Supporting Information

Photocatalytic alkylation of pyrroles and indoles with α-diazo esters

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1. General Information

All solvents and commercially available reagents were purchased as reagent grade and were used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC), using 0.20 mm Merck silica plates (60F-254) and visualized using UV-light, anisaldehyde or cerium molybdate stain, with heat as a developing agent. Colum chromatography was performed on Merck silica gel 60 (230-400 mesh). Yields refer to spectroscopically (^{1}H NMR) homogeneous materials.

NMR spectra were recorded on Bruker 400 MHz and calibrated using residual undeuterated solvent ($CHCl_3$ – 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR) or TMS as an internal reference. Low-resolution mass spectra (LRMS) were recorded on an Applied Biosystems API 365 mass spectrometer using electrospray ionization (ESI) technique. High-resolution mass spectra (HRMS) were recorded on a Waters AutoSpec Premier instrument using electron ionization (EI) or a Waters SYNAPT G2-S HDMS instrument using electrospray ionization (ESI) with time of flight detector (TOF). Elemental analysis (C, H, N) were performed using a PERKIN-ELMER 240 Elemental Analyzer. Cyclic voltammograms were recorded using Bio-Logic SP-50 potentiostat. GC analyses were performed using Shimadzu GCMS-QP2010 SE gas chromatograph with additional FID detector and Zebron ZB 5MSi column. Fluorescence quenching experiments were performed using a Hitachi F-7000 fluorescence spectrophotometer.

2. Photoreactor Setup

Photoredox reactions were carried out in bottom plane irradiated vials in specially constructed photoreactor composed of cooling block and LED plate connected to constant current (0,7 A) power supply (Figure S1). This particular setup was obtained by courtesy of Dr. Burkhard König. Aluminum cooling block can be replaced by 3D printed holder with fan which allowed to keep reaction vials at 28 °C (Figure S2). 3D model of the holder is available on the ACS Publication website at http://dx.doi.org/10.1021/acs.orglett.9b02612 and DG group webpage (https://ww2.icho.edu.pl/gryko_group/3dprintedphotoreactor) and can be easily printed on hobby-tier printer (eg. Prusa i3 MK3 by Prusa Research). LED plates are commercially available radiators (Fischer Elektronik part no. SK 105 100 SA) with 6 epoxy-glued star-cased 3W LEDs (ProLight Opto Technology Corporation part no. PM2B-3LBS-SD) connected in series.

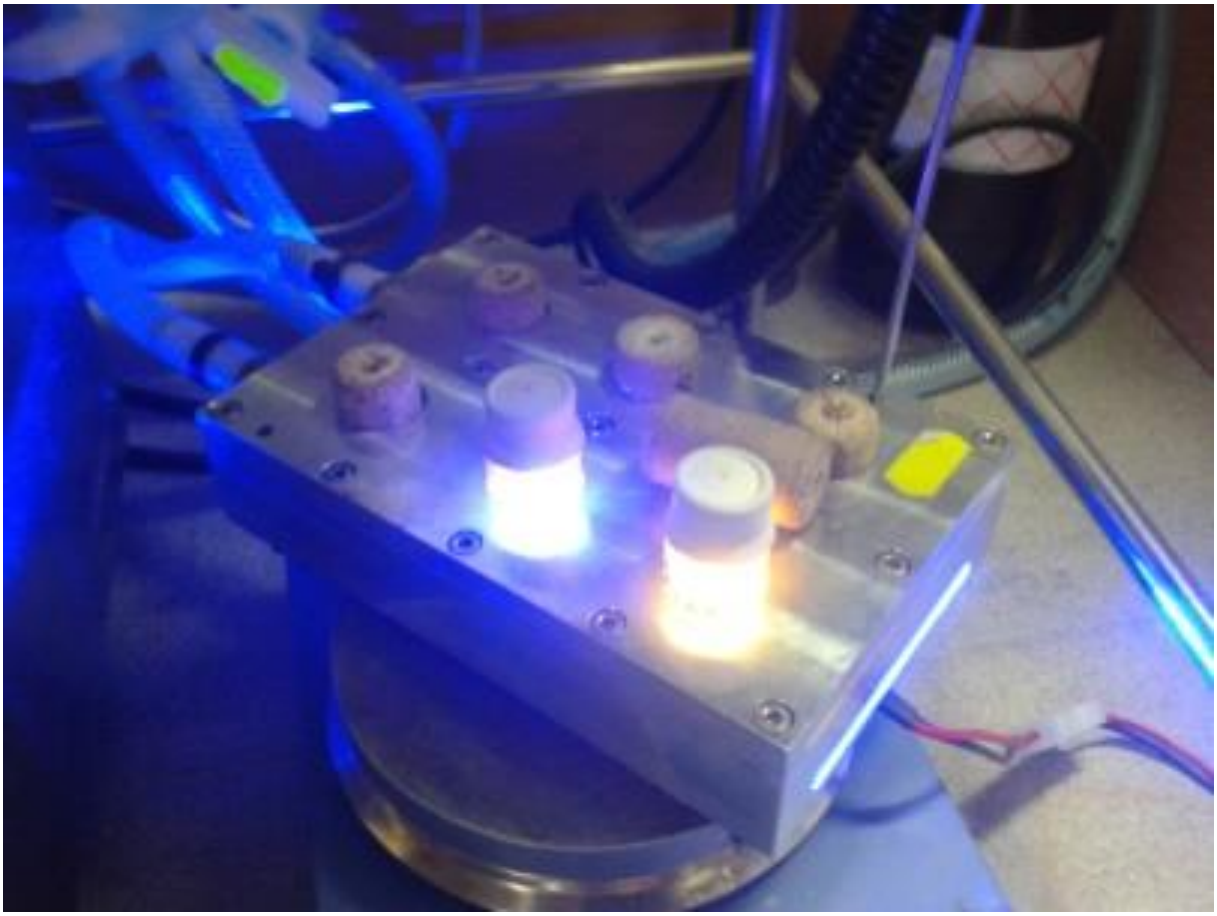


Figure S1 Photoreactor setup with aluminum cooling block

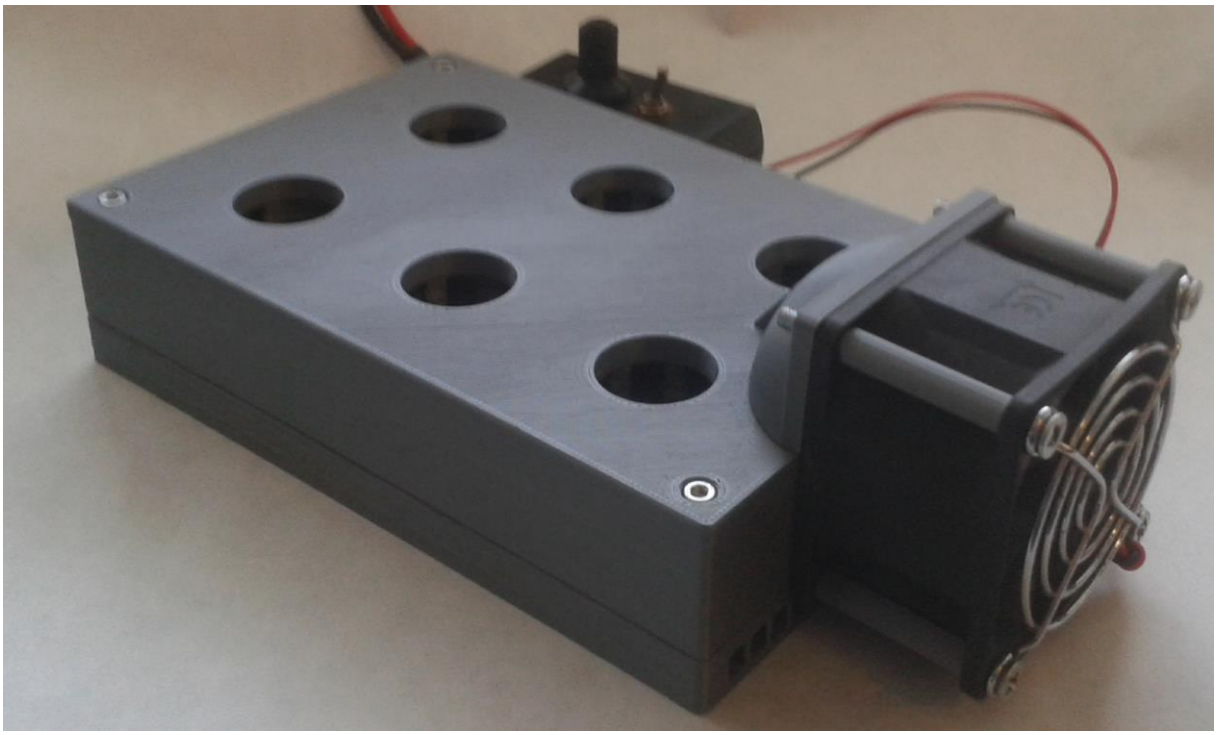
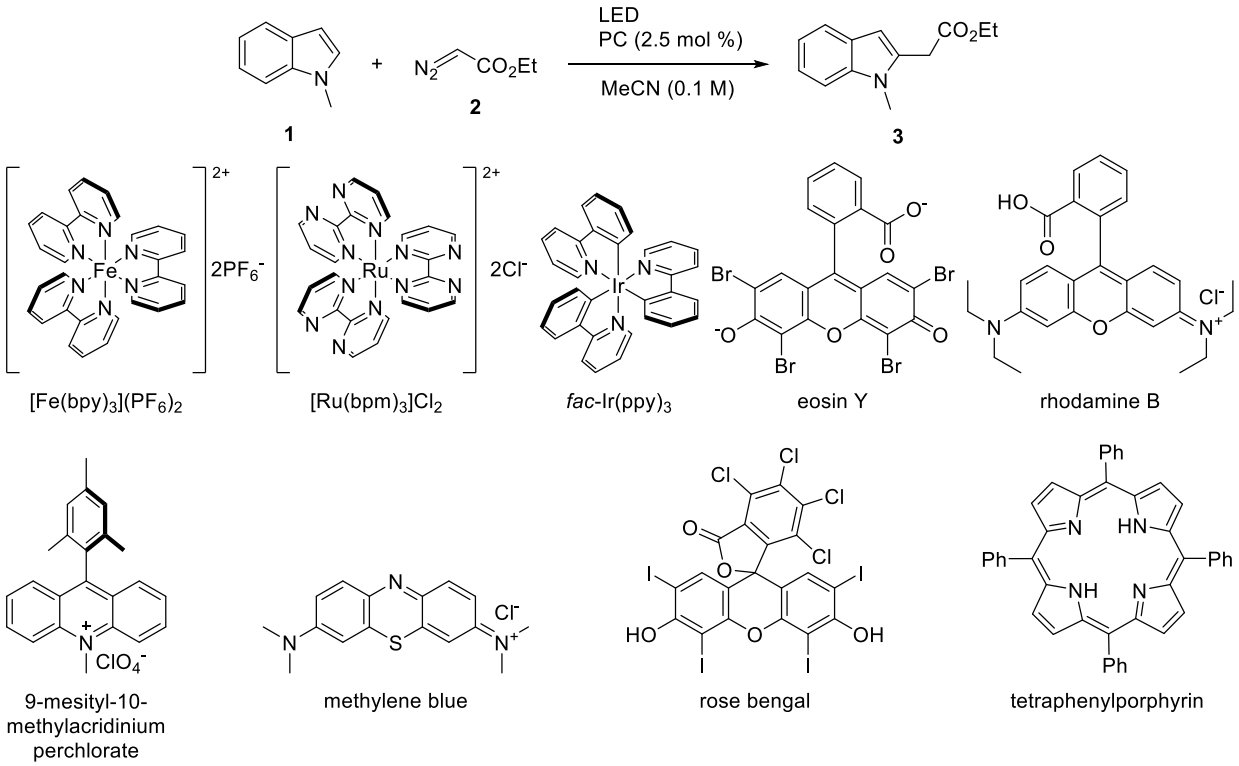


Figure S2 3D printed fan-cooled vial holder

3. Optimization studies

3.1. Screening of photocatalysts

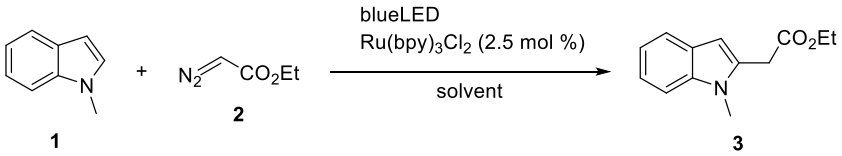


Scheme S1 Photocatalysts tested in the model reaction

LED color (dominant wavelength) was chosen to match the absorption maxima of the tested photocatalyst. None of the above catalyzed the reaction.

3.2. Screening of solvents

Table S1 Screening of the solvent

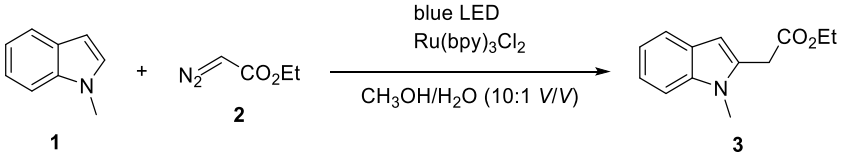


entry	solvent	yield[a] [%]
1	DMSO	traces
2	CH_3CN	30
3	DMSO/buffer pH 4 (10:1 *V*/*V*)	44
4	CH_3CN/buffer pH 4 (10:1 *V*/*V*)	59
5	DMF/buffer pH 4 (10:1 *V*/*V*)	54
6	CH_3OH/buffer pH 4 (10:1 *V*/*V*)	65
7	CH_3CN/H_2O (10:1 *V*/*V*)	60
8	**CH_3OH/H_2O (10:1 *V*/*V*)**	**74**
9	CH_3OH	69
10	C_2H_5OH/H_2O (10:1 *V*/*V*)	62
11	$CH_3CH(OH)CH_3$ (10:1 *V*/*V*)	traces
12	$CF_3CF(OH)CF_3$ (10:1 *V*/*V*)	69

Reaction conditions: 1.25 mmol of 1-methylindol (**1**), 0.25 mmol of ethyl diazoacetate (**2**) and 6.25 μmol of $Ru(bpy)_3Cl_2$ in solvent (2.5 mL), irradiation at 455 nm for 8 h. [a] GC yield.

3.3. Catalyst loading

Table S2 Catalyst loading studies.

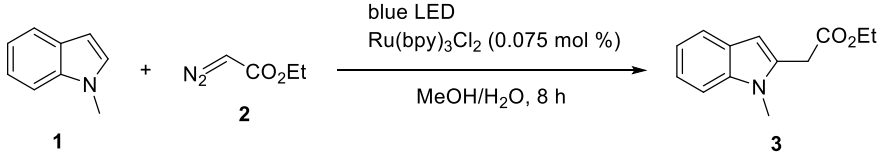


entry	catalyst loading [mol %]	yield[a] [%]
1	2.5	74
2	1	77
3	0.25	76
4	0.1	72
5	0.01	45
6	0.025	66
7	0.05	68
8	**0.075**	**76**

Reaction conditions: 1.25 mmol of 1-methylindol (**1**), 0.25 mmol of ethyl diazoacetate (**2**) and $Ru(bpy)_3Cl_2$ in 2.75 mL of CH_3OH/H_2O (10:1 *V*/*V*) mixture, irradiation at 455 nm for 8 h. [a] GC yield.

3.4. Concentration effects

Table S3 Influence of the concentration and MeOH/H_2O ratio on the product yield.

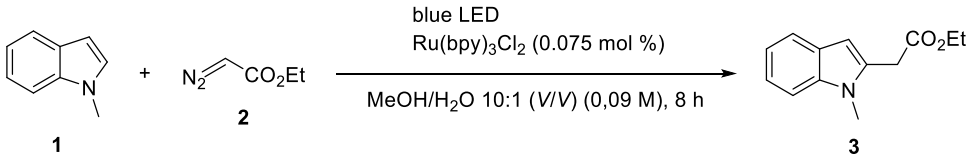


entry	concentration [M]	MeOH/H_2O ratio	yield [a] [%]
1	**0.09**	**10:1**	**76**
2	0.25	10:1	72
3	0.05	10:1	62
4	0.09	50:1	65
5	0.09	2:1	57

Reaction conditions: 1.25 mmol of *N*-methylindol (**1**), 0.25 mmol of ethyl diazoacetate (**2**) and $Ru(bpy)_3Cl_2$ (187.5 nmol, 0.075 mol %) in CH_3OH/H_2O, irradiation at 455 nm for 8 h. [a] GC yield.

3.5. Substrate ratio and gradual addition of EDA (**2**) studies

Table S4 Influence of the indole **1** to EDA (**2**) ratio on the product yield.



entry	indole **1**/EDA (**2**)	EDA (**2**) addition rate	yield [a] [%]
1	2:1	-	53
2	1:5	-	32
3	2:1	variable	62
4	2:1	variable	59
5	2:1	82 µmol/h	55
6	2:1	34 µmol/h	56
7	4,5:1	-	73
8	4:1	-	72
9	3,5:1	-	66

Reaction conditions: 1-methylindole (**1**), ethyl diazoacetate (**2**) and $Ru(bpy)_3Cl_2$ (187 nmol, 0.075 mol %) in 2.75 mL of CH_3OH/H_2O (10:1 *V*/*V*) mixture, irradiation at 455 nm for 8 h. [a] GC yield.

3.6. Optimization of the reaction time

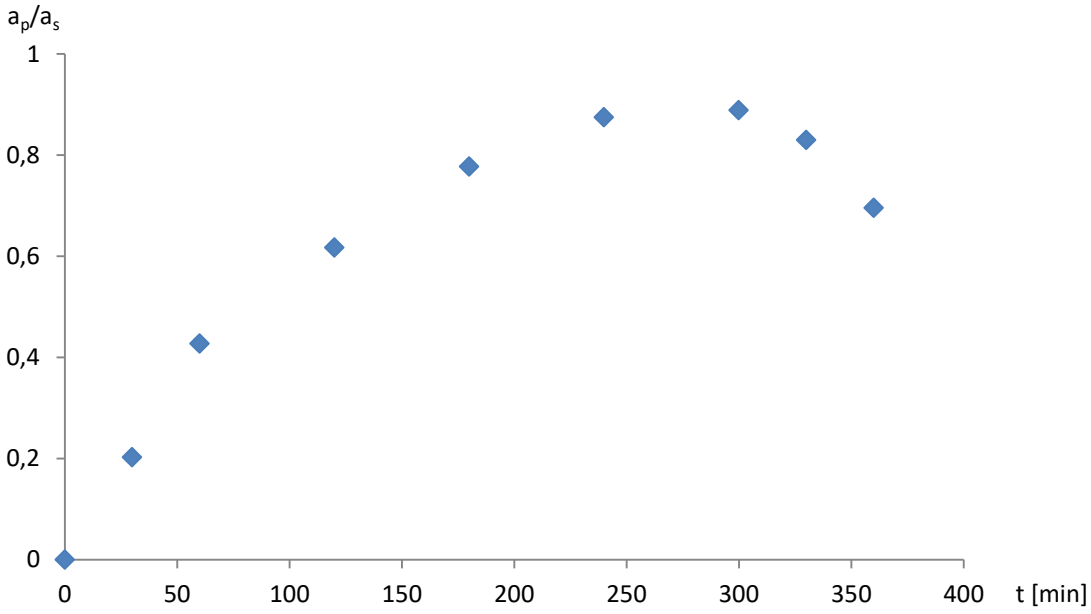
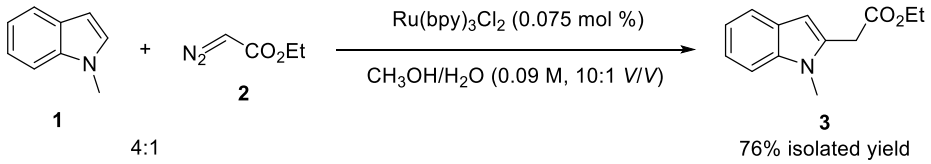


Figure S3 Correlation between the relative yield of the product ($a_{product}/a_{standard}$) and reaction time.

3.7. Optimization summary

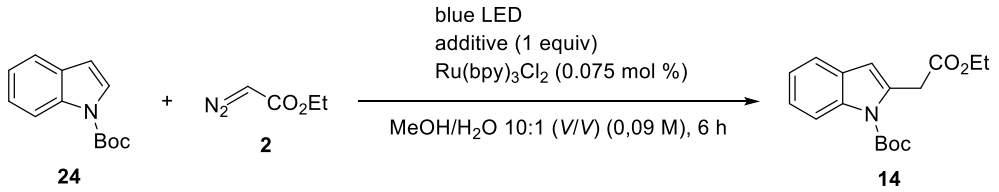


Scheme S2 Optimized reaction conditions

Reaction conditions: *N*-methylindole (**1**, 4.0 equiv, 1.0 mmol), ethyl diazoacetate (**2**, 1.0 equiv, 0.25 mmol) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.075 mol %, 188 nmol), CH_3OH/H_2O (10:1 *V*/*V*, 0.09 M, 2.75 mL) irradiation with 3 W blue (λ_{max} = 455 nm) LED for 4.5 h.

3.8. Screening of additives

Table S5 Screening of an additive.



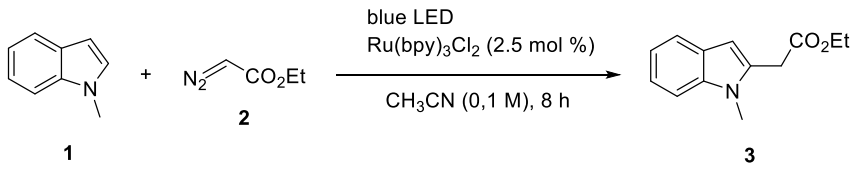
24 **2** **14**

entry	additive	E_{ox} [V vs SCE]	yield [a] [%]
1	DABCO	0.70	0
2	quinuclidine	1.01	0
3	*N*,*N*-dimethylaniline	0.75	29
4	4,*N*,*N*-trimethylaniline	0.65	28
5	4-methoxytriphenylamine	0.76	54
6	4-methoxy-*N*,*N*-dimethylaniline (**25**)	0.49	59
7[b]	4-methoxy-*N*,*N*-dimethylaniline (**25**)	0.49	60

Reaction conditions: *N*-Boc-indole (**24**, 4.0 equiv, 1.0 mmol), ethyl diazoacetate (**2**, 1.0 equiv, 0.25 mmol) additive (1 equiv, 0.25 mmol) and $Ru(bpy)_3Cl_2$ (188 nmol, 0.075 mol %) in CH_3OH/H_2O (10:1 *V*/*V*, 2.75 mL), irradiation at 455 nm for 6 h. [a] isolated yield, [b] 10 mol %, of amine **25** (0.025 mmol) was used.

4. Mechanistic studies

4.1. Background reactions

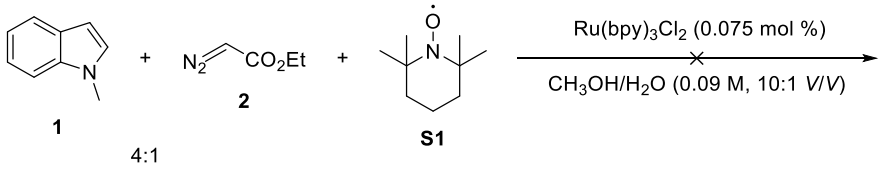


entry	PC	light	yield[a] /%
1	$Ru(bpy)_3Cl_2$	+	30
2	none	+	nr
3	$Ru(bpy)_3Cl_2$	-	nr
4[b]	$Ru(bpy)_3Cl_2$	+	nr

Reaction conditions: 1.25 mmol of *N*-methylindol (**1**), 0.25 mmol of ethyl diazoacetate (**2**) and 6.25 μmol of $Ru(bpy)_3Cl_2$ in acetonitrile (2.5 mL), irradiation at 455 nm for 8 h. [a] GC yield, [b] reaction mixture was not degassed.

4.2. Experiments with TEMPO

Addition of free radical scavenger – TEMPO (**S1**) to the reaction mixture stops the reaction completely, however no radical addition products were not detected either by TLC analysis or mass spectroscopy.

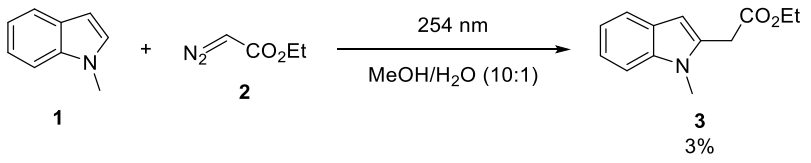


Scheme S3 Reaction with the addition of TEMPO (**S1**)

4.3. Experiments confirming the lack of carbene/carbenoid species in the reaction pathway

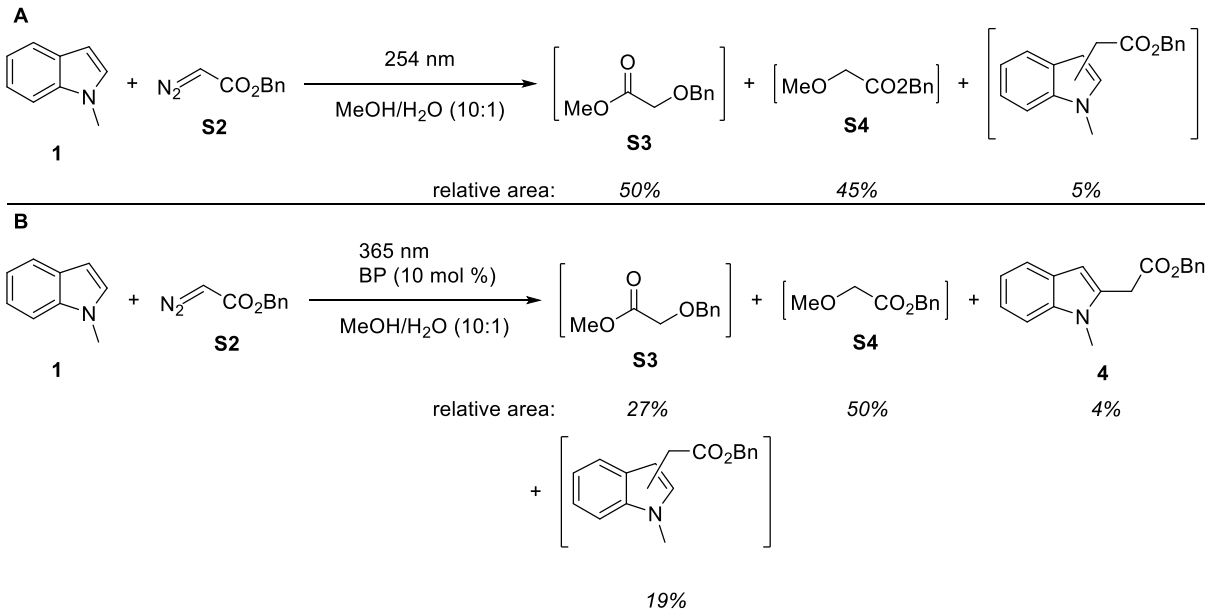
In order to exclude the formation of free carbene by photosensitized decomposition of diazo compounds in the presence of $Ru(bpy)_3Cl_2$ several experiments were performed:

Direct photolysis of diazo compounds leads to formation of the corresponding carbene in singlet or triplet state (depending on the substituents). Therefore if the reaction does not involve carbenes, for the model reaction conducted with no photocatalyst, under UV (254 nm) irradiation ***different products should be observed.*** In fact for the reaction of ethyl diazoacetate (**2**) only 3% of product **3** was formed (GC), despite of full conversion of the starting material (Scheme S4). Other products were not observed by GC-MS due to their high volatility.



Scheme S4 Direct decomposition of ethyl diazoacetate (**2**) in the presence of *N*-methylindole (**1**)

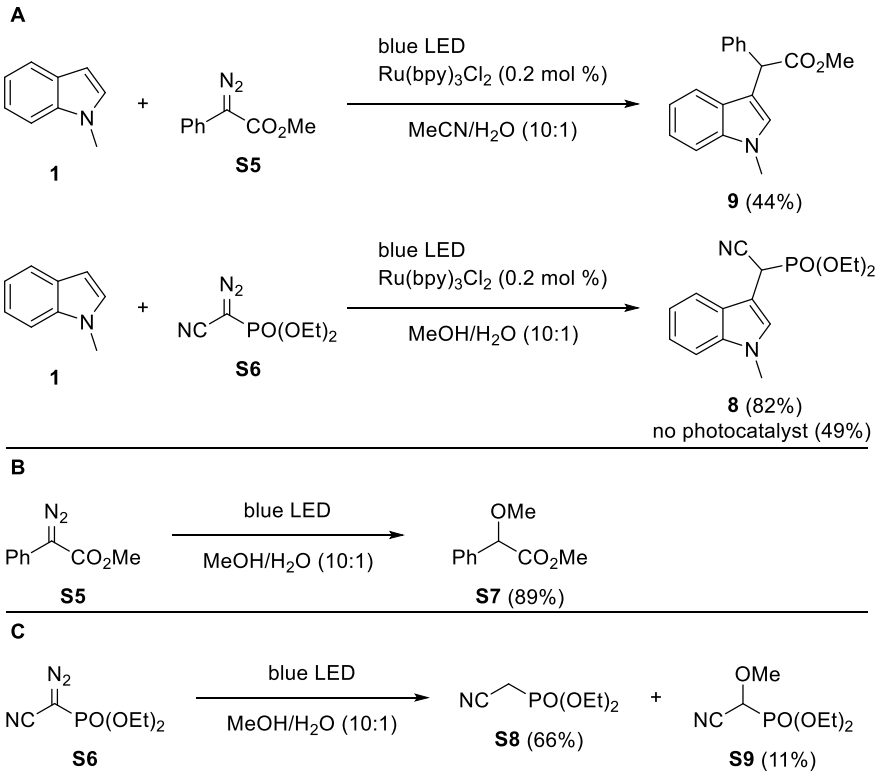
GC-MS analysis of a similar reaction for benzyl diazoacetate (**S2**) shows only traces of the corresponding product (GC-MS and TLC analysis) and two peaks with *m*/*z* = 164 corresponding to $[C_{10}H_{12}O_2]^{\bullet+}$. Fragmentation analysis suggests two possible products **S3** and **S4**. Product **S3** may result from Wolff rearrangement of the corresponding carbene followed by the attack of MeOH, whereas **S4** may be formed by direct insertion of a carbene into methanol O-H bond (Scheme S5A). In fact UVA (365 nm) irradiation of a mixture of benzyl diazoacetate (**S2**) and 1-methylindole (**1**) in the presence of common triplet sensitizer – benzophenone leads to the mixture of products **S3** and **S4** and due to the low power of the light source conversion after 16 h was still not full (Scheme S5B).



Scheme S4 Direct and sensitized decomposition of benzyl diazoacetate (**S2**) in the presence of 1-methylindole (**1**)

Some of the tested diazo compounds namely methyl diazo(phenyl)acetate (**S5**) and diethyl (cyano(diazo)methyl)phosphonate (**S6**) give corresponding C3 substituted products **9** and **8**, suggesting that carbenes are involved in those reactions. In fact under optimized conditions diazo compound **S5** gives product **9** and methyl methoxy(phenyl)acetate (**S7**) as inseparable mixture. Changing the solvent to MeCN/H_2O allowed to isolate product **9** in 44% yield (Scheme S6A). This different behavior of **S5** is caused by the conjugation of diazo group with phenyl ring lowering the excitation energy, observed as batochromic shift of the absorption UV-Vis spectrum. Direct irradiation of a solution of **S5** in MeOH/H_2O mixture with blue light (455 nm) leads to the formation of **S7** in 89% after just 3 hours (Scheme S6B). Although diazo compound **S6** gives corresponding product **8** in very good 82% yield or acceptable 49% without the photocatalyst, its direct, blue light irradiation in MeOH/H_2O gives reduced compound **S8** (66%) and OH insertion product **S9** (11%) (Scheme S6C).

In conclusion for diazo compounds that are not absorbing in visible region, carbenes are not formed and the process is C2-selective. For visible light absorbing diazo compounds C3 selectivity is observed and usually other byproducts are formed.



Scheme S6 Carbene-mediated light induced reactions of selected diazocompounds.

4.4. Fluorescence quenching experiments (the Stern Volmer analysis)

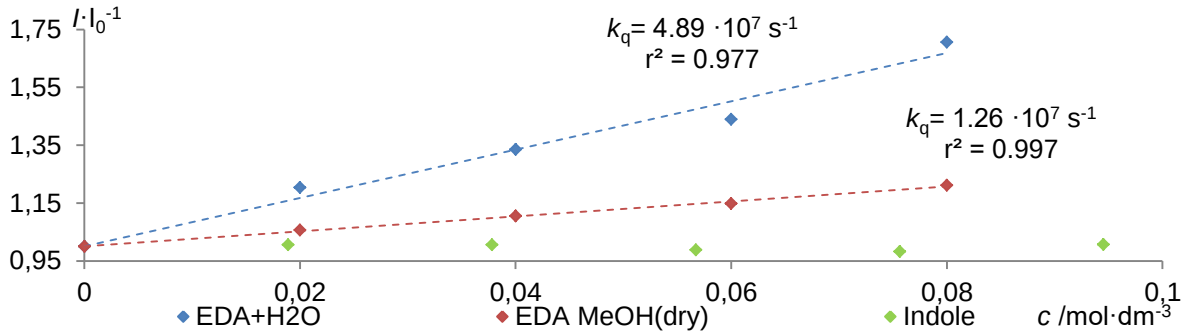


Figure S4 Quenching of the excited state of the photoredox catalyst by ethyl diazoacetate (**2**) and indole

Indole does not quench excited state of the photocatalyst. On the other hand quenching by ethyl diazoacetate was observed, and the quenching constant is increased in the presence of H_2O (10:1) in comparison with that observed in anhydrous MeOH (Figure S4). This suggest that protonated ethyl diazoacetate may act as an actual quencher.

N,*N*-dimethyl-4-methoxyaniline (**25**) quenches the excited state of the photocatalyst with two orders of magnitude higher constant (Figure S5), what suggest that different mechanism should operate in this case.

Procedure for Stern-Volmer experiments:

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ was dissolved in absolute MeOH or in HPLC-grade MeOH or in the mixture of MeOH with H_2O (10:1) to obtain solution with c = 5-10 10^{-6} M which absorbance at the maximum (λ = 450 nm) in the range of 0.1 to 0.2. Mixtures were degassed by freeze-pump-thaw cycle (x3), and 1.5

mL was transferred into a glass cuvette equipped with threaded cap and septum. Stock solutions of reagents in MeOH were prepared (0.75 M for EDA (**2**), 0.71 M for indole and 0.98 M for **25**). After the addition of quencher the solution was degassed for 1 min by bubbling Ar through the mixture. Excitation was performed at 450 nm and the emission was observed at 608 nm. Quenching constant was calculated based on the equation:

$$\frac{I_0}{I} = k_q \cdot \tau \cdot c_{\text{quencher}}$$

Where τ is lifetime of the fluorescence of the photocatalyst, which for $Ru(bpy)_3Cl_2$ in MeOH is equal to 205.7 ns.[1]

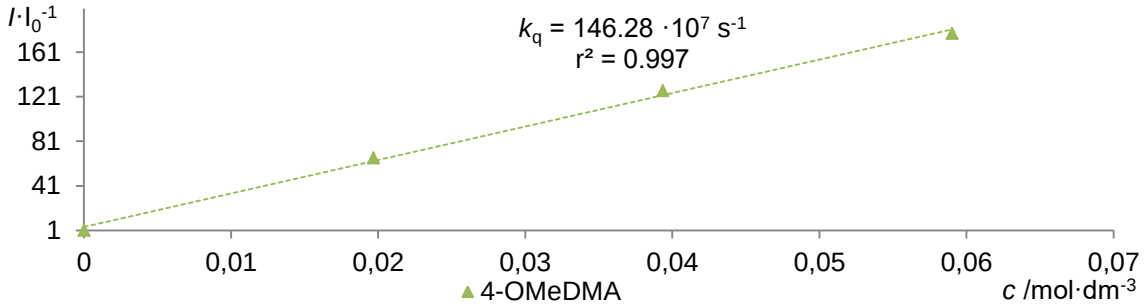


Figure S5 Quenching of the excited state of the photoredox catalyst by *N*,*N*-dimethyl-4-methoxyaniline (**25**).

4.5. Cyclic voltammetry measurements

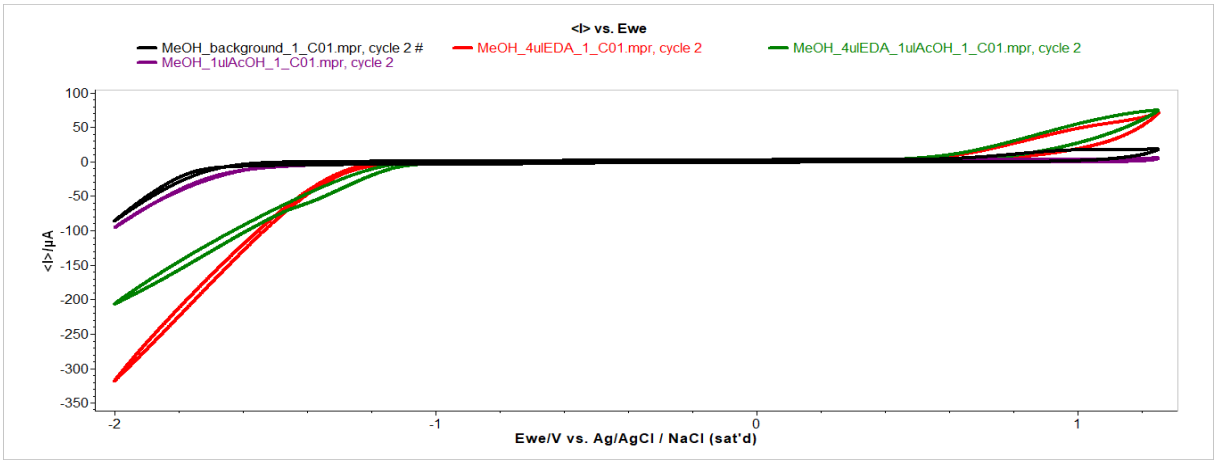


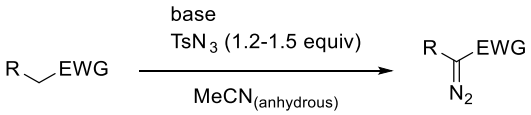
Figure S6 Cyclic voltammetry of ethyl diazoacetate (**2**) in MeOH with (green trace) and without (red trace) the addition of CH_3CO_2H

The peak corresponding to the reduction of ethyl diazoacetate cannot be observed in the MeOH due to its narrow electrochemical window. However a rise of the current resulting from reduction of EDA (**2**) can be observed at potentials around -1.2 V vs Ag/AgCl/NaCl(sat.). An addition of acetic acid increases the potential at which the current rises to about -1.1 V vs Ag/AgCl/NaCl(sat.) (Figure S6), what indicates that the protonation of diazoacetate may occur even in the presence of minute amounts of weak acids.

5. General synthetic procedures

5.1. Preparation of diazo compounds **S5**, **S10**-**S12**, **S6**, **S14** and **S15**

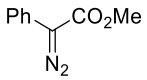
Diazo compounds **S5**, **S10**-**S12** were prepared by diazo transfer with tosyl azide according to slightly modified literature procedures:[2-5]



Scheme S7 Synthesis of diazo compounds **S5**, **S10**-**S12**

A solution of carbanion precursor in anhydrous MeCN (1 M) was stirred under argon atmosphere at 0 °C. Tosyl azide (1.2-1.5 equiv) and an appropriate base were added, then cooling bath were removed. The mixture was stirred until full conversion of the starting material was observed by the TLC. The reaction was quenched with sat. NH_4Cl and extracted with DCM (3 times), combined organic layers were washed with brine and dried over magnesium sulfate. The mixture was then filtered and evaporated in *vacuo*, crude product was purified by column chromatography.

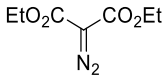
Methyl diazo(phenyl)acetate (S5)[2]



S5

Synthesized according to the general procedure from 750 mg (5.0 mmol) of methyl phenylacetate using 1.12 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (7.5 mmol, 1.5 equiv) as a base. Column chromatography (AcOEt/hexane) afforded 706 mg of **S5** (4.01 mmol, 80%) as red oil.

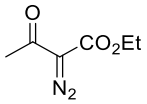
Diethyl 2-diazomalonate (S10)[3]



S10

Synthesized according to the general procedure from 320 mg (2.0 mmol) of ethyl malonate using 335 μL of Et_3N (2.4 mmol, 1.2 equiv) as a base. Column chromatography (AcOEt/hexane) afforded 171 mg of **S10** (0.92 mmol, 46%) as pale yellow oil.

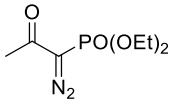
Ethyl 2-diazoacetylacetate (S11)[4]



S11

Synthesized according to the general procedure from 260 mg (2.0 mmol) of ethyl acetoacetate using 335 μL of Et_3N (2.4 mmol, 1.2 equiv) as a base. Column chromatography (AcOEt/hexane) afforded 187 mg of **S11** (1.20 mmol, 60%) as pale yellow oil.

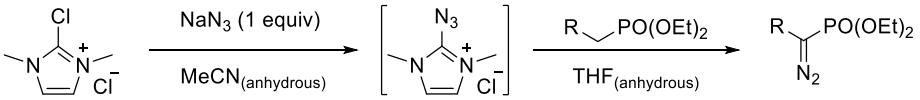
Diethyl (1-diazo-2-oxopropyl)phosphonate (S12)[5]



S12

Synthesized according to the general procedure from 388 mg (2.0 mmol) of diethyl (2-oxopropyl)phosphonate using 348 μL of Et_3N (2.5 mmol, 1.2 equiv) as a base. Column chromatography (AcOEt/hexane, 3:2) afforded 430 mg of **S12** (1.95 mmol, 97%) as pale yellow oil.

Diazo compounds **S6** and **S14** were prepared according to the literature procedure:[6]

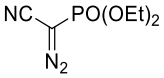


S13

Scheme S8 Synthesis of diazo compounds **S6** and **S14**

To a stirred solution of 2-chloro-1,3-dimethyl-imidazolinium chloride (**S13**, 1.0 equiv) in anhydrous MeCN (0.75 M) sodium azide (1 equiv) was added at 0 °C. After 30 minutes a solution of phosphonate (0.67 equiv) and Et_3N (1.33 equiv) in anhydrous THF (0.25 M) was added and stirring was continued until consumption of phosphonate (monitored by TLC). The reaction was quenched with H_2O and extracted with DCM (3 times), combined organic layers were washed with brine, dried over sodium sulfate, and the solvent was removed in *vacuo*. The crude product was purified by column chromatography (AcOEt/hexane).

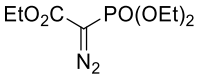
Diethyl (cyano(diazo)methyl)phosphonate (S6)



S6

The product was synthesized using 0.98 g of **S6**(5.8 mmol, 2.1 equiv) 234 mg of NaN_3 (3.6 mmol, 1.3 equiv), 452 µL of diethyl (cyanomethyl)phosphonate (2.8 mmol, 1.0 equiv) and 0.80 mL (5.8 mmol, 2.1 equiv) of Et_3N. Column chromatography (AcOEt:hexane 2:3) afforded 562 mg of **S6** (2.77 mmol, 99%) as yellow oil.

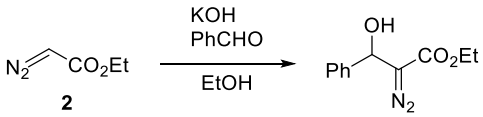
Ethyl diazo(diethylphosphono)acetate (S14)



S14

The product was synthesized using 1.27 g of **S14** (7.5 mmol, 1.5 equiv) 488 mg of NaN_3 (7.5 mmol, 1.5 equiv), 1,00 mL of triethylphosphonoacetate (5.0 mmol, 1.0 equiv) and 1.4 mL (10 mmol, 2 equiv) of Et_3N. Column chromatography (AcOEt:hexane 2:3) afforded 874 mg of **S14** (3.50 mmol, 70%) as yellowish oil.

Diazo compound **S15** was prepared according to the literature procedure:[7]



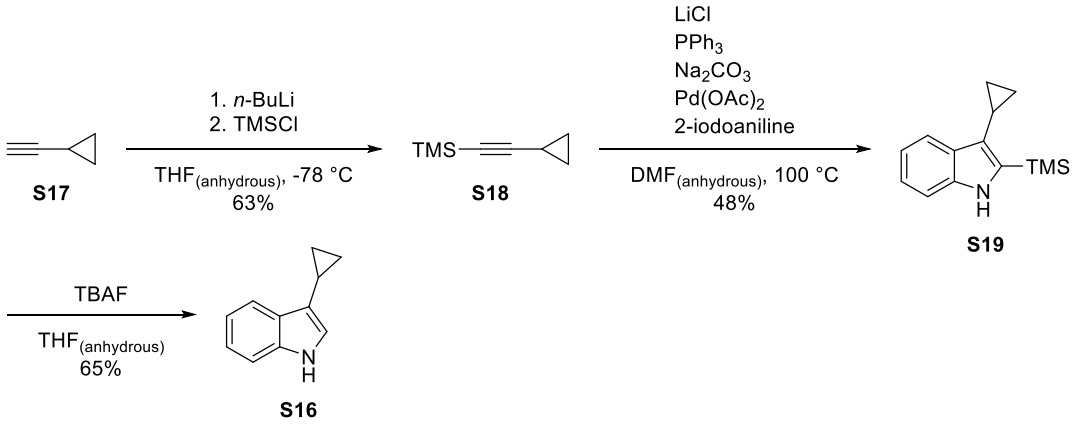
2 **S15** (99%)

Scheme S9 Synthesis of diazo compound **S15**.

To a stirred mixture of ethyl diazoacetate (**2**, 600 µL, 5.0 mmol, 1.0 equiv) and benzaldehyde (505 µL, 5.0 mmol, 1.0 equiv) in EtOH (1 mL) 190 µL of KOH solution in EtOH (10% wt.) was added dropwise. After 2 h in r.t. the reaction was diluted with H_2O and extracted with CH_2Cl_2 (3x10mL), combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. Column chromatography (16-25% AcOEt in hexane) afforded 1.088 g of ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (**S15**) (4.94 mmol, 99%) as yiellow oil.

5.2. Preparation of indole derivatives **S16**, **S20-S26**, **24**

Indole **S16** was prepared in three-step synthesis from commercially available 2-iodoaniline and cyclopropylacetylene (**S17**).



Scheme S10 Three-step synthesis of 3-cyclopropyl-1*H*-indole (**S16**).

Trimethylsillyl cyclopropylacetylene (S18):[8]

To a stirred solution of cyclopropylacetylene (**S17**) (1.85 mL, 21.8 mmol) in anhydrous THF (7 mL) at -78 °C 10.5 mL of 2.5 M *n*-BuLi in hexane (26.2 mmol, 1.2 equiv) was added dropwise. After stirring for 30 min, 2.9 mL of TMSCl (22.8 mmol, 1.04 equiv) was added dropwise and the mixture was stirred for 1 hour at -78 °C. The reaction was allowed to warm up to rt and was diluted with Et_2O and filtred through a pad of Na_2SO_4 layered eluting Et_2O:pentane (1:4). Filtrate was concentrated in *vacuo*, affording in 1.893 g of **S18** as colorless oil (13.69 mmol, 63%).

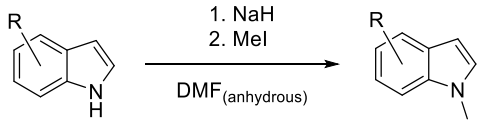
3-cyclopropyl-2-(trimethylsilyl)-1*H*-indole (S19):[9]

To a stirred solution of 2-iodoaniline (438 mg, 2.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.4 mg 0.1 mmol, 0.05 equiv), PPh_3 (26.2 mg, 0.1 mmol 0.05 equiv), LiCl (85 mg, 2.0 mmol, 1.0 equiv) and Na_2CO_3 (636 mg, 6.0 mmol, 3.0 equiv) in anhydrous DMF, 415 mg of **S18** (3.0 mmol, 1.5 equiv) was added. The mixture was heated (100 °C) in a sealed flask for 16 h, diluted with H_2O, filtered through cotton, extracted with AcOEt (3 times), dried over Na_2SO_4 and concentrated in *vacuo*. Column chromatography (4% AcOEt/hexane) afforded 221.7 mg of **S19** as beige solid (0.97 mmol, 49%).

3-Cyclopropyl-1*H*-indole (S16):

To a stirred solution of **S19** (214.6 mg 0.94 mmol, 1.0 equiv) in anhydrous THF (8 mL) 1.5 mL of 1 M solution of TBAF in THF (1.5 mmol, 1.6 equiv) was added. The mixture was refluxed for 2 h, then quenched with H_2O, extracted using EtOAc (3 times), dried over Na_2SO_4 and concentrated in *vacuo*. Column chromatography (5% AcOEt in hexane) afforded 95.6 mg of **S16** as yellow solid (0.60 mmol, 65%).

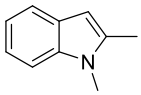
Indoles **S20**-**S26** were prepared by *N*-methylation of commercially available starting materials with methyl iodide, according to the literature procedure:[10]



Scheme S11 *N*-Methylation of indole derivatives.

To a stirred solution of 1-*H*-indole derivative (1.0 equiv) in anhydrous MeCN (0.8 M), sodium hydride (1.12 equiv) was added at 0 °C. After 30 min methyl iodide (1.0 equiv) was added and the reaction mixture was allowed to warm up to rt, stirring was continued for 16 h. Then the reaction was quenched with H_2O and aqueous layer were extracted with AcOEt (3 times), combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in *vacuo*. Column chromatography using AcOEt/hexane afforded products **S20**-**S26**.

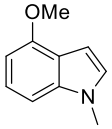
1,2-Dimethyl-1*H*-indole (S20)



S20

The product was synthesized according to the general procedure from 656 mg of 2-methyl-*1H*-indole (5.0 mmol, 1.0 equiv) Column chromatography (10% AcOEt in hexane) afforded 634 mg of **S20** (4.37 mmol, 87%) as dark red solid.

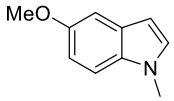
4-Methoxy-1-methyl-1*H*-indole (S21)



S21

The product was synthesized according to the general procedure from 294 mg of 4-methoxy-*1H*-indole (2.0 mmol, 1.0 equiv) Column chromatography (5% AcOEt in hexane) afforded 323.1 mg of **S21** (2.0 mmol, 99%) as greenish solid.

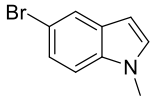
5-Methoxy-1-methyl-1*H*-indole (S22)



S22

The product was synthesized according to the general procedure from 753 mg of 5-methoxy-*1H*-indole (5.11 mmol, 1.0 equiv) Column chromatography (7% AcOEt in hexane) afforded 823 mg of **S22** (5.11 mmol, 99%) as dark orange solid.

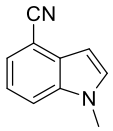
5-Bromo-1-methyl-1*H*-indole (S23)



S23

The product was synthesized according to the general procedure from 980 mg of 5-bromo-*1H*-indole (5.0 mmol, 1.0 equiv) Column chromatography (7% AcOEt in hexane) afforded 782 mg of **S23** (3.72 mmol, 74%) as light orange solid.

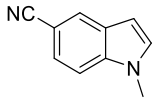
1-Methyl-1*H*-indole-4-carbonitrile (S24)



S24

The product was synthesized according to the general procedure from 711 mg of *1H*-indole-4-carbonitrile (5.0 mmol, 1.0 equiv) Column chromatography (20% AcOEt in hexane) afforded 754 mg of **S24** (4.83 mmol, 97%) as light pink solid.

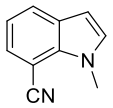
1-Methyl-1*H*-indole-5-carbonitrile (S25)



S25

The product was synthesized according to the general procedure from 711 mg of *1H*-indole-5-carbonitrile (5.0 mmol, 1.0 equiv) Column chromatography (25% AcOEt in hexane) afforded 416 mg of **S25** (2.66 mmol, 53%) as beige solid.

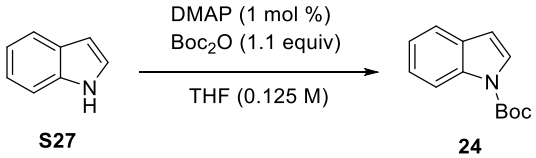
1-Methyl-1*H*-indole-7-carbonitrile (S26)



S26

The product was synthesized according to the general procedure from 284 mg of *1H*-indole-7-carbonitrile (2.0 mmol, 1.0 equiv) Column chromatography (6% AcOEt in hexane) afforded 248 mg of **S27** (1.59 mmol, 80%) as beige solid.

tert-Butyl 1*H*-indole-1-carboxylate (**24**) was synthesized according to the literature procedure:[11]



S27 **24**

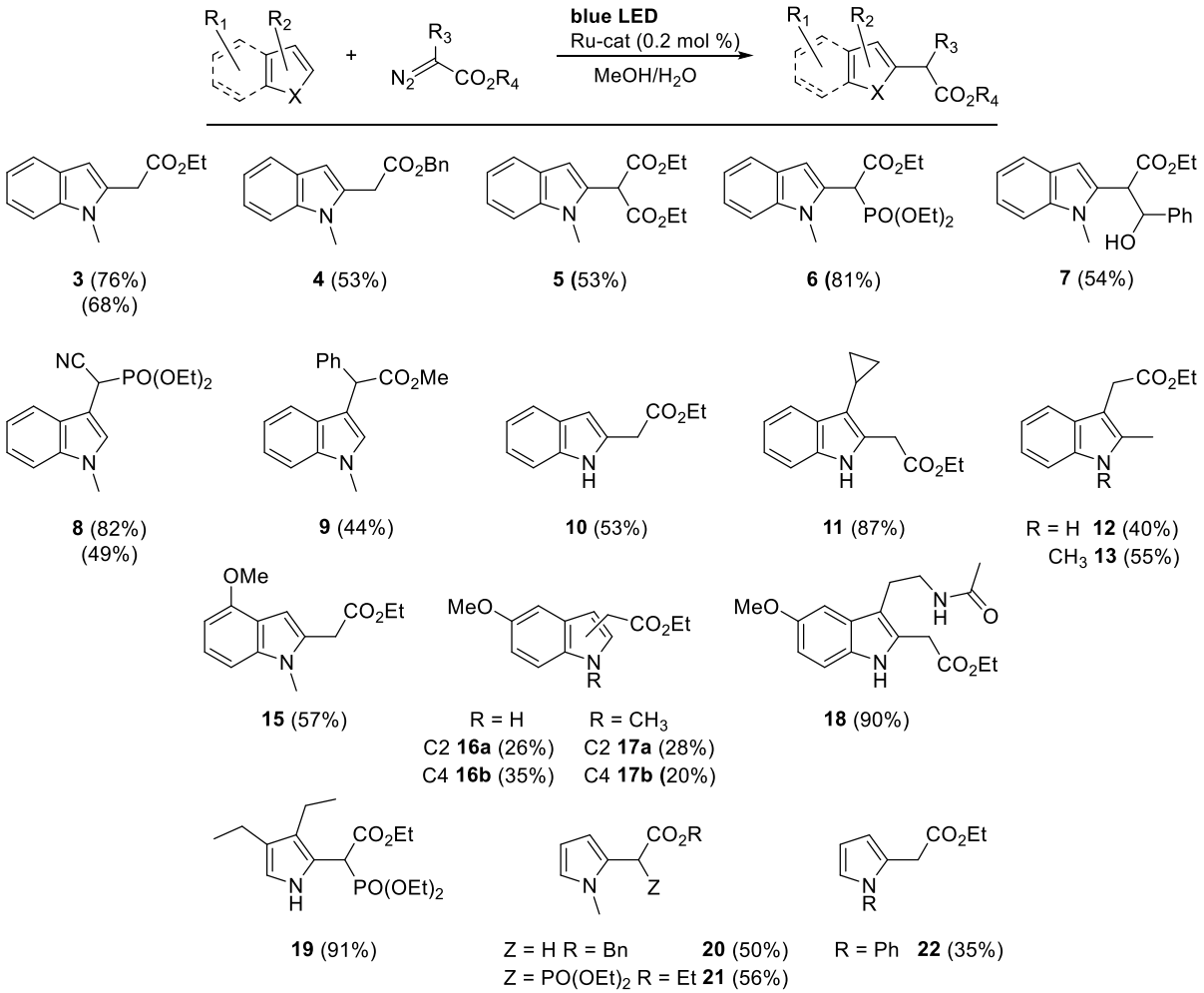
Scheme S12 Boc protection of 1-*H*-indole (**24**).

To a stirred solution of 1-*H*-indole (**S27**, 586 mg, 5.0 mmol, 1.0 equiv) and DMAP (6.1 mg. 0.05 mmol, 0.01 equiv) in THF (40 mL) 1.20 g of Boc_2O (5.5 mmol, 1.1 equiv) was added and the mixture was stirred at rt for 2 hours. Evaporation followed by column chromatography (0-6% AcOEt in hexane) afforded 1.074 g (4.94 mmol, 99%) of **24** as colorless oil.

5.3. General procedure for the photocatalytic alkylation of electron-rich indoles and pyrroles.

A glass vial (outer diameter ~20 mm) equipped with a stirring bar was charged with solid reagents [indole or pyrrole derivative (1.0 mmol, 4.0 equiv), and a diazo compound (0.25 mmol, 1.0 eqiuv), if solid], MeOH (2.5 mL), H_2O (0.25 mL) and 97 μL (0.5 μmol, 0.2 mol %) of stock solution of $Ru(bpy)_3Cl_2$ (c = 5.15 $\mu mol \cdot mL^{-1}$ in MeOH) was added and the vial was sealed by crimping with an appropriate cap equipped with a rubber septum. The mixture was degassed 3x by simplified freeze-thaw method using dry ice as a cooling agent (bubbling the mixture with Ar for 10 min in the ultrasonic bath proven to perform equally good), then the remaining reagents (heteroarene and diazo compound, if liquid) were added. The resulted mixture was cooled again and Ar gas was evacuated to prevent rising of the pressure (during the reaction nitrogen gas is evolving). The reaction mixture was irradiated with 3W blue LED (λ = 455 nm) through the bottom of the vial until full conversion of the

starting material (4.5-8 h). Then the reaction mixture was concentrated in *vacuo* and purified by column chromatography on silica gel to give the products (Scheme S13).



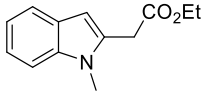
Scheme S13 Scope and limitation studies part I.

Table S6 Determination of yields of other isomers.*

Compound	Isolated yield (main product) /%	Content of isomers /% (determined by)	Calculated yield of other isomers /%
3	76 **C2**	88 / 9 / 2 / 1 (GC)	10
4	53 **C2**	81 / 14 / 2 / 2 / 1 (GC)	13
5	53 **C2**	77 / 11 /5 / 4 / 3 (GC)	16
6	81 **C2**	82 / 7 / 7 / 2 / 2(GC)	18
7	54 **C2**	76 (NMR)	17
8	82 **C3**	93 / 3 / 2 / 1 (GC)	6
9	44 **C3**	92 / 4 / 2 / 2 / 1 (GC)	4
10	53 **C2**	74 / 11 / 10 / 5(GC)	18
12	40 **C3**	69 / 22 / 6 / 3 (GC)	18
13	55 **C3**	76 / 15 / 3 / 3 / 2 / 1 (GC)	17
15	57 **C2**	83 / 12 / 5 / 1 (GC)	10
16a	26 **C2**	70 (NMR)	26
16b	35 **C4**		
17a	28 **C2**	53 / 33 / 7 / 4 / 2 / 1 (GC)	9
17b	20 **C4**		
20	50 **C2**	99 (GC)	1
21	56 **C2**	99 (GC)	1

*Chromatograms on page S36

Ethyl (1-methyl-1*H*-indol-2-yl)acetate (3)



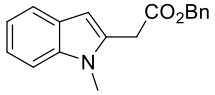
3

Synthesized according to the general procedure from 125 μL (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-indole (**1**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 41.3 mg (0.19 mmol, 76% yield) of yellowish oil, by column chromatography (4-9% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.15 – 7.06 (m, 1H), 6.44 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 3.72 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 137.8, 132.8, 127.7, 121.5, 120.4, 119.6, 109.2, 102.0, 61.4, 33.5, 30.0, 14.3.

Benzyl (1-methyl-1*H*-indol-2-yl)acetate (4)



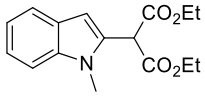
4

Synthesized according to the general procedure from 125 μL (1.0 mmol, 3.89 equiv) of 1-methyl-1*H*-indole (**1**) and 49.5 mg (0.257 mmol, 1.0 equiv) of benzyl diazoacetate (**S2**, containing ~10% of DCM as a stabilizer). Product isolated as 38.1 mg (0.136 mmol, 53% yield) of orange solid, by column chromatography (4-7% AcOEt in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.40 – 7.27 (m, 6H), 7.21 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.10 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 6.44 (d, *J* = 0.8 Hz, 1H), 5.17 (s, 2H), 3.90 – 3.85 (m, 2H), 3.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 137.8, 135.7, 132.5, 128.7, 128.5, 128.4, 127.7, 121.5, 120.4, 119.7, 109.2, 102.1, 67.1, 33.5, 29.9.
Elemental analysis (%) calculated for $C_{18}H_{17}NO_2$: C 77.40, H 6.13,N 5.01, found: C 77.23, H 6.05, N 4.92.
HRMS (EI) calculated [M^+] ($C_{18}H_{17}NO_2$) *m*/*z* = 279.1259, found 279.1263.

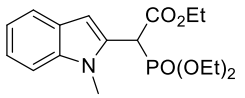
Diethyl (1-methyl-1*H*-indol-2-yl)propanedioate (5)



5

Synthesized according to the general procedure from 125 μL (1.0 mmol, 4.20 equiv) of 1-methyl-1*H*-indole (**1**) and 44.4 mg (0.238 mmol, 1.0 equiv) of diethyl diazomalonate (**S10**). Product isolated as 36.5 mg (0.126 mmol, 53% yield) of yellowish oil, by column chromatography (4-10% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[13]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.32 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.24 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.11 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 6.60 (s, 1H), 4.94 (s, 1H), 4.28 (qq, *J* = 7.3, 3.7 Hz, 4H), 3.73 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ 167.1, 138.1, 131.1, 127.4, 122.1, 120.9, 119.8, 109.4, 103.1, 62.3, 51.5, 30.4, 14.2.

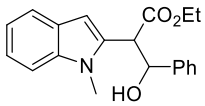
Ethyl (diethylphosphono)(1-methyl-1*H*-indol-2-yl)acetate (6)



6

Synthesized according to the general procedure from 125 μL (1.0 mmol, 4.07 equiv) of 1-methyl-1*H*-indole (**1**) and 61.5 mg (0.246 mmol, 1.0 equiv) of ethyl diazo(diethylphosphono)acetate (**S14**). Product isolated as 70.1 mg (0.198 mmol, 81% yield) of colorless oil, by column chromatography (25-60% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dq, *J* = 7.8, 0.9 Hz, 1H), 7.31 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.21 (ddt, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.83 (d, *J* = 3.3 Hz, 1H), 4.55 (d, *J* = 23.9 Hz, 1H), 4.34 – 4.01 (m, 6H), 3.78 (s, 3H), 1.33 – 1.22 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.6, 137.8, 129.1, 129.1, 127.6, 127.6, 121.9, 120.8, 119.8, 109.4, 103.4, 103.3, 63.8, 63.7, 63.7, 62.3, 45.7, 44.3, 30.1, 16.5, 16.5, 16.4, 16.4, 14.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 16.83.

Ethyl 3-hydroxy-2-(1-methyl-1*H*-indol-2-yl)-3-phenylpropanoate (7)

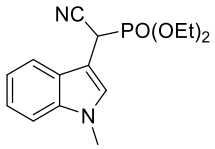


7

Synthesized according to the general procedure from 125 μL (1.0 mmol, 3.57 equiv) of 1-methyl-1*H*-indole (**1**) and 61.6 mg (0.280 mmol, 1.0 equiv) of 2-diazo-3-hydroxy-3-phenylpropanoate (**S15**). Product isolated as 48.6 mg (0.150 mmol, 54% yield) of orange oil, by column chromatography (20-25% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.21 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.12 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 1H), 6.74 (s, 1H), 5.39 (d, *J* = 7.1 Hz, 1H), 4.16 (d, *J* = 7.1 Hz, 1H), 4.04 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.49 (s, 3H), 2.95 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 140.8, 137.6, 133.8, 128.6, 128.4, 127.7, 126.8, 121.8, 120.8, 119.9, 109.5, 101.4, 74.9, 61.5, 51.8, 29.7, 14.0.

Elemental analysis (%) calculated for $C_{20}H_{21}NO_3$: C 74.28, H 6.55, N 4.33, found: C 74.10, H 6.77, N 4.15.
HRMS (ESI+) calculated [M+Na^+] ($C_{20}H_{21}NO_3Na$) *m*/*z* = 346.1414 found 346.1424.

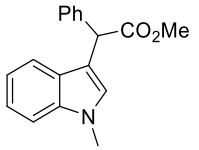
Diethyl (cyano(1-methyl-1*H*-indol-3-yl)methyl)phosphonate (8)



8

Synthesized according to the general procedure from 125 μL (1.0 mmol, 4.08 equiv) of 1-methyl-1*H*-indole (**1**) and 49.8 mg (0.245 mmol, 1.0 equiv) of diethyl (cyano(diazo)methyl)phosphonate (**S6**). Product isolated as 61.8 mg (0.202 mmol, 82% yield) of orange oil, by column chromatography (70% AcOEt in hexane).
Also synthesized via the reaction with no photocatalyst added - 37.8 mg (0.123 mmol, 49% yield) orange oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.18 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 4.52 (dd, *J* = 25.9, 0.7 Hz, 1H), 4.23 – 3.92 (m, 4H), 3.79 (d, *J* = 0.9 Hz, 3H), 1.26 (dtd, *J* = 23.2, 7.1, 0.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 137.1, 129.0, 129.0, 126.3, 126.2, 122.6, 120.2, 119.1, 115.9, 115.8, 109.8, 100.4, 100.3, 64.7, 64.7, 64.4, 64.4, 33.2, 29.1, 27.6, 16.5, 16.4, 16.4.
^{31}P NMR (162 MHz, $CDCl_3$) δ 15.12.
Elemental analysis (%) calculated for $C_{15}H_{19}N_2O_3P$: C 58.82, H 6.25, N 9.15, found: C 58.89, H 6.15, N 9.00.
HRMS (ESI+) calculated [M+Na^+] ($C_{15}H_{19}N_2O_3PNa$) *m*/*z* = 329.1026, found 329.1028.

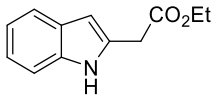
Methyl (1-methyl-1*H*-indol-3-yl)(phenyl)acetate (9)



9

Synthesized according to the general procedure with the change of solvent for acetonitrile from 125 μL (1.0 mmol, 3.88 equiv) of 1-methyl-1*H*-indole (**1**) and 45.4 mg (0.258 mmol, 1.0 equiv) of methyl diazo(phenyl)acetate (**S5**). Product isolated as 31.7 (0.113 mmol, 44% yield) of yellow oil, by column chromatography (4-7% AcOEt in hexane) (peaks corresponding to dimerized diazocompound are visible in both ^{1}H and ^{13}CNMR spectra. The spectroscopic data are consistent with those reported in literature.[15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H), 7.37 – 7.20 (m, 6H), 7.13 – 7.05 (m, 2H), 5.29 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 138.9, 137.2, 128.7, 128.5, 128.0, 127.3, 127.2, 122.0, 119.4, 119.2, 112.2, 109.4, 52.4, 48.9, 32.9.

Ethyl 1*H*-indol-2-ylacetate (10)



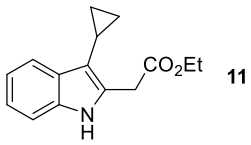
10

Synthesized according to the general procedure from 117 mg (1.0 mmol, 4.0 equiv) of 1*H*-indole (S**27**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 26.9 mg (0.132 mmol 53% yield) of yellowish oil, by column chromatography (8-15% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.59 – 7.54 (m, 1H), 7.38 – 7.33 (m, 1H), 7.17 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.41 – 6.34 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 1.0 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.75, 136.48, 130.72, 128.36, 121.83, 120.24, 119.93, 110.92, 101.93, 61.50, 34.09, 14.28.

Ethyl (3-cyclopropyl-1*H*-indol-2-yl)acetate (11)



11

Synthesized according to the general procedure from 79 mg (0.5 mmol, 4.0 equiv) of 3-cyclopropyl-1*H*-indole (**S16**): and 15 μL (0.125 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 26.6 mg (0.109 mmol, 87% yield) of colorless oil, by column chromatography (9% AcOEt in hexane). In addition 55.9 mg (70%) of indole **S16** was recovered.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.38 – 7.27 (m, 1H), 7.13 (dtd, *J* = 22.0, 7.0, 1.2 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 1.79 (tt, *J* = 8.4, 5.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.00 – 0.90 (m, 2H), 0.73 – 0.65 (m, 2H).

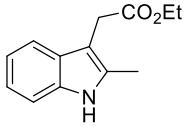
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 135.5, 128.8, 128.7, 121.7, 119.4, 119.1, 114.6, 110.9, 61.4, 32.2, 14.3, 5.2, 5.0.

Elemental analysis (%) calculated for $C_{15}H_{17}NO_2$: C 74.05, H 7.04, N 5.76, found: C 73.92, H 6.89, N 5.75.

HRMS (EI) calculated [M^+] ($C_{15}H_{17}NO_2$) *m*/*z* = 243.1259, found 243.1261.

Ethyl (2-methyl-1*H*-indol-3-yl)acetate (12) and ethyl (2-methyl-1*H*-indol-4-yl)acetate (S28)

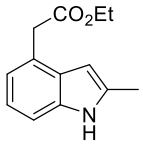
Synthesized according to the general procedure from 131 mg (1.0 mmol, 4.0 equiv) of 2-methyl-1*H*-indole: and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product **12** isolated as 21.5 mg (0.099 mmol, 40% yield) of greenish solid and product **S28** as 6.0 mg (0.027 mmol, 11% yield) of brown oil, by column chromatography (6-15% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[17]



12

(**12**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.59 – 7.49 (m, 1H), 7.29 – 7.22 (m, 1H), 7.16 – 7.05 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 2H), 2.40 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

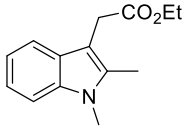
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 135.3, 132.8, 128.7, 121.3, 119.6, 118.3, 110.4, 104.8, 60.8, 30.6, 14.4, 11.8.



S28

(**S28**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.1, 7.2 Hz, 1H), 6.97 (dd, *J* = 7.2, 0.9 Hz, 1H), 6.28 (dt, *J* = 2.3, 1.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 2.44 (d, *J* = 0.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 136.2, 135.2, 128.9, 125.2, 121.2, 120.6, 109.5, 99.1, 60.8, 39.6, 14.4, 13.9.

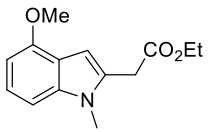
Ethyl (1,2-dimethyl-1*H*-indol-3-yl)acetate (13)



13

Synthesized according to the general procedure from 146 mg (1.0 mmol, 4.0 equiv) of 1,2-dimethyl-1*H*-indole (**S20**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 31.8 mg (0.137 mmol, 55% yield) of orange oil, by column chromatography (9% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[18]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.16 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 2H), 3.67 (s, 3H), 2.41 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 136.7, 134.6, 127.7, 120.9, 119.3, 118.2, 108.7, 104.0, 60.8, 30.9, 29.7, 14.4, 10.5.

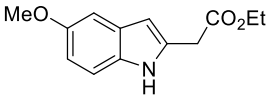
Ethyl (4-methoxy-1-methyl-1*H*-indol-2-yl)acetate (15)



15

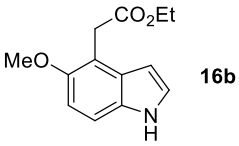
Synthesized according to the general procedure from 161 mg (1.0 mmol, 4.0 equiv) of 4-methoxy-1-methyl-1*H*-indole (**S21**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 35.4 mg (0.143 mmol, 57% yield) of dark red oil, by column chromatography (12% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.58 – 6.47 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 3.81 (s, 2H), 3.69 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 153.2, 139.3, 131.2, 122.3, 118.2, 102.8, 99.8, 99.2, 61.3, 55.5, 33.6, 30.3, 14.3.
Elemental analysis (%) calculated for $C_{14}H_{17}NO_3$: C 68.00, H 6.93, N 5.66, found: C 68.24, H 7.08, N 5.43.
HRMS (EI) calculated [M^+] ($C_{14}H_{17}NO_3$) *m*/*z* = 247.1208, found 247.1217.

Ethyl (5-methoxy-1*H*-indol-2-yl)acetate (16a) and ethyl (5-methoxy-1*H*-indol-4-yl)acetate (16b)
Synthesized according to the general procedure from 147 mg (1.0 mmol, 4.0 equiv) of 5-methoxy-1*H*-indole and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product **16a** isolated as 15.4 mg (0.066 mmol, 26% yield) of green oil, and product **16b** as 20.3 mg (0.087 mmol, 35% yield) by column chromatography (10-18% AcOEt in hexane). Spectroscopic data for compound **16a** is consistent with reported in literature.[19]



16a

(**16a**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.28 (dd, *J* = 2.1, 1.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.80 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 154.4, 131.7, 131.4, 128.8, 111.9, 111.6, 102.3, 101.8, 61.5, 56.0, 34.1, 14.3.

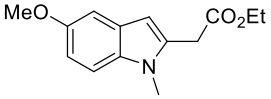


16b

(**16b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.24 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.17 (t, *J* = 2.8 Hz, 1H), 6.49 (ddd, *J* = 3.1, 2.0, 0.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 3.86 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 151.7, 131.5, 129.1, 125.5, 114.0, 110.4, 109.5, 100.8, 60.7, 58.0, 33.0, 14.4.
Elemental analysis (%) calculated for $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00, found: C 67.07, H 6.41, N 5.75.
HRMS (ESI+) calculated [M+Na$^+$] ($C_{13}H_{15}NO_3Na$) *m*/*z* = 256.0944, found 256.0946.

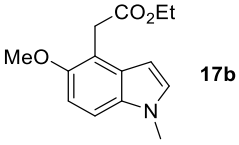
Ethyl (5-methoxy-1-methyl-1*H*-indol-2-yl)acetate (17a) and ethyl (5-methoxy-1-methyl-1*H*-indol-4-yl)acetate (17b)

Synthesized according to the general procedure from 161 mg (1.0 mmol, 4.0 equiv) of 5-methoxy-1-methyl-1*H*-indole (**S22**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product **17a** isolated as 17.3 mg (0.070 mmol, 28% yield) of yellow oil, and product **17b** as 12.4mg (0.050 mmol, 20% yield) of yellow oil by column chromatography (10% AcOEt in hexane). Spectroscopic data for compound **17a** is consistent with reported in literature.[20]



17a

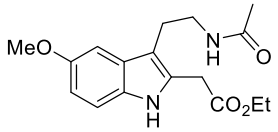
(**17a**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.9 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.34 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.79 (s, 2H), 3.68 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 154.3, 133.3, 133.2, 128.0, 111.6, 109.9, 102.4, 101.6, 61.4, 56.1, 33.6, 30.1, 14.3.



17b

(**17b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.42 (dd, *J* = 3.1, 0.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 151.6, 132.6, 130.0, 129.6, 114.2, 109.2, 108.6, 98.9, 60.6, 58.1, 33.1, 33.0, 14.4.
HRMS (ESI+) calculated [M+Na$^+$] ($C_{14}H_{17}NO_3Na$) *m*/*z* = 270.1101, found 270.1106.

Ethyl (3-(2-(acetylamino)ethyl)-5-methoxy-1*H*-indol-2-yl)acetate (18)



18

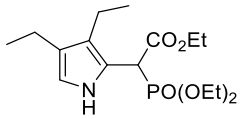
Synthesized according to the general procedure using lowered amount of heteroarene - 116 mg (0.5 mmol, 2 equiv) of melatonin and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 71.8 mg (0.226 mmol, 90% yield) of brownish solid, by column chromatography (50% acetone in hexane). In addition 56.6 mg (0.244 mmol) of unreacted melatonin was recovered.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.24 – 7.16 (m, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.97 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 2H), 3.53 (q, *J* = 6.2 Hz, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 1.90 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.5, 154.3, 131.1, 128.6, 128.4, 112.3, 111.8, 110.6, 100.6, 61.7, 56.1, 39.8, 32.1, 24.1, 23.3, 14.3.

HRMS (ESI+) calculated [M+Na^+] ($C_{17}H_{22}N_2O_4Na$) *m*/*z* = 341.1472, found 341.1474.

Ethyl (diethylphosphono)(3,4-diethyl-1*H*-pyrrol-2-yl)acetate (19)



19

Synthesized according to the general procedure from 134 μL (1.0 mmol, 4.0 equiv) of 3,4-diethyl-1*H*-pyrrole and 62.5 mg (0.25 mmol, 1.0 equiv) of ethyl diazo(diethylphosphono)acetate (**S14**). Product isolated as 78.3 mg (0.227 mmol, 91% yield) of brown oil, by column chromatography (60% AcOEt in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 6.56 – 6.44 (m, 1H), 4.34 (d, *J* = 23.9 Hz, 1H), 4.25 – 4.14 (m, 2H), 4.14 – 4.03 (m, 2H), 3.98 (dp, *J* = 10.1, 7.2 Hz, 1H), 3.81 (ddq, *J* = 10.2, 8.2, 7.0 Hz, 1H), 2.48 – 2.35 (m, 4H), 1.29 (dt, *J* = 9.0, 7.1 Hz, 6H), 1.16 (q, *J* = 7.3 Hz, 6H), 1.08 (t, *J* = 7.6 Hz, 3H).

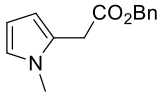
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 167.6, 124.6, 124.6, 122.9, 122.8, 115.1, 115.0, 114.8, 114.7, 63.7, 63.6, 63.2, 63.2, 62.0, 44.2, 42.9, 18.6, 17.3, 17.3, 16.5, 16.4, 16.4, 16.3, 16.0, 16.0, 14.7, 14.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.65.

Elemental analysis (%) calculated for $C_{16}H_{28}NO_5P$: C 55.64, H 8.17, N 4.06, found: C 55.39, H 8.21, N 4.19.

HRMS (ESI+) calculated [M+Na^+] ($C_{16}H_{28}NO_5PNa$) *m*/*z* = 368.1597, found 368.1597.

Benzyl (1-methyl-1*H*-pyrrol-2-yl)acetate (20)



20

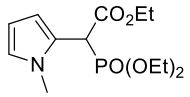
Synthesized according to the general procedure from 89 μL (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-pyrrole and 42 μL (0.25 mmol, 1.0 equiv) of benzyl diazoacetate (**S5**, containing ~10% of DCM as a stabilizer). Product isolated as 28.5 mg (0.124 mmol, 50% yield) of yellowish oil, by column chromatography (9% AcOEt in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 6.60 (dd, *J* = 2.7, 1.9 Hz, 1H), 6.14 – 6.03 (m, 2H), 5.16 (s, 2H), 3.68 (d, *J* = 0.7 Hz, 2H), 3.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 135.9, 128.7, 128.4, 128.3, 124.8, 122.7, 109.0, 107.2, 66.8, 34.0, 32.8.

Elemental analysis (%) calculated for $C_{14}H_{15}NO_2$: C 73.34, H 6.59, N 6.11, found: C 73.34, H 6.58, N 6.06.
HRMS (EI) calculated [M^+] ($C_{14}H_{15}NO_2$) *m*/*z* = 229.1097, found 229.1104.

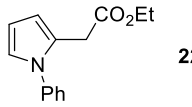
Ethyl (diethylphosphono)(1-methyl-1*H*-pyrrol-2-yl)acetate (21)



21

Synthesized according to the general procedure from 89 μL (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-pyrrole and 62.7 mg (0.251 mmol, 1.0 equiv) of ethyl diazo(diethylphosphono)acetate (**S14**). Product isolated as 42.8 mg (0.141 mmol, 56% yield) of yellowish oil, by column chromatography (50% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (q, *J* = 2.0 Hz, 1H), 6.41 (td, *J* = 3.4, 1.8 Hz, 1H), 6.07 (dd, *J* = 3.7, 2.8 Hz, 1H), 4.32 (d, *J* = 23.9 Hz, 1H), 4.27 – 3.96 (m, 6H), 3.62 (s, 3H), 1.32 – 1.18 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.9, 123.4, 123.3, 121.0, 121.0, 110.3, 110.3, 107.5, 107.4, 63.6, 63.5, 63.5, 62.0, 45.2, 43.8, 34.2, 16.5, 16.4, 16.4, 14.1.
^{31}P NMR (162 MHz, $CDCl_3$) δ 17.52.
Elemental analysis (%) calculated for $C_{13}H_{22}NO_5P$: C 51.48, H 7.31, N 4.62, found: C 51.64, H 7.15, N 4.42.
HRMS (EI) calculated [M^+] ($C_{13}H_{22}NO_5P$) *m*/*z* = 303.1230, found 303.1241.

Ethyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (22)



22

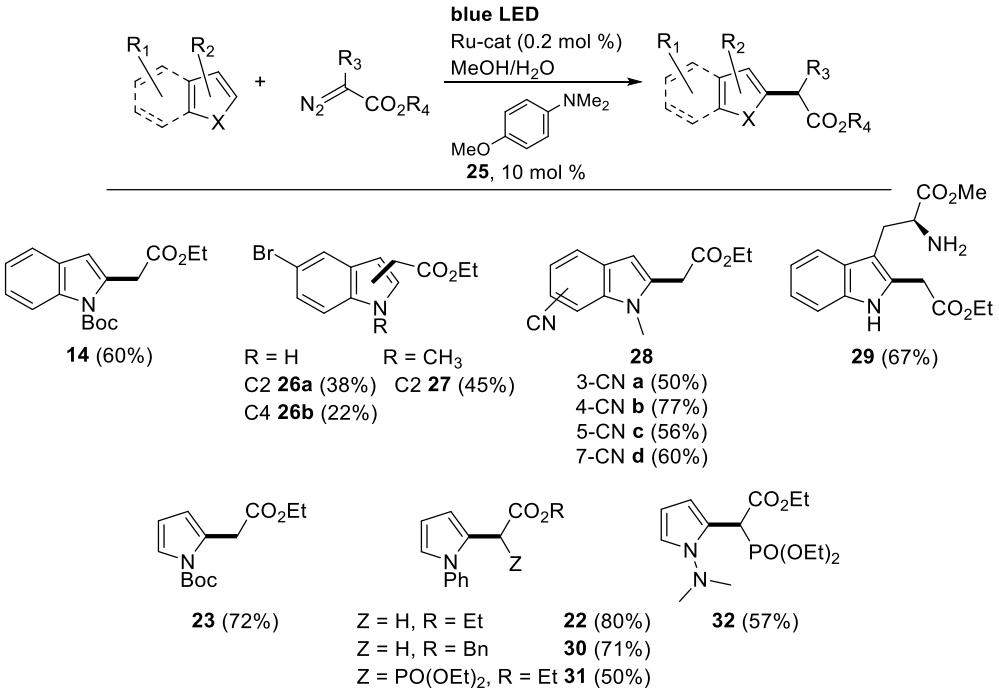
Synthesized according to the general procedure from 143 mg (1.0 mmol, 4.0 equiv) of 1-phenyl-1*H*-pyrrole and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 19.9 mg (0.087 mmol 35% yield) of brownish solid, by column chromatography (3-5% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[21]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.28 (m, 5H), 6.80 (dd, *J* = 2.8, 1.9 Hz, 1H), 6.28 – 6.22 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 2H), 1.17 (t, *J* = 7.1 Hz, 3H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 140.1, 129.3, 127.6, 126.5, 125.7, 122.8, 110.0, 108.6, 61.0, 33.0, 14.3.

5.4. The reaction on the preparative scale (5 mmol) – procedure.

100 mL Schlenk flask equipped with a stirring bar was charged with 2.0 mg of $Ru(bpy)_3Cl_2$ hexahydrate (2.7 μmol, 0.054 mol %). Then 50 mL of HPLC-grade MeOH and 5 mL of H_2O was added and the flask was capped with a septum. The solution was degassed 3x by simplified freeze-thaw method using dry ice as a cooling agent, then 2.50 mL (20 mmol, 4.0 equiv) of 1-methylindole (**1**) and 600 μL (5.0 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer) were added. The reaction mixture was cooled again to -78 °C and Ar gas was evacuated to prevent rising of the pressure (during the reaction nitrogen gas is evolving). The reaction mixture was irradiated with 9 W blue LED tape (λ = 455 nm) for 26 h (after full conversion of **2** was observed by TLC analysis). Then it was concentrated in *vacuo* and purified by column chromatography on silica gel (5-12% AcOEt in hexane) to give 743 mg (3.42 mmol, 68% yield) of product **3** as brown solid. In addition 1.90 g (14.48 mmol, 72%) of 1-methylindole (**1**) was recovered.

5.5. General procedure for the photocatalytic alkylation of indoles and pyrroles with EWG substituents

A glass vial (outer diameter ~20 mm) equipped with a stirring bar was charged with 3.8 mg (25 μmol, 10 mol %) of *N*,*N*-dimethyl-4-methoxyaniline (**25**), other solid reagents [indole or pyrrole derivative (1.0 mmol, 4.0 equiv), and diazo compound (0.25 mmol 1 eqiuv.), if solid], MeOH (2.5 mL), H_2O (0.25 mL) and 97 μL (0.5 μmol, 0.2 mol %) of stock solution of $Ru(bpy)_3Cl_2$ (c = 5.15 μmol·mL^{-1}) in MeOH was added and the vial was sealed by crimping with an appropriate cap equipped with a rubber septum. The mixture was degassed 3x by simplified freeze-thaw method from dry ice as a cooling agent (bubbling the mixture with Ar for 10 min in the ultrasonic bath proven to perform equally well), then the remaining reagents (heteroarene and diazo compound, if liquid) were added. The reaction mixture was cooled again and Ar gas was evacuated to prevent rising of the pressure (during the reaction nitrogen gas is evolving) and then irradiated with 3W blue LED (λ = 455 nm) through the bottom plane of the vial until full conversion of the starting material (4.5-8 h). Then the reaction mixture was concentrated in *vacuo* and purified by column chromatography on silica gel to give the products (Scheme S14).



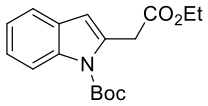
Scheme S14 Scope and limitation studies part II.

Table S7 Determination of yield of other isomers.*

Compound	Isolated yield (main product) /%	Content of isomers /% (determined by)	Calculated yield of other isomers /%
14	60 **C2**	82 (NMR)	14
22	80 **C2**	93 / 4 / 3 (GC)	6
23	72 **C2**	96 / 3 / 1 (GC)	3
26a	38 **C2**	46 / 38 / 5 / 4 / 3 / 2 / 1 (GC)	11
26b	22 **C4**		
27	45 **C2**	72 / 18 / 6 / 2 / 2 (GC)	18
28a	50 **C2**	93 / 4 / 2 (GC)	4
28b	77 **C2**	88 / 8 / 2 / 2 (GC)	10
28c	56 **C2**	71 / 21 / 7 / 1 (GC)	23
28d	60 **C2**	74 / 16 / 8 / 1 (GC)	22
29	67 **C2**	77 / 18 / 3 / 1 (GC)	20
31	50 **C2**	75 / 14 / 9 / 2 (GC)	17
32	57 **C2**	88 / 8 / 4 (GC)	8

*Chromatograms on page S36

***tert*-Butyl 2-(2-ethoxy-2-oxoethyl)-1*H*-indole-1-carboxylate (14)**



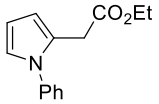
14

Synthesized according to the general procedure from 203 μL (1.0 mmol, 4.0 equiv) of *tert*-butyl 1*H*-indole-1-carboxylate (**24**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 45.3 mg (0.149 mmol 60% yield) of colorless oil, by column chromatography (2-4% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.49 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.28 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.21 (td, *J* = 7.4, 1.1 Hz, 1H), 6.49 – 6.45 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 0.9 Hz, 2H), 1.67 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 150.6, 136.7, 133.6, 129.0, 124.0, 122.8, 120.4, 115.9, 110.4, 84.3, 61.0, 36.5, 28.3, 14.3.

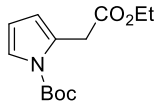
Ethyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (22)



22

Synthesized according to the general procedure from 143 mg (1.0 mmol, 4.0 equiv) of 1-phenyl-1*H*-pyrrole and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 46.1 mg (0.201 mmol 80% yield) of brownish solid, by column chromatography (3-5% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[21]

***tert*-Butyl 2-(2-ethoxy-2-oxoethyl)-1*H*-pyrrole-1-carboxylate (23)**



23

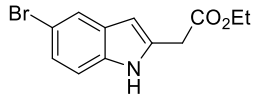
Synthesized according to the general procedure from 167 μL (1.0 mmol, 4.0 equiv) of *tert*-butyl-1*H*-pyrrole-1-carboxylate and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 45.6mg (0.180 mmol 72% yield) of yellow oil, by column chromatography (7% AcOEt in hexane). The spectroscopic data are consistent with those reported in literature.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.11 (t, *J* = 3.3 Hz, 1H), 6.07 (tt, *J* = 2.1, 0.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.86 (d, *J* = 0.8 Hz, 2H), 1.56 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 149.5, 127.5, 121.8, 114.2, 110.1, 83.9, 60.9, 35.1, 28.1, 14.3.

Ethyl (5-bromo-1*H*-indol-2-yl)acetate (26a) and ethyl (5-bromo-1*H*-indol-4-yl)acetate (26b)

Synthesized according to the general procedure from 196 mg (1.0 mmol, 4.0 equiv) of 5-bromo-1*H*-indole and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product **26a** isolated as 26.7 mg (0.095 mmol, 38% yield) of brownish solid, and product **26b** as 15.4 mg (0.055 mmol, 22% yield) of brownish solid by column chromatography (15% AcOEt in hexane).



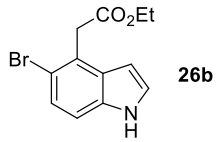
26a

(**26a**) ^{1}H NMR (400 MHz, CDCl3) δ 8.79 (s, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.28 (d, *J* = 2.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 135.0, 132.1, 130.1, 124.7, 122.7, 113.1, 112.4, 101.5, 61.7, 33.8, 14.3.

Elemental analysis (%) calculated for $C_{12}H_{12}BrNO_2$: C 51.09, H 4.29, N 4.96, found: C 51.27, H 4.55, N 4.83.

HRMS (ESI+) calculated [M+Na^+] ($C_{12}H_{12}BrNO_2Na$) *m*/*z* = 303.9944, found 303.9925.



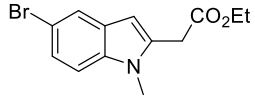
26b

(**26b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.21 – 7.10 (m, 2H), 6.53 (ddd, *J* = 3.2, 2.1, 1.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 134.7, 129.6, 126.1, 125.9, 125.4, 116.0, 111.8, 101.6, 61.1, 39.1, 14.3.

HRMS (ESI+) calculated [M+Na^+] ($C_{12}H_{12}BrNO_2Na$) *m*/*z* = 303.9944, found 303.9938.

Ethyl (5-bromo-1-methyl-1*H*-indol-2-yl)acetate (27)

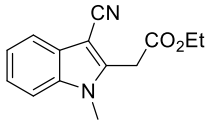


27

Synthesized according to the general procedure from 210 mg (1.0 mmol, 4.0 equiv) of 5-bromo-1-methyl-1*H*-indole (**S23**) and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 33.4 mg (0.113 mmol 45% yield) of brown oil, by column chromatography (8% AcOEt in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.21 (m, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.39 – 6.31 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 3.68 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 136.5, 134.1, 129.3, 124.3, 122.9, 112.9, 110.7, 101.6, 61.5, 33.5, 30.2, 14.3.
HRMS (ESI+) calculated [M+Na^+] ($C_{13}H_{14}BrNO_2Na$) *m*/*z* = 318.0100, found 318.0093.

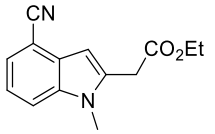
Ethyl (3-cyano-1-methyl-1*H*-indol-2-yl)acetate (28a)



28a

Synthesized according to the general procedure from 156 mg (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-indole-3-carbonitrile and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 30.2 mg (0.124 mmol 50% yield) of beige solid, by column chromatography (15% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.41 – 7.24 (m, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 3.77 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 140.9, 136.8, 127.0, 123.9, 122.4, 119.7, 115.9, 110.3, 87.0, 62.1, 32.4, 30.9, 14.3.
HRMS (ESI+) calculated [M+Na^+] ($C_{14}H_{14}N_2O_2Na$) *m*/*z* = 265.0947, found 265.0945.

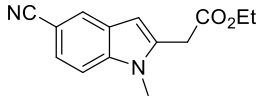
Ethyl (4-cyano-1-methyl-1*H*-indol-2-yl)acetate (28b)



28b

Synthesized according to the general procedure from 156 mg (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-indole-4-carbonitrile and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 46.5 mg (0.192 mmol 77% yield) of off-white solid, by column chromatography (18% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.43 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.21 (dd, *J* = 8.3, 7.4 Hz, 1H), 6.64 (t, *J* = 0.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.86 (d, *J* = 0.6 Hz, 2H), 3.75 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 137.5, 136.0, 129.1, 125.1, 121.1, 118.9, 113.9, 102.7, 101.2, 61.7, 33.5, 30.4, 14.3.
Elemental analysis (%) calculated for $C_{14}H_{14}N_2O_2$: C 69.41, H 5.82, N 11.56, found: C 69.57, H 5.75, N 11.62.
HRMS (ESI+) calculated [M+Na^+] ($C_{14}H_{14}N_2O_2Na$) *m*/*z* = 265.0947, found 265.0953.

Ethyl (5-cyano-1-methyl-1*H*-indol-2-yl)acetate (28c)

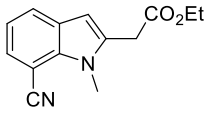


28c

Synthesized according to the general procedure from 156 mg (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-indole-5-carbonitrile and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 33.8 mg (0.140 mmol 56% yield) of brown solid, by column chromatography (18% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.6 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.50 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 3.74 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 139.3, 135.5, 127.4, 125.9, 124.6, 120.9, 110.1, 103.0, 102.8, 61.7, 33.4, 30.3, 14.3.
HRMS (ESI+) calculated [M+H$^+$] ($C_{14}H_{15}N_2O_2$) *m*/*z* = 243.1128, found 243.1127.

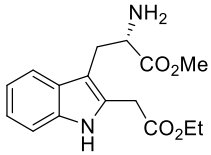
Ethyl (7-cyano-1-methyl-1*H*-indol-2-yl)acetate (28d)



28d

Synthesized according to the general procedure from 156 mg (1.0 mmol, 4.0 equiv) of 1-methyl-1*H*-indole-7-carbonitrile and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 36.2 mg (0.149 mmol 60% yield) of brownish solid, by column chromatography (12% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 0.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 3.83 (d, *J* = 0.7 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 135.9, 135.3, 129.3, 128.6, 125.8, 119.4, 119.0, 103.3, 93.8, 61.7, 33.4, 31.5, 14.3.
HRMS (ESI+) calculated [M+Na$^+$] ($C_{14}H_{14}N_2O_2Na$) *m*/*z* = 265.0947, found 265.0944.

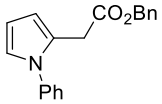
Methyl (2*S*)-2-amino-3-(2-(2-ethoxy-2-oxoethyl)-1*H*-indol-3-yl)propanoate (29)



29

Synthesized according to the general procedure from 218 mg (1.0 mmol, 4.0 equiv) of methyl (2*S*)-2-amino-3-(1*H*-indol-3-yl)propanoate and 30 μL (0.25 mmol, 1.0 equiv) of ethyl diazoacetate (**2**, containing ~13% of DCM as a stabilizer). Product isolated as 51.1 mg (0.168 mmol 67% yield) of light brown oil, by column chromatography (5% MeOH, 1% Et_3N in DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.55 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.31 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.16 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.09 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.85 – 3.79 (m, 3H), 3.70 (s, 3H), 3.25 (dd, *J* = 14.4, 5.1 Hz, 1H), 2.98 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.69 (s, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 170.8, 135.9, 128.7, 128.2, 122.2, 119.8, 118.6, 111.0, 108.9, 61.6, 55.3, 52.2, 32.0, 30.0, 14.3.
HRMS (ESI+) calculated [M+H$^+$] ($C_{16}H_{21}N_2O_4$) *m*/*z* = 305.1501, found 305.1514.

Benzyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (30)

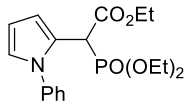


30

Synthesized according to the general procedure from 143 mg (1.0 mmol, 4.0 equiv) of 1-phenyl-1*H*-pyrrole and 42 μL (0.25 mmol, 1.0 equiv) of benzyl diazoacetate (**S2**, containing ~10% of DCM as a stabilizer). Product isolated as 51.6 mg (0.177 mmol 71% yield) of yellow oil, by column chromatography (4% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 6H), 7.27 (ddd, *J* = 8.1, 5.0, 1.7 Hz, 4H), 6.81 (dd, *J* = 2.7, 1.9 Hz, 1H), 6.27 (dd, *J* = 2.4, 1.4 Hz, 2H), 5.07 (s, 2H), 3.66 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.0, 135.9, 129.3, 128.6, 128.4, 127.6, 126.5, 125.4, 122.8, 110.1, 108.6, 66.7, 32.9.

Elemental analysis (%) calculated for $C_{19}H_{17}NO_2$: C 78.33, H 5.88, N 4.81, found: C 78.47, H 5.90, N 4.70.
HRMS (EI) calculated [M^+] ($C_{19}H_{17}NO_2$) *m*/*z* = 291.1254, found 291.1259.

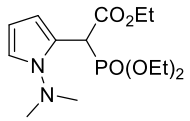
Ethyl (diethylphosphono)(1-phenyl-1*H*-pyrrol-2-yl)acetate (31)



31

Synthesized according to the general procedure from 143 mg (1.0 mmol, 4.0 equiv) of 1-phenyl-1*H*-pyrrole and 62.5 mg (0.25 mmol, 1.0 equiv) of ethyl diazo(diethylphosphono)acetate (**S14**). Product isolated as 45.4 mg (0.124 mmol, 50% yield) of yellow oil, by column chromatography (60% AcOEt in hexane).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 6.79 (dt, *J* = 3.0, 1.5 Hz, 1H), 6.65 (td, *J* = 3.3, 1.8 Hz, 1H), 6.27 (t, *J* = 3.3 Hz, 1H), 4.28 (d, *J* = 24.2 Hz, 1H), 4.22 – 3.97 (m, 6H), 1.23 (qd, *J* = 6.4, 5.8, 2.9 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 167.2, 139.3, 129.5, 128.0, 127.0, 123.3, 123.3, 121.9, 121.9, 111.5, 111.4, 109.0, 108.9, 63.7, 63.6, 63.2, 63.2, 62.0, 44.5, 43.1, 16.5, 16.5, 16.4, 16.4, 14.1.
Elemental analysis (%) calculated for $C_{18}H_{24}NO_5P$: C 59.17, H 6.62, N 3.83, found: C 59.20, H 6.85, N 3.66.
HRMS (EI) calculated [M^+] ($C_{18}H_{24}NO_5P$) *m*/*z* = 365.1387, found 365.1400.

Ethyl (diethylphosphono)(1-(dimethylamino)-1*H*-pyrrol-2-yl)acetate (32)

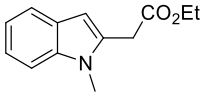


32

Synthesized according to the general procedure from 121 μL (1.0 mmol, 4.1 equiv) of *N*,*N*-dimethyl-1*H*-pyrrol-1-amine and 60.6 mg (0.242 mmol, 1.0 equiv) of ethyl diazo(diethylphosphono)acetate (**S14**). Product isolated as 45.8 mg (0.138 mmol, 57% yield) of brown oil, by column chromatography (75% AcOEt in hexane).
H NMR (400 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 3.0, 1.4 Hz, 1H), 6.26 (ddd, *J* = 4.3, 2.6, 1.8 Hz, 1H), 6.13 (dd, *J* = 4.0, 3.1 Hz, 1H), 4.95 (d, *J* = 24.1 Hz, 1H), 4.30 – 3.99 (m, 6H), 2.76 (d, *J* = 12.1 Hz, 6H), 1.32 – 1.21 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 167.5, 121.2, 121.1, 113.0, 113.0, 107.2, 107.2, 106.1, 106.1, 63.3, 63.3, 63.1, 63.0, 61.7, 48.0, 47.8, 43.1, 41.7, 16.5, 16.5, 16.4, 14.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 18.53.
Elemental analysis (%) calculated for $C_{14}H_{25}N_2O_5P$: C 50.60, H 7.58, N 8.43, found: C 50.51, H 7.67, N 8.25.
HRMS (ESI+) calculated [M+Na^+] ($C_{14}H_{25}N_2O_5PNa$) *m*/*z* = 355.1393, found 355.1398.

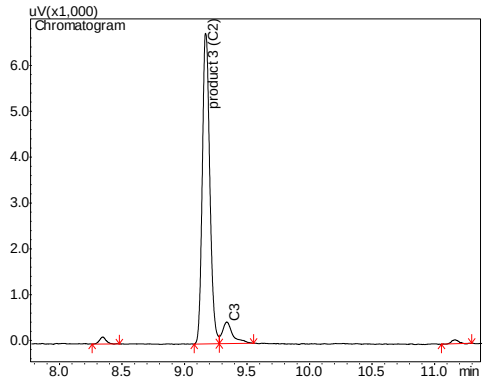
6. GC Chromatograms – parts showing content of isomers in crude reaction mixtures.

Ethyl (1-methyl-1*H*-indol-2-yl)acetate (3)

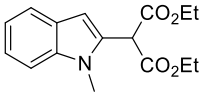


3

Isolated yield (main product) /%	Content of isomers /%
76 **C2**	88 / 9 / 2 / 1

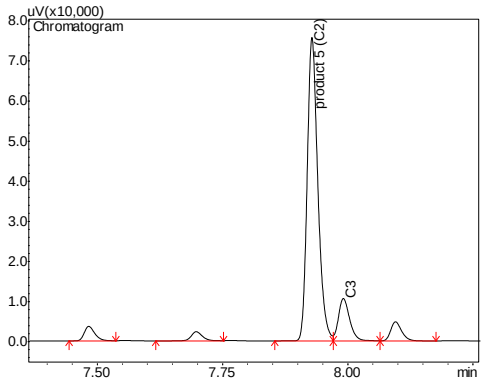


Diethyl (1-methyl-1*H*-indol-2-yl) propane-dioate (5)

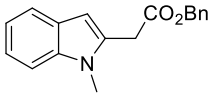


5

Isolated yield (main product) /%	Content of isomers /%
53 **C2**	77 / 11 /5 / 4 / 3

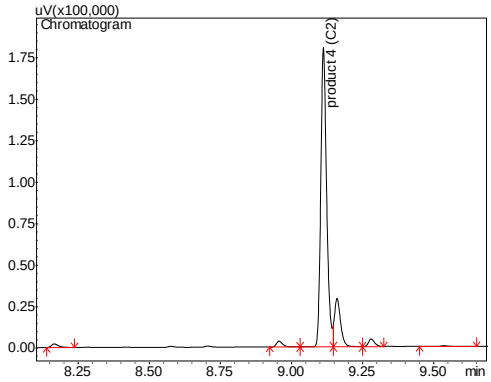


Benzyl (1-methyl-1*H*-indol-2-yl)acetate (4)

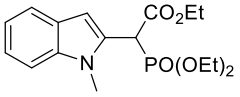


4

Isolated yield (main product) /%	Content of isomers /%
53 **C2**	81 / 14 / 2 / 2 / 1

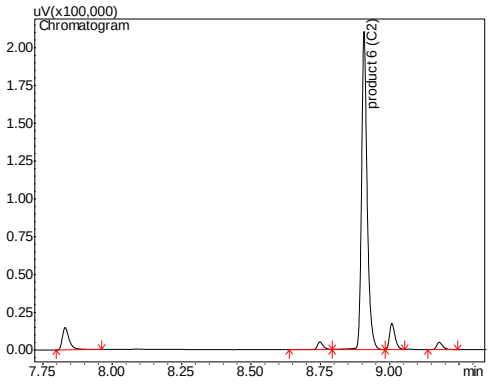


Ethyl (diethylphosphono)(1-methyl-1*H*-indol-2-yl)acetate (6)

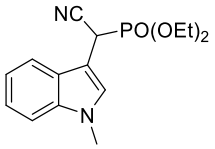


6

Isolated yield (main product) /%	Content of isomers /%
81 **C2**	82 / 7 / 7 / 2 / 2

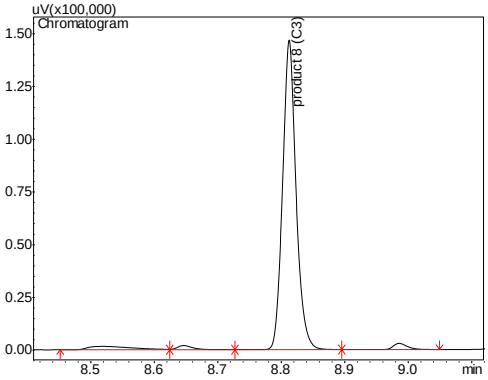


Diethyl (cyano(1-methyl-1*H*-indol-3-yl) methyl) phosphonate (8)

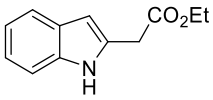


8

Isolated yield (main product) /%	Content of isomers /%
82 **C3**	93 / 3 / 2 / 1

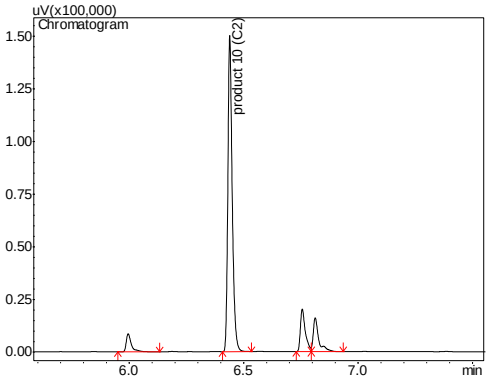


Ethyl 1*H*-indol-2-ylacetate (10)

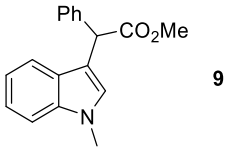


10

Isolated yield (main product) /%	Content of isomers /%
53 **C2**	74 / 11 / 10 / 5

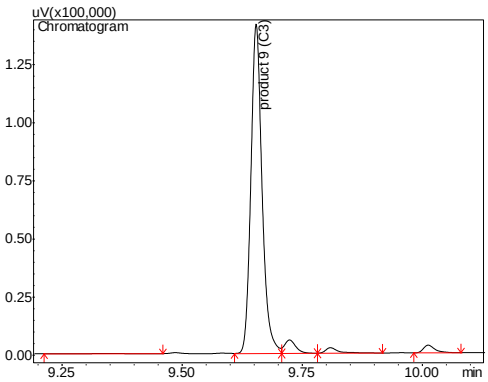


Methyl (1-methyl-1*H*-indol-3-yl)(phenyl)acetate (9)

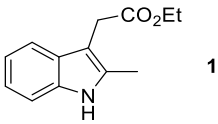


9

Isolated yield (main product) /%	Content of isomers /%
44 **C3**	92 / 4 / 2 / 2 / 1

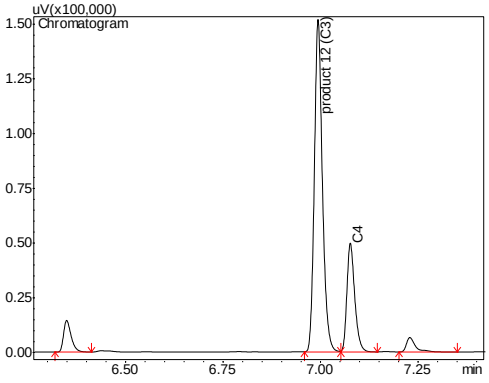


Ethyl (2-methyl-1*H*-indol-3-yl)acetate (12)

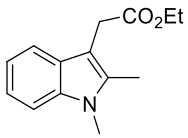


12

Isolated yield (main product) /%	Content of isomers /%
40 **C3**	69 / 22 / 6 / 3

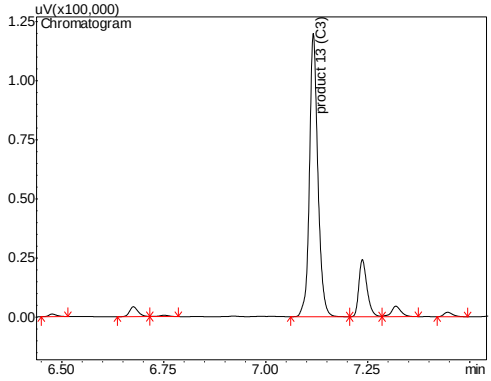


Ethyl (1,2-dimethyl-1*H*-indol-3-yl)acetate (13)

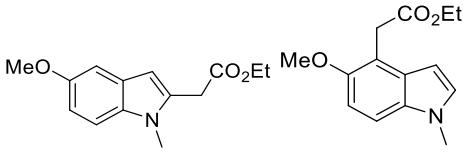


13

Isolated yield (main product) /%	Content of isomers /%
55 **C3**	76 / 15 / 3 / 3 / 2 / 1

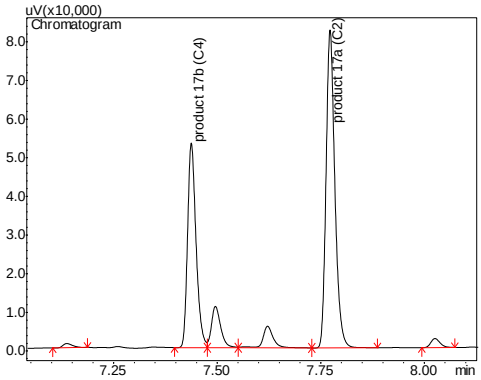


Ethyl (5-methoxy-1-methyl-1*H*-indol-2-yl) acetate (17a) and ethyl (5-methoxy-1-methyl-1*H*-indol-4-yl)acetate (17b)

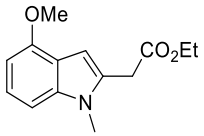


17a 17b

Isolated yield /%	Content of isomers /%
28 **C2**	53 / 33 / 7 / 4 / 2 / 1
20 **C4**	

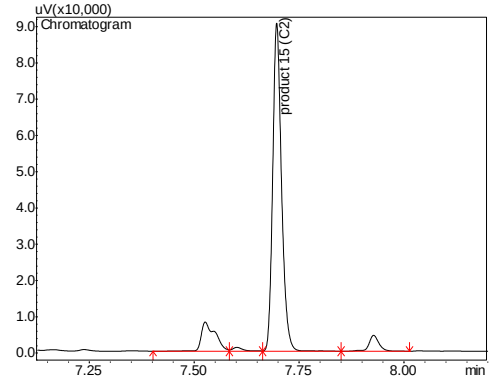


Ethyl (4-methoxy-1-methyl-1*H*-indol-2-yl) acetate (15)

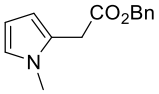


15

Isolated yield (main product) /%	Content of isomers /%
57 **C2**	83 / 12 / 5 / 1

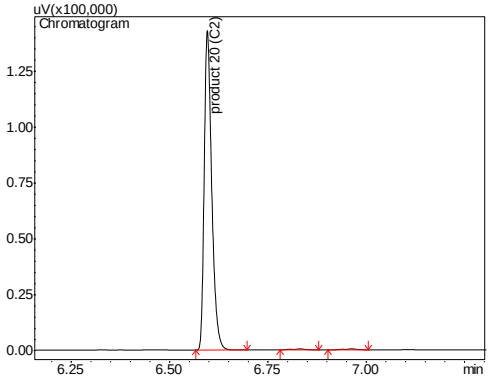


Benzyl (1-methyl-1*H*-pyrrol-2-yl)acetate (20)

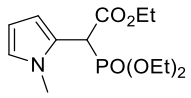


20

Isolated yield (main product) /%	Content of isomers /%
50 **C2**	99

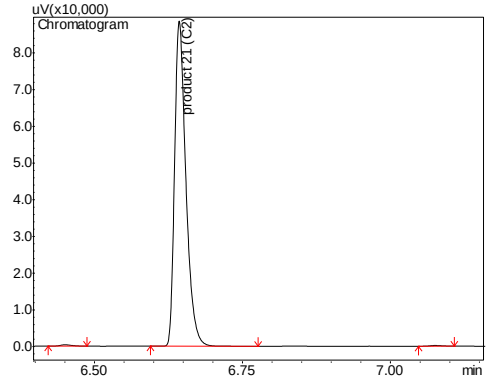


Ethyl (diethylphosphono)(1-methyl-1*H*-pyrrol-2-yl)acetate (21)

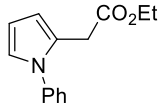


21

Isolated yield (main product) /%	Content of isomers /%
56 **C2**	99

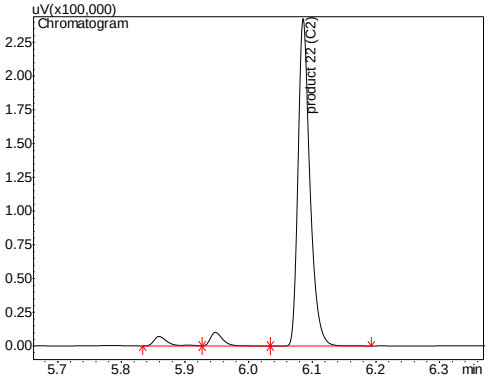


Ethyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (22)

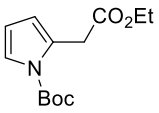


22

Isolated yield (main product) /%	Content of isomers /%
80 **C2**	93 / 4 / 3

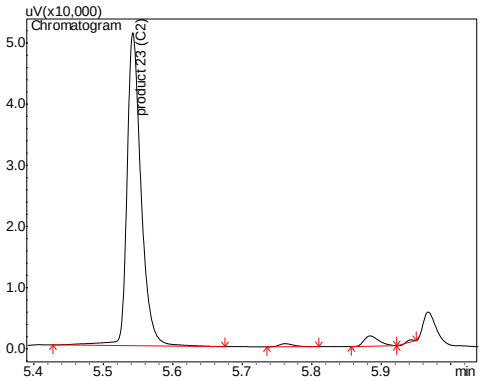


***tert*-Butyl 2-(2-ethoxy-2-oxoethyl)-1*H*-pyrrole-1-carboxylate (23)**

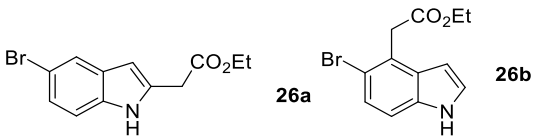


23

Isolated yield (main product) /%	Content of isomers /%
72 **C2**	96 / 3 / 1

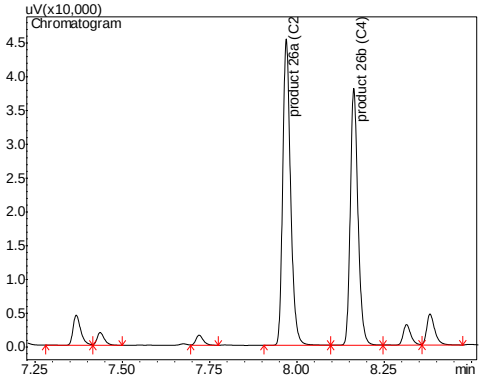


Ethyl (5-bromo-1*H*-indol-2-yl)acetate (26a) and ethyl (5-bromo-1*H*-indol-4-yl)acetate (26b)

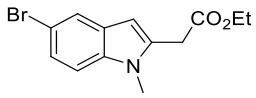


26a **26b**

Isolated yield (main product) /%	Content of isomers /%
38 **C2**	46 / 38 / 5 / 4 / 3 / 2 / 1
22 **C4**	

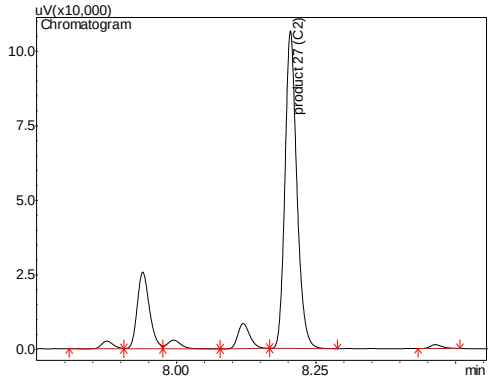


Ethyl (5-bromo-1-methyl-1*H*-indol-2-yl) acetate (27)

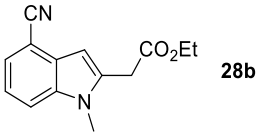


27

Isolated yield (main product) /%	Content of isomers /%
45 **C2**	72 / 18 / 6 / 2 / 2

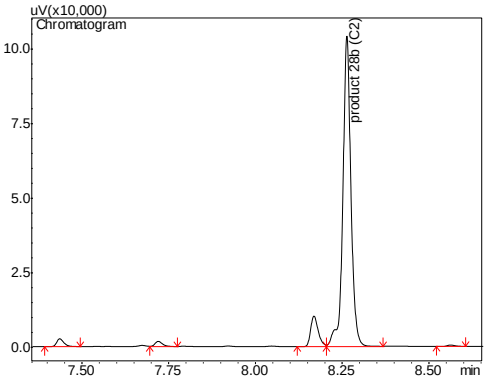


Ethyl (4-cyano-1-methyl-1*H*-indol-2-yl) acetate (28b)

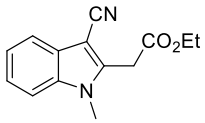


28b

Isolated yield (main product) /%	Content of isomers /%
77 **C2**	88 / 8 / 2 / 2

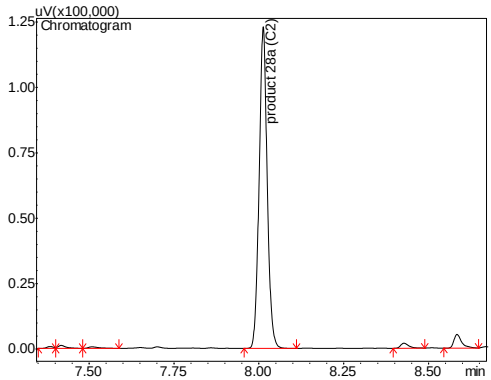


Ethyl (3-cyano-1-methyl-1*H*-indol-2-yl) acetate (28a)

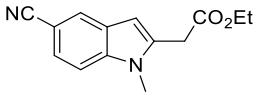


28a

Isolated yield (main product) /%	Content of isomers /%
50 **C2**	93 / 4 / 2

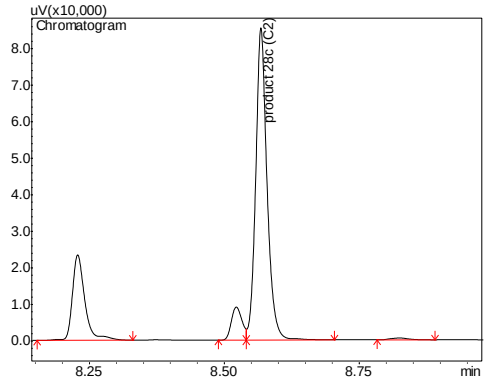


Ethyl (5-cyano-1-methyl-1*H*-indol-2-yl) acetate (28c)

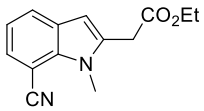


28c

Isolated yield (main product) /%	Content of isomers /%
56 **C2**	71 / 21 / 7 / 1

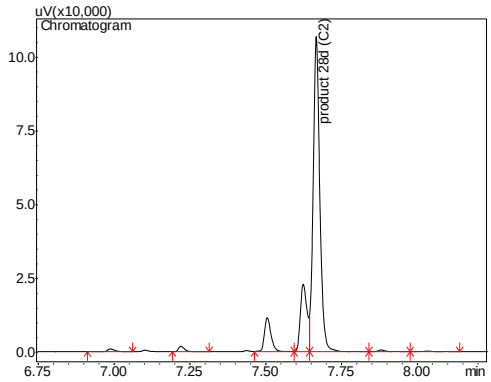


Ethyl (7-cyano-1-methyl-1*H*-indol-2-yl) acetate (28d)

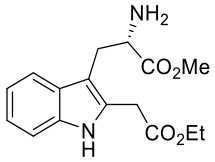


28d

Isolated yield (main product) /%	Content of isomers /%
60 **C2**	74 / 16 / 8 / 1

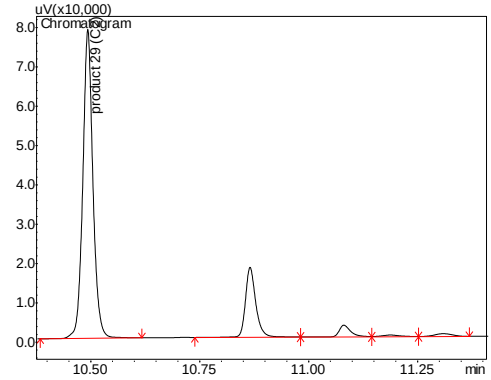


Methyl (2*S*)-2-amino-3-(2-(2-ethoxy-2-oxo ethyl)-1*H*-indol-3-yl)propanoate (29)

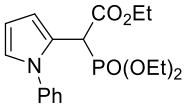


29

Isolated yield (main product) /%	Content of isomers /%
67 **C2**	77 / 18 / 3 / 1

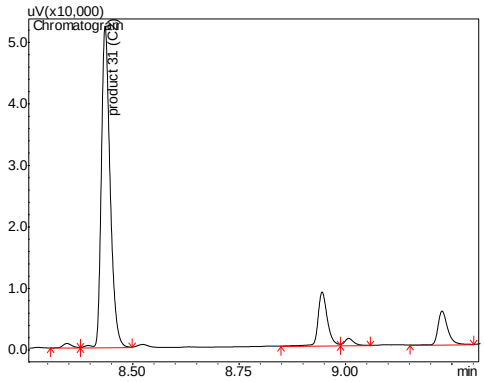


Ethyl (diethylphosphono)(1-phenyl-1*H*-pyrrol-2-yl)acetate (31)

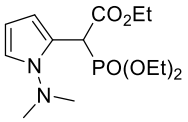


31

Isolated yield (main product) /%	Content of isomers /%
50 **C2**	75 / 14 / 9 / 2

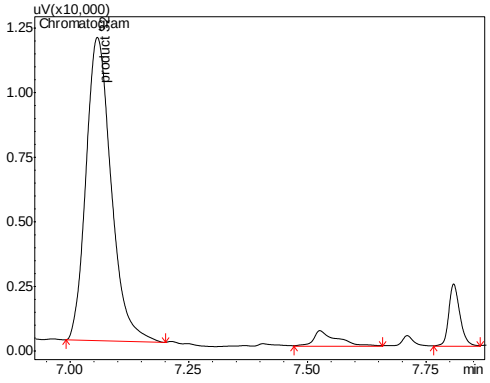


Ethyl (diethylphosphono)(1-(dimethyl amino)-1*H*-pyrrol-2-yl)acetate (32)



32

Isolated yield (main product) /%	Content of isomers /%
57 **C2**	88 / 8 / 4



7. References

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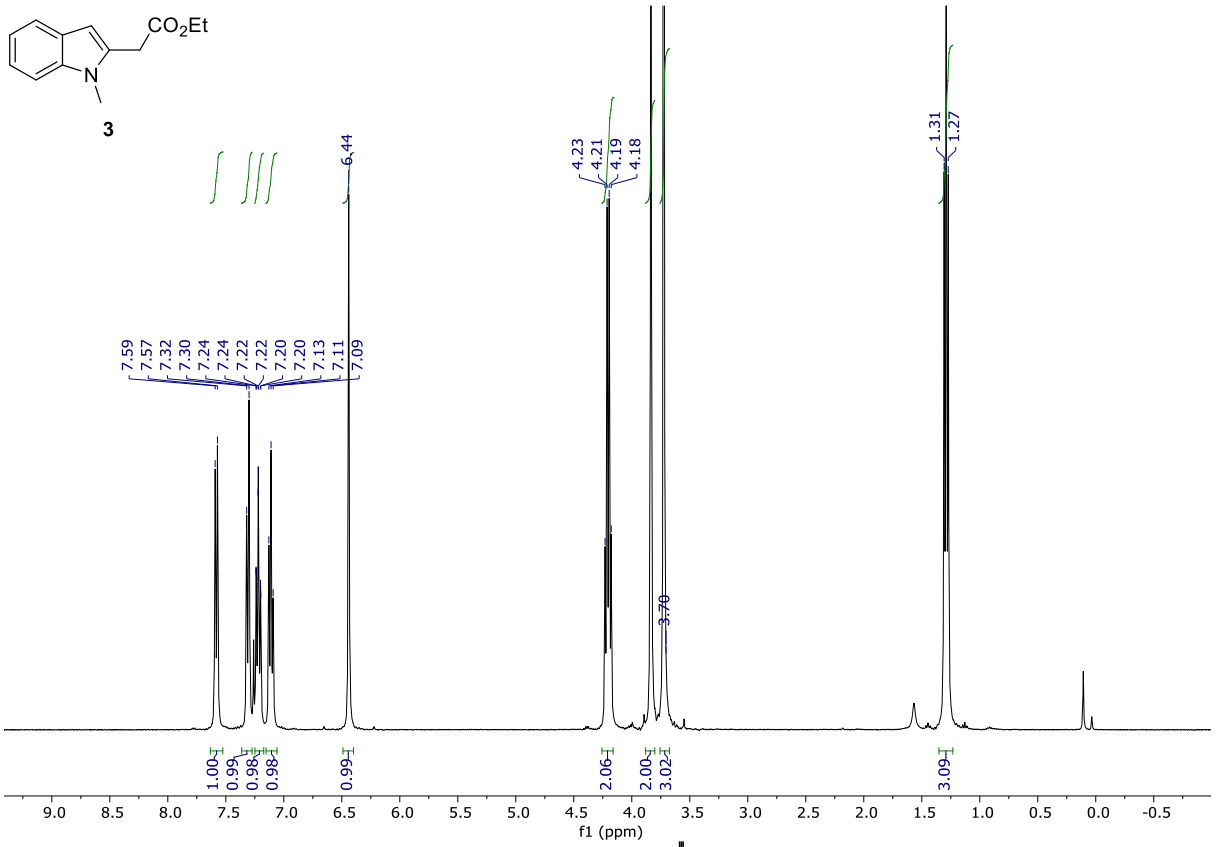
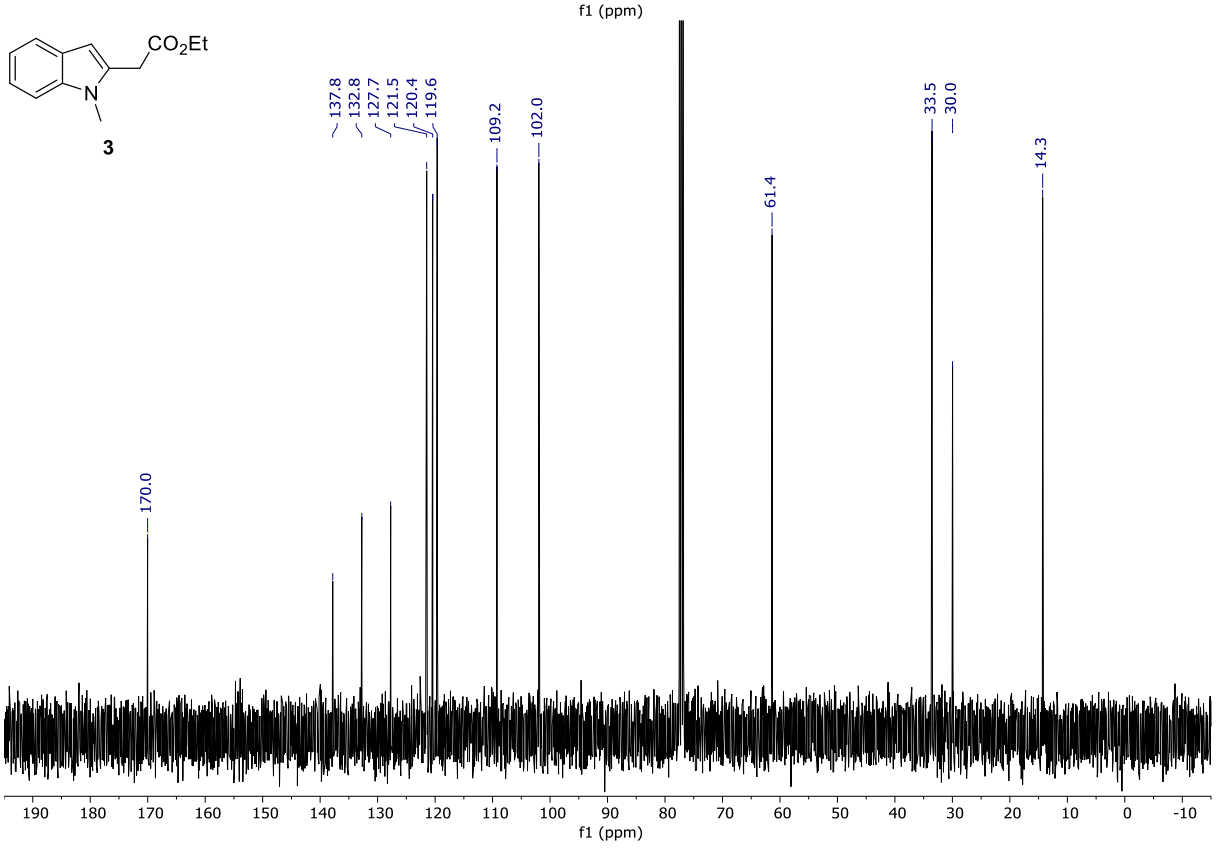
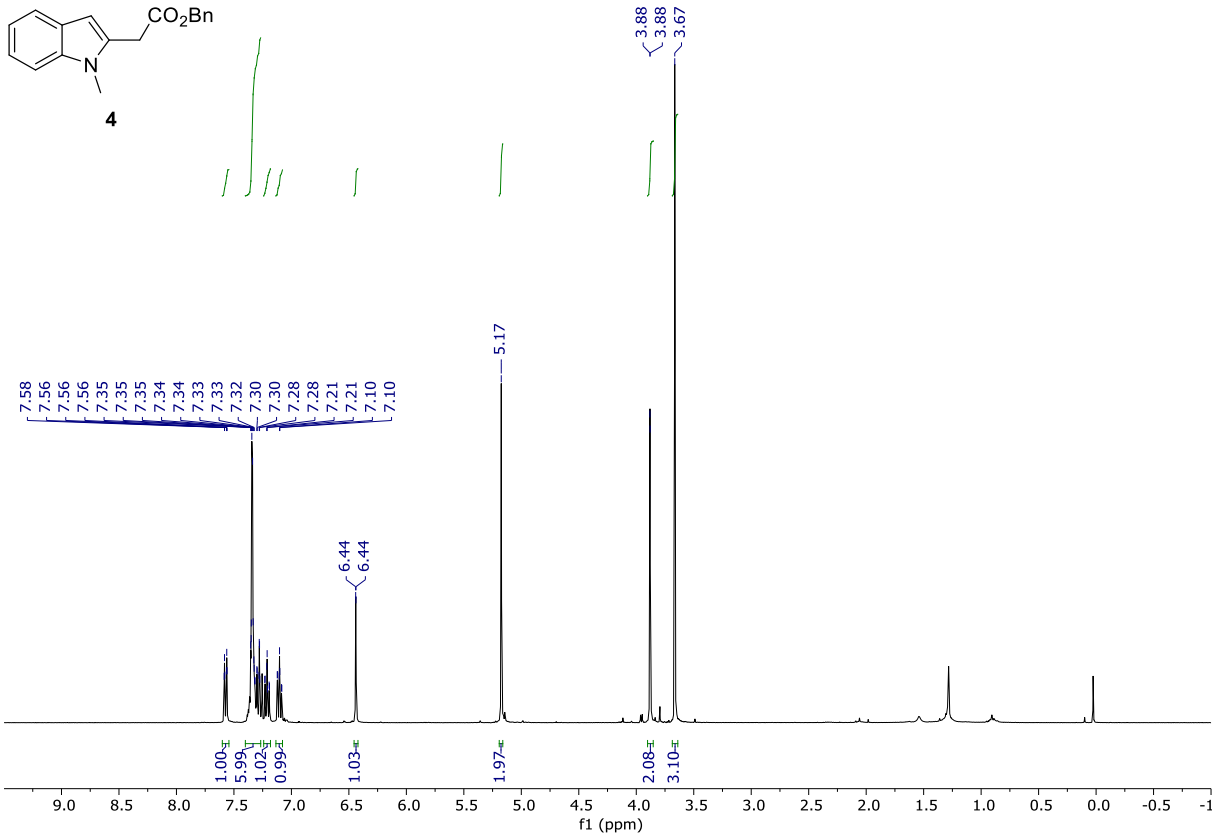
8. NMR spectra

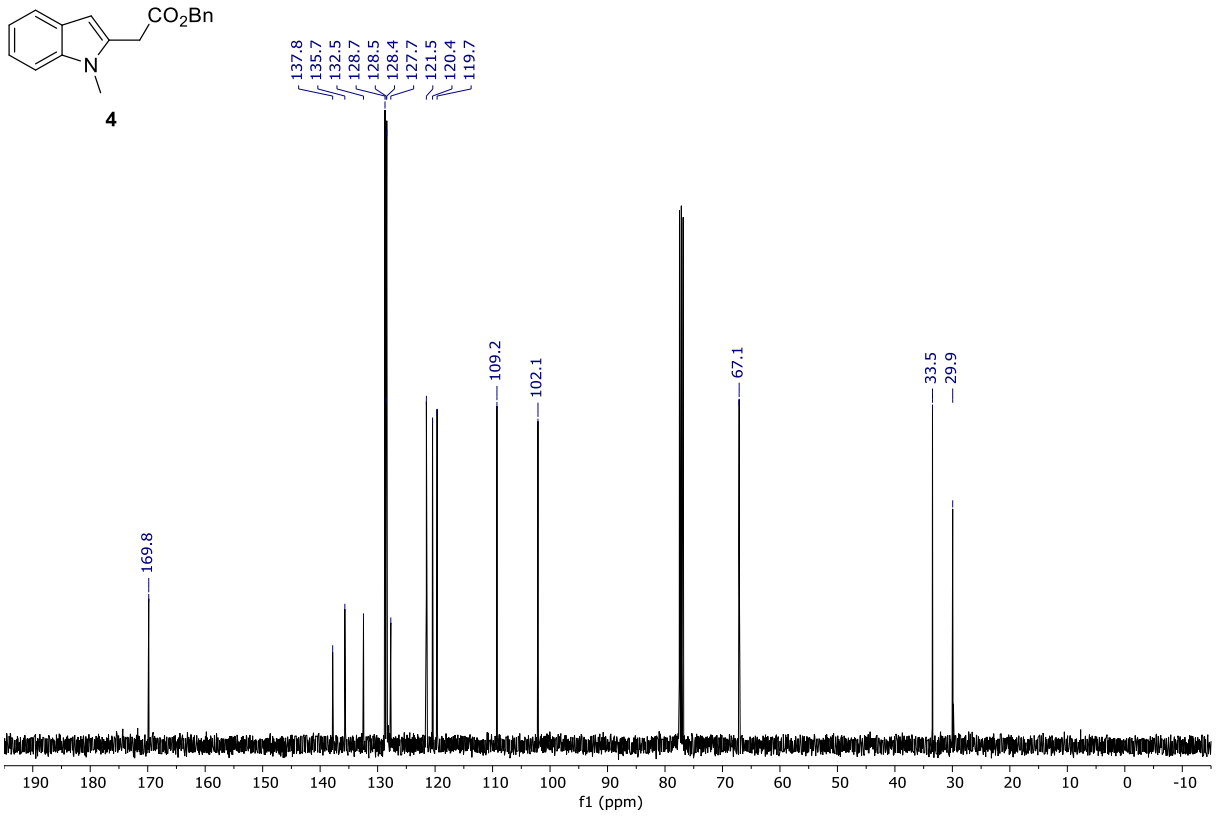
Ethyl (1-methyl-1*H*-indol-2-yl)acetate (**3**)



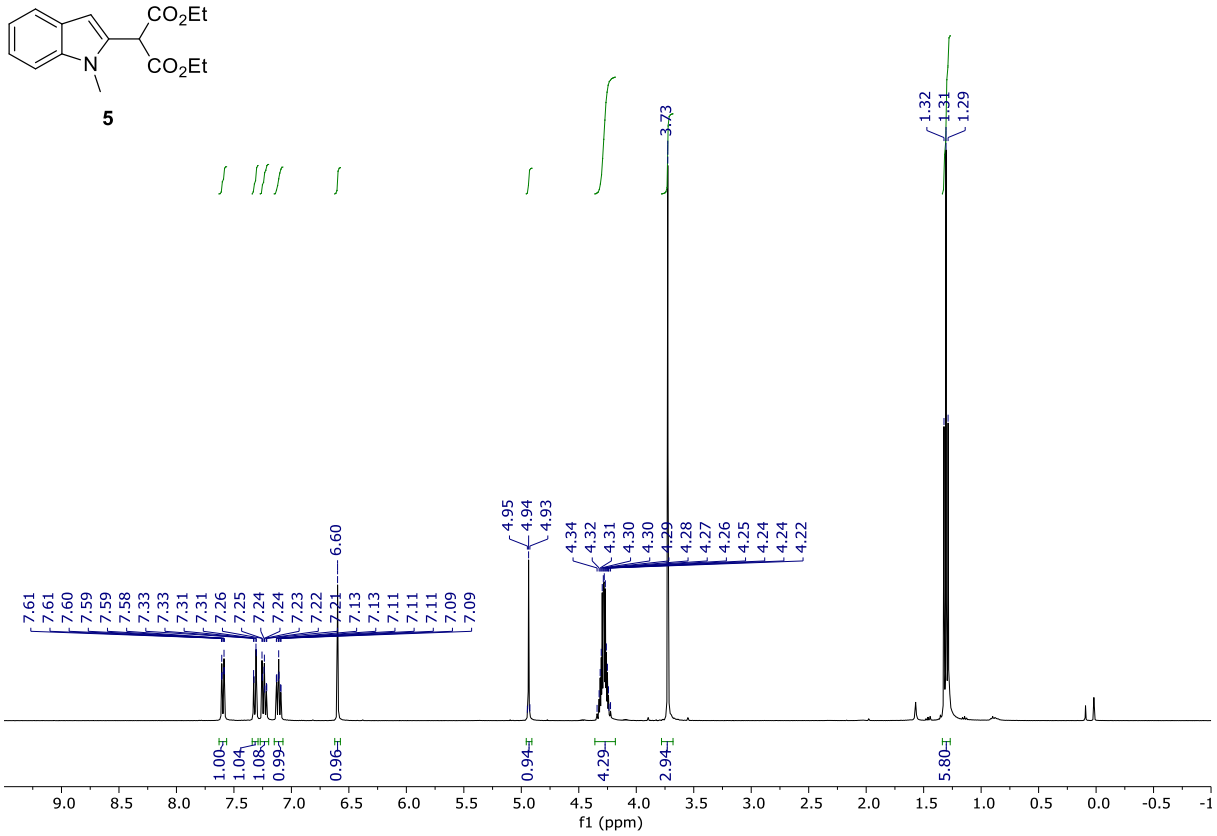


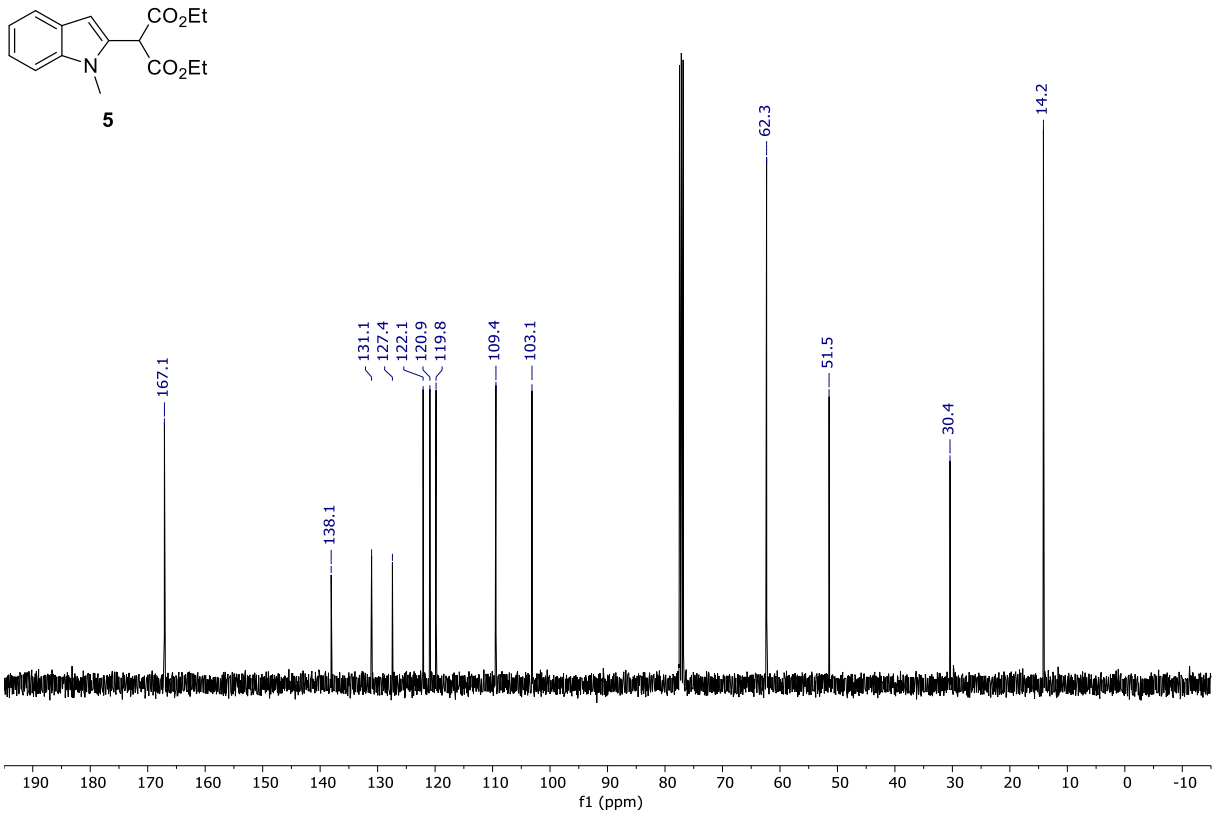
Benzyl (1-methyl-1*H*-indol-2-yl)acetate (**4**)



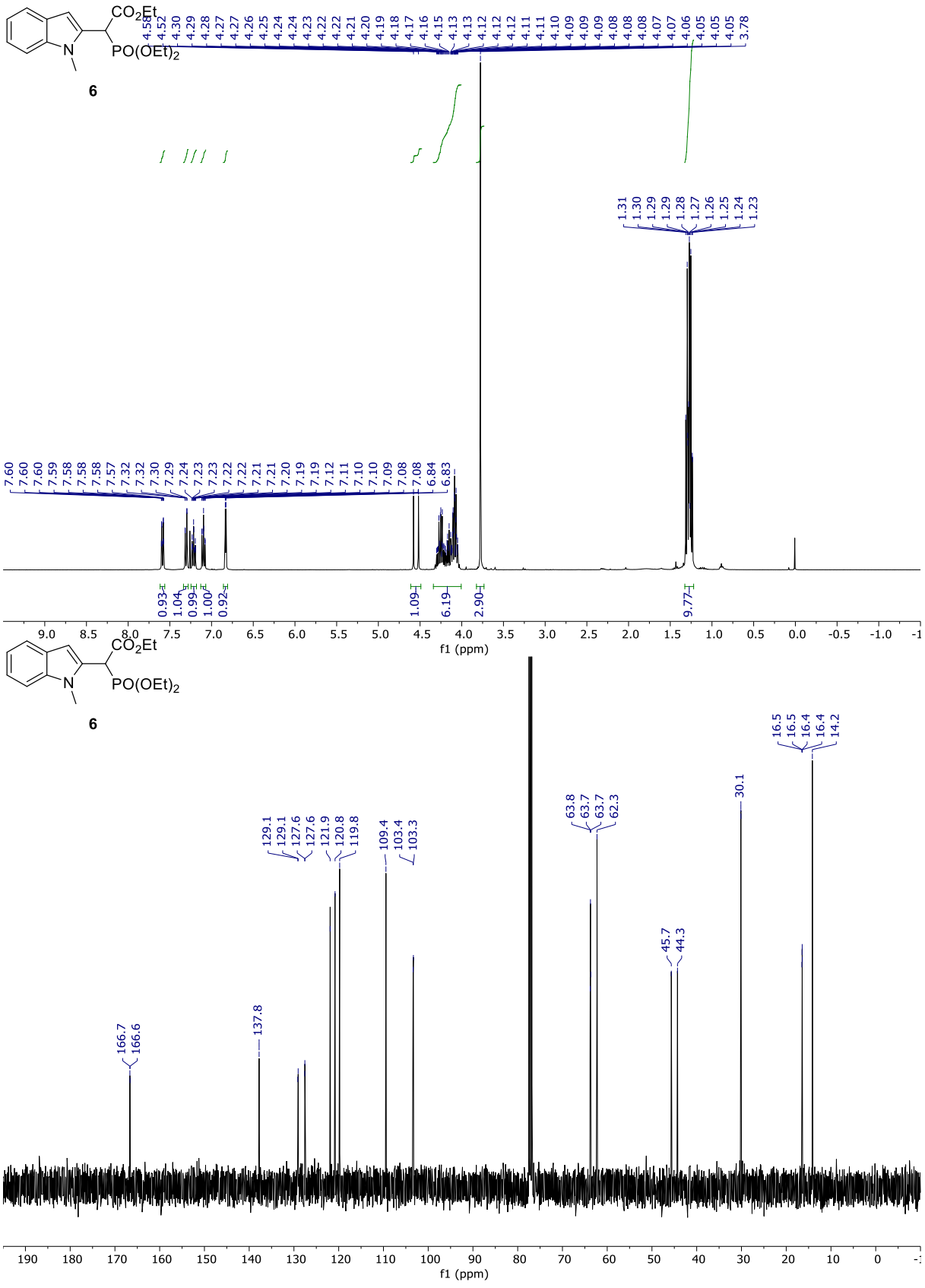


Diethyl (1-methyl-1*H*-indol-2-yl)propanedioate (**5**)

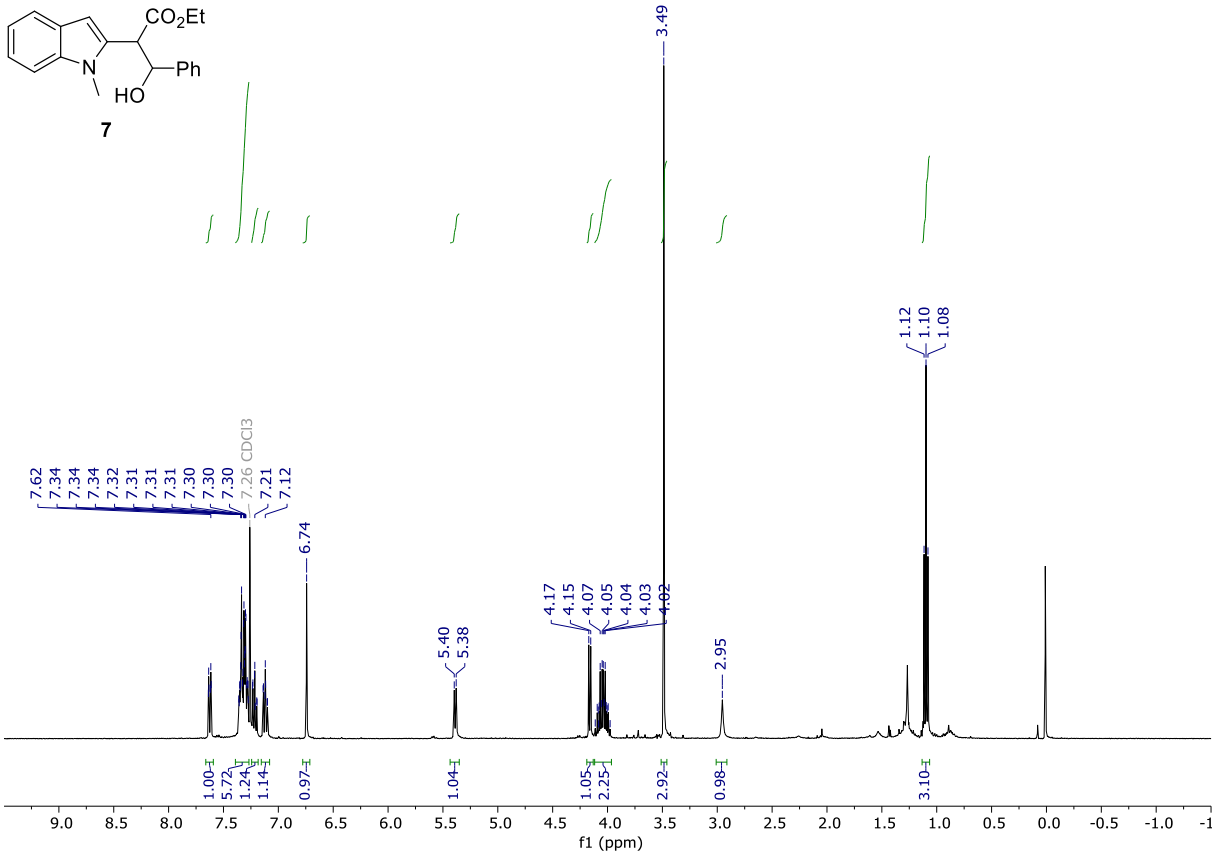


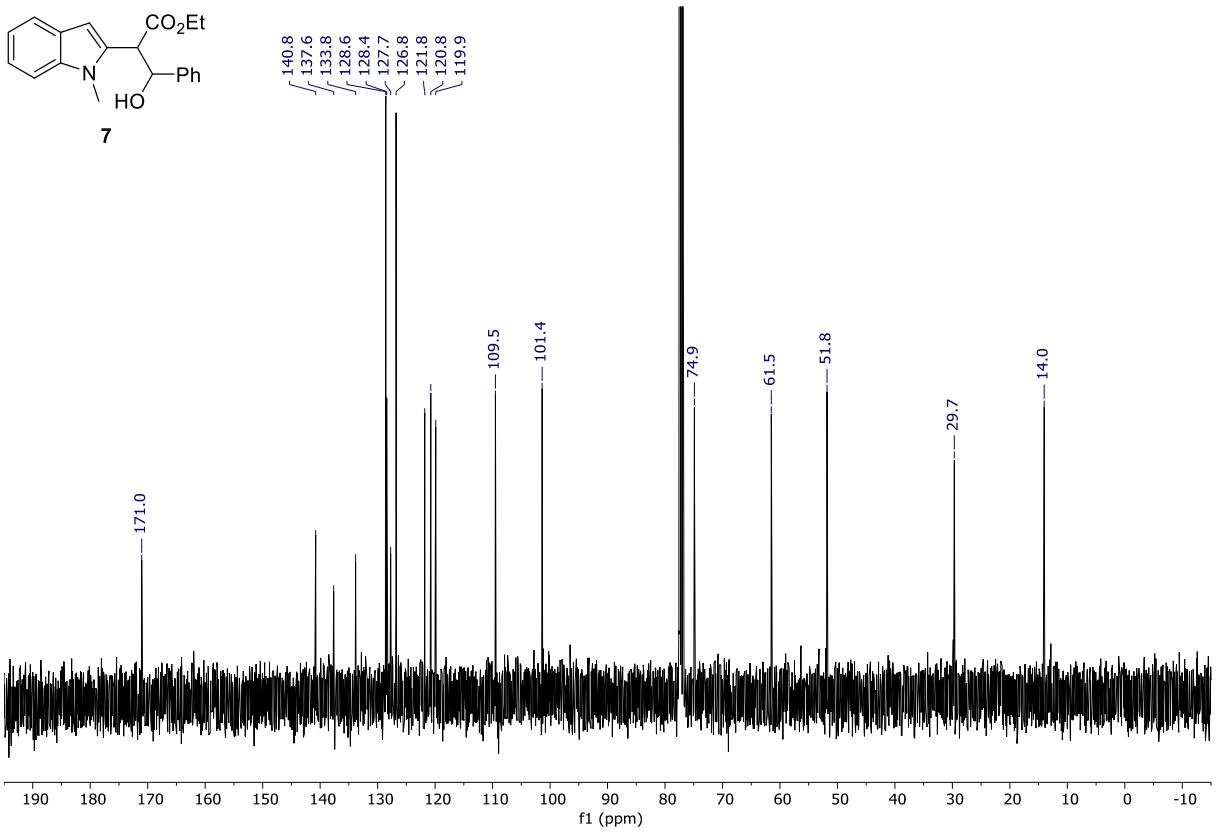


Ethyl (diethylphosphono)(1-methyl-1*H*-indol-2-yl)acetate (**6**)

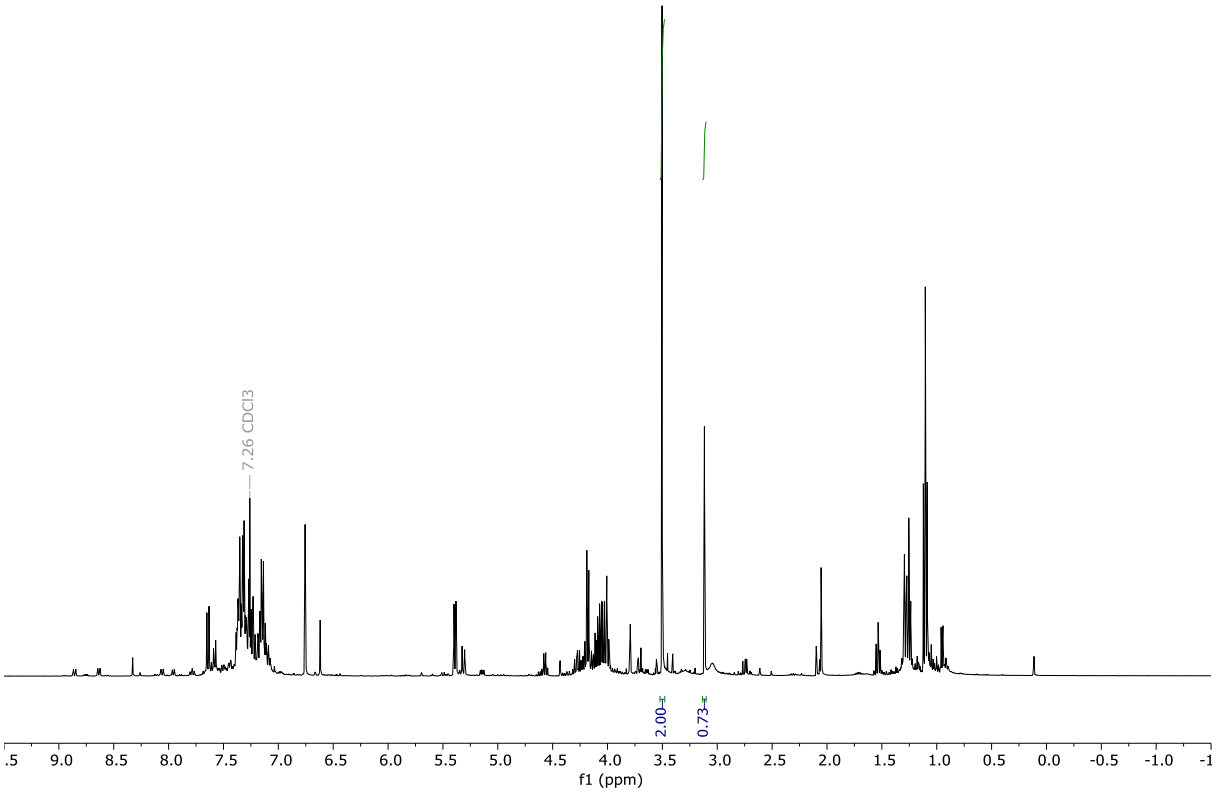


Ethyl 3-hydroxy-2-(1-methyl-1*H*-indol-2-yl)-3-phenylpropanoate (**7**)

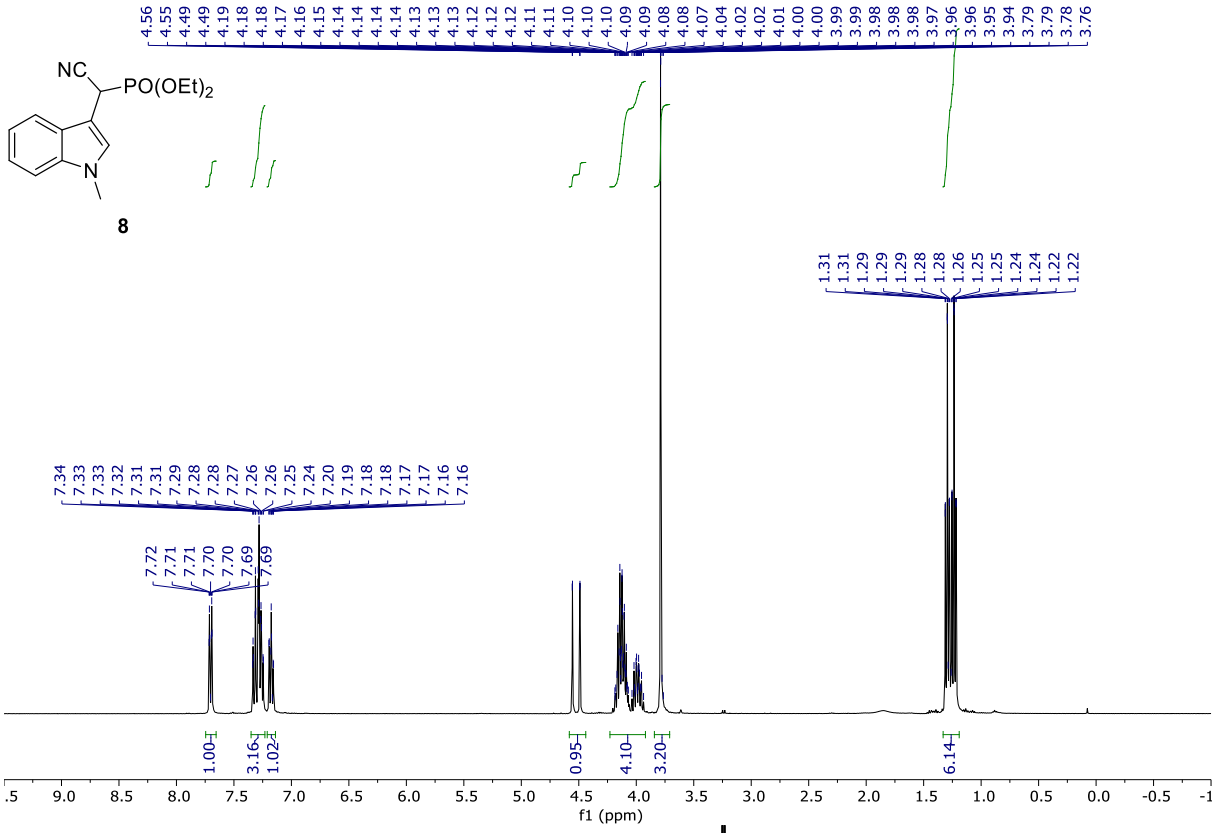


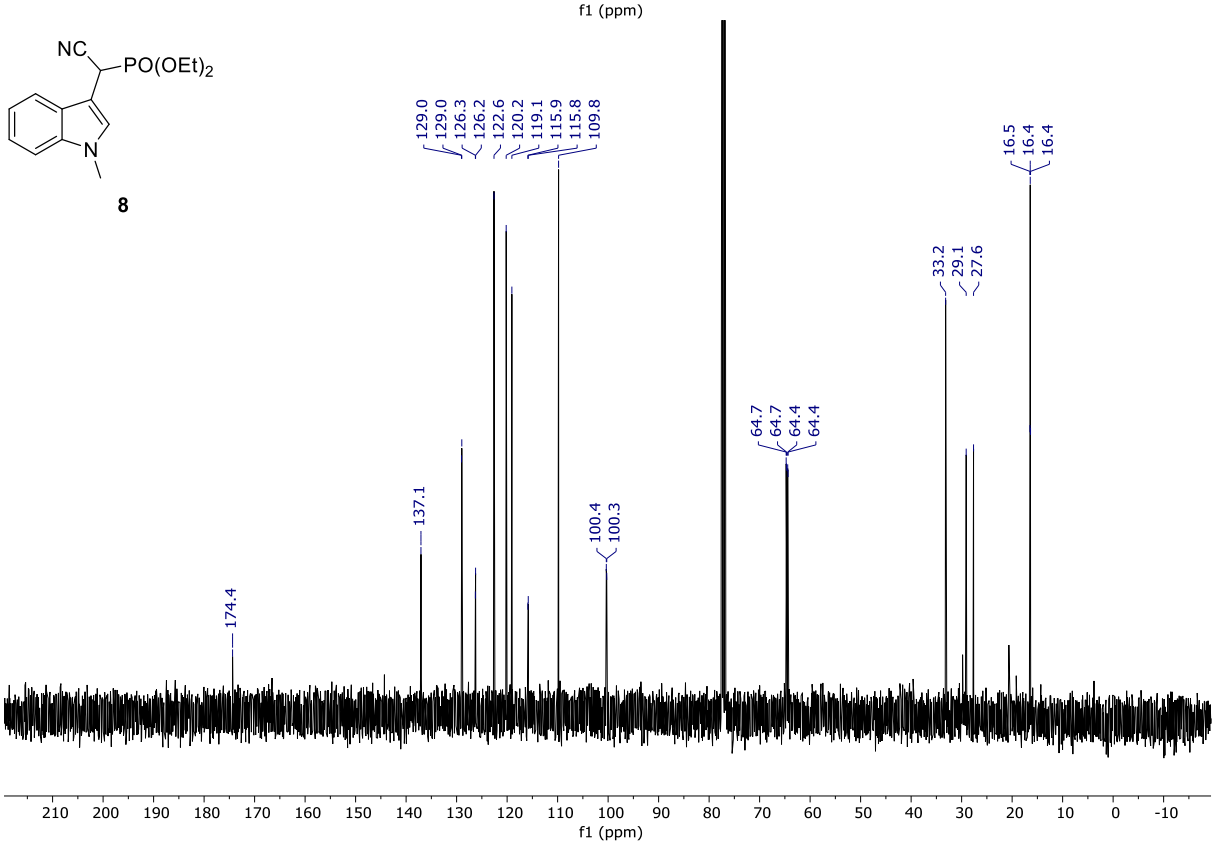


^{1}HNMR of crude reaction mixture (1-methylindole excess removed by column chromatography):

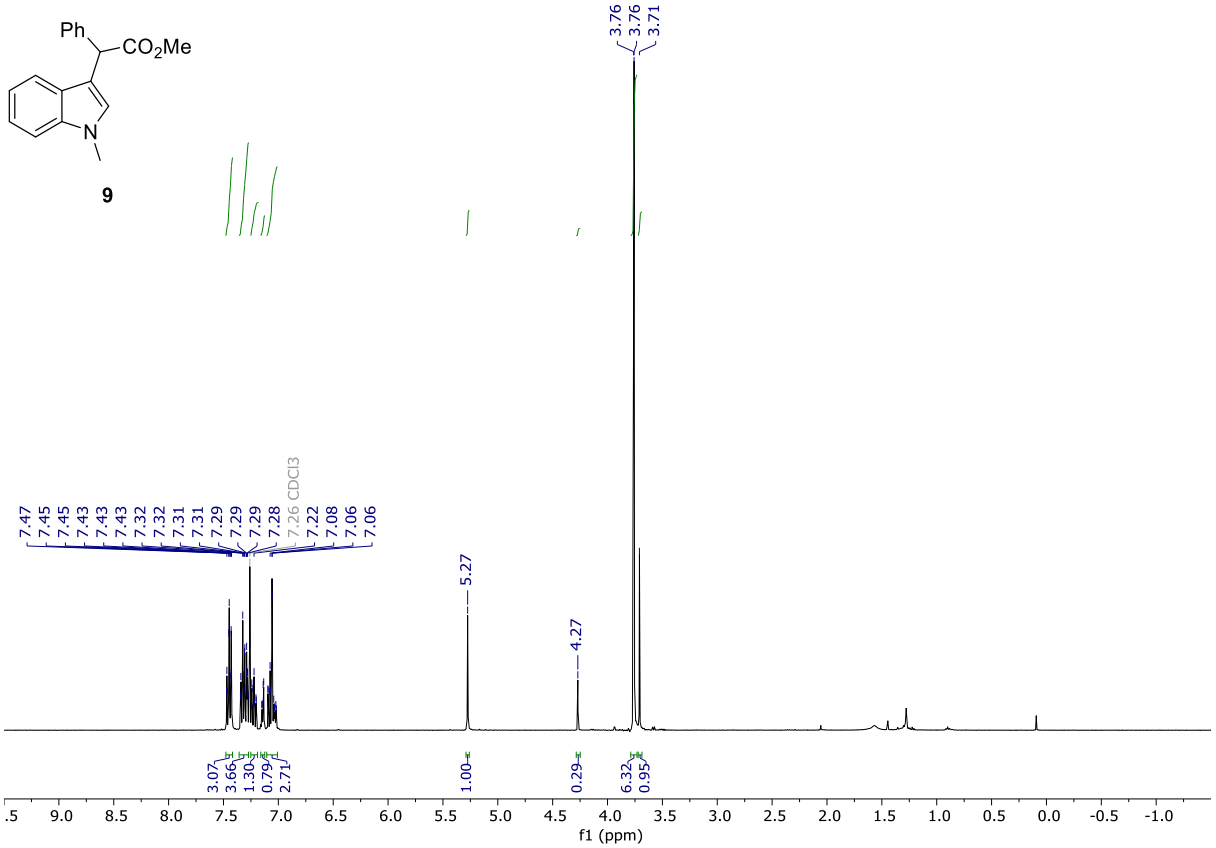


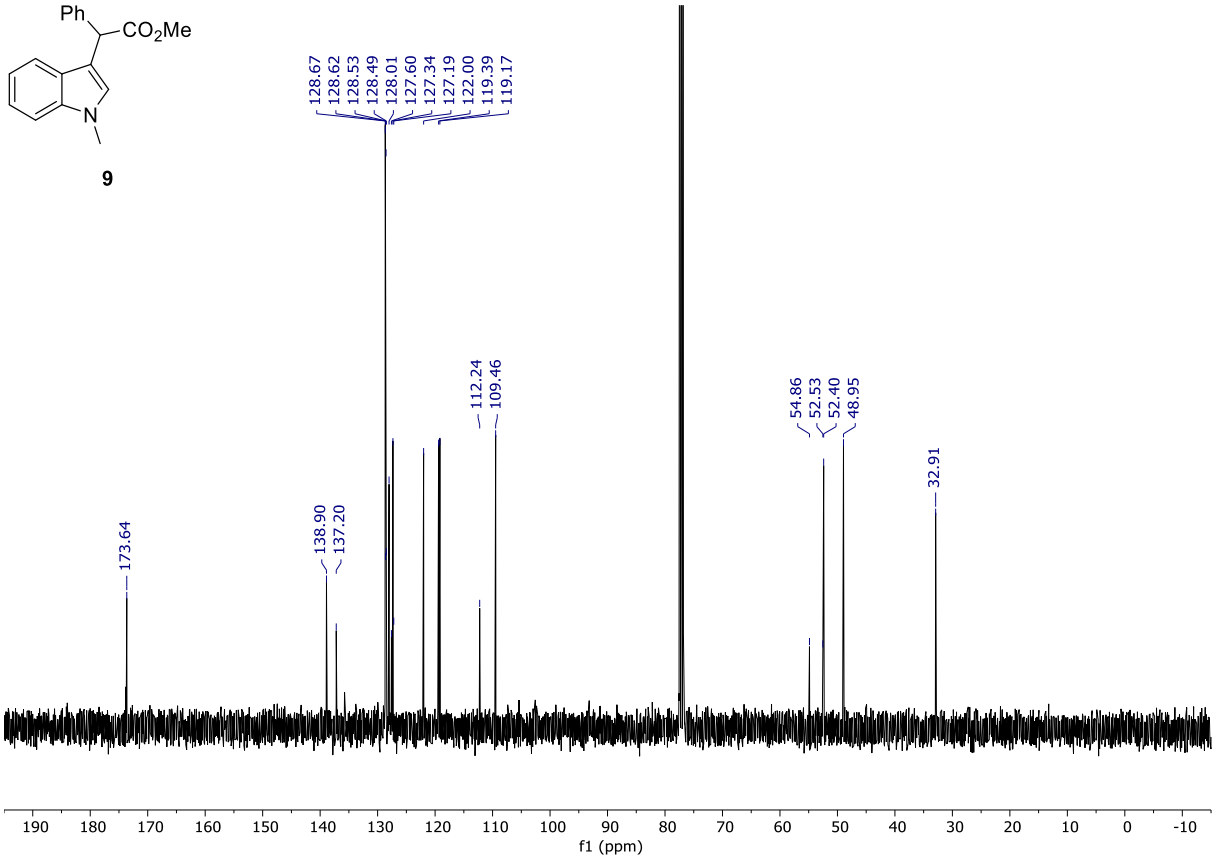
Diethyl (cyano(1-methyl-1*H*-indol-3-yl)methyl)phosphonate (**8**)



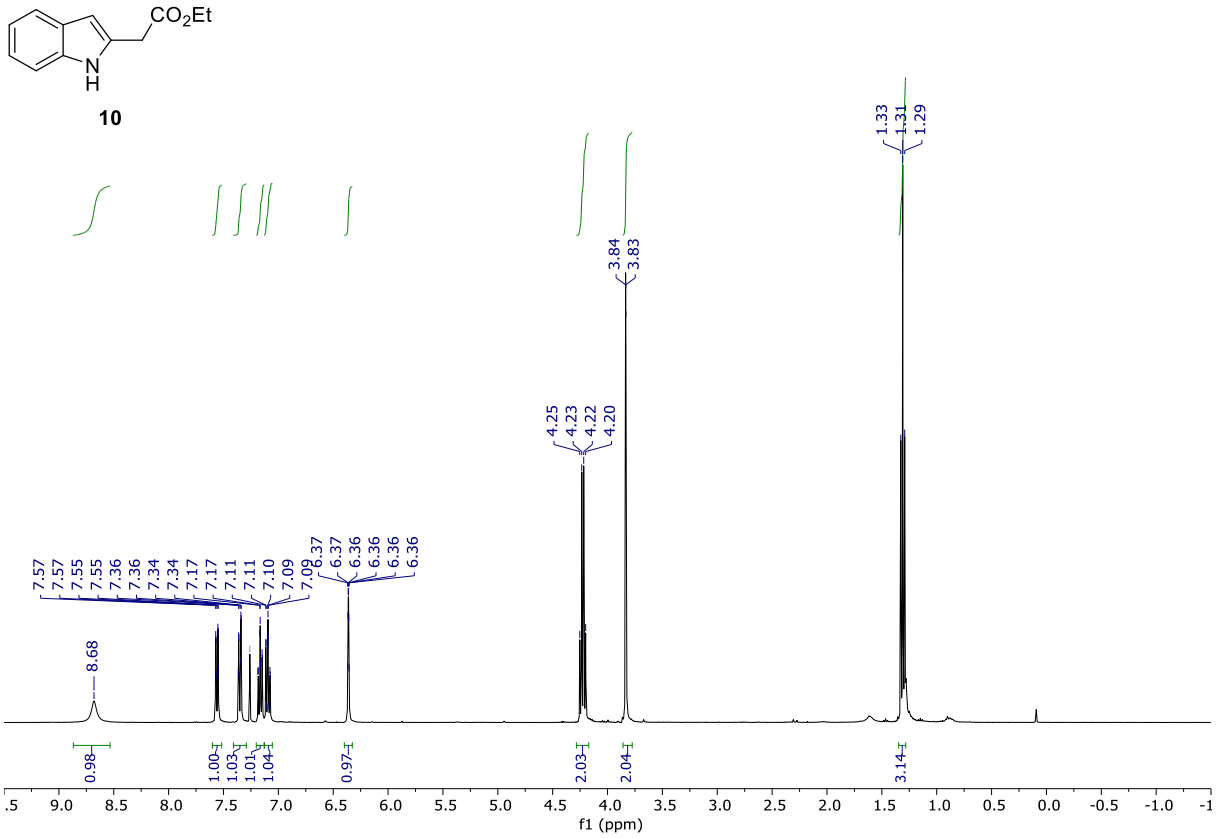


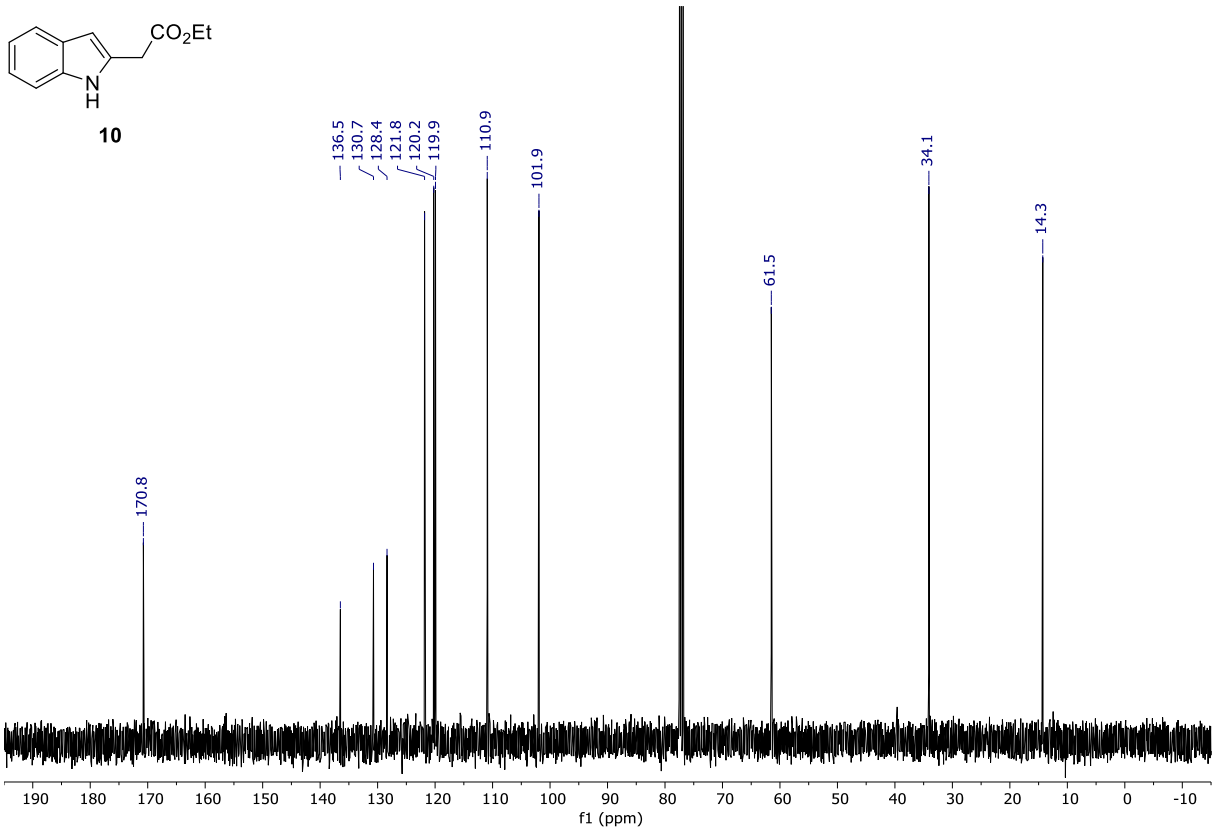
Methyl (1-methyl-1*H*-indol-3-yl)(phenyl)acetate (**9**)



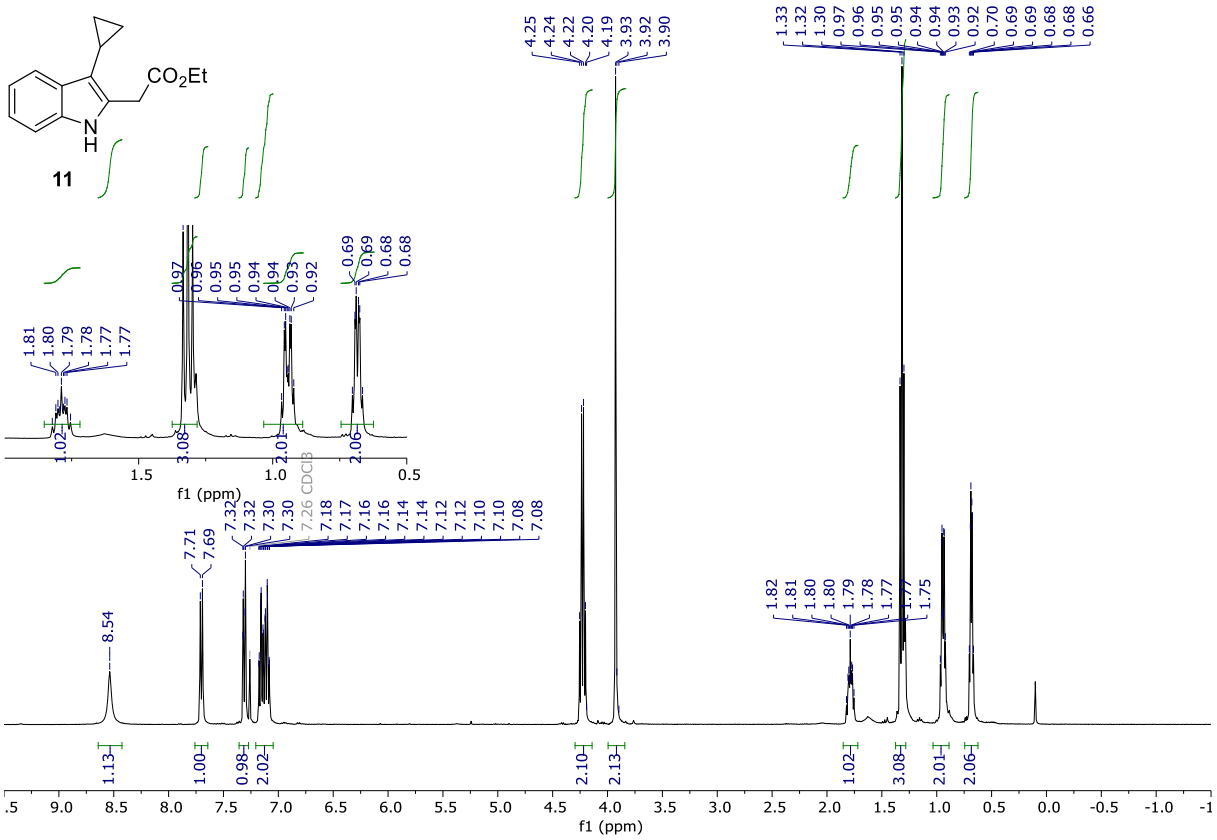


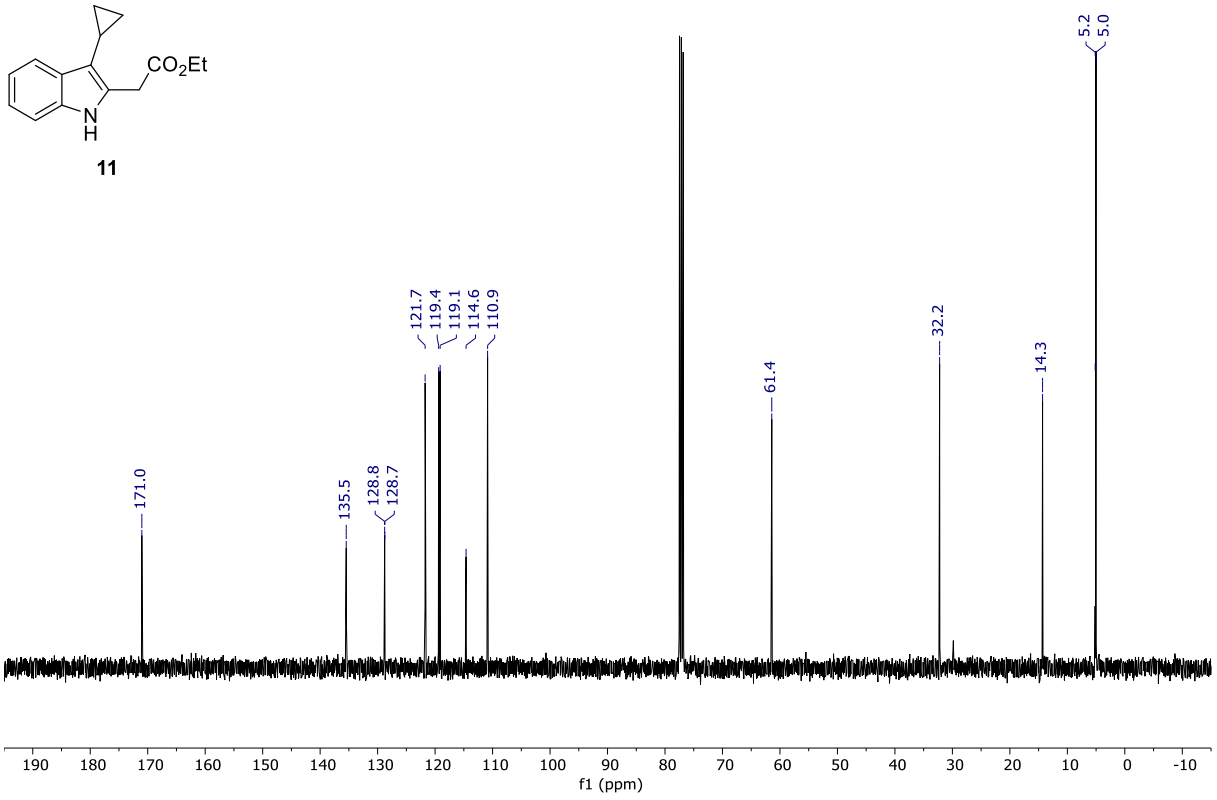
Ethyl 1*H*-indol-2-ylacetate (**10**)



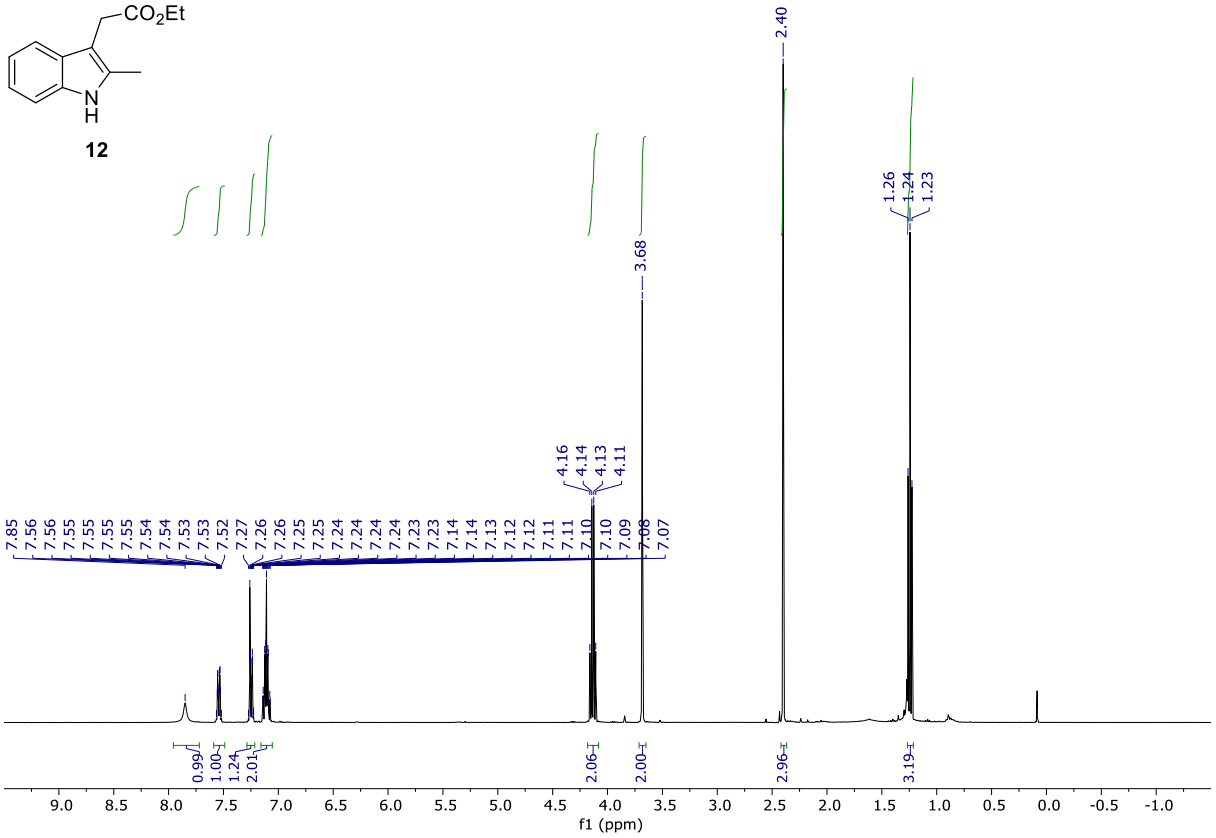


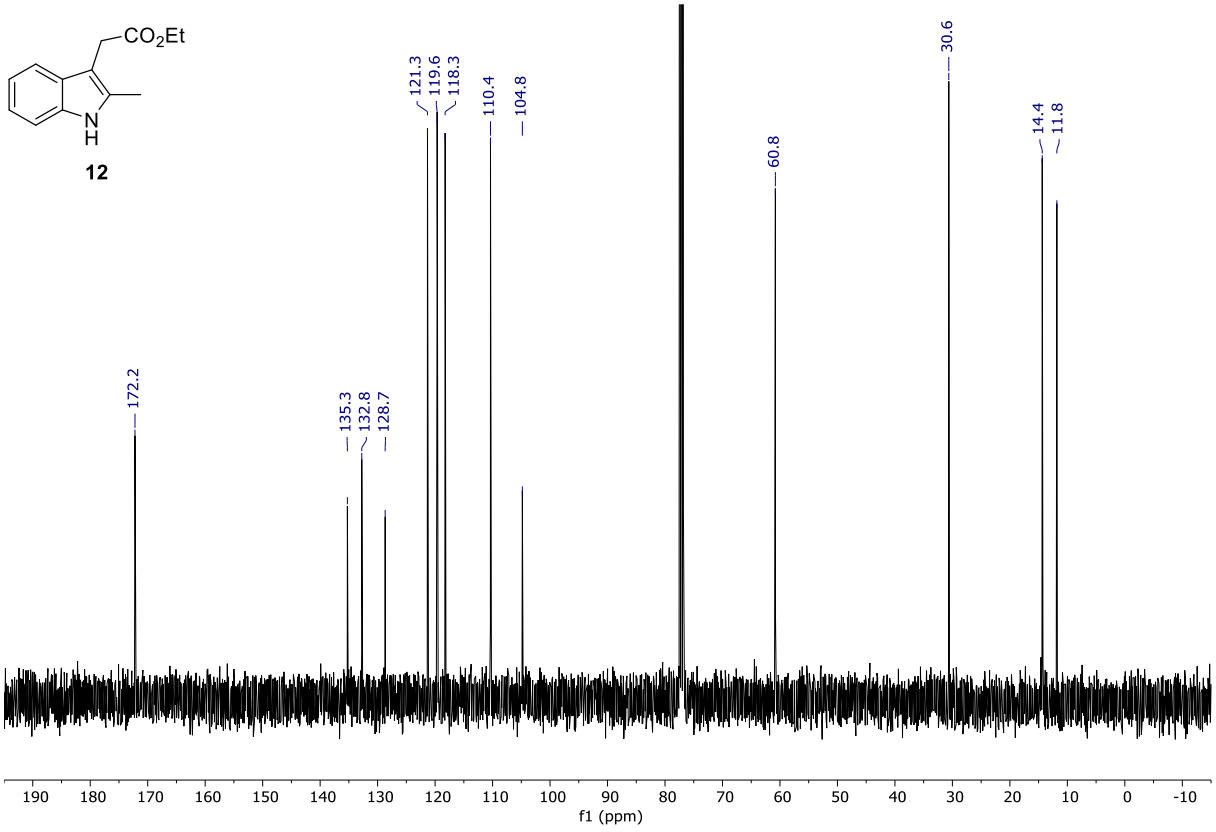
Ethyl (3-cyclopropyl-1*H*-indol-2-yl)acetate (**11**)



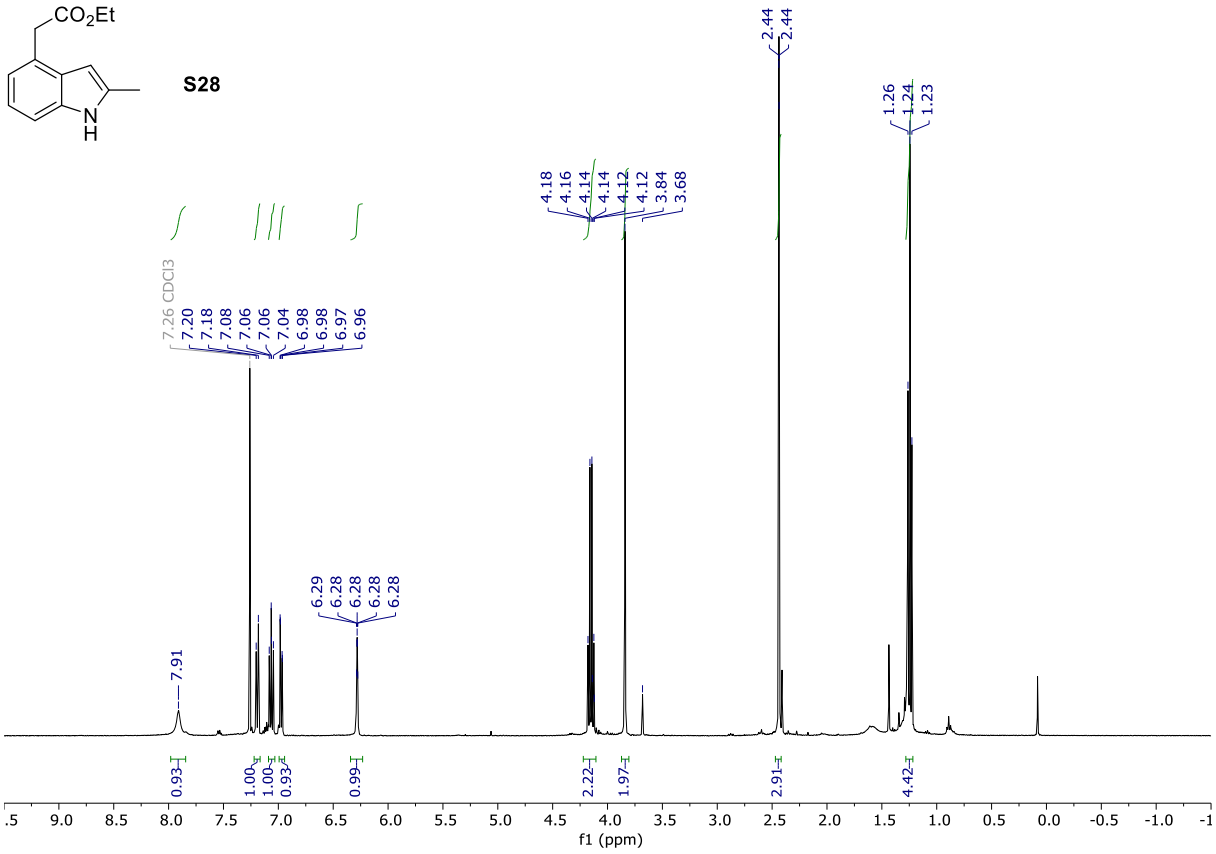


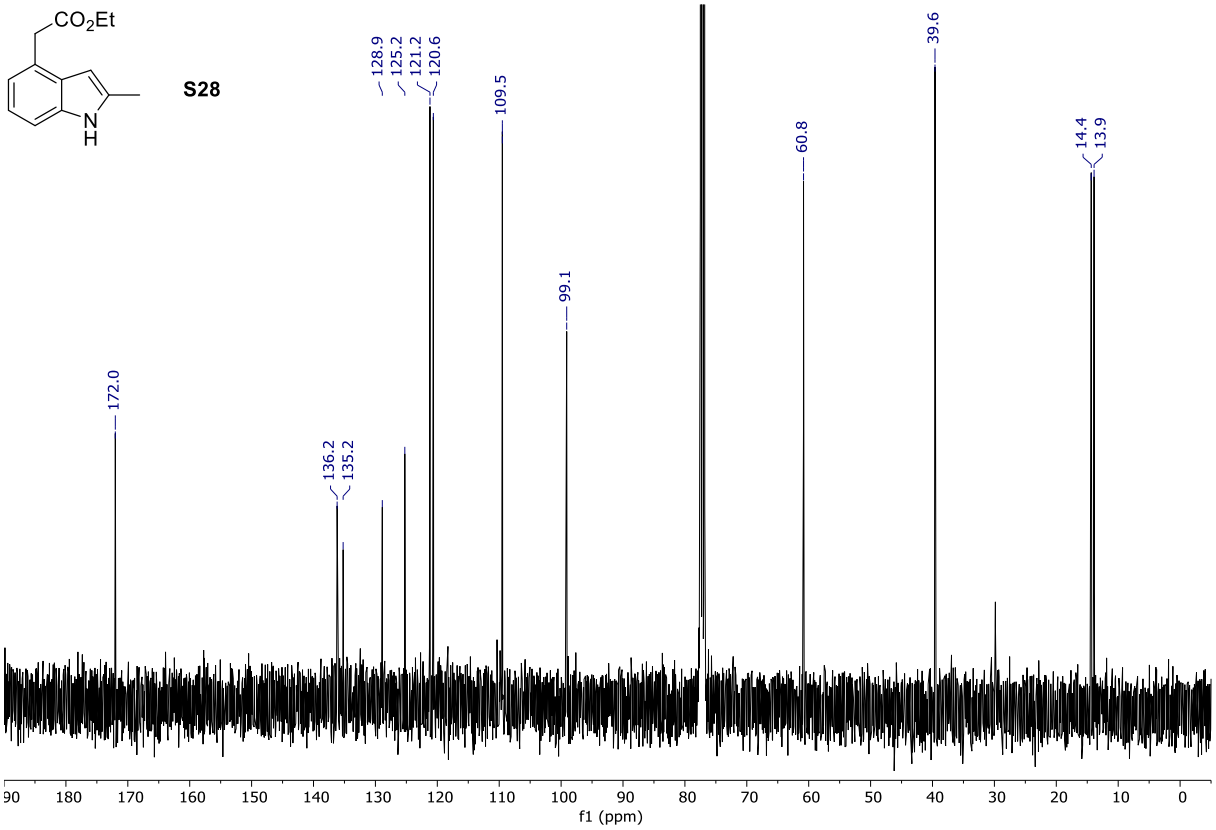
Ethyl (2-methyl-1*H*-indol-3-yl)acetate (**12**)

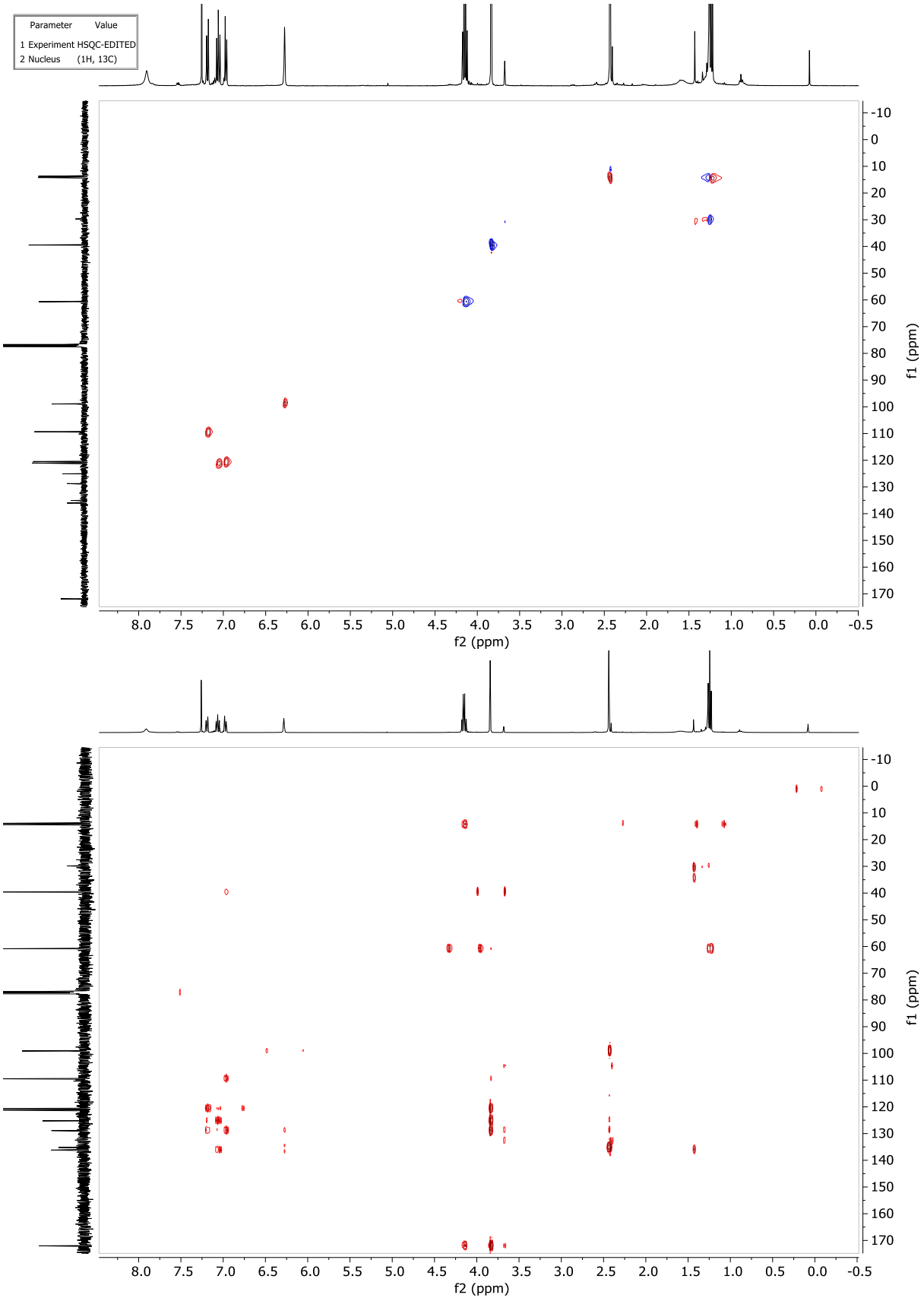




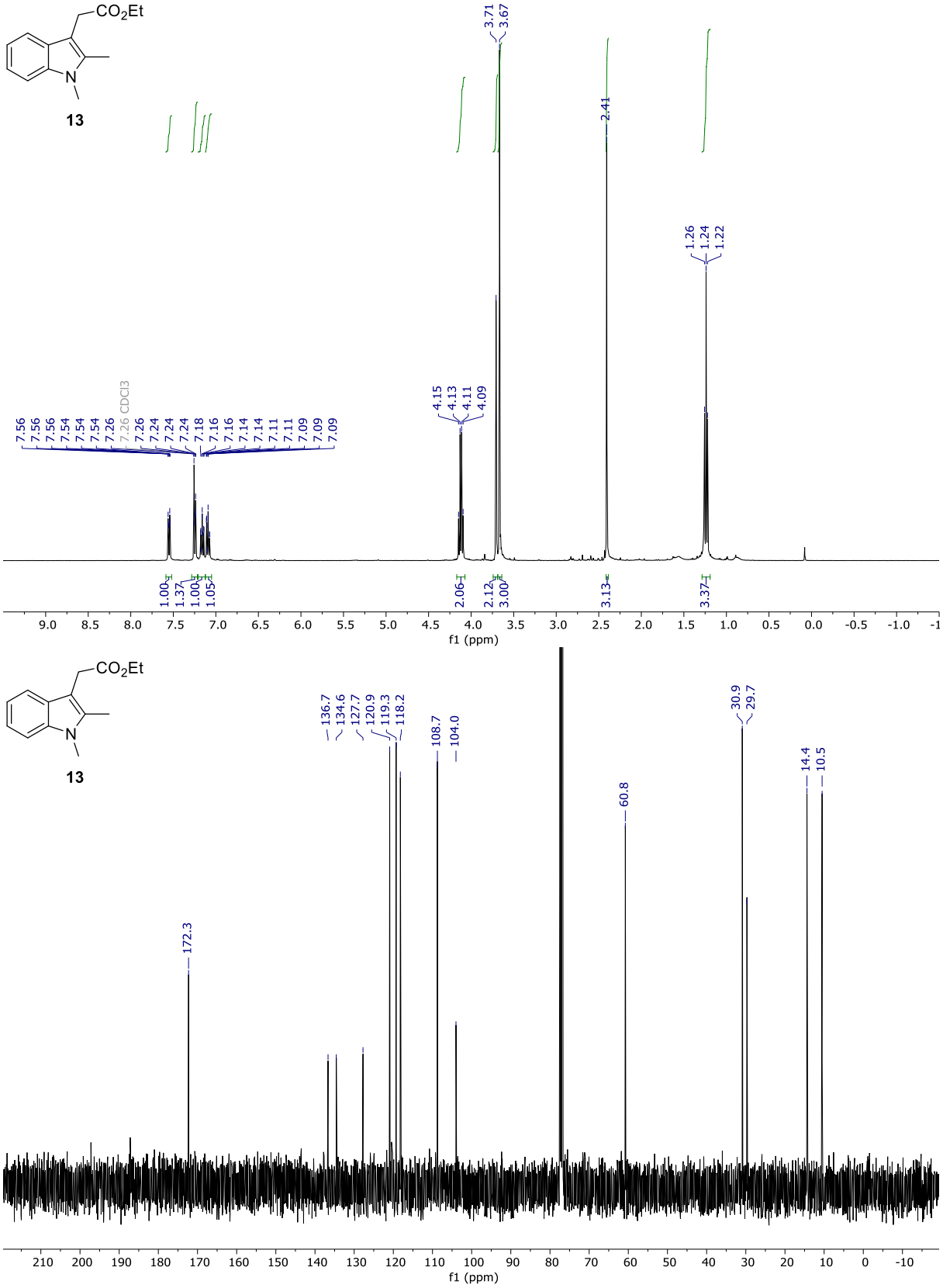
Ethyl (2-methyl-1*H*-indol-4-yl)acetate (**S28**)



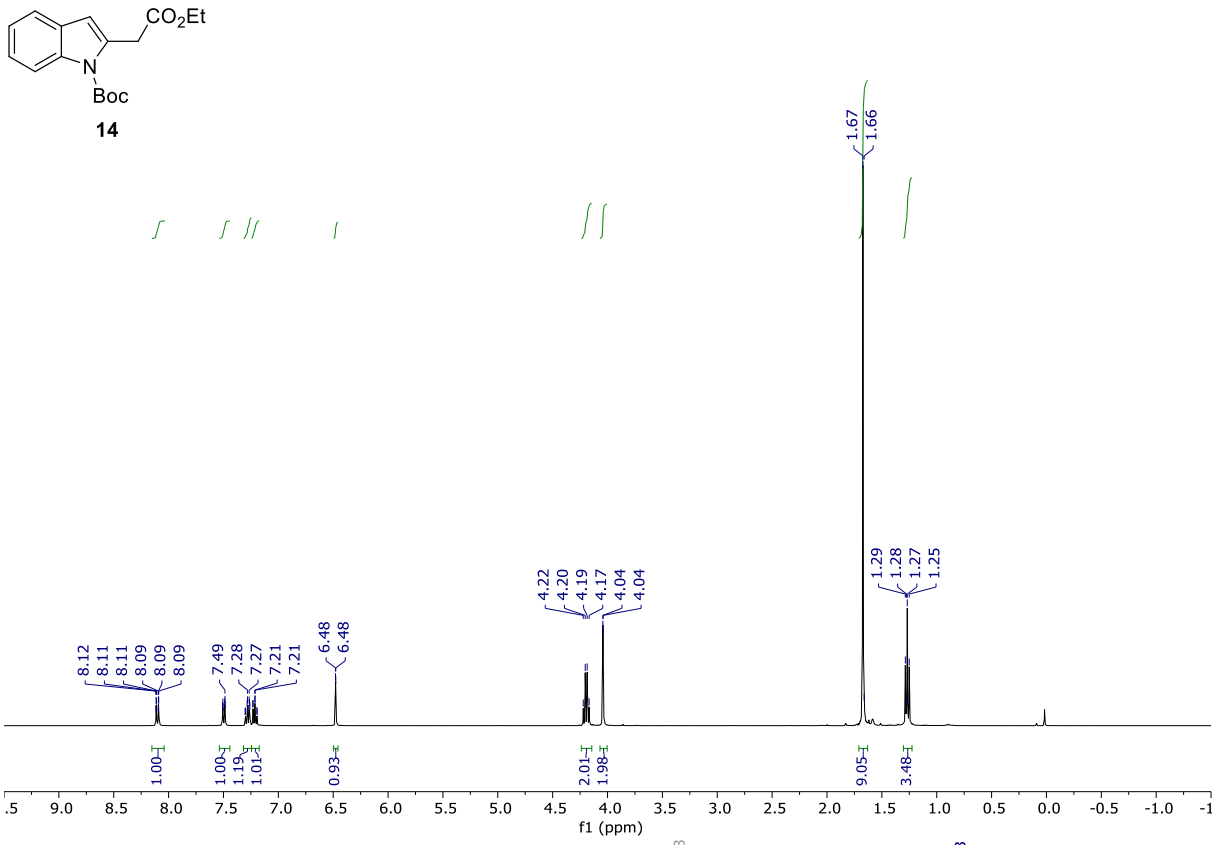


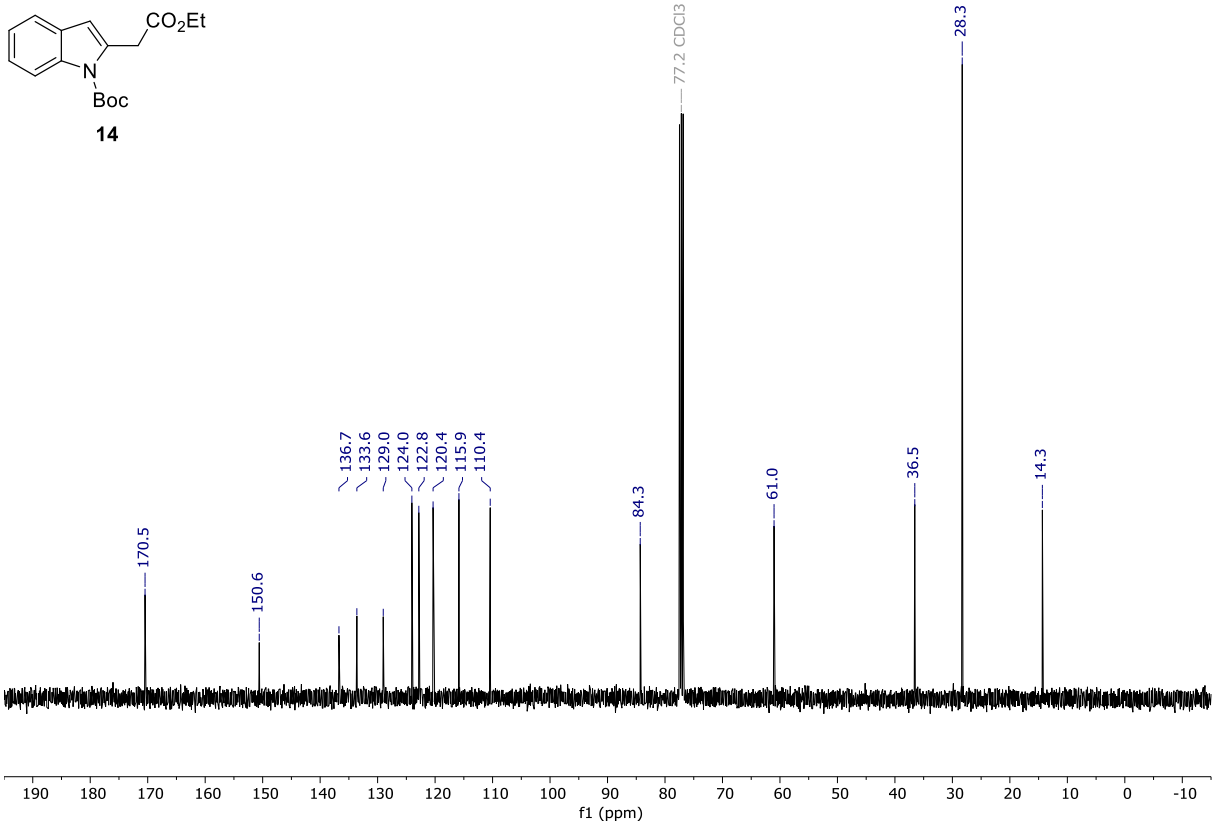

Parameter Value
1 Experiment HSQC-EDITED
2 Nucleus (1H, 13C)
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170

Ethyl (1,2-dimethyl-1*H*-indol-3-yl)acetate (**13**)

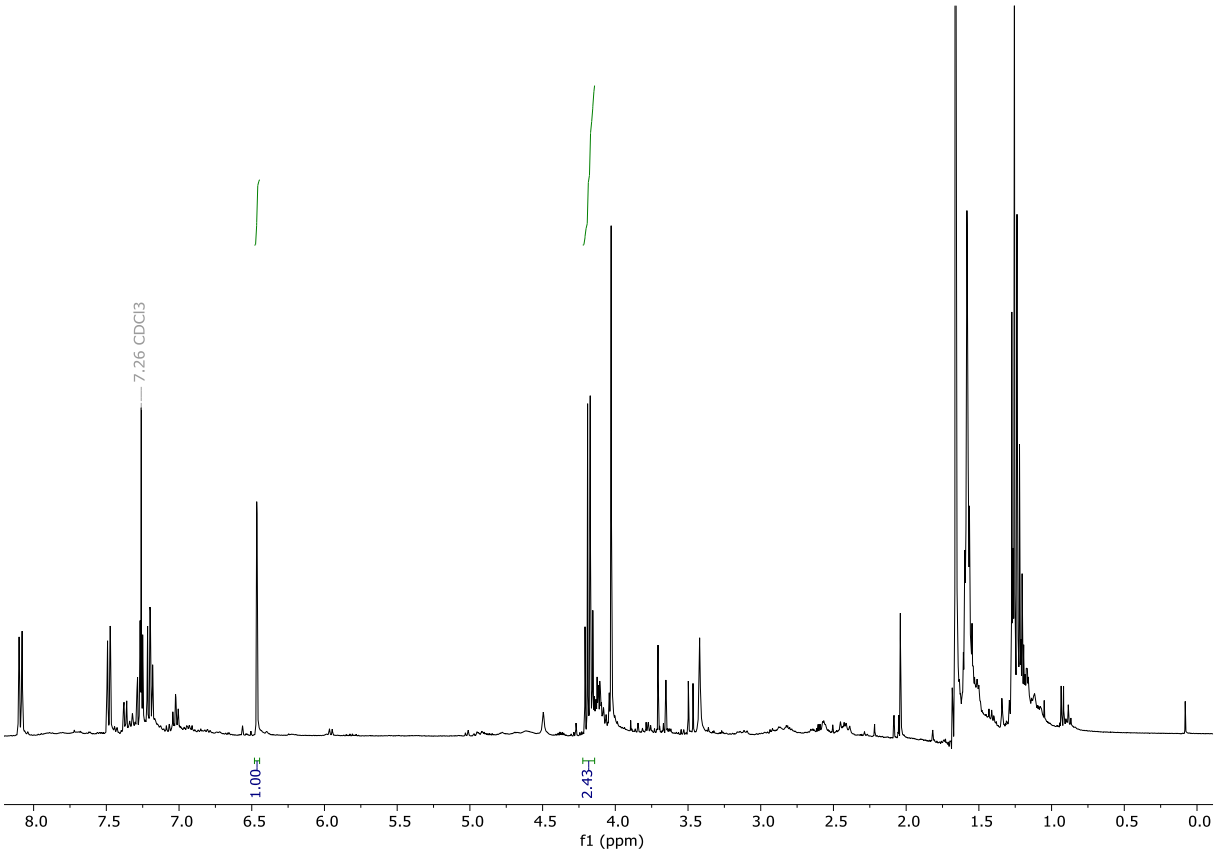


tert-Butyl 2-(2-ethoxy-2-oxoethyl)-1*H*-indole-1-carboxylate (**14**)

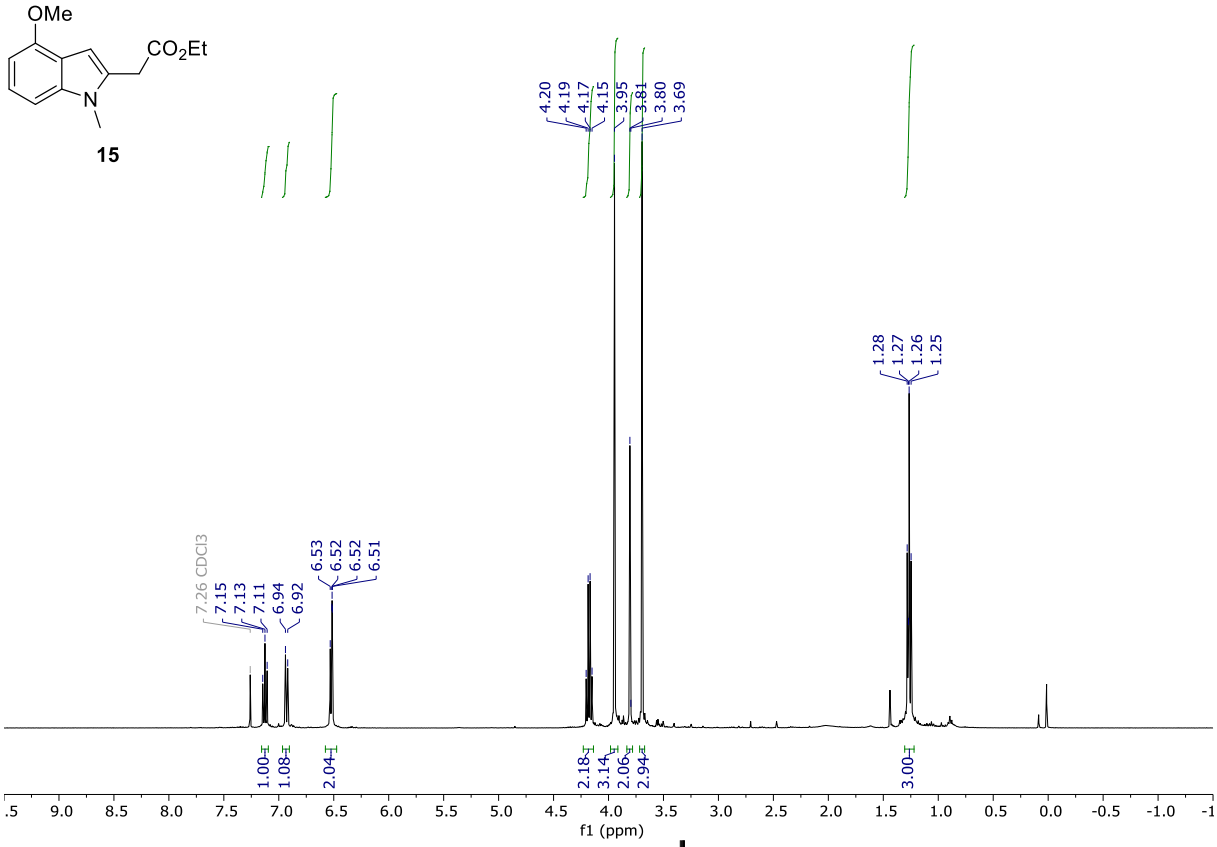


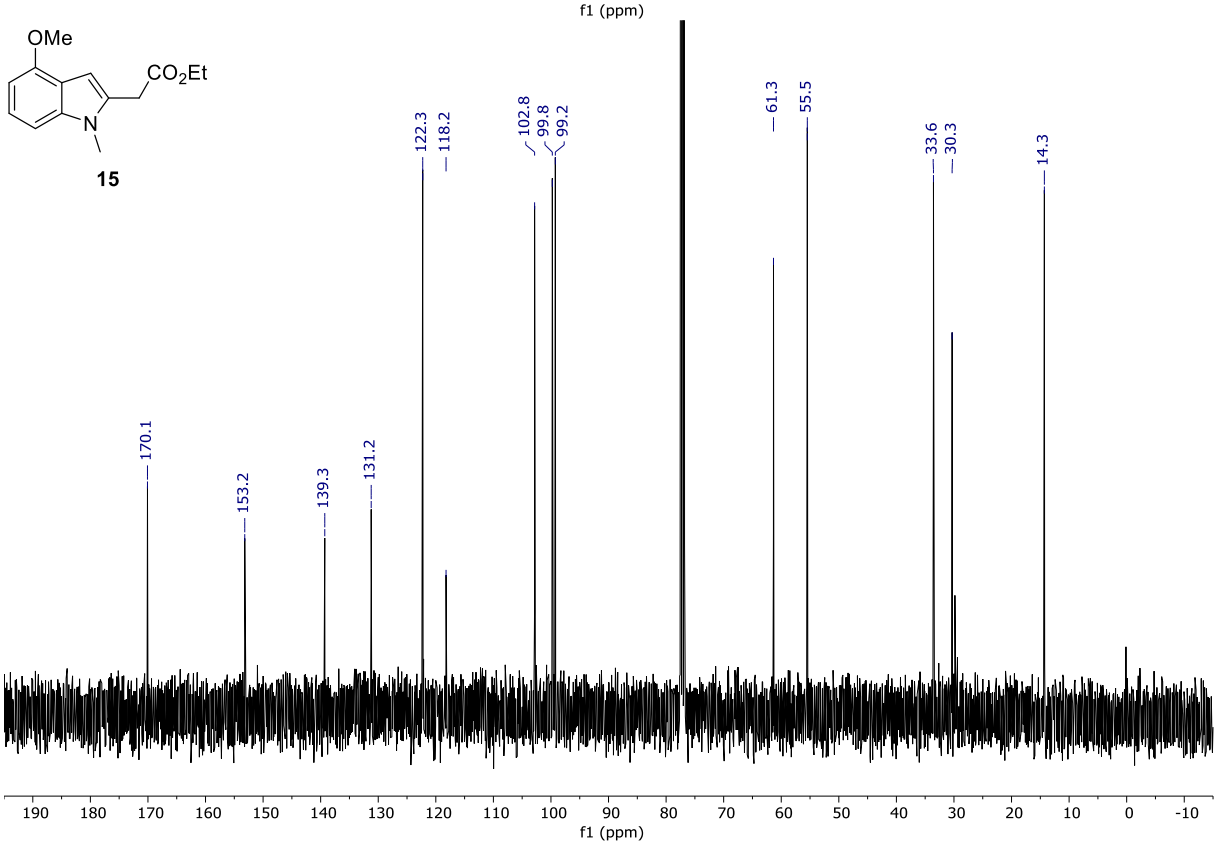


^{1}HNMR of crude reaction mixture (1-Bocindole excess removed by column chromatography):

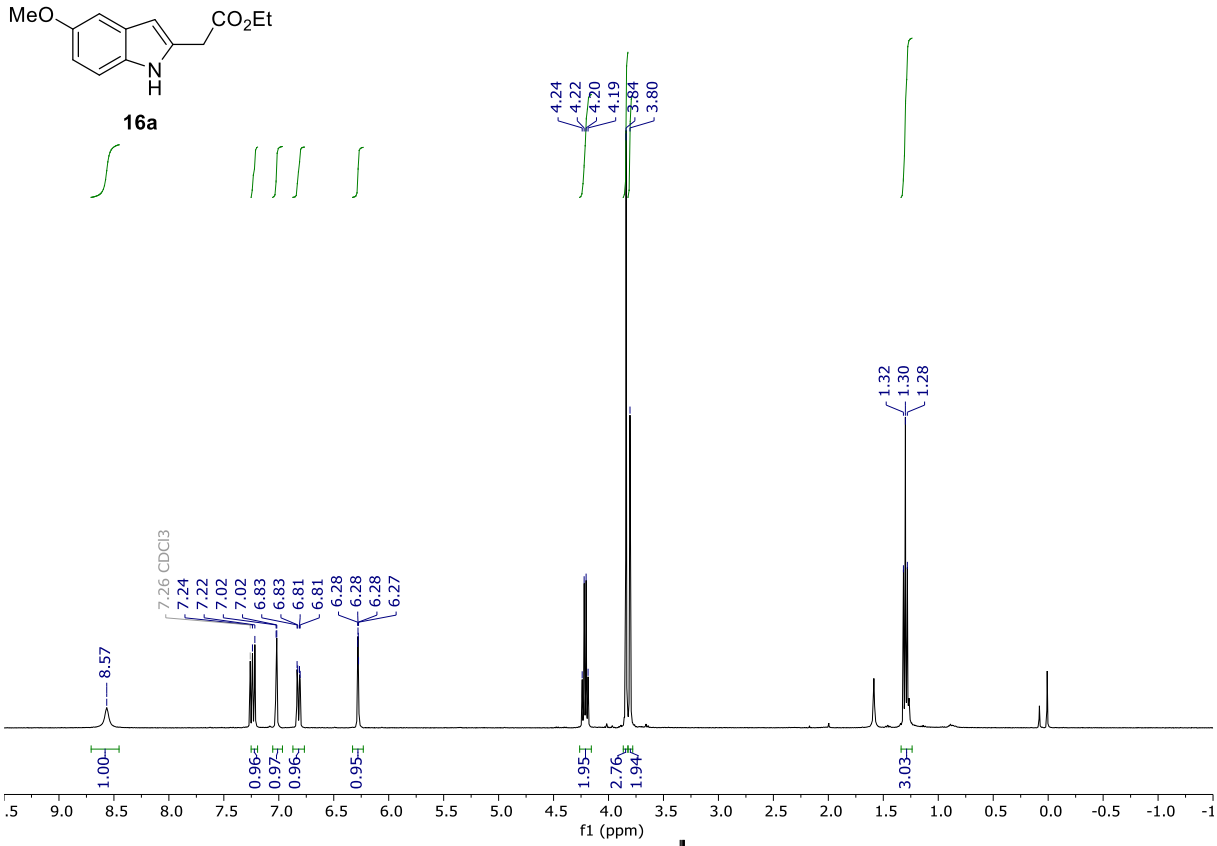


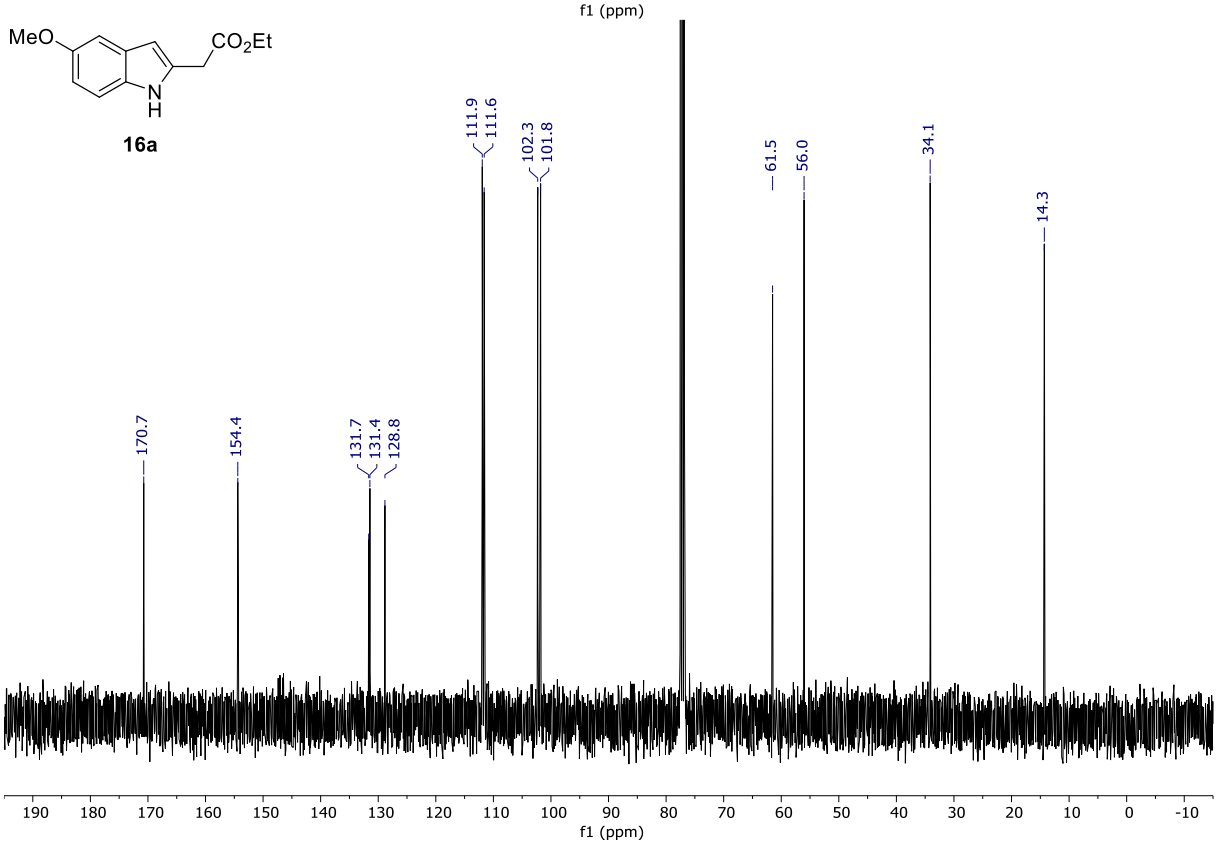
Ethyl (4-methoxy-1-methyl-1*H*-indol-2-yl)acetate (**15**)



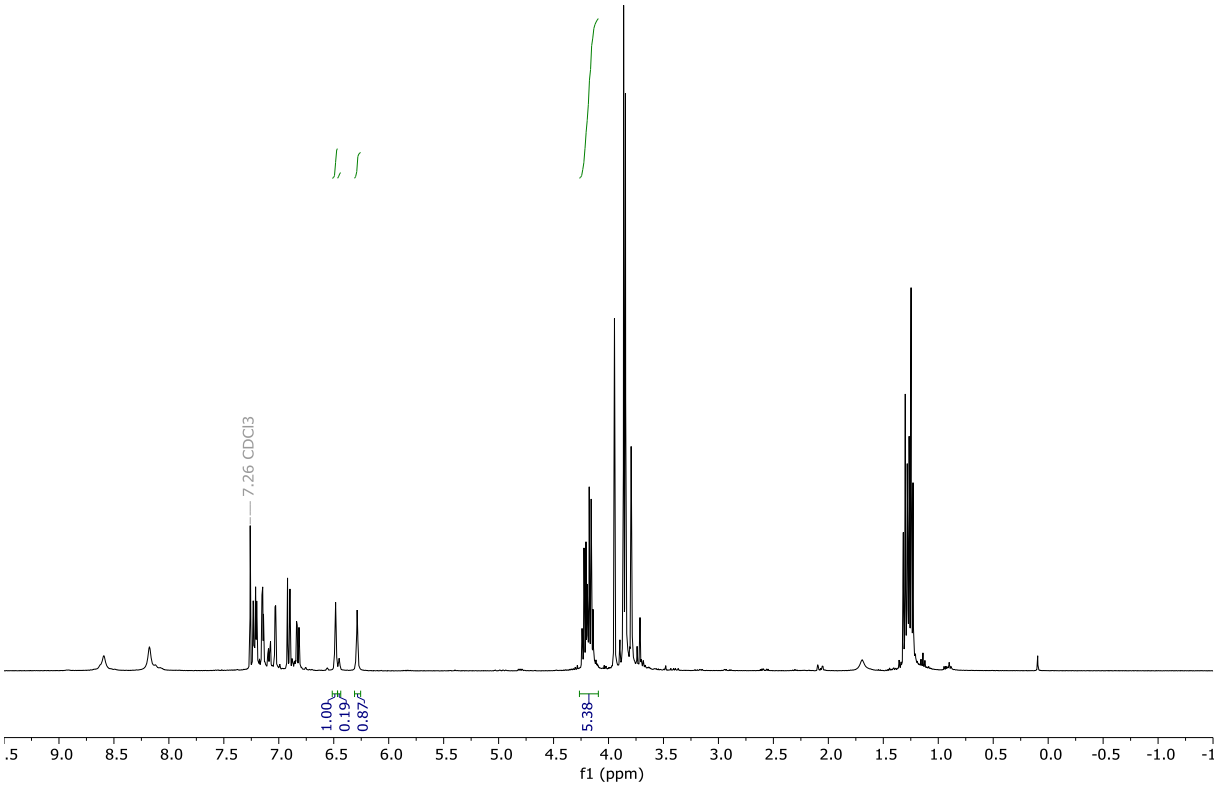


Ethyl (5-methoxy-1*H*-indol-2-yl)acetate (**16a**)

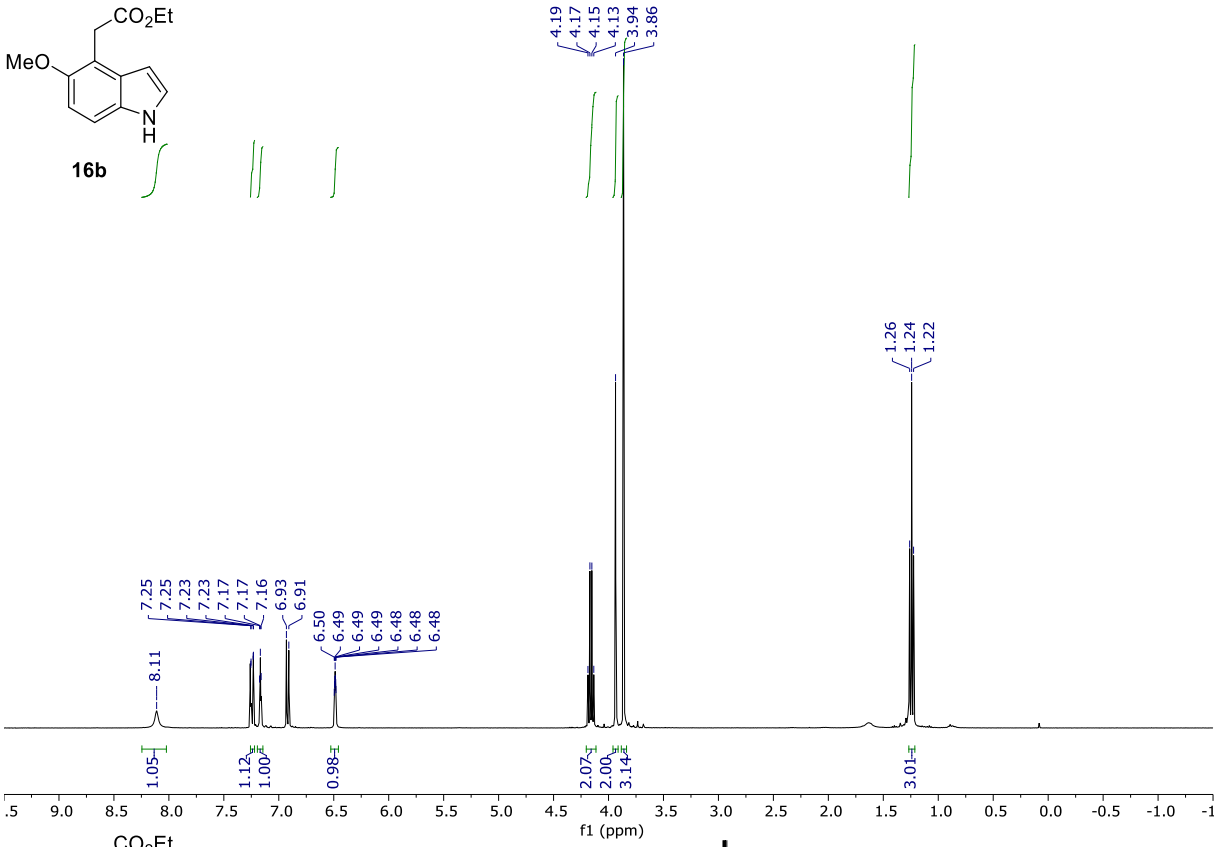


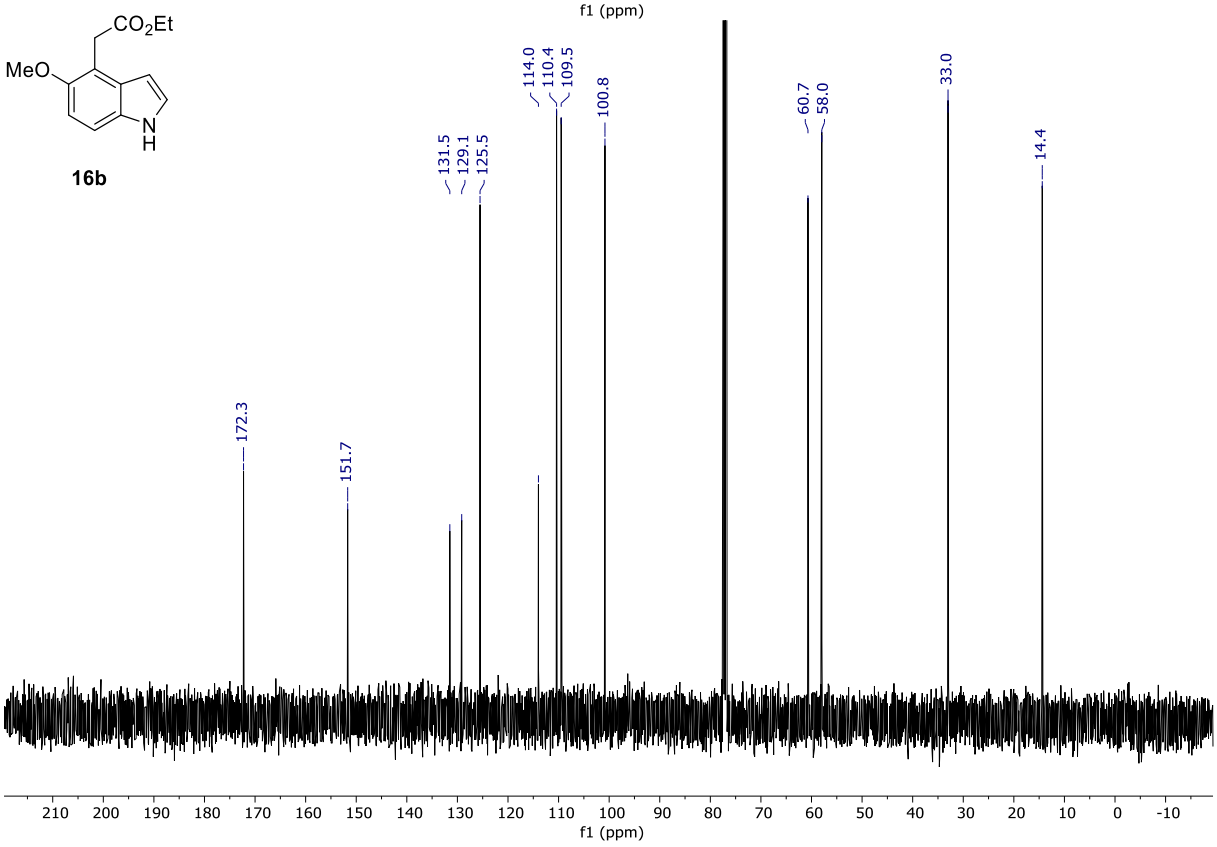


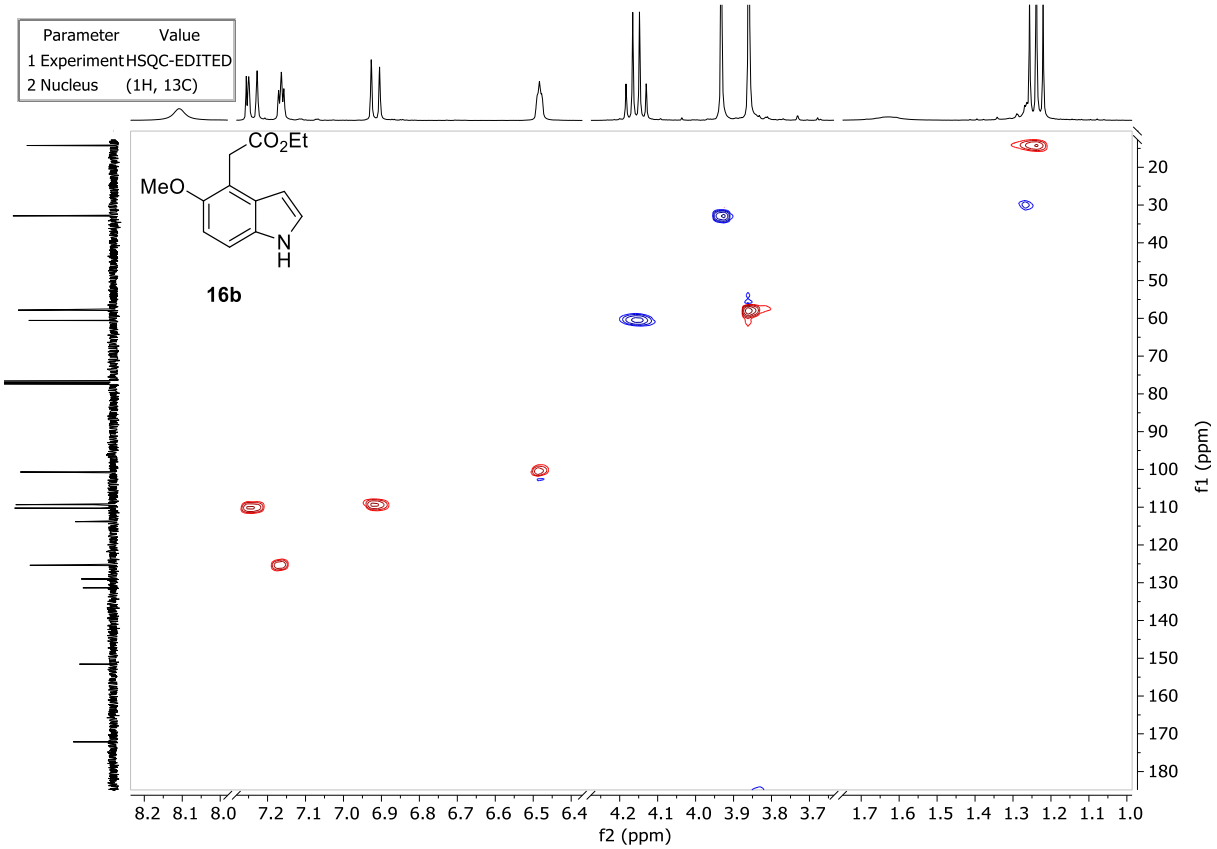
[1]HNMR of crude reaction mixture (5-methoxyindole excess removed by column chromatography):

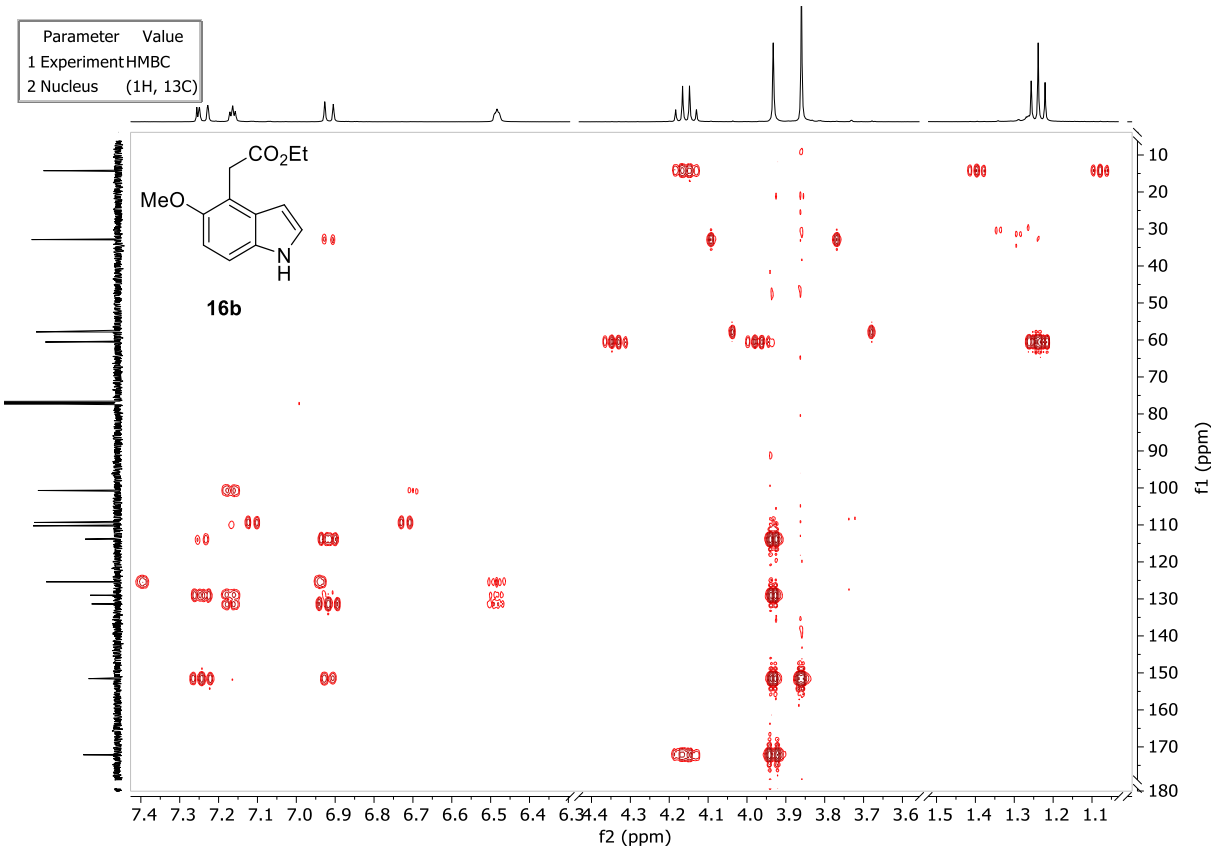


Ethyl (5-methoxy-1*H*-indol-4-yl)acetate (**16b**)

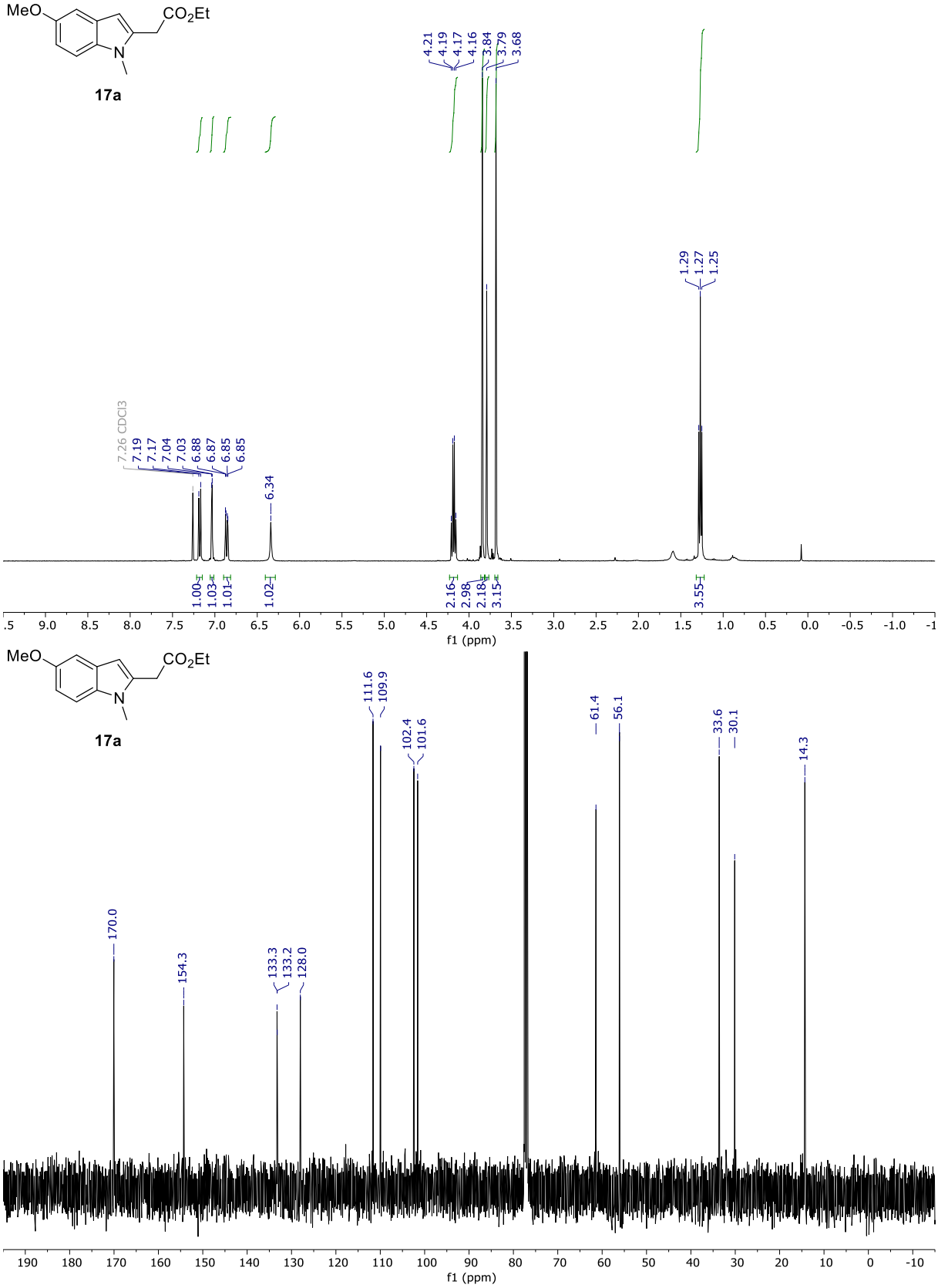




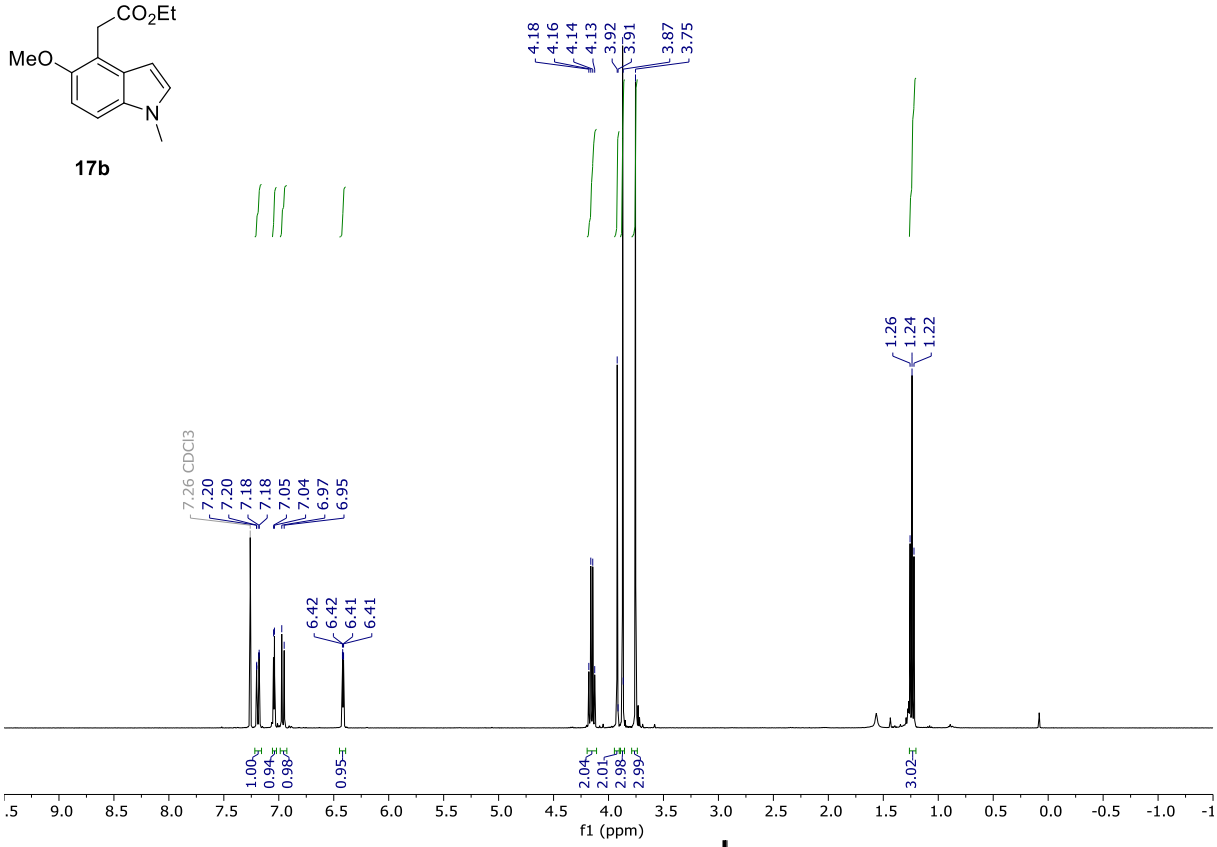

Parameter Value
1 Experiment HSQC-EDITED
2 Nucleus (1H, 13C)
CO2Et
MeO
N
H
16b
f2 (ppm)
f1 (ppm)

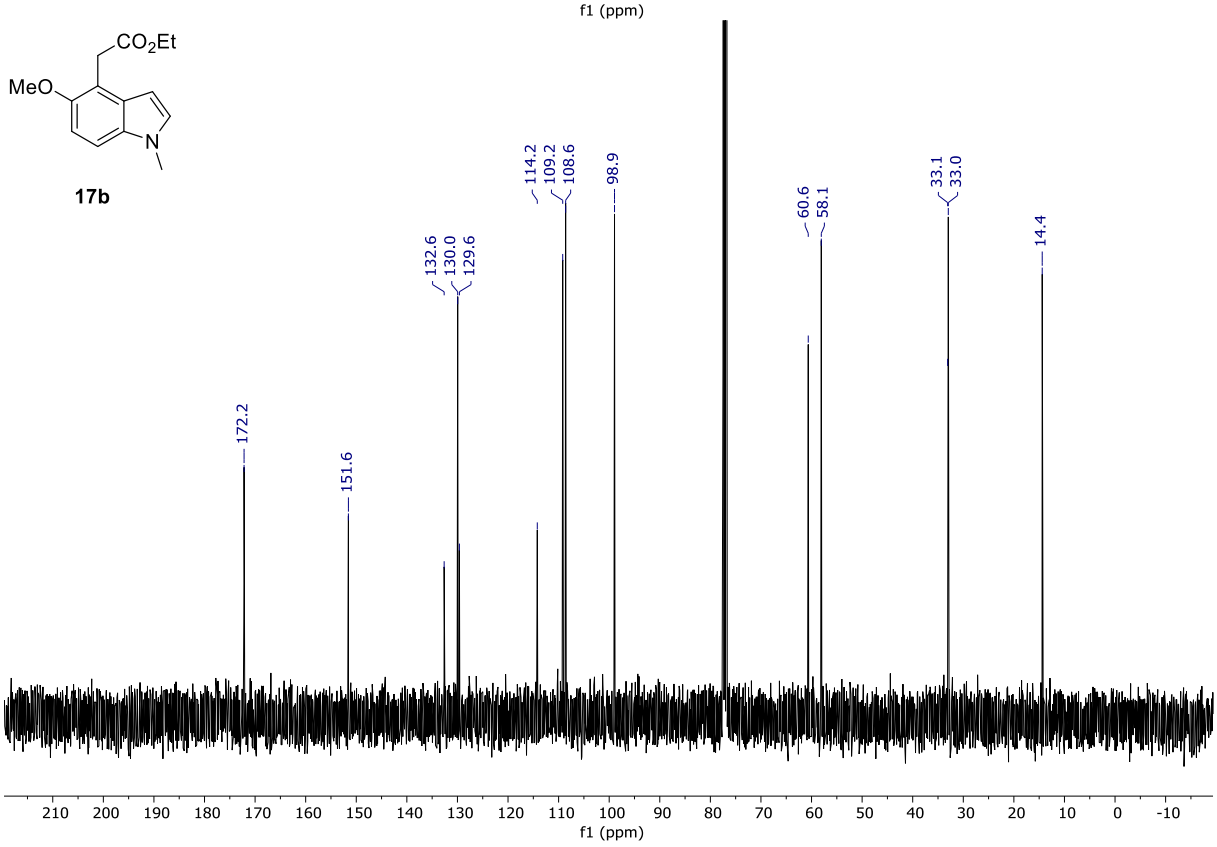

Parameter Value
1 Experiment HMBC
2 Nucleus (1H, 13C)
CO2Et
MeO
N
H
16b
f2 (ppm)
f1 (ppm)

Ethyl (5-methoxy-1-methyl-1*H*-indol-2-yl)acetate (**17a**)

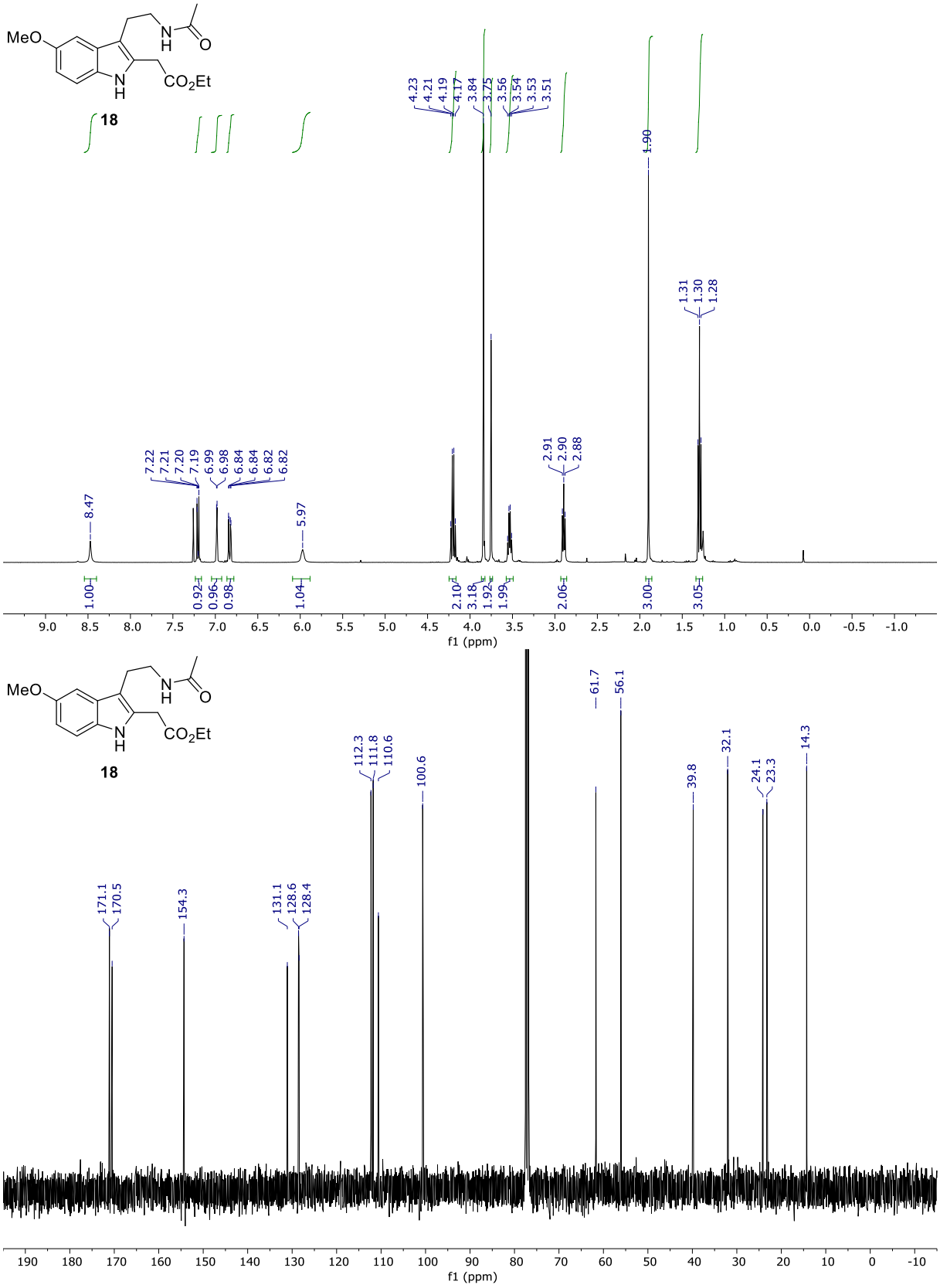


Ethyl (5-methoxy-1-methyl-1*H*-indol-4-yl)acetate (**17b**)

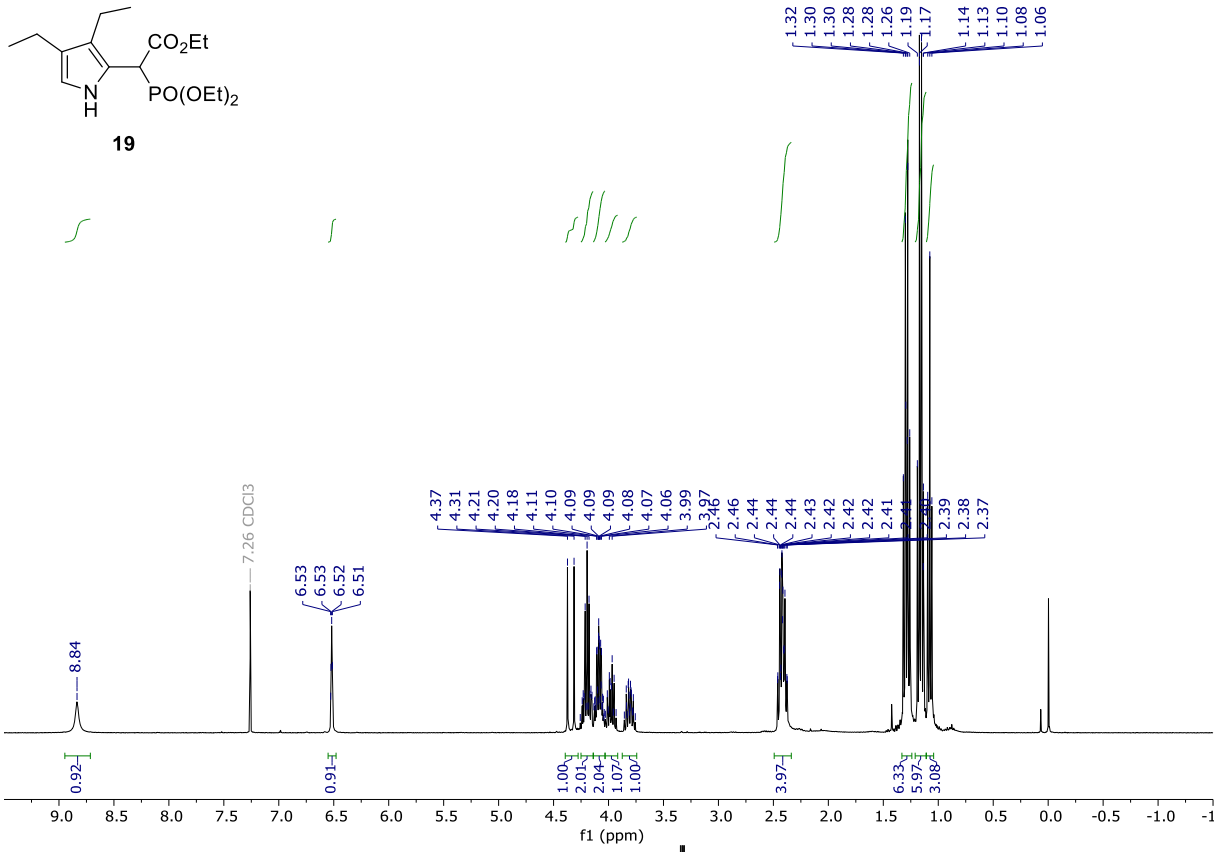


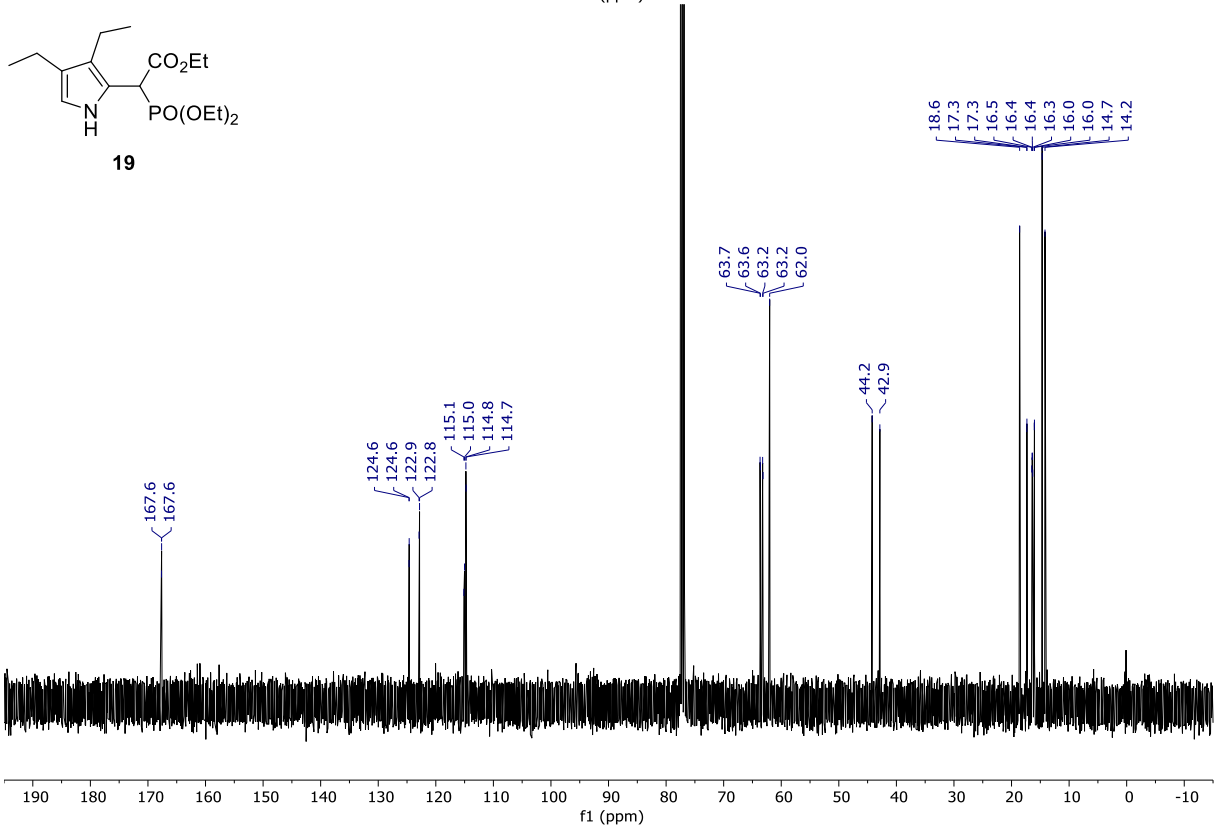


Ethyl (3-(2-(acetylamino)ethyl)-5-methoxy-1*H*-indol-2-yl)acetate (**18**)

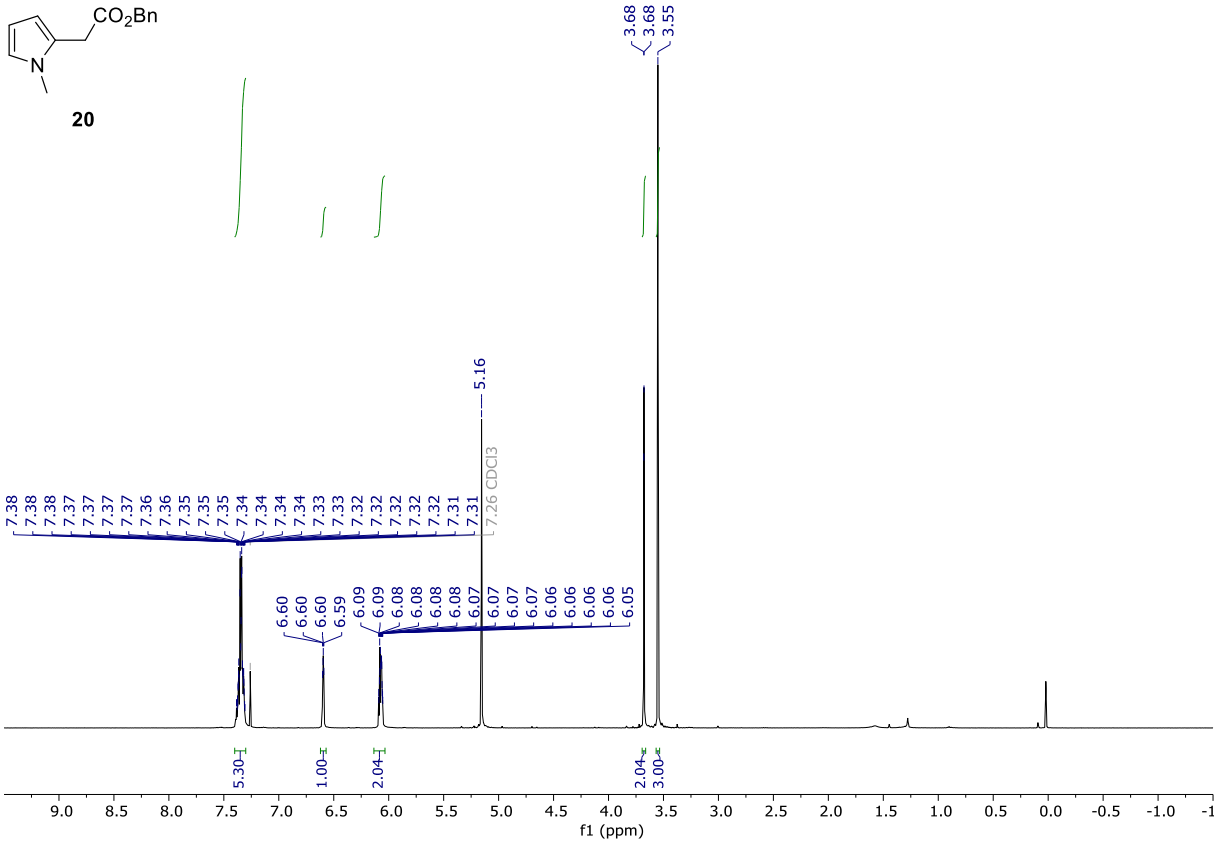


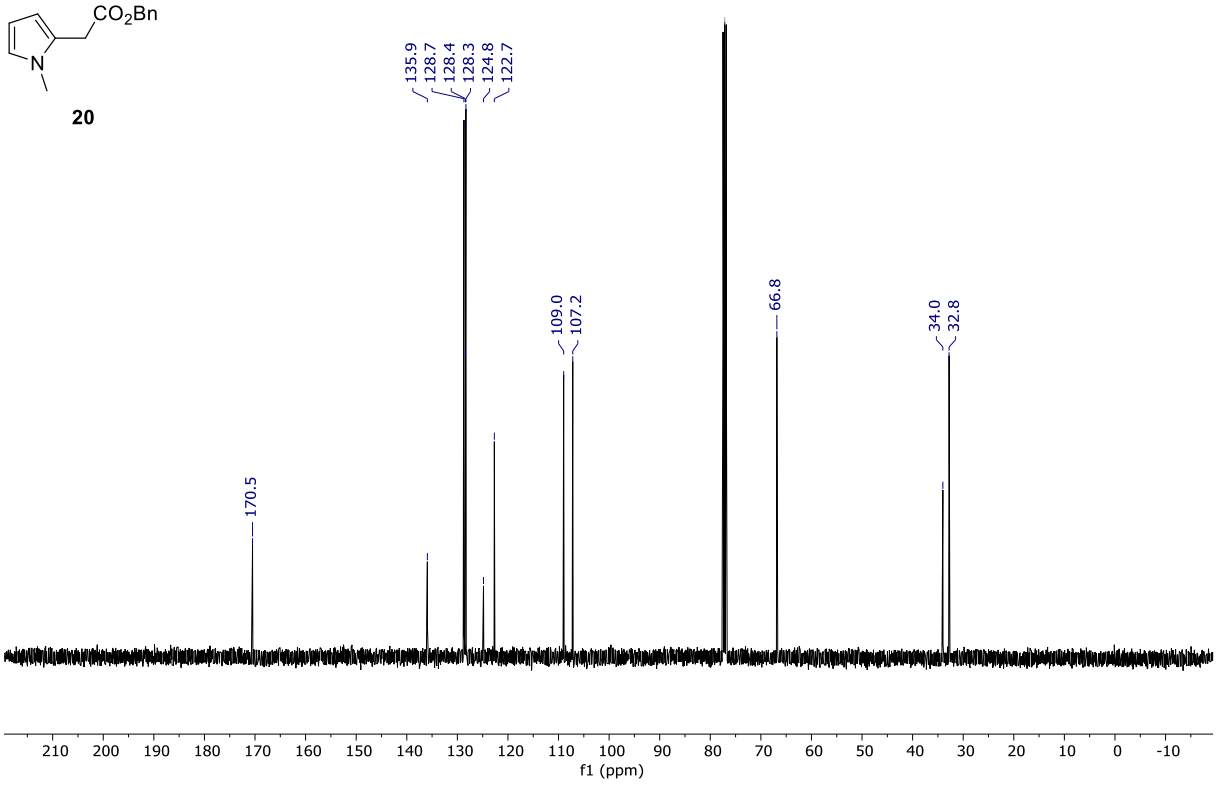
Ethyl (diethylphosphono)(3,4-diethyl-1*H*-pyrrol-2-yl)acetate (**19**)



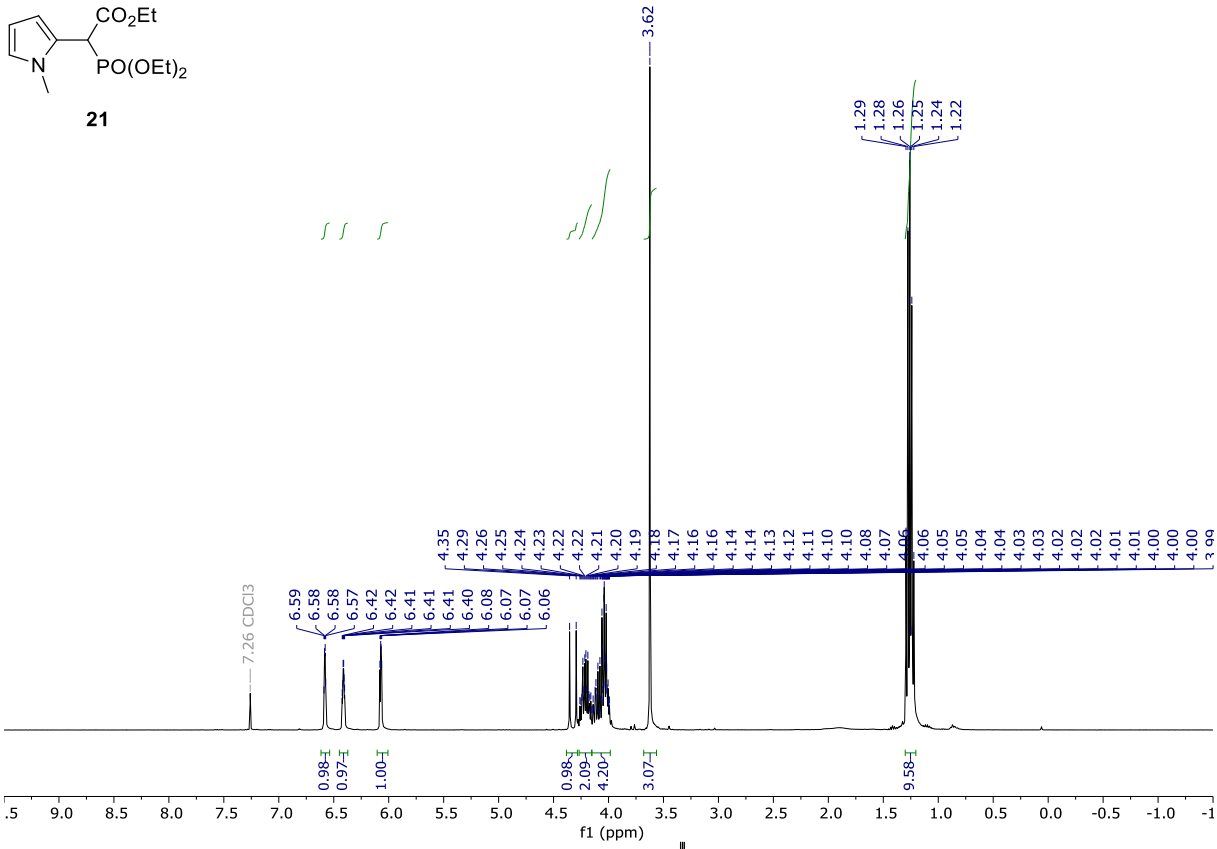


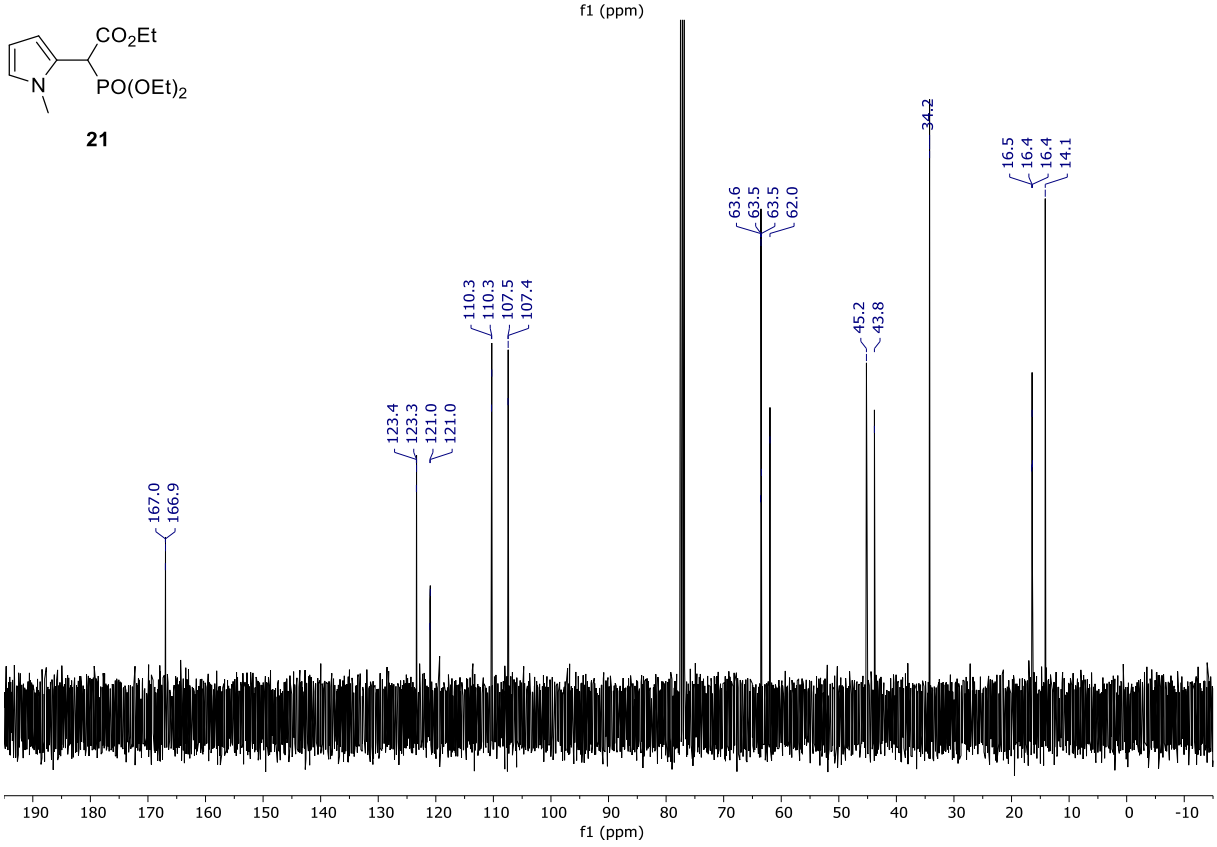
Benzyl (1-methyl-1*H*-pyrrol-2-yl)acetate (**20**)



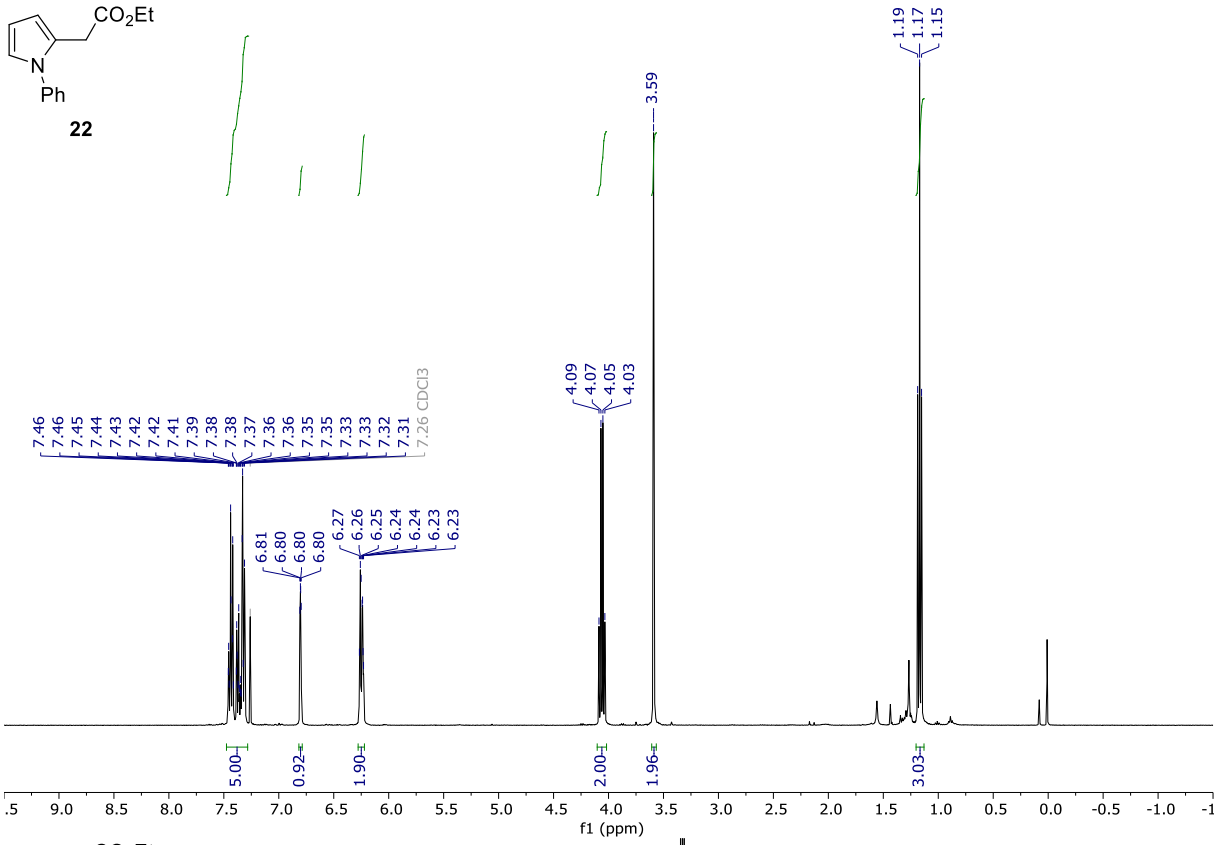


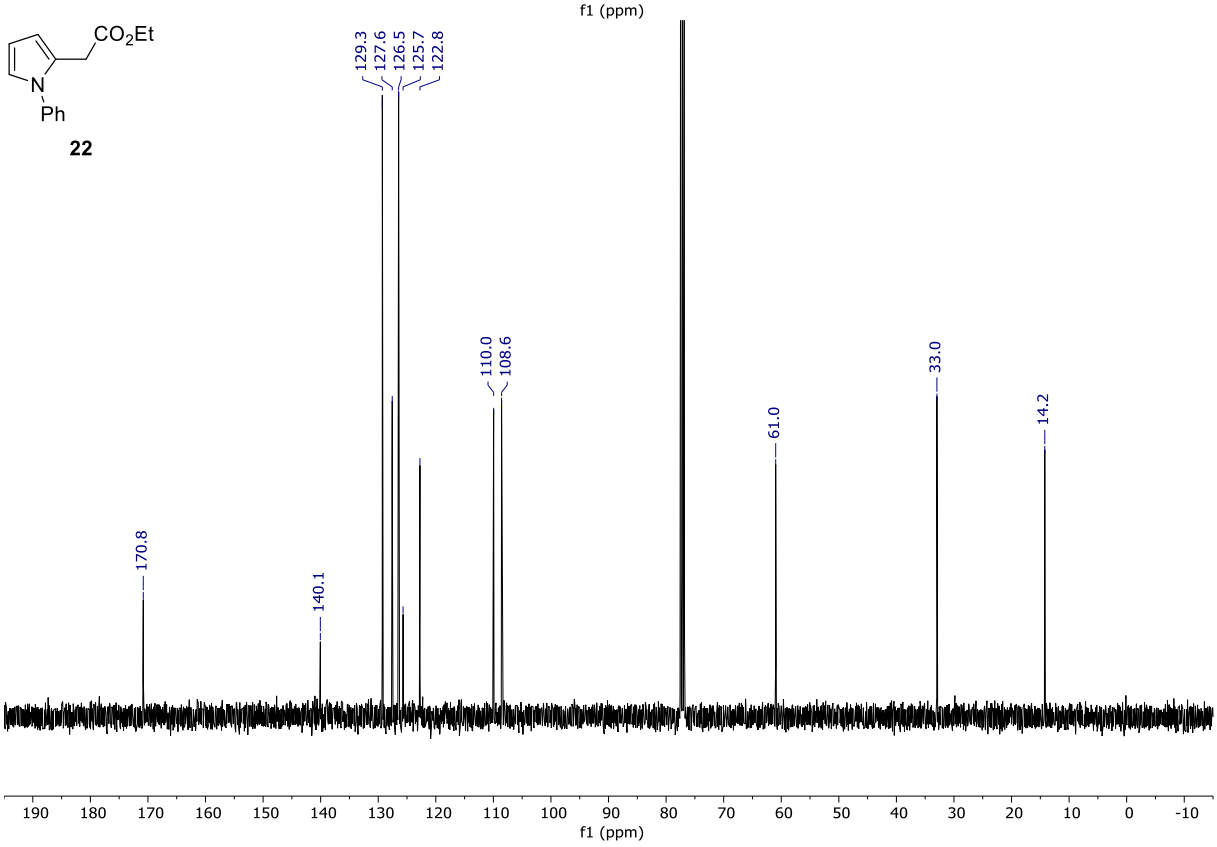
Ethyl (diethylphosphono)(1-methyl-1*H*-pyrrol-2-yl)acetate (**21**)



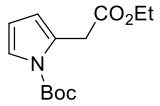


Ethyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (**22**)

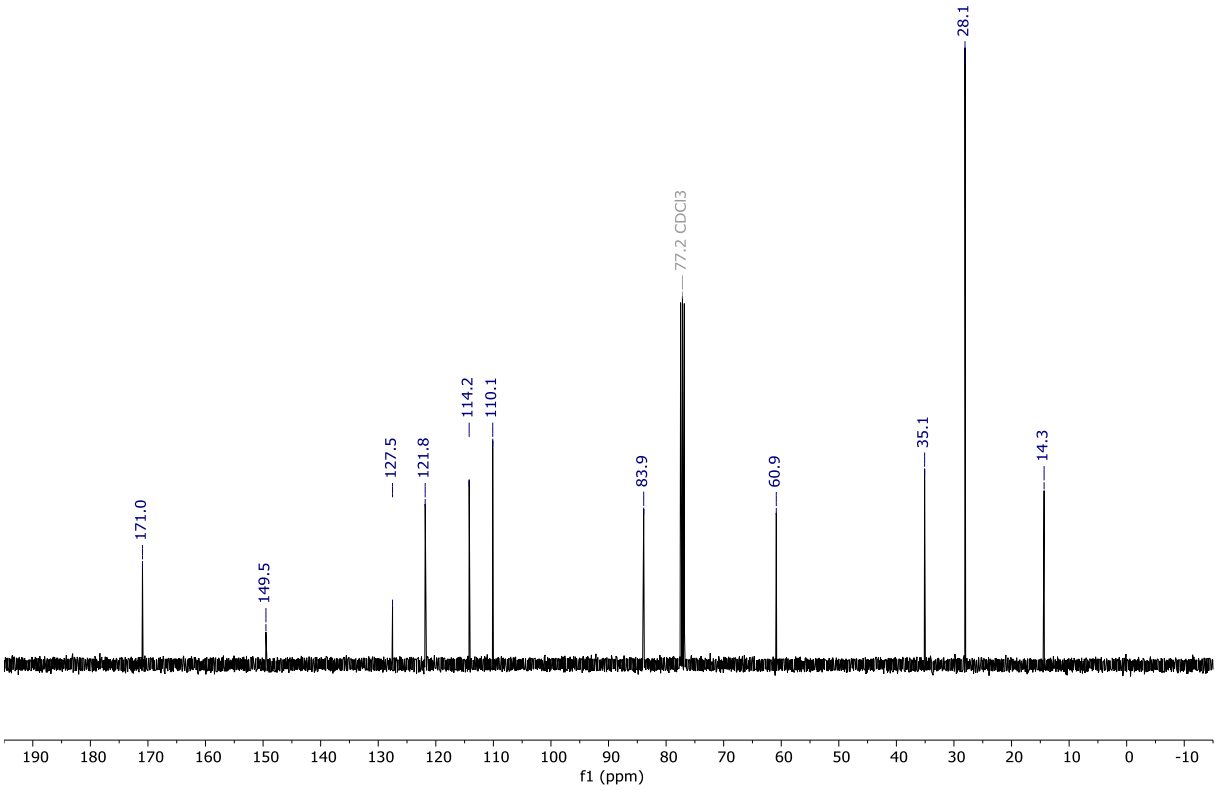




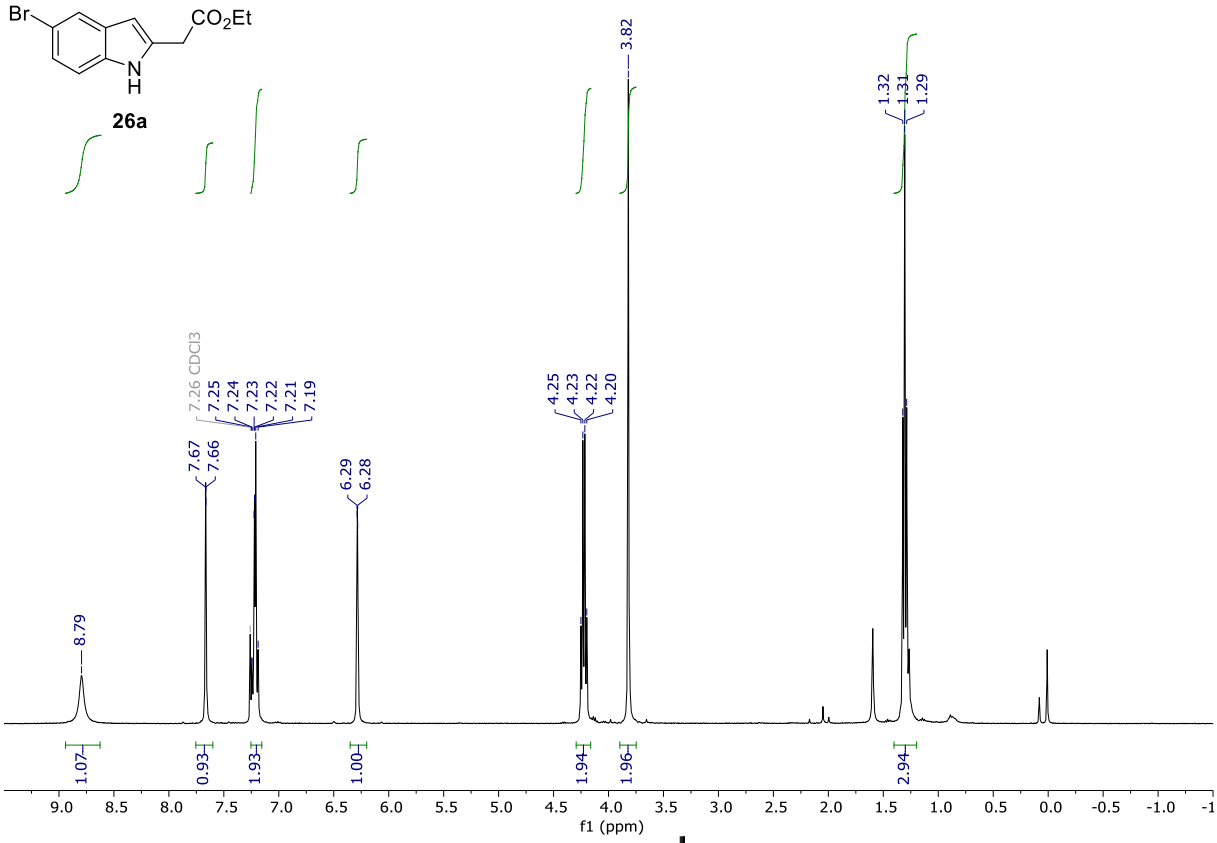
tert-Butyl 2-(2-ethoxy-2-oxoethyl)-1*H*-pyrrole-1-carboxylate (**23**)

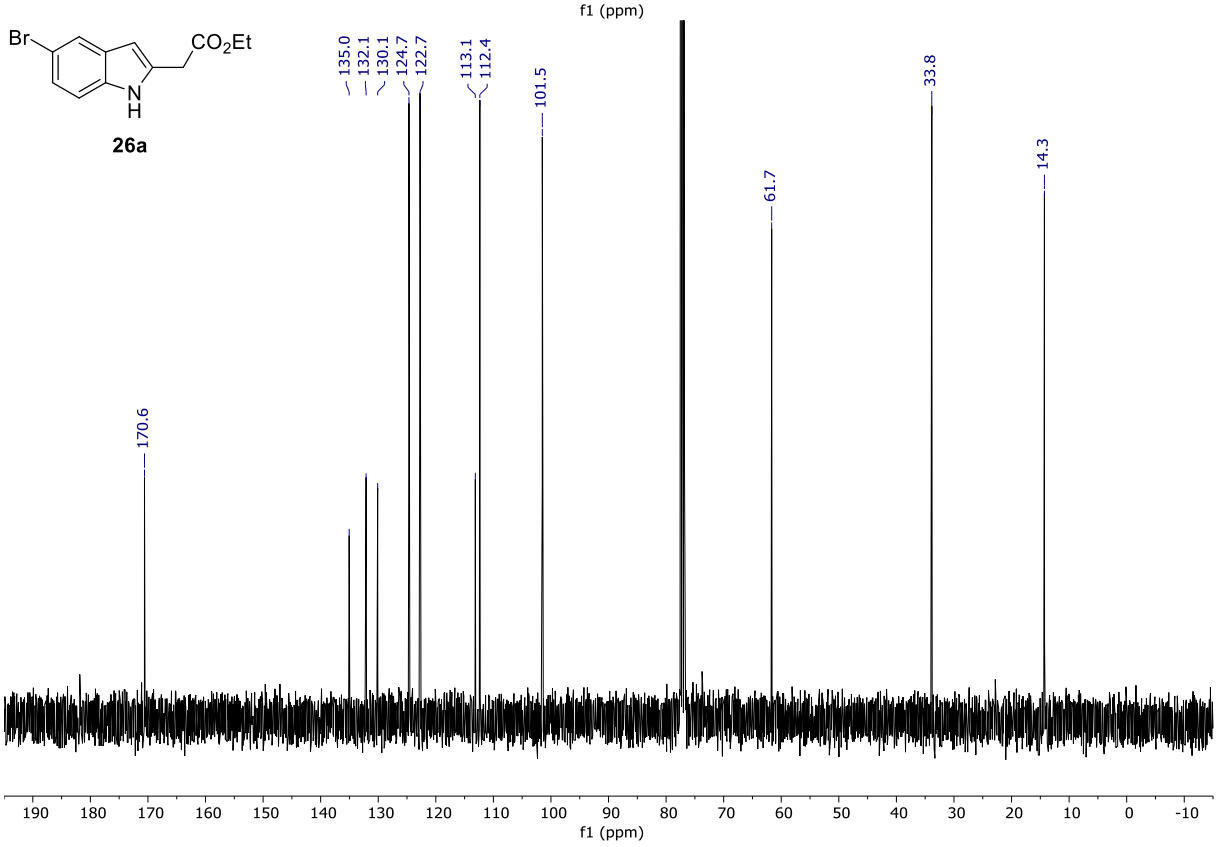


23

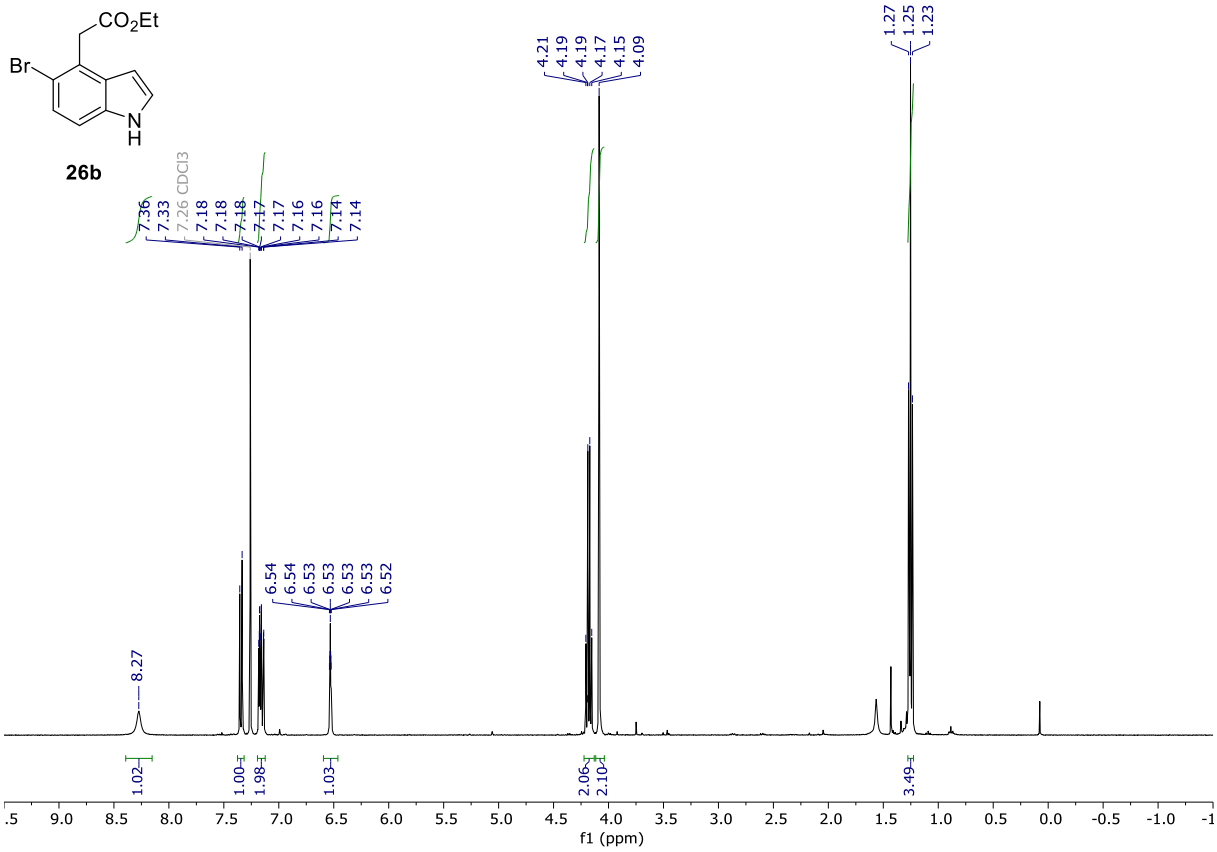


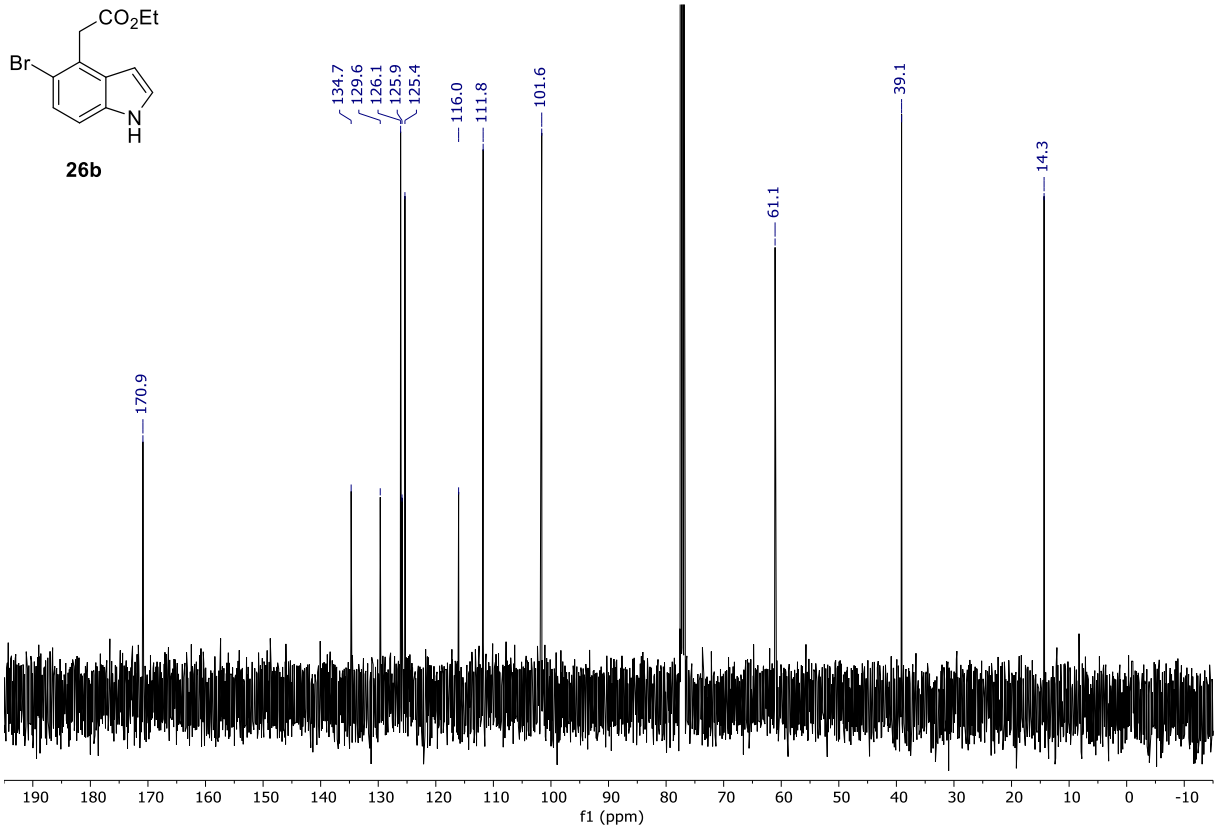
Ethyl (5-bromo-1*H*-indol-2-yl)acetate (**26a**)



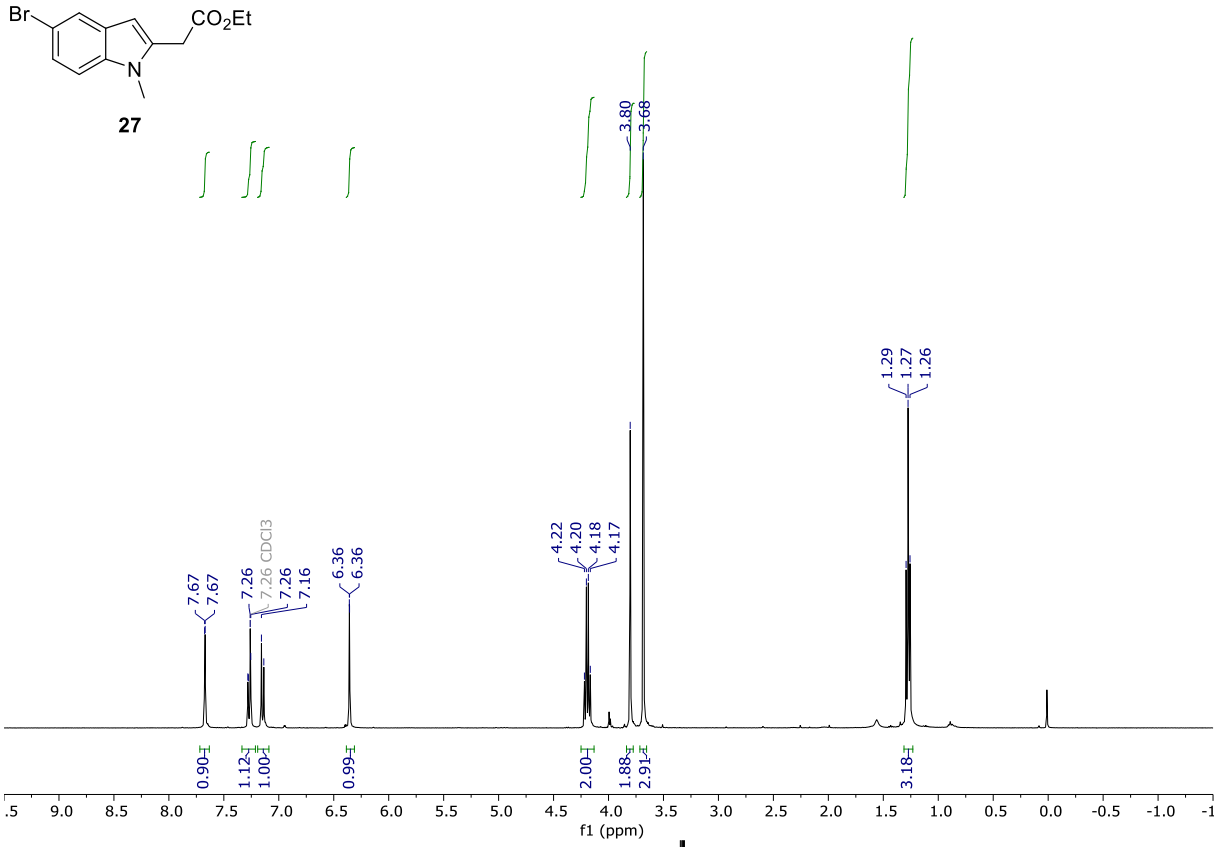


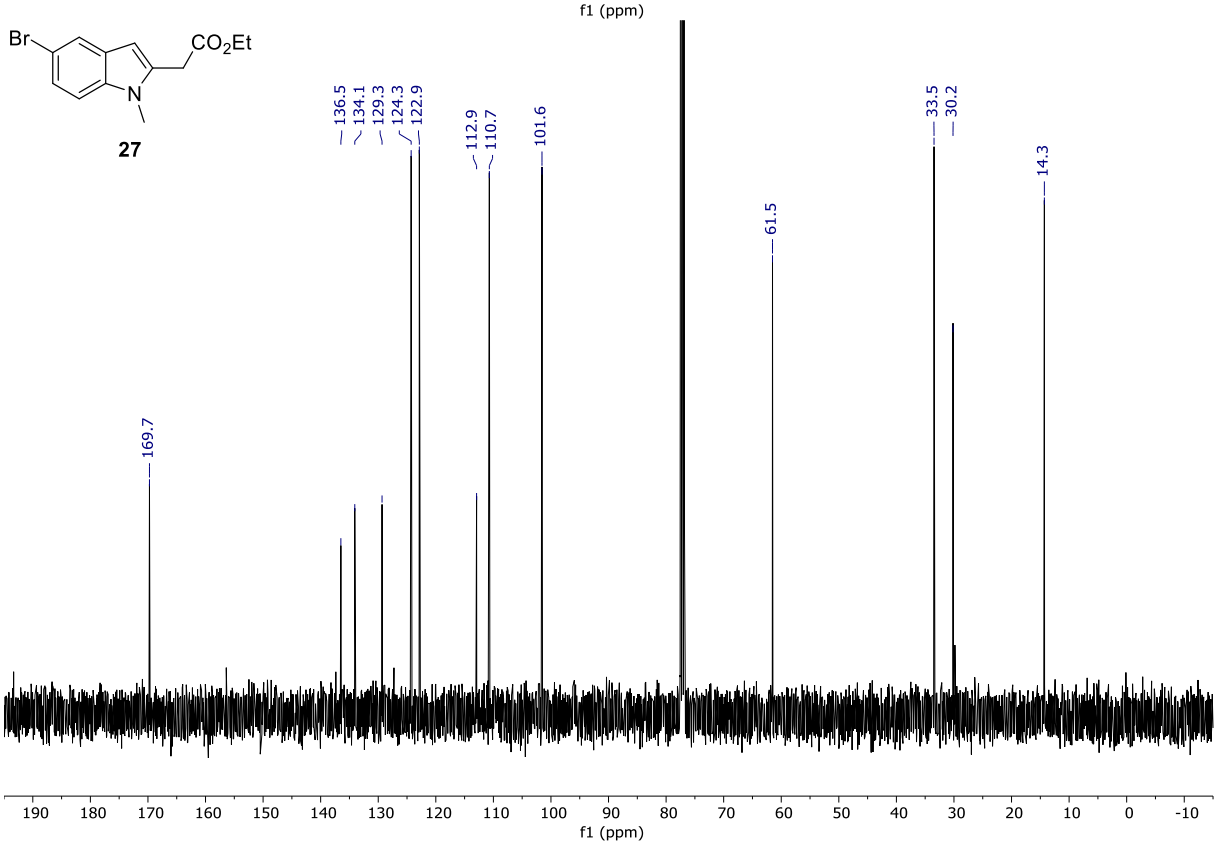
Ethyl (5-bromo-1*H*-indol-3-yl)acetate (**26b**)



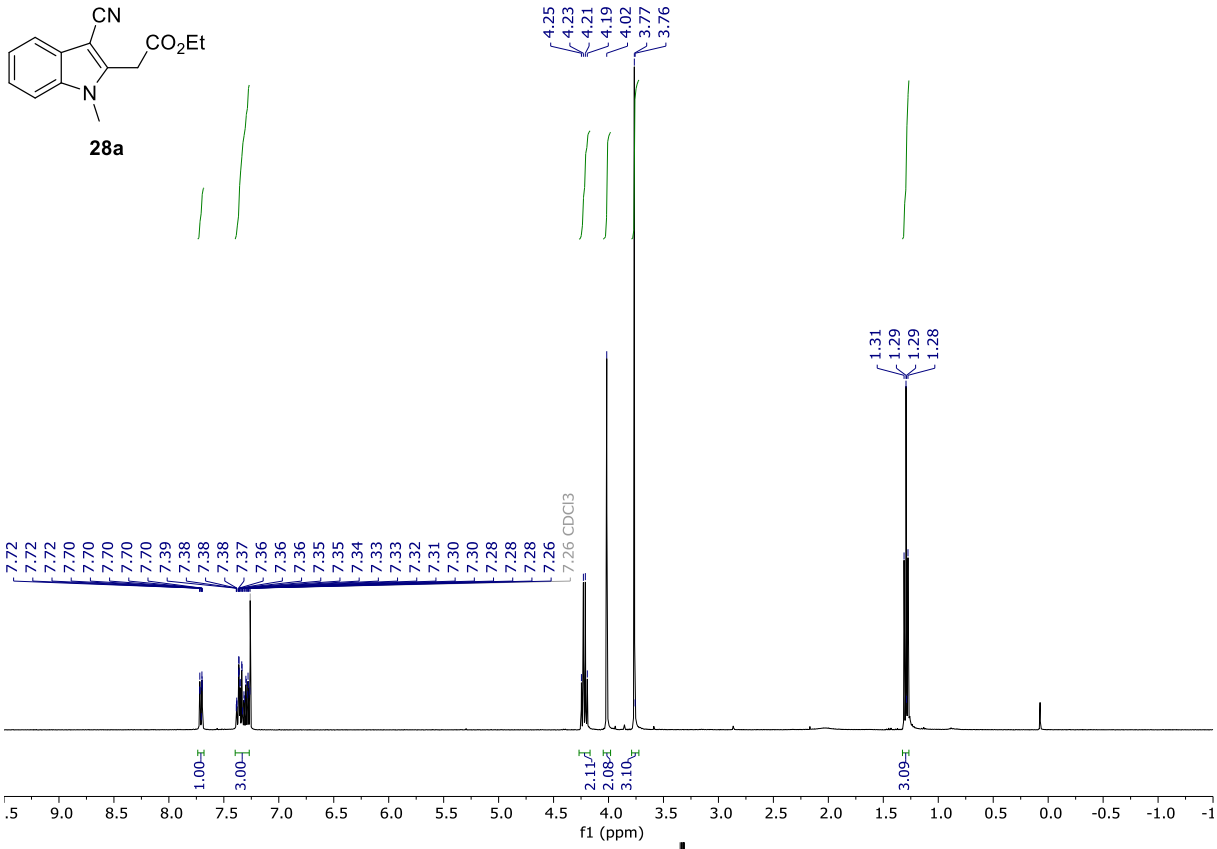


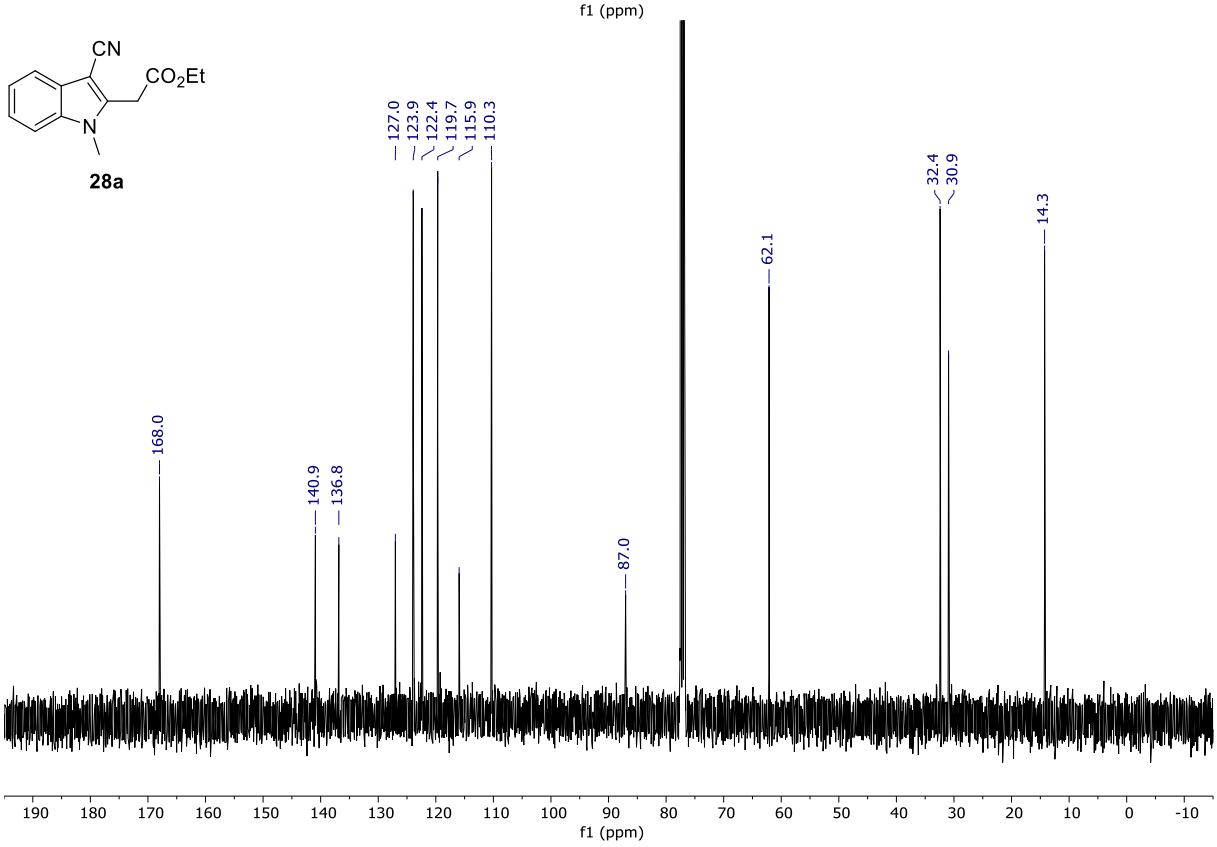
Ethyl (5-bromo-1-methyl-1*H*-indol-2-yl)acetate (**27**)



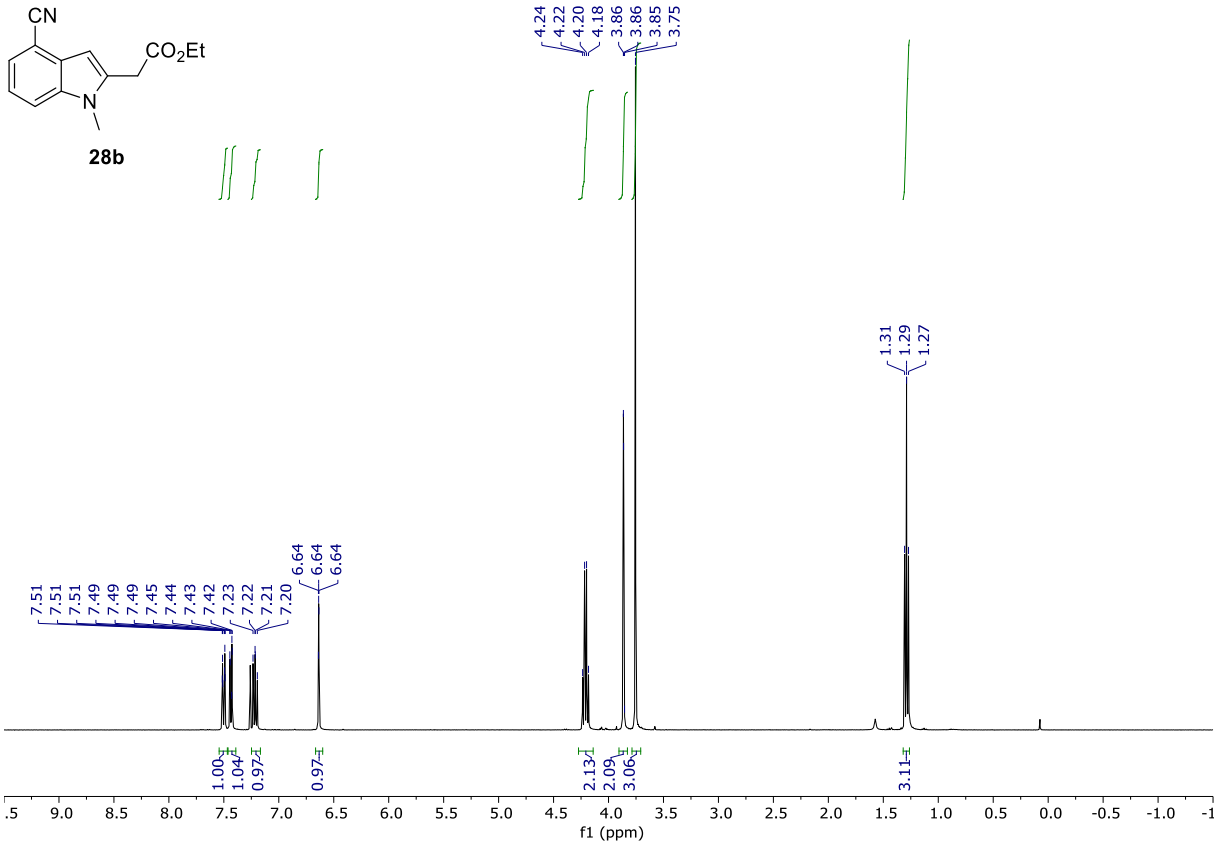


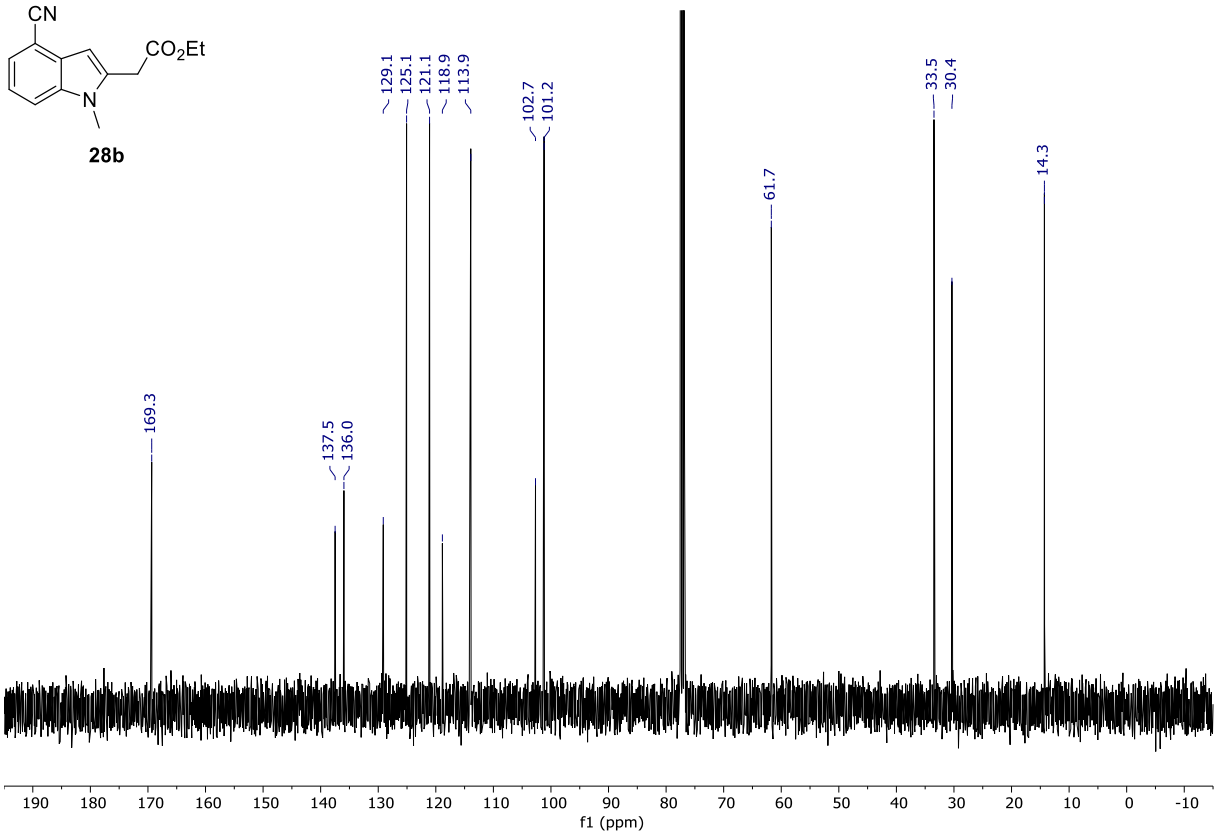
Ethyl (3-cyano-1-methyl-1*H*-indol-2-yl)acetate (**28a**)



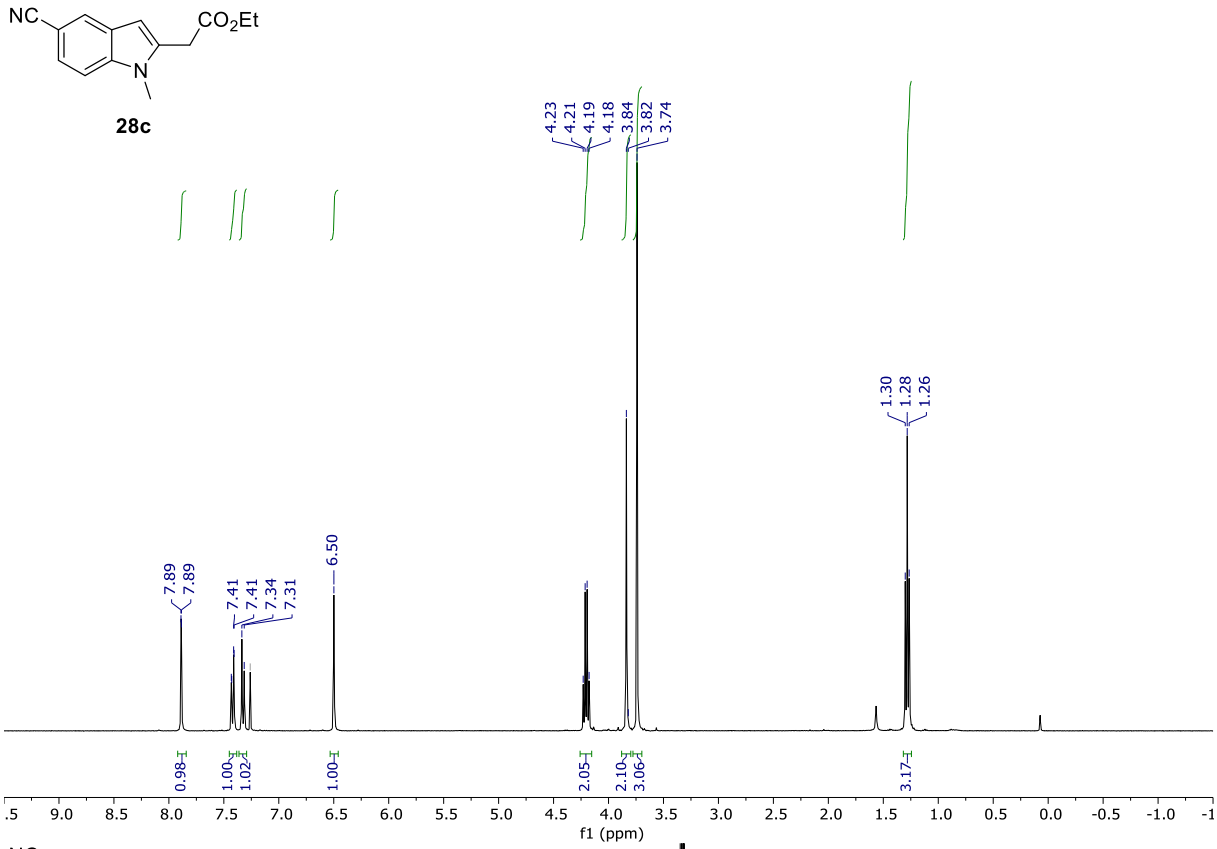


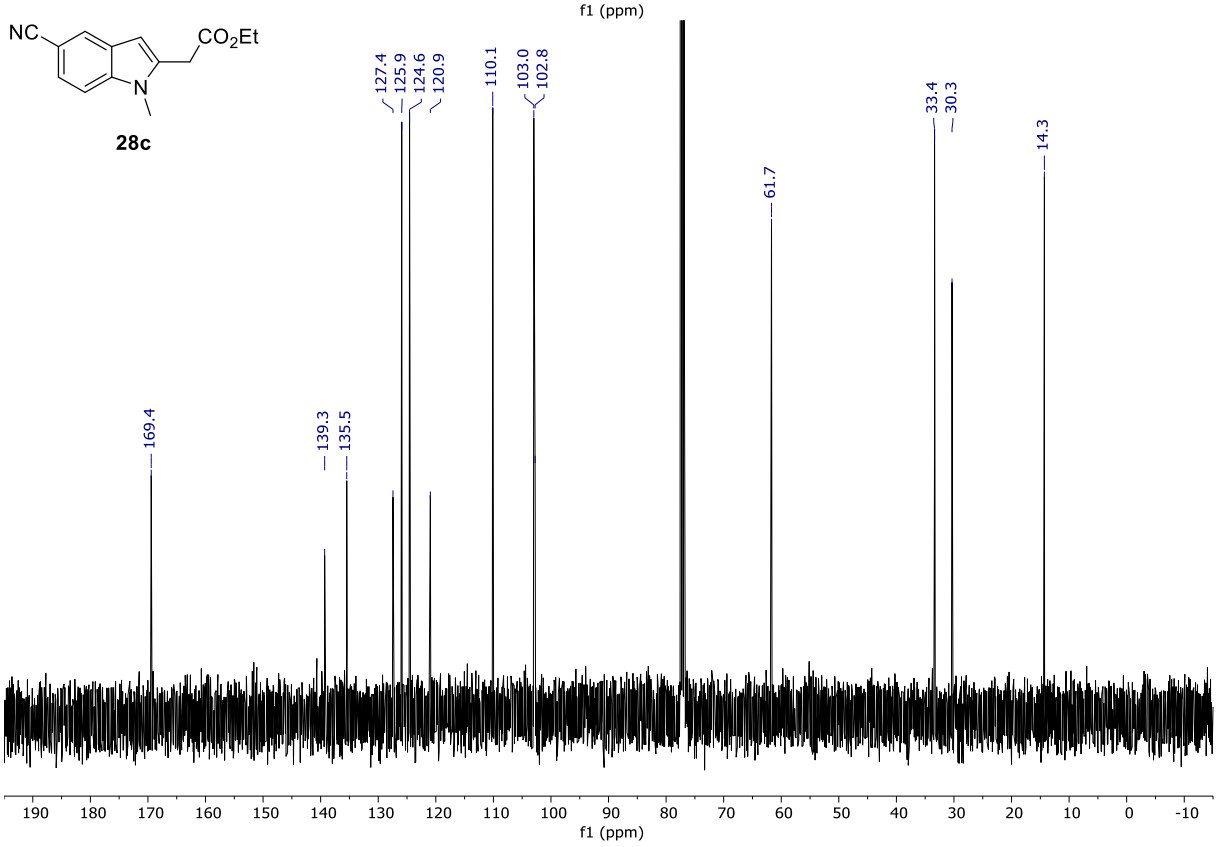
Ethyl (4-cyano-1-methyl-1*H*-indol-2-yl)acetate (**28b**)



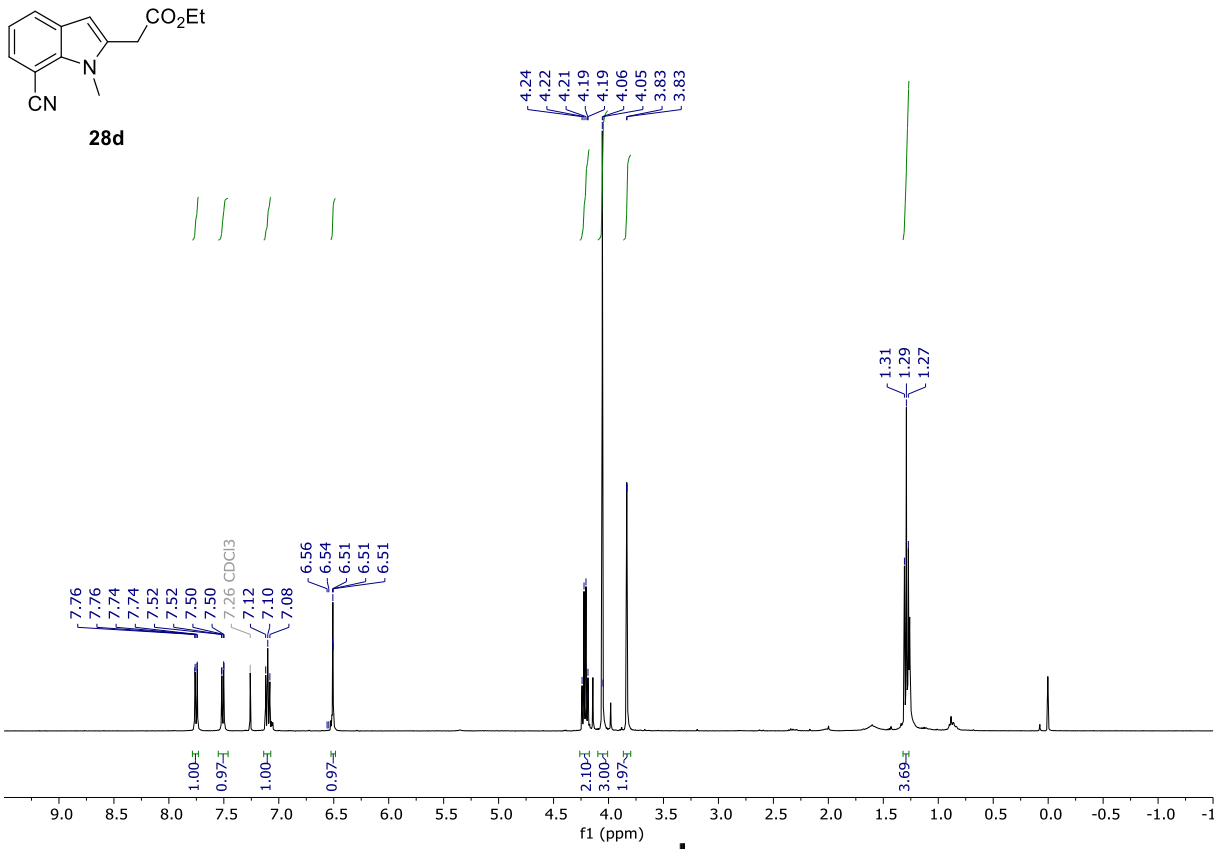


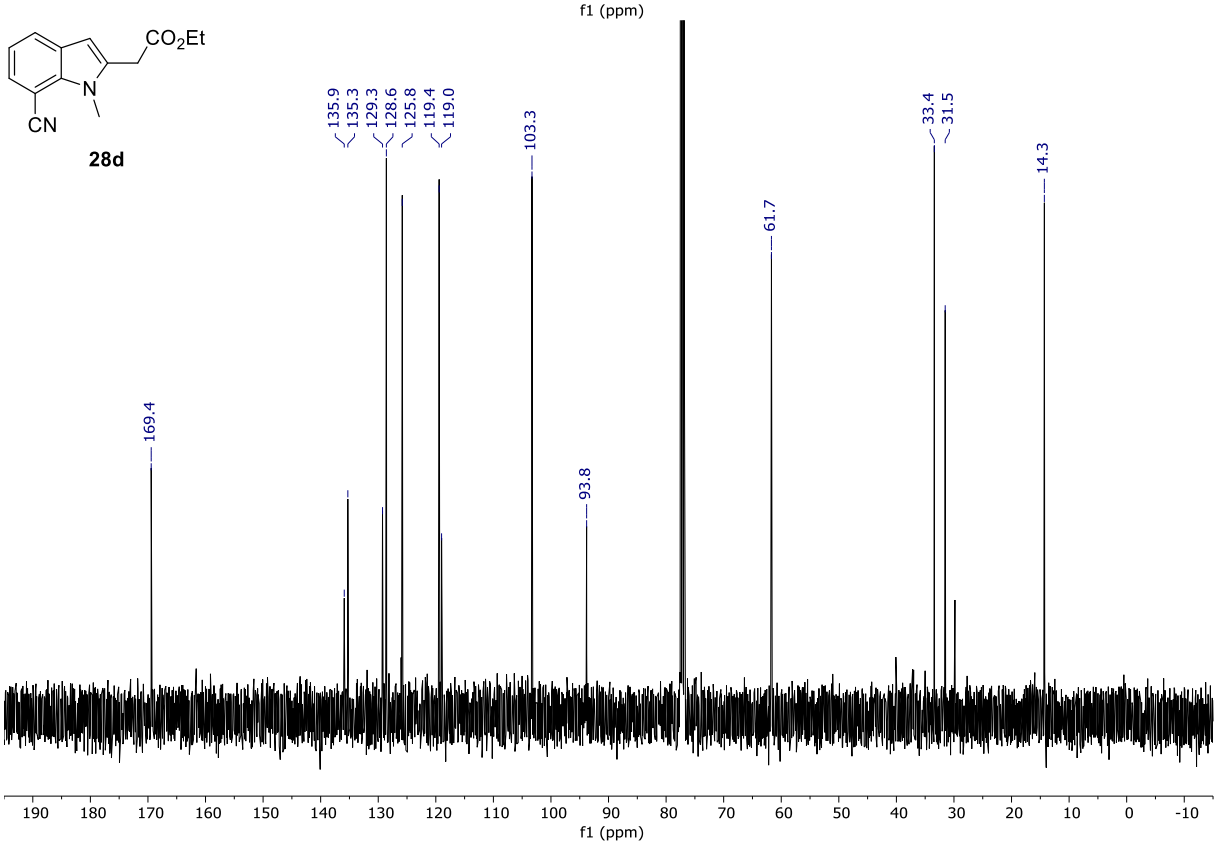
Ethyl (5-cyano-1-methyl-1*H*-indol-2-yl)acetate (**28c**)



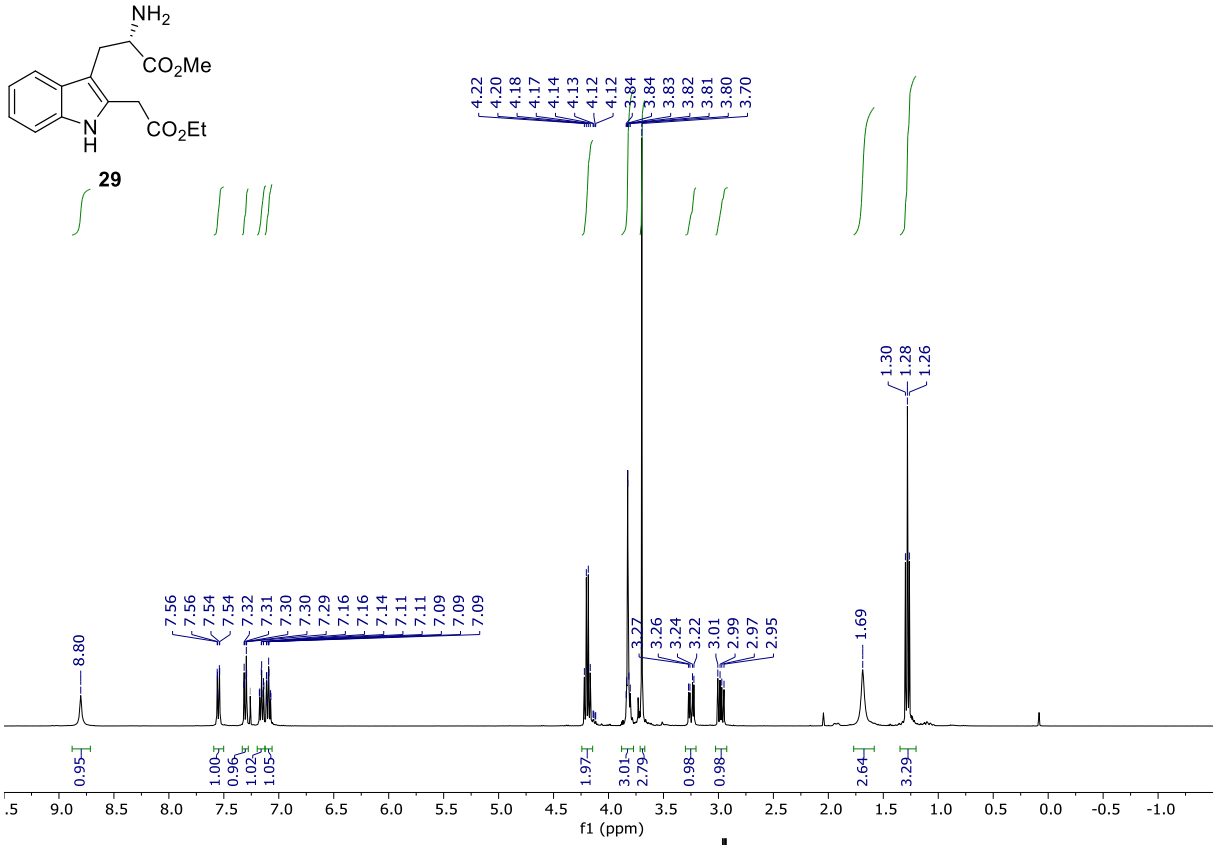


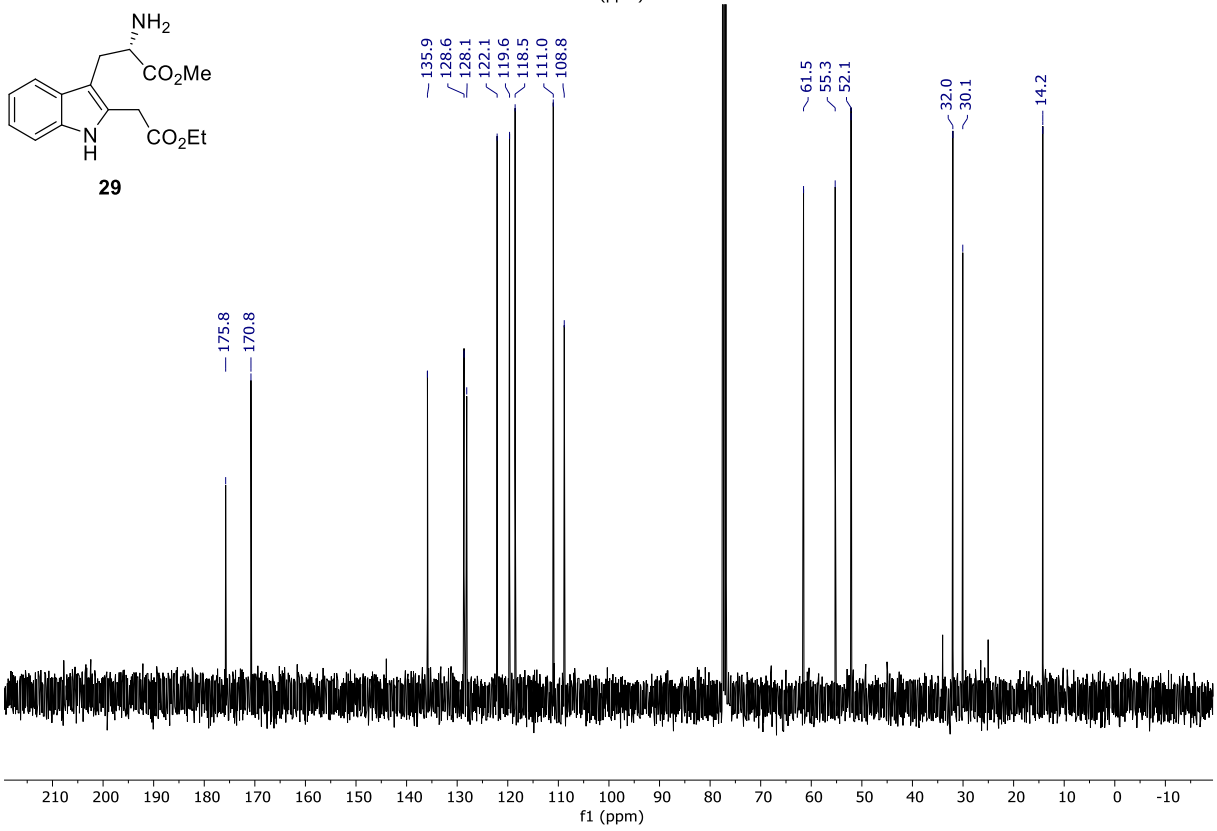
Ethyl (7-cyano-1-methyl-1*H*-indol-2-yl)acetate (**28d**)



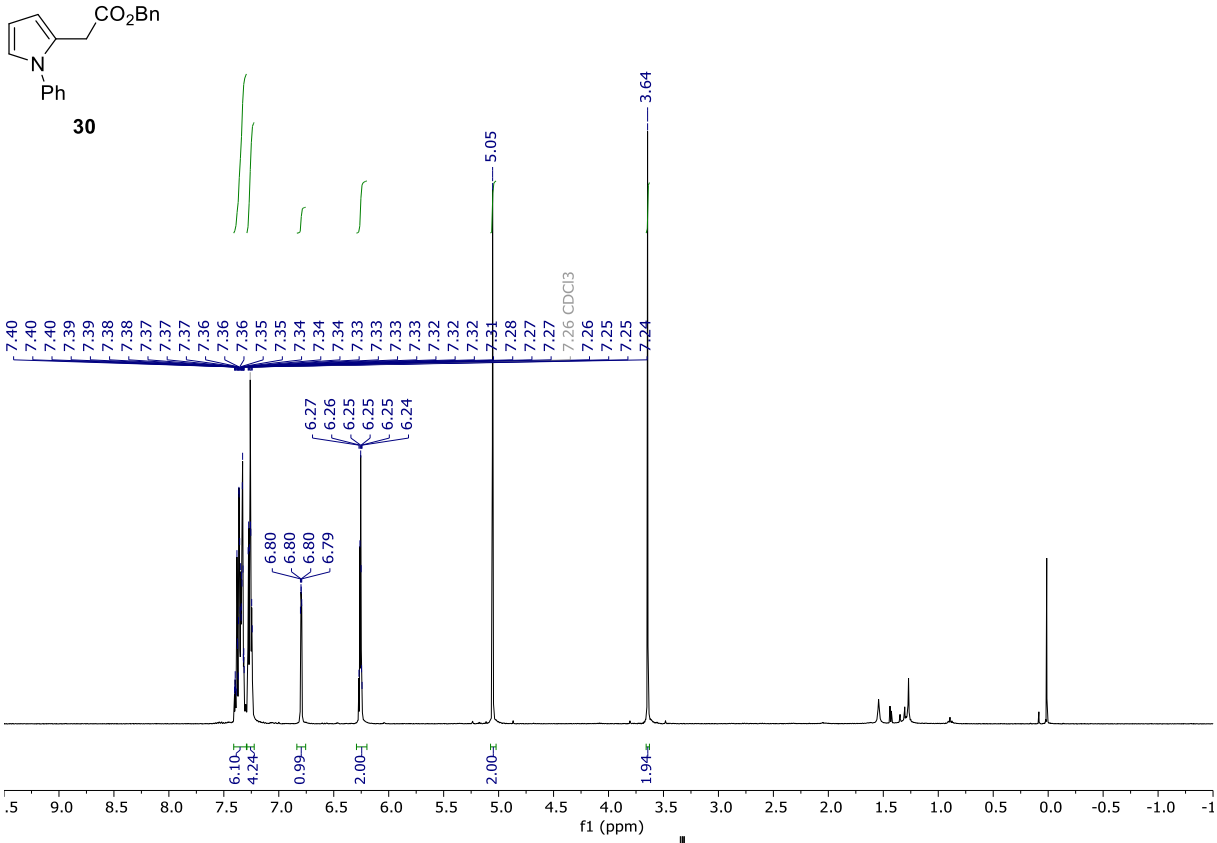


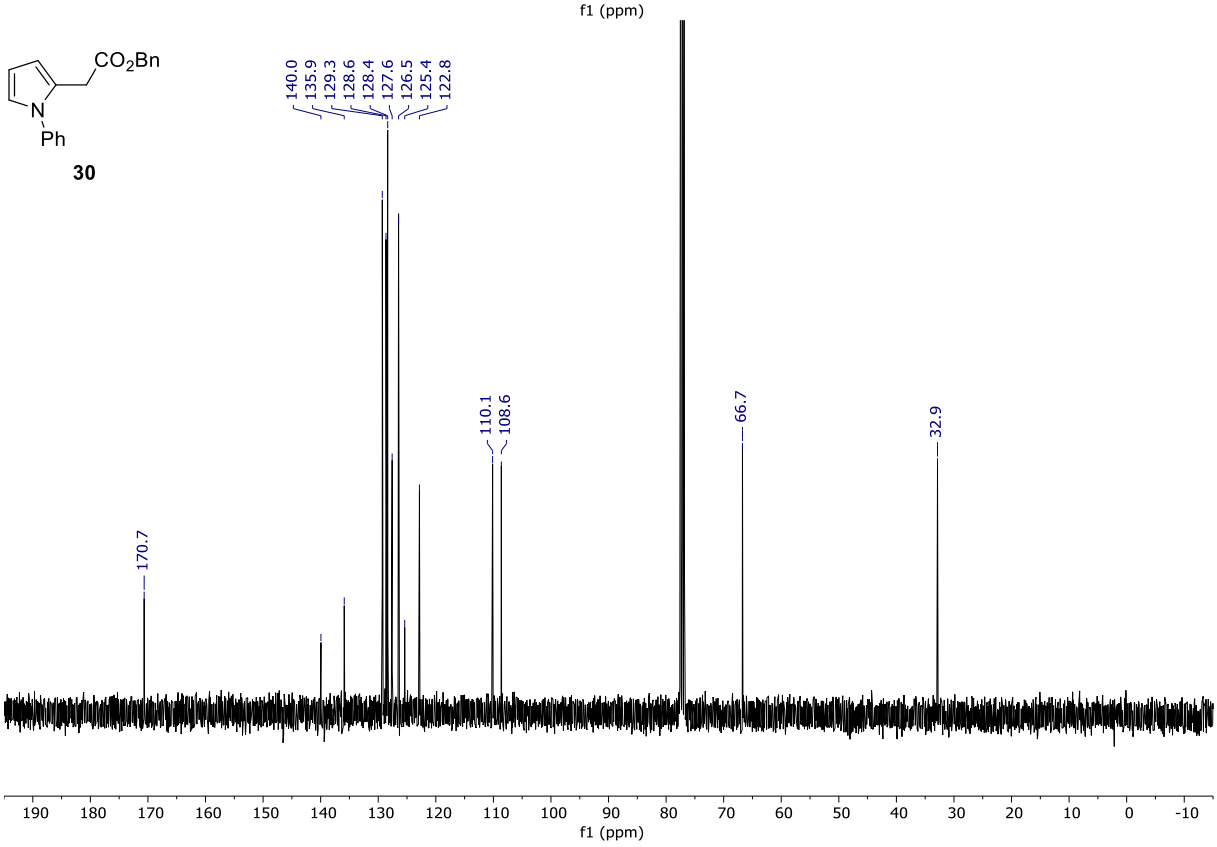
Methyl (2*S*)-2-amino-3-(2-(2-ethoxy-2-oxoethyl)-1*H*-indol-3-yl)propanoate (**29**)



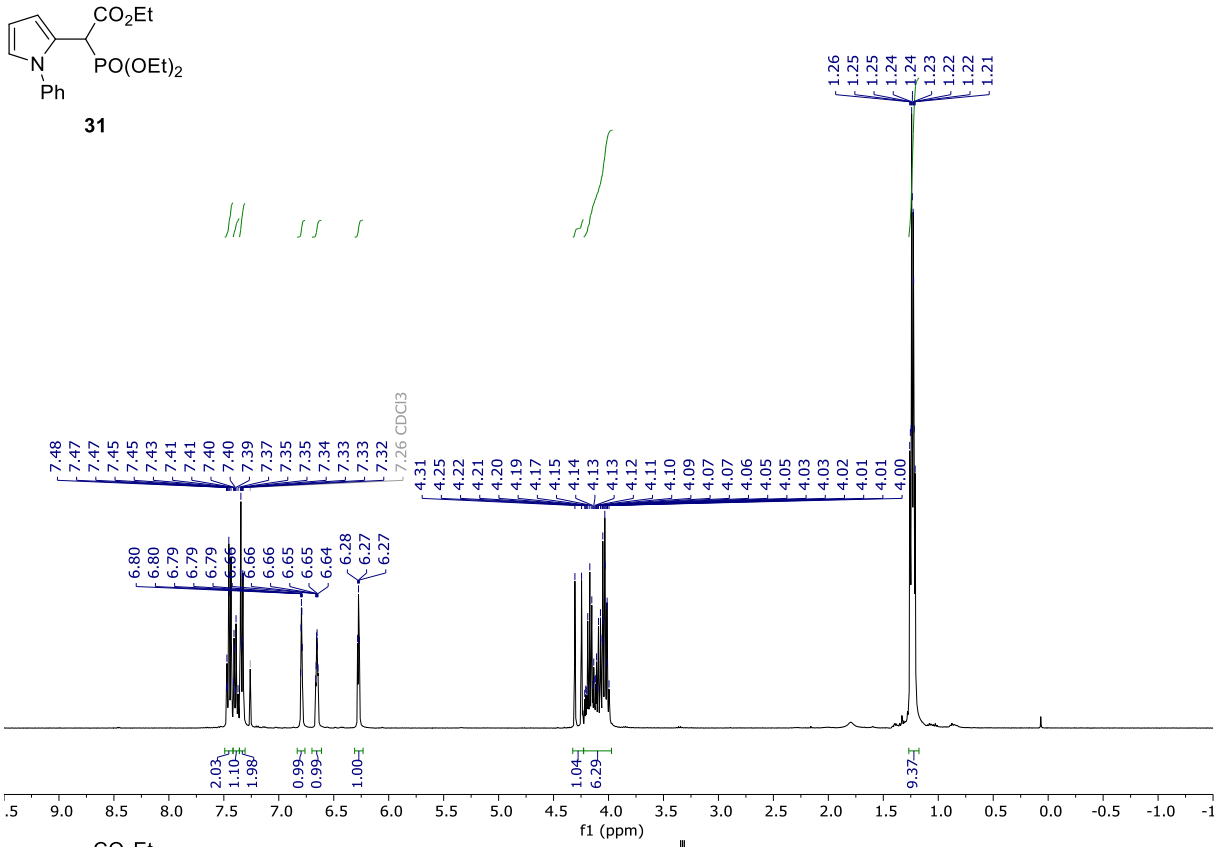


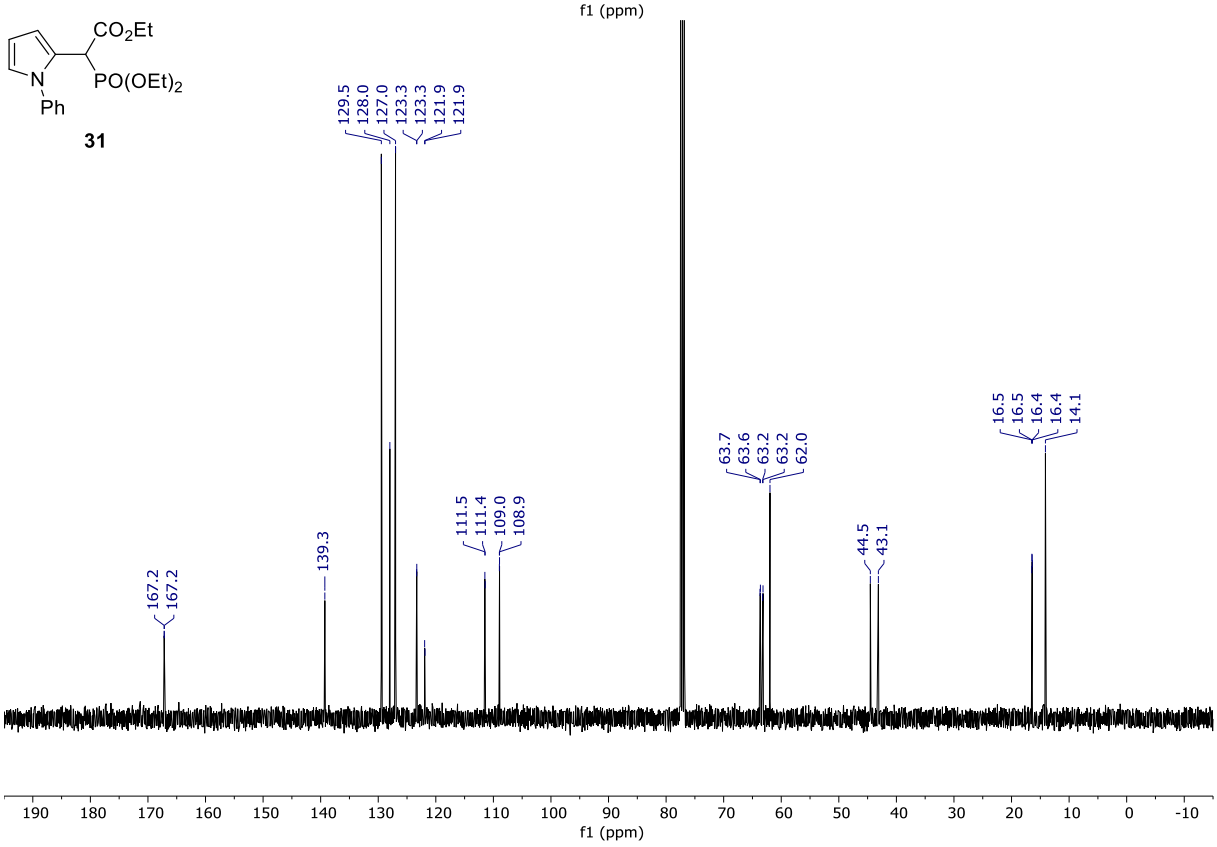
Benzyl (1-phenyl-1*H*-pyrrol-2-yl)acetate (**30**)





Ethyl (diethylphosphono)(1-phenyl-1*H*-pyrrol-2-yl)acetate (**31**)





Ethyl (diethylphosphono)(1-(dimethylamino)-1*H*-pyrrol-2-yl)acetate (**32**)