Supporting Information

Regioselective Synthesis of 2-Substituted Indoles from Benzotriazoles and Alkynes by Photoinitiated Denitrogenation

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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. The solvents used were purified by distillation over standard drying agents and were stored over molecular sieves and transferred under argon. Blue LEDs (5 W, λ_{max} = 455 nm or 3 W, λ_{max} = 420 nm) and UVA LEDs (3 W, λ_{max} = 365 nm) were used for blue and UVA light irradiation, respectively (see figure S1).

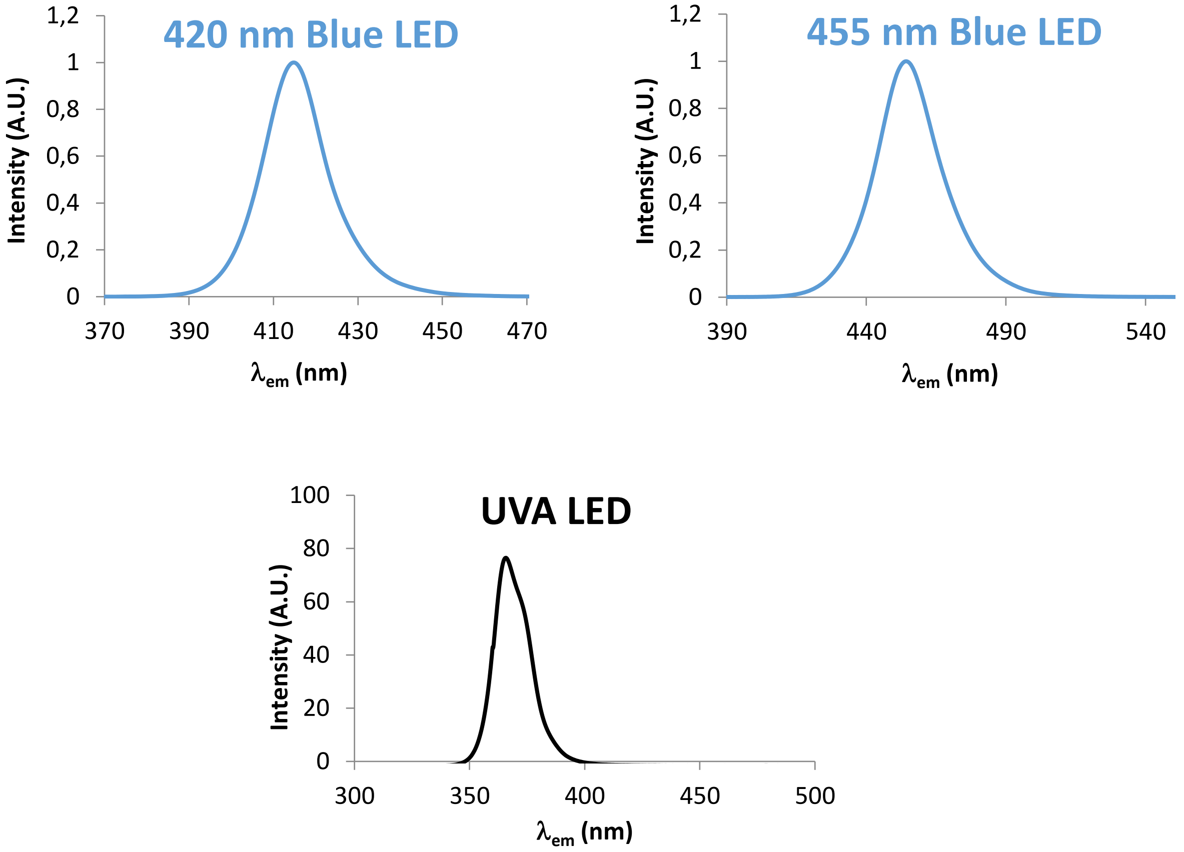


Figure S1. Emission spectra of the used LEDs.

In each case, the light source was placed ~ 5 cm from the reaction vessel. A custom made "light box" was used with 6 LEDs arranged around the reaction vessels (see figure S2). A fan attached to the apparatus was used to maintain the temperature inside the "box" at no more than 9 °C above room temperature.

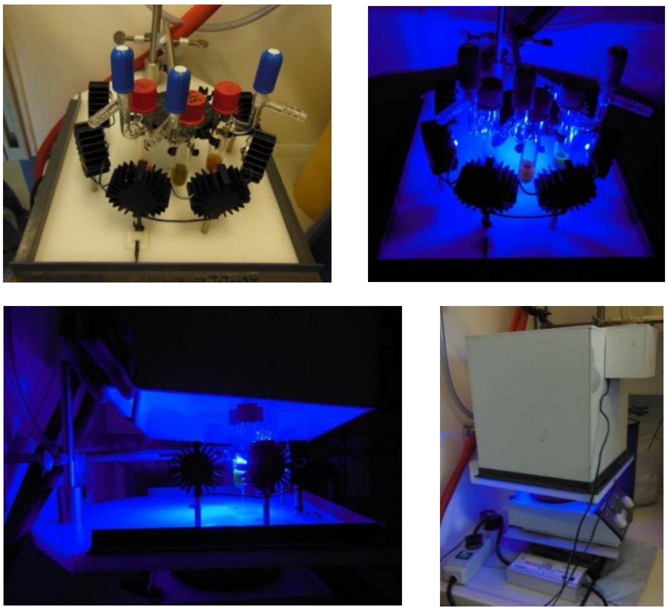
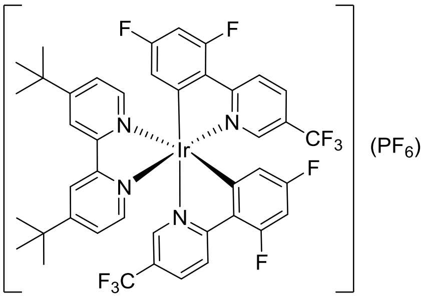


Figure S2. Photographs of the custom-made “light box” used for reactions conducted under blue LED irradiation.

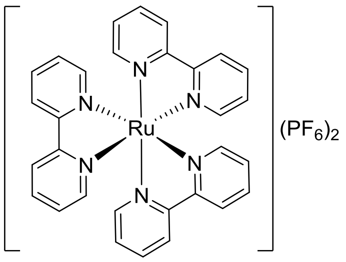
N-Substituted benzotriazoles were prepared following literature procedures: 1-(Benzoyl) benzotriazole (**1a**), 1-(benzoyl)-5-methyl benzotriazole (**1b**),[1] 1-(benzoyl)-5-chloro benzotriazole (**1c**),[1] 1-(benzoyl)-5,6-dimethyl benzotriazole (**1d**),[1] 1-(4-(methoxy)benzoyl) benzotriazole (**1e**),[1] 1-(4-(trifluoromethyl)benzoyl) benzotriazole (**1Ha**),[1] 1-(4-(trifluoromethyl)benzoyl) 5,6-dimethylbenzotriazole (**1Hd**)[1] and 1-(4-(trifluoromethyl)benzoyl) 5-chlorobenzotriazole (**1He**).[1] (Ethynyl-*d*)benzene was synthesized according to literature procedures.[2] (*E*)-*N*-(2-styrylphenyl)benzamide (**15**) was synthesized according to a procedure from Youn et al.[3] All 1*H*-benzotriazoles, all the alkyne derivatives (**2**), diisopropylethylamine (**4**) and any other compounds used in the study were commercially available and used as received. Photocatalysts $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (**16**, $dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-3-trifluoromethylpyridine),[4] $[Ru(bpy)_3]_2(PF_6)_2$ (**17**, bpy = 2,2′-bipyridine), [5] $[Ru(phen)_3](PF_6)_2$ (**18**, phen = 1,10-phenanthroline),[6] $[Ir(ppy)_2(dtbbpy)](PF_6)$ (**3**, ppy = 2-phenylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine),[7] $[Ru(bpz)_3](PF_6)_2$ (**19**, bpz = 2,2′-bipyrazine),[8] *fac*-$[Ir(ppy)_3]$[9] (**20**), $[Ir(ppy)_2(NHC\text{-}F_2)]$ (**21**, $NHC\text{-}F_2$ = 1-(2,4-difluorophenyl)-3-methyl-2,3-dihydro-1H-imidazolydene),[10] and *fac*-$[Ir(dF\text{-}ppy)_3]$ (**22**, dF(ppy) = 2-(2,4-difluorophenyl)pyridine)[10] were prepared according to literature procedures (see figure S3).

Flash chromatography was performed on Merck silica gel (40-63 mesh) using standard techniques.

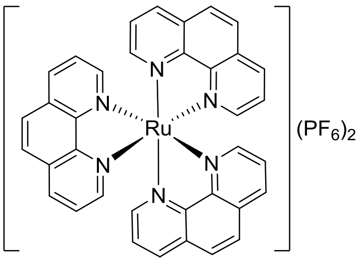
NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.13 ppm). ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (*J*) are quoted in Hz.



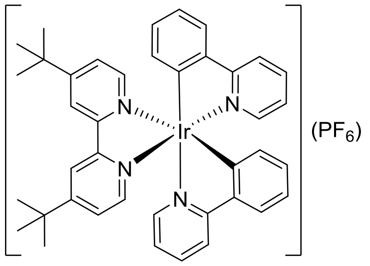
[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$
(**16**)
λ_{em} = 472 nm



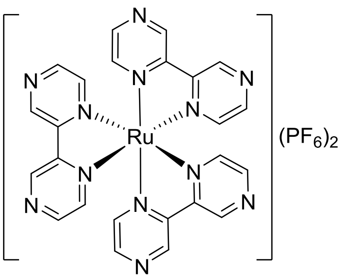
[Ru(bpy)$_3$](PF$_6$)$_2$
(**17**)
λ_{em} = 598 nm



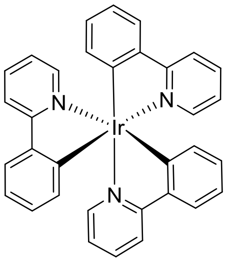
[Ru(phen)$_3$](PF$_6$)$_2$
(**18**)
λ_{em} = 584 nm



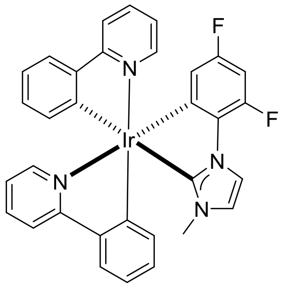
[Ir(ppy)$_2$(dtbbpy)]PF$_6$
(**3**)
λ_{em} = 581 nm



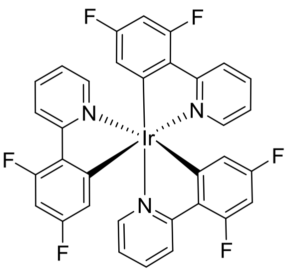
[Ru(bpz)$_3$](PF$_6$)$_2$
(**19**)
λ_{em} = 591 nm



fac-[Ir(ppy)$_3$]
(**20**)
λ_{em} = 494 nm



[Ir(ppy)$_2$(NHC-F$_2$)]
(**21**)
λ_{em} = 491 nm



fac-[Ir(dF(ppy)$_3$)]
(**22**)
λ_{em} = 473 nm

Figure S3. Structures of photocatalysts **16-22** and **3**.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 µm). The major signals are quoted in *m/z* with the relative intensity in parentheses. The method indicated as '50_40' starts with the injection temperature T_0 (50 °C); after holding this temperature for 3 min, the column is heated by 40 °C/min to temperature T_1 (290 °C or 320 °C) and this temperature is held for an additional time t.

GC-FID analysis was undertaken on an Agilent Technologies 6890A equipped with an HP-5 quartz column (0.32 mm x 30 m, film: 0.25 µm) using flame ionization detection. Method: Initial temperature 50 °C, hold 3 min, increment 40 °C/min, final temperature 280 °C, hold 3 min.

ESI mass spectra were recorded on a Bruker Daltonics MicroTof spectrometer.

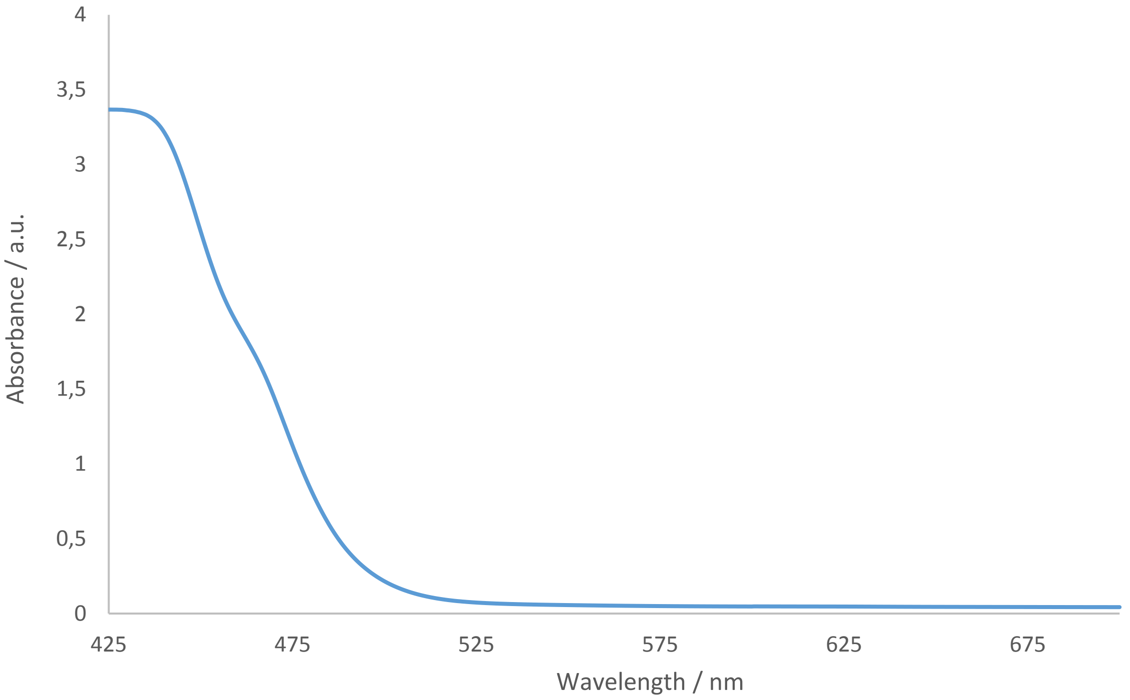
Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur or on a Shimadzu FTIR 8400S spectrometer. The wave numbers (ν) of recorded IR-signals are quoted in cm^{-1}.

Stern-Volmer luminescence quenching analysis was conducted using a Jasco FP-8300 spectrofluorometer. The following parameters were employed: Excitation bandwidth = 5 nm, data interval = 0.2 nm, scan speed = 500 nm/min, response time = 0.2 sec.

UV/vis absorption spectra were recorded on a Jasco V-650 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 1.4 mL, H × W × D = 46 mm × 12.5 mm, 12.5 mm) fitted with a PTFE stopper.

UV/vis absorption spectra and extinction coefficients at 455 nm and 420 nm for $[Ir(ppy)_2(dtbbpy)](PF_6)$ (**3**) can be found in figure S4.

$[Ir(ppy)_2(dtbbpy)](PF_6)$ (3)



Extinction coefficient:

Irradiation wavelength / nm	Extinction coefficient ϵ / L mol^{-1} cm^{-1}
455	4255
420	11881

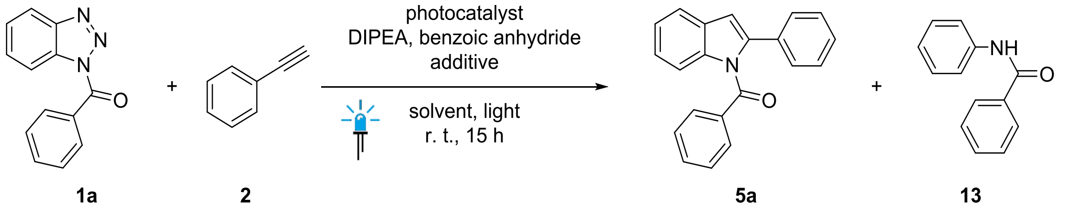
Figure S4. UV/vis absorption spectra and extinction coefficients at 420 nm and 455 nm for $[Ir(ppy)_2(dtbbpy)](PF_6)$ (**3**). The photocatalyst concentration was 0.5 mM. Extinction coefficients were determined using three data points.

2. Photoinitiated Synthesis of 2-Substituted Indoles From 1-(Benzoyl) benzotriazoles

2.1. Optimisation Studies

GENERAL PROCEDURE

1-(Benzoyl) benzotriazole (**1a**, 22 mg, 0.10 mmol, 1.0 equiv), the photocatalyst, phenylacetylene (**2a**), di*iso*propylethylamine (DIPEA, **4**), benzoic anhydride (**7**), the additive and the solvent were added to a dried Schlenk tube in the absence of light. The mixture was degassed using three freeze-pump-thaw cycles, flushed with argon, sealed and stirred under irradiation with the mentioned visible light source. After the specified time, the solution was filtered through a short pad of silica (eluent = EtOAc) and analysed by GC-MS and GC-FID.



Entry	Ratio 1a:2	Solvent	Photocatalyst (mol%)	Equiv DIPEA	Light source	Equiv BA[a]	Additive (equiv)	Yield 5a[b]	Yield 13[b]
1	1:10	DMSO (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	/	/	12	24
2	1:10	DMSO (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	/	/	/	/	/
3	1:10	DMSO (0.1 M)	/	3	455 nm	/	/	1	16
4	1:10	DMSO (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	/	455 nm	/	/	/	/
5	1:10	DMSO (0.1 M)	[Ir(ppy)$_2$(NHC-F$_2$)] (2.5)	3	455 nm	/	/	13	43
6	1:10	DMSO (0.1 M)	[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)] (PF$_6$) (2.5)	3	455 nm	/	/	11	21
7	1:10	DMSO (0.1 M)	*fac*-[Ir(dF(ppy)$_3$)] (2.5)	3	455 nm	/	/	9	22
8	1:10	DMSO (0.1 M)	*fac*-[Ir(ppy$_3$)] (2.5)	3	455 nm	/	/	13	25
9	1:10	DMSO (0.1 M)	[Ru(bpy)$_3$]$_2$(PF$_6$)$_2$ (2.5)	3	455 nm	/	/	6	16
10	1:10	DMSO (0.1 M)	[Ru(bpz)$_3$](PF$_6$)$_2$ (2.5)	3	455 nm	/	/	/	28
11	1:10	DMSO (0.1 M)	[Ru(phen)$_3$](PF$_6$)$_2$ (2.5)	3	455 nm	/	/	5	16
12	1:10	DMF (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	/	/	3	43
13	1:10	Acetone (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	/	/	15	23
14	1:10	MeCN (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	/	/	1	10
15	1:10	CHCl$_3$ (0.1 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	/	/	/	7
16	1:10	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	/	32	27
17	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	/	40	11
18	1:10	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NBr (1.0)	47	20

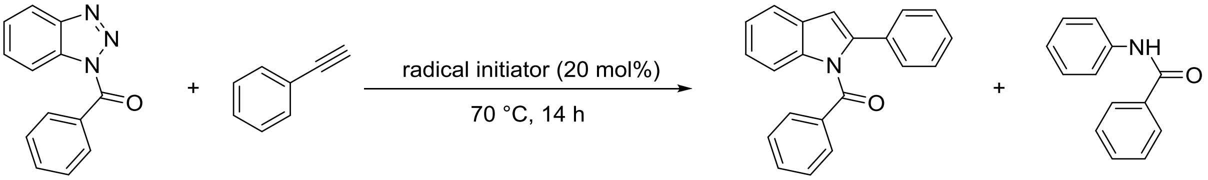
19	1:10	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NI (1.0)	10	17
20	1:10	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NCl (1.0)	60	17
21	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NCl (1.0)	63	8
22	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NCl (2.0)	73	7
23	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	2	^{n}Bu$_4$NCl (0.5)	53	8
24	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	5	455 nm	2	^{n}Bu$_4$NCl (2.0)	69	7
25	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	2	455 nm	2	^{n}Bu$_4$NCl (2.0)	58	6
26	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	69	8
27	neat	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	75	3
28[c]	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2.5)	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	55	9
29	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (1.0)	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	69	7
30	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (5.0)	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	70	9
31	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (1.0)	3	420 nm	0.5	^{n}Bu$_4$NCl (2.0)	67	9
32	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (1.0)	3	365 nm	0.5	^{n}Bu$_4$NCl (2.0)	40	14
33	1:20	DMSO (0.2 M)	/	3	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	3	16
34	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (1.0)	3	/	0.5	^{n}Bu$_4$NCl (2.0)	/	/
35	1:20	DMSO (0.2 M)	[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (1.0)	/	455 nm	0.5	^{n}Bu$_4$NCl (2.0)	/	/

[a] BA = benzoic anhydride. [b] Yields were determined by GC-FID using mesitylene as internal standard. [c] *In situ* generation of 1-(benzoyl) benzotriazole (**1a**) from 1*H*-benzotriazole (12 mg, 0.1 mmol, 1.0 equiv) and benzoic anhydride.

2.2 Attempts to use radical initiators for the denitrogenative synthesis of 2-phenylindoles

GENERAL PROCEDURE

1-(Benzoyl) benzotriazole (**1a**, 22 mg, 0.10 mmol, 1.0 equiv), the radical initiator (20.0 mol%) and phenylacetylene (220 µL, 2 mmol, 20.0 equiv) were added to a dried Schlenk tube in the absence of light and dissolved in DMSO (1 mL, 0.1 M). The mixture was degassed using three freeze-pump-thaw cycles, flushed with argon, sealed and stirred at 70°C for 14 h. After this time, mesitylene (14 µL) was added as an internal standard and the solution was filtered through a short pad of silica (eluent = EtOAc) and analysed by GC-MS and GC-FID.



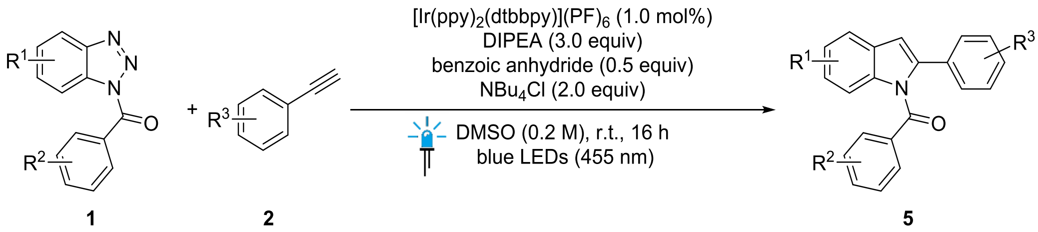
1a **2** **5a** **13**

Entry	Ratio 1a:2	Solvent	Radical initiator (mol%)	Yield 5a[a]	Yield 13[a]	Recovered 1a[a]
1	1:20	DMSO (0.1 M)	Zn (20)	/	8	84
2	1:20	DMSO (0.1 M)	$\mathrm{SmI_2}$ (20)	/	2	81
3	1:20	DMSO (0.1 M)	AIBN (20)	/	4	91
4	1:20	DMSO (0.1 M)	DBPO (20)	/	7	87
5	1:20	DMSO (0.1 M)	$^{n}\mathrm{Bu_4NI}$	/	8	82

[a] Yields were determined by GC-FID using mesitylene as internal standard. DBPO = dibenzoylperoxide, AIBN = Azobis(isobutyronitril), $^{n}\mathrm{Bu_4NI}$ = tetrabutylammonium chloride.

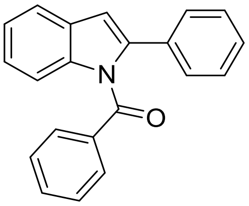
2.3. Scope and Limitation Studies

General Procedure (GP1) for the denitrogenative indole synthesis from 1-(benzoyl) benzotriazoles (1)



[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**3**, 2.7 mg, 0.003 mmol, 1.0 mol%), the 1-(benzoyl) benzotriazole derivative **1** (0.3 mmol, 1.0 equiv), di*iso*propylethylamine (**4**, 154 µL, 0.9 mmol, 3.0 equiv), the corresponding benzoic anhydride (**7**, 0.15 mmol, 0.5 equiv.), the alkyne derivative (**2**, 6.0 mmol, 20.0 equiv) and tetrabutylammonium chloride (**6**, 168 mg, 0.6 mmol, 2.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (1.5 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was backfilled with argon. The reaction mixture was allowed to stir at room temperature for 16 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). After the indicated reaction time, EtOAc (50 mL) was added. The organic layer was washed with distilled water (3 x 40 mL) and brine (50 mL). The mixture was dried over anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. The crude reaction products were purified by column chromatography over silica gel (solvent gradient: eluent = pentane (100%) to pentane/ethyl acetate 90:10) to afford the pure products.

N-Benzoyl-2-phenylindole (5a)[11]

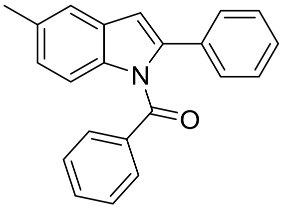


5a

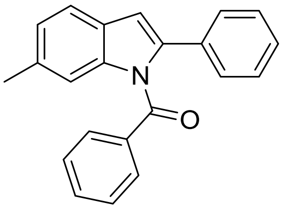
Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (62.4 mg, 70%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.69 (m, 1H), 7.64 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.29 – 7.24 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.15 – 7.11 (m, 1H), 6.78 (s, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 170.2, 141.4, 138.3, 135.2, 132.9, 130.4, 129.4, 128.5, 128.3, 127.7, 124.4, 123.2, 120.8, 114.2, 109.6; **R$_f$ (pentane:EtOAc = 9:1)**: 0.45; **GC-MS: t$_R$ (50_40):** 10.73 min; **EI-MS:** *m/z* (%): 297 (57), 192 (10), 165 (27), 105 (100), 77 (65), 51 (15); **HR-MS (ESI):** *m/z* calculated for [$C_{21}H_{16}NO$]$^+$ ([M+H]$^+$): 298.1226, measured: 298.1228; calculated for [$C_{21}H_{15}NONa$]$^+$ ([M+Na]$^+$): 320.1046, measured: 320.1049; calculated for [($C_{21}H_{15}NO)_2Na$]$^+$ ([M$_2$+Na]$^+$): 617.2199, measured: 617.2205; **IR (ATR): ν (cm^{-1}):** 1681, 1597, 1558, 1489, 1450, 1357, 1319, 1280, 1226, 1149, 918, 748, 694.

N-Benzoyl-2-phenyl 5-methylindole (5b1) / *N*-Benzoyl-2-phenyl 6-methylindole (5b2)



5b1

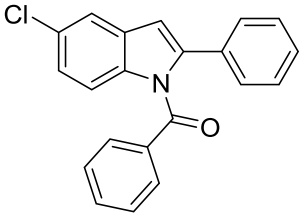


5b2

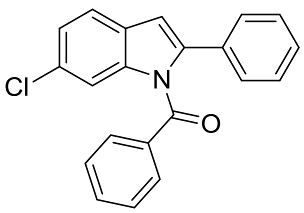
Prepared from 1-(benzoyl) 5-methyl benzotriazole (**1b**, 71.1 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as white solid (48.3 mg, 52%). Products **5b1** and **5b2** were obtained as a mixture which could not be separated using column chromatography. The characterization data for the product mixture is given below. The ratio of **5b1** and **5b2** was determined by NMR to be 60:40.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.64 – 7.55 (m, 3H), 7.53 (d, *J* = 7.7 Hz, 0.38H), 7.43 (m, 68H), 7.41 – 7.33 (m, 1.35H), 7.32 – 7.20 (m, 4H), 7.20 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 7.10 – 7.06 (m, 1H), 6.72 (s, 0.4H), 6.71 (s, 0.6H), 2.47 (s, 1.84H), 2.45 (s, 1.12H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 170.3, 170.1, 141.4, 140.7, 138.8, 136.7, 135.4, 134.5, 133.4, 133.3, 132.8, 130.3, 129.6, 128.5, 128.34, 128.3, 127.6, 127.4, 125.8, 124.8, 120.7, 120.1, 114.4, 114.0, 109.5, 109.4, 22.1, 21.5; **R$_f$ (pentane:EtOAc = 9:1**): 0.36; **GC-MS: t$_R$ (50_40):** 11.21 min; **EI-MS:** *m/z* (%): 311 (40), 206 (14), 204 (15), 179 (15), 105 (100), 77 (88), 51 (16); **HR-MS (ESI):** *m/z* calculated for $[C_{22}H_{18}NO]^+$ ($[M+H]^+$): 312.1383, measured: 312.1374; calculated for $[C_{22}H_{17}NONa]^+$ ($[M+Na]^+$): 334.1202, measured: 334.1198; calculated for $[(C_{22}H_{17}NO)_2Na]^+$ ($[M_2+Na]^+$): 645.2512, measured: 645.2496; **IR (ATR): ν (cm^{-1}):** 1681, 1604, 1489, 1450, 1311, 1296, 1249, 763, 694.

N-Benzoyl-2-phenyl 5-chloroindole (5c1) / *N*-Benzoyl-2-phenyl 6-chloroindole (5c2)



5c1

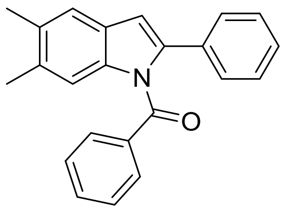


5c2

Prepared from 1-(benzoyl) 5-chloro benzotriazole (**1c**, 77.1 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (65.4 mg, 85%). Products **5c1** and **5c2** were obtained as a mixture which could not be separated using column chromatography. The characterization data for the product mixture is given below. The ratio of **5c1** and **5c2** was determined by NMR to be 62:38.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82 (d, *J* = 1.8 Hz, 0.60H), 7.65 (d, *J* = 8.8 Hz, 0.38H) 7.63 – 7.53 (m, 3H), 7.42 – 7.35 (m, 1.21H), 7.30 – 7.21 (m, 5.2H), 7.21 – 7.09 (m, 3H), 6.74 (s, 0.62H), 6.71 (s, 0.37H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 169.8, 142.5, 141.8, 138.5, 136.5, 134.7, 134.6, 133.0, 132.6, 132.5, 130.3, 130.2, 130.2, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 124.3, 123.8, 121.4, 120.2, 115.1, 114.3, 108.7, 108.4; **R$_f$ (pentane:EtOAc = 9:1**): 0.46; **GC-MS: t$_R$ (50_40):** 11.98 min; **EI-MS:** *m/z* (%): 331 (11), 106 (8), 105 (100), 77 (42), 51 (6); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{14}ClNONa]^+$ ($[M+Na]^+$): 354.0656, measured: 354.0663; calculated for $[(C_{21}H_{14}ClNO)_2Na]^+$ ($[M_2+Na]^+$): 685.1420, measured: 685.1429; **IR (ATR): ν (cm^{-1}):** 1681, 1597, 1450, 1350, 1311, 1280, 1219, 1072, 902, 756, 740, 694.

N-Benzoyl-2-phenyl-5,6-dimethylindole (5d)

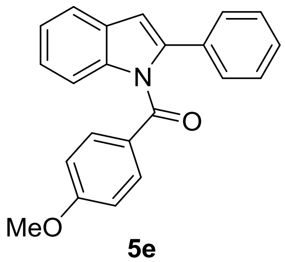


5d

Prepared from 1-(benzoyl)-5,6-dimethyl benzotriazole (**1d**, 75.3 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as yellow oil (71.8 mg, 74%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61 – 7.55 (m, 3H), 7.39 (s, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.17 (m, 4H), 7.13 (tt, *J* = 6.6, 1.1 Hz, 2H), 7.10 – 7.05 (m, 1H), 6.66 (s, 1H), 2.35 (s, 3H), 2.33 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.2, 140.4, 137.2, 135.4, 133.5, 132.6, 132.0, 130.2, 128.3, 128.1, 127.5, 127.2, 120.9, 114.7, 109.3, 20.7, 20.1; **R$_f$ (pentane:EtOAc = 9:1**): 0.39; **GC-MS: t$_R$ (50_40):** 10.15 min; **EI-MS:** *m/z* (%): 325 (23), 106 (8), 105 (100), 77 (36); **HR-MS (ESI):** *m/z* calculated for $[C_{23}H_{20}NO]^+$ ($[M+H]^+$): 326.1539, measured: 326.1536; calculated for $[C_{23}H_{19}NONa]^+$ ($[M+Na]^+$): 348.1359, measured: 348.1356; calculated for $[(C_{23}H_{19}NO)_2Na]^+$ ($[M_2+Na]^+$): 673.2825, measured: 673.2826; **IR (ATR): ν (cm^{-1}):** 1681, 1597, 1458, 1319, 1280, 1226, 1172, 1026, 918, 871, 756, 694, 671.

N-(4-Methoxy)benzoyl-2-phenylindole (5e)

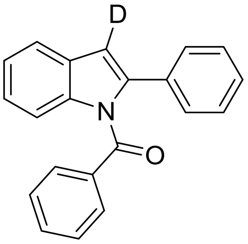


5e

Prepared from N-((4-methoxy)benzoyl) benzotriazole (**1e**, 75.9 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (77.8 mg, 79%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70 – 7.65 (m, 3H), 7.61 – 7.58 (m, 1H), 7.38 – 7.36 (m, 2H), 7.28 – 7.22 (m, 4H), 7.20 – 7.17 (m, 1H), 6.82 – 6.78 (m, 3H), 3.81 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 169.3, 163.5, 141.4, 138.3, 133.0, 132.8, 129.2, 128.2, 128.2, 127.5, 127.2, 123.9, 122.7, 120.7, 113.7, 113.7, 55.5; **R$_f$ (pentane:EtOAc = 95:5**): 0.23; **GC-MS: t$_R$ (50_40):** 12.33 min; **EI-MS:** *m/z* (%): 327 (9), 165 (6), 135 (100), 92 (10), 77 (16); **HR-MS (ESI):** *m/z* calculated for $[C_{22}H_{18}NO_2]^+$ ($[M+H]^+$): 328.1332, measured: 328.1330; calculated for $[C_{22}H_{17}NO_2Na]^+$ ($[M+Na]^+$): 350.1151, measured: 350.1153; calculated for $[(C_{22}H_{17}NO_2)_2Na]^+$ ($[M_2+Na]^+$): 677.2411, measured: 677.2407; **IR (ATR): ν (cm^{-1}):** 1681, 1604, 1512, 1450, 1311, 1257, 1172, 1026, 763, 694.

N-Benzoyl-2-phenyl-3-deuteriumindole (5f)

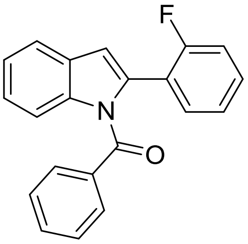


5f

Prepared from 1-(benzoyl) benzotriazole (**1a**, 22.3 mg, 0.1 mmol) and (ethynyl-*d*)benzene (220 µL, 2.0 mmol) following general procedure **GP1** to give the product as white solid (20.1 mg, 67%); 94% deuterium incorporation (determined by ESI-MS).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 – 7.67 (m, 1H), 7.66 – 7.60 (m, 3H), 7.41 – 7.37 (m, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.24 (m, 4H), 7.20 – 7.16 (m, 2H), 7.14 – 7.11 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 170.0, 141.2, 138.2, 135.1, 133.0, 132.8, 129.2, 128.3, 128.1, 127.5, 124.2, 123.1, 120.7, 114.1; **R$_f$ (pentane:EtOAc = 9:1**): 0.44; **GC-MS: t$_R$ (50_40):** 11.21 min; **EI-MS:** *m/z* (%): 298 (42), 166 (7), 105 (100), 77 (33); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{15}DNO]^+$ ($[M+H]^+$): 299.1289, measured: 299.1309; calculated for $[C_{21}H_{14}DNONa]^+$ ($[M+Na]^+$): 321.1109, measured: 321.1126; calculated for $[(C_{21}H_{14}DNO)_2Na]^+$ ($[M_2+Na]^+$): 619.2325, measured: 619.2394; **IR (ATR): ν (cm^{-1}):** 1681, 1489, 1450, 1350, 1319, 1280, 1219, 1149, 902, 748, 694.

N-Benzoyl-2-(2-fluorophenyl)indole (5g)

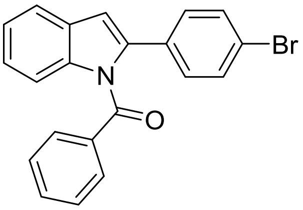


5g

Prepared from N-(benzoyl) benzotriazole (**1a**, 75.9 mg, 0.3 mmol) and 2-ethynyl fluorobenzene (680 µL, 6.0 mmol) following general procedure **GP1** to give the product as beige solid (64.1 mg, 65%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.69 – 7.63 (m, 3H), 7.55 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 7.33 – 7.13 (m, 5H), 7.07 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (ddd, *J* = 10.4, 8.2, 1.2 Hz, 1H), 6.80 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 169.6, 158.8 (d, *J* = 247 Hz), 137.9, 135.2, 134.6, 132.7, 130.4 (d, *J* = 3.1 Hz), 130.3, 129.8 (d, *J* = 8.0 Hz), 129.1, 128.2, 124.4, 124.2 (d, *J* = 16.1 Hz), 123.0, 121.7, 121.6, 120.9, 115.4 (d, *J* = 22.1 Hz), 114.3, 111.0; **^{13}F{^{1}H} NMR (282 MHz, CDCl$_3$):** δ -112.9 Hz; **R$_f$ (pentane:EtOAc = 9:1**): 0.36; **GC-MS: t$_R$ (50_40):** 10.72 min; **EI-MS:** *m/z* (%): 325 (55), 183 (28), 105 (100), 77 (62), 51 (13); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{14}FNONa]^+$ ($[M+Na]^+$): 338.0952, measured: 338.0962; calculated for $[(C_{21}H_{14}FNO)_2Na]^+$ ($[M_2+Na]^+$): 653.2011, measured: 653.2039; **IR (ATR): ν (cm^{-1}):** 1689, 1489, 1450, 1319, 1280, 1219, 925, 748, 702, 655.

N-Benzoyl-2-(4-bromophenyl)indole (5h)

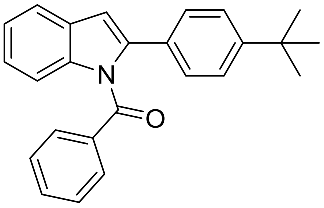


5h

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-bromo phenylacetylene (1.08 g, 6.0 mmol) following general procedure **GP1** to give the product as yellow solid (70.7 mg, 63%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.64 (m, 3H), 7.59 (d, *J* = 7.8 Hz 1H), 7.47 (d, *J* = 7.5 Hz 1H), 7.35 – 7.23 (m, 6H), 7.20 – 7.16 (m, 2H), 6.78 (s, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 170.0, 140.1, 138.4, 135.0, 133.3, 132.1, 131.5, 130.4, 129.8, 129.2, 128.6, 124.6, 123.4, 121.8, 121.0, 114.2, 110.1; **R$_f$ (pentane:EtOAc = 95:5)**: 0.37; **GC-MS: t$_R$ (50_40):** 12.33 min; **EI-MS:** *m/z* (%):377 (27), 375 (27), 191 (16), 190 (17), 105 (100), 77 (55); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{15}BrNO]^+$ ($[M+H]^+$): 378.0332, measured: 378.0312; calculated for $[C_{21}H_{14}BrNONa]^+$ ($[M+Na]^+$): 398.0151, measured: 398.0144; **IR (ATR): ν (cm^{-1}):** 1681, 1597, 1489, 1450, 1319, 1288, 1219, 1149, 1072, 1010, 918, 887, 833, 810, 732, 694.

N-Benzoyl-2-(4-*tert*-butylphenyl)indole (5i)

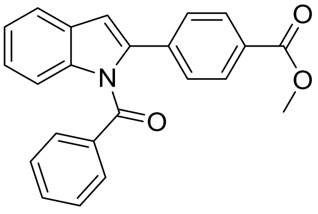


5i

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-(*tert*-butyl)phenylacetylene (1080 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (97.8 mg, 92%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68 – 7.59 (m, 4H), 7.39 – 7.35 (m, 1H), 7.27 – 7.17 (m, 8H), 6.76 (s, 1H), 1.23 (s, 9H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.3, 150.6, 141.5, 138.3, 135.3, 132.7, 130.3, 130.2, 129.5, 128.3, 125.2, 124.1, 123.2, 120.7, 114.2, 109.1, 34.6, 31.2; **R$_f$ (pentane:EtOAc = 9:1)**: 0.43; **GC-MS: t$_R$ (50_40):** 12.63 min; **EI-MS:** *m/z* (%): 353 (33), 105 (100), 77 (32); **HR-MS (ESI):** *m/z* calculated for $[C_{25}H_{23}NONa]^+$ ($[M+Na]^+$): 376.1672, measured: 376.1682; calculated for $[(C_{25}H_{23}NO)_2Na]^+$ ($[M_2+Na]^+$): 729.3451, measured: 729.3460; **IR (ATR): ν (cm^{-1}):** 2360, 1681, 1597, 1504, 1473, 1450, 1357, 1311, 1273, 1226, 1149, 1018, 925, 833, 810, 748, 702.

N-Benzoyl-2-(methyl)benzoateindole (5j)

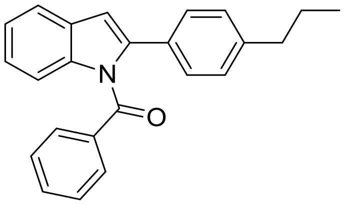


5j

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and methyl-4-ethynylbenzoate (961 mg, 6.0 mmol) following general procedure **GP1** (NMR-yield using CH_2Br_2: 46%). Product decomposition observed during purification process.

R_f (pentane:EtOAc = 9:1): 0.34; **GC-MS: t_R (50_40):** 13.52 min; **EI-MS:** *m/z* (%): 355 (12), 105 (100), 77 (33); **HR-MS (ESI):** *m/z* calculated for $[C_{23}H_{17}NO_3Na]^+$ ($[M+Na]^+$): 378.1101, measured: 378.1105; **IR (ATR) (crude): ν (cm^{-1}):** 1720, 1651, 1604, 1543, 1435, 1280, 1111, 1018, 763.

N-Benzoyl-2-(4-propylphenyl)indole (5k)

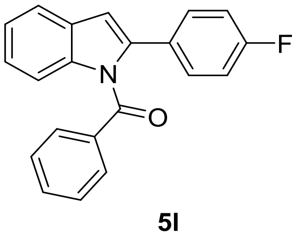


5k

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-propylphenylacetylene (955 µL, 6.0 mmol) following general procedure **GP1** to give the product as yellowish oil (49.1 mg, 49%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 1H), 7.67 – 7.58 (m, 3H), 7.40 – 7.35 (m, 1H), 7.30 – 7.18 (m, 6H), 6.98 (dd, *J* = 8.3, 2.3 Hz, 2H), 6.76 (s, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 1.59 – 1.53 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 170.3, 142.2, 141.6, 138.3, 135.4, 132.7, 130.5, 130.3, 129.5, 128.4, 128.4, 128.3, 124.2, 123.2, 120.7, 114.2, 109.0, 37.7, 24.4, 13.7; **R_f (pentane:EtOAc = 9:1**): 0.37; **GC-MS: t_R (50_40):** 12.37 min; **EI-MS:** *m/z* (%): 339 (19), 204 (9), 105 (100), 77 (34); **HR-MS (ESI):** *m/z* calculated for $[C_{24}H_{21}NONa]^+$ ($[M+Na]^+$): 362.1515, measured: 362.1518; calculated for $[(C_{24}H_{21}NO)_2Na]^+$ ($[M_2+Na]^+$): 701.3138, measured: 701.3140; **IR (ATR): ν (cm^{-1}):** 1684, 1604, 1450, 1311, 1280, 111, 1018, 748, 702, 624.

N-Benzoyl-2-(2-fluorophenyl)indole (5l)

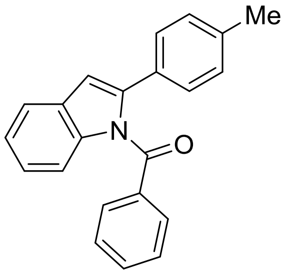


5l

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-flurophenylacetylene (688 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (67.2 mg, 71%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.68 – 7.59 (m, 4H), 7.46 – 7.42 (m, 1H), 7.31 – 7.24 (m, 6H), 6.92 – 6.86 (m, 2H), 6.75 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 170.05, 162.2 (d, *J* = 240 Hz), 140.2, 138.3, 135.1, 133.1, 130.3, 130.1 (d, *J* = 8.5 Hz), 129.4 (d, *J* = 3.7 Hz), 129.3, 128.5, 124.4, 123.3, 120.8, 115.4 (d, *J* = 22 Hz), 114.2, 109.6; **^{13}F{^{1}H} NMR (282 MHz, CDCl$_3$):** δ -113.8 Hz; **R_f (pentane:EtOAc = 9:1**): 0.41; **GC-MS: t_R (50_40):** 10.58 min; **EI-MS:** *m/z* (%): 315 (52), 208 (10), 183 (28), 105 (100), 77 (59), 51 (13); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{15}FNO]^+$ ($[M+H]^+$): 316.1132, measured: 316.1128; calculated for $[C_{21}H_{14}FNONa]^+$ ($[M+Na]^+$): 338.0952, measured: 338.0956; calculated for $[(C_{21}H_{14}FNO)_2Na]^+$ ($[M_2+Na]^+$): 653.2011, measured: 653.2020; **IR (ATR): ν (cm^{-1}):** 1681, 1597, 1504, 1450, 1311, 1288, 1226, 1157, 925, 840, 810, 759, 702, 663, 617.

N-Benzoyl-2-(4-methylphenyl)indole (5m)

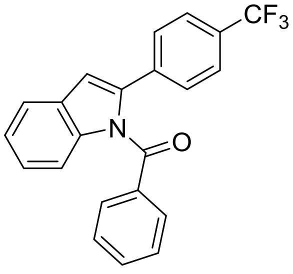


5m

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-methylphenylacetylene (761 µL, 6.0 mmol) following general procedure **GP1** to give the product as light yellow solid (72 mg, 77%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 – 7.50 (m, 4H), 7.35 – 7.29 (m, 1H), 7.21 – 7.08 (m, 6H), 6.93 – 6.88 (m, 2H), 6.66 (s, 1H), 2.16 (s, 3H).; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.2, 141.6, 138.2, 137.5, 135.2, 132.9, 130.4, 130.2, 129.5, 129.0, 128.4, 128.3, 124.1, 123.1, 120.7, 114.1, 109.1, 21.3; **R_f (pentane/EtOAc = 99:1):** 0.5; **GC-MS: t_R (50_40):** 11.64 min; **EI-MS:** *m/z* 311 (38), 207 (12), 105 (100), 77 (34). **HR-MS (ESI):** *m/z* calculated for $[C_{22}H_{17}NONa]^+$ ($[M+Na]^+$): 334.1202, measured 334.1211; **IR (ATR): ν (cm^{-1}):** 1681, 1651, 1543, 1504, 1450, 1319, 1288, 925, 802, 748, 702, 555.

N-Benzoyl-2-(4-(trifluoromethyl)phenyl)indole (5n)



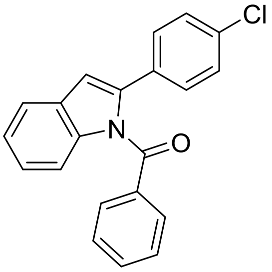
5n

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-(trifluoromethyl)-phenylacetylene (989 µL, 6.0 mmol) following general procedure **GP1** to give the product as a light yellow solid (92 mg, 84%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 – 7.60 (m, 1H), 7.54 (dd, *J* = 7.7, 1.8 Hz, 3H), 7.51 – 7.38 (m, 5H), 7.35 – 7.27 (m, 3H), 7.24 (d, *J* = 2.3 Hz, 1H), 6.85 (s, 1H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ

169.8, 139.8, 138.5, 136.7, 134.9, 133.4, 130.4, 129.4 (q, *J* = 32.5 Hz), 129.2, 128.5, 125.3 (q, *J* = 3.8 Hz), 124.9, 123.5, 121.2, 114.3, 111.0 (1 signal missing); **^{19}F NMR{^{1}H} (282 MHz, CDCl$_3$):** δ -62.7; **R$_f$ (Pentane/EtOAc = 99/1):** 0.1; **GC-MS: t$_R$ (50_40):** 10.42 min; **EI-MS:** *m/z* (%): 365 (15), 233 (5), 105 (100), 77 (39); **HR-MS (ESI):** *m/z* calculated for $[C_{22}H_{14}F_3NONa]^+$ ($[M+Na]^+$): 388.0920, measured 388.0924; **IR (ATR): ν (cm^{-1}):** 1674, 1620, 1450, 1319, 1111, 1072, 1018, 817, 745, 702.

N-Benzoyl-2-(4-chlorophenyl)indole (5o)

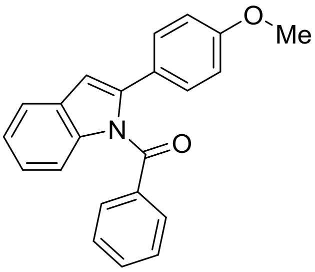


5o

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-chlorophenylacetylene (819 mg, 6.0 mmol) following general procedure **GP1** to give the product as a yellow oil (78 mg, 79%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.7 – 7.6 (m, 4H), 7.5 (t, *J* = 7.5 Hz, 1H), 7.4 – 7.1 (m, 8H), 6.8 (s, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 169.9, 140.1, 138.3, 135.0, 133.6, 133.2, 131.6, 130.3, 129.5, 129.2, 128.6, 128.5, 124.6, 123.3, 120.9, 114.2, 110.0; **R$_f$ (pentane/EtOAc = 99:1):** 0.2; **GC-MS: t$_R$ (50_40):** 11.63 min; **EI-MS:** *m/z* (%) 331 (41), 199 (15), 190 (14), 105 (100), 77 (56), 51 (12); **HR-MS (ESI):** *m/z* calculated for calculated for $[C_{21}H_{14}ClNONa]^+$ ($[M+Na]^+$): 354.0656, measured 354.0692; **IR (ATR): ν (cm^{-1}):** 1681, 1489, 1450, 1319, 1288, 1226, 1067, 1010, 918, 833, 810, 732, 702, 578.

N-Benzoyl-2-(4-methoxyphenyl)indole (5p)

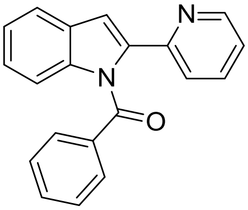


5p

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 4-methoxyphenylacetylene (778 µL, 6.0 mmol) following general procedure **GP1** to give the product as a yellow oil (64 mg, 65%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.7 – 7.6 (m, 4H), 7.4 (t, *J* = 7.4 Hz, 1H), 7.3 – 7.2 (m, 6H), 6.7 (m, 3H), 3.7 (s, 3H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 170.3, 159.1, 141.2, 138.1, 135.2, 132.9, 130.3, 129.7, 129.5, 128.4, 125.7, 124.0, 123.1, 120.6, 114.1, 113.8, 108.6, 55.3; **R$_f$ (pentane/EtOAc = 95:5):** 0.1; **GC-MS: t$_R$ (50_40):** 12.19 min; **EI-MS:** *m/z* (%) 327 (25), 178 (7), 105 (100), 77 (38); **HR-MS (ESI):** *m/z* calculated for calculated for $[C_{22}H_{17}NO_2Na]^+$ ($[M+Na]^+$): 350.1151, measured 350.1167; **IR (ATR): ν (cm^{-1}):** 1681, 1612, 1504, 1450, 1319, 1280, 1249, 1226, 1180, 1026, 925, 833, 810, 748, 702.

N-Benzoyl-2-(pyridin-2-yl)indole (5q)

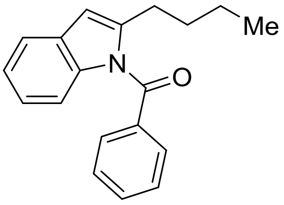


5q

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 2-ethynylpyridine (606 µL, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (70.4 mg, 79%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.29 (dt, *J* = 4.9, 1.5 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.71 – 7.67 (m, 1H), 7.67 – 7.61 (m, 2H), 7.55 – 7.52 (m, 2H), 7.40 – 7.20 (m, 5H), 7.05 (s, 1H), 6.94 (ddd, *J* = 6.0, 4.9, 2.6 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.3, 151.2, 149.1, 140.2, 138.7, 136.2, 132.56, 129.8, 128.8, 128.3, 125.0, 123.0, 122.4, 121.7, 121.4, 113.9, 109.6; **R$_f$ (pentane:EtOAc = 9:1)**: 0.29; **GC-MS: t$_R$ (50_40):** 11.37 min; **EI-MS:** *m/z* (%): 298 (13), 270 (10), 105 (100), 77 (49); **HR-MS (ESI):** *m/z* calculated for $[C_{20}H_{15}N_2O]^+$ ($[M+H]^+$): 299.1179, measured: 299.1182; calculated for $[C_{20}H_{14}N_2ONa]^+$ ($[M+Na]^+$): 321.0998, measured: 32.1003; calculated for $[(C_{20}H_{14}N_2O)_2Na]^+$ ($[M_2+Na]^+$): 619.2104, measured: 619.2097; **IR (ATR): ν (cm^{-1}):** 3063, 1697, 1589, 1558, 1442, 1311, 1273, 1226, 1149, 926, 887, 779, 748, 702, 655, 563.

N-Benzoyl-2-butylindole (5u)

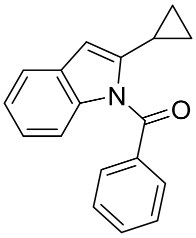


5u

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and 1-hexyne (689 µL, 6.0 mmol) following general procedure **GP1** to give the product as a yellow solid (17 mg, 21%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 – 7.71 (m, 2H), 7.66 – 7.61 (m, 1H), 7.49 (td, *J* = 7.9, 1.8 Hz, 3H), 7.13 (ddd, *J* = 7.9, 7.2, 1.0 Hz, 1H), 6.98 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 6.86 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.48 (q, *J* = 1.0 Hz, 1H), 2.84 (t, *J* = 7.2 Hz, 2H), 1.62 (dt, *J* = 15.4, 7.5 Hz, 2H), 1.34 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.1, 143.2, 137.4, 135.6, 133.2, 130.0, 129.6, 128.9, 122.6, 122.5, 120.1, 114.2, 107.4, 31.3, 28.7, 22.6, 14.0; **R$_f$ (pentane/EtOAc = 99:1):** 0.3; **GC-MS: t$_R$ (50_40):** 10.05 min; **EI-MS:** *m/z* (%) 267 (5), 256 (51), 255 (12), 239 (10), 183 (36), 178 (28), 165 (14); **HR-MS (ESI):** *m/z* calculated for $[C_{19}H_{19}NONa]^+$ ($[M+Na]^+$): 300.1359, measured 300.1363; **IR (ATR): ν (cm^{-1}):** 1681, 1651, 1519, 1458, 1396, 1319, 1257, 748, 609, 555.

(2-Cyclopropyl-1*H*-indol-1-yl)(phenyl)methanone (5v)

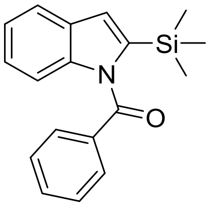


5v

Prepared from 1-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol) and cyclopropylacetylene (507 µL, 6.0 mmol) following general procedure **GP1** to give the product as a yellow oil (24 mg, 31%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.46 (m, 3H), 7.30 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 6.33 (t, *J* = 1.0 Hz, 1H), 1.81 (dddd, *J* = 12.1, 8.2, 5.4, 1.2 Hz, 1H), 0.77 – 0.65 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 170.2, 144.3, 137.5, 136.0, 132.8, 129.9, 129.3, 128.7, 123.2, 122.8, 120.1, 114.4, 106.0, 10.5, 8.5; **R$_f$ (pentane/EtOAc = 99:1):** 0.2; **GC-MS: t$_R$ (50_40):** 10.03 min; **EI-MS:** *m/z* (%) 261 (25), 233 (11), 105 (100), 77 (42) **HR-MS (ESI):** *m/z* calculated for $[C_{18}H_{15}NONa]^+$ ($[M+Na]^+$): 284.1046, measured 284.1058; **IR (ATR): ν (cm^{-1}):** 1681, 1519, 1451, 1319, 1296, 1211, 1172, 878, 748, 702, 571.

N-Benzoyl-2-trimethylsilylindole (5w)

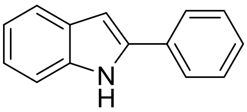


5w

Prepared from *N*-(benzoyl) benzotriazole (**1a**, 75.9 mg, 0.3 mmol) and trimethylsilylacetylene (831 µL, 6.0 mmol) following general procedure **GP1** to give the product as colorless oil (35.1 mg, 40%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 – 7.68 (m, 2H), 7.65 (ddt, *J* = 8.8, 7.9, 1.3 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.12 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.00 (s, 1H), 6.94 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 0.41 (s, 9H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 169.8, 143.3, 138.7, 135.5, 132.5, 131.7, 123.7, 122.7, 121.0, 120.7, 114.7, 0.1; **R$_f$ (pentane:EtOAc = 9:1**): 0.57; **GC-MS: t$_R$ (50_40):** 9.51 min; **EI-MS:** *m/z* (%): 293 (6), 280 (6), 279 (25), 278 (100), 105 (48), 77 (37); **HR-MS (ESI):** *m/z* calculated for $[C_{18}H_{19}NOSiNa]^+$ ($[M+Na]^+$): 316.1128, measured: 316.1141; calculated for $[(C_{18}H_{19}NOSi)_2Na]^+$ ($[M_2+Na]^+$): 609.2364, measured: 609.2372; **IR (ATR): ν (cm^{-1}):** 2360, 2337, 1681, 1357, 1327, 1249, 1111, 1087, 1026, 848, 748, 702, 665.

2-Phenylindole (5Ha)[12]

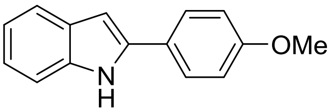


5Ha

Prepared from 1-(4-(trifluoromethyl)benzoyl) benzotriazole (**1a**, 87.3 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as white solid (30.6 mg, 53%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.41 – 8.29 (bs, 1H), 7.70 – 7.63 (m, 3H), 7.47 – 7.40 (m, 3H), 7.36 – 7.32 (m, 1H), 7.23 – 7.19 (m, 1H), 7.14 (m, 1H), 6.85 (s, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.0, 136.9, 132.5, 129.4, 129.2, 127.8, 125.3, 122.5, 120.8, 120.4, 111.0, 100.1; **R$_f$ (pentane:EtOAc = 9:1)**: 0.32; **GC-MS: t$_R$ (50_40):** 9.12 min; **EI-MS:** *m/z* (%): 193 (100), 165 (26), 89 (10); **HR-MS (ESI):** *m/z* calculated for [$C_{14}H_{11}NNa$]$^+$ ([M+Na]$^+$): 216.0784, measured: 216.0777; **IR (ATR): ν (cm^{-1}):** 2360, 1681, 1643, 1450, 1327, 1265, 794, 740, 686.

2-(4-Methoxyphenyl)indole (5Hb)[13]

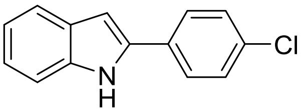


5Hb

Prepared from 1-(4-(trifluoromethyl)benzoyl) benzotriazole (**1a**, 87.3 mg, 0.3 mmol) and ethynylanisole (777 mg, 6.0 mmol) following general procedure **GP1** to give the product as pale yellow solid (23.1 mg, 35%).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.4 (s, 1H), 7.8 (d, *J* = 8.9 Hz, 2H), 7.5 (d, *J* = 8.2 Hz, 1H), 7.4 (d, *J* = 7.0 Hz, 1H), 7.1 – 6.9 (m, 4H), 6.8 (d, *J* = 1.3 Hz, 1H), 3.8 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, DMSO-d$_6$):** δ 158.8, 137.8, 136.9, 128.8, 126.4, 124.9, 121.1, 119.7, 119.2, 114.4, 111.1, 97.3, 55.2; **R$_f$ (pentane:EtOAc = 20:1)**: 0.08; **GC-MS: t$_R$ (50_40):** 10.15 min; **EI-MS:** *m/z* (%): 223 (100), 208 (74), 180 (28), 152 (13), 111 (17).

2-(4-Chlorophenyl)indole (5Hc)[14]

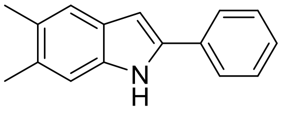


5Hc

Prepared from 1-(4-(trifluoromethyl)benzoyl) benzotriazole (**1a**, 87.3 mg, 0.3 mmol) and 4-clorophenylacetylene (816 mg, 6.0 mmol) following general procedure **GP1** to give the product as off-white solid (42.1 mg, 62%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.4 (s, 1H), 7.6 (d, *J* = 7.8 Hz, 1H), 7.6 – 7.5 (m, 2H), 7.5 – 7.3 (m, 3H), 7.2 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.2 – 7.1 (m, 1H), 6.8 (d, *J* = 1.3 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$):** δ 137.0, 136.8, 133.5, 131.0, 129.3, 129.2, 126.4, 122.8, 120.8, 120.5, 111.1, 100.5; **R$_f$ (pentane:EtOAc = 20:1)**: 0.29; **GC-MS: t$_R$ (50_40):** 9.95 min; **EI-MS:** *m/z* (%): 227 (100), 165 (18), 114 (14); **HR-MS (ESI):** *m/z* calculated for [$C_{14}H_{11}ClN$]$^+$ ([M+H]$^+$): 228.0575, measured: 228.0575.

5,6-Dimethyl-2-phenylindole (5Hd)[15]

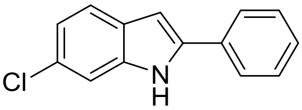


5Hd

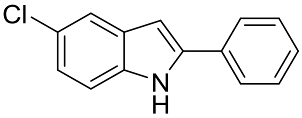
Prepared from 1-(4-(trifluoromethyl)benzoyl) 5,6-dimethylbenzotriazole (**1Hd**, 95.7 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give the product as white solid (24.8 mg, 37%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16 (bs, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.5, 2H), 7.34 – 7.27 (m, 2H), 7.18 (s, 1H), 6.72 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** 137.0, 135.9, 132.7, 131.5, 129.0, 128.9, 127.6, 127.3, 124.9, 120.7, 111.3, 99.4, 20.6, 20.1; **R$_f$ (pentane:EtOAc = 9:1**): 0.37; **GC-MS: t$_R$ (50_40):** 10.27 min; **EI-MS:** *m/z* (%): 221 (100), 220 (47), 206 (35), 204 (26), 115 (28); **HR-MS (ESI):** *m/z* calculated for $[C_{16}H_{16}N]^+$ ($[M+H]^+$): 222.1277, measured: 122.1265.

5-Chloro-2-phenylindole (5Hea) / 6-Chloro-2-phenylindole (5Heb)[16]



5Heb



5Hea

Prepared from 1-(4-(trifluoromethyl)benzoyl) 5-chlorobenzotriazole (**1He**, 97.5 mg, 0.3 mmol) and phenylacetylene (658 µL, 6.0 mmol) following general procedure **GP1** to give 6-Chloro-2-phenylindole (**5Hea**, 24.5 mg, 36%, white solid) and 5-Chloro-2-phenylindole (**5Heb**, 16 mg, 23%, white solid).

Characterization data for 6-Chloro-2-phenylindole (5Heb)

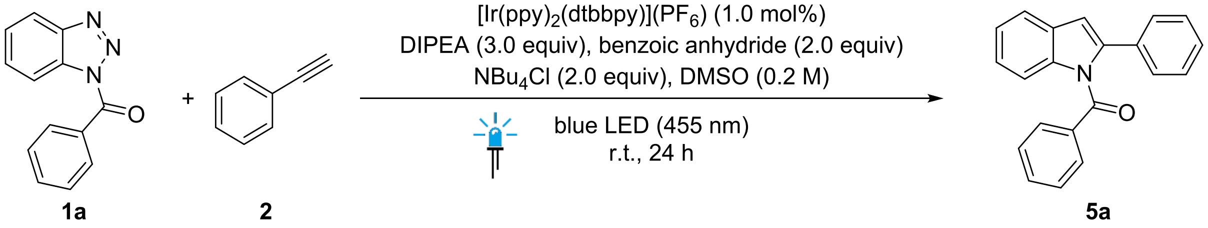
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (s, 1H), 7.68 – 7.63 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.80 (dd, *J* = 2.2, 1.0 Hz, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 138.8, 137.2, 132.0, 129.2, 128.1, 127.9, 125.3, 121.6, 121.1, 111.0, 100.0; **R$_f$ (pentane:EtOAc = 9:1**): 0.38; **GC-MS: t$_R$ (50_40):** 10.04 min; **EI-MS:** *m/z* (%):227 (100), 199 (5), 192 (10), 191 (10), 165 (16), 89 (11); **HR-MS (ESI):** *m/z* calculated for $[C_{14}H_{11}ClN]^+$ ($[M+H]^+$): 228.0575, measured: 228.0564.

Characterization data for 6-Chloro-2-phenylindole (5Heb)

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.40 – 7.29 (m, 2H), 7.14 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.76 (s, 1H); **^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$):** δ 139.3, 135.1, 131.9, 130.3, 129.1, 128.1, 125.2, 122.6, 112.0, 111.9, 99.5; **R$_f$ (pentane:EtOAc = 9:1**): 0.33; **GC-MS: t$_R$ (50_40):** 10.02 min; **EI-MS:** *m/z* (%): 227 (100), 192 (13), 165 (18) 89 (11); **HR-MS (ESI):** *m/z* calculated for $[C_{14}H_{11}ClN]^+$ ($[M+H]^+$): 228.0575, measured: 228.0571.

2.4. Reaction Scale-up

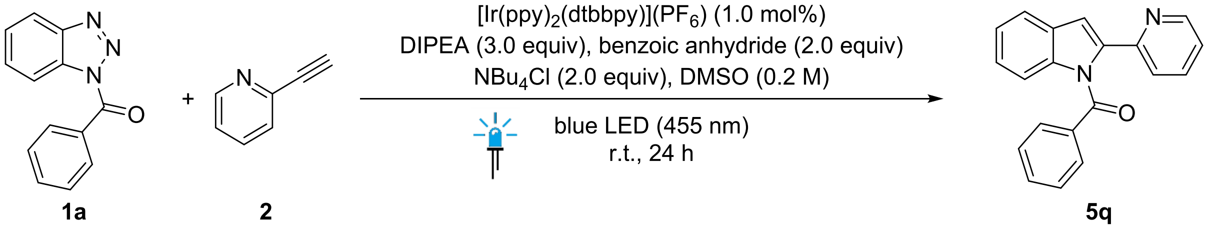
N-benzoyl-2-phenylindole (5a)



[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**3**, 27 mg, 0.03 mmol, 1.0 mol%), *N*-(benzoyl) benzotriazole (**1a**, 669 mg, 3.0 mmol, 1.0 equiv), di*iso*propylethylamine (**4**, 1.54 mL, 9 mmol, 3.0 equiv), benzoic anhydride (**7**, 340 mg, 1.5 mmol, 0.5 equiv), phenylacetylene (**2a**, 6.6 mL, 60 mmol, 20.0 equiv) and tetrabutylammonium chloride (**6**, 1.68 g, 6 mmol, 2.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (15 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature for 24 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). After the indicated reaction time, EtOAc (150 mL) was added. The organic layer was washed with distilled water (3 x 150 mL) and brine (200 mL). The mixture was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction product was purified by column chromatography over silica gel (pentane/ethyl acetate 90:10) to afford the pure product **5a** as a white solid (543 mg, 61%). Unreacted phenyl acetylene (6.1 mL, 55.5 mmol, 92.5% of starting material) was recovered, resulting in an effective use of 4.5 mmol phenylacetylene (1.5 equiv).

The characterization data fits to the data reported before.

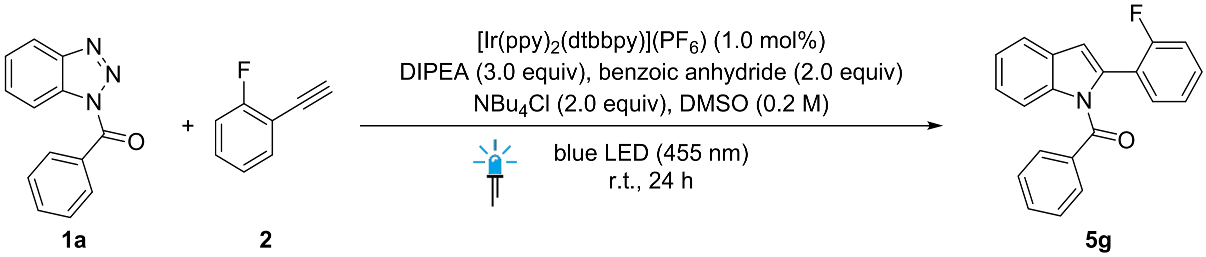
N-Benzoyl-2-(pyridin-2-yl)indole (5q)



[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**3**, 27 mg, 0.03 mmol, 1.0 mol%), *N*-(benzoyl) benzotriazole (**1a**, 669 mg, 3.0 mmol, 1.0 equiv), di*iso*propylethylamine (**4**, 1.54 mL, 9 mmol, 3.0 equiv), benzoic anhydride (**7**, 340 mg, 1.5 mmol, 0.5 equiv), 2-ethynylpyridine (3.03 mL, 30 mmol, 10.0 equiv) and tetrabutylammonium chloride (**6**, 1.68 g, 6 mmol, 2.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (15 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature for 24 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). After the indicated reaction time, EtOAc (150 mL) was added. The organic layer was washed with distilled water (3 x 150 mL) and brine (200 mL). The mixture was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction product was purified by column chromatography over silica gel (pentane/ethyl acetate 95:5) to afford the pure product **5q** as a white solid (546 mg, 61%).

The characterization data fits to the data reported before.

N-Benzoyl-2-(2-fluorophenyl)indole (5g)



1a **2** **5g**

[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**3**, 27 mg, 0.03 mmol, 1.0 mol%), *N*-(benzoyl) benzotriazole (**1a**, 669 mg, 3.0 mmol, 1.0 equiv), di*iso*propylethylamine (**4**, 1.54 mL, 9 mmol, 3.0 equiv), benzoic anhydride (**7**, 340 mg, 1.5 mmol, 0.5 equiv), 1-ethynyl-2-fluorobenzene (6.80 mL, 60 mmol, 10.0 equiv) and tetrabutylammonium chloride (**6**, 1.68 g, 6 mmol, 2.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (15 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature for 24 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). After 24 h, fluorobenzene (281 µL, 3.0 mmol, 1.0 equiv) was added as an internal ^{19}F standard and the yield was determined to be 59% using ^{19}F spectroscopy.

3. Mechanistic Experiments

3.1. Stern-Volmer Luminescence Quenching Analysis

All samples used in the luminescence quenching-based screening studies were prepared under oxygen-free conditions. The photocatalysts and potential quenchers were weighed into vials and placed inside a glovebox (a common glovebag can alternatively be used) under a positive pressure of argon. Acetonitrile was degassed by argon sparging for one hour and also placed inside along with micropipettes and their tips, cuvettes, empty vials, waste containers and parafilm. Stern-Volmer luminescence quenching studies were carried out using a 2 x 10^{-6} M solution of $[Ir(ppy)_2(dtbbpy)](PF_6)$ (**3**) and variable concentrations of *N*-(benzoyl)benzotriazole (**1a**), di*iso*propylethylamine (**4**), phenylacetylene (**2a**), benzoic anhydride (**7**) and tetrabutylammonium chloride (**6**) in dry acetonitrile at room temperature under an argon atmosphere. The samples were prepared in 1.4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside an argon filled glove-box. The solutions were irradiated at 420 nm and the luminescence was measured at 471 nm (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed intensity as a function of the quencher concentration).

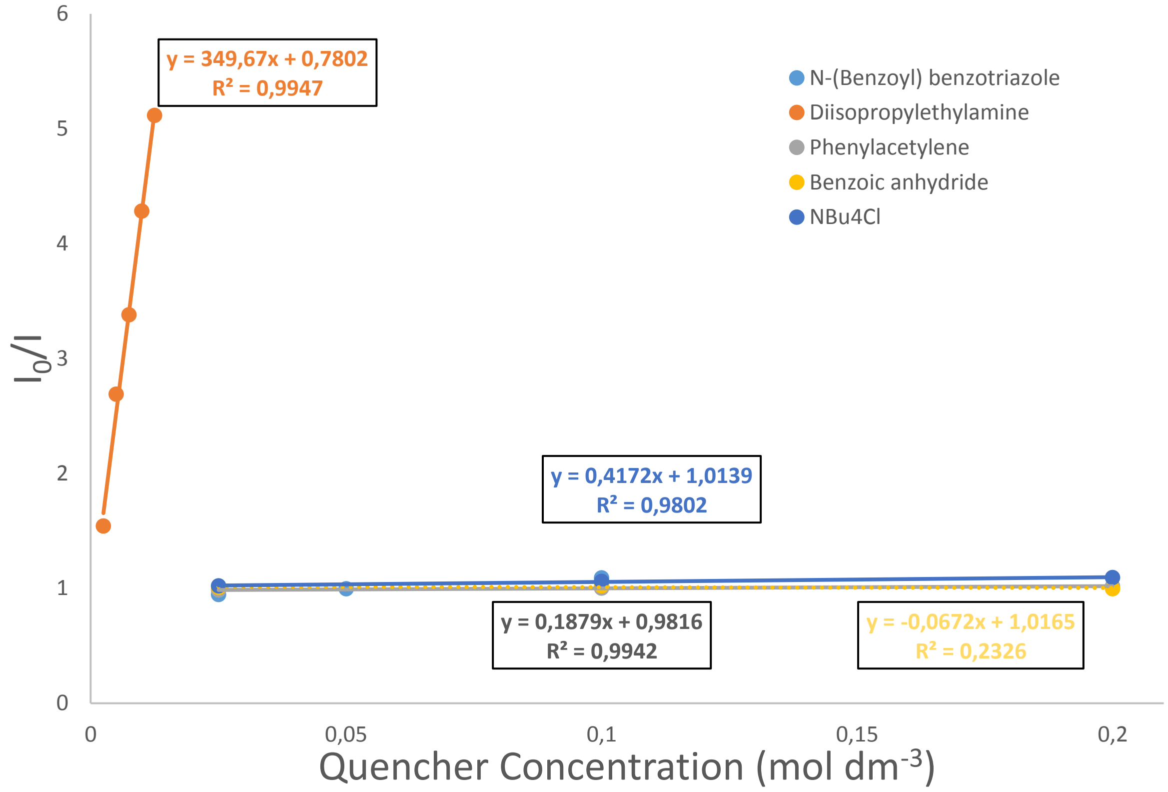


Figure S5. Stern-Volmer luminescence quenching analysis for the denitrogenative indole synthesis using $[Ir(ppy)_2(dtbbpy)](PF_6)$ (2 x 10^{-6} M).

3.2. Determination of the Reaction Quantum Yield (Φ) for the Denitrogenative Indole Synthesis

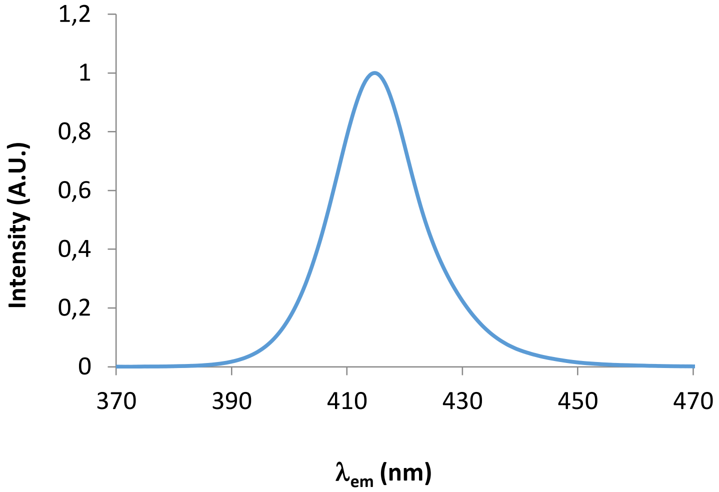


Figure S6. Emission spectrum of blue LED used for quantum yield experiments (λ_{max} = 420 nm).

Determination of the light intensity at 420 nm:

According to the procedure of Yoon,[17] the photon flux of the LED (λ_{max} = 420 nm) was determined by standard ferrioxalate actinometry.[18,19,20] A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (25 mg) and sodium acetate (5.63 g) in H_2SO_4 (25 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (1.0 mL) was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 420 nm (figure S6). After irradiation, the phenanthroline solution (0.175 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1.5 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

$$\text{mol Fe}^{2+} = \frac{\text{V} \bullet \Delta\text{A}(510\text{ nm})}{\text{l} \bullet \varepsilon} \tag{1}$$

where V is the total volume (0.001175 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $\text{Lmol}^{-1}\text{cm}^{-1}$).[20] The photon flux can be calculated using eq 2.

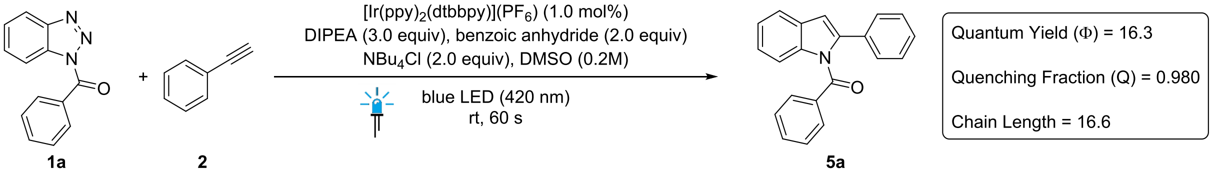
$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \bullet \text{t} \bullet \text{f}} \tag{2}$$

where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at λ_{ex} = 420 nm),[21] t is the irradiation time (90 s), and f is the fraction of light absorbed at λ_{ex} = 420 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A(420 nm) is the absorbance of the ferrioxalate solution at 420 nm. An absorption spectrum gave an A(415 nm) value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$\text{f} = 1 - 10^{-A(415\,nm)} \tag{3}$$

The photon flux was thus calculated (average of three experiments) to be 2.04 × 10^{-9} einsteins s^{-1}.

Determination of the reaction quantum yield:



[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (0.9 mg, 0.001 mmol, 1.0 mol%), 1-(benzoyl)benzotriazole (22.3 mg, 0.1 mmol, 1.0 equiv), di*iso*propylethylamine (52 µL, 0.3 mmol, 3.0 equiv), benzoic anhydride (11.3 mg, 0.05 mmol, 0.5 equiv), tetrabutylammonium chloride (52 mg, 0.2 mmol, 2.0 equiv) and phenylacetylene (220 µL, 2.0 mmol, 20 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (0.5 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. 0.5 mL of the reaction mixture (containing 0.10 mmol of **1a**) was transferred into a quartz cuvette under an argon atmosphere. The cuvette was capped with a PTFE stopper and sealed with *Parafilm*. The sample was stirred and irradiated at λ_{max} = 420 nm (see figure S6 for an emission spectrum of the LED used) for 60 s. After irradiation, the yield of product **5a** formed was determined by GC-FID analysis. The yield of **5a** was determined to be 2% (2×10^{-6} mol). The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 2.06×10^{-9} einsteins s^{-1} (determined by actinometry as described above), t is the reaction time (60 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq 3. An absorption spectrum of the reaction mixture gave an absorbance value of > 3 at 420 nm, indicating that essentially all the incident light (f > 0.999) is absorbed by the photocatalyst.

$$\Phi = \frac{\text{mol of product formed}}{\text{Photon flux} \bullet \text{t} \bullet \text{f}} \tag{4}$$

The reaction quantum yield (Φ) was thus determined to be 16.3.

Determination of the quenching fraction:

Simple quenching experiments, following a modification of the procedure described by Yoon,[19] were conducted to determine the quenching fraction of the reaction. The reaction with 1-(benzoyl)benzotriazole (**1a**) was prepared as described above and 0.5 mL of the reaction mixture was transferred to a cuvette under an argon atmosphere, which was then capped with a PTFE stopper and sealed with *Parafilm*. The luminescence intensity under the reaction conditions (I) was recorded (λ_{em} = 571 nm) while being irradiated at λ_{ex} = 420 nm in a Jasco FP-8300 spectrofluorometer. The same reaction was set up in the absence of the quencher **4** and the luminescence intensity (I_0) was measured in the same fashion. The quenching fraction (Q) was determined using eq 5.

$$\text{Q} = \frac{I_0 - \text{I}}{I_0} \tag{5}$$

A quenching fraction (Q) of 0.98 was determined for the reaction.

Chain length calculation:

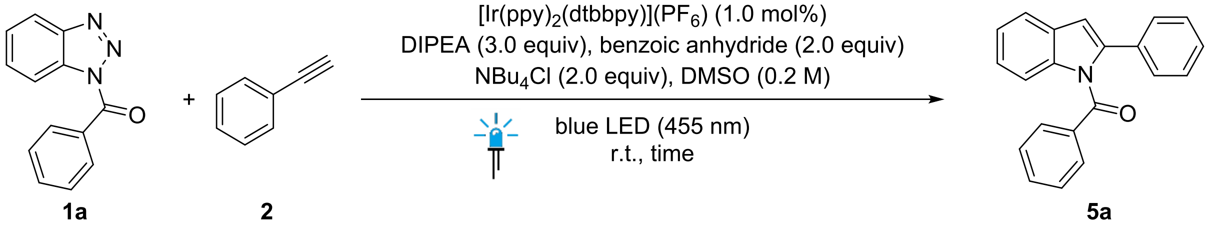
The chain length value was calculated using the method described by Yoon,[19] and is a lower limit approximation of the actual chain length. Using Q, as determined from the simple quenching experiments described above, the chain length of the denitrogenative indole synthesis was determined using eq 6.

$$\text{chain length} = \frac{\Phi}{Q} \tag{6}$$

The chain length of the reaction was thus determined to be 16.6.

3.3. Reaction Profile for the Denitrogenative Indole Synthesis

The reaction profile for the denitrogenative indole synthesis under the standard reaction conditions was determined using mesitylene as internal standard in combination with GC-FID. A stock solution of [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (7.2 mg, 0.008 mmol, 1.0 mol%), 1-(benzoyl)benzotriazole (178.4 mg, 0.8 mmol, 1.0 equiv), di*iso*propylethylamine (416 µL, 2.4 mmol, 3.0 equiv), benzoic anhydride (90.4 mg, 0.4 mmol, 0.5 equiv), tetrabutylammonium chloride (416 mg, 1.6 mmol, 2.0 equiv) and phenylacetylene (1760 µL, 16.0 mmol, 20 equiv.) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous DMSO (4.0 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was backfilled with argon. 0.5 mL of the reaction mixture (containing 0.10 mmol of **1a**) was transferred into another dried Schlenk tube containing a magnetic stirring bar. The solutions were degassed one more time and backfilled with argon. The samples were irradiated with visible light from blue LEDs (455 nm) for the respective time. After the indicated time, mesitylene (14 µL, 0.1 mmol) was added as internal standard and the yield of the product **5a** was determined using GC-FID. The reaction profile of the denitrogenative indole synthesis can be seen in figure S7.



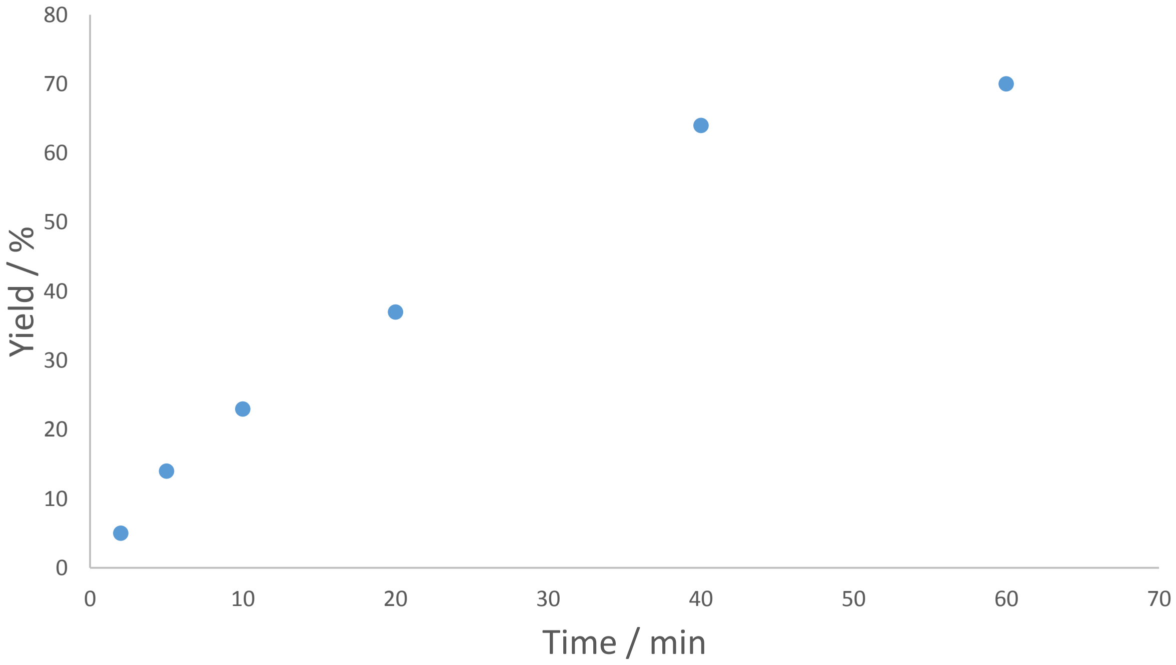


Figure S7. Reaction profile for the denitrogenative indole synthesis to give **5a**.

3.4. UV/vis Analysis of the Starting Materials and Reaction Mixtures

UV/vis absorption spectroscopy has been performed using a Jasco V-650 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 1.4 mL, H × W × D = 46 mm × 12.5 mm, 12.5 mm) fitted with a PTFE stopper. Stock solutions of the educts 1-(benzoyl)benzotriazole (**1a**), benzoic anhydride (**7**), phenylacetylene (**2**), di*iso*propylethylamine (**4**), tetrabutylammonium chloride (**6**) and of the photocatalyst [Ir(ppy)$_2$(dttbpy)](PF$_6$) (**3**) were prepared with the same concentration used in the reaction in the presence of air using DMSO as solvent.

Phenylacetylene was identified as only starting material absorbing slightly at 455 nm. All other starting materials did not show any absorption (see figure S8).

To proof that the photocatalyst is the mainly absorbing species within the reaction mixture, UV/vis absorption spectra of the reaction mixture with and without the photocatalyst were measured. The concentration of all reaction compounds is identical to those used under the scope reaction conditions. As one can see below, the photocatalyst is the mainly absorbing species at a wavelength around 455 nm. However, in the absence of a photocatalyst the absorbtion spectra shows some absorption probably arising from phenylacetylene due to comparable curve shape. This observation is in agreement with the identification of some reactivity even in the absence of a photocatalyst.

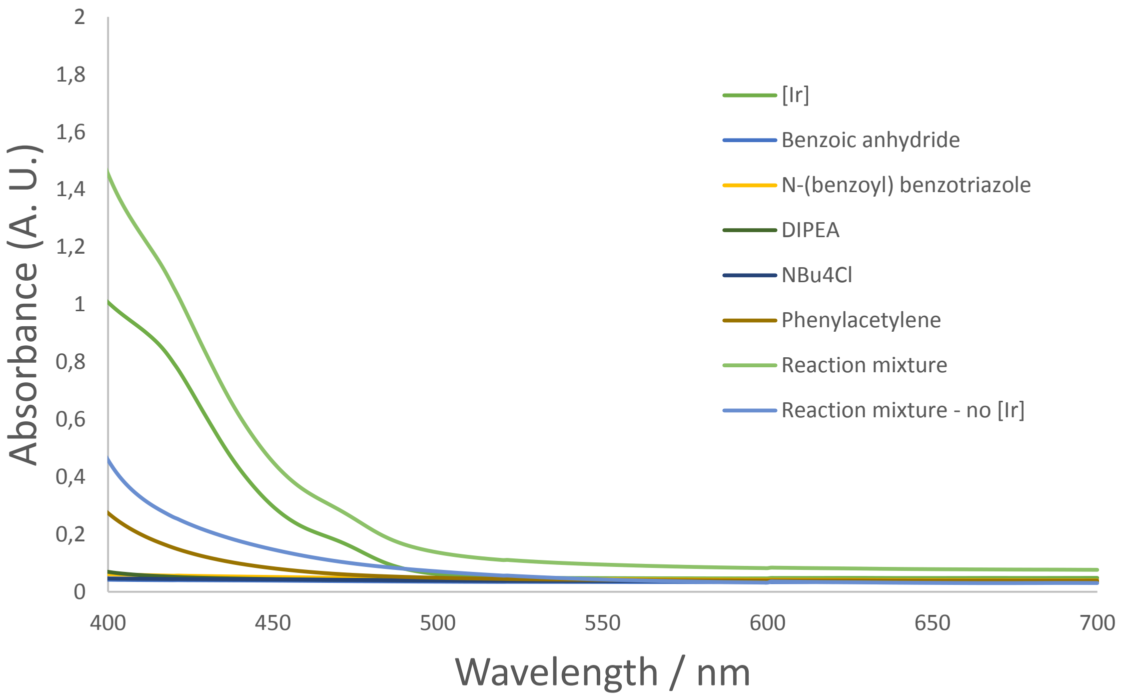
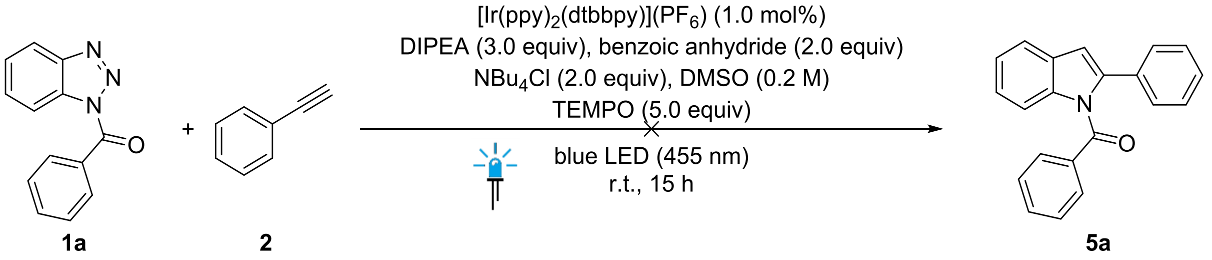


Figure S8. UV/vis absorption spectra of the starting materials in isolation and combined recorded in DMSO as solvent.

3.5. TEMPO Radical Trapping Experiment



[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (0.9 mg, 0.001 mmol, 1.0 mol%), 1-(benzoyl) benzotriazole (22.3 mg, 0.1 mmol, 1.0 equiv), diisopropylethylamine (52 µL, 0.3 mmol, 3.0 equiv), benzoic anhydride (11.3 mg, 0.05 mmol, 0.5 equiv), tetrabutylammonium chloride (52 mg, 0.2 mmol, 2.0 equiv), phenylacetylene (220 µL, 2.0 mmol, 20 equiv) and 2,2,6,6-tetramethylpiperidinyloxyl (78.0 mg, 0.5 mmol, 5.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous dimethylsulfoxid (0.5 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The solution was irradiated with visible light from blue LEDs (455 nm) for 15 h. EtOAc (50 mL) was added, the organic layer was washed with distilled water (3 x 40 mL) and brine (50 mL). The mixture was dried over anhydrous MgSO$_4$, filtered and concentrated *in vacuo* and analysed using HR-ESI-MS (see figure S9) and GC-MS.

The formation of the indole product **5a** was not observed via GC-MS and ESI-MS analysis. Furthermore, no trapped intermediates (for example TEMPO+Phenylradical) could be identified.

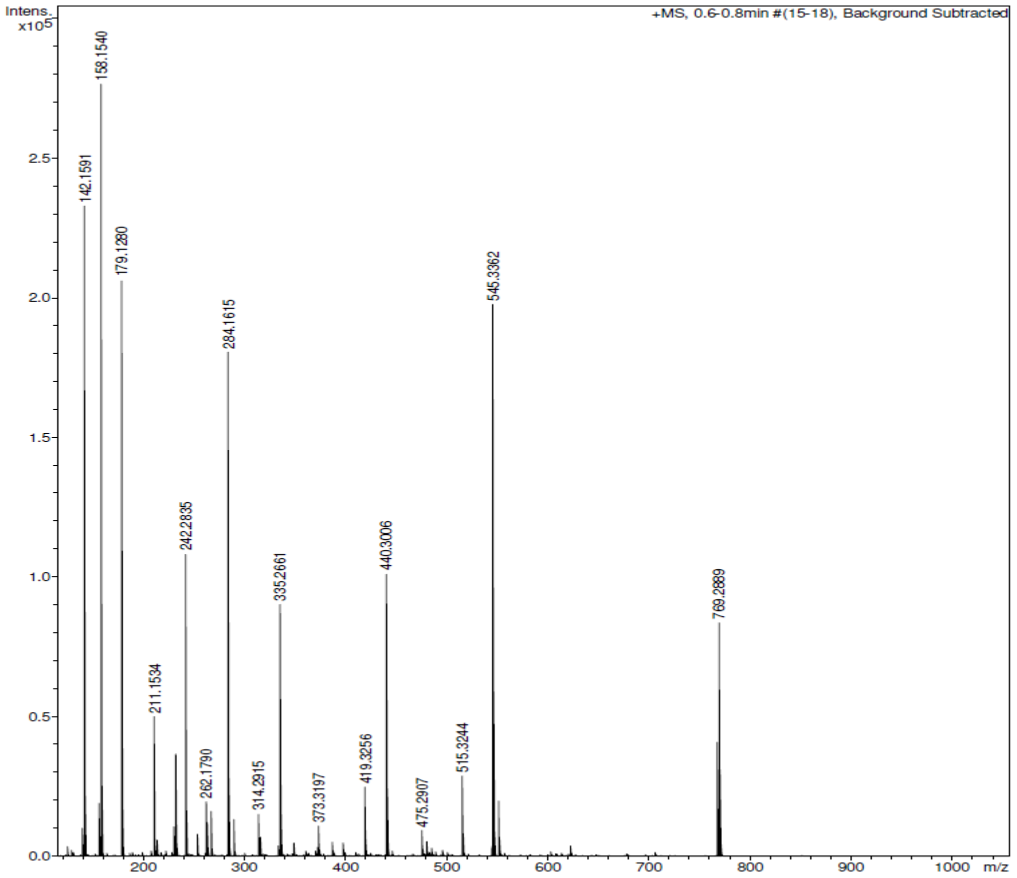
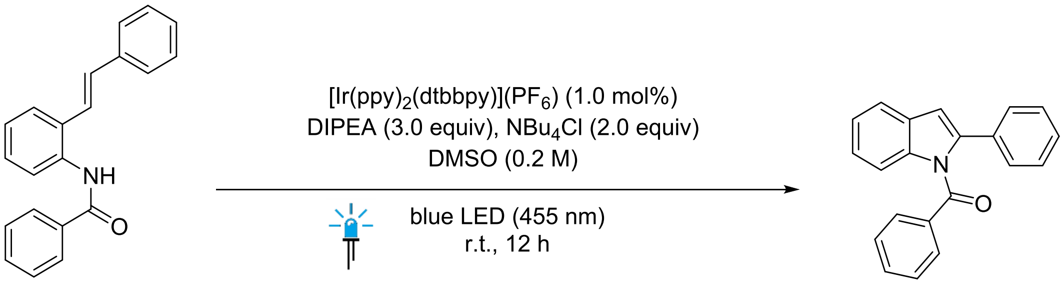


Figure S9. ESI-MS trace of the radical trapping experiment using TEMPO.

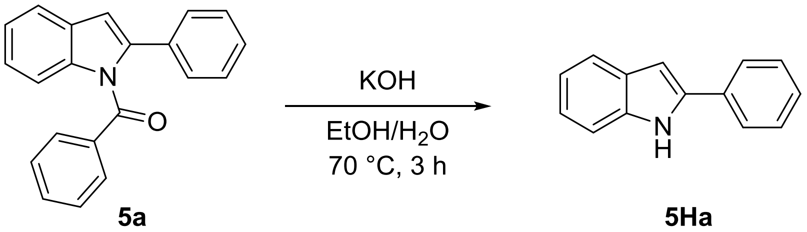
3.6. Attempt of the Photocatalytic Annulation of (*E*)-*N*-(2-styrylphenyl)benzamide to give *N*-(benzoyl)-2-aryl indoles



To validate the mechanistic proposal and to exclude a cascade reaction mechanism, (*E*)-*N*-(2-styrylphenyl)benzamide (**15**, 89.7 mg, 0.3 mmol, 1.0 equiv), [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (**3**, 2.7 mg, 0.003 mmol, 1.0 mol%), diisopropylethylamine (**4**, 154 µL, 0.9 mmol, 3.0 equiv) and tetrabutylammonium chloride (**6**, 168 mg, 0.6 mmol, 2.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous dimethylsulfoxid (1.5 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature for 12 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). Only trace amounts of the indole product were observed using GC-FID in combination with mesitylene as internal standard. A mechanistic cascade scenario, in which **15** is formed and later on transformed to the 2-arylindole product **5a** therefore seems to be unlikely.

4. Follow-up Reactions

Product Deprotection – Synthesis of 2-Phenylindole (5Ha)

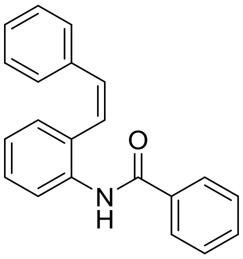


The deprotection of the *N*-(benzoyl)-2-aryl indole products can be achieved by using a published procedure from Taylor et al.[22] *N*-(benzoyl)-2-aryl indole (**5a**, 89.1 mg, 0.3 mmol, 1.0 equiv) was dissolved in a schlenk tube using 6 mL of EtOH and 10 mL of a 2M KOH solution in EtOH as well as a few drops of water were added. The tube was sealed and the mixture was refluxed for 3 h. After this time, the mixture was allowed to cool down to room temperature. Ethanol (50 mL) was added and the organic solution was washed with brine (2 x 50 mL) and water (30 mL). The organic layer was dried over $MgSO_4$ and the solution was dried *in vacuo* to give the crude product, which was purified by flash column chromatography using pentane/EtOAc (8:2) as solvent system. The clean product **5Ha** (53.9 mg, 93%) was obtained as white solid.

The characterization data fits to those reported before.

(*Z*)-*N*-(2-styrylphenyl)benzamide (8)

$[Ir(ppy)_2(dtbbpy)](PF_6)$ (2.7 mg, 0.003 mmol, 1.0 mol%), *N*-(benzoyl) benzotriazole (**1a**, 66.9 mg, 0.3 mmol, 1.0 equiv), diisopropylethylamine (**4**, 154 µL, 0.9 mmol, 3.0 equiv), benzoic anhydride (**7**, 33.4 mg, 0.15 mmol, 0.5 equiv.) and phenyl acetylene (**2**, 658 µL, 6.0 mmol, 20.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous acetonitrile (3.0 mL, 0.1 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. The reaction mixture was allowed to stir at room temperature for 16 h under irradiation with visible light from six 5 W blue LEDs (λ_{max} = 455 nm). After the indicated reaction time, EtOAc (50 mL) was added. The organic layer was washed with distilled water (3 x 40 mL) and brine (50 mL). The mixture was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction product was purified by column chromatography over silica gel (pentane/ethyl acetate 90:10) to afford the pure product **8** as white solid (49.4 mg, 55%).



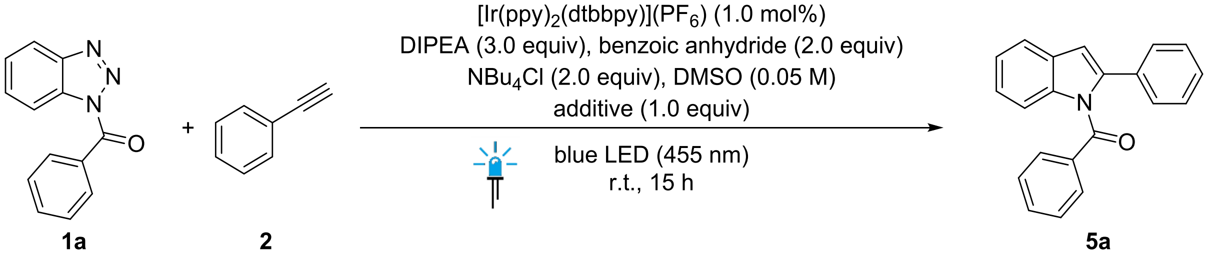
8

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.96 (s, 1H), 7.51 – 7.45 (m, 3H), 7.39 – 7.34 (m, 3H), 7.29 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.16 (ddddd, *J* = 11.2, 8.8, 7.5, 5.1, 1.9 Hz, 6H), 6.80 (d, *J* = 12.2 Hz, 1H), 6.63 (d, *J* = 12.2 Hz, 1H); **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):** δ 165.4, 135.8, 135.1, 134.7, 133.4, 131.7, 129.4, 128.8, 128.7, 128.6, 128.5, 128.0, 127.0, 125.7, 124.6, 121.6; **R_f (pentane:EtOAc = 9:1)**: 0.38; **GC-MS: t_R (50_40):** 11.05 min; **EI-MS:** *m/z* (%): 299 (24), 281 (10), 194 (100), 165 (13), 105 (34), 77 (54), 51 (15); **HR-MS (ESI):** *m/z* calculated for $[C_{21}H_{17}NONa]^+$ ($[M+Na]^+$): 322.1202, measured: 322.1195.

5. Additive-based Robustness Screen – General Procedure and Results

In order to evaluate the robustness and the functional group preservation of the investigated reaction, we decided to apply an intermolecular additive-based screen to this transformation.[23] This screening technique, previously reported by our group, evaluates the tolerance of a given reaction to a series of additives (robustness), as well as the stability of these additives to the reaction conditions (functional group preservation).[7]

The protocol requires to carry out the desired transformation under the standard reaction conditions in the presence of equimolar amounts of a single functionalized additive. After a pre-determined reaction time, the yield of the product and the remaining additive and starting materials are determined by GC-FID analysis.[7] Calibration of the additives and products of the reaction was done using a single point batch calibration.



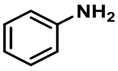
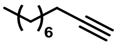
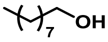
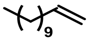
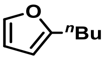
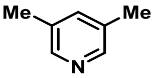
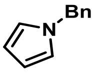
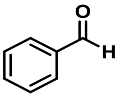
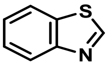
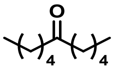
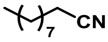
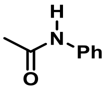
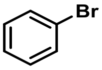
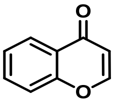
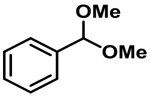
[Ir(ppy)$_2$(dtbbpy)](PF$_6$) (0.9 mg, 0.001 mmol, 1.0 mol%), 1-(benzoyl) benzotriazole (22.3 mg, 0.1 mmol, 1.0 equiv.), diisopropylethylamine (52 µL, 0.3 mmol, 3.0 equiv), benzoic anhydride (11.3 mg, 0.05 mmol, 0.5 equiv.), tetrabutylammonium chloride (52 mg, 0.2 mmol, 2.0 equiv), phenylacetylene (220 µL, 2.0 mmol, 20 equiv.) and the additive (1.0 equiv) were added to a dried Schlenk tube containing a magnetic stirring bar. In the absence of light, anhydrous dimethylsulfoxid (0.5 mL, 0.2 M) was added via syringe under an argon stream. The resulting solution was degassed using three freeze-pump-thaw cycles and the tube was finally backfilled with argon. After 15 h of irradiation, the yield of the product **5a** and the remaining additive yield was determined by GC-FID analysis.

Color-coding should help the ready assessment of the yields: green (> 66%), yellow (34…66%), red (< 34%). The color-coding for facilitated assessment of the reactions yield is scaled using these percentages relative to the yield of the standard reaction in the absence of any additive.

Note:

- Change in volume of the stock solution due to addition of liquid starting materials was not accounted for, hence a control reaction (no additive) was carried out to determine the maximum yield of the reaction in the screen.
- Acetanilide should be filtered through Celite® when preparing samples for GC analysis.

Table S1. Results of the additive-based screening for the denitrogenative indole synthesis.

		Yield Product	Additive remaining
A1		34	19
A2		64	98
A3		56	74
A4		63	94
A5		65	102
A6		56	105
A7		65	94
A8		46	28
A9		58	95
A10		62	105
A11		59	92
A12		58	94
A13		63	79
A14		10	22
A15		56	92
	none	67	-
Average Yield		**54**	**80**

The color-coding for facilitated assessment of the results is scaled relative to the yield of the standard reaction in the absence of any additive, representing > 44% in green, 22…44% in yellow and < 22% in red for the product yields and > 66% in green, 34…66% in yellow and < 34% in red for the additive recovery in both protocols.

6. References

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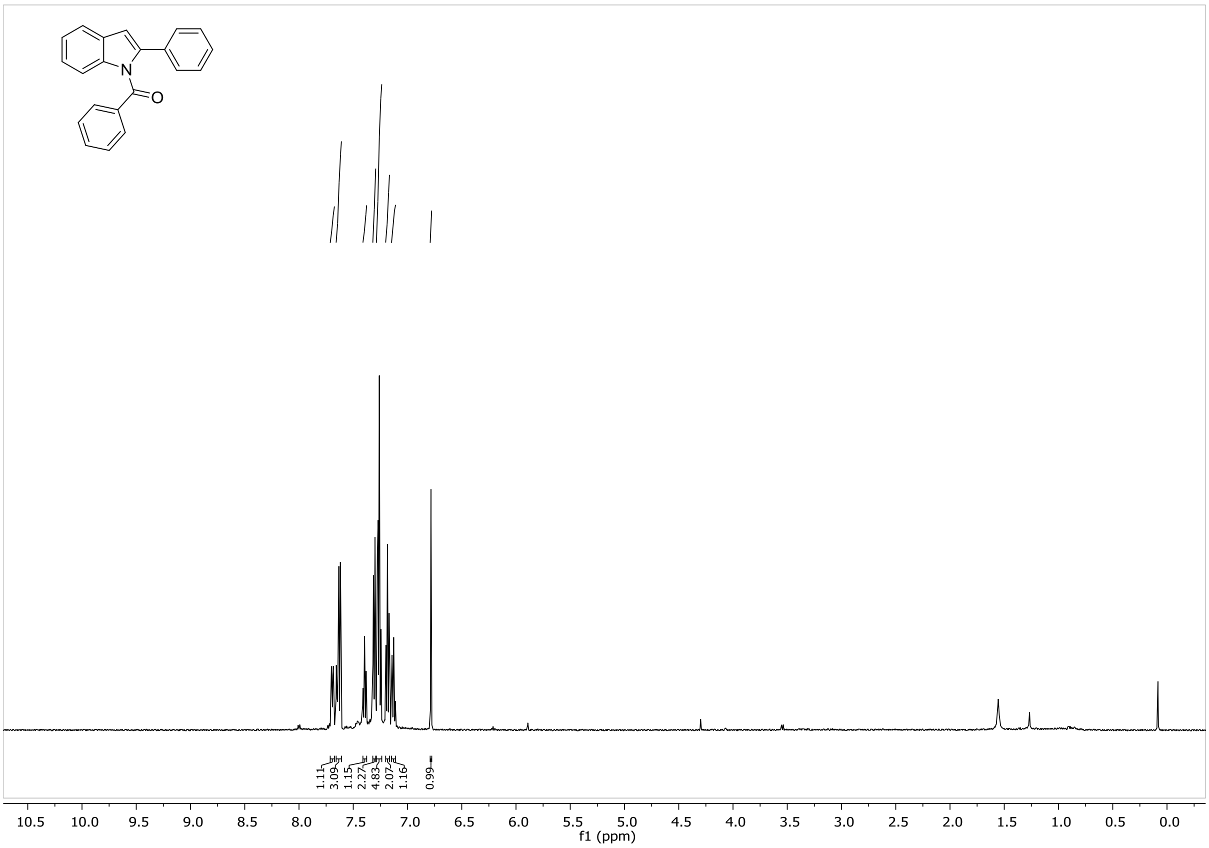
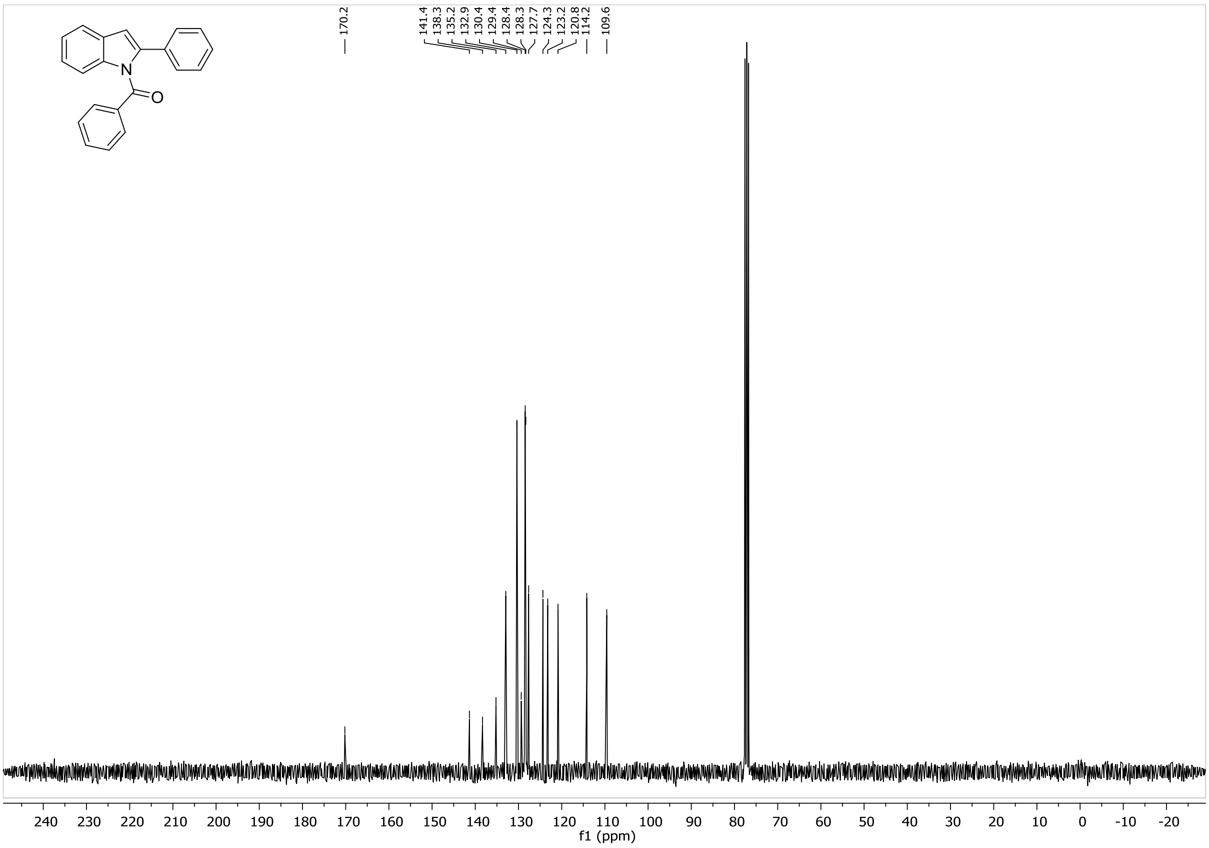
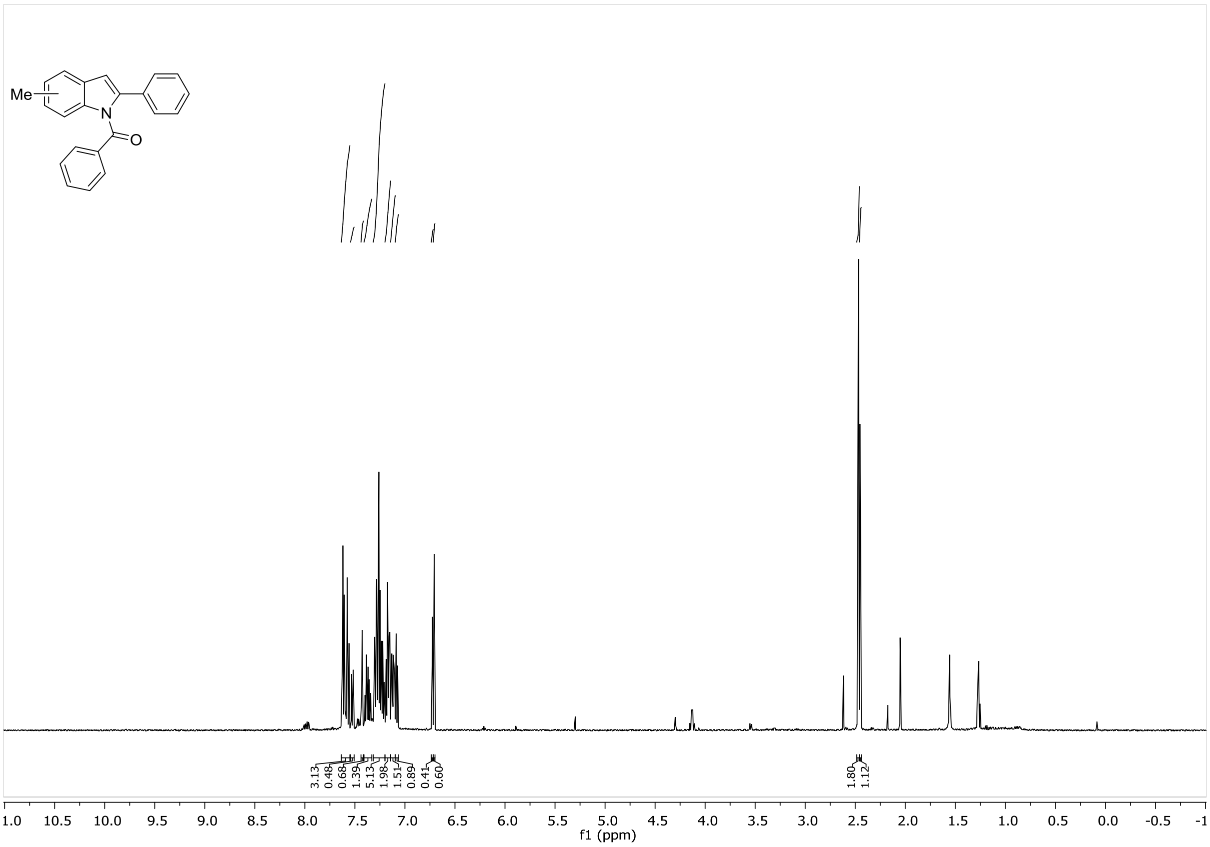
7. Product Spectra

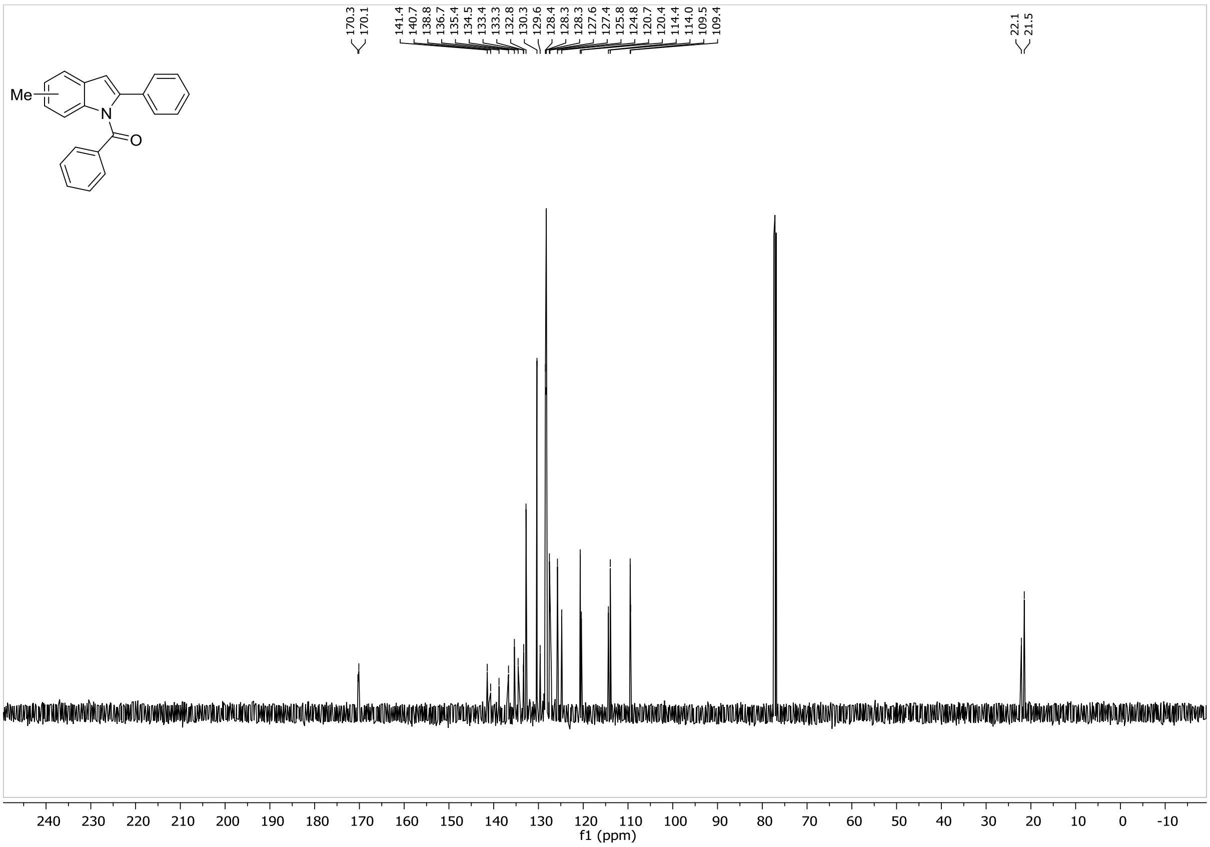
N-Benzoyl-2-phenylindole (5a)



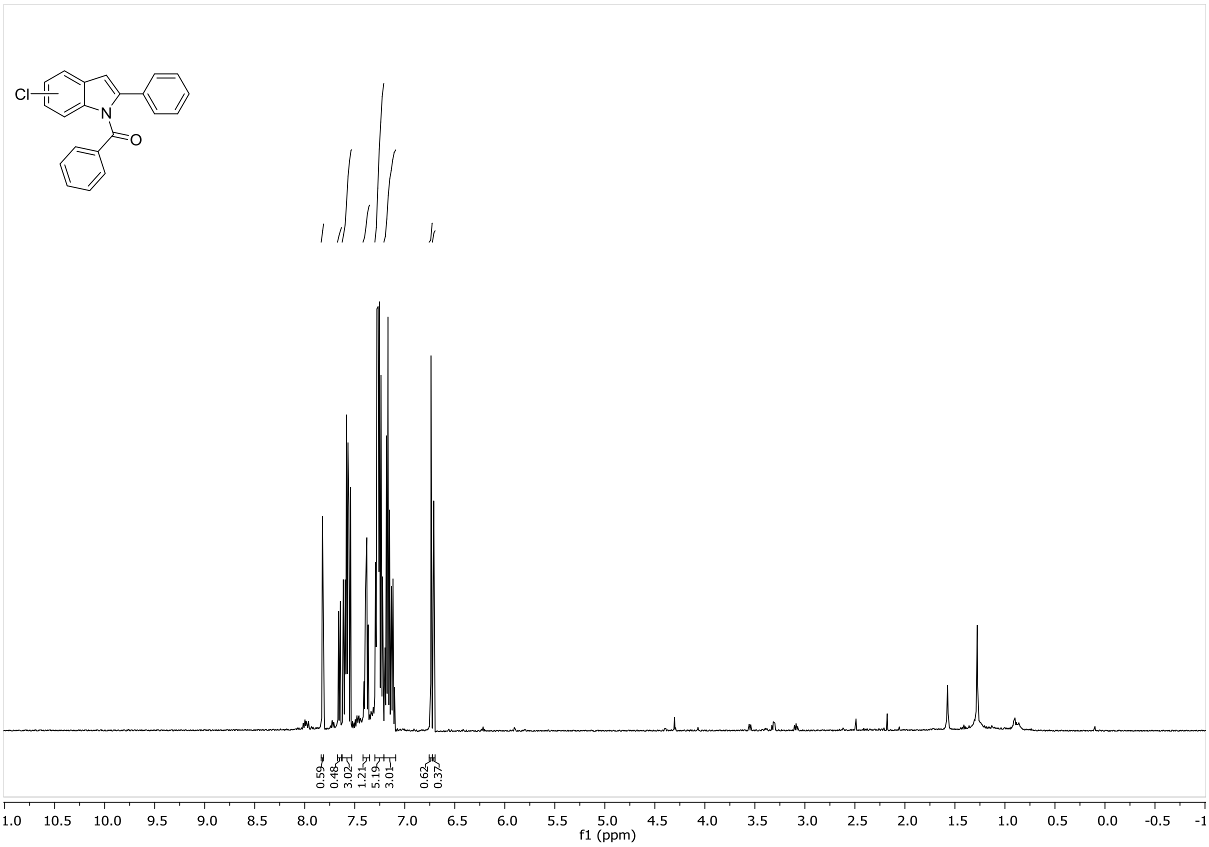


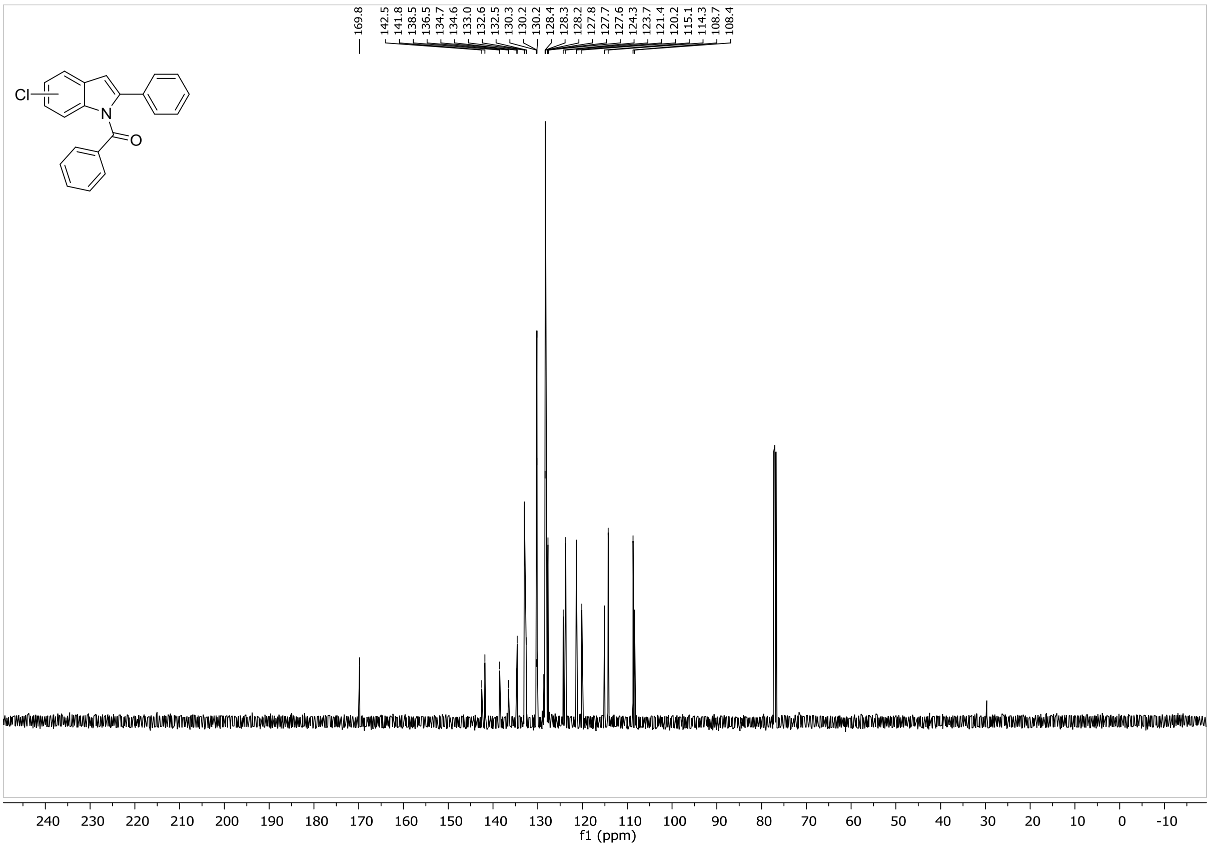
N-Benzoyl-2-phenyl 5-methylindole (5b1) / *N*-Benzoyl-2-phenyl 6-methylindole (5b2)





N-Benzoyl-2-phenyl 5-chloroindole (5c1) / *N*-Benzoyl-2-phenyl 6-chloroindole (5c2)





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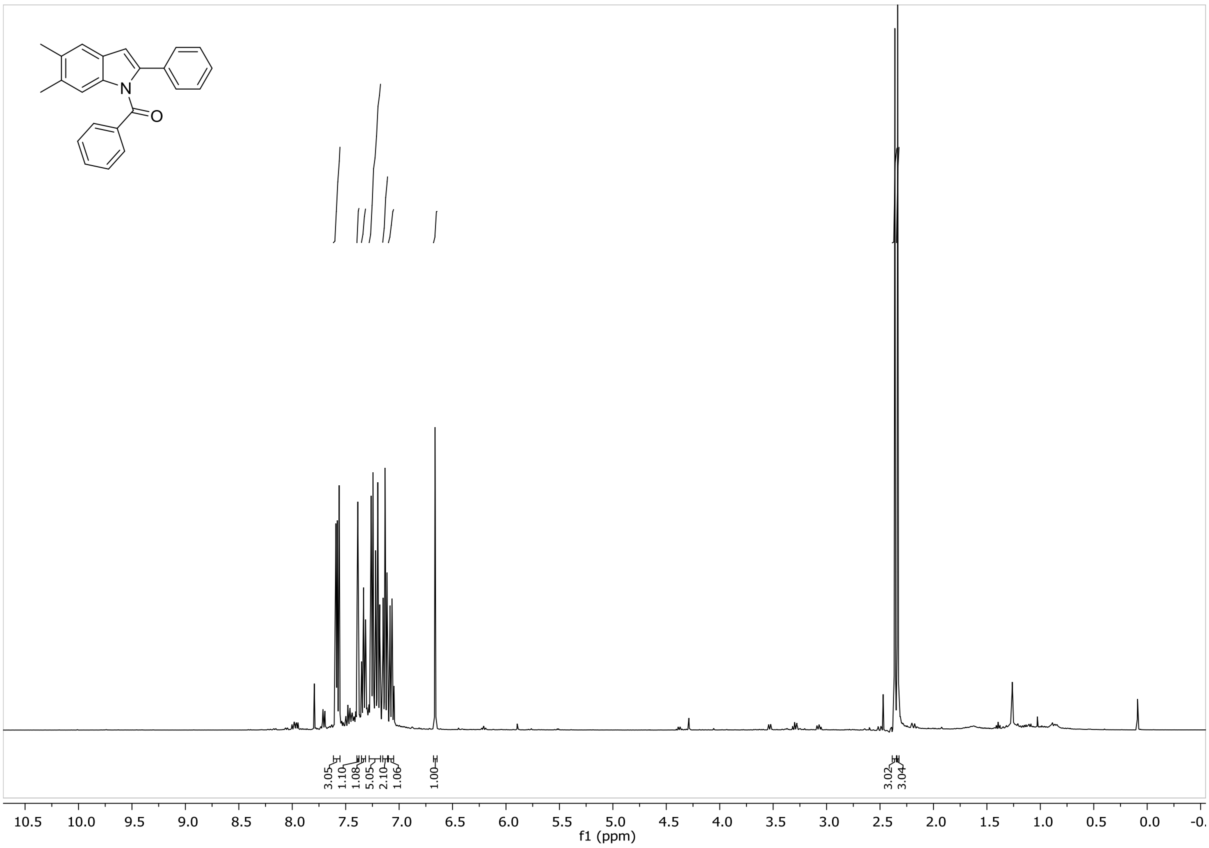

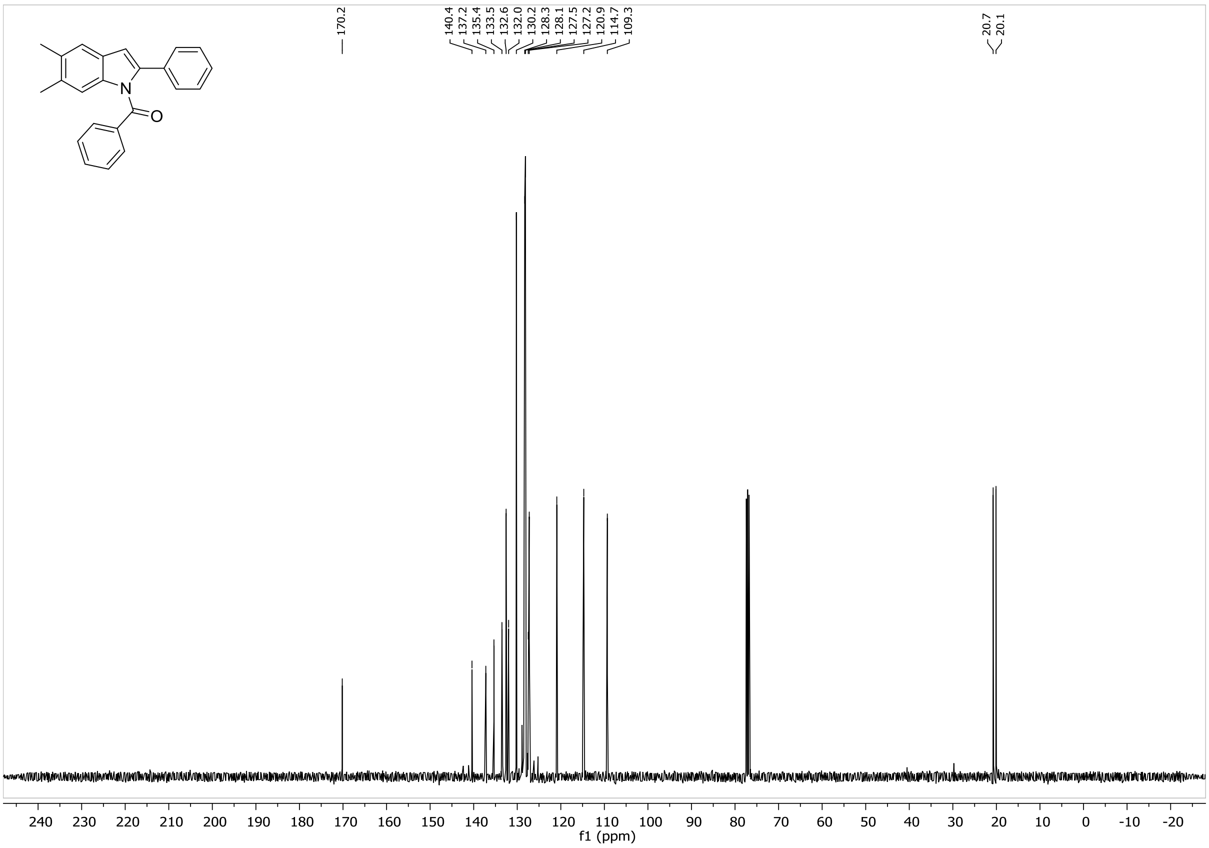

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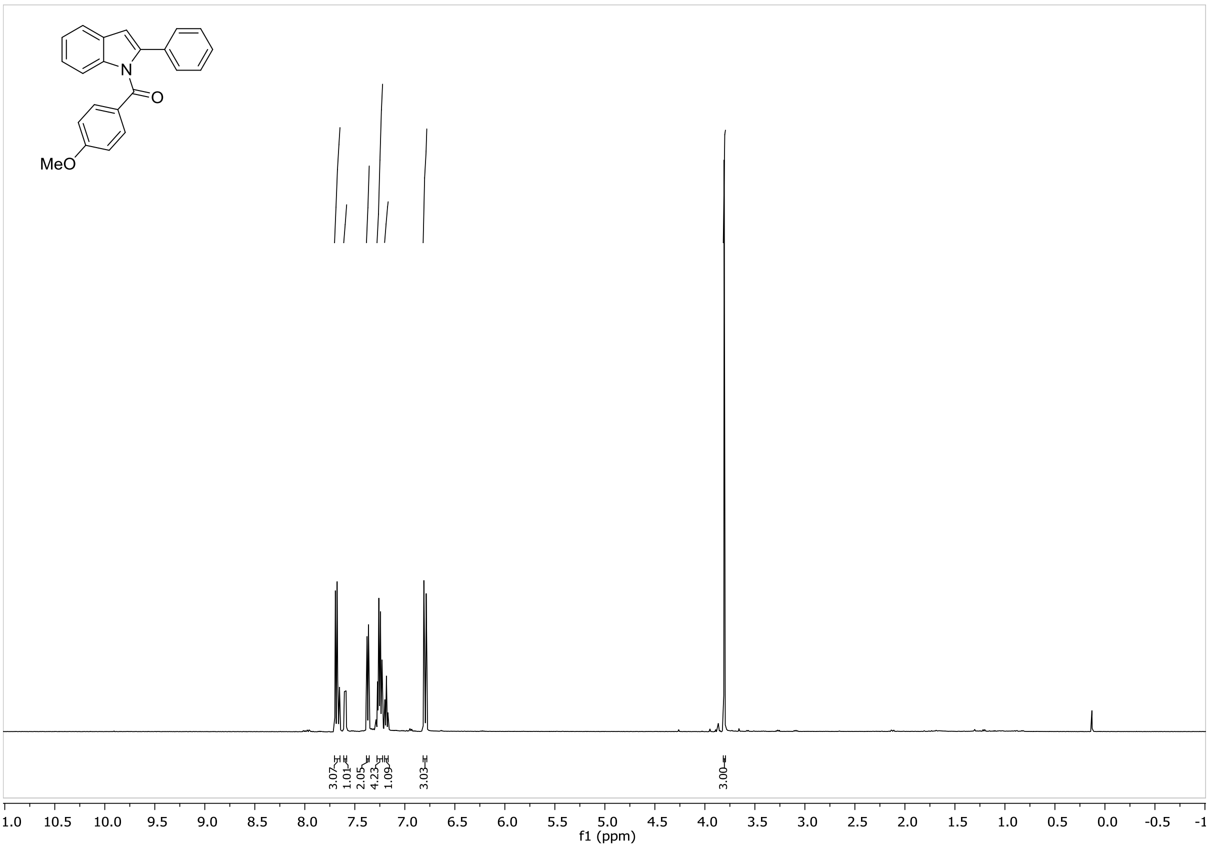
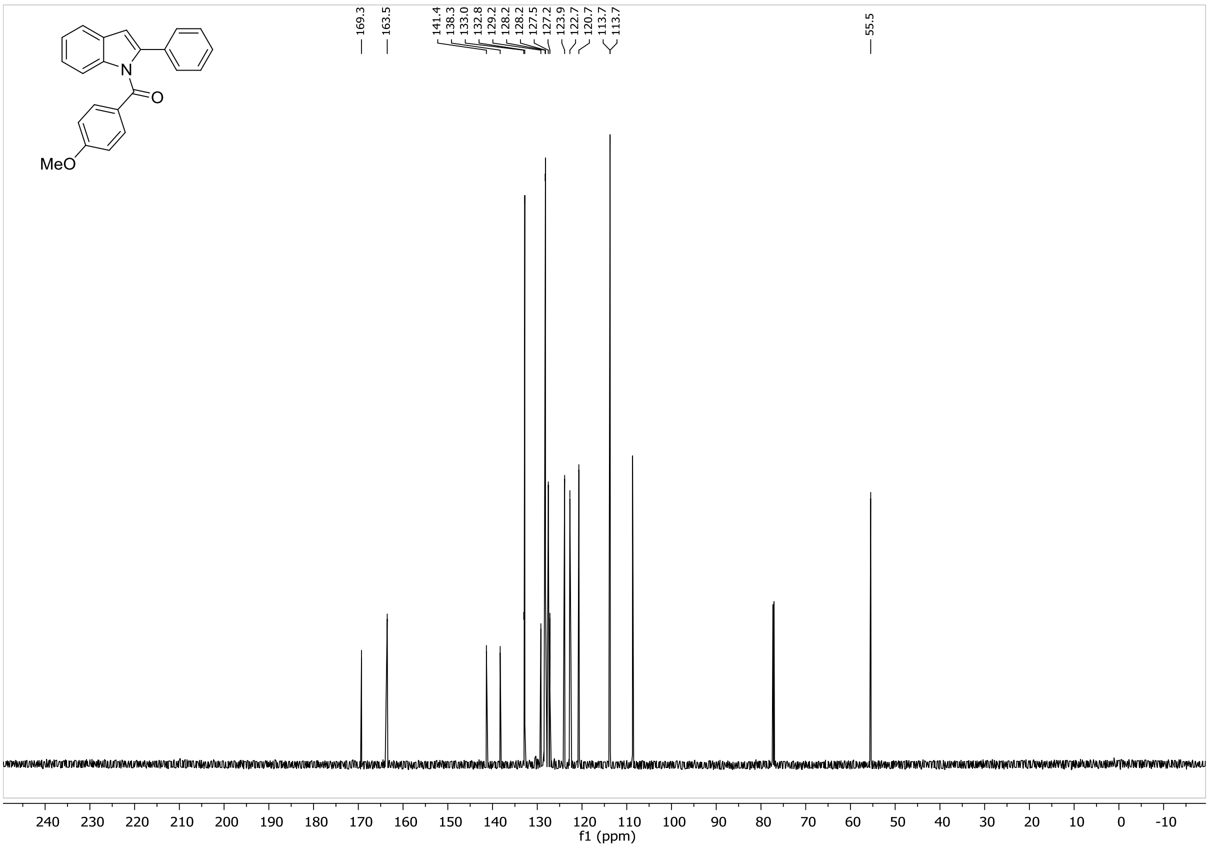
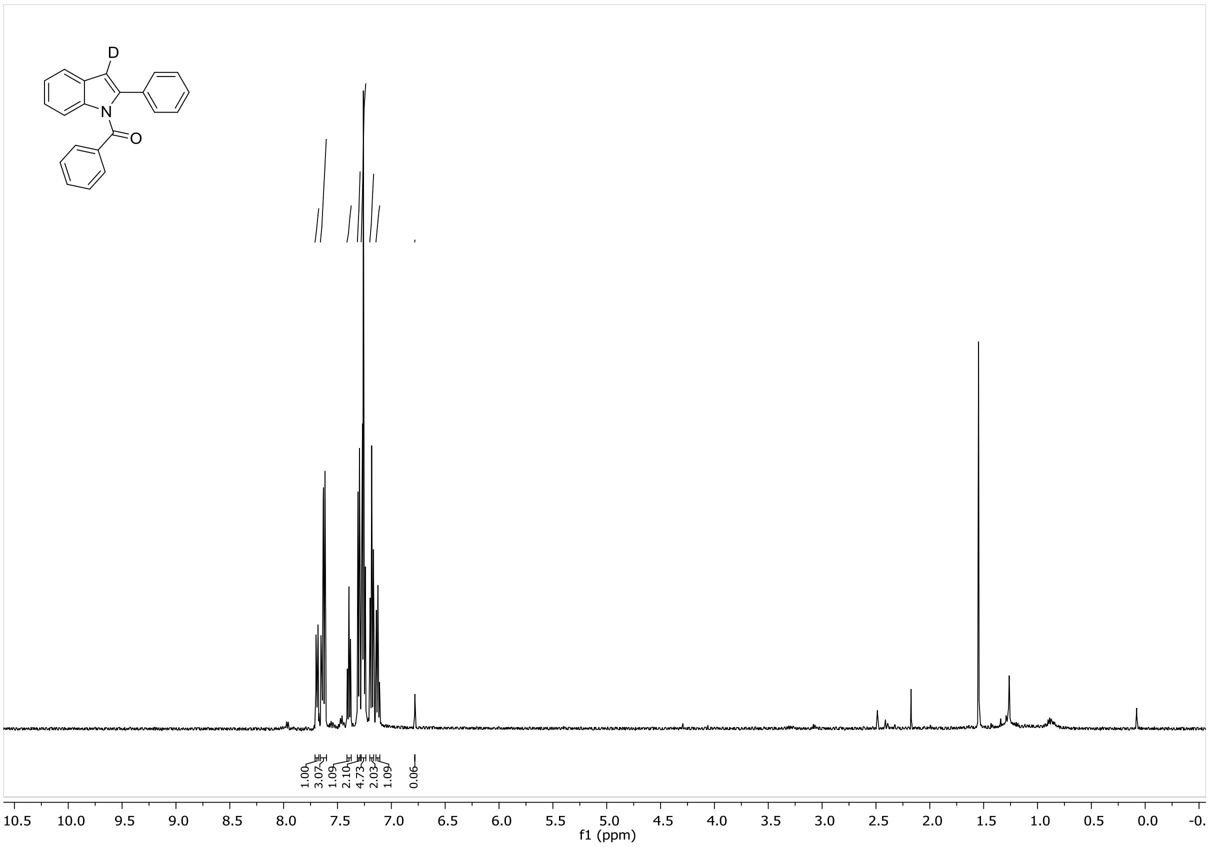
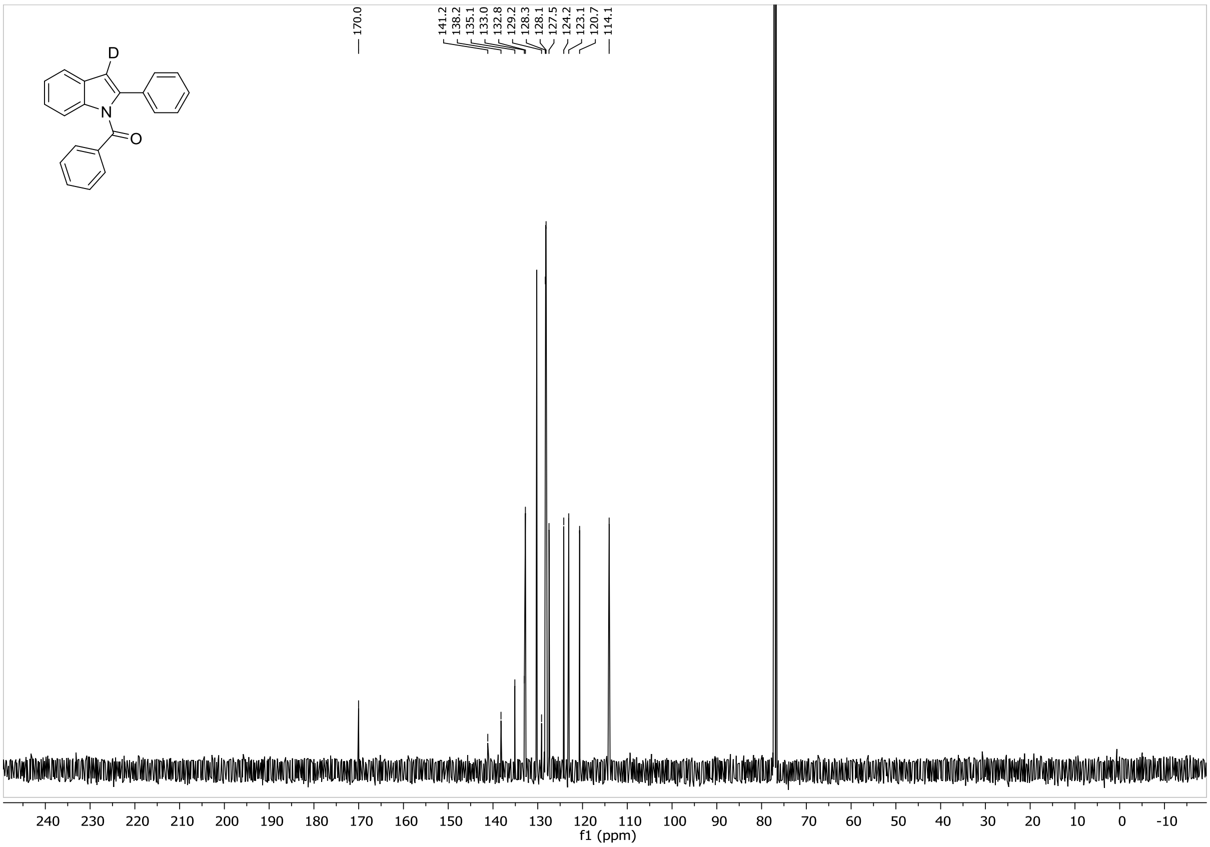




N-Benzoyl-2-phenyl-3-deuteriumindole (5f)





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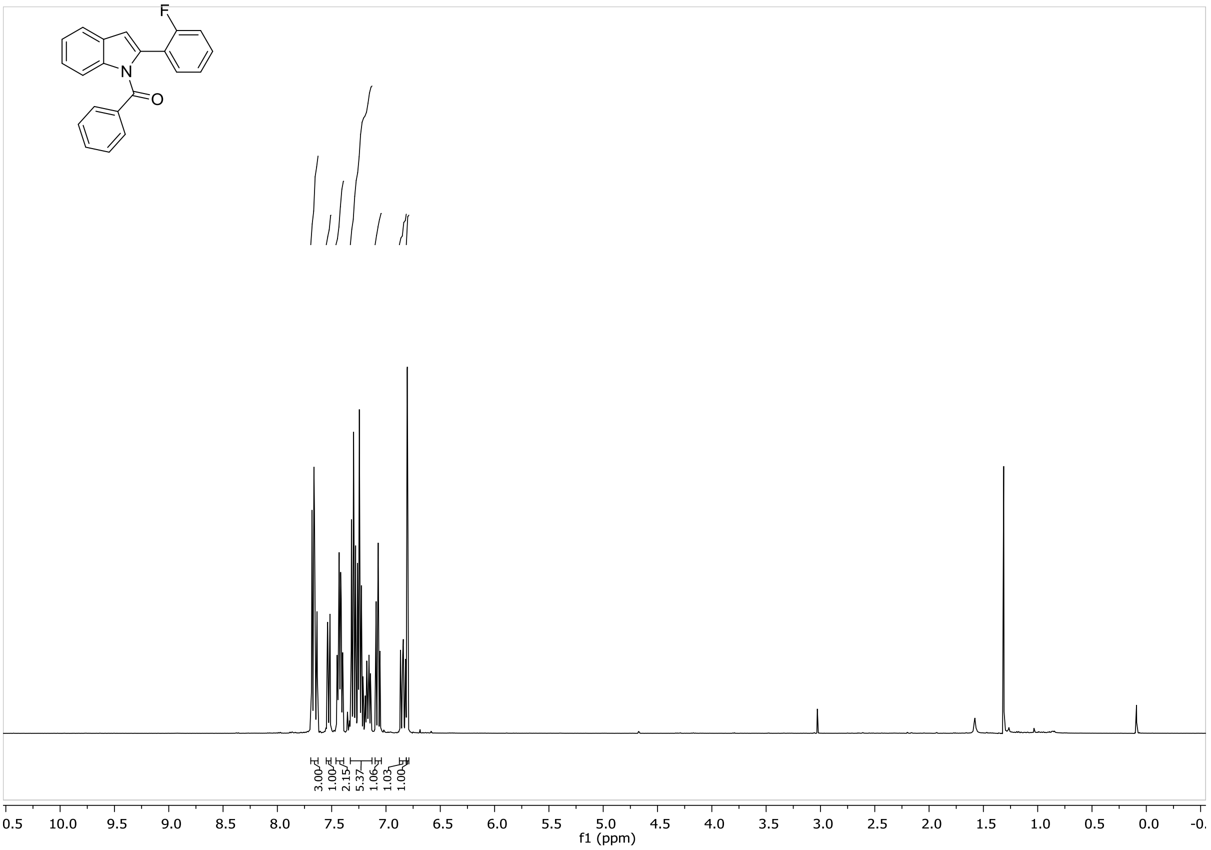

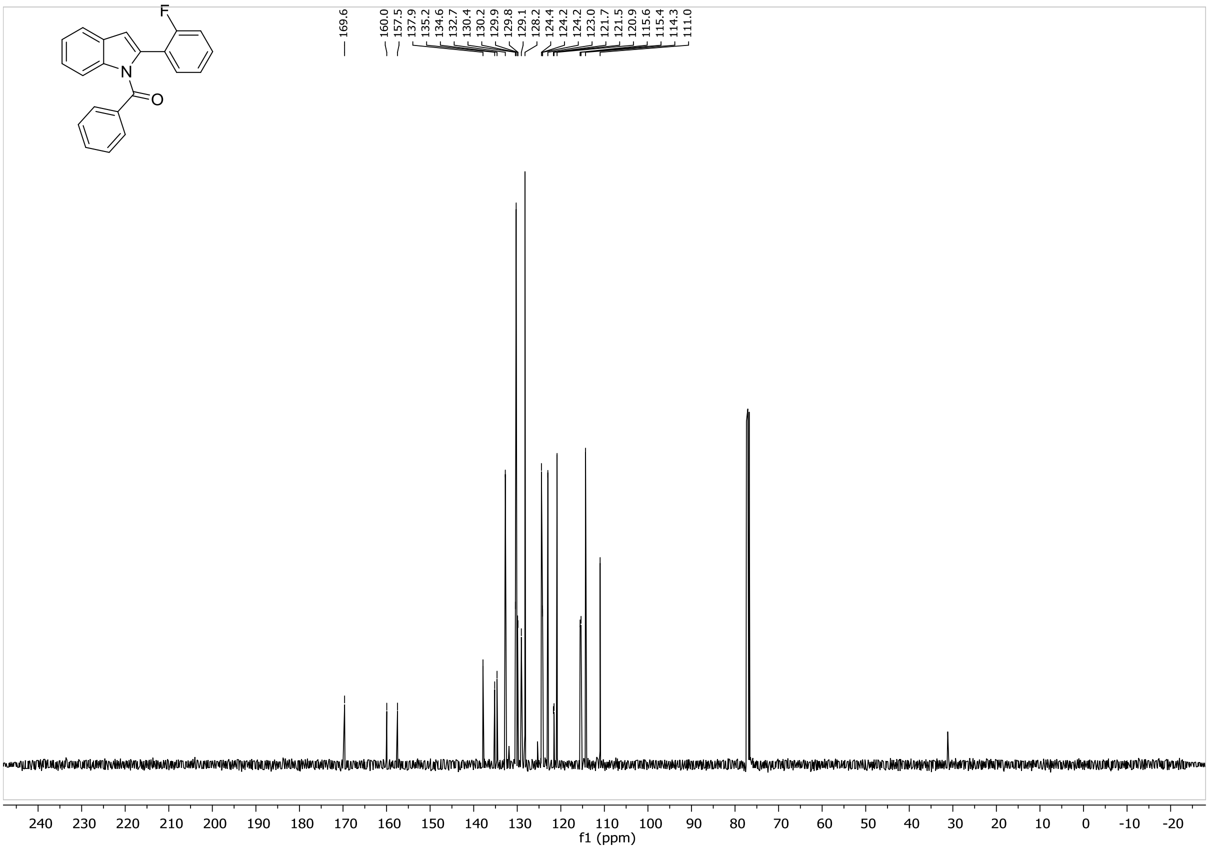

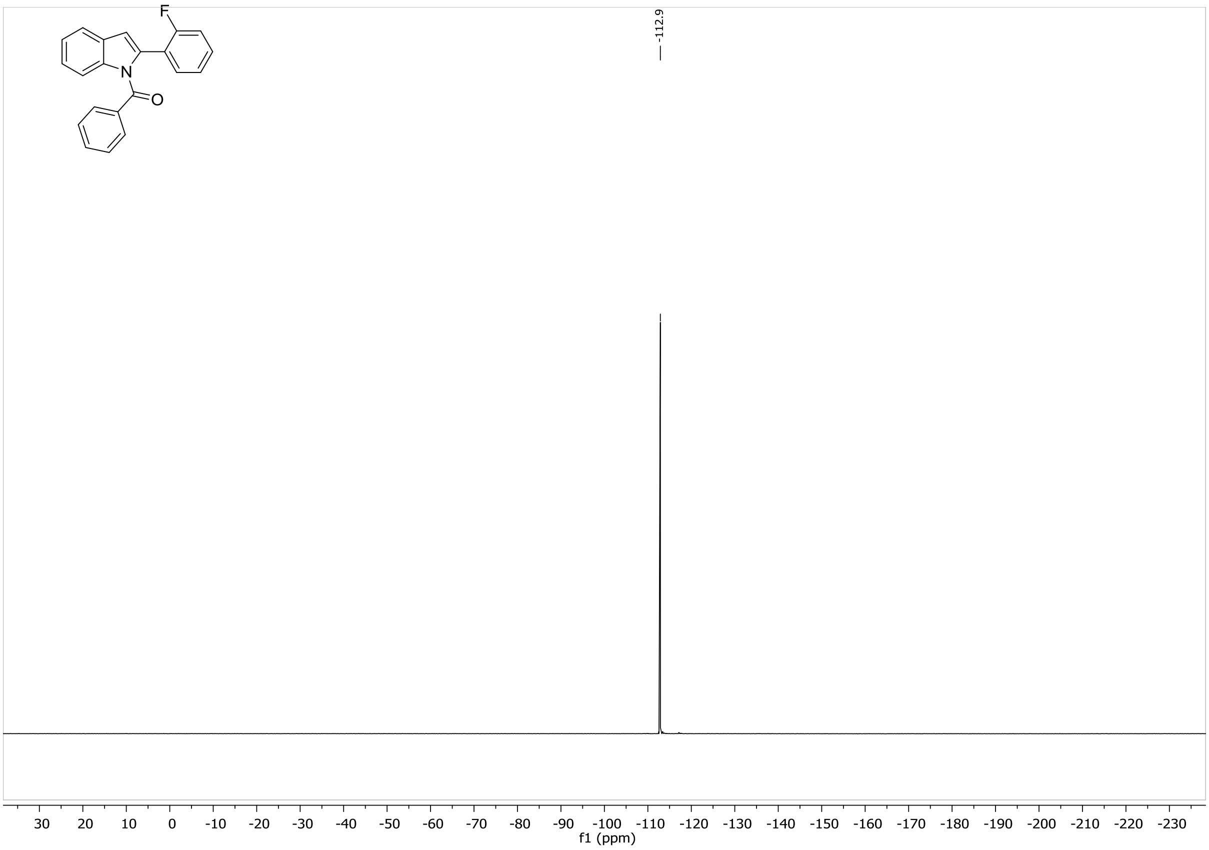
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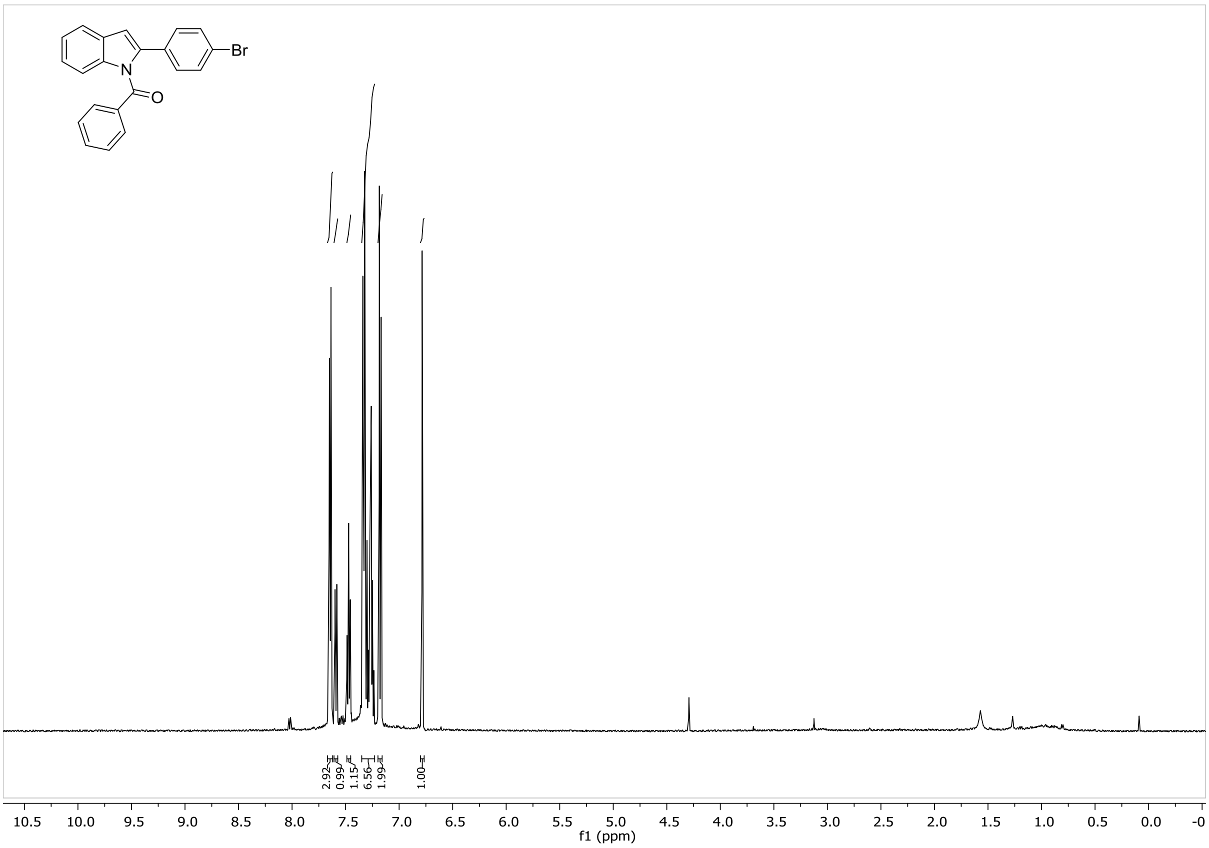
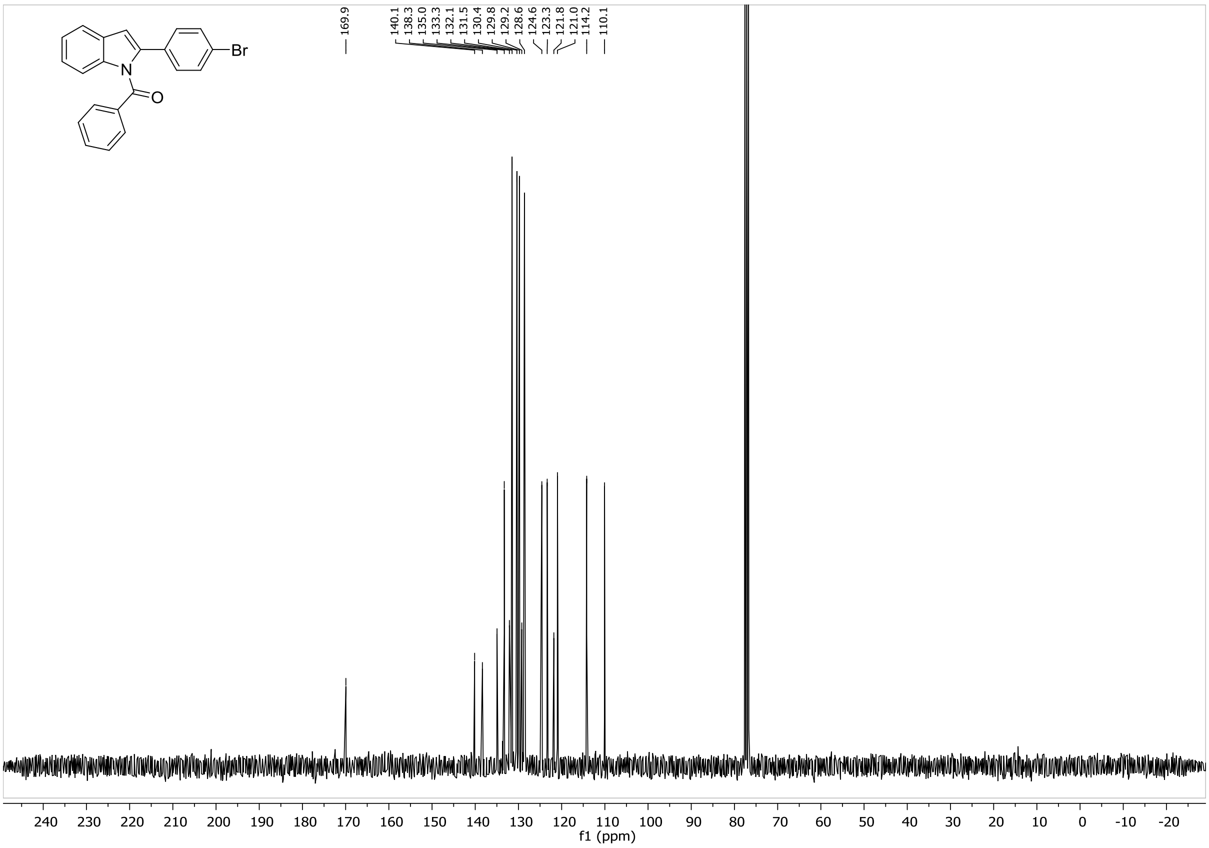
f1 (ppm)

N-Benzoyl-2-(4-bromo phenyl)indole (5h)





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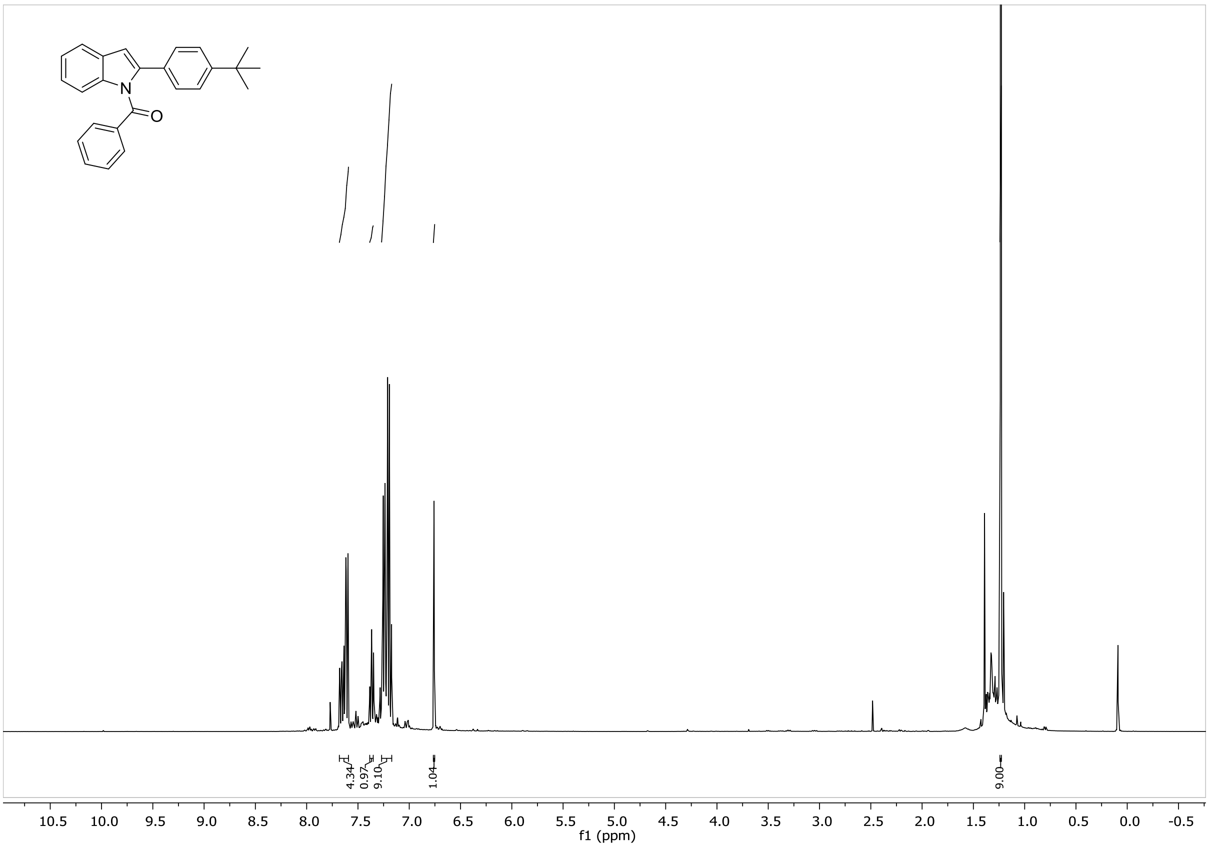

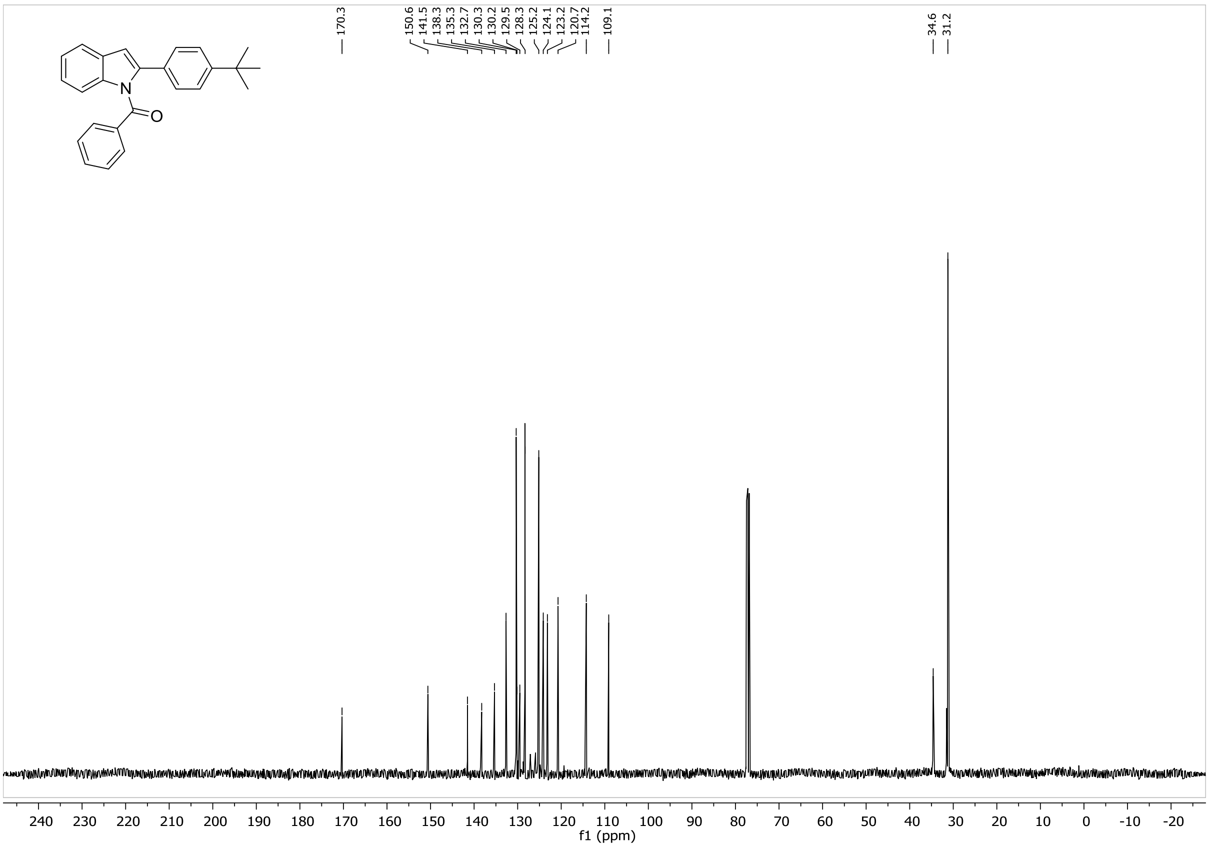

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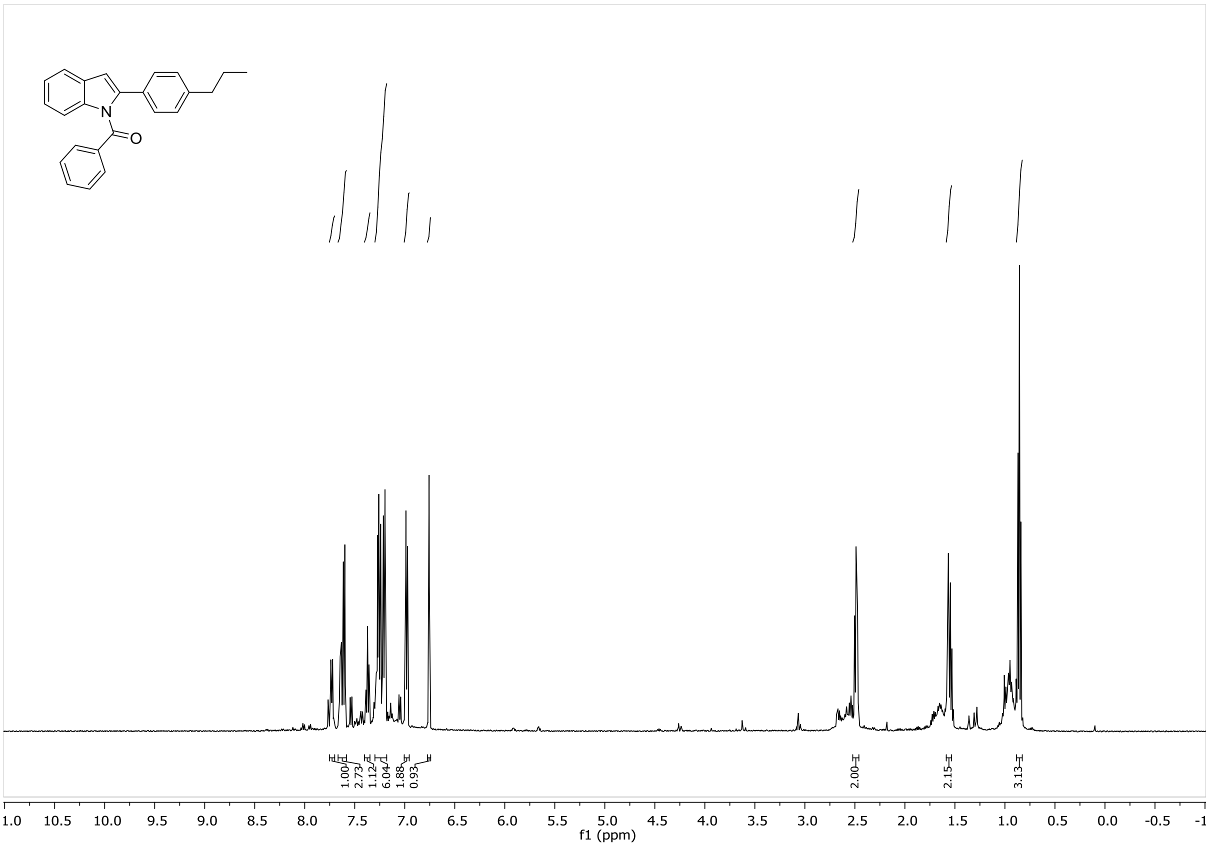
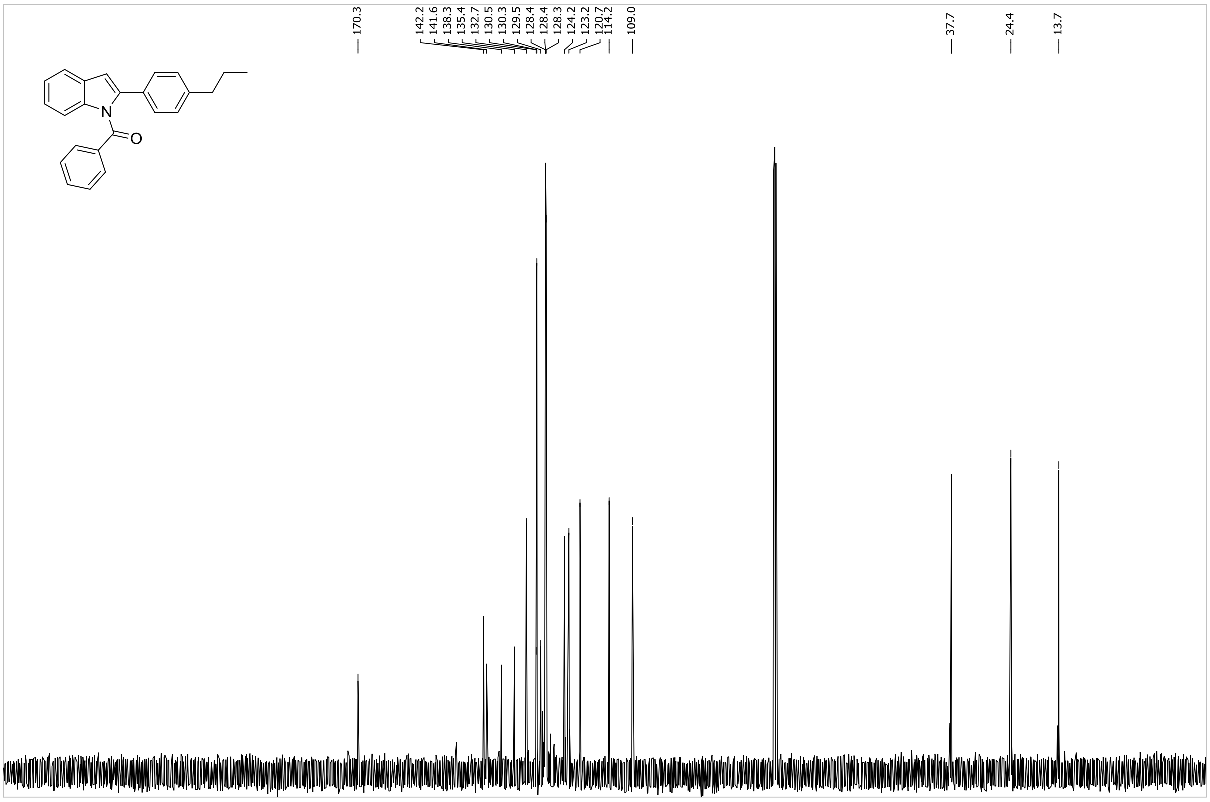
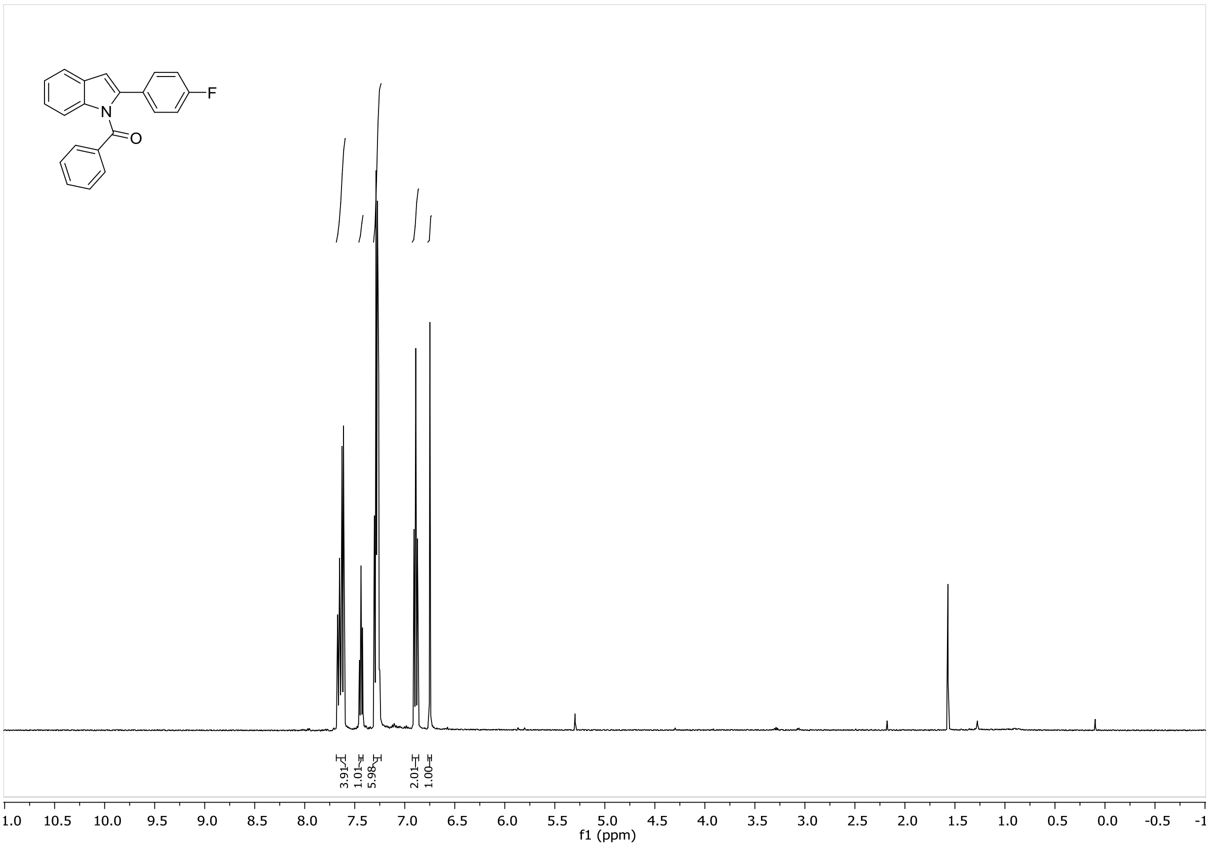
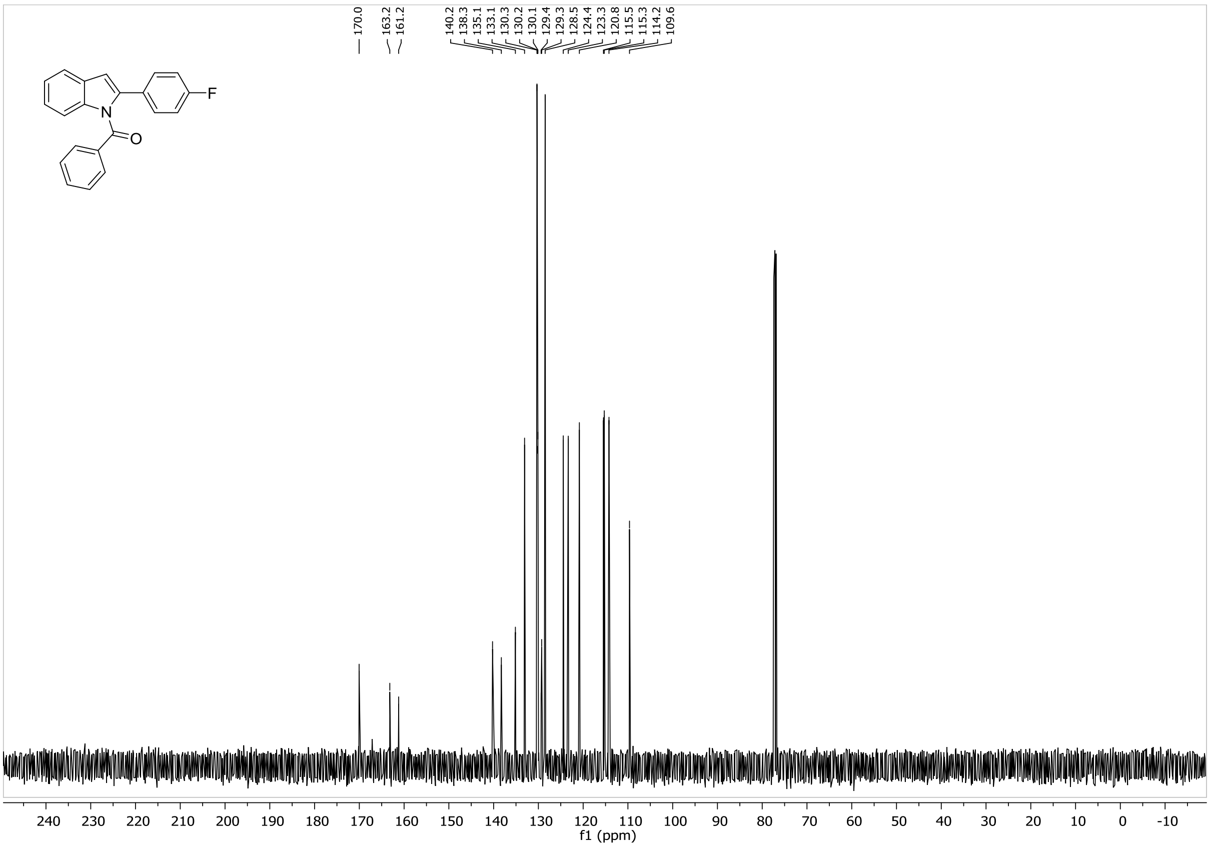
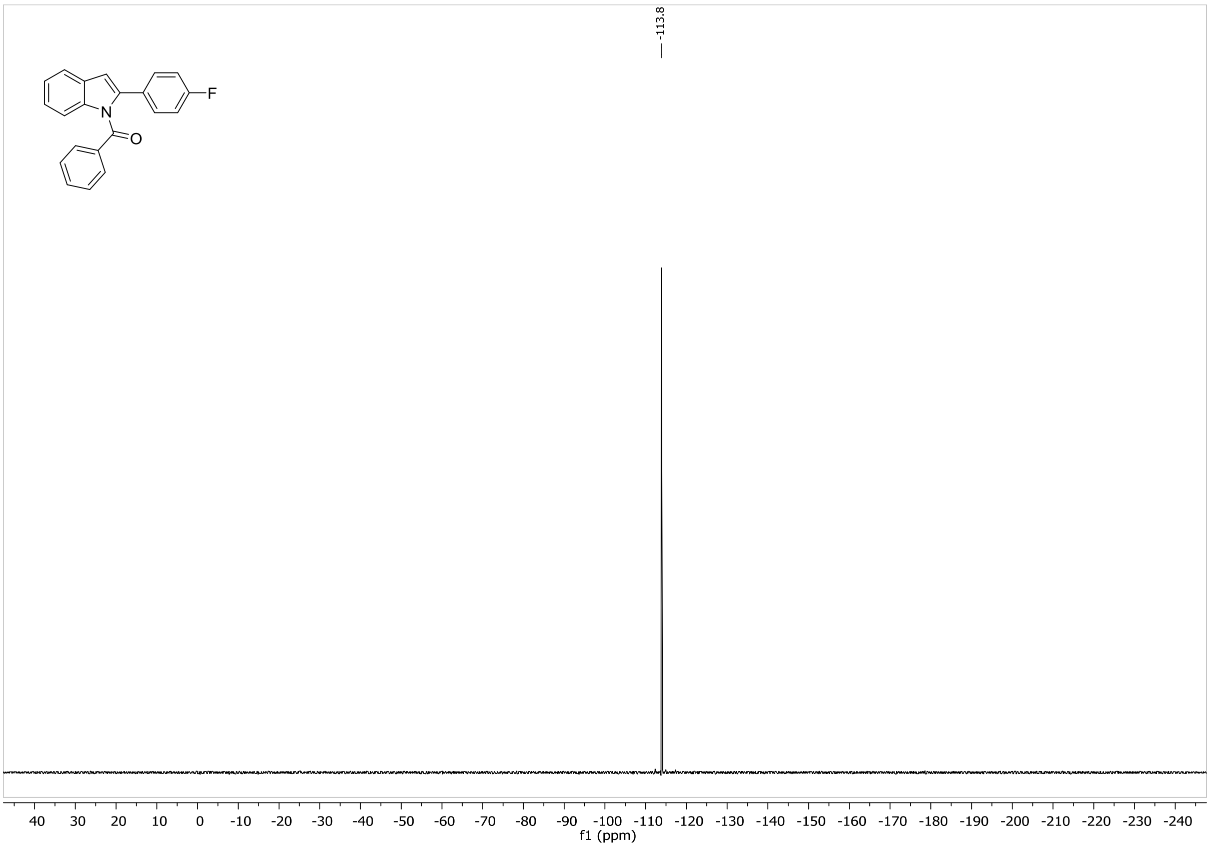




N-Benzoyl-2-(2-fluoro phenyl)indole (5l)



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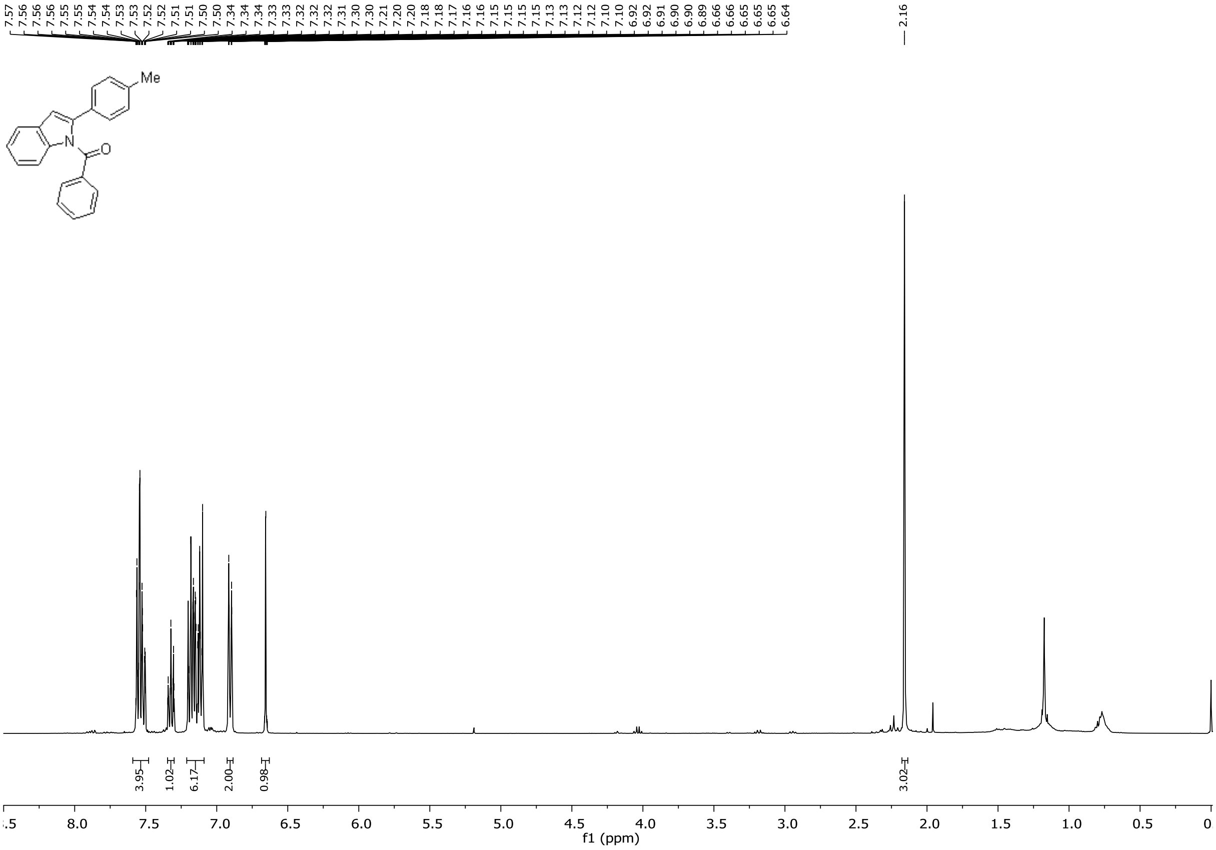
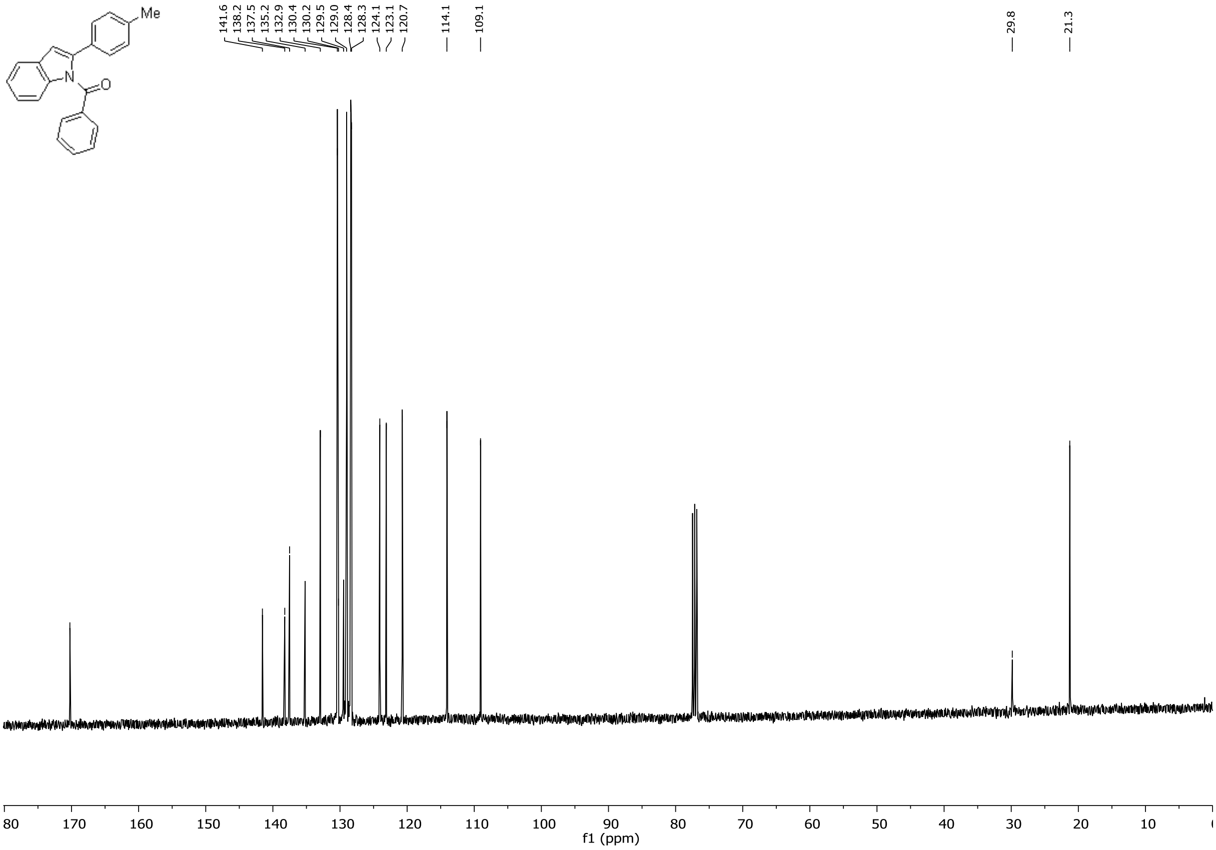
f1 (ppm)

N-Benzoyl-2-(4-methyl phenyl)indole (5m)





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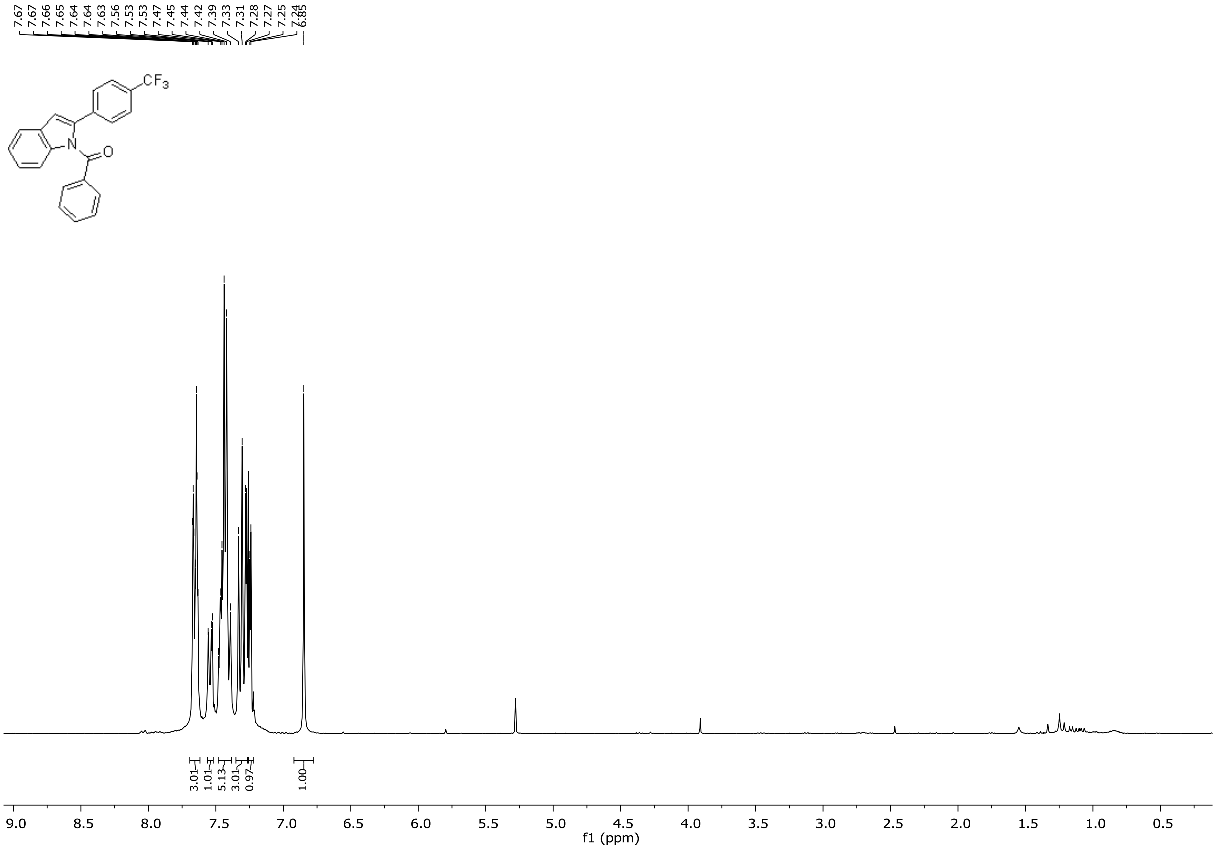

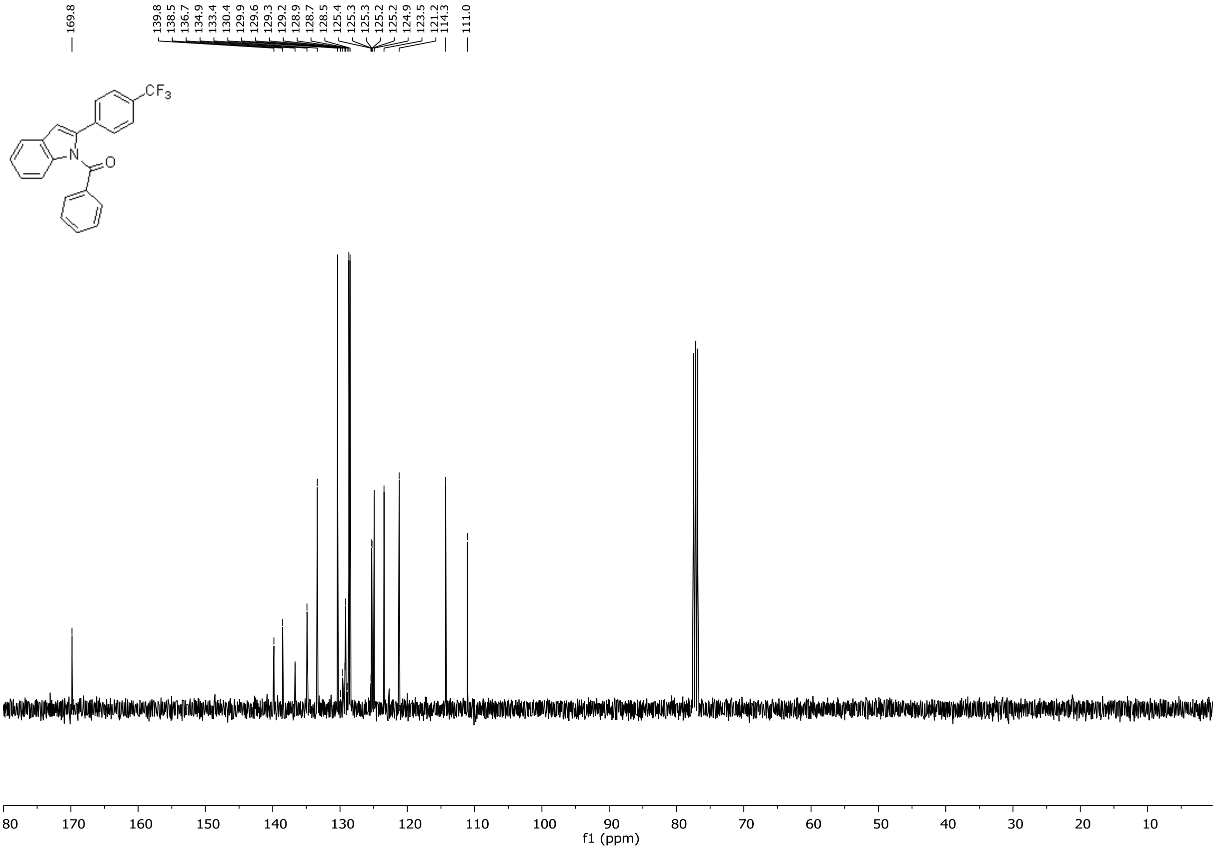

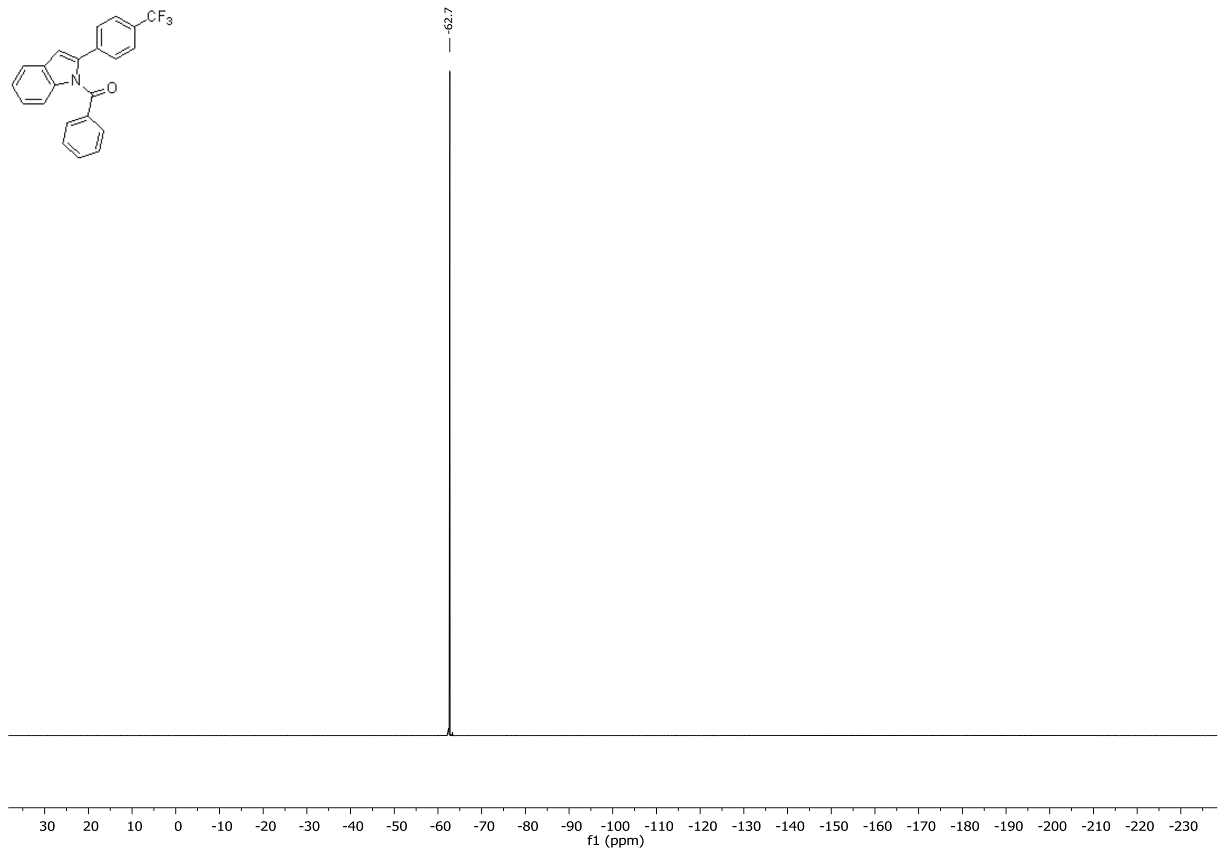
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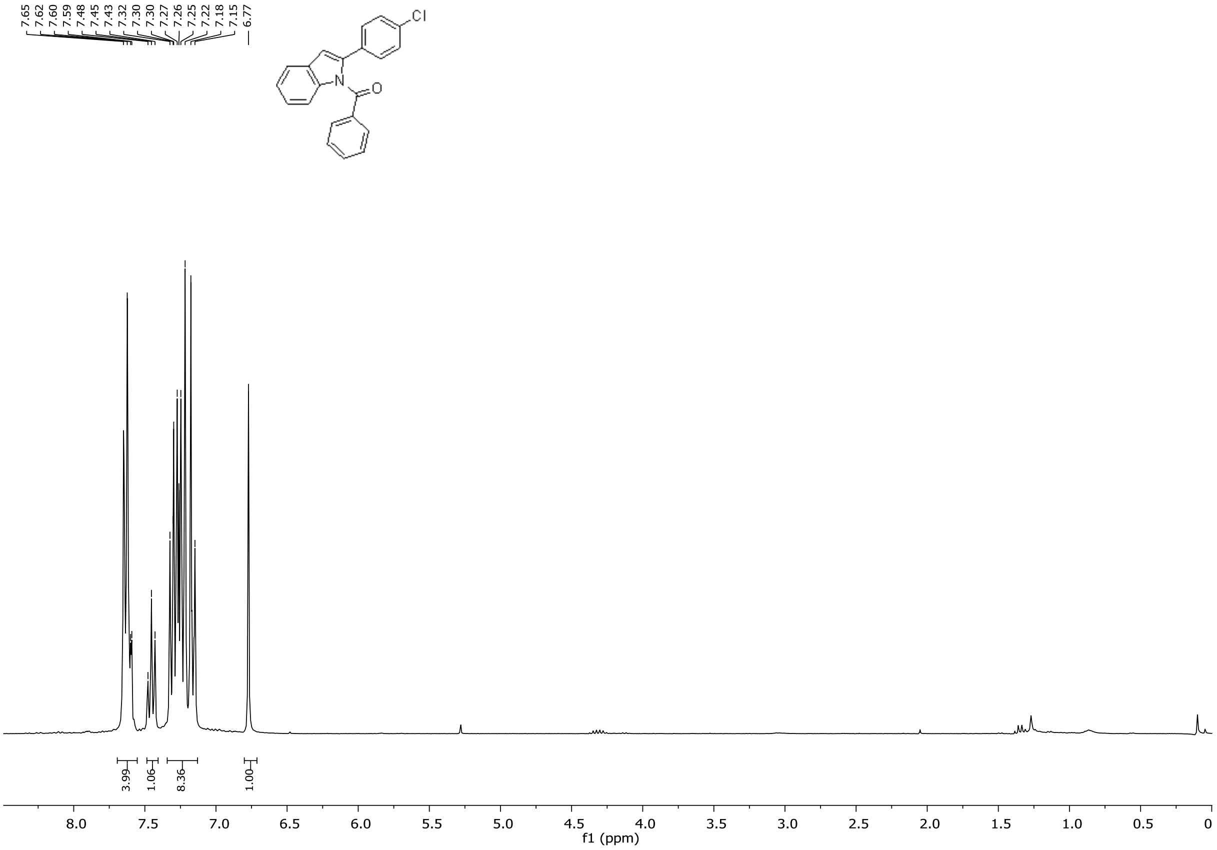
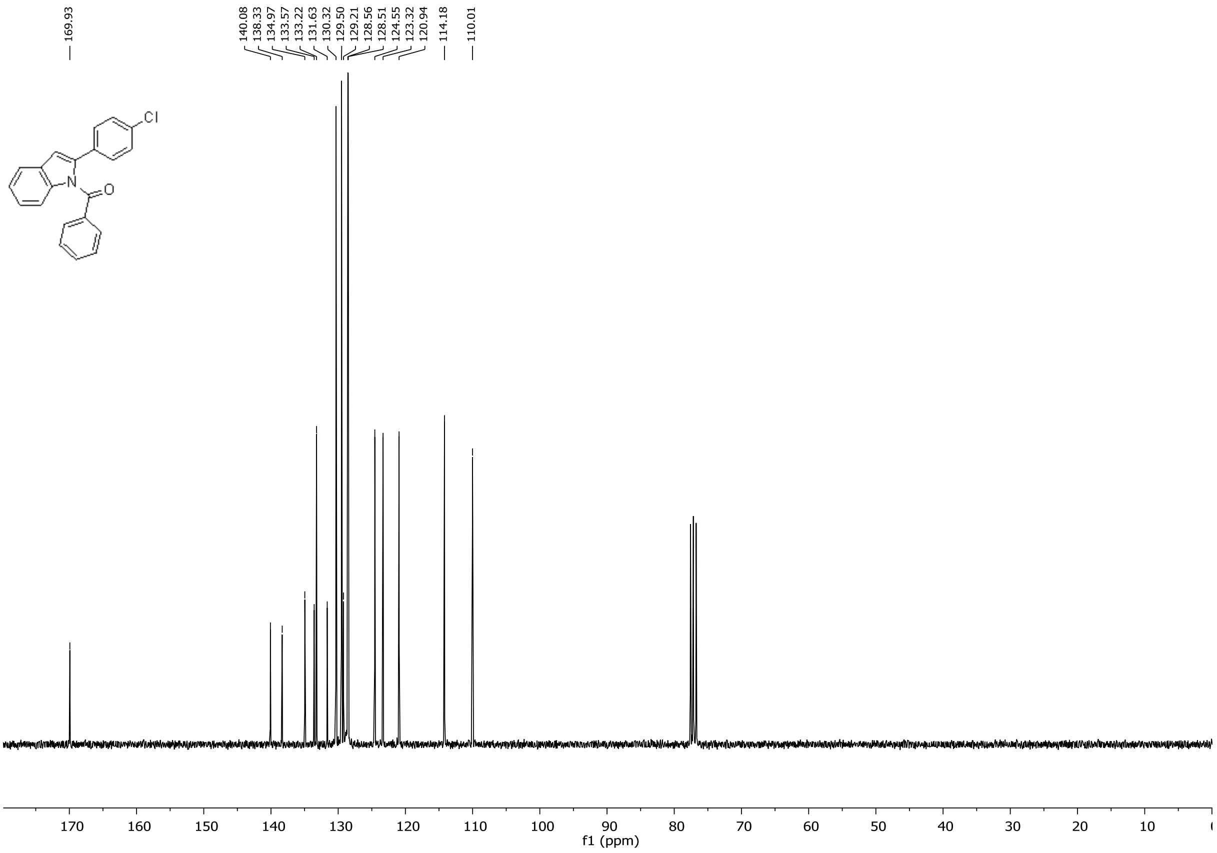
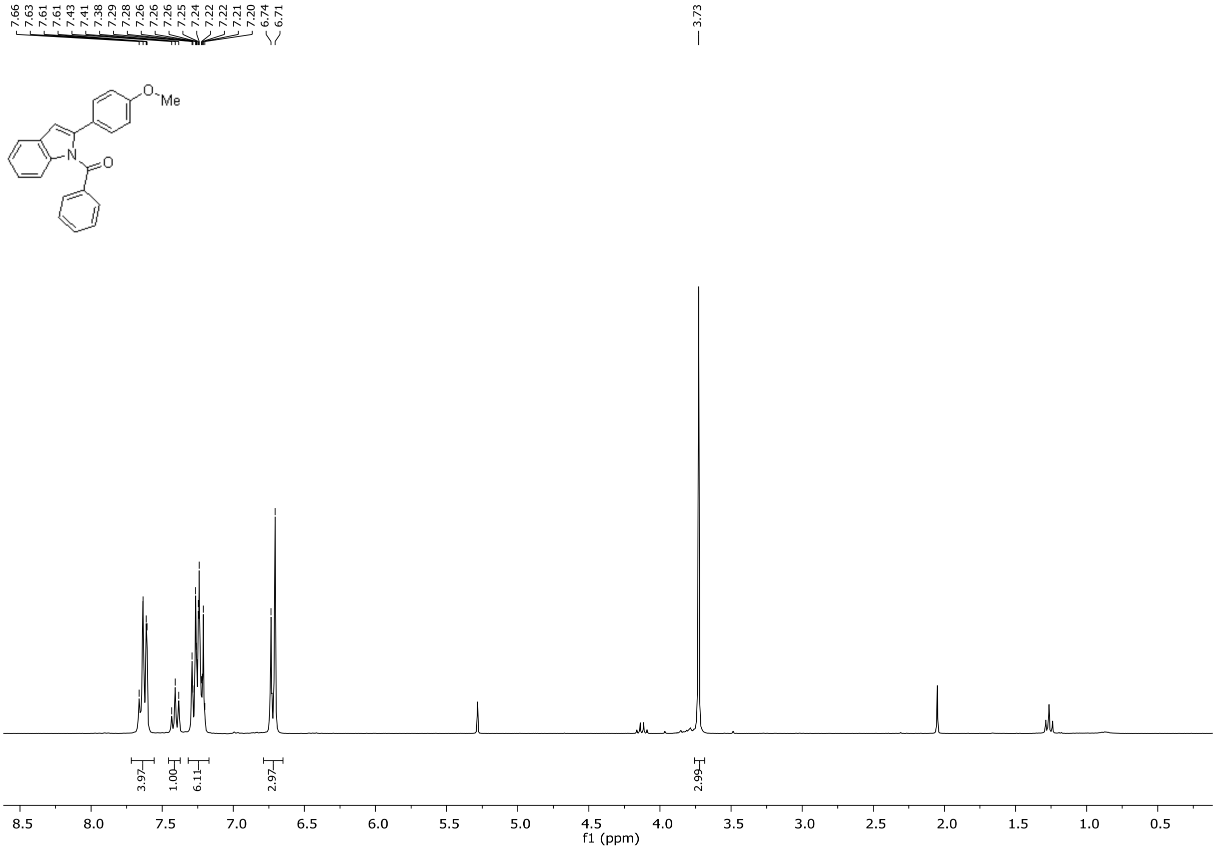
f1 (ppm)

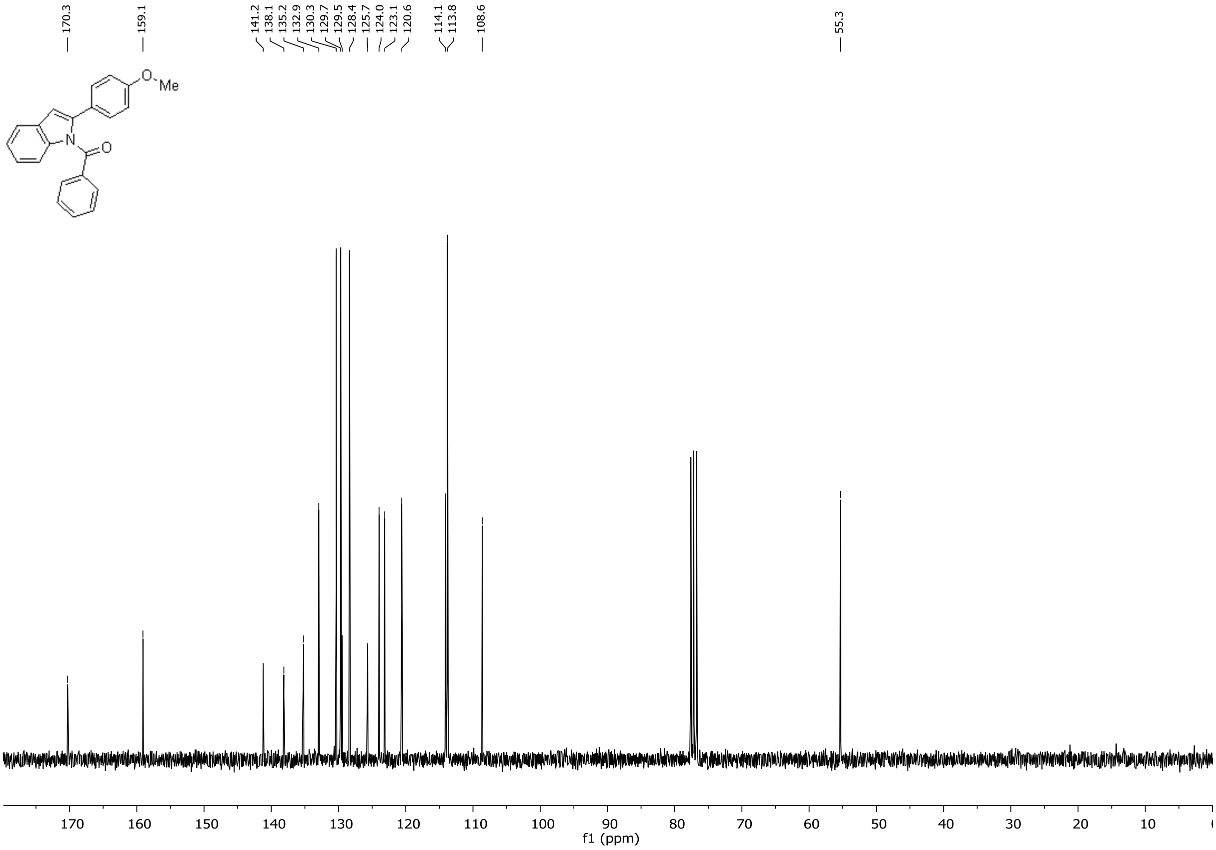
N-Benzoyl-2-(4-chlorophenyl)indole (5o)



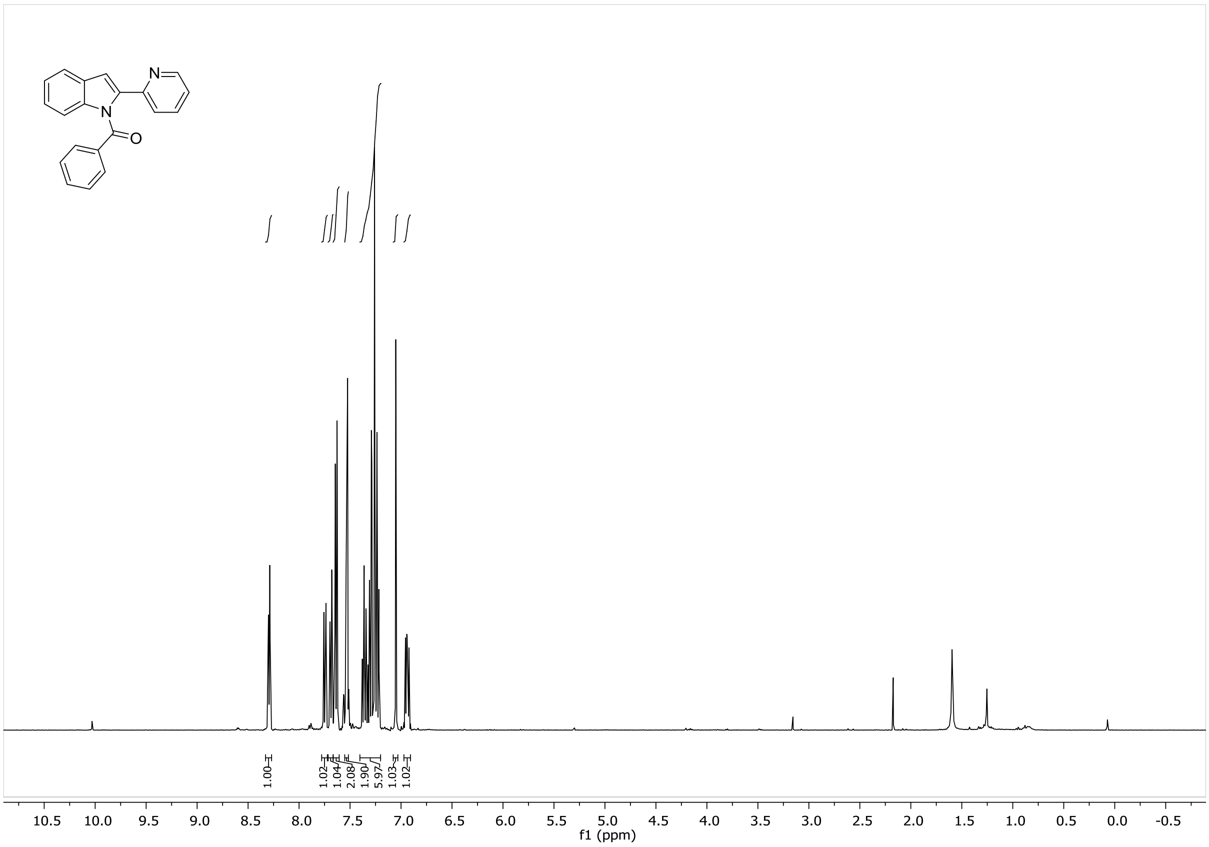


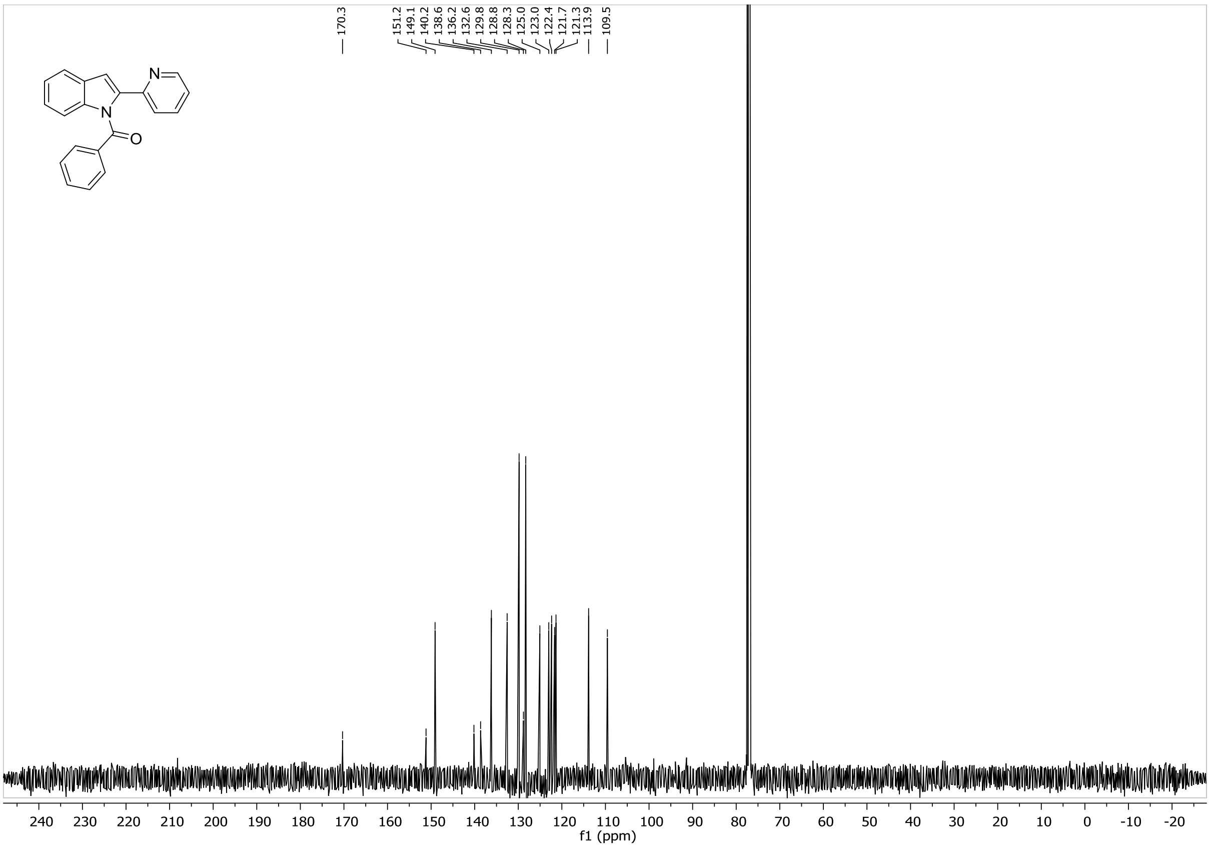
N-Benzoyl-2-(4-methoxyphenyl)indole (5p)





N-Benzoyl-2-(pyridin-2-yl)indole (5q)





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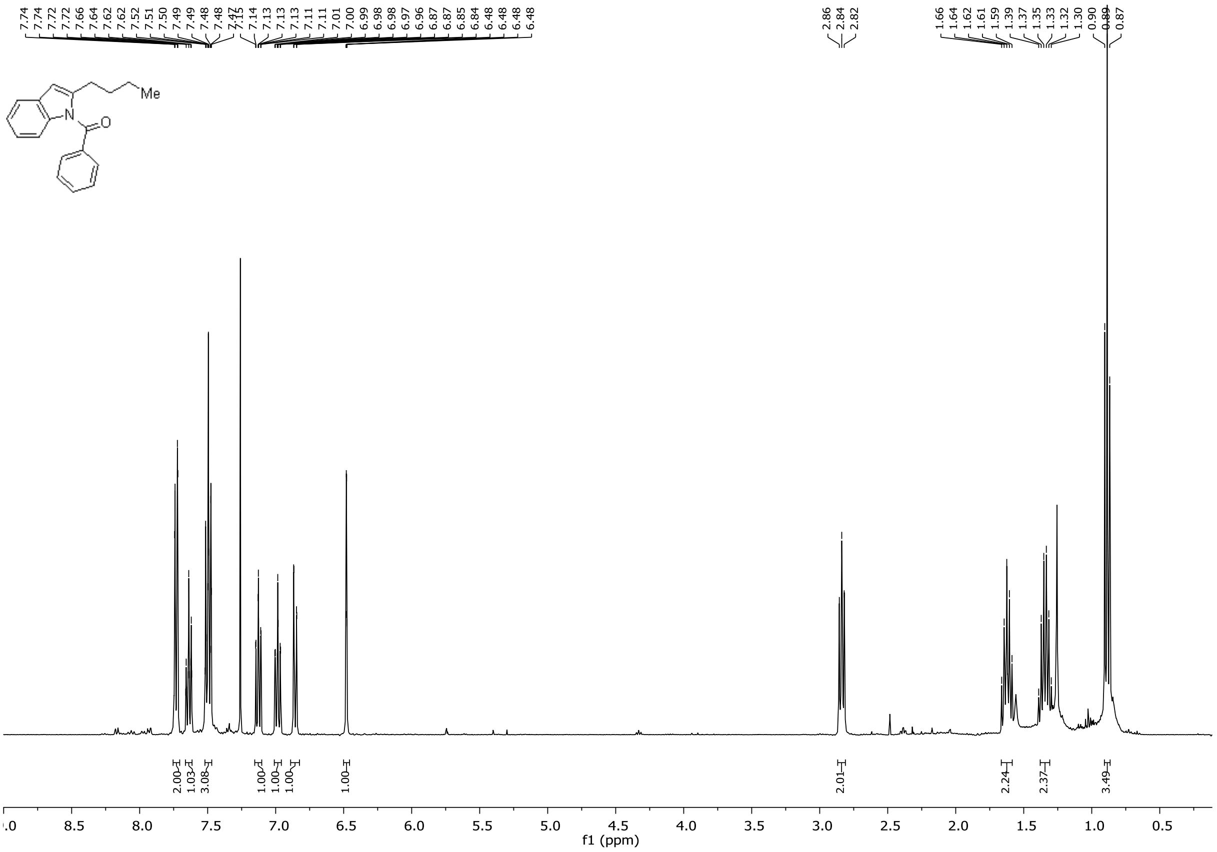

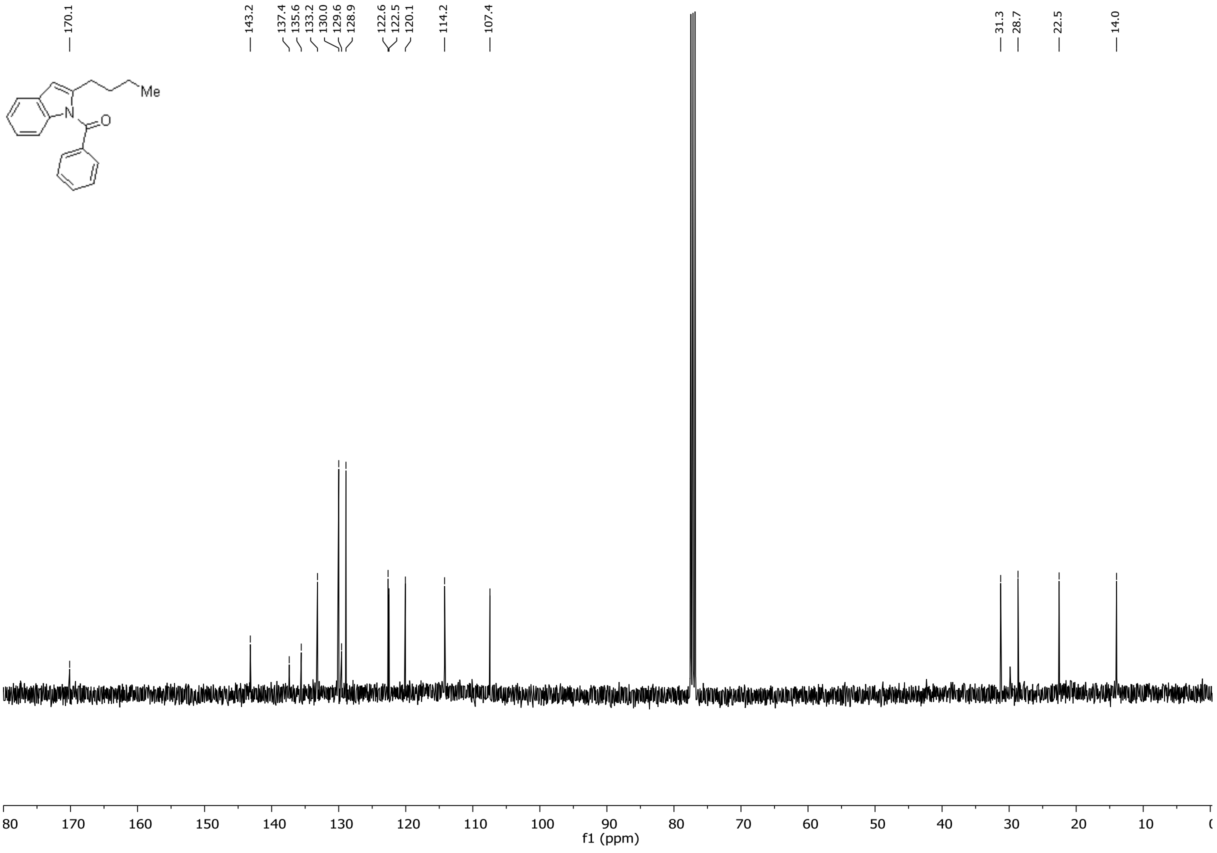

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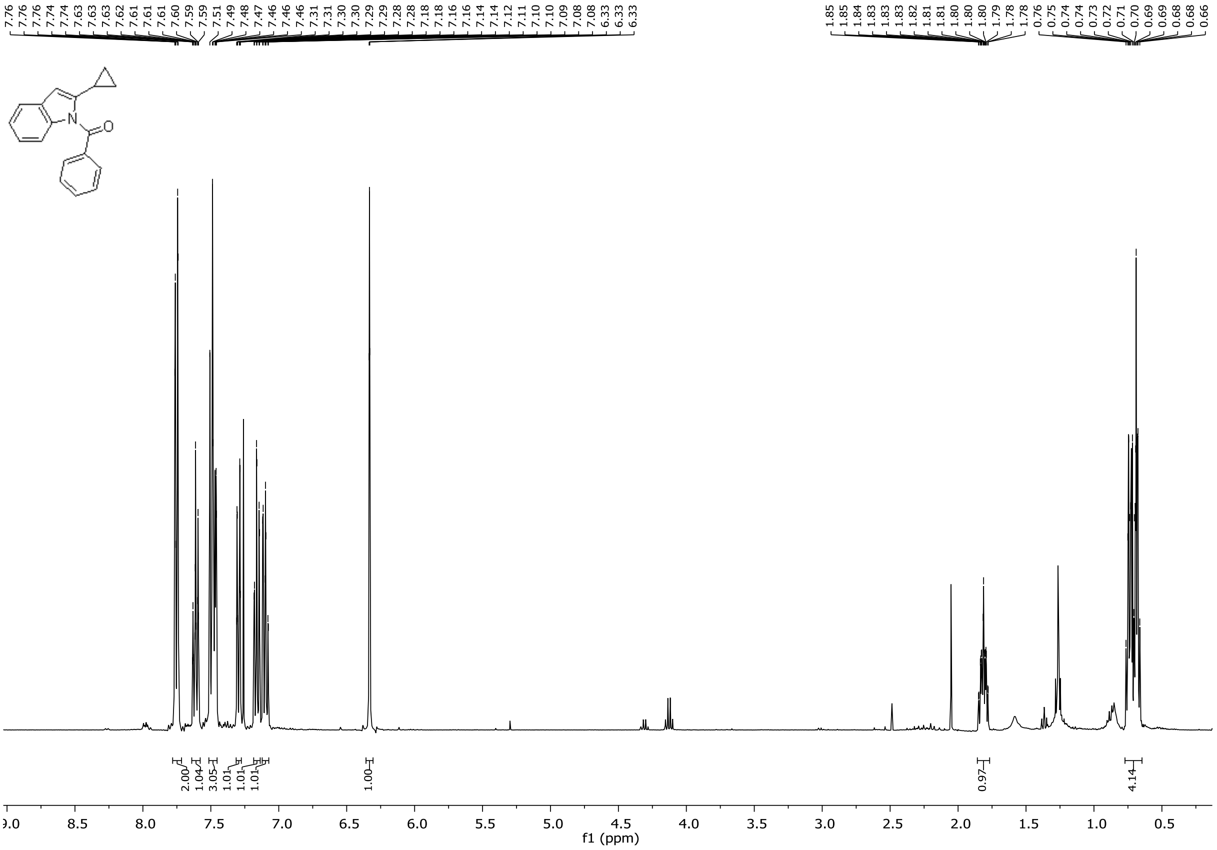
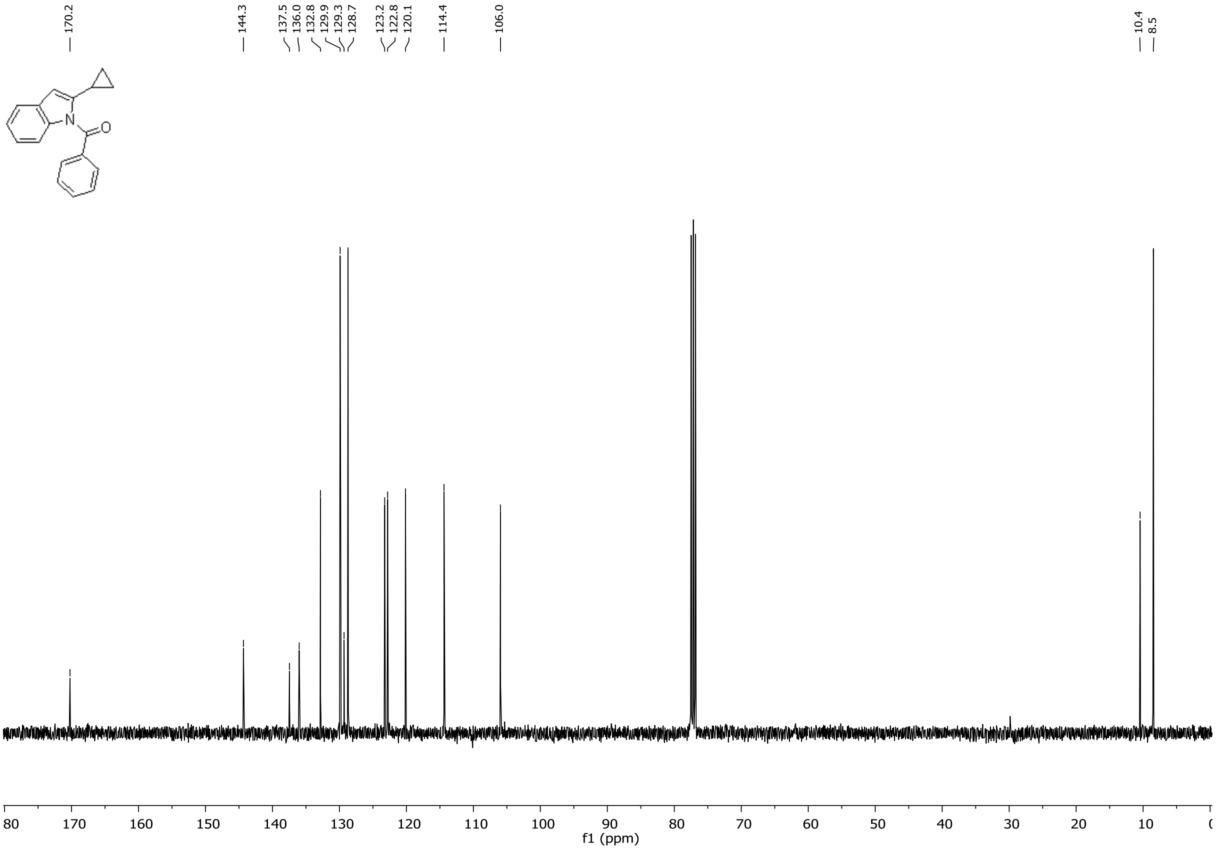
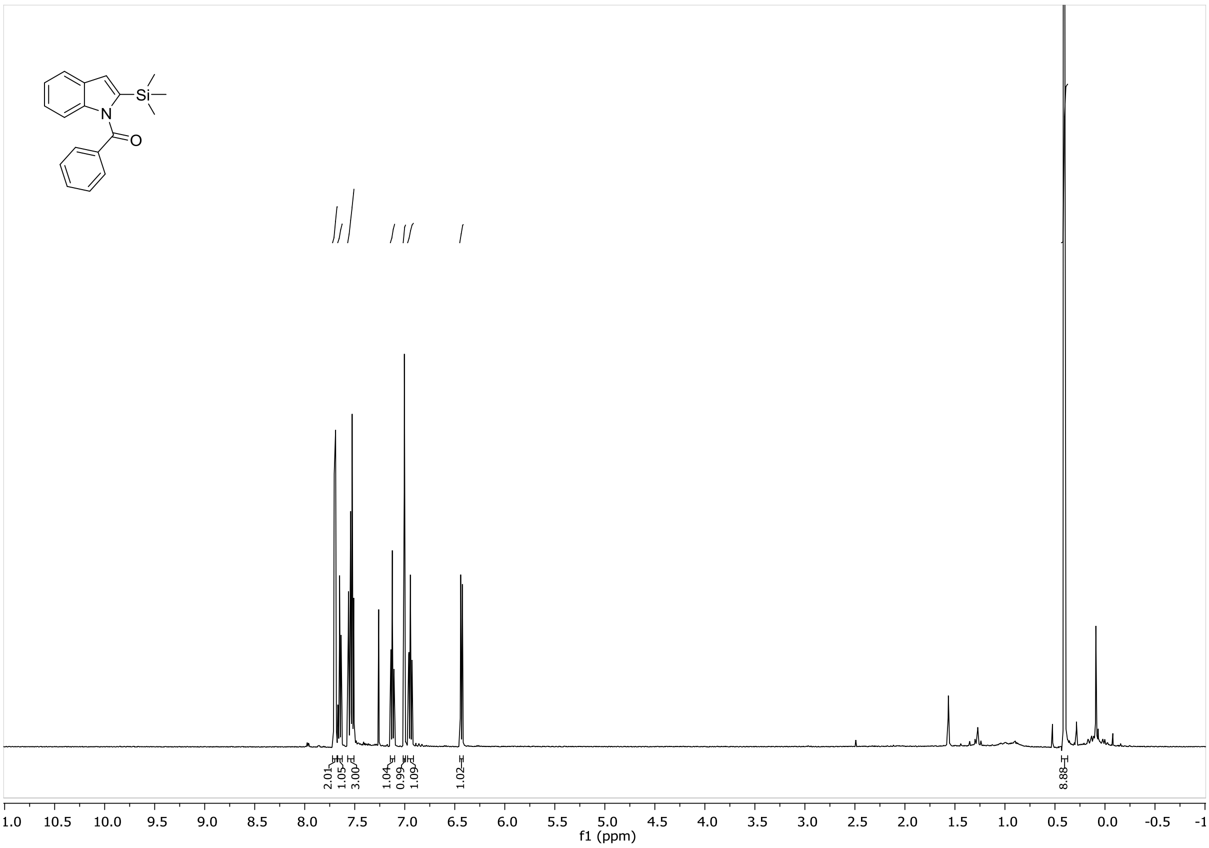
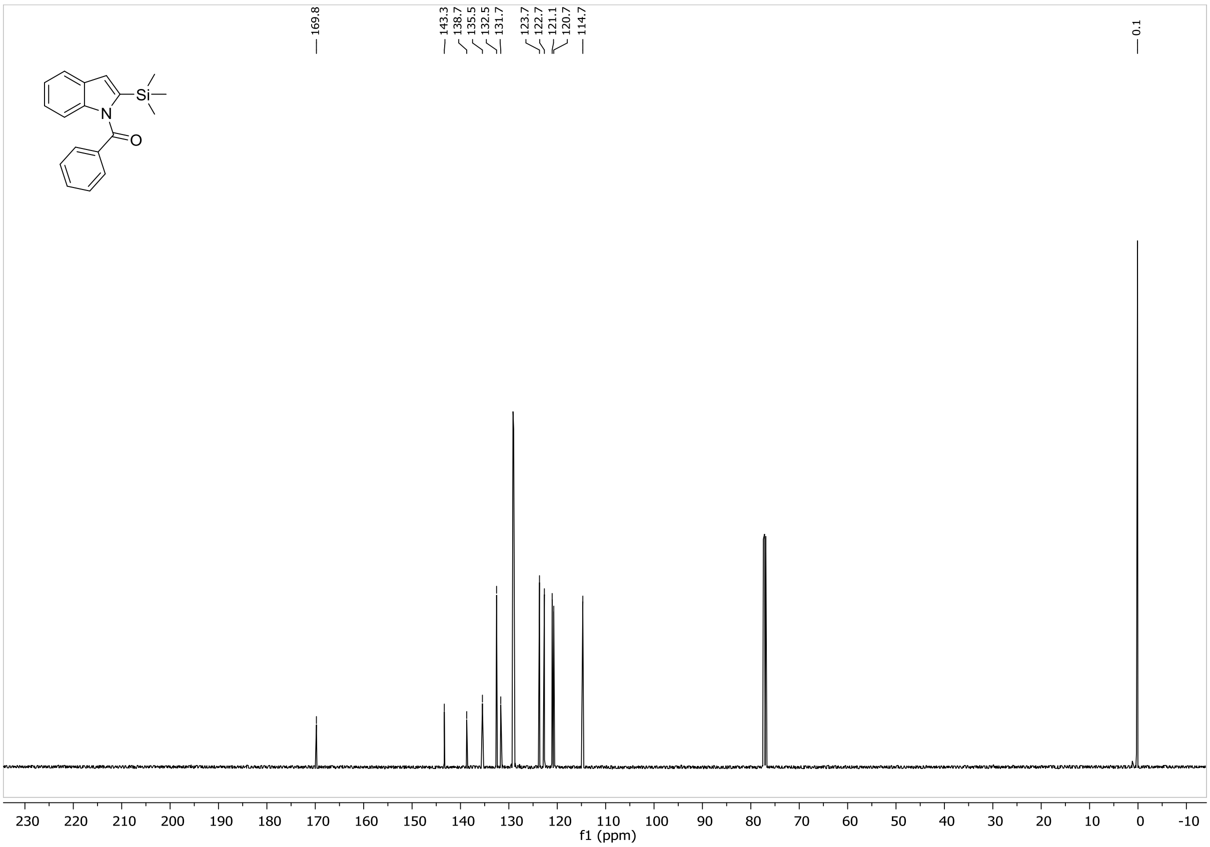


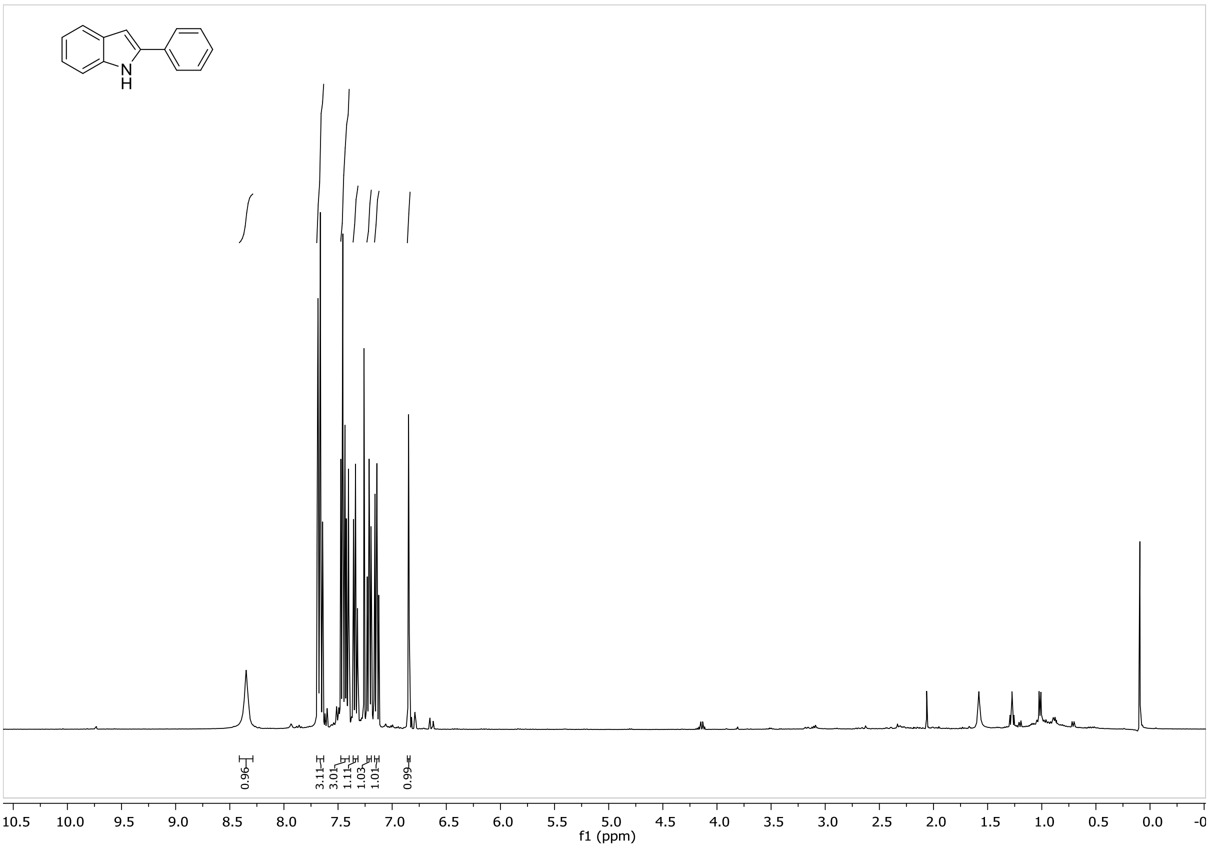


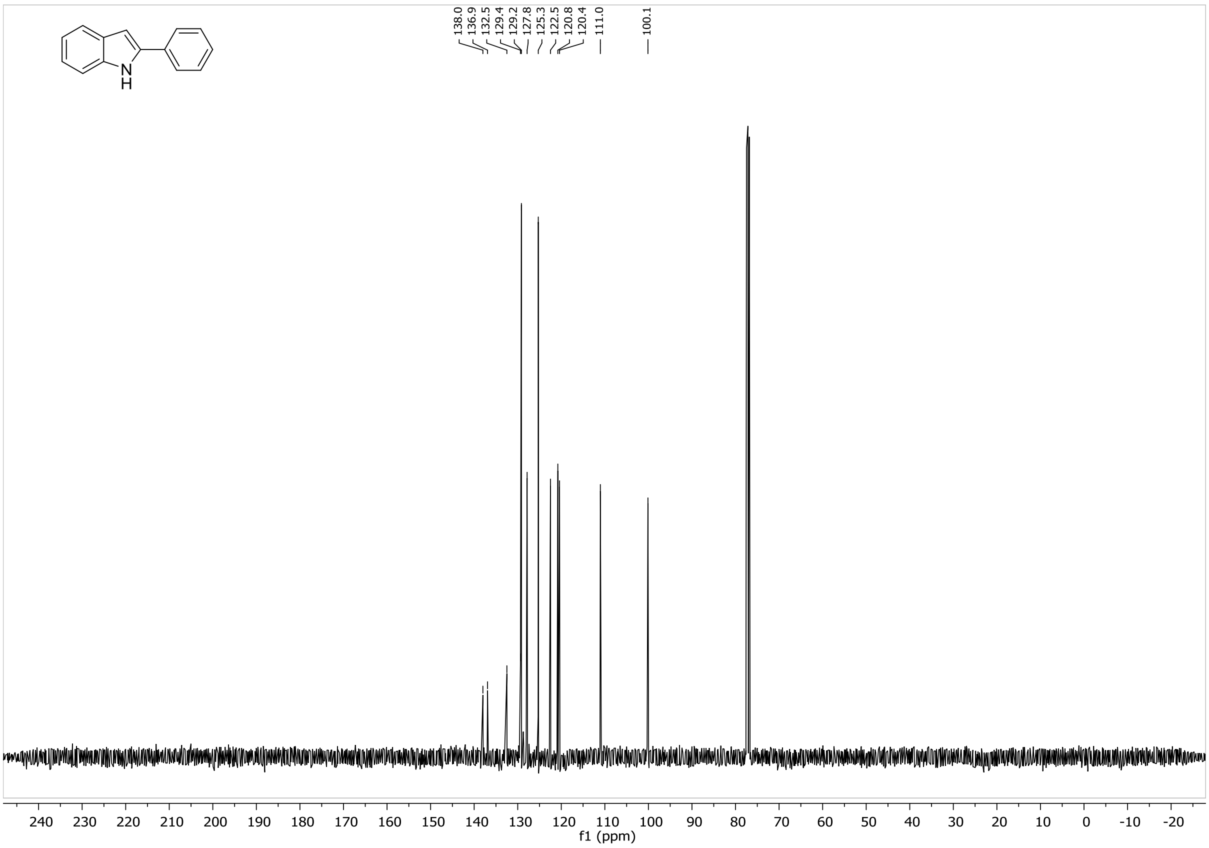
N-Benzoyl-2-trimethylsilylindole (5w)





2-Phenylindole (5Ha)





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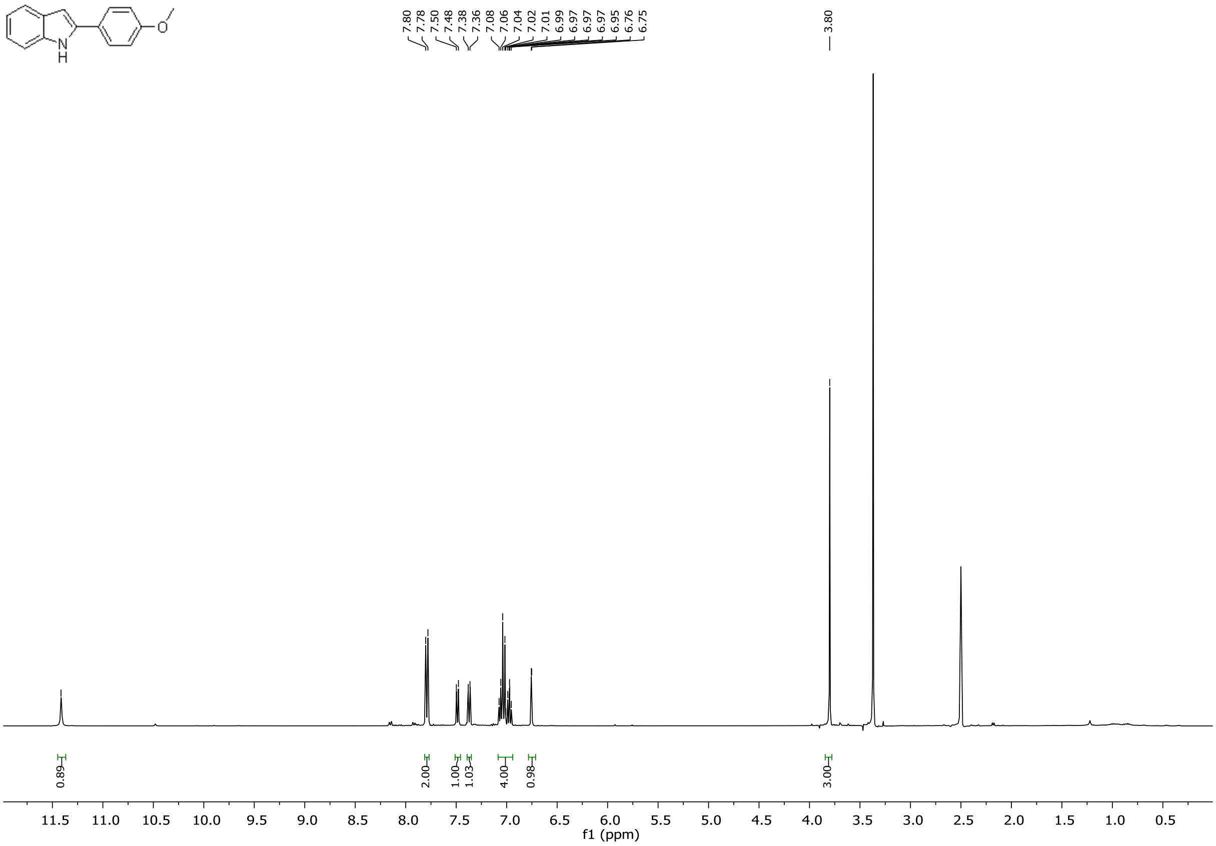
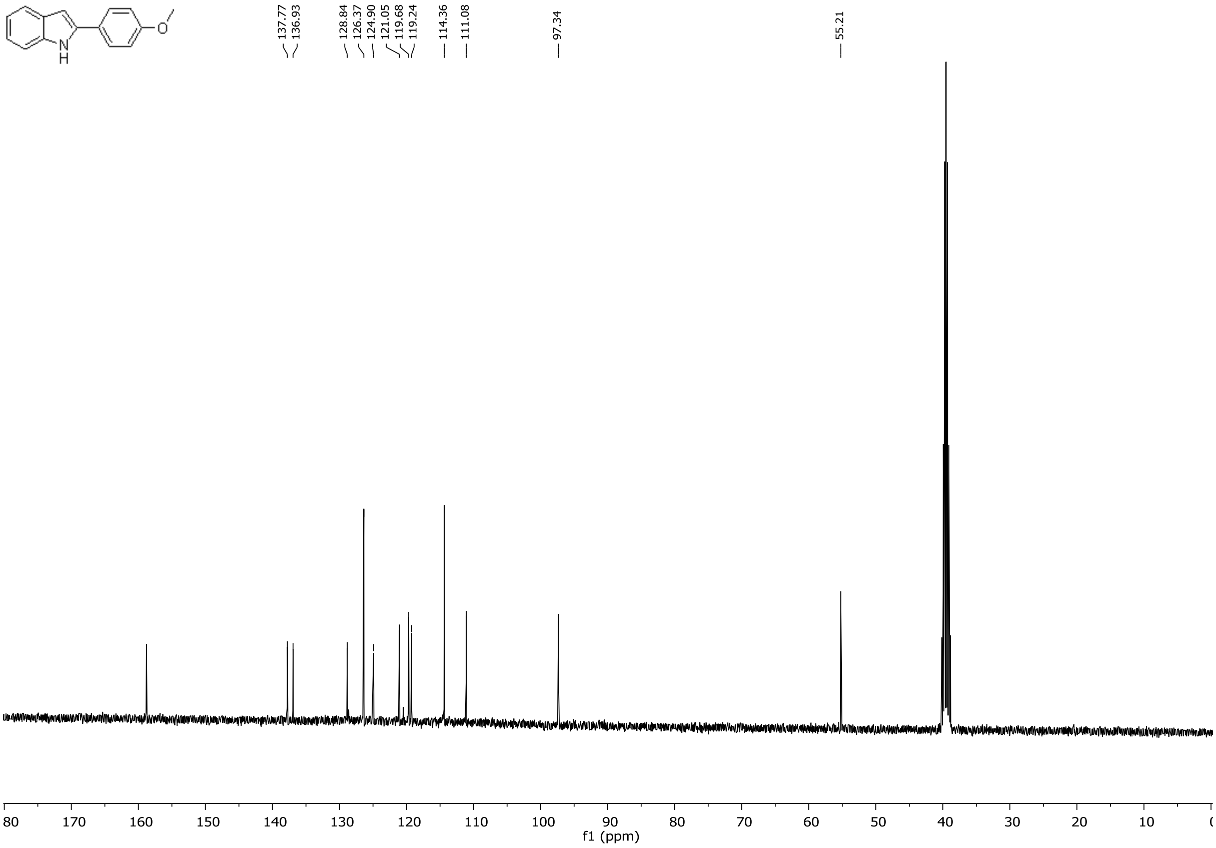
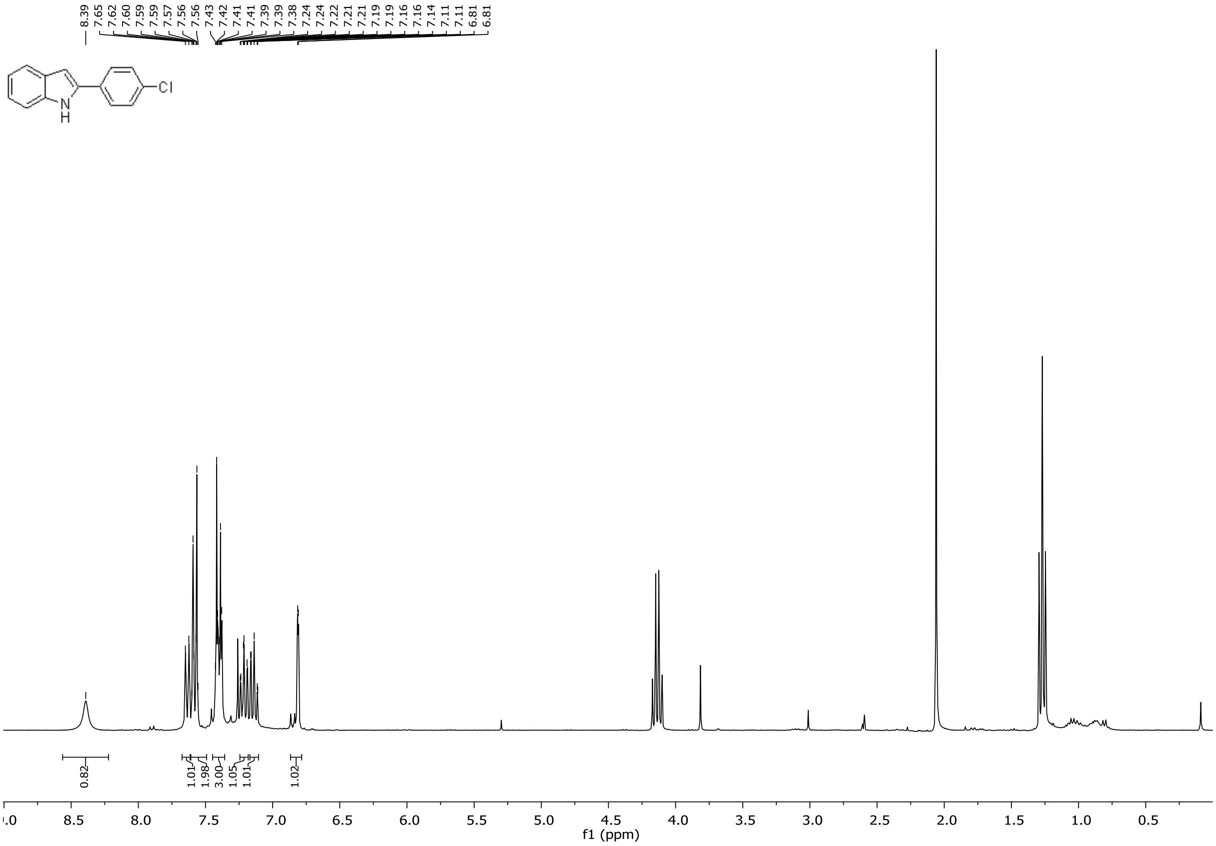
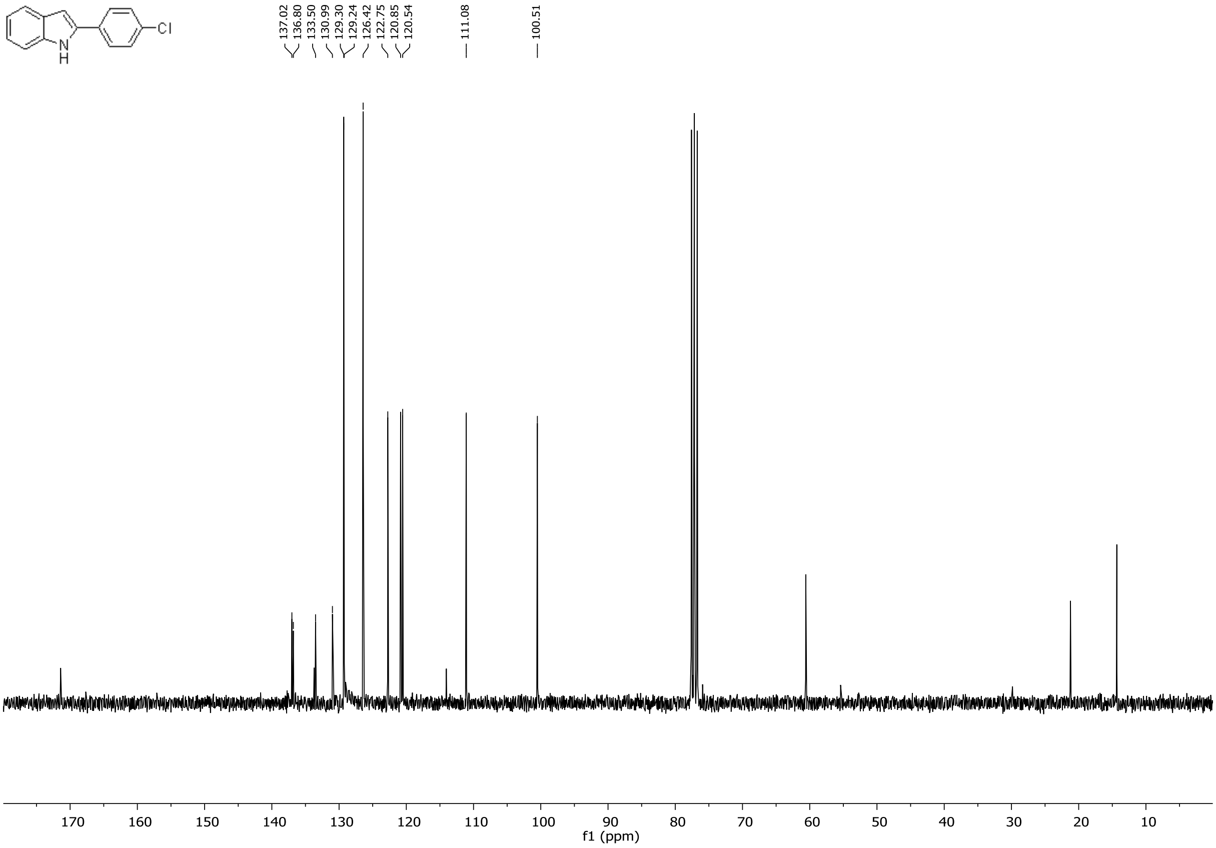


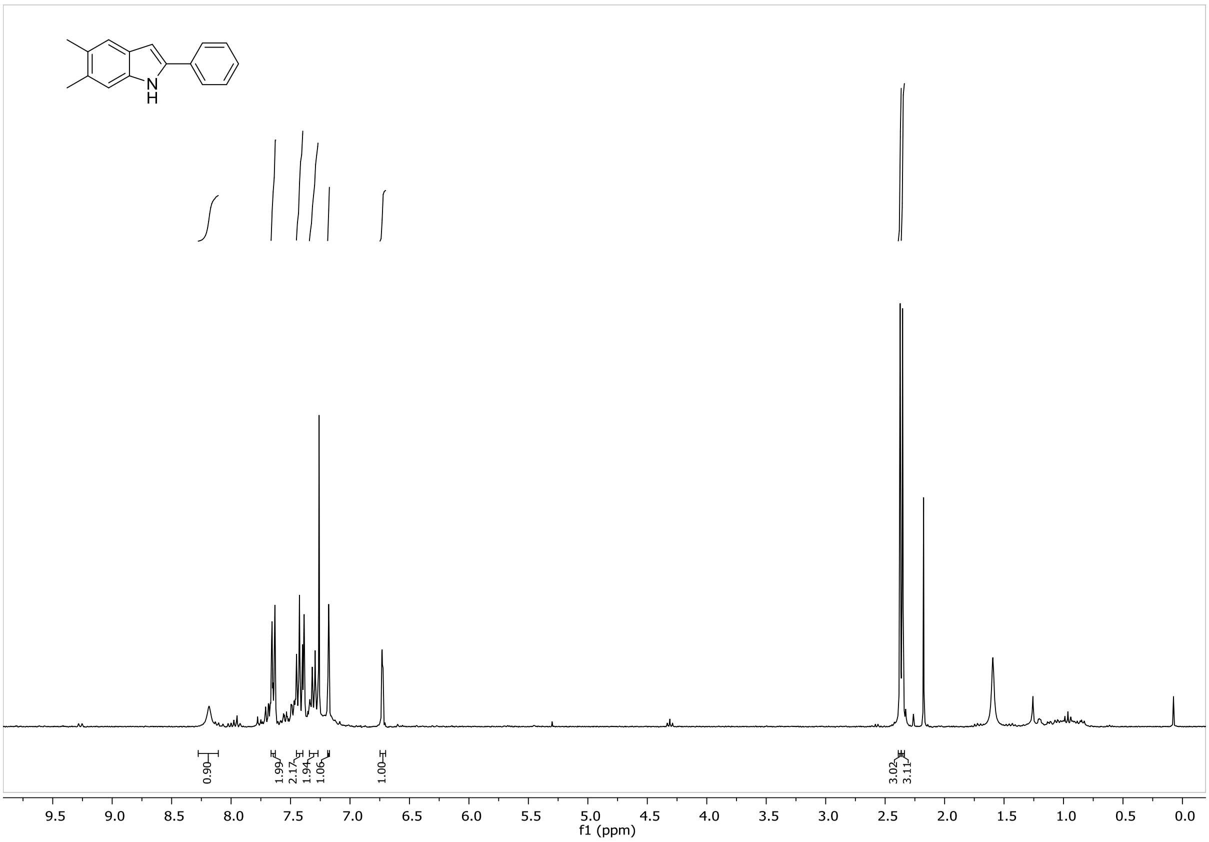


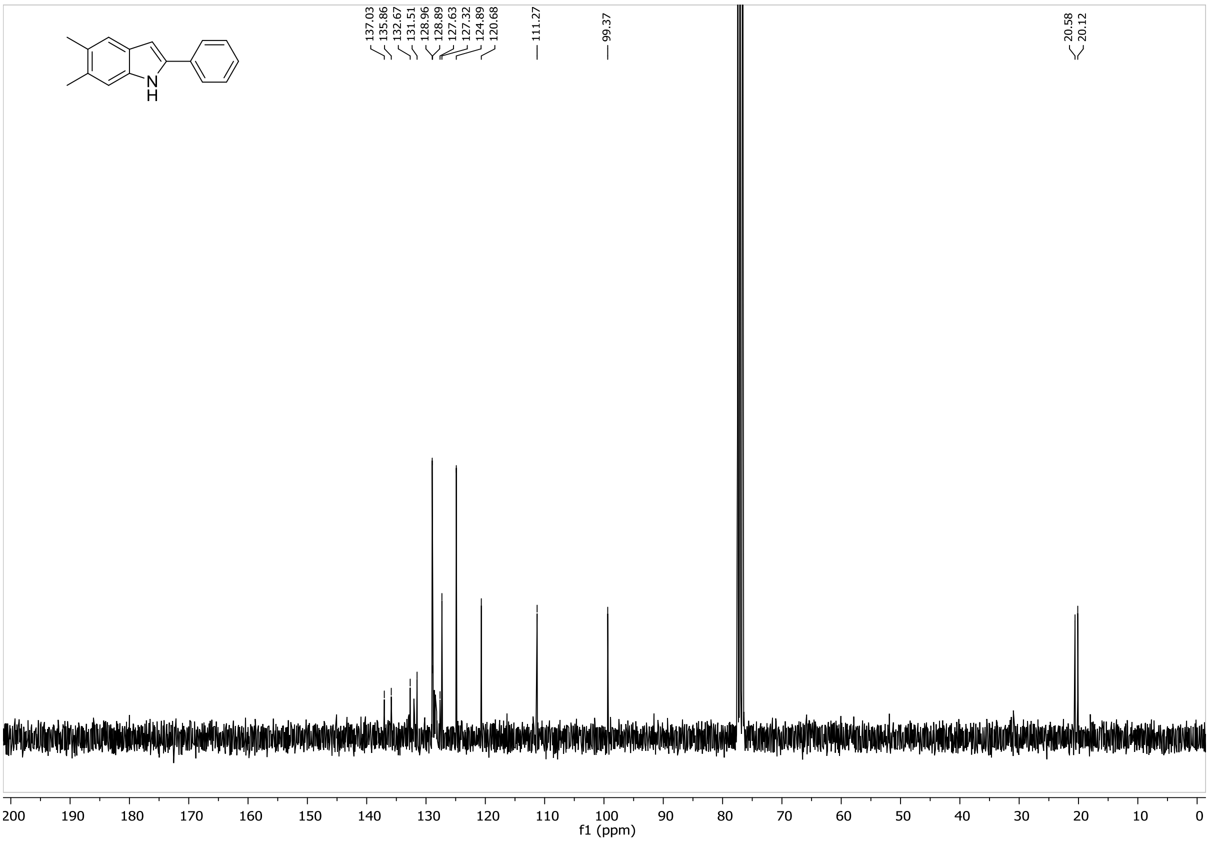
2-(4-Chlorophenyl)indole (5Hc)



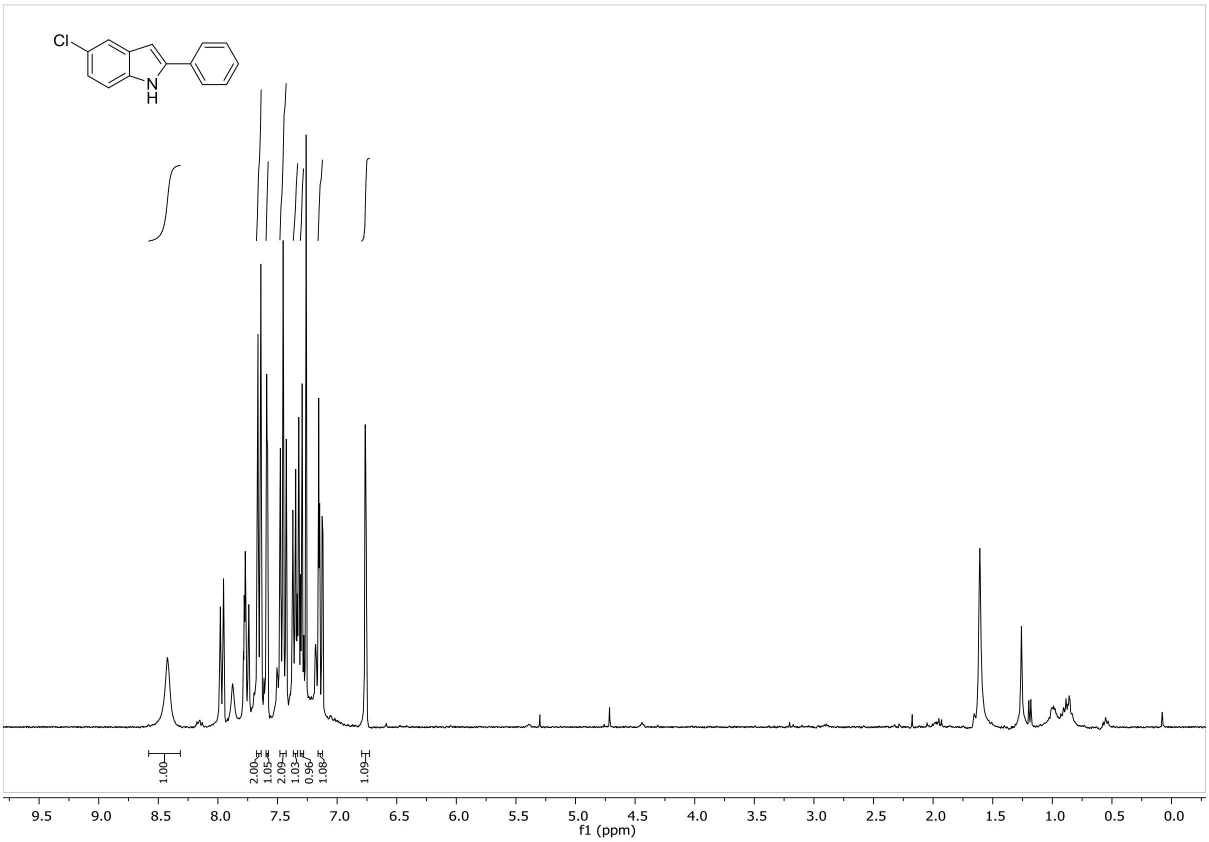


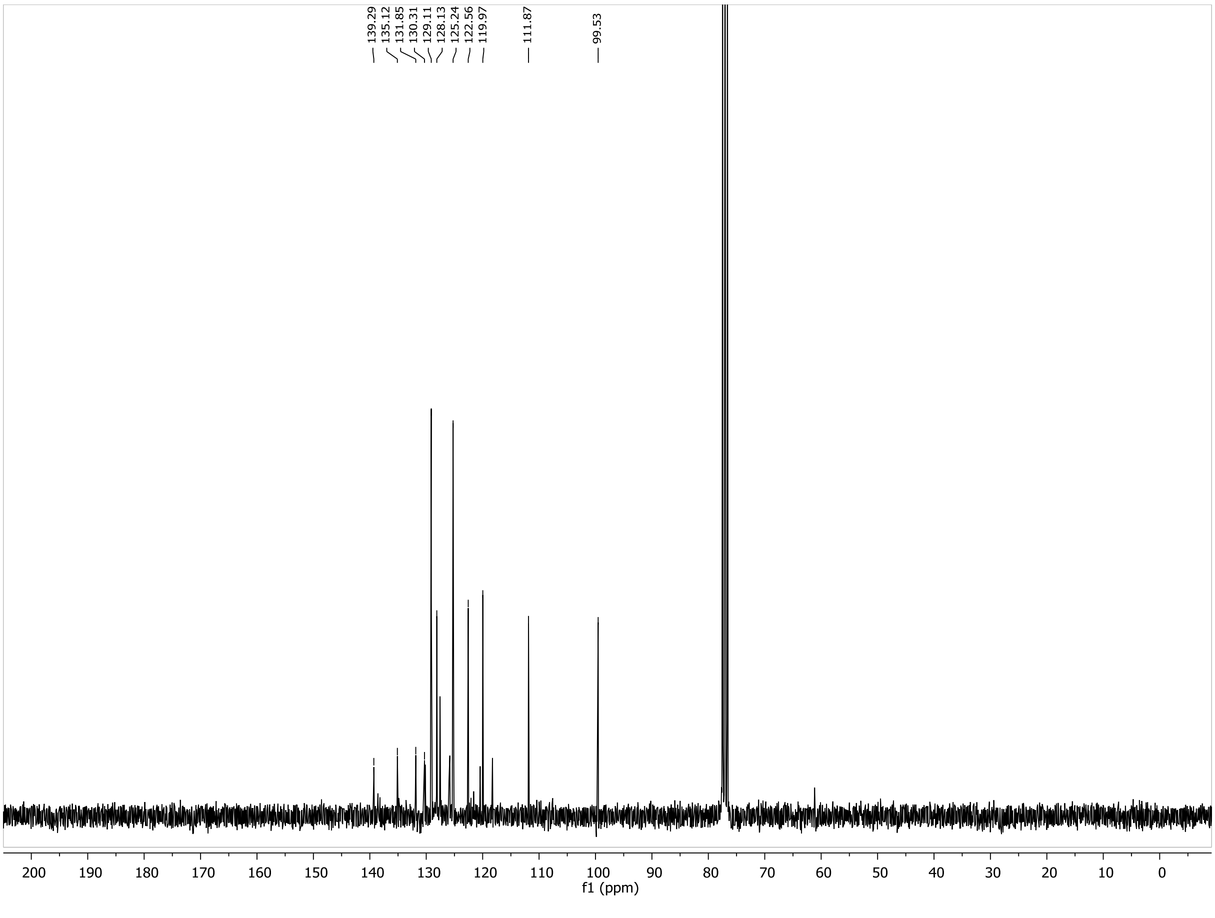
5,6-Dimethyl-2-phenylindole (5Hd)



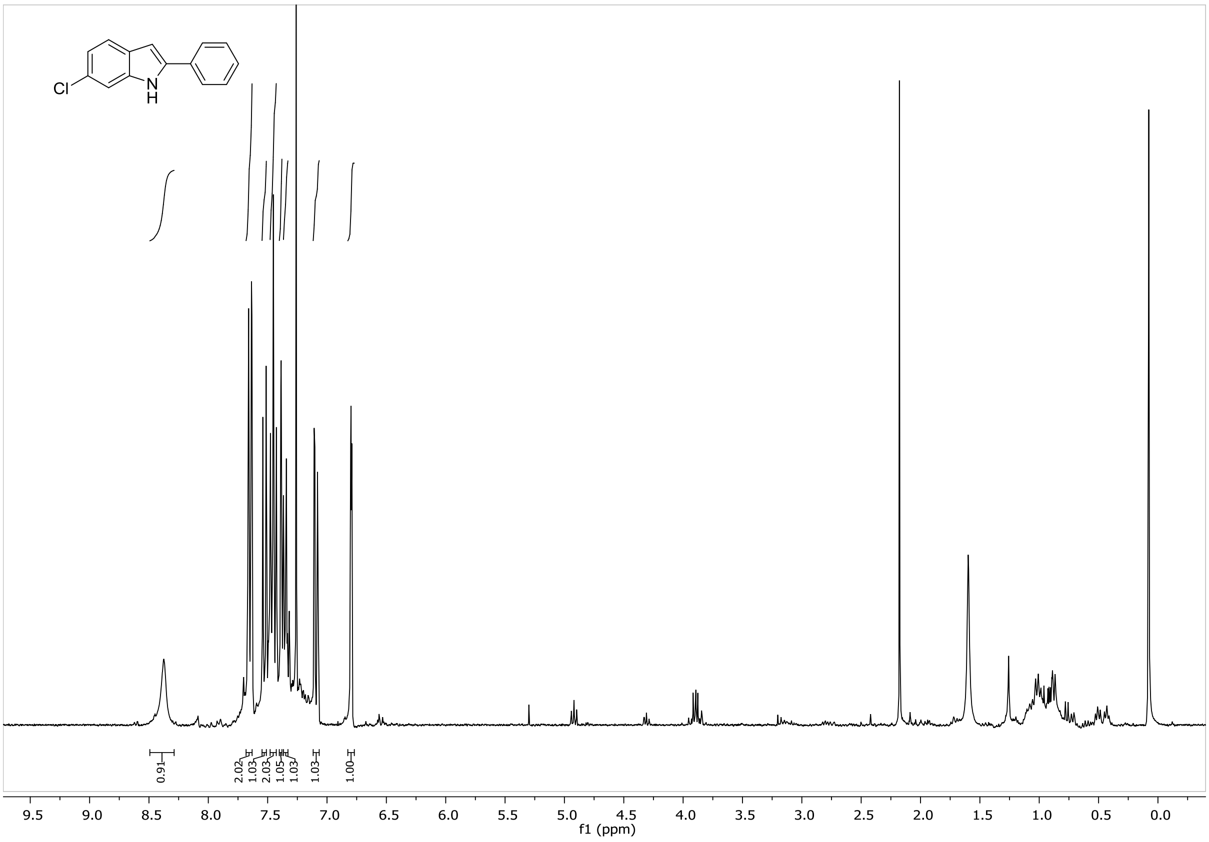


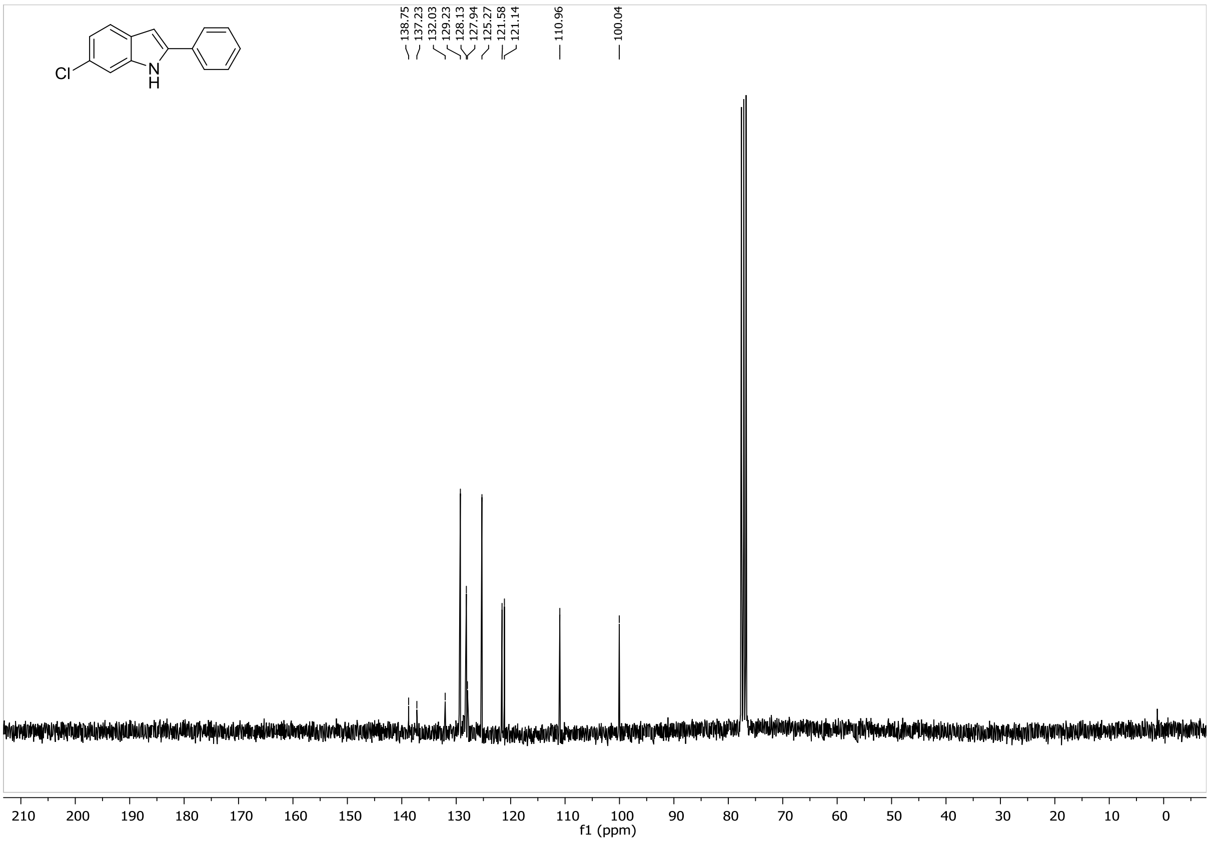
5-Chloro-2-phenylindole (5Hea)





6-Chloro-2-phenylindole (5Heb)





(*Z*)-*N*-(2-styrylphenyl)benzamide (8)