

Intramolecular Radical Cyclization Approach to Access Highly Substituted Indolines and 2,3- Dihydrobenzofurans under Visible-Light

Clarice A. D. Caiuby,[a] Akbar Ali,[a] Vinicius T. Santana,[b] Francisco W. de S. Lucas, [a] Marília S. Santos,[a] Arlene G. Corrêa,[a] Otaciro R. Nascimento,[b] Hao Jiang[a] and Márcio W. Paixão [a],*

[a] Center of Excellence for Research in Sustainable Chemistry (CERSusChem), Department of Chemistry, Federal University of São Carlos – UFSCar, Rodovia Washington Luís, km 235 - SP-310 - São Carlos - São Paulo - Brazil -13565-905

E-mail: mwpaixao@ufscar.br

[b] Group of Molecular Biophysics "Sérgio Mascarenhas", São Carlos Institute of Physics – IFSC/USP, University of São Paulo, Avenida Trabalhador São Carlense, 400, São Carlos, SP – Brazil – 13560-970

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1. GENERAL INFORMATION

Commercially available reagents were used throughout, without purification unless otherwise stated or purified according to the procedures outlined in Purification of Common Laboratory Chemicals¹. All solvents were freshly dried and distilled. Oven or flame-dried glassware was used for all reactions which were stirred magnetically unless otherwise specified. Reactions were monitored by thin layer chromatography employing aluminium plates (Merck Kieselgel 60 GF254, 0.25 mm thickness) and visualized under ultraviolet light at 254 nm and stained with an ethanolic solution of potassium permanganate or acid vanillin. Column flash chromatography was performed using silica gel 60 (230–400 mesh).

NMR spectra were recorded at 400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as an internal standard. Coupling constant (*J*) are given in Hz. The following abbreviations (or combinations thereof) were used to explain the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, br = broad, dd = doublet of doublet, ddd = doublet of doublet of doublets, dt = doublet of triplet, ddt = doublet of doublet of triplets, tdd = triplet of doublet of doublet.

Melting points were determined using a Büchi M-560 Basic Melting Point Apparatus.

The mass spectra of high resolution were obtained using a micrOTOF Q II - TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA, USA) equipped with an ESI ion source (positive ionization mode). Protonated molecular ions (M+H)⁺, sodium adducts (M+Na)⁺ or potassium adducts (M+K)⁺ were used for empirical formula confirmation.

1.1. The reactor's LEDs and photochemical set up

The experiments under a light-emitting diode (LED RGB 5 m strip, 12 V DC, 150 LED/m) strip as a light source were performed using a photoreactor (aluminum flask 166 mm x 130 mm), equipped with a fan (100 mm) which can emit a red, green, blue and white light (Figure S1). The reactions were conducted in a sealed 5 mL transparent borosilicate glass vial equipped with a Teflon-coated magnetic bar.



Figure S1. Photochemical set up.

1.2. Determination of the Reactor's LEDs spectra and irradiance

The characterization of the emission spectra of the reactor's LEDs (Figure S1) was performed with aid of a spectrofluorometer (RF-5301PC Shimadzu Scientific Instruments). The reactor was placed in front of the spectrofluorometer detector, and the spectra of the white, blue, green and red LEDs were measured. After that, the determination of the irradiance of each LEDs at an area of 4.91 cm^2 in the reactor center was done by using a radiometer (laser power/energy meter, model FieldMaxII-TOP™ coupled to an EnergyMax Sensor™, model J-25MB-LE, Coherent Inc.). Figure S2 below shows the LEDs spectra and irradiance.

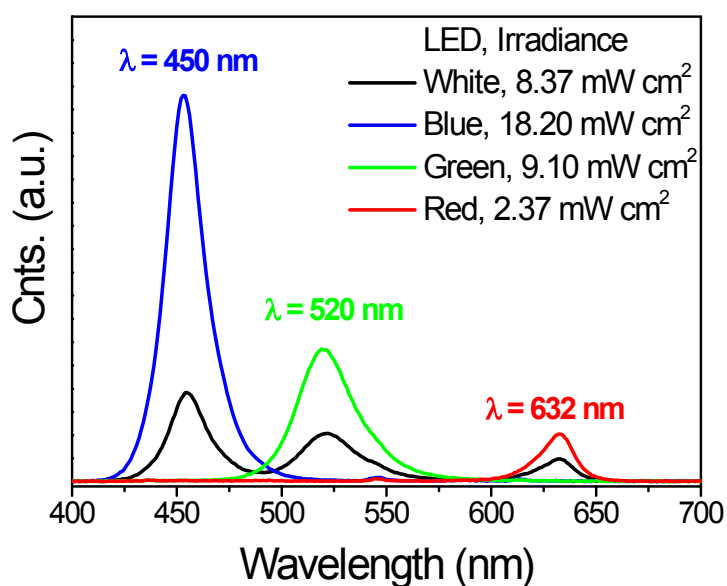
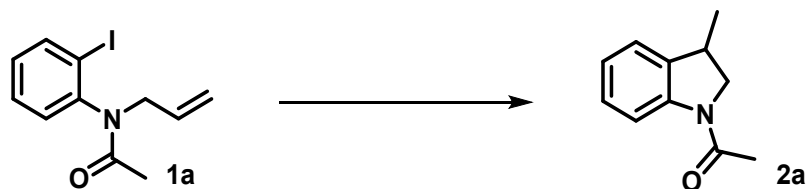


Figure S2. White, blue, green and red LED's spectra and their respective irradiances.

2. OPTIMIZATION STUDIES

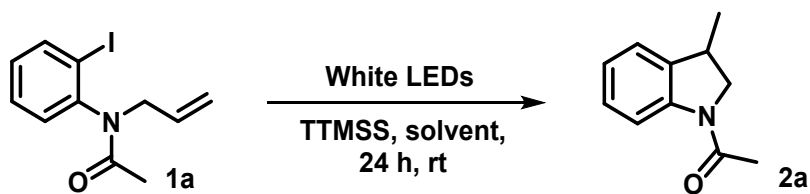
2.1. Screening and Control Experiments for Indoline Synthesis

Table S1. Reaction conditions and silane compound selection.^a



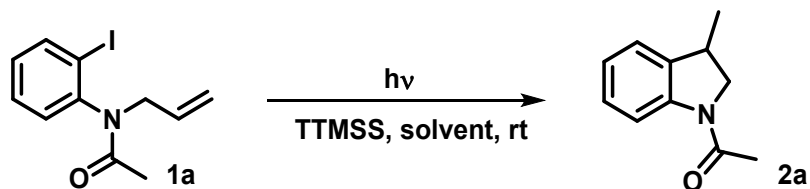
Entry	Silane	<i>hν</i>	Temp (°C)	Time (h)	Yield (%) ^b
1 ^{c,d}	TTMSS	CFL	rt	24	47
2 ^{c,e}	TTMSS	CFL	rt	24	50
3 ^c	TTMSS	CFL	rt	24	70
4 ^f	TTMSS	LEDs	rt	24	92
5 ^g	TTMSS	UV	rt	0.5	65
6 ^f	Et ₃ SiH	LEDs	rt	48	-
7 ^f	PhSiH ₃	LEDs	rt	48	-
8	TTMSS	darkness	rt	72	70
9	TTMSS	darkness	50	5	72
10	-	darkness	50	48	-
11 ^f	-	LED	rt	48	-

a] Unless otherwise specified reactions were performed using **1a** (0.20 mmol), silane (2 equiv), MeCN (0.4 mL). [b] Yield of isolated products. [c] Reaction vessel placed between two 12 W CFL lamp. [d] 1 equiv of TTMSS was used. [e] Reaction was performed with 1 equiv of TTMSS and 5 equiv. of EtOH. [f] Irradiated with a white LEDs strip. [g] UV radiation (40 W).

Table S2. Solvent screening.

Entry ^a	Solvent	Yield (%) ^b
1	DCM	40
2	THF	71
3	Dioxane	72
4	AcOEt	60
5	MeOH	43
6	EtOH	71
7	Acetone	91
8	MeCN	92

[a] Reactions were performed on 0.20 mmol scale, 2 equiv of TTMSS, 0.4 mL of solvent and using a white light-emitting diode (LED) strip as a light source. [b] Isolated yield.

Table S3. Wavelength evaluation.^a

Entry	λ (nm) ^b	Solvent	Time (h)	Yield (%) ^c
1	632	MeCN	12	46
2	520	MeCN	7	85
3	450	MeCN	5	98
4	450	Acetone	24	93

[a] Unless otherwise specified reactions were performed using **1a** (0.20 mmol), TTMSS (2 equiv, 0.40 mmol) and specified solvent (0.4 mL). [b] Irradiated with a LEDs strip. [c] Yield of isolated products.

Table S4. Analysis of the effect of substituents X and R.

White LEDs
TTMSS
MeCN, time, rt

Entry	R	X	Time (h)	Yield (%)
1	Acetyl	I	5	98
2	Acetyl	Br	24	49
3	Acetyl	H	48	-
4	Pivaloyl	I	24	90
5	Tosyl	I	48	86
6	Benzyl	I	48	Traces ^c
7	Ethyl	I	48	Traces ^c
8	H	I	48	Traces ^c

[a] Reactions were performed on 0.20 mmol scale, 2 equiv of TTMSS, 0.4 mL of solvent and using a white light-emitting diode (LEDs) strip as a light source. [b] Isolated yield. [c] Observed by GC-MS.

2.2. Screening and Control Experiments for 2,3-dihydrobenzofuran Synthesis

Table S5. Analysis of the effect light source.

LEDs Strip
TTMSS, solvent, rt

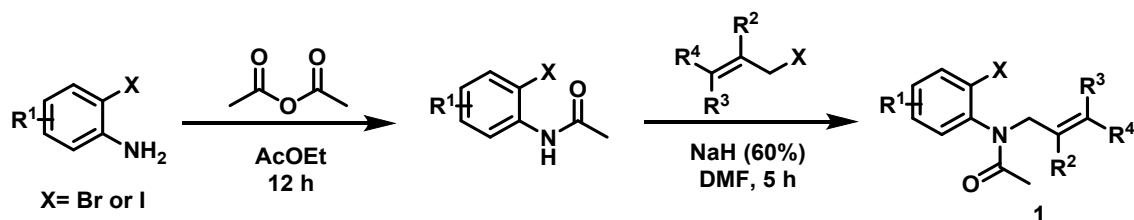
3b **4b**

Entry ^a	X	Light Source	Time (h)	Temperature (°C)	Yield (%) ^b
1	2	Blue (λ_{\max} = 450) ^c	12	25°C	74
2	2	Green (λ_{\max} = 520) ^c	24	25°C	54
3	2	Red (λ_{\max} = 632) ^c	24	25°C	Traces ^c
4	2	White^d	10	25°C	86
5	1	White ^d	24	25°C	63
6 ^e	2	-	24	50°C	60
7 ^e	2	-	48	25°C	-

[a] Reactions were performed on 0.20 mmol scale using 0.4 mL of solvent. [b] Isolated yields. [c] Reaction performed using light-emitting diode (LEDs). [d] Reaction performed using two 12 W LEDs lamp. [e] Reaction performed without light. [f] Observed by GC-MS.

3. EXPERIMENTAL PROCEDURES

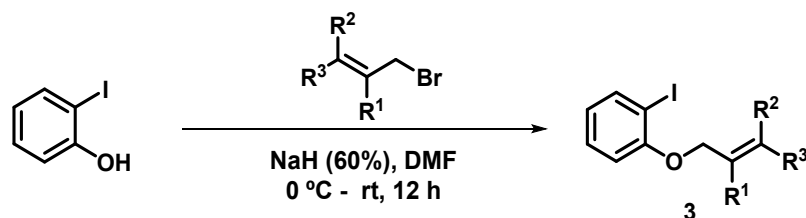
3.1. Synthesis of *N*-allyl-*N*-(2-halophenyl)acetamides



In a round bottom flask containing a solution of 2-iodoaniline (2.0 mmol, 428 mg) in 8 mL of EtOAc, acetic anhydride (4.0 mmol, 408 mg) was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude solid was recrystallized from a mixture of hexane and ethyl acetate to provide the *N*-(2-iodophenyl)acetamide as a white solid.²

To a solution of *N*-(2-iodophenyl)acetamide (1.0 mmol, 261 mg) in DMF (3.0 mL) was slowly added NaH (60% in mineral oil, 1.5 mmol, 60 mg) at 0 °C under nitrogen atmosphere. After vigorous evolution of hydrogen gas, the reaction mixture was treated with allyl bromide (1.5 mmol, 182 mg) and warmed up to room temperature. After stirring for 5 h, the reaction mixture was quenched by careful addition of H₂O (20 mL) and extracted with DCM (50 mL). The organic layers were washed successively with water (4 x 20 mL), and brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography provided the desired *N*-allyl-*N*-(2-iodophenyl)acetamide (**1**).³

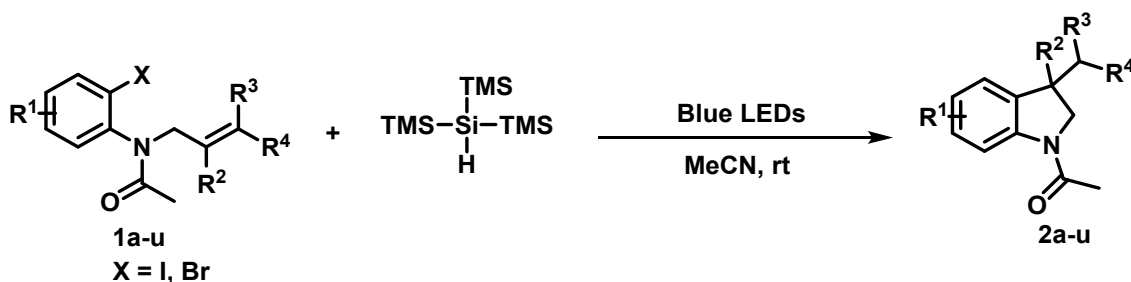
3.2. Synthesis of *O*-(allyloxy)-2-iodobenzene



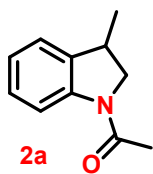
To a solution of 2-iodophenol (1.0 mmol, 220 mg, 1 equiv) in DMF (3.0 mL) was slowly added NaH (60% in mineral oil, 1.2 mmol, 50 mg) at 0 °C under a nitrogen atmosphere. The corresponding allyl bromide (1.2 mmol, 146 mg) was added dropwise and stirring at 0 °C during 20 min. After that, the resulting mixture was stirred at room temperature for 12 h. Upon completion, the reaction

mixture was quenched by careful addition of H₂O (20 mL) and extracted with DCM (50 mL). The organic layers were washed successively with water (4 x 20 mL), washed with brine (20 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash column chromatography provided the desired product.⁴

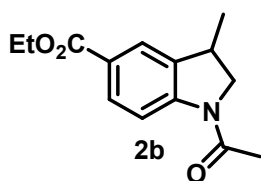
3.3. General procedure for the photochemical intramolecular cyclization reaction - Indoline synthesis.



To a transparent borosilicate glass vial (5 mL) equipped with a Teflon-coated magnetic stirring bar was added the organohalide substrate **1** (0.2 mmol, 1 equiv.), 0.4 mL of acetonitrile (0.5 M) and TTMSS (0.4 mmol, 2 equiv) at room temperature (degassing is unnecessary). The mixture was placed in the irradiation apparatus equipped with a blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature until the starting material was completely consumed as monitored by TLC. After complete consumption of the starting material, the reaction mixture was purified by flash column chromatography on silica gel, which furnished the title compounds as described.

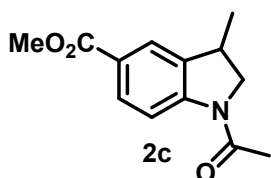


1-(3-methylindolin-1-yl)ethan-1-one⁵ (2a): According to general procedure, the *N*-allyl-*N*-(2-iodophenyl)acetamide (**1a**) (60.2 mg, 0.2 mmol) afforded **2a** (98%, 34.4mg) as a colorless solid. **MP:** 71 - 73 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.19 (d, J = 8.1 Hz, 1H), 7.24 – 7.09 (m, 3H), 7.04 (td, J = 7.4, 0.9 Hz, 1H), 4.21 (t, J = 9.6 Hz, 1H), 3.57 (dd, J = 9.9, 6.7 Hz, 1H), 3.53 – 3.44 (m, 1H), 2.22 (s, 3H), 1.36 (d, J = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.6, 142.4, 136.3, 127.7, 123.7, 123.3, 116.9, 57.0, 34.8, 24.2, 20.3.



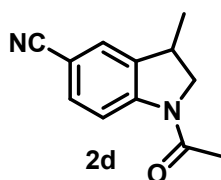
Ethyl 1-acetyl-3-methylindoline-5-carboxylate (2b):

According to general procedure, the ethyl 4-(*N*-allylacetamido)-3-iodobenzoate (**1b**) (74.6 mg, 0.2 mmol) afforded **2b** (75%, 37.4 mg) as a colorless solid. **MP**: 73 – 75 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.83 (s, 1H), 4.40 – 4.32 (m, 2H), 4.27 (t, *J* = 9.8 Hz, 1H), 3.64 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.58 – 3.47 (m, 1H), 2.24 (s, 3H), 1.42 – 1.35 (m, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 166.4, 146.2, 136.5, 130.3, 125.7, 124.8, 116.1, 60.8, 57.3, 34.4, 24.3, 20.3, 14.4. **HRMS**: calculated for C₁₄H₁₈NO₃ (*M*+*H*)⁺ 248.1281; found 248.1289.



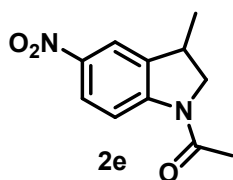
Methyl 1-acetyl-3-methylindoline-5-carboxylate (2c):

According to general procedure, the methyl 4-(*N*-allylacetamido)-3-iodobenzoate (**1c**) (71.8mg, 0.2mmol) afforded **2c** (65%, 30.3 mg) as a colorless solid. **MP**: 78 – 80 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.92 (ddd, *J* = 8.5, 1.8, 0.7 Hz, 1H), 7.83 (s, 1H), 4.27 (t, *J* = 9.8 Hz, 1H), 3.89 (s, 3H), 3.64 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.52 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 166.9, 146.3, 136.5, 130.4, 125.4, 124.9, 116.2, 57.3, 52.0, 34.4, 24.3, 20.3. **HRMS**: calculated for C₁₃H₁₆NO₃ (*M*+*H*)⁺ 234.1125; found 234.1132.



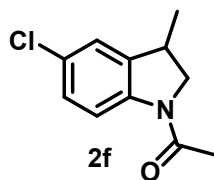
1-acetyl-3-methylindoline-5-carbonitrile⁶ (2d): According to general procedure, the *N*-allyl-*N*-(4-cyano-2-iodophenyl)acetamide (**1d**) (65.3 mg, 0.2 mmol) afforded **2d** (88%, 35.3mg) as a colorless solid. **MP**: 105 – 107 °C. **¹H**

NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.51 (ddd, *J* = 8.4, 1.7, 0.6 Hz, 1H), 7.41 (s, 1H), 4.28 (t, *J* = 9.9 Hz, 1H), 3.66 (dd, *J* = 10.2, 6.7 Hz, 1H), 3.54 (m, 1H), 2.25 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.4, 146.1, 137.3, 132.9, 127.1, 119.3, 117.1, 106.5, 57.0, 34.4, 24.3, 20.2.



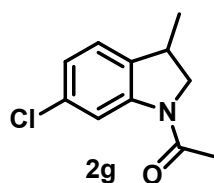
1-(3-methyl-5-nitroindolin-1-yl)ethan-1-one⁷ (2e):

According to general procedure, the *N*-allyl-*N*-(2-iodo-4-nitrophenyl)acetamide (**1e**) (69.2 mg, 0.2 mmol) afforded **2e** (45%, 20mg) as a yellow solid. **MP**: 116 – 118 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.27 (d, *J* = 10.3 Hz, 1H), 8.14 (dd, *J* = 8.9, 2.4 Hz, 1H), 8.03 (s, 1H), 4.35 (t, *J* = 9.9 Hz, 1H), 3.72 (dd, *J* = 10.3, 6.8 Hz, 1H), 3.58 (m, 1H), 2.28 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.5, 147.8, 143.7, 137.6, 124.8, 119.3, 116.2, 57.5, 34.3, 24.3, 20.2. **HRMS**: calculated for C₁₁H₁₃N₂O₃ (M+H)⁺ 221.0921; found 221.0929.



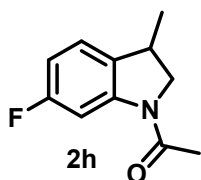
1-(5-chloro-3-methylindolin-1-yl)ethan-1-one (2f): According to general procedure, the *N*-allyl-*N*-(4-chloro-2-iodophenyl)acetamide (**1f**) (67.2 mg, 0.2 mmol) afforded **2f** (78%, 32.8 mg) as a colorless solid. **MP**: 121 – 123 °C. **¹H**

NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.6 Hz, 1H), 7.15 (ddd, *J* = 8.6, 2.2, 0.7 Hz, 1H), 7.10 (s, 1H), 4.21 (t, *J* = 9.8 Hz, 1H), 3.58 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.47 (m, 1H), 2.20 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.6, 141.0, 138.2, 128.5, 127.6, 123.6, 117.8, 57.0, 34.6, 24.1, 20.1. **HRMS**: calculated for C₁₁H₁₃NOCl (M+H)⁺ 210.0680; found 210.0686.



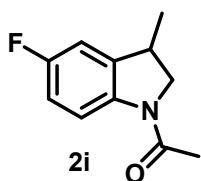
1-(6-chloro-3-methylindolin-1-yl)ethan-1-one (2g):

According to general procedure, the *N*-allyl-*N*-(5-chloro-2-iodophenyl)acetamide (**1g**) (67.2 mg, 0.2 mmol) afforded **2g** (73%, 31 mg) as a colorless solid. **MP**: 98 – 99 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.22 (t, *J* = 9.8 Hz, 1H), 3.59 (dd, *J* = 10.1, 6.7 Hz, 1H), 3.51 – 3.41 (m, 1H), 2.21 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.8, 143.4, 134.8, 133.2, 124.0, 123.6, 117.1, 57.3, 34.4, 24.1, 20.3. **HRMS**: calculated for C₁₁H₁₂NOCl (M+H)⁺ 210.0680; found 210.0687.

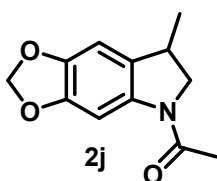


1-(6-fluoro-3-methylindolin-1-yl)ethan-1-one (2h): According to general procedure, the *N*-allyl-*N*-(5-fluoro-2-iodophenyl)acetamide (**1h**) (63.8 mg, 0.2 mmol) afforded **2h**

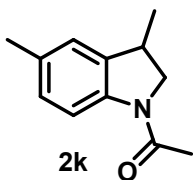
(85%, 32.8 mg) as a colorless solid. **MP**: 78 – 79 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.07 (dd, *J* = 8.7, 4.9 Hz, 1H), 6.84 – 6.75 (m, 2H), 4.16 (t, *J* = 9.8 Hz, 1H), 3.53 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.47 – 3.36 (m, 1H), 2.14 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.3, 159.5 (d, *J* = 241.8 Hz), 138.5, 138.3, 117.7 (d, *J* = 7.9 Hz), 113.9 (d, *J* = 22.6 Hz), 110.6 (d, *J* = 23.9 Hz), 57.1, 34.8, 23.9, 20.0. **HRMS**: calculated for C₁₁H₁₃NOF (M+H)⁺ 194.0976; found 194.0982.



1-(5-fluoro-3-methylindolin-1-yl)ethan-1-one⁸ (2i): According to general procedure, the *N*-allyl-*N*-(4-fluoro-2-bromophenyl)acetamide (**1i**) (54.3 mg, 0.2 mmol) afforded **2i** (40%, 32.8 mg) as a colorless solid. **MP**: 112 – 114 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.94 (dd, *J* = 10.6, 2.4 Hz, 1H), 7.05 (dd, *J* = 7.7, 5.8 Hz, 1H), 6.71 (td, *J* = 8.6, 2.5 Hz, 1H), 4.24 (t, *J* = 9.8 Hz, 1H), 3.61 (dd, *J* = 10.1, 6.6 Hz, 1H), 3.52 – 3.41 (m, 1H), 2.21 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.8, 162.5 (d, *J* = 242.1 Hz), 143.5 (d, *J* = 12.5 Hz), 131.7, 123.7 (d, *J* = 9.9 Hz), 110.0 (d, *J* = 23.1 Hz), 105.0 (d, *J* = 29.0 Hz), 57.6, 34.2, 24.1, 20.4. **HRMS**: calculated for C₁₁H₁₃NOF (M+H)⁺ 194.0976; found 194.0985.

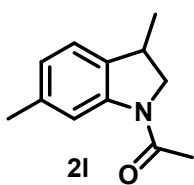


1-(7-methyl-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-5-yl)ethan-1-one (2j): According to general procedure, the *N*-allyl-*N*-(6-iodobenzo[d][1,3]dioxol-5-yl)acetamide (**1j**) (69 mg, 0.2 mmol) afforded **2j** (60%, 26.3 mg) as a colorless solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.84 (s, 1H), 6.61 (s, 1H), 5.92 (m, 2H), 4.20 (t, *J* = 10.1 Hz, 1H), 3.56 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.43 – 3.34 (m, 1H), 2.19 (s, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 167.9, 146.7, 143.9, 136.6, 129.0, 103.8, 101.3, 99.8, 57.5, 34.6, 24.0, 20.5. **HRMS**: calculated for C₁₂H₁₄NO₃ (M+H)⁺ 220.0968; found 220.0972



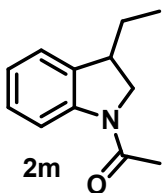
1-(3,5-dimethylindolin-1-yl)ethan-1-one (2k): According to general procedure, the *N*-allyl-*N*-(2-iodo-4-methylphenyl)acetamide (**1k**) (63.0 mg, 0.2 mmol) afforded **2k**

(83%, 31.5 mg) as a colorless solid. **MP**: 89 – 90 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 6.6 Hz, 1H), 6.96 (s, 1H), 4.18 (t, *J* = 9.7 Hz, 1H), 3.55 (dd, *J* = 10.0, 6.7 Hz, 1H), 3.45 (m, 1H), 2.31 (s, 3H), 2.20 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.2, 140.1, 136.4, 133.3, 128.2, 124.0, 116.6, 57.1, 34.7, 24.1, 21.0, 20.2. **HRMS**: calculated for C₁₂H₁₆NO (M+H)⁺ 190.1226; found 190.1231.



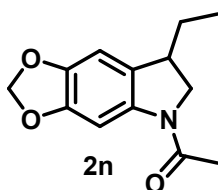
1-(3,6-dimethylindolin-1-yl)ethan-1-one (2l): According to general procedure, the *N*-allyl-*N*-(2-bromo-5-methylphenyl)acetamide (**1l**) (53.6 mg, 0.2 mmol) afforded **2l** (60%, 22.6 mg) as a colorless solid. **MP**: 98 – 100 °C. **¹H NMR**

(400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 7.6, 0.7 Hz, 1H), 4.19 (t, *J* = 9.7 Hz, 1H), 3.56 (dd, *J* = 10.0, 6.7 Hz, 1H), 3.45 (m, 1H), 2.34 (s, 3H), 2.21 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.6, 142.5, 137.7, 133.5, 124.4, 123.0, 117.6, 57.3, 34.4, 24.2, 21.6, 20.4. **HRMS**: calculated for C₁₂H₁₆NO (M+H)⁺ 190.1226; found 190.1234.



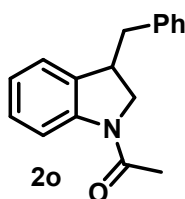
1-(3-ethylindolin-1-yl)ethan-1-one⁹ (2m): According to general procedure, the *N*-(but-2-en-1-yl)-*N*-(2-iodophenyl)acetamide (**1m**) (63.0 mg, 0.2 mmol) afforded **2m** (92%, 35 mg) as a colorless solid. **MP**: 73 – 75 °C. **¹H NMR (400 MHz, CDCl₃)** δ 8.13 (d, *J* =

8.0 Hz, 1H), 7.17 – 7.03 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 4.08 (t, *J* = 9.9 Hz, 1H), 3.61 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.17 (s, 3H), 1.84 – 1.73 (m, 1H), 1.58 – 1.46 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.7, 142.7, 135.0, 127.8, 123.8, 123.6, 116.9, 54.7, 41.5, 28.1, 24.3, 11.2.

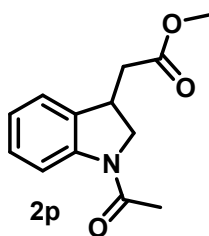


1-(7-ethyl-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-5-yl)ethan-1-one (2n): According to general procedure, the *N*-(but-2-en-1-yl)-*N*-(6-iodobenzo[d][1,3]dioxol-5-yl)acetamide (**1n**) (71.8 mg, 0.2 mmol) afforded **2n** (92%, 42 mg) as a

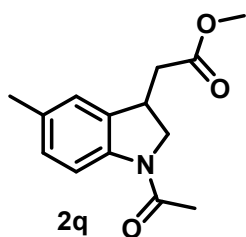
colorless solid. . **MP**: 123 – 124 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.85 (s, 1H), 6.62 (s, 1H), 5.92 (s, 2H), 4.14 (t, *J* = 9.6 Hz, 1H), 3.67 (dd, *J* = 10.4, 5.8 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.19 (s, 3H), 1.79 – 1.72 (m, 1H), 1.54 (m, *J* = 14.7, 7.4 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 167.9, 146.7, 143.8, 137.0, 127.5, 104.1, 101.2, 99.8, 55.2, 41.3, 28.2, 24.0, 10.9. **HRMS**: calculated for C₁₃H₁₆NO₃ (M+H)⁺ 234.1126; found 234.1129



1-(3-benzylindolin-1-yl)ethan-1-one² (2o): According to general procedure, the *N*-cinnamyl-*N*-(2-iodophenyl)acetamide (**1o**) (75.4 mg, 0.2 mmol) afforded **2o** (32%, 16.0 mg) as a yellow oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.70 (m, 2H), 7.67 – 7.54 (m, 1H), 7.17 – 7.14 (m, 1H), 7.32 – 7.10 (m, 2H), 7.02 – 6.97 (m, 1H), 6.93 (td, *J* = 7.4, 1.0 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.69 – 3.59 (m, 2H), 3.06 (dd, *J* = 13.9, 5.3 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.9 Hz, 1H), 2.07 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.8, 142.7, 138.8, 134.4, 129.0, 128.7, 128.1, 126.7, 124.0, 123.6, 117.1, 54.5, 41.5, 24.2.



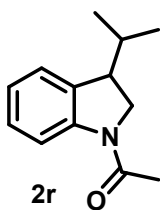
Methyl 2-(1-acetylindolin-3-yl)acetate⁸ (2p): According to general procedure, the methyl 4-(*N*-(2-iodophenyl)acetamido)but-2-enoate (**1p**) (71.8 mg, 0.2 mmol) afforded **2p** (86%, 41.1 mg) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 11.5, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 4.24 (dd, *J* = 10.3, 9.3 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.66 (s, 3H), 2.77 (dd, *J* = 16.6, 4.4 Hz, 1H), 2.49 (dd, *J* = 16.6, 10.0 Hz, 1H), 2.15 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.2, 168.8, 142.6, 133.0, 128.4, 123.8, 123.6, 117.1, 55.1, 51.9, 39.6, 36.5, 24.2.



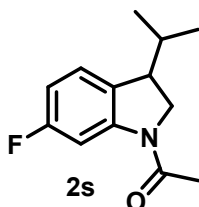
Methyl 2-(1-acetyl-5-methylindolin-3-yl)acetate (2q): According to general procedure, the methyl 4-(*N*-(2-iodo-4-methylphenyl)acetamido)but-2-enoate (**1q**) (74.6 mg, 0.2 mmol) afforded **2q** (70%, 34.7 mg) as a yellow solid. . **MP**:

47 – 49 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.99 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* =

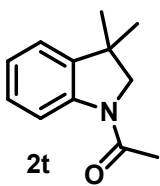
7.1 Hz, 1H), 6.87 (s, 1H), 4.21 (t, J = 9.5 Hz, 1H), 3.78 – 3.68 (m, 1H), 3.68 – 3.61 (m, 4H), 2.76 (dd, J = 16.6, 4.2 Hz, 1H), 2.46 (dd, J = 16.5, 9.9 Hz, 1H), 2.22 (s, 3H), 2.12 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3)** δ 172.3, 168.5, 140.3, 133.4, 133.1, 128.8, 124.2, 116.8, 55.3, 51.9, 39.6, 36.5, 24.1, 21.0. **HRMS:** calculated for $\text{C}_{14}\text{H}_{18}\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 248.1281; found 248.1279



1-(3-isopropylindolin-1-yl)ethan-1-one¹⁰ (2s): According to general procedure, the *N*-(2-iodophenyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (**1s**) (65.8 mg, 0.2 mmol) afforded **2s** (85%, 34.6 mg) as a yellow oil. **^1H NMR (400 MHz, CDCl_3)** δ 8.13 (d, J = 8.1 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.95 (td, J = 7.5, 1.0 Hz, 1H), 3.93 (t, J = 10.2 Hz, 1H), 3.72 (dd, J = 10.6, 5.0 Hz, 1H), 3.27 (dt, J = 9.4, 4.6 Hz, 1H), 2.16 (s, 3H), 2.03 – 1.94 (m, 1H), 0.91 (d, J = 6.9 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, CDCl_3)** δ 168.6, 143.2, 133.7, 127.8, 124.3, 123.4, 116.8, 51.2, 47.0, 31.9, 24.3, 20.0, 17.3.

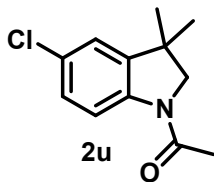


1-(6-fluoro-3-isopropylindolin-1-yl)ethan-1-one (2s): According to general procedure, the *N*-(5-fluoro-2-iodophenyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (**1s**) (69.4 mg, 0.2 mmol) afforded **2s** (75%, 34 mg) as a yellow oil. **^1H NMR (400 MHz, CDCl_3)** δ 7.88 (dd, J = 10.7, 2.5 Hz, 1H), 6.99 (dd, J = 7.7, 5.7 Hz, 1H), 6.63 (td, J = 8.6, 2.5 Hz, 1H), 3.97 (t, J = 10.2 Hz, 1H), 3.74 (dd, J = 10.6, 4.9 Hz, 1H), 3.23 (m, 1H), 2.16 (s, 3H), 2.00 – 1.90 (m, 1H), 0.89 (d, J = 6.9 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, CDCl_3)** δ 168.8, 162.5 (d, J = 241.8 Hz), 144.3 (d, J = 12.5 Hz), 129.1, 124.7 (d, J = 9.9 Hz), 109.8 (d, J = 22.9 Hz), 104.9 (d, J = 28.9 Hz), 51.9, 45.3, 31.9, 24.2, 19.8, 17.3. **HRMS:** calculated for $\text{C}_{13}\text{H}_{17}\text{NOF}$ ($\text{M}+\text{H}$) $^+$ 222.1289; found 222.1297.



1-(3,3-dimethylindolin-1-yl)ethan-1-one¹¹ (2t): According to general procedure, the *N*-(2-iodophenyl)-*N*-(2-methylallyl)acetamide (**1t**) (63 mg, 0.2 mmol) afforded **2t** (85%, 32.2 mg) as a colorless oil. **^1H NMR (400 MHz, CDCl_3)** δ 8.11 (d, J = 8.1 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.06 (dd, J = 7.4, 0.9 Hz, 1H), 6.98 (td, J =

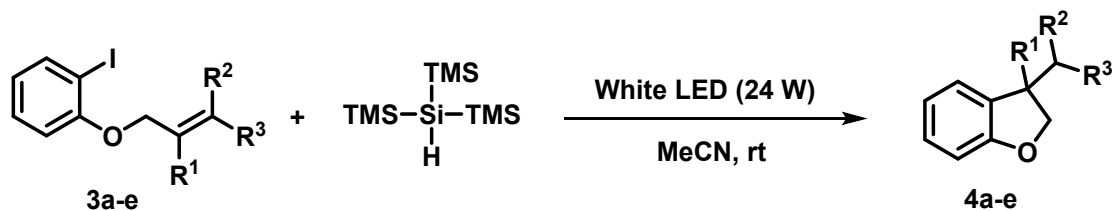
7.4, 1.0 Hz, 1H), 3.70 (s, 2H), 2.15 (s, 3H), 1.29 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 141.5, 140.4, 127.7, 123.9, 121.8, 116.9, 63.7, 40.2, 28.3, 24.2.



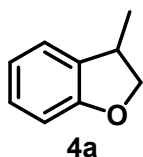
1-(5-chloro-3,3-dimethylindolin-1-yl)ethan-1-one (2u):

According to general procedure, the *N*-(5-chloro-2-iodophenyl)-*N*-(2-methylallyl) acetamide (**1u**) (70 mg, 0.2 mmol) afforded **2u** (73%, 32.7 mg) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 3.72 (s, 2H), 2.14 (s, 3H), 1.28 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 142.3, 140.2, 128.7, 127.7, 122.2, 117.9, 63.7, 40.3, 28.5, 24.1.

3.4. General procedure for synthesis of 2,3-dihydrobenzofuran

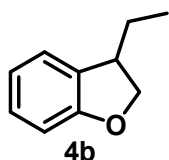


To a transparent borosilicate glass vial (5 mL) equipped with a Teflon-coated magnetic stirring bar was added the organohalide **3** (0.2 mmol, 1 equiv.), 0.4 mL acetonitrile (0.5 M) and TTMSS (0.4 mmol, 2 equiv) at room temperature (degassing is unnecessary). The mixture was placed in approximately 5 cm away from the light source, two 12 W light-emitting diode (LEDs) lamps. The resulting mixture was stirred at room temperature until the starting material was completely consumed as monitored by TLC. The reaction mixture was purified by flash column chromatography on silica gel, which furnished the title compounds as described.

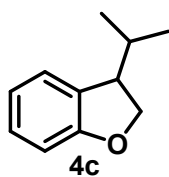


3-methyl-2,3-dihydrobenzofuran⁸ (4a): According to general procedure, the *O*-(allyloxy)-2-iodobenzene (**3a**) (52 mg, 0.2 mmol) afforded **4a** (49%, 13 mg) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.98 – 6.89 (m, 2H), 6.67 (td, *J* = 7.4, 0.9 Hz, 1H), 6.60 (d, *J* = 8.0 Hz,

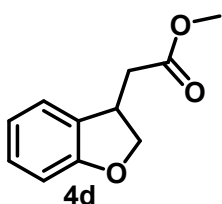
1H), 4.48 (t, J = 8.8 Hz, 1H), 3.87 (dd, J = 8.6, 7.5 Hz, 1H), 3.35 (sex, 1H), 1.13 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.3, 132.8, 128.6, 124.4, 121.0, 110.0, 79.0, 37.1, 19.9.



3-ethyl-2,3-dihydrobenzofuran⁸ (4b): According to general procedure, the 1-(but-2-en-1-yloxy)-2-iodobenzene (**3b**) (54.8 mg, 0.2mmol) afforded **4b** (84%, 25 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.05 (m, 1H) 7.00 (m, 1H), 6.74 (td, J = 7.4, 1.0 Hz, 1H), 6.68 – 6.65 (m, 1H), 4.51 (t, J = 12.2, 5.5 Hz, 1H), 4.10 (dd, J = 8.8, 6.4 Hz, 1H), 3.25 (ddd, J = 14.5, 8.5, 6.0 Hz, 1H), 1.74 – 1.63 (m, 1H), 1.54 – 1.42 (m, 1H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 130.9, 128.1, 124.4, 120.3, 109.5, 76.6, 43.4, 27.7, 11.4.

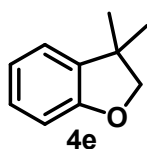


3-isopropyl-2,3-dihydrobenzofuran⁸ (4c): According to general procedure, the 1-iodo-2-((3-methylbut-2-en-1-yl)oxy)benzene (**3c**) (57.6 mg, 0.2 mmol) afforded **4c** (52%, 17 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.08 – 7.03 (m, 1H), 6.99 (tdd, J = 8.1, 1.4, 0.7 Hz, 1H), 6.72 (td, J = 7.4, 1.0 Hz, 1H), 6.67 – 6.62 (m, 1H), 4.39 (t, J = 9.1 Hz, 1H), 4.25 (dd, J = 9.0, 5.1 Hz, 1H), 3.23 – 3.17 (m, 1H), 1.90 – 1.78 (m, 1H), 0.83 (d, J = 6.8 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 129.4, 128.1, 125.1, 120.1, 109.3, 73.8, 48.1, 31.7, 19.8, 18.4.



Methyl 2 - (2,3-dihydrobenzofuran-3-yl) acetate¹² (4d): According to general procedure, the methyl 4-(2-iodophenoxy)but-2-enoate (**3d**) (63.6 mg, 0.2 mmol) afforded **4d** (88%, 34 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 6.98 – 6.93 (m, 2H), 6.67 (td, J = 7.5, 1.0 Hz, 1H), 6.63 – 6.60 (m, 1H), 4.56 (t, J

= 9.1 Hz, 1H), 4.06 (dd, J = 9.2, 6.3 Hz, 1H), 3.69 (m, 1H), 3.53 (s, 3H), 2.61 (dd, J = 16.5, 5.3 Hz, 1H), 2.40 (dd, J = 16.5, 9.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 160.5, 129.8, 129.4, 124.9, 121.3, 110.5, 77.4, 52.6, 40.0, 39.0.



3,3-dimethyl-2,3-dihydrobenzofuran⁸ (4e): According to general procedure, the 1-iodo-2-((2-methylallyl)oxy)benzene (**3e**) (54.8 mg, 0.2 mmol) afforded **4e** (95%, 25 mg) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.04 – 6.98 (m, 2H), 6.78 (td, J = 7.5, 1.0 Hz, 1H), 6.69 (dt, J = 7.7, 0.9 Hz, 1H), 4.12 (s, 2H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 136.5, 127.9, 122.3, 120.6, 109.6, 84.4, 41.9, 27.5.

4. MECHANISTIC STUDIES

4.1. EDA-complex characterization

The formation of the EDA-complex between the compound **1a** and the **TTMSS** was proved by UV-vis spectroscopy in the absorbance mode. The following solutions were prepared in MeCN (100 μL each):

- Solution A: 0.4 mol L^{-1} of **1a**
- Solution B: 0.8 mol L^{-1} of **TTMSS**
- Solution C: 0.4 mol L^{-1} of **1a** + 0.8 mol L^{-1} of **TTMSS** (reaction mixture, **RM**)
- Solution D: 0.4 mol L^{-1} of the reactional product **2a**.
- Solution E: Saturated KI (~ 0.1 mol L^{-1}).

All these solutions were maintained under N_2 atmosphere for inhibiting the reaction with atmospheric oxygen, mainly concerned about the **TTMSS**. Each solution was prepared in duplicated and, after 30 min under darkness, a replicate of each solution was diluted forty (40) times with MeCN and its absorbance spectrum was recorded. At the same time, the replicates of the solutions were exposed to the blue LEDs light, inside the reactor, for 10 min and, then, diluted and analyzed by UV-vis spectroscopy, as it was done for the non-irradiated solutions. The spectra of these experiments are shown in Figure S3A. A. Additionally, the spectrum of the **RM** (not diluted), after EDA-complex formation, was taken and, from it, the fraction of light absorbed was calculated ($f = 1 - 10^{\text{absorbance}}$) as a function of wavelength, being the graph shown in Figure 2XB.

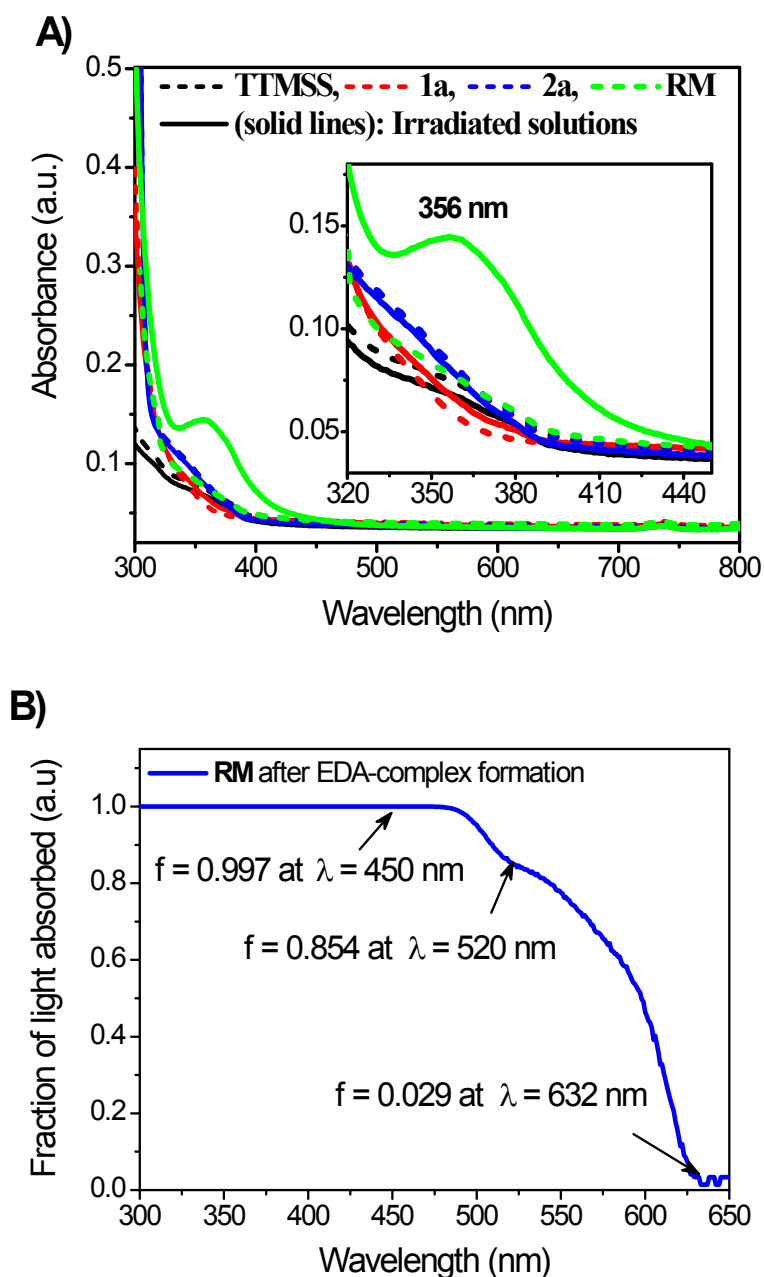


Figure S3. **A)** Absorbance spectra for the solutions 0.02 mol.L⁻¹ **TTMSS** (black lines), 0.01 mol L⁻¹ **1a** (red lines), 0.01 mol.L⁻¹ **2a** (blue lines) and the mixture 0.02 mol.L⁻¹ **TTMSS** + 0.01 mol.L⁻¹ **1a** (**RM**, green lines). The solid lines represent the replicates of the solutions that were exposed to the blue LEDs light for 10 min. **B)** The fraction of light absorbed versus wavelength for **RM** (not diluted, i.e 0.8 mol L⁻¹ of **TTMSS** + 0.4 mol.L⁻¹ of **1a**) after 10 min of exposing to the blue LEDs light.

As can be seen in Figure S3A, the solutions of the separated compounds are not affected by the exposure to the blue light (comparing the solid lines with the dotted ones). However, we can clearly see that the spectrum of the **RM** solution (**1a** + **TTMSS**) shows a new absorption band at 356 nm after

illumination. This absorption band can be attributed to the formation of an EDA-complex between the compound **1a** and the **TTMSS**, which is only formed after irradiation. It is worth to mention that the absorption spectrum of the product **2a** and of the iodide ions (I^- ions liberated from compound **1a** after reaction, graph not presented) do not show the band at this region, confirming that this phenomenon is related to the EDA-complex.

In Figure S3B, we can see the spectrum of the f for EDA-complex formed from the **RM** after 10 min of blue light irradiation. As can be seen, this complex absorb almost 100% of light at a wavelength of 450 nm (blue light); while the fraction of light absorbed is ~ 85 and 3% under green and red light, respectively. This effect added to the fact that the green and the red LEDs have lower irradiance, explain the lower yield observed for the reaction performed under these LEDs illumination.

4.2. Determination of blue LEDs photon flux at the reactional vial position

To estimate the quantum yield of the studied photocatalytic reaction, an important parameter that might be known is the light flux that reaches the reactional vial (where the photocatalytic reactions were performed). Thus, the light flux was measured by actinometry; a 0.15 mol.L^{-1} solution of potassium ferrioxalate (the most common and standard actinometer) was used, according to the similar procedure described by Cismesia and Yoon¹³ and other authors.¹⁴ First of all, the following solutions were prepared in a dark-room and stored in the dark for inhibit their photodegradation:

- Solution E: Actinometer solution was prepared by dissolving 0.82 g of potassium trioxalatoferrate(III) trihydrate (ferrioxalate) in 10 mL of H_2SO_4 (0.05 mol.L^{-1}).
- Solution F: Buffered 0.5% 1,10-phenanthroline solution was prepared in 25 mL of H_2SO_4 (0.5 mol.L^{-1}) + sodium acetate (0.1 mol.L^{-1}).

To determine the photon flux that reaches the vessel, 0.5 mL of the solution E was placed in a vial at the reactor center (as it was done for the photocatalytic reactions) and irradiated for 15 min at the blue LED light. It is worth to mention that the reactor was turned on 30 min before the experiments in order to equilibrate the flux of the LEDs. Under this conditions, the

actinometer reacts almost quantitatively with each photon that reaches the system, being converted to Fe(II)-oxalate.

After irradiation, 1.165 mL of the solution F was added to the vial (total volume of 1.665). The solution was then kept in the dark, under magnetic stirring and N₂ atmosphere for 1 h to allow the ferrous ions to be completely coordinated by the 1,10-phenanthroline (red coordination-complex). Then, 0.5 mL of this resulting solution was transferred to a quartz cuvette and diluted with 2.8 mL of water (dilution factor of 6.6), in order to correctly measure the absorbance spectrum of the solution (respecting the linear behavior of the Beer-Lambert law; absorbance ≤ 1 at 510 nm). For such measurement, a spectrophotometer (UV-Vis-NIR Varian Cary 5E®) was used and the value of the absorbance was taken at 510 nm. A non-irradiated sample was also prepared. The quantity of ferrous ions generated was calculated using Eq. 1.

$$mol Fe^{2+} = \frac{V \times d \times \Delta Abs}{l \times \epsilon(510\text{ nm})} \text{ (Eq.1)}$$

where V is the total volume (1.660×10^{-3} L) of the solution after addition of the solution F, d is the dilution factor (in our case, 6.6), ΔAbs is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the optical path length (1.000 cm), and ϵ is the molar absorptivity of Fe(II)-phenanthroline complex at 510 nm ($11,100 \text{ L mol}^{-1} \text{ cm}^{-1}$).^{3a}

As the quantum yield of this actinometer is well known in the literature³ the photon flux can be calculated using Eq. 2. where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at $\lambda = 450 \text{ nm}$),³ t is the time of exposure (900 s), and f is the fraction of light absorbed by the actinometer at $\lambda = 450 \text{ nm}$ (see Figure S4 below that shows the graph of f versus wavelength for the actinometer).

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \times f \times t} \text{ (Eq.2)}$$

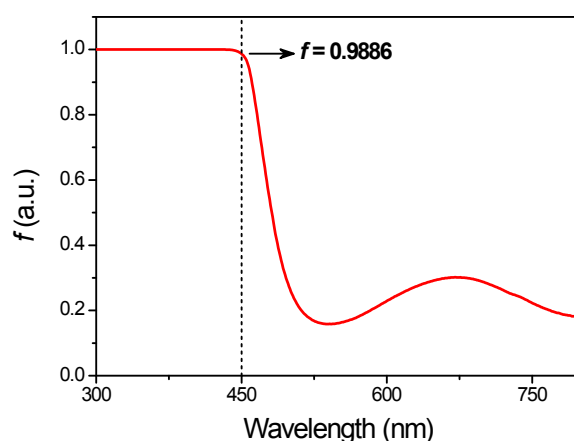


Figure S4. Determination of the fraction of light absorbed by the actinometer at LEDs emission peak ($\lambda = 450$ nm).

The Figure S5 below shows the absorbance spectra of the three irradiated actinometer replicates and of the non-irradiated sample.

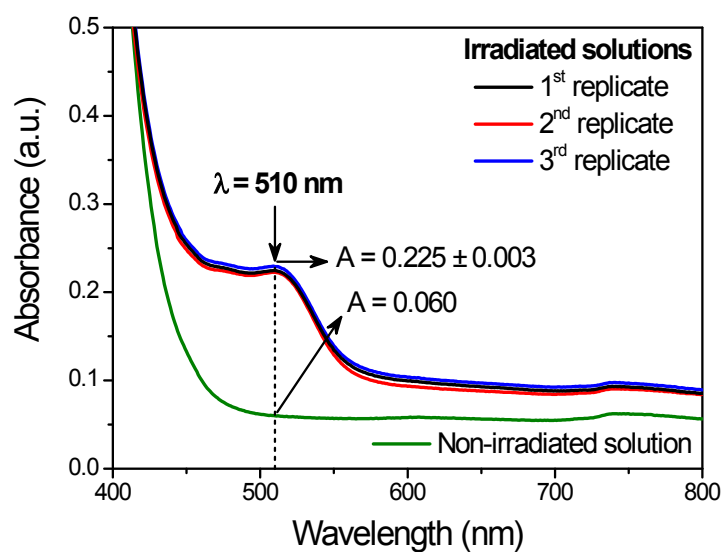


Figure S5. Absorbance spectra for the diluted irradiated and non-irradiated solutions of actinometer after complexing with 1,10-phenanthroline.

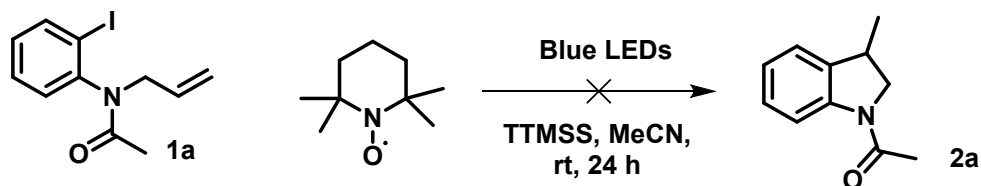
Thus, using the Eq. 1 and 2:

$$\text{mol } Fe^{2+} = \frac{1.660 \times 10^{-3} \text{ L} \times 6.6 \times (0.225 - 0.060)}{1.000 \text{ cm} \times 1.110 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}} = 1.634 \times 10^{-7} \text{ mol}$$

$$\text{photon flux} = \frac{1.634 \times 10^{-7} \text{ mol}}{1.01 \times 0.9886 \times 900 \text{ s}} = 1.81 \times 10^{-10} \text{ einstein s}^{-1}$$

In conclusion, the photon flux calculated from the average of three experiments was of 1.81×10^{-10} einstein s^{-1} .

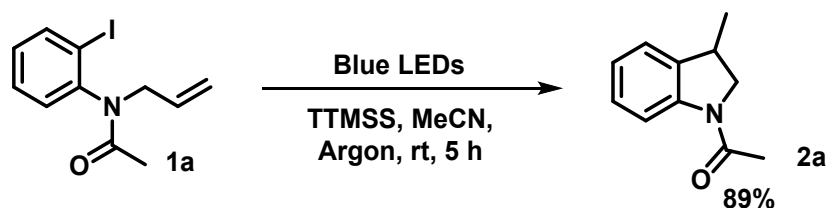
4.3. TEMPO radical trapping experiment



To a transparent borosilicate glass vial (5 mL) equipped with a Teflon-coated magnetic stirring bar was added *N*-allyl-*N*-(2-iodophenyl)acetamide (**1a**) (0.2 mmol, 1 equiv.), 0.4 mL of acetonitrile (0.5 M), TTMSS (0.4 mmol, 2 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (0.4 mmol, 2 equiv.) at room temperature. The mixture was placed in the irradiation apparatus equipped with a blue light-emitting diode (LEDs) strip. The resulting mixture was monitored by GC-FID during 24 hours. No formation of the desired product was observed by calibrated GC-MS analysis and the starting material was recovered.

4.4. Control experiments

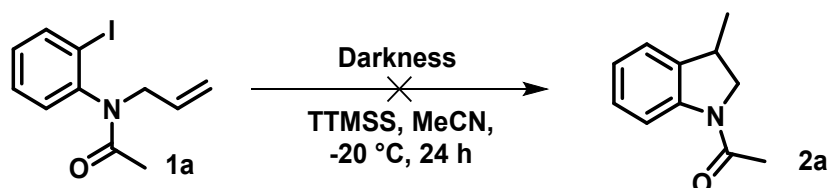
a. Impact of the molecular oxygen absence



An oven-dried Schlenk tube equipped with a Teflon-coated magnetic stirring bar was charged with *N*-allyl-*N*-(2-iodophenyl)acetamide (**1a**) (0.2 mmol, 1.0 equiv., 60 mg), TTMSS (0.4 mmol, 2.0 equiv., 0.14 mL) and acetonitrile (0.4 mL) under an argon atmosphere. The tube was evacuated and backfilled with argon and the reaction mixture degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon the tube was placed in a irradiation apparatus equipped with a blue light-emitting diode (LEDs) strip. The resulting

mixture was stirred at room temperature and monitored by TLC. After 5 hours the starting material was completely consumed, and the reaction mixture was purified by flash column chromatography on silica gel and employing as eluent a mixture of hexane/ethyl acetate (80:20). The compound **2a** was obtained in 89% yield.

b. Impact of low temperature and visible-light absence



To a transparent borosilicate glass vial (5 mL) equipped with a Teflon-coated magnetic stirring bar was added *N*-allyl-*N*-(2-iodophenyl)acetamide **1a** (0.2 mmol, 1 equiv.), 0.4 mL of acetonitrile (0.5 M), TTMSS (0.4 mmol, 2 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (0.4 mmol, 2 equiv.). The reaction was carried out under -20°C and darkness. The resulting mixture was monitored by GC-FID during 24 hours. No formation of the desired product was observed by calibrated GC-MS analysis and the starting material was recovered.

4.5. Determination of quantum yield

First of all, for the quantum yield experiments of the model reaction, we decided to construct a calibration curve for the product **2a**, in order to have an exact and precise determination of the quantity of the product that was generated after an exposure to a specific quantity of light flux (or quantity of photons).

a) GC-MS calibration curves

Following the common analytical procedures,¹⁵ a stock solution 0.4 mol.L⁻¹ of the compound **2a** was prepared in MeCN and, then, seven standard solutions with different concentrations were obtained by diluting the stock with ethyl acetate. Aliquots of 1 µL of each standard solution (in triplicate) were injected on a Shimadzu GCMS-QP2010S Gas Chromatograph coupled to a MS detector. The Figure S6 below shows a representative chromatogram, the

column temperature profile, and the calibration curve for the compound **2a** (the standard deviations are presented with 95% of confidence).

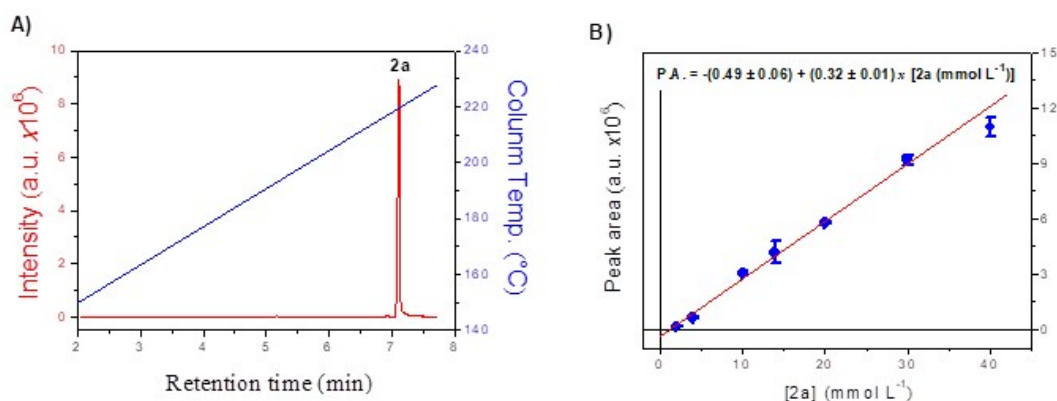


Figure S6. **A)** Representative chromatogram for the standard solution 10 mmol L⁻¹ of the compound **2a**, as well as the column temperature profile. **B)** Calibration curves for compound **2a** with statistical errors (n =3) in 95% of confidence.

As can be seen in Figure S6B, the calibration curve showed a good linear region with six (6) points and it was observed saturation for the higher concentration.

b) Quantum yield

At the same conditions (vessel, light irradiation and temperature), 0.5 mL of **RM** was exposed to the blue LEDs light for 1h. Then, for quantification of the product **2a** formed after this time, 0.25 mL of this solution was taken, diluted four (4) times with ethyl acetate, and injected in the GC-MS at same conditions used for the calibration curve construction (replicates 1-3, Table S6). The other part of the solution was kept under the dark and N₂ atmosphere during 3 h, and after that, it was also quantified (replicates 4-6, Table S1) to verify if the reaction is propagated in the absence of light. These experiments were performed in triplicate, the peak area of the compound **2a** for each experiment, as well as the concentrations (**[2a]**) extracted from the calibration curve, and the number of moles of this compound (taking into account the dilution factor) are organized in Table S1. From the data organized in Table S6, the calculation of the quantum yield (Φ) can be done using the following equation.

$$\Phi = \frac{\text{mol } 2a}{E \times f \times t} \text{ (Eq.3)}$$

where E is the photon flux, *f* is the fraction of light absorbed by EDA-complex at $\lambda = 450 \text{ nm}$ (0.997, *vide* Figure S3B).

Table S6. Quantum yield experiments

Replicate	Peak area (a.u)	[2a] (mmol L ⁻¹)	mmols of 2a produced*	Φ
1	2.34×10^6	8.86	1.17×10^{-5}	27.3
2	2.78×10^6	10.23	2.05×10^{-5}	31.5
3	2.25×10^6	8.56	1.71×10^{-5}	26.4
Mean (1-3)	2.46×10^6	9.21	1.84×10^{-5}	28.4
4**	3.09×10^6	11.19	2.24×10^{-5}	---
5**	3.39×10^6	12.13	3.43×10^{-5}	---
6**	4.99×10^6	17.13	2.43×10^{-5}	---
Mean (4-6)	3.82×10^6	13.49	2.70×10^{-5}	---
Mean (4-6) – Mean (1-3)			0.86×10^{-5}	---

* Quantity of compound **2a** produced for 0.5 mL of reaction mixture. ** Replicates that remained in the dark for 3 h after the irradiation.

As can be seen in Table S6, Φ of the reaction is $\gg 1$, what means that this reaction has radical chain propagation.

To verify the radical chain process, after illumination, the reaction was left in the dark for 3 h. The data shown in Table S1 probe that the reaction is propagated in the dark (even that slower than under light), producing almost 50 % more product after 3 h.

4.6. EPR studies

The starting material **1a**, the **TTMSS** and the reaction mixture (**RM = 1a + TTMSS**, 1: 1 ratio) were characterized by electron paramagnetic resonance from the following solutions:

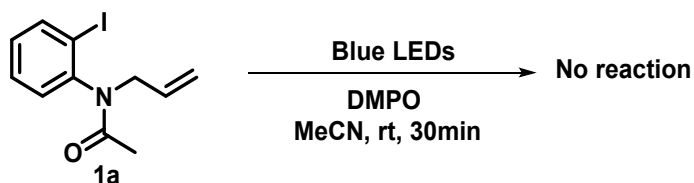
- 0.36 mol.L⁻¹ of 1a in acetonitrile.
- 0.36 mol.L⁻¹ of TTMSS in acetonitrile.
- 0.36 mol.L⁻¹ of 1a + 0.36 mol L⁻¹ of TTMSS in acetonitrile.

- 10 mol.L⁻¹ of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) in water.

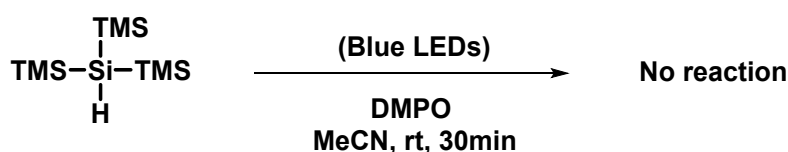
The resulting solutions containing the radical DMPO adducts were measured by electron paramagnetic resonance (EPR) spectroscopy on a Varian E-109 spectrometer operating in an X band (9.5 GHz). The irradiated samples were transferred to a quartz cell adapted to a microwave cavity operating under the following conditions: modulation amplitude 0.05 mT, microwave power 20 mW, room temperature, measurement time of 1 minute, field of 10 mT.

The free Easyspin package was used to simulate the nitrogen and hydrogen hyperfine interacting with the electronic density of the nitroxide radical of the DMPO molecule.

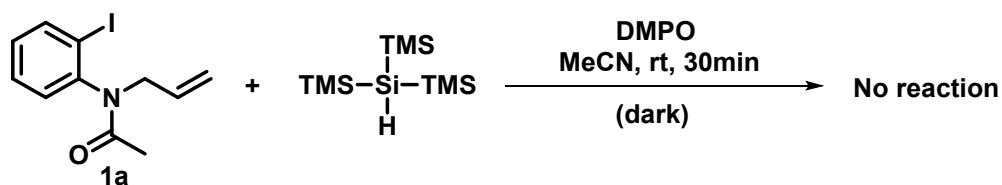
Experiment 1: A 100 μ L aliquot of **1a** solution and 1 μ L of the DMPO solution were transferred to a quartz cuvette and irradiated for 30 min by the blue LEDs. The EPR spectrum was recorded and no signal was observed.



Experiment 2: A 100 μ L aliquot of the TTMSS solution and 1 μ L of the DMPO solution were transferred to a quartz cuvette and irradiated for 30 min by the blue LEDs. The spectrum was recorded and EPR signal was not also observed.



Experiment 3: A 100 μ L aliquot of the RM solution and 4 μ L of the DMPO solution were added to a transparent borosilicate glass vial, equipped with a Teflon-coated magnetic stirring bar, and stirred for 30 min in the dark. Then, the resulting mixture was transferred into a quartz cuvette for EPR analysis. No EPR signal was observed.



Experiment 4: A similar reaction mixture used in experiment 3 was now irradiated for 30 min by the blue LEDs under stirring. Then, this resulting solution was transferred to a quartz cuvette and the spectra were recorded (Figure S7).

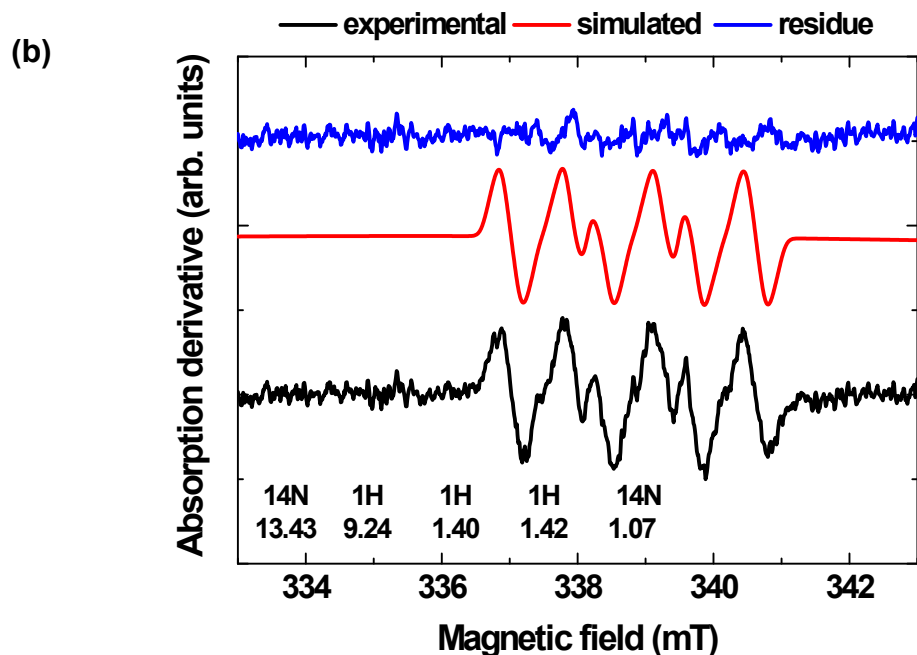
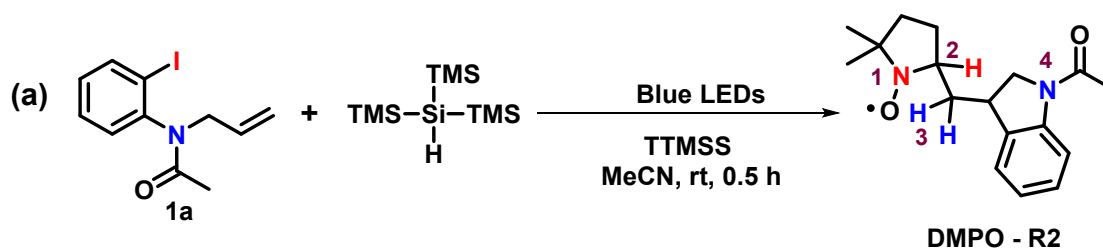


Figure S7. (a) Proposed formation of a DMPO-R2 adduct. (b) The EPR spectrum of DMPO – R2.

The EPR spectrum of the DMPO-R2 adduct system was simulated in the steps described in the following. The first simulation was performed considering the hyperfine coupling of the radical with the N and H nuclei labeled

in red in figure S7a, positions 1 and 2, respectively, present in the DMPO molecule. The simulated spectrum (black line) had a good agreement with the central field position and linewidth of the experimental spectrum (red line) as shown in Figure S7a. However, the lineshape and spectrum structure does not match accurately. Due to the low concentration of trapped radical, the signal was too noisy and reducing the modulation amplitude to resolve all the hyperfine structure of the spectrum was not possible. Nevertheless, including hyperfine coupling with nuclei from the expected trapped radical R2 allowed to reduce the linewidth of the simulated spectrum and to improve the accordance with the experimental data. Then, the spectrum was simulated including the hyperfine coupling of the hydrogen atoms (labeled in blue, position 3 in figure S7a) in addition to the nitrogen and hydrogen typically present in the DMPO molecule. The comparison between experiment and simulation for this case can be seen in figure S7b. The best agreement between the experimental (red line) and simulated spectrum (black line) was obtained in a third step, when including the more distant nitrogen (labeled blue, position 4). The hyperfine constants (a) were adjusted to the values shown in Figure S8a-c. The best fit indicated higher values of hyperfine for the nitrogen and hydrogen nuclei closer to the $\text{NO}\cdot$ radical (1.33 mT and 0.937 mT, respectively). The two hydrogens symmetrically disposed on the carbon (labeled in blue, position 3) showed close hyperfine values (0.0981 and 0.152 mT), and the more distant nitrogen (labeled in blue, position 4) had a lower value of hyperfine (0.088 mT).

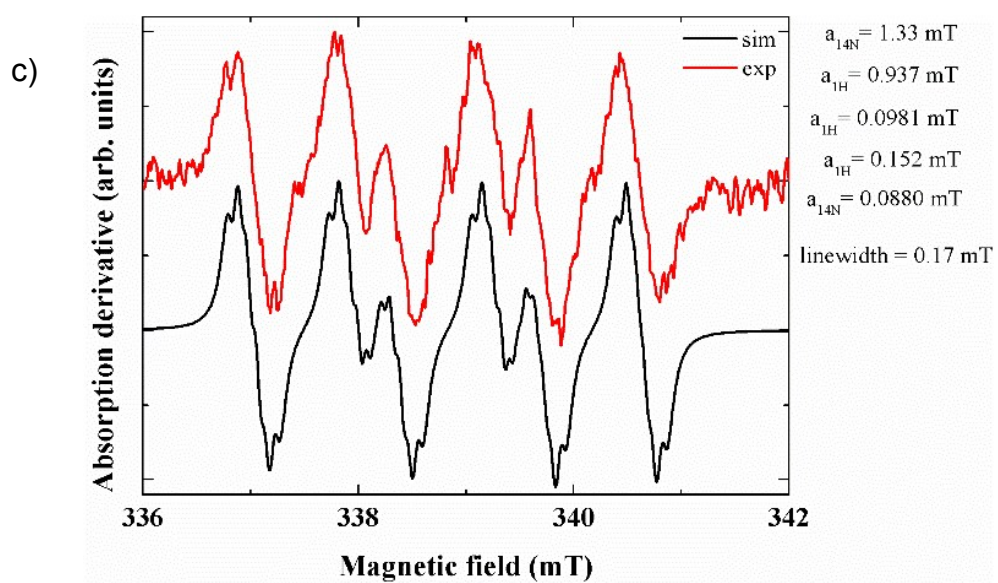
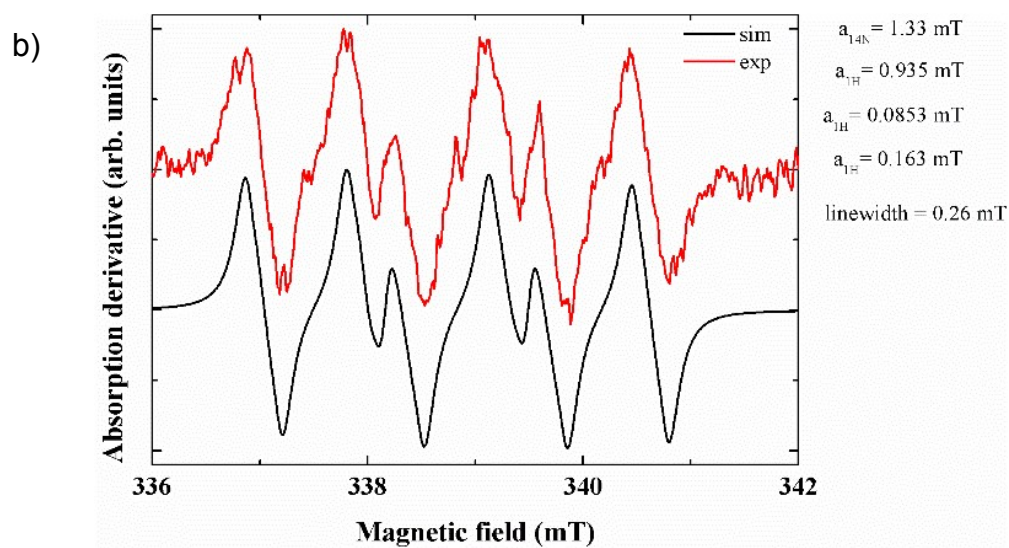
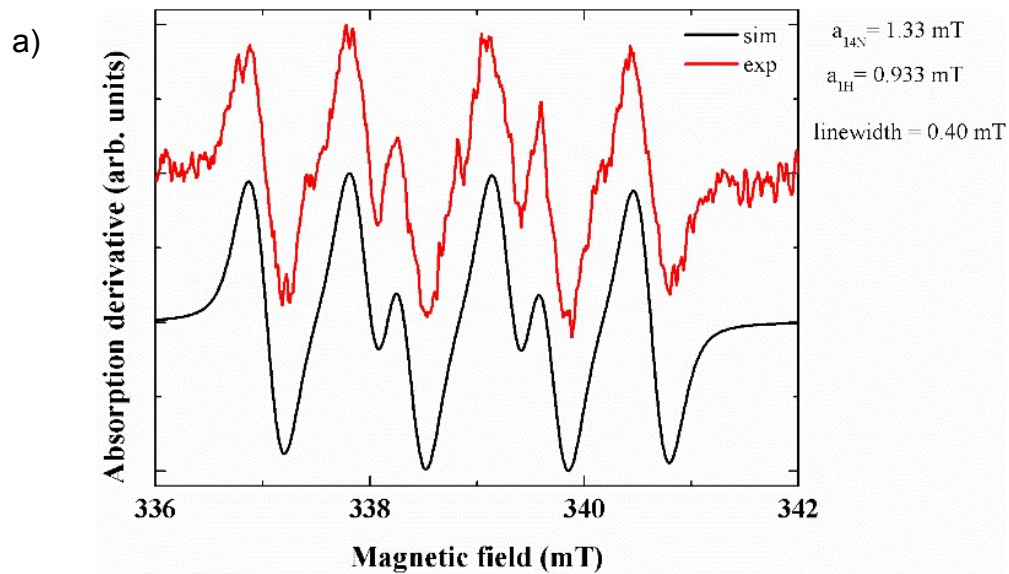


Figure S8. The EPR spectrum of DMPO – R2 and simulation considering different nuclei coupled to the NO radical.

5. NMR Spectra of Compounds

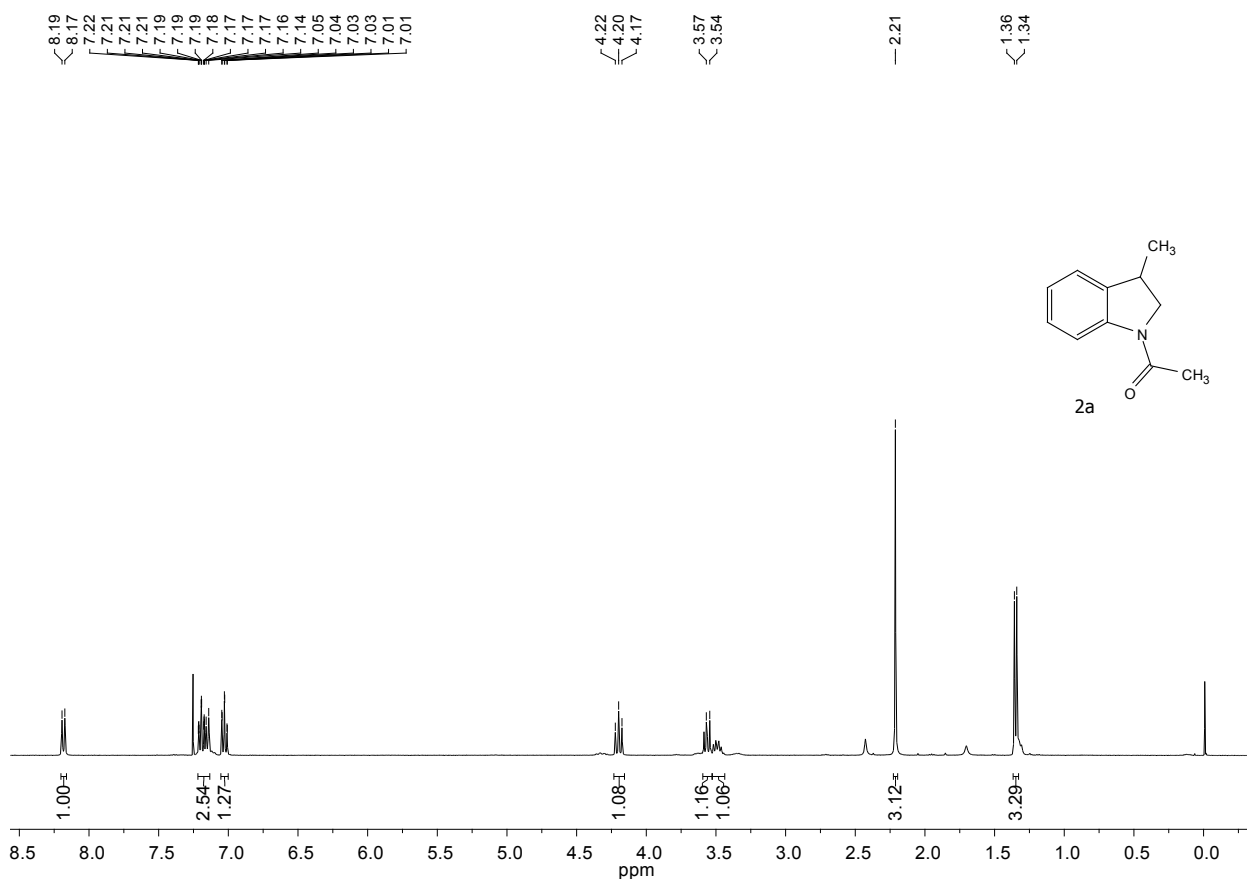


Figure S9. ¹H NMR of compound **2a** (400 MHz, CDCl₃).

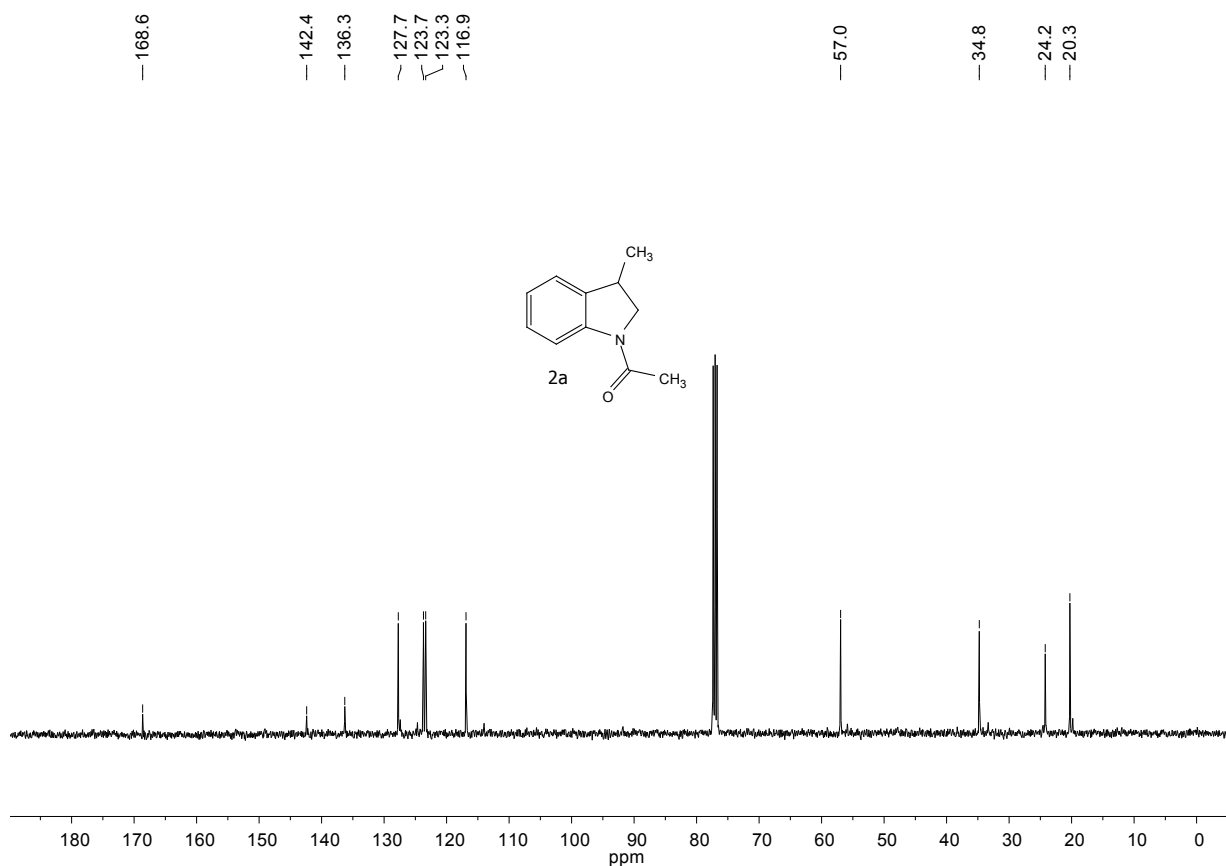


Figure S10. ¹³C NMR of compound **2a** (100 MHz, CDCl₃).

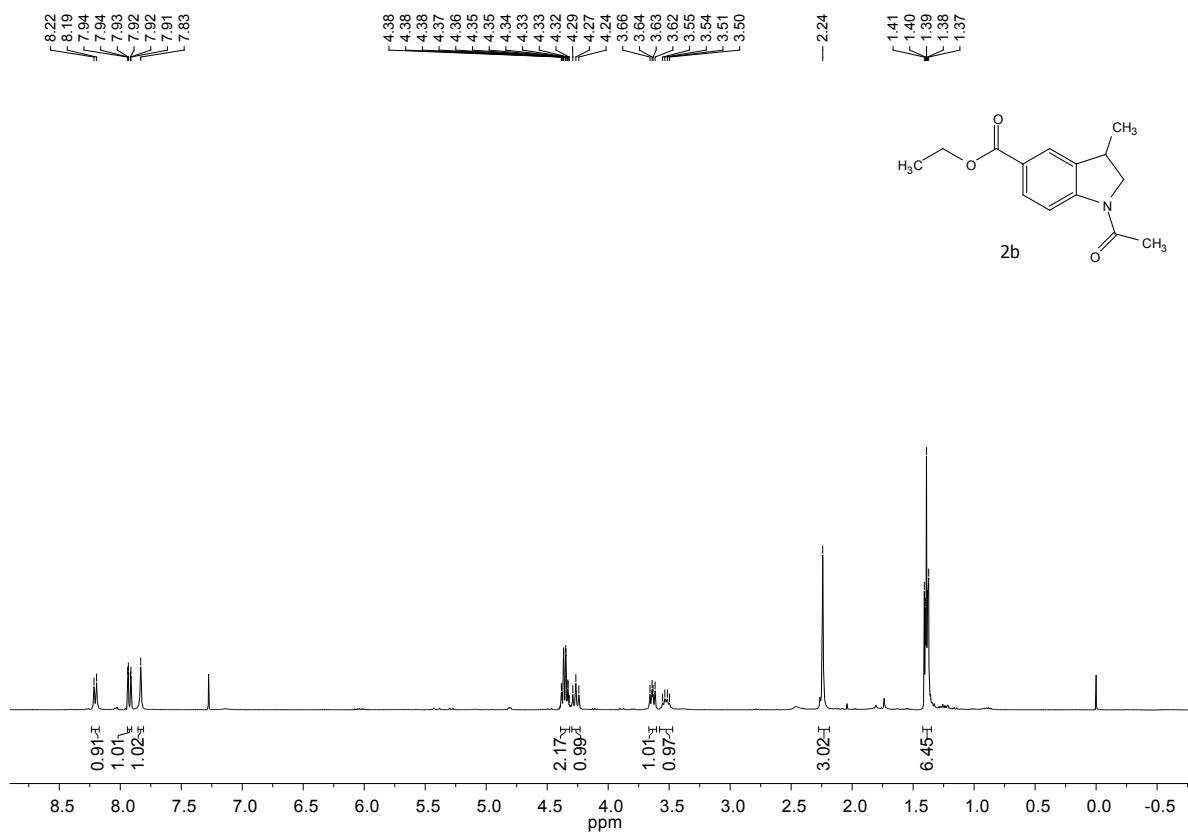


Figure S11. ¹H NMR of compound **2b** (400 MHz, CDCl₃).

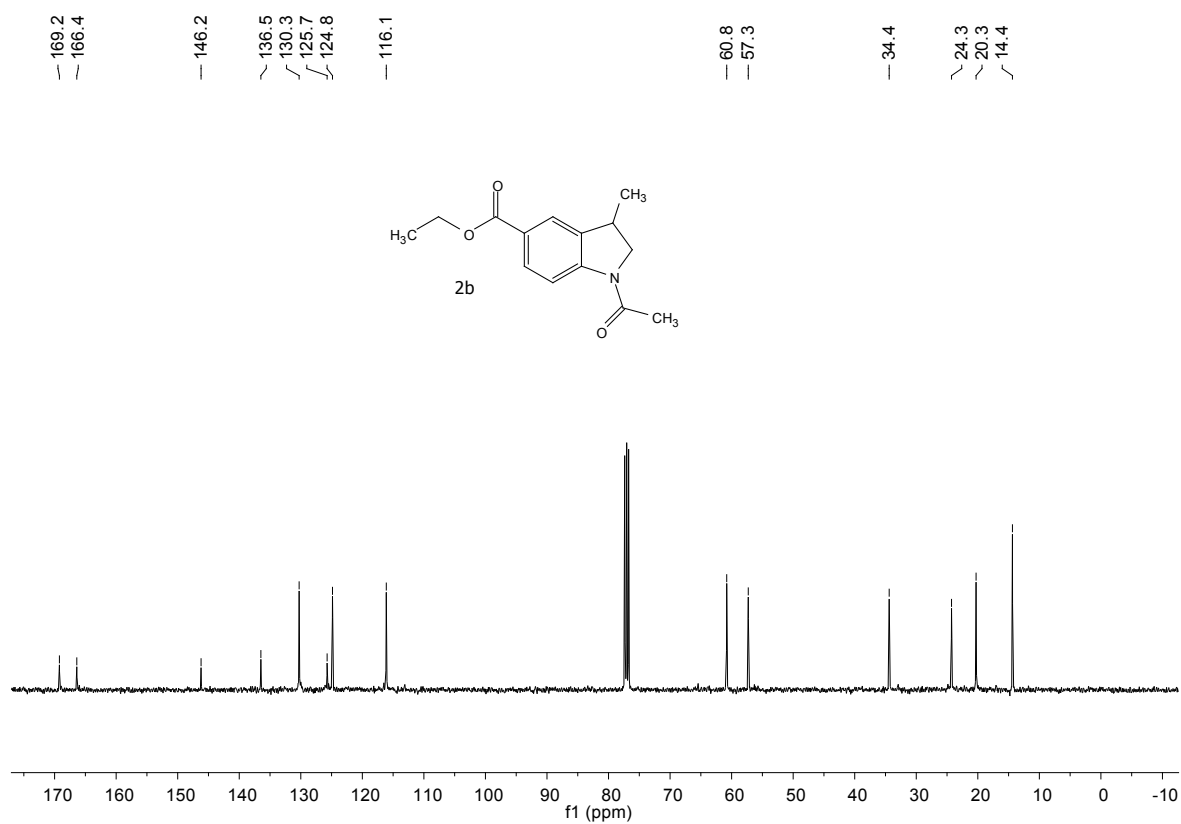


Figure S12. ¹³C NMR of compound **2b** (100 MHz, CDCl₃).

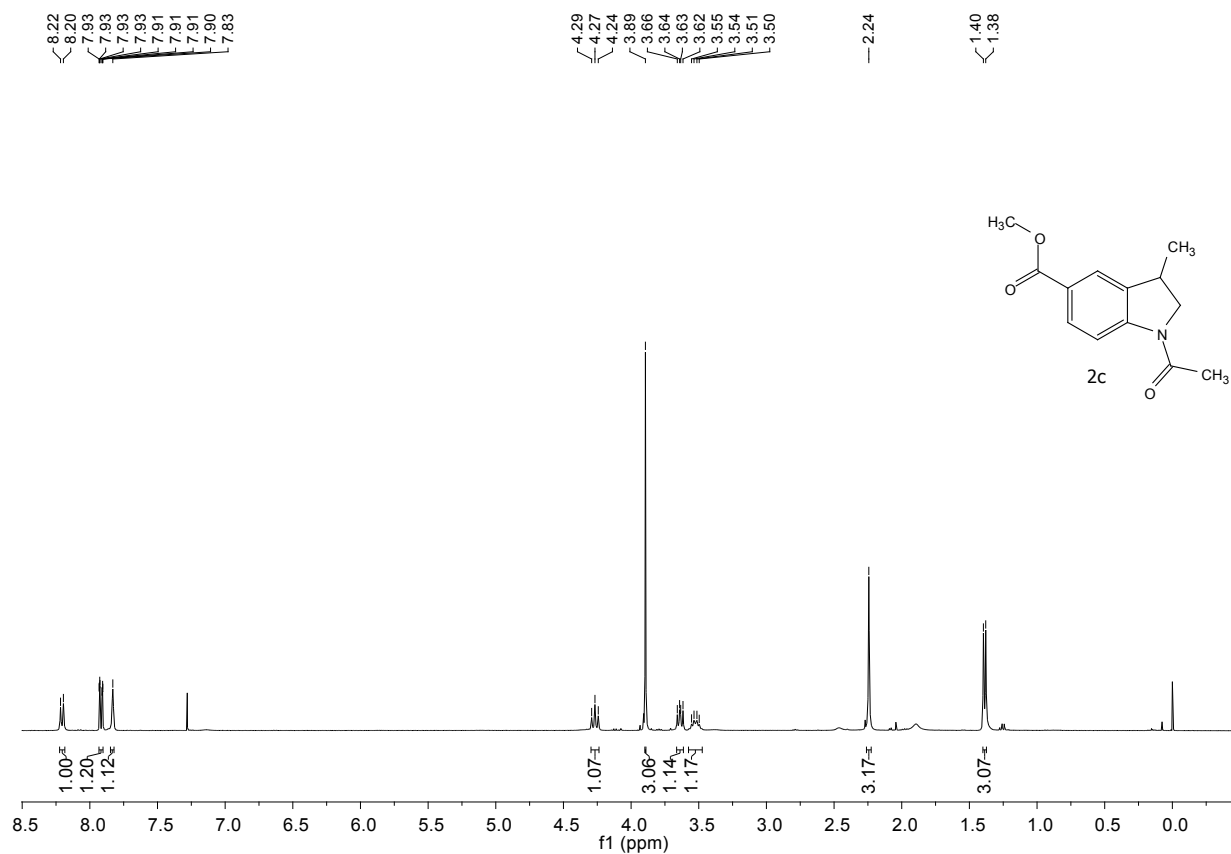


Figure S13. ¹H NMR of compound **2c** (400 MHz, CDCl₃).

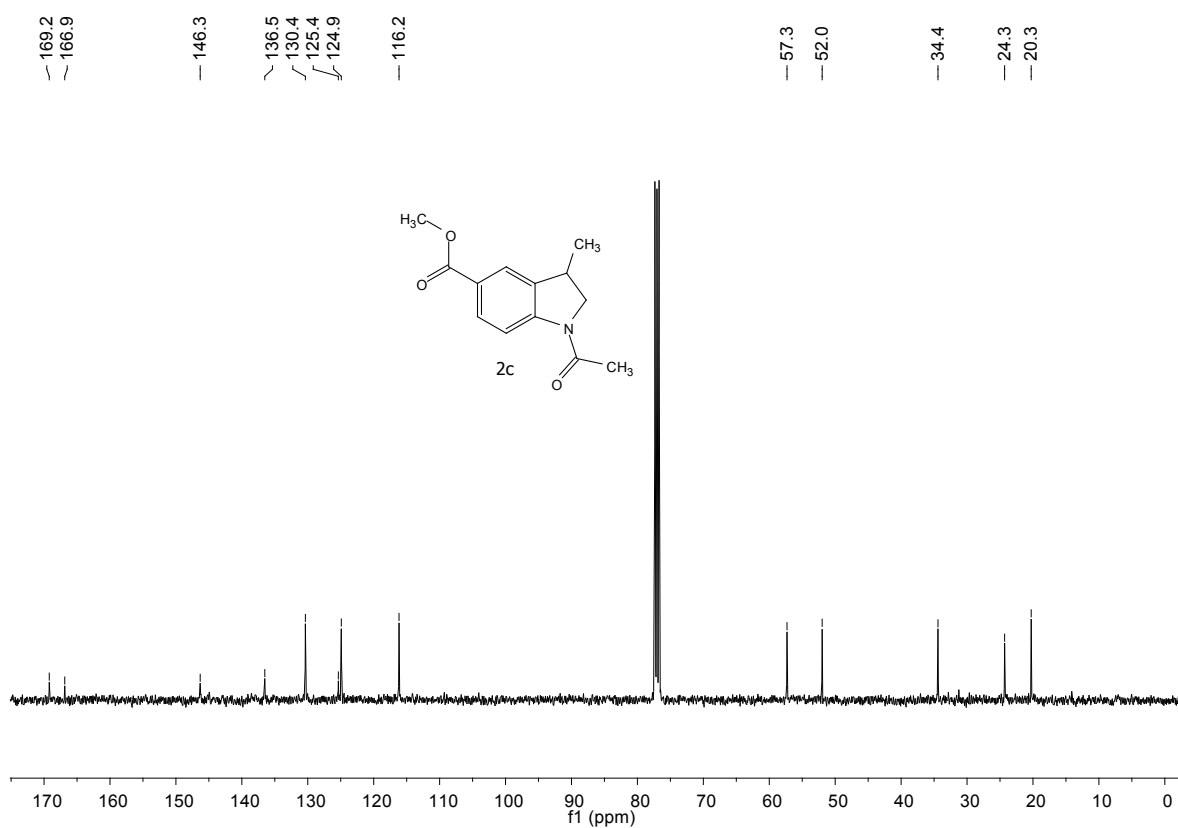


Figure S14. ¹³C NMR of compound **2c** (100 MHz, CDCl₃)

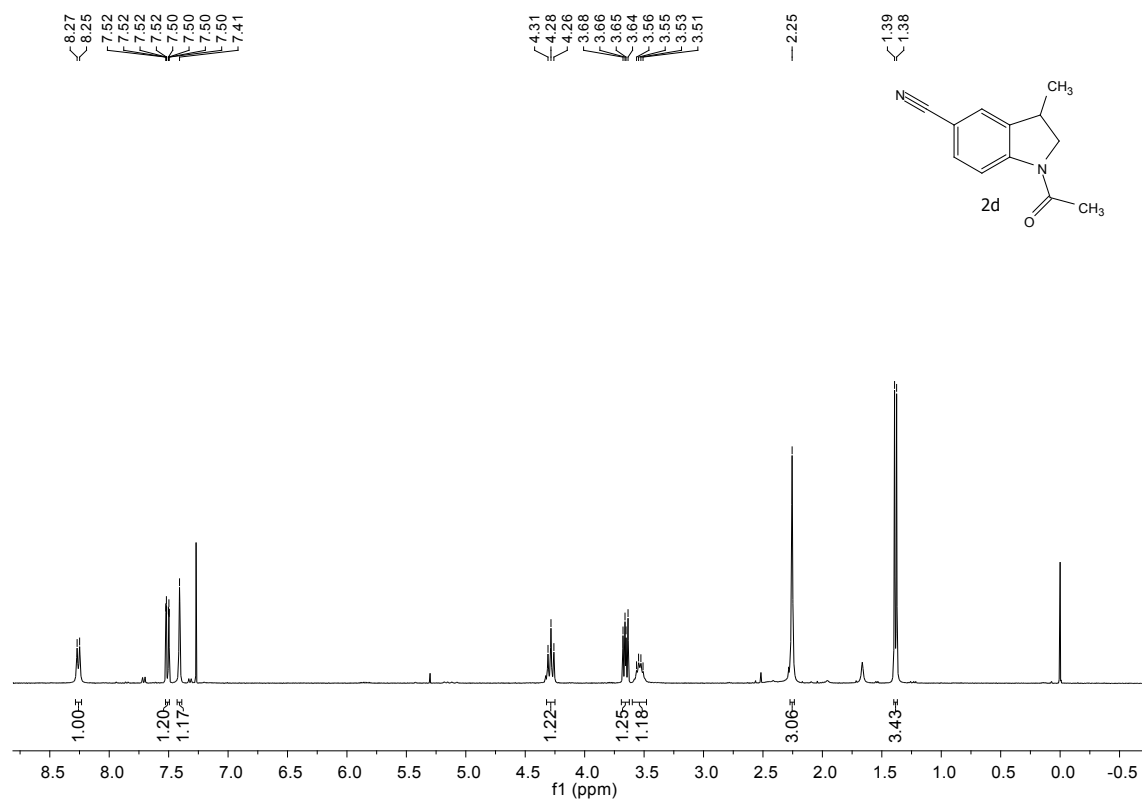


Figure S15. ¹H NMR of compound **2d** (400 MHz, CDCl₃).

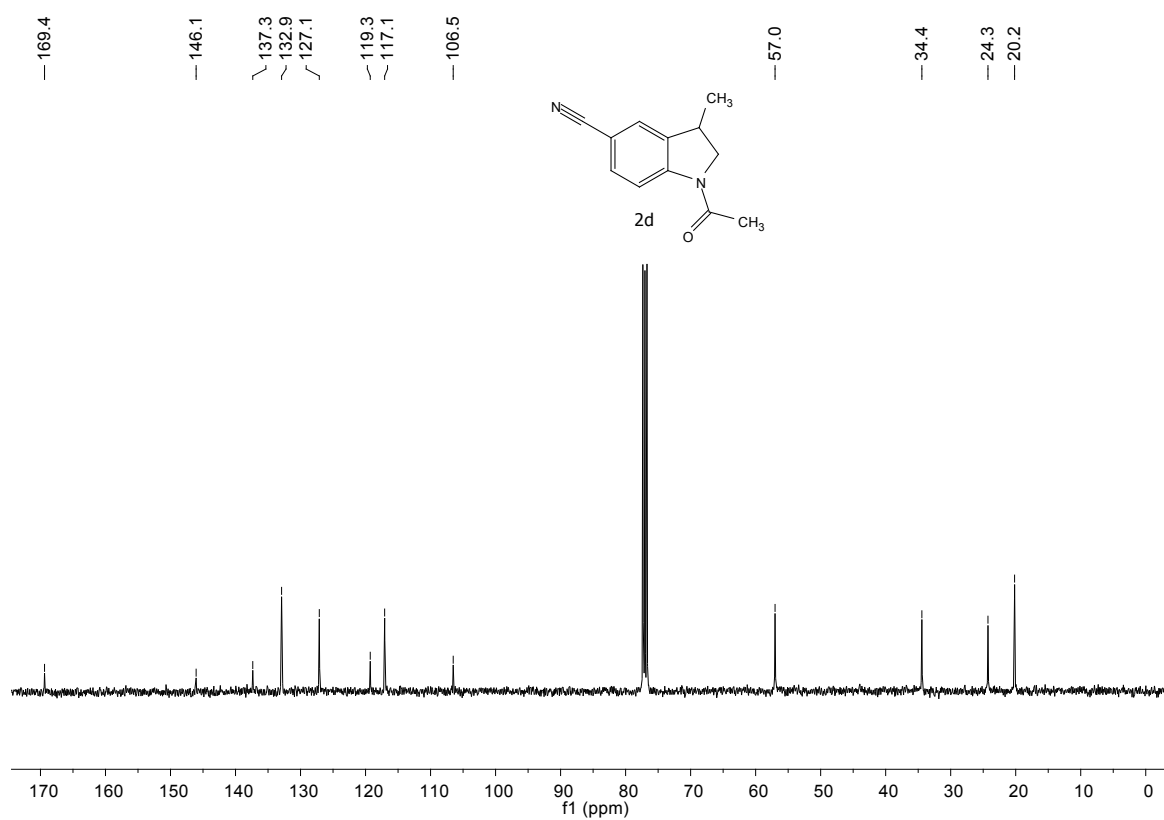


Figure S16. ¹³C NMR of compound **2d** (100 MHz, CDCl₃).

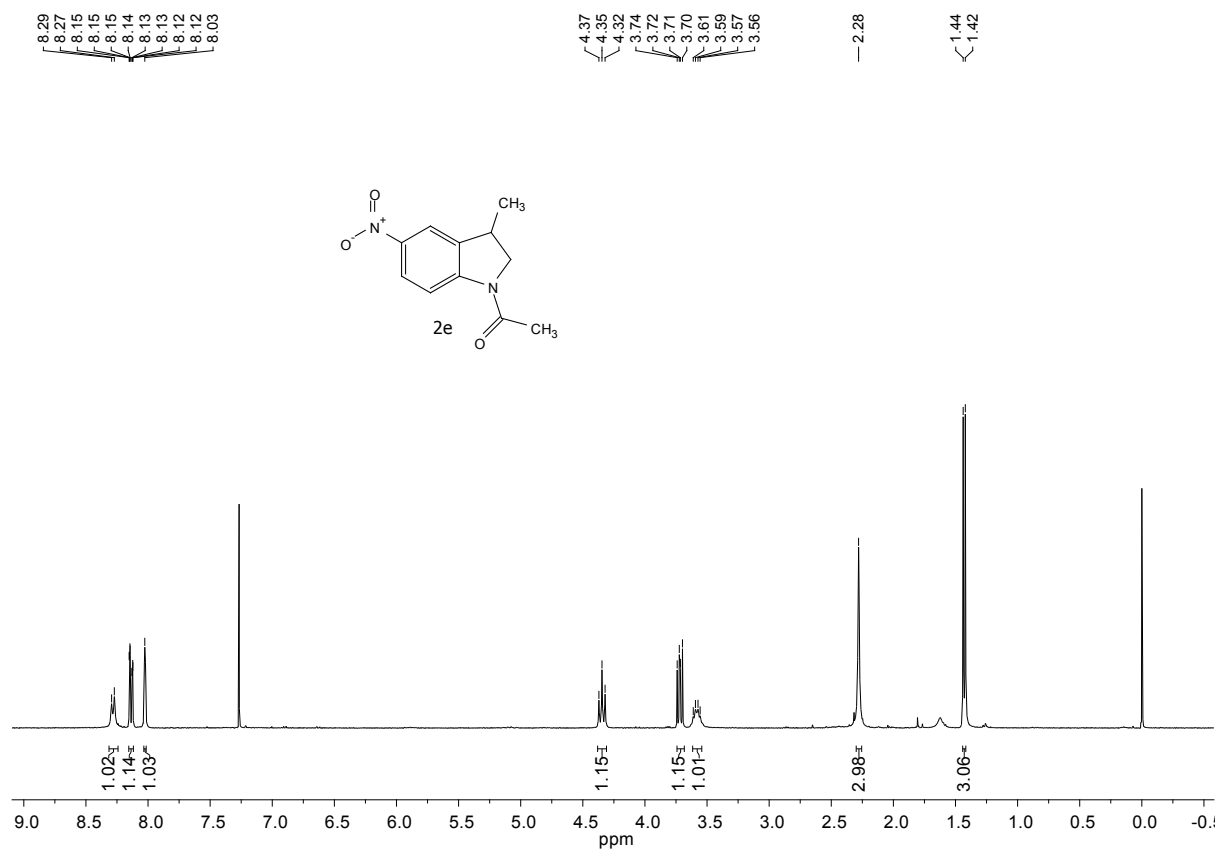


Figure S17. ¹H NMR of compound **2e** (400 MHz, CDCl₃).

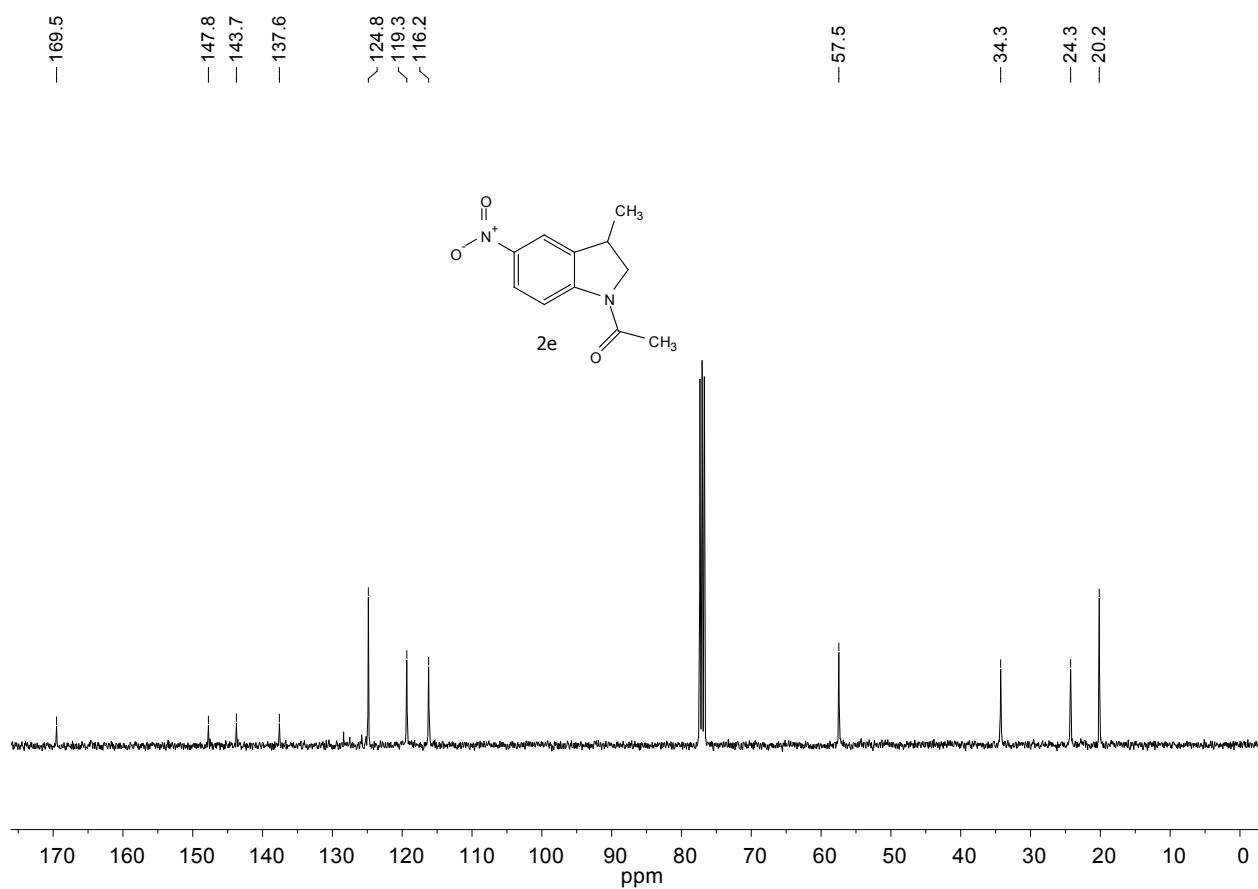


Figure S18. ¹³C NMR of compound **2e** (100 MHz, CDCl₃).

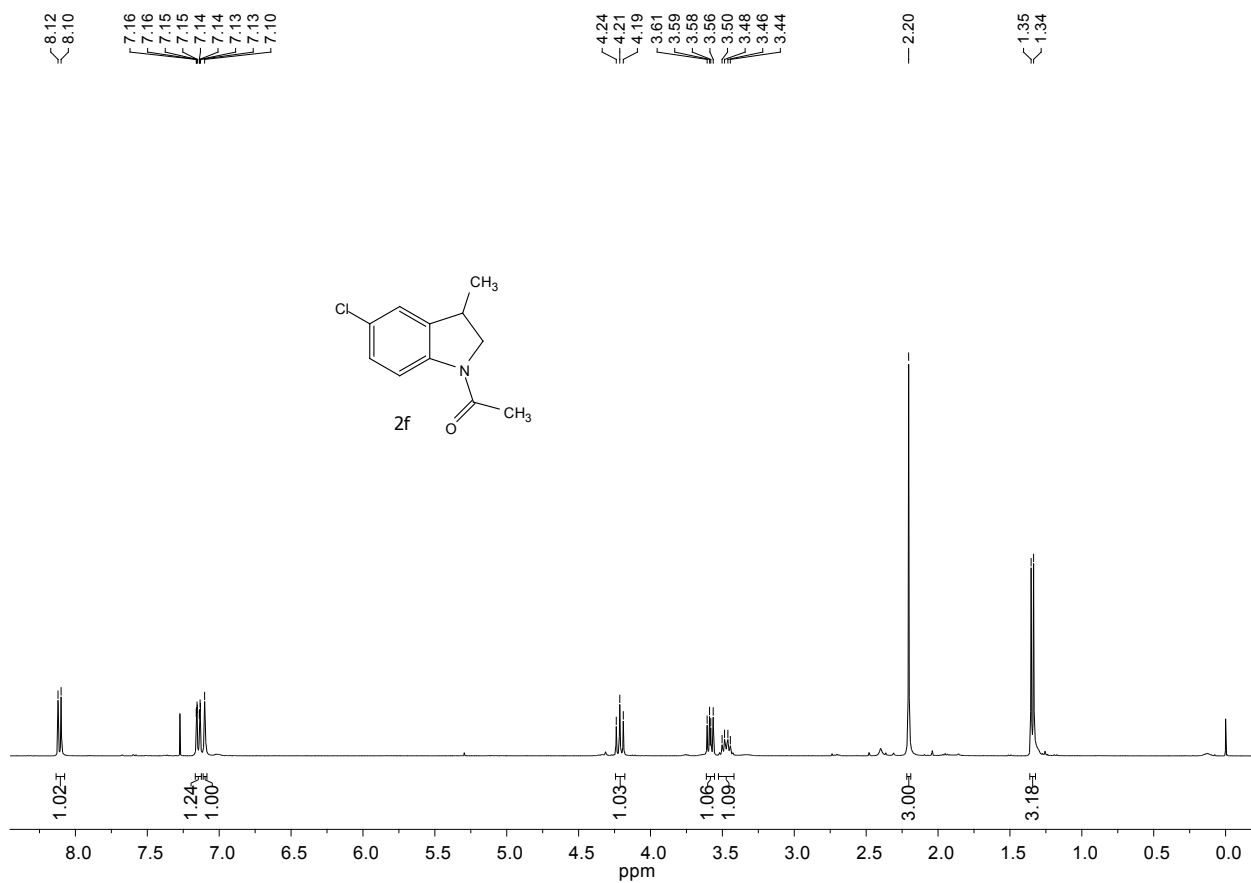


Figure S19. ¹H NMR of compound **2f** (400 MHz, CDCl₃).

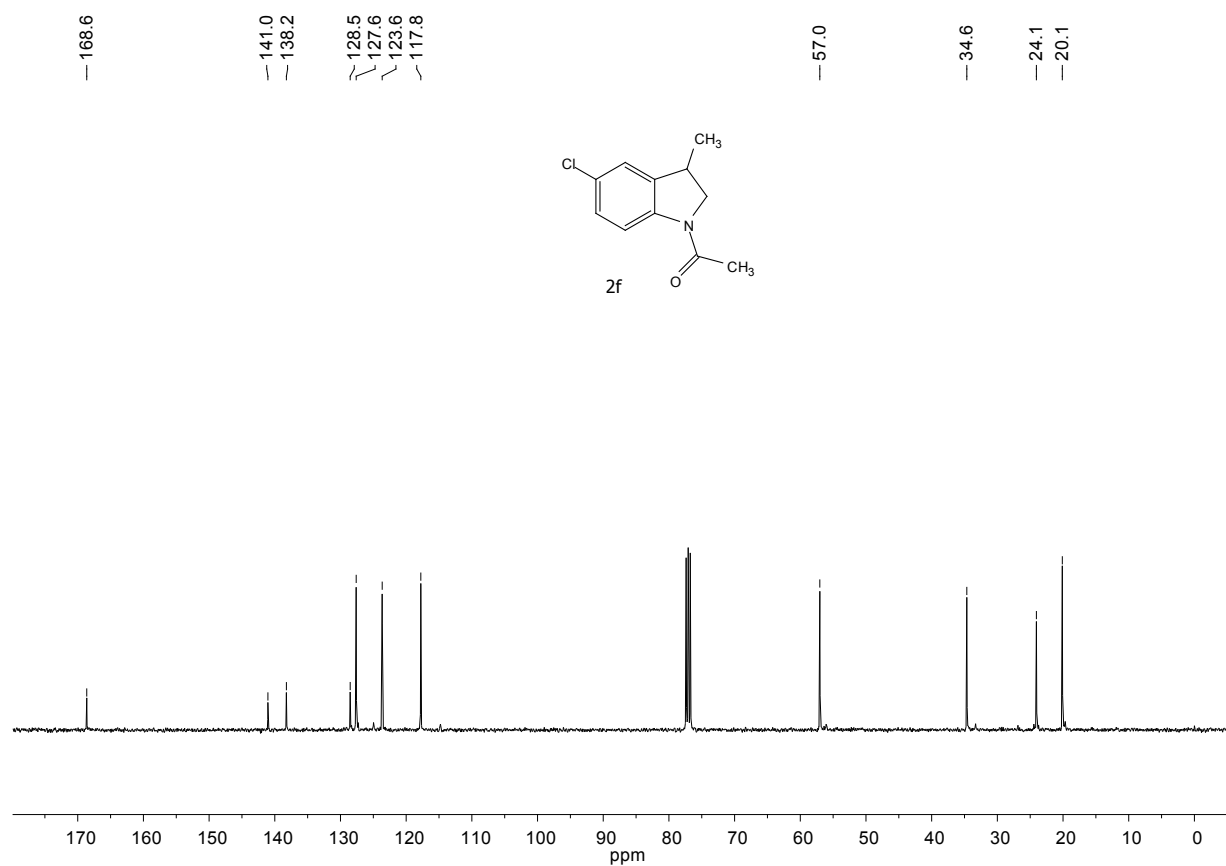


Figure S20. ¹³C NMR of compound **2f** (100 MHz, CDCl₃).

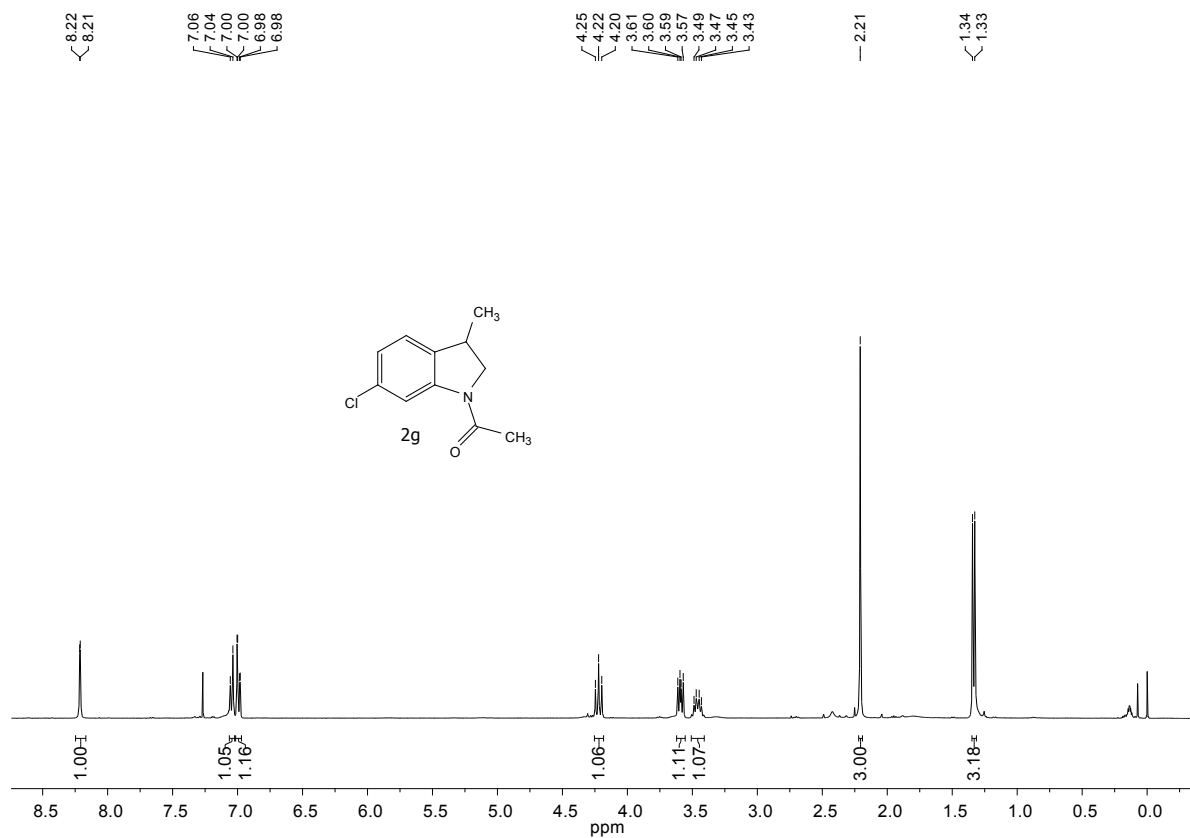


Figure S21. ¹H NMR of compound **2g** (400 MHz, CDCl₃).

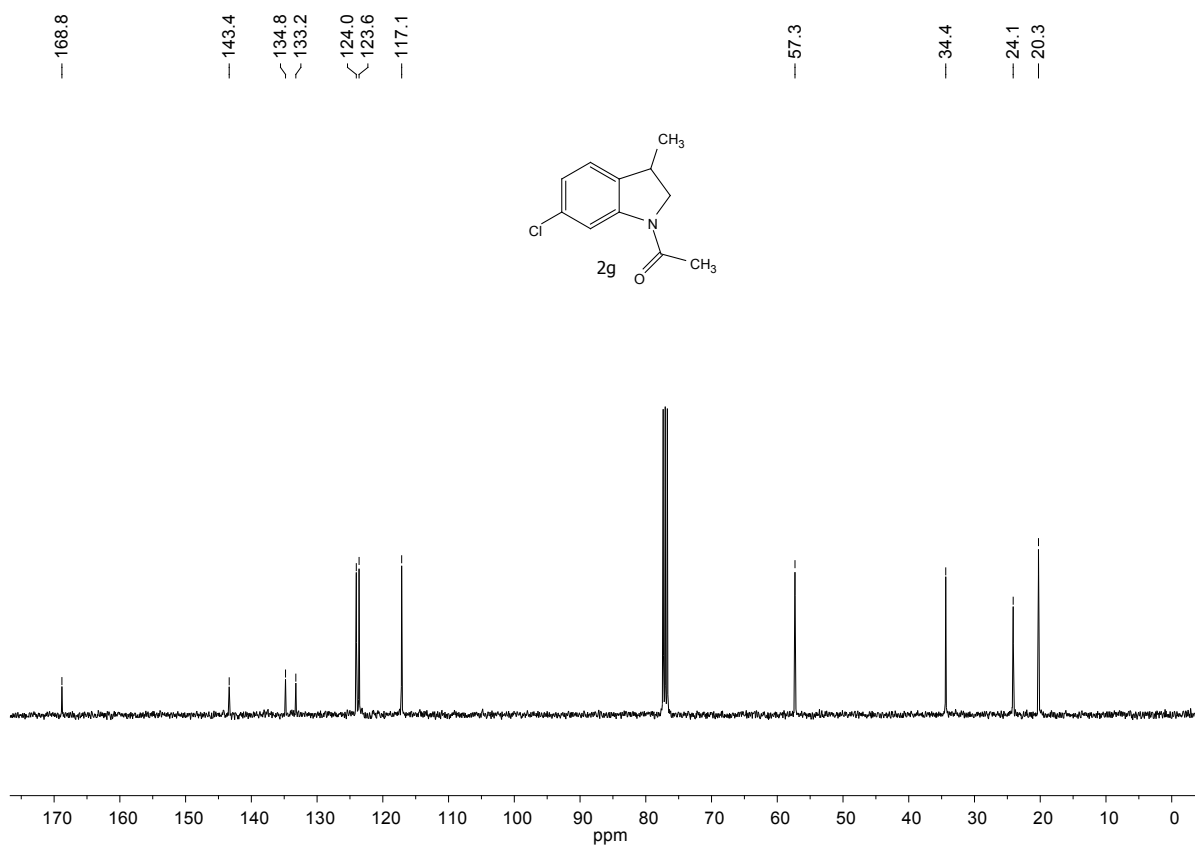


Figure S22. ¹³C NMR of compound **2g** (100 MHz, CDCl₃).

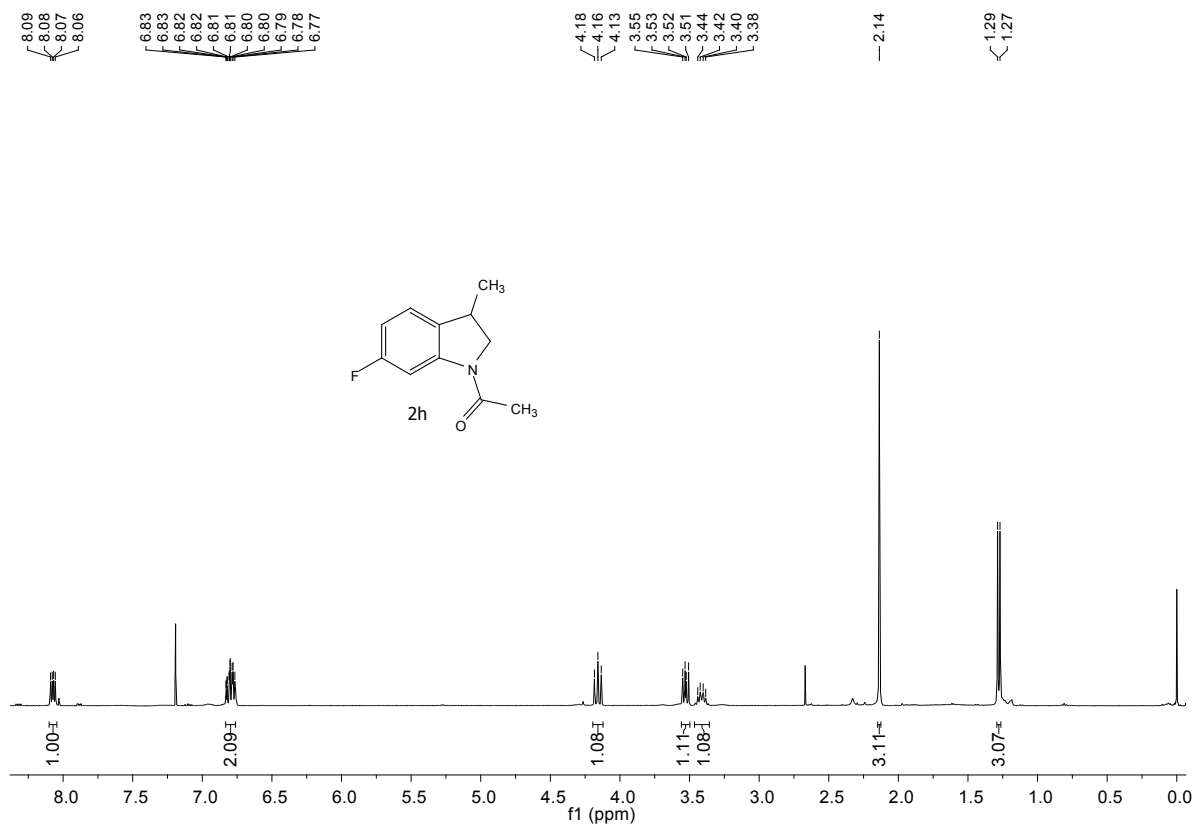


Figure S23. ¹H NMR of compound **2h** (400 MHz, CDCl₃).

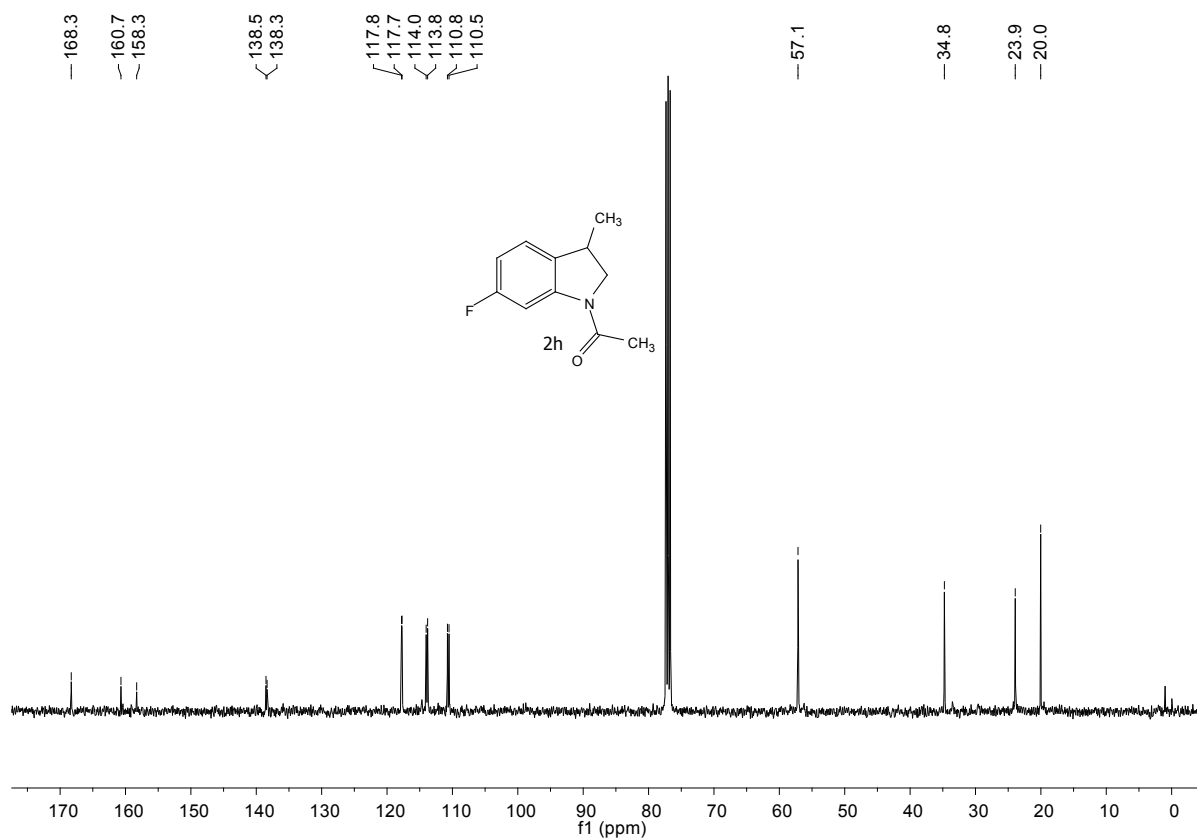


Figure S24. ¹³C NMR of compound **2h** (100 MHz, CDCl₃).

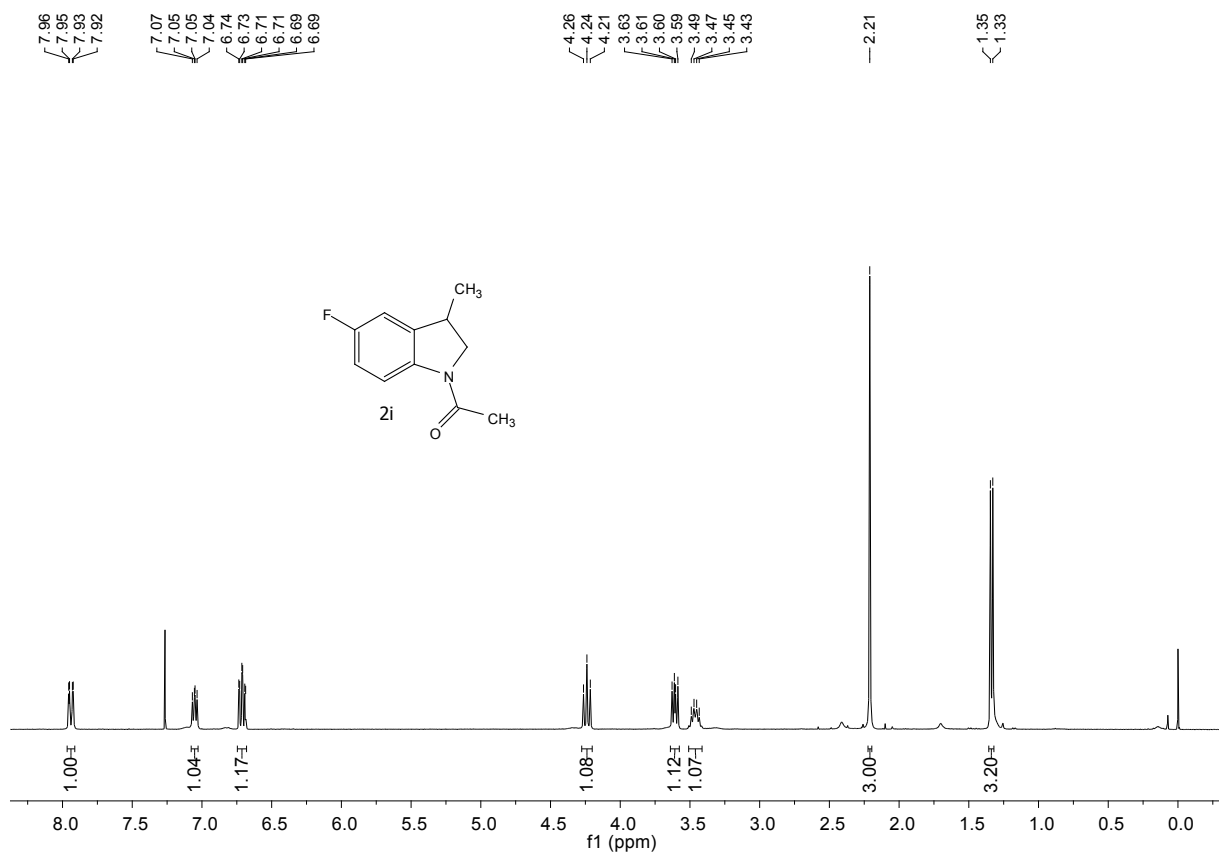


Figure S25. ¹H NMR of compound **2i** (400 MHz, CDCl₃).

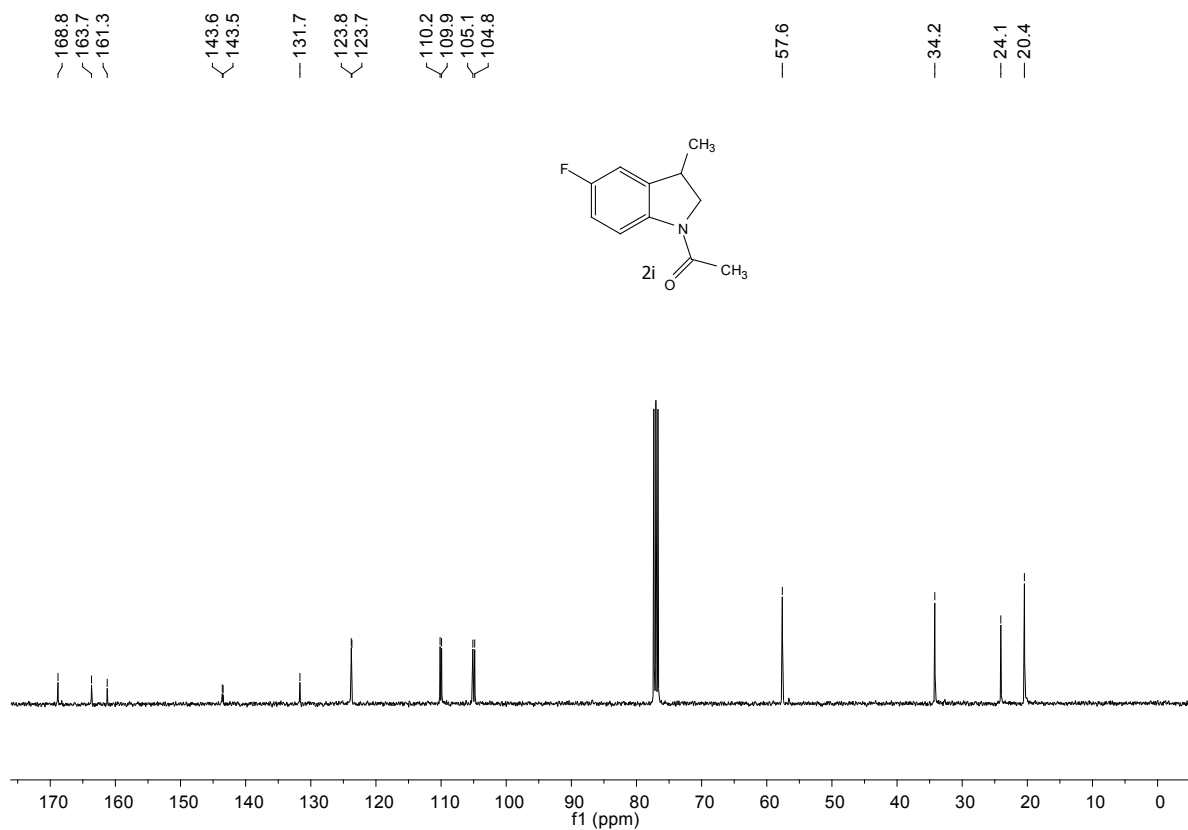


Figure S26. ¹³C NMR of compound **2i** (100 MHz, CDCl₃).

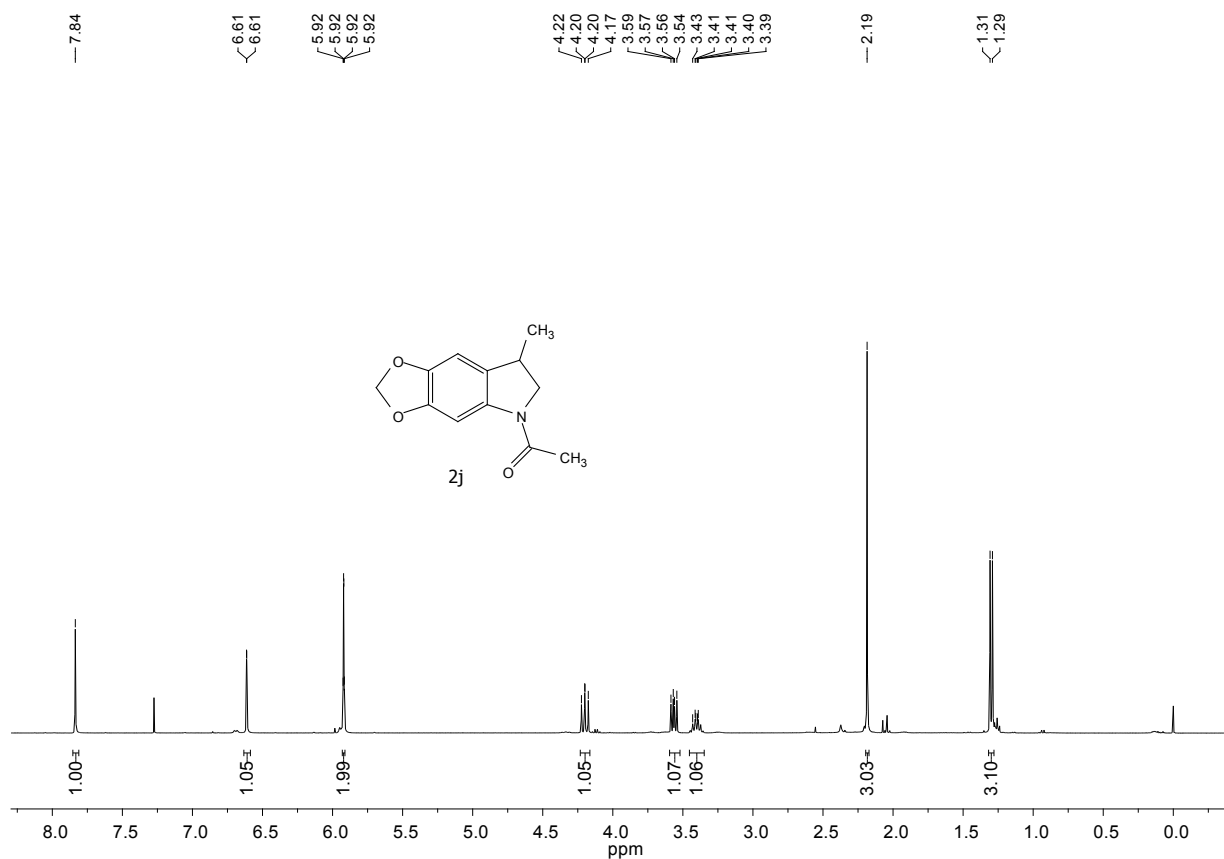


Figure S27. ^1H NMR of compound **2j** (400 MHz, CDCl_3).

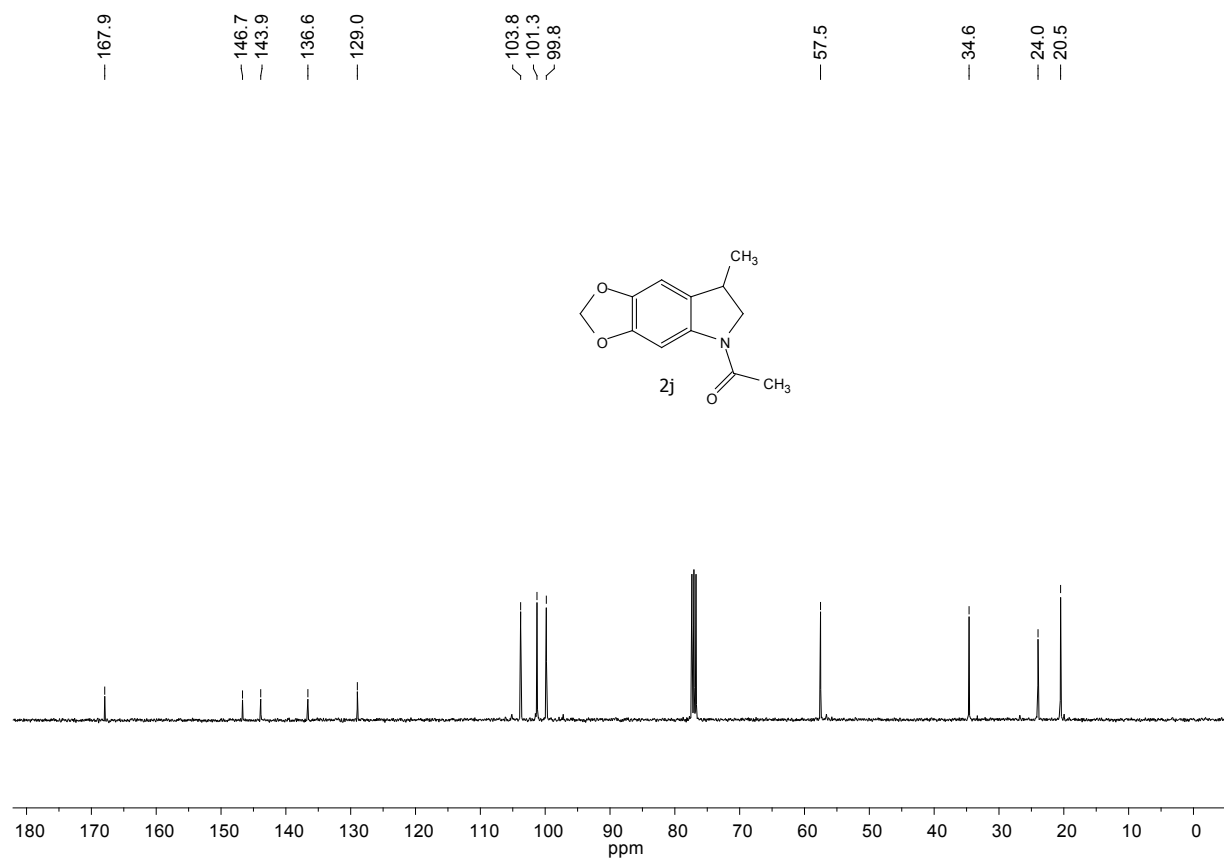


Figure S28. ^{13}C NMR of compound **2j** (100 MHz, CDCl_3).

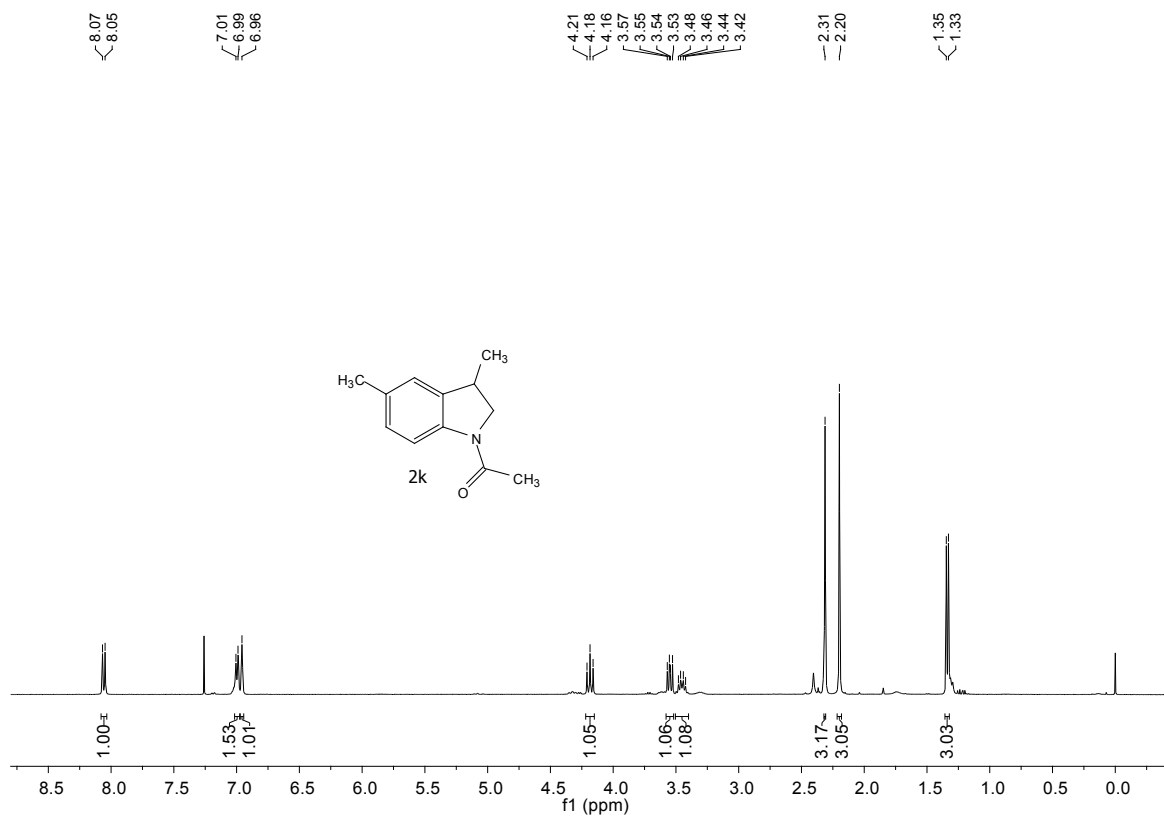


Figure S29. ¹H NMR of compound **2k** (400 MHz, CDCl₃).

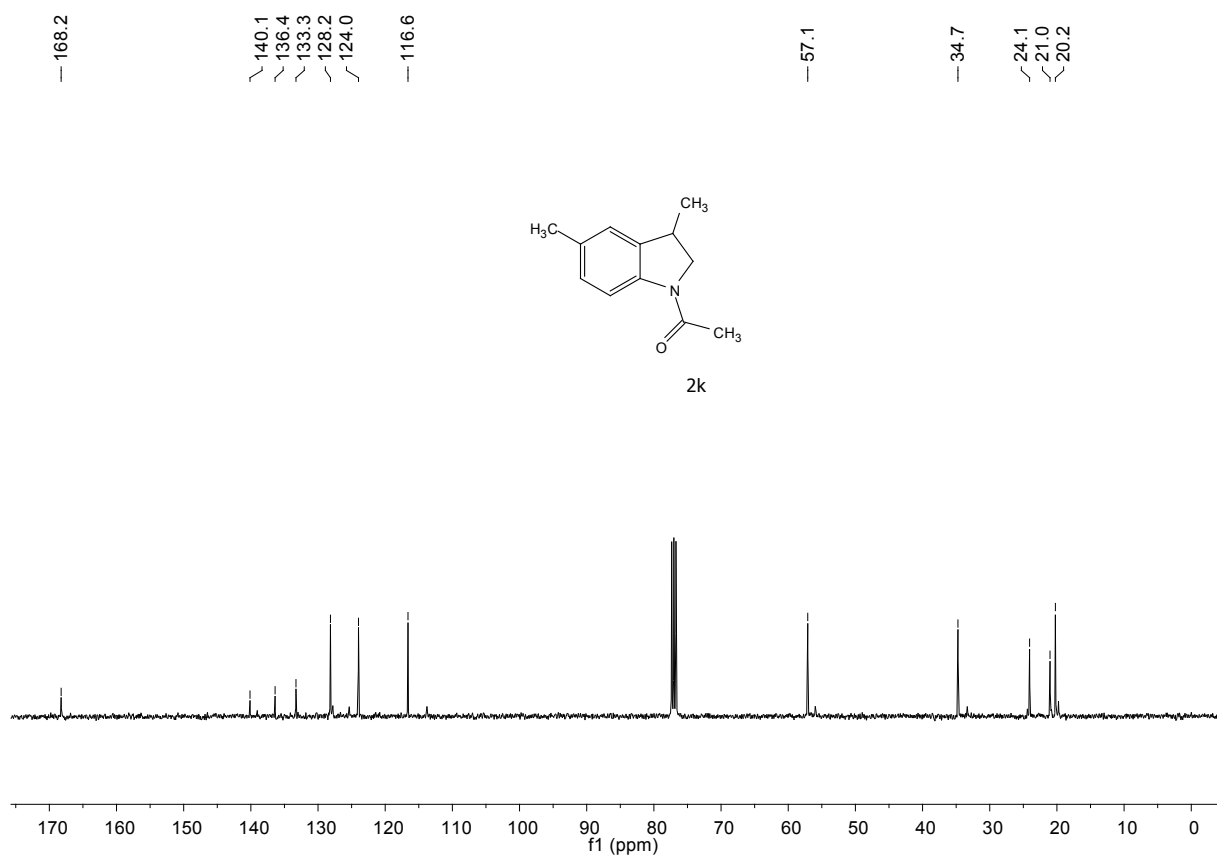


Figure S30. ¹³C NMR of compound **2k** (100 MHz, CDCl₃).

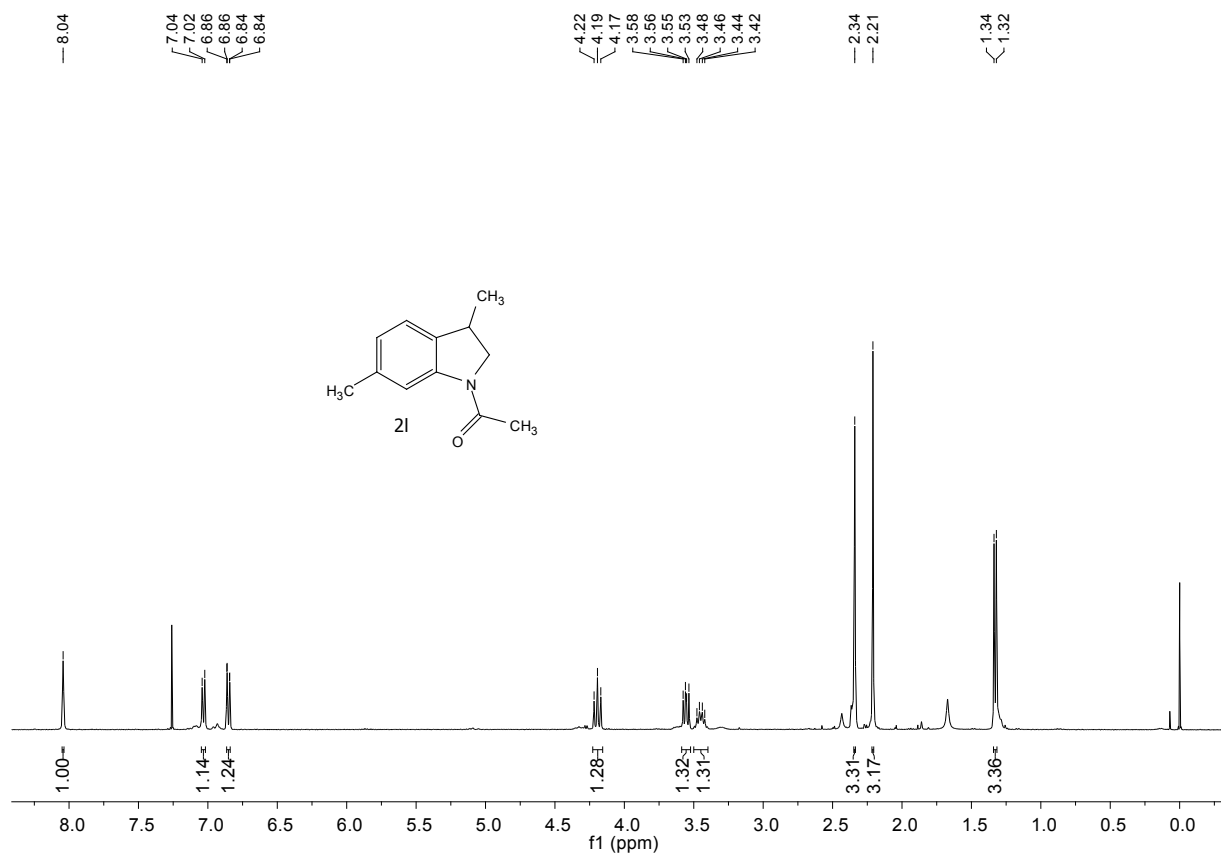


Figure S31. ¹H NMR of compound **2I** (400 MHz, CDCl₃).

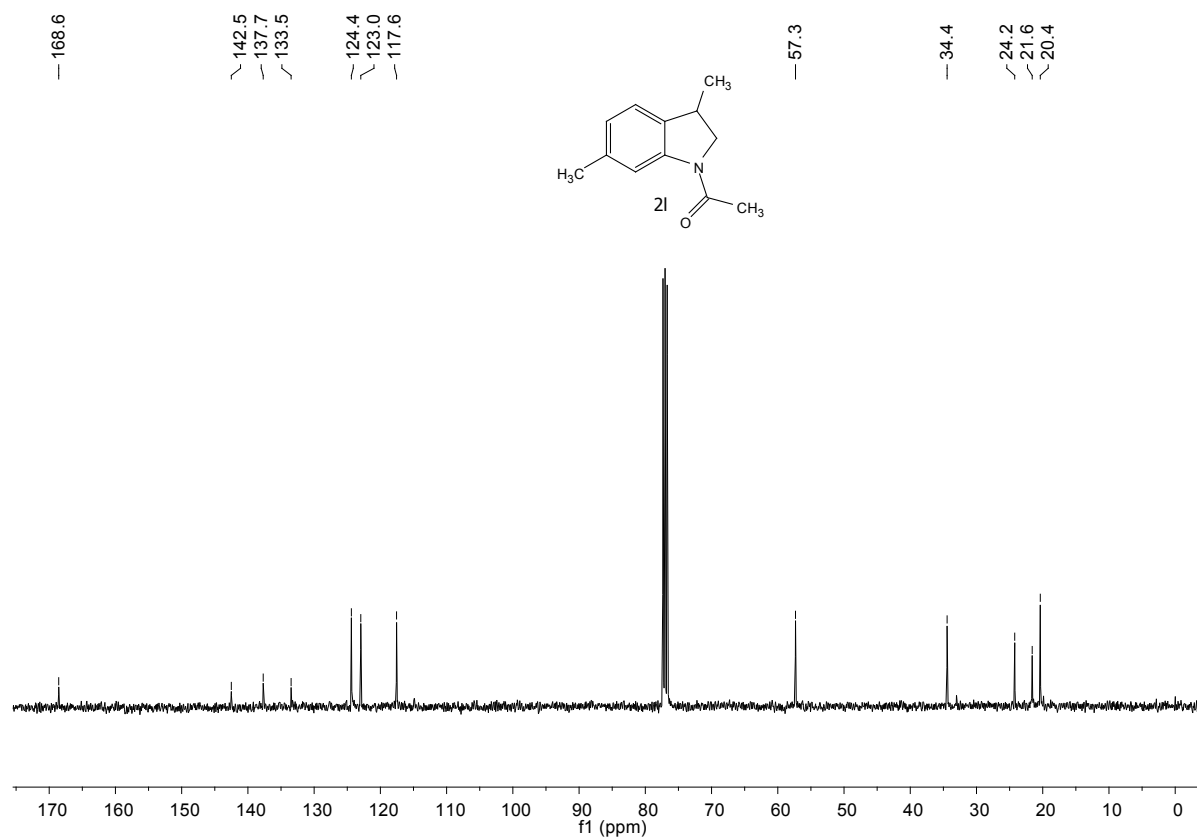


Figure S32. ¹³C NMR of compound **2I** (100 MHz, CDCl₃).

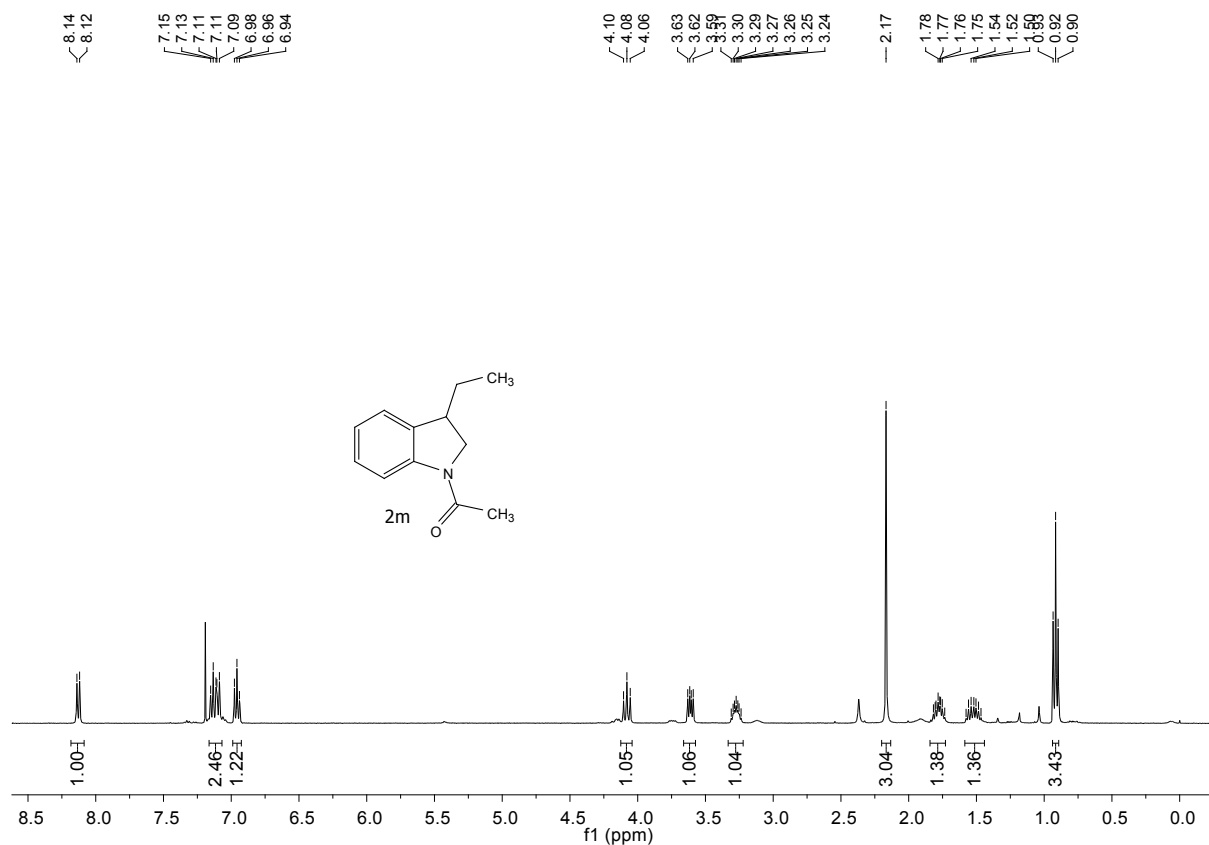


Figure S33. ¹H NMR of compound **2m** (400 MHz, CDCl₃).

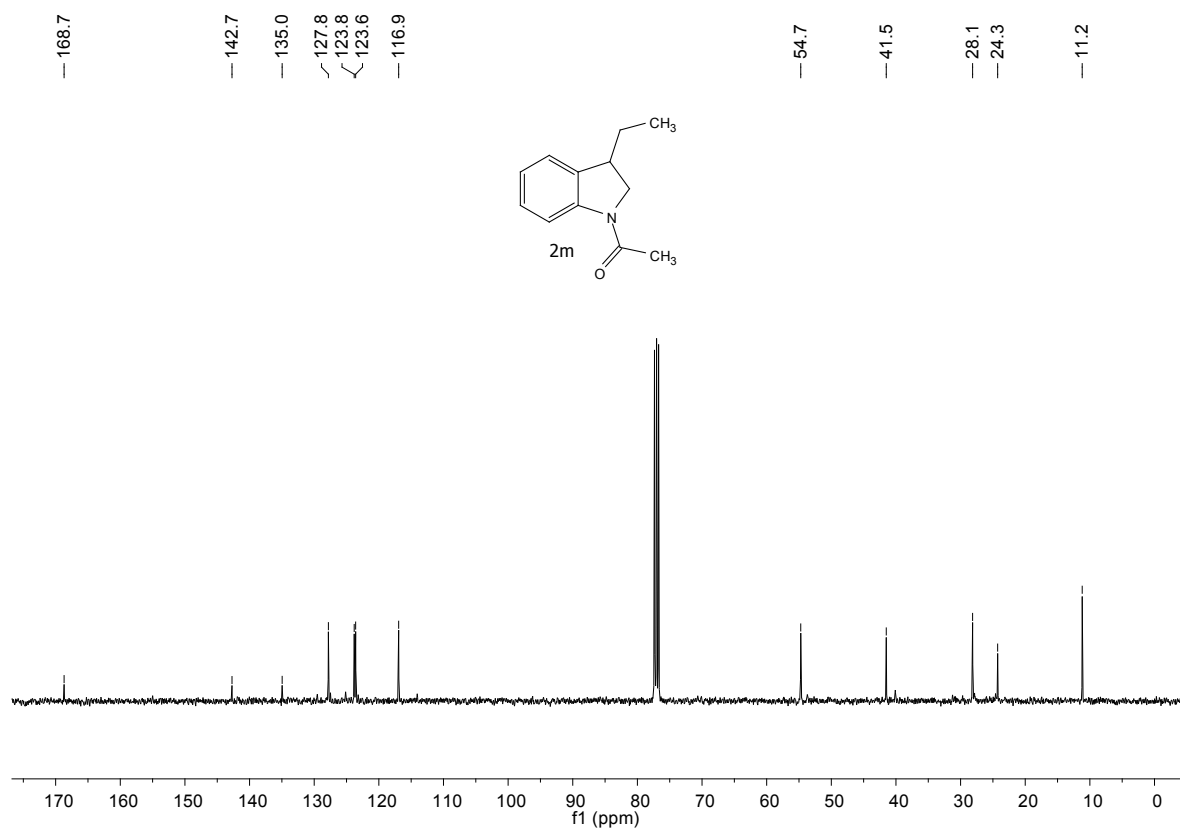


Figure S34. ¹³C NMR of compound **2m** (100 MHz, CDCl₃).

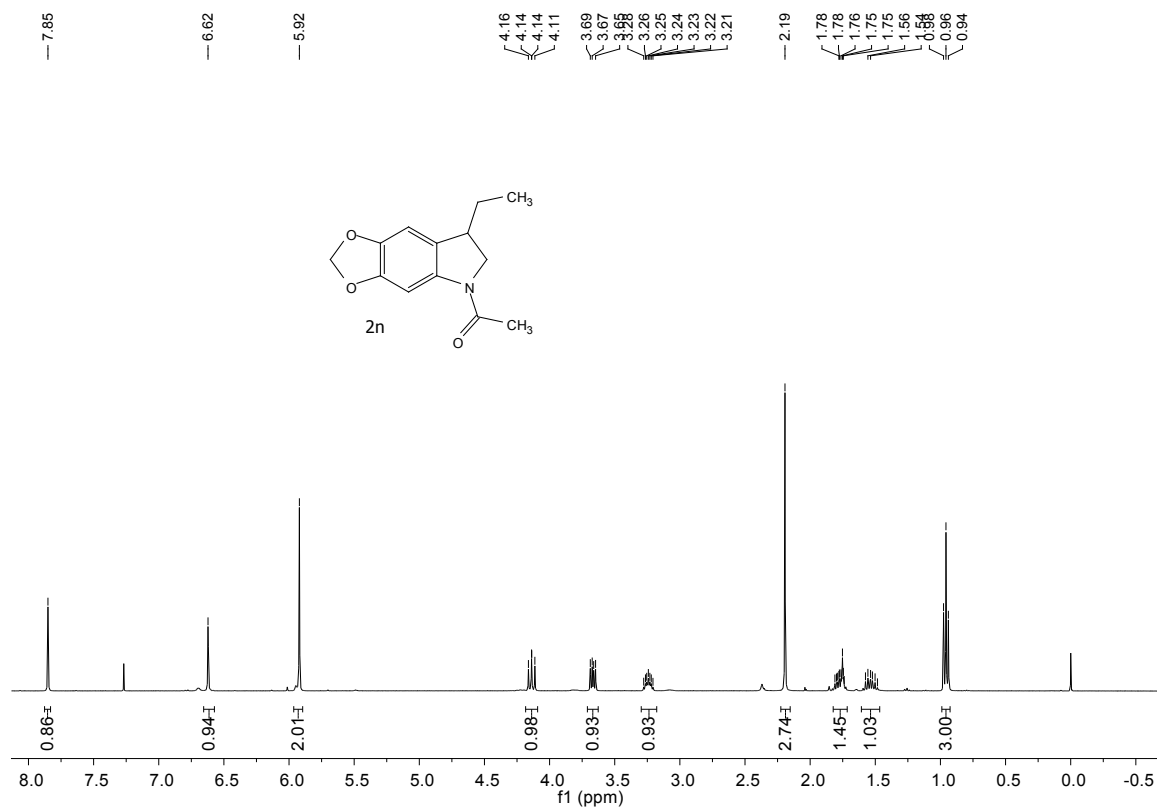


Figure S35. ^1H NMR of compound **2n** (400 MHz, CDCl_3).

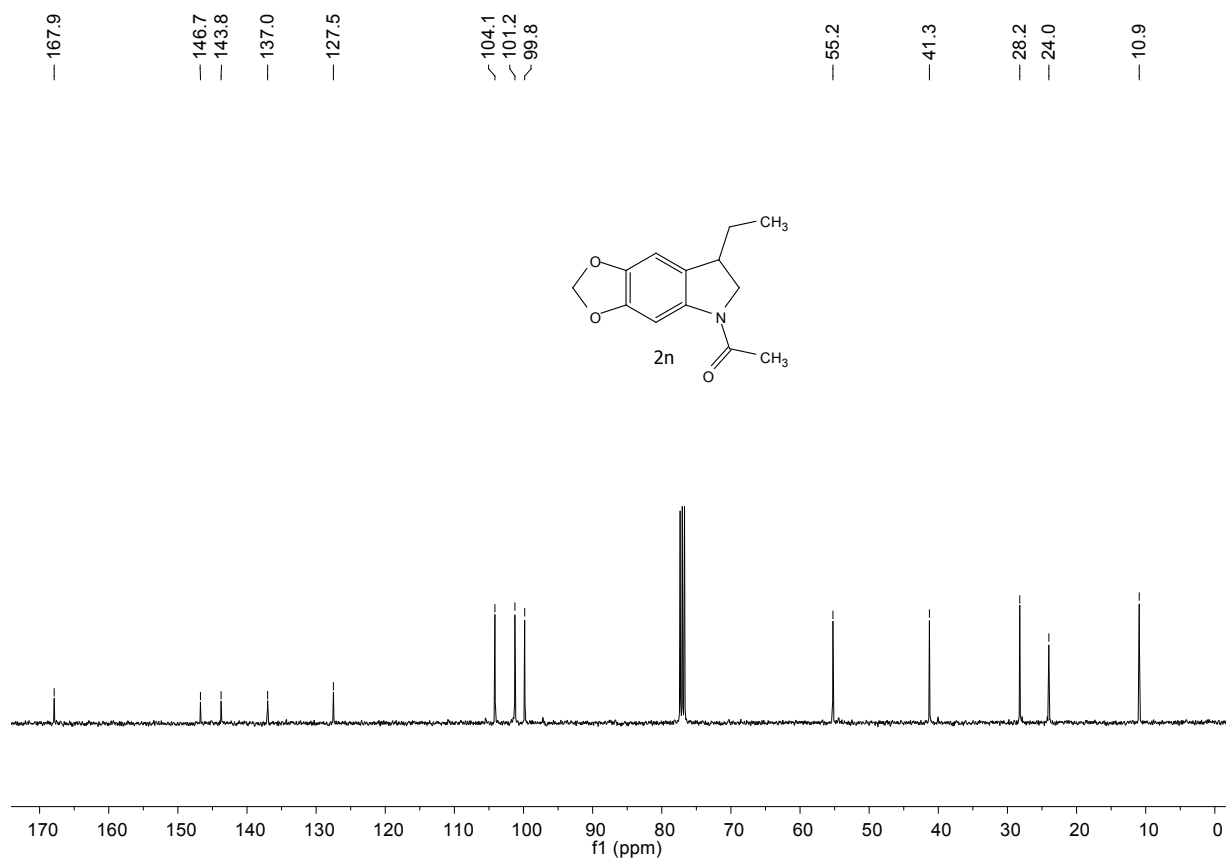


Figure S36. ^{13}C NMR of compound **2n** (100 MHz, CDCl_3).

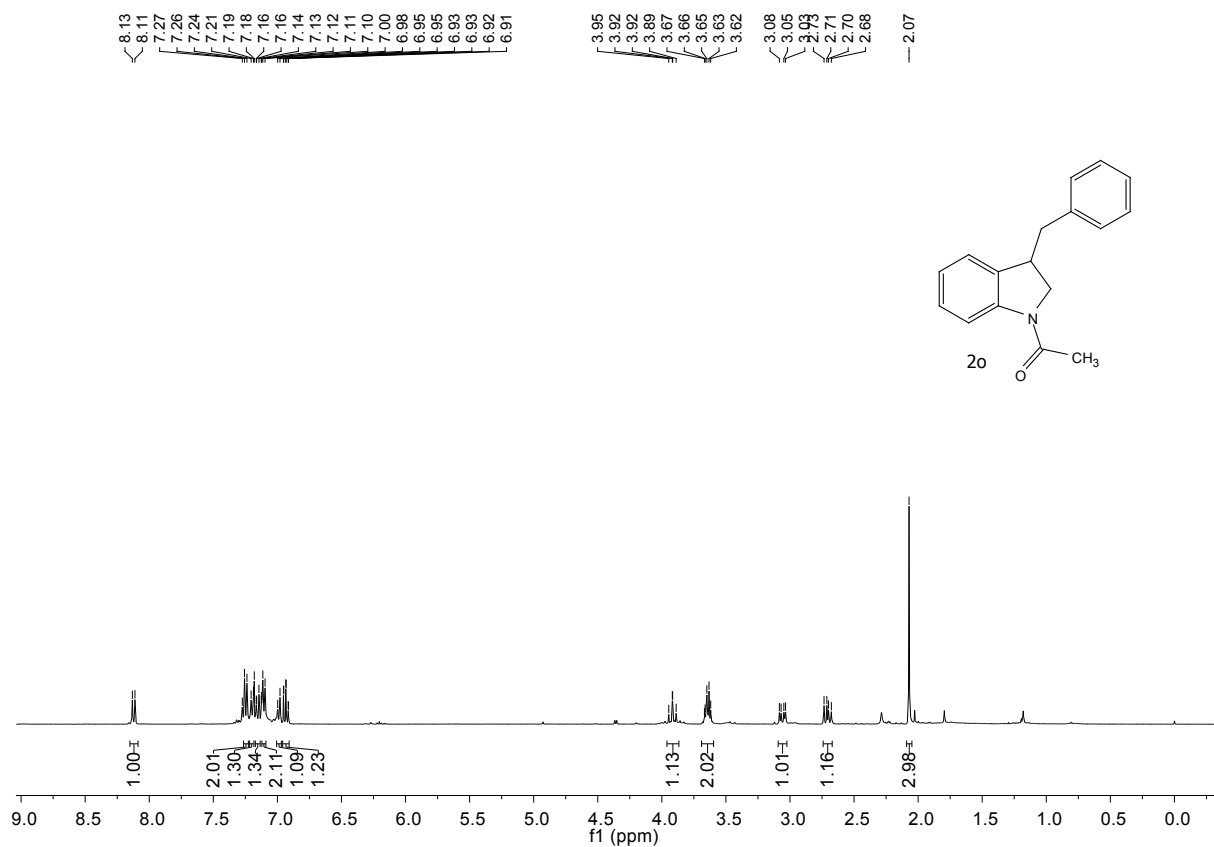


Figure S37. ¹H NMR of compound **2o** (400 MHz, CDCl₃).

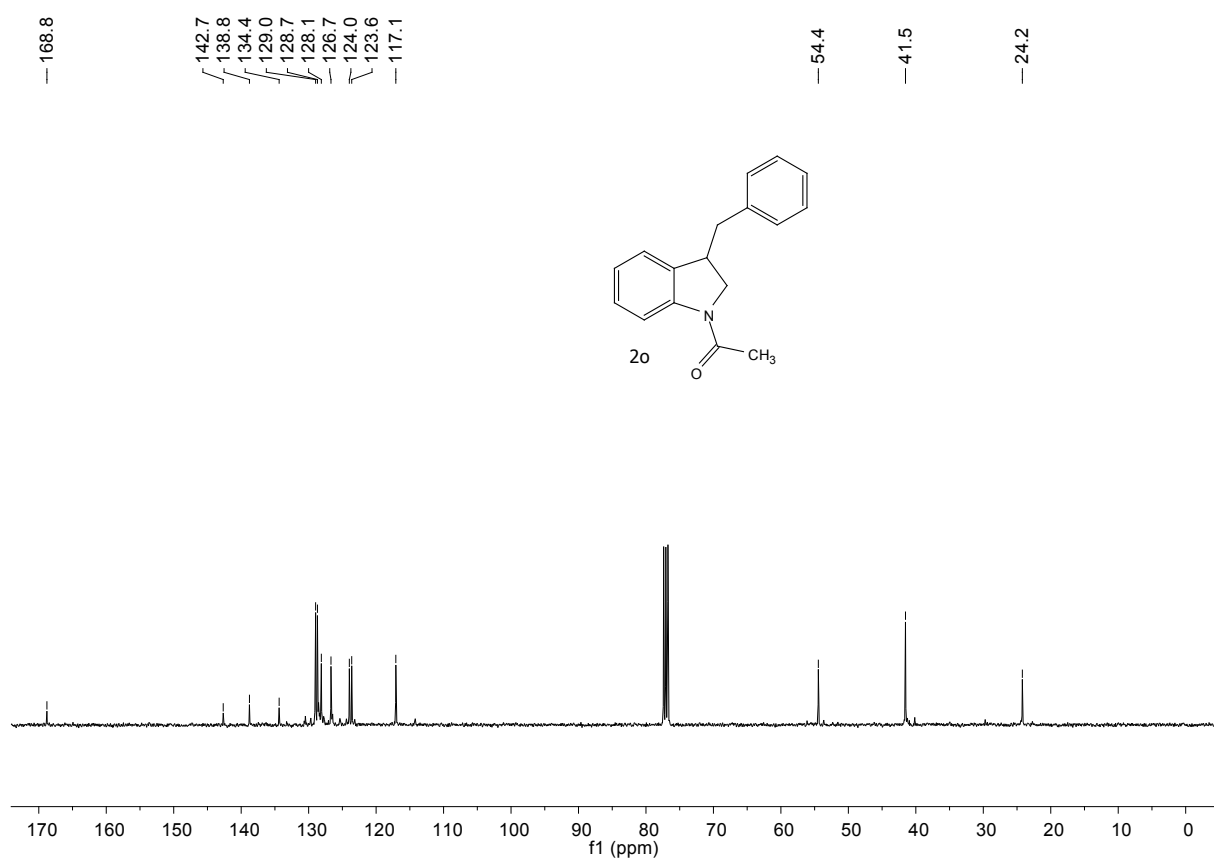


Figure S38. ¹³C NMR of compound **2o** (100 MHz, CDCl₃).

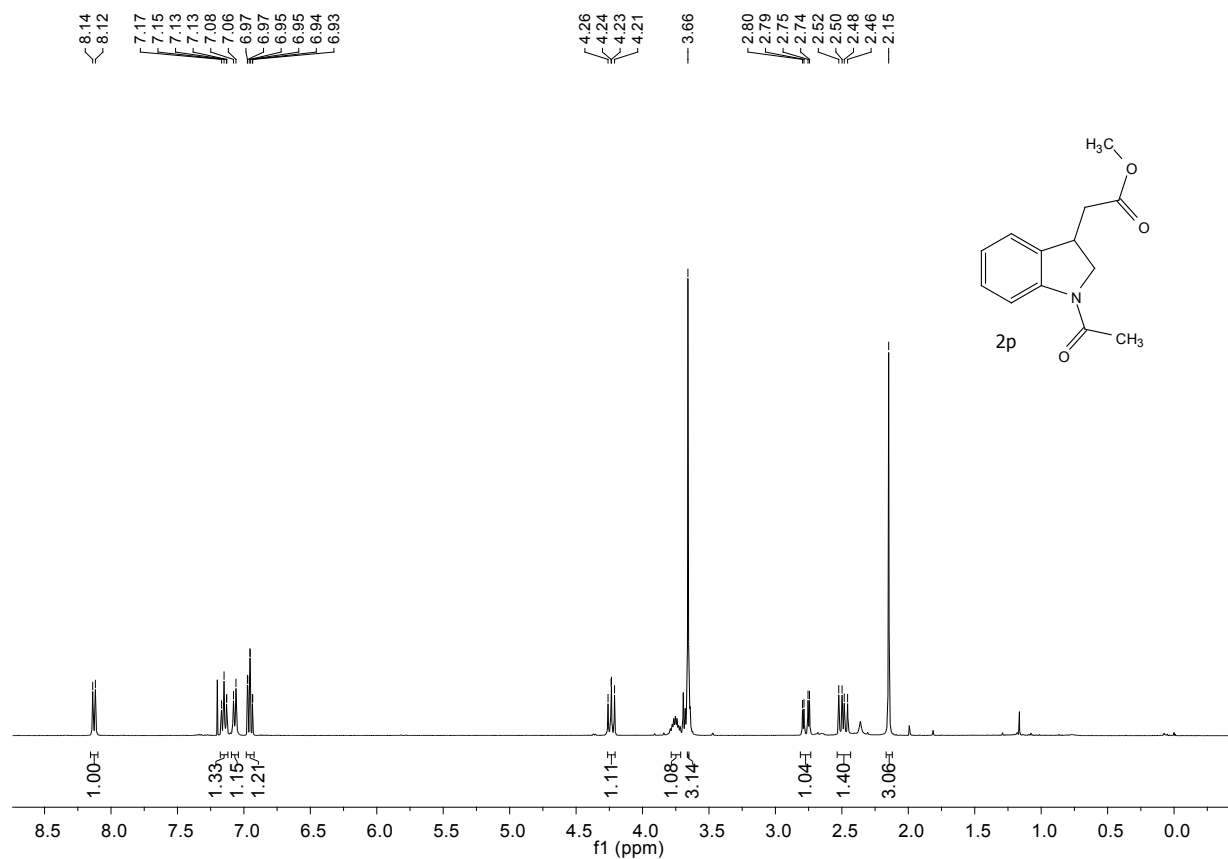


Figure S39. ¹H NMR of compound **2p** (400 MHz, CDCl₃).

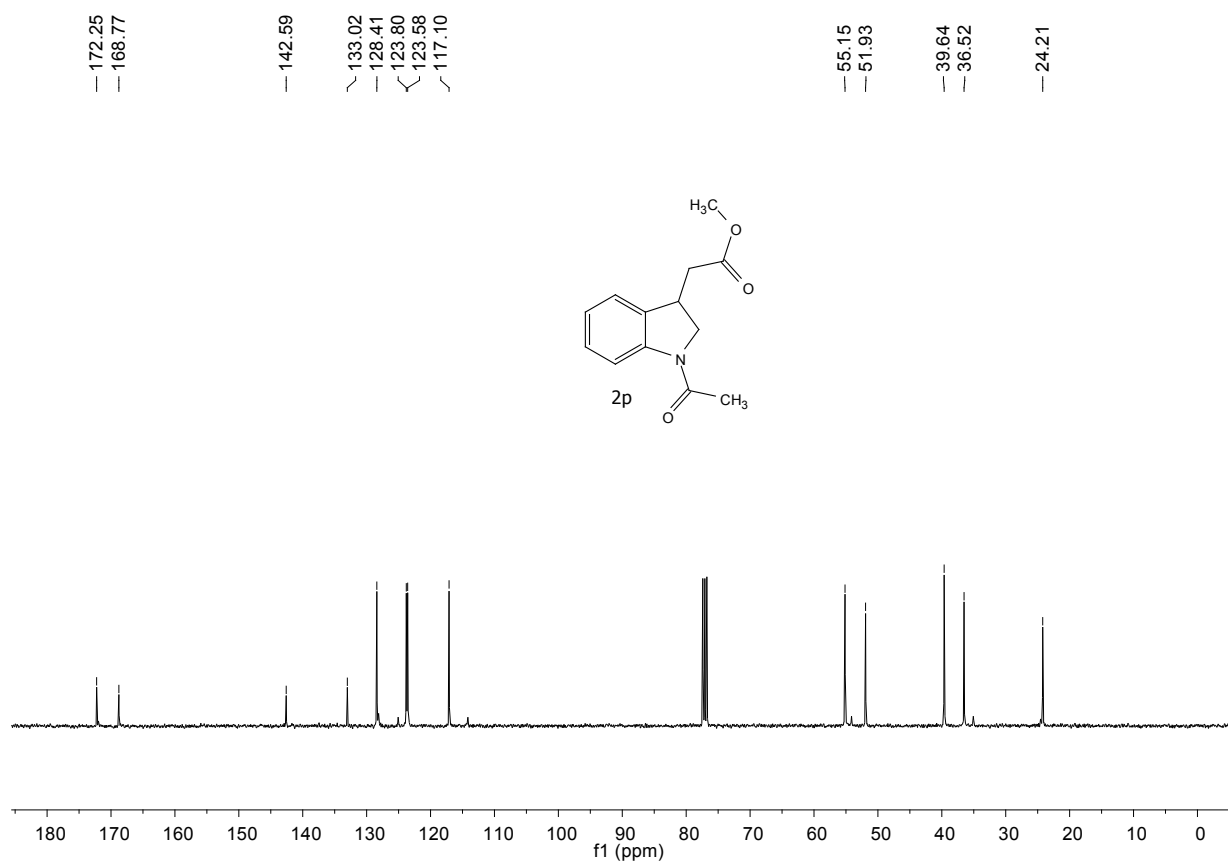


Figure S40. ¹³C NMR of compound **2p** (100 MHz, CDCl₃).

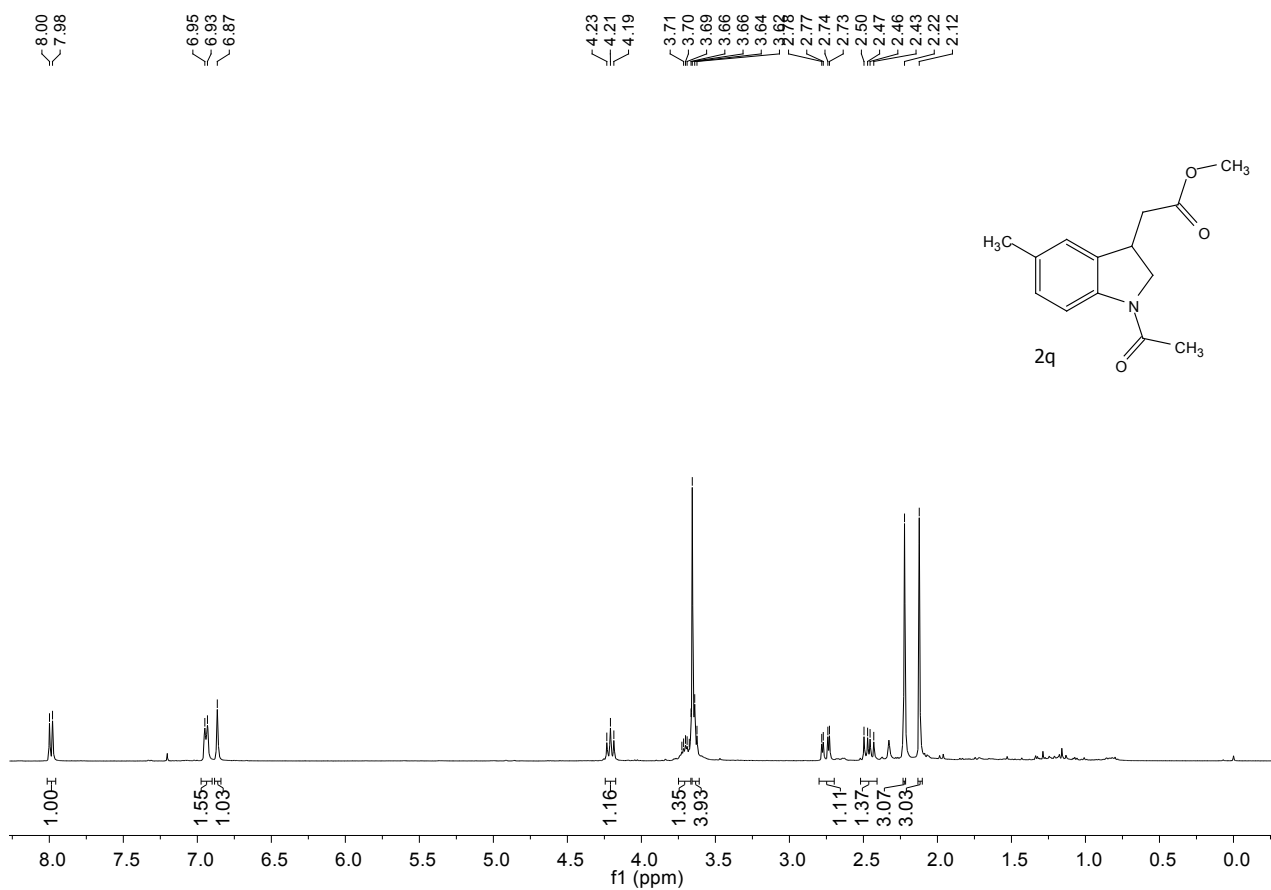


Figure S41. ¹H NMR of compound **2q** (400 MHz, CDCl₃).

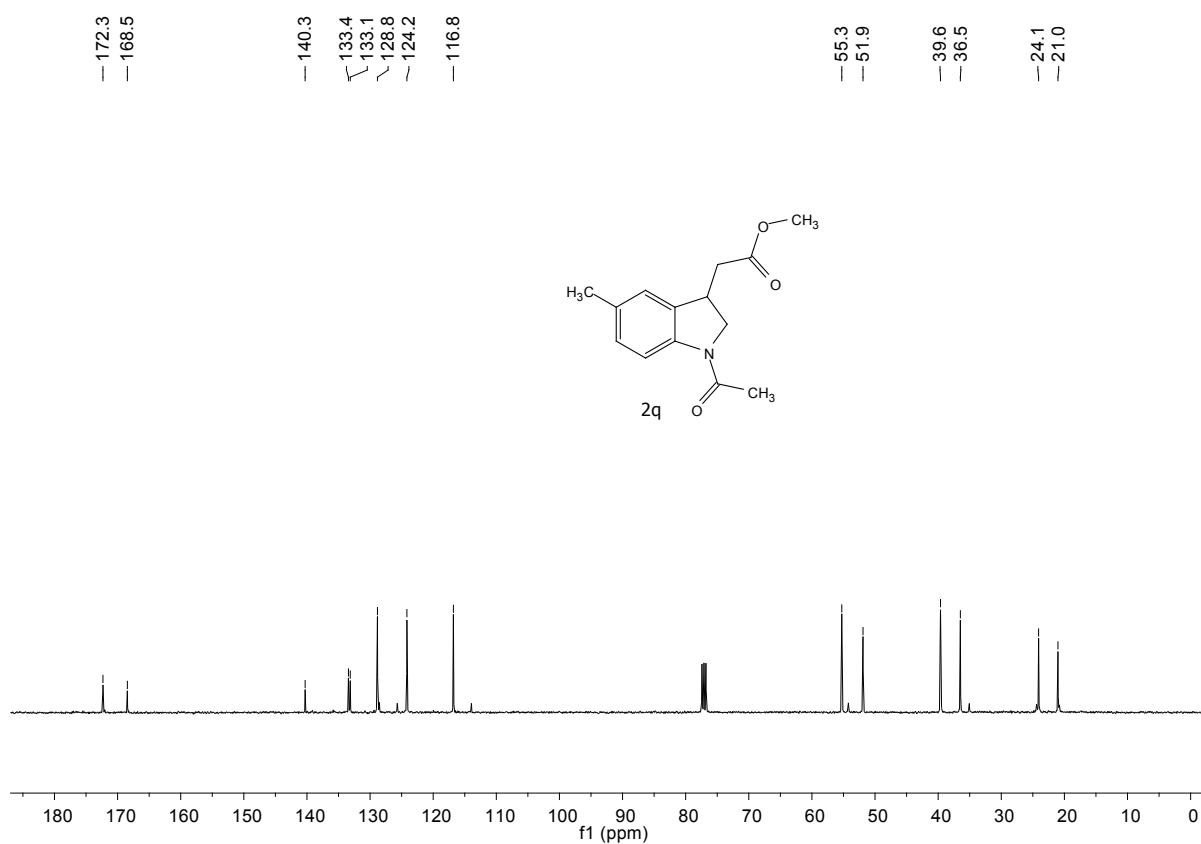


Figure S 42. ¹³C NMR of compound **2q** (100 MHz, CDCl₃).

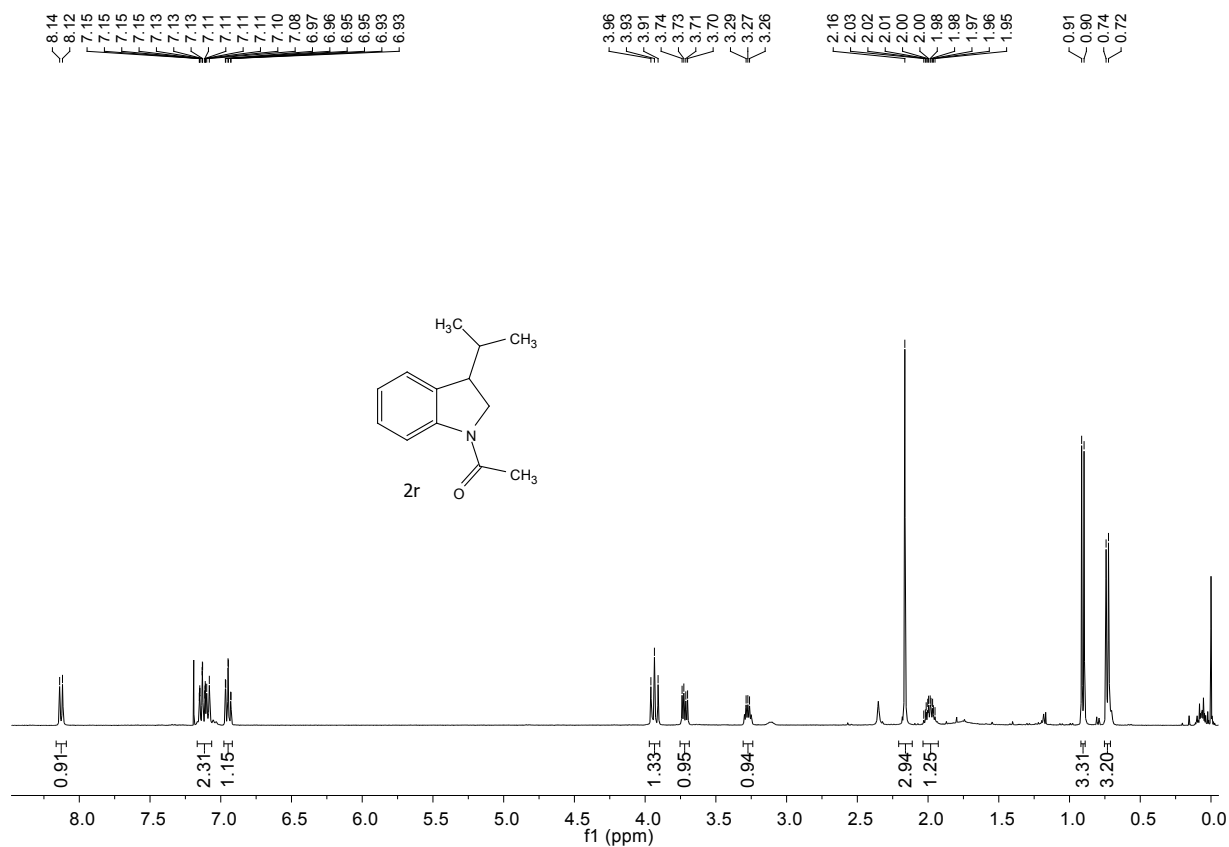


Figure S43. ¹H NMR of compound **2r** (400 MHz, CDCl₃).

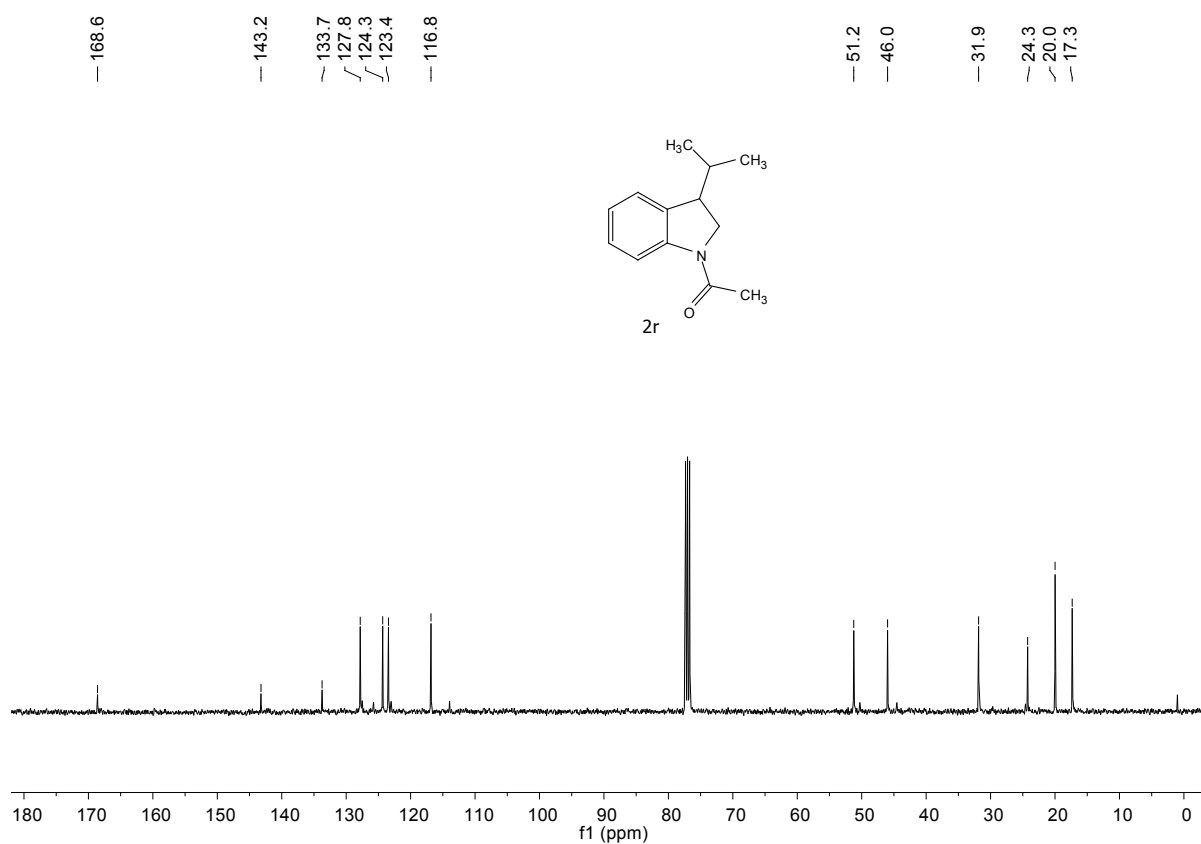


Figure S44. ¹³C NMR of compound **2r** (100 MHz, CDCl₃).

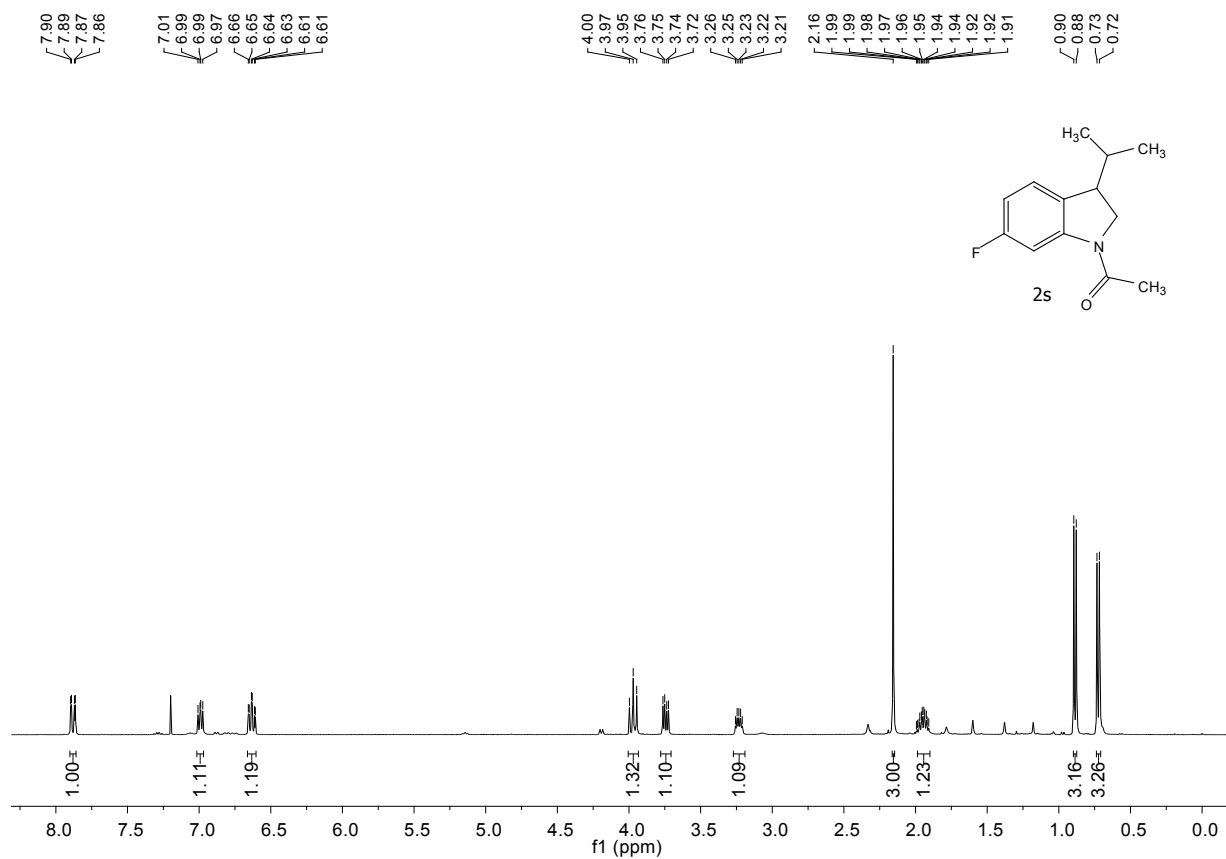


Figure S45. ¹H NMR of compound **2s** (400 MHz, CDCl₃).

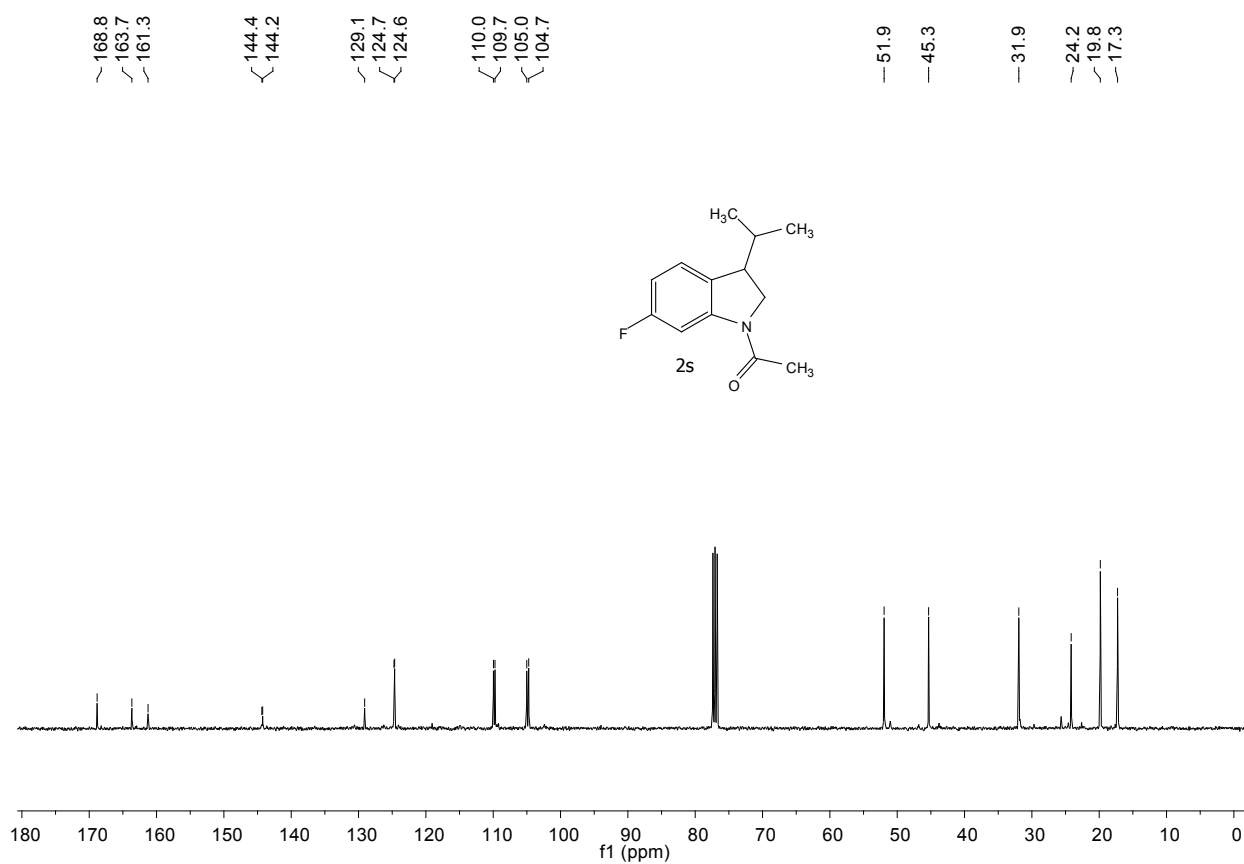


Figure S46. ¹³C NMR of compound **2s** (100 MHz, CDCl₃).

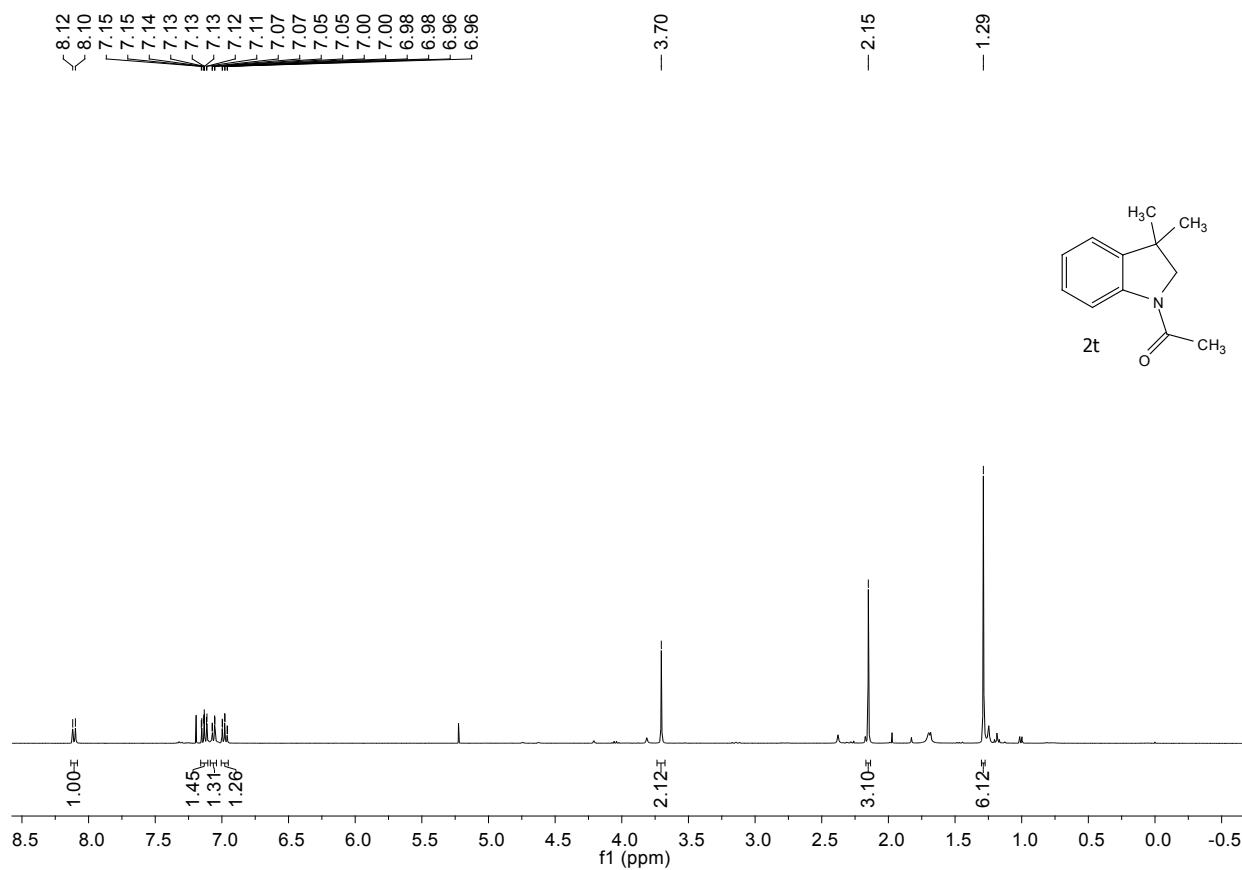


Figure S47. ¹H NMR of compound **2t** (400 MHz, CDCl₃).

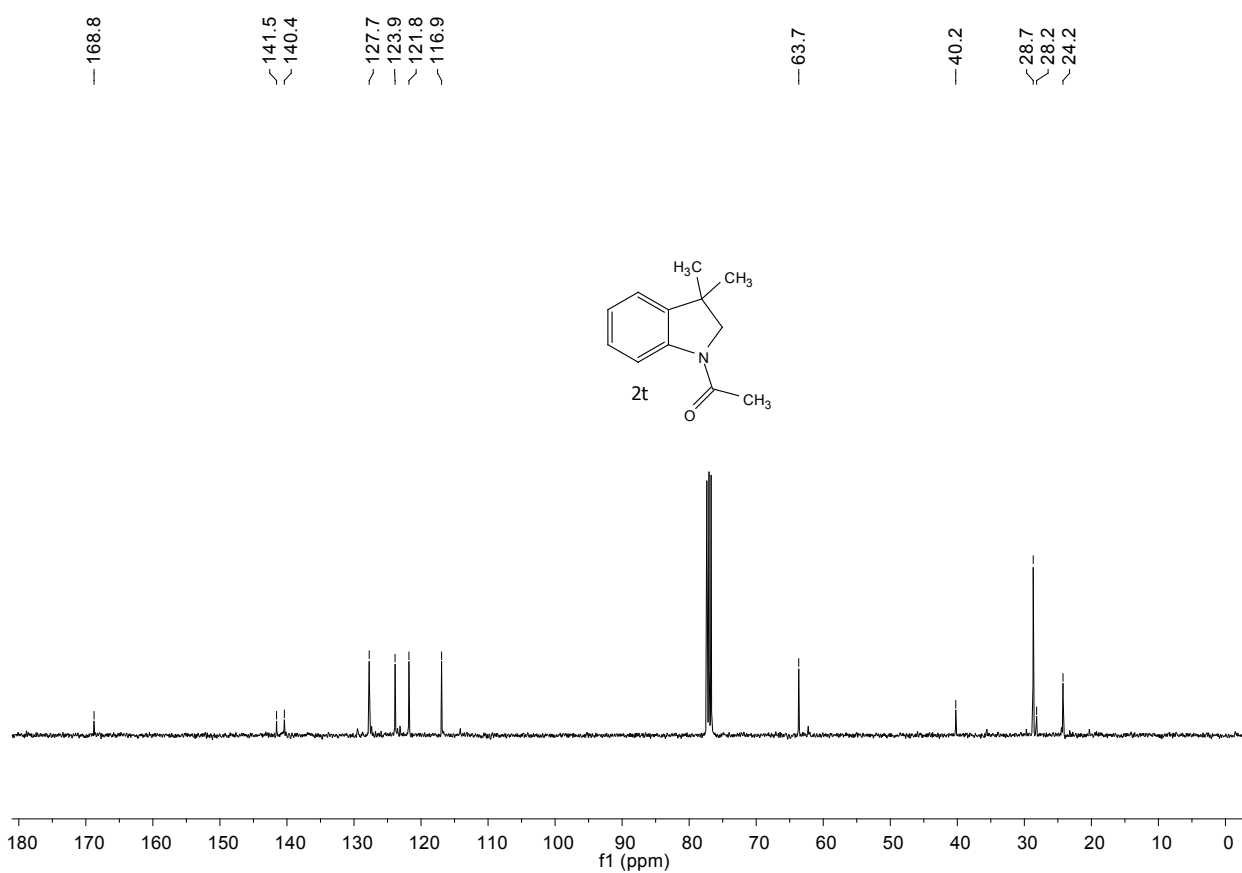


Figure S48. ¹³C NMR of compound **2t** (100 MHz, CDCl₃).

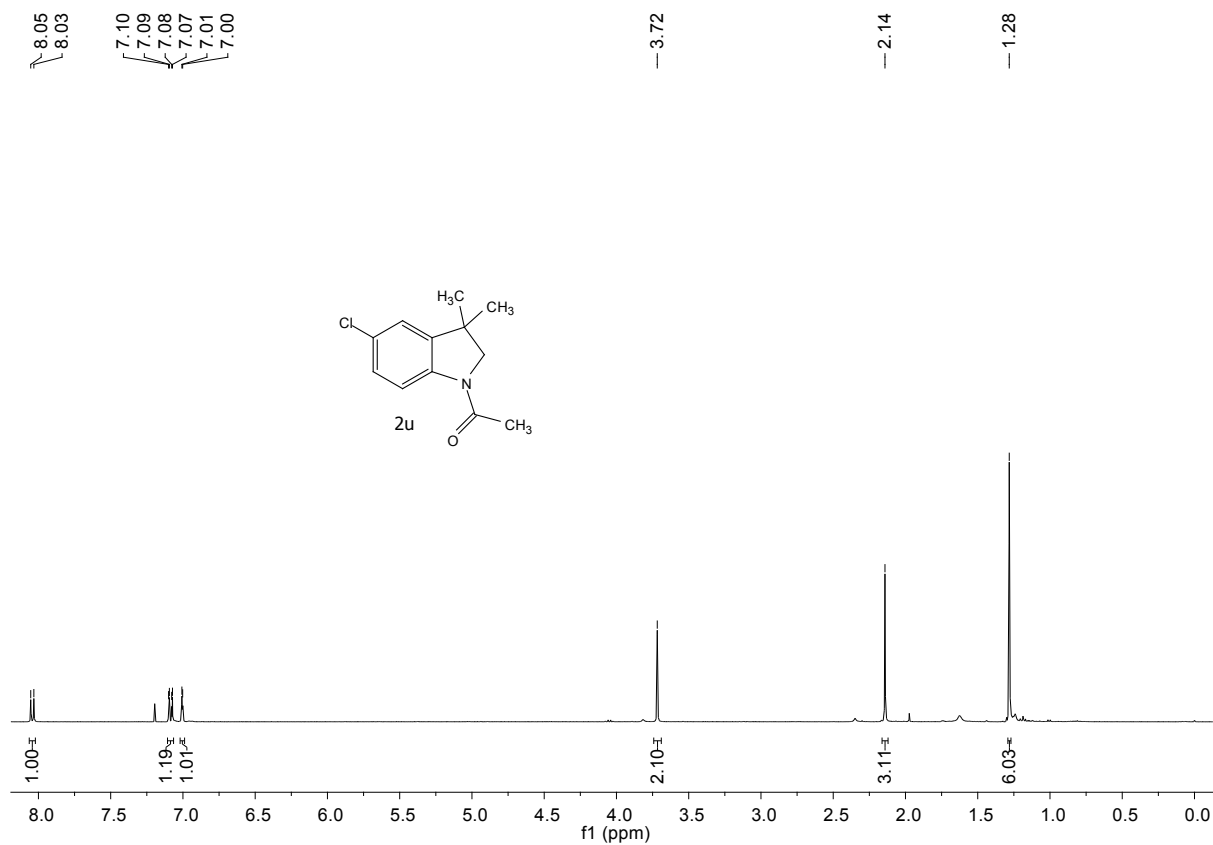


Figure S49. ¹H NMR of compound **2u** (400 MHz, CDCl₃).

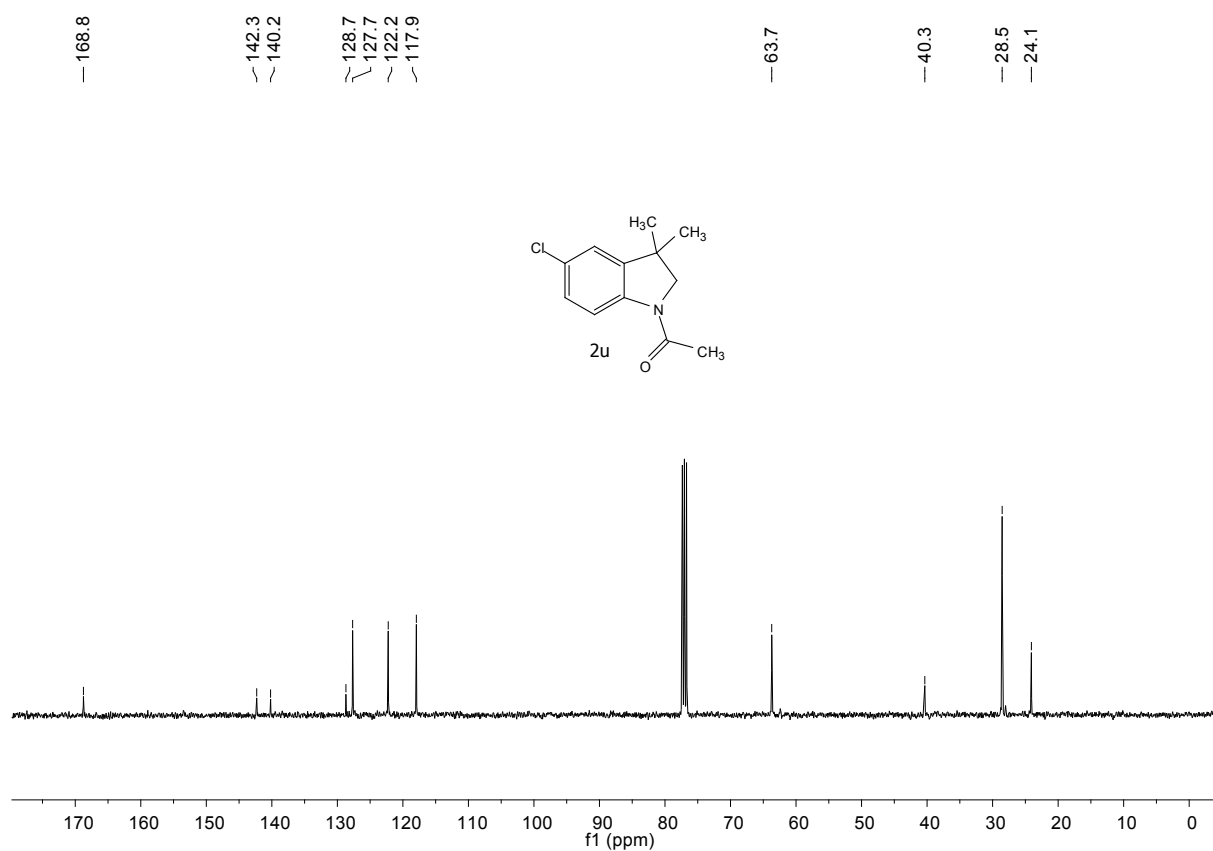


Figure S50. ¹³C NMR of compound **2u** (100 MHz, CDCl₃).

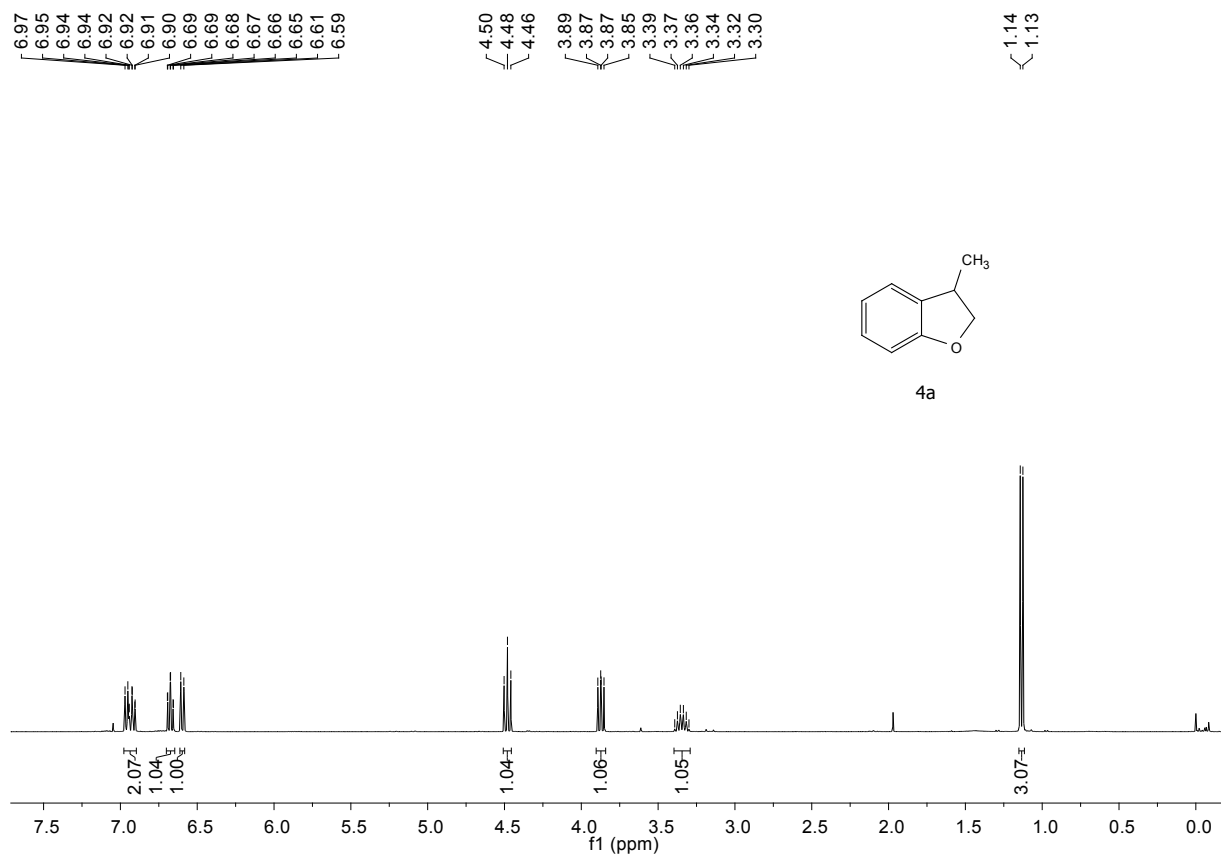


Figure S51. ¹H NMR of compound **4a** (400 MHz, CDCl₃).

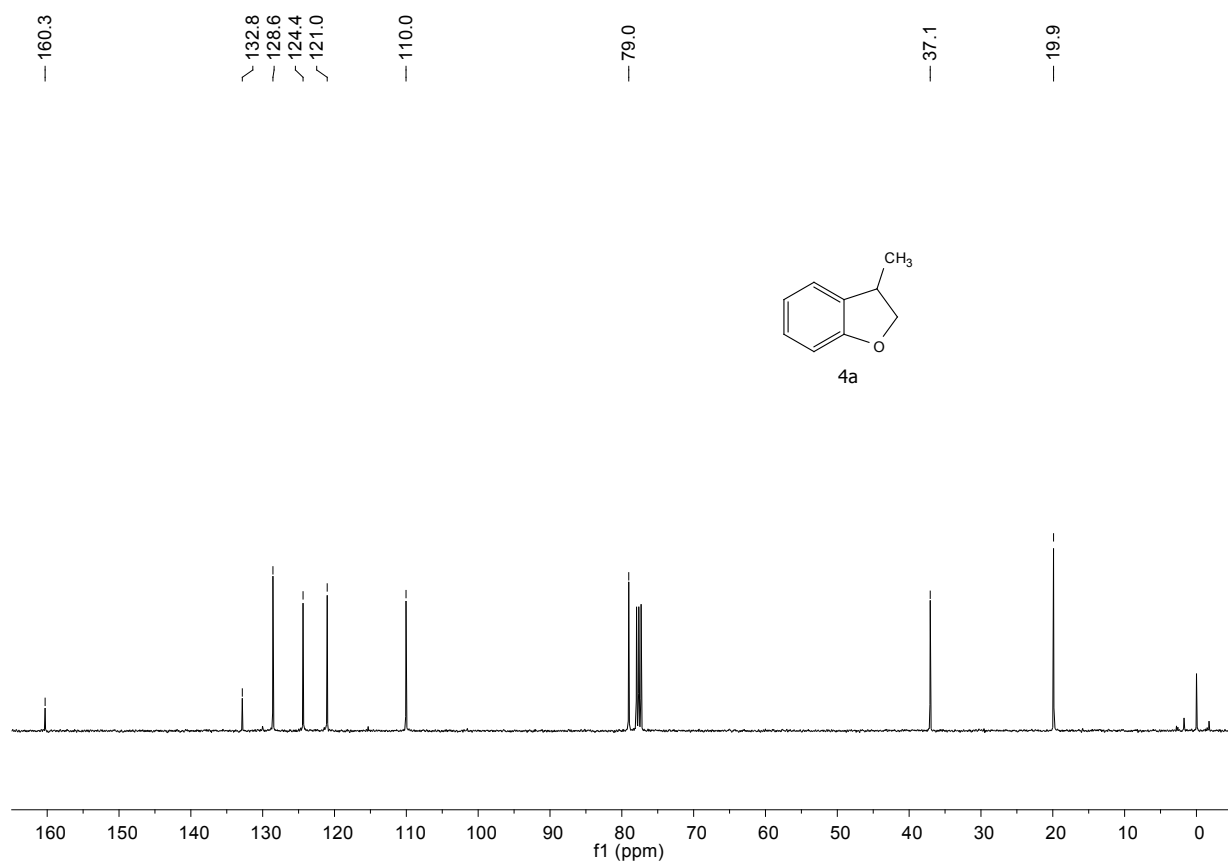


Figure S52. ¹³C NMR of compound **4a** (100 MHz, CDCl₃).

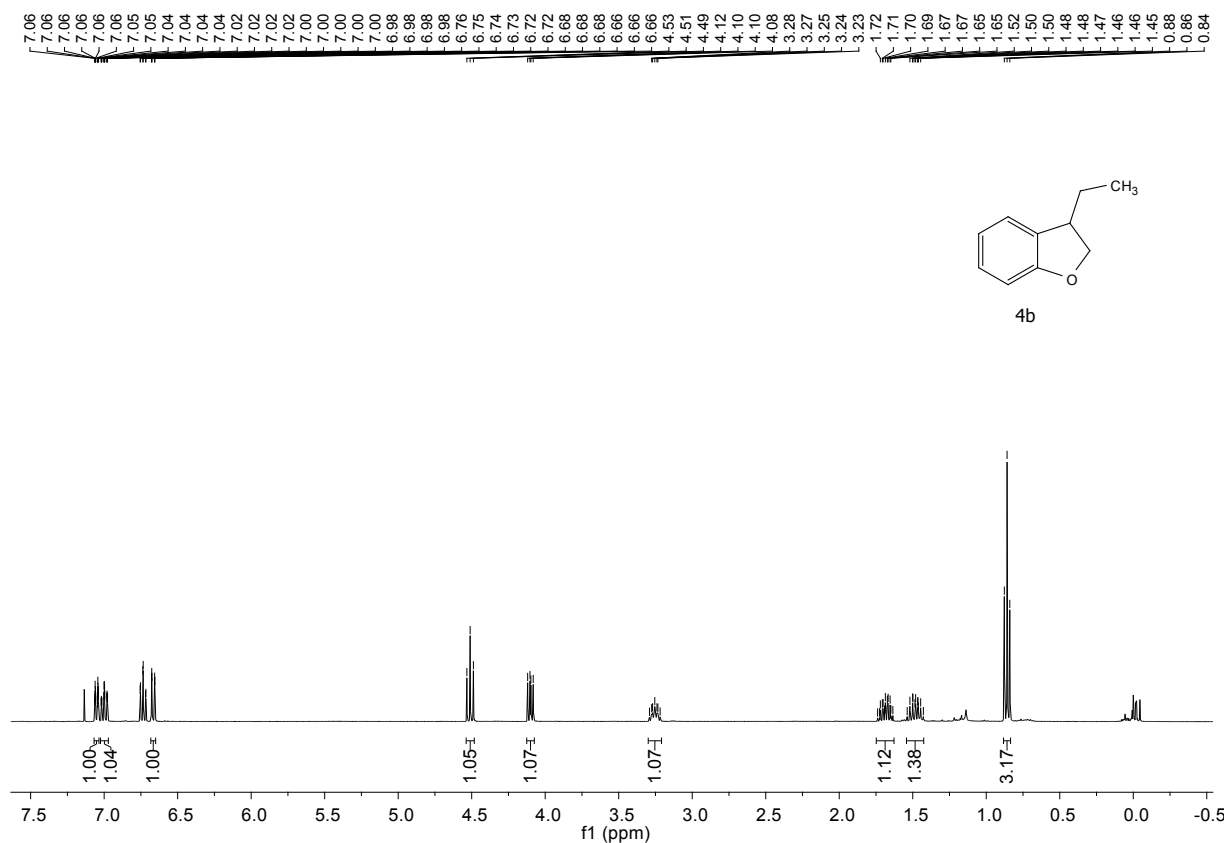


Figure S53. ¹H NMR of compound **4b** (400 MHz, CDCl₃).

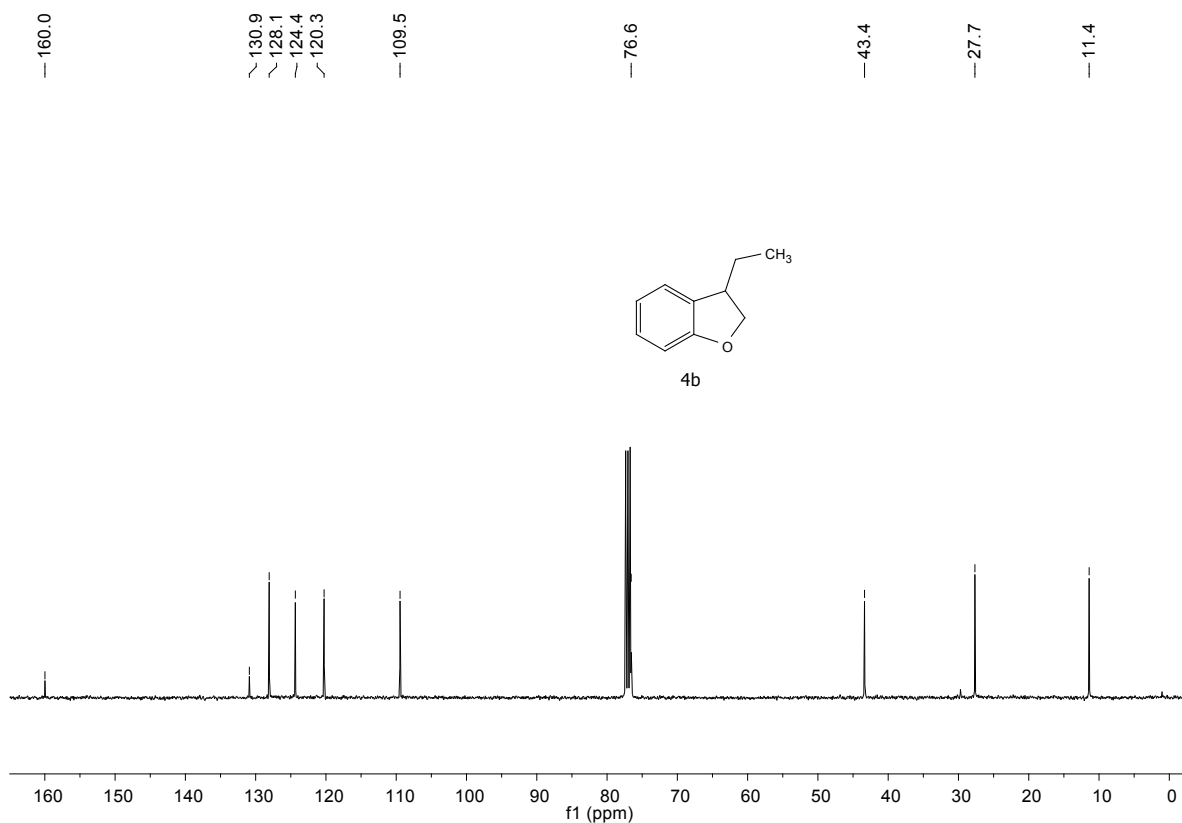


Figure S54. ¹³C NMR of compound **4b** (100 MHz, CDCl₃).

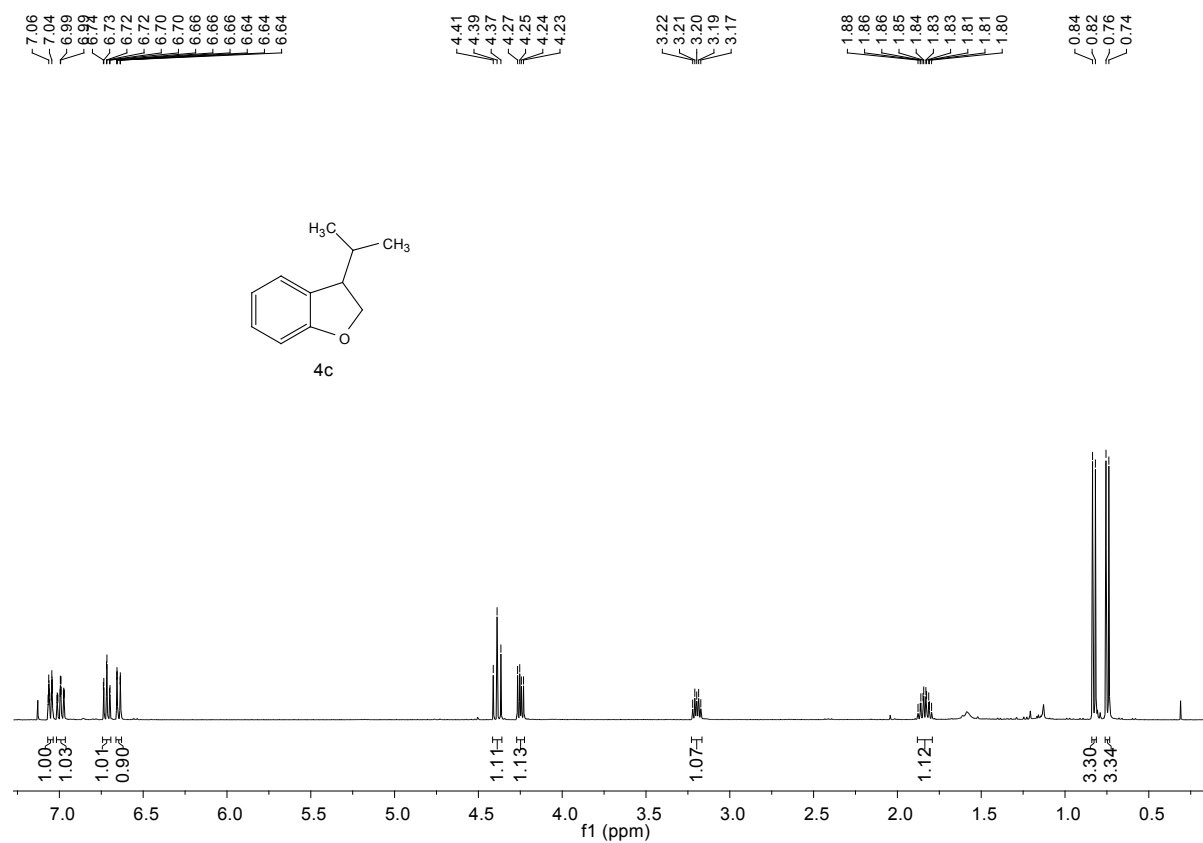


Figure S55. ¹H NMR of compound **4c** (400 MHz, CDCl₃).

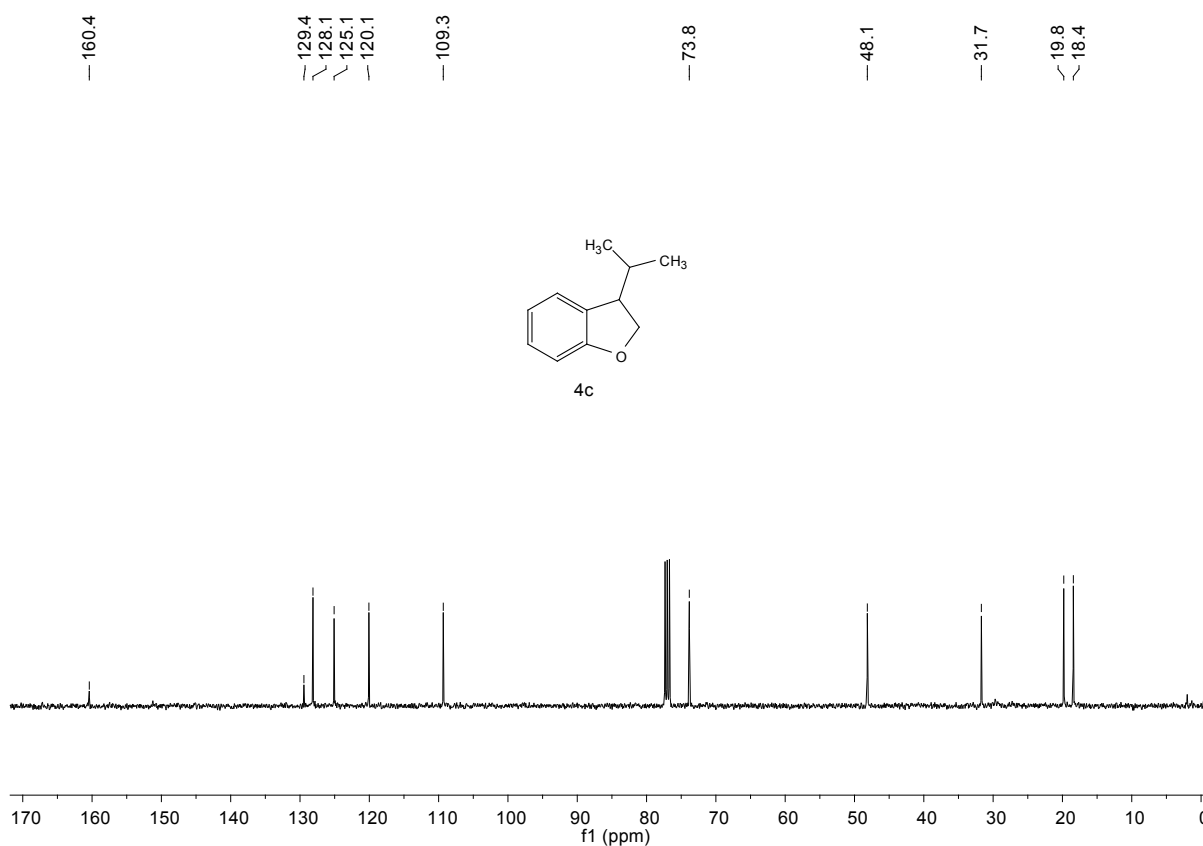


Figure S56. ¹³C NMR of compound **4c** (100 MHz, CDCl₃).

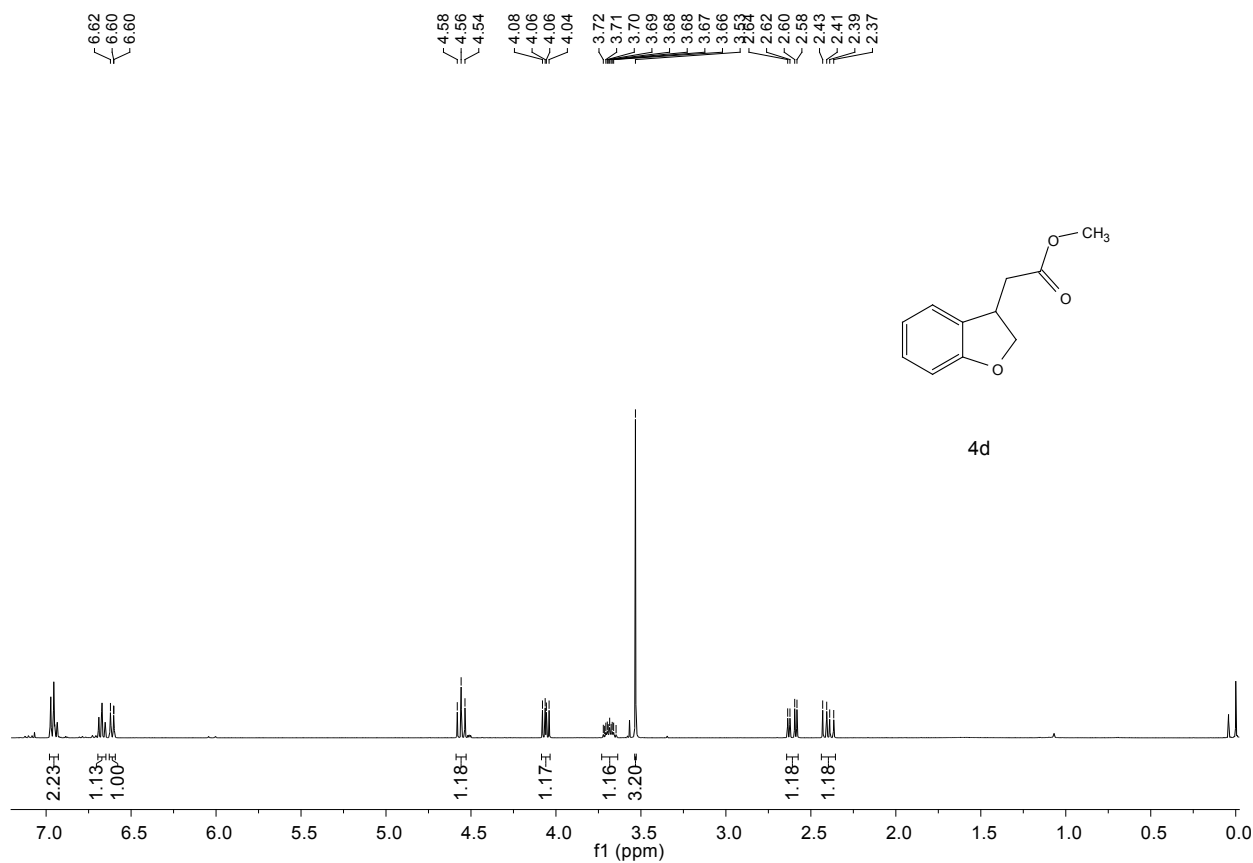


Figure S57. ¹H NMR of compound **4d** (400 MHz, CDCl₃).

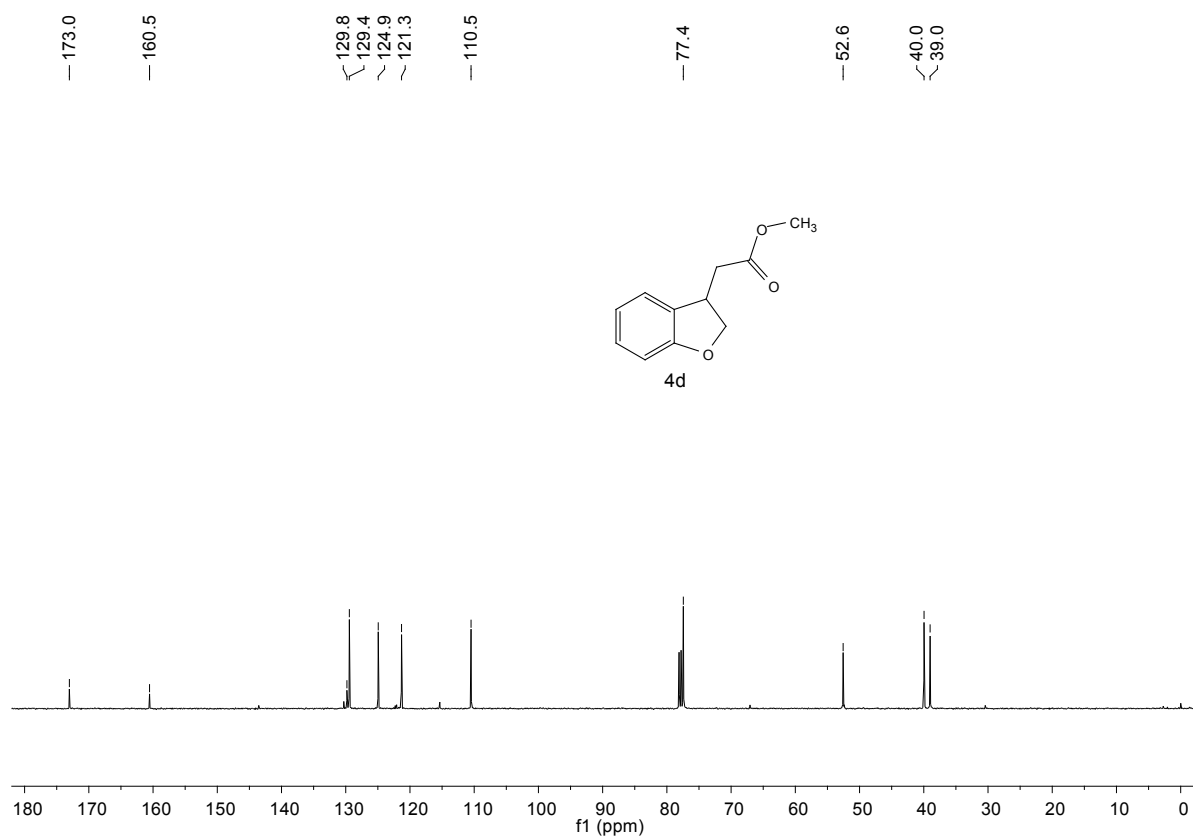


Figure S58. ¹³C NMR of compound **4d** (100 MHz, CDCl₃).

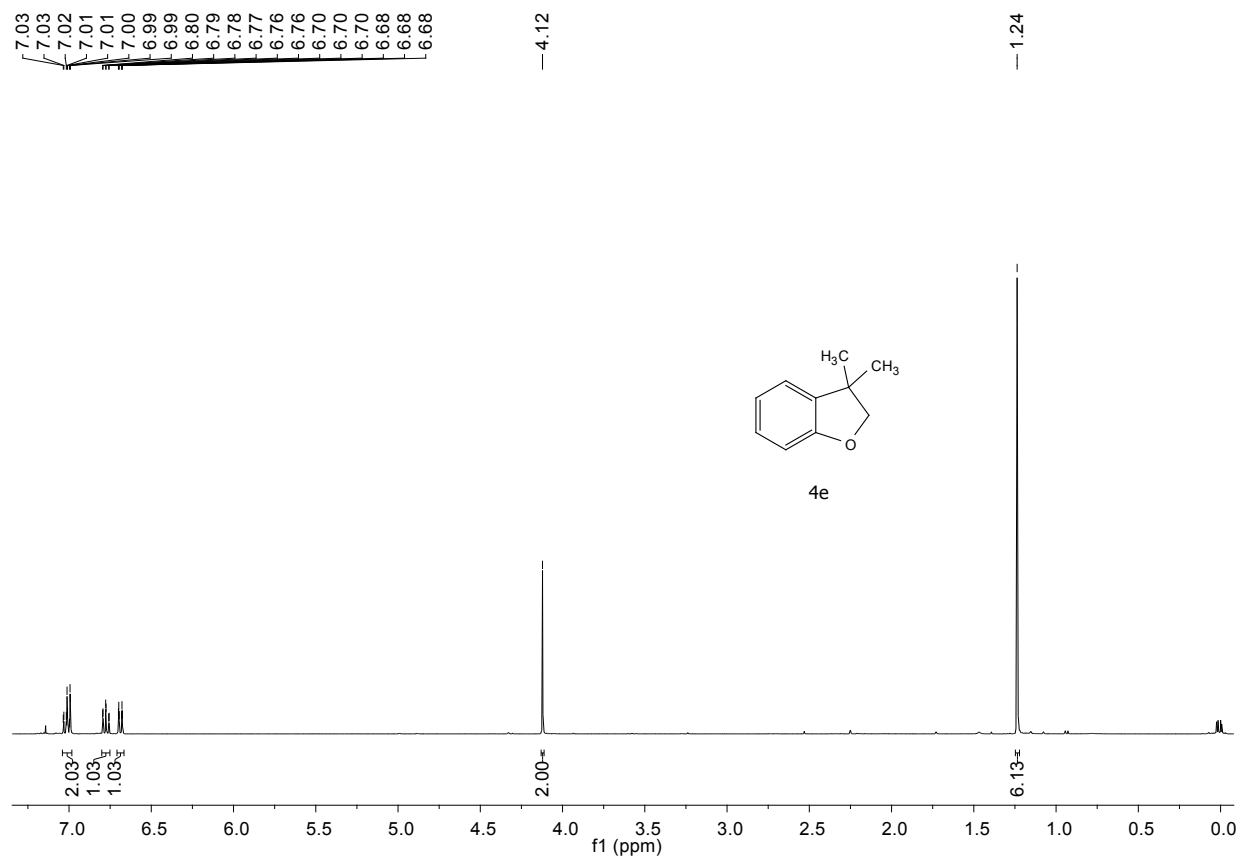


Figure S59. ¹H NMR of compound **4e** (400 MHz, CDCl₃).

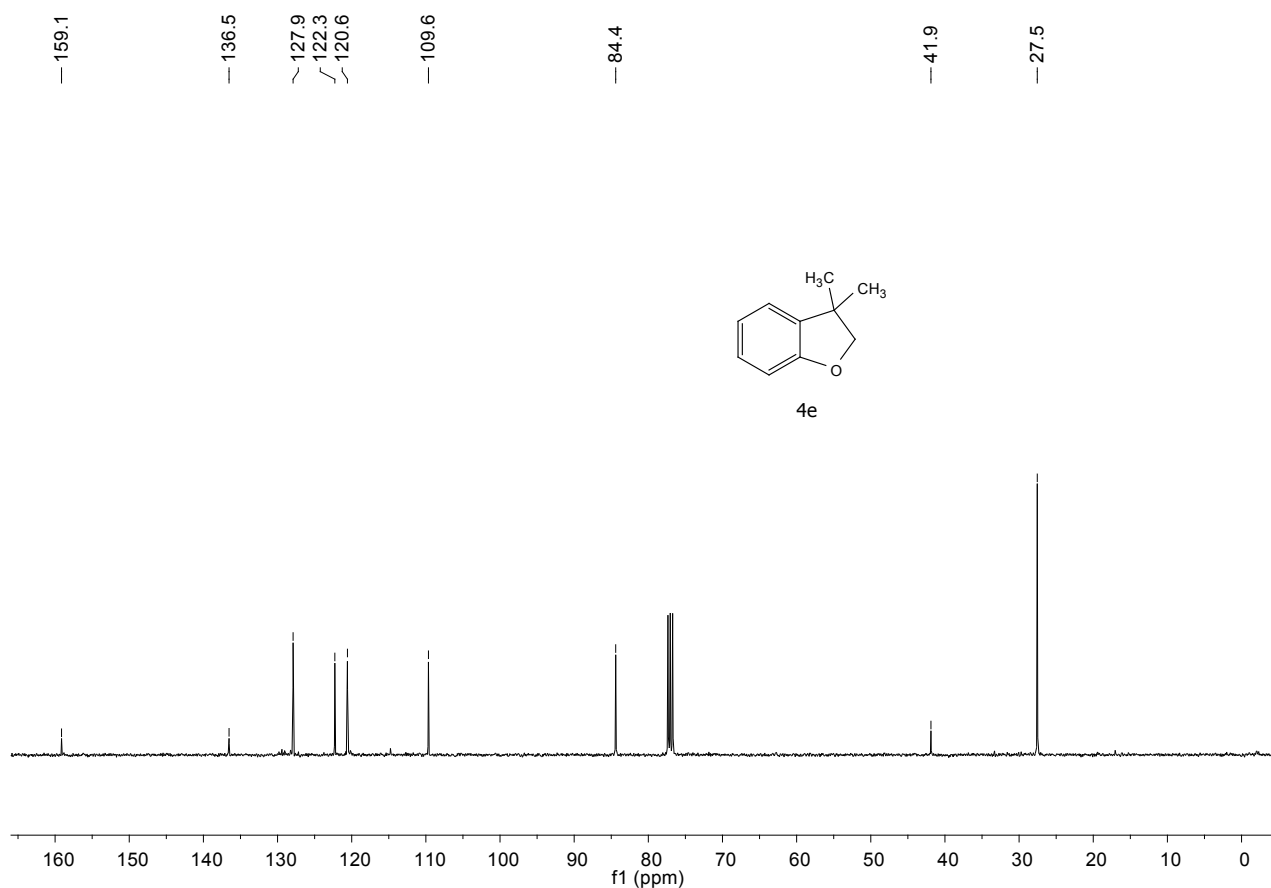


Figure S60. ¹³C NMR of compound **4e** (100 MHz, CDCl₃).

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