Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

Manganese catalyzed C–H functionalization of indoles with alkynes to synthesize bis/trisubstituted indolylalkenes and carbazoles: the acid is the key to control selectivity

Lijun Shi,[a,b] Xiang Zhong,[b] Houde She,[a] Ziqiang Lei*[a] and Fuwei Li*[b]

[a] *Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China. Fax: +86-931-7975121; E-mail: Leizq@nwnu.edu.cn*

[b] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, 730000, China. Fax: (+86)-931-4968129; Email: fuweili@licp.cas.cn*

1. General information

All solvents before use were dried and degassed by standard methods and stored under nitrogen. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. N-2-pyridylindole, N-2-Pyrimidylpyrrole and N-2-Pyrimidylindoles used here were prepared according to the reported methods.[1] NMR spectra of the products were recorded using a Bruker Avance TM Ⅲ spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. High resolution mass spectrum (HRMS) were obtained on a Bruker Daltonics micro TOF-Q Ⅱ spectrometer. High-performance liquid chromatography (HPLC) analysis (acetonitrile/H_2O = 75/25, 0.8 mL/min, λ = 254 nm) was performed by Agilent 1260 Infinity with an Agilent ZORBAX C18 column using biphenyl as inner standard for product **4a**. Isolated yield was obtained by column chromatography (300-400 mesh), and Ethyl acetate/ Petroleum ether was used as the eluent.

2. General procedure for Mn-catalyzed alkenylation of indoles with alkynes.

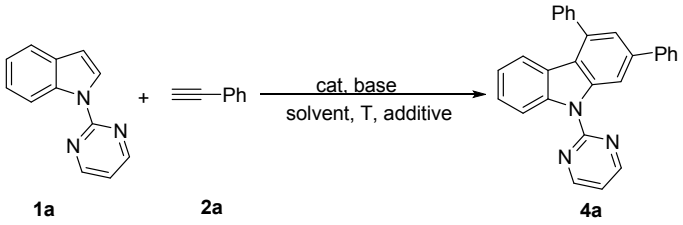
A flame-dried 50 mL Young-type tube with a magnetic stir bar was charged with N-2-pyrimidylindole (**1a**) (0.2 mmol), phenylacetylene (**2a**) (0.3 mmol), $MnBr(CO)_5$ (0.02 mmol), $PhCO_2H$ (0.04 mmol), N,N-diisopropylethylamine (DIPEA) (0.04 mmol) and diethyl ether (1.0 mL). The reaction mixture was stirred vigorously at 80 °C for 12 h under argon atmosphere. After cooling to room temperature, the reaction mixture was directly loaded onto a silica gel column to afford the desired product (**3aa**).

3. General procedure for the manganese-catalyzed addition of various indoles to phenylacetylenes.

A flame-dried 50 mL Young-type tube with a magnetic stir bar was charged with N-2-pyrimidylindole (**1a**) (0.3 mmol), phenylacetylene (**2a**) (0.75 mmol), $MnBr(CO)_5$ (0.06 mmol) , DIPEA (0.06 mmol) and diethyl ether (1.0 mL). The reaction mixture was stirred vigorously at 80 °C for 24 h under argon atmosphere. After cooling to room temperature, the reaction mixture was directly loaded onto a silica gel column to afford the desired product (**4a**).

4. Optimization of the reaction conditions for carbazole.

Table S1. Survey of the reaction parameters [a]



1a **2a** **4a**

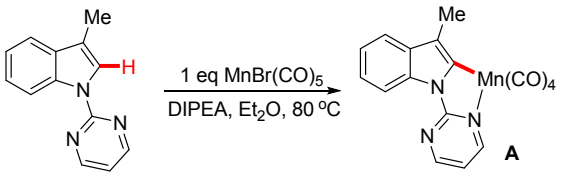
Entry	Base/Additive	Solvent	T(°C) /time	Yield(%)[b]/**4**
1	Et_2NH	Et_2O	100/6h	23.3
2	$(Pr)_2NH$	Et_2O	100/6h	13.3
3	Pyrrolidine	Et_2O	100/6h	2.6

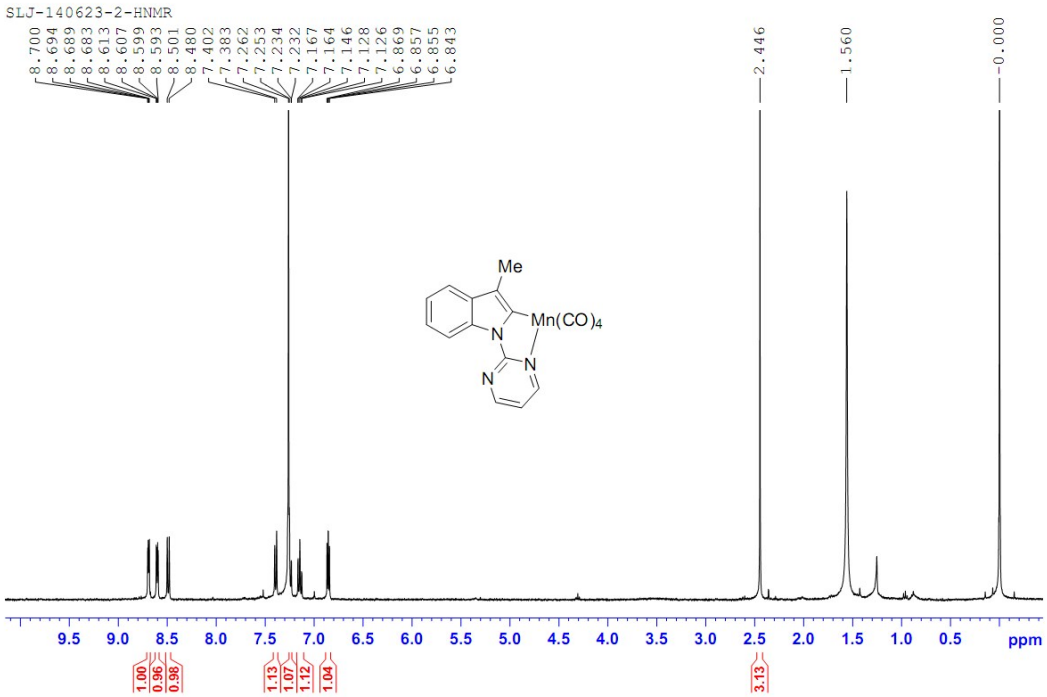
4	Piperidine	Et_2O	100/6h	15.1
5	DBU	Et_2O	100/6h	5.3
6	DABCO	Et_2O	100/6h	21.3
7	Pyridine	Et_2O	100/6h	15.2
8	DIPEA	Et_2O	100/6h	29.8
9	NEt_3	Et_2O	100/6h	28.9
10	^{t}BuOk	Et_2O	100/6h	22.8
11	$BuNH_2$	Et_2O	100/6h	5.8
12	DIPEA	Et_2O	100/6h	29.8
13	DIPEA	Toluene	100/6h	13.9
14	DIPEA	DMSO	100/6h	trace
15	DIPEA	DMAc	100/6h	2.96
16	DIPEA	Toluene	100/6h	6.8
17[c]	DIPEA	Et_2O	100/12h	35.8
18[d]	DIPEA	Et_2O	100/12h	36.6
19	DIPEA	Et_2O	100/12h	37.2
20	DIPEA/TBAB	Et_2O	100/12h	12
21	DIPEA/$(PhCO_2)_2$	Et_2O	100/12h	25
22	DIPEA /Pyridine	Et_2O	100/12h	14.1
23	DIPEA /$(Ph)_3P$	Et_2O	100/12h	18.1
24	DIPEA /$(Py)_2$	Et_2O	100/12h	12.9
25	DIPEA/4A	Et_2O	100/12h	36.3
26	DIPEA/$PhCO_2H$	Et_2O	100/12h	7
27	DIPEA/Ag(TFA)	Et_2O	100/12h	n.r.
28	DIPEA	Et_2O	80/12h	38.7
29	DIPEA	Et_2O	50/12h	n.r.
30[e]	DIPEA	Et_2O	80/12h	46(20)
31[e]	DIPEA	Et_2O	80/24h	58(29)*67*
32[e]	DIPEA	Et_2O	80/36h	(18)

[a]Reaction conditions: 0.2 mmol of **1a**, 2.5equiv **2a**, 10% mol of $MnBr(CO)_5$, 0.20 equiv DIPEA and $PhCO_2H$, 1 mL of solvent, Argon atmosphere. [b]The yields were determined by HPLC analysis with biphenyl as an internal standard. [c] under the CO atmosphere. [d] under O_2 atmosphere. [e] 20% mol of catalyst, recovery yields of **1a** in italics .

5. Procedure for the synthesis of Mn-complex A.

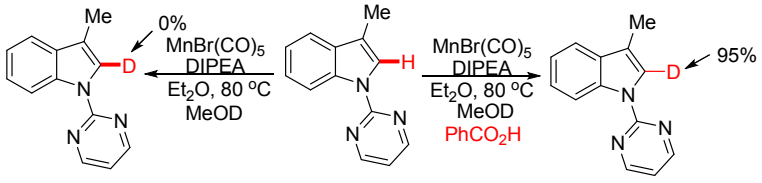
To a flame-dried Teflom-screw-capped tube was equipped with a magnetic stie bar. 3-methyl-N-2-pyrimidylindole (**1j**) (0.3 mmol), $MnBr(CO)_5$ (0.3 mmol) , DIPEA (0.36 mmol) were added to 2.0 mL diethyl ether under argon atmosphere. The closed tube was put into a pre-heated oil bath at 80 ºC and stirred for 12 h. After cooling to room temperature, the reaction mixture was directly loaded onto a silica gel column to afford the five-membered manganacycle Mn-**A**.

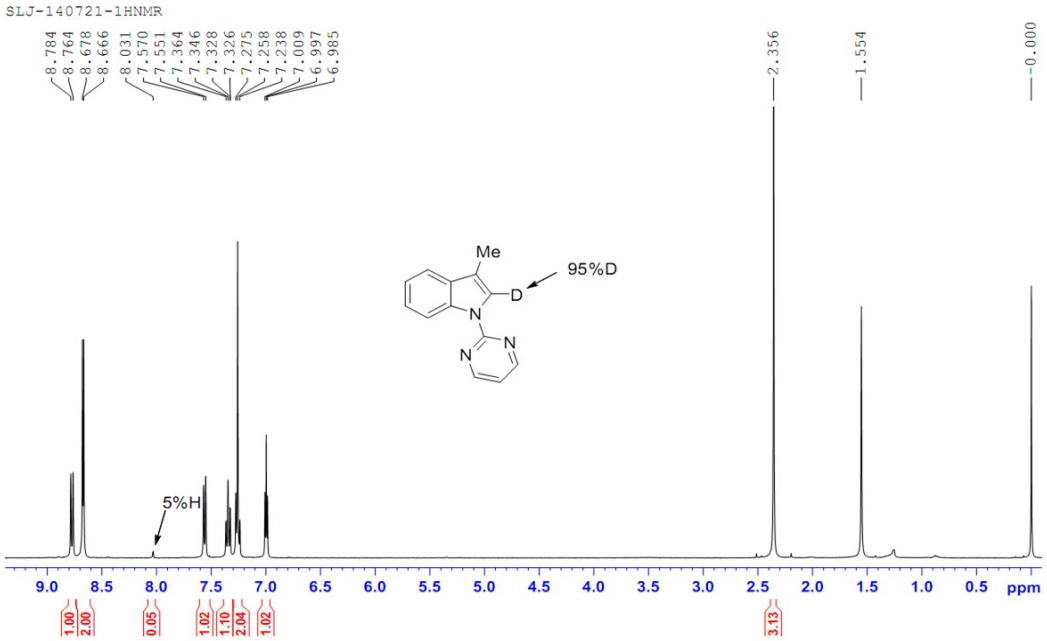




6. Procedure for deuterium-labeling experiments and kinetic isotope effect (KIE) experiments.

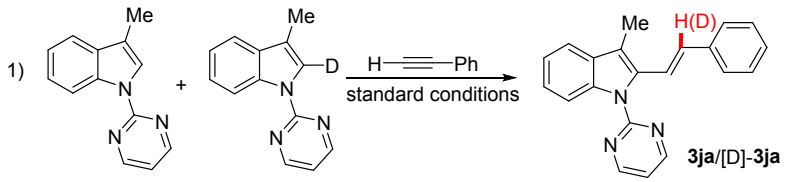
To a flame-dried Teflom-screw-capped tube was equipped with a magnetic stie bar. 3-methyl-N-2-pyrimidylindole (**1j**) (0.2 mmol), MeOD (0.3 mmol), $MnBr(CO)_5$ (0.06 mmol) , DIPEA (0.06 mmol) and $PhCO_2H$ (0.06 mmol) were added to 1.0 mL diethyl ether under argon atmosphere. The closed tube was put into a pre-heated oil bath at 80 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was directly loaded onto a silica gel column to afford the deuterium-labeling product. Without the acid addition, all of **1a** was recovered.





Kinetic isotope effect (KIE) experiments:

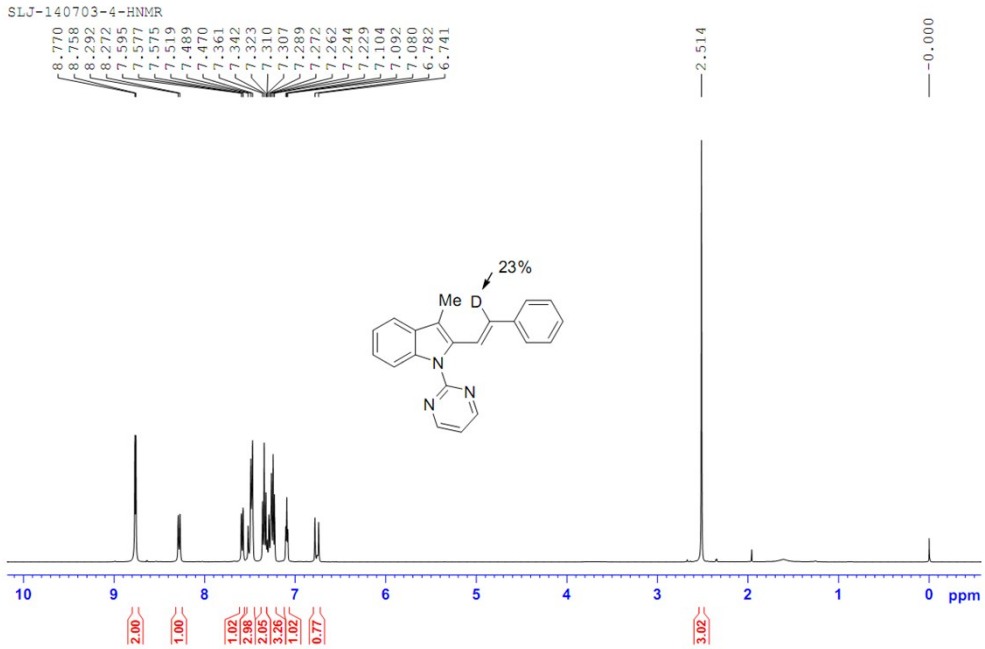
1) To a flame-dried Teflom-screw-capped tube was equipped with a magnetic stie bar. 3-methyl-N-2-pyrimidylindole (**1j**) and D-3-methyl-N-2-pyrimidylindole (D-**1j**) (1:1) (0.2 mmol), phenylacetylene (0.1 mmol), $MnBr(CO)_5$ (0.06 mmol) , DIPEA (0.06 mmol) and $PhCO_2H$ (0.06 mmol) were added to 1.0 mL diethyl ether under argon atmosphere. The closed tube was put into a pre-heated oil bath at 80 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was directly loaded onto a silica gel column to afford the deuterium-labeling product. The KIE value was determined by NMR.



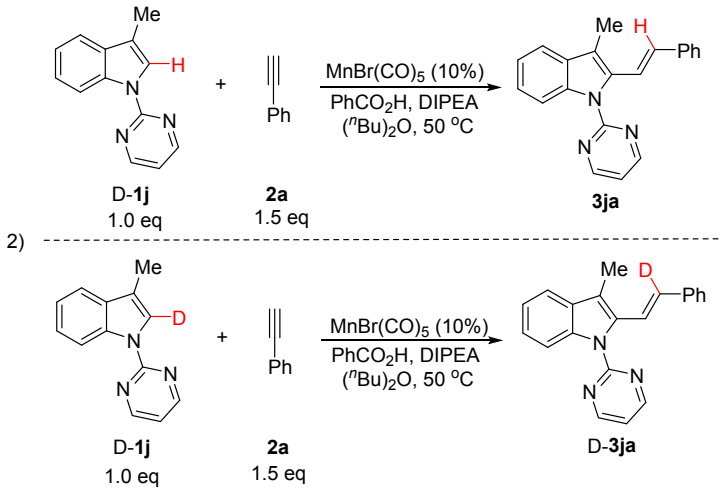
1j + [D]-**1j**

1 : 1

KIE = **3ja**/[D]-**3ja** = 3.45



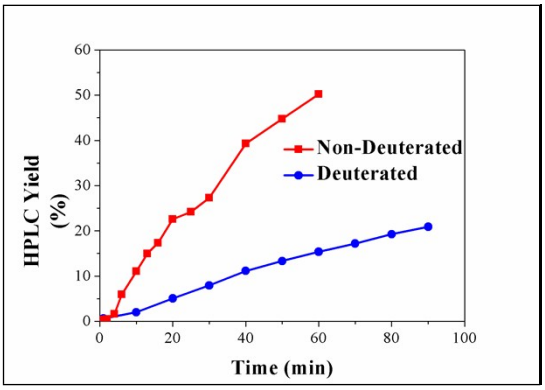
2) Two parallel reactions of **2a** with **1j** and D-**1j** respectively were performed to determine the corresponding KIE value. **1j** (0.2 mmol) and D-**1j** (0.2 mmol) were placed in a flame-dried Schlenk tube equipped with a magnetic stir bar, respectively. Then to both tubes were added the same mixture of **2a** (0.3 mmol), $MnBr(CO)_5$ (0.06 mmol) , DIPEA (0.06 mmol) and $PhCO_2H$ (0.06 mmol) in 2.0 mL 1-butoxybutane. The closed tube was put into a pre-heated oil bath at 50 ^oC under argon atmosphere. Each reaction was sampled at the following indicated points and analyzed by HPLC with the biphenyl as inner standard. And the results and curves are shown in the below.

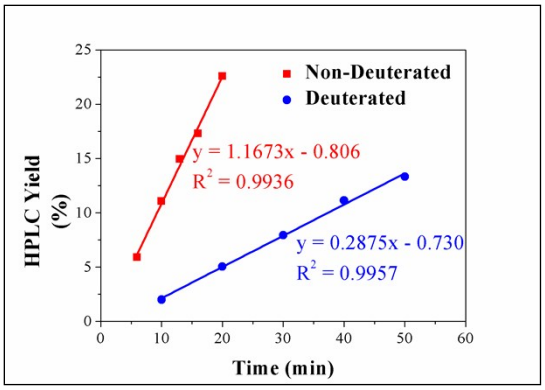


Time (min)	1	2	4	6	10	13	16	20	25	30
HPLC yield of **3ja** (%)	0.34	0.50	1.61	5.92	11.07	14.95	17.32	22.58	24.18	27.31

Time (min)	40	50	60
HPLC yield of **3ja**	39.32	44.73	50.22

(%)										
Time (min)	1	10	20	30	40	50	60	70	80	90
HPLC yield of D-**3ja** (%)	0.60	2.01	5.05	7.94	11.15	13.33	15.38	17.19	19.25	20.89





KIE = 1.167/0.288 = 4.05

Thus, the KIE value from the two parallel reactions was determined to be 4.05. So these two types of KIE values were measured by the above experiments indicated that the cleavage of the C–H bond might be the rate-determining step of the reaction.

7. GC analysis of the gas composition of the reaction and GC-MS analysis of the styrene.

Experimental procedure:

A) In an oven-dried Schlenk tube under Ar atmosphere, a mixture of **1j** (0.2 mmol), **2a** (0.3 mmol), $MnBr(CO)_5$ (0.02 mmol), DIPEA (0.04 mmol) and $PhCO_2H$ (0.04 mmol) in Et_2O (1 mL) was stirred at 80 °C for 12 h. When the reaction mixture cooled down to room temperature, the mixed gas of the reaction was taken using a syringe and GC analysis of the gas composition was carried out. There was only CO generated after the reaction, according to the GC spectrum of the mixture (Figure S1) and those of the corresponding standard samples (Figures S3 and S4). In addition, the styrene was not detected according to the GC-MS spectrum (Figure S5).

B) In an oven-dried Schlenk tube under Ar atmosphere, a mixture of **1j** (0.2 mmol), **2a** (0.3 mmol), $MnBr(CO)_5$ (0.04 mmol), DIPEA (0.04 mmol) in Et_2O (1 mL) was stirred at 80 °C for 12 h. When the reaction mixture cooled down to room temperature, the mixed gas of the reaction was taken using a syringe and GC analysis of the gas composition was carried out. The H_2 combined with CO were generated after the reaction, according to the GC spectrum of the mixture (Figure S2). In figure S6, the definitely peak certificated that the styrene was generated in this process.

GC analysis of the gas composition

Figure S1. GC spectrum of the mixed gas **(A)**

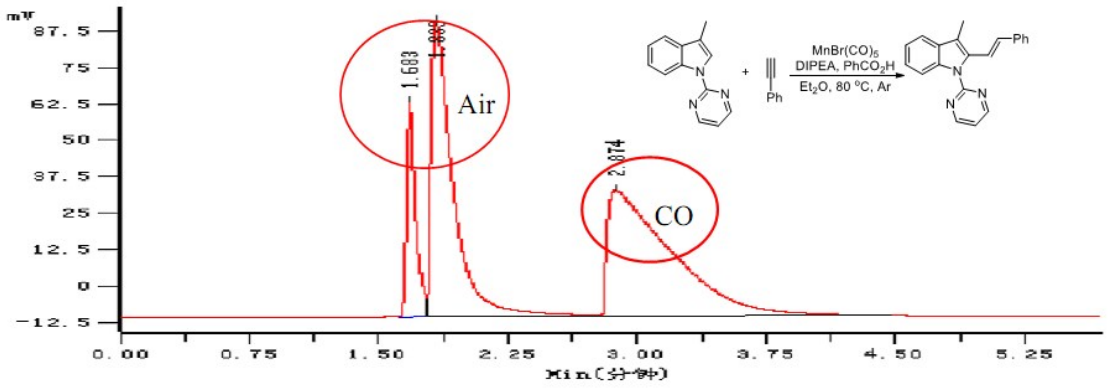


Figure S2. GC spectrum of the mixed gas **(B)**

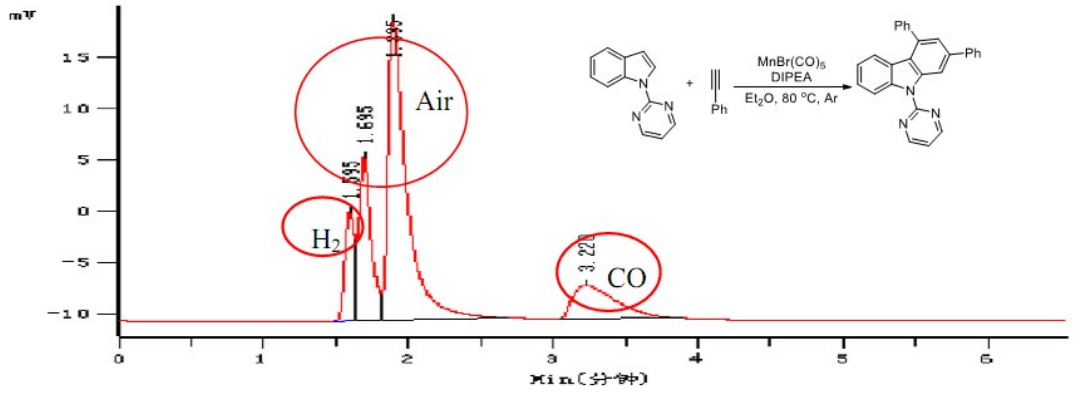


Figure S3. GC spectrum of standard sample H_2

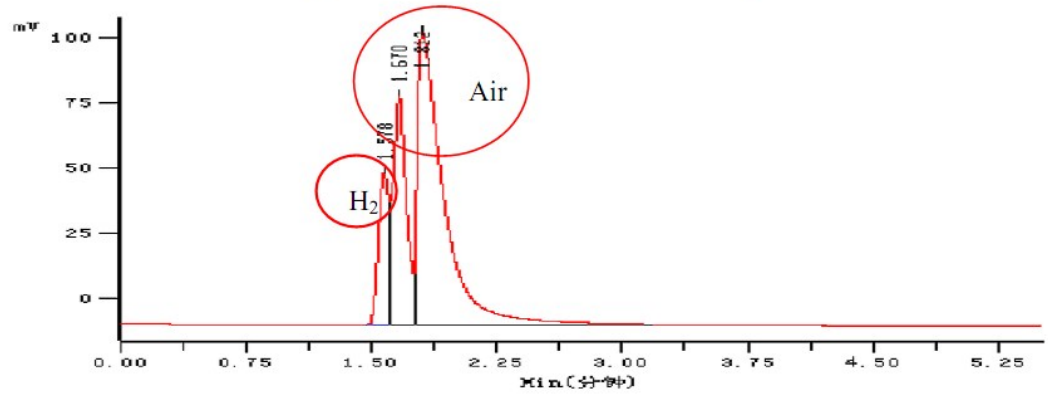
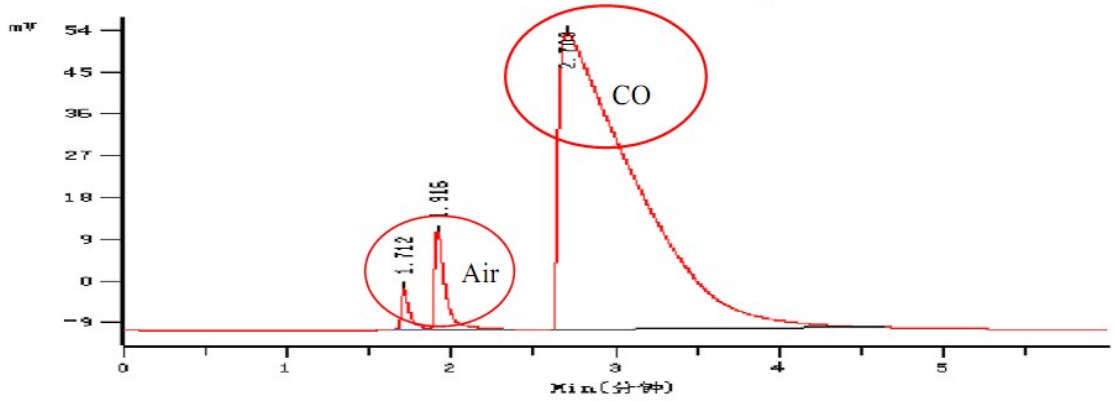


Figure S4. GC spectrum of standard sample CO



GC-MS analysis of the styrene

Figure S5. GC-MS spectrum of experiment **A**

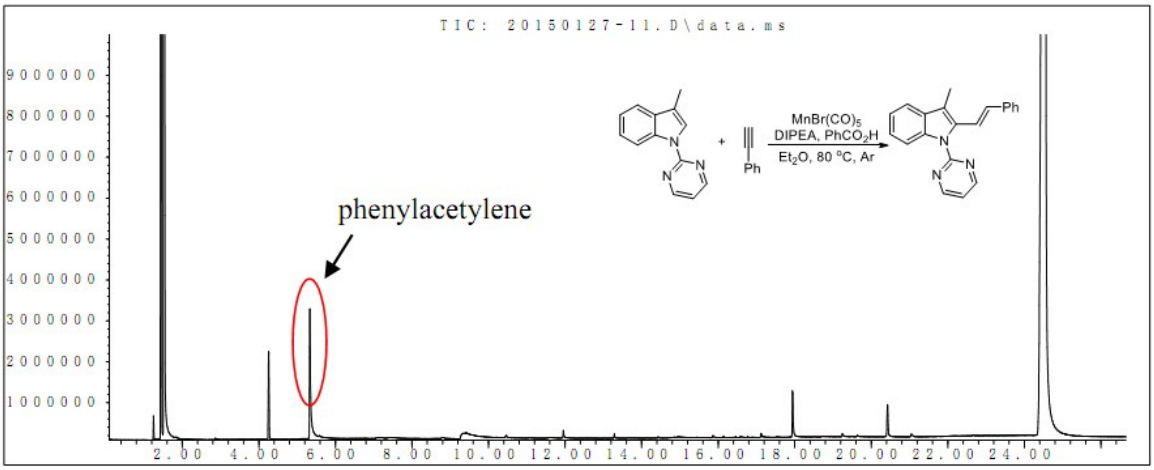
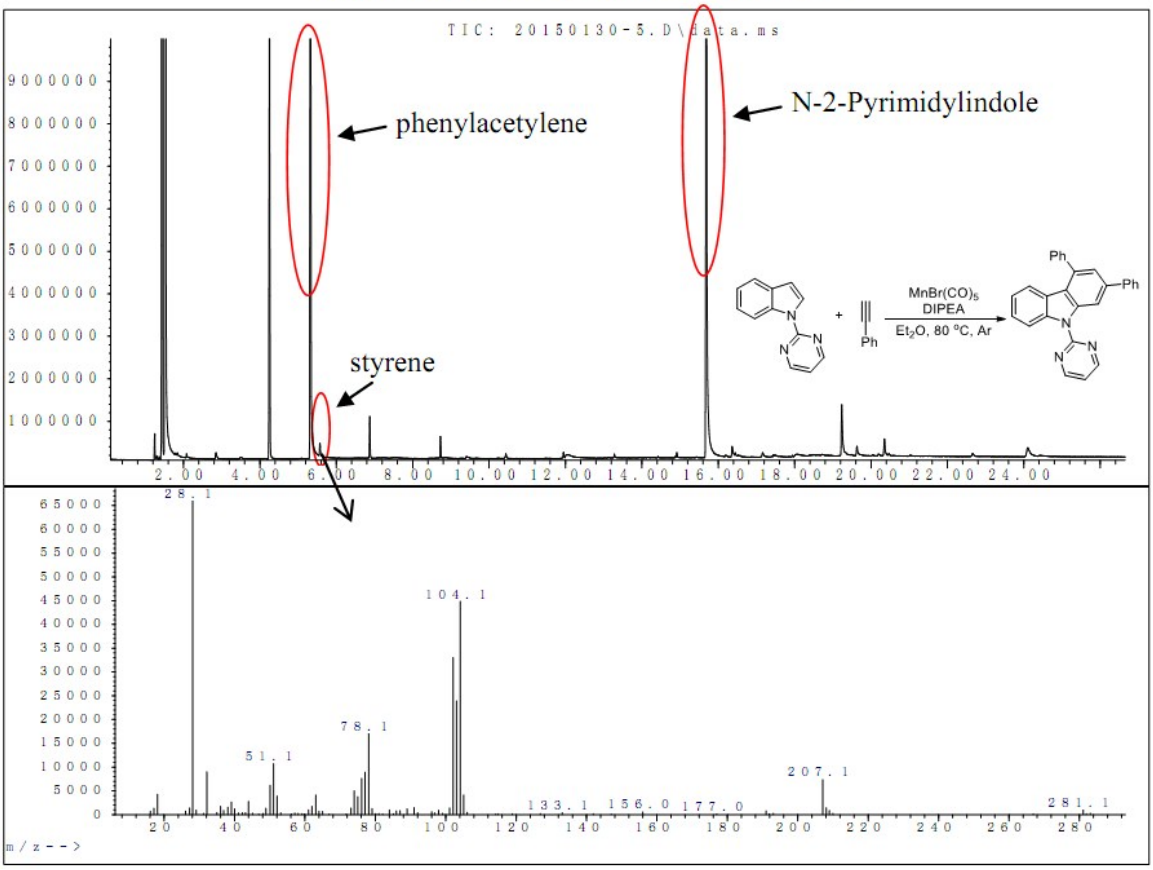
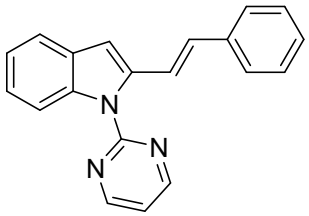


Figure S6. GC-MS spectrum of experiment **B**



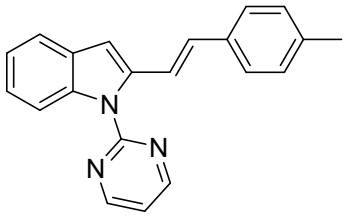
8. Characterization data for products.

(*E*)-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3aa**)



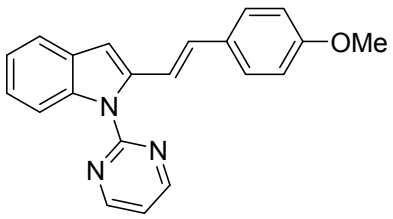
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.85 (d, *J* = 4.8 Hz, 2H), 8.29 (d, *J* = 8.2, 1H), 7.69 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.18-7.29 (m, 4H), 7.16 (d, *J* = 16.2 Hz, 1H), 7.02 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.2, 138.8, 137.5, 137.4, 129.6, 129.4, 128.6, 127.6, 126.6, 123.5, 122.3, 120.7, 120.4, 117.3, 114.0, 105.3. HRMS (ESI): *m/z* calculated for $C_{20}H_{15}N_3Na^+$ [M+Na$^+$]: 320.1158, found 320.1145.

(*E*)-2-(4-methylstyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ab**)



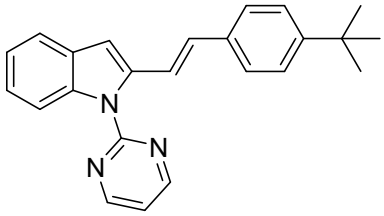
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 4.4 Hz, 2H), 8.27 (d, *J* = 8.0, 1H), 7.58-7.64 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.19-7.27 (m, 2H), 7.10-7.14 (m, 4H), 6.98 (s, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.2, 139.1, 137.6, 137.4, 134.8, 129.7, 129.5, 129.4, 126.6, 123.4, 122.3, 120.3, 119.7, 117.3, 114.0, 105.0, 21.4. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na$^+$]: 334.1315, found 334.1306.

(*E*)-2-(4-methoxystyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ac**)



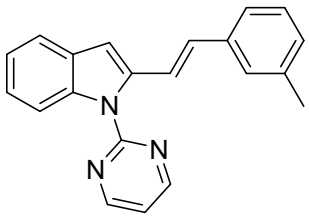
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.6 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.57-7.62(m, 1H), 7.53 (d, *J* = 16.1 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.18-7.30(m, 2H), 7.16 (t, *J* = 4.7 Hz, 1H), 7.11 (d, *J* = 16.1 Hz, 1H), 6.96 (s, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 158.4, 158.2, 139.3, 137.4, 130.4, 129.6, 129.4, 128.0, 123.4, 122.4, 120.3, 118.5, 117.4, 114.2, 114.0, 104.8, 55.4. HRMS (ESI): *m/z* calculated for $C_{21}H_{18}N_3O^+$ [M+H$^+$]: 328.1444, found 328.1436.

(*E*)-2-(4-*tert*-butylstyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ad**)



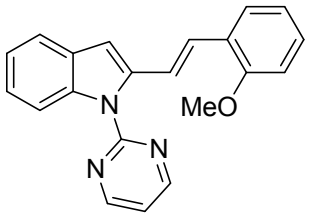
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.27 (d, *J* = 8.2, 1H), 7.64 (d, *J* = 16.4 Hz, 2H), 7.58-7.60 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 4H), 7.19-7.27 (m, 2H), 7.11-7.15 (m, 2H), 6.99 (s, 1H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 158.2, 150.9, 139.2, 137.4, 134.9, 129.64, 129.56, 126.5, 125.7, 123.5, 122.4, 120.4, 120.0, 117.3, 114.1, 105.1, 34.7, 31.4. HRMS (ESI): *m/z* calculated for $C_{24}H_{23}N_3Na^+$ [M+Na^+]: 376.1784, found 376.1773.

(*E*)-2-(3-methylstyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ae**)



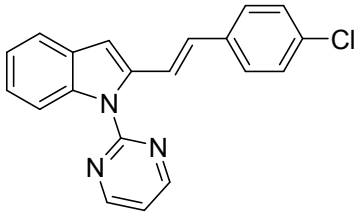
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.82 (d, *J* = 4.6 Hz, 2H), 8.28 (d, *J* = 8.1, 1H), 7.65 (d, *J* = 16.2 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.19-7.30 (m, 5H), 7.10-7.16 (m, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.1, 139.0, 138.2, 137.5, 137.4, 129.8, 129.4, 128.6, 128.5, 127.4, 123.8, 123.5, 122.3, 120.5, 120.4, 117.3, 114.0, 105.2, 21.5. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na^+]: 334.1315, found 334.1300.

(*E*)-2-(2-methoxystyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3af**)



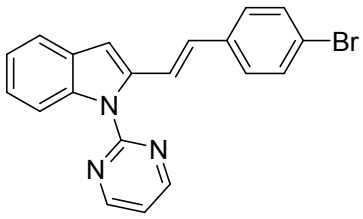
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.26 (d, *J* = 8.1, 1H), 7.71 (d, *J* = 16.4 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.49-7.56 (m, 2H), 7.18-7.26 (m, 3H), 7.10 (t, *J* = 4.8 Hz, 1H), 7.04 (s, 1H). 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.2, 157.1, 139.6, 137.4, 129.6, 128.8, 126.74, 126.65, 124.6, 123.4, 122.3, 120.9, 120.8, 120.4, 117.3, 114.0, 111.1, 105.1, 55.6. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3ONa^+$ [M+Na^+]: 350.1264, found 350.1272.

(*E*)-2-(4-chlorostyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ag**)



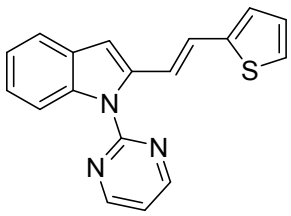
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 8.0, 1H), 7.67 (d, *J* = 16.2 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.19-7.28 (m, 3H), 7.09 (d, *J* = 16.2 Hz, 1H), 7.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 158.2, 138.6, 137.5, 136.2, 133.3, 129.5, 128.9, 128.3, 127.9, 123.9, 122.6, 121.4, 120.6, 117.4, 114.2, 105.7. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}ClN_3Na^+$ [M+Na$^+$]: 354.0768, found 354.0759.

(*E*)-2-(4-bromostyryl)-1-(pyrimidin-2-yl)-1*H*-indole (**3ah**)



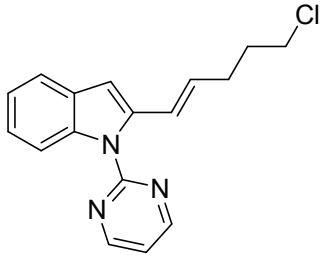
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.84 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 8.2, 1H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.18-7.30 (m, 3H), 7.07 (d, *J* = 16.2 Hz, 1H), 7.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 158.2, 138.5, 137.5, 136.6, 131.9, 129.4, 128.3, 128.2, 123.9, 122.5, 121.5, 121.4, 120.5, 117.4, 114.2, 105.7. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}BrN_3Na^+$ [M+Na$^+$]: 398.0263, found 398.0258.

(*E*)-1-(pyrimidin-2-yl)-2-(2-(thiophen-2-yl)vinyl)-1*H*-indole (**3ai**)



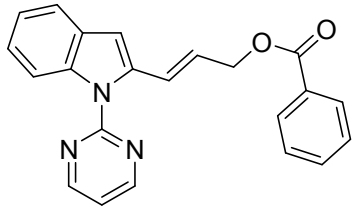
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.84 (d, *J* = 4.7 Hz, 2H), 8.29 (d, *J* = 8.2, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 15.9 Hz, 1H), 7.17-7.28 (m, 5H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.99-7.01 (m, 1H), 6.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 158.2, 143.2, 138.4, 137.4, 129.5, 127.8, 126.2, 124.5, 123.7, 122.8, 122.5, 120.43, 120.36, 117.4, 114.1, 105.3. HRMS (ESI): *m/z* calculated for $C_{18}H_{13}N_3SNa^+$ [M+Na$^+$]: 326.0722, found 326.0715.

(*E*)-2-(5-chloropent-1-enyl)-1-(pyrimidin-2-yl)-1*H*-indole (**3aj**)



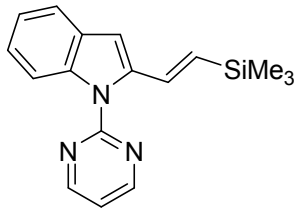
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.1, 1H), 7.55 (dd, *J* = 7.2, 0.7 Hz, 1H), 7.13-7.26 (m, 3H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.78 (s, 1H), 6.19 (dt, *J* = 15.6, 7.1 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.40 (qd, *J* = 7.1, 1.2 Hz, 2H), 1.96 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.1, 138.8, 137.1, 130.0, 129.4, 123.7, 123.3, 122.3, 120.2, 117.3, 114.0, 104.8, 44.4, 31.9, 30.1. HRMS (ESI): *m/z* calculated for $C_{17}H_{16}ClN_3Na^+$ [M+Na^+]: 320.0925, found 320.0918.

(*E*)-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)allylbenzoate (**3ak**)



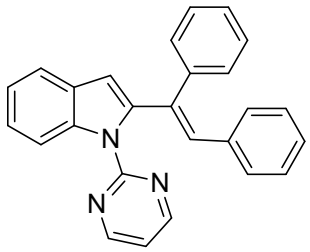
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.7 Hz, 2H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 2H), 7.54-7.59 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 15.8 Hz, 1H), 7.19-7.28 (m, 2H), 7.13 (t, *J* = 4.7 Hz, 1H), 6.93 (s, 1H), 6.45 (dt, *J* = 15.6, 6.2 Hz, 1H), 5.02 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 158.3, 158.1, 137.4, 137.3, 133.1, 130.4, 129.8, 129.2, 128.5, 126.2, 124.2, 123.8, 122.4, 120.6, 117.3, 114.3, 106.1, 65.5. HRMS (ESI): *m/z* calculated for $C_{22}H_{17}N_3O_2Na^+$ [M+Na^+]: 378.1213, found 378.1210.

(*E*)-1-(pyrimidin-2-yl)-2-(2-(trimethylsily)vinyl)-1*H*-indole (**3al**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.6 Hz, 2H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 19.1 Hz, 1H), 7.15-7.27 (m, 3H), 6.94 (s, 1H), 6.49 (d, *J* = 19.1 Hz, 1H), 0.15 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.1, 140.2, 137.4, 135.3, 130.8, 129.2, 123.7, 122.3, 120.6, 117.4, 114.0, 105.7, -1.1. HRMS (ESI): *m/z* calculated for $C_{17}H_{19}N_3SiNa^+$ [M+Na^+]: 316.1240, found 316.1237.

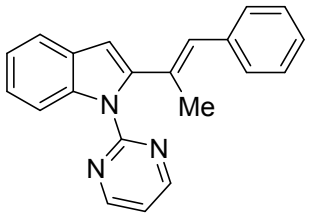
(E)-2-(1, 2-diphenylvinyl)-1-(pyrimidin-2-yl)-1*H*-indole (**3am**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.6 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.08-7.29 (m, 9H), 7.01-7.06 (m, 4H), 6.88 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ

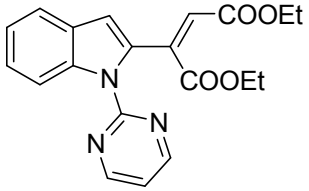
158.1, 157.6, 142.8, 138.6, 137.9, 137.2, 135.4, 130.5, 129.8, 128.9, 128.8, 128.0, 127.8, 127.3, 127.0, 123.9, 122.1, 120.7, 117.2, 112.9, 110.1. HRMS (ESI): *m/z* calculated for $C_{26}H_{19}N_3Na^+$ [M+Na^+]: 396.1471, found 396.1472.

(E)-2-(1-phenylprop-1-en-2-yl)-1-(pyrimidin-2-yl)-1H-indole (**3an**)



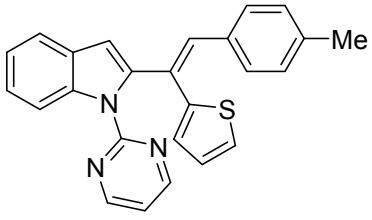
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.18-7.30 (m, 3H), 7.12 (dt, *J* = 4.8, 1.0 Hz, 1H), 6.74 (s, 1H), 6.66 (s, 1H), 2.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 158.4, 144.6, 138.0, 137.9, 131.4, 129.4, 129.3, 129.2, 128.3, 126.7, 123.6, 122.3, 120.6, 117.5, 113.4, 107.4, 19.3. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na^+]: 334.1315, found 334.1298.

Diethyl-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)maleate (**3ao**)



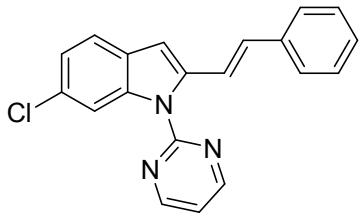
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.5, 0.7 Hz, 1H), 8.65 (d, *J* = 4.8 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.34-7.38 (m, 1H), 7.22-7.26 (m, 1H), 7.03 (t, *J* = 4.8 Hz, 1H), 6.95 (s, 1H), 6.70 (d, *J* = 0.6 Hz, 1H), 4.00-4.10 (m, 4H), 1.00 (dt, *J* = 7.1, 3.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 165.9, 157.9, 157.6, 138.7, 136.7, 132.1, 129.5, 127.0, 124.4, 122.5, 121.0, 116.35, 116.31, 111.5, 61.5, 60.9, 14.0, 13.9. HRMS (ESI): *m/z* calculated for $C_{20}H_{19}N_3O_4Na^+$ [M+Na^+]: 388.1268, found 388.1284.

1-(pyrimidin-2-yl)-2-(1-(thiophen-2-yl)-2-(p-tolyl)vinyl)-1*H*-indole (**3ap**)



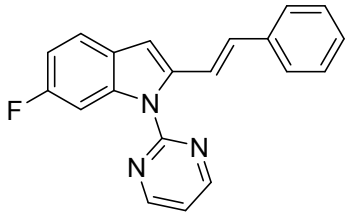
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.8 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.60 (m, 1H), 7.28-7.18 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 7.02 (dd, *J* = 5.0, 0.6 Hz, 1H), 6.99-6.95 (m, 3H), 6.90 (d, *J* = 3.3 Hz, 1H), 6.86-6.84 (m, 1H), 6.80 (s, 1H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2, 158.0, 142.8, 140.9, 138.4, 137.8, 135.0, 133.3, 130.5, 129.1, 129.0, 128.9, 126.4, 125.6, 123.8, 122.2, 122.1, 120.7, 117.4, 112.8, 109.9, 21.5. HRMS (ESI): *m/z* calculated for $C_{25}H_{19}N_3SNa^+$ [M+Na^+]: 416.1192, found 416.1209.

(*E*)-6-chloro-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3ba**)



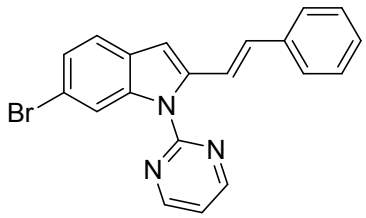
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.35 (s, 1H), 7.55 (d, *J* = 16.2, 1H), 7.47 (d, *J* = 8.3 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23-7.26 (m, 1H), 7.15-7.19 (m, 2H), 7.12 (d, *J* = 16.4 Hz, 1H), 6.93 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 157.8, 139.6, 137.6, 137.3, 130.1, 129.2, 128.7, 127.9, 127.8, 126.7, 122.9, 121.0, 120.4, 117.6, 114.4, 104.9. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}ClN_3Na^+$ [M+Na^+]: 354.0768, found 354.0754.

(*E*)-6-fluoro-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3ca**)



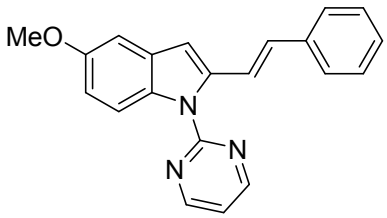
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.09 (dd, *J* = 11.0, 2.0 Hz, 1H), 7.69 (d, *J* = 16.2, 1H), 7.48-7.52 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24-7.27 (m, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.11 (d, *J* = 16.2 Hz, 1H), 6.99 (m, 1H), 6.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.9, 159.5, 158.5, 158.1, 139.6, 139.5, 137.62, 137.56, 137.5, 129.5, 128.8, 127.8, 126.8, 125.9, 121.0, 120.9, 120.8, 117.5, 111.0, 110.8, 105.2, 101.8, 101.5. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}FN_3Na^+$ [M+Na^+]: 338.1064, found 338.1067.

(*E*)-6-bromo-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3da**)



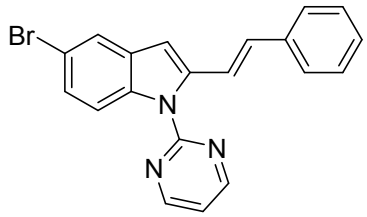
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (d, *J* = 4.5 Hz, 2H), 8.5 (s, 1H), 7.65 (d, *J* = 16.2, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 8.3 Hz, 1H), 7.31-7.36 (m, 3H), 7.24-7.27 (m, 1H), 7.18-7.20 (m, 1H), 7.14 (d, *J* = 16.2 Hz, 1H), 6.94 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 157.9, 139.6, 138.0, 137.4, 130.3, 128.8, 128.3, 127.9, 126.8, 125.7, 121.4, 120.4, 117.7, 117.3, 117.1, 105.0. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}BrN_3Na^+$ [M+Na^+]: 398.0263, found 398.0252.

(*E*)-5-methoxy-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3ea**)



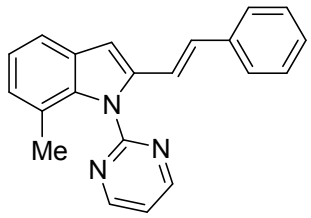
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.24 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 16.2 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.22-7.26 (m, 1H), 7.09-7.14 (m, 2H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.93 (s, 1H), 6.90 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.2, 155.8, 139.5, 137.6, 132.4, 130.2, 129.5, 128.7, 127.7, 126.7, 121.0, 117.1, 115.3, 112.9, 105.3, 102.3, 55.8. HRMS (ESI): *m/z* calculated for $C_{21}H_{18}N_3O^+$ [M+H$^+$]: 328.1444, found 328.1433.

(*E*)-5-bromo-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3fa**)



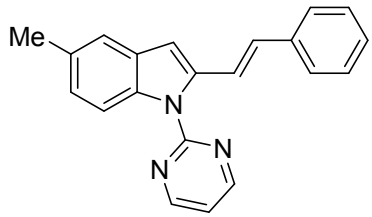
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.85 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.32-7.38 (m, 3H), 7.26-7.29 (m, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 7.16 (d, *J* = 16.2 Hz, 1H), 6.93 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 158.0, 140.2, 137.4, 136.1, 131.3, 130.7, 128.8, 128.0, 126.9, 126.3, 122.9, 120.4, 117.7, 115.8, 115.7, 104.4. HRMS (ESI): *m/z* calculated for $C_{20}H_{14}BrN_3Na^+$ [M+Na$^+$]: 398.0263, found 398.0252.

(*E*)-7-methyl-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3ga**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.9 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.34-7.38 (m, 2H), 7.24-7.31 (m, 3H), 7.18-7.22 (m, 1H), 7.07-7.12 (m, 3H), 6.97-6.98 (m, 2H), 1.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 158.6, 139.6, 137.5, 137.2, 131.0, 129.8, 128.7, 127.8, 126.6, 126.0, 122.1, 121.9, 119.6, 118.7, 118.0, 102.9, 20.0. HRMS (ESI): *m/z* calculated for $C_{21}H_{18}N_3^+$ [M+H$^+$]: 312.1495, found 312.1489.

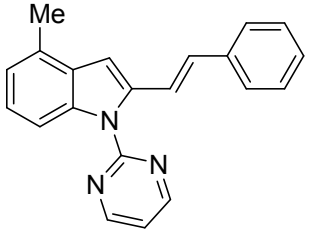
(*E*)-5-methyl-1-(pyrimidin-2-yl)-2-styryl-1*H*-indole (**3ha**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 16.2 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.30-7.36 (m, 3H), 7.18-7.26 (m, 1H), 7.02 -7.15 (m, 3H), 6.91 (s, 1H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.3, 158.2, 138.9, 137.6, 135.7, 131.7,

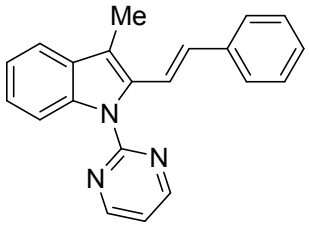
129.7, 129.3, 128.7, 127.6, 126.7, 125.1, 121.0, 120.2, 117.0, 114.0, 105.2, 21.4. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na$^+$]: 334.1315, found 334.1304.

(E)-4-methyl-1-(pyrimidin-2-yl)-2-styryl-1H-indole (**3ia**)



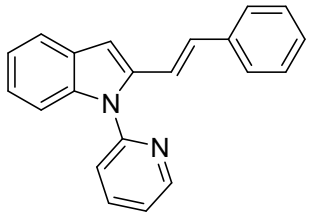
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 3.2 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.11-7.25 (m, 4H), 7.01-7.04 (m, 2H), 2.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.4, 158.2, 138.3, 137.7, 137.2, 129.8, 129.4, 129.1, 128.7, 127.6, 126.7, 123.7, 122.7, 120.8, 117.3, 111.6, 103.8, 18.8. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na$^+$]: 334.1315, found 334.1306.

(E)-3-methyl-1-(pyrimidin-2-yl)-2-styryl-1H-indole (**3ja**)



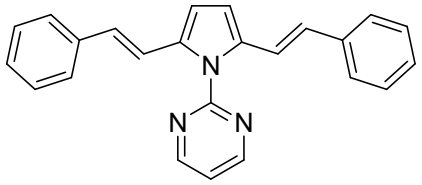
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.29 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.59-7.61 (m, 1H), 7.48-7.52 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.23-7.32 (m, 4H), 7.14 (t, *J* = 4.8 Hz, 1H), 6.77 (d, *J* = 16.4 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.5, 158.4, 137.9, 136.7, 134.0, 131.3, 130.0, 128.8, 127.6, 126.5, 124.1, 122.0, 120.8, 118.9, 117.0, 115.8, 113.8, 10.7. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_3Na^+$ [M+Na$^+$]: 334.1315, found 334.1299.

(*E*)-1-(pyridin-2-yl)-2-styryl-1*H*-indole (**3ka**)



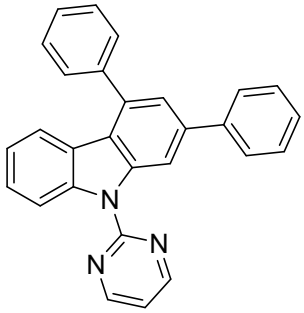
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.73 (m, 1H), 7.88 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62-7.64 (m, 1H), 7.50-7.52 (m, 1H), 7.39-7.42 (m, 3H), 7.29-7.36 (m, 3H), 7.15-7.25 (m, 3H), 7.10 (d, *J* = 6.2 Hz, 1H), 6.99 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4, 149.7, 138.4, 138.2, 137.9, 137.2, 130.6, 128.7, 127.8, 126.6, 123.0, 122.1, 121.6, 121.5, 120.6, 118.4, 111.0, 102.4. HRMS (ESI): *m/z* calculated for $C_{21}H_{17}N_2^+$ [M+H$^+$]: 297.1386, found 297.1382.

2-(2, 5-distyryl-1H-pyrrol-1-yl)pyrimidine (**3la**)



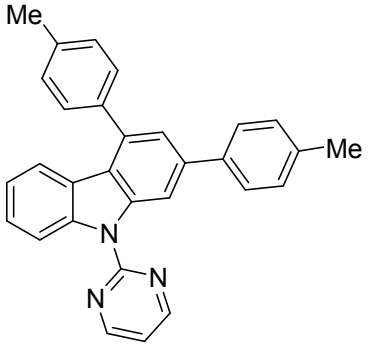
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.8 Hz, 2H), 7.34-7.37 (m, 5H), 7.25-7.3 (m, 4H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 16.2 Hz, 2H), 6.91 (d, *J* = 16.1 Hz, 2H), 6.73 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.8, 157.6, 138.0, 134.6, 128.7, 127.2, 127.1, 126.3, 119.2, 118.8, 109.9. HRMS (ESI): *m/z* calculated for $C_{24}H_{19}N_3Na^+$ [M+Na^+]: 372.1471, found 372.1457.

2, 4-diphenyl-9-(pyrimidin-2-yl)-9H-carbazole (**4a**)



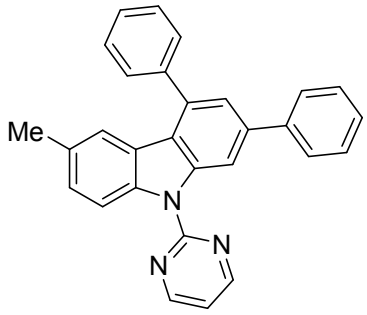
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.5 Hz, 1H), 8.87 (d, *J* = 4.8 Hz, 2H), 8.76 (d, *J* = 8.4 Hz, 1H), 7.76-7.79 (m, 2H), 7.63-7.66 (m, 2H), 7.37-7.57 (m, 8H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 4.7 Hz, 1H), 7.06-7.10 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 158.2, 142.0, 141.2, 140.2, 140.0, 139.5, 137.5, 129.5, 128.9, 128.7, 127.8, 127.3, 126.4, 125.2, 123.7, 122.4, 122.1, 122.0, 116.5, 115.5, 113.4. HRMS (ESI): *m/z* calculated for $C_{28}H_{19}N_3Na^+$ [M+Na^+]: 420.1471, found 420.1455.

9-(pyrimidin-2-yl)-2, 4-dip-tolyl-9H-carbazole (**4b**)



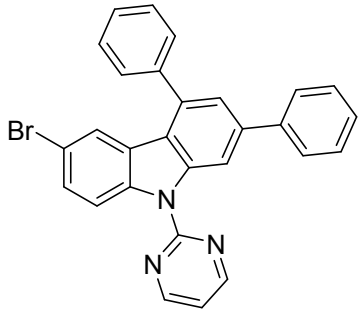
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 1.1 Hz, 1H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.76 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 1.2 Hz, 1H), 7.39-7.42 (m, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.06-7.13 (m, 2H), 2.50 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 158.1, 140.2, 139.9, 139.4, 139.2, 138.3, 137.5, 137.4, 137.0, 129.6, 129.3, 127.6, 126.3, 125.4, 123.6, 122.2, 122.1, 121.9, 116.4, 115.5, 113.0, 21.5, 21.3. HRMS (ESI): *m/z* calculated for $C_{30}H_{23}N_3Na^+$ [M+Na^+]: 448.1784, found 448.1784.

6-methyl-2, 4-diphenyl-9-(pyrimidin-2-yl)-9H-carbazole (**4c**)



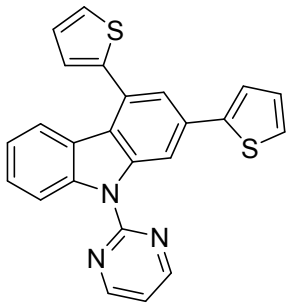
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 1.5 Hz, 1H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.67 (d, *J* = 8.6 Hz, 1H), 7.76-7.78 (m, 2H), 7.63-7.65 (m, 2H), 7.51-7.57 (m, 3H), 7.45-7.49 (m, 3H), 7.34-7.38 (m, 1H), 7.21-7.24 (m, 1H), 7.10-7.12 (m, 2H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 158.1, 142.1, 141.2, 140.4, 139.3, 138.2, 137.4, 131.3, 129.5, 128.8, 128.6, 127.8, 127.6, 127.2, 125.4, 123.6, 122.4, 122.2, 116.2, 115.4, 113.5, 21.6. HRMS (ESI): *m/z* calculated for $C_{29}H_{21}N_3Na^+$ [M+Na^+]: 434.1628, found 434.1629.

6-bromo-2, 4-diphenyl-9-(pyrimidin-2-yl)-9H-carbazole (**4d**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.5 Hz, 1H), 8.85 (d, *J* = 4.7 Hz, 2H), 8.68 (d, *J* = 9.0 Hz, 1H), 7.75-7.77 (m, 2H), 7.53-7.62 (m, 5H), 7.46-7.50 (m, 4H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.36-7.39 (m, 1H), 7.16 (t, *J* = 4.82 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 158.2, 141.8, 140.5, 140.4, 140.2, 138.7, 137.7, 129.3, 129.0, 128.9, 128.8, 128.2, 127.8, 127.5, 127.1, 124.6, 123.9, 121.3, 117.2, 116.7, 115.0, 113.6. HRMS (ESI): *m/z* calculated for $C_{28}H_{18}N_3BrNa^+$ [M+Na^+]: 498.0576, found 498.0560.

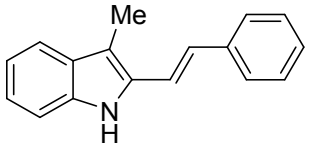
9-(pyrimidin-2-yl)-2, 4-di(thiophen-2-yl)-9H-carbazole (**4e**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 1.5 Hz, 1H), 8.86 (d, *J* = 4.9 Hz, 2H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.51 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.41-7.46 (m, 3H), 7.29-7.32 (m, 2H), 7.23-7.25 (m, 1H), 7.10-7.16 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 158.1, 145.1, 141.5, 140.0, 132.3, 129.5, 128.2, 127.5, 127.3, 126.7, 126.1, 125.04, 125.00, 123.8, 123.71,

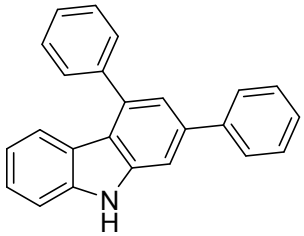
123.69, 122.3, 122.0, 116.6, 115.7, 113.2. HRMS (ESI): *m/z* calculated for $C_{24}H_{15}N_3S_2Na^+$ [M+Na^+]: 432.0600, found 432.0600.

(E)-3-methyl-2-styryl-1H-indole (**5a**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34-7.38 (m, 2H), 7.25-7.28 (m, 2H), 7.17-7.23 (m, 2H), 7.08-7.11 (m, 1H), 6.74 (d, *J* = 16.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 136.6, 132.4, 129.8, 128.9, 127.6, 126.3, 125.7, 123.3, 119.6, 119.1, 117.3, 112.8, 110.5, 8.9. HRMS (ESI): *m/z* calculated for $C_{17}H_{15}NNa^+$ [M+Na^+]: 256.1097, found 256.1090.

2, 4-diphenyl-9H-carbazole (**6a**)

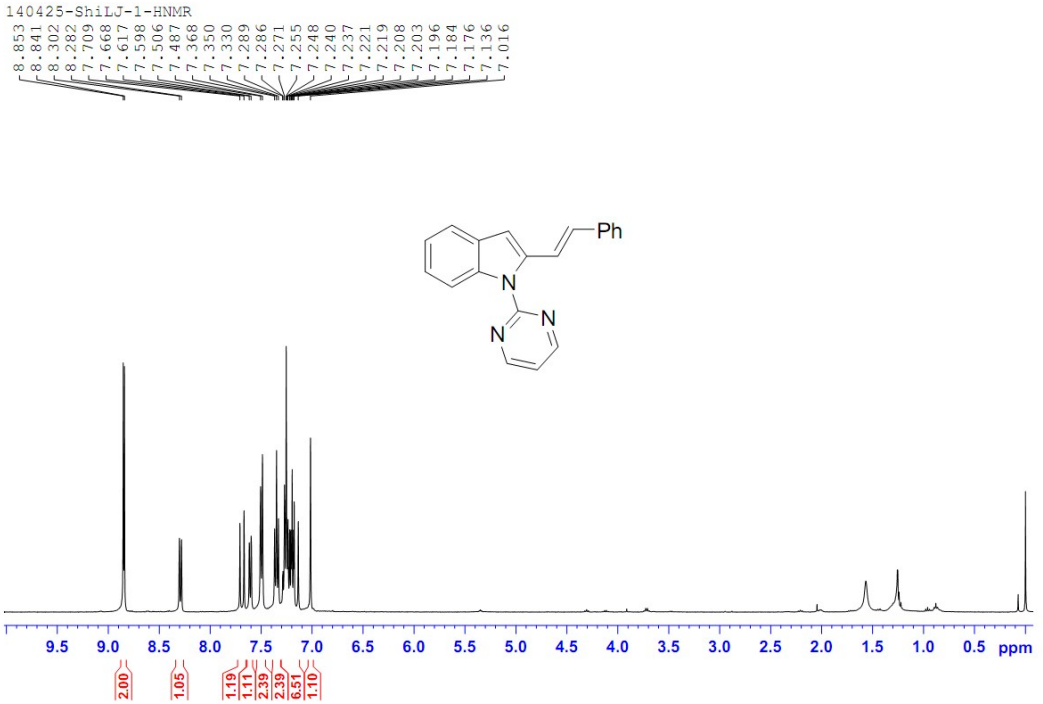


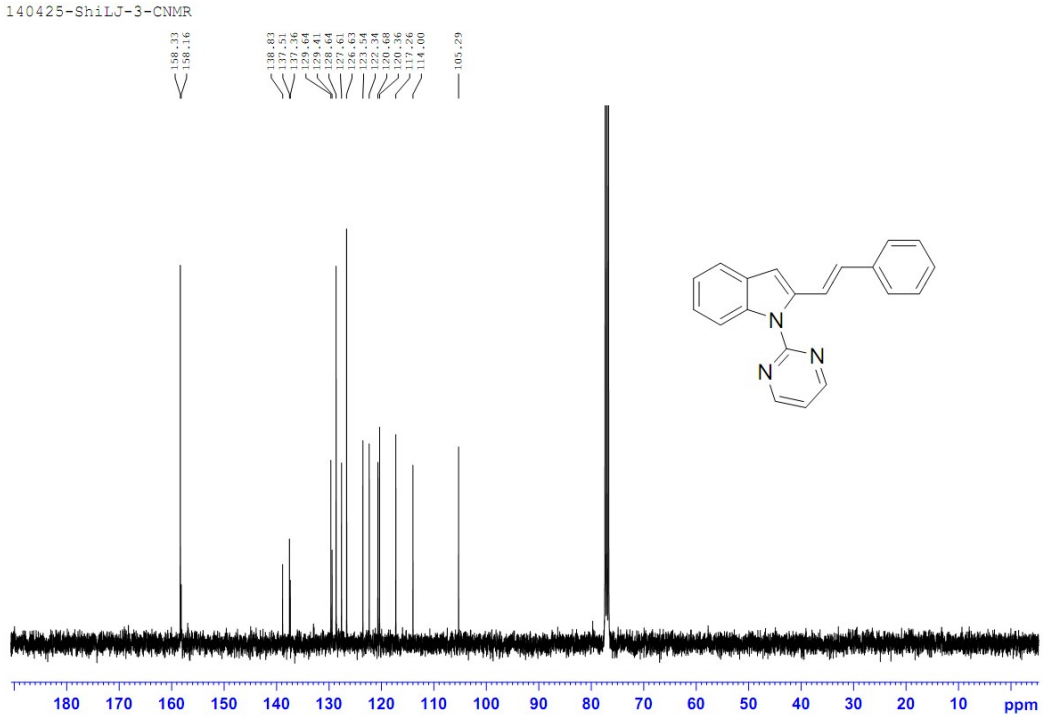
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66-7.72 (m, 4H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.43-7.56 (m, 6H), 7.32-7.29 (m, 4H), 6.97-7.01 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.7, 141.3, 140.6, 140.3, 139.1, 138.0, 129.4, 128.9, 128.6, 127.8, 127.6, 127.3, 125.9, 122.8, 123.7, 122.5, 121.0, 119.3, 110.6, 108.1. HRMS (ESI): *m/z* calculated for $C_{24}H_{17}NNa^+$ [M+Na^+]: 342.1253, found 342.1240.

9. References

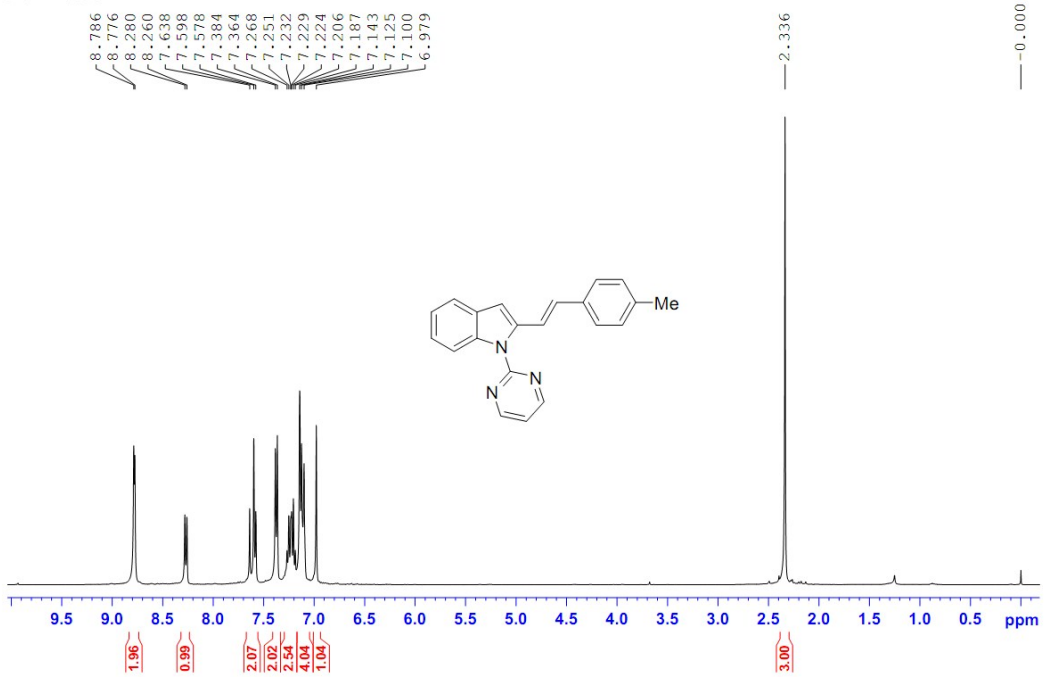
1. (a) Z. Ding and N. Yoshikai, *Angew. Chem. Int. Ed.*, 2012, **51**, 4698; (b) L. Ackermann and A. V. Lygin, *Org. Lett.*, 2011, **13**, 3332.

10. ^{1}H NMR and ^{13}C NMR copies of products.

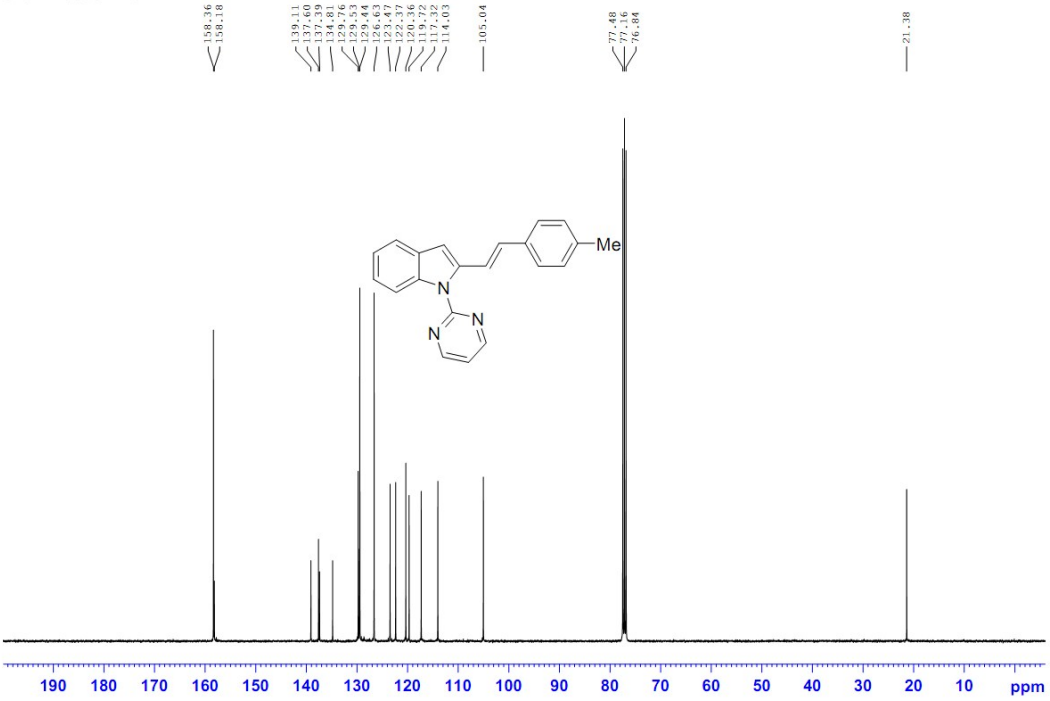




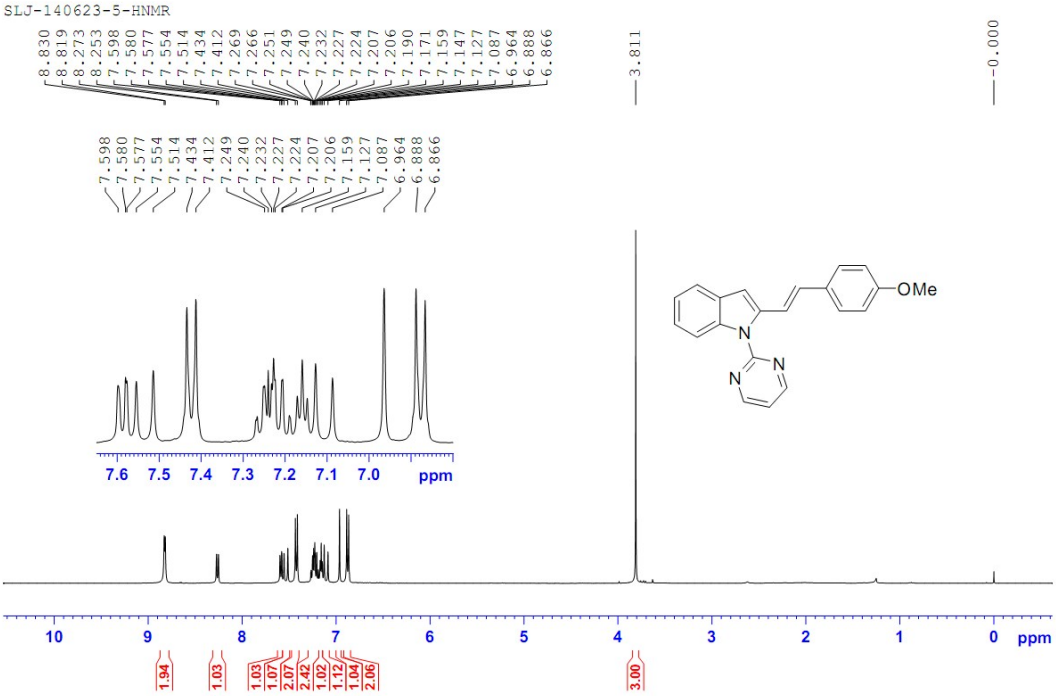
SLJ-140606-4-HNMR



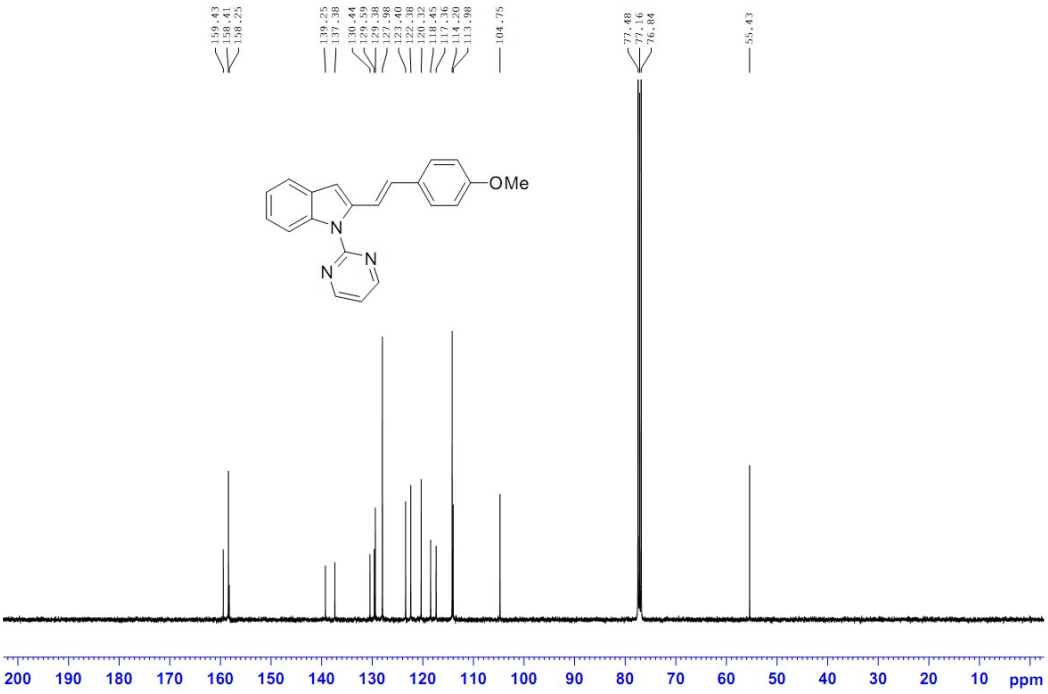
SLJ-140606-4-CNMR



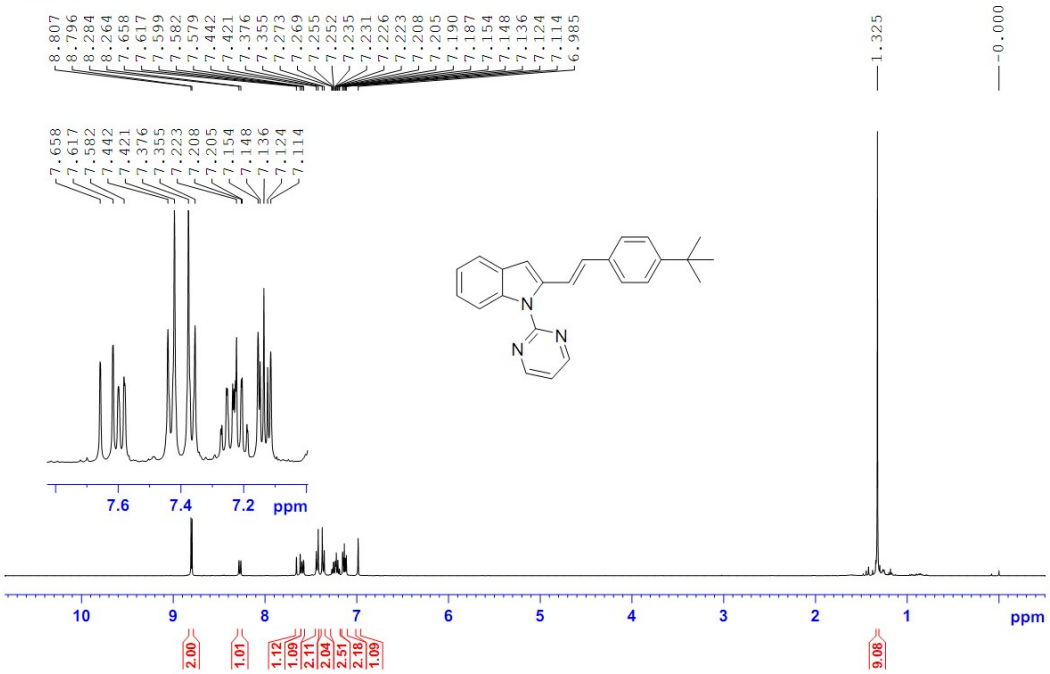
SLJ-140623-5-HNMR



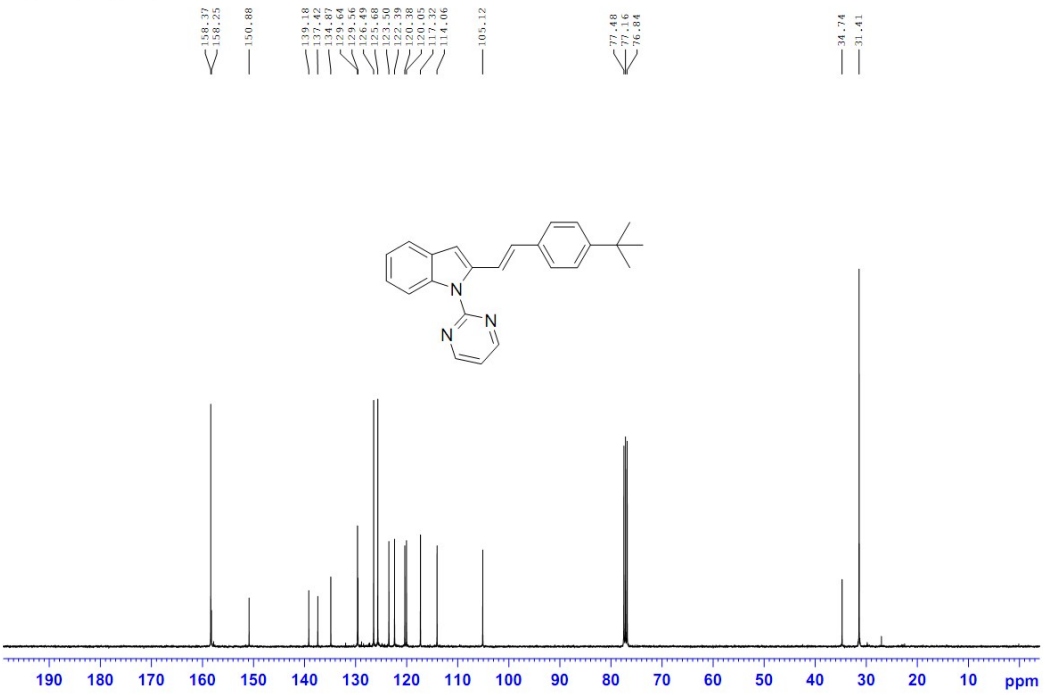
SLJ-140623-5-CNMR



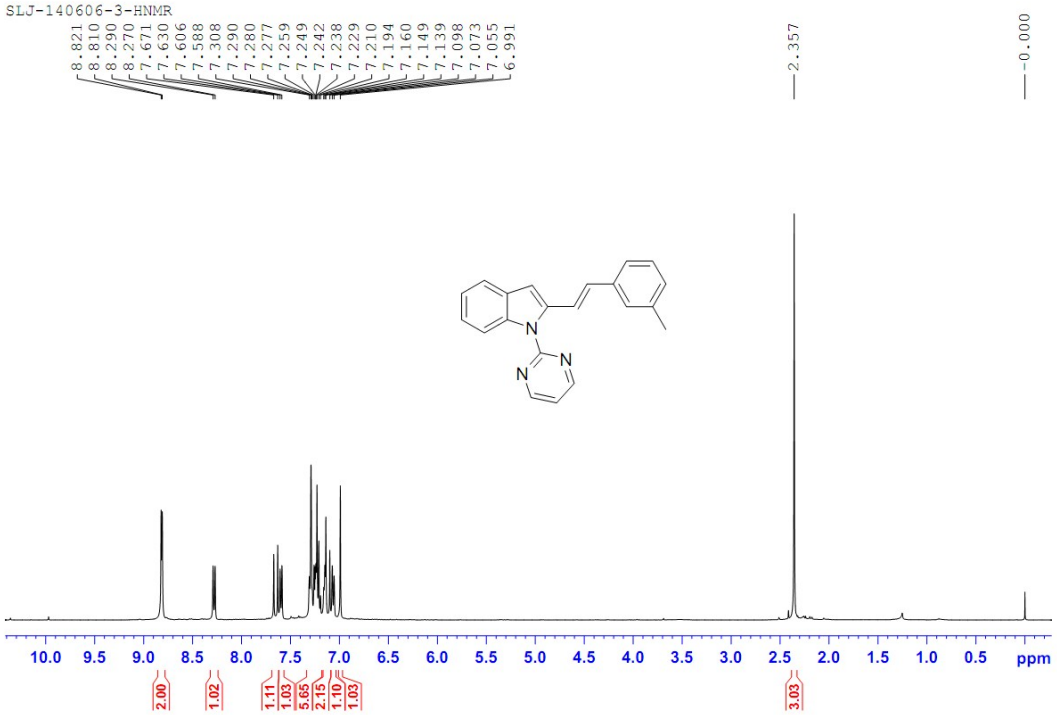
140509-ShiLJ-1-HNMR



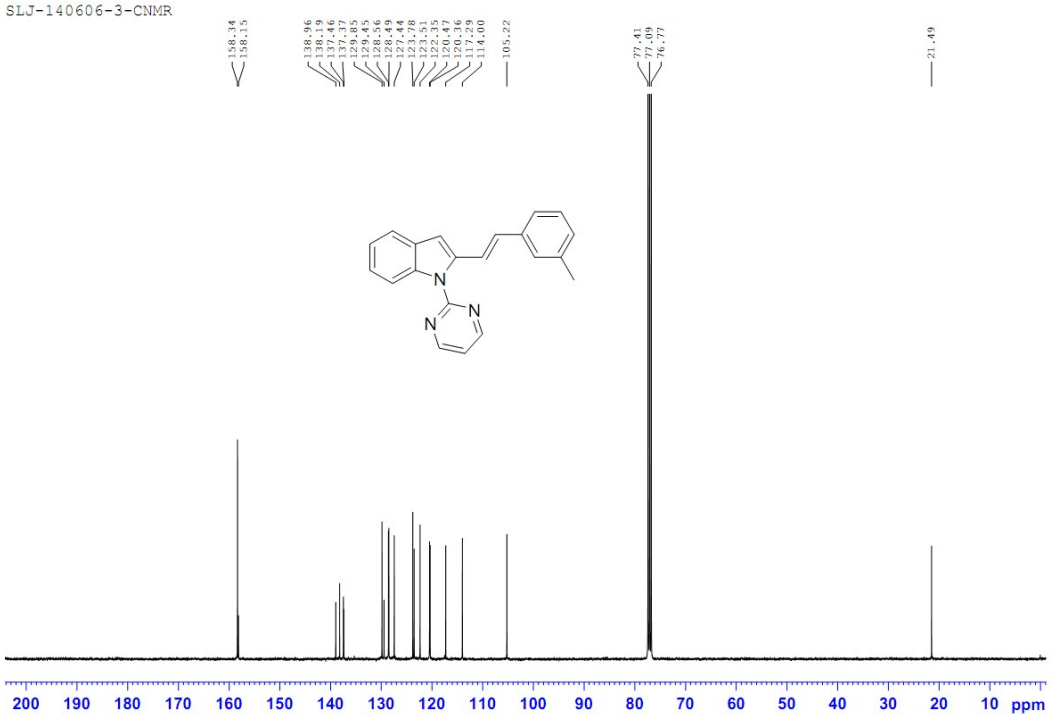
140512-ShiLJ-2-CNMR



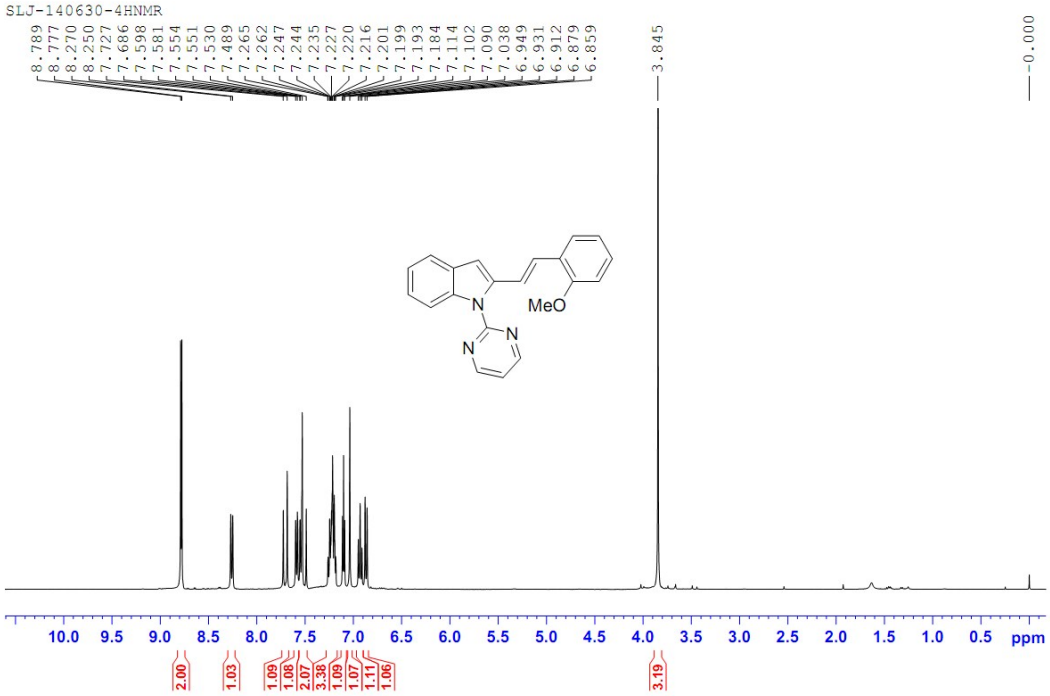
SLJ-140606-3-HNMR



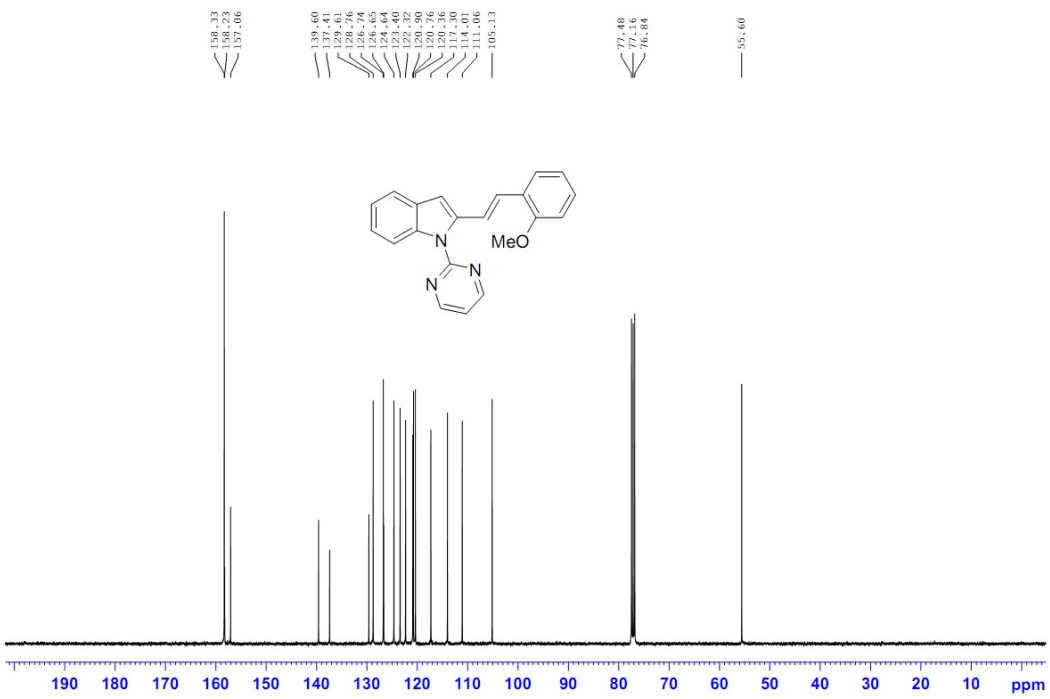
SLJ-140606-3-CNMR

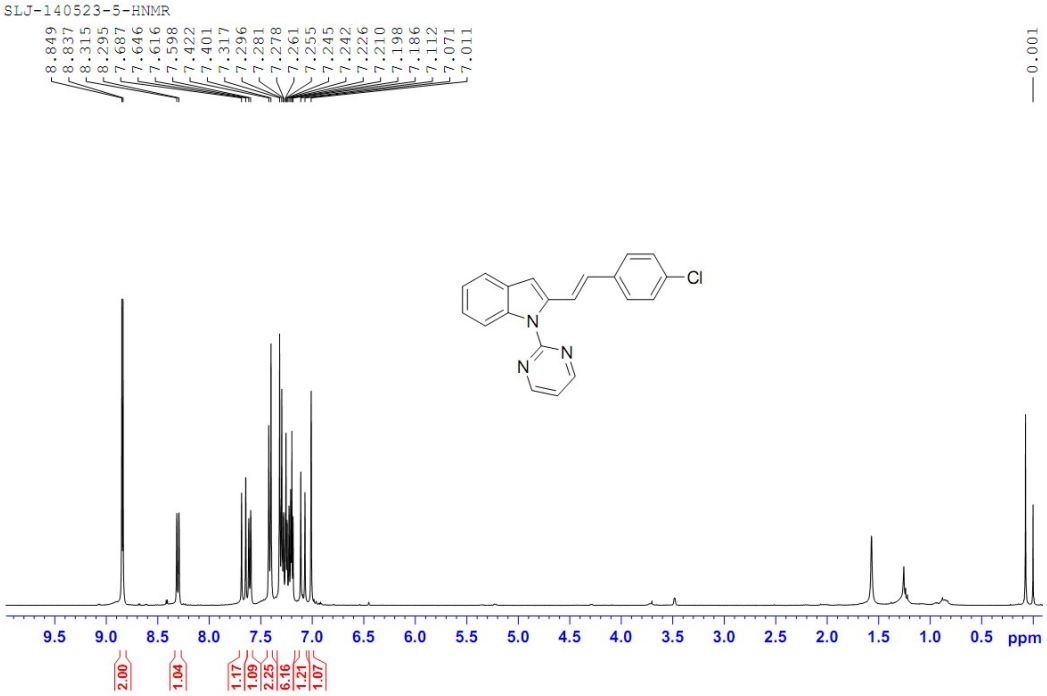


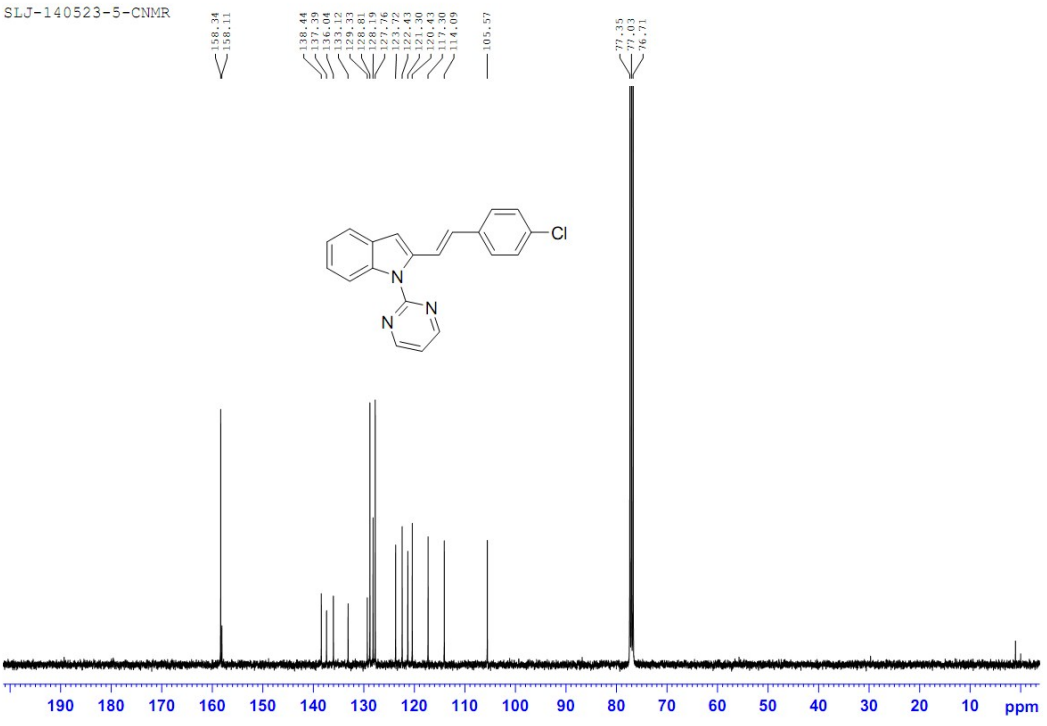
SLJ-140630-4HNMR



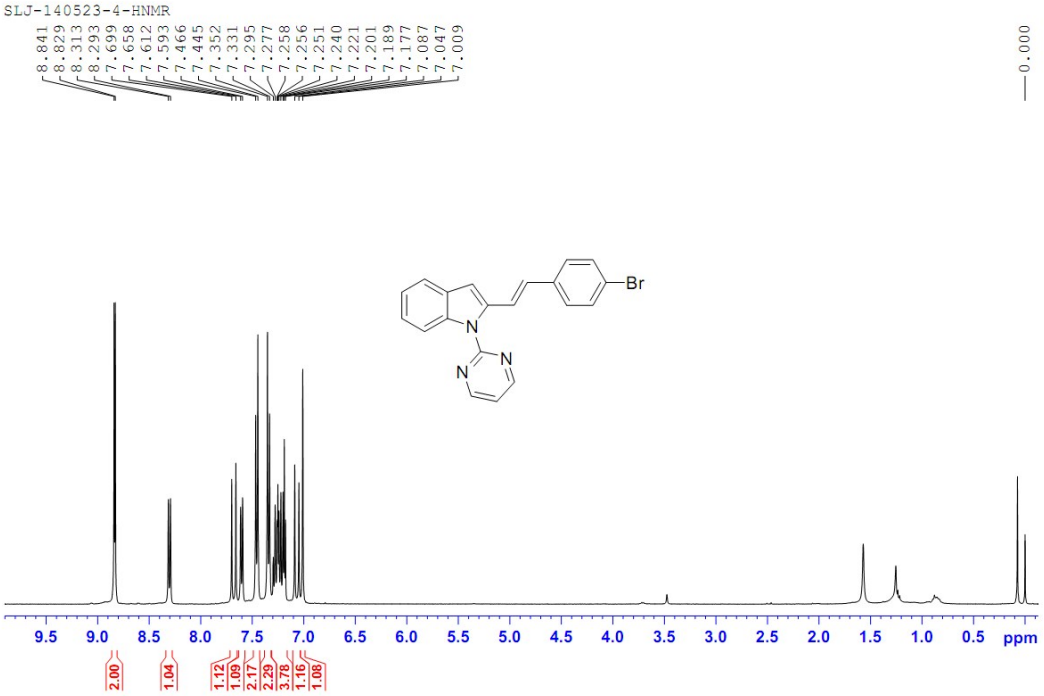
SLJ-140630-4CNMR



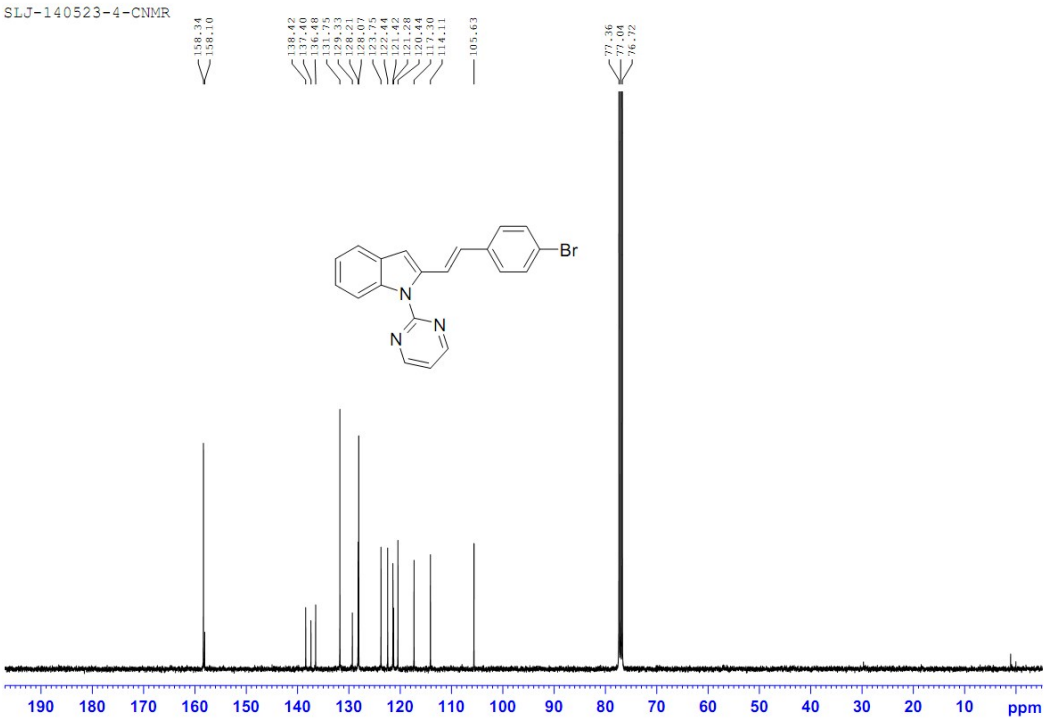

SLJ-140523-5-HNMR
8.849
8.837
8.315
8.295
7.687
7.646
7.616
7.598
7.422
7.401
7.317
7.296
7.281
7.278
7.261
7.255
7.245
7.242
7.226
7.210
7.198
7.186
7.112
7.071
7.011
0.001
Cl
N
N
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.04
1.17
1.09
2.25
6.16
1.21
1.07


SLJ-140523-5-CNMR
158.34
158.11
138.44
137.39
136.04
133.12
129.33
128.81
128.19
127.76
123.72
122.43
121.30
120.43
117.30
114.09
105.57
77.35
77.03
76.71
Cl
N
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

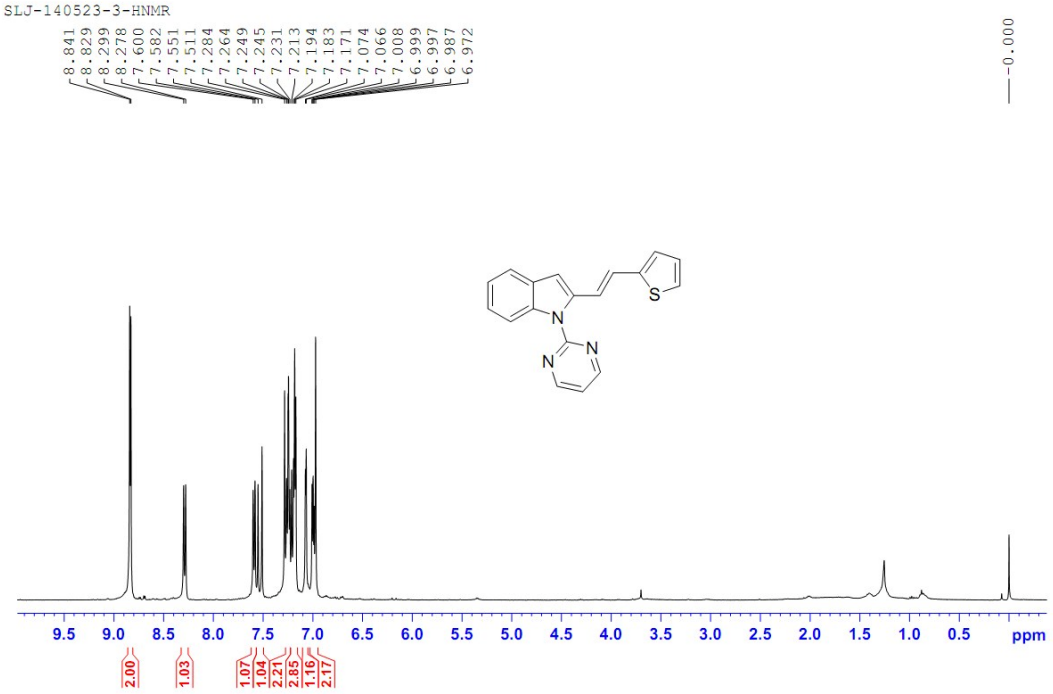
SLJ-140523-4-HNMR



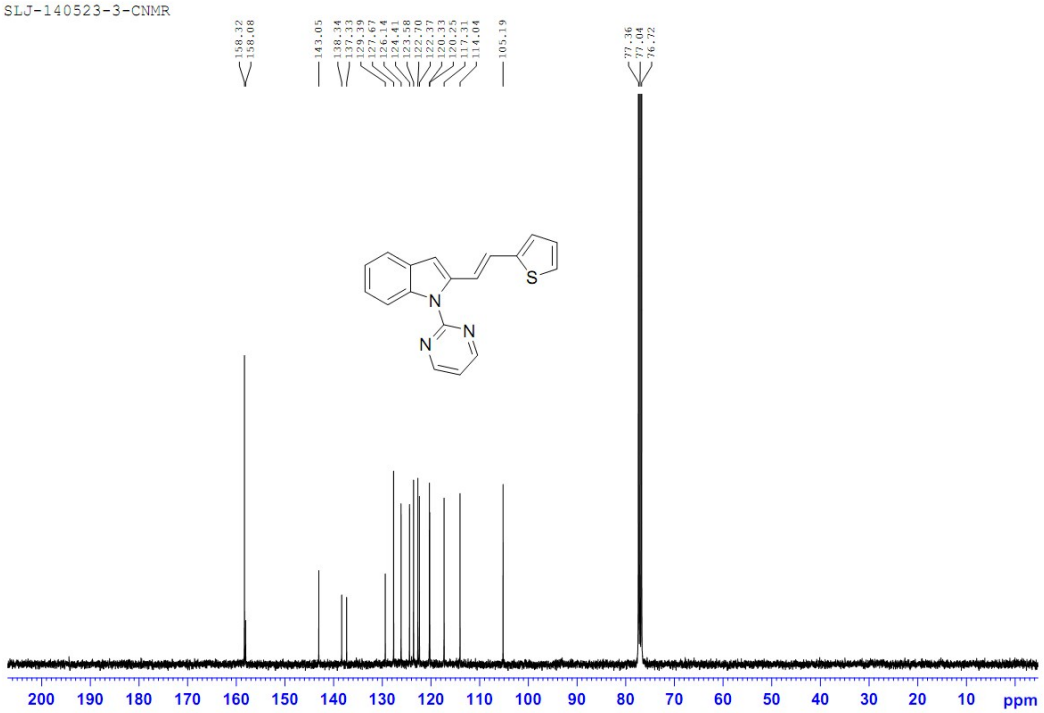
SLJ-140523-4-CNMR



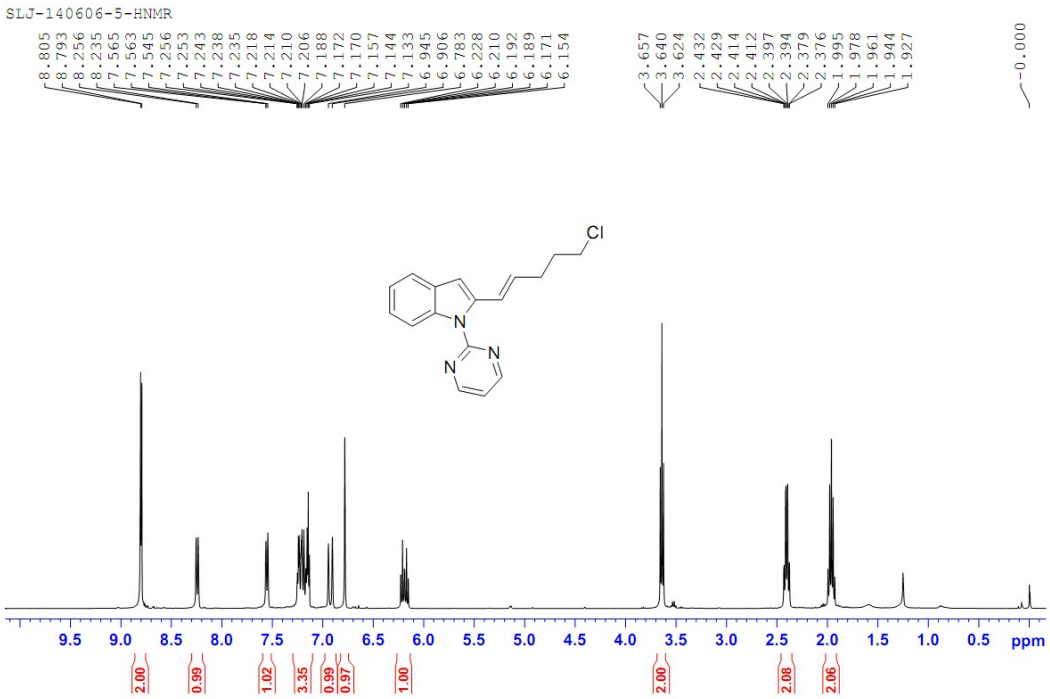
SLJ-140523-3-HNMR



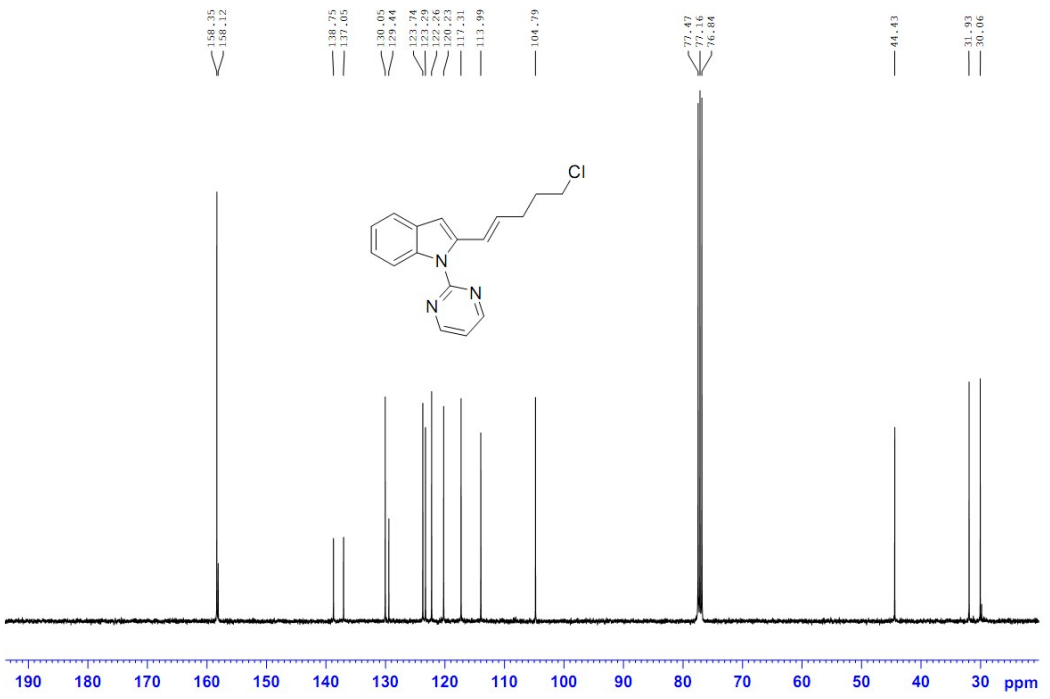
SLJ-140523-3-CNMR



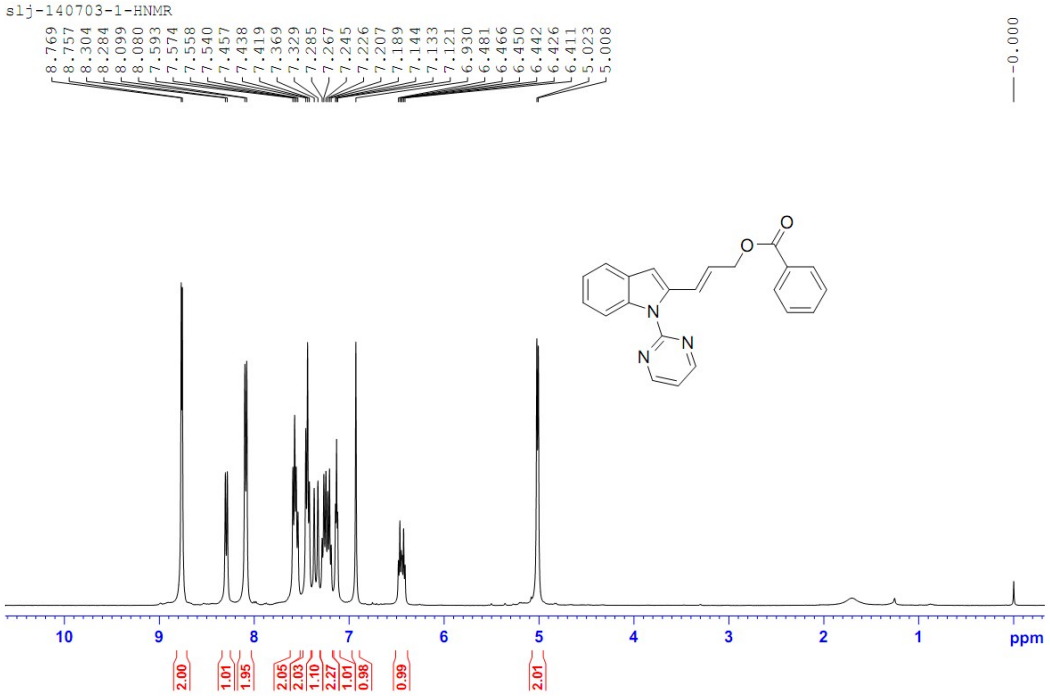
SLJ-140606-5-HNMR



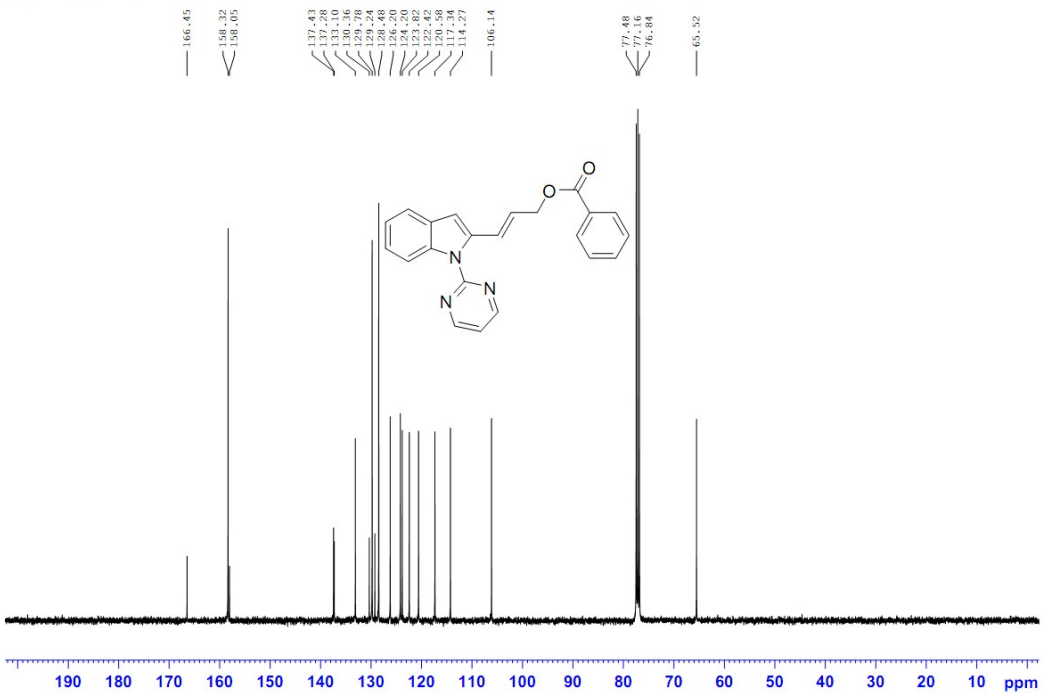
SLJ-140606-5-CNMR



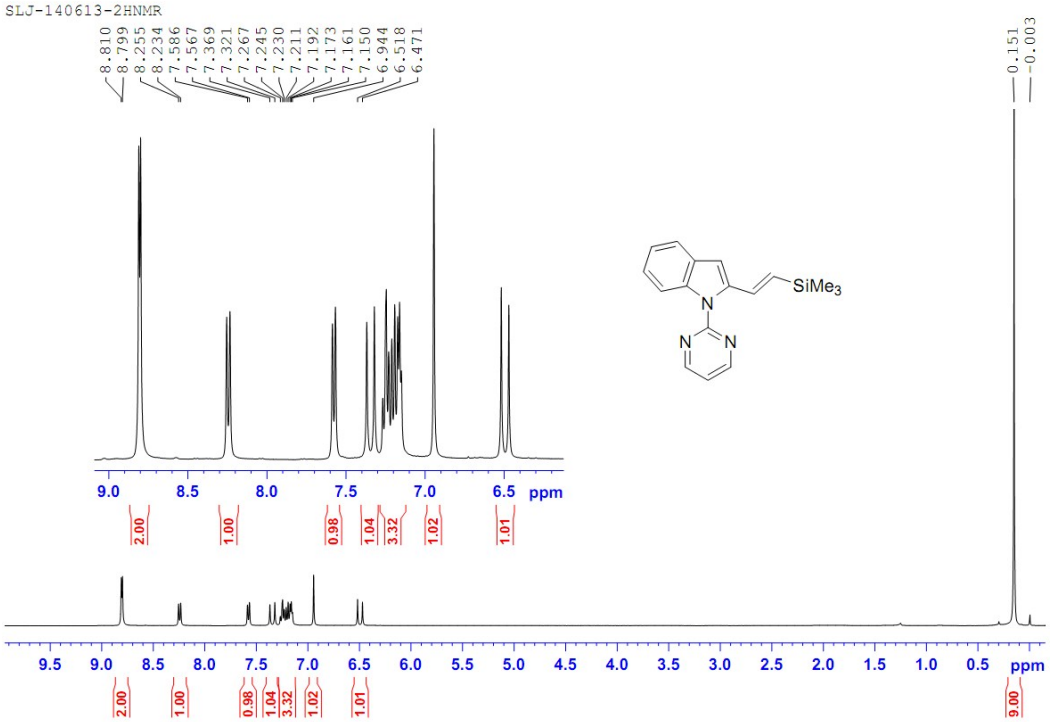
slj-140703-1-HNMR



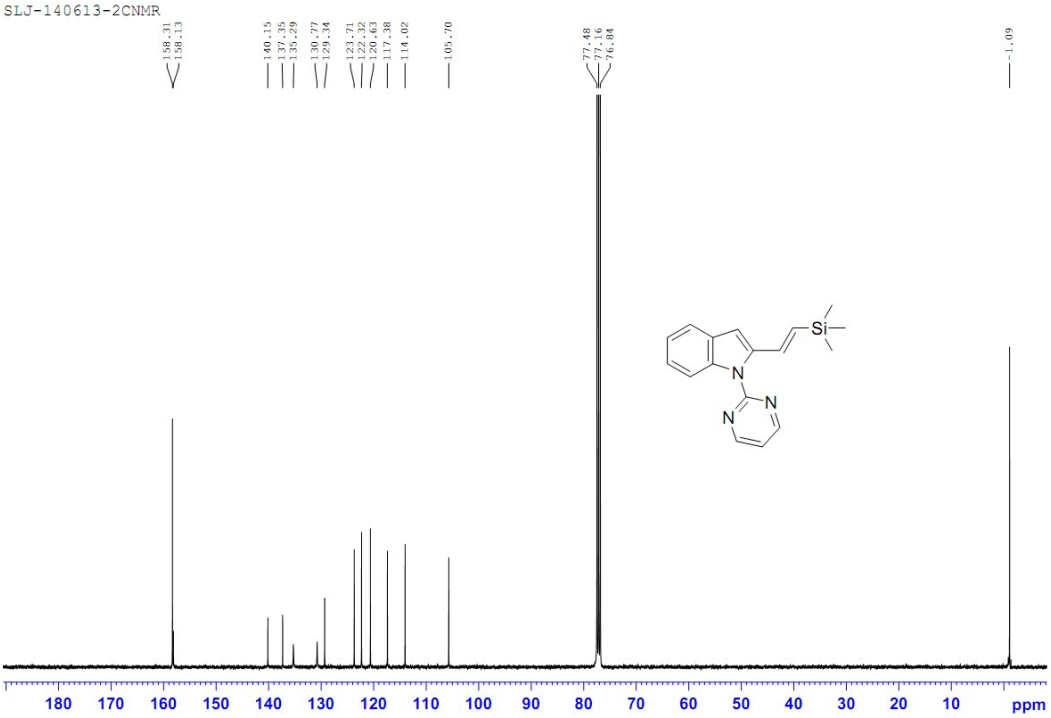
slj-140703-1-CNMR



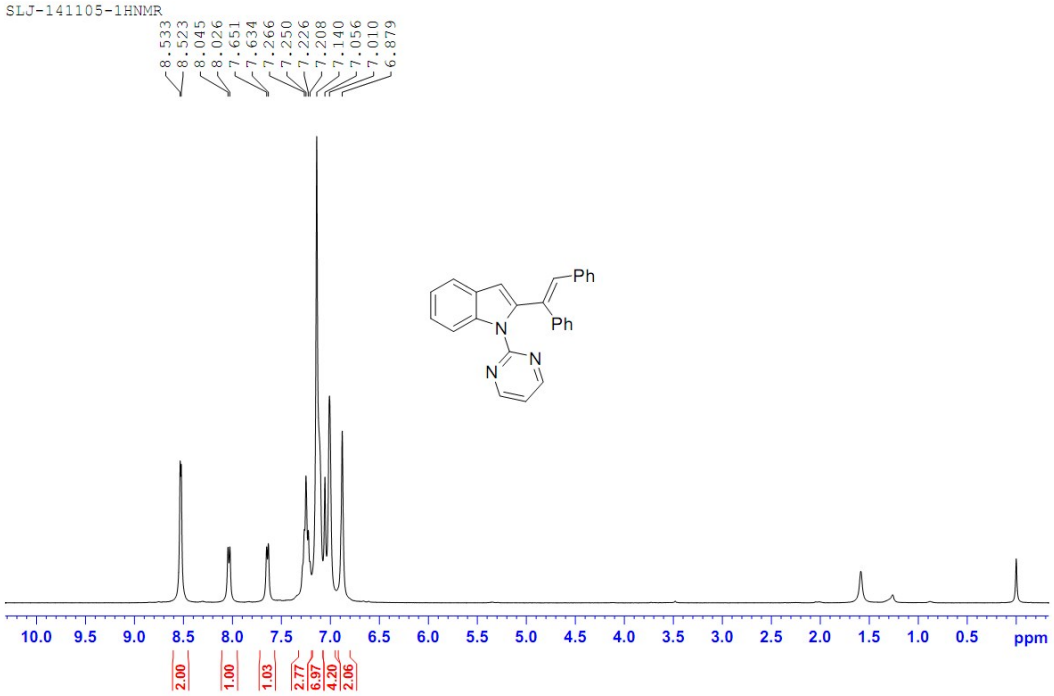
SLJ-140613-2HNMR



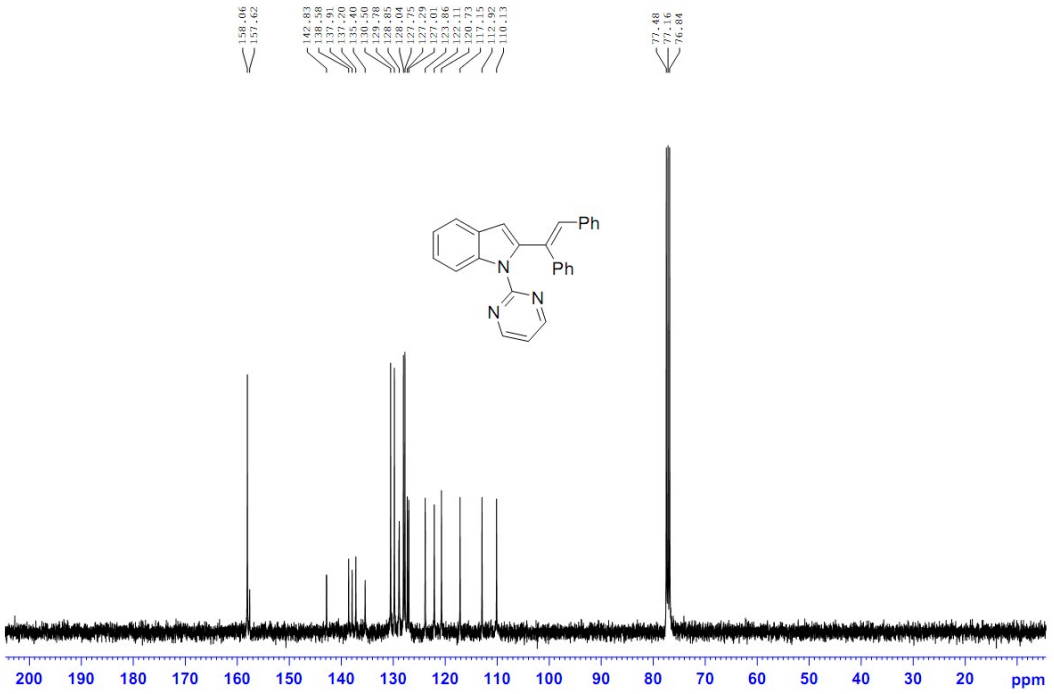
SLJ-140613-2CNMR



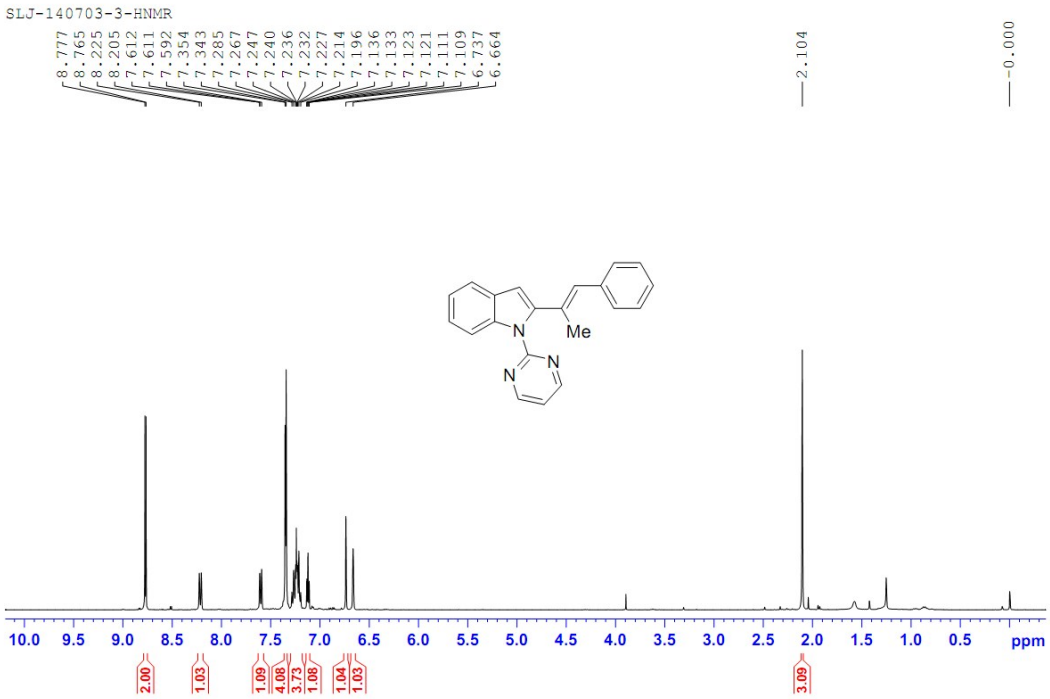
SLJ-141105-1HNMR



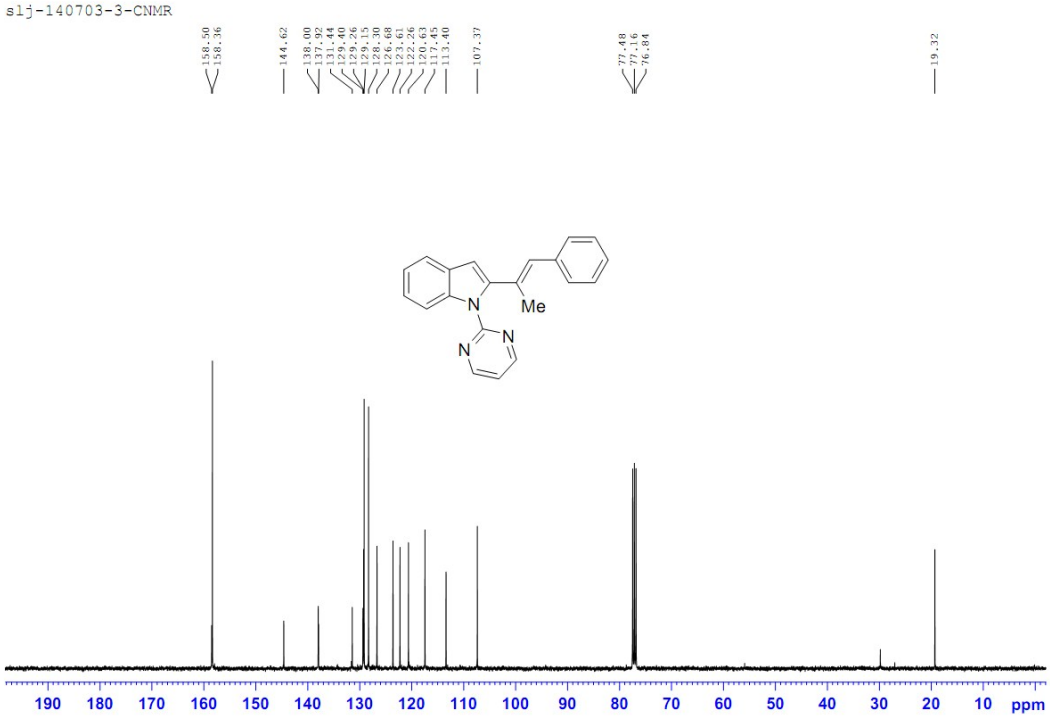
SLJ-141104-2-HNMR



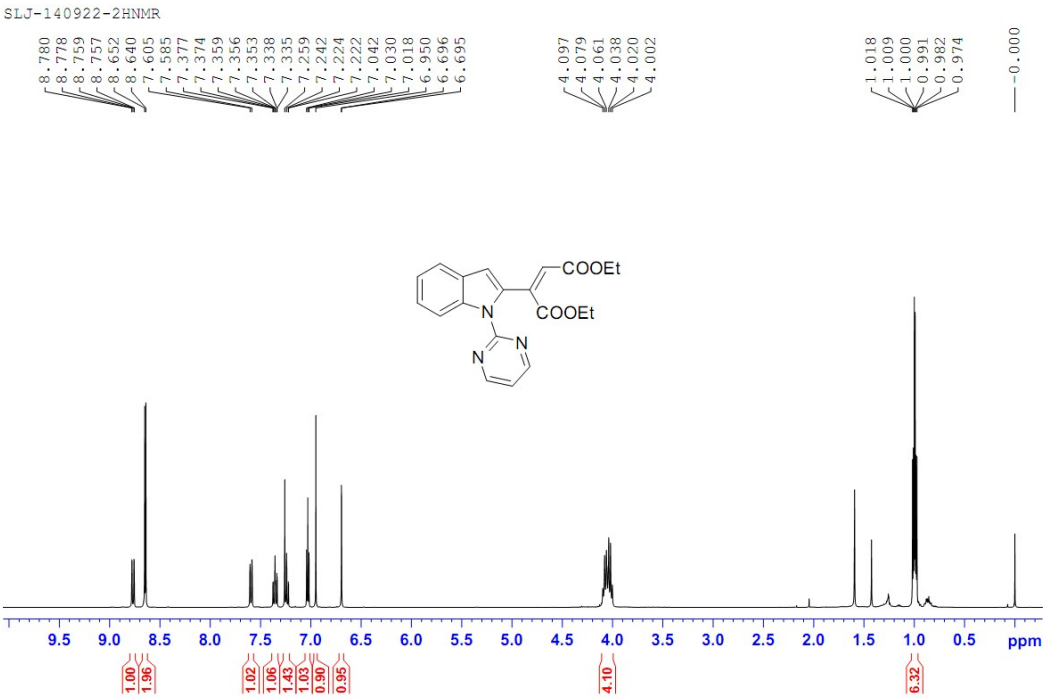
SLJ-140703-3-HNMR



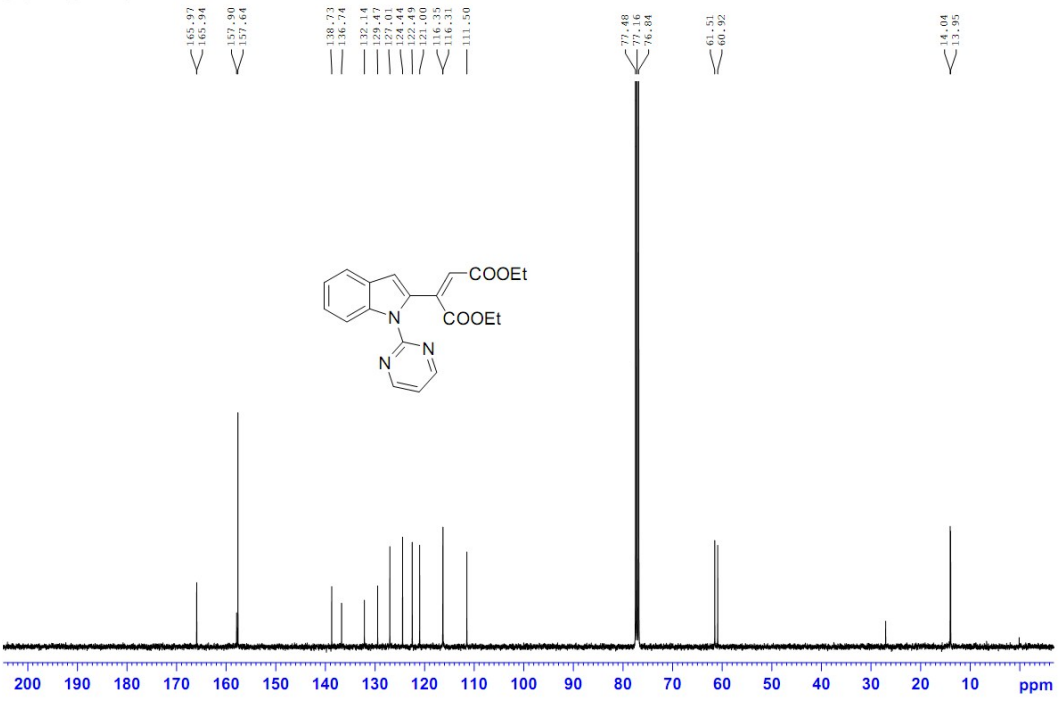
slj-140703-3-CNMR



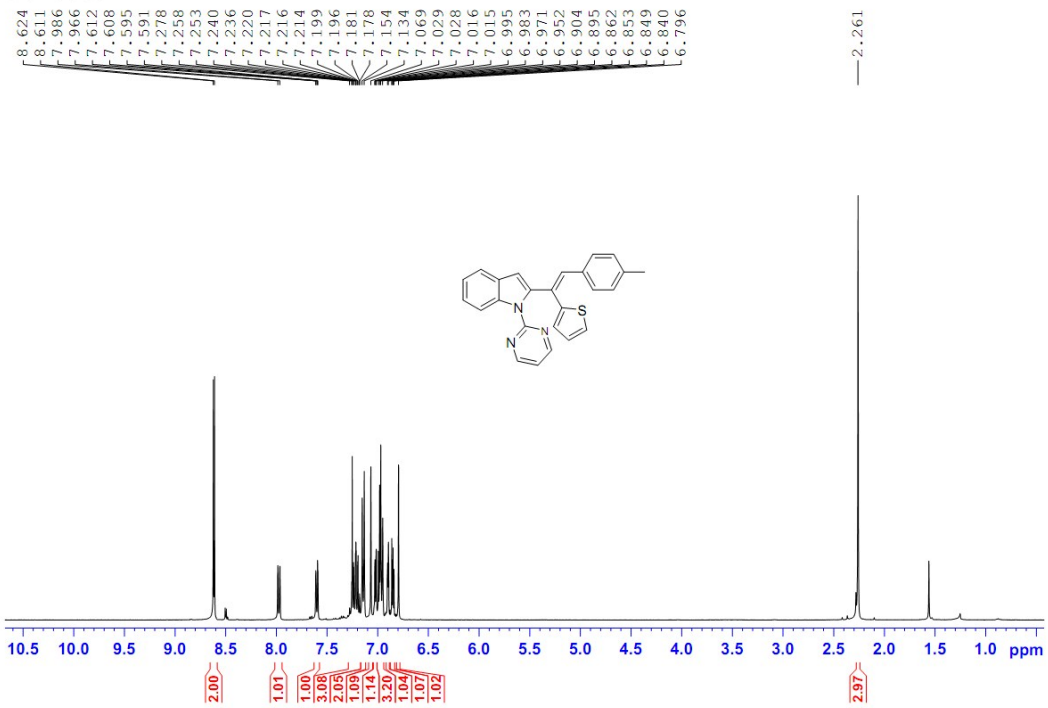
SLJ-140922-2HNMR



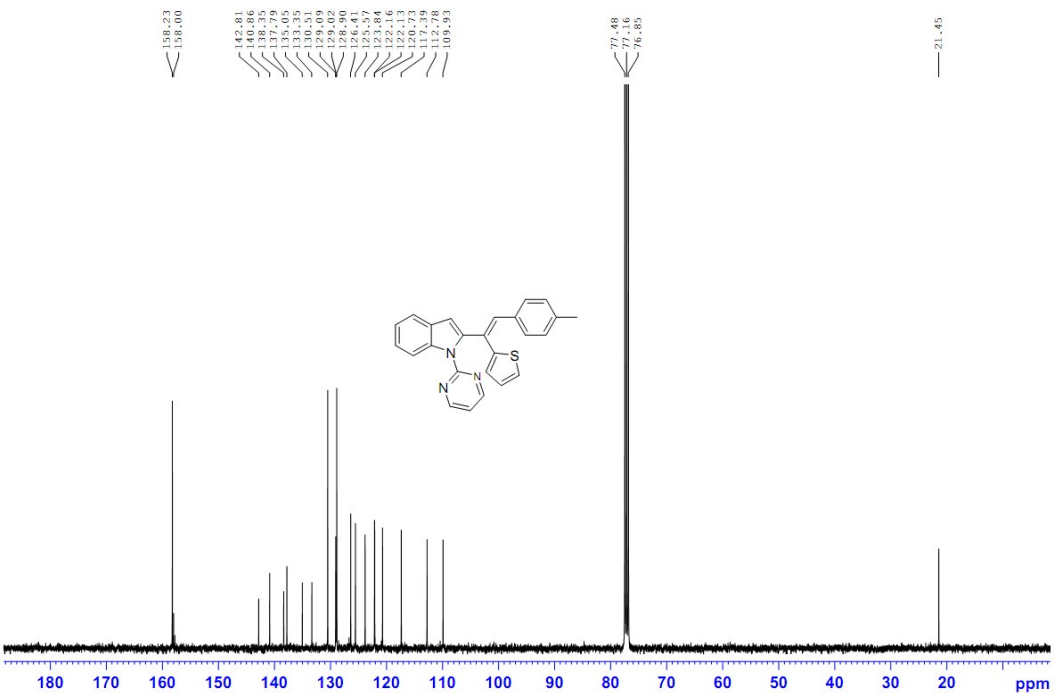
SLJ-140922-2CNMR



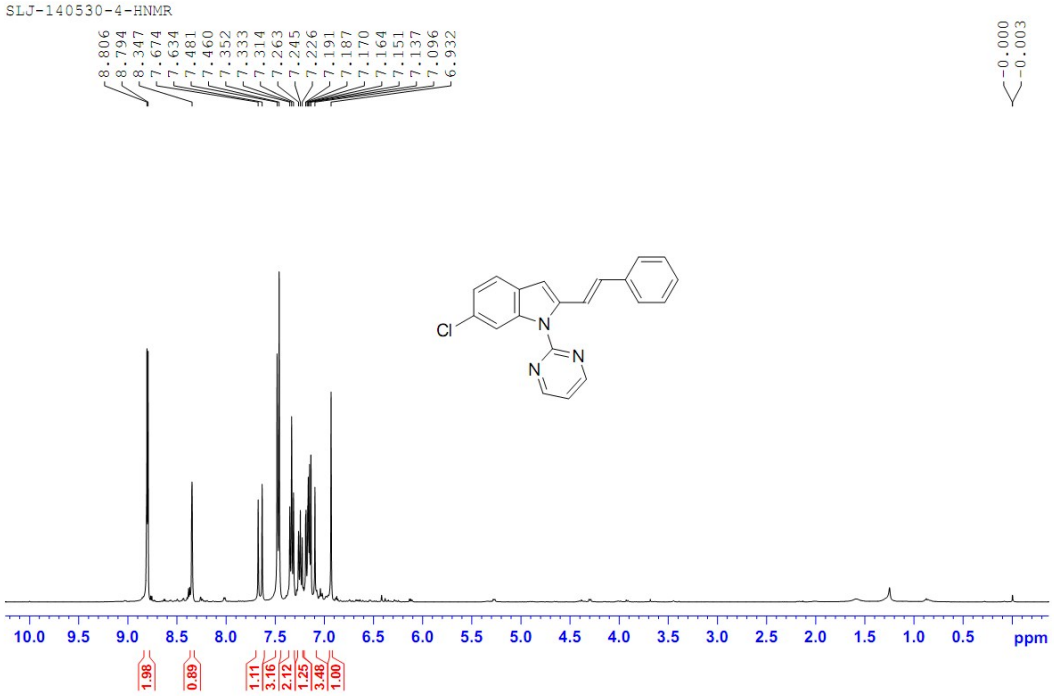
SLJ-150205-4-HNMR



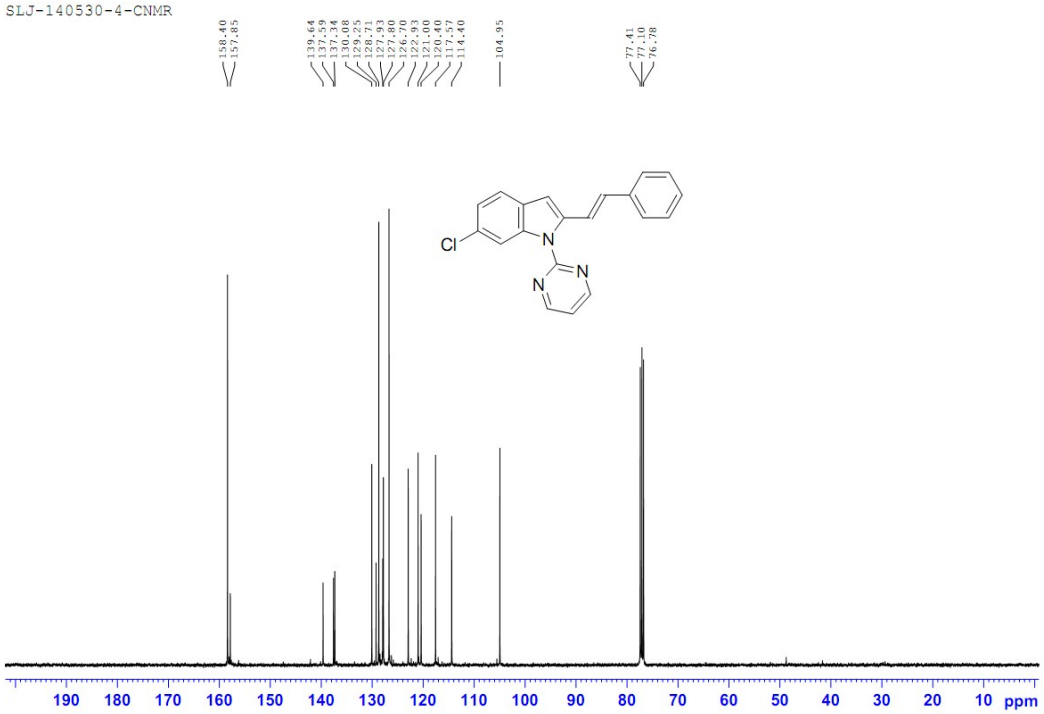
SLJ-150205-4-CNMR



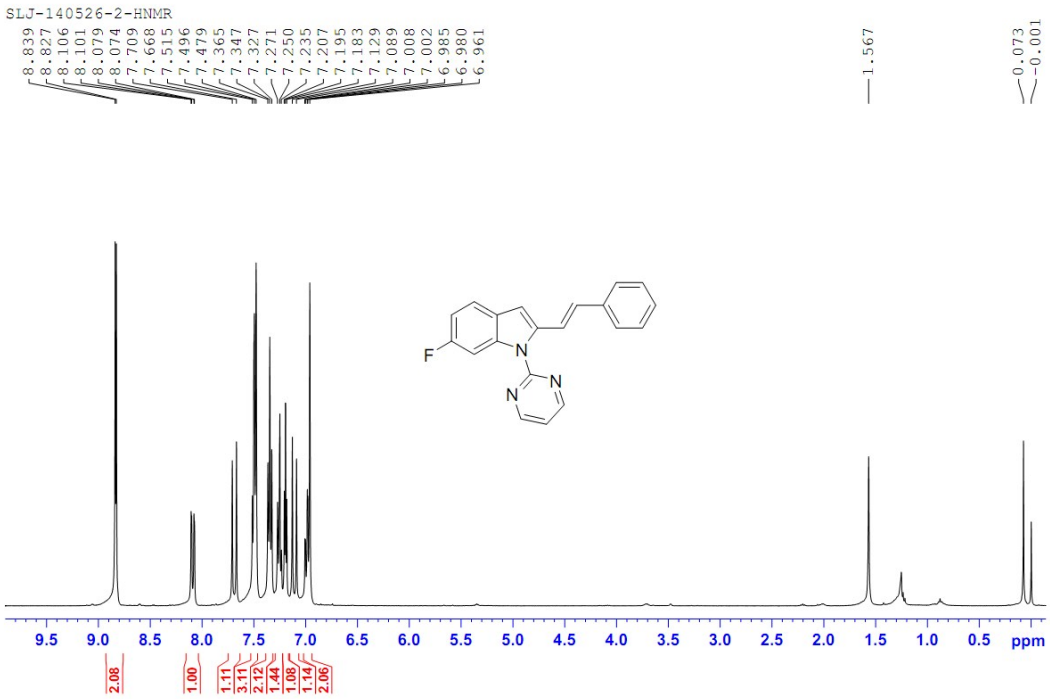
SLJ-140530-4-HNMR



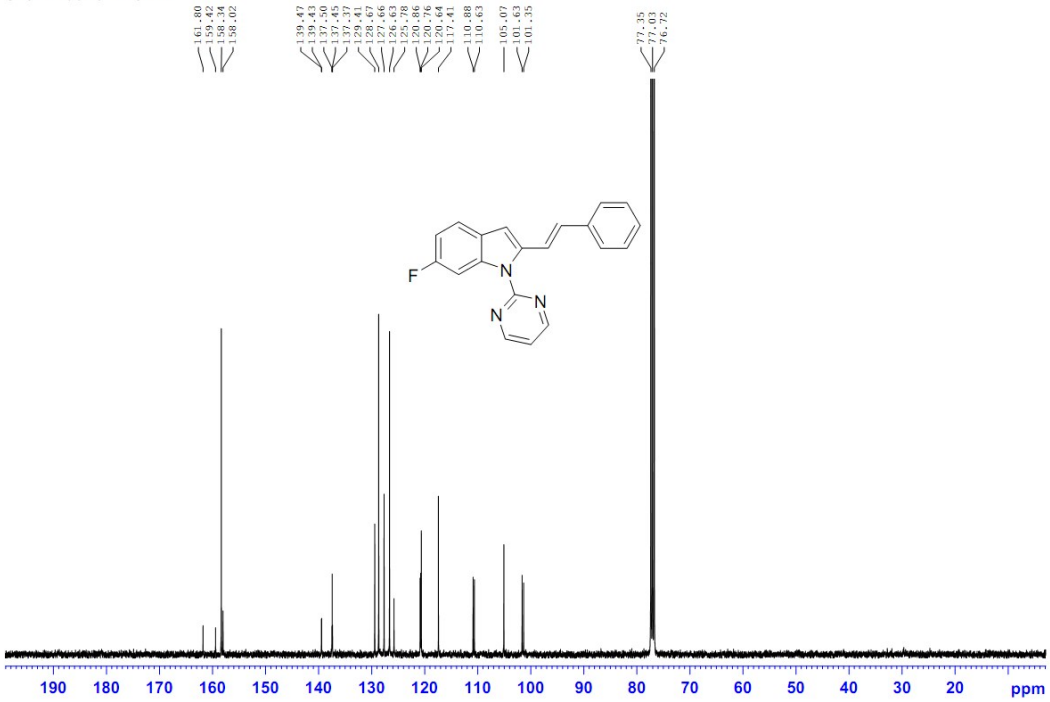
SLJ-140530-4-CNMR



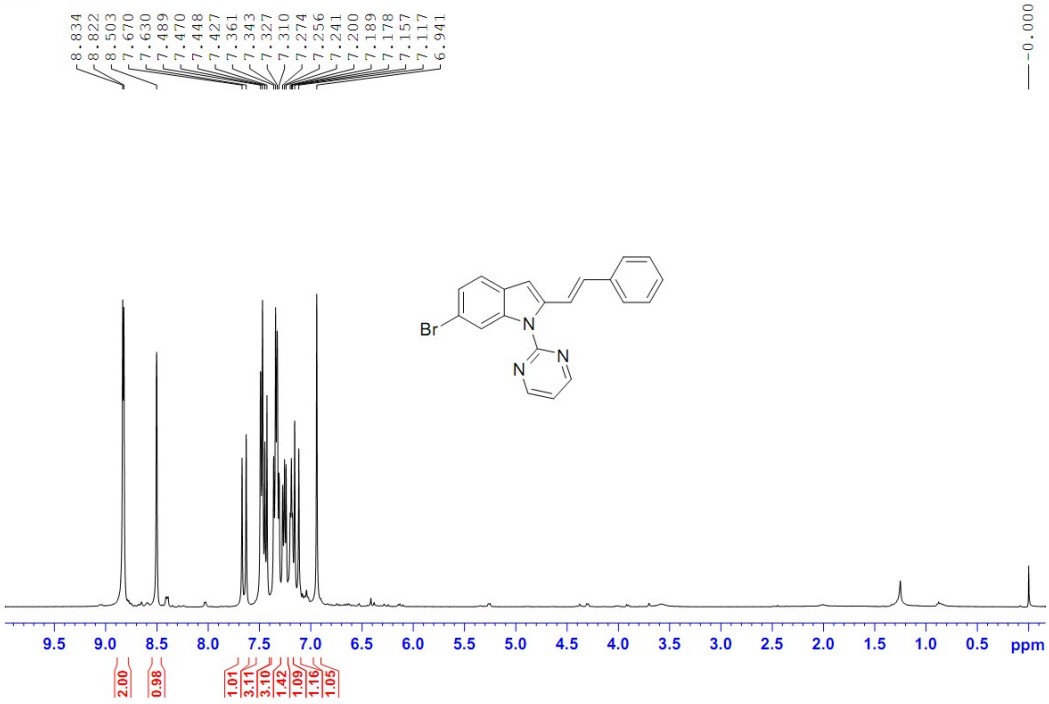
SLJ-140526-2-HNMR



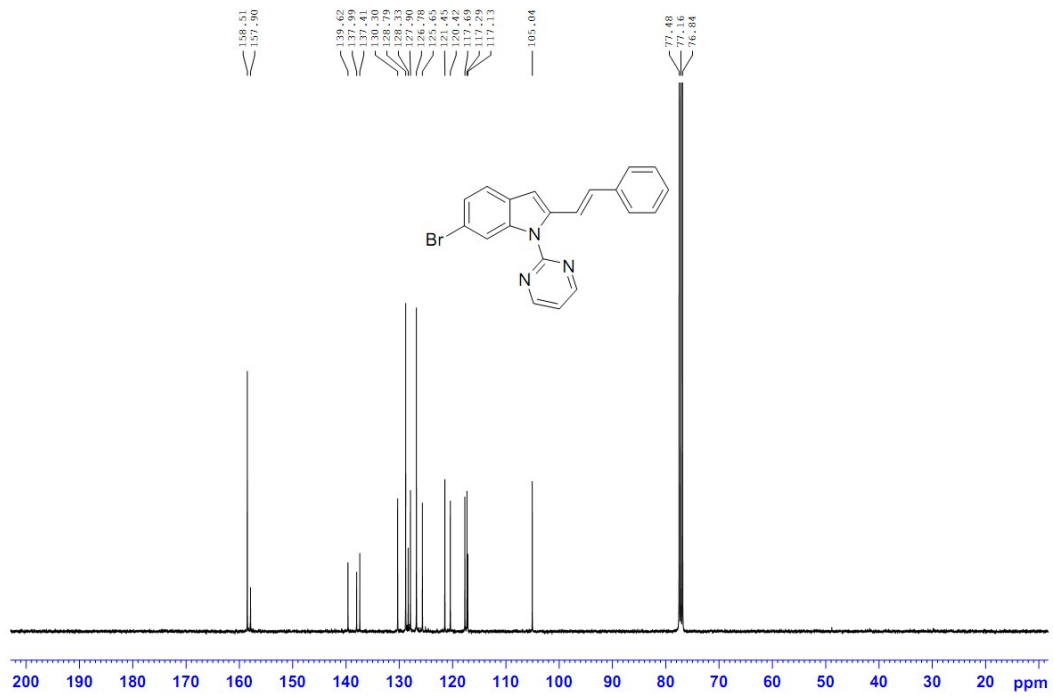
SLJ-140526-2-CNMR



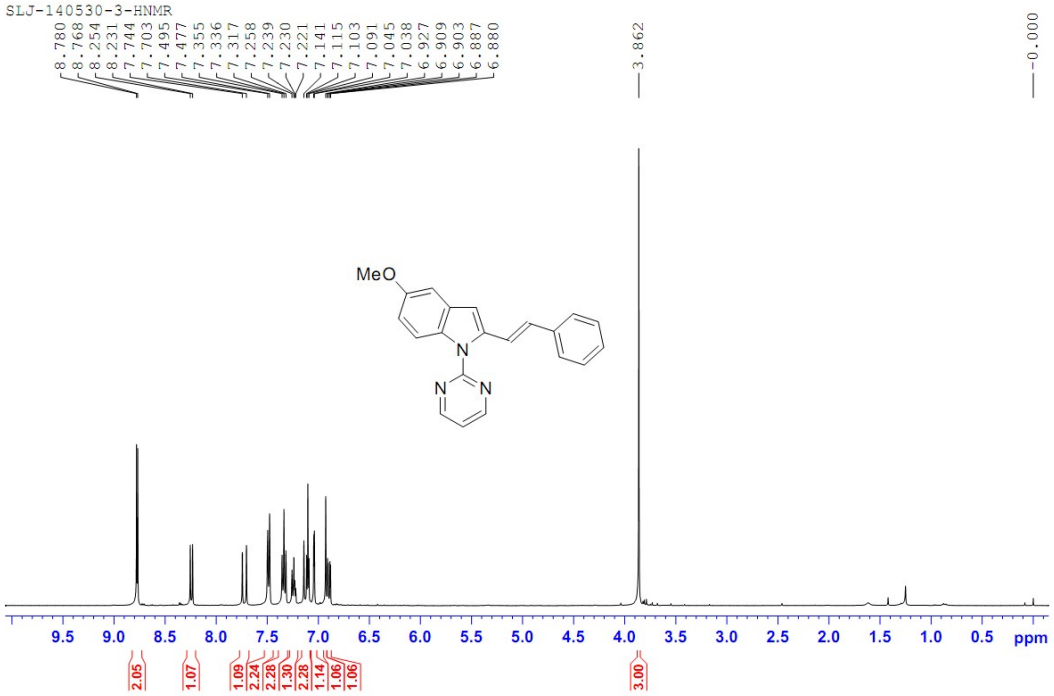
SLJ-140606-1-HNMR



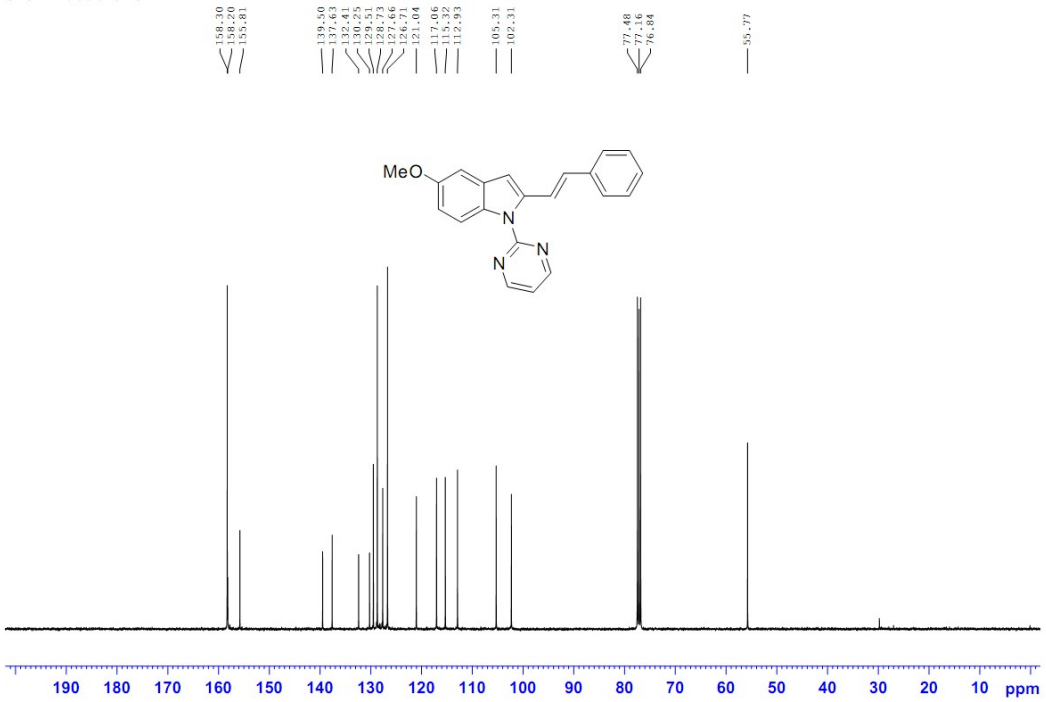
SLJ-140606-1-CNMR



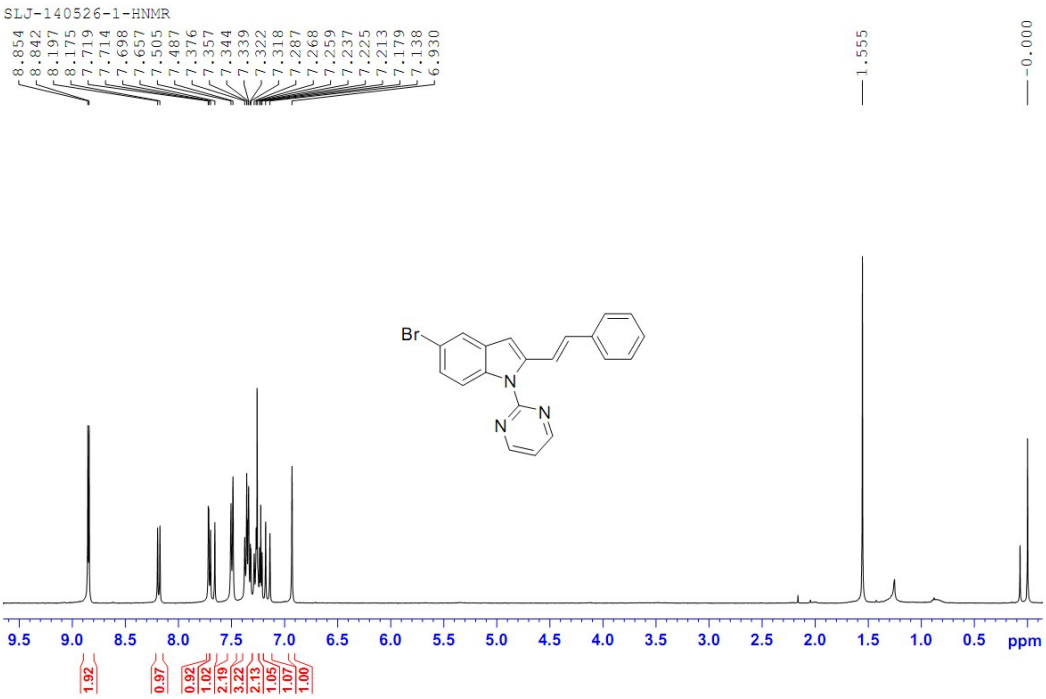
SLJ-140530-3-HNMR



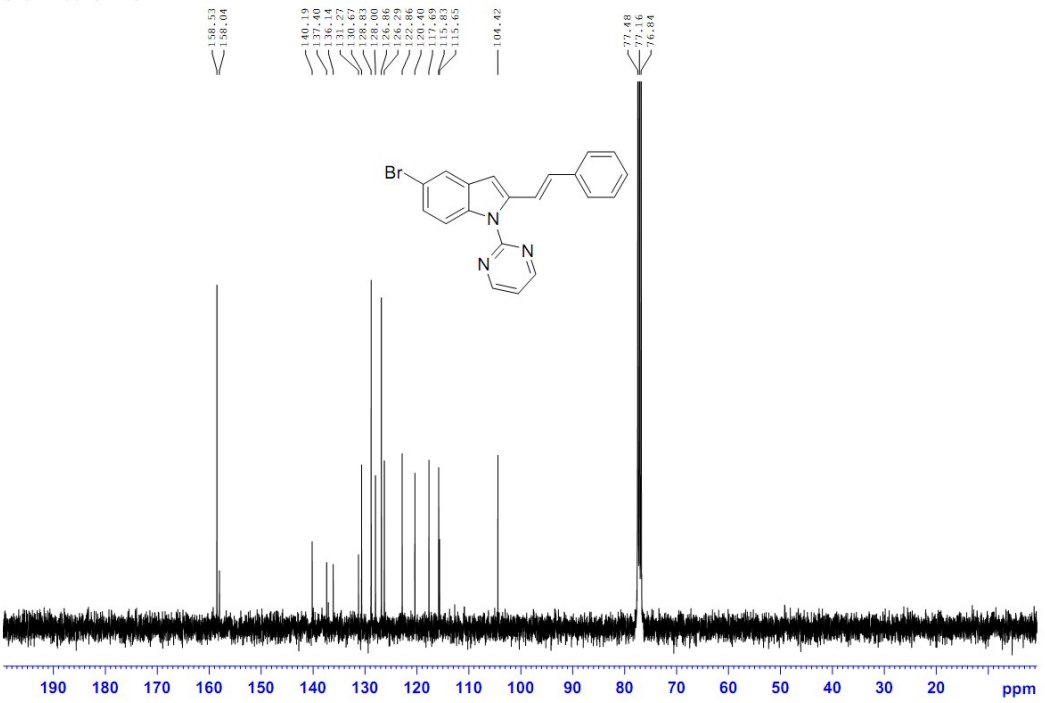
SLJ-140606-9-CNMR



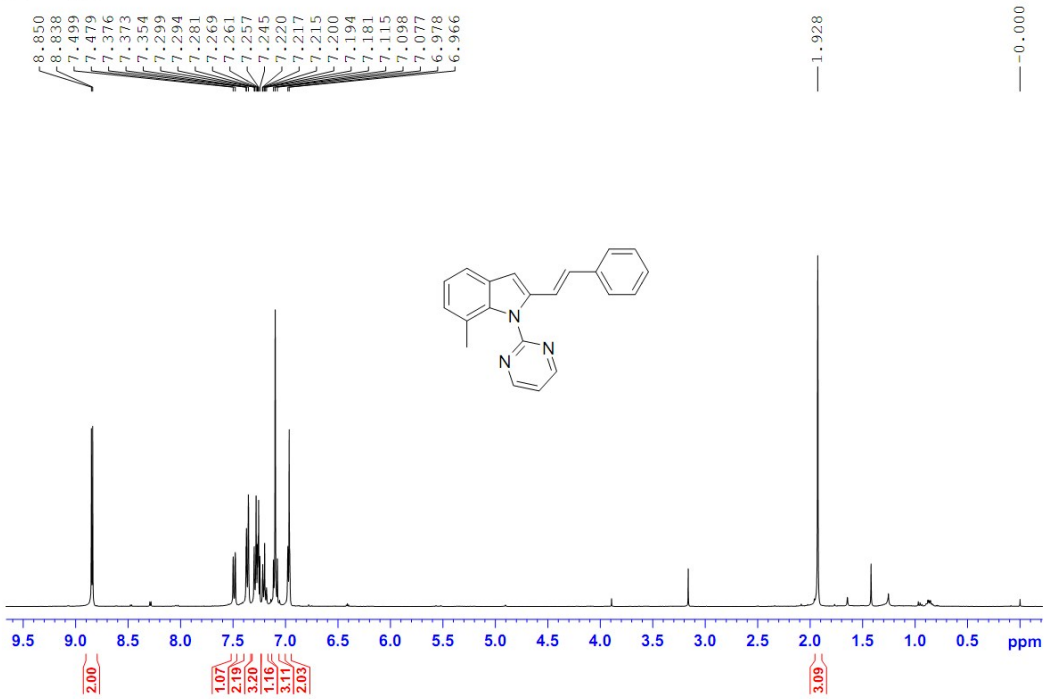
SLJ-140526-1-HNMR



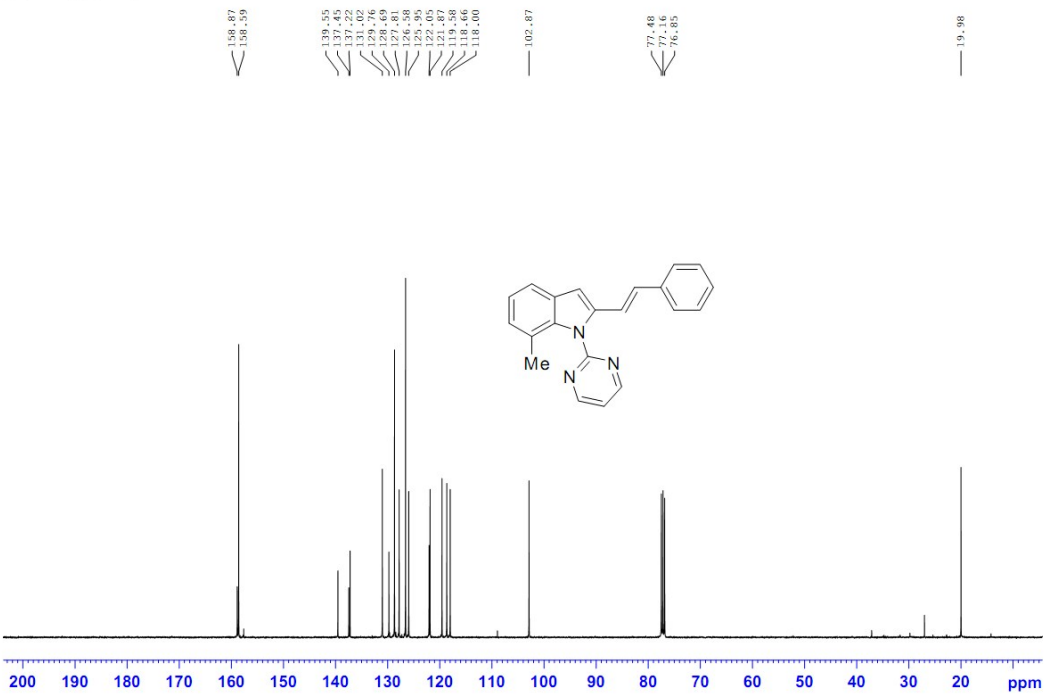
SLJ-140526-1-CNMR



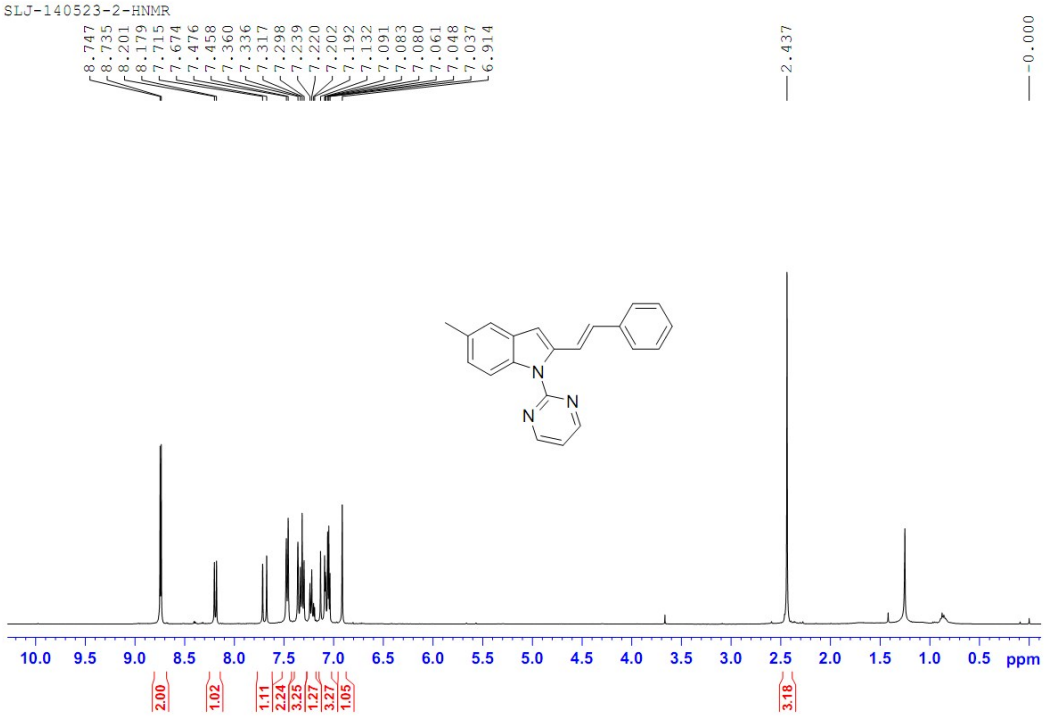
SLJ-140606-2-HNMR



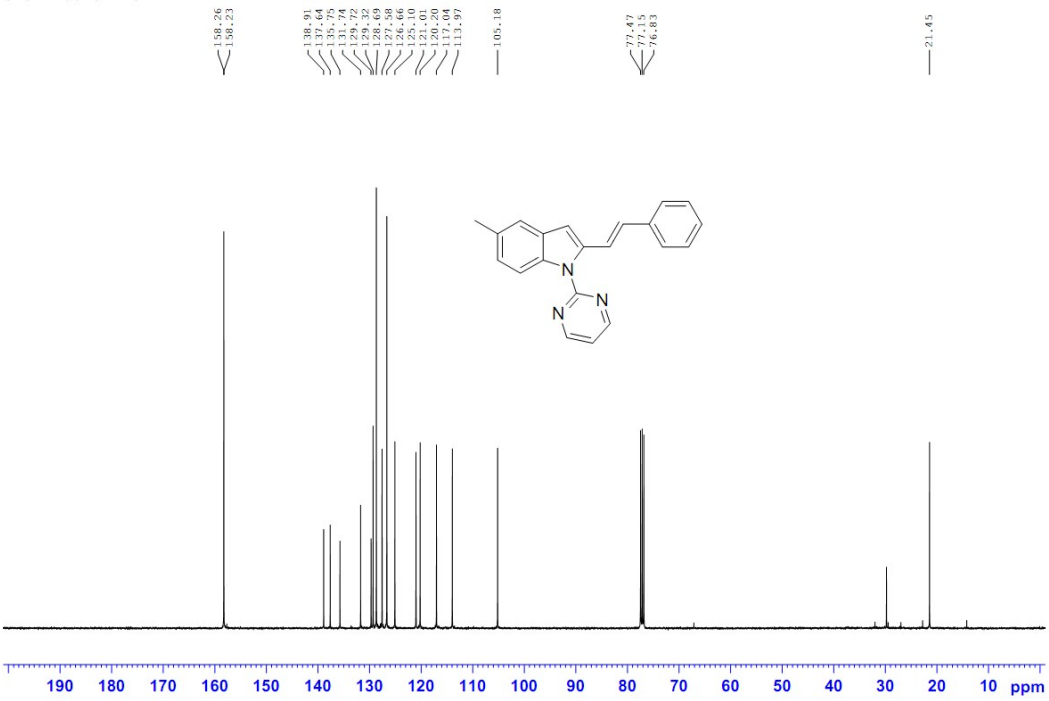
SLJ-140606-2-CNMR



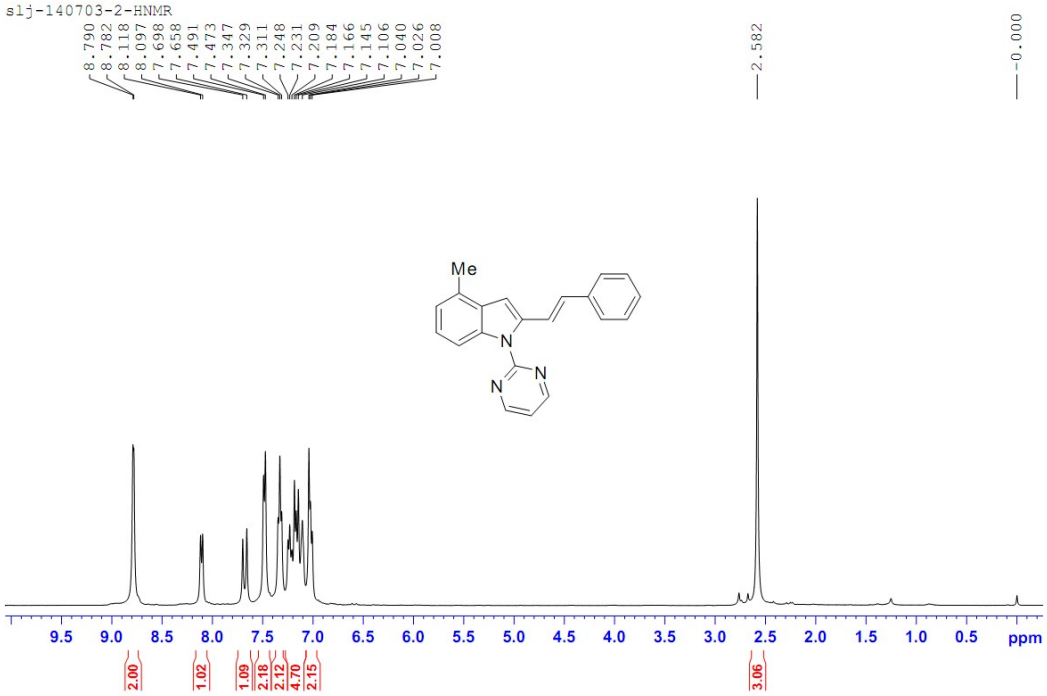
SLJ-140523-2-HNMR



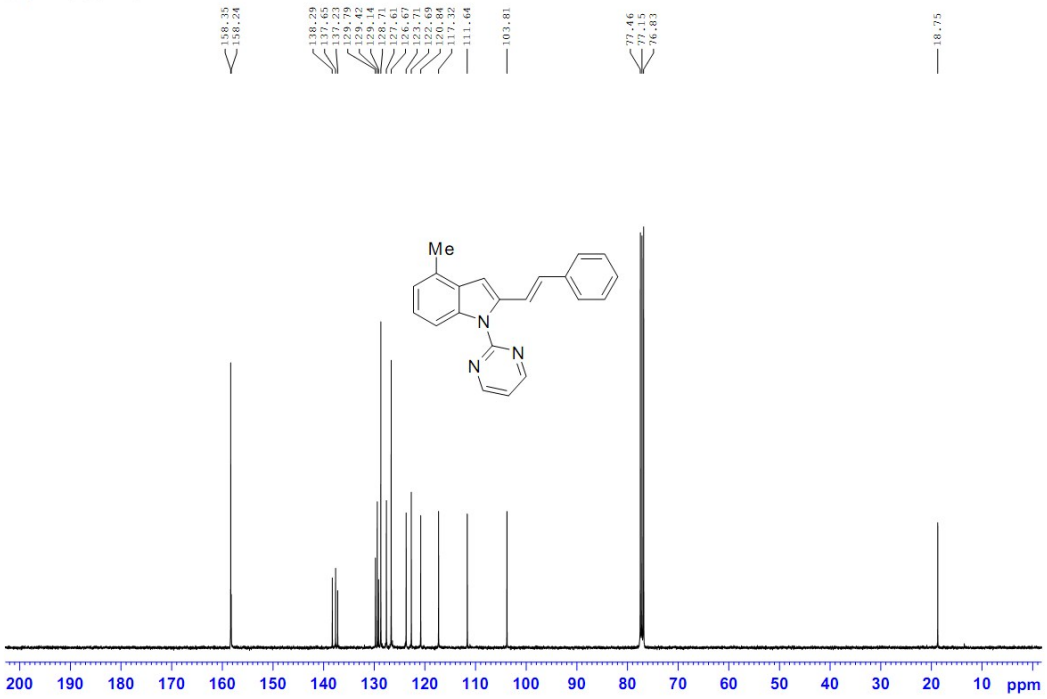
SLJ-140523-2-CNMR



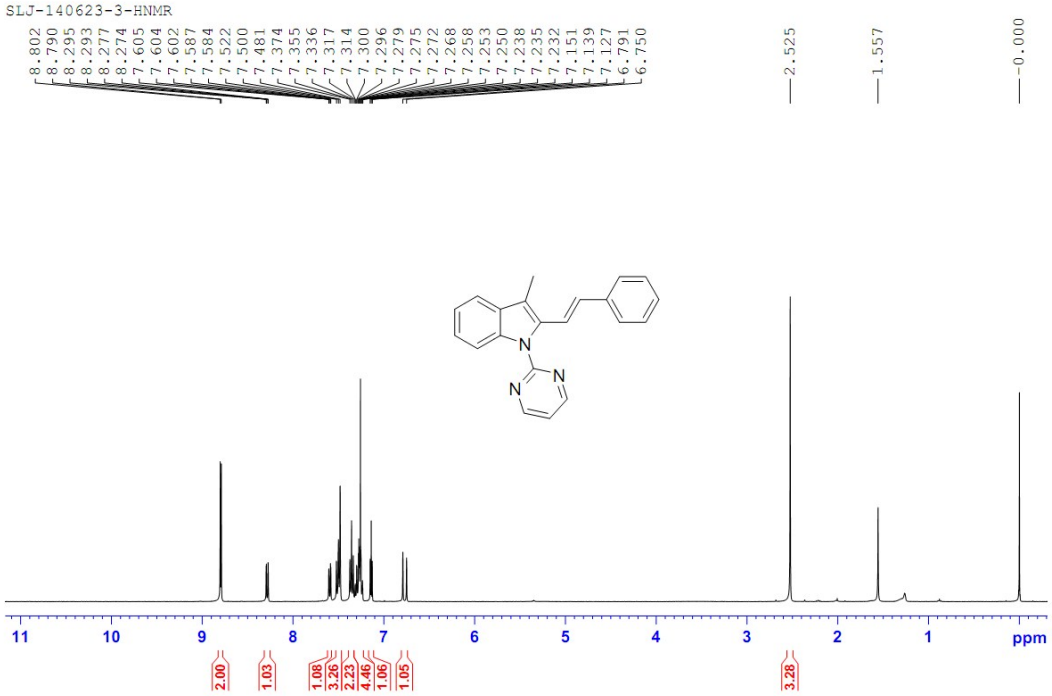
slj-140703-2-HNMR



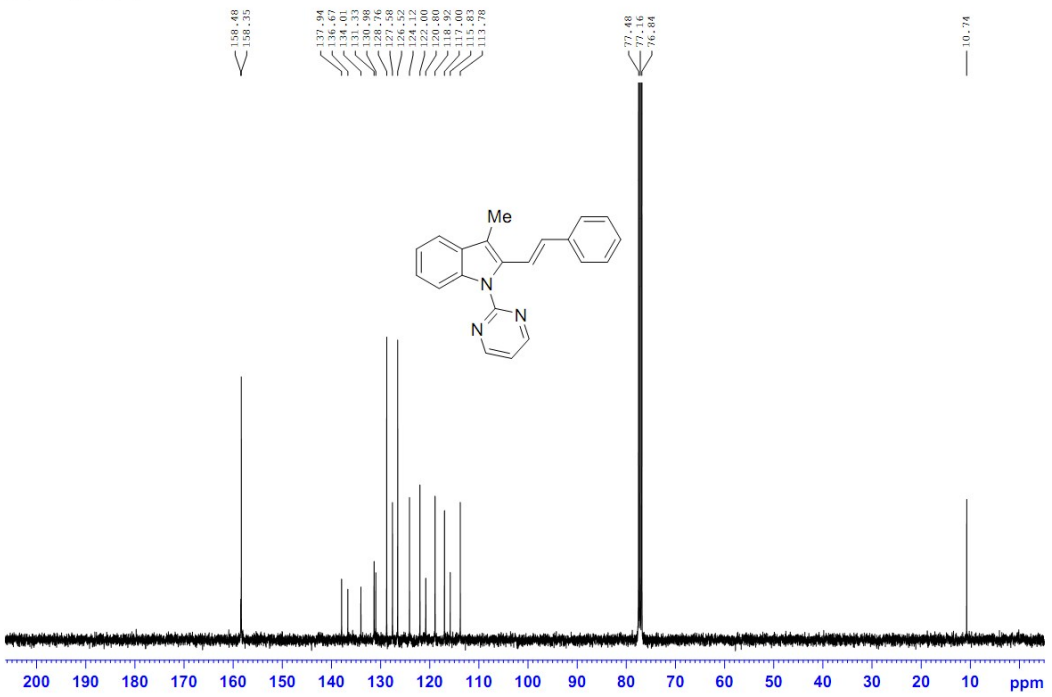
slj-140703-2-CNMR



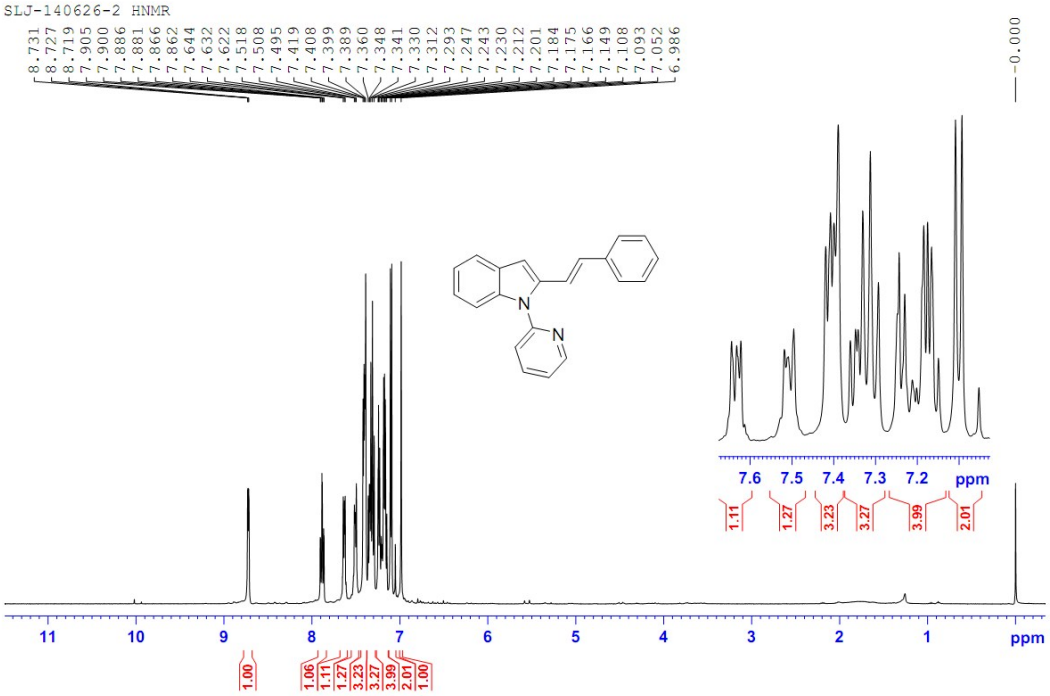
SLJ-140623-3-HNMR



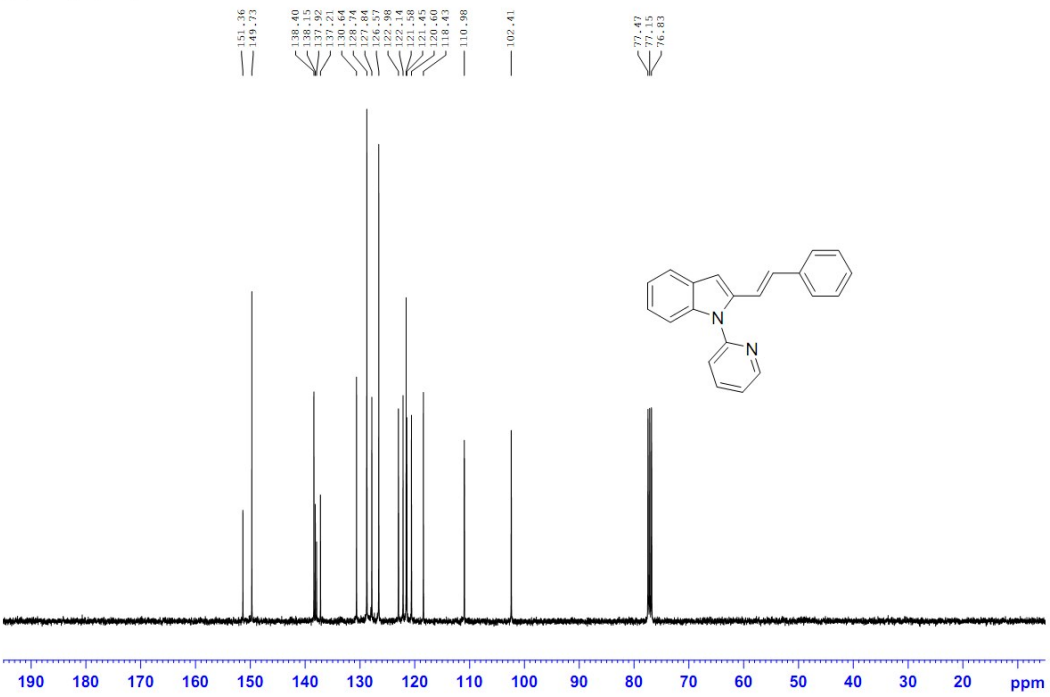
SLJ-140626-3 CNMR



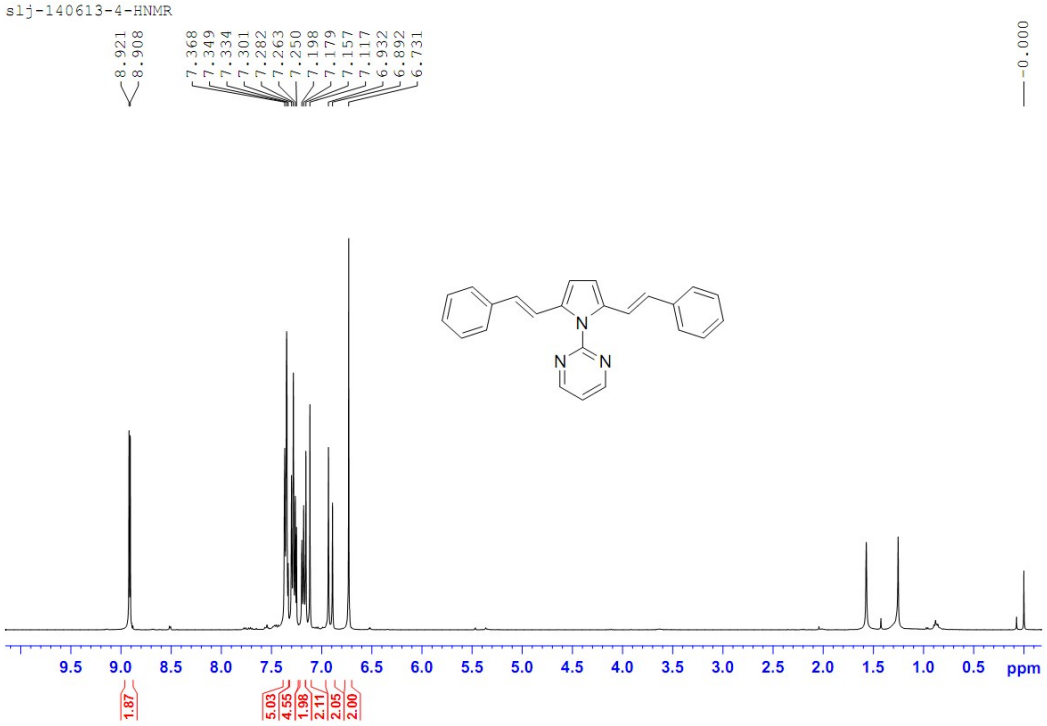
SLJ-140626-2 HNMR



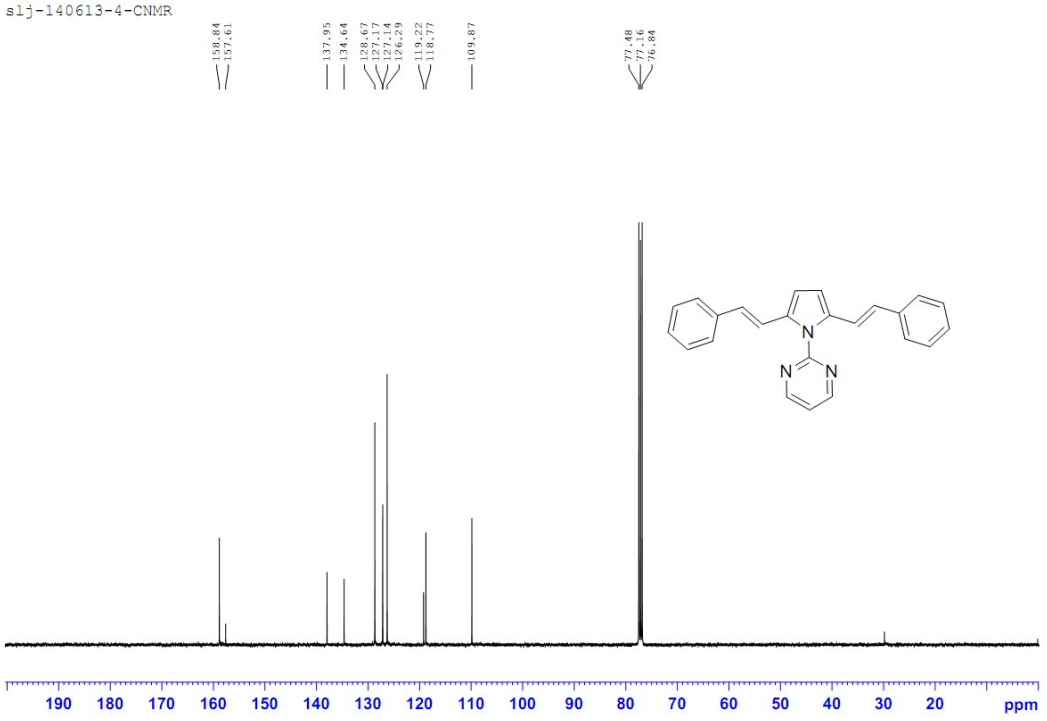
SLJ-140623-4-CNMR



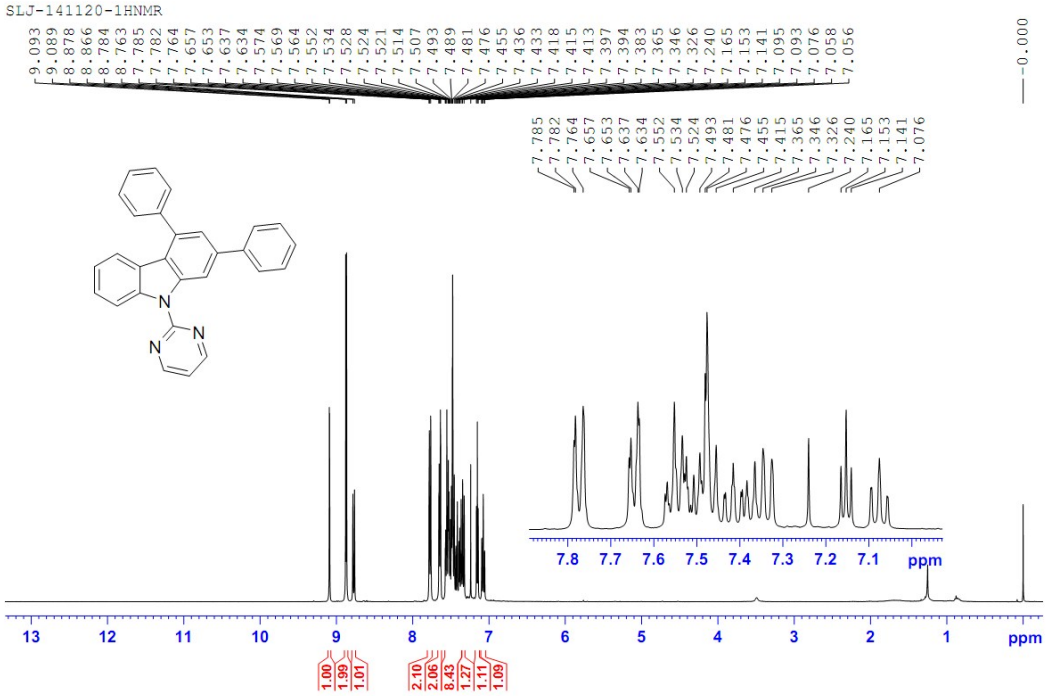
slj-140613-4-HNMR



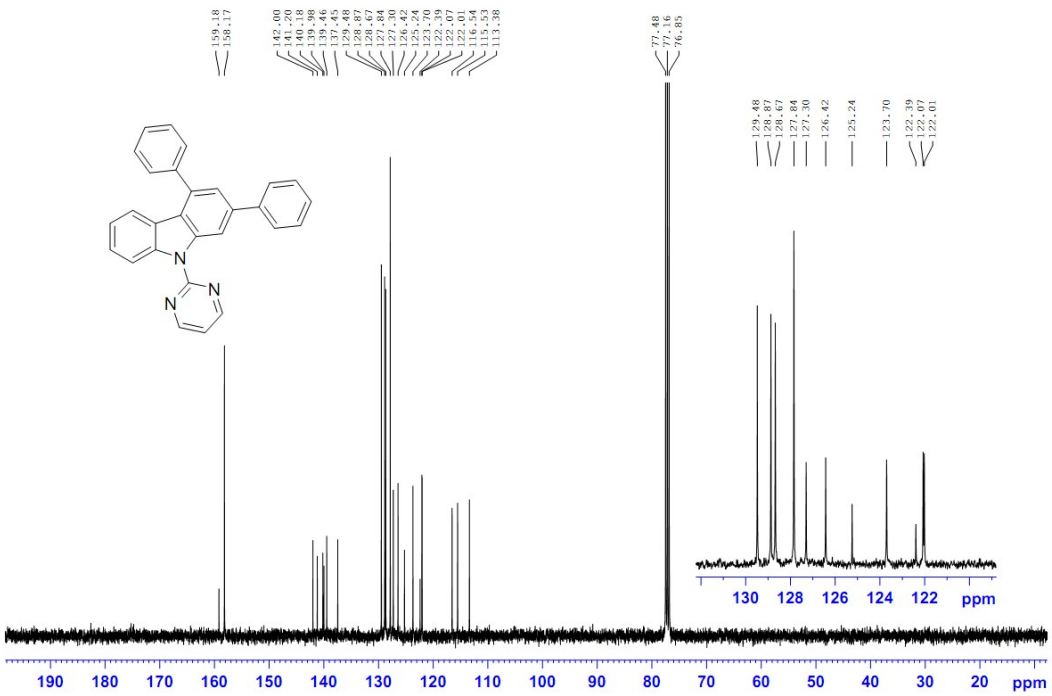
slj-140613-4-CNMR

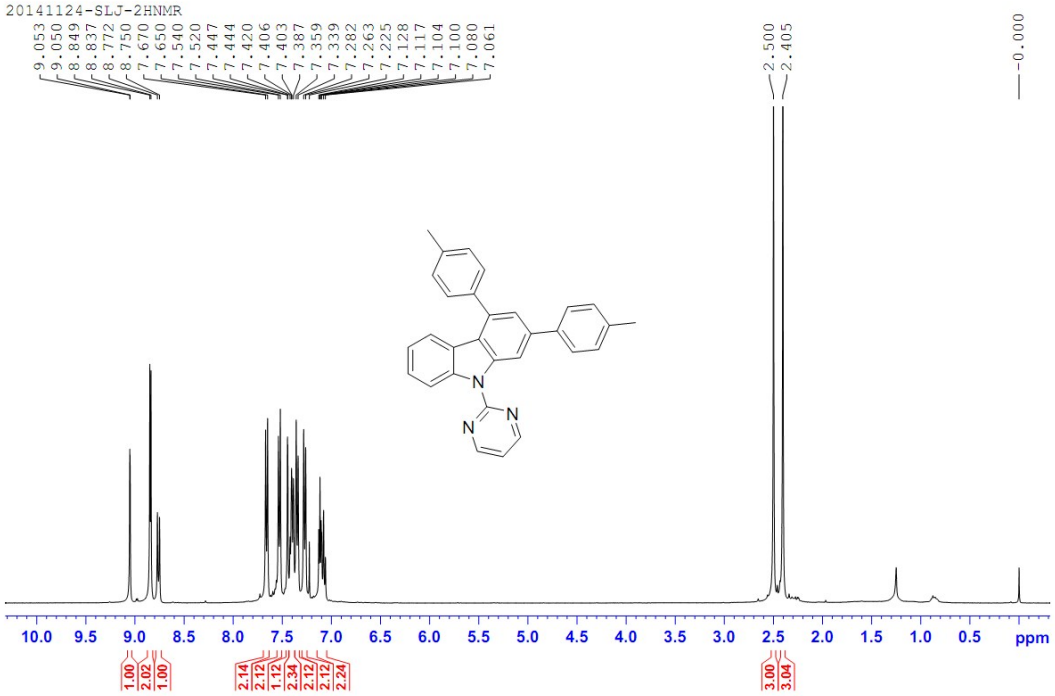


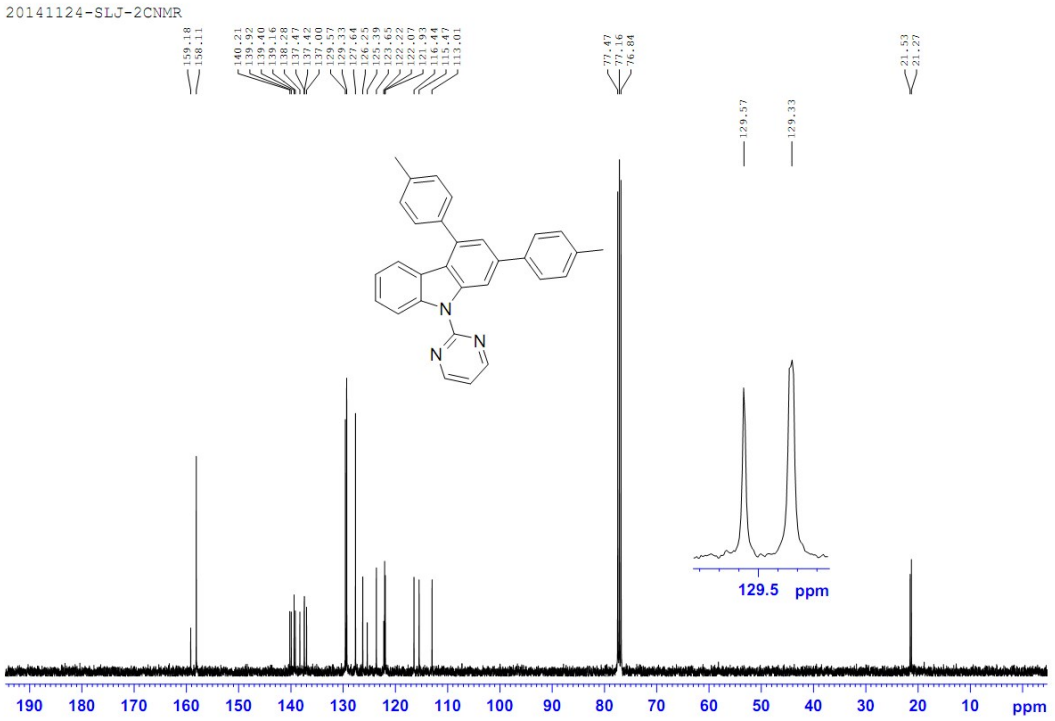
SLJ-141120-1HNMR



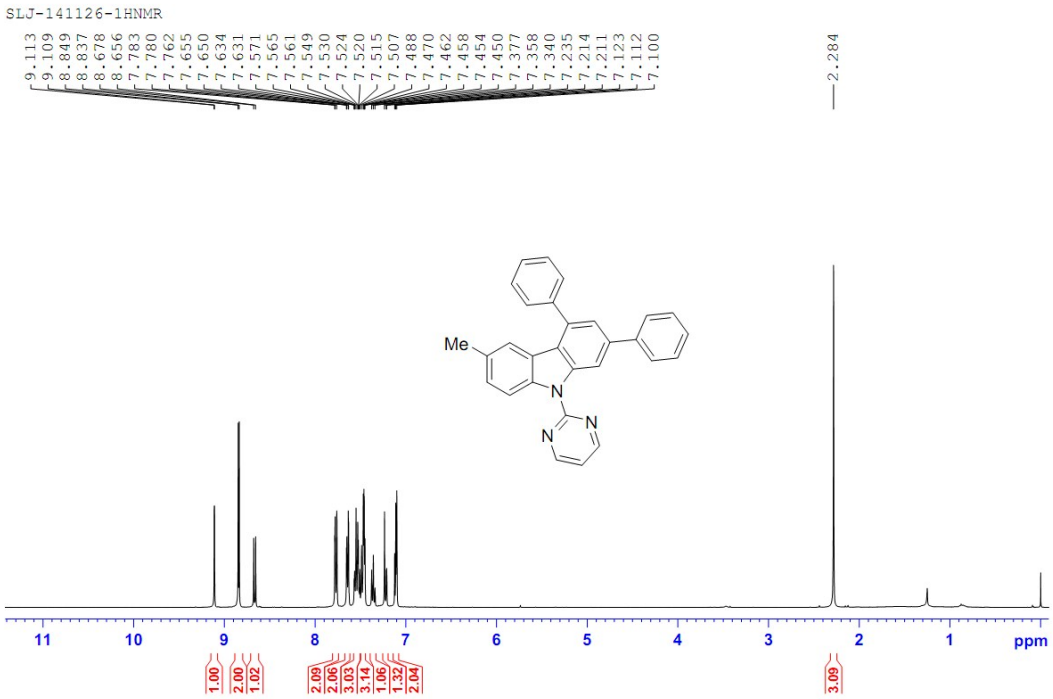
SLJ-141120-1CNMR



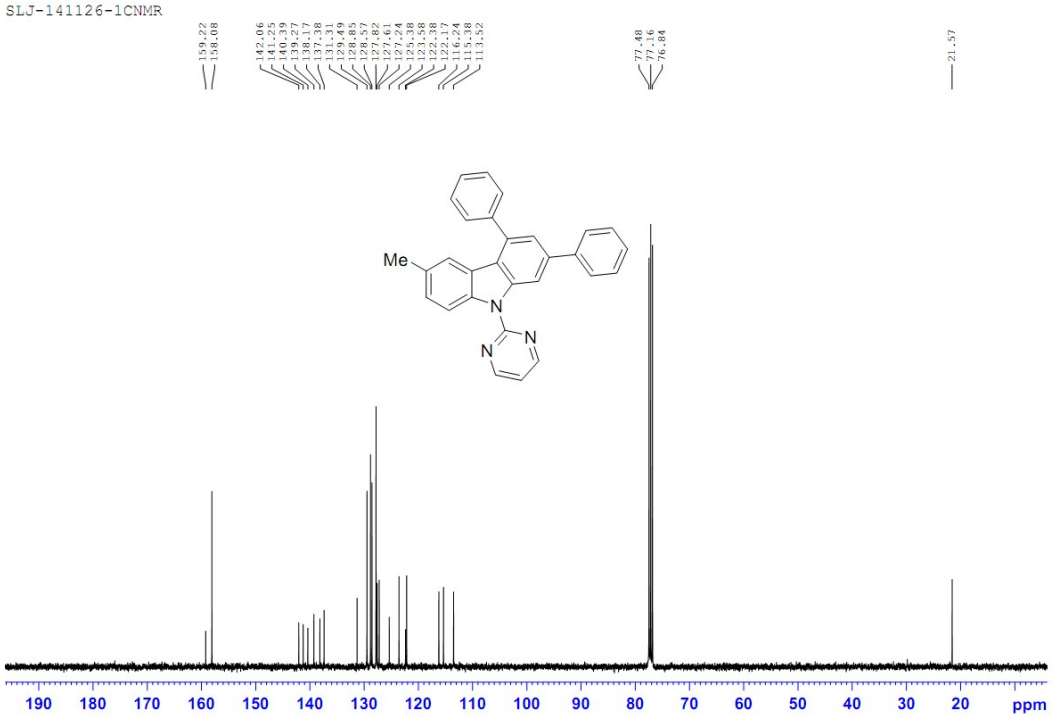

20141124-SLJ-2HNMR
9.053
9.050
8.849
8.837
8.772
8.750
7.670
7.650
7.540
7.520
7.447
7.444
7.420
7.406
7.403
7.387
7.359
7.339
7.282
7.263
7.225
7.128
7.117
7.104
7.100
7.080
7.061
2.500
2.405
0.000
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.02
1.00
2.14
2.12
1.12
2.34
2.12
2.12
2.24
3.00
3.04


20141124-SLJ-2CNMR
159.18
158.11
140.21
139.92
139.40
139.16
138.28
137.47
137.42
137.00
129.57
129.33
127.64
126.25
125.39
123.65
122.22
122.07
121.93
116.44
115.47
113.01
77.47
77.16
76.84
129.57
129.33
21.53
21.27
N
N
129.5 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

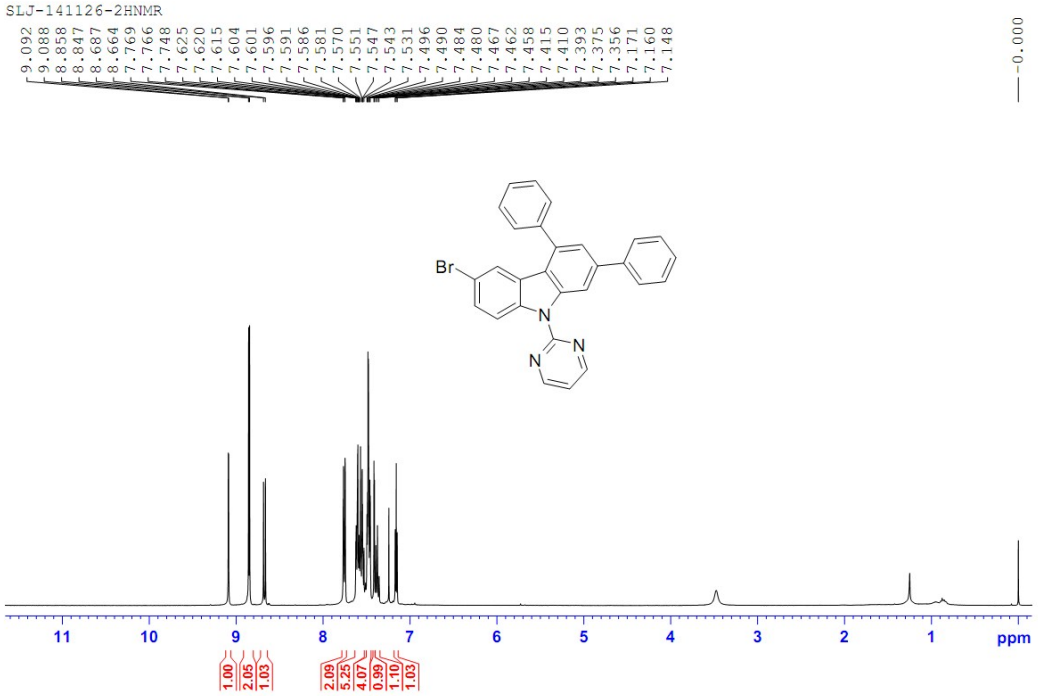
SLJ-141126-1HNMR



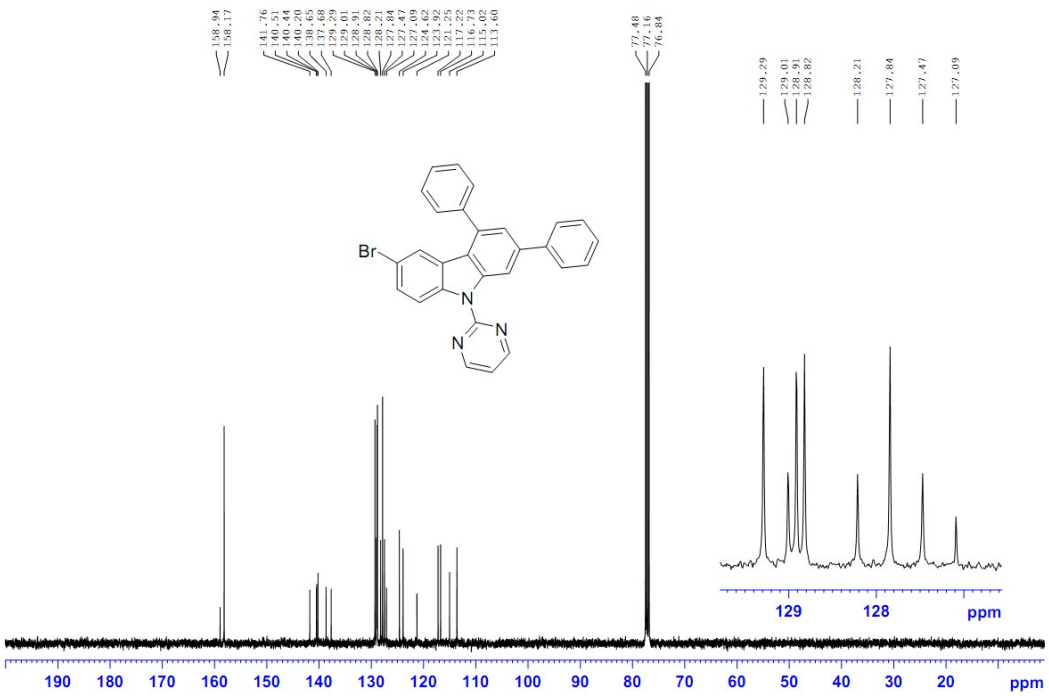
SLJ-141126-1CNMR



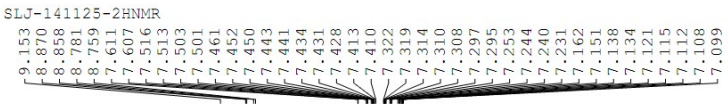
SLJ-141126-2HNMR

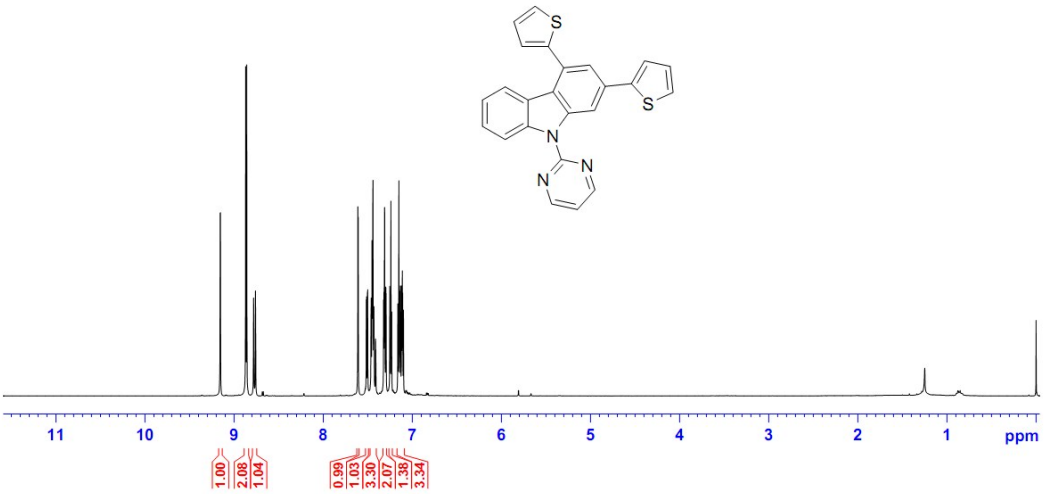


SLJ-141126-2CNMR

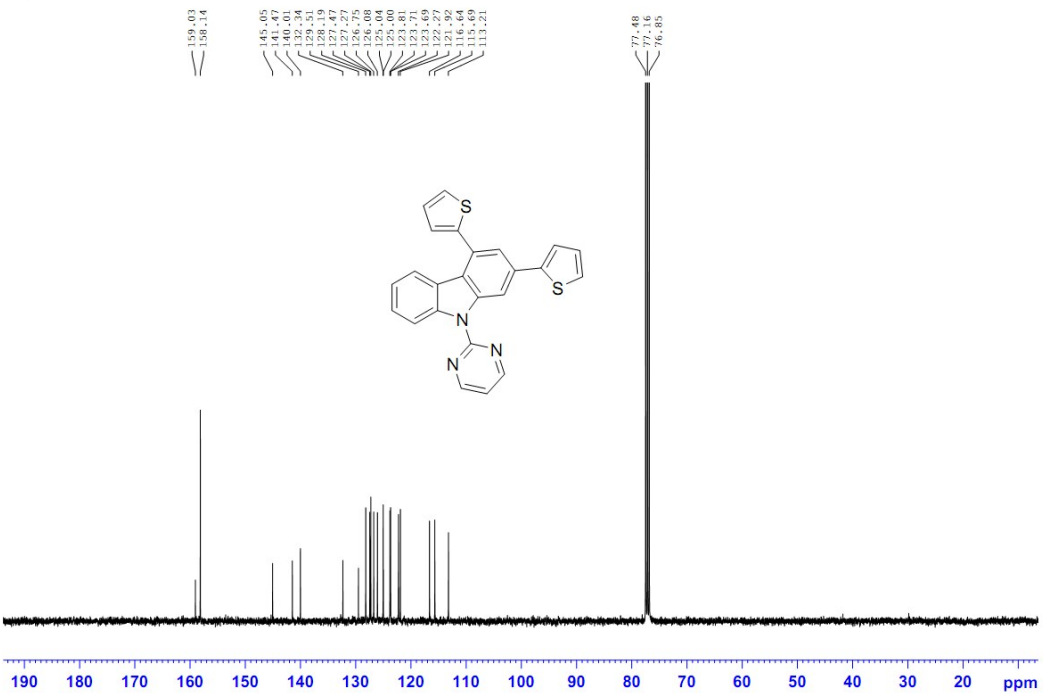


SLJ-141125-2HNMR

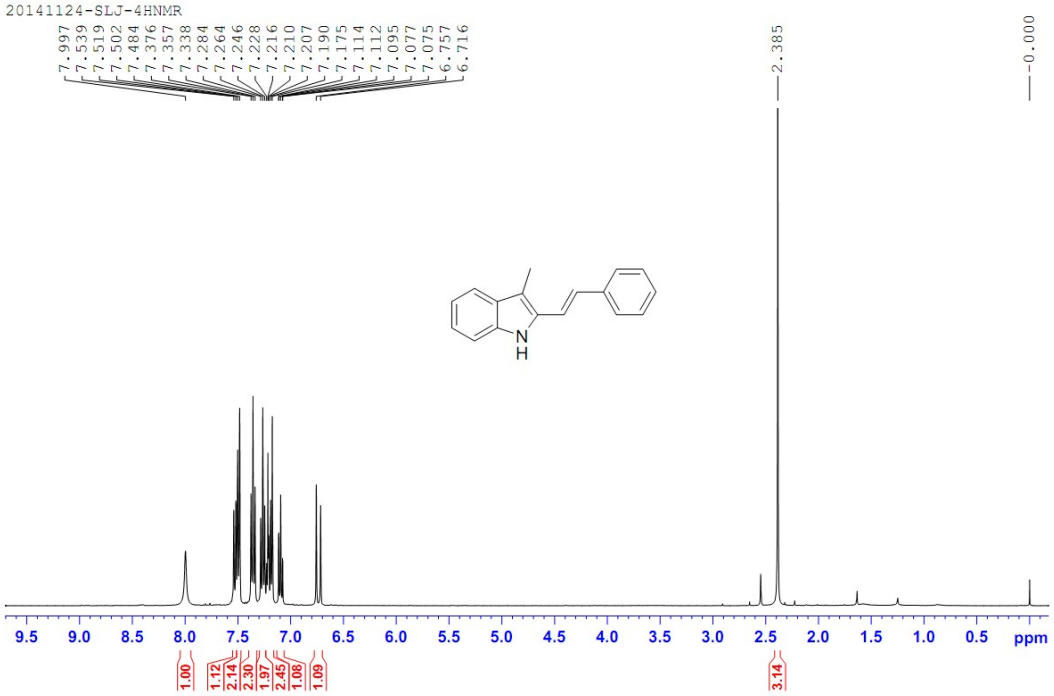




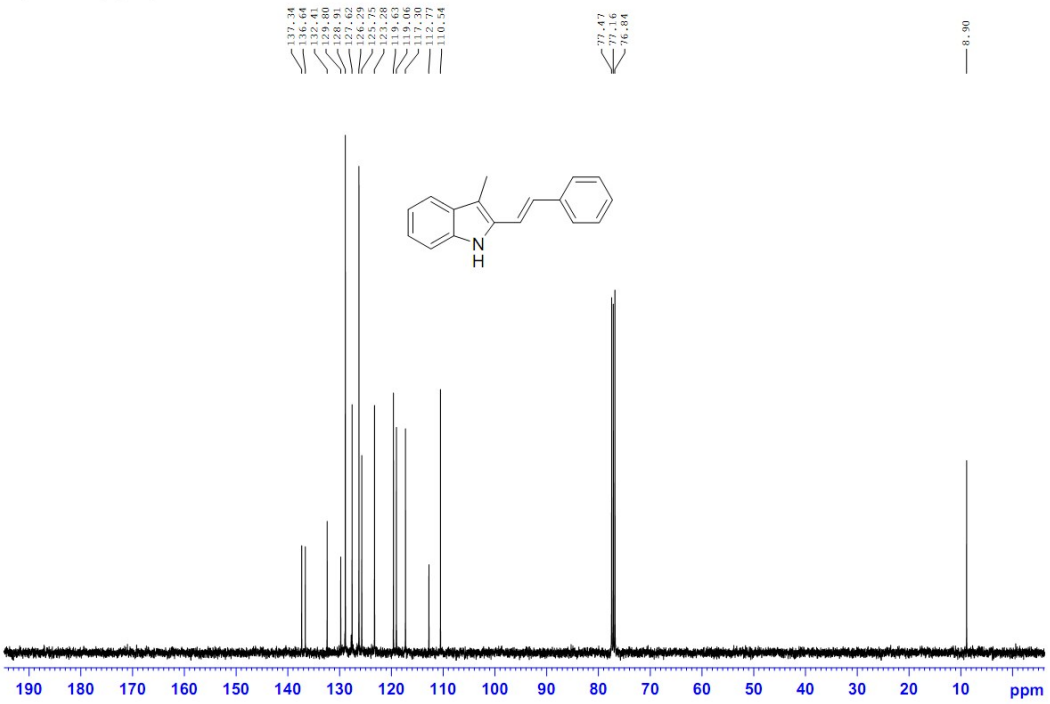
SLJ-141125-2CNMR



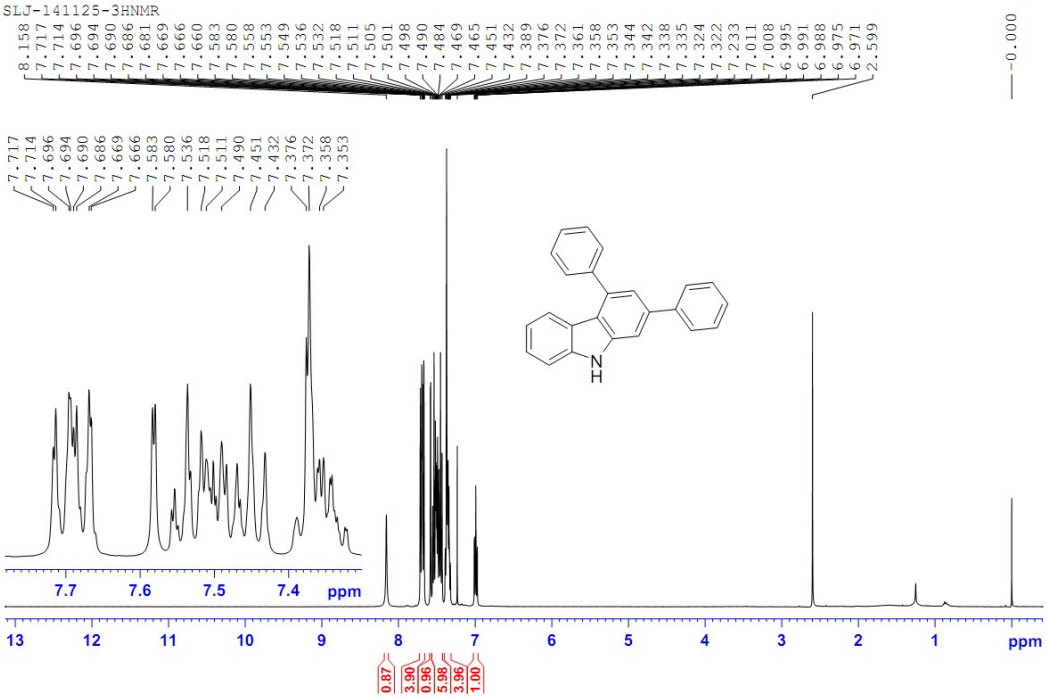
20141124-SLJ-4HNMR



20141124-SLJ-4CNMR



SLJ-141125-3HNMR



SLJ-141125-3CNMR