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# One-pot sequential synthesis of unsymmetrical diarylmethanes by using methylene chloride as a $C_I$ -synthon

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# **Supporting Information**

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#### 1. General Considerations

The reagents used in this experiment were all commercially purchased.  $^{1}$ H were recorded on a Bruker AV 500 in deuterated solvents as indicate. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ( $d_6$ -DMSO:  $\delta_{\rm H} = 2.50$  ppm,  $\delta_{\rm C} = 39.52$  ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, J, were reported in hertz unit (Hz). Chemical shifts were reported in parts per million relatively to tetramethylsilane ( $\delta = 0$ ). High-resolution mass spectra (HRMS) were produced by Thermo Fisher Scientific. Analytical thin layer chromatography was performed on Polygram SIL  $G/UV_{254}$  plates. Visualization was accomplished with short wave UV light, or KMnO<sub>4</sub> staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique.

# 2. Optimization of the reaction conditions

We first selected 6-nitroindole (1a, 0.2 mmol) and indole (2a, 1.0 eq.) as the model substrates in the reaction. In the first attempt, the reaction was conducted in DCM (0.2 M) in a one-pot synthesis as proposed, however, no desired product was formed. Then, a trial with diethylamine (Et2NH) as a base was performed for the reaction, the desired BIM (3aa) was generated in yield of 11%. (Table 1)

Table 1. The initial reaction

Entry	Amine (1.0 eq.)	T	Solvent	Yield (%) <sup>c</sup>
01	-	90	DCM	ND
02	Et <sub>2</sub> NH	90	DCM	11

<sup>a</sup> ND: not detected. <sup>b</sup> NR: no reaction. <sup>c</sup> isolated yield.

Under the optimized reaction conditions, the substrate scope of indole with 6-nitroindole (1a) was investigated, as shown in table 2-5.

Table 2. Screening of the base

Entry	Amine (1.0 eq.)	T <sub>1</sub> [°C]	Solvent	T <sub>2</sub> [°C]	Yield (%) <sup>c</sup>
01	Et <sub>2</sub> NH	90	HFIP	80	38
02	$Et_3N$	90	HFIP	80	10
03	Pyridine	90	HFIP	80	$\mathrm{ND}^\mathrm{a}$
04	Pyrrolidine	90	HFIP	80	2
05	morpholine	90	HFIP	80	27
06	None	90	HFIP	80	$NR^b$

<sup>&</sup>lt;sup>a</sup> ND: not detected. <sup>b</sup> NR: no reaction. <sup>c</sup> isolated yield.

Table 3. Screening study for the base loading

Entry	Et <sub>2</sub> NH (x eq.)	$T_1$ [°C]	Solvent	T <sub>2</sub> [°C]	Yield (%) <sup>a</sup>
01	0.5	90	HFIP	80	29
02	1.0	90	HFIP	80	38
03	2.0	90	HFIP	80	49
04	3.0	90	HFIP	80	54
05	4.0	90	HFIP	80	55

<sup>&</sup>lt;sup>a</sup> isolated yield.

Table 4. Screening of the solvent

Entry	Et <sub>2</sub> NH (x eq.)	T <sub>1</sub> [°C]	Solvent	T <sub>2</sub> [°C]	Yield (%) <sup>a</sup>
01	3.0	90	HFIP	80	54
02	3.0	90	DCM	80	10
03	3.0	90	MeOH	80	15

04	3.0	90	MeCN	80	Trace
05	3.0	90	TFE	80	40
06	3.0	90	THF	80	6

<sup>&</sup>lt;sup>a</sup> isolated yield.

Table 5. Screening of the temperature

Entry	Et <sub>2</sub> NH (x eq.)	T <sub>1</sub> [°C]	Solvent	T <sub>2</sub> [°C]	Yield (%) <sup>a</sup>
01	3.0	90	HFIP	80	54
02	3.0	90	HFIP	60	18
03	3.0	90	HFIP	70	34
04	3.0	80	HFIP	80	54
05	3.0	100	HFIP	80	42
06	3.0	100	HFIP	100	48
07	3.0	100	HFIP	50	16
08	3.0	90	HFIP	90	41
09	3.0	80	HFIP	80	38
10	3.0	50	HFIP	50	7
11	3.0	50	HFIP	80	18
12 <sup>b</sup>	3.0	90	HFIP	80	11
13 <sup>c</sup>	3.0	90	HFIP	80	$ND^f$
$14^{d}$	3.0	90	HFIP	80	$ND^f$
$14^e$	3.0	90	HFIP	80	28

<sup>&</sup>lt;sup>a</sup> isolated yield. <sup>b</sup> using CH<sub>2</sub>Br<sub>2</sub> as solvent and C1 source. <sup>c</sup> using CHCl<sub>3</sub> as solvent and C1 source. <sup>d</sup> using CCl<sub>4</sub> as solvent and C1 source. <sup>b</sup> using morpholine as base. <sup>f</sup> ND: not detected.

# 3. General Procedure

General procedur A

Typical procedure for preparation of 3

A 15 mL-schlenk tube charged with a stirring bar, was added 6-nitroindole 1a (0.2

mmol, 1.0 equiv), diethylamine (0.60 mmol, 3.0 equiv) and dichloromethane (1.0 mL) and reacted at 90 °C overnight; after that, dichloromethane was removed under reduced pressure and different substituted indoles **2** (0.2 mmol, 1.0 equiv) and hexafluoroisopropanol (HFIP, 2.0 mL) were added. The reaction was carried out at 80 °C for 5.0 h. The reaction mixture was then diluted with EtOAc (10.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

# General procedur B

Typical procedure for preparation of 6 and 7

A 15 mL-schlenk tube charged with a stirring bar, was added 6-nitroindole **1a** (0.2 mmol, 1.0 equiv), diethylamine (0.60 mmol, 3.0 equiv) and dichloromethane (1.0 mL) and reacted at 90 °C overnight; after that, dichloromethane was removed under reduced pressure and different substituted phenols **4** or anilines **5** (0.2 mmol, 1.0 equiv) and hexafluoroisopropanol (HFIP, 2.0 mL) were added. The reaction was carried out at 80 °C for 5.0 h. The reaction mixture was then diluted with EtOAc (10.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **6** or **7**.

# 4. Characterization of Products 3, 6, 7, 8 and 9

# 3-((1H-indol-3-yl)methyl)-6-nitro-1H-indole (3aa)

The title compound was prepared *via* the general procedure 
$$\bf A$$
, after purification by silica gel column chromatography (PE/EA = 4/1), **3aa** was obtained as a yellow oil (31.5 mg, 0.108 mmol, 54 %).  $\bf R_f = 0.46$  (PE/EA = 2/1).

<sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ) δ 11.59 (s, 1H), 10.78 (s, 1H), 8.30 (s, 1H), 7.82 (dd, J = 8.8, 1.9 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 1.9 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 1.6 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 4.17 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ) δ 141.9, 136.6, 134.8, 132.0, 130.3, 127.1, 123.1, 121.1, 119.1, 118.7, 118.4, 116.1, 113.7, 113.6, 111.6, 108.4, 20.7. ESI-MS: calculated for C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>[M+Na]<sup>+</sup>: 314.0899, found: 314.0898.

# 1-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ab)

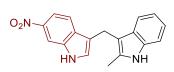
O<sub>2</sub>N HN N

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ab** was obtained as a yellow powder (36.6

mg, 60% yield); R<sub>f</sub> = 0.87 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.31 (d, J = 1.8 Hz, 1H), 7.83 (dd, J = 8.8, 1.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.64 – 7.62 (d, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.97 (t, J = 7.5 Hz, 1H), 4.18 (s, 2H), 3.69 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.7, 136.8, 134.7, 131.8, 130.3, 127.3, 121.1, 118.9, 118.8, 118.3, 115.7, 113.5, 113.0, 109.6, 108.3, 32.3, 20.4.

ESI-MS: calculated for C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>: 328.1056, found: 328.1052.

# 2-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ac)



The title compound was prepared via the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ac** was obtained as a white solid (22.0 mg,

0.072 mmol, 36 %).  $R_f = 0.6$  (PE/EA = 2/1).

<sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ) δ 11.51 (s, 1H), 10.73 (s, 1H), 8.27 (s, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.46 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 8.2 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 4.10 (s, 2H), 2.40 (s, 3H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 141.7, 135.3, 134.7, 131.7, 131.6, 130.1, 128.2, 119.9, 118.7, 118.1, 117.7, 116.4, 113.4, 110.4, 108.8, 108.2, 19.3, 11.5.

ESI-MS: calculated for  $C_{18}H_{15}N_3O_2 [M+H]^+$ : 306.1237, found:306.1167.

# Methyl 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-2-carboxylate (3ad)

O<sub>2</sub>N HN MeOOC NH

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **3ad** was obtained as a yellow powder (35.6)

mg, 51% yield);  $R_f$ = 0.51 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.66 (s, 1H), 11.56 (s, 1H), 8.27 (d, J= 2.1 Hz, 1H), 7.84 (dd, J= 8.9, 2.1 Hz, 1H), 7.74 (d, J= 8.9 Hz, 1H), 7.65 (d, J= 8.2 Hz, 1H), 7.52 (d, J= 2.4 Hz, 1H), 7.41 (d, J= 8.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.01 – 6.97 (m, 1H), 4.58 (s, 2H), 3.92 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  162.3, 141.7, 136.5, 134.5, 131.6, 130.4, 127.0, 125.0, 122.7, 121.8, 120.8, 119.6, 118.7, 115.6, 113.6, 112.6, 108.3, 51.7, 19.9.

ESI-MS: calculated for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>: 372.0954, found:372.0951.

#### 4-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ae)

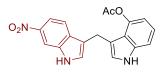
O<sub>2</sub>N NH

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **3ae** was obtained as a yellow oil (21.4 mg,

35% yield);  $R_f$ = 0.48 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.56 (s, 1H), 10.77 (s, 1H), 8.33 (s, 1H), 7.85 (dd, J= 8.8, 2.1 Hz, 1H), 7.69 (d, J= 8.8 Hz, 1H), 7.32 (d, J= 2.1 Hz, 1H), 7.17 (d, J= 8.1 Hz, 1H), 6.96 (d, J= 2.2 Hz, 1H), 6.92 (t, J= 7.2, 7.9 Hz,1H), 6.65 (d, J= 7.2 Hz, 1H), 4.33 (s, 2H), 2.49 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8, 137.0, 134.8, 131.6, 130.4, 129.7, 125.6, 123.5, 121.0, 119.8, 118.8, 117.1, 113.9, 113.5, 109.5, 108.3, 22.6, 19.8.

ESI-MS: calculated for  $C_{18}H_{15}N_3O_2$   $Na^+$   $[M+Na]^+$ : 328.1056, found: 328.1055.

## 2-((6-nitro-1H-indol-3-yl)methyl)-1H-indol-4-yl acetate (3af)



The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3af** was obtained as a yellow powder (34.0

mg, 49% yield); R<sub>f</sub> = 0.36 (PE/EA = 2/1);  $^{1}$ H NMR (500 MHz, DMSO- $d_{6}$ )  $\delta$  11.56 (s, 1H), 11.04 (s, 1H), 8.33 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 8.8, 2.1 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 2.2 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.05 (t, J = 7.9 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 4.16 (s, 2H), 2.01 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_{6}$ )  $\delta$  169.6 , 143.8 , 141.8 , 138.9 , 134.8 , 131.7 , 130.3 , 124.3 , 121.2 , 119.6 , 118.8 , 116.2 , 113.6 , 111.9 , 111.8 , 109.6 , 108.4 , 21.6 , 20.7 .

ESI-MS: calculated for  $C_{19}H_{15}N_3O_4$   $Na^+$   $[M+Na]^+:372.0954$ , found: 372.0951.

## 5-methoxy-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ag)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography

(PE/EA = 2/1), **3ag** was obtained as a yellow powder (38.6)

mg, 60% yield);  $R_f$  = 0.37 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (s, 1H), 10.63 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.11 (d, J = 2.3 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.71 – 6.68 (m, 1H), 4.15 (s, 2H), 3.70 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  152.9 , 141.7 , 134.7 , 131.9 , 131.6 , 130.2 , 127.3 , 123.6 , 118.9 , 115.9 , 113.4 , 113.3 , 112.0 , 110.9 , 108.3 , 100.6 , 55.4 , 20.6 .

ESI-MS: calculated for  $C_{18}H_{15}N_3O_3$   $Na^+$   $[M+Na]^+:344.1005$ , found: 344.1001.

#### 6-fluoro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ah)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ah** was obtained as a brown powder (35.3 mg, 57% yield);  $R_f = 0.70$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 10.92 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.31 (dd, J = 8.8, 4.6 Hz, 1H), 7.28 (d, J = 2.2 Hz, 1H), 7.24 (dd, J = 10.1, 2.5 Hz, 1H), 6.89 – 6.85 (m, 1H), 4.15 (s, 2H).

125.1, 118.9, 115.6, 113.9 (d, J = 4.6 Hz), 113.4, 112.3 (d, J = 9.8 Hz), 109.0 (d, J =

26.1 Hz), 108.3, 103.2 (d, J = 23.0 Hz), 20.5.

ESI-MS: calculated for  $C_{17}H_{12}FN_3O_2$   $Na^+$   $[M+Na]^+$ :332.0805, found: 332.0802.

#### 5-iodo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ai)

O<sub>2</sub>N NH

The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $\bf 3ai$  was obtained as a yellow powder (49.2 mg,

59% yield);  $R_f$  = 0.76 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.60 (s, 1H), 11.03 (s, 1H), 8.30 (d, J = 2.0 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 2.3 Hz, 1H), 7.29 (dd, J = 8.5, 1.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 4.15 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8, 135.5, 134.8, 131.8, 130.3, 129.8, 128.9, 127.1, 124.2, 118.9, 115.6, 114.0, 113.5, 113.1, 108.4, 82.1, 20.4.

ESI-MS: calculated for C<sub>17</sub>H<sub>12</sub>IN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:439.9866, found: 439.9862.

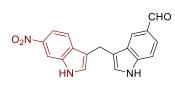
#### 1-(3-((6-nitro-1H-indol-3-yl)methyl)-1H-indol-5-yl)ethan-1-one (3aj)

O<sub>2</sub>N Ac

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3aj** was obtained as a yellow powder (45.3

mg, 68% yield);  $R_f$  = 0.21 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ ) δ 11.60 (s, 1H), 11.21 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 8.23 – 8.23 (m, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.69 (dd, J = 8.7, 1.7 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 4.26 (s, 2H), 2.55 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ ) δ 197.5 , 141.8 , 139.1 , 134.8 , 131.8 , 130.3 , 128.3 , 126.6 , 124.8 , 121.3 , 120.9 , 118.9 , 115.7 , 115.6 , 113.5 , 111.4 , 108.4 , 26.6 , 20.4 . ESI-MS: calculated for  $C_{19}H_{15}N_3O_3$   $Na^+$  [M+Na] $^+$ :356.1005, found:356.0999.

## 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-5-carbaldehyde (3ak)



The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), 3ak was obtained as a yellow oil (46.1 mg,

72% yield); R<sub>f</sub>= 0.23 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.60 (s, 1H), 11.38 (s, 1H), 9.92 (s, 1H), 8.30 (d, J = 2.0 Hz, 1H), 8.16 – 8.15 (m, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.66 (s, 1H), 7.61 – 7.59 (m, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 1.6 Hz, 1H), 4.26 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  192.5, 141.8, 139.9, 134.8, 131.8, 130.3, 128.3, 126.9, 125.2, 124.1, 121.1, 118.9, 115.9, 115.4, 113.5, 112.2, 108.3, 20.4.

ESI-MS: calculated for  $C_{18}H_{13}N_3O_3 Na^+ [M+Na]^+$ : 342.0849, found: 342.0844.

# 6-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3al)

The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $\bf 3al$  was obtained as a yellow powder (32.4)

mg, 53% yield);  $R_f = 0.80$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (s, 1H), 10.63 (s, 1H), 8.30 – 8.27 (d, 1H), 7.83 – 7.80 (dd, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.61 – 7.59 (d, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.14 (s, 2H), 2.34 (s, 3H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.7 , 136.9 , 134.7 , 131.9 , 130.2 , 129.8 , 125.0 , 122.2 , 119.9 , 118.9 , 118.3 , 116.0 , 113.4 , 113.4 , 111.3 , 108.3 , 21.4 , 20.7 .

ESI-MS: calculated for  $C_{18}H_{15}N_3O_2$   $Na^+$   $[M+Na]^+:328.1056$ , found:328.1051.

## 6-(benzyloxy)-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3am)

O<sub>2</sub>N OBn

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3am** was obtained as a

yellow oil (32.2 mg, 41% yield);  $R_f$  = 0.49 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (s, 1H), 10.59 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 2.2 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 6.4 Hz, 3H), 7.30 (d, J = 7.3 Hz, 1H), 7.02 (d, J = 1.9 Hz, 1H), 6.90 (d, J = 2.2 Hz, 1H), 6.66 (dd, J = 8.6, 2.2 Hz, 1H), 5.07 (s, 2H), 4.13 (s, 2H).

<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 154.5 , 141.7 , 137.7 , 137.1 , 134.7 , 131.9 , 130.2 , 128.4 , 127.7 , 127.5 , 121.7 , 119.2 , 118.9 , 116.0 , 113.6 , 113.4 , 109.1 , 108.3 , 96.0 , 69.5 , 20.7 .

ESI-MS: calculated for  $C_{24}H_{19}N_3O_3$   $Na^+$  [M+Na] $^+$ :420.1318, found: 420.1313.

## 6-nitro-3-((6-(trifluoromethyl)-1H-indol-3-yl)methyl)-1H-indole (3an)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3an** was obtained as a brown yellow powder (31.6 mg, 44% yield);  $R_f = 0.51$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 11.29 (s, 1H), 8.30 (d, J = 1.9 Hz, 1H), 7.83 (dd, J = 8.8, 1.9 Hz, 1H), 7.69 (d, J = 7.9 Hz, 3H), 7.64 (d, J = 1.8 Hz, 1H)), 7.45 (s, 1H), 7.21 (d, J = 8.5 Hz, 1H), 4.23 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8, 135.2, 134.8, 131.7, 130.3, 129.4, 126.6, 125.6 (d, J = 271.3 Hz), 121.4 (d, J = 31.0 Hz), 119.4, 118.9, 115.5, 114.5, 114.2, 113.5, 108.8, 108.3, 20.4.

ESI-MS: calculated for  $C_{18}H_{12}F_3N_3O_2$   $Na^+$   $[M+Na]^+$ :382.0773, found: 382.0770.

## 6-fluoro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ao)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ao** was obtained as a brown yellow powder (40.1 mg, 65% yield);  $R_f = 0.38$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.60 (s, 1H), 10.88 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 2.3 Hz, 1H), 7.46 (dd, J = 8.7, 5.5 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 7.11 (dd, J = 10.2, 2.3 Hz, 1H), 6.78 (td, J = 9.3, 8.7, 2.3 Hz, 1H), 4.17 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  159.8, 158.0, 141.8, 136.3 (d, J = 12.7 Hz), 134.8, 131.9, 130.3, 123.7 (d, J = 47.4 Hz), 119.6 (d, J = 10.3 Hz), 118.9, 115.7, 113.9, 113.5, 108.3, 106.7 (d, J = 24.3 Hz), 97.4 (d, J = 25.3 Hz), 20.6.

ESI-MS: calculated for C<sub>17</sub>H<sub>12</sub>FN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>: 332.0805, found: 332.0805.

#### 6-chloro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ap)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ap** was obtained as a yellow powder (27.4 mg, 42% yield); R<sub>f</sub>= 0.49 (PE/EA = 2/1);  $^{1}$ H NMR (500 MHz, DMSO- $^{2}$ d<sub>6</sub>)  $^{1}$ 8 11.59 (s, 1H), 10.95 (s, 1H), 8.30 (d,  $^{2}$  = 2.0 Hz, 1H), 7.82 (dd,  $^{2}$  = 8.8, 2.0 Hz, 1H), 7.67 (d,  $^{2}$  = 8.8 Hz, 1H), 7.62 (d,  $^{2}$  = 2.0Hz, 1H), 7.48 (d,  $^{2}$  = 8.4 Hz, 1H), 7.37 (d,  $^{2}$  = 1.7 Hz, 1H), 7.22 (d,  $^{2}$  = 1.9 Hz, 1H), 6.93 (dd,  $^{2}$  = 8.4, 2.0 Hz, 1H), 4.17 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $^{2}$ d<sub>6</sub>)  $^{3}$ 8 141.8, 136.8, 134.7, 131.8, 130.3, 125.8, 125.8, 124.2, 120.0, 118.9, 118.6, 115.6, 114.0, 113.5, 111.1, 108.3, 20.5.

ESI-MS: calculated for C<sub>17</sub>H<sub>21</sub>ClN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>: 348.0510, found: 348.0508.

#### 6-bromo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3aq)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3aq** was obtained as a yellow powder (47.2 mg, 64% yield);  $R_f = 0.42$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 10.96 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.83 – 7.81 (m, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.52 (d, J = 1.7 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 2.3 Hz, 1H), 7.05 (d, J = 6.7 Hz, 1H), 4.17 (s, 2H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8 , 137.3 , 134.7 , 131.8 , 130.2 , 126.1 , 124.1 , 121.1 , 120.4 , 118.9 , 115.6 , 114.0 , 114.0 , 113.8 , 113.5 , 108.3 , 20.5 .

ESI-MS: calculated for C<sub>17</sub>H<sub>12</sub>BrN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:392.0005 found:391.9999.

# Methyl 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-6-carboxylate (3ar)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ar** was obtained as a yellow solid (34.9 mg, 50% yield);  $R_f = 0.30$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 11.26 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 8.03 (s, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.68 (d, J

= 8.8 Hz, 1H), 7.63 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.4, 1.1 Hz, 1H), 7.45 (d, J = 2.2 Hz, 1H), 4.21 (s, 2H), 3.83 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  167.4, 141.8, 135.7, 134.8, 131.8, 130.5, 130.3, 127.2, 122.0, 119.0, 118.9, 118.4, 115.6, 114.3, 113.5, 113.5, 108.3, 51.8, 20.4.

ESI-MS: calculated for  $C_{19}H_{15}N_3O_4$   $Na^+$  [M+Na] $^+$ :372.0954, found: 372.0952.

#### 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-6-carbonitrile (3as)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3as** was obtained as a yellow solid (24.0 mg, 38% yield);  $R_f = 0.38$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 11.42 (s, 1H), 8.29 (d, J = 2.0 Hz, 1H), 7.82 (dd, J = 8.9, 2.0 Hz, 2H), 7.67 (dd, J = 8.9, 8.2Hz, 2H), 7.65 (d, J = 2.4 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.26 (dd, J = 8.2, 1.4 Hz, 1H), 4.22 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8 , 135.2 , 134.7 , 131.7 , 130.3 , 130.0 , 127.8 , 121.0 , 120.8 , 119.8 , 118.8 , 116.4 , 115.4 , 114.8 , 113.5 , 108.3 , 102.3 , 20.3 .

ESI-MS: calculated for  $C_{18}H_{12}N_4O_2$   $Na^+$   $[M+Na]^+:339.0852$ , found: 339.0851.

## 7-chloro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3at)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography

(PE/EA = 2/1), **3at** was obtained as a yellow solid (55.0 mg,

84% yield);  $R_f$ = 0.54 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.60 (s, 1H), 11.19 (s, 1H), 8.31 (d, J = 2.1 Hz, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.9,7.5 Hz, 1H), 4.20 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8, 134.7, 133.2, 131.8, 130.3, 129.0, 124.3, 120.5, 119.3, 118.8, 117.7, 115.8, 115.5, 115.1, 113.5, 108.3, 20.6.

ESI-MS: calculated for  $C_{17}H_{12}ClN_3O_2 Na^+ [M+Na]^+:348.0510$ , found: 348.0511.

#### 5,6-dichloro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3au)

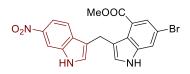
The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $3\mathbf{au}$  was obtained as a

yellow oil (59.1 mg, 82% yield);  $R_f$ = 0.69 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 11.13 (s, 1H), 8.30 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.58 (s, 1H), 7.32 (s, 1H), 4.17 (s, 2H).

<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 141.8 , 135.3 , 134.8 , 131.8 , 130.4 , 127.1 , 125.9 , 123.3 , 120.9 , 119.8 , 118.9 , 115.4 , 113.8 , 113.5 , 113.0 , 108.4 , 20.3 .

ESI-MS: calculated for C<sub>17</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:382.0120, found: 382.0111.

# Methyl 6-bromo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-4-carboxylate (3av)

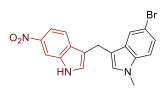


The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3av** was obtained as a

yellow power (57.4 mg, 67% yield);  $R_f = 0.34$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.50 – 11.49 (m, 1H), 11.41 (d, J = 2.0 Hz, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 2.5 Hz, 1H), 4.26 (s, 2H), 3.58 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  167.0 , 141.8 , 138.8 , 134.7 , 131.7 , 130.0 , 127.9 , 125.2 , 123.2 , 122.6 , 118.8 , 117.9 , 115.9 , 114.0 , 113.3 , 112.1 , 108.2 , 52.0 , 22.4 .

ESI-MS: calculated for C<sub>19</sub>H<sub>14</sub>BrN<sub>3</sub>O<sub>4</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:450.0059, found: 450.0051.

# $5\text{-}bromo\text{-}1\text{-}methyl\text{-}3\text{-}((6\text{-}nitro\text{-}1H\text{-}indol\text{-}3\text{-}yl)methyl)\text{-}1H\text{-}indole\ (3aw)}$



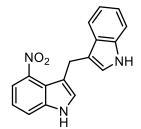
The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3av** was obtained as a yellow oil (23.8 mg,

31% yield);  $R_f = 0.53$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.69 – 7.67 (m, 3H), 7.35 (d, J = 8.7 Hz,

1H), 7.22 - 7.20 (m, 1H), 7.19 (s, 1H), 4.15 (s, 2H), 3.70 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.8, 135.5, 134.7, 131.7, 130.3, 129.0, 128.9, 123.5, 121.0, 118.9, 115.4, 113.5, 112.8, 111.8, 111.1, 108.3, 32.5, 20.2.

ESI-MS: calculated for C<sub>18</sub>H<sub>14</sub>BrN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:406.0161, found: 406.0154.

# 3-((1H-indol-3-yl)methyl)-4-nitro-1H-indole (3ba)



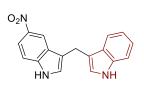
The title compound was prepared via the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ba** was obtained as a white solid (22.8 mg, 0.078 mmol, 39%). Rf = 0.6 (PE/EA = 2/1).

<sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ) δ 11.67 (s, 1H), 10.68 (s, 1H), 7.76 (d, J = 5.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 10.1 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.89 (t, J = 8.6 Hz, 1H), 6.78 (s, 1H), 4.21 (s, 2H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 142.5, 139.4, 136.4, 129.1, 127.0, 122.5, 120.9, 119.8, 118.5, 118.1, 117.9, 116.3, 114.1, 113.5, 111.3, 22.8.

ESI-MS: calculated for  $C_{17}H_{13}N_3O_2[M+H]^+$ :292.1080, found:292.1014.

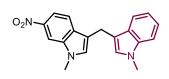
## 3-((1H-indol-3-yl)methyl)-5-nitro-1H-indole (3ca)



The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **3ca** was obtained as a yellow solid (11.0 mg, 19% yield);

 $R_f$ = 0.38 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.55 (s, 1H), 10.80 (s, 1H), 8.48 (d, J = 2.2 Hz, 1H), 7.95 (dd, J = 9.0, 2.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.44 (d, J = 2.3 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.04 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.92 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 4.22 (s, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  140.0, 139.6, 136.5, 127.0, 126.8, 126.5, 123.0, 120.9, 118.6, 118.2, 117.3, 116.3, 116.0, 113.4, 111.8, 111.4, 20.7.

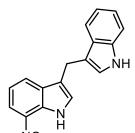
# 1-methyl-3-((1-methyl-1H-indol-3-yl)methyl)-6-nitro-1H-indole (3da)



The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3da** was obtained as a yellow solid (32.0 mg,

50% yield);  $R_f = 0.29$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.41 (d, J = 2.0 Hz, 1H), 7.86 (dd, J = 8.8, 2.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.58 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 4.16 (s, 2H), 3.86 (s, 3H), 3.70 (s, 3H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  141.9, 136.8, 135.2, 134.3, 132.0, 127.3, 127.2, 121.1, 119.1, 118.7, 118.3, 115.1, 113.5, 112.8, 109.6, 106.9, 32.8, 32.3, 20.2.

# 3-((1H-indol-3-yl)methyl)-7-nitro-1H-indole (3ea)



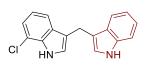
The title compound was prepared via the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ea** was obtained as a white solid (19.27 mg, 0.066 mmol, 33 %). Rf = 0.6 (PE/EA = 2/1).

<sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 10.79 (s, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 1.6 Hz, 1H), 7.30 (s, 1H), 7.19 (s, 1H), 7.17 (t, J = 8.7 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 6.5 Hz, 1H), 4.20 (s, 2H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 136.4, 132.4, 131.6, 128.6, 127.5, 127.0, 126.1, 123.0, 120.9, 118.6, 118.4, 118.2, 118.0, 116.6, 113.4, 111.4, 20.5.

ESI-MS: calculated for  $C_{17}H_{13}N_3O_2 [M+H]^+$ :292.1080, found:292.1012.

# 3-((1H-indol-3-yl)methyl)-7-chloro-1H-indole (3fa)



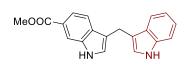
The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3fa** was obtained as a white solid (21 mg, 37% yield); R<sub>f</sub>

= 0.40 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.12 (s, 1H), 10.76 (s, 1H), 7.50 (dd, J = 8.0, 2.9 Hz, 1H), 7.31 (dt, J = 8.0, 0.9 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H),

7.15 (d, J = 2.4 Hz, 1H), 7.11 (dd, J = 7.6, 0.9 Hz, 1H), 7.03 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 6.92 (q, J = 8.1 Hz, 2H), 4.13 (s, 2H).

<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 136.4 , 133.2 , 129.2 , 127.1 , 124.2 , 122.9 , 120.9 , 120.4 , 119.2 , 118.7 , 118.1 , 117.9 , 115.8 , 113.8 , 111.4 , 21.0 .

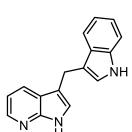
# Methyl 3-((1H-indol-3-yl)methyl)-1H-indole-6-carboxylate (3ga)



The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **3ga** was obtained as a orange oil (12.2 mg,

20% yield); R<sub>f</sub>= 0.45 (PE/EA = 2/1);  $^{1}$ H NMR (500 MHz, DMSO- $d_{6}$ )  $\delta$  11.20 (s, 0H), 10.76 (s, 1H), 8.01 (d, J = 1.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 8.4, 1.4 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 2.4 Hz, 1H), 7.31(d, J = 8.0 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 7.03 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.91 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 4.15 (s, 2H), 3.83 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_{6}$ )  $\delta$  167.4, 136.4, 135.6, 130.7, 127.1, 127.0, 122.9, 121.8, 120.8, 118.8, 118.6, 118.5, 118.1, 115.0, 113.9, 113.4, 111.4, 51.8, 20.8.

# 3-((1H-indol-3-yl)methyl)-1H-pyrrolo[2,3-b]pyridine (3ha)



The title compound was prepared via the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ha** was obtained as a white solid (23.3 mg, 0.08 mmol, 47 %). Rf = 0.3 (PE/EA = 2/1).

H NMR (600 MHz, DMSO) δ 11.27 (s, 1H), 10.75 (s, 1H), 8.14 (d, J = 4.5 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.27 (s, 1H), 7.16 (s, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.96 (dd, J = 7.9, 4.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 4.13 (s, 2H).

<sup>13</sup>C NMR (151 MHz, DMSO) δ 148.8, 142.2, 136.4, 127.1, 126.8, 123.1, 122.8, 120.8, 119.4, 118.6, 118.1, 114.7, 113.8, 113.2, 111.4, 21.0.

ESI-MS: calculated for  $C_{16}H_{13}N_3$  [M+H]<sup>+</sup> :248.1182, found:248.1125.

# 4-((6-nitro-1H-indol-3-yl)methyl)benzene-1,2-diol (6aa)

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA =1/1), **6aa** was obtained as a yellow solid (7.0 mg,

11% yield);  $R_f = 0.58$  (PE/EA = 1/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.62 (s, 1H), 8.68 (d, J = 34.2 Hz, 2H), 8.30 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.58 (s, 1H), 7.55 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 2.0 Hz, 1H), 6.53 (dd, J = 8.0, 2.0 Hz, 1H), 3.90 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  145.1, 143.4, 141.8, 134.7, 131.9, 131.8, 130.4, 119.0, 118.9, 116.1, 115.8, 115.4, 113.5, 108.3, 29.9.

ESI-MS: calculated for  $C_{15}H_{12}N_2O_4$  Na<sup>+</sup> [M+Na]<sup>+</sup>:307.0689, found: 307.0685.

#### 2-allyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ab)

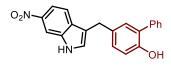
O<sub>2</sub>N Allyl OH

The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1), **6ab** was obtained as a yellow oil (25.2 mg,

41% yield);  $R_f = 0.60$  (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.62 (s, 1H), 9.15 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.58 – 7.55 (m, 2H), 6.95 (d, J = 2.1 Hz, 1H), 6.90 (dd, J = 8.1, 2.1 Hz, 1H), 6.69 (d, J = 8.1 Hz, 1H), 5.94 – 5.88 (m, 1H), 5.01 – 4.94 (m, 2H), 3.94 (s, 2H), 3.22 (d, J = 6.6 Hz, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  153.1 , 141.8 , 137.2 , 134.7 , 131.7 , 131.2 , 130.3 , 129.8 , 127.0 , 125.7 , 118.9 , 116.3 , 115.2 , 114.8 , 113.5 , 108.3 , 33.9 , 29.9 .

ESI-MS: calculated for  $C_{18}H_{16}N_2O_3$   $Na^+$  [M+Na]<sup>+</sup>:331.1053, found: 331.1049.

# **5-**((6-nitro-1H-indol-3-yl)methyl)-[1,1'-biphenyl]-2-ol (6ac)



The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **6ac** was obtained as a yellow power (16.6

mg, 24% yield);  $R_f = 0.38$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.64 (s, 1H), 9.35 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.64 (m, 2H),

7.50 – 7.47 (m, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 7.06 (dd, J = 8.2, 2.1 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 4.03 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  152.4 , 141.8 , 138.7 , 134.7 , 131.9 , 131.7 , 130.4 , 130.3, 129.1, 128.4, 127.9 , 127.5, 126.5, 118.9 , 116.1 , 116.0 , 113.6 , 108.3 , 29.8 . ESI-MS: calculated for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:367.1053, found: 367.1048.

#### 2-ethyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ad)

The title compound was prepared *via* the general procedure  $O_2N$   $O_1$   $O_2N$   $O_2N$   $O_3N$   $O_4N$   $O_4N$ 

## 2-isopropyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ae)

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **6ae** was obtained as a yellow solid (28.3 mg, 46% yield); R<sub>f</sub> = 0.54 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 9.02 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.3 Hz, 1H), 6.83 (dd, J = 8.1, 2.2 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 3.96 (s, 2H), 3.16 – 3.12 (m, 1H), 1.11 (d, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  152.4, 141.8, 134.7, 133.9, 131.7, 131.1, 130.2, 126.1, 126.0, 118.9, 116.4, 114.8, 113.5, 108.3, 30.1, 26.4, 22.6.

ESI-MS: calculated for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:333.1209, found: 333.1210.

# 4-(tert-butyl)-2-((6-nitro-1H-indol-3-yl)methyl)phenol (6af)

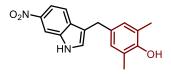
O<sub>2</sub>N HN HO

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **6af** was obtained as a yellow oil (11.0 mg,

17% yield);  $R_f = 0.43$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (s, 1H), 9.23 (s, 1H), 8.29 (d, J = 1.9 Hz, 1H), 7.84 (dd, J = 8.8, 1.9 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.54 (s, 1H), 7.14 (d, J = 2.1 Hz, 1H), 6.99 (dd, J = 8.3, 2.1 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 3.97 (s, 2H), 1.15 (s, 9H).  $^{13}C$  NMR (125MHz, DMSO- $d_6$ )  $\delta$  152.5 , 141.7 , 140.9 , 134.5 , 131.9 , 130.5 , 126.8 , 126.3 , 123.5 , 119.0 , 115.7 , 114.5 , 113.4 , 108.3 , 33.6 , 31.5 , 25.0 .

ESI-MS: calculated for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:347.1366, found: 347.1364.

#### 2,6-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ag)

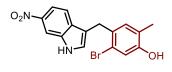


The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **6ag** was obtained as a yellow oil (39.7 mg,

67% yield);  $R_f = 0.57$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.61 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.97 (s, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 6.80 (s, 2H), 3.90 (s, 2H), 2.08 (s, 6H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  151.2, 141.8, 134.7, 131.7, 131.4, 130.3, 128.1, 124.0, 118.8, 116.3, 113.5, 108.3, 29.8, 16.7.

ESI-MS: calculated for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:319.1053, found: 319.1051.

#### 5-bromo-2-methyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ah)



The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1), **6ah** was obtained as a yellow power (54.9)

mg, 76% yield);  $R_f = 0.54$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.65 (s, 1H), 9.64 (s, 1H), 8.31 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 8.8, 2.1 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 7.00 (d, J = 6.0 Hz, 2H), 4.02 (s, 2H), 1.99 (s,

3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  154.7 , 141.9 , 134.7 , 132.3 , 131.6 , 130.7 , 129.5 , 124.0 , 120.2 , 118.7 , 118.0 , 114.7 , 113.7 , 108.4 , 30.0 , 15.6 .

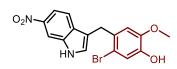
ESI-MS: calculated for C<sub>16</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>3</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:383.0001, found: 383.0001.

## 2,4-dimethyl-3-((6-nitro-1H-indol-3-yl)methyl)phenol (6ai)

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **6ai** was obtained as a yellow oil (14.4 mg,

28% yield);  $R_f = 0.58$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 8.13 (s, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 2.4 Hz, 1H), 6.71 (s, 1H), 6.68 (s, 1H), 3.99 (s, 2H), 2.14 (s, 3H), 2.06 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  150.3 , 141.7 , 134.5 , 131.9 , 130.6 , 129.1 , 127.8 , 127.7 , 127.6 , 124.5 , 118.9 , 115.5 , 113.5 , 108.3 , 24.9 , 20.2 , 16.7 . ESI-MS: calculated for  $C_{17}H_{16}N_2O_3$  Na<sup>+</sup> [M+Na]<sup>+</sup>:319.1053, found: 319.1049.

#### 5-bromo-2-methoxy-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6aj)

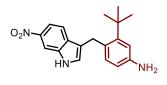


The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1), **6aj** was obtained as a yellow solid (37.0 mg,

49% yield);  $R_f = 0.31$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.66 (s, 1H), 9.39 (s, 1H), 8.31 (d, J = 2.1 Hz, 1H), 7.87 (dd, J = 8.8, 2.1 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 4.06 (s, 2H), 3.46 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  147.4 , 146.1 , 141.9 , 134.7 , 131.5 , 130.7 , 130.0 , 118.9 , 118.8 , 114.6 , 114.5 , 113.7 , 113.4 , 108.4 , 55.8 , 30.6 .

ESI-MS: calculated for C<sub>16</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>4</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:398.9950, found: 398.9948.

## 3-(tert-butyl)-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7aa)



The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **7aa** was obtained as a yellow oil (22.0 mg,

34% yield);  $R_f = 0.44$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.62 (s, 1H), 8.31 (d, J = 2.1 Hz, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 2.3 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.48 (dd, J = 7.9, 1.9 Hz, 1H), 4.83 (s, 2H), 3.86 (s, 2H), 1.19 (s, 9H).

<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 149.0 , 145.5 , 141.7 , 134.7 , 132.0 , 130.7 , 128.8 , 121.2 , 119.0 , 114.4 , 113.5 , 113.3 , 111.9 , 108.3 , 33.9 , 31.3 , 25.8 .

ESI-MS: calculated for  $C_{19}H_{21}N_3O_2$   $Na^+$   $[M+Na]^+$ :346.1525, found: 346.1522.

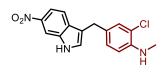
# 2-iodo-5-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ab)

The title compound was prepared via the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **7ab** was obtained as a yellow oil (32.6 mg,

40% yield); R<sub>f</sub> = 0.63 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ) δ 11.64 (s, 1H), 8.31 (d, J = 2.0 Hz, 1H), 7.84 (dd, J = 8.8, 2.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.40 (d, J = 2.3 Hz, 1H), 7.26 (s, 1H), 6.59 (s, 1H), 4.95 (s, 2H), 3.88 (s, 2H), 2.10 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ) δ 146.7 , 141.9 , 138.2 , 137.1 , 134.7 , 131.0 , 130.5 , 129.2 , 118.8 , 116.3 , 115.1 , 113.6 , 108.4 , 80.0 , 27.0 , 19.1 .

ESI-MS: calculated for  $C_{16}H_{14}IN_3O_2\ Na^+\ [M+Na]^+:430.0022$ , found: 430.0019.

# 2-chloro-N-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ac)



The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7ac** was obtained as a yellow solid (39.8 mg,

63% yield);  $R_f = 0.75$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.64 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 1.9 Hz, 1H), 7.07 (dd, J = 8.3, 1.8 Hz, 1H), 6.54 (d, J = 8.3 Hz, 1H), 5.28 (d, J = 4.9 Hz, 1H), 3.95 (s, 2H), 2.70 (d, J = 5.0 Hz, 3H).  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  143.4 , 141.8 , 134.8 , 131.6 , 130.4 , 129.1 , 128.6 , 128.0 , 118.8 , 117.6 , 115.9 , 113.6 , 110.6 , 108.3 , 30.0 , 29.3 .

ESI-MS: calculated for  $C_{16}H_{14}ClN_3O_2 Na^+ [M+Na]^+:338.0666$ , found: 338.0661.

#### *N*,3-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ad)

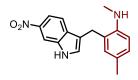
O<sub>2</sub>N N

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7ad** was obtained as a yellow oil (23.6 mg, 40%)

yield);  $R_f$ = 0.56 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 2.3 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.35 (d, J = 2.1 Hz, 1H), 6.28 (dd, J = 8.2, 2.3 Hz, 1H), 5.34 (s, 1H), 3.90 (s, 2H), 2.62 (s, 3H), 2.15 (s, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  148.3 , 141.8 , 136.1 , 134.8 , 131.8 , 130.3 , 129.7 , 125.8 , 118.9 , 115.8 , 113.8 , 113.5 , 109.3 , 108.3 , 30.0 , 27.7 , 19.6 .

ESI-MS: calculated for  $C_{17}H_{18}N_3O_2^+$  [M+H]<sup>+</sup>:296.1393, found: 296.1390.

# *N*,4-dimethyl-3-((6-nitro-1H-indol-3-yl)methyl)aniline (7ae)

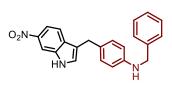


The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **7ae** was obtained as a yellow oil (11.9 mg, 20% yield);  $R_f$ =

0.62 (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.63 (s, 1H), 8.32 (d, J = 1.8 Hz, 1H), 7.84 (dd, J = 8.8, 2.1 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 2.1 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 1.8 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 3.88 (s, 2H), 2.70 (s, 3H), 2.06 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  145.0, 141.8, 134.7, 132.1, 130.8, 129.5, 127.4, 124.4, 123.8, 119.0, 114.1, 113.6, 109.3, 108.4, 30.5, 26.0, 20.2.

ESI-MS: calculated for  $C_{17}H_{18}N_3O_2^+$  [M+H]<sup>+</sup>:296.1393, found: 296.1390.

# N-benzyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7af)



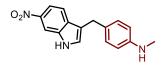
The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7af** was obtained as a yellow power (32.2 mg,

45% yield);  $R_f = 0.75$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H),

8.28 (d, J = 2.1 Hz, 1H), 7.81 (dd, J = 8.8, 2.1 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.55 (s, 1H), 7.32 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 6.05 (t, J = 6.0 Hz, 1H), 4.20 (d, J = 6.0 Hz, 2H), 3.89 (s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  146.8, 141.7, 140.5, 134.7, 131.7, 130.2, 128.8, 128.3, 128.1, 127.2, 126.6, 118.9, 116.6, 113.5, 112.3, 108.3, 46.7, 29.8.

ESI-MS: calculated for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:380.1369, found: 380.1362.

#### N-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ag<sub>1</sub>)

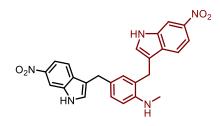


The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $7\mathbf{ag_1}$  was obtained as a yellow solid (16.6 mg,

30% yield);  $R_f = 0.56$  (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.60 (s, 1H), 8.29 (s, 1H), 7.82 (dd, J = 8.8, 1.9 Hz, 1H), 7.57 (d, J = 9.3 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 6.44 (d, J = 8.3 Hz, 2H), 5.41 (s, 1H), 3.91 (s, 2H), 2.61 (s,3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  148.2 , 141.8 , 134.8 , 131.8 , 130.2 , 128.9 , 127.8 , 118.9 , 116.7 , 113.5 , 111.7 , 108.3 , 30.0 , 29.9 .

ESI-MS: calculated for  $C_{16}H_{15}N_3O_2 Na^+ [M+Na]^+:304.1056$ , found: 304.1053.

#### N-methyl-2,4-bis((6-nitro-1H-indol-3-yl)methyl)aniline (7ag<sub>2</sub>)



The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $\bf 7ag_2$  was obtained as a yellow solid (9.0 mg, 20% yield);  $\bf R_f$ = 0.29 (PE/EA

= 2/1);  ${}^{1}$ H NMR (500 MHz, DMSO- $d_{6}$ )  $\delta$  11.55 (d, J = 10.9 Hz, 2H), 8.25 (dd, J = 4.4, 2.1 Hz, 2H), 7.71 – 7.69 (m, 1H), 7.62 (dd, J = 8.8, 2.1 Hz, 1H), 7.55 (d, J = 2.2 Hz, 1H), 7.49 (s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 6.96 (dd, J = 8.1, 1.7 Hz, 1H), 6.86 (d, J = 1.7 Hz, 1H), 6.42 (d, J = 8.2 Hz, 1H), 5.04 – 5.00 (m, 1H), 3.85 (d, J = 3.6 Hz, 4H), 2.68 (d, J = 3.7 Hz, 3H).  ${}^{13}$ C NMR (125 MHz, DMSO- $d_{6}$ )  $\delta$  145.3, 141.7, 134.7, 131.9, 131.6, 130.7, 130.0, 129.2, 127.8, 127.0, 124.2, 118.9,

118.8, 116.6, 113.8, 113.3, 113.3, 109.2, 108.2, 108.2, 30.4, 29.9, 26.4.

ESI-MS: calculated for  $C_{25}H_{21}N_5O_4$  Na<sup>+</sup> [M+Na]<sup>+</sup>: 478.1485, found: 478.1482.

#### N-isopropyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ah<sub>1</sub>)

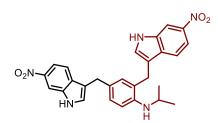
O<sub>2</sub>N HN

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1),  $7\mathbf{ah}_1$  was obtained as a yellow solid (28.5)

mg, 46% yield);  $R_f = 0.69$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 6.45 (d, J = 8.4 Hz, 2H), 5.11 (d, J = 7.9 Hz, 1H), 3.90 (s, 2H), 3.47 – 3.43 (m, 1H), 1.08 (d, J = 6.3 Hz, 6H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  146.8 , 142.2 , 135.2 , 132.2 , 130.6 , 129.4 ,127.9 , 119.3 , 117.1 , 113.9 , 112.9 , 108.7 , 43.5 , 30.2 , 23.0 .

ESI-MS: calculated for  $C_{18}H_{19}N_3O_2$   $Na^+$  [M+Na]<sup>+</sup>:332.1369, found: 332.1365.

#### N-isopropyl-2,4-bis((6-nitro-1H-indol-3-yl)methyl)aniline (7ah<sub>2</sub>)



The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1),  $7ah_2$  was obtained as a yellow oil (15.1 mg, 31% yield);  $R_f = 0.30$  (PE/EA

= 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (d, J = 18.0 Hz, 2H), 8.27 (t, J = 2.4 Hz, 2H), 7.73 (dd, J = 8.8, 2.1 Hz, 1H), 7.63 (dd, J = 8.8, 2.1 Hz, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 9.6 Hz, 2H), 6.49 (d, J = 8.1 Hz, 1H), 4.22 (d, J = 7.9 Hz, 1H), 3.88 (d, J = 14.8 Hz, 4H), 3.53 – 3.48 (m, 1H), 1.04 (d, J = 6.2 Hz, 6H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  143.5, 141.7, 134.7, 131.9, 131.7, 130.7, 130.1, 129.7, 128.0, 127.0, 124.6, 118.9, 118.8, 116.6, 113.8, 113.4, 113.3, 110.8, 108.2, 108.2, 43.4, 29.9, 26.7, 22.5.

ESI-MS: calculated for C<sub>27</sub>H<sub>25</sub>N<sub>5</sub>O<sub>4</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:506.1798, found: 506.1796.

# N-cyclohexyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ai<sub>1</sub>)

O<sub>2</sub>N HN H

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7ai**<sub>1</sub> was obtained as a yellow power (43.0

mg, 62% yield);  $R_f = 0.75$  (PE/EA = 2/1);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 7.82 (dd, J = 8.8, 2.1 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.46 (d, J = 8.5 Hz, 2H), 5.16 (d, J = 7.6 Hz, 1H), 3.89 (s, 2H), 1.87 (d, J = 12.4 Hz, 2H), 1.67 (dt, J = 12.7, 3.4 Hz, 2H), 1.58 – 1.54 (m, 1H), 1.30 – 1.22 (m, 3H), 1.16 – 1.06 (m, 3H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  146.2 , 141.7 , 134.7 , 131.7 , 130.2 , 128.9 , 127.4 , 118.9 , 116.7 , 113.5 , 112.4 , 108.2 , 50.6 , 32.7 , 29.8 , 25.7 , 24.6 .

ESI-MS: calculated for  $C_{21}H_{23}N_3O_2$   $Na^+$   $[M+Na]^+$ :372.1682, found: 372.1674.

# N-cyclohexyl-2,4-bis((6-nitro-1H-indol-3-yl)methyl)aniline (7ai<sub>2</sub>)

 $O_2N$ 

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **7ai**<sub>2</sub> was obtained as a yellow solid (15.4 mg, 29% yield); R<sub>f</sub> = 0.53 (PE/EA

= 2/1);  $^{1}$ H NMR (500 MHz, DMSO- $d_{6}$ )  $\delta$  11.58 (d, J = 13.6 Hz, 2H), 8.26 (t, J = 2.0 Hz, 2H), 7.74 (dd, J = 8.8, 2.1 Hz, 1H), 7.62 (dd, J = 8.8, 2.1 Hz, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.52 (d, J = 2.1 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 9.6 Hz, 2H), 6.49 (d, J = 8.2 Hz, 1H), 4.21 (d, J = 6.8 Hz, 1H), 3.88 (d, J = 10.8 Hz, 4H), 1.79 (d, J = 10.0 Hz, 2H), 1.57 – 1.49 (m, 3H), 1.27 – 1.20 (m, 4H), 1.09 – 1.05 (m, 2H).  $^{13}$ C NMR (125 MHz, DMSO- $d_{6}$ )  $\delta$  143.2 , 141.7 , 134.7 , 131.9 , 131.7 , 130.7 , 130.1 , 129.8 , 127.9 , 127.0 , 124.4 , 118.9 , 118.8 , 116.6 , 113.8 , 113.4 , 113.3 , 110.7 , 108.2 , 108.2 , 50.8 , 32.6 , 31.2 , 29.9 , 29.9 , 26.9 , 25.6 , 24.5 .

ESI-MS: calculated for C<sub>30</sub>H<sub>29</sub>N<sub>5</sub>O<sub>4</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>: 546.2111, found: 546.2106.

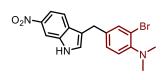
## *N,N*-diethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7aj)

The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7aj** was obtained as a yellow oil (41.8 mg,

65% yield);  $R_f$  = 0.69 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.62 (s, 1H), 8.30 (s, 1H), 7.83 (dd, J = 8.8, 2.1 Hz, 1H), 7.59 (d, J = 11.0 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 3.92 (s, 2H), 3.24 (q, J = 5.9, 5.1 Hz, 4H), 1.01 (t, J = 6.9 Hz, 6H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  145.7, 141.8, 134.8, 131.7, 130.2, 129.1, 127.3, 118.9, 116.6, 113.5, 111.7, 108.3, 43.7, 29.6, 12.4.

ESI-MS: calculated for  $C_{19}H_{21}N_3O_2$   $Na^+$   $[M+Na]^+$ :346.1525, found: 346.1520.

#### 2-bromo-N,N-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ak)

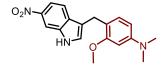


The title compound was prepared *via* the general procedure  $\bf A$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7ak** was obtained as a yellow oil (19.0 mg, 25%)

yield);  $R_f$  = 0.75 (PE/EA = 2/1);  $^1$ H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.68 (s, 1H), 8.31 (d, J = 2.0 Hz, 1H), 7.85 (dd, J = 8.8, 2.0 Hz, 1H), 7.67 (d, J = 2.4 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 8.2, 2.0 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 4.03 (s, 2H), 2.63 (s, 6H).  $^{13}$ C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  149.4 , 141.9 , 137.4 , 134.7 , 133.1 , 131.5 , 130.6 , 128.4 , 120.9 , 118.8 , 118.4 , 115.2 , 113.7 , 108.4 , 43.9 , 29.2 .

ESI-MS: calculated for C<sub>17</sub>H<sub>16</sub>BrN<sub>3</sub>O<sub>2</sub> Na<sup>+</sup> [M+Na]<sup>+</sup>:396.0318, found: 396.0315.

#### 3-methoxy-N,N-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7al<sub>1</sub>)



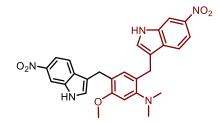
The title compound was prepared *via* the general procedure  $\mathbf{A}$ , after purification by silica gel column chromatography (PE/EA = 2/1), **7al**<sub>1</sub> was obtained as a yellow power (20.7 mg,

32% yield);  $R_f = 0.63$  (PE/EA = 2/1);  ${}^{1}H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.57 (s, 1H), 8.29 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.8, 2.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 6.31 (d, J = 2.1 Hz, 1H), 6.17 (dd, J = 8.3, 2.1 Hz, 1H), 3.89 (s, 2H), 3.80 (s, 3H), 2.84 (s, 6H).  ${}^{13}C$  NMR (125 MHz, DMSO- $d_6$ )

δ 157.4, 150.5, 141.7, 134.6, 131.9, 130.4, 129.8, 118.9, 116.7, 116.0, 113.5, 108.3, 104.5, 96.4, 55.1, 40.5, 23.9.

ESI-MS: calculated for  $C_{18}H_{19}N_3O_3$   $Na^+$   $[M+Na]^+$ :348.1318, found: 348.1314.

# 5-methoxy-N,N-dimethyl-2,4-bis((6-nitro-1H-indol-3-yl)methyl)aniline (7al<sub>2</sub>)



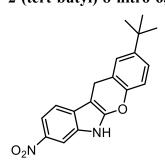
The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **7al**<sub>2</sub> was obtained as a yellow power (26.7 mg, 54% yield); R<sub>f</sub> = 0.38

(PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.51 (d, J = 24.4 Hz, 2H), 8.23 (d, J = 2.0 Hz, 1H), 8.18 (d, J = 2.0 Hz, 1H), 7.67 (dd, J = 8.8, 2.0 Hz, 1H), 7.56 (dd, J = 8.8, 2.0 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H), 7.39 (d, J = 1.5 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 6.81 (s, 1H), 6.73 (s, 1H), 3.97 (s, 2H), 3.82 (s, 2H), 3.80 (s, 3H), 2.65 (s, 6H).

<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 155.4 , 151.2 , 141.7 , 141.6 , 134.6 , 134.5 , 131.8 , 131.7 , 130.9 , 130.3 , 130.3 , 126.3 , 123.1 , 118.7 , 118.5 , 116.0 , 114.9 , 113.4 , 113.2 , 108.1 , 108.1 , 102.4 , 55.3 , 44.9 , 24.9 , 24.4 .

ESI-MS: calculated for  $C_{27}H_{25}N_5O_5$  Na<sup>+</sup> [M+Na]<sup>+</sup>:522.1747, found: 522.1742.

# 2-(tert-butyl)-8-nitro-6,11-dihydrochromeno[2,3-b]indole (8)



To a solution of 6af in DCM and THF (v/v = 1/1) was added MBS (1.1 eq) and PPTS (1.1 eq) at -78 °C. The result mixture was stirred for 15 min at -78 °C. The reaction mixture was then diluted with EtOAc (10.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The

organic layers were combined, washed with brine and dried over  $Na_2SO_4$ . After purification by silica gel column chromatography (PE/EA = 8/1), **8** was obtained as a white solid (7 mg, 0.021 mmol, 43 %). Rf = 0.4 (PE/EA = 8/1).

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  12.28 (s, 1H), 8.14 (d, J = 2.1 Hz, 1H), 7.95 (dd, J

= 8.7, 2.2 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 2.5 Hz, 1H), 7.33 (dd, J = 8.6, 2.6 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 4.08 (s, 2H), 1.30 (s, 9H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 150.0, 148.3, 147.0, 140.4, 131.4, 129.4, 127.2, 125.0, 119.1, 116.6, 116.5, 115.3, 107.2, 87.6, 34.1, 31.2, 22.1.

ESI-MS: calculated for  $C_{19}H_{18}N_2O_3$  [M+H]<sup>+</sup>:323.1390, found:323.1391.

#### N-ethyl-*N*-((6-nitro-1H-indol-3-yl)methyl)ethanamine (int I)

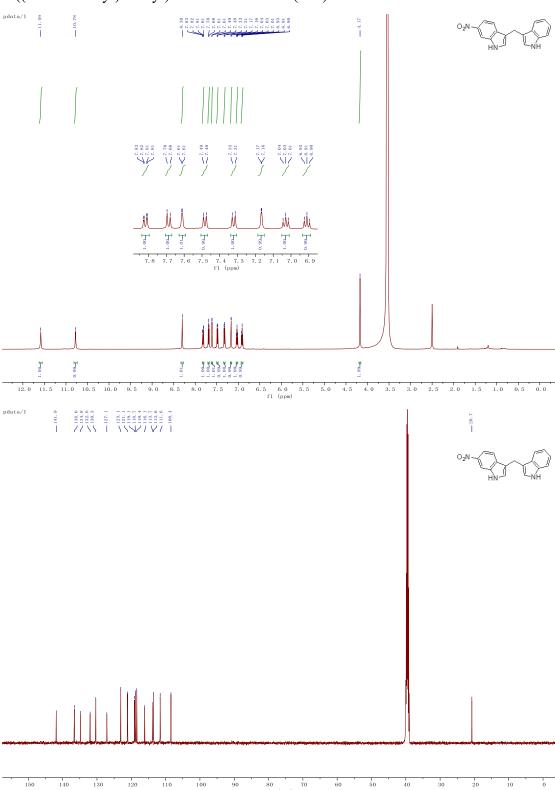
The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), int **I** was obtained as a yellow solid (quantitative yield); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  12.28 (s, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.09 (s, 1H), 8.00 (dd, J = 3.7, 2.0 Hz, 2H), 4.51 (d, J = 4.9 Hz, 2H), 3.08 (q, J = 6.5, 5.8 Hz, 4H), 1.27 (t, J = 7.2 Hz, 6H).

ESI-MS: calculated for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 248.1393, found: 248.1389.

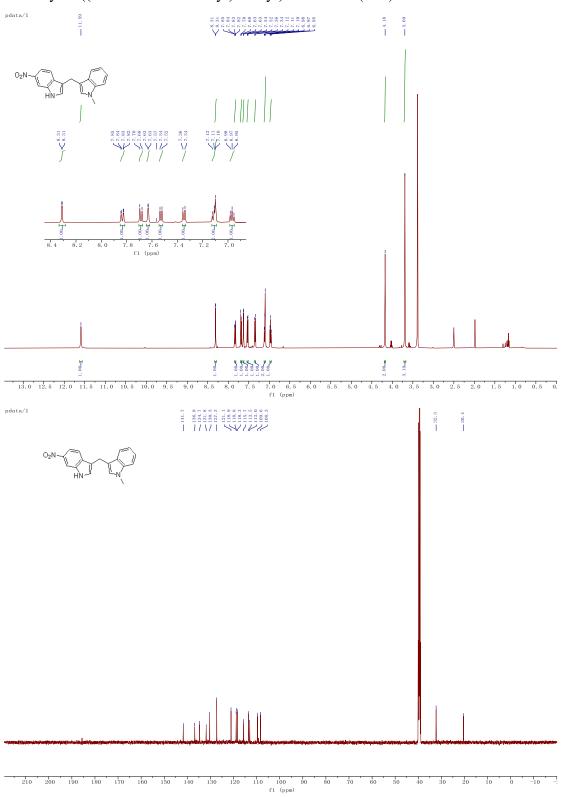
#### 3,3'-(phenylmethylene)bis(6-nitro-1H-indole) (9)

The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 2/1), **9** was obtained as a yellow solid (65.0 mg, 79% yield);  $R_f = 0.34$  (PE/EA = 2/1); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  11.69 (s, 1H), 8.33 (d, J = 2.2 Hz, 2H), 7.78 (dd, J = 8.8, 2.2 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.34 – 7.27 (m, 4H), 7.22 (t, J = 7.3 Hz, 1H), 6.02 (s, 1H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta$  143.7 , 141.9 , 135.0 , 131.1 , 130.8 , 128.5 , 128.2 , 126.4 , 119.2 , 118.9 , 113.7 , 108.5 .

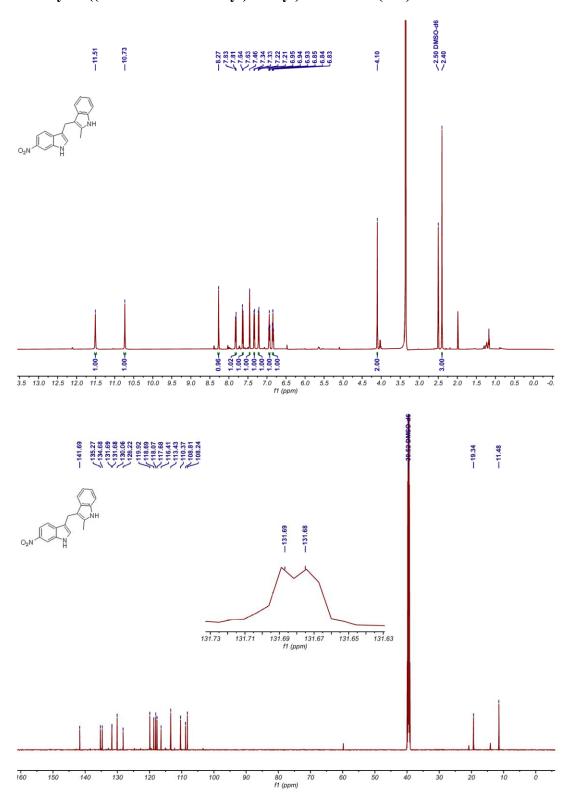
# $3\hbox{-}((1H\hbox{-}indol\hbox{-} 3\hbox{-}yl)methyl)\hbox{-} 6\hbox{-}nitro\hbox{-} 1H\hbox{-}indole\ (\textbf{3aa})$



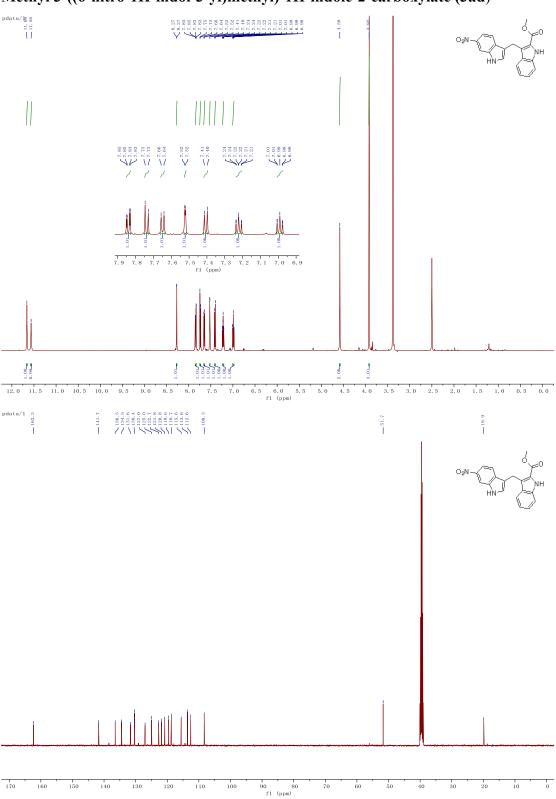
# $1\text{-methyl-}3\text{-}((6\text{-nitro-}1\text{H-indol-}3\text{-yl})\text{methyl})\text{-}1\text{H-indole}\;(\textbf{3ab})$



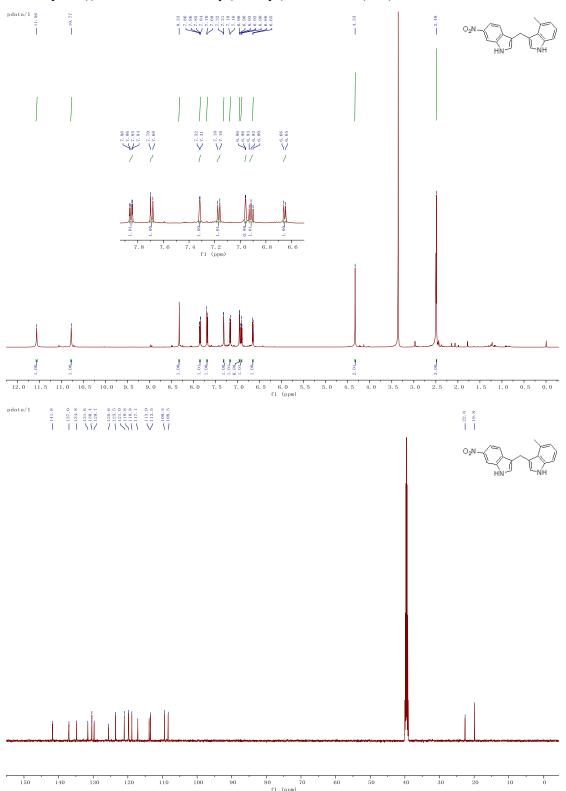
# 2-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ac)



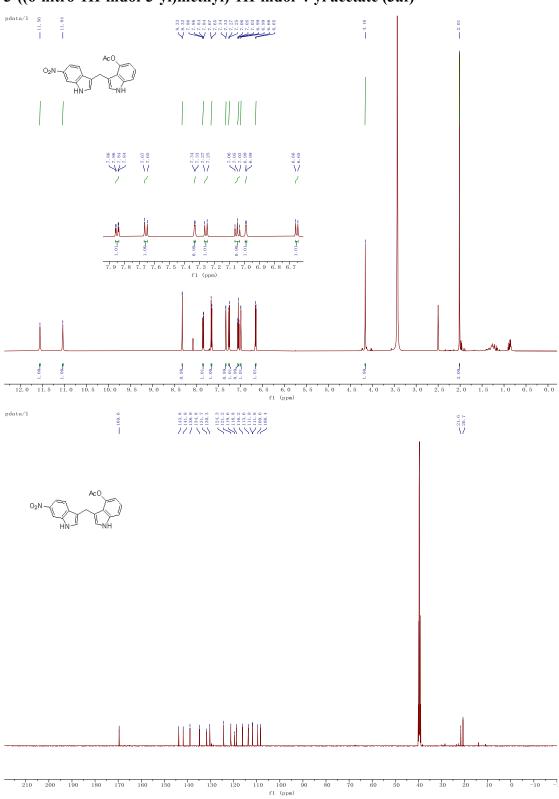
# Methyl 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-2-carboxylate (3ad)



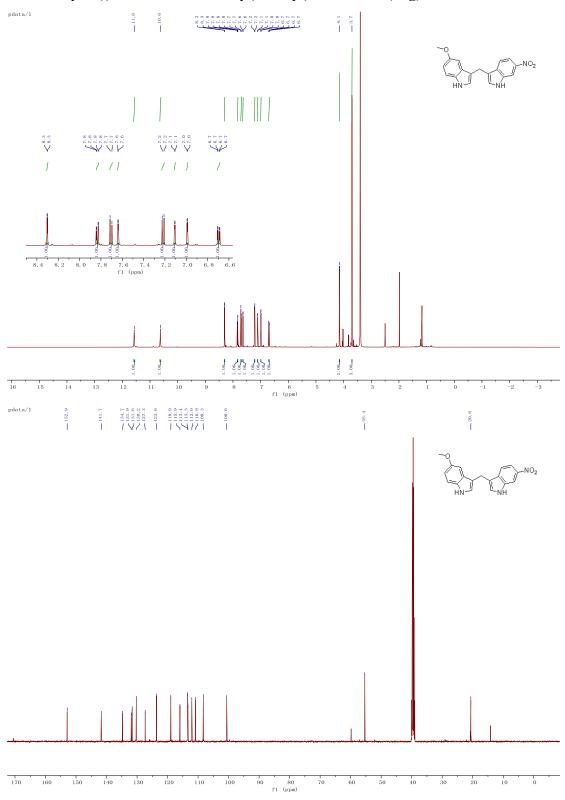
# $4\text{-methyl-}3\text{-}((6\text{-nitro-}1\text{H-indol-}3\text{-yl})\text{methyl})\text{-}1\text{H-indole}\;(\textbf{3ae})$



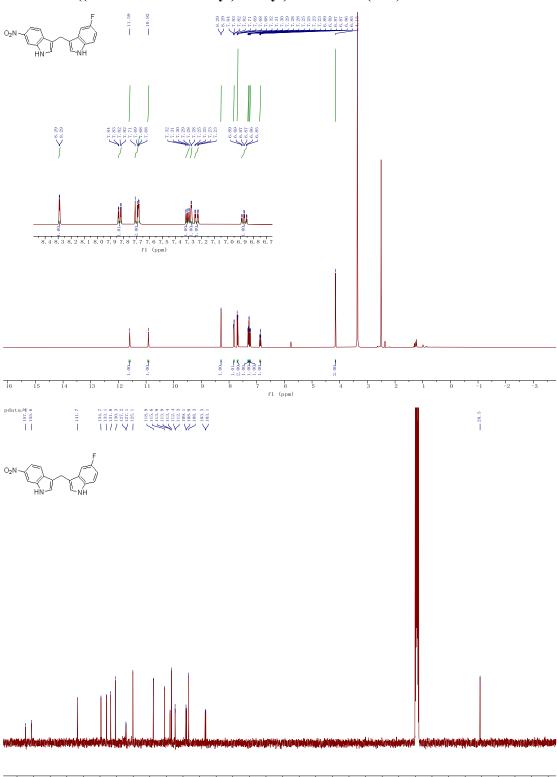
# 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indol-4-yl acetate (3af)



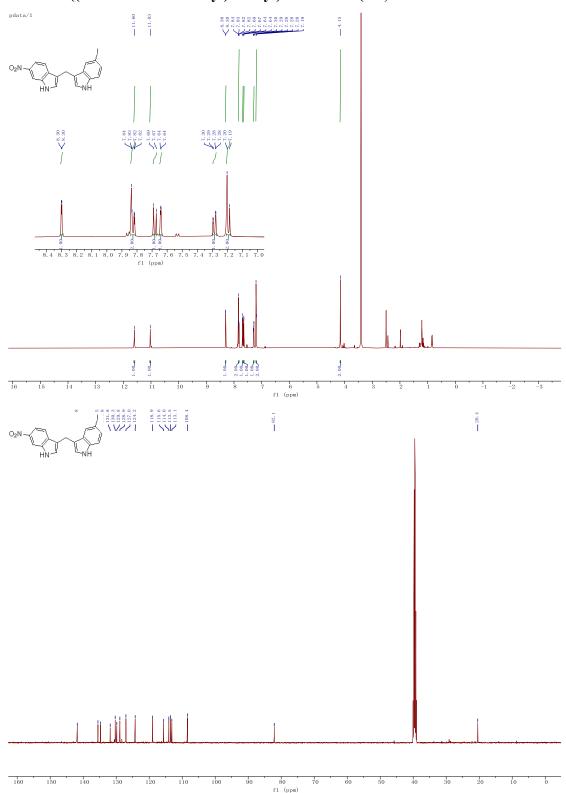
# $5\text{-methoxy-3-}((6\text{-nitro-1}H\text{-indol-3-yl})\text{methyl})\text{-}1H\text{-indole}\ (3\text{ag})$



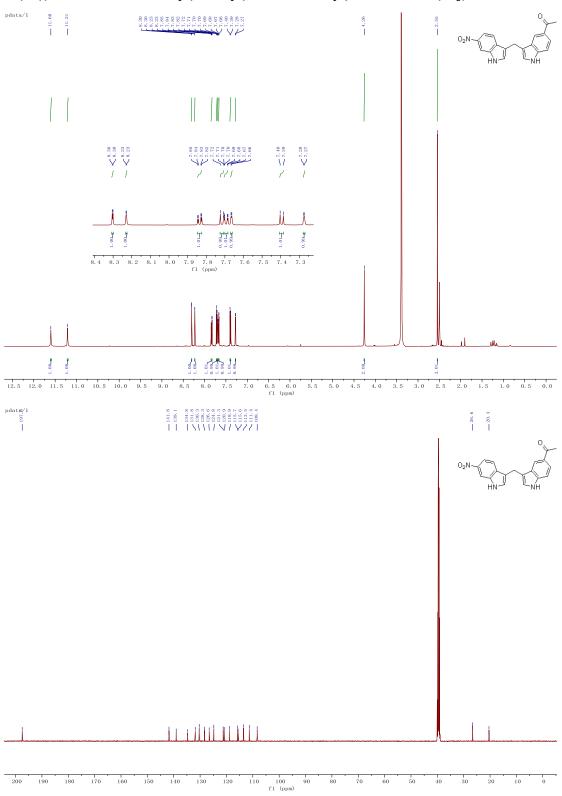
## $5-fluoro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole\ (3ah)$



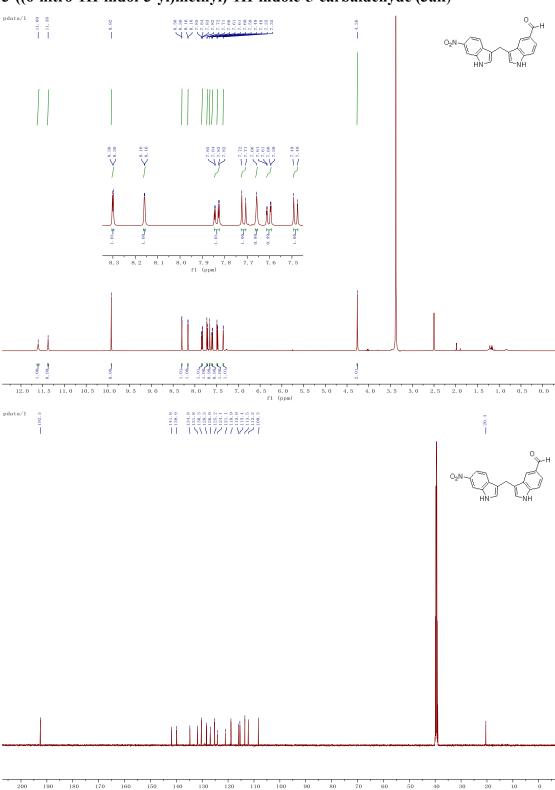
5-iodo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ai)



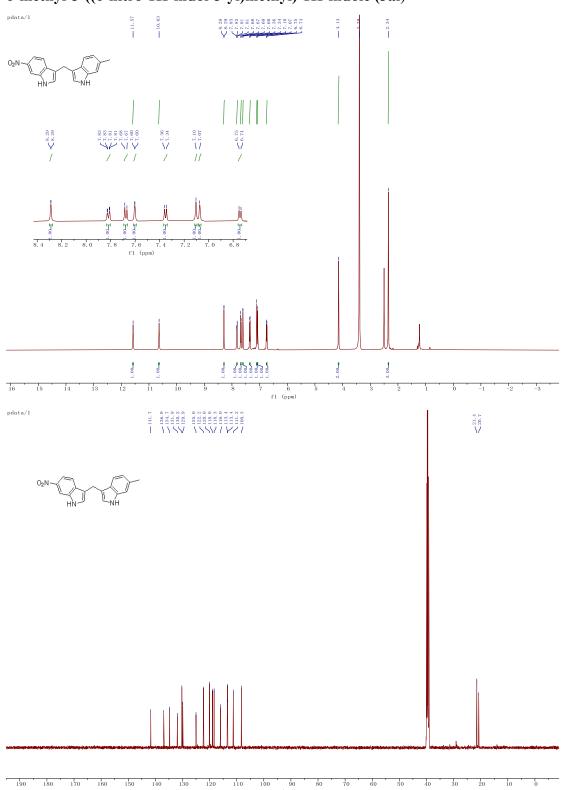
### $1\hbox{-}(3\hbox{-}((6\hbox{-nitro-}1H\hbox{-indol-}3\hbox{-}yl)methyl)\hbox{-}1H\hbox{-indol-}5\hbox{-}yl)ethan\hbox{-}1\hbox{-}one\ (3aj)$



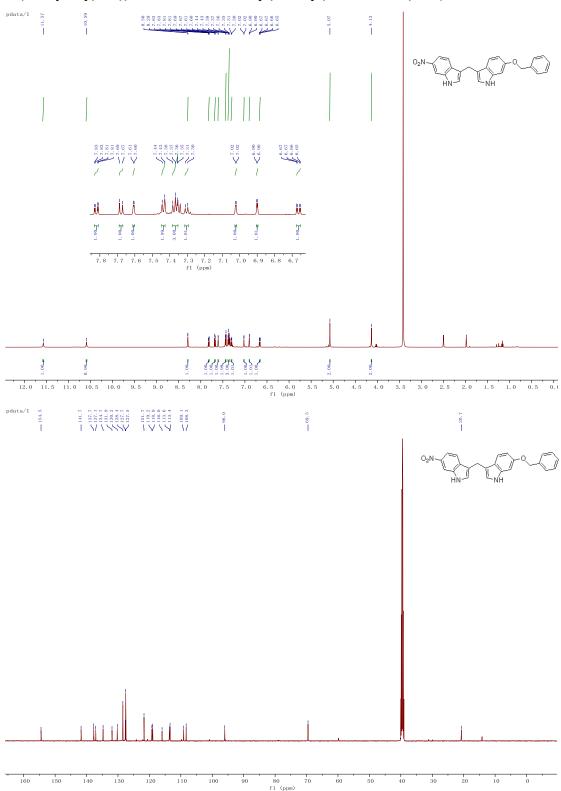
### $3\hbox{-}((6\hbox{-}nitro\hbox{-}1H\hbox{-}indol\hbox{-}3\hbox{-}yl)methyl)\hbox{-}1H\hbox{-}indole\hbox{-}5\hbox{-}carbaldehyde} \ (3ak)$



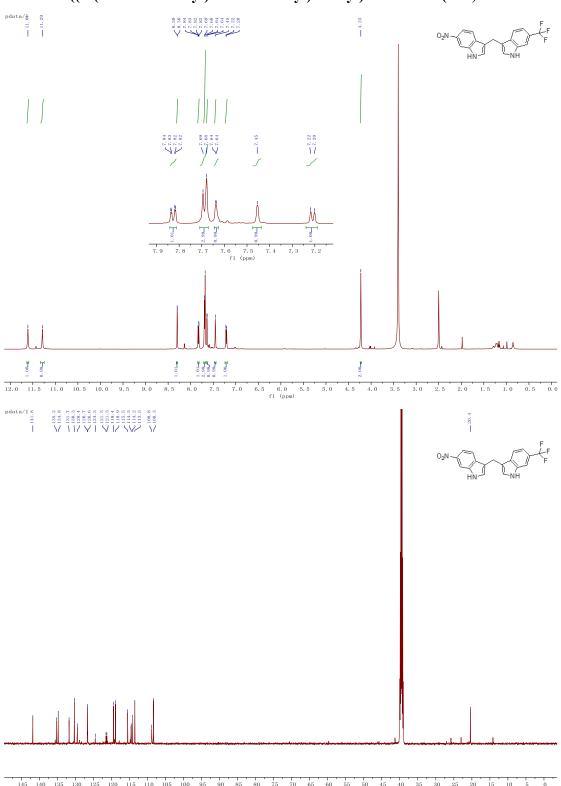
#### 6-methyl-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3al)



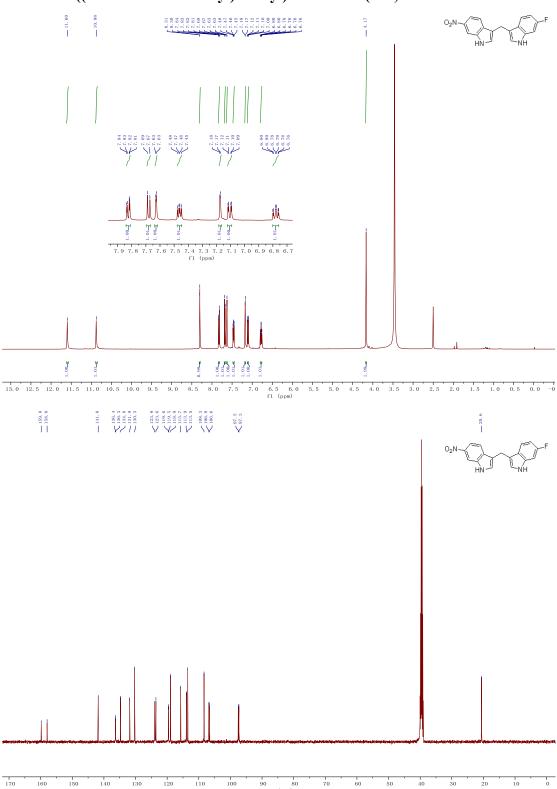
### $\hbox{6-(benzyloxy)-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole\ (3am)}$



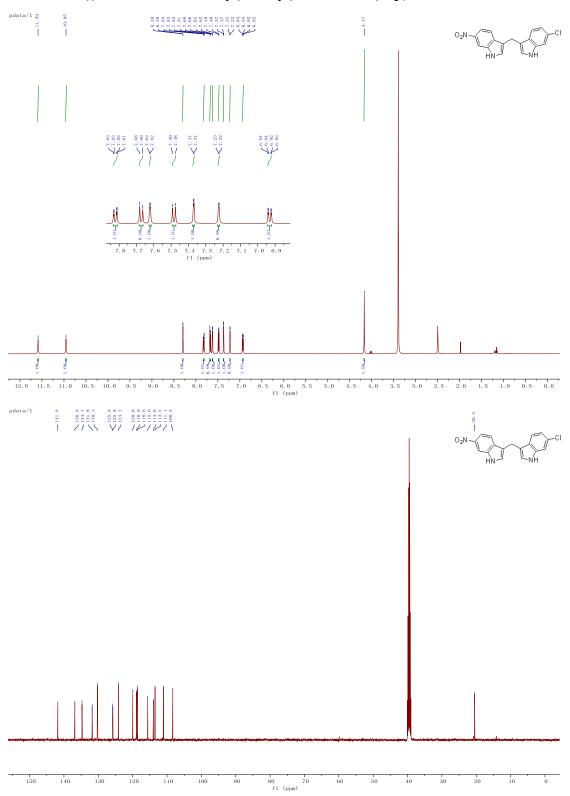
### $6\hbox{-nitro-3-((6-(trifluoromethyl)-1H-indol-3-yl)} methyl)-1H-indole~(3an)$



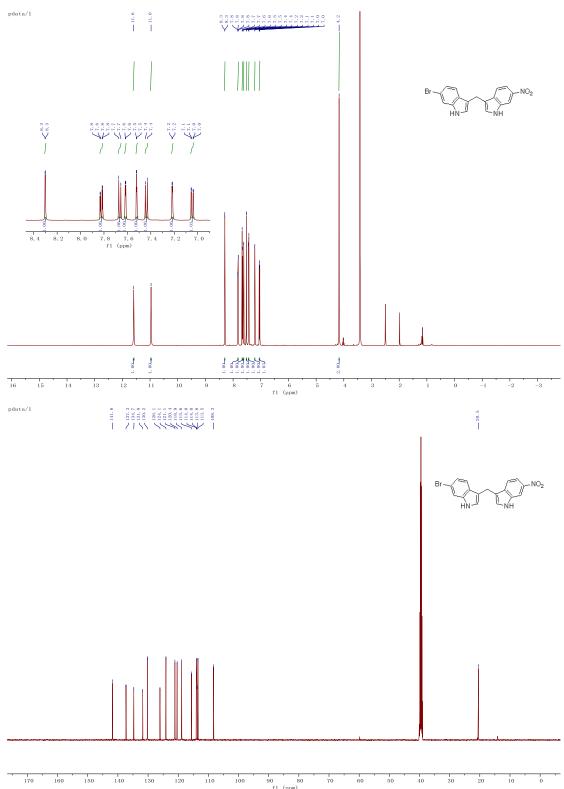
#### 6-fluoro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ao)



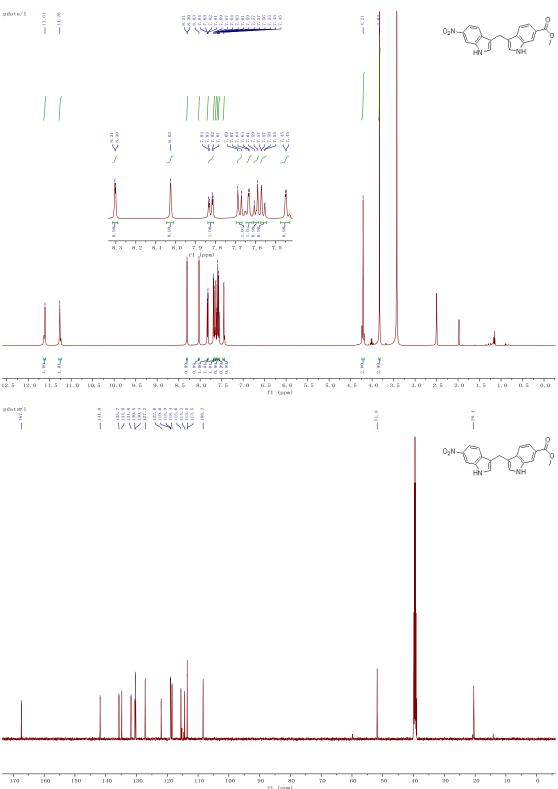
#### 6-chloro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3ap)



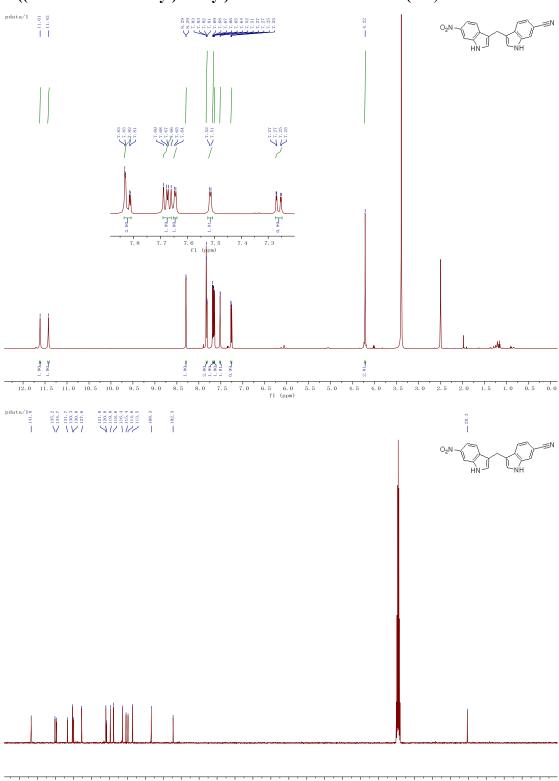
### $\hbox{6-bromo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole\ (3aq)}$



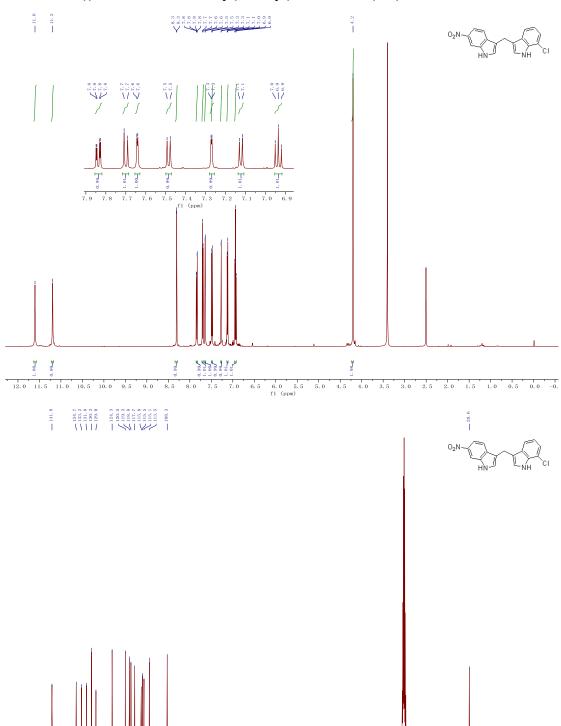
#### Methyl 3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-6-carboxylate (3ar)



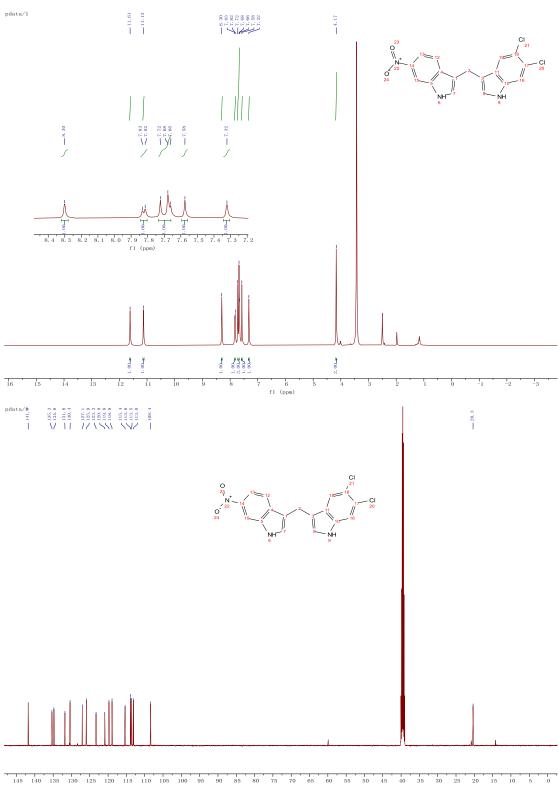
### $3\hbox{-}((6\hbox{-}nitro\hbox{-}1H\hbox{-}indol\hbox{-}3\hbox{-}yl)methyl)\hbox{-}1H\hbox{-}indole\hbox{-}6\hbox{-}carbonitrile}\ (3as)$



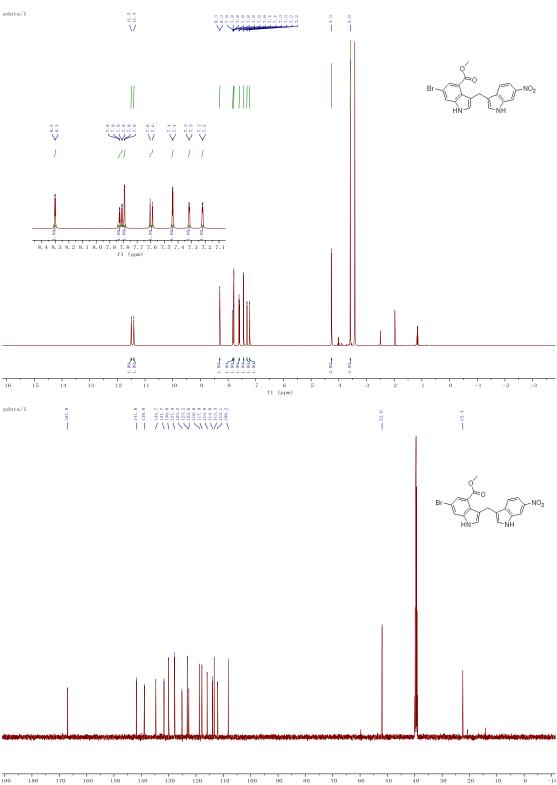
#### 7-chloro-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole (3at)



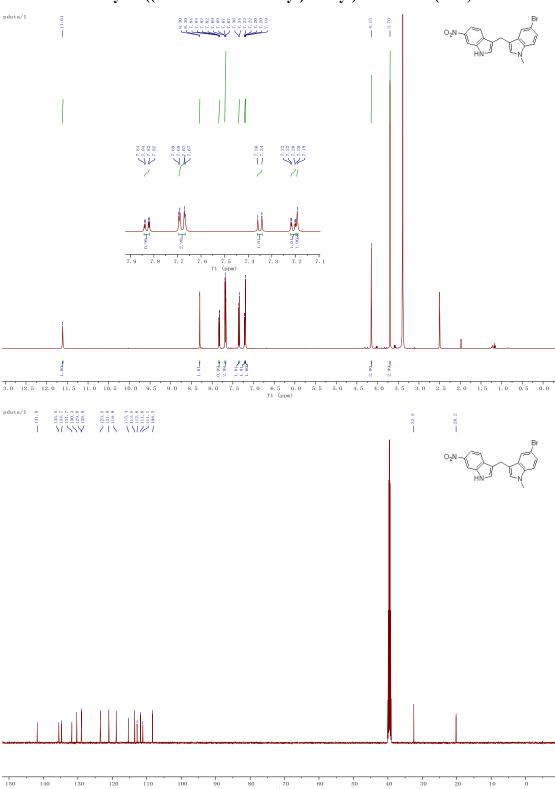
### $5,\!6\text{-}dichloro-3\text{-}((6\text{-}nitro-1H\text{-}indol-3\text{-}yl)methyl)\text{-}1H\text{-}indole\ (3au)$



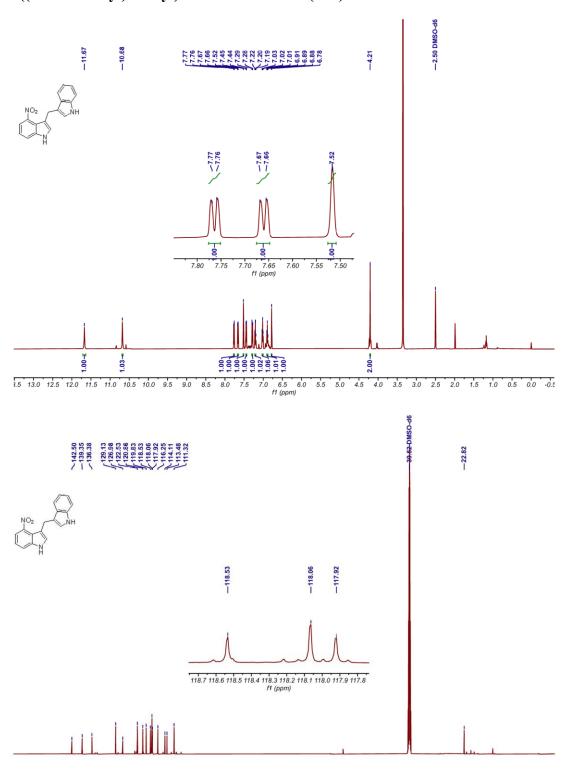
### $Methyl\ 6-bromo-3-((6-nitro-1H-indol-3-yl)methyl)-1H-indole-4-carboxylate\ (3av)$



## $5\text{-}bromo\text{-}1\text{-}methyl\text{-}3\text{-}((6\text{-}nitro\text{-}1H\text{-}indol\text{-}3\text{-}yl)methyl)\text{-}1H\text{-}indole\ (3aw)}$

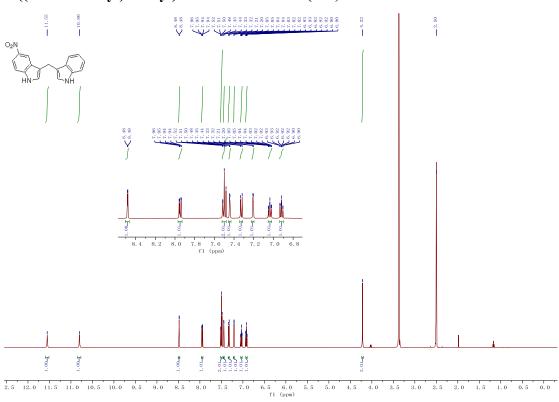


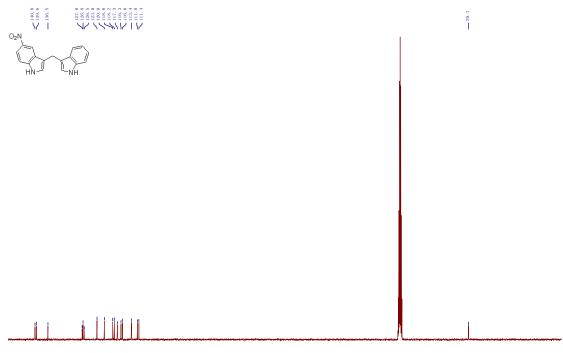
#### 3-((1H-indol-3-yl)methyl)-4-nitro-1H-indole (3ba)



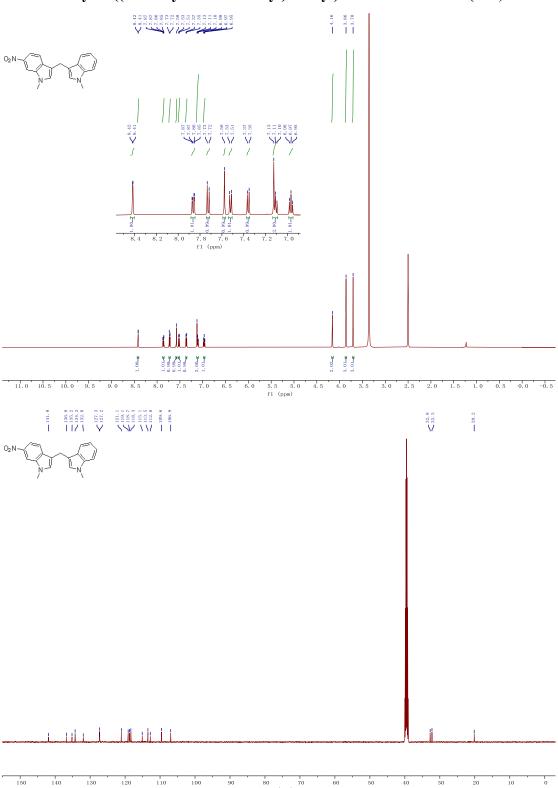
f1 (ppm) 

# $3\hbox{-}((1H\hbox{-}indol\hbox{-} 3\hbox{-}yl)methyl)\hbox{-} 5\hbox{-}nitro\hbox{-} 1H\hbox{-}indole\ (3ca)$

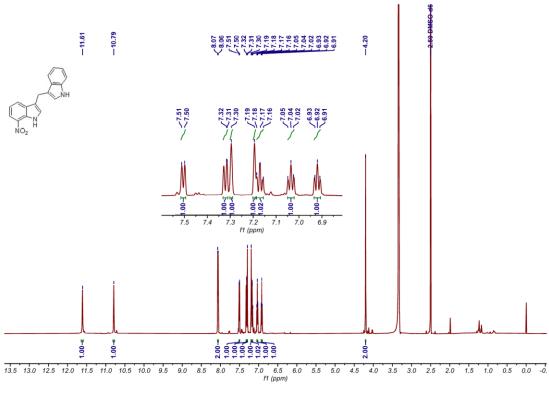


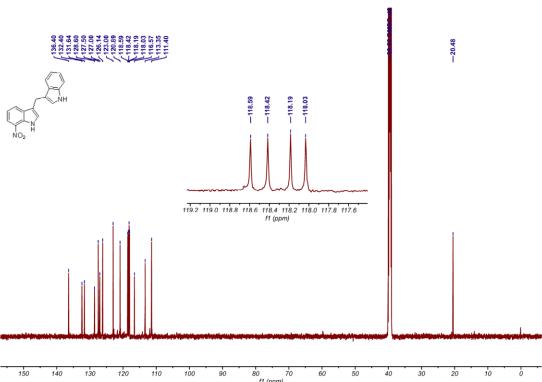


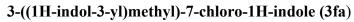
#### 1-methyl-3-((1-methyl-1H-indol-3-yl)methyl)-6-nitro-1H-indole (3da)

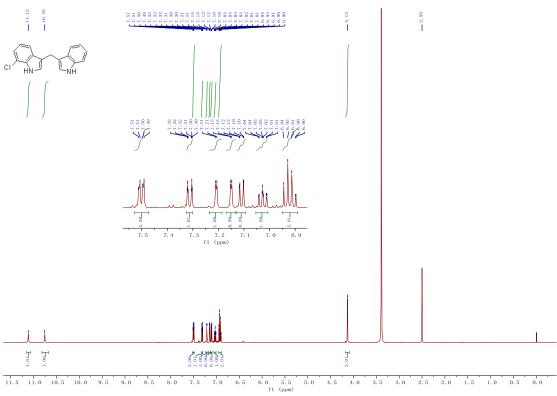


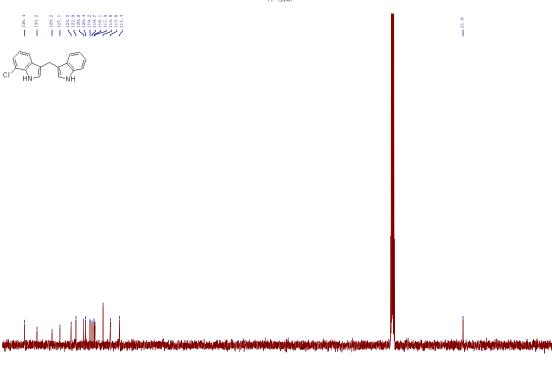
#### 3-((1H-indol-3-yl)methyl)-7-nitro-1H-indole (3ea)



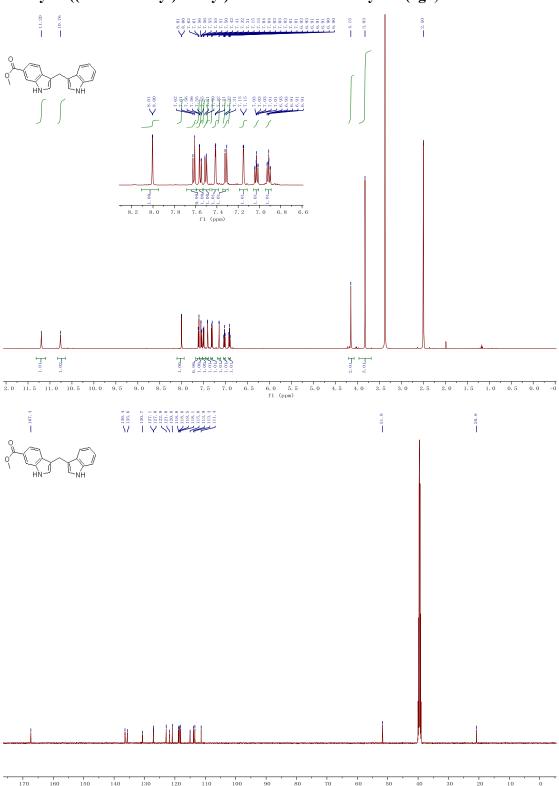




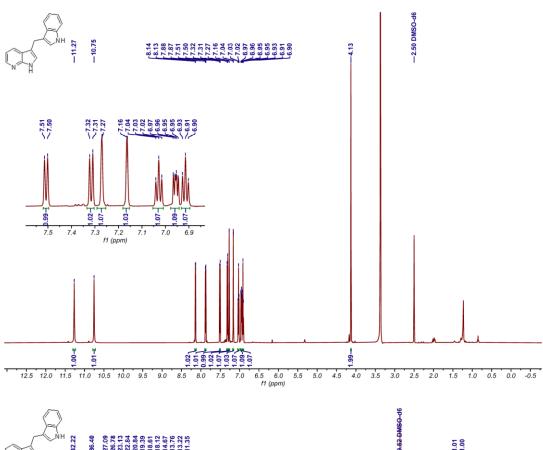


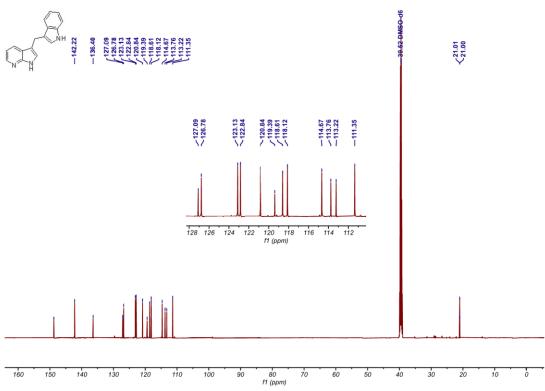


#### Methyl 3-((1H-indol-3-yl)methyl)-1H-indole-6-carboxylate (3ga)

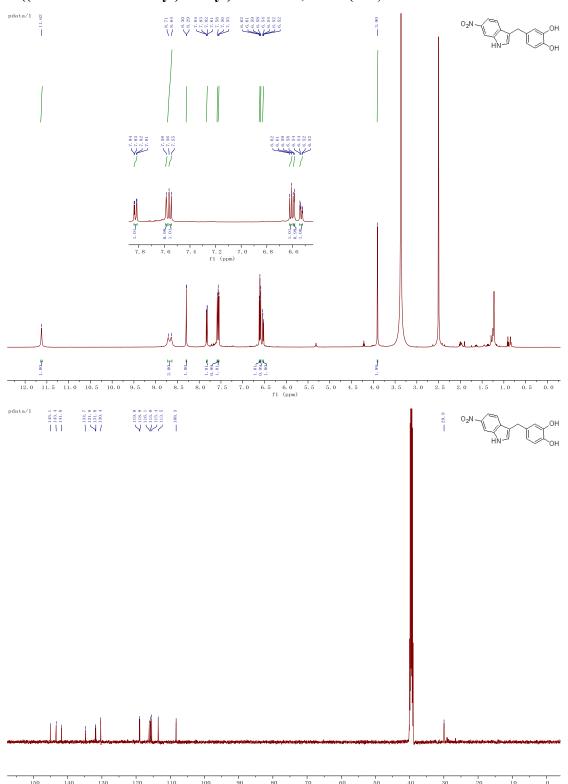


#### 3-((1H-indol-3-yl)methyl)-1H-pyrrolo[2,3-b]pyridine (3ha)

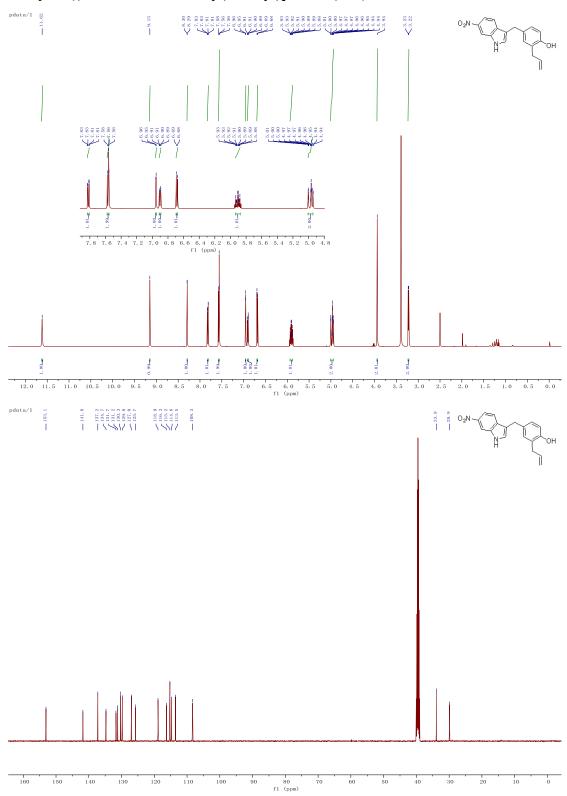




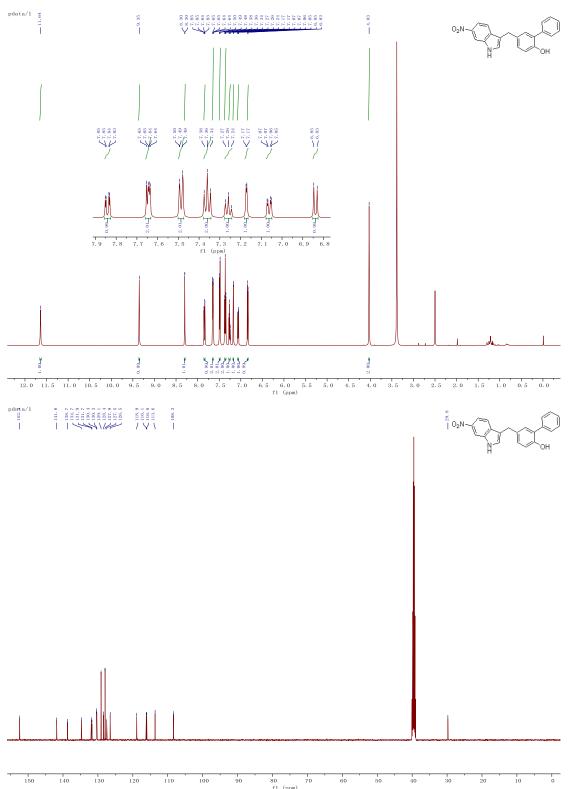
### $\hbox{\it 4-((6-nitro-1H-indol-3-yl)} methyl) benzene-1, \hbox{\it 2-diol (6aa)}$



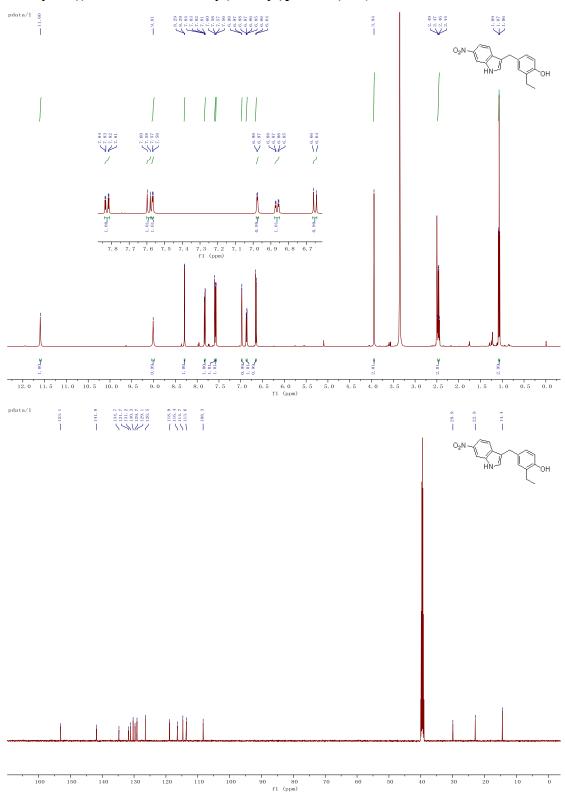
#### 2-allyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ab)



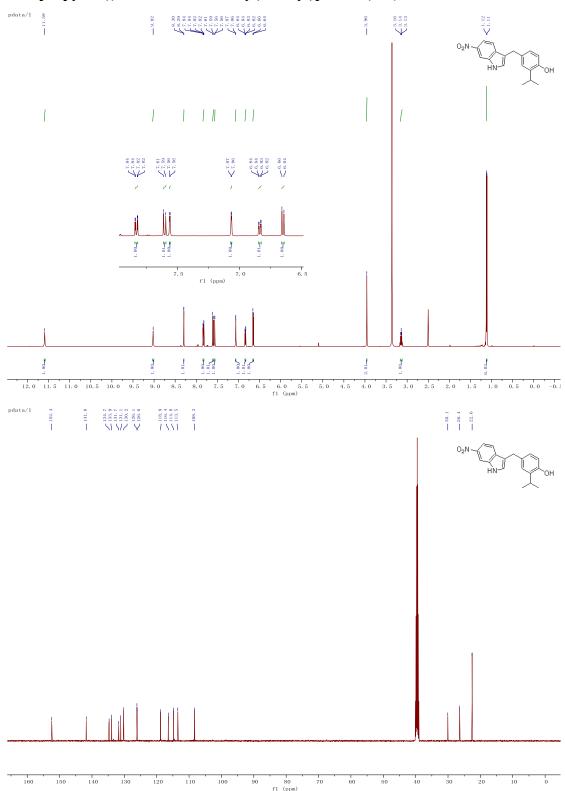
### $5\hbox{-}((6\hbox{-}nitro\hbox{-}1H\hbox{-}indol\hbox{-}3\hbox{-}yl)methyl)\hbox{-}[1,1'\hbox{-}biphenyl]\hbox{-}2\hbox{-}ol\ (6ac)$



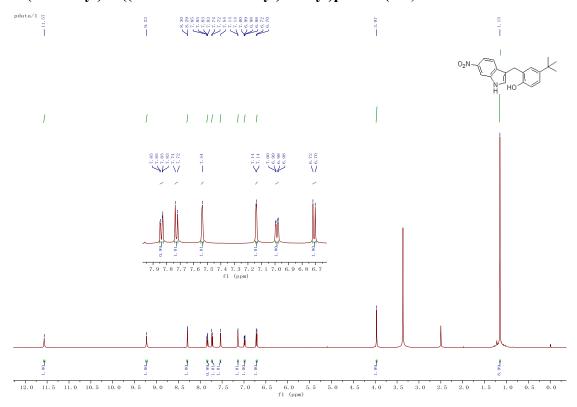
#### 2-ethyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ad)

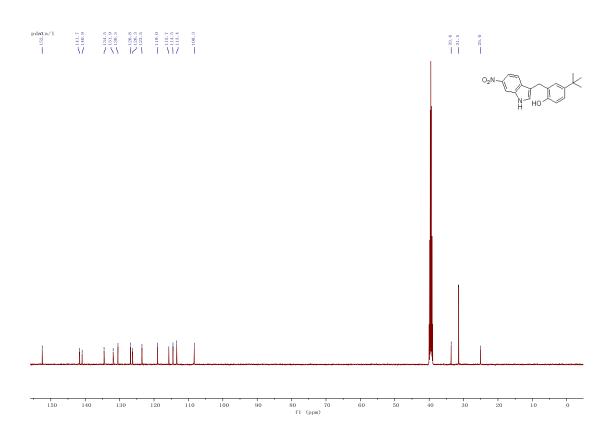


#### 2-isopropyl-4-((6-nitro-1H-indol-3-yl)methyl)phenol (6ae)

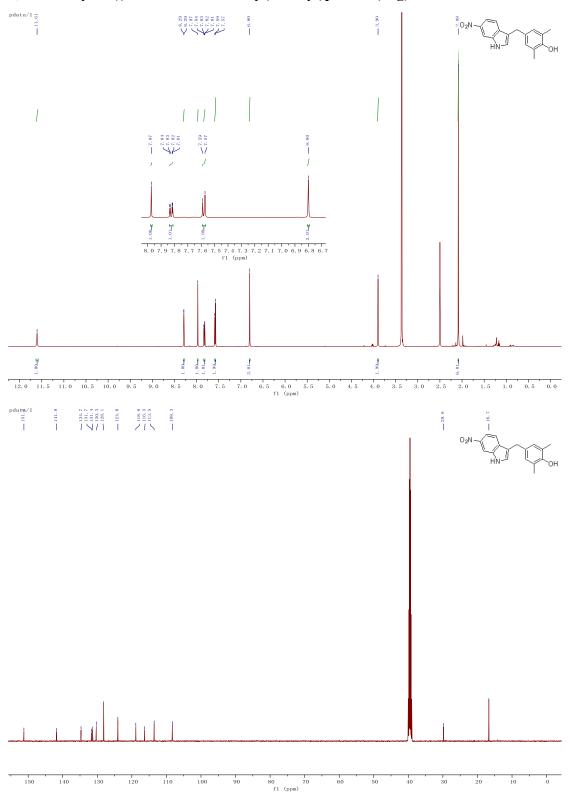


### $\hbox{4-(tert-butyl)-2-((6-nitro-1 H-indol-3-yl)methyl)} phenol~(6af)$

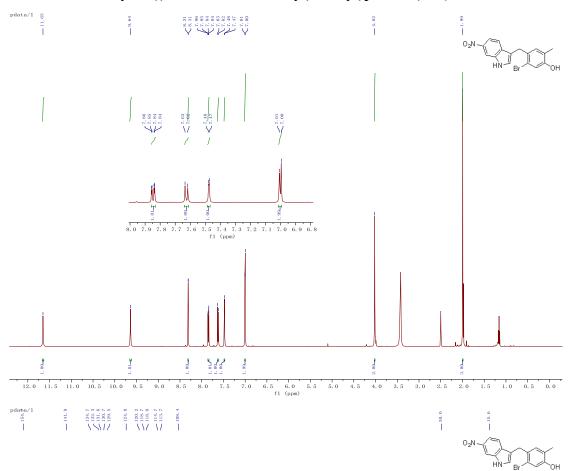


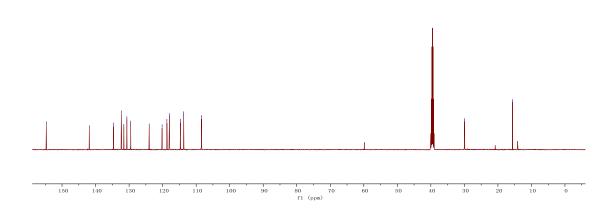


### $2,\!6\text{-}dimethyl-4\text{-}((6\text{-}nitro\text{-}1H\text{-}indol\text{-}3\text{-}yl)methyl)phenol~(6ag)$

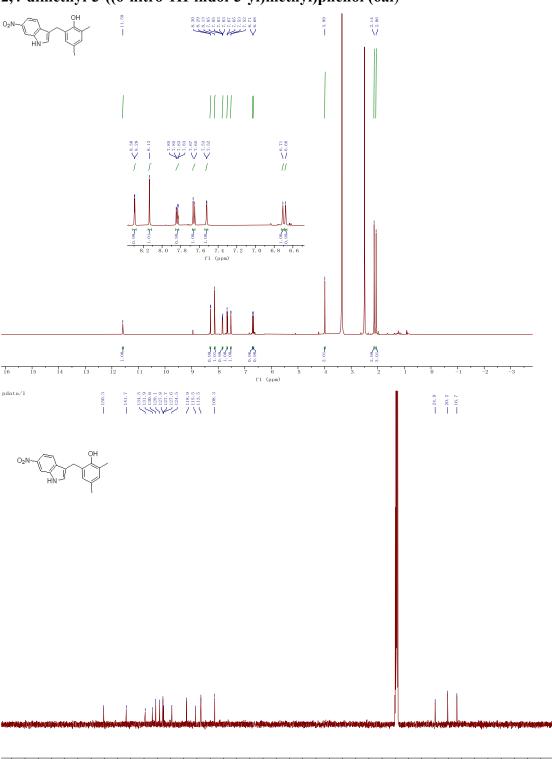


### $5\text{-}bromo\text{-}2\text{-}methyl\text{-}4\text{-}((6\text{-}nitro\text{-}1H\text{-}indol\text{-}3\text{-}yl)methyl)phenol~(6ah)}$

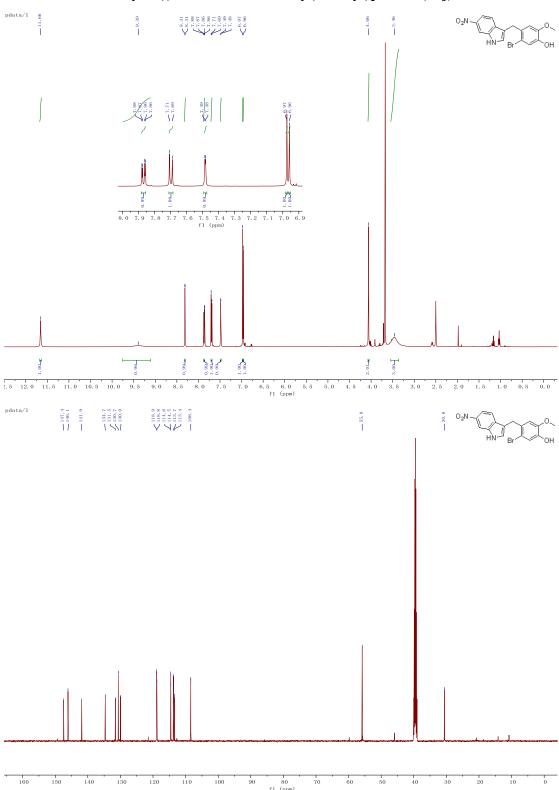




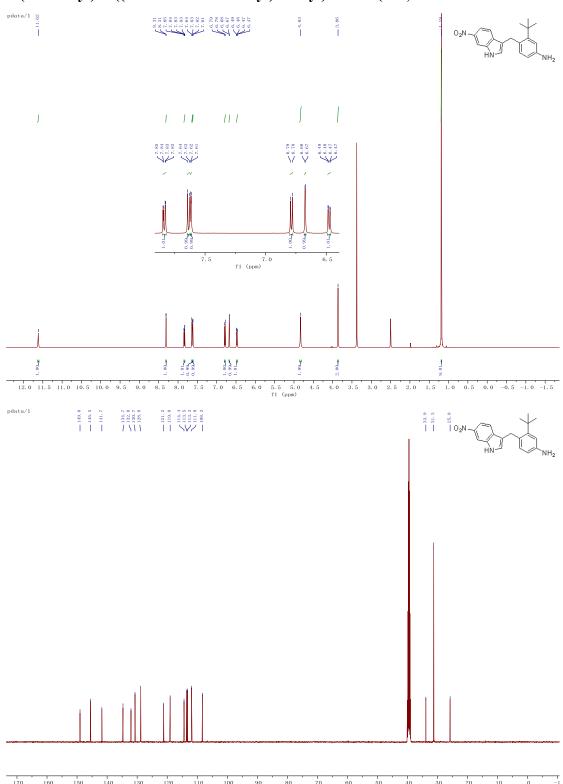
### $2,\!4\text{-}dimethyl-\!3\text{-}((6\text{-}nitro\text{-}1H\text{-}indol\text{-}3\text{-}yl)methyl)phenol~(6ai)$



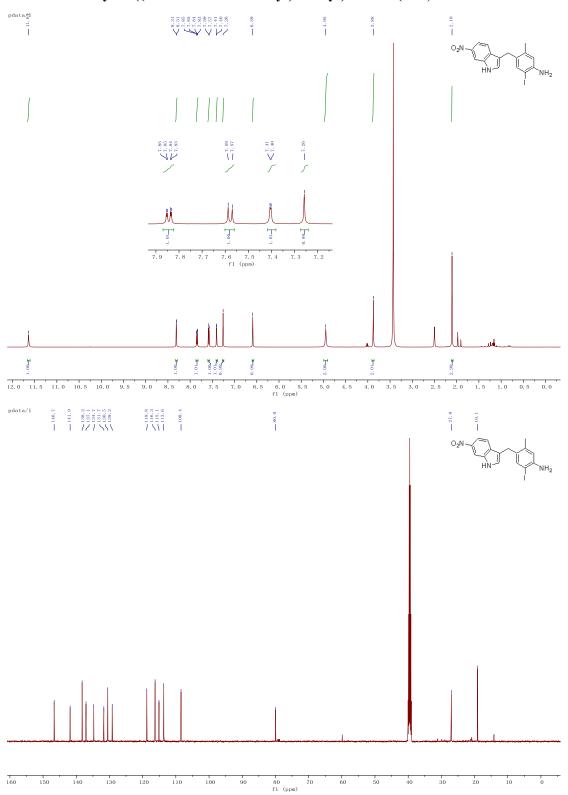
# 5-bromo-2-methoxy-4-((6-nitro-1H-indol-3-yl)methyl)phenol~(6aj)



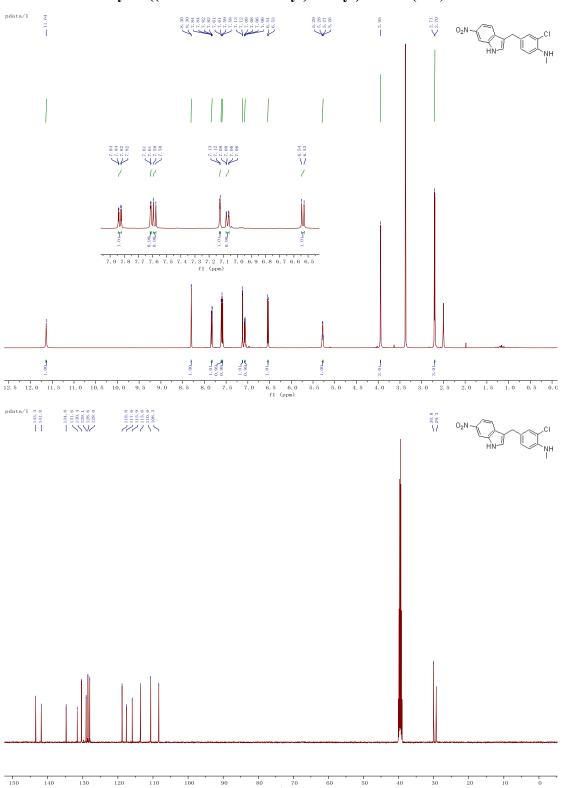
# $3\hbox{-}(tert\hbox{-}butyl)\hbox{-}4\hbox{-}((6\hbox{-}nitro\hbox{-}1H\hbox{-}indol\hbox{-}3\hbox{-}yl)methyl) aniline\ (7aa)$



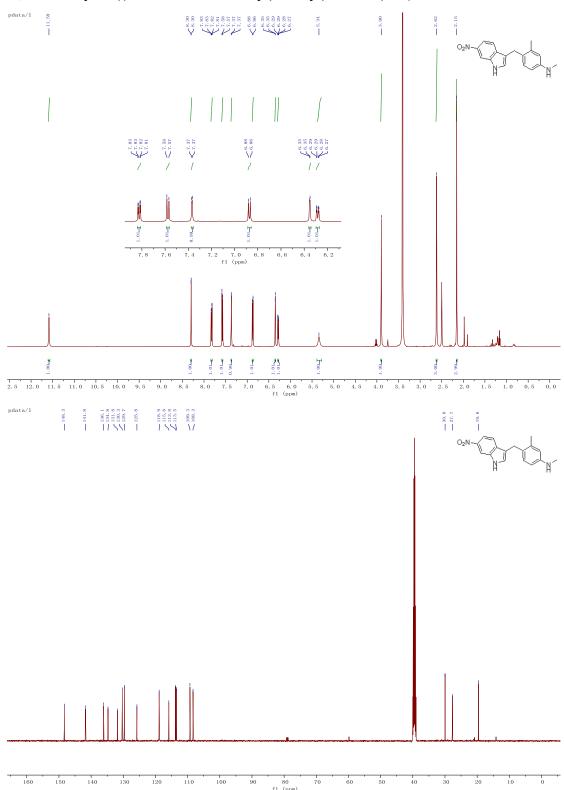
### 2-iodo-5-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ab)



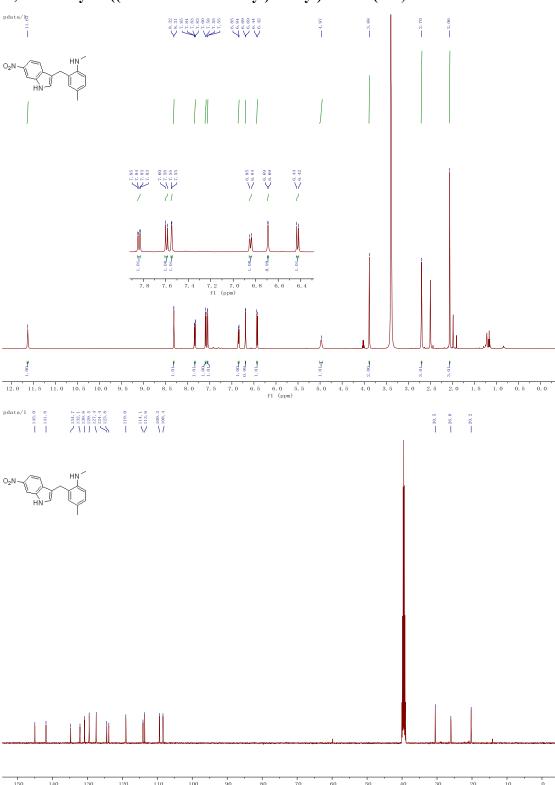
## 2-chloro-N-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ac)



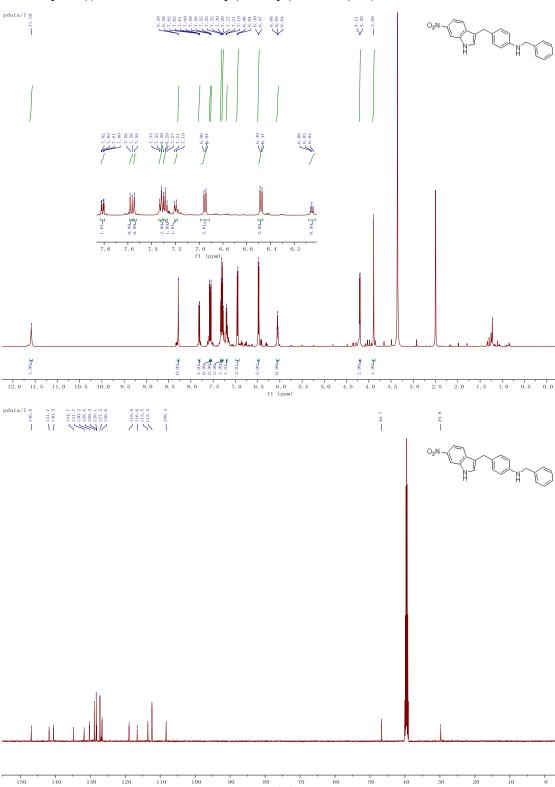
# N,3-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ad)



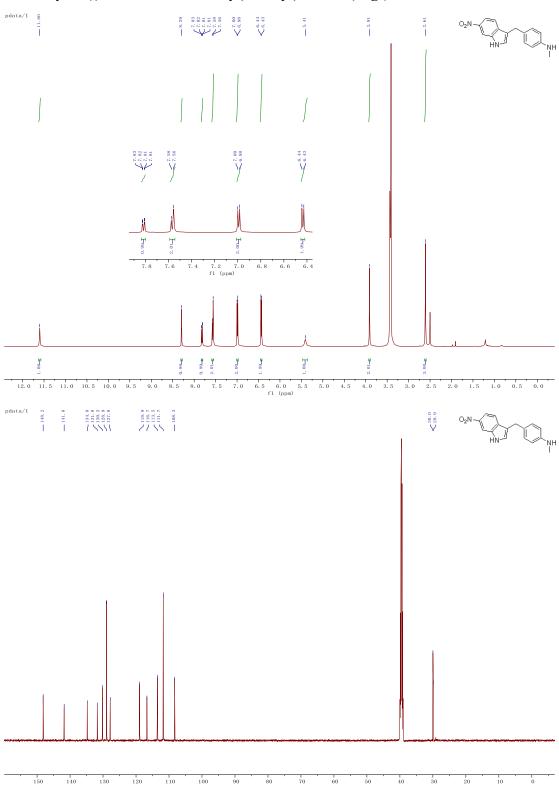
# N,4-dimethyl-3-((6-nitro-1H-indol-3-yl)methyl)aniline (7ae)



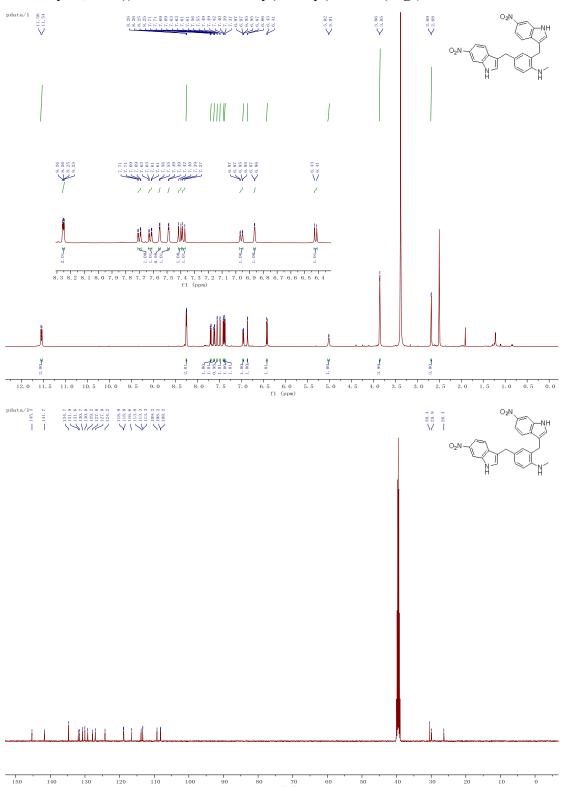
#### N-benzyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7af)



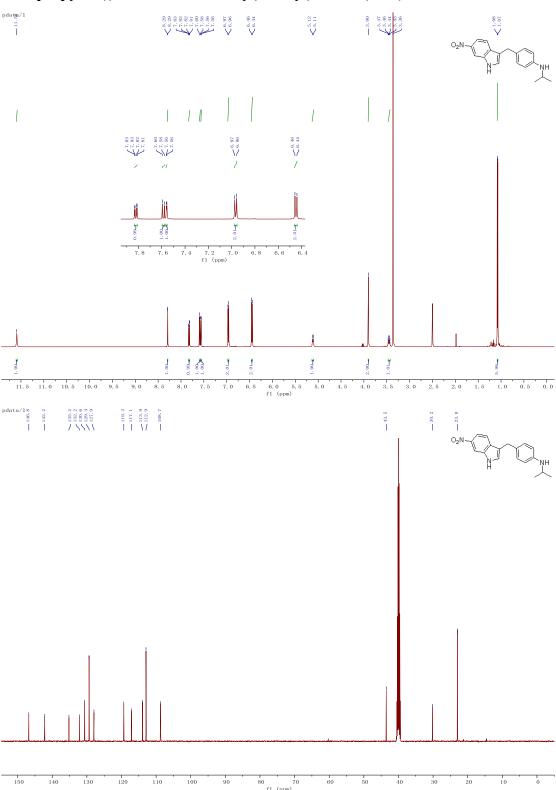
## N-methyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ag1)



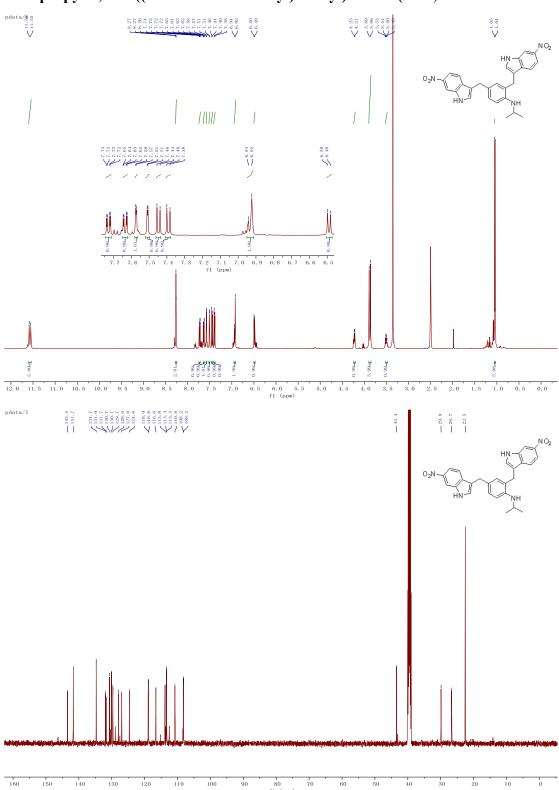
#### *N*-methyl-2,4-bis((6-nitro-1H-indol-3-yl)methyl)aniline (7ag<sub>2</sub>)



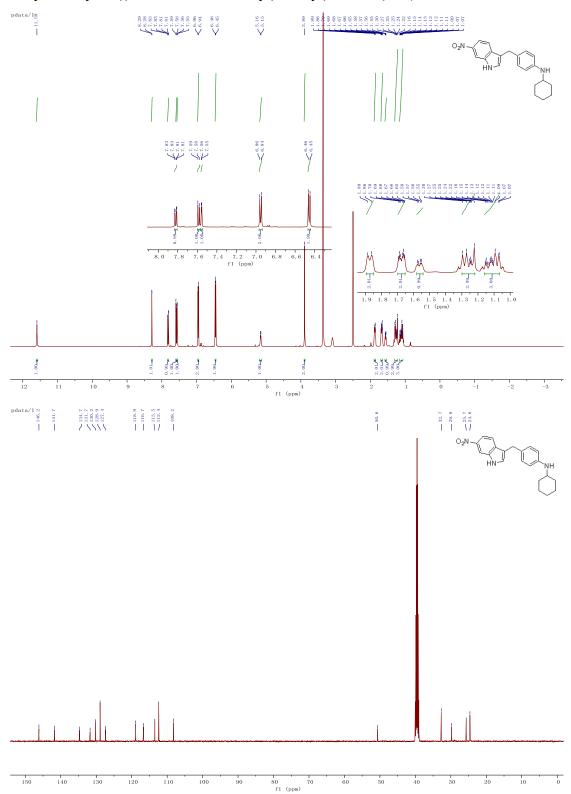
## $N-isopropyl-4-((6-nitro-1H-indol-3-yl)methyl) aniline\ (7ah_1)$



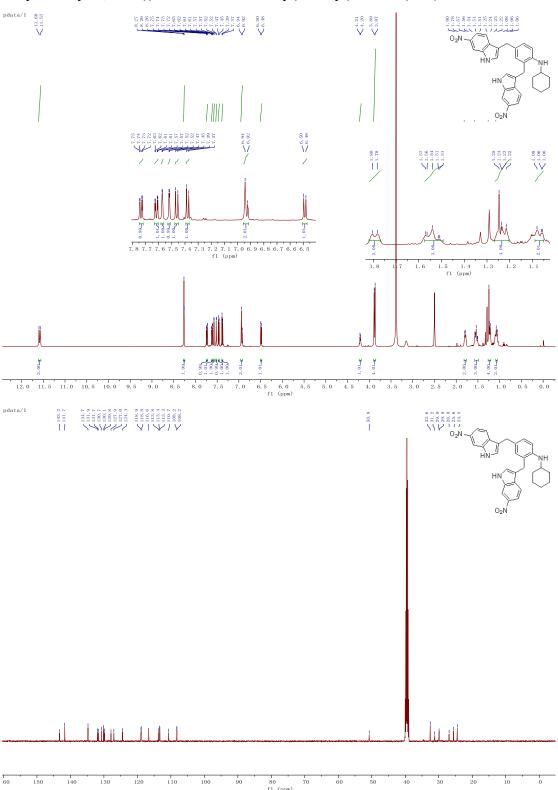
## $N-is opropyl-2, 4-bis ((6-nitro-1H-indol-3-yl)methyl) aniline \ (7ah_2)$



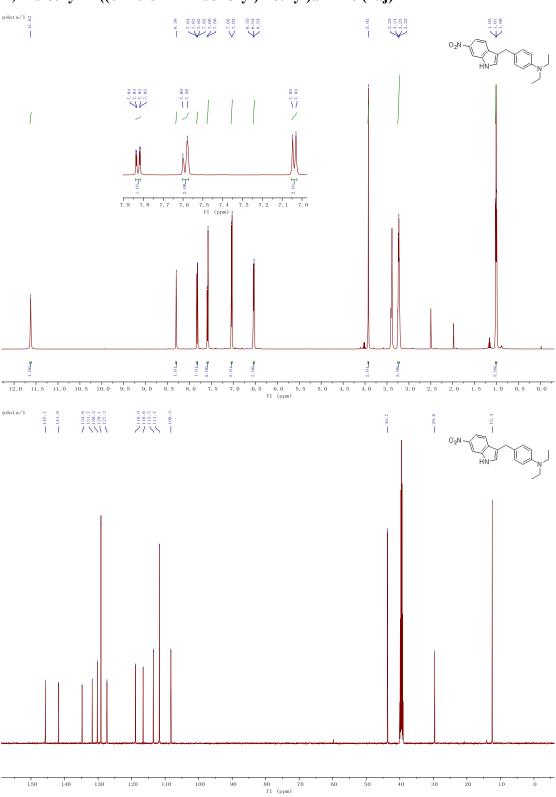
## N-cyclohexyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ai<sub>1</sub>)



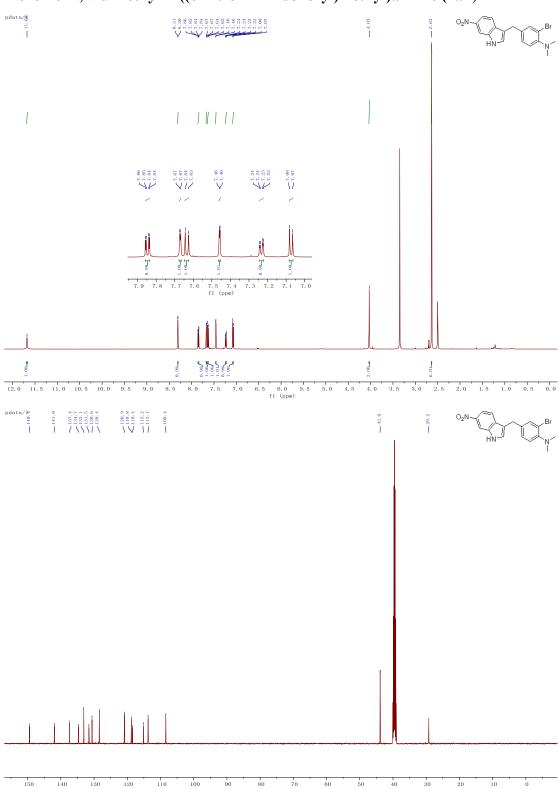
## $N\hbox{-cyclohexyl-2,4-bis} ((6\hbox{-nitro-1H-indol-3-yl}) methyl) aniline~(7\hbox{ai}_2)$



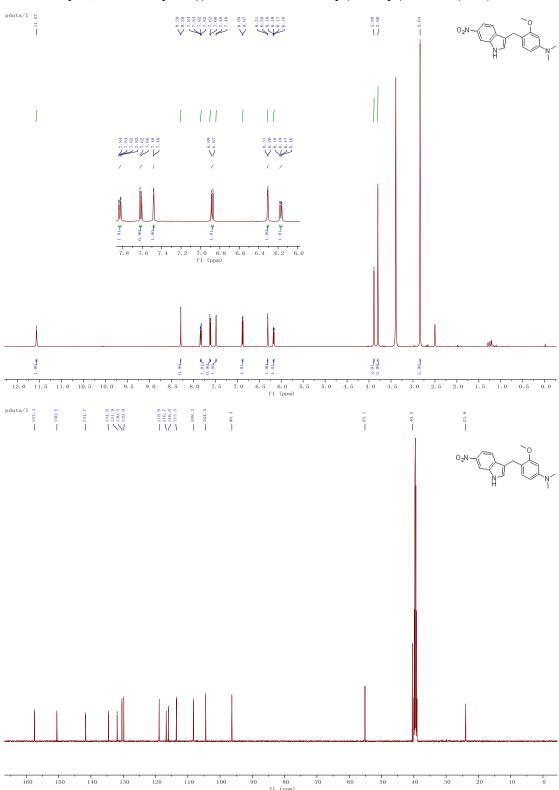
#### N,N-diethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7aj)



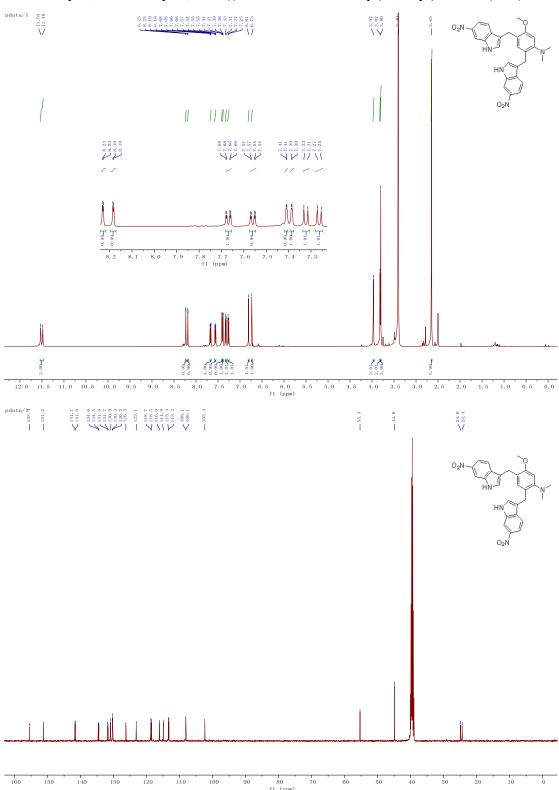
#### $\hbox{$2$-bromo-N,N-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7ak)$}$



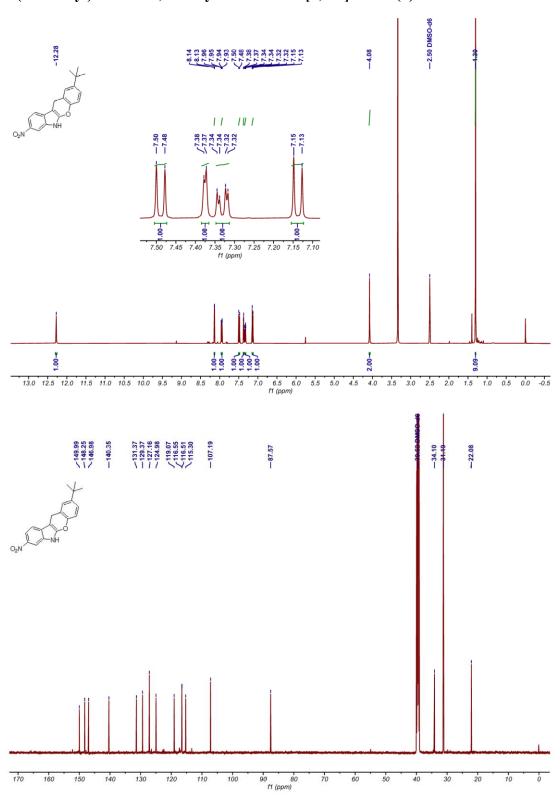
## 3-methoxy-N,N-dimethyl-4-((6-nitro-1H-indol-3-yl)methyl)aniline (7al<sub>1</sub>)



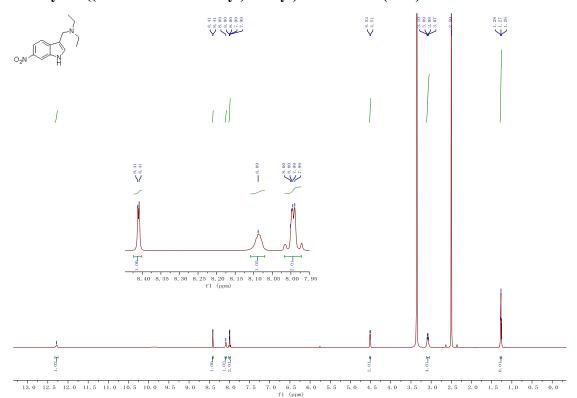
## $5-methoxy-N, N-dimethyl-2, 4-bis ((6-nitro-1H-indol-3-yl)methyl) aniline \ (7al_2)$



#### 2-(tert-butyl)-8-nitro-6,11-dihydrochromeno[2,3-b]indole (8)



#### N-ethyl-N-((6-nitro-1H-indol-3-yl)methyl)ethanamine (int I)



# 3,3'-(phenylmethylene)bis(6-nitro-1H-indole) (9)

