Supplementary information for

Merocyanine-Based Photoacids as Recyclable Catalysts in Visible-Light-Driven Transformations

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This PDF file includes:

1. Materials and methods - general information

Reagents and solvents: Commercially available chemicals and solvents of the highest commercial quality were purchased and used without further purification unless noted otherwise. All photochemical reactions were conducted in dried and degassed solvents. Solvents for column chromatography were used without further purification. Commercially available starting materials and reagents were purchased and checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used without further purification.

Gas Chromatography: Gas Chromatography (GC) measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent Chem Station Rev.C.01.04. GC–MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD Chem Station E.02.02.1431. A capillary column HP-5MS/30 mx 0.25 mm/0.25µM film and helium as carrier gas (flow rate of 1 mL/min) were used. The GC oven temperature program was adjusted as follows: initial temperature 40 ºC was kept for 3 minutes, and the temperature was increased at a rate of 15 ºC/min over 16 minutes until 280 ºC was reached and kept for 5 minutes, the temperature was again increased at a rate of 25 ºC/min over seconds until the final temperature (300 ºC) was reached and kept for 5 minutes.

Column and Thin-Layer Chromatography: Column chromatography was performed in the *Biotage* Isolera One 3.0 or on the normal-grade silica gel (SiO_2, 60 Å) in a cylindrical glass column with isocratic elution (composition of the eluent is given for each experiment). Chromatography solvents were distilled before use. Analytical thin-layer chromatography (TLC) was performed on silica gel-coated alumina plates (MN pre-coated TLC-sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 nm or 366 nm) or staining with $KMnO_4$.

NMR Spectroscopy: All NMR spectra of the isolated compounds were measured at room temperature using a *Bruker* Avance 400 (400 MHz for ^{1}H, 101 MHz for $^{13}C\{^{1}H\}$ and 377 MHz for $^{19}F\{^{1}H\}$) NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant J, number of protons). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, DMSO-d6: 2.50 ppm) and $^{13}C\{^{1}H\}$ NMR spectra are reported relative to TMS and were referenced via the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, DMSO-d6: 39.52 ppm). Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H NMR: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet and br. = broad; ^{13}C-NMR: (1^{o}) = primary, (2^{o}) = secondary, (3^{o}) = tertiary, (4^{o}) = quaternary carbon. Spectra were analyzed using Bruker Topspin 4.1.4.

High-Resolution Mass Spectroscopy: 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 2013 IUPAC recommendations. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A, or Agilent Q-TOF 6540 UHD instrument.

2. Detailed description of the photoreactor setup

Photoreactions were irradiated with LEDs (Model: ELP8X3LS, λ_{max} = 505 nm, average radiant flux 210 ± 10 mW, 89 V, 700 mA). Reaction mixtures were exposed to light under stirring (1200 rpm, magnetic stirrer) from the bottom side of the vial. The system's temperature was controlled by a water-cooling circuit consisting of an aluminum cooling block connected to a thermostat.

Fig. S1: (i) LED-s; (ii) Cooling block; (iii) 5 mL crimp-capped vial charged with reaction mixture and a stirring bar; (iv) Irradiation and cooling setup.

3. Description of the *in situ* irradiated NMR setup

For sample preparation, a Schlenk technique with argon as an inert gas was employed (**Fig. S2a**).

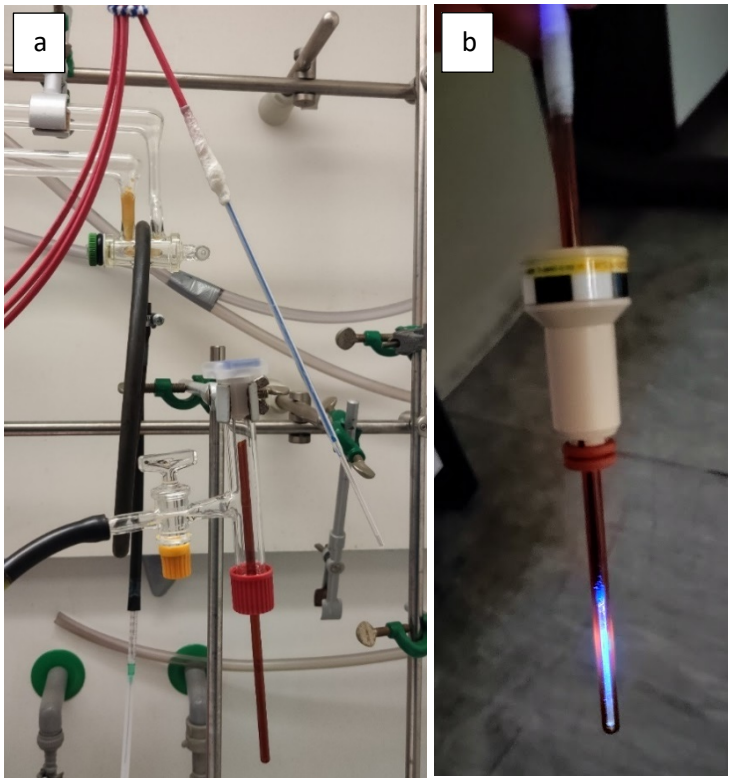


Fig. S2: a) Setup for the preparation of the NMR sample under argon atmosphere. b) Inserted glass fiber into the amberized NMR tube during irradiation.

For the irradiation in NMR spectrometer, the *in situ* illumination setup described by Gschwind and co-workers[1] was employed. The glass fiber, positioned within an insert inside the NMR tube, secured with Parafilm®, was linked to an LED placed in a custom-built illumination chamber (**Fig. S2b**).

For the illumination, LED OSRAM OSLON® SSL 80 (LD CQ7P-2U3U-W5-1-K) was utilized as a light source with λ_{max} = 451 nm, operating at a current of 1000 mA.

The NMR experiments were conducted at 298 K on a Bruker AVANCE III-HD 600 MHz spectrometer equipped with TBI (Triple resonance broadband inverse) 5 mm CPPBBO 1H/19F-BB probe head with Z-gradient and BVT unit.

4. Synthetic procedures

Synthesis of ethylene alcohol-functionalized spiropyran (SP-OH)
Ethylene alcohol-functionalized spiropyran was prepared according to the reported procedure.[2]

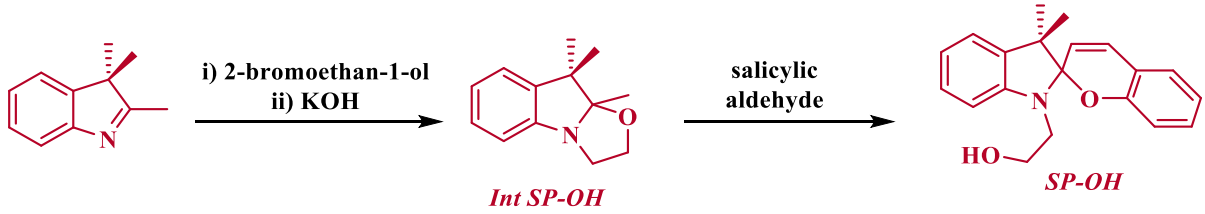
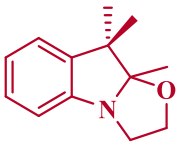


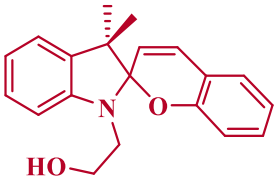
Fig. S3: Synthesis of ethylene alcohol-functionalized spiropyran (SP-OH).

9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (Int-SP-OH)



Preparation: A solution of 2,3,3-trimethyl-3H-indole (2.60 g. 16 mmol) and 2-bromo ethanol (2.48 g, 20 mmol) in MeCN (20 mL) was heated for 24 h under reflux and argon atmosphere. After cooling to ambient temperature, the solvent was distilled under reduced pressure. The residue was suspended in hexane (25 mL) and the mixture was sonicated and filtered. The resulting solid was washed with DCM, (35 mL) to afford 1-(2-Hydroxyethyl)-2,3,3-trimethyl-3H-indolium bromide as a pink solid. Next, the solid was dissolved in H_2O (50 mL), and KOH (0.92 g, 16 mmol) was added. The reaction was stirred at ambient temperature for 10 min and the product was extracted with Et_2O (3×20 mL). The organic phase was concentrated under reduced pressure and purified by column chromatography on silica gel. Elution with petroleum ether/ ethyl acetate (PE/EA) 5:1.
Isolated yield: 73 % (237 mg, pale yellow oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.11 (s, 3H), 1.32 (s, 3H), 1.36 (s, 3H), 3.45 (m, 2H), 3.65 (m, 1H), 3.77 (m, 1H), 6.69 (d, J = 7.90 Hz, 1H), 6.85 (m, 1H), 7.00 (m, 1H), 7.06 (m, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 17.58, 20.79, 28.09, 46.94, 50.08, 62.98, 108.96, 111.96, 121.68, 122.40, 127.48, 140.00, 150.53 ppm.
Spectral data match those reported in the literature.[2]

2-(3',3'-dimethylspiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol (SP-OH)



Preparation: A solution of 2-hydroxy-benzaldehyde (0.75 g, 6 mmol) and Int-SP-OH (0.82 g, 4 mmol) in EtOH (10 mL) was heated for 3 h under reflux and argon. After cooling to ambient temperature, the solvent was removed, and the product purified by column chromatography on silica gel. Elution with PE/EA 4:1.
Isolated yield: 71% (869 mg purple, hygroscopic solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.17 (s, 3H), 1.31 (s, 3H), 1.93 (t, J = 6.32 Hz, 1H), 3.34 (dt, ^2J = 14.78 Hz, ^3J = 5.13 Hz, 1H), 3.49-3.56 (m, 1H), 3.71-3.79 (m, 2H), 5.67 (d, J = 10.23 Hz, 1H), 6.63 (d, J = 7.75 Hz, 1H), 6.70 (d, J = 8.16 Hz, 1H), 6.81-6.88 (m, 3H), 3.34 (dd, ^3J = 7.48 Hz, ^4J = 1.55 Hz, 1H), 7.07-7.12 (m, 2H), 7.17 (td, ^3J = 7.65 Hz, ^4J = 1.23 Hz, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 20.36, 25.87, 46.12, 52.31, 60.87, 104.56, 106.62, 115.07, 118.63, 119.34, 119.61, 120.45, 121.88, 126.85, 127.59, 129.53, 129.91, 136.45, 147.38, 153.89 ppm.
HRMS: *m/z* for $[C_{20}H_{22}NO_2]^+$ $[M+H]^+$ calcd: 308.1645, found: 308.1649.
Spectral data match those reported in the literature.[3]

Synthesis of alkyl sulfonate-functionalized merocyanines (HMC-3 and HMC-4)

Alkyl sulfonate group containing merocyanines – **HMC-3,** and **HMC-4** were prepared according to the reported procedure.[4]

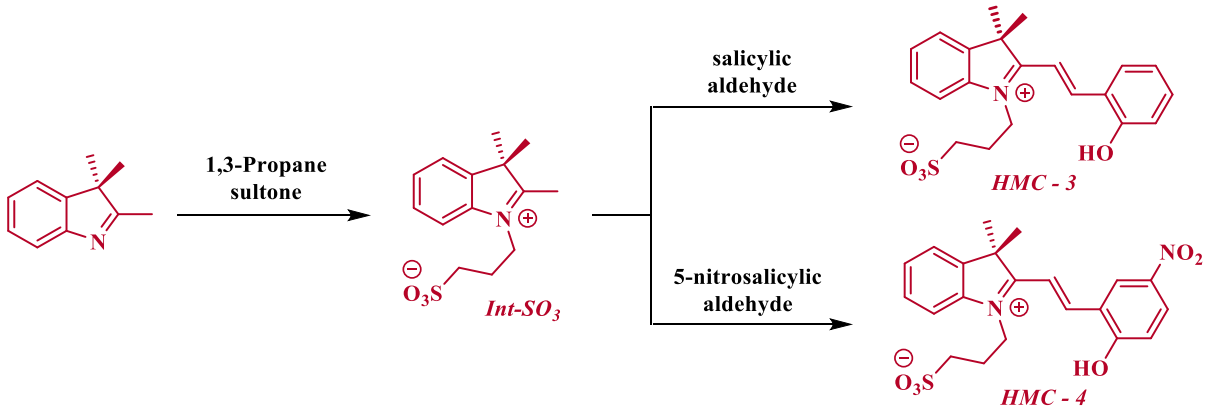
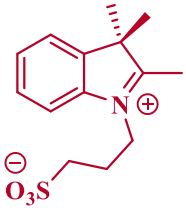


Fig. S4: Synthesis of alkyl sulfonate-functionalized merocyanines (HMC-3 and HMC-4).

3-(2,3,3- trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (Int-SO_3)



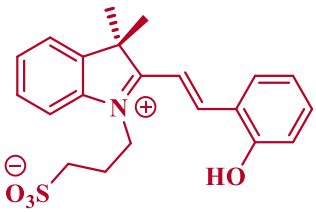
Preparation according to a modified literature procedure:[5] A solution of 1,3-propane sultone (2.30 g, 18.8 mmol, 1.00 eq.) and 2,3,3-trimethyl-3H-indole (3.18 g, 20 mmol, 1.00 eq.) in toluene (110 mL) was heated to 135 °C for 2.5 days. After letting the solution return to r.t. the purple precipitate was collected by vacuum filtration and washed with petroleum ether (ca. 15 mL, two times). The precipitate was dried *in vacuo* for ca. 6 h and was used in the consecutive reaction without further purification.

Isolated yield: 81% (4.27 mg purple, hygroscopic solid.).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 1.52 (s, 6H), 2.10-2.19 (m, 2H), 2.60-2.65 (m, 2H), 2.82 (s, 3H), 4.65 (t, J = 7.93 Hz, 2H), 7.57-7.64 (m, 2H), 7.80-7.83 (m, 1H), 8.02-8.05 (m, 1H) ppm.

Spectral data matches those reported in the literature.[6]

(E)-3-(2-(2-hydroxystyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 3)



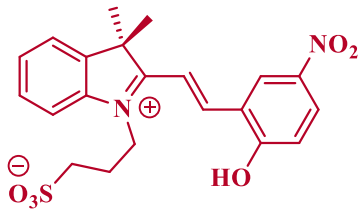
Preparation: salicylaldehyde (45 mg, 37 µmol, 1.37 eq.) was added to a solution of the substituted indolinium (96 mg, ca. 80 w %, 270 µmol, 1.00 eq.) in anhydrous ethanol (136 mM, 2.00 mL). The reaction mixture was heated to 95 °C for 16 h and let cool down to room temperature. The resulting orange precipitate was collected by vacuum filtration, washed with ethanol (ca. 2 mL) and dried *in vacuo* giving an orange powder.

Isolated yield: 80% (83 mg, 215 µmol, orange powder).

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 1.76 (s, 6H), 2.17 (m, 2H), 2.65 (m, 2H), 4.80 (m, 2H), 6.98 (dd, ^3J = 7.67, ^3J = 7.46 Hz, 1H), 7.03 (d, J = 7.85 Hz, 1H), 7.46 (m, 1H), 7.56-7.65 (m, 2H), 7.82-7.86 (m, 1H), 7.87 (d, J = 16.61 Hz, 1H), 8.01 (m, 1H), 8.27 (dd, ^3J = 8.00, ^4J = 1.27 Hz, 1H), 8.59 (d, J = 16.48 Hz, 1H), 11.02 (s, 1H) ppm.

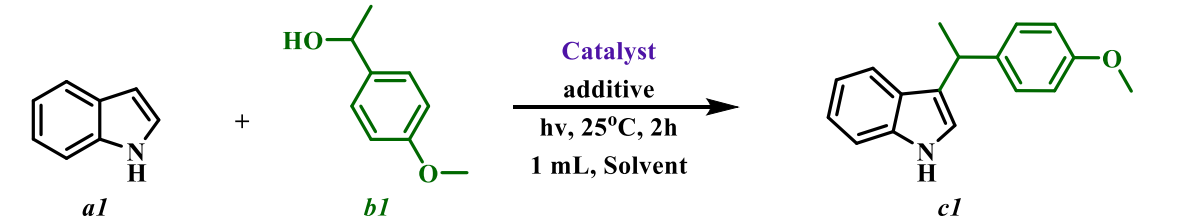
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) δ = 25.06, 26.91, 46.01, 47.81, 52.37, 111.92, 115.56, 117.09, 120.53, 121.81, 123.45, 129.60, 129.62, 130.24, 136.21, 141.40, 143.95, 149.16, 159.49, 182.23 ppm.
Note: In a given condition (r.t., ^{1}H NMR (400 MHz, $(CD_3)_2SO$), ~ 0.1 M) exclusively merocyanine form was detected, in the NMR sample four equivalents of water were observed.
HRMS: *m/z* for ($[C_{21}H_{23}NO_4S]+H^+$) $[(M+H)^+]$ calcd: 386.1421, found: 386.1424.
Spectral data matches those reported in the literature.[6]

(E)-3-(2-(2-hydroxy-5-nitrostyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 4)



Preparation: 2-hydroxy-5-nitrobenzaldehyde (196 mg, 1.17 mmol, 1.10 eq.) was added to a solution of the substituted indolinium (300 mg, 1.07 mmol, 1.00 eq.) in anhydrous ethanol (178 mM, 6.00 mL). The reaction mixture was heated to 100°C for 22 h and let cool down to room temperature. The dark yellow precipitate was collected by vacuum filtration, washed with ice-cold ethanol (ca. 4 mL) and dried *in vacuo*.
Isolated yield: 50% (230 mg, dark yellow powder).
^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 1.79 (s, 6H), 2.20 (m, 2H), 2.64 (m, 2H), 4.83 (m, 2H), 7.19 (d, J = 9.17 Hz, 1H), 7.63-7.66 (m, 2H), 7.87-7.90 (m, 1H), 8.06 (d, J = 16.39 Hz, 1H), 8.07-8.10 (m, 1H), 8.29 (dd, ^{3}J = 9.26, ^{4}J = 2.85 Hz, 1H), 8.48 (d, J = 16.39 Hz, 1H), 9.08 (d, J = 2.8 Hz, 1H), 12.63 (s, 1H) ppm.
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2SO$) δ = 25.19, 26.36, 46.67, 48.03, 52.84, 115.24, 116.09, 117.76, 121.85, 123.53, 127.89, 129.71, 129.91, 130.15, 140.72, 141.35, 144.38, 147.80, 164.61, 182.68 ppm.
HRMS: *m/z* for ($[C_{21}H_{22}N_2O_6S]+H^+$) $[(M+H)^+]$ calcd: 431.1271, found: 431.1272.
Spectral data matches those reported in the literature.[6]

5. Optimization of reaction conditions



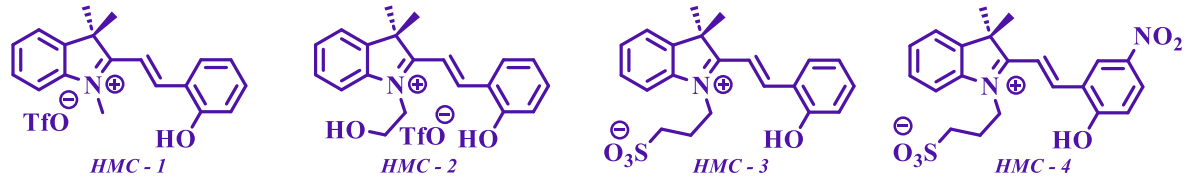


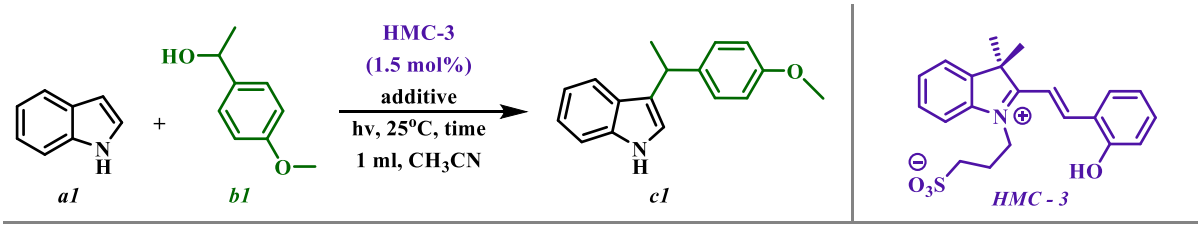
Table S1: Optimization of reaction conditions (screening of catalysts, solvents, additives). Yields were determined by GC-FID using 1,4-Bis(trifluoromethyl)benzene as an internal standard.

Entry	Catalyst	Conditions	Time	Conv.	Yield
1	**HMC – 1** 10 mol%	HFIP, λ = 470 nm	2 h	90 %	75 %
2	**HMC – 1** 10 mol%	HFIP, No light	2 h	3 %	2 %
3	**HMC – 1** 10 mol%	CH_3CN, HFIP 0.5 mmol, λ = 470 nm	2 h	99 %	78 %
4	**HMC – 1** 1 mol%	CH_3CN, HFIP 0.1 mmol, λ = 470 nm	2 h	88 %	82 %
5	**HMC – 1** 1 mol%	CH_3CN, HFIP 0.1 mmol, No light	2 h	12 %	10 %
6	**HMC – 1** 1 mol%	DCM, HFIP 0.1 mmol, λ = 470 nm	2 h	95 %	68 %
7	**HMC – 1** 1 mol%	Toluene, HFIP 0.1 mmol, λ = 470 nm	2 h	83 %	62 %
8	**HMC – 2** 1 mol%	CH_3CN, HFIP 0.1 mmol, λ = 470 nm	2 h	92 %	86 %
9	**HMC – 2** 1 mol%	CH_3CN, HFIP 0.1 mmol, No light	2 h	5 %	4 %
10	**HMC – 2** 1 mol%	DCM, HFIP 0.1 mmol, λ = 470 nm	2 h	92 %	66 %
11	**HMC – 2** 1 mol%	DCM, HFIP 0.1 mmol, No light	2 h	21 %	19 %
12	**HMC – 2** 1 mol%	CH_3OH, HFIP 0.1 mmol, λ = 470 nm	2 h	0 %	0 %
13	**HMC – 3** 1 mol%	CH_3CN, HFIP 0.1 mmol, λ = 470 nm	2 h	99 %	90 %
14	**HMC – 3** 1 mol%	CH_3CN, λ = 470 nm	2 h	97 %	87 %
15	**HMC – 3** 1 mol%	CH_3CN, λ = 505 nm	2 h	95 %	86 %
16	**HMC – 3** 2 mol%	CH_3CN, λ = 505 nm	**2 h**	**99 %**	**91 %**
17	**HMC – 3** 2 mol%	CH_3CN, No light	2 h	0 %	0 %
18	**HMC – 3** 1 mol%	DMSO, λ = 505 nm	2 h	0 %	0 %
19	**HMC – 3** 1 mol%	H_2O, λ = 505 nm	2 h	0 %	0 %

20	**HMC – 3** 1 mol%	CH_3CN, H_2O 1 mmol, λ = 470 nm	2 h	90 %	80 %
21	**HMC – 4** 1 mol%	CH_3CN, λ = 505 nm	2 h	0 %	0 %
22	**p-Toluenesulfonic acid** 1 mol%	CH_3CN, No light	2 h	100 %	90 %
23	**Schreiner's Thiourea Catalyst** 1 mol%	CH_3CN, λ = 365 nm	2 h	3 %	2 %
24	**8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS)** 1 mol%	CH_3CN, λ = 395 nm	2 h	0 %	0 %
25	**HPTS** 1 mol%	H_2O, λ = 395 nm	2 h	0 %	0 %
26	**HPTS** 1 mol%	CH_3OH, λ = 395 nm	2 h	0 %	0 %
27	**HPTS** 1 mol%	DMSO, λ = 395 nm	2 h	0 %	0 %

Evaluation of the optimal quantity of HFIP (as an additive)

Table S2: Evaluation of the optimal quantity of HFIP. Yields were determined by GC-FID using 1,4-Bis(trifluoromethyl)benzene as an internal standard.



Entry	Additive	Time	Yield
1	HFIP, 0.2 mmol	1 h	84 %
2	HFIP, 0.2 mmol	10 min	32 %
3	HFIP, 0.05 mmol	10 min	23 %
4	HFIP, 0.1 mmol	10 min	27 %
5	HFIP, 0.3 mmol	10 min	43 %
6	HFIP, 0.4 mmol	10 min	52 %
7	HFIP, 0.5 mmol	10 min	53 %
8	HFIP, 1 mmol	10 min	58 %
9	HFIP, 1.5 mmol	10 min	55 %
10	HFIP, 2 mmol	10 min	47 %
11	HFIP, 2.5 mmol	10 min	46 %

6. General synthetic procedures

General synthetic procedure – 1 (GP-1) for the substrate scope

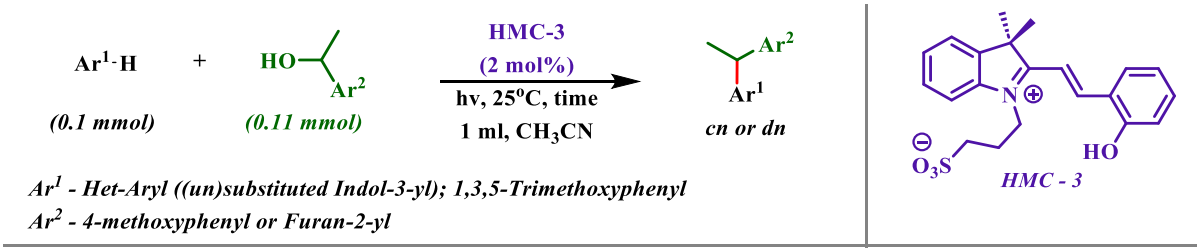
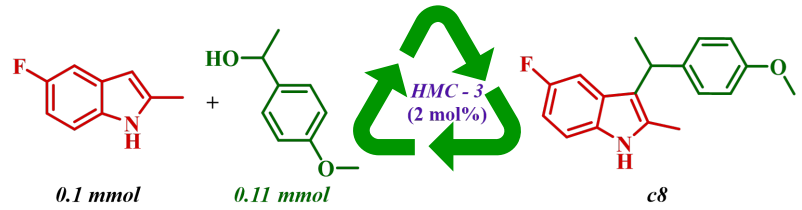


Fig. S5: Metastable-state photoacid catalyzed Friedel-Crafts alkylation of electron-rich aromatic compounds by benzylic alcohols.

A 5 mL crimp-top vial was charged with electron-rich arene Ar^1-H (0.1 mmol, 1 equiv), the corresponding benzylic alcohol (0.11 mmol, 1.1 equiv), HMC-3 (2 mol%), acetonitrile (1 mL) and a stirring bar. The vial was then crimped, and a freeze-pump-thaw cycle was applied three times to degas the sample. The vial was placed in an aluminum cooling block and stirred for 2 h at room temperature under a single green LED irradiation (λ_{Max} = 505 ± 15 nm light optical power ~ 0.2 W). The reaction mixture was quenched with 100 µL conc. $NaHCO_3$ solution and extracted/washed with EtOAc (2 × 2 mL). The combined organic phases were dried on Na_2SO_4. The solvent was removed by vacuum. Finally, crude product ***cn*** or ***dn*** was purified using petroleum ether/ethyl acetate mixture as eluent by flash column chromatography.

General synthetic procedure – 2 (GP-2) catalyst recovery by washing



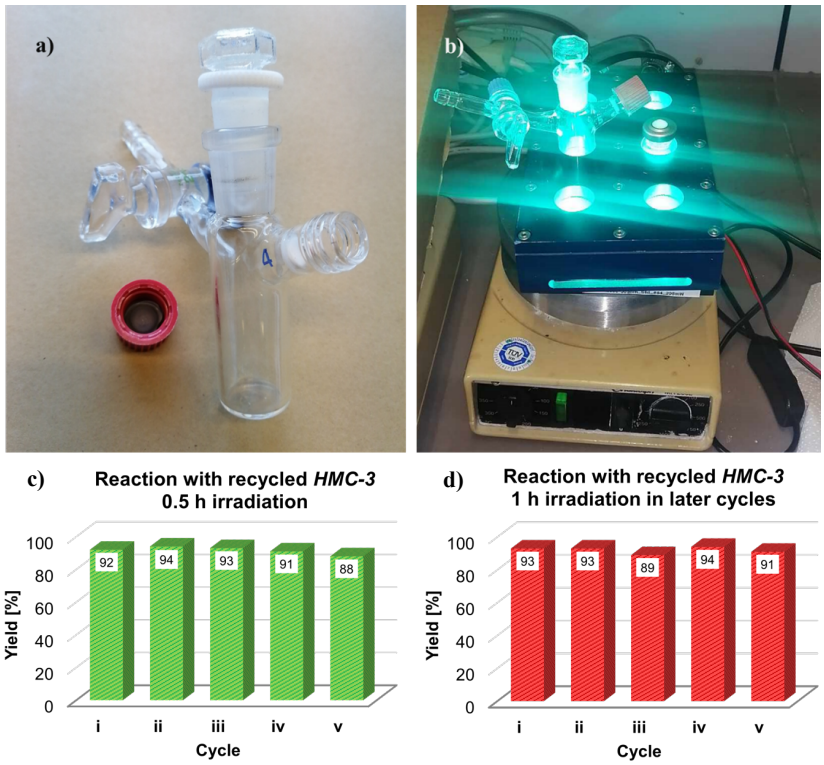


Fig S6: Recycling of the catalyst HMC – 3. a) Filter attached Schlenk tube. b) Stirred under irradiation of 505 nm LED light (0.202 Watt). c) Reaction yields with recycled catalyst, irradiation time – 0.5 h for all five

cycles. d) Reaction yields with recycled catalyst, irradiation time – 0.5 h for first three cycles and irradiation time – 1 h for last two cycles.

The filter-attached Schlenk tube (Fig 5. a)) was charged with HMC-3 (2 mol%) and (1 mL) stock solution containing 0.1 M 5-fluoro-2-methyl-1H-indole and 1M 1-(4-methoxyphenyl)ethan-1-ol. The tube was sealed and a freeze-pump-thaw cycle was applied three times to degas the sample. Then it was placed in an aluminum cooling block and stirred for 0.5 h at room temperature under a single green LED irradiation (λ_{Max} = 505 ± 15 nm light optical power ~ 0.2 W) and another 0.5 h in the dark. The reaction mixture was evaporated and the crude product was washed out by 4 X 1 mL (4 mL in total) cyclohexane. Residual orange precipitate was reused as the catalyst for the following cycles. Yields for each cycle (shown in Fig 5. c)) were determined using $^{19}F\{^{1}H\}$ NMR spectroscopy, with 1-ethyl-4-fluorobenzene employed as an external standard.
**Over time the activity of the catalyst was reduced, and longer irradiation times (1 h instead of 0.5 h) for the fourth and the fifth cycles solved the minor drop in yield. (Fig 5. d))

General synthetic procedure – 3 (GP-3) on simple catalyst recovery *via* precipitation

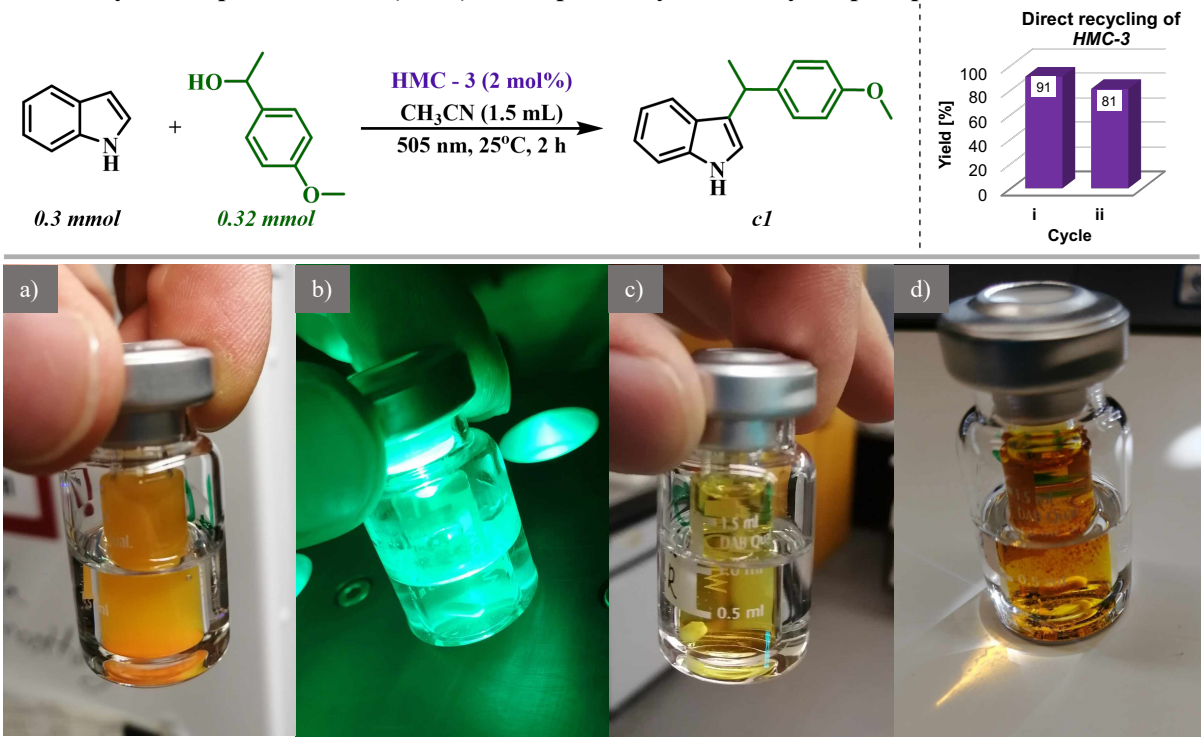
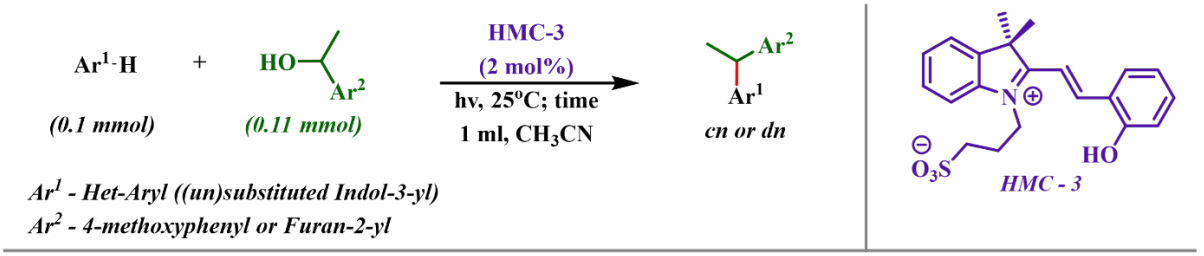


Fig. S7: Direct recycling of the catalyst HMC – 3. Yields were determined by GC-FID using 1,4-Bis(trifluoromethyl)benzene as an internal standard. a) Sample before irradiation. b) Stirred under irradiation of 505 nm LED light (0.202 Watt). c) Sample after 1h irradiation. d) Sample after 16 h thermal relaxation (in the dark).

A 2 mL crimp-top vial was charged with 0.006 mmol HMC-3 (2 mol%) and 1.5 mL stock solution (in acetonitrile) containing 0.3 mmol indole (1 equiv) and 0.32 mmol 1-(4-methoxyphenyl)ethan-1-ol (1.07 equiv.) The vial was then crimped, and a freeze-pump-thaw cycle was applied three times to degas the sample. The vial was placed in an aluminum cooling block and stirred for 2 h at room temperature under a single green LED irradiation (λ_{Max} = 505 ± 15 nm light optical power ~ 0.2 W). The reaction mixture was kept in the dark for 16 hours to relax thermally and the catalyst was thus precipitated as shown in (Fig 6. e)). To separate suspended solids from the liquid centrifuge was applied, the acetonitrile solution of a crude product was removed by decantation and the precipitated catalysts were collected and reused for the second cycle.

General Procedure – 4 (GP-4) for the near-IR irradiation



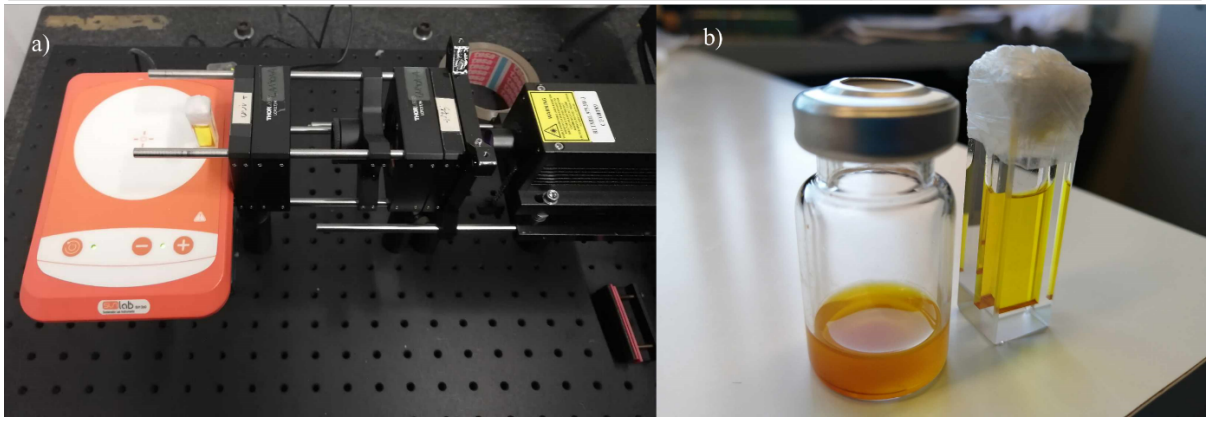


Fig. S8: Near IR promoted acid-catalyzed FC alkylation of indoles. a) Irradiated by laser beam λ = 975 nm. b) Before (in a vial) and after (in a cuvette) irradiation; after irradiation, suspension of HMC – 3 turns into the transparent solution which indicates effective merocyanine to spiropyran photoisomerization. (At the bottom of the cuvette, the presence of some of the HMC – 3 precipitate could be explained by inefficient diffusion).

A ~ 0.55 mL (height:length: width 2.75:1:0.2) cuvette was charged with electron-rich arene Ar^1-H (0.06 mmol, 1 equiv), the corresponding benzylic alcohol (0.07 mmol, 1.17 equiv), HMC-3 (0.0012 mmol 2 mol%), HFIP (0.3 mmol) acetonitrile (0.4 mL). The cuvette was then sealed, degassed, and refilled with argon using the Schlenk line technique (three times). The cuvette was irradiated for 9 h (or for 4 h) at room temperature via the near-IR laser beam (λ_{Max} = 975 nm light optical power ~ 1 W). The reaction mixture was quenched with 60 µL conc. $NaHCO_3$ solution.

It should be noted that the solubility of HMC-3 in acetonitrile is very limited, leading to significant dilution even in saturated solutions. Given the inherently low efficiency of two-photon absorption, we hypothesized that using HFIP as an additive to enhance HMC-3 solubility could facilitate more efficient switching. Although HFIP is a weakly acidic additive, a control experiment conducted in the dark (Entry 3) yielded only trace amounts of the target product, suggesting that it does not function as an efficient Brønsted acid catalyst. However, since HFIP is recognized as a privileged solvent/additive for Friedel–Crafts reactions,[7] its optimal quantity has been determined (see Section 5, Table 2 in the Supporting Information).

Entry	***Substrates***	***Time***	***λ***	***Conv.***	***Yield***
1	*Indole and 1-(4-methoxyphenyl)ethan-1-ol*	***9.5 h***	*975 nm*	1.5 %	1.1 %[a,b]
2	*Indole and 1-(4-methoxyphenyl)ethan-1-ol*	***9.5 h***	No light	0 %	0 %[a,b]
3	*Indole and 1-(4-methoxyphenyl)ethan-1-ol*	***9.5 h***	*975 nm*	93 %	89 %[b]
4	*Indole and 1-(4-methoxyphenyl)ethan-1-ol*	***9.5 h***	No light	1 %	1 %[b]
5	*5-fluoro-2-methyl-1H-indole and 1-(furan-2-yl)ethan-1-ol*	***4.5 h***	*975 nm*	14 %	13 %[c]

6	*5-fluoro-2-methyl-1H-indole and 1-(furan-2-yl)ethan-1-ol*	***4.5 h***	No light	0 %	0 %[c]

Table 3: The reaction was carried out in acetonitrile without HFIP.[a] The yield was estimated either by GC-FID using 1,4-Bis(trifluoromethyl)benzene as an internal standard[b] or using 19F{^{1}H} NMR spectroscopy, with 1-ethyl-4-fluorobenzene employed as an external standard[c].

General synthetic procedure – 5 (GP-5) for gram scale reaction

A 10 mL crimp-top vial was charged with indole (10 mmol, 1.171 g, 1 equiv.), 1-(4-methoxyphenyl)ethan-1-ol (10.7 mmol, 1,627 g, 1.07 equiv), HMC-3 (0.0212 g, 0.55 mol%), acetonitrile (10 mL), and a stirring bar. The vial was then crimped, and a freeze-pump-thaw cycle was applied three times to degas the sample. The vial was placed in an aluminum cooling block and stirred for 5 h at room temperature (until the conversion reached over 99 %) under a single green LED irradiation (λ_{Max} = 505 ± 15 nm light optical power ~ 0.2 W). The reaction mixture was quenched with 1 mL conc. $NaHCO_3$ solution and extracted/washed with EtOAc (3 × 50 mL). The combined organic phases were dried on Na_2SO_4, and the solvent was removed by vacuum. Finally, the crude product was purified using a petroleum ether/ethyl acetate mixture (9/1) as eluent by column chromatography. Yielding 2.210 g, 88 % of 3-(1-(4-methoxyphenyl)ethyl)-1H-indole.

7. UV-Vis absorption measurements of HMC-3

HMC–3 has limited solubility in acetonitrile, so it was not possible to prepare a 10^{-6} M solution and UV-Vis measurements were conducted with sub-ppm molar solution. In a visible region, the absorption maximum is given at about ~425 nm, (characteristic for protonated trans merocyanine HMC-3[7]). Irradiation via 470 nm light causes the instantaneous decrease of the main sharp MCH-3 characteristic absorption band and an increase of a peak with the λ_{max} ~ 300 nm which is characteristic for protonated spiropyran.[7] Thermal relaxation has a slower rate and after 16 hours the important portion of protonated spiropyrans relaxed back to its merocyanine.

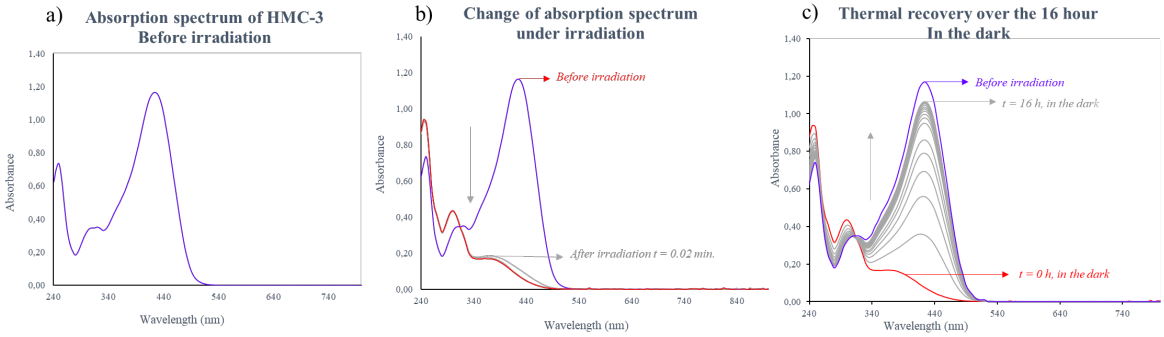


Fig. S9: a) Absorption spectrum of HMC-3 before irradiation. b) Change of absorption spectrum under 470 nm LED light irradiation; measurement interval – 0.02 minute; after ~ 0.04 minutes equilibrium between protonates MC/SP isomers is achieved. c) Thermal recovery of a system measurement interval – 2 hours.

To estimate the time for full thermal recovery in the absence of the light at ambient temperature 176 h. UV-Vis measurement experiment was conducted, and after ~ 80 hours the initial equilibrium between isomers was fully recovered and afterward no more considerable changes in the spectrum were noticeable.

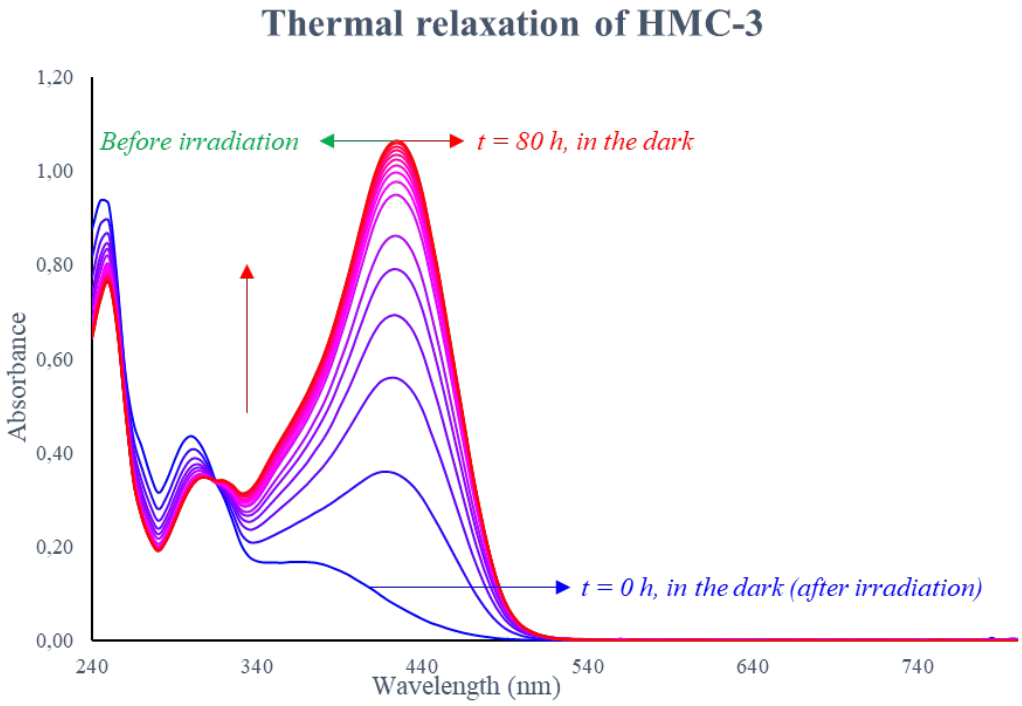


Fig. S10: The full thermal relaxation of the system containing HMC-3 solution in acetonitrile in the dark.

In the presence of HFIP, (HFIP:CH_3CN – 1:19 volume ratio) the solubility of HMC-3 was increased and 10^{-6} M solution was possible to be prepared. The absorption spectrum of the solution before irradiation was similar to the one in pure acetonitrile with a slightly sharp absorbance band in a visible region λ_{max} ~ 425 nm. As in a previous case the equilibrium between photoswitch isomers under irradiation was achieved almost instantaneously (in less than 0.1 min). and thermal relaxation in the dark is considerably accelerated in 4 hour the system is almost fully relaxed (for full relaxation ~ 16 hour is needed).

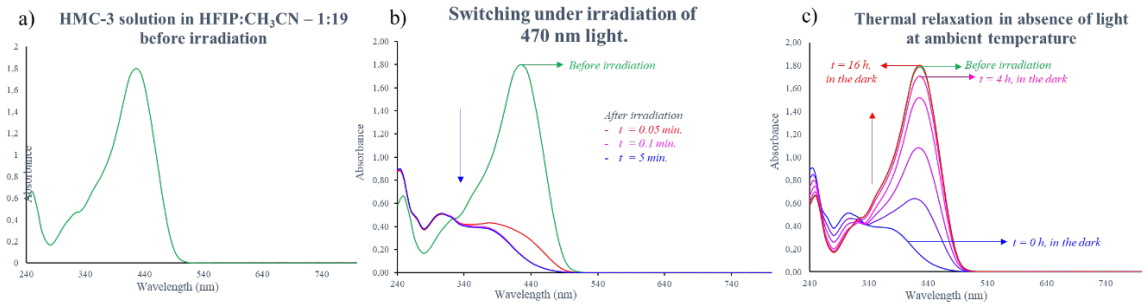


Fig. S11: a) Absorption spectrum of HMC-3 in HFIP:CH_3CN – 1:19 volume ratio, before irradiation. b) Change of absorption spectrum under 470 nm LED light irradiation; measurement interval – 0.05 minute; after ~ 0.1 minutes equilibrium between protonates MC/SP isomers is achieved. c) Thermal recovery of a system measurement interval – 1 hours.

8. Monitoring kinetics by ^{1}H-NMR spectroscopy

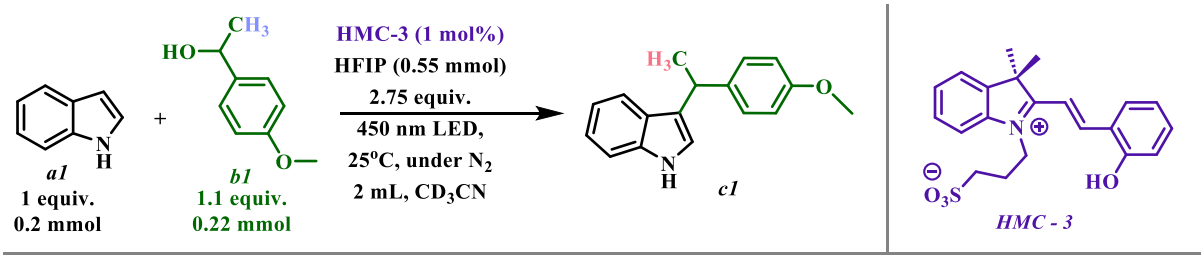


Fig. S12: Model reaction for the ^{1}H-NMR monitoring.

General NMR samples preparation for the *in situ* irradiated kinetic measurements

A 5 mL crimp-top vial was charged with indole (23.4 mg, 0.2 mmol, 1 equiv), 1-(4--methoxyphenyl)ethan-1-ol (31 µL, 0.22 mmol, 1.1 equiv), HMC-3 (0.8 mg, 0.002 mmol, 0.01 equiv), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 59 µL, 0.55 mmol, 2.75 equiv), acetonitrile-d3 (2 mL), and a stirring bar. The vial was crimped, and the sample was degassed by three freeze-pump-thaw cycles. An aliquot of 0.3 mL was transferred into the dry amberized NMR tube under argon atmosphere. Then, under an argon stream, a glass fiber was inserted into the NMR tube and secured with Parafilm®. The reaction kinetic data were obtained according to the procedure described in the *Setup for the in situ Irradiation Kinetics*.

To guarantee quantitative results, the relaxation delay (d1) was set to 28 s, which ensured full relaxation of the nuclei (d1 ≥ 5·T_1). Spectra were acquired for 1 s (AQ = 1 s) with 1 scan (NS = 1). The distance between the data points was varying from approximately 30 s to 10 min.

Processing of the NMR spectra was executed in MestReNova v15.0.0-34764. Phase and baseline correction were applied to all spectra.

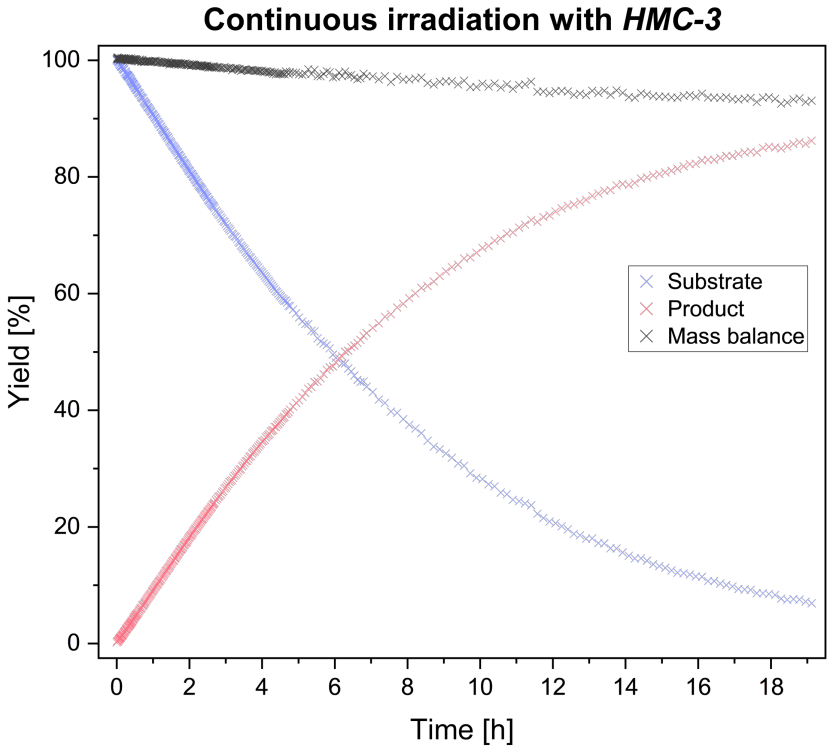


Fig. S13: ^{1}H-NMR kinetics under continuous irradiation. Violet – consumption of the starting material (*b1*) in time, light red – formation of the product (*c1*) in time, grey – mass balance.

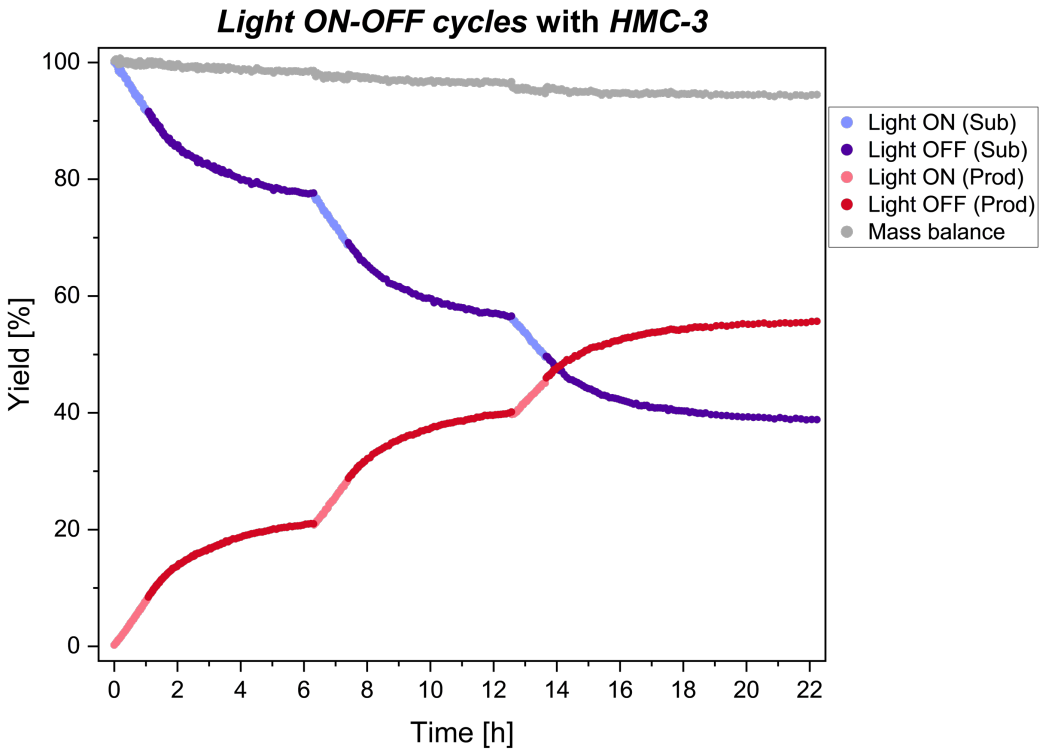


Fig. S14: ^{1}H-NMR kinetics under light ON-OFF cycles. Light violet – consumption of the starting material (*b1*) under irradiation, dark violet – consumption of the starting material (*b1*) in dark, light red – formation of the product (*c1*) under irradiation, red – formation of the product (*c1*) in dark, grey – mass balance.

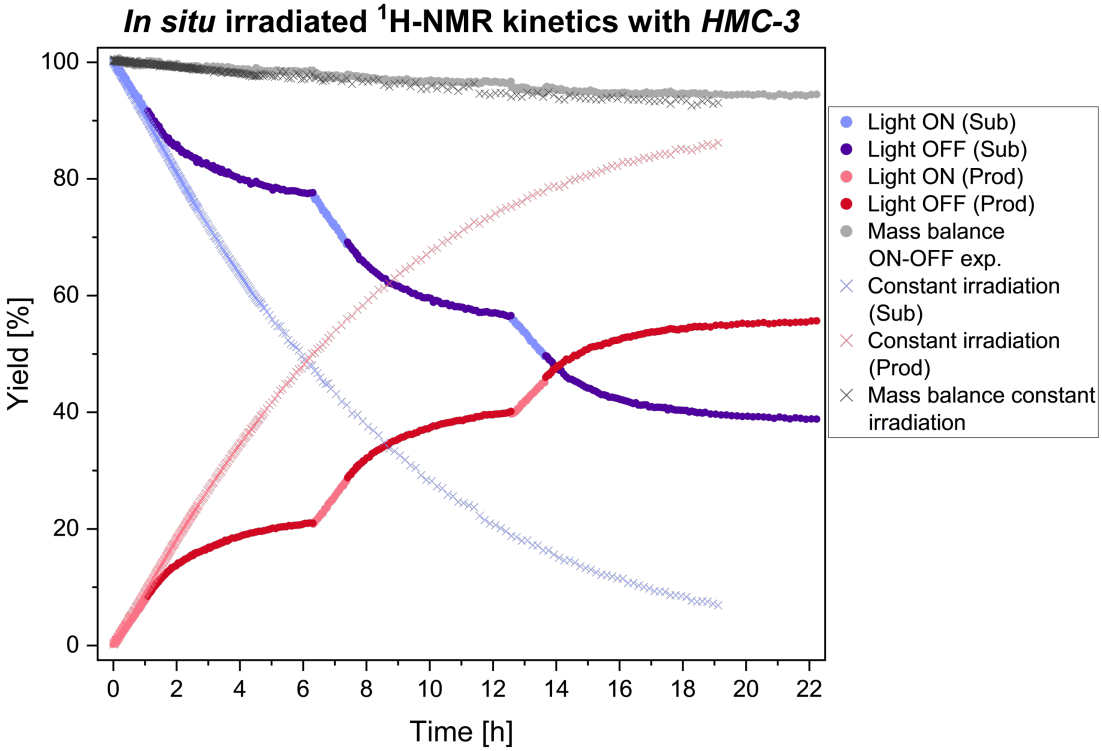
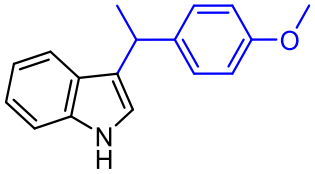


Fig. S15: Comparison of the ^{1}H-NMR kinetics under continuous irradiation and light ON-OFF cycles. Violet - consumption of the starting material (*b1*) under irradiation (ON-OFF cycles – dots, continous irradiation – crosses), dark violet dots – consumption of the starting material (*b1*) in dark, light red – formation of the product (*c1*) under irradiation (ON-OFF cycles – dots, continous irradiation – crosses), red dots – formation of the product (*c1*) in dark, grey – mass balance (ON-OFF cycles – dots, continous irradiation – crosses).

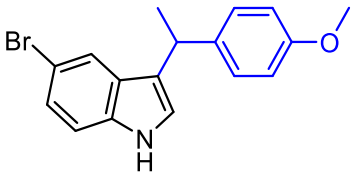
9. Characterization data of final products

3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c1)



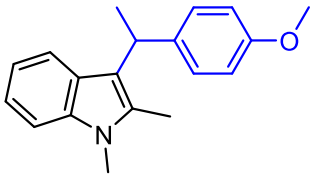
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 89% (22.3 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.72 (d, *J* = 7.13 Hz, 3H), 3.81 (s, 3H), 4.37 (q, *J* = 7.12 Hz, 1H), 6.86 (m, 2H), 6.99 (d, *J* = 1.41 Hz, 1H), 7.05 (m, 1H), 7.19 (m, 1H), 7.25 (m, 2H), 7.34 (d, *J* = 8.09 Hz, 1H), 7.34 (d, *J* = 7.96 Hz, 1H), 7.92 (br. s, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 22.6, 36.1, 55.3, 111.1, 113.7, 119.2, 119.8, 121.1, 121.8, 122.0, 126.9, 128.4, 136.7, 139.1, 157.8 ppm.
HRMS: *m/z* for $[C_{17}H_{17}NO]^+$ [M^+] calcd: 251.1305, found: 251.1302.
Spectral data matches those reported in the literature.[8]

5-bromo-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c2)



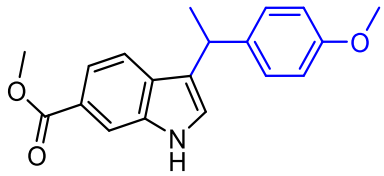
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 92% (30.3 mg, pale yellow solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.75 (d, *J* = 7.15 Hz, 3H), 3.88 (s, 3H), 4.35 (q, *J* = 7.12 Hz, 1H), 6.92 (m, 2H), 7.07 (d, *J* = 1.07 Hz, 1H), 7.25-7.35 (m, 4H), 7.59 (d, *J* = 1.68 Hz, 1H), 8.06 (br. s, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 22.6, 35.9, 55.3, 112.5, 112.5, 113.8, 121.6, 122.2, 122.3, 124.8, 128.2, 128.7, 135.3, 138.5, 157.9 ppm.
HRMS: *m/z* for $[C_{17}H_{16}BrNO]^+$ [M^+] calcd: 329.0415, found: 329.0410.
Spectral data matches those reported in the literature.[9]

3-(1-(4-methoxyphenyl)ethyl)-1,2-dimethyl-1H-indole (c3)



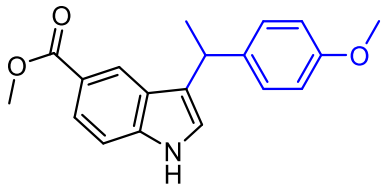
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 3:97)
Isolated yield: 94% (26.1 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.77 (d, *J* = 7.33 Hz, 3H), 2.35 (s, 3H), 3.66 (s, 3H), 3.78 (s, 3H), 4.42 (q, *J* = 7.31 Hz, 1H), 6.82 (m, 2H), 6.98 (td, ^{3}J = 7.49 Hz, ^{4}J = 0.98 Hz, 1H), 7.13 (td, ^{3}J = 7.09 Hz, ^{4}J = 1.03 Hz, 1H), 7.24-7.30 (m, 3H), 7.42 (d, *J* = 7.94 Hz, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 10.6, 21.0, 29.5, 35.0, 55.3, 108.6, 113.5, 115.7, 118.5, 119.4, 120.3, 126.7, 128.3, 132.4, 136.8, 138.5, 157.5 ppm.
HRMS: *m/z* for $[C_{19}H_{21}NO]^+$ [M^+] calcd: 279.1623, found: 279.1617.
Spectral data matches those reported in the literature.[10]

Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-6-carboxylate (c4)



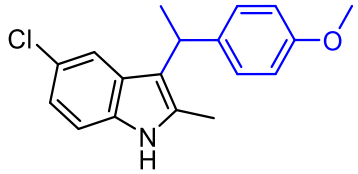
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:9)
Isolated yield: 91% (28.1 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.77 (d, *J* = 7.14 Hz, 3H), 3.86 (s, 3H), 4.00 (s, 3H), 4.42 (q, *J* = 7.11 Hz, 1H), 6.91 (m, 2H), 7.23-7.30 (m, 3H), 7.46 (d, *J* = 8.41 Hz, 1H), 7.78 (dd, ^{3}J = 8.41 Hz, ^{4}J = 1.32 Hz, 1H), 8.20 (s, 1H) 8.48 (br. s, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 22.5, 36.0, 52.0, 55.3, 113.5, 113.8, 119.3, 120.2, 122.2, 123.6, 124.5, 128.3, 130.4, 136.0, 138.6, 157.9, 168.3 ppm.
HRMS: *m/z* for $[C_{19}H_{19}NO_3]^+$ [M^+] calcd: 309.1365, found: 309.1353.

Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-5-carboxylate (c5)



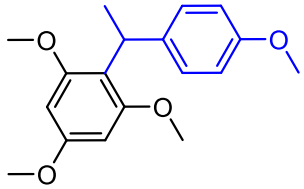
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:9)
Isolated yield: 92% (28.4 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.74 (d, *J* = 7.16 Hz, 3H), 3.83 (s, 3H), 4.00 (s, 3H), 4.43 (q, *J* = 7.14 Hz, 1H), 6.88 (m, 2H), 7.07 (d, *J* = 1,43 Hz, 1H), 7.27 (m, 2H), 7.38 (d, *J* = 8.92 Hz, 1H), 7.92 (dd, ^{3}J = 8.55 Hz, ^{4}J = 1.49 Hz, 1H), 8.27 (d, *J* = 0.65 Hz, 1H) 8.34 (br. s, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 22.6, 35.8, 51.8, 55.2, 110.8, 113.8, 121.3, 122.3, 122.6, 123.4, 123.4, 126.5, 128.3, 138.5, 139.3, 157.9, 168.3 ppm.
HRMS: *m/z* for $[C_{19}H_{19}NO_3]^+$ [M^+] calcd: 309.1365, found: 309.1359.

5-chloro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c6)



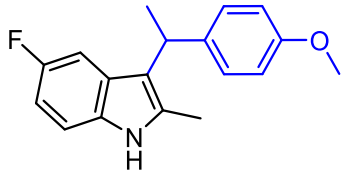
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 91% (29.3 mg, pale yellow solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.78 (d, *J* = 7.33 Hz, 3H), 2.38 (s, 3H), 3.84 (s, 3H), 4.38 (q, *J* = 7.31 Hz, 1H), 6.87 (m, 2H), 7.07 (dd, ^{3}J = 8.52 Hz, ^{4}J = 1.99 Hz, 1H), 7.20 (d, *J* = 8.52 Hz, 1H), 7.24-7.3 (m, 2H), 7.40 (d, *J* = 1.75 Hz, 1H), 7.79 (br. s, 1H) ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 12.3, 20.7, 34.5, 55.3, 111.1, 113.6, 116.3, 118.7, 120.9, 124.6, 128.2, 128.9, 132.1, 133.7, 137.8, 157.6 ppm.
HRMS: *m/z* for $[C_{18}H_{18}ClNO]^+$ [M^+] calcd: 299.1077, found: 299.1069.

1,3,5-trimethoxy-2-(1-(4-methoxyphenyl)ethyl)benzene (c7)



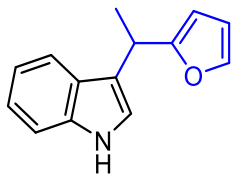
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 93 % (28.1 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.69 (d, *J* = 7.30 Hz, 3H), 3.77 (s, 6H), 3.83 (s, 3H), 3.86 (s, 3H), 4.77 (q, *J* = 7.29 Hz, 1H), 6.20 (s, 2H), 6.84 (m, 2H), 7.27 (m, 2H), ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 18.1, 32.3, 55.2, 55.3, 55.8, 91.5, 113.0, 116.0, 128.2, 138.9, 157.1, 159.0, 159.4 ppm.
HRMS: *m/z* for $[C_{18}H_{22}O_4]^+$ [M^+] calcd: 302.1513, found: 302.1512.
Spectral data matches those reported in the literature.[11]

5-fluoro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c8)



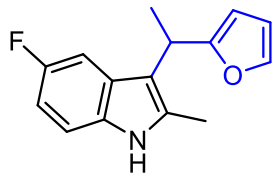
Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 93 % (26.0 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.76 (d, *J* = 7.33 Hz, 3H), 2.39 (s, 3H), 3.82 (s, 3H), 4.36 (q, *J* = 7.33 Hz, 1H), 6.81-6.89 (m, 3H), 7.04 (dd, ^{3}J = 10.24 Hz, ^{4}J = 2.46 Hz, 1H), 7.19 (dd, ^{3}J = 8.72 Hz, ^{4}J = 4.48 Hz, 1H), 7.24-7.29 (m, 2H), 7.74 (br. s, 1H), ppm.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ = -125.62 (s, 1F), ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 12.3, 20.5, 34.55, 55.3, 104.4, (d, *J* = 23.71 Hz), 108.7, (d, *J* = 26.14 Hz), 110.6, (d, *J* = 9.76 Hz), 113.6, 116.7, (d, *J* = 4.46 Hz), 128.2, 132.1, (d, *J* = 68.01 Hz), 137.9, 157.4 (d, *J* = 233.13 Hz), 157.6 ppm.
HRMS: *m/z* for $[C_{18}H_{18}ClNO]^+$ [M^+] calcd: 283.1367, found: 283.1368.
Spectral data matches those reported in the literature.[12]

3-(1-(furan-2-yl)ethyl)-1H-indole (d1)



Synthesized by using General Procedure – 1. Purified by flash column chromatography (EA/PE 1:19)
Isolated yield: 81 % (17.1 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.71 (d, *J* = 7.19 Hz, 3H), 4.44 (q, *J* = 7.16 Hz, 1H), 6.03 (d, *J* = 3.18 Hz, 1H), 6.28 (dd, ^{3}J = 3.13 Hz, ^{4}J = 1.24 Hz, 1H), 7.02 (d, *J* = 1.24 Hz, 1H), 7.08 (m, 1H), 7.18 (m, 1H), 7.31 (m, 1H), 7.35 (d, *J* = 8.15 Hz, 1H), 7.54 (d, *J* = 7.96 Hz, 1H), 7.96 (br. s, 1H), ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 20.0, 30.8, 104.5, 110.0, 111.1, 119.1, 119.3, 119.5, 121.1, 122.0, 126.5, 136.5, 140.9, 159.3 ppm.
HRMS: *m/z* for ($[C_{14}H_{13}NO]+H^+$) $[(M+H)^+]$ calcd: 212.1070, found: 212.1067.

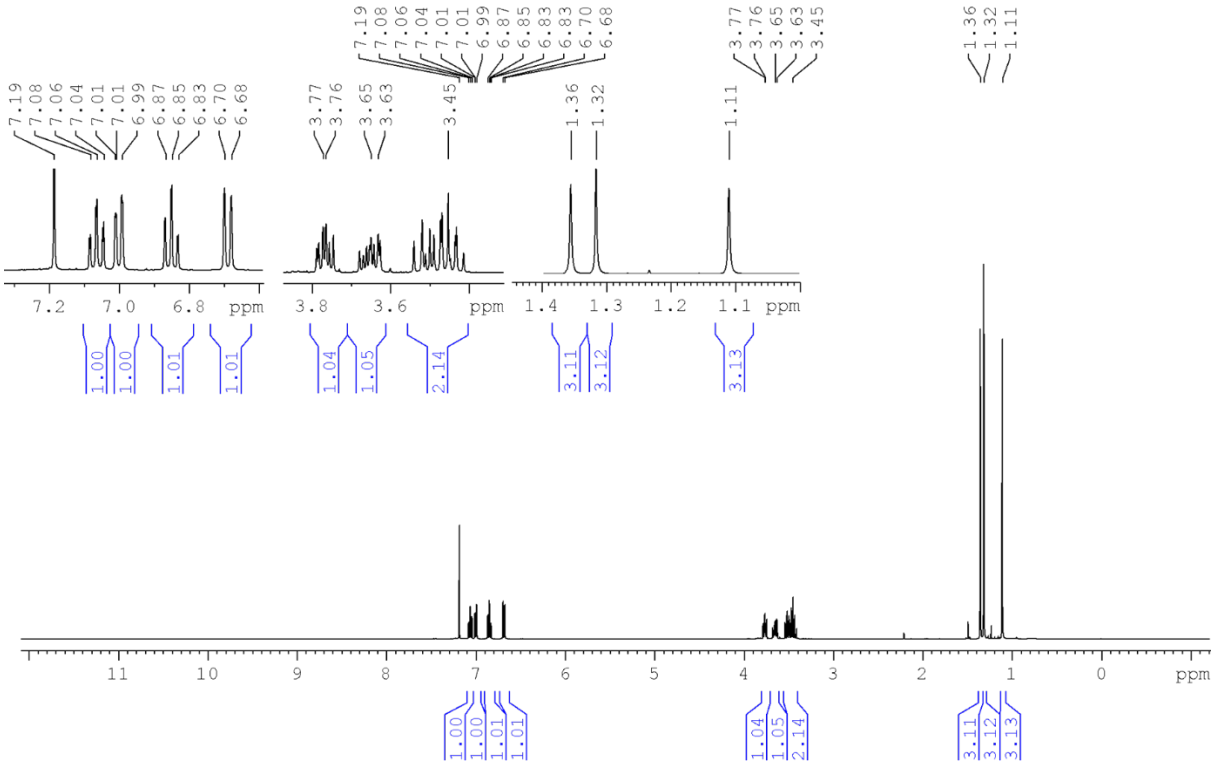
5-fluoro-3-(1-(furan-2-yl)ethyl)-2-methyl-1H-indole (d2)



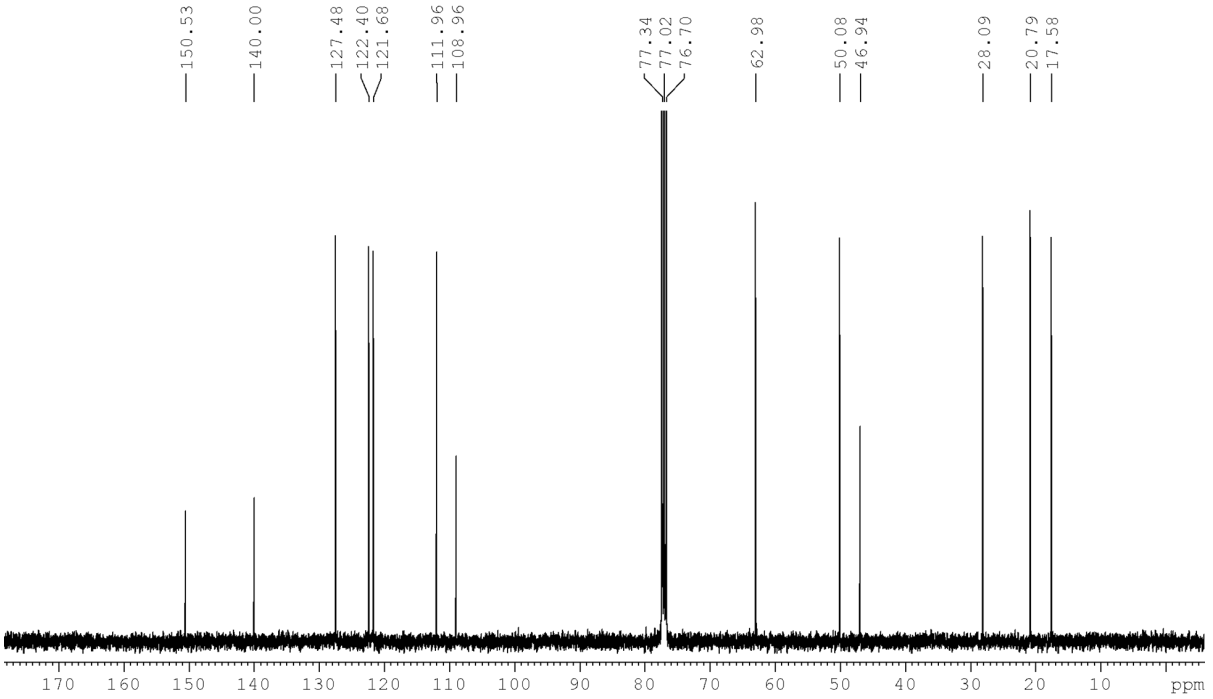
Synthesized by using General Procedure – 1. Purified by flash column chromatography (PE/EA 19:1)
Isolated yield: 93 % (20.6 mg, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.66 (d, *J* = 7.25 Hz, 3H), 2.35 (s, 3H), 4.32 (q, *J* = 7.12 Hz, 1H), 6.11 (m, 1H), 6.31 (dd, ^{3}J = 3.12 Hz, ^{4}J = 1.89 Hz, 1H), 6.81 (td, ^{3}t = 9.04 Hz, ^{4}J = 2.51 Hz, 1H), 6.98 (dd, ^{3}J = 10.24 Hz, ^{4}J = 2.51 Hz, 1H), 7.15 (dd, ^{3}J = 8.74 Hz, ^{4}J = 4.47 Hz, 1H), 7.31 (m, 1H), 7.72 (br. s, 1H), ppm.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ = -125.56 (s, 1F), ppm.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 12.0 19.0, 30.2, 103.9, 104.2, 104.9, 108.8, (d, *J* = 26.35 Hz), 110.0, 110.6, (d, *J* = 9.88 Hz), 114.0, (d, *J* = 4.77 Hz), 127.8, (d, *J* = 9.90 Hz), 132.2, (d, *J* = 93.99 Hz), 141.1, 157.5, (d, *J* = 233.28 Hz), 158.7 ppm.
HRMS: *m/z* for ($[C_{15}H_{14}FNO]+H^{+}$) $[(M+H)^{+}]$ calcd: 244.1132, found: 244.1131.

10. NMR spectra of isolated compounds

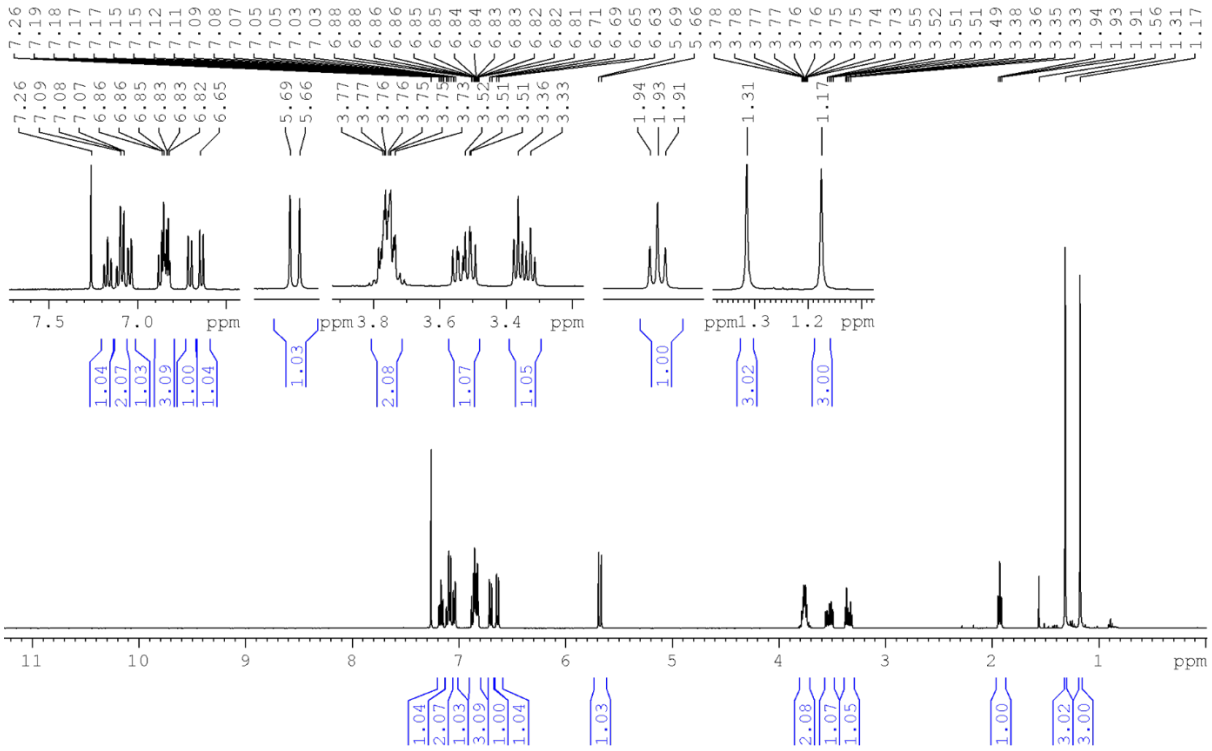
^{1}H NMR spectrum of 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (Int-SP-OH) (400 MHz, $CDCl_3$)



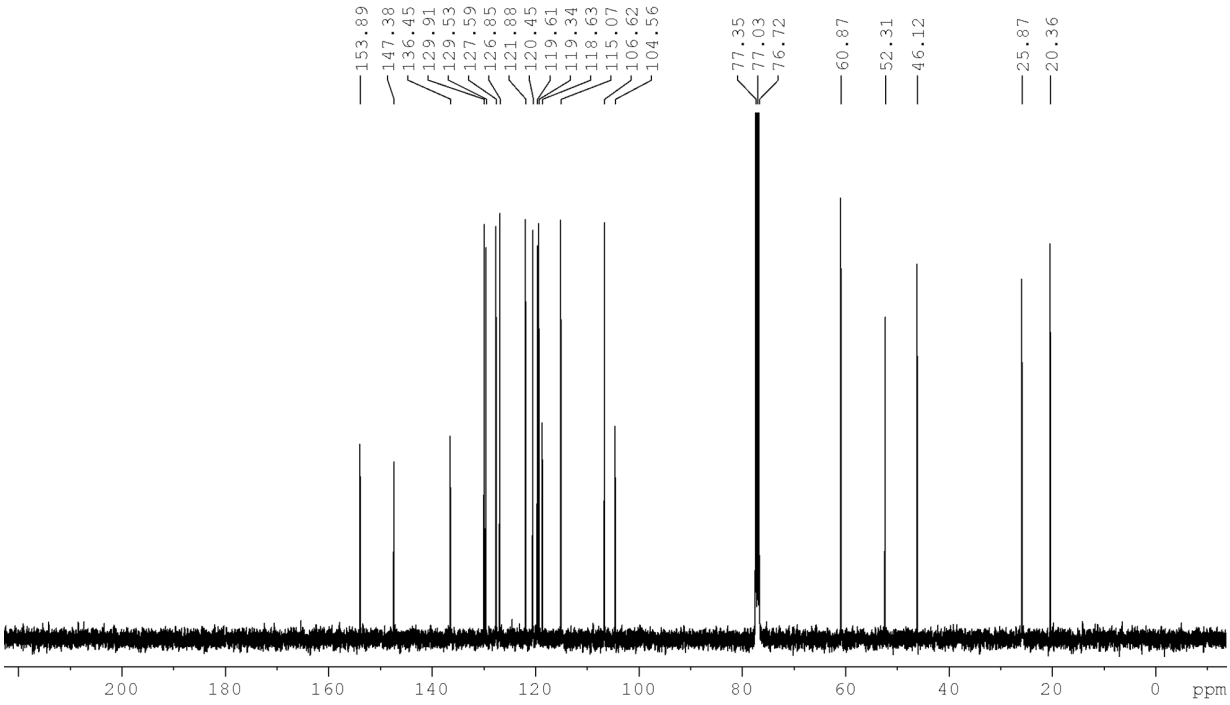
^{13}C{^{1}H} NMR spectrum of 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (Int-SP-OH) (101 MHz, $CDCl_3$)



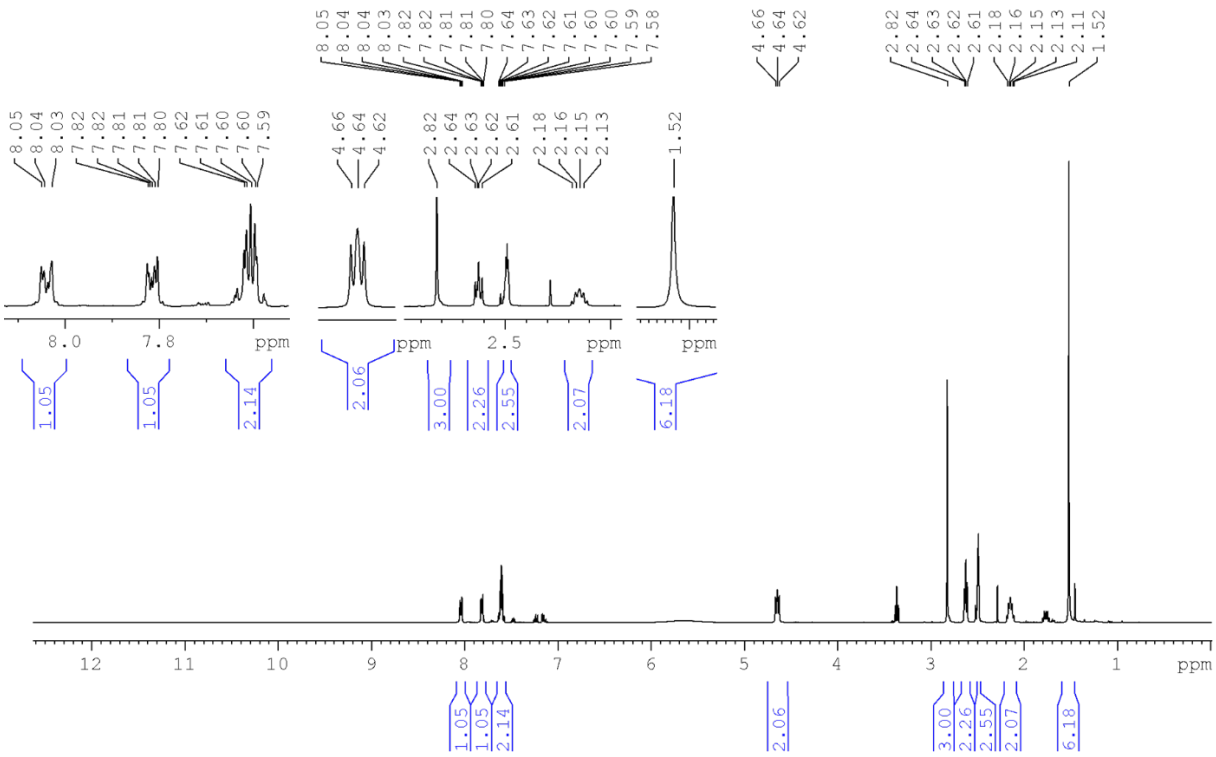
^{1}H NMR spectrum of 2-(3',3'-dimethylspiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol (SP-OH) (400 MHz, $CDCl_3$)



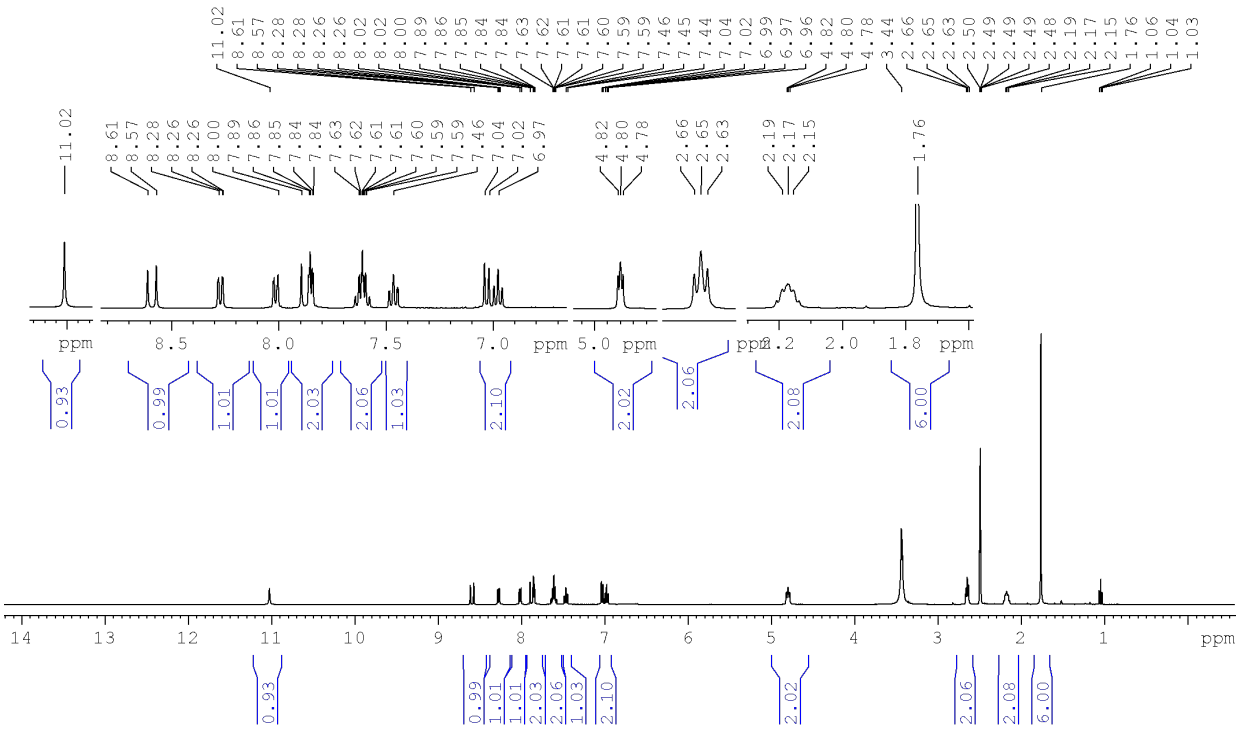
^{13}C{^{1}H} NMR spectrum of 2-(3',3'-dimethylspiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol (SP-OH) (101 MHz, $CDCl_3$)



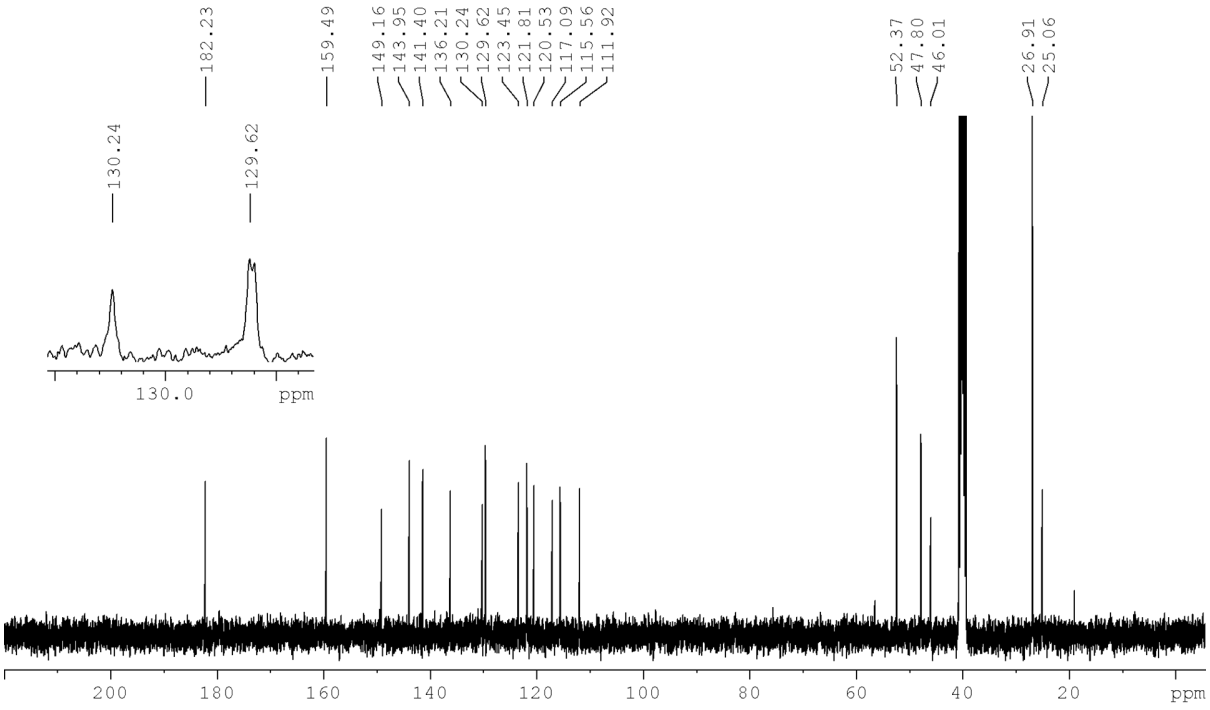
^{1}H NMR spectrum of 3-(2,3,3- trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (Int-SO3) (400 MHz, $(CD_3)_2SO$)



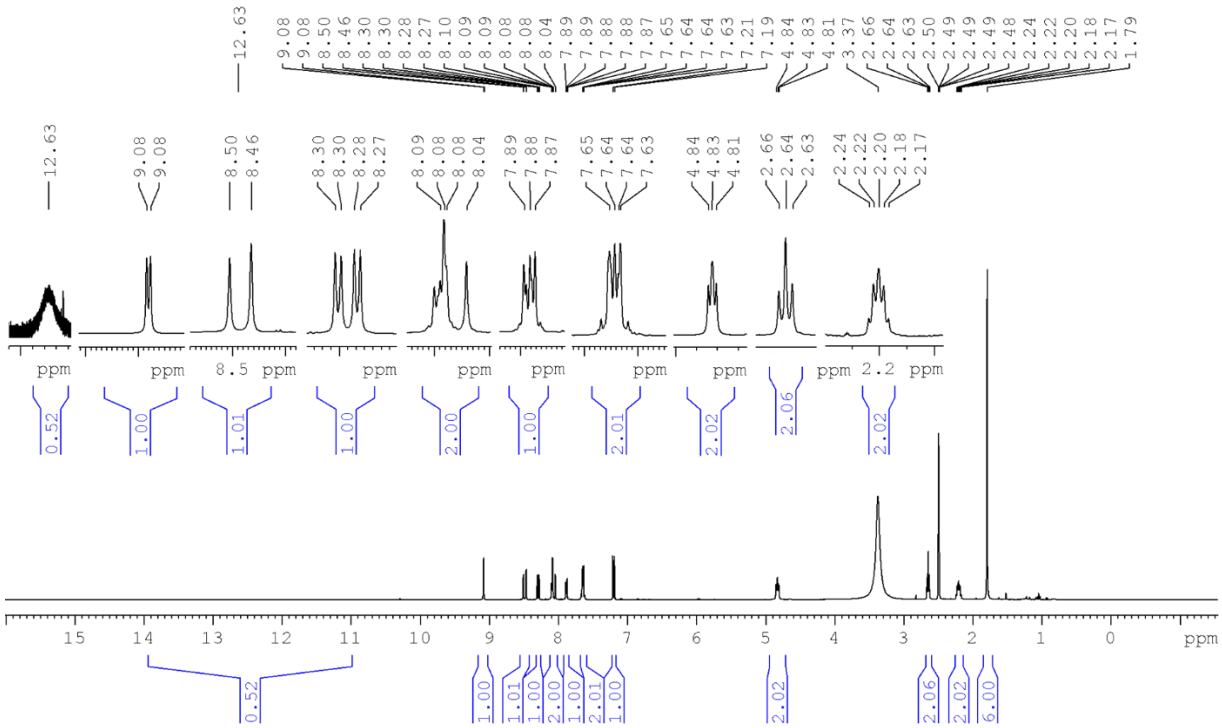
^{1}H NMR spectrum of (E)-3-(2-(2-hydroxystyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 3) (400 MHz, $(CD_3)_2SO$)



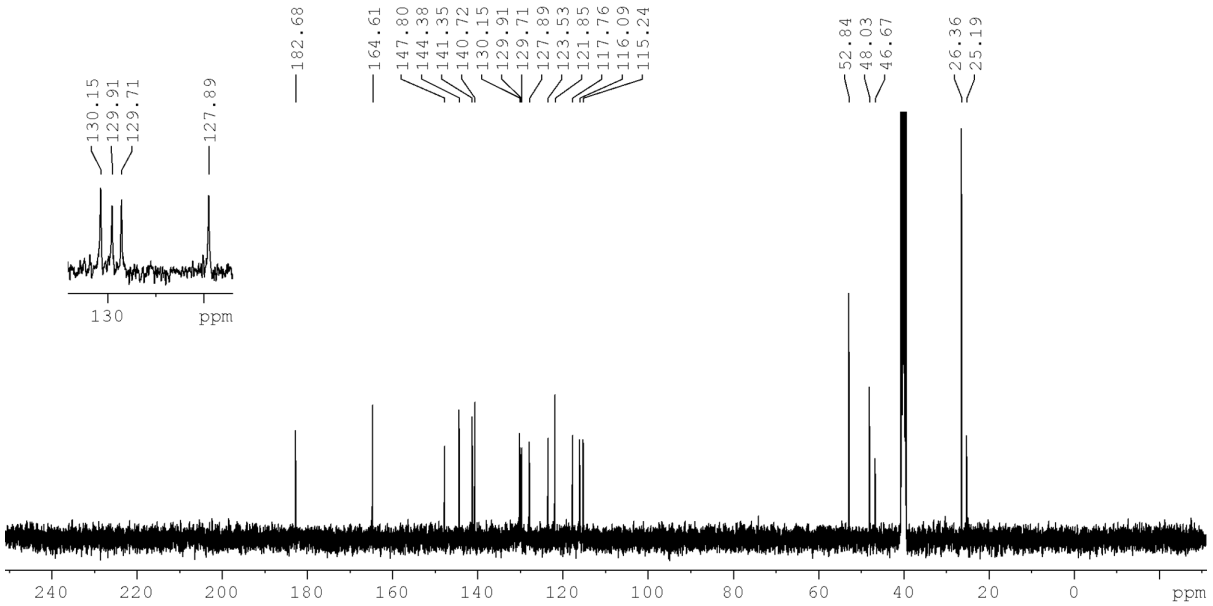
$^{13}C\{^{1}H\}$ NMR spectrum of (E)-3-(2-(2-hydroxystyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 3) (101 MHz, $(CD_3)_2SO$)



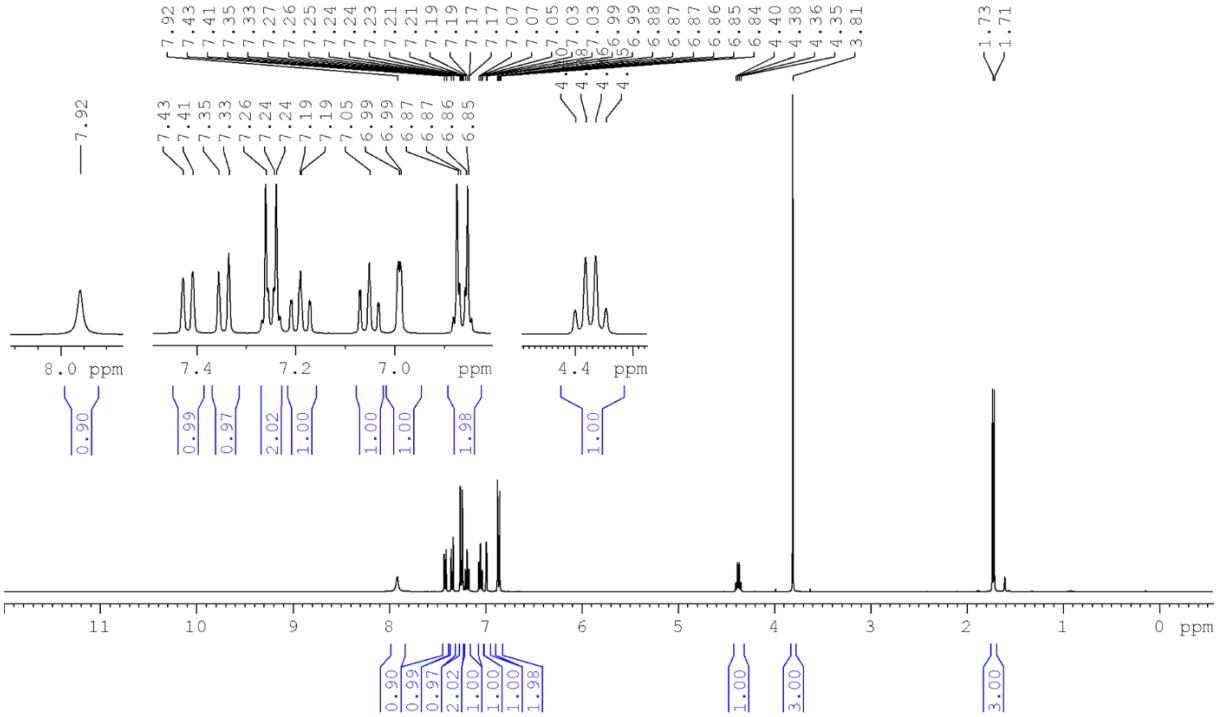
^{1}H NMR spectrum of (E)-3-(2-(2-hydroxy-5-nitrostyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 4) (101 MHz, $(CD_3)_2SO$)



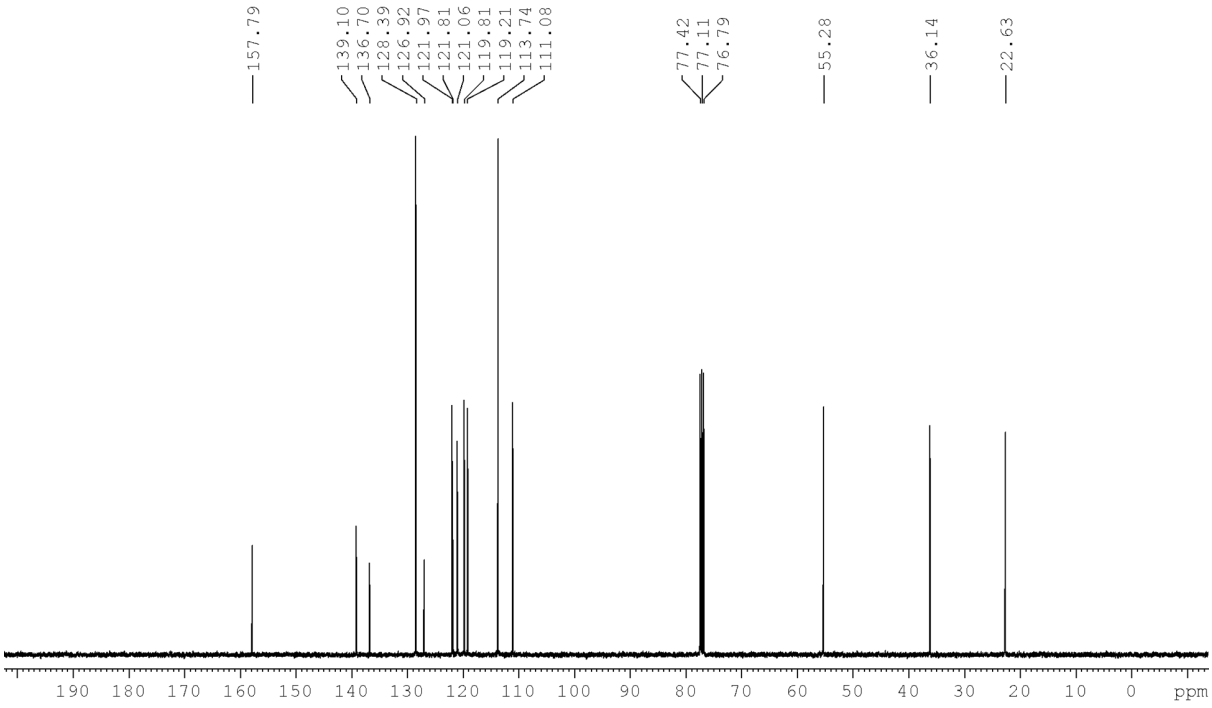
^{13}C{^{1}H} NMR spectrum of (E)-3-(2-(2-hydroxy-5-nitrostyryl)-3,3-dimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (MCH - 4) (101 MHz, $(CD_3)_2SO$)



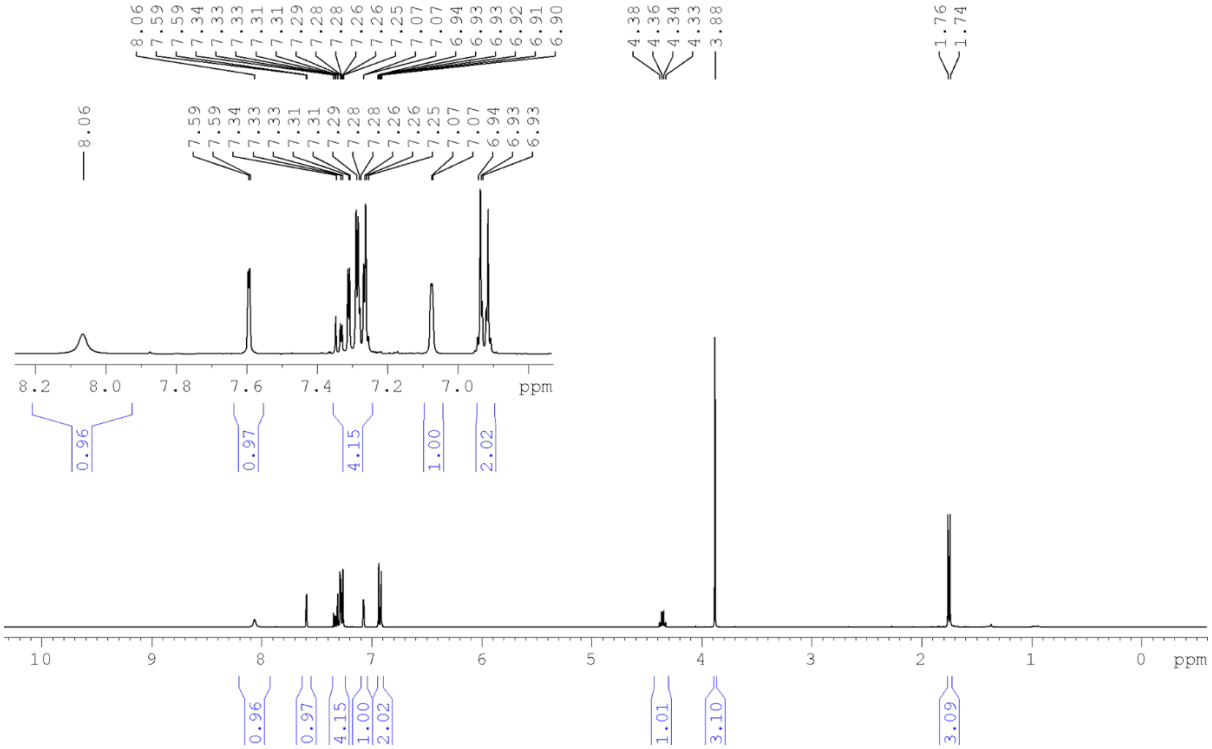
^{1}H NMR spectrum of 3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c1) (400 MHz, $CDCl_3$)



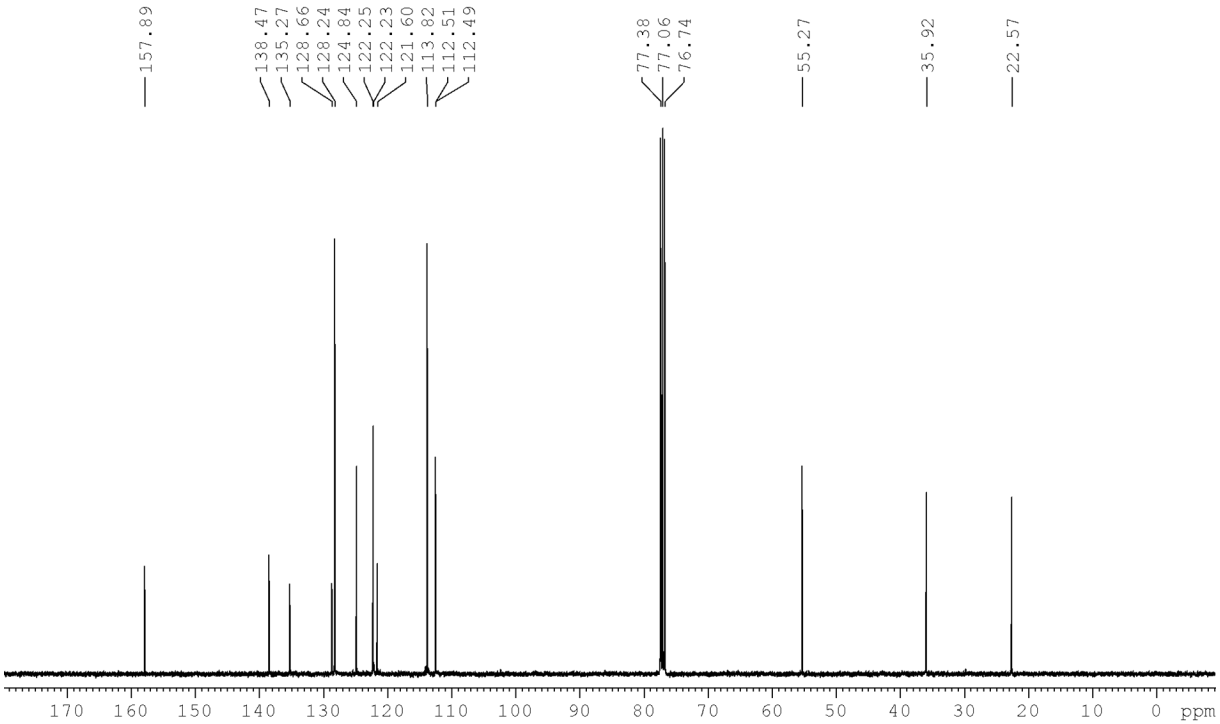
^{13}C{^{1}H} NMR spectrum of 3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c1) (101 MHz, $CDCl_3$)



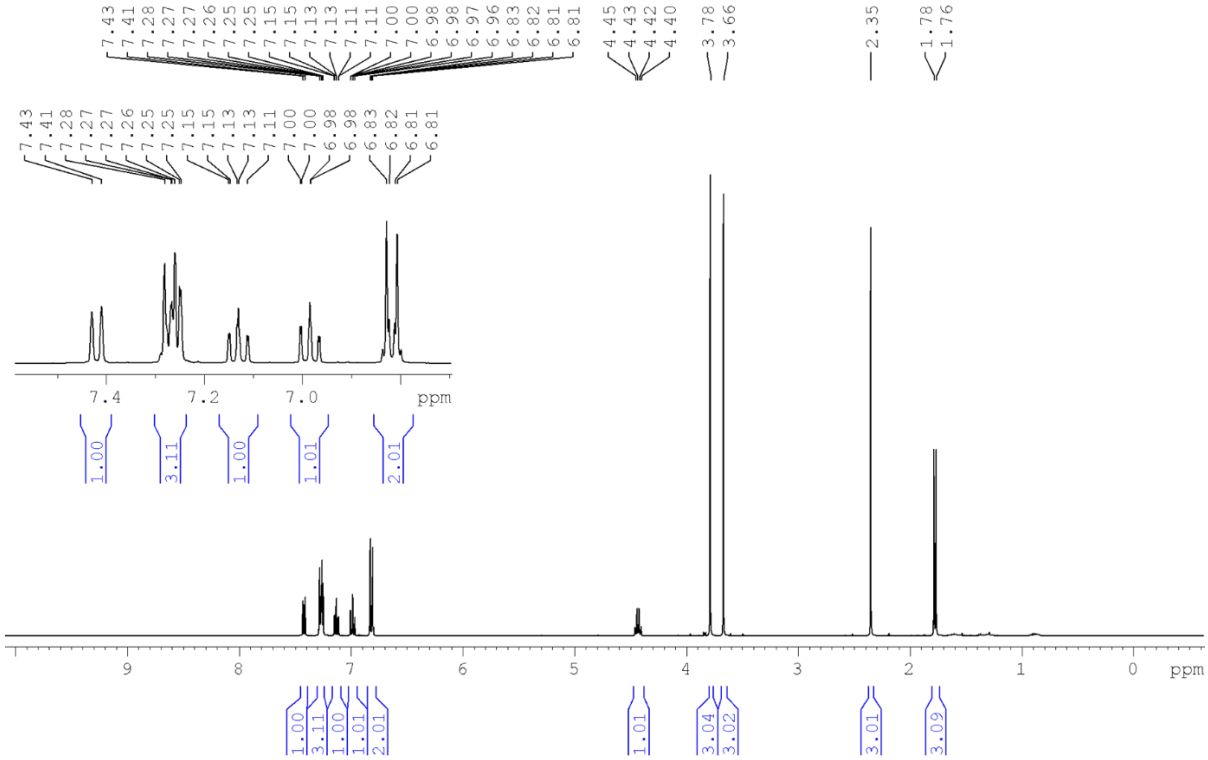
^{1}H NMR spectrum of 5-bromo-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c2) (400 MHz, $CDCl_3$)



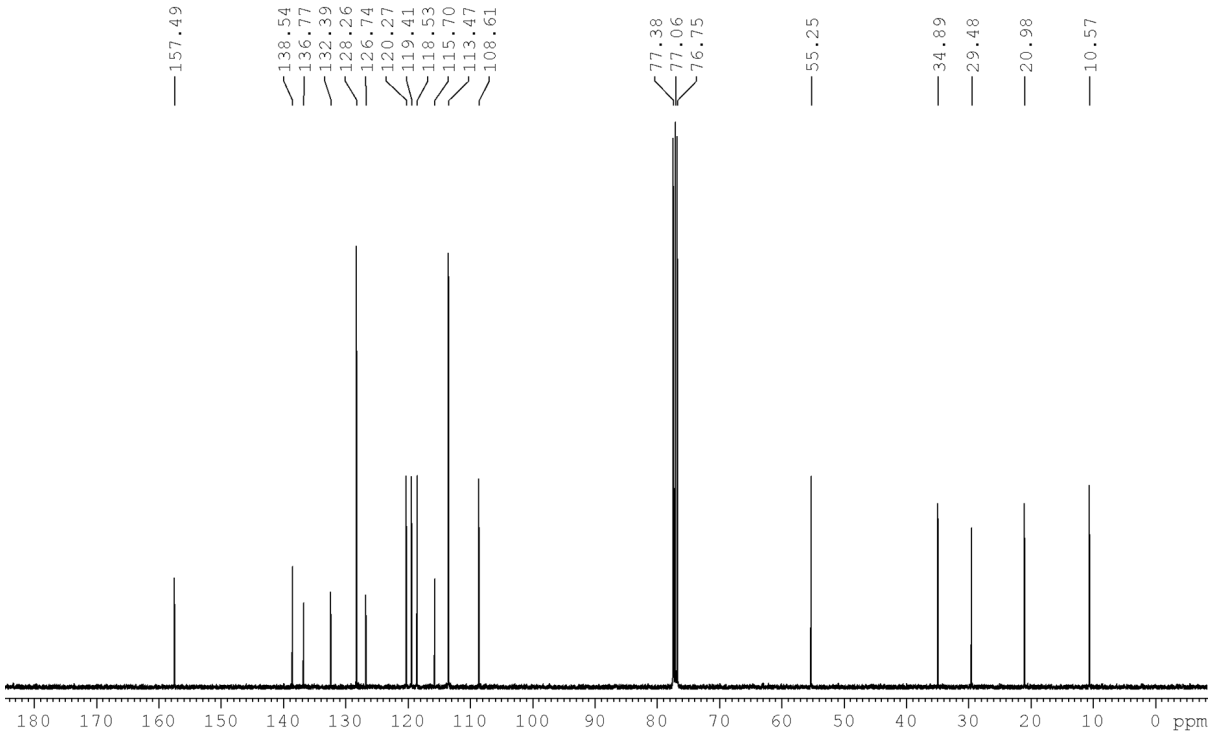
^{13}C{^{1}H} NMR spectrum of 5-bromo-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (c2) (101 MHz, $CDCl_3$)



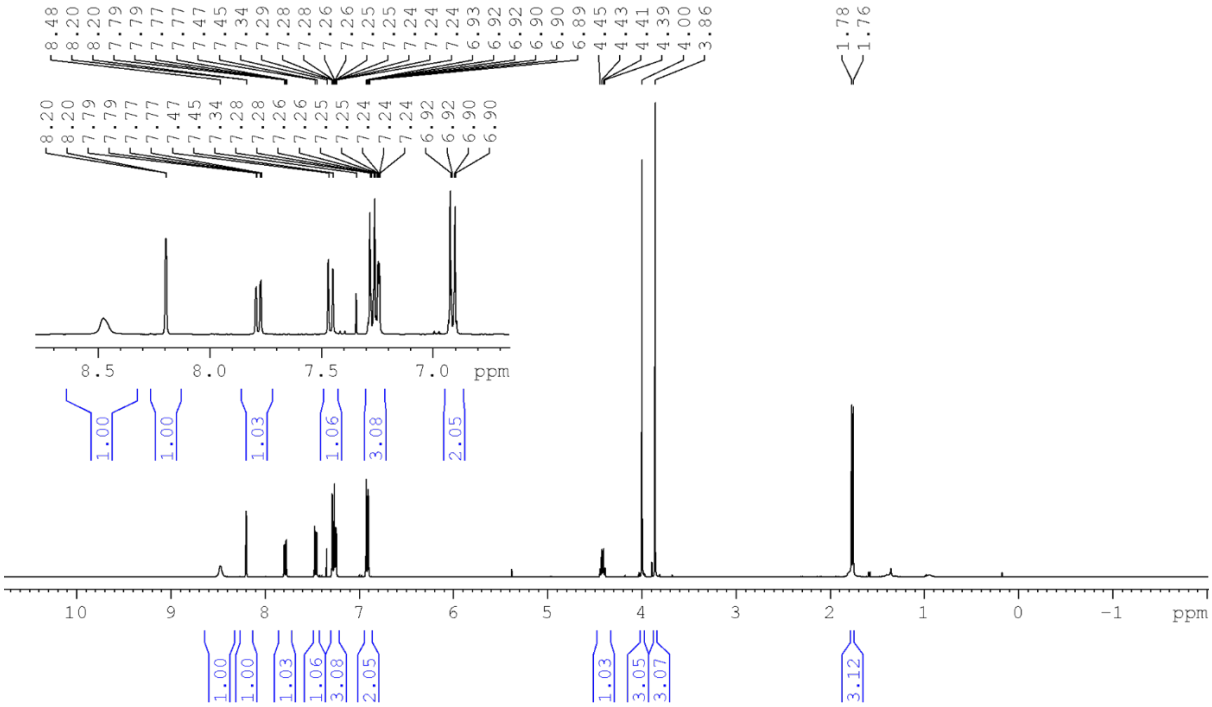
^{1}H NMR spectrum of 3-(1-(4-methoxyphenyl)ethyl)-1,2-dimethyl-1H-indole (c3)(400 MHz, $CDCl_3$)



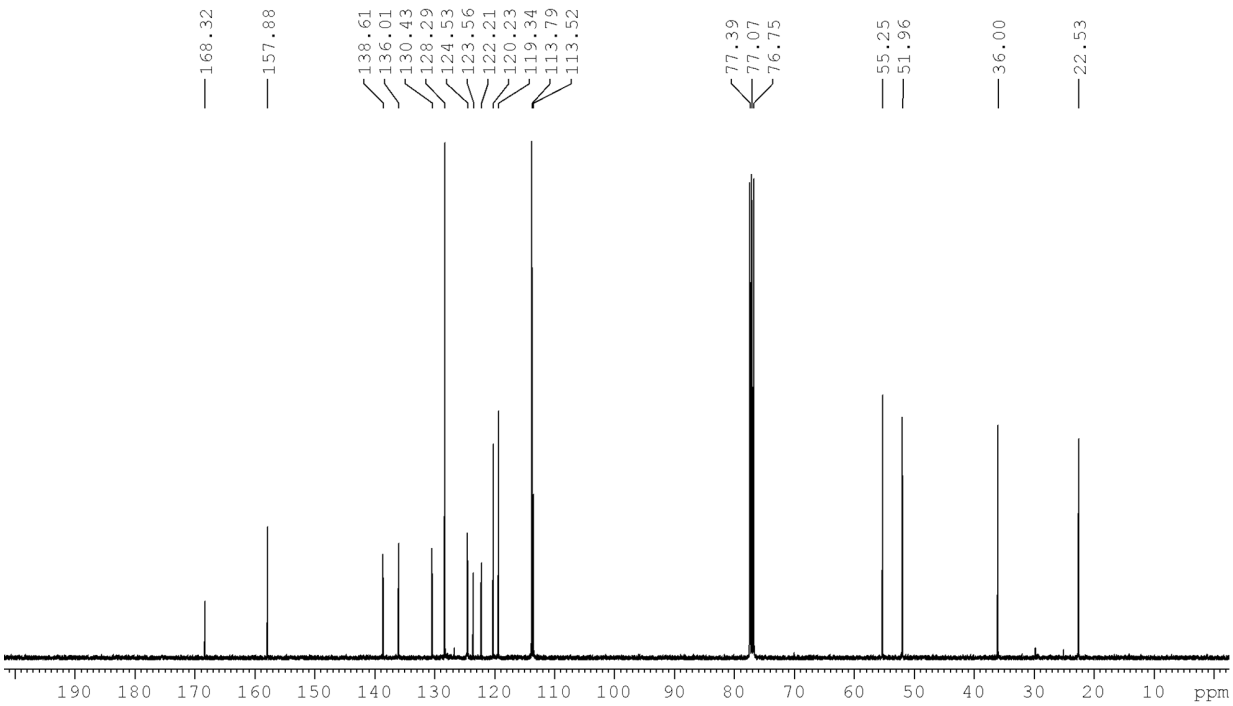
^{13}C{^{1}H} NMR spectrum of 3-(1-(4-methoxyphenyl)ethyl)-1,2-dimethyl-1H-indole (c3) (101 MHz, $CDCl_3$)



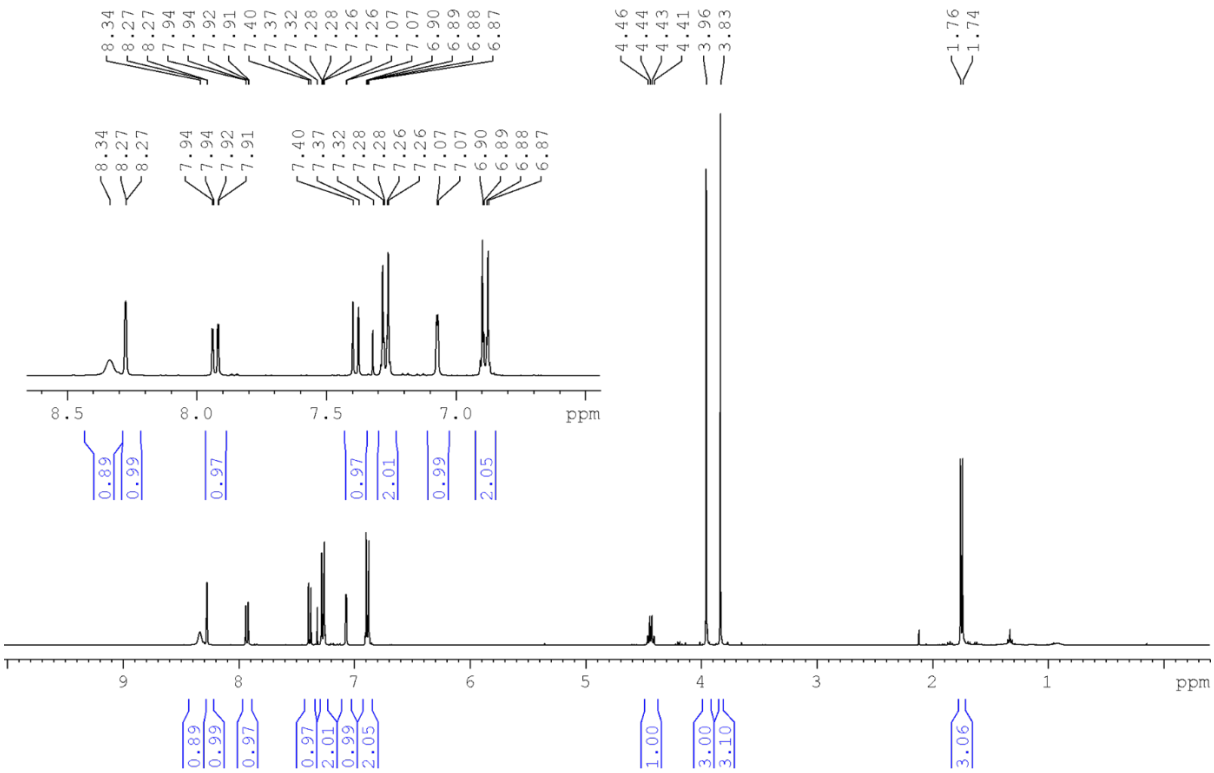
^{1}H NMR spectrum of Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-6-carboxylate (c4) (400 MHz, $CDCl_3$)



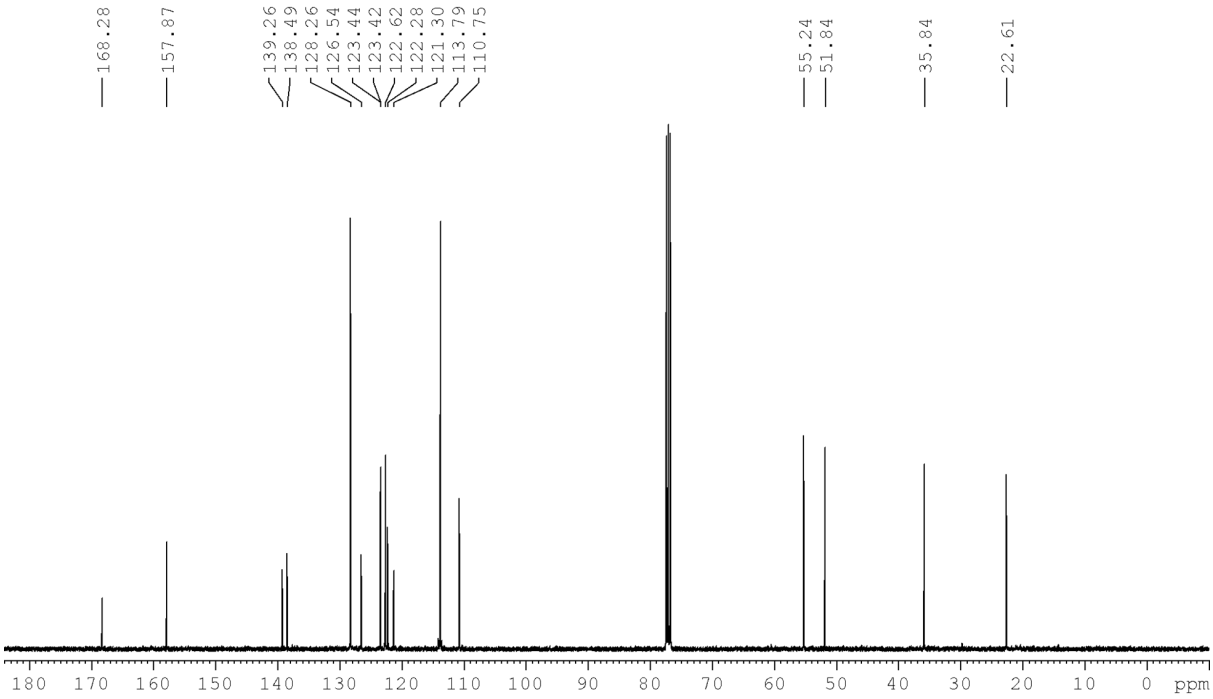
^{13}C{^{1}H} NMR spectrum of Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-6-carboxylate (c4) (101 MHz, $CDCl_3$)



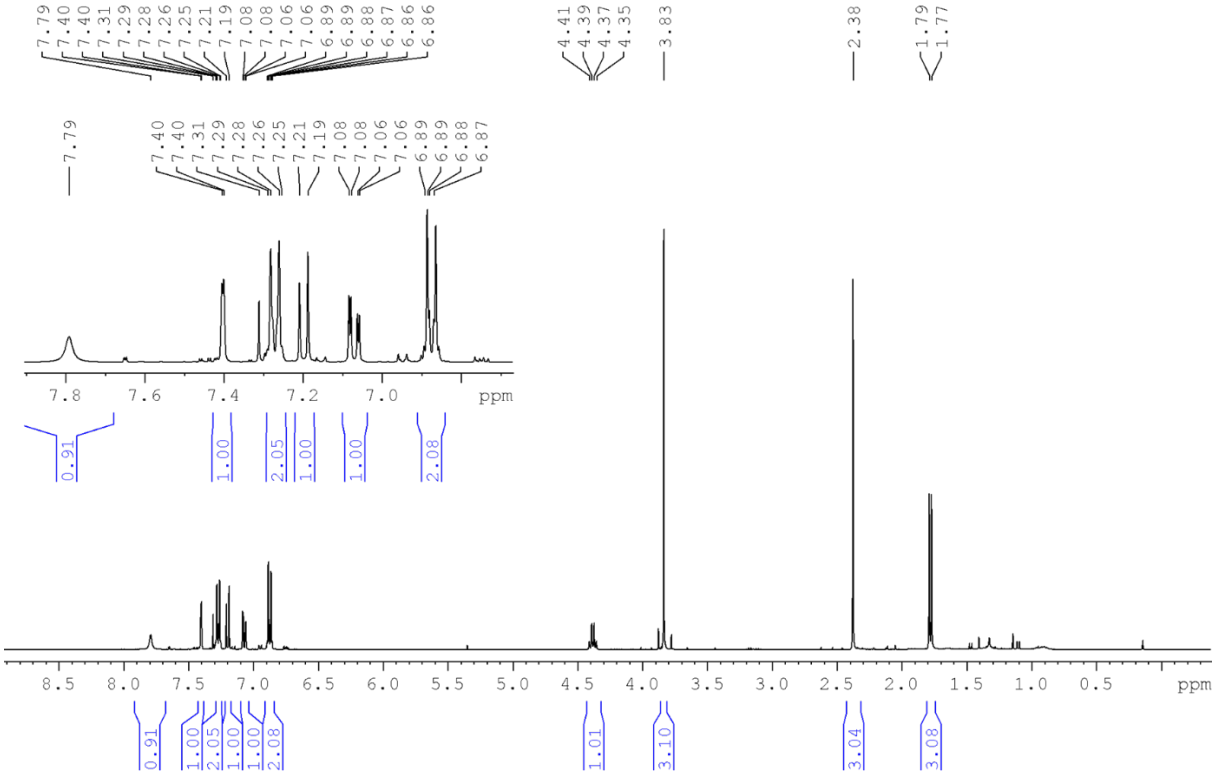
^{1}H NMR spectrum of Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-5-carboxylate (c5) (400 MHz, $CDCl_3$)



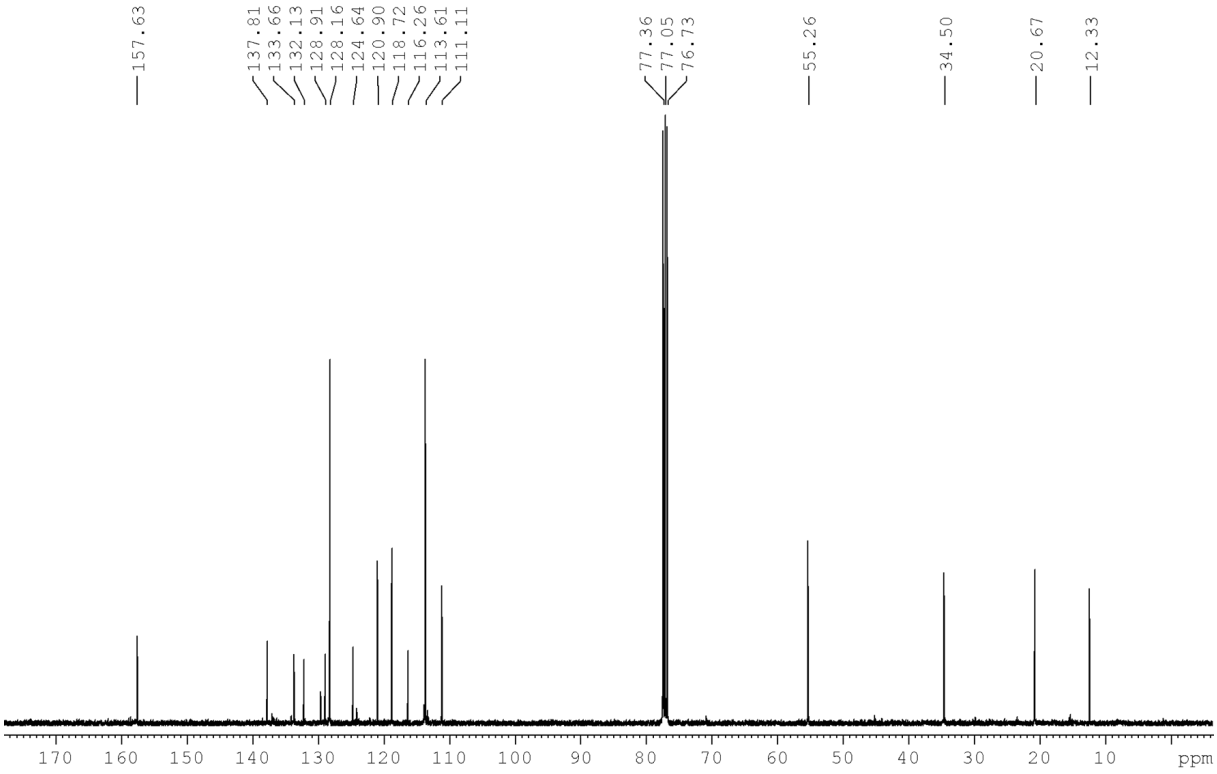
^{13}C{^{1}H} NMR spectrum of Methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-5-carboxylate (c5) (101 MHz, $CDCl_3$)



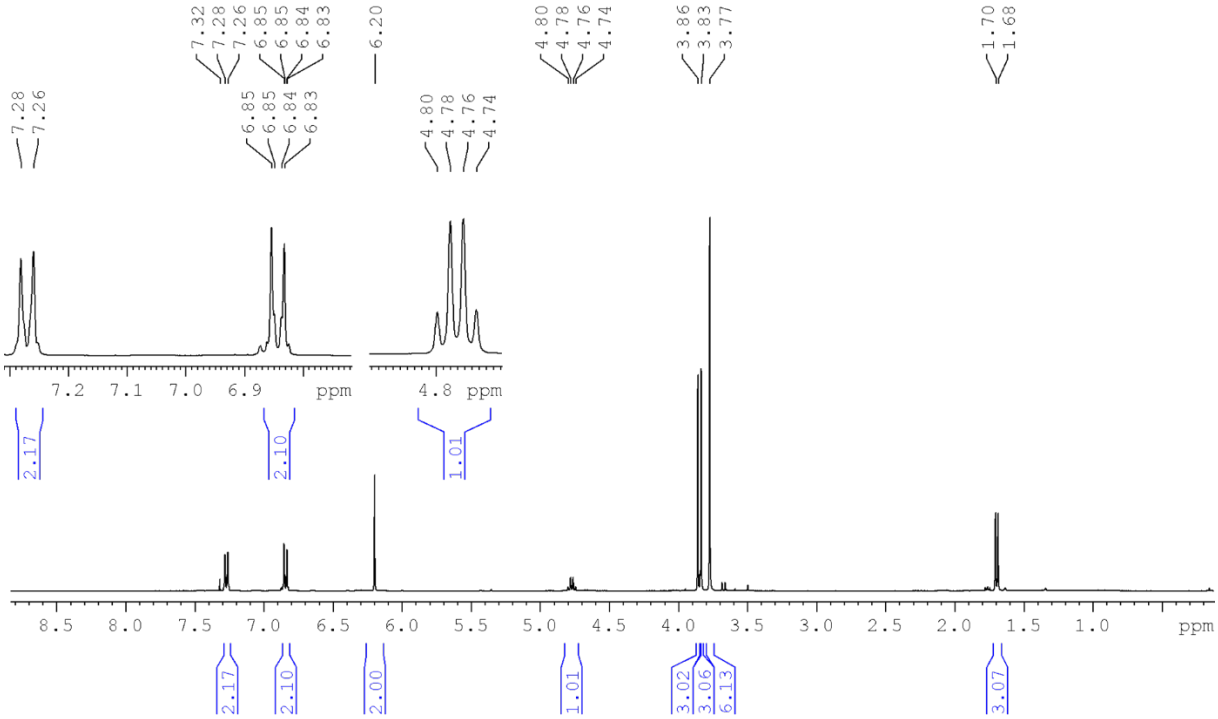
^{1}H NMR spectrum of 5-chloro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c6) (400 MHz, $CDCl_3$)



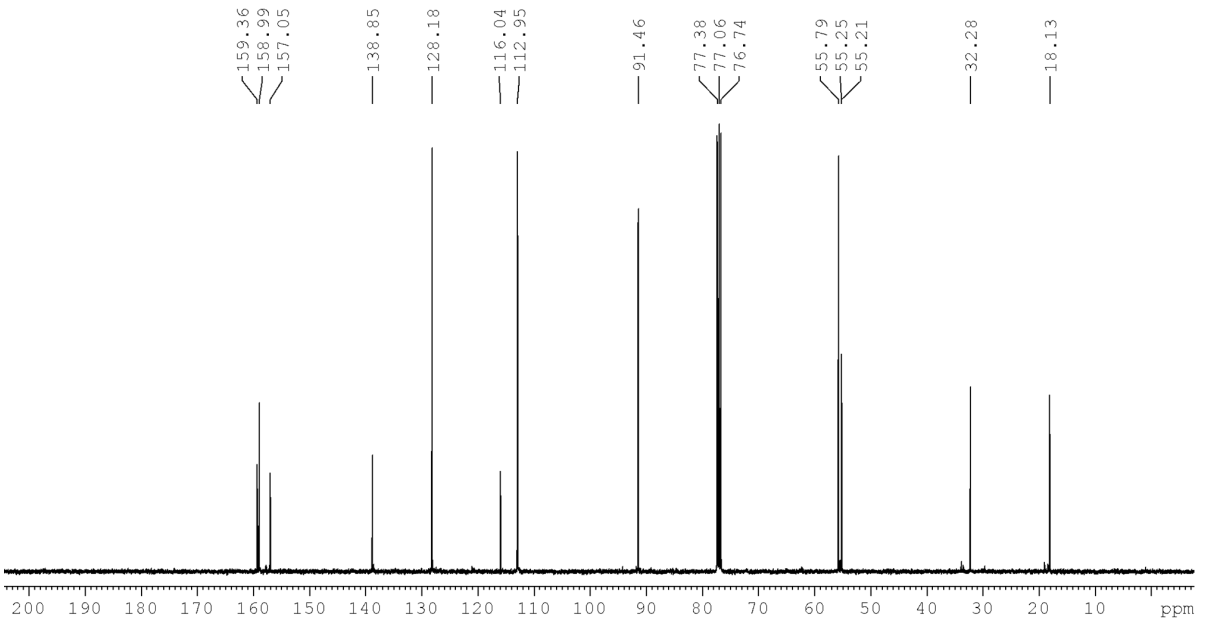
^{13}C{^{1}H} NMR spectrum of Methyl 5-chloro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c6) (101 MHz, $CDCl_3$)



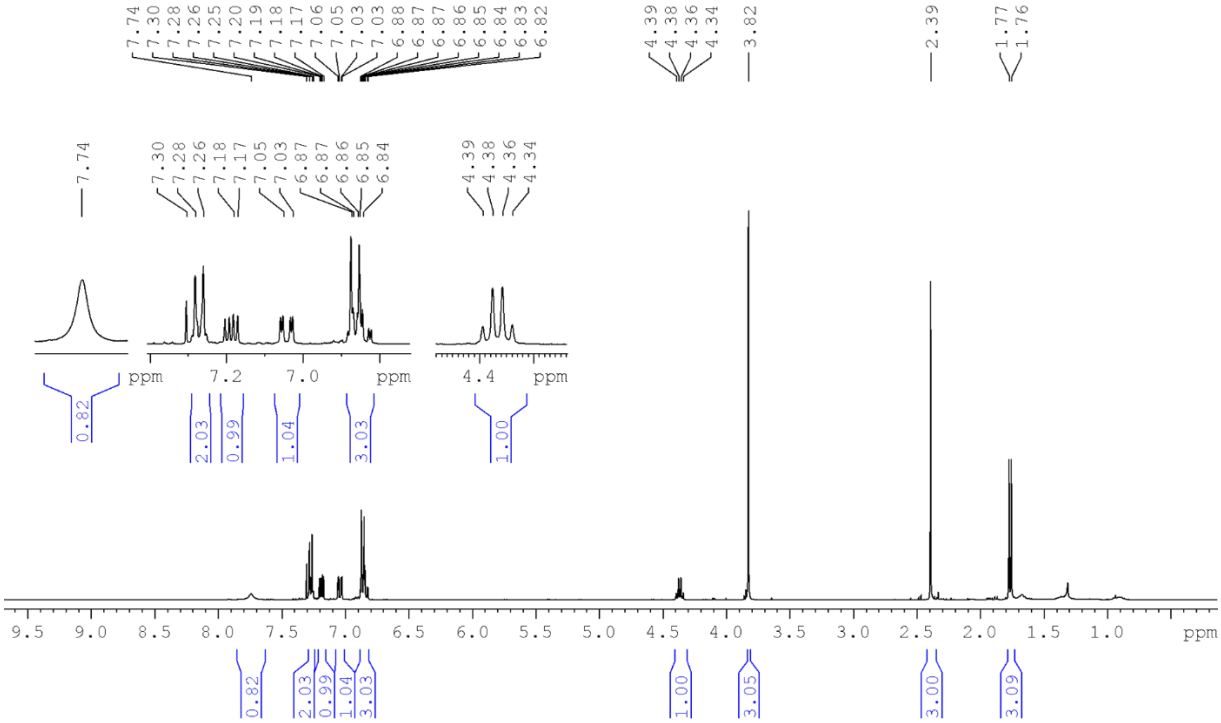
^{1}H NMR spectrum of 1,3,5-trimethoxy-2-(1-(4-methoxyphenyl)ethyl)benzene (c7) (400 MHz, $CDCl_3$)



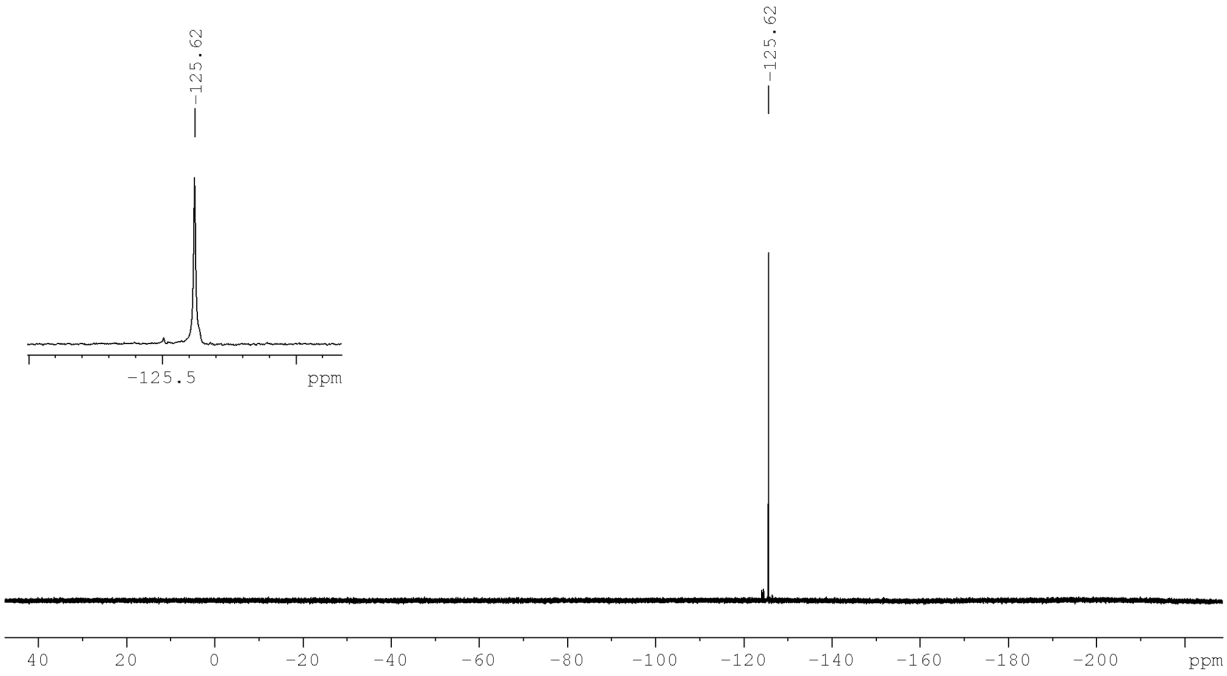
^{13}C{^{1}H} NMR spectrum of 1,3,5-trimethoxy-2-(1-(4-methoxyphenyl)ethyl)benzene (c7) (101 MHz, $CDCl_3$)



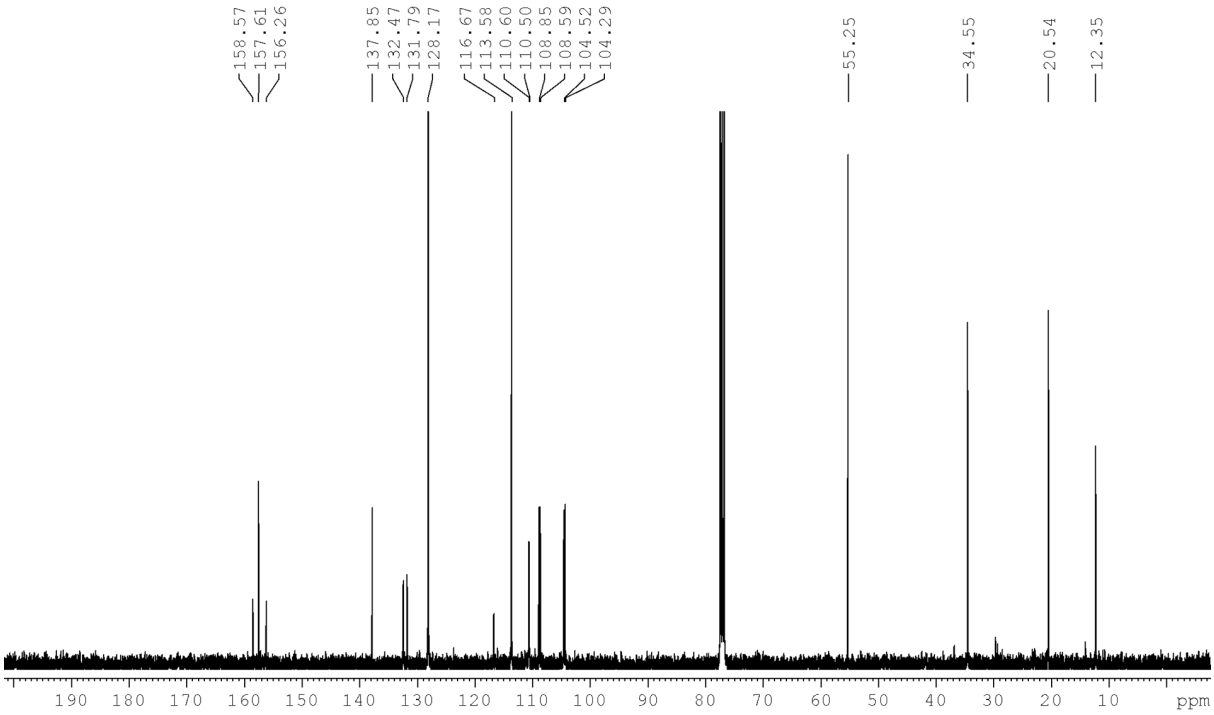
^{1}H NMR spectrum of 5-fluoro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c8) (400 MHz, $CDCl_3$)



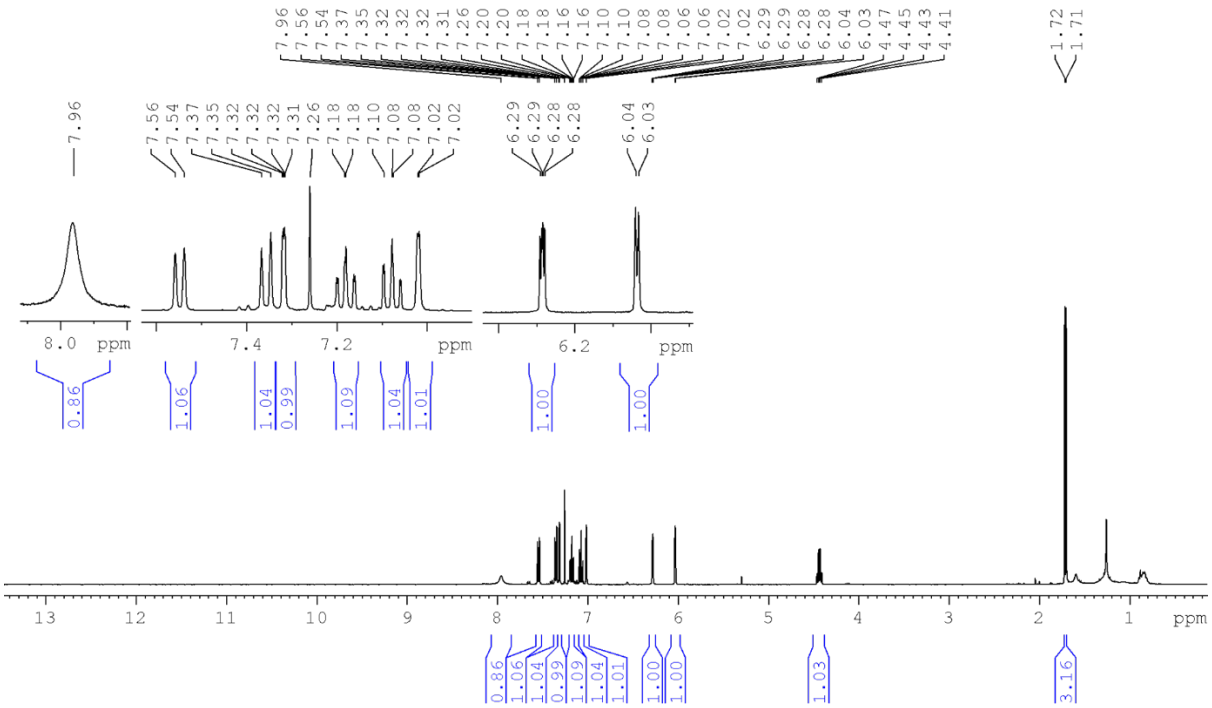
^{19}F{1H} NMR spectrum of 5-fluoro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c8) (377 MHz, $CDCl_3$)



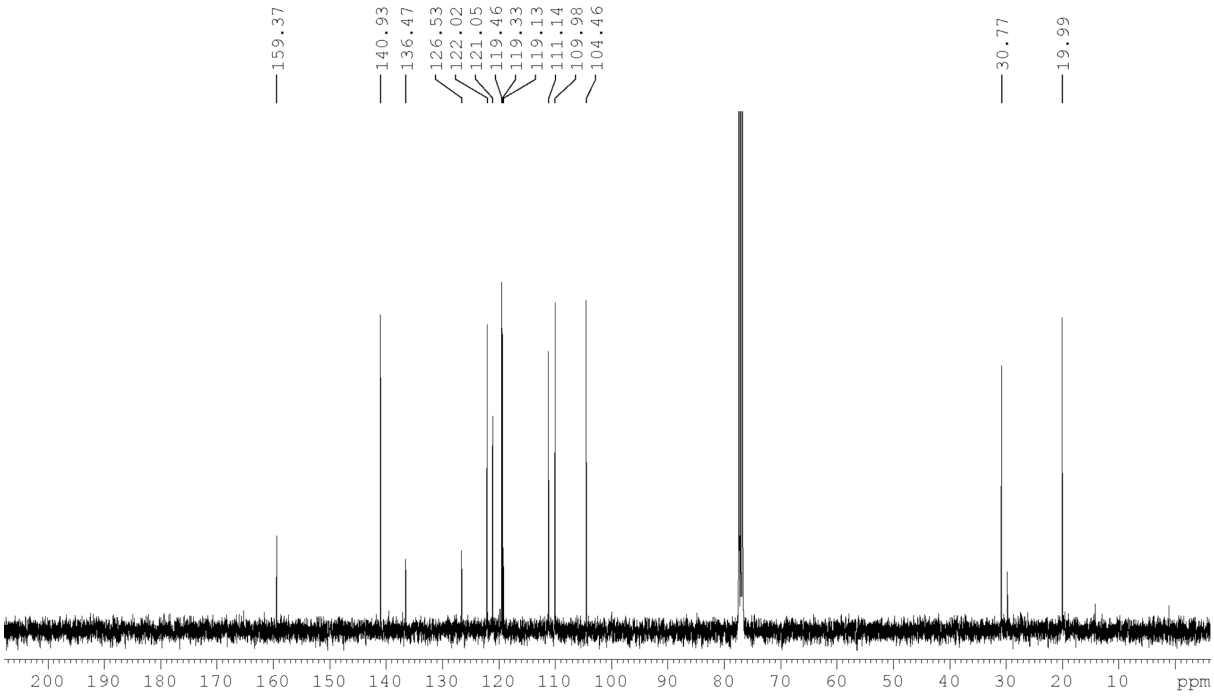
$^{13}C\{^{1}H\}$ NMR spectrum of 5-fluoro-3-(1-(4-methoxyphenyl)ethyl)-2-methyl-1H-indole (c8) (101 MHz, $CDCl_3$)



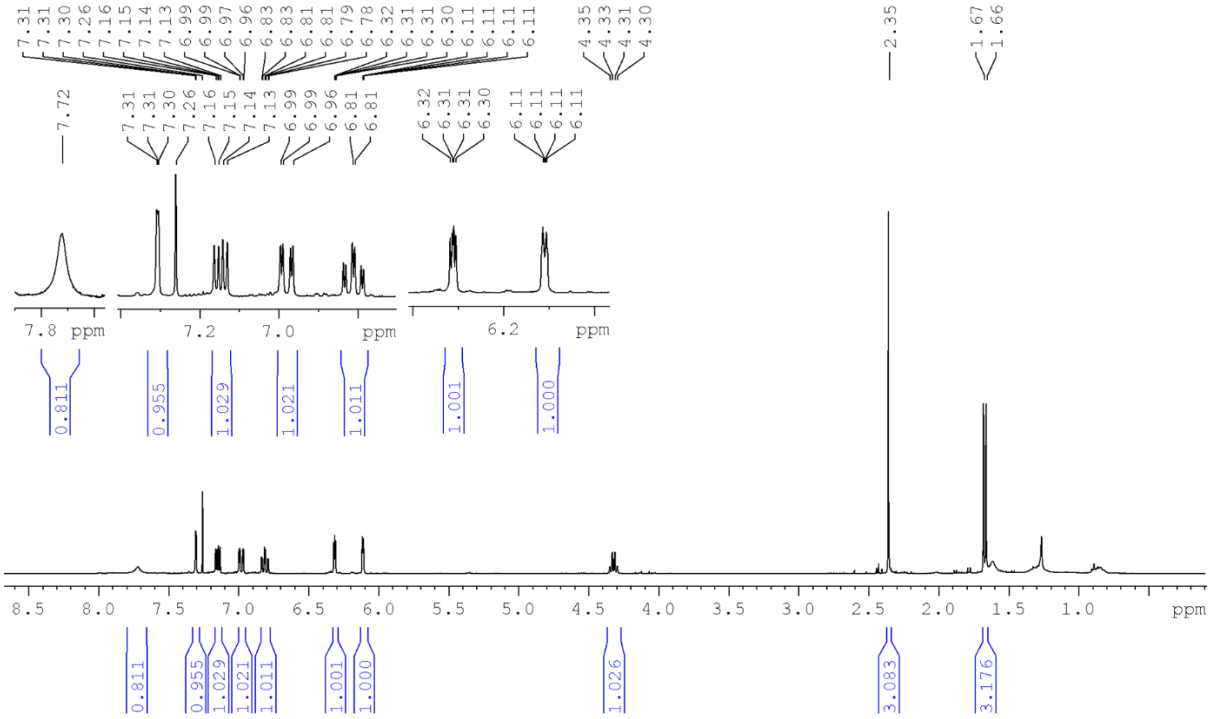
^{1}H NMR spectrum of 3-(1-(furan-2-yl)ethyl)-1H-indole (d1) (400 MHz, $CDCl_3$)



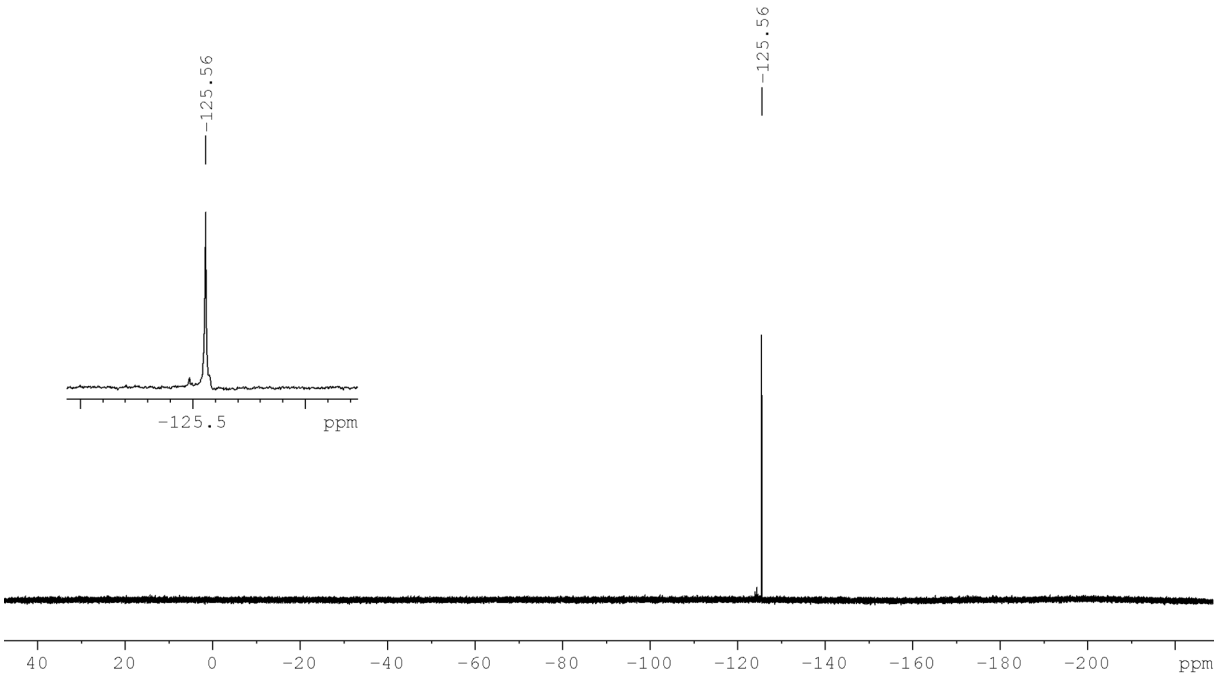
^{13}C{^{1}H} NMR spectrum of 3-(1-(furan-2-yl)ethyl)-1H-indole (d1) (101 MHz, $CDCl_3$)



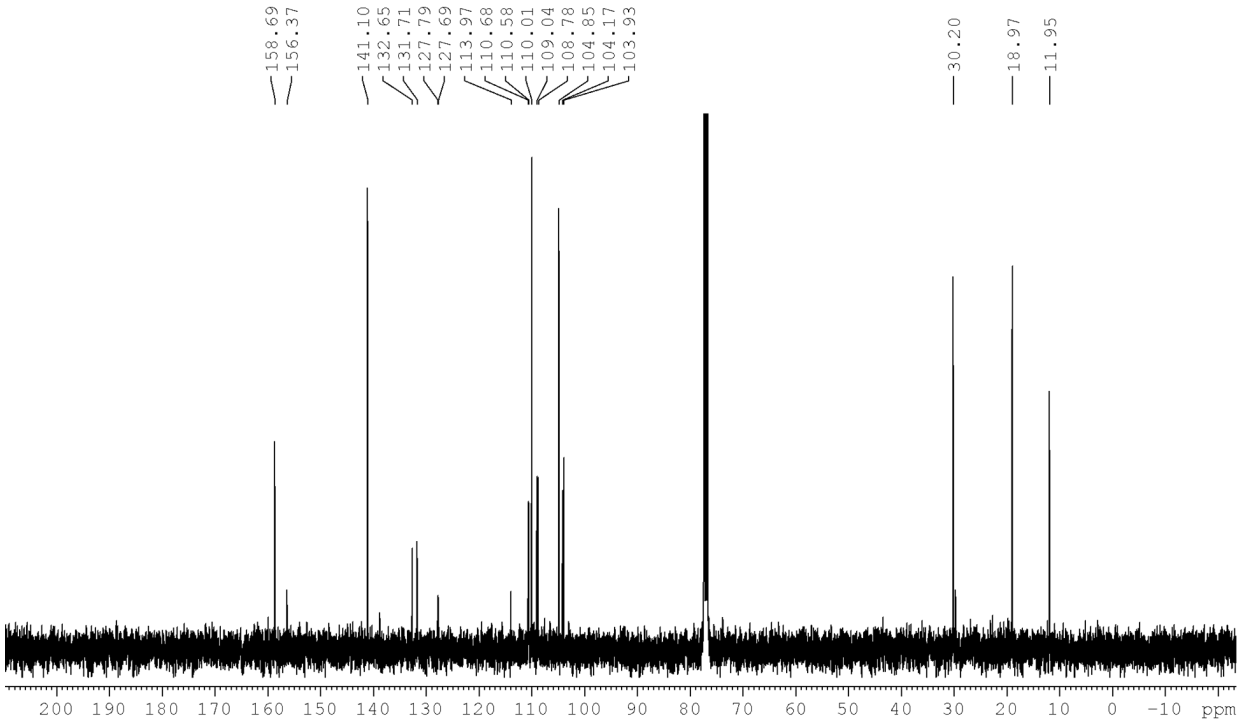
^{1}H NMR spectrum of 5-fluoro-3-(1-(furan-2-yl)ethyl)-2-methyl-1H-indole (d2) (400 MHz, $CDCl_3$)



^{19}F{1H} NMR spectrum of 5-fluoro-3-(1-(furan-2-yl)ethyl)-2-methyl-1H-indole (d2) (377 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum of 5-fluoro-3-(1-(furan-2-yl)ethyl)-2-methyl-1H-indole (d2) (101 MHz, $CDCl_3$)



11. References

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