Content

General experimental details

All manipulations of air and moisture sensitive species were performed under argon atmosphere unless otherwise stated. Dry solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. Starting materials were acquired from commercial sources and used without further purification. (*E*)-1-(2-alkynylphenyl)-2-phenyldiazenes were synthesized according to previously reported procedures.[1]

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60FS-254) using UV light for visualization. Silica gel grade 60 (230-400 mesh, Silicycle Inc.) was used for column chromatography. Melting points were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on either a Varian Mercury VX-300, Varian Unity 300, Bruker Avance Neo 400 or Varian Unity 500 MHz spectrometers at room temperature. Chemical shifts are given in ppm (δ) downfield from TMS. Coupling constants (*J*) are in Hertz (Hz) and signals are described as follows: s, singlet; d, doublet; dd, doublet of doublets; dt, double of triplets; dq, double of quadruplets; ddd, doublet of doublet of doublets; t, triplet; td, triplet of doublets, q, quadruplet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Absorption spectra were recorded in a UV-VIS FLS980 Spectrophotometer (Edinburgh Instruments) equipped with a detector (200-1000 nm) that is allowed for absorbance measurements. High-resolution analysis (HRMS) was performed on an Agilent 6545 Q-TOF. Crystals for X-ray diffraction were grown by vapor diffusion crystallization, the X-ray diffractometer used for the measurements was D8 VENTURE Dual-source configuration. The irradiations were carried out with a 30 W blue LED strip (ALED light 5050), Kessil LED lights A160WE Tuna Blue or two 50 W Chip led COB EPISTAR 35mil.

Experiments for 11*H*-indolo[1,2-*b*]indazoles 2

Reaction set up

For the synthesis of indolo[1,2-*b*]indazoles **2** the reaction was exposed to a Kessil 40 W blue LED lamp (model: A160WE Tuna Blue) positioned at approximately 3 cm from the Schlenk tube. A fan was placed on top of the Schlenk tube to maintain the temperature at 30 °C (**Figure S1**). The emission spectra of the Kessil 40 W blue LED lamp is presented in **Figure S2**.

Figure S1. Photochemical experimental setup for the synthesis of indolo[1,2-*b*]indazoles **2**.

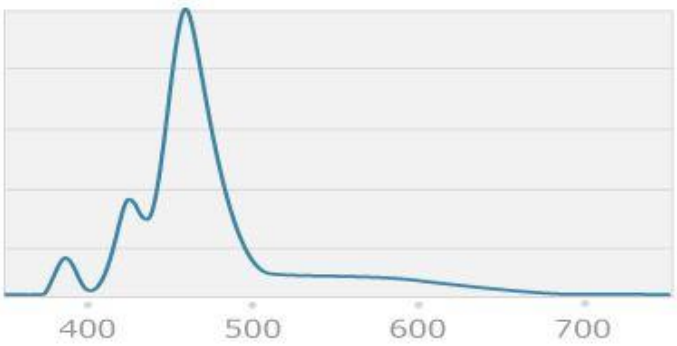


Figure S2. Emission spectrum of the Kessil blue LED lamp.

Optimization of reaction conditions

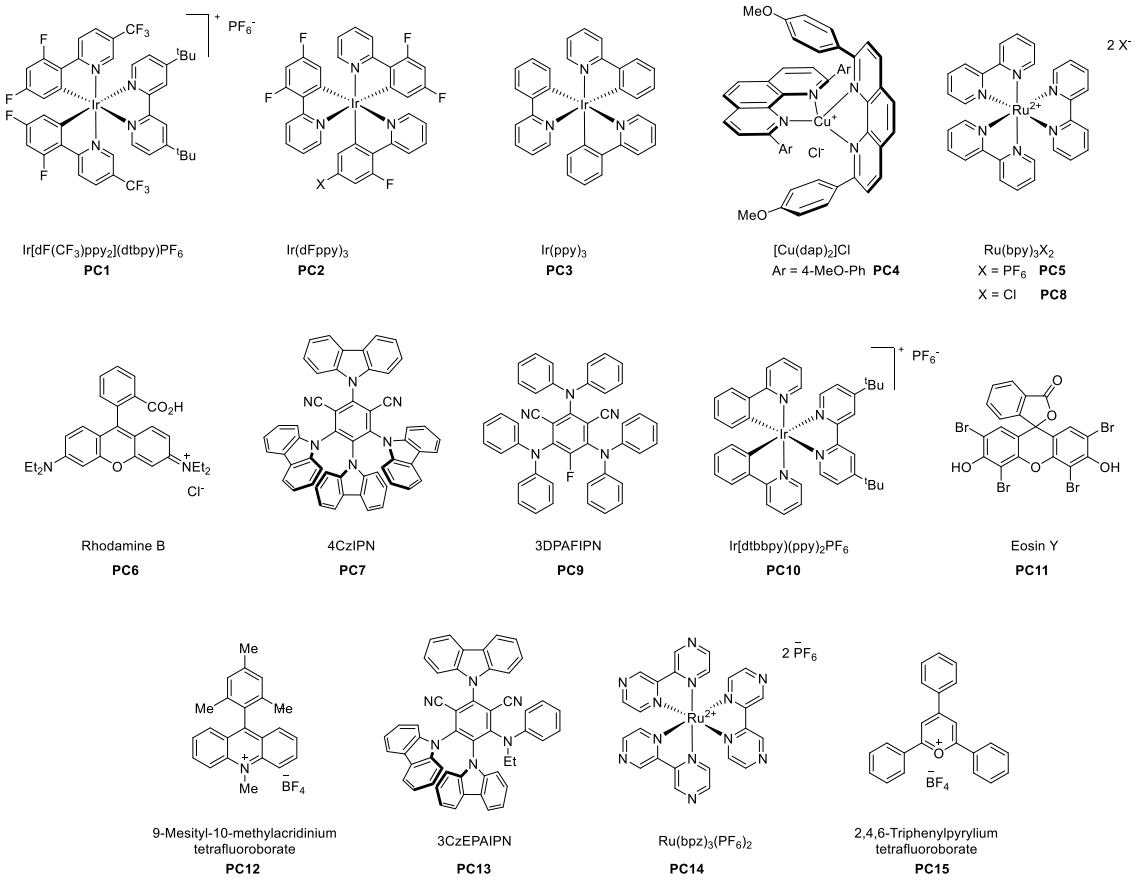
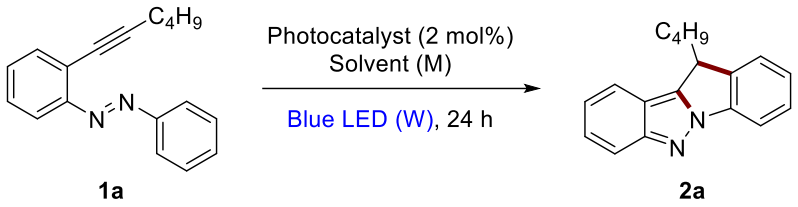


Figure S3. Photocatalysts used in the optimizations.

Table S1. Optimization of the conditions for the cyclization of 2-alkynylazobenzene **1a** to indolo[1,2-*b*]indazole **2a**.



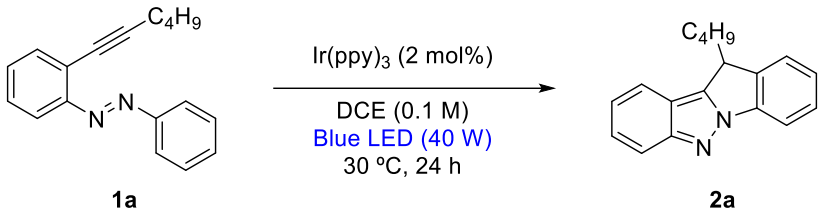
1a **2a**

Entry	Blue LED (W)	Photocatalyst	Solvent	Concentration (M)	Yield[a] (%)
1	40	-	MeCN	0.1	33
2	40	PC1	MeCN	0.1	34
3	40	PC2	MeCN	0.1	47
4	40	PC3	MeCN	0.1	62
5	40	PC4	MeCN	0.1	33
6	40	PC5	MeCN	0.1	15
7	40	PC6	MeCN	0.1	34
8	40	PC7	MeCN	0.1	24
9	40	PC10	MeCN	0.1	30
10	40	PC11	MeCN	0.1	28
11	40	PC12	MeCN	0.1	22
12	40	PC13	MeCN	0.1	24
13	40	PC3	MeCN	0.05	43
14	40	PC3	MeCN	0.2	52
15	40	PC3	MeCN	0.5	17
16	**40**	**PC3**	**DCE**	**0.1**	**85**
17	40	PC3	Acetone	0.1	72
18	40	PC3	MeOH	0.1	0[b]
19	50	PC3	DCE	0.1	85
20	100	PC3	DCE	0.1	86

[a] Isolated yields by column chromatography. [b] 3-(1-Methoxypentyl)-2-phenyl-2*H*-indazole was obtained with a 90% yield.

Control experiments

Table S2. Control experiments

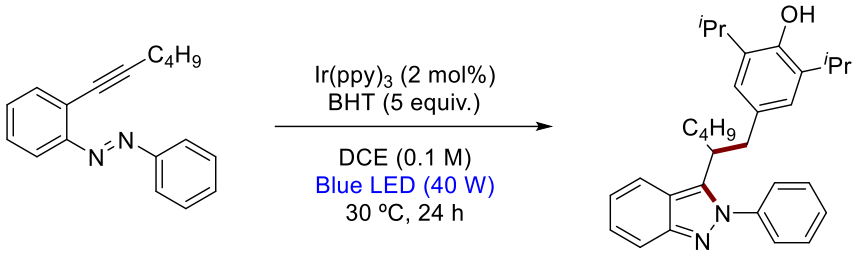


1a **2a**

Entry	Photocatalyst	Blued LED (W)	Yield (%)
1	-	-	0
2	$Ir(ppy)_3$	-	0
3	-	40	33[a]

[a] (*E*)-3-(pent-1-en-1-yl)-2-phenyl-2*H*-indazole was obtained as the major product with a 56% yield.

Radical inhibitor experiment



1a **6** (39%)

Kinetic study

To a flame dried J-Young NMR tube, (*E*)-1-(2-(hex-1-yn-1-yl)phenyl)-2-phenyldiazene (**1a**, 0.06 mmol) and $Ir(ppy)_3$ (2 mol%) were added under a flow of argon. The NMR tube was evacuated and then filled back with argon (three times). Then, deuterated dichloroethane (0.1 M) was added. Time zero (t = 0) ^{1}H-NMR spectrum was recorded prior to irradiation. Then the NMR tube was placed in the photoreactor under blue light irradiation (40 W). After the allotted time, the light was turned off and reaction solution was analyzed by ^{1}H-NMR. Temporal concentrations (%) of all compounds were calculated based on the integration of the corresponding signals and they were plotted against time in minutes.

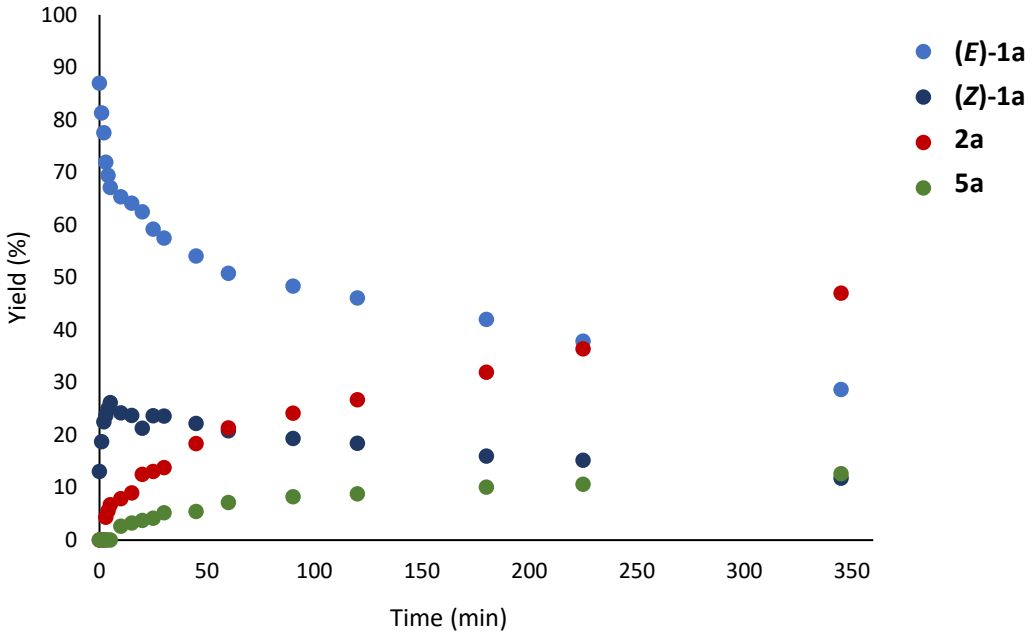


Figure S4. Kinetics of the reaction during the first 6 hours.

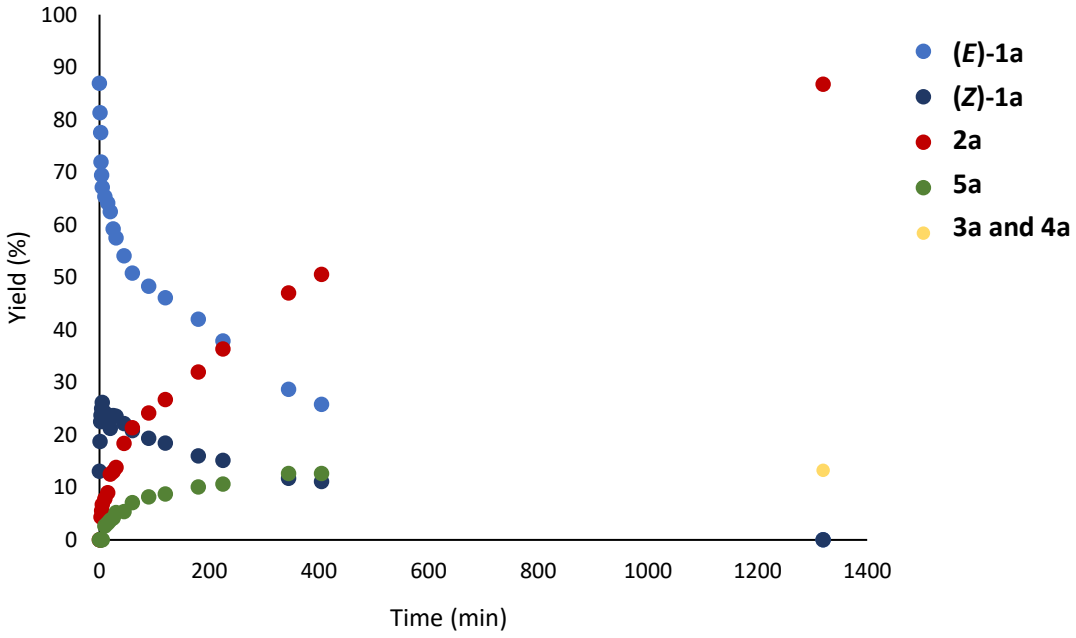
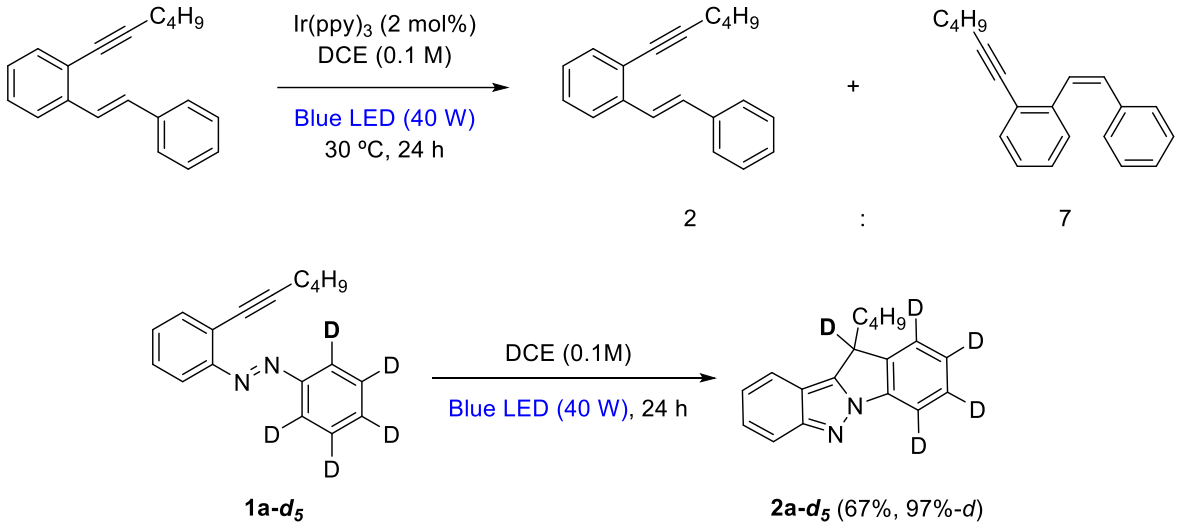


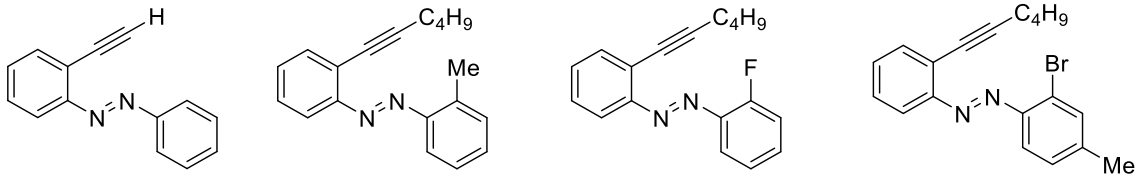
Figure S5. Kinetics for the reaction of 2-alkynylazobenzene **1a** in the presence of $Ir(ppy_3)$ in deuterated dichloroethane (24 h).

Additional experiments



Limitations

No noteworthy results were obtained with the following substrates under the standard reaction conditions, even with modifications such as extended reaction times, reduced LED intensity, or increased photocatalyst amounts.



Cyclic voltammetry of 1a

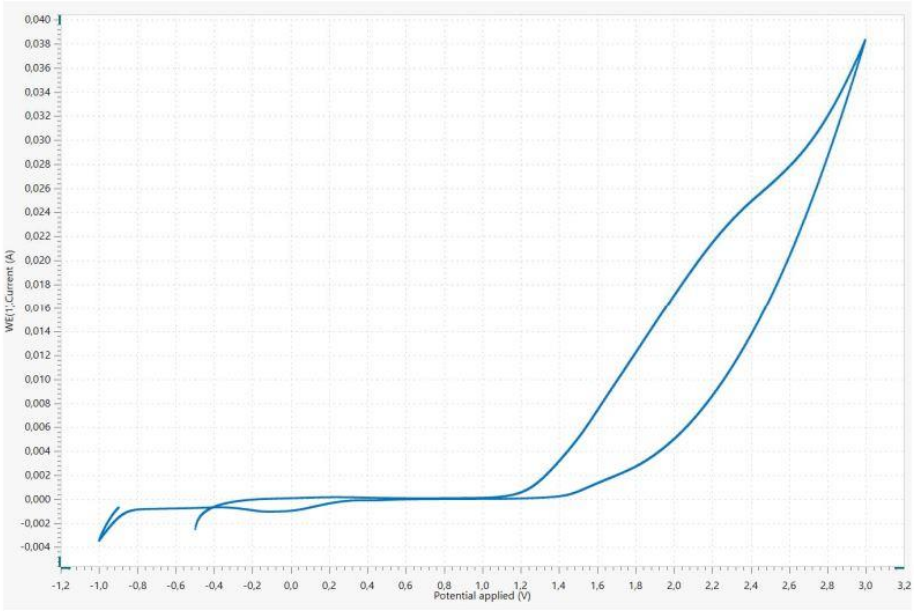


Figure S7. CV of 2-alkenylazobenzene **1a**. (Anode: Pt. Cathode: Pt. Reference electrode: Ag/AgCl. Solvent: MeOH. Electrolyte: NaClO4. Potential range: -1.0 V: +3.0 V).

Experiments for indazolo[2,3-*a*]quinolines 3 and 4

Reaction set up

For the synthesis of 5,6-dihydroindazolo[2,3-*a*]quinolines **3**, the reaction was exposed to a 30 W blue LED strip (ALED light 5050) wrapped around a 600 mL beaker. The Schlenk tube was placed in the center of the beaker, approximately 3 cm from the LED strip. A fan was positioned above the Schlenk tube to maintain the temperature at room temperature. (**Figure S6**).

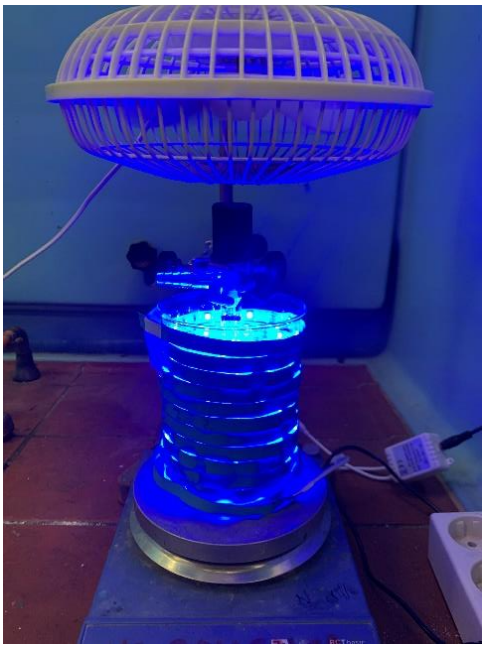


Figure S6. Photochemical experimental setup for the synthesis of 5,6-dihydroindazolo[2,3-*a*]quinolines **3**.

For the synthesis of indazolo[2,3-*a*]quinolines **4**, the reaction was initially exposed to a custom-made photoreactor equipped with two 50 W Chip LED COB EPISTAR 35mil lights. The Schlenk tube was positioned in the center, approximately at 2 cm from the LEDs. One fan was placed above the Schlenk tube and another on the side to maintain the temperature at 70 °C (

Figure S7). The emission spectrum of the 50 W blue LED chips is presented in **Figure S8**.

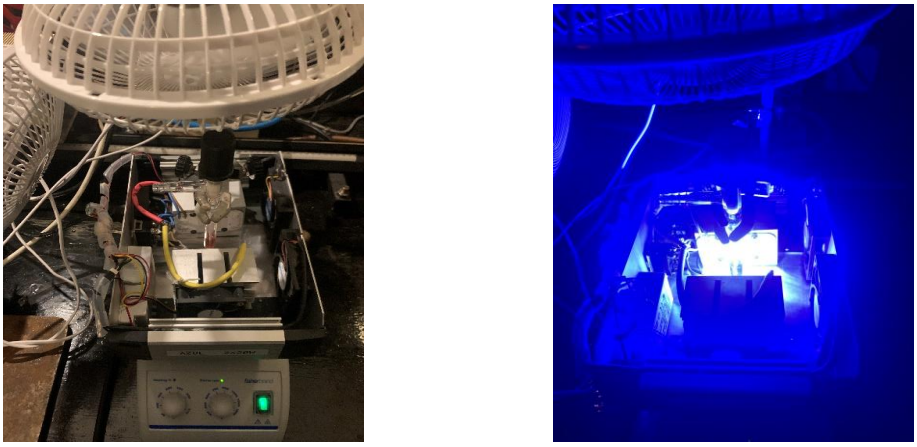


Figure S7. Photochemical experimental setup for the first step in the synthesis of indazolo[2,3-*a*]quinolines **4**.

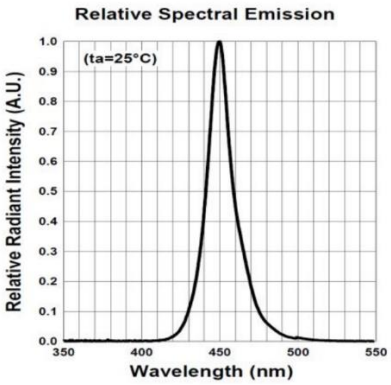


Figure S8. Emission spectra of the 50 W blue LED chips.

In the second reaction step, the reaction was exposed to two Kessil 40 W blue LED lamps (model: A160WE Tuna Blue), positioned approximately 3 cm from the Schlenk tube. One fan was placed above the Schlenk tube and another on the side to maintain the temperature at 50°C (

Figure S9).

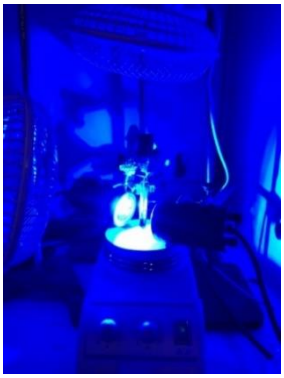
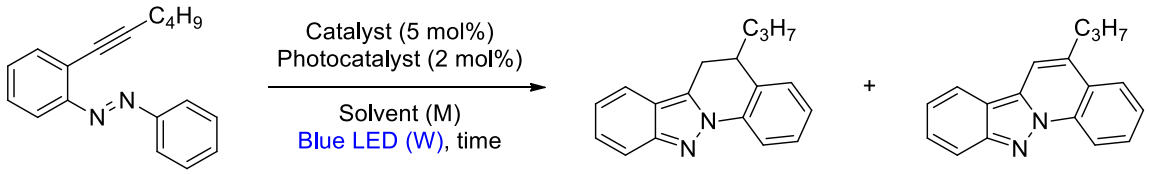


Figure S9. Photochemical experimental setup for the second step of the synthesis of indazolo[2,3-*a*]quinolines **4**.

Optimization of reaction conditions

Table S3. Optimization of the conditions for the cyclization of 2-alkynylazobenzene **1a** to furnish indazolo[2,3-*a*]quinolines **3a** and **4a**.

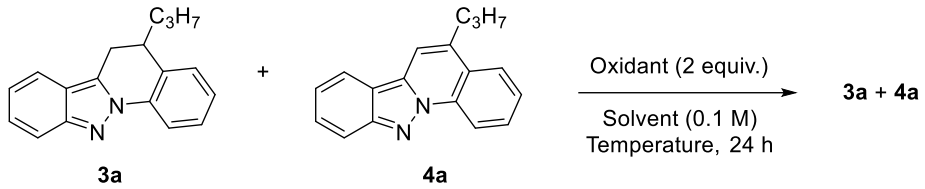


Entry	Blue LED (W)	Catalyst	Photocatalyst	Solvent	Time (hours)	Yield 3 (%)[a]	Yield 4 (%)[a]
1	40	$AuCl_3$	-	MeCN	24	20	5
2	80	$AuCl_3$	PC1	MeCN	24	29	10
3	100	$AuCl_3$	PC1	MeCN	24	50	30
4	180	$AuCl_3$	PC1	MeCN	24	0	0
5	100	$AuBr_3$	PC1	MeCN	24	49	24
6	100	$Au(OAc)_3$	PC1	MeCN	24	29	Traces
7	100	Cu_2O	PC1	MeCN	24	34	Traces
8	100	$Cu(MeCN)_4BF_4$	PC1	MeCN	24	38	17
9	100	$AuCl_3$	PC3	MeCN	24	13	Traces
10	100	$AuCl_3$	PC4	MeCN	24	-	-
11	100	$AuCl_3$	PC8	MeCN	24	25	Traces
12	100	$AuCl_3$	PC9	MeCN	24	38	5
13	100	$AuCl_3$	PC12	MeCN	24	-	-
14	100	$AuCl_3$	PC14	MeCN	24	14	Traces
15	100	$AuCl_3$	PC15	MeCN	24	Traces	-
16	100	$AuCl_3$	PC1	DCE	24	15	Traces
17	100	$AuCl_3$	PC1	Acetone	24	50	30

18	100	$AuCl_3$	PC1	MeCN	48	42	32
19	100	$AuCl_3$	PC1	MeCN	96	23	38
20	100	$AuCl_3$	PC1	MeCN	240	11	35

[a] Yields calculated by ^{1}H-NMR, using dibromomethane as internal standard.

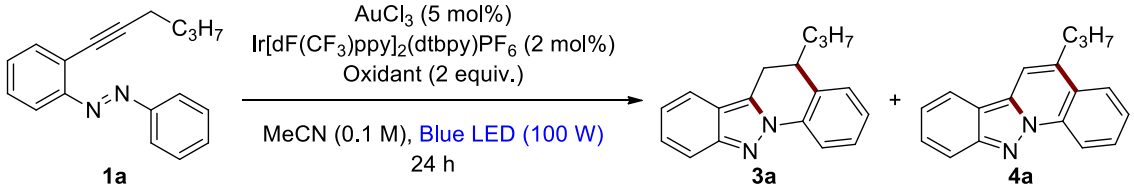
Table S4. Treatment of a mixture 5:3 of 5,6-dihydroindazolo[2,3-*a*]quinoline **3a** and indazolo[2,3-*a*]quinoline **4a** with different oxidants.



Entry	Oxidant	Solvent	Temperature (°C)	Ratio	
				3a	4a
1	Air	MeCN	r.t.	1.7	1
2	DDQ	MeCN	r.t.	1.7	1
3	DDQ	MeCN	85	1.7	1
4	$PhI(OAc)_2$	MeCN	r.t.	1.7	1
5	$PhI(OAc)_2$	MeCN	85	1.7	1
6	TBP/$[CPh_3]^+BF_4^-$	DCE	75	1.7	1

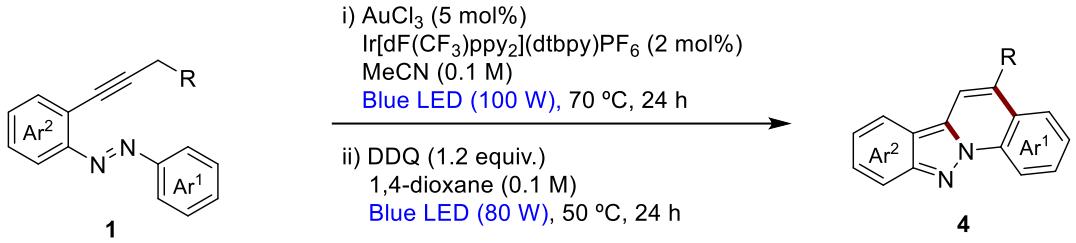
A series of additional experiments were conducted by adding various oxidants into the reaction mixture before irradiating for 24 hours. In all the cases oxidation of the 2-alkynylazobenzene **1a** was also observed.

Table S5. Optimization of the cyclization of 2-alkynylazobenzene **3a** to indazolo[2,3-a]quinoline **4a** in the presence of different oxidants.



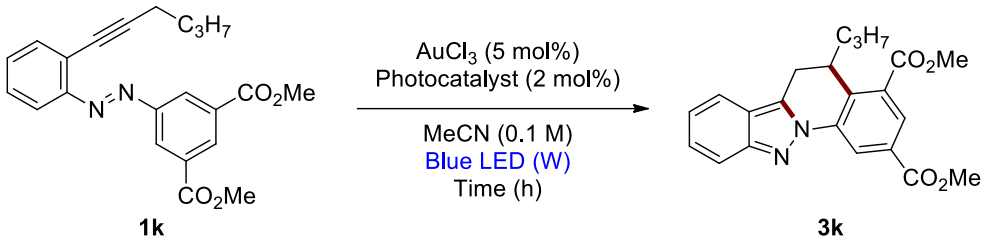
Entry	Oxidant	^{1}H-NMR yield	Ratio	
		3a + 4a	18a	19a
1	(Diacetoxyiodo)benzene	18	0	1
2	DDQ	32	0	1
3	NBS	24	1	5
4	IBX	-	-	-
5	Cyclooctene	20	1	1.5
6	MnO_2	22	1	1.3

Since DDQ had proved to be the most effective oxidant, an alternative approach was explored to prevent oxidation of the starting material. The oxidant was added after the reaction had been irradiated for 24 hours and filtered through silica. Surprisingly, no complete oxidation to the desired indazolo[2,3-*a*]quinoline **4a** was observed; instead, a 1:5 ratio of **3a** to **4a** was detected, along with decomposition byproducts. To minimize decomposition while promoting the oxidation of 5,6-dihydroindazolo[2,3-*a*]quinoline **3a**, the reaction conditions were slightly modified. This involved adding only 1.2 equivalents of DDQ, using 1,4-dioxane as the solvent for the second step, and employing 80 W of blue LED irradiation. Under these conditions, the desired indazolo[2,3-*a*]quinoline **4a** was isolated by column chromatography with 46% yield, along with 5,6-dihydroindazolo[2,3-*a*]quinoline **3a**.



Optimization of the reaction conditions for the synthesis of 5,6-dihydroindazolo[2,3-*a*]quinoline 3l

Table S6. Optimization of the conditions for the cyclization of 2-alkynylazobenzene **1a** to furnish 5,6-dihydroindazolo[2,3-*a*]quinoline **3l**.

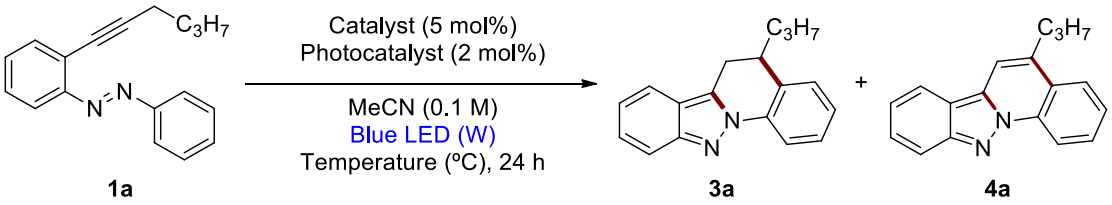


Entry	Photocatalyst	Blue LED (W)	Time (h)	Yield (%)
1	PC8	40	3	20
2	PC1	100	1	30
3	PC1	100	2	52[a]
4	PC1	100	1.5	40[a]
5	PC1	40	2	47
6	**PC1**	**30**	**24**	**51**

[a]Traces of indazolo[2,3-*a*]quinoline **4k** were detected.

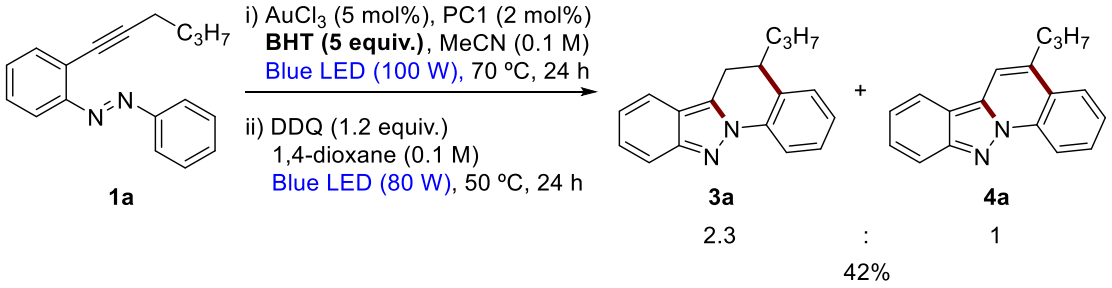
Control experiments

Table S7. Control experiments for the synthesis of indazolo[2,3-*a*]quinoline **3a** and **4a** form 2-alkynylazobenzene **1a**.

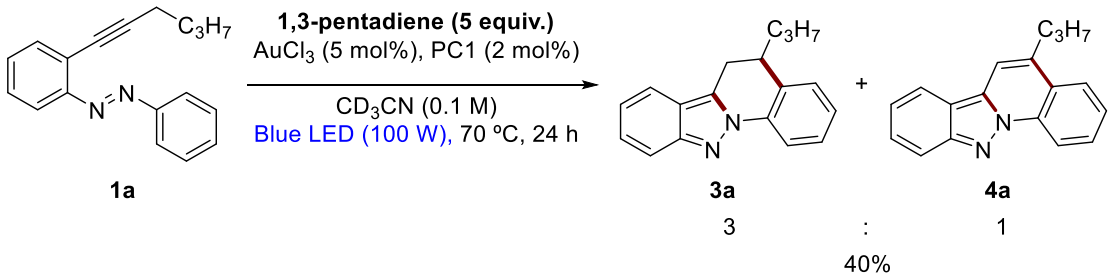


Entry	Catalyst	Photocatalyst	Blue LED (W)	Temperature (ºC)	^{1}H-NMR yield (%)	
					3a	**4a**
1	-	PC1	100	70	18	Traces
2	$AuCl_3$	-	100	70	22	12
3	$AuCl_3$	PC1	-	r.t.	-	-
4	$AuCl_3$	PC1	-	90	-	-

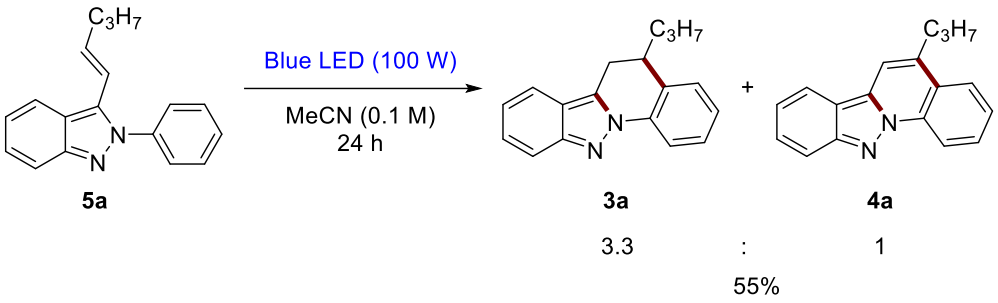
Radical inhibitor experiment



Triplet quencher experiment



Additional experiments



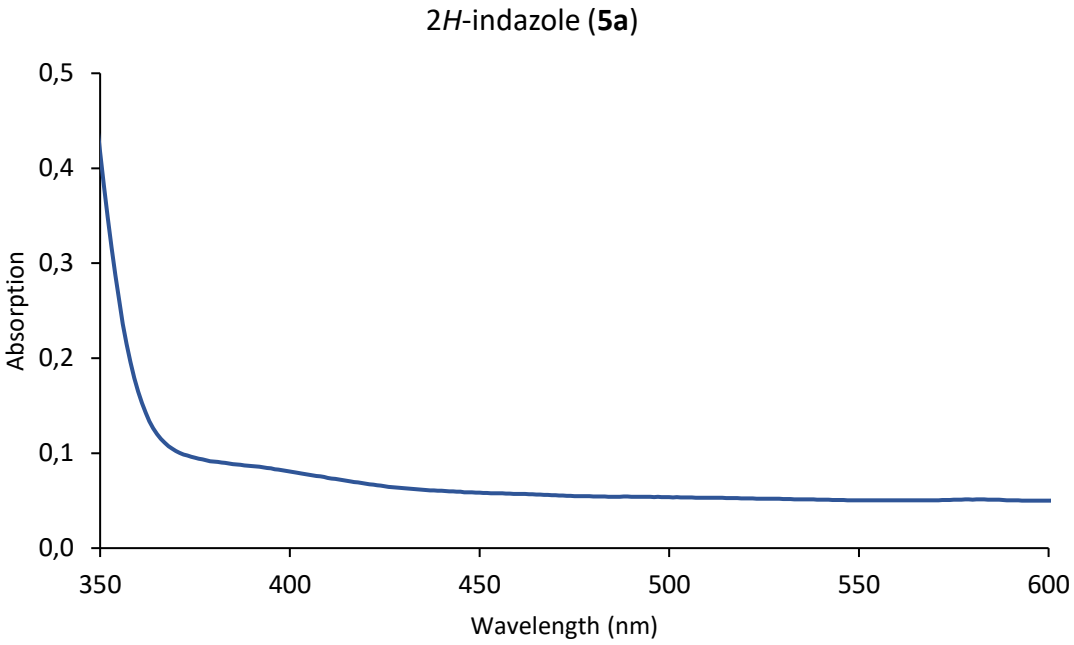
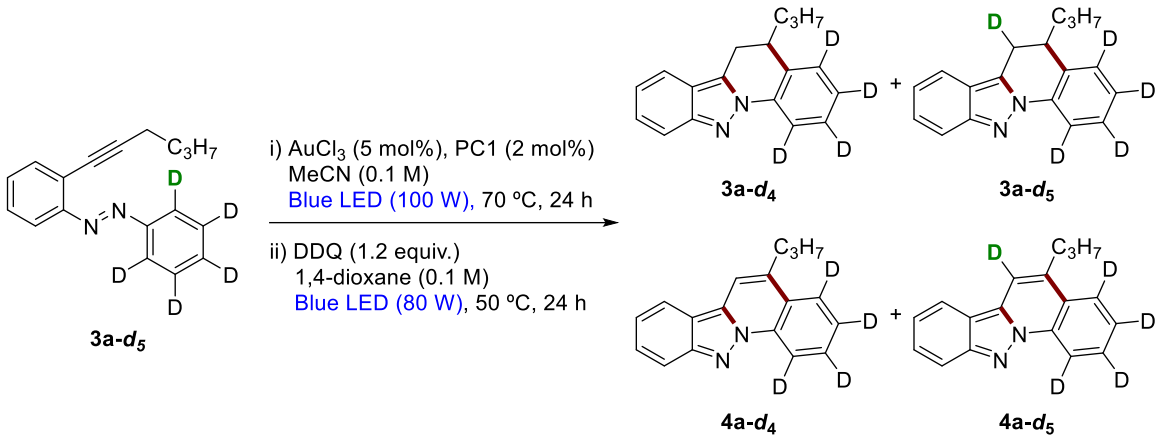
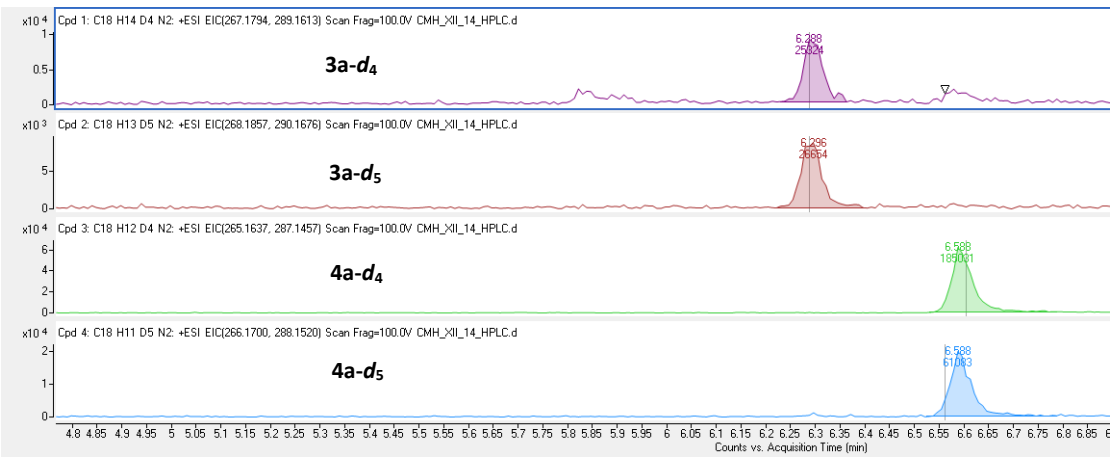
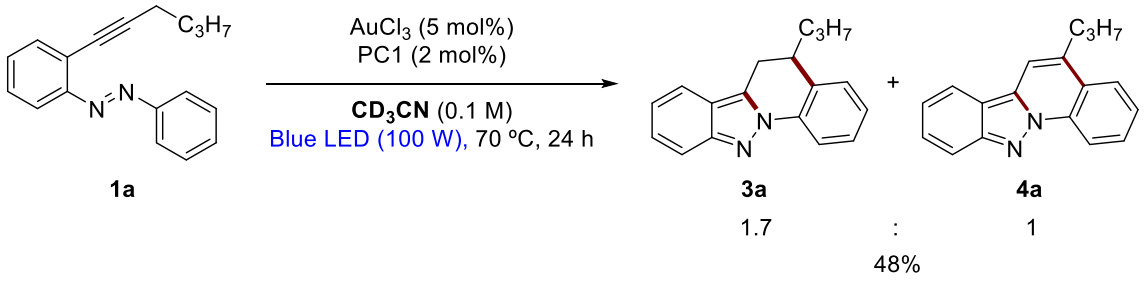


Figure S13. UV-vis spectra of 2*H*-indazole **5a**.

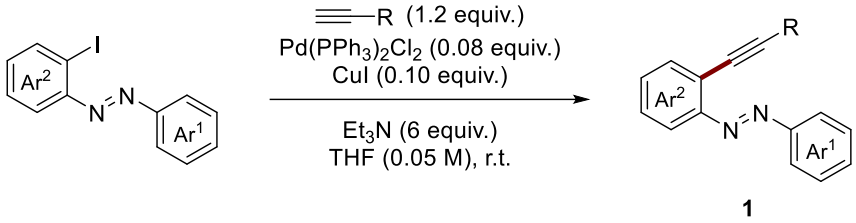

i) AuCl3 (5 mol%), PC1 (2 mol%)
MeCN (0.1 M)
Blue LED (100 W), 70 ºC, 24 h
ii) DDQ (1.2 equiv.)
1,4-dioxane (0.1 M)
Blue LED (80 W), 50 ºC, 24 h
3a-d5
3a-d4
3a-d5
4a-d4
4a-d5


Cpd 1: C18 H14 D4 N2: +ESI EIC(267.1794, 289.1613) Scan Frag=100.0V CMH_XII_14_HPLC.d
3a-d4
Cpd 2: C18 H13 D5 N2: +ESI EIC(268.1857, 290.1676) Scan Frag=100.0V CMH_XII_14_HPLC.d
3a-d5
Cpd 3: C18 H12 D4 N2: +ESI EIC(265.1637, 287.1457) Scan Frag=100.0V CMH_XII_14_HPLC.d
4a-d4
Cpd 4: C18 H11 D5 N2: +ESI EIC(266.1700, 288.1520) Scan Frag=100.0V CMH_XII_14_HPLC.d
4a-d5
Counts vs. Acquisition Time (min)


AuCl3 (5 mol%)
PC1 (2 mol%)
CD3CN (0.1 M)
Blue LED (100 W), 70 ºC, 24 h
1a
3a
4a
1.7 : 1
48%

General synthetic procedure and characterization

2-Alkynylazobenzenes 1

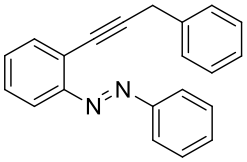


1

In a 50 mL Schlenk tube under argon flow, the corresponding 1-(2-iodophenyl)-2-phenyldiazene (0.97 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.08 mmol, 0.08 equiv.), and CuI (0.1 mol, 0.1 equiv.) were dissolved in THF (0.05 M) at room temperature. Then, Et_3N (5.8 mmol, 6 equiv.) was added dropwise. After 10 minutes, the appropriate alkyne (1.2 mmol, 1.2 equiv.) was added. The reaction was stirred at room temperature until completion. The mixture was diluted with AcOEt (20 mL), washed with NH_4Cl (2 x 20 mL), dried over $MgSO_4$, and filtered. The solvent was concentrated *in vacuo* and the resulting (*E*)-1-(2-alkynylphenyl)-2-phenyldiazene **1** was purified by flash chromatography using a mixture hexane:EtOAc.

2-Alkynylazobenzenes **1a**-**1z** were prepared as previously described in the literature.[1,2]

(*E*)-1-Phenyl-2-[2-(3-phenylprop-1-yn-1-yl)phenyl]diazene (1aa)



Eluent: Hexane/EtOAc (100:1). Red oil (164 mg, 56% yield).

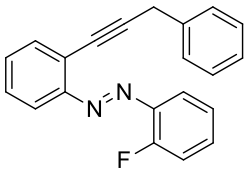
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.08 – 7.93 (m, 2H), 7.80 – 7.72 (m, 1H), 7.72 – 7.64 (m, 1H), 7.61 – 7.45 (m, 5H), 7.47 – 7.26 (m, 5H), 3.99 (s, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 153.5, 152.9, 136.8, 133.5, 131.3, 130.6, 129.2, 128.6, 128.6, 128.2, 126.7, 124.3, 123.4, 116.0, 94.2, 80.2, 26.3.

HRMS (ESI+) m/z calculated for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386, found $[M+H]^+$: 297.1390.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (226, 28640), (253, 17755), (322, 16249), (440, 865).

(*E*)-1-(2-Fluorophenyl)-2-(2-(3-phenylprop-1-yn-1-yl)phenyl)diazene (1ab)



Eluent: Hexane. Red oil (102 mg, 37% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.73 (m, 2H), 7.72 – 7.63 (m, 1H), 7.61 – 7.22 (m, 9H), 7.17 (td, *J* = 7.8, 1.4 Hz, 1H), 3.98 (s, 2H).

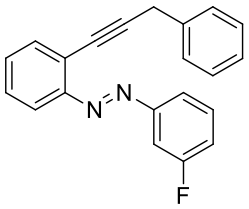
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) -123.69 – -124.31 (m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 160.6 (d, *J* = 255.0 Hz), 153.6, 141.0 (d, *J* = 6.8 Hz), 136.8, 133.5, 132.8 (d, *J* = 8.3 Hz), 131.1, 128.7, 128.6, 128.6, 128.2, 126.7, 124.8, 124.4 (d, *J* = 3.8 Hz), 118.2, 117.1 (d, *J* = 20.0 Hz), 116.3, 94.4, 80.1, 26.3.

HRMS (ESI+) m/z calculated for $C_{21}H_{16}FN_2$ $[M+H]^+$: 315.1292, found $[M+H]^+$: 315.1291.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (231, 22117), (254, 16225), (328, 14460), (440, 1129).

(*E*)-1-(3-Fluorophenyl)-2-(2-(3-phenylprop-1-yn-1-yl)phenyl)diazene (1ac)



Eluent: Hexane. Red oil (47 mg, 16% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.77 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.70 – 7.59 (m, 2H), 7.56 – 7.13 (m, 9H), 3.96 (s, 2H).

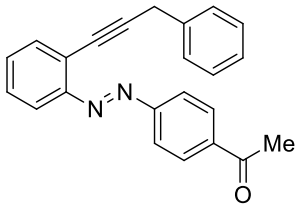
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) -111.85 (td, *J* = 9.2, 6.3 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 163.4 (d, *J* = 247.6 Hz), 154.4 (d, *J* = 6.8 Hz), 153.1, 136.7, 133.7, 131.1, 130.4 (d, *J* = 8.4 Hz), 128.7, 128.6, 128.1, 126.8, 121.1 (d, *J* = 2.9 Hz), 118.1 (d, *J* = 22.1 Hz), 116.1, 108.6 (d, *J* = 22.8 Hz), 94.6, 80.0, 26.3.

HRMS (ESI+) m/z calculated for $C_{21}H_{16}FN_2$ $[M+H]^+$: 315.1292, found $[M+H]^+$: 315.1292.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (253, 30971), (315, 28452), (440, 12633).

(*E*)-1-[4-((2-(3-Phenylprop-1-yn-1-yl)phenyl)diazenyl)phenyl]ethan-1-one (1ad)



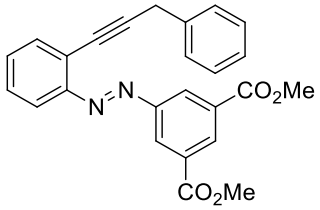
Eluent: Hexane/EtOAc (50:1). Red oil (30 mg, 10% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.09 – 8.03 (m, 2H), 7.99 – 7.92 (m, 2H), 7.73 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.53 – 7.38 (m, 4H), 7.36 – 7.24 (m, 3H), 3.96 (s, 2H), 2.67 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 197.5, 155.2, 153.1, 138.4, 136.6, 133.6, 131.3, 129.4, 128.6, 128.5, 128.1, 126.7, 125.0, 123.3, 115.8, 94.7, 79.9, 26.9, 26.2.

HRMS (ESI+) m/z calculated for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1492, found $[M+H]^+$: 339.1495.

(*E*)-Dimethyl 5-((2-(3-phenylprop-1-yn-1-yl)phenyl)diazenyl)isophthalate (1ae)



Eluent: Hexane/EtOAc (20:1). Red oil (90 mg, 26% yield).

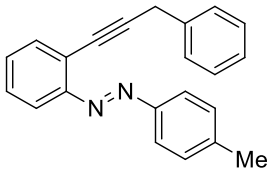
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.82 – 8.73 (m, 2H), 8.80 – 8.73 (m, 2H), 7.72 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.53 – 7.32 (m, 5H), 7.32 – 7.15 (m, 3H), 3.98 (s, 3H), 3.91 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 165.7, 153.0, 152.9, 136.5, 135.3, 133.6, 132.5, 131.8, 131.4, 128.6, 128.5, 128.2, 128.1, 128.0, 126.6, 125.0, 116.0, 94.9, 79.8, 52.6, 26.2.

HRMS (ESI+) m/z calculated for $C_{25}H_{21}N_2O_4$ $[M+H]^+$: 413.1496, found $[M+H]^+$: 413.1494.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (319, 15563), (440, 1558).

(*E*)-1-[2-(3-Phenylprop-1-yn-1-yl)phenyl]-2-(*p*-tolyl)diazene (1af)



Eluent: Hexane/EtOAc (100:1). Red oil (70 mg, 29% yield).

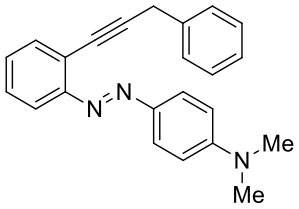
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 – 7.85 (m, 2H), 7.80 – 7.70 (m, 1H), 7.71 – 7.63 (m, 1H), 7.61 – 7.48 (m, 2H), 7.45 – 7.25 (m, 7H), 3.99 (s, 2H), 2.48 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 153.6, 151.1, 141.9, 136.8, 133.5, 130.3, 129.8, 128.6, 128.5, 128.2, 126.7, 124.1, 123.4, 116.0, 94.0, 80.3, 26.3, 21.7.

HRMS (ESI+) m/z calculated for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found $[M+H]^+$: 311.1547.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (236, 51572), (330, 33902), (439, 1783).

(*E*)-*N*,*N*-Dimethyl-4-((2-(3-phenylprop-1-yn-1-yl)phenyl)diazenyl)aniline (1ag)



Eluent: Hexane/EtOAc (5:1). Red oil (220 mg, 78% yield).

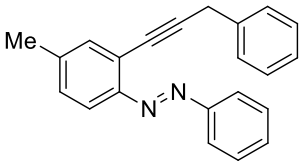
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.09 – 7.94 (m, 2H), 7.79 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.51 – 7.24 (m, 5H), 6.81 – 6.69 (m, 2H), 4.03 (s, 2H), 3.07 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 154.1, 152.5, 144.0, 136.9, 133.3, 128.9, 128.5, 128.5, 128.1, 126.5, 125.6, 125.5, 122.9, 115.9, 111.4, 93.3, 80.8, 40.2, 26.2.

HRMS (ESI+) m/z calculated for $C_{23}H_{22}N_3$ $[M+H]^+$: 340.1808, found $[M+H]^+$: 340.1808.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (270, 10665), (423, 15125).

(*E*)-1-(4-Methyl-2-(3-phenylprop-1-yn-1-yl)phenyl)-2-phenyldiazene (1ah)



Eluent: Hexane/EtOAc (100:1). Red oil (203 mg, 70% yield).

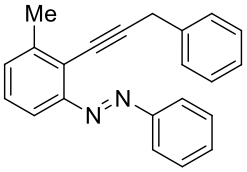
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.98 (dt, *J* = 7.3, 1.8 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.44 (m, 6H), 7.42 – 7.27 (m, 3H), 7.21 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.00 (s, 2H), 2.42 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 153.0, 151.5, 141.2, 136.8, 133.8, 131.0, 129.5, 129.1, 128.6, 128.2, 126.7, 124.5, 123.3, 115.8, 93.8, 80.4, 26.3, 21.3.

HRMS (ESI+) m/z calculated for $C_{23}H_{19}N_2O$ $[M+H]^+$: 311.1543, found $[M+H]^+$: 311.1542.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (228, 27827), (260, 17717), (329, 17940), (440, 1817).

(*E*)-1-[3-Methyl-2-(3-phenylprop-1-yn-1-yl)phenyl]-2-phenyldiazene (1ai)



Eluent: Hexane/EtOAc (100:1). Red oil (50 mg, 52% yield).

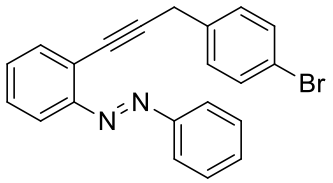
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.93 (m, 2H), 7.59 – 7.47 (m, 6H), 7.35 – 7.26 (m, 5H), 4.04 (s, 2H), 2.60 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 154.0, 153.0, 141.8, 137.0, 131.5, 131.1, 129.2, 128.6, 128.2, 127.8, 126.7, 123.4, 120.7, 113.3, 98.8, 78.8, 26.5, 21.0.

HRMS (ESI+) m/z calculated for $C_{23}H_{19}N_2O$ $[M+H]^+$: 311.1543, found $[M+H]^+$: 311.1546.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (264, 18379), (318, 16797), (438, 645).

(*E*)-1-[2-(3-(4-Bromophenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1aj)



Eluent: Hexane. Black oil (21 mg, 6 % yield).

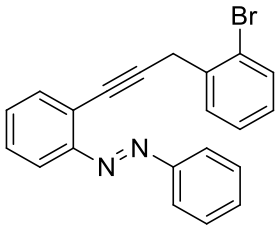
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.90 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.64 – 7.60 (m, 1H), 7.52 – 7.48 (m, 3H), 7.42 – 7.34 (m, 6H), 3.89 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 153.6, 153.0, 135.9, 133.5, 131.7, 131.5, 130.6, 130.0, 129.3, 128.8, 124.0, 123.4, 120.6, 116.2, 93.5, 81.0, 25.8.

HRMS (ESI+) m/z calculated for $C_{21}H_{15}BrN_2$ $[M+H]^+$: 375.0497, found $[M+H]^+$: 375.0489.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (266, 47348).

(*E*)-1-[2-(3-(2-Bromophenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1ak)



Eluent: Hexane. Black oil (21 mg, 16 % yield).

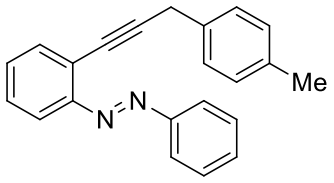
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.96 – 7.94 (m, 2H), 7.84 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.67 – 7.65 (m, 1H), 7.56 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.50 – 7.49 (m, 3H), 7.43 – 7.40 (m, 2H), 7.23 – 7.19 (m, 1H), 7.16 – 7.10 (m, 2H), 4.01 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 153.6, 153.0, 136.2, 133.6, 132.6, 131.4, 130.7, 130.1, 129.1, 128.8, 128.5, 127.8, 124.1, 124.0, 123.5, 116.1, 92.9, 81.3, 27.4.

HRMS (ESI+) m/z calculated for $C_{21}H_{15}BrN_2$ $[M+H]^+$: 375.04914, found $[M+H]^+$: 375.04922.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (270, 98510).

(*E*)-1-Phenyl-2-[2-(3-(*p*-tolyl)prop-1-yn-1-yl)phenyl]diazene (1al)



Eluent: Hexane. Red oil (122 mg, 40% yield).

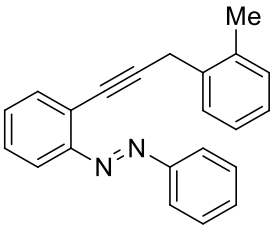
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.98 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.76 7.73 (m, 1H), 7.68 – 7.66 (m, 1H), 7.53 – 7.51 (m, 3H), 7.43 – 7.40 (m, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.94 (s, 2H), 2.38 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 152.9, 136.2, 133.7, 133.5, 131.3, 130.6, 129.3, 129.2, 128.5, 128.1, 124.4, 123.5, 116.0, 94.6, 79.9, 25.9, 21.2.

HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_2$ $[M+H]^+$: 311.1548, found $[M+H]^+$: 311.1541.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (224, 20180), (238, 16630), (255, 11700), (274, 6401), (317, 9724).

(*E*)-1-Phenyl-2-[2-(3-(*o*-tolyl)prop-1-yn-1-yl)phenyl]diazene (1am)



Eluent: Hexane. Red oil (60 mg, 19% yield).

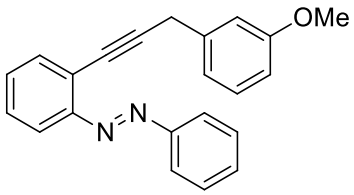
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.94 – 7.91 (m, 2H), 7.72 – 7.70 (m, 1H), 7.65-7.62 (m, 2H), 7.52 – 7.49 (m, 3H), 7.41 – 7.38 (m, 2H), 7.20 – 7.18 (m, 3H), 3.87 (s, 2H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 153.3, 153.0, 136.2, 135.1, 133.6, 131.3, 130.6, 130.2, 129.2, 128.6, 128.5, 126.9, 126.4, 124.4, 123.5, 116.0, 94.0, 80.3, 24.5, 19.5.

HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_2$ $[M+H]^+$: 311.1548, found $[M+H]^+$: 311.1543

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (227, 19771), (238, 17460), (255, 12377), (320, 10713).

(*E*)-1-[2-(3-(3-Methoxyphenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1an)



Eluent: Hexane. Red oil (76 mg, 23% yield).

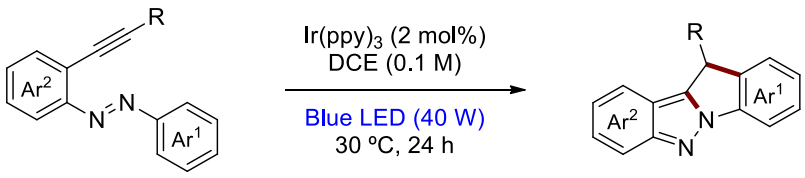
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.94 – 7.92 (m, 2H), 7.72 – 7.70 (m, 1H), 7.65 – 7.62 (m, 1H), 7.50 – 7.46 (m, 3H), 7.41 – 7.38 (m, 2H), 7.23 (t, *J* = 2.1 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.03 (s, 1H), 6.80 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.93 (s, 2H), 3.75 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 160.0, 153.5, 153.0, 138.4, 134.0, 131.3, 130.6, 129.6, 129.2, 128.6, 124.4, 123.5, 120.6, 116.1, 113.8, 112.3, 94.1, 80.2, 55.3, 26.4.

HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_2O$ $[M+H]^+$: 327.1497, found $[M+H]^+$: 327.1492.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (271, 72216).

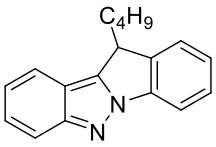
11*H*-Indolo[1,2-*b*]indazoles 2



1 **2**

The corresponding 2-alkynylazobenzene **1** (0.15 mmol, 1 equiv.) and $Ir(ppy)_3$ (0.003 mmol, 2 mol%) were dissolved in DCE (0.1 M) in a 5 mL Schlenk tube. The reaction mixture was irradiated with a 40 W blue LED until completion. The solvents were removed under reduced pressure, and the crude was purified by column chromatography using mixtures of hexane and ethyl acetate as the eluent to yield the corresponding indolo[1,2-*b*]indazole **2**.

11-Butyl-11*H*-indolo[1,2-*b*]indazole (2a)



Eluent: Hexane/EtOAc (20:1). White solid (29 mg, 83%; 1mmol scale: 194 mg, 74%).

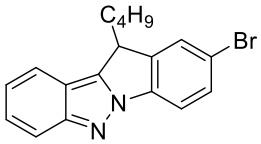
M.p. 79-80 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.19 – 7.07 (m, 1H), 4.34 (t, *J* = 6.6 Hz, 1H), 2.29 – 2.12 (m, 1H), 2.02 – 1.86 (m, 1H), 1.54 – 1.30 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.4, 141.5, 140.2, 139.7, 128.4, 126.5, 126.2, 125.2, 121.7, 120.0, 118.6, 117.4, 112.3, 41.8, 32.4, 29.0, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543, found $[M+H]^+$: 263.1545.

2-Bromo-11-butyl-11*H*-indolo[1,2-*b*]indazole (2b)



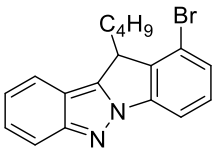
Eluent: Hexane/EtOAc (20:1). White solid (26 mg, 52%). **M.p.** 72-73 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 8.8 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.62 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.34 (ddd, *J* = 8.8, 6.7, 1.2 Hz, 1H), 7.18 – 7.10 (m, 1H), 4.35 (t, *J* = 6.8 Hz, 1H), 2.27 – 2.13 (m, 1H), 1.99 – 1.85 (m, 1H), 1.50 – 1.31 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.7, 141.7, 141.3, 139.3, 131.6, 128.6, 126.8, 122.1, 120.0, 119.6, 118.7, 117.5, 113.5, 41.8, 32.3, 29.0, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{18}H_{18}BrN_2$ $[M+H]^+$: 341.0648, found $[M+H]^+$: 341.0650.

1-Bromo-11-butyl-11*H*-indolo[1,2-*b*]indazole (2c)



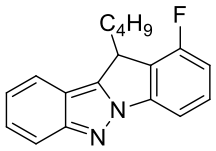
Eluent: Hexane/EtOAc (20:1). Yellow oil (23 mg, 53%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86 – 7.77 (m, 2H), 7.73 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.14 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 4.46 (dd, *J* = 8.0, 3.6 Hz, 1H), 2.59-2.48 (m, 1H), 2.19 – 2.06 (m, 1H), 1.34 – 1.14 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.6, 141.7, 141.4, 138.4, 130.2, 130.0, 126.9, 122.1, 120.1, 119.8, 118.7, 117.3, 111.3, 43.3, 29.5, 27.9, 22.6, 13.9.

HRMS (ESI+) m/z calculated for $C_{18}H_{18}BrN_2$ $[M+H]^+$: 341.0648, found $[M+H]^+$: 341.0649.

11-Butyl-1-fluoro-11*H*-indolo[1,2-*b*]indazole (2d)



Eluent: Hexane/EtOAc (20:1). Yellow solid (12 mg, 37%).

M.p. 85-86 ^{o}C.

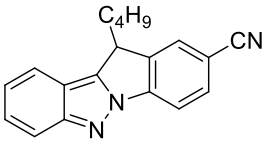
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.81 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.74 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.70 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.35 (ddd, *J* = 8.9, 6.6, 1.1 Hz, 1H), 7.15 (ddd, *J* = 8.5, 6.7, 0.9 Hz, 1H), 7.04 (ddd, *J* = 9.2, 8.3, 0.8 Hz, 1H), 4.57 (dd, *J* = 7.9, 4.6 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.07 – 1.92 (m, 1H), 1.45 – 1.26 (m, 4H), 0.91 – 0.83 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -117.85 (dd, *J* = 9.4, 5.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 159.5 (d, *J* = 248.9 Hz), 153.6, 142.2 (d, *J* = 9.4 Hz), 141.6, 130.6 (d, *J* = 8.1 Hz), 127.0, 125.1 (d, J = 20.7 Hz), 122.2, 120.1, 118.7, 117.3, 113.8 (d, *J* = 20.5 Hz), 108.5 (d, *J* = 3.5 Hz), 77.5, 77.2, 76.8, 40.4, 40.4, 30.8, 30.8, 28.7, 22.7, 13.9.

HRMS (ESI+) m/z calculated for $C_{18}H_{18}FN_2$ $[M+H]^+$: 281.1449, found $[M+H]^+$: 281.1451.

11-Butyl-11*H*-indolo[1,2-*b*]indazole-2-carbonitrile (2e)



Eluent: Hexane/EtOAc (5:1). Yellow solid (23 mg, 74%).

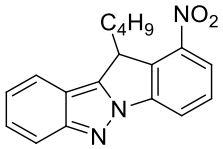
M.p. 123-124 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.99 – 7.90 (m, 1H), 7.86 – 7.77 (m, 3H), 7.73 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.37 (ddd, *J* = 8.9, 6.6, 1.1 Hz, 1H), 7.22 – 7.11 (m, 1H), 4.42 (t, *J* = 6.6 Hz, 1H), 2.21 (ddd, *J* = 15.6, 7.7, 5.8 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.49 – 1.33 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 154.4, 143.3, 142.5, 140.7, 133.6, 128.9, 127.6, 122.7, 120.1, 118.9, 118.8, 117.5, 112.9, 109.6, 41.8, 32.2, 29.0, 22.7, 14.0.

HRMS (ESI+) m/z calculated for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495, found $[M+H]^+$: 288.1497.

11-Butyl-1-nitro-11*H*-indolo[1,2-*b*]indazole (2f)



Eluent: Hexane/EtOAc (10:1). Yellow solid (17 mg, 45%).

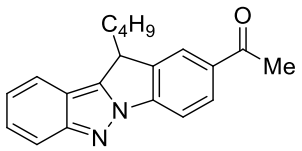
M.p. 125-126 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.74 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.68 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.30 (ddd, *J* = 8.9, 6.6, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 5.05 (dd, *J* = 8.2, 3.7 Hz, 1H), 2.34 – 2.21 (m, 1H), 1.84 – 1.70 (m, 1H), 1.30 – 1.11 (m, 4H), 0.75 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 154.5, 146.3, 142.7, 142.5, 135.8, 130.4, 127.8, 122.9, 121.8, 120.6, 119.1, 117.9, 117.7, 43.5, 31.2, 28.9, 22.8, 14.2.

HRMS (ESI+) m/z calculated for $C_{18}H_{18}N_3O_2$ $[M+H]^+$: 308.1394, found $[M+H]^+$: 308.1401.

1-(11-Butyl-11H-indolo[1,2-*b*]indazol-2-yl)ethanone (2g)



Eluent: Hexane/EtOAc (20:1). Yellow solid (22 mg, 67%).

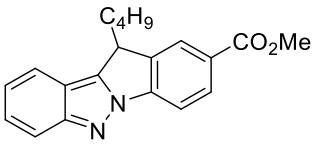
M.p. 135-136 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.17 (dd, *J* = 1.6, 0.8 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.76 (m, 1H), 7.72 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.9, 6.6, 1.1 Hz, 1H), 7.14 (dd, *J* = 8.5, 6.6 Hz, 1H), 4.39 (dd, *J* = 7.6, 5.5 Hz, 1H), 2.67 (s, 3H), 2.31-2.17 (m, 1H), 2.01 – 1.85 (m, 1H), 1.50 – 1.29 (m, 4H), 0.94 – 0.83 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 197.1, 154.2, 143.5, 142.9, 140.2, 135.2, 130.2, 127.3, 125.0, 122.3, 120.2, 118.8, 117.5, 111.8, 41.8, 32.2, 29.0, 26.9, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{20}H_{20}N_2O$ $[M+H]^+$: 305.1648, found $[M+H]^+$: 305.1652.

Methyl 11-butyl-11*H*-indolo[1,2-*b*]indazole-2-carboxylate (2h)



Eluent: Hexane/EtOAc (20:1). Yellow solid (20 mg, 60%).

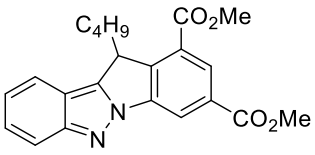
M.p. 122-123 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 – 8.19 (m, 2H), 7.92 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.81 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.73 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.35 (ddd, *J* = 8.9, 6.6, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.4, 6.6, 1.0 Hz, 1H), 4.41 (t, *J* = 6.5 Hz, 1H), 3.97 (s, 3H), 2.33 – 2.19 (m, 1H), 2.01 – 1.89 (m, 1H), 1.48 – 1.32 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 166.7, 154.0, 143.5, 142.8, 139.8, 131.0, 128.1, 127.3, 126.6, 122.3, 120.2, 118.8, 117.5, 112.0, 52.5, 41.8, 32.2, 28.9, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598, found $[M+H]^+$: 321.1607.

Dimethyl 11-butyl-11H-indolo[1,2-*b*]indazole-1,3-dicarboxylate (2i)



Eluent: Hexane/EtOAc (10:1). Yellow solid (37 mg, 87%).

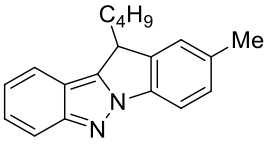
M.p. 127-128 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.66 (d, *J* = 1.4 Hz, 1H), 8.61 (d, *J* = 1.3 Hz, 1H), 7.79 (dt, *J* = 8.9, 1.1 Hz, 1H), 7.72 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.19 – 7.08 (m, 1H), 4.96 (dd, *J* = 8.4, 3.7 Hz, 1H), 4.03 (s, 3H), 3.99 (s, 3H), 2.43 – 2.34 (m, 1H), 1.85 – 1.72 (m, 1H), 1.31 – 1.20 (m, 4H), 0.81 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.5, 165.3, 153.9, 146.3, 142.7, 141.5, 131.3, 129.2, 128.1, 127.2, 122.3, 120.33, 118.7, 117.4, 116.5, 52.8, 52.7, 43.2, 31.9, 28.7, 22.6, 13.9.

HRMS (ESI+) m/z calculated for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1652, found $[M+H]^+$: 379.1654.

11-Butyl-2-methyl-11*H*-indolo[1,2-*b*]indazole (2j)



Eluent: Hexane/EtOAc (20:1). Yellow solid (22 mg, 72%).

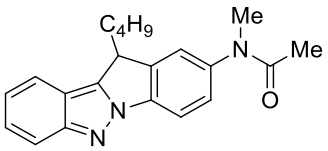
M.p. 113-114 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 – 7.70 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.64 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.04 (ddd, *J* = 8.3, 6.6, 0.9 Hz, 1H), 4.22 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.38 (s, 3H), 2.17 – 2.05 (m, 1H), 1.90 – 1.76 (m, 1H), 1.40 – 1.23 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.2, 141.3, 139.9, 138.1, 136.3, 128.9, 126.2, 125.9, 121.6, 120.0, 118.5, 117.4, 111.9, 41.7, 32.5, 29.1, 22.8, 21.7, 14.0.

HRMS (ESI+) m/z calculated for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, found $[M+H]^+$: 277.1700.

***N*-(11-Butyl-11*H*-indolo[1,2-*b*]indazol-2-yl)-*N*-methylacetamide (2k)**



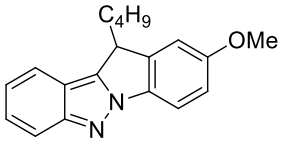
Eluent: Hexane/EtOAc (2:1). Yellow oil (21 mg, 64%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 8.2 Hz, 1H), 7.81 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.74 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.41 – 7.28 (m, 3H), 7.21 – 7.09 (m, 1H), 4.39 (dd, *J* = 7.7, 5.6 Hz, 1H), 3.33 (s, 3H), 2.28 – 2.15 (m, 1H), 1.98-1.89 (m, 4H), 1.49 – 1.34 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 170.7, 153.7, 142.8, 141.9, 141.5, 139.5, 127.7, 126.9, 124.3, 122.2, 120.0, 118.7, 117.6, 113.1, 41.9, 37.6, 32.3, 29.1, 22.8, 22.7, 14.0.

HRMS (ESI+) m/z calculated for $C_{21}H_{24}N_3O$ $[M+H]^+$: 334.1914, found $[M+H]^+$: 334.1920.

11-Butyl-2-methoxy-11*H*-indolo[1,2-*b*]indazole (2l)



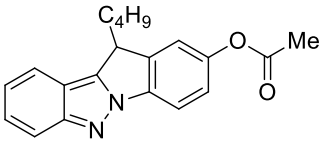
Eluent: Hexane/EtOAc (5:1). Orange oil (19 mg, 43%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87 – 7.75 (m, 2H), 7.72 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.8, 6.6, 1.1 Hz, 1H), 7.18 – 7.08 (m, 2H), 6.99 (dd, *J* = 8.6, 2.5 Hz, 1H), 4.32 (t, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 2.19 (m, 1H), 1.99 – 1.88 (m, 1H), 1.48 – 1.33 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 158.8, 153.0, 141.4, 140.9, 134.1, 126.1, 121.6, 119.8, 118.4, 117.6, 112.8, 112.8, 112.1, 56.0, 41.9, 32.5, 28.9, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648, found $[M+H]^+$: 293.1657.

11-Butyl-11*H*-indolo[1,2-*b*]indazol-2-yl acetate (2m)



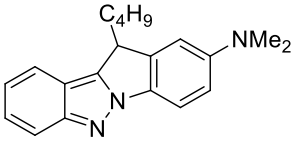
Eluent: Hexane/EtOAc (10:1). Yellow oil (19 mg, 52%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87 (d, *J* = 8.4 Hz, 1H), 7.81 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.73 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.20 – 7.08 (m, 1H), 4.37 (t, *J* = 6.6 Hz, 1H), 2.35 (s, 3H), 2.25 – 2.10 (m, 1H), 2.03 – 1.84 (m, 1H), 1.53 – 1.30 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 169.7, 153.4, 149.1, 141.7, 141.0, 137.9, 126.7, 122.0, 121.7, 120.0, 119.3, 118.6, 117.6, 112.7, 42.0, 32.3, 29.1, 22.8, 21.3, 14.0.

HRMS (ESI+) m/z calculated for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598, found $[M+H]^+$: 321.1601.

11-Butyl-2-methyl-11*H*-indolo[1,2-*b*]indazole (2n)



Eluent: Hexane/EtOAc (5:1). Yellow solid (17 mg, 35%).

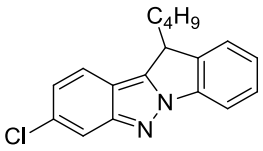
M.p. 93-94 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.80 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.35 – 7.26 (m, 1H), 7.10 (ddd, *J* = 8.5, 6.7, 0.9 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.29 (dd, *J* = 7.8, 5.3 Hz, 1H), 3.04 (s, 6H), 2.27 – 2.16 (m, 1H), 1.99 – 1.81 (m, 1H), 1.53 – 1.30 (m, 4H), 0.95 – 0.84 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 152.7, 149.6, 141.0, 139.8, 130.7, 125.3, 121.0, 119.4, 118.0, 117.39, 112.4, 111.5, 109.3, 41.8, 41.0, 32.6, 28.8, 22.6, 13.8.

HRMS (ESI+) m/z calculated for $C_{20}H_{24}N_3$ $[M+H]^+$: 306.1965, found $[M+H]^+$: 306.1967.

11-Butyl-8-chloro-11*H*-indolo[1,2-*b*]indazole (2o)



Eluent: Hexane/EtOAc (20:1). White solid (20 mg, 63%).

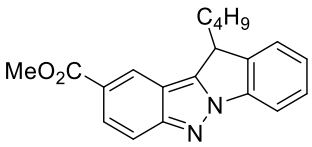
M.p. 115-116 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.49 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.08 (dd, *J* = 8.9, 1.8 Hz, 1H), 4.34 (dd, *J* = 7.5, 5.6 Hz, 1H), 2.20 – 2.14 (m, 1H), 2.02 – 1.84 (m, 1H), 1.44 – 1.33 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 141.9, 140.1, 139.5, 132.3, 128.6, 126.5, 125.3, 123.3, 121.2, 117.6, 115.9, 112.4, 41.8, 32.3, 29.0, 22.8, 14.0.

HRMS (ESI+) m/z calculated for $C_{18}H_{17}ClN_2$ $[M+H]^+$: 297.1153, found $[M+H]^+$: 297.1155.

Methyl 11-butyl-11*H*-indolo[1,2-*b*]indazole-9-carboxylate (2p)



Eluent: Hexane/EtOAc (20:1). Yellow solid (26 mg, 70%).

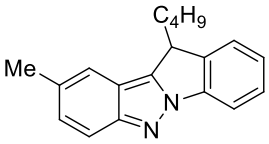
M.p. 134-135 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.58 (dd, *J* = 1.6, 0.9 Hz, 1H), 7.95 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.90 (dt, *J* = 7.9, 0.8 Hz, 1H), 7.81 (dd, *J* = 9.2, 0.9 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.55 – 7.46 (m, 1H), 7.38 (td, *J* = 7.5, 1.1 Hz, 1H), 4.41 (t, *J* = 6.5 Hz, 1H), 3.96 (s, 3H), 2.29 – 2.17 (m, 1H), 2.08 – 1.98 (m, 1H), 1.44 – 1.34 (m, 4H), 0.93 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 167.6, 154.6, 144.0, 139.9, 139.6, 128.7, 126.8, 126.4, 125.4, 124.6, 123.8, 118.3, 116.8, 112.6, 52.3, 42.0, 32.1, 28.8, 22.8, 13.9.

HRMS (ESI+) m/z calculated for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598, found $[M+H]^+$: 321.1605.

11-Butyl-9-methyl-11*H*-indolo[1,2-*b*]indazole (2q)



Eluent: Hexane/EtOAc (20:1). Yellow solid (21 mg, 66%).

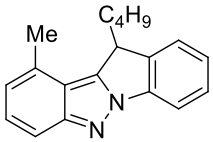
M.p. 129-130 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.58 – 7.41 (m, 3H), 7.33 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.17 (dd, *J* = 8.9, 1.6 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 1H), 2.47 (s, 3H), 2.28 – 2.10 (m, 1H), 2.01-1.89 (m, 1H), 1.49 – 1.32 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 167.6, 154.6, 144.0, 139.9, 139.6, 128.7, 126.8, 126.4, 125.4, 124.6, 123.8, 118.3, 116.8, 112.6, 52.3, 42.0, 32.1, 28.8, 22.8, 13.9.

HRMS (ESI+) m/z calculated for $C_{29}H_{21}N_2$ $[M+H]^+$: 277.1699, found $[M+H]^+$: 277.1703.

11-Butyl-10-methyl-11H-indolo[1,2-*b*]indazole (2r)



Eluent: Hexane/EtOAc (20:1). Yellow solid (25 mg, 84%).

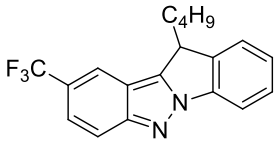
M.p. 117-118 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.69 – 7.59 (m, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.7, 1.1 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.22 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.91 – 6.82 (m, 1H), 4.46 (dd, *J* = 6.4, 3.7 Hz, 1H), 2.68 (s, 3H), 2.39 – 2.17 (m, 2H), 1.27 – 1.14 (m, 2H), 1.03 – 0.87 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.7, 141.3, 140.4, 139.3, 130.3, 128.4, 126.8, 126.1, 125.0, 121.4, 118.7, 115.9, 112.1, 41.6, 32.5, 26.9, 22.8, 20.9, 13.9.

HRMS (ESI+) m/z calculated for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, found $[M+H]^+$: 277.1703.

11-Butyl-9-(trifluoromethyl)-11*H*-indolo[1,2-*b*]indazole (2s)



Eluent: Hexane/EtOAc (20:1). White solid (23 mg, 65%).

M.p. 98-99 ^{o}C.

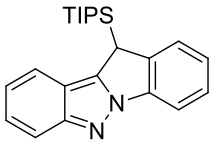
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.11 – 8.04 (m, 1H), 7.95 – 7.86 (m, 2H), 7.63 – 7.57 (m, 1H), 7.57 – 7.45 (m, 2H), 7.45 – 7.34 (m, 1H), 4.40 (t, *J* = 6.5 Hz, 1H), 2.29 – 2.14 (m, 1H), 2.08 – 1.91 (m, 1H), 1.49 – 1.32 (m, 4H), 0.95 – 0.84 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -61.72.

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.7, 143.3, 139.9, 139.6, 128.7, 126.9, 125.4, 124.9 (q, *J* = 272.7 Hz), 123.9 (q, *J* = 31.8 Hz), 122.4 (q, *J* = 2.9 Hz), 119.6, 118.7 (q, *J* = 4.9 Hz), 116.1, 112.7, 42.0, 32.2, 28.9, 22.7, 13.9.

HRMS (ESI+) m/z calculated for $C_{19}H_{18}F_3N_2$ $[M+H]^+$: 331.1417, found $[M+H]^+$: 331.1425.

11-(Triisopropylsilyl)-11*H*-indolo[1,2-*b*]indazole (2t)



Eluent: hexane/EtOAc (20:1). Yellow solid (11 mg, 27%).

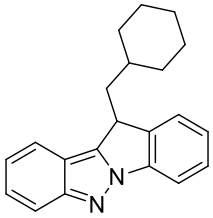
M.p. 132-133 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 – 7.96 (m, 1H), 7.81 (dt, *J* = 8.7, 1.0 Hz, 1H), 7.71 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.57 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.37 – 7.28 (m, 2H), 7.09 (ddd, *J* = 8.5, 6.7, 1.0 Hz, 1H), 4.50 (s, 1H), 1.36 (sext, *J* = 7.3 Hz, 4H), 0.98 (d, *J* = 7.5 Hz, 9H), 0.90 (d, *J* = 7.6 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 141.1, 139.5, 138.1, 127.1, 126.3, 125.5, 125.1, 121.0, 120.2, 118.4, 116.5, 112,6, 31.7, 18.6, 18.3, 11.6.

HRMS (ESI+) m/z calculated for $C_{23}H_{31}N_2Si$ $[M+H]^+$: 363.2251, found $[M+H]^+$: 363.2254.

11-(Cyclohexylmethyl)-11*H*-indolo[1,2-*b*]indazole (2u)



Eluent: Hexane/EtOAc (20:1). Yellow solid (22 mg, 65%).

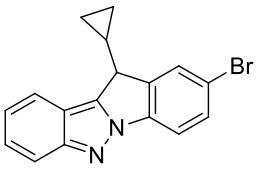
M.p. 148-149 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.89 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.69 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.57 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.14 (ddd, *J* = 8.6, 6.7, 0.9 Hz, 1H), 4.41 (dd, *J* = 9.4, 5.9 Hz, 1H), 2.17 – 2.06 (m, 1H), 2.03 – 1.63 (m, 7H), 1.46 – 1.01 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.4, 141.8, 140.3, 140.0, 128.4, 126.5, 126.2, 125.3, 121.9, 120.1, 118.6, 117.5, 112.4, 40.8, 39.4, 35.7, 34.1, 32.9, 26.6, 26.3.

HRMS (ESI+) m/z calculated for $C_{21}H_{23}N_2$ $[M+H]^+$: 303.1856, found $[M+H]^+$: 303.1859.

2-Bromo-11-cyclopropyl-11*H*-indolo[1,2-*b*]indazole (2v)



Eluent: Hexane/EtOAc (20:1). Yellow solid (24 mg, 72%).

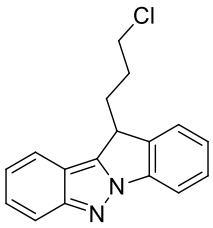
M.p. 150-151 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.91 – 7.69 (m, 4H), 7.62 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.40 – 7.28 (m, 1H), 7.15 (dd, *J* = 8.2, 6.8 Hz, 1H), 3.61 (d, *J* = 9.3 Hz, 1H), 1.05-0.95 (m, 1H), 0.92-0.79 (m, 3H), 0.75 – 0.65 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.7, 141.6, 141.0, 139.2, 131.8, 128.9, 126.9, 122.2, 120.2, 119.6, 118.6, 117.5, 113.5, 46.6, 13.5, 4.6, 3.6.

HRMS (ESI+) m/z calculated for $C_{17}H_{14}BrN_2$ $[M+H]^+$: 325.0335, found $[M+H]^+$: 325.0336.

11-(3-Chloropropyl)-11*H*-indolo[1,2-*b*]indazole (2w)



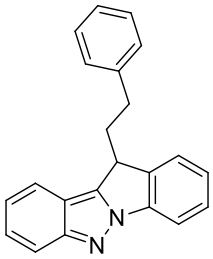
Eluent: Hexane/EtOAc (20:1). Yellow oil (19 mg, 62%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 7.9 Hz, 1H), 7.83 (dt, *J* = 8.8, 1.1 Hz, 1H), 7.95 – 7.78 (m, 2H), 7.72 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.42 – 7.28 (m, 2H), 7.15 (dd, *J* = 8.3, 6.8 Hz, 1H), 4.44 (t, *J* = 6.1 Hz, 1H), 3.55 – 3.46 (m, 2H), 2.54 – 2.36 (m, 1H), 2.26 – 2.08 (m, 1H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 140.5, 140.3, 138.8, 128.8, 126.7, 126.5, 125.2, 122.1, 119.7, 118.7, 117.4, 112.4, 44.8, 40.9, 29.6, 29.3.

HRMS (ESI+) m/z calculated for $C_{17}H_{15}ClN_2$ $[M+H]^+$: 283.0997, found $[M+H]^+$: 283.1000.

11-Phenethyl-11*H*-indolo[1,2-*b*]indazole (2x)



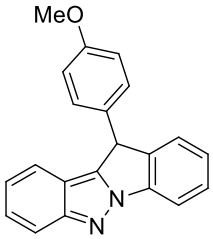
Eluent: Hexane/EtOAc (20:1). Yellow oil (19 mg, 66%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.91 (d, *J* = 7.8 Hz, 1H), 7.84 (dt, *J* = 8.8, 1.0 Hz, 1H), 7.79 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (td, *J* = 7.7, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.6, 7.0, 1.2 Hz, 2H), 7.31 – 7.19 (m, 2H), 7.21 – 7.07 (m, 4H), 4.45 (t, *J* = 6.2 Hz, 1H), 2.81 – 2.63 (m, 2H), 2.63 – 2.45 (m, 1H), 2.40 – 2.22 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 153.5, 141.2, 141.0, 140.4, 139.2, 128.7, 128.6, 128.4, 126.56 126.4, 126.3, 125.2, 122.0, 119.9, 118.7, 117.4, 112.4, 41.5, 34.4, 33.0.

HRMS (ESI+) m/z calculated for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543, found $[M+H]^+$: 311.1549.

11-(4-Methoxyphenyl)-11*H*-indolo[1,2-*b*]indazole (2y)



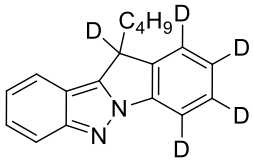
Eluent: Hexane/EtOAc (20:1). Yellow oil (22 mg, 65%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.27 (m, 2H), 7.16 – 7.08 (m, 2H), 7.07 – 7.01 (m, 1H), 6.88 – 6.82 (m, 2H), 5.41 (s, 1H), 3.78 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 159.4, 153.6, 141.0, 140.2, 140.0, 129.5, 129.1, 128.8, 126.7, 126.7, 126.0, 122.0, 119.7, 118.7, 117.3, 114.7, 112.4, 55.4, 46.4.

HRMS (ESI+) m/z calculated for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335, found $[M+H]^+$: 313.1341.

11-Butyl-11*H*-indolo[1,2-*b*]indazole-1,2,3,4,11-d_5 (2a-d_5)



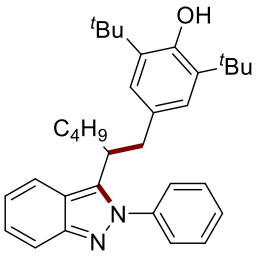
Eluent: Hexane/EtOAc (20:1). Yellow oil (16 mg, 67% yield, >97% deuteration).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.83 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.75 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.39 – 7.29 (m, 1H), 7.19 – 7.08 (m, 1H), 2.28 – 2.13 (m, 1H), 2.02 – 1.86 (m, 1H), 1.52 – 1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 153.5, 141.5, 140.3, 139.6, 126.5, 121.8, 120.1, 118.7, 117.4, 32.3, 29.0, 22.8, 14.0. *C coupled with deuterium are not observed.

HRMS (ESI+) m/z calculated for $C_{18}H_{14}D_5N_2$ $[M+H]^+$: 268.18566, found $[M+H]^+$: 268.18602.

2,6-Di-*tert*-butyl-4-[2-(2-phenyl-2*H*-indazol-3-yl)hexyl]phenol (6)



Eluent: Hexane/EtOAc (20:1). Yellow oil (19 mg, 39% yield).

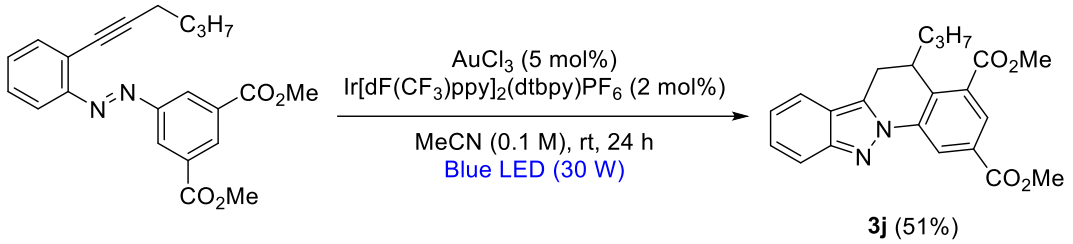
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.71 (dt, *J* = 8.7, 1.0 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.12 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 6.74 – 6.66 (m, 2H), 6.43 (s, 2H), 4.99 (s, 1H), 3.23 – 3.04 (m, 2H), 2.91 (dd, *J* = 12.2, 3.9 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.93 – 1.82 (m, 1H), 1.21 (s, 18H), 1.18 – 1.05 (m, 4H), 0.78 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 152.3, 148.9, 140.1, 139.4, 135.8, 130.2, 128.8, 128.7, 127.1, 126.3, 125.6, 121.0, 120.9, 119.5, 118.2, 41.8, 41.7, 35.4, 34.2, 30.3, 30.2, 22.7, 14.0.

HRMS (ESI+) m/z calculated for $C_{33}H_{43}N_2O$ $[M+H]^+$: 483.33699, found $[M+H]^+$: 483.33707.

5,6-Dihydroindolo[2,3-*a*]quinolines 3

Dimethyl 5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-2,4-dicarboxylate (3j)



3j (51%)

2-Alkynylazobenzene **1j** (59 mg, 0.16 mmol, 1 equiv.), $AuCl_3$ (2.4 mg, 0.008 mmol, 5 mol%) and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (3.6 mg, 0.003 mmol, 2 mol%) were dissolved in MeCN (0.1 M, 1.6 mL) in a 5 mL Schlenk tube. The reaction mixture was irradiated with a 30 W blue LED strip at room temperature for 24 hours. After filtration through Celite, the solvent was removed under reduced pressure, and the crude was purified by column chromatography using a mixture of hexane and EtOAc (5:1) as eluent. This yielded the corresponding 5,6-dyhydroindazolo[2,3-*a*]quinoline **3j** as a yellow solid (31 mg, 51% yield).

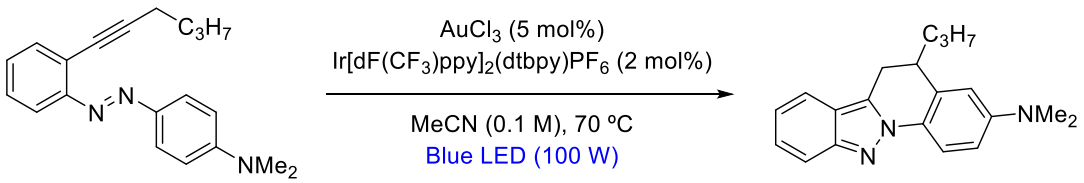
M.p 149-150 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.03 (d, *J* = 1.8 Hz, 1H), 8.53 (d, *J* = 1.8 Hz, 1H), 7.75 (dt, *J* = 8.9, 0.9 Hz, 1H), 7.63 (dt, *J* = 8.5, 1.1 Hz, 1H), 7.33 (ddd, *J* = 8.9, 6.6, 1.2 Hz, 1H), 7.12 – 7.04 (m, 1H), 4.36 – 4.23 (m, 1H), 3.98 (s, 3H), 3.98 (s, 3H), 3.52 (dd, *J* = 16.6, 1.9 Hz, 1H), 3.21 (dd, *J* = 16.6, 5.6 Hz, 1H), 1.42 – 1.28 (m, 4H), 0.82 (t, *J* = 6.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 166.7, 165.7, 149.8, 139.3, 137.0, 130.6, 130.2, 130.2, 129.8, 127.9, 122.8, 121.8, 120.9, 120.0, 118.0, 52.7, 52.6, 35.7, 32.1, 23.7, 20.2, 14.0.

HRMS (ESI+) m/z calculated for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1652, found $[M+H]^+$: 379.1654.

N,N-Dimethyl-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinolin-3-amine (3m)



3m

The corresponding 2-alkynylazobenzene (0.16 mmol, 1 equiv.), $AuCl_3$ (0.007 mmol, 5 mol%) and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (0.003 mmol, 2 mol%) were dissolved in MeCN (0.1 M, 1.6 mL) in a 5 mL Schlenk tube. The reaction mixture was irradiated with blue LED chips (2 x 50 W) at 70 ^{o}C

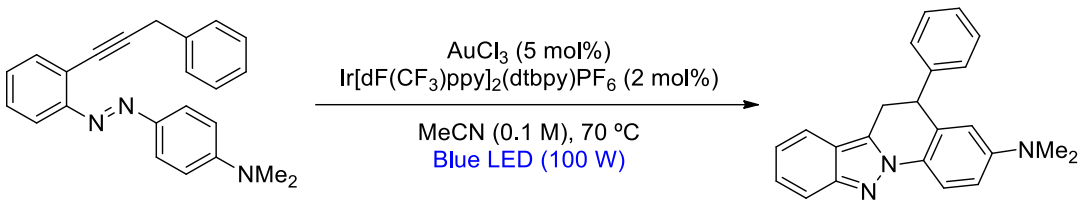
until the 2*H*-indazole intermediate **5n** had been fully consumed. After filtration through Celite, the solvent was removed under reduced pressure and the crude was purified by column chromatography using a mixture of hexane and EtOAc as eluent (5:1). This yielded the corresponding 5,6-dyhydroindazolo[2,3-*a*]quinoline **3m** as a yellow oil (43 mg, 86% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.12 – 8.02 (m, 1H), 7.79 – 7.70 (m, 1H), 7.65 – 7.56 (m, 1H), 7.34 – 7.27 (m, 1H), 7.08 – 7.00 (m, 1H), 6.74 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 3.31 (d, *J* = 4.3 Hz, 2H), 3.01 (s, 7H), 1.49 – 1.30 (m, 4H), 0.91 – 0.80 (m, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.4, 148.9, 133.5, 128.9, 126.4, 126.3, 120.7, 120.6, 119.5, 119.0, 117.4, 111.8, 111.4, 40.8, 36.9, 36.7, 25.7, 20.3, 14.1.

HRMS (ESI+) m/z calculated for $C_{20}H_{23}N_3$ $[M+H]^+$: 306.19647, found $[M+H]^+$: 306.19777.

***N*,*N*-dimethyl-5-phenyl-5,6-dihydroindazolo[2,3-*a*]quinolin-3-amine (3ag)**



1ag **3ag**

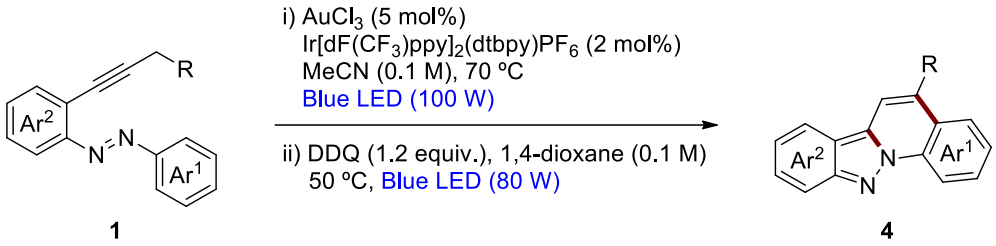
The corresponding 2-alkynylazobenzene **1ag** (0.15 mmol, 1 equiv.), $AuCl_3$ (0.007 mmol, 5 mol%) and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (0.003 mmol, 2 mol%) were dissolved in MeCN (0.1 M, 1.5 mL) in a Schlenk tube (5 mL). The reaction mixture was irradiated with blue LED chips (2 x 50 W) at 70 °C until the 2*H*-indazole intermediate **6ag** had been fully consumed. The mixture was filtered over Celite, and the solvents were removed under reduced pressure. This yielded the corresponding 5,6-dyhydroindazolo[2,3-*a*]quinoline **3ag** as a yellow solid (34 mg, 76% yield). **M.p.** 145-146 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 8.9 Hz, 1H), 7.74 (dt, *J* = 8.8, 0.9 Hz, 1H), 7.50 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.33 – 7.19 (m, 4H), 7.21 – 7.12 (m, 2H), 7.00 (ddd, *J* = 8.2, 6.5, 0.7 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.37 (dd, *J* = 2.7, 0.9 Hz, 1H), 4.37 (t, *J* = 7.0 Hz, 1H), 3.71 – 3.44 (m, 2H), 2.90 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 149.6, 148.9, 142.6, 131.9, 129.8, 128.9, 128.6, 128.0, 127.2, 126.4, 122.8, 120.8, 120.3, 119.5, 119.0, 117.3, 112.3, 111.8, 42.6, 40.6, 29.2.

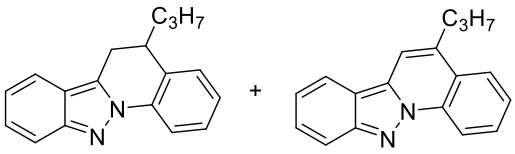
HRMS (ESI+) m/z calculated for $C_{23}H_{22}N_3$ $[M+H]^+$: 340.1808, found $[M+H]^+$: 340.1808.

Indazolo[2,3-*a*]quinolines 4



The corresponding 2-alkynylazobenzene **1** (0.16 mmol, 1 equiv.), $AuCl_3$ (0.008 mmol, 5 mol%) and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (0.003 mmol, 2 mol %) were dissolved in MeCN (0.1 M, 1.6 mL) in a Schlenk tube (5 mL). The reaction mixture was irradiated with blue LED chips (2 x 50 W) at 70 ^oC until the 2*H*-indazole intermediate **6** had been fully consumed. The mixture was filtered through silica and the solvents were removed under reduced pressure. The crude mixture was dissolved in 1,2-dioxane (0.1 M, 1.6 mL) in a Schlenk tube (5 mL), DDQ (0.19 mmol, 1.2 equiv.) was added, and the reaction mixture was irradiated with blue LED Kessil (2 x 40 W) at 50 ^oC until completion. The mixture was diluted with EtOAc and washed with $NaHCO_3$ (3 x 10 mL). The organic layer was dried over $MgSO_4$ and filtered. The solvents were removed under reduced pressure and the crude was purified by column chromatography using a mixture of hexane and EtOAc as eluent to yield the corresponding indazolo[2,3-*a*]quinolines **4**.

5-Propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 5-propylindazolo[2,3-*a*]quinoline (3a and 4a)



3a **4a**

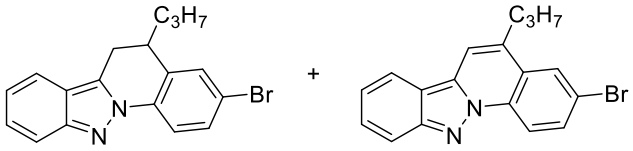
Eluent: Hexane/EtOAc (50:1). The mixture was obtained in a 1:5.7 ratio (**3a:4a**) as a yellow oil (22 mg, 43% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) δ 9.00 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.12 – 8.01 (m, 2H), 7.93 (dt, *J* = 8.7, 1.0 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.62 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.7, 6.7, 1.2 Hz, 1H), 7.23 (ddd, *J* = 8.3, 6.7, 0.9 Hz, 1H), 3.16 – 3.04 (m, 2H), 1.88 (sext, *J* = 7.5 Hz, 2H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.4, 134.8, 134.3, 132.3, 129.2, 128.1, 126.0, 125.1, 124.9, 121.3, 120.4, 120.0, 117.9, 116.6, 114.5, 34.8, 23.3, 14.3.

HRMS (ESI+) m/z calculated for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.13862, found $[M+H]^+$: 261.13889.

3-Bromo-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 3-bromo-5-propylindazolo[2,3-*a*]quinoline (3b and 4b)



3b **4b**

Eluent: Hexane/EtOAc (50:1). The mixture was obtained in a 1:5 ratio (**3b:4b**) as a yellow solid (33 mg, 51% yield).

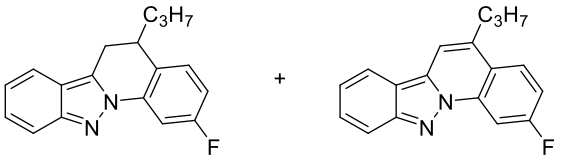
M.p. 168-169 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.87 (d, *J* = 8.9 Hz, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.96 – 7.83 (m, 2H), 7.82 (s, 1H), 7.58 – 7.50 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 3.04 (t, *J* = 7.7 Hz, 2H), 1.88 (sext, *J* = 7.3 Hz, 2H), 1.12 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.5 (C), 133.6 (C), 133.1 (C), 132.2 (CH), 132.2 (C), 128.4 (CH), 127.7 (CH), 126.5 (C), 120.8 (CH), 120.0 (C), 119.9 (CH), 119.6 (CH), 117.9 (C), 116.6 (CH), 115.5 (CH), 34.6 (CH_2), 23.0 (CH_2), 14.2 (CH_3).

HRMS (ESI+) m/z calculated for $C_{18}H_{16}BrN_2$ $[M+H]^+$: 339.0491, found $[M+H]^+$: 339.0493.

2-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 2-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3d and 4d)



Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1:1.9 ratio as a yellow oil (8 mg, 18% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (dd, *J* = 9.8, 2.7 Hz), 8.10 – 8.01 (m), 7.98 – 7.88 (m), 7.77 (s), 7.76 – 7.68 (m), 7.60 (d, *J* = 8.5 Hz), 7.54 (ddd, *J* = 8.7, 6.7, 1.2 Hz), 7.41 – 7.29 (m), 7.26 – 7.19 (m), 7.06 (ddd, *J* = 8.5, 6.5, 0.9 Hz), 6.96 (td, *J* = 8.3, 2.7 Hz), 3.34 (dd, *J* = 4.8, 3.1 Hz), 3.13 – 3.04 (m), 1.88 (sext, *J* = 7.4 Hz), 1.50 – 1.31 (m), 1.11 (t, *J* = 7.4 Hz), 0.86 (t, *J* = 7.2 Hz).

^{19}F-NMR (282 MHz, $CDCl_3$) δ (ppm) -108.44 – -109.25 (m), -113.17 – -113.36 (m).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 162.9 (C, d, *J* = 251 Hz), 161.2 (C), 149.6 (C), 134.5 (C), 134.5 (C), 132.7 (C), 130.8 (C), 129.8 (CH, d, *J* = 8.1 Hz), 128.5 (CH), 127.6 (CH), 127.4 (CH, d, *J* = 10.1

Hz), 127.0 (C), 121.6 (CH), 121.6 (C), 121.5 (C), 121.3 (C), 120.8 (C), 120.6 (CH), 120.1 (CH), 119.9 (CH), 117.9 (CH), 116.6 (CH), 116.5 (C), 114.8 (CH, d, *J* = 24.2 Hz), 113.7 (CH, d, *J* = 2.0 Hz), 113.5 (CH, d, *J* = 21.2 Hz), 106.0 (CH, d, *J* = 27.3 Hz) 104.1 (CH, d, *J* = 26.3 Hz), 36.8 (CH_2), 35.4 (CH), 34.9 (CH_2), 25.8 (CH_2), 23.3 (CH_2), 20.2 (CH_2), 14.3 (CH_3), 14.1 (CH_3).

HRMS (ESI+) for **3d**: m/z calculated for $C_{18}H_{18}FN_2$ $[M+H]^+$: 281.1449, found $[M+H]^+$: 281.1452.

HRMS (ESI+) for **4d**: m/z calculated for $C_{18}H_{16}FN_2$ $[M+H]^+$: 279.1292, found $[M+H]^+$: 279.1297.

4-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 2-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3d' and 4d')

Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1:1.3 ratio as a yellow oil (13 mg, 29% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.84 (dt, *J* = 8.5, 1.0 Hz), 8.05 (dt, *J* = 8.3, 1.1 Hz), 8.01 (d, *J* = 8.1 Hz), 7.92 (dt, *J* = 8.8, 1.0 Hz), 7.76 (s), 7.76 – 7.65 (m), 7.61 (dt, *J* = 8.4, 1.1 Hz), 7.54 (ddd, *J* = 8.8, 6.7, 1.1 Hz), 7.41 – 7.25 (m), 7.26 – 7.20 (m), 7.11 – 6.98 (m), 3.55 (q, *J* = 6.5 Hz), 3.45 (dd, *J* = 16.4, 1.6 Hz), 3.26 (dd, *J* = 16.4, 6.1 Hz), 3.24 – 3.14 (m), 1.89 – 1.75 (m), 1.45 – 1.33 (m), 1.26 – 1.18 (m), 1.09 (t, *J* = 7.3 Hz), 0.82 (t, *J* = 6.9 Hz).

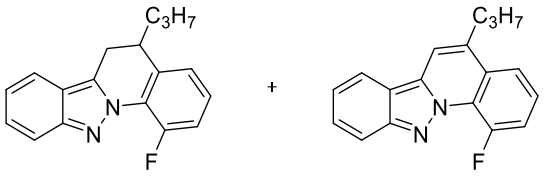
^{19}F-NMR (282 MHz, $CDCl_3$) δ (ppm) -110.86 – -111.05 (m), -117.56 – -117.76 (m).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 160.2 (C, d, *J* = 254.5 Hz), 160.2 (C, d, *J* = 244.4 Hz) 149.6 (2 x C), 138.8 (C, d, *J* = 7.1 Hz), 137.1 (C, d, *J* = 7.1 Hz) 133.6 (C, d, *J* = 5.1 Hz), 132.2 (C), 130.4 (C), 129.5 (CH, d, *J* = 10.1 Hz), 128.7 (CH, d, *J* = 9.1 Hz), 128.5 (CH), 127.5 (CH), 121.6 (CH), 120.9 (C), 120.8 (CH), 120.2 (C, d, *J* = 21.1 Hz), 120.0 (CH), 119.9 (CH), 117.9 (CH), 116.6 (CH), 116.4 (C), 116.2 (CH, d, *J* = 1 Hz), 115.2 (C, d, *J* = 15.2 Hz), 114.0 (CH, d, *J* = 4.0 Hz), 114.0 (CH, d, *J* = 4.0 Hz), 113.8 (CH, d, *J* = 22.2 Hz), 112.7 (CH, d, *J* = 24.2 Hz), 38.4 (CH_2, d, *J* = 11.1 Hz), 36.3 (CH_2), 28.9 (CH, d, *J* = 1.0 Hz), 25.0 (CH_2), 24.4 (CH_2, d, *J* = 4.0 Hz), 20.1 (CH_2), 14.2 (CH_3), 14.0 (CH_3).

HRMS (ESI+) for **3d'**: m/z calculated for $C_{18}H_{18}FN_2$ $[M+H]^+$: 281.1449, found $[M+H]^+$: 281.1451.

HRMS (ESI+) for **4d'**: m/z calculated for $C_{18}H_{16}FN_2$ $[M+H]^+$: 279.1292, found $[M+H]^+$: 279.1296.

1-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 1-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3e and 4e)



Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1:2.2 ratio as a yellow oil (14 mg, 30% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.05 (dt, *J* = 8.3, 1.1 Hz), 8.01 (dt, *J* = 8.7, 0.9 Hz), 7.89 – 7.83 (m), 7.80 (dt, *J* = 8.9, 1.0 Hz), 7.60 (dt, *J* = 8.5, 1.1 Hz), 7.57 – 7.51 (m), 7.33 – 7.27 (m), 7.26 – 7.19 (m), 7.12 – 7.03 (m), 3.33 (dd, J = 4.3, 1.4 Hz), 3.15 – 3.09 (m), 3.07 (t, *J* = 7.6, 7.1 Hz), 1.88 (sext, J = 7.4 Hz), 1.36 – 1.32 (m), 1.26 – 1.22 (m), 1.11 (t, *J* = 7.4 Hz), 0.83 (t, *J* = 6.9 Hz).

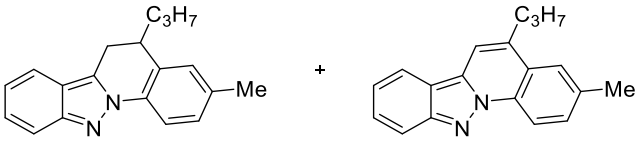
^{19}F-NMR (282 MHz, $CDCl_3$) δ (ppm) -116.30 – -116.46 (m), -121.39 – -121.55 (m).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 154.9 (C), 152.8 (C), 150.0 (C), 149.9 (C), 148.0 (C), 136.3 (C), 134.1 (C), 133.3 (C), 132.7 (C), 131.8 (C), 128.2 (CH), 128.0 (C), 127.5 (CH, d, *J* = 8.8 Hz), 127.2 (CH), 125.7 (CH, d, *J* = 7.6 Hz), 124.1 (CH, d, *J* = 2.5 Hz), 121.7 (CH), 121.0 (CH), 120.7 (CH, d, *J* = 3.8 Hz), 119.6 (CH), 119.5 (CH), 118.4 (CH), 117.2 (CH), 116.9 (CH, d, *J* = 21.4 Hz), 116.3 (CH, d, *J* = 22.9 Hz), 115.5 (CH, d, *J* = 1.3 Hz), 115.3 (C), 115.4 (C), 37.0 (CH, d, *J* = 2.0 Hz), 36.0 (CH_2), 35.3 (CH_2), 25.7 (CH_2), 22.9 (CH_2), 20.3 (CH_2), 14.3 (CH_3), 14.0 (CH_3).

HRMS (ESI+) for **3e**: m/z calculated for $C_{18}H_{18}FN_2$ $[M+H]^+$: 281.1449, found $[M+H]^+$: 281.1451.

HRMS (ESI+) for **4e**: m/z calculated for $C_{18}H_{16}FN_2$ $[M+H]^+$: 279.1292, found $[M+H]^+$: 279.1296.

3-Methyl-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 3-methyl-5-propylindazolo[2,3-*a*]quinoline (3k and 4k)



Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1.4:1 ratio as a yellow oil (18 mg, 34% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.88 (d, *J* = 8.5 Hz), 8.11 – 8.02 (m), 7.92 (dt, *J* = 8.8, 0.9 Hz), 7.84 (s), 7.79 (s), 7.73 (dt, *J* = 8.8, 1.0 Hz), 7.65 – 7.57 (m), 7.52 (ddd, *J* = 8.7, 6.7, 1.1 Hz), 7.29 (ddd, *J* = 8.7, 6.6, 1.1 Hz), 7.26 – 7.17 (m), 7.13 – 7.08 (m), 7.05 (ddd, *J* = 8.4, 6.6, 0.9 Hz), 3.32

(dd, *J* = 4.7, 1.9 Hz), 3.13 – 3.03 (m), 2.61 (s), 2.40 (s), 1.96 – 1.82 (m), 1.51 – 1.34 (m), 1.33 – 1.22 (m), 1.12 (t, *J* = 7.4 Hz), 0.85 (t, *J* = 7.1 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.3 (C), 149.3 (C), 136.7 (C), 135.9 (C), 134.6 (C), 133.7 (C), 132.5 (C), 132.3 (C), 131.9 (C), 130.8 (CH), 130.2 (C), 129.1 (CH), 128.7 (CH), 127.9 (CH), 127.0 (CH), 125.0 (C), 124.7 (CH), 121.1 (CH), 120.7 (C), 120.2 (CH), 119.9 (CH), 119.8 (CH), 118.0 (CH), 117.8 (CH), 117.7 (CH), 116.6 (C), 116.4 (CH), 114.4 (CH), 36.8 (CH_2), 35.9 (CH), 34.8 (CH), 25.7 (CH_2), 23.2 (CH_2), 21.9 (CH_3), 21.4 (CH_3), 20.3 (CH_2), 14.3 (CH_3), 14.1 (CH_3).

HRMS (ESI+) for **3k**: m/z calculated for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, found $[M+H]^+$: 277.1701.

HRMS (ESI+) for **4k**: m/z calculated for $C_{19}H_{19}N_2$ $[M+H]^+$: 275.1543, found $[M+H]^+$: 275.1545.

_N_-Methyl-_N_-(5-propyl-5,6-dihydroindazolo[2,3-_a_]quinolin-3-yl)acetamide and _N_-methyl-_N_-(5-propylindazolo[2,3-_a_]quinolin-3-yl)acetamide (3l and 4l)

Eluent: Hexane/EtOAc, 2:1. The mixture was obtained in a 1:1.2 ratio as a yellow oil (17 mg, 42% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 8.8 Hz), 8.24 (d, *J* = 8.5 Hz), 8.06 (dt, *J* = 8.4, 1.1 Hz), 7.93 (dd, *J* = 8.7, 1.0 Hz), 7.87 (s), 7.72 (dd, *J* = 8.8, 1.0 Hz), 7.61 (ddd, *J* = 8.5, 3.2, 1.9 Hz), 7.55 (ddd, *J* = 8.8, 6.7, 1.1 Hz), 7.36 – 7.29 (m), 7.27 – 7.20 (m), 7.13 (d, *J* = 2.4 Hz), 7.10 – 7.03 (m), 3.41 (s), 3.37 (dd, *J* = 9.3, 4.8 Hz), 3.31 (s), 3.18 – 3.09 (m), 3.06 (t, *J* = 7.6 Hz), 1.95 (s), 1.94 (s), 1.87 (sext, *J* = 7.4 Hz), 1.52 – 1.44 (m), 1.42 – 1.34 (m), 1.30 – 1.23 (m), 1.12 (t, *J* = 7.3 Hz), 0.87 (t, *J* = 7.2 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 170.7 (C=O), 170.6 (C=O), 149.7 (C), 149.6 (C), 142.9 (C), 142.3 (C), 134.0 (C), 133.8 (C), 133.2 (C), 132.3 (C), 130.5 (C), 128.5 (CH), 128.0 (CH), 127.6 (CH), 127.2 (CH), 126.8 (CH), 125.8 (C), 123.4 (CH), 121.7 (CH), 120.9 (CH), 120.8 (CH), 120.0 (2 x CH), 119.9 (CH), 119.6 (C), 119.5 (C), 117.9 (CH), 116.7 (CH), 116.6 (CH), 115.6 (C), 37.7 (CH_3), 37.4 (CH_3), 36.6 (CH_2), 35.9 (CH), 34.7 (CH_2), 25.6 (CH_2), 23.3 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 20.3 (CH_2), 14.2 (CH_3), 14.0 (CH_3).

HRMS (ESI+) for **3l**: m/z calculated for $C_{21}H_{24}N_3O$ $[M+H]^+$: 334.1914, found $[M+H]^+$: 334.1918.

HRMS (ESI+) for **4l**: m/z calculated for $C_{21}H_{22}N_3O$ $[M+H]^+$: 332.1757 , found $[M+H]^+$: 332.1762.

9-Chloro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 9-chloro-5-propylindazolo[2,3-*a*]quinoline (3p and 4p)

Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1.5:1 ratio as a yellow oil (20 mg, 34% yield).

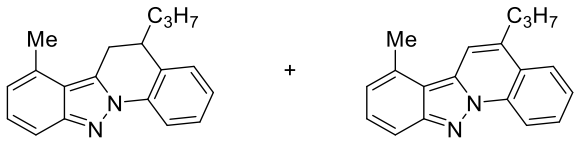
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, *J* = 8.5, 1.3 Hz), 8.16 (dd, *J* = 7.9, 1.2 Hz), 8.08 (dd, *J* = 8.3, 1.4 Hz), 7.96 (dd, *J* = 8.7, 0.7 Hz), 7.89 (dd, *J* = 1.7, 0.7 Hz), 7.82 – 7.77 (m), 7.76 (s), 7.72 (dd, *J* = 1.8, 0.7 Hz), 7.67 – 7.60 (m), 7.54 (dd, *J* = 8.9, 0.8 Hz), 7.41 (ddd, *J* = 8.0, 6.6, 2.2 Hz), 7.32 – 7.27 (m), 7.16 (dd, *J* = 8.7, 1.7 Hz), 7.00 (dd, *J* = 8.9, 1.7 Hz), 3.39 – 3.23 (m), 3.16 – 3.05 (m), 1.94 – 1.84 (m), 1.49 – 1.35 (m), 1.11 (t, *J* = 7.3 Hz), 0.86 (t, *J* = 7.2 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.6 (C), 149.5 (C), 135.8 (C), 135.7 (C), 134.0 (C), 133.0 (C), 132.4 (C), 132.2 (C), 131.4 (C), 131.1 (C), 129.7 (C), 129.5 (CH), 128.6 (CH), 128.2 (CH), 127.1 (CH), 126.3 (CH), 125.2 (CH), 124.9 (C), 122.9 (CH), 121.6 (CH), 121.2 (CH), 121.1 (CH), 119.2 (C), 118.2 (CH), 117.9 (CH), 116.8 (CH), 115.7 (CH), 114.1 (CH), 36.7 (CH_2), 35.7 (CH), 34.8 (CH_2), 25.7 (CH_2), 23.2 (CH_2), 20.2 (CH_2), 14.3 (CH_3), 14.1 (CH_3).

HRMS (ESI+) for **3p**: m/z calculated for $C_{18}H_{18}ClN_2$ $[M+H]^+$: 297.1153, found $[M+H]^+$: 297.1135.

HRMS (ESI+) for **4p**: m/z calculated for $C_{18}H_{16}ClN_2$ $[M+H]^+$: 295.0997, found $[M+H]^+$: 295.1001.

7-Methyl-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 7-methyl-5-propylindazolo[2,3-*a*]quinoline (3s and 4s)



Eluent: Hexane/EtOAc, 50:1. The mixture was obtained in a 1:1.3 ratio as a yellow oil (33 mg, 0.09 mmol, 55% yield).

M.p. 98-99 °C.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.01 (d, *J* = 8.4 Hz), 8.20 (d, *J* = 7.9 Hz), 8.05 (d, *J* = 8.3 Hz), 7.89 (s), 7.81 – 7.75 (m), 7.65 – 7.58 (m), 7.57 (d, *J* = 8.7 Hz), 7.42 (dd, *J* = 8.7, 6.8 Hz), 7.32 – 7.23 (m), 7.17 (dd, *J* = 8.7, 6.7 Hz), 6.97 (d, *J* = 6.8 Hz), 6.76 (d, *J* = 6.6 Hz), 3.59 (dd, *J* = 16.1, 3.4 Hz),

3.47 (dd, *J* = 16.0, 5.7 Hz), 3.11 – 3.05 (m), 2.87 (s), 2.66 (s), 1.88 (sext, *J* = 7.5 Hz), 1.53 – 1.45 (m), 1.46 – 1.36 (m), 1.35 – 1.24 (m), 1.12 (t, *J* = 7.3 Hz), 0.87 (t, *J* = 7.2 Hz).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.7 (C), 149.6 (C), 136.0 (C), 134.5 (C), 134.2 (C), 132.7 (C), 132.1 (C), 132.1 (C), 131.4 (C), 130.8 (C), 129.1 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 126.7 (CH), 125.9 (CH), 124.9 (CH), 124.4 (C), 121.5 (CH), 120.9 (CH), 120.9 (C), 118.2 (CH), 117.8 (CH), 116.3 (C), 116.1 (CH), 115.6 (CH), 114.2 (CH), 36.7 (CH_2), 36.0 (CH), 35.0 (CH_2), 27.3 (CH_2), 23.4 (CH_2), 20.6 (CH_3), 20.5 (CH_2), 20.2 (CH_3), 14.3 (CH_3), 14.1 (CH_3).

HRMS (ESI+) for **3s**: m/z calculated for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, found $[M+H]^+$: 277.1699.

HRMS (ESI+) for **4s**: m/z calculated for $C_{19}H_{19}N_2$ $[M+H]^+$: 275.1543, found $[M+H]^+$: 275.1547.

5-(2-Chloroethyl)-5,6-dihydroindazolo[2,3-*a*]quinoline and 5-(2-chloroethyl)indazolo[2,3-*a*]quinoline (3x and 4x)

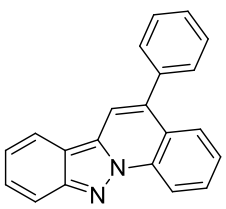
Eluent: Hexane/EtOAc (50:1). The mixture was obtained in a 1:5 ratio as a yellow oil (20 mg, 42% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.02 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.06 (dt, *J* = 8.4, 1.1 Hz, 1H), 8.01 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.95 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.81 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.65 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.7, 6.6, 1.1 Hz, 1H), 7.28 – 7.24 (m, 1H), 3.93 (t, *J* = 7.4 Hz, 2H), 3.58 (t, *J* = 7.4 Hz, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.4 (C), 134.4 (C), 131.8 (C), 129.7 (C), 129.6 (CH), 128.3 (CH), 126.4 (CH), 124.4 (CH), 124.3 (C), 120.9 (CH), 119.9 (CH), 118.1 (CH), 116.8 (C), 116.7 (CH), 116.1 (CH), 43.4 (CH_2), 35.9 (CH_2).

HRMS (ESI+) m/z calculated for $C_{17}H_{14}ClN_2$ $[M+H]^+$: 281.0840, found $[M+H]^+$: 281.0844.

5-Phenylindazolo[2,3-*a*]quinoline (4aa)



Eluent: Hexane/EtOAc (50:1). Yellow solid (16 mg, 41% yield).

M.p. 145-146 ^{o}C.

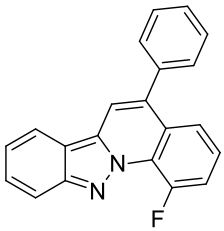
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.05 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.07 (dt, *J* = 8.3, 1.1 Hz, 1H), 8.01 – 7.93 (m, 3H), 7.82 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.62 – 7.50 (m, 7H), 7.28 – 7.25 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.5, 138.7, 136.0, 134.3, 132.1, 130.0, 129.6, 128.8, 128.3, 128.3, 127.5, 126.1, 124.6, 120.9, 119.9, 117.6, 117.1, 116.7, 115.8.

HRMS (ESI+) m/z calculated for $C_{21}H_{15}N_2$ $[M+H]^+$: 295.1230, found $[M+H]^+$: 295.1233.

UV-vis (MeOH) [λ (nm), ε (l/mol·cm)]: (275, 22470), (285, 25960), (304, 15590), (373, 15465), (388, 14095).

1-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ab)



Eluent: Hexane/EtOAc (50:1). Yellow solid (11 mg, 22% yield).

M.p. 155-156 ^{o}C.

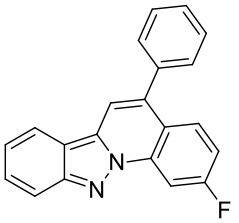
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 – 8.02 (m, 2H), 7.98 (s, 1H), 7.82 – 7.64 (m, 2H), 7.61 – 7.51 (m, 6H), 7.46 (td, *J* = 8.1, 4.6 Hz, 1H), 7.32 – 7.27 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -116.80 (dd, *J* = 12.3, 4.6 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 153.7 (d, *J* = 258.5 Hz), 150.1 (d, *J* = 5.5 Hz), 138.6, 135.4 (d, *J* = 2.0 Hz), 133.2, 130.0, 129.9 (d, *J* = 64 Hz), 128.9, 128.5, 128.4, 127.8, 125.8 (d, *J* = 8.4 Hz), 123.2 (d, *J* = 4.3 Hz), 121.5, 119.4, 117.4, 116.9 (d, *J* = 1.6 Hz), 116.6 (d, *J* = 21.0 Hz), 115.9.

HRMS (ESI+) m/z calculated for $C_{21}H_{16}FN_2$ $[M+H]^+$: 313.1136, found $[M+H]^+$: 313.1136.

2-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ac)



Eluent: Hexane/EtOAc (50:1). Yellow solid (10 mg, 24% yield).

M.p. 147-148 ^{o}C.

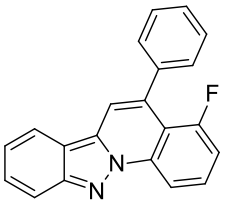
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.71 (dd, *J* = 9.7, 2.7 Hz, 1H), 8.06 (dt, *J* = 8.3, 1.1 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.91 (s, 1H), 7.63 – 7.49 (m, 6H), 7.33 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -108.08 (td, *J* = 9.0, 5.6 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 163.0 (d, *J* = 251.1 Hz), 149.6, 138.3, 135.5 (d, *J* = 1.5 Hz), 135.2 (d, *J* = 11.3 Hz), 132.3, 129.9, 129.7 (d, *J* = 9.4 Hz), 128.8, 128.4 (d, *J* = 15.8 Hz), 121.1, 121.0, 119.9, 116.8 (d, *J* = 27.5 Hz), 115.0, 114.9 (d, *J* = 2.5 Hz), 114.7, 103.7.

HRMS (ESI+) m/z calculated for $C_{21}H_{16}FN_2$ $[M+H]^+$: 313.1136, found $[M+H]^+$: 313.1135.

4-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ac')



Eluent: Hexane/EtOAc (50:1). Yellow solid (9 mg, 23% yield).

M.p. 158-159 ^{o}C.

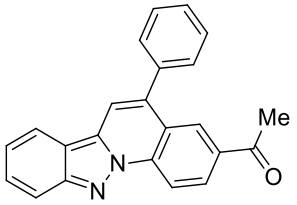
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.89 (dt, *J* = 8.6, 1.1 Hz, 1H), 8.04 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.98 (dt, *J* = 8.8, 0.9 Hz, 1H), 7.86 (s, 1H), 7.76 (td, *J* = 8.3, 5.2 Hz, 1H), 7.64 – 7.43 (m, 6H), 7.33 – 7.27 (m, 1H), 7.24 – 7.19 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -103.77 (dd, *J* = 12.2, 5.3 Hz).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 159.6 (d, *J* = 256.5 Hz), 149.8, 141.1 (d, *J* = 3.9 Hz), 135.4 (d, *J* = 5.5 Hz), 130.0 (d, *J* = 9.8 Hz), 128.9 (d, *J* = 3.9 Hz), 128.7, 128.0, 127.8, 121.4, 119.9, 118.2, 117.1, 116.9, 114.6 (d, *J* = 13.5 Hz), 113.8 (d, *J* = 4.1 Hz), 112.8 (d, *J* = 22.4 Hz).

HRMS (ESI+) m/z calculated for $C_{21}H_{16}FN_2$ $[M+H]^+$: 313.1136, found $[M+H]^+$: 313.1137.

1-(5-Phenylindazolo[2,3-*a*]quinolin-3-yl)ethan-1-one (4ad)



Eluent: Hexane/EtOAc (10:1). Yellow solid (13 mg, 34% yield).

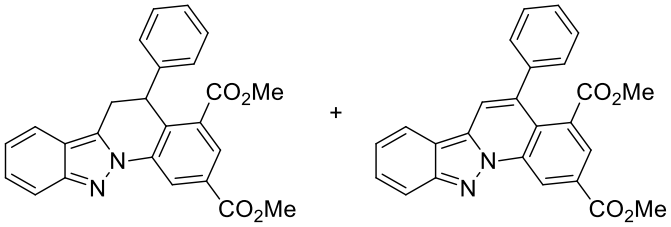
M.p. 196-197 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.08 (d, *J* = 8.8 Hz, 1H), 8.57 (d, *J* = 1.9 Hz, 1H), 8.36 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.07 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.99 – 7.96 (m, 2H), 7.67 – 7.52 (m, 6H), 7.33 – 7.25 (m, 1H), 2.63 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 197.2, 150.1, 138.1, 136.6, 136.1, 134.5, 132.7, 130.0, 129.1, 128.9, 128.7, 128.7, 128.6, 124.1, 121.5, 120.0, 118.1, 117.2, 117.0, 116.8, 26.8.

HRMS (ESI+) m/z calculated for $C_{23}H_{17}N_2O$ $[M+H]^+$: 337.1335, found $[M+H]^+$: 337.134.

Dimethyl 5-phenyl-5,6-dihydroindazolo[2,3-*a*]quinoline-2,4-dicarboxylate and dimethyl 5-phenylindazolo[2,3-*a*]quinoline-2,4-dicarboxylate (3ae and 4ae)



Eluent: Hexane/EtOAc (6:1). Yellow oil (27 mg, 44% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.87 (d, *J* = 1.9 Hz, 1H), 9.19 (d, *J* = 1.6 Hz, 1H), 8.57 (d, *J* = 1.9 Hz, 1H), 8.39 (d, *J* = 1.8 Hz, 1H), 8.13 – 8.03 (m, 2H), 8.01 (dt, *J* = 8.7, 0.9 Hz, 1H), 7.72 (dt, *J* = 8.9, 1.0 Hz, 1H), 7.60 (ddd, *J* = 8.8, 6.7, 1.1 Hz, 1H), 7.54 – 7.42 (m, 6H), 7.35 – 7.26 (m, 2H), 7.12 – 7.03 (m, 3H), 6.99 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1H), 6.88 – 6.80 (m, 2H), 5.70 (dd, *J* = 5.2, 3.2 Hz, 1H), 4.06 (s, 3H), 4.01 (s, 4H), 3.86 (s, 3H), 3.68 – 3.63 (m, 2H), 3.21 (s, 3H).

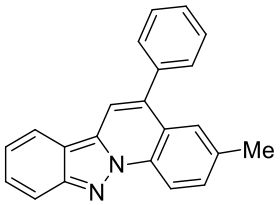
^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 168.3 (C=O), 166.1 (C=O), 165.4 (C=O), 165.4 (C=O), 149.8 (C), 149.6 (C), 141.6 (C), 140.3 (C), 137.8 (C), 136.1 (C), 134.8 (C), 133.9 (C), 133.1 (C), 131.8 (C), 130.5 (C), 130.4 (CH), 129.9 (C), 129.8 (C), 129.6 (C), 129.1 (C), 128.8 (2 x CH), 128.7 (2 x CH), 128.6 (2 x CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.0 (2 x CH), 126.9 (CH), 124.5 (C), 123.0

(CH), 121.8 (CH), 121.7 (CH), 121.7 (CH), 121.0 (CH), 120.9 (CH), 120.0 (CH), 119.7 (CH), 117.8 (CH), 117.2 (C), 117.0 (CH), 52.7 (CH_3), 52.6 (CH_3), 52.5 (CH_3), 52.2 (CH_3), 37.3 (CH), 28.4 (CH_2).

HRMS (ESI+) for **3ae** m/z calculated for $C_{25}H_{21}N_2O_4$ $[M+H]^+$: 413.1496, found $[M+H]^+$: 413.1493.

HRMS (ESI+) for **4ae** m/z calculated for $C_{25}H_{19}N_2O_4$ $[M+H]^+$: 411.1339, found $[M+H]^+$: 411.1340.

3-Methyl-5-phenylindazolo[2,3-*a*]quinoline (4af)



Eluent: Hexane/EtOAc (50:1). Yellow solid (20 mg, 39% yield).

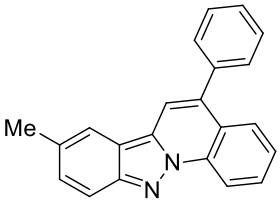
M.p. 180-181 ^oC.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.93 (d, *J* = 8.5 Hz, 1H), 8.05 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.97 (dt, *J* = 8.7, 1.0 Hz, 1H), 7.91 (s, 1H), 7.71 (s, 1H), 7.64 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.61 – 7.48 (m, 6H), 7.26 – 7.21 (m, 1H), 2.50 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.4, 138.9, 136.1, 135.7, 132.5, 131.7, 131.2, 130.0, 128.8, 128.2, 128.1, 126.8, 124.6, 120.7, 119.8, 117.5, 117.2, 116.6, 115.9, 21.7.

HRMS (ESI+) m/z calculated for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1386, found $[M+H]^+$: 309.1389.

8-Methyl-5-phenylindazolo[2,3-*a*]quinoline (4ah)



Eluent: Hexane/EtOAc (50:1). Yellow solid (24 mg, 41% yield).

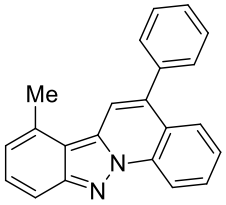
M.p. 140-141 ^oC.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.01 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.94 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.90 – 7.88 (m, 2H), 7.85 – 7.75 (m, 2H), 7.63 – 7.48 (m, 6H), 7.41 (dd, *J* = 8.8, 1.7 Hz, 1H), 2.55 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 148.3, 138.7, 135.2, 134.2, 131.3, 130.9, 130.3, 129.9, 129.3, 128.6, 128.1, 127.3, 125.8, 124.4, 118.2, 117.4, 117.2, 116.4, 115.8, 21.9.

HRMS (ESI+) m/z calculated for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1386, found $[M+H]^+$: 309.1387.

7-Methyl-5-phenylindazolo[2,3-*a*]quinoline (4ai)



Eluent: Hexane/EtOAc (50:1). Yellow solid (23 mg, 46% yield).

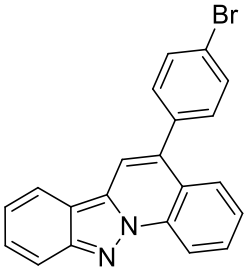
M.p. 148-149 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.06 (d, *J* = 8.5 Hz, 1H), 8.04 (s, 1H), 7.97 – 7.88 (m, 1H), 7.88 – 7.75 (m, 2H), 7.65 – 7.50 (m, 6H), 7.46 (ddd, *J* = 8.4, 6.8, 1.1 Hz, 1H), 7.05 – 6.96 (m, 1H), 2.86 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.7, 139.0, 135.7, 134.2, 132.5, 132.1, 130.1, 129.5, 128.8, 128.3, 127.3, 126.0, 124.1, 121.4, 117.7, 117.5, 116.9, 114.4, 20.6.

HRMS (ESI+) m/z calculated for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1386, found $[M+H]^+$: 309.1396.

5-(4-Bromophenyl)indazolo[2,3-*a*]quinoline (4aj)



Eluent: Hexane/ EtOAc (60:1) Brown solid (3 mg, 15 % yield).

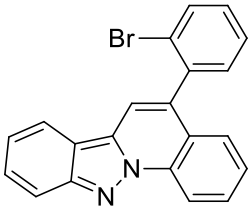
M.p. 126-127 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.99 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.93 (s, 1H), 7.89 (d, *J* = 8.3 H, 1H), 7.85 – 7.81 (m, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 7.7, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.6, 137.6, 134.5, 134.3, 132.0, 131.9, 131.7, 129.8, 128.4, 127.1, 126.3, 124.3, 122.6, 121.1, 119.9, 117.8, 117.2, 116.9, 115.9.

HRMS (ESI+) m/z calculated for $C_{21}H_{13}BrN_2$ $[M+H]^+$: 373.0340, found $[M+H]^+$: 373.0331

5-(2-Bromophenyl)indazolo[2,3-*a*]quinoline (4ak)



Eluent: Hexane/ EtOAc (85:1). Brown solid (8 mg, 16 % yield).

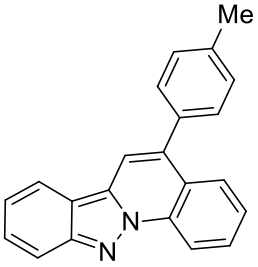
M.p. 147-148 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.05 (d, *J* = 8.5 Hz, 1H), 8.07 (dt, *J* = 8.2, 1.1 Hz, 1H), 8.00 (dt, *J* = 8.8, 1.0 Hz, 1H), 7.92 (s, 1H), 7.84 – 7.79 (m, 2H), 7.60 – 7.56 (m, 1H), 7.52 (td, *J* = 5.8, 1.2 Hz, 3H), 7.49 – 7.48 (m, 1H), 7.42 – 7.37 (m, 1H), 7.30 – 7.26 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.6, 139.3, 134.8, 134.1, 133.2, 132.1, 131.8, 130.1, 129.7, 128.3, 127.7, 127.4, 126.2, 124.5, 124.4, 121.1, 119.9, 117.6, 117.3, 116.9, 116.5.

HRMS (ESI+) m/z calculated for $C_{21}H_{13}BrN_2$ $[M+H]^+$: 373.03349, found $[M+H]^+$: 373.03419.

5-(*p*-Tolyl)indazolo[2,3-*a*]quinoline (4al)



Eluent: Hexane/ EtOAc (60:1). Yellow solid (13 mg, 26 % yield).

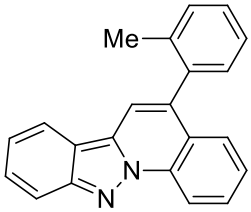
M.p. 138-139 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.05 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.07 (dt, *J* = 8.3, 1.1 Hz, 1H), 8.00 – 7.96 (m, 2H), 7.93 (s, 1H), 7.84 – 7.79 (m, 1H), 7.59 – 7.47 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.26 (dt, *J* = 8.3, 1.1, 1H), 2.50 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 149.6, 138.2, 136.0, 135.8, 134.3, 132.1, 129.9, 129.5, 29.5, 128.3, 127.5, 126.1, 124.7, 120.8, 119.9, 117.6, 117.1, 116.7, 115.7, 21.5.

HRMS (ESI+) m/z calculated for $C_{22}H_{16}N_2$ $[M+H]^+$: 309.13862, found $[M+H]^+$: 309.13987.

5-(*o*-Tolyl)indazolo[2,3-*a*]quinoline (4am)



Eluent: Hexane/ EtOAc (80:1). Yellow solid (7 mg, 20 % yield).

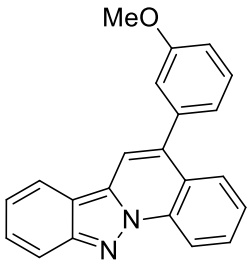
M.p. 137-138 ^{o}C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 8.5 Hz, 1H), 8.60 (dt, *J* = 8.3, 1.1 Hz, 1H), 8.00 (dt, *J* = 8.8, 1.0 Hz, 1H), 7.89 (s, 1H), 7.80 (dt, *J* = 8.5, 4.2 Hz, 1H), 7.89 (s, 1H), 7.83 – 7.78 (m, 1H), 7.57 (ddd, *J* = 8.7, 6.7, 1.1 Hz, 1H), 7.51 – 7.50 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 –7.34 (m, 2H), 7.28 – 7.24 (m, 1H), 2.13 (s, 3H)

.^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 149.6, 138.1, 137.1, 135.7, 134.1, 132.1, 130.4, 130.4, 129.6, 128.6, 128.3, 127.5, 126.2, 126.1, 125.0, 120.9, 119.9, 117.5, 117.0, 116.8, 115.8, 20.3.

HRMS (ESI+) m/z calculated for $C_{22}H_{16}N_2$ $[M+H]^+$: 309.13862, found $[M+H]^+$: 309.13965.

5-(3-Methoxyphenyl)indazolo[2,3-*a*]quinoline (4an)



Eluent: Hexane/ EtOAc (80:1). Yellow solid (9 mg, 24 % yield).

M.p. 142-143 ^{o}C.

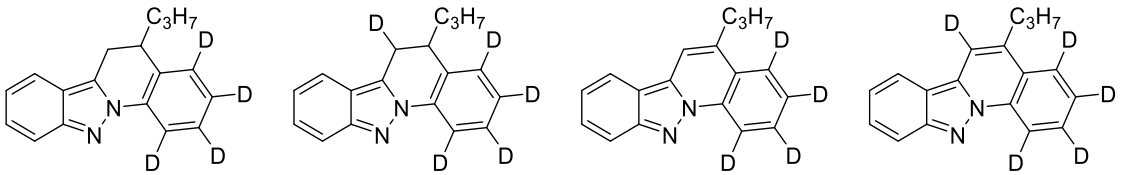
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 9.05 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.08, (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.96 (s, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.48 (t, *J* = 7.9 Hz, 1H),

7.28 – 7.25 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 2.1 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.90 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) 159.9, 149.6, 140.1, 135.8, 134.3, 132.0, 129.8, 129.6, 128.3, 127.5, 126.2, 124.6, 122.5, 120.9, 119.5, 117.6, 117.2, 116.8, 115.8, 115.7, 113.8, 55.6.

HRMS (ESI+) m/z calculated for $C_{22}H_{16}N_2O$ $[M+H]^+$: 325.1341, found $[M+H]^+$: 325.1334.

5-Propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-1,2,3,4-*d*$_4$, 5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-1,2,3,4,6-*d*$_5$, 5-propylindazolo[2,3-*a*]quinoline-1,2,3,4-*d*$_4$ and 5-propylindazolo[2,3-*a*]quinoline-1,2,3,4,6-*d*$_5$ (3a-*d*$_4$, 3a-*d*$_5$, 4a-*d*$_4$ and 4a-*d*$_5$)



Eluent: Hexane/EtOAc (50:1). The mixture was isolated as a yellow solid (17 mg, 45% yield).

M.p. 149-150 ^{o}C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J* = 8.3 Hz), 7.94 (d, *J* = 8.7 Hz), 7.81 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.22 (t, *J* = 7.4 Hz), 7.06 (t, *J* = 7.6 Hz), 3.39 – 3.27 (m), 3.12 – 3.05 (m), 1.89 (sext, *J* = 7.4 Hz), 1.53 – 1.40 (m), 1.42 – 1.26 (m), 1.11 (t, *J* = 7.4 Hz), 0.85 (t, *J* = 6.9 Hz).

^{13}C-NMR (126 MHz, $CDCl_3$) δ (ppm) 149.4 (C), 134.8 (C), 132.3 (C), 128.1 (CH), 127.2 (CH), 124.8 (C), 121.3 (CH), 120.4 (CH), 120.0 (CH), 119.9 (CH), 117.9 (CH), 116.5 (CH), 114.4 (CH), 36.7 (CH_2), 35.8 (CH), 34.8 (CH_2), 25.7 (CH_2), 23.2 (CH_2), 20.3 (CH_2), 14.3 (CH_3), 14.1 (CH_3). *C coupled with deuterium are not observed.

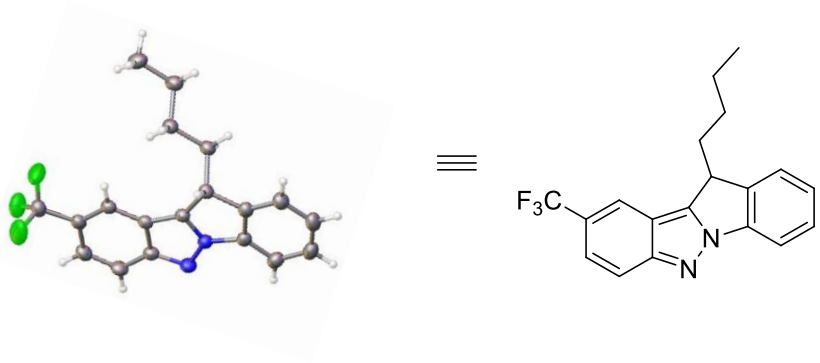
HRMS (ESI+) for **3a-*d*$_4$**: m/z calculated for $C_{18}H_{15}D_4N_2$ $[M+H]^+$: 266.1721, found $[M+H]^+$: 266.1722.

HRMS (ESI+) for **3a-*d*$_5$**: m/z calculated for $C_{18}H_{14}D_5N_2$ $[M+H]^+$: 267.1784, found $[M+H]^+$: 267.1785.

HRMS (ESI+) for **4a-*d*$_4$**: m/z calculated for $C_{18}H_{13}D_4N_2$ $[M+H]^+$: 264.1565, found $[M+H]^+$: 264.1569.

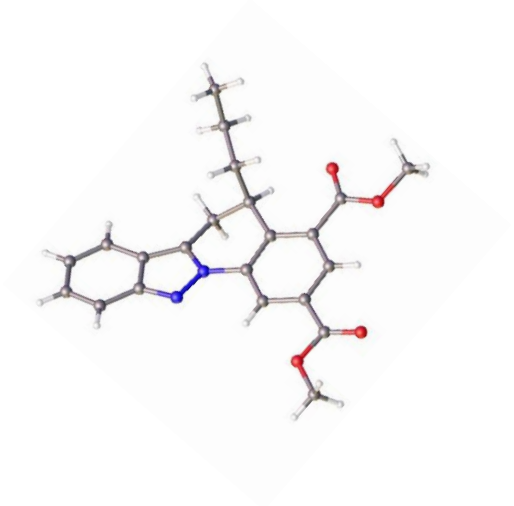
HRMS (ESI+) for **4a-*d*$_5$**: m/z calculated for $C_{18}H_{12}D_5N_2$ $[M+H]^+$: 265.1627, found $[M+H]^+$: 264.1569.

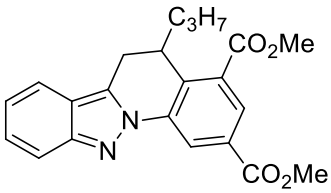
X-Ray crystallographic data



X-Ray Crystallographic Data for **2s** (CCDC 2374941)

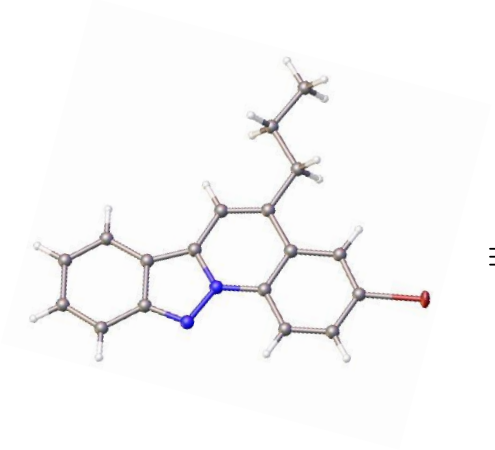
Empirical formula	$C_{19}H_{17}F_3N_2$
Formula weight	330.34
Temperature/K	220.0
Crystal system	triclinic
Space group	P-1
a/Å	8.541(10)
b/Å	10.615(6)
c/Å	10.654(8)
α/°	119.18(5)
β/°	95.86(5)
γ/°	104.41(7)
Volume/Å^3	787.8(13)
Z	2
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	0.904
F(000)	344.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.684 to 144.632
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	20367
Independent reflections	2954 [R_{int} = 0.0362, R_{sigma} = 0.0243]
Data/restraints/parameters	2954/0/219
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1266
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.1286
Largest diff. peak/hole / e Å^{-3}	0.24/-0.26

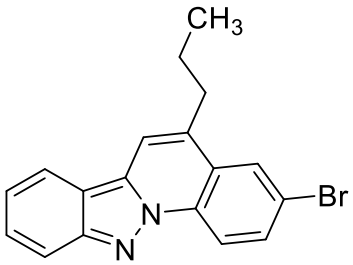




X-Ray Crystallographic Data for **3j** (CCDC 2374943)

Empirical formula	$C_{22}H_{22}N_2O_4$
Formula weight	378.41
Temperature/K	299.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3106(4)
b/Å	27.0052(10)
c/Å	7.1569(3)
α/°	90
β/°	104.419(3)
γ/°	90
Volume/Å^3	1929.99(13)
Z	4
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.737
F(000)	800.0
Crystal size/mm^3	0.08 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	11.02 to 144.544
Index ranges	-12 ≤ h ≤ 12, -33 ≤ k ≤ 33, -8 ≤ l ≤ 8
Reflections collected	25657
Independent reflections	3793 [R_{int} = 0.0659, R_{sigma} = 0.0363]
Data/restraints/parameters	3793/0/256
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1527
Final R indexes [all data]	R_1 = 0.1014, wR_2 = 0.1999
Largest diff. peak/hole / e Å^{-3}	0.28/-0.18





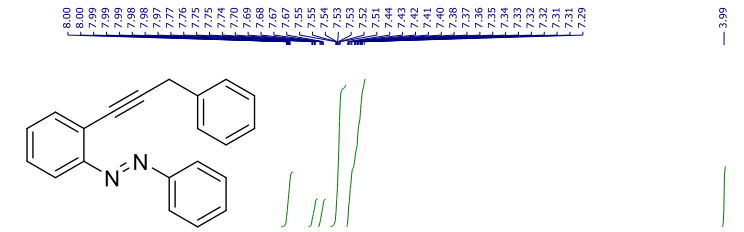
X-Ray Crystallographic Data for **4b** (CCDC 2374942)

Empirical formula	$C_{18}H_{15}BrN_2$
Formula weight	339.23
Temperature/K	240.0
Crystal system	triclinic
Space group	P-1
a/Å	7.6346(5)
b/Å	9.5012(7)
c/Å	10.3414(7)
α/°	87.704(2)
β/°	75.290(2)
γ/°	89.836(3)
Volume/Å^3	724.95(9)
Z	2
ρ_{calc}g/cm^3	1.554
μ/mm^{-1}	3.800
F(000)	344.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.848 to 145.512
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12
Reflections collected	9760
Independent reflections	2778 [R_{int} = 0.0610, R_{sigma} = 0.0537]
Data/restraints/parameters	2778/0/191
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1774
Final R indexes [all data]	R_1 = 0.0719, wR_2 = 0.1819
Largest diff. peak/hole / e Å^{-3}	1.45/-1.27

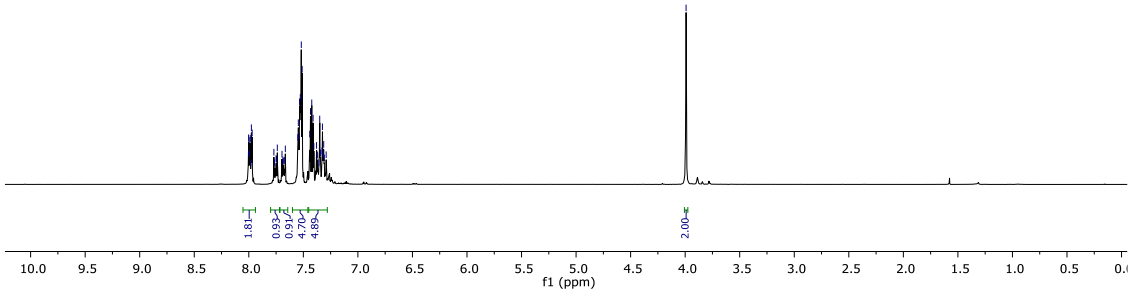
NMR spectra

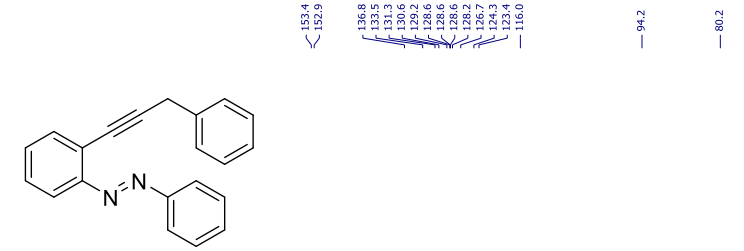
2-Alkynylazobenzenes 1

(*E*)-1-Phenyl-2-(2-(3-phenylprop-1-yn-1-yl)phenyl)diazene (1aa)

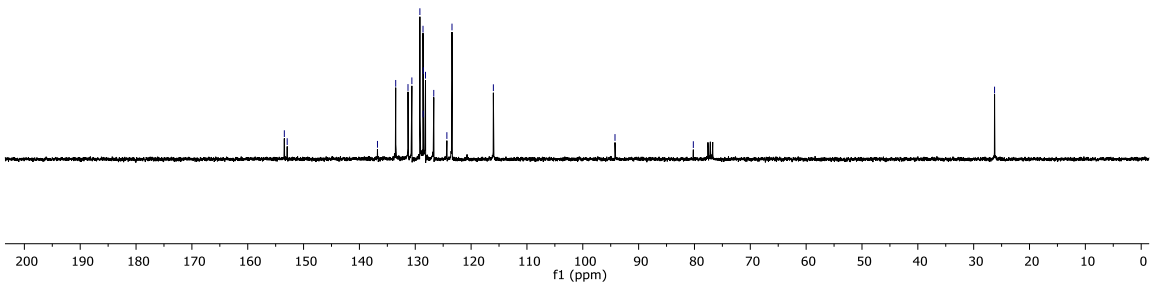


^{1}H-NMR (300 MHz, $CDCl_3$)

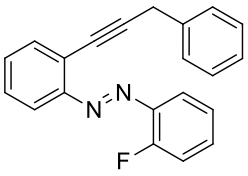




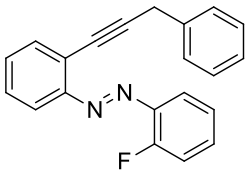
^{13}C-NMR (75 MHz, $CDCl_3$)



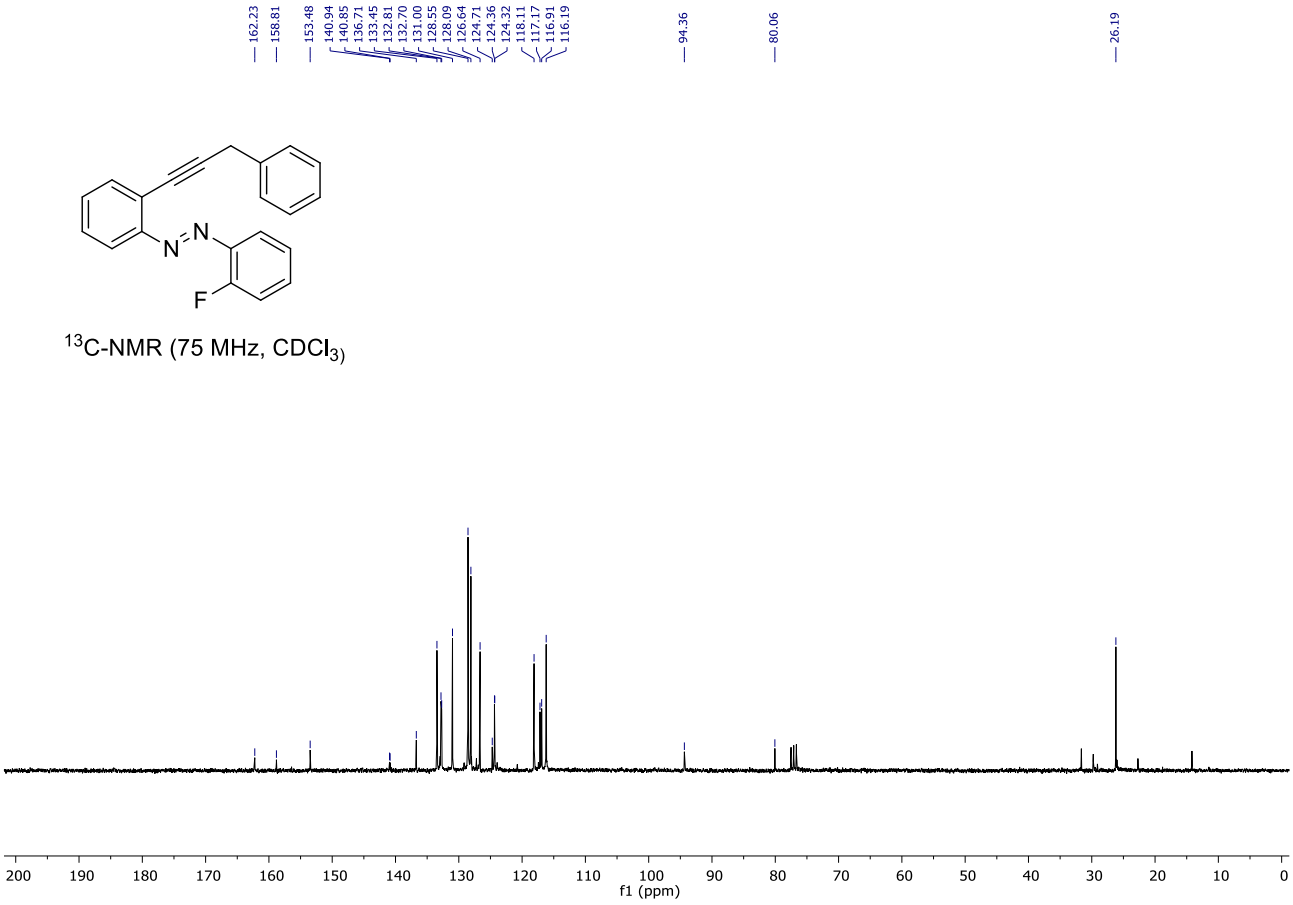
(*E*)-1-(2-Fluorophenyl)-2-(2-(3-phenylprop-1-yn-1-yl)phenyl)diazene (1ab)



^{1}H-NMR (300 MHz, $CDCl_3$)

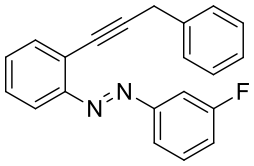


^{19}F-NMR (282 MHz, $CDCl_3$)

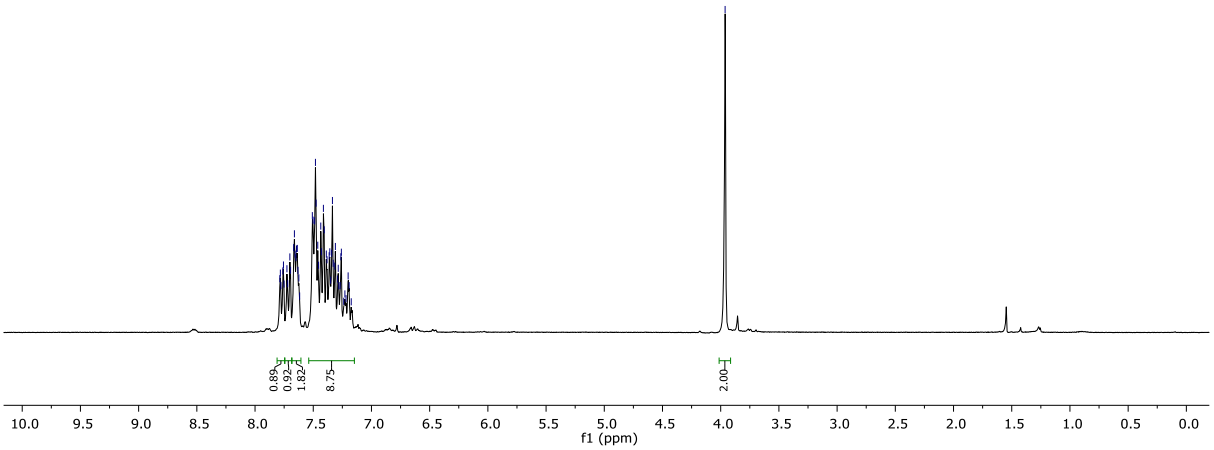


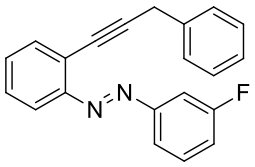
^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-1-(3-Fluorophenyl)-2-[2-(3-phenylprop-1-yn-1-yl)phenyl]diazene (1ac)

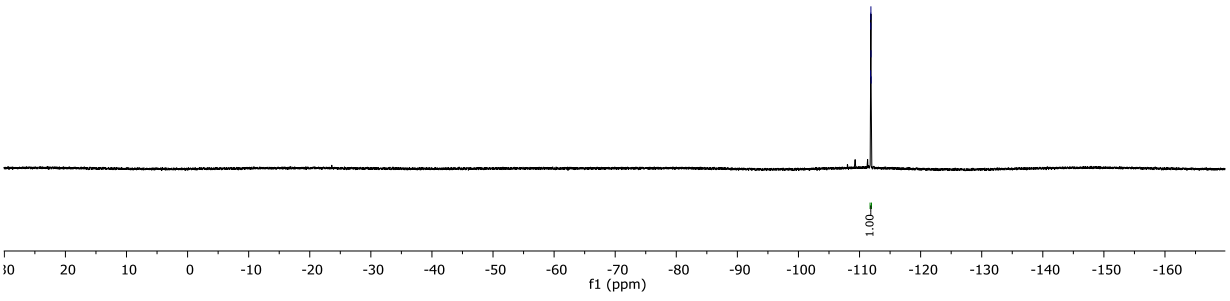


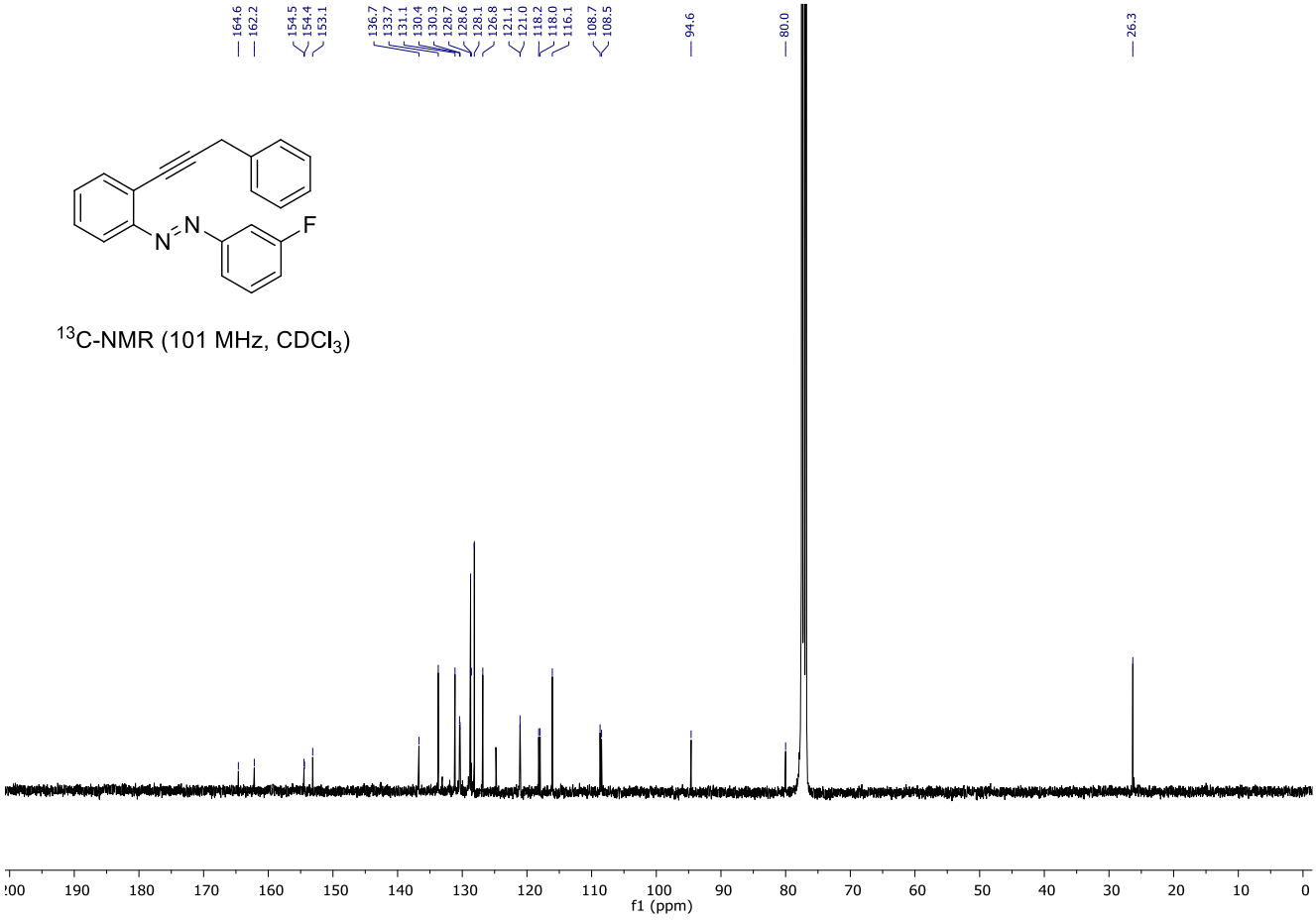
^{1}H-NMR (300 MHz, $CDCl_3$)





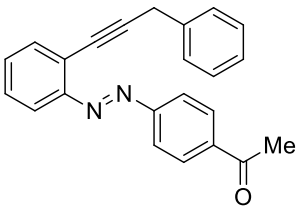
^{19}F-NMR (282 MHz, $CDCl_3$)



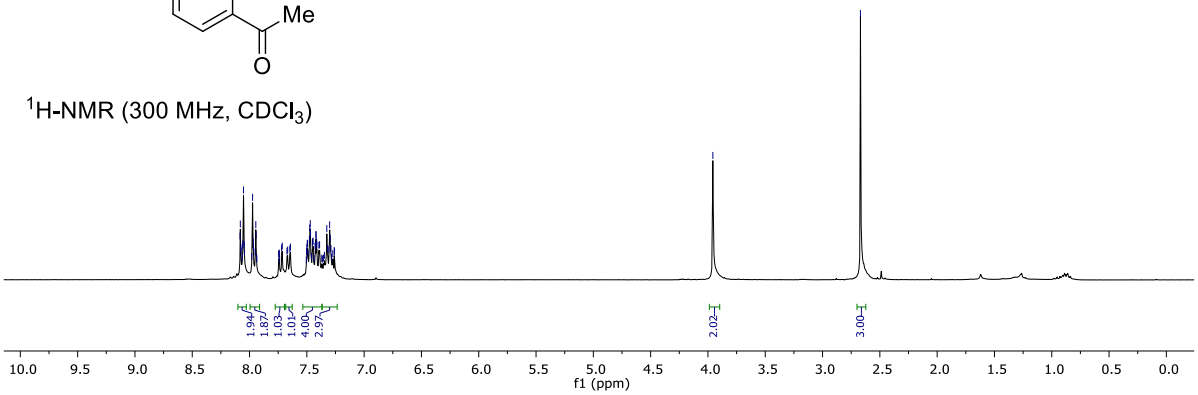


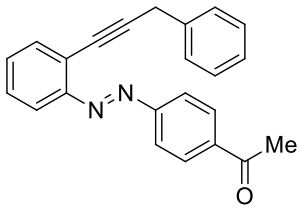
^{13}C-NMR (101 MHz, $CDCl_3$)

(*E*)-1-[4-((2-(3-Phenylprop-1-yn-1-yl)phenyl)diazenyl)phenyl]ethan-1-one (1ad)

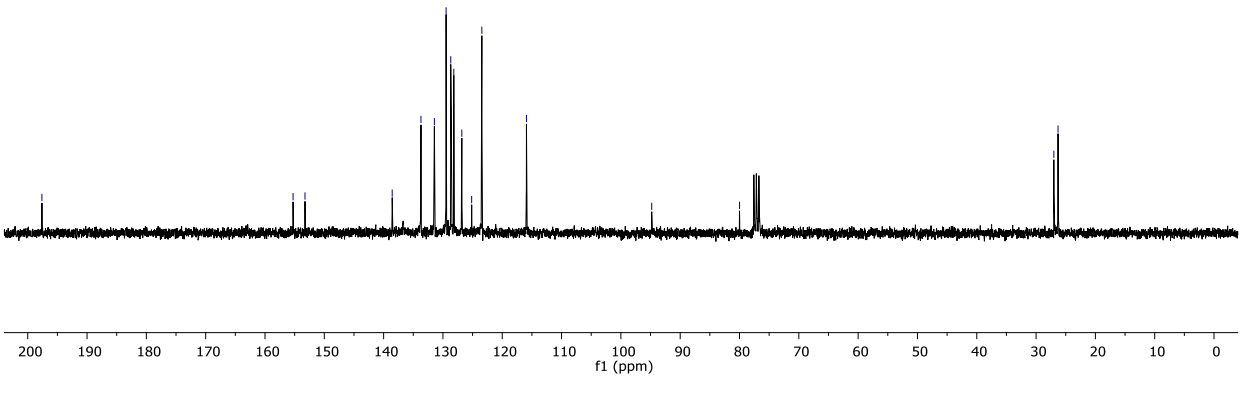


^{1}H-NMR (300 MHz, $CDCl_3$)

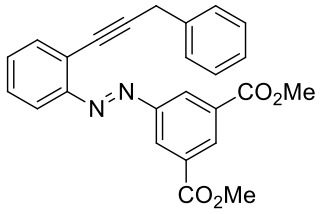




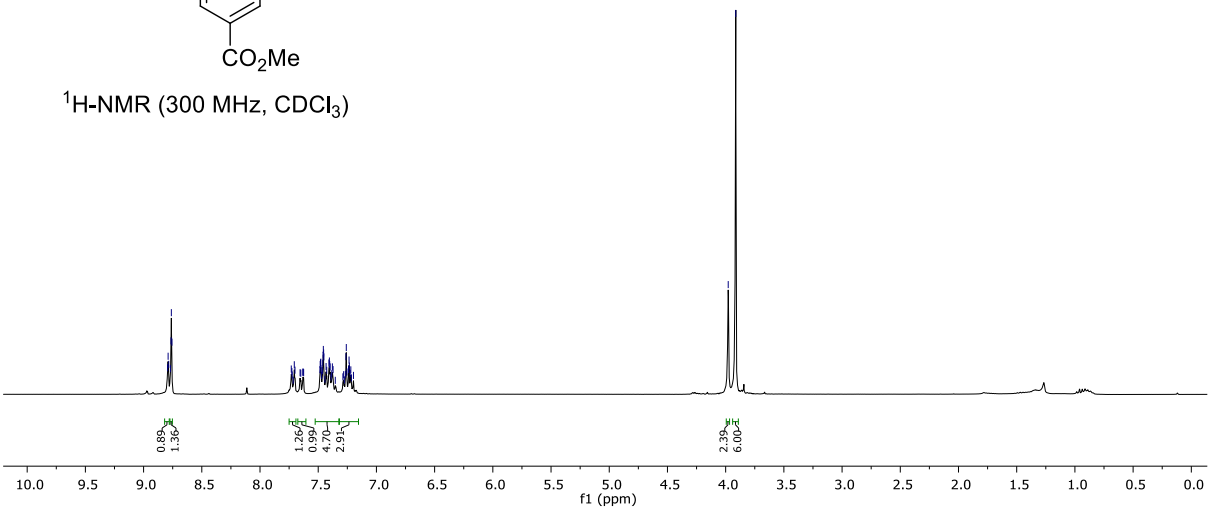
^{13}C-NMR (75 MHz, $CDCl_3$)

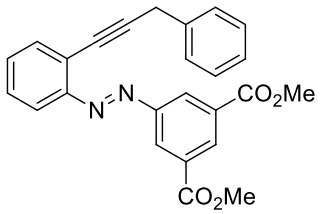


(*E*)-Dimethyl 5-((2-(3-phenylprop-1-yn-1-yl)phenyl)diazenyl)isophthalate (1ae)

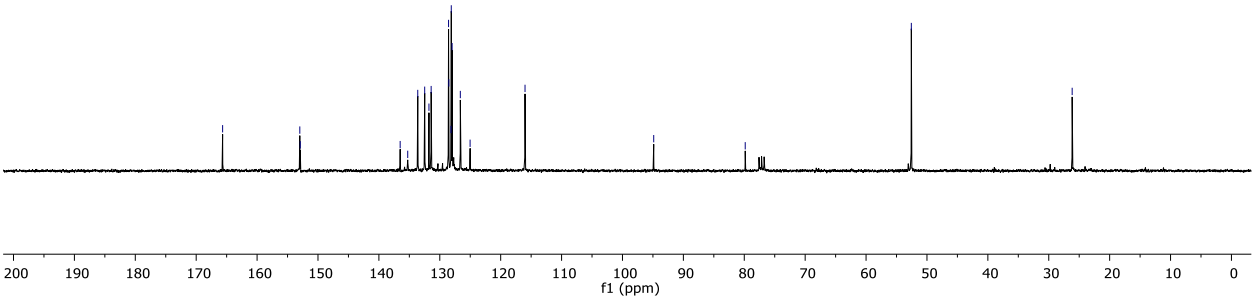


^{1}H-NMR (300 MHz, $CDCl_3$)

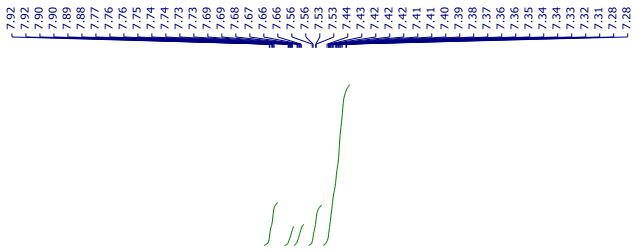


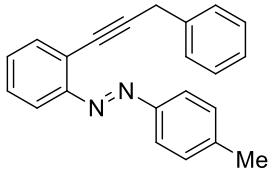


^{13}C-NMR (75 MHz, $CDCl_3$)

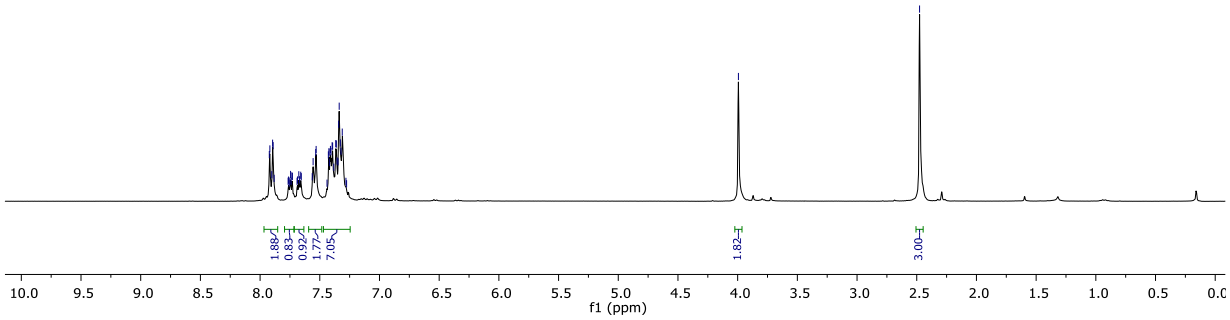


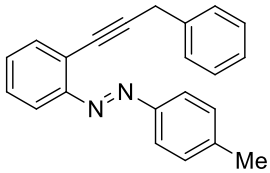
(*E*)-1-[2-(3-Phenylprop-1-yn-1-yl)phenyl]-2-(*p*-tolyl)diazene (1af)



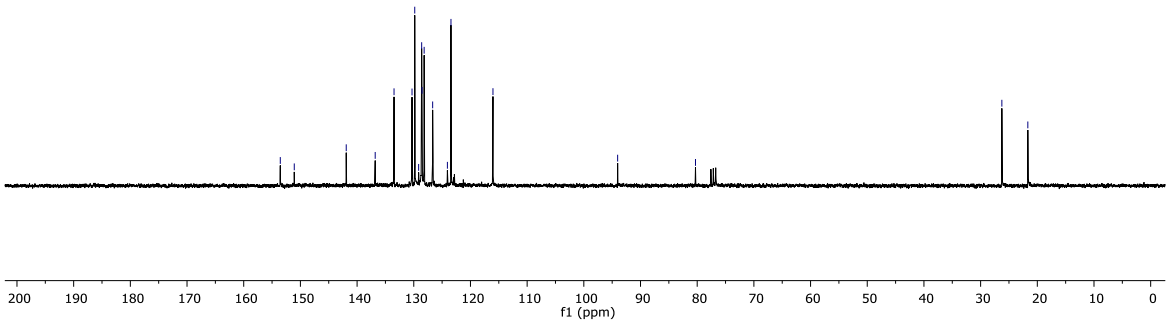


^{1}H-NMR (300 MHz, $CDCl_3$)

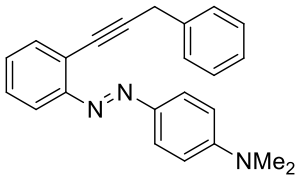




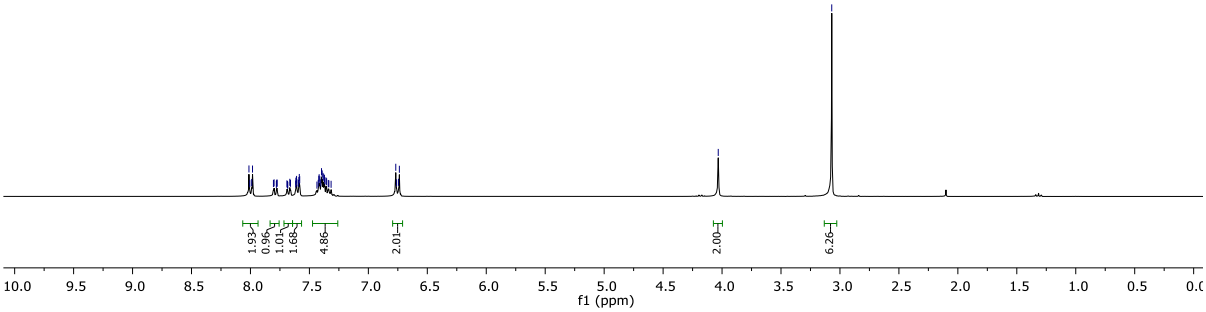
^{13}C-NMR (75 MHz, $CDCl_3$)

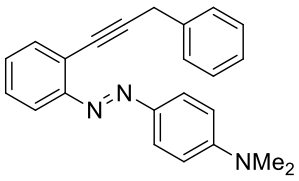


(*E*)-*N*,*N*-dimethyl-4-((2-(3-phenylprop-1-yn-1-yl)phenyl)diazenyl)aniline (1ag)

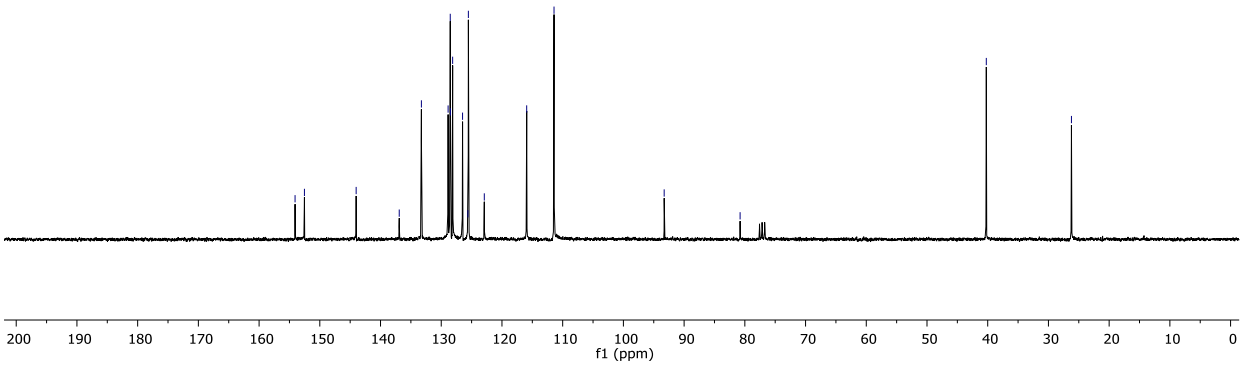


^{1}H-NMR (300 MHz, $CDCl_3$)

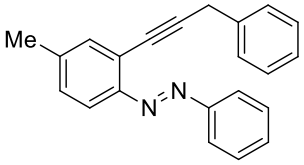




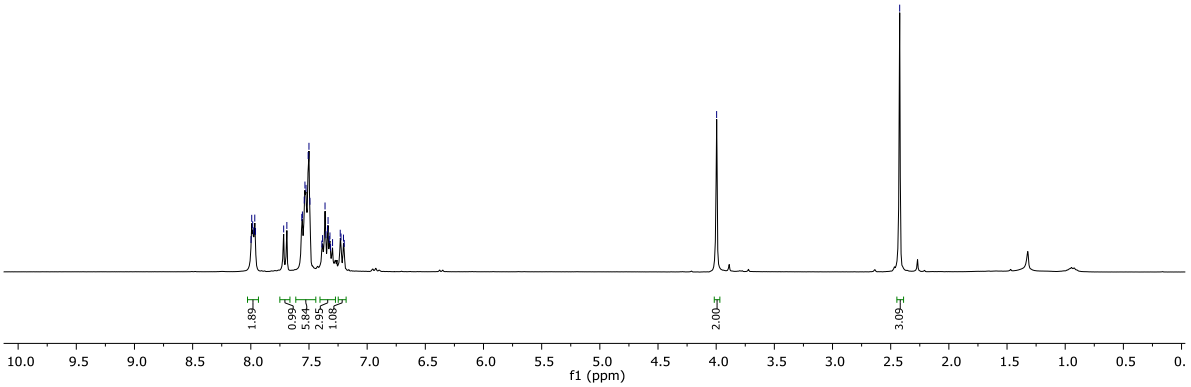
^{13}C-NMR (75 MHz, $CDCl_3$)

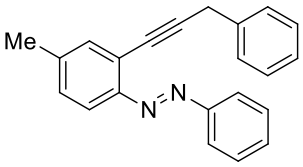


(*E*)-1-(4-Methyl-2-(3-phenylprop-1-yn-1-yl)phenyl)-2-phenyldiazene (1ah)

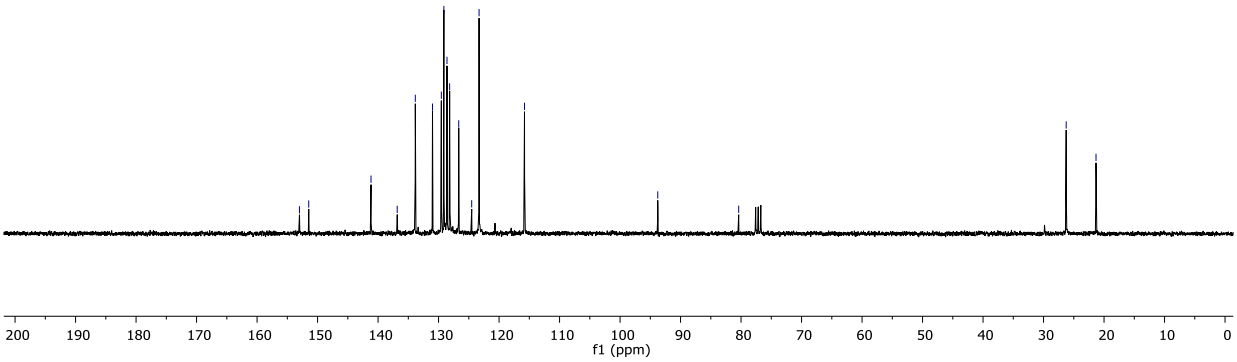


^{1}H-NMR (300 MHz, $CDCl_3$)

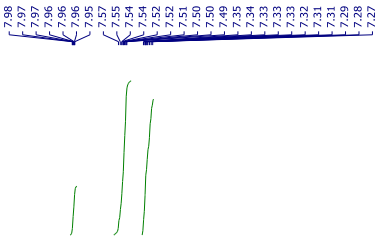


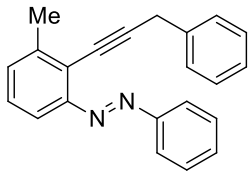


^{13}C-NMR (75 MHz, $CDCl_3$)

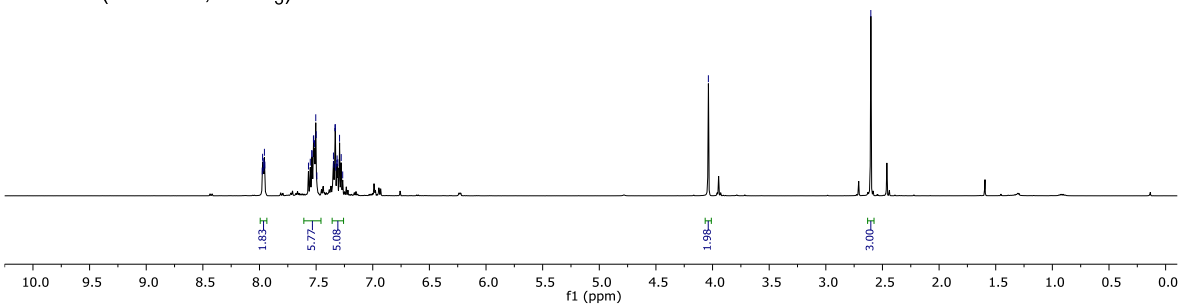


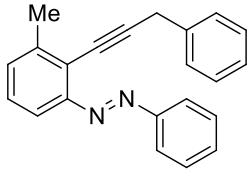
(*E*)-1-[3-Methyl-2-(3-phenylprop-1-yn-1-yl)phenyl]-2-phenyldiazene (1ai)



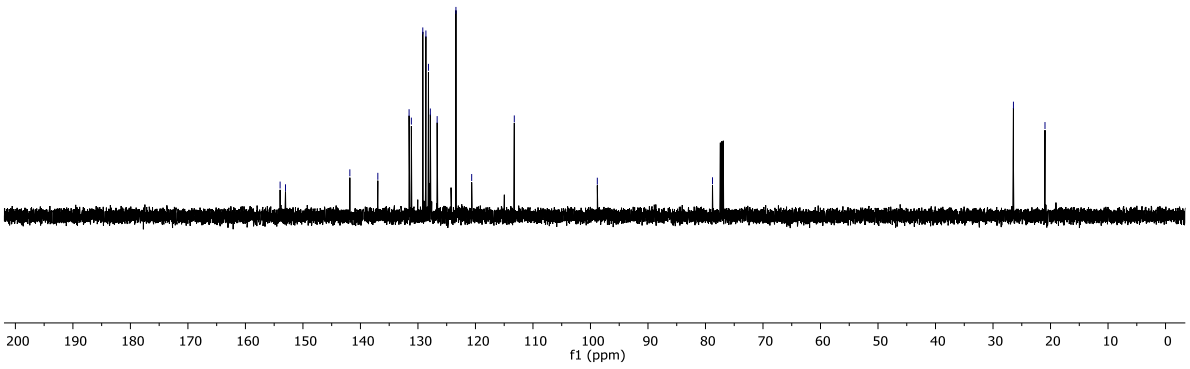


^{1}H-NMR (300 MHz, $CDCl_3$)

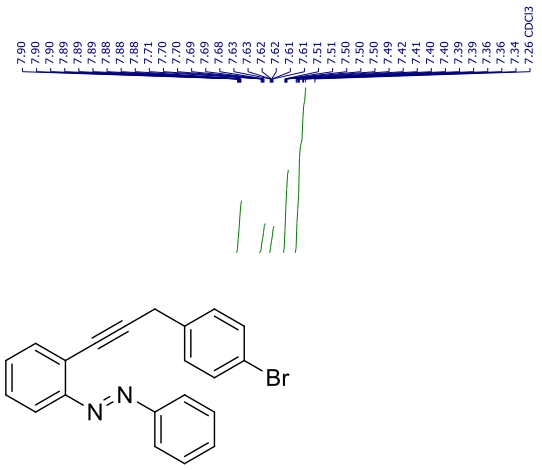




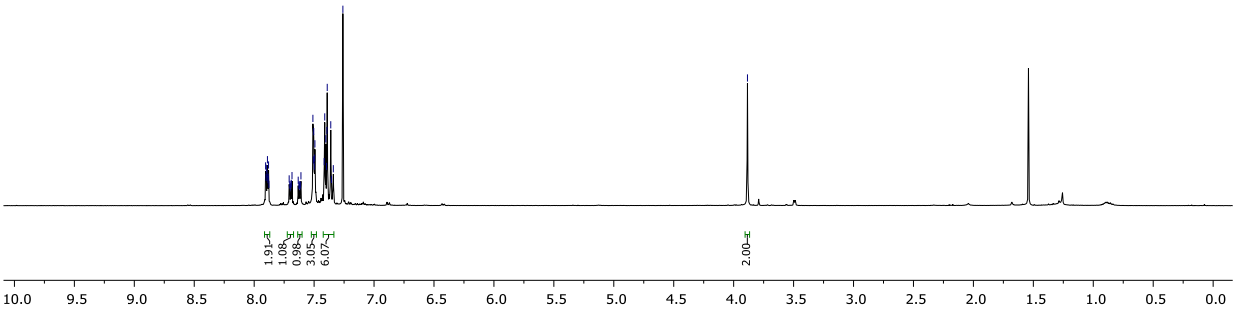
^{13}C-NMR (75 MHz, $CDCl_3$)

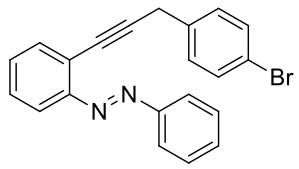


(*E*)-1-[2-(3-(4-Bromophenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1aj)



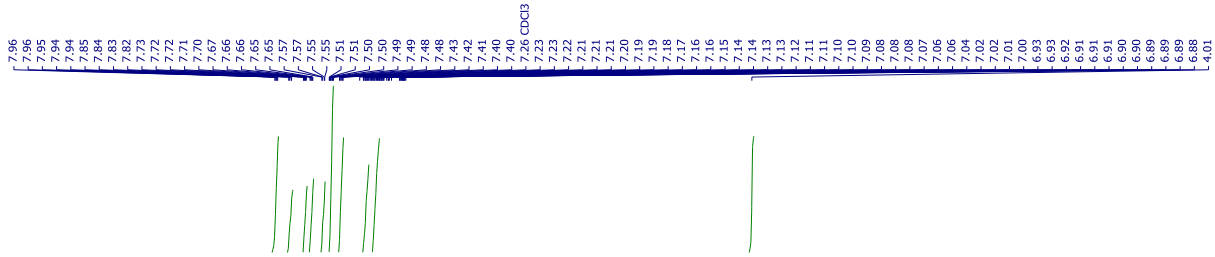
^{1}H-NMR (400 MHz, $CDCl_3$)

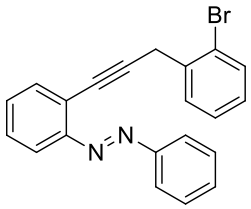




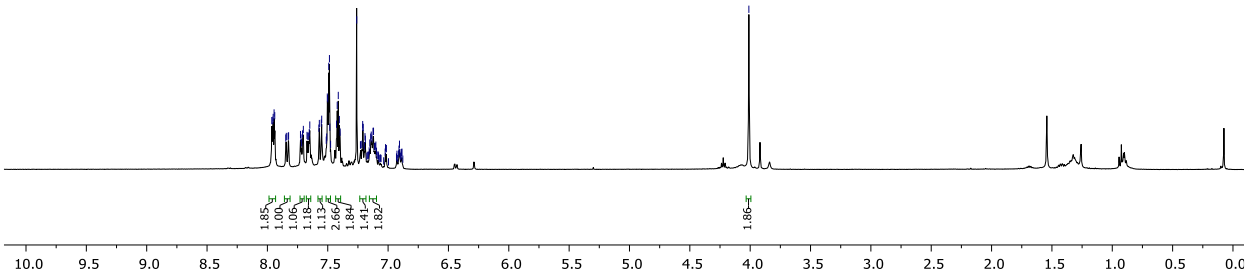
^{13}C-NMR (101 MHz, $CDCl_3$)

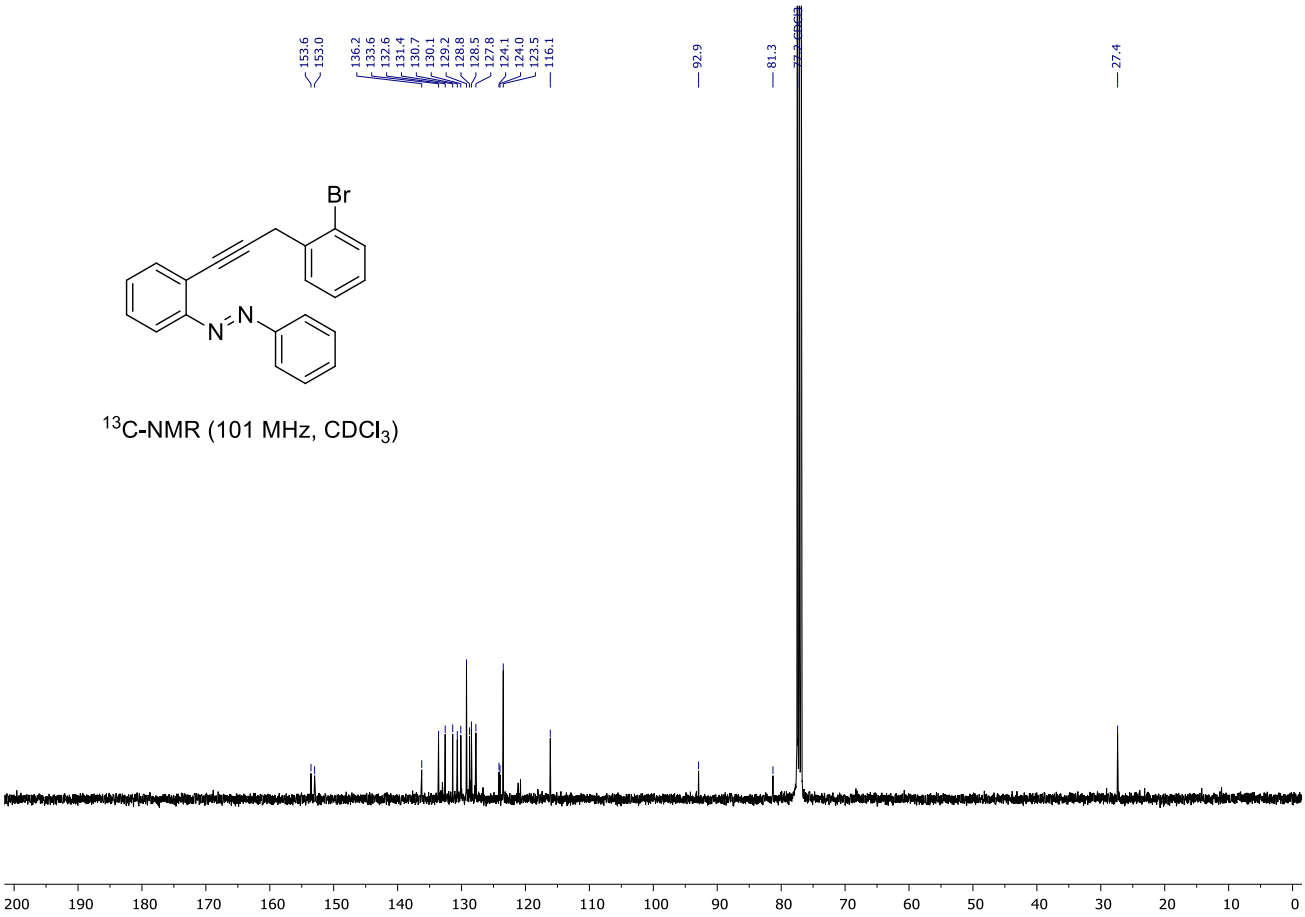
(*E*)-1-[2-(3-(2-bromophenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1ak)





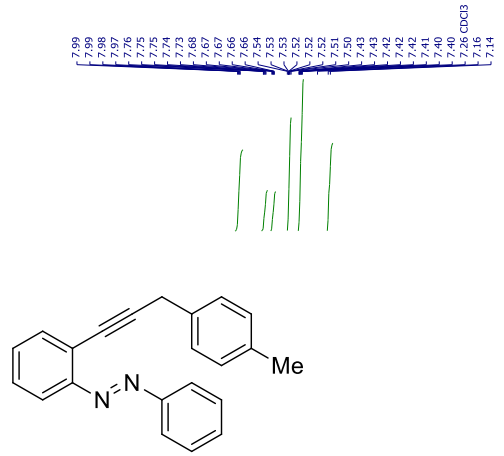
^{1}H-NMR (400 MHz, $CDCl_3$)



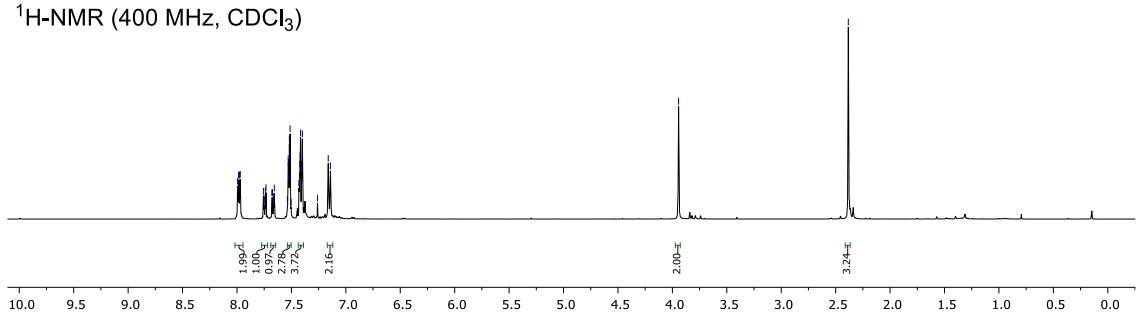


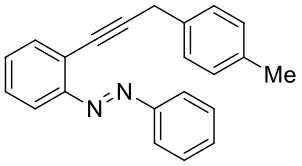
^{13}C-NMR (101 MHz, $CDCl_3$)

(*E*)-1-Phenyl-2-[2-(3-(*p*-tolyl)prop-1-yn-1-yl)phenyl]diazene (1al)

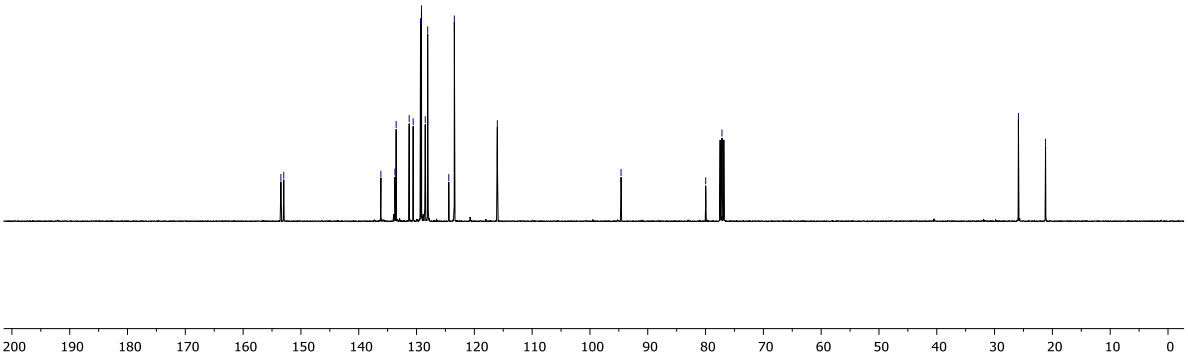


^{1}H-NMR (400 MHz, $CDCl_3$)

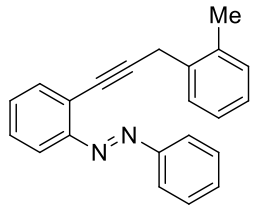




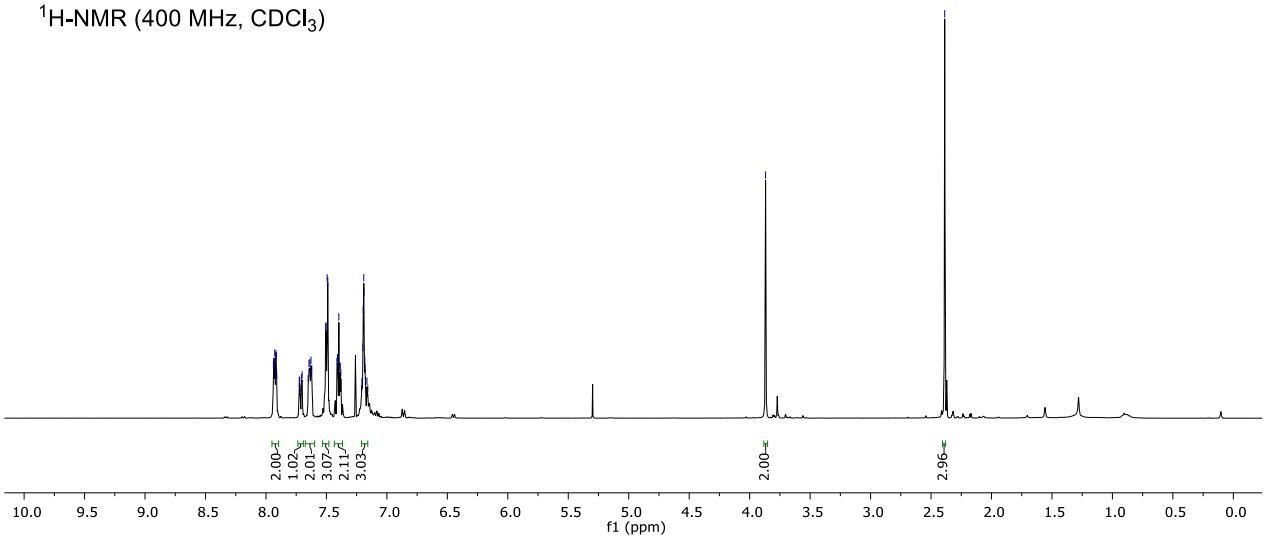
^{13}C-NMR (101 MHz, $CDCl_3$)

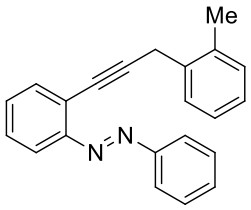


(*E*)-1-Phenyl-2-[2-(3-(*o*-tolyl)prop-1-yn-1-yl)phenyl]diazene (1am)

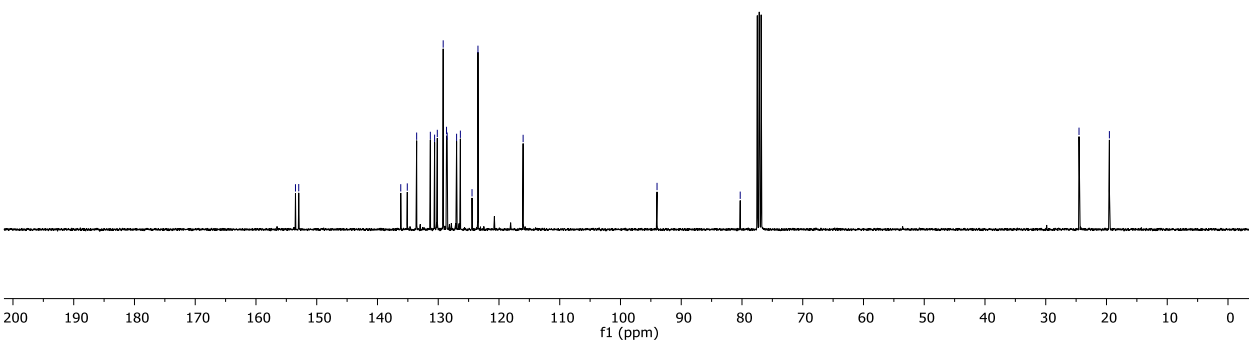


^{1}H-NMR (400 MHz, $CDCl_3$)

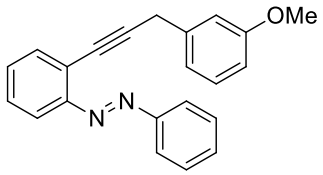




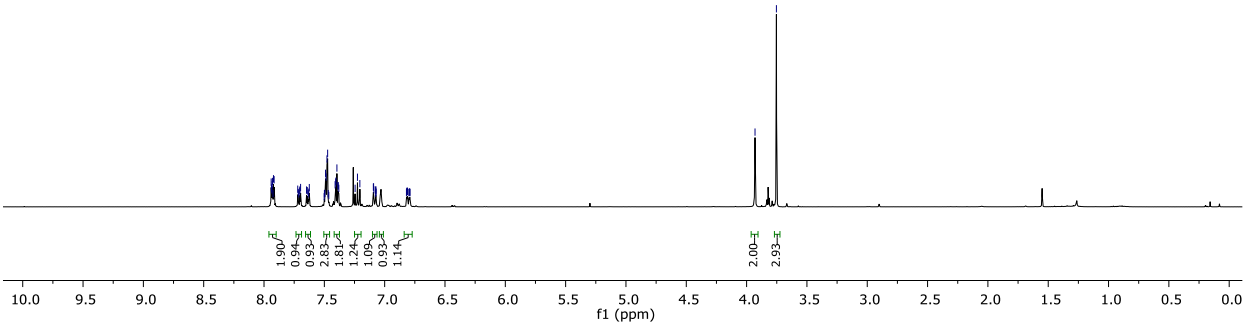
^{13}C-NMR (101 MHz, $CDCl_3$)

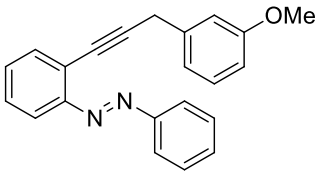


(*E*)-1-[2-(3-(3-Methoxyphenyl)prop-1-yn-1-yl)phenyl]-2-phenyldiazene (1an)

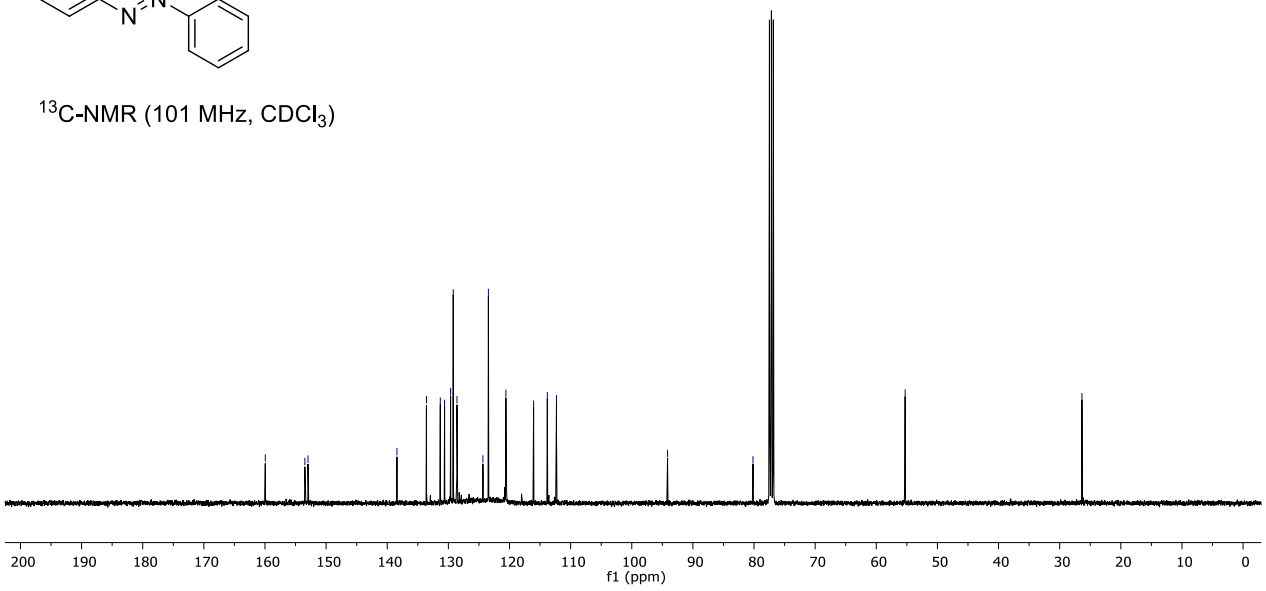


^{1}H-NMR (400 MHz, $CDCl_3$)



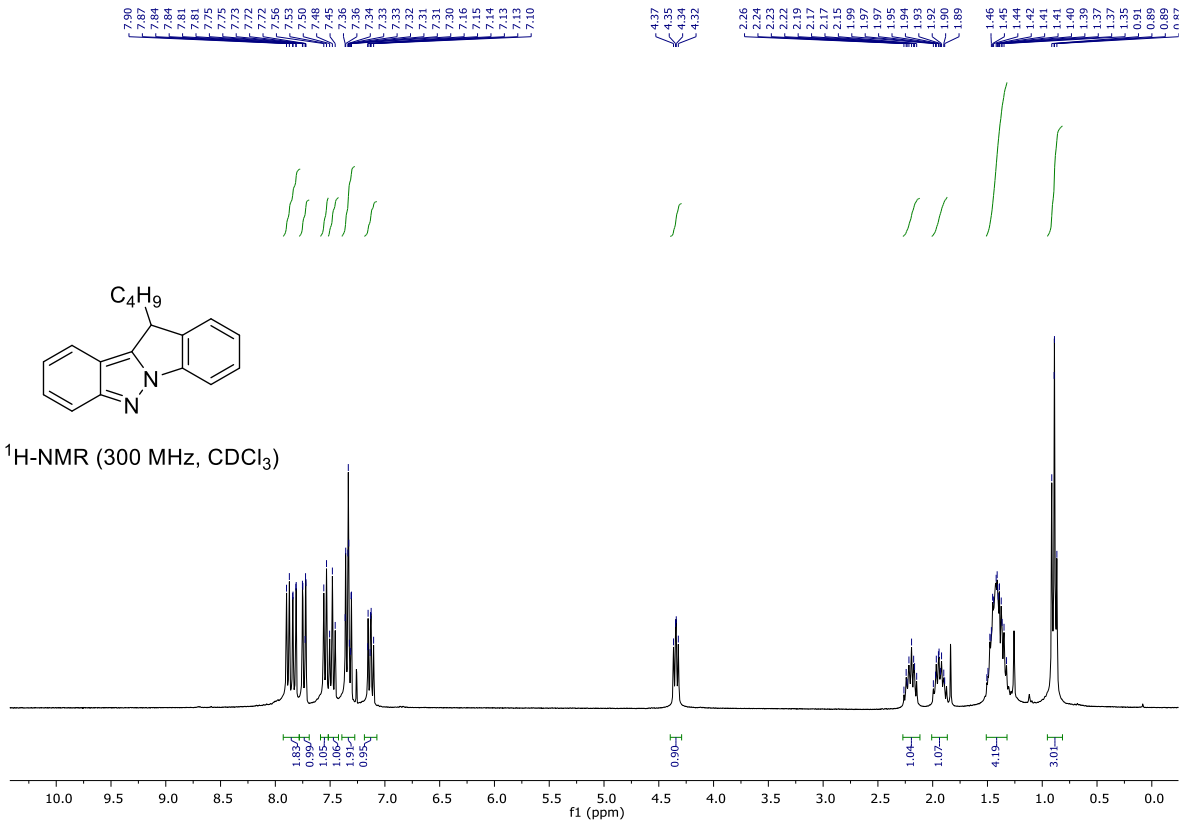


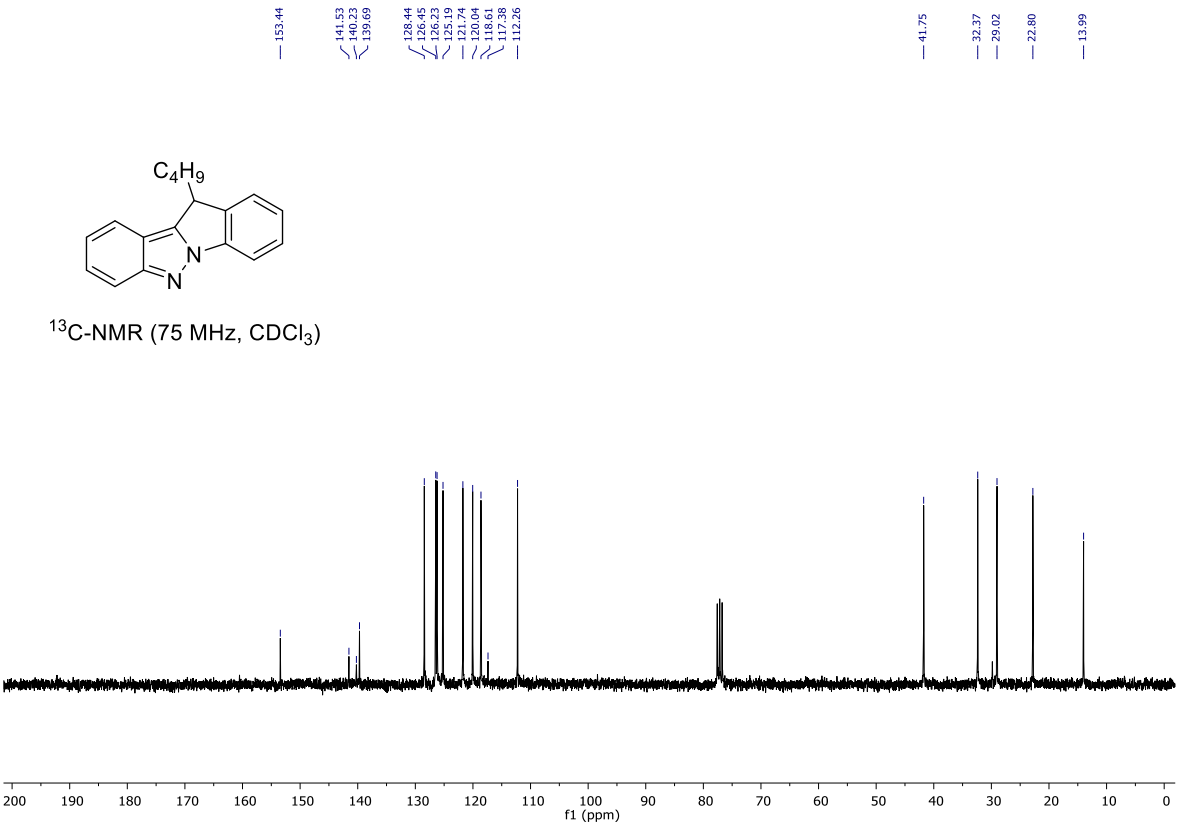
^{13}C-NMR (101 MHz, $CDCl_3$)



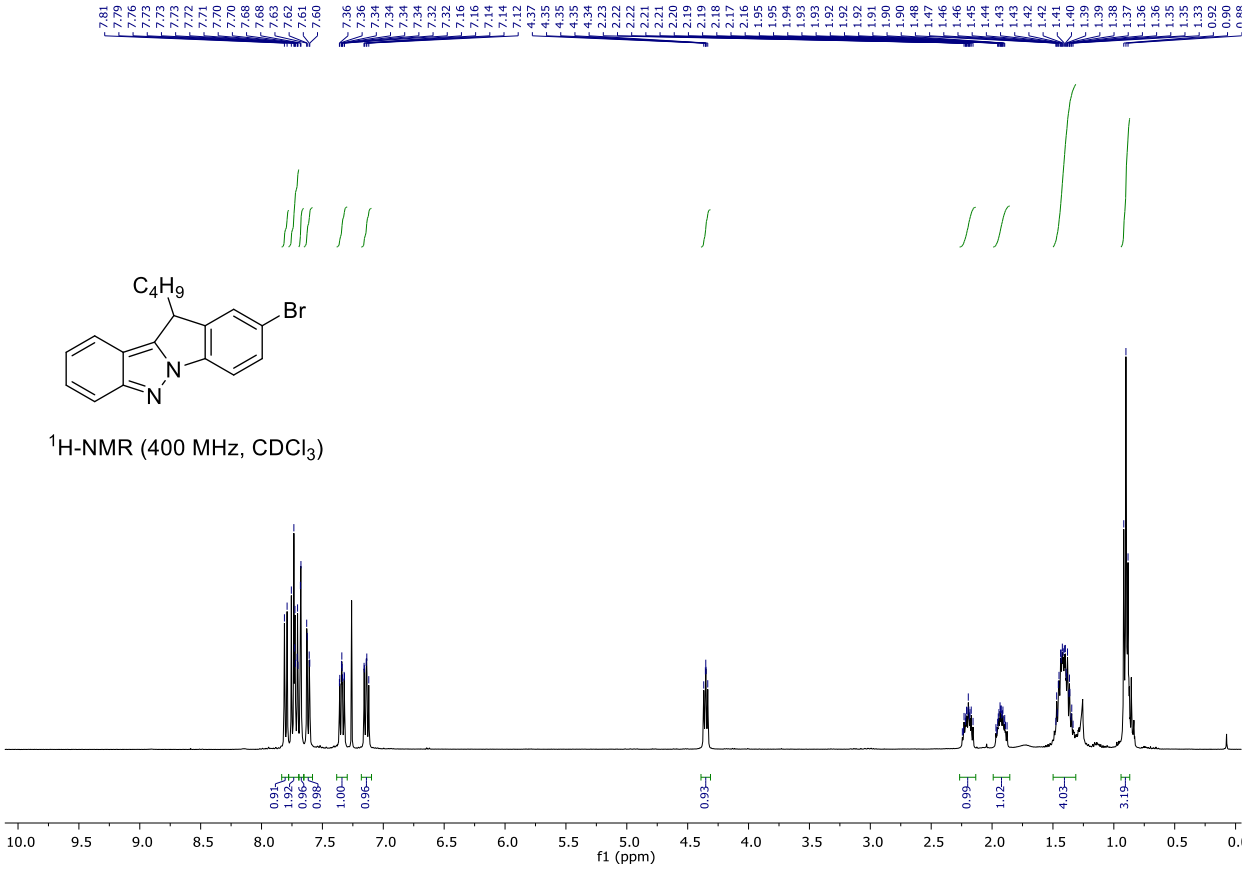
11*H*-Indolo[1,2-*b*]indazoles 2

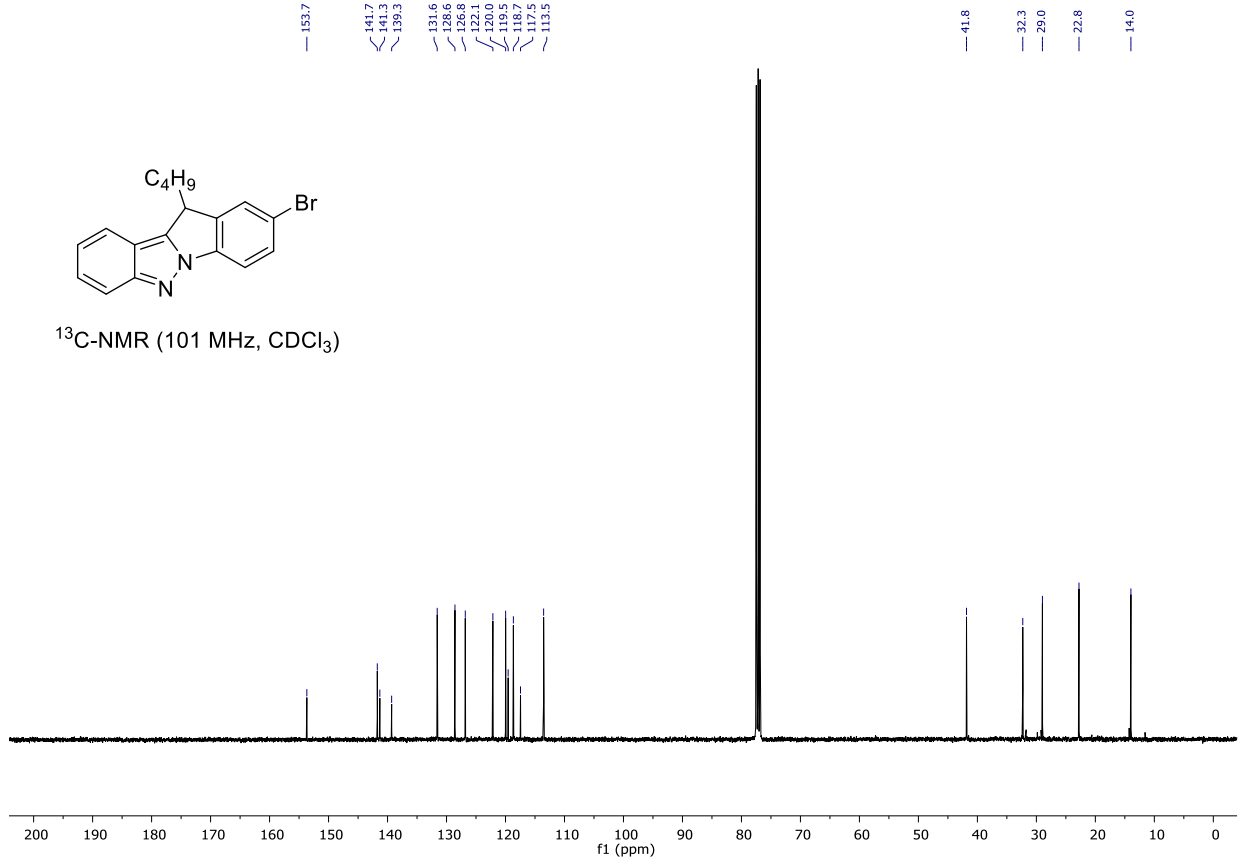
11-Butyl-11*H*-indolo[1,2-*b*]indazole (2a)



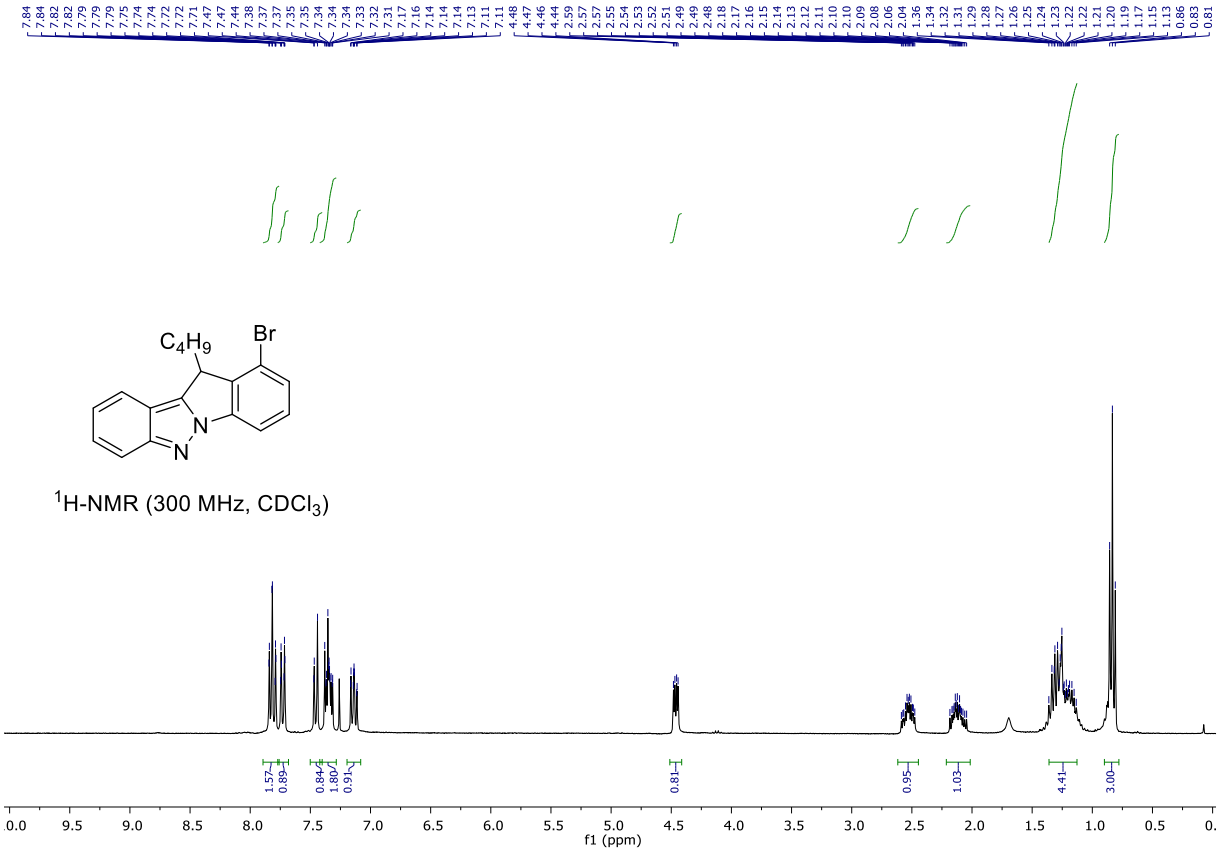


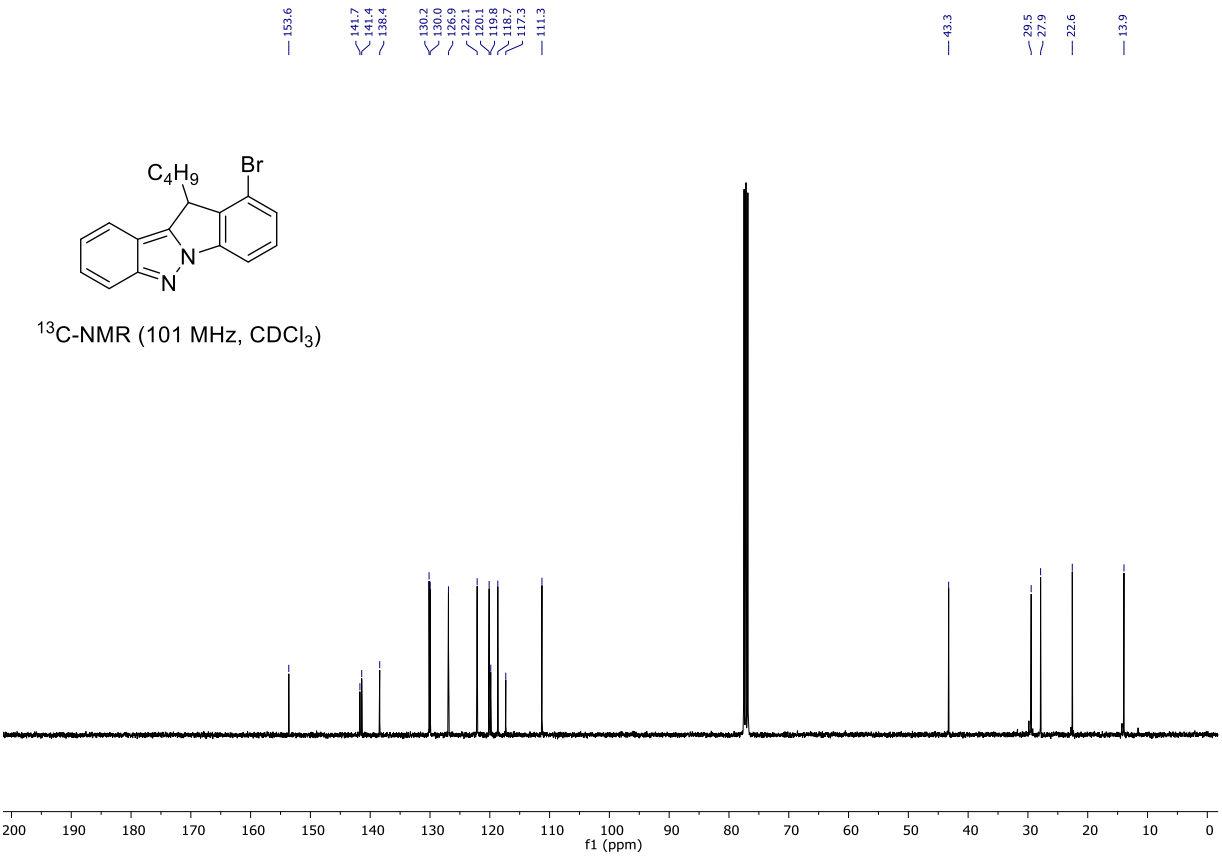
2-Bromo-11-butyl-11*H*-indolo[1,2-*b*]indazole (2b)



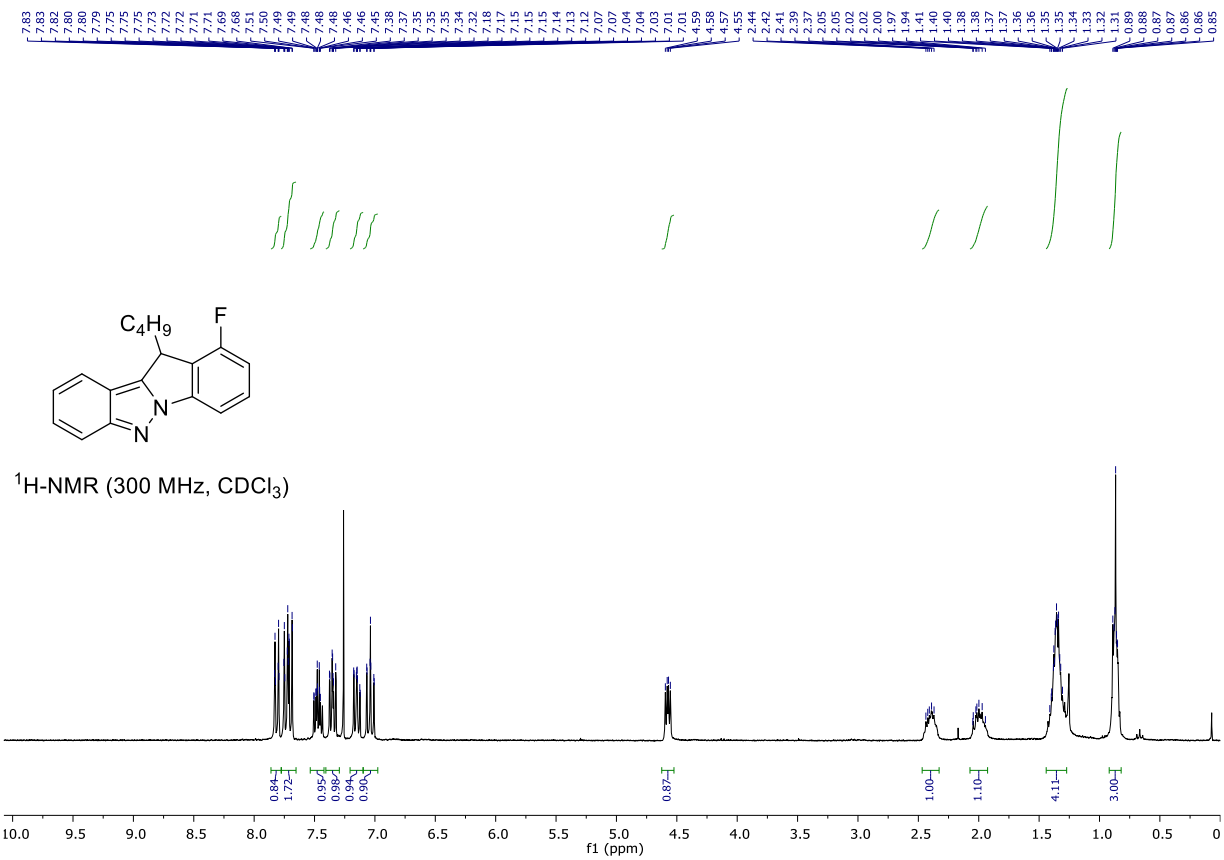


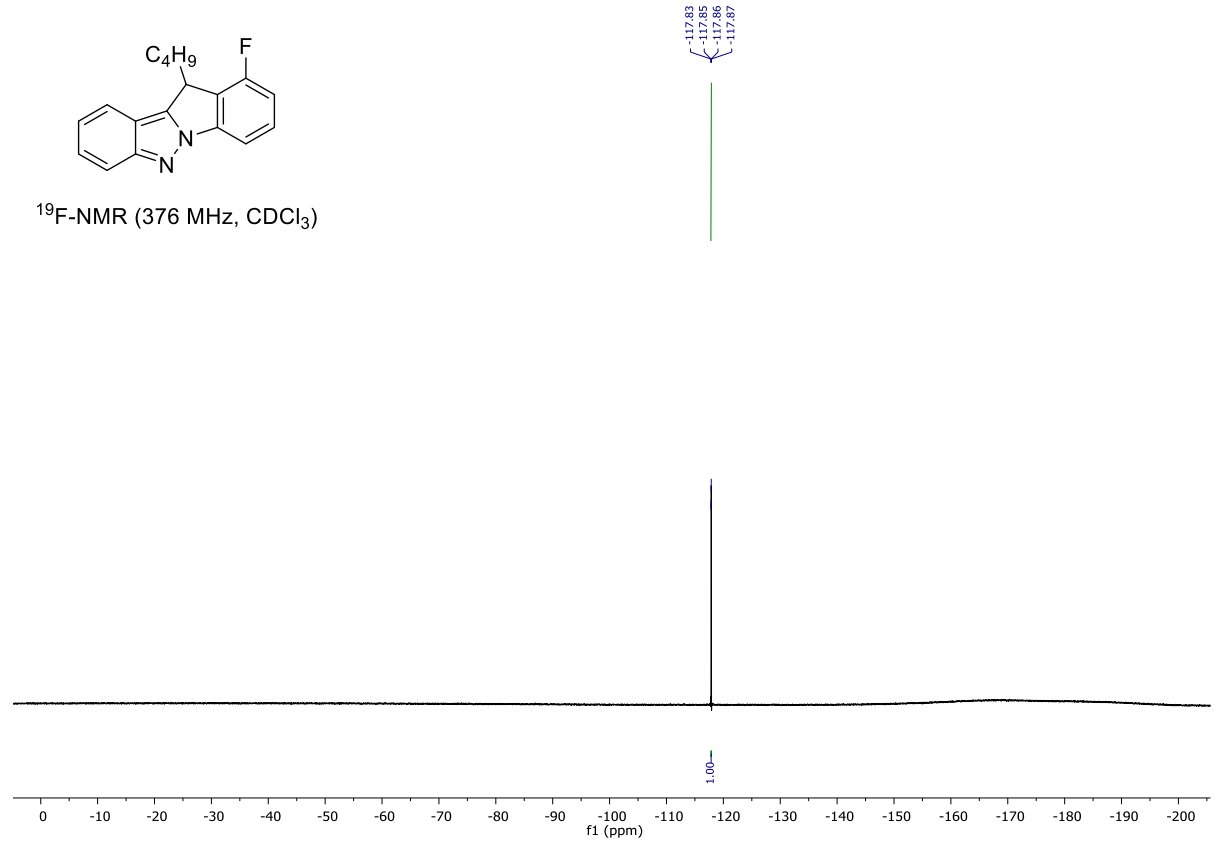
1-Bromo-11-butyl-11*H*-indolo[1,2-*b*]indazole (2c)

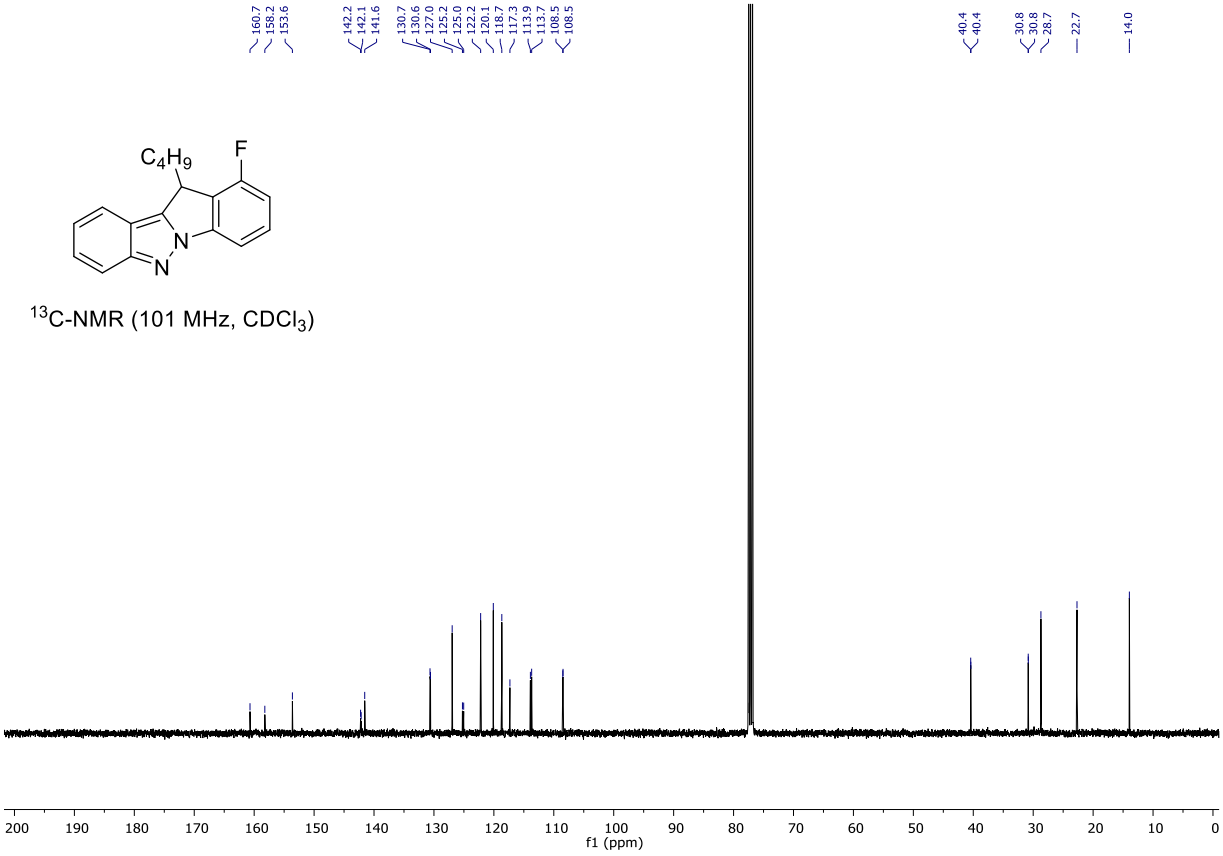




11-Butyl-1-fluoro-11*H*-indolo[1,2-*b*]indazole (2d)

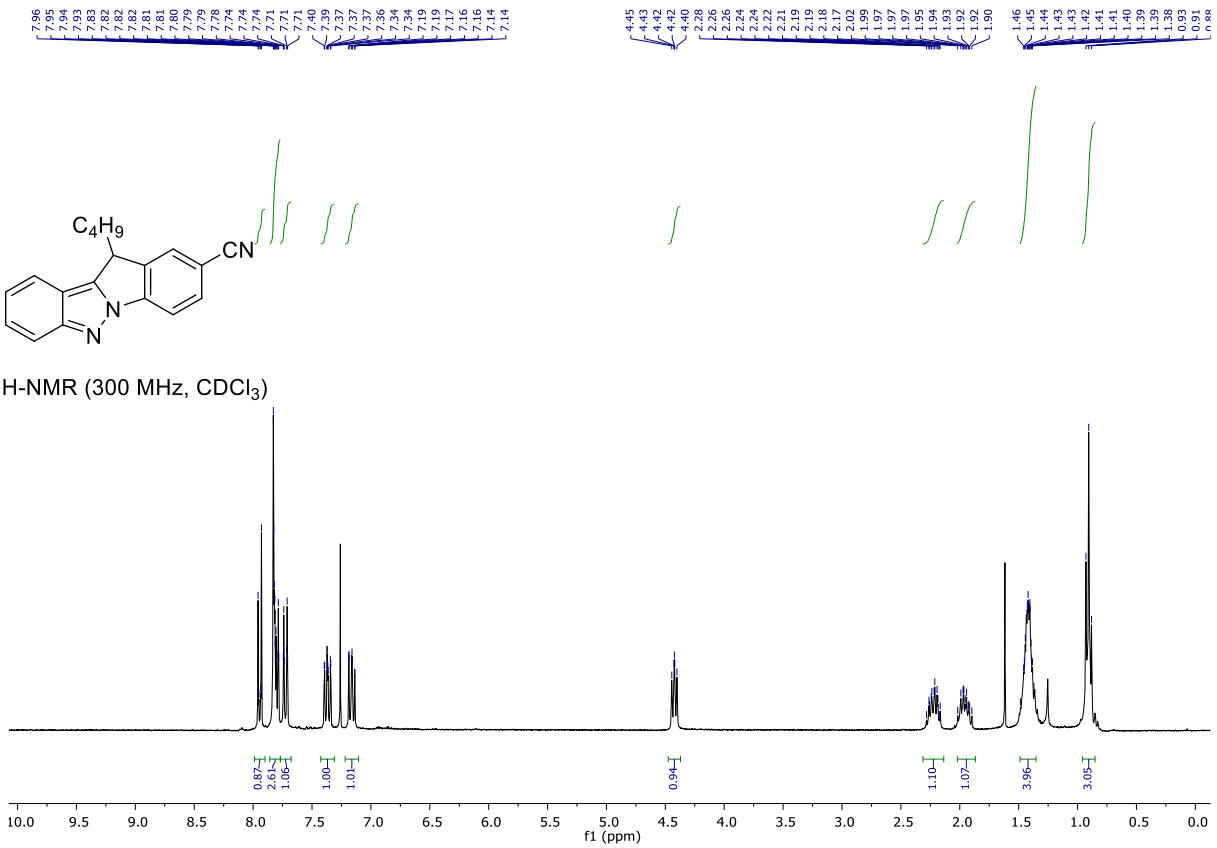


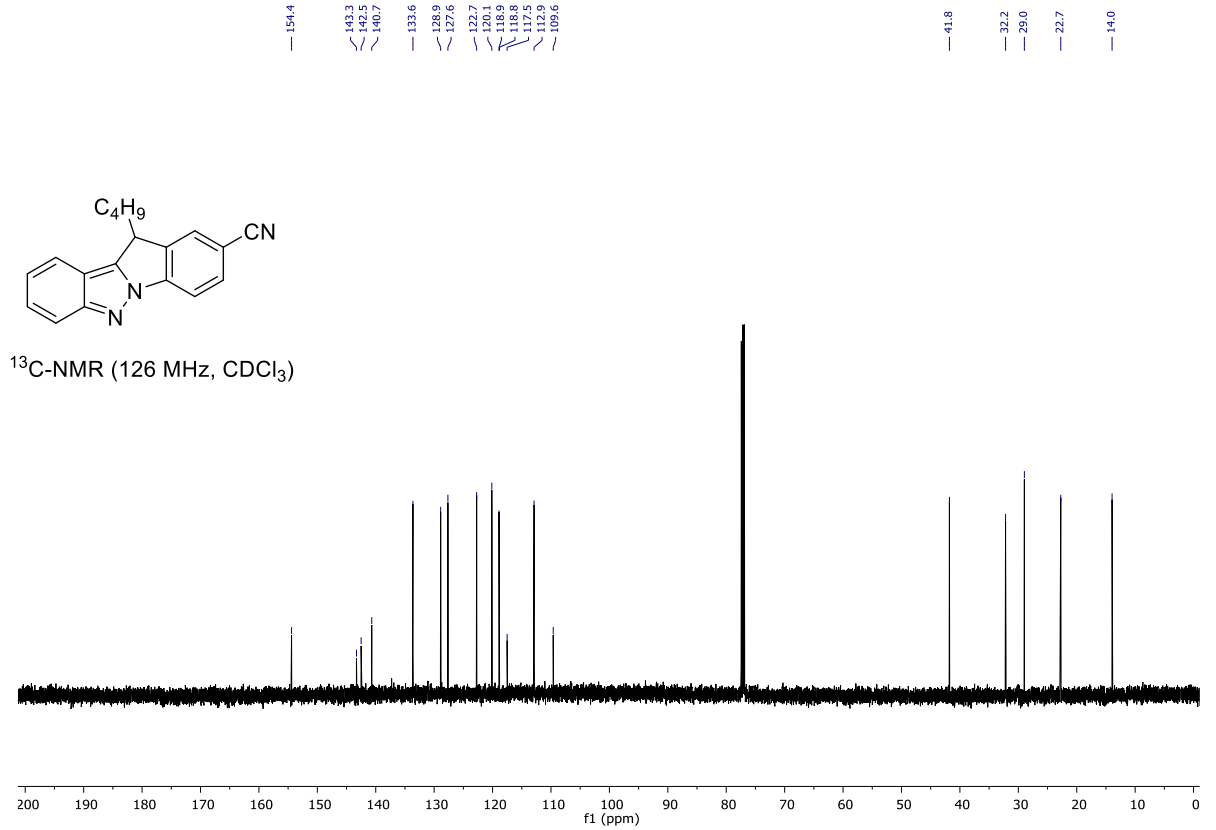




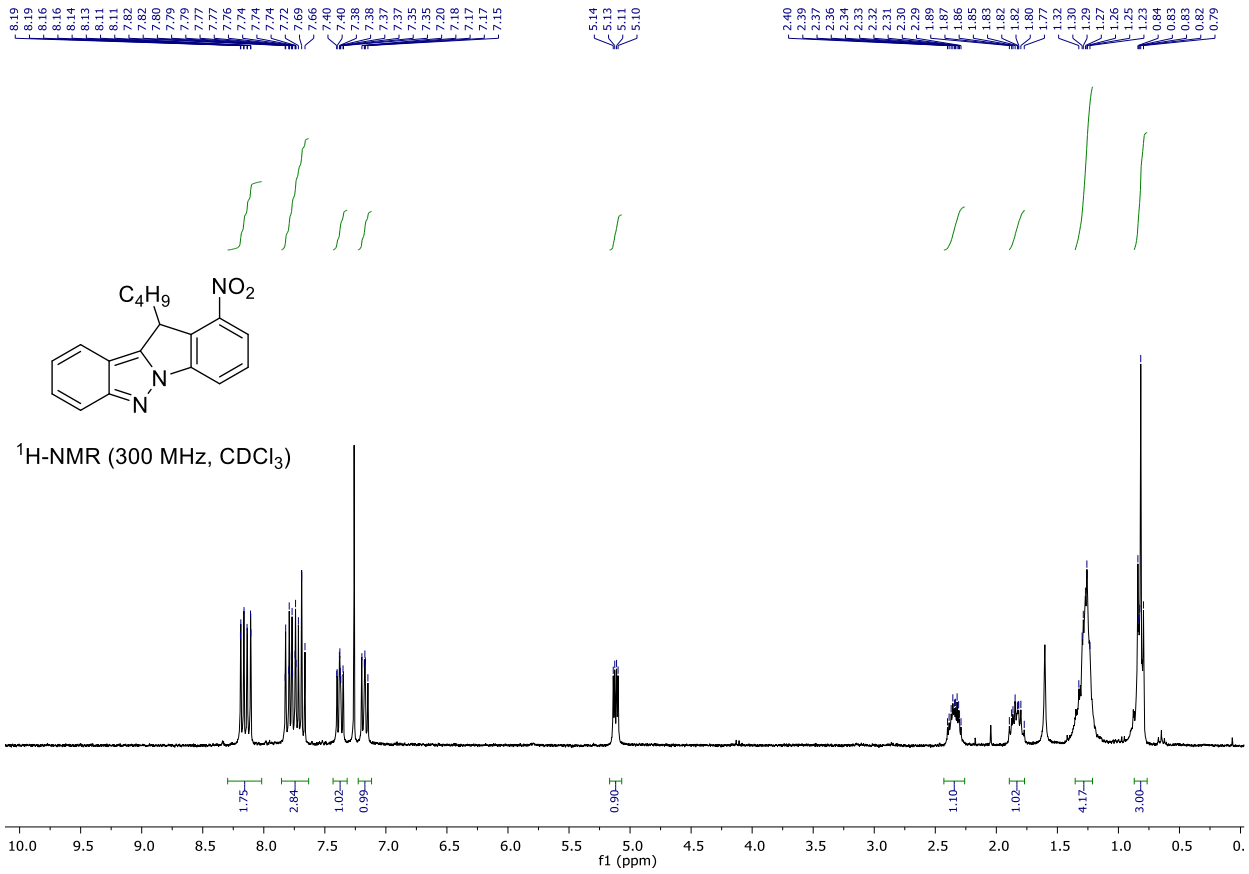
^{13}C-NMR (101 MHz, $CDCl_3$)

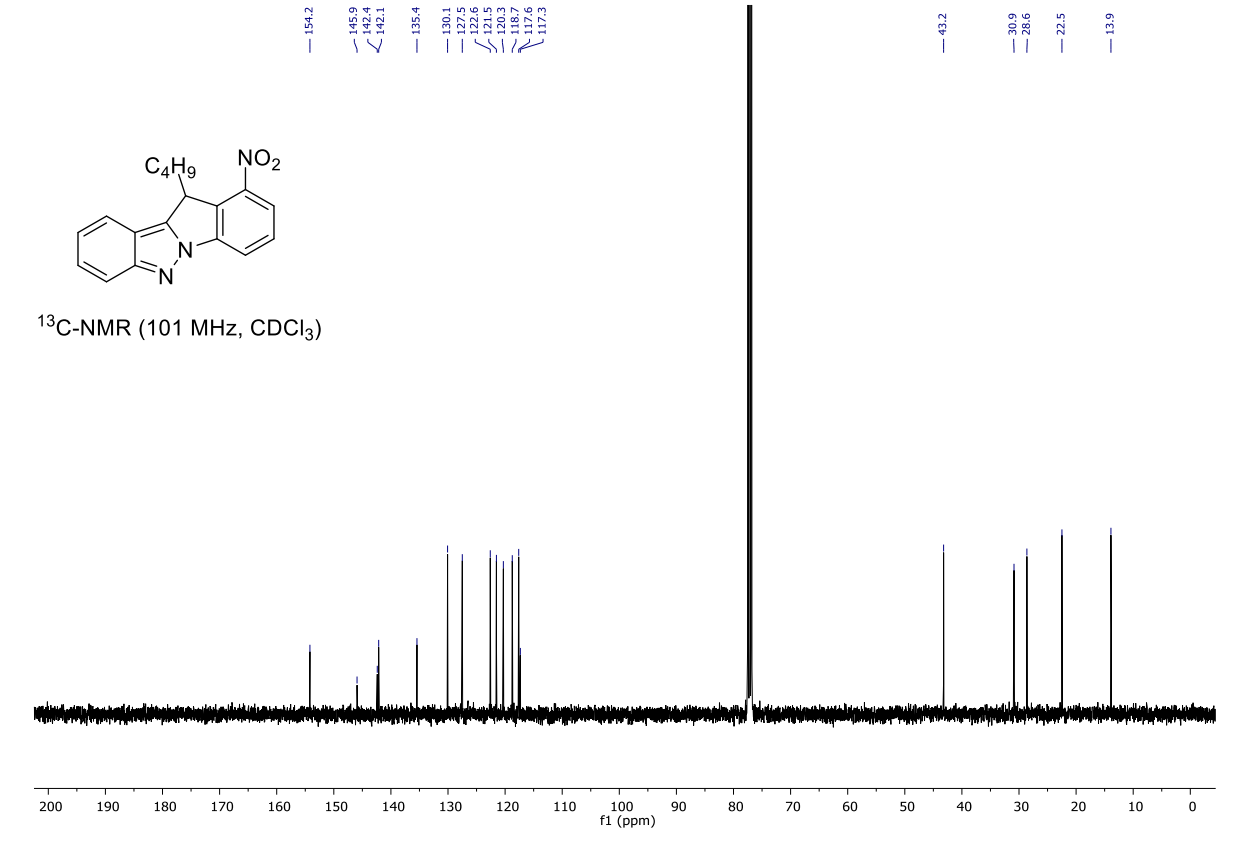
11-Butyl-11*H*-indolo[1,2-*b*]indazole-2-carbonitrile (2e)



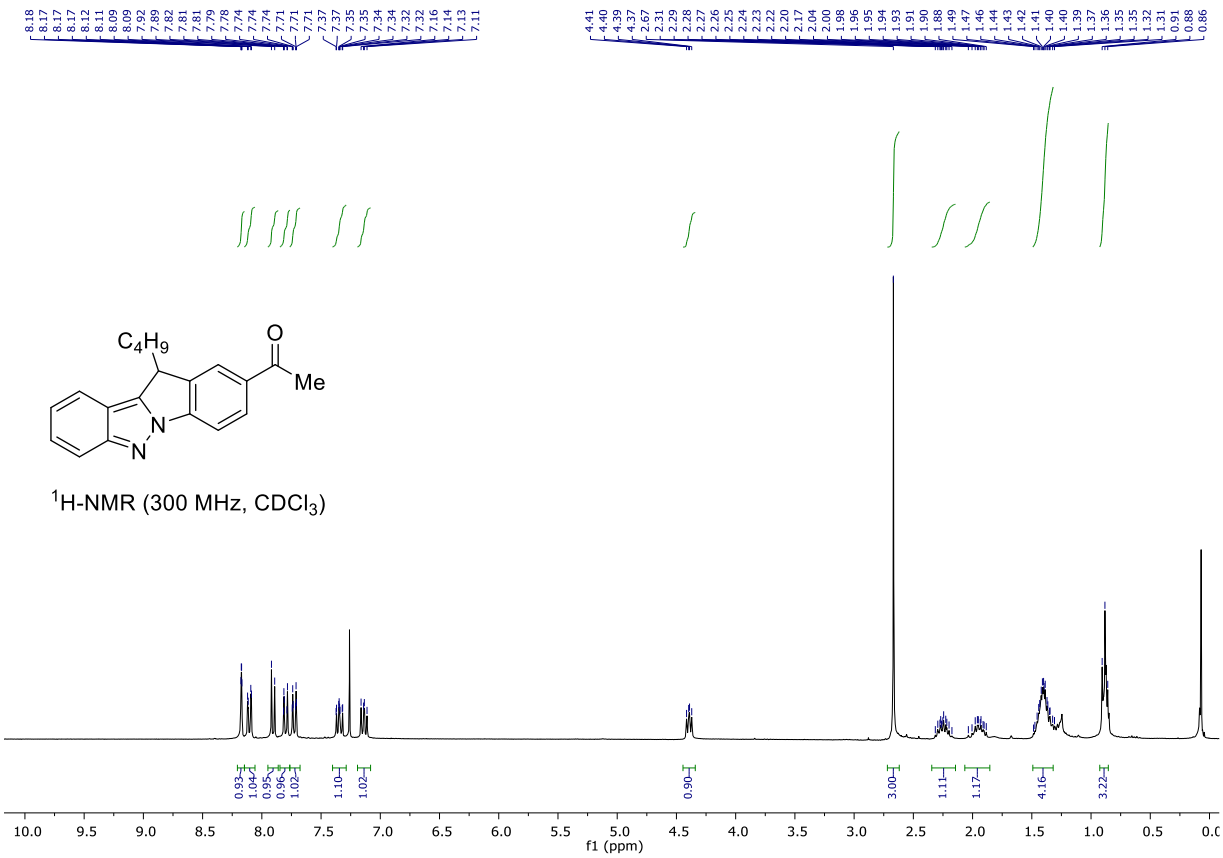


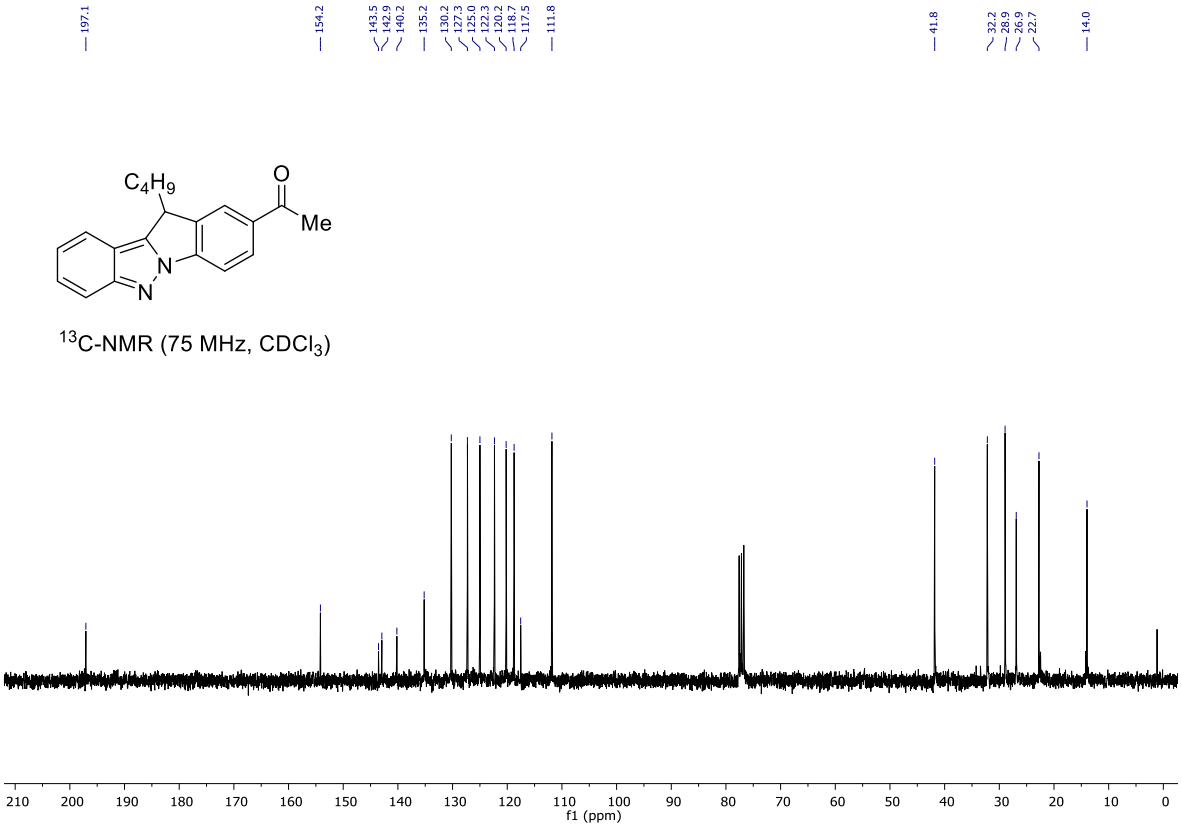
11-Butyl-1-nitro-11*H*-indolo[1,2-*b*]indazole (2f)



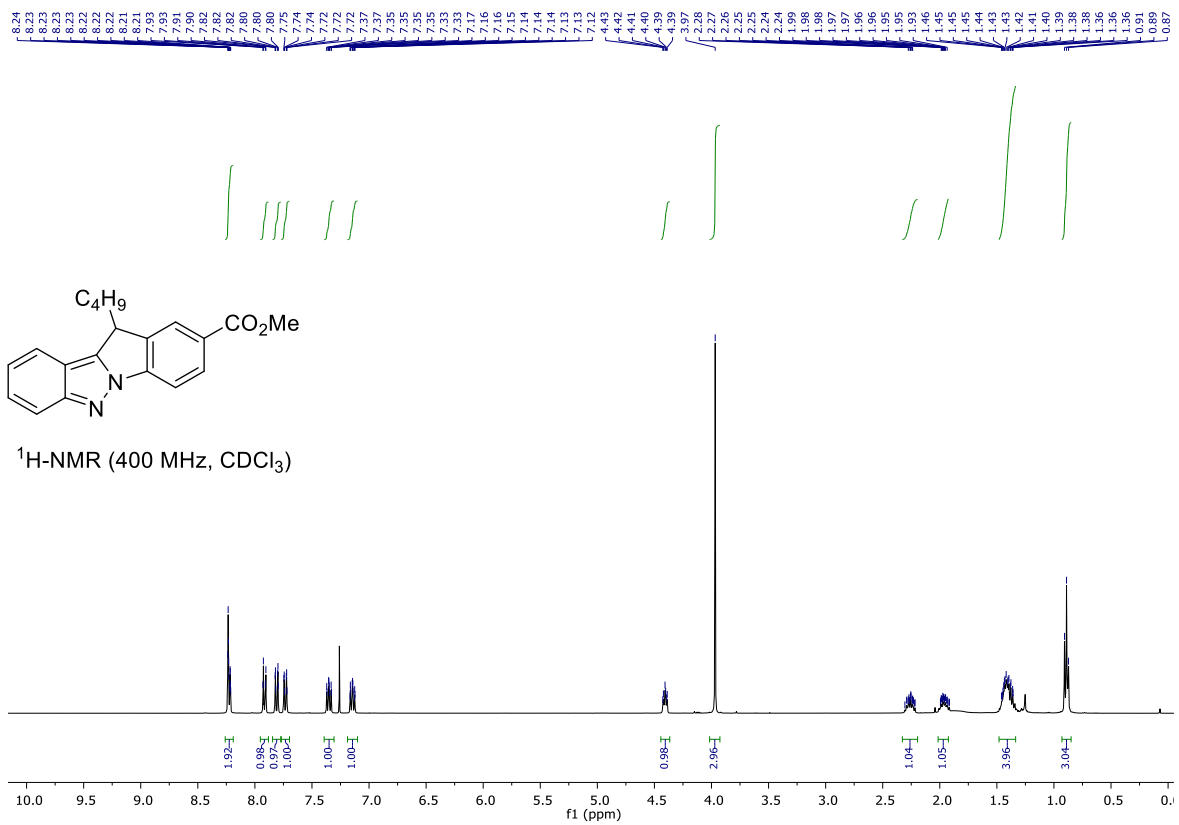


1-(11-Butyl-11*H*-indolo[1,2-*b*]indazol-2-yl)ethanone (2g)

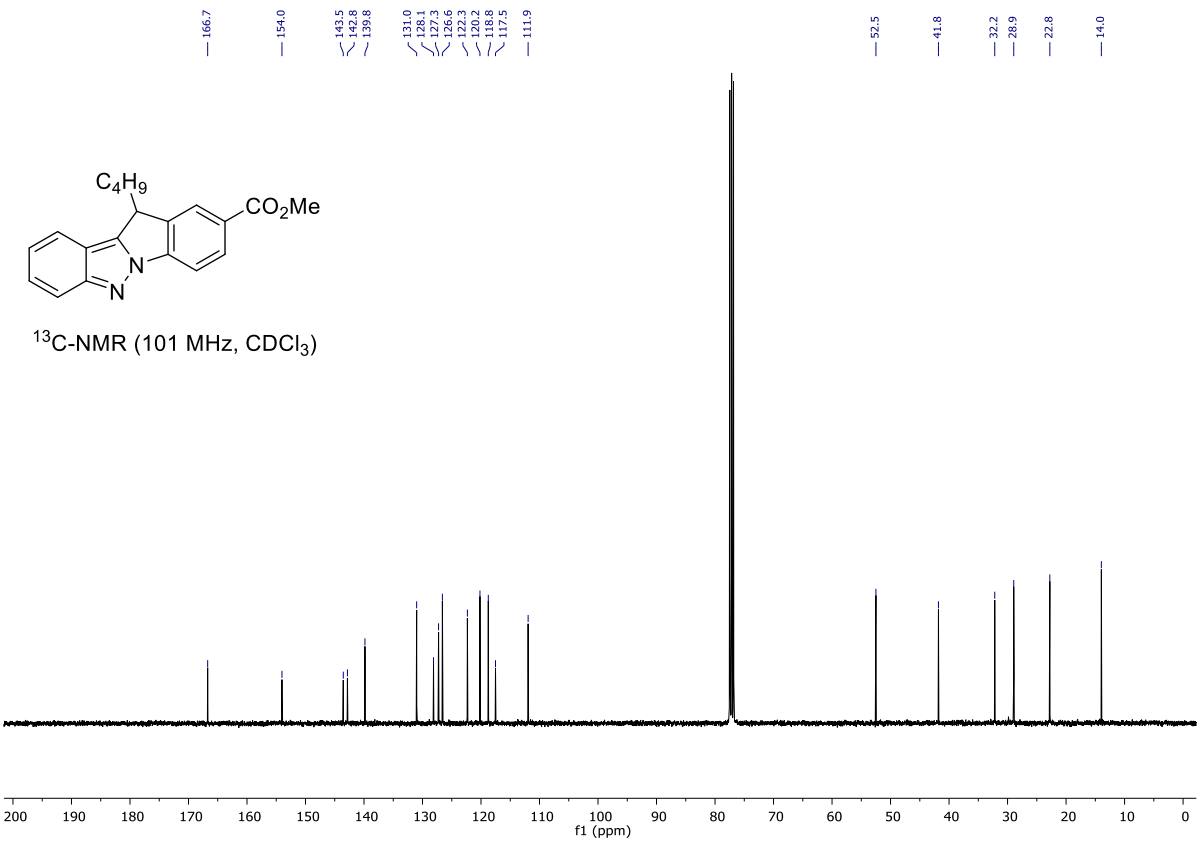




Methyl 11-butyl-11*H*-indolo[1,2-*b*]indazole-2-carboxylate (2h)

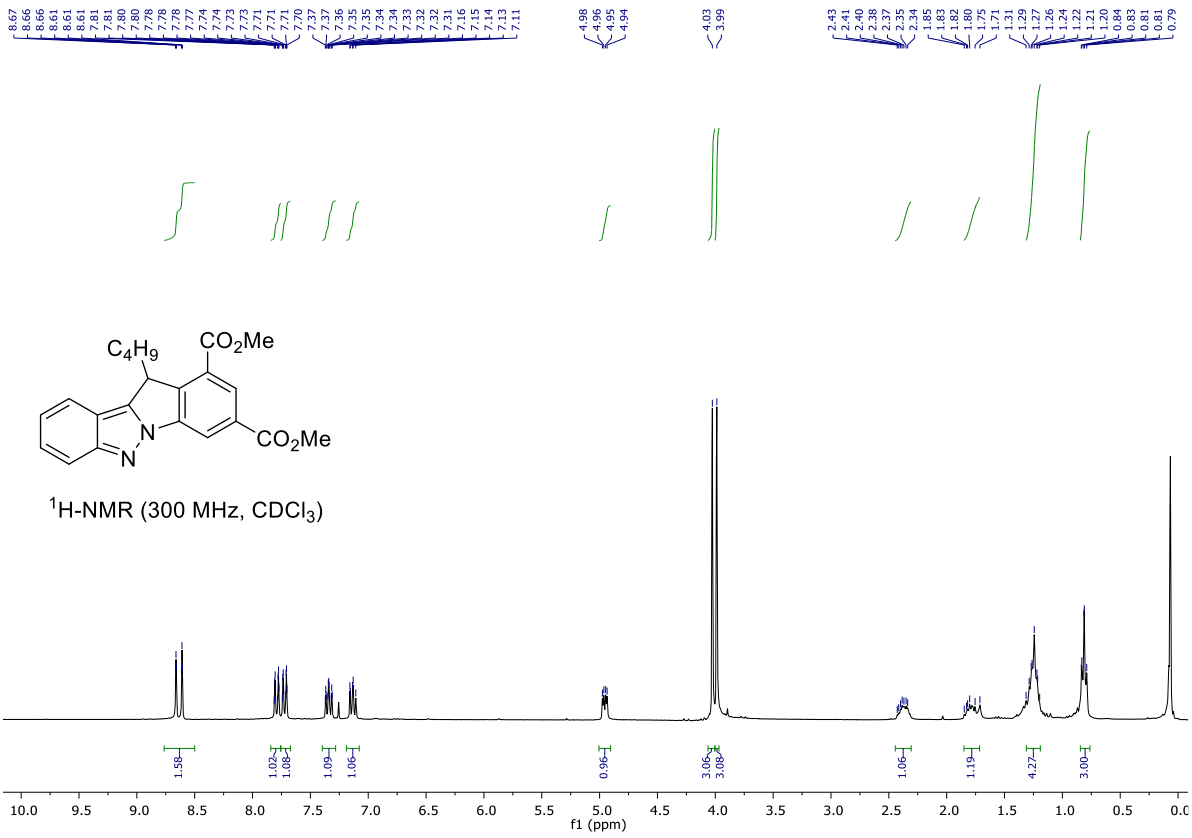


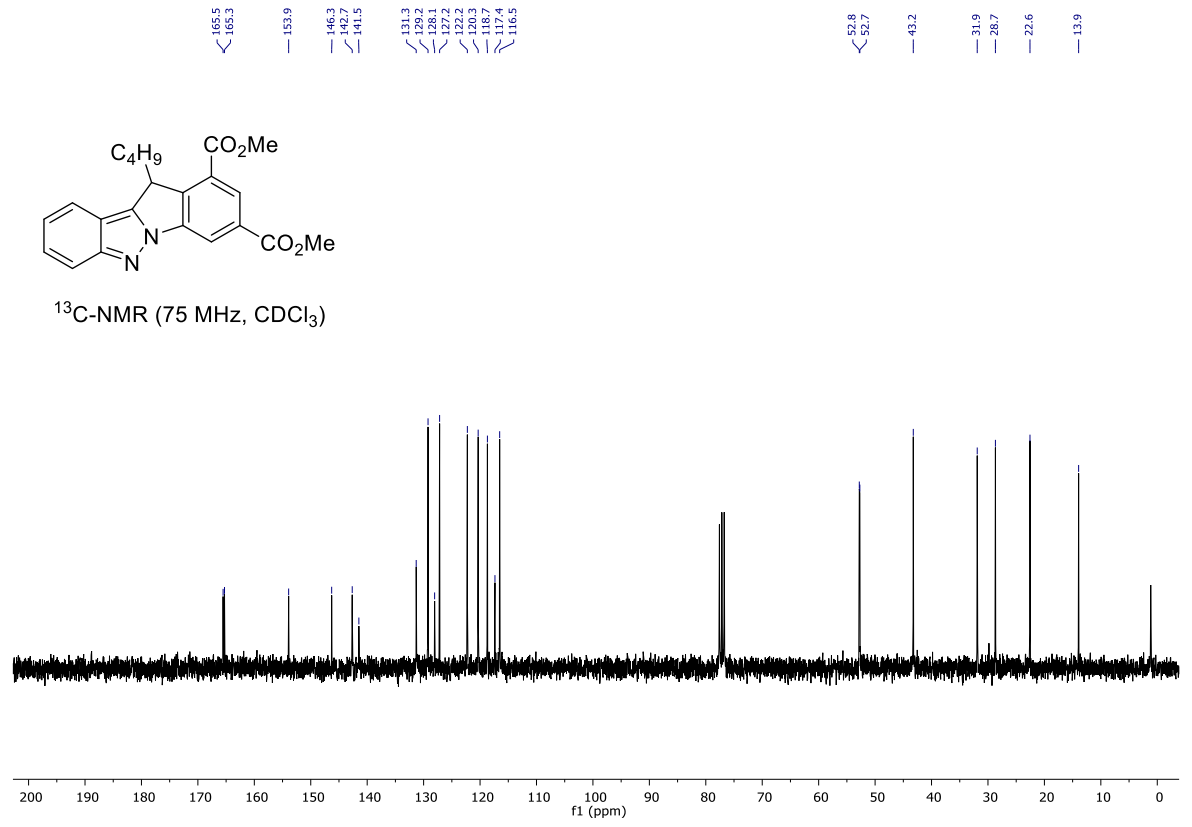
^{1}H-NMR (400 MHz, $CDCl_3$)



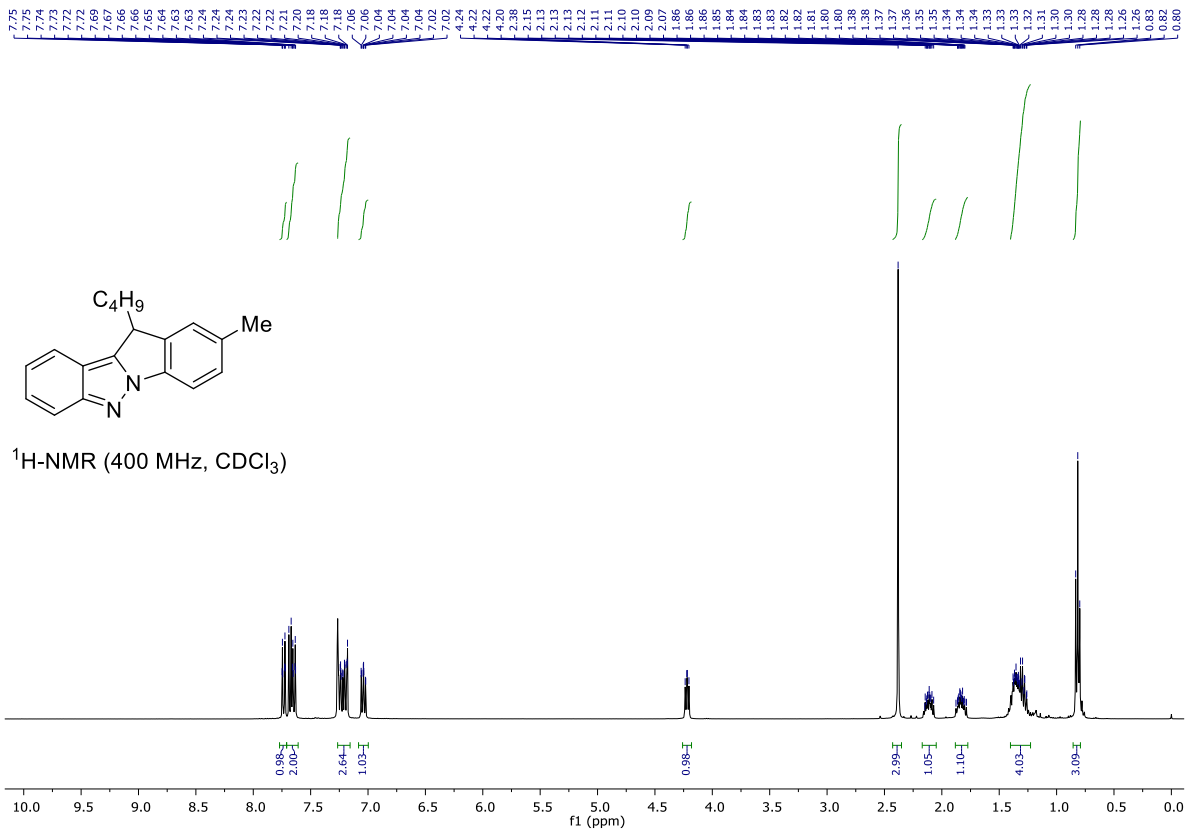
^{13}C-NMR (101 MHz, $CDCl_3$)

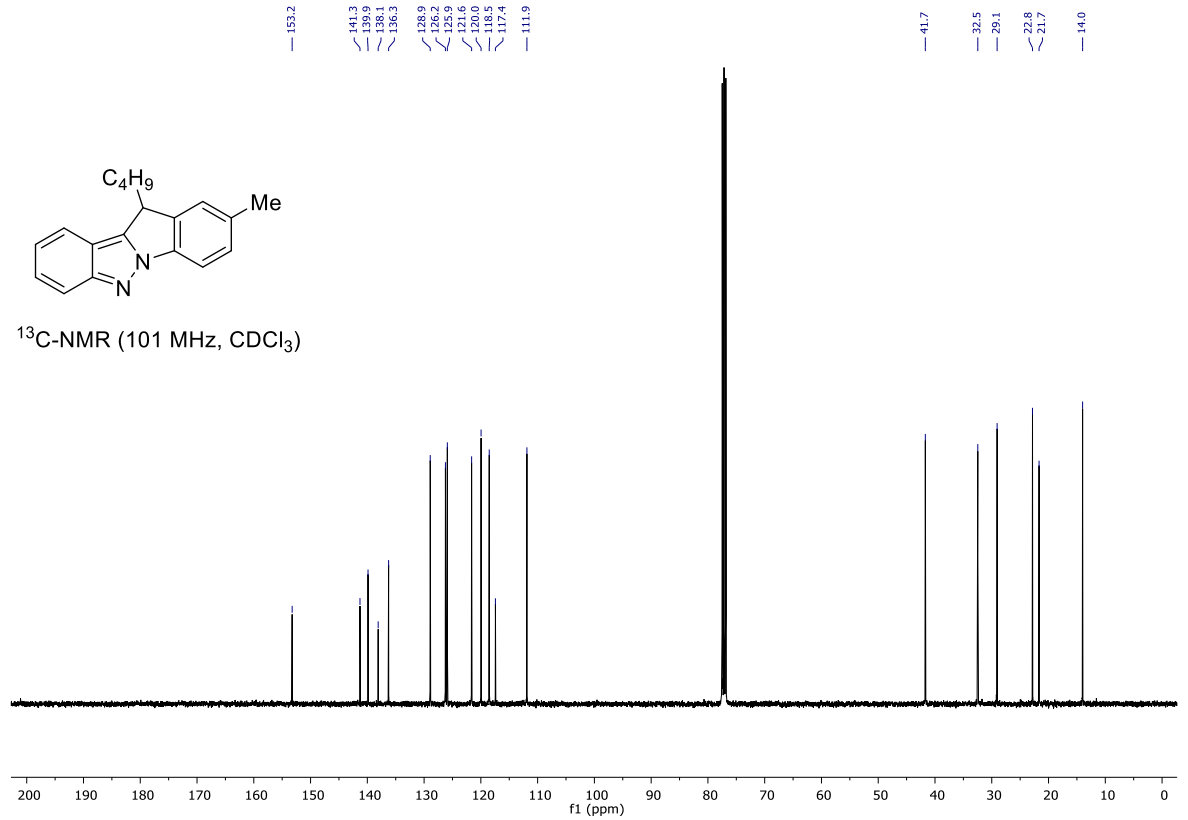
Dimethyl 11-butyl-11*H*-indolo[1,2-*b*]indazole-1,3-dicarboxylate (2i)



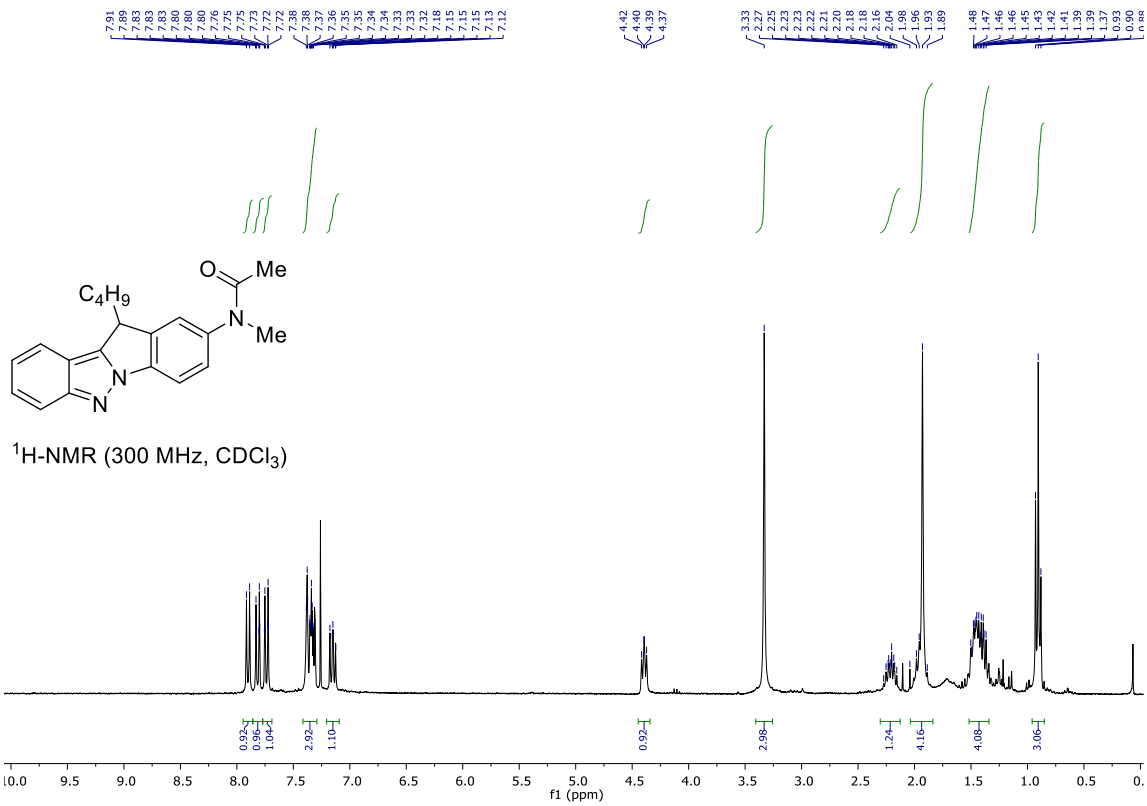


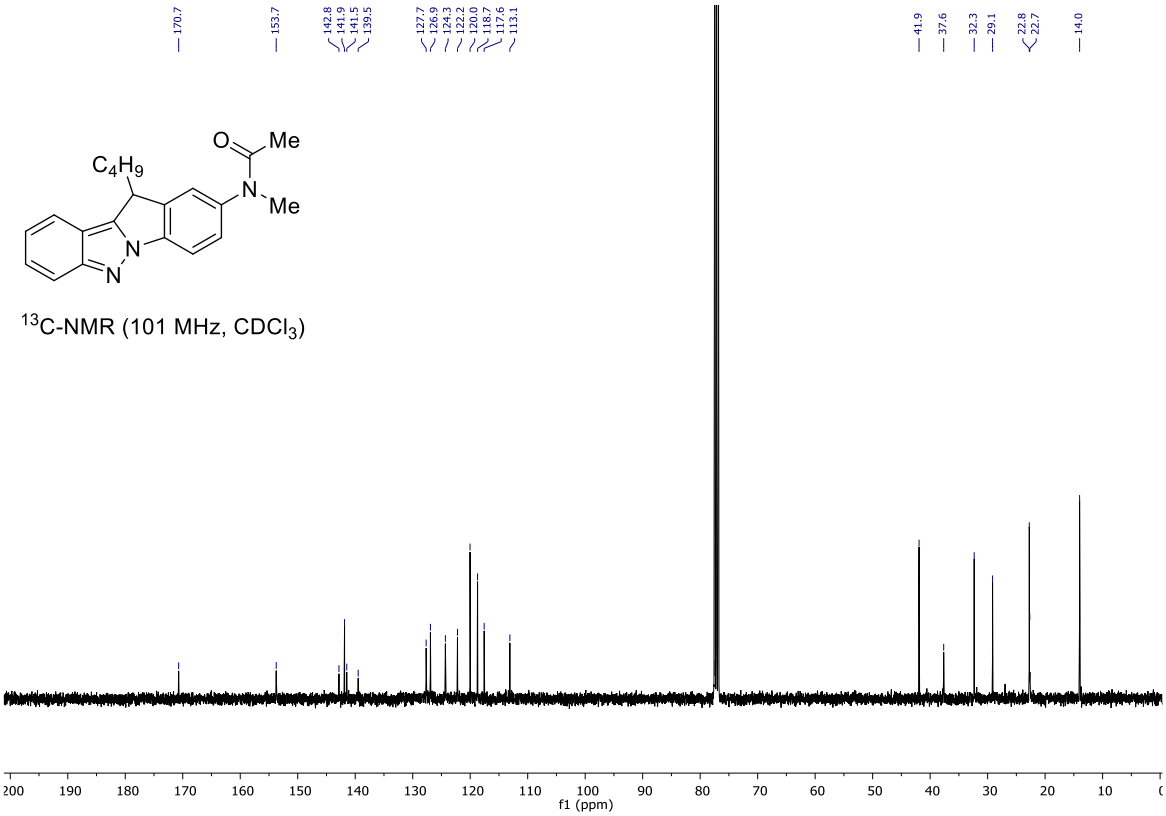
11-Butyl-2-methyl-11*H*-indolo[1,2-*b*]indazole (2j)



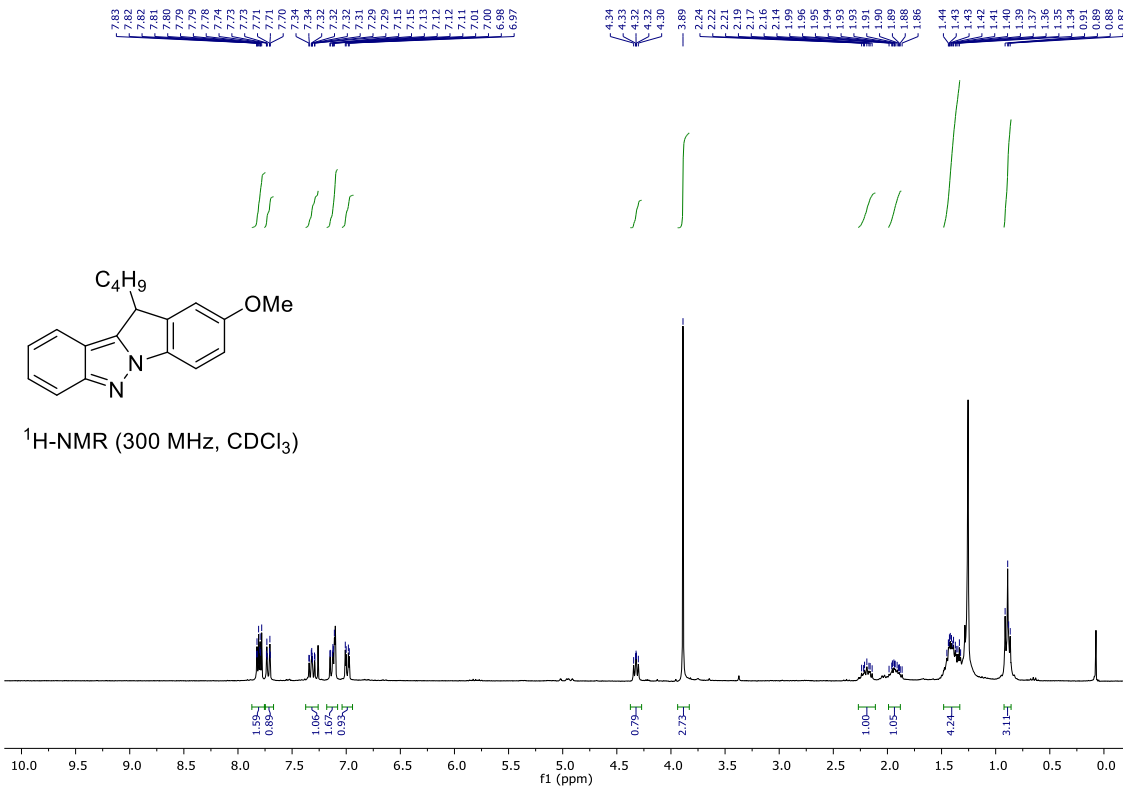


_N_-(11-Butyl-11_H_-indolo[1,2-_b_]indazol-2-yl)-_N_-methylacetamide (2k)

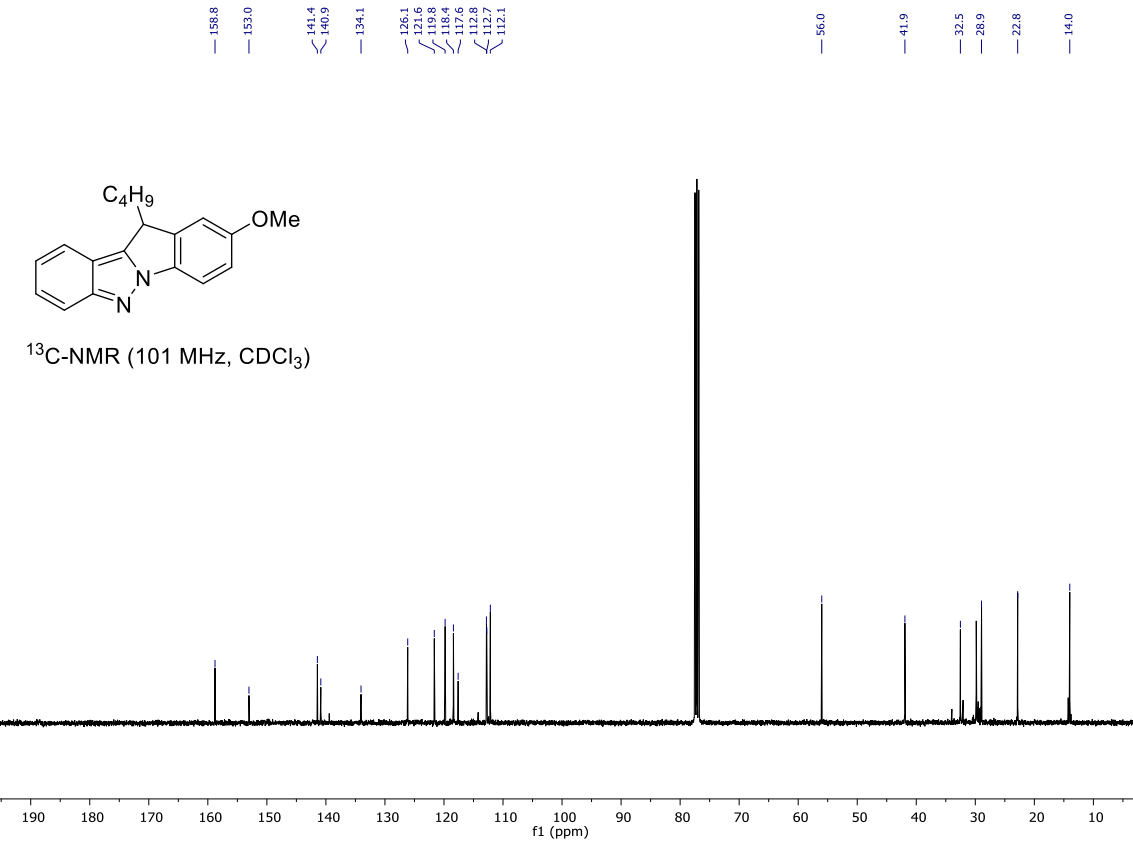




11-Butyl-2-methoxy-11*H*-indolo[1,2-*b*]indazole (2l)

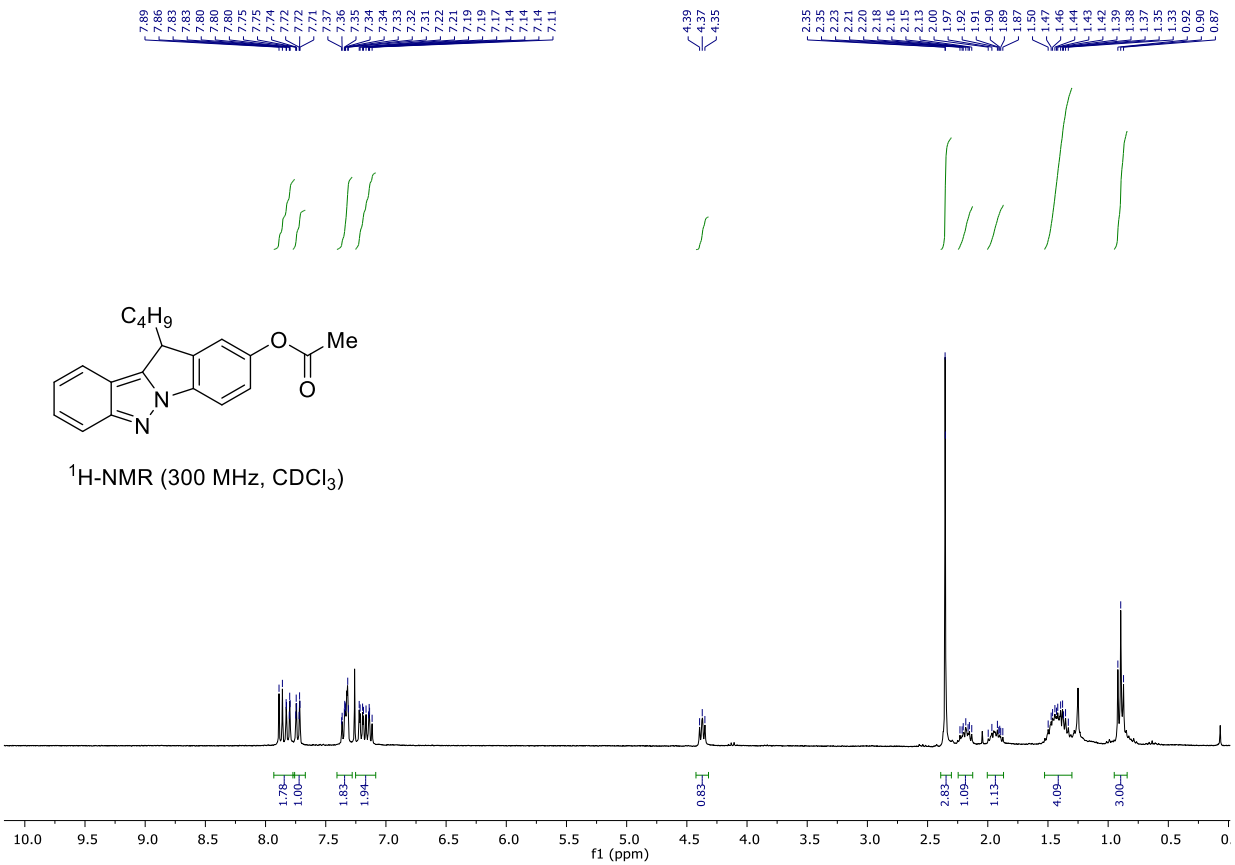


^{1}H-NMR (300 MHz, $CDCl_3$)

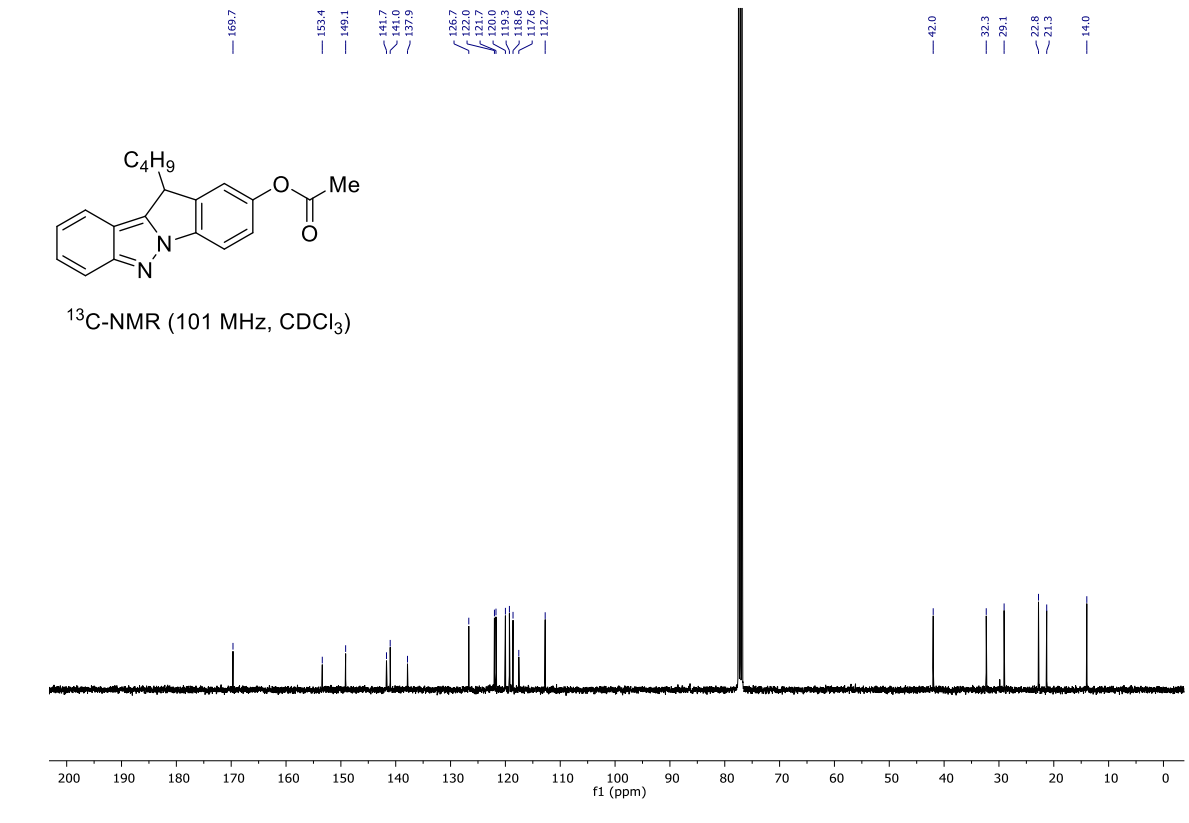


^{13}C-NMR (101 MHz, $CDCl_3$)

11-Butyl-11*H*-indolo[1,2-*b*]indazol-2-yl acetate (2m)

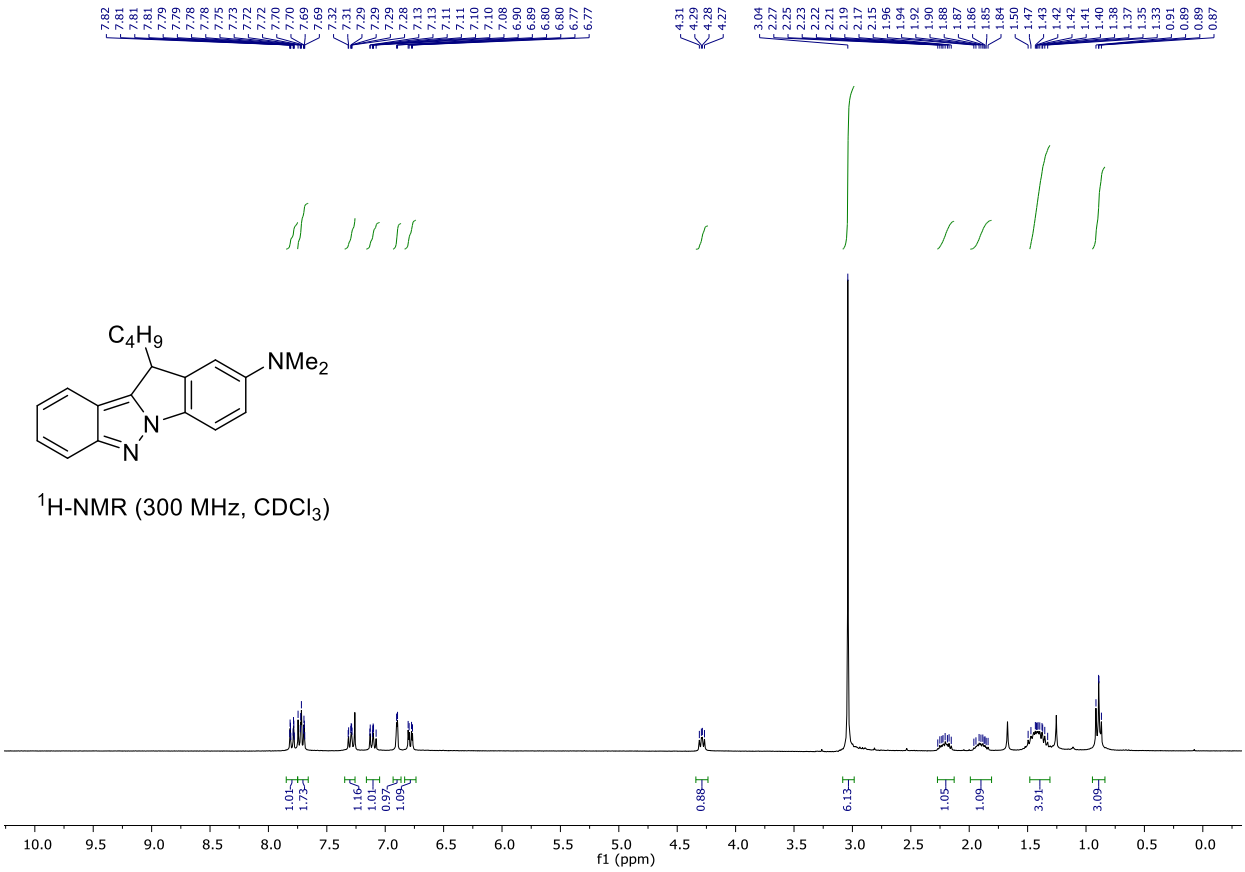


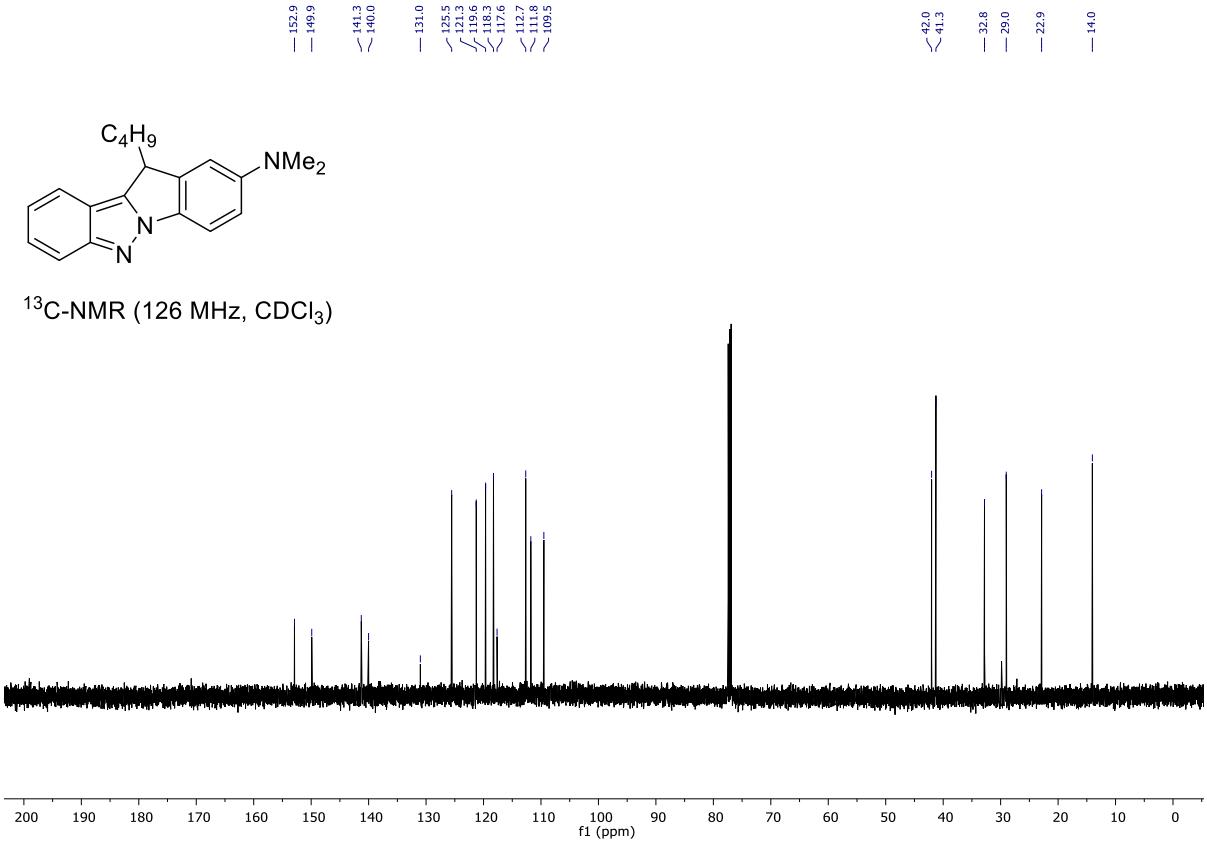
^{1}H-NMR (300 MHz, $CDCl_3$)



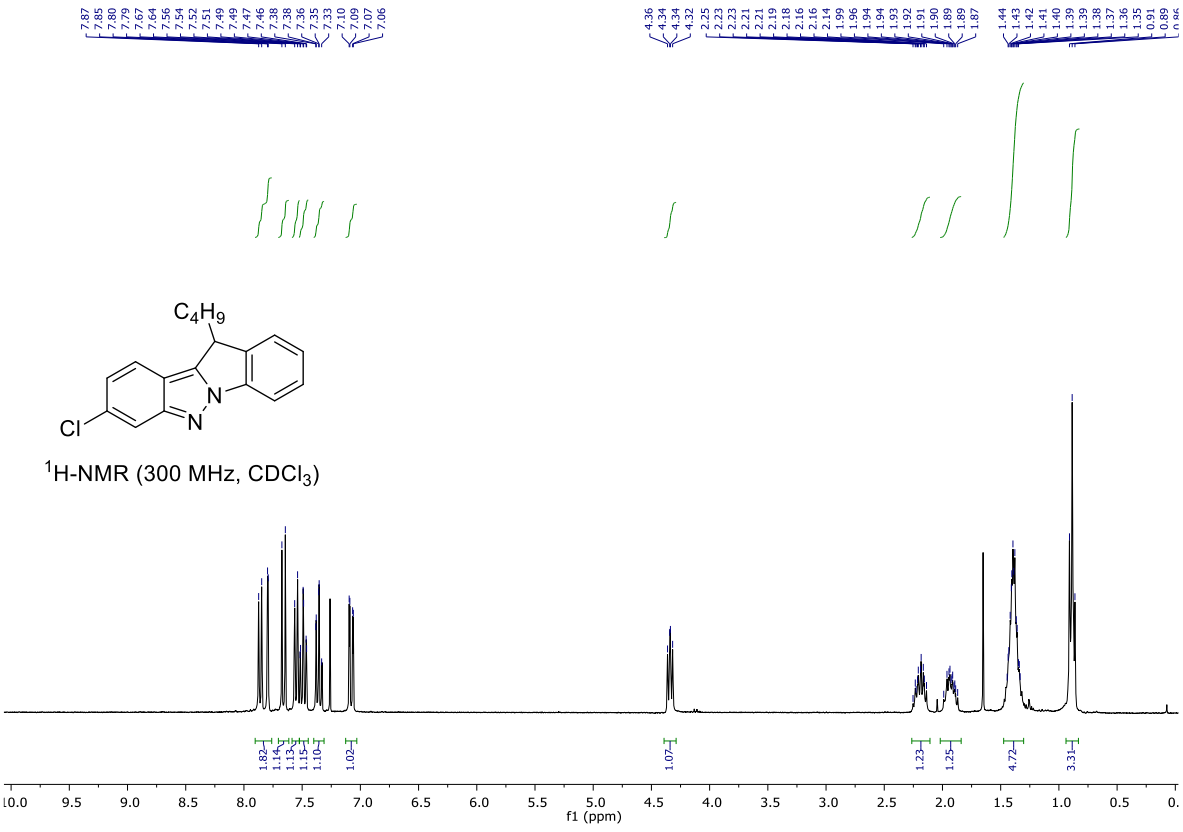
^{13}C-NMR (101 MHz, $CDCl_3$)

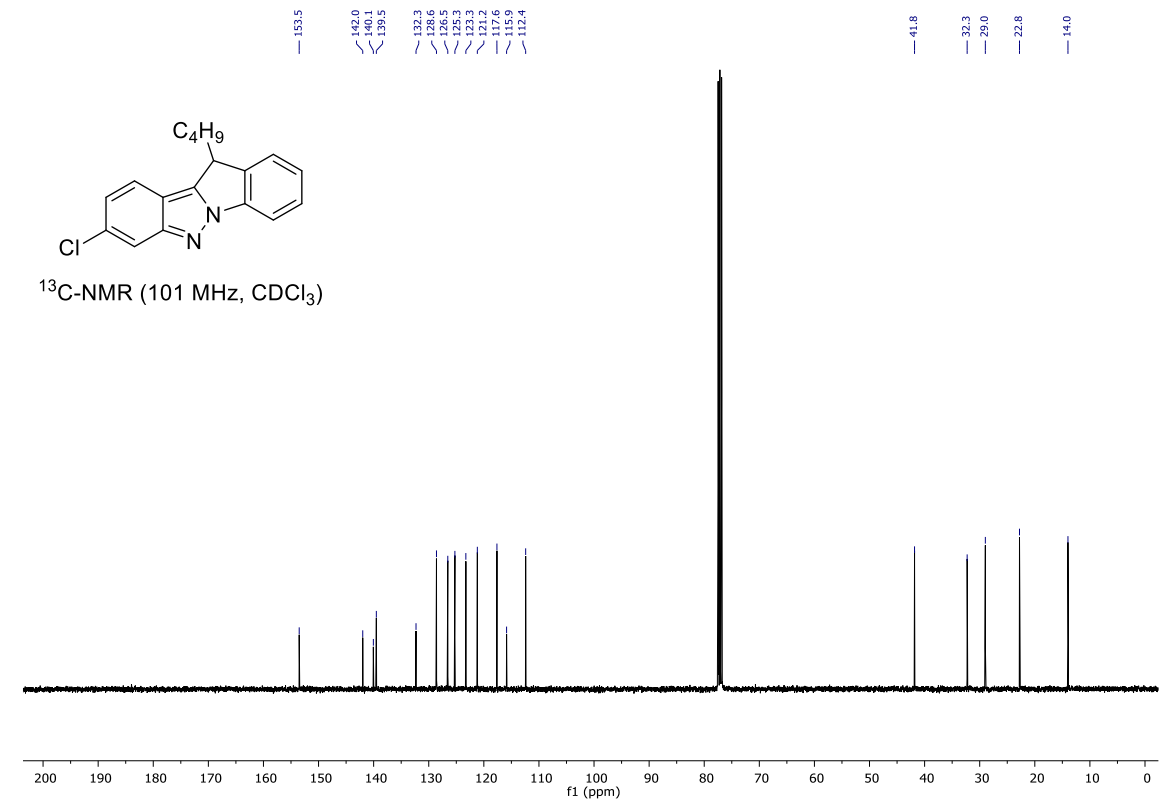
11-Butyl-2-methyl-11*H*-indolo[1,2-*b*]indazole (2n)



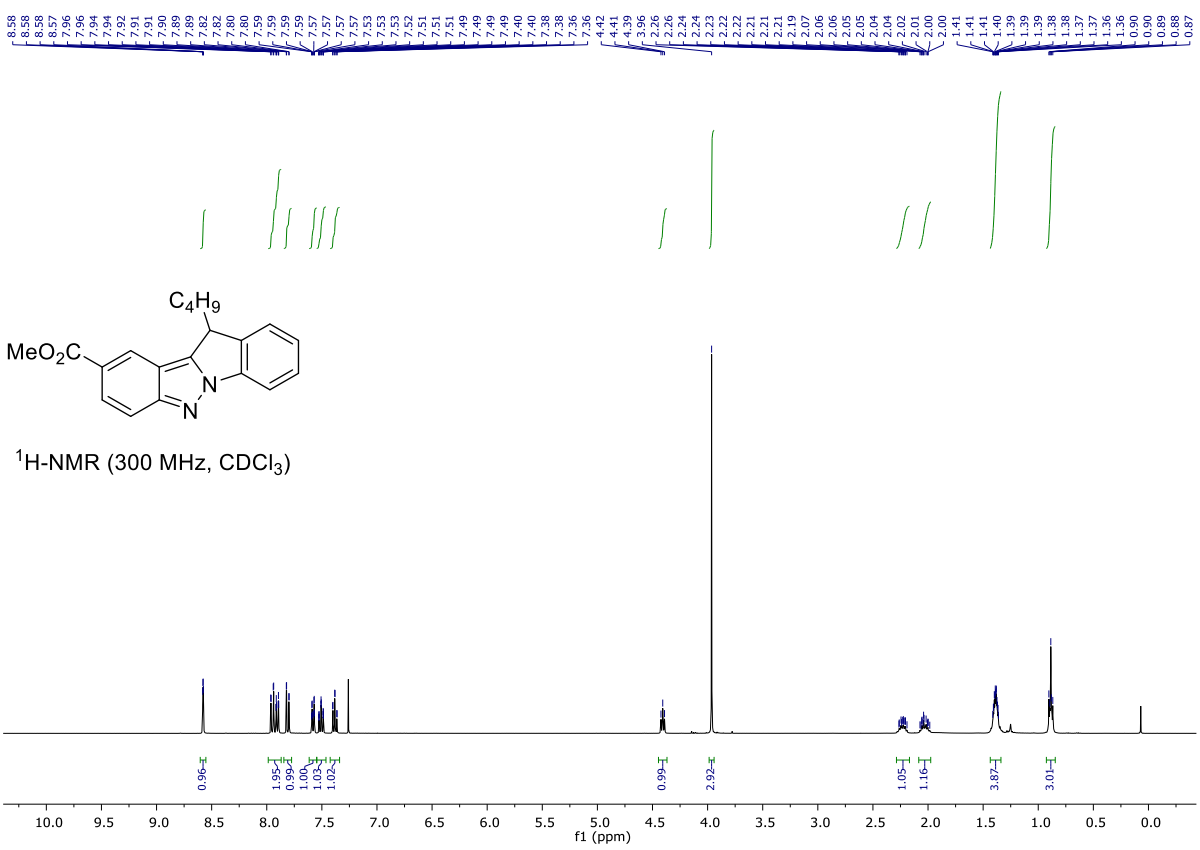


11-Butyl-8-chloro-11*H*-indolo[1,2-*b*]indazole (2o)

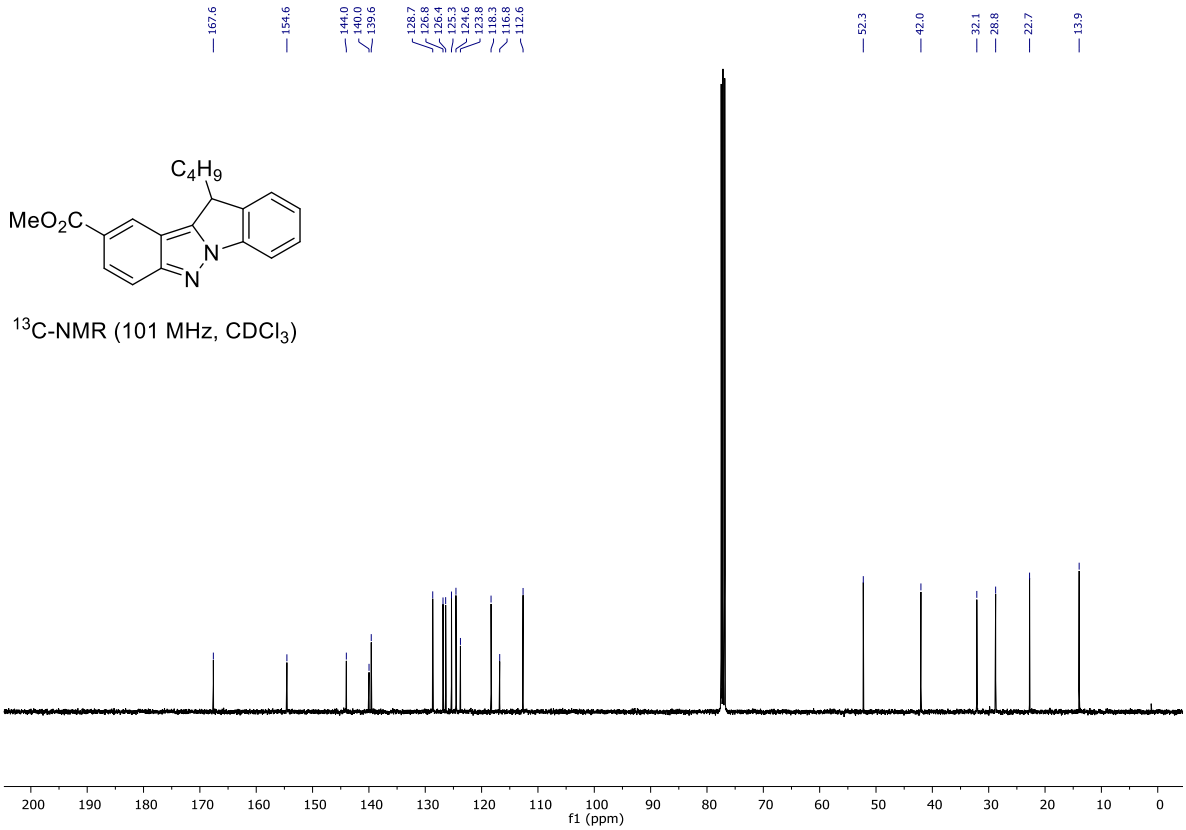




Methyl 11-butyl-11*H*-indolo[1,2-*b*]indazole-9-carboxylate (2p)

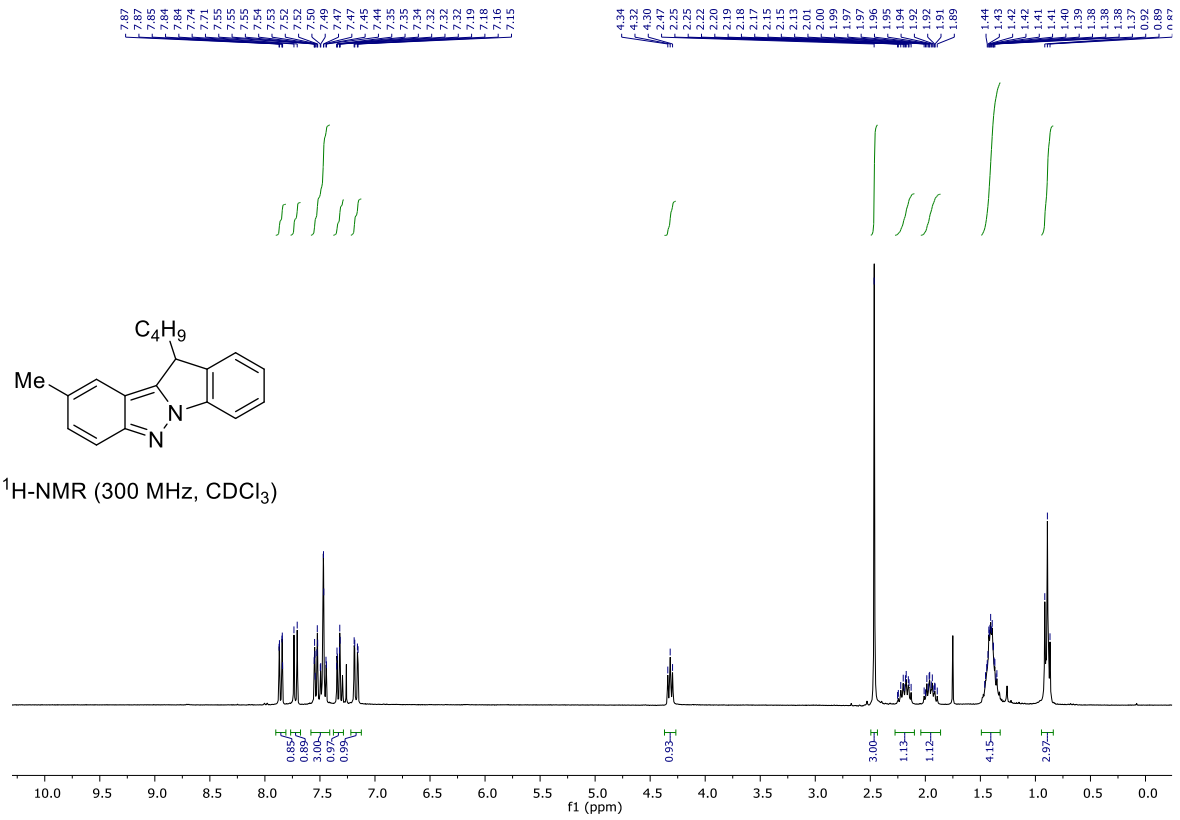


^{1}H-NMR (300 MHz, $CDCl_3$)

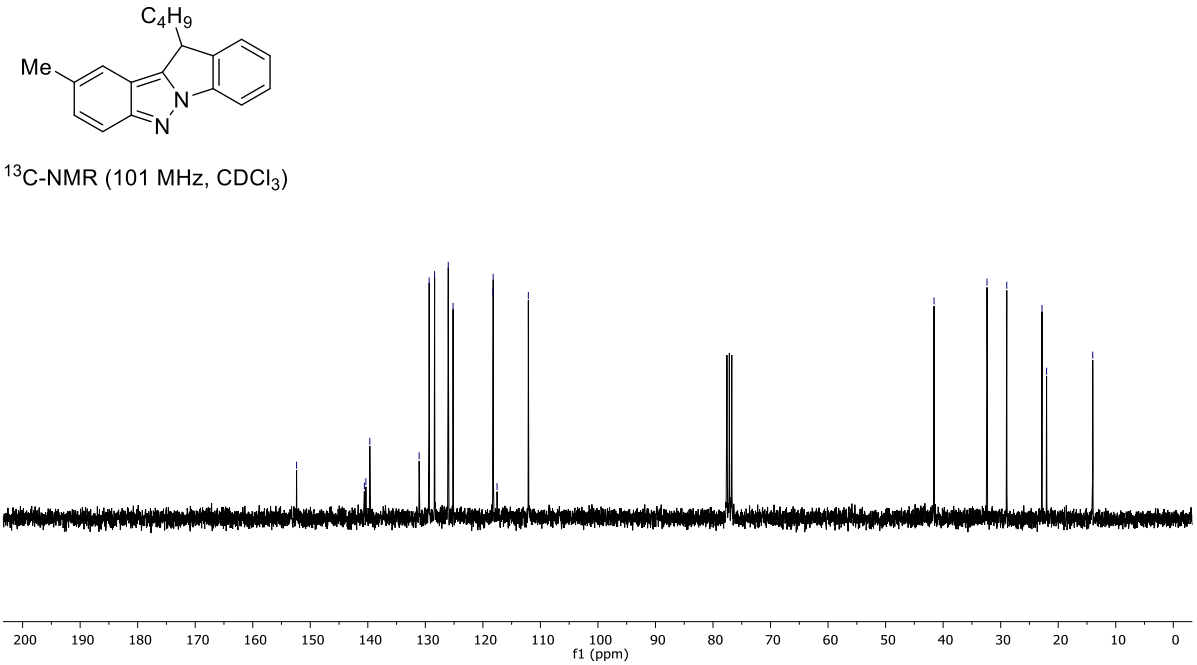


^{13}C-NMR (101 MHz, $CDCl_3$)

11-Butyl-9-methyl-11*H*-indolo[1,2-*b*]indazole (2q)

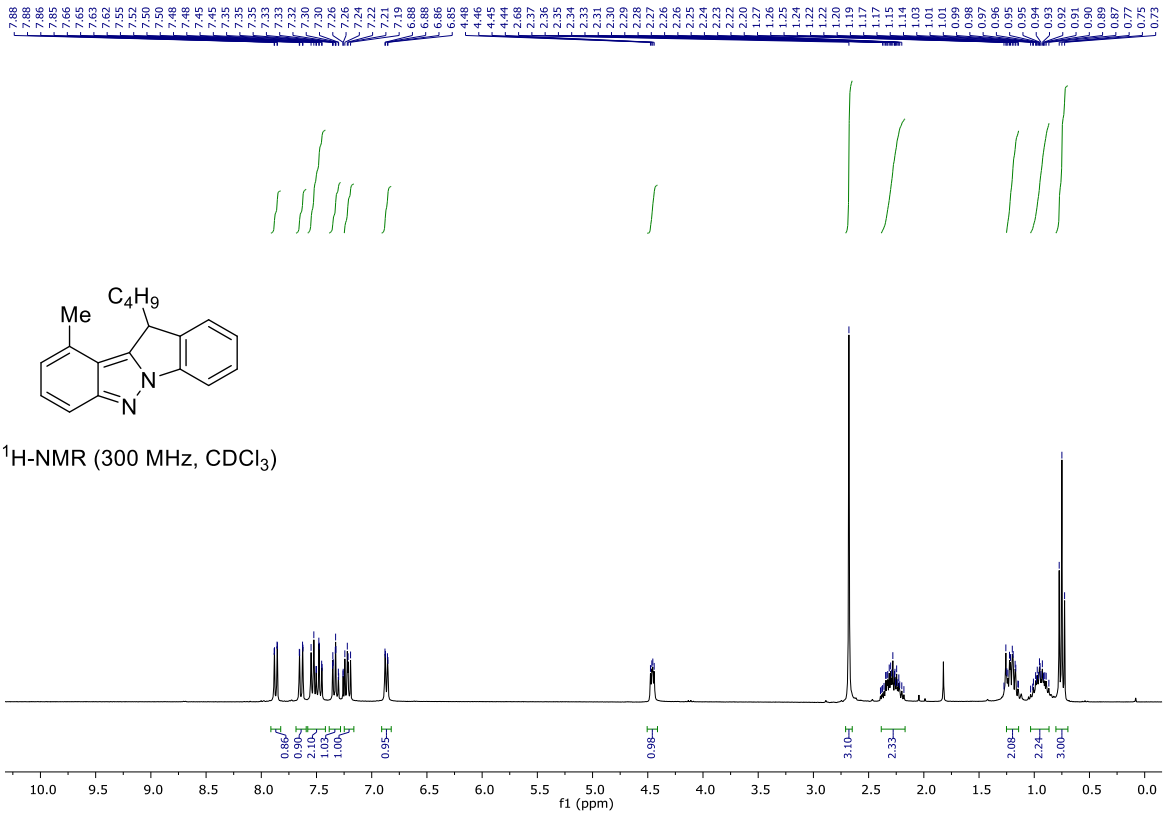


^{1}H-NMR (300 MHz, $CDCl_3$)

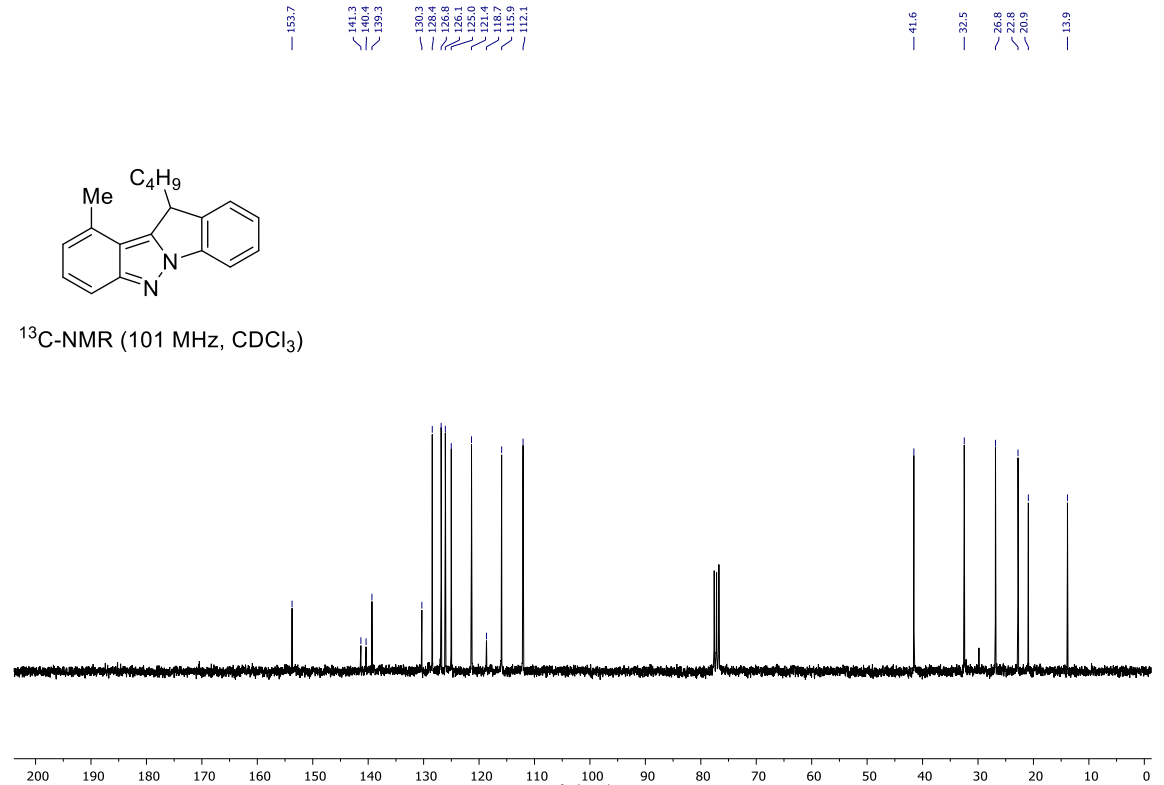


^{13}C-NMR (101 MHz, $CDCl_3$)

11-Butyl-10-methyl-11*H*-indolo[1,2-*b*]indazole (2r)

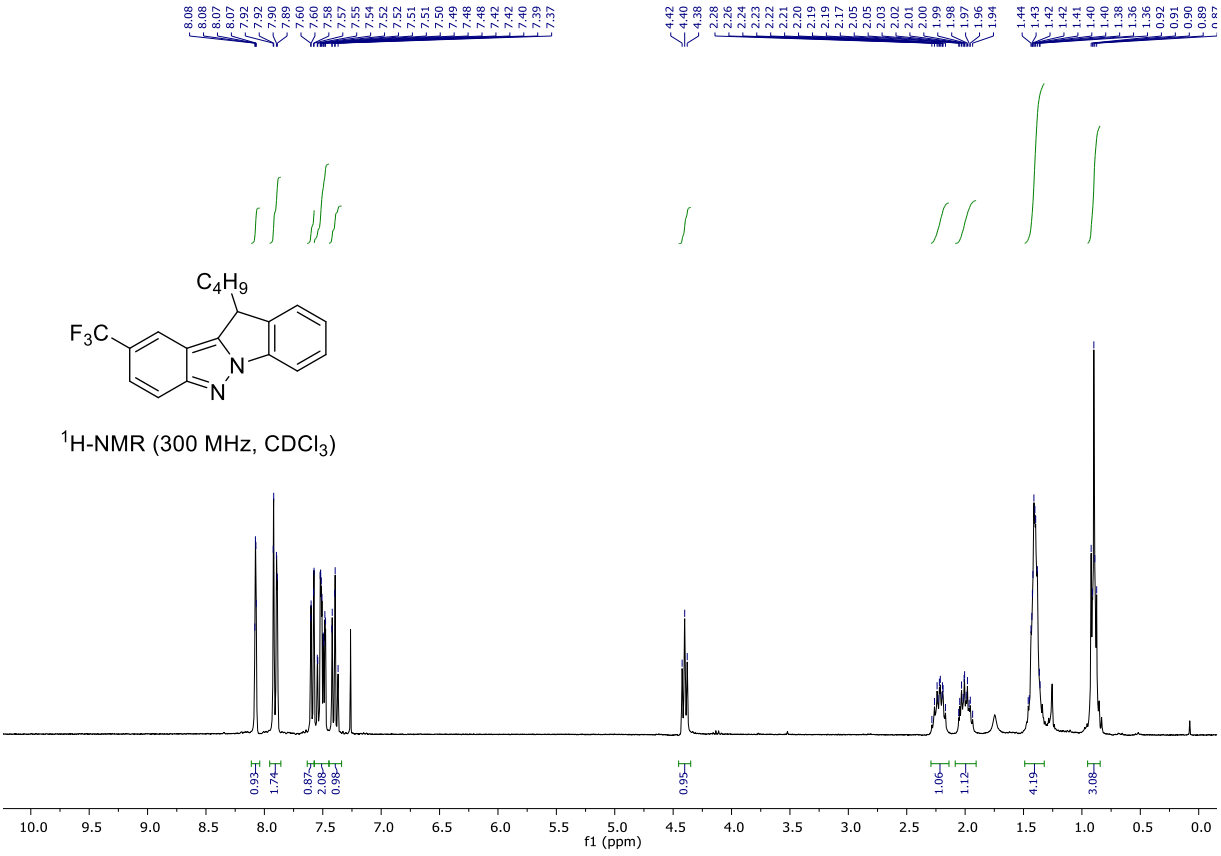


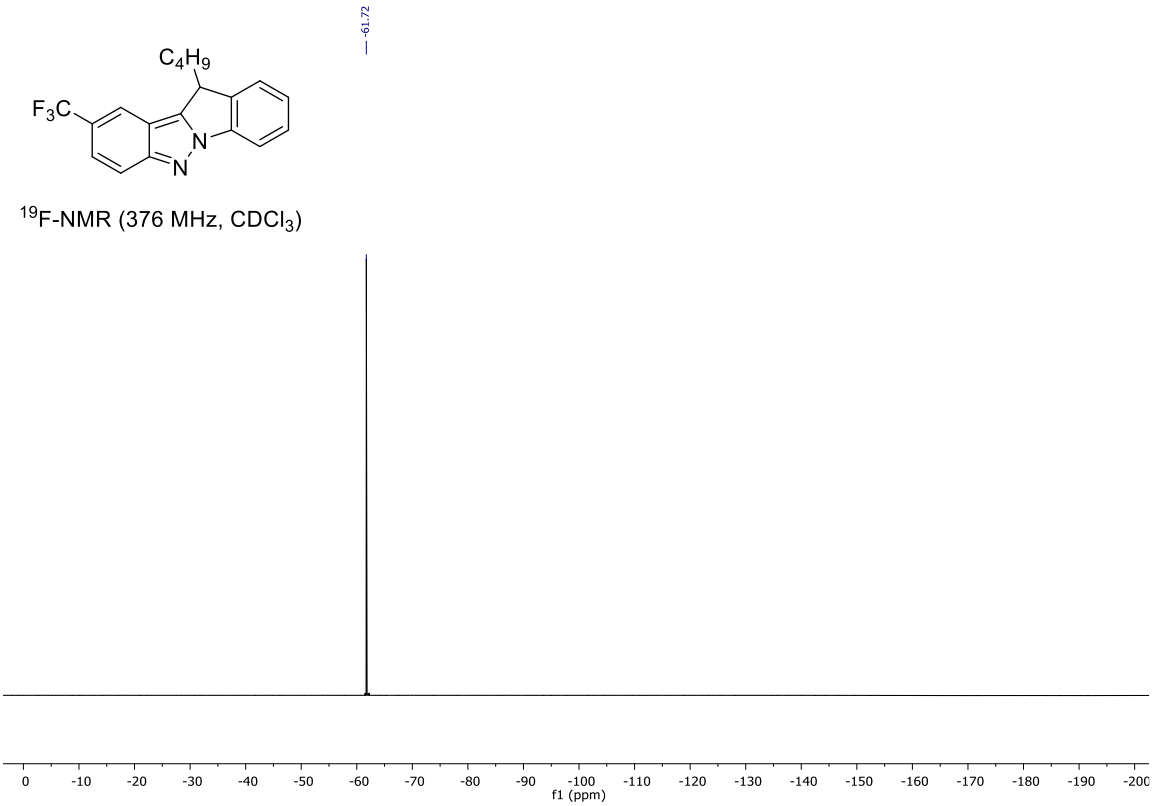
^{1}H-NMR (300 MHz, $CDCl_3$)

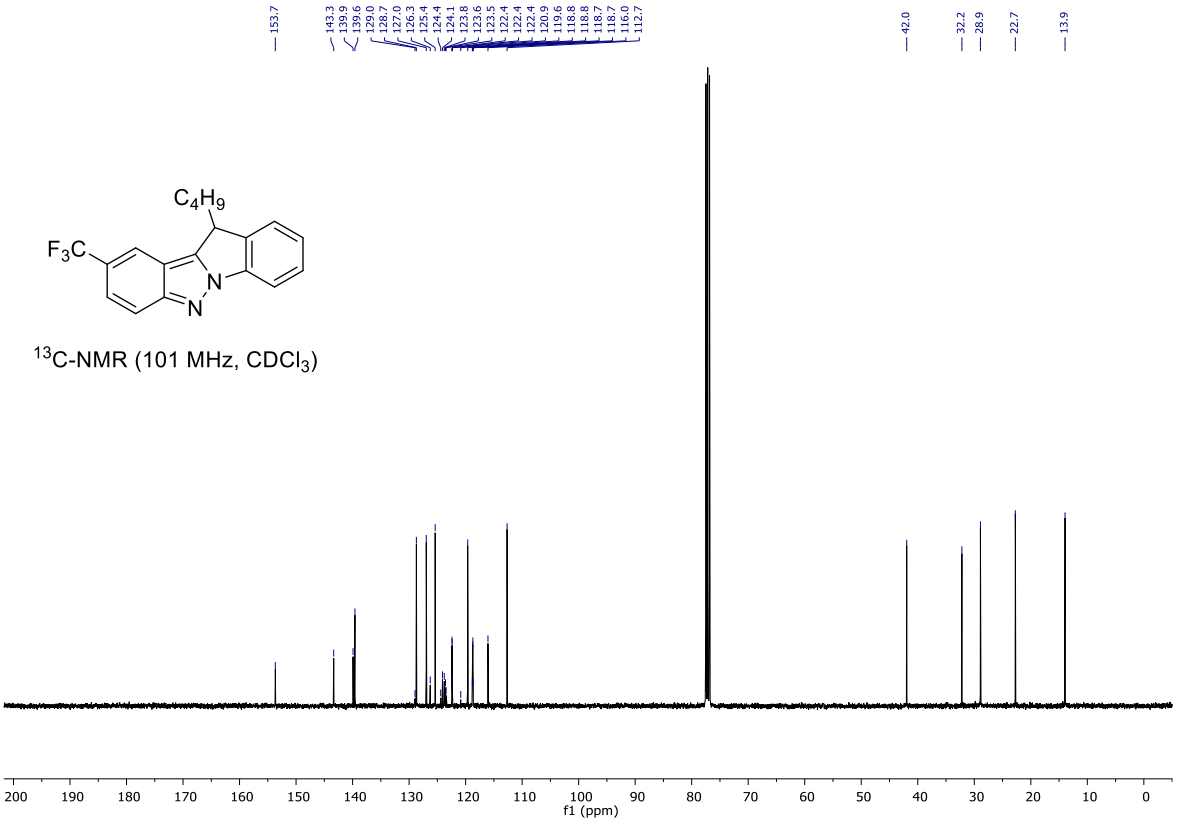


^{13}C-NMR (101 MHz, $CDCl_3$)

1-Butyl-9-(trifluoromethyl)-11*H*-indolo[1,2-*b*]indazole (2s)

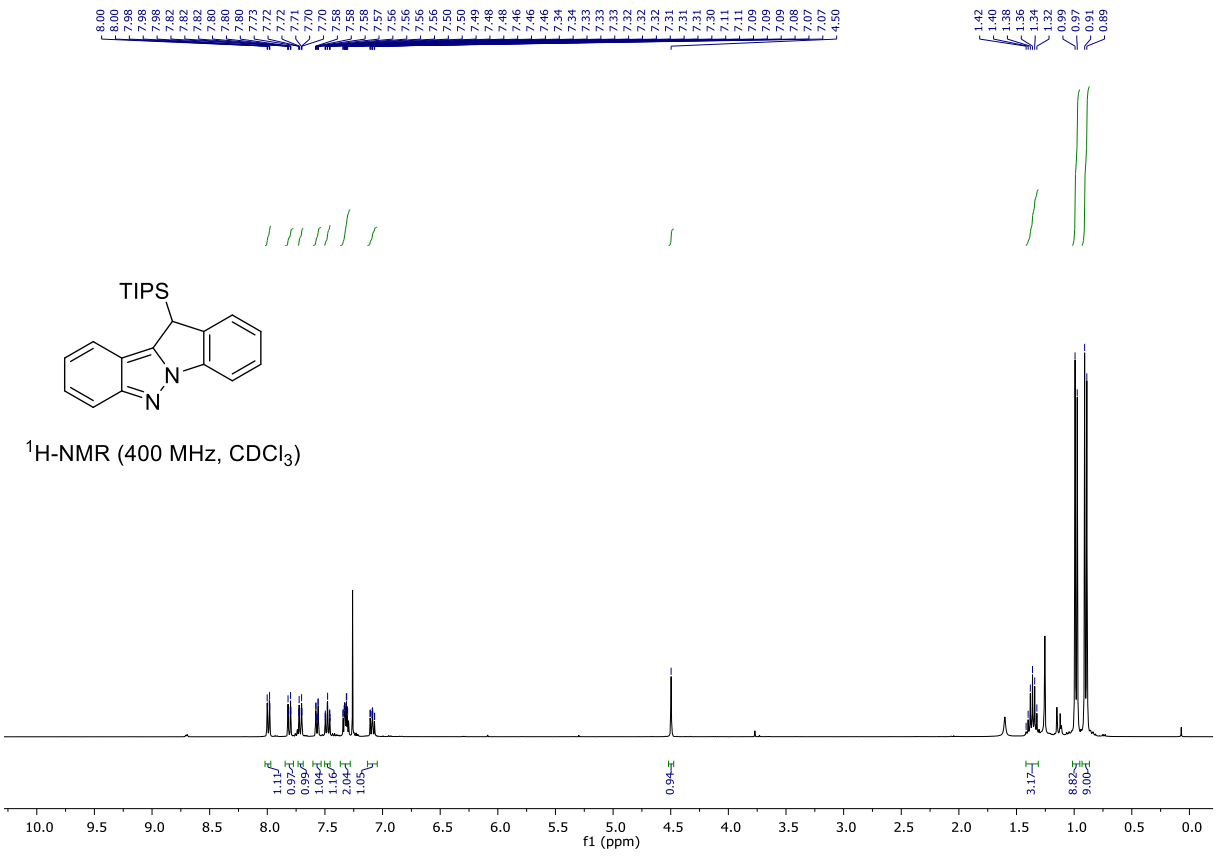




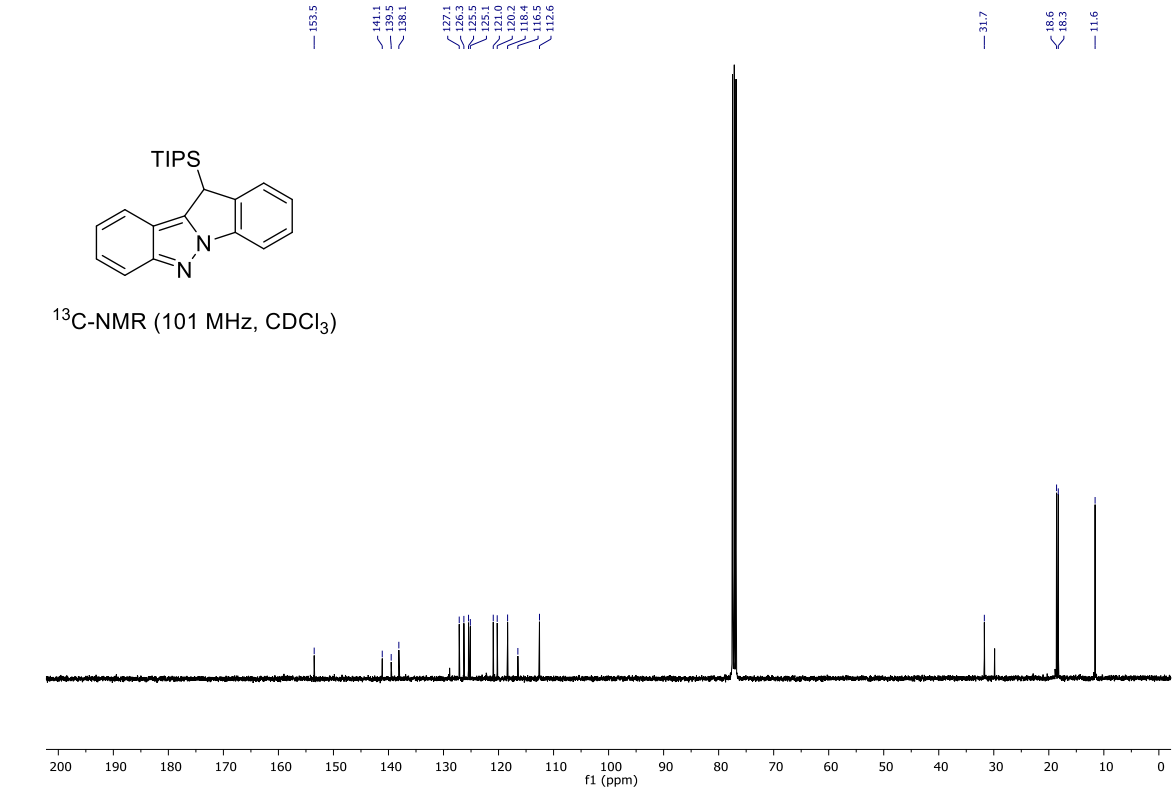


^{13}C-NMR (101 MHz, $CDCl_3$)

11-(Triisopropylsilyl)-11*H*-indolo[1,2-*b*]indazole (2t)

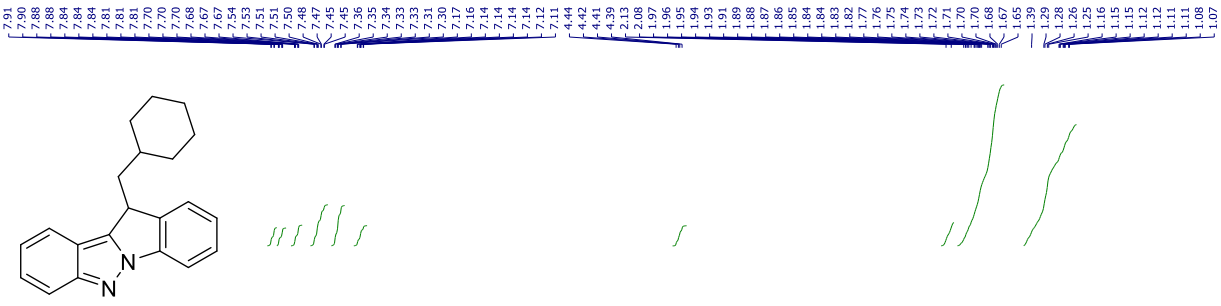


^{1}H-NMR (400 MHz, $CDCl_3$)

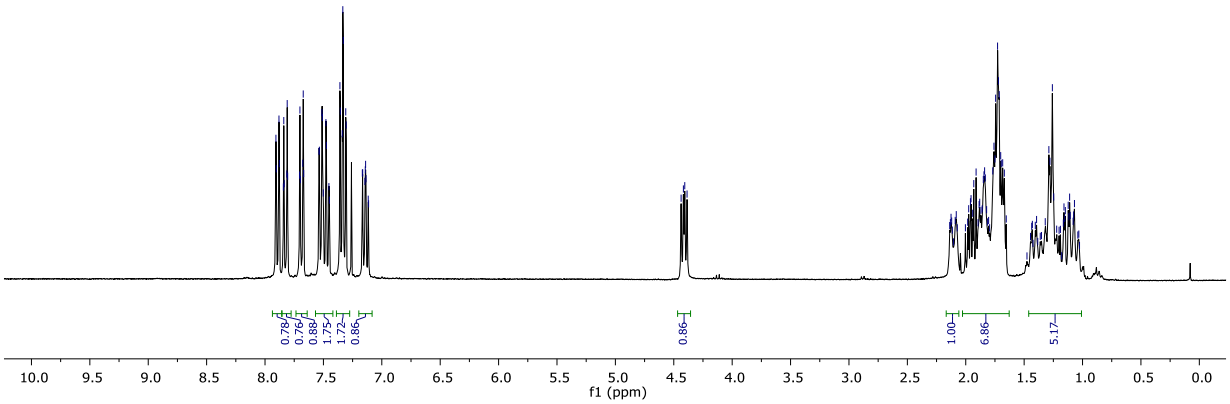


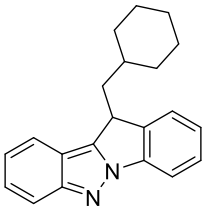
^{13}C-NMR (101 MHz, $CDCl_3$)

11-(Cyclohexylmethyl)-11*H*-indolo[1,2-*b*]indazole (2u)



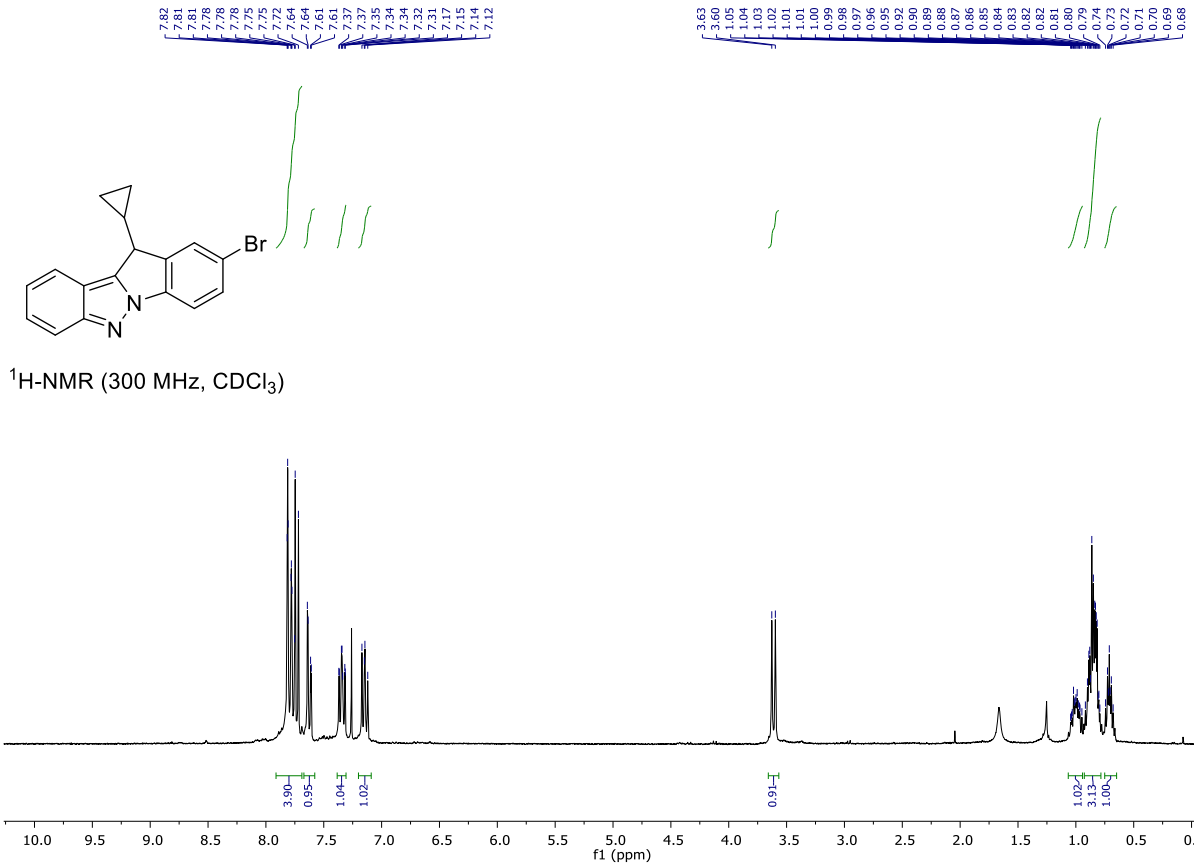
^{1}H-NMR (300 MHz, $CDCl_3$)



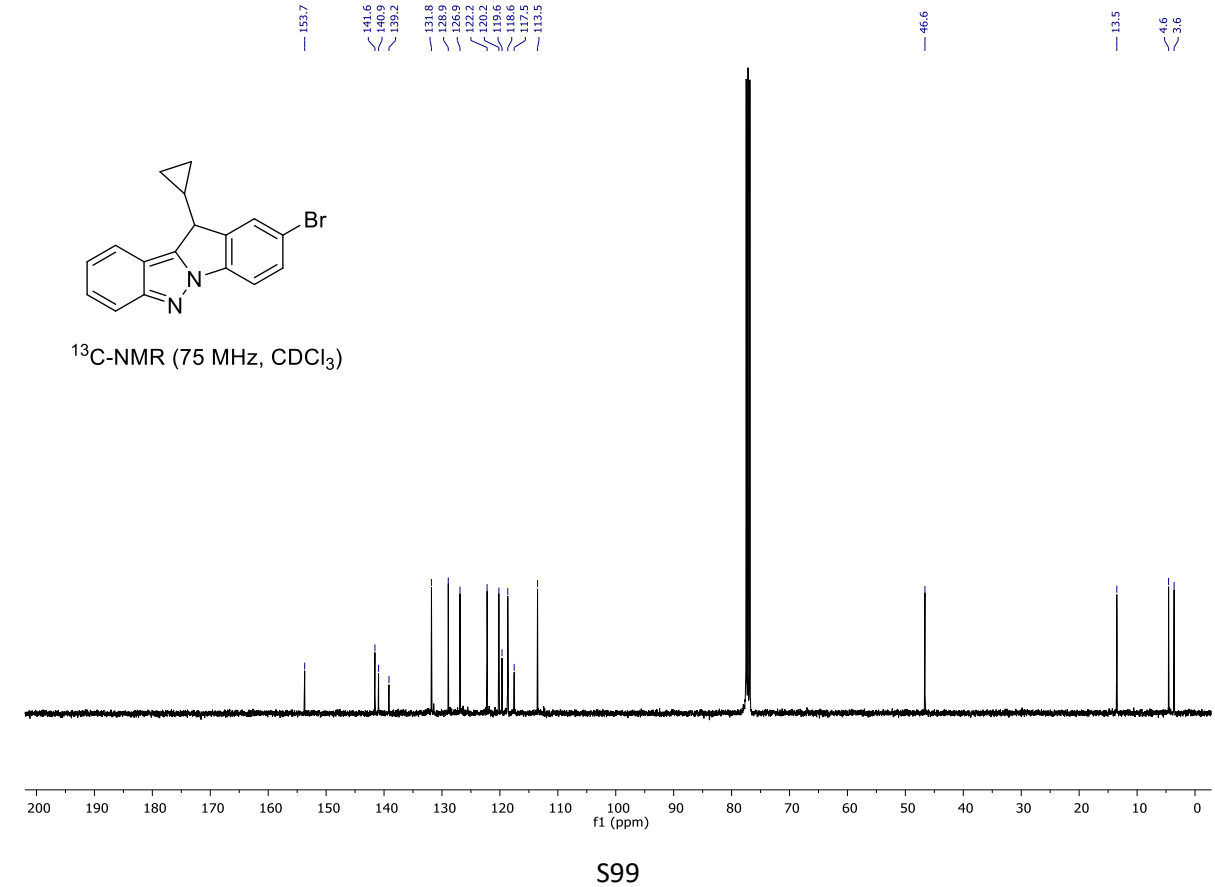


^{13}C-NMR (75 MHz, $CDCl_3$)

2-Bromo-11-cyclopropyl-11*H*-indolo[1,2-*b*]indazole (2v)

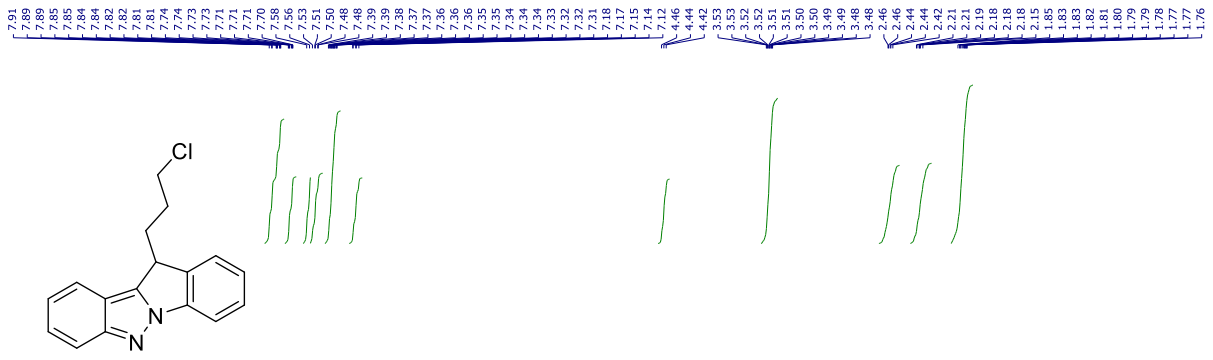


^{1}H-NMR (300 MHz, $CDCl_3$)

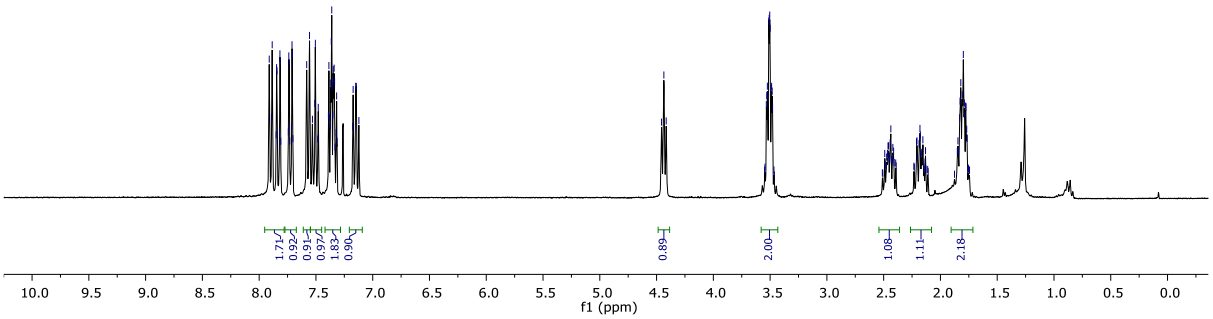


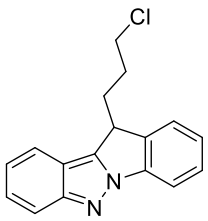
^{13}C-NMR (75 MHz, $CDCl_3$)

11-(3-Chloropropyl)-11*H*-indolo[1,2-*b*]indazole (2w)



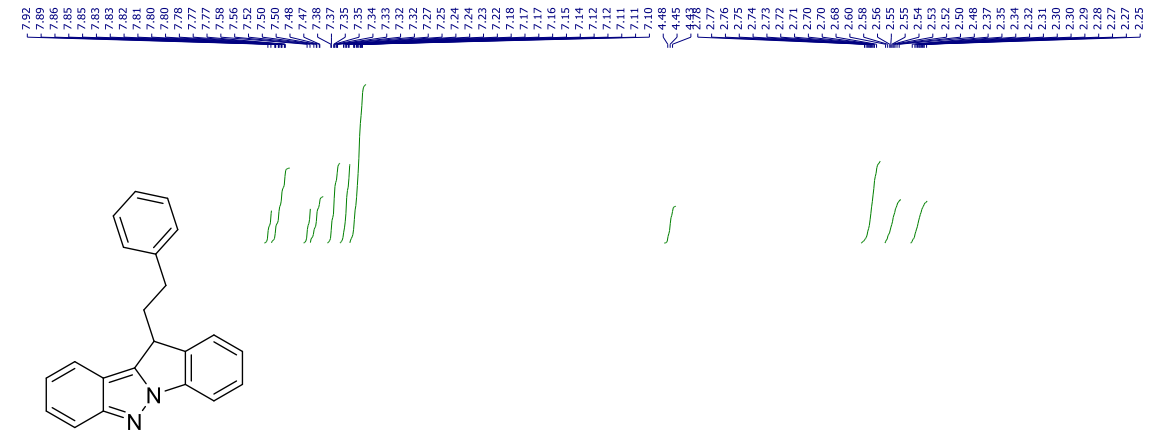
^{1}H-NMR (300 MHz, $CDCl_3$)



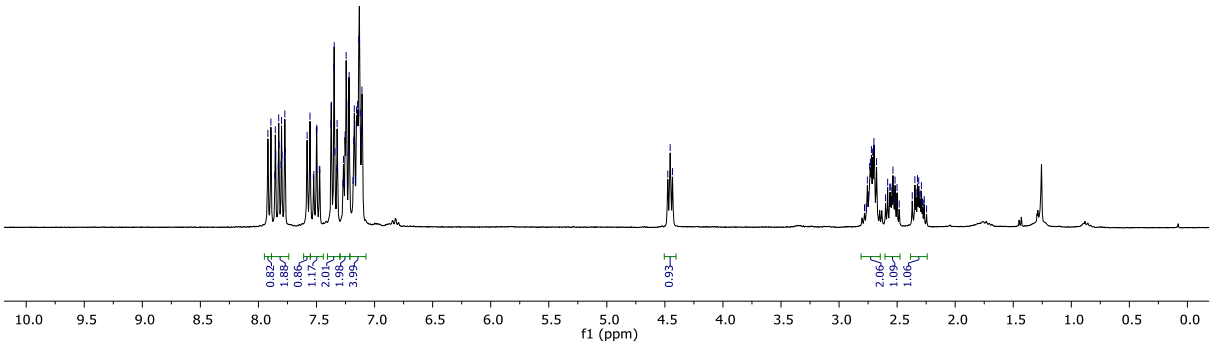


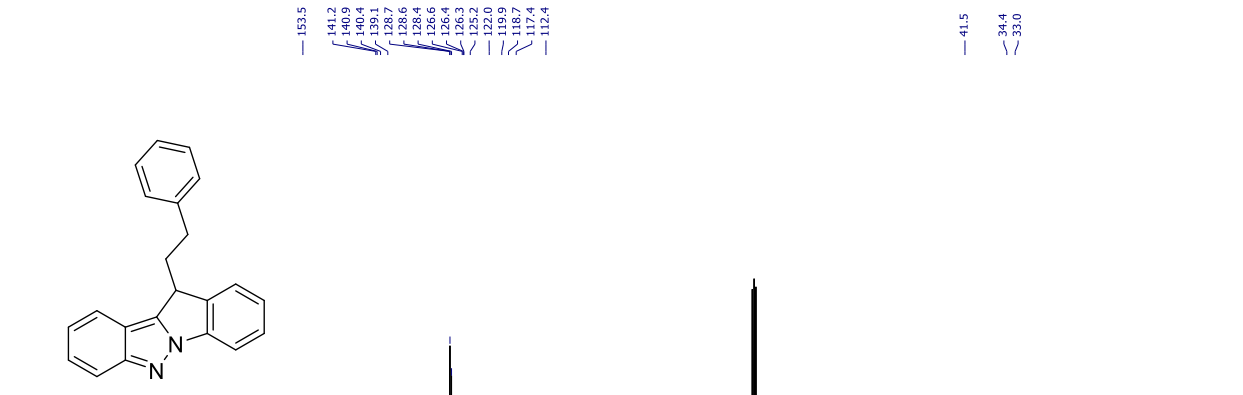
^{13}C-NMR (101 MHz, $CDCl_3$)

11-Phenethyl-11*H*-indolo[1,2-*b*]indazole (2x)

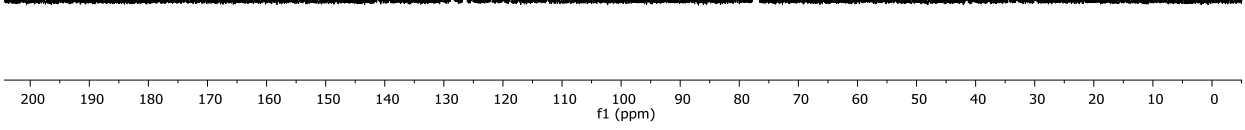


^{1}H-NMR (300 MHz, $CDCl_3$)

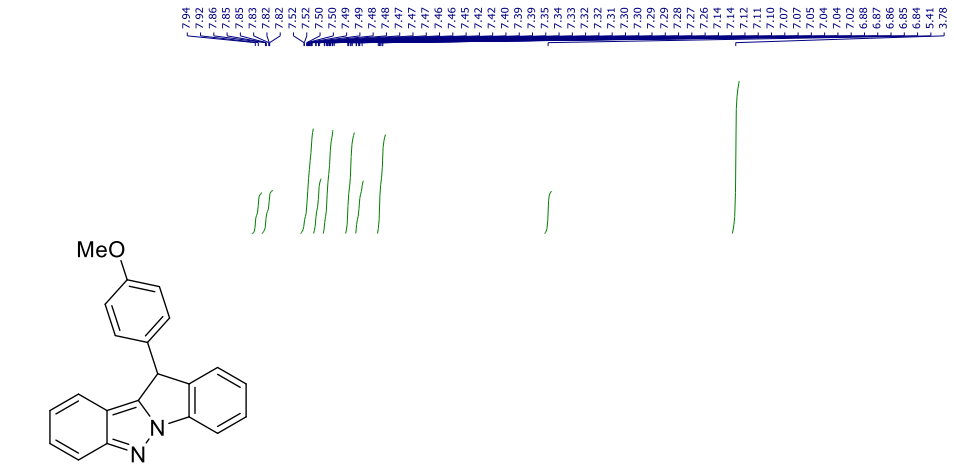




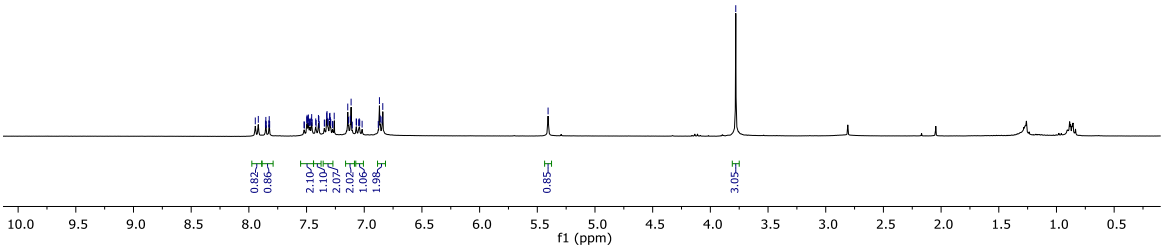
^{13}C-NMR (101 MHz, $CDCl_3$)

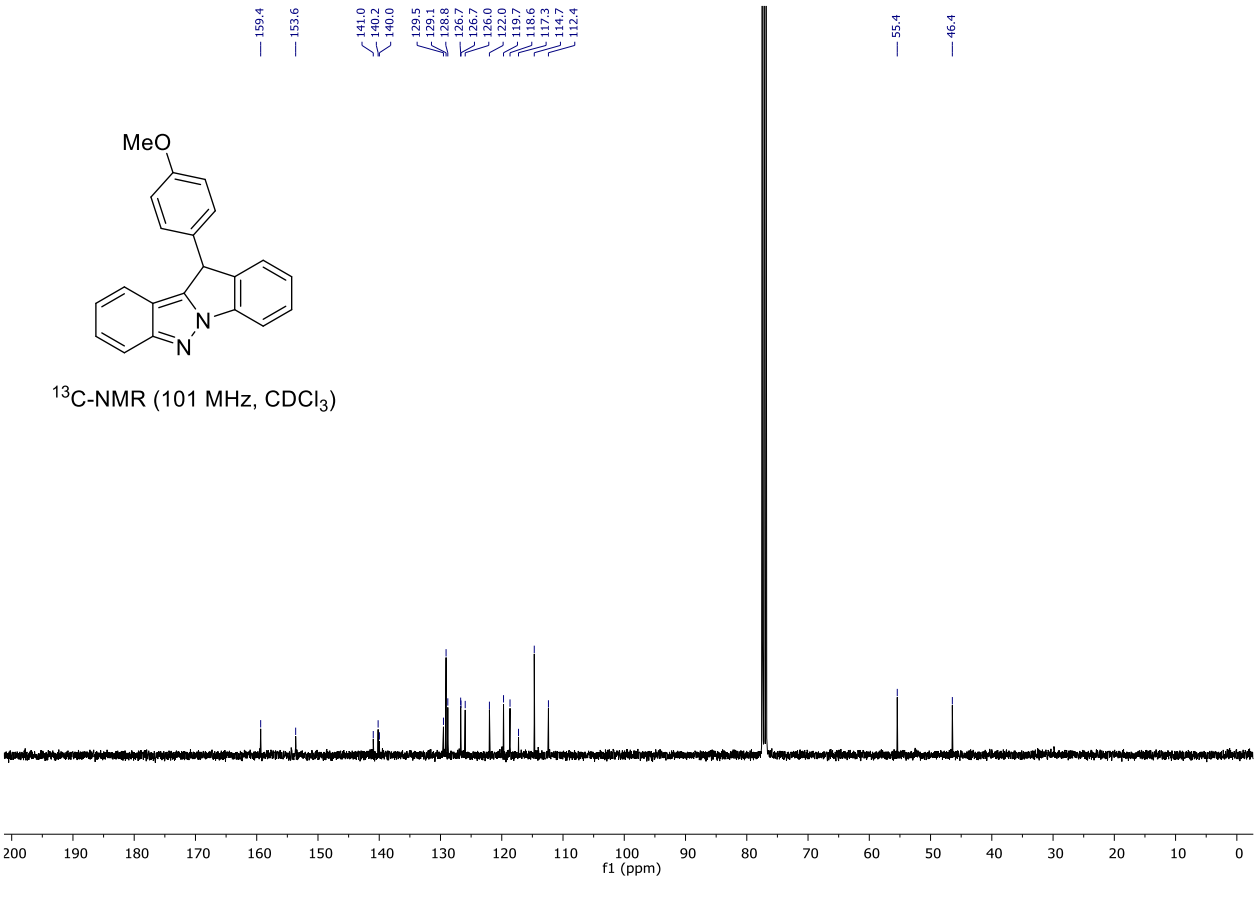


11-(4-Methoxyphenyl)-11*H*-indolo[1,2-*b*]indazole (2y)



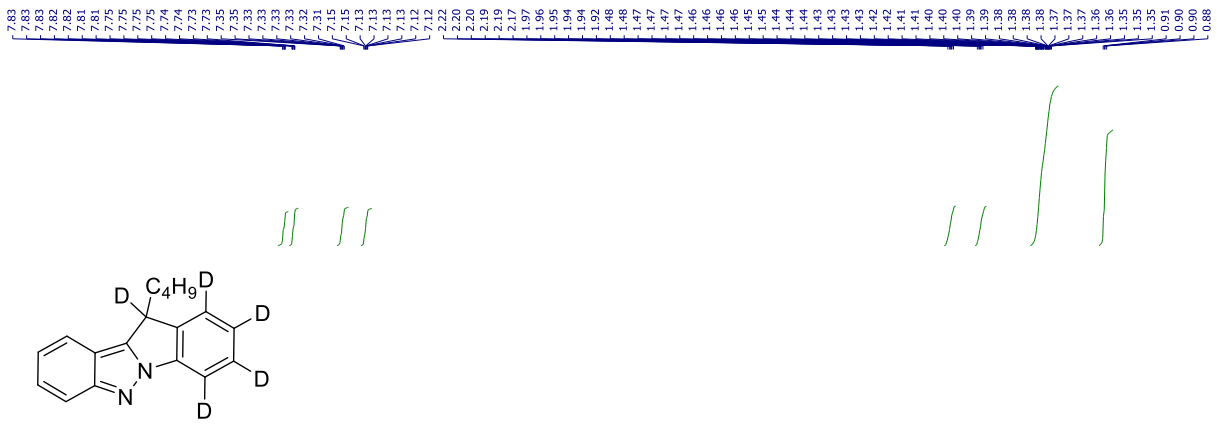
^{1}H-NMR (300 MHz, $CDCl_3$)



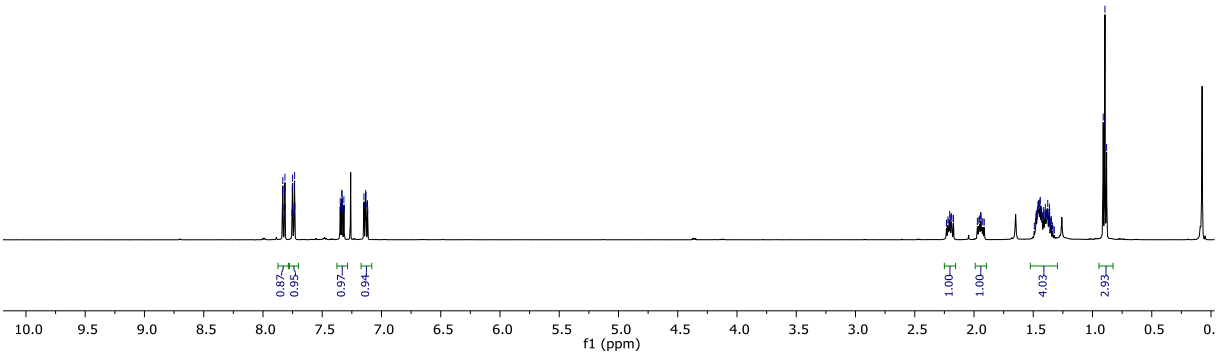


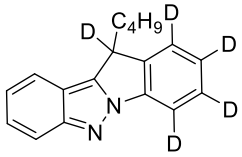
^{13}C-NMR (101 MHz, $CDCl_3$)

11-Butyl-11*H*-indolo[1,2-*b*]indazole-1,2,3,4,11-*d*5 (2a-d_5)

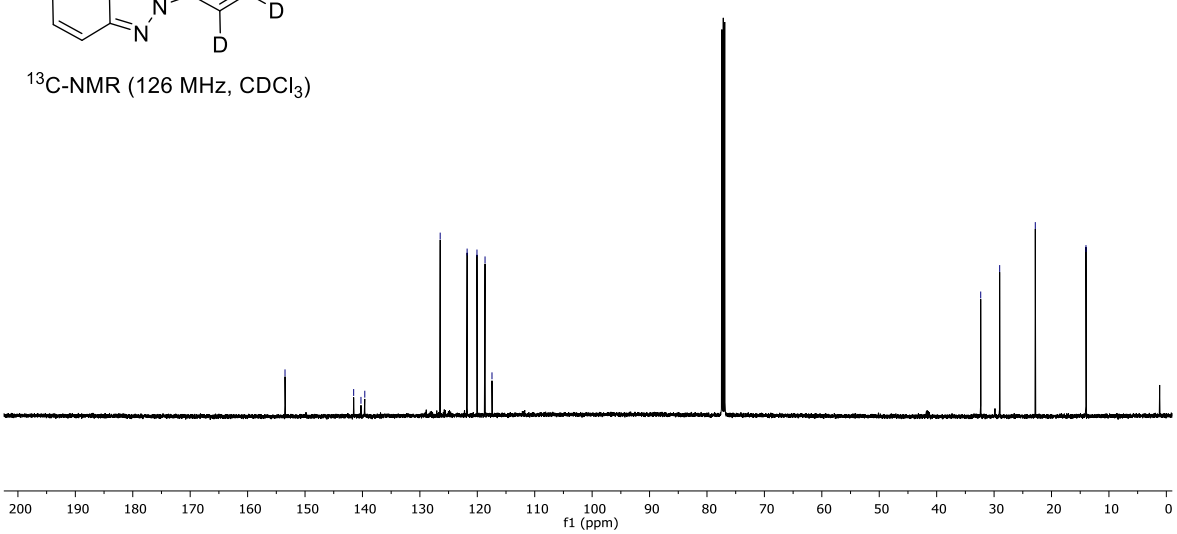


^{1}H-NMR (300 MHz, $CDCl_3$)

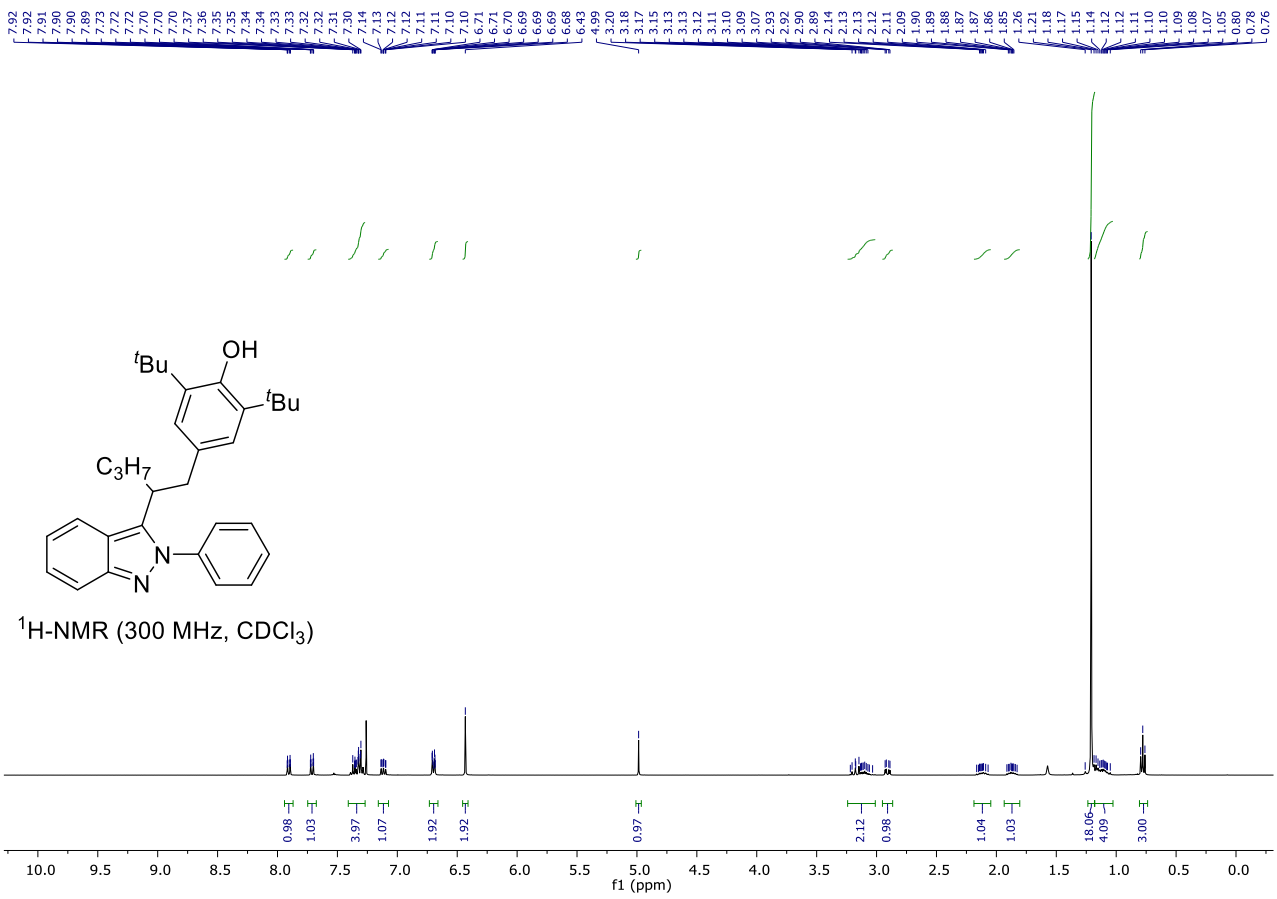




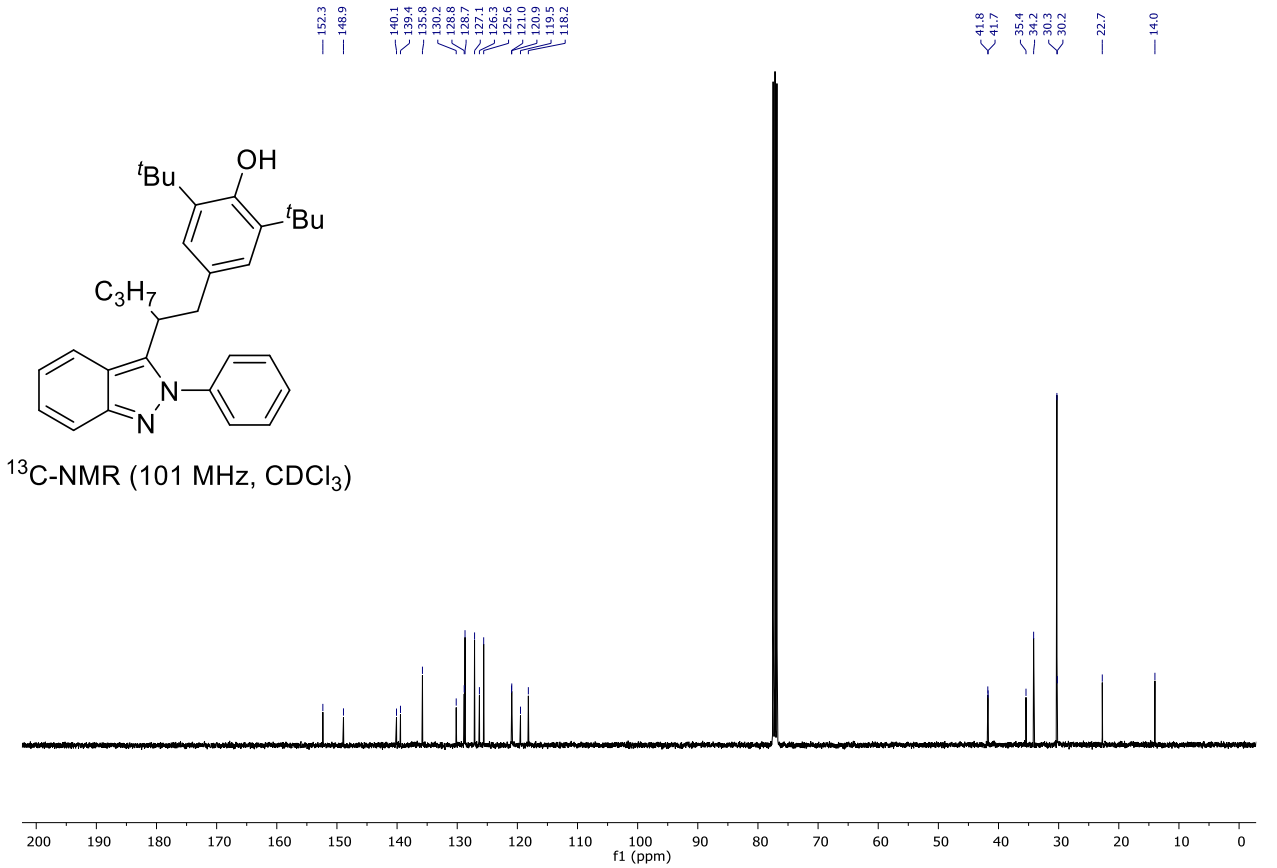
^{13}C-NMR (126 MHz, $CDCl_3$)



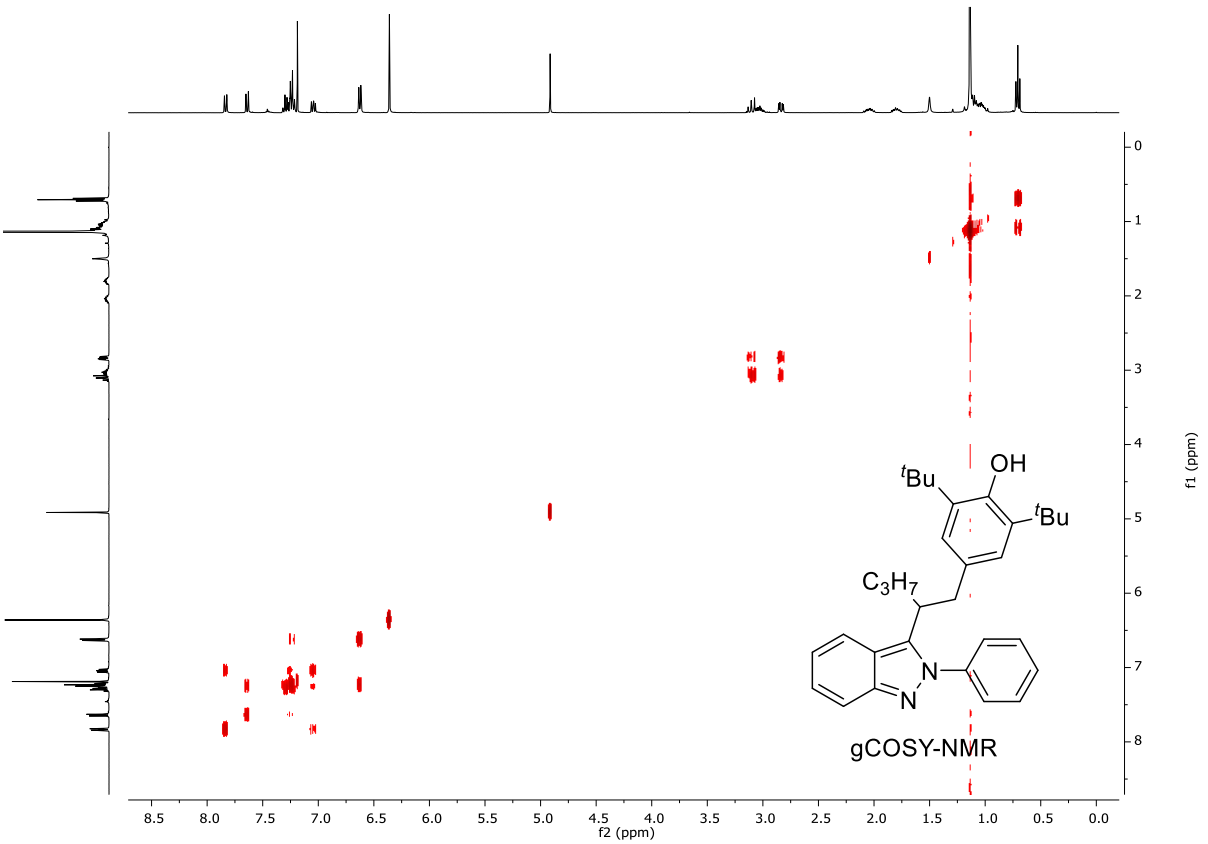
2,6-Di-tert-butyl-4-(2-(2-phenyl-2*H*-indazol-3-yl)hexyl)phenol (6)

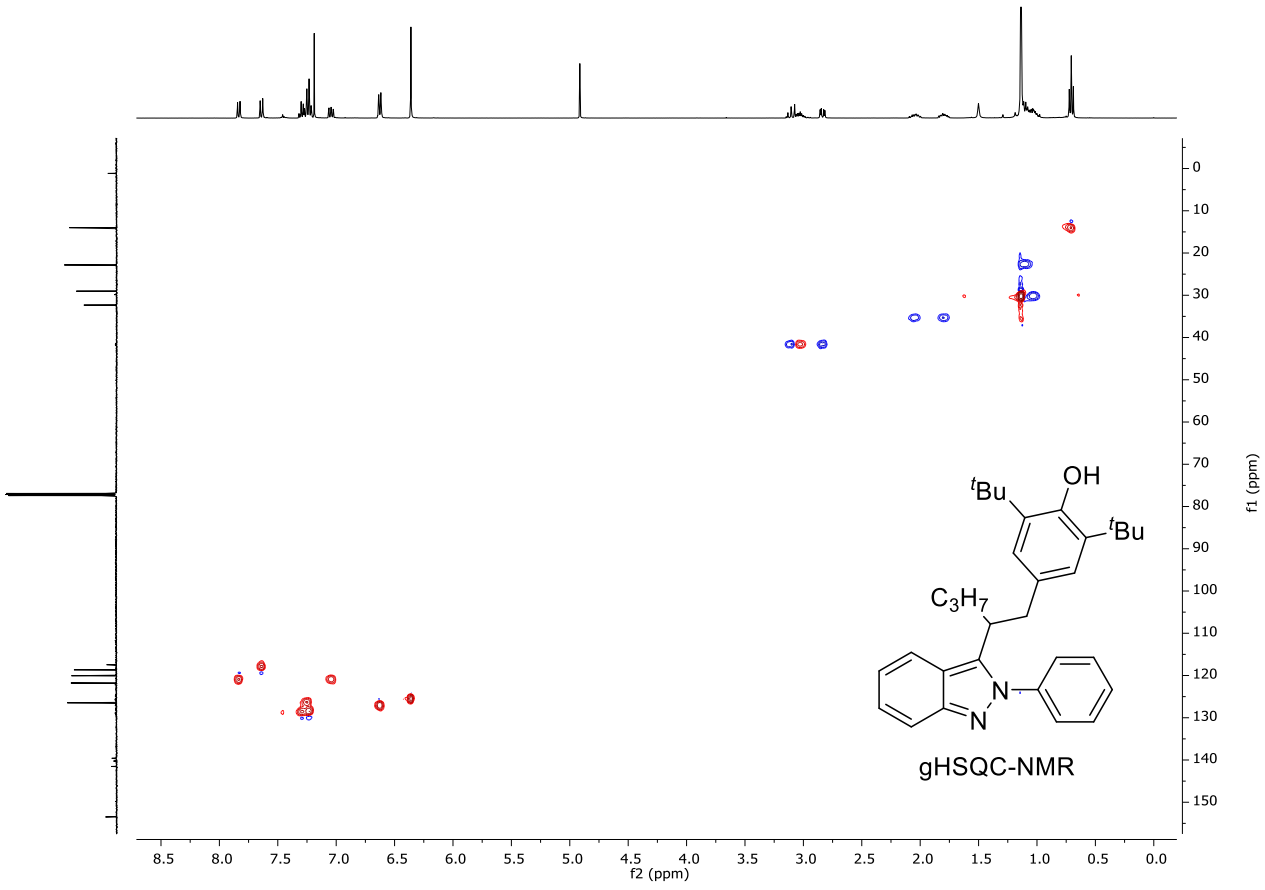


^{1}H-NMR (300 MHz, $CDCl_3$)



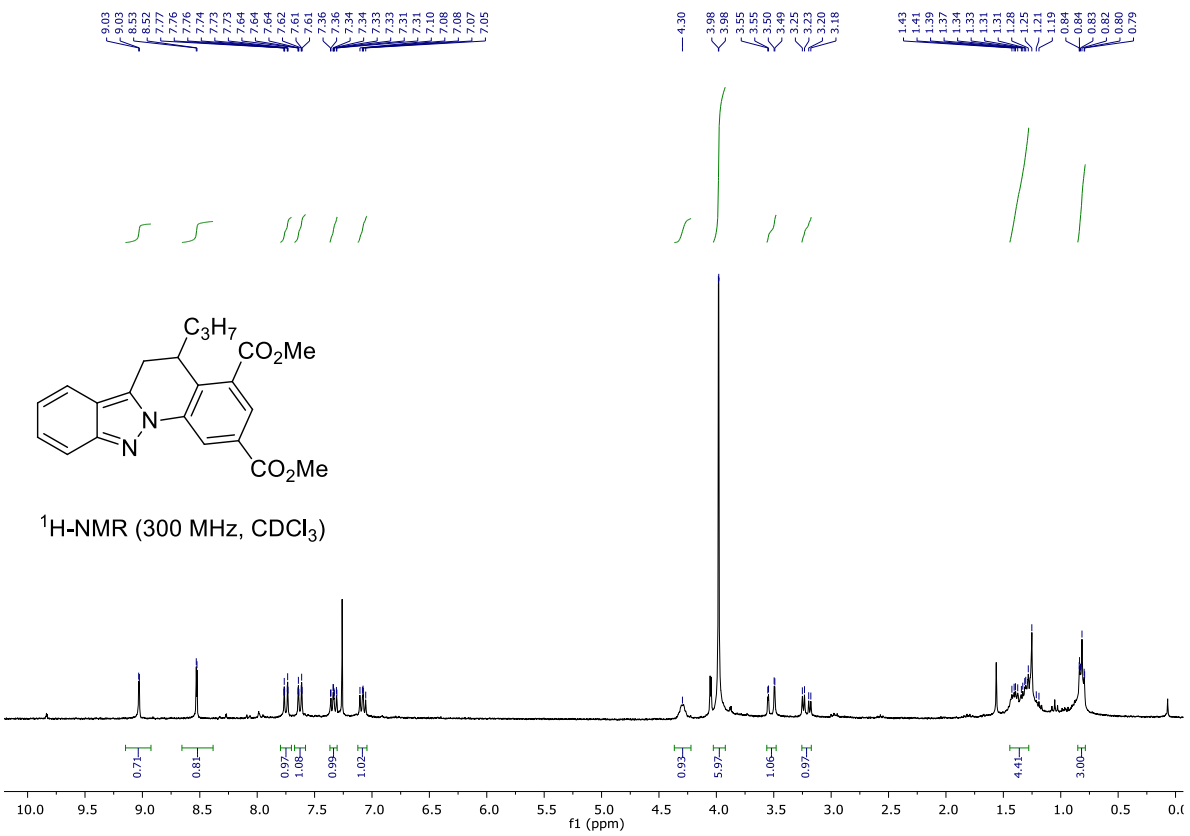
^{13}C-NMR (101 MHz, $CDCl_3$)


OH
tBu
tBu
C3H7
N
N
gCOSY-NMR
f2 (ppm)
f1 (ppm)

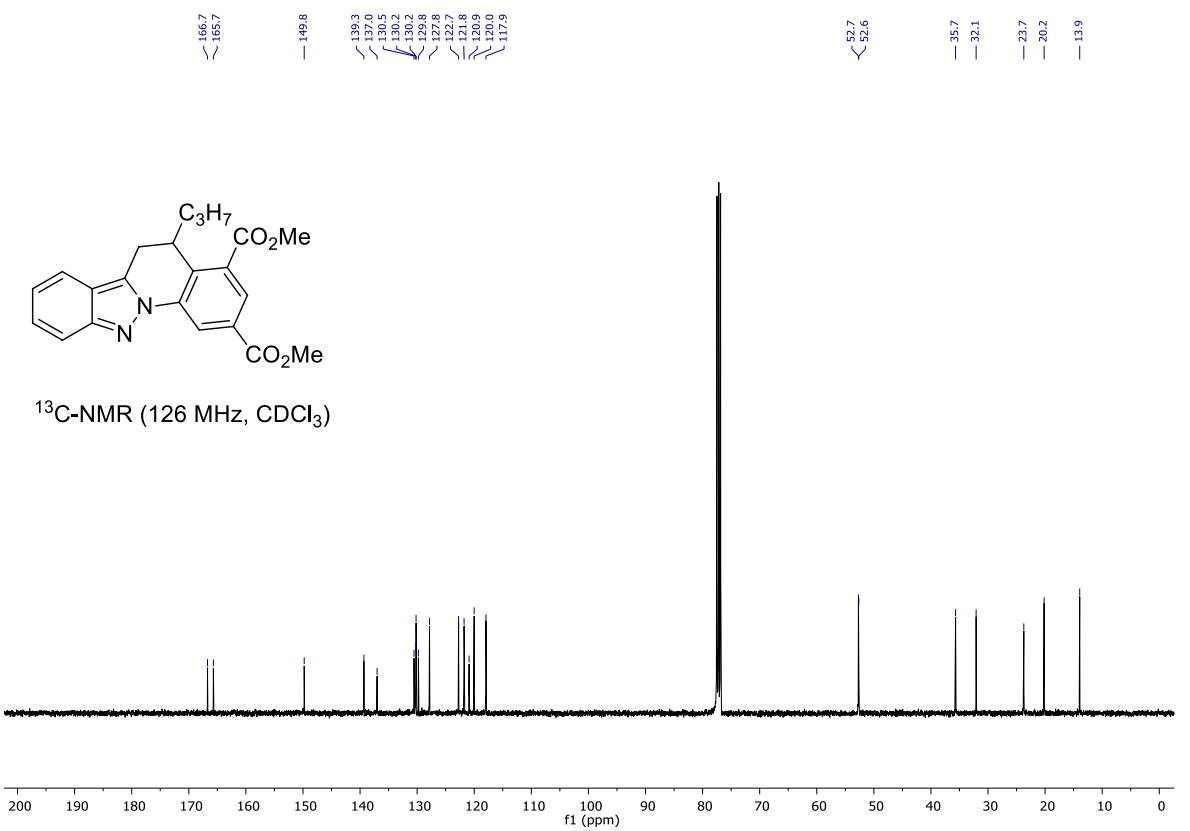

OH
tBu
tBu
C3H7
N
N
gHSQC-NMR
f2 (ppm)
f1 (ppm)

5,6-Dihydroindazolo[2,3-*a*]quinolines 3

Dimethyl 5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-2,4-dicarboxylate (3j)

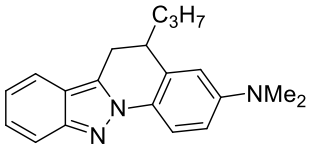


^{1}H-NMR (300 MHz, $CDCl_3$)

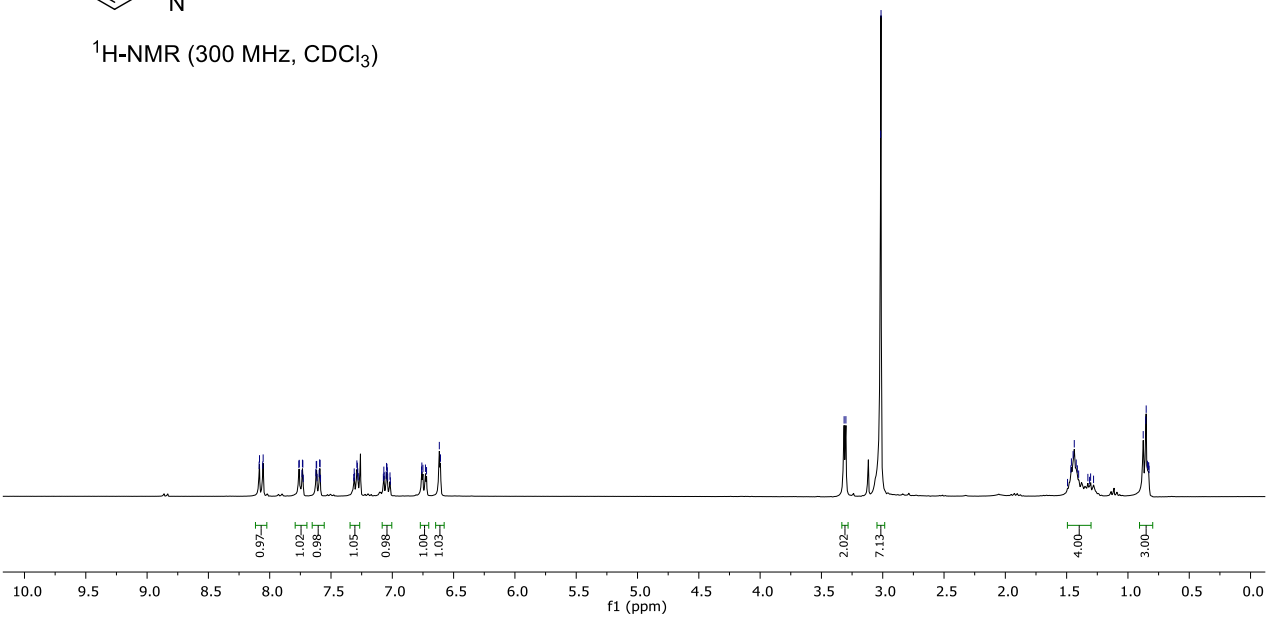


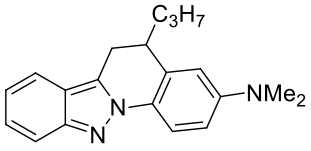
^{13}C-NMR (126 MHz, $CDCl_3$)

N,N-Dimethyl-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinolin-3-amine (3m)

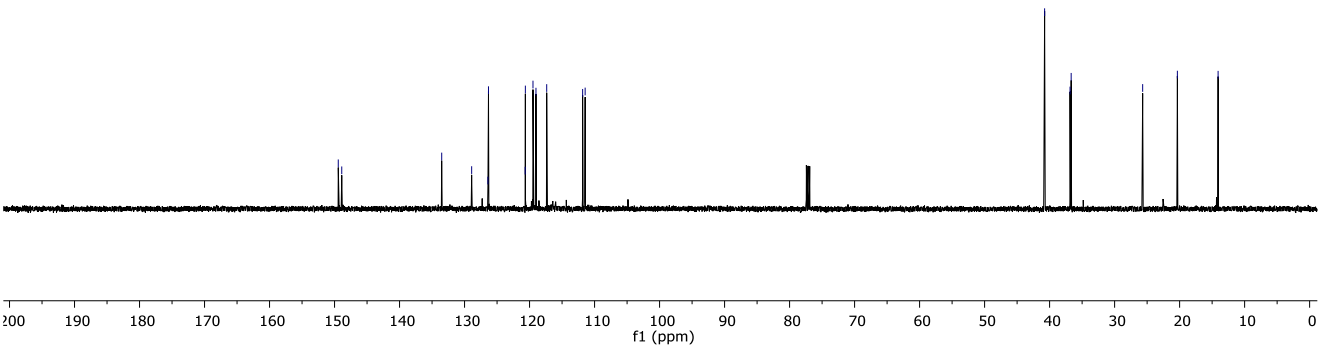


^{1}H-NMR (300 MHz, $CDCl_3$)

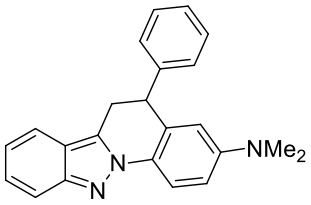




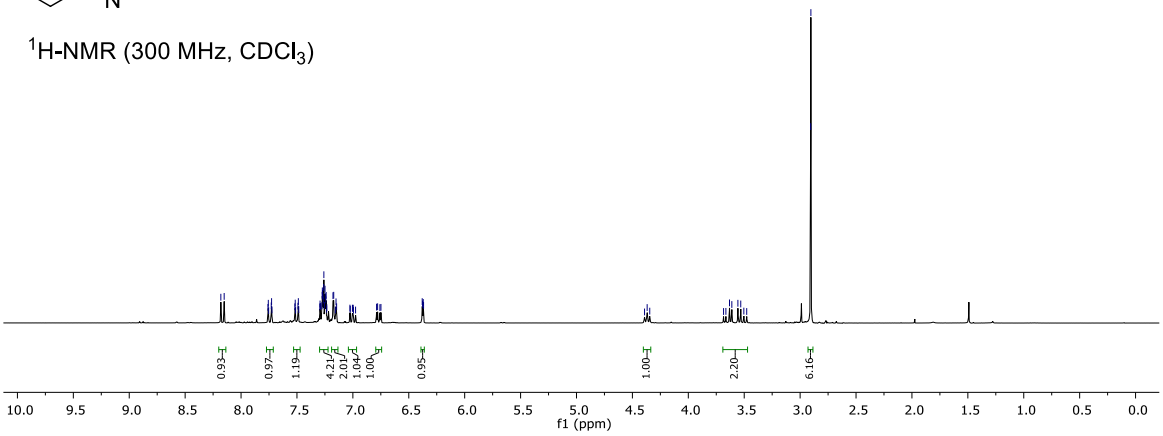
^{13}C-NMR (75 MHz, $CDCl_3$)

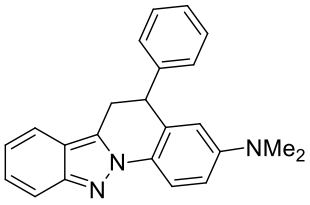


N,*N*-dimethyl-5-phenyl-5,6-dihydroindazolo[2,3-*a*]quinolin-3-amine (3ag)

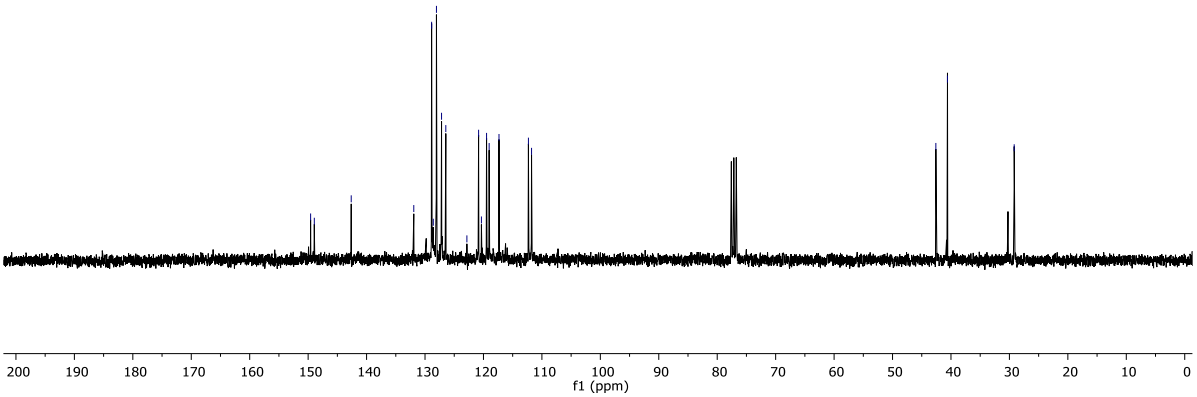


^{1}H-NMR (300 MHz, $CDCl_3$)



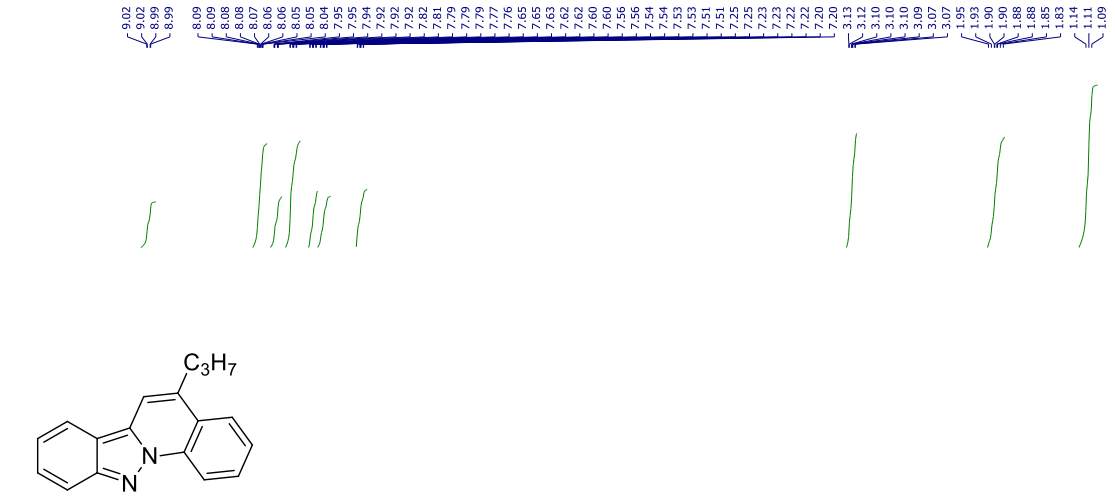


^{13}C-NMR (75 MHz, $CDCl_3$)

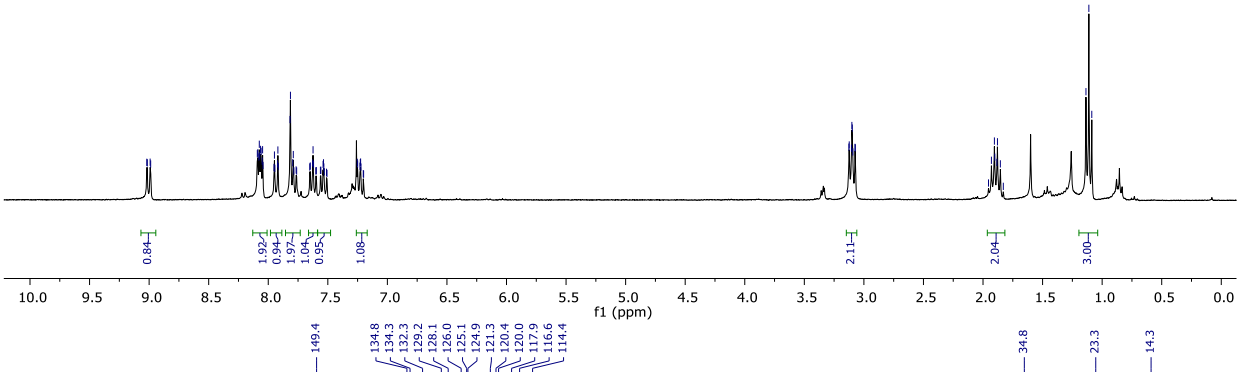


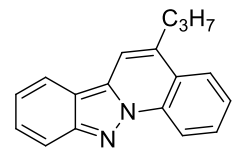
Indazolo[2,3-*a*]quinolines 4

5-Propylindazolo[2,3-*a*]quinoline (4a)

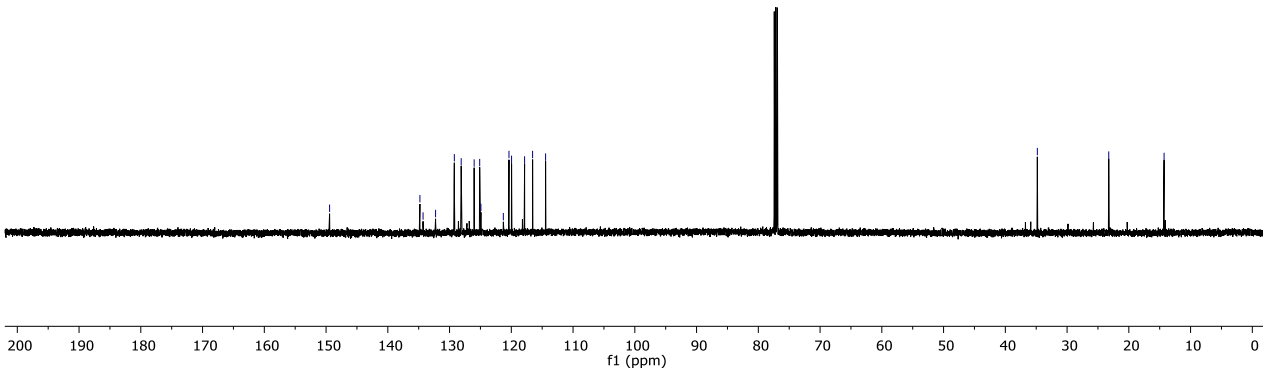


^{1}H-NMR (300 MHz, $CDCl_3$)

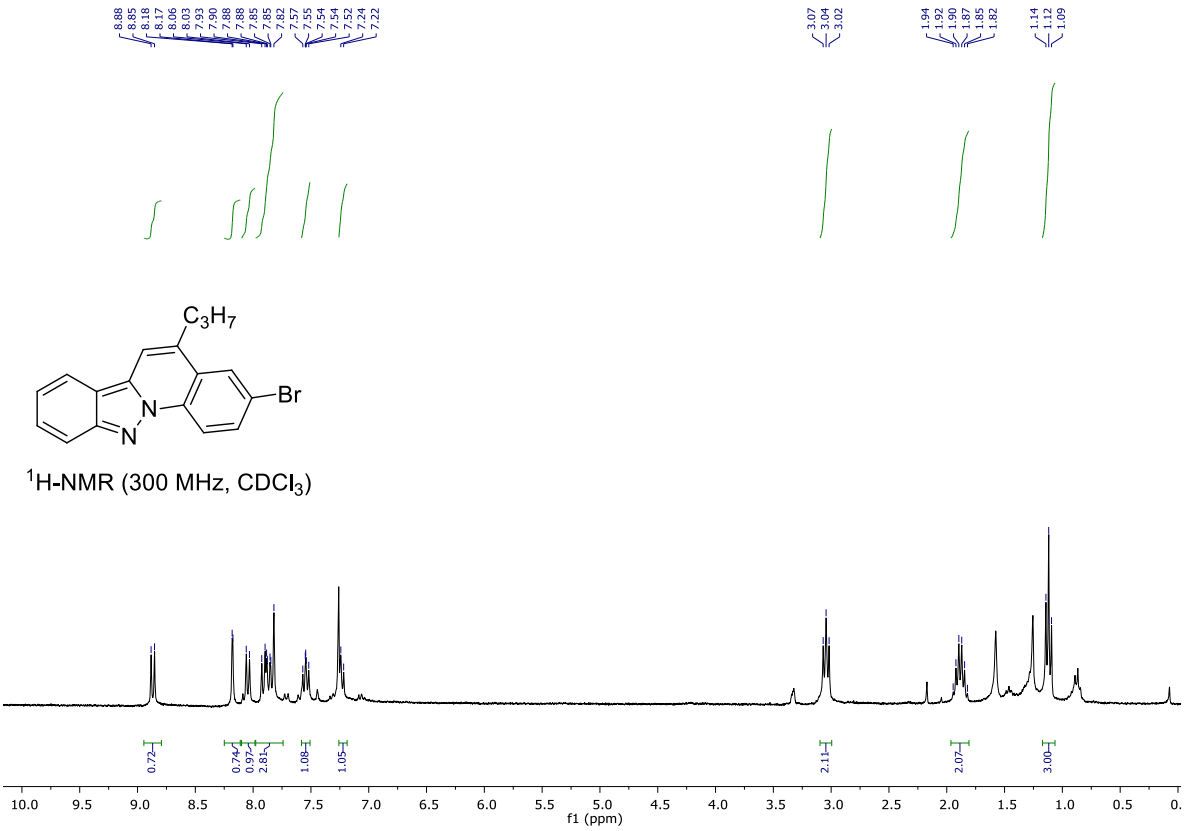


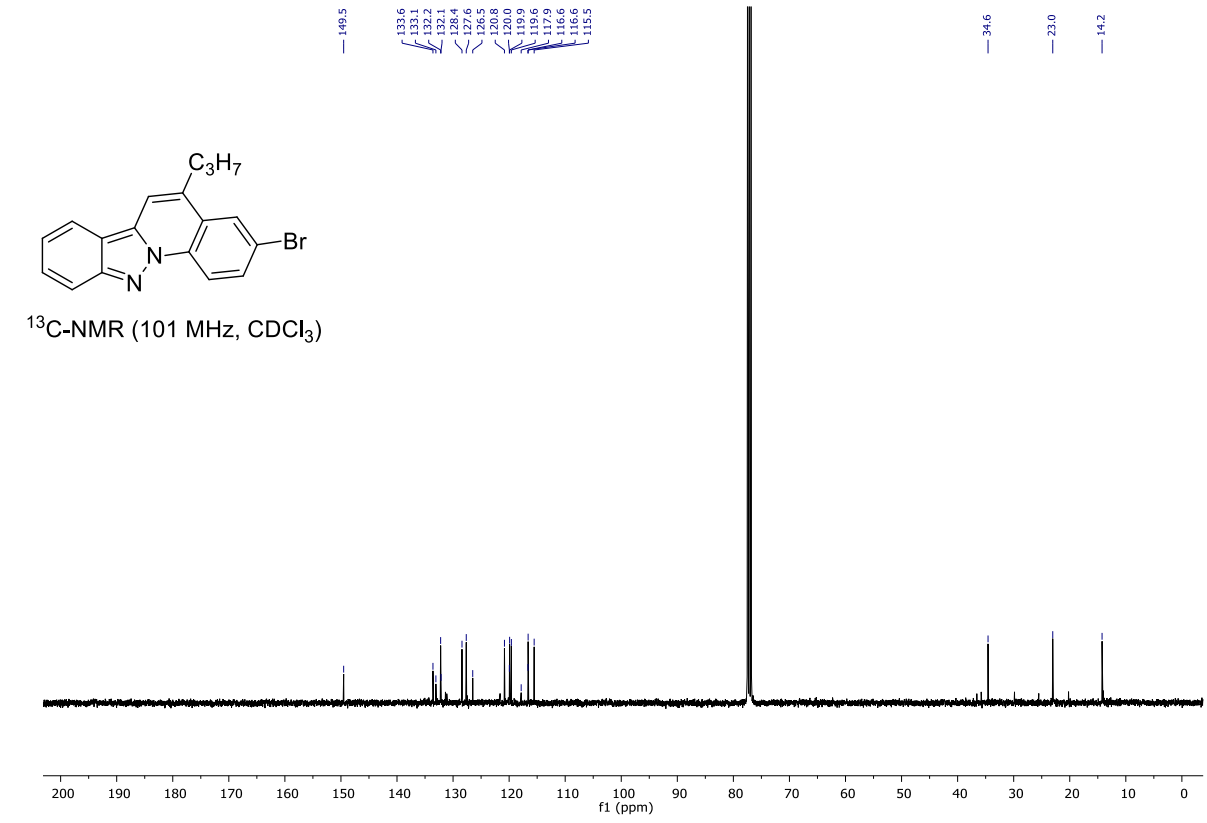


^{13}C-NMR (126 MHz, $CDCl_3$)

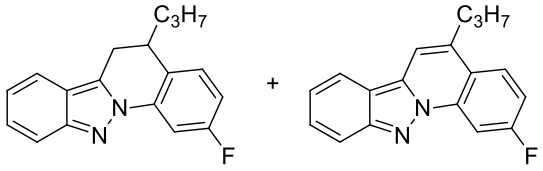


3-Bromo-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 3-bromo-5-propylindazolo[2,3-*a*]quinoline (3b and 4b)

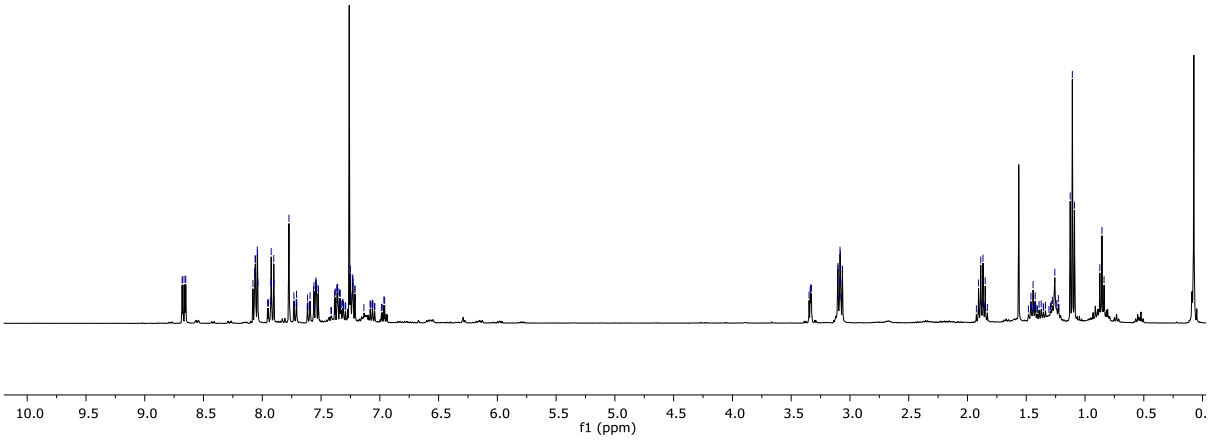


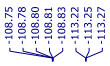


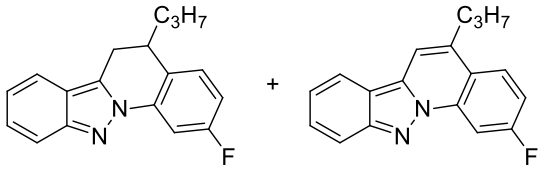
2-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 2-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3d and 4d)



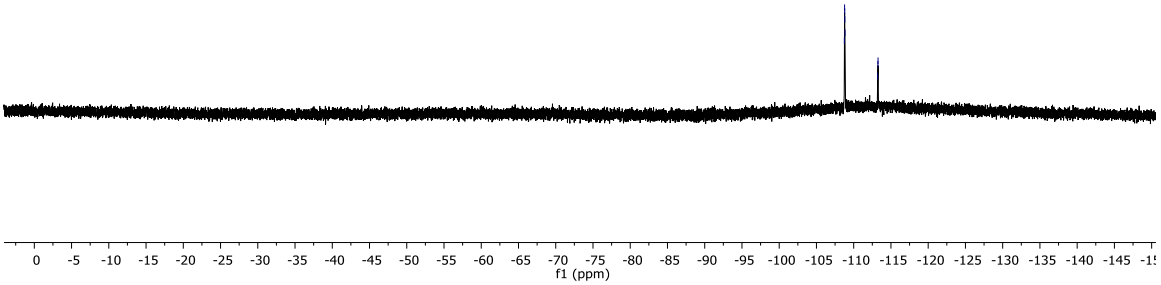
^{1}H-NMR (400 MHz, $CDCl_3$)

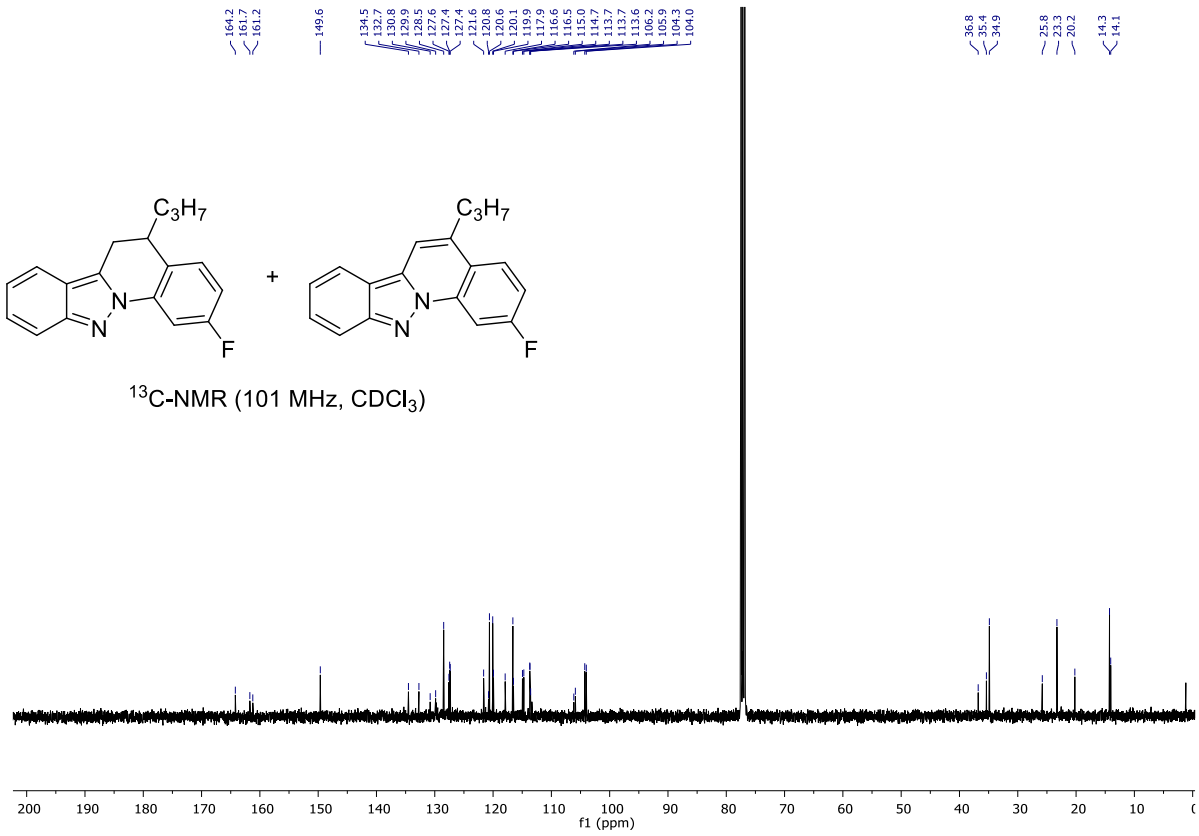




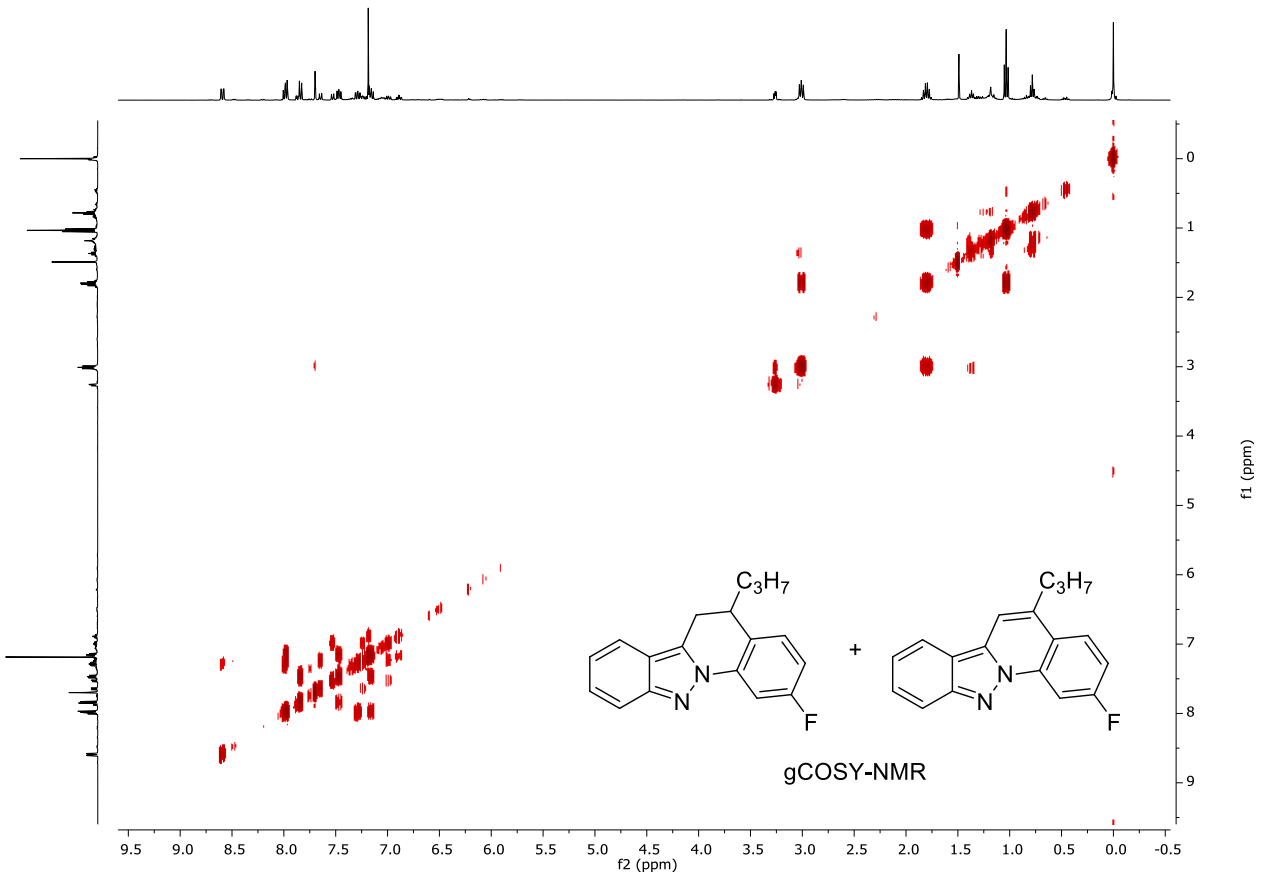


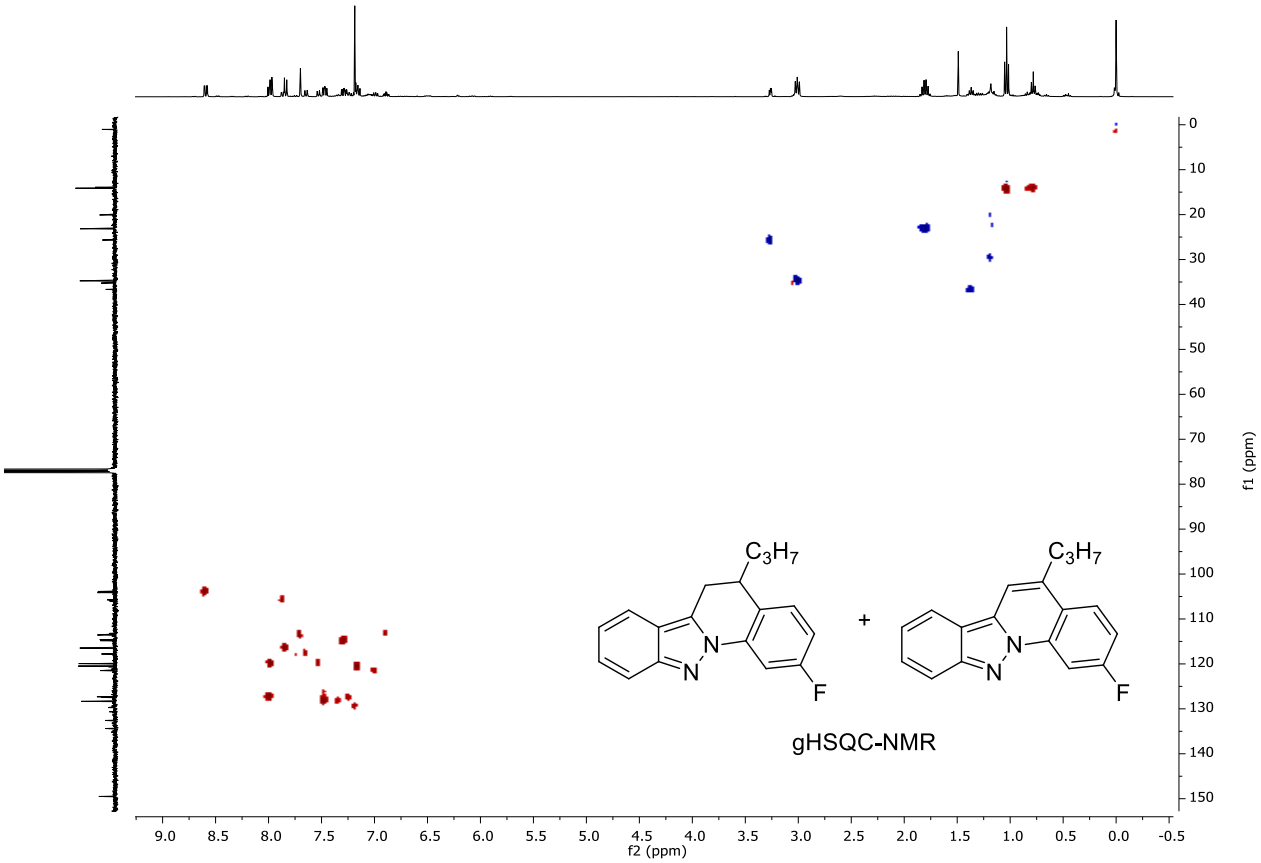
^{19}F-NMR (282 MHz, $CDCl_3$)



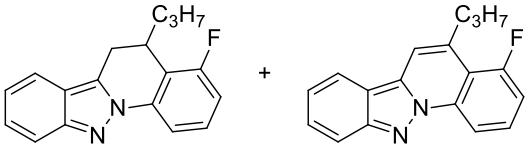


^{13}C-NMR (101 MHz, $CDCl_3$)

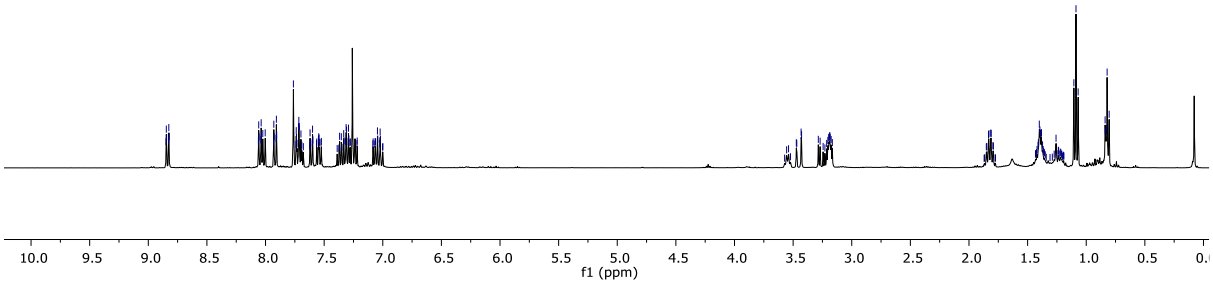


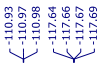

f2 (ppm)
f1 (ppm)
C3H7
N
N
F
+
C3H7
N
N
F
gHSQC-NMR

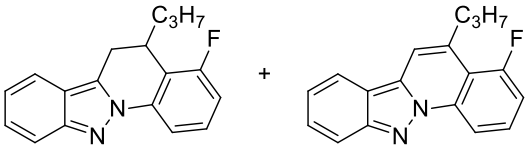
4-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 2-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3d' and 4d')



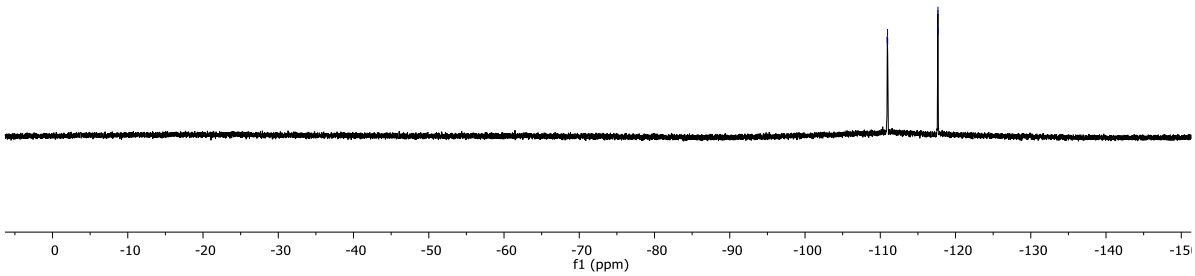
^{1}H-NMR (400 MHz, $CDCl_3$)

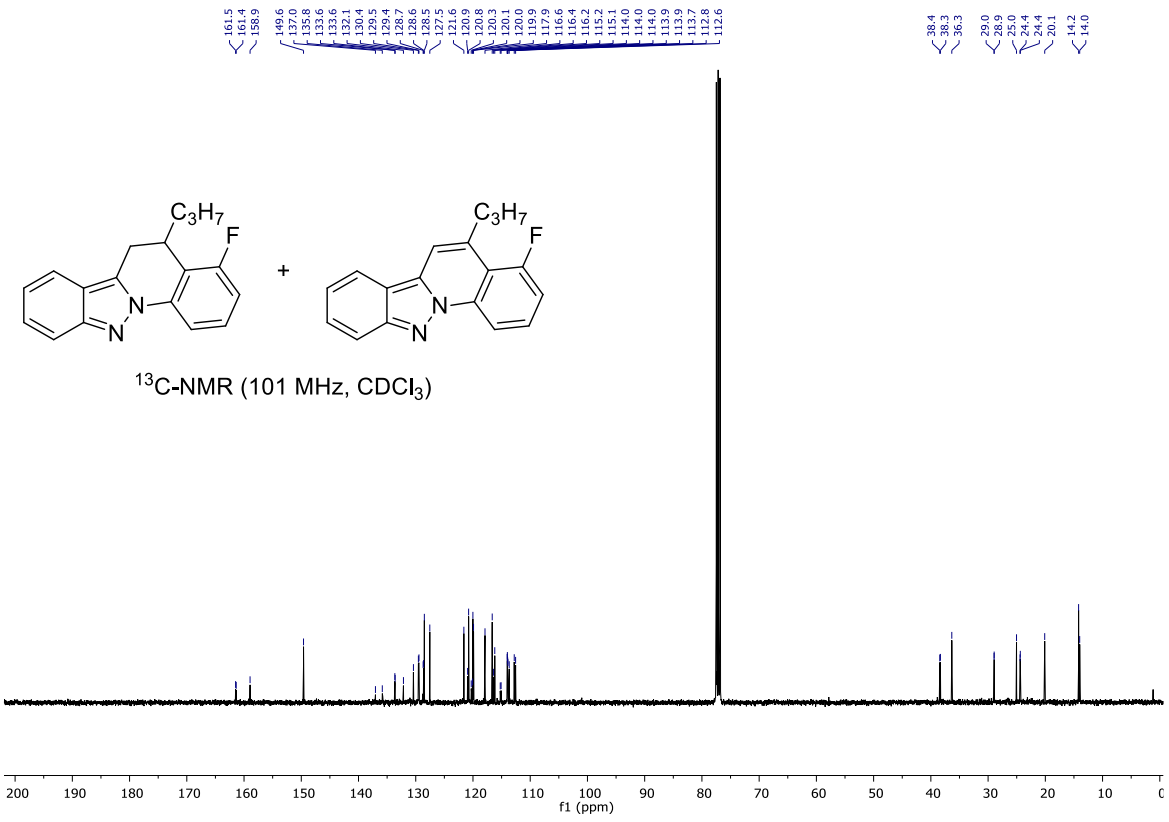


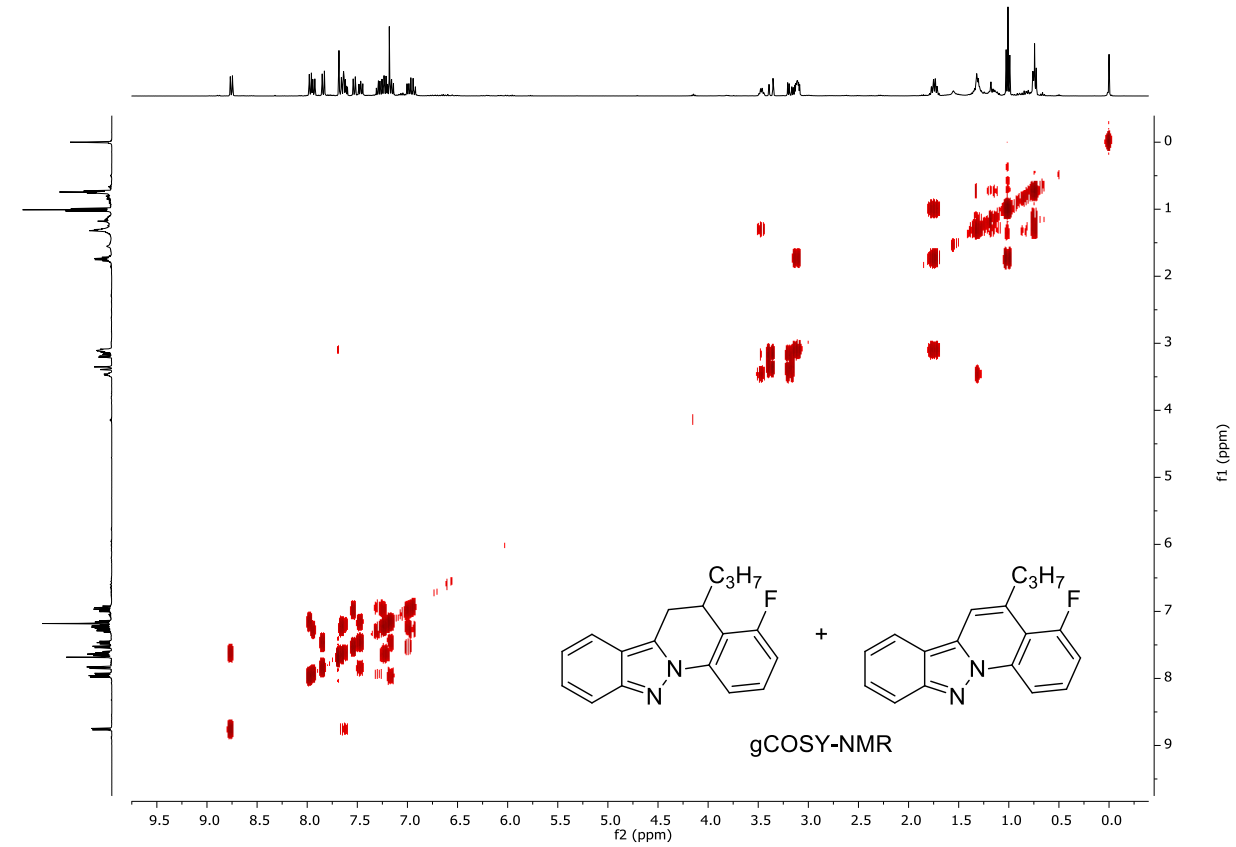


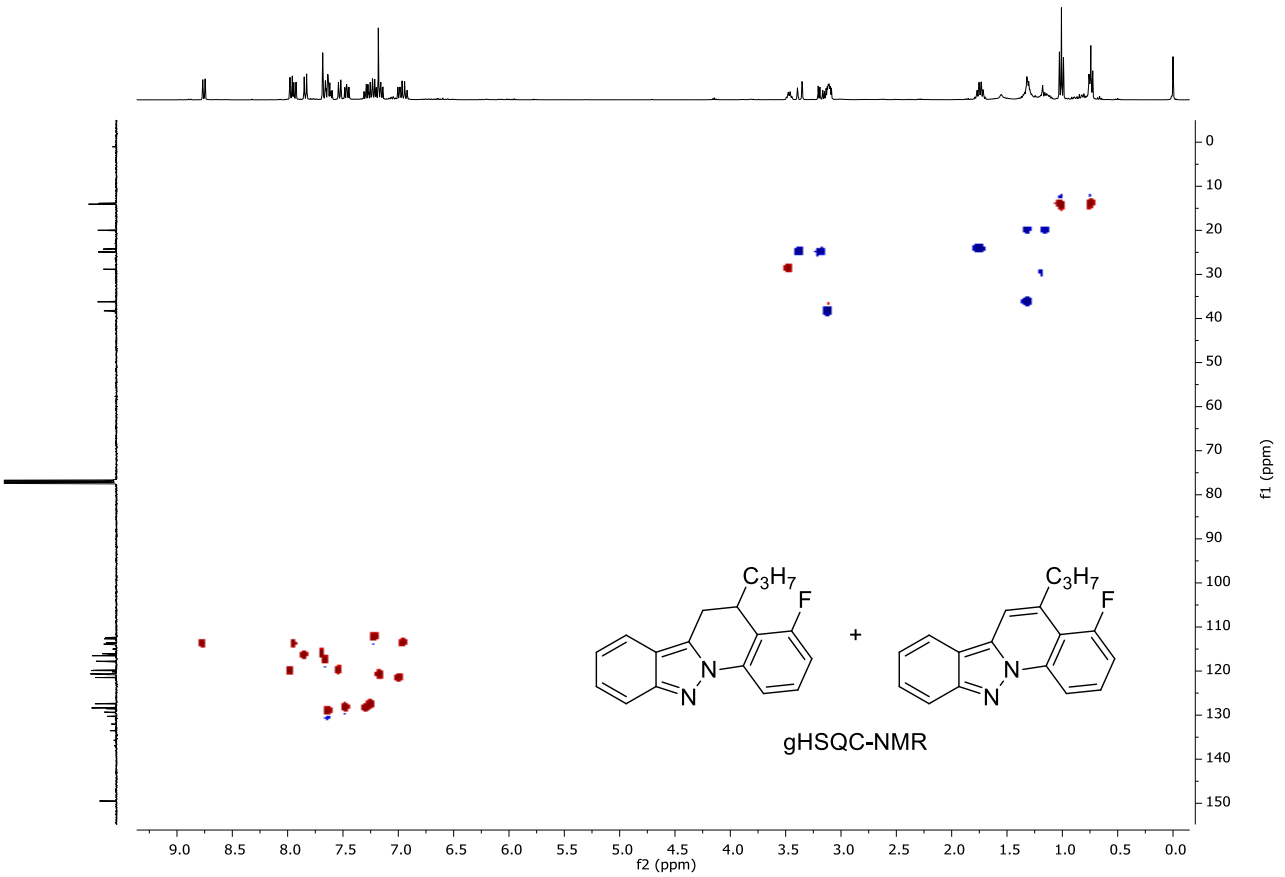


^{19}F-NMR (282 MHz, $CDCl_3$)

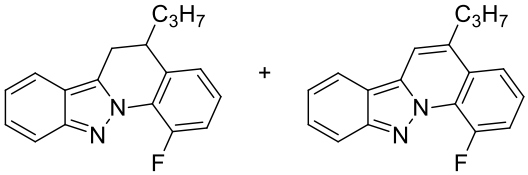



161.5
161.4
158.9
149.6
137.0
135.8
133.6
133.6
132.1
130.4
129.5
129.4
128.7
128.6
128.5
127.5
121.6
120.9
120.8
120.3
120.1
120.0
119.9
117.9
116.6
116.4
116.2
115.2
115.1
114.0
114.0
114.0
113.9
113.9
113.7
112.8
112.6
38.4
38.3
36.3
29.0
28.9
25.0
24.4
24.4
20.1
14.2
14.0
C_3H_7
F
N
N
+
C_3H_7
F
N
N
^{13}C-NMR (101 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

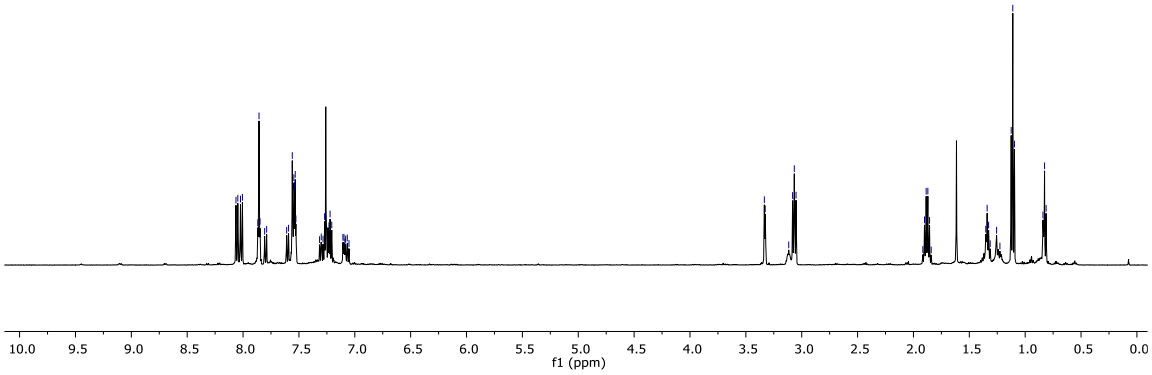

0
1
2
3
4
5
6
7
8
9
f1 (ppm)
C_3H_7
F
N
N
+
C_3H_7
F
N
N
gCOSY-NMR
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

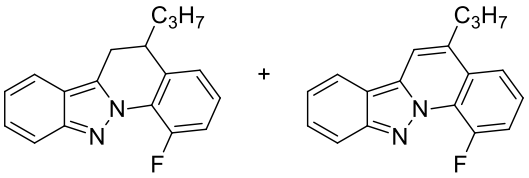

C3H7
F
N
N
+
C3H7
F
N
N
gHSQC-NMR
f2 (ppm)
f1 (ppm)

1-Fluoro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 1-fluoro-5-phenylindazolo[2,3-*a*]quinoline (3e and 4e)

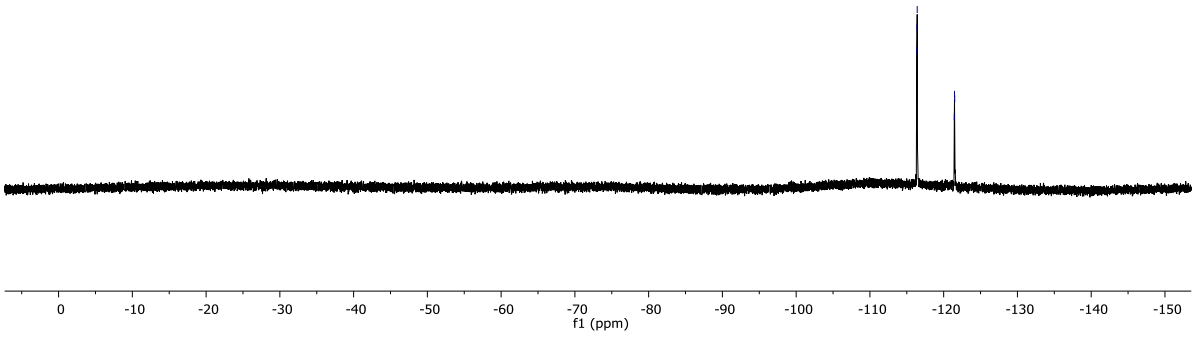


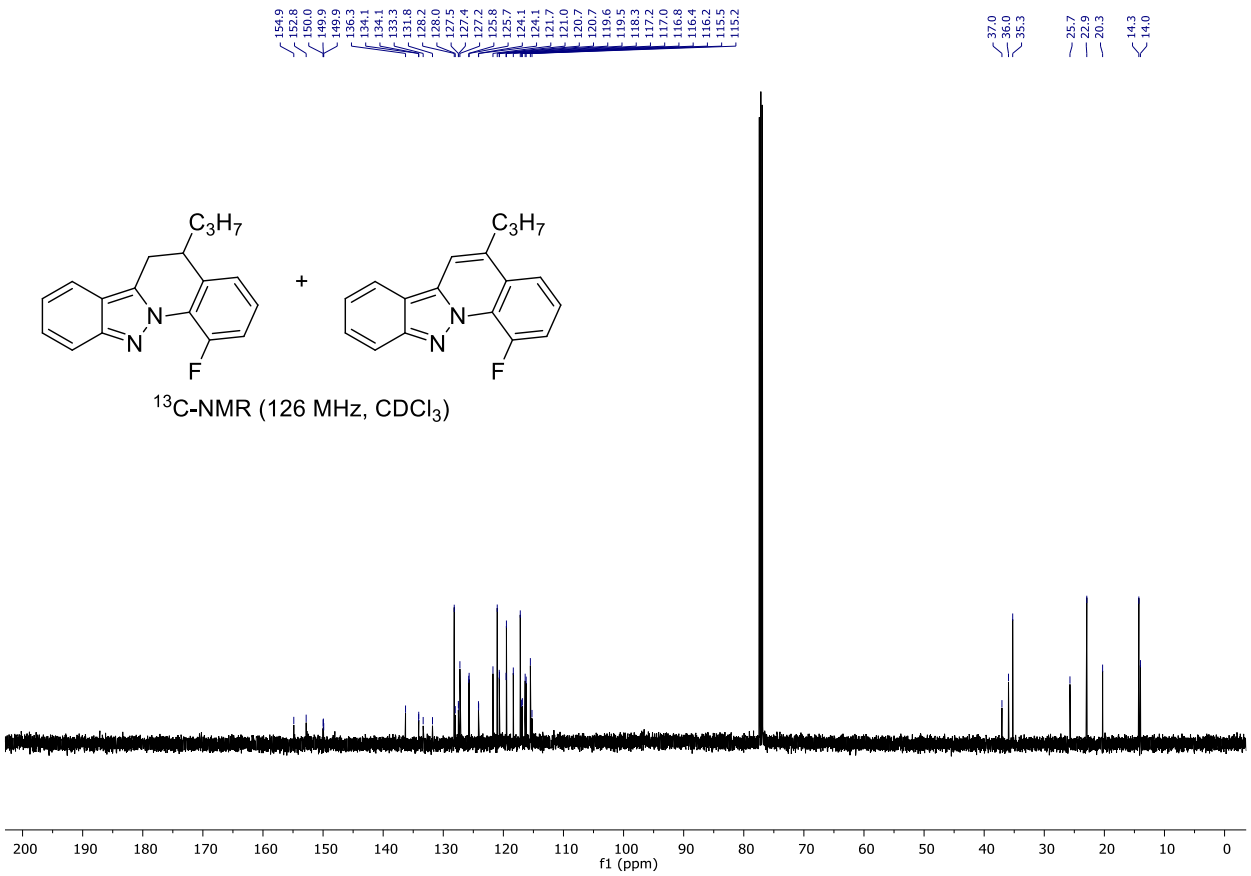
^{1}H-NMR (500 MHz, $CDCl_3$)

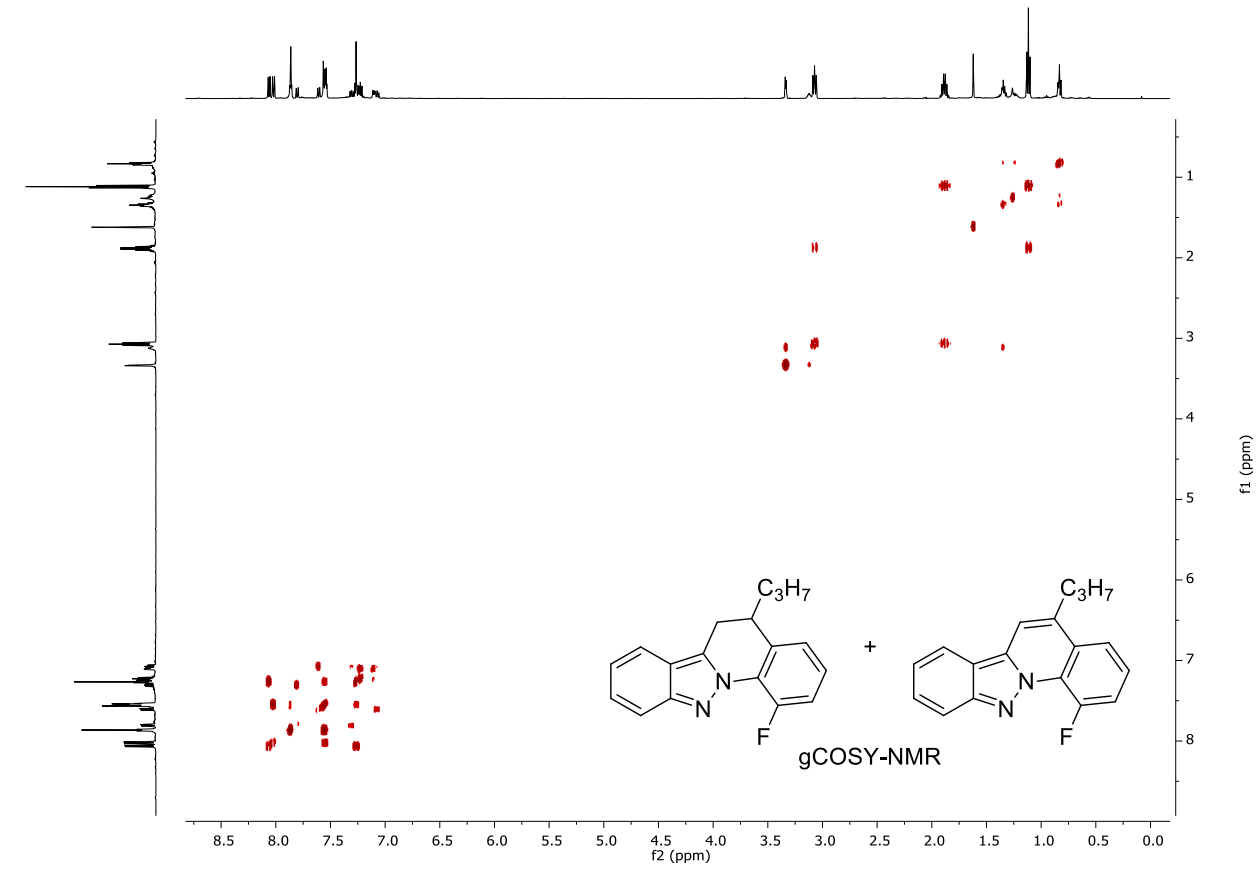


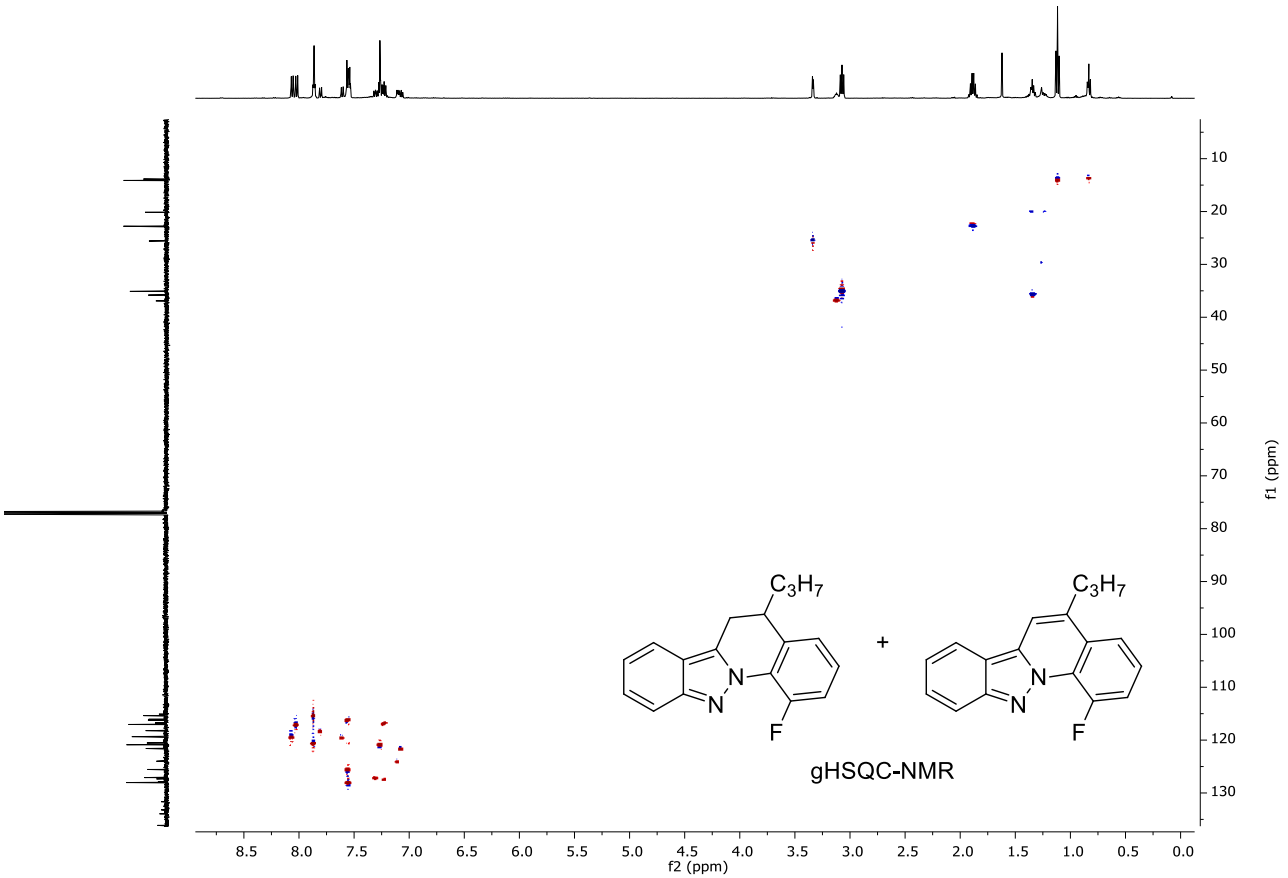


^{19}F-NMR (282 MHz, $CDCl_3$)

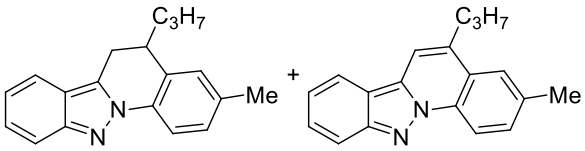



154.9
152.8
150.0
149.9
149.9
136.3
134.1
134.1
133.3
131.8
128.2
128.0
127.5
127.4
127.2
125.8
125.7
124.1
124.1
121.7
121.0
120.7
120.7
119.6
119.5
118.3
117.2
117.0
116.8
116.4
116.2
115.5
115.2
37.0
36.0
35.3
25.7
22.9
20.3
14.3
14.0
C_3H_7
N
N
F
+
C_3H_7
N
N
F
^{13}C-NMR (126 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

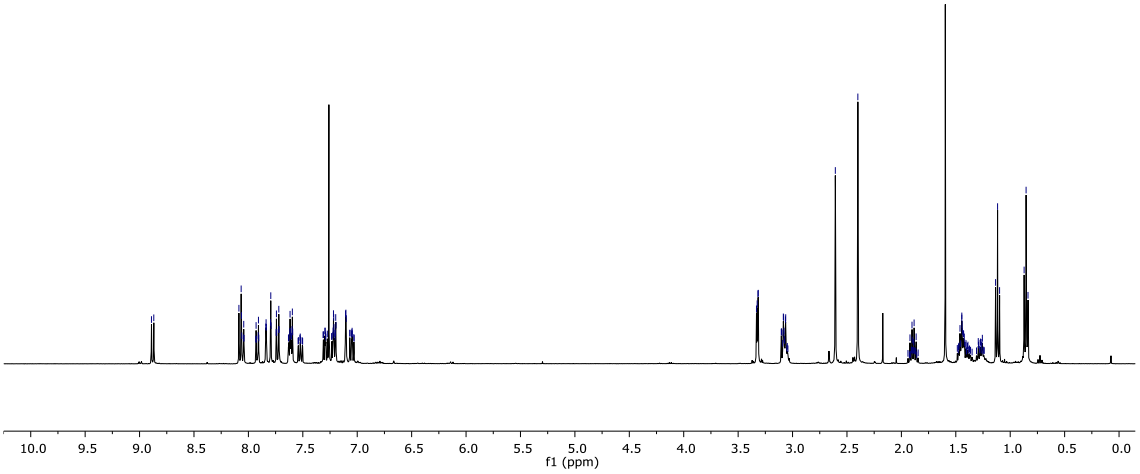

1 2 3 4 5 6 7 8
f1 (ppm)
C_3H_7
N
N
F
+
C_3H_7
N
N
F
gCOSY-NMR
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

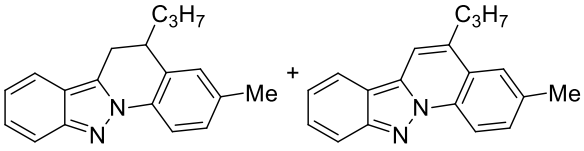

f1 (ppm)
f2 (ppm)
C3H7
N
N
F
+
C3H7
N
N
F
gHSQC-NMR

3-Methyl-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 3-methyl-5-propylindazolo[2,3-*a*]quinoline (3k and 4k)

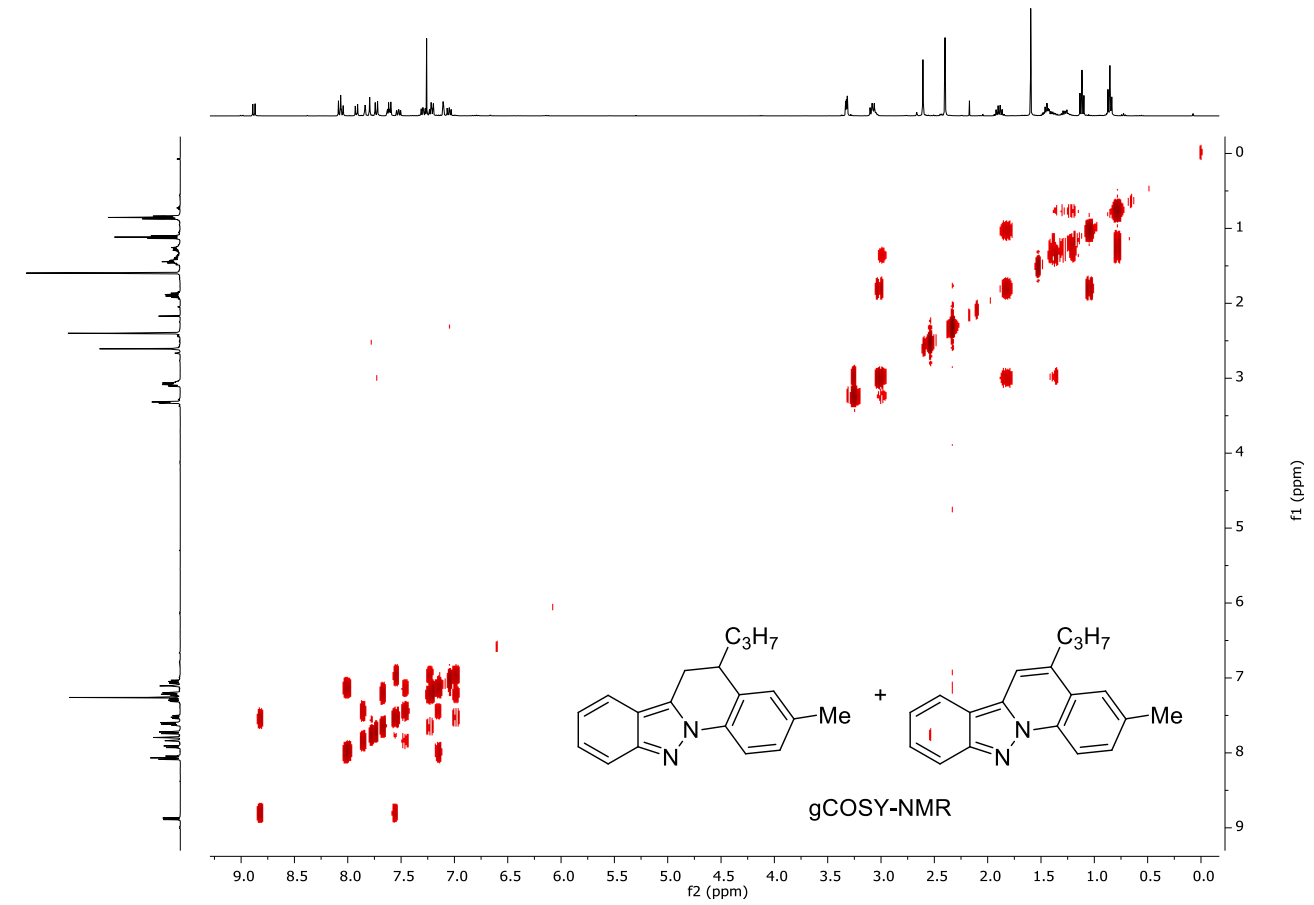


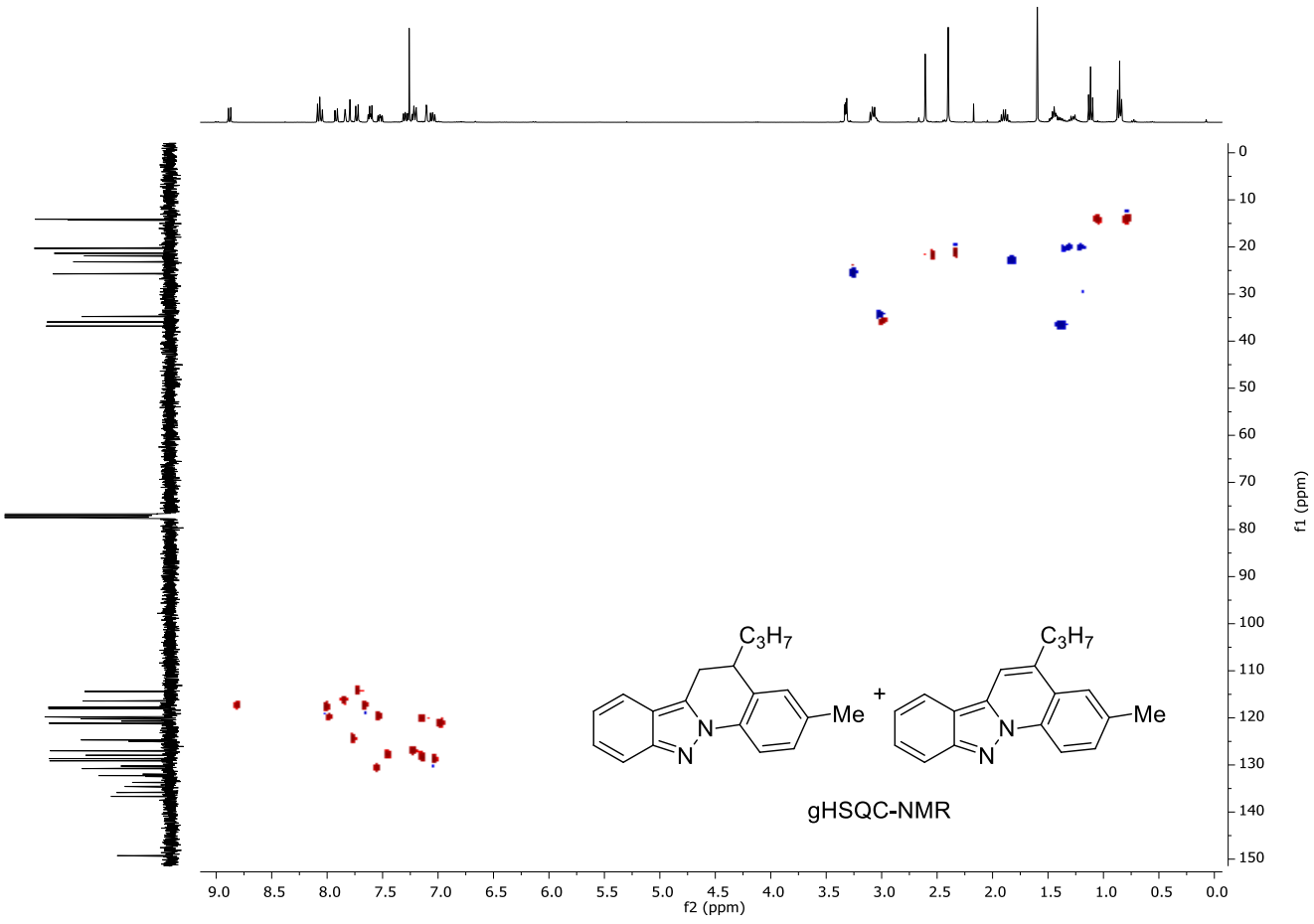
^{1}H-NMR (400 MHz, $CDCl_3$)



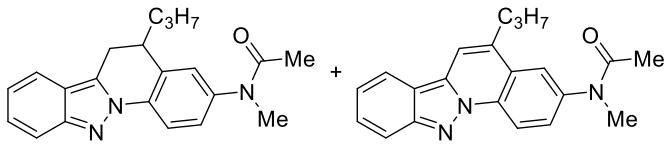


^{13}C-NMR (101 MHz, $CDCl_3$)

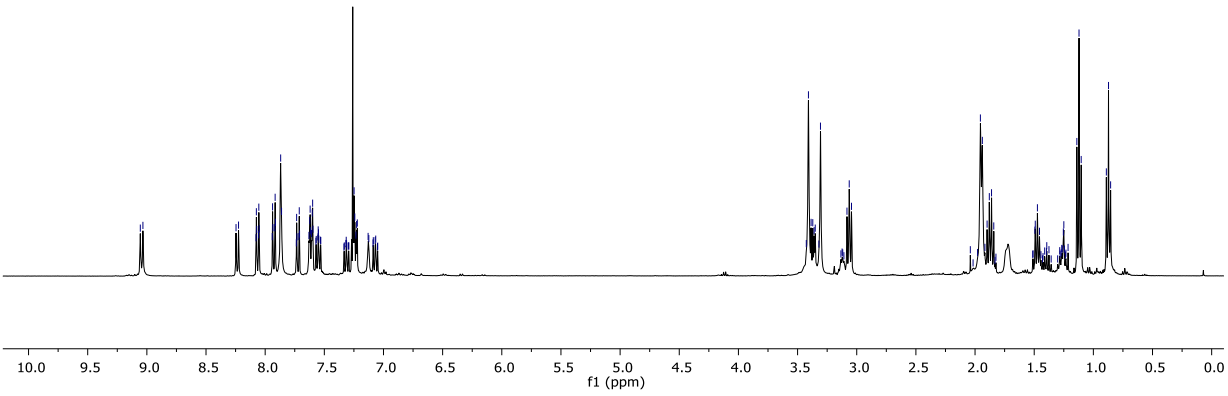

f2 (ppm)
f1 (ppm)
C3H7
Me
N
N
+
gCOSY-NMR

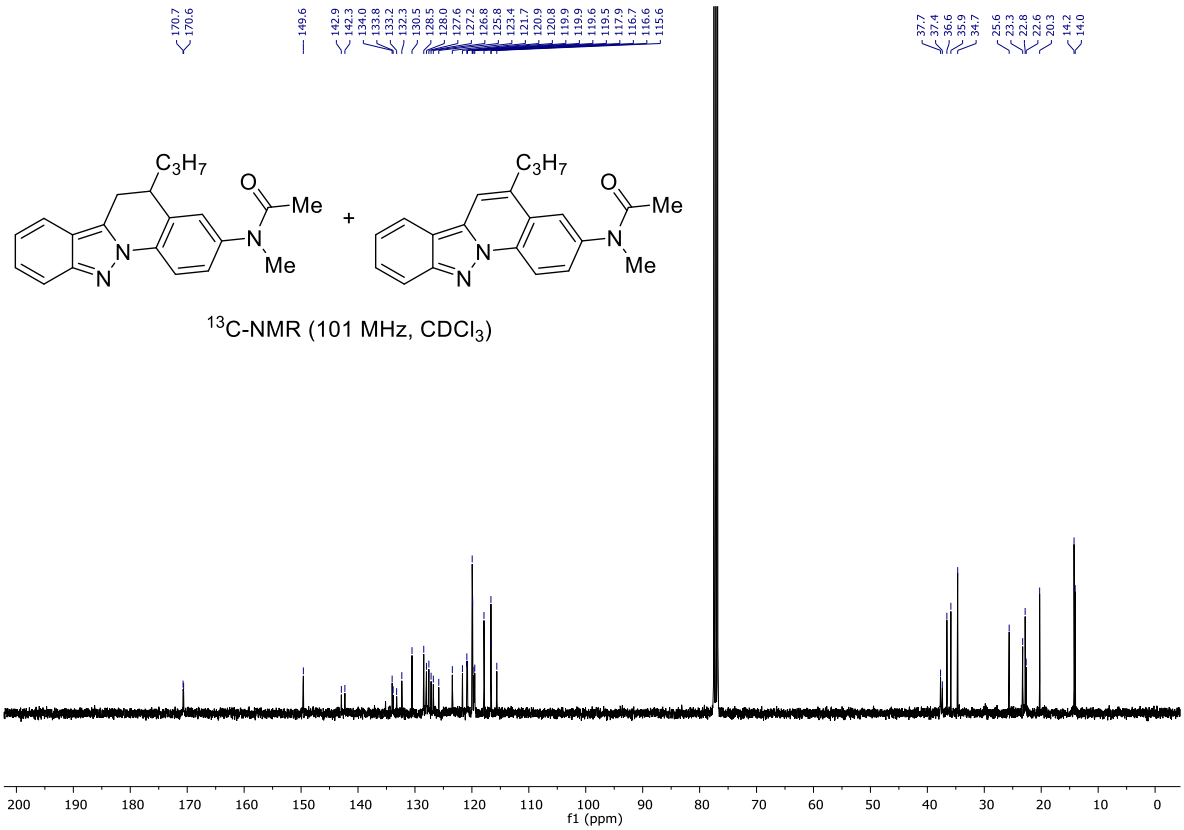

f2 (ppm)
f1 (ppm)
C3H7
Me
N
N
+
gHSQC-NMR

_N_-Methyl-_N_-(5-propyl-5,6-dihydroindazolo[2,3-_a_]quinolin-3-yl)acetamide and _N_-methyl-_N_-(5-propylindazolo[2,3-_a_]quinolin-3-yl)acetamide (3l and 4l)

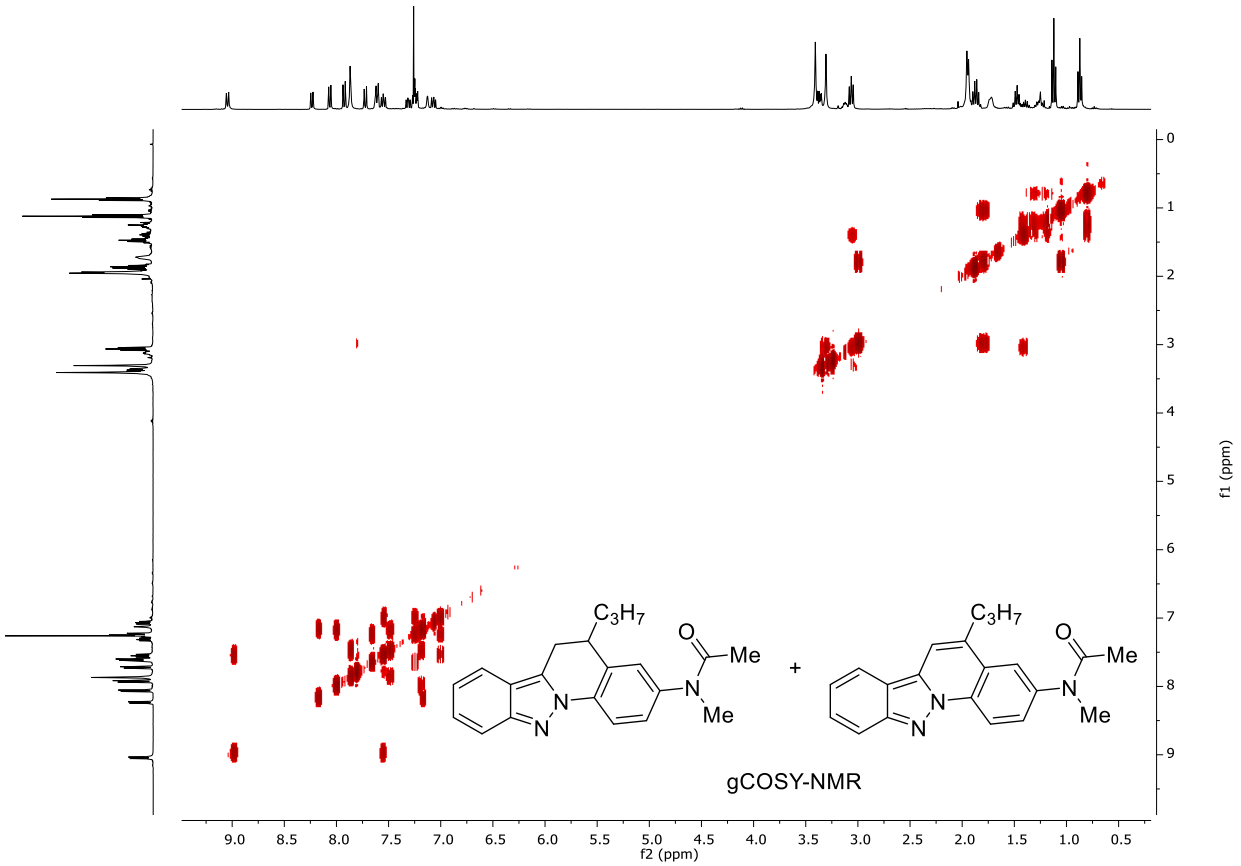


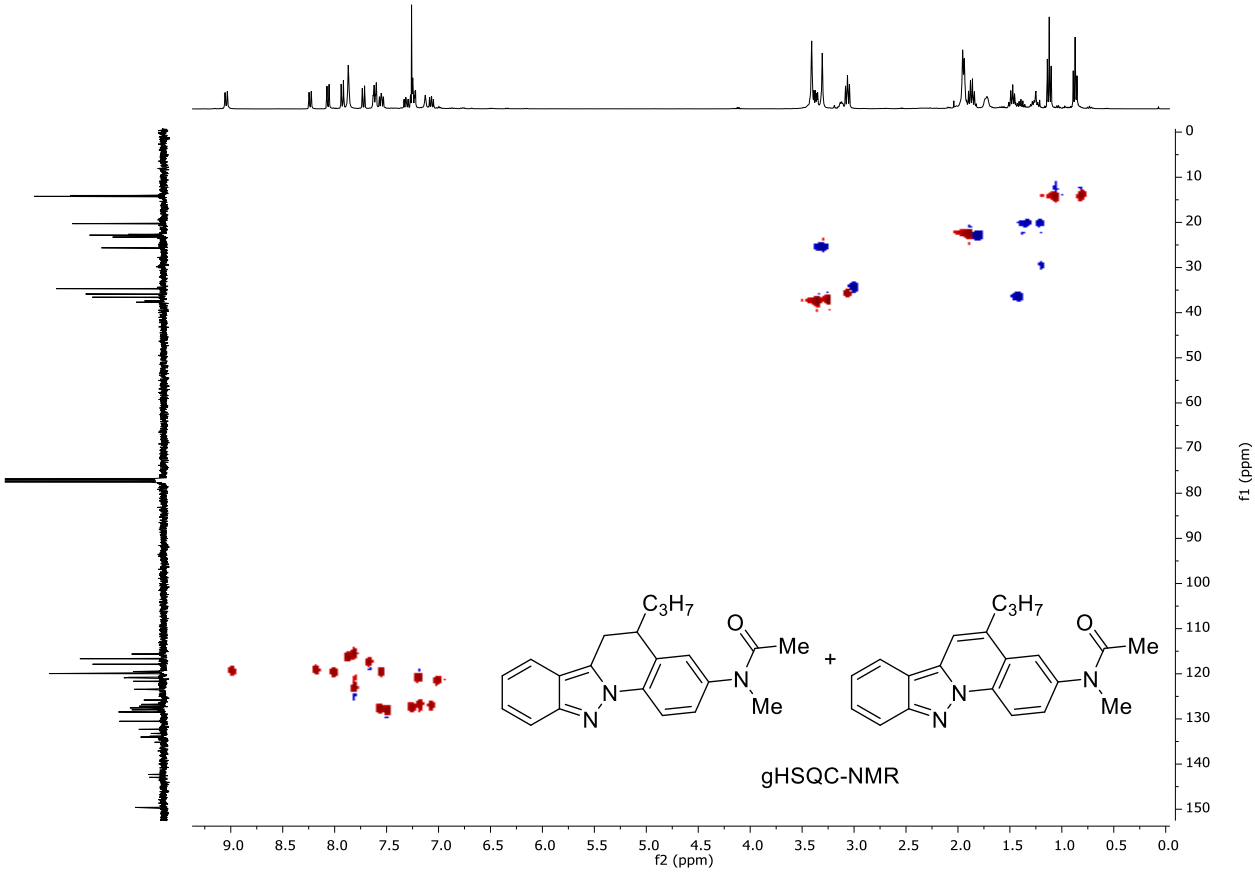
^{1}H-NMR (400 MHz, $CDCl_3$)



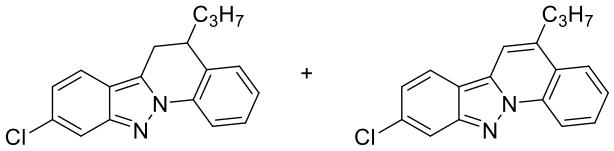


^{13}C-NMR (101 MHz, $CDCl_3$)

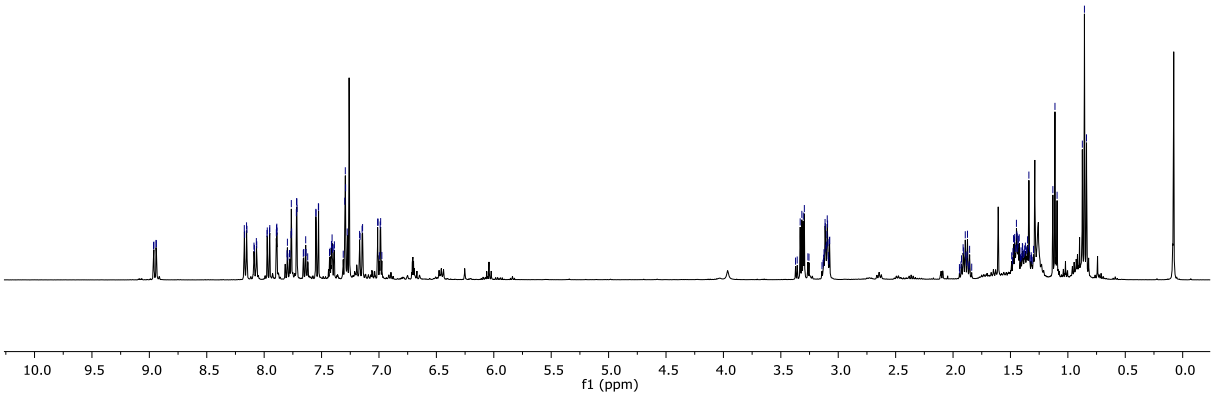

f2 (ppm)
f1 (ppm)
C3H7
O
Me
N
Me
+
gCOSY-NMR

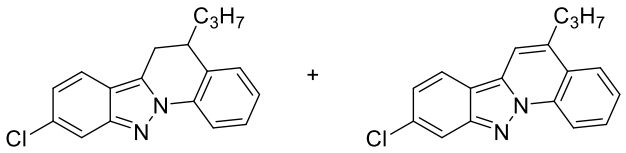

f2 (ppm)
f1 (ppm)
C3H7
O
Me
N
Me
+
gHSQC-NMR

9-Chloro-5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline and 9-chloro-5-propylindazolo[2,3-*a*]quinoline (3p and 4p)

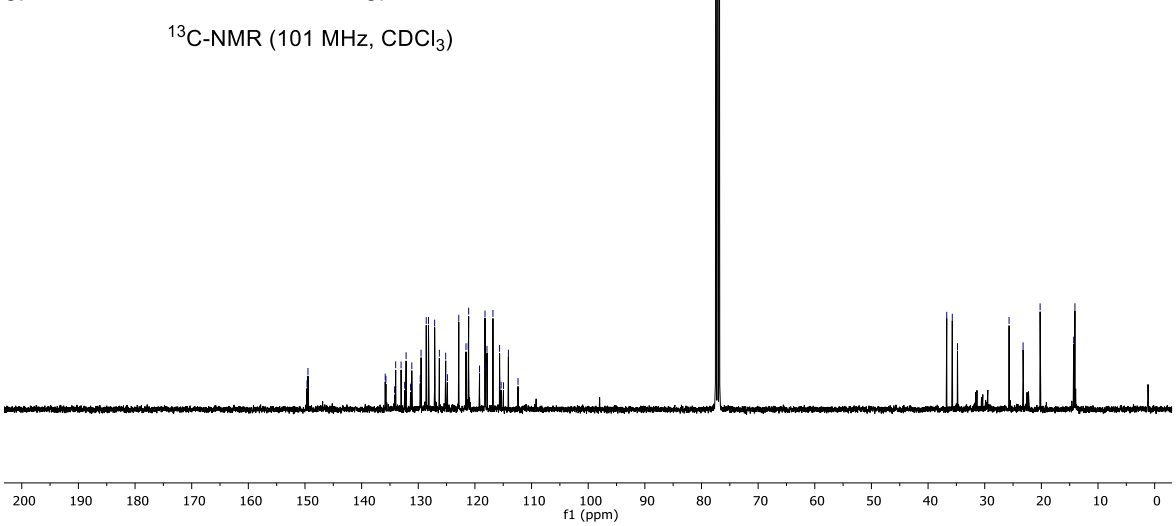


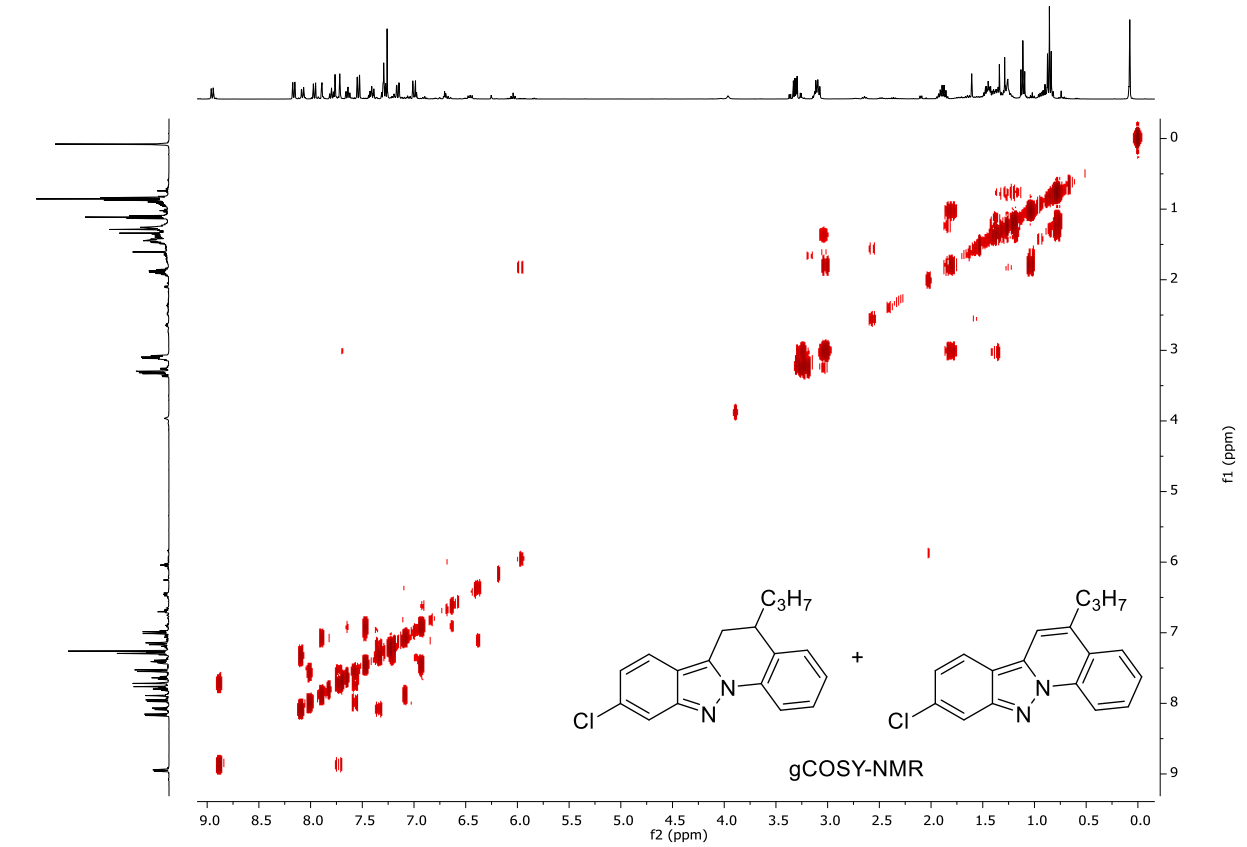
^{1}H-NMR (400 MHz, $CDCl_3$)

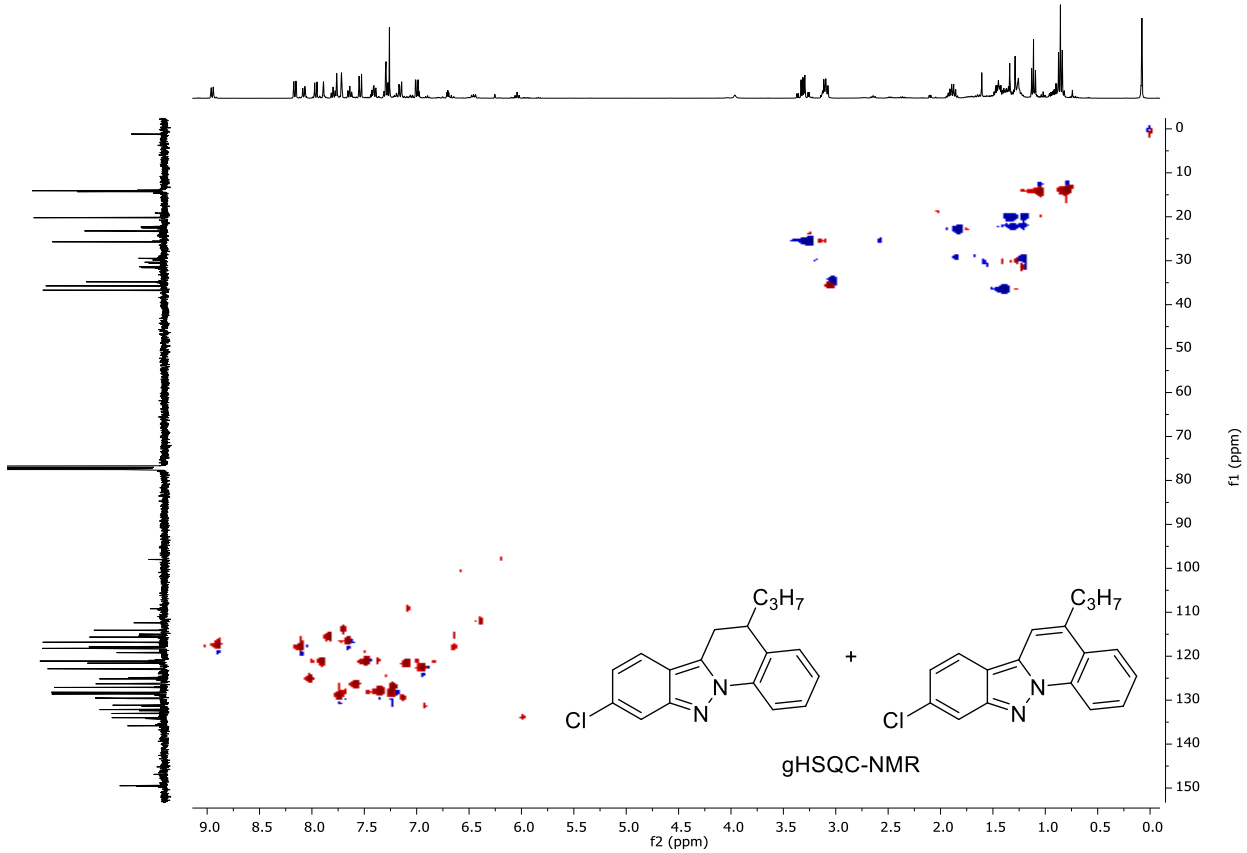




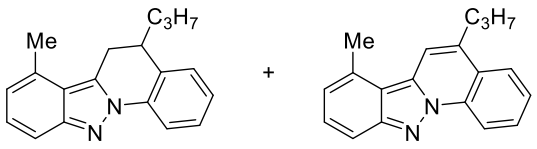
^{13}C-NMR (101 MHz, $CDCl_3$)



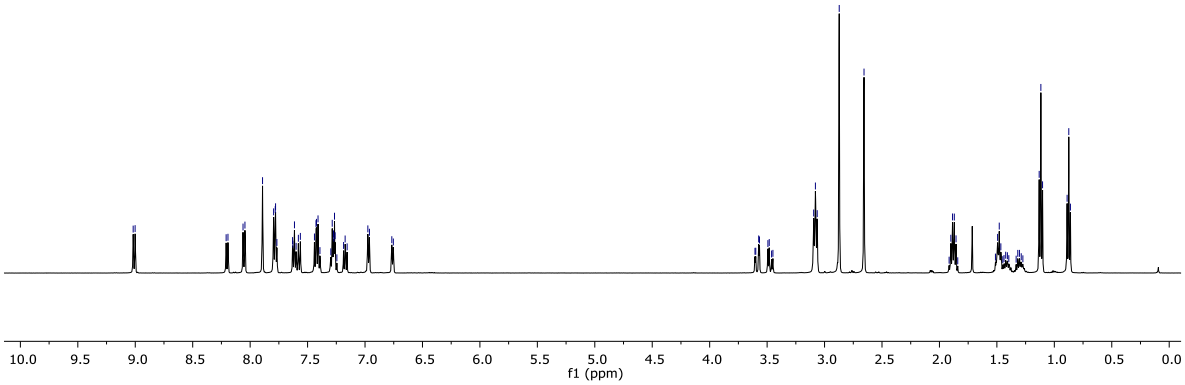

f1 (ppm)
f2 (ppm)
gCOSY-NMR
Cl
N
N
C_3H_7
+

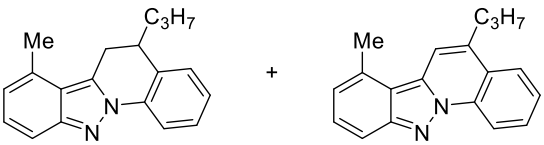

f1 (ppm)
f2 (ppm)
gHSQC-NMR
Cl
N
N
C_3H_7
+

7-Methyl-5-propyl-5,6-dihydroindazolo[2,3-a]quinoline and 7-methyl-5-propylindazolo[2,3-*a*]quinoline (3s and 4s)

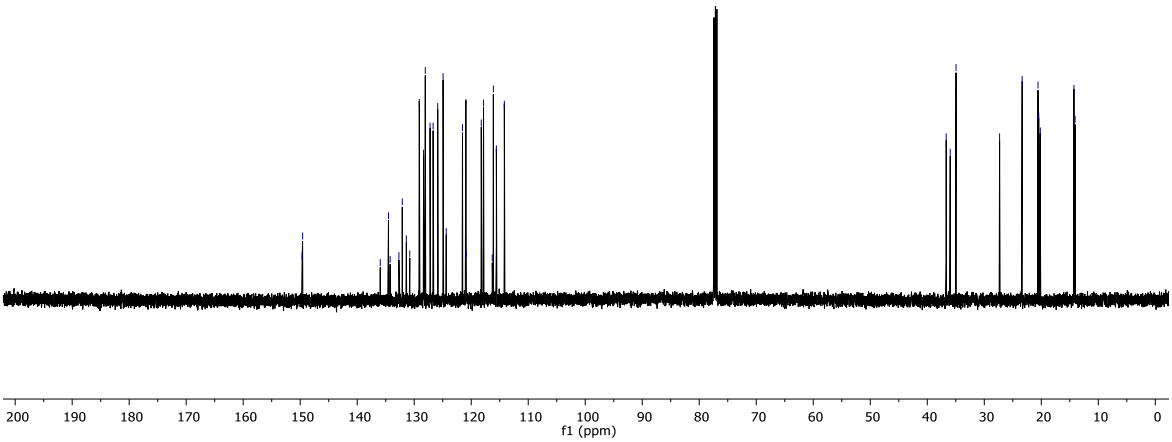


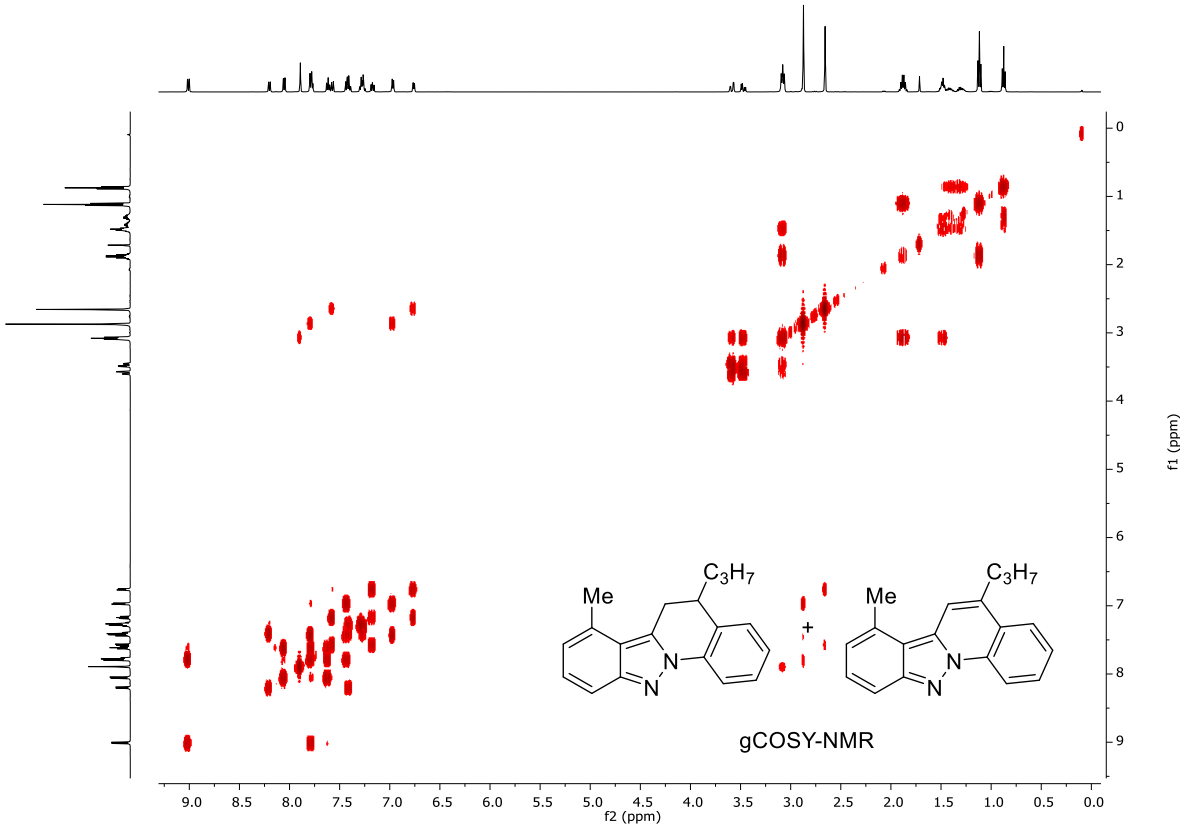
^{1}H-NMR (500 MHz, $CDCl_3$)

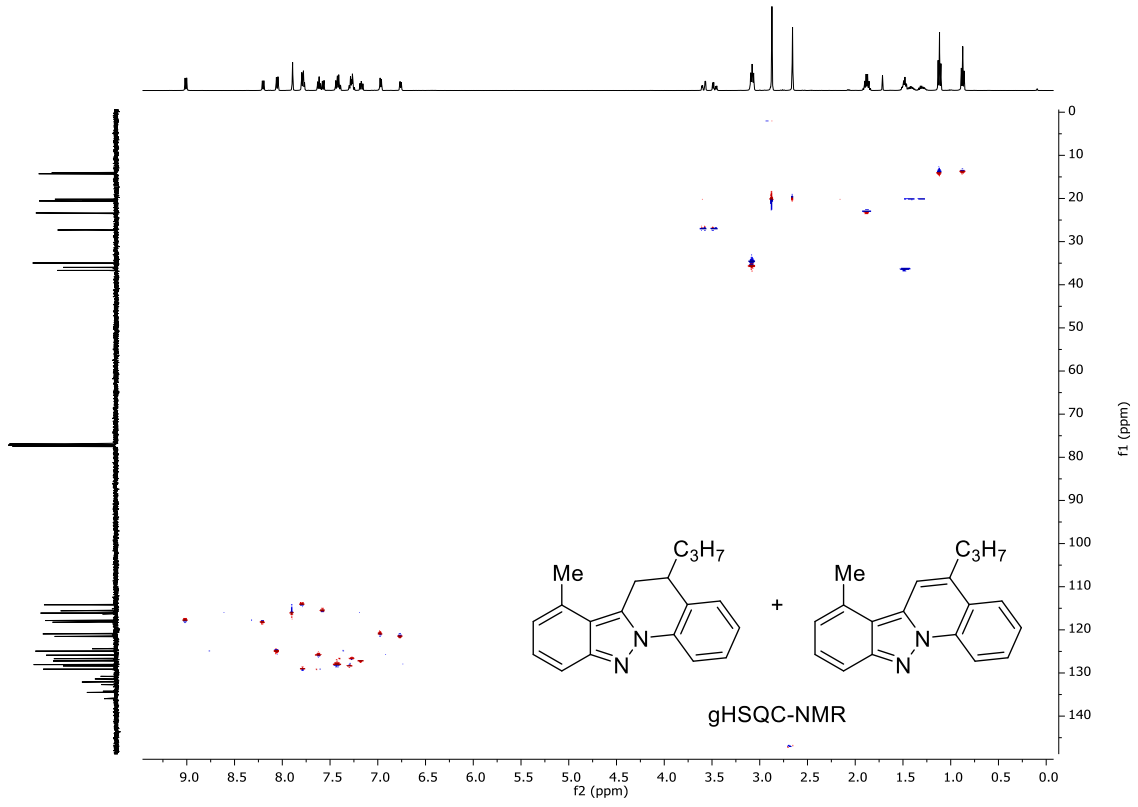




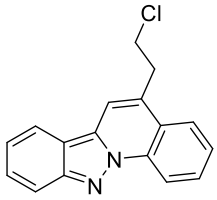
^{13}C-NMR (126 MHz, $CDCl_3$)



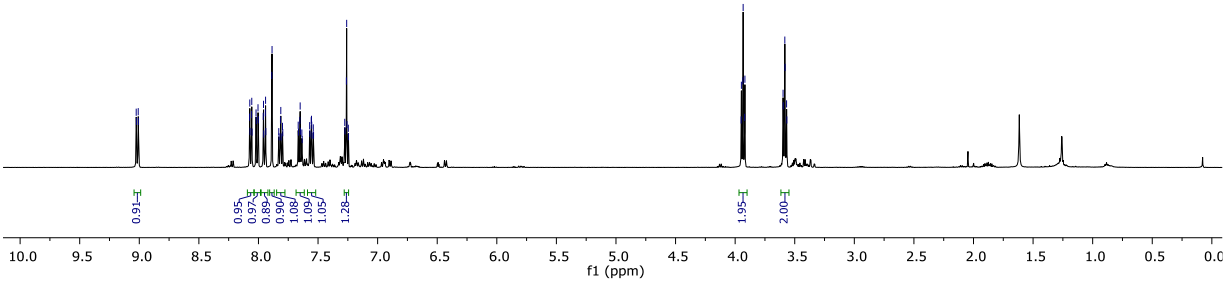

f2 (ppm)
f1 (ppm)
Me
C3H7
N
N
+
gCOSY-NMR

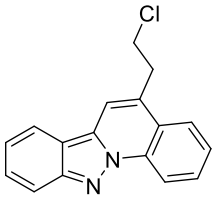

f2 (ppm)
f1 (ppm)
Me
C3H7
N
N
+
gHSQC-NMR

5-(2-Chloroethyl)indazolo[2,3-*a*]quinoline (4x)

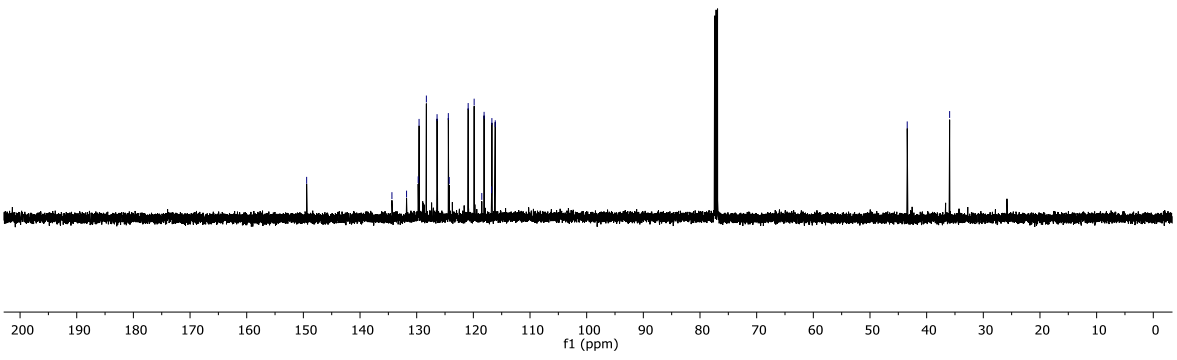


^{1}H-NMR (500 MHz, $CDCl_3$)

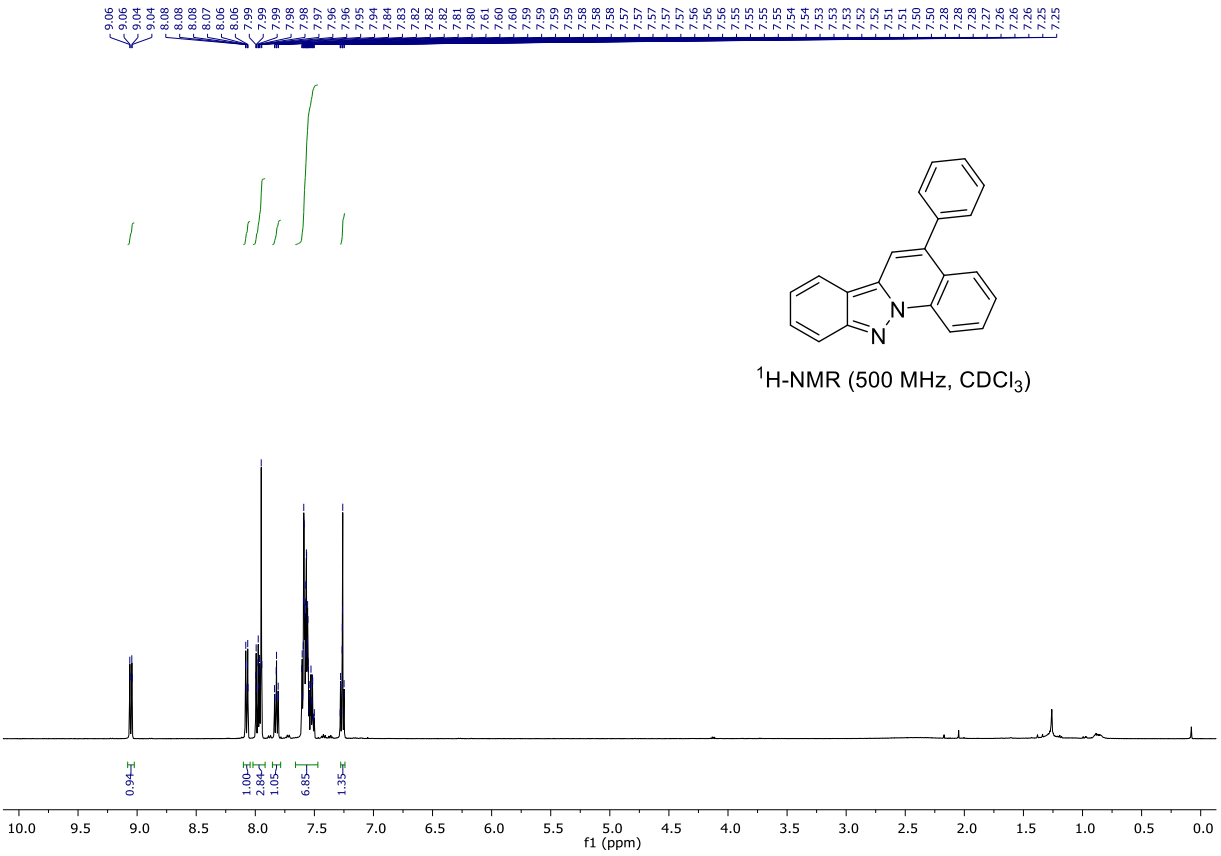




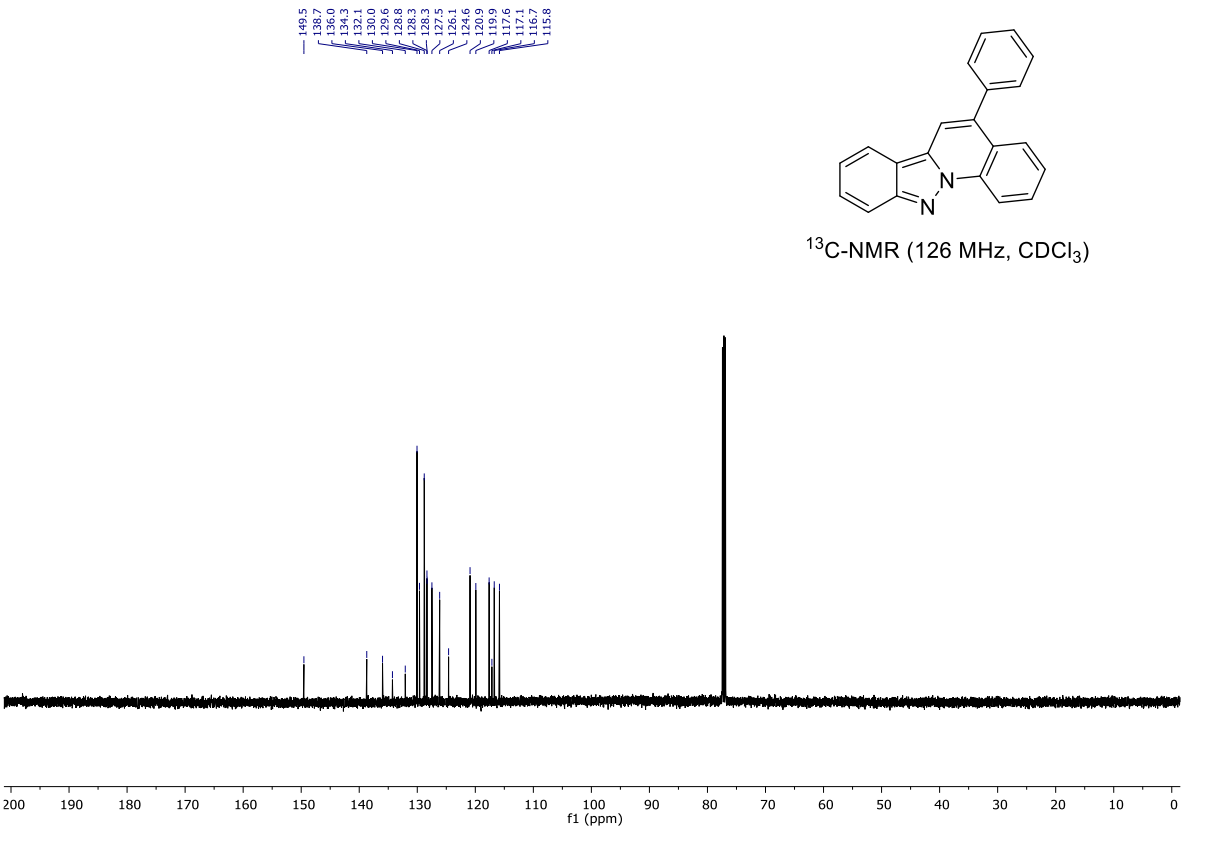
^{13}C-NMR (126 MHz, $CDCl_3$)



5-Phenylindazolo[2,3-*a*]quinoline (4aa)

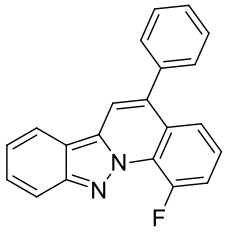


^{1}H-NMR (500 MHz, $CDCl_3$)

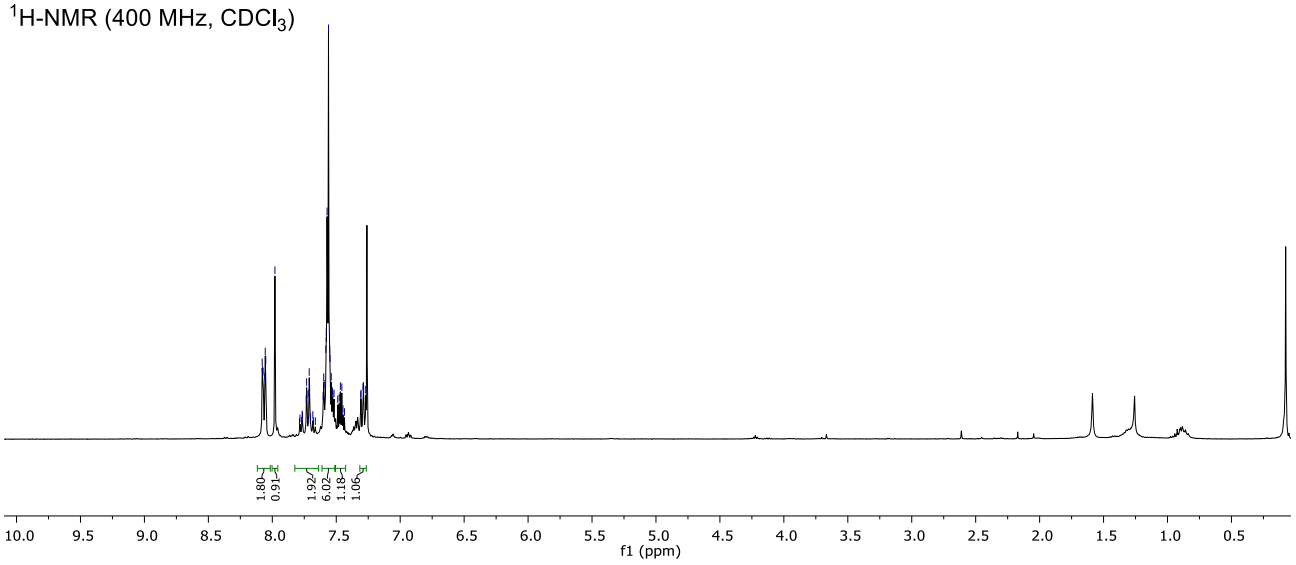


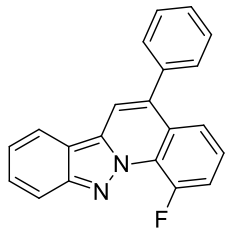
^{13}C-NMR (126 MHz, $CDCl_3$)

1-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ab)

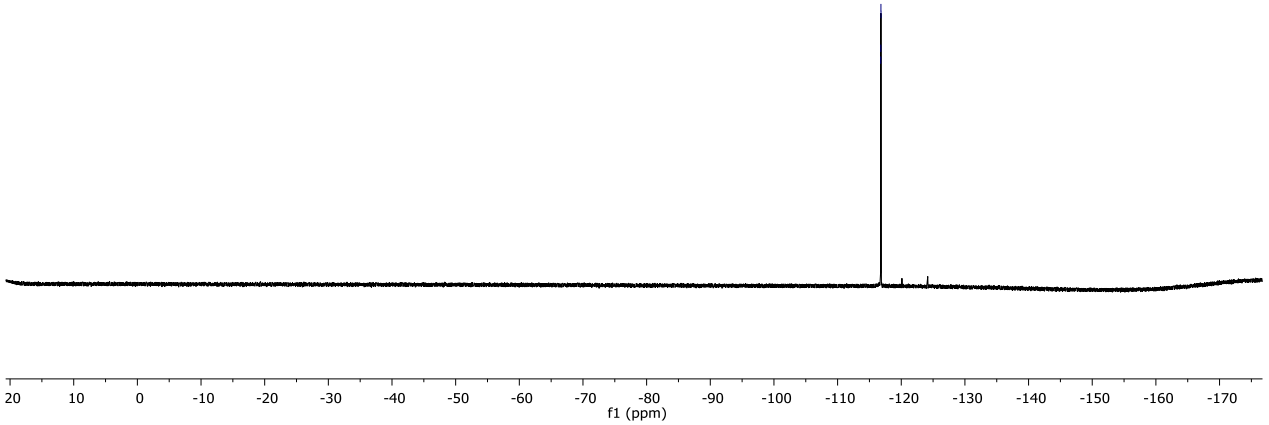


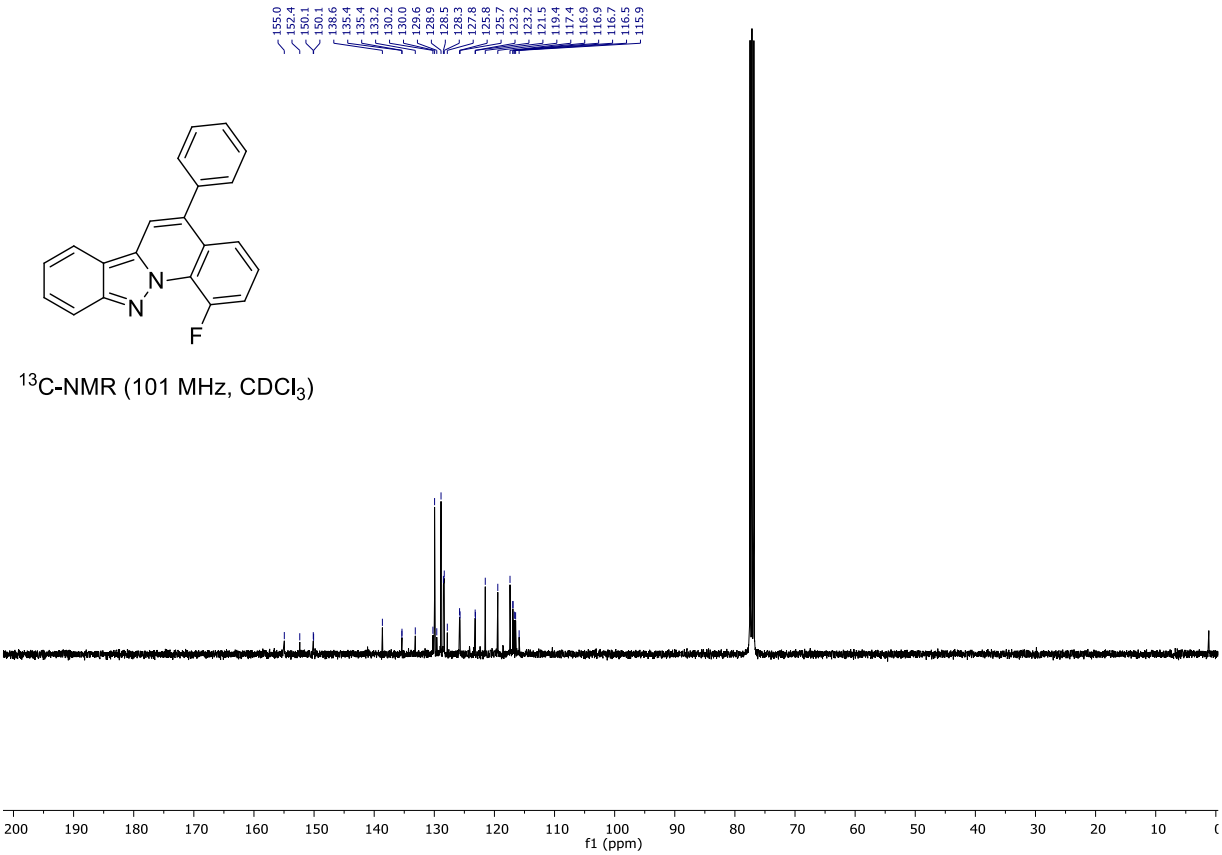
^{1}H-NMR (400 MHz, $CDCl_3$)





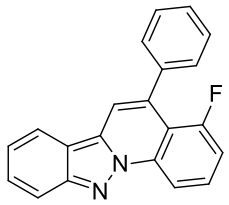
^{19}F-NMR (376 MHz, $CDCl_3$)



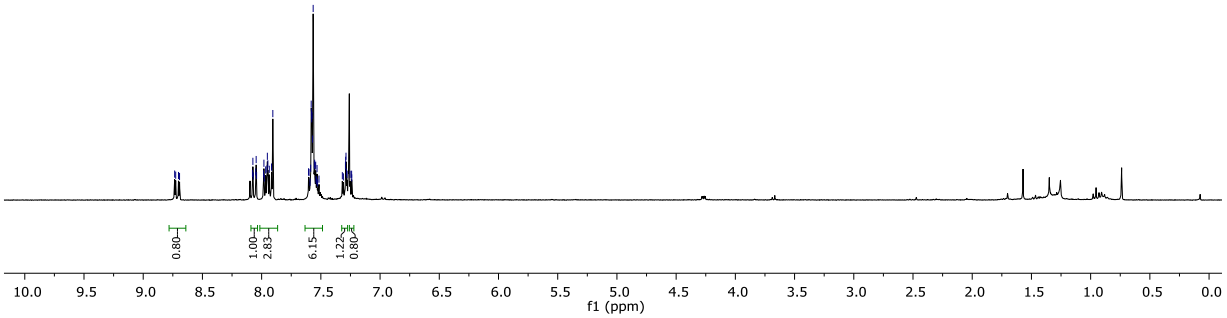


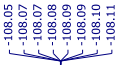
^{13}C-NMR (101 MHz, $CDCl_3$)

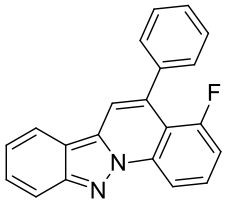
4-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ac)



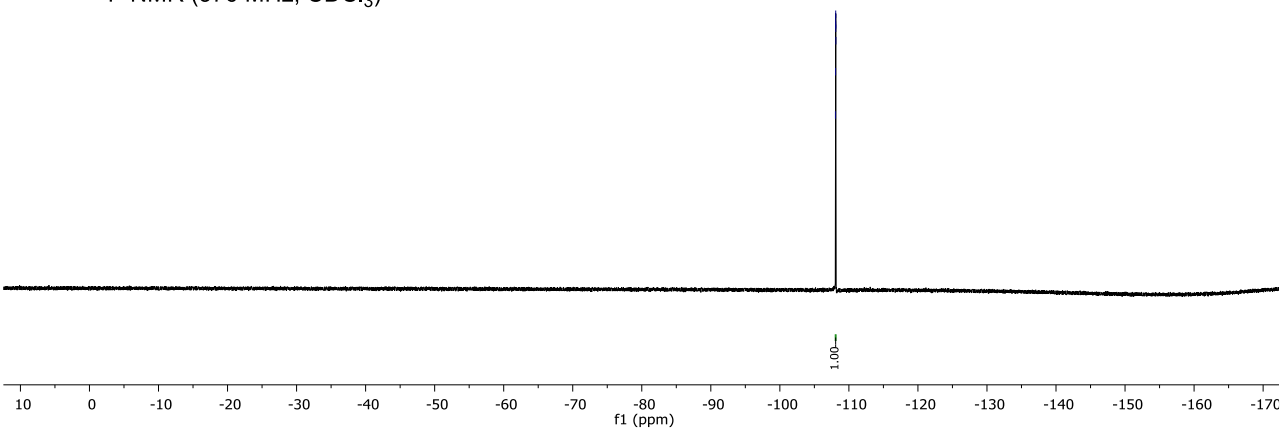
^{1}H-NMR (300 MHz, $CDCl_3$)

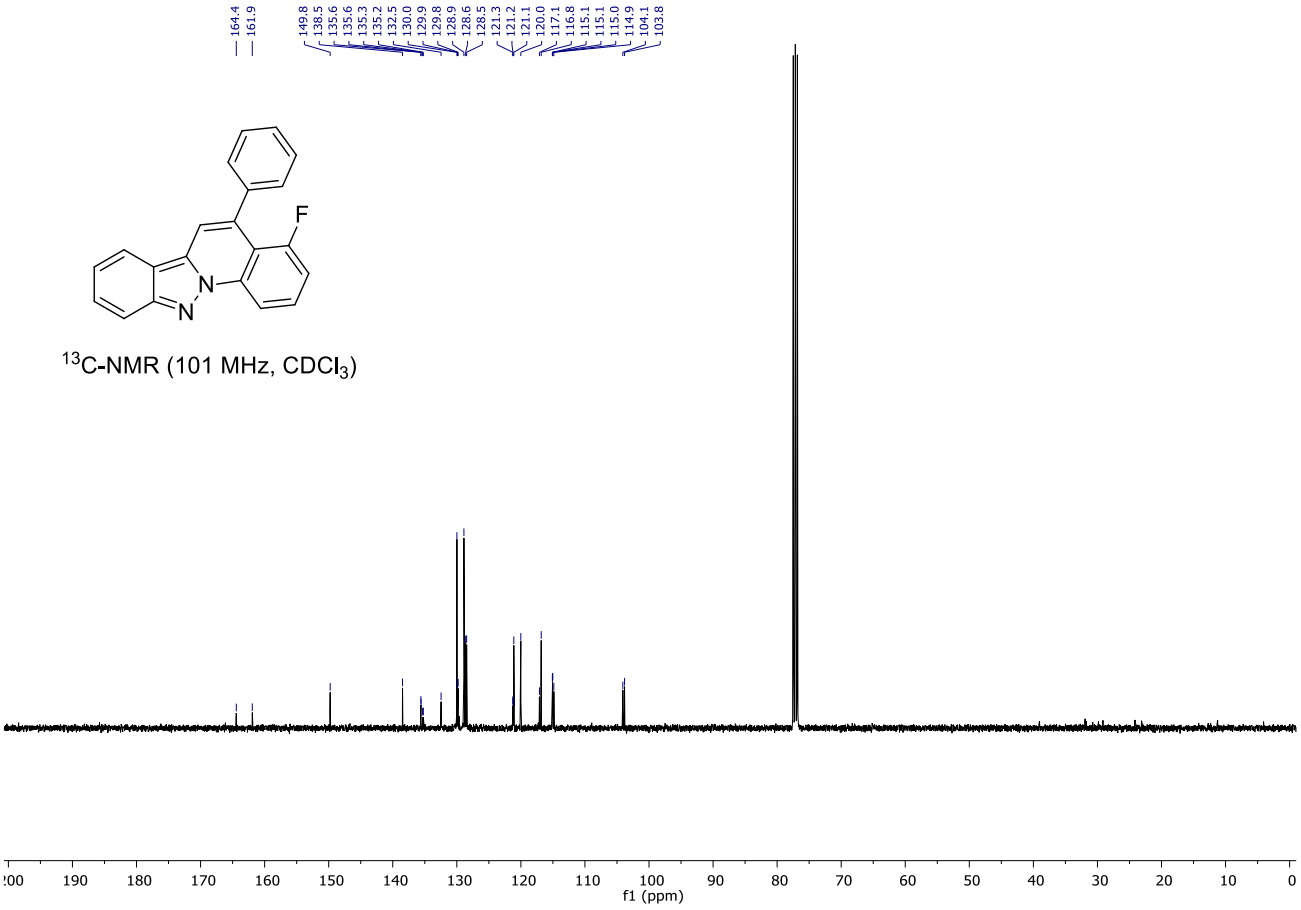






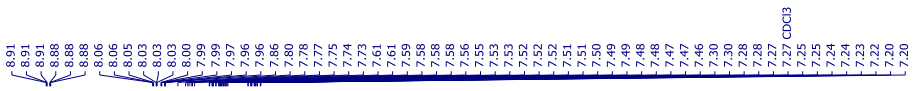
^{19}F-NMR (376 MHz, $CDCl_3$)

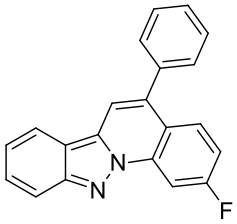




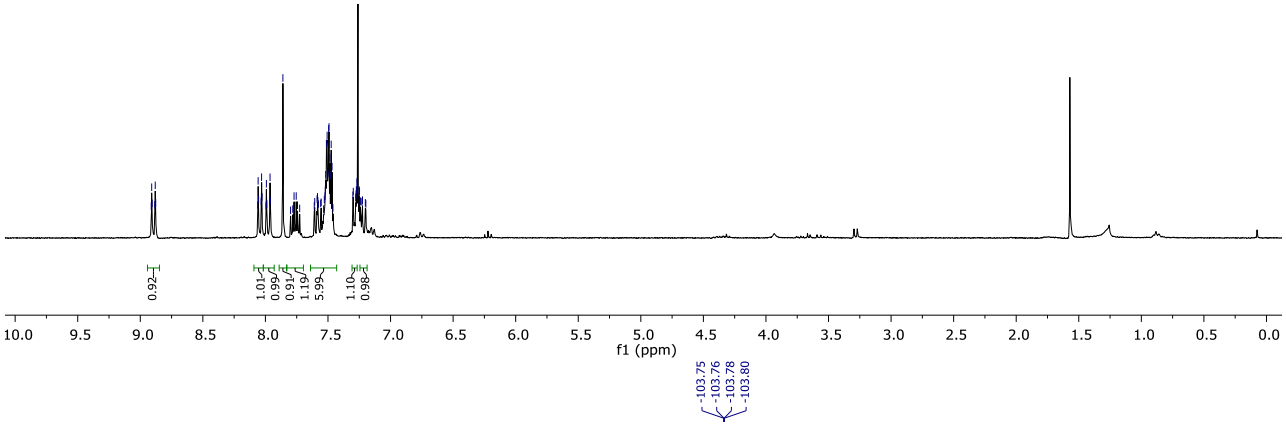
^{13}C-NMR (101 MHz, $CDCl_3$)

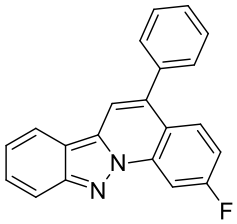
2-Fluoro-5-phenylindazolo[2,3-*a*]quinoline (4ac')



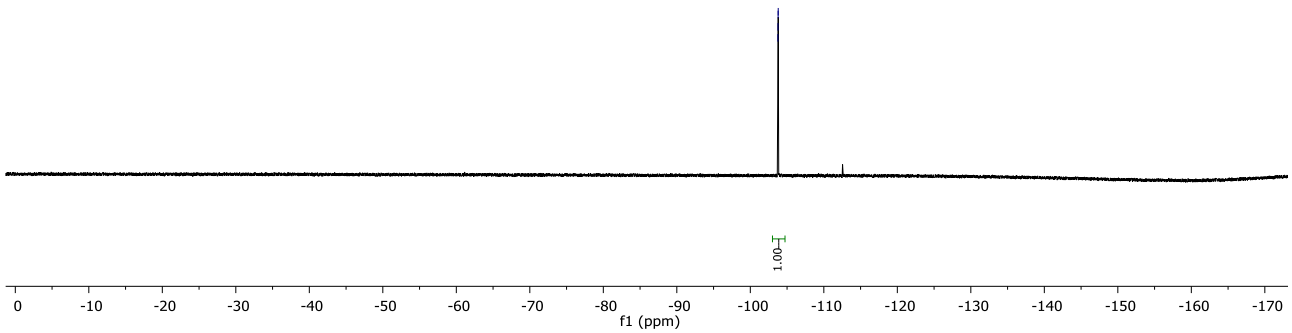


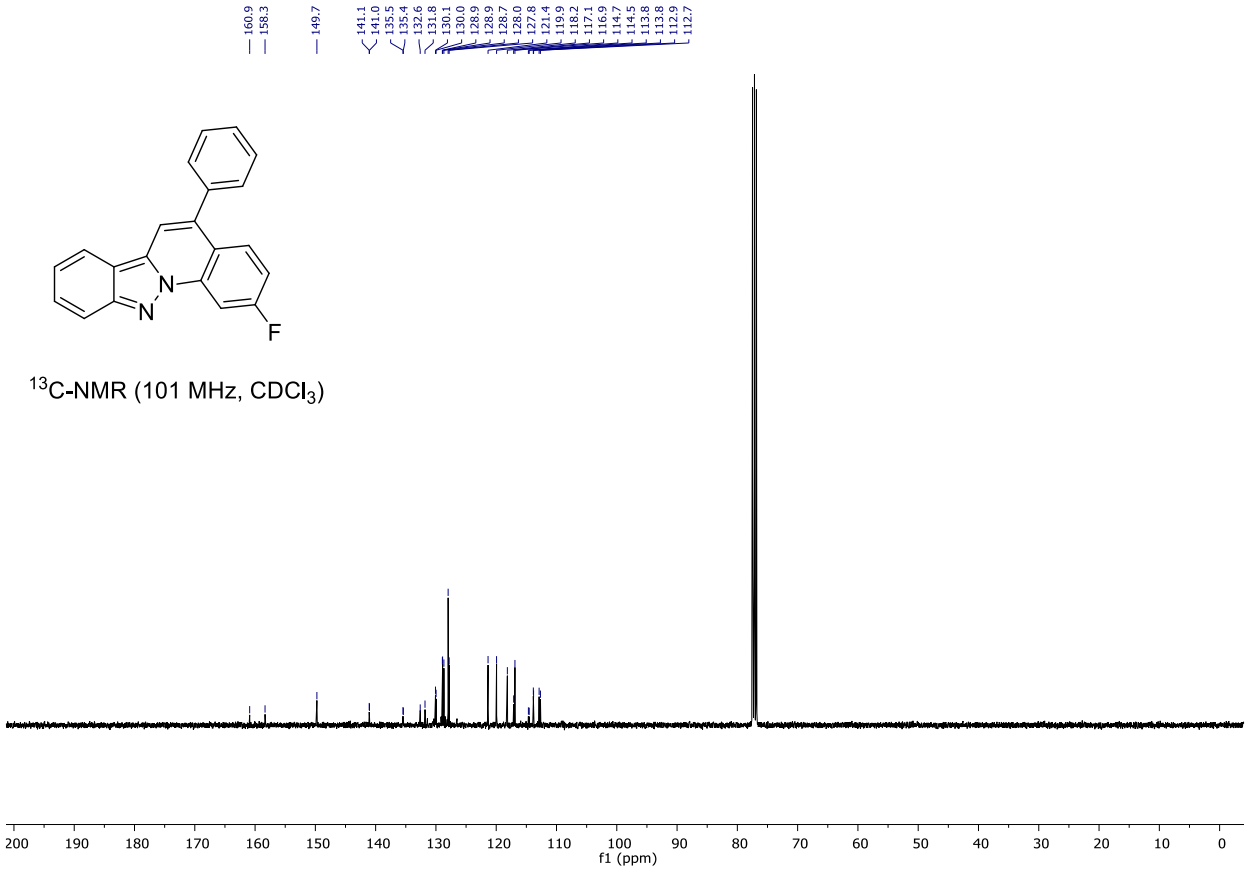
^{1}H-NMR (300 MHz, $CDCl_3$)





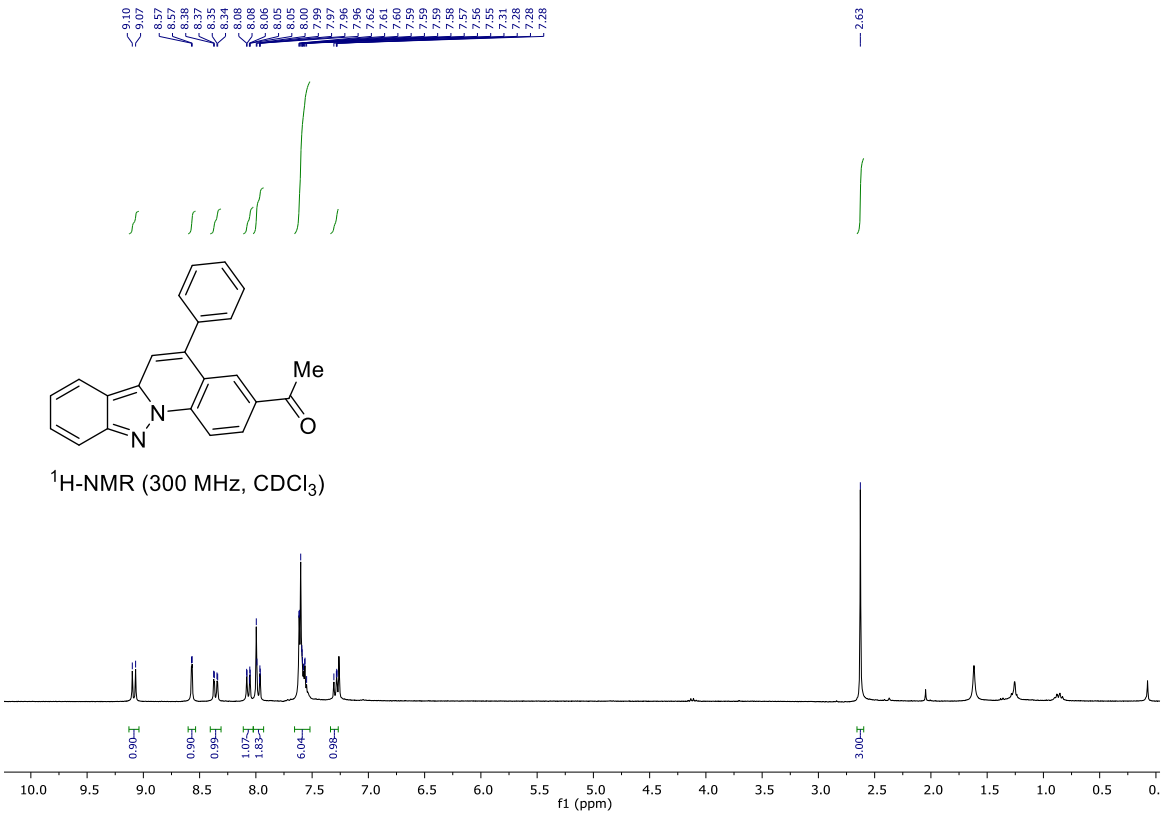
^{19}F-NMR (376 MHz, $CDCl_3$)



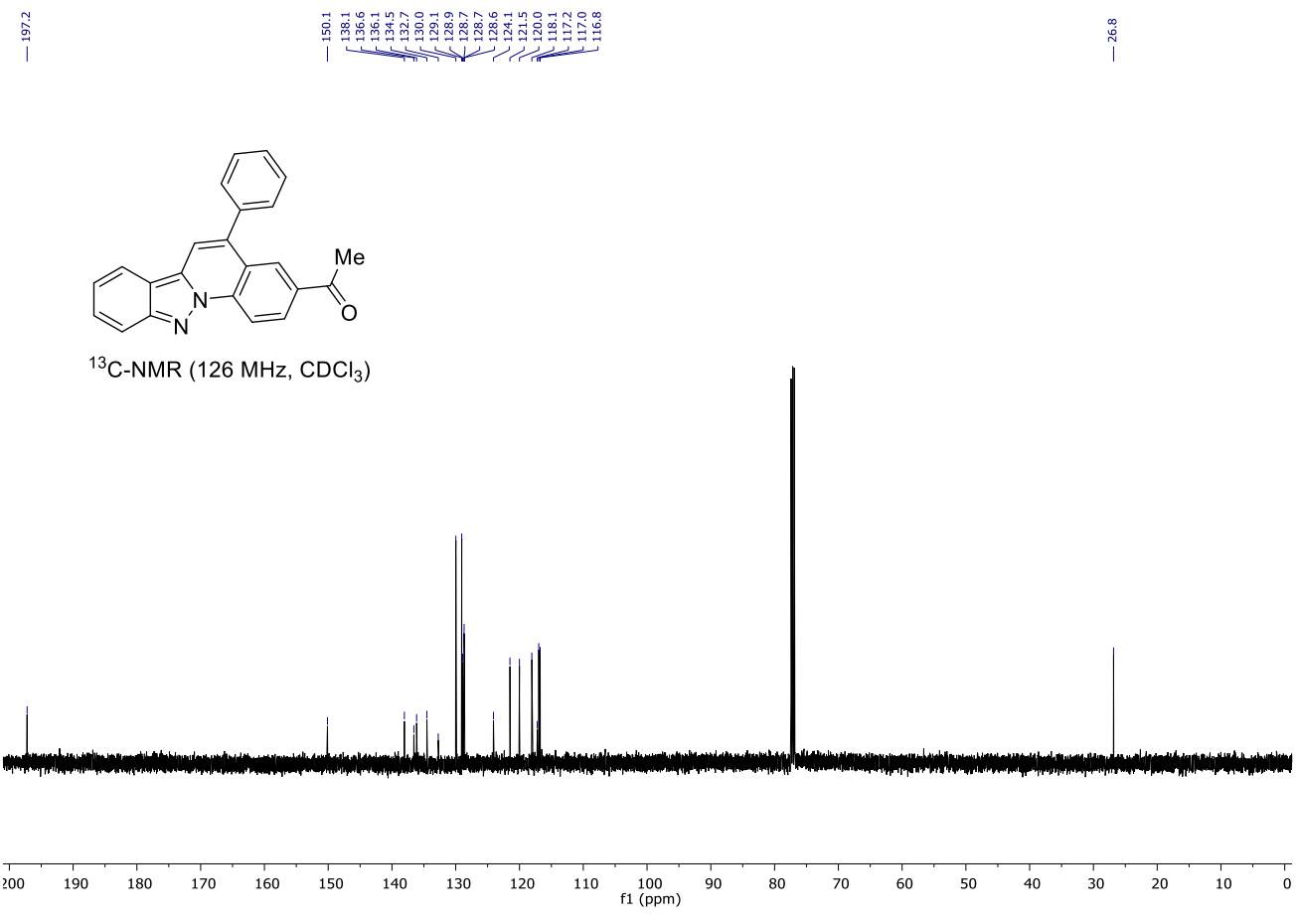


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(5-Phenylindazolo[2,3-*a*]quinolin-3-yl)ethan-1-one (4ad)

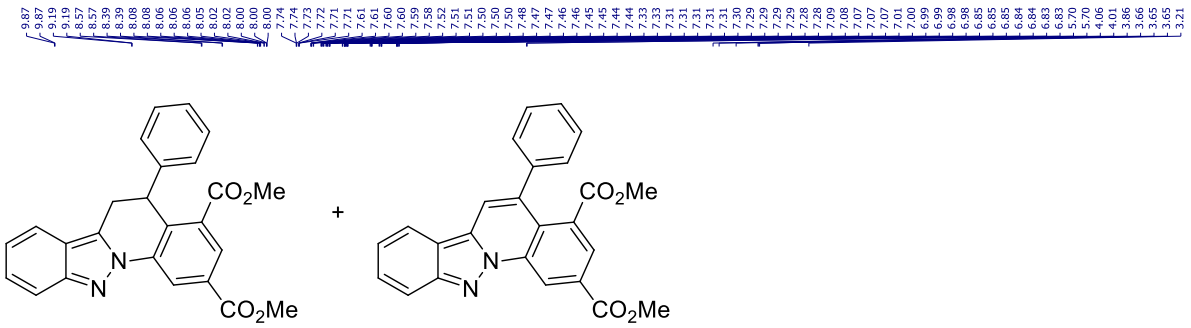


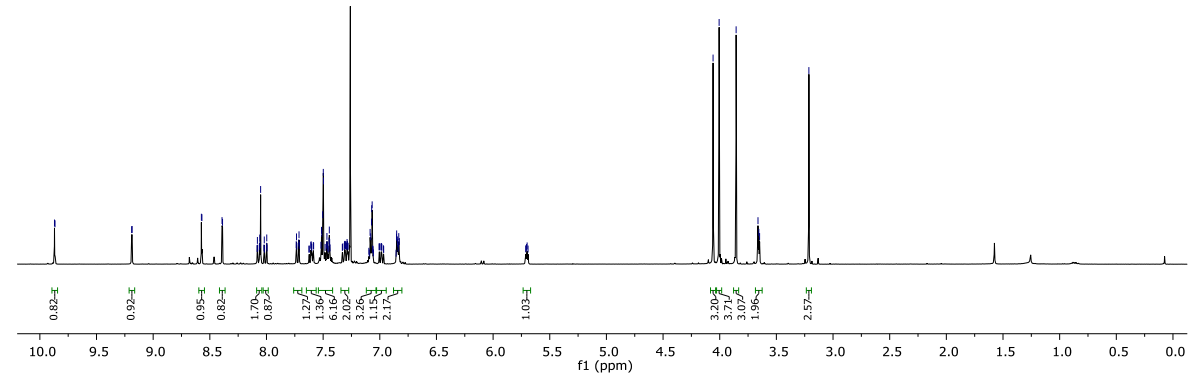
^{1}H-NMR (300 MHz, $CDCl_3$)



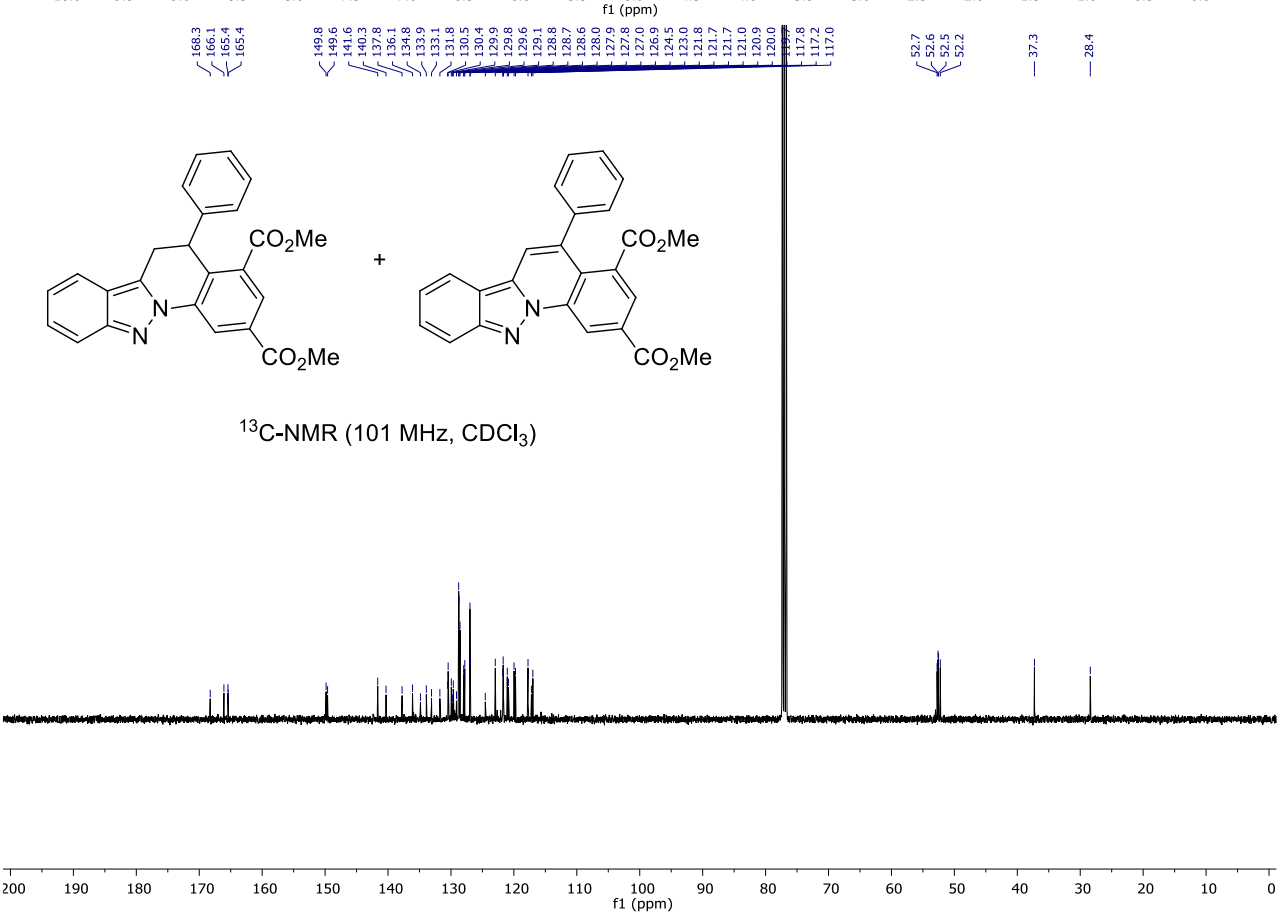
^{13}C-NMR (126 MHz, $CDCl_3$)

Dimethyl 5-phenyl-5,6-dihydroindazolo[2,3-*a*]quinoline-2,4-dicarboxylate and dimethyl 5-phenylindazolo[2,3-*a*]quinoline-2,4-dicarboxylate (3ae and 4ae)

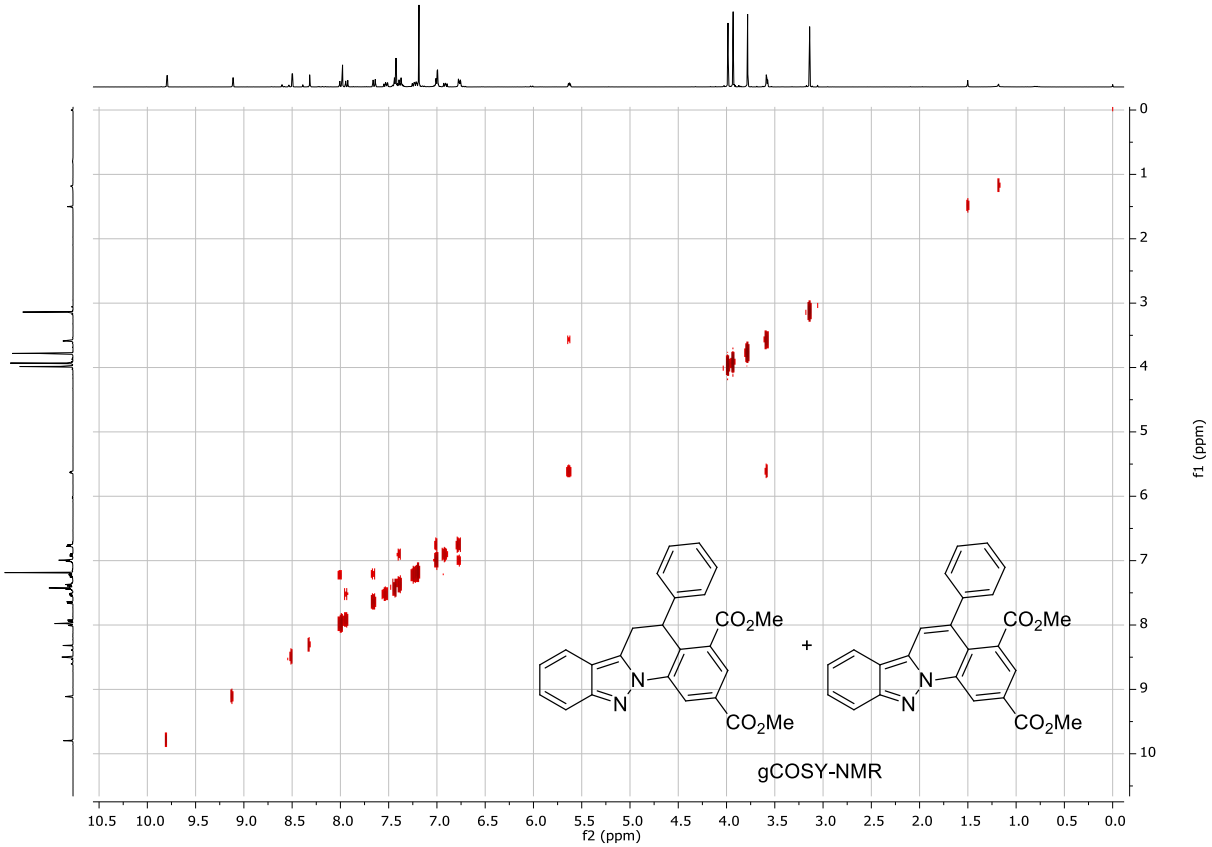


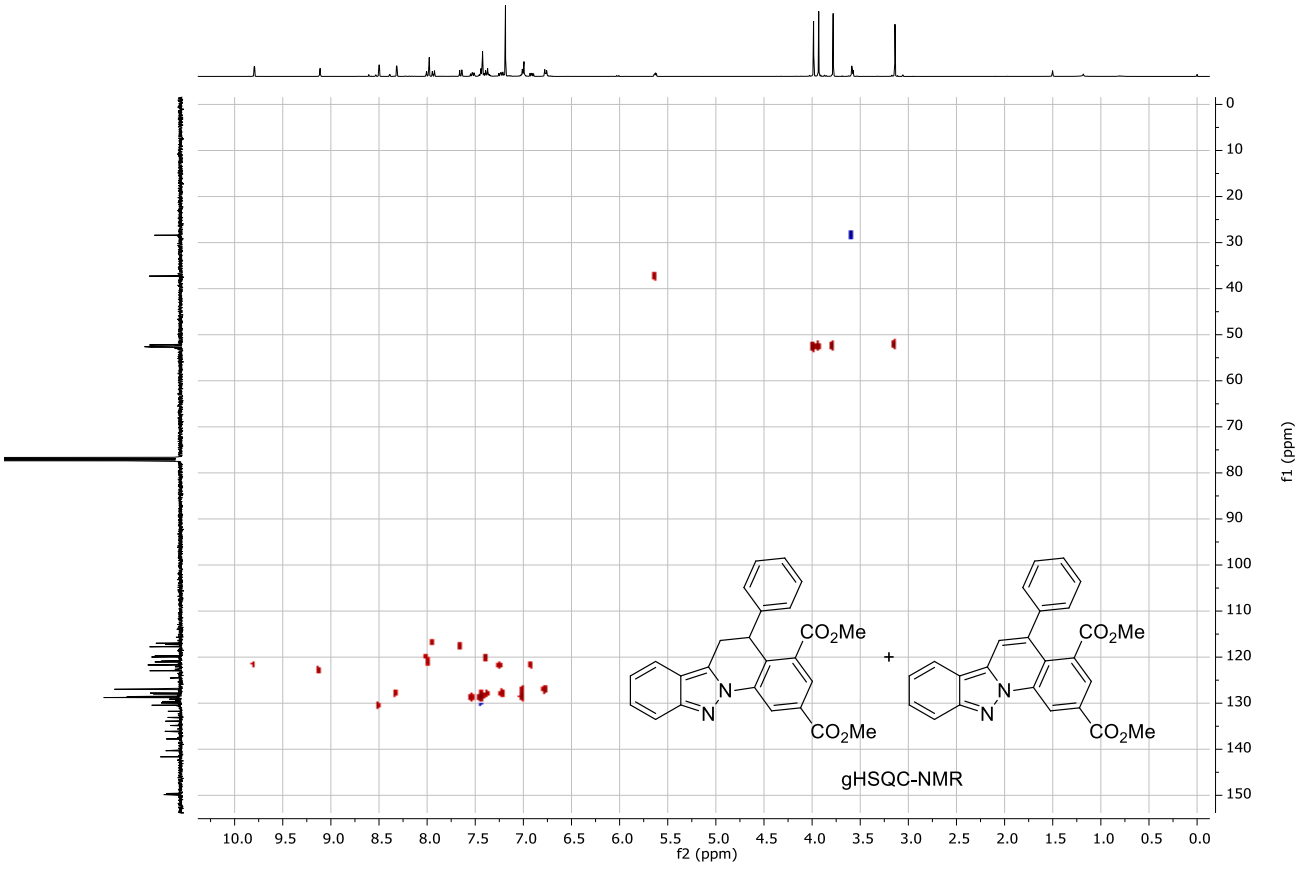


^{1}H-NMR (400 MHz, $CDCl_3$)

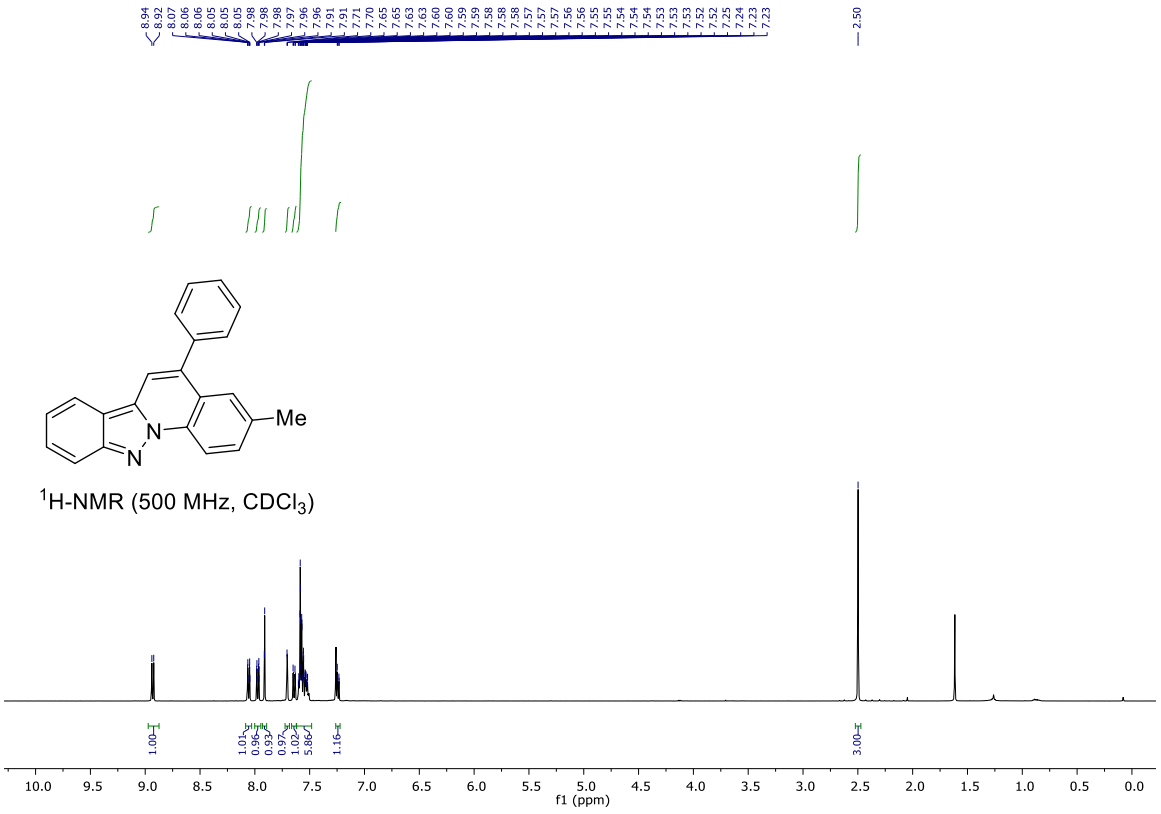


^{13}C-NMR (101 MHz, $CDCl_3$)

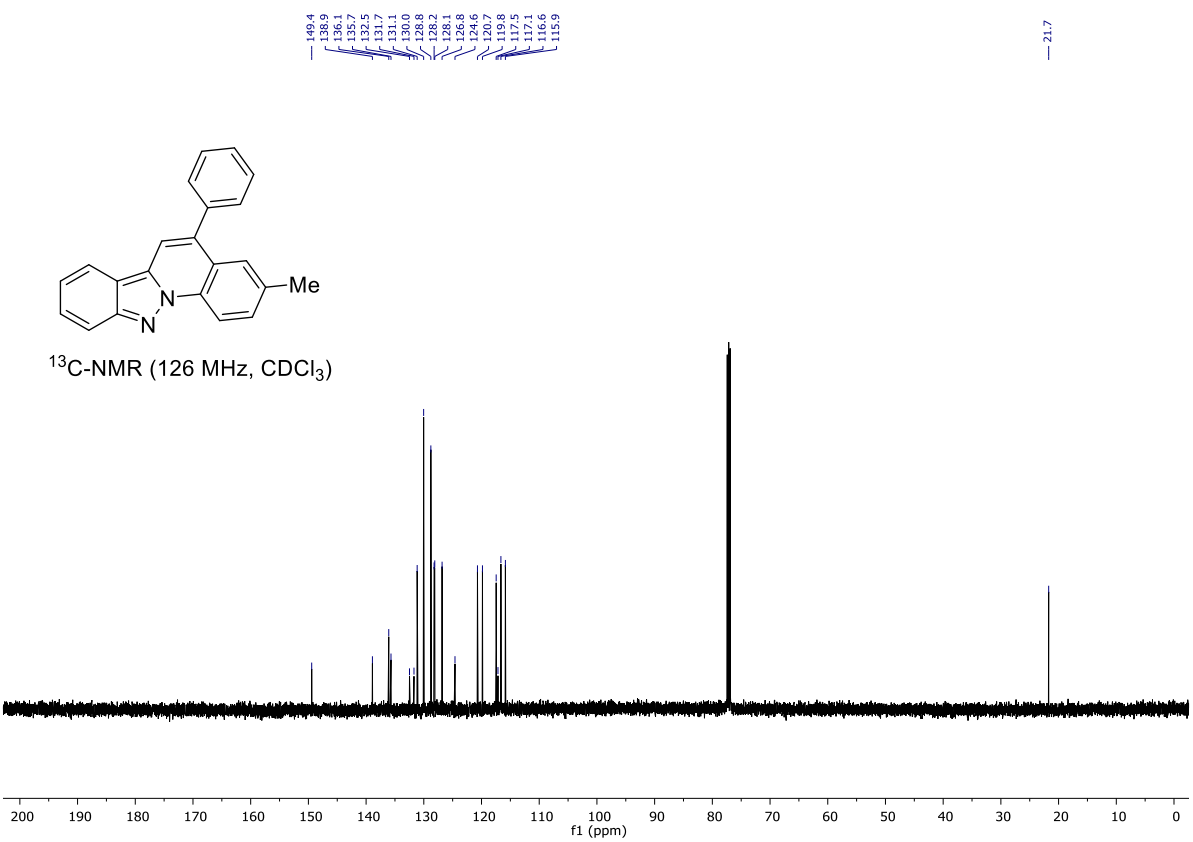

f2 (ppm)
f1 (ppm)
CO2Me
CO2Me
+
CO2Me
CO2Me
gCOSY-NMR


f2 (ppm)
f1 (ppm)
CO2Me
CO2Me
+
CO2Me
CO2Me
gHSQC-NMR

3-Methyl-5-phenylindazolo[2,3-*a*]quinoline (4af)

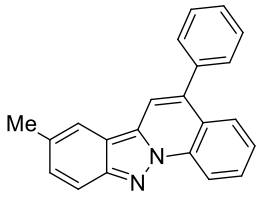


^{1}H-NMR (500 MHz, $CDCl_3$)

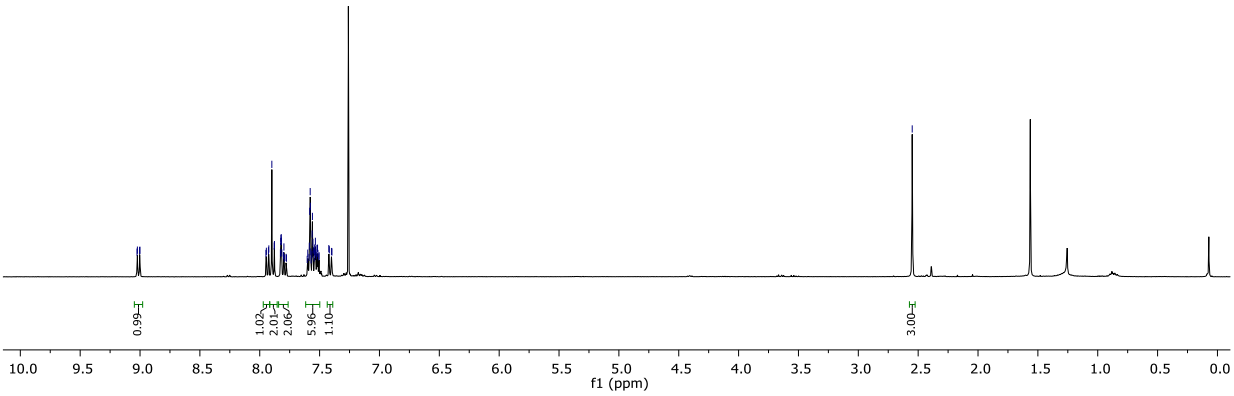


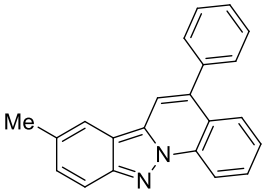
^{13}C-NMR (126 MHz, $CDCl_3$)

8-Methyl-5-phenylindazolo[2,3-*a*]quinoline (4ah)



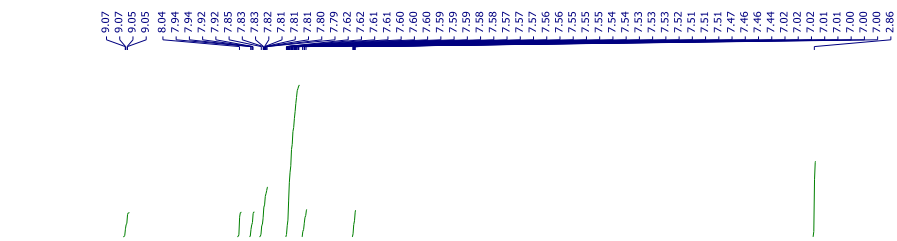
^{1}H-NMR (400 MHz, $CDCl_3$)

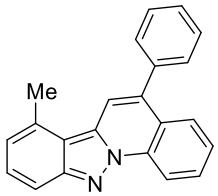




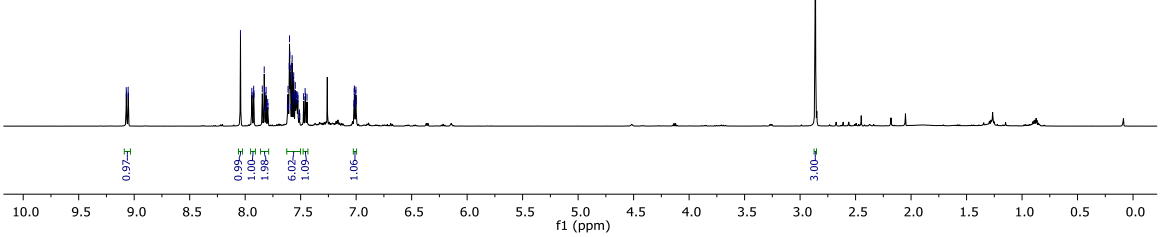
^{13}C-NMR (101 MHz, $CDCl_3$)

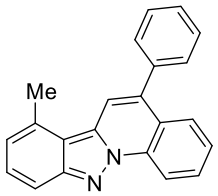
7-Methyl-5-phenylindazolo[2,3-a]quinoline (4ai)



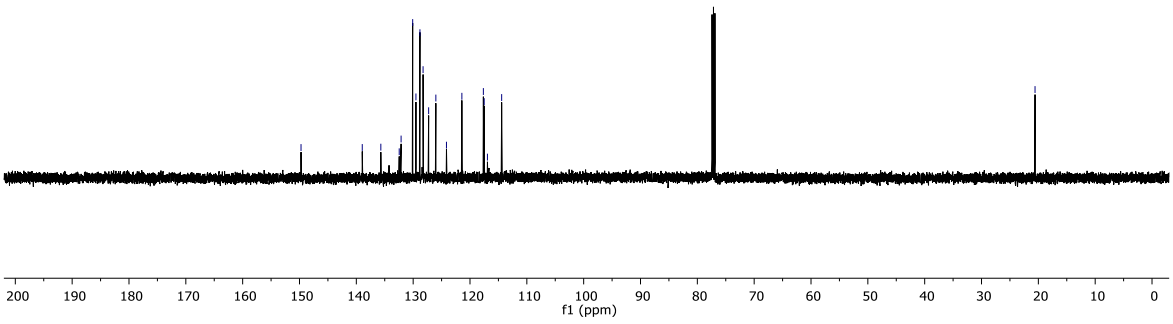


^{1}H-NMR (500 MHz, $CDCl_3$)

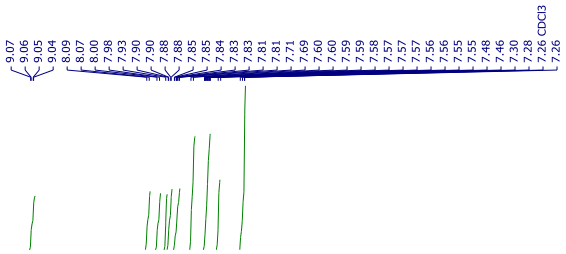


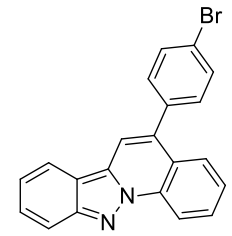


^{13}C-NMR (126 MHz, $CDCl_3$)

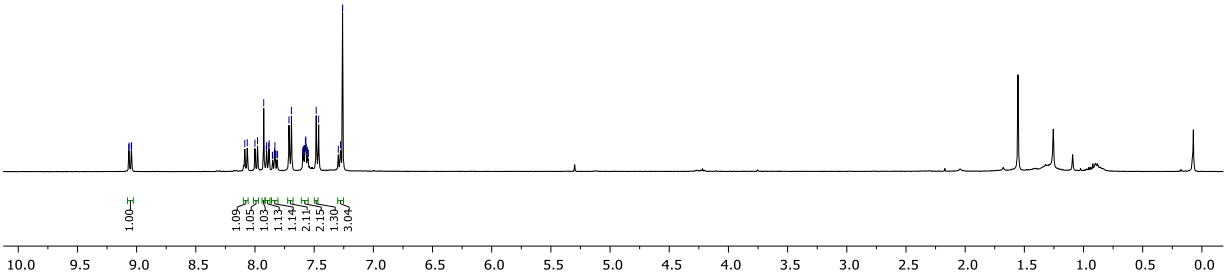


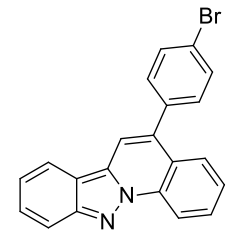
5-(4-Bromophenyl)indazolo[2,3-*a*]quinoline (4aj)





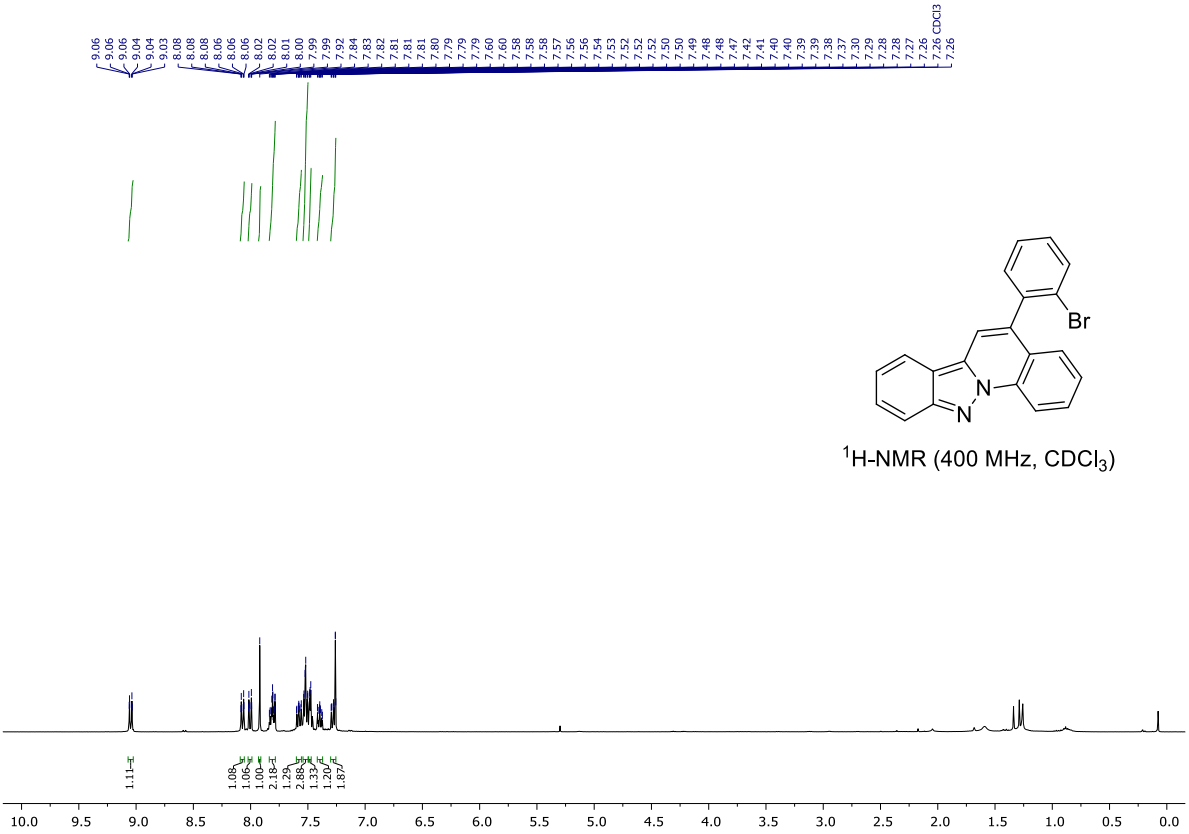
^{1}H-NMR (400 MHz, $CDCl_3$)



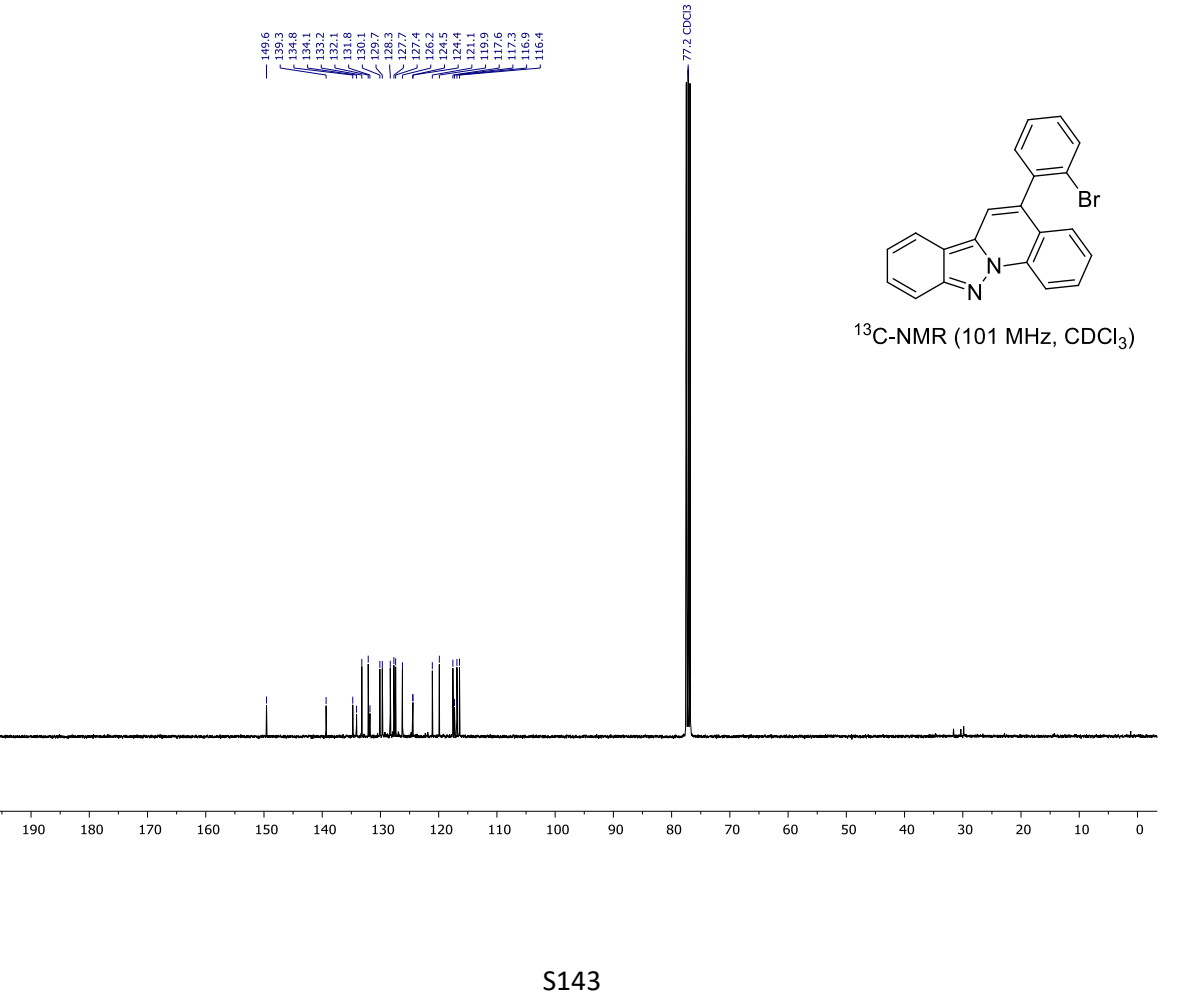


^{13}C-NMR (101 MHz, $CDCl_3$)

5-(2-bromophenyl)indazolo[2,3-a]quinoline (4ak)

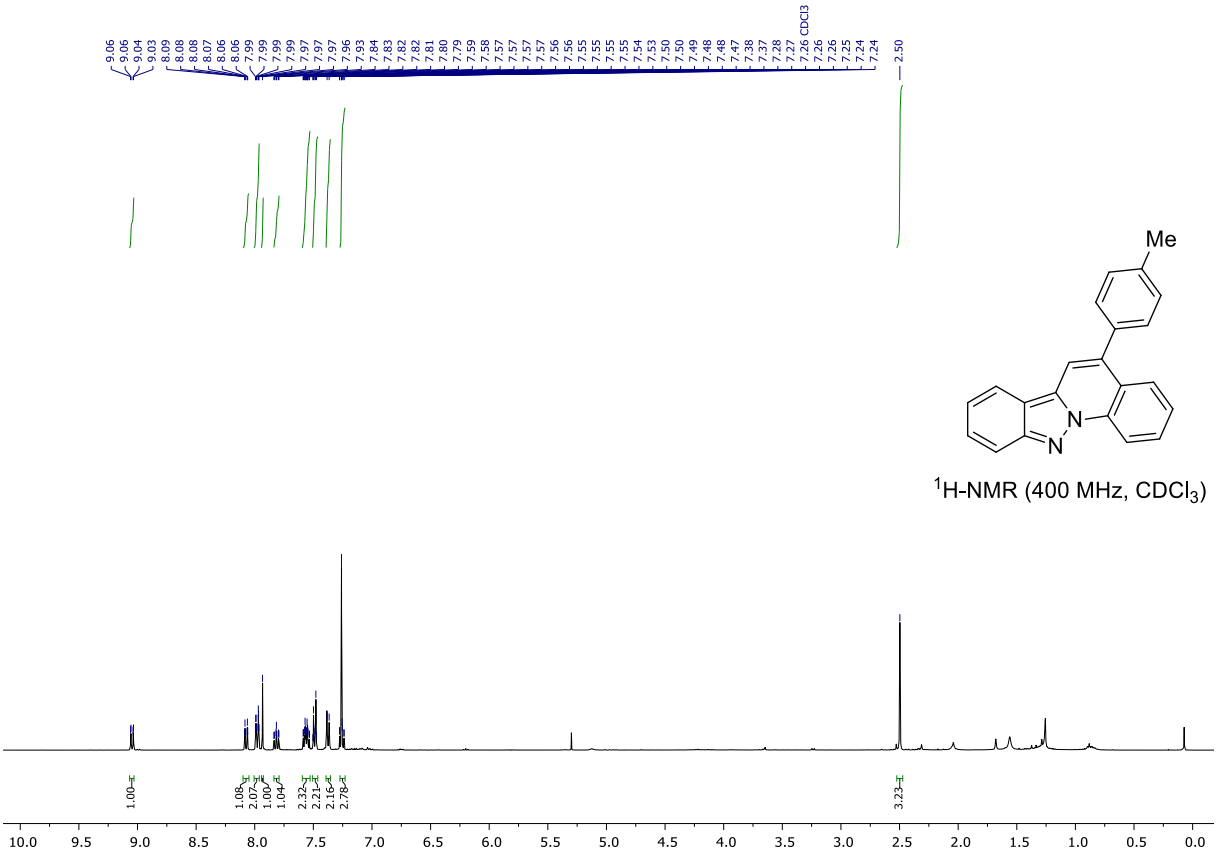


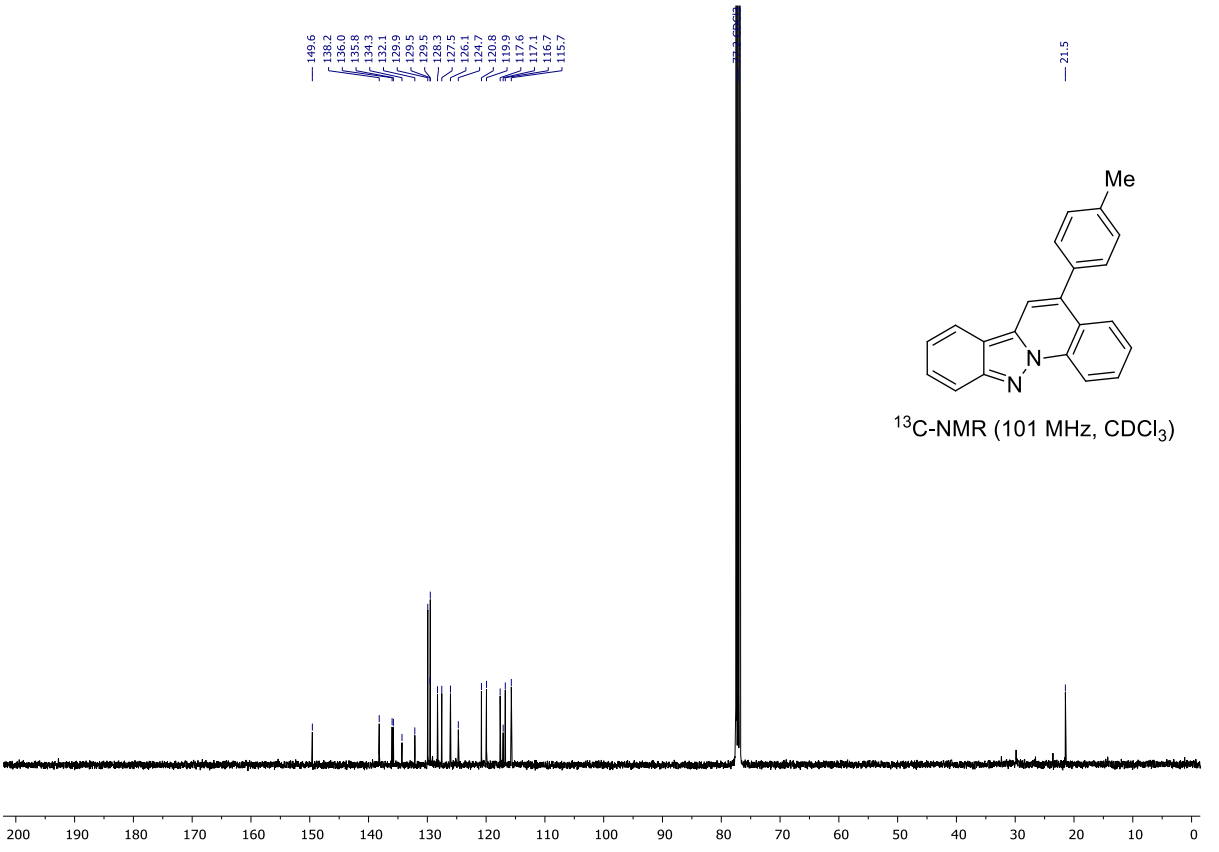
^{1}H-NMR (400 MHz, $CDCl_3$)



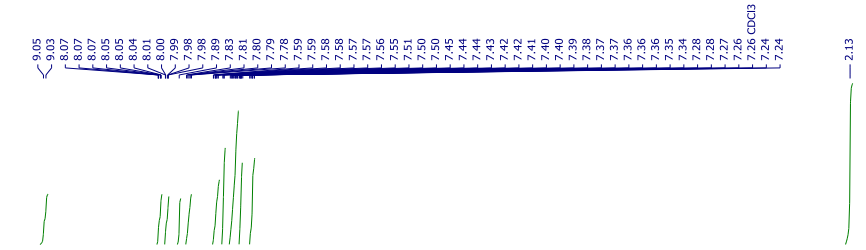
^{13}C-NMR (101 MHz, $CDCl_3$)

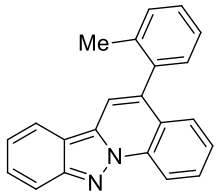
5-(*p*-Tolyl)indazolo[2,3-*a*]quinoline (4al)



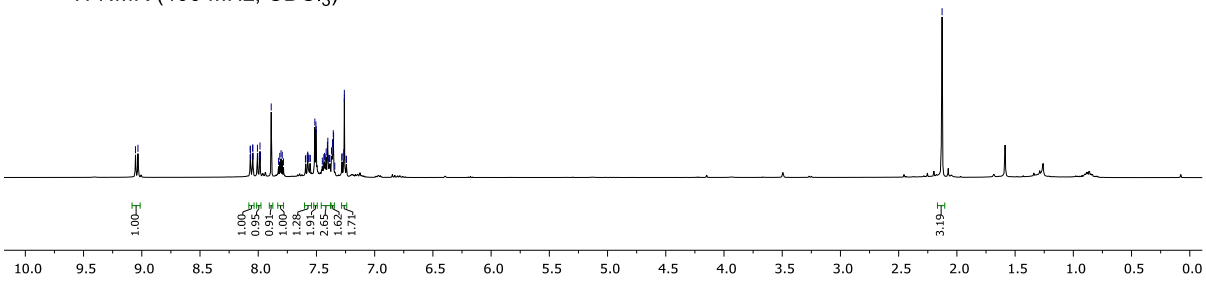


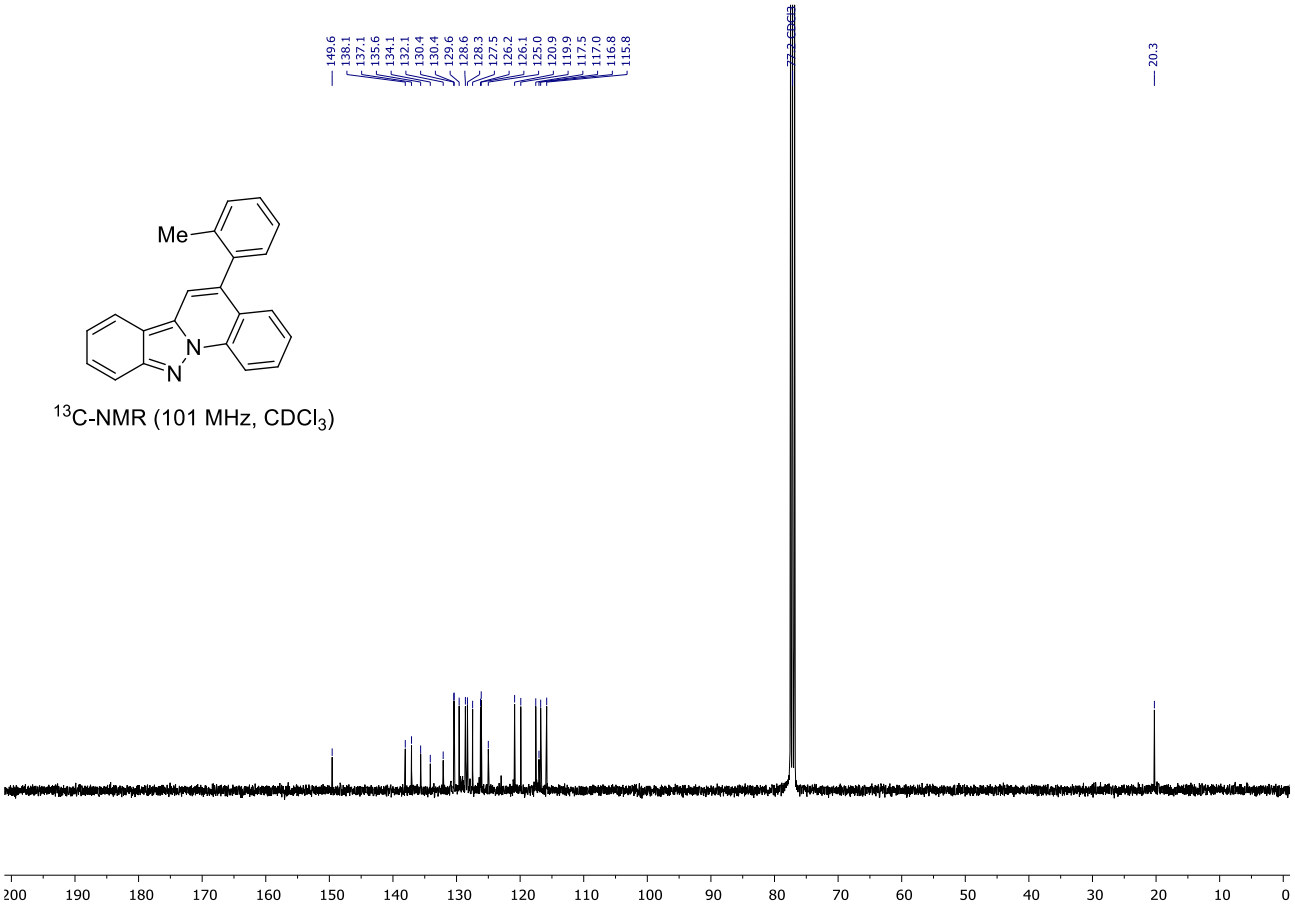
5-(*o*-Tolyl)indazolo[2,3-*a*]quinoline (4am)





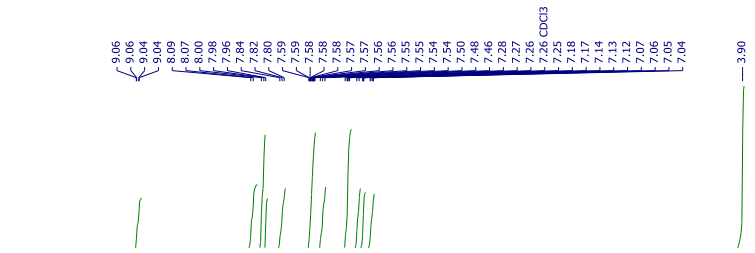
^{1}H-NMR (400 MHz, $CDCl_3$)

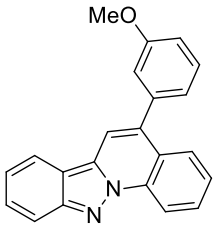




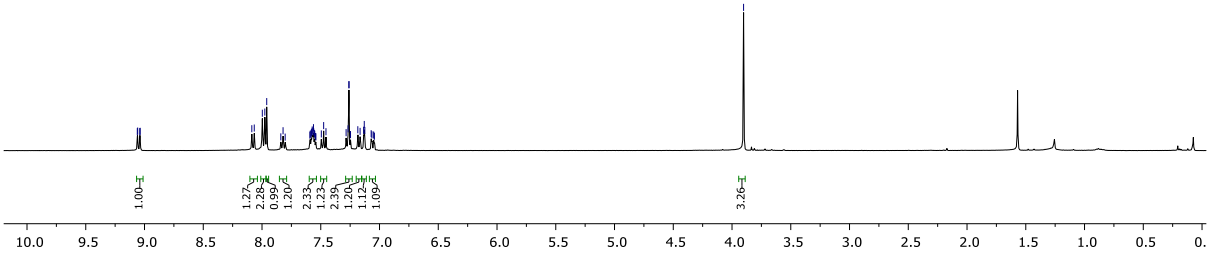
^{13}C-NMR (101 MHz, $CDCl_3$)

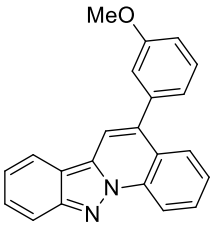
5-(3-Methoxyphenyl)indazolo[2,3-*a*]quinoline (4an)



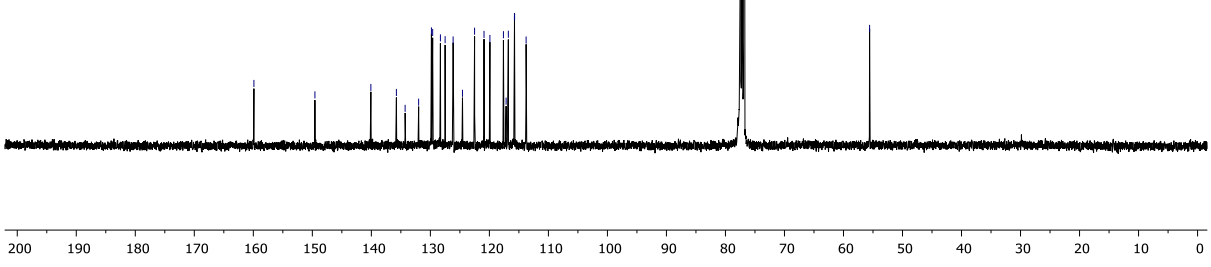


^{1}H-NMR (400 MHz, $CDCl_3$)

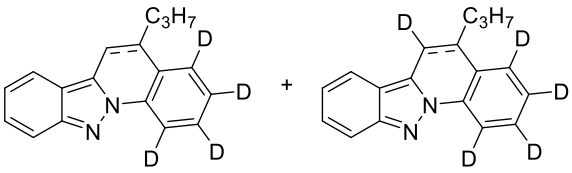




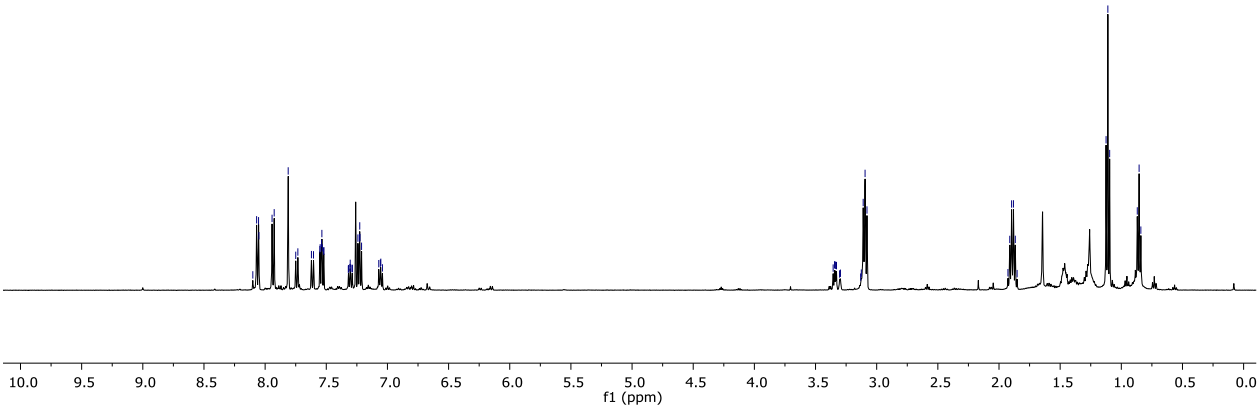
^{13}C-NMR (101 MHz, $CDCl_3$)

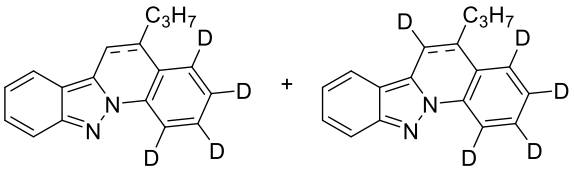


5-Propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-1,2,3,4-*d*4, 5-propyl-5,6-dihydroindazolo[2,3-*a*]quinoline-1,2,3,4,6-*d5*, 5-propylindazolo[2,3-*a*]quinoline-1,2,3,4-*d*4 and 5-propylindazolo[2,3-*a*]quinoline-1,2,3,4,6-*d*5 (*d*$_4$-3a, *d*$_5$-4a, *d*$_4$-3a and *d*$_5$-4a)

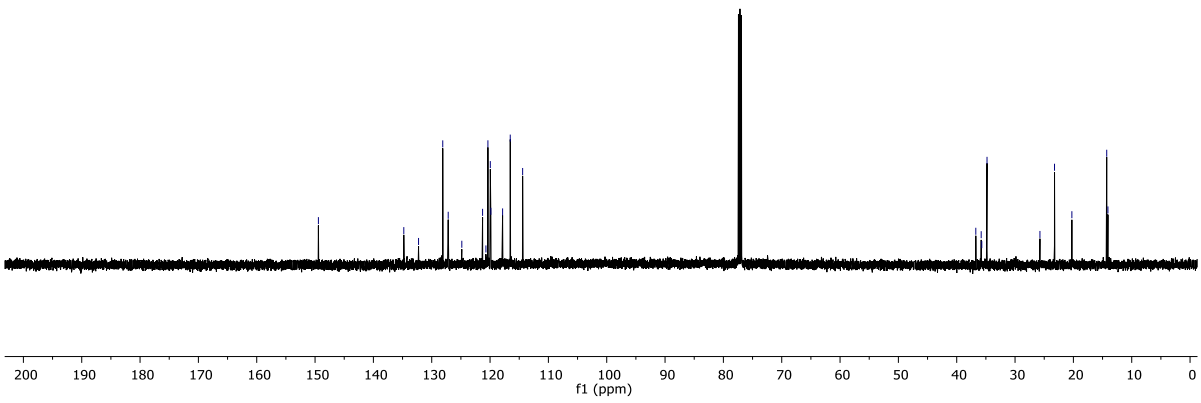


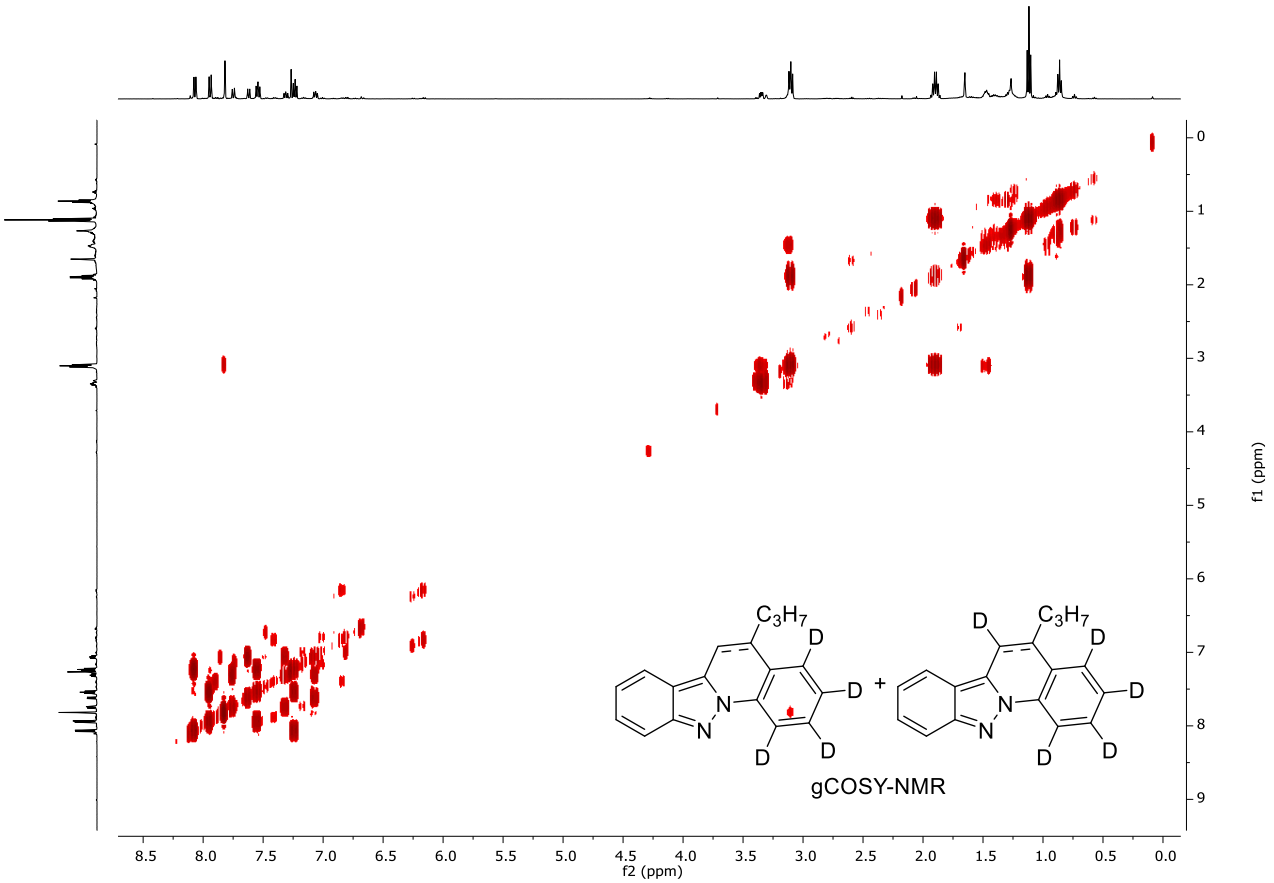
^{1}H-NMR (500 MHz, $CDCl_3$)

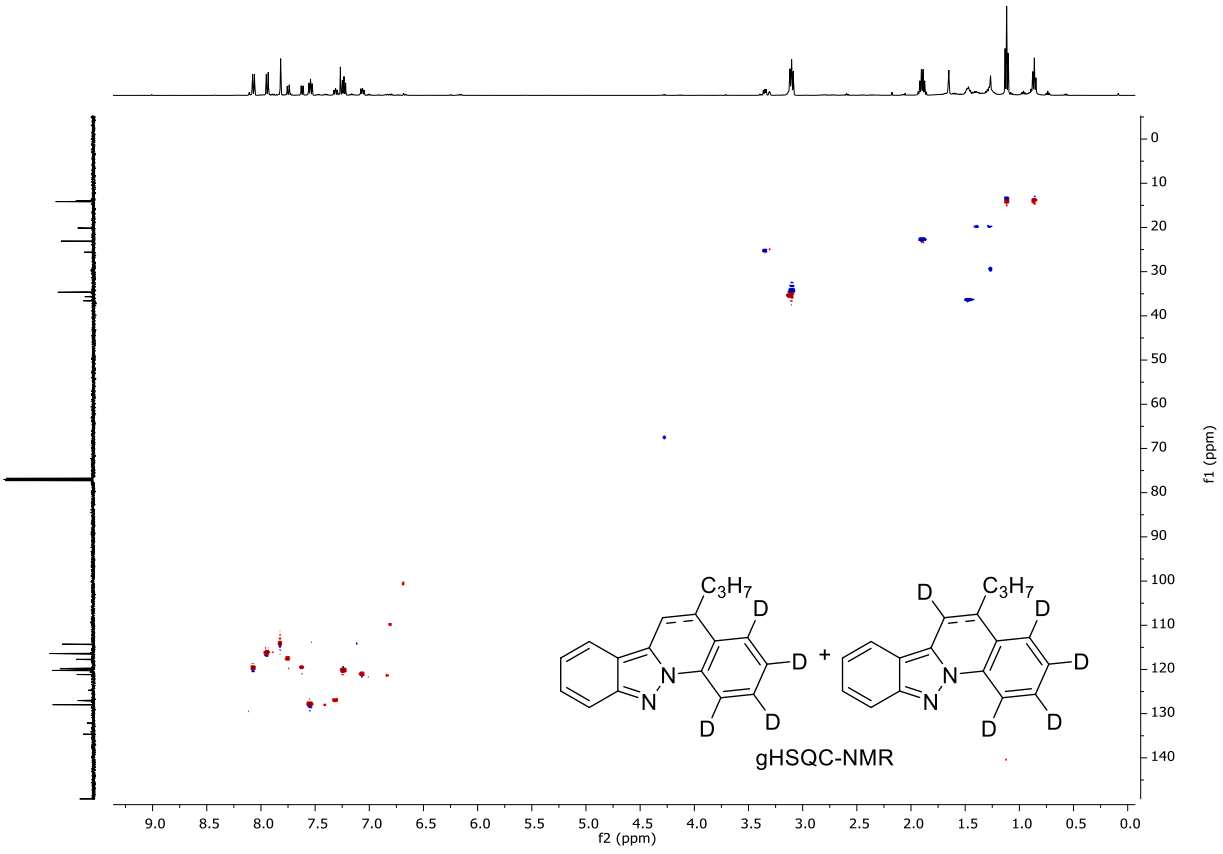




^{13}C-NMR (126 MHz, $CDCl_3$)




f2 (ppm)
f1 (ppm)
gCOSY-NMR


f2 (ppm)
f1 (ppm)
gHSQC-NMR

DFT Calculations

All reported structures were optimized at Density Functional Theory level as implemented in Gaussian 16.[3] The geometry optimizations were performed using B3LYP functional[4] with a mixed basis set of LANL2DZ[5] for Ir and 6-31+G(d,p) basis set for other atoms and M06 functional[6] with a mixed basis set of SDD[7] for Au and 6-311g(d,p) basis set for other atoms. Solvent effects were considered in all the calculations applying the polarizable continuum model (IEFPCM) using 1,2-dichloroethane or acetonitrile as solvent at 298.15 K. Reported energy values correspond to Gibbs Free (G) energies in kcal·mol^{-1}. All structures were optimized without geometrical constraint. Stationary points were characterized by frequency calculations (no negative frequency for minima and one negative frequency for transition states).

Cartesian coordinates of the computed structures:

$Ir(ppy)_3$

Ir	0.00029800	-0.00059800	0.03805600
C	-1.71656700	1.49386700	-2.16557100
C	-0.64400600	2.86992600	-0.59773200
C	-2.27839900	2.57982500	-2.82671700
H	-1.89964100	0.47755000	-2.49684000
C	-1.18623600	4.00559600	-1.22558600
C	-2.00393200	3.86302300	-2.34100100
H	-2.91256000	2.41980200	-3.69163000
H	-0.96918900	4.99388700	-0.83836700
H	-2.42369400	4.73946100	-2.82534000
C	0.23007500	2.88411300	0.58414600
C	0.62291800	4.08290900	1.21133100
C	0.65795900	1.61275200	1.07363200
C	1.44849500	4.05746700	2.33260100
H	0.28751900	5.04292100	0.82900200
C	1.49591100	1.63058500	2.20878100
C	1.88472200	2.82059200	2.82928700
H	1.74816300	4.98456300	2.81292000
H	1.84863800	0.68951200	2.62038900
H	2.53021800	2.78701800	3.70439300
N	-0.92193900	1.62793500	-1.08796500
C	2.80693800	-0.87919500	-0.60204800
C	2.14709300	0.73318700	-2.17269000
C	4.06009600	-0.97875300	-1.23267100
C	3.36682200	0.67523700	-2.83677800
H	1.35729300	1.39871500	-2.50362900
C	4.34242100	-0.20233500	-2.35096300
H	4.80865500	-1.65951700	-0.84535000
H	3.54286400	1.30201000	-3.70396800
H	5.31013600	-0.27805700	-2.83750700
C	2.38517300	-1.64000400	0.58298800
C	3.22870600	-2.57729600	1.21126300
C	1.07131100	-1.37368400	1.07470300
C	2.79693100	-3.27564200	2.33613600
H	4.22700000	-2.76761400	0.82728000
C	0.67095400	-2.10413000	2.21363000
C	1.50889300	-3.03347000	2.83527500
H	3.45138600	-3.99682400	2.81738200
H	-0.31927200	-1.93757500	2.62727700
H	1.15951500	-3.57260300	3.71327000
N	1.86889900	-0.01900800	-1.09220300
C	-2.16710600	-1.99049300	-0.59624000
C	-0.44217100	-2.23058200	-2.16754700
C	-2.88251000	-3.02496400	-1.22551800
C	-1.10484700	-3.25709900	-2.83030100
H	0.52974400	-1.88204300	-2.49930400
C	-2.35329300	-3.65992200	-2.34349000
H	-3.84677600	-3.33036700	-0.83737400
H	-0.65146900	-3.72491700	-3.69714900
H	-2.90477500	-4.45938000	-2.82894800
C	-2.61275300	-1.24287000	0.58838500
C	-3.84598500	-1.50231100	1.21816200
C	-1.72307800	-0.23900000	1.07810500
C	-4.23238800	-0.77788700	2.34303100
H	-4.51185300	-2.27068300	0.83536600
C	-2.15293700	0.47410900	2.21727600
C	-3.37635000	0.21526300	2.84065400
H	-5.18402900	-0.98206800	2.82542100
H	-1.51203900	1.24767400	2.62984800
H	-3.66650800	0.78823300	3.71878700
N	-0.95258800	-1.61128900	-1.08746300

SCF Done: E(RB3LYP) = -1541.10779604
Zero-point correction= 0.480491 (Hartree/Particle)
Thermal correction to Energy= 0.509267
Thermal correction to Enthalpy= 0.510211
Thermal correction to Gibbs Free Energy= 0.420937
Sum of electronic and zero-point Energies= -1540.627305
Sum of electronic and thermal Energies= -1540.598529
Sum of electronic and thermal Enthalpies= -1540.597585
Sum of electronic and thermal Free Energies= -1540.686859

$Ir(ppy)_3^+$

Ir	-0.00028800	0.00108800	-0.06901300
C	-0.99587500	-2.07183800	2.12847800
C	0.58487800	-2.87601700	0.58609800
C	-1.07664700	-3.30073200	2.76991100
H	-1.58530100	-1.22406400	2.45759900
C	0.54420700	-4.13918800	1.19919200
C	-0.28798900	-4.35290600	2.29152100
H	-1.74081500	-3.42615600	3.61732700
H	1.15877700	-4.94642100	0.82066600
H	-0.32404100	-5.32841600	2.76577500
C	1.40802100	-2.52247700	-0.57735300
C	2.28139600	-3.43495800	-1.19337700
C	1.30716200	-1.17923800	-1.05154000
C	3.06351200	-3.03854000	-2.27598400
H	2.36061300	-4.45583500	-0.83392700
C	2.12949900	-0.80317700	-2.13202100
C	2.98545700	-1.71901300	-2.74408500
H	3.73223100	-3.74994300	-2.75059000
H	2.08150200	0.21029600	-2.51557600
H	3.59324800	-1.40828100	-3.58947700
N	-0.18646300	-1.86195000	1.07349700
C	2.19670900	1.94352700	0.59632400
C	2.28205600	0.17278500	2.13893400
C	3.30997000	2.53781900	1.21295100
C	3.38492400	0.71563500	2.78453700
H	1.84081100	-0.76168500	2.46581800
C	3.90572700	1.92369600	2.30795500
H	3.70542400	3.47216800	0.83464300
H	3.82129600	0.20247800	3.63369900
H	4.76791500	2.37883800	2.78478500
C	1.48453800	2.48090100	-0.56989500
C	1.84230600	3.69253300	-1.18525600
C	0.37191200	1.72358300	-1.04735900
C	1.11224200	4.17230100	-2.27049500
H	2.68686300	4.27016900	-0.82385400
C	-0.36119100	2.24903200	-2.13004700
C	0.00815500	3.44711600	-2.74145700
H	1.39751800	5.10610100	-2.74507000
H	-1.21438900	1.70170000	-2.51624900
H	-0.56146000	3.81887400	-3.58877300
N	1.70018600	0.76944700	1.08181200
C	-2.78409400	0.92640800	0.59141700
C	-1.29980000	1.87629200	2.14748600

C	-3.85859700	1.58592500	1.21037300
C	-2.32491700	2.55367800	2.79415300
H	-0.27131000	1.95946400	2.47848700
C	-3.62957900	2.40173400	2.31168700
H	-4.86438700	1.46065400	0.82908700
H	-2.10306800	3.18242000	3.64868300
H	-4.45748200	2.91486100	2.79036600
C	-2.88812100	0.04792800	-0.58082500
C	-4.11387200	-0.24428400	-1.20307000
C	-1.67445800	-0.53398900	-1.05748800
C	-4.16024100	-1.10999200	-2.29355400
H	-5.03780500	0.19606200	-0.84253900
C	-1.75833800	-1.42444000	-2.14571000
C	-2.97832400	-1.70025600	-2.76357300
H	-5.10981300	-1.32747400	-2.77271200
H	-0.85617300	-1.88757500	-2.53071100
H	-3.01196600	-2.37476000	-3.61476300
N	-1.52084100	1.08302300	1.08236800

SCF Done: E(UB3LYP) = -1540.91610443
Zero-point correction= 0.480902 (Hartree/Particle)
Thermal correction to Energy= 0.510081
Thermal correction to Enthalpy= 0.511025
Thermal correction to Gibbs Free Energy= 0.418791
Sum of electronic and zero-point Energies= -1540.435203
Sum of electronic and thermal Energies= -1540.406024
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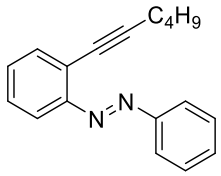
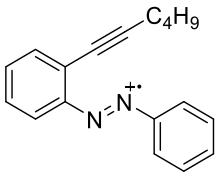
Sum of electronic and thermal Free Energies= -1540.497313



1a

C	1.40029500	4.29140200	-0.38323400
C	0.05157800	4.61659900	-0.17127700
C	1.81418400	2.96684300	-0.31059100
C	-0.87210600	3.61536200	0.11226200
H	-0.27537100	5.65045900	-0.22700600
C	0.89143800	1.94401500	-0.02532800
C	-0.47522500	2.26326100	0.19180000
H	-1.91536400	3.86370100	0.27672300
H	2.12127300	5.07286700	-0.60324500
H	2.85203200	2.69946700	-0.47069400
N	1.23621400	0.57428600	0.06809800
N	2.44745800	0.30493600	-0.15202400
C	2.79312700	-1.06719700	-0.05457000
C	4.13995500	-1.36670500	-0.31283000
C	1.89431100	-2.10032400	0.27407700
C	4.59136200	-2.68617800	-0.24589000
H	4.81562600	-0.55485200	-0.56391400
C	2.35219100	-3.41310000	0.33927700
H	0.85647400	-1.85979100	0.47264100
C	3.69887800	-3.71137400	0.08010500
H	5.63399400	-2.91257100	-0.44683900
H	1.66125000	-4.21185500	0.59278500
H	4.04617400	-4.73889800	0.13349500
C	-1.45327200	1.26283000	0.48535700
C	-2.33629400	0.46833300	0.74575400
C	-3.38868600	-0.50781300	1.03246200
H	-4.11291400	-0.06350200	1.72823900
H	-2.94813500	-1.36826600	1.55362900
C	-4.13006000	-0.99992500	-0.23127500
H	-3.40266300	-1.44403600	-0.92239100
H	-4.56873400	-0.13666500	-0.74751500
C	-5.22648300	-2.02120400	0.09489200
H	-5.94402300	-1.57098500	0.79442900
H	-4.77963700	-2.87680100	0.61945600
C	-5.96926200	-2.51665300	-1.15121300
H	-5.28202200	-3.00182300	-1.85433400
H	-6.74534800	-3.24337900	-0.88788500
H	-6.45389400	-1.68665200	-1.67876300

SCF Done: E(RB3LYP) = -806.233638359
Zero-point correction= 0.312887 (Hartree/Particle)
Thermal correction to Energy= 0.331774
Thermal correction to Enthalpy= 0.332718
Thermal correction to Gibbs Free Energy= 0.261192
Sum of electronic and zero-point Energies= -805.920752
Sum of electronic and thermal Energies= -805.901865
Sum of electronic and thermal Enthalpies= -805.900921
Sum of electronic and thermal Free Energies= -805.972446

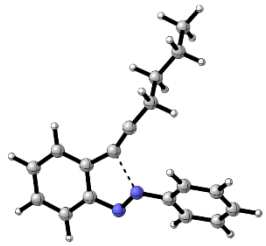


I

C	-4.55580800	1.86698900	0.31731200
C	-3.78042500	2.97433500	-0.06837800
C	-3.95633700	0.62705700	0.45826600
C	-2.41363700	2.85001700	-0.31333700
H	-4.25100000	3.94518100	-0.18453200
C	-2.57172200	0.49112300	0.22538700
C	-1.76737600	1.60821400	-0.18442000
H	-1.83189500	3.71260400	-0.61721100
H	-5.61791500	1.98198000	0.50176000
H	-4.52341000	-0.24943300	0.75104900
N	-2.03744000	-0.76241600	0.38792200
N	-0.84150700	-1.01920200	0.48706500
C	-0.24354900	-2.24601000	0.24599900
C	-0.88274200	-3.25315800	-0.51253900
C	1.05338100	-2.42791200	0.76656200
C	-0.21451000	-4.45024300	-0.72158200
H	-1.87670600	-3.08114800	-0.91061200
C	1.70468100	-3.63600100	0.54607300
H	1.51603600	-1.62739000	1.33310400
C	1.07406900	-4.64321000	-0.19539400
H	-0.69020500	-5.23917200	-1.29442400
H	2.69975900	-3.79505500	0.94668100
H	1.58675700	-5.58393400	-0.36851900
C	-0.38536600	1.46314800	-0.43645800
C	0.80673200	1.39403500	-0.69496600
C	2.23257700	1.31131600	-0.97515600
H	2.41411200	1.72310100	-1.97743900
H	2.52384500	0.25341700	-1.01677100
C	3.10503900	2.06028700	0.06091500
H	2.90624900	1.65026600	1.05844600

H	2.80471900	3.11465100	0.08438400
C	4.60049400	1.95002500	-0.26025900
H	4.78503600	2.34965400	-1.26632300
H	4.88762700	0.89031700	-0.29018200
C	5.47859200	2.69037700	0.75472000
H	5.33842000	2.29061100	1.76581100
H	6.53959400	2.59409000	0.50166400
H	5.23706300	3.75924000	0.78174300

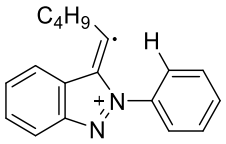
SCF Done: E(UB3LYP) = -806.016192475
Zero-point correction= 0.312617 (Hartree/Particle)
Thermal correction to Energy= 0.331551
Thermal correction to Enthalpy= 0.332495
Thermal correction to Gibbs Free Energy= 0.261359
Sum of electronic and zero-point Energies= -805.703576
Sum of electronic and thermal Energies= -805.684642
Sum of electronic and thermal Enthalpies= -805.683698
Sum of electronic and thermal Free Energies= -805.754834



TSI-II

C	-4.04607300	-2.68322400	0.23398400
C	-2.95523000	-3.51534100	-0.06539700
C	-3.87598200	-1.30396000	0.31494800
C	-1.67731600	-2.99383600	-0.28863600
H	-3.10248200	-4.58884000	-0.12249000
C	-2.59762500	-0.78342000	0.09160200
C	-1.48332600	-1.61122600	-0.20358800
H	-0.84443900	-3.64956800	-0.51498100
H	-5.02568100	-3.11721000	0.40090500
H	-4.69998200	-0.63601700	0.53965400
N	-2.33879800	0.57950300	0.12714400
C	-0.24632900	-0.92185100	-0.38594600
C	0.99599200	-0.87214800	-0.53339100
C	2.42499400	-0.69494700	-0.66294600
H	2.67737800	0.33716000	-0.37595800
H	2.70145300	-0.80497800	-1.72010200
C	3.24290400	-1.68788100	0.20814700
H	2.98611100	-2.71208900	-0.08476300
H	2.94927700	-1.56704600	1.25698600
C	4.75171300	-1.45996400	0.05329600
H	4.99320300	-0.42733100	0.33766700
H	5.02752400	-1.56532500	-1.00416000
C	5.57925500	-2.43375300	0.89941800
H	5.38235500	-3.47331900	0.61338900
H	6.65088000	-2.24933700	0.77158000
H	5.34652200	-2.32936500	1.96534800
N	-1.17839400	0.87771200	-0.19811500
C	-0.62164600	2.15955600	-0.08189200
C	0.41593400	2.50725800	-0.96105600
C	-1.09006600	3.05895900	0.89433000
C	0.97952800	3.77755300	-0.87070600
H	0.74435300	1.80305300	-1.71707200
C	-0.51135100	4.32100700	0.97173800
H	-1.88148500	2.75729800	1.57098700
C	0.52037300	4.68172000	0.09392100
H	1.77273200	4.06317800	-1.55322600
H	-0.85938400	5.02423000	1.72115600
H	0.96752100	5.66798200	0.16491400

Frequency= -272.9803
SCF Done: E(UB3LYP) = -806.010052861
Zero-point correction= 0.312533 (Hartree/Particle)
Thermal correction to Energy= 0.330456
Thermal correction to Enthalpy= 0.331401
Thermal correction to Gibbs Free Energy= 0.263947
Sum of electronic and zero-point Energies= -805.697462
Sum of electronic and thermal Energies= -805.679538
Sum of electronic and thermal Enthalpies= -805.678594
Sum of electronic and thermal Free Energies= -805.746048

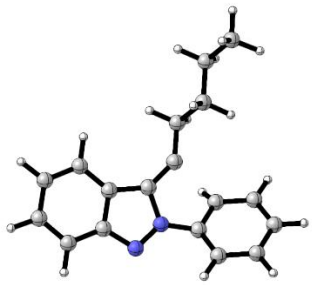


II

C	-2.61902000	-3.85810700	-0.07753700
C	-3.38247100	-2.69585200	0.17735100
C	-1.23850000	-3.79525000	-0.20452000
C	-2.79674800	-1.43478100	0.31335000
H	-4.45975200	-2.78779700	0.27070500
C	-0.65069700	-2.52632300	-0.06752500
C	-1.41111200	-1.35881800	0.18881000
H	-3.40132900	-0.55632300	0.50872300
H	-3.12555800	-4.81225900	-0.17358200
H	-0.63273600	-4.67301900	-0.39945400
N	0.68781500	-2.23410400	-0.13482000
C	-0.43929300	-0.28049800	0.24202600
C	-0.62380900	1.03730300	0.30977400
C	-0.18513800	2.41587700	0.28180300
H	0.82812500	2.47261400	-0.14665200
C	-1.14433100	3.36900000	-0.48398300
H	-1.24758400	3.01611700	-1.51646800
H	-0.64473900	4.34323500	-0.52983800
C	-2.52231900	3.51562300	0.17006000
H	-2.39598100	3.86644100	1.20290700
H	-3.00307500	2.53031500	0.23405700
C	-3.43364700	4.48209400	-0.59397600
H	-3.60335400	4.13824800	-1.62077900
H	-4.40928400	4.57123900	-0.10535500
H	-2.99279700	5.48430900	-0.64553100
N	0.82665900	-0.96176000	0.05625600
C	2.12718500	-0.36181200	0.03132800
C	2.51006100	0.48745400	1.07431400
C	2.99146900	-0.67285600	-1.02356700
C	3.78817800	1.04696400	1.04685900
C	4.26476100	-0.10516800	-1.03460100
H	2.66282900	-1.33356800	-1.81794200
C	4.66249700	0.75482600	-0.00470700
H	4.10251100	1.69928700	1.85473200
H	4.94302100	-0.33035000	-1.85090900
H	5.65499200	1.19344400	-0.01985100
H	-0.10015100	2.75371500	1.32704900

H	1.84114500	0.67734800	1.90658900

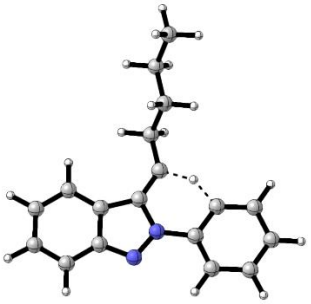
SCF Done: E(UB3LYP) = -806.030433940
Zero-point correction= 0.314946 (Hartree/Particle)
Thermal correction to Energy= 0.332525
Thermal correction to Enthalpy= 0.333469
Thermal correction to Gibbs Free Energy= 0.267159
Sum of electronic and zero-point Energies= -805.715488
Sum of electronic and thermal Energies= -805.697909
Sum of electronic and thermal Enthalpies= -805.696965
Sum of electronic and thermal Free Energies= -805.763275



TSII-III

C	-4.72264600	-1.32527500	-0.27255600
C	-3.82800100	-2.39571100	-0.04371100
C	-4.28003200	-0.01009900	-0.30445400
C	-2.46369600	-2.18627200	0.15674600
H	-4.21547500	-3.40903100	-0.02200200
C	-2.90738200	0.20777500	-0.10176500
C	-1.99986000	-0.86901100	0.12644800
H	-1.79653800	-3.02236800	0.33345600
H	-5.77495000	-1.54049600	-0.42477400
H	-4.95393000	0.82124900	-0.47918800
N	-2.27078300	1.42966000	-0.07190500
C	-0.71210400	-0.22760300	0.25245000
C	0.60131500	-0.53053600	0.33232000
C	1.44916900	-1.69504700	0.56073800
H	0.85446700	-2.60240300	0.36644300
H	1.69342700	-1.72317300	1.63484400
C	2.75239800	-1.71851900	-0.26976900
H	3.33140200	-0.81433400	-0.04914500
H	2.49702300	-1.68212600	-1.33542600
C	3.59645200	-2.96500500	0.02296500
H	3.00188300	-3.86401200	-0.18699000
H	3.83661800	-2.99515000	1.09421700
C	4.89155500	-3.00470000	-0.79537200
H	5.52289400	-2.13472900	-0.58066200
H	5.47292400	-3.90387400	-0.56687300
H	4.68042700	-3.00747000	-1.87096000
N	-1.01570900	1.16299600	0.13263800
C	0.06167200	2.05212200	0.19240400
C	1.17837800	1.55194800	0.92570900
C	0.13756600	3.19803400	-0.59630600
C	2.42298200	2.20768900	0.75978500
C	1.37069000	3.84048400	-0.70305700
H	-0.72625700	3.53042200	-1.16054900
C	2.51267100	3.32917100	-0.05350700
H	3.28370200	1.86606100	1.32428300
H	1.45719900	4.72283300	-1.32813400
H	3.46287900	3.84112500	-0.16356400
H	1.01098800	1.01221100	1.85548500

Frequency= -352.1943
SCF Done: E(UB3LYP) = -806.019988676
Zero-point correction= 0.314038 (Hartree/Particle)
Thermal correction to Energy= 0.330886
Thermal correction to Enthalpy= 0.331830
Thermal correction to Gibbs Free Energy= 0.267596
Sum of electronic and zero-point Energies= -805.705951
Sum of electronic and thermal Energies= -805.689103
Sum of electronic and thermal Enthalpies= -805.688158
Sum of electronic and thermal Free Energies= -805.752392

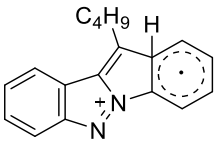


TSII-V

C	-2.43326500	4.01065600	0.21534600
C	-1.06881000	4.18624500	-0.09761100
C	-2.97787300	2.73955000	0.34959700
C	-0.20157400	3.10441800	-0.28700200
H	-0.67792800	5.19381100	-0.19470100
C	-2.10705700	1.65592100	0.15954600
C	-0.73260500	1.82326400	-0.15575700
H	0.84101200	3.27534300	-0.52634300
H	-3.06208700	4.88352700	0.35214600
H	-4.02289300	2.57910700	0.58945100
N	-2.43831400	0.32588600	0.24453700
C	-0.21542400	0.47188000	-0.26365600
C	0.97264500	-0.10899600	-0.53398900
C	2.31034700	0.41786000	-0.83795300
H	2.28853700	1.51065200	-0.92659100
H	2.61156900	0.01653500	-1.81679200
C	3.36569400	-0.01396400	0.21680500
H	3.38362100	-1.10850500	0.28092500
H	3.06107700	0.36089800	1.20113600
C	4.76458300	0.51097300	-0.13258300
H	4.73243300	1.60547500	-0.21103500
H	5.05387600	0.13567400	-1.12294600
C	5.81845700	0.10126700	0.90200400
H	5.89630400	-0.98931700	0.97823300
H	6.80545300	0.48850100	0.62866600
H	5.57044200	0.49003400	1.89632600
N	-1.36519400	-0.35358500	0.00565400
C	-1.34587500	-1.77586300	0.01147500
C	-0.13497500	-2.39962500	-0.26039600
C	-2.48964400	-2.53968500	0.27805400
C	0.00516800	-3.77186100	-0.28204000
C	-2.36649900	-3.92951400	0.26028300
H	-3.43658300	-2.05749000	0.49060100
C	-1.13877200	-4.54490600	-0.01514900
H	0.95867500	-4.24322800	-0.49637300

H	-3.24014400	-4.53941300	0.46393200
H	-1.06537700	-5.62793800	-0.02411000
H	0.77945100	-1.40547700	-0.47569900

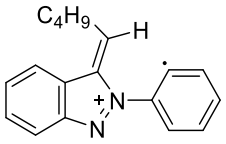
Frequency= -1649.7253
SCF Done: E(UB3LYP) = -806.006639537
Zero-point correction= 0.309588 (Hartree/Particle)
Thermal correction to Energy= 0.325957
Thermal correction to Enthalpy= 0.326901
Thermal correction to Gibbs Free Energy= 0.264240
Sum of electronic and zero-point Energies= -805.697051
Sum of electronic and thermal Energies= -805.680683
Sum of electronic and thermal Enthalpies= -805.679738
Sum of electronic and thermal Free Energies= -805.742400



III

C	-4.57525100	1.17812500	0.30417000
C	-3.69108500	2.21307600	-0.08096300
C	-4.13778900	-0.13016300	0.44856100
C	-2.34006300	1.96704500	-0.33280400
H	-4.07369600	3.22342800	-0.18122800
C	-2.77712400	-0.39279800	0.19500900
C	-1.87736500	0.65706100	-0.19690700
H	-1.67714300	2.77473900	-0.62197700
H	-5.61712300	1.41731400	0.49014600
H	-4.80742500	-0.93025300	0.74409000
N	-2.16686500	-1.61806400	0.28596500
C	-0.60929700	-0.00090200	-0.34982800
C	0.71683700	0.13240900	-0.65470900
C	1.48573400	1.36205400	-0.99276200
H	0.81602900	2.11433500	-1.42126000
H	2.23265200	1.12077300	-1.75845500
C	2.20435000	1.96667200	0.24369800
H	2.85604600	1.21161700	0.70079700
H	1.45302500	2.23091500	0.99760900
C	3.03220200	3.20565900	-0.12216300
H	2.37646200	3.95335700	-0.58753100
H	3.77738300	2.93159300	-0.88058400
C	3.73633100	3.82340300	1.09101000
H	4.42411100	3.10808200	1.55679800
H	4.31741000	4.70506900	0.80115700
H	3.01243700	4.13562700	1.85258800
N	-0.89641600	-1.36497500	-0.03833700
C	0.20446300	-2.14231200	-0.10576600
C	1.28756000	-1.27904500	-0.67042200
C	0.42675200	-3.44443400	0.34142400
C	2.66596500	-1.70255900	-0.28771500
C	1.75016600	-3.84022400	0.46913100
H	-0.39222800	-4.07692900	0.66302300
C	2.85489800	-2.96079700	0.19503900
H	3.50191800	-1.05335500	-0.52434300
H	1.96410600	-4.83545900	0.84491300
H	3.85970100	-3.31817600	0.39243100
H	1.27560000	-1.50499900	-1.76558500

SCF Done: E(UB3LYP) = -806.070196615
Zero-point correction= 0.316427 (Hartree/Particle)
Thermal correction to Energy= 0.333110
Thermal correction to Enthalpy= 0.334054
Thermal correction to Gibbs Free Energy= 0.270633
Sum of electronic and zero-point Energies= -805.753769
Sum of electronic and thermal Energies= -805.737087
Sum of electronic and thermal Enthalpies= -805.736143
Sum of electronic and thermal Free Energies= -805.799564

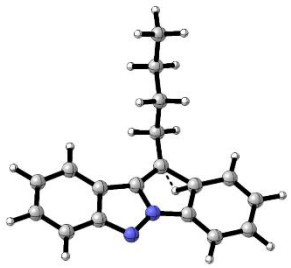


V

C	-4.72546400	-0.86592200	0.08056100
C	-3.99784700	-2.04080900	-0.22319400
C	-4.08119400	0.34913300	0.25425200
C	-2.60807000	-2.04369200	-0.35898200
H	-4.54021200	-2.97124000	-0.35652700
C	-2.68152100	0.34460600	0.11230200
C	-1.94577200	-0.82782900	-0.19036700
H	-2.07939400	-2.96144200	-0.59319000
H	-5.80417800	-0.92341900	0.17658600
H	-4.61608500	1.26245800	0.48887700
N	-1.84924200	1.42431700	0.20945700
C	-0.55841200	-0.40500000	-0.21070900
C	0.54512100	-1.20337100	-0.26875100
C	1.99177100	-0.92239600	-0.07794800
H	2.14360600	0.00884000	0.47051100
C	2.74184500	-2.08757600	0.61141500
H	2.23422300	-2.34179500	1.55071900
H	3.73106300	-1.70597100	0.89011300
C	2.91541800	-3.34389200	-0.25157000
H	3.43595900	-3.07164800	-1.17935600
H	1.93749100	-3.74202600	-0.55293500
C	3.69692100	-4.44645100	0.47272500
H	3.18121400	-4.76096300	1.38740700
H	3.81629400	-5.32854800	-0.16455300
H	4.69726600	-4.09948200	0.75590500
N	-0.63112700	1.00330200	0.01875800
C	0.42441600	1.96959100	-0.01898100
C	1.33000800	2.00646500	-1.06065400
C	0.51268900	2.95961200	0.97379200
C	2.32888100	2.93849500	-1.19984500
C	1.51275900	3.92731000	0.87352000
H	-0.18833100	2.95562100	1.80213100
C	2.41377700	3.92411700	-0.19840600
H	3.01734900	2.92912400	-2.03898800
H	1.59129300	4.68984500	1.64089300
H	3.18657200	4.68399800	-0.26372000
H	2.43149900	-0.76354300	-1.07679800
H	0.29500200	-2.24750000	-0.44952700

SCF Done: E(UB3LYP) = -806.015281604
Zero-point correction= 0.315068 (Hartree/Particle)
Thermal correction to Energy= 0.332722
Thermal correction to Enthalpy= 0.333666
Thermal correction to Gibbs Free Energy= 0.266747
Sum of electronic and zero-point Energies= -805.700213
Sum of electronic and thermal Energies= -805.682559

Sum of electronic and thermal Enthalpies= -805.681615
Sum of electronic and thermal Free Energies= -805.748535

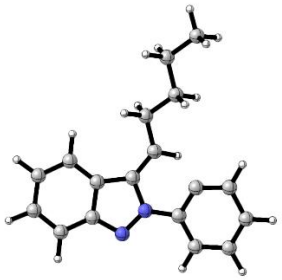


TS_{III-IV}

C	-4.65652900	0.49042900	0.16011100
C	-3.92441300	1.60855900	-0.30223300
C	-4.03054000	-0.71526900	0.43744300
C	-2.53925200	1.55584200	-0.50218800
H	-4.45117800	2.53499100	-0.50613000
C	-2.63257700	-0.78736800	0.23849000
C	-1.88870800	0.35351000	-0.23492000
H	-1.99958300	2.42859700	-0.85218000
H	-5.72826600	0.58309000	0.29950700
H	-4.58019800	-1.57991400	0.79271100
N	-1.84845100	-1.87710500	0.45030100
C	-0.53878400	-0.12363200	-0.29791400
C	0.79001500	0.18521500	-0.64962400
C	1.38784900	1.51794500	-0.99281800
H	0.69912900	2.07070300	-1.64039700
H	2.30812300	1.36756800	-1.56686700
C	1.70154100	2.35065300	0.27314300
H	2.38299500	1.78459400	0.92020200
H	0.77773000	2.50444300	0.84449400
C	2.32626500	3.70890400	-0.07131700
H	1.64300300	4.26591500	-0.72600400
H	3.24655800	3.54820400	-0.64833700
C	2.64076100	4.54532900	1.17405300
H	3.34804600	4.02625300	1.83120200
H	3.08448200	5.50789700	0.89938100
H	1.73315800	4.74868800	1.75409200
N	-0.60633800	-1.43595100	0.13166600
C	0.61345100	-2.07160500	0.09104400
C	1.55124700	-1.09391900	-0.41669800
C	1.00425100	-3.34898000	0.47340900
C	2.94397000	-1.42023100	-0.45526900
C	2.36394300	-3.64337200	0.38347800
H	0.28555900	-4.06970200	0.84476500
C	3.31586900	-2.68907000	-0.06326200
H	3.67179100	-0.69583900	-0.80224600
H	2.70842800	-4.62982600	0.67472000
H	4.36386500	-2.96681500	-0.08974900
H	1.11971600	-0.77509900	-1.57248900

Frequency= -1108.7972
SCF Done: E(UB3LYP) = -806.047766372
Zero-point correction= 0.313094 (Hartree/Particle)
Thermal correction to Energy= 0.329506
Thermal correction to Enthalpy= 0.330451
Thermal correction to Gibbs Free Energy= 0.267934
Sum of electronic and zero-point Energies= -805.734672

Sum of electronic and thermal Energies= -805.718260
Sum of electronic and thermal Enthalpies= -805.717316
Sum of electronic and thermal Free Energies= -805.779832

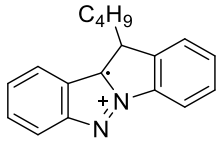


TS_{V-IV}

C	-4.42668300	-1.83215400	-0.29165200
C	-3.39518900	-2.78841400	-0.16371700
C	-4.15772700	-0.46950200	-0.24095800
C	-2.06192400	-2.41798300	0.02108600
H	-3.64688600	-3.84270600	-0.21119900
C	-2.81694700	-0.09050200	-0.06884300
C	-1.76740900	-1.05032400	0.05382600
H	-1.29181100	-3.17343800	0.12228700
H	-5.44766900	-2.17215700	-0.42778000
H	-4.94067600	0.27619000	-0.32105000
N	-2.33069900	1.19090000	-0.01934100
C	-0.59406600	-0.26060300	0.29559900
C	0.72214400	-0.52272600	0.64293700
C	1.42794800	-1.80497900	0.37849800
H	0.96178800	-2.34528000	-0.45057100
H	1.30387000	-2.42474700	1.28340600
C	2.93918000	-1.61567000	0.12484900
H	3.38202200	-1.07771500	0.97294300
H	3.07592900	-0.98329200	-0.76126300
C	3.66624200	-2.95108300	-0.07589400
H	3.20822900	-3.49069900	-0.91520300
H	3.52085200	-3.57837300	0.81358100
C	5.16531500	-2.77180500	-0.33955800
H	5.65682800	-2.26259900	0.49753300
H	5.65817200	-3.73967200	-0.47757800
H	5.34012200	-2.17606500	-1.24295700
N	-1.04860800	1.07251300	0.21278200
C	-0.11403700	2.11987400	0.07954900
C	1.19119800	1.74735700	-0.19969900
C	-0.42437800	3.48248800	0.18635900
C	2.24117900	2.61891700	-0.34796500
C	0.60831900	4.40389400	0.01221800
H	-1.43939300	3.79604900	0.40501500
C	1.92129700	3.98733600	-0.25181200
H	3.25460400	2.28932500	-0.55062700
H	0.38969300	5.46351800	0.08843200
H	2.70737100	4.72348800	-0.38943500
H	1.21533600	0.16954600	1.32144000

Frequency= -204.6385
SCF Done: E(UB3LYP) = -806.014172004
Zero-point correction= 0.314365 (Hartree/Particle)
Thermal correction to Energy= 0.331160
Thermal correction to Enthalpy= 0.332104
Thermal correction to Gibbs Free Energy= 0.267941

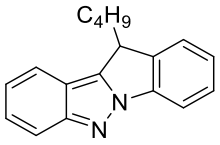
Sum of electronic and zero-point Energies= -805.699807
Sum of electronic and thermal Energies= -805.683012
Sum of electronic and thermal Enthalpies= -805.682068
Sum of electronic and thermal Free Energies= -805.746231



IV

C	3.11343200	-3.24901600	-0.06051100
C	3.52349600	-2.01808000	0.45799200
C	1.76854300	-3.48727400	-0.41372100
C	2.61298000	-0.95877800	0.64137000
H	4.56294900	-1.87234300	0.72983100
C	0.86237200	-2.44320400	-0.23240700
C	1.27484500	-1.16875300	0.28184000
H	2.94638900	-0.01631300	1.06031600
H	3.84068200	-4.04306500	-0.18949000
H	1.44847600	-4.44588800	-0.80704100
N	-0.49197800	-2.47700600	-0.48239800
C	0.08346100	-0.40936300	0.31536000
C	-0.52620000	0.91817400	0.65683600
C	-0.00317900	2.12320500	-0.18267300
H	-0.67011800	2.96122200	0.04810400
H	-0.13675500	1.89625700	-1.24660200
C	1.44410900	2.53729700	0.09814000
H	2.13129800	1.74230200	-0.21706300
H	1.58606200	2.67294800	1.17929600
C	1.82851500	3.83346800	-0.63127900
H	1.15423800	4.63894800	-0.31163000
H	1.66477900	3.70289100	-1.70936900
C	3.28160500	4.25125800	-0.38050800
H	3.98093500	3.48103000	-0.72653500
H	3.52168700	5.18041300	-0.90775100
H	3.46736400	4.41568500	0.68739100
N	-0.89717100	-1.26515700	-0.14344400
C	-2.17898600	-0.67212900	-0.10432400
C	-2.00550800	0.62633600	0.39797900
C	-3.40657400	-1.21582100	-0.45979700
C	-3.12548000	1.43327400	0.55886600
C	-4.52043300	-0.38825400	-0.29121000
H	-3.49254600	-2.22581500	-0.84349100
C	-4.38182300	0.91380900	0.21215900
H	-3.03794800	2.44302200	0.94689100
H	-5.50504900	-0.76178500	-0.55154700
H	-5.26460700	1.53245500	0.33649300
H	-0.34484800	1.13628800	1.71841500

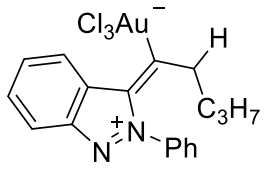
SCF Done: E(UB3LYP) = -806.100702486
Zero-point correction= 0.317543 (Hartree/Particle)
12202- Thermal correction to Energy= 0.334142
Thermal correction to Enthalpy= 0.335086
Thermal correction to Gibbs Free Energy= 0.271975
Sum of electronic and zero-point Energies= -805.783160
Sum of electronic and thermal Energies= -805.766561
Sum of electronic and thermal Enthalpies= -805.765617
Sum of electronic and thermal Free Energies= -805.828727



2a

C	-3.11184100	3.25181000	-0.05771300
C	-3.52834000	1.98616100	0.45607500
C	-1.79818800	3.49851800	-0.39904100
C	-2.63553600	0.94762600	0.62331800
H	-4.57191100	1.84495300	0.72120000
C	-0.85676000	2.45195100	-0.22936200
C	-1.27603600	1.16000700	0.27254900
H	-2.96536300	-0.00597900	1.02207700
H	-3.85216500	4.03796000	-0.17520600
H	-1.48120000	4.46362900	-0.78227700
N	0.47785500	2.49865000	-0.47713400
C	-0.09050800	0.40877600	0.29826200
C	0.53111500	-0.92544000	0.65223800
C	0.03345300	-2.14336200	-0.16783100
H	0.69264400	-2.98688700	0.07239200
H	0.17195400	-1.93049100	-1.23537700
C	-1.41849400	-2.55374600	0.10040100
H	-2.09541800	-1.74946400	-0.21210100
H	-1.56698100	-2.68827500	1.18162200
C	-1.81260500	-3.84620200	-0.62863100
H	-1.14102200	-4.65697700	-0.31466800
H	-1.65242100	-3.71470300	-1.70749500
C	-3.26675200	-4.26025100	-0.37534200
H	-3.96367000	-3.48413400	-0.71324800
H	-3.51513500	-5.18550800	-0.90644400
H	-3.44947800	-4.42911200	0.69265200
N	0.87657100	1.25911000	-0.14351900
C	2.16116900	0.68074200	-0.10177400
C	2.00872100	-0.62490900	0.39153000
C	3.38715100	1.23221800	-0.44823400
C	3.13807600	-1.42084600	0.54452500
C	4.51459000	0.41572200	-0.28551200
H	3.46409700	2.24633700	-0.82377400
C	4.39360900	-0.89056900	0.20462900
H	3.05824300	-2.43528100	0.92436100
H	5.49479200	0.80520200	-0.54247100
H	5.28243100	-1.50226300	0.32463300
H	0.37267500	-1.14256200	1.71817600

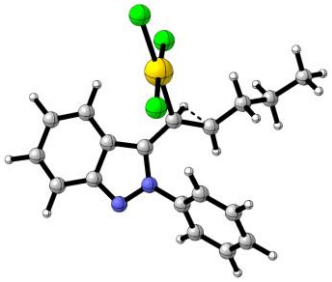
SCF Done: E(RB3LYP) = -806.315336942
Zero-point correction= 0.318311 (Hartree/Particle)
Thermal correction to Energy= 0.334735
Thermal correction to Enthalpy= 0.335679
Thermal correction to Gibbs Free Energy= 0.273609
Sum of electronic and zero-point Energies= -805.997026
Sum of electronic and thermal Energies= -805.980602
Sum of electronic and thermal Enthalpies= -805.979658
Sum of electronic and thermal Free Energies= -806.041728



II

SCF Done: E(RM06) = -2322.20441401
Zero-point correction= 0.318865 (Hartree/Particle)
Thermal correction to Energy= 0.343646
Thermal correction to Enthalpy= 0.344590
Thermal correction to Gibbs Free Energy= 0.260091
Sum of electronic and zero-point Energies= -2321.885549
Sum of electronic and thermal Energies= -2321.860768
Sum of electronic and thermal Enthalpies= -2321.859824
Sum of electronic and thermal Free Energies= -2321.944323

C	0.30555500	-0.17732400	-0.25333400
C	0.72150800	1.11063500	-0.08135200
C	1.09168400	-1.33455600	-0.71700800
H	0.59333900	-1.66592700	-1.64215500
H	2.10500900	-1.03447200	-1.00748400
C	1.16056100	-2.52317900	0.25375400
H	0.16323600	-2.97076300	0.35905700
H	1.44846800	-2.16593400	1.24892800
C	2.15281200	-3.57144800	-0.22568700
H	2.20822400	-4.35862500	0.53575500
H	3.15560500	-3.12153300	-0.27258900
C	1.79351300	-4.18303500	-1.56804600
H	2.46888100	-5.00448800	-1.82261000
H	0.77212700	-4.58154100	-1.55583000
H	1.85517400	-3.45214700	-2.38179000
C	-0.00708600	2.35310200	-0.06191200
C	-1.34626300	2.73174800	-0.07594400
C	0.98825700	3.35303600	-0.10793600
C	-1.63545500	4.08439700	-0.11310300
H	-2.15543300	2.01048500	-0.05517100
C	0.69447300	4.72032600	-0.15453300
C	-0.63384700	5.07039000	-0.15366900
H	-2.67466800	4.39559300	-0.11084700
H	1.49309100	5.45191400	-0.19286700
H	-0.92071500	6.11514800	-0.18664100
N	2.23047500	2.80586900	-0.07520300
N	2.08392700	1.52593300	-0.06967000
C	3.24435000	0.70466800	0.12314200
C	3.32467700	-0.08807000	1.25853400
C	4.25853700	0.75135400	-0.82079300
C	4.44795700	-0.88141400	1.43351300
H	2.52531300	-0.07157800	1.99364800
C	5.37414000	-0.04928300	-0.63219800
H	4.15749500	1.39079600	-1.69108100
C	5.46544700	-0.86732800	0.48738200
H	4.52888800	-1.50821600	2.31499100
H	6.17309100	-0.03692800	-1.36522700
H	6.33970800	-1.49405400	0.62721600
Cl	-1.14876100	-0.70864600	2.36486600
Au	-1.66751400	-0.60084200	0.06521100
Cl	-1.99061300	-0.35304100	-2.25597000
Cl	-3.98468000	-1.17230800	0.45123800

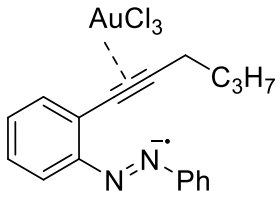


$TS_{II\text{-}III}$

C	-0.66753000	2.32293300	-0.60222000
C	-1.84623300	3.07554800	-0.35322700
C	-1.85501800	4.47921600	-0.48628300
C	-0.68931700	5.08362400	-0.86703300
C	0.48809800	4.33332300	-1.12465300
C	0.51825000	2.96924000	-1.00384100
C	-1.05340900	0.99521900	-0.37496400
H	-2.76138100	5.04167500	-0.29054800
H	-0.65458400	6.16223500	-0.97982800
H	1.38616000	4.86162400	-1.42774800
H	1.42402200	2.40875300	-1.21500700
N	-2.86802500	2.28160500	0.01365200
N	-2.37541000	1.05039000	-0.00448500
C	-3.22951400	-0.04036400	0.35259400
C	-4.44097800	-0.17915600	-0.31053100
C	-2.83171600	-0.93829700	1.33361900
C	-5.26199600	-1.24940100	0.00940200
H	-4.72294000	0.54418200	-1.06787300
C	-3.65800300	-2.01186600	1.63459400
H	-1.89313700	-0.79061000	1.86103300
C	-4.86849700	-2.16942700	0.97326600
H	-6.20995000	-1.36938300	-0.50395600
H	-5.51155300	-3.00937100	1.21384000
C	-0.29311700	-0.22435600	-0.49668100
H	-3.35661900	-2.72013500	2.39886600
C	-0.83147600	-1.42329600	-0.96047700
H	-1.81706600	-1.36960600	-1.43661700
H	-0.01892400	-0.48586700	-1.68673100
C	-0.20006100	-2.75106400	-0.89210900
H	0.85116600	-2.67335300	-0.58894500
H	-0.71801100	-3.24148400	-0.04660500
C	-0.36767000	-3.58584800	-2.15590300
H	-1.43173700	-3.63634400	-2.41780000
H	0.13556900	-3.07614400	-2.98741200
C	0.20005300	-4.97955600	-1.97410500
H	-0.31146200	-5.50860900	-1.16285100
H	0.08964300	-5.57305200	-2.88481000
H	1.26622800	-4.94078100	-1.72673200
Au	1.62615700	-0.20208500	0.33501000

Cl	0.62459400	-0.23118000	2.46664100
Cl	2.48001000	-0.24110900	-1.87023400
Cl	3.82604300	-0.12899300	1.29836000

Frequency= -641.6240
SCF Done: E(RM06) = -2322.16825583
Zero-point correction= 0.314120 (Hartree/Particle)
Thermal correction to Energy= 0.338858
Thermal correction to Enthalpy= 0.339802
Thermal correction to Gibbs Free Energy= 0.255876
Sum of electronic and zero-point Energies= -2321.854136
Sum of electronic and thermal Energies= -2321.829398
Sum of electronic and thermal Enthalpies= -2321.828454
Sum of electronic and thermal Free Energies= -2321.912380

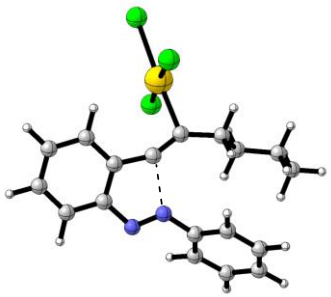


V

C	1.78869800	2.42431700	-0.77584400
C	-0.29606400	3.07726400	-1.81749100
C	0.05813200	4.40829800	-1.69567700
C	1.26410500	4.75522600	-1.09431800
C	2.10977700	3.76827400	-0.61854100
H	-1.25296200	2.79543700	-2.24467200
H	-0.61464000	5.17977600	-2.05414100
H	1.53911100	5.79906400	-0.98706900
H	3.04706800	4.01570000	-0.13057000
C	3.60199800	-0.57185900	-0.34701900
C	3.60235800	-1.77870900	-1.04214900
C	4.33270700	-0.43798400	0.83531900
C	4.31447800	-2.86179600	-0.55100800
H	3.02117000	-1.84623400	-1.95740000
C	5.04671400	-1.51872100	1.31601700
H	4.31952500	0.50968100	1.36222200
C	5.03423800	-2.73188100	0.62889900
H	4.30742200	-3.80584800	-1.08542300
H	5.61611000	-1.42497200	2.23524700
H	5.59241200	-3.57735000	1.01850600
N	2.69918000	1.49055700	-0.24786300
N	2.79018800	0.43671400	-0.90747300
C	0.55845500	2.06109100	-1.36929700
C	0.12445500	0.71371600	-1.45589600
C	-0.32112500	-0.42251800	-1.51699900
C	-0.62132400	-1.80552800	-1.86418400
H	-0.24920600	-1.97607700	-2.88465700
H	-0.03297600	-2.46006800	-1.20497800
C	-2.09732700	-2.18110800	-1.78514500
H	-2.68743800	-1.48736500	-2.39980600
H	-2.45052100	-2.04831200	-0.75115700
C	-2.34197200	-3.61122300	-2.23037600
H	-1.73144200	-4.28890500	-1.61715600
H	-1.98709900	-3.73396700	-3.26330100
C	-3.80509300	-4.00018000	-2.13443700
H	-3.97420800	-5.03100900	-2.45854300
H	-4.16752800	-3.91044600	-1.10405900
H	-4.42560500	-3.34762100	-2.75919000

Au	-1.22931200	0.07463900	0.76066000
Cl	-3.09967700	1.33491200	-0.22067600
Cl	-2.14859400	0.36394300	3.08611400
Cl	0.58366000	-1.37349900	1.56928200

SCF Done: E(UM06) = -2322.33631822
Zero-point correction= 0.314033 (Hartree/Particle)
Thermal correction to Energy= 0.341217
Thermal correction to Enthalpy= 0.342161
Thermal correction to Gibbs Free Energy= 0.250115
Sum of electronic and zero-point Energies= -2322.022285
Sum of electronic and thermal Energies= -2321.995101
Sum of electronic and thermal Enthalpies= -2321.994157
Sum of electronic and thermal Free Energies= -2322.086203

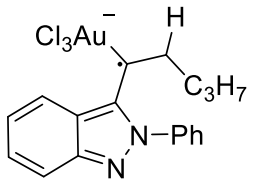


$TS_{V\text{-}VI}$

C	0.02187300	2.29752600	-0.25911100
C	1.06314500	3.18168000	0.07991400
C	0.82081900	4.51554900	0.38569000
C	-0.47626700	4.98923500	0.32830100
C	-1.51710300	4.12920800	-0.02275600
C	-1.28039600	2.79680200	-0.32002900
C	0.37868700	0.94774000	-0.50531200
H	1.65635800	5.15438600	0.65062900
H	-0.68610400	6.02848400	0.55468300
H	-2.53393800	4.50550500	-0.05933700
H	-2.09995800	2.13517400	-0.58610600
N	2.35207400	2.66027200	0.11381100
N	2.40568800	1.53905300	-0.42713600
C	3.59597800	0.79338100	-0.29691300
C	4.38096000	0.86936100	0.85295000
C	3.92591200	-0.07844600	-1.33041600
C	5.49554500	0.05626000	0.96374800
H	4.09092600	1.54405400	1.65119400
C	5.05233500	-0.87511700	-1.21741900
H	3.30085000	-0.10810100	-2.21774000
C	5.83114900	-0.81580500	-0.06709800
H	6.10281700	0.09477500	1.86192800
H	6.70262600	-1.45513100	0.02895900
C	0.13424600	-0.29296400	-0.61638900
H	5.32000000	-1.54972600	-2.02376500
C	0.84304400	-1.54445600	-0.97200300
H	0.13413100	-2.28982400	-1.35153100
H	1.53949000	-1.33120900	-1.79341400
C	1.61036300	-2.12578900	0.21516800
H	2.29603000	-1.36302000	0.61340600
H	0.90715900	-2.36134300	1.02537000
C	2.40032100	-3.36278500	-0.17469200
H	1.70726600	-4.14902100	-0.50456300
H	3.03238500	-3.12814700	-1.04374100
C	3.26600300	-3.86632100	0.96473300

H	2.65969300	-4.09934700	1.84760500
H	3.81670800	-4.77066600	0.68987600
H	3.99888100	-3.10437700	1.25849900
Cl	-1.16728300	-0.56357600	2.43288000
Cl	-4.29556000	-1.09924900	0.70200700
Cl	-2.52338200	-0.65846900	-2.44680600
Au	-1.93371600	-0.62501400	0.02333800

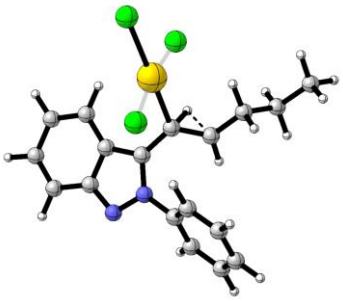
Frequency= -245.8055
SCF Done: E(UM06) = -2322.33287538
Zero-point correction= 0.313966 (Hartree/Particle)
Thermal correction to Energy= 0.340040
Thermal correction to Enthalpy= 0.340985
Thermal correction to Gibbs Free Energy= 0.251775
Sum of electronic and zero-point Energies= -2322.018909
Sum of electronic and thermal Energies= -2321.992835
Sum of electronic and thermal Enthalpies= -2321.991891
Sum of electronic and thermal Free Energies= -2322.081100



VI

C	0.32756000	-0.18467700	-0.29681800
C	0.74102900	1.12488200	-0.15767600
C	1.08308600	-1.38088500	-0.74854100
H	0.60814200	-1.74866300	-1.67073600
H	2.09723600	-1.07324900	-1.04290900
C	1.18005400	-2.52884200	0.25863800
H	0.18717800	-2.98490300	0.38820200
H	1.46136800	-2.12742800	1.23977800
C	2.18040500	-3.59331700	-0.16620000
H	2.25209300	-4.34442400	0.63038700
H	3.17803400	-3.13425000	-0.24193200
C	1.82620500	-4.27683000	-1.47614400
H	2.50980100	-5.10285600	-1.69334200
H	0.80921200	-4.68604600	-1.44041600
H	1.87346600	-3.58509500	-2.32395900
C	0.00827400	2.35964300	-0.14017800
C	-1.34696600	2.71313900	-0.16648900
C	0.99727900	3.37646400	-0.14771700
C	-1.68233600	4.04977900	-0.18138400
H	-2.13454200	1.96448900	-0.17571000
C	0.64229100	4.73876900	-0.16901900
C	-0.69219800	5.05544700	-0.18204000
H	-2.72865000	4.33717600	-0.19586300
H	1.41529300	5.50042000	-0.17236200
H	-0.99848700	6.09688400	-0.19523400
N	2.24574100	2.87305700	-0.12958000
N	2.07697700	1.53853100	-0.11935700
C	3.22661700	0.73034800	0.10453700
C	3.29828500	-0.05805300	1.24532100
C	4.27184900	0.76290200	-0.80873800
C	4.41639400	-0.85178000	1.45335800
H	2.47778100	-0.04583700	1.95739000
C	5.38978900	-0.02766700	-0.58837600
H	4.19264800	1.39810900	-1.68495000
C	5.45978700	-0.84129800	0.53596700
H	4.47425000	-1.47607700	2.33938000
H	6.20732700	-0.01368100	-1.30170300
H	6.33302600	-1.46396000	0.70123300
Cl	-1.14167600	-0.53555600	2.38218000
Au	-1.65239300	-0.59949000	0.07291900
Cl	-1.99498700	-0.53405400	-2.26767700
Cl	-4.03390000	-1.16804800	0.51218800

SCF Done: E(UM06) = -2322.37404474
Zero-point correction= 0.316797 (Hartree/Particle)
Thermal correction to Energy= 0.341873
Thermal correction to Enthalpy= 0.342817
Thermal correction to Gibbs Free Energy= 0.257352
Sum of electronic and zero-point Energies= -2322.057248
Sum of electronic and thermal Energies= -2322.032172
Sum of electronic and thermal Enthalpies= -2322.031228
Sum of electronic and thermal Free Energies= -2322.116692



TS_{VI-VII}

C	0.82379200	2.21251000	0.70067400
C	2.05091700	2.91068000	0.53762900
C	2.12117900	4.30430600	0.75283500
C	0.97233400	4.94641900	1.12269200
C	-0.25501900	4.24878800	1.28903300
C	-0.34638600	2.89771600	1.08909100
C	1.14095200	0.87865900	0.42477200
H	3.06100700	4.83150800	0.62686200
H	0.98912600	6.01764600	1.29725300
H	-1.13684600	4.80892400	1.58323600
H	-1.28531200	2.36688200	1.22512300
N	3.04121900	2.08471500	0.16243400
N	2.47206300	0.87694600	0.10849700
C	3.26521000	-0.23489300	-0.30946400
C	4.48527200	-0.45253800	0.31580500
C	2.80847200	-1.07397800	-1.31733600
C	5.25437500	-1.54012500	-0.06752600
H	4.81492400	0.22714800	1.09394900
C	3.58323700	-2.16622900	-1.68234700
H	1.86389300	-0.86373900	-1.81574700
C	4.80163600	-2.40172600	-1.05909300
H	6.20818000	-1.71993100	0.41712100
H	5.40366800	-3.25587300	-1.35108700
C	0.28239600	-0.29041700	0.46152300
H	3.23552800	-2.82857700	-2.46819100
C	0.73309500	-1.50380900	0.97006300
H	1.71936500	-1.53760300	1.44788900
H	-0.10968300	-0.55841300	1.62140100
C	-0.01542700	-2.77718300	0.92755500
H	-1.03550400	-2.60140400	0.56208200
H	0.48998100	-3.37981000	0.15306100

C	-0.01798300	-3.53118500	2.25162100
H	1.01583900	-3.73495300	2.55802300
H	-0.45210600	-2.88363400	3.02498700
C	-0.80892700	-4.82041100	2.15070100
H	-0.39029400	-5.47997200	1.38252200
H	-0.80873600	-5.36537300	3.09810500
H	-1.85151300	-4.61648300	1.88147200
Au	-1.62967700	-0.09147500	-0.43309200
Cl	-0.46947800	0.01175700	-2.77602700
Cl	-2.54885800	-0.39696000	2.08090300
Cl	-3.85547400	0.23397000	-1.38544500

Frequency= -728.0166
SCF Done: E(UM06) = -2322.34669294
Zero-point correction= 0.312371 (Hartree/Particle)
Thermal correction to Energy= 0.338047
Thermal correction to Enthalpy= 0.338992
Thermal correction to Gibbs Free Energy= 0.250131
Sum of electronic and zero-point Energies= -2322.034322
Sum of electronic and thermal Energies= -2322.008646
Sum of electronic and thermal Enthalpies= -2322.007701
Sum of electronic and thermal Free Energies= -2322.096562

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