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Supporting Information

Controllable C2 arylation and C3 diazenylation of indoles with arytriazenes under ambient conditions

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I. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial sources (Adamas-beta, Alfa Aesar) and used without further purification.

NMR spectrum

^{1}H and ^{13}C NMR spectra were collected on 400 MHz NMR spectrometers (Varian Inova-400). Chemical shifts for protons were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to residual protium in the NMR solvents ($CDCl_3$ = δ 7.26, DMSO-d_6 = δ 2.50). Chemical shifts for carbon resonances were reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the carbon resonances of the solvents ($CDCl_3$ = δ 77.00, DMSO-d_6 = δ 39.70). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants J were reported in hertz unit (Hz).

Melting point

Melting point (M.P.) were recorded on BÜCHI (M-560).

GC-MS

GC-MS were recorded on SHIMADZU (GCMS-QP2010Plus).

HRMS

High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Scientific Q-Exactive.

Column Chromatography

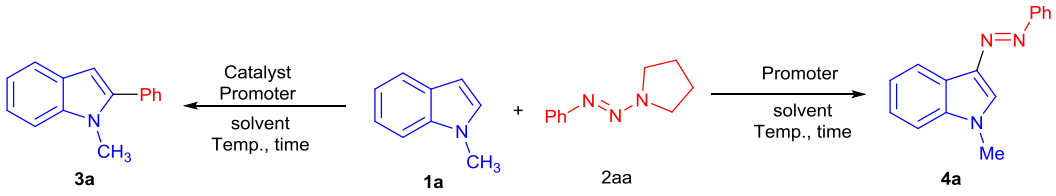
Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F_{254} plates. Column chromatography was undertaken on silica gel (300-400 mesh) using a proper eluent.

UV light

Visualization on TLC was achieved by the use of UV light (254 nm).

II. Optimization of C2 Arylation and C3 Diazenylation of Indole

Table S1. Optimization for HPF_6 activated reaction

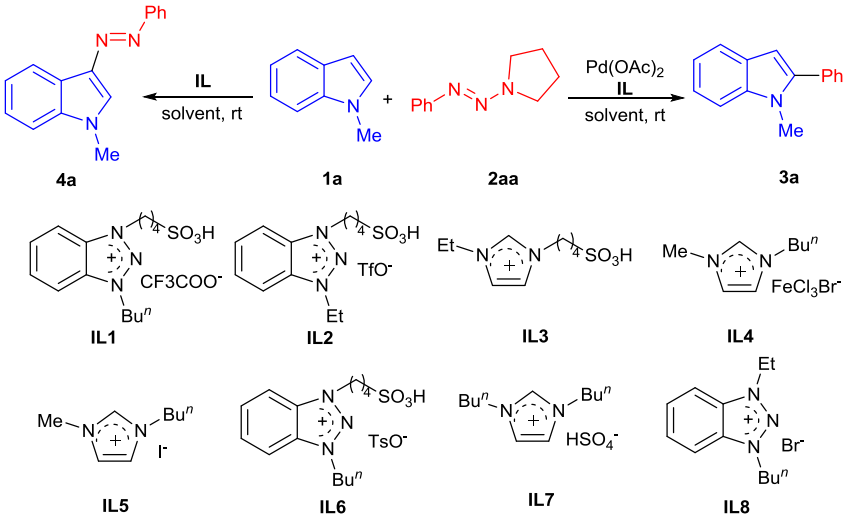


Entry[a]	Catalyst (mol%)	Promoter (equiv.)	Temp. (^oC)	Solvent (mL)	Yield (%)[b]	
					3a	**4a**
1	$Pd(OAc)_2$ (5)	TFA (1.0)	60	DMF (2)	18	33
2	$Pd(OAc)_2$ (5)	TCA (1.0)	60	DMF (2)	13	30
3	$Pd(OAc)_2$ (5)	HCl (1.0)	60	DMF (2)	Trace	11
4	$Pd(OAc)_2$ (5)	AcOH (1.0)	60	DMF (2)	Trace	20
5	$Pd(OAc)_2$ (5)	HBF_4 (1.0)	60	DMF (2)	50	22
6	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	DMF (2)	53	5
7	$PdCl_2$ (5)	HPF_6 (1.0)	60	DMF (2)	13	6
8	$Pd(Ph_3)_4$ (5)	HPF_6 (1.0)	60	DMF (2)	ND	ND
9	$Pd_2(dba)_3$ (5)	HPF_6 (1.0)	60	DMF (2)	15	ND
10	-	HPF_6 (1.0)	60	DMF (2)	ND	37
11	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	EtOH (2)	5	47
12	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	THF (2)	41	26
13	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	DMAC (2)	53	11
14	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	TFE (2)	trace	67
15	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	DCE (2)	ND	15
16	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	CH_3CN (2)	ND	19
17	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	NMP (2)	37	23
18	$Pd(OAc)_2$ (5)	HPF_6 (1.0)	60	H_2O (2)	ND	17
19[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (1.0)	60	DMF (2)	68	4
20[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (1.0)	40	DMF (2)	67	2
21[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (1.0)	rt	DMF (2)	67	Trace

Entry[a]	Catalyst (mol%)	Promoter (equiv.)	Temp. (°C)	Solvent (mL)	Yield (%)[b]	
					3a	**4a**
22[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (1.0)	0	DMF (2)	53	7
23[c,d]	$Pd(OAc)_2$ (2.5)	HPF_6 (1.0)	rt	DMF (2)	48[e]	6
24[c,d]	$Pd(OAc)_2$ (7.5)	HPF_6 (1.0)	rt	DMF (2)	78[e]	ND
25[c,d]	$Pd(OAc)_2$ (10)	HPF_6 (1.0)	rt	DMF (2)	84[e]	ND
26[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (0.8)	rt	DMF (2)	77[e]	ND
27[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (0.6)	rt	DMF (2)	78[e]	ND
28[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (0.4)	rt	DMF (2)	71[e]	ND
29[c,d]	$Pd(OAc)_2$ (5.0)	HPF_6 (0.6)	rt	DMF (1)	82[e]	ND
30[c,d,f]	$Pd(OAc)_2$ (5.0)	HPF_6 (0.6)	rt	DMF (1)	84[e]	ND
31	—	HPF_6 (1.0)	40	TFE (1)	ND	85
32	—	HPF_6 (1.0)	40	THF (1)	ND	39
33	—	HPF_6 (1.0)	40	EtOH (1)	ND	77
34	—	HPF_6 (1.0)	40	H_2O (1)	ND	72
35	—	HPF_6 (1.0)	40	CH_3CN (1)	ND	53
36	—	HPF_6 (1.0)	40	NMP (1)	ND	64
37	—	HPF_6 (1.0)	rt	TFE (1)	ND	83
38[c,d]	—	HPF_6 (1.0)	rt	TFE (1)	ND	93
39[c,d]	—	HPF_6 (1.0)	rt	TFE (1)	ND	93[e]
40[c,d]	—	HPF_6 (1.0)	rt	TFE (2)	ND	95[e]
41[c,d]	—	HPF_6 (0.8)	rt	TFE (2)	ND	95[e]
42[c,d]	—	HPF_6 (0.6)	rt	TFE (2)	ND	94[e]
43[c,d]	—	HPF_6 (0.4)	rt	TFE (2)	ND	83[e]

[a] Reaction conditions: **1a** (0.2 mmol), **2aa** (0.24 mmol), promoter (1 equiv.), solvent (2.0 mL), 12 h. [b] GC yield, benzophenone as internal standard. [c] HPF_6 was added slowly over 30 min. [d] The reaction time is determined by TLC detection. [e] Isolated yield. [f] **1aa** (0.26 mmol). ND = no detection. TFA = Trifluoroacetic acid. TCA = Trichloroacetic acid.

Table S2. Optimization for **IL** activated reaction



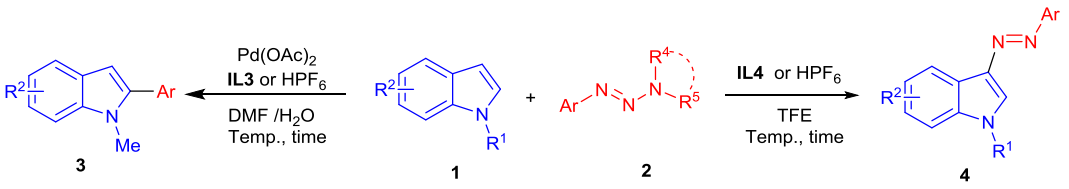
Entry[a]	Catalyst (mol %)	**IL** (equiv.)	Solvent	Yield (%)[b]	
				3a	**4a**
1	$Pd(OAc)_2$ (5.0)	**IL1** (1)	DMF	32	ND
2	$Pd(OAc)_2$ (5.0)	**IL2** (1)	DMF	54	ND
3	$Pd(OAc)_2$ (5.0)	**IL3** (1)	DMF	57	ND
4	$Pd(OAc)_2$ (5.0)	**IL4** (1)	DMF	Trace	ND
5	$Pd(OAc)_2$ (5.0)	**IL5** (1)	DMF	Trace	ND
6	$Pd(OAc)_2$ (5.0)	**IL6** (1)	DMF	50	ND
7	$Pd(OAc)_2$ (5.0)	**IL7** (1)	DMF	27	ND
8	$Pd(OAc)_2$ (5.0)	**IL8** (1)	DMF	Trace	ND
9	$Pd(OAc)_2$ (5.0)	**IL3** (1)	H_2O	ND	ND
10	$Pd(OAc)_2$ (5.0)	**IL3** (1)	THF	37	ND
11	$Pd(OAc)_2$ (5.0)	**IL3** (1)	DCM	40	ND
12	$Pd(OAc)_2$ (5.0)	**IL3** (1)	DMAC	52	ND
13	$Pd(OAc)_2$ (5.0)	**IL3** (0.8)	DMF	62	ND
14	$Pd(OAc)_2$ (5.0)	**IL3** (0.6)	DMF	55	ND
15[c]	$Pd(OAc)_2$ (5.0)	**IL3** (0.8)	DMF/H_2O	83	ND
16[d]	$Pd(OAc)_2$ (5.0)	**IL3** (0.8)	DMF/H_2O	74	ND
17[e]	$Pd(OAc)_2$ (5.0)	**IL3** (0.8)	DMF/H_2O	77	ND

Entry[a]	Catalyst (mol %)	**IL** (equiv.)	Solvent	Yield (%)[b]	
				3a	**4a**
18[c]	$Pd(OAc)_2$ (2.5)	**IL3** (0.8)	DMF/H_2O	70	ND
19[c]	$Pd(OAc)_2$ (7.5)	**IL3** (0.8)	DMF/H_2O	85	ND
20[c]	$Pd(OAc)_2$ (5.0)	**IL3** (0.8)	DMF/H_2O	83[f]	ND
21	-	**IL1** (1)	TFE	ND	41
22	-	**IL2** (1)	TFE	ND	90
23	-	**IL3** (1)	TFE	ND	92
24	-	**IL4** (1)	TFE	ND	96
25	-	**IL5** (1)	TFE	ND	Trace
26	-	**IL6** (1)	TFE	ND	65
27	-	**IL7** (1)	TFE	ND	48
28	-	**IL8** (1)	TFE	ND	Trace
29	-	**IL4** (1)	H_2O	ND	58
30	-	**IL4** (1)	EtOH	ND	88
31	-	**IL4** (1)	CH_3CN	ND	6
32	-	**IL4** (0.8)	TFE	ND	96
33	-	**IL4** (0.6)	TFE	ND	95
34	-	**IL4** (0.4)	TFE	ND	87
35	-	**IL4** (0.6)	TFE	ND	95[f]

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), $Pd(OAc)_2$ (5.0 mol %), **IL**, Solvent (2 mL). [b] GC yield, benzophenone as internal standard, the reaction time is determined by TLC detection. [c] DMF : H_2O (1 : 1). [d] DMF : H_2O (2 : 1). [e] DMF : H_2O (1 : 2). [f] Isolated yields. ND = No detection. DMAC = Dimethylacetamide

III. The Synthetic Procedure for selective C2 Arylation and C3 Diazenylation of 1-substituted indole.

Schem S1. Selective C2 Arylation and C3 Diazenylation of 1-substituted indole



Synthesis of 3a-3d, 3f-3i, 3k-3o. A tube was charged with 1-substituted indole (0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 5.0 mol%), aryltriazene (0.26 mmol) and DMF (1 mL). HPF_6 (60 wt.% solution in water, 18 μL, 0.12 mmol) in DMF was introduced over 30 min to the mixture at 0°C, then the reaction mixture stirred at room temperature for 4 h [or **IL3** (46 mg / 0.16 mmol) in 1 mL of H_2O was dropped slowly to the mixture, then stirred at room temperature for 5 h]. When the reaction completed, 5 mL of water was added to the mixture, the aqueous mixture was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash column chromatography (petroleum ether / ethyl acetate 100:1-50:1) to afford the desired product.

Synthesis of 3e, 3j and 3q activated by IL3. A tube was charged with 1-methyl indole (0.2 mmol), Pd $(OAc)_2$ (2.2 mg, 5 mol%), aryltriazene (0.24 mmol) and DMF (1 mL). **IL3** (46 mg, 0.16 mmol) in 1 mL of water was dropped slowly to the mixture. The reaction mixture was stirred at 60 °C for 5 h, then cooled it to room temperature when the reaction completed. 5 mL of water was added to the mixture, the aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash column chromatography (petroleum ether / ethyl acetate 100:1-10:1) to afford the desired product.

Synthesis of 3j, 3p and 3q activated by HPF_6. A tube was charged with 1-methyl indole (0.2 mmol), Pd $(OAc)_2$ (2.2 mg, 5.0 mol%), aryltriazene (0.26 mmol) and DMF (1 mL). HPF_6 (60 wt.% solution in water, 18 μL, 0.12 mmol) in DMF was introduced over 30 min to the mixture at 0 °C. The mixture stirred at 60 °C for 10 h, then cooled it to room temperature when the reaction completed. 5 mL of water was added to the

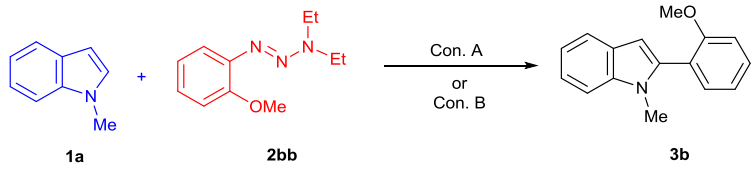
mixture, the aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash column chromatography (petroleum ether / ethyl acetate 100:1:1-10:1) to afford the desired product.

Synthesis of 4a-4q activated by HPF_6. A tube was charged with 1-substituted indole (0.2 mmol), aryltriazene (0.24 mmol) and CF_3CH_2OH (2 mL). HPF_6 (60 wt.% solution in water, 18 μL, 0.12 mmol) in CF_3CH_2OH was introduced over 30 min to the mixture at 0 ^oC. The mixture was stirred at room temperature until the reaction completion (about 1-4h). 5 mL of water was added to the mixture, the aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 50:1-15:1) to afford the desired product.

Synthesis of 4a- 4q activated by IL4. A tube was charged with indole (0.2 mmol), aryltriazene (0.24 mmol) and CF_3CH_2OH (1 mL). **IL4** (46 mg, 0.12 mmol) in CF_3CH_2OH was dropped slowly to the mixture at 0 ^oC. Then the reaction stirred at room temperature for 2 h. When the reaction completed, 5 mL of water was added to the mixture, the aqueous layer was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 50:1-15:1) to afford the desired product.

IV. Gram-Scale experiments and Late-Stage Modification of Drugs

Scheme S2. Gram-Scale experiments for C2-arylation of 1-methylindole

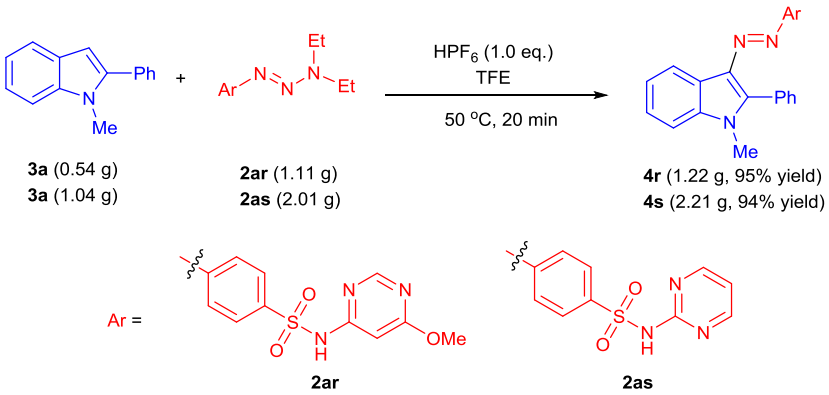


1a **2bb** **3b**

Con. A: A 100 mL round-bottomed flask was charged with 1-methylindole (5 mmol, 0.65 g), Pd $(OAc)_2$ (0.25 mmol, 56 mg), (*E*)-3,3-diethyl-1-(2-methoxyphenyltriaz)-1-ene (5.5 mmol, 1.14 g) and DMF (20 mL), stirring until complete dissolution. An aqueous solution of **IL3** (4 mmol of IL3 was dissolved with 20 mL of H_2O) was introduced slowly to the above mixture at 0 ^oC. The reaction stirred at room temperature for 12 h. The reaction mixture was diluted with water (30 mL), and the aqueous solution was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (petroleum ether / ethyl acetate 100:1-20:1) to afford the product **3b** (colorless oil, 0.88 g, 74% yield).

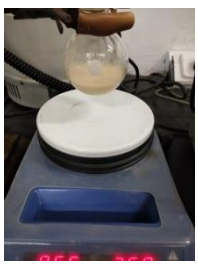
Con. B: A 100 mL round-bottomed flask was charged with 1-methylindole (5 mmol, 0.65 g), Pd $(OAc)_2$ (0.25 mmol, 56 mg) and (*E*)-3,3-diethyl-1-(2-methoxyphenyl)triaz-1-ene (6.5 mmol, 1.33 g) and DMF (30 mL). A solution of HPF_6 (60 wt.% solution in water, 0.73 mL, 5 mmol) in DMF(30 mL) was dropped slowly over 30 min to the reaction mixture at 0 ^oC. After that, the resulting mixture was then stirred at 60 ^oC for 1 h. The reaction mixture cooled to room temperature and diluted with water (30 mL), the aqueous solution was extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether / ethyl acetate 100:1-20:1) to afford the desired product **3b** (colorless oil, 0.96 g, 81% yield).

Scheme S3. Gram-scale and late-stage modification of drugs



Gram-scale synthesis of 4r. A round-bottomed flask was charged with 1-methyl-2-phenylindole (0.53 g, 2.6 mmol), (*E*)-*N*-(6-methoxypyrimidin-4-yl)-4-(pyrrolidin-1-yldiazenyl)benzenesulfonamide (1.11 g, 3.1 mmol) and TFE (20 mL). HPF_6 (60 wt.% solution in water, 0.377 mL, 2.6 mmol) in 30 mL of CF_3CH_2OH was dropped slowly over 30 min to the mixture at 0°C. The mixture was then reacted at 50 °C for 20 min. The reaction mixture cooled to room temperature and 100 mL of water was added, the generated precipitation was filtered and recrystallized with ethanol to afford the 4r (1.22 g, 95% yield).

Gram-scale synthesis of 4s. A round-bottomed flask was charged with 1-methyl-2-phenylindole (1.04 g, 5 mmol), (*E*)-*N*-(pyrimidin-2-yl)-4-(pyrrolidin-1-yldiazenyl)benzenesulfonamide (2.01 g, 6 mmol) and solvent (30 mL). HPF_6 (60 wt.% solution in water, 0.725 mL, 5 mmol) in 30 mL of CF_3CH_2OH was dropped slowly over 30 min to the mixture at 0°C. The mixture was then reacted at 50 °C for 20 min. The reaction mixture cooled to room temperature and 100 mL water was added, the generated precipitation was filtered and recrystallized with ethanol to afford the 4s (2.21 g, 94% yield).



Starting materials in solvent

HPF_6 was added by dropwise

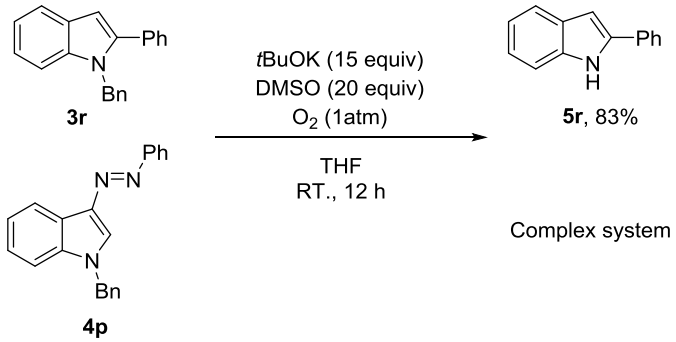
Continuous addition of HPF_6

Complete addition of HPF_6

The reaction mixture at 10 min | Upon completion of the reaction | Water was added to the mixture | The isolated product **4r**

Figure S1. The reaction process diagram for gram-scale and late-stage modification of drugs

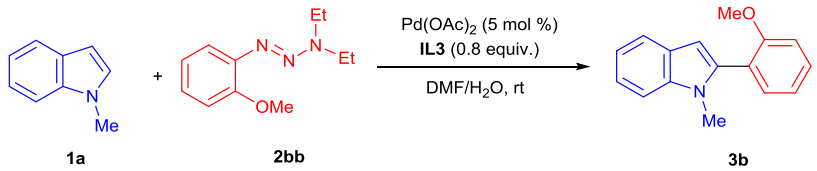
V. N-debenzylation of N-benzylated products [10]



Synthesis of **5r**: A flame-dried flask was added compound **3r** (0.3 mmol) and DMSO (6 mmol), the mixture stirred at room temperature until the clear solution. KO*t*Bu (4.5 mmol, 1 M soln in THF) was then added dropwise. After that, oxygen was bubbled into the solution through a gas dispersor for 10 min. Upon completion (determined by TLC) the reaction was quenched with saturated ammonium chloride. The product was extracted with EtOAc (3× 10mL). The organic layer were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (V_{DCM} / V_{MeOH} = 15:1-10:1).

VI. ILs Recycling Experiment

Scheme S4. **IL3** recycling experiment for C2 arylation of 1-methylindole



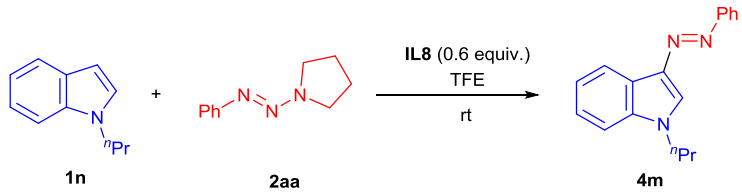
A tube was charged with 1-methylindole (25.6 μL, 0.2 mmol), Pd $(OAc)_2$ (2.2 mg, 5 mol %), (*E*)-3,3-diethyl-1-(*o*-tolyl)triaz-1-ene (42 mg, 0.22 mmol) and DMF (1 mL). **IL3** (46 mg, 0.16 mmol) dissolved in water (1 mL) and introduced slowly to the reaction mixture at 0^oC. The reaction was monitored by TLC plate and quenched it

upon disappearance of the starting material. For each cycle, water (10 mL) and ethyl acetate (10 mL) were added, the organic phase was extracted with water (3×10 mL). The aqueous phase were combined, concentrated, and **IL3** was recovered and recycled for the next reaction after drying it in vacuo at 90 °C. For the first run, the reaction conditions remain the same. In the subsequent two cycles, another 2 mol % of **IL3** was needed, and the reaction time also expended from 1.5h to 7h and 12h. In the fourth cycle, the desired product was obtained after adding another 5 mol % of **IL3** and expending the time to 12 h. The corresponding results were listed in Table S3.

Table S3. The results of **IL3** recycling experiments for C2-arylation of 1-methylindole

Run	1	2	3	4
Yield (%)	96	87	70	55

Scheme S5. **IL4** recycling experiment for C3 diazenylation of 1-propylindole

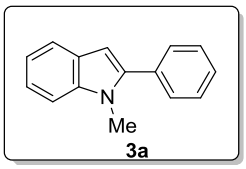


A tube was charged with 1-propylindole (31.8 mg, 0.2 mmol), (*E*)-1-(phenyldiazenyl)pyrrolidine (38.5 mg, 0.22 mmol) and CF_3CH_2OH (1 mL). **IL4** (46 mg, 0.12 mmol) dissolved in water (1 mL) and introduced slowly to the reaction mixture at 0°C. The reaction was monitored by TLC plate and quenched it upon disappearance of the starting material (Scheme S5). For each cycle, water (10 mL) and ethyl acetate (10 mL) were added, the organic phase was extracted with water (3×10 mL). The aqueous phase were combined,, concentrated, and **IL4** was recovered and recycled for the next reaction after drying it in vacuo at 90 °C. For the first run, the reaction conditions remain the same. In the subsequent two cycles, the reaction time expended from 2 h to 4 h and 7 h. In the fourth cycle, the desired product was obtained after adding another 2 mol % of **IL4** and expending the time to 12 h. The corresponding results were listed in Table S5.

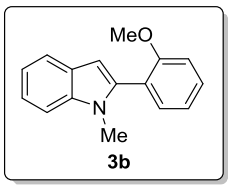
Table S4. The results of **IL4** recycling experiment for C3 diazenylation of 1-propylindole

Run	1	2	3	4
Yield (%)	98	95	90	83

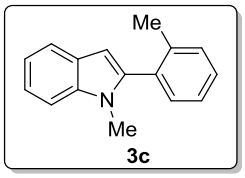
VII. The data for C2 Arylation and C3 Diazenylation of 1-substituted indole



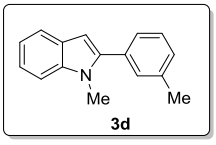
1-methyl-2-phenyl-1*H*-indole **3a**[1]: Colorless crystals, mp 91.0-92.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.78 (s, 3 H), 6.59 (d, *J* = 0.8 Hz, 1 H), 7.15-7.19 (m, 1 H), 7.26-7.30 (m, 1 H), 7.38-7.45 (m, 2 H), 7.48-7.52 (m, 2 H), 7.53-7.56 (m. 2 H), 7.66 (d, *J* = 8, 1H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.17, 101.61, 109.58, 119.83, 120.44, 121.63, 127.83, 127.91, 128.47, 129.35, 132.81, 138.30, 141.54 ppm. MS m/z: 207.



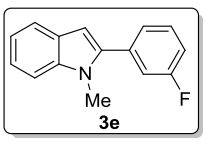
2-(2-methoxyphenyl)-1-methyl-1*H*-indole **3b**[3]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.50 (s, 3 H), 3.72 (s, 3 H), 6.41 (s, 1 H), 6.92 (d, *J* = 8 Hz, 1 H), 6.95-6.99 (m, 1 H), 7.02-7.06 (m, 1 H), 7.13-7.17 (m, 1 H), 7.26-7.30 (m, 2 H), 7.32-7.36 (m, 1 H), 7.54-7.57 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 30.69, 55.42, 101.68, 109.30, 110.82, 119.34, 120.40, 120.63, 121.22, 127.91, 130.03, 132.51, 137.58, 138.52, 154.46 ppm. MS m/z: 237.



1-methyl-2-(*o*-tolyl)-1*H*-indole **3c**[2]: Colorless solid, mp 88.7-90.8 °C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.26 (s, 3 H), 3.56 (s, 3 H), 6.50 (d, *J* = 0.8 Hz, 1 H), 7.19-7.23 (m, 1 H), 7.26-7.42 (m, 6 H), 7.69-7.71 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 20.22, 30.49, 101.66, 109.57, 119.81, 120.54, 121.43, 125.71, 128.15, 128.81, 130.22, 131.29, 132.69, 137.44, 138.22, 140.66 ppm. MS m/z: 221.

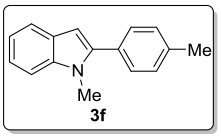


1-methyl-2-(m-tolyl)-1*H*-indole **3d**[7]: Colorless solid, mp 45.4-46.8 °C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.43 (s, 3 H), 3.74 (s, 3 H), 6.55 (d, *J* = 0.8 Hz, 1 H), 7.12-7.16 (m, 1 H), 7.20-7.26 (m, 2 H), 7.29-7.37 (m, 4 H), 7.62-7.64 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 21.51, 31.16, 101.48, 109.55, 119.76, 120.39, 121.53, 126.42, 127.92, 128.32, 128.61, 130.06, 132.71, 138.15, 138.26, 141.70 ppm. MS m/z: 221.

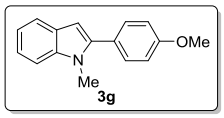


2-(3-fluorophenyl)-1-methyl-1*H*-indole **3e**[9]: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.78 (s, 3 H), 6.62 (s, 1 H), 7.07-7.25 (m, 3 H), 7.28-7.34 (m, 2 H), 7.37-7.49 (m, 2 H), 7.68 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.20, 102.23, 109.67, 114.69 (J_{C-F} = 21

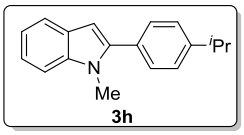
Hz), 116.12 ($J_{C\text{-}F}$ = 22 Hz), 120.02, 120.63, 122.04, 124.95, 127.76, 128.73, 130.02 ($J_{C\text{-}F}$ = 8.5 Hz), 134.90 ($J_{C\text{-}F}$ = 8.3 Hz), 138.48, 140.10 ($J_{C\text{-}F}$ = 2.1 Hz), 162.66 ($J_{C\text{-}F}$ = 245 Hz) ppm. MS m/z: 225.



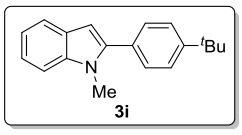
1-methyl-2-(p-tolyl)-1*H*-indole **3f**[1]: Colorless solid, mp 87.7-89.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.42 (s, 3 H), 3.73 (s, 3 H), 6.53 (s, 1 H), 7.11-7.15 (m, 1 H), 7.21-7.28 (m, 3 H), 7.34-7.41 (m, 3 H), 7.61-7.63 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 21.27, 31.11, 101.25, 109.52, 119.75, 120.32, 121.45, 127.93, 129.17, 129.24, 129.87, 137.73, 138.20, 141.61 ppm. MS m/z: 221.



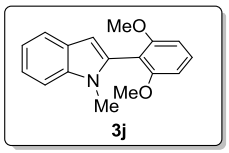
2-(4-methoxyphenyl)-1-methyl-1*H*-indole **3g**[3]: Colorless solid, mp 117.8-118.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.75 (s, 3 H), 3.90 (s, 3 H), 6.54 (s, 1 H), 7.02-7.05 (m, 2 H), 7.15-7.19 (m, 1 H), 7.25-7.29 (m, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.45-7.49 (m, 2 H), 7.65-7.67 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.01, 55.33, 101.02, 109.48, 113.96, 119.75, 120.25, 121.36, 125.28, 128.02, 130.59, 138.15, 141.40, 159.45 ppm. MS m/z: 237.



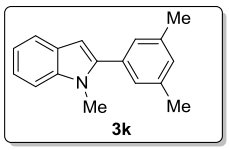
2-(4-isopropylphenyl)-1-methyl-1*H*-indole **3h**[5]: Colorless solid, mp 135.3-135.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.30 (s, 3 H), 1.32 (s, 3 H), 2.94-3.01 (m, 1 H), 3.74 (s, 3 H), 6.54 (s, 1 H), 7.11-7.15 (m, 1 H), 7.21-7.25 (m, 1 H), 7.31-7.36 (m, 3 H), 7.42-7.45 (m, 2 H), 7.63 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 23.96, 31.14, 33.93, 101.31, 109.52, 119.75, 120.34, 121.45, 126.55, 127.99, 129.31, 130.25, 138.25, 141.68, 148.62 ppm. MS m/z: 249.



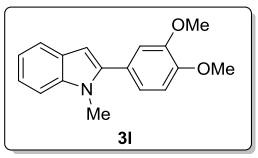
2-(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indole **3i**[1]: Yellowish solid, mp 108.4-109.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.38 (s, 9 H), 3.75 (s, 3 H), 6.54 (s, 1 H), 7.11-7.15 (m, 1 H), 7.21-7.25 (m, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.43-7.50 (m, 4 H), 7.63 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.18, 31.33, 34.67, 101.30, 109.52, 119.74, 120.33, 121.44, 125.41, 127.95, 129.02, 129.85, 138.22, 141.59, 150.85 ppm. MS m/z: 263.



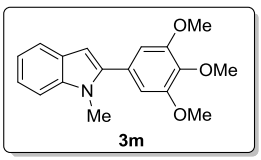
2-(2,6-dimethoxyphenyl)-1-methyl-1*H*-indole **3j**[6]: White solid, mp 154.7-156.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.54 (s, 3 H), 3.77 (s, 6 H), 6.51 (d, *J* = 0.8 Hz, 1 H), 6.84 (s, 1 H), 6.70 (s, 1 H), 7.10-7.14 (m, 1 H), 7.20-7.26 (m, 1 H), 7.36-7.42 (m, 2 H), 7.65-7.67(m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 30.17, 55.84, 102.28, 103.85, 109.23, 110.16, 118.94, 120.43, 120.64, 127.99, 130.29, 133.01, 137.16, 159.22 ppm. MS m/z: 267.



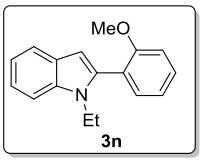
2-(3,5-dimethylphenyl)-1-methyl-1*H*-indole **3k**[1]: Yellowish liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.40 (s, 6 H), 3.77 (s, 3 H), 6.55 (s, 1 H), 7.07 (s, 1 H), 7.14-7.18 (m, 3 H), 7.24-7.28 (m, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 21.38, 31.17, 101.39, 109.52, 119.71, 120.36, 121.45, 127.17, 127.96, 129.53, 132.68, 138.00, 138.25, 141.86. MS m/z: 235.



2-(3,4-dimethoxyphenyl)-1-methyl-1*H*-indole **3l**[8]: Light yellow, mp 86.4-88.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.74 (s, 3H), 3.93 (s, 3 H), 3.95 (s, 3 H), 6.52 (s, 1 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 7.02-7.07 (m, 2 H), 7.12-7.16 (m, 1 H), 7.22-7.24 (m, 1 H), 7.34-7.37 (m, 1 H), 7.61-7.63 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.10, 55.99, 101.10, 109.51, 111.10, 112.76, 119.83, 120.28, 121.49, 121.93, 125.53, 127.93, 138.14, 141.49, 148.85, 148.99 ppm. MS m/z: 267.

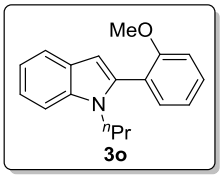


1-methyl-2-(3,4,5-trimethoxyphenyl)-1*H*-indole **3m**[4]: White solid, mp 101.4-102.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.76 (s, 3H), 3.90 (s, 6H), 3.92 (s, 3H), 6.54 (s, 1H), 6.70 (s, 2H), 7.12-7.16 (m, 1H), 7.23-7.27 (m, 1H), 7.36 (d, *J* = 8 Hz 1H), 7.63 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.18, 56.18, 60.95, 101.36, 106.62, 109.55, 119.91, 120.37, 121.70, 127.76, 128.30, 137.89, 138.18, 141.48, 153.12. MS m/z: 297.

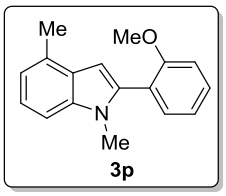


1-ethyl-2-(2-methoxyphenyl)-1*H*-indole **3n**: Colorless solid, mp 75.8-77.0 °C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.21 (t, 3 H), 3.77 (s, 3 H), 4.01 (q, 2 H), 6.44 (s, 1 H), 6.97-7.12 (m, 3 H), 7.18-7.22 (m, 1 H), 7.32-7.41 (m, 3 H), 7.62 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 15.01, 38.85, 55.41, 102.07, 109.65, 110.86, 119.24, 120.54, 120.57,

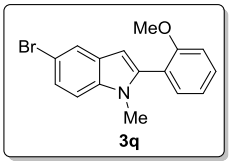
121.08, 122.26, 128.38, 130.03, 132.63, 136.38, 137.69, 157.53 ppm. HRMS (ESI) calcd. for $C_{17}H_{18}NO$ ($[M+H]^+$): 252.13829, found: 252.13797.



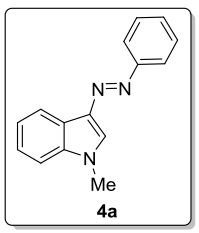
2-(2-methoxyphenyl)-1-propyl-1*H*-indole **3o**: Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 0.73 (t, 3 H), 1.63-1.72 (m, 2 H), 3.80 (s, 3 H), 3.96 (t, 2 H), 6.47 (s, 1 H), 7.00-7.14 (m, 3 H), 7.20-7.26 (m, 1 H), 7.36-7.46 (m, 3 H), 7.65 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 11.37, 23.00, 45.80, 55.44, 102.01, 109.84, 110.88, 119.20, 120.50, 120.57, 121.01, 122.42, 128.27, 129.97, 132.73, 136.77, 138.10, 157.43 ppm. HRMS (ESI) calcd. for $C_{18}H_{20}NO$ ($[M+H]^+$): 266.15394, found: 266.15366.



2-(2-methoxyphenyl)-1,4-dimethyl-1*H*-indole **3p:** Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.56 (s, 3 H), 3.57 (s, 3 H), 3.80 (s, 3 H), 6.50 (s, 1 H), 6.92 (d, *J* = 6.8 Hz, 1 H), 7.00-7.07 (m, 2 H), 7.11-7.20 (m, 2 H), 7.37-7.42 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 18.68, 30.84, 55.45, 100.26, 106.94, 110.82, 119.59, 120.66, 121.45, 122.18, 127.81, 129.92, 129.98, 132.56, 137.36, 137.93, 157.52 ppm. HRMS (ESI) calcd. for $C_{17}H_{18}NO$ ($[M+H]^+$): 252.13829, found: 252.13794.

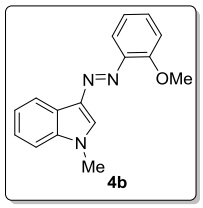


5-bromo-2-(2-methoxyphenyl)-1-methyl-1*H*-indole **3q**: White solid, mp 75.4-77.2 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.56 (s, 3 H), 3.82 (s, 3 H), 6.43 (s, 1 H), 7.01-7.08 (m, 2 H), 7.20-7.26 (m, 1 H), 7.30 (q, *J* = 8.8 Hz, 1 H), 7.35 (d, *J* = 7.4 Hz, 1 H), 7.42-7.48 (m, 1 H), 7.75 (d, *J* = 2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 30.85, 55.48, 101.26, 110.76, 110.93, 112.64, 120.73, 121.43, 122.80, 123.99, 129.56, 130.36, 132.44, 136.29, 139.79, 157.43 ppm. HRMS (ESI) calcd. for $C_{16}H_{15}BrNO$ ($[M+H]^+$): 316.03315, found: 316.03287.

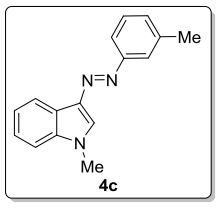


(*E*)-1-methyl-3-(phenyldiazenyl)-1*H*-indole **4a**: Yellow solid, mp 95.8-97.3 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.89 (s, 3 H), 7.33-7.40 (m, 4 H), 7.49-7.52 (m, 2 H), 7.87-7.89 (m, 3 H), 8.57-8.59 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.45, 109.43, 119.47, 121.68, 122.89, 123.15, 123.98, 128.81, 128.89, 134.71, 135.47,

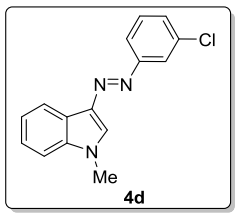
137.30, 153.87 ppm. HRMS (ESI) calcd. for $C_{15}H_{14}N_3$ ($[M+H]^+$): 236.11822, found: 236.11787.



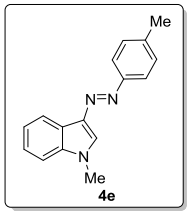
(*E*)-3-((2-methoxyphenyl)diazenyl)-1-methyl-1*H*-indole **4b**: Yellow solid, mp 132.5-133.7 ^oC, ^1H NMR (400 MHz, $CDCl_3$). δ: 3.86 (s, 3 H), 4.01 (s, 3 H), 7.04-7.10 (m, 2 H), 7.32-7.37 (m, 4 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.86 (s, 1 H), 8.59-8.61 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.38, 56.44, 109.26, 112.67, 116.15, 119.72, 120.80, 122.99, 123.11, 123.88, 130.03, 133.98, 136.41, 137.19, 143.27, 156.01 ppm. HRMS (ESI) calcd. for $C_{16}H_{16}N_3O$ ($[M+H]^+$): 266.12879, found: 266.12860.



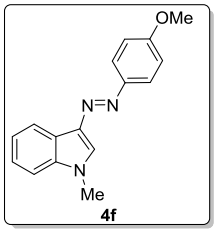
(*E*)-1-methyl-3-(*m*-tolyldiazenyl)-1*H*-indole **4c**: Yellow solid, mp 133.7-135.8 ^oC, ^1H NMR (400 MHz, $CDCl_3$). δ: 2.47 (s, 3 H), 3.87 (s, 3 H), 7.19-7.22 (m, 1 H), 7.32-7.41 (m, 4 H), 7.69-7.71 (m, 2 H), 7.86 (s, 1 H), 8.57-8.60 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 21.43, 33.41, 109.39, 119.19, 119.50, 121.94, 122.83, 123.16, 123.93, 128.71, 129.63, 134.53, 138.48, 137.29, 138.67, 153.93 ppm. HRMS (ESI) calcd. for $C_{16}H_{16}N_3$ ($[M+H]^+$): 250.13387, found: 250.13367.



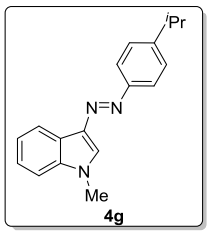
(*E*)-3-((3-chlorophenyl)diazenyl)-1-methyl-1*H*-indole **4d**: Yellow solid, mp 137.8-138.4 ^oC, ^1H NMR (400 MHz, $CDCl_3$). δ: 3.89 (s, 3 H), 7.31-7.37 (m, 4 H), 7.42 (t, *J* = 16 Hz, 1 H), 7.75-7.78 (m, 1 H), 7.86-7.88 (m, 2 H), 8.52-8.54 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.53, 109.53, 119.31, 120.71, 121.14, 123.16, 123.20, 124.21, 128.41, 129.90, 134.86, 135.48, 135.61, 137.41, 154.87 ppm. HRMS (ESI) calcd. for $C_{15}H_{13}ClN_3$ ($[M+H]^+$): 270.07925, found: 270.07913.



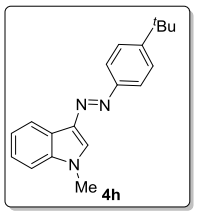
(*E*)-1-methyl-3-(*p*-tolyldiazenyl)-1*H*-indole **4e**: Yellow solid, mp 110.0-110.9 ^oC, ^1H NMR (400 MHz, $CDCl_3$). δ: 2.43 (s, 3 H), 3.88 (s, 3 H), 7.28-7.38 (m, 5 H), 7.81 (t, 3 H), 8.56-8.59 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 21.33, 33.32, 109.36, 119.54, 121.61, 122.68, 123.10, 123.82, 129.53, 134.12, 135.34, 137.24, 138.96, 151.86 ppm. HRMS (ESI) calcd. for $C_{16}H_{16}N_3$ ($[M+H]^+$): 250.13387, found: 250.13377.



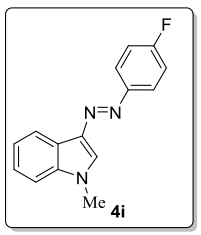
(*E*)-3-((4-methoxyphenyl)diazenyl)-1-methyl-1*H*-indole **4f**: Yellow solid, mp 98.4-100.1 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.86 (s, 3 H), 3.88 (s, 3 H), 7.00 (t, *J* =5 .2 Hz, 1 H), 7.02 (t, *J* = 5.2 Hz, 1 H), 7.30-7.36 (m, 3 H), 7.81-7.89 (m, 3 H), 8.56-8.59 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.35, 55.48, 109.36, 114.04, 119.61, 122.54, 123.06, 123.17, 123.76, 133.54, 135.21, 137.21, 148.07, 160.35 ppm. HRMS (ESI) calcd. for $C_{16}H_{16}N_3O$ ($[M+H]^+$): 266.12879, found: 266.12869.



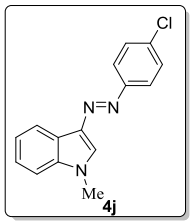
(*E*)-3-((4-isopropylphenyl)diazenyl)-1-methyl-1*H*-indole **4g**: Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.31 (s, 3 H), 1.32 (s, 3 H), 2.99 (m, 1 H), 3.87 (s, 3 H), 7.30-7.36 (m, 5 H), 7.80-7.84 (m, 3 H), 8.57 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 23.97, 33.38, 34.00, 109.36, 119.61, 121.67, 122.70, 123.15, 123.84, 126.90, 134.07, 135.46, 137.27, 149.91, 152.21 ppm. HRMS (ESI) calcd. for $C_{18}H_{20}N_3$ ($[M+H]^+$): 278.16517, found: 278.16483.



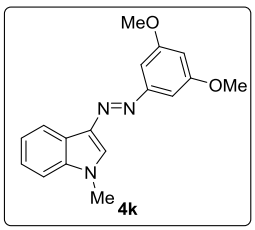
(*E*)-3-((4-(*tert*-butyl)phenyl)diazenyl)-1-methyl-1*H*-indole **4h**: Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.41 (s, 9 H), 3.85 (s, 3 H), 7.32-7.39 (m, 3 H), 7.52-7.56 (m, 2 H), 7.82-7.86 (m, 3 H), 8.59-8.62 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.35, 33.33, 34.78, 109.35, 119.56, 121.32, 122.68, 123.12, 123.82, 125.78, 134.12, 135.44, 137.23, 151.75, 152.07 ppm. HRMS (ESI) calcd. for $C_{19}H_{22}N_3$ ($[M+H]^+$): 292.18082, found: 292.18042.



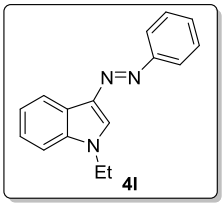
(*E*)-3-((4-fluorophenyl)diazenyl)-1-methyl-1*H*-indole **4i**: Yellow solid, mp 124.7-125.3 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.86 (s, 3 H), 7.15-7.21 (m, 2 H), 7.32-7.39 (m, 3 H), 7.83 (s, 1 H), 7.86-7.91 (m, 2 H), 8.55-8.57 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.89, 109.45, 115.68 ($J_{C\text{-}F}$ = 23 Hz), 122.88, 123.05, 123.32 (d, $J_{C\text{-}F}$ = 8.5 Hz), 123.99, 134.64, 135.26, 137.30, 150.34, 163.02 (d, $J_{C\text{-}F}$ = 247 Hz) ppm. HRMS (ESI) calcd. for $C_{15}H_{13}FN_3$ ($[M+H]^+$): 254.10880, found: 254.10854.



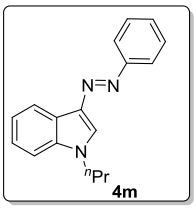
(*E*)-3-((4-chlorophenyl)diazenyl)-1-methyl-1*H*-indole **4j**: Yellow solid, mp 130.2-130.4 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.80 (s, 3 H), 7.22-7.35 (m, 3 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 7.79 (d, *J* = 8.8 Hz, 3 H), 8.52 (d, *J* = 6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.42, 109.50, 119.36, 122.89, 123.05, 123.07, 124.09, 129.02, 134.22, 135.14, 135.38, 137.34, 152.23 ppm. HRMS (ESI) calcd. for $C_{15}H_{13}ClN_3$ ($[M+H]^+$): 270.07925, found: 270.07916.



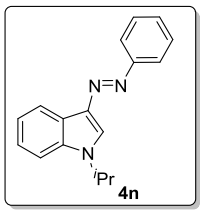
(*E*)-3-((3,5-dimethoxyphenyl)diazenyl)-1-methyl-1*H*-indole **4k.** Orange red solid, mp 142.8-143.6 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.86 (s, 3 H), 3.96 (s, 3 H), 4.00 (s, 3 H), 6.99 (d, *J* = 8.4 Hz, 1 H), 7.30-7.34 (m, 3 H), 7.51 (d, *J* = 2 Hz, 1 H), 7.54 (dd, *J* = 8.4 Hz, 1 H), 7.82 (s, 1 H), 8.58 (d, *J* = 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 33.34, 55.86, 56.02, 101.71, 109.36, 110.56, 118.02, 119.60, 122.56, 123.09, 123.79, 133.58, 135.16, 137.24, 148.12, 149.43, 150.04 ppm. MS m/z: 295.



(*E*)-1-ethyl-3-(phenyldiazenyl)-1*H*-indole **4l.** Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.55-1.59 (t, 3 H), 4.25 (q, 2 H), 7.32-7.40 (m, 4 H), 7.48-7.53 (m, 2 H), 7.92 (t, 3 H), 8.60 (t, *J* = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 15.09, 41.55, 109.52, 119.73, 121.67, 122.87, 123.23, 123.88, 128.77, 128.90, 132.97, 135.60, 136.45, 153.91 ppm. HRMS (ESI) calcd. for $C_{16}H_{16}N_3$ ($[M+H]^+$): 250.13387, found: 250.13365.

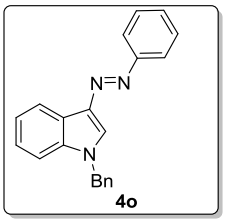


(*E*)-3-(phenyldiazenyl)-1-propyl-1*H*-indole **4m.** Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.01 (t, 3 H), 1.92-2.01 (m, 2 H), 4.16 (t, 2 H), 7.32-7.41 (m, 4 H), 7.49-7.53 (m, 2 H), 7.91 (t, 3 H), 8.61 (t, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 11.39, 23.14, 48.56, 109.64, 119.70, 121.67, 122.81, 123.21, 123.84, 128.75, 128.88, 133.79, 135.48, 136.72, 153.94 ppm. HRMS (ESI) calcd. for $C_{17}H_{18}N_3$ ($[M+H]^+$): 264.14952, found: 264.14932.



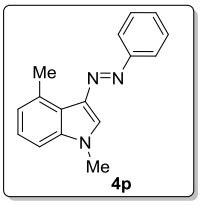
(*E*)-1-isopropyl-3-(phenyldiazenyl)-1*H*-indole **4n.** Yellow solid, mp 134.0-134.3 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 1.62 (s, 3 H),

1.64 (s, 3 H), 4.69-4.4.79 (m, 1 H), 7.31-7.43 (m, 4 H), 7.47-7.52 (m, 2 H), 7.89 (d, 2 H), 8.06 (s, 1 H), 8.61 (q, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 22.64, 47.65, 109.65, 119.69, 121.64, 122.88, 123.22, 123.76, 128.72, 128.89, 130.05, 135.77, 136.34, 153.95 ppm. HRMS (ESI) calcd. for $C_{17}H_{18}N_3$ ($[M+H]^+$): 264.14952, found: 264.14926.



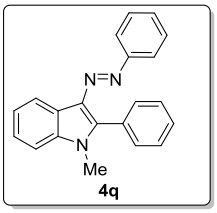
4o

(*E*)-1-phenyl-3-(phenyldiazenyl)-1*H*-indole **4o**: Red liquid, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 5.39 (s, 2 H), 7.23-7.26 (m, 2 H), 7.29-7.40 (m, 7 H), 7.47-7.51 (m, 2 H), 7.88-7.96 (m, 3 H), 8.60 (d, *J* = 9.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 50.74, 109.99, 121.72, 123.09, 123.23, 124.16, 127.15, 128.17, 128.91, 128.95, 129.01, 133.99, 135.85, 136.96 ppm. HRMS (ESI) calcd. for $C_{21}H_{18}N_3$ ($[M+H]^+$): 312.14952, found: 312.14923.



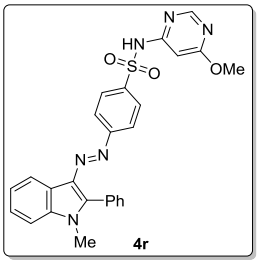
4p

(*E*)-1, 4-dimethyl-3-(phenyldiazenyl)-1*H*-indole **4p**: Red solid, mp 93.1-95.7 °C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 2.96 (s, 3 H), 3.84 (s, 3 H), 7.12-7.14 (m, 1 H), 7.20-7.26 (m, 2 H), 7.37-7.42 (m, 1 H), 7.49-7.53 (m, 2 H), 7.65 (s, 1 H), 7.88-7.90 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 20.79, 33.51, 107.49, 117.20, 122.02, 122.71, 123.21, 124.67, 128.94, 129.00, 132.17, 136.92, 137.14, 153.59 ppm. HRMS (ESI) calcd. For $C_{16}H_{16}N_3$ ($[M+H]^+$): 250.13387, found: 250.13370.



4q

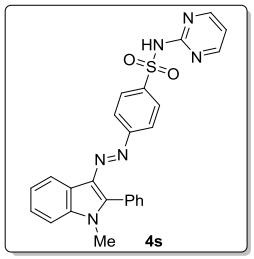
(*E*)-1-methyl-2-phenyl-3-(phenyldiazenyl)-1*H*-indole **4q**: Yellow solid, mp 147.4-147.6 °C, ^{1}H NMR (400 MHz, $CDCl_3$). δ: 3.84 (s, 3 H), 7.32-7.36 (m, 1 H), 7.40-7.48 (m, 5 H), 7.52-7.60 (m, 3 H), 7.67-7.70 (m, 2 H), 7.82-7.85 (m, 2 H), 8.74-8.76 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 31.48, 109.51, 118.81, 121.89, 123.28, 123.33, 124.03, 127.99, 128.46, 128.75, 128.86, 129.65, 131.63, 132.66, 137.45, 146.21, 154.24 ppm. HRMS (ESI) calcd. for $C_{21}H_{18}N_3$ ($[M+H]^+$): 312.14952, found: 312.14908.



4r

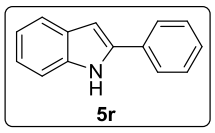
(*E*)-*N*-(6-methoxypyrimidin-4-yl)-4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)benzenesulfonamide **4r** was obtained. Red solid (1.22 g, 95%), mp 248.6-250.0 °C, ^{1}H NMR (400 MHz,

DMSO-d_6). δ: 3.84 (s, 6 H), 6.36 (d, J = 0.4 Hz, 1 H), 7.35-7.44 (m, 2 H), 7.59-7.64 (m, 3 H), 7.70 (d, J = 8 Hz, 1 H), 7.74-7.79 (m, 4 H), 7.99 (d, J = 8.8 Hz, 2 H), 8.42 (s, 1 H), 8.51 (d, J = 7.6 Hz, 1 H), 12.23 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6). δ: 31.97, 54.43, 91.07, 111.19, 117.85, 121.76, 122.67, 124.11, 124.79, 128.33, 128.38, 128.79, 129.67, 131.74, 137.50, 148.43, 156.17, 158.62, 170.13 ppm. HRMS (ESI) calcd. for $C_{26}H_{23}N_6O_3S$ ($[M+H]^+$): 499.15469, found: 499.15427.



4s

(*E*)-4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)-*N*-(pyrimidin-2-yl)benzenesulfonamide **4s** was obtained. Red solid (2.21 g, 94%), mp 254.9-256.3 ^{o}C, ^{1}H NMR (400 MHz, DMSO-d_6). δ: 3.82 (s, 3 H), 7.03 (t, J = 9.6 Hz, 1 H), 7.35-7.44 (m, 2 H), 7.56-7.64 (m, 3 H), 7.68 (d, J = 8 Hz, 1 H), 7.73-7.77 (m, 4 H), 8.05 (d, J = 8.4 Hz, 2 H), 8.50 (t, J = 8.8 Hz, 3 H), 11.88 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6). δ: 31.98, 111.20, 115.97, 117.89, 121.47, 122.71, 124.13, 124.81, 128.41, 128.82, 129.06, 129.69, 131.77, 132.73, 137.51, 139.32, 148.41, 156.21, 157.05, 158.55 ppm. HRMS (ESI) calcd. for $C_{25}H_{21}N_6O_2S$ ($[M+H]^+$): 469.14412, found: 469.14380.



5r

2-phenyl-1*H*-indole **5r** (48 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$). δ: 6.85 (d, J = 4 Hz, 1 H), 7.12-7.16 (m, 1 H), 7.19-7.23 (m, 1 H), 7.34 (t, J = 16 Hz, 1 H), 7.40-7.48 (m, 3 H), 7.64-7.69 (m, 3 H), 8.34 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$). δ: 99.94, 110.87, 120.24, 120.64, 122.32, 125.12, 127.69, 128.98, 129.00, 129.21, 132.32, 136.75, 137.83 ppm. HRMS (ESI) calcd. for $C_{14}H_{12}N$ ($[M+H]^+$): 194.09643, found: 194.09610.

VIII. References

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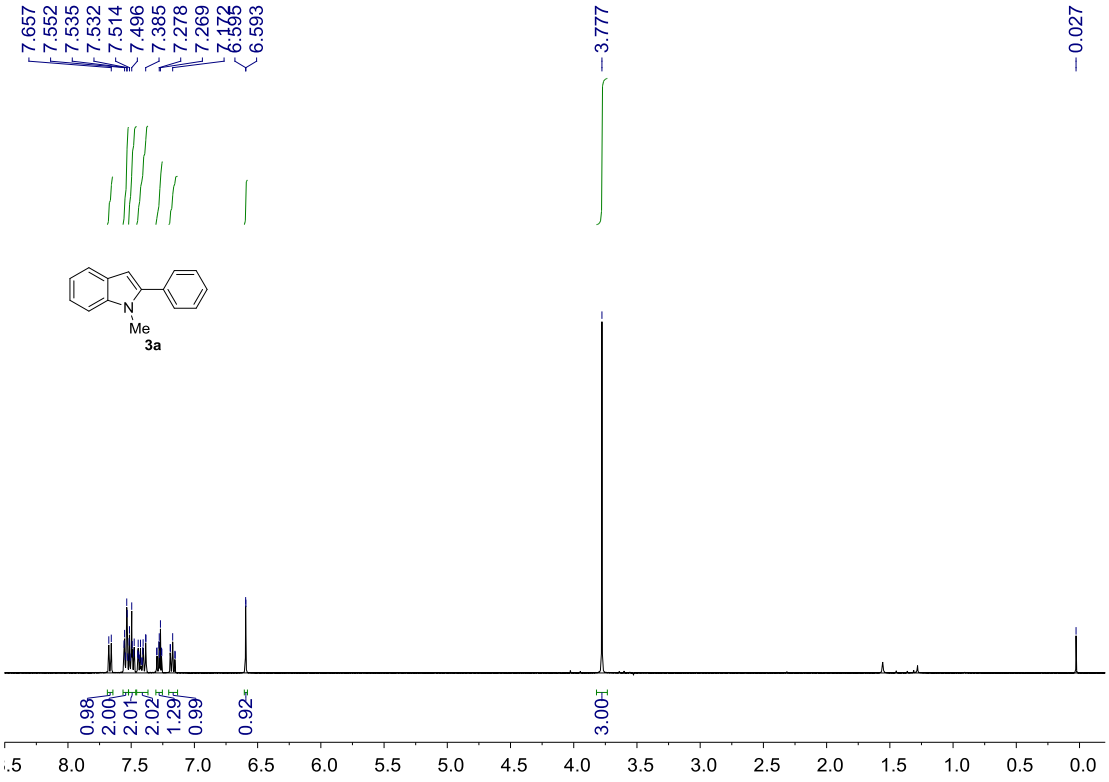
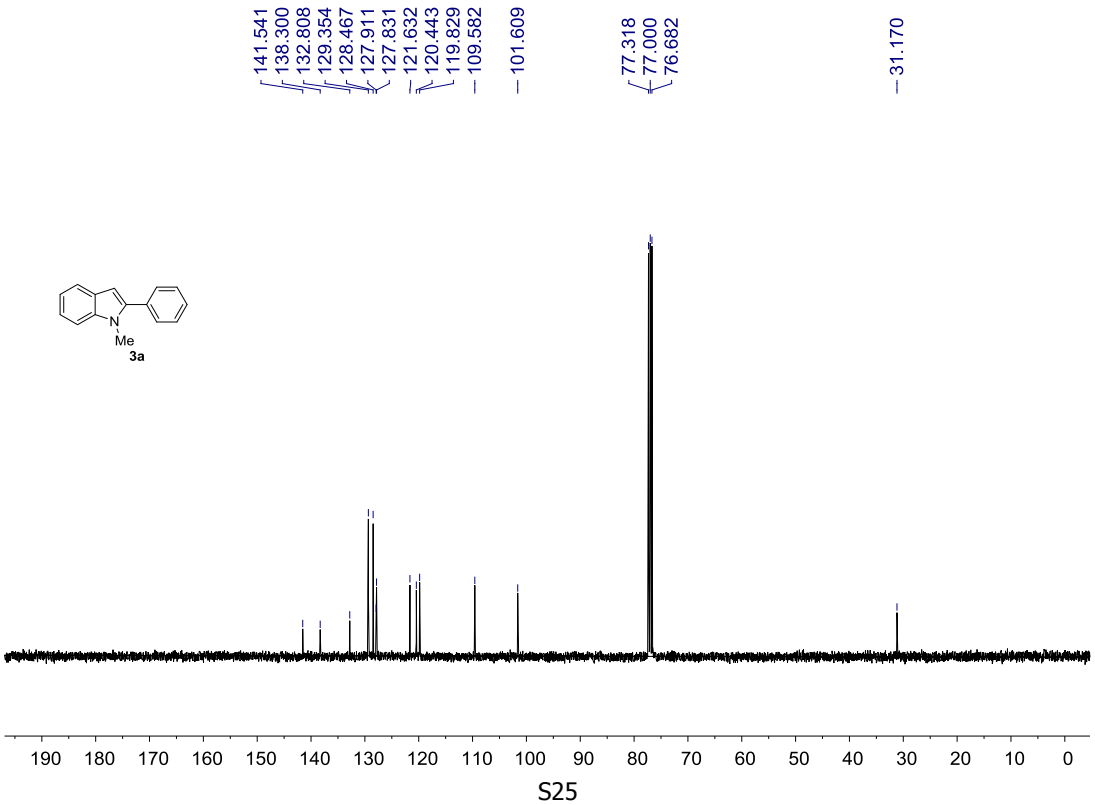
Ⅸ. Copies of ^{1}H NMR and ^{13}C NMR

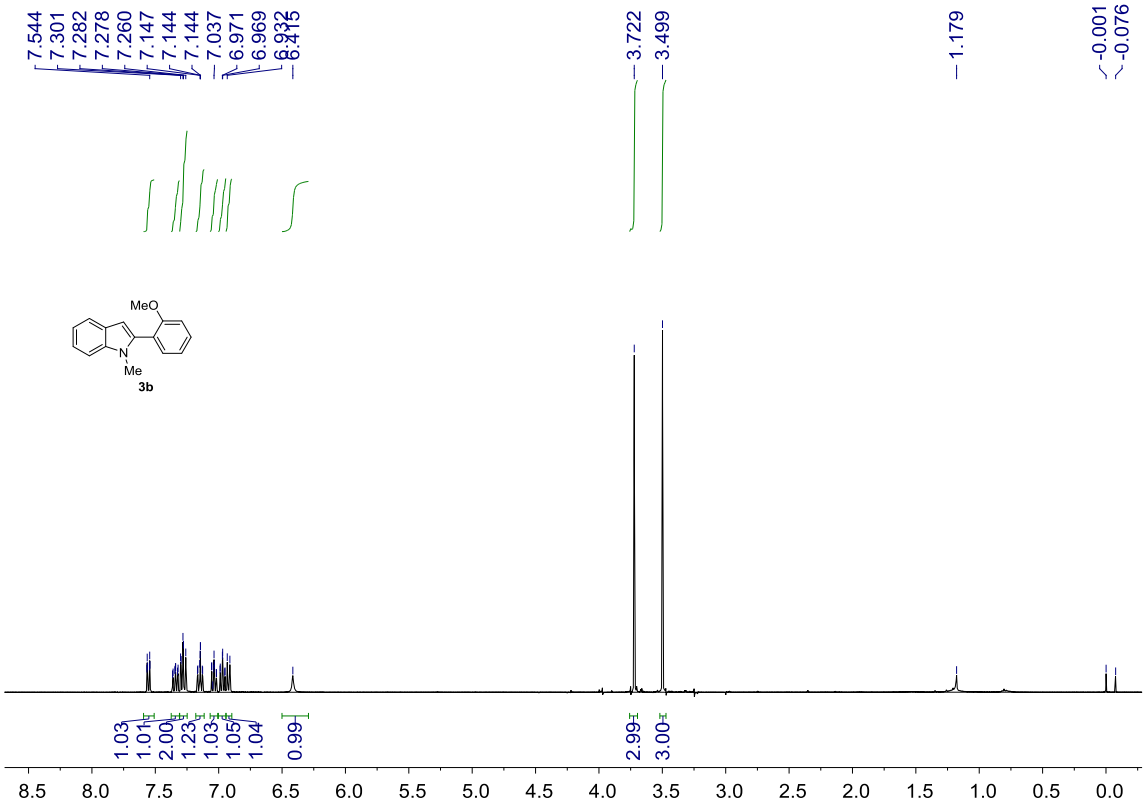
^{1}H NMR



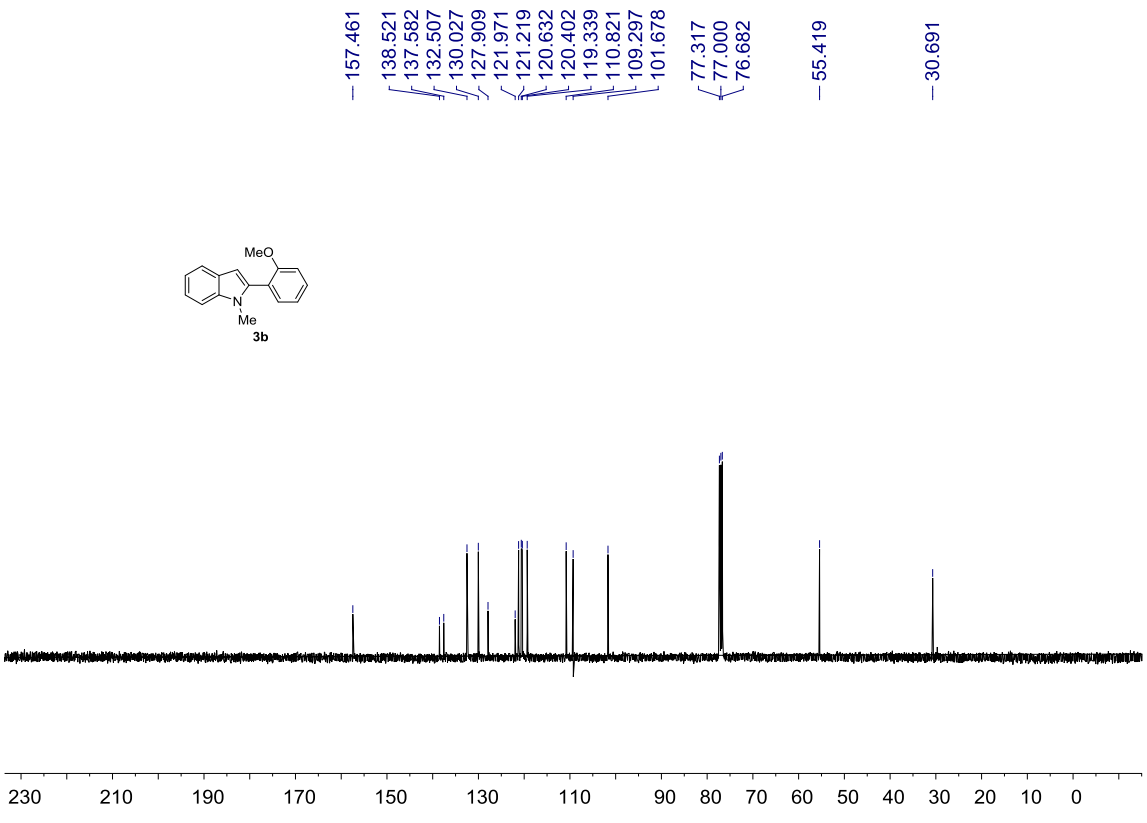
^{13}C NMR



^{1}H NMR



^{13}C NMR



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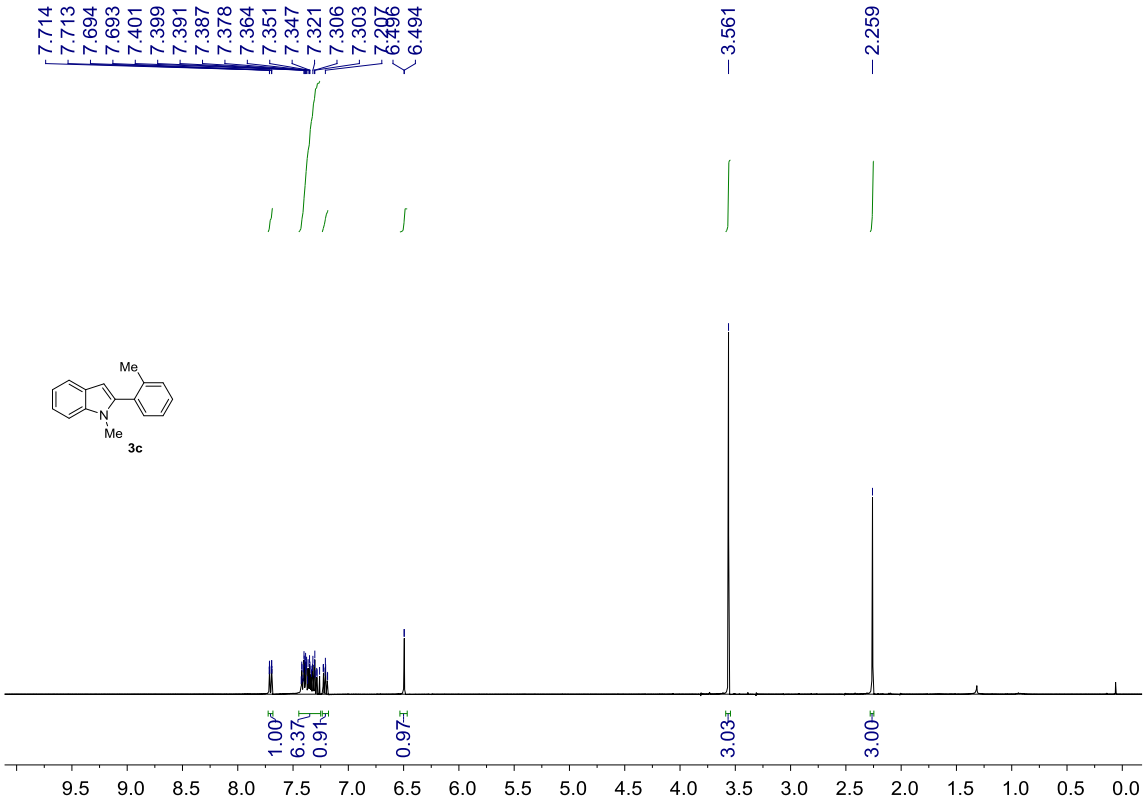

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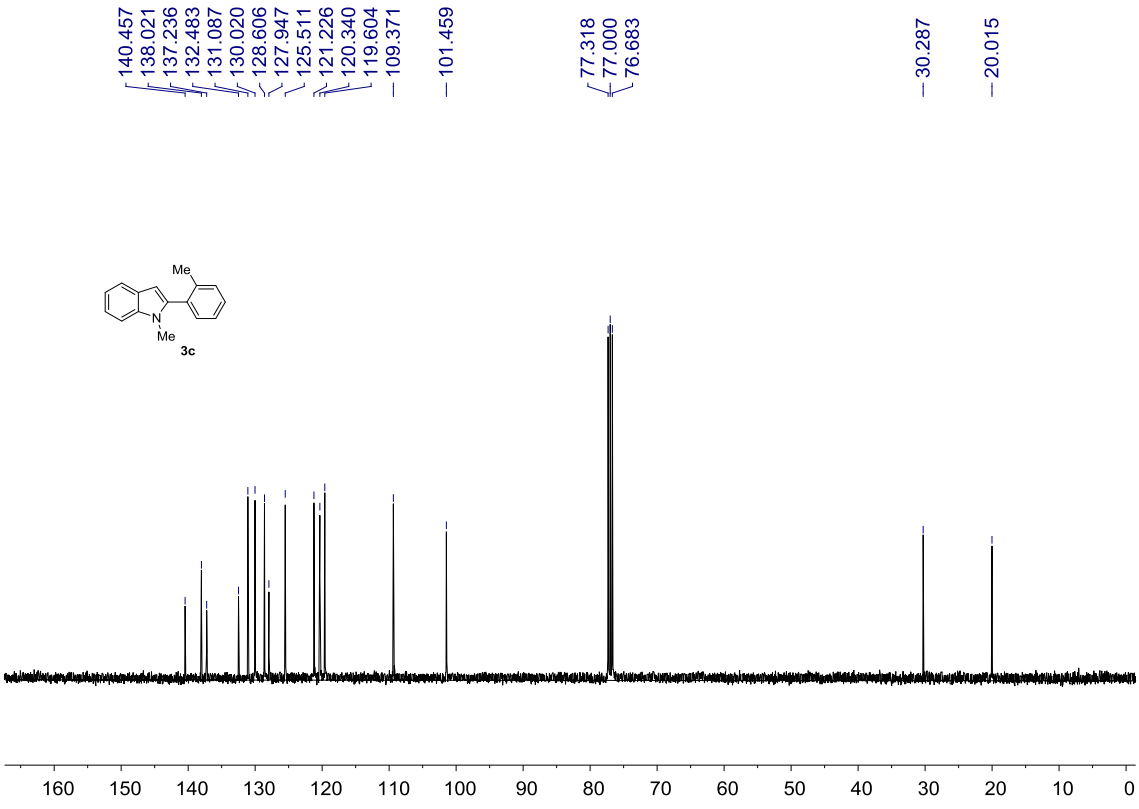

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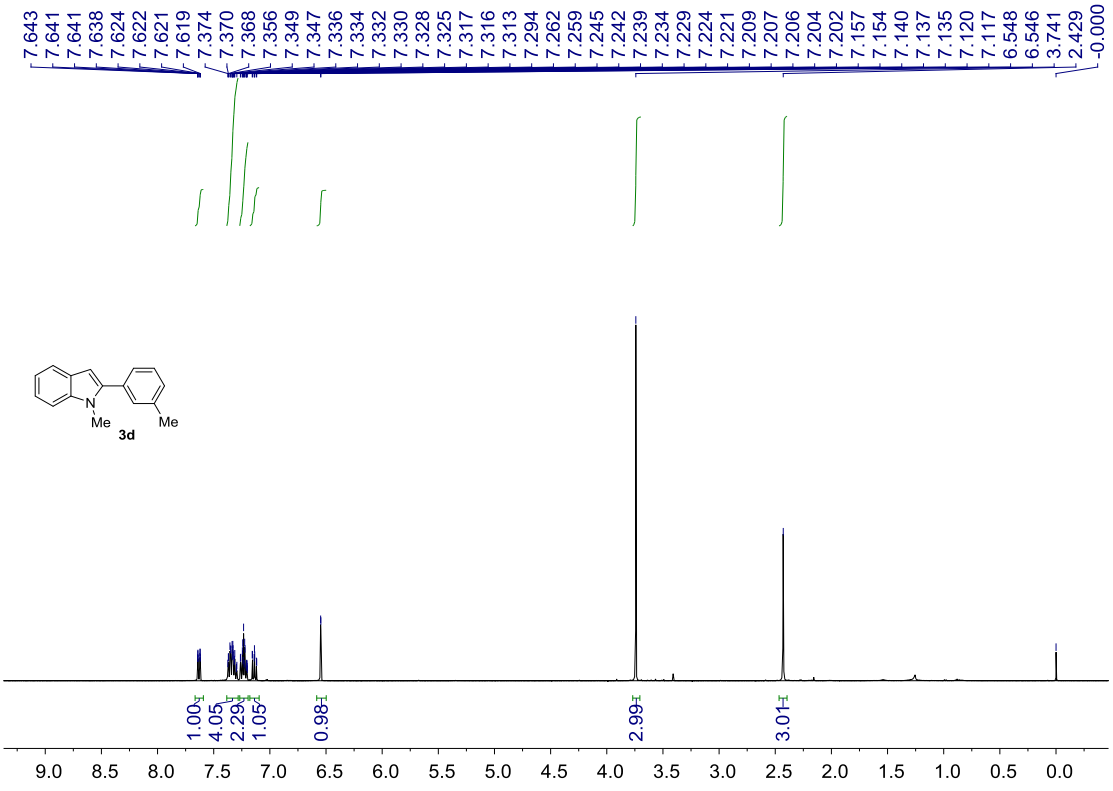

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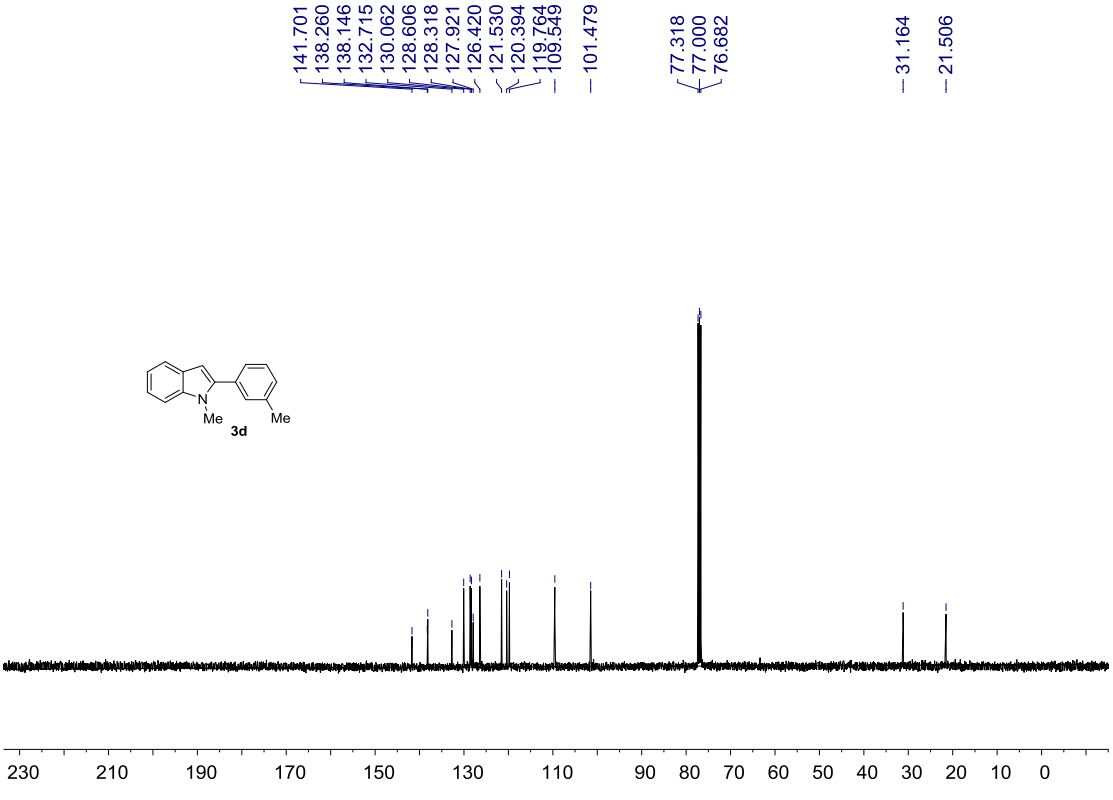

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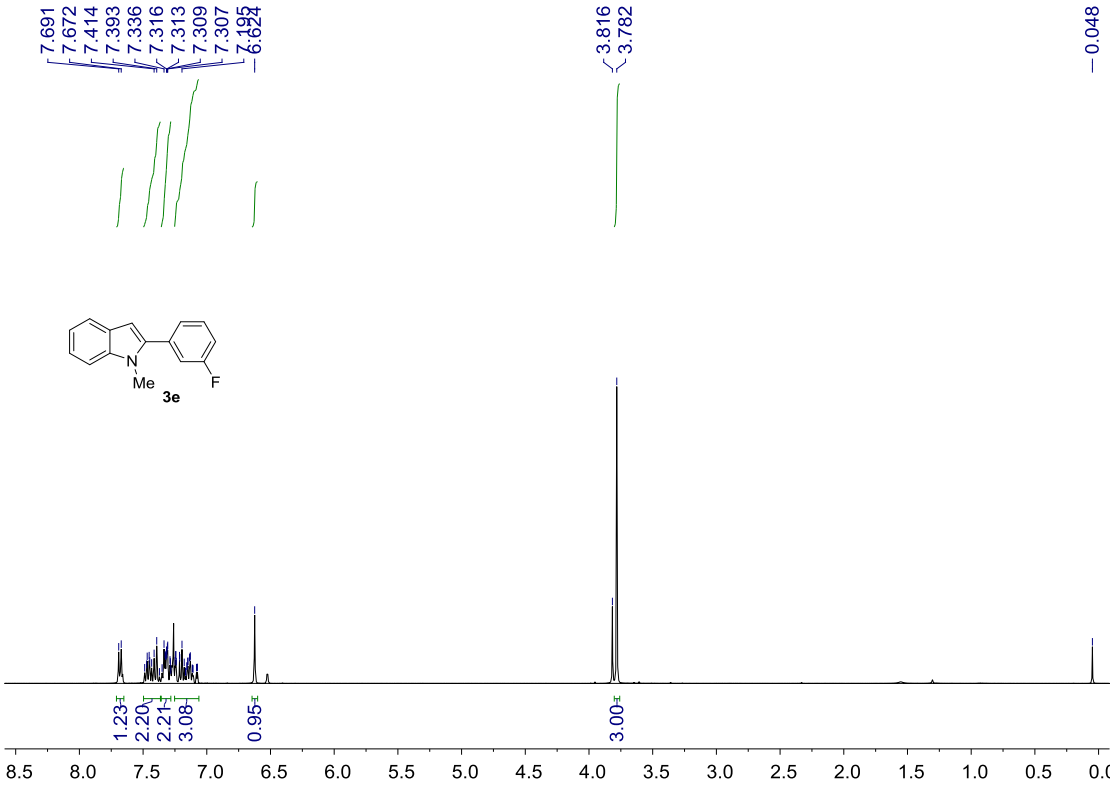

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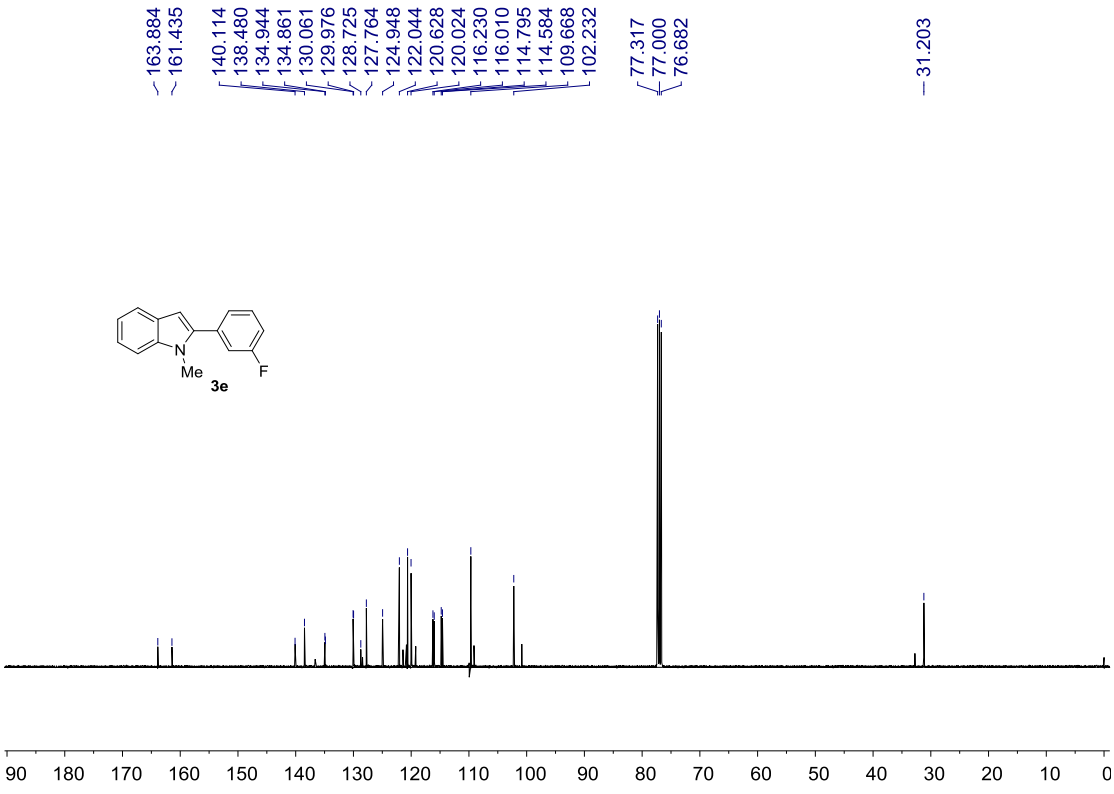

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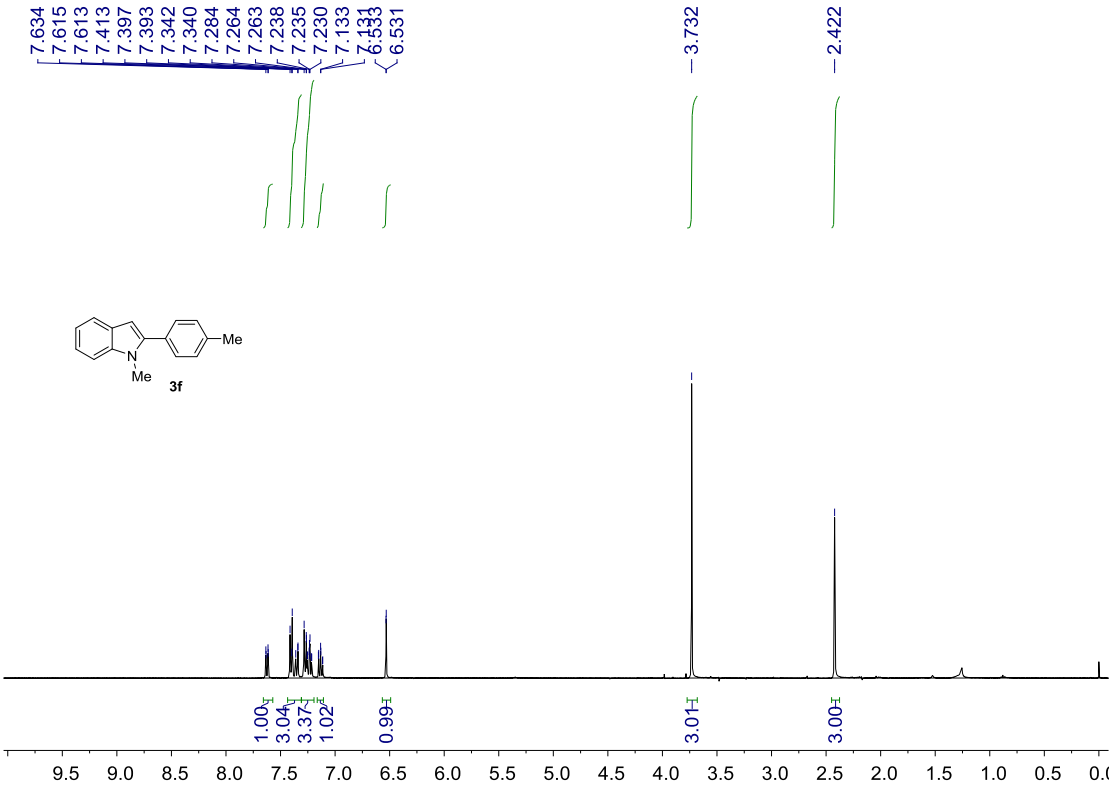

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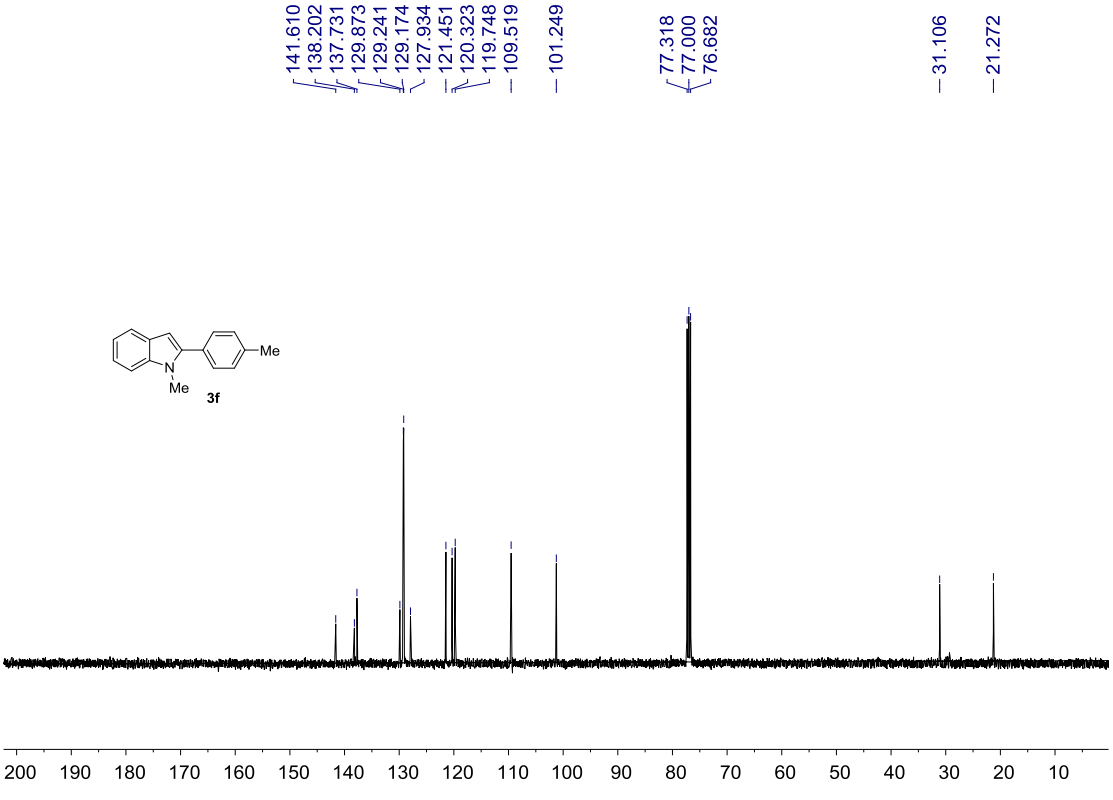

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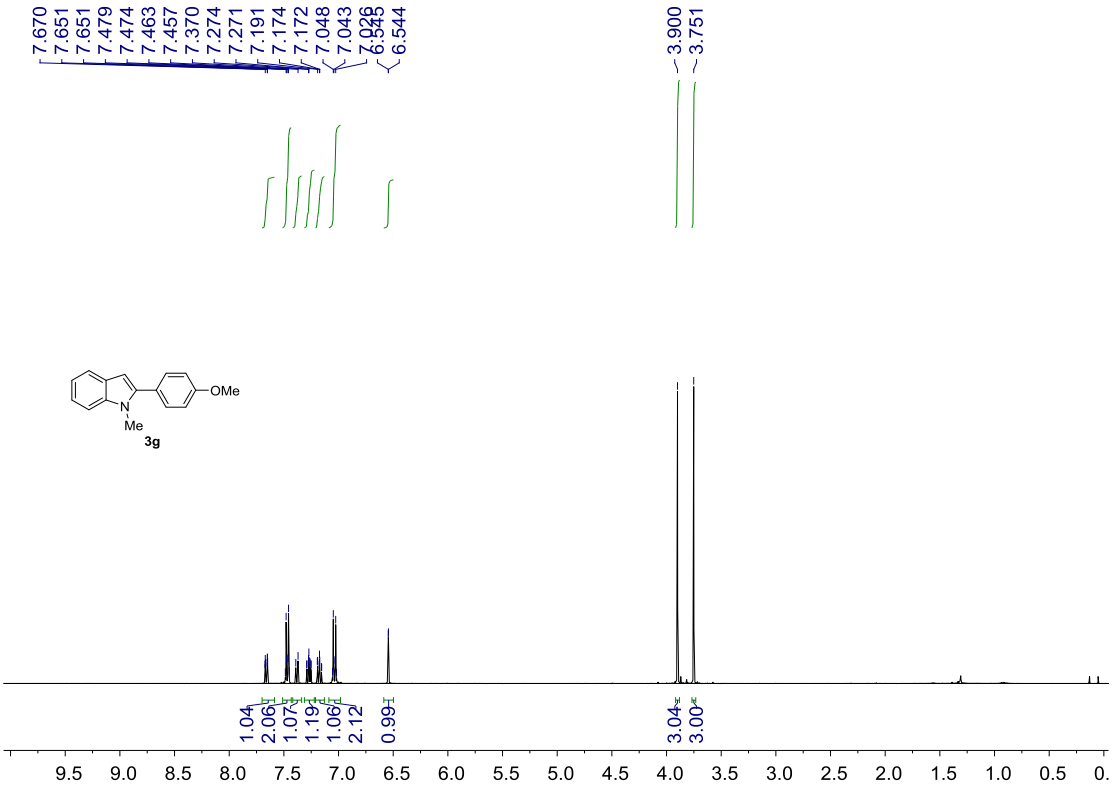

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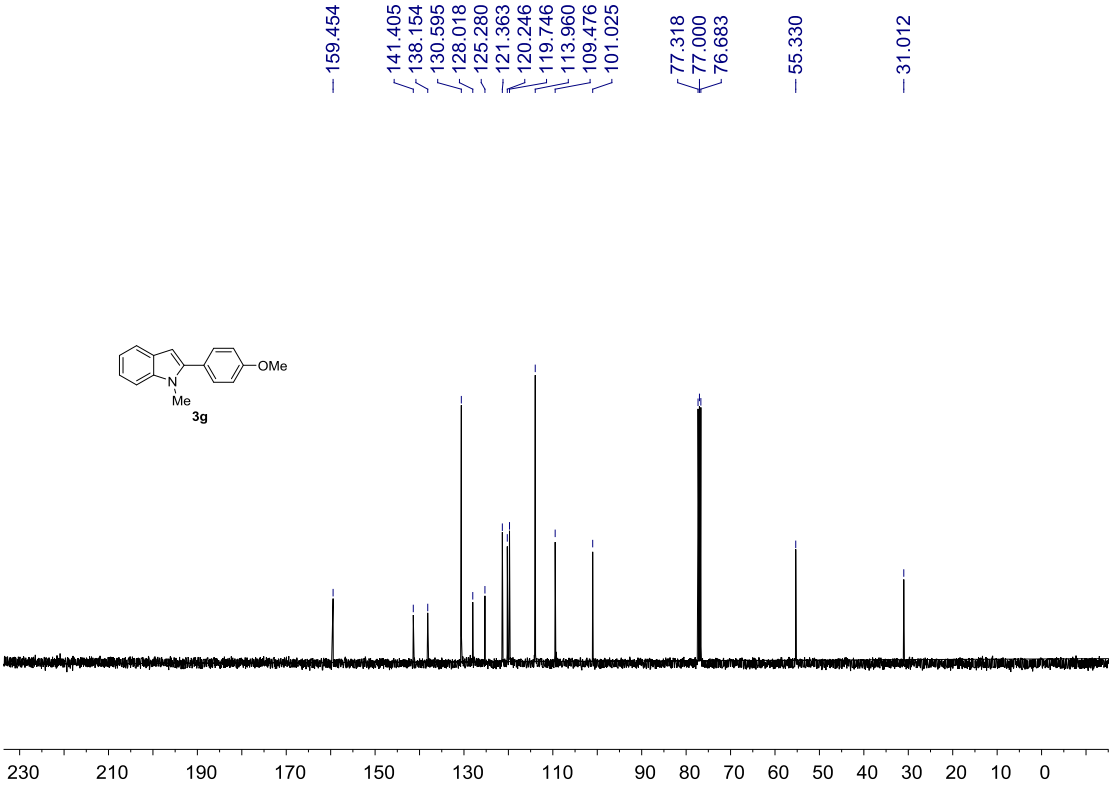

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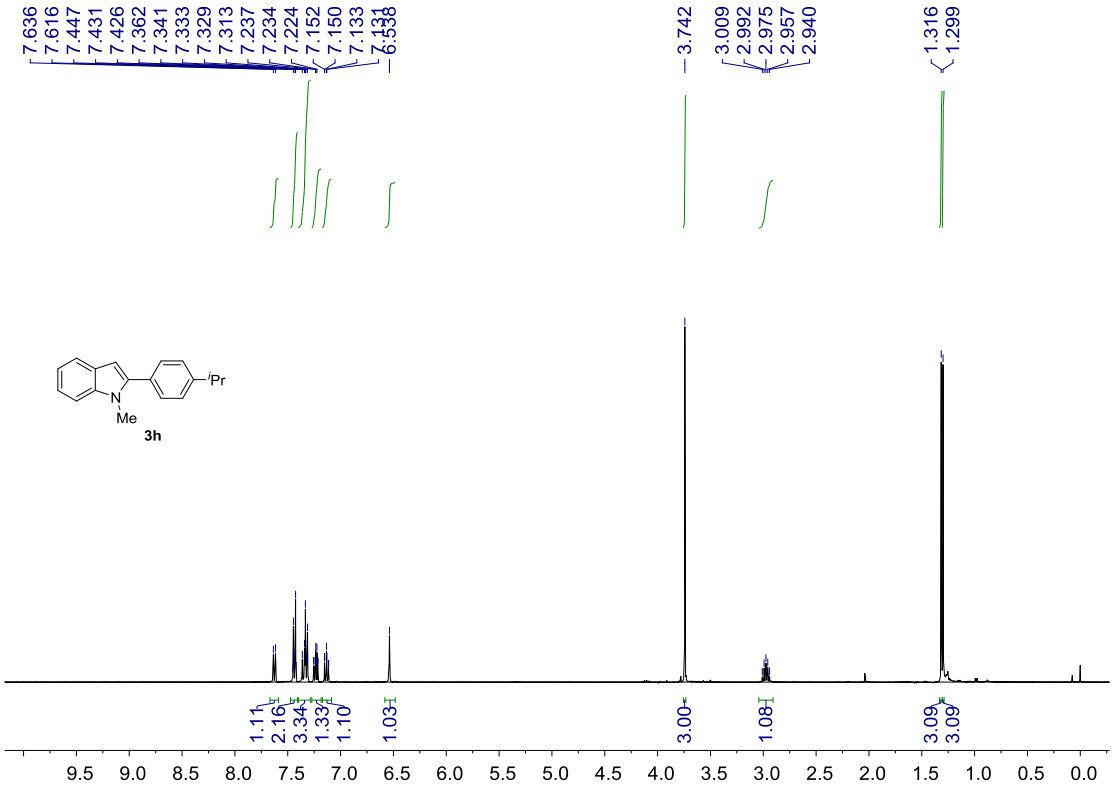

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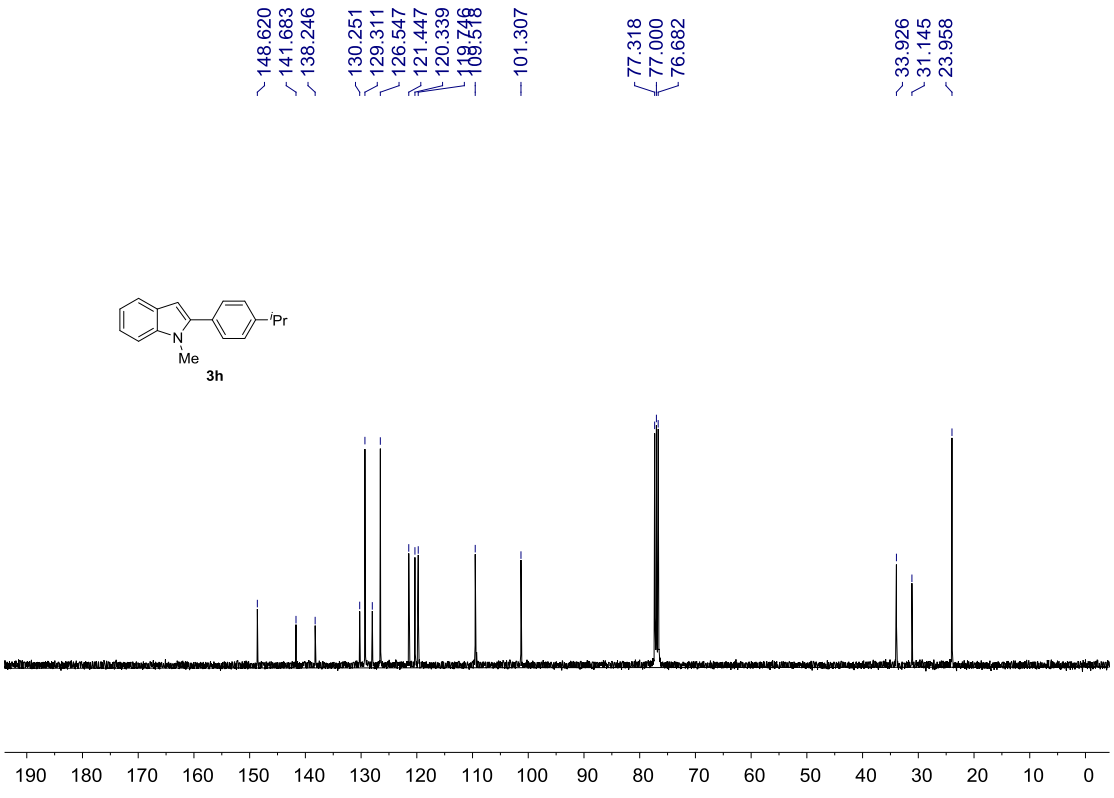

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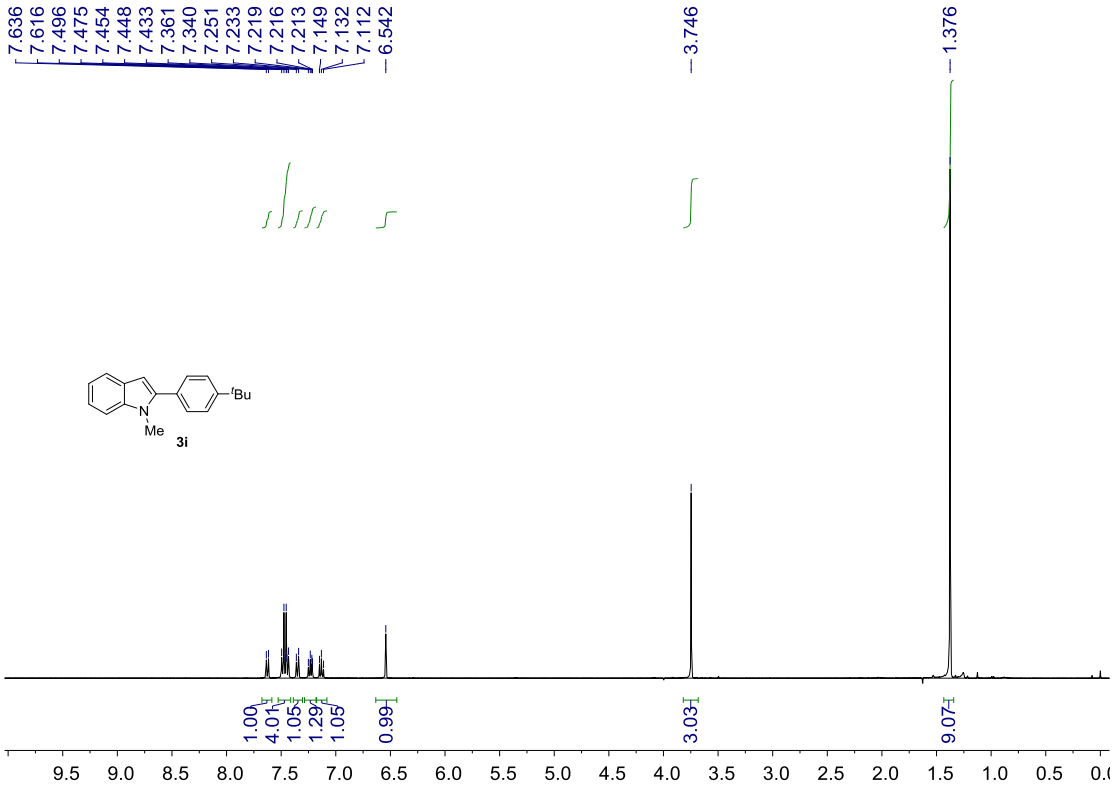

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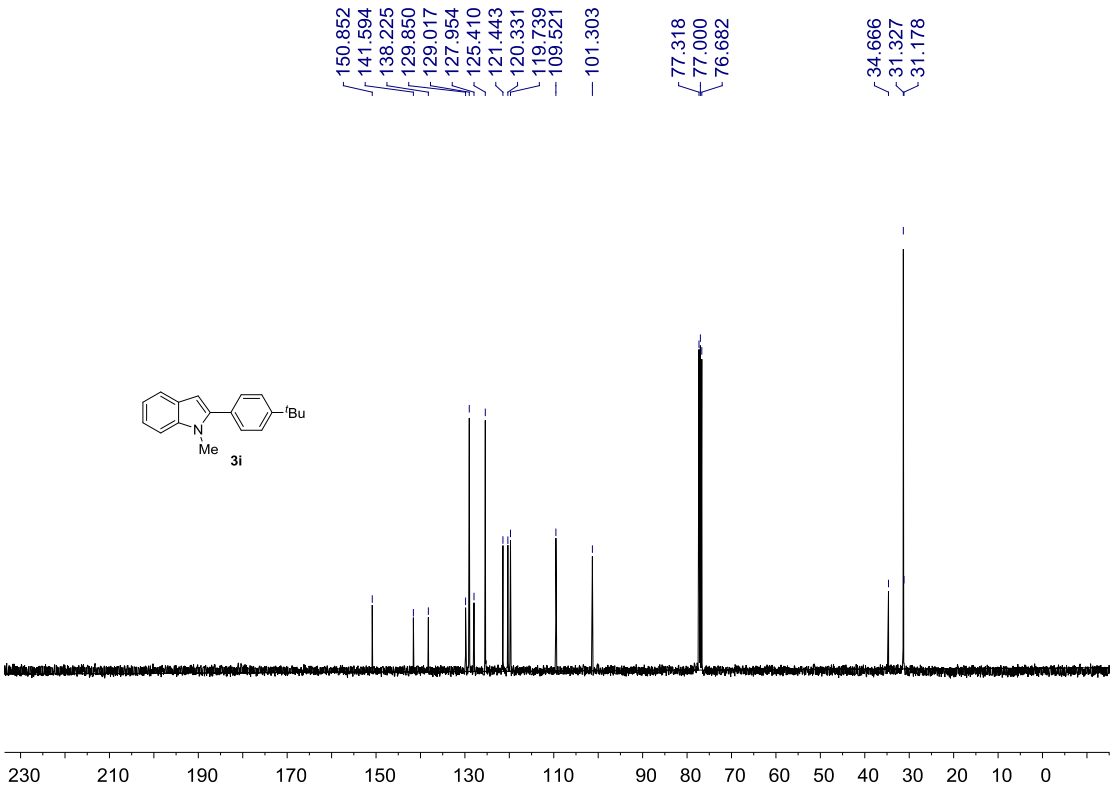

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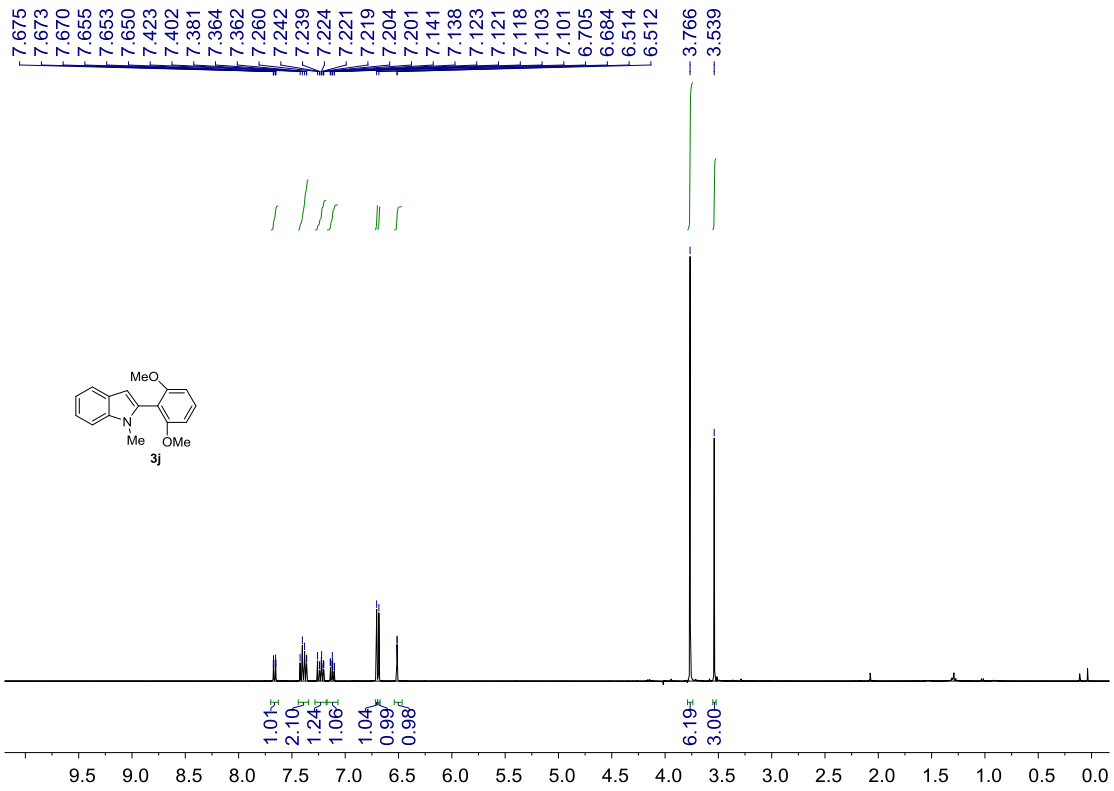

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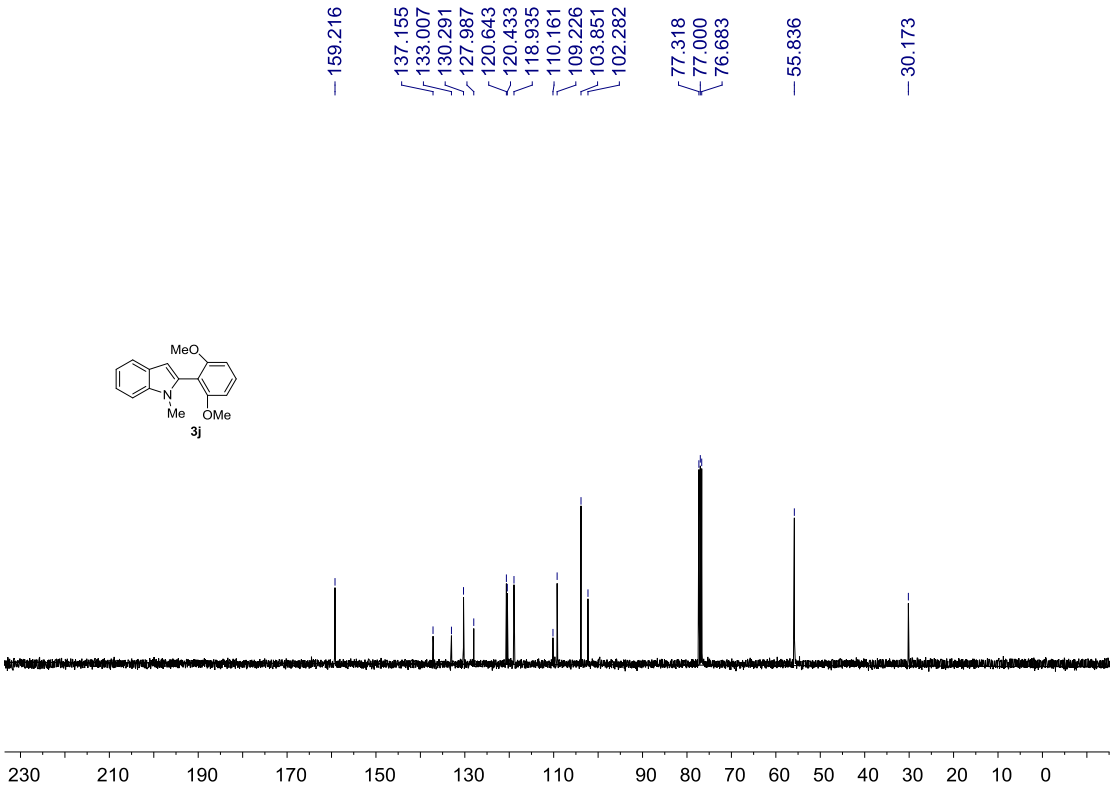

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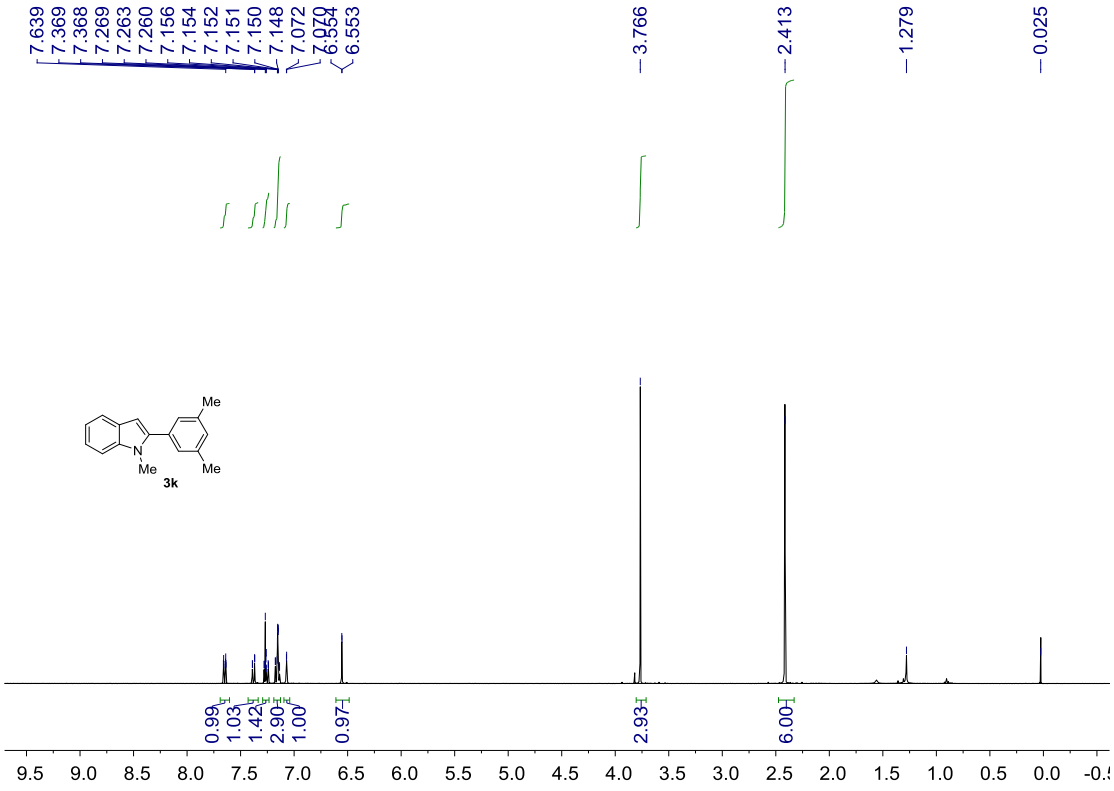

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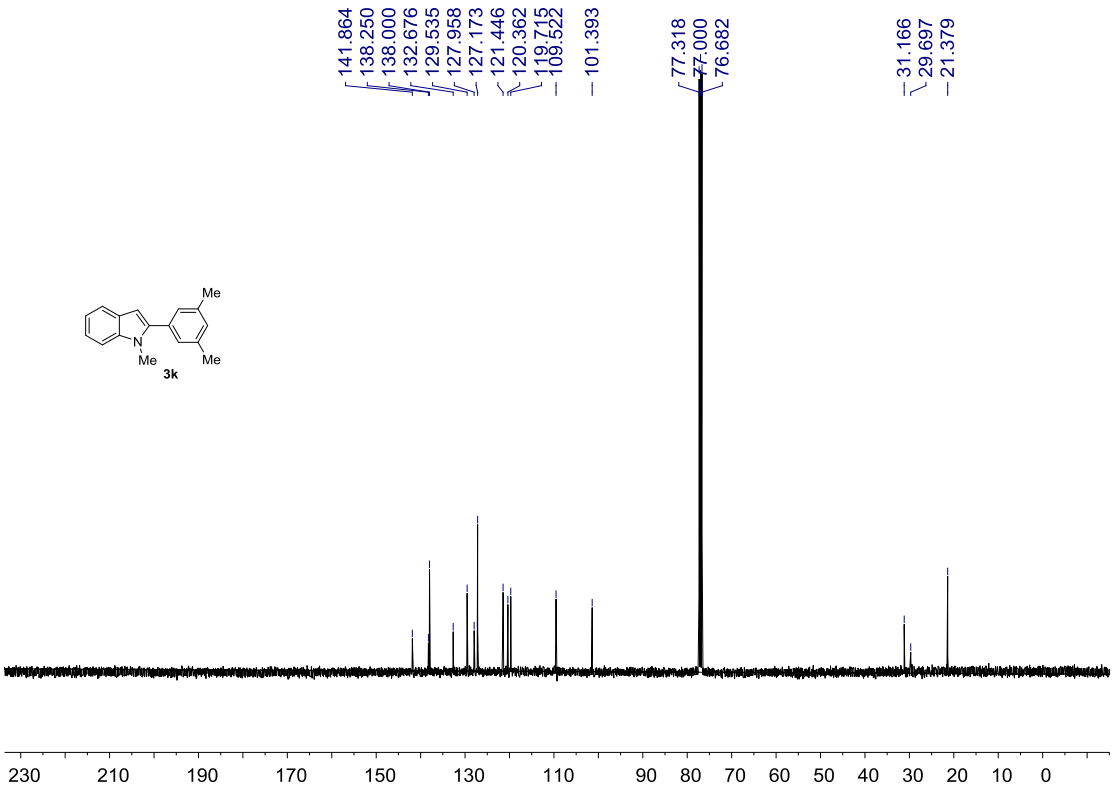

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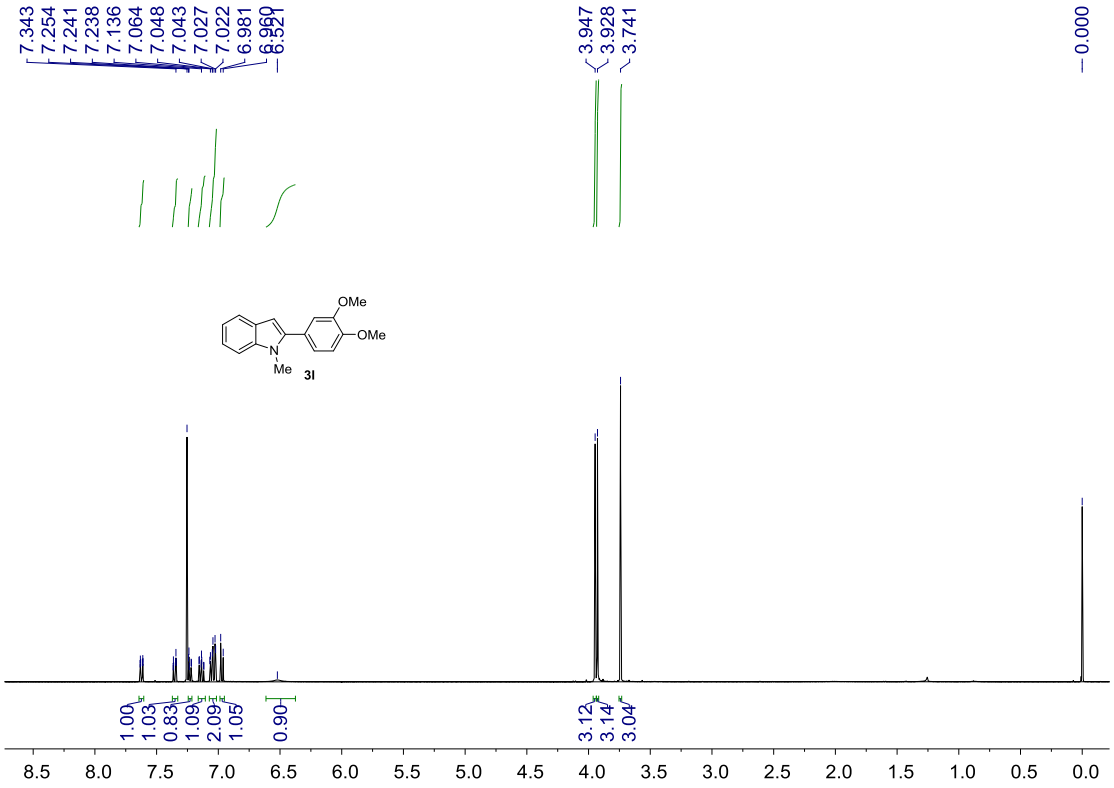

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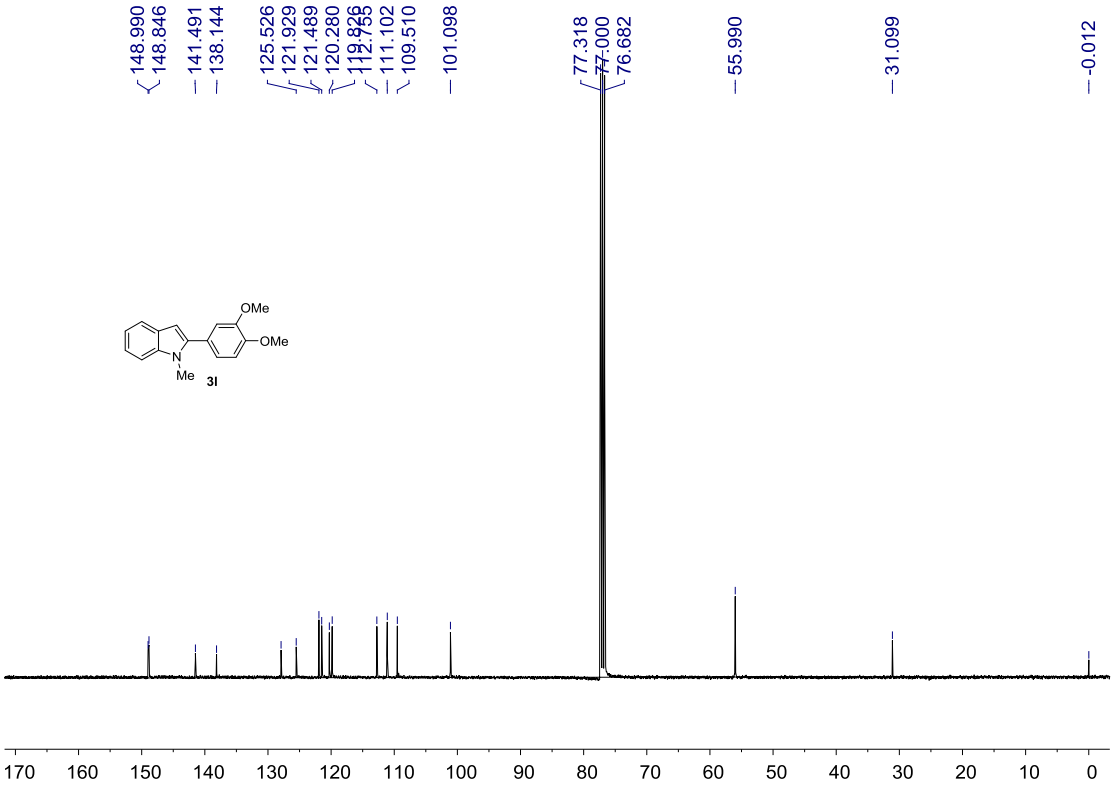

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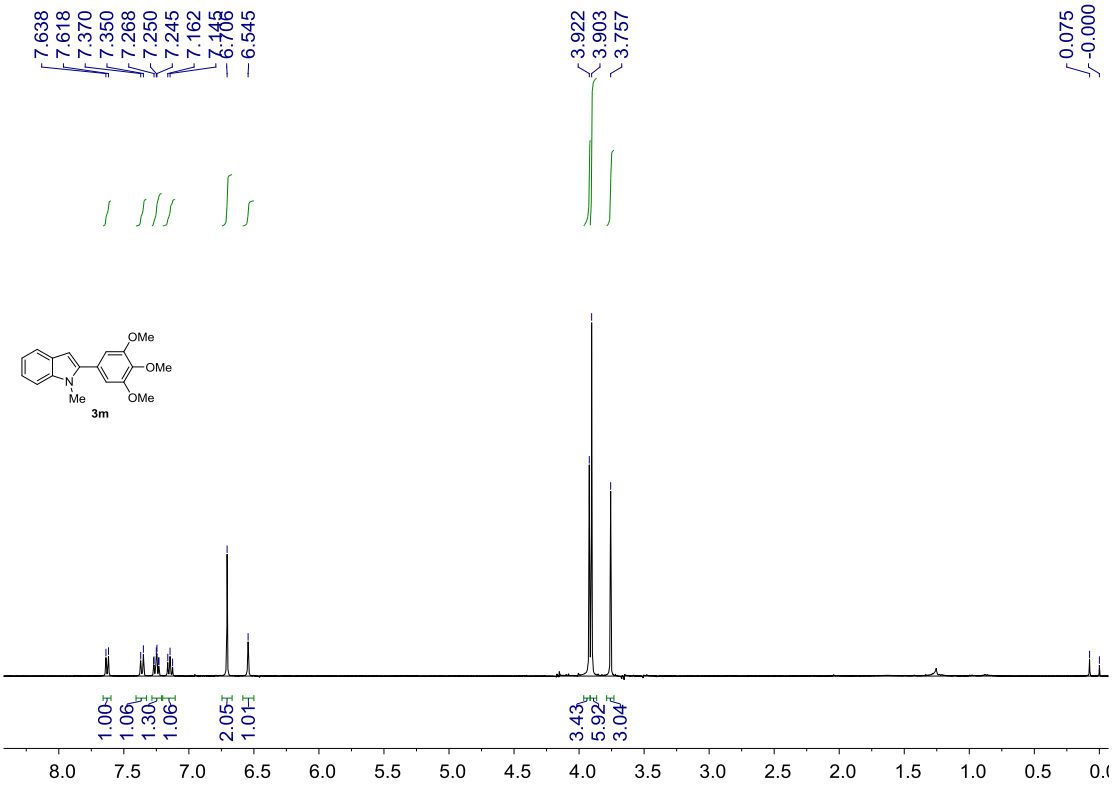

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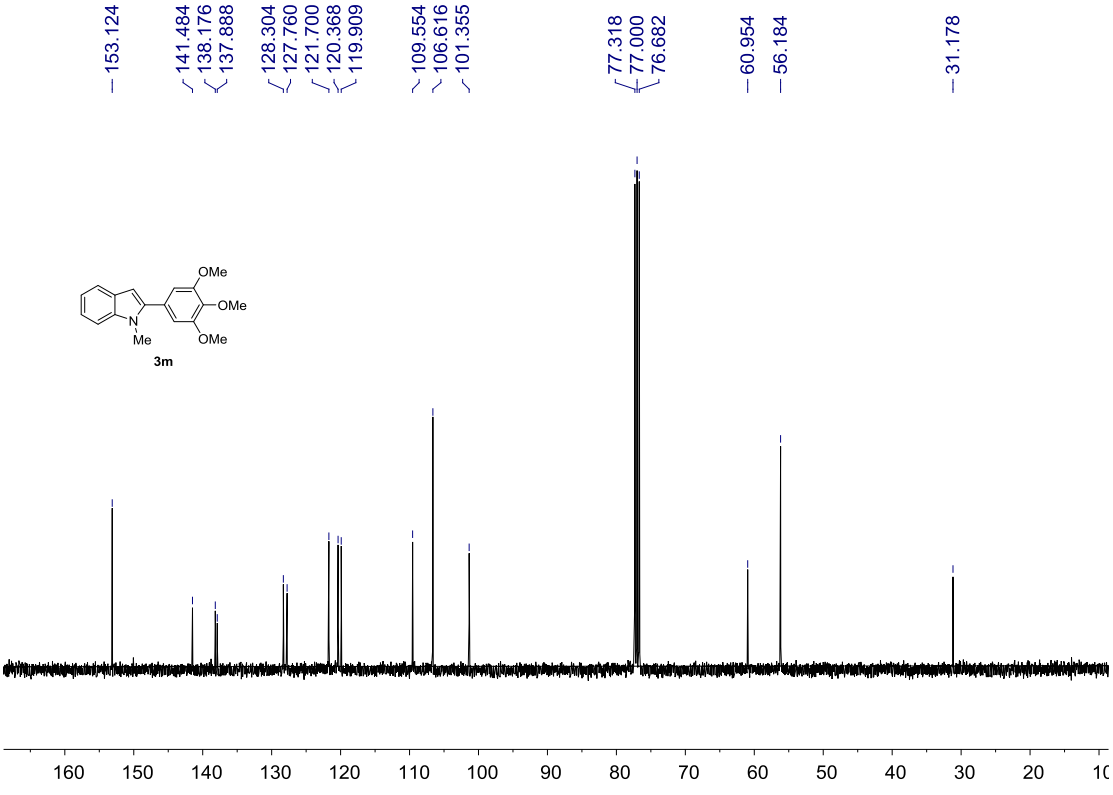

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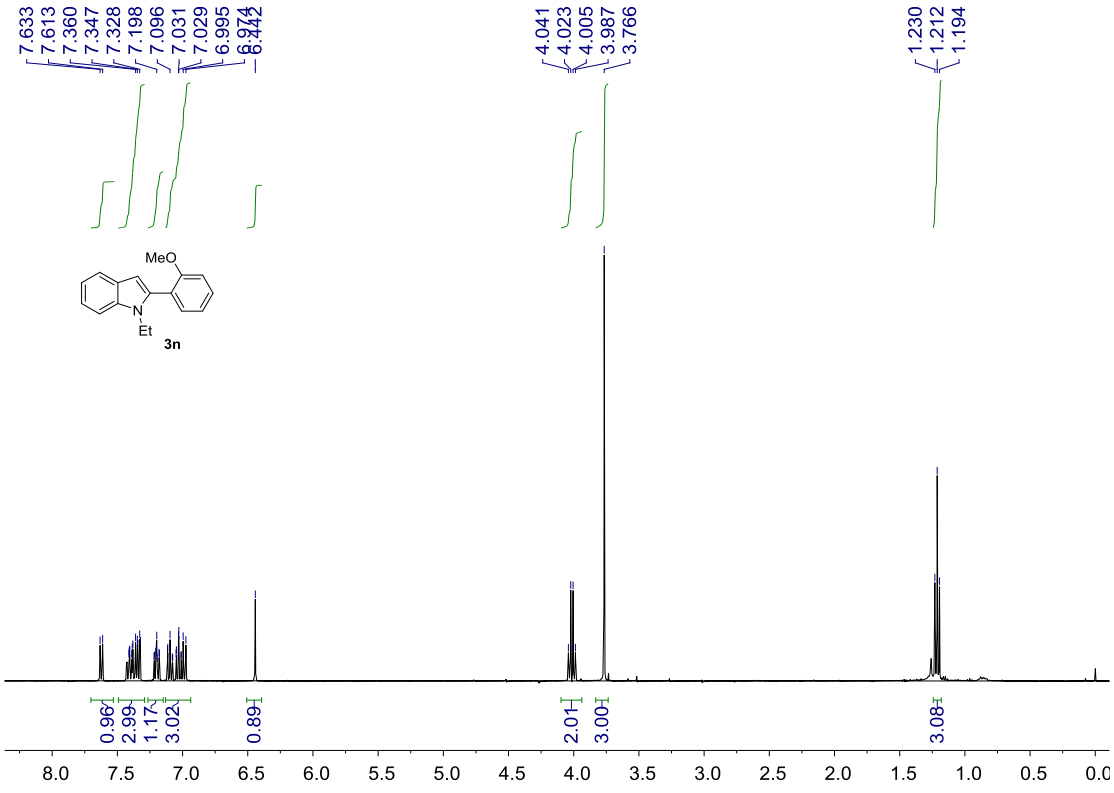

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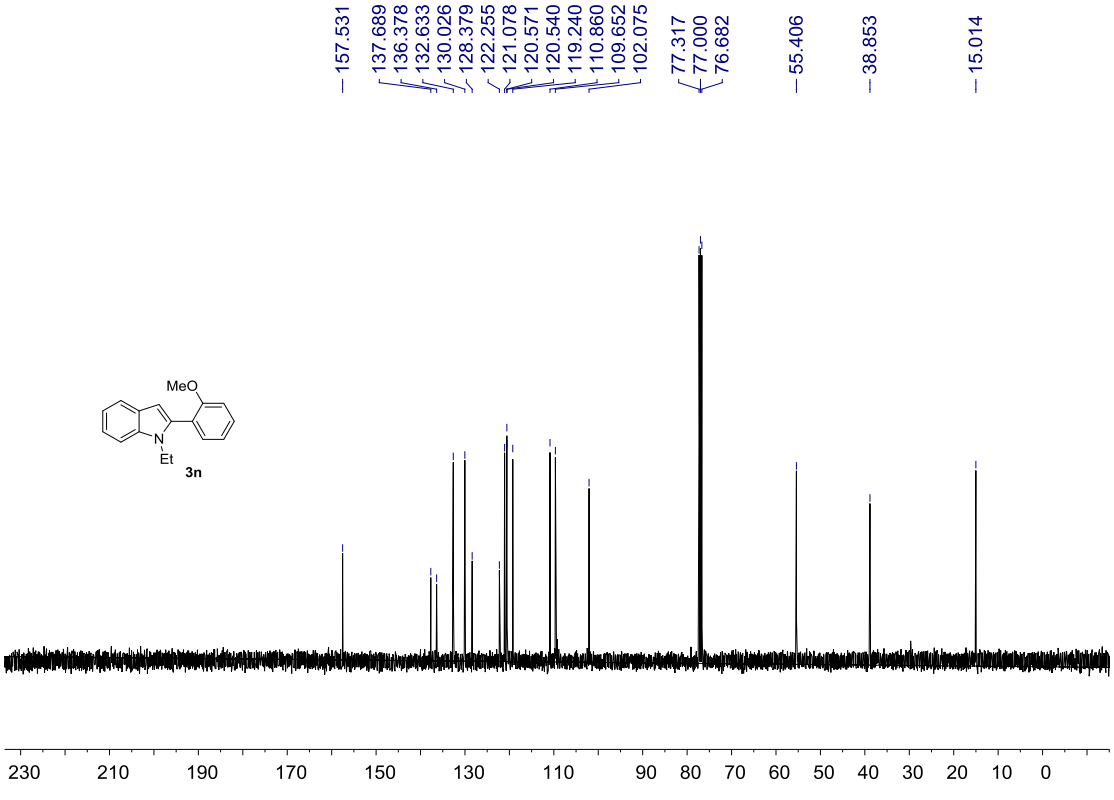

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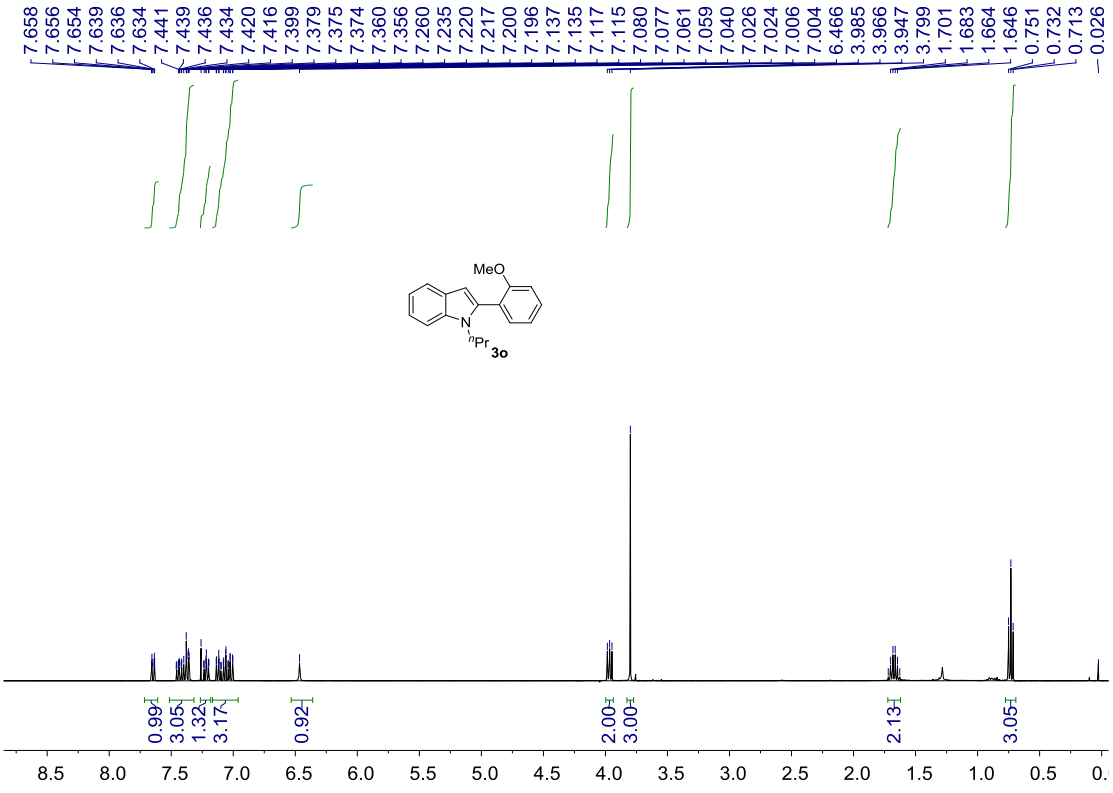

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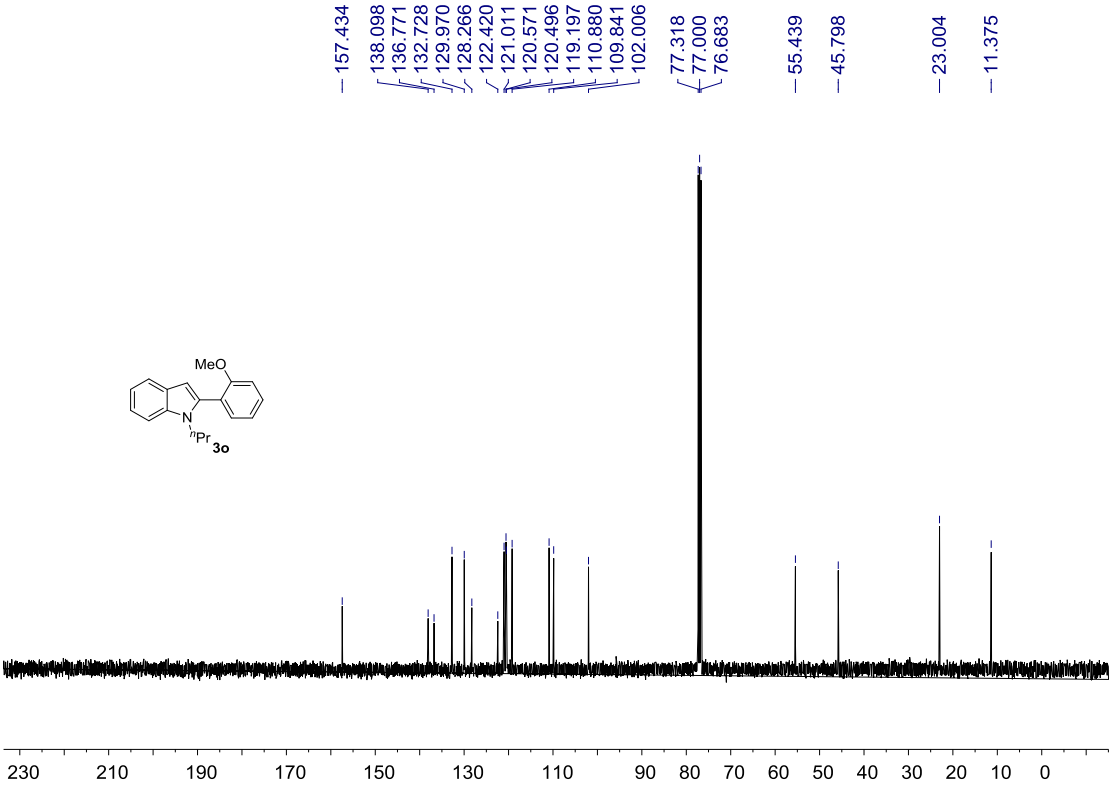

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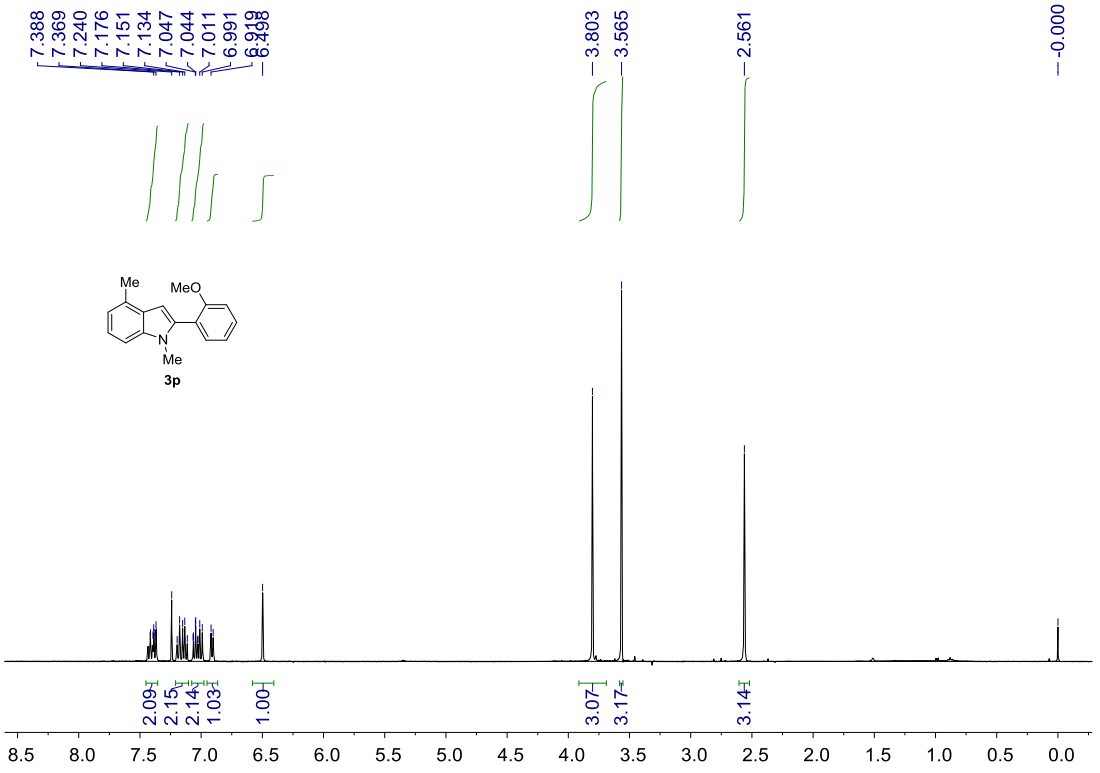

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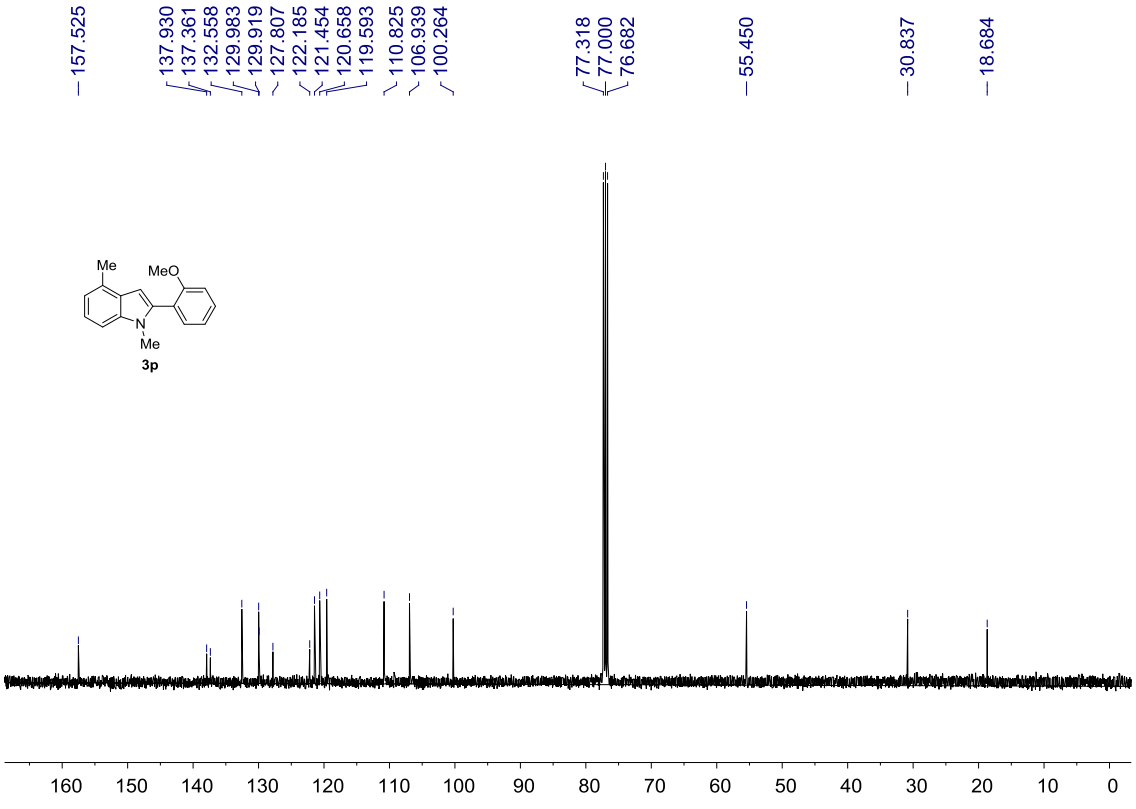

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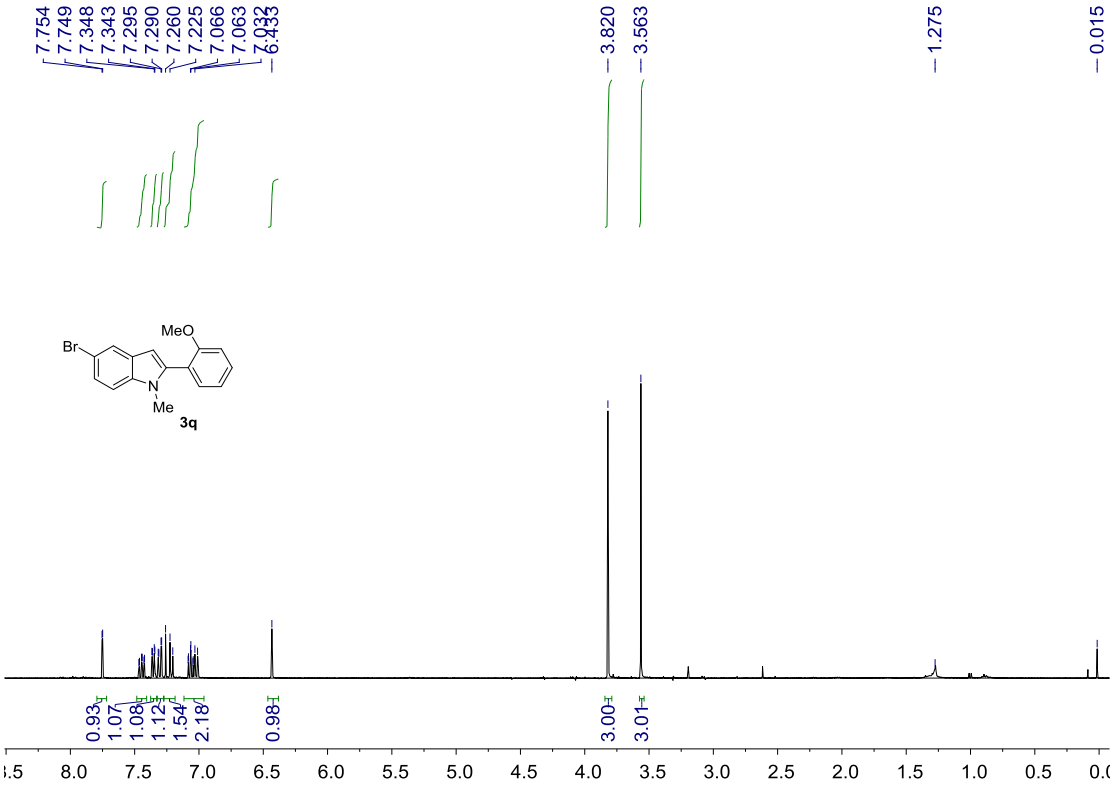

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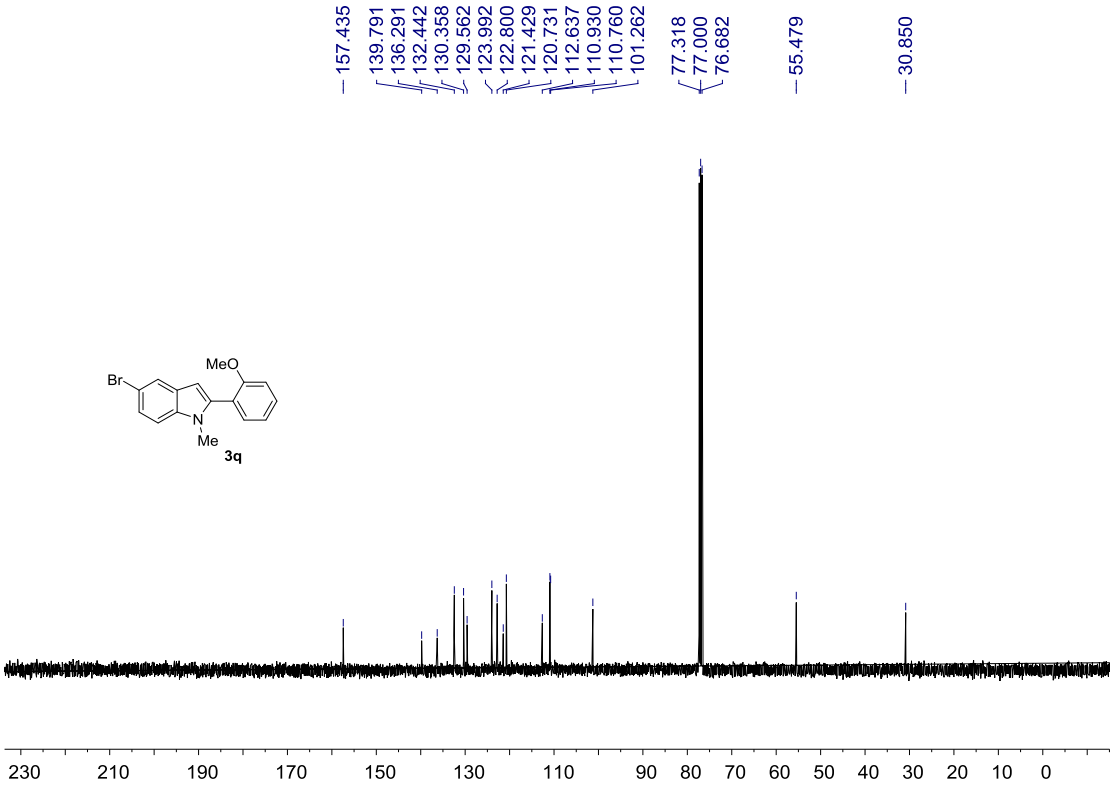

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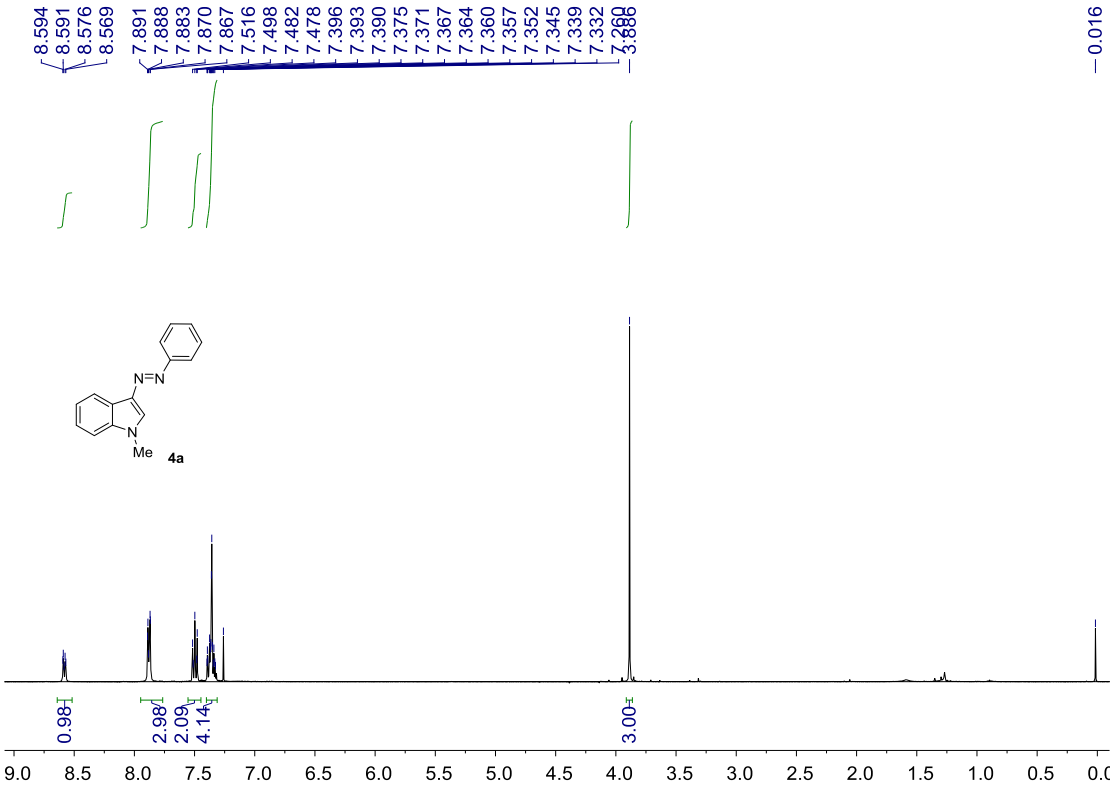

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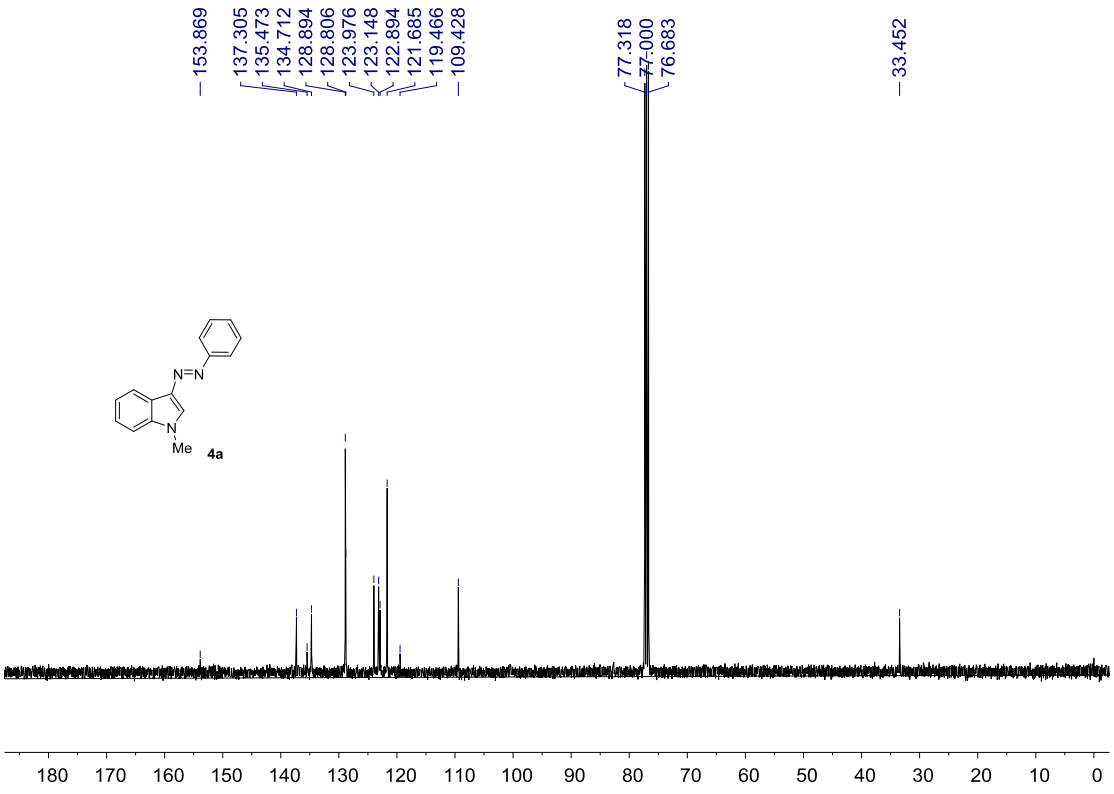

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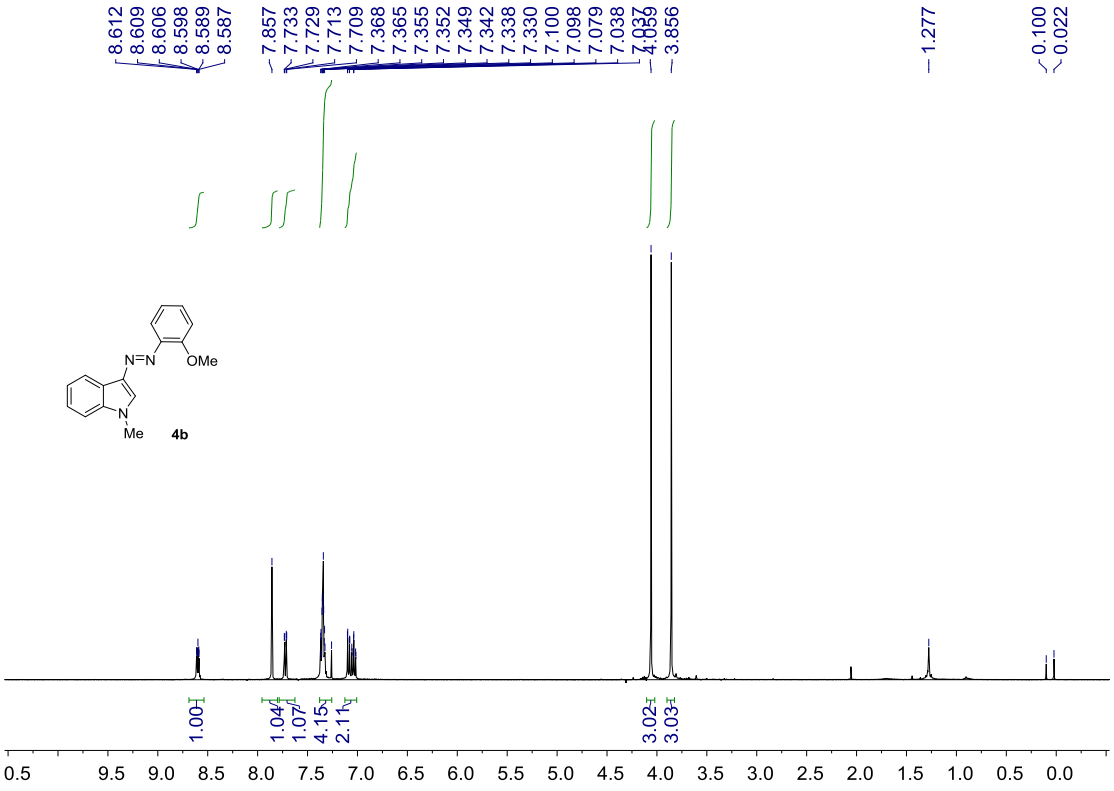

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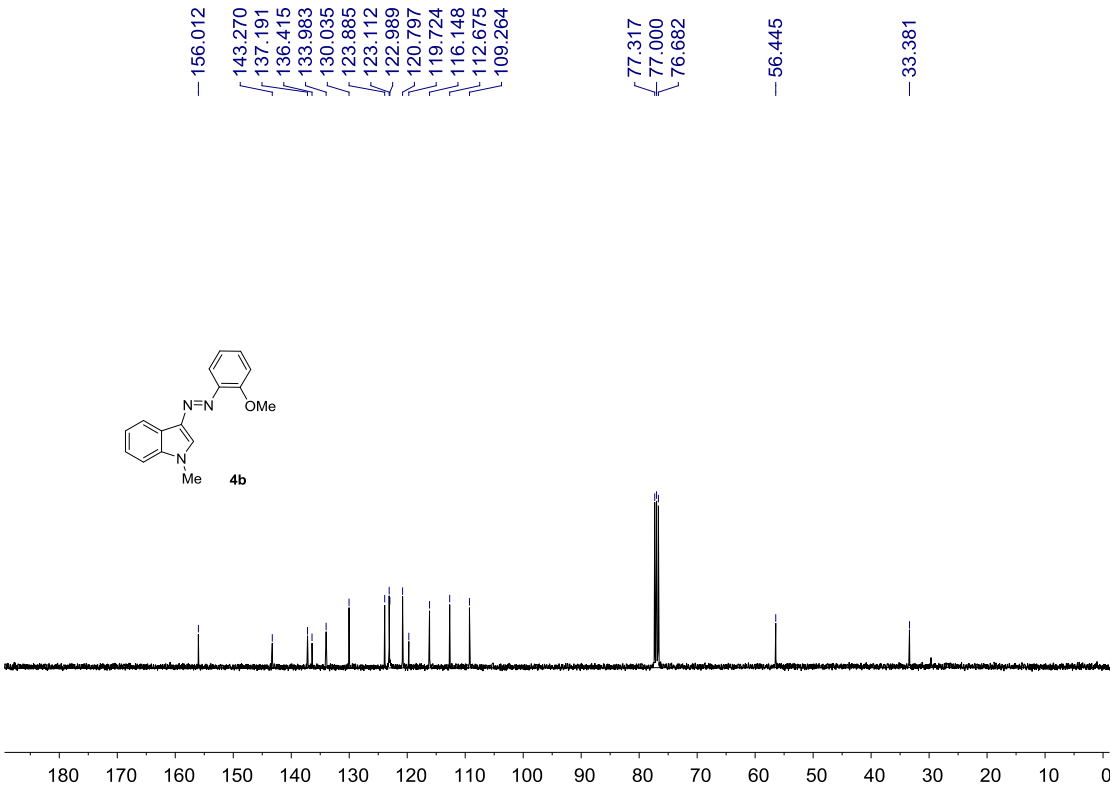

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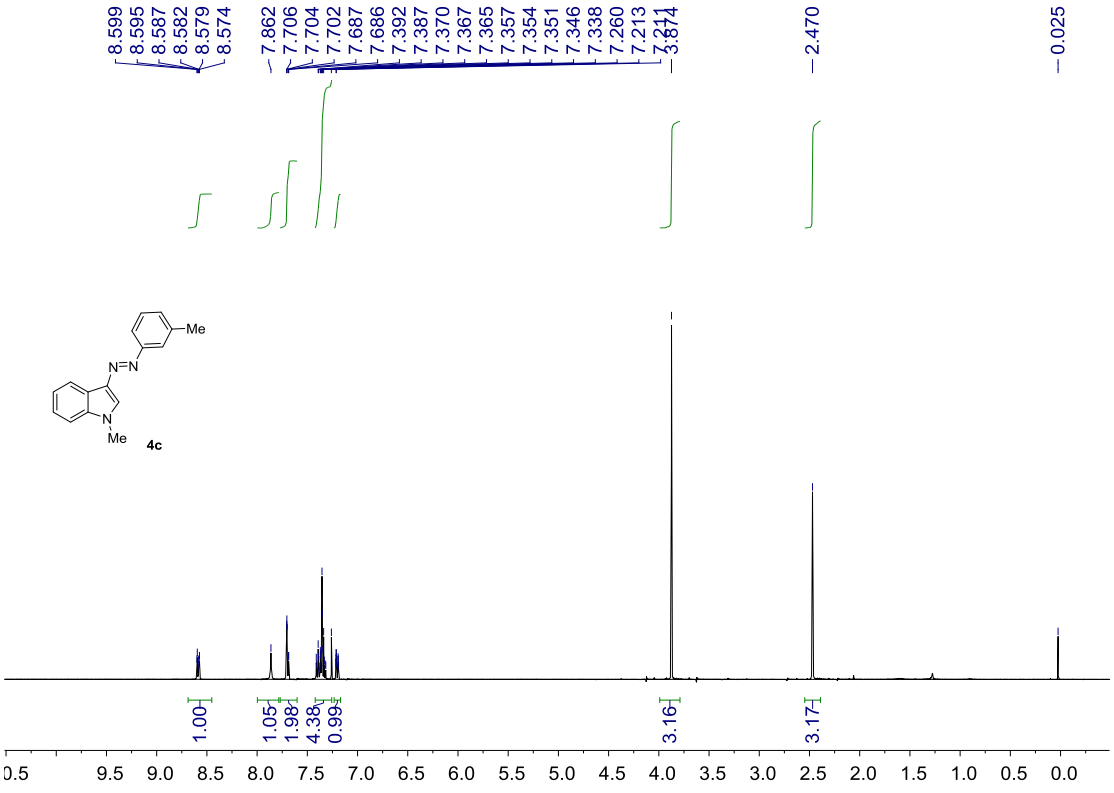

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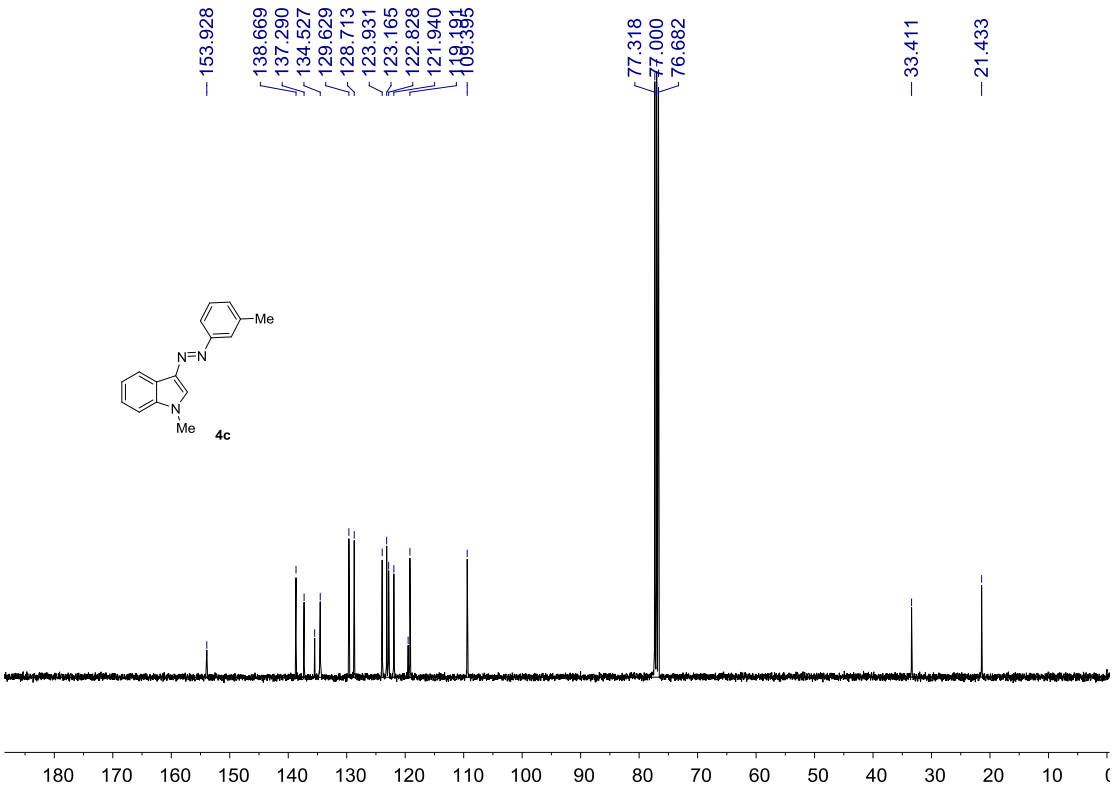

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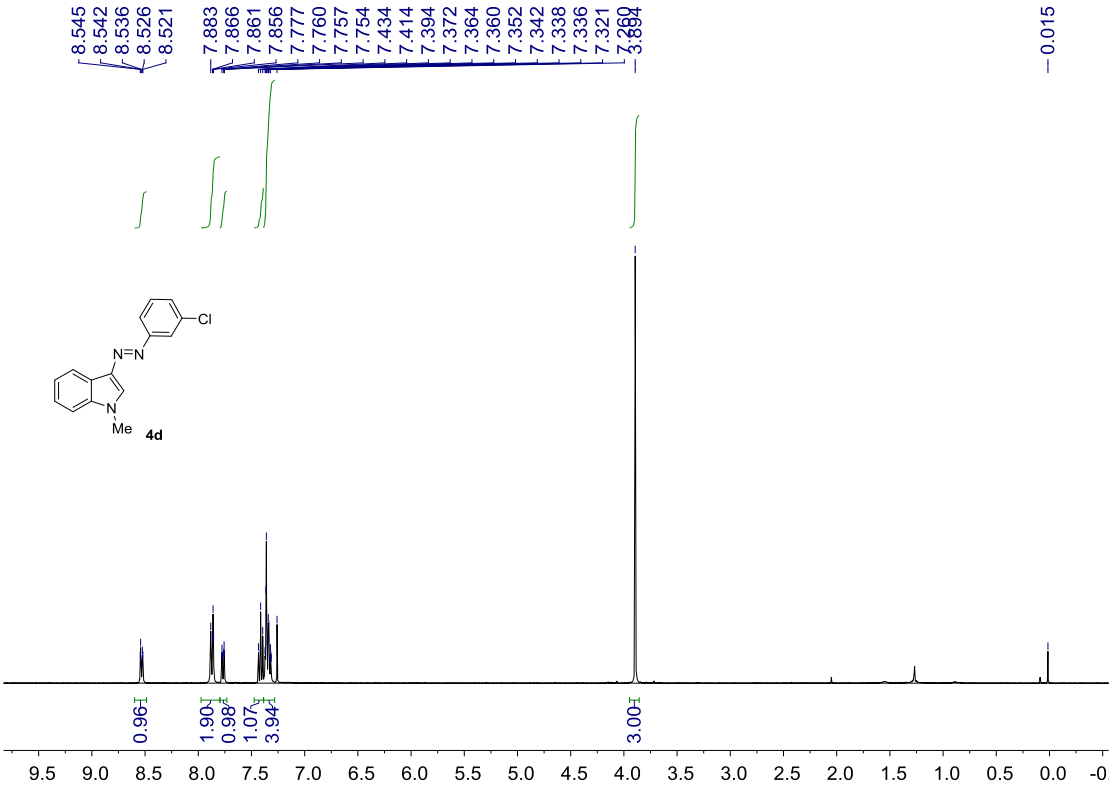

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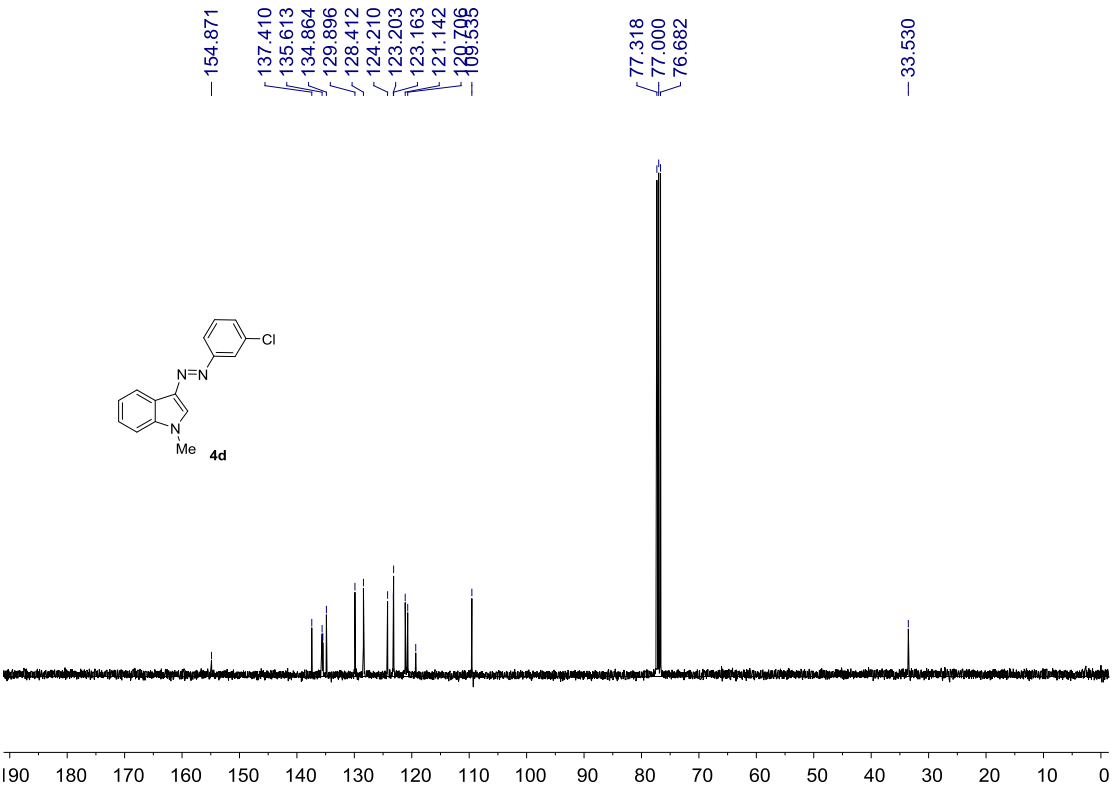

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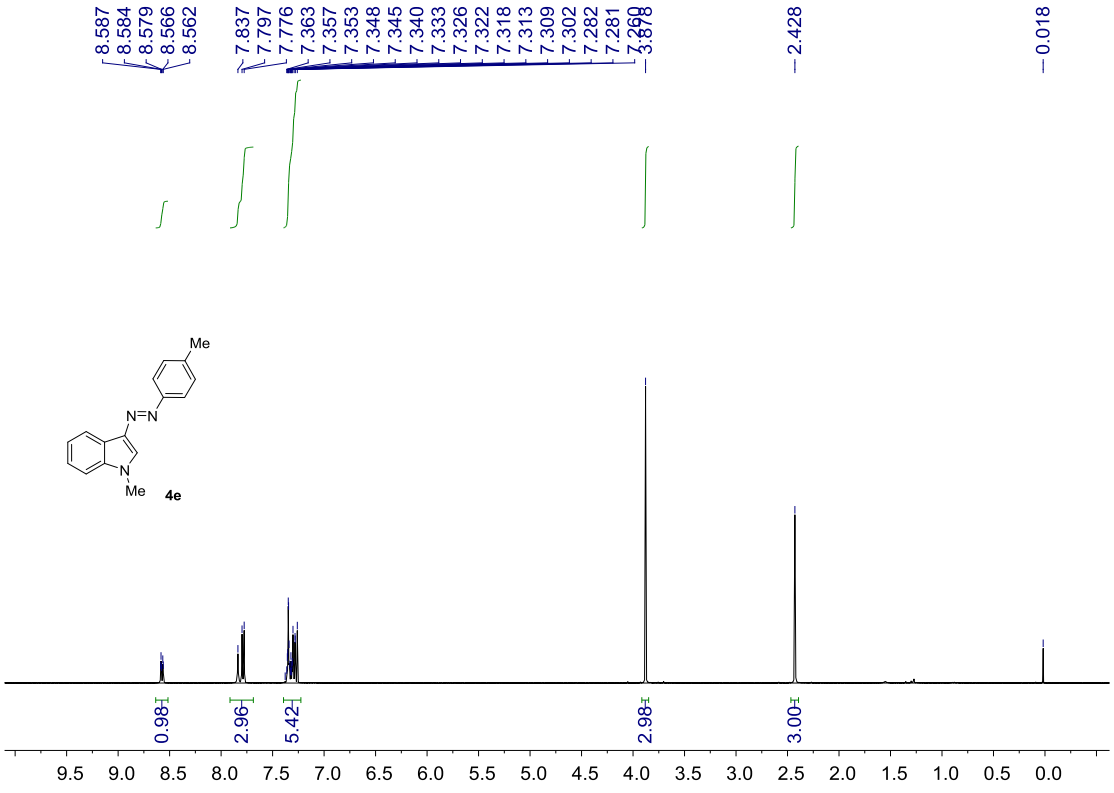

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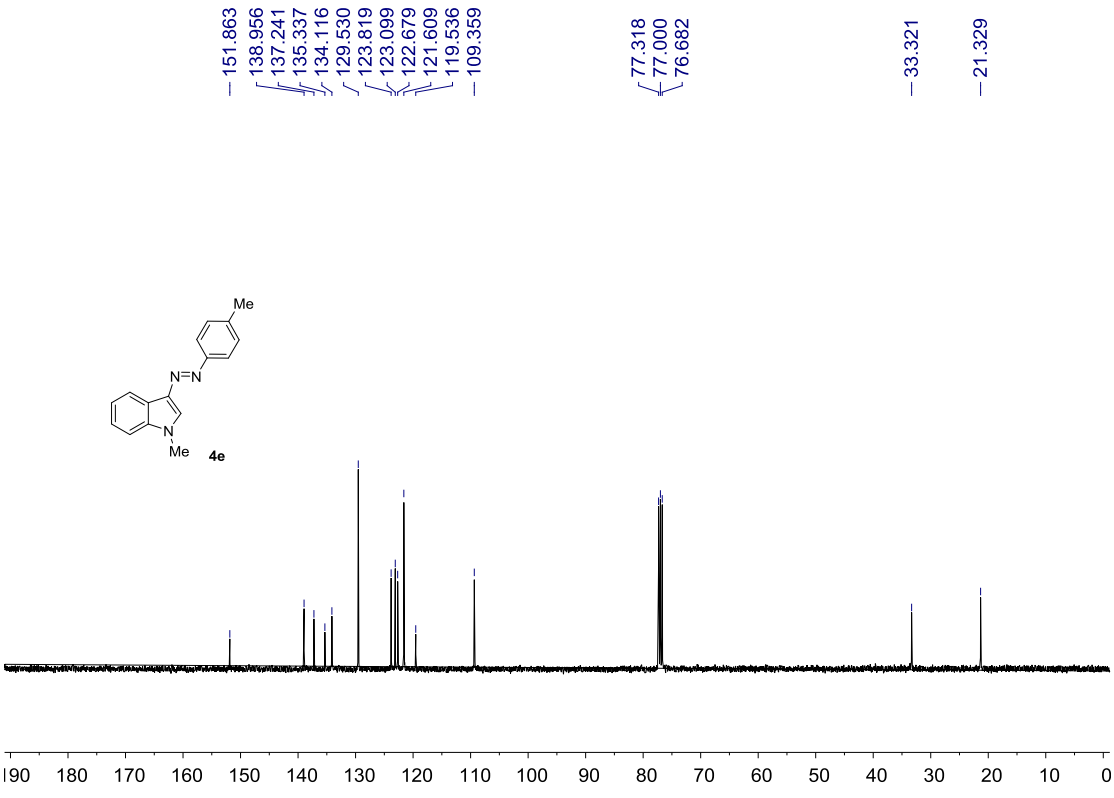

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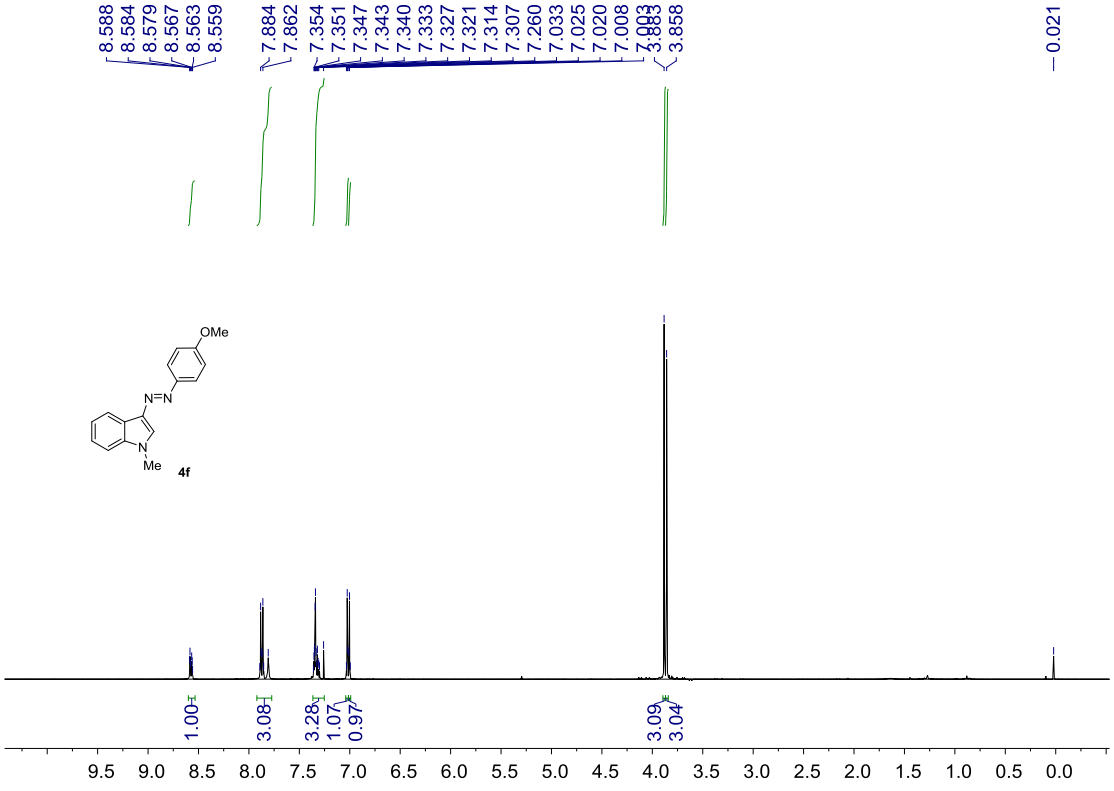

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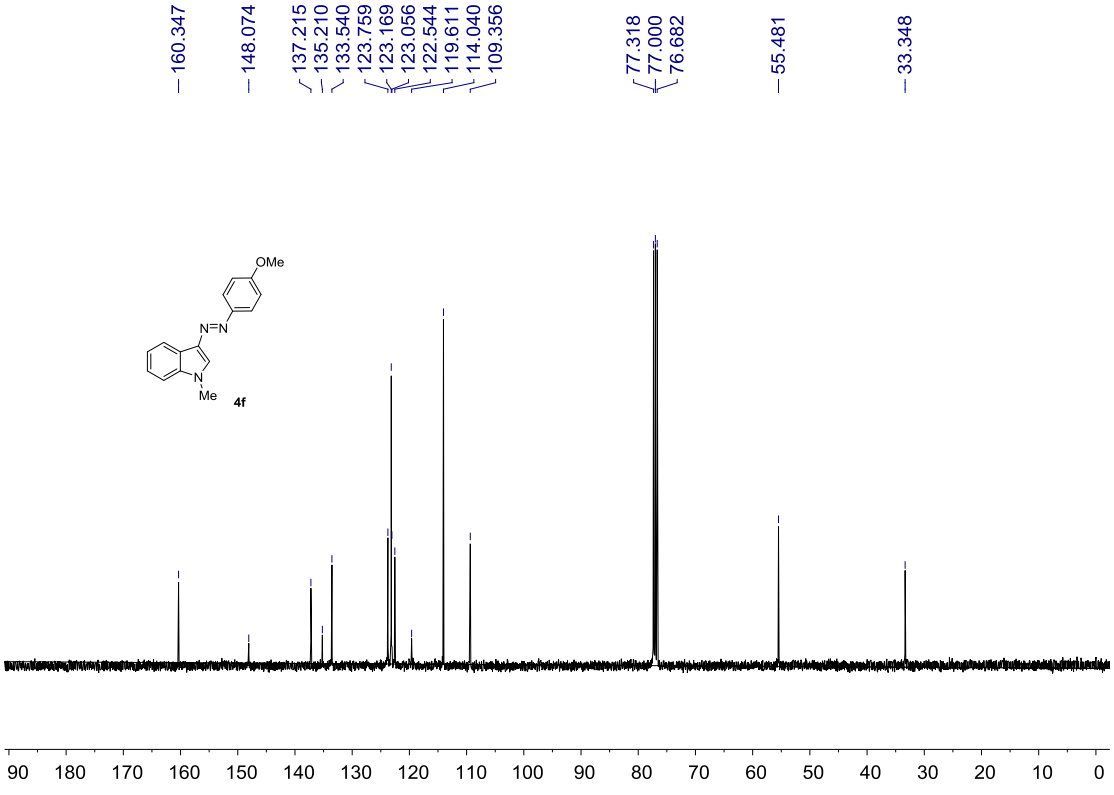

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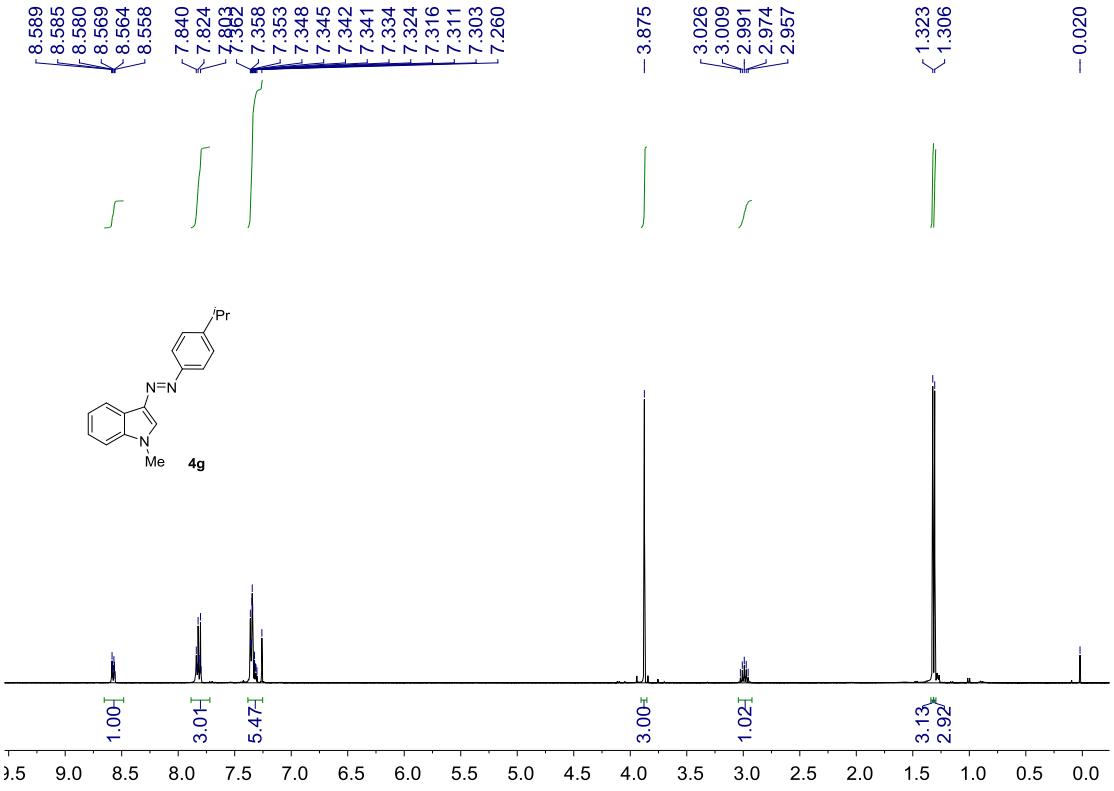

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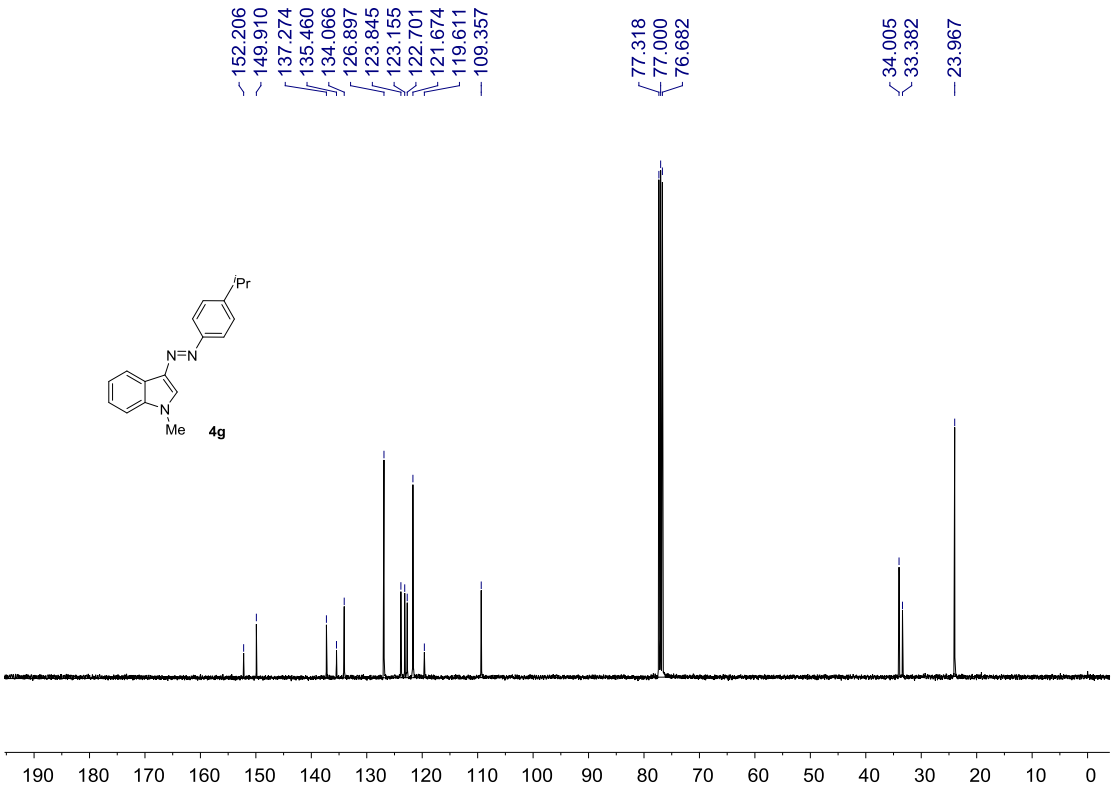

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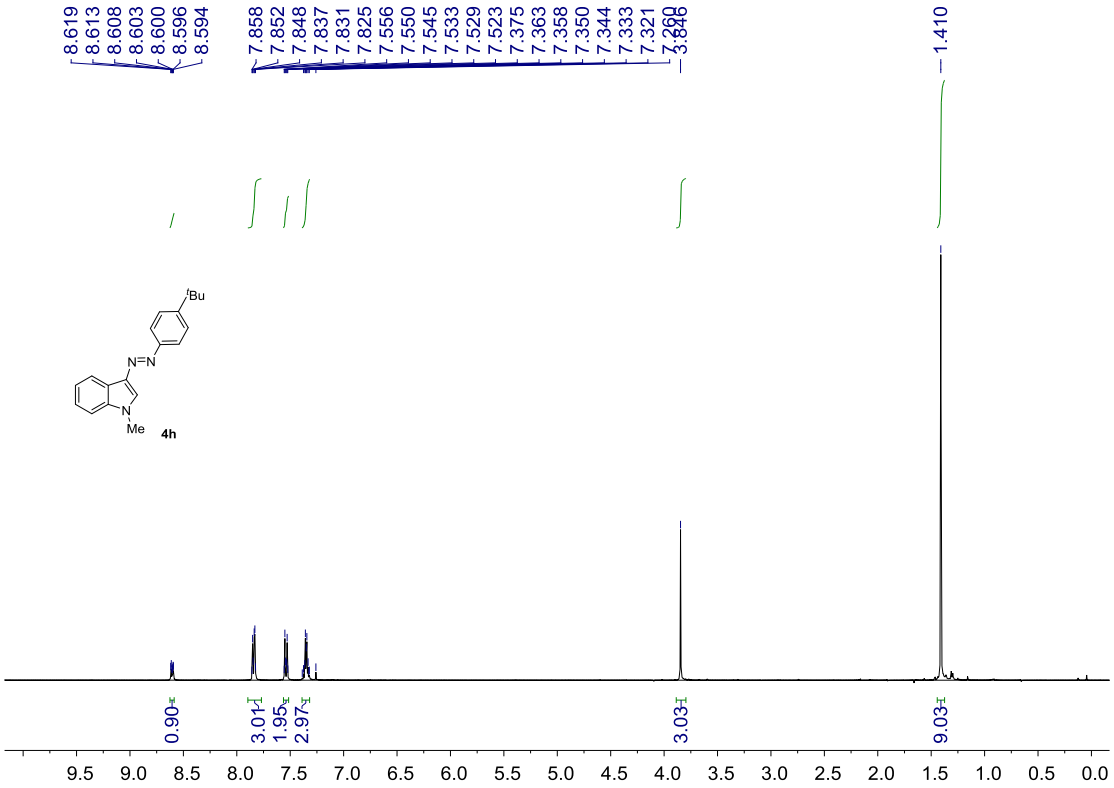

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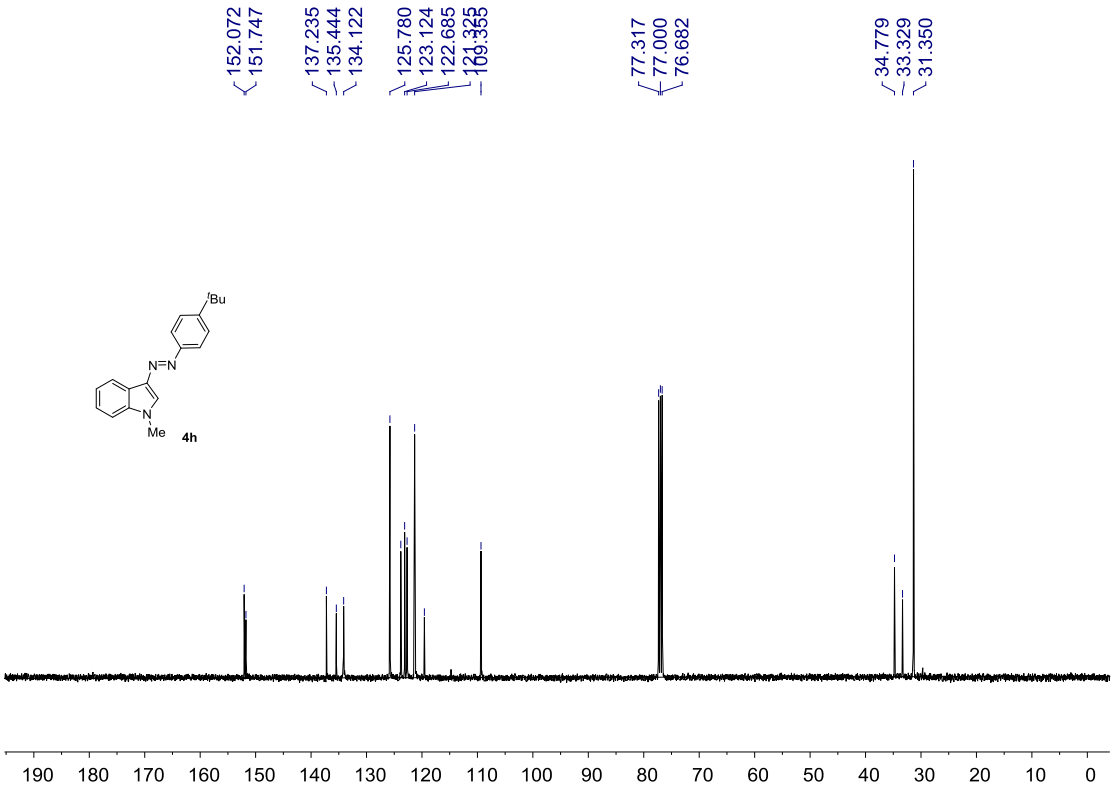

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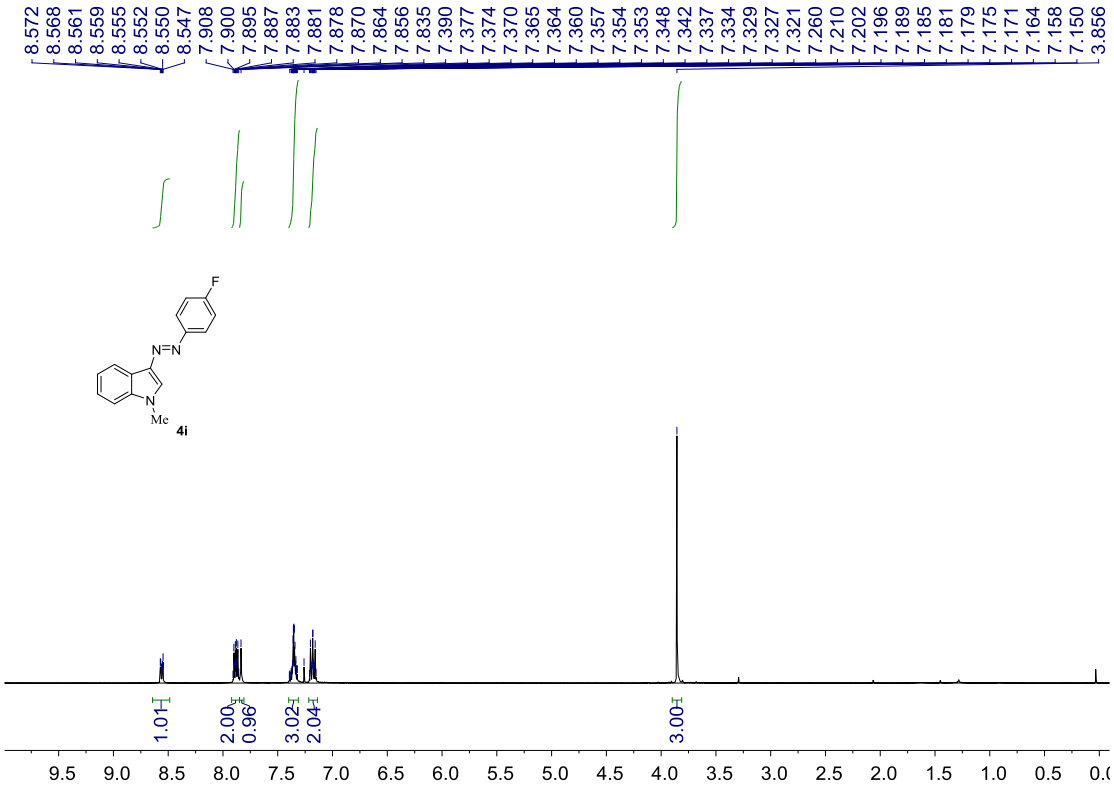

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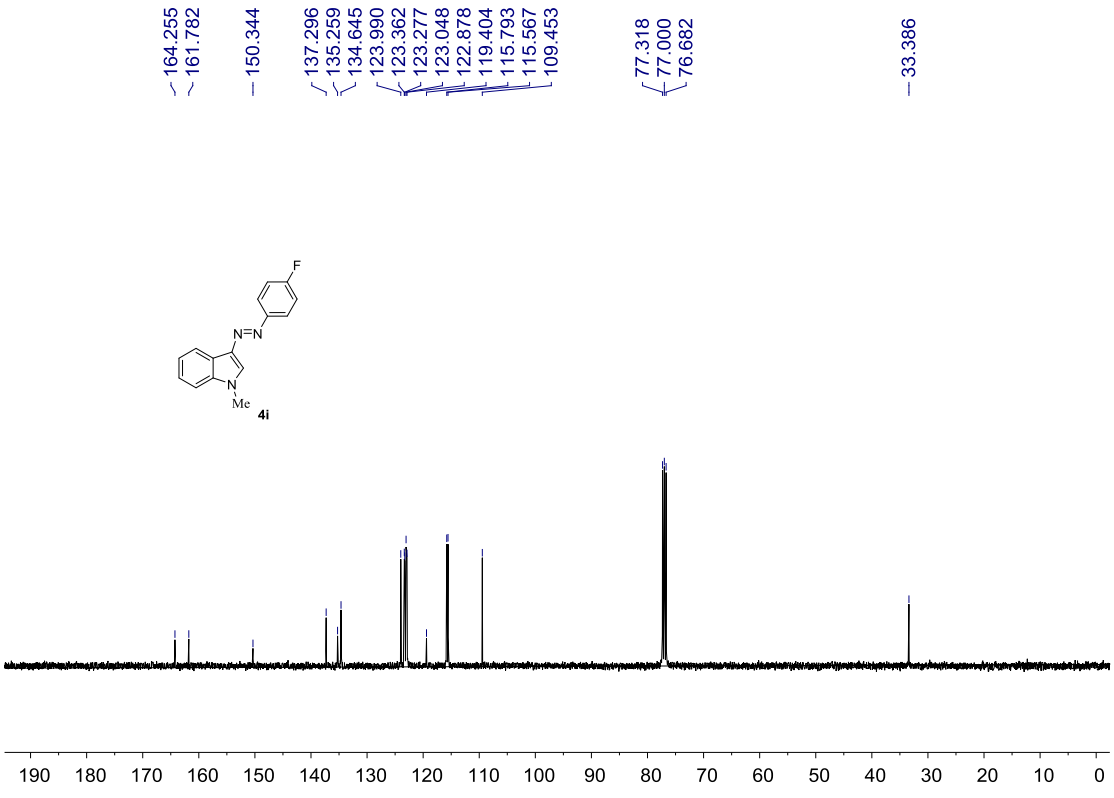

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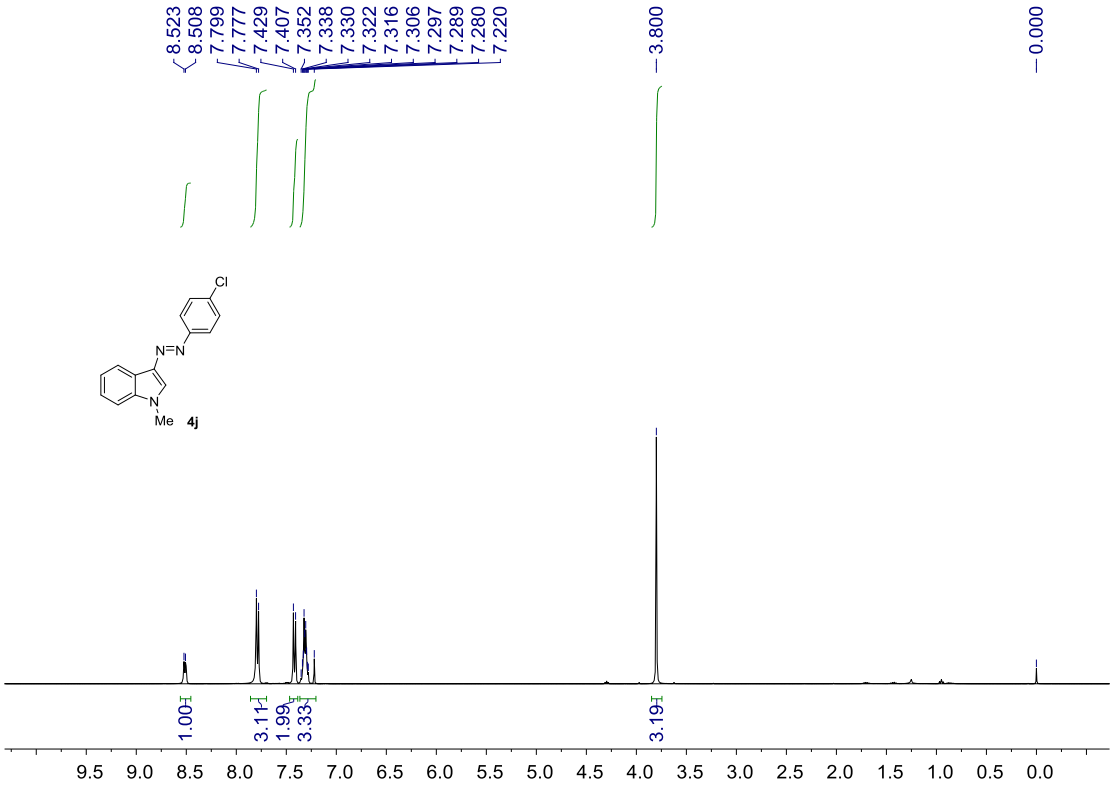

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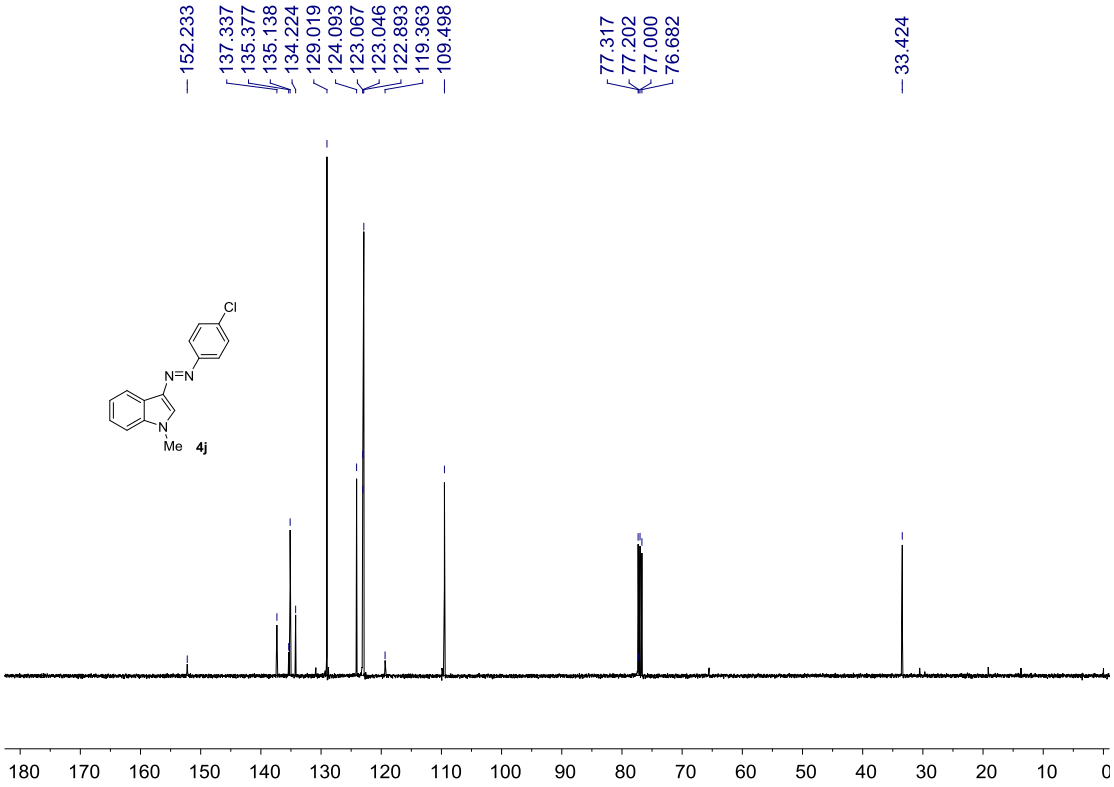

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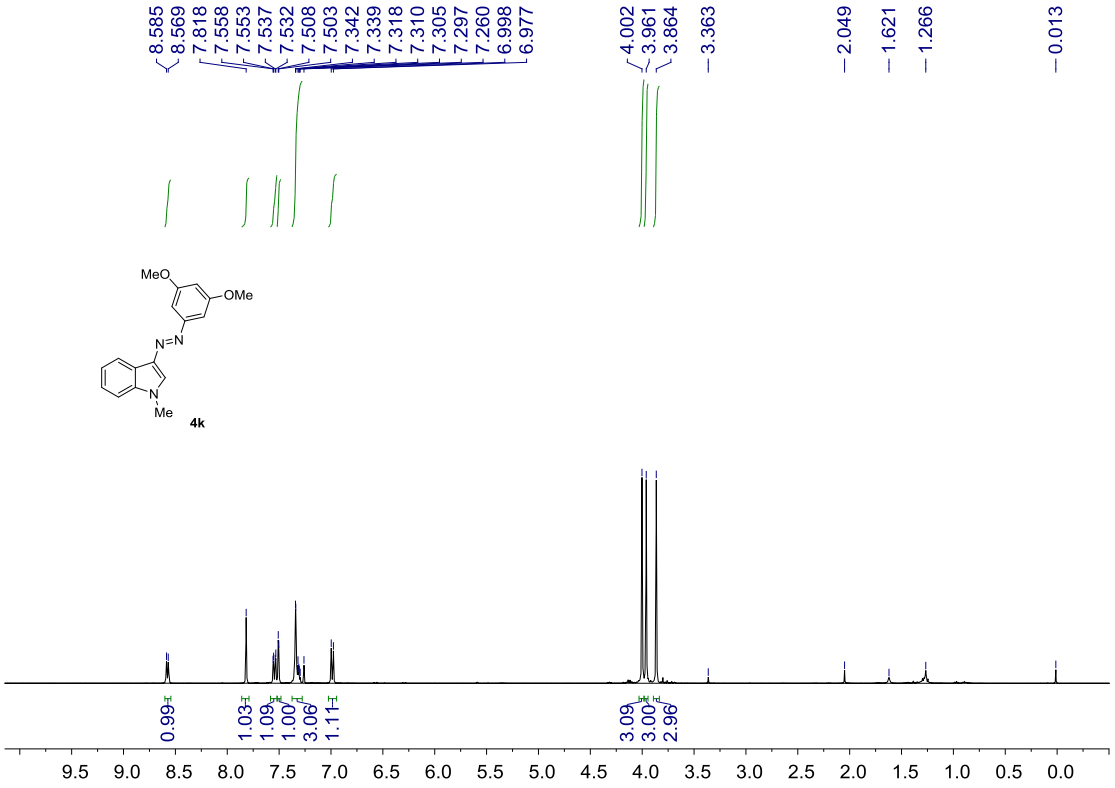

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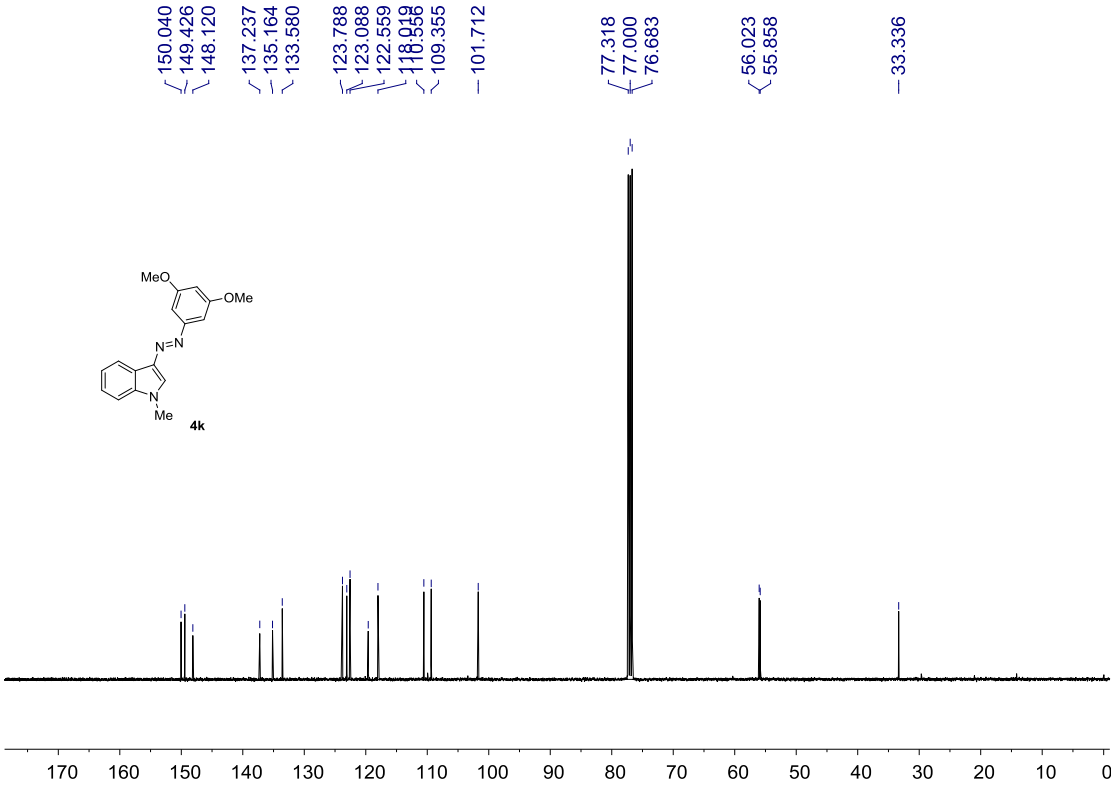

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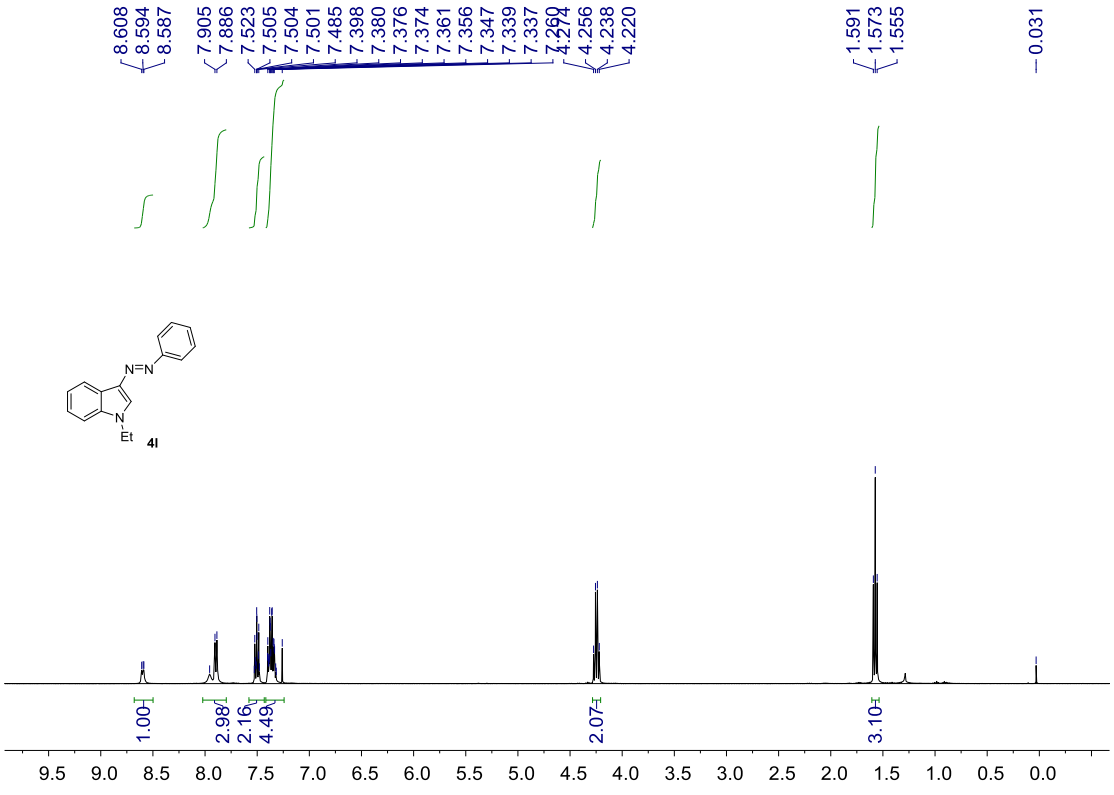

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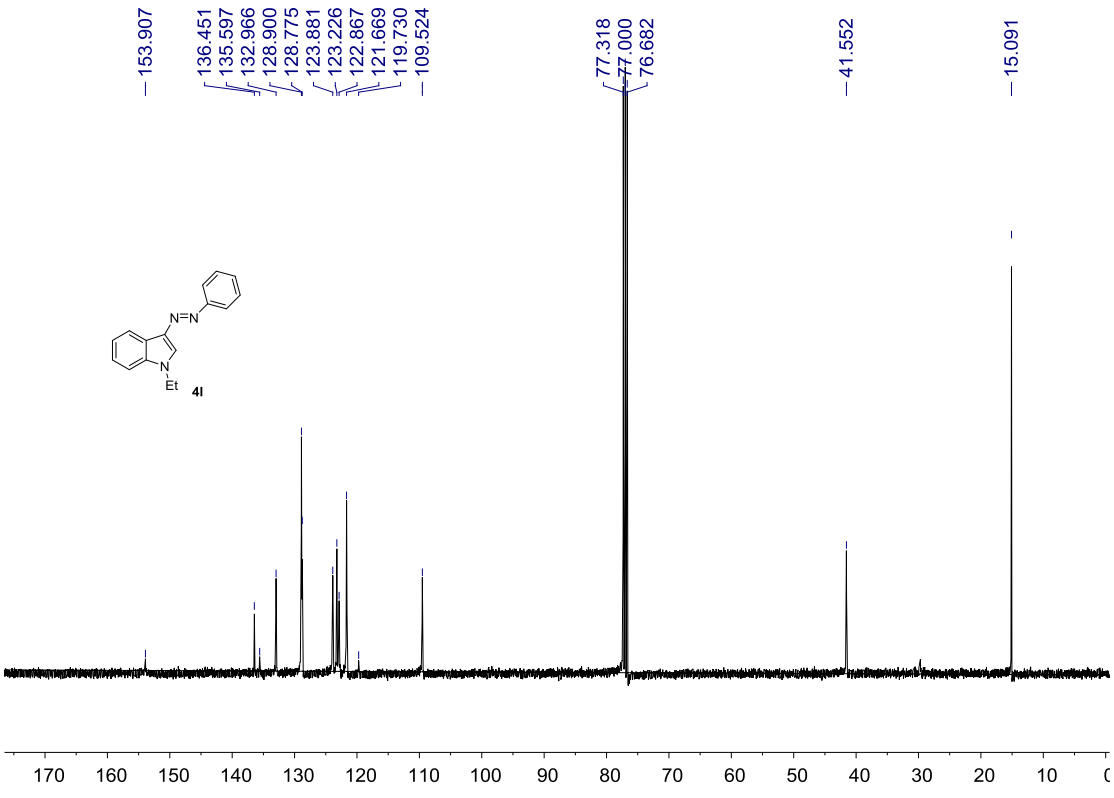

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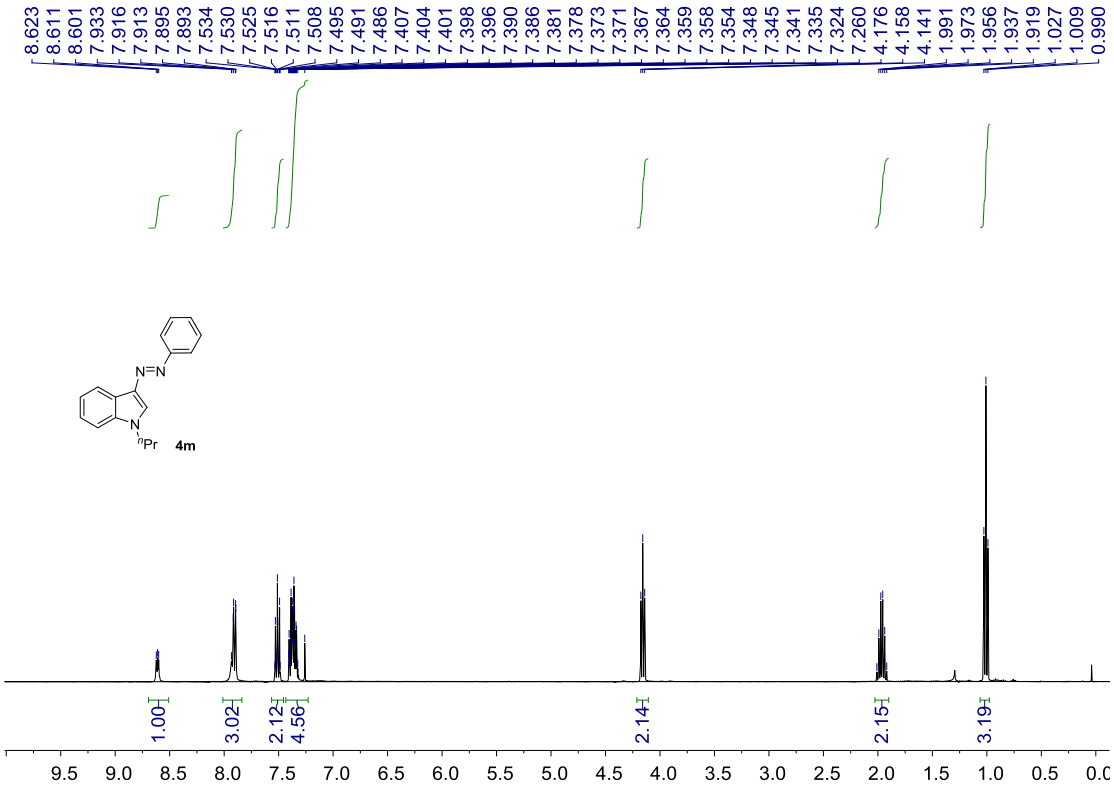

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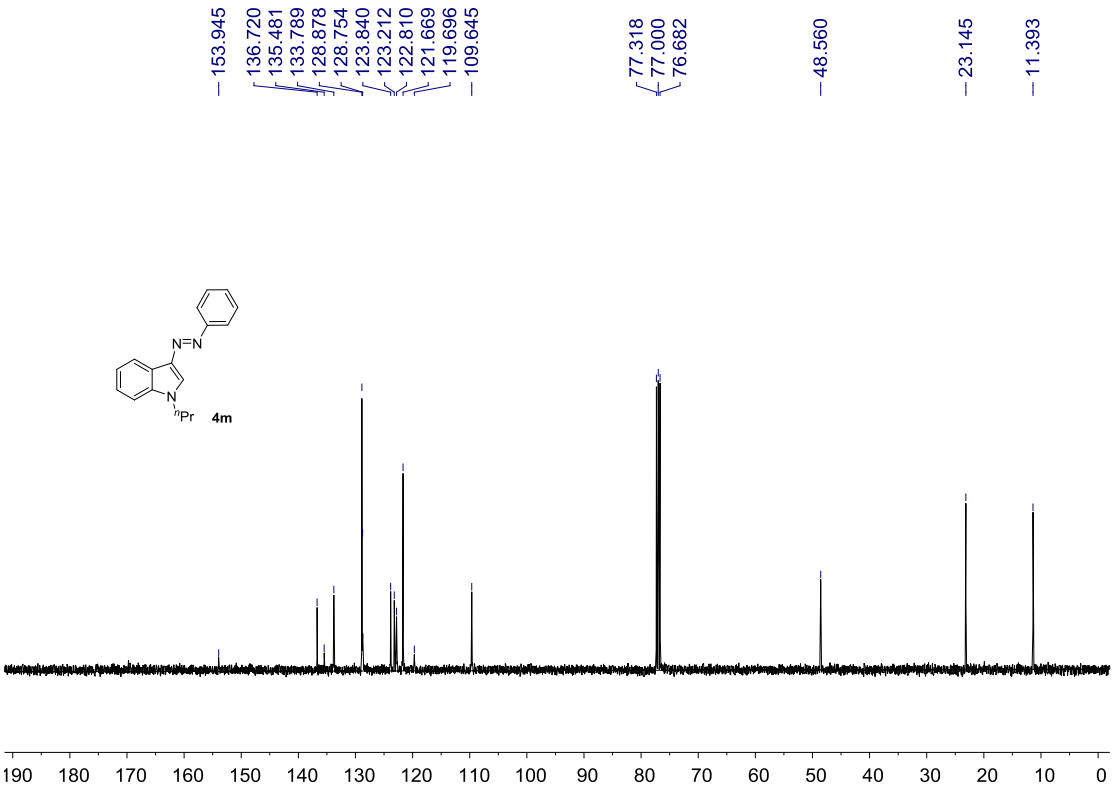
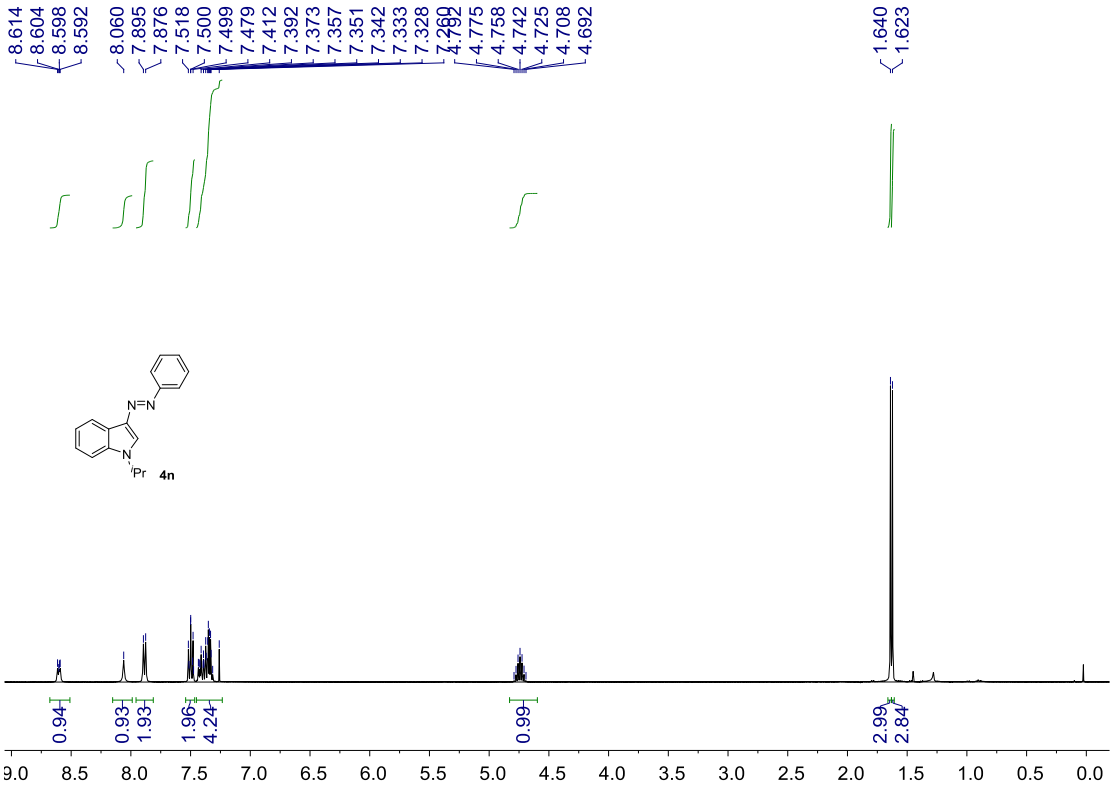
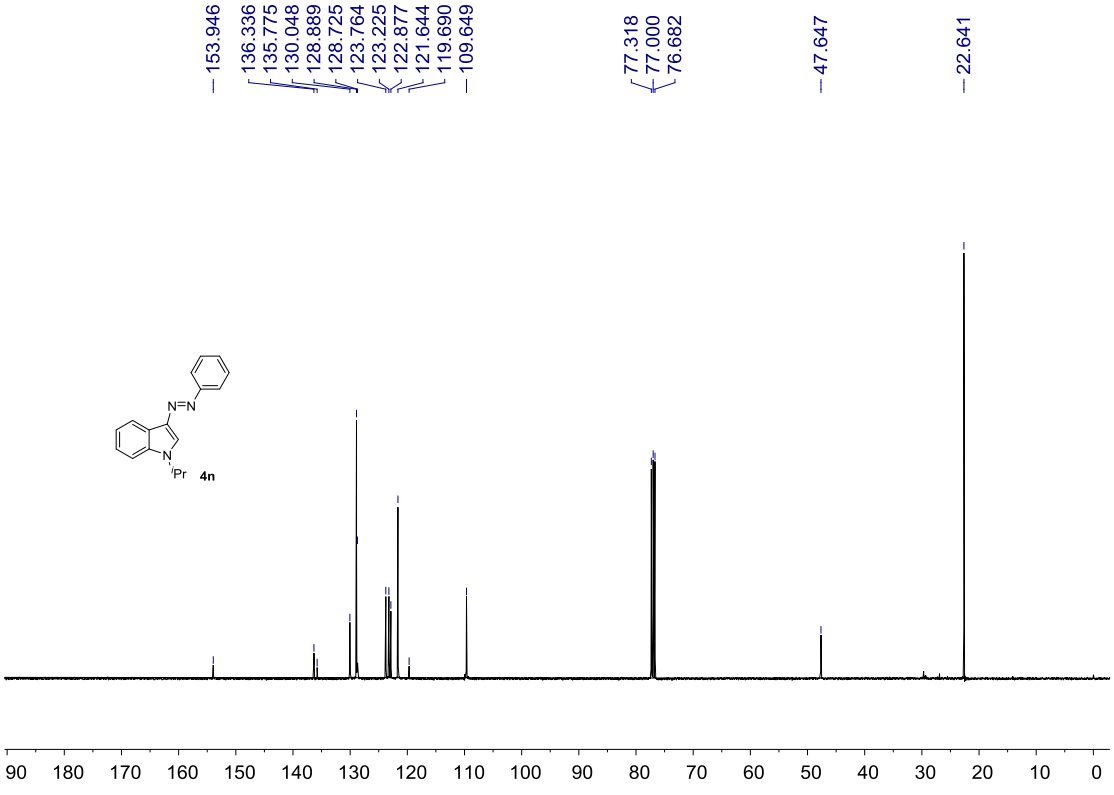


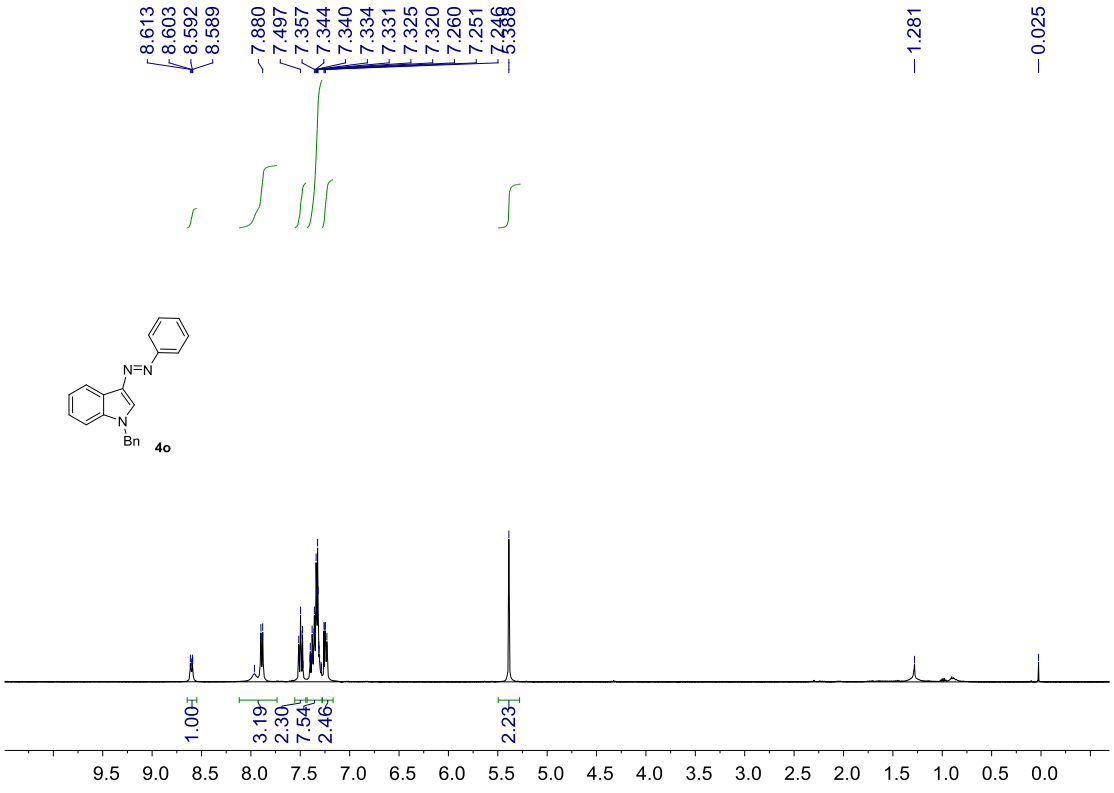
^{1}H NMR



^{13}C NMR



^{1}H NMR



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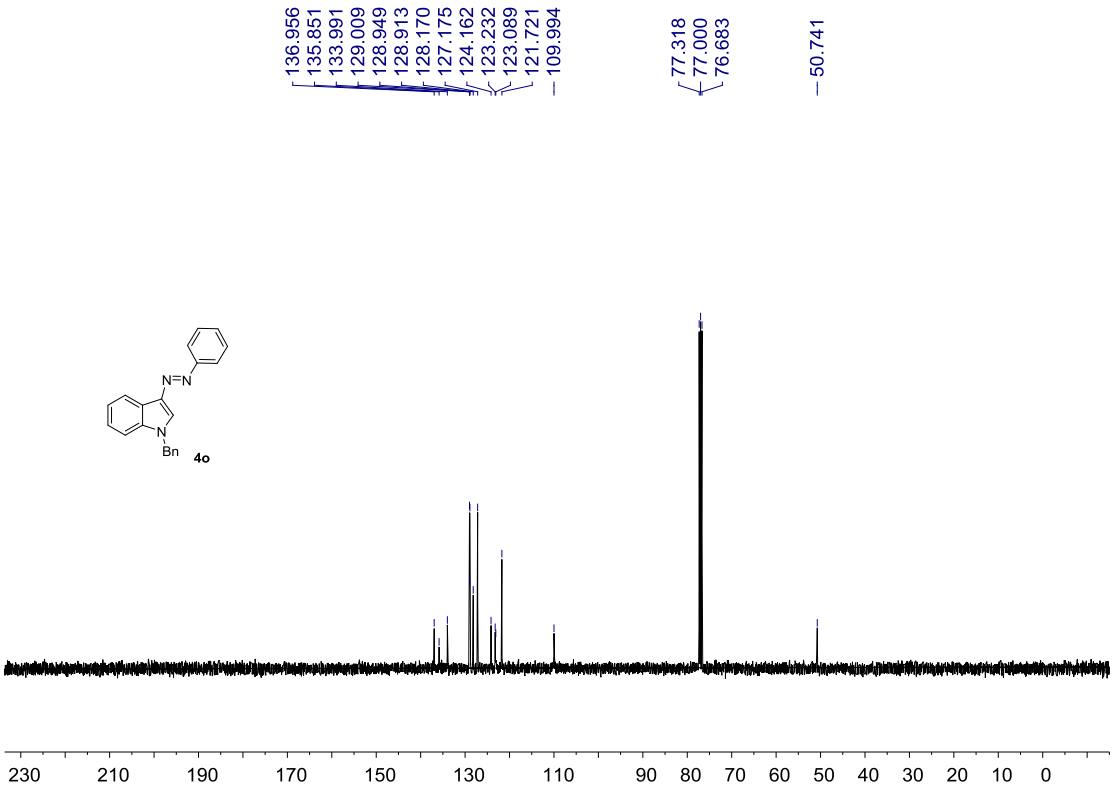

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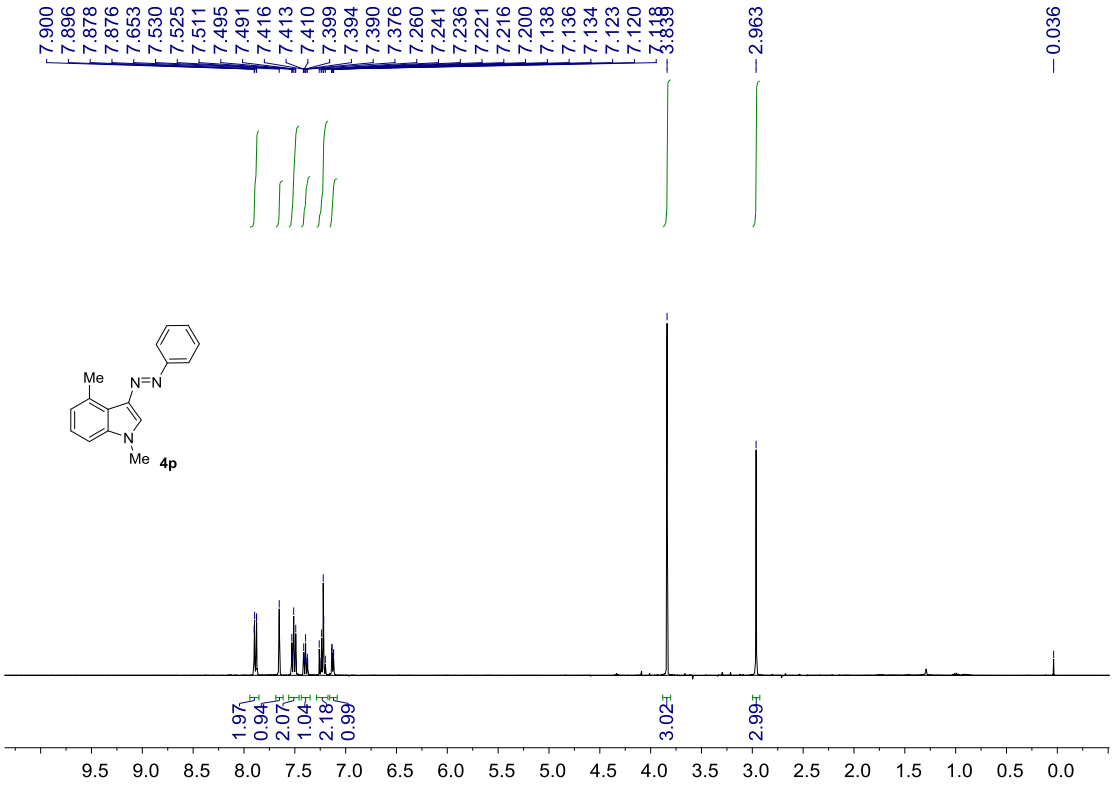

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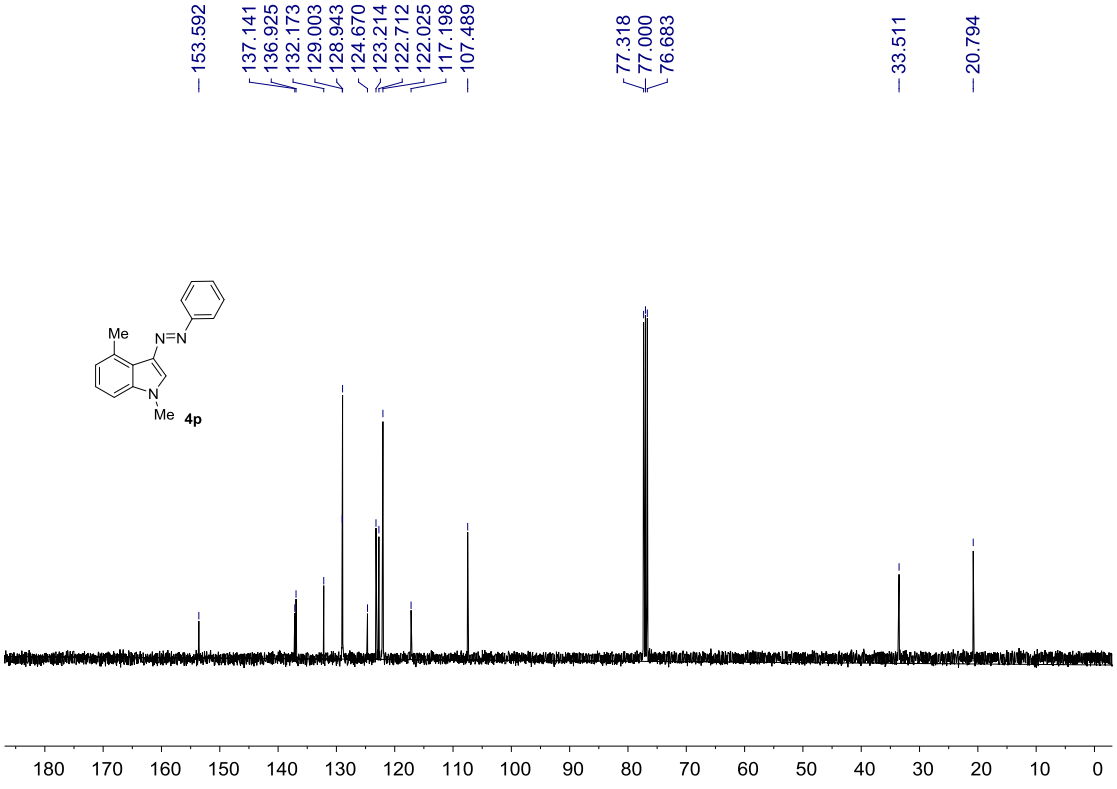

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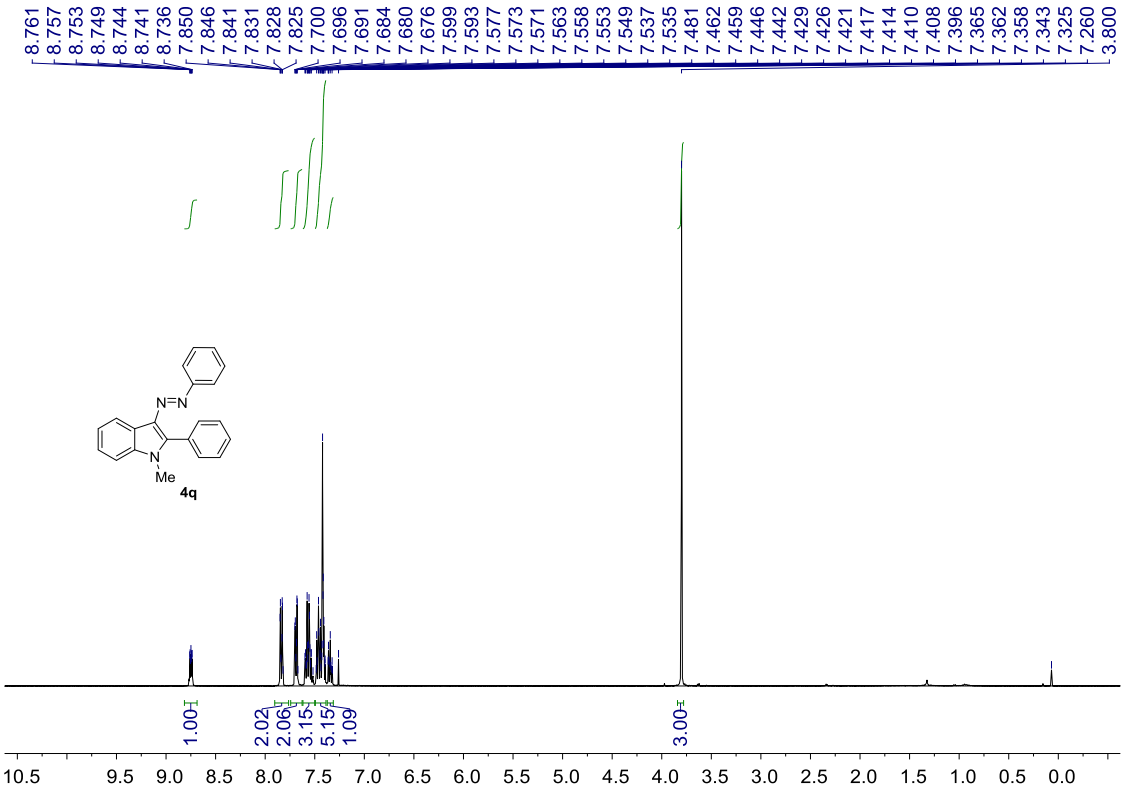

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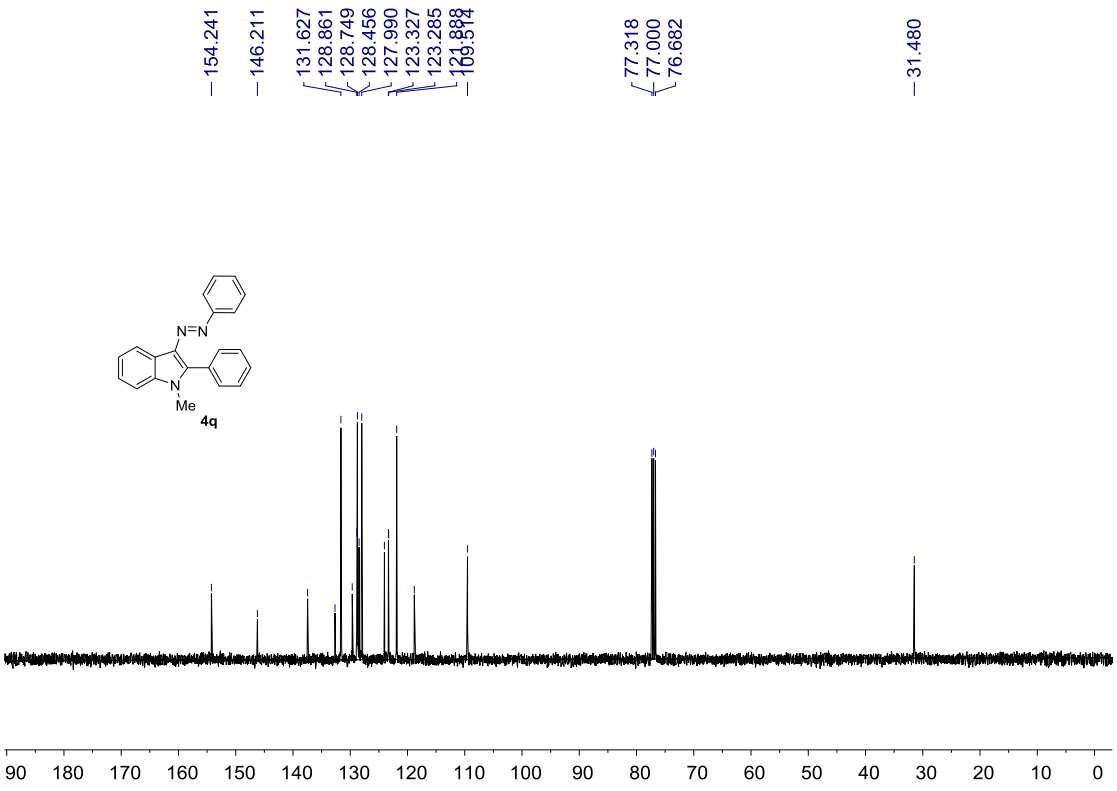

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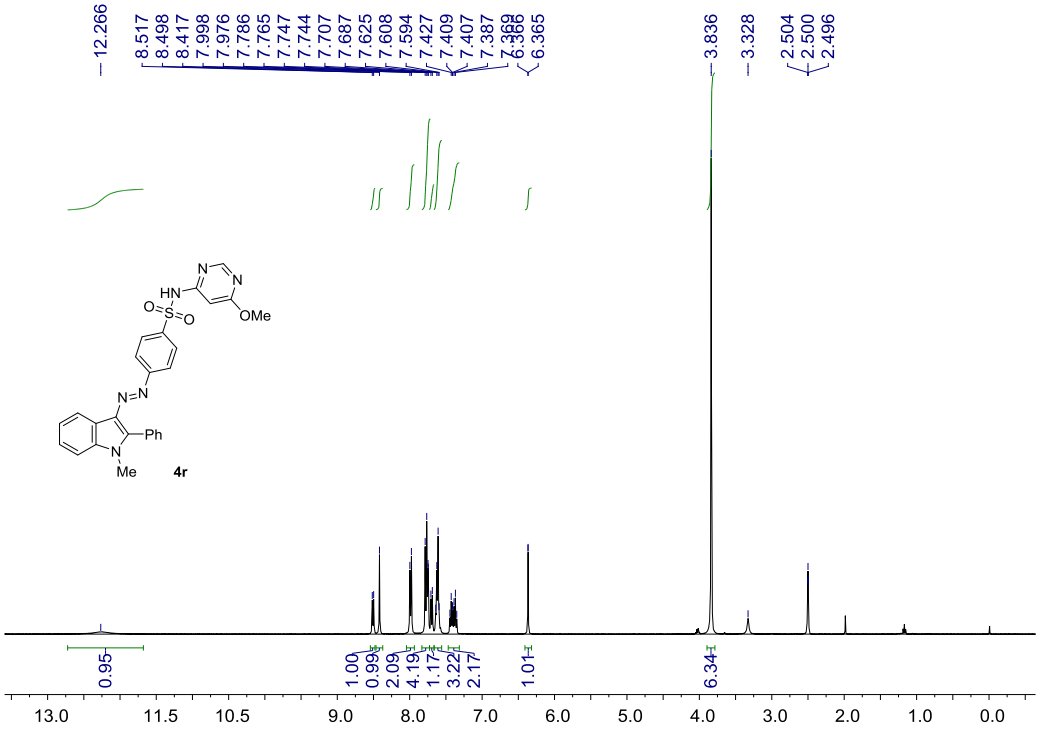

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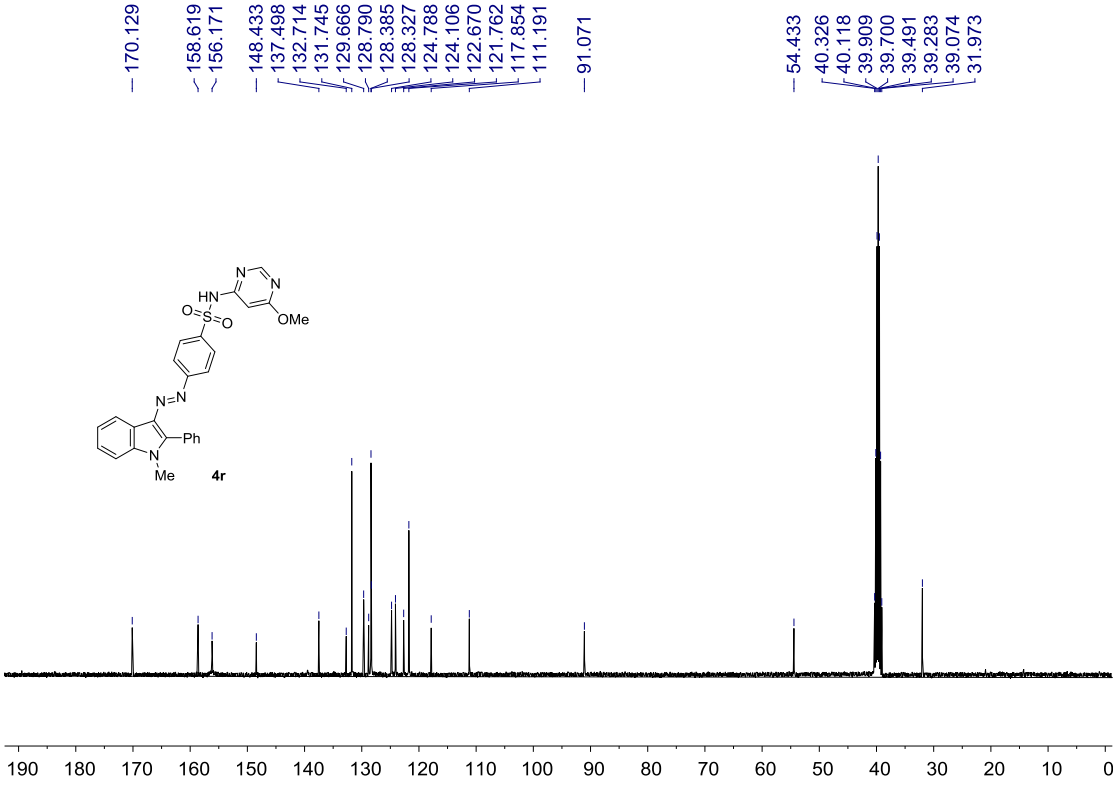

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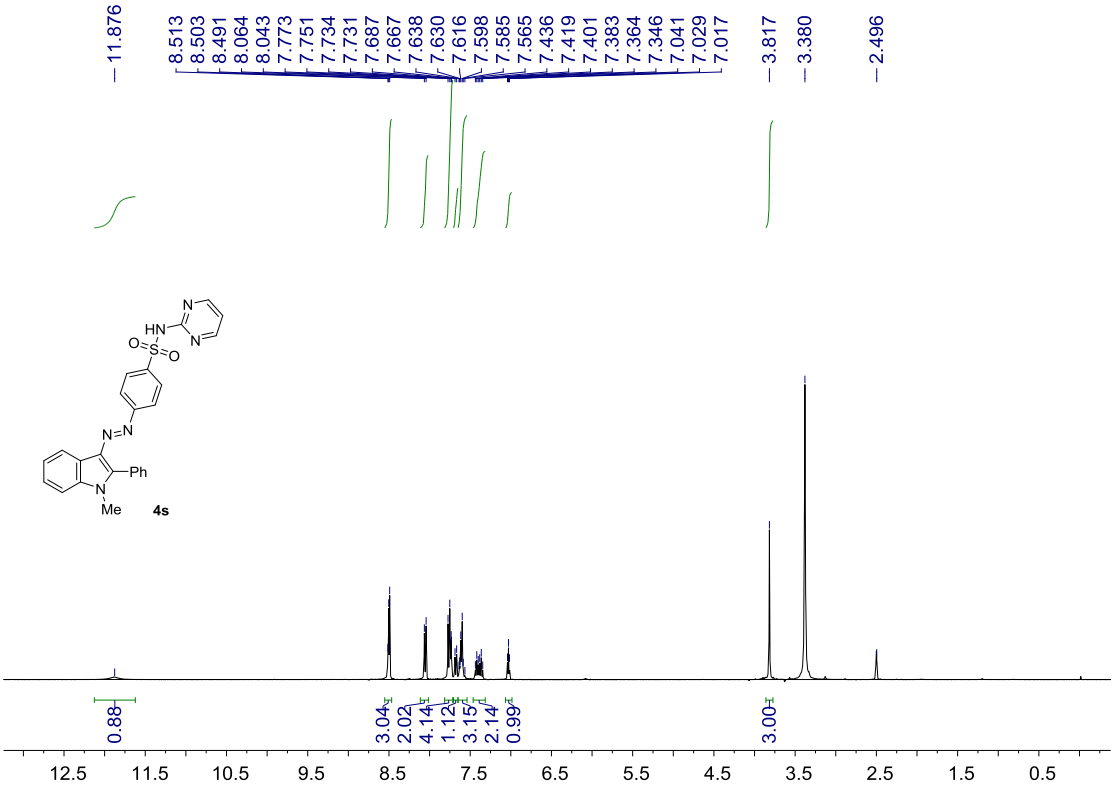

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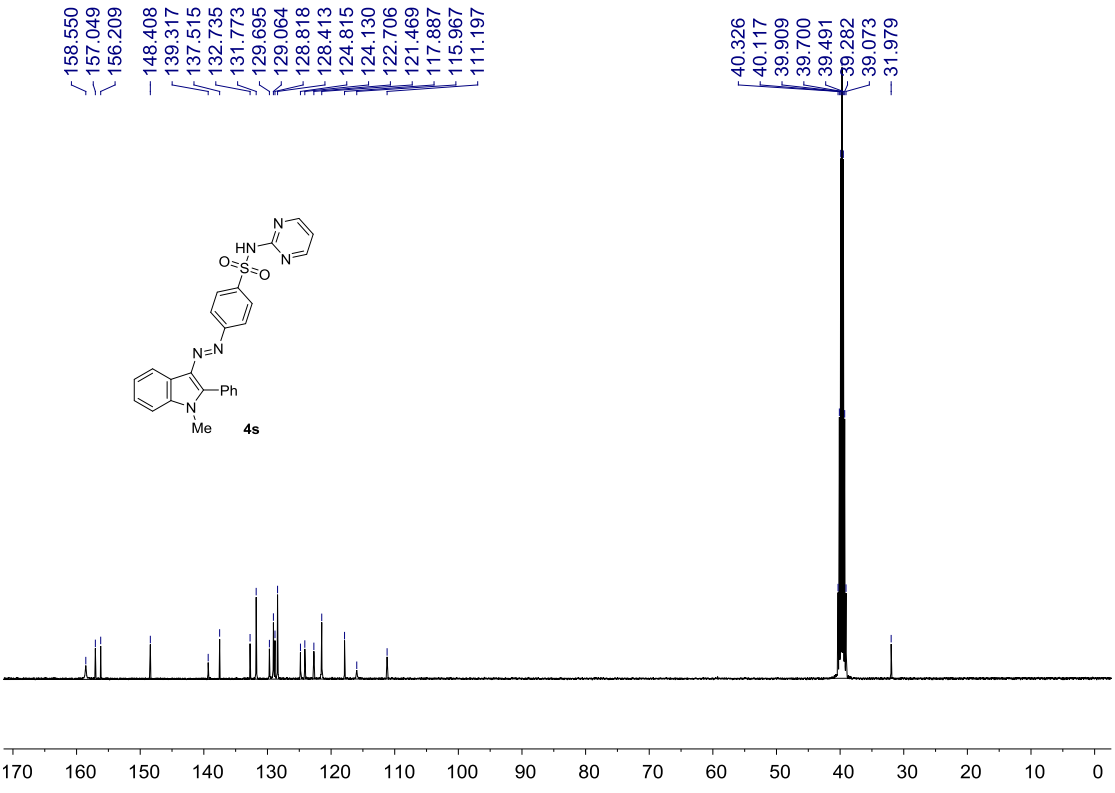

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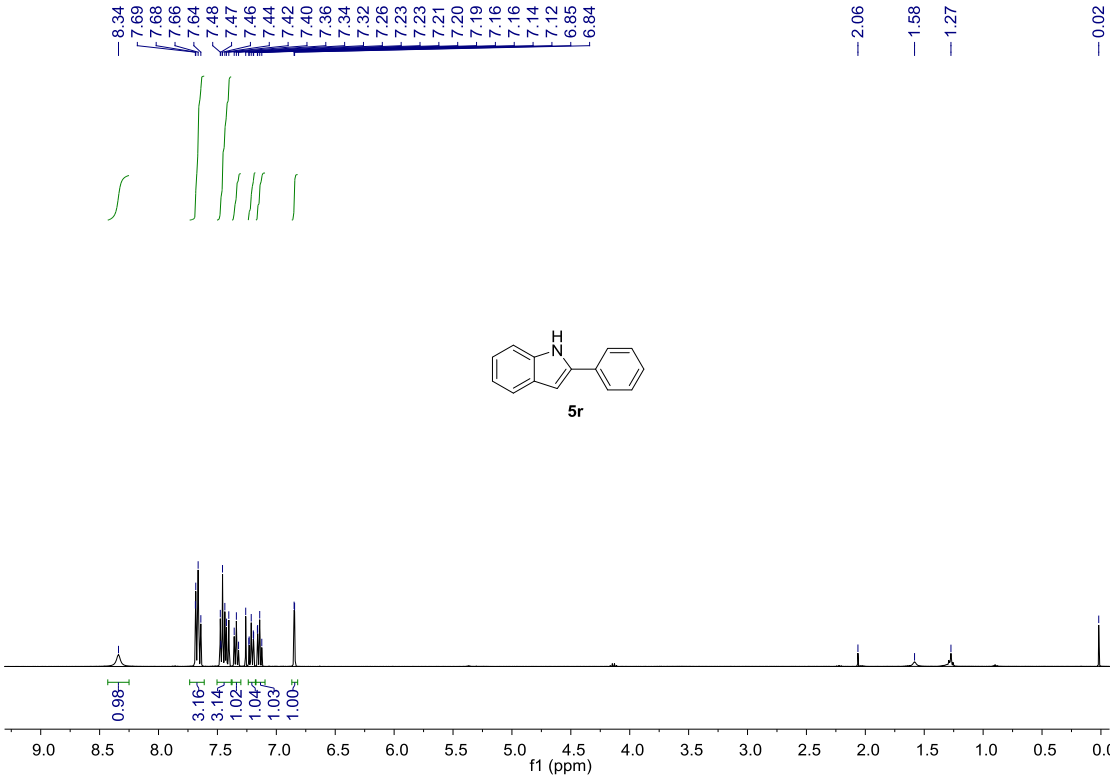

^{13}C NMR