Supporting Information

Modular Counter-Fischer-Indole Synthesis through Radical-Enolate Coupling

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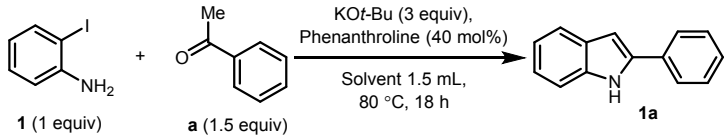
1. General remarks

All commercially available reagents were purchased from Aldrich, Alfa, Acros, TCI, and Strem were used without further purification. Anhydrous tetrahydrofuran (THF) and methylene chloride (CH_2Cl_2) were dried using a solvent purification system. Anhydrous toluene and acetonitrile (CH_3CN) were distilled according to the standard protocols. DMF, DMA, DMSO, DMPU, DMI, 1,4-Dioxane and NMP were purchased in anhydrous form and used without further purification. 2-Iodoaniline, KO*t*-Bu, and Bathophenanthroline were purchased from Alfa. All reactions were carried out under nitrogen gas. $CDCl_3$ and DMSO-D_6 were purchased from Deutero. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. TLC plates were visualized by ultraviolet light and treated with $KMnO_4$ or p-anisaldehyde stain followed by gentle heating. Flash column chromatography was carried out on Merck 60 silica gel (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively). ^{1}H NMR spectra were taken in DMSO or $CDCl_3$ and were referenced to DMSO (2.50 ppm) or $CDCl_3$ (7.26 ppm) and reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of the ^{13}C NMR spectra were measured relative to DMSO (39.52 ppm) or $CDCl_3$ (77.16). The nature of the carbons (C, CH, CH_2, CH_3) was determined by recording the DEPT-135 NMR, and is given in parentheses. High-Resolution Mass Spectra (TOF MS) were obtained at the National Instrumentation Center for Environmental Management (NICEM, Seoul, South Korea).

2. Optimization data

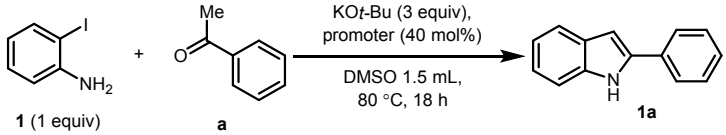
A. Optimization of reaction parameters: Solvent



	solvent	promoter	temp [°C]	yield [%]
1	DMF	Phenanthroline	80	37%
2	DMA	Phenanthroline	80	51%
3	DMSO	Phenanthroline	80	55%
4	DMPU	Phenanthroline	80	22%
5	DMI	Phenanthroline	80	15%
6	1,4-Dioxane	Phenanthroline	80	24%
7	Chlorobenzene	Phenanthroline	80	13%
8	NMP	Phenanthroline	80	51%

Reaction conditions: 2-Iodoaniline (0.5 mmol), acetophenone (0.75 mmol), KO*t*-Bu (1.5 mmol), phenanthroline (0.2 mmol), solvent (1.5 mL). 80°C, 18 h, N_2. Yields are determined by GC using dodecane as an internal standard.

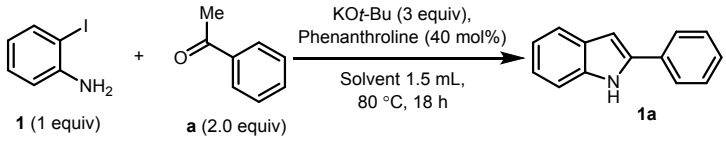
B. Optimization of reaction parameters: Promoter



	a	promoter	temp [°C]	yield [%]
1	1.5 equiv.	-	80	10%
2	1.5 equiv.	Phenanthroline	80	55%
3	1.5 equiv.	Indoline	80	39%
4	1.5 equiv.	DMEDA	80	39%
5	1.5 equiv.	1,2-dianilinoethane	80	19%
6	1.5 equiv.	*N*-methyl-*p*-anisidine	80	48%
7	1.5 equiv.	1,10-phenanthroline-4,7-diol	80	44%
8	1.5 equiv.	5-Chloro-1,10-phenanthroline	80	41%
9	1.5 equiv.	Bathophenanthroline	80	63%
10	2.0 equiv.	Bathophenanthroline	80	83%

Reaction conditions: 2-Iodoaniline (0.5 mmol), KO*t*-Bu (1.5 mmol), promoter (0.2 mmol), DMSO (1.5 mL), 80 °C, 18 h, N_2. Yields are determined by GC using dodecane as an internal standard.

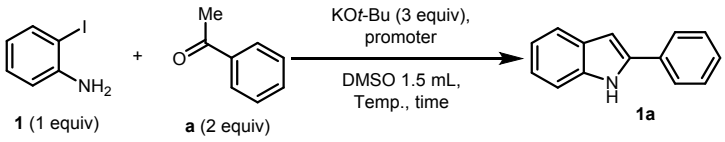
C. Sensitivity to moisture and air



	promoter	additive	yield [%]
1	Phenanthroline	-	64%
2	Phenanthroline	H_2O 1 equiv.	60%
3	Phenanthroline	$MgSO_4$ 1 equiv.	56%
4	Phenanthroline	M.S 4Å	54%
5	Phenanthroline	Open air	34%

Reaction conditions: 2-Iodoaniline (0.5 mmol), acetophenone (1.0 mmol) KO*t*-Bu (1.5 mmol), promoter (0.2 mmol), DMSO (1.5 mL), 80 °C, 18 h, N_2. Yields are determined by GC using dodecane as an internal standard.

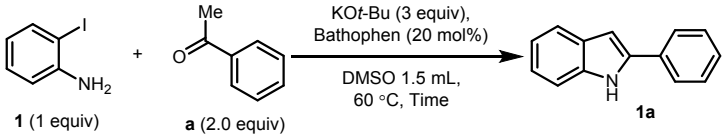
D. Optimization of reaction conditions: Promoter loading, Temperature



	Promoter	Temp [°C]	Time [h]	Yield
1	Bathophenanthroline 0.4 equiv	80	18	85%
2	Bathophenanthroline 0.2 equiv	80	18	87%
3	Bathophenanthroline 0.1 equiv	80	18	86%
4	Bathophenanthroline 0.4 equiv	60	18	82%
5	Bathophenanthroline 0.2 equiv	60	18	83%
6	Bathophenanthroline 0.1 equiv	60	18	73%
7	Bathophenanthroline 0.4 equiv	50	18	76%
8	Bathophenanthroline 0.2 equiv	50	18	70%
9	Bathophenanthroline 0.1 equiv	50	18	52%
10	Bathophenanthroline 0.4 equiv	40	18	58%
11	Bathophenanthroline 0.4 equiv	40	48	82%
12	Bathophenanthroline 0.4 equiv	30	18	22%
13	Bathophenanthroline 0.4 equiv	30	72	80%

Reaction conditions: 2-Iodoaniline (0.5 mmol), acetophenone (1.0 mmol), KO*t*-Bu (1.5 mmol), DMSO (1.5 mL), N_2. Yields are determined by GC using dodecane as an internal standard

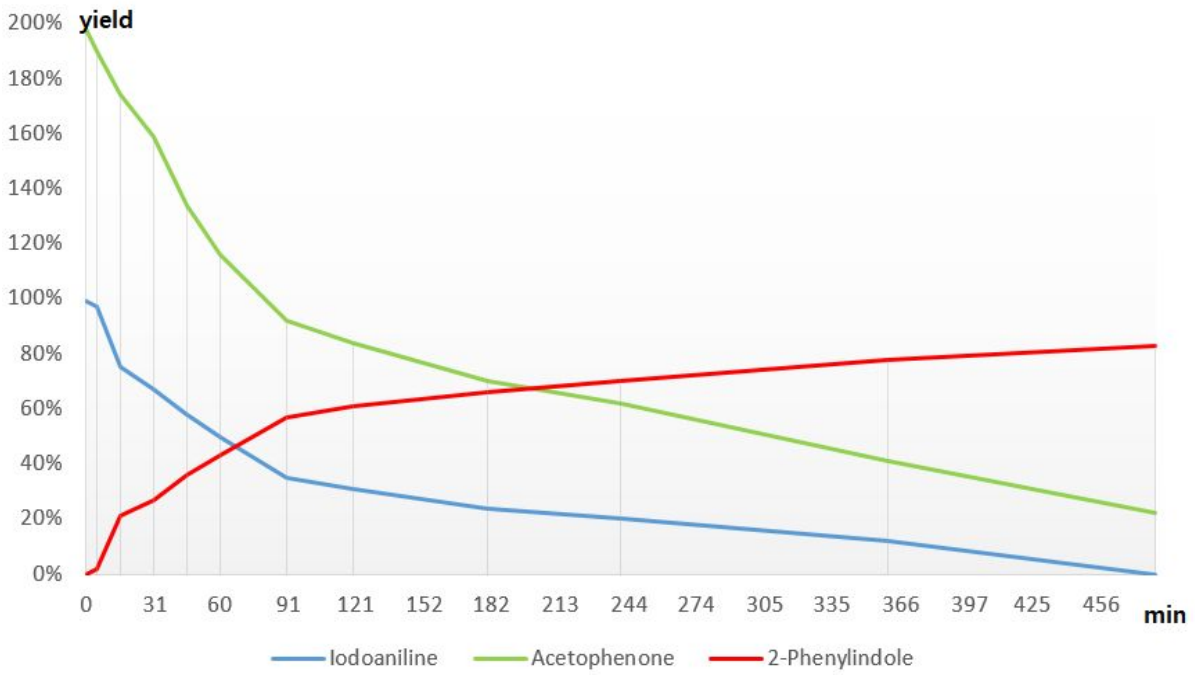
E. Optimization of reaction conditions: Time



	Promoter	Time [h]	Yield
1	Bathophenanthroline	1.5	57%
2	Bathophenanthroline	3	66%
3	Bathophenanthroline	4.5	72%
4	Bathophenanthroline	6	78%
5	Bathophenanthroline	7	80%
6	Bathophenanthroline	8	82%
7	Bathophenanthroline	18	82%

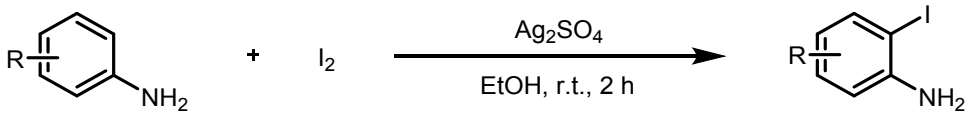
Reaction conditions: 2-Iodoaniline (0.5 mmol), acetophenone (1.0 mmol), KO*t*-Bu (1.5 mmol), DMSO (1.5 mL), N_2. Yields are determined by GC using dodecane as an internal standard

Reaction time tracking



3. General procedure for synthesis of starting materials

A. Synthesis of 2-iodoaniline derivatives[1]

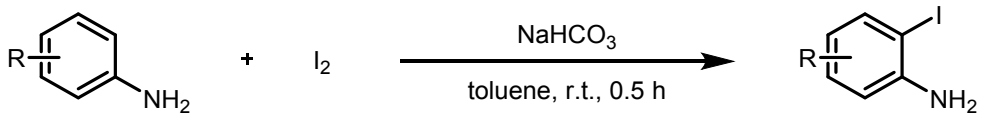


R = 4-*t*Bu (**2**), 4-CN (**5**), 4-NO_2 (**6**), 4-CO_2*t*Bu (**7**), 6-Cl-4-Me (**13**), 4-Br-6-Cl (**16**), 6-Br-4-Cl (**17**)

For compounds **2**, **5**, **6**, **7**, **13**, **16**, and **17**.

Reactions were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of aniline derivatives (10.0 mmol) in ethanol (25 mL) were added I_2 (10.0 mmol) and Ag_2SO_4 (10.0 mmol). The flask was purged with N_2 gas, and the reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was filtered over a short pad of celite and the filter cake was washed with DCM. The combined organic phase was washed with saturated aqueous $Na_2S_2O_3$ solution (3 x 15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of **2**, **5**, **6**, **7**, **13**, **16**, and **17** were confirmed based on reported NMR spectra.[1]

B. Synthesis of 2-iodoaniline derivatives[2]

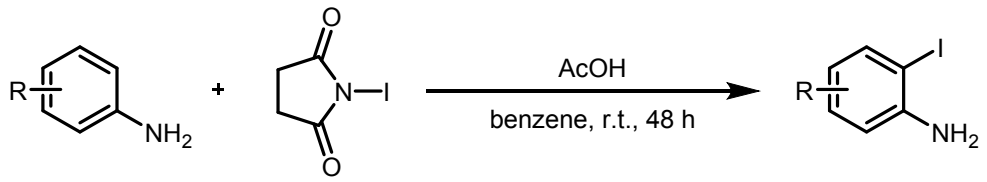


R = 4-Br (**9**), 4-Cl (**10**)

For compounds **9**, and **10**.

Reactions were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of aniline derivatives (12.0 mmol) in toluene (25 mL) was added $NaHCO_3$ (20.0 mmol) and the reaction mixture was stirred at room temperature. After 15 min, I_2 (10 mmol) was added to a solution and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was then poured into water and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic phase was washed with aqueous $Na_2S_2O_3$ solution (1 x 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of **9** and **10** were confirmed based on reported NMR spectra.[2]

C. Synthesis of 2-iodoaniline derivatives[3]

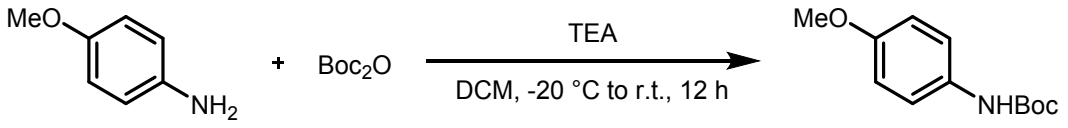


R = 5-Me (**3**), 5-OMe (**4**), Naphthyl (**8**), 4-Cl-6-Cl (**14**), 4-Br-6-Br (**15**)

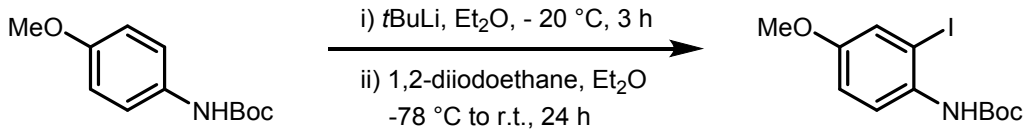
For compounds **3**, **4**, **8**, **14**, and **15**.

Reactions were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of aniline derivatives (10.0 mmol) in benzene (25 mL) were added *N*-iodosuccinimide (10 mmol) and glacial acetic acid (10.5 mmol). The reaction mixture was stirred at room temperature for 48 hours. The crude reaction mixture was then poured into saturated aqueous $NaHCO_3$ solution (30 mL), stirred at room temperature for another 10 min, and extracted with EtOAc (3 x 30 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of **3**, **4**, **8**, and **14** were confirmed based on reported NMR spectra.[3]

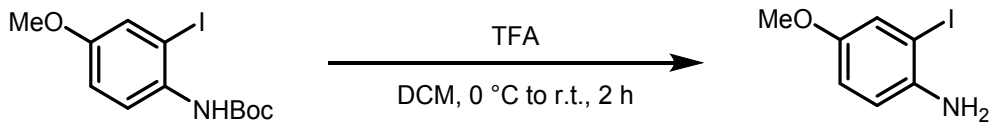
D. Synthesis of 4-methoxy-2-iodoaniline (3 step synthesis)[4]



A reaction was performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of *p*-anisidine (10.0 mmol) in dry DCM (25 mL) maintained at -20 °C were added triethylamine (20.0 mmol) and *tert*-butyl dicarbonate (12.0 mmol). The flask was evacuated and backfilled with N_2. The reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was then diluted with DCM (25 mL), washed with brine (3 x 30 mL), dried over $MgSO_4$ filtered and concentrated under reduced pressure. The product was isolated by flash column chromatography. The identity of synthesized product was confirmed based on reported NMR spectra.[4]

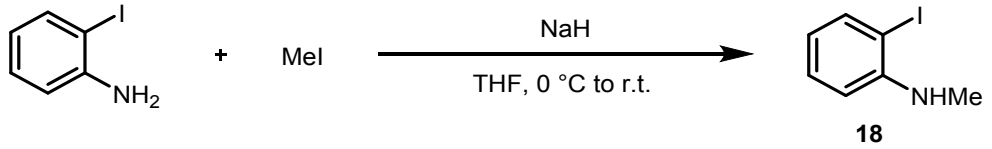


A reaction was performed in a 100 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of *tert*-butyl(methoxyphenyl)carbamate (10.0 mmol) in anhydrous diethyl ether (20 mL) maintained at –20 °C was added *tert*-butyllithium (20.0 mmol). After stirring at –20 °C for 3 hours, the reaction mixture was cooled to –78 °C and 1,2-diiodoethane (15.0 mmol) in dry diethyl ether (15 mL) was added and the reaction mixture was then gradually warmed up to room temperature over 16 hours. After the addition of aqueous Na_2SO_3 solution, it was extracted with diethyl ether (3 x 30 mL) and the combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was isolated by flash column chromatography. The identity of synthesized product was confirmed based on reported NMR spectra.[4]

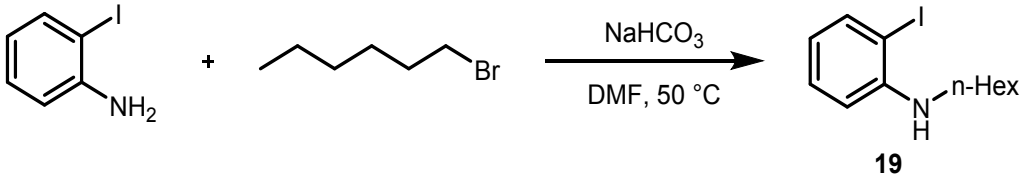


A reaction was performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of *tert*-butyl(2-iodo-4-methoxyphenyl)-carbamate (10.0 mmol) in anhydrous DCM (25 mL) maintained at 0 °C under N_2 was added TFA (12 mmol). After stirring at room temperature for 3 hours, sodium hydroxide (2 M, 10 mL) was added followed by hydrochloric acid (2 M) until neutral pH. The crude reaction mixture was extracted with DCM (3 x 20 mL), the combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was isolated by flash column chromatography. The identity of synthesized product was confirmed based on reported NMR spectra.[4]

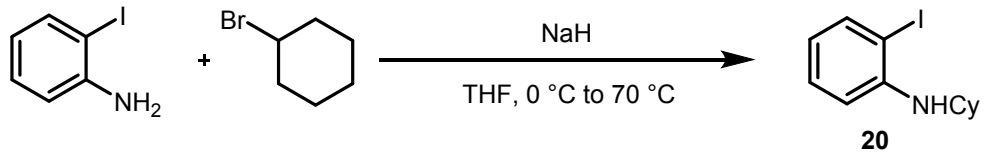
E. Synthesis of *N*-substituted iodoaniline derivatives[5,6,7]



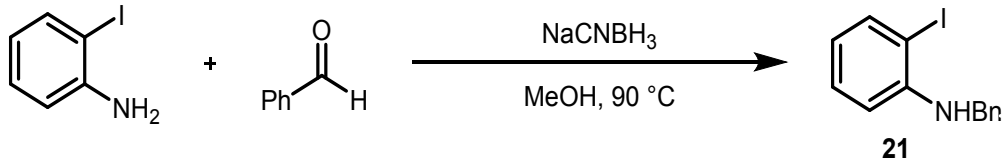
A round-bottom flask equipped with a magnetic stirrer bar was charged with 2-iodoaniline (12.0 mmol) and NaH (60% in mineral oil, 40.0 mmol) dissolved in THF (30 mL). The resulting mixture was stirred at 0 °C for 30 min. Then iodomethane (10.0 mmol) was added dropwise for 10 min. The reaction mixture was quenched with water and the organic layer was extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography. The identity of **18** was confirmed based on reported NMR spectra.[5]



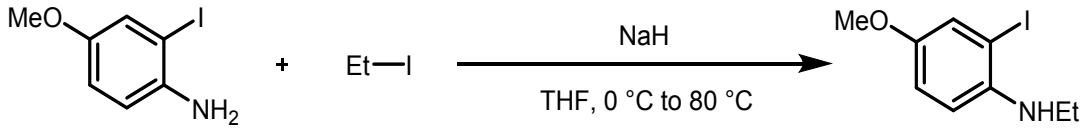
A round-bottom flask equipped with a magnetic stirrer bar was charged with 2-iodoaniline (10.0 mmol), 1-bromohexane (12.0 mmol), $NaHCO_3$ (20.0 mmol), and DMF (30 mL). The reaction mixture was stirred at 50 °C (oil bath) until complete consumption of starting material. Then the reaction was quenched with brine and the organic layer was extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with brine (3 x 30 mL), dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography. Identity of **19** was confirmed based on reported NMR spectra.[6]



A round-bottom flask equipped with a magnetic stirrer bar was charged with 2-iodoaniline (12.0 mmol) and NaH (60% in mineral oil, 40.0 mmol) dissolved in THF (30 mL). The resulting mixture was stirred at 0 °C for 30 min. Then cyclohexylbromide (10.0 mmol) was added dropwise. The ice bath was removed and the reaction mixture was allowed to warm up to 70 °C (oil bath). The reaction mixture was stirred for 2 h. The reaction mixture was quenched with water and the organic layer extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography. The identity of **20** was confirmed based on reported NMR spectra.[5]

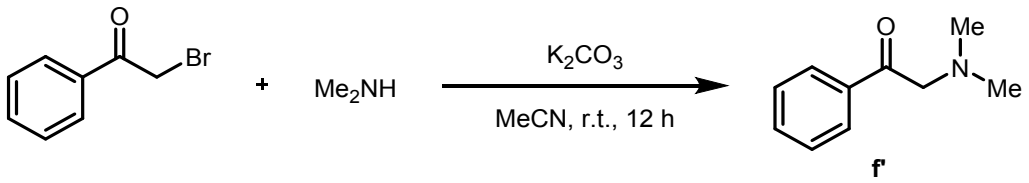


A round-bottom flask equipped with a magnetic stirrer bar was charged with the 2-iodoaniline (10.0 mmol) and a 2:1 (v/v) solution of MeOH and glacial acetic acid (30 mL). To this solution were added benzaldehyde (12.0 mmol) and $NaCNBH_3$ (12.0 mmol). The reaction mixture was heated to 90 °C (oil bath) and then stirred for 12 hours. Upon full consumption of starting material, the reaction was cooled to room temperature, quenched with 1M NaOH, and then extracted with Diethyl ether (3 x 30 mL). The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography. The identity of **21** was confirmed based on reported NMR spectra.[7]



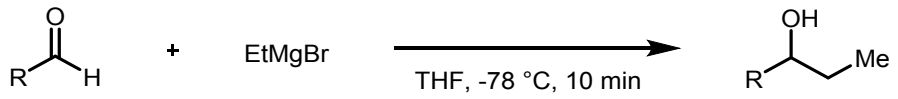
A round-bottom flask equipped with a magnetic stirrer bar was charged with 2-iodo-4-methoxyaniline (12.0 mmol) and NaH (60% in mineral oil, 40.0 mmol) dissolved in THF (30 mL). The resulting mixture was stirred at 0 °C for 30 min. Then iodoethane (10.0 mmol) was added dropwise. The ice bath was removed and the reaction mixture was allowed to warm up to 80 °C. The reaction mixture was stirred for 2 h. The reaction mixture was quenched with water and the organic layer extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography.

F. Synthesis of amino ketone derivatives[8]



A reaction was performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of a-bromoacetophenone (10.0 mmol) in MeCN (25 mL) were treated sequentially with K_2CO_3 (30.0 mmol) and Me_2NH (30.0 mmol). After stirring overnight at room temperature, the reaction mixture was charged with aqueous 1N NaOH and the organic layer was separated. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of **f'** was confirmed based on reported NMR spectra.[8]

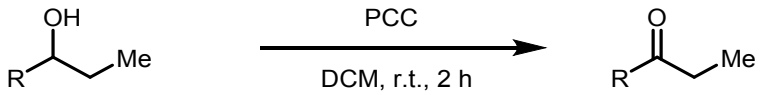
G. Synthesis of ketone derivatives (2 step synthesis)



R = 3-pentyl (**n'**), cyclohexyl (**o'**)

For compounds **n'**, and **o'**.

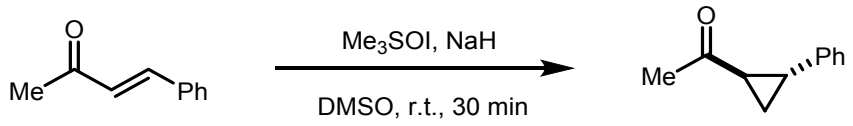
Reactions were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of aldehyde (10.0 mmol) in THF (25 mL) maintained at –78 °C under an atmosphere of nitrogen gas was added EtMgBr (12.0 mmol). After 10 min, the ice bath was removed and the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 25 mL) . The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of synthesized product was confirmed based on reported NMR spectra.



R = 3-pentyl (**n'**), cyclohexyl (**o'**)

Reactions were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of pyridinium chlorochromate (25.0 mmol) in DCM (30.0 mL) was added alcohol (10.0 mmol). After 2 hours, the reaction was quenched with water. The aqueous layer was extracted with DCM (3 x 25 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of **n'** and **o'** was confirmed based on reported NMR spectra.

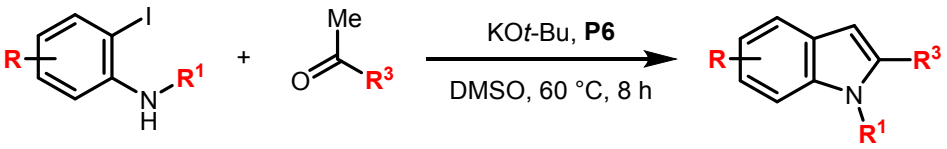
H. Synthesis of *trans*-1-(2-phenylcyclopropyl)ethan-1-one[9]



Reaction was performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. To a solution of ketone (10.0 mmol) in DMSO (20.0 mL) was added NaH (13.0 mmol). After 10 min stirring, trimethylsulfoxonium iodide (13.0 mmol) was added to a reaction solution. The reaction mixture was quenched with water after 30 min. The aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was isolated by flash column chromatography eluting with hexane and ethyl acetate. The identity of synthesized product was confirmed based on reported NMR spectra.[9]

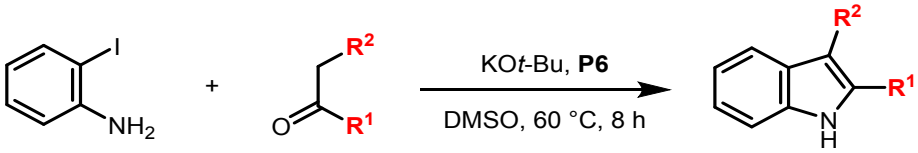
4. General procedure for synthesis of indole derivatives

A. General procedure for the reactions in Scheme 2 and Scheme 3



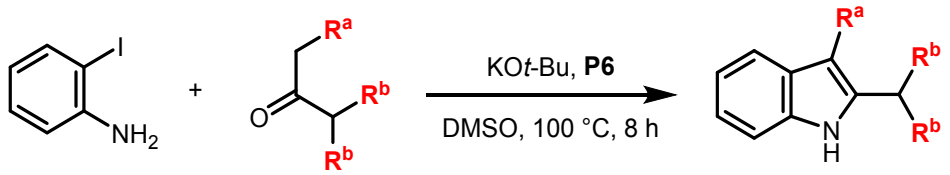
Reactions were performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. Aniline derivatives (0.5 mmol), KO*t*-Bu (1.5 mmol), and **P6** (20 mol%) were added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via a syringe and the reaction mixture was stirred at 60 °C (oil bath) for 8 hours. After the solution was cooled to room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give the desired indole product.

B. General procedure for the reactions in Scheme 4



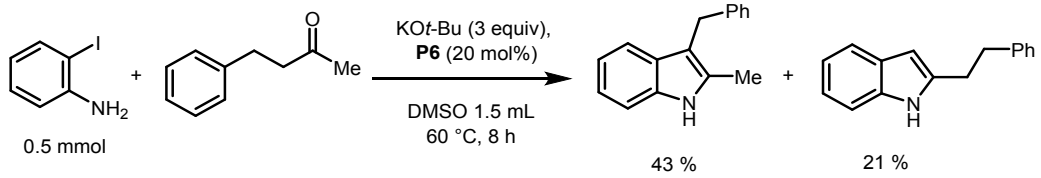
Reactions were performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. Aniline derivatives (0.5 mmol), KO*t*-Bu (1.5 mmol), and **P6** (20 mol%) were added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via a syringe and the reaction mixture was stirred at 60 °C (oil bath) for 8 hours. After the solution was cooled to room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give the desired indole product.

C. General procedure for the reactions in Scheme 5

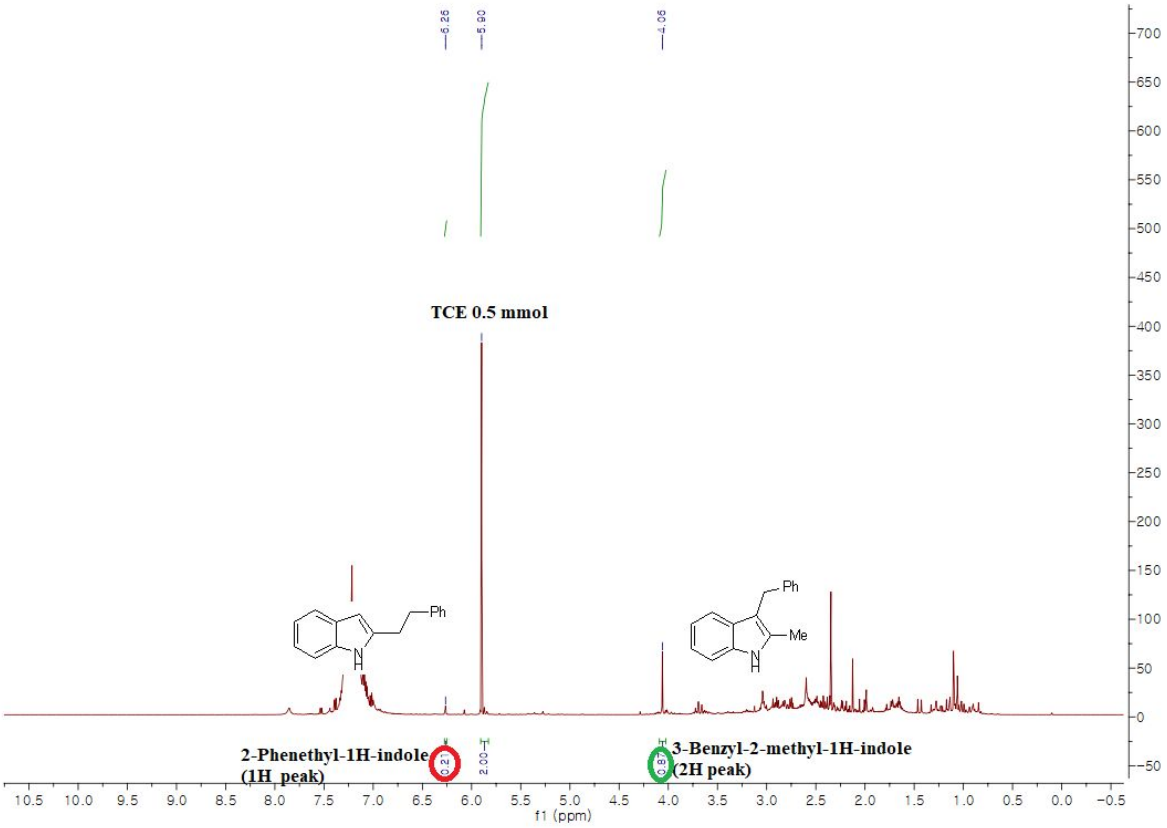


Reactions were performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. Aniline derivatives (0.5 mmol), KO*t*-Bu (1.5 mmol) and **P6** (40 mol%) were added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via a syringe and stirred at 100 °C (oil bath) for 8 hours. After the solution was cooled to room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give the desired indole product.

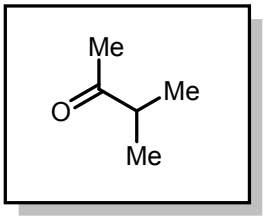
5. Determination of 1' and byproduct



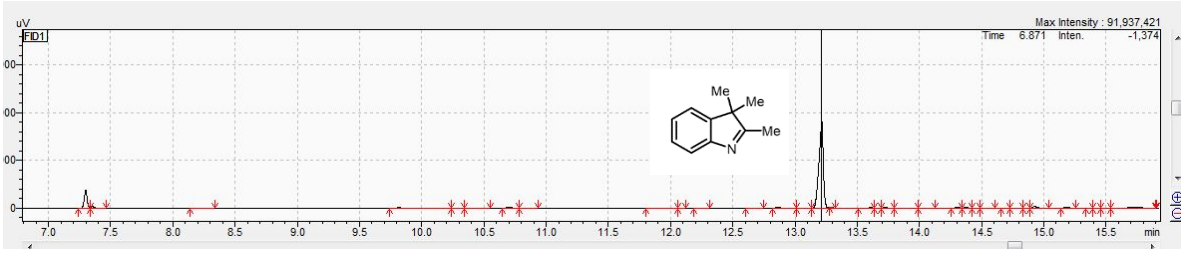
The reaction of 2-iodoaniline with 4-phenyl-2-butanone afforded two regioisomers (3-benzyl-2methyl-*1H*-indole and 2-phenethyl-*1H*-indole). Two isomers were difficult to be isolated, thus the yield and ratio of the products were determined by ^{1}H NMR using TCE as an internal standard. The identities of two regioisomers were confirmed based on reported NMR spectra.[32,33]



6. Determination of byproduct in Scheme 5



A. Fischer conditions - (product retention time – 13.215)



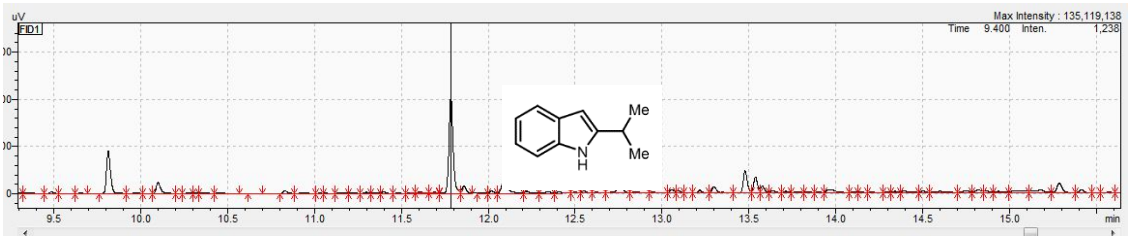
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
14	8,210	7888	4227		0,000		
15	9,816	16283	9261	SV	0,000		
16	10,295	3466	970	V	0,000		
17	10,364	3487	795	V	0,000		
18	10,696	29289	7604		0,000		
19	10,798	5755	2086	V	0,000		
20	11,886	13347	3378	V	0,000		
21	12,096	1284	316	V	0,000		
22	12,214	1746	716	V	0,000		
23	12,668	1342	361	V	0,000		
24	12,860	23587	11677	V	0,000		
25	13,096	2723	685	V	0,000		
26	13,215	4383035	1782153	SV	0,000		
27	13,291	10453	7873	T	0,000		
28	13,609	11015	3911	TV	0,000		
29	13,655	9437	3342	TV	0,000		
30	13,723	17189	8332	TV	0,000		
31	13,868	6684	1302	TV	0,000		
32	14,048	3073	742	TV	0,000		

FID1 - Ch1

Data Anal...

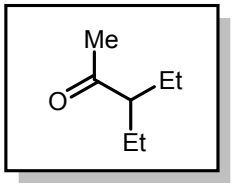
B. Our conditions – Crude reaction mixture (product retention time – 11.786)



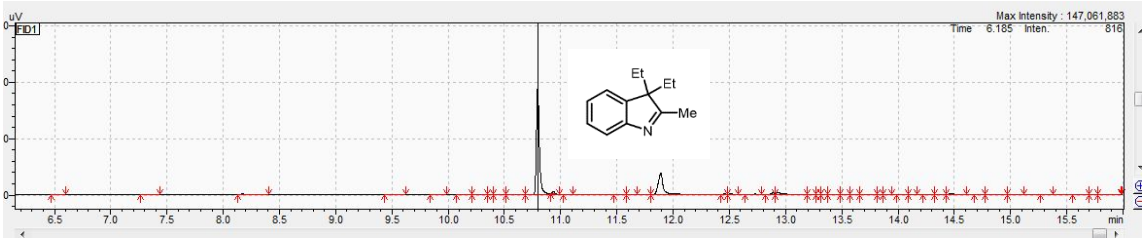
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
59	11,786	3437051	203720	V	0,000		
60	11,861	253853	15375	V	0,000		
61	11,963	4055	1819	V	0,000		
62	12,019	8478	5068	V	0,000		
63	12,096	72189	29549	SV	0,000		
64	12,223	8621	4183	V	0,000		
65	12,346	9820	3858	V	0,000		
66	12,408	7758	2254	V	0,000		
67	12,498	5740	2375	V	0,000		
68	12,552	9766	4944	V	0,000		
69	12,623	6149	2575	V	0,000		
70	12,752	45886	16249	V	0,000		
71	12,861	11169	2539	V	0,000		
72	12,946	7144	3291	V	0,000		
73	13,057	13811	7730	V	0,000		
74	13,094	9023	5187	V	0,000		
75	13,143	2343	1346	V	0,000		
76	13,218	13139	5974	V	0,000		
77	13,300	30554	13532	V	0,000		

FID1 - Ch1



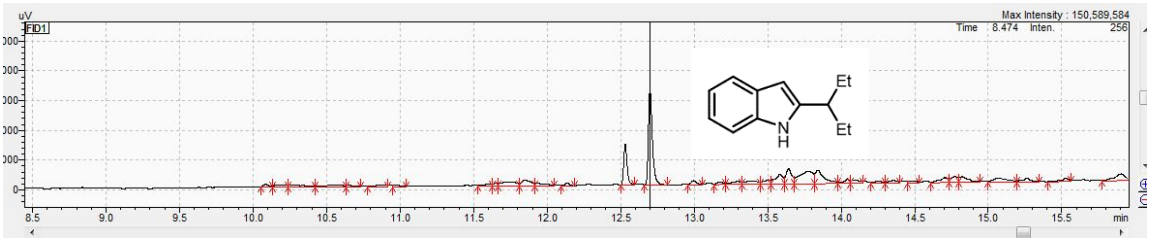
A. Fischer conditions - (product retention time – 10.796)



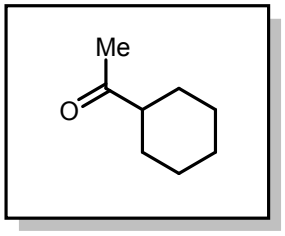
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
12	9,905	1161	223	V	0,000		
13	10,145	1366	467	V	0,000		
14	10,280	5186	932	V	0,000		
15	10,383	2304	753	V	0,000		
16	10,463	4956	724	V	0,000		
17	10,567	6152	681	V	0,000		
18	10,796	920599	472078	SV	0,000		
19	10,935	16458	10415	T	0,000		
20	11,042	1193	627	T	0,000		
21	11,530	1370	506	TV	0,000		
22	11,619	2490	1099	TV	0,000		
23	11,891	377305	96501	SV	0,000		
24	12,453	6077	3741	TV	0,000		
25	12,510	8516	5077	TV	0,000		
26	12,729	6149	3203	T	0,000		
27	12,886	19884	7403	T	0,000		
28	12,933	50398	8286	TV	0,000		
29	13,237	2756	885	TV	0,000		
30	13,286	1110	460	TV	0,000		

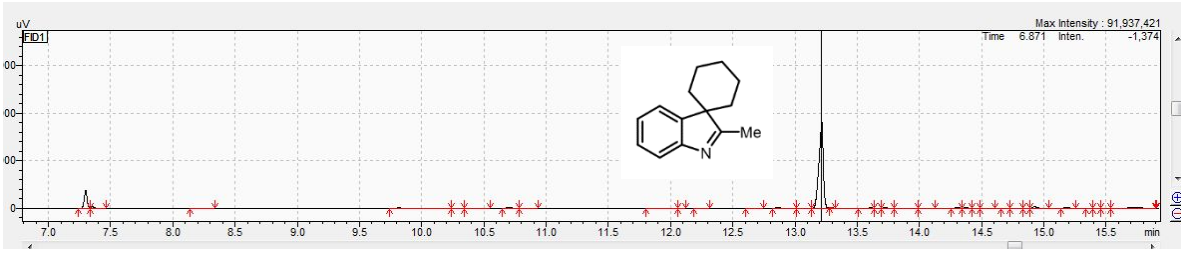
B. Our conditions - Crude reaction mixture (product retention time – 12.700)



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam
11	10,086	1538	470	V	0,000			
12	10,197	2353	443	V	0,000			
13	10,288	2694	347	V	0,000			
14	10,521	2805	333	V	0,000			
15	10,696	1244	209	V	0,000			
16	10,883	1881	326	V	0,000			
17	10,965	1162	326	V	0,000			
18	11,608	1791	410	V	0,000			
19	11,653	1039	517	V	0,000			
20	11,750	5120	681	V	0,000			
21	11,850	4705	1029	V	0,000			
22	11,933	2355	500	V	0,000			
23	12,138	1116	467	V	0,000			
24	12,531	11343	6779	V	0,000			
25	12,700	37705	15979	V	0,000			
26	12,996	1091	695	V	0,000			
27	13,175	1457	400	V	0,000			



A. Fischer conditions - (product retention time – 13.215)



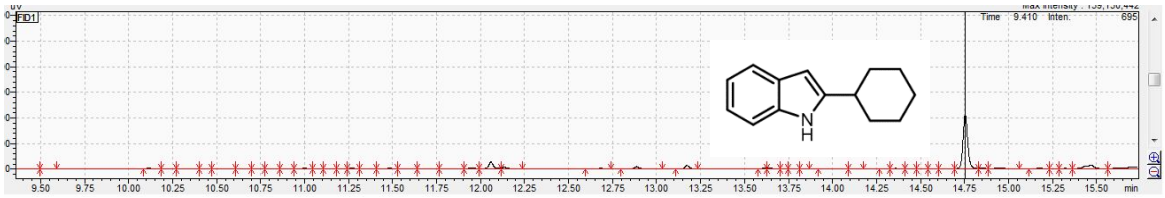
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
14	8,210	7888	4227		0,000		
15	9,816	16283	9261	SV	0,000		
16	10,295	3466	970	V	0,000		
17	10,364	3487	795	V	0,000		
18	10,696	29289	7604		0,000		
19	10,798	5755	2086	V	0,000		
20	11,886	13347	3378	V	0,000		
21	12,096	1284	316	V	0,000		
22	12,214	1746	716	V	0,000		
23	12,668	1342	361	V	0,000		
24	12,860	23587	11677	V	0,000		
25	13,096	2723	685	V	0,000		
26	13,215	4383035	1782153	SV	0,000		
27	13,291	10453	7873	T	0,000		
28	13,609	11015	3911	TV	0,000		
29	13,655	9437	3342	TV	0,000		
30	13,723	17189	8332	TV	0,000		
31	13,868	6684	1302	TV	0,000		
32	14,048	3073	742	TV	0,000		

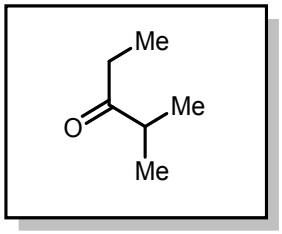
\FID1 - Ch1 /

Data Anal...

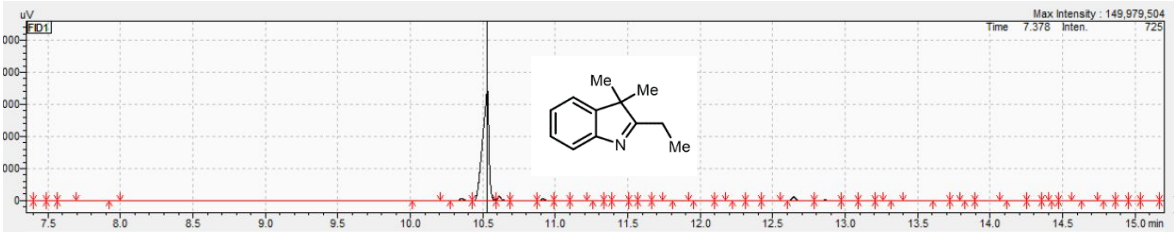
B. Our conditions - Crude reaction mixture (product retention time – 14.754)



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam
78	12,887	10191	4597	TV	0,000			
79	13,172	12903	6924	TV	0,000			
80	13,613	2832	1892	TV	0,000			
81	13,641	4071	1700	TV	0,000			
82	13,729	1369	673	TV	0,000			
83	13,767	1961	896	TV	0,000			
84	13,840	1398	663	TV	0,000			
85	13,989	2505	745	TV	0,000			
86	14,134	1917	849	T	0,000			
87	14,307	1513	597	TV	0,000			
88	14,358	3378	935	TV	0,000			
89	14,429	1373	561	TV	0,000			
90	14,510	1977	823	TV	0,000			
91	14,566	1837	731	TV	0,000			
92	14,633	3172	735	TV	0,000			
93	14,754	199290	105740	TV	0,000			
94	14,854	2992	1289	TV	0,000			



A. Fischer conditions - (product retention time – 10.529)

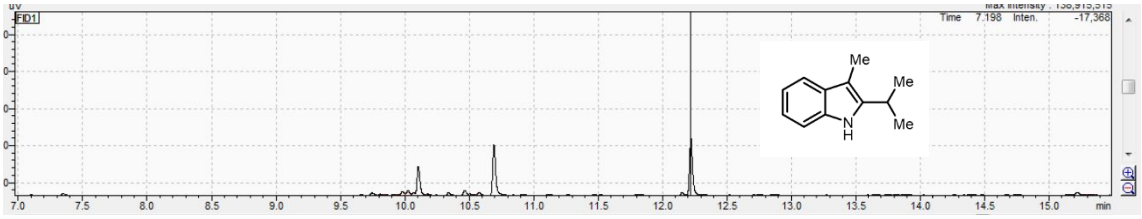


Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
27	7,368	2049	572	TV	0,000		
28	7,422	2114	532	TV	0,000		
29	7,531	1473	365	TV	0,000		
30	7,646	2313	390	TV	0,000		
31	7,966	1097	306	TV	0,000		
32	10,096	2530	517	TV	0,000		
33	10,353	113893	63336	TV	0,000		
34	10,529	10482863	9462490	TV	0,000		
35	10,612	226599	132787	TV	0,000		
36	10,699	24051	4396	TV	0,000		
37	10,914	82070	50033	TV	0,000		
38	11,035	7434	3065	TV	0,000		
39	11,135	6829	2574	TV	0,000		
40	11,312	1644	461	TV	0,000		
41	11,359	1178	383	TV	0,000		
42	11,439	5371	1494	TV	0,000		
43	11,521	1077	432	TV	0,000		
44	11,625	1226	335	TV	0,000		
45	11,704	1029	427	TV	0,000		

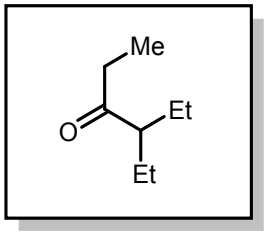
\FID1 - Ch1

B. Our conditions - Crude reaction mixture (product retention time – 12.222)

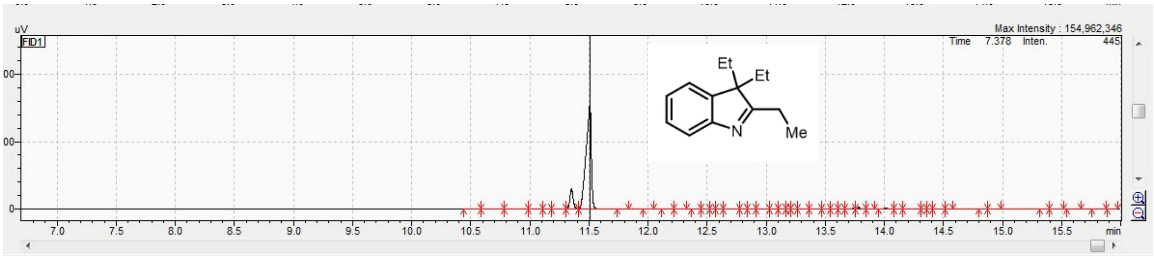


Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
35	10,024	10885	6533	V	0,000		
36	10,106	68398	38886	V	0,000		
37	10,181	4078	1999	V	0,000		
38	10,242	1479	587	V	0,000		
39	10,341	7763	3678	V	0,000		
40	10,466	16975	6728	V	0,000		
41	10,579	7613	3694	V	0,000		
42	10,694	112239	67367	V	0,000		
43	10,843	1818	567	V	0,000		
44	10,927	3298	835	V	0,000		
45	11,120	3585	1263	V	0,000		
46	11,270	1925	863	V	0,000		
47	11,474	1571	696	V	0,000		
48	11,519	2461	556	V	0,000		
49	11,832	4682	1544	V	0,000		
50	11,918	1932	428	V	0,000		
51	12,154	6334	3704	V	0,000		
52	12,222	121725	75721	SV	0,000		
53	12,411	1112	521	I	0,000		



A. Fischer conditions - (product retention time – 11.509)



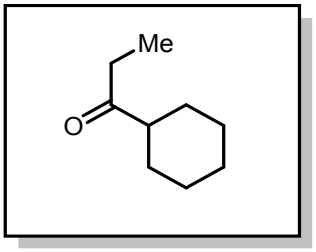
Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
9	10,816	10483	1338	V	0,000		
10	11,076	5544	1014	V	0,000		
11	11,147	7321	2839	V	0,000		
12	11,247	14780	2859	V	0,000		
13	11,352	1428634	744913	V	0,000		
14	11,509	12005765	3874761	SV	0,000		
15	11,773	1048	319	T	0,000		
16	11,988	6241	3595	T	0,000		
17	12,157	3101	1111	TV	0,000		
18	12,247	1721	726	TV	0,000		
19	12,421	19829	11220	TV	0,000		
20	12,458	21759	7009	TV	0,000		
21	12,540	5258	2732	TV	0,000		
22	12,619	5275	1523	TV	0,000		
23	12,696	13795	3641	TV	0,000		
24	12,814	3423	1035	TV	0,000		
25	12,881	5812	1562	TV	0,000		
26	12,948	11433	4938	TV	0,000		
27	13,078	29259	16999	TV	0,000		

FID1 - Ch1

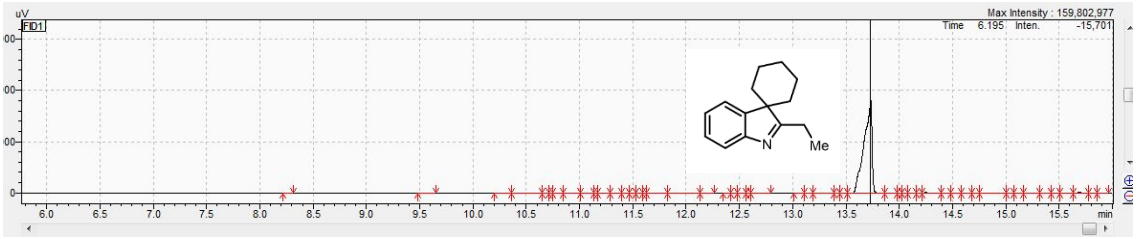
B. Our conditions – Crude reaction mixture (product retention time – 13.118)

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
7	2,591	1221	611	V	0,000		
8	3,694	142759	48848	S	0,000		
9	4,111	4149	2007	T	0,000		
10	5,359	1929	1015	V	0,000		
11	5,521	29418	16502	SV	0,000		
12	6,451	24965	9092	S	0,000		
13	9,515	3919	332		0,000		
14	11,348	2622	773	V	0,000		
15	11,477	3222	974	V	0,000		
16	12,347	1193	610	V	0,000		
17	12,401	17013	10325	V	0,000		
18	12,491	3418	2162	V	0,000		
19	12,550	17012	9626	V	0,000		
20	12,659	39729	25205	V	0,000		
21	12,757	12559	5402	SV	0,000		
22	12,909	2452	1449	V	0,000		
23	12,998	41229	23508	V	0,000		
24	13,118	51665	31599	SV	0,000		
Total		295805584	146129124		0,000		

FID1 - Ch1



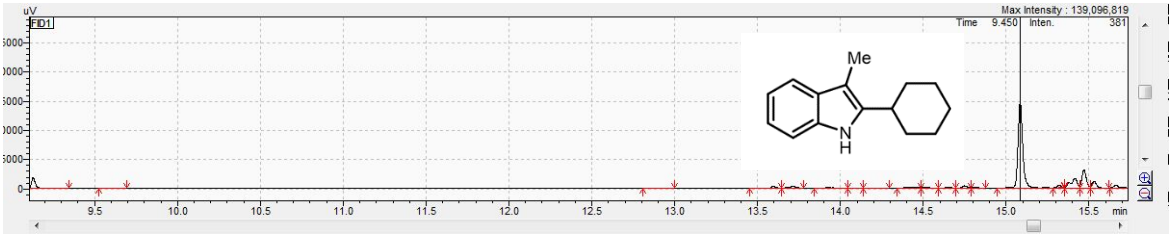
A. Fischer conditions - (product retention time – 13.732)



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
25	12,161	2106	359	V	0,000		
26	12,399	1504	545	V	0,000		
27	12,460	2608	762	V	0,000		
28	12,499	2937	819	V	0,000		
29	12,591	1061	371	V	0,000		
30	12,643	7034	1744	V	0,000		
31	13,090	3597	1600	V	0,000		
32	13,178	25716	12433	V	0,000		
33	13,208	29216	12619	SV	0,000		
34	13,410	2517	980	V	0,000		
35	13,476	7581	3168	V	0,000		
36	13,732	23287438	4494656	V	0,000		
37	13,905	96095	13798	V	0,000		
38	13,997	3942	1688	V	0,000		
39	14,037	4288	1541	V	0,000		
40	14,116	25195	11848	V	0,000		
41	14,178	6179	2624	V	0,000		
42	14,251	76030	25833	V	0,000		
43	14,441	13394	4341	V	0,000		

FID1 - Ch1

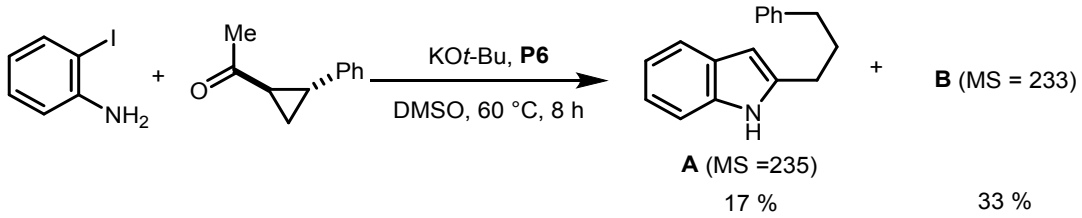
B. Our conditions - Crude reaction mixture (product retention time – 15.085)



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#
17	12,909	1588	351	V	0,000		
18	13,596	4099	1681		0,000		
19	13,713	5955	1897	V	0,000		
20	13,925	3952	513	V	0,000		
21	14,080	1470	292	V	0,000		
22	14,254	2575	335	V	0,000		
23	14,412	3975	832	V	0,000		
24	14,515	2317	621	V	0,000		
25	14,653	2016	533	V	0,000		
26	14,749	4378	1929	V	0,000		
27	14,806	1541	400	V	0,000		
28	15,085	148525	73192	SV	0,000		
29	15,319	3322	1934		0,000		
30	15,414	22839	8097	V	0,000		
31	15,469	28819	15167	V	0,000		
32	15,530	10888	5595	V	0,000		
33	15,661	4755	2104		0,000		
34	15,860	91023	45776	V	0,000		
Total		296912247	152625791		0,000		

7. Radical clock experiment

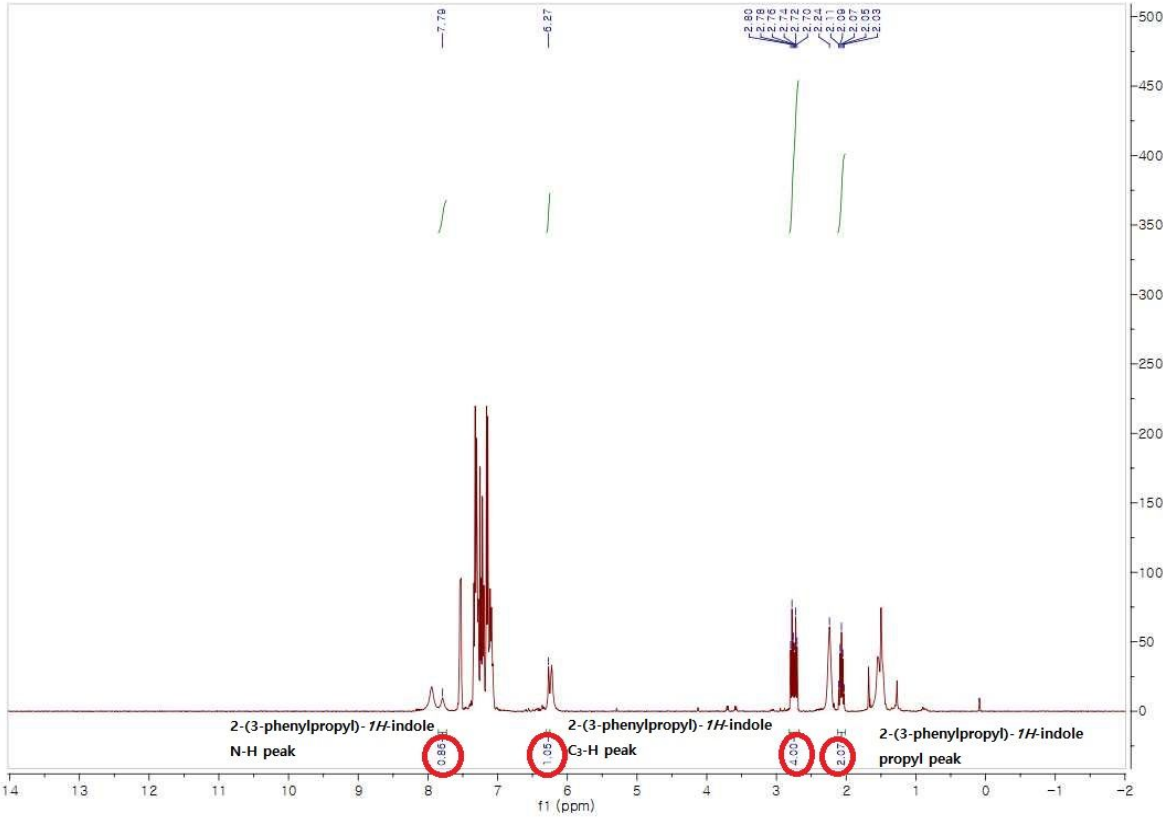
a. General procedure for radical clock experiment

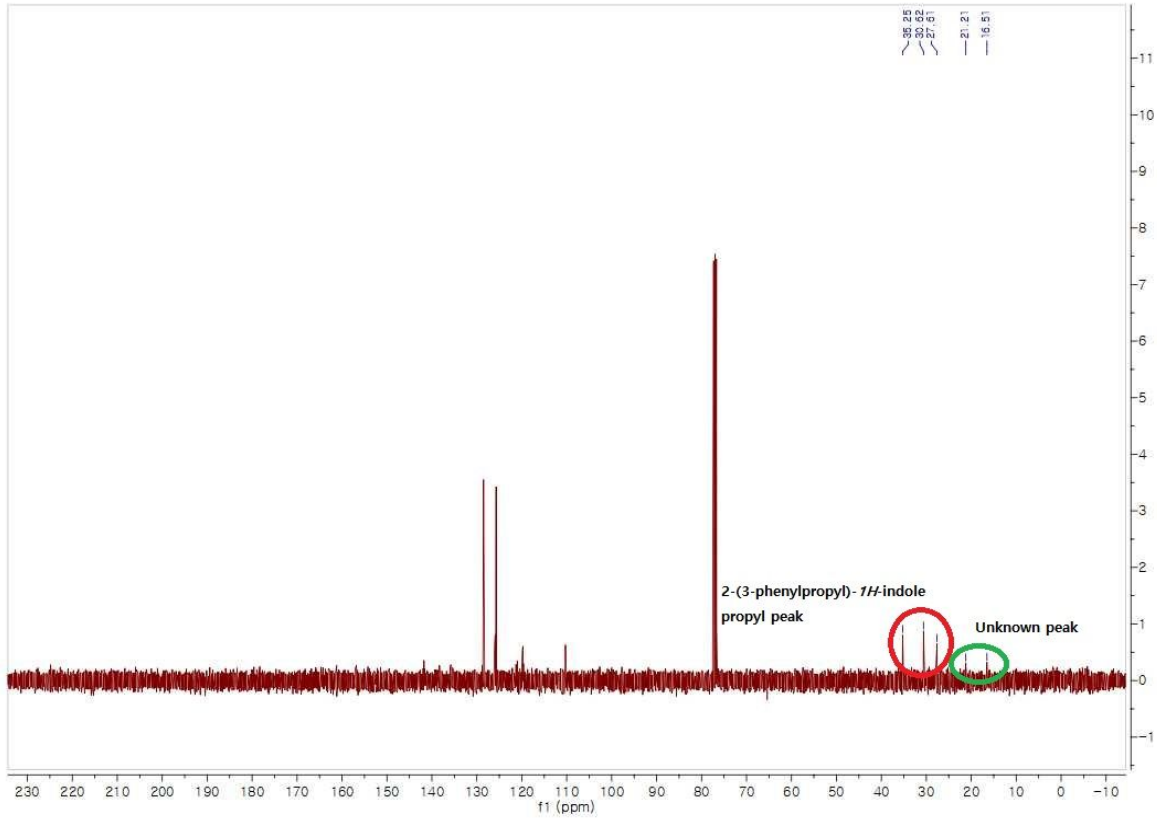


Reaction was performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. Aniline derivatives (0.5 mmol), KO*t*-Bu (1.5 mmol) and **P6** (20 mol%) were added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via a syringe and the reaction mixture was stirred at 60 °C (oil bath) for 8 hours. After the solution was cooled to room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give A and B as an inseparable mixture.

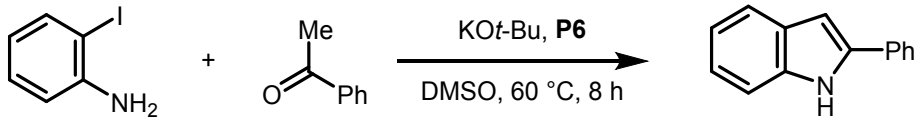
b. Characterization of ring opening indole product

After the reaction, expected indole product **A** (MS=235) was obtained by column chromatography with another indole compound **B** (MS=233) which could not be separated by silica-gel chromatography in a ratio of 1:1.94. The identity of the expected ring opening indole product **A** was confirmed by the reported NMR spectra.[10] Although the identity of the compound **B** could not be clearly identified in this stage, the observed MS value (233) suggests the formation of 2-(2-phenylcyclopropyl)-*1H*-indole.


2-(3-phenylpropyl)-1H-indole
N-H peak
2-(3-phenylpropyl)-1H-indole
C3-H peak
2-(3-phenylpropyl)-1H-indole
propyl peak
f1 (ppm)

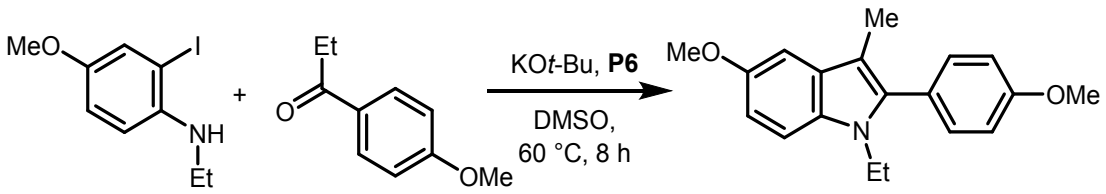

2-(3-phenylpropyl)-1H-indole
propyl peak
Unknown peak
f1 (ppm)

8. Gram-scale experiment and synthesis of Zindoxifene



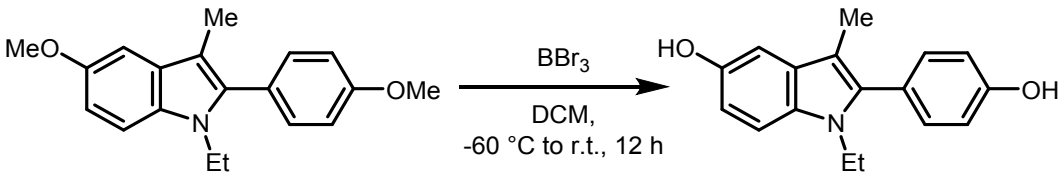
A Reaction was performed in a 50 mL Schlenk tube equipped with a magnetic stirring bar. 2-Iodoaniline (10.0 mmol), KO*t*-Bu (15.0 mmol) and **P6** (20 mol%) were added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via a syringe and the reaction mixture was stirred at 60 °C (oil bath) for 8 hours. After the solution was cooled to room temperature, the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give the 2-phenylindole. (1.41 g, 73%)

General procedure for synthesis of Zindoxifene (3 step synthesis)

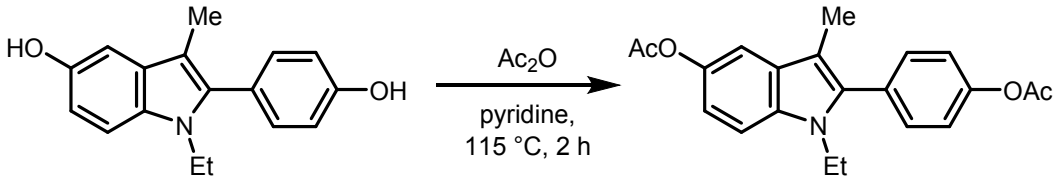


A reaction was performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. *N*-Ethyl-4-methoxy-2-iodoaniline (0.5 mmol), KO*t*-Bu (1.5 mmol) and **P6** (20 mol%) was added to the Schlenk tube. The tube was sealed, evacuated, and backfilled with N_2. A solution of ketone (1.0 mmol) in DMSO (1.5 mL) was added to the Schlenk tube via syringe and the reaction mixture was stirred at 60 °C (oil bath) for 8 hours. After the solution was cooled to room temperature the reaction mixture was quenched with water. The aqueous layer was extracted with ethyl acetate (3 x 5mL) and the combined organic

layer was concentrated under reduced pressure. This crude material was purified by column chromatography to give the desired indole product.

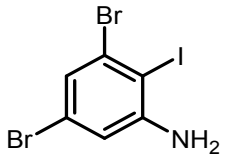


A reaction was performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. A solution of the methoxy-substituted 2-phenylindole (0.5 mmol) in dry DCM (2 mL) was cooled to –60 °C under a nitrogen atmosphere, and then BBr_3 (2 mmol) was added via syringe. After 30 min the cooling bath was removed and the mixture was stirred overnight. The reaction mixture poured into an aqueous solution of $NaHCO_3$. The organic layer was extracted with ethyl acetate (3 x 5mL) and the combined organic layer was, washed with water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was used for next acetylation step without further purification.



A reaction was performed in a 20 mL Schlenk tube equipped with a magnetic stirring bar. To a solution of the dihydroxy indole derivative (0.5 mmol) in pyridine (2 mL) was added Ac_2O (3 mmol). After refluxing (oil bath) for 2 hours, the reaction mixture was poured in to ice and extracted with DCM (3 x 5mL). The organic layer was washed twice with 2N HCl and water. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography to give the desired product, Zindoxifene.

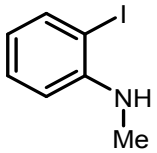
9. Characterization of synthesized compounds



15

3,5-dibromo-2-iodoaniline – Isolation: 2.54 g (68%) (**15**)

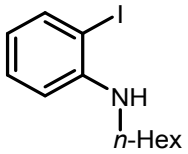
White film; Rf: 0.3 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 4.41 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0 (C), 131.3 (C), 124.4 (CH), 123.3 (C), 115.1 (CH), 89.7 (C) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_6H_5Br_2IN$ 375.7828; found 375.7826.



18

2-iodo-*N*-methylaniline – Isolation: 2.12 g (91%) (**18**)

Colorless oil; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.24 (m, 1H), 6.67 – 6.59 (m, 1H), 6.52 – 6.44 (m, 1H), 2.90 (s, 3H); The identity of synthesized product was confirmed based on reported NMR spectra.[5]

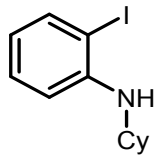


19

N-hexyl-2-iodoaniline – Isolation: 2.69 g (89%) (**19**)

Colorless oil; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.44 (t, J = 7.5 Hz, 1H), 4.36 (s, 1H), 3.15 (t, J = 7.1 Hz, 2H), 1.68 (m, 2H),

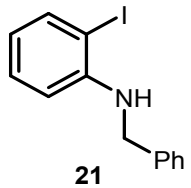
1.38 (m, 6H), 0.91 (t, J = 7.0 Hz, 3H); The identity of synthesized product was confirmed based on reported NMR spectra.[6]



20

N-cyclohexyl-2-iodoaniline – Isolation: 1.53 g (51%) (**20**)

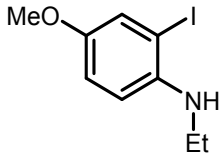
Colorless oil; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.2 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.59 (d, J = 8.1 Hz, 1H), 6.44 – 6.34 (m, 1H), 4.23 (s, 1H), 3.38 – 3.23 (m, 1H), 2.09 – 1.95 (m, 2H), 1.84 – 1.70 (m, 2H), 1.65 – 1.61 (m, 1H), 1.44 – 1.16 (m, 5H); The identity of synthesized product was confirmed based on reported NMR spectra.[5]



21

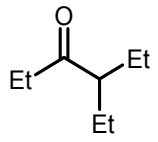
N-benzyl-2-iodoaniline – Isolation: 1.92 g (62%) (**21**)

Colorless oil; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.8, 1.4 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.31 – 7.29 (m, 1H), 7.20 – 7.13 (m, 1H), 6.61 (d, J = 8.1 Hz, 1H), 6.51 – 6.47 (m, 1H), 4.42 (s, 2H); The identity of synthesized product was confirmed based on reported NMR spectra.[7]



N-ethyl-2-iodo-4-methoxyaniline – Isolation: 2.47 g (89%)

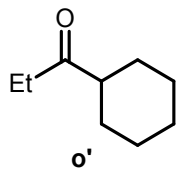
White film; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 1H), 6.82 (m, 1H), 6.51 (m, 1H), 3.70 (d, J = 1.4 Hz, 3H), 3.11 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (C), 142.2 (C), 124.6 (CH), 115.6 (CH), 111.4 (CH), 85.5 (C), 56.1 (CH_3), 39.8 (CH_2), 14.9 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_9H_{13}INO$ 278.0036; found 278.0029.



n'

4-ethylhexan-3-one – Isolation: 0.99 g (78%) (**n'**)

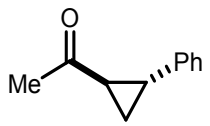
Colorless oil; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (q, *J* = 7.3 Hz, 2H), 2.33 – 2.25 (m, 1H), 1.61 – 1.50 (m, 2H), 1.47 – 1.31 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 6H); The identity of synthesized product was confirmed based on reported NMR spectra.[30]



o'

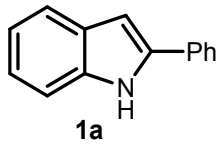
1-cyclohexylpropan-1-one – Isolation: 1.12 g (80%) (**o'**)

Colorless oil; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (q, *J* = 7.3 Hz, 2H), 2.39 – 2.26 (m, 1H), 1.80 (m, 4H), 1.66 (m, 1H), 1.41 – 1.14 (m, 5H), 1.03 (t, *J* = 7.3 Hz, 3H); The identity of synthesized product was confirmed based on reported NMR spectra.[31]



Trans-1-(2-phenylcyclopropyl)ethan-1-one – Isolation: 1.46 g (91 %)

Colorless oil; Rf: 0.3 (Hex/EA 10:1) Purified by column chromatography eluting with Hexane:EA (40:1 to 40:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.22 (m, 1H), 7.12 – 7.07 (m, 2H), 2.53 (m, 1H), 2.31 (s, 3H), 2.22 (m, 1H), 1.68 (m, 1H), 1.39 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9 (C), 140.4 (C), 128.6 (CH), 126.6 (CH), 126.1 (CH), 33.0 (CH), 31.0 (CH_3), 29.1 (CH), 19.2 (CH_2) ppm; The identity of synthesized product was confirmed based on reported NMR spectra.[9]



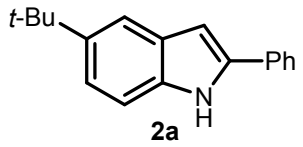
1a

2-phenyl-*1H*-indole– Isolation: 80 mg (83%) (Scheme 2, **1a**)

White solid; m.p. 187-189 ℃; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.49 (s, 1H), 7.83 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.86 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.6 (C), 137.1 (C), 132.2 (C), 128.9 (CH), 128.6 (C), 127.4 (CH), 125.0 (CH), 121.6 (CH), 120.0 (CH), 119.4 (CH), 111.3 (CH), 98.7 (CH) ppm; The identity of **1a** was confirmed based on reported NMR spectra.[11]

An identical experiment was repeated in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 78 mg, 0.5 mmol, 1equiv). After silicagel chromatography 15 mg (16% yield) of 2-phenyl-*1H*-indole was isolated.

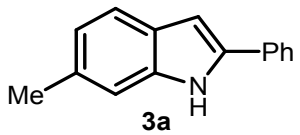
Additionally, the stability of TEMPO under the given reaction conditions was assessed. Due to the unstable nature of TEMPO, quantitative analysis in its original form was not viable. An indirect measurement was made by the following. TEMPO (78 mg, 0.5 mmol, 1 equiv) was exposed to KO*t*-Bu (168 mg, 1.5 mmol, 3 equiv) and **P6** (66 mg, 0.1 mmol, 0.2 equiv) in DMSO (1.5 mL). The mixture was heated to 60 °C with vigorous stirring for 8 hours. At the end of the reaction, diluted with water and organic phase was extracted with ethyl acetate three times. The combined organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Silica-gel chromatography (Hex/EA = 10/1) furnished an identical material that could be obtained from TEMPO with an identical purification procedure. 78 mg (0.5 mmol) of commercial TEMPO provided 56 mg of the title material after silica-gel chromatography. From the reaction mixture, 34 mg (61%) of the title material was recovered. The identity of the title material from both batches were matched by ^{1}H-NMR comparison.



2a

5-(*tert*-butyl)-2-phenyl-*1H*-indole– Isolation: 100 mg (80%) (Scheme 2, **2a**)

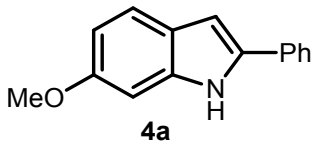
White film; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.40 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.51 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.20 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.85 (s, 1H), 1.35 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 141.6 (C), 137.6 (C), 135.4 (C), 132.4 (C), 128.9 (CH), 128.5 (CH), 127.2 (C), 124.8 (CH), 119.8 (CH), 115.7 (CH), 110.8 (CH), 98.8 (CH), 34.2 (C), 31.8 (CH_3) ppm. HRMS (TOF MS EI^{+}) m/z: [M + H]$^{+}$ Calcd for $C_{18}H_{20}N$ 250.1587; found 250.1593.



3a

6-methyl-2-phenyl-*1H*-indole– Isolation: 86 mg (81%) (Scheme 2, **3a**)

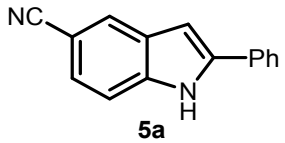
White film; Rf: 0.7 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.31 (s, 1H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.38 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.16 (s, 1H), 6.82 – 6.72 (m, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.6 (C), 137.0 (C), 132.4 (C), 130.7 (C), 128.8 (CH), 127.1 (CH), 126.5 (C), 124.8 (CH), 121.2 (CH), 119.7 (CH), 111.1 (CH), 98.6 (CH), 21.5 (CH_3) ppm; The identity of **3a** was confirmed based on reported NMR spectra.[12]



4a

6-methoxy-2-phenyl-*1H*-indole– Isolation: 79 mg (70%) (Scheme 2, **4a**)

White solid; m.p. 175-177 ℃; Rf: 0.2 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:2 to 100:8); ^{1}H NMR (400 MHz, DMSO) δ 11.27 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.24 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H), 6.71 (s, 1H), 6.58 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.69 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 155.9 (C), 138.0 (C), 136.5 (C), 132.5 (C), 128.9 (CH), 126.9 (CH), 124.5 (CH), 123.0 (C), 120.8 (CH), 109.6 (CH), 98.7 (CH), 94.4 (CH), 55.2 (CH_3) ppm; The identity of **4a** was confirmed based on reported NMR spectra.[13]

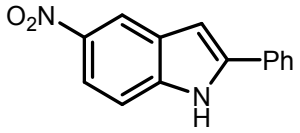


5a

2-phenyl-*1H*-indole-5-carbonitrile– Isolation: 90 mg (83%) (Scheme 2, **5a**)

White solid; m.p. 199-201 ℃; Rf: 0.5 (Hex/DCM 1:1); Purified by column chromatography eluting with Hexane:DCM (100:10 to 100:40); ^{1}H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 8.05 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.39 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 140.3 (C), 138.9 (C), 131.2 (C), 129.1 (CH), 128.4 (C), 128.3 (CH), 125.5 (CH), 125.4

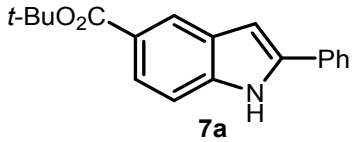
(CH), 124.3 (CH), 120.7 (C), 112.5 (CH), 101.5 (C), 99.3 (CH) ppm; The identity of **5a** was confirmed based on reported NMR spectra.[12]



6a

5-nitro-2-phenyl-*1H*-indole– Isolation: 60 mg (50%) (Scheme 2, **6a**)

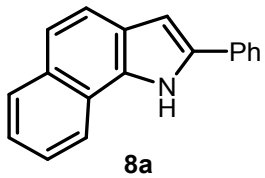
Yellow solid; m.p. 197-199 °C; Rf: 0.1 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:5 to 100:15); ^{1}H NMR (400 MHz, DMSO) δ 12.29 (s, 1H), 8.52 (d, *J* = 2.2 Hz, 1H), 8.01 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.16 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 141.4 (C), 141.0 (C), 140.4 (C), 131.0 (C), 129.1 (CH), 128.5 (CH), 128.0 (C), 125.5 (CH), 117.0 (CH), 111.7 (CH), 100.9 (CH) ppm; The identity of **6a** was confirmed based on reported NMR spectra.[14]



7a

tert-butyl 2-phenyl-*1H*-indole-5-carboxylate– Isolation: 79 mg (54%) (Scheme 2, **7a**)

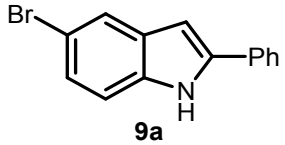
Yellow foam; Rf: 0.4 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:2 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.88 (s, 1H), 8.18 (s, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.69 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.47 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 1.57 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 166.0 (C), 139.5 (C), 139.3 (C), 131.6 (C), 129.0 (CH), 128.1 (C), 127.9 (CH), 125.2 (CH), 122.7 (C), 122.5 (CH), 122.3 (CH), 111.0 (CH), 99.8 (CH), 79.7 (C), 28.0 (CH_3) ppm; HRMS (TOF MS EI^{+}) m/z: $[M + H]^{+}$ Calcd for $C_{19}H_{20}NO_2$ 294.1488; found 294.1488.



8a

2-phenyl-*1H*-benzo[*g*]indole– Isolation: 105 mg (86%) (Scheme 2, **8a**)

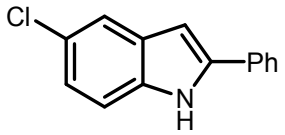
White solid; m.p. 169-171 °C; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.70 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 8.0, 5.8 Hz, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.4 (C), 132.4 (C), 131.8 (C), 130.0 (C), 128.9 (CH), 128.5 (CH), 127.1 (CH), 125.3 (CH), 125.1 (CH), 124.7 (C), 123.7 (CH), 122.1 (C), 121.3 (CH), 120.6 (CH), 120.4 (CH), 100.9 (CH) ppm; The identity of **8a** was confirmed based on reported NMR spectra.[15]



9a

5-bromo-2-phenyl-*1H*-indole – Isolation: 79 mg (58%) (Scheme 2, **9a**)

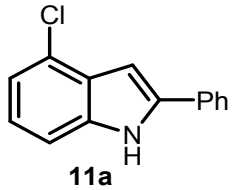
White to yellow solid; m.p. 192-194 °C; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:4); ^{1}H NMR (400 MHz, DMSO) δ 11.76 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.70 (s, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.87 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 139.2 (C), 135.8 (C), 131.7 (C), 130.5 (C), 129.0 (CH), 127.9 (CH), 125.2 (CH), 124.0 (CH), 122.2 (CH), 113.3 (CH), 111.9 (C), 98.3 (CH) ppm; The identity of **9a** was confirmed based on reported NMR spectra.[14]



10a

5-chloro-2-phenyl-*1H*-indole– Isolation: 68 mg (60%) (Scheme 2, **10a**)

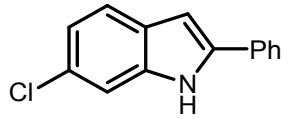
White to yellow solid; m.p. 199-201 °C; Rf: 0.3 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:5 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.75 (s, 1H), 7.85 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.88 (d, *J* = 1.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 139.2 (C), 135.8 (C), 131.7 (C), 130.5 (C), 129.0 (CH), 127.9 (CH), 125.2 (CH), 124.0 (C), 122.2 (CH), 113.3 (CH), 111.9 (CH), 98.3 (CH) ppm; The identity of **10a** was confirmed based on reported NMR spectra.[11]



11a

4-chloro-2-phenyl-*1H*-indole – Isolation: 89 mg (78%) (Scheme 2, **11a**)

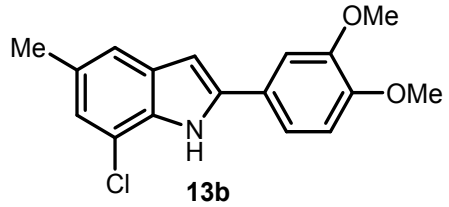
White solid; m.p. 75-77 °C; Rf: 0.3 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.92 (s, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.96 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 138.7 (C), 137.9 (C), 131.5 (C), 129.0 (CH), 128.0 (CH), 127.2 (C), 125.3 (CH), 124.2 (C), 122.4 (CH), 119.0 (CH), 110.4 (CH), 96.7 (CH) ppm; HRMS (TOF MS EI^{+}) m/z: $[M + H]^{+}$ Calcd for $C_{14}H_{11}ClN$ 228.0574; found 228.0569.



12a

6-chloro-2-phenyl-*1H*-indole– Isolation: 70 mg (62%) (Scheme 2, **12a**)

White solid; m.p. 180-182 °C; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 7.86 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46 (m, *J* = 10.9, 4.2 Hz, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.91 (d, *J* = 1.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 138.8 (C), 137.5 (C), 131.8 (C), 129.0 (CH), 127.7 (CH), 127.5 (C), 126.1 (C), 125.1 (CH), 121.4 (CH), 119.8 (CH), 110.80 (CH), 98.8 (CH) ppm; The identity of **12a** was confirmed based on reported NMR spectra.[11]

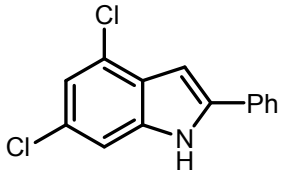


13b

7-chloro-2-(3,4-dimethoxyphenyl)-5-methyl-1H-indole– Isolation: 84 mg (56%) (Scheme 2, **13b**)

White to red foam; Rf: 0.6 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:5 to 100:15); ^{1}H NMR (400 MHz, DMSO) δ 11.24 (s, 1H), 7.52 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.15 (s, 1H), 6.99 – 6.86 (m, 2H), 6.71 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 148.9 (C), 148.7 (C), 139.8 (C), 132.2 (C), 131.0 (C), 129.4 (C), 124.6 (C), 122.1 (CH), 118.5

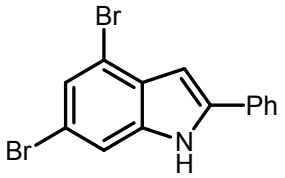
(CH), 118.4 (CH), 115.1 (C), 111.9 (CH), 109.6 (CH), 98.8 (CH), 55.8 (CH_3), 55.5 (CH_3), 20.8 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}ClNO_2$ 302.0942; found 302.0938.



14a

4,6-dichloro-2-phenyl-*1H*-indole– Isolation: 72 mg (55%) (Scheme 2, **14a**)

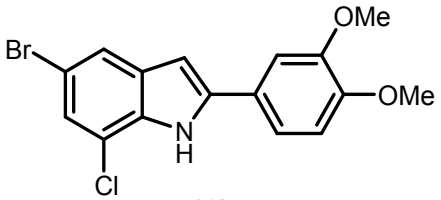
White to yellow solid**;** m.p. 111-113 ℃; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.97 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 (s, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 139.8 (C), 137.7 (C), 131.1 (C), 129.0 (CH), 128.3 (CH), 126.2 (C), 125.9 (C), 125.4 (CH), 124.8 (C), 119.0 (CH), 110.2 (CH), 96.9 (CH) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}Cl_2N$ 262.0184; found 262.0180.



15a

4,6-dibromo-2-phenyl-*1H*-indole– Isolation: 70 mg (40%) (Scheme 2, **15a**)

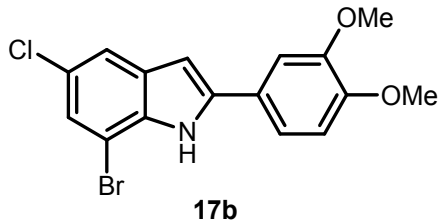
Yellow foam**;** Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 12.02 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.53 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.26 (m, 2H), 6.84 (d, *J* = 1.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 139.6 (C), 137.7 (C), 131.0 (C), 129.0 (CH), 128.4 (C), 128.3 (CH), 125.4 (CH), 124.1 (CH), 113.8 (C), 113.6 (C), 113.4 (CH), 98.6 (CH) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}Br_2N$ 349.9174; found 349.9173.



16b

5-bromo-7-chloro-2-(3,4-dimethoxyphenyl)-*1H*-indole– Isolation: 91 mg (50%) (Scheme 2, **16b**)

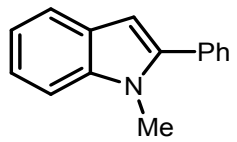
White foam**;** Rf: 0.4 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:7 to 100:20); ^{1}H NMR (400 MHz, DMSO) δ 11.65 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 149.1 (C), 148.9 (C), 141.3 (C), 132.8 (C), 132.0 (C), 123.8 (C), 122.5 (CH), 120.9 (CH), 118.9 (CH), 116.5 (C), 111.9 (CH), 111.3 (C), 109.8 (CH), 98.9 (CH), 55.8 (CH_3), 55.6 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}BrClNO_2$ 365.9890; found 365.9889.



17b

7-bromo-5-chloro-2-(3,4-dimethoxyphenyl)-*1H*-indole– Isolation: 64 mg (35%) (Scheme 2, **17b**)

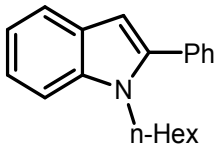
White to yellow foam; Rf: 0.4 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:8 to 100:13); ^{1}H NMR (400 MHz, DMSO) δ 11.42 (s, 1H), 7.52 (d, *J* = 1.7 Hz, 2H), 7.47 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 149.1 (C), 148.9 (C), 141.6 (C), 134.2 (C), 131.0 (C), 124.2 (C), 123.9 (C), 123.1 (CH), 119.0 (CH), 118.3 (CH), 111.9 (CH), 110.0, (CH) 104.1 (C), 99.4 (CH), 55.8 (CH_3), 55.6 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}BrClNO_2$ 365.9890; found 365.9890.



18a

1-methyl-2-phenyl-*1H*-indole– Isolation: 60 mg (58%) (Scheme 2, **18a**)

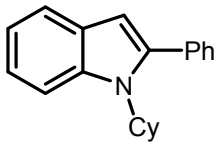
White solid; m.p. 98-100 ℃; Rf: 0.8 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (200:0 to 200:1); ^{1}H NMR (400 MHz, DMSO) δ 7.57 (t, *J* = 8.8 Hz, 3H), 7.49 (m, 3H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.55 (s, 1H), 3.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 140.9 (C), 138.1 (C), 132.2 (C), 129.0 (CH), 128.7 (CH), 127.9 (CH), 127.4 (C), 121.4 (CH), 120.0 (CH), 119.6 (CH), 110.2 (CH), 101.1 (CH), 31.1 (CH_3) ppm; The identity of **18a** was confirmed based on reported NMR spectra.[16]



19a

1-hexyl-2-phenyl-*1H*-indole– Isolation: 97 mg (70%) (Scheme 2, **19a**)

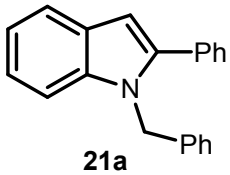
Yellow oil; Rf: 0.8 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (200:0 to 200:1); ^{1}H NMR (400 MHz, DMSO) δ 7.55 – 7.43 (m, 6H), 7.43 – 7.36 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 4.14 (t, *J* = 7.4 Hz, 2H), 1.55 – 1.43 (m, 2H), 1.10 – 0.91 (m, 6H), 0.69 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 140.8 (C), 137.2 (C), 132.7 (C), 129.0 (CH), 128.6 (CH), 127.9 (CH), 127.7 (C), 121.3 (CH), 120.2 (CH), 119.5 (CH), 110.4 (CH), 101.7 (CH), 43.1 (CH_2), 30.5 (CH_2), 29.2 (CH_2), 25.6 (CH_2), 21.8 (CH_2), 13.7 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{20}H_{24}N$ 278.1903; found 278.1908.



20a

1-cyclohexyl-2-phenyl-*1H*-indole– Isolation: 95 mg (69%) (Scheme 2, **20a**)

Colorless oil; m.p. 104-106 ℃; Rf: 0.8 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (200:0 to 200:1); ^{1}H NMR (400 MHz, DMSO) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.51 (m, 3H), 7.44 (d, *J* = 7.3 Hz, 3H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.01 (m, 1H), 6.41 (s, 1H), 4.18 – 4.08 (m, 1H), 2.48 (dt, *J* = 3.6, 1.7 Hz, 1H), 2.30 (m, 2H), 1.79 (m, 4H), 1.59 (m, 1H), 1.34 – 1.09 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 141.0 (C), 135.4 (C), 133.0 (C), 129.2 (CH), 128.7 (CH), 128.4 (C), 128.1 (CH), 120.9 (CH), 120.5 (CH), 119.2 (CH), 112.8 (CH), 101.9 (CH), 55.9 (CH), 30.8 (CH_2), 25.9 (CH_2), 24.7 (CH_2) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{20}H_{22}N$ 276.1746; found 276.1745.

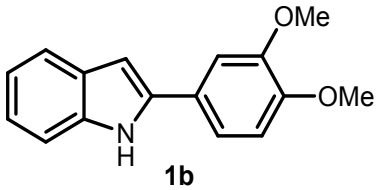


21a

1-cyclohexyl-2-phenyl-*1H*-indole– Isolation: 88 mg (62%) (Scheme 2, **21a**)

White solid; m.p. 93-95 ℃; Rf: 0.8 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (200:0 to 200:1); ^{1}H NMR (400 MHz, DMSO) δ 7.60 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.38 (m, 5H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.15 (m, 3H), 7.09 (ddd, *J* = 14.9, 10.3, 4.1 Hz, 2H), 6.89 (d, *J* = 7.0 Hz, 2H), 6.65 (s, 1H), 5.46 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 141.1 (C), 138.3 (C), 137.6 (C), 132.2 (C), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.2 (CH), 127.8 (C), 127.0 (CH), 125.9

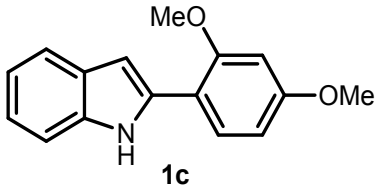
(CH), 121.7 (CH), 120.3 (CH), 119.9 (CH), 110.8 (CH), 102.2 (CH), 46.8 (CH_2) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{21}H_{18}N$ 284.1433; found 284.1432.



1b

2-(3,4-dimethoxyphenyl)-*1H*-indole– Isolation: 119 mg (94%) (Scheme 3, **1b**)

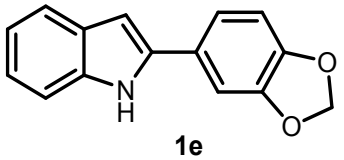
White to yellow solid; m.p. 189-191 °C; Rf: 0.3 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:20); ^{1}H NMR (400 MHz, DMSO) δ 11.41 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.40 (t, *J* = 8.7 Hz, 2H), 7.10 – 6.94 (m, 3H), 6.81 (d, *J* = 1.4 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 149.0 (C), 148.4 (C), 138.0 (C), 136.9 (C), 128.8 (C), 125.1 (C), 121.1 (CH), 119.7 (CH), 119.2 (CH), 117.5 (CH), 112.2 (CH), 111.0 (CH), 109.0 (CH), 97.6 (CH), 55.6 (CH_3), 55.6 (CH_3) ppm; The identity of **1b** was confirmed based on reported NMR spectra.[17]



1c

2-(2,4-dimethoxyphenyl)-*1H*-indole– Isolation: 88 mg (70%) (Scheme 3, **1c**)

White to yellow foam; Rf: 0.7 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:7); ^{1}H NMR (400 MHz, DMSO) δ 11.08 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.94 (s, 3H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 160.0 (C), 157.3 (C), 136.2 (C), 134.9 (C), 128.6 (CH), 128.4 (C), 120.8 (CH), 119.5 (CH), 118.9 (CH), 113.7 (C), 111.1 (CH), 105.6 (CH), 100.1 (CH), 99.0 (CH), 55.6 (CH_3), 55.3 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1175, found 254.1167.

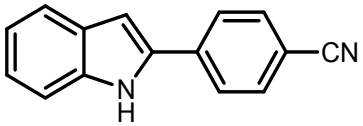


1e

2-(benzo[d][1,3]dioxol-5-yl)-*1H*-indole – Isolation: 51 mg (43%) (Scheme 3, **1e**)

White solid; m.p. 163-165 °C; Rf: 0.7 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.38 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 7.0 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.78 (s,

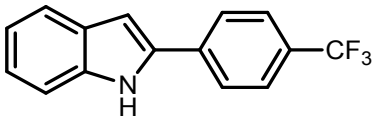
1H), 6.07 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 147.9 (C), 146.7 (C), 137.6 (C), 136.9 (C), 128.7 (C), 126.5 (C), 121.2 (CH), 119.8 (CH), 119.3 (CH), 118.7 (CH), 111.1 (CH), 108.7 (CH), 105.6 (CH), 101.2 (CH_2), 98.0 (CH) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}NO_2$ 238.0862; found 238.0856.



1f

4-(*1H*-indol-2-yl)benzonitrile– Isolation: 62 mg (60%) (Scheme 3, **1f**)

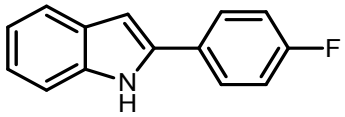
White solid**;** m.p. 192-194 ℃; Rf: 0.2 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:3 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.76 (s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.06 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.7 (C), 136.5 (C), 135.6 (C), 132.8 (CH), 128.4 (C), 125.3 (CH), 122.8 (C), 120.7 (CH), 119.8 (CH), 119.0 (CH), 111.7 (C), 109.2 (CH), 101.6 (CH) ppm; The identity of **1f** was confirmed based on reported NMR spectra.[18]



1g

2-(4-(trifluoromethyl)phenyl)-*1H*-indole– Isolation: 91 mg (70%) (Scheme 3, **1g**)

White solid; m.p. 239-241 ℃; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0.5 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.75 (s, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.6 (C) , 136.1 (C), 135.9 (C), 128.4 (C), 127.3 (C-F, $1J_{C\text{-}F}$ = 32.0 Hz), 125.8 (C-F, $2J_{C\text{-}F}$ = 3.8 Hz), 125.3 (CH), 123.0 (CH), 122.4 (CH), 120.5 (CH), 119.7 (CH), 111.6 (CH), 100.7 (CH) ppm; ^{19}F NMR (376 MHz, DMSO) δ -61.0 ppm; The identity of **1g** was confirmed based on reported NMR spectra.[19]

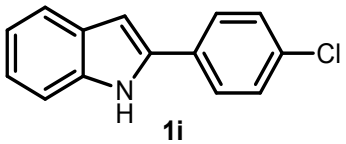


1h

2-(4-fluorophenyl)-*1H*-indole– Isolation: 30 mg (28%) (Scheme 3, **1h**)

White solid; m.p. 188-190 ℃; Rf: 0.7 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0.5 to 100:1); ^{1}H NMR (400 MHz, DMSO) δ 11.53 (s, 1H), 7.90 (dd, J = 8.8, 5.4 Hz,

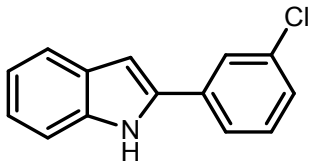
2H), 7.53 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.9 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.86 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 161.5 (C-F, $1J_{C\text{-}F}$ = 244.6 Hz), 137.1 (C), 136.7 (C), 128.9 (C-F, $4J_{C\text{-}F}$ = 3.1 Hz), 128.6 (C), 127.0 (C-F, $3J_{C\text{-}F}$ = 8.0 Hz), 121.6 (CH), 120.0 (CH), 119.4 (CH), 115.8 (C-F, $2J_{C\text{-}F}$ = 21.6 Hz), 111.3 (CH), 98.7 (CH) ppm; ^{19}F NMR (376 MHz, DMSO) δ -114.7 ppm; The identity of **1h** was confirmed based on reported NMR spectra.[11]



1i

2-(4-chlorophenyl)-*1H*-indole– Isolation: 68 mg (61%) (Scheme 3, **1i**)

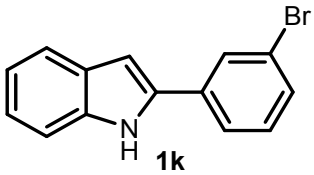
White to yellow solid; m.p. 200-202 °C; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.58 (s, 1H), 7.88 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 7.7 Hz, 3H), 7.40 (d, J = 8.2 Hz, 1H), 7.11 (t, J = 7.1 Hz, 1H), 7.00 (t, J = 7.1 Hz, 1H), 6.93 (d, J = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.2 (C), 136.4 (C), 131.8 (C), 131.1 (C), 128.9 (CH), 128.5 (C), 126.6 (CH), 121.9 (CH), 120.2 (CH), 119.5 (CH), 111.4 (CH), 99.3 (CH) ppm; The identity of **1i** was confirmed based on reported NMR spectra.[20]



1j

2-(3-chlorophenyl)-*1H*-indole– Isolation: 70 mg (63%) (Scheme 3, **1j**)

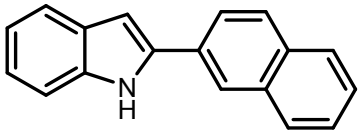
White solid; m.p. 144-146 °C; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.56 (s, 1H), 7.89 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.37 (dd, J = 16.2, 8.1 Hz, 2H), 7.26 (d, J = 7.9 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.93 (dd, J = 14.3, 4.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.3 (C), 136.0 (C), 134.3 (C), 133.8 (C), 130.7 (CH), 128.4 (C), 127.0 (CH), 124.4 (CH), 123.6 (CH), 122.1 (CH), 120.3 (CH), 119.6 (CH), 111.4 (CH), 99.9 (CH) ppm; The identity of **1j** was confirmed based on reported NMR spectra.[21]



1k

2-(3-bromophenyl)-*1H*-indole– Isolation: 41 mg (30%) (Scheme 3, **1k**)

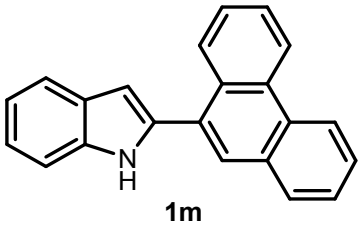
White solid; m.p. 154-156 °C; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:1.5); ^{1}H NMR (400 MHz, DMSO) δ 11.62 (s, 1H), 8.09 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.05 – 6.96 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.3 (C), 135.9 (C), 134.6 (C), 131.0 (CH), 129.9 (CH), 128.4 (C), 127.2 (CH), 124.0 (CH), 122.5 (C), 122.1 (CH), 120.3 (CH), 119.6 (CH), 111.4 (CH), 99.9 (CH) ppm; The identity of **1k** was confirmed based on reported NMR spectra.[22]



1l

2-(naphthalen-2-yl)-*1H*-indole– Isolation: 83 mg (68%) (Scheme 3, **1l**)

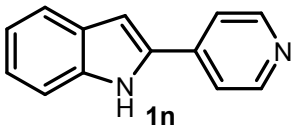
White solid; m.p. 200-202 °C; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.71 (s, 1H), 8.39 (s, 1H), 8.02 (m, 2H), 7.93 (t, *J* = 7.4 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 – 7.00 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.6 (C), 137.4 (C), 133.3 (C), 132.3 (C), 129.7 (C), 128.7 (C), 128.4 (CH), 127.9 (CH), 127.7 (CH), 126.7 (CH), 126.0 (CH), 123.8 (CH), 122.8 (CH), 121.8 (CH), 120.1 (CH), 119.5 (CH), 111.3 (CH), 99.6 (CH) ppm; The identity of **1l** was confirmed based on reported NMR spectra.



1m

2-(phenanthren-9-yl)-*1H*-indole– Isolation: 116 mg (80%) (Scheme 3, **1m**)

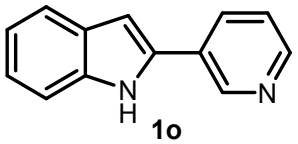
White foam; Rf: 0.7 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.71 (s, 1H), 8.94 (d, *J* = 8.0 Hz, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.12 – 8.02 (m, 2H), 7.82 – 7.62 (m, 5H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.7 (C), 136.4 (C), 130.9 (C), 130.3 (C), 130.0 (C), 129.7 (C), 129.5 (C), 128.8 (CH), 128.4 (C), 128.1 (CH), 127.3 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 123.4 (CH), 122.9 (CH), 121.5 (CH), 120.1 (CH), 119.4 (CH), 111.4 (CH), 102.8 (CH) ppm; HRMS (TOF MS EI^{+}) m/z: [M + H]$^{+}$ Calcd for $C_{22}H_{16}N$ 294.1277; found 294.1272.



1n

2-(pyridin-4-yl)-*1H*-indole– Isolation: 85 mg (88%) (Scheme 3, **1n**)

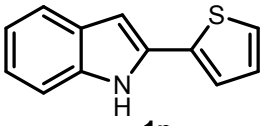
White solid; m.p. 240-242 °C; Rf: 0.2 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:50 to 100:100); ^{1}H NMR (400 MHz, DMSO) δ 11.82 (s, 1H), 8.62 (dd, *J* = 4.7, 1.5 Hz, 2H), 7.82 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 150.2 (CH), 139.1 (C), 137.7 (C), 134.7 (C), 128.3 (C), 122.9 (CH), 120.8 (CH), 119.9 (CH), 119.1 (CH), 111.7 (CH), 101.7 (CH) ppm; HRMS (TOF MS EI^{+}) m/z: [M + H]$^{+}$ Calcd for $C_{13}H_{11}N_2$ 195.0916; found 195.0908.



1o

2-(pyridin-3-yl)-*1H*-indole– Isolation: 79 mg (81%) (Scheme 3, **1o**)

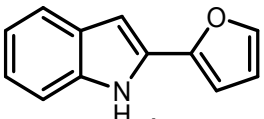
White solid; m.p. 168-170 °C; Rf: 0.2 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:20 to 100:100); ^{1}H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 9.16 (d, *J* = 2.0 Hz, 1H), 8.51 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.25 – 8.19 (m, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.07 – 7.01 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 148.2 (CH), 146.3 (CH), 137.4 (C), 134.6 (C), 132.1 (CH), 128.5 (C), 128.2 (C), 123.9 (CH), 122.2 (CH), 120.4 (CH), 119.7 (CH), 111.5 (CH), 100.0 (CH) ppm; The identity of **1o** was confirmed based on reported NMR spectra.[23]



1p

2-(thiophen-2-yl)-*1H*-indole– Isolation: 50 mg (50%) (Scheme 3, **1p**)

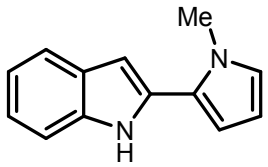
White solid; m.p. 166-168 °C; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.54 (s, 1H), 7.51 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.8 (C), 135.5 (C), 132.4 (C), 128.5 (C), 128.1 (CH), 125.1 (CH), 123.5 (CH), 121.7 (CH), 119.9 (CH), 119.5 (CH), 111.1 (CH), 98.7 (CH) ppm; The identity of **1p** was confirmed based on reported NMR spectra.[24]



1q

2-(furan-2-yl)-*1H*-indole– Isolation: 38 mg (41%) (Scheme 3, **1q**)

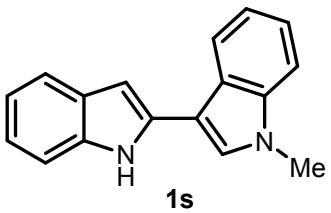
White solid; m.p. 122-124 ℃; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:1 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.54 (s, 1H), 7.77 – 7.72 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 3.3 Hz, 1H), 6.69 (s, 1H), 6.62 (dd, *J* = 3.3, 1.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 147.8 (C), 142.6 (CH), 136.6 (C), 129.4 (C), 128.2 (C), 121.8 (CH), 120.1 (CH), 119.5 (CH), 111.9 (CH), 111.3 (CH), 105.8 (CH), 97.7 (CH) ppm; The identity of **1q** was confirmed based on reported NMR spectra.[25]



1r

2-(1-methyl-1H-pyrrol-2-yl)-*1H*-indole– Isolation: 75 mg (77%) (Scheme 3, **1r**)

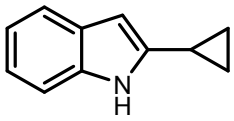
White to pale purple solid; m.p. 92-94 ℃; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 11.18 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.56 (dd, *J* = 3.8, 1.5 Hz, 2H), 6.13 (dd, *J* = 3.5, 2.8 Hz, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.2 (C), 131.0 (C), 128.8 (C), 126.0 (C), 124.9 (CH), 121.1 (CH), 119.6 (CH), 119.1 (CH), 110.8 (CH), 108.5 (CH), 107.4 (CH), 98.0 (CH), 35.6 (CH_3) ppm; The identity of **1r** was confirmed based on reported NMR spectra.[26]



1s

1'-methyl-*1H*,*1'H*-2,3'-biindole– Isolation: 49 mg (40%) (Scheme 3, **1s**)

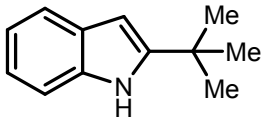
White to purple solid**;** m.p. 142-144 ℃; Rf: 0.5 (Hex/EA 3:1); Purified by column chromatography eluting with Hexane:EA (100:5 to 100:10); ^{1}H NMR (400 MHz, DMSO) δ 11.23 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.82 (s, 1H), 7.52 (dd, *J* = 7.9, 4.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (m, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.76 (s, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.1 (C), 136.1 (C), 133.7 (C), 129.2 (C), 127.3 (CH), 125.0 (C), 121.9 (CH), 120.4 (CH), 120.0 (CH), 119.9 (CH), 119.1 (CH), 118.9 (CH), 110.5 (CH), 110.3 (CH), 107.7 (C), 97.0 (CH), 32.8 (CH_3) ppm; The identity of **1s** was confirmed based on reported NMR spectra.[26]



1t

2-cyclopropyl-*1H*-indole– Isolation: 39 mg (50%) (Scheme 3, **1t**)

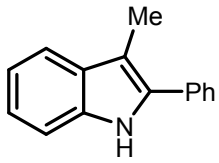
White solid; m.p. 60-62 ℃; Rf: 0.4 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:2); ^{1}H NMR (400 MHz, DMSO) δ 10.81 (s, 1H), 7.38 – 7.27 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.91 (m, 2H), 6.04 (s, 1H), 2.08 – 1.87 (m, 1H), 0.93 (qd, *J* = 6.4, 4.0 Hz, 2H), 0.86 – 0.63 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 142.2 (C), 135.8 (C), 128.4 (C), 119.8 (CH), 118.8 (CH), 118.6 (CH), 110.4 (CH), 96.3 (CH), 9.1 (CH), 8.0 (CH_2) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_{12}N$ 158.0964; found 158.0952.



1u

2-(*tert*-butyl)-*1H*-indole– Isolation: 57 mg (66%) (Scheme 3, **1u**)

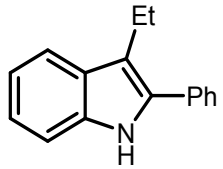
Yellow to White solid**;** m.p. 72-74 ℃; Rf: 0.5 (Hex/DCM 5:1); Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:30); ^{1}H NMR (400 MHz, DMSO) δ 10.82 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.95 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.87 (td, *J* = 7.5, 1.0 Hz, 1H), 6.06 (d, *J* = 1.5 Hz, 1H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 149.1 (C), 136.2 (C), 127.8 (C), 120.0 (CH), 119.3 (CH), 118.4 (CH), 110.6 (CH), 95.5 (CH), 31.7 (C), 30.0 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{16}N$ 174.1277; found 174.1271.



1a'

3-methyl-2-phenyl-*1H*-indole– Isolation: 88 mg (85%) (Scheme 4, **1a'**)

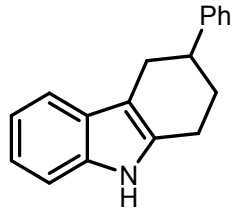
White solid; m.p. 94-96 ℃; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:1); ^{1}H NMR (400 MHz, DMSO) δ 11.31 (s, 1H), 7.84 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.72 – 7.64 (m, 3H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 2.58 (s, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.0 (C), 133.8 (C), 133.1 (C), 129.4 (C), 128.7 (CH), 127.5 (CH), 127.0 (CH), 121.6 (CH), 118.6 (CH), 118.4 (CH), 111.0 (CH), 106.8 (C), 9.9 (CH_3) ppm; The identity of **1a'** was confirmed based on reported NMR spectra.[27]



1b'

3-ethyl-2-phenyl-*1H*-indole– Isolation: 74 mg (67%) (Scheme 4, **1b'**)

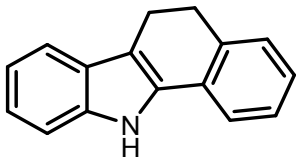
White solid; m.p. 85-87 °C; Rf: 0.6 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.10 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.1 (C), 133.4 (C), 133.1 (C), 128.8 (CH), 128.4 (C), 127.6 (CH), 127.2 (CH), 121.5 (CH), 118.6 (CH), 118.5 (CH), 113.6 (C), 111.2 (CH), 17.5 (CH_2), 15.7 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N$ 222.1277; found 222.1267.



1c'

3-phenyl-2,3,4,9-tetrahydro-*1H*-carbazole– Isolation: 46 mg (37%) (Scheme 4, **1c'**)

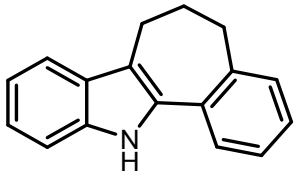
White solid; m.p. 128-130 °C; Rf: 0.3 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:5 to 100:15); ^{1}H NMR (400 MHz, DMSO) δ 10.65 (s, 1H), 7.42 – 7.06 (m, 7H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 2.99 – 2.68 (m, 4H), 2.68 – 2.55 (m, 1H), 2.05 – 1.89 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 146.8 (C), 136.0 (C), 134.1 (C), 128.3 (CH), 127.1 (C), 126.9 (CH), 126.0 (CH), 120.1 (CH), 118.1 (CH), 117.2 (CH), 110.6 (CH), 108.2 (C), 40.7 (CH), 30.1 (CH_2), 29.3 (CH_2), 23.0 (CH_2) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}N$ 248.1433; found 248.1422.



1d'

6,11-dihydro-*5H*-benzo[*a*]carbazole– Isolation: 66 mg (60%) (Scheme 4, **1d'**)

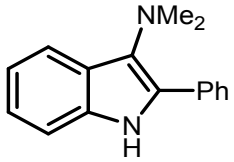
White solid; m.p. 164-166 ℃; Rf: 0.5 (Hex/DCM 5:1); Purified by column chromatography eluting with Hexane:DCM (100:1 to 100:5); ^{1}H NMR (400 MHz, DMSO) δ 11.37 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.14 – 7.00 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.1 (C), 135.9 (C), 133.1 (C), 129.1 (C), 128.2 (CH), 126.7 (C), 126.7 (CH), 126.5 (CH), 121.6 (CH), 120.9 (CH), 118.9 (CH), 118.4 (CH), 111.3 (CH), 110.7 (C), 29.0 (CH_2), 19.3 (CH_2) ppm; The identity of **1d'** was confirmed based on reported NMR spectra.[28]



1e'

5,6,7,12-tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]indole– Isolation: 73 mg (63%) (Scheme 4, **1e'**)

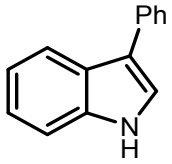
White foam; Rf: 0.5 (Hex/DCM 5:1); Purified by column chromatography eluting with Hexane:DCM (100:1 to 100:5); ^{1}H NMR (400 MHz, DMSO) δ 11.00 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.21 – 7.03 (m, 3H), 6.94 (t, *J* = 7.4 Hz, 1H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.84 – 2.76 (m, 2H), 1.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 141.3 (C), 136.4 (C), 132.5 (C), 131.5 (C), 129.5 (CH), 129.2 (C), 126.7 (CH), 126.3 (CH), 126.3 (CH), 122.1 (CH), 118.5 (CH), 118.2 (CH), 112.9 (C), 110.9 (CH), 35.0 (CH_2), 26.2 (CH_2), 25.9 (CH_2) ppm; HRMS (TOF MS EI^{+}) m/z: [M + H]$^{+}$ Calcd for $C_{17}H_{16}N$ 234.1277; found 234.1270.



1f'

N,N-dimethyl-2-phenyl-*1H*-indol-3-amine– Isolation:56 mg (47%) (Scheme 4, **1f'**)

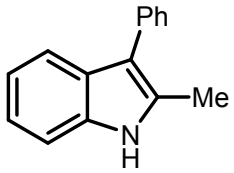
White foam; Rf: 0.5 (Hex/EA 10:1); Purified by column chromatography eluting with Hexane:EA (100:0 to 100:1); ^{1}H NMR (400 MHz, DMSO) δ 11.03 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 2.86 (s, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 134.9 (C), 132.4 (C), 129.0 (C), 128.4 (CH), 127.2 (C), 126.8 (CH), 126.6 (CH), 124.8 (C), 121.4 (CH), 119.8 (CH), 118.4 (CH), 111.8 (CH), 45.0 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{16}H_{17}N_2$ 237.1386; found 236.1378.



1g'

3-phenyl-*1H*-indole– Isolation:24 mg (25%) (Scheme 4, **1g'**)

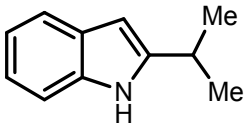
White solid; m.p. 81-83 °C; Rf: 0.5 (Hex/EA 10:1) Purified by column chromatography eluting with Hexane:EA (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 11.33 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 3H), 7.47 – 7.35 (m, 3H), 7.23 – 7.02 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.9 (C), 135.9 (C), 128.8 (CH), 126.5 (CH), 125.2 (CH), 125.0 (C), 123.4 (CH), 121.4 (CH), 119.6 (CH), 119.0 (CH), 115.7 (C), 112.0 (CH) ppm; The identity of **1g'** was confirmed based on reported NMR spectra.[29]



1h'

2-methyl-3-phenyl-*1H*-indole– Isolation: 57 mg (55%) (Scheme 4, **1h'**)

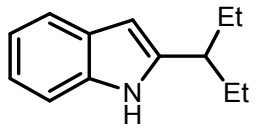
White solid; m.p. 61-63 °C; Rf: 0.5 (Hex/EA 10:1) Purified by column chromatography eluting with Hexane:EA (100:0 to 100:4); ^{1}H NMR (400 MHz, DMSO) δ 11.15 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.08 – 7.02 (m, 1H), 7.01 – 6.96 (m, 1H), 2.53 – 2.47 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 136.0 (C), 135.7 (C), 132.7 (C), 129.1 (CH), 129.0 (CH), 127.4 (C), 125.7 (CH), 121.0 (CH), 119.6 (CH), 118.1 (CH), 112.8 (C), 111.2 (CH), 12.8 (CH_3) ppm; The identity of **1h'** was confirmed based on reported NMR spectra.[29]



1j'

2-isopropyl-*1H*-indole– Isolation: 41 mg (52%) (Scheme 5, **1j'**)

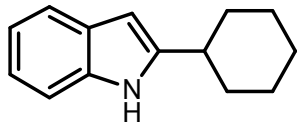
White solid; m.p. 75-77 °C; Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 10.84 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.91 (m, 2H), 6.07 (s, 1H), 2.99 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 146.3 (C), 136.0 (C), 128.1 (C), 120.0 (CH), 119.2 (CH), 118.5 (CH), 110.6 (CH), 96.0 (CH), 27.2 (CH), 22.4 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_{14}N$ 160.1120; found 160.1110.



1k'

2-(pentan-3-yl)-*1H*-indole– Isolation: 36 mg (38%) (Scheme 5, **1k'**)

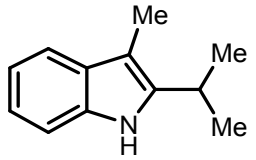
Colorless oil; Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 10.80 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 6.92 (m, 2H), 6.10 (d, *J* = 1.5 Hz, 1H), 2.59 – 2.50 (m, 1H), 1.64 (M, 4H), 0.76 (t, *J* = 7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 143.2 (C), 136.0 (C), 128.2 (C), 119.8 (CH), 119.0 (CH), 118.4 (CH), 110.6 (CH), 98.1 (CH), 42.1 (CH), 27.3 (CH_2), 11.9 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{13}H_{18}N$ 188.1433; found 188.1425.



1l'

2-cyclohexyl-*1H*-indole– Isolation: 50 mg (50%) (Scheme 5, **1l'**)

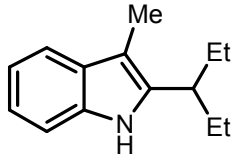
White solid; m.p. 103-105 °C; Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 10.81 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 6.90 (m, 2H), 6.05 (s, 1H), 2.66 (m, 1H), 1.99 (m, 2H), 1.79 – 1.72 (m, 2H), 1.65 (m, 1H), 1.46 – 1.31 (m, 4H), 1.27 – 1.18 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 145.8 (C), 136.2 (C), 128.5 (C), 120.3 (CH), 119.6 (CH), 118.8 (CH), 111.0 (CH), 96.5 (CH), 37.2 (CH), 32.9 (CH_2), 26.3 (CH_2), 26.2 (CH_2) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{18}N$ 200.1433; found 200.1431.



1m'

2-isopropyl-*1H*-indole– Isolation: 52 mg (60%) (Scheme 5, **1m'**)

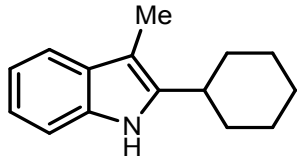
Colorless to yellow oil**;** Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 9.74 (s, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 6.11 (m, 2H), 2.36 (m, 1H), 1.33 (s, 3H), 0.43 (d, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 140.9 (C), 135.1 (C), 128.8 (C), 119.9 (CH), 117.9 (CH), 117.4 (CH), 110.5 (CH), 103.0 (C), 25.3 (CH), 22.4 (CH_3), 8.3 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{16}N$ 174.1277; found 174.1267.



1n'

3-methyl-2-(pentan-3-yl)-*1H*-indole– Isolation: 43 mg (43%) (Scheme 5, **1n'**)

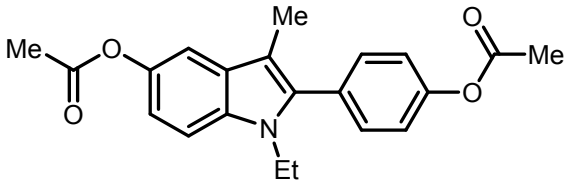
Colorless to yellow oil**;** Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 10.48 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.81 (m, 2H), 2.66 (m, 1H), 2.16 (s, 3H), 1.79 – 1.49 (m, 4H), 0.72 (t, *J* = 7.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 137.9 (C), 135.5 (C), 128.6 (C), 119.8 (CH), 117.7 (CH), 117.4 (CH), 110.3 (CH), 105.9 (C), 40.1 (CH), 27.6 (CH_2), 12.2 (CH_3), 8.6 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{20}N$ 202.1590; found 202.1580.



1o'

2-cyclohexyl-3-methyl-*1H*-indole – Isolation: 54 mg (51%) (Scheme 5, **1o'**)

Colorless to yellow oil**;** Rf: 0.5 (Hex/DCM 10:1) Purified by column chromatography eluting with Hexane:DCM (100:0 to 100:3); ^{1}H NMR (400 MHz, DMSO) δ 10.53 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.01 – 6.79 (m, 2H), 2.79 (m, 1H), 2.15 (s, 3H), 1.85 – 1.68 (m, 5H), 1.59 (m, 2H), 1.51 – 1.33 (m, 2H), 1.33 – 1.18 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 140.3 (C), 135.1 (C), 128.7 (C), 119.8 (CH), 117.9 (CH), 117.4 (CH), 110.5 (CH), 103.2 (C), 35.4 (CH), 32.3 (CH_2), 26.3 (CH_2), 25.7 (CH_2), 8.4 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: [M + H]$^+$ Calcd for $C_{15}H_{20}N$ 214.1590; found 214.1582.



Zindoxifene

4-(5-acetoxy-1-ethyl-3-methyl-*1H*-indol-2-yl)phenyl acetate – final step isolation: 97 mg (3steps total yield: 55%) (Zindoxifene) - (Scheme 8)

White solid; m.p. 150-152 ℃; Rf: 0.5 (Hex/EA 2:1) Purified by column chromatography eluting with Hexane:EA (100:10 to 100:30); ^{1}H NMR (400 MHz, DMSO) δ 7.44 (dd, *J* = 8.6, 4.0 Hz, 3H), 7.25 (m, 3H), 6.89 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.03 (q, *J* = 6.9 Hz, 2H), 2.27 (m, 6H), 2.10 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 169.9 (C), 169.2 (C), 150.3 (C), 143.8 (C), 137.2 (C), 133.4 (C), 131.3 (CH), 128.9 (C), 128.2 (CH), 122.1 (CH), 115.9 (C), 110.9 (CH), 110.3 (CH), 108.3 (C), 38.3 (CH_2), 20.9 (CH_3), 15.1 (CH_3), 9.1 (CH_3) ppm; HRMS (TOF MS EI$^+$) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}NO_4$ 352.1543; found 352.1543.

10. References

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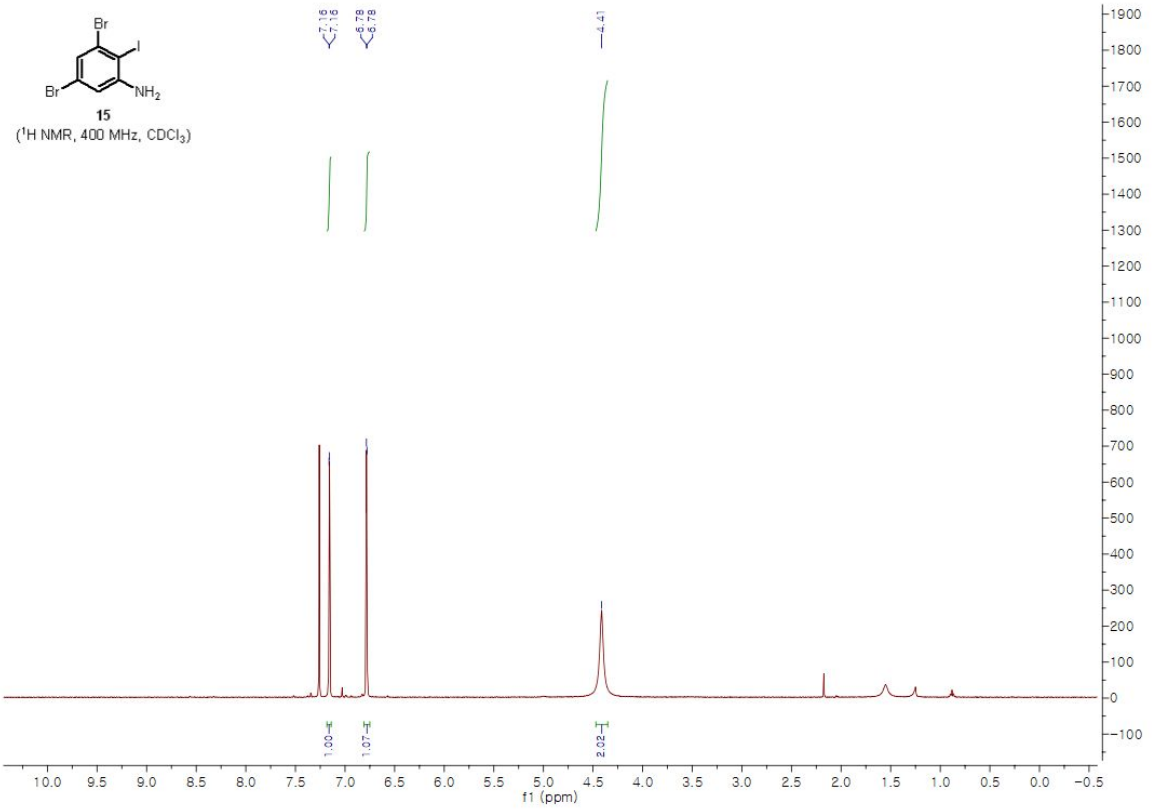
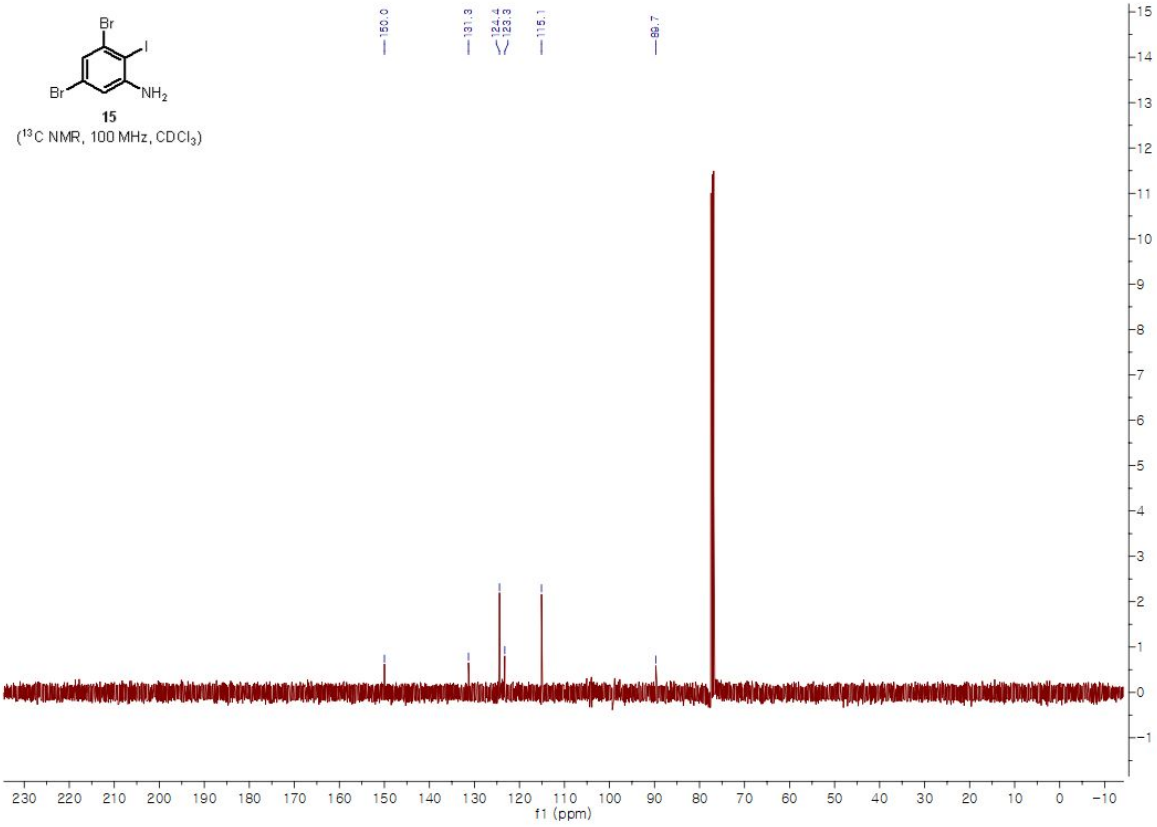
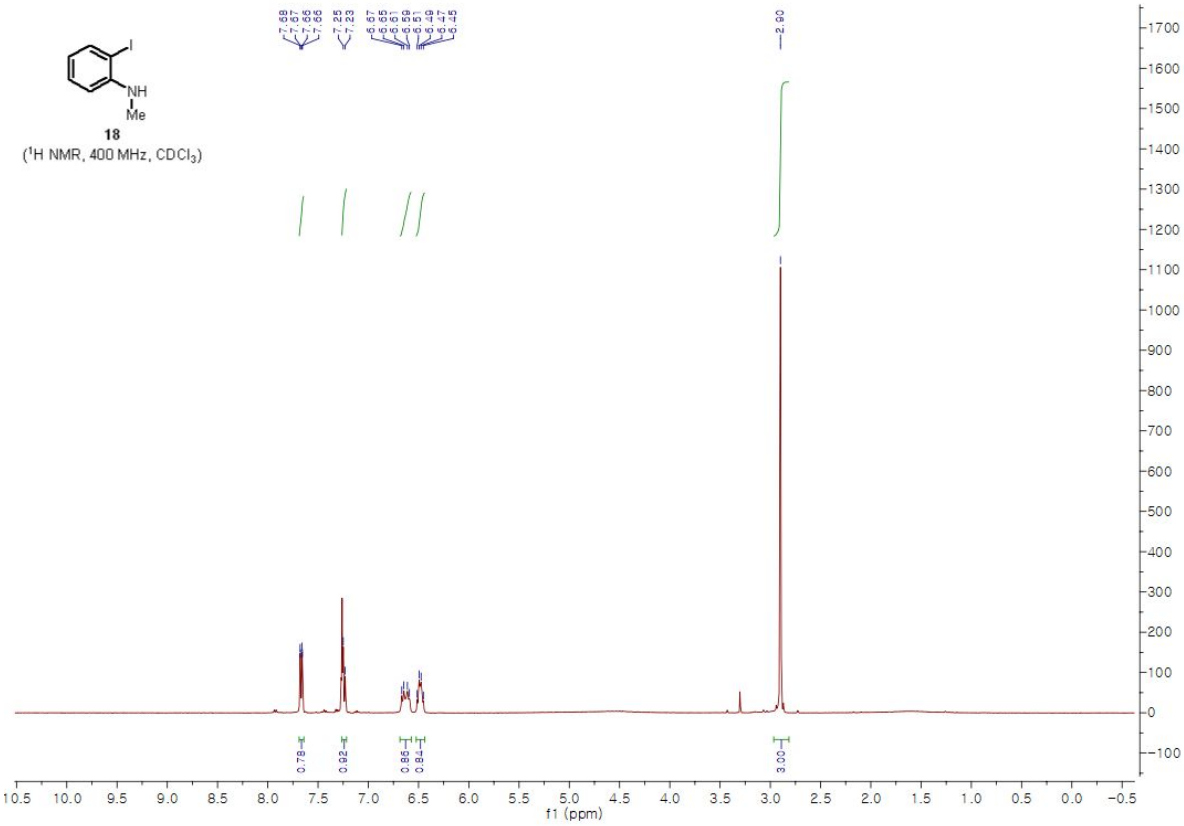
11. NMR Spectra of synthesized indole compounds

3,5-dibromo-2-iodoaniline (**15**)

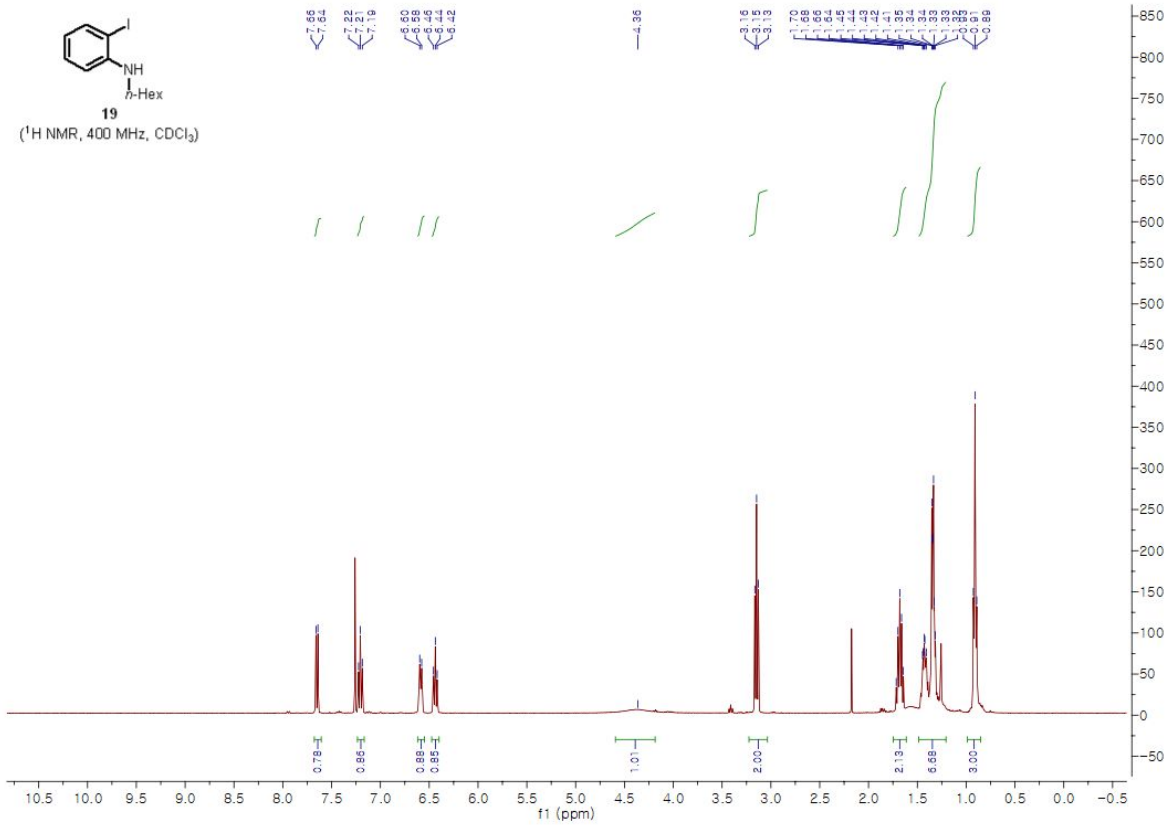




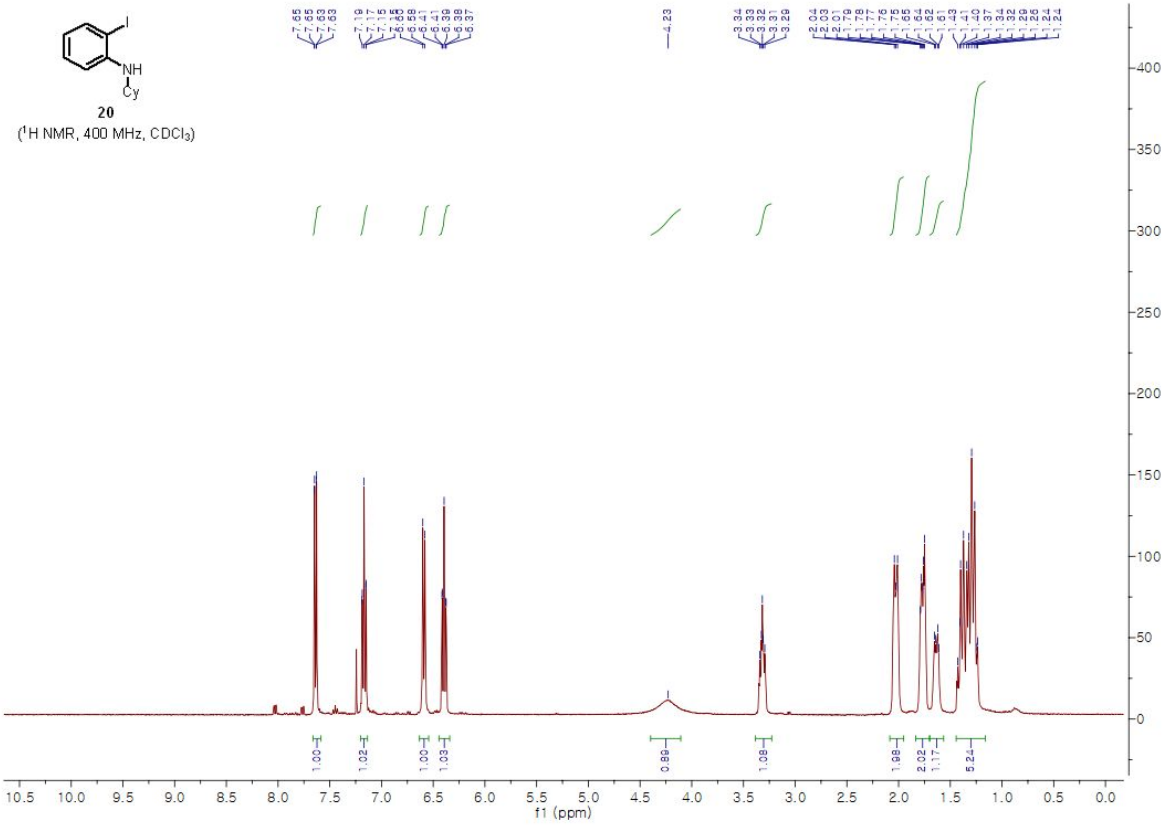
2-iodo-*N*-methylaniline (**18**)



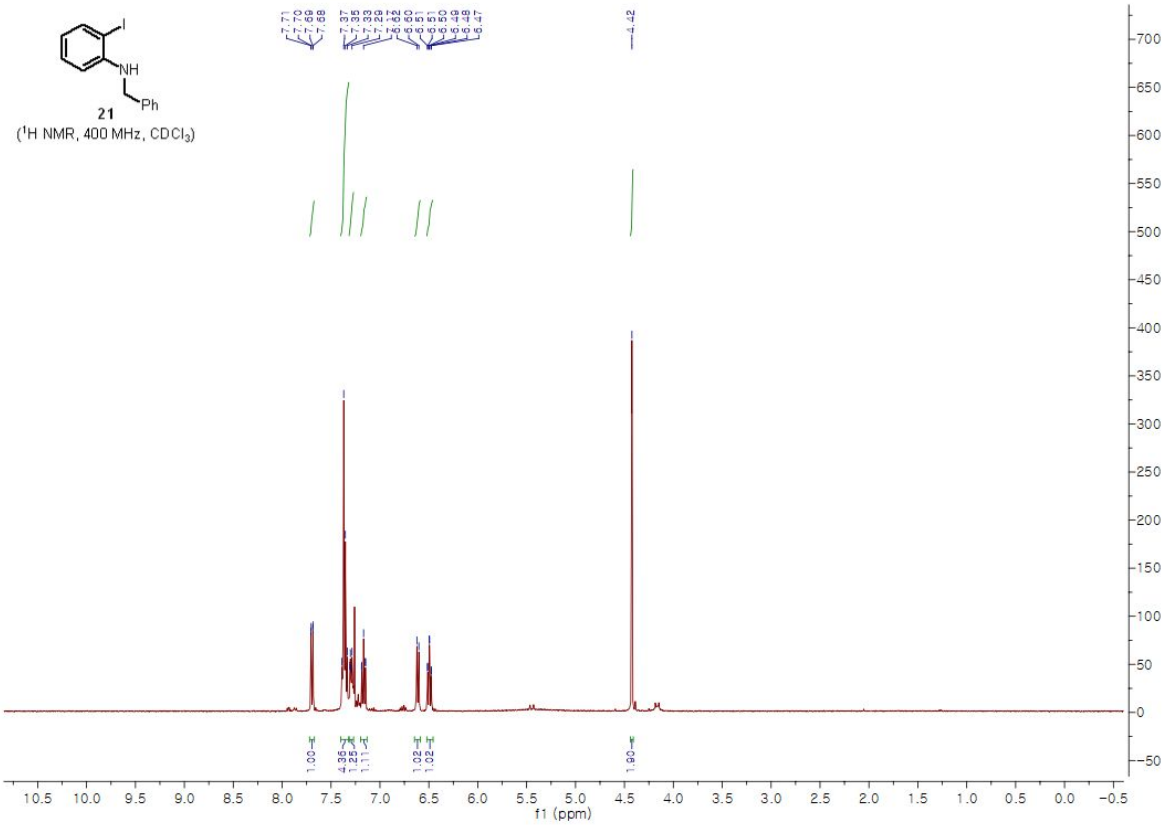
N-hexyl-2-iodoaniline (**19**)



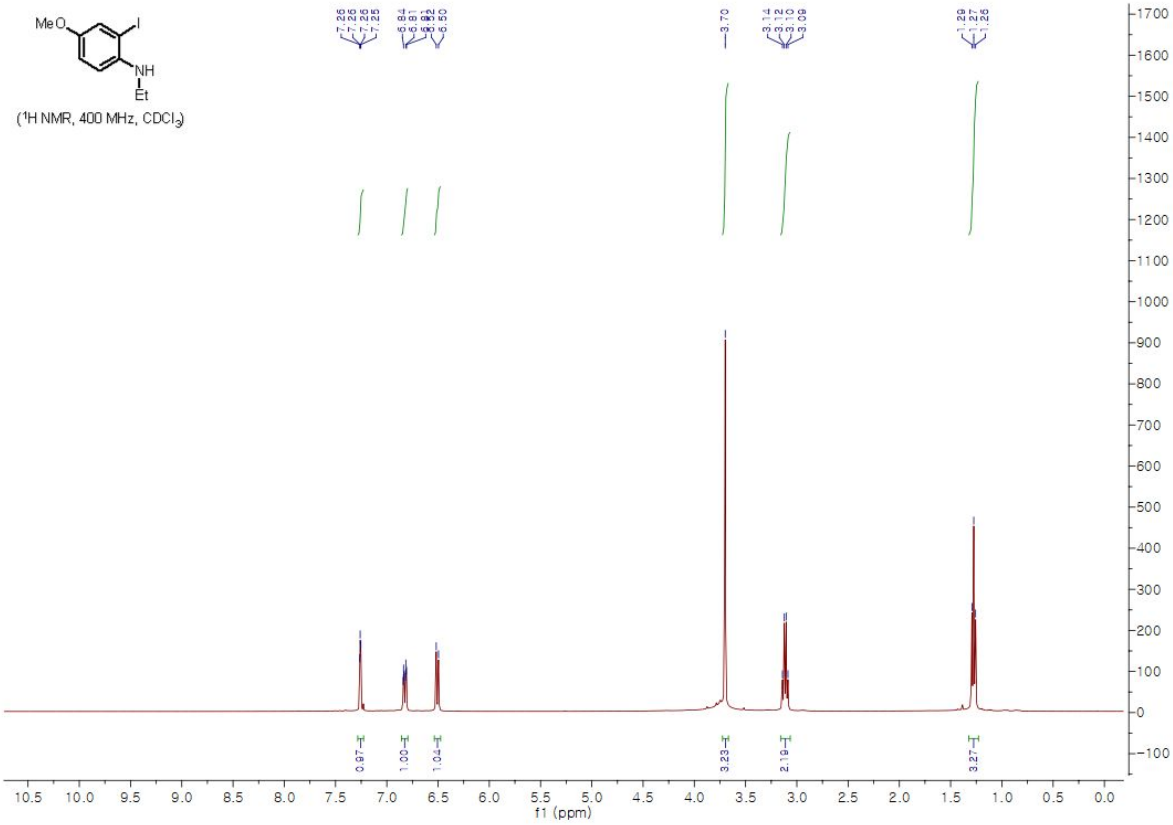
N-cyclohexyl-2-iodoaniline (**20**)

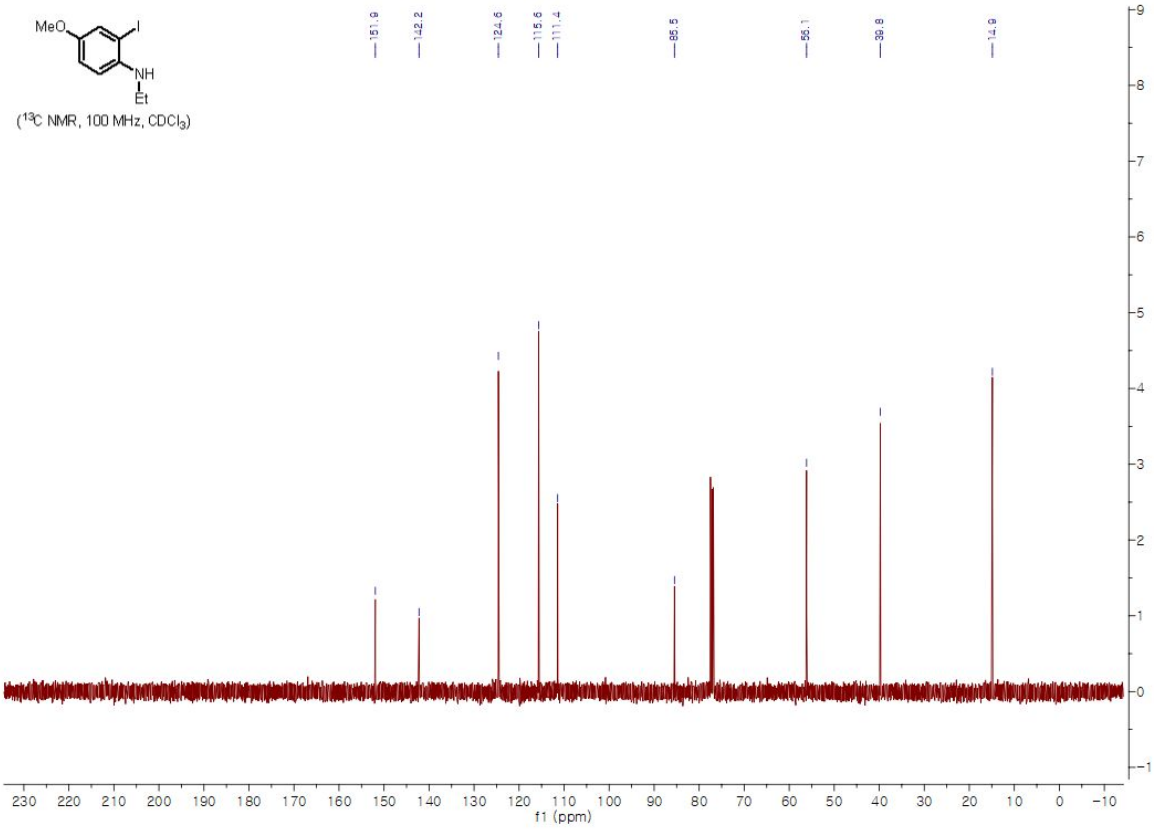


N-benzyl-2-iodoaniline

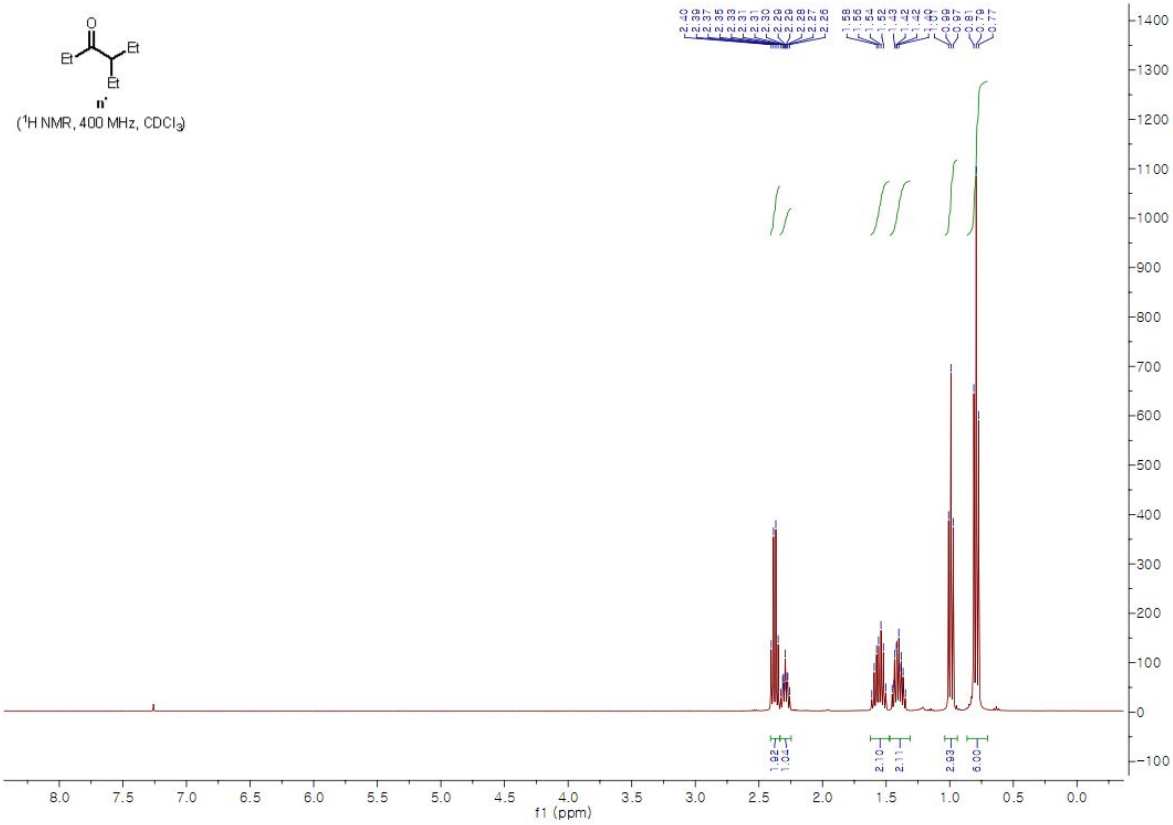


N-ethyl-2-iodo-4-methoxyaniline

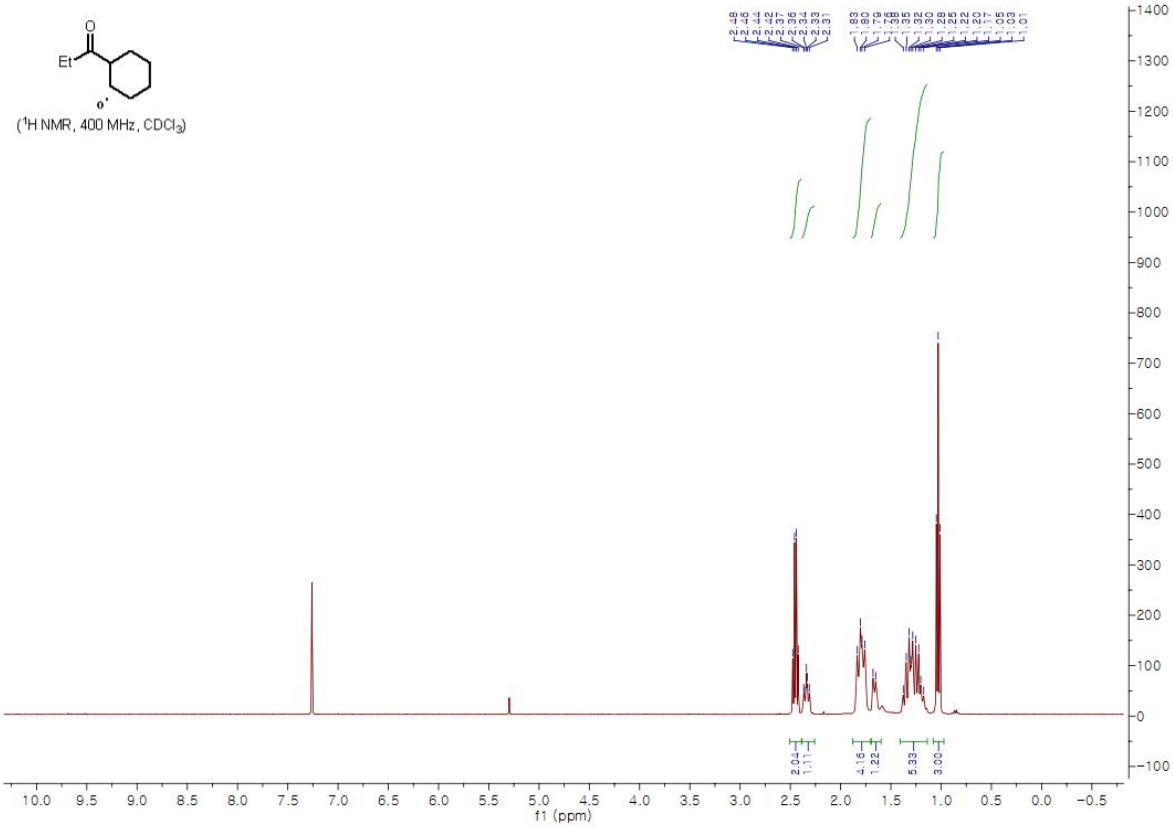




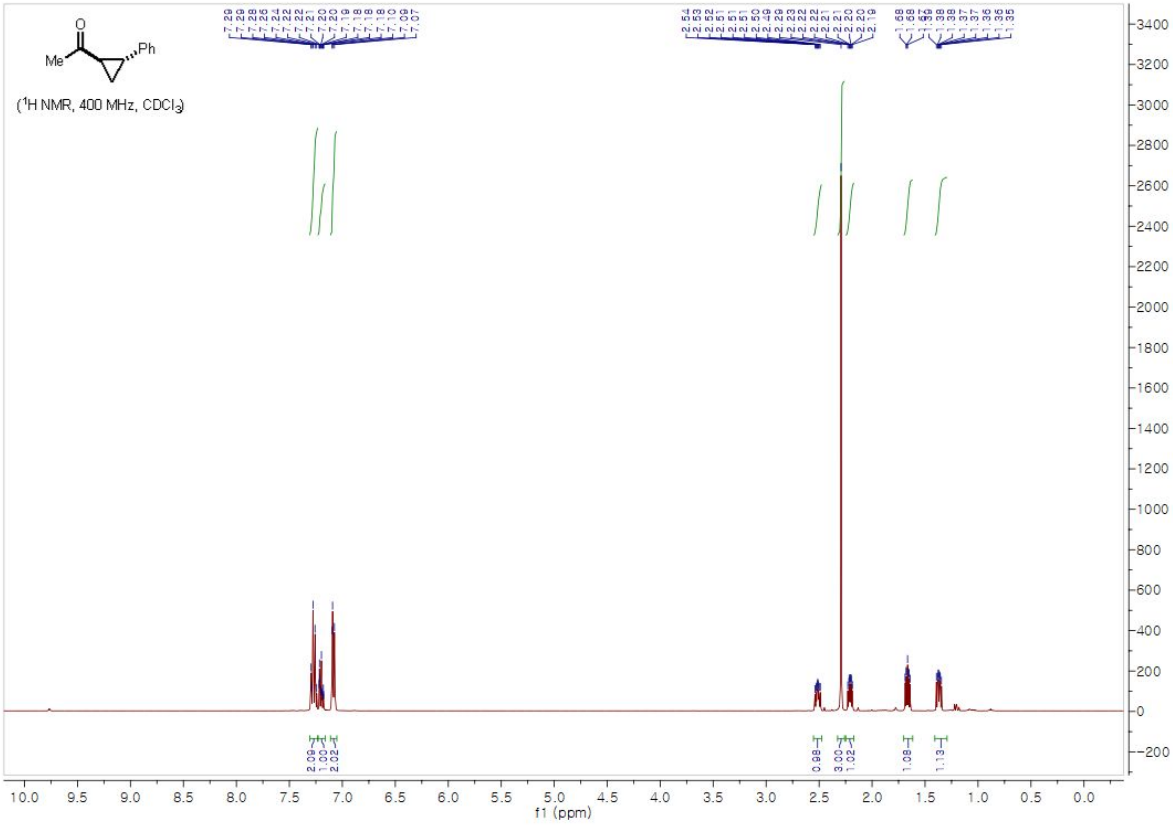
4-ethylhexan-3-one (**n'**)

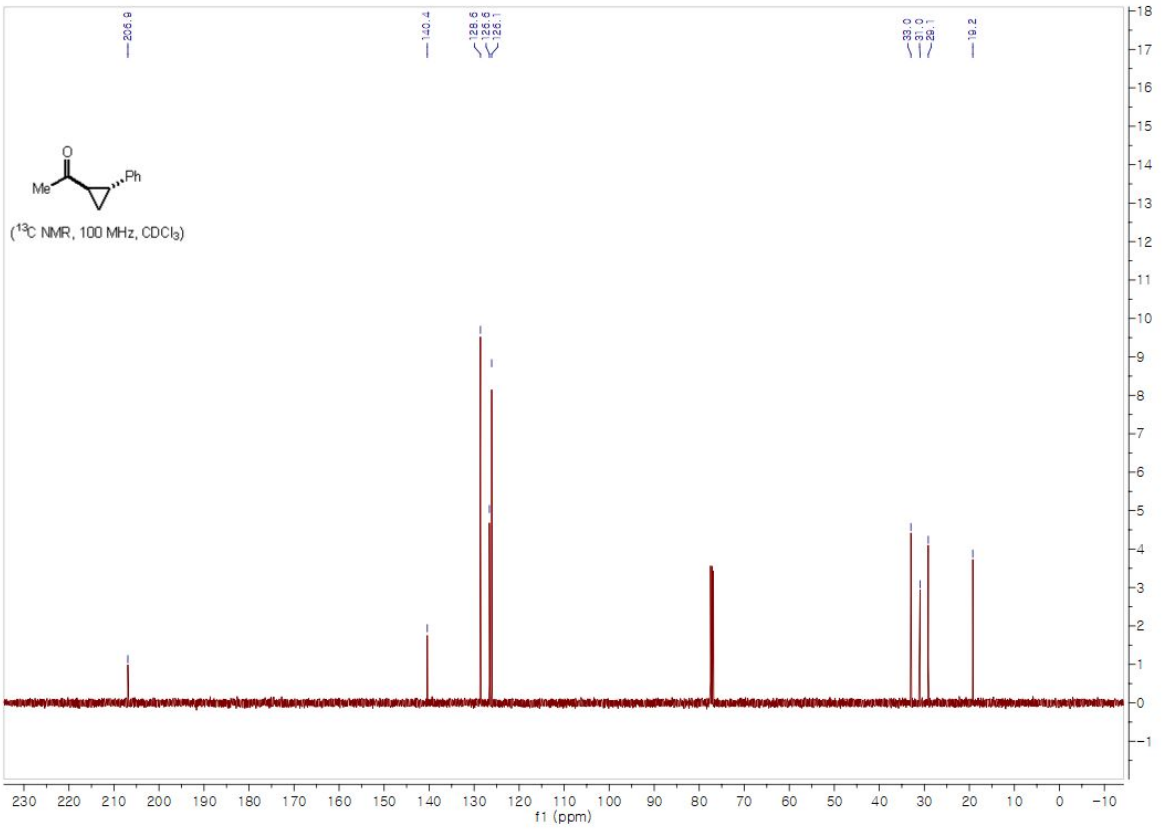


1-cyclohexylpropan-1-one (**o'**)

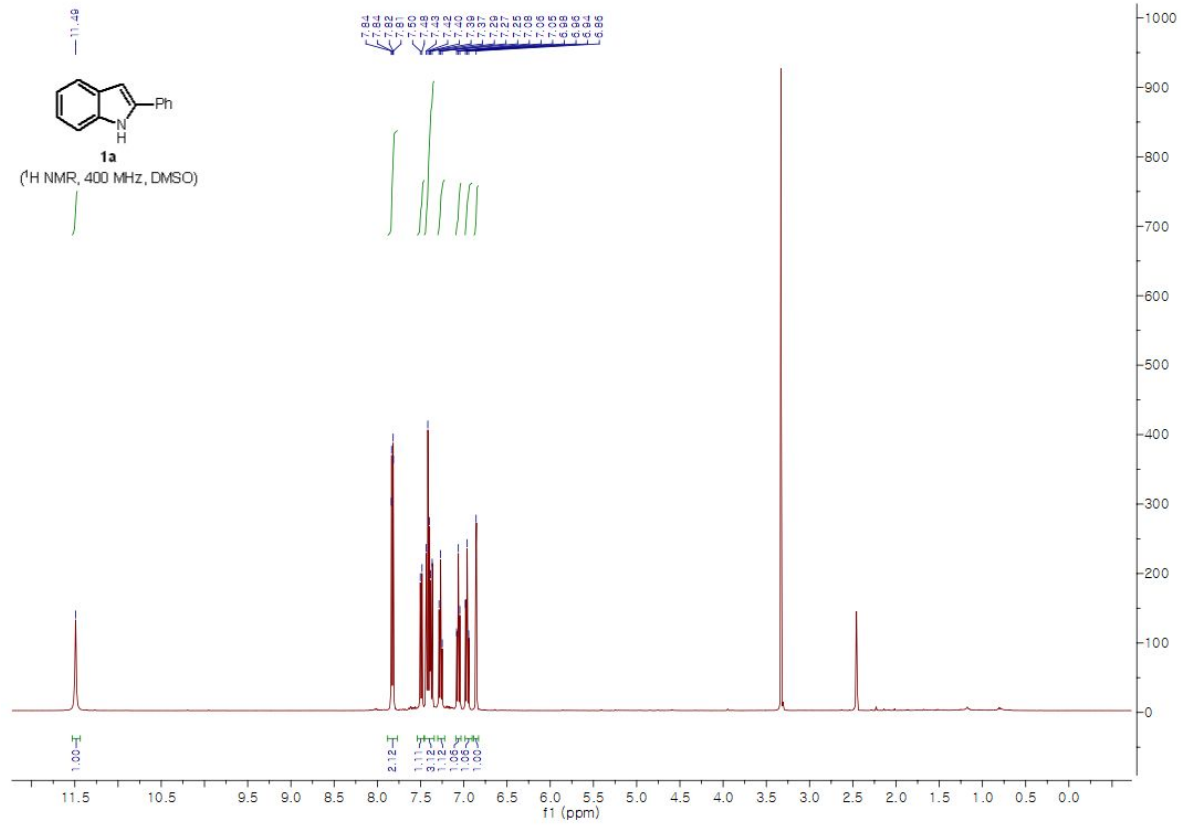


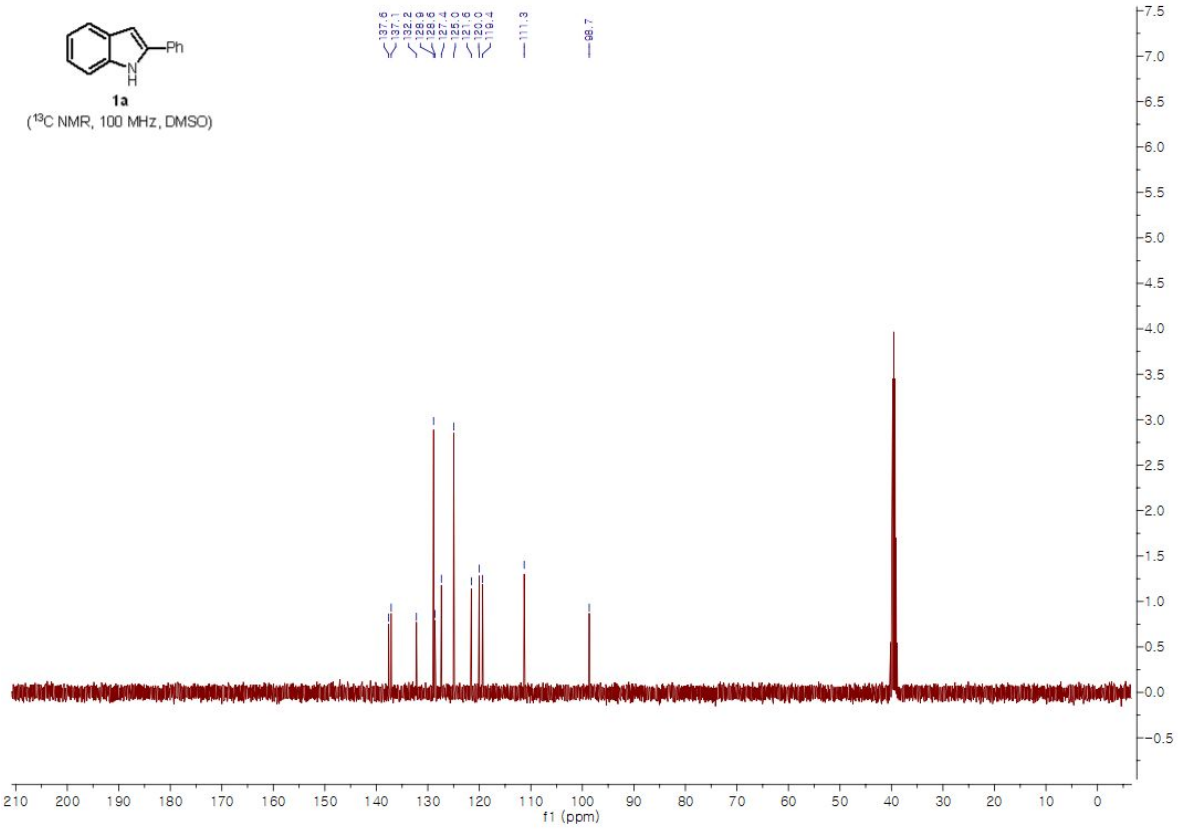
Trans-1-(2-phenylcyclopropyl)ethan-1-one



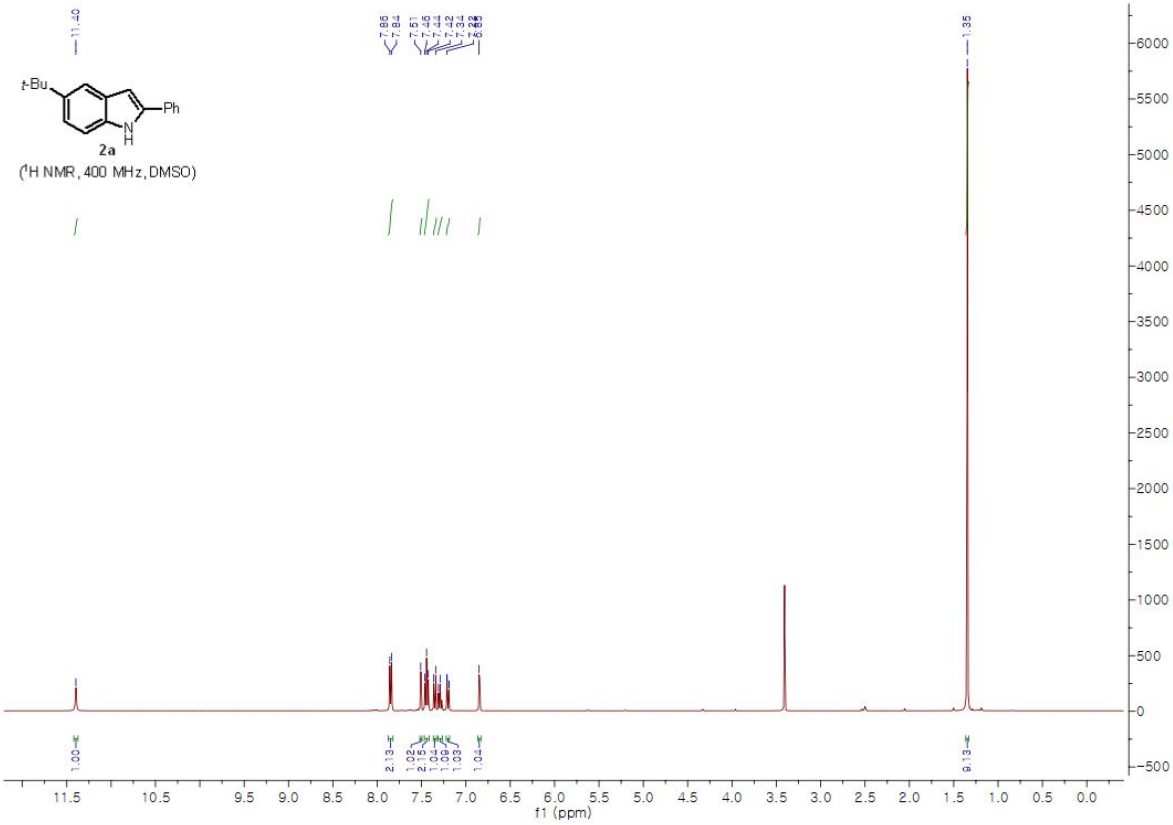


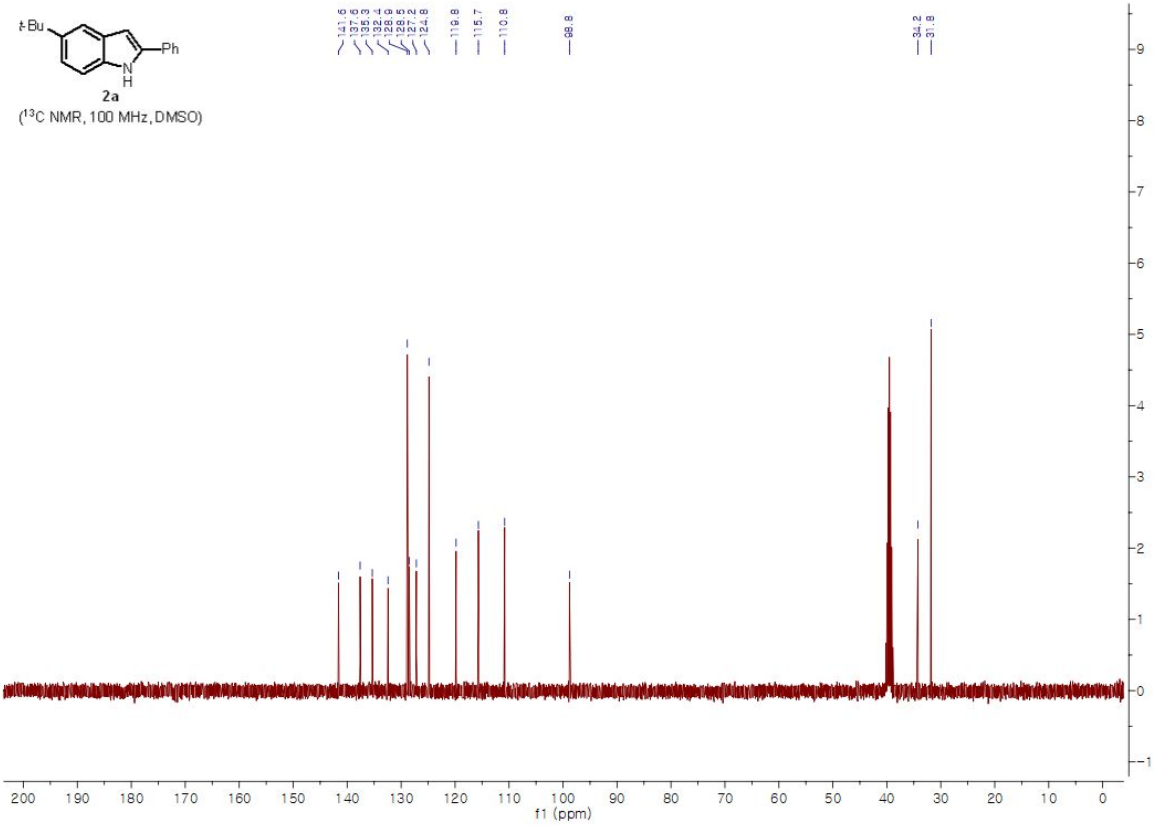
2-phenyl-*1H*-indole (Table 1, **1a**)



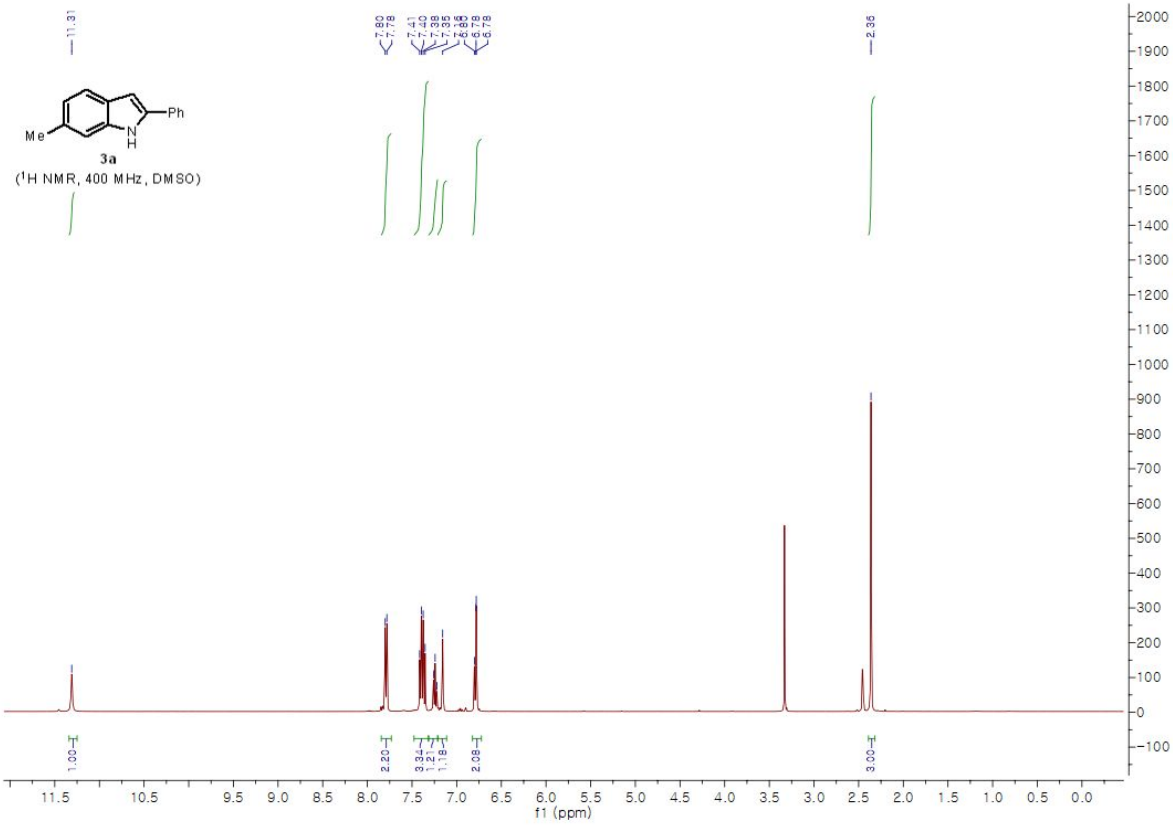


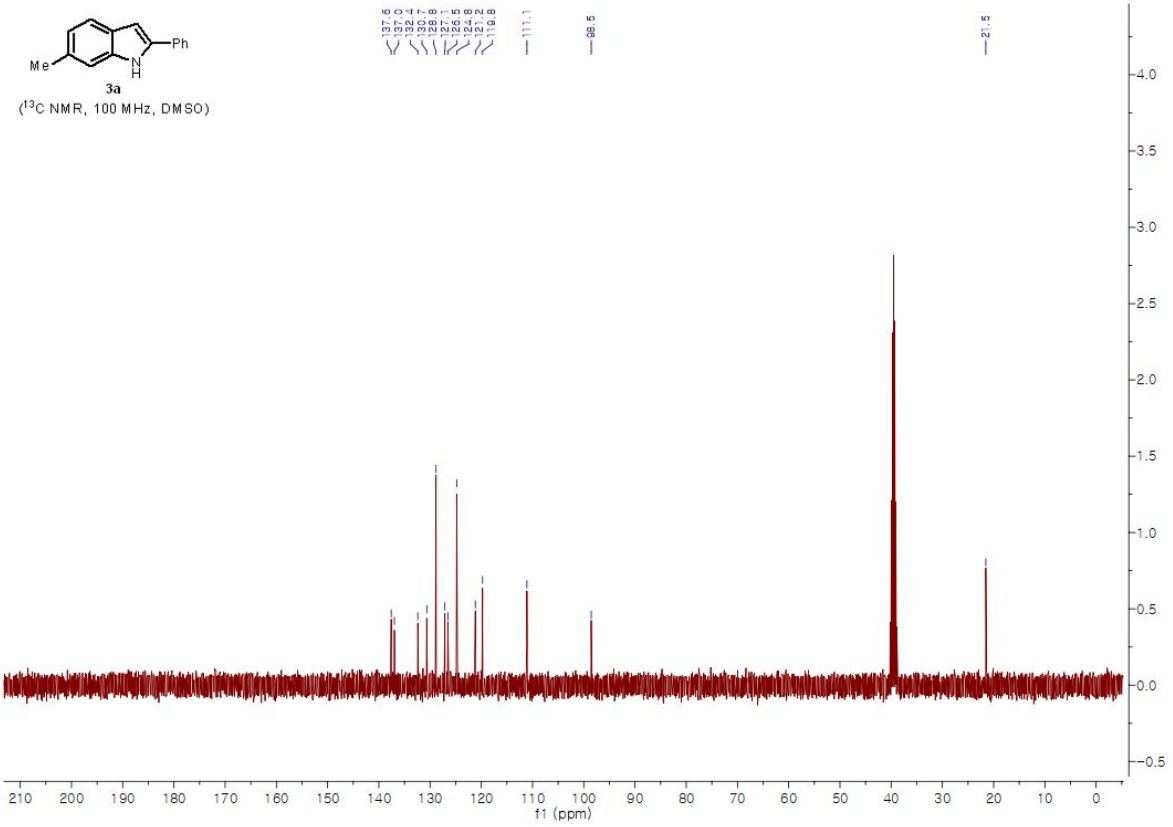
5-(*tert*-butyl)-2-phenyl-*1H*-indole (Scheme 2, **2a**)



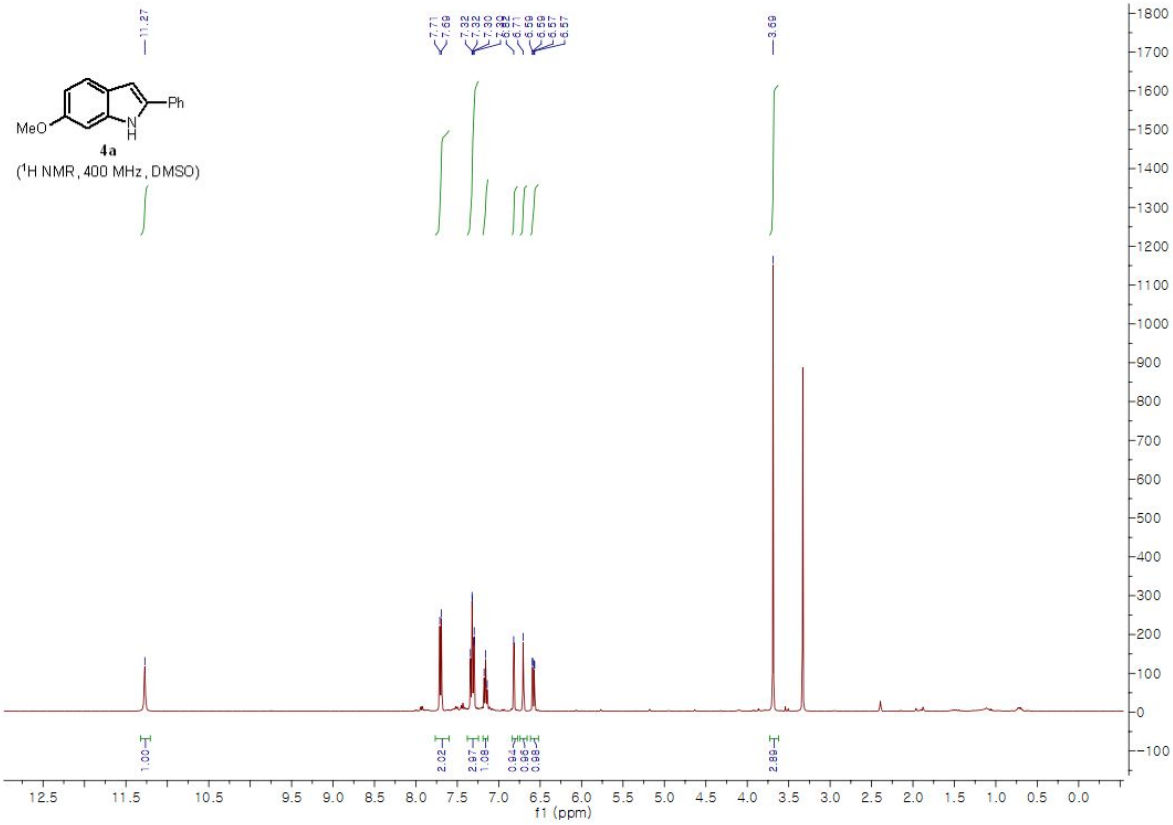


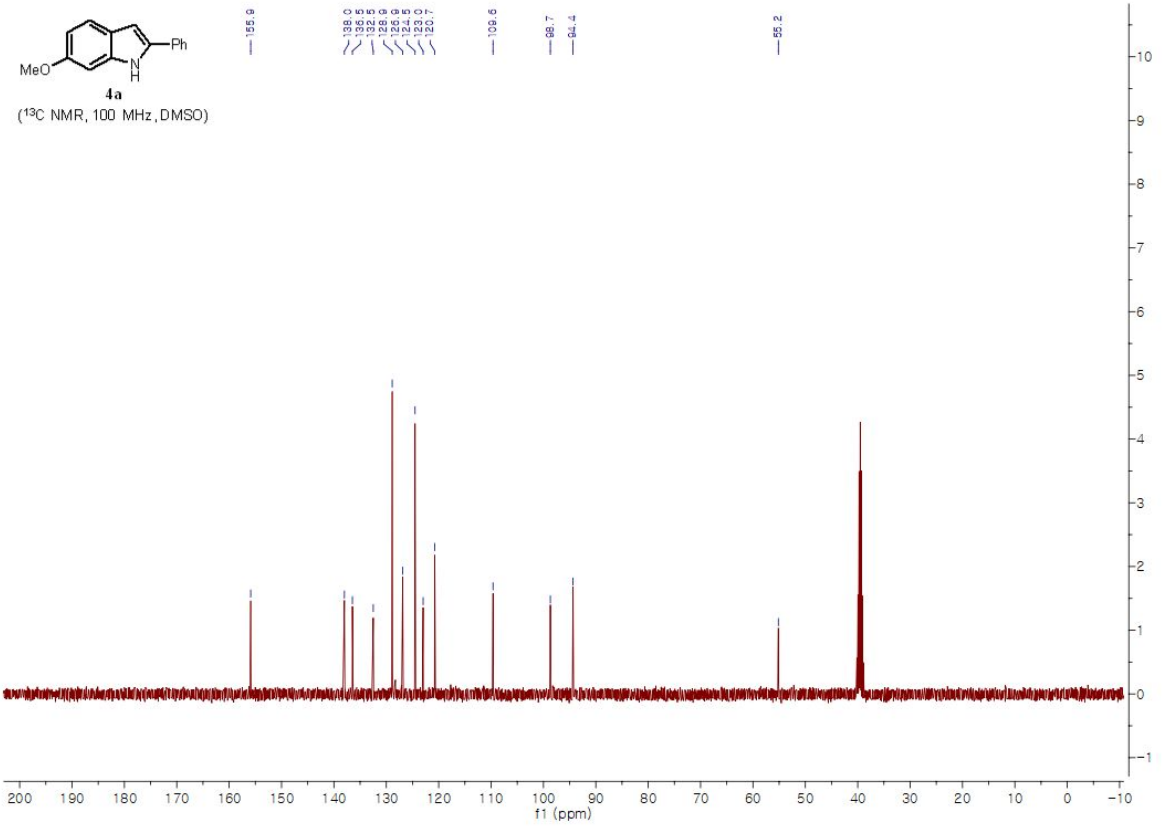
6-methyl-2-phenyl-*1H*-indole (Scheme 2, **3a**)



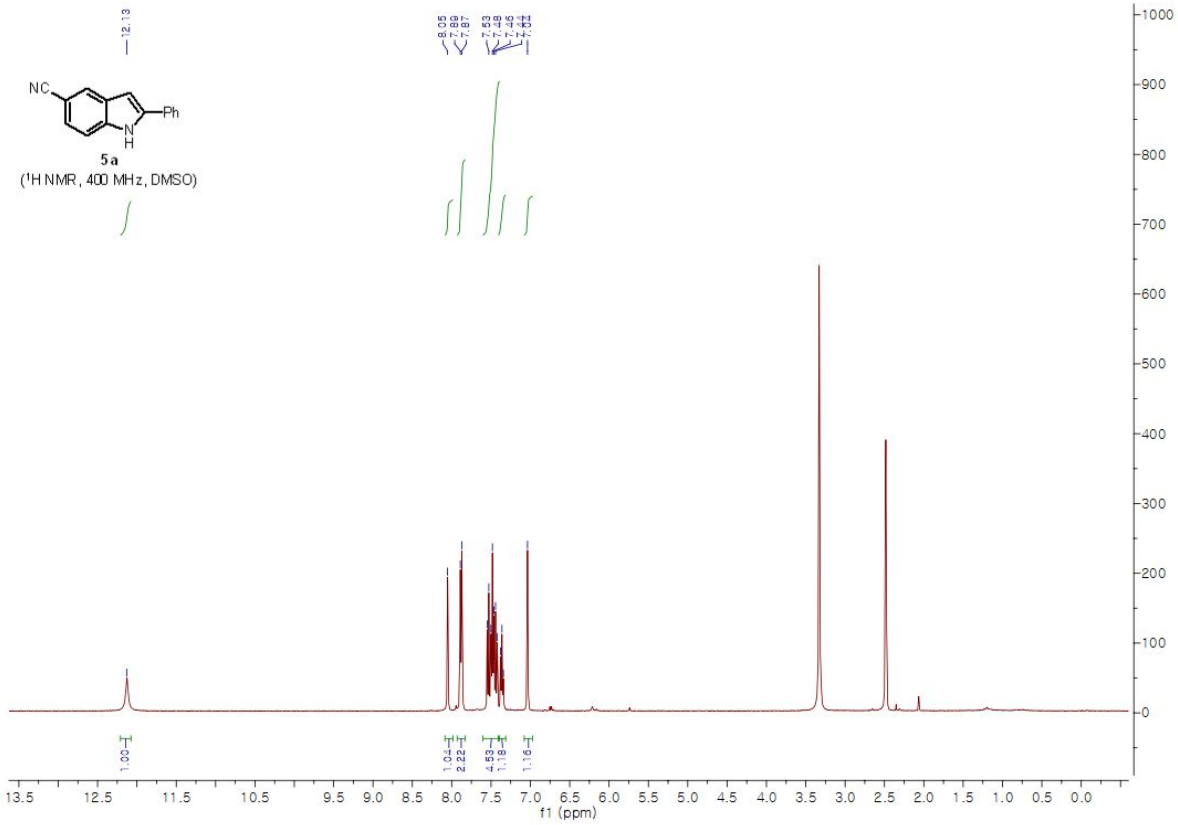


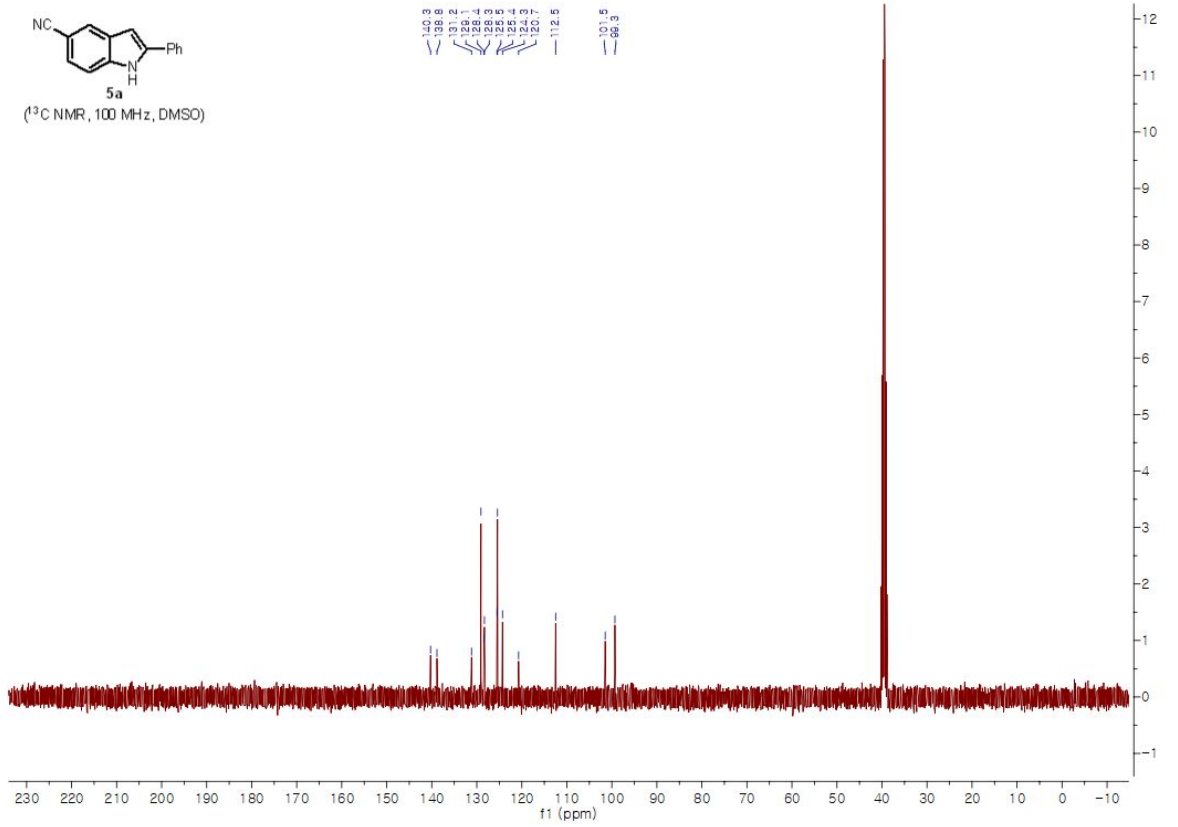
6-methoxy-2-phenyl-*1H*-indole (Scheme 2, **4a**)



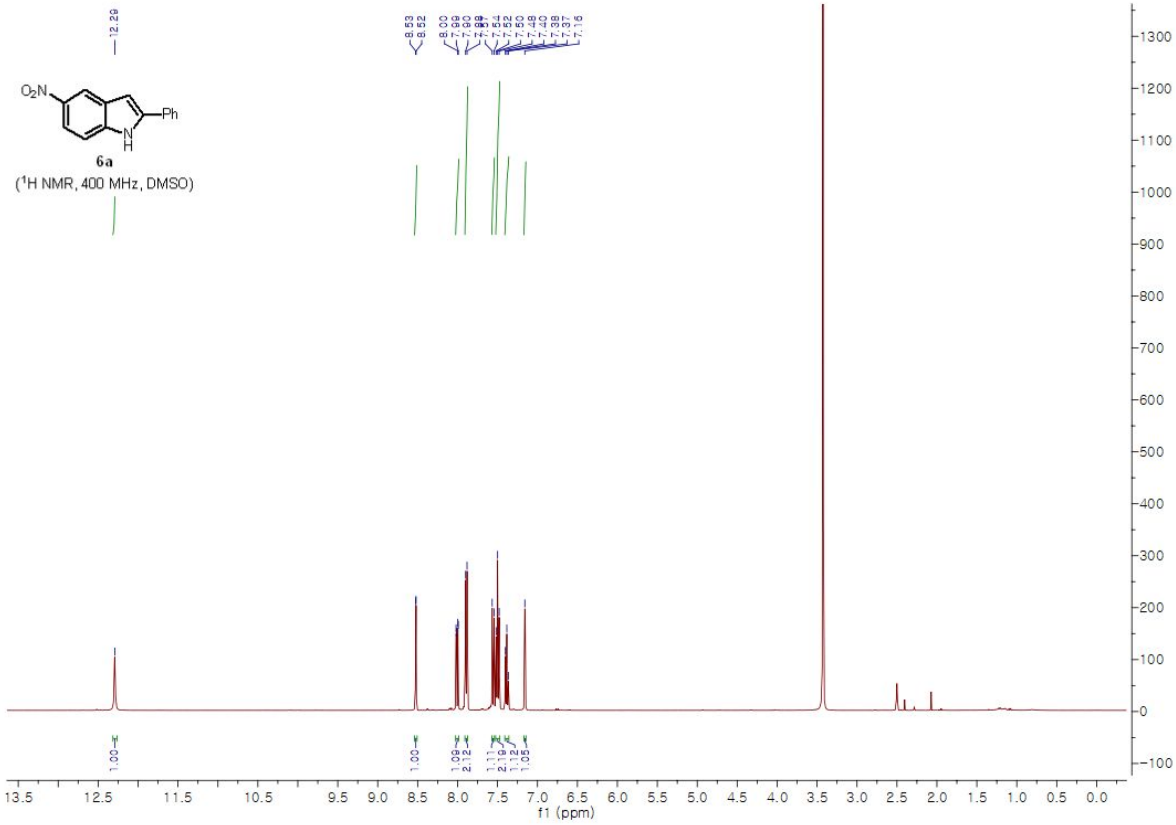


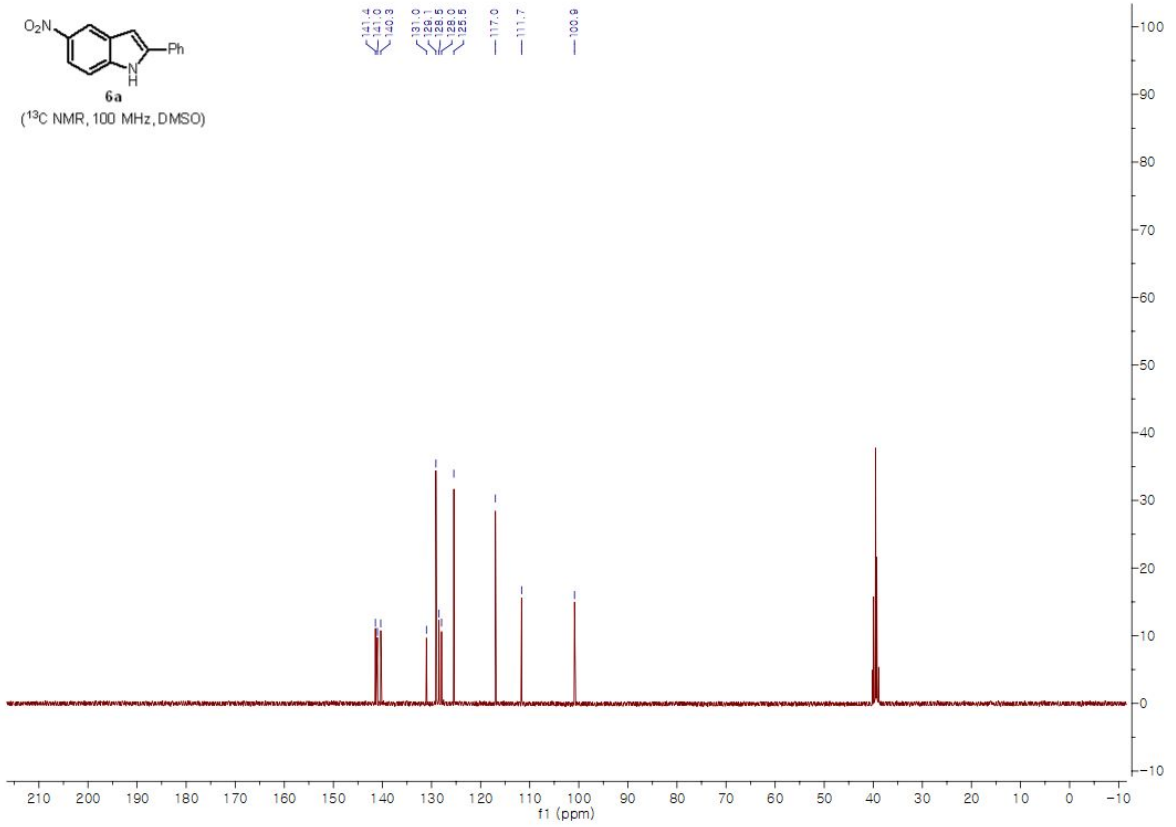
2-phenyl-*1H*-indole-5-carbonitrile (Scheme 2, **5a**)



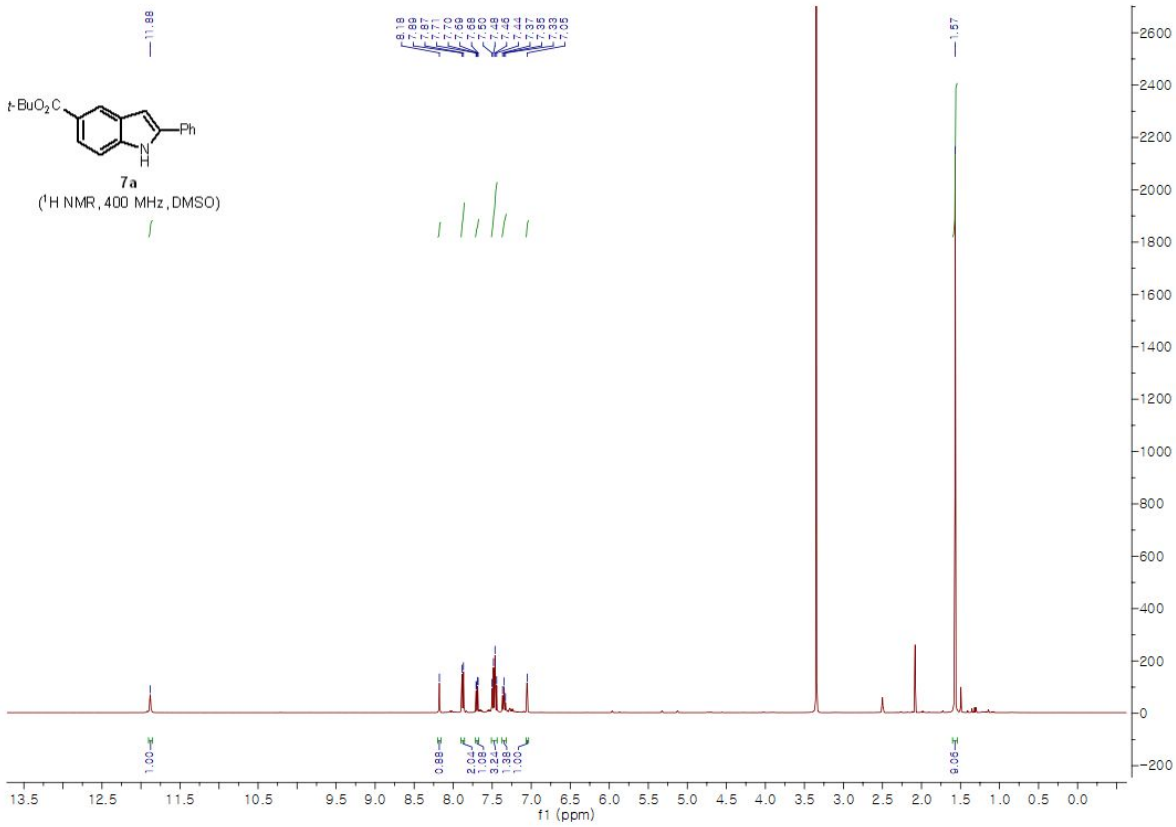


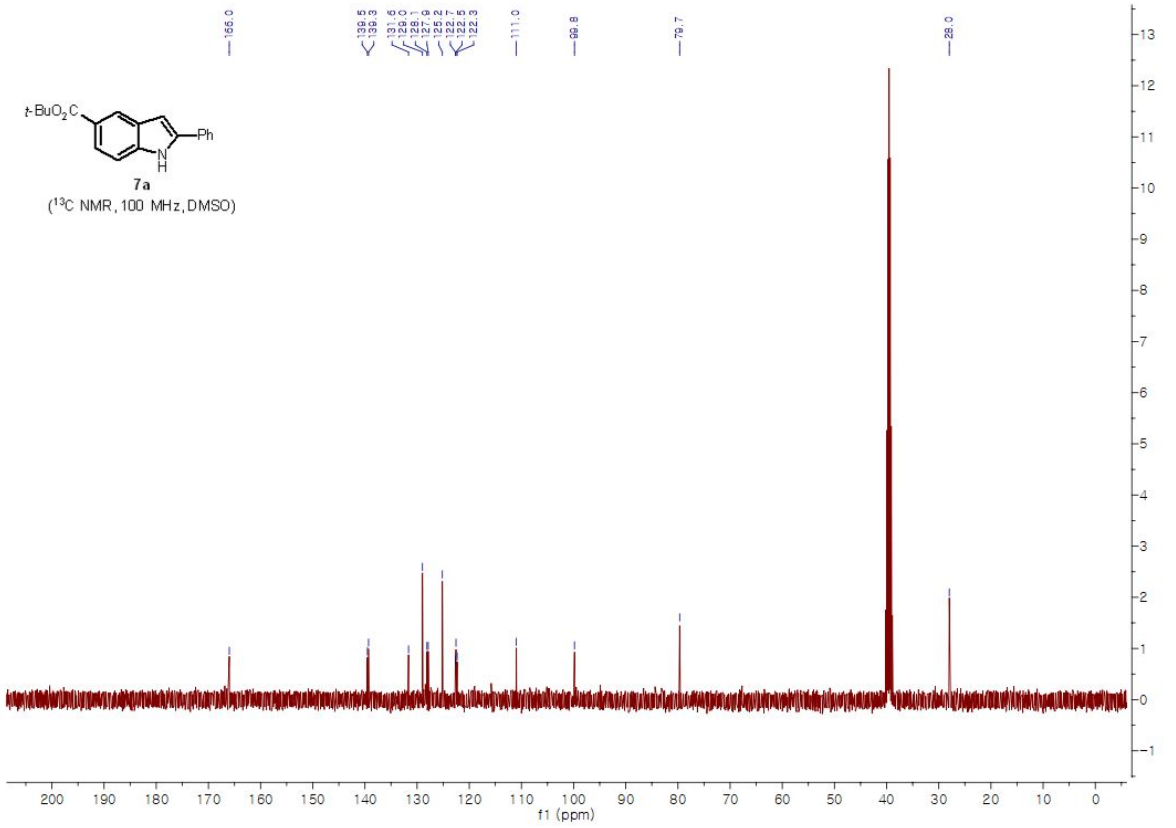
5-nitro-2-phenyl-*1H*-indole (Scheme 2, **6a**)



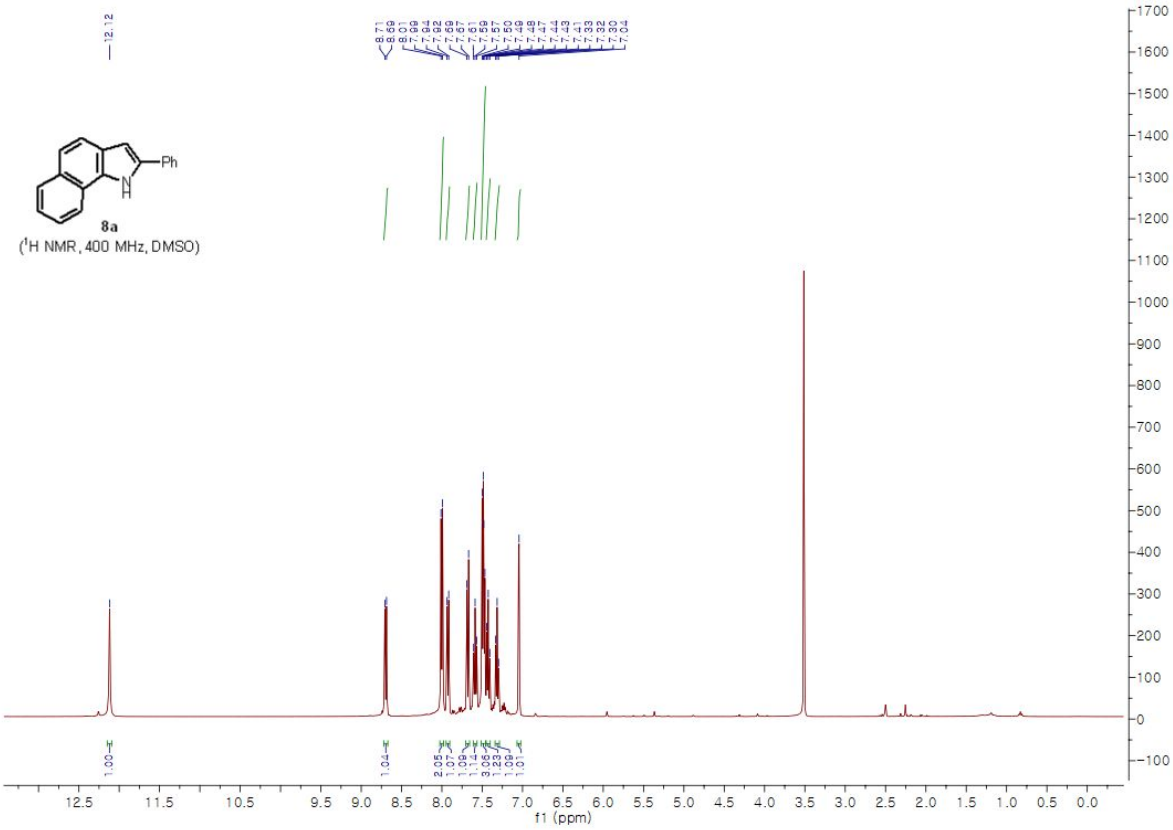


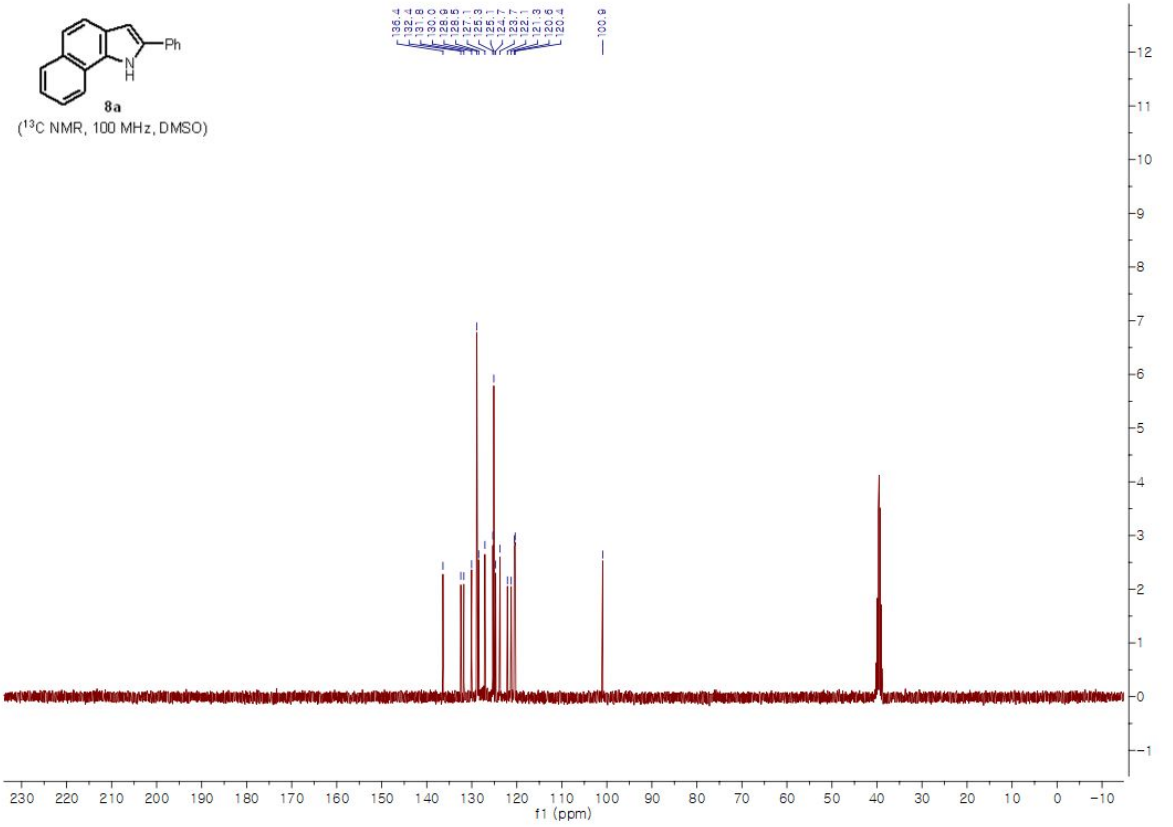
tert-butyl 2-phenyl-*1H*-indole-5-carboxylate (Scheme 2, **7a**)



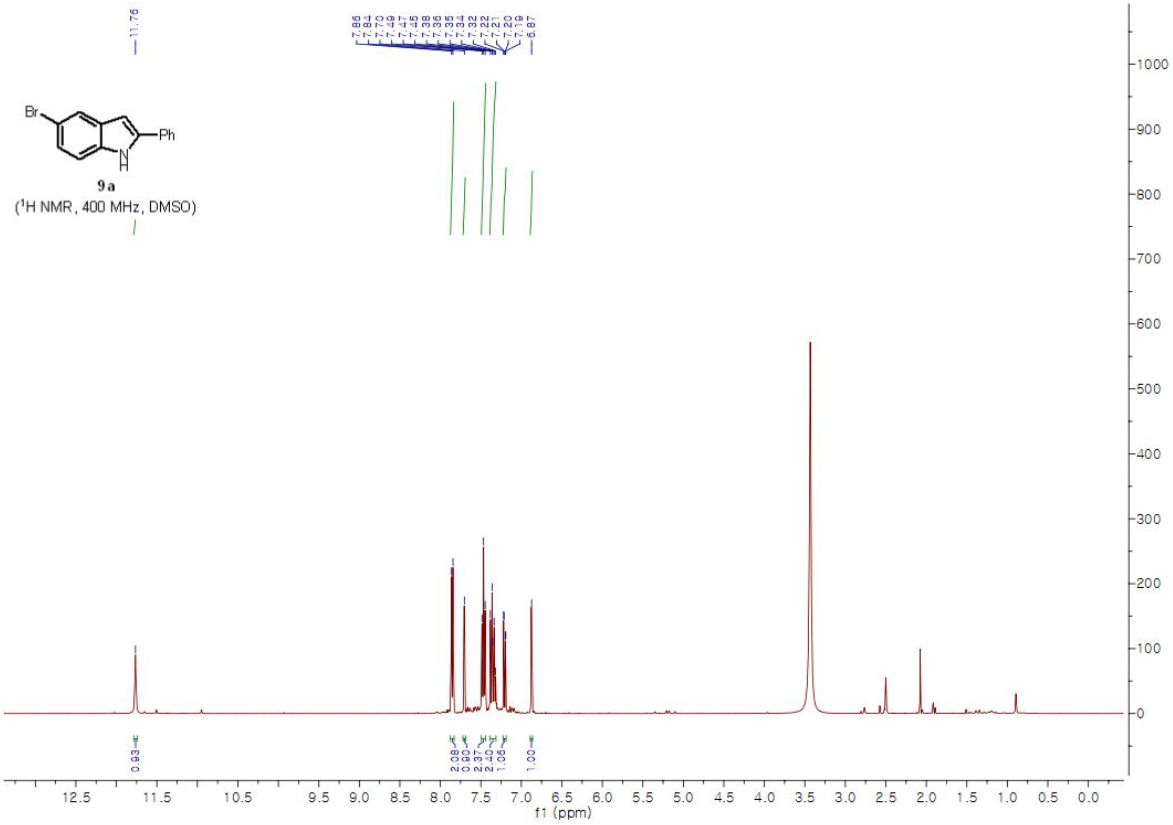


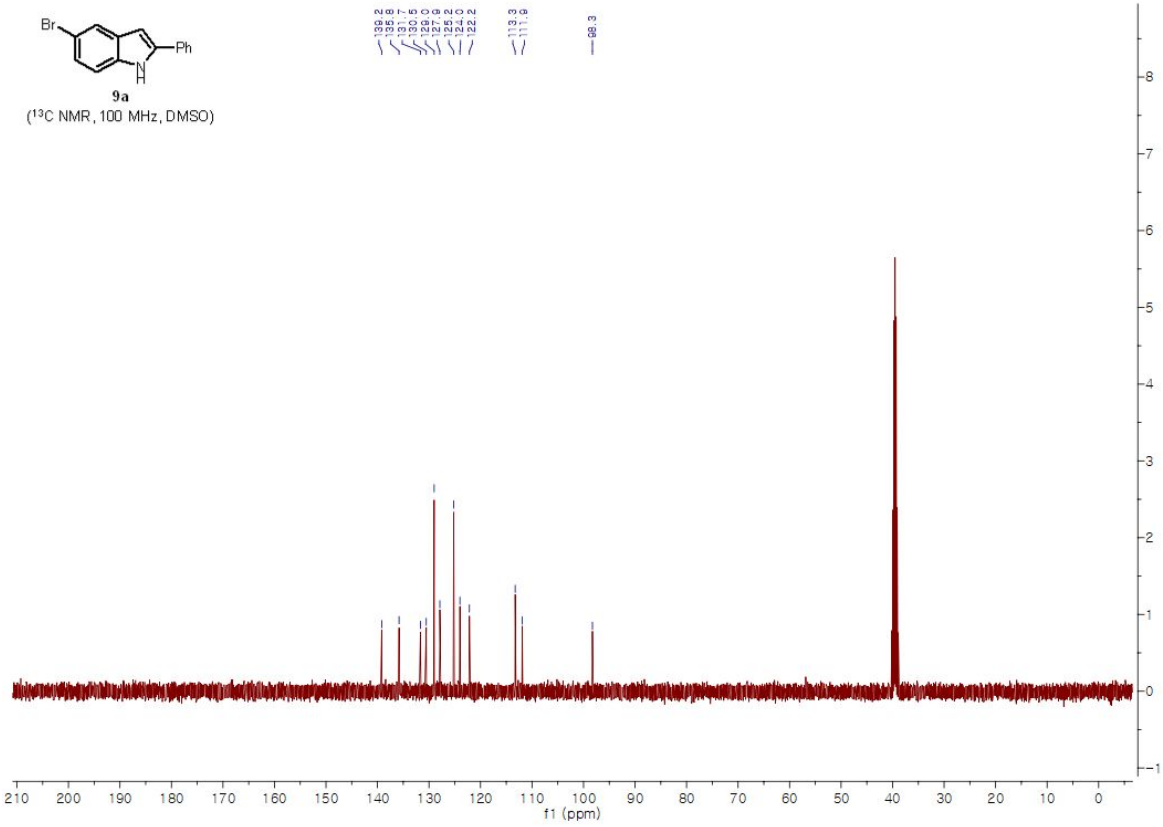
2-phenyl-*1H*-benzo[*g*]indole (Scheme 2, **8a**)



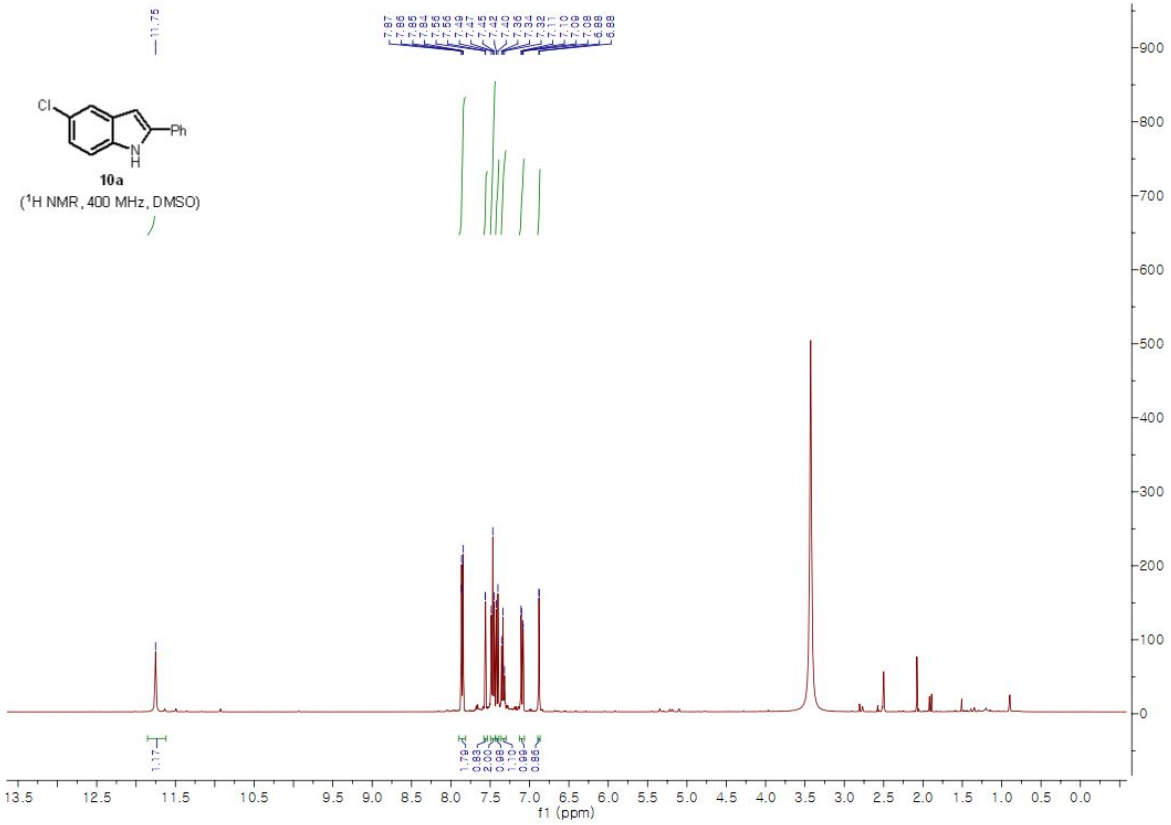


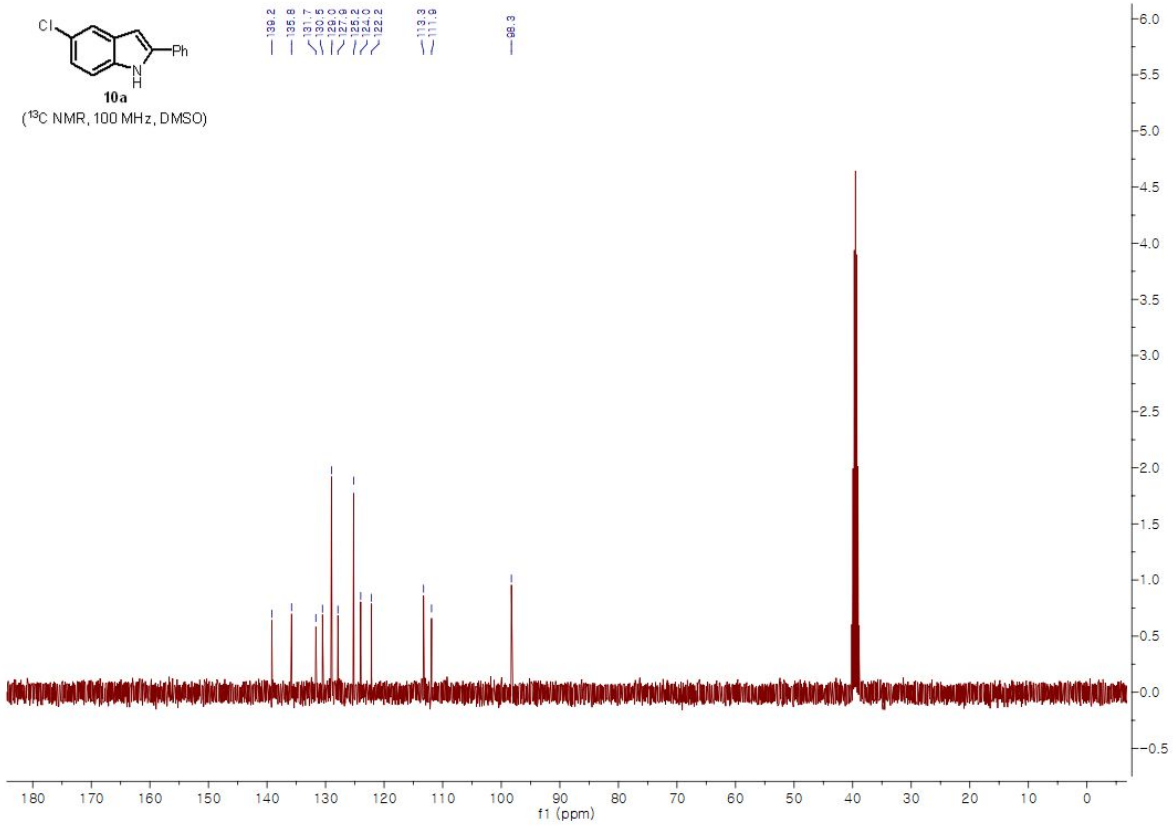
5-bromo-2-phenyl-*1H*-indole (Scheme 2, **9a**)



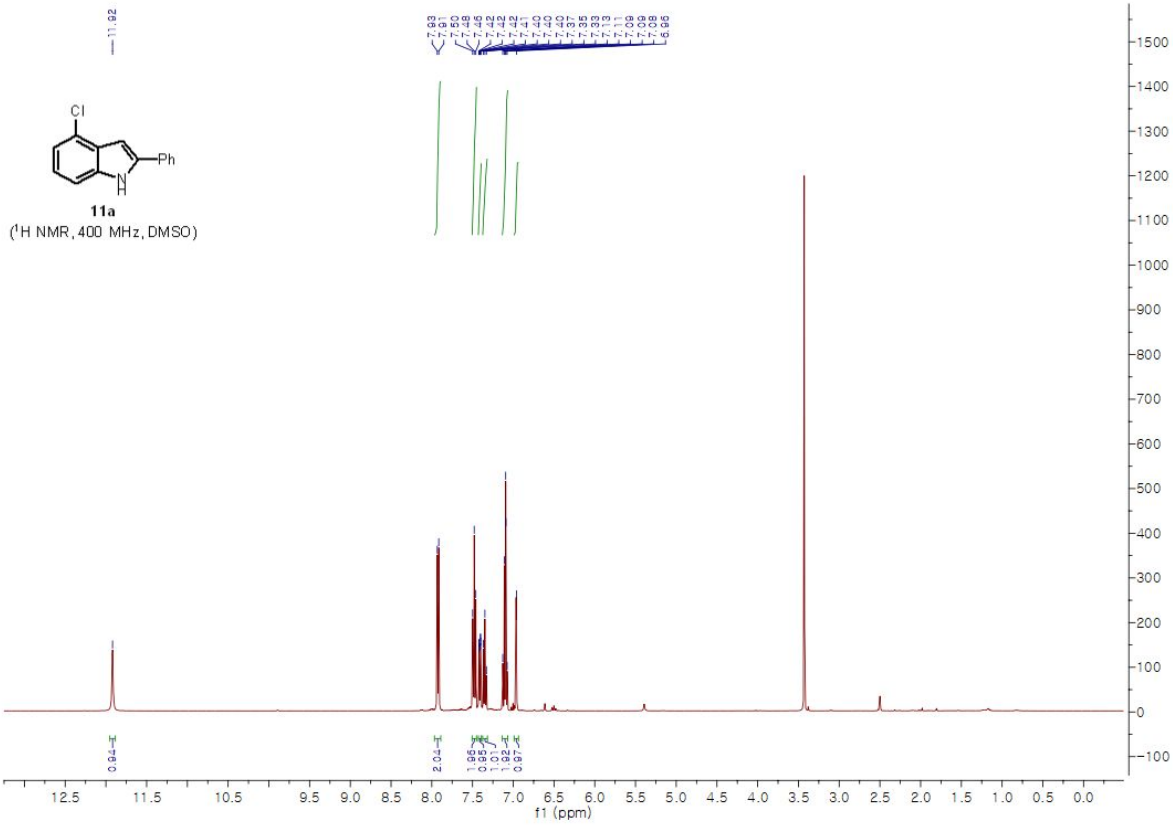


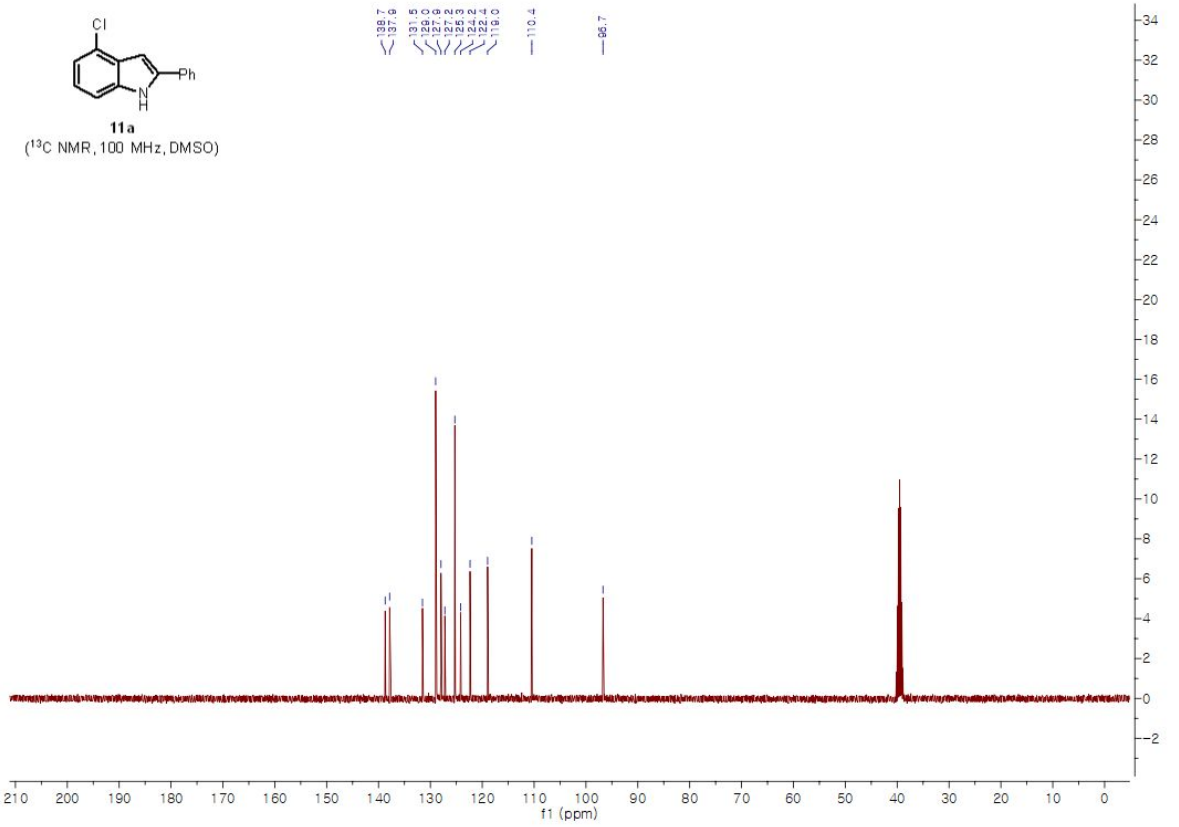
5-chloro-2-phenyl-*1H*-indole (Scheme 2, **10a**)



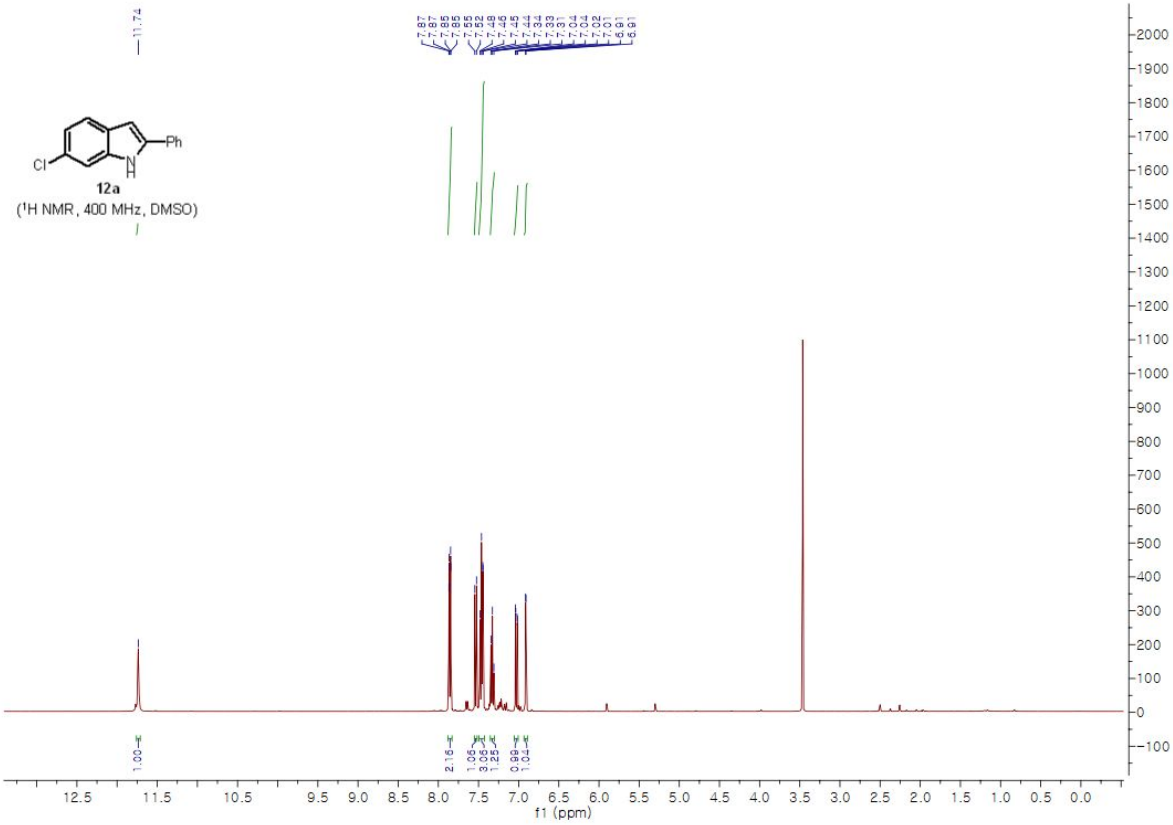


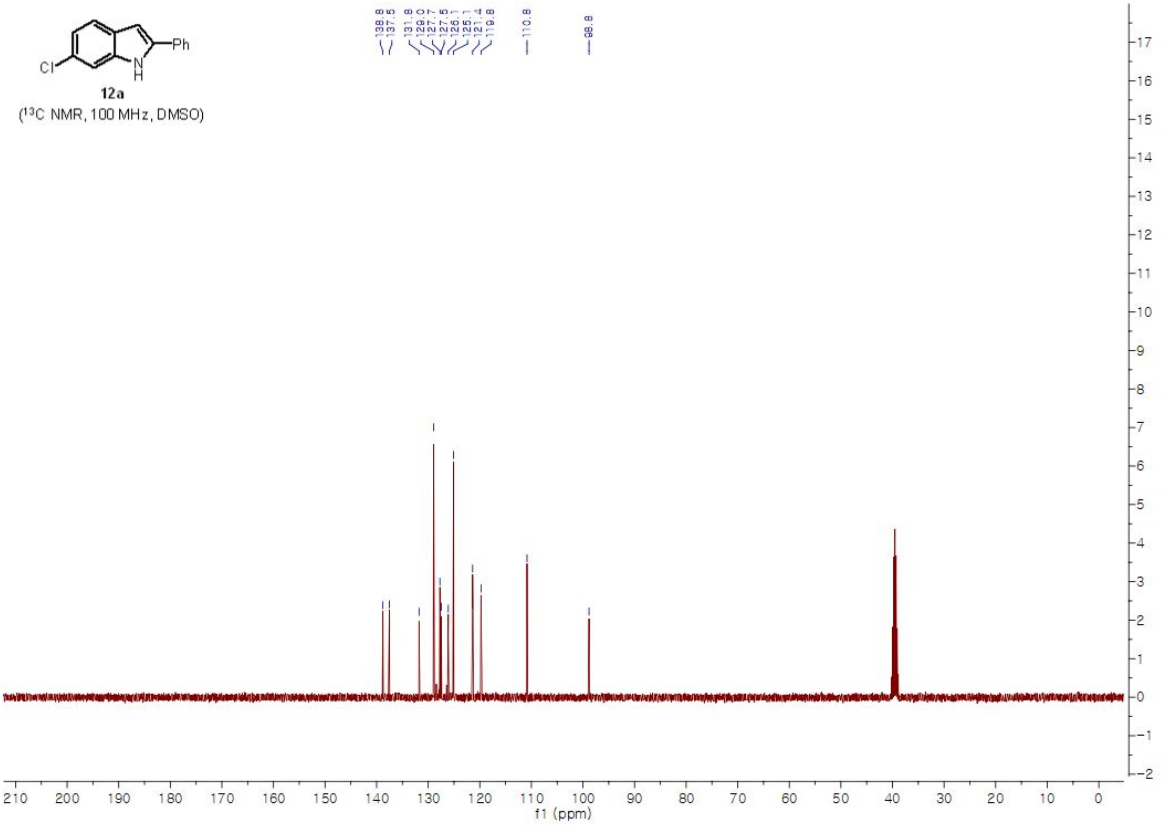
4-chloro-2-phenyl-*1H*-indole (Scheme 2, **11a**)



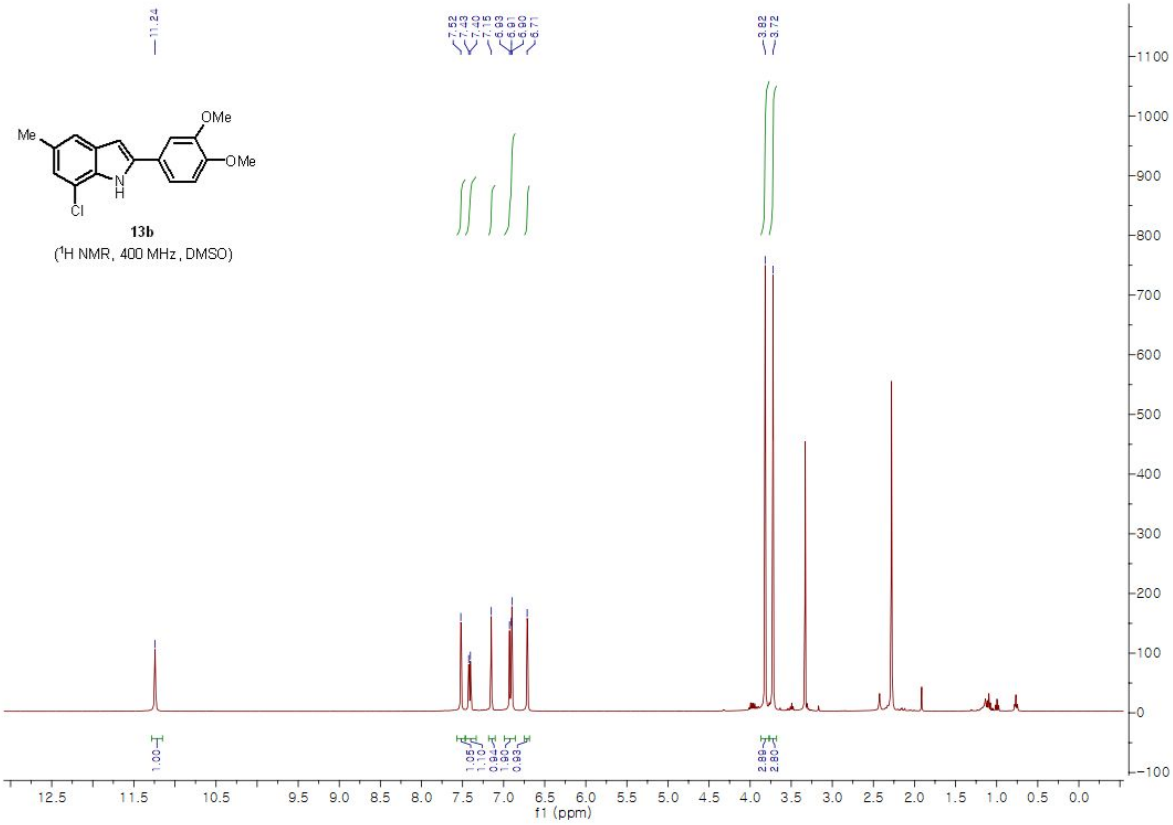


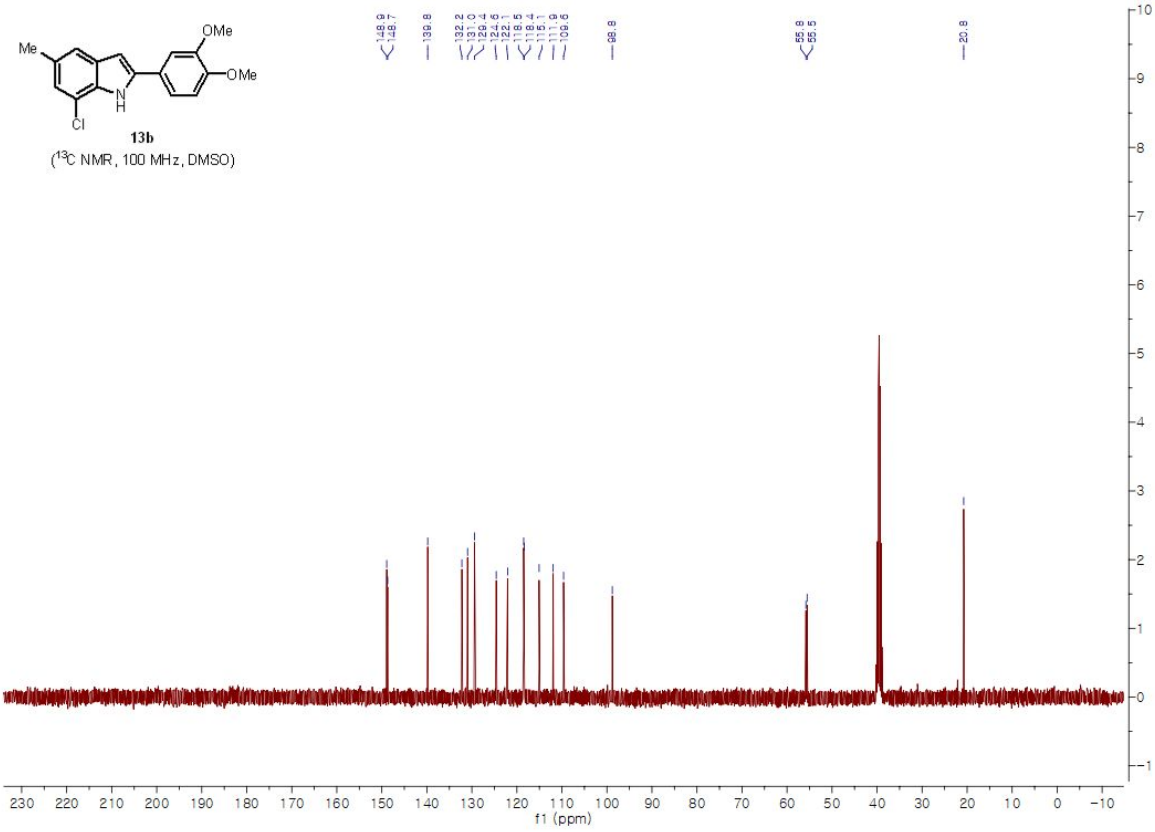
6-chloro-2-phenyl-*1H*-indole (Scheme 2, **12a**)



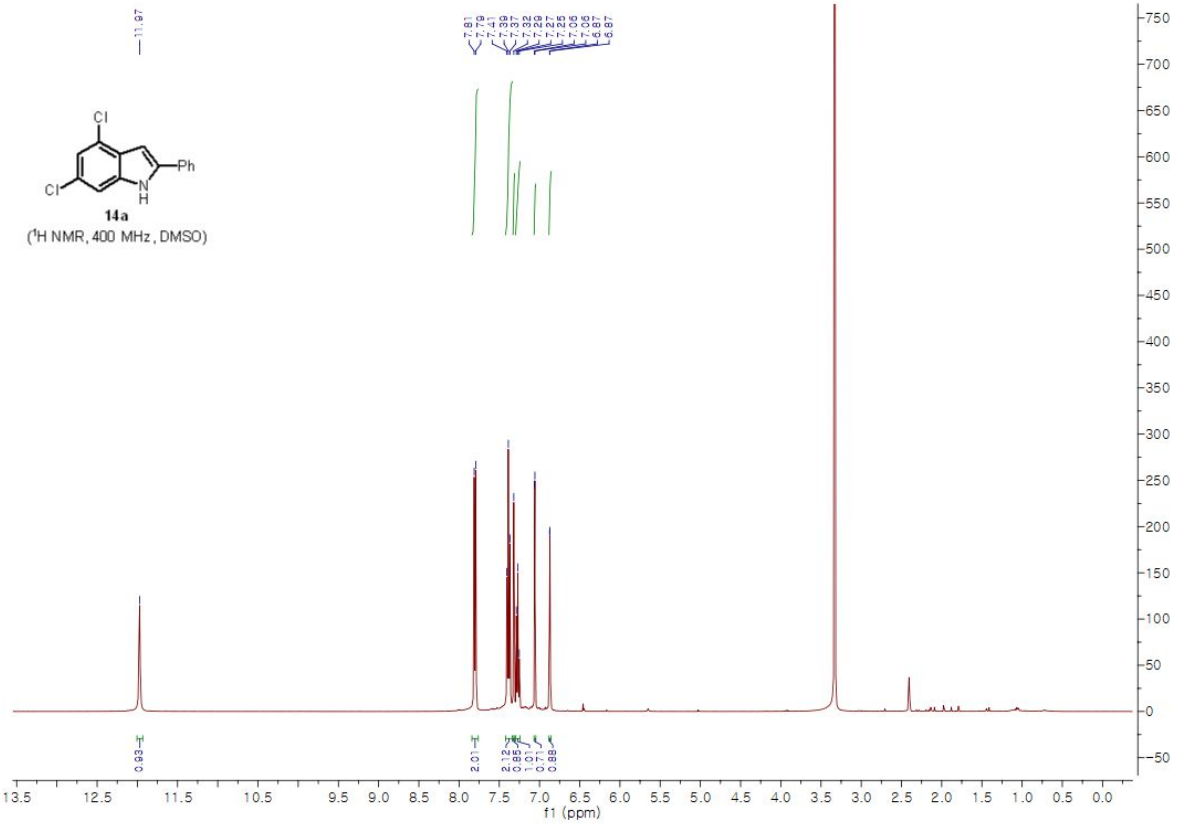


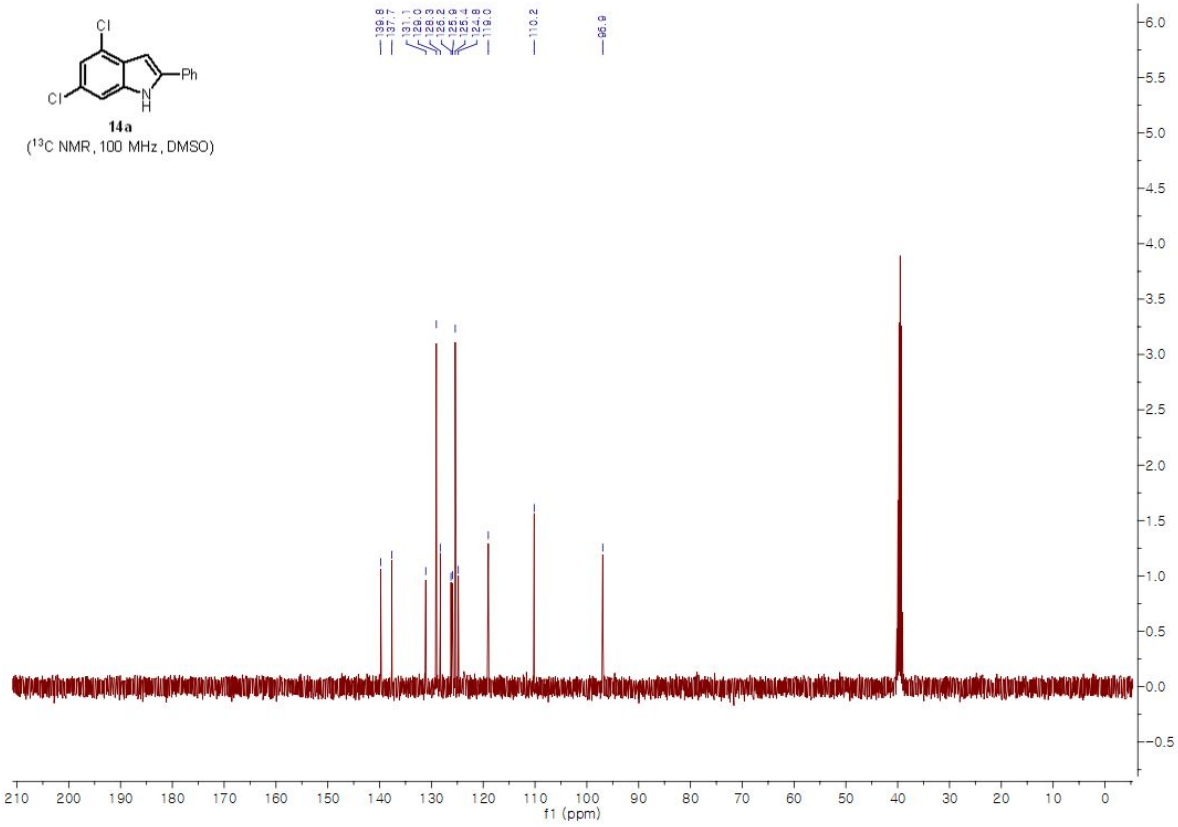
7-chloro-2-(3,4-dimethoxyphenyl)-5-methyl-*1H*-indole (Scheme 2, **13b**)



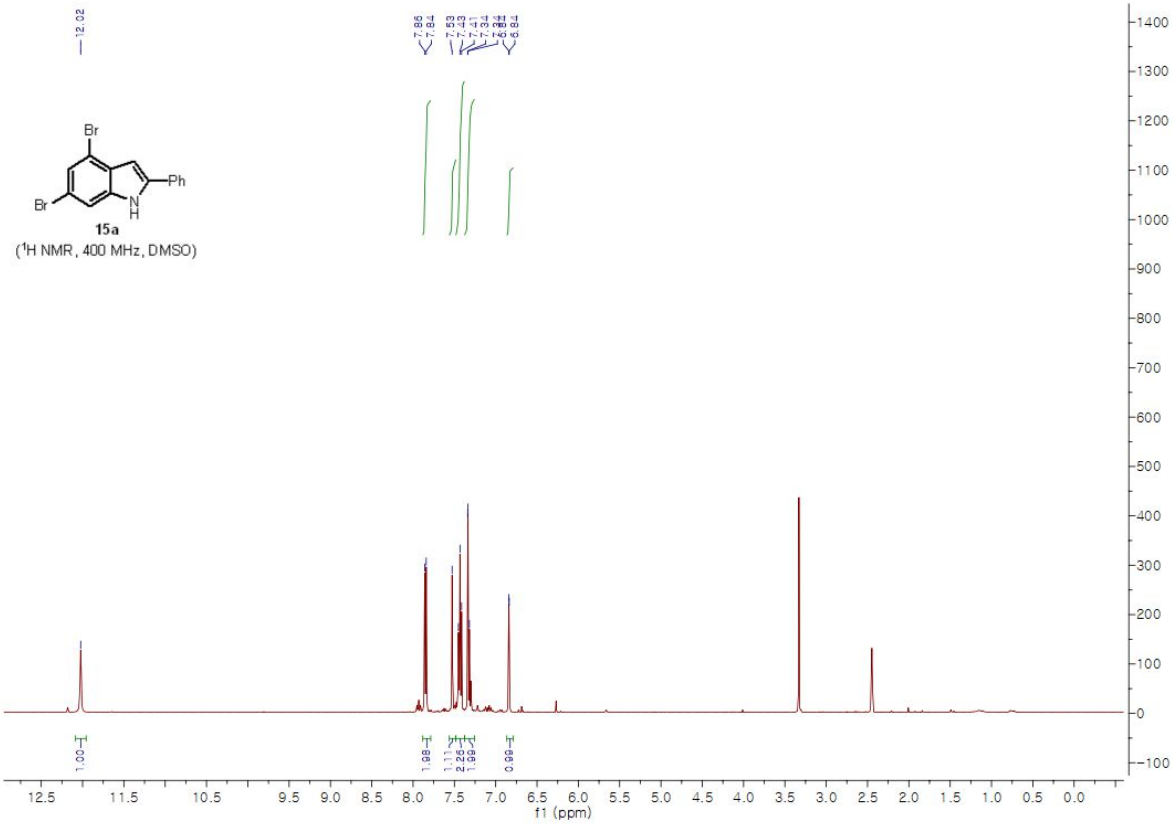


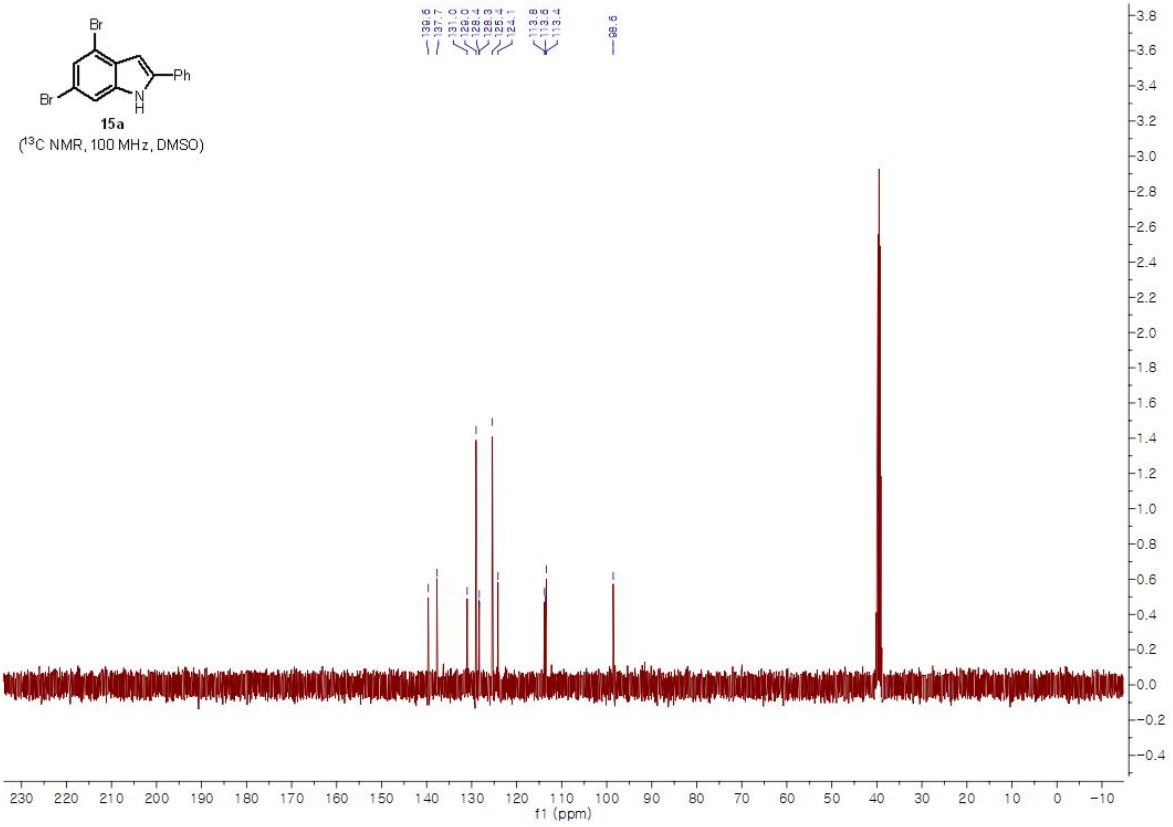
4,6-dichloro-2-phenyl-*1H*-indole (Scheme 2, **14a**)



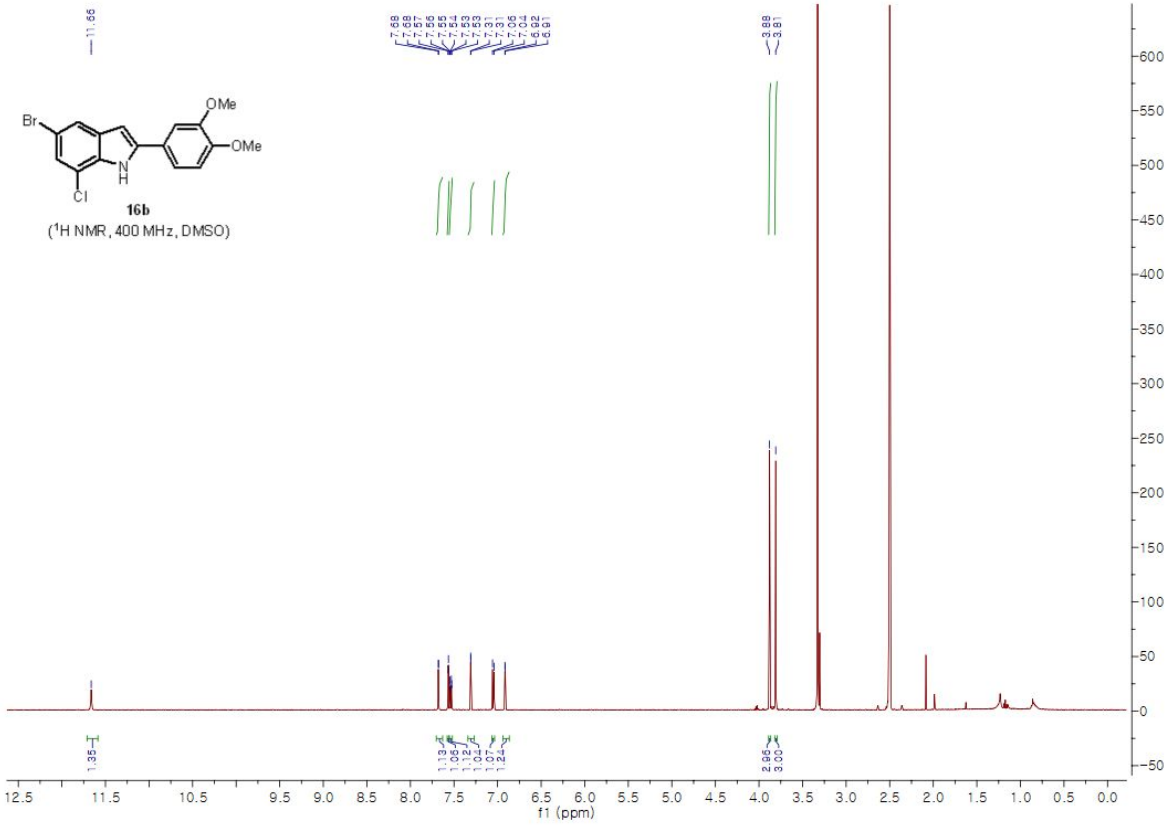


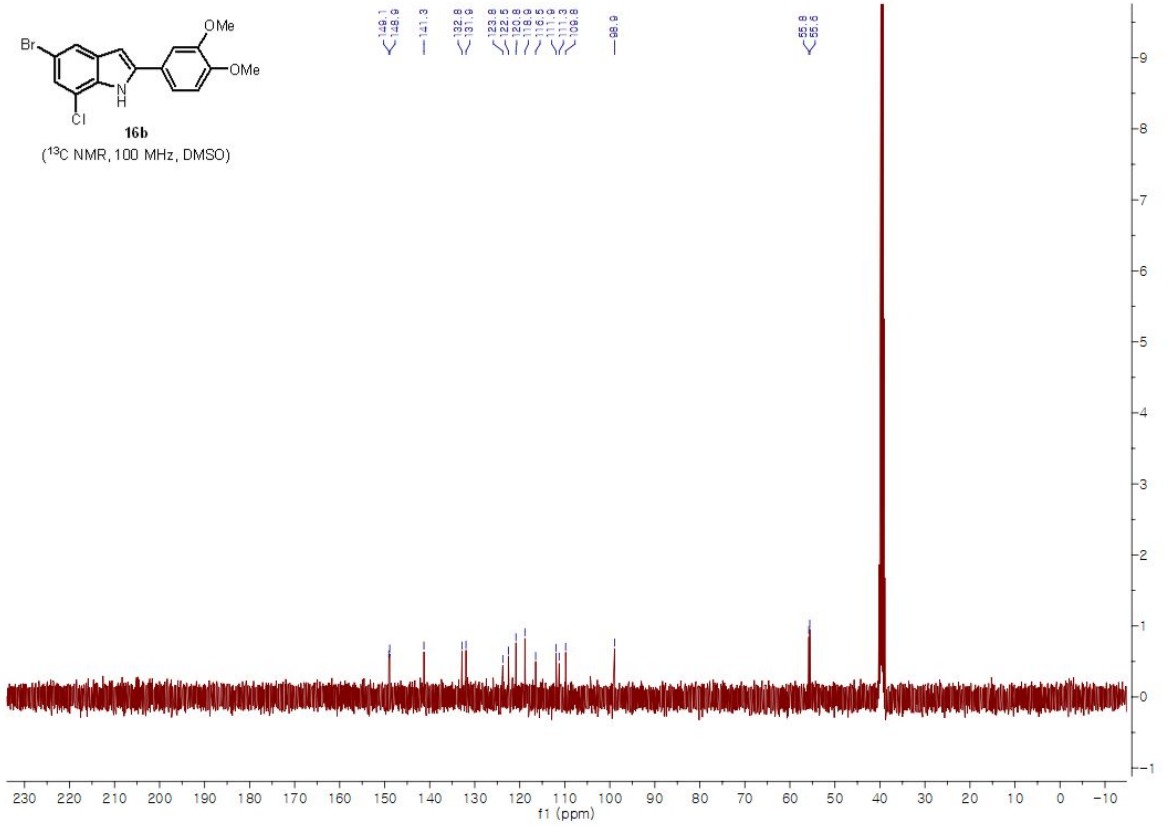
4,6-dibromo-2-phenyl-*1H*-indole (Scheme 2, **15a**)



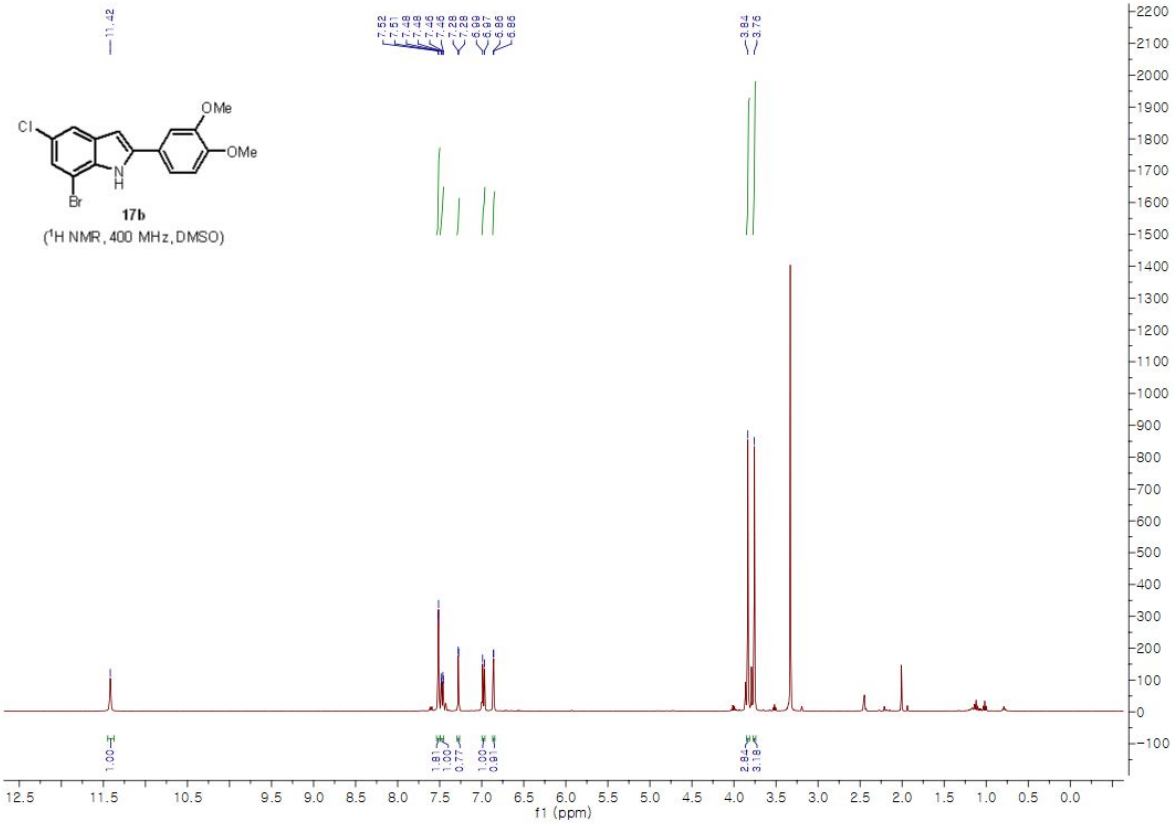


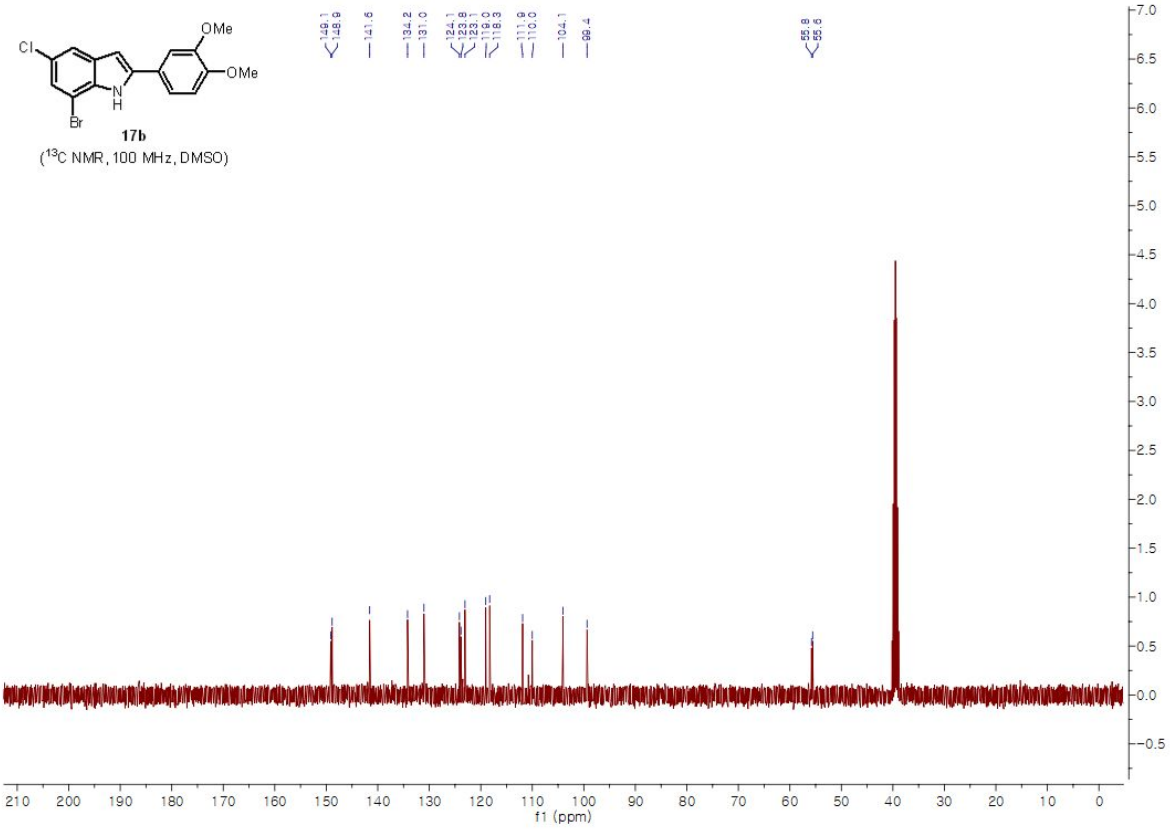
5-bromo-7-chloro-2-(3,4-dimethoxyphenyl)-*1H*-indole (Scheme 2, **16b**)



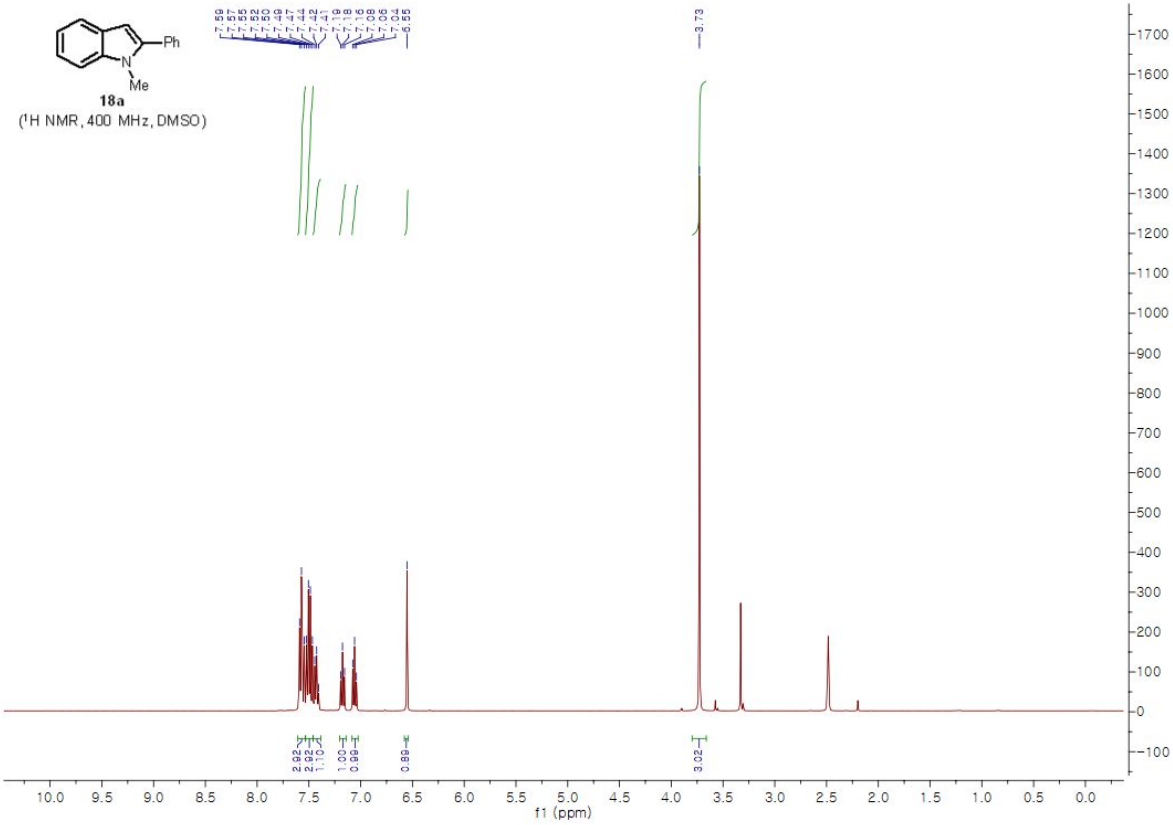


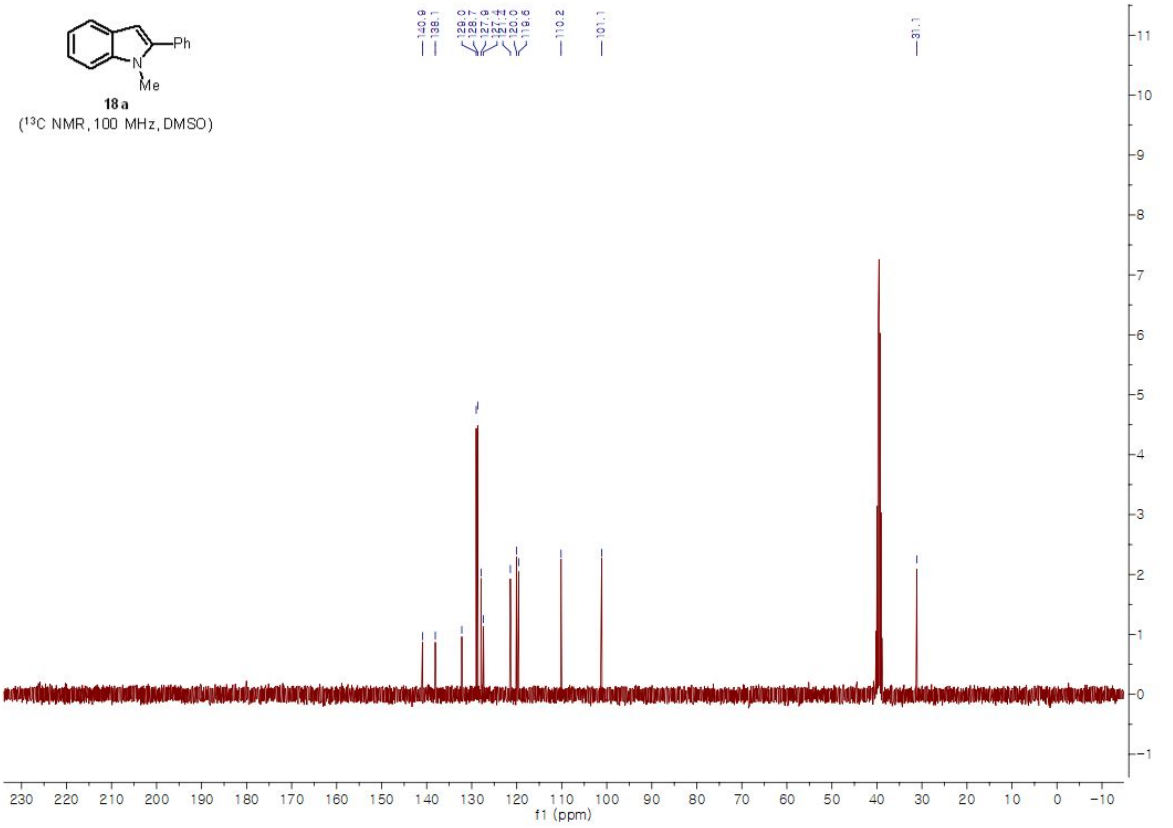
7-bromo-5-chloro-2-(3,4-dimethoxyphenyl)-*1H*-indole (Scheme 2, **17b**)



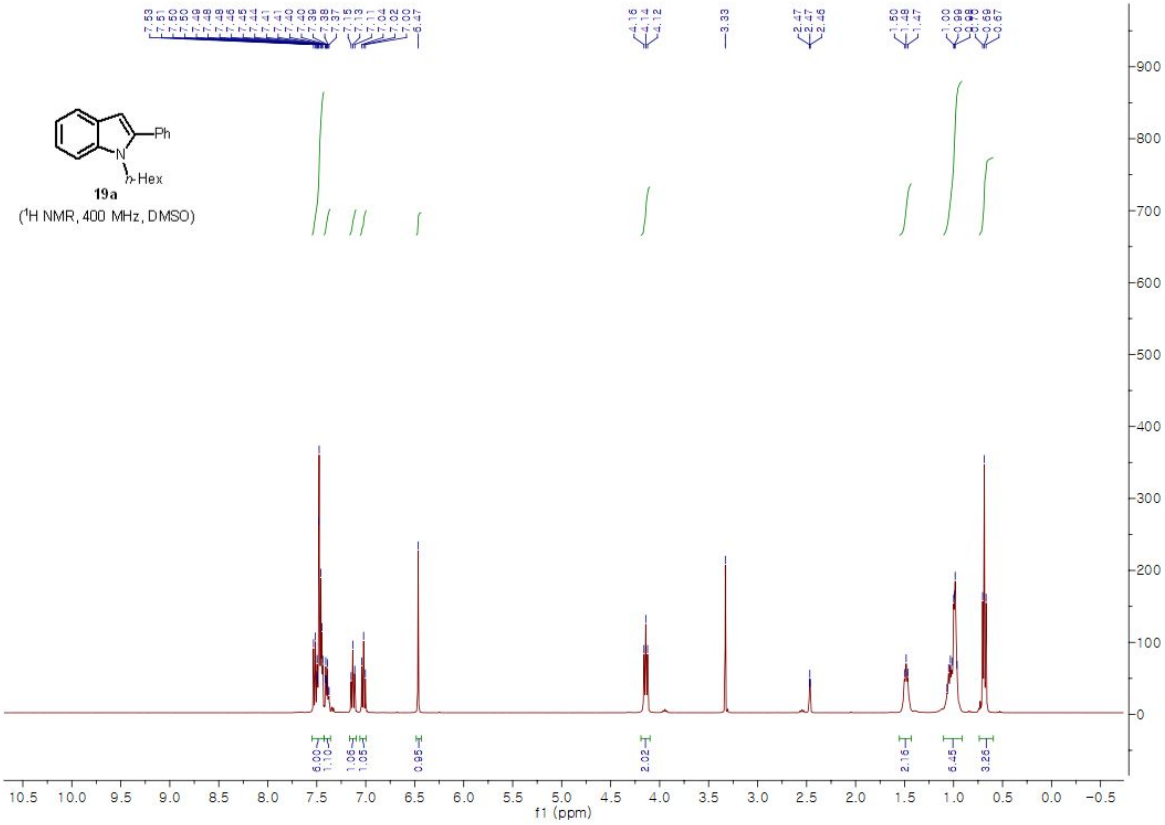


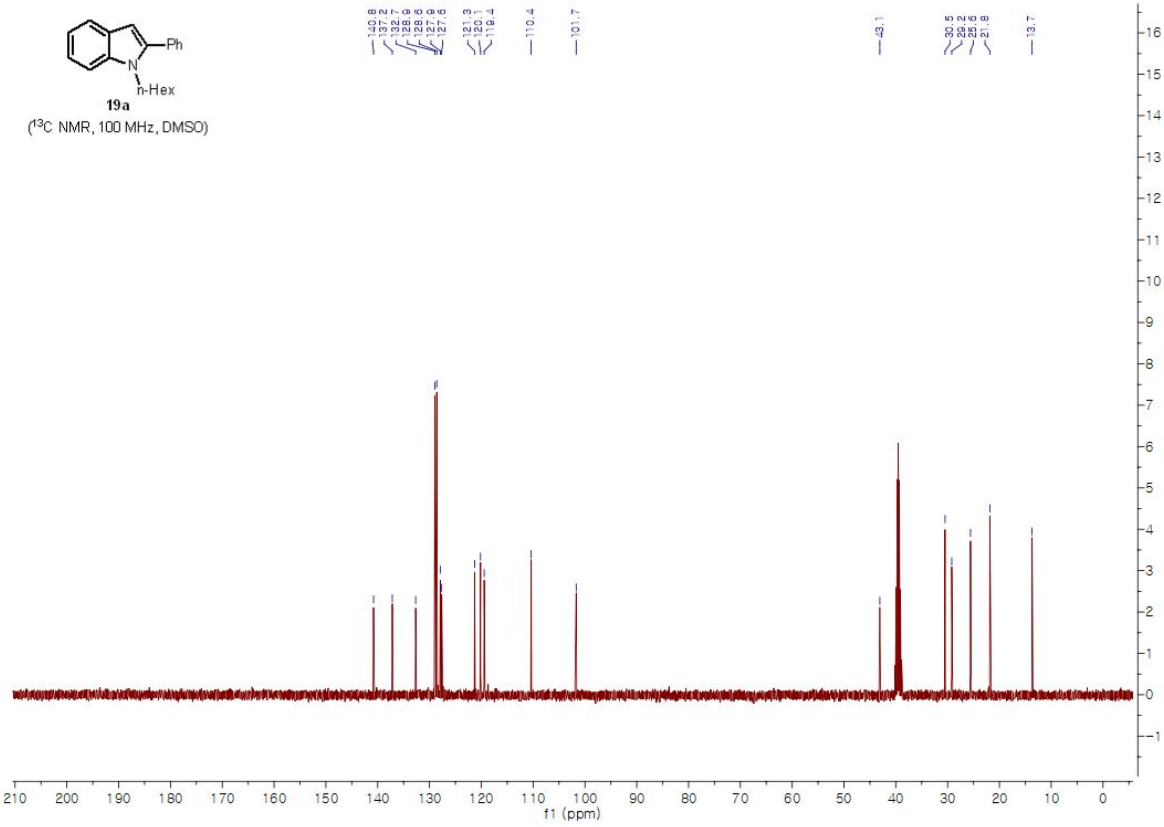
1-methyl-2-phenyl-*1H*-indole (Scheme 2, **18a**)



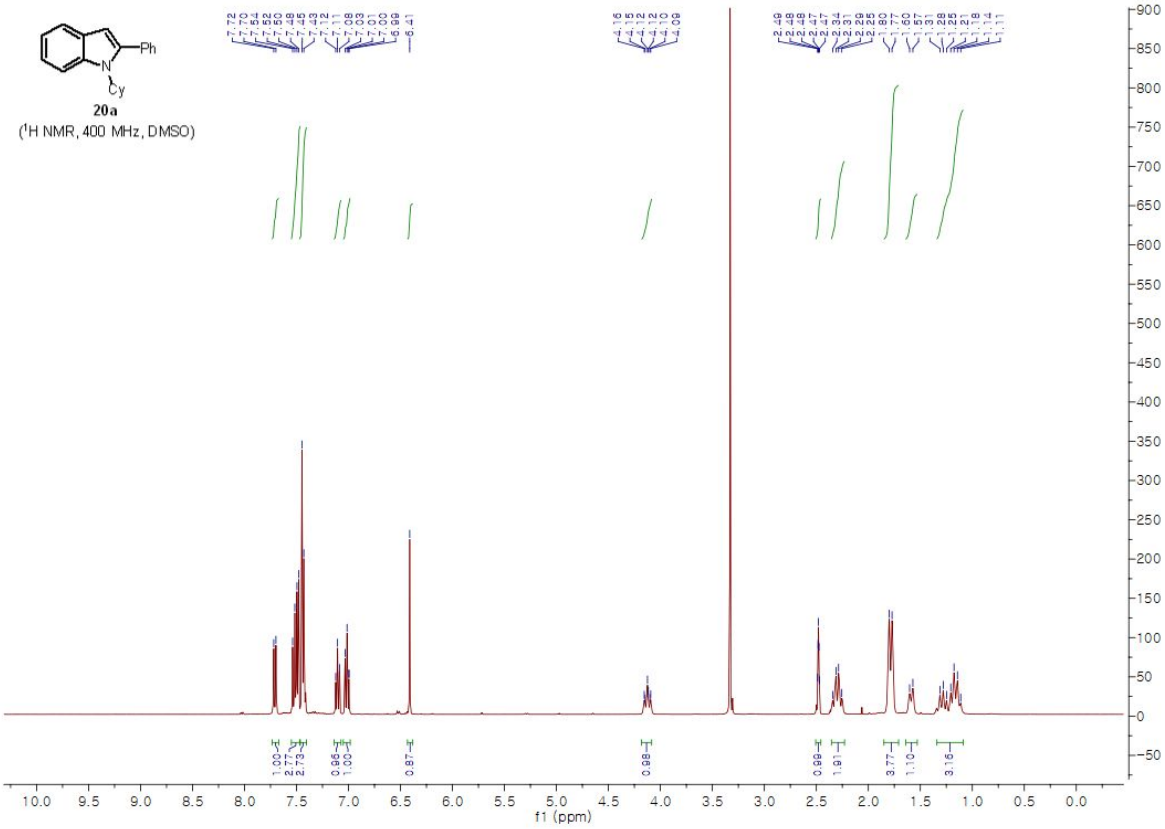


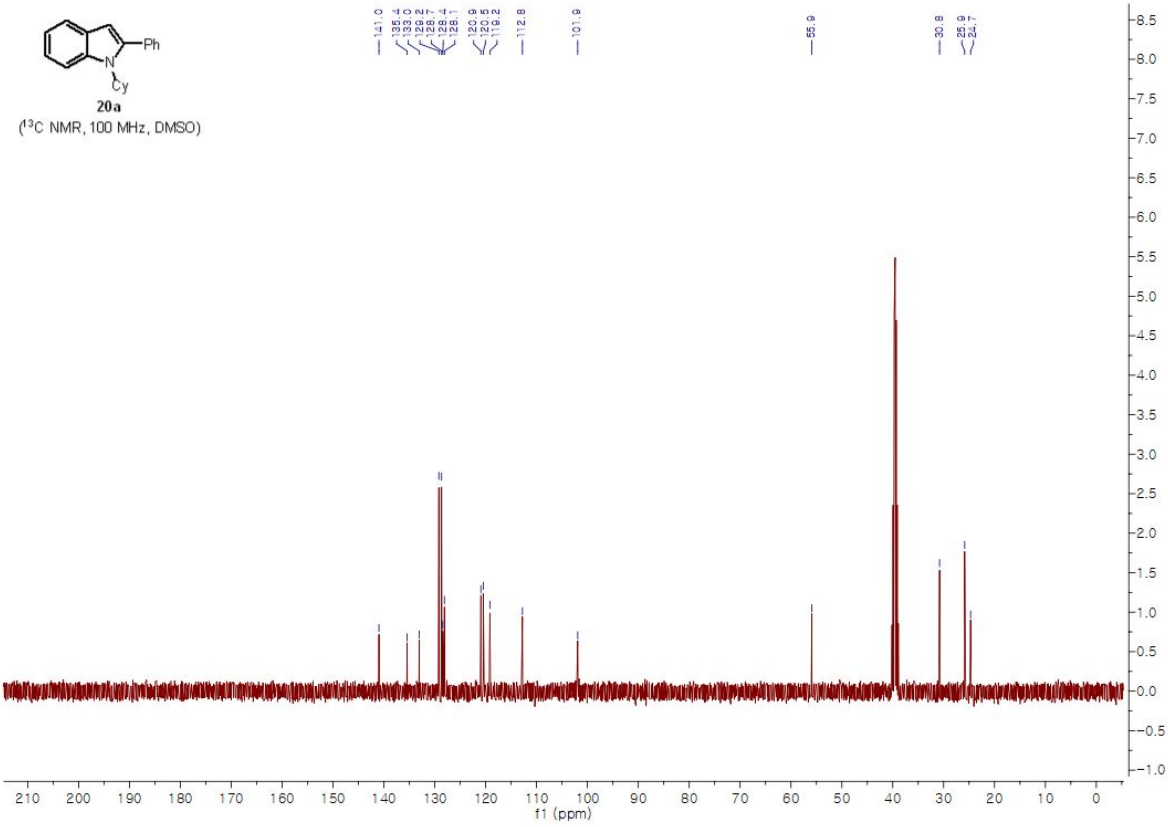
1-hexyl-2-phenyl-*1H*-indole (Scheme 2, **19a**)



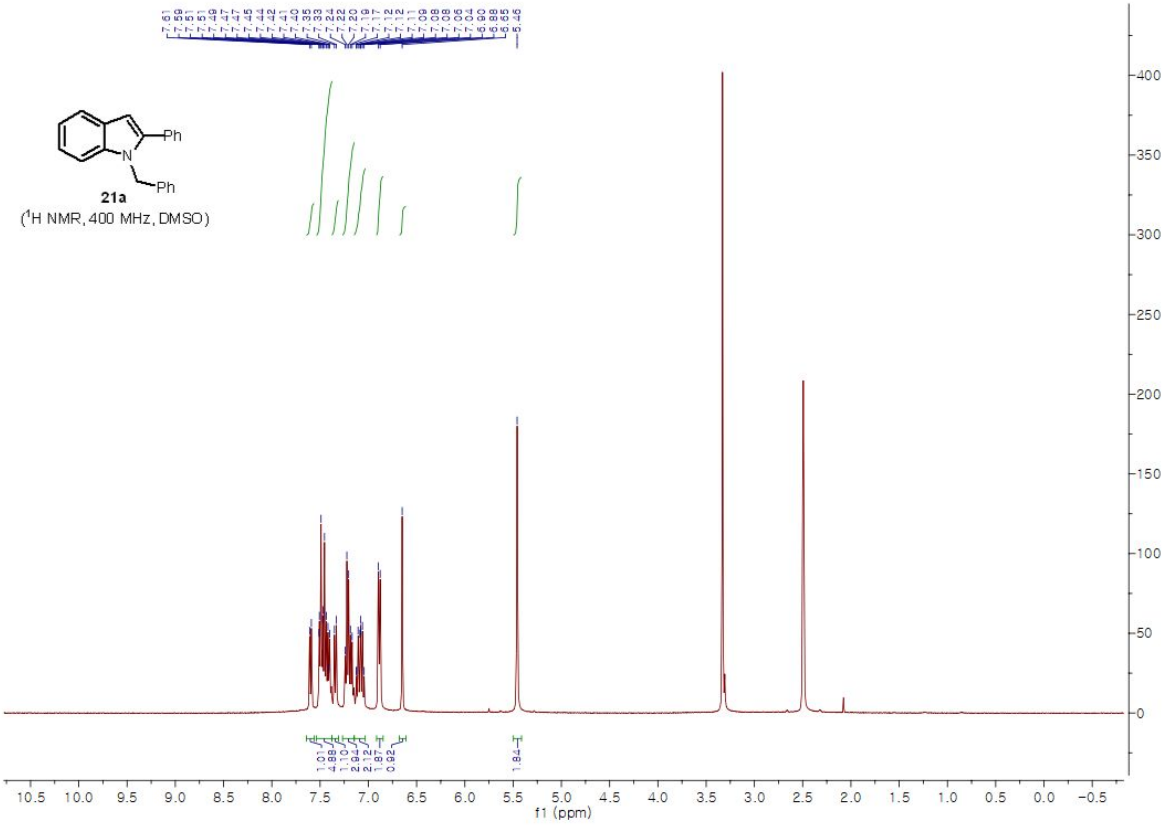


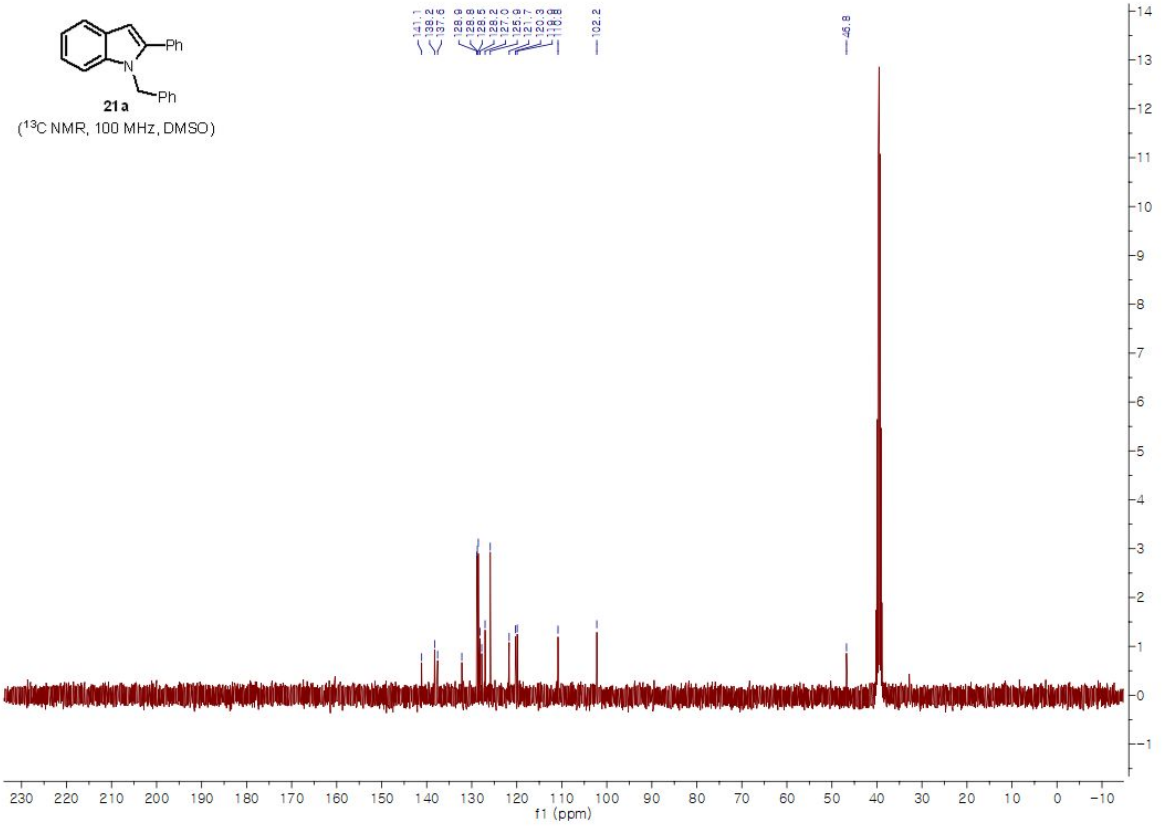
1-cyclohexyl-2-phenyl-*1H*-indole (Scheme 2, **20a**)



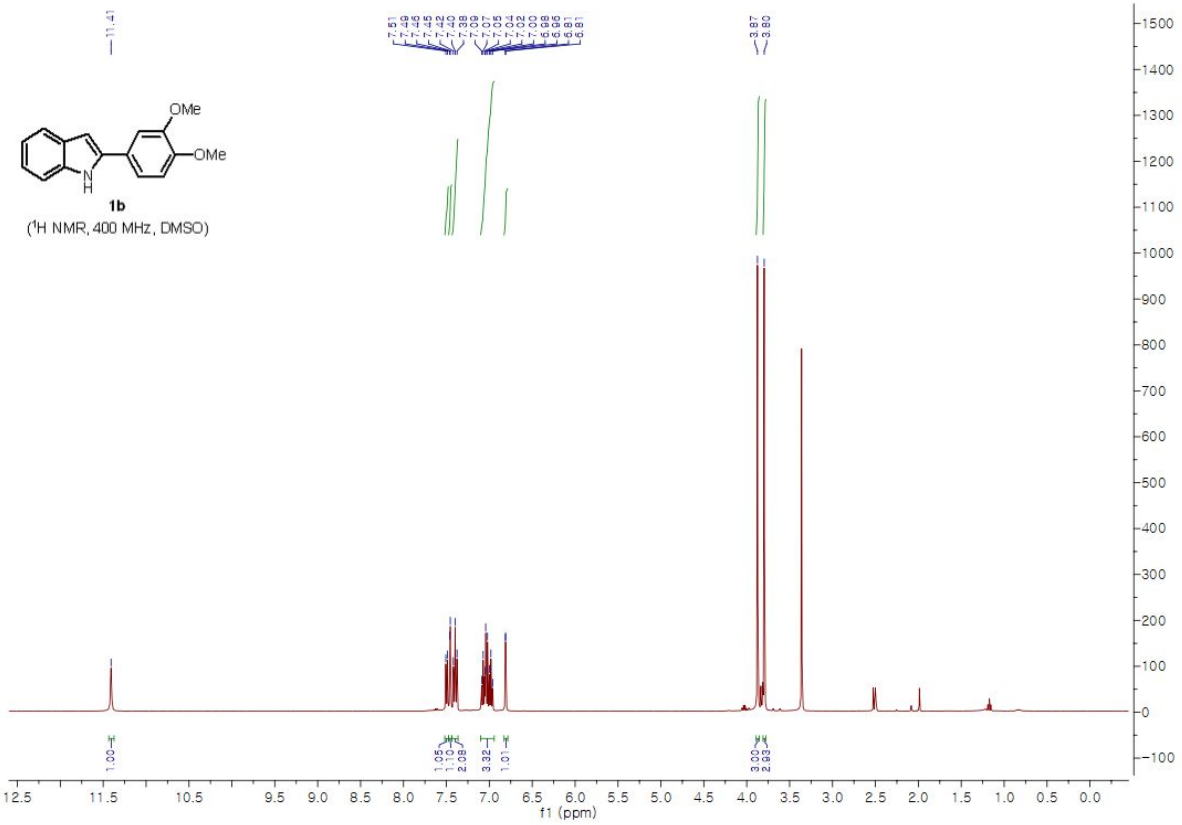


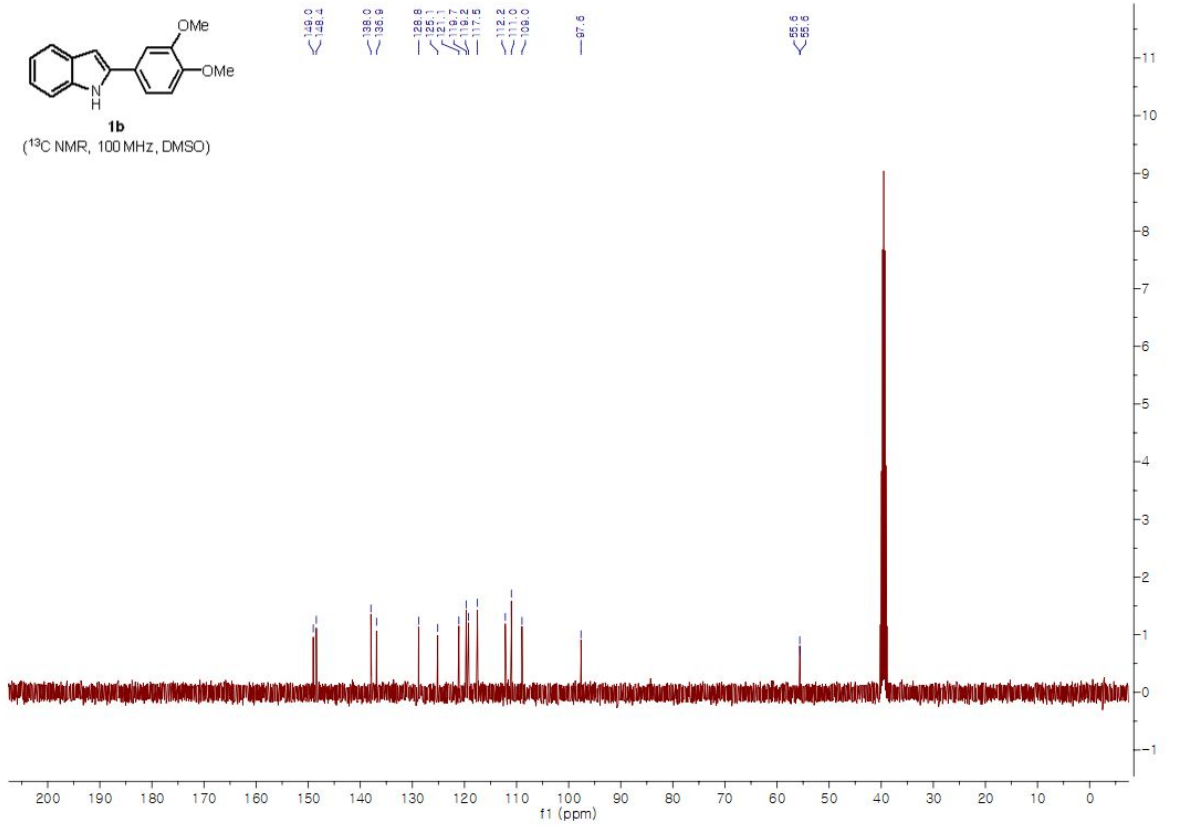
1-benzyl-2-phenyl-*1H*-indole (Scheme 2, **21a**)



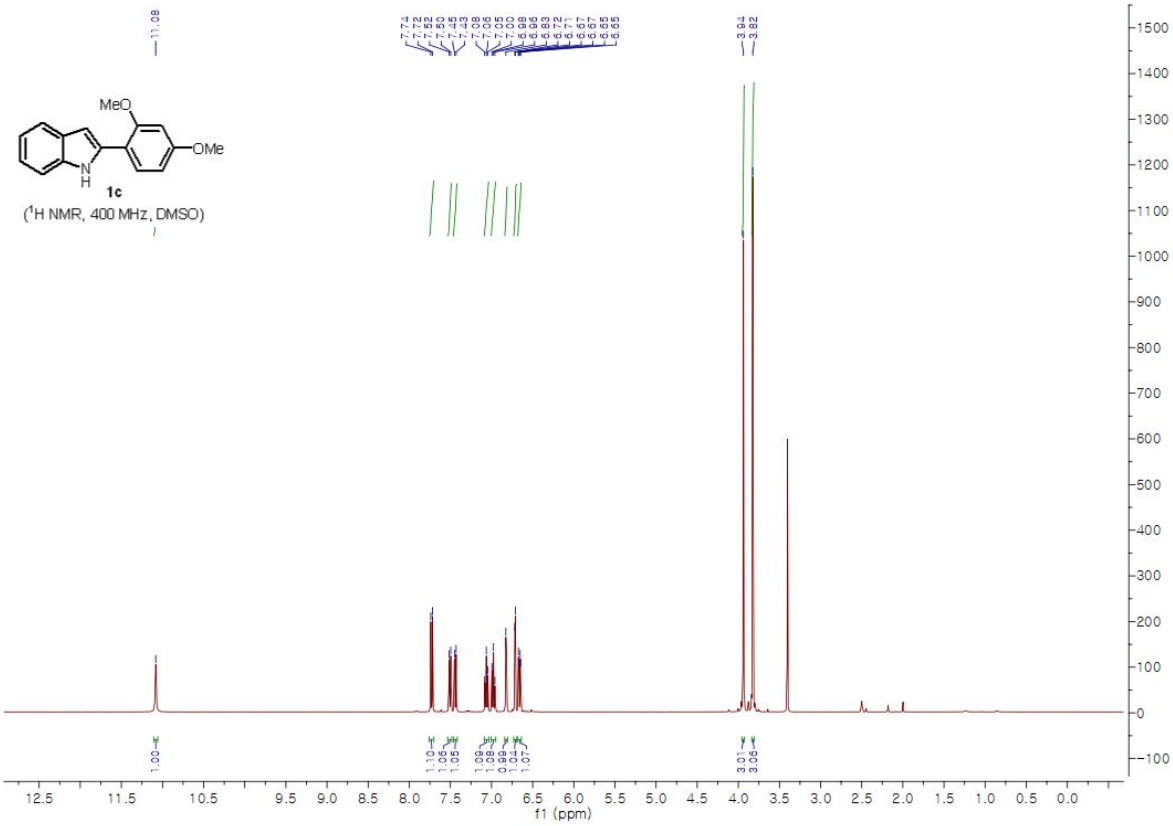


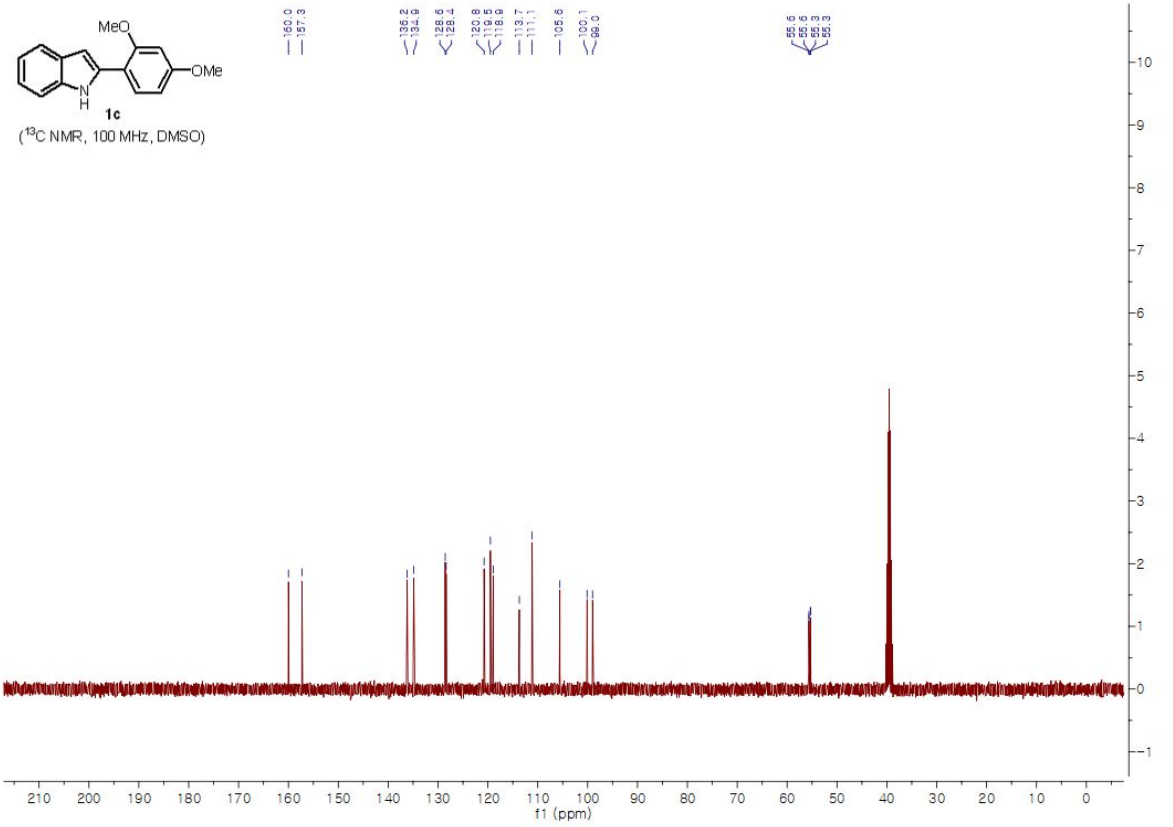
2-(3,4-dimethoxyphenyl)-*1H*-indole (Scheme 3, **1b**)



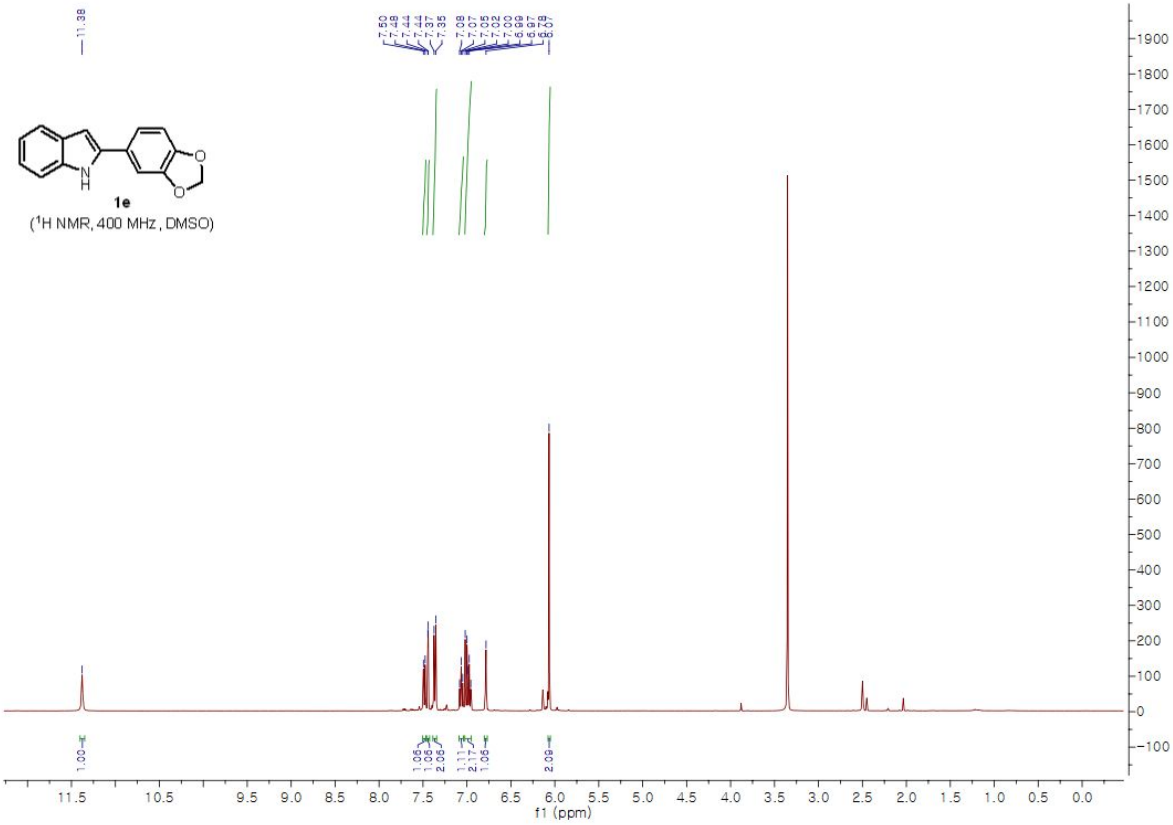


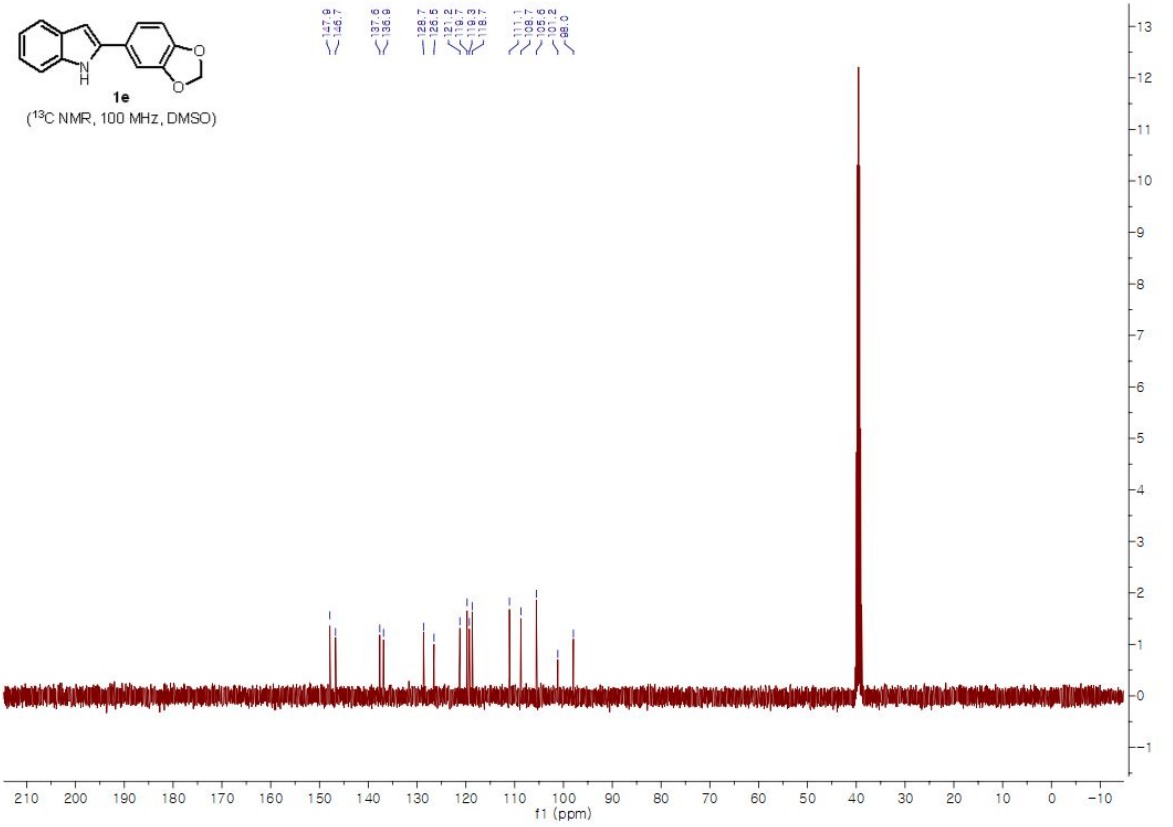
2-(2,4-dimethoxyphenyl)-*1H*-indole (Scheme 3, **1c**)



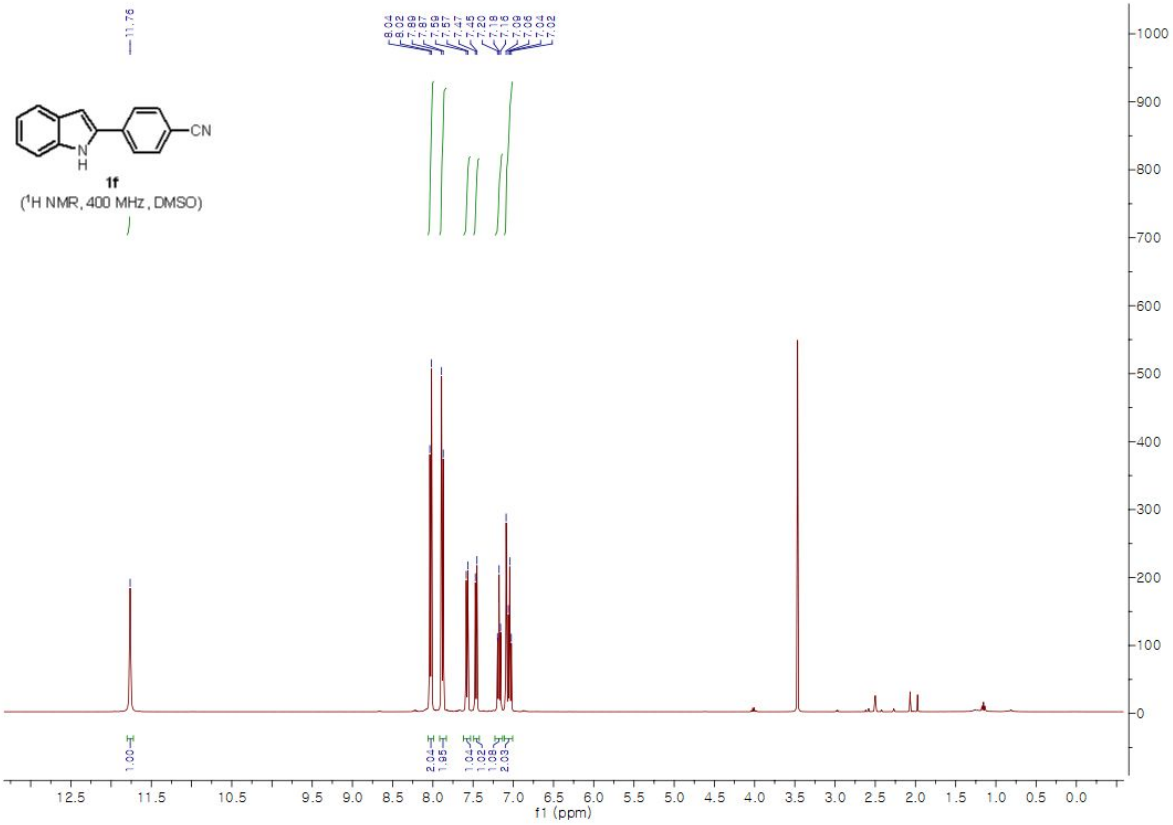


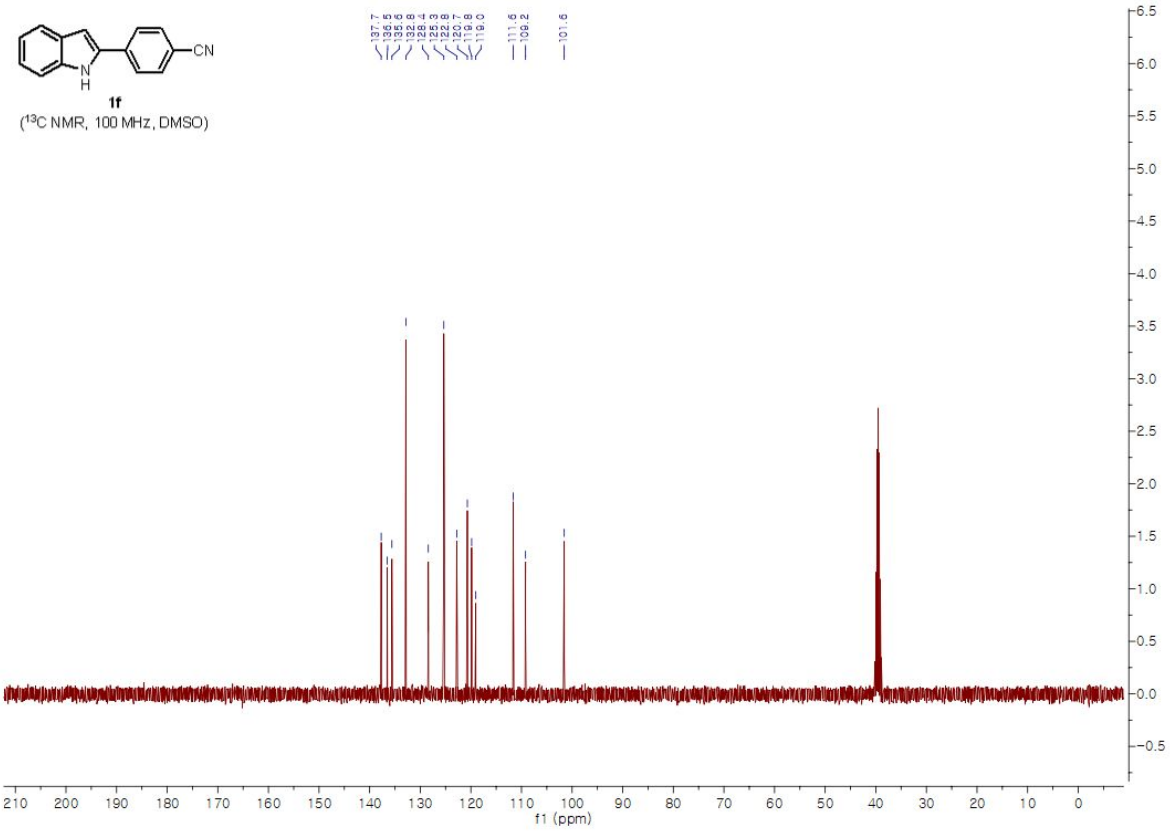
2-(benzo[d][1,3]dioxol-5-yl)-*1H*-indole (Scheme 3, **1e**)



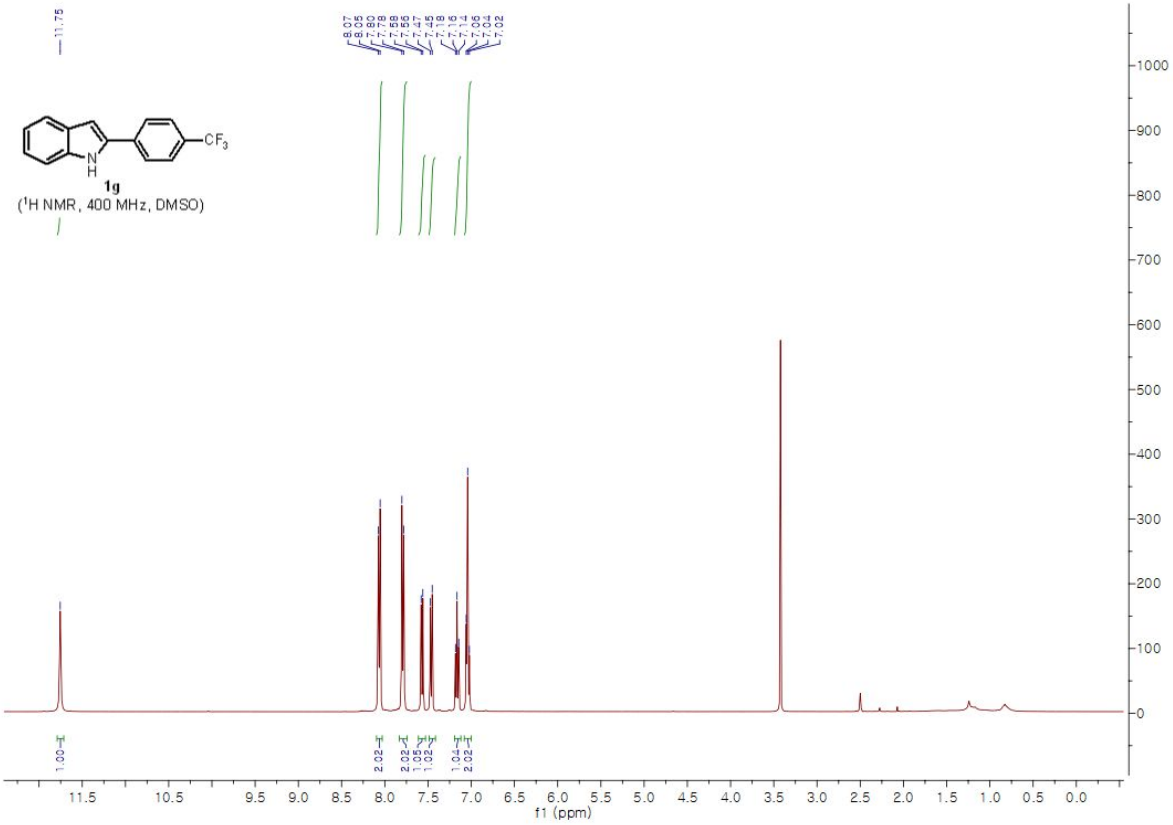


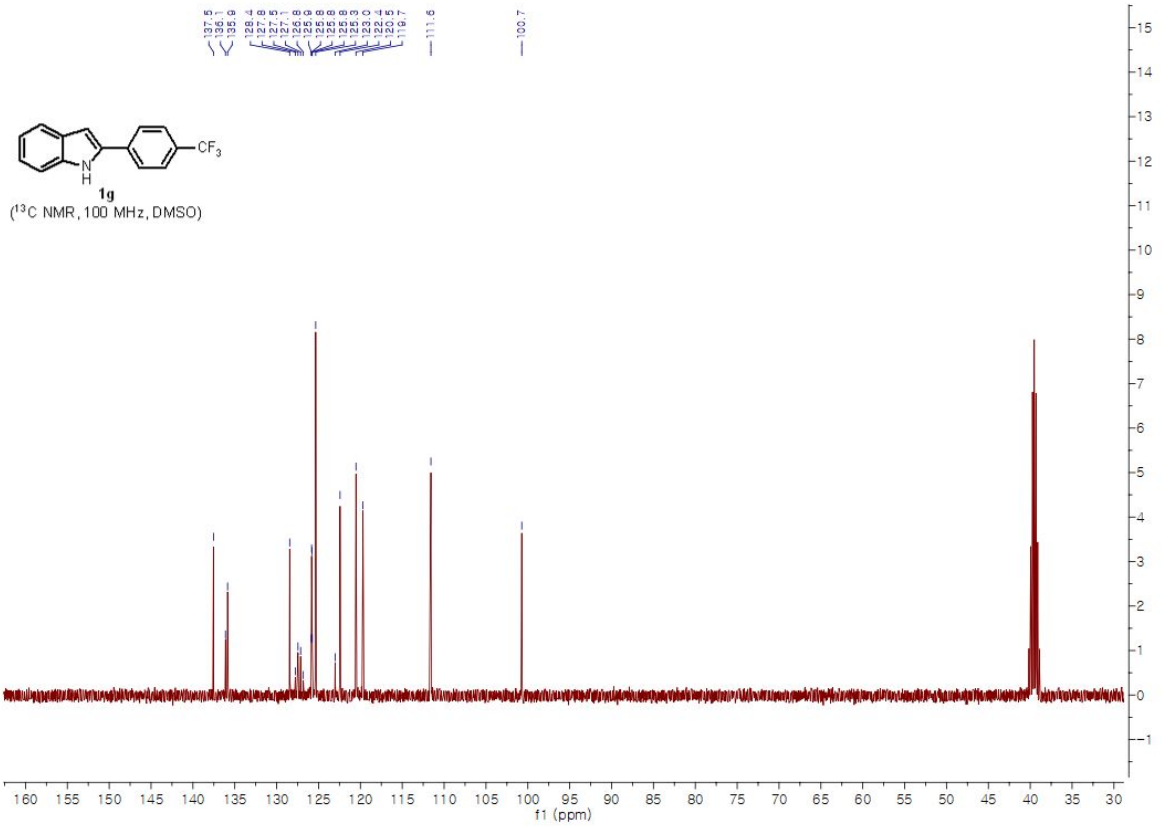
4-(*1H*-indol-2-yl)benzonitrile (Scheme 3, **1f**)

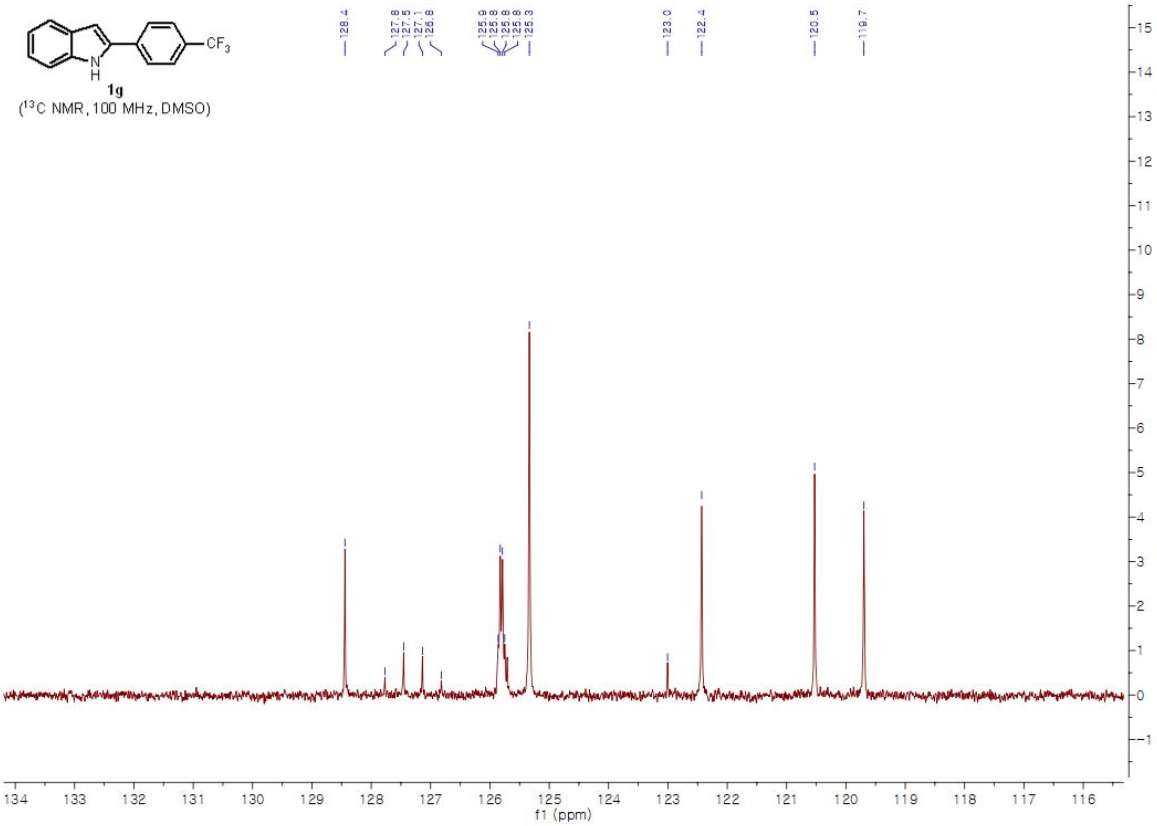


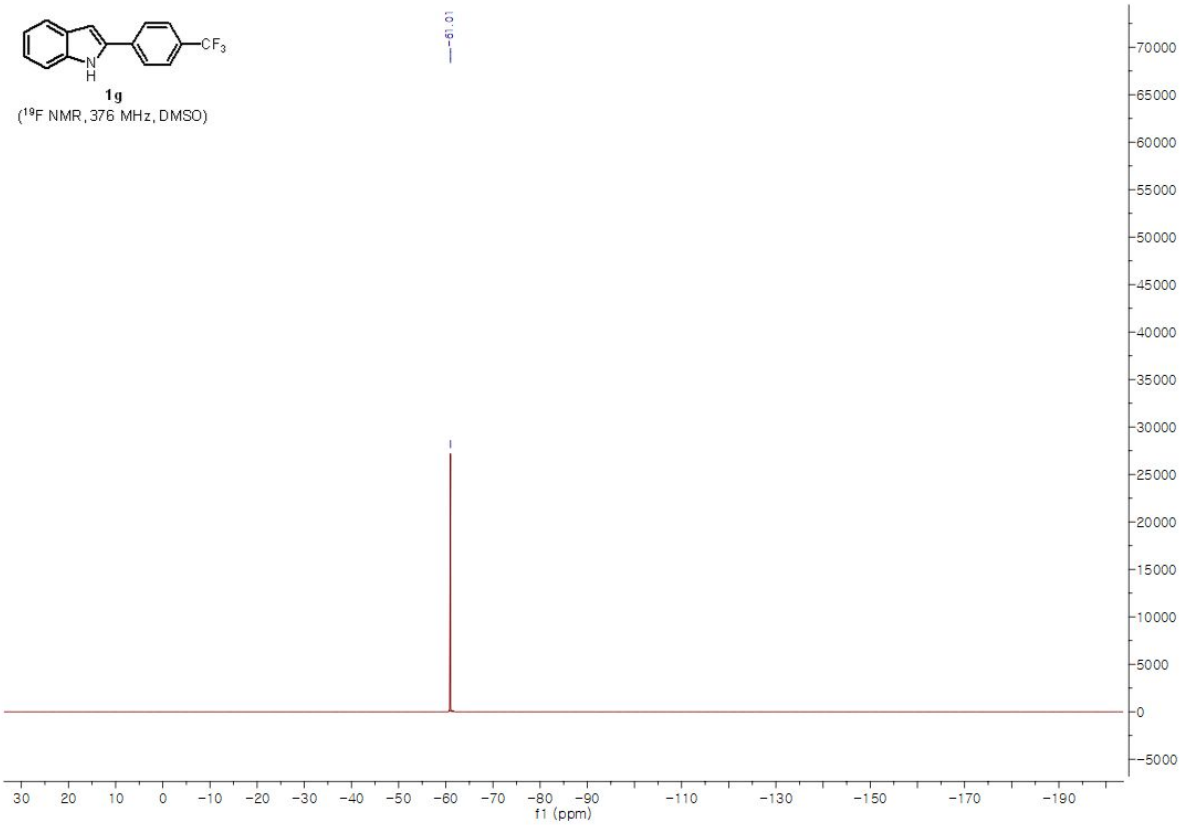


2-(4-(trifluoromethyl)phenyl)-*1H*-indole (Scheme 3, **1g**)

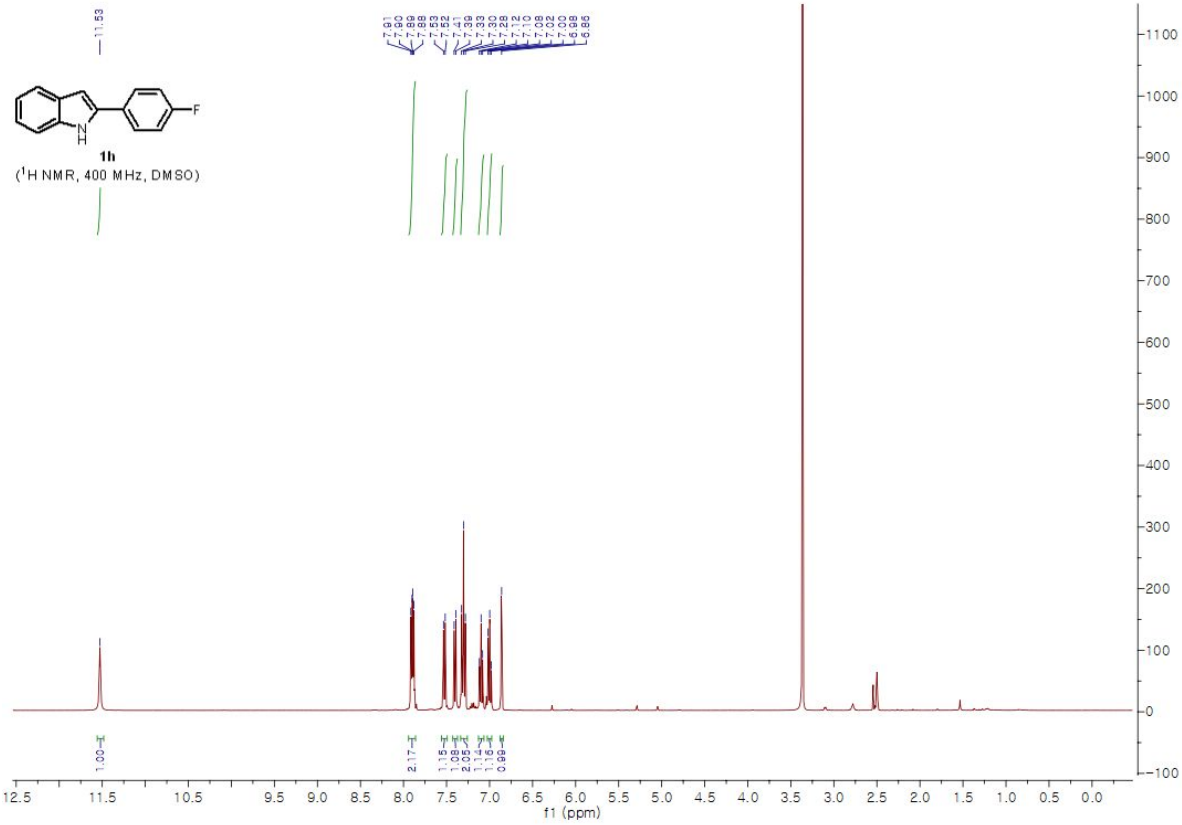


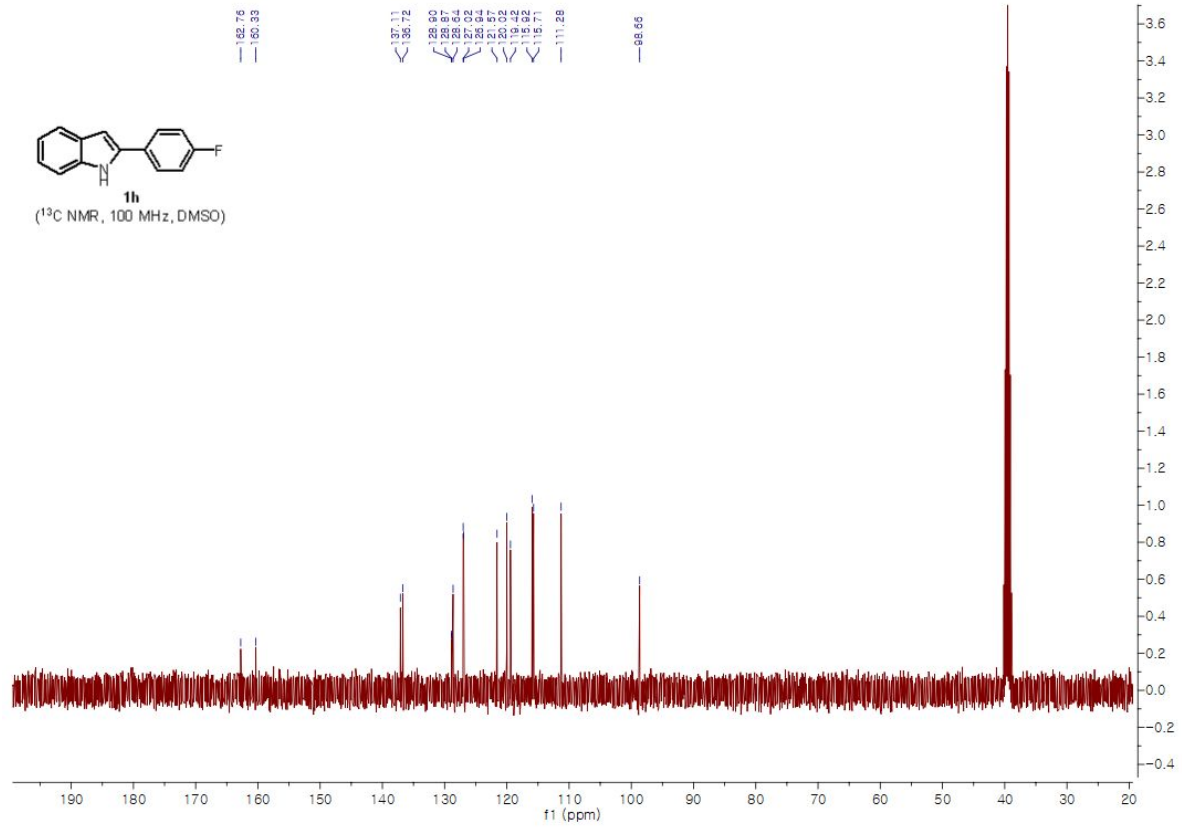


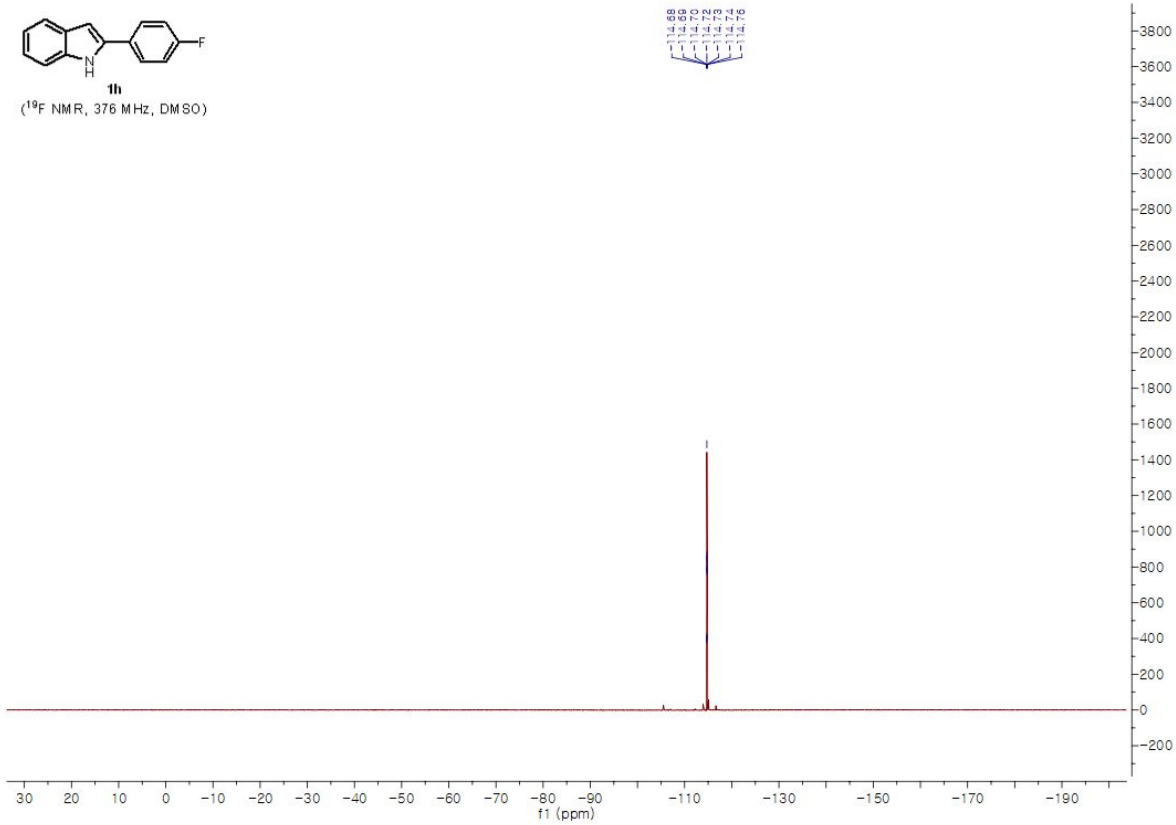

CF3
N
H
1g
(13C NMR, 100 MHz, DMSO)
128.4
127.8
127.5
127.1
126.8
125.9
125.8
125.8
125.8
125.3
123.0
122.4
120.5
119.7
f1 (ppm)

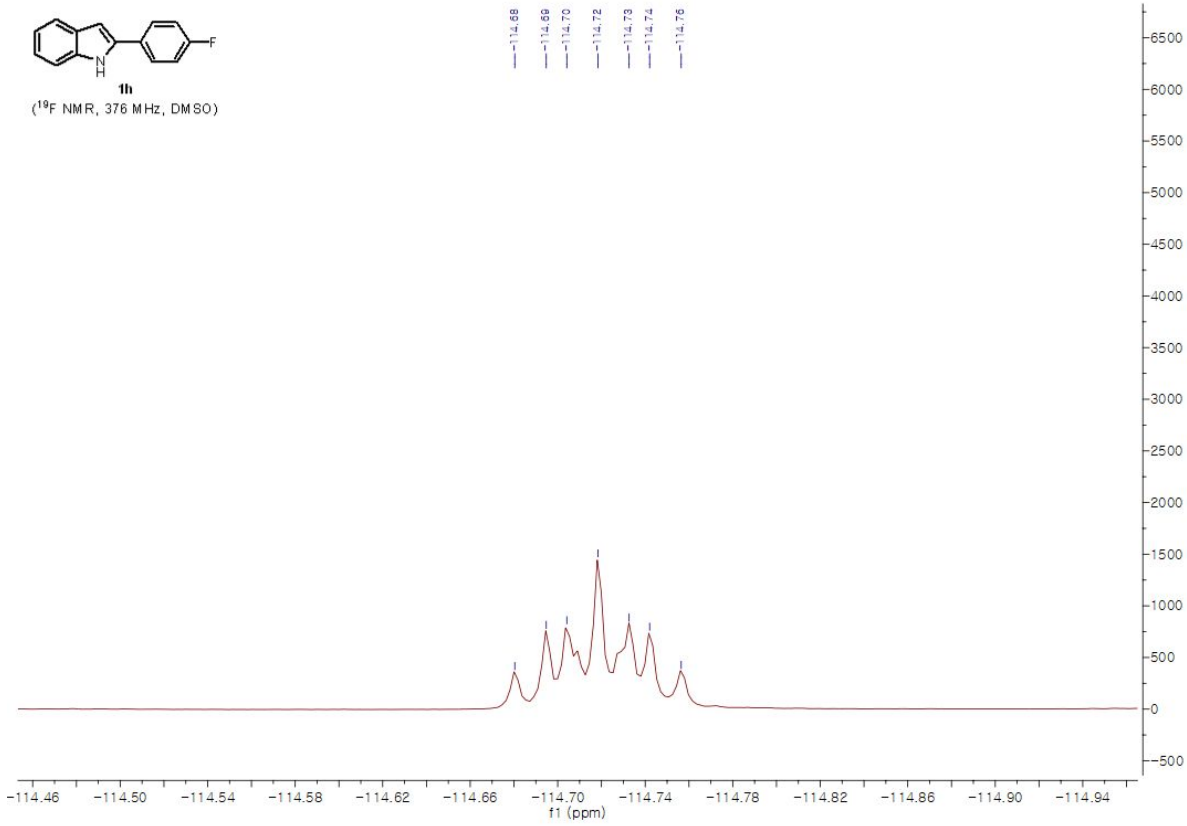

CF3
N
H
1g
(19F NMR, 376 MHz, DMSO)
-61.01
f1 (ppm)

2-(4-fluorophenyl)-*1H*-indole (Scheme 3, **1h**)

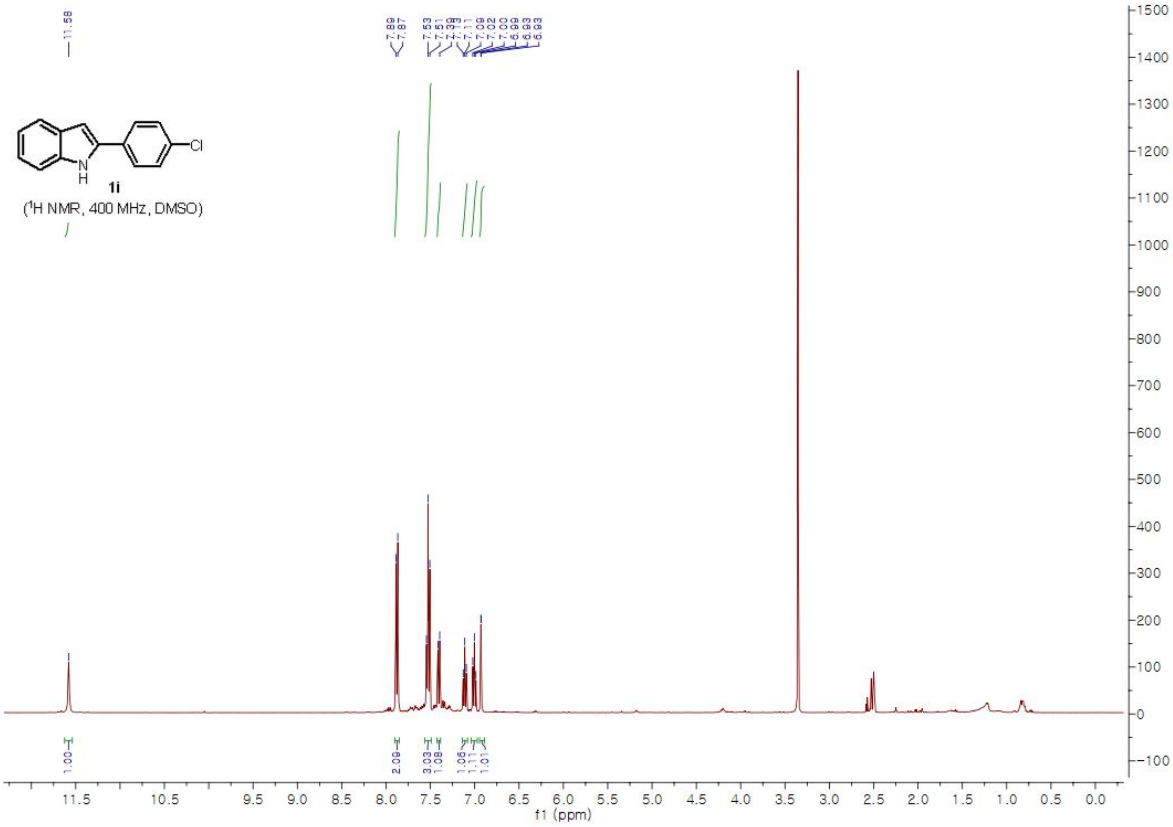


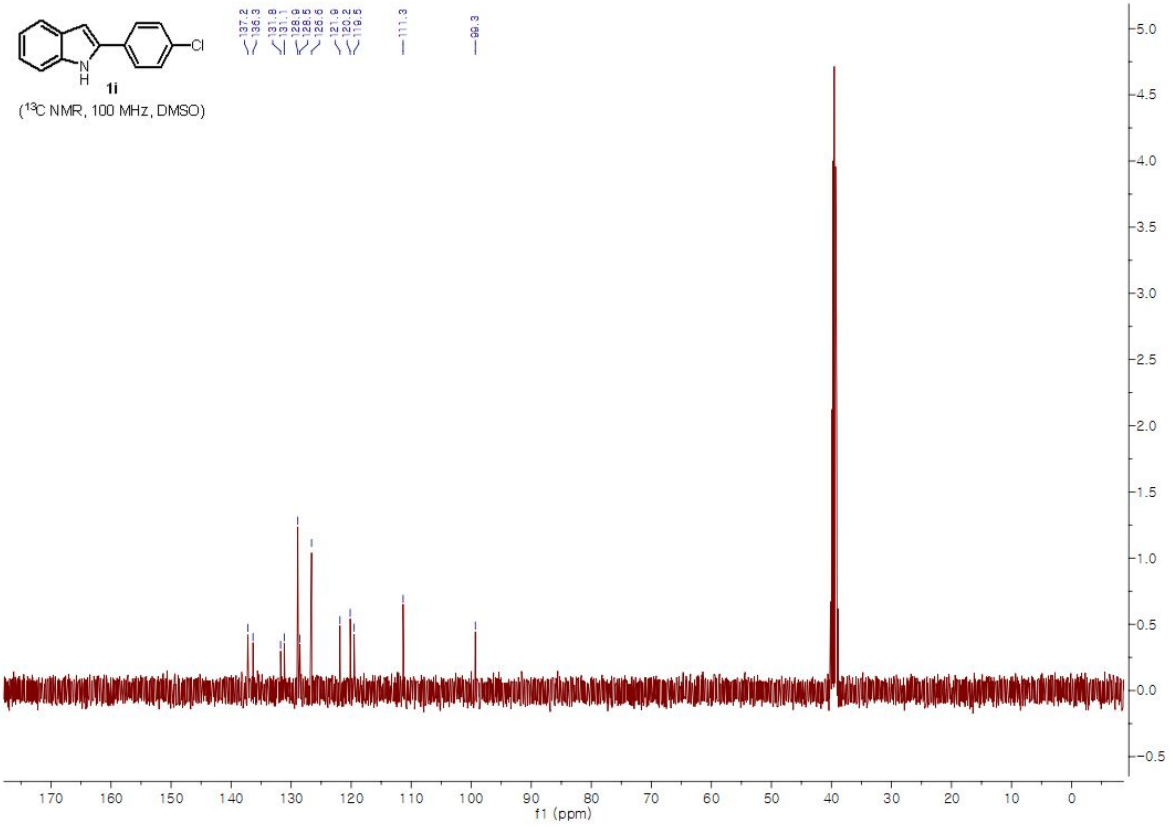



1h
(19F NMR, 376 MHz, DMSO)
f1 (ppm)

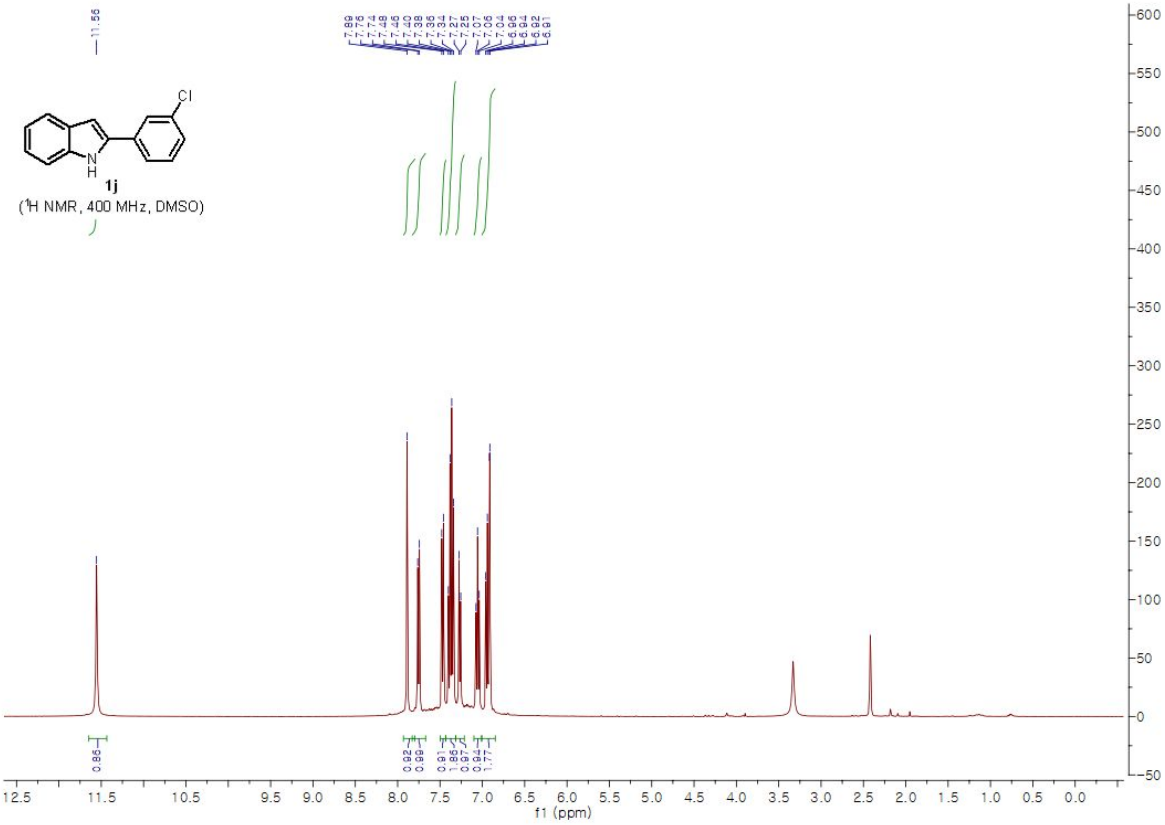

1h
(19F NMR, 376 MHz, DMSO)
f1 (ppm)

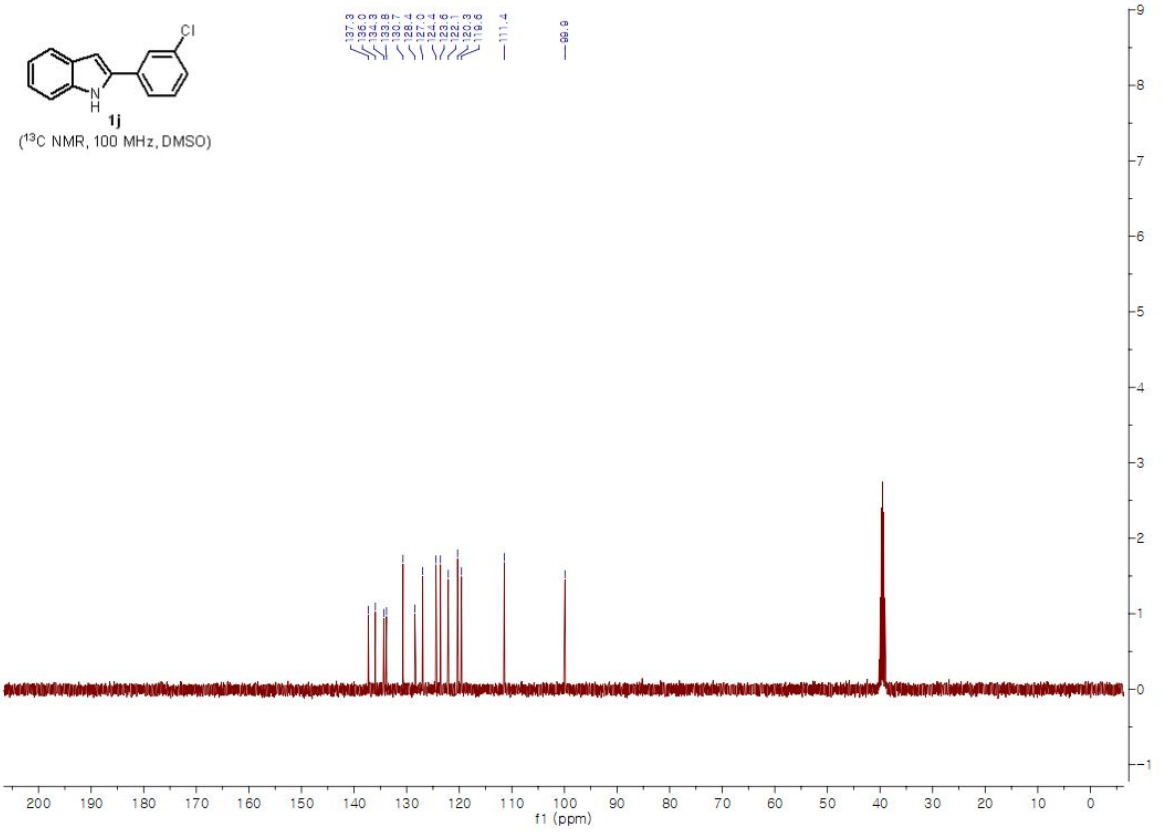
2-(4-chlorophenyl)-*1H*-indole (Scheme 3, **1i**)



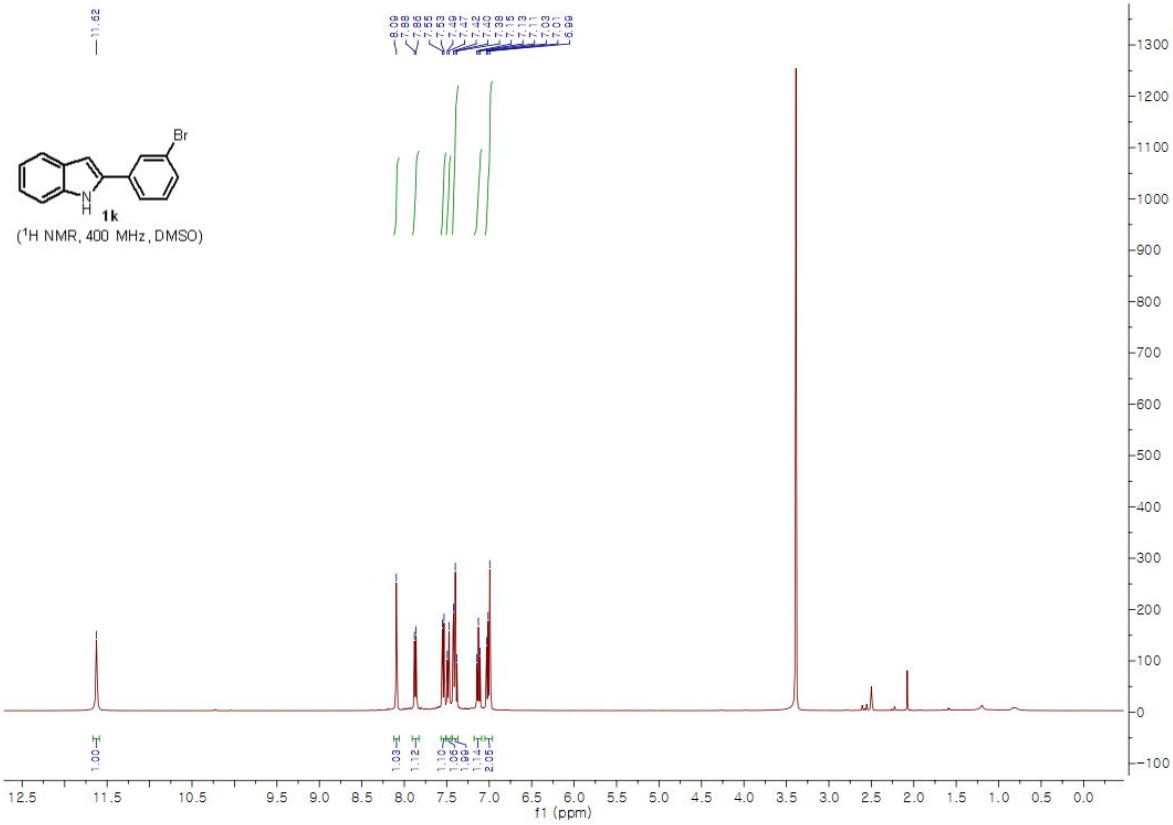


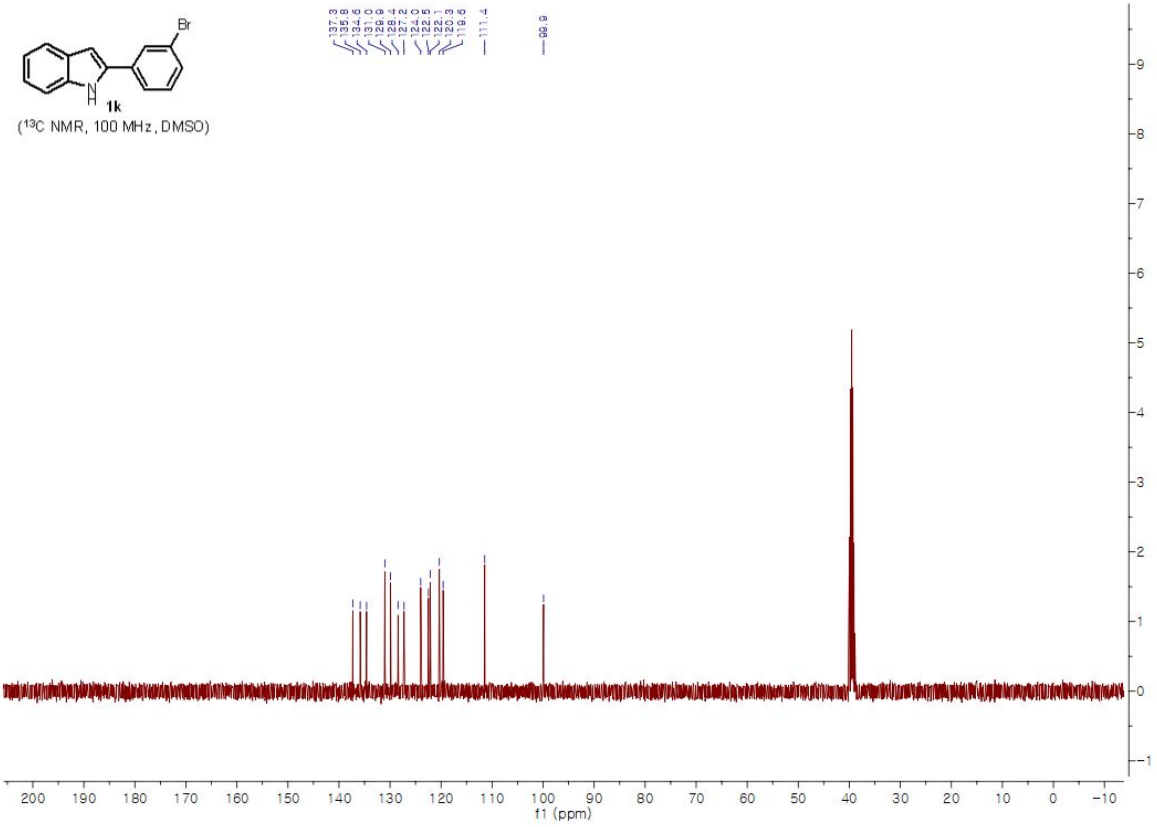
2-(3-chlorophenyl)-*1H*-indole (Scheme 3, **1j**)



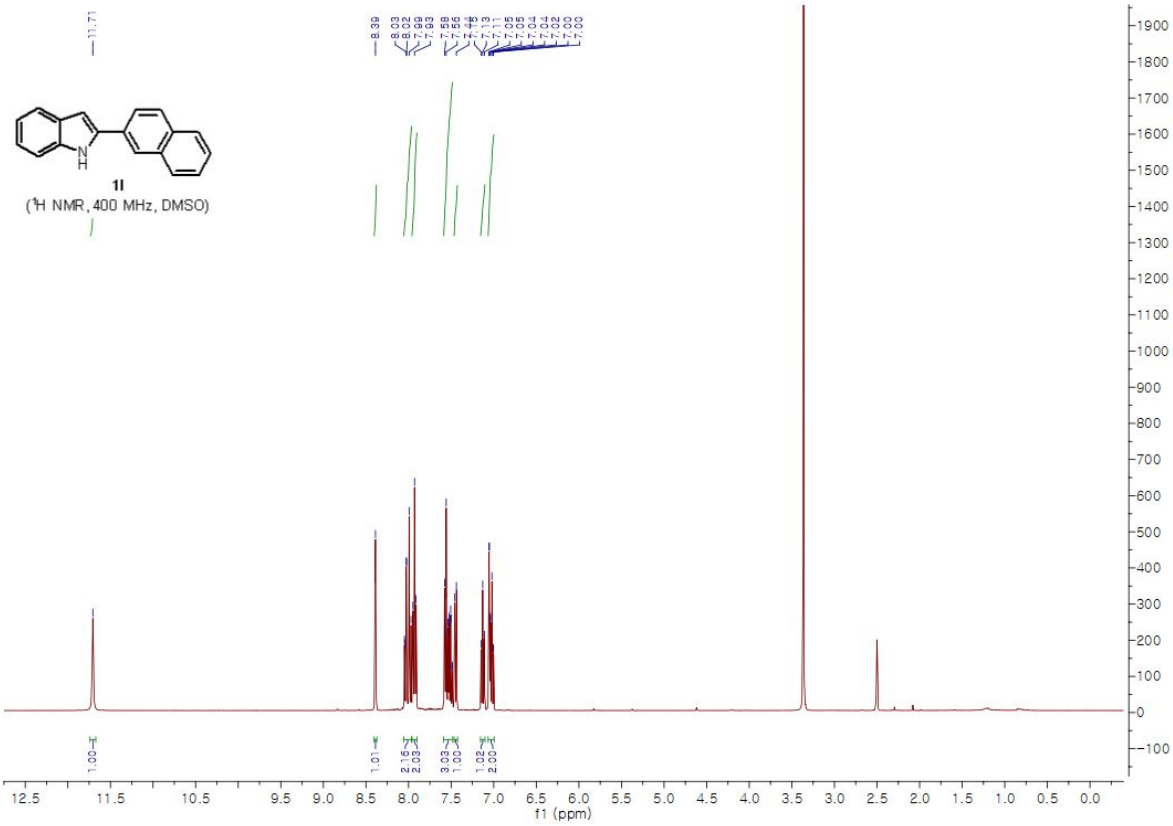


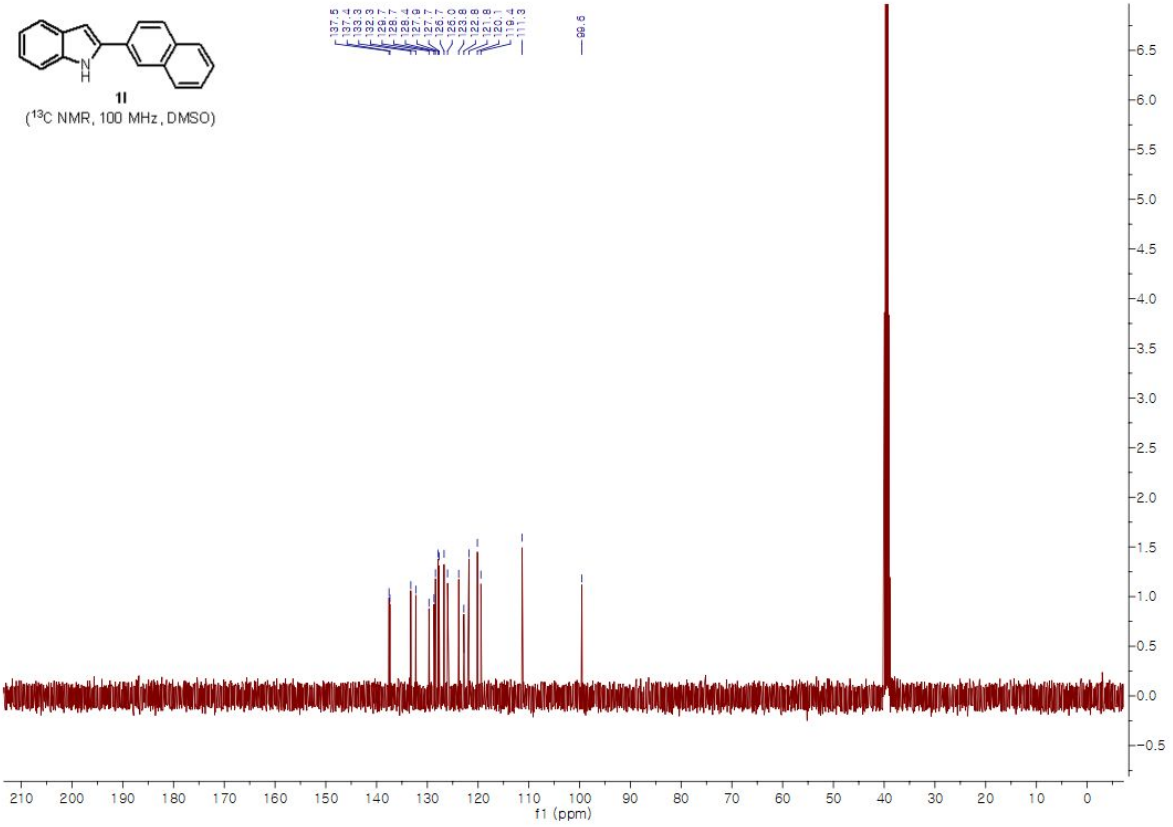
2-(3-bromophenyl)-*1H*-indole (Scheme 3, **1k**)



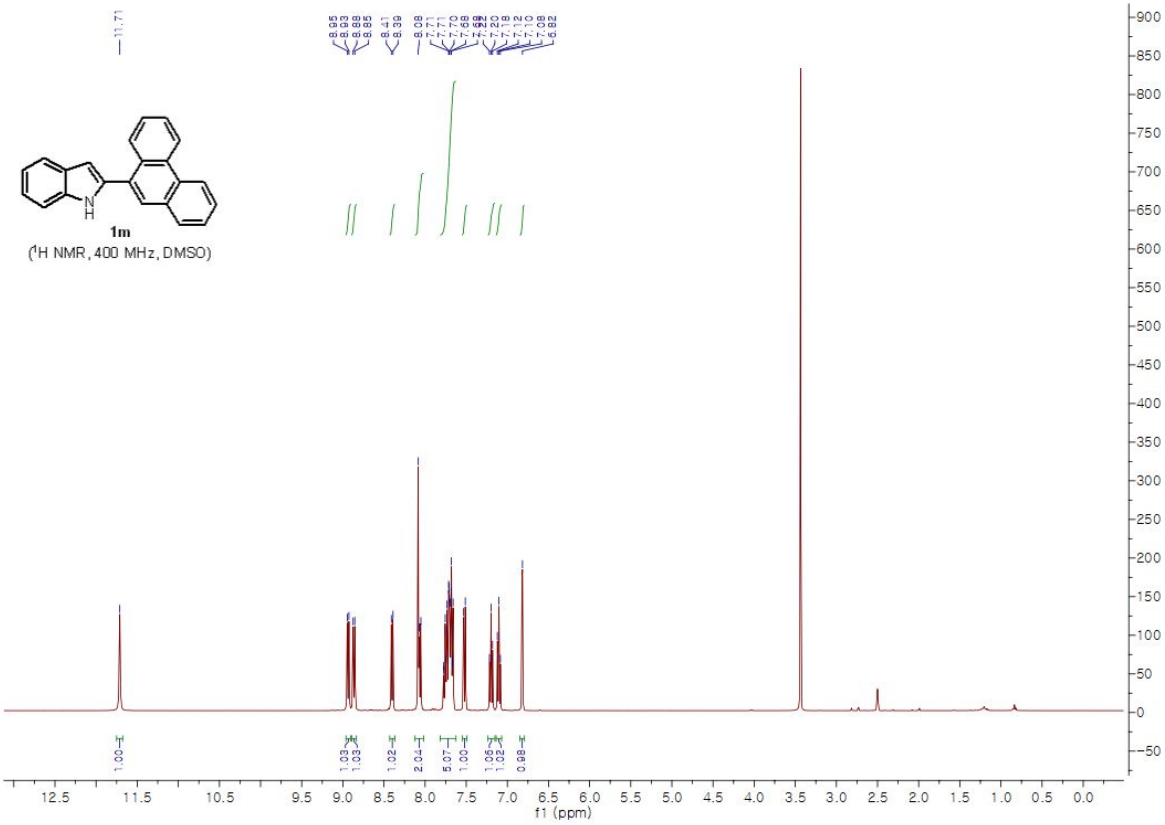


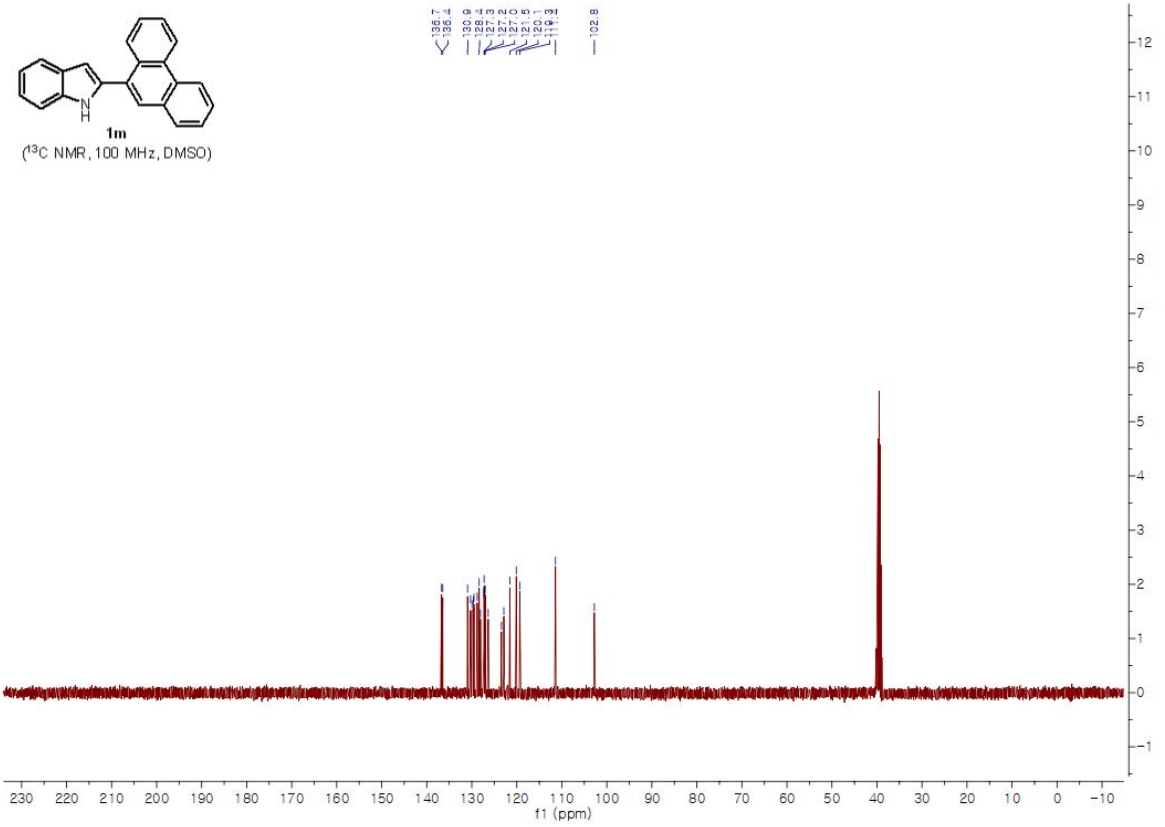
2-(naphthalen-2-yl)-*1H*-indole (Scheme 3, **1l**)



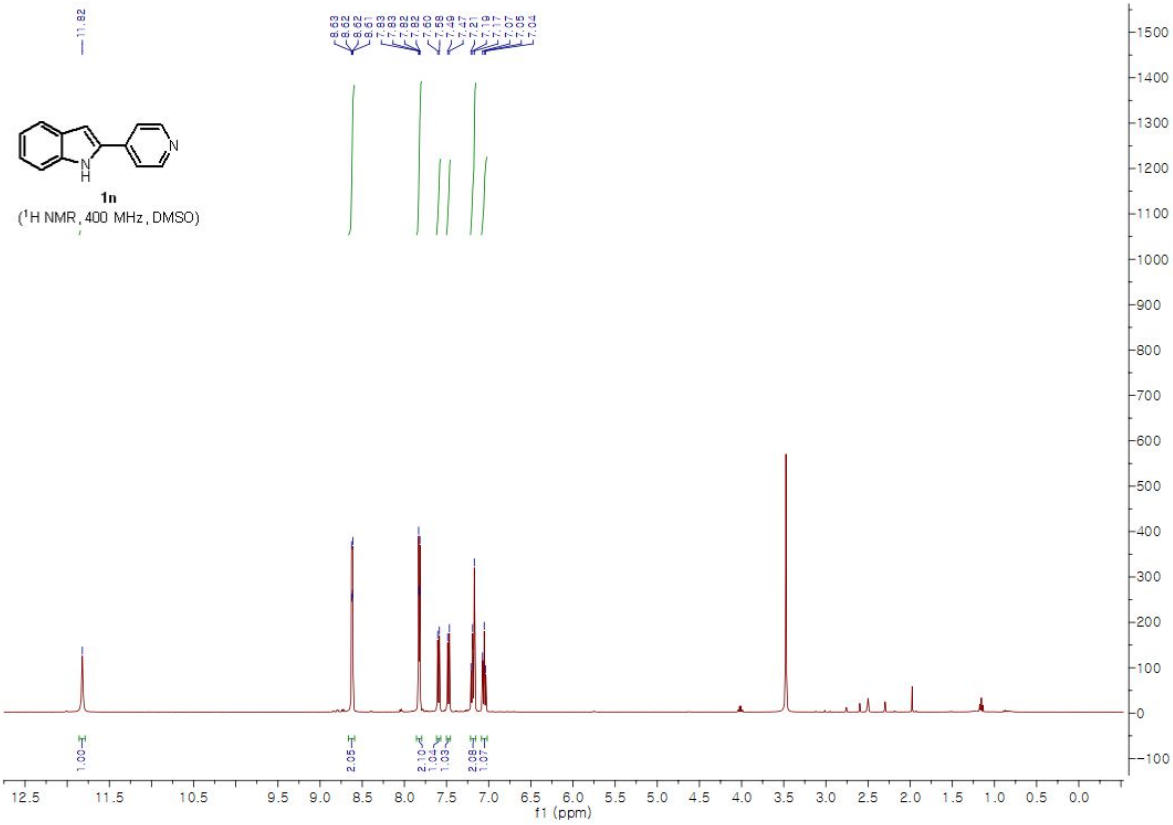


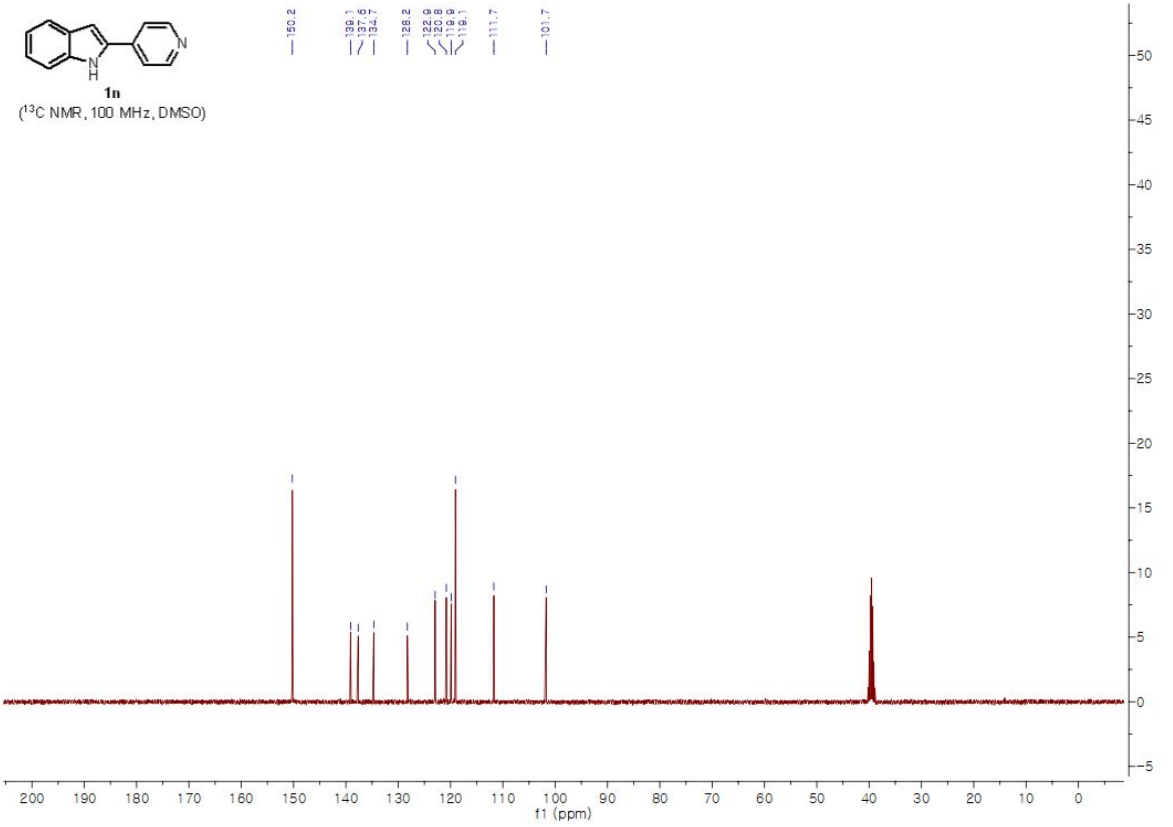
2-(phenanthren-9-yl)-*1H*-indole (Scheme 3, **1m**)



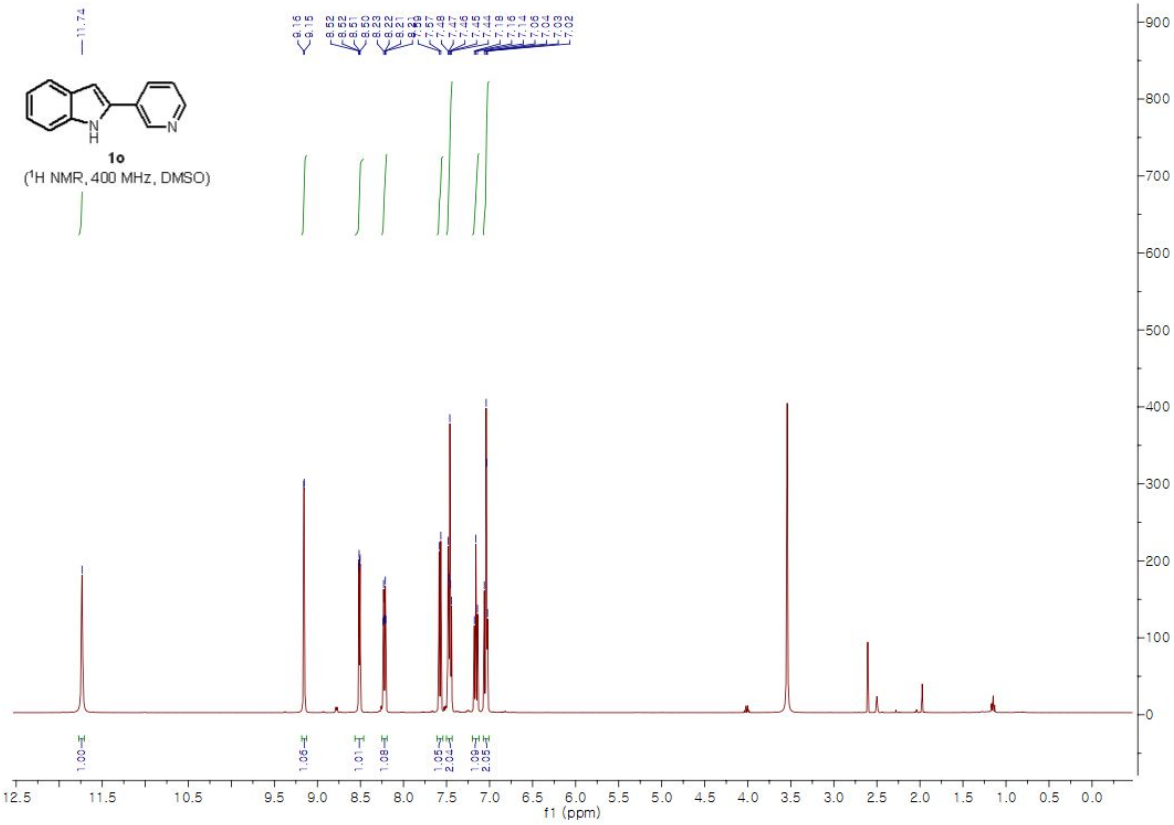


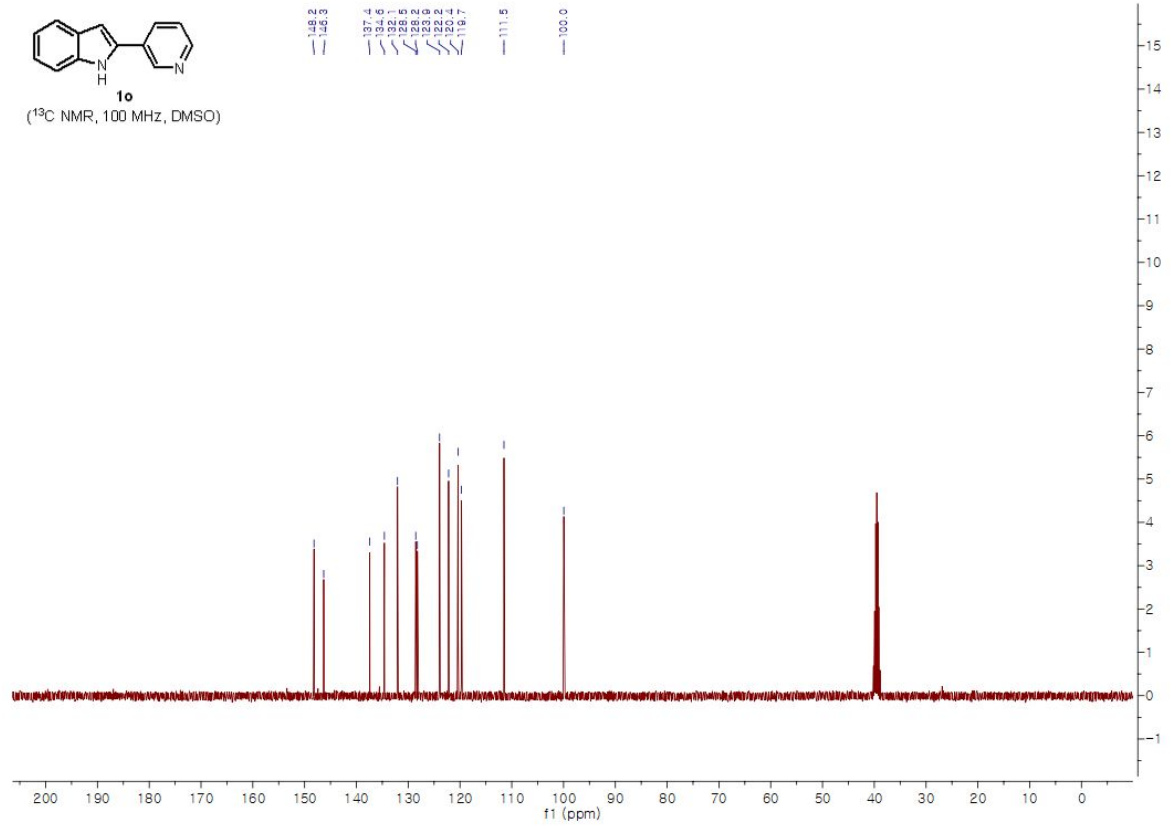
2-(pyridin-4-yl)-*1H*-indole (Scheme 3, **1n**)



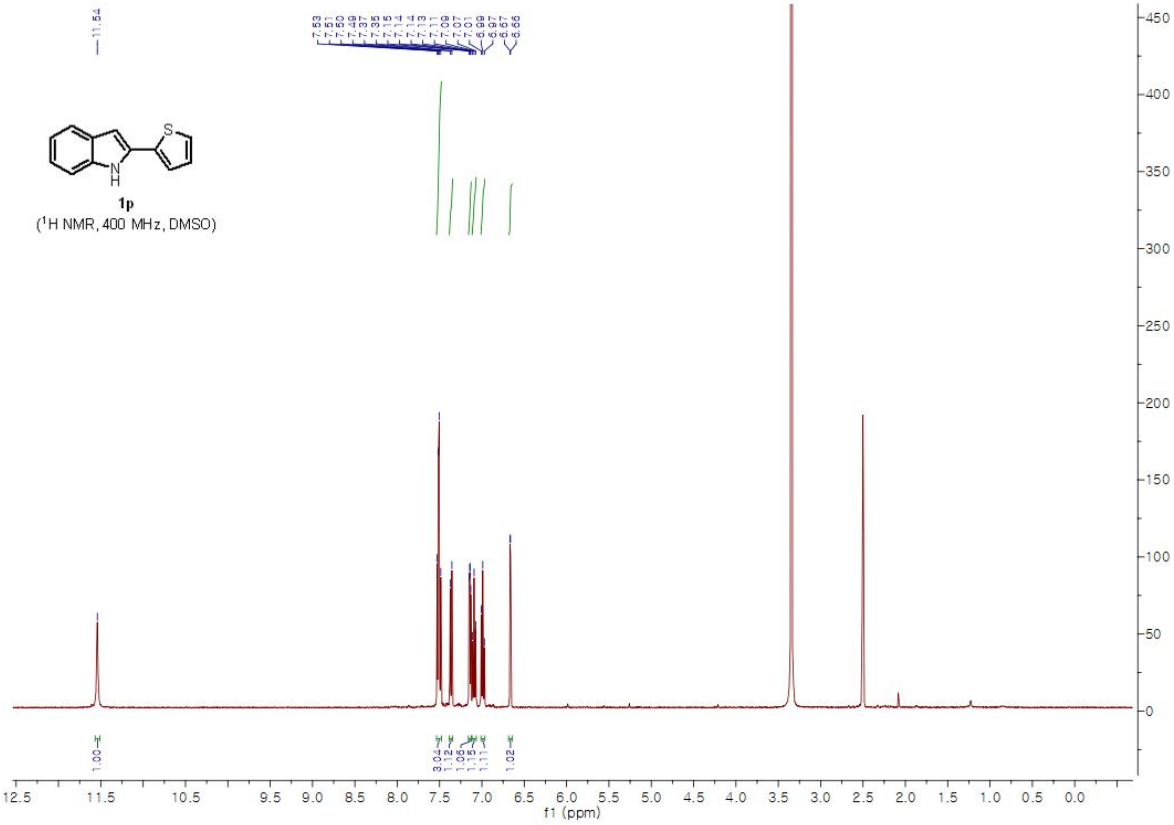


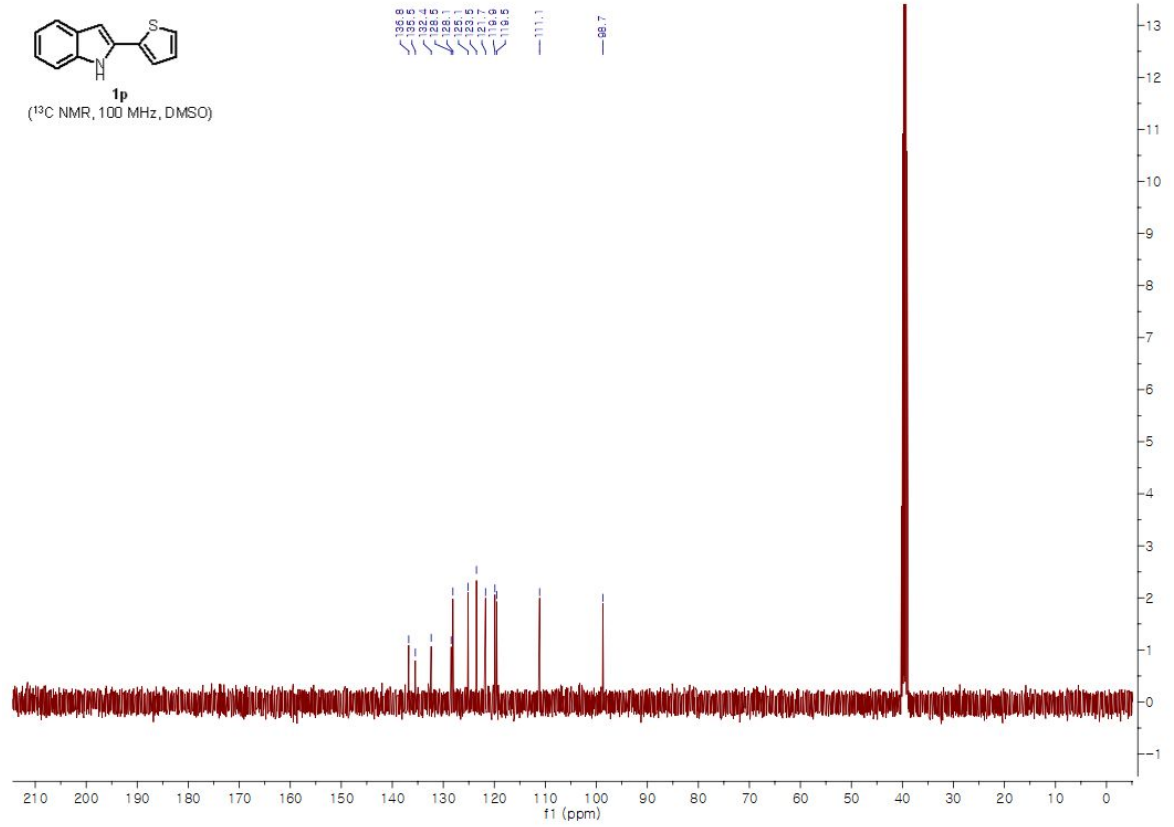
2-(pyridin-3-yl)-*1H*-indole (Scheme 3, **1o**)



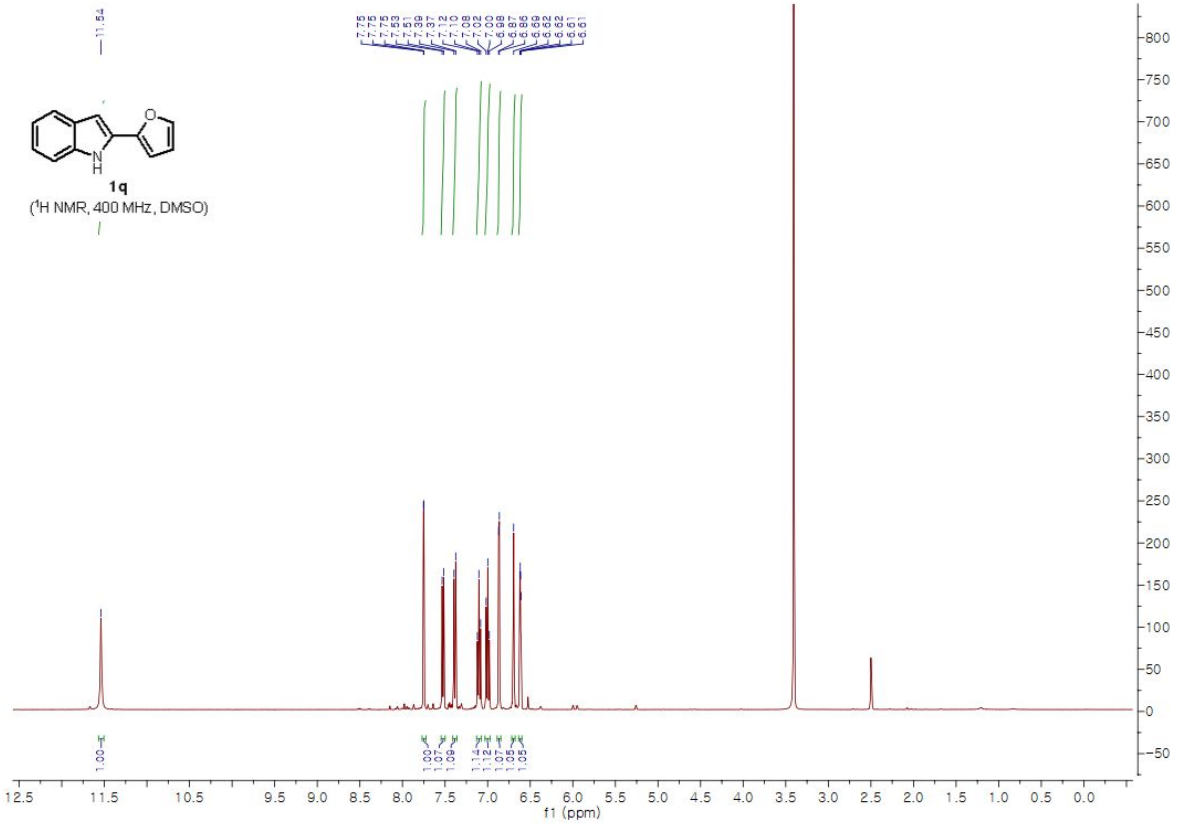


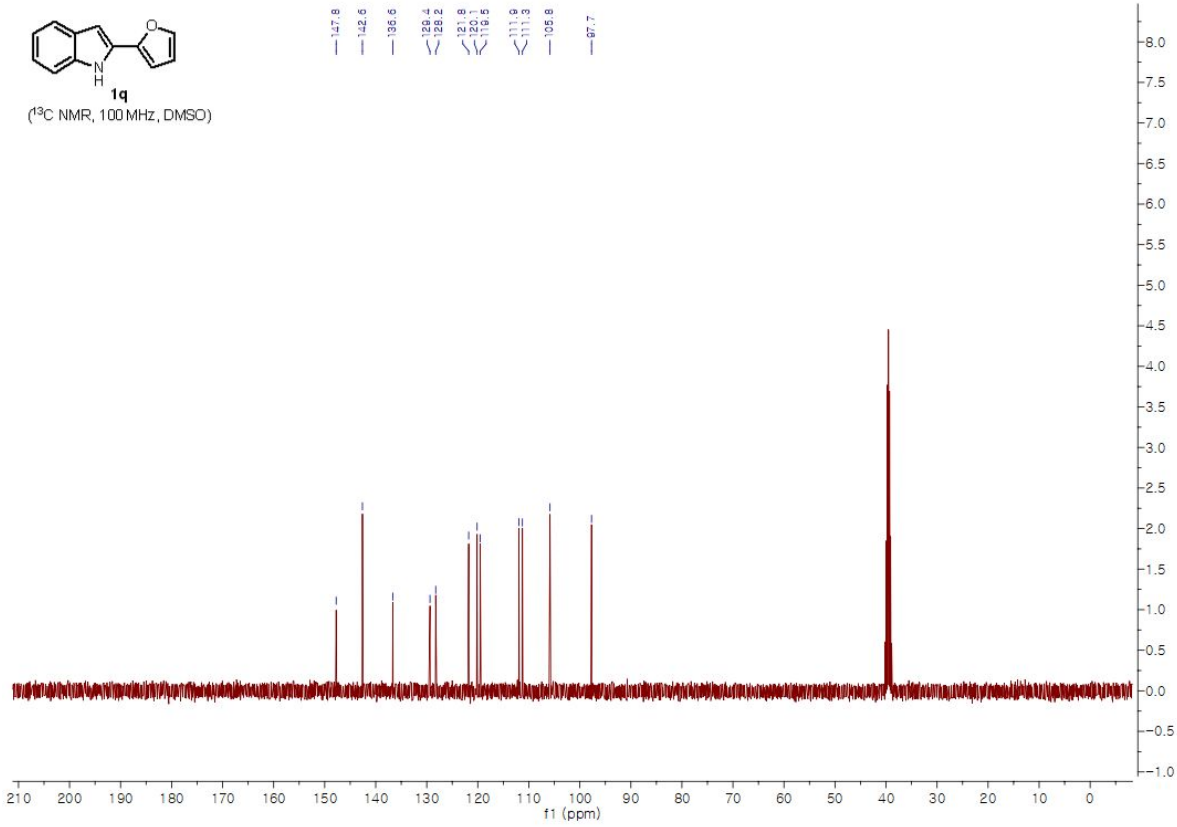
2-(thiophen-2-yl)-*1H*-indole (Scheme 3, **1p**)



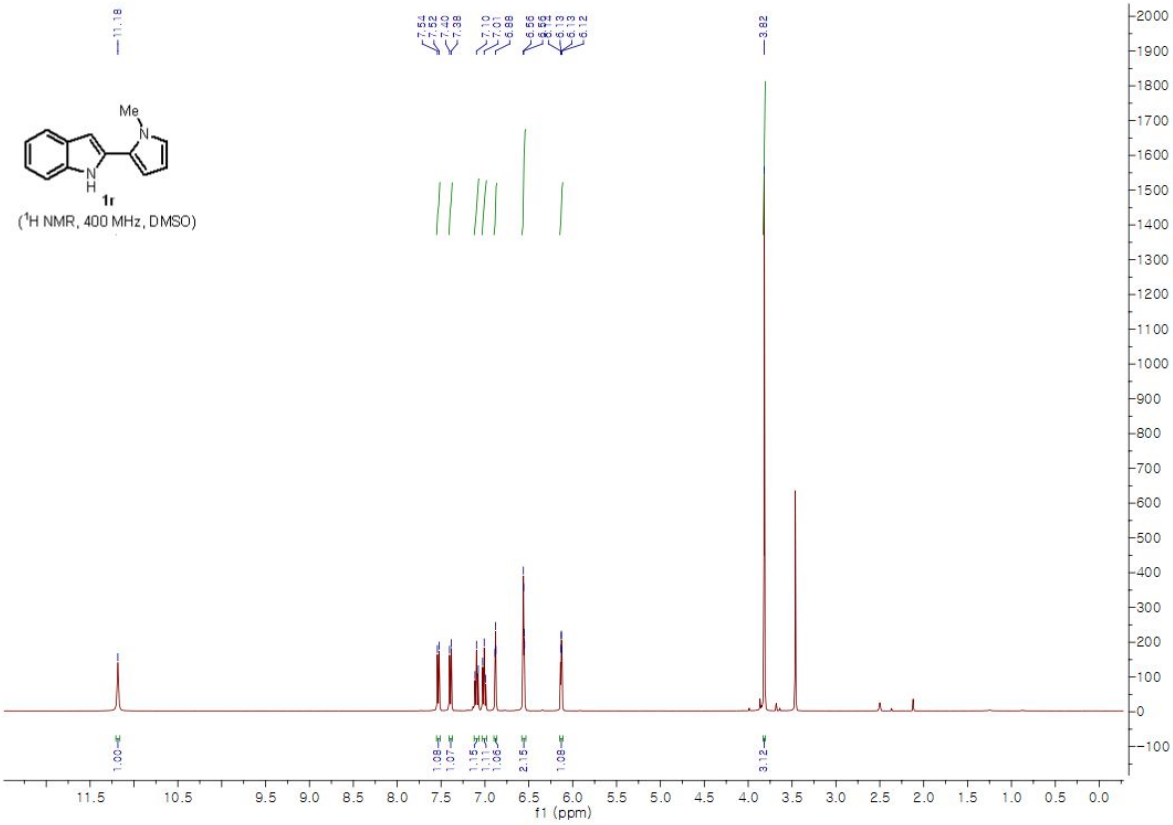


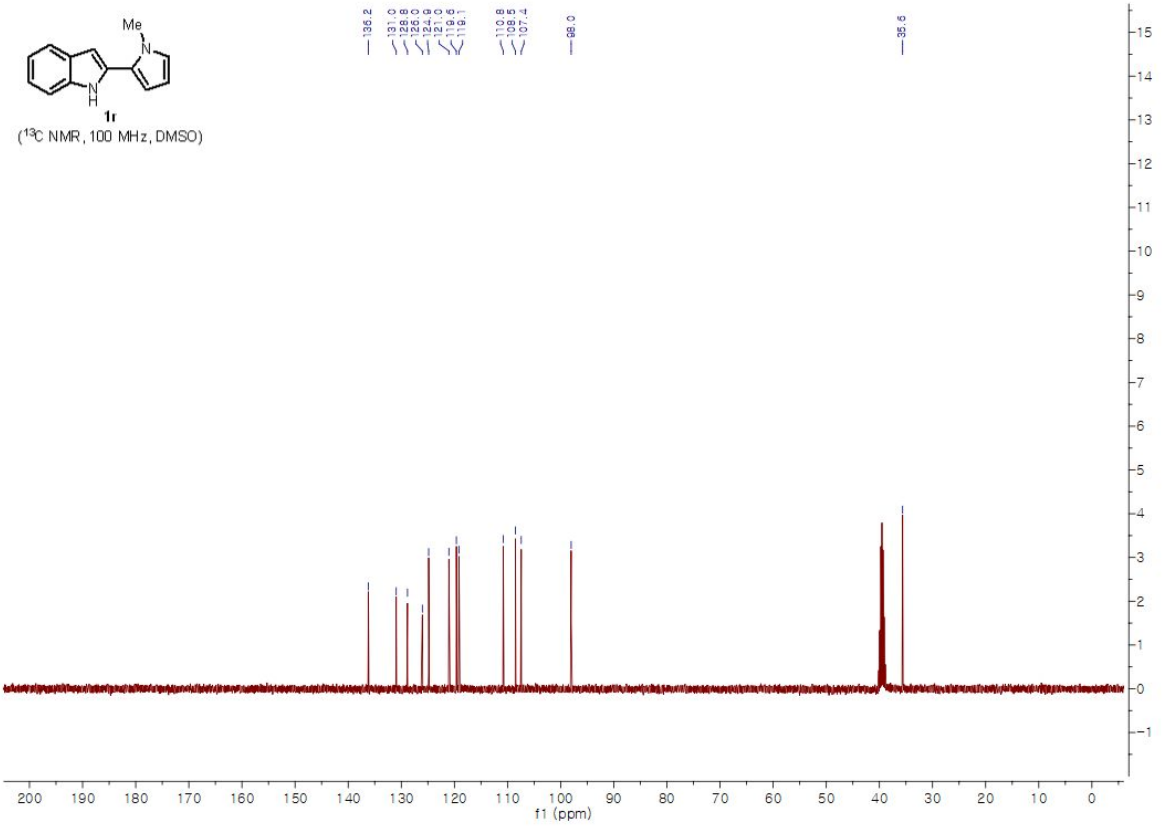
2-(furan-2-yl)-*1H*-indole (Scheme 3, **1q**)



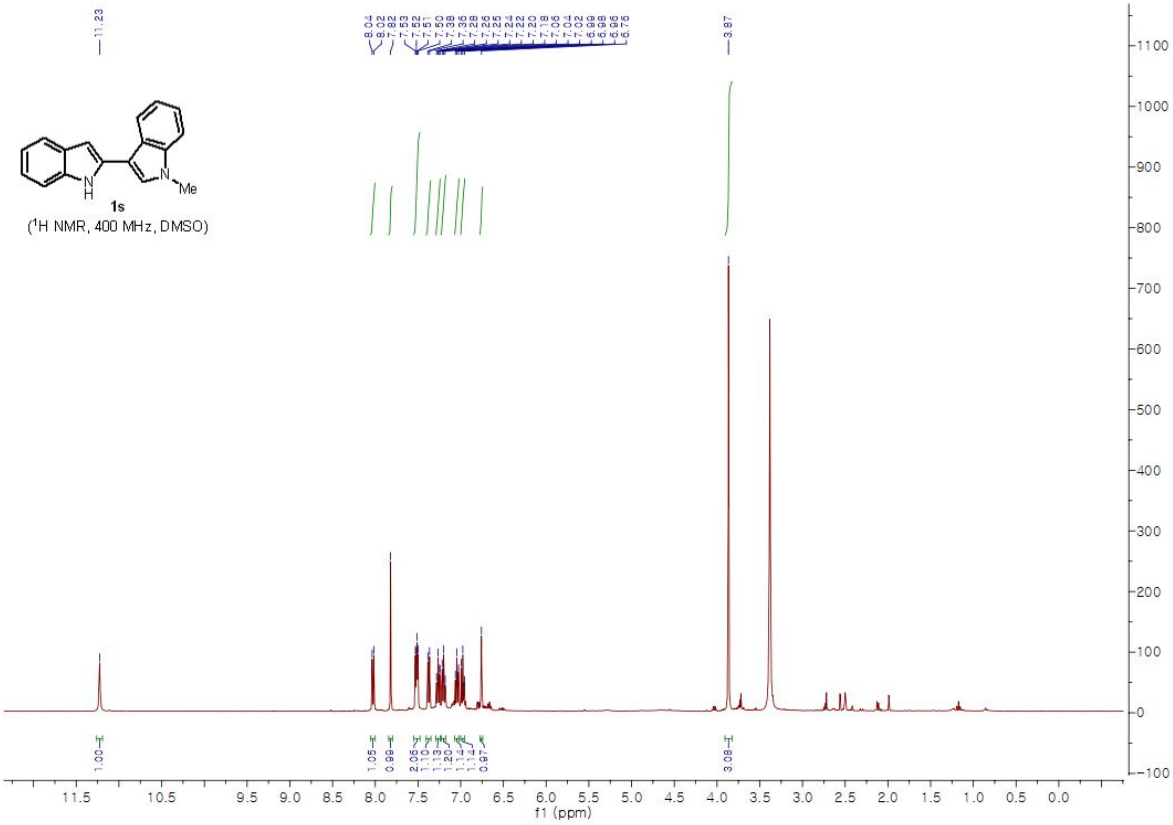


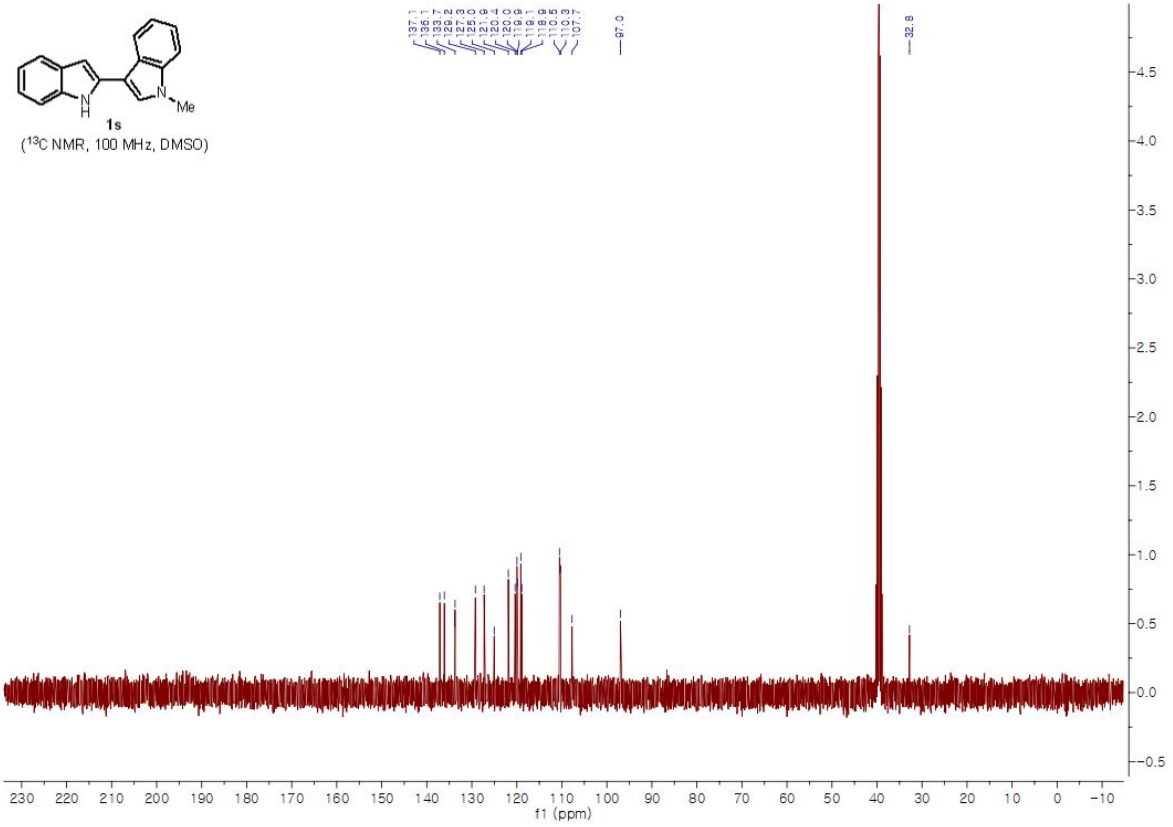
2-(1-methyl-1H-pyrrol-2-yl)-*1H*-indole (Scheme 3, **1r**)



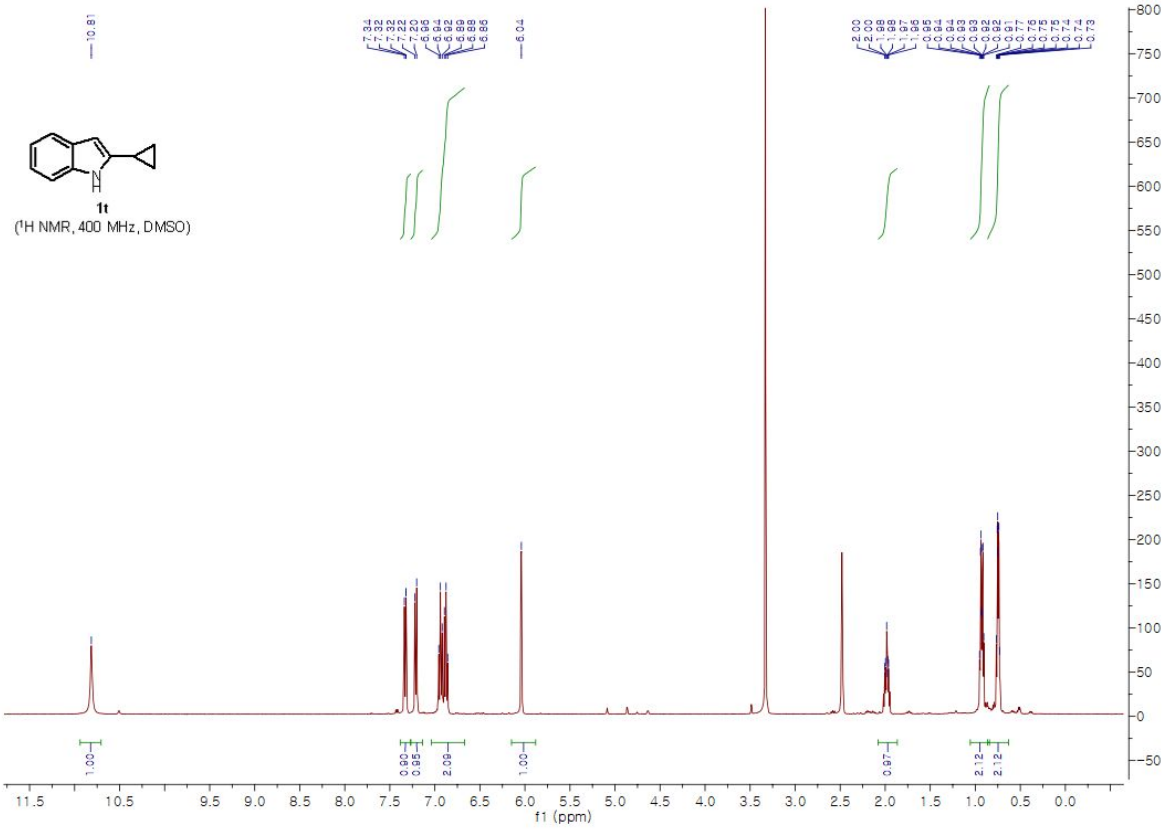


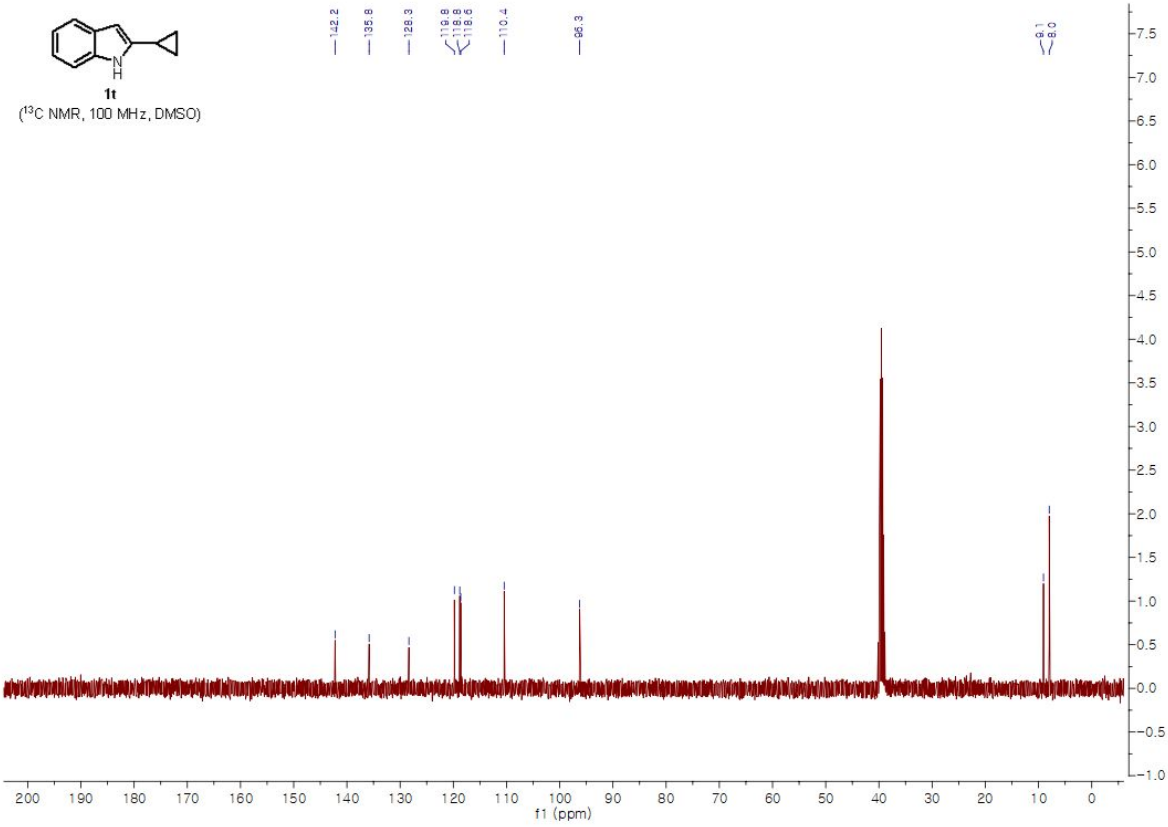
1'-methyl-*1H*,*1'H*-2,3'-biindole (Scheme 3, **1s**)



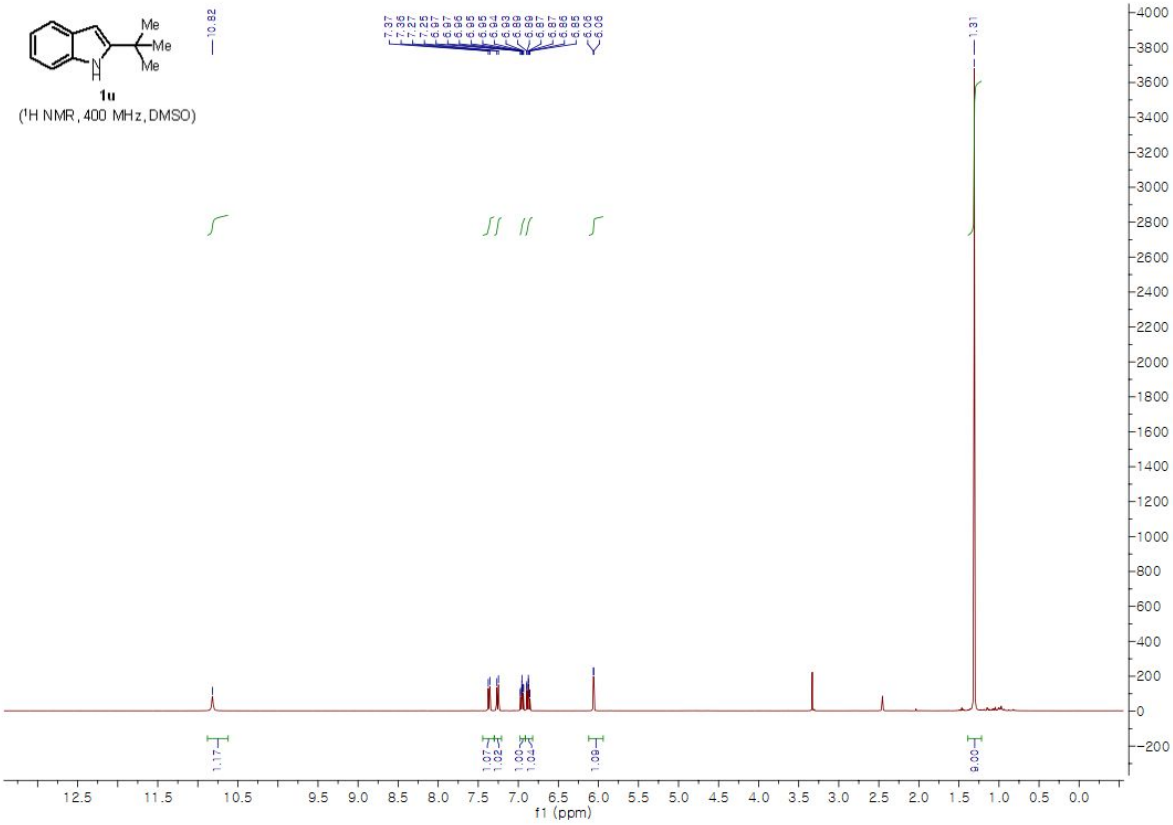


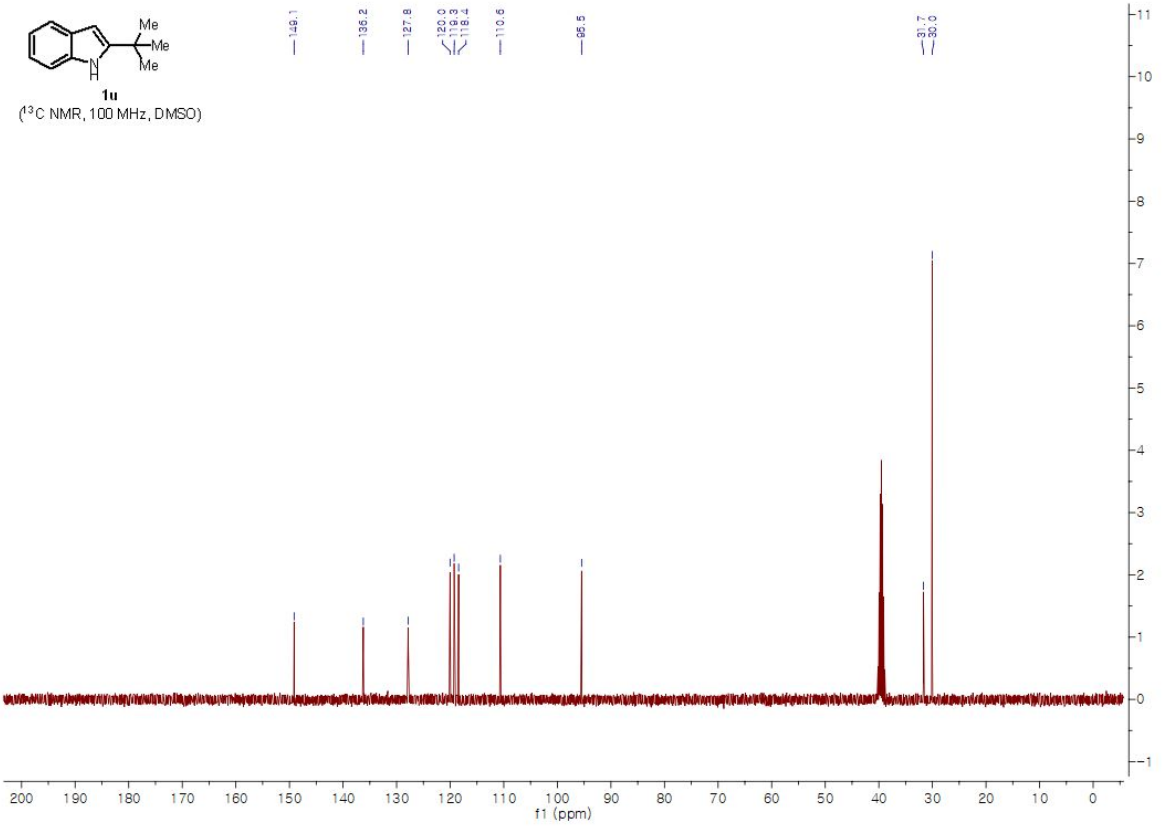
2-cyclopropyl-*1H*-indole (Scheme 3, **1t**)



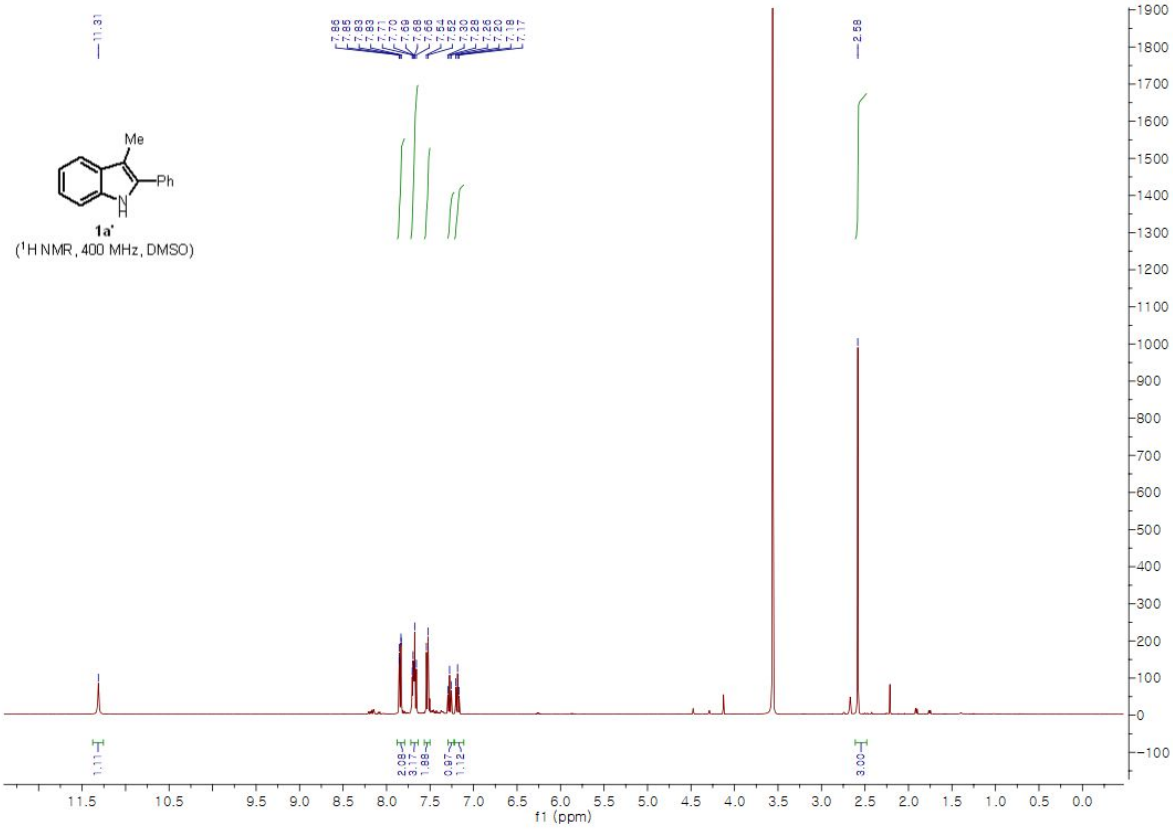


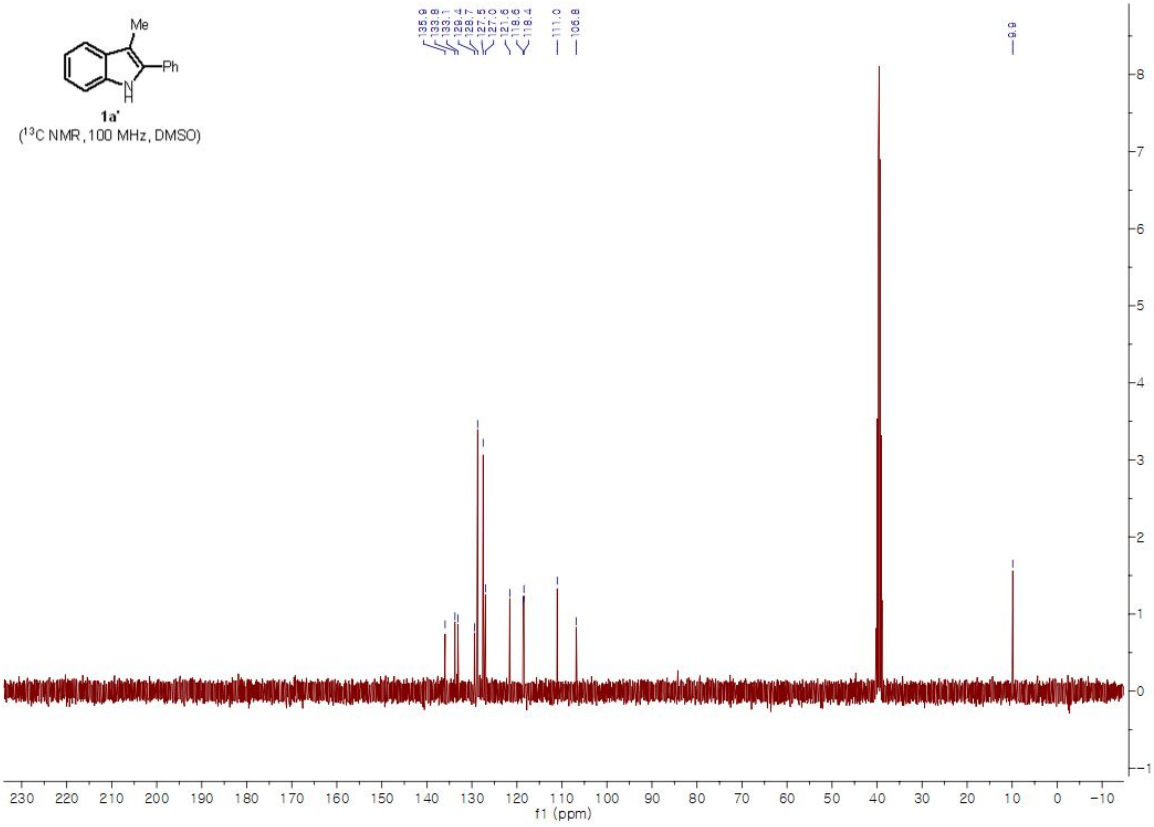
2-(*tert*-butyl)-*1H*-indole (Scheme 3, **1u**)



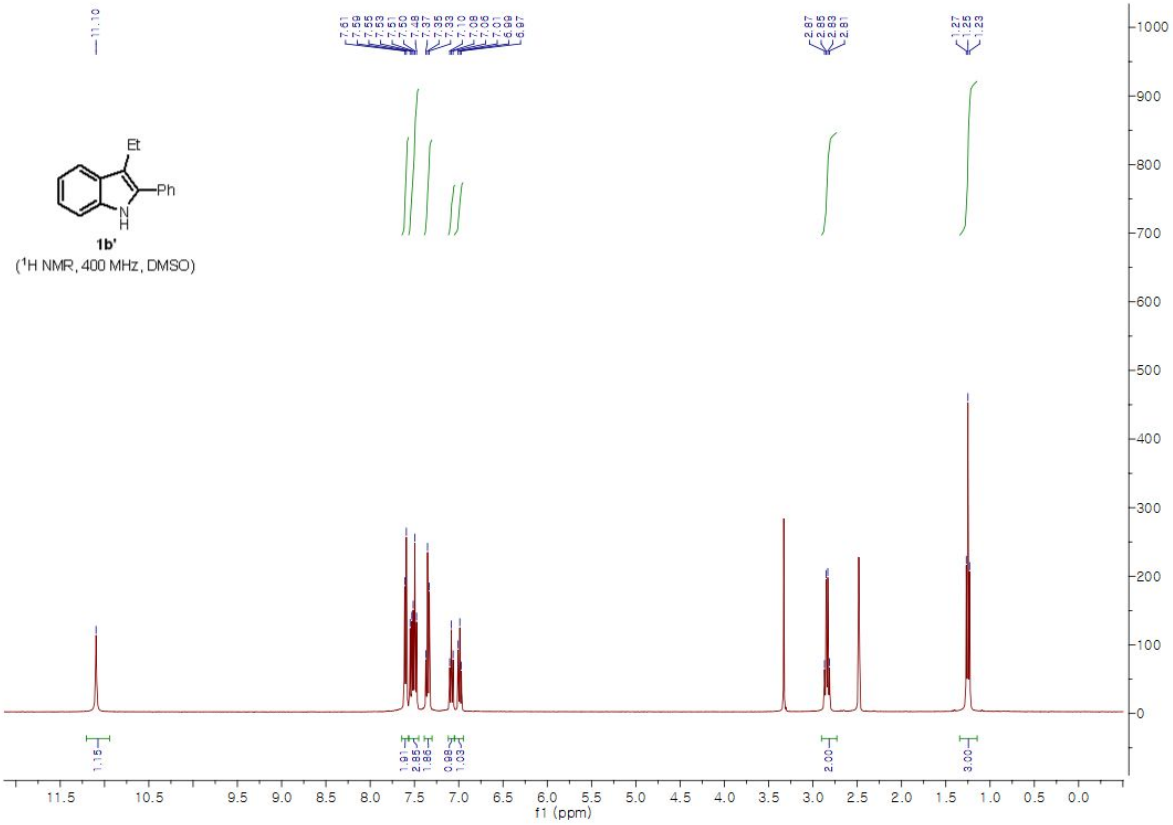


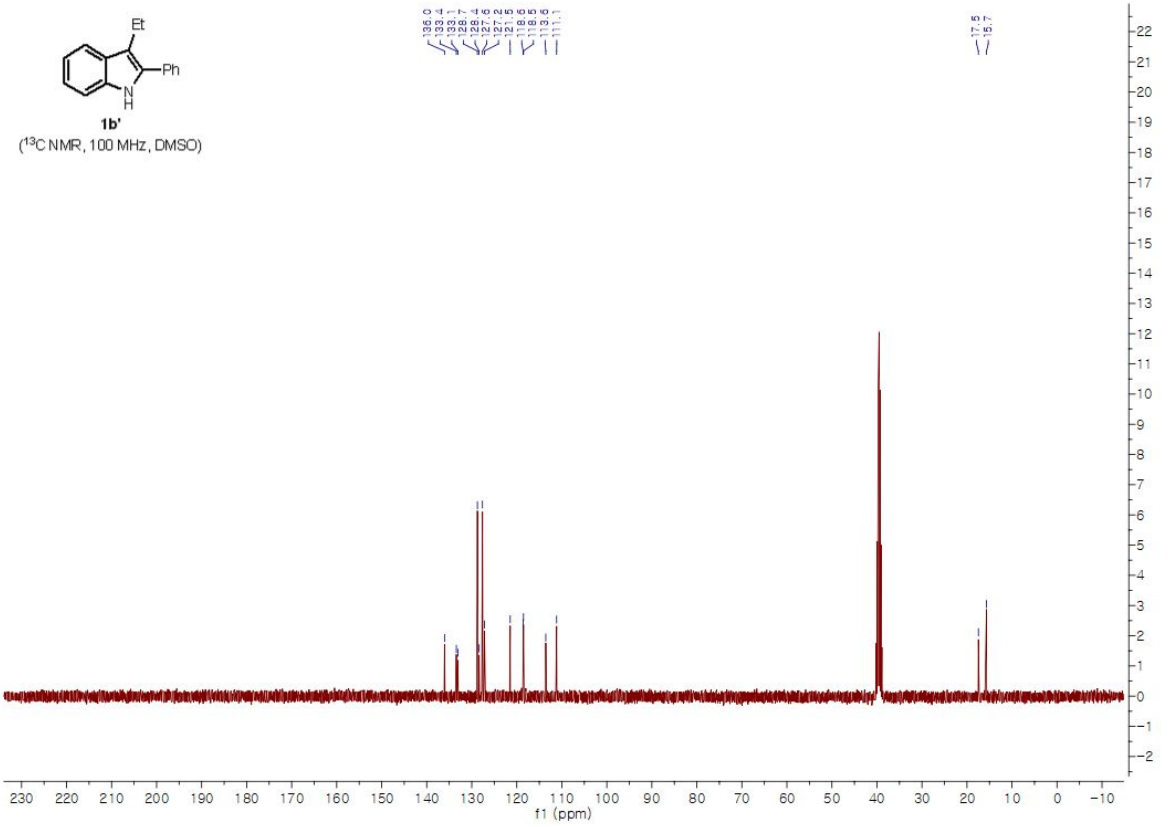
3-methyl-2-phenyl-*1H*-indole (Scheme 4, **1a'**)



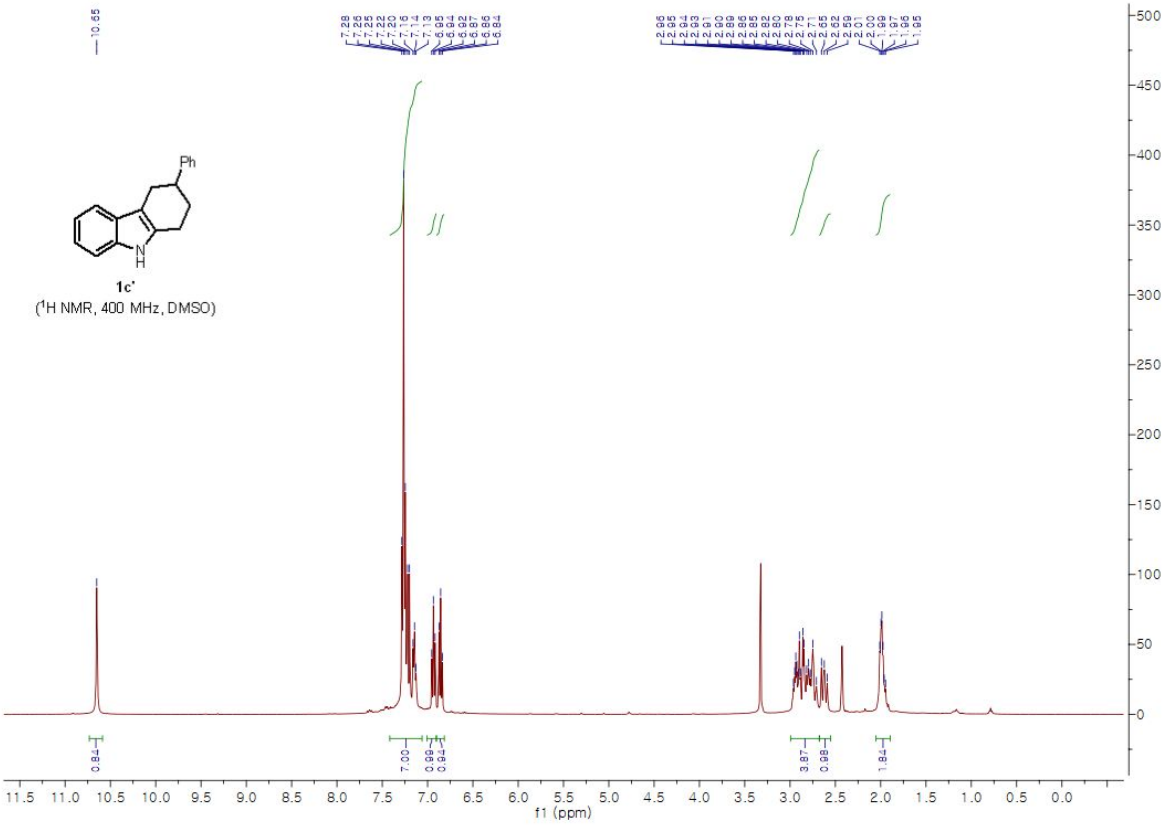


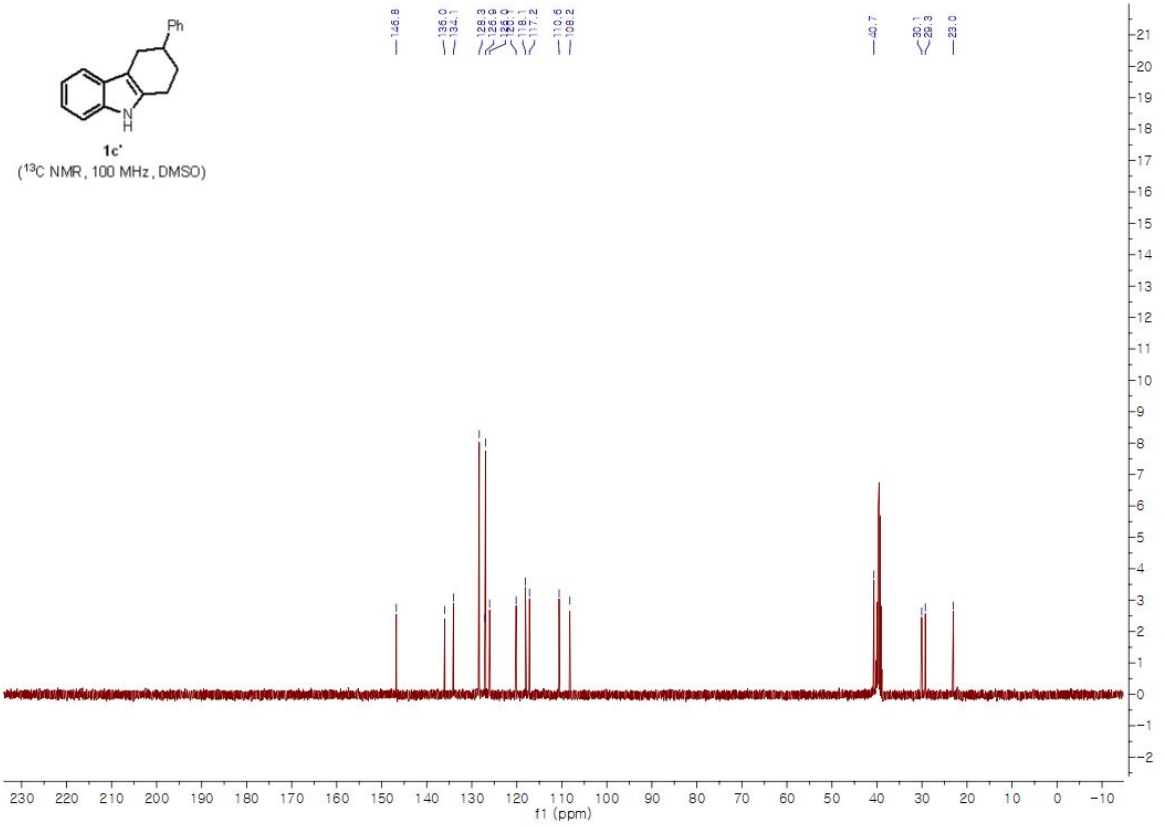
3-ethyl-2-phenyl-*1H*-indole (Scheme 4, **1b'**)



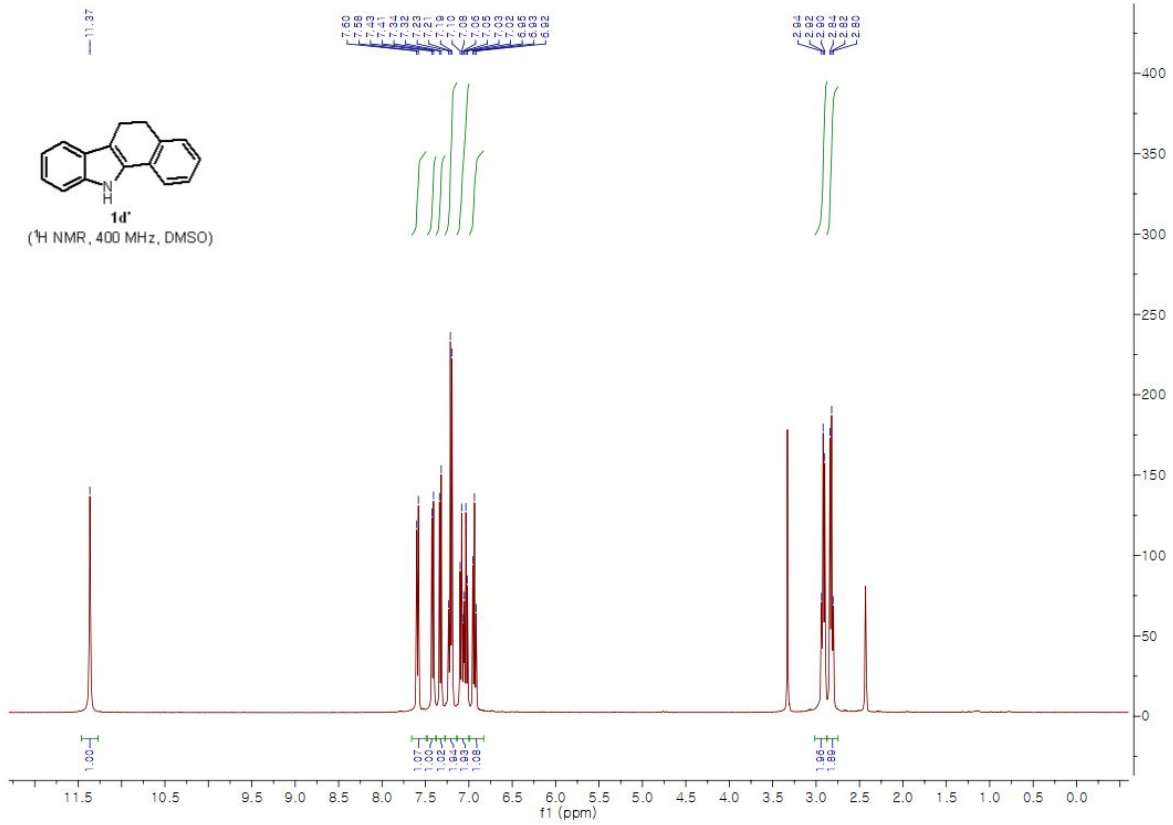


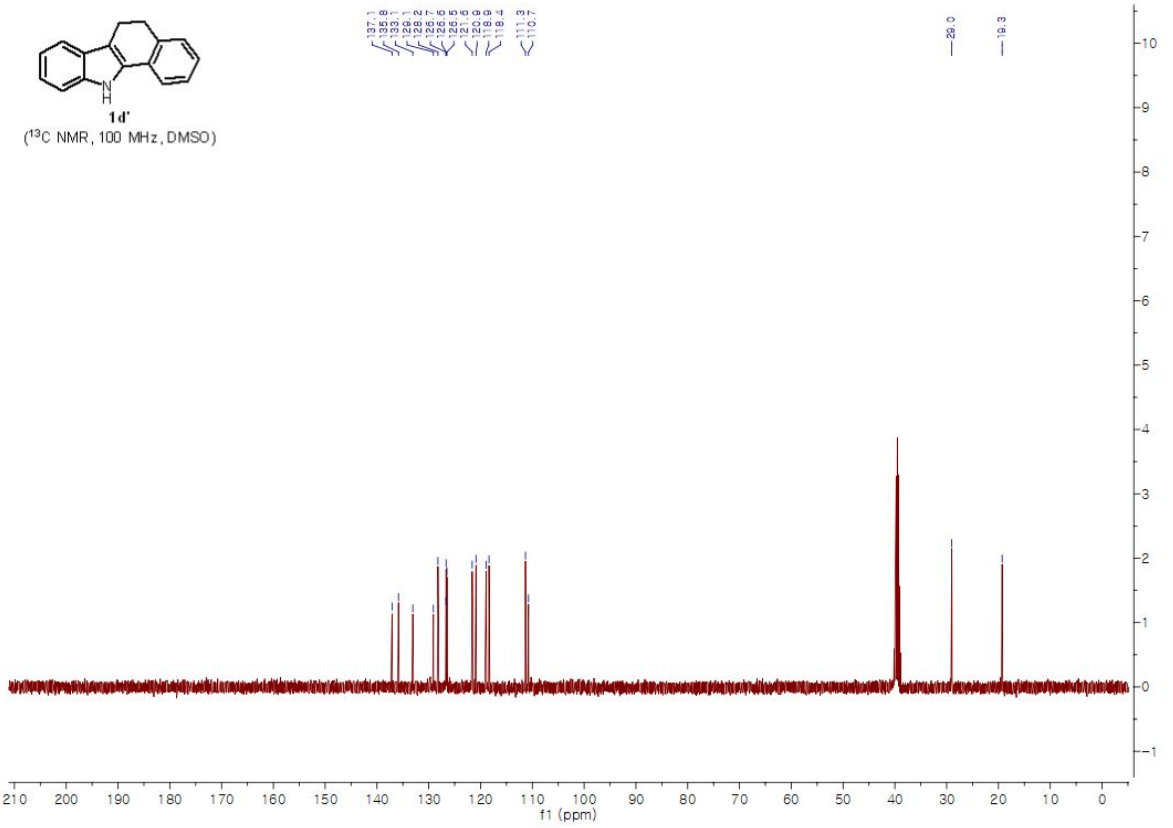
3-phenyl-2,3,4,9-tetrahydro-*1H*-carbazole (Scheme 4, **1c'**)



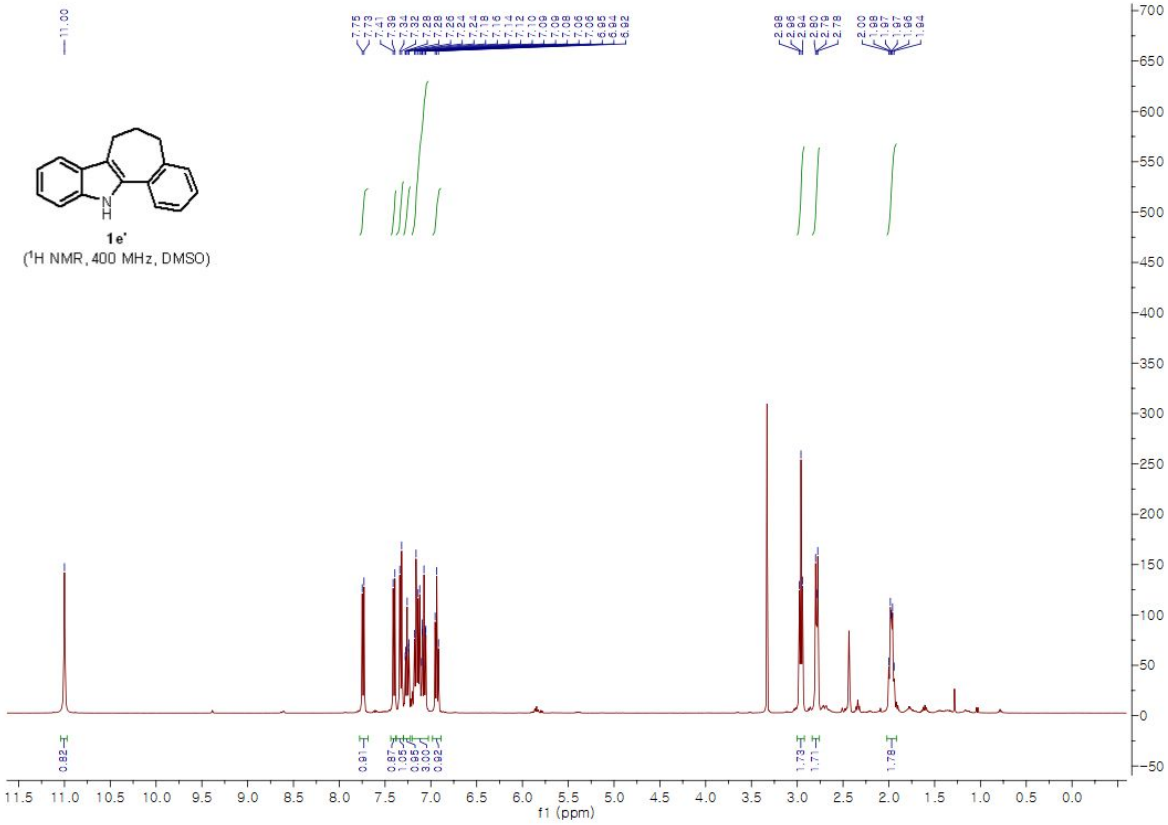


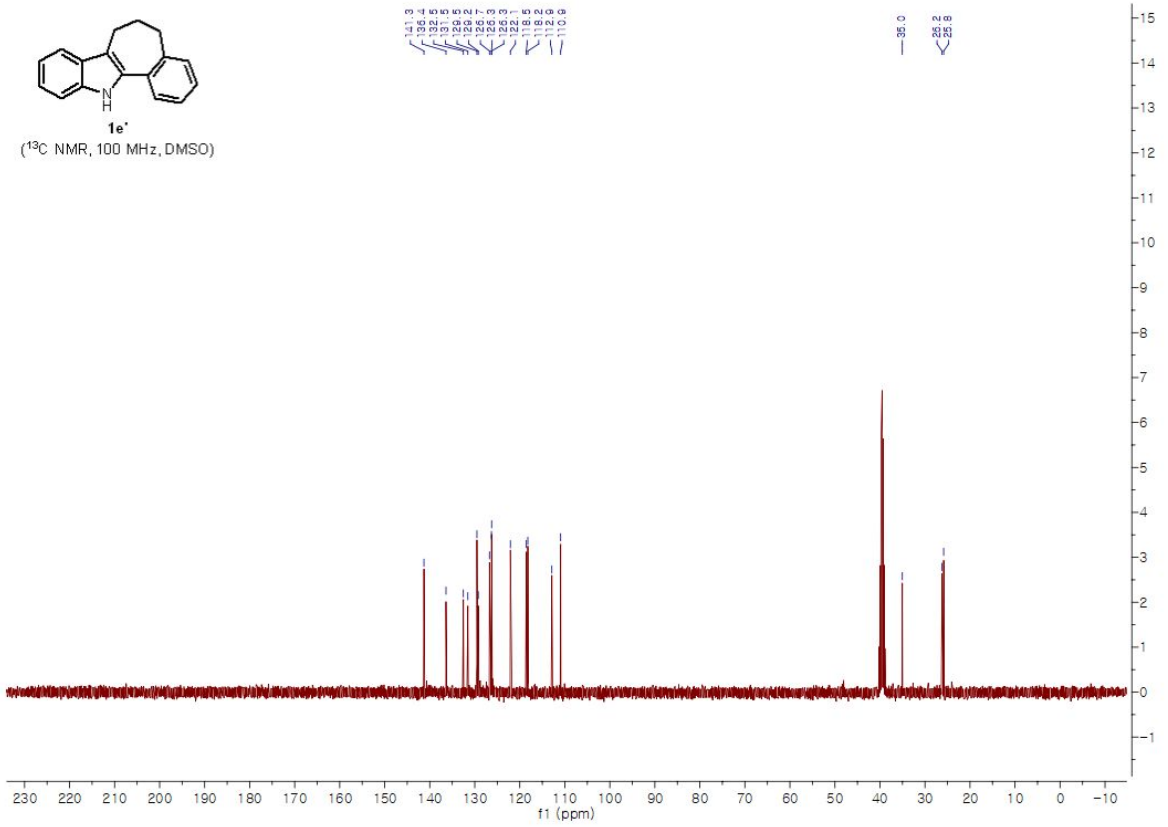
6,11-dihydro-*5H*-benzo[*a*]carbazole (Scheme 4, **1d'**)



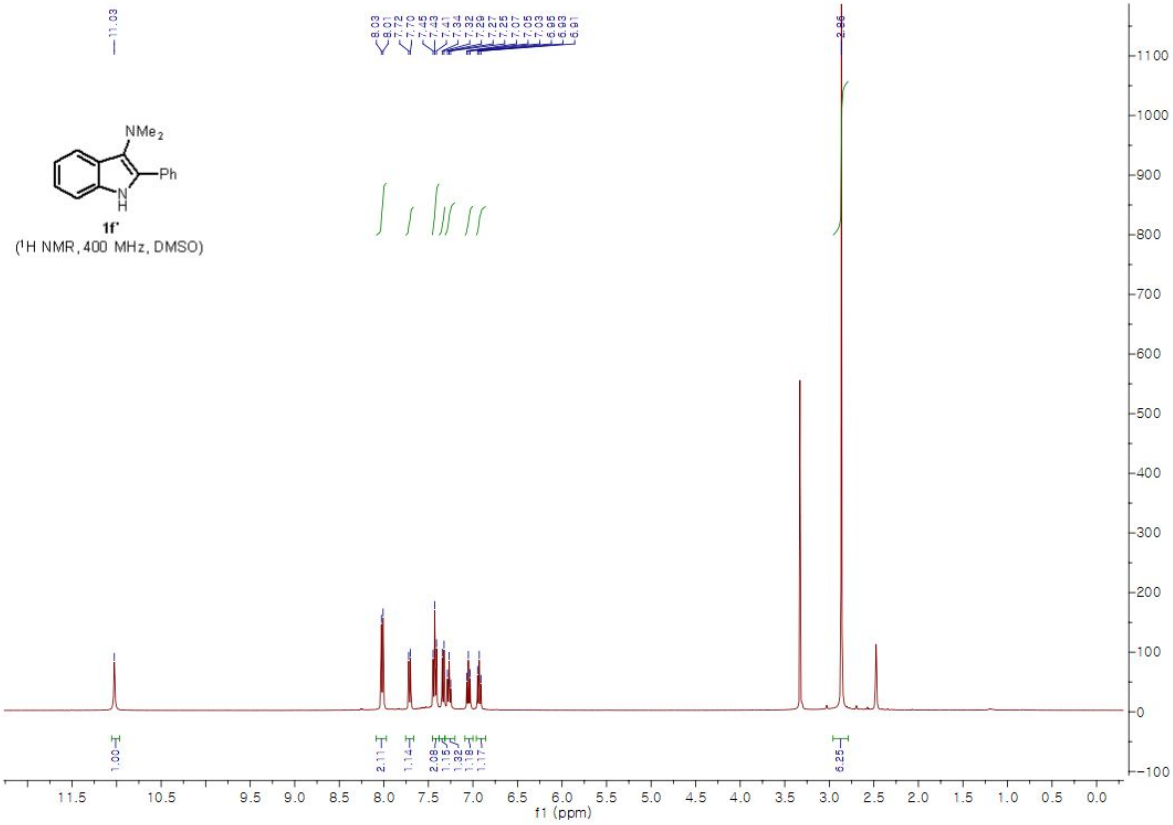


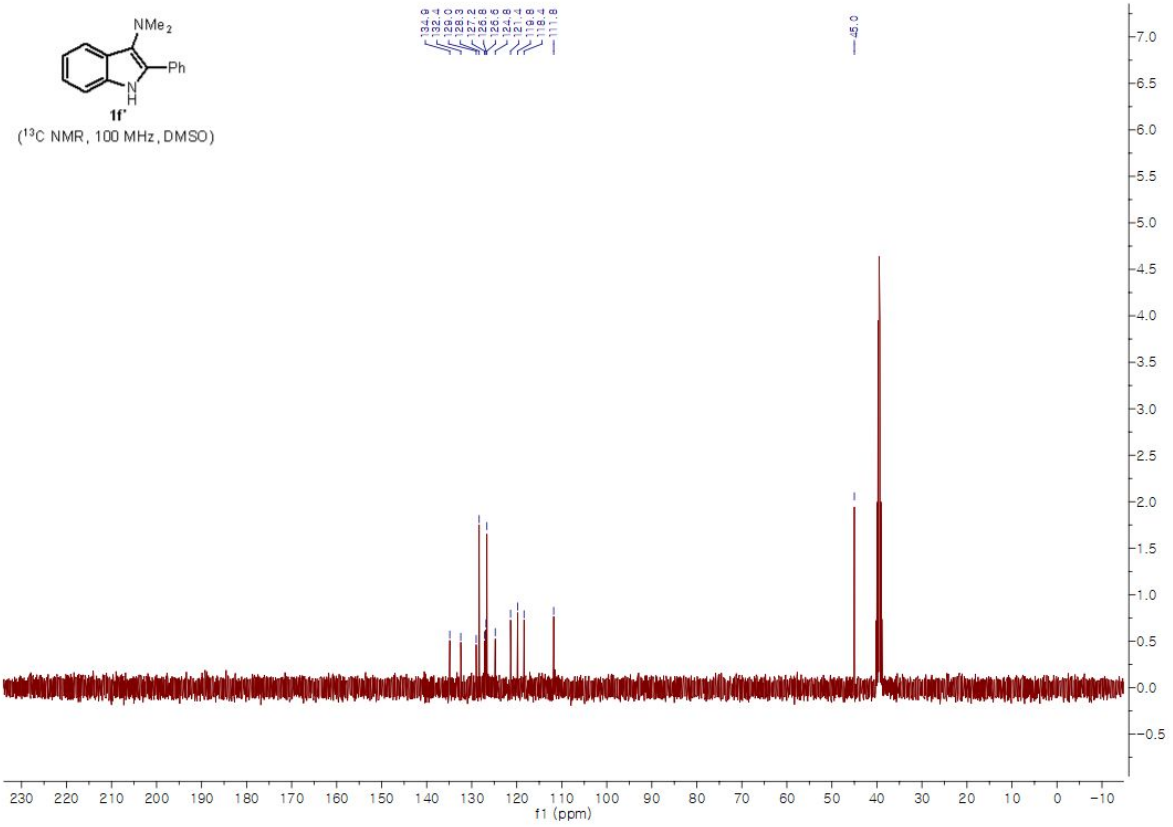
5,6,7,12-tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]indole (Scheme 4, **1e'**)



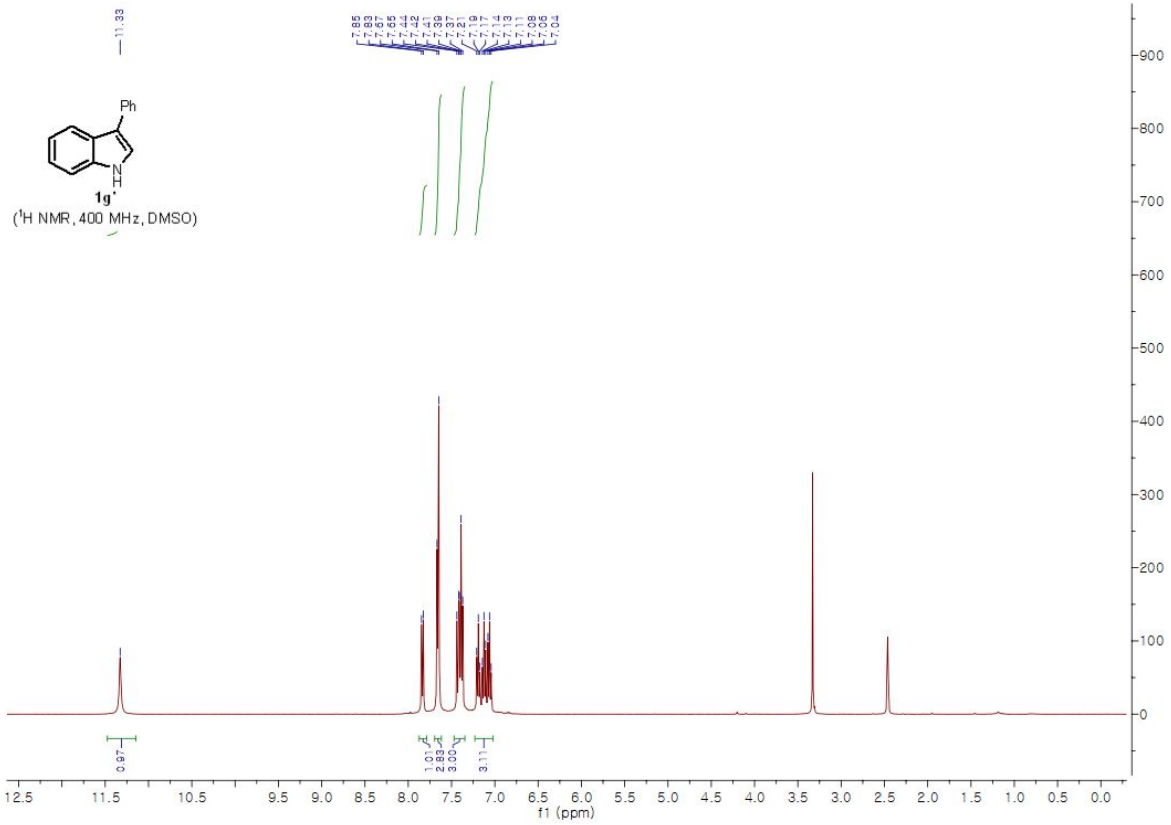


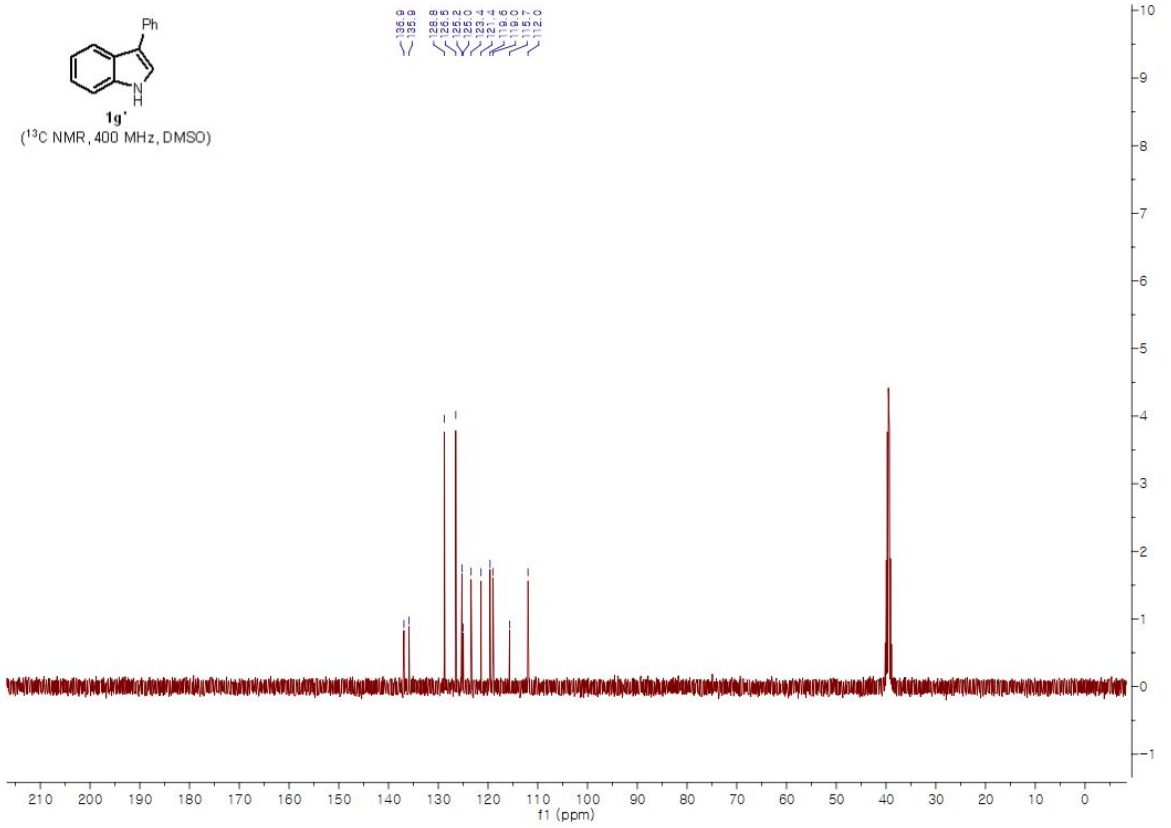
2-methyl-3-phenyl-*1H*-indole (Scheme 4, **1f'**)



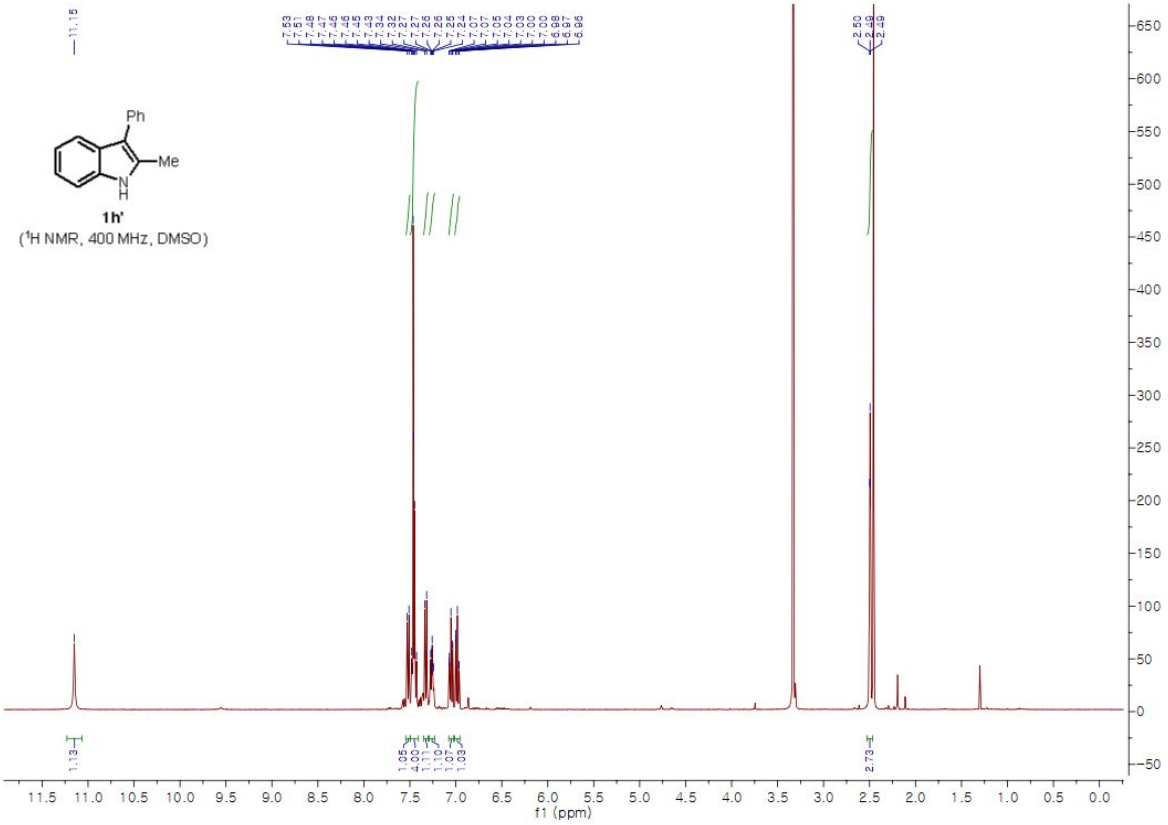


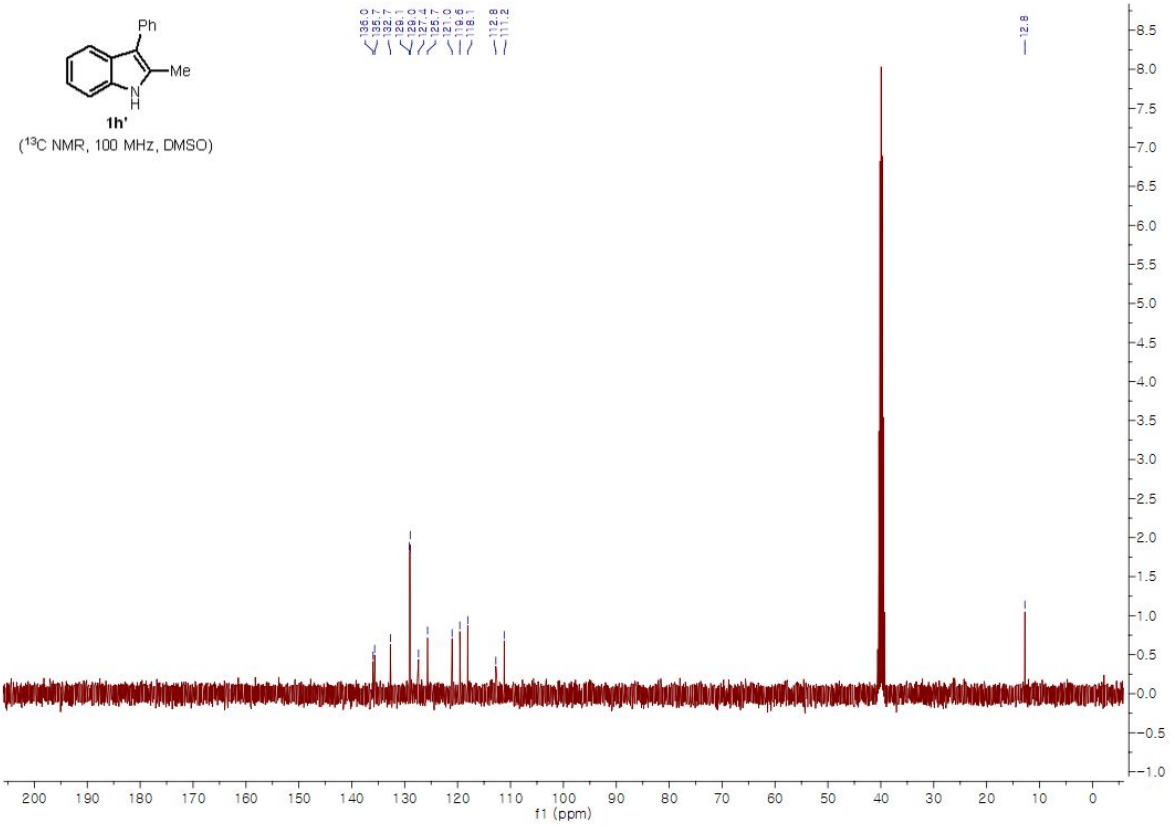
3-phenyl-*1H*-indole (Scheme 5, **1g'**)



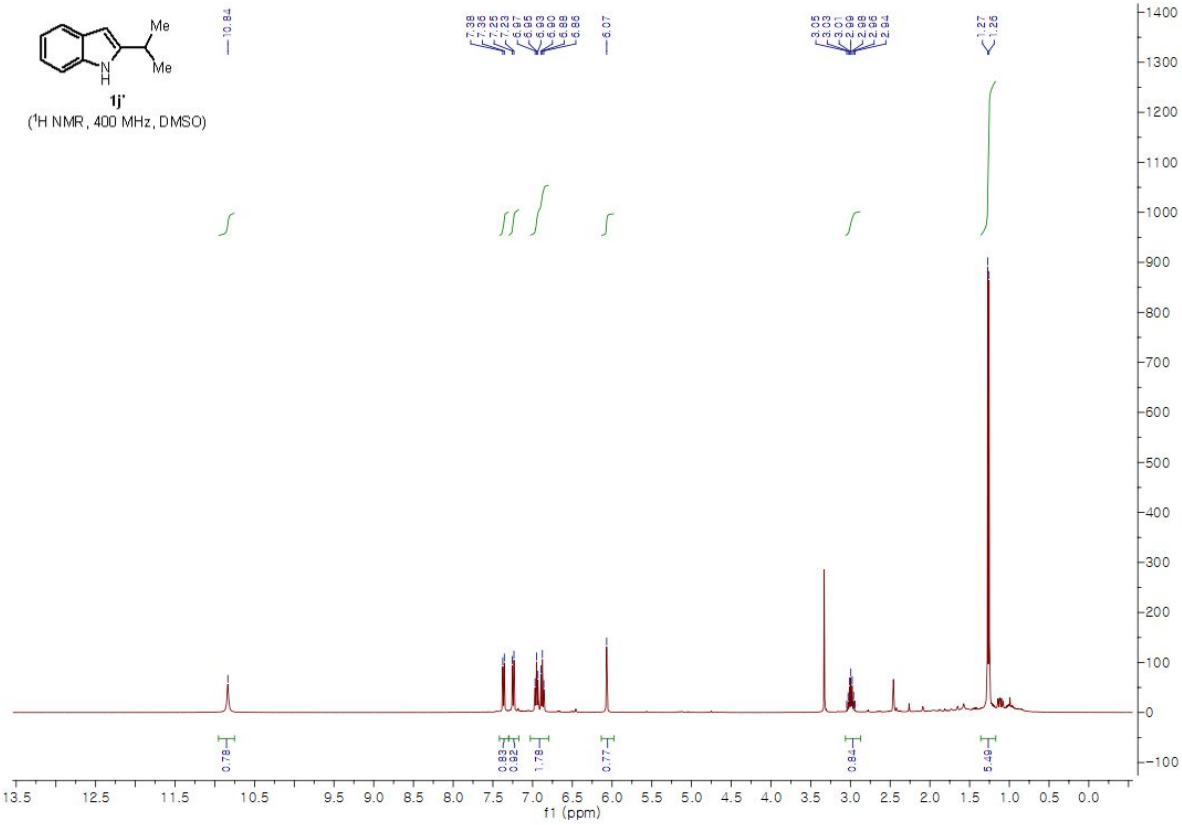


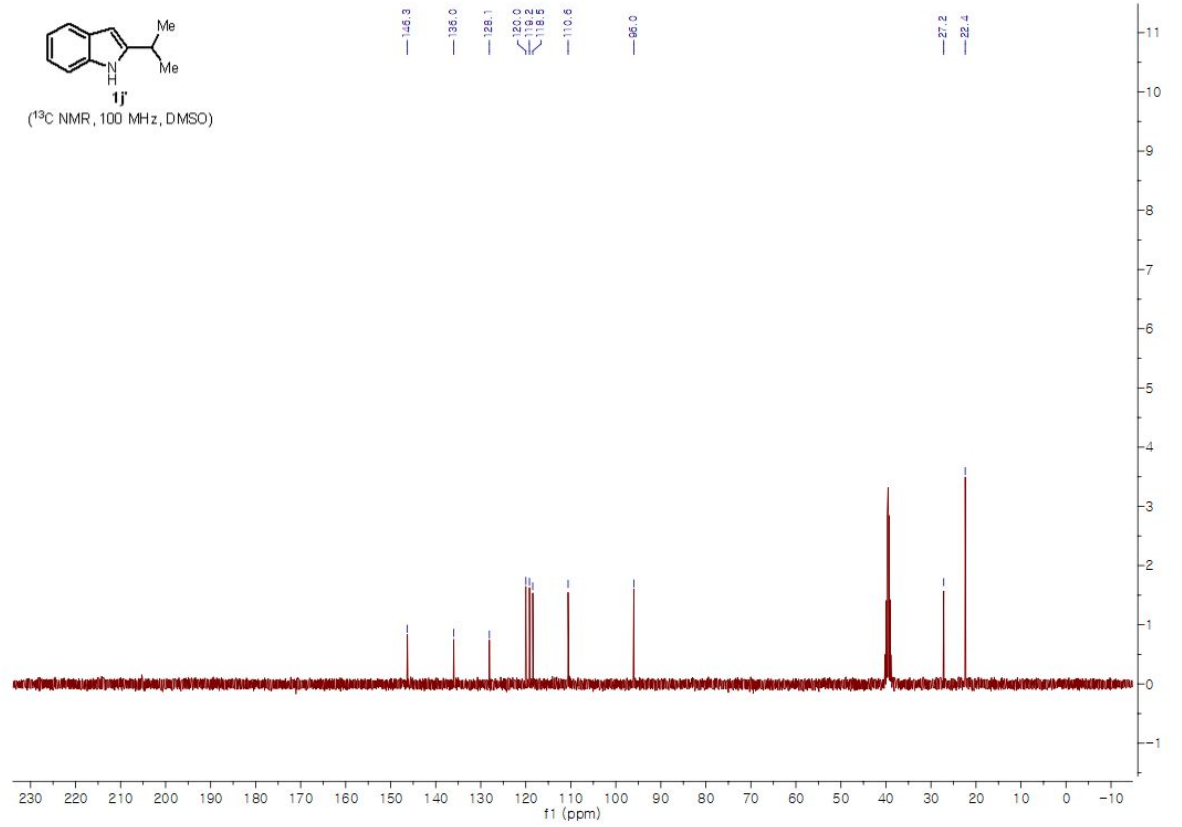
2-methyl-3-phenyl-*1H*-indole (Scheme 5, **1h'**)



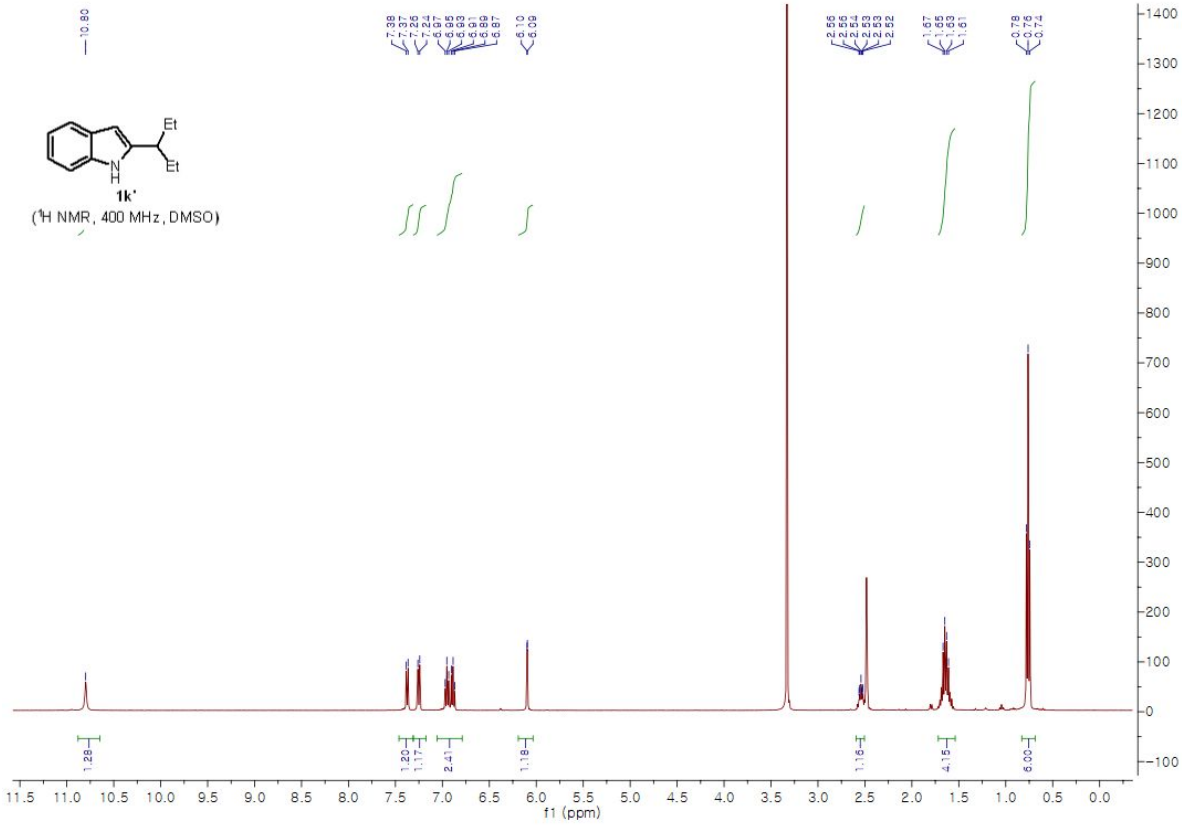


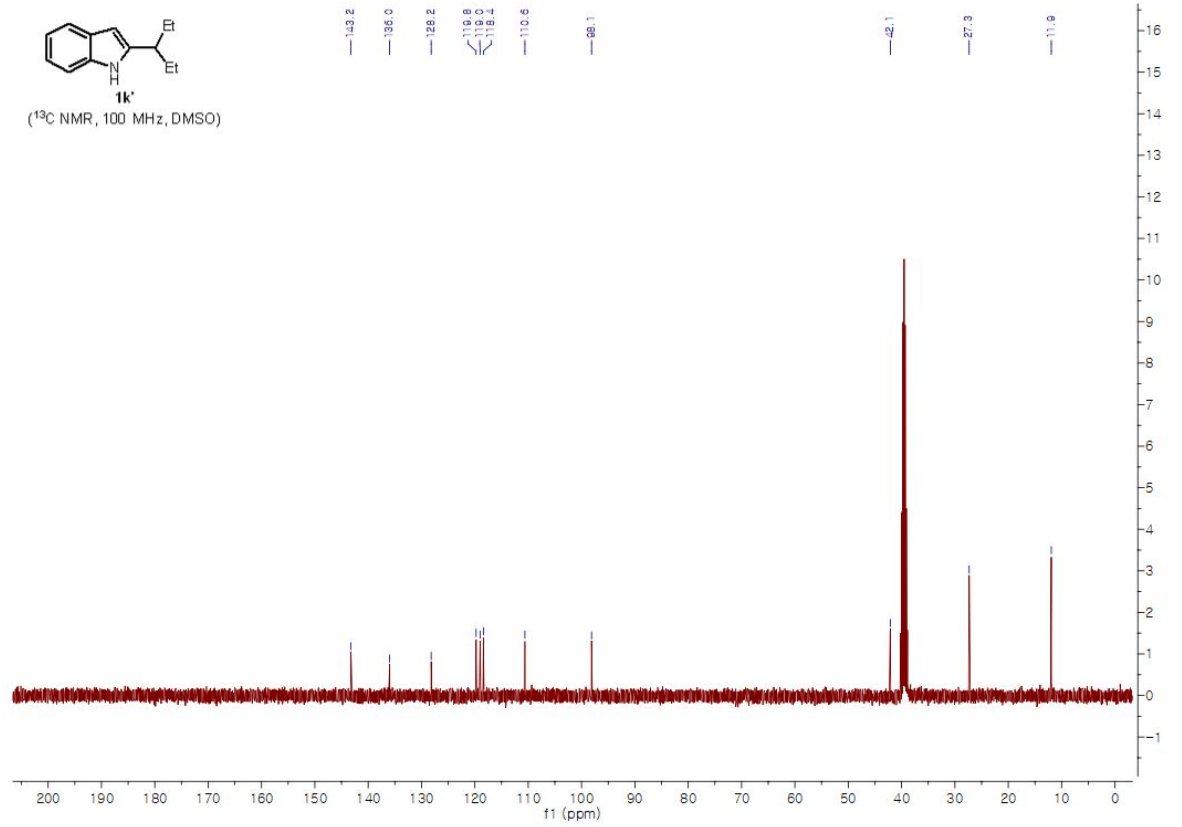
2-isopropyl-*1H*-indole (Scheme 5, **1j'**)



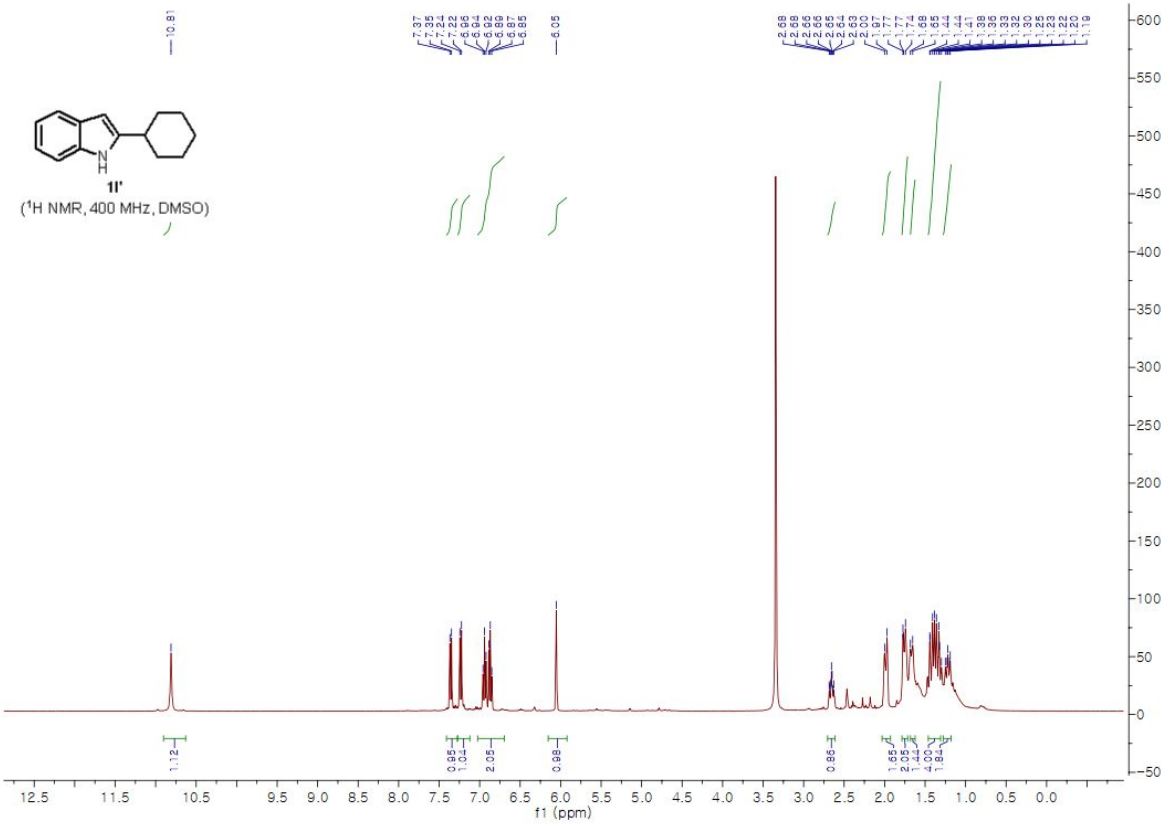


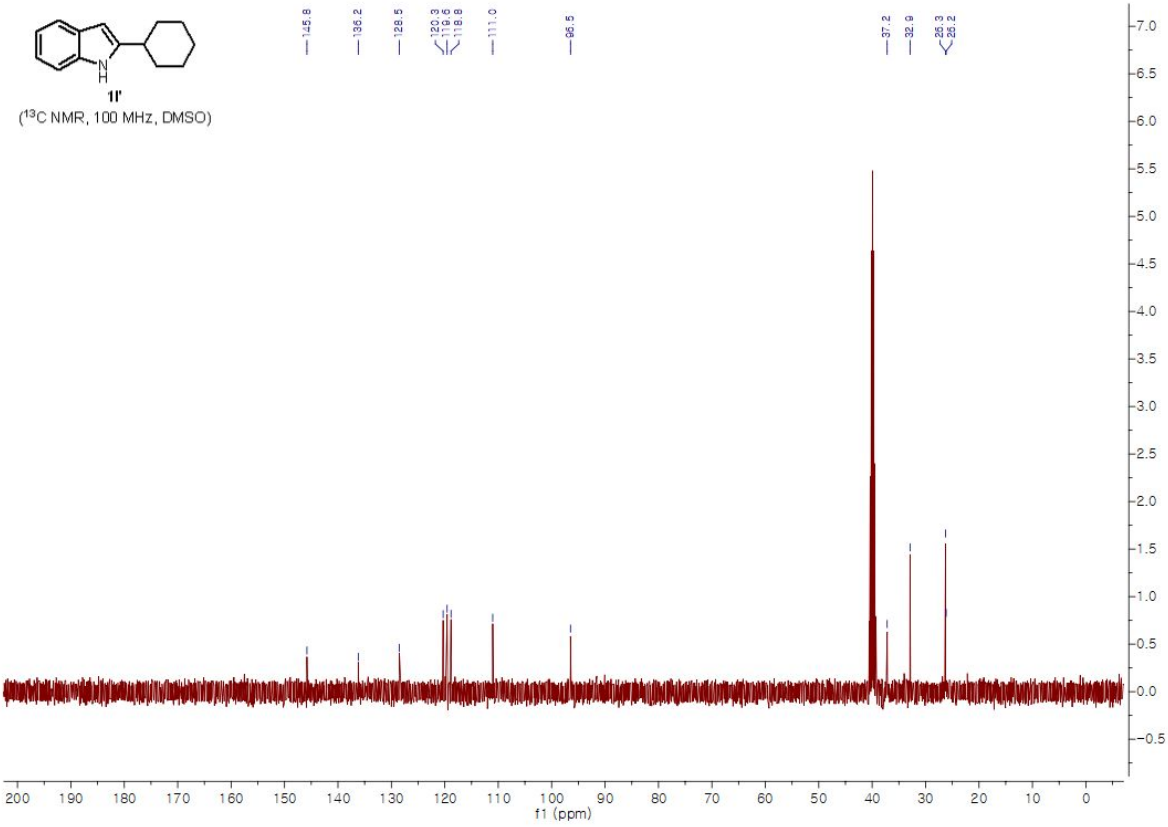
2-(pentan-3-yl)-*1H*-indole (Scheme 5, **1k'**)



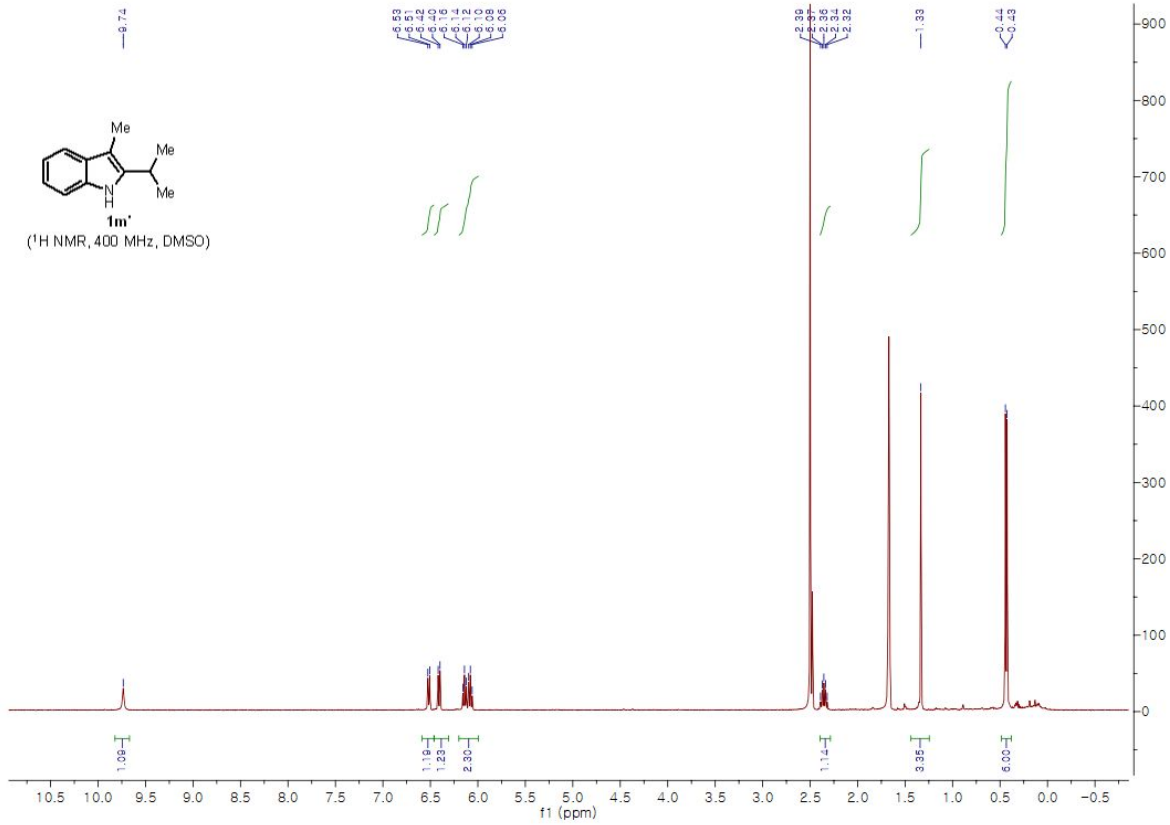


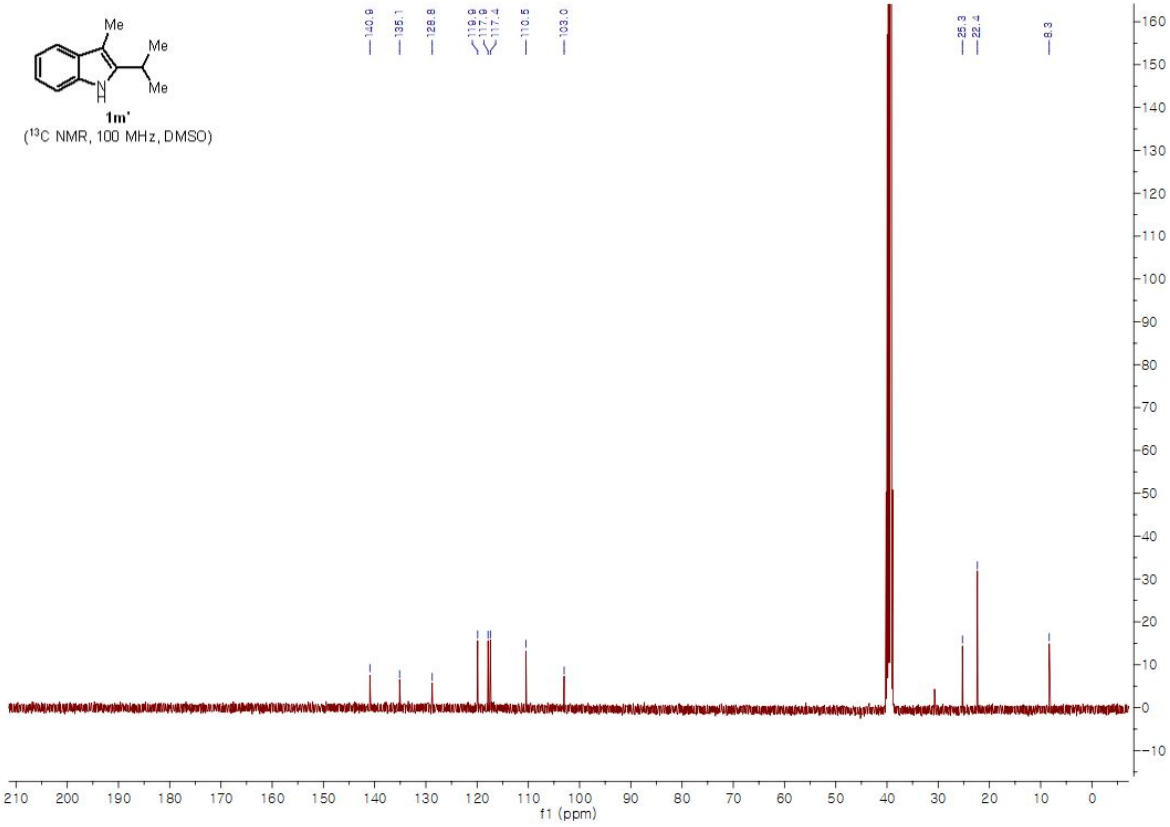
2-cyclohexyl-*1H*-indole (Scheme 5, **1l'**)



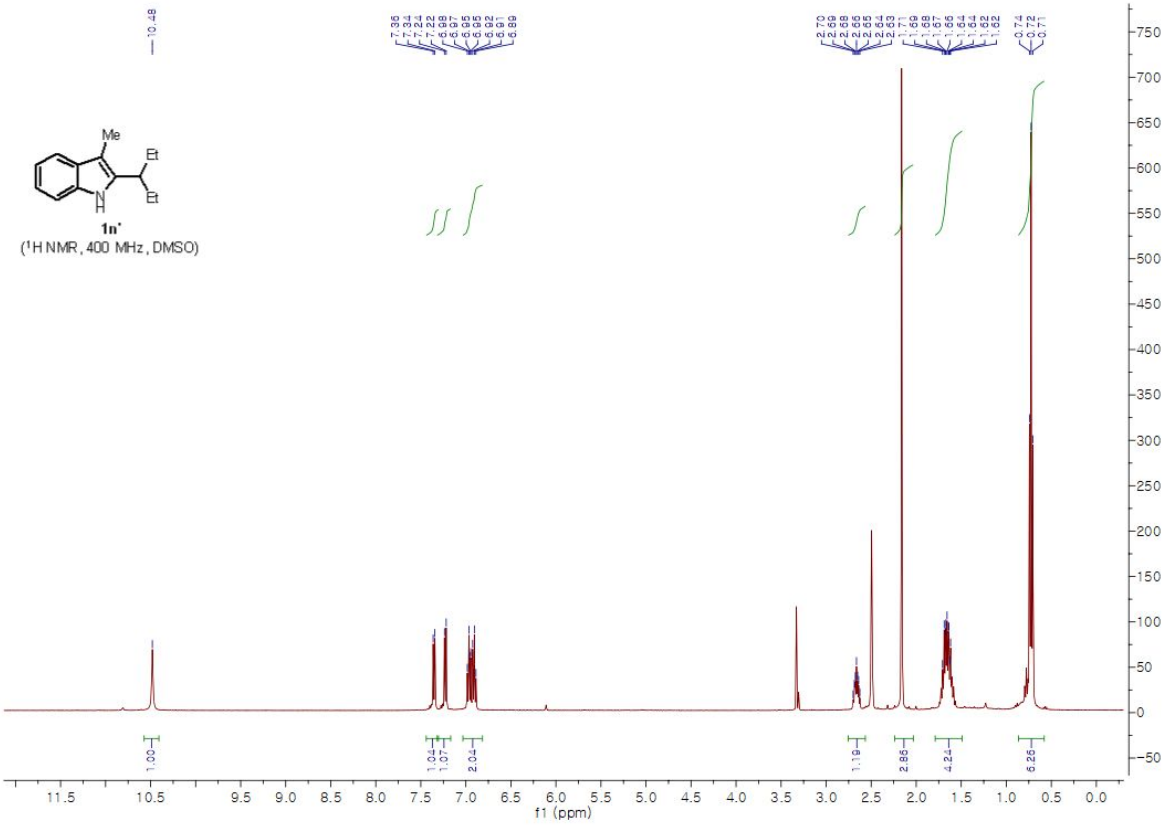


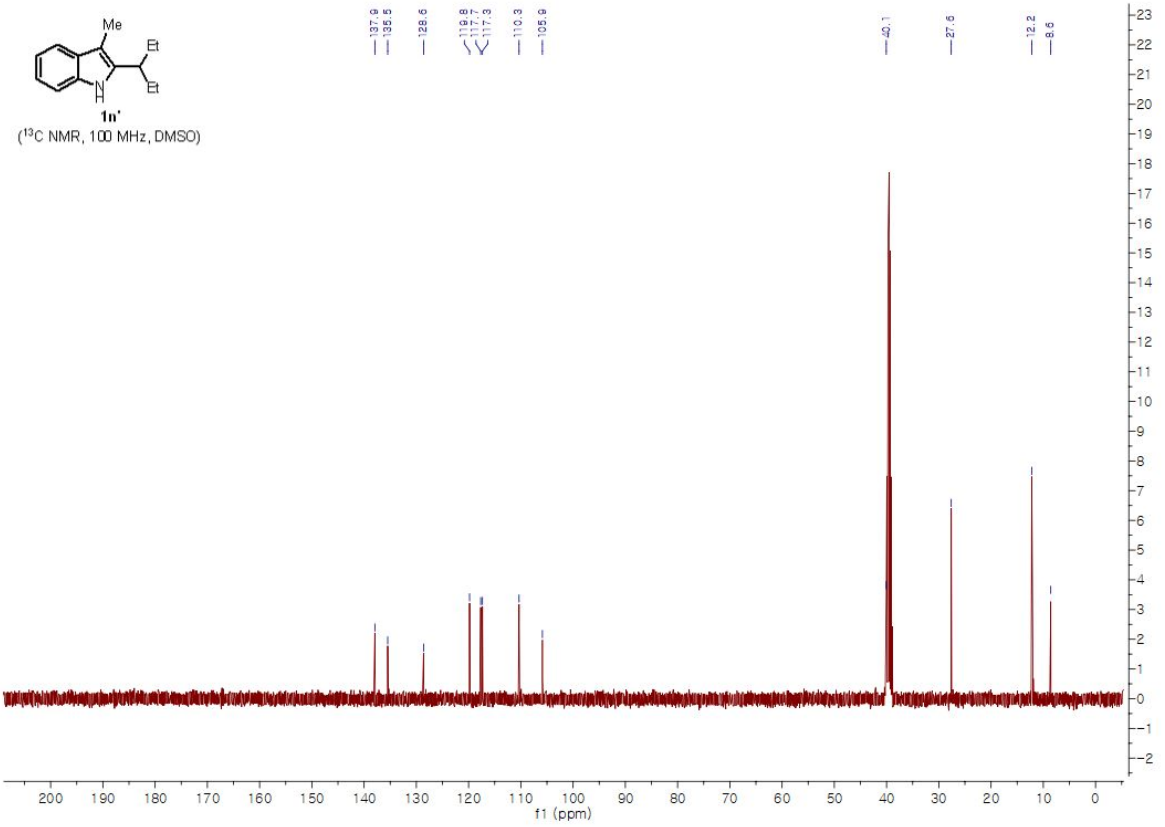
2-isopropyl-*1H*-indole (Scheme 5, **1m'**)

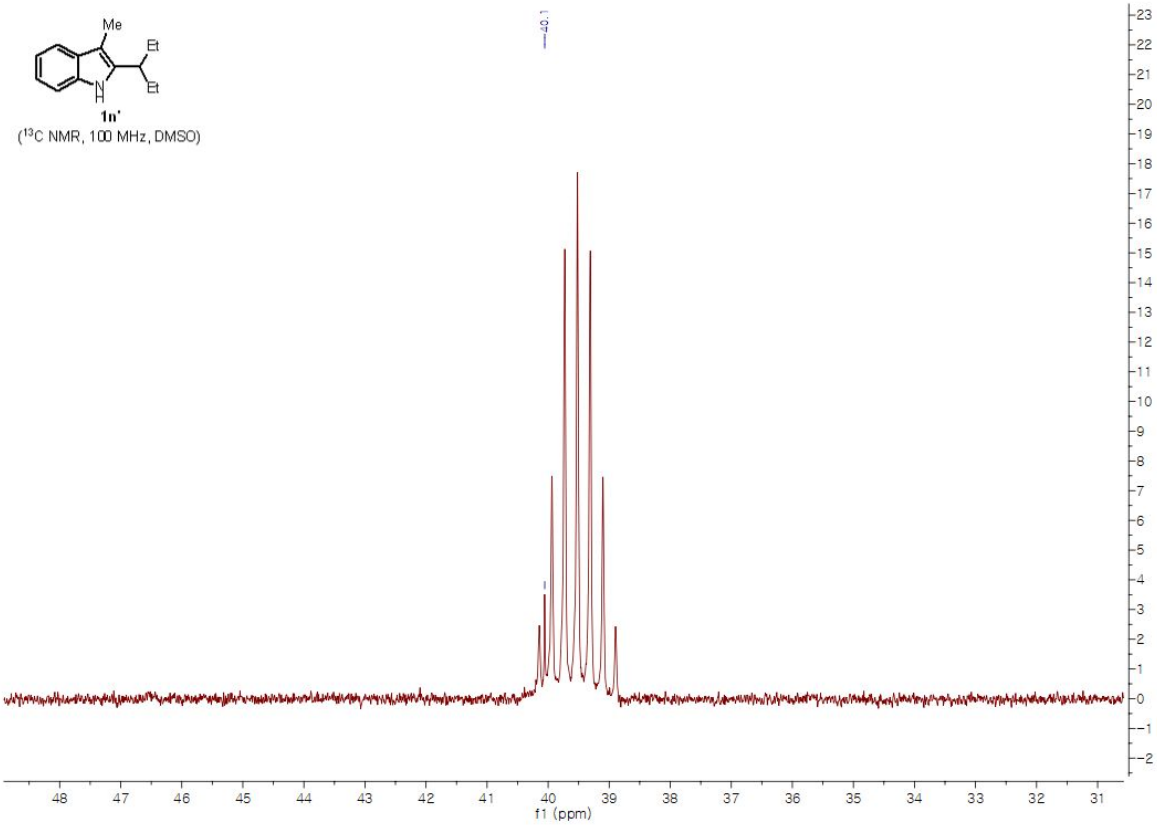




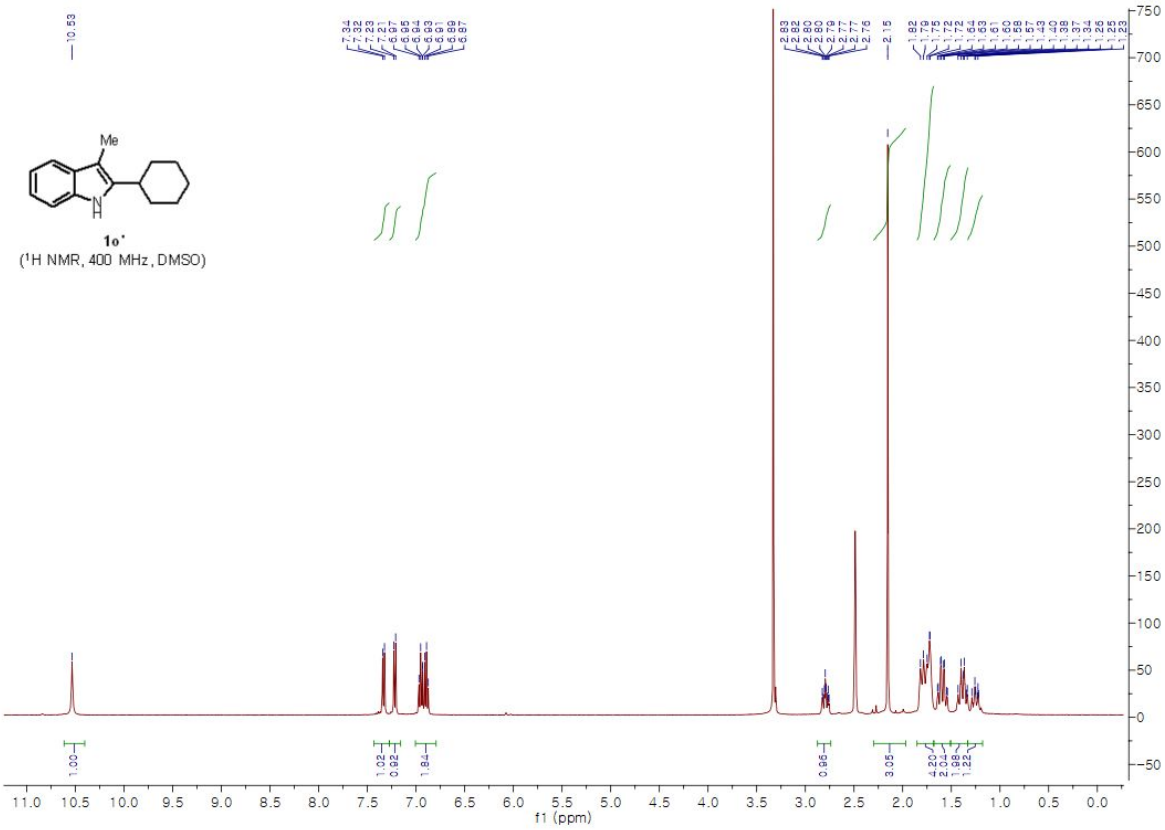
3-methyl-2-(pentan-3-yl)-*1H*-indole (Scheme 5, **1n'**)

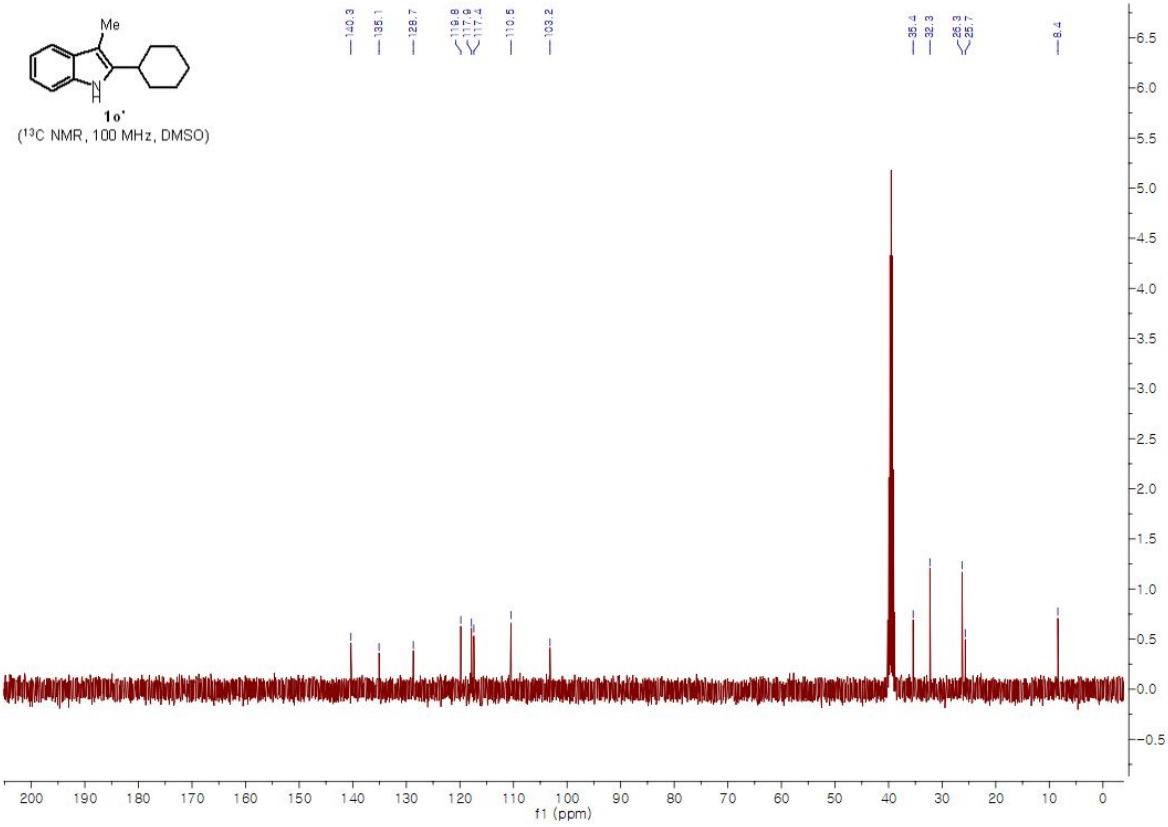




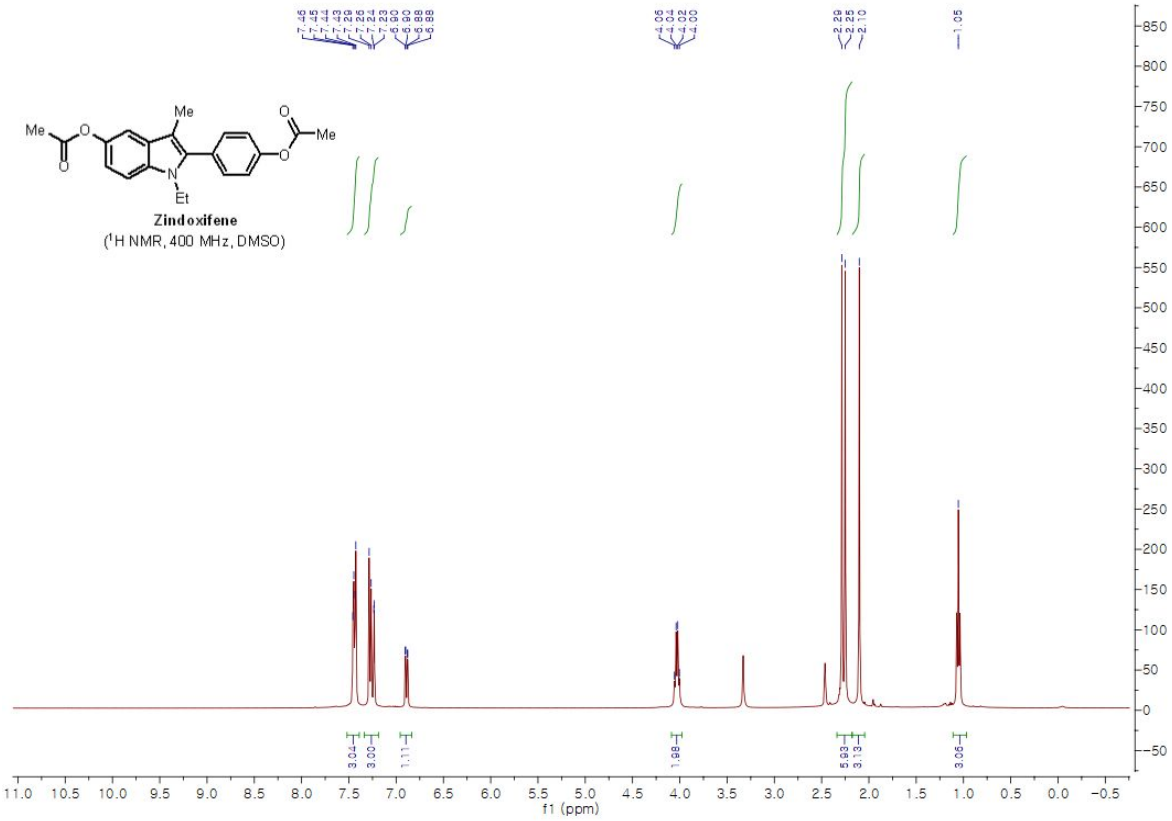

Me
Et
Et
N
H
1n'
(13C NMR, 100 MHz, DMSO)
40.1
f1 (ppm)

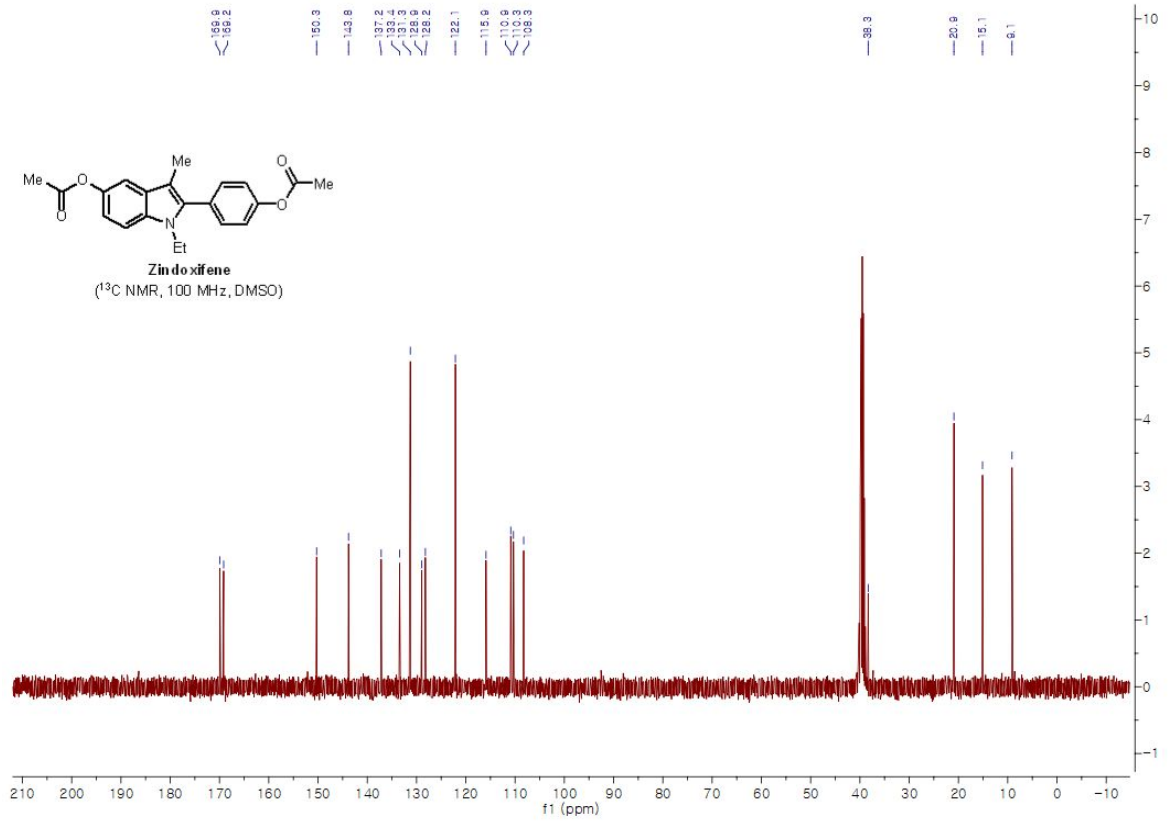
2-cyclohexyl-3-methyl-*1H*-indole (Scheme 5, **1o'**)





Zindoxifene (Scheme 8)





1. Complete authorship of software packages used in this work

Gaussian 16, Revision A.03

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, **2016**.

CYLview

CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

GaussView, Version 6.0.16

Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

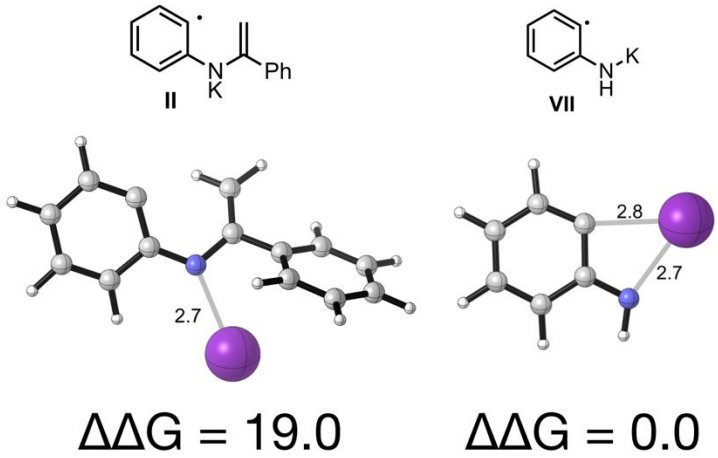
Schrodinger Macromodel

Schrödinger Release 2019-4: MacroModel, Schrödinger, LLC, New York, NY, 2019.

2. General Computational Procedures

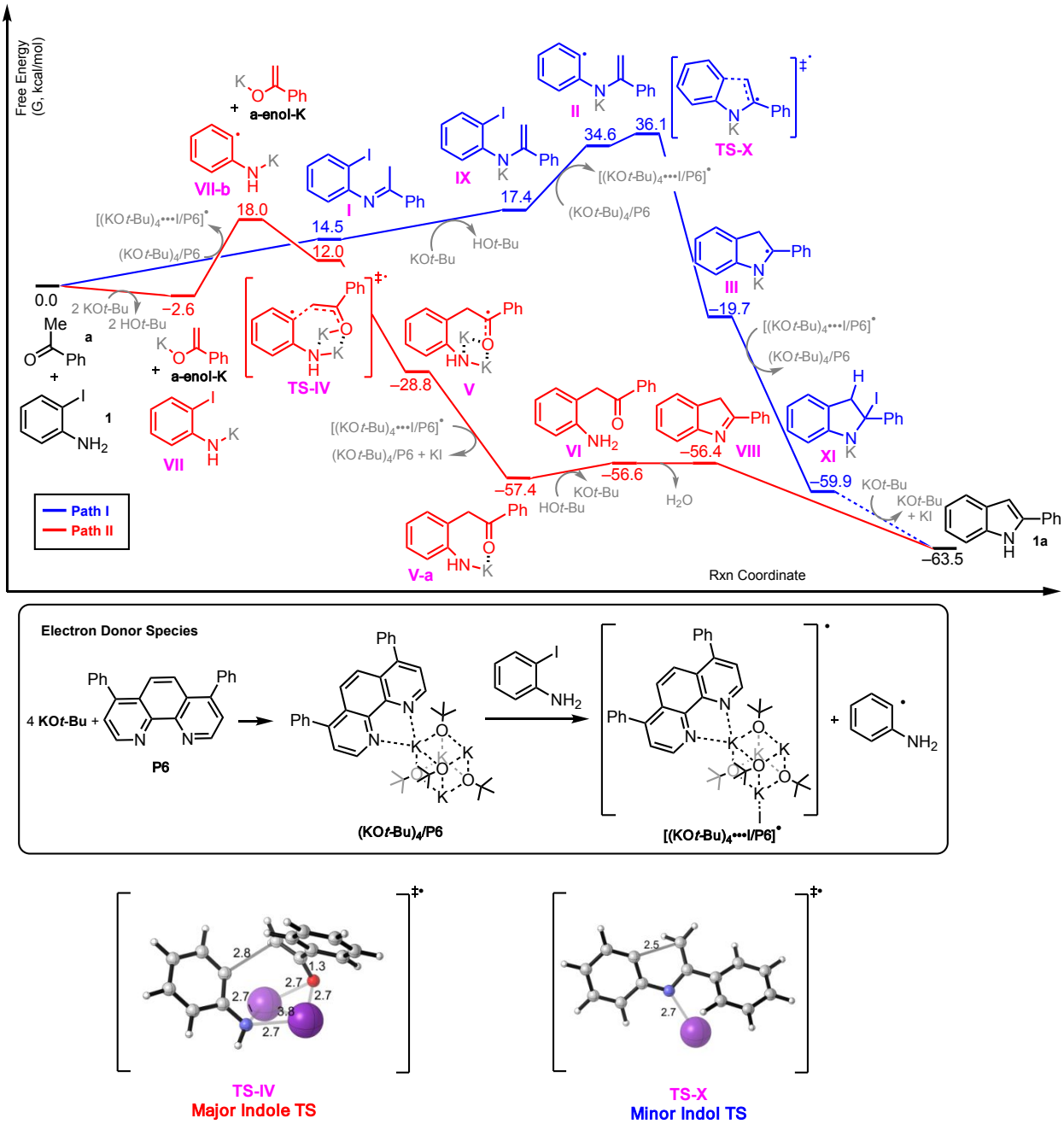
All computations were performed using Density Functional Theory (DFT) using the Gaussian 16 software package (see above reference). All reactants, intermediates, and products were optimized using PBE functional with LANL2DZ basis set for I and 6-31G(d) for all other atoms in DMSO using SMD solvation method. All reported energy values are free energies in kcal/mol, and all distances are in Ångströms (Å). Conformational search was performed using Schrodinger Macromodel software package.

3. Comparison of Radical Stabilities of II (Path I) and VII (Path II)



4. Reaction Coordinate Diagram of the Two Proposed Mechanistic Pathways

Figure S1. Reaction coordinate diagram for the two proposed mechanistic routes of the reaction of 2-iodoaniline (**1**) and acetophenone (**a**) with **(KO*t*-Bu)$_4$/P6** complex, as reported in main manuscript.

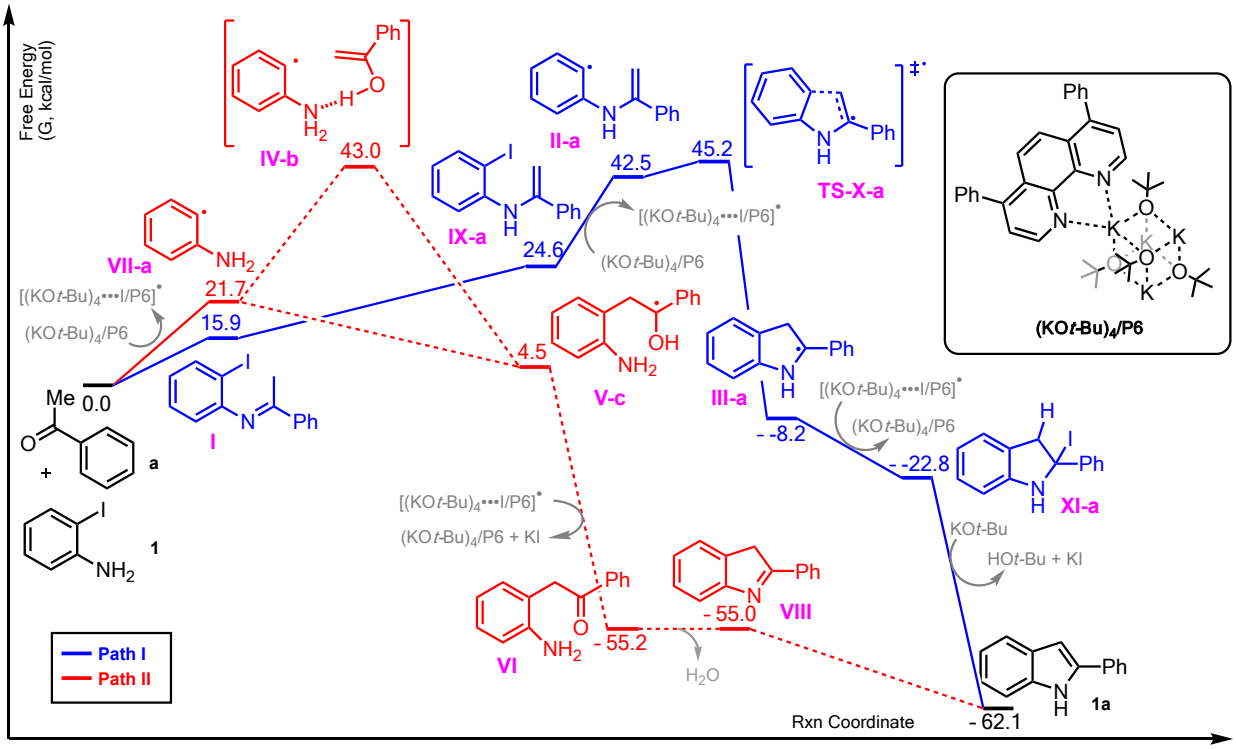


TS-IV
Major Indole TS

TS-X
Minor Indol TS

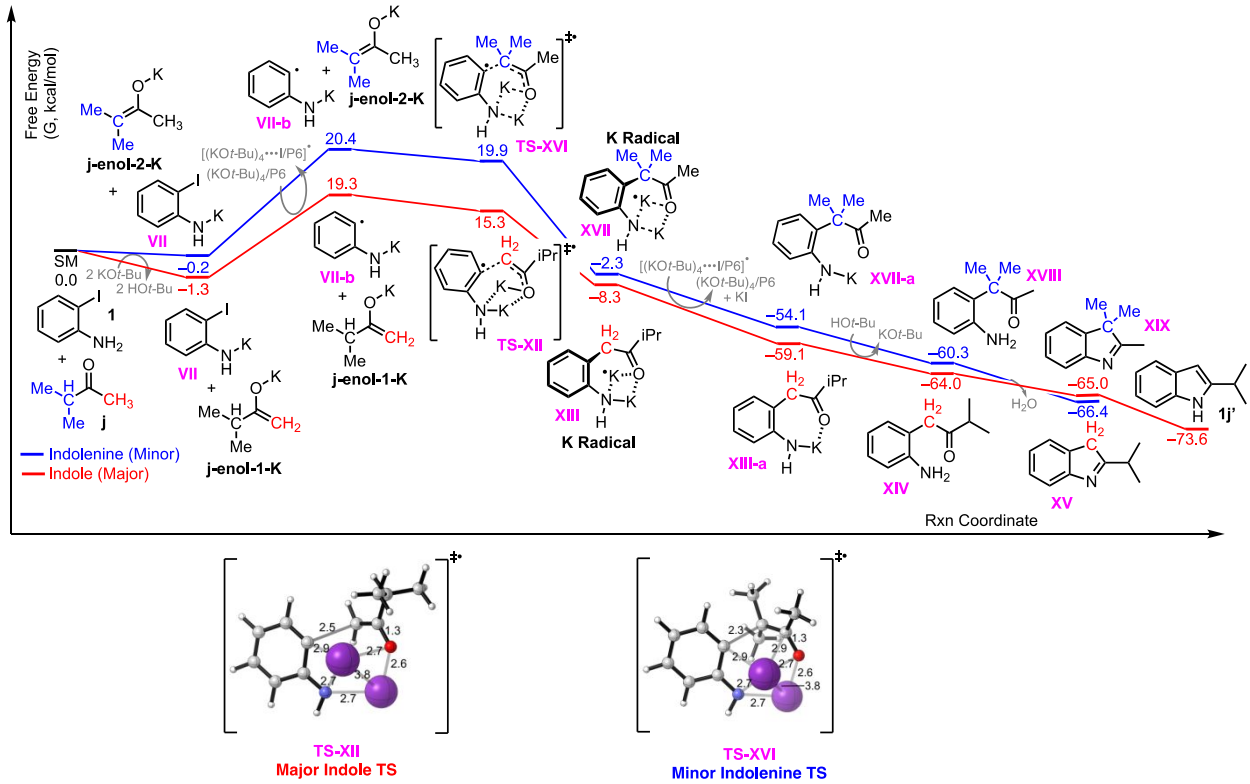
Figure S2. Reaction coordinate diagram for the two proposed mechanistic routes of the reaction of 2-iodoaniline (**1**) and acetophenone (**a**) with **(KO*t*-Bu)$_4$/P6** complex with no deprotonation state of the nitrogen.

–The transition structure of aryl radical adding to enol in path 2 in a 7-endo-trig fashion was not a stationary point on the potential energy surface. Upon incrementally shrinking the C–C bond, the energy lowers monotonically without a barrier and forms the C–C bond. In contrast, there was a transition structure in path 1. We attribute the presence of barrier in path 1 to the structural reorganization necessary to achieve an orbitally poorly aligned 5-endo-trig in path 1. In path 2, the significantly expanded ring size to 7-endo-trig fashion now requires minimal structural reorganization and leads to a barrierless process.

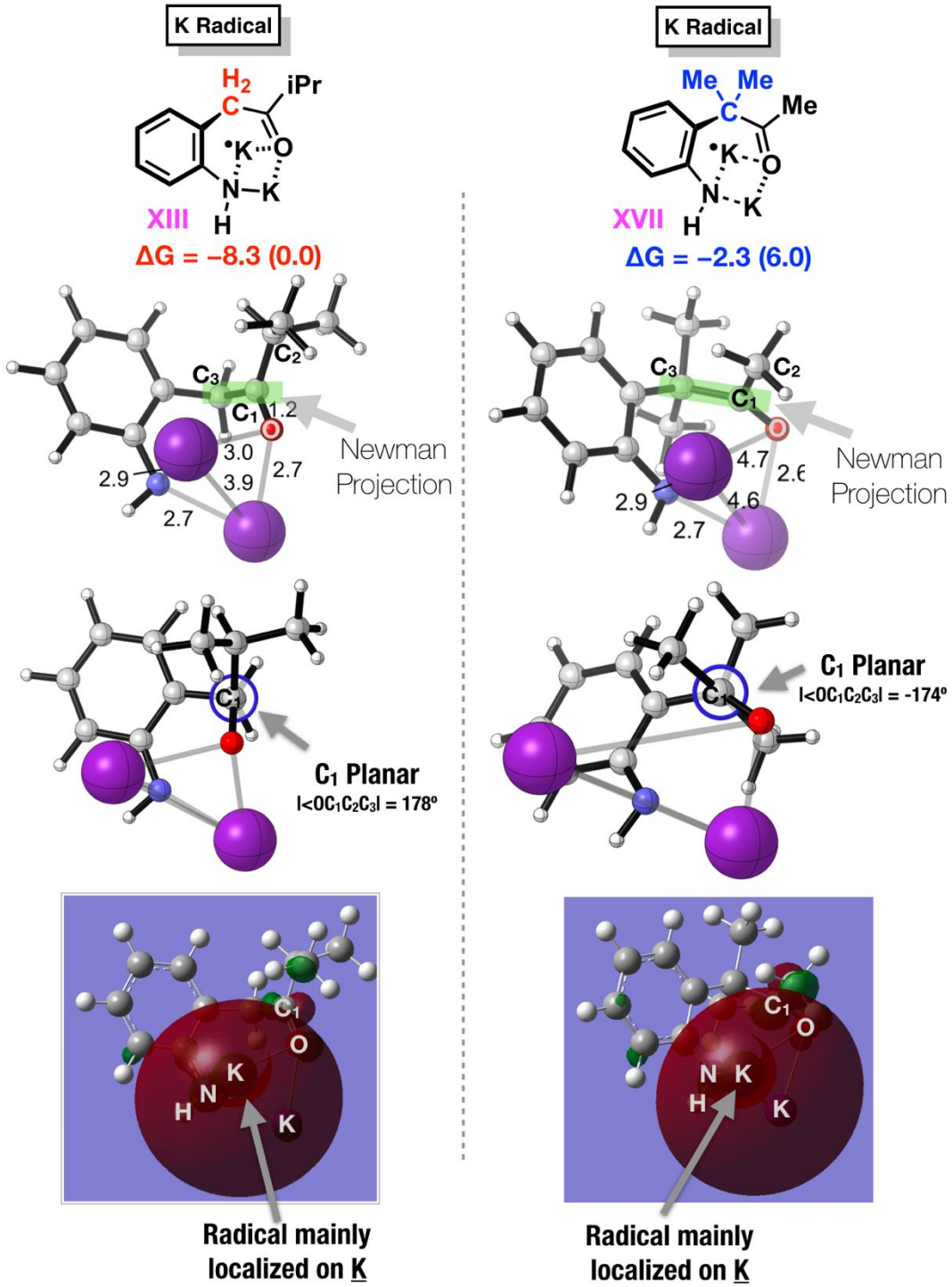


5. Reaction Coordinate Diagram for the Regiocontrolled Formation of Indole Product 1j'

Figure S3. Reaction coordinate diagram for regioselectivity of the reaction of 2-iodoaniline (**1**) and methyl isopropyl ketone (**j**) with **(KO*t*-Bu)$_4$/P6** complex.

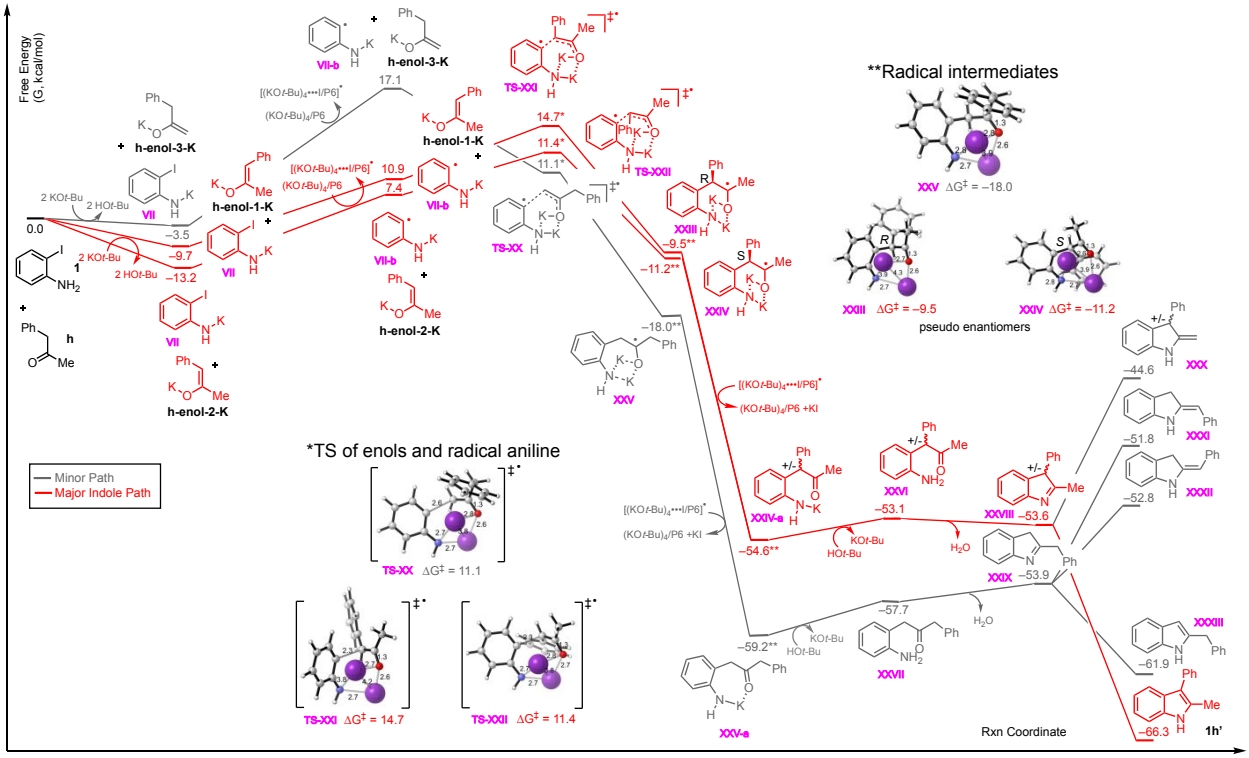


6. Di-Potassium Radical Aniline Enolate Adducts: Molecular Orbitals, Geometries:
–The radicals of **XIII** and **XVII** in the reaction coordinate diagram of Figure S3, following C-C bond formation, are localized on one single potassium atom rather than distributed over two potassium atoms or shared over the C_1, O atoms of the former enol substrate.



7. Reaction Coordinate Diagram for the Regiocontrolled Formation of Indole Product 1h'

Figure S4. Reaction coordinate diagram for regioselectivity of the reaction of 2-iodoaniline (**1**) and benzyl methyl ketone (**h**) with **(KO*t*-Bu)$_4$/P6** complex.

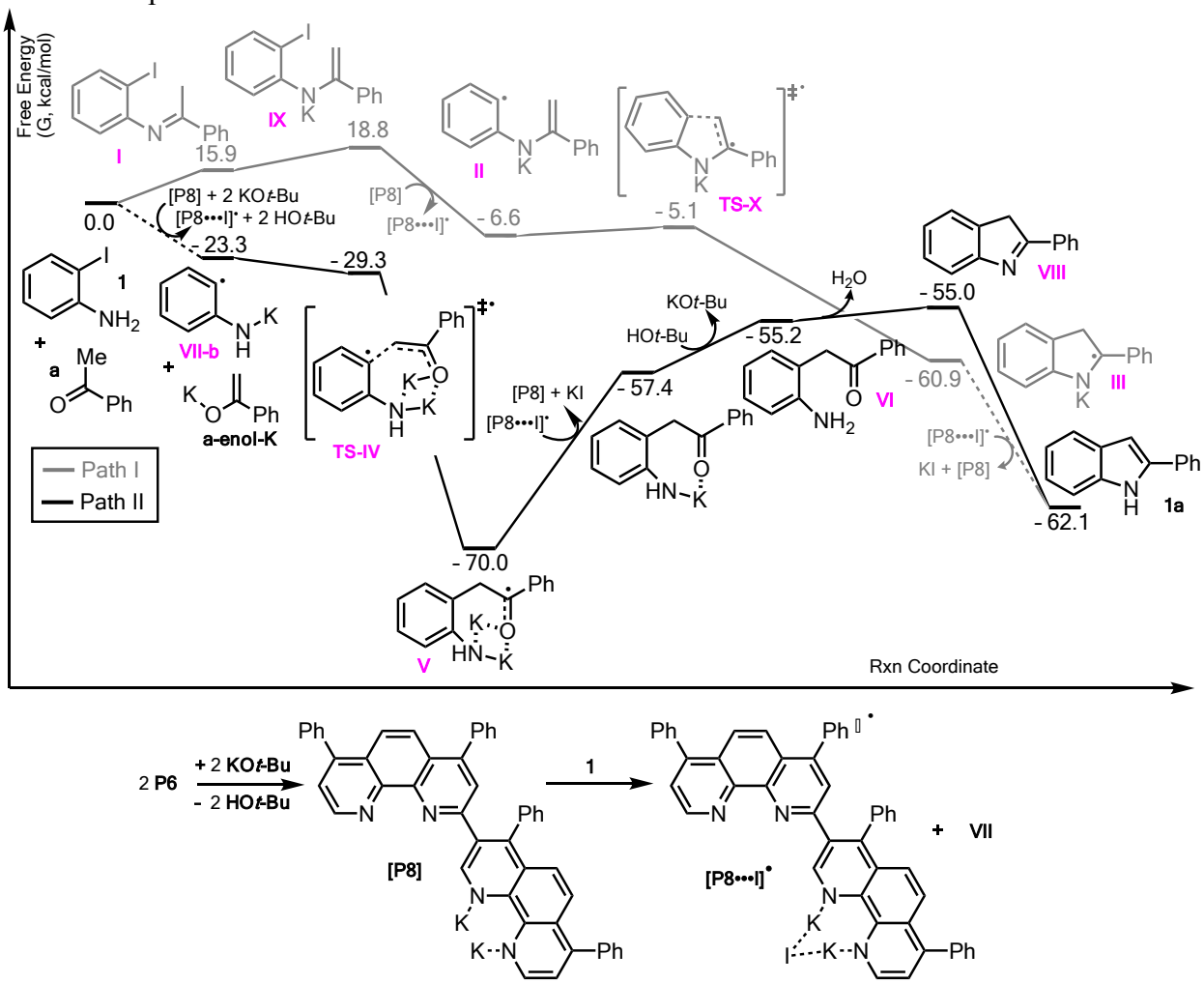


8. Reaction Coordinate Diagrams of the Regioselective Reaction with dimeric Bathophenanthroline and KO*t*Bu complex

–There were literature reports of SET processes mediated by bathophenanthroline dimer and KO*t*Bu complex **P8**.[S1-S4] There are no immediate experimental evidence to suggest that such a complex exists in our reaction. Considering the relative concentrations of KO*t*-Bu, bathophenanthroline **P6** and the energetics of their complexes, it is very likely that most of the bathophenanthroline **P6** are probably sequestered in complexes with KO*t*-Bu.

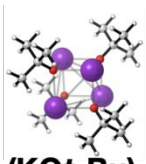
–We nevertheless computed the process as mediated by complex **P8** (shown in Figure S5). The results show that none of the general conclusions reported in the main text change. For an example, the preferred mechanism of the title reaction is still Path 2.

Figure S5. Reaction coordinate diagram for the two proposed mechanistic routes of the reaction of 2-iodoaniline (**1**) and acetophenone (**a**) with bathophenanthroline dimer and KO*t*Bu complex **P8**.

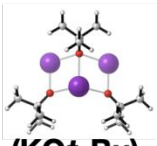


9. Dissociation of Tetramer KO*t*-Bu to Trimer, Dimer, and Monomer

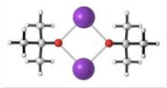
The dissociation of **(KO*t*-Bu)$_4$** was computed by different DFT and solvation methods. We were able to reproduce the DFT results reported by Liu using the method reported in their work (method 1).[S5] Using Gaussian 16 and PBE structures, we obtained results comparable to the Gaussian 09 method used by Liu (method 2). We then changed the solvent to DMSO to match the experimental conditions of this work (method 3). The thermodynamics of the reactions were surprisingly different than in THF (methods 1 and 2). We also realized that M06-2X single points were not necessary to achieve similar results (method 4, highlighted in blue), and this is the DFT method used in the main manuscript and further computations herein.



(KO*t*-Bu)$_4$



(KO*t*-Bu)$_3$



(KO*t*-Bu)$_2$

KO*t*-Bu

(KO*t*-Bu)$_4$	⟶	2 (KO*t*-Bu)$_2$ ⟶ 4 KO*t*-Bu	Eq. 0
(KO*t*-Bu)$_4$	⟶	(KO*t*-Bu)$_3$ + KO*t*-Bu	Eq. 1
(KO*t*-Bu)$_4$	⟶	(KO*t*-Bu)$_3$K$^{\oplus}$ + *t*-BuO$^{\ominus}$	Eq. 2
(KO*t*-Bu)$_4$	⟶	(KO*t*-Bu)$_3$ + K$^{\oplus}$ + *t*-BuO$^{\ominus}$	Eq. 3

	Method	Eq.0	Eq.1	Eq.2	Eq. 3
1	G09: M06-2X/6-311+G(d,p)-CPCM(THF)//B3LYP/6-31G(d)	36.5	15.3	25.9	36.0
2	G16: M06-2X/6-311+G(d,p)-CPCM(THF)//PBE/6-31G(d)-SMD(THF)	26.7	16.8	28.5	38.7
3	G16: M06-2X/6-311+G(d,p)-SMD(DMSO)//PBE/6-31G(d)-SMD(DMSO)	102.9	44.9	38.2	67.4
4	G16: PBE/6-31G(d)-SMD(DMSO)	75.6	35.6	42.2	65.3

10. SET by Tetramer KO*t*-Bu and Monomer KO*t*-Bu with Promoter

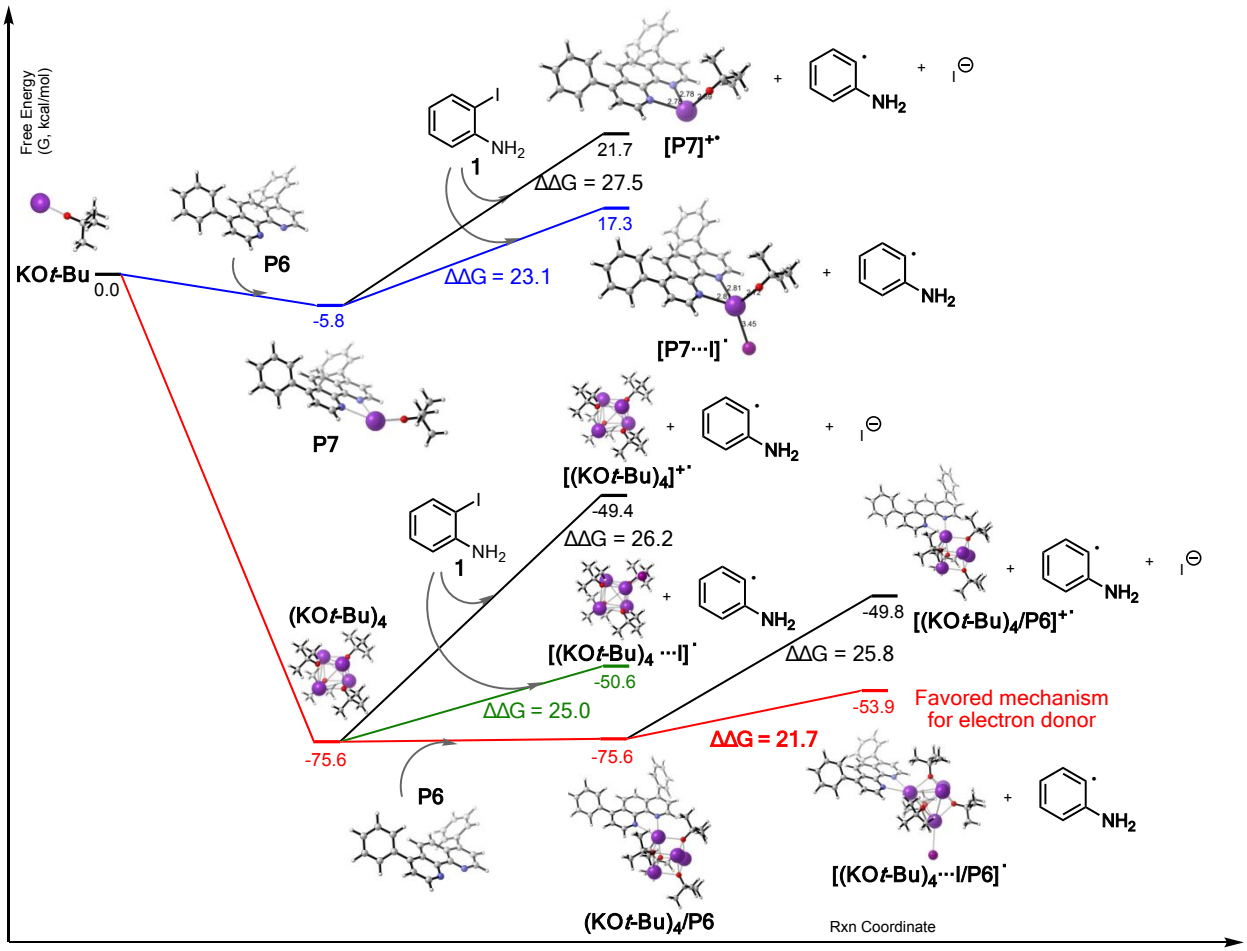
–Experimentally **KO*t*-Bu** by itself was ineffective for the title reaction, but the addition of bathophenanthroline (**P6**) led to a successful reaction with an approximate experimental barrier of ~26 kcal/mol (83% yield, 60ºC and 8 hours; Table 1, entry 10).

–DFT investigations of the probable SET pathways were explored, and the summary results are shown below.

–The most favorable pathway for the formation of the aniline radical via SET is by the **(KO*t*-Bu)$_4$/P6** complex (highlighted in red), a ΔΔG = 21.7 kcal/mol thermodynamic process.

–The SET process via the **P7** complex is energetically similar, at ΔΔG = 23.1 kcal/mol or 1.4 kcal/mol higher than the SET by **(KO*t*-Bu)$_4$/P6** (highlighted in blue). Additionally, the formation of the KOt-Bu tetramer complex, **(KOt-Bu)$_4$**, is shown extremely favorable at –75.6 kcal/mol, further favoring the **(KO*t*-Bu)$_4$/P6** pathway.

–The SET process via the **(KO*t*-Bu)$_4$** by itself is a ΔΔG = 25.0 kcal/mol process (highlighted in green) or 3.3 kcal/mol higher in energy than the SET process by **(KO*t*-Bu)$_4$/P6**. At the reaction conditions of 60ºC, all else being equal, this translates to the **(KO*t*-Bu)$_4$** process being ~147x slower than the process by **(KO*t*-Bu)$_4$/P6**.



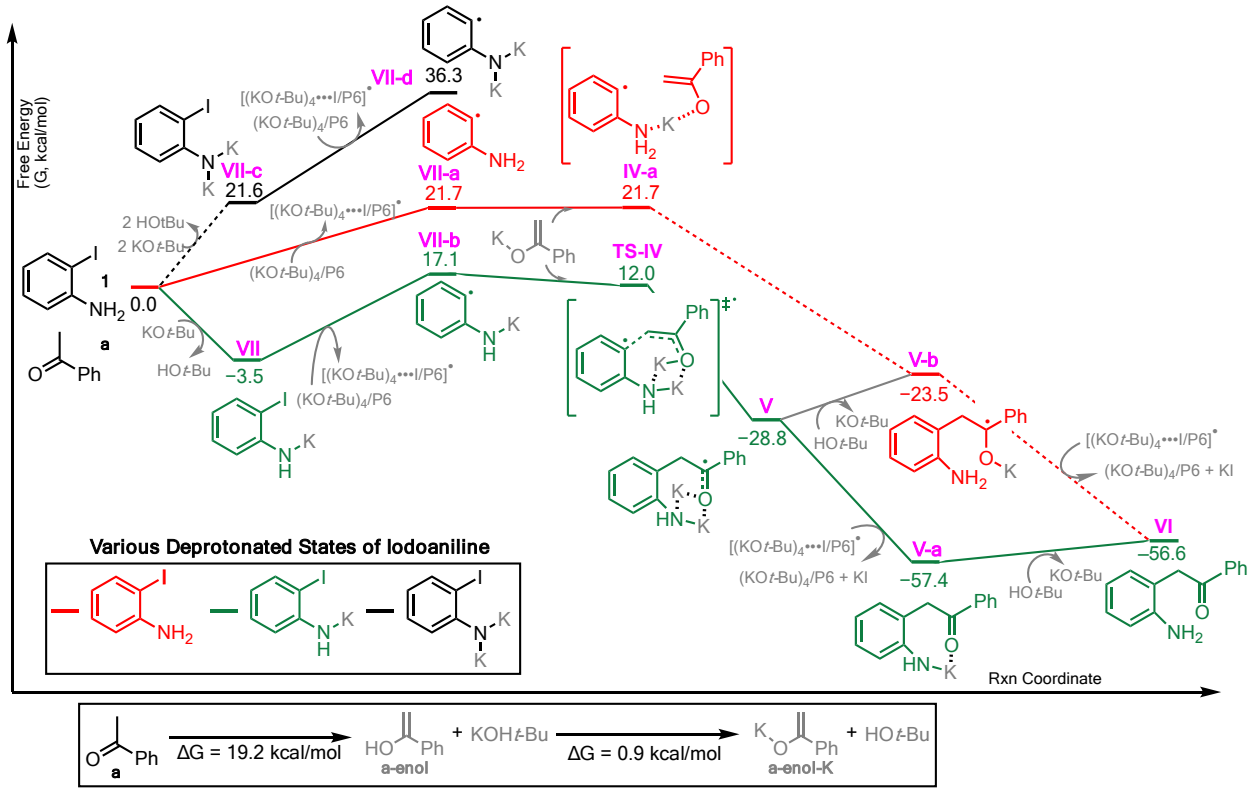
11. Reaction Coordinate Diagram for the Deprotonation States

–The most favorable pathway for the formation of the potassium aryl radical (**VII-b**) via deprotonation by **KO*t*-Bu** and subsequent SET by **(KO*t*-Bu)$_4$/P6** complex (highlighted in green), at 17.1 kcal/mol or at ΔΔG = 20.6 kcal/mol thermodynamic process.

–The formation of the aryl radical (**VII-a**) via SET by **(KO*t*-Bu)$_4$/P6** complex (highlighted in red) at 21.7 kcal/mol or 4.6 kcal/mol higher than the potassium aryl radical (**VII-b**). This pathway leads to a barrierless C-C formation of aryl radical adding to potassium enolate (**IV-a**).

–The formation of the di-potassium aryl radical (**VII-d**) via two steps of deprotonation by **KO*t*-Bu** and subsequent SET by **(KO*t*-Bu)$_4$/P6** complex (highlighted in black), at 36.3 kcal/mol or 19.2 kcal/mol higher than the potassium aryl radical (**VII-b**). Double deprotonation of 2-iodoaniline is energetically unfavorable.

Figure S6. Reaction coordinate diagram for the various deprotonation states of 2-iodoaniline (**1**) and acetophenone (**a**) by **KO*t*-Bu** followed by SET of complex **(KO*t*-Bu)$_4$/P6**.



We attempted to identify additional transition states leading to C–C bond formation without metal coordination by DFT calculation. We were unable to locate such a transition structure. In examining the potential energy surface by incrementally shrinking the C–C bond to locate this transition structure, we find that no such transition structure exists – the energy lowers monotonically without a barrier and forms the C–C bond. In the absence of such transition state, we believe it is helpful to analyze at the intermediate preceding the transition state. The non-coordinated (i.e. uncomplexed) enolate and aniline radical exhibit a free energy of 30.3 kcal/mol. This is 9.7 kcal/mol higher in energy than the corresponding coordinated intermediate of the favored mechanism and 15.7 kcal/mol higher in energy than the favored C-C bonding transition state structure (Main manuscript, Scheme 2b). These observations strongly suggest that the non-coordinated mechanism is very likely to be significantly energetically disfavored. Overall it does not change our conclusion that the metal-assisted pathway is the preferred one.

12. Computed Structures, Electronic Energies, and Thermal Corrections, as well as the Input Parameters

A. Reactants & Products

Supporting Information: 1 (2-iodoaniline)

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # opt=(gdiis,maxcycle=250) freq=noraman pbepbe/genecp/auto
 scrf=(smd,solvent=dmso) density=current 10f 6d
 scf=(maxcycle=300,direct,tight,yqc)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C6H6IN     C1[X(C6H6IN)]   #Atoms= 14
 Charge = 0        Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -298.039588371        Predicted Change= -2.345448D-08
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00003 ||   0.00045     [ YES ]        0.00001 ||   0.00030     [ YES ]
 Displ        0.00034 ||   0.00180     [ YES ]        0.00034 ||   0.00180     [ YES ]
---------------------------------------------------------------------------
        Atomic              Coordinates (Angstroms)
         Type          X                Y          Z
---------------------------------------------------------------------------
         C          -3.312102        -0.387101        0.002402
         C          -2.693253         0.864331        0.001312
         C          -1.278595         0.996709       -0.006002
         C          -0.531936        -0.207670       -0.002059
         C          -1.145549        -1.465284        0.003306
         C          -2.545059        -1.563561        0.003400
         H          -4.406091        -0.442382        0.009035
         H          -3.295336         1.780522        0.005542
         H          -0.530069        -2.369609        0.007921
         H          -3.021788        -2.548601        0.005712
         I           1.627115        -0.131626       -0.000133
         N          -0.697506         2.254655       -0.082863
         H          -1.303460         3.016347        0.229154
         H           0.241143         2.332742        0.315587
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
```

```
=========================================================================
===
 SCF Energy=       -298.039588371 Predicted Change= -2.345448D-08
 Zero-point correction (ZPE)=            -297.9352   0.10429
 Internal Energy (U)=                    -297.9278   0.11170
 Enthalpy (H)=                           -297.9269    0.11264
 Gibbs Free Energy (G)=                  -297.9685     0.07099
-------------------------------------------------------------------------------
 Frequencies --      125.8459                    188.7356                    236.3603
```

Supporting Information: a (acetophenone)

```
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 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
-------------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C8H8O     C1[X(C8H8O)]   #Atoms= 17
 Charge = 0        Multiplicity = 1
-------------------------------------------------------------------------------
 SCF Energy= -384.425459567       Predicted Change= -3.210960D-08
=========================================================================
===
 Optimization completed.                {Found          2          times}
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 Displ        0.00057 ||   0.00180    [ YES ]       0.00057 ||   0.00180    [ YES ]
-------------------------------------------------------------------------------
        Atomic              Coordinates (Angstroms)
         Type        X              Y              Z
-------------------------------------------------------------------------------
         C           2.603010        0.110384       -0.000015
         C           1.830396        1.282327        0.000087
         C           0.431092        1.202113        0.000109
         C          -0.210808       -0.055147        0.000016
         C           0.577379       -1.226526       -0.000090
         C           1.973029       -1.146261       -0.000101
         H           3.696473        0.175512       -0.000026
         H           2.319322        2.262261        0.000153
         H          -0.158558        2.124176        0.000193
         H           0.068013       -2.195651       -0.000160
         H           2.574341       -2.061710       -0.000179
         C          -1.706811       -0.199892        0.000031
         O          -2.228350       -1.321170        0.000208
         C          -2.557701        1.055414       -0.000189
```

```
        H          -2.344477          1.678223          0.887397
        H          -2.344587          1.677855         -0.888060
        H          -3.621243          0.774234         -0.000067
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -384.425459567      Predicted Change= -3.210960D-08
 Zero-point correction (ZPE)=              -384.2908       0.13460
 Internal Energy (U)=                    -384.2828       0.14262
 Enthalpy (H)=                         -384.2818       0.14357
 Gibbs Free Energy (G)=                  -384.3237       0.10166
 Entropy (S)=                                0.00014055
---------------------------------------------------------------------------
 Frequencies --       59.1285                    146.0499                    163.3298
```

Supporting Information: a-enol

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # opt=(gdiis,maxcycle=250) freq=noraman pbepbe/6-31g(d)/auto
 scrf=(smd,solvent=dmso) geom=connectivity density=current
 scf=(maxcycle=300,direct,tight,yqc)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C8H8O     C1[X(C8H8O)]   #Atoms= 17
 Charge = 0        Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -384.394935132        Predicted Change= -1.921184D-07
===========================================================================
===
 Optimization completed.                  {Found          1          times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00012 ||   0.00045     [ YES ]        0.00001 ||   0.00030     [ YES ]
 Displ        0.00451 ||   0.00180     [ NO ]         0.00451 ||   0.00180     [ YES ]
---------------------------------------------------------------------------
        Atomic             Coordinates (Angstroms)
         Type          X                Y          Z
---------------------------------------------------------------------------
        C          -2.610413         -0.016517          0.014620
        C          -1.925165          1.203401         -0.113126
        C          -0.526216          1.230826         -0.128026
        C           0.220634          0.037349         -0.004685
        C          -0.478842         -1.184370          0.113762
        C          -1.880335         -1.208916          0.124960
```

H	-3.705507	-0.035958	0.021165
H	-2.484140	2.140060	-0.213064
H	-0.008852	2.187257	-0.255388
H	0.083669	-2.117625	0.205727
H	-2.402861	-2.166820	0.222122
C	1.704952	0.050140	0.001452
O	2.229072	-1.196644	-0.247973
C	2.474775	1.139370	0.237212
H	3.568620	1.077293	0.214975
H	2.034052	2.109646	0.474211
H	3.206098	-1.128397	-0.162987

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
SCF Energy= -384.394935132 Predicted Change= -1.921184D-07
Zero-point correction (ZPE)= -384.2604 0.13449
Internal Energy (U)= -384.2526 0.14233
Enthalpy (H)= -384.2516 0.14328
Gibbs Free Energy (G)= -384.2931 0.10181

Frequencies -- 46.3634 148.8956 223.7755

Supporting Information: a-enol-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C8H7KO C1[X(C8H7KO)] #Atoms= 17
Charge = 0 Multiplicity = 1

SCF Energy= -983.522447925 Predicted Change= -4.199135D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00132 ||	0.00180	[YES]	0.00132 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.395771	-0.470335	0.364441
C	-2.986792	0.873352	0.403366
C	-1.661010	1.219496	0.104064
C	-0.710884	0.231770	-0.237752

C	-1.143132	-1.110663	-0.288218
C	-2.465901	-1.462523	0.013756
H	-4.432380	-0.739142	0.596260
H	-3.707600	1.658460	0.659508
H	-1.369431	2.275540	0.115741
H	-0.405931	-1.867029	-0.578580
H	-2.774965	-2.513779	-0.026082
C	0.743118	0.527301	-0.582747
O	1.391474	-0.420753	-1.191559
C	1.299240	1.739538	-0.174616
H	2.286486	2.043198	-0.551450
H	0.733358	2.497819	0.374405
K	3.182392	-0.488246	0.596258

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -983.522447925 Predicted Change= -4.199135D-09
Zero-point correction (ZPE)= -983.4001 0.12233
Internal Energy (U)= -983.3904 0.13199
Enthalpy (H)= -983.3895 0.13294
Gibbs Free Energy (G)= -983.4371 0.08534

Frequencies -- 26.9830 39.8370 122.0668

Supporting Information: j (methyl isopropyl ketone)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C5H10O C1[X(C5H10O)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -271.433094841 Predicted Change= -6.362603D-10

==========
==

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00067 ||	0.00180	[YES]	0.00067 ||	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-0.746533	-0.324396	0.020274
O	-0.923180	-1.453599	-0.439122
C	-1.914463	0.624402	0.237410
H	-1.802486	1.211941	1.164970
H	-1.963787	1.347064	-0.599018
H	-2.858994	0.058769	0.257792
C	0.650931	0.191552	0.386930
H	0.598375	0.464410	1.461574
C	1.727693	-0.878619	0.188223
H	1.814139	-1.160547	-0.875782
H	2.709397	-0.501187	0.523445
H	1.497340	-1.794661	0.757597
C	0.978041	1.482472	-0.397060
H	0.255653	2.289946	-0.190882
H	1.980829	1.848651	-0.115693
H	0.980962	1.291938	-1.485682

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -271.433094841 Predicted Change= -6.362603D-10
Zero-point correction (ZPE)= -271.2954 0.13759
Internal Energy (U)= -271.2875 0.14551
Enthalpy (H)= -271.2866 0.14646
Gibbs Free Energy (G)= -271.3273 0.10573

Frequencies -- 51.5437 124.2139 194.0196

Supporting Information: j-enol-1-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,xqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C5H9KO C1[X(C5H9KO)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -870.524731671 Predicted Change= -1.399750D-08

==========
===

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00245 ||	0.00180	[NO]	0.00245 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.566734	-0.453389	-0.000036
O	0.655002	0.027602	0.000080
C	-0.619077	-1.984695	-0.000001
H	-1.627478	-2.432132	-0.000889
H	-0.077281	-2.372684	-0.885418
H	-0.078866	-2.372792	0.886351
C	-1.716247	0.325851	-0.000132
C	-3.138726	-0.179445	0.000013
H	-3.714978	0.182669	0.882740
H	-3.715384	0.183516	-0.882087
H	-3.224690	-1.279183	-0.000472
C	-1.585348	1.830336	0.000016
H	-2.067262	2.305761	-0.884437
H	-2.067610	2.305575	0.884380
H	-0.518510	2.113549	0.000225
K	3.032044	0.205945	-0.000011

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -870.524731671 Predicted Change= -1.399750D-08
Zero-point correction (ZPE)= -870.3999 0.12473
Internal Energy (U)= -870.3899 0.13477
Enthalpy (H)= -870.3890 0.13572
Gibbs Free Energy (G)= -870.4370 0.08768

Frequencies -- 27.5255 38.1217 121.0231

Supporting Information: j-enol-2-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,xqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C5H9KO C1[X(C5H9KO)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -870.529455745 Predicted Change= -4.291633D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00152 ||	0.00180	[YES]	0.00152 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.266357	-0.642748	-0.042955
O	-0.225751	-0.209503	-1.163461
C	-0.315219	-1.608991	0.776220
C	1.580705	0.028156	0.434823
C	2.711942	-0.280107	-0.562119
H	2.426874	0.068406	-1.570824
H	3.654926	0.220360	-0.274594
H	2.908479	-1.366360	-0.622682
H	1.857605	-0.385627	1.423879
C	1.381555	1.547961	0.570019
H	0.643729	1.789660	1.359102
H	2.324960	2.064292	0.827327
H	1.009741	1.959488	-0.385391
H	-1.151301	-2.225582	0.410274
H	0.161416	-1.933804	1.708140
K	-2.409603	0.379977	-0.032814

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -870.529455745 Predicted Change= -4.291633D-09
Zero-point correction (ZPE)= -870.4036 0.12576
Internal Energy (U)= -870.3943 0.13509
Enthalpy (H)= -870.3934 0.13603
Gibbs Free Energy (G)= -870.4386 0.09080

Frequencies -- 43.2633 63.0776 149.1957

Supporting Information: h (benzyl methyl ketone)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
=================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
-------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C9H10O     C1[X(C9H10O)]   #Atoms= 20
 Charge = 0        Multiplicity = 1
-------------------------------------------------------------------------
 SCF Energy= -423.680081348        Predicted Change= -6.864989D-09
=================================================================
===
 Optimization completed on the basis of negligible forces.                {Found          2
times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00000 ||   0.00045     [ YES ]        0.00000 ||   0.00030     [ YES ]
 Displ        0.00455 ||   0.00180     [ NO ]         0.00455 ||   0.00180     [ YES ]
-------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
-------------------------------------------------------------------------
         O           1.840478       0.977987       1.059489
         C           2.157528       0.166897       0.193711
         C           1.145334      -0.435227      -0.795237
         C          -0.304279      -0.234982      -0.429010
         C          -1.072011      -1.304152       0.071730
         C          -2.416935      -1.120734       0.428750
         C          -3.015114       0.141242       0.291690
         C          -2.259610       1.215664      -0.205430
         C          -0.916351       1.027983      -0.561696
         C           3.585731      -0.308435       0.011987
         H           1.381582      -1.507684      -0.923479
         H           1.375312       0.036733      -1.772895
         H          -0.609290      -2.292671       0.179162
         H          -2.998345      -1.966776       0.811700
         H          -4.065557       0.286635       0.566672
         H          -2.719425       2.203697      -0.319376
         H          -0.334239       1.869358      -0.954604
         H           4.278412       0.313141       0.599756
         H           3.875810      -0.297558      -1.053773
         H           3.666156      -1.358311       0.351955
-------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=================================================================
===
```

SCF Energy= -423.680081348 Predicted Change= -6.864989D-09
Zero-point correction (ZPE)= -423.5186 0.16146
Internal Energy (U)= -423.5089 0.17115
Enthalpy (H)= -423.5079 0.17209
Gibbs Free Energy (G)= -423.5550 0.12499
Entropy (S)= 0.00015798

Frequencies -- 26.3258 48.3071 92.4272

Supporting Information: h-enol-1-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C9H9KO C1[X(C9H9KO)] #Atoms= 20
Charge = 0 Multiplicity = 1

SCF Energy= -1022.78605842 Predicted Change= -7.732358D-09
==========
===
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.01120 ||	0.00180	[NO]	0.01120 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.693386	2.369899	-0.011090
C	-1.110908	0.897280	-0.003673
O	-2.384317	0.677916	-0.002072
K	-4.256219	-0.895143	0.004137
C	-0.175854	-0.153913	0.000195
C	1.270282	-0.182887	0.001081
C	2.160753	0.939431	0.010382
C	3.552670	0.779986	0.009717
C	4.147304	-0.493008	0.000820
C	3.300083	-1.617953	-0.006834
C	1.912436	-1.466083	-0.006653
H	-0.077522	2.627769	-0.892957
H	-0.104597	2.643248	0.884683

H	-1.602902	2.992226	-0.029700
H	-0.643300	-1.151578	0.001339
H	1.762841	1.956567	0.019706
H	4.185346	1.676595	0.017023
H	5.236532	-0.607148	0.000508
H	3.728821	-2.627925	-0.013275
H	1.277210	-2.361876	-0.013033

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1022.78605842 Predicted Change= -7.732358D-09
Zero-point correction (ZPE)= -1022.6363 0.14975
Internal Energy (U)= -1022.6247 0.16128
Enthalpy (H)= -1022.6238 0.16222
Gibbs Free Energy (G)= -1022.6798 0.10622
Entropy (S)= 0.00018783

Frequencies -- 3.7286 14.8905 17.1165

Supporting Information: h-enol-2-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C9H9KO C1[X(C9H9KO)] #Atoms= 20
Charge = 0 Multiplicity = 1

SCF Energy= -1022.79752213 Predicted Change= -3.202652D-08

==========
===

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00007 ||	0.00045	[YES]	0.00001 ||	0.00030	[YES]
Displ	0.00307 ||	0.00180	[NO]	0.00307 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.285740	1.407864	0.081851
C	1.972803	0.666069	0.349024

O	2.051383	-0.429567	1.029263
K	0.935445	-1.852845	-0.814219
C	0.791264	1.208986	-0.198436
C	-0.569094	0.745993	0.003096
C	-1.631486	1.303265	-0.776396
C	-2.955674	0.881117	-0.636339
C	-3.300071	-0.122639	0.290730
C	-2.282790	-0.676700	1.085333
C	-0.950091	-0.257312	0.954459
H	3.735540	1.721572	1.043023
H	4.015711	0.729783	-0.399670
H	3.163290	2.303450	-0.551367
H	0.897980	2.091493	-0.841746
H	-1.388918	2.085860	-1.506951
H	-3.733639	1.339434	-1.259039
H	-4.338152	-0.455441	0.395360
H	-2.527668	-1.443700	1.830697
H	-0.172272	-0.671721	1.605822

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1022.79752213 Predicted Change= -3.202652D-08
Zero-point correction (ZPE)= -1022.6473 0.15016
Internal Energy (U)= -1022.6361 0.16135
Enthalpy (H)= -1022.6352 0.16229
Gibbs Free Energy (G)= -1022.6854 0.11207
Entropy (S)= 0.00016843

Frequencies -- 53.6875 67.7012 83.7706

Supporting Information: h-enol-3-K

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C9H9KO C1[X(C9H9KO)] #Atoms= 20
Charge = 0 Multiplicity = 1

SCF Energy= -1022.78244689 Predicted Change= -5.224987D-09

==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00067 ||	0.00180	[YES]	0.00067 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.752327	-0.256088	0.970735
C	-2.024037	-0.459384	-0.193567
O	-1.937276	0.342449	-1.202828
K	-0.388387	1.838722	0.214525
C	-1.070920	-1.702831	-0.233406
C	0.341603	-1.180602	-0.130030
C	0.994964	-0.650680	-1.266755
C	2.204519	0.055619	-1.141812
C	2.788614	0.243072	0.123376
C	2.164237	-0.302975	1.260539
C	0.953346	-1.003467	1.131907
H	-3.452393	0.587953	1.043795
H	-2.779609	-1.003718	1.770833
H	-1.291729	-2.403696	0.589803
H	-1.223451	-2.225428	-1.195239
H	0.533641	-0.774329	-2.251709
H	2.688538	0.466661	-2.034975
H	3.727592	0.798176	0.221915
H	2.617221	-0.176163	2.250141
H	0.457751	-1.400758	2.026171

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
===
SCF Energy= -1022.78244689 Predicted Change= -5.224987D-09
Zero-point correction (ZPE)= -1022.6323 0.15013
Internal Energy (U)= -1022.6213 0.16104
Enthalpy (H)= -1022.6204 0.16199
Gibbs Free Energy (G)= -1022.6699 0.11251
Entropy (S)= 0.00016594

Frequencies -- 59.6708 63.1185 82.2285

Supporting Information: 1a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
-----------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H11N     C1[X(C14H11N)]   #Atoms= 26
 Charge = 0        Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -594.149777208        Predicted Change= -2.935584D-09
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00082 ||   0.00180    [ YES ]       0.00082 ||   0.00180    [ YES ]
-----------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
-----------------------------------------------------------------------------
         C          1.842568       -0.649028       0.076305
         C          1.896946        0.776596      -0.093044
         C          3.163665        1.402649      -0.172603
         C          4.314551        0.617379      -0.073918
         C          4.233781       -0.787681       0.102638
         C          2.999246       -1.440658       0.179737
         C         -0.290827        0.125509      -0.011067
         C          0.541993        1.237474      -0.142497
         H          3.237750        2.487806      -0.307164
         H          5.299799        1.092524      -0.132461
         H          5.155751       -1.374001       0.178564
         H          2.933524       -2.525486       0.314738
         N          0.511487       -1.006624       0.107946
         C         -1.754722        0.044731      -0.004863
         C         -2.432616       -1.178896      -0.219639
         C         -2.529474        1.209522       0.213773
         C         -3.832279       -1.233793      -0.210549
         H         -1.866967       -2.095904      -0.417537
         C         -3.927044        1.150986       0.214163
         H         -2.027435        2.164765       0.400021
         C         -4.587714       -0.071129       0.004970
         H         -4.334292       -2.192388      -0.380841
         H         -4.504600        2.065391       0.387933
         H         -5.681873       -0.116046       0.010455
         H          0.170541       -1.947582       0.300631
         H          0.208947        2.265323      -0.290390
-----------------------------------------------------------------------------
```

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -594.149777208 Predicted Change= -2.935584D-09
Zero-point correction (ZPE)= -593.9440 0.20572
Internal Energy (U)= -593.9327 0.21701
Enthalpy (H)= -593.9318 0.21796
Gibbs Free Energy (G)= -593.9818 0.16797
Entropy (S)= 0.00016767

Frequencies -- 46.3265 58.3141 106.1810

Supporting Information: 1j'

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C11H13N C1[X(C11H13N)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -481.156250716 Predicted Change= -6.165716D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00422 ||	0.00180	[NO]	0.00422 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.073093	-0.826618	-0.000809
C	0.897809	0.599471	0.000092
C	1.981844	1.493070	0.000975
C	3.270073	0.945159	0.000932
C	3.470350	-0.457678	0.000012
C	2.388683	-1.344398	-0.000863
C	-0.244616	-1.401998	-0.001490
C	-1.162099	-0.360189	-0.000820
H	1.822136	2.576757	0.001808
H	4.137697	1.613836	0.001666
H	4.492440	-0.852195	-0.000010

H	2.557843	-2.427569	-0.001516
N	-0.462158	0.840829	0.000026
C	-2.669923	-0.389546	-0.000747
H	-2.957949	-1.456822	-0.002920
C	-3.252311	0.269332	-1.269067
H	-2.869813	-0.212992	-2.185306
H	-4.353638	0.187239	-1.271636
H	-2.995736	1.343452	-1.315660
C	-3.251433	0.263949	1.270829
H	-4.352837	0.182846	1.273312
H	-2.869069	-0.223035	2.184638
H	-2.993774	1.337561	1.322370
H	-0.892527	1.765034	0.001019
H	-0.498493	-2.463237	-0.002216

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -481.156250716 Predicted Change= -6.165716D-08
Zero-point correction (ZPE)= -480.9470 0.20919
Internal Energy (U)= -480.9360 0.22017
Enthalpy (H)= -480.9351 0.22112
Gibbs Free Energy (G)= -480.9837 0.17251

Frequencies -- 36.5982 79.5119 146.7013

Supporting Information: 1h'

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.411145015 Predicted Change= -4.282649D-08

==========
===

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00203 ||	0.00180	[NO]	0.00203 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.406122	3.054499	0.319014
C	0.375070	1.789194	0.158554
C	-0.037772	0.455084	0.038219
C	-1.426191	-0.036795	0.007631
C	-1.787713	-1.229838	0.681641
C	-3.105054	-1.706283	0.655594
C	-4.102357	-1.001210	-0.037046
C	-3.763517	0.183394	-0.709371
C	-2.443716	0.655313	-0.694336
C	1.170565	-0.346598	-0.038722
C	1.440136	-1.724581	-0.203844
C	2.768874	-2.158335	-0.263978
C	3.846149	-1.244336	-0.168373
C	3.615512	0.128101	-0.022240
C	2.279819	0.557171	0.036142
N	1.757703	1.829639	0.154526
H	-1.418671	2.846219	0.699198
H	0.096554	3.736947	1.027559
H	-0.515208	3.599532	-0.637797
H	-1.028231	-1.775677	1.251320
H	-3.355412	-2.630049	1.189302
H	-5.132506	-1.372905	-0.054860
H	-4.528938	0.739484	-1.262290
H	-2.189504	1.560737	-1.255528
H	0.621234	-2.446670	-0.291324
H	2.980958	-3.225704	-0.389952
H	4.875765	-1.614786	-0.215689
H	4.441806	0.844326	0.040170
H	2.306147	2.682401	0.264904

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -633.411145015 Predicted Change= -4.282649D-08
Zero-point correction (ZPE)= -633.1781 0.23297
Internal Energy (U)= -633.1652 0.24592
Enthalpy (H)= -633.1642 0.24687
Gibbs Free Energy (G)= -633.2174 0.19371
Entropy (S)= 0.0001783

Frequencies -- 62.0445 78.3738 86.9629

B. Intermediates

Supporting Information: I

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/genecp/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman 6d 10f
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H12IN     C1[X(C14H12IN)]   #Atoms= 28
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -606.110199184       Predicted Change= -3.597699D-09
=========================================================================
===
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00182 ||   0.00180    [ NO ]        0.00182 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
---------------------------------------------------------------------------
         C          -2.487211        3.051601       -0.622886
         C          -1.182172        2.552028       -0.560288
         C          -0.930510        1.176385       -0.319554
         C          -2.057831        0.338309       -0.148390
         C          -3.365218        0.831594       -0.188105
           C          -3.583246        2.196937       -0.433511
         H          -2.646270        4.117358       -0.818604
         H          -0.325361        3.214555       -0.721096
         H          -4.211338        0.155211       -0.036602
         H          -4.607277        2.580602       -0.481204
         N           0.354948        0.637121       -0.389783
         C           1.349492        1.025823        0.351773
         C           1.241717        2.001965        1.500615
         H           1.790918        2.935540        1.281569
         H           0.194150        2.260293        1.713041
         H           1.691733        1.571785        2.412141
         C           2.684384        0.425982        0.059373
         C           3.840989        0.823234        0.767012
         C           2.816793       -0.556172       -0.950295
         C           5.088940        0.255571        0.473980
         H           3.775451        1.584719        1.549581
         C           4.060755       -1.123944       -1.238290
```

H	1.923298	-0.866109	-1.500767
C	5.204015	-0.720054	-0.526709
H	5.974231	0.578585	1.031941
H	4.142285	-1.886067	-2.020856
H	6.178975	-1.164997	-0.752895
I	-1.744355	-1.758809	0.227998

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -606.110199184 Predicted Change= -3.597699D-09
Zero-point correction (ZPE)= -605.8951 0.21500
Internal Energy (U)= -605.8807 0.22948
Enthalpy (H)= -605.8797 0.23043
Gibbs Free Energy (G)= -605.9394 0.17072
Entropy (S)= 0.00020027

Frequencies -- 25.2703 34.8224 61.2353

Supporting Information: II

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H11KN(2) C1[X(C14H11KN)] #Atoms= 27
Charge = 0 Multiplicity = 2

SCF Energy= -1193.73547153 Predicted Change= -1.088756D-08

==========
===

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00154 ||	0.00180	[YES]	0.00154 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.194894	1.044248	0.162355
C	2.809271	1.147543	-0.003098
C	1.952628	-0.003422	0.020247

C	2.631121	-1.234572	0.225106
C	4.006341	-1.367000	0.327615
C	4.816651	-0.206289	0.333974
H	4.803610	1.956418	0.142292
H	2.357074	2.133672	-0.183322
H	4.474466	-2.354963	0.444931
H	5.900278	-0.282089	0.481756
N	0.588020	0.170792	-0.093338
C	-0.196055	-0.947156	-0.285537
C	-1.646338	-0.720043	0.038639
C	-2.017809	0.044450	1.171647
C	-2.675272	-1.218083	-0.792211
C	-3.367226	0.305381	1.458793
H	-1.231501	0.417365	1.839413
C	-4.024100	-0.961643	-0.503953
H	-2.404425	-1.794908	-1.683595
C	-4.376049	-0.194595	0.618399
H	-3.630358	0.891909	2.346178
H	-4.803862	-1.351217	-1.167794
H	-5.429095	0.011276	0.838029
C	0.192298	-2.196275	-0.732930
H	1.187730	-2.377681	-1.147634
H	-0.511022	-3.035994	-0.729652
K	-0.980588	2.296600	-0.671658

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1193.73547153 Predicted Change= -1.088756D-08
Zero-point correction (ZPE)= -1193.5361 0.19928
Internal Energy (U)= -1193.5214 0.21404
Enthalpy (H)= -1193.5204 0.21498
Gibbs Free Energy (G)= -1193.5807 0.15467
Entropy (S)= 0.00020229

Frequencies -- 30.7811 35.8309 50.1802

Supporting Information: II-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# opt=(gdiis,maxcycle=250) freq=noraman pbepbe/6-31g(d)/auto
scrf=(smd,solvent=dmso) density=current
scf=(maxcycle=300,direct,tight,yqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

```
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H12N(2)     C1[X(C14H12N)]   #Atoms= 27
 Charge = 0        Multiplicity = 2
---------------------------------------------------------------------------
 SCF Energy= -594.625578796        Predicted Change= -6.680778D-08
=========================================================================
============
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00007 ||   0.00045    [ YES ]        0.00001 ||   0.00030    [ YES ]
 Displ        0.00353 ||   0.00180    [ NO ]         0.00353 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type          X                Y          Z
---------------------------------------------------------------------------
         C          -4.062211        -1.244237        -0.362582
         C          -2.676487        -1.301724        -0.547229
         C          -1.848746        -0.211050        -0.160030
         C          -2.512430         0.885142         0.398399
         C          -3.878763         0.991489         0.569067
         C          -4.679692        -0.110126         0.193208
         H          -4.672224        -2.101480        -0.667139
         H          -2.210637        -2.185545        -1.001769
         H          -4.335858         1.890299         1.000622
         H          -5.764632        -0.075730         0.339665
         N          -0.469728        -0.295126        -0.318682
         H          -0.121795        -1.171535        -0.710950
         C           0.471852         0.714215        -0.104178
         C           1.879176         0.227802        -0.021775
         C           2.182418        -1.045314         0.511317
         C           2.943728         1.038730        -0.474263
         C           3.509761        -1.488251         0.595972
         H           1.375750        -1.684843         0.886540
         C           4.269257         0.597305        -0.381987
         H           2.721910         2.014102        -0.920188
         C           4.558467        -0.669009         0.151975
         H           3.723943        -2.475516         1.019339
         H           5.079799         1.239872        -0.742471
         H           5.595088        -1.016424         0.216914
         C           0.151383         2.028917         0.055860
         H          -0.867536         2.401229        -0.086549
         H           0.918006         2.748130         0.354235
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=========================================================================
===
```

SCF Energy= -594.625578796 Predicted Change= -6.680778D-08
Zero-point correction (ZPE)= -594.4127 0.21284
Internal Energy (U)= -594.4000 0.22553
Enthalpy (H)= -594.3990 0.22648
Gibbs Free Energy (G)= -594.4533 0.17222

Frequencies -- 32.6328 52.4741 70.2789

Supporting Information: III

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H11KN(2) C1[X(C14H11KN)] #Atoms= 27
Charge = 0 Multiplicity = 2

SCF Energy= -1193.82697886 Predicted Change= -3.058181D-09
==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00088 ||	0.00180	[YES]	0.00088 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.925641	0.277877	-0.415720
C	-2.116175	-1.030315	0.135212
C	-3.394198	-1.516246	0.399002
C	-4.516249	-0.703519	0.114024
C	-4.332318	0.585667	-0.424361
C	-3.049959	1.091138	-0.692062
C	0.145747	-0.495106	-0.199019
C	-0.739842	-1.623233	0.332160
H	-3.537282	-2.518446	0.823041
H	-5.526607	-1.076287	0.313323
H	-5.208373	1.208779	-0.641155
H	-2.918860	2.094240	-1.116077
H	-0.592301	-2.574873	-0.220450
N	-0.588885	0.597297	-0.605133
C	1.573657	-0.529964	-0.248988

C	2.344838	0.497752	-0.911022
C	2.328235	-1.583769	0.377160
C	3.742130	0.484688	-0.895808
H	1.817987	1.260387	-1.499275
C	3.721283	-1.581216	0.377958
H	1.792109	-2.399482	0.875500
C	4.454994	-0.543422	-0.244551
H	4.287477	1.279450	-1.420224
H	4.255602	-2.401610	0.872755
H	5.549608	-0.549374	-0.237983
H	-0.530811	-1.868395	1.395828
K	0.806034	2.283291	0.992986

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1193.82697886 Predicted Change= -3.058181D-09
Zero-point correction (ZPE)= -1193.6247 0.20225
Internal Energy (U)= -1193.6109 0.21598
Enthalpy (H)= -1193.6100 0.21692
Gibbs Free Energy (G)= -1193.6672 0.15971
Entropy (S)= 0.00019189

Frequencies -- 41.4819 45.7843 55.8745

Supporting Information: III-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H12N(2) C1[X(C14H12N)] #Atoms= 27
Charge = 0 Multiplicity = 2

SCF Energy= -594.710356156 Predicted Change= -1.289811D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00170 ||	0.00180	[YES]	0.00170 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.853921	0.654264	0.000048
C	-1.934611	-0.760969	0.000208
C	-3.183092	-1.380408	0.000031
C	-4.347299	-0.582370	-0.000294
C	-4.247673	0.820615	-0.000412
C	-2.999117	1.465444	-0.000252
C	0.336749	-0.068935	0.000343
C	-0.525109	-1.318967	0.000565
H	-3.262457	-2.473659	0.000130
H	-5.332789	-1.059084	-0.000459
H	-5.159155	1.428366	-0.000647
H	-2.921590	2.557461	-0.000350
H	-0.324900	-1.961662	-0.881959
N	-0.514772	1.027039	0.000179
H	-0.206795	1.998678	0.000401
C	1.754994	0.000072	0.000208
C	2.479623	1.240055	0.000358
C	2.532488	-1.206699	-0.000164
C	3.873707	1.257693	0.000034
H	1.940869	2.194363	0.000714
C	3.925809	-1.168738	-0.000487
H	2.020077	-2.174767	-0.000209
C	4.617862	0.059976	-0.000407
H	4.394313	2.222550	0.000138
H	4.486334	-2.110899	-0.000778
H	5.712317	0.084058	-0.000690
H	-0.325270	-1.960875	0.883779

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -594.710356156 Predicted Change= -1.289811D-08
Zero-point correction (ZPE)= -594.4954 0.21493
Internal Energy (U)= -594.4835 0.22678
Enthalpy (H)= -594.4826 0.22773
Gibbs Free Energy (G)= -594.5340 0.17626

Frequencies -- 47.8067 79.0472 107.6506

Supporting Information: TS-IV

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd)
 opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
 guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
-------------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H12K2NO(2)     C1[X(C14H12K2NO)]   #Atoms=
30
 Charge = 0       Multiplicity = 2
-------------------------------------------------------------------------------
 SCF Energy= -1869.22226297       Predicted Change= -4.900316D-10
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]        0.00000 ||   0.00030    [ YES ]
 Displ        0.00077 ||   0.00180    [ YES ]        0.00077 ||   0.00180    [ YES ]
-------------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
-------------------------------------------------------------------------------
         C           2.234012       0.127799       0.832889
         C           2.032503       0.412505      -0.562732
         C           2.691709       1.411808      -1.261409
         C           3.688065       2.198719      -0.628662
         C           3.948492       1.948283       0.731286
         C           3.255324       0.957589       1.437094
         N           1.545284      -0.851695       1.500466
         C          -0.109449      -0.312866      -2.195822
         H           2.461933       1.590581      -2.322654
         H           4.233223       2.971761      -1.182530
         H           4.704848       2.543026       1.260173
         H           3.472390       0.800608       2.505095
         H           0.497983      -1.033202      -2.757259
         C          -1.074112      -0.753691      -1.287615
         H          -0.127297       0.703607      -2.596348
         C          -3.929188       2.055942       0.411563
         C          -2.664450       2.512339       0.003343
         C          -1.738387       1.625778      -0.565361
         C          -2.056307       0.257858      -0.739555
         C          -3.328383      -0.189887      -0.307643
         C          -4.258006       0.699336       0.251949
         H          -4.650135       2.750822       0.855410
         H          -2.392344       3.565324       0.138294
         H          -0.745396       1.989101      -0.851744
```

H	-3.579087	-1.249952	-0.430366
H	-5.242171	0.331819	0.564189
O	-1.168937	-1.970829	-0.825118
K	-1.146890	-1.183364	1.785046
H	1.931402	-0.895046	2.457644
K	1.453112	-2.503427	-0.640739

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1869.22226297 Predicted Change= -4.900316D-10
Zero-point correction (ZPE)= -1869.0096 0.21257
Internal Energy (U)= -1868.9915 0.23075
Enthalpy (H)= -1868.9905 0.23169
Gibbs Free Energy (G)= -1869.0592 0.16296
Entropy (S)= 0.00023052

Frequencies -- -103.7702 19.3820 30.7123

Supporting Information: IV-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H13KNO(2) C1[X(C14H13KNO)] #Atoms= 30
Charge = 0 Multiplicity = 2

SCF Energy= -1270.10098349 Predicted Change= -2.636077D-08

==========
===

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00650 ||	0.00180	[NO]	0.00650 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.720679	-0.791105	0.139031
C	3.426800	0.158198	1.120321
C	3.717584	1.506076	1.069709

C	4.347964	1.988578	-0.100956
C	4.654371	1.087468	-1.133417
C	4.349577	-0.277358	-1.027036
N	3.296711	-2.133541	0.228920
C	-0.770687	1.373305	0.311081
H	3.470432	2.184624	1.894378
H	4.591720	3.052365	-0.191406
H	5.147795	1.449849	-2.041555
H	4.603316	-0.970811	-1.839234
H	3.841033	-2.765633	-0.366526
H	3.285820	-2.486732	1.191206
H	0.246624	1.460040	0.718065
C	-1.557506	0.267694	0.631775
H	-1.161785	2.247754	-0.217467
C	-5.764571	0.098839	-0.515138
C	-5.106715	1.340472	-0.498970
C	-3.754762	1.421840	-0.134713
C	-3.024756	0.264913	0.218249
C	-3.705938	-0.971194	0.211617
C	-5.056083	-1.058819	-0.155082
H	-6.821464	0.036996	-0.797512
H	-5.652953	2.253377	-0.763403
H	-3.268992	2.403420	-0.106025
H	-3.138831	-1.859163	0.511144
H	-5.560000	-2.032709	-0.157638
O	-1.127633	-0.810776	1.215540
K	0.710823	-1.158201	-0.525243

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1270.10098349 Predicted Change= -2.636077D-08
Zero-point correction (ZPE)= -1269.8759 0.22504
Internal Energy (U)= -1269.8582 0.24270
Enthalpy (H)= -1269.8573 0.24365
Gibbs Free Energy (G)= -1269.9288 0.17211
Entropy (S)= 0.00023995

Frequencies -- 10.4404 14.6720 17.2351

Supporting Information: IV-b

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)

density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H14NO(2) C1[X(C14H14NO)] #Atoms= 30
Charge = 0 Multiplicity = 2

SCF Energy= -670.971679799 Predicted Change= -3.061864D-09
==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00117 ||	0.00180	[YES]	0.00117 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.010680	0.438811	-0.629946
C	3.325273	-0.916623	-0.576928
C	4.178951	-1.522796	0.320613
C	4.787094	-0.693820	1.291629
C	4.506264	0.681722	1.292623
C	3.634856	1.248217	0.351020
N	2.070226	0.968994	-1.548814
C	-0.470552	-1.396487	-0.632171
H	4.384008	-2.599274	0.293651
H	5.469723	-1.128381	2.029808
H	4.977418	1.331607	2.037652
H	3.428968	2.326146	0.358501
H	2.238490	1.962844	-1.743143
H	2.066860	0.454147	-2.436796
H	0.578200	-1.434412	-0.945631
C	-1.142849	-0.219280	-0.528235
H	-0.946655	-2.345171	-0.375375
C	-5.265950	0.109656	0.735159
C	-4.772072	-1.118129	0.263214
C	-3.441251	-1.231810	-0.155915
C	-2.568358	-0.121422	-0.104952
C	-3.080444	1.110257	0.360414
C	-4.413820	1.223096	0.778315
H	-6.308755	0.197658	1.058656
H	-5.431091	-1.991704	0.210893
H	-3.082311	-2.189682	-0.546641
H	-2.418498	1.980026	0.397209
H	-4.787349	2.187427	1.140331
O	-0.596622	1.001839	-0.776348

```
        H            0.385456         0.902742        -1.015675
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -670.971679799      Predicted Change= -3.061864D-09
 Zero-point correction (ZPE)=              -670.7336        0.23802
 Internal Energy (U)=                    -670.7184        0.25323
 Enthalpy (H)=                         -670.7174        0.25418
 Gibbs Free Energy (G)=                  -670.7801        0.19154
 Entropy (S)=                                0.00021007
---------------------------------------------------------------------------
 Frequencies --        17.3572                    22.2617                    36.2462
```

Supporting Information: V

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H12K2NO(2)     C1[X(C14H12K2NO)]   #Atoms=
30
 Charge = 0       Multiplicity = 2
---------------------------------------------------------------------------
 SCF Energy= -1869.29357227        Predicted Change= -3.275135D-08
===========================================================================
===
 Optimization completed.                  {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00138 ||   0.00180    [ YES ]       0.00138 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
---------------------------------------------------------------------------
         C           2.092114        0.587626        0.411031
         C           1.288190        1.043289       -0.712897
         C           1.252086        2.413893       -1.026061
         C           1.945721        3.396389       -0.295794
         C           2.723891        2.973645        0.798071
         C           2.793445        1.619819        1.133567
         N           2.176408       -0.737269        0.752679
```

C	0.521740	0.073841	-1.612019
H	0.658508	2.722366	-1.898487
H	1.887672	4.452352	-0.580307
H	3.287094	3.705247	1.392170
H	3.415956	1.303574	1.983349
H	1.223725	-0.651355	-2.076005
C	-0.604952	-0.752646	-0.967873
H	0.110233	0.663134	-2.455992
C	-4.332935	1.041848	0.308206
C	-3.347843	1.829257	-0.335659
C	-2.143202	1.276368	-0.766237
C	-1.845138	-0.120402	-0.577170
C	-2.876866	-0.906626	0.061101
C	-4.075809	-0.334471	0.490581
H	-5.275259	1.486841	0.644037
H	-3.533074	2.897869	-0.503254
H	-1.408585	1.922674	-1.255566
H	-2.711995	-1.985923	0.164506
H	-4.832845	-0.971572	0.966159
O	-0.409861	-2.019686	-0.722672
K	-0.315185	-1.165166	1.878308
H	2.844897	-0.794222	1.540202
K	2.001241	-2.955023	-0.765744

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1869.29357227 Predicted Change= -3.275135D-08
Zero-point correction (ZPE)= -1869.0769 0.21662
Internal Energy (U)= -1869.0595 0.23403
Enthalpy (H)= -1869.0585 0.23497
Gibbs Free Energy (G)= -1869.1242 0.16934
Entropy (S)= 0.00022014

Frequencies -- 28.6854 46.8806 50.8510

Supporting Information: V-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H12KNO C1[X(C14H12KNO)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -1269.59059267 Predicted Change= -4.821175D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00041 ||	0.00180	[YES]	0.00041 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.360087	-0.741787	-0.053927
C	-1.067726	-0.995583	0.568891
C	-0.467132	-2.262526	0.472887
C	-1.061182	-3.335224	-0.211165
C	-2.313809	-3.116617	-0.823959
C	-2.937470	-1.874354	-0.744913
N	-2.971517	0.462552	0.037892
C	-0.384249	0.108262	1.368927
H	0.499110	-2.417746	0.970346
H	-0.569012	-4.312216	-0.257014
H	-2.808225	-3.932315	-1.367711
H	-3.914063	-1.724379	-1.227094
H	-3.896656	0.360574	-0.413240
H	0.196754	-0.326093	2.199252
C	0.514472	0.915668	0.440476
H	-1.144978	0.787437	1.793868
C	4.583313	-0.258737	-0.435519
C	3.927215	-0.831890	0.664556
C	2.601113	-0.484403	0.955952
C	1.912101	0.453508	0.153403
C	2.592307	1.034503	-0.942545
C	3.909930	0.676779	-1.240178
H	5.617848	-0.536603	-0.663902
H	4.449853	-1.553686	1.301139
H	2.114274	-0.936907	1.824348
H	2.061003	1.769712	-1.554944
H	4.417558	1.128353	-2.099374
O	0.089261	1.939221	-0.135341
K	-2.296301	3.011402	-0.038184

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===
SCF Energy= -1269.59059267 Predicted Change= -4.821175D-10
Zero-point correction (ZPE)= -1269.3722 0.21831
Internal Energy (U)= -1269.3568 0.23370
Enthalpy (H)= -1269.3559 0.23464
Gibbs Free Energy (G)= -1269.4167 0.17383
Entropy (S)= 0.00020398

Frequencies -- 31.1362 39.2362 48.7406

Supporting Information: V-b

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H13KNO(2) C1[X(C14H13KNO)] #Atoms= 30
Charge = 0 Multiplicity = 2

SCF Energy= -1270.18548282 Predicted Change= -3.222366D-08
==========
===
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00358 ||	0.00180	[NO]	0.00358 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.528730	-0.451951	0.407046
C	-1.507568	0.368931	0.985625
C	-1.431662	1.721520	0.598735
C	-2.324415	2.284509	-0.330255
C	-3.331785	1.476866	-0.884617
C	-3.432117	0.125968	-0.518637
N	-2.617783	-1.803877	0.763686
C	-0.444036	-0.248171	1.885711
H	-0.643379	2.344751	1.038158
H	-2.236313	3.339303	-0.610222
H	-4.037780	1.891881	-1.612435
H	-4.210261	-0.509009	-0.960115

H	-3.230211	-2.339344	0.141491
H	-1.672145	-2.231302	0.819637
H	-0.902766	-0.983934	2.574272
C	0.570617	-0.976480	0.994082
H	0.021343	0.538176	2.501891
C	4.214030	0.861753	-0.444873
C	3.420118	1.527519	0.519431
C	2.247413	0.957815	1.012336
C	1.793399	-0.333967	0.566665
C	2.626987	-0.996617	-0.410454
C	3.796559	-0.408684	-0.895530
H	5.132474	1.319293	-0.826565
H	3.729366	2.512935	0.889477
H	1.666722	1.511841	1.757507
H	2.334767	-2.001024	-0.738172
H	4.401524	-0.950775	-1.633638
O	0.186110	-2.101881	0.453523
K	-0.291084	-0.550245	-1.748782

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1270.18548282 Predicted Change= -3.222366D-08
Zero-point correction (ZPE)= -1269.9560 0.22943
Internal Energy (U)= -1269.9404 0.24506
Enthalpy (H)= -1269.9394 0.24600
Gibbs Free Energy (G)= -1270.0008 0.18459

Frequencies -- 28.2123 38.3059 51.3125

Supporting Information: V-c

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

#pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
guess=(mix,always)
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H14NO(2) C1[X(C14H14NO)] #Atoms= 30
Charge = 0 Multiplicity = 2

SCF Energy= -671.040140060 Predicted Change= -1.305953D-08

==========
===

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00138 ||	0.00180	[YES]	0.00138 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.532354	0.666688	-0.179583
C	1.615854	-0.118145	0.581731
C	1.779557	-1.513987	0.606827
C	2.809690	-2.157931	-0.095848
C	3.708458	-1.380490	-0.843333
C	3.572074	0.011112	-0.883169
N	2.467762	2.061448	-0.170381
C	0.493429	0.535947	1.390138
H	1.083365	-2.109005	1.210727
H	2.911711	-3.247130	-0.052659
H	4.521476	-1.857765	-1.402084
H	4.275113	0.618931	-1.465893
H	3.002313	2.503568	-0.921549
H	1.523092	2.453103	-0.107763
H	0.901477	1.394346	1.960787
C	-0.661492	1.049589	0.570484
H	0.124082	-0.191663	2.132092
C	-4.174992	-1.133076	-0.557445
C	-3.122307	-1.769859	0.130749
C	-1.979202	-1.066016	0.503258
C	-1.832407	0.328731	0.199131
C	-2.924682	0.958751	-0.488622
C	-4.060200	0.237952	-0.856482
H	-5.069419	-1.692816	-0.848661
H	-3.196463	-2.835180	0.376885
H	-1.175412	-1.591731	1.026174
H	-2.908366	2.033835	-0.708322
H	-4.875009	0.755163	-1.375451
O	-0.477253	2.357683	0.180181
H	-1.111078	2.579153	-0.540059

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -671.040140060 Predicted Change= -1.305953D-08
Zero-point correction (ZPE)= -670.7991 0.24101
Internal Energy (U)= -670.7850 0.25509
Enthalpy (H)= -670.7840 0.25604

Gibbs Free Energy (G)= -670.8413 0.19874

Frequencies -- 19.1123 43.1649 85.6635

Supporting Information: VI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

#pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman

#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H13NO C1[X(C14H13NO)] #Atoms= 29

Charge = 0 Multiplicity = 1

SCF Energy= -670.488666578 Predicted Change= -1.018756D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00260 ||	0.00180	[NO]	0.00260 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.543515	0.642840	-0.101353
C	-1.575640	-0.148401	0.586952
C	-1.646778	-1.548905	0.495293
C	-2.655378	-2.191420	-0.237971
C	-3.617887	-1.410054	-0.898798
C	-3.563053	-0.014128	-0.832445
N	-2.529113	2.032999	0.007650
C	-0.495852	0.522639	1.426741
H	-0.895818	-2.145684	1.027020
H	-2.692703	-3.284457	-0.285780
H	-4.415506	-1.889631	-1.477367
H	-4.309639	0.594860	-1.356444
H	-1.588421	2.444027	0.069271
H	-3.105311	2.509279	-0.689973
H	-0.072749	-0.203447	2.137080
C	0.582122	1.136401	0.529878
H	-0.933379	1.353568	2.011018
C	4.195522	-0.972331	-0.529592
C	3.283106	-1.579510	0.346587
C	2.102688	-0.915727	0.706450

C	1.819352	0.367634	0.188333
C	2.747085	0.967345	-0.694772
C	3.924520	0.305121	-1.050223
H	5.118304	-1.493236	-0.806865
H	3.491292	-2.574341	0.753889
H	1.407020	-1.406966	1.392557
H	2.520160	1.961389	-1.092427
H	4.634612	0.781413	-1.734495
O	0.401022	2.269151	0.048561

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -670.488666578 Predicted Change= -1.018756D-08
Zero-point correction (ZPE)= -670.2571 0.23152
Internal Energy (U)= -670.2437 0.24496
Enthalpy (H)= -670.2427 0.24590
Gibbs Free Energy (G)= -670.2983 0.19034
Entropy (S)= 0.00018637

Frequencies -- 24.1736 40.1972 67.4187

Supporting Information: VII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman 10f 6d
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C6H5IKN C1[X(C6H5IKN)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -897.143051789 Predicted Change= -5.213158D-09

==========
===

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00024 ||	0.00180	[YES]	0.00024 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	-3.571914	0.946779	-0.000056
C	-2.430047	1.744167	-0.000087
C	-1.076639	1.218792	0.000028
C	-1.063587	-0.221918	0.000035
C	-2.196151	-1.035520	-0.000024
C	-3.480210	-0.459634	0.000039
H	-4.557094	1.430233	0.000017
H	-2.530961	2.838283	-0.000055
H	-2.083854	-2.124836	-0.000022
H	-4.371136	-1.095035	0.000132
I	0.871853	-1.233061	-0.000004
N	0.031765	1.983955	0.000131
H	-0.279524	2.968214	-0.000044
K	2.647541	1.804825	-0.000019

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -897.143051789 Predicted Change= -5.213158D-09
Zero-point correction (ZPE)= -897.0515 0.09154
Internal Energy (U)= -897.0421 0.10089
Enthalpy (H)= -897.0412 0.10183
Gibbs Free Energy (G)= -897.0890 0.05396
Entropy (S)= 0.00016056

Frequencies -- 34.0485 83.1072 117.1758

Supporting Information: VII-a (aryl radical)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# opt=(gdiis,maxcycle=250) freq=noraman pbepbe/6-31g(d)/auto
scrf=(smd,solvent=dmso) geom=connectivity density=current
scf=(maxcycle=300,direct,tight,yqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C6H6N(2) C1[X(C6H6N)] #Atoms= 13
Charge = 0 Multiplicity = 2

SCF Energy= -286.562051627 Predicted Change= -5.874005D-09

==========
===

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]

Displ 0.00087 || 0.00180 [YES] 0.00087 || 0.00180 [YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.122858	1.193449	0.002168
C	0.278606	1.161475	-0.001904
C	0.983782	-0.074453	-0.008697
C	0.167017	-1.209467	-0.005451
C	-1.210774	-1.232036	0.005512
C	-1.883884	0.013132	0.004676
H	-1.628826	2.165241	0.008798
H	0.855742	2.095329	0.003850
H	-1.774588	-2.172674	0.013934
H	-2.978669	0.046198	0.007857
N	2.375207	-0.133863	-0.084872
H	2.850694	0.687575	0.295682
H	2.777855	-0.997226	0.286149

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -286.562051627 Predicted Change= -5.874005D-09
Zero-point correction (ZPE)= -286.4603 0.10172
Internal Energy (U)= -286.4544 0.10761
Enthalpy (H)= -286.4534 0.10855
Gibbs Free Energy (G)= -286.4901 0.07189

Frequencies -- 207.9086 338.8596 369.1114

Supporting Information: VII-b (potassium aryl radical)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C6H5KN(2) C1[X(C6H5KN)] #Atoms= 13
Charge = 0 Multiplicity = 2

SCF Energy= -885.666154834 Predicted Change= -5.539803D-06

==========
===

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00026 ||	0.00045	[YES]	0.00004 ||	0.00030	[YES]
Displ	0.26964 ||	0.00180	[NO]	0.26964 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.695133	0.401342	-0.052966
C	-1.594924	1.246506	-0.014874
C	-0.252627	0.699369	0.023679
C	-0.013312	-0.744860	0.039500
C	-1.186472	-1.526519	0.059761
C	-2.496565	-0.999744	-0.022033
H	-3.710505	0.813241	-0.090893
H	-1.731953	2.337621	0.010495
H	-1.104565	-2.625745	0.101672
H	-3.365162	-1.669898	-0.070088
N	0.829974	1.517789	0.055658
H	0.509642	2.502739	0.055032
K	2.790890	-0.338897	-0.031276

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -885.666154834 Predicted Change= -5.539803D-06
Zero-point correction (ZPE)= -885.5775 0.08865
Internal Energy (U)= -885.5696 0.09653
Enthalpy (H)= -885.5686 0.09748
Gibbs Free Energy (G)= -885.6124 0.05367
Entropy (S)= 0.00014694

Frequencies -- 21.6463 132.2998 158.3750

Supporting Information: VII-c

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman 10f 6d
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C6H4IK2N C1[X(C6H4IK2N)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -1496.20028621 Predicted Change= -3.684748D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00117 ||	0.00180	[YES]	0.00117 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.816244	1.971640	0.666786
C	-2.452191	0.635296	0.849304
C	-1.120652	0.015167	0.531404
C	-0.230982	1.153340	0.160342
C	-0.571714	2.484845	-0.032053
C	-1.895928	2.932198	0.202174
H	-3.844879	2.276101	0.909633
H	-3.185555	-0.053547	1.298908
H	0.193171	3.196364	-0.363723
H	-2.167097	3.982152	0.055087
I	1.920925	0.575754	-0.282021
N	-0.875879	-1.260971	0.571942
K	1.225541	-2.732930	0.692989
K	-2.917502	-1.806237	-0.967942

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1496.20028621 Predicted Change= -3.684748D-08
Zero-point correction (ZPE)= -1496.1220 0.07826
Internal Energy (U)= -1496.1103 0.08996
Enthalpy (H)= -1496.1093 0.09090
Gibbs Free Energy (G)= -1496.1639 0.03635
Entropy (S)= 0.00018297

Frequencies -- 33.1959 52.2892 56.5247

Supporting Information: VII-d

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)

freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C6H4K2N(2) C1[X(C6H4K2N)] #Atoms= 13
Charge = 0 Multiplicity = 2

SCF Energy= -1484.73352428 Predicted Change= -3.538179D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.02266 ||	0.00180	[NO]	0.02266 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.379203	-1.788772	-0.413241
C	1.001557	-1.556862	-0.391030
C	0.445347	-0.269243	0.006716
C	1.358626	0.781859	0.506911
C	2.719422	0.416402	0.557145
C	3.261492	-0.808462	0.079809
H	2.766841	-2.749986	-0.779246
H	0.308174	-2.341853	-0.732872
H	3.454736	1.149232	0.940054
H	4.344982	-0.990248	0.088185
N	-0.882883	-0.067641	-0.100225
K	-0.633112	2.608504	-0.235652
K	-3.139964	-1.305514	0.188683

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1484.73352428 Predicted Change= -3.538179D-08
Zero-point correction (ZPE)= -1484.6569 0.07656
Internal Energy (U)= -1484.6471 0.08637
Enthalpy (H)= -1484.6462 0.08732
Gibbs Free Energy (G)= -1484.6966 0.03686
Entropy (S)= 0.00016924

Frequencies -- 15.1017 45.6269 62.8273

Supporting Information: VIII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
-----------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H11N     C1[X(C14H11N)]   #Atoms= 26
 Charge = 0        Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -594.137384026        Predicted Change= -3.298044D-08
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00172 ||   0.00180    [ YES ]       0.00172 ||   0.00180    [ YES ]
-----------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
-----------------------------------------------------------------------------
         C          1.804071       -0.643023       0.000015
         C          1.937863        0.769566       0.000163
         C          3.201903        1.359333       0.000166
         C          4.334390        0.519787       0.000155
         C          4.197057       -0.880808       0.000101
         C          2.927669       -1.482827      -0.000010
         C         -0.281507        0.044429      -0.000198
         C          0.540695        1.325841      -0.000351
         H          3.321182        2.448713       0.000189
         H          5.335188        0.964592       0.000183
         H          5.093006       -1.510966       0.000113
         H          2.812401       -2.571880      -0.000092
         H          0.319471        1.953014      -0.885155
         N          0.451761       -1.049404      -0.000067
         C         -1.749135        0.002696      -0.000144
         C         -2.429470       -1.239131      -0.000100
         C         -2.510870        1.193983      -0.000004
         C         -3.825931       -1.284774       0.000035
         H         -1.841556       -2.162341      -0.000109
         C         -3.910650        1.143864       0.000180
         H         -2.006944        2.166102      -0.000135
         C         -4.573032       -0.093397       0.000210
         H         -4.338050       -2.253000       0.000065
         H         -4.486300        2.075478       0.000334
         H         -5.667601       -0.131254       0.000375
         H          0.318566        1.954134       0.883398
-----------------------------------------------------------------------------
```

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -594.137384026 Predicted Change= -3.298044D-08
Zero-point correction (ZPE)= -593.9326 0.20474
Internal Energy (U)= -593.9213 0.21599
Enthalpy (H)= -593.9204 0.21694
Gibbs Free Energy (G)= -593.9704 0.16692
Entropy (S)= 0.00016776

Frequencies -- 44.9337 61.4899 108.0423

Supporting Information: IX

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman 6d 10f
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H11IKN C1[X(C14H11IKN)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -1205.20465930 Predicted Change= -1.310225D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00261 ||	0.00180	[NO]	0.00261 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.180703	-0.132489	3.011449
C	0.628031	0.265865	1.746021
C	-0.182229	0.152929	0.558039
C	-1.486045	-0.390470	0.804838
C	-1.941378	-0.789602	2.060604
C	-1.104986	-0.666308	3.186767
H	0.851367	-0.018517	3.871639
H	1.644912	0.664273	1.642844
H	-2.950168	-1.200145	2.169182
H	-1.461921	-0.981665	4.172077

I	-2.834439	-0.591032	-0.880858
N	0.154468	0.637687	-0.675775
C	1.467247	0.878849	-1.033706
C	2.562035	-0.094532	-0.677487
C	2.298355	-1.482051	-0.664379
C	3.876245	0.337348	-0.392352
C	3.316282	-2.405943	-0.390680
H	1.285974	-1.834570	-0.888836
C	4.893934	-0.585954	-0.112957
H	4.095660	1.410789	-0.374655
C	4.619124	-1.962715	-0.112205
H	3.090539	-3.478160	-0.395958
H	5.904669	-0.227176	0.111850
H	5.413191	-2.684400	0.107961
C	1.792622	1.959102	-1.831395
H	1.008234	2.615230	-2.233583
H	2.794904	2.078757	-2.251902
K	0.102474	3.158543	0.451048

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1205.20465930 Predicted Change= -1.310225D-08
Zero-point correction (ZPE)= -1205.0024 0.20221
Internal Energy (U)= -1204.9861 0.21850
Enthalpy (H)= -1204.9852 0.21945
Gibbs Free Energy (G)= -1205.0497 0.15494
Entropy (S)= 0.00021635

Frequencies -- 25.4033 37.5788 44.0115

Supporting Information: IX-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

#pbepbe/genecp/auto scf=(maxcycle=300,direct,tight,yqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman 6d 10f
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H12IN C1[X(C14H12IN)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -606.094927016 Predicted Change= -6.151439D-11

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00008 ||	0.00180	[YES]	0.00008 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.165873	2.940613	0.849993
C	-0.615507	1.622093	0.968026
C	0.209704	0.526695	0.608284
C	1.519956	0.833171	0.160714
C	1.982151	2.149378	0.065160
C	1.133067	3.215872	0.399103
H	-0.835678	3.758864	1.135168
H	-1.615480	1.421270	1.361734
H	3.001820	2.343553	-0.279473
H	1.493193	4.245501	0.310791
I	2.876501	-0.754182	-0.388246
N	-0.230286	-0.797015	0.690972
H	0.496347	-1.473972	0.937254
C	-1.543598	-1.224868	0.982967
C	-2.650447	-0.666758	0.155175
C	-2.435887	-0.301813	-1.192590
C	-3.948462	-0.528402	0.694156
C	-3.492993	0.172629	-1.980193
H	-1.436446	-0.410424	-1.626439
C	-5.004630	-0.056765	-0.096180
H	-4.121002	-0.776995	1.746925
C	-4.781463	0.296545	-1.436561
H	-3.309516	0.443645	-3.025587
H	-6.003772	0.046556	0.340772
H	-5.605846	0.672069	-2.052196
C	-1.748307	-2.215241	1.889041
H	-0.925167	-2.608219	2.495403
H	-2.727297	-2.690002	1.993318

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -606.094927016 Predicted Change= -6.151439D-11
Zero-point correction (ZPE)= -605.8797 0.21518
Internal Energy (U)= -605.8653 0.22953
Enthalpy (H)= -605.8644 0.23047
Gibbs Free Energy (G)= -605.9234 0.17145

Frequencies -- 27.4112 45.1504 51.5477

Supporting Information: TS-X

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

#pbepbe/6-31g(d)/auto scrf=(smd,solvent=dmso) guess=(mix,always)
density=current scf=(maxcycle=300,direct,vshift=200,tight,yqc)
opt=(calcfc,ts,gdiis,maxcycle=250,noeigentest,nofreeze) freq=noraman
#P Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H11KN(2) C1[X(C14H11KN)] #Atoms= 27
Charge = 0 Multiplicity = 2

SCF Energy= -1193.73436725 Predicted Change= -6.133867D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00072 ||	0.00180	[YES]	0.00072 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.936369	0.060100	0.012012
C	2.463603	-1.255465	0.126656
C	3.821768	-1.499831	0.285746
C	4.726093	-0.417036	0.424568
C	4.228479	0.896250	0.346578
C	2.863804	1.138606	0.139580
C	-0.186170	-0.791258	-0.389846
C	0.315915	-1.991597	-0.899368
H	4.210596	-2.527861	0.342325
H	5.793806	-0.600762	0.596184
H	4.916301	1.745799	0.437908
H	2.498494	2.172054	0.048988
H	-0.283555	-2.909383	-0.854011
N	0.582367	0.321798	-0.148889
C	-1.619805	-0.679386	0.004479
C	-2.011173	0.142257	1.093511
C	-2.638385	-1.353218	-0.712278
C	-3.362549	0.295238	1.438454
H	-1.232333	0.629852	1.693038
C	-3.986545	-1.211696	-0.358168
H	-2.359783	-1.974873	-1.570594

```
        C          -4.357769        -0.379888         0.711939
        H          -3.636994         0.929336         2.289125
        H          -4.755551        -1.741306        -0.931627
        H          -5.413163        -0.262153         0.979849
        H           1.166404        -2.013359        -1.583984
        K          -0.954873         2.451664        -0.723587
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -1193.73436725      Predicted Change= -6.133867D-10
 Zero-point correction (ZPE)=            -1193.5351       0.19918
 Internal Energy (U)=                  -1193.5212       0.21313
 Enthalpy (H)=                       -1193.5202       0.21407
 Gibbs Free Energy (G)=                -1193.5783       0.15601
 Entropy (S)=                                0.00019476
---------------------------------------------------------------------------
Frequencies --    -183.0764                    37.0681                    46.2719
```

Supporting Information: TS-X-a

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest)
 freq=noraman guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C14H12N(2)     C1[X(C14H12N)]   #Atoms= 27
 Charge = 0       Multiplicity = 2
---------------------------------------------------------------------------
 SCF Energy= -594.622582250       Predicted Change= -7.153669D-09
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00002 ||   0.00045    [ YES ]        0.00000 ||   0.00030    [ YES ]
 Displ        0.00099 ||   0.00180    [ YES ]        0.00099 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type          X              Y          Z
---------------------------------------------------------------------------
        C           1.820992        -0.286218         0.336686
        C           2.209383         0.862776        -0.368925
        C           3.511893         1.062776        -0.798857
```

C	4.467092	0.041412	-0.580907
C	4.088952	-1.126627	0.102831
C	2.778550	-1.300330	0.571675
C	-0.424764	0.589512	0.441462
C	0.047525	1.882654	0.302846
H	3.806004	1.978024	-1.329296
H	5.492986	0.162237	-0.947345
H	4.827737	-1.915075	0.283446
H	2.497259	-2.203282	1.128087
H	-0.562111	2.638569	-0.201634
N	0.491369	-0.404707	0.754558
H	0.163776	-1.311670	1.089836
C	-1.809784	0.176897	0.140508
C	-2.114268	-1.137902	-0.288445
C	-2.874279	1.098605	0.289359
C	-3.435592	-1.512566	-0.561272
H	-1.308207	-1.863916	-0.440127
C	-4.191076	0.724506	0.001219
H	-2.660325	2.108739	0.654719
C	-4.479371	-0.584157	-0.420950
H	-3.649224	-2.532826	-0.897743
H	-4.999765	1.453269	0.122420
H	-5.511986	-0.879113	-0.635663
H	0.892770	2.249962	0.888010

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -594.622582250 Predicted Change= -7.153669D-09
Zero-point correction (ZPE)= -594.4100 0.21250
Internal Energy (U)= -594.3982 0.22436
Enthalpy (H)= -594.3972 0.22531
Gibbs Free Energy (G)= -594.4491 0.17345

Frequencies -- -225.1734 46.3366 68.6451

Supporting Information: XI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman 10f 6d
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C14H11IKN C1[X(C14H11IKN)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -1205.32576013 Predicted Change= -5.804816D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00994 ||	0.00180	[NO]	0.00994 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.663439	-1.074240	-0.408840
C	-3.545840	-0.674552	0.625862
C	-4.538904	-1.543485	1.079094
C	-4.638531	-2.816243	0.483191
C	-3.758708	-3.207351	-0.543323
C	-2.754801	-2.339856	-1.004891
C	-1.983456	0.967731	0.070266
C	-3.142005	0.719089	1.017622
H	-5.227166	-1.250167	1.879391
H	-5.411995	-3.511806	0.825284
H	-3.858181	-4.202544	-0.989513
H	-2.071452	-2.639404	-1.807337
H	-2.825262	0.801463	2.075439
N	-1.724150	-0.059449	-0.716073
C	-1.200173	2.208967	0.008551
C	-1.058459	3.034263	1.147732
C	-0.559971	2.594570	-1.196185
C	-0.268830	4.189475	1.091837
H	-1.548790	2.756141	2.086150
C	0.228547	3.750099	-1.246122
H	-0.741030	2.016301	-2.110253
C	0.383440	4.546544	-0.098915
H	-0.159774	4.813165	1.985111
H	0.708622	4.039077	-2.186976
H	0.999457	5.450845	-0.137815
H	-3.942129	1.471519	0.880649
I	3.674209	-1.222127	0.435501
K	0.969497	-0.351883	-1.406550

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===
SCF Energy= -1205.32576013 Predicted Change= -5.804816D-09
Zero-point correction (ZPE)= -1205.1202 0.20555
Internal Energy (U)= -1205.1040 0.22174
Enthalpy (H)= -1205.1030 0.22268
Gibbs Free Energy (G)= -1205.1729 0.15284
Entropy (S)= 0.00023424

Frequencies -- 2.3789 6.4120 30.7383

Supporting Information: XI-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# opt=(gdiis,maxcycle=250) freq=noraman pbepbe/genecp/auto
scrf=(smd,solvent=dmso) guess=(mix,always) density=current 10f 6d
scf=(maxcycle=300,direct,tight,yqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---
Pointgroup= C1 Stoichiometry= C14H12IN C1[X(C14H12IN)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -606.170633520 Predicted Change= -6.915027D-09
==========
===
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00354 ||	0.00180	[NO]	0.00354 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.969155	-0.244561	-0.242669
C	2.237584	0.670319	0.540806
C	2.814532	1.897515	0.870515
C	4.113998	2.169212	0.403821
C	4.823185	1.236328	-0.377525
C	4.258613	-0.001763	-0.720442
C	0.975211	-1.289657	0.165715
C	0.901637	0.050595	0.842859
H	2.271945	2.631117	1.474916
H	4.583270	3.126230	0.652674
H	5.832118	1.478437	-0.725394

H	4.795584	-0.736205	-1.327582
H	0.044671	0.640386	0.440602
N	2.163099	-1.386949	-0.429343
C	-0.053909	-2.307684	0.136207
C	-1.297467	-2.037756	0.763179
C	0.142050	-3.560878	-0.501856
C	-2.314359	-2.994972	0.750067
H	-1.467416	-1.074067	1.252295
C	-0.880145	-4.510009	-0.506904
H	1.090501	-3.802382	-0.992638
C	-2.108922	-4.231389	0.117625
H	-3.270657	-2.775589	1.234510
H	-0.719921	-5.473948	-0.999500
H	-2.906703	-4.981253	0.110000
H	0.695740	-0.062647	1.924052
I	-2.416053	2.148334	-0.235980
H	2.473025	-2.194921	-0.980003

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -606.170633520 Predicted Change= -6.915027D-09
Zero-point correction (ZPE)= -605.9523 0.21824
Internal Energy (U)= -605.9383 0.23230
Enthalpy (H)= -605.9373 0.23324
Gibbs Free Energy (G)= -605.9989 0.17172

Frequencies -- 15.8388 17.1088 35.0748

Supporting Information: TS-XII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd)
opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C11H14K2NO(2) C1[X(C11H14K2NO)] #Atoms= 29
Charge = 0 Multiplicity = 2

SCF Energy= -1756.22636895 Predicted Change= -1.856591D-11

==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00007 ||	0.00180	[YES]	0.00007 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.653479	0.314065	0.081063
C	2.213775	0.438491	0.139092
C	1.507191	-0.774057	-0.195034
C	2.149720	-1.938721	-0.598615
C	3.564616	-2.023191	-0.639029
C	4.297196	-0.871727	-0.294841
H	4.256500	1.201342	0.330254
H	1.557589	-2.823789	-0.880297
H	4.067933	-2.952496	-0.931423
H	5.394680	-0.892355	-0.326907
N	1.557895	1.585698	0.509213
H	2.278805	2.283483	0.755881
C	-0.694167	-0.469324	-1.394371
H	-0.074627	0.364076	-1.741446
H	-0.592503	-1.393908	-1.971855
C	-1.831687	-0.257401	-0.602869
C	-2.830995	-1.419826	-0.416625
H	-2.493389	-2.274258	-1.033262
C	-2.892091	-1.881454	1.052881
H	-3.165052	-1.037818	1.714441
H	-3.654358	-2.669526	1.192105
H	-1.927236	-2.309700	1.388551
C	-4.228222	-0.986714	-0.897232
H	-4.565112	-0.100454	-0.331024
H	-4.217337	-0.720063	-1.969879
H	-4.969467	-1.793896	-0.754595
O	-2.077663	0.843166	0.056010
K	-0.274024	0.138453	1.911203
K	-0.548780	2.834879	-0.693289

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
===
SCF Energy= -1756.22636895 Predicted Change= -1.856591D-11
Zero-point correction (ZPE)= -1756.0100 0.21636
Internal Energy (U)= -1755.9923 0.23400

Enthalpy (H)= -1755.9914 0.23494
Gibbs Free Energy (G)= -1756.0575 0.16885
Entropy (S)= 0.00022168

Frequencies -- -87.7659 36.6147 46.6689

Supporting Information: XIII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C11H14K2NO(2) C1[X(C11H14K2NO)] #Atoms= 29
Charge = 0 Multiplicity = 2

SCF Energy= -1756.26808657 Predicted Change= -3.192979D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00127 ||	0.00180	[YES]	0.00127 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.994925	-0.417785	0.051463
C	-1.662667	-0.575484	-0.486924
C	-1.034796	0.651974	-0.947337
C	-1.716716	1.879835	-0.863328
C	-3.013221	1.989634	-0.337009
C	-3.643112	0.815163	0.123759
H	-3.508204	-1.324049	0.402186
H	-1.214127	2.776952	-1.248757
H	-3.523259	2.957633	-0.301433
H	-4.657434	0.863927	0.540097
N	-1.015285	-1.774444	-0.541106
H	-1.693881	-2.494904	-0.238257
C	0.369576	0.616974	-1.537687
H	0.516663	-0.293594	-2.147027
H	0.532568	1.502477	-2.176341
C	1.343387	0.644018	-0.368638

C	1.742592	2.014482	0.176131
H	0.937362	2.728371	-0.074930
C	1.971105	2.008386	1.691714
H	2.711823	1.242549	1.979068
H	2.342852	2.992198	2.027256
H	1.031953	1.807416	2.241113
C	3.017222	2.451132	-0.587631
H	3.859118	1.772998	-0.361237
H	2.860205	2.455207	-1.680677
H	3.303368	3.472144	-0.280884
O	1.779658	-0.403807	0.153109
K	-0.185992	-1.253936	2.199724
K	1.401784	-2.813314	-1.021007

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1756.26808657 Predicted Change= -3.192979D-09
Zero-point correction (ZPE)= -1756.0463 0.22170
Internal Energy (U)= -1756.0287 0.23929
Enthalpy (H)= -1756.0278 0.24023
Gibbs Free Energy (G)= -1756.0951 0.17297
Entropy (S)= 0.0002256

Frequencies -- 24.0434 35.0177 46.4321

Supporting Information: XIII-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C11H14KNO C1[X(C11H14KNO)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -1156.60066686 Predicted Change= -2.461617D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00086 ||	0.00180	[YES]	0.00086 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.522666	1.179721	0.995975
C	-1.259664	0.933362	0.349956
C	-1.279758	-0.066787	-0.699541
C	-2.464694	-0.732284	-1.037389
C	-3.685698	-0.465691	-0.386568
C	-3.691078	0.500655	0.638494
H	-2.551417	1.929032	1.799925
H	-2.429196	-1.487902	-1.834757
H	-4.598942	-1.001322	-0.665937
H	-4.625076	0.729172	1.168844
N	-0.088974	1.547671	0.663395
H	-0.267931	2.150836	1.484583
C	0.020417	-0.357635	-1.411339
H	0.356682	0.495082	-2.037779
H	-0.122283	-1.215089	-2.101241
C	1.202637	-0.719720	-0.506842
C	0.980590	-1.760369	0.591239
H	-0.078001	-1.701524	0.901751
C	1.219670	-3.160895	-0.021409
H	2.260842	-3.258950	-0.377660
H	1.043025	-3.938778	0.741938
H	0.543327	-3.359657	-0.870950
C	1.892687	-1.513048	1.798841
H	2.955516	-1.543191	1.503270
H	1.685597	-0.525708	2.248928
H	1.725592	-2.283607	2.571699
O	2.342989	-0.288237	-0.747335
K	2.289816	2.287366	-0.266643

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1156.60066686 Predicted Change= -2.461617D-09
Zero-point correction (ZPE)= -1156.3795 0.22109
Internal Energy (U)= -1156.3643 0.23628
Enthalpy (H)= -1156.3634 0.23722
Gibbs Free Energy (G)= -1156.4230 0.17762
Entropy (S)= 0.00019991

Frequencies -- 33.6497 35.8917 58.9859

Supporting Information: XIV

```
---------------------------------------------------------------------------
Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C11H15NO     C1[X(C11H15NO)]   #Atoms= 28
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -557.498231225       Predicted Change= -1.573274D-08
===========================================================================
===
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00233 ||   0.00180    [ NO ]        0.00233 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type          X              Y          Z
---------------------------------------------------------------------------
         C          -2.979219       -0.557782       -0.478199
         C          -1.725622       -0.866152        0.102806
         C          -0.908775        0.203775        0.577098
         C          -1.357130        1.527095        0.423751
         C          -2.596069        1.824303       -0.164137
         C          -3.407651        0.767757       -0.608818
         H          -3.609355       -1.380902       -0.836297
         H          -0.719684        2.339807        0.793004
         H          -2.925291        2.863554       -0.264002
         H          -4.380393        0.974891       -1.069140
         N          -1.325718       -2.191404        0.277943
         H          -1.854540       -2.860453       -0.286483
         H          -0.311985       -2.340262        0.187312
         C           0.422010       -0.090579        1.255304
         H           0.311625       -0.931406        1.965891
         H           0.754054        0.800957        1.812133
         C           1.469548       -0.484369        0.208327
         C           2.410182        0.609826       -0.288778
         H           1.817523        1.544122       -0.341371
         C           3.518182        0.817181        0.772657
         H           4.135000       -0.093343        0.874902
         H           4.178241        1.645743        0.462876
         H           3.103811        1.066536        1.764681
         C           3.003261        0.287579       -1.663474
         H           3.579946       -0.652411       -1.633113
```

```
        H          2.213991        0.174813       -2.426708
        H          3.679641        1.097744       -1.986452
        O          1.526893       -1.642671       -0.222757
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -557.498231225 Predicted Change= -1.573274D-08
 Zero-point correction (ZPE)=            -557.2634   0.23476
 Internal Energy (U)=                    -557.2502   0.24798
 Enthalpy (H)=                           -557.2492   0.24893
 Gibbs Free Energy (G)=                  -557.3033   0.19492
---------------------------------------------------------------------------
Frequencies --       34.9006                    52.0367                    75.2110
```

Supporting Information: XV

```
---------------------------------------------------------------------------
Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C11H13N     C1[X(C11H13N)]   #Atoms= 25
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -481.142735826       Predicted Change= -6.722625D-10
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00036 ||   0.00180    [ YES ]       0.00036 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic             Coordinates (Angstroms)
         Type          X              Y          Z
---------------------------------------------------------------------------
        C          1.081882       -0.772334       -0.153683
        C          0.909112        0.622426        0.030465
        C          2.005051        1.474413        0.220016
        C          3.289935        0.903127        0.222500
        C          3.466827       -0.480418        0.040326
        C          2.360051       -1.332658       -0.149307
        C         -0.298534       -1.347007       -0.318659
        C         -1.154196       -0.092153       -0.202193
```

H	1.860012	2.550815	0.361602
H	4.165566	1.545063	0.368274
H	4.477776	-0.901880	0.045859
H	2.509068	-2.409381	-0.289947
H	-0.458153	-1.852578	-1.290982
N	-0.460069	1.000984	-0.007344
H	-0.557502	-2.092822	0.457305
C	-2.659495	-0.104443	-0.305087
H	-2.905440	-0.612264	-1.260689
C	-3.267937	1.303765	-0.327078
H	-2.854145	1.912463	-1.148855
H	-4.361731	1.240120	-0.461039
H	-3.069148	1.837418	0.618813
C	-3.276349	-0.959465	0.827293
H	-4.374064	-0.993619	0.714946
H	-2.902480	-1.997317	0.811832
H	-3.047354	-0.524416	1.816739

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -481.142735826 Predicted Change= -6.722625D-10
Zero-point correction (ZPE)= -480.9347 0.20800
Internal Energy (U)= -480.9237 0.21898
Enthalpy (H)= -480.9228 0.21992
Gibbs Free Energy (G)= -480.9719 0.17083

Frequencies -- 22.1699 83.7711 153.9632

Supporting Information: TS-XVI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd)
opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C11H14K2NO(2) C1[X(C11H14K2NO)] #Atoms= 29
Charge = 0 Multiplicity = 2

SCF Energy= -1756.21977095 Predicted Change= -2.530044D-09

==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00058 ||	0.00180	[YES]	0.00058 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.781564	-1.529651	-0.110494
C	-1.416922	-1.065435	-0.001421
C	-1.250638	0.376565	0.055445
C	-2.369829	1.212885	0.051103
C	-3.699136	0.726389	-0.012151
C	-3.881694	-0.664983	-0.109440
H	-2.950350	-2.616026	-0.184560
H	-2.228202	2.303709	0.098104
H	-4.554691	1.412913	0.003074
H	-4.893619	-1.084935	-0.188254
N	-0.349772	-1.930799	0.085023
H	-0.742660	-2.887609	0.073351
C	0.632197	1.395812	-0.872458
C	1.702523	1.282078	0.067198
C	0.074689	2.783707	-1.140681
H	0.787496	3.396101	-1.733966
H	-0.861439	2.731693	-1.722789
H	-0.142622	3.349649	-0.218193
C	0.664862	0.495748	-2.102156
H	1.674142	0.470601	-2.566714
H	0.350802	-0.537991	-1.873875
H	-0.033582	0.866787	-2.873520
C	1.923919	2.396772	1.092186
H	1.028482	2.584761	1.726258
H	2.766054	2.122258	1.750229
H	2.164134	3.370548	0.624129
O	2.428757	0.205565	0.204346
K	0.612617	-0.439133	2.139930
K	2.180223	-2.090904	-0.910772

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
===
SCF Energy= -1756.21977095 Predicted Change= -2.530044D-09
Zero-point correction (ZPE)= -1756.0038 0.21592
Internal Energy (U)= -1755.9861 0.23363

Enthalpy (H)= -1755.9851 0.23457
Gibbs Free Energy (G)= -1756.0502 0.16954
Entropy (S)= 0.0002181

Frequencies -- -193.5473 48.4763 61.8423

Supporting Information: XVII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C11H14K2NO(2) C1[X(C11H14K2NO)] #Atoms= 29
Charge = 0 Multiplicity = 2

SCF Energy= -1756.25908685 Predicted Change= -4.079235D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00109 ||	0.00180	[YES]	0.00109 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.176492	-1.008424	-1.143580
C	-0.911270	-0.402456	-0.806584
C	-0.980458	0.927834	-0.220228
C	-2.234693	1.511581	0.021217
C	-3.452623	0.879429	-0.297818
C	-3.406453	-0.389882	-0.897163
H	-2.153264	-1.991281	-1.638006
H	-2.277729	2.511074	0.466873
H	-4.406164	1.378256	-0.095550
H	-4.333876	-0.906528	-1.175835
N	0.283830	-1.044567	-0.981988
H	0.080391	-1.916114	-1.504463
C	0.324562	1.694834	0.064429
C	1.258172	0.883118	0.990184
C	0.094474	3.018397	0.848591
H	1.064710	3.500872	1.061642

```
H          -0.500209          3.722069          0.240823
H          -0.430194          2.861241          1.805897
C           1.032483          2.049398         -1.261614
H           2.043088          2.454340         -1.079852
H           1.111513          1.162894         -1.913064
H           0.444123          2.812200         -1.800328
C           0.684252          0.353585          2.290278
H          -0.414313          0.259682          2.271689
H           1.160515         -0.610897          2.548084
H           0.945175          1.053684          3.105948
O           2.471932          0.754252          0.761339
K          -0.609073         -2.810930          1.158634
K           2.951823         -0.984756         -1.107946
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=========================================================================
===
 SCF Energy=       -1756.25908685      Predicted Change= -4.079235D-09
 Zero-point correction (ZPE)=            -1756.0382       0.22087
 Internal Energy (U)=                  -1756.0207       0.23833
 Enthalpy (H)=                       -1756.0198       0.23928
 Gibbs Free Energy (G)=                -1756.0855       0.17356
 Entropy (S)=                                0.00022044
---------------------------------------------------------------------------
 Frequencies --        30.6709                    35.1129                    50.5828
```

Supporting Information: XVII-a

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C11H14KNO     C1[X(C11H14KNO)]   #Atoms= 28
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1156.59366210       Predicted Change= -1.024013D-09
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00000 ||   0.00045     [ YES ]        0.00000 ||   0.00030     [ YES ]
 Displ        0.00032 ||   0.00180     [ YES ]        0.00032 ||   0.00180     [ YES ]
```

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.111192	-1.916100	-0.186207
C	0.911721	-1.125930	-0.051025
C	1.120231	0.295823	0.201172
C	2.424546	0.809191	0.269256
C	3.572627	0.006418	0.120613
C	3.393129	-1.371329	-0.105705
H	1.987901	-2.993149	-0.371159
H	2.564557	1.881774	0.446351
H	4.573066	0.447694	0.181617
H	4.264883	-2.028556	-0.224077
N	-0.338681	-1.641309	-0.162792
H	-0.230900	-2.647564	-0.377972
C	-0.111171	1.185724	0.425679
C	-1.111808	1.031514	-0.742446
C	0.215517	2.705873	0.429617
H	-0.712672	3.290192	0.558831
H	0.880259	2.947901	1.276799
H	0.708263	3.040589	-0.498689
C	-0.778535	0.848236	1.778003
H	-1.768852	1.328214	1.870077
H	-0.889386	-0.243495	1.895372
H	-0.142206	1.208433	2.604800
C	-0.565759	1.056241	-2.156128
H	-0.399944	0.006806	-2.462332
H	-1.309606	1.499122	-2.837941
H	0.396886	1.583867	-2.241058
O	-2.337977	0.977236	-0.555092
K	-2.944095	-1.410764	0.308563

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1156.59366210 Predicted Change= -1.024013D-09
Zero-point correction (ZPE)= -1156.3732 0.22038
Internal Energy (U)= -1156.3580 0.23558
Enthalpy (H)= -1156.3571 0.23652
Gibbs Free Energy (G)= -1156.4150 0.17859
Entropy (S)= 0.0001943

Frequencies -- 50.1367 67.6538 91.5788

```
---------------------------------------------------------------------------
Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C11H15NO     C1[X(C11H15NO)]   #Atoms= 28
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -557.487293249       Predicted Change= -6.649185D-09
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00072 ||   0.00180    [ YES ]       0.00072 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type          X              Y          Z
---------------------------------------------------------------------------
         C            2.423077       -1.132082       0.022805
         C            1.030522       -0.979604       0.230818
         C            0.456401        0.331994       0.183637
         C            1.318894        1.415320      -0.076642
         C            2.697976        1.255687      -0.277748
         C            3.248879       -0.032954      -0.225356
         H            2.846261       -2.143408       0.059647
         H            0.901603        2.425177      -0.124921
         H            3.328425        2.128578      -0.475932
         H            4.321834       -0.188198      -0.384635
         N            0.284473       -2.123064       0.537585
         H           -0.708585       -2.108612       0.301825
         H            0.717725       -2.994116       0.222588
         C           -1.048319        0.547452       0.434567
         C           -1.885356       -0.275443      -0.585959
         C           -1.497136        2.015833       0.206360
         H           -2.586733        2.095852       0.363688
         H           -1.005625        2.682037       0.936190
         H           -1.268768        2.385028      -0.806969
         C           -1.424113        0.166388       1.883806
         H           -2.513934        0.244123       2.031144
         H           -1.119656       -0.860470       2.142498
         H           -0.924840        0.856965       2.584779
         C           -1.505751       -0.187852      -2.054246
         H           -0.847413       -1.044934      -2.292273
```

```
        H          -2.409670        -0.282332        -2.677203
        H          -0.956153         0.730683        -2.311568
        O          -2.832028        -0.976669        -0.223026
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=========================================================================
===
 SCF Energy=       -557.487293249 Predicted Change= -6.649185D-09
 Zero-point correction (ZPE)=            -557.2538   0.23339
 Internal Energy (U)=                    -557.2403   0.24695
 Enthalpy (H)=                           -557.2393   0.24790
 Gibbs Free Energy (G)=                  -557.2928   0.19440
---------------------------------------------------------------------------
 Frequencies --       55.1301                    76.1023                    93.8275
```

Supporting Information: XIX

```
---------------------------------------------------------------------------
Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C11H13N     C1[X(C11H13N)]   #Atoms= 25
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -481.143225474       Predicted Change= -1.157702D-08
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]        0.00000 ||   0.00030    [ YES ]
 Displ        0.00130 ||   0.00180    [ YES ]        0.00130 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic             Coordinates (Angstroms)
         Type          X              Y          Z
---------------------------------------------------------------------------
        C           0.456394        -0.450234         0.000060
        C           0.699953         0.942867         0.000027
        C           2.003214         1.456113        -0.000032
        C           3.071204         0.540553        -0.000005
        C           2.834679        -0.845857         0.000082
        C           1.519192        -1.354086         0.000121
        C          -1.049084        -0.640893         0.000031
        C          -1.489848         0.833323         0.000228
```

H	2.180240	2.537098	-0.000071
H	4.101383	0.913012	-0.000042
H	3.682394	-1.539564	0.000130
H	1.345119	-2.436705	0.000186
N	-0.506320	1.696140	0.000122
C	-2.921207	1.258370	0.000300
H	-3.452592	0.860675	0.885333
H	-3.000071	2.356870	0.001105
H	-3.452200	0.862019	-0.885589
C	-1.547319	-1.372741	-1.268419
H	-1.148896	-2.402171	-1.289322
H	-2.649720	-1.432720	-1.275185
H	-1.219999	-0.857403	-2.187665
C	-1.547518	-1.373740	1.267718
H	-1.148994	-2.403145	1.287925
H	-1.220473	-0.859100	2.187457
H	-2.649913	-1.433884	1.274217

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -481.143225474 Predicted Change= -1.157702D-08
Zero-point correction (ZPE)= -480.9357 0.20751
Internal Energy (U)= -480.9244 0.21873
Enthalpy (H)= -480.9235 0.21967
Gibbs Free Energy (G)= -480.9717 0.17147

Frequencies -- 79.7963 118.7784 139.2886

Supporting Information: TS-XX

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd)
opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H14K2NO(2) C1[X(C15H14K2NO)] #Atoms= 33
Charge = 0 Multiplicity = 2

SCF Energy= -1908.48199217 Predicted Change= -4.003716D-09

==========
===
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00182 ||	0.00180	[NO]	0.00182 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-2.112260	0.855014	-1.350299
C	-2.519294	-0.234860	-0.623271
C	-3.713785	-0.999428	-0.910818
C	-4.102343	-2.112831	-0.155514
C	-3.336897	-2.558003	0.938387
C	-2.159868	-1.832658	1.255041
C	-1.760426	-0.745399	0.489452
C	-0.403560	0.877807	1.991071
C	0.814216	1.298707	1.449485
O	0.952214	2.142948	0.471729
K	0.501762	0.026064	-1.284390
C	2.111907	0.613097	1.962829
C	2.684903	-0.283840	0.888312
C	3.492021	0.248225	-0.142701
C	3.871511	-0.540057	-1.243213
C	3.455135	-1.880107	-1.331577
C	2.672571	-2.430294	-0.299690
C	2.292259	-1.638348	0.796458
H	-2.792340	0.982483	-2.117444
H	-4.343095	-0.669410	-1.752189
H	-5.027527	-2.639432	-0.424945
H	-3.638995	-3.431502	1.528276
H	-1.552713	-2.153314	2.115976
H	-1.330530	1.432118	1.808398
H	-0.425430	0.202106	2.851418
H	1.902307	0.031475	2.876588
H	2.835051	1.410361	2.215933
H	3.813318	1.293644	-0.084445
H	4.493372	-0.105659	-2.034044
H	3.747612	-2.494124	-2.190165
H	2.354239	-3.477479	-0.350716
H	1.665359	-2.068951	1.586615
K	-1.287163	3.230090	-0.333321

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===
SCF Energy= -1908.48199217 Predicted Change= -4.003716D-09
Zero-point correction (ZPE)= -1908.2414 0.24052
Internal Energy (U)= -1908.2221 0.25988
Enthalpy (H)= -1908.2211 0.26082
Gibbs Free Energy (G)= -1908.2919 0.19006
Entropy (S)= 0.00023733

Frequencies -- -112.0554 26.1340 41.6905

Supporting Information: TS-XXI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd)
opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C15H14K2NO(2) C1[X(C15H14K2NO)] #Atoms=
33
Charge = 0 Multiplicity = 2

SCF Energy= -1908.46910978 Predicted Change= 4.599024D-09
==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00094 ||	0.00180	[YES]	0.00094 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-2.015298	1.120402	-1.424860
C	-2.619691	0.140153	-0.694699
C	-3.921623	-0.412912	-1.017899
C	-4.535810	-1.422008	-0.264932
C	-3.911929	-1.967700	0.871507
C	-2.633146	-1.455682	1.219352
C	-2.027851	-0.455580	0.476233
C	0.242182	-0.213198	1.288344
C	0.990693	-1.072382	0.352773
C	1.059581	-0.793435	-1.041089

C	1.904600	-1.528182	-1.888818
C	2.695863	-2.575242	-1.380317
C	2.600886	-2.901547	-0.014045
C	1.759531	-2.165075	0.835157
C	0.542081	1.164731	1.415925
O	1.280994	1.852952	0.586665
K	3.502504	0.564021	0.151470
C	-0.084109	1.929379	2.574382
H	-2.647609	1.331526	-2.216716
H	-4.439518	-0.013190	-1.904818
H	-5.523652	-1.788471	-0.576455
H	-4.390421	-2.756535	1.464442
H	-2.115853	-1.874125	2.098710
H	-0.117164	-0.708217	2.198169
H	0.414294	-0.008294	-1.452897
H	1.940320	-1.286451	-2.957894
H	3.361474	-3.140587	-2.041079
H	3.194578	-3.726855	0.395230
H	1.717187	-2.413509	1.902915
H	-0.604668	1.272461	3.291806
H	0.686510	2.509780	3.115085
H	-0.825854	2.666294	2.199593
K	-0.300295	3.101339	-1.026555

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1908.46910978 Predicted Change= 4.599024D-09
Zero-point correction (ZPE)= -1908.2295 0.23953
Internal Energy (U)= -1908.2096 0.25947
Enthalpy (H)= -1908.2086 0.26042
Gibbs Free Energy (G)= -1908.2816 0.18742
Entropy (S)= 0.00024482

Frequencies -- -163.8134 25.9531 32.5133

Supporting Information: TS-XXII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd)
opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest) freq=noraman
guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq

---
Pointgroup= C1 Stoichiometry= C15H14K2NO(2) C1[X(C15H14K2NO)] #Atoms= 33
Charge = 0 Multiplicity = 2

SCF Energy= -1908.47385314 Predicted Change= -7.970428D-10
==========
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00296 ||	0.00180	[NO]	0.00296 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.977187	2.089167	0.948268
C	-1.936315	1.202937	-0.082020
C	-3.086933	0.820450	-0.880081
C	-2.979395	0.017533	-2.029294
C	-1.734704	-0.517358	-2.424757
C	-0.601097	-0.227937	-1.612464
C	-0.670358	0.597706	-0.488306
C	0.758238	-0.032970	1.114201
C	2.006962	-0.282081	0.386635
C	2.987739	0.747055	0.304043
C	4.186114	0.571821	-0.398350
C	4.457528	-0.646053	-1.046712
C	3.511179	-1.683140	-0.965651
C	2.306931	-1.508238	-0.270421
C	-0.014690	-1.067111	1.758327
O	-0.097060	-2.279187	1.349485
K	-2.353469	-2.110917	0.055046
C	-0.859155	-0.630018	2.957635
H	-2.954062	2.409849	1.050956
H	-4.069731	1.230249	-0.599625
H	-3.882340	-0.199831	-2.615415
H	-1.640511	-1.121636	-3.335257
H	0.367946	-0.672112	-1.890299
H	0.772240	0.902060	1.691848
H	2.824000	1.688613	0.848079
H	4.918221	1.387462	-0.430696
H	5.394908	-0.787410	-1.595460
H	3.713595	-2.644278	-1.453875
H	1.580682	-2.321816	-0.189404
H	-1.384299	0.322563	2.746901

```
        H          -1.595519        -1.412224         3.216180
        H          -0.227075        -0.462759         3.852011
        K           0.290652         3.222234         0.120406
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -1908.47385314      Predicted Change= -7.970428D-10
 Zero-point correction (ZPE)=            -1908.2337       0.24007
 Internal Energy (U)=                  -1908.2141       0.25966
 Enthalpy (H)=                       -1908.2132       0.26061
 Gibbs Free Energy (G)=                -1908.2849       0.18895
 Entropy (S)=                                0.00024035
---------------------------------------------------------------------------
 Frequencies --     -221.2427                    14.7021                    36.5730
```

Supporting Information: XXIII

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C15H14K2NO(2)     C1[X(C15H14K2NO)]   #Atoms=
33
 Charge = 0       Multiplicity = 2
---------------------------------------------------------------------------
 SCF Energy= -1908.50943670       Predicted Change= -4.543491D-08
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00177 ||   0.00180    [ YES ]       0.00177 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X             Y             Z
---------------------------------------------------------------------------
        N           1.567069        -1.054858        -1.368886
        C           2.276405        -0.083592        -0.735615
        C           3.623894         0.264874        -1.128018
        C           4.386971         1.251246        -0.499089
        C           3.857003         1.971317         0.587585
```

C	2.546369	1.661508	0.997392
C	1.737322	0.686026	0.381519
C	0.328727	0.489135	0.986502
C	-0.786283	1.128745	0.174934
C	-1.033913	0.785628	-1.174568
C	-2.131231	1.325749	-1.867631
C	-3.010952	2.223981	-1.227647
C	-2.772057	2.582151	0.110469
C	-1.674666	2.035073	0.803442
C	-0.037443	-0.955169	1.414370
O	-1.078994	-1.594976	0.929580
K	-3.360514	-0.588169	0.456818
C	1.017481	-1.736488	2.154042
H	2.173296	-1.407021	-2.130651
H	4.052004	-0.287818	-1.977566
H	5.405690	1.454014	-0.856016
H	4.439450	2.742759	1.103029
H	2.115003	2.216516	1.843833
H	0.374255	1.074710	1.930826
H	-0.343191	0.078403	-1.655853
H	-2.305170	1.044832	-2.913161
H	-3.867446	2.641859	-1.767864
H	-3.442228	3.284324	0.619585
H	-1.506110	2.311438	1.851827
H	1.720123	-1.082638	2.701884
H	0.554695	-2.433471	2.877398
H	1.657532	-2.373285	1.477370
K	0.027294	-3.143509	-0.816039

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1908.50943670 Predicted Change= -4.543491D-08
Zero-point correction (ZPE)= -1908.2677 0.24173
Internal Energy (U)= -1908.2482 0.26118
Enthalpy (H)= -1908.2473 0.26212
Gibbs Free Energy (G)= -1908.3172 0.19215
Entropy (S)= 0.00023469

Frequencies -- 32.9059 44.6041 52.6435

Supporting Information: XXIV

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

```
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C15H14K2NO(2)     C1[X(C15H14K2NO)]   #Atoms=
33
 Charge = 0       Multiplicity = 2
---------------------------------------------------------------------------
 SCF Energy= -1908.51068931       Predicted Change= -7.820060D-08
===========================================================================
===
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]        0.00000 ||   0.00030    [ YES ]
 Displ        0.00779 ||   0.00180    [ NO ]         0.00779 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
---------------------------------------------------------------------------
         N          -2.148843       1.164475      -0.732045
         C          -1.784123      -0.122227      -0.929315
         C          -2.678700      -1.144288      -1.433737
         C          -2.308312      -2.486699      -1.554907
         C          -1.010884      -2.912116      -1.194788
         C          -0.099128      -1.937017      -0.733224
         C          -0.441256      -0.585241      -0.587665
         C           0.517200       0.435506       0.008219
         C           2.001055       0.101866      -0.149101
         C           2.735617       0.641211      -1.224678
         C           4.095583       0.341375      -1.390737
         C           4.748201      -0.504022      -0.479129
         C           4.029865      -1.045022       0.598296
         C           2.668966      -0.742447       0.762664
         C           0.211874       0.739305       1.491025
         O          -0.462252      -0.025260       2.213355
         K          -2.208028      -1.869821       1.542101
         C           0.725283       2.052579       2.022011
         H          -3.136260       1.240267      -1.033401
         H          -3.695966      -0.834569      -1.710848
         H          -3.040158      -3.213177      -1.930918
         H          -0.707133      -3.958852      -1.295518
         H           0.916147      -2.251776      -0.462947
         H           0.350765       1.396365      -0.527630
         H           2.232099       1.306600      -1.936856
         H           4.648275       0.774468      -2.231936
         H           5.811416      -0.735481      -0.605107
```

H	4.530044	-1.702301	1.318295
H	2.120451	-1.163494	1.613377
H	-0.040789	2.851124	1.842823
H	0.881189	2.005603	3.111674
H	1.649086	2.381661	1.519816
K	-1.699692	3.814965	-0.567519

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1908.51068931 Predicted Change= -7.820060D-08
Zero-point correction (ZPE)= -1908.2670 0.24366
Internal Energy (U)= -1908.2473 0.26333
Enthalpy (H)= -1908.2464 0.26428
Gibbs Free Energy (G)= -1908.3187 0.19189
Entropy (S)= 0.00024278

Frequencies -- 22.5041 29.8948 39.3452

Supporting Information: XXIV-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H14KNO C1[X(C15H14KNO)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1308.84089126 Predicted Change= -2.081364D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00125 ||	0.00180	[YES]	0.00125 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.591793	-1.760929	-1.486988
C	1.519213	-1.329602	-0.592775
C	2.625204	-2.128918	-0.122297

C	3.538307	-1.674468	0.829863
C	3.423485	-0.384039	1.384299
C	2.374084	0.437535	0.931588
C	1.447161	0.013844	-0.034080
C	0.350545	0.939096	-0.559510
C	-1.032386	0.707487	0.040674
C	-2.181244	0.936448	-0.749060
C	-3.469044	0.685333	-0.246194
C	-3.631478	0.201360	1.065185
C	-2.496857	-0.009259	1.868564
C	-1.210477	0.245492	1.360236
C	0.781405	2.413994	-0.434982
C	1.753836	2.902850	-1.492871
O	0.359867	3.153982	0.452728
H	0.885641	-2.706195	-1.788941
H	2.733655	-3.139797	-0.541149
H	4.353962	-2.337163	1.148379
H	4.130708	-0.023166	2.138165
H	2.281859	1.451469	1.342494
H	0.266551	0.722802	-1.644322
H	-2.060762	1.295057	-1.778746
H	-4.344942	0.856522	-0.881621
H	-4.632646	-0.007163	1.456701
H	-2.611656	-0.380409	2.892928
H	-0.329655	0.056005	1.983365
H	2.483188	2.123747	-1.769973
H	2.274278	3.810885	-1.150498
H	1.180880	3.152215	-2.407006
K	-1.914899	-2.185425	-0.616028

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1308.84089126 Predicted Change= -2.081364D-09
Zero-point correction (ZPE)= -1308.5965 0.24429
Internal Energy (U)= -1308.5791 0.26169
Enthalpy (H)= -1308.5782 0.26264
Gibbs Free Energy (G)= -1308.6434 0.19748
Entropy (S)= 0.00021854

Frequencies -- 27.7356 43.0001 53.9013

Supporting Information: XXV

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

```
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
-------------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C15H14K2NO(2)     C1[X(C15H14K2NO)]   #Atoms=
33
 Charge = 0       Multiplicity = 2
-------------------------------------------------------------------------------
 SCF Energy= -1908.53292418       Predicted Change= -1.135001D-07
=========================================================================
===
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00001 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00522 ||   0.00180    [ NO ]        0.00522 ||   0.00180    [ YES ]
-------------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
-------------------------------------------------------------------------------
         N          -2.245333       0.394537      -1.151684
         C          -2.009754      -0.816262      -0.555815
         C          -2.159988      -2.073995      -1.245133
         C          -1.905496      -3.312410      -0.645122
         C          -1.484144      -3.381260       0.695798
         C          -1.328106      -2.172063       1.399868
         C          -1.553206      -0.908498       0.823854
         C          -1.343541       0.337950       1.681353
         C          -0.056285       1.136421       1.451091
         O          -0.005342       2.147209       0.630070
         K           0.555213       0.457094      -1.466164
         C           1.224361       0.672358       2.140621
         C           2.185144       0.158659       1.086465
         C           2.984005       1.079613       0.345772
         C           3.709669       0.661711      -0.784894
         C           3.674009      -0.679830      -1.205411
         C           2.917928      -1.615823      -0.452082
         C           2.189202      -1.196246       0.670069
         H          -2.609807       0.193109      -2.098501
         H          -2.511140      -2.039027      -2.287086
         H          -2.047013      -4.231685      -1.228482
         H          -1.298696      -4.343545       1.185338
         H          -1.020106      -2.204233       2.455013
         H          -2.209741       1.023213       1.547887
         H          -1.367194       0.014836       2.743005
```

H	0.999953	-0.119799	2.878600
H	1.692515	1.527193	2.682758
H	3.028288	2.126075	0.667913
H	4.311308	1.391639	-1.340868
H	4.238126	-1.002649	-2.086956
H	2.908335	-2.673038	-0.741968
H	1.589136	-1.927512	1.225928
K	-2.250302	2.963119	-0.376992

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -1908.53292418 Predicted Change= -1.135001D-07
Zero-point correction (ZPE)= -1908.2899 0.24298
Internal Energy (U)= -1908.2711 0.26179
Enthalpy (H)= -1908.2701 0.26274
Gibbs Free Energy (G)= -1908.3383 0.19460
Entropy (S)= 0.00022854

Frequencies -- 38.6569 41.3500 54.8131

Supporting Information: XXV-a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H14KNO C1[X(C15H14KNO)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1308.84716244 Predicted Change= -2.544074D-08

==========
===

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.01302 ||	0.00180	[NO]	0.01302 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z

N	2.592668	1.271962	-0.776616
C	2.635781	-0.043104	-0.459967
C	3.344712	-1.030184	-1.245655
C	3.394740	-2.381348	-0.909777
C	2.748712	-2.863124	0.248599
C	2.052877	-1.936154	1.042973
C	1.974999	-0.569055	0.726791
C	1.213084	0.368033	1.653225
C	-0.209931	0.583989	1.147798
C	-1.205771	-0.540391	1.449520
C	-2.396830	-0.598735	0.523186
C	-3.572106	0.126672	0.798330
C	-4.666475	0.080159	-0.078756
C	-4.599978	-0.693461	-1.248231
C	-3.432724	-1.420175	-1.533398
C	-2.340902	-1.371319	-0.654139
O	-0.558463	1.601809	0.535882
H	3.179502	1.393783	-1.619335
H	3.860397	-0.676170	-2.150000
H	3.950899	-3.073988	-1.555249
H	2.797156	-3.920035	0.530090
H	1.561016	-2.281687	1.962981
H	1.155059	-0.077502	2.663832
H	1.720135	1.347968	1.724274
H	-1.530947	-0.362792	2.495808
H	-0.661539	-1.500482	1.460039
H	-3.631670	0.726463	1.714255
H	-5.574957	0.646598	0.154476
H	-5.454976	-0.733608	-1.931911
H	-3.373466	-2.030788	-2.441224
H	-1.431445	-1.941948	-0.878421
K	1.058565	3.394483	-0.512808

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1308.84716244 Predicted Change= -2.544074D-08
Zero-point correction (ZPE)= -1308.6018 0.24533
Internal Energy (U)= -1308.5848 0.26230
Enthalpy (H)= -1308.5839 0.26325
Gibbs Free Energy (G)= -1308.6507 0.19638
Entropy (S)= 0.00022428

Frequencies -- 10.4949 14.1460 31.8954

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C15H15NO C1[X(C15H15NO)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -709.737469843 Predicted Change= -1.342704D-08
==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00151 ||	0.00180	[YES]	0.00151 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.000703	-1.616257	1.913841
C	-1.659846	-1.143876	0.774519
C	-2.846931	-1.771727	0.330527
C	-3.555504	-1.279327	-0.770696
C	-3.089000	-0.152837	-1.464973
C	-1.913252	0.478171	-1.029527
C	-1.190655	0.014221	0.084714
C	0.084352	0.703605	0.581318
C	1.364525	0.008565	0.130361
C	2.365539	-0.299047	1.073196
C	3.560784	-0.920287	0.677739
C	3.773677	-1.236695	-0.672127
C	2.783312	-0.931619	-1.620337
C	1.587772	-0.316539	-1.222574
C	0.064280	2.205653	0.198441
C	-0.731434	3.096836	1.128772
O	0.655423	2.640821	-0.785770
H	0.019338	-1.542911	1.886809
H	-1.277850	-2.565114	2.177839
H	-3.202858	-2.660715	0.865129
H	-4.471038	-1.788136	-1.092567
H	-3.630927	0.234450	-2.333663
H	-1.550049	1.359600	-1.569761
H	0.054827	0.673750	1.688671

H	2.205421	-0.045856	2.128689
H	4.324248	-1.156938	1.426937
H	4.704455	-1.722597	-0.984540
H	2.941300	-1.177171	-2.676402
H	0.815579	-0.095917	-1.966759
H	-1.693398	2.630437	1.403219
H	-0.901462	4.083279	0.671138
H	-0.161765	3.230488	2.068408

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -709.737469843 Predicted Change= -1.342704D-08
Zero-point correction (ZPE)= -709.4801 0.25731
Internal Energy (U)= -709.4645 0.27295
Enthalpy (H)= -709.4635 0.27389
Gibbs Free Energy (G)= -709.5240 0.21338
Entropy (S)= 0.00020296

Frequencies -- 32.4238 42.6439 52.7711

Supporting Information: XXVII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H15NO C1[X(C15H15NO)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -709.744592909 Predicted Change= -5.969090D-10

==========
===

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00326 ||	0.00180	[NO]	0.00326 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

N	2.413777	1.527920	-1.601826
C	2.792234	0.477115	-0.765385
C	3.781464	-0.451096	-1.170400
C	4.203101	-1.475339	-0.315636
C	3.648366	-1.603553	0.968322
C	2.675009	-0.681456	1.381888
C	2.242906	0.363150	0.546597
C	1.215045	1.372221	1.038419
C	-0.151326	1.104319	0.400059
C	-1.130344	0.291479	1.243883
C	-2.403533	-0.112287	0.541917
C	-3.588431	0.628841	0.711921
C	-4.767805	0.261267	0.046076
C	-4.777861	-0.856540	-0.802328
C	-3.601890	-1.603337	-0.979492
C	-2.425633	-1.233151	-0.311873
O	-0.416192	1.500673	-0.737873
H	2.684610	1.394943	-2.578938
H	1.424863	1.796752	-1.519139
H	4.207457	-0.359649	-2.176882
H	4.966107	-2.182347	-0.660446
H	3.973600	-2.403119	1.641572
H	2.245152	-0.756710	2.388192
H	1.136518	1.314123	2.136647
H	1.521356	2.398268	0.759259
H	-1.344100	0.898351	2.146182
H	-0.572589	-0.591919	1.613588
H	-3.586082	1.501037	1.376634
H	-5.681349	0.847685	0.194032
H	-5.698140	-1.146783	-1.320910
H	-3.601473	-2.479803	-1.636922
H	-1.510643	-1.821453	-0.450909

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -709.744592909 Predicted Change= -5.969090D-10
Zero-point correction (ZPE)= -709.4861 0.25847
Internal Energy (U)= -709.4710 0.27350
Enthalpy (H)= -709.4701 0.27445
Gibbs Free Energy (G)= -709.5313 0.21327
Entropy (S)= 0.00020517

Frequencies -- 8.7277 20.9512 46.4359

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C15H13N     C1[X(C15H13N)]   #Atoms= 29
 Charge = 0        Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -633.388485457        Predicted Change= -6.005027D-09
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item         Max Val.      Criteria      Pass?         RMS Val.      Criteria      Pass?
 Force         0.00000 ||   0.00045     [ YES ]         0.00000 ||   0.00030     [ YES ]
 Displ         0.00174 ||   0.00180     [ YES ]         0.00174 ||   0.00180     [ YES ]
---------------------------------------------------------------------------
        Atomic              Coordinates (Angstroms)
         Type         X              Y              Z
---------------------------------------------------------------------------
         C          -0.527940        3.068489        -0.092841
         C           0.364650        1.873261        -0.108527
         N           1.560488        1.868799         0.418038
         C           2.101562        0.570007         0.211643
         C           3.364019        0.118393         0.615450
         C           3.711389       -1.212543         0.321510
         C           2.818490       -2.060822        -0.357413
         C           1.550432       -1.598715        -0.764990
         C           1.202793       -0.278942        -0.478059
         C          -0.035873        0.542944        -0.768162
         C          -1.359546       -0.032930        -0.283045
         C          -2.432080       -0.216285        -1.175581
         C          -3.654942       -0.740320        -0.727284
         C          -3.820750       -1.085181         0.621913
         C          -2.756417       -0.903148         1.520745
         C          -1.535301       -0.382481         1.072163
         H          -0.804066        3.365100        -1.121889
         H          -1.474784        2.843330         0.432261
         H          -0.034934        3.917531         0.405763
         H           4.053851        0.783612         1.145559
         H           4.691351       -1.594032         0.628186
         H           3.110697       -3.094314        -0.571864
         H           0.858958       -2.266588        -1.291321
         H          -0.124274        0.730016        -1.858506
```

H	-2.306077	0.052058	-2.231115
H	-4.477882	-0.879231	-1.436851
H	-4.774111	-1.494131	0.973483
H	-2.877308	-1.168963	2.576628
H	-0.707758	-0.246346	1.778275

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -633.388485457 Predicted Change= -6.005027D-09
Zero-point correction (ZPE)= -633.1567 0.23174
Internal Energy (U)= -633.1437 0.24474
Enthalpy (H)= -633.1428 0.24568
Gibbs Free Energy (G)= -633.1972 0.19120
Entropy (S)= 0.00018271

Frequencies -- 25.4898 53.6002 66.5156

Supporting Information: XXIX

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========
===

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.388655347 Predicted Change= -1.020566D-07

==========
===

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00008 ||	0.00045	[YES]	0.00001 ||	0.00030	[YES]
Displ	0.00129 ||	0.00180	[YES]	0.00129 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.838008	-0.505411	-0.000126
C	2.500985	-1.739230	-0.000203
C	3.907206	-1.730204	-0.000075
C	4.622851	-0.519401	0.000112

C	3.949685	0.719285	0.000183
C	2.554329	0.717899	0.000067
C	1.518729	1.809828	0.000093
C	0.237554	0.990589	-0.000050
C	-1.124218	1.634819	-0.000184
C	-2.292404	0.670912	-0.000059
C	-2.842728	0.208615	1.211056
C	-3.917456	-0.693089	1.213341
C	-4.457890	-1.147907	0.000188
C	-3.917779	-0.693038	-1.213086
C	-2.843049	0.208668	-1.211045
N	0.430372	-0.302523	-0.000232
H	1.936865	-2.678003	-0.000353
H	4.453012	-2.679978	-0.000130
H	5.717970	-0.538442	0.000200
H	4.516980	1.656988	0.000322
H	1.571173	2.474068	-0.884239
H	1.571033	2.473847	0.884601
H	-1.178903	2.306492	-0.879852
H	-1.178940	2.306790	0.879251
H	-2.426528	0.564108	2.161298
H	-4.335518	-1.038665	2.165259
H	-5.299488	-1.849186	0.000286
H	-4.336093	-1.038571	-2.164908
H	-2.427104	0.564204	-2.161383

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -633.388655347 Predicted Change= -1.020566D-07
Zero-point correction (ZPE)= -633.1565 0.23206
Internal Energy (U)= -633.1438 0.24478
Enthalpy (H)= -633.1429 0.24572
Gibbs Free Energy (G)= -633.1976 0.19100
Entropy (S)= 0.00018355

Frequencies -- 24.5844 28.9882 53.7795

Supporting Information: XXX

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.374048515 Predicted Change= -1.281522D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00182 ||	0.00180	[NO]	0.00182 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.444610	3.055215	-0.118755
C	0.328116	1.947953	-0.181367
N	1.641829	1.832709	0.282017
C	2.136130	0.538622	0.165553
C	3.378753	0.025032	0.564744
C	3.630104	-1.338123	0.321172
C	2.674819	-2.160180	-0.299161
C	1.429137	-1.625538	-0.693680
C	1.164778	-0.278199	-0.460483
C	-0.056511	0.578179	-0.784064
C	-1.384902	0.026865	-0.281423
C	-2.436762	-0.226219	-1.180834
C	-3.663543	-0.737474	-0.726394
C	-3.852029	-1.003462	0.637165
C	-2.807029	-0.755092	1.543592
C	-1.584584	-0.244723	1.088040
H	-0.077481	3.988591	0.319826
H	-1.465026	3.038265	-0.509708
H	2.120359	2.578889	0.785706
H	4.124546	0.661532	1.052022
H	4.593178	-1.761933	0.626875
H	2.894012	-3.218124	-0.475657
H	0.677470	-2.264404	-1.171904
H	-0.139869	0.694921	-1.882724
H	-2.292580	-0.019762	-2.248145
H	-4.471231	-0.926982	-1.441842
H	-4.807491	-1.402424	0.994678
H	-2.945569	-0.960798	2.610778
H	-0.774332	-0.053873	1.801357

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -633.374048515 Predicted Change= -1.281522D-08
Zero-point correction (ZPE)= -633.1423 0.23166
Internal Energy (U)= -633.1294 0.24464
Enthalpy (H)= -633.1284 0.24559
Gibbs Free Energy (G)= -633.1829 0.19105
Entropy (S)= 0.00018292

Frequencies -- 26.3991 37.1175 63.6277

Supporting Information: XXXI

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.387251328 Predicted Change= -9.605497D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00149 ||	0.00180	[YES]	0.00149 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.071157	0.533341	-0.041265
N	-0.675736	0.499199	0.032826
C	-2.913851	1.640672	-0.203164
C	-4.300329	1.401798	-0.232783
C	-4.820251	0.103271	-0.103272
C	-3.953261	-0.998831	0.056526
C	-2.576889	-0.780836	0.085069
C	-1.402657	-1.724264	0.232764
C	-0.185822	-0.801430	0.126603
C	1.116440	-1.222837	0.114520
C	2.356400	-0.453783	0.059353

C	3.548392	-1.126377	-0.328923
C	4.776519	-0.462355	-0.405873
C	4.867037	0.904300	-0.089666
C	3.709472	1.584430	0.320469
C	2.477413	0.921592	0.399395
H	-0.100216	1.296500	-0.235427
H	-2.508921	2.652750	-0.305165
H	-4.982793	2.249262	-0.359819
H	-5.903011	-0.056660	-0.128582
H	-4.358641	-2.012779	0.150948
H	-1.382321	-2.509566	-0.545295
H	-1.412015	-2.252195	1.205335
H	1.243738	-2.312428	0.114954
H	3.491691	-2.192815	-0.578966
H	5.671132	-1.015312	-0.714442
H	5.827077	1.427575	-0.151467
H	3.764791	2.643819	0.595884
H	1.614918	1.475315	0.783746

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -633.387251328 Predicted Change= -9.605497D-09
Zero-point correction (ZPE)= -633.1546 0.23264
Internal Energy (U)= -633.1418 0.24537
Enthalpy (H)= -633.1409 0.24632
Gibbs Free Energy (G)= -633.1944 0.19279
Entropy (S)= 0.00017954

Frequencies -- 34.8808 57.0949 79.4528

Supporting Information: XXXII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.388560550 Predicted Change= -3.211982D-09

==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00146 ||	0.00180	[YES]	0.00146 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.493432	-0.719542	-0.000058
N	-1.301433	-1.435666	-0.000186
C	-3.812475	-1.194595	-0.000155
C	-4.845060	-0.239199	-0.000025
C	-4.567643	1.138231	0.000185
C	-3.232330	1.595814	0.000287
C	-2.196478	0.663893	0.000174
C	-0.689776	0.823193	0.000188
C	-0.176121	-0.615127	-0.000092
C	1.099031	-1.116652	-0.000209
C	2.377222	-0.419853	-0.000135
C	3.561788	-1.211363	0.000332
C	4.835434	-0.635712	0.000454
C	4.984125	0.762060	0.000110
C	3.831977	1.564732	-0.000376
C	2.553215	0.992540	-0.000508
H	-1.247252	-2.454117	-0.000366
H	-4.029757	-2.267550	-0.000334
H	-5.885401	-0.582534	-0.000103
H	-5.389943	1.860951	0.000269
H	-3.015233	2.670198	0.000451
H	-0.325311	1.380219	-0.884290
H	-0.325298	1.379800	0.884933
H	1.175001	-2.212914	-0.000346
H	3.462285	-2.303863	0.000611
H	5.720088	-1.282935	0.000820
H	5.980383	1.216851	0.000214
H	3.926451	2.656862	-0.000660
H	1.687143	1.658172	-0.000928

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
===
SCF Energy= -633.388560550 Predicted Change= -3.211982D-09
Zero-point correction (ZPE)= -633.1559 0.23257
Internal Energy (U)= -633.1432 0.24531

Enthalpy (H)= -633.1422 0.24626
Gibbs Free Energy (G)= -633.1959 0.19265
Entropy (S)= 0.0001798

Frequencies -- 28.4306 57.1571 85.6393

Supporting Information: XXXIII

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C15H13N C1[X(C15H13N)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -633.402636535 Predicted Change= -5.675750D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00132 ||	0.00180	[YES]	0.00132 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.946553	-0.559939	-0.309007
N	-0.658804	-0.487083	-0.802555
C	-2.805335	-1.661964	-0.160666
C	-4.075706	-1.422108	0.375722
C	-4.478838	-0.117194	0.753838
C	-3.621743	0.977626	0.604834
C	-2.330766	0.772873	0.066383
C	-1.208852	1.623040	-0.227483
C	-0.205938	0.824649	-0.758315
C	1.176220	1.183229	-1.231235
C	2.281340	0.488044	-0.444415
C	3.022157	-0.562894	-1.016666
C	4.028401	-1.214160	-0.284508
C	4.306955	-0.820079	1.032422
C	3.573358	0.228200	1.612927
C	2.567837	0.874204	0.880574
H	-0.107435	-1.279134	-1.132176

H	-2.490401	-2.669192	-0.454096
H	-4.770139	-2.259272	0.505033
H	-5.480769	0.033621	1.170479
H	-3.945305	1.982289	0.900873
H	-1.141020	2.701172	-0.074312
H	1.282805	0.927930	-2.302917
H	1.284450	2.278845	-1.148990
H	2.812595	-0.868741	-2.048843
H	4.596402	-2.028794	-0.747187
H	5.093361	-1.324411	1.604410
H	3.786767	0.544775	2.639903
H	1.995094	1.689330	1.339264

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -633.402636535 Predicted Change= -5.675750D-09
Zero-point correction (ZPE)= -633.1693 0.23331
Internal Energy (U)= -633.1566 0.24602
Enthalpy (H)= -633.1556 0.24696
Gibbs Free Energy (G)= -633.2105 0.19211
Entropy (S)= 0.00018396

Frequencies -- 23.0474 26.0884 40.6165

C. Solvents & Ions

Supporting Information: H_2O

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current scrf=(pcm,solvent=dmso) opt=(gdiis,maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C2V Stoichiometry= H2O C2V[C2(O),SGV(H2)] #Atoms= 3
Charge = 0 Multiplicity = 1

SCF Energy= -76.3305401603 Predicted Change= -1.884601D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00009 ||	0.00045	[YES]	0.00007 ||	0.00030	[YES]
Displ	0.00014 ||	0.00180	[YES]	0.00014 ||	0.00180	[YES]

```
---------------------------------------------------------------------------
        Atomic          Coordinates (Angstroms)
         Type        X              Y        Z
---------------------------------------------------------------------------
         O          -0.000000        0.000000        0.122880
         H           0.000000        0.759849       -0.491520
         H          -0.000000       -0.759849       -0.491520
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -76.3305401603        Predicted Change= -1.884601D-08
 Zero-point correction (ZPE)=              -76.3098  0.02067
 Internal Energy (U)=                      -76.3070  0.02351
 Enthalpy (H)=                            -76.3060   0.02445
 Gibbs Free Energy (G)=                          -76.3275     0.00298
---------------------------------------------------------------------------
 Frequencies --     1683.8097                 3642.2187                 3751.0896
```

Supporting Information: HO*t*-Bu

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C4H10O     C1[X(C4H10O)]   #Atoms= 15
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -233.364442550  Predicted Change= -3.432897D-07
===========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00027 ||   0.00045    [ YES ]        0.00004 ||   0.00030    [ YES ]
 Displ        0.00147 ||   0.00180    [ YES ]        0.00147 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic          Coordinates (Angstroms)
         Type        X              Y        Z
---------------------------------------------------------------------------
         C          -0.007390       -0.000001        0.016673
         C           0.683302       -1.264621       -0.522214
         H           1.751071       -1.278780       -0.233115
         H           0.204488       -2.170589       -0.111077
```

```
H          0.634084      -1.314689      -1.624577
C          0.682903       1.264871      -0.522141
H          0.633680       1.314982      -1.624501
H          0.203794       2.170661      -0.110958
H          1.750663       1.279358      -0.233028
C         -1.498016      -0.000223      -0.338552
H         -1.995034      -0.894693       0.076384
H         -1.995315       0.894062       0.076449
H         -1.640078      -0.000203      -1.432518
O          0.037025      -0.000035       1.464924
H          0.991644       0.000020       1.694959
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -233.364442550       Predicted Change= -3.432897D-07
 Zero-point correction (ZPE)=            -233.2321  0.13228
 Internal Energy (U)=                    -233.2252  0.13917
 Enthalpy (H)=                           -233.2243   0.14011
 Gibbs Free Energy (G)=                          -233.2613     0.10314
---------------------------------------------------------------------------
 Frequencies --      197.3012                    250.8993                    259.4072
```

Supporting Information: ⁻O*t*Bu.log

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C4H9O(1-)     C1[X(C4H9O)]   #Atoms= 14
 Charge = -1      Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -232.820124332       Predicted Change= -6.448438D-07
===========================================================================
===
 Optimization completed.                 {Found          1          times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00010 ||   0.00045     [ YES ]        0.00003 ||   0.00030     [ YES ]
 Displ        0.00643 ||   0.00180     [ NO ]         0.00643 ||   0.00180     [ NO ]
---------------------------------------------------------------------------
        Atomic              Coordinates (Angstroms)
```

Type	X	Y	Z
C	1.459087	-0.083383	-0.440423
C	0.000166	0.000023	0.163162
H	2.052570	0.774050	-0.065494
H	1.951096	-1.003075	-0.066102
H	1.529170	-0.087184	-1.550760
C	-0.801857	-1.222164	-0.438949
C	-0.657904	1.304620	-0.440368
H	-1.844146	-1.187966	-0.064027
H	-0.840751	-1.281097	-1.549248
H	-0.356178	-2.165139	-0.064285
H	-0.689364	1.367272	-1.550720
H	-1.697403	1.389479	-0.065725
H	-0.107953	2.190823	-0.065578
O	0.000750	0.001032	1.497676

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -232.820124332 Predicted Change= -6.448438D-07
Zero-point correction (ZPE)= -232.7028 0.11732
Internal Energy (U)= -232.6961 0.12394
Enthalpy (H)= -232.6952 0.12488
Gibbs Free Energy (G)= -232.7316 0.08843
Entropy (S)= 0.00012225

Frequencies -- 209.5062 258.0136 262.0175

Supporting Information: KO*t*-Bu

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,yqc) density=current
scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C4H9KO C1[X(C4H9KO)] #Atoms= 15
Charge = 0 Multiplicity = 1

SCF Energy= -832.460389697 Predicted Change= -9.240517D-10

==========

Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?

```
 Force        0.00000 ||   0.00045     [ YES ]        0.00000 ||   0.00030     [ YES ]
 Displ        0.00071 ||   0.00180     [ YES ]        0.00071 ||   0.00180     [ YES ]
---------------------------------------------------------------------------
        Atomic          Coordinates (Angstroms)
         Type        X              Y        Z
---------------------------------------------------------------------------
         C          1.081322        0.000009       -0.007364
         C          1.563104       -1.262319        0.772464
         H          1.089435       -1.282620        1.772692
         H          1.241364       -2.174372        0.234142
         H          2.661776       -1.316730        0.912776
         C          1.563231        1.260982        0.774572
         H          2.661915        1.315063        0.914920
         H          1.241534        2.173970        0.237813
         H          1.089626        1.279636        1.774862
         C          1.784246        0.001146       -1.400161
         H          1.468487       -0.890450       -1.974912
         H          1.468668        0.893789       -1.973385
         H          2.891823        0.000997       -1.347639
         O         -0.279611        0.000183       -0.145680
         K         -2.606798        0.000018       -0.011731
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=================================================================
===
 SCF Energy=       -832.460389697       Predicted Change= -9.240517D-10
 Zero-point correction (ZPE)=            -832.3407  0.11964
 Internal Energy (U)=                    -832.3320  0.12835
 Enthalpy (H)=                          -832.3310   0.12929
 Gibbs Free Energy (G)=                          -832.3761     0.08421
---------------------------------------------------------------------------
 Frequencies --        14.8356                    33.1134                    216.7410
```

Supporting Information: KI

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=================================================================
===
 # pbepbe/genecp/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman 6d 10f
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C*V     Stoichiometry= IK     C*V[C*(KI)]   #Atoms= 2
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -611.171273552   Predicted Change= -8.127107D-10
```

```
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||  0.00045    [ YES ]       0.00000 ||  0.00030    [ YES ]
 Displ        0.00016 ||  0.00180    [ YES ]       0.00016 ||  0.00180    [ YES ]
-----------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type         X              Y         Z
-----------------------------------------------------------------------------
         K            0.000000         0.000000        -2.461374
         I           0.000000         0.000000         0.882379
-----------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
=========================================================================
===
 SCF Energy=       -611.171273552       Predicted Change= -8.127107D-10
 Zero-point correction (ZPE)=            -611.1710  0.00026
 Internal Energy (U)=                    -611.1679  0.00332
 Enthalpy (H)=                          -611.1670   0.00427
 Gibbs Free Energy (G)=                          -611.1968    -0.02562
-----------------------------------------------------------------------------
 Frequencies --      115.6539
```

Supporting Information: K^+

```
-----------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
-----------------------------------------------------------------------------
 Pointgroup= OH     Stoichiometry= K(1+)     OH[O(K)]   #Atoms= 1
 Charge = 1        Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -599.582015872       Predicted Change= -0.000000D+00
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||  0.00045    [ YES ]       0.00000 ||  0.00030    [ YES ]
 Displ        0.00000 ||  0.00180    [ YES ]       0.00000 ||  0.00180    [ YES ]
-----------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
```

```
        Type        X             Y             Z
---------------------------------------------------------------------------
        K           0.000000      0.000000      0.000000
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin        Pressure= 1.00000 Atm
=========================================================================
===
 SCF Energy=       -599.582015872      Predicted Change= -0.000000D+00
 Zero-point correction (ZPE)=              -599.5820       0.00000
 Internal Energy (U)=                   -599.5806       0.00141
 Enthalpy (H)=                       -599.5796       0.00236
 Gibbs Free Energy (G)=                -599.5971      -0.01517
 Entropy (S)=                                5.882e-05
---------------------------------------------------------------------------
```

Supporting Information: I^-

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/genecp/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman 6d 10f
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= OH     Stoichiometry= I(1-)     OH[O(I)]   #Atoms= 1
 Charge = -1      Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -11.5708341451       Predicted Change= -0.000000D+00
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00000 ||   0.00045    [ YES ]       0.00000 ||   0.00030    [ YES ]
 Displ        0.00000 ||   0.00180    [ YES ]       0.00000 ||   0.00180    [ YES ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
        Type        X             Y             Z
---------------------------------------------------------------------------
        I           0.000000      0.000000      0.000000
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin        Pressure= 1.00000 Atm
=========================================================================
===
 SCF Energy=       -11.5708341451      Predicted Change= -0.000000D+00
 Zero-point correction (ZPE)=               -11.5708       0.00000
```

Internal Energy (U)= -11.5694 0.00141
Enthalpy (H)= -11.5684 0.00236
Gibbs Free Energy (G)= -11.5876 -0.01684
Entropy (S)= 6.443e-05

D. KO*t*-Bu Dimers

Supporting Information: (KO*t*-Bu)$_2$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C8H18K2O2 C1[X(C8H18K2O2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -1664.97800998 Predicted Change= -1.971942D-09
==========
===
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00065 ||	0.00180	[YES]	0.00065 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
K	0.000228	1.815437	0.501125
O	1.770164	-0.000281	0.526410
O	-1.770091	0.000231	0.526243
K	-0.000158	-1.815473	0.501116
C	2.964810	-0.000058	-0.165944
C	-2.964833	0.000070	-0.165948
C	4.175580	0.000216	0.810845
H	5.158193	0.000395	0.298774
H	4.128360	0.892556	1.463598
H	4.128714	-0.892097	1.463658
C	3.084372	-1.258192	-1.080662
H	2.239847	-1.283432	-1.797502
H	4.023543	-1.294803	-1.667295
H	3.042232	-2.178900	-0.464899
C	3.083898	1.258058	-1.080757

H	4.023014	1.294920	-1.667459
H	2.239318	1.282976	-1.797544
H	3.041545	2.178810	-0.465067
C	-4.175461	0.000021	0.811016
H	-4.128402	0.892395	1.463733
H	-5.158151	-0.000102	0.299091
H	-4.128239	-0.892258	1.463851
C	-3.084392	1.258122	-1.080775
H	-4.023616	1.294738	-1.667323
H	-3.042139	2.178884	-0.465105
H	-2.239928	1.283234	-1.797689
C	-3.084183	-1.258119	-1.080621
H	-3.041852	-2.178810	-0.464845
H	-4.023382	-1.294930	-1.667195
H	-2.239700	-1.283203	-1.797515

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1664.97800998 Predicted Change= -1.971942D-09
Zero-point correction (ZPE)= -1664.7369 0.24110
Internal Energy (U)= -1664.7181 0.25983
Enthalpy (H)= -1664.7172 0.26077
Gibbs Free Energy (G)= -1664.7864 0.19157
Entropy (S)= 0.0002321

Frequencies -- 21.6333 27.1810 30.5578

Supporting Information: (KO*t*-Bu)$_3$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= C1 Stoichiometry= C12H27K3O3 C1[X(C12H27K3O3)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -2497.48899582 Predicted Change= -6.456593D-08

==========

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?

Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00891 ||	0.00180	[NO]	0.00891 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	0.010574	1.956278	-0.180989
O	2.147130	-1.038863	-0.286803
O	-2.177216	-0.996625	-0.270351
K	-2.211583	1.257313	-1.346118
K	2.195353	1.204870	-1.386137
K	-0.005018	-0.478306	1.027275
C	0.031500	3.122870	0.577586
C	3.079218	-2.001033	0.040869
C	-3.103510	-1.970790	0.037608
C	-1.220851	4.006082	0.297663
H	-2.145833	3.469473	0.590930
H	-1.212481	4.961082	0.857319
H	-1.280932	4.250675	-0.780915
C	1.292262	3.982506	0.264141
H	1.314693	4.939290	0.820366
H	2.214523	3.430487	0.536619
H	1.330114	4.222206	-0.816517
C	0.048571	2.796442	2.100300
H	0.944069	2.193345	2.349217
H	0.066920	3.700047	2.740093
H	-0.852728	2.212890	2.373783
C	-4.551012	-1.391894	0.020395
H	-4.784117	-0.995533	-0.987608
H	-5.332282	-2.134444	0.278600
H	-4.625011	-0.554000	0.740056
C	-3.040806	-3.142978	-0.984653
H	-2.025320	-3.583536	-0.983310
H	-3.767694	-3.953437	-0.777364
H	-3.236779	-2.760068	-2.004545
C	-2.846092	-2.563446	1.458213
H	-1.836943	-3.020213	1.499839
H	-2.889064	-1.756110	2.215289
H	-3.575777	-3.343629	1.753058
C	3.029019	-3.190481	-0.961838
H	3.761613	-3.991567	-0.738857
H	2.017067	-3.638986	-0.956352
H	3.225193	-2.822839	-1.987283
C	4.522726	-1.412071	0.019639
H	4.587492	-0.561045	0.724700
H	5.308084	-2.144241	0.294547
H	4.757947	-1.032233	-0.994268

```
        C          2.820882        -2.571766         1.470316
        H          2.857691        -1.752136         2.214501
        H          1.814036        -3.033059         1.516467
        H          3.553897        -3.343040         1.779968
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=       -2497.48899582      Predicted Change= -6.456593D-08
 Zero-point correction (ZPE)=            -2497.1267       0.36223
 Internal Energy (U)=                  -2497.0976       0.39131
 Enthalpy (H)=                       -2497.0967       0.39226
 Gibbs Free Energy (G)=                -2497.1923       0.29664
 Entropy (S)=                                0.00032071
---------------------------------------------------------------------------
 Frequencies --       16.9012                    17.5377                    21.4838
```

Supporting Information: $(KOt\text{-}Bu)_3K^+$

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C12H27K4O3(1+)     C1[X(C12H27K4O3)]   #Atoms=
46
 Charge = 1        Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -3097.12496455        Predicted Change= -1.438168D-05
===========================================================================
===
 Optimization completed.                {Found          1          times}
 Item        Max Val.     Criteria     Pass?        RMS Val.     Criteria     Pass?
 Force        0.00006 ||   0.00045    [ YES ]        0.00001 ||   0.00030    [ YES ]
 Displ        0.11099 ||   0.00180    [ NO ]         0.11099 ||   0.00180    [ NO ]
---------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type        X              Y              Z
---------------------------------------------------------------------------
        O           1.857255         1.032622        -0.170025
        O          -0.033559        -2.124991        -0.171731
        O          -1.823373         1.092082        -0.170911
        K           0.040316         2.505023        -1.316025
```

K	2.151550	-1.288327	-1.314757
K	-2.189692	-1.216941	-1.316859
K	-0.000552	-0.000541	1.452875
C	2.993400	1.665716	0.337057
C	-0.054785	-3.424792	0.337011
C	-2.939340	1.759474	0.337044
C	3.076551	3.146049	-0.136521
H	2.209460	3.723746	0.242741
H	3.986948	3.662785	0.222126
H	3.081330	3.194919	-1.243283
C	4.295275	0.949523	-0.126176
H	5.214209	1.450648	0.232854
H	4.324347	-0.089466	0.259870
H	4.343879	0.920556	-1.232620
C	2.979774	1.665579	1.892821
H	2.957135	0.625440	2.274002
H	3.865765	2.160991	2.334365
H	2.082084	2.196892	2.266448
C	-2.973106	3.243797	-0.129964
H	-2.975163	3.297590	-1.236522
H	-3.866281	3.788895	0.229980
H	-2.087602	3.790700	0.252359
C	-4.262984	1.088218	-0.131750
H	-4.327018	0.049241	0.250101
H	-5.165779	1.617640	0.227601
H	-4.310175	1.065237	-1.238374
C	-2.928660	1.751738	1.892819
H	-2.939829	0.709657	2.269196
H	-2.015197	2.252478	2.270408
H	-3.799217	2.273117	2.335148
C	-1.327464	-4.193171	-0.123848
H	-1.354660	-5.238545	0.237977
H	-2.240898	-3.696418	0.261224
H	-1.377266	-4.223704	-1.230186
C	1.183840	-4.239323	-0.137270
H	2.119011	-3.778082	0.239733
H	1.175215	-5.285672	0.222633
H	1.221860	-4.269144	-1.244056
C	-0.046392	-3.410804	1.892723
H	0.863497	-2.899319	2.264496
H	-0.934942	-2.869802	2.274288
H	-0.060758	-4.425159	2.335712

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===

SCF Energy= -3097.12496455 Predicted Change= -1.438168D-05
Zero-point correction (ZPE)= -3096.7601 0.36482
Internal Energy (U)= -3096.7298 0.39515
Enthalpy (H)= -3096.7288 0.39609
Gibbs Free Energy (G)= -3096.8247 0.30022
Entropy (S)= 0.00032156

Frequencies -- 17.1978 18.6705 27.6597

Supporting Information: (KO*t*-Bu)$_4$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current scrf=(solvent=dmso,smd) freq=noraman
---
Pointgroup= C1 Stoichiometry= C16H36K4O4 C1[X(C16H36K4O4)] #Atoms= 60
Charge = 0 Multiplicity = 1

SCF Energy= -3330.03244488 Predicted Change= -4.349871D-06
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005 ||	0.00045	[YES]	0.00001 ||	0.00030	[YES]
Displ	0.07414 ||	0.00180	[NO]	0.07414 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.537942	0.491814	-1.616359
O	1.336833	1.819032	0.356281
O	1.283585	-1.763561	-0.681369
O	-1.078755	-0.545953	1.936761
K	-1.287211	1.774674	0.683781
K	1.084596	0.549213	-1.950649
K	-1.340537	-1.829129	-0.362069
K	1.547552	-0.492685	1.624451
C	-2.476787	0.788135	-2.590629
C	2.147087	2.921172	0.573621
C	2.062772	-2.832421	-1.092369
C	-1.734612	-0.877603	3.110791
C	-3.379225	1.981735	-2.155919
H	-2.756286	2.880405	-1.977099
H	-4.147178	2.250651	-2.907629
H	-3.905635	1.732593	-1.213329

C	-3.403889	-0.433518	-2.866299
H	-4.170257	-0.239532	-3.642329
H	-2.798036	-1.298242	-3.202179
H	-3.933742	-0.722338	-1.937029
C	-1.788553	1.176124	-3.933599
H	-1.136180	2.058685	-3.781689
H	-1.158182	0.337802	-4.290539
H	-2.505344	1.423854	-4.741079
C	2.903977	3.326230	-0.726749
H	2.176504	3.568403	-1.526609
H	3.564399	4.206068	-0.596799
H	3.533097	2.483318	-1.075109
C	3.212153	2.626811	1.672241
H	3.883157	3.484126	1.876961
H	2.709617	2.360062	2.623001
H	3.845568	1.771558	1.364051
C	1.309961	4.150051	1.039551
H	0.776043	3.908202	1.979821
H	1.920971	5.055365	1.224551
H	0.555553	4.406343	0.269611
C	-2.623984	0.300852	3.609021
H	-3.378332	0.556174	2.838691
H	-3.166825	0.077066	4.548381
H	-1.997026	1.196431	3.789321
C	-2.656979	-2.116967	2.907611
H	-2.054138	-2.985661	2.576611
H	-3.201255	-2.416663	3.824721
H	-3.411600	-1.901585	2.125421
C	-0.720151	-1.219888	4.242861
H	-0.084785	-2.073632	3.934611
H	-0.061202	-0.350020	4.434521
H	-1.204158	-1.491323	5.201621
C	1.190106	-4.097811	-1.347839
H	1.775614	-4.977489	-1.680269
H	0.656245	-4.381950	-0.419449
H	0.434465	-3.883379	-2.129279
C	2.818328	-2.500583	-2.414099
H	3.471611	-1.618413	-2.263779
H	3.454802	-3.330747	-2.778679
H	2.090755	-2.259760	-3.214249
C	3.127195	-3.197892	-0.014719
H	3.785444	-2.327183	0.175491
H	2.625029	-3.466031	0.935841
H	3.773522	-4.049739	-0.304169

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========
===
SCF Energy= -3330.03244488 Predicted Change= -4.349871D-06
Zero-point correction (ZPE)= -3329.5487 0.48371
Internal Energy (U)= -3329.5097 0.52266
Enthalpy (H)= -3329.5088 0.52360
Gibbs Free Energy (G)= -3329.6253 0.40712
Entropy (S)= 0.00039068

Frequencies -- 16.3746 21.1664 23.4882

Supporting Information: [(KO*t*-Bu)$_4$]$^{+\bullet}$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
===
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) freq=noraman guess=(mix,always)

Pointgroup= C1 Stoichiometry= C16H36K4O4(1+,2) C1[X(C16H36K4O4)] #Atoms=
60
Charge = 1 Multiplicity = 2

SCF Energy= -3329.87904413 Predicted Change= -3.352203D-03
==========
===
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.01254 ||	0.00045	[NO]	0.00299 ||	0.00030	[NO]
Displ	0.10557 ||	0.00180	[NO]	0.10557 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.537942	0.491814	-1.616359
O	1.336833	1.819032	0.356281
O	1.283585	-1.763561	-0.681369
O	-1.078755	-0.545953	1.936761
K	-1.287211	1.774674	0.683781
K	1.084596	0.549213	-1.950649
K	-1.340537	-1.829129	-0.362069
K	1.547552	-0.492685	1.624451
C	-2.476787	0.788135	-2.590629
C	2.147087	2.921172	0.573621
C	2.062772	-2.832421	-1.092369
C	-1.734612	-0.877603	3.110791
C	-3.379225	1.981735	-2.155919

H	-2.756286	2.880405	-1.977099
H	-4.147178	2.250651	-2.907629
H	-3.905635	1.732593	-1.213329
C	-3.403889	-0.433518	-2.866299
H	-4.170257	-0.239532	-3.642329
H	-2.798036	-1.298242	-3.202179
H	-3.933742	-0.722338	-1.937029
C	-1.788553	1.176124	-3.933599
H	-1.136180	2.058685	-3.781689
H	-1.158182	0.337802	-4.290539
H	-2.505344	1.423854	-4.741079
C	2.903977	3.326230	-0.726749
H	2.176504	3.568403	-1.526609
H	3.564399	4.206068	-0.596799
H	3.533097	2.483318	-1.075109
C	3.212153	2.626811	1.672241
H	3.883157	3.484126	1.876961
H	2.709617	2.360062	2.623001
H	3.845568	1.771558	1.364051
C	1.309961	4.150051	1.039551
H	0.776043	3.908202	1.979821
H	1.920971	5.055365	1.224551
H	0.555553	4.406343	0.269611
C	-2.623984	0.300852	3.609021
H	-3.378332	0.556174	2.838691
H	-3.166825	0.077066	4.548381
H	-1.997026	1.196431	3.789321
C	-2.656979	-2.116967	2.907611
H	-2.054138	-2.985661	2.576611
H	-3.201255	-2.416663	3.824721
H	-3.411600	-1.901585	2.125421
C	-0.720151	-1.219888	4.242861
H	-0.084785	-2.073632	3.934611
H	-0.061202	-0.350020	4.434521
H	-1.204158	-1.491323	5.201621
C	1.190106	-4.097811	-1.347839
H	1.775614	-4.977489	-1.680269
H	0.656245	-4.381950	-0.419449
H	0.434465	-3.883379	-2.129279
C	2.818328	-2.500583	-2.414099
H	3.471611	-1.618413	-2.263779
H	3.454802	-3.330747	-2.778679
H	2.090755	-2.259760	-3.214249
C	3.127195	-3.197892	-0.014719
H	3.785444	-2.327183	0.175491
H	2.625029	-3.466031	0.935841
H	3.773522	-4.049739	-0.304169

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -3329.87904413 Predicted Change= -3.352203D-03
Zero-point correction (ZPE)= -3329.3960 0.48299
Internal Energy (U)= -3329.3568 0.52215
Enthalpy (H)= -3329.3559 0.52310
Gibbs Free Energy (G)= -3329.4742 0.40475
Entropy (S)= 0.00039695

Frequencies -- 10.2101 11.8752 18.6516

Supporting Information: [(KO*t*-Bu)$_4$•••I]$^{\bullet}$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman guess=(mix,always) 6d 10f
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/GenECP/Auto Freq
---
Pointgroup= C1 Stoichiometry= C16H36IK4O4(2) C1[X(C16H36IK4O4)] #Atoms= 61
Charge = 0 Multiplicity = 2

SCF Energy= -3341.46627036 Predicted Change= -1.791790D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00524 ||	0.00180	[NO]	0.00524 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-3.282467	-0.000046	-0.113681
O	-0.321187	-0.000197	2.168801
O	-0.313919	1.884415	-0.969148
O	-0.313894	-1.883871	-0.969848
K	-1.903283	-1.895764	1.166728
K	-1.903575	1.895524	1.167283
K	-1.687599	0.000422	-2.255536
K	1.356504	0.000212	0.046998

C	-4.673975	-0.000395	-0.216810
C	0.112936	-0.000250	3.495012
C	0.082534	3.074966	-1.579338
C	0.082878	-3.074379	-1.579924
C	-5.259343	-1.259198	0.483214
H	-4.985186	-1.266099	1.555603
H	-6.362573	-1.293597	0.418767
H	-4.866641	-2.178233	0.007220
C	-5.124832	-0.000945	-1.700940
H	-6.225167	-0.001306	-1.811498
H	-4.739137	0.898635	-2.218870
H	-4.738583	-0.900583	-2.218350
C	-5.259821	1.258629	0.482429
H	-4.985676	1.266302	1.554817
H	-4.867425	2.177490	0.005861
H	-6.363063	1.292570	0.417944
C	-0.427217	1.258219	4.231997
H	-1.534235	1.264003	4.226784
H	-0.097189	1.293106	5.286668
H	-0.061075	2.177771	3.736144
C	1.660918	0.000162	3.577566
H	2.030542	0.000133	4.619976
H	2.071454	-0.897604	3.077091
H	2.070950	0.898283	3.077316
C	-0.426529	-1.259210	4.231643
H	-0.060166	-2.178425	3.735329
H	-0.096229	-1.294371	5.286219
H	-1.533546	-1.265436	4.226706
C	-0.519656	-4.305598	-0.852859
H	-1.626236	-4.260571	-0.871815
H	-0.220016	-5.262247	-1.319646
H	-0.182356	-4.332236	0.201674
C	-0.379907	-3.095237	-3.063989
H	0.064287	-2.245880	-3.617446
H	-0.077838	-4.025670	-3.579235
H	-1.483420	-3.024390	-3.122499
C	1.632602	-3.188849	-1.553003
H	2.090926	-2.339652	-2.093454
H	1.997521	-3.180839	-0.508727
H	1.983809	-4.123580	-2.027934
C	-0.380653	3.095860	-3.063277
H	-0.078855	4.026390	-3.578505
H	0.063531	2.246643	-3.616966
H	-1.484174	3.024878	-3.121527
C	-0.519949	4.306080	-0.852046
H	-0.182449	4.332627	0.202423
H	-0.220484	5.262796	-1.318811

```
        H          -1.626529          4.260959          -0.870784
        C           1.632263          3.189594          -1.552837
        H           1.997454          3.181483          -0.508658
        H           2.090501          2.340492          -2.093512
        H           1.983269          4.124406          -2.027754
        I          4.893082         -0.000092         -0.138577
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin          Pressure= 1.00000 Atm
===========================================================================
===
 SCF Energy=        -3341.46627036      Predicted Change= -1.791790D-07
 Zero-point correction (ZPE)=              -3340.9811        0.48514
 Internal Energy (U)=                   -3340.9395        0.52670
 Enthalpy (H)=                        -3340.9386        0.52764
 Gibbs Free Energy (G)=                 -3341.0638        0.40241
 Entropy (S)=                                0.00042004
---------------------------------------------------------------------------
 Frequencies --        15.6523                    16.0351                    21.7416
```

E. Monomeric and Complex SET Promoters

Supporting Information: P6 (bathophenanthroline)

```
---------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
===========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
 density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C24H16N2     C1[X(C24H16N2)]   #Atoms= 42
 Charge = 0        Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1032.46084315        Predicted Change= -3.590649D-08
===========================================================================
===
 Optimization completed.                {Found          1          times}
 Item         Max Val.      Criteria      Pass?         RMS Val.      Criteria      Pass?
 Force         0.00004 ||   0.00045     [ YES ]         0.00000 ||   0.00030     [ YES ]
 Displ         0.00344 ||   0.00180     [ NO ]          0.00344 ||   0.00180     [ YES ]
---------------------------------------------------------------------------
        Atomic              Coordinates (Angstroms)
         Type         X              Y              Z
---------------------------------------------------------------------------
        C           -0.731845          1.869829          0.024739
```

C	-2.690529	3.075604	0.153758
C	0.731889	1.869822	-0.024675
C	-1.439032	0.620893	0.005400
C	-3.484341	1.911863	0.119908
H	-3.174987	4.059069	0.219945
C	1.439067	0.620884	-0.005329
C	-0.686372	-0.601823	0.000808
C	-2.874908	0.658757	0.022720
H	-4.575538	1.996872	0.137016
C	2.874949	0.658742	-0.022726
C	0.686398	-0.601830	-0.000661
C	2.690579	3.075589	-0.153757
H	-1.220336	-1.555794	0.011318
C	3.484383	1.911844	-0.119945
H	1.220346	-1.555811	-0.011098
H	3.175040	4.059052	-0.219937
H	4.575579	1.996850	-0.137104
N	1.357709	3.077719	-0.091482
N	-1.357664	3.077728	0.091536
C	-3.724511	-0.560687	-0.055794
C	-4.771664	-0.745996	0.874291
C	-3.552060	-1.519251	-1.079918
C	-5.611120	-1.864893	0.793028
H	-4.913319	-0.013011	1.676058
C	-4.398664	-2.633124	-1.163469
H	-2.767351	-1.376629	-1.830291
C	-5.427083	-2.812760	-0.225517
H	-6.410692	-1.996622	1.529857
H	-4.256215	-3.360473	-1.969831
H	-6.084698	-3.686168	-0.290195
C	3.724521	-0.560720	0.055727
C	3.551756	-1.519494	1.079610
C	4.771934	-0.745864	-0.874093
C	4.398305	-2.633403	1.163179
H	2.766823	-1.377005	1.829778
C	5.611339	-1.864798	-0.792814
H	4.913839	-0.012724	-1.675675
C	5.426990	-2.812871	0.225482
H	4.255607	-3.360913	1.969352
H	6.411117	-1.996397	-1.529443
H	6.084569	-3.686304	0.290166

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1032.46084315 Predicted Change= -3.590649D-08

Zero-point correction (ZPE)= -1032.1364 0.32435
Internal Energy (U)= -1032.1172 0.34360
Enthalpy (H)= -1032.1162 0.34454
Gibbs Free Energy (G)= -1032.1850 0.27579
Entropy (S)= 0.0002306

Frequencies -- 34.6966 38.7168 43.8117

Supporting Information: P7 (bathophenanthroline and KO*t*-Bu complex)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# opt=(gdiis,maxcycle=250) freq=noraman pbepbe/6-31g(d)/auto
scrf=(smd,solvent=dmso) density=current
scf=(maxcycle=300,direct,tight,yqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C28H25KN2O C1[X(C28H25KN2O)] #Atoms= 57
Charge = 0 Multiplicity = 1

SCF Energy= -1864.94842687 Predicted Change= -1.181339D-07
==========
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00742 ||	0.00180	[NO]	0.00742 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.063648	3.477779	-0.554612
C	1.276040	2.883876	-0.197206
C	1.329177	1.448378	-0.170547
C	0.125559	0.720472	-0.453810
C	-1.056248	2.670964	-0.829152
C	2.534862	0.717943	0.098407
C	0.141918	-0.742765	-0.409475
C	1.377334	-1.427036	-0.156161
C	2.557934	-0.653903	0.104576
C	1.368006	-2.863716	-0.148385
C	0.137966	-3.501200	-0.324854
C	-1.021202	-2.735143	-0.548190
H	3.458342	1.269144	0.293540
H	-0.030721	4.567447	-0.590828

H	-2.011123	3.142940	-1.095883
H	3.494972	-1.172020	0.324013
H	0.074695	-4.593686	-0.325688
H	-1.983791	-3.241155	-0.699924
C	2.592866	-3.687693	0.035095
C	2.590703	-4.744193	0.972994
C	3.746889	-3.484972	-0.755254
C	3.716019	-5.564307	1.127608
H	1.704096	-4.908844	1.594975
C	4.867424	-4.312944	-0.603985
H	3.754584	-2.693045	-1.511647
C	4.858052	-5.351293	0.340112
H	3.699998	-6.371892	1.867304
H	5.749348	-4.148195	-1.232091
H	5.736428	-5.994505	0.458989
C	2.440156	3.750178	0.131632
C	2.801996	4.796937	-0.745377
C	3.161882	3.595134	1.336700
C	3.866432	5.653297	-0.434505
H	2.253169	4.925426	-1.684713
C	4.220048	4.459487	1.648671
H	2.873691	2.811187	2.044810
C	4.579074	5.487349	0.763119
H	4.139757	6.452551	-1.131590
H	4.761749	4.331266	2.591834
H	5.409286	6.158573	1.007188
N	-1.050234	1.335943	-0.769841
N	-1.036320	-1.400253	-0.611073
K	-3.445531	-0.077796	-1.271580
O	-5.473865	-0.054989	-0.039251
C	-6.637952	-0.052895	0.677072
C	-6.668063	-1.230430	1.701544
C	-6.803249	1.278763	1.474627
C	-7.875972	-0.204665	-0.261513
H	-6.562226	-2.191475	1.162566
H	-5.807935	-1.141159	2.392534
H	-7.593568	-1.279299	2.310879
H	-6.797291	2.133350	0.771121
H	-7.733533	1.336261	2.075840
H	-5.944015	1.407755	2.160422
H	-8.850312	-0.208049	0.268341
H	-7.887942	0.624848	-0.994329
H	-7.793563	-1.149648	-0.832031

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
=========================================================================
===
 SCF Energy=       -1864.94842687 Predicted Change= -1.181339D-07
 Zero-point correction (ZPE)=          -1864.5035   0.44486
 Internal Energy (U)=                  -1864.4734   0.47495
 Enthalpy (H)=                         -1864.4725    0.47589
 Gibbs Free Energy (G)=                -1864.5705     0.37790
-----------------------------------------------------------------------------
 Frequencies --       11.8303                    13.2380                    18.4477
```

Supporting Information: [P7]$^{+\bullet}$

```
-----------------------------------------------------------------------------
 Using   Gaussian 16:   ES64L-G16RevA.03 25-Dec-2016
=========================================================================
===
 # pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,tight,xqc) density=current
 scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250) freq=noraman
 guess=(mix,always)
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/6-31G(d)/Auto Freq
-----------------------------------------------------------------------------
 Pointgroup= C1     Stoichiometry= C28H25KN2O(1+,2)     C1[X(C28H25KN2O)]
#Atoms= 57
 Charge = 1        Multiplicity = 2
-----------------------------------------------------------------------------
 SCF Energy= -1864.79664095        Predicted Change= -1.139317D-09
=========================================================================
===
 Optimization completed.                {Found          2          times}
 Item        Max Val.      Criteria      Pass?        RMS Val.      Criteria      Pass?
 Force        0.00000 ||   0.00045     [ YES ]        0.00000 ||   0.00030     [ YES ]
 Displ        0.00097 ||   0.00180     [ YES ]        0.00097 ||   0.00180     [ YES ]
-----------------------------------------------------------------------------
        Atomic            Coordinates (Angstroms)
         Type          X              Y          Z
-----------------------------------------------------------------------------
         C          -1.986327        -3.227057        -0.641496
         C          -2.618716        -2.059670        -0.209104
         C          -1.853817        -0.843687        -0.232102
         C          -0.477897        -0.914257        -0.633074
         C          -0.635407        -3.187249        -1.031255
         C          -2.415715         0.434128         0.100311
         C           0.333092         0.304253        -0.638232
         C          -0.280518         1.560663        -0.316619
         C          -1.665337         1.581725         0.058204
         C           0.532355         2.744639        -0.356591
         C           1.889534         2.585419        -0.643527
         C           2.398479         1.305102        -0.928340
```

H	-3.469758	0.494254	0.382927
H	-2.523502	-4.180262	-0.646084
H	-0.140194	-4.111883	-1.355055
H	-2.128785	2.534732	0.325773
H	2.554269	3.453729	-0.682509
H	3.464254	1.187103	-1.165364
C	-0.003480	4.109891	-0.107977
C	0.651934	4.963391	0.807169
C	-1.122631	4.604065	-0.815484
C	0.189719	6.268383	1.022400
H	1.518322	4.591046	1.364714
C	-1.575549	5.913417	-0.605043
H	-1.621760	3.968341	-1.554330
C	-0.925222	6.747542	0.317414
H	0.702696	6.912288	1.744699
H	-2.437819	6.283888	-1.169538
H	-1.283950	7.768877	0.483422
C	-4.032503	-2.126227	0.248418
C	-4.996495	-2.780517	-0.550552
C	-4.429078	-1.605849	1.501036
C	-6.323797	-2.895134	-0.117042
H	-4.702025	-3.184623	-1.525240
C	-5.755444	-1.731423	1.935645
H	-3.687930	-1.126483	2.149096
C	-6.707593	-2.371155	1.127101
H	-7.060484	-3.395185	-0.754776
H	-6.043351	-1.332162	2.913963
H	-7.744468	-2.464038	1.467112
N	0.116932	-2.081683	-1.017092
N	1.657665	0.191635	-0.949449
O	4.421272	-2.763497	0.440696
C	5.340513	-1.974587	1.076719
C	5.985860	-0.933152	0.136742
C	4.439923	-1.211887	2.144228
C	6.390834	-2.817626	1.833507
H	6.528235	-1.449185	-0.675051
H	5.222985	-0.268970	-0.307441
H	6.706639	-0.305233	0.687644
H	3.969981	-1.931207	2.831553
H	5.127409	-0.551294	2.700056
H	3.669549	-0.609342	1.638171
H	7.058623	-2.166761	2.422341
H	5.897657	-3.533191	2.511893
H	7.002162	-3.382903	1.108624
K	2.818348	-2.238003	-1.660584

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1864.79664095 Predicted Change= -1.139317D-09
Zero-point correction (ZPE)= -1864.3508 0.44575
Internal Energy (U)= -1864.3207 0.47593
Enthalpy (H)= -1864.3197 0.47688
Gibbs Free Energy (G)= -1864.4175 0.37911

Frequencies -- 12.1151 13.1467 25.8577

Supporting Information: [P7•••I]•

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# opt=(gdiis,maxcycle=250) freq=noraman pbepbe/genecp/auto
scrf=(smd,solvent=dmso) density=current 6d 10f
scf=(maxcycle=300,direct,tight,yqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/GenECP/Auto Freq
---
Pointgroup= C1 Stoichiometry= C28H25IKN2O(2) C1[X(C28H25IKN2O)] #Atoms= 58
Charge = 0 Multiplicity = 2

SCF Energy= -1876.38164690 Predicted Change= -5.898799D-09
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00542 ||	0.00180	[NO]	0.00542 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.216333	3.566283	-0.315289
C	-2.400501	2.829114	-0.250174
C	-2.288159	1.408234	-0.069247
C	-0.975263	0.831076	-0.029604
C	0.023730	2.904615	-0.250309
C	-3.427911	0.552934	0.100442
C	-0.830580	-0.617191	0.125959
C	-2.000411	-1.427440	0.309310
C	-3.290614	-0.800019	0.281719
C	-1.826054	-2.842766	0.484701
C	-0.526481	-3.347326	0.403696

C	0.553831	-2.467783	0.204909
H	-4.428355	0.993083	0.095300
H	-1.244753	4.651594	-0.451901
H	0.951324	3.487838	-0.317082
H	-4.184672	-1.417757	0.398178
H	-0.337701	-4.417955	0.528555
H	1.575570	-2.866938	0.155031
C	-2.954564	-3.777255	0.742338
C	-3.078658	-4.953567	-0.030050
C	-3.878470	-3.551184	1.787618
C	-4.108430	-5.869060	0.223872
H	-2.371210	-5.137950	-0.845802
C	-4.901311	-4.474037	2.044782
H	-3.777505	-2.662295	2.419110
C	-5.023213	-5.632204	1.261566
H	-4.196079	-6.769960	-0.392678
H	-5.602393	-4.288405	2.865390
H	-5.826437	-6.349305	1.461378
C	-3.704321	3.535546	-0.367753
C	-3.952632	4.680878	0.421057
C	-4.685803	3.127074	-1.298922
C	-5.156002	5.387233	0.295013
H	-3.201374	5.005390	1.149235
C	-5.884196	3.841833	-1.428966
H	-4.496012	2.261953	-1.942870
C	-6.125682	4.969991	-0.629851
H	-5.336386	6.266176	0.922995
H	-6.629580	3.517250	-2.162738
H	-7.064992	5.524069	-0.730105
N	0.161268	1.580263	-0.129113
N	0.428678	-1.141796	0.086065
K	2.733070	0.455804	-0.118320
O	3.525737	-0.032424	-2.673944
C	3.736732	-1.219628	-3.321095
C	4.186663	-2.347567	-2.366617
C	2.284646	-1.562361	-3.869515
C	4.690571	-1.053114	-4.525220
H	5.150047	-2.077957	-1.899080
H	3.439502	-2.518946	-1.571409
H	4.323565	-3.293523	-2.917831
H	1.938119	-0.774021	-4.554710
H	2.383515	-2.517763	-4.412937
H	1.575239	-1.678576	-3.035194
H	4.770200	-1.996664	-5.090853
H	4.327721	-0.260289	-5.200111
H	5.696184	-0.775323	-4.164265
I	5.261493	1.065514	2.151493

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1876.38164690 Predicted Change= -5.898799D-09
Zero-point correction (ZPE)= -1875.9361 0.44552
Internal Energy (U)= -1875.9031 0.47849
Enthalpy (H)= -1875.9022 0.47943
Gibbs Free Energy (G)= -1876.0121 0.36951

Frequencies -- 5.3095 7.6236 11.6196

Supporting Information: (KO*t*-Bu)$_4$/P6

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C40H52K4N2O4 C1[X(C40H52K4N2O4)] #Atoms= 102
Charge = 0 Multiplicity = 1

SCF Energy= -4362.51189443 Predicted Change= -6.700702D-08
==========
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.02004 ||	0.00180	[NO]	0.02004 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-2.086296	0.027260	1.975455
O	-2.880524	-1.940917	-1.213998
O	-2.829104	1.812370	-1.348710
O	-5.534867	0.041549	0.567021
K	-3.803807	-1.846738	1.253867
K	-1.010690	-0.058624	-0.508343
K	-3.736832	1.910003	1.124009
K	-4.602626	-0.062804	-1.900905

C	-1.555777	0.059544	3.253262
C	-2.704367	-3.074494	-1.988533
C	-2.633580	2.889201	-2.196138
C	-6.870567	0.083343	0.928626
C	-1.958329	1.367785	4.002345
H	-3.061441	1.433102	4.090560
H	-1.540536	1.435644	5.026207
H	-1.601052	2.251476	3.437269
C	-0.000642	-0.006988	3.222284
H	0.459972	0.012046	4.230028
H	0.323925	-0.934247	2.713217
H	0.398828	0.848352	2.645508
C	-2.063739	-1.141723	4.109808
H	-3.169198	-1.114079	4.186680
H	-1.771302	-2.097906	3.631953
H	-1.659942	-1.148992	5.141470
C	-2.499290	-4.336543	-1.096872
H	-3.402352	-4.519023	-0.480453
H	-2.300739	-5.260349	-1.675722
H	-1.645979	-4.172380	-0.410668
C	-1.461057	-2.934722	-2.917080
H	-1.306338	-3.809177	-3.580209
H	-1.574200	-2.037015	-3.555103
H	-0.544096	-2.805233	-2.311182
C	-3.943076	-3.337612	-2.899829
H	-4.071244	-2.508470	-3.624908
H	-3.866515	-4.274284	-3.486752
H	-4.858999	-3.398380	-2.280152
C	-7.244971	-1.127654	1.835064
H	-6.622701	-1.119051	2.751646
H	-8.307134	-1.131418	2.150005
H	-7.051884	-2.076124	1.295880
C	-7.198163	1.387048	1.717127
H	-6.967280	2.272917	1.092930
H	-8.259667	1.461437	2.025407
H	-6.578102	1.439472	2.633833
C	-7.793782	0.041781	-0.326162
H	-7.574967	0.905922	-0.984068
H	-7.605365	-0.885785	-0.901898
H	-8.873831	0.071539	-0.081158
C	-3.842273	3.077304	-3.164643
H	-3.748169	3.967587	-3.817441
H	-3.944105	2.195363	-3.829006
H	-4.778661	3.181189	-2.582215
C	-2.465990	4.213254	-1.390540
H	-1.632544	4.106980	-0.669325
H	-2.256802	5.095701	-2.027263

H	-3.389286	4.429650	-0.816399
C	-1.359288	2.693909	-3.071117
H	-0.462980	2.609459	-2.427783
H	-1.448516	1.755065	-3.651109
H	-1.185353	3.522748	-3.786043
C	2.821531	-0.738524	-0.121919
C	1.644443	-2.724051	-0.172864
C	2.804003	0.725221	-0.124383
C	4.073942	-1.428717	0.003423
C	2.817211	-3.496969	-0.073269
H	0.669317	-3.224743	-0.237336
C	4.039323	1.445686	0.000115
C	5.272182	-0.662751	0.197676
C	4.061105	-2.865121	-0.008311
H	2.749483	-4.589342	-0.081584
C	3.991688	2.881330	-0.014545
C	5.255620	0.709297	0.196408
C	1.579292	2.681556	-0.181887
H	6.214142	-1.187221	0.379467
C	2.732973	3.482808	-0.082335
H	6.184631	1.256646	0.377435
H	0.592368	3.158361	-0.249124
H	2.638901	4.573211	-0.092909
N	1.594042	1.346032	-0.223496
N	1.626752	-1.388682	-0.217599
C	5.297010	-3.690940	0.045487
C	5.381681	-4.769497	0.954222
C	6.375253	-3.464874	-0.839832
C	6.517462	-5.589063	0.986524
H	4.555895	-4.952087	1.650506
C	7.505790	-4.292579	-0.811268
H	6.314397	-2.653205	-1.572493
C	7.582905	-5.353972	0.103638
H	6.569824	-6.413877	1.705223
H	8.327046	-4.109681	-1.512377
H	8.469009	-5.997171	0.126532
C	5.207393	3.736642	0.039593
C	5.266119	4.816526	0.948762
C	6.291086	3.536356	-0.845265
C	6.382440	5.662387	0.982155
H	4.436043	4.979157	1.644906
C	7.401951	4.390218	-0.815633
H	6.249666	2.723478	-1.577966
C	7.453583	5.452761	0.099750
H	6.415075	6.487881	1.701249
H	8.227670	4.226942	-1.516349
H	8.324429	6.116445	0.123579

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4362.51189443 Predicted Change= -6.700702D-08
Zero-point correction (ZPE)= -4361.7037 0.80818
Internal Energy (U)= -4361.6430 0.86888
Enthalpy (H)= -4361.6420 0.86982
Gibbs Free Energy (G)= -4361.8103 0.70151
Entropy (S)= 0.0005645

Frequencies -- 6.5331 8.9524 13.1328

Supporting Information: [(KO*t*-Bu)$_4$/P6]$^{+\bullet}$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) freq=noraman guess=(mix,always)

Pointgroup= C1 Stoichiometry= C40H52K4N2O4(1+,2) C1[X(C40H52K4N2O4)]
#Atoms= 102
Charge = 1 Multiplicity = 2

SCF Energy= -4362.36478972 Predicted Change= -6.291105D-05
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00074 ||	0.00045	[NO]	0.00011 ||	0.00030	[YES]
Displ	0.06041 ||	0.00180	[NO]	0.06041 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.116429	-0.008701	1.972940
O	2.871550	1.773049	-1.245440
O	2.988689	-1.982521	-1.055230
O	5.535759	0.093948	0.509180
K	3.765160	1.950839	1.256300
K	0.963599	-0.127031	-0.500470
K	3.958089	-1.855481	1.417890
K	4.603529	-0.094732	-1.980470
C	1.423219	-0.043601	3.184280
C	2.641870	2.886739	-2.053570

C	2.782709	-3.173861	-1.750760
C	6.897200	0.193578	0.796850
C	2.396729	-0.193961	4.383440
H	3.133180	0.631879	4.389590
H	1.871819	-0.187441	5.357000
H	2.955619	-1.148251	4.317700
C	0.421879	-1.231541	3.199790
H	-0.136291	-1.288651	4.152960
H	-0.311341	-1.131741	2.378500
H	0.958349	-2.189981	3.063980
C	0.615110	1.273639	3.364610
H	1.295910	2.145739	3.400360
H	-0.081130	1.413049	2.518090
H	0.027530	1.268379	4.301480
C	2.427650	4.163229	-1.198030
H	3.346390	4.410089	-0.630190
H	2.174250	5.047999	-1.811180
H	1.604260	4.002159	-0.476680
C	1.392030	2.654629	-2.947230
H	1.212970	3.499299	-3.638420
H	1.525040	1.737129	-3.550200
H	0.487360	2.532299	-2.323700
C	3.863800	3.122089	-2.989680
H	3.984170	2.279919	-3.698450
H	3.745920	4.042359	-3.590970
H	4.789000	3.220048	-2.391130
C	7.191860	1.530658	1.534070
H	6.629210	1.578698	2.486120
H	8.265030	1.644688	1.774340
H	6.897510	2.388508	0.899150
C	7.332799	-0.976792	1.723040
H	7.142139	-1.948322	1.227810
H	8.410089	-0.932742	1.968080
H	6.768969	-0.943592	2.674770
C	7.747249	0.145168	-0.500000
H	7.574749	-0.808912	-1.035210
H	7.471050	0.982298	-1.170340
H	8.832310	0.223568	-0.301480
C	4.107769	-3.607341	-2.446130
H	4.002609	-4.588581	-2.944740
H	4.404229	-2.873742	-3.220370
H	4.922349	-3.682392	-1.702310
C	2.346789	-4.307501	-0.785030
H	1.451749	-3.995361	-0.215120
H	2.103989	-5.245371	-1.318550
H	3.153739	-4.538751	-0.062600
C	1.698339	-2.990671	-2.846770

H	0.723299	-2.735511	-2.390470
H	1.984659	-2.168701	-3.529190
H	1.554009	-3.905821	-3.451120
C	-2.803200	0.722850	-0.198530
C	-1.539880	2.653979	-0.113400
C	-2.849101	-0.739250	-0.255360
C	-4.028900	1.464940	-0.116400
C	-2.681220	3.474690	-0.041430
H	-0.542690	3.112869	-0.106560
C	-4.113951	-1.409260	-0.147720
C	-5.270920	0.749040	-0.050200
C	-3.952920	2.898630	-0.070180
H	-2.565210	4.562110	0.000660
C	-4.124811	-2.845730	-0.157290
C	-5.311041	-0.622140	-0.062790
C	-1.719691	-2.743491	-0.455800
H	-6.205680	1.310200	0.026720
C	-2.902341	-3.496630	-0.336190
H	-6.278181	-1.129040	-0.014730
H	-0.760231	-3.261321	-0.584640
H	-2.852631	-4.589800	-0.350540
N	-1.669121	-1.408081	-0.403210
N	-1.577660	1.321279	-0.212930
C	-5.152260	3.778260	-0.046570
C	-5.252510	4.801110	0.922700
C	-6.175700	3.658090	-1.013580
C	-6.353580	5.667470	0.935470
H	-4.468160	4.902480	1.680740
C	-7.270590	4.532740	-1.003840
H	-6.098840	2.892450	-1.792860
C	-7.366400	5.536090	-0.027210
H	-6.420199	6.447050	1.701840
H	-8.049380	4.431501	-1.767180
H	-8.225439	6.215271	-0.018850
C	-5.362031	-3.653270	0.016410
C	-6.230071	-3.446470	1.112380
C	-5.652701	-4.696080	-0.891200
C	-7.360981	-4.255670	1.287180
H	-6.002351	-2.665670	1.845570
C	-6.789481	-5.496600	-0.718660
H	-4.989071	-4.865180	-1.746200
C	-7.647591	-5.278879	0.370480
H	-8.017021	-4.087829	2.147870
H	-7.005132	-6.292680	-1.439190
H	-8.534382	-5.906809	0.506680

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4362.36478972 Predicted Change= -6.291105D-05
Zero-point correction (ZPE)= -4361.5555 0.80924
Internal Energy (U)= -4361.4947 0.87003
Enthalpy (H)= -4361.4938 0.87098
Gibbs Free Energy (G)= -4361.6600 0.70472
Entropy (S)= 0.00055764

Frequencies -- 8.5366 11.0300 19.0238

Supporting Information: [(KO*t*-Bu)$_4$•••I/P6]$^{\bullet}$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current scrf=(solvent=dmso,smd) freq=noraman guess=(mix,always) 6d 10f
---
Pointgroup= C1 Stoichiometry= C40H52IK4N2O4(2) C1[X(C40H52IK4N2O4)]
#Atoms= 103
Charge = 0 Multiplicity = 2

SCF Energy= -4373.94770794 Predicted Change= -1.089565D-03
==========
Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00816 ||	0.00045	[NO]	0.00209 ||	0.00030	[NO]
Displ	0.13334 ||	0.00180	[NO]	0.13334 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.069893	-1.478539	2.465775
O	-2.000444	-1.392142	-1.198131
O	-2.494357	1.609124	1.087569
O	-4.620073	-1.393339	1.314401
K	-2.536336	-2.997439	0.842202
K	-0.260505	0.083680	0.349286
K	-3.184284	0.001273	3.072496
K	-4.022158	0.298049	-0.710921
C	-0.259578	-1.979689	3.484306
C	-1.724366	-1.857843	-2.494622
C	-2.454589	3.001741	1.163738

C	-5.895842	-1.877789	1.567940
C	-0.922608	-1.768024	4.874707
H	-1.924304	-2.244276	4.891035
H	-0.325551	-2.209678	5.699204
H	-1.042433	-0.690016	5.084160
C	1.124092	-1.282327	3.487255
H	1.778990	-1.645297	4.301809
H	1.646978	-1.451937	2.526426
H	0.996870	-0.185770	3.621985
C	-0.042406	-3.506667	3.275303
H	-1.010894	-4.045830	3.348980
H	0.403927	-3.705083	2.281129
H	0.630926	-3.935414	4.040634
C	-1.387471	-3.367044	-2.477620
H	-2.256056	-3.955957	-2.130003
H	-1.113031	-3.752696	-3.481515
H	-0.535010	-3.562697	-1.805115
C	-0.519564	-1.070251	-3.098294
H	-0.310263	-1.391479	-4.140804
H	-0.744572	0.009202	-3.102110
H	0.388270	-1.237608	-2.492932
C	-2.961975	-1.627875	-3.412962
H	-3.175714	-0.546009	-3.522255
H	-2.791619	-2.037482	-4.425623
H	-3.845796	-2.132676	-2.979988
C	-6.398708	-1.358030	2.951533
H	-6.416155	-0.251037	2.946749
H	-7.423929	-1.702701	3.175097
H	-5.737905	-1.710509	3.764589
C	-6.903085	-1.428375	0.475268
H	-6.563449	-1.799515	-0.520467
H	-7.920570	-1.821185	0.643386
H	-6.961221	-0.332753	0.438999
C	-5.886311	-3.432291	1.627280
H	-5.551925	-3.848331	0.650438
H	-5.194426	-3.787482	2.410759
H	-6.881230	-3.854788	1.841737
C	-3.889804	3.548984	1.438352
H	-3.893578	4.652312	1.525741
H	-4.570036	3.275414	0.609533
H	-4.300683	3.130434	2.375953
C	-1.543849	3.435423	2.354018
H	-0.522892	3.030379	2.209962
H	-1.481907	4.536352	2.436374
H	-1.939402	3.043377	3.307658
C	-1.916372	3.625730	-0.146291
H	-0.896856	3.265619	-0.358192

H	-2.559360	3.336862	-1.003797
H	-1.886961	4.730408	-0.106053
C	3.515183	-0.511335	-0.314245
C	2.354691	-2.502765	-0.495135
C	3.491942	0.928582	-0.029075
C	4.762566	-1.152436	-0.621914
C	3.519520	-3.223642	-0.822511
H	1.393303	-3.021333	-0.435495
C	4.727146	1.658108	0.013583
C	5.966863	-0.372842	-0.592036
C	4.741043	-2.552252	-0.917941
H	3.454688	-4.291045	-1.038052
C	4.679279	3.062193	0.330055
C	5.950028	0.968471	-0.287702
C	2.266732	2.831671	0.434694
H	6.920406	-0.855590	-0.811768
C	3.420658	3.632861	0.509948
H	6.888061	1.529763	-0.285036
H	1.280723	3.293025	0.586374
H	3.326089	4.701364	0.744941
N	2.280247	1.521833	0.194277
N	2.323395	-1.181326	-0.265193
C	5.956546	-3.312757	-1.315015
C	6.274072	-4.528135	-0.656300
C	6.785669	-2.891331	-2.385301
C	7.389286	-5.282379	-1.044503
H	5.639195	-4.866726	0.169562
C	7.894578	-3.653337	-2.777489
H	6.535551	-1.970509	-2.926409
C	8.198133	-4.852594	-2.106190
H	7.616957	-6.214447	-0.517677
H	8.512401	-3.314224	-3.607995
H	9.068085	-5.435876	-2.416635
C	5.894325	3.907152	0.463295
C	6.964037	3.527373	1.310959
C	5.964521	5.139294	-0.218961
C	8.074337	4.375456	1.463405
H	6.912303	2.595545	1.871396
C	7.080549	5.969987	-0.062025
H	5.143378	5.440911	-0.873943
C	8.139177	5.590808	0.779086
H	8.889749	4.072127	2.134341
H	7.132820	6.922107	-0.604783
H	9.010060	6.242000	0.891408
I	-6.019767	2.144524	-2.975170

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4373.94770794 Predicted Change= -1.089565D-03
Zero-point correction (ZPE)= -4373.1386 0.80908
Internal Energy (U)= -4373.0750 0.87264
Enthalpy (H)= -4373.0741 0.87358
Gibbs Free Energy (G)= -4373.2541 0.69356
Entropy (S)= 0.0006038

Frequencies -- 2.8000 3.9420 9.2014

Supporting Information: P8

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/6-31g(d)/auto scf=(maxcycle=300,direct,vshift=200,tight,yqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq
---
Pointgroup= C1 Stoichiometry= C48H30K2N4 C1[X(C48H30K2N4)] #Atoms= 84
Charge = 0 Multiplicity = 1

SCF Energy= -3263.15056165 Predicted Change= -1.010786D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00284 ||	0.00180	[NO]	0.00284 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.884523	-3.570785	-0.373274
C	6.459349	-2.296471	-0.338620
C	5.584387	-1.166684	-0.123022
C	4.163188	-1.434539	-0.050678
C	4.491661	-3.718386	-0.244742
C	6.046363	0.169413	0.049799
C	3.212714	-0.310550	0.091132
C	3.750446	1.011455	0.322930
C	5.151913	1.211502	0.280013
C	2.777732	2.064801	0.565440
C	1.431479	1.760484	0.427751
C	0.982260	0.437247	0.108307

H	7.119149	0.378660	0.030087
H	6.512746	-4.453409	-0.536285
H	4.041667	-4.719978	-0.272675
H	5.548631	2.222592	0.419510
H	0.694367	2.537339	0.648958
C	3.165605	3.434634	0.996169
C	2.552343	4.566959	0.409168
C	4.104072	3.653762	2.033479
C	2.863223	5.863740	0.840192
H	1.834155	4.422648	-0.405884
C	4.412956	4.950695	2.464834
H	4.575634	2.795507	2.523723
C	3.797055	6.063452	1.868946
H	2.377153	6.722498	0.363725
H	5.134346	5.091803	3.277440
H	4.043399	7.076842	2.203846
C	7.928386	-2.163486	-0.527209
C	8.812671	-3.018571	0.171551
C	8.482017	-1.239178	-1.444455
C	10.197348	-2.947315	-0.032135
H	8.405074	-3.734804	0.893717
C	9.866233	-1.173328	-1.651568
H	7.817267	-0.584572	-2.017711
C	10.731303	-2.023503	-0.943915
H	10.861831	-3.614312	0.528124
H	10.270327	-0.457290	-2.375632
H	11.813429	-1.966899	-1.103499
N	3.644857	-2.687558	-0.107992
N	1.902142	-0.579085	-0.016900
C	-0.420963	0.080619	-0.002495
C	-1.536565	0.977094	-0.290845
C	-0.766992	-1.280137	0.247357
C	-2.853191	0.467208	-0.195470
H	0.061154	-1.984476	0.403726
C	-3.084841	-0.921903	0.158915
C	-4.031845	1.247037	-0.487809
C	-4.399307	-1.459373	0.285140
C	-5.300749	0.734068	-0.387689
H	-3.914508	2.293286	-0.784383
C	-5.559279	-0.632870	-0.011473
H	-6.148878	1.394670	-0.589782
C	-6.859611	-1.184534	0.117673
C	-5.806324	-3.262005	0.835902
C	-6.963922	-2.530636	0.592414
H	-5.885250	-4.309056	1.163108
H	-7.944268	-3.003099	0.704117
C	-1.306903	2.347936	-0.825631

C	-1.824165	3.504188	-0.191665
C	-0.558467	2.531017	-2.015005
C	-1.619221	4.783049	-0.732411
H	-2.381459	3.396169	0.745695
C	-0.355194	3.806687	-2.556111
H	-0.142496	1.653742	-2.523368
C	-0.886452	4.943077	-1.918594
H	-2.030809	5.659067	-0.218329
H	0.214022	3.915342	-3.486355
H	-0.726956	5.940734	-2.341593
N	-1.991014	-1.790955	0.353152
N	-4.540592	-2.800508	0.684260
K	-2.802908	-3.965103	-1.114173
K	-2.800962	-2.729155	2.819623
C	-8.105550	-0.445913	-0.200008
C	-8.268263	0.289913	-1.400648
C	-9.213818	-0.519190	0.680983
C	-9.473513	0.942872	-1.691322
H	-7.449748	0.323679	-2.127393
C	-10.416701	0.136472	0.390406
H	-9.116268	-1.083385	1.615311
C	-10.553784	0.874684	-0.796711
H	-9.572790	1.497778	-2.630964
H	-11.251621	0.072824	1.097290
H	-11.495180	1.385455	-1.025681

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -3263.15056165 Predicted Change= -1.010786D-08
Zero-point correction (ZPE)= -3262.5265 0.62406
Internal Energy (U)= -3262.4821 0.66840
Enthalpy (H)= -3262.4812 0.66935
Gibbs Free Energy (G)= -3262.6092 0.54133

Frequencies -- 10.5074 13.6354 18.5193

Supporting Information: [P8•••I]˙

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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# pbepbe/genecp/auto scf=(maxcycle=300,direct,vshift=200,tight,xqc)
density=current scrf=(solvent=dmso,smd) opt=(gdiis,maxcycle=250)
freq=noraman 10f 6d guess=(mix,always)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk UPBEPBE/GenECP/Auto Freq

---
Pointgroup= C1 Stoichiometry= C48H30IK2N4(2) C1[X(C48H30IK2N4)] #Atoms= 85
Charge = 0 Multiplicity = 2

SCF Energy= -3274.65552220 Predicted Change= -3.037133D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00388 ||	0.00180	[NO]	0.00388 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.767467	3.097721	-1.237199
C	-6.454406	1.921013	-0.929474
C	-5.678497	0.786657	-0.502278
C	-4.244719	0.922361	-0.491473
C	-4.361252	3.128327	-1.163301
C	-6.262896	-0.443431	-0.062232
C	-3.410784	-0.225529	-0.104645
C	-4.053928	-1.422247	0.367434
C	-5.478177	-1.497693	0.362157
C	-3.193558	-2.496036	0.806162
C	-1.820355	-2.340332	0.653194
C	-1.270177	-1.138813	0.117439
H	-7.351235	-0.543608	-0.043390
H	-6.315053	3.986932	-1.566372
H	-3.823658	4.053315	-1.411043
H	-5.963266	-2.420372	0.694285
H	-1.154812	-3.130010	1.011235
C	-3.712532	-3.741855	1.434112
C	-3.240679	-5.001544	0.999805
C	-4.633062	-3.704093	2.507084
C	-3.680561	-6.183617	1.610825
H	-2.533830	-5.049965	0.163854
C	-5.067747	-4.887142	3.119956
H	-4.989748	-2.738241	2.880230
C	-4.596744	-6.131742	2.672631
H	-3.307135	-7.149132	1.252437
H	-5.772937	-4.834588	3.956630
H	-4.940631	-7.055269	3.150627
C	-7.937309	1.893053	-1.053436
C	-8.710192	2.929577	-0.483035
C	-8.601830	0.882873	-1.785847

C	-10.103915	2.948163	-0.627841
H	-8.210354	3.716594	0.092306
C	-9.995064	0.907815	-1.935672
H	-8.019304	0.087437	-2.262347
C	-10.751833	1.937043	-1.354081
H	-10.685208	3.755223	-0.168995
H	-10.490134	0.121340	-2.515434
H	-11.840930	1.952225	-1.468923
N	-3.607888	2.078660	-0.821405
N	-2.072064	-0.097451	-0.226155
C	0.178701	-0.910217	-0.004847
C	1.186231	-1.908544	-0.232148
C	0.627767	0.428463	0.161832
C	2.550511	-1.498922	-0.243921
H	-0.132803	1.203282	0.322040
C	2.886119	-0.114513	-0.032358
C	3.639942	-2.406312	-0.498066
C	4.255191	0.326799	-0.038611
C	4.947194	-1.988963	-0.522287
H	3.419945	-3.463428	-0.669632
C	5.315535	-0.614738	-0.312847
H	5.734729	-2.727468	-0.695603
C	6.662501	-0.147085	-0.327102
C	5.798192	2.057121	0.235243
C	6.885858	1.215534	-0.016905
H	5.970173	3.120598	0.450546
H	7.900768	1.623799	-0.017284
C	0.830256	-3.319820	-0.558687
C	1.238484	-4.396754	0.261068
C	0.071935	-3.608055	-1.716468
C	0.901191	-5.718229	-0.068001
H	1.813137	-4.191613	1.171141
C	-0.259227	-4.929002	-2.047546
H	-0.250314	-2.786121	-2.365391
C	0.152961	-5.990438	-1.223844
H	1.223760	-6.537372	0.584009
H	-0.837087	-5.131031	-2.956141
H	-0.107145	-7.022412	-1.482539
N	1.895236	0.841123	0.172400
N	4.507891	1.667082	0.218398
K	2.630010	3.061879	-1.415092
K	2.809694	2.381877	2.378545
C	7.828369	-1.011419	-0.643644
C	7.858457	-1.837373	-1.792127
C	8.976875	-0.971984	0.181728
C	8.990912	-2.606130	-2.093155
H	6.998461	-1.853400	-2.469852

C	10.105247	-1.745912	-0.118078
H	8.972351	-0.339664	1.076498
C	10.116976	-2.568216	-1.255996
H	8.995317	-3.231178	-2.992760
H	10.978448	-1.708286	0.542350
H	11.000300	-3.171056	-1.492115
I	1.943220	5.459458	1.008307

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -3274.65552220 Predicted Change= -3.037133D-08
Zero-point correction (ZPE)= -3274.0284 0.62706
Internal Energy (U)= -3273.9817 0.67376
Enthalpy (H)= -3273.9808 0.67470
Gibbs Free Energy (G)= -3274.1187 0.53680

Frequencies -- 7.1431 9.4504 10.9753

12. References

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[S3] Barham J. P.; Coulthard G.; Emery K. J.; Doni E.; Cumine F.; Nocera G.; John M. P.; Berlouis L. E.; McGuire T.; Tuttle T.; Murphy J. A. KO*t*Bu: A Privileged Reagent for Electron Transfer Reactions? *J. Am. Chem. Soc.*, **2016**, *138*(23), 7402-7410.

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