Supporting Information

Rhodium(III)-catalyzed tunable coupling reaction of indole derivatives with alkylidenecyclopropanes via C−H activation

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CONTENTS

(A) General Remarks

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, respectively. HRMS spectra were recorded by ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, HRMS was measured on Agilent 6224 LC/MS instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure.

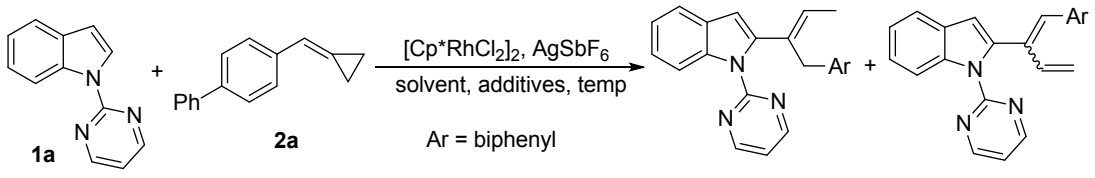
(B) Experimental Procedure and Condition Optimization

General Procedure for the Preparation of 3aa

To a Schlenk tube with a magnetic stirring bar was added 1-(pyrimidin-2-yl)-1H-indole **1a**, methylenecyclopropane **2a**, $[RhCp^*Cl_2]_2$, and $AgSbF_6$. Then, DMF was injected to the reaction mixture and HOAc was added. The reaction mixture was stirred and it was turned to dark purple within 60 seconds. Next, the reaction was carried out at 120 ^oC. After the reaction was complete, the reaction mixture was filtered through a celite to remove the salts. The solution was concentrated under reduced pressure and the residue was purified with a silica gel column chromatography to afford the product.

Preliminary Condition Optimization

Table S1 Preliminary Condition Optimization of **3aa** and **4aa**



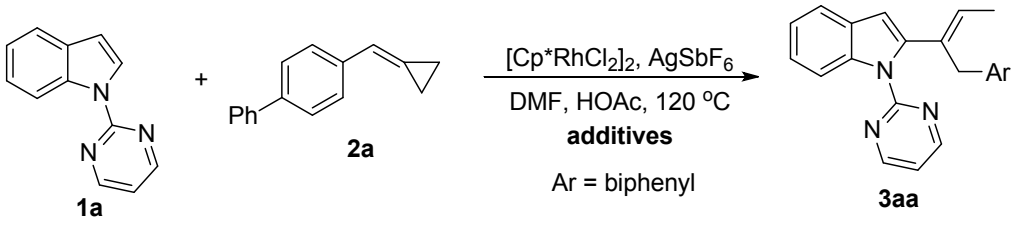
entry	solvent	temp.	additives	yield of **3aa**/**4aa** (%)
1	DMF	20	HOAc	1/30
2	DMF	70	HOAc	16/43
3	DMF	120	HOAc	17/62
4	DMF	120	PivOH	30/52
5	DMF	120	PhCOOH	28/60
6	DMF	120	AdCOOH	28/62
7	DMF	120	-	12/55
8	DCE	120	HOAc	31/48
9	MeCN	120	HOAc	15/58
10	EtOH	120	HOAc	32/49

[a] **1a** (0.10 mmol), **2a** (0.12 mmol), HOAc (0.20 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (20 mol %), additives (2 equiv) were added. All the reactions were carried out in a 0.10 mmol scale in solvent (1.0 mL) at 120 ^oC for 12 h.

Condition Optimization of Halide Effect

To a Schlenk tube with a magnetic stirring bar was added 1-(pyrimidin-2-yl)-1H-indole **1a**, methylenecyclopropane **2a**, $[RhCp^*Cl_2]_2$, and $AgSbF_6$. Then, DMF was injected to the reaction mixture and HOAc was added. The reaction mixture was stirred and it was turned to dark purple within 60 seconds. Next, alkali metal halide was added into the mixture and the reaction was carried out at 120 °C. After reaction was complete, the mixture was filtered through a celite to remove the salts. The solution was concentrated under reduced pressure and the residue was purified with a silica gel column chromatography to afford the product. KBr and KI may poison the rhodium catalyst due to the large ionic radius and high coordination ability of Br^- or I^-, resulting none of the desired product being formed.

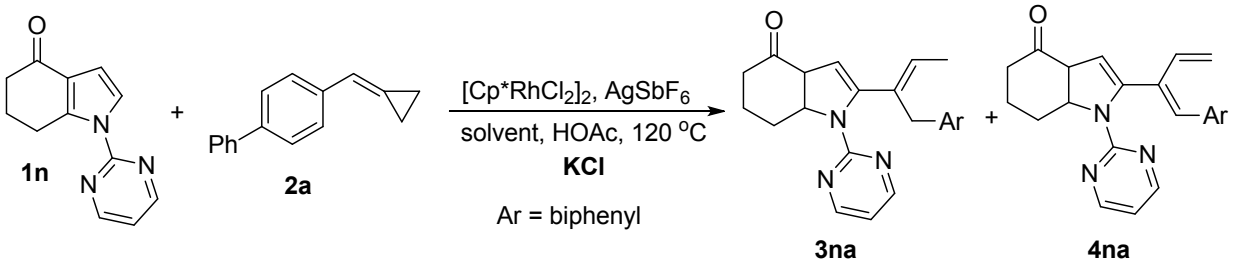
Table S2 Condition Optimization of Halide Effect of **3aa** and **4aa**



entry[a]	**additives** (equiv)	solvents	yield/[%]
1	LiCl (2.0)	DMF	63
2	NaCl (2.0)	DMF	70
3	KCl (2.0)	DMF	88
4	CsCl (2.0)	DMF	88
5	KI (2.0)	DMF	0
6	KBr (2.0)	DMF	9
7	C_2Cl_6 (2.0)	DMF	72
8	Me_4NCl (2.0)	DMF	35
9	KCl (1.0)	DMF	65
10	KCl (3.0)	DMF	83
11	KCl (5.0)	DMF	71
12[b]	KCl (2.0)	DMF	-

[a] **1a** (0.10 mmol), **2a** (0.12 mmol), HOAc (0.20 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (20 mol %), DMF (1.0 mL) and halide (2.0 equiv) were added. All the reactions were carried out in a 0.10 mmol scale in DMF (1.0 mL) at 120 °C for 12 h. [b] Without $AgSbF_6$.

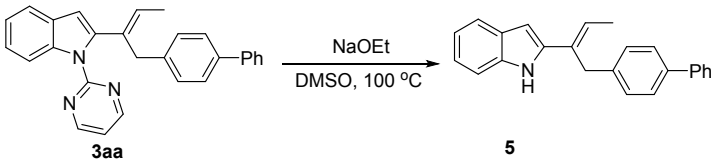
Table S3 Condition Optimization of **3na** and **4na**



entry[a]	solvent	yield/[%] **3na/4na**
1	DMF	38/38
2	DCE	35/36
3	EtOH	37/37

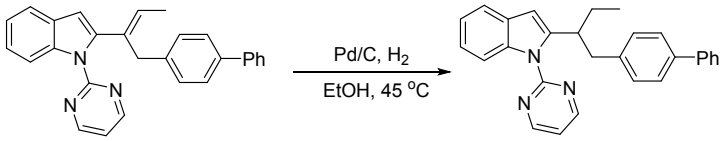
[a] **1n** (0.10 mmol), **2a** (0.12 mmol), HOAc (0.20 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (20 mol %), solvent (1.0 mL) and KCl (2.0 equiv) were added. All the reactions were carried out in a 0.10 mmol scale in DMF (1.0 mL) at 120 °C for 12 h.

(C) Derivatization of Reaction Products



3aa **5**

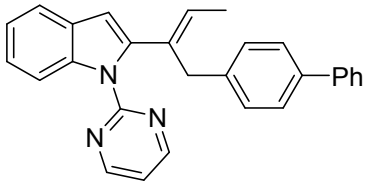
To a Schlenk tube with a magnetic stirring bar was added product **3aa** and NaOEt. Then DMSO was injected to the mixture. The reaction was carried out at 100 °C. After reaction was completed, the mixture was washed by water and dried over anhydrous Na_2SO_4. The solvent was removed under the reduced pressure and the residue was purified with a silica gel column chromatography to afford the product **5** in 86% yield.



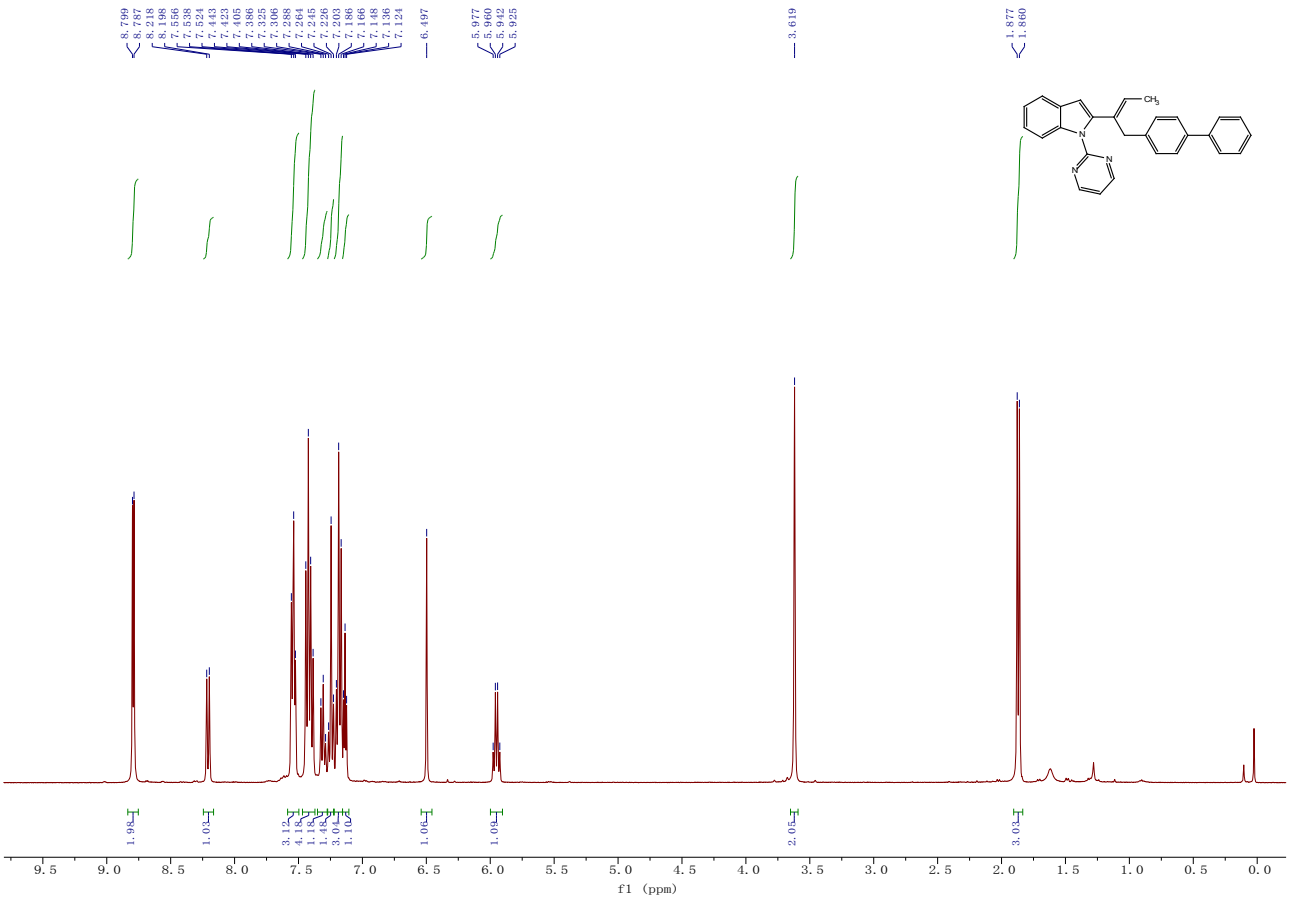
3aa **6**

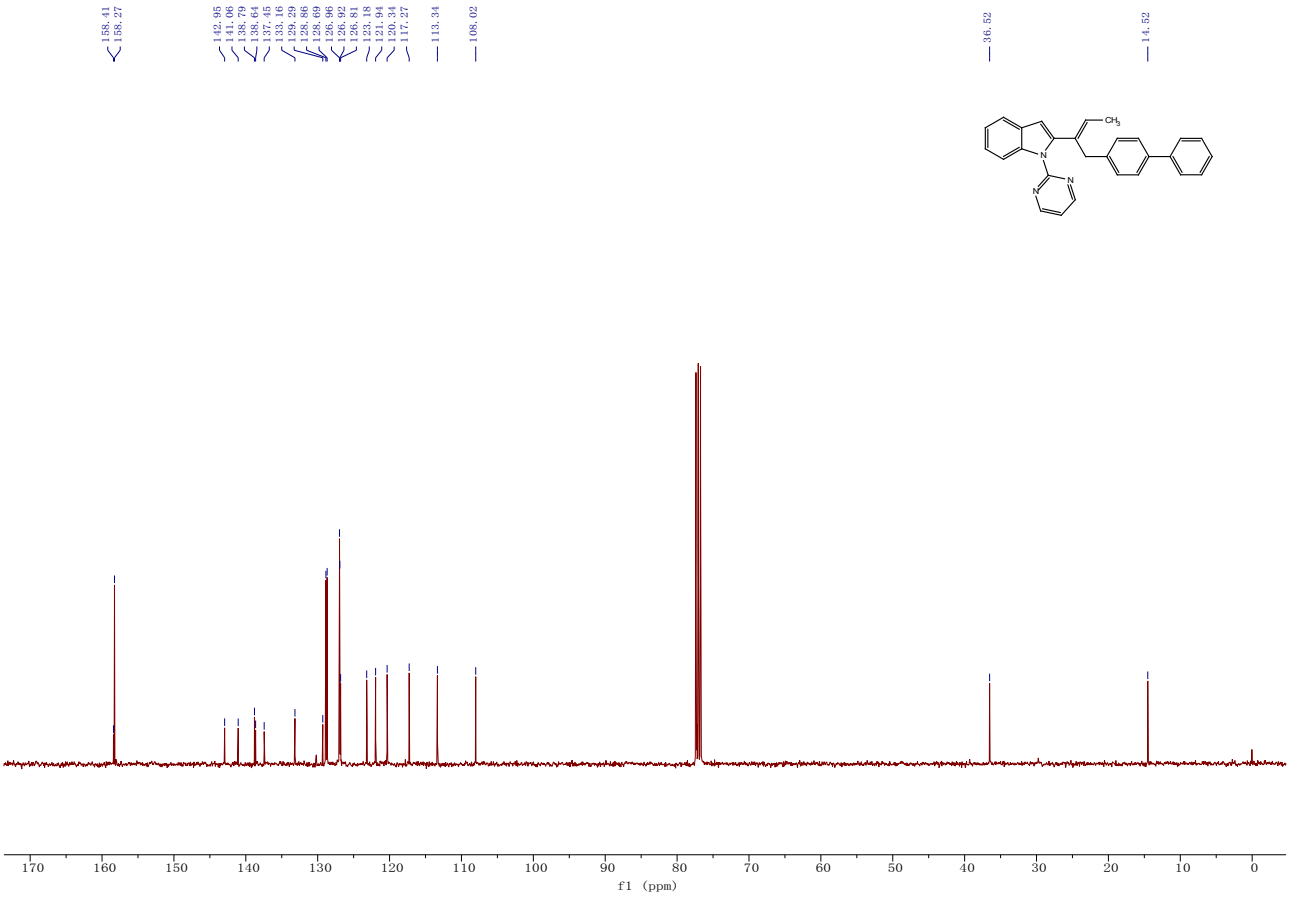
To a Schlenk tube with a magnetic stirring bar was added product **3aa** and palladium on coral. Then EtOH was injected to the mixture. The system was vacuumed and refilled with H_2 three times. The reaction was carried out at 45 °C. After reaction was completed, the mixture was filtered through a celite to remove the catalysts. The solvent was removed under reduced pressure and the residue was purified with a silica gel column chromatography to afford the product **6** in 91% yield.

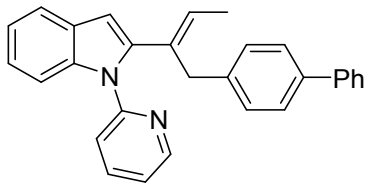
(D) Product Characterization



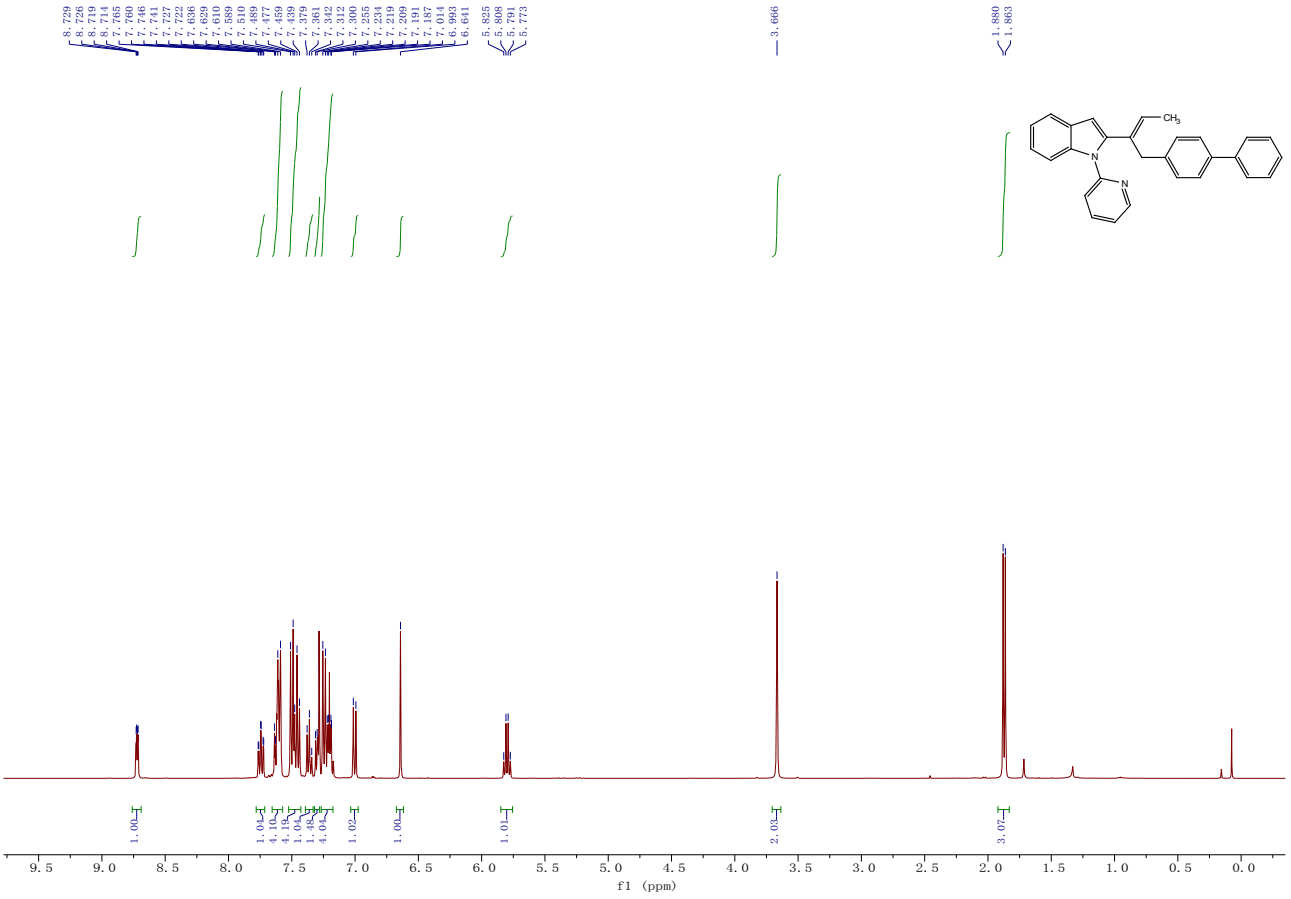
Compound 3aa: yellow (35.3 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.85 (d, *J* = 7.0 Hz, 3H), 3.60 (s, 2H), 5.93 (q, *J* = 7.0 Hz, 1H), 6.47 (s, 1H), 7.13 – 7.18 (m, 4H), 7.20 – 7.25 (m, 1H), 7.27 – 7.33 (m, 1H), 7.36 – 7.43 (m, 4H), 7.52 (dd, *J* = 7.2 Hz, 3H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.5, 108.0, 113.3, 117.3, 120.3, 121.9, 123.2, 126.8, 126.9, 127.0, 128.7, 128.9, 129.3, 130.2, 133.2, 137.4, 138.6, 138.8, 141.1, 142.9, 158.3, 158.4. IR (neat) ν 3021, 2919, 2846, 1570, 1559, 1486, 1336, 1311, 1256, 1184, 1121, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{24}N_3$ requires (M^++H): 402.1965, Found: 402.1968.







Compound 3ba: yellow oil (36.8 mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.87 (d, *J* = 7.0 Hz, 3H), 3.67 (s, 2H), 5.80 (q, *J* = 7.0 Hz, 1H), 6.62 – 6.67 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.27 (m, 4H), 7.28 – 7.32 (m, 1H), 7.36 (dd, *J* = 7.3 Hz, 1H), 7.43 – 7.52 (m, 4H), 7.57 – 7.66 (m, 4H), 7.71 – 7.78 (m, 1H), 8.72 (dd, *J* = 4.9, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.6, 35.9, 105.1, 111.2, 120.4, 121.1, 121.5, 121.7, 122.7, 127.0, 127.1, 128.5, 128.8, 128.9, 129.0, 131.2, 138.0, 138.2, 138.6, 138.9, 141.0, 142.0, 149.2, 152.7. IR (neat) ν 3047, 2912, 2846, 1561, 1451, 1379, 1345, 1213, 1173, 1121, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{25}N_2$ requires (M^++H): 401.2012, Found: 401.2020.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3.07
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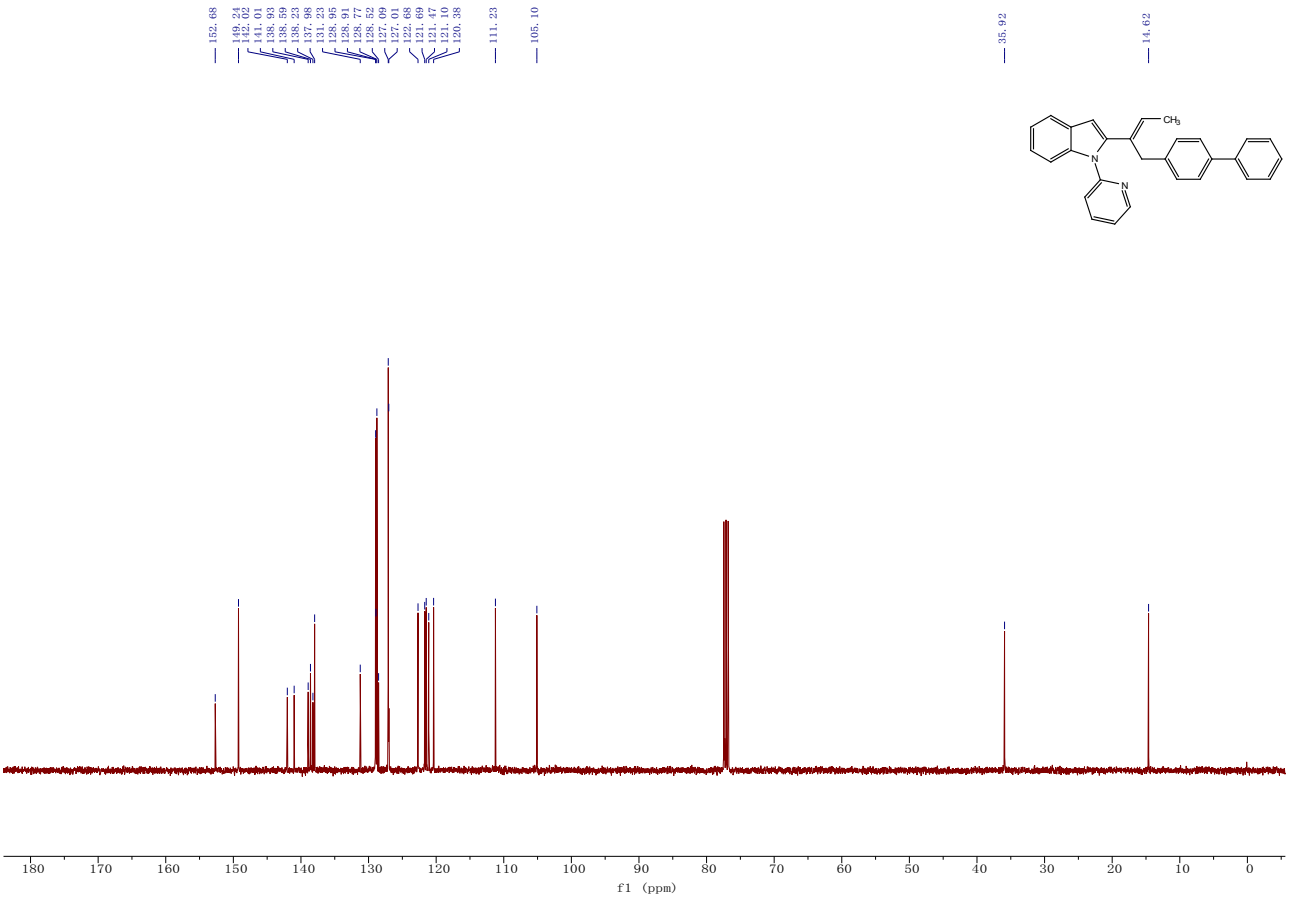
f1 (ppm)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N
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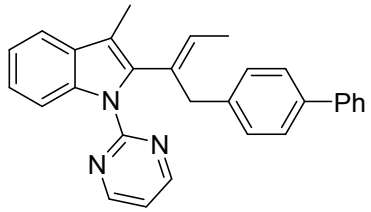
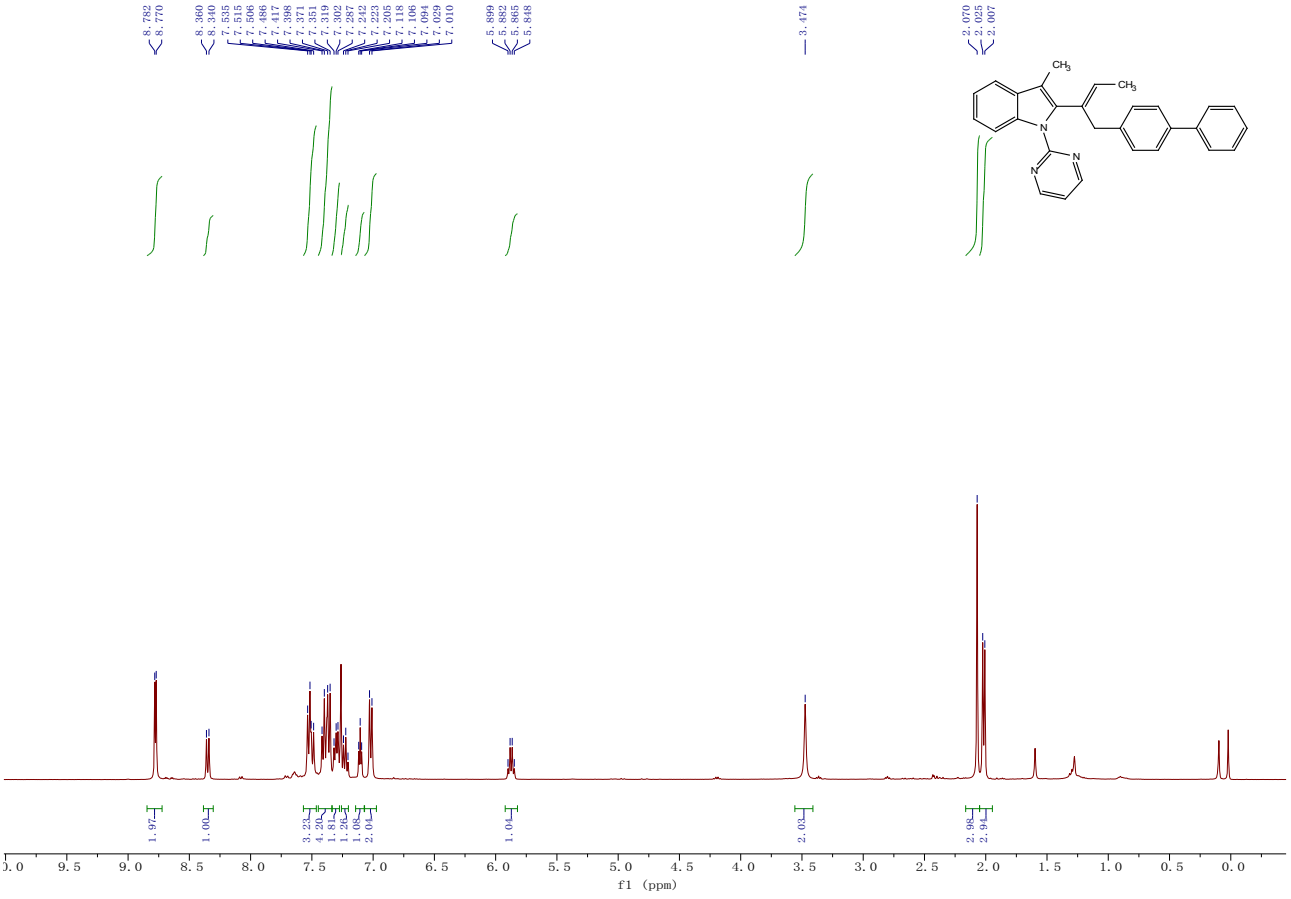
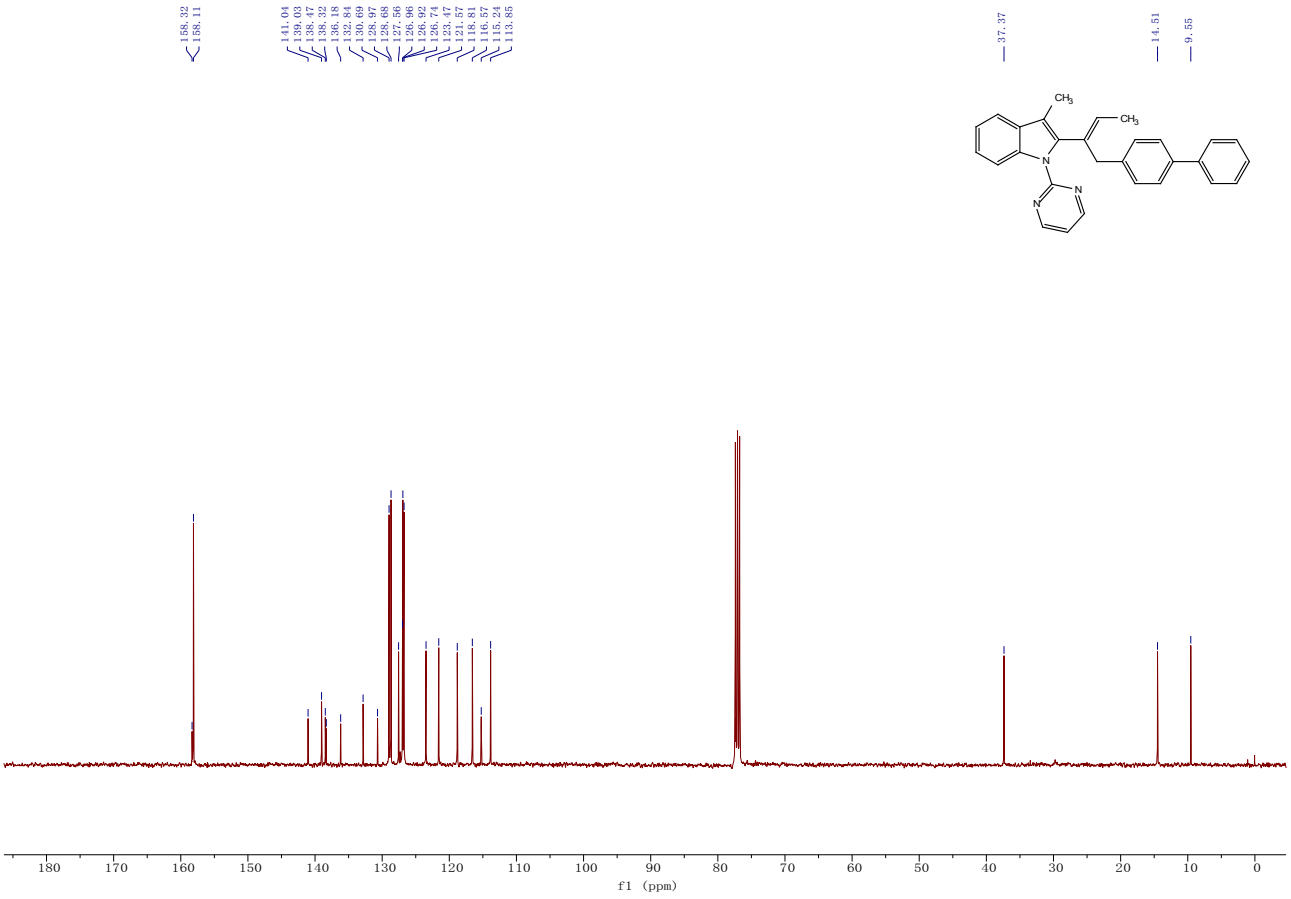
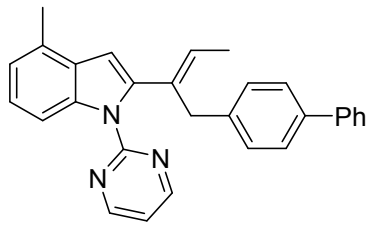
f1 (ppm)



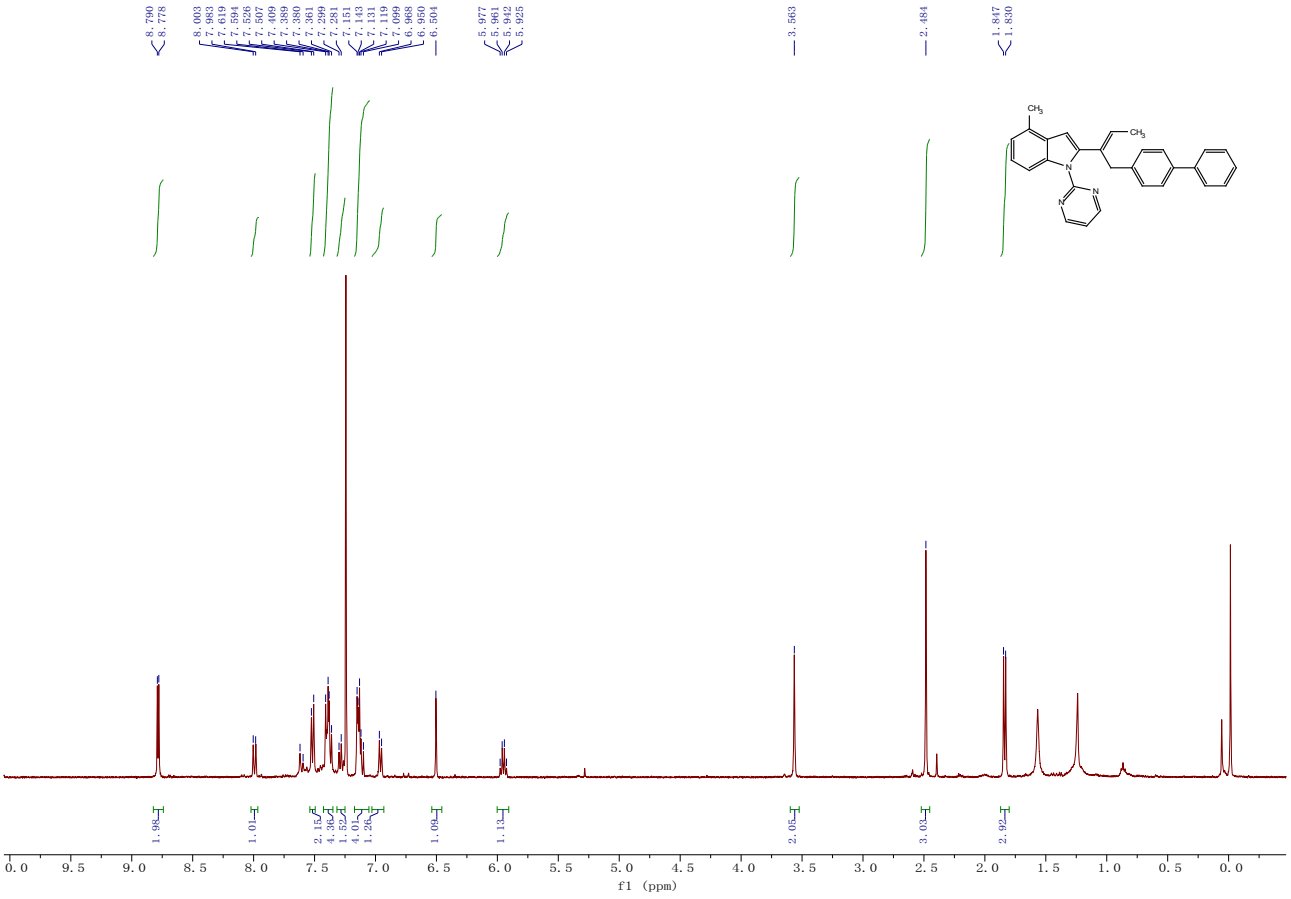
Compound 3da: yellow oil (37.8 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.02 (d, *J* = 6.8 Hz, 3H), 2.07 (s, 3H), 3.47 (s, 2H), 5.87 (q, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 4.8 Hz, 1H), 7.20 – 7.26 (m, 1H), 7.27 – 7.34 (m, 2H), 7.33 – 7.45 (m, 4H), 7.46 – 7.57 (m, 3H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.78 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 9.5, 14.5, 37.4, 113.8, 115.2, 116.6, 118.8, 121.6, 123.5, 126.7, 126.9, 127.0, 127.6, 128.7, 129.0, 130.7, 132.8, 136.2, 138.3, 138.5, 139.0, 141.0, 158.1, 158.3. IR (neat) ν 3034, 2914, 2844, 1561, 1507, 1451, 1380, 1348, 1257, 1120, 1037, 1017 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{26}N_3$ requires (M^++H): 416.2121, Found: 416.2138







Compound 3ea: yellow oil (34.0 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) 1.84 (d, *J* = 6.9 Hz, 3H), 2.48 (s, 3H), 3.56 (s, 2H), 5.95 (q, *J* = 7.0 Hz, 1H), 6.50 (s, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 7.05 – 7.17 (m, 4H), 7.28 (dd, *J* = 7.2 Hz, 2H), 7.35 – 7.43 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.78 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 18.6, 36.5, 106.5, 110.9, 117.3, 122.3, 123.3, 126.6, 126.9, 127.0, 128.7, 128.9, 129.7, 133.3, 137.3, 138.6, 138.8, 141.1, 142.4, 158.3, 158.5. IR (neat) ν 3037, 2925, 2849, 1562, 1451, 1379, 1345, 1213, 1173, 1121, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{26}N_3$ requires (M^++H): 416.2121, Found: 416.2126.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7.281
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7.119
7.000
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6.950
6.504
5.977
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5.942
5.925
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1.830
1.98
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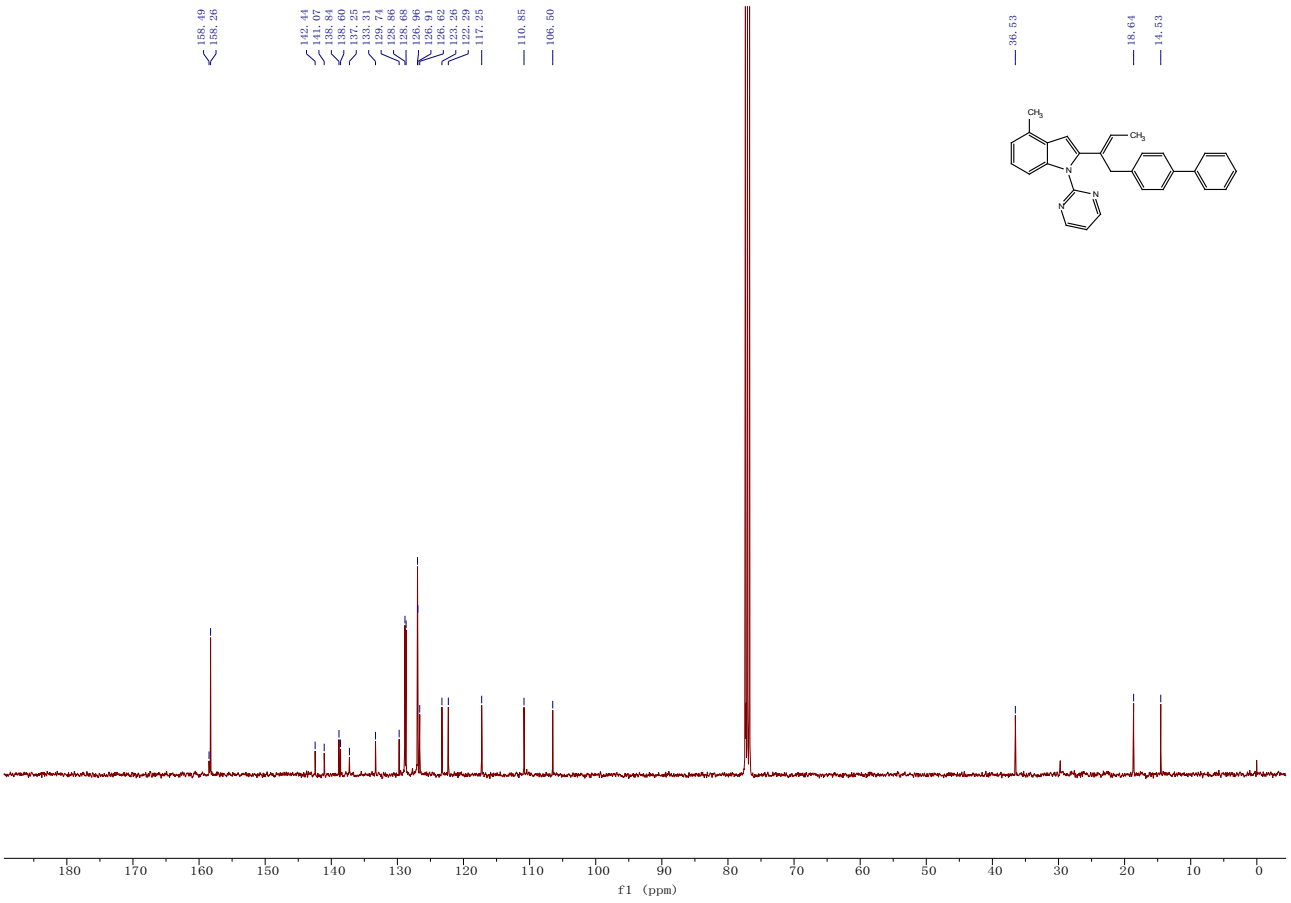
3.03
2.92
f1 (ppm)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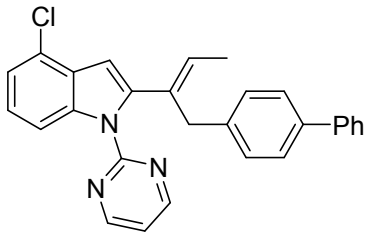
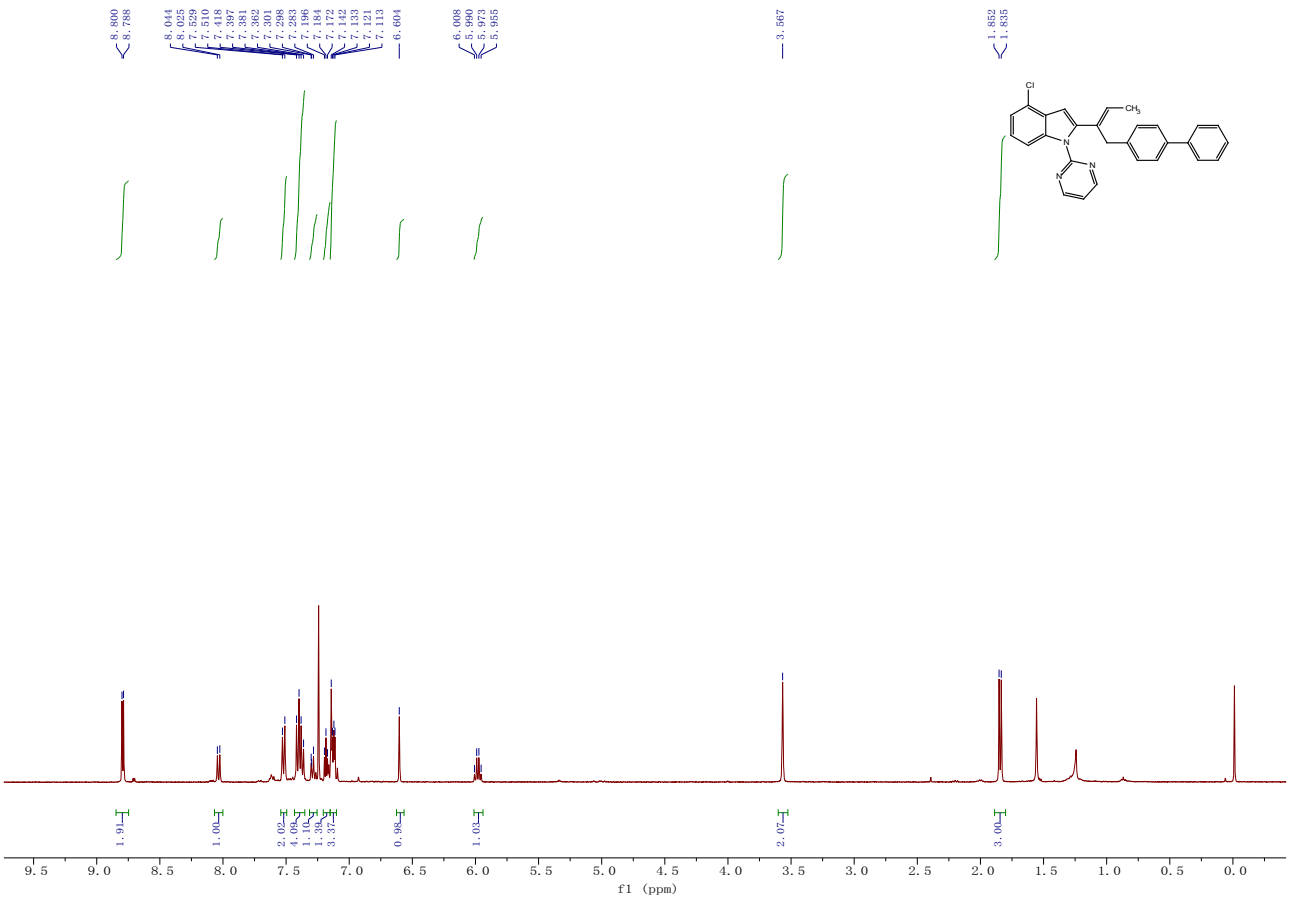
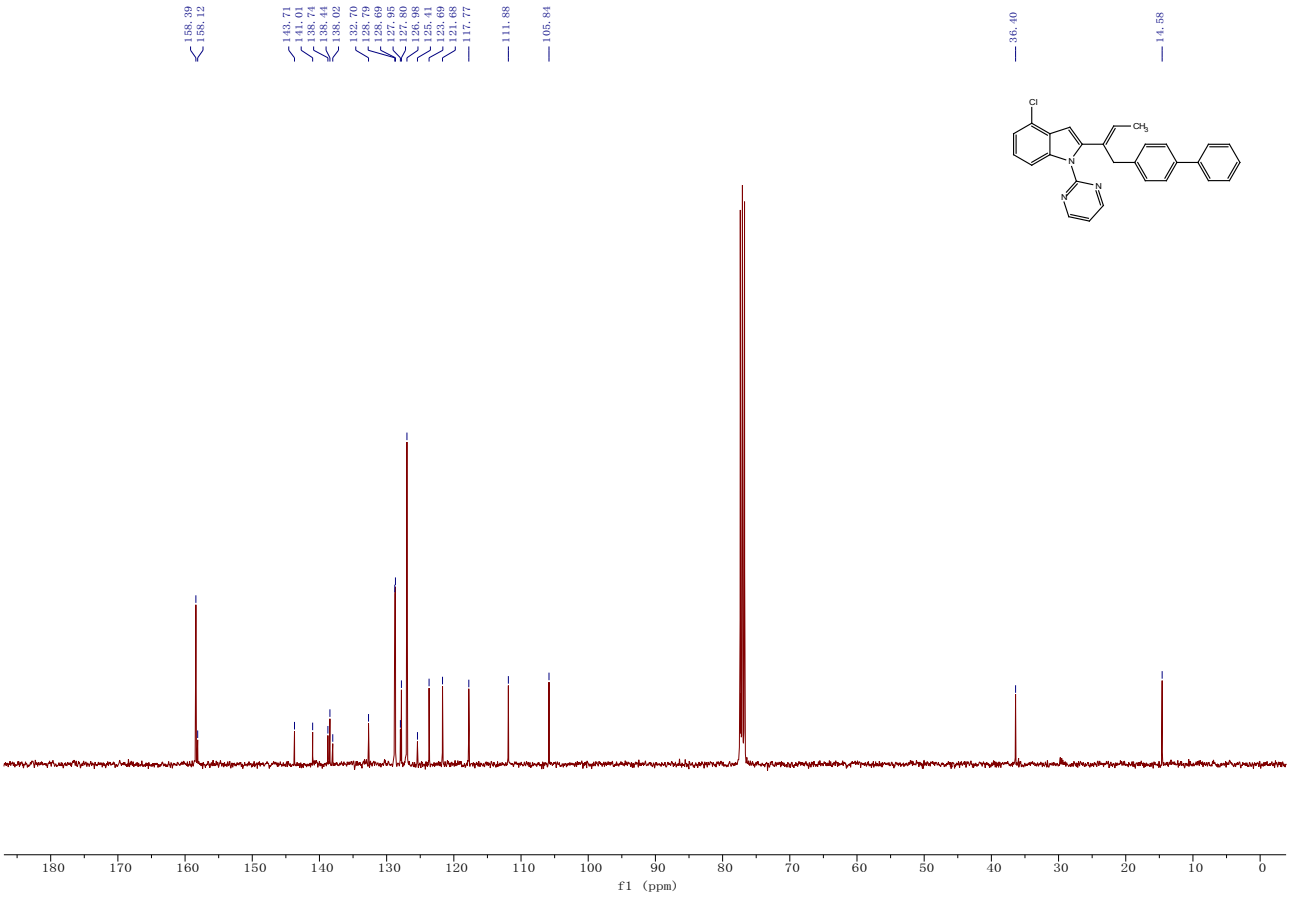
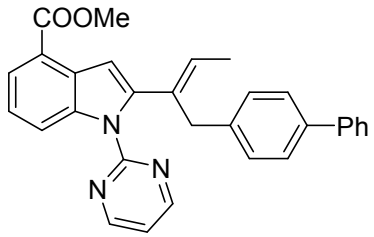
14.53
f1 (ppm)



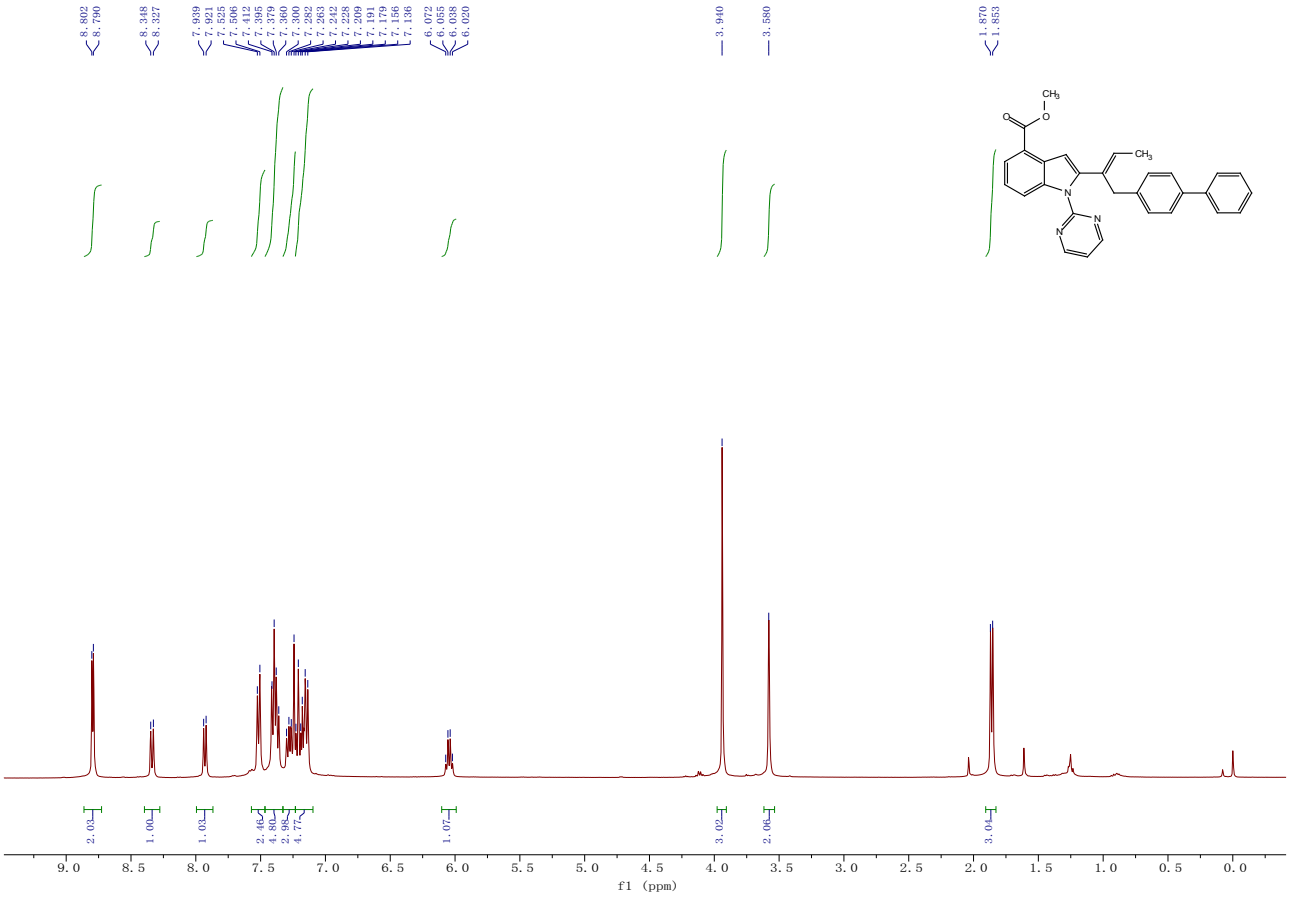
Compound 3fa: yellow oil (37.4 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 5.98 (q, *J* = 7.0 Hz, 1H), 6.60 (s, 1H), 7.13 (dd, *J* = 8.1, 3.6 Hz, 3H), 7.15 – 7.21 (m, 1H), 7.28 (dd, *J* = 7.3 Hz, 1H), 7.35 – 7.43 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.6, 36.4, 105.8, 111.9, 117.8, 121.7, 123.7, 125.4, 127.0, 127.8, 128.0, 128.7, 128.8, 132.7, 138.0, 138.4, 138.7, 141.0, 143.7, 158.1, 158.4. IR (neat) ν 2922, 2849, 1561, 1507, 1451, 1380, 1348, 1213, 1173, 1121, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{23}ClN_3$ requires (M^++H): 436.1575, Found: 436.1575.







Compound 3ga: yellow oil (29.4 mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.86 (d, *J* = 7.0 Hz, 3H), 3.58 (s, 2H), 3.94 (s, 3H), 6.05 (q, *J* = 6.9 Hz, 1H), 7.11 – 7.24 (m, 5H), 7.26 – 7.31 (m, 2H), 7.35 – 7.43 (m, 4H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.6, 36.4, 51.8, 108.6, 117.8, 121.1, 122.4, 125.0, 127.0, 127.0, 128.1, 128.7, 128.8, 129.2, 132.7, 138.2, 138.5, 138.7, 141.0, 145.2, 158.1, 158.4, 167.8. IR (neat) ν 3021, 2922, 2850, 1682, 1562, 1486, 1379, 1353, 1321, 1254, 1222, 1173, 1121, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{30}H_{26}N_3O_2$ requires (M^++H): 460.2020, Found: 460.2023.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7.179
7.156
7.136
6.072
6.055
6.038
6.020
3.940
3.580
1.870
1.853
CH3
O
O
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N
N
N
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1.00
1.03
2.46
4.80
2.98
4.77
1.07
3.02
2.06
3.04
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8.0
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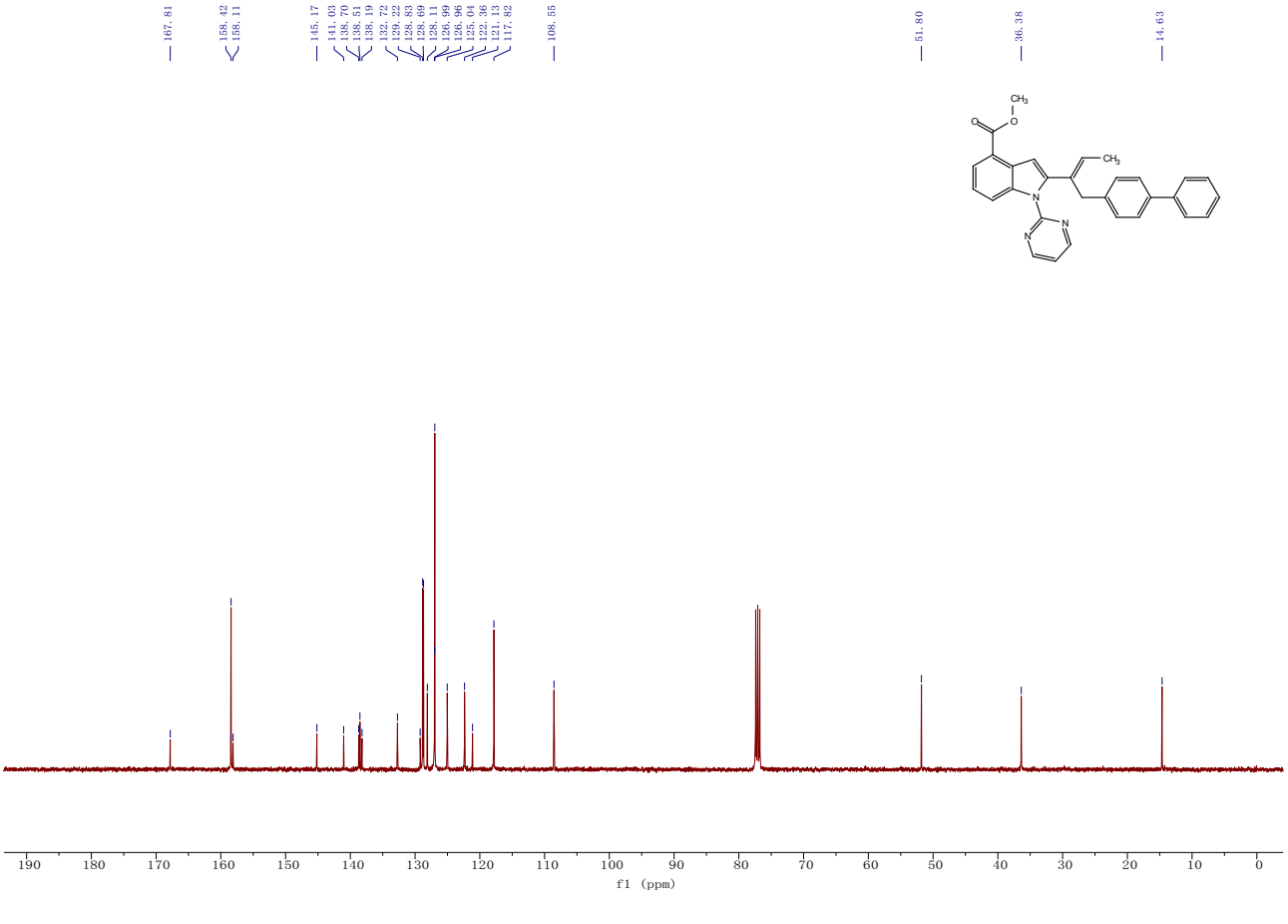
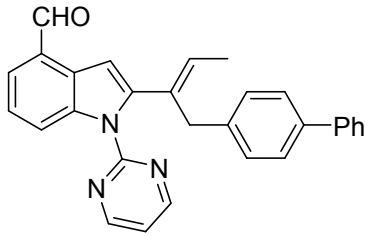
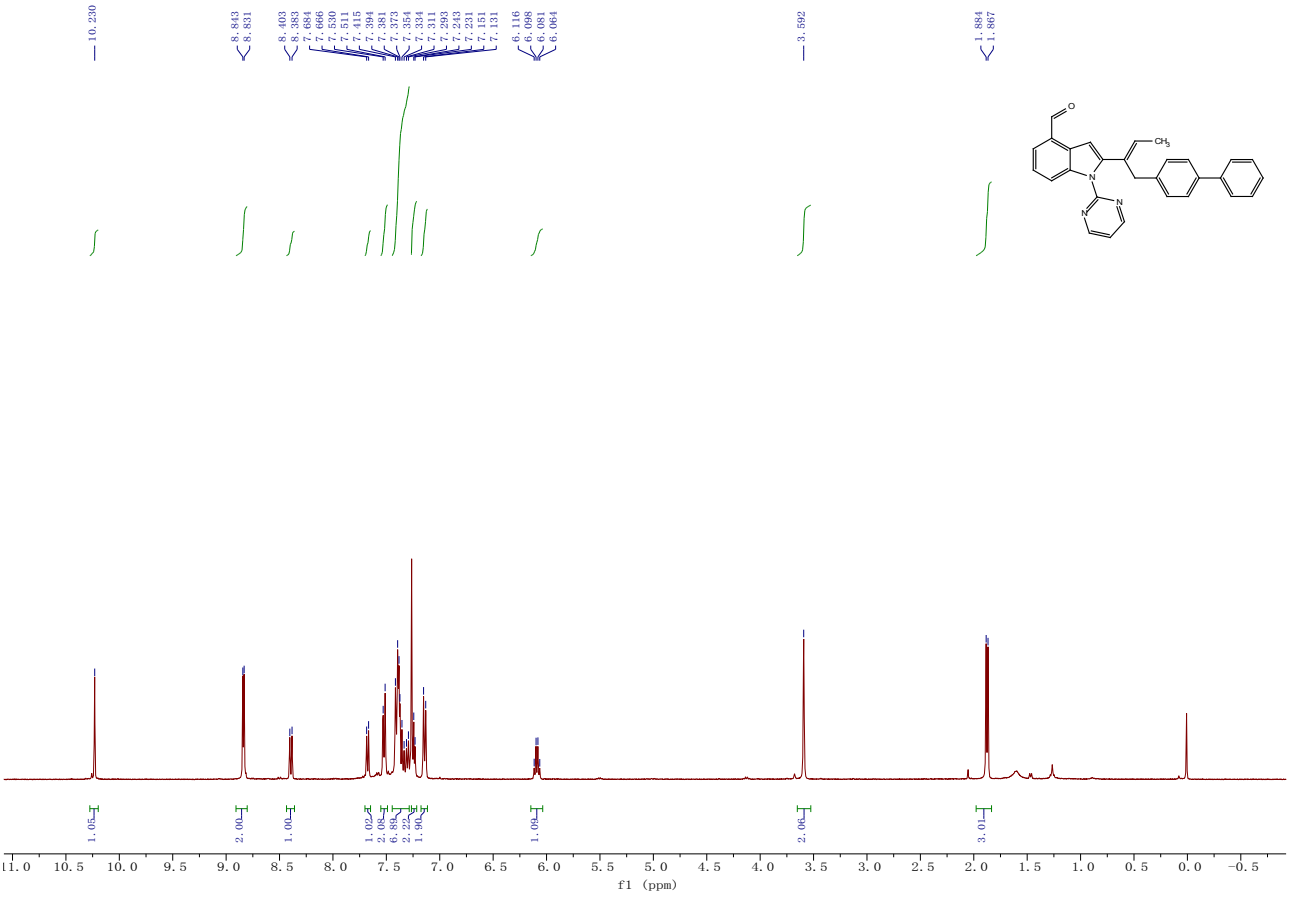
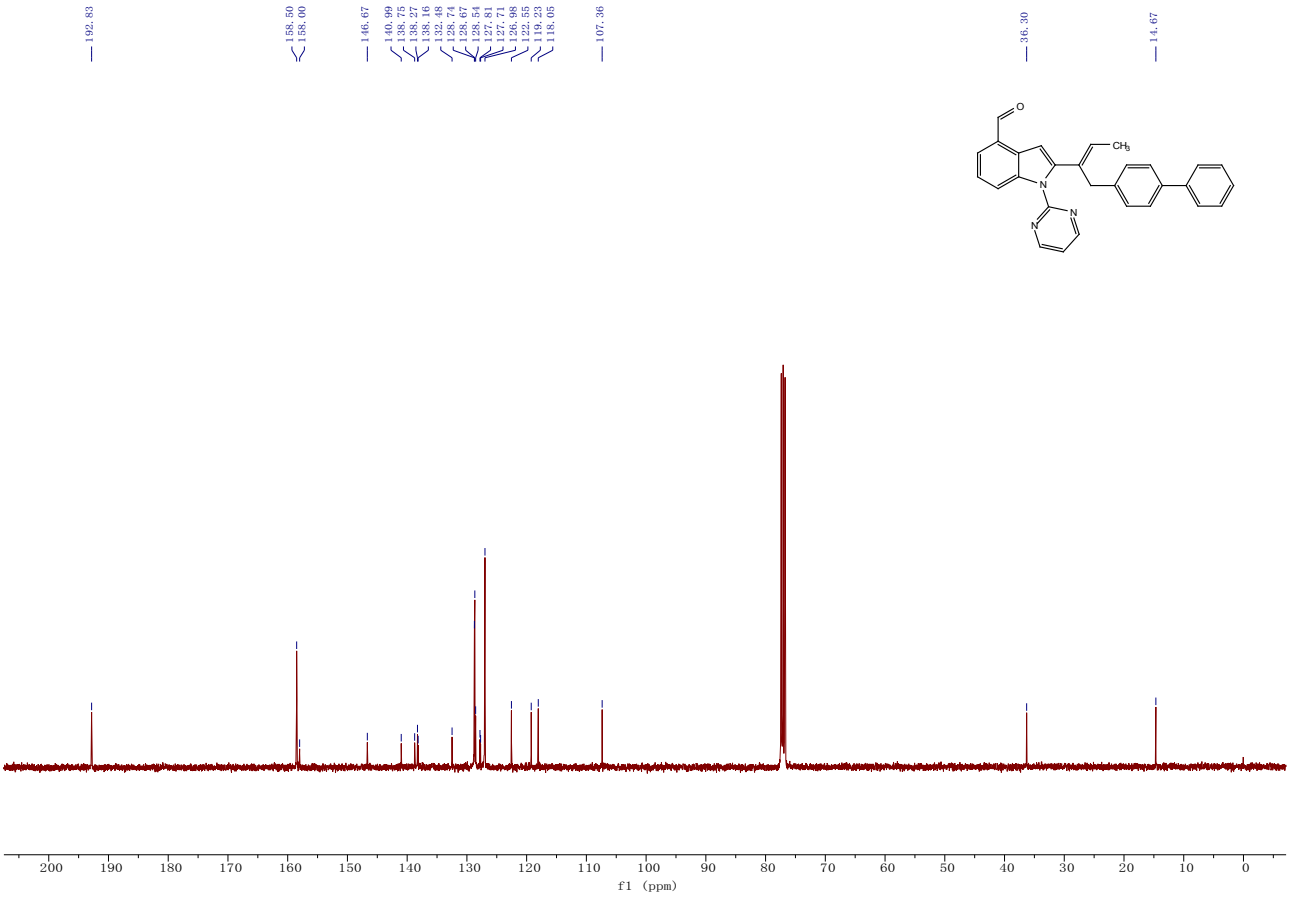
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

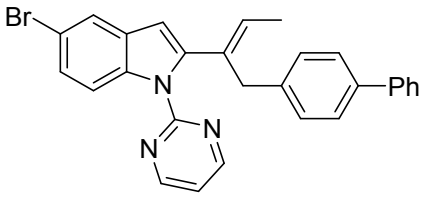

167.81
158.42
158.11
145.17
141.03
138.70
138.51
138.19
132.72
129.22
128.83
128.69
128.11
126.99
126.96
125.04
122.36
121.13
117.82
108.55
51.80
36.38
14.63
CH3
O
O
CH3
N
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



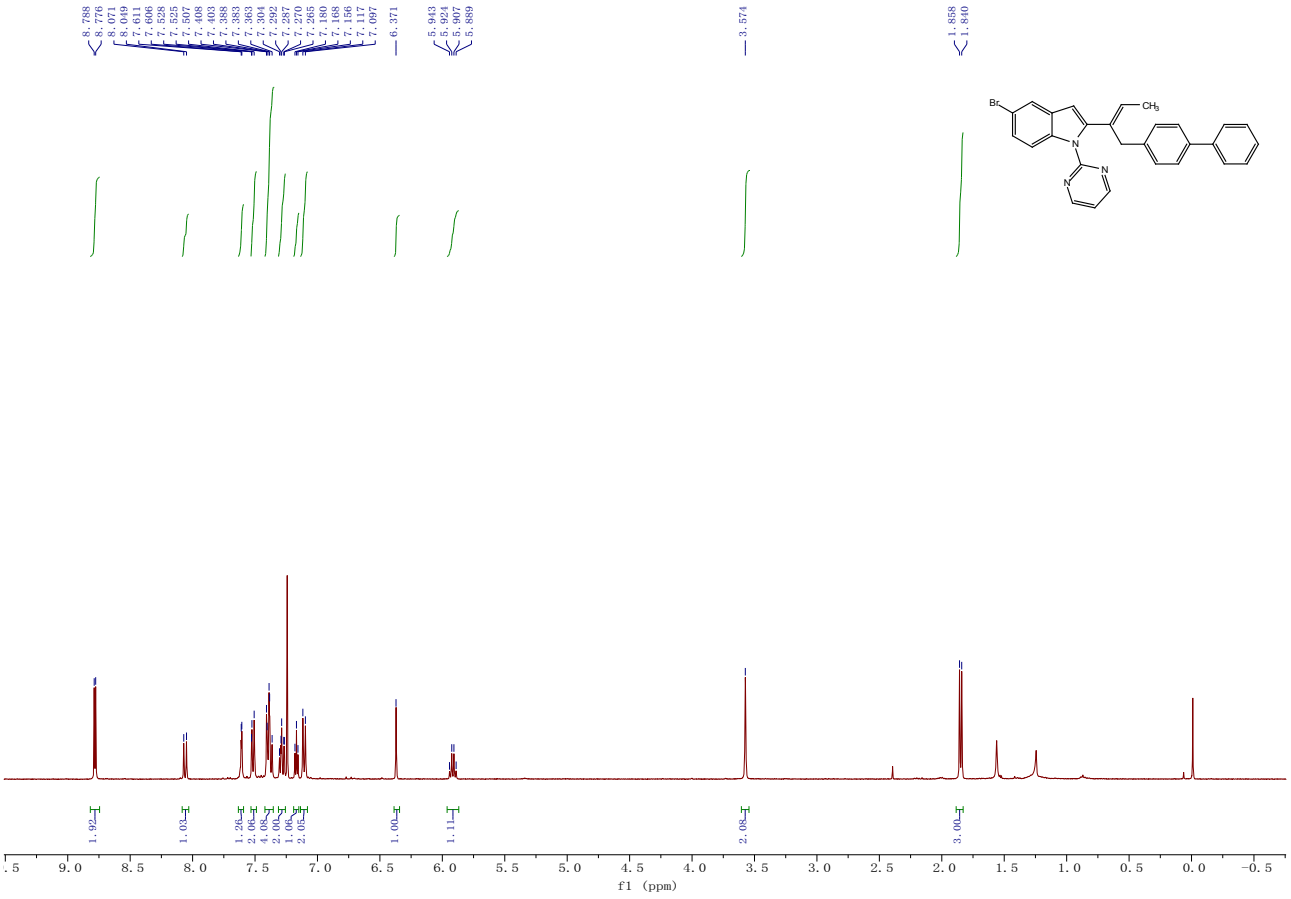
Compound 3ha: yellow oil (33.5 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.88 (d, *J* = 6.9 Hz, 3H), 3.59 (s, 2H), 6.09 (q, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 4.8 Hz, 2H), 7.29 – 7.44 (m, 7H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 1H), 8.39 (d, *J* = 8.2 Hz, 1H), 8.84 (d, *J* = 4.8 Hz, 2H), 10.23 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.7, 36.3, 107.4, 118.1, 119.2, 122.5, 127.0, 127.7, 127.8, 128.5, 128.67, 128.74, 132.5, 138.2, 138.3, 138.7, 141.0, 146.7, 158.0, 158.5, 192.8. IR (neat) ν 3027, 2921, 2850, 1681, 1563, 1519, 1486, 1354, 1321, 1223, 1163, 1087, 1039 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{24}N_3O$ requires (M^++H): 430.1914, Found: 430.1921.

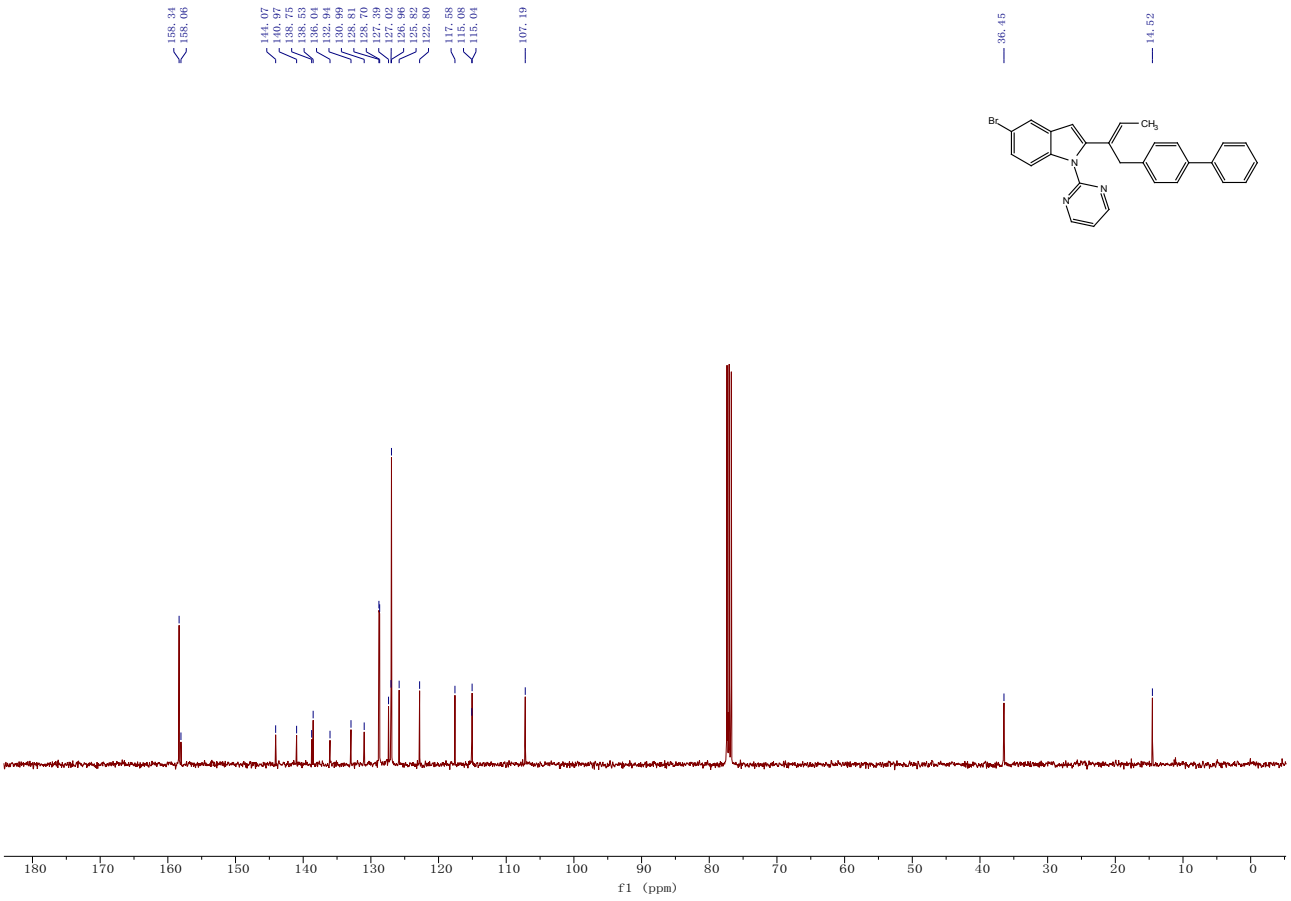


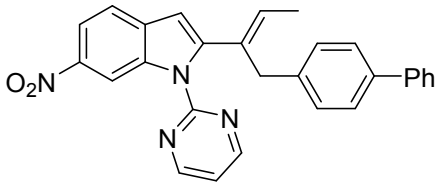




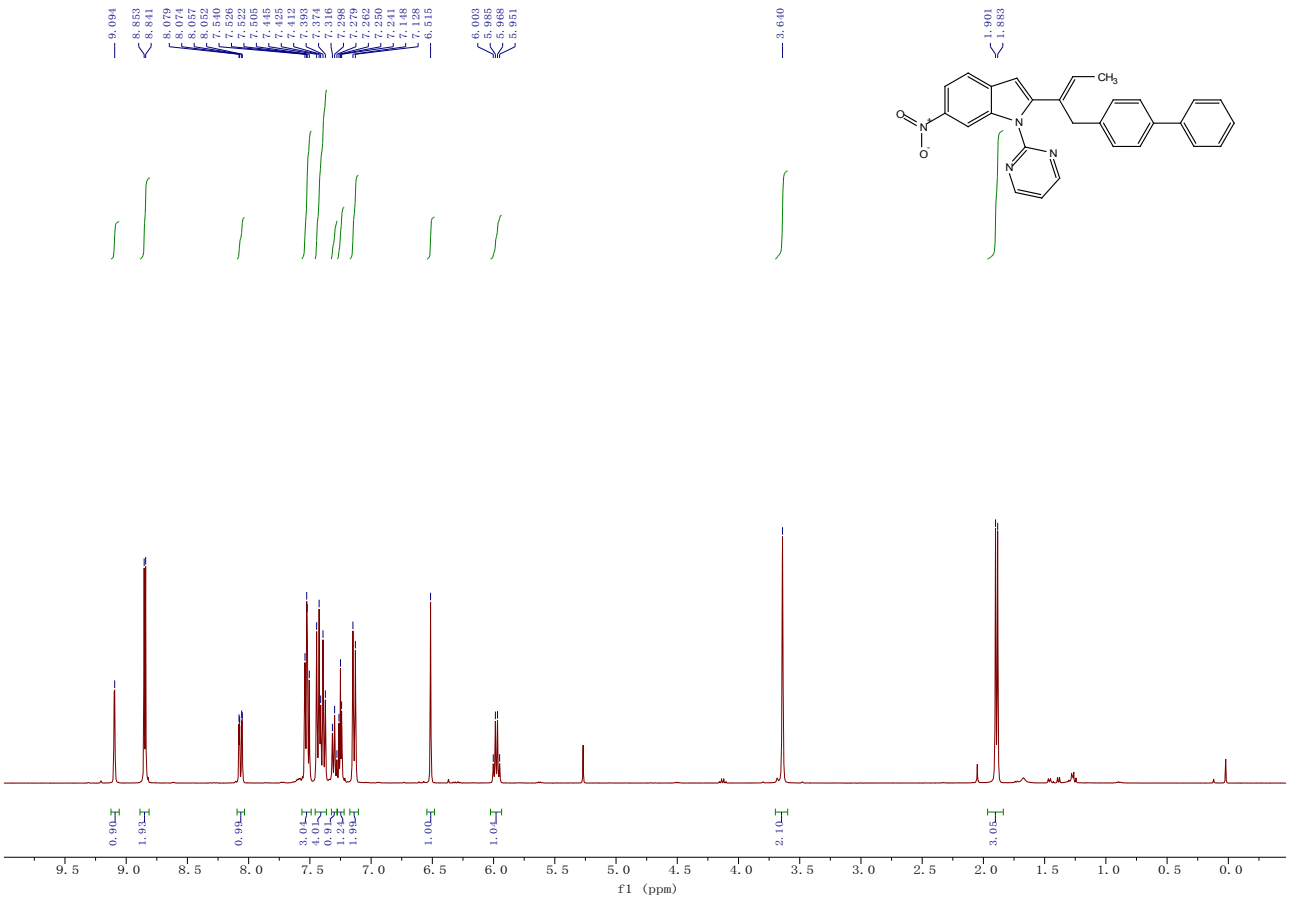
Compound 3ia: yellow oil (35.0 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.85 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 5.92 (q, *J* = 7.2 Hz, 1H), 6.37 (s, 1H), 7.05 – 7.14 (m, 2H), 7.17 (dd, *J* = 4.8 Hz, 1H), 7.24 – 7.33 (m, 1H), 7.34 – 7.49 (m, 4H), 7.49 – 7.55 (m, 2H), 7.61 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.5, 107.2, 115.0, 115.1, 117.6, 122.8, 125.8, 127.0, 127.02, 127.4, 128.7, 128.8, 131.0, 132.9, 136.0, 138.5, 138.8, 141.0, 144.1, 158.1, 158.3. IR (neat) ν 3026, 2925, 2844, 1569, 1486, 1465, 1449, 1345, 1337, 1257, 1147, 1110, 1057 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{23}BrN_3$ requires (M^++H): 480.1070, Found: 480.1063.

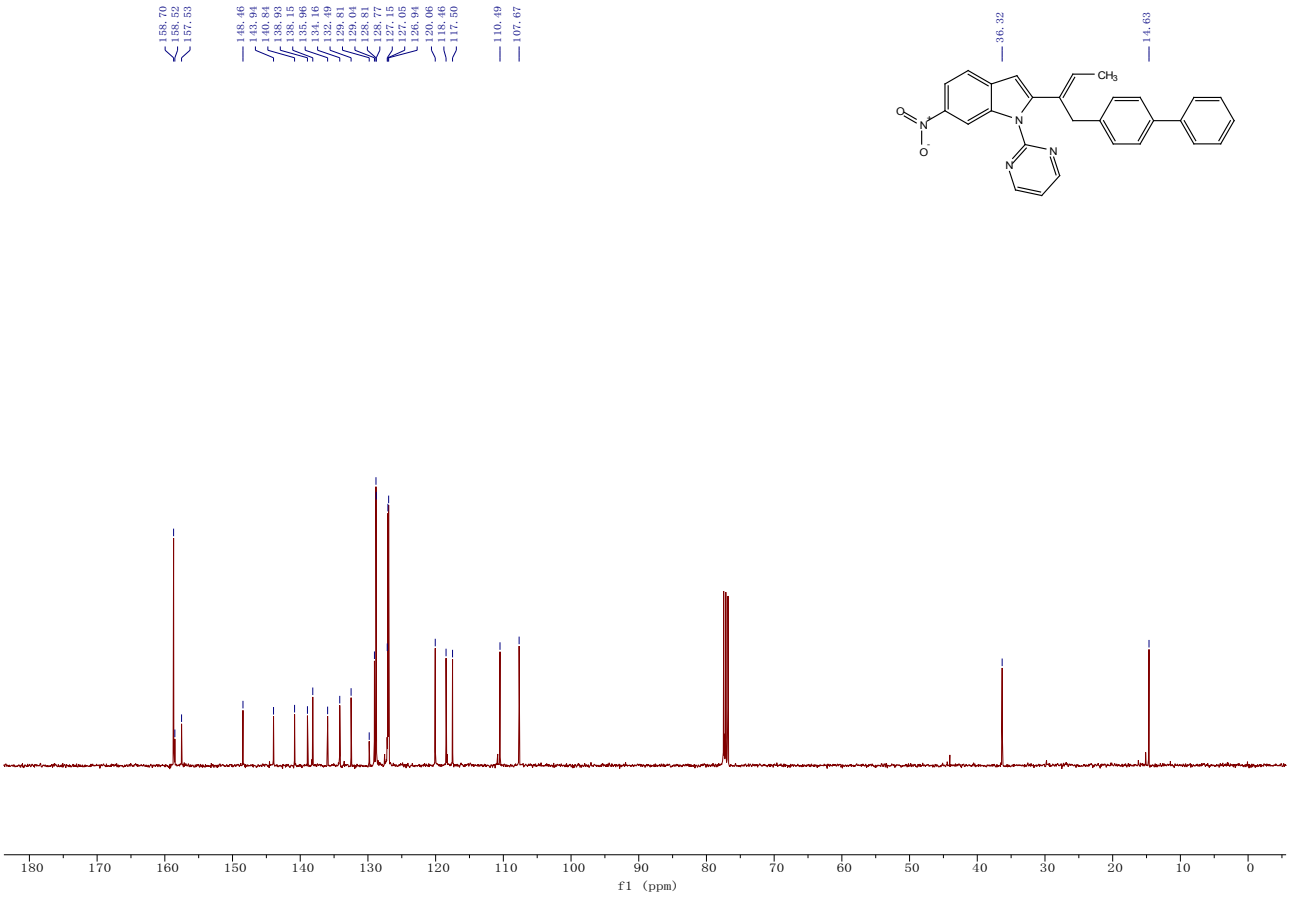

8.788
8.776
8.071
8.049
7.611
7.606
7.528
7.525
7.497
7.408
7.403
7.388
7.383
7.363
7.304
7.292
7.287
7.270
7.265
7.180
7.168
7.156
7.117
7.097
6.371
5.943
5.924
5.907
5.889
3.574
1.858
1.840
Br
CH3
N
N
N
1.92
1.03
1.26
2.06
4.08
2.00
1.06
2.05
1.00
1.11
2.08
3.00
f1 (ppm)

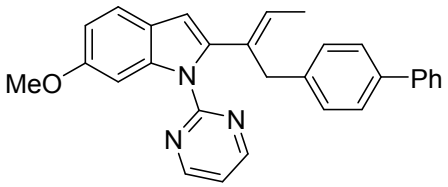

158.34
158.06
144.07
140.97
138.75
138.53
136.04
132.84
130.99
128.81
128.70
127.39
127.02
126.96
125.82
122.80
117.58
115.08
115.04
107.19
36.45
14.52
Br
CH3
N
N
N
f1 (ppm)



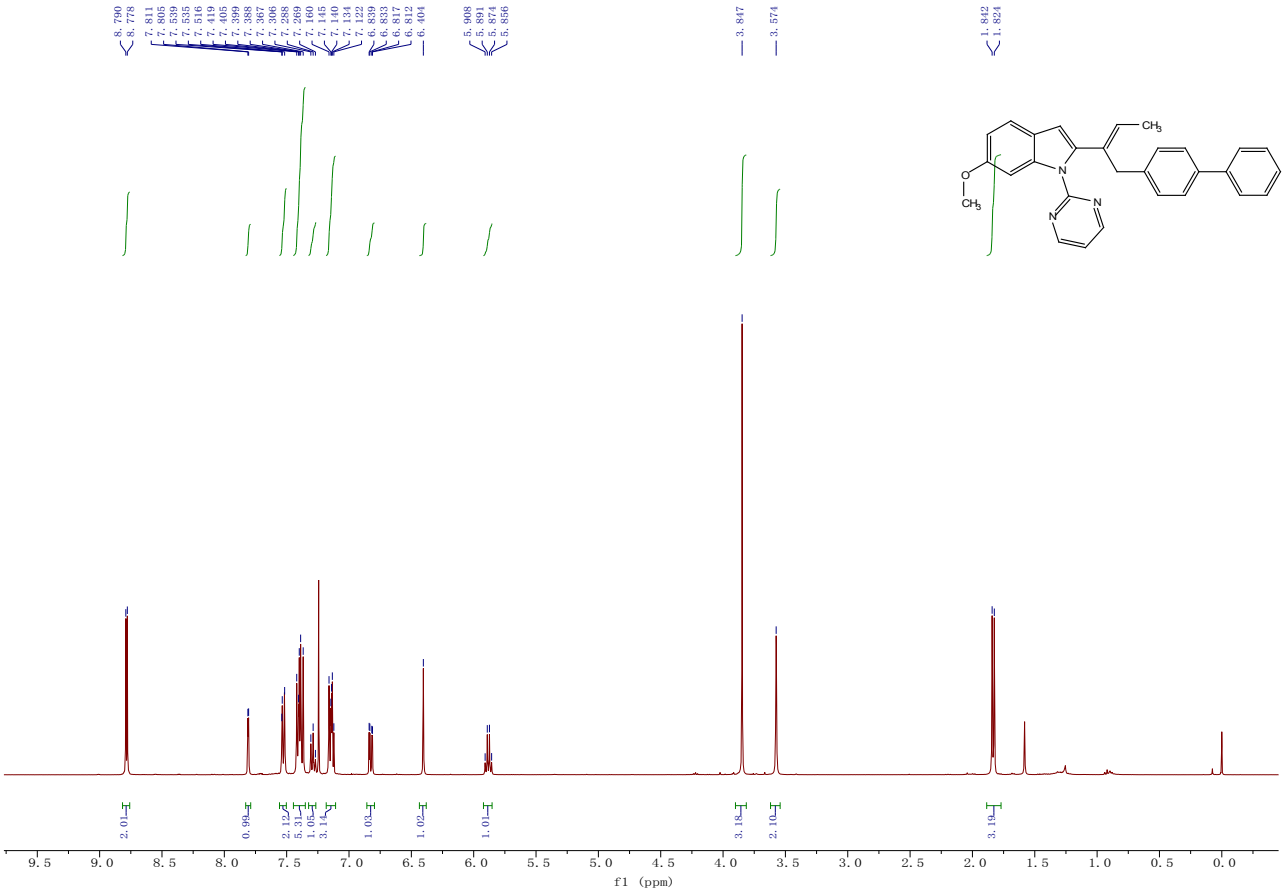
Compound 3ka: yellow oil (34.3 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.89 (d, *J* = 7.0 Hz, 3H), 3.64 (s, 2H), 5.98 (q, *J* = 6.9 Hz, 1H), 6.51 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 4.3 Hz, 1H), 7.30 (dd, *J* = 7.3 Hz, 1H), 7.37 – 7.46 (m, 4H), 7.49 – 7.57 (m, 3H), 8.07 (dd, *J* = 8.7, 2.0 Hz, 1H), 8.85 (d, *J* = 4.9 Hz, 2H), 9.09 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.6, 36.3, 107.7, 110.5, 117.5, 118.5, 120.1, 126.9, 127.1, 127.15, 128.77, 128.81, 129.0, 129.8, 132.5, 134.2, 136.0, 138.1, 138.9, 140.8, 143.9, 148.5, 157.5, 158.5, 158.7. IR (neat) ν 3057, 3016, 1763, 1693, 1654, 1593, 1572, 1489, 1444, 1419, 1348, 1276, 1211, 1075 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{23}N_4O_2$ requires (M^++H): 447.1816, Found: 447.1817.

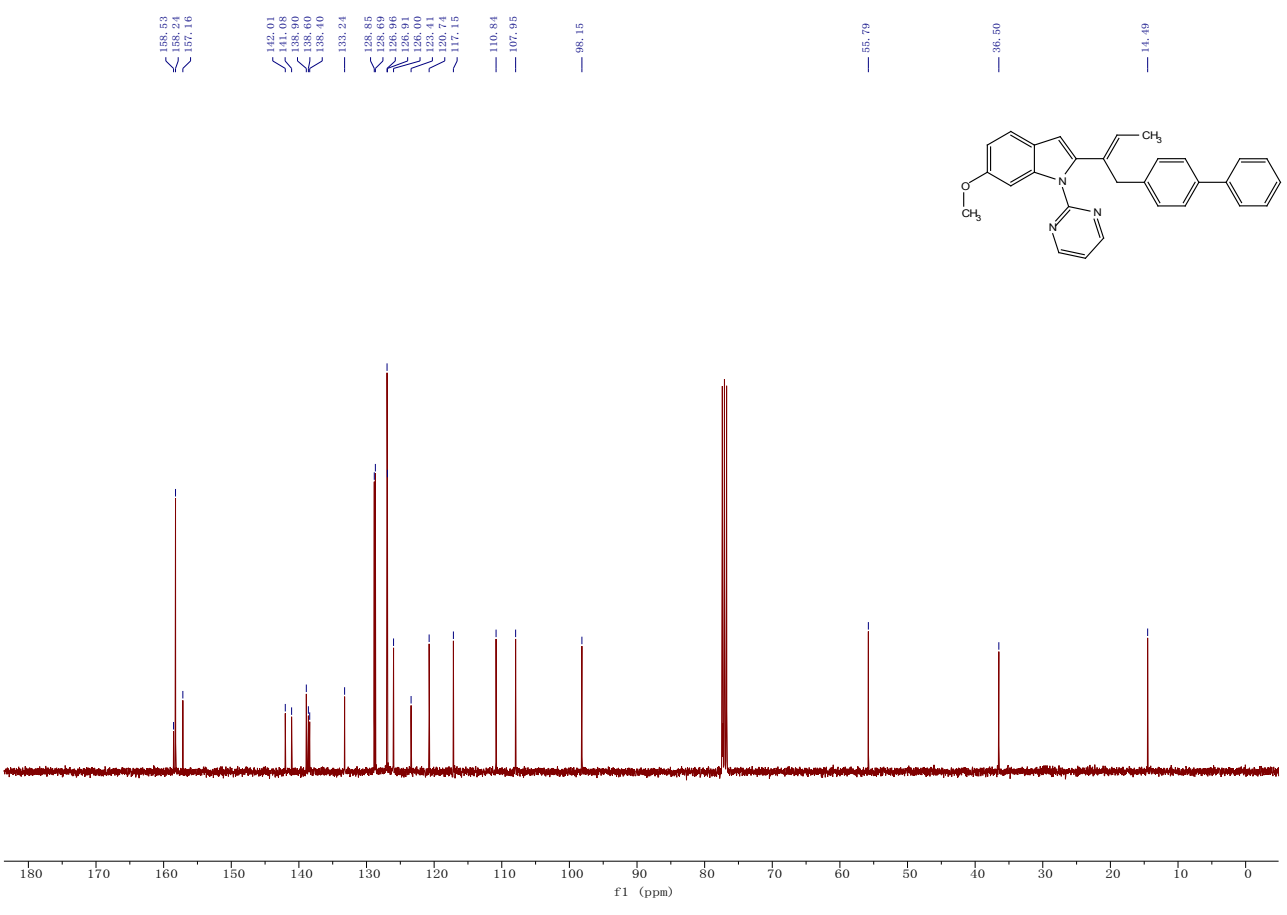


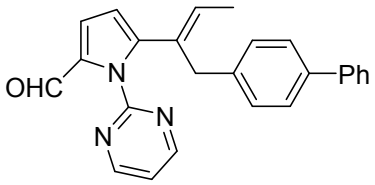




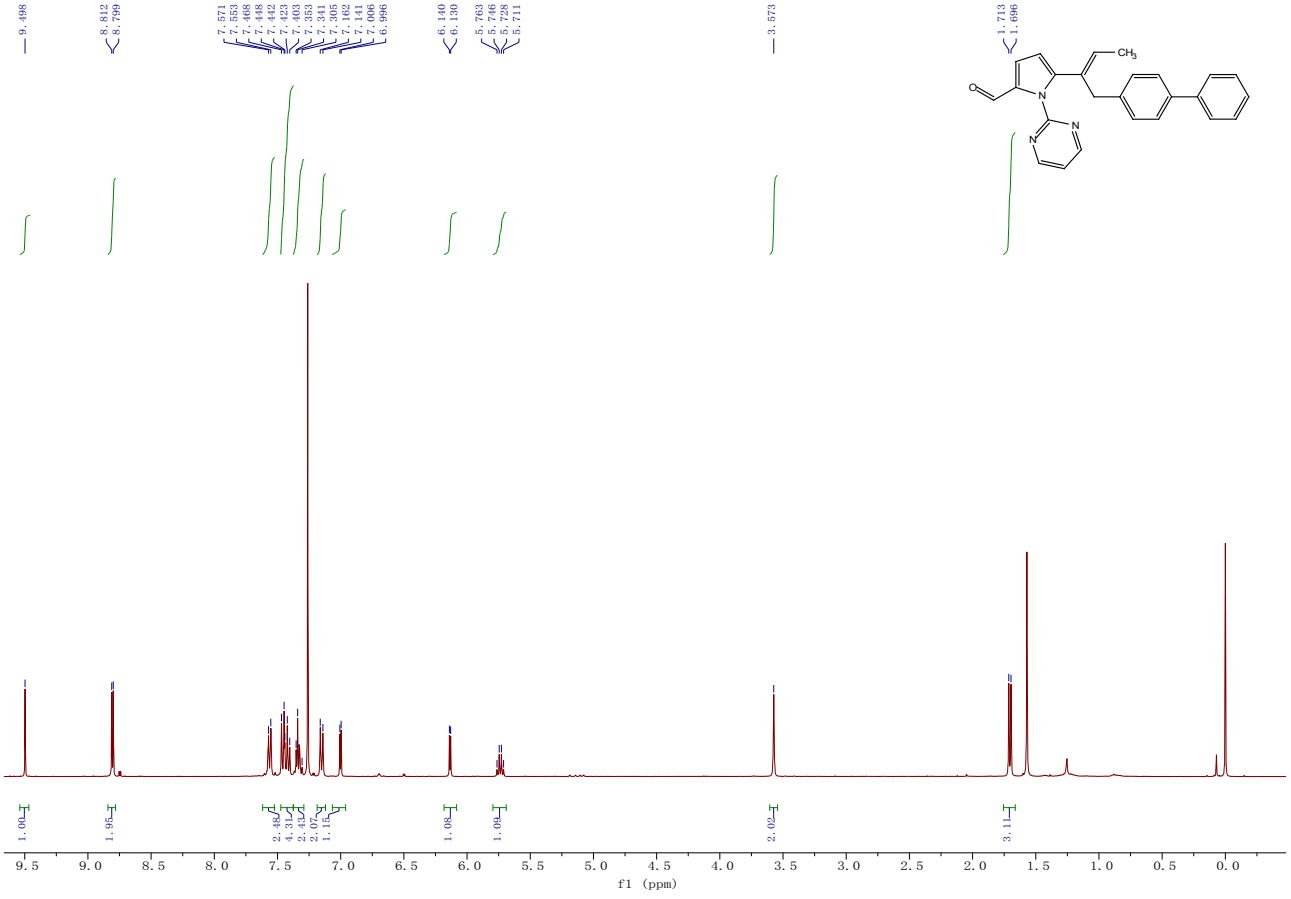
Compound 3la: yellow oil (29.7 mg, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.83 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 3.85 (s, 3H), 5.88 (q, *J* = 7.0 Hz, 1H), 6.40 (s, 1H), 6.83 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.10 – 7.18 (m, 3H), 7.29 (dd, *J* = 6.8 Hz, 1H), 7.35 – 7.45 (m, 5H), 7.49 – 7.56 (m, 2H), 7.81 (d, *J* = 2.3 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.5, 55.8, 98.1, 108.0, 110.8, 117.2, 120.7, 123.4, 126.0, 126.9, 127.0, 128.7, 128.9, 133.2, 138.4, 138.6, 138.9, 141.1, 142.0, 157.2, 158.2, 158.5. IR (neat) ν 2919, 2850, 1556, 1507, 1485, 1342, 1312, 1225, 1180, 1056, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{26}N_3O$ requires (M^++H): 432.2076, Found: 432.2070.

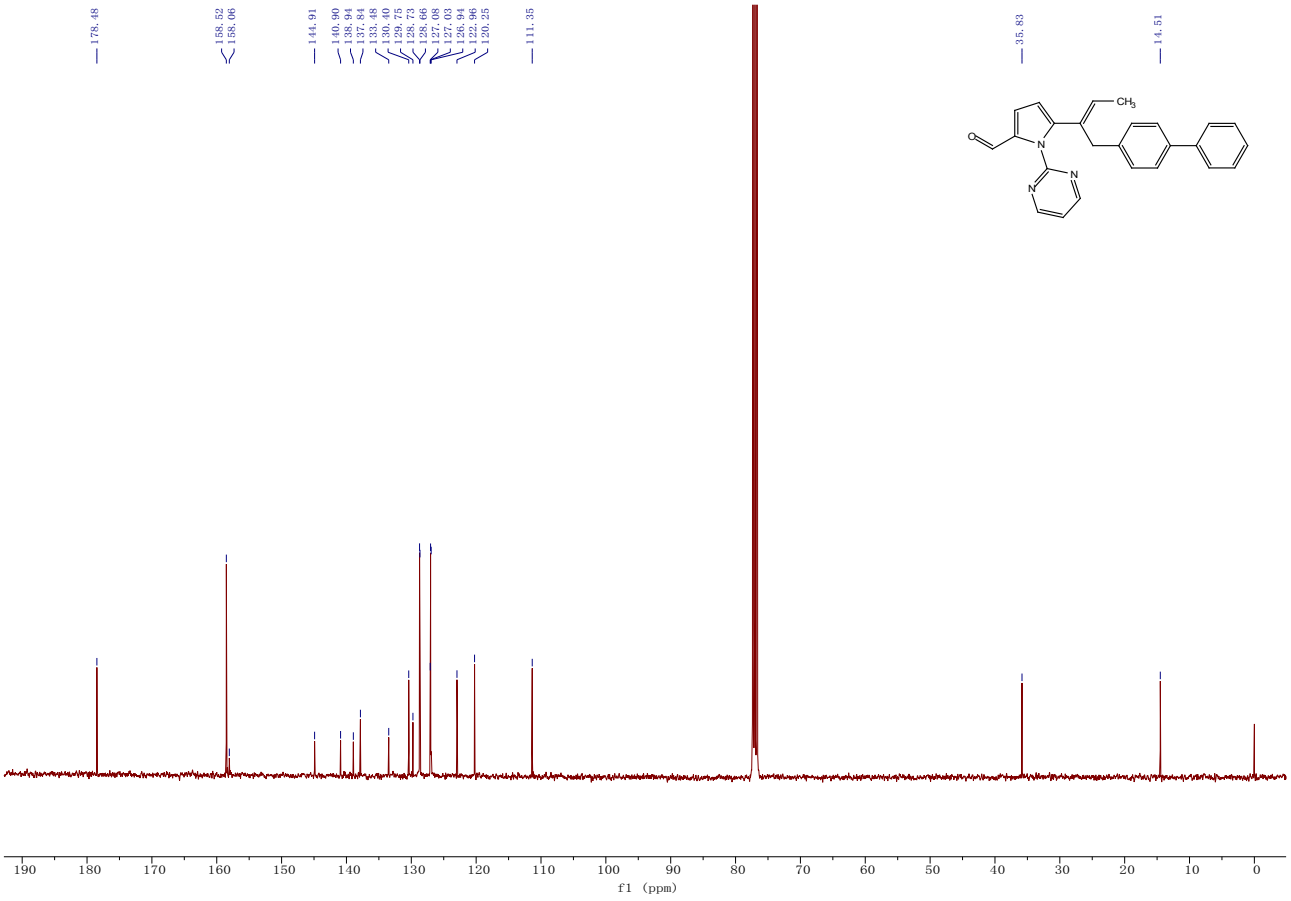

8.790
8.778
7.811
7.805
7.539
7.535
7.516
7.419
7.405
7.399
7.388
7.367
7.306
7.298
7.289
7.160
7.145
7.140
7.134
7.122
6.839
6.833
6.817
6.812
6.404
5.908
5.893
5.874
5.856
3.847
3.574
1.842
1.824
CH3
O
CH3
N
N
N
2.01
0.99
2.12
2.31
1.05
3.14
1.03
1.02
1.01
3.18
2.10
3.19
f1 (ppm)

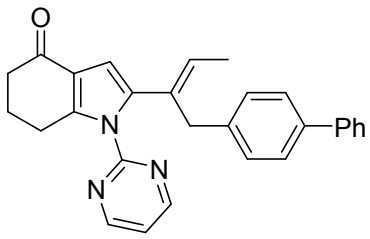

158.53
158.24
157.16
142.01
141.08
138.90
138.60
138.40
133.24
128.85
128.69
126.96
126.91
126.00
123.41
120.74
117.15
110.84
107.95
98.15
55.79
36.50
14.49
CH3
O
CH3
N
N
N
f1 (ppm)



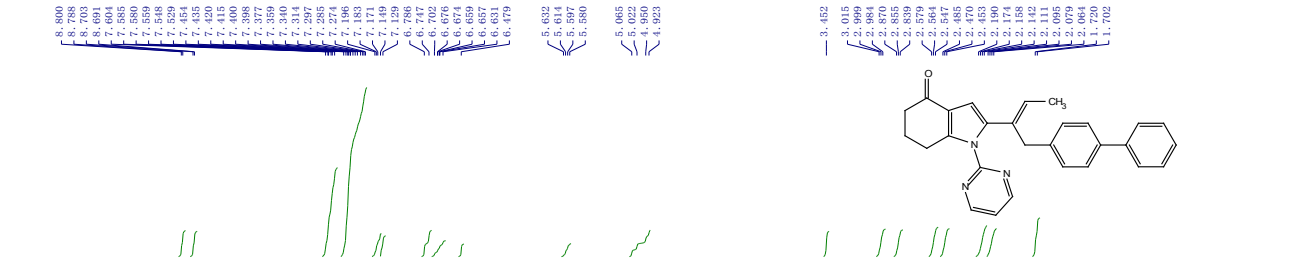
Compound 3ma: yellow oil (16.3 mg, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.70 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 5.74 (q, *J* = 7.0 Hz, 1H), 6.13 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.37 (m, 2H), 7.37 – 7.47 (m, 4H), 7.56 (d, *J* = 7.2 Hz, 2H), 8.81 (d, *J* = 4.8 Hz, 2H), 9.50 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 35.8, 111.4, 120.2, 123.0, 126.9, 127.0, 127.1, 128.66, 128.73, 129.7, 130.4, 133.5, 137.8, 138.9, 140.9, 144.9, 158.1, 158.5, 178.5. IR (neat) ν 3047, 2912, 2846, 1682, 1559, 1486, 1342, 1312, 1225, 1180, 1059, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{22}N_3O$ requires (M^++H): 380.1757, Found: 380.1764.







Compound 3na: yellow oil (15.9 mg, 38%). ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.71 (d, *J* = 6.9 Hz, 3H), 2.09 (q, *J* = 6.3 Hz, 2H), 2.17 (q, *J* = 6.3 Hz, 2H), 2.47 (t, *J* = 6.4 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.2 Hz, 2H), 3.00 (t, *J* = 6.2 Hz, 2H), 3.45 (s, 2H), 4.91 – 5.08 (m, 2H), 5.61 (q, *J* = 6.9 Hz, 1H), 6.48 (s, 1H), 6.61 – 6.72 (m, 1H), 6.77 (d, *J* = 15.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.22 (m, 2H), 7.26 – 7.48 (m, 13H), 7.51 – 7.63 (m, 7H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.79 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 35.8, 111.4, 120.2, 123.0, 126.9, 127.0, 127.1, 128.66, 128.73, 129.7, 130.4, 133.5, 137.8, 138.9, 140.9, 144.9, 158.1, 158.5, 178.5. IR (neat) ν 3063, 3021, 1693, 1593, 1573, 1486, 1342, 1312, 1276, 1225, 1150, 1069, 1018 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_3O$ requires (M^++H): 419.1998, Found: 419.1995.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7.559
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7.528
7.454
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7.415
7.400
7.398
7.377
7.359
7.340
7.314
7.297
7.285
7.274
7.196
7.183
7.171
7.149
7.129
6.786
6.747
6.702
6.676
6.674
6.659
6.657
6.643
6.479
5.632
5.614
5.597
5.580
5.065
5.022
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4.923
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3.015
2.999
2.984
2.870
2.855
2.839
2.579
2.564
2.547
2.485
2.470
2.453
2.190
2.174
2.158
2.142
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2.095
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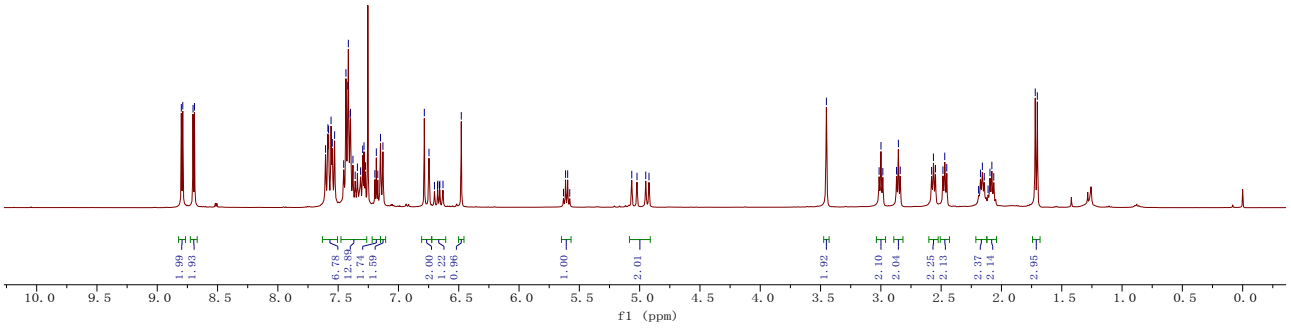
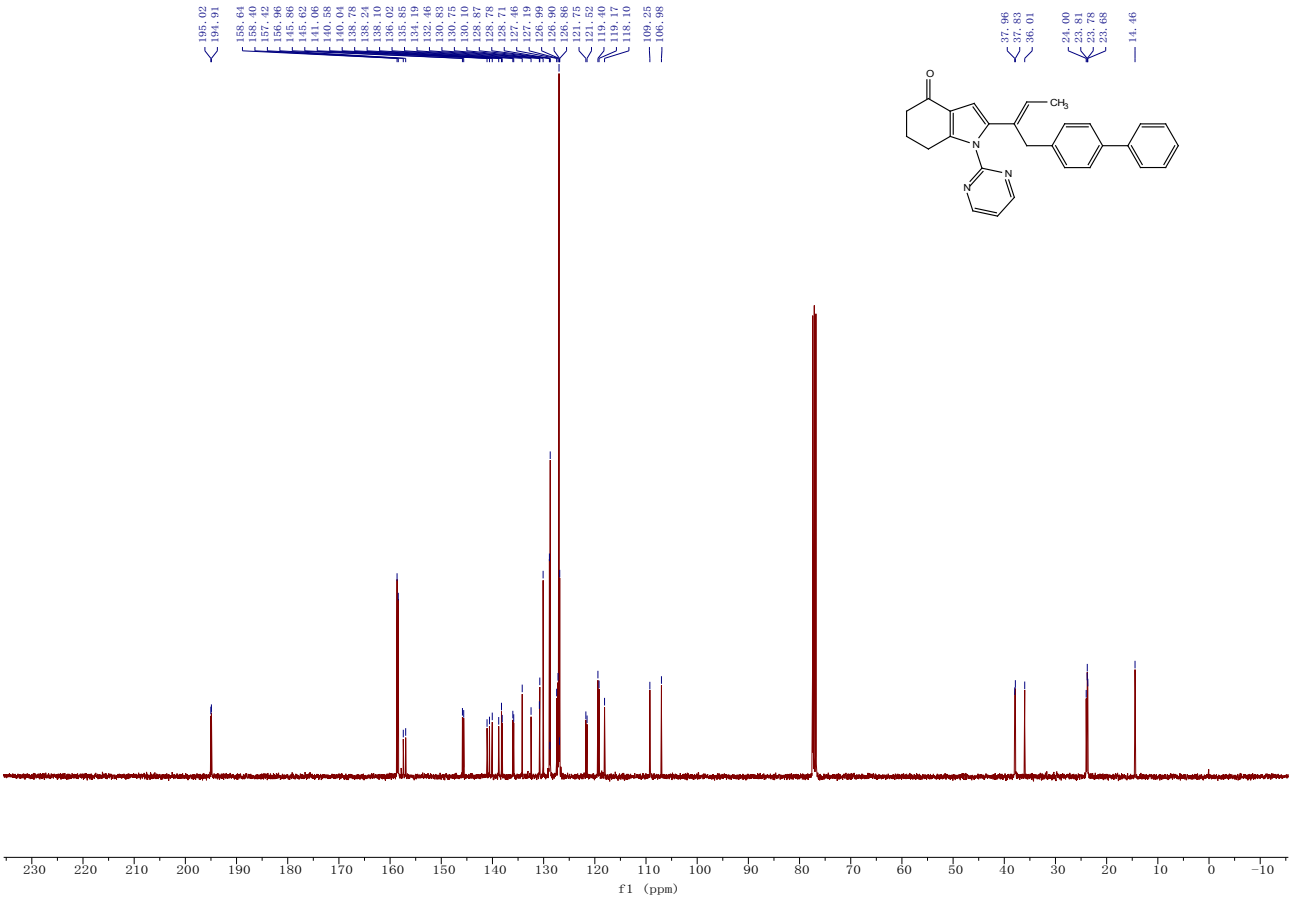
2.063
2.046
1.720
1.702
O
CH3
N
N
N


1.99
1.93
6.78
12.89
1.74
1.59
2.00
1.22
0.96
1.00
2.01
1.92
2.10
2.04
2.25
2.13
2.37
2.14
2.95
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
0.0
f1 (ppm)


195.02
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158.40
157.42
156.96
145.86
145.62
141.06
140.58
140.04
138.78
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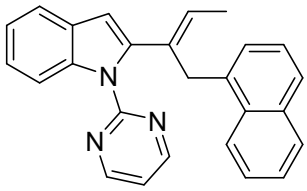
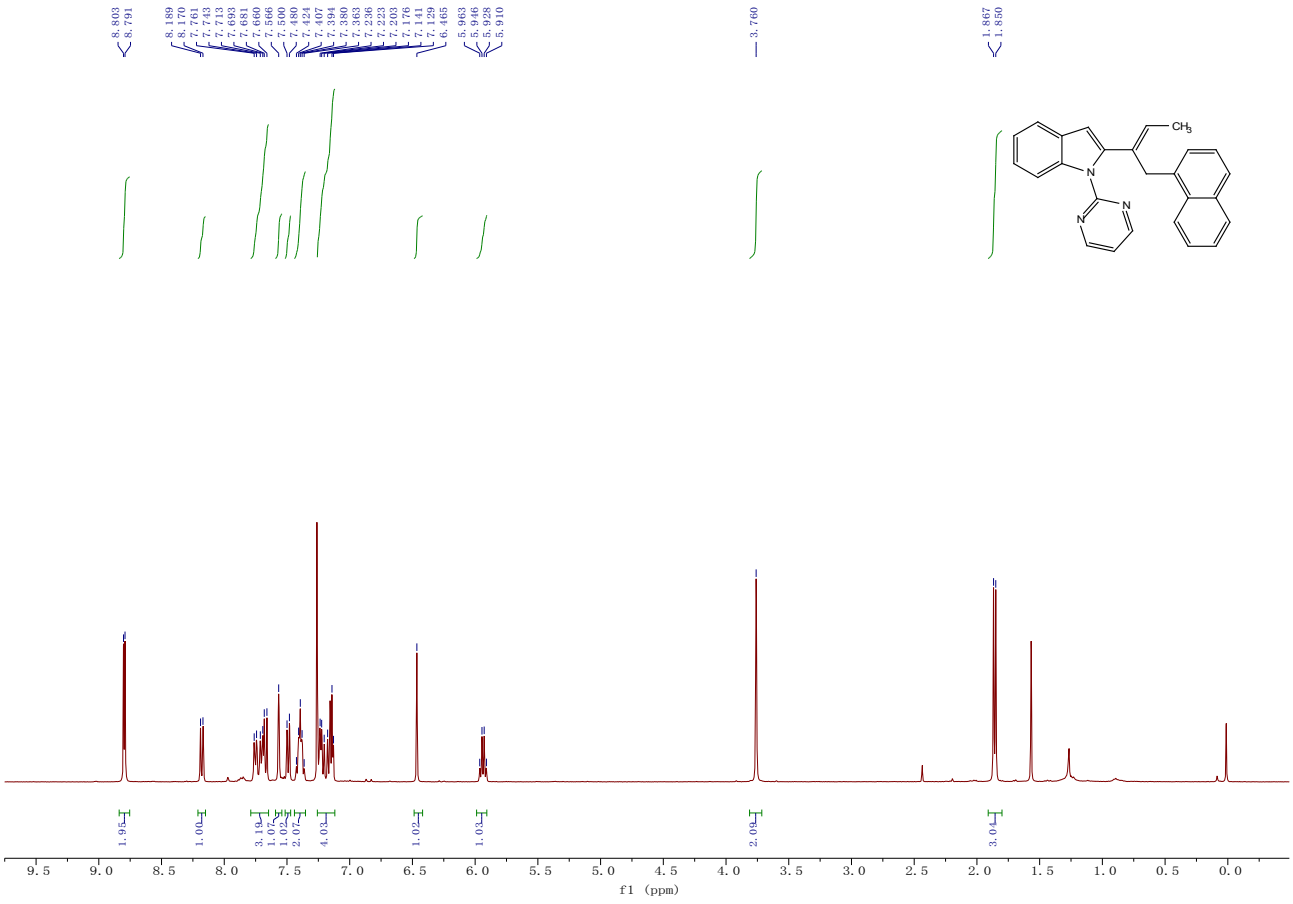
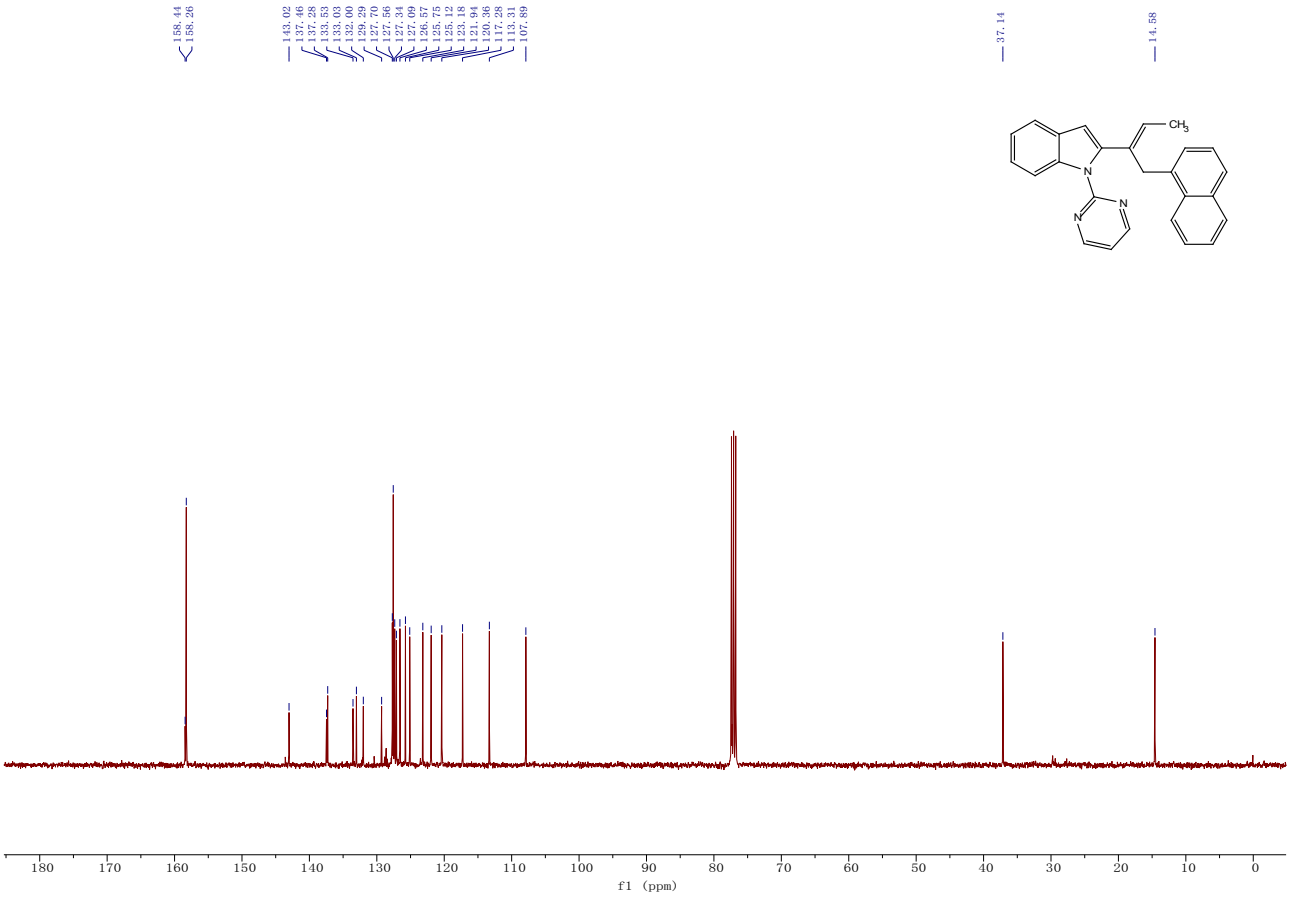
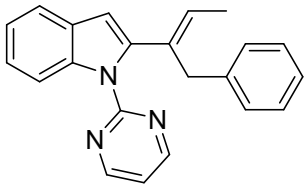
138.10
136.02
135.85
134.19
132.46
132.03
130.75
130.10
128.87
128.78
128.71
127.46
127.19
126.99
126.90
126.86
121.75
121.52
119.40
119.17
118.10
109.25
106.98
37.96
37.83
36.01
24.00
23.81
23.78
23.68
14.46
O
CH3
N
N
N
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



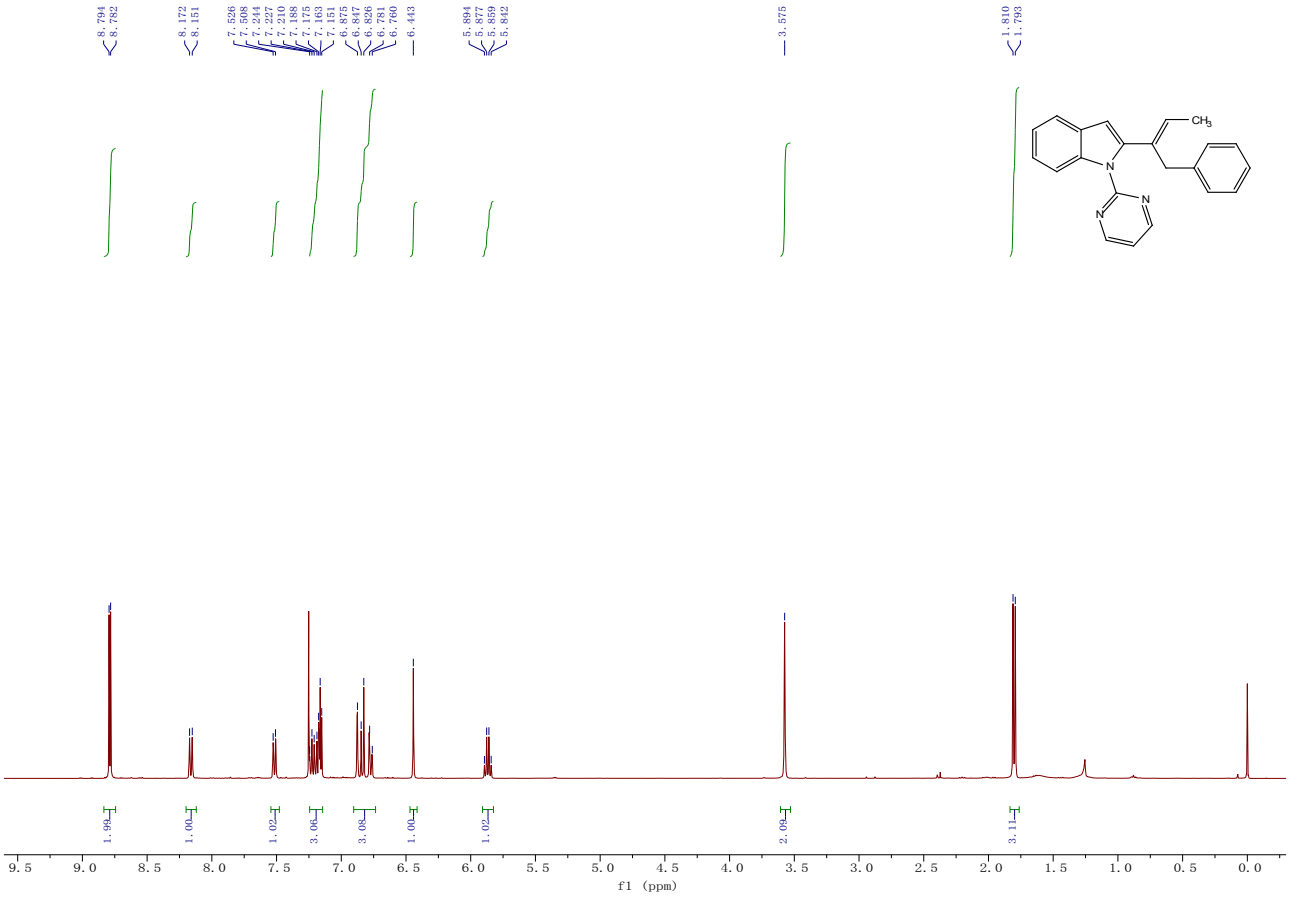
Compound 3ab: yellow oil (33.4 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.86 (d, *J* = 7.0 Hz, 3H), 3.76 (s, 2H), 5.94 (q, *J* = 7.1 Hz, 1H), 6.46 (s, 1H), 7.11 – 7.26 (m, 4H), 7.34 – 7.45 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.64 – 7.79 (m, 3H), 8.18 (d, *J* = 7.7 Hz, 1H), 8.80 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 23.7, 23.8, 23.8, 24.0, 36.0, 37.8, 107.0, 109.2, 118.1, 119.2, 119.4, 121.5, 121.8, 126.9, 127.0, 127.2, 127.5, 128.7, 128.9, 130.1, 130.8, 130.8, 132.5, 134.2, 135.8, 136.0, 138.1, 138.2, 138.8, 140.0, 140.6, 141.1, 145.6, 145.9, 157.0, 157.4, 158.4, 158.6, 194.9, 195.0. IR (neat) ν 3042, 2917, 2852, 1561, 1486, 1342, 1312, 1225, 1180, 1059, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{22}N_3$ requires (M^++H): 376.1808, Found: 376.1823.

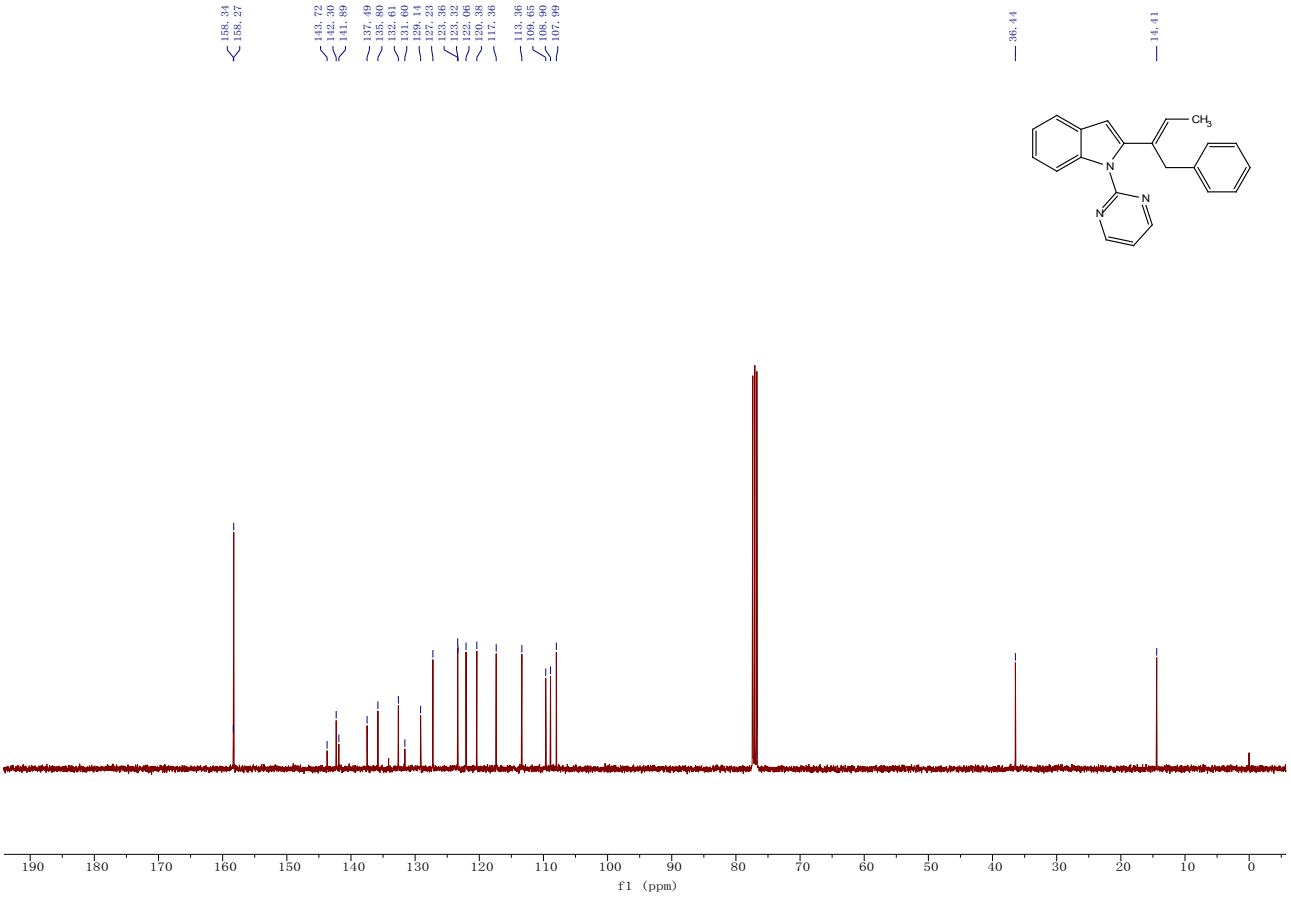


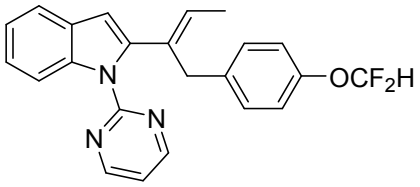




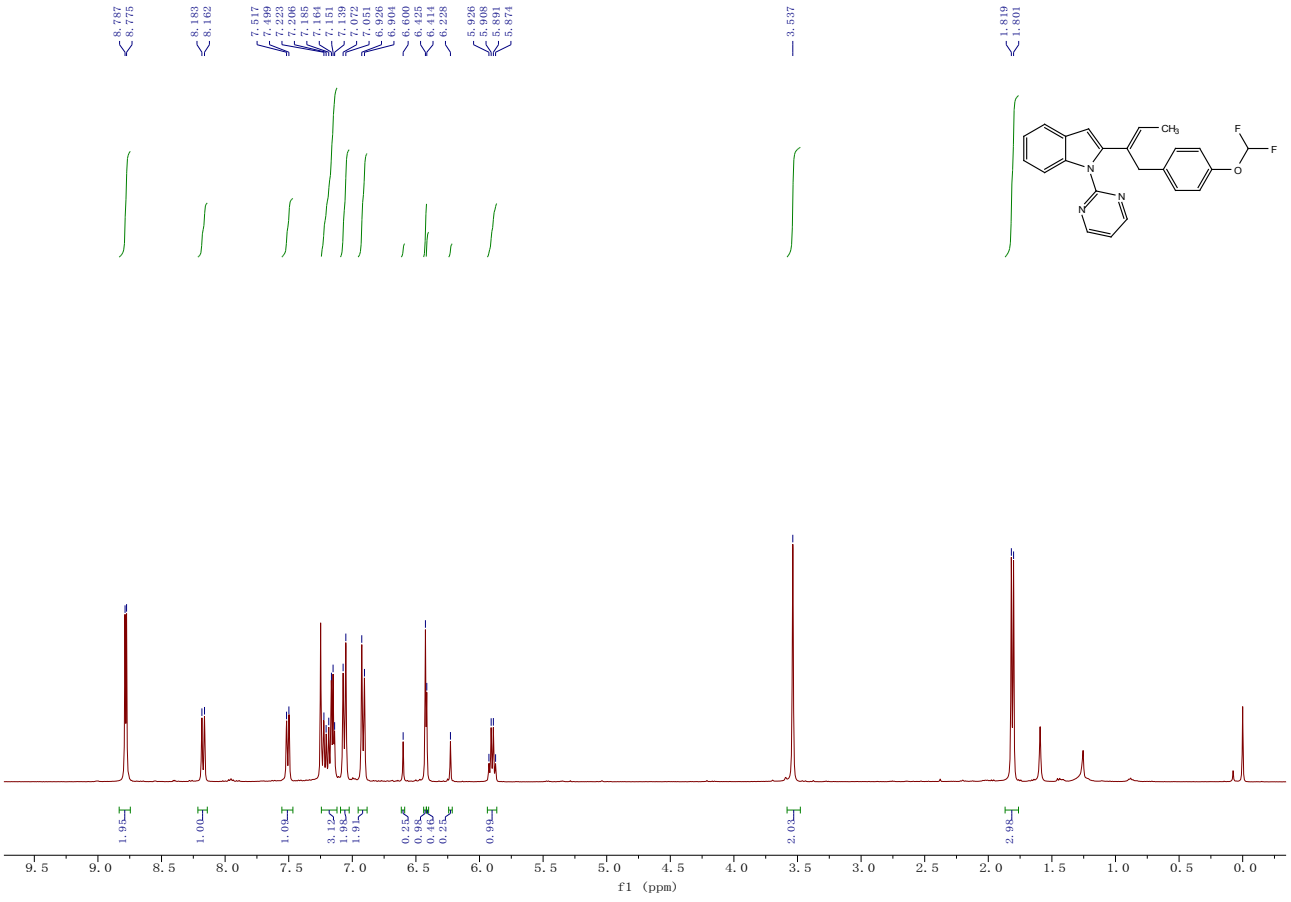
Compound 3ac: yellow oil (28.0 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.80 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 5.87 (q, *J* = 7.0 Hz, 1H), 6.44 (s, 1H), 6.74 – 6.90 (m, 3H), 7.14 – 7.24 (m, 3H), 7.52 (d, *J* = 7.3 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.4, 36.4, 108.0, 108.9, 109.6, 113.4, 117.4, 120.4, 122.1, 123.3, 123.4, 127.2, 129.1, 131.6, 132.6, 135.8, 137.5, 141.9, 142.3, 143.7, 158.27, 158.34. IR (neat) ν 3039, 2917, 2846, 1561, 1507, 1451, 1420, 1380, 1348, 1320, 1225, 1180, 1120, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{20}N_3$ requires (M^++H): 326.1652, Found: 326.1652.

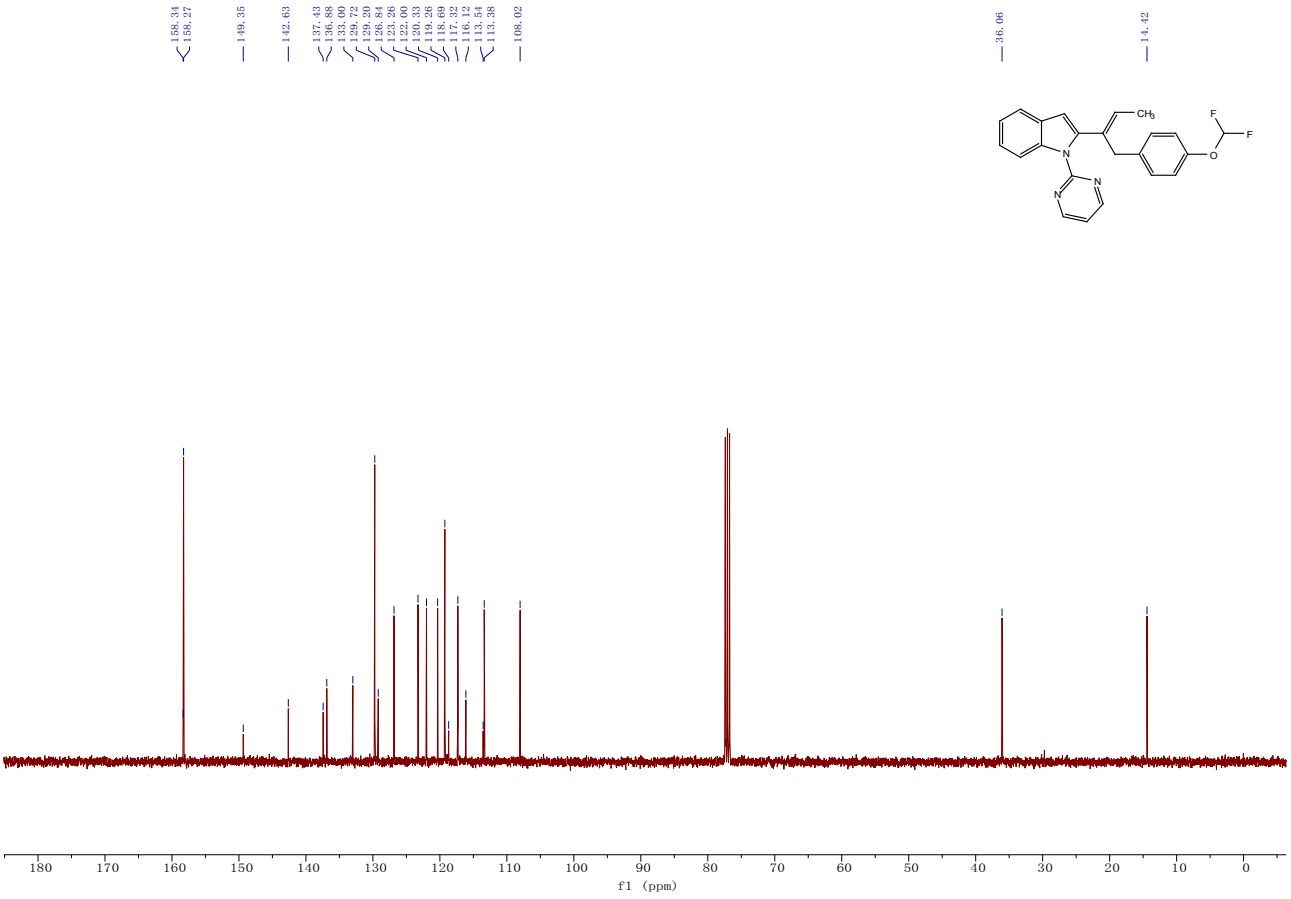

8.794
8.782
8.172
8.151
7.526
7.508
7.244
7.227
7.210
7.188
7.175
7.163
7.151
6.875
6.847
6.808
6.781
6.760
6.443
5.894
5.877
5.859
5.842
3.575
1.810
1.793
CH3
N
N
N
1.99
1.00
1.02
3.06
3.08
1.00
1.02
2.09
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

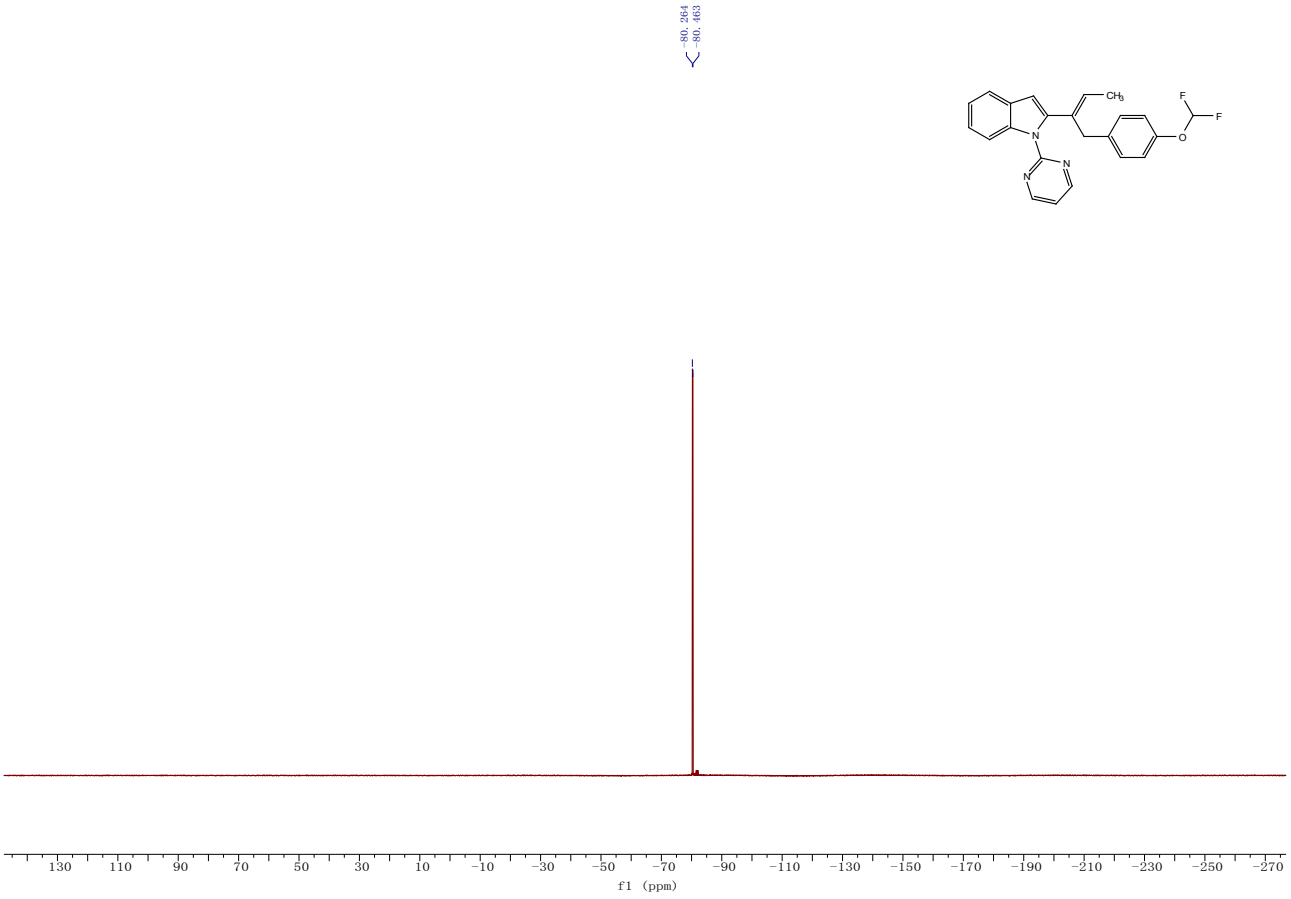

158.34
158.27
143.72
142.30
141.89
137.49
135.80
132.61
131.60
129.14
127.23
123.36
123.32
122.06
120.38
117.36
113.36
109.65
108.90
107.99
36.44
14.41
CH3
N
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

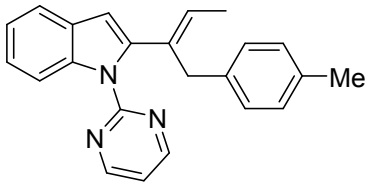


Compound 3ad: yellow oil (37.1 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.82 (d, *J* = 6.9 Hz, 3H), 3.55 (s, 2H), 5.91 (q, *J* = 7.0 Hz, 1H), 6.427 (t, *J* = 74.4 Hz, 1H), 6.438 (s, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.13 – 7.25 (m, 3H), 7.26 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 8.79 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.4, 36.1, 108.0, 113.4, 116.1 (t, *J* = 257 Hz), 117.3, 119.3, 120.3, 122.0, 123.3, 126.8, 129.2, 129.7, 133.0, 136.9, 137.4, 142.6, 149.3, 158.27, 158.34. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.4, -80.2. IR (neat) ν 3039, 2912, 2846, 1561, 1507, 1452, 1425, 1384, 1352, 1307, 1255, 1182, 1120, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{20}F_2N_3O$ requires (M^++H): 392.1569, Found: 392.1575.

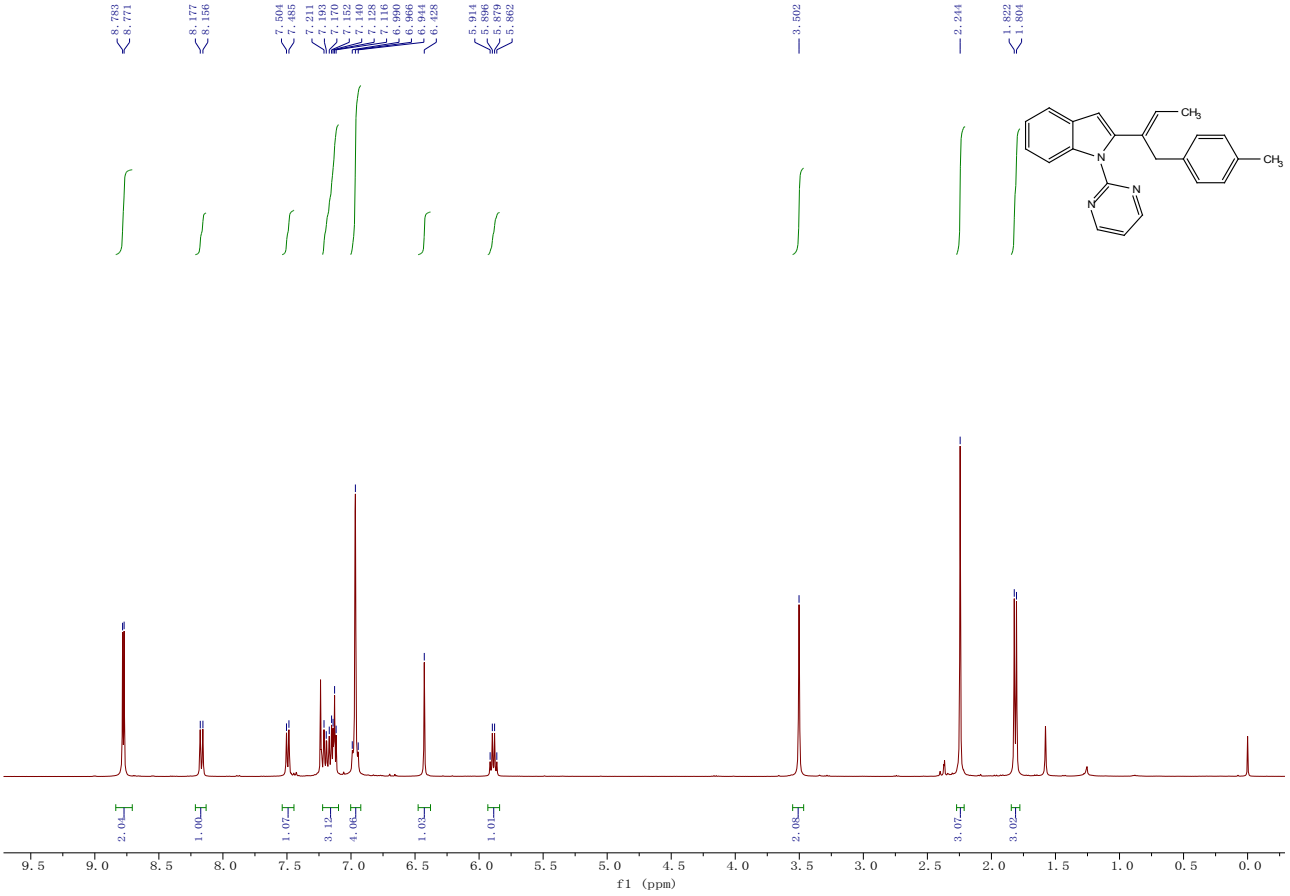


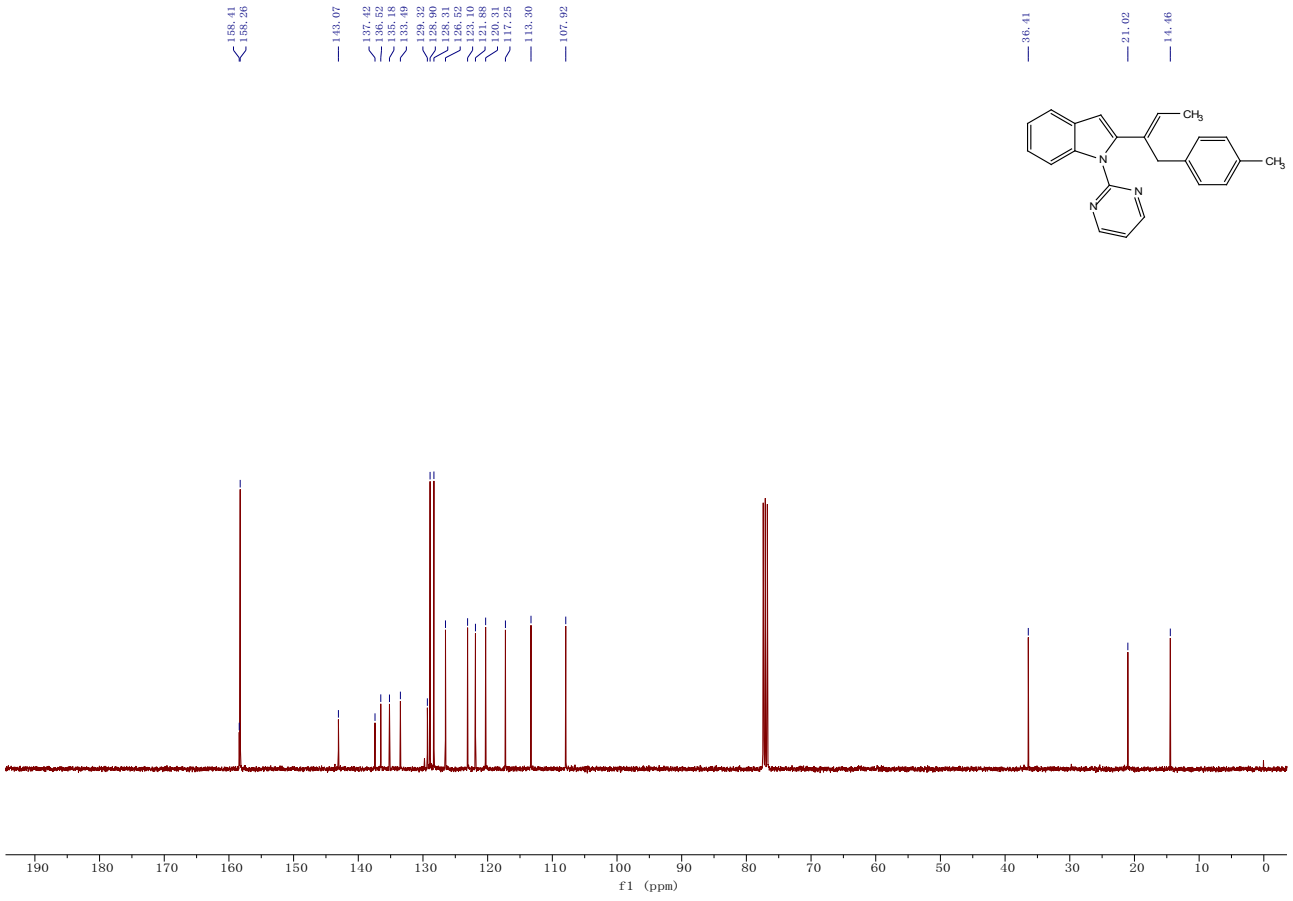

158.34
158.27
149.35
142.63
137.43
136.88
133.00
129.72
129.20
126.84
123.26
122.00
120.33
119.26
118.69
117.32
116.12
113.54
113.38
108.02
36.06
14.42
CH3
F
F
O
N
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

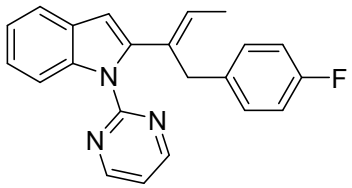

-80.264
-80.463
CH3
F
F
O
N
N
N
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)



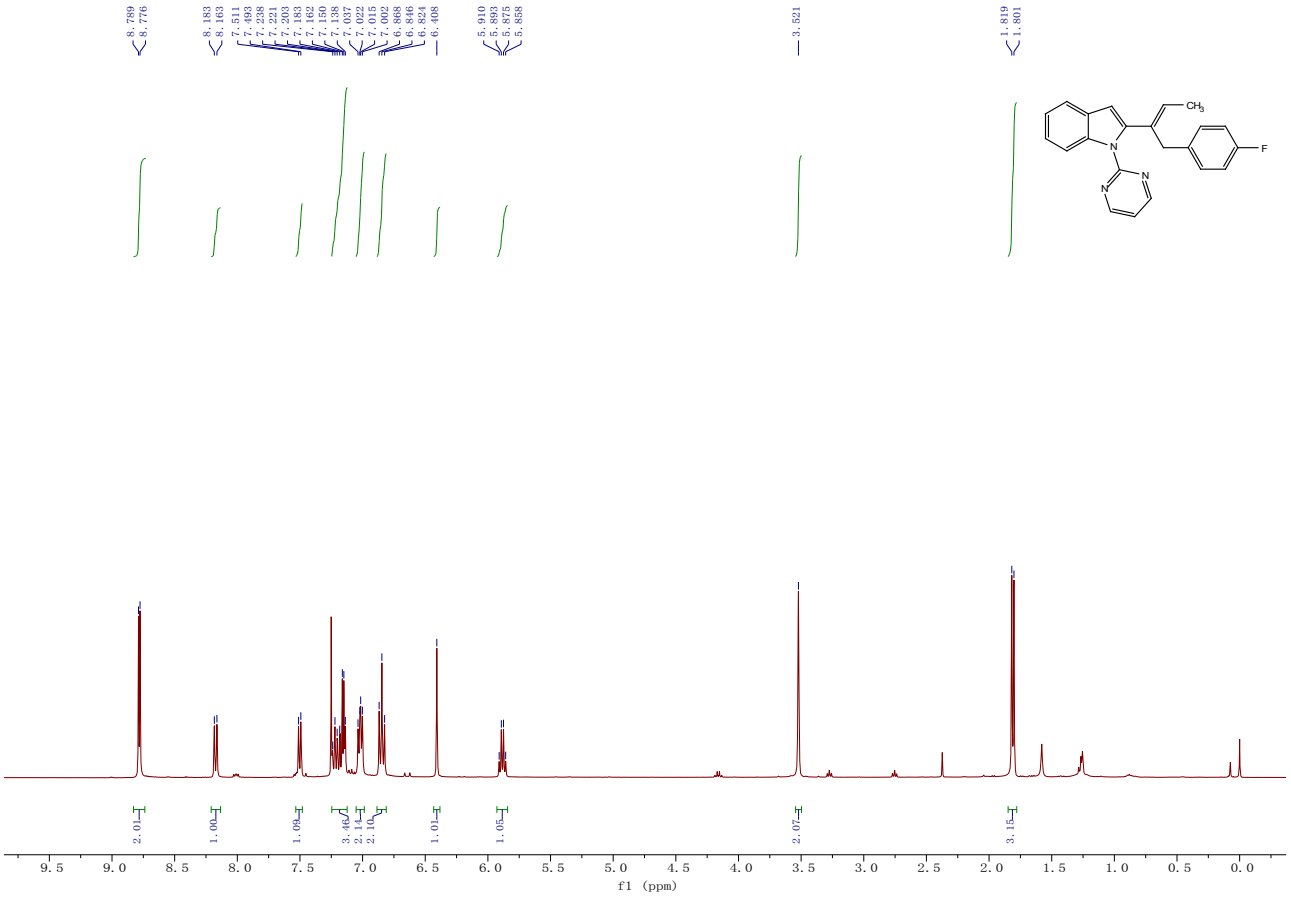
Compound 3ae: yellow oil (26.4 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.81 (d, *J* = 7.0 Hz, 3H), 2.24 (s, 3H), 3.50 (s, 2H), 5.89 (q, *J* = 7.0 Hz, 1H), 6.43 (s, 1H), 6.97 (s, 4H), 7.10 – 7.22 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 21.0, 36.4, 107.9, 113.3, 117.3, 120.3, 121.9, 123.1, 126.5, 128.3, 128.9, 129.3, 133.5, 135.2, 136.5, 137.4, 143.1, 158.3, 158.4. IR (neat) ν 3034, 2923, 2845, 1561, 1508, 1450, 1421, 1375, 1345, 1318, 1213, 1178, 1120, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{22}N_3$ requires (M^++H): 340.1808, Found: 340.1808.

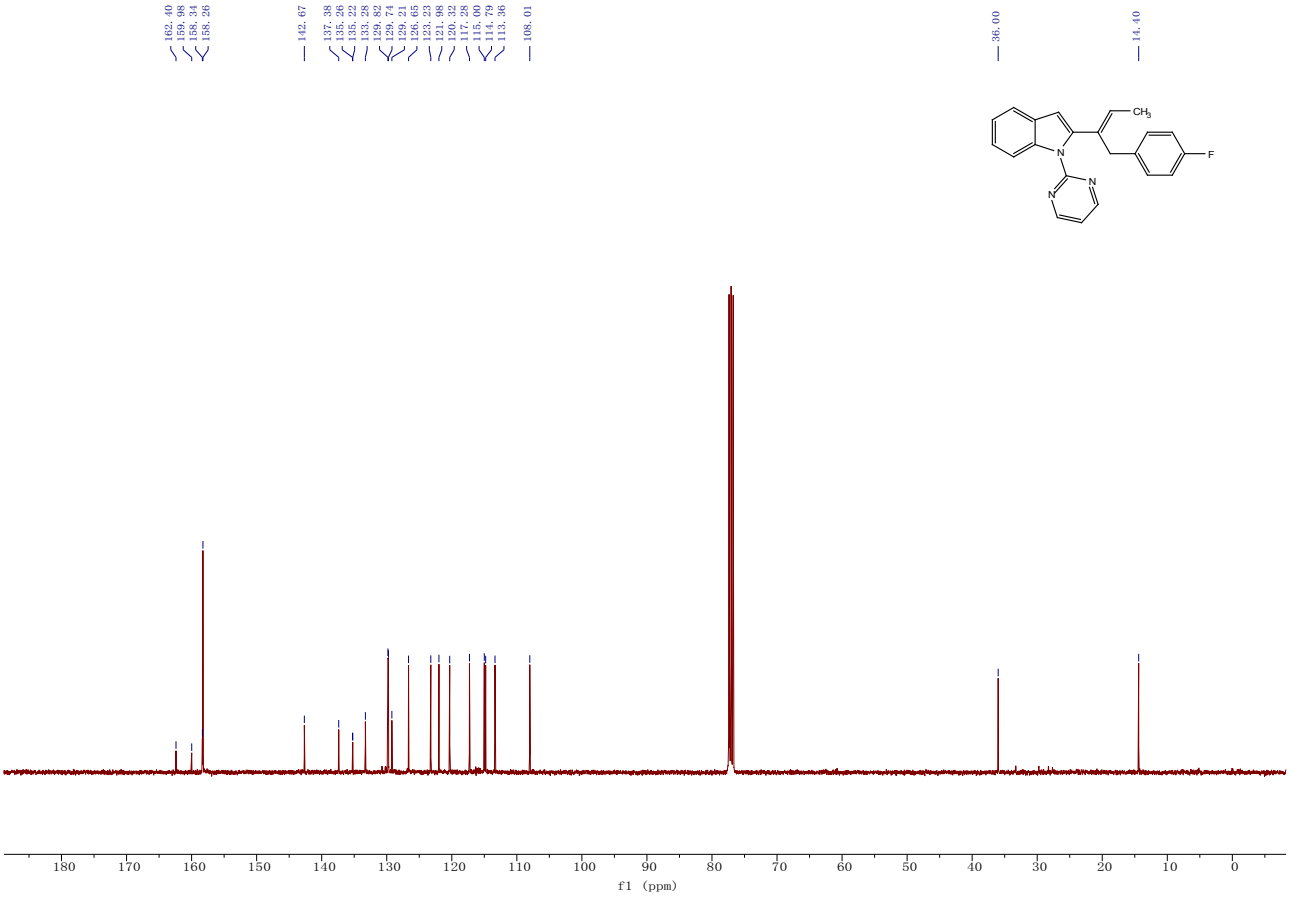


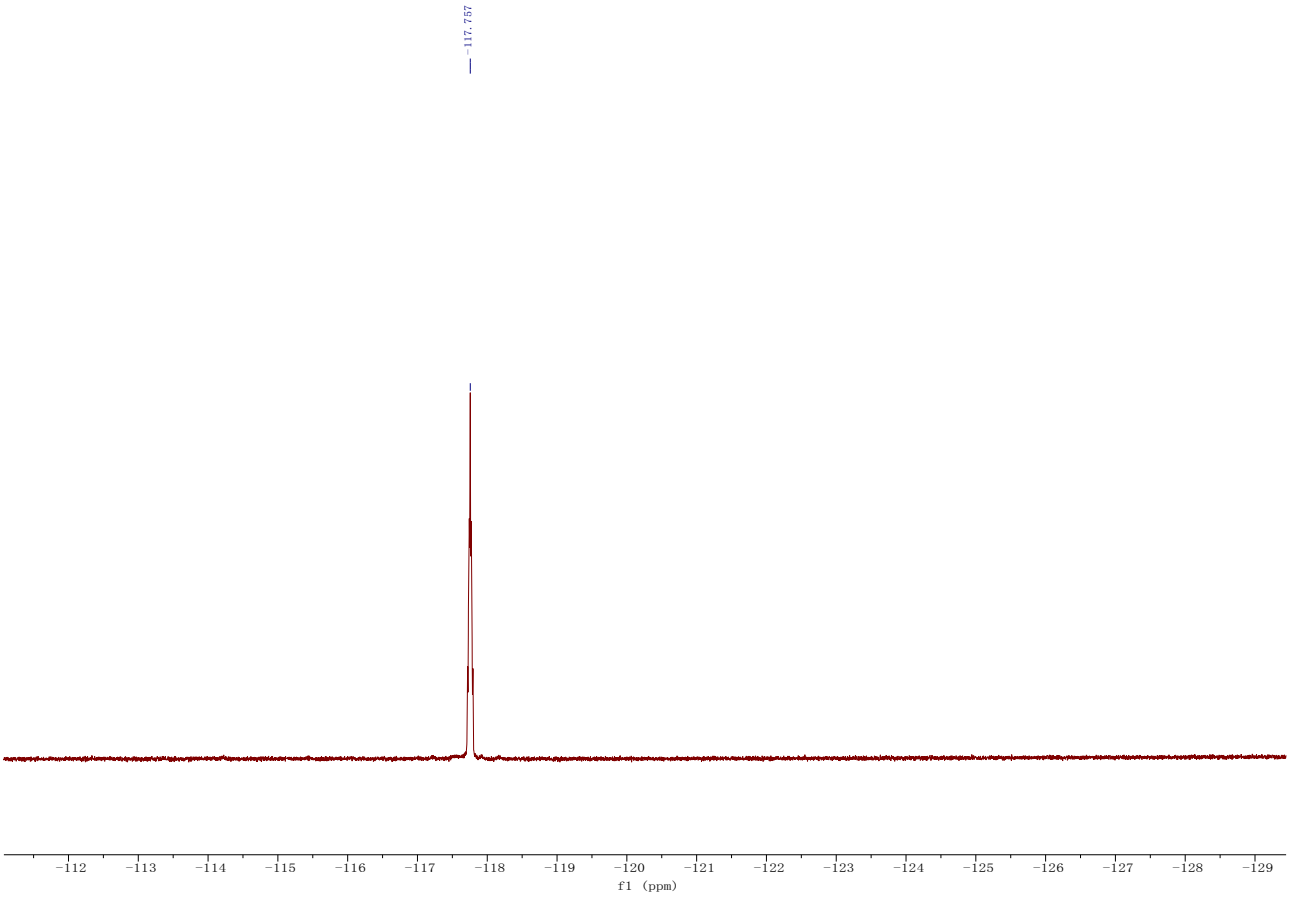


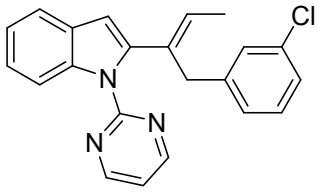


Compound 3af: yellow oil (27.1 mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.81 (d, *J* = 7.0 Hz, 3H), 3.52 (s, 2H), 5.88 (q, *J* = 6.9 Hz, 1H), 6.41 (s, 1H), 6.85 (dd, *J* = 8.7 Hz, 2H), 6.99 – 7.05 (m, 2H), 7.12 – 7.25 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.4, 36.0, 108.0, 113.4, 114.8, 115.0, 117.3, 120.3, 122.0, 123.2, 126.6, 129.2, 129.8 (d, *J* = 7.7 Hz), 133.3, 135.3 (d, *J* = 4.0 Hz), 137.4, 142.7, 158.26, 158.34, 161.2 (d, *J* = 243.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.8. IR (neat) ν 2920, 2846, 1580, 1560, 1495, 1449, 1379, 1348, 1317, 1225, 1156, 1064, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{19}FN_3$ requires (M^++H): 344.1558, Found: 344.1562.

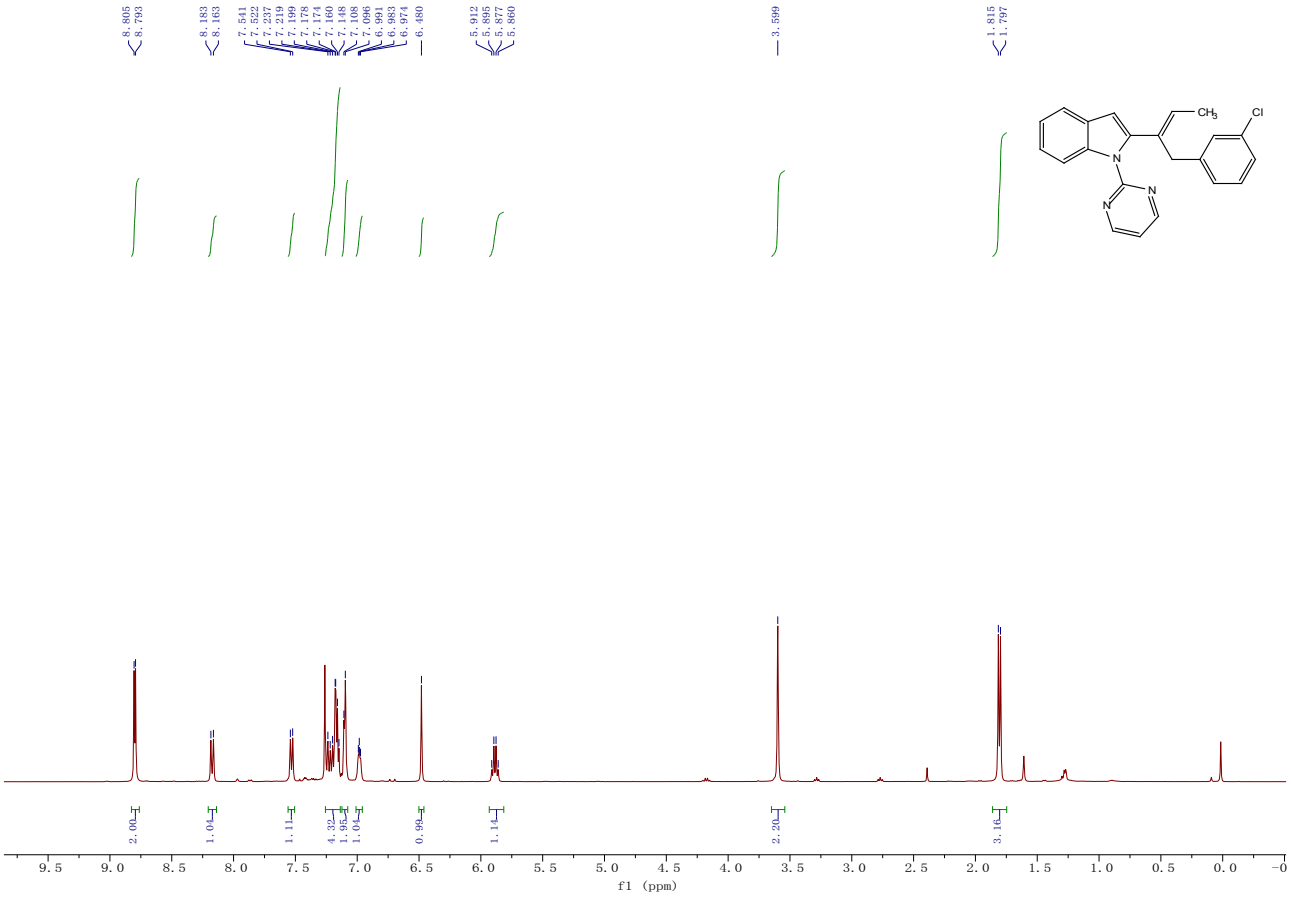

8.789
8.776
8.183
8.163
7.511
7.493
7.238
7.221
7.203
7.183
7.162
7.150
7.138
7.037
7.022
7.015
7.002
6.898
6.846
6.824
6.408
5.910
5.893
5.875
5.858
3.521
1.819
1.801
CH3
F
N
N
N
2.01
1.00
1.09
3.46
2.14
2.10
1.01
1.05
2.07
3.15
f1 (ppm)

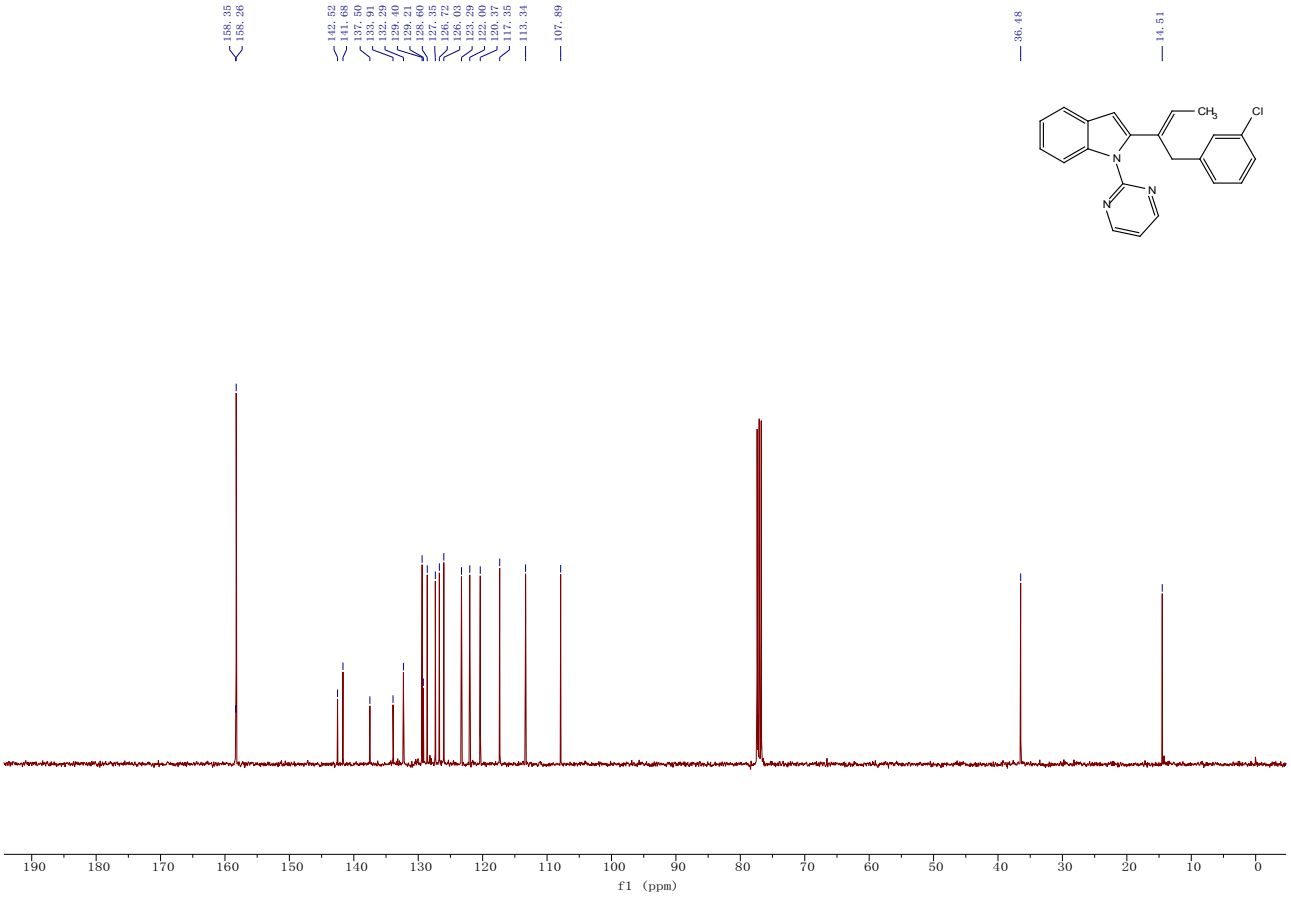

162.40
159.98
158.34
158.26
142.67
137.38
135.36
135.22
133.28
129.82
129.74
129.21
126.65
123.23
121.98
120.32
117.28
115.00
114.79
113.36
108.01
36.00
14.40
CH3
F
N
N
N
f1 (ppm)

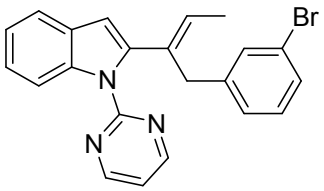




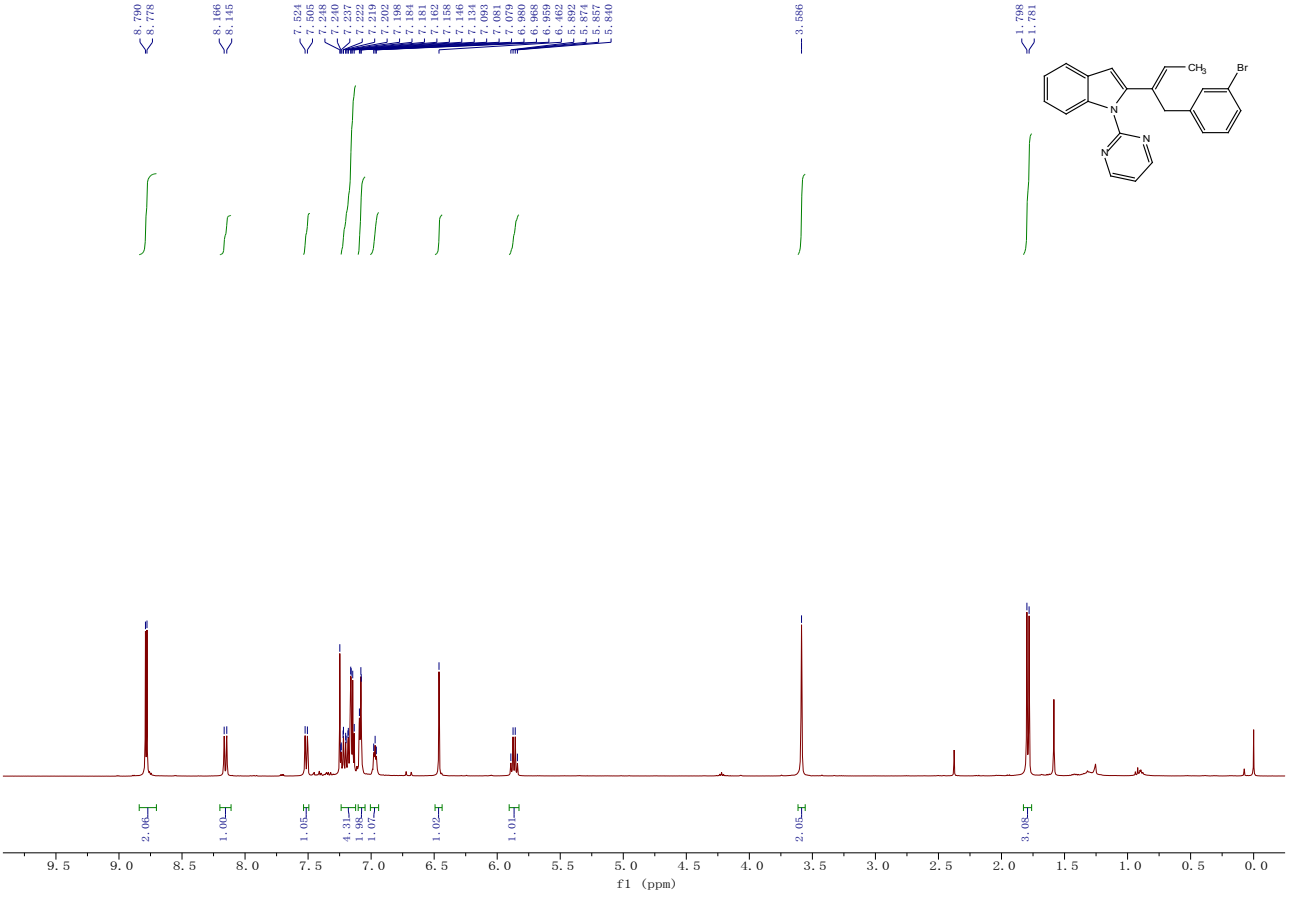
Compound 3ah: yellow oil (30.9 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.81 (d, *J* = 6.9 Hz, 3H), 3.60 (s, 2H), 5.89 (q, *J* = 6.9 Hz, 1H), 6.48 (s, 1H), 6.96 – 7.01 (m, 1H), 7.08 – 7.12 (m, 2H), 7.14 – 7.26 (m, 4H), 7.53 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.80 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.5, 107.9, 113.3, 117.4, 120.4, 122.0, 123.3, 126.0, 126.7, 127.3, 128.6, 129.2, 129.4, 132.3, 133.9, 137.5, 141.7, 142.5, 158.3, 158.4. IR (neat) ν 3035, 2918, 2849, 1570, 1559, 1507, 1486, 1420, 1380, 1348, 1320, 1256, 1184, 1058, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{19}ClN_3$ requires (M^++H): 360.1262, Found: 360.1279.

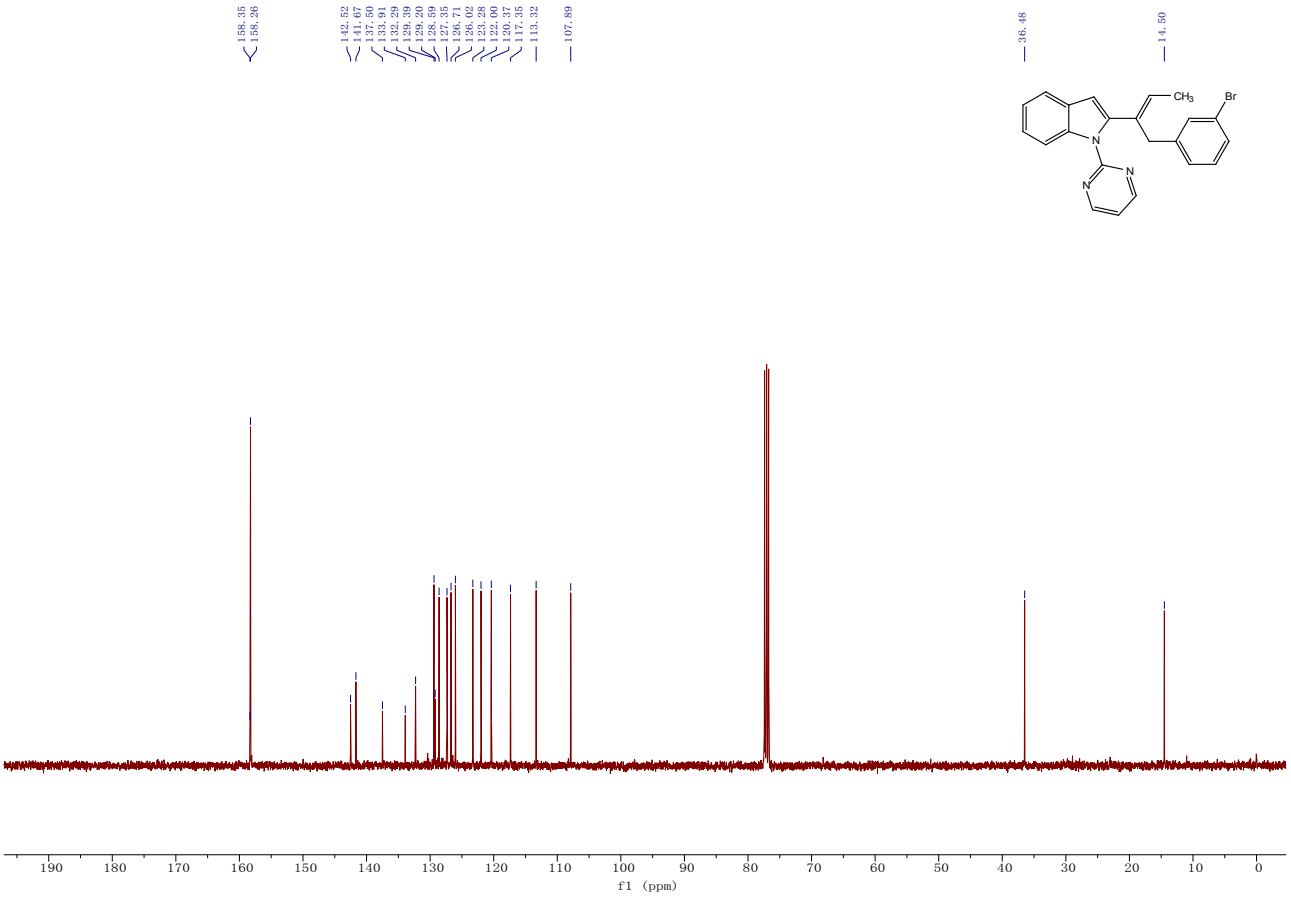

8.805
8.793
8.183
8.163
7.541
7.522
7.237
7.219
7.199
7.178
7.174
7.160
7.148
7.108
7.096
6.991
6.983
6.974
6.480
5.912
5.895
5.877
5.860
3.599
1.815
1.797
CH3
Cl
N
N
N
2.00
1.04
1.11
4.32
1.95
1.04
0.99
1.14
2.20
3.16
f1 (ppm)

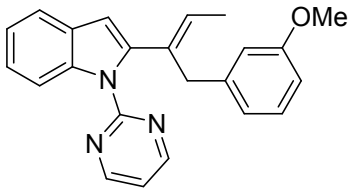

158.35
158.26
142.52
141.68
137.50
133.91
132.29
132.40
129.21
128.60
127.35
126.72
126.03
123.29
122.00
120.37
117.35
113.34
107.89
36.48
14.51
CH3
Cl
N
N
N
f1 (ppm)



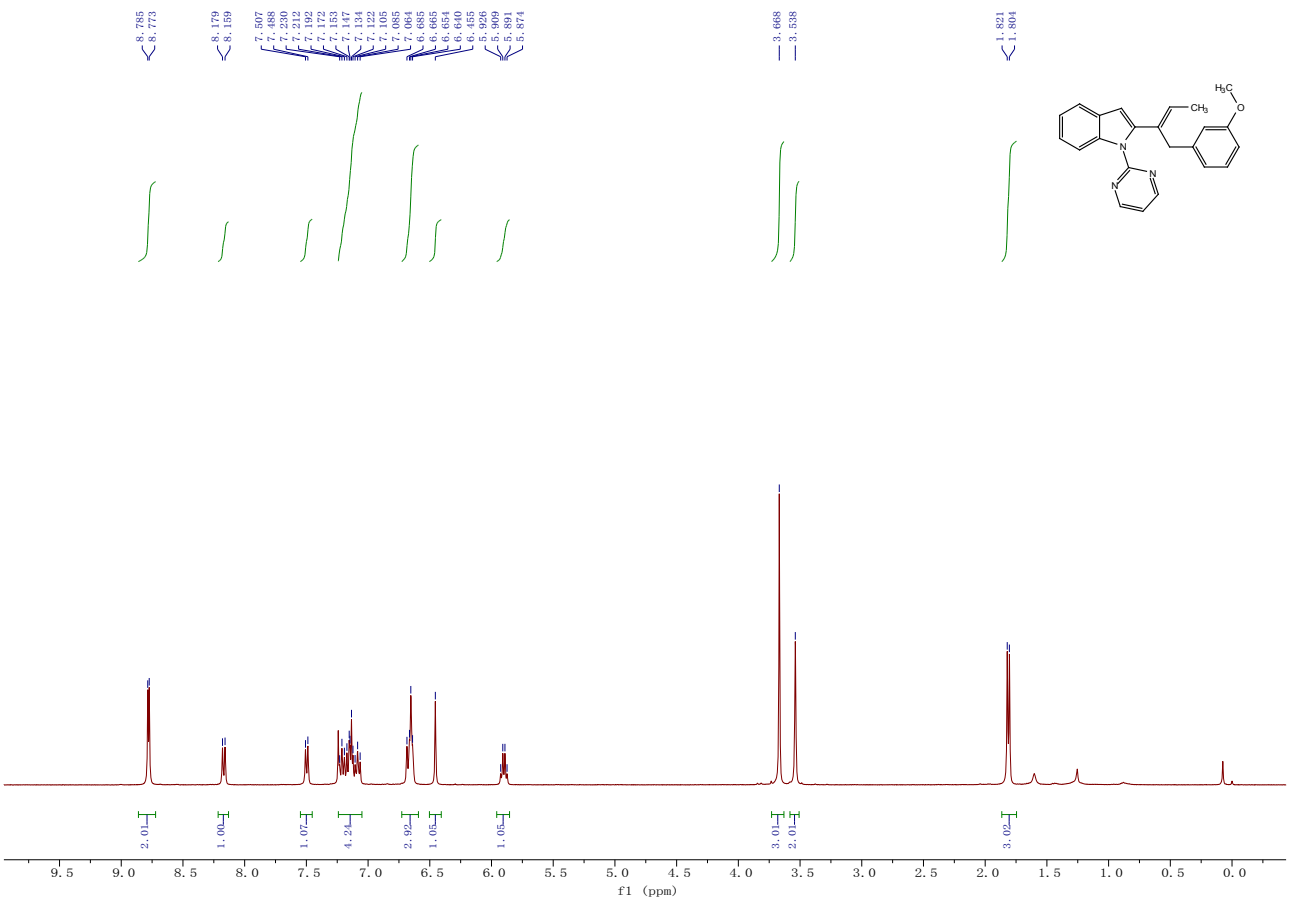
Compound 3ai: yellow oil (38.4 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.79 (d, *J* = 7.0 Hz, 3H), 3.59 (s, 2H), 5.87 (q, *J* = 6.9 Hz, 1H), 6.46 (s, 1H), 6.94 – 7.01 (m, 1H), 7.05 – 7.10 (m, 2H), 7.11 – 7.24 (m, 4H), 7.51 (d, *J* = 7.3 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.5, 107.9, 113.3, 117.4, 120.4, 122.0, 123.3, 126.0, 126.7, 127.3, 128.6, 129.2, 129.4, 132.3, 133.9, 137.5, 141.7, 142.5, 158.26, 158.35. IR (neat) ν 3039, 2919, 2846, 1559, 1507, 1451, 1422, 1380, 1348, 1321, 1226, 1146, 1127, 1052 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{19}BrN_3$ requires (M^++H): 404.0757, Found: 404.0757.

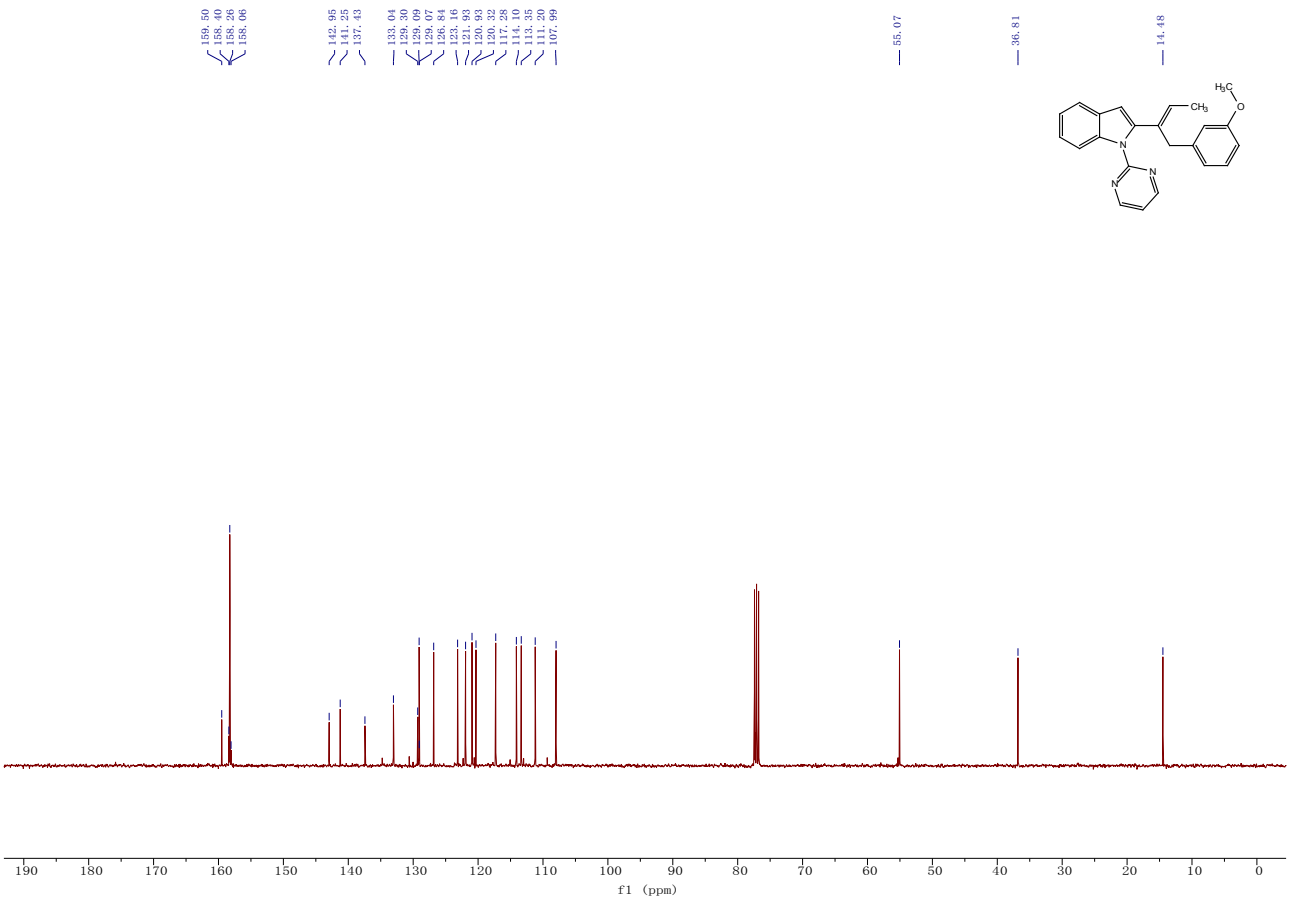






Compound 3aj: yellow oil (25.6 mg, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.81 (d, *J* = 6.9 Hz, 3H), 3.54 (s, 2H), 3.67 (s, 3H), 5.90 (q, *J* = 6.8 Hz, 1H), 6.46 (s, 1H), 6.61 – 6.71 (m, 3H), 7.05 – 7.24 (m, 4H), 7.50 (d, *J* = 7.7 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.78 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.8, 55.1, 108.0, 111.2, 113.3, 114.1, 117.3, 120.3, 120.9, 121.9, 123.2, 126.8, 129.07, 129.09, 129.3, 133.0, 137.4, 141.2, 142.9, 158.1, 158.3, 158.4, 159.5. IR (neat) ν 3039, 2917, 2850, 1559, 1507, 1451, 1422, 1385, 1345, 1323 1228, 1164, 1120, 1055 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{22}N_3O$ requires (M^++H): 356.1757, Found: 356.1766.


8.785
8.773
8.179
8.159
7.607
7.588
7.230
7.212
7.192
7.172
7.153
7.147
7.134
7.122
7.105
7.085
7.064
6.685
6.665
6.654
6.640
6.455
5.926
5.909
5.891
5.874
3.668
3.538
1.821
1.804
2.01
1.00
1.07
4.24
2.92
1.05
1.05
3.01
2.01
3.02
f1 (ppm)


159.50
158.40
158.26
158.06
142.95
141.25
137.43
133.04
129.30
129.09
129.07
126.84
123.16
121.83
120.93
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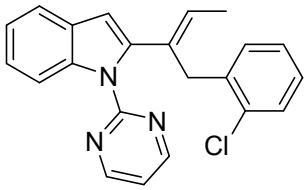
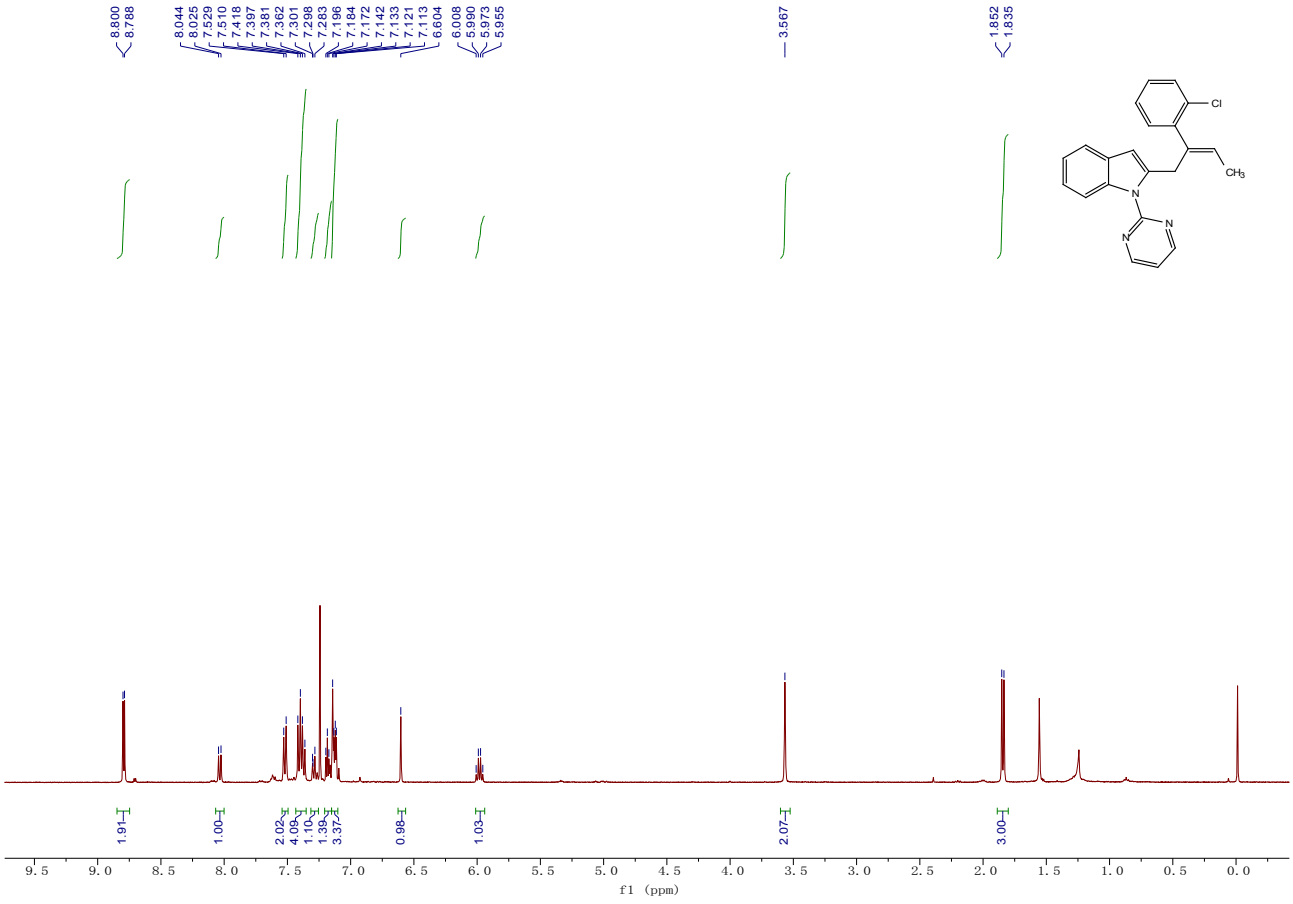
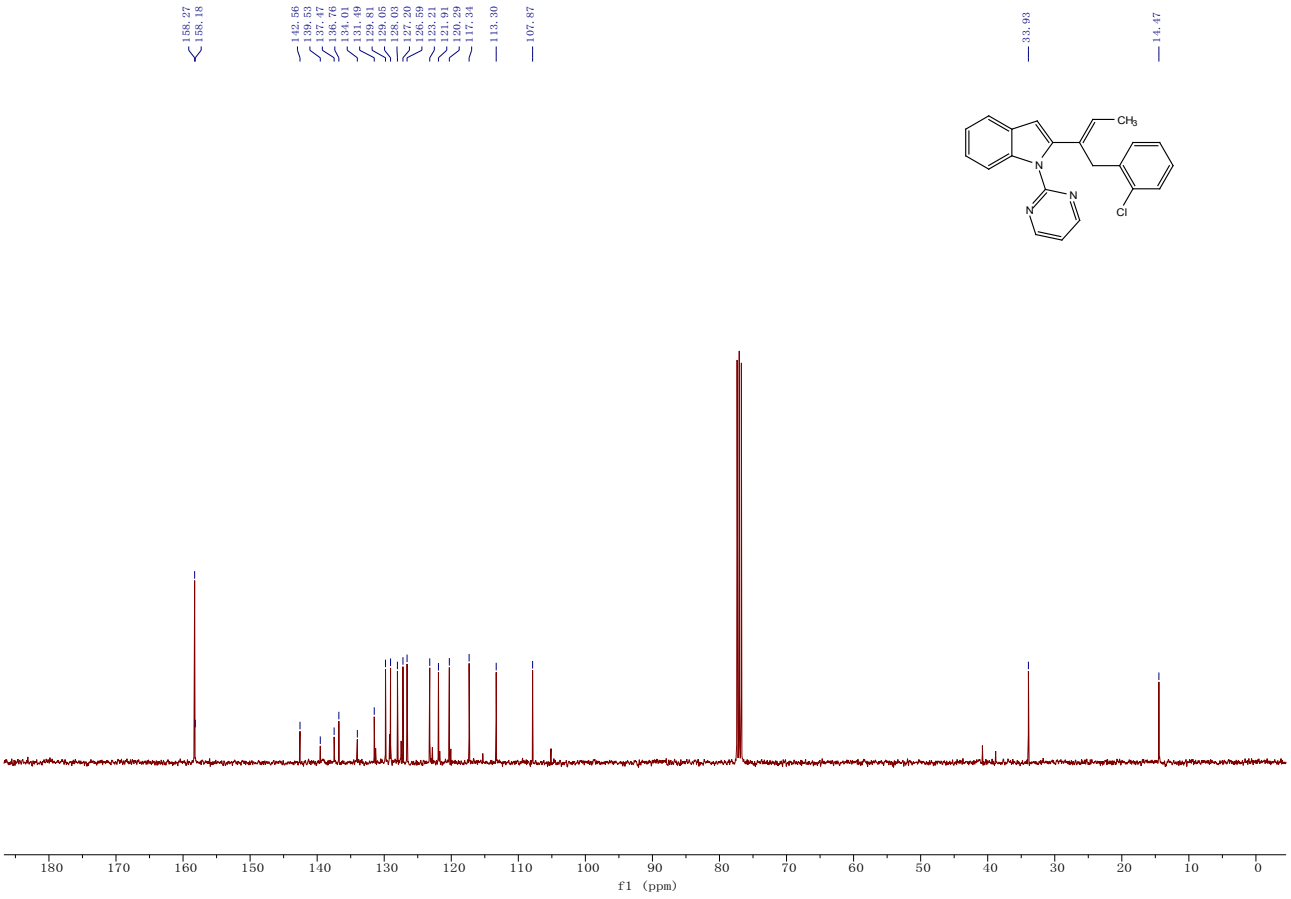
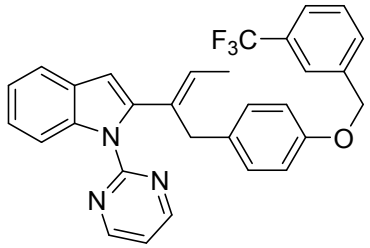
117.28
114.10
113.35
111.20
107.99
55.07
36.81
14.48
f1 (ppm)



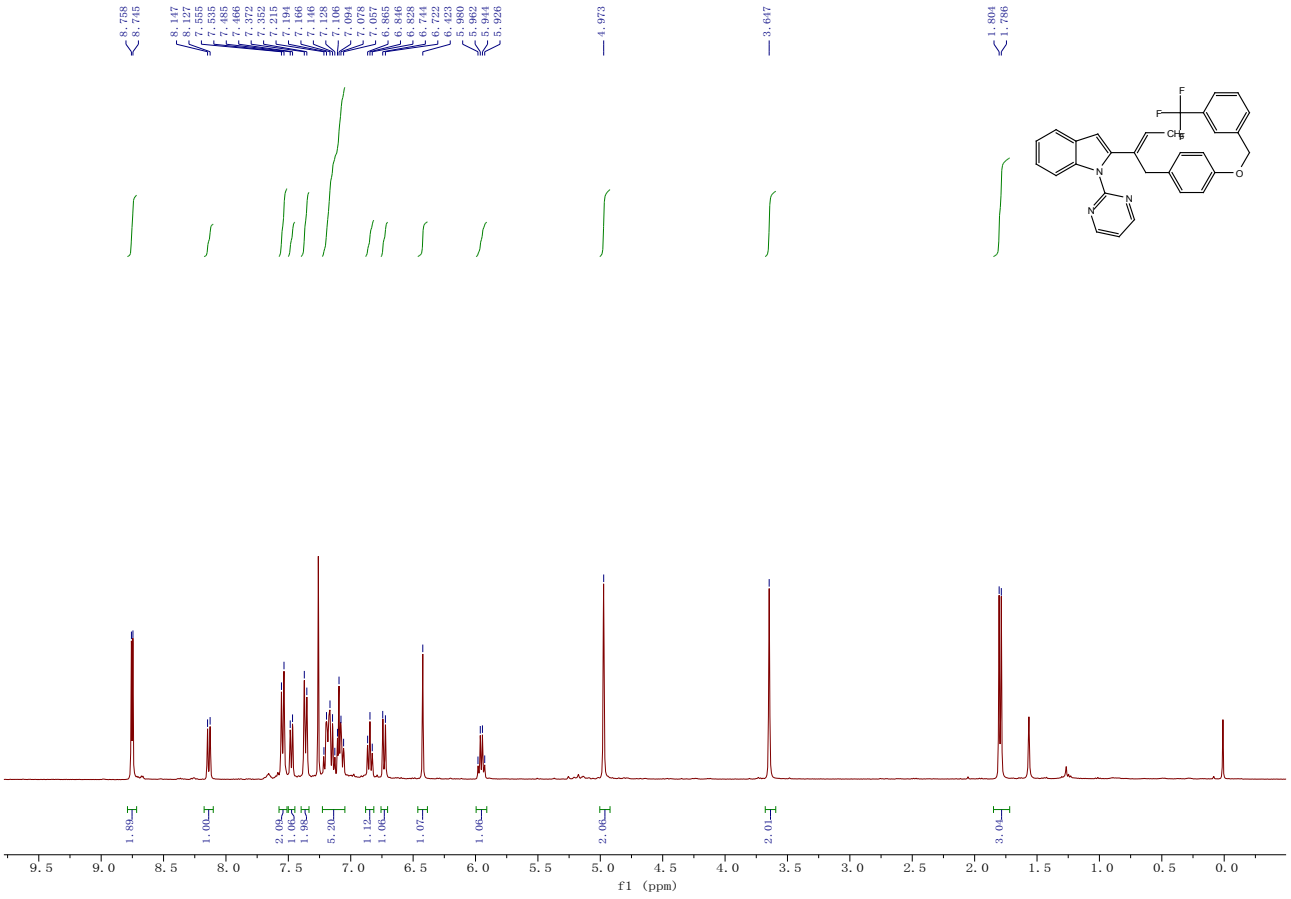
Compound 3ak: yellow oil (24.5 mg, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 (d, *J* = 7.0 Hz, 3H), 3.57 (s, 2H), 5.98 (q, *J* = 7.0 Hz, 1H), 6.60 (s, 1H), 7.13 (dd, *J* = 8.1, 3.6 Hz, 3H), 7.15 – 7.21 (m, 1H), 7.28 (dd, *J* = 7.3 Hz, 1H), 7.35 – 7.43 (m, 4H), 7.52 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.79 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 33.9, 107.9, 113.3, 117.3, 120.3, 121.9, 123.2, 126.6, 127.2, 128.0, 129.1, 129.8, 131.5, 134.0, 136.8, 137.5, 139.5, 142.6, 158.2, 158.3. IR (neat) ν 3021, 2922, 2850, 1570, 1559, 1486, 1440, 1336, 1310, 1256, 1225, 1184, 1058 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{19}ClN_3$ requires (M^++H): 360.1262, Found: 360.1267.

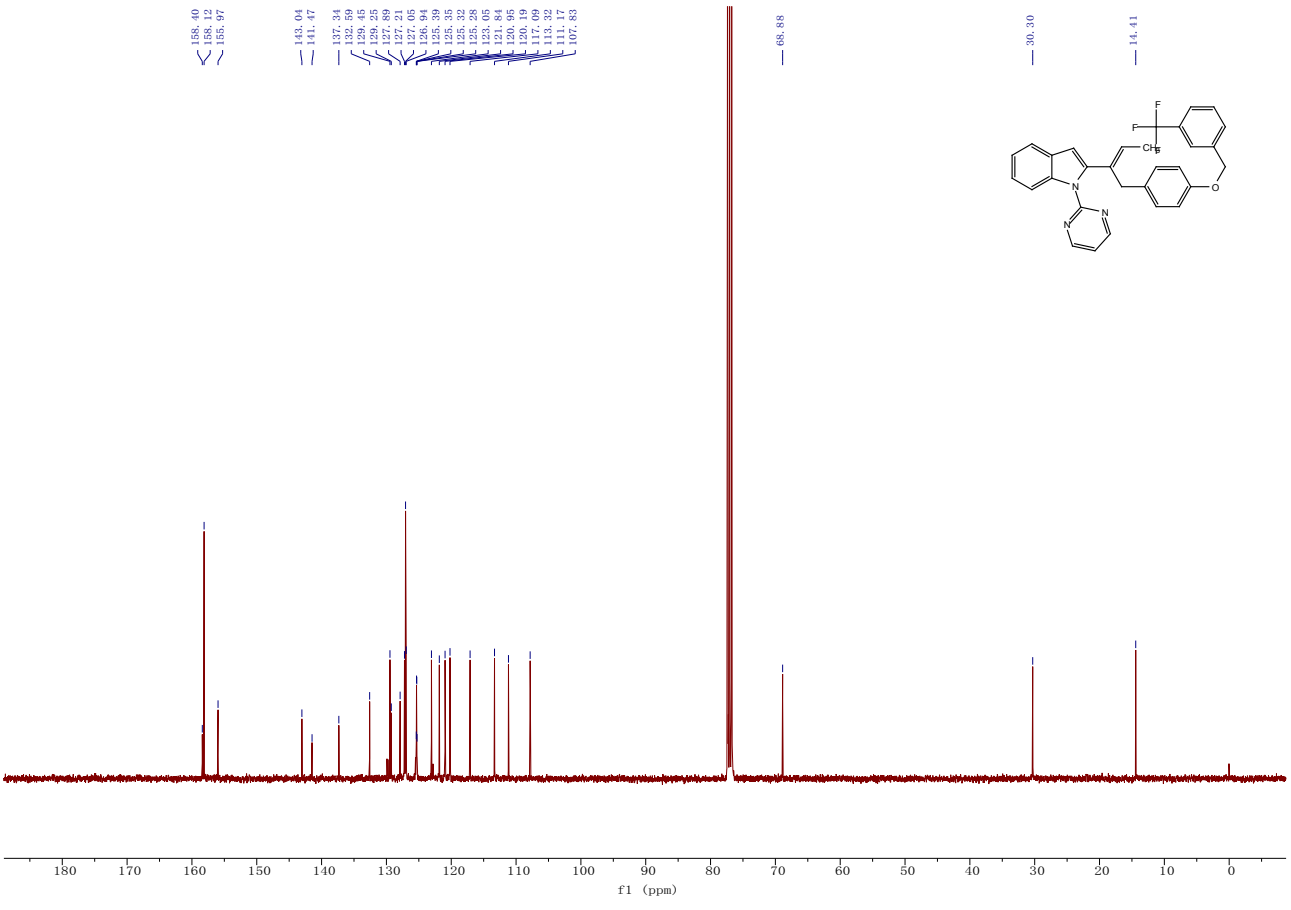


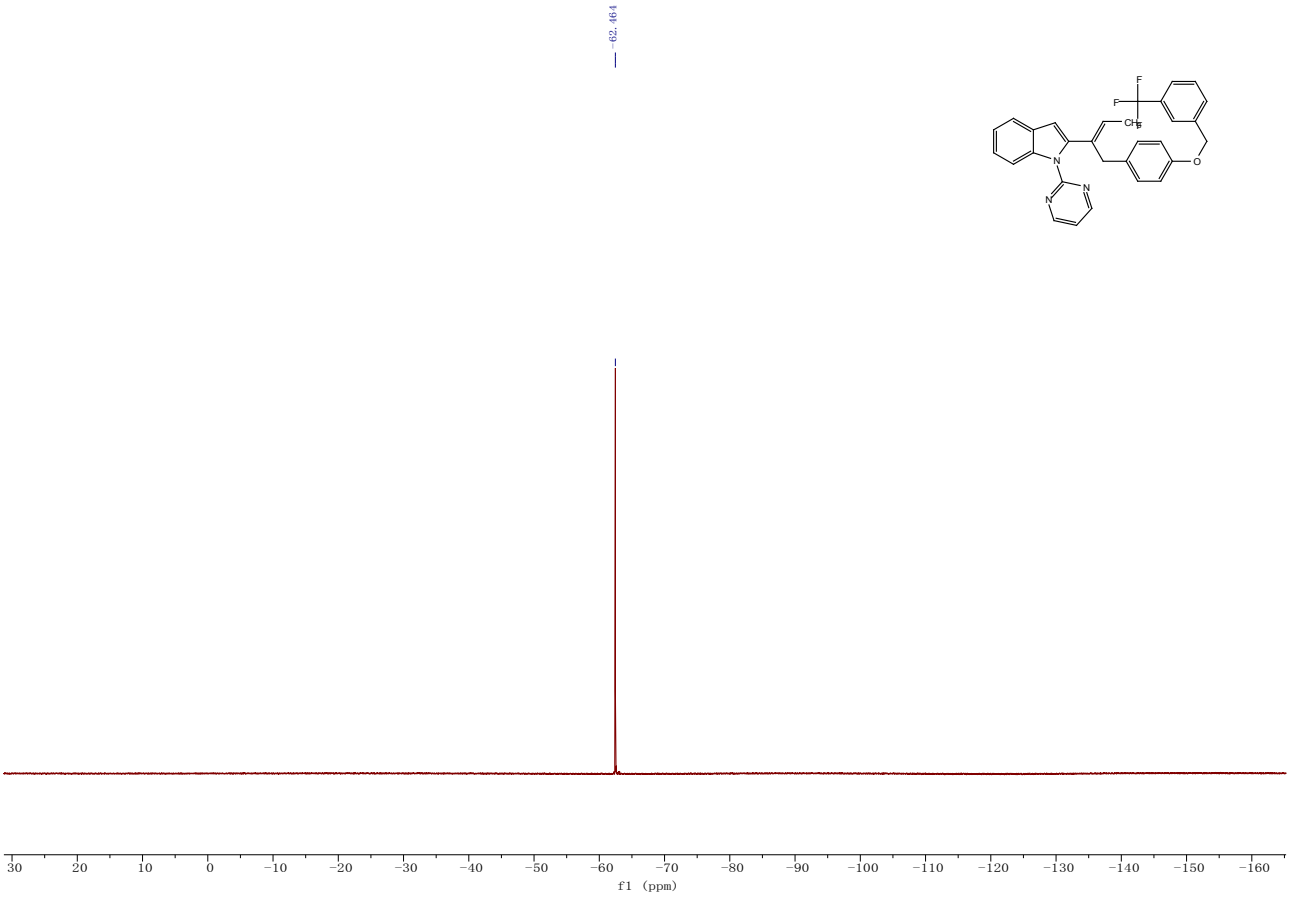


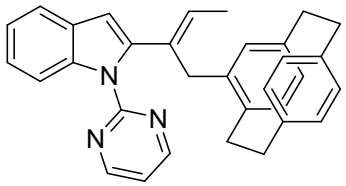


Compound 3al: yellow oil (37.5 mg, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.79 (d, *J* = 6.9 Hz, 3H), 3.65 (s, 2H), 4.97 (s, 2H), 5.95 (q, *J* = 7.3 Hz, 1H), 6.42 (s, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 7.4 Hz, 1H), 7.05 – 7.23 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.75 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.4, 30.3, 68.9, 107.8, 111.2, 113.3, 117.1, 120.2, 121.0, 121.8, 123.1, 124.2 (q, *J* = 270 Hz), 125.3 (q, *J* = 3.9 Hz), 126.97, 127.05 127.2, 127.9, 129.2, 129.5, 129.7 (q, *J* = 32.0 Hz), 132.6, 137.3, 141.5, 143.0, 156.0, 158.1, 158.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.5. IR (neat) ν 3035, 2914, 2849, 1561, 1557, 1507, 1447, 1423, 1355, 1321, 1253, 1182, 1129, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{30}H_{25}F_3N_3O$ requires (M^++H): 500.1944, Found: 500.1946.

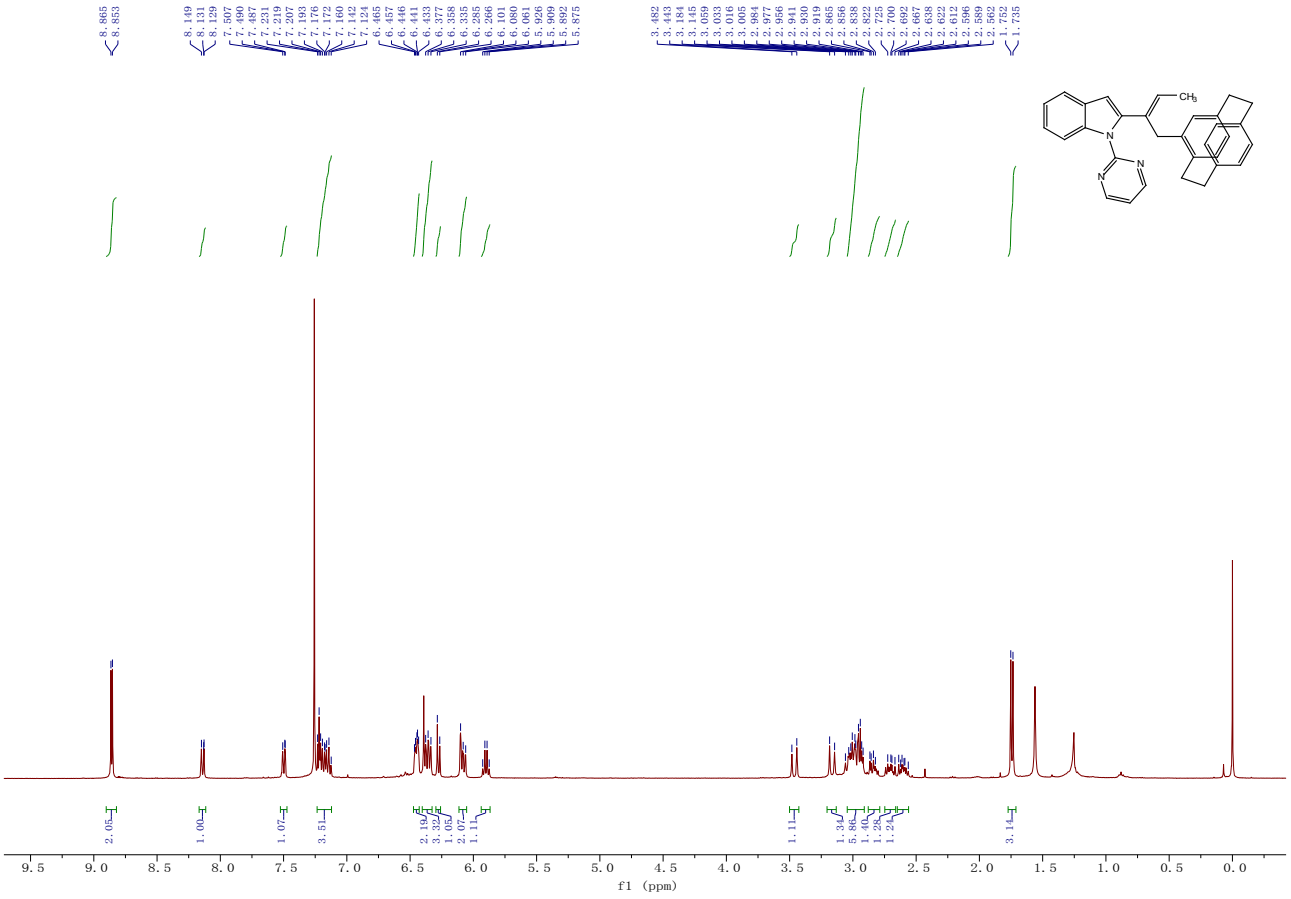

8.758
8.745
8.147
8.127
7.555
7.535
7.485
7.466
7.372
7.352
7.215
7.194
7.166
7.146
7.128
7.106
7.094
7.078
7.057
6.865
6.846
6.808
6.774
6.722
6.423
5.980
5.962
5.944
5.926
4.973
3.647
1.804
1.786
F
F
CH3
N
N
N
O
1.89
1.00
2.09
1.06
1.98
5.20
1.12
1.06
1.07
1.06
2.06
2.01
3.04
f1 (ppm)

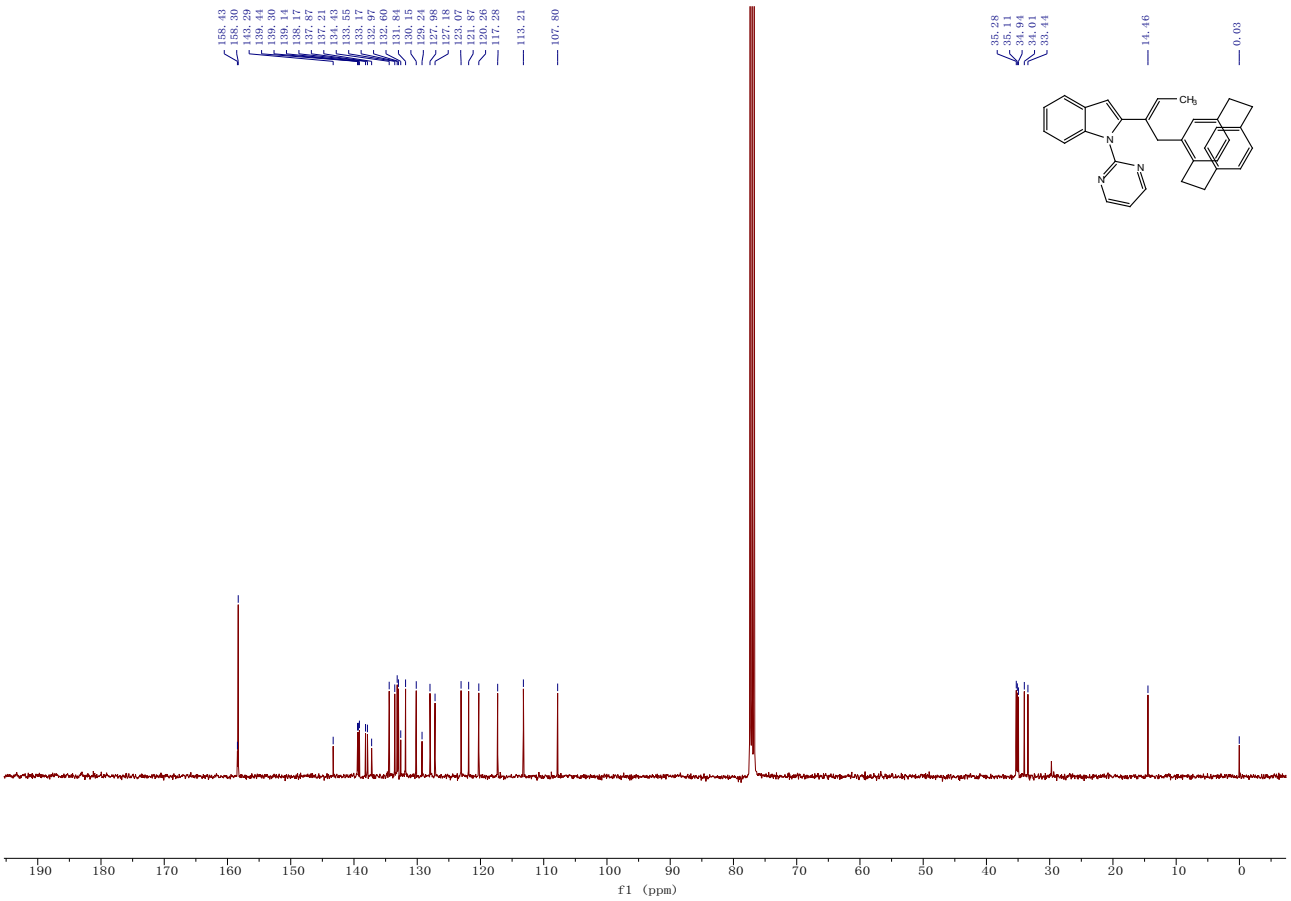

158.40
158.12
155.97
143.04
141.47
137.34
132.59
129.45
129.25
127.89
127.21
127.05
126.94
125.39
125.35
125.32
125.28
123.05
121.84
120.95
120.19
117.09
113.32
111.17
107.83
68.88
30.30
14.41
F
F
CH3
N
N
N
O
f1 (ppm)

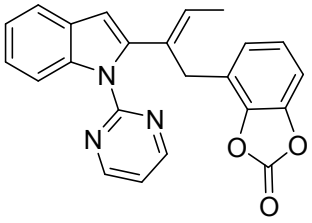




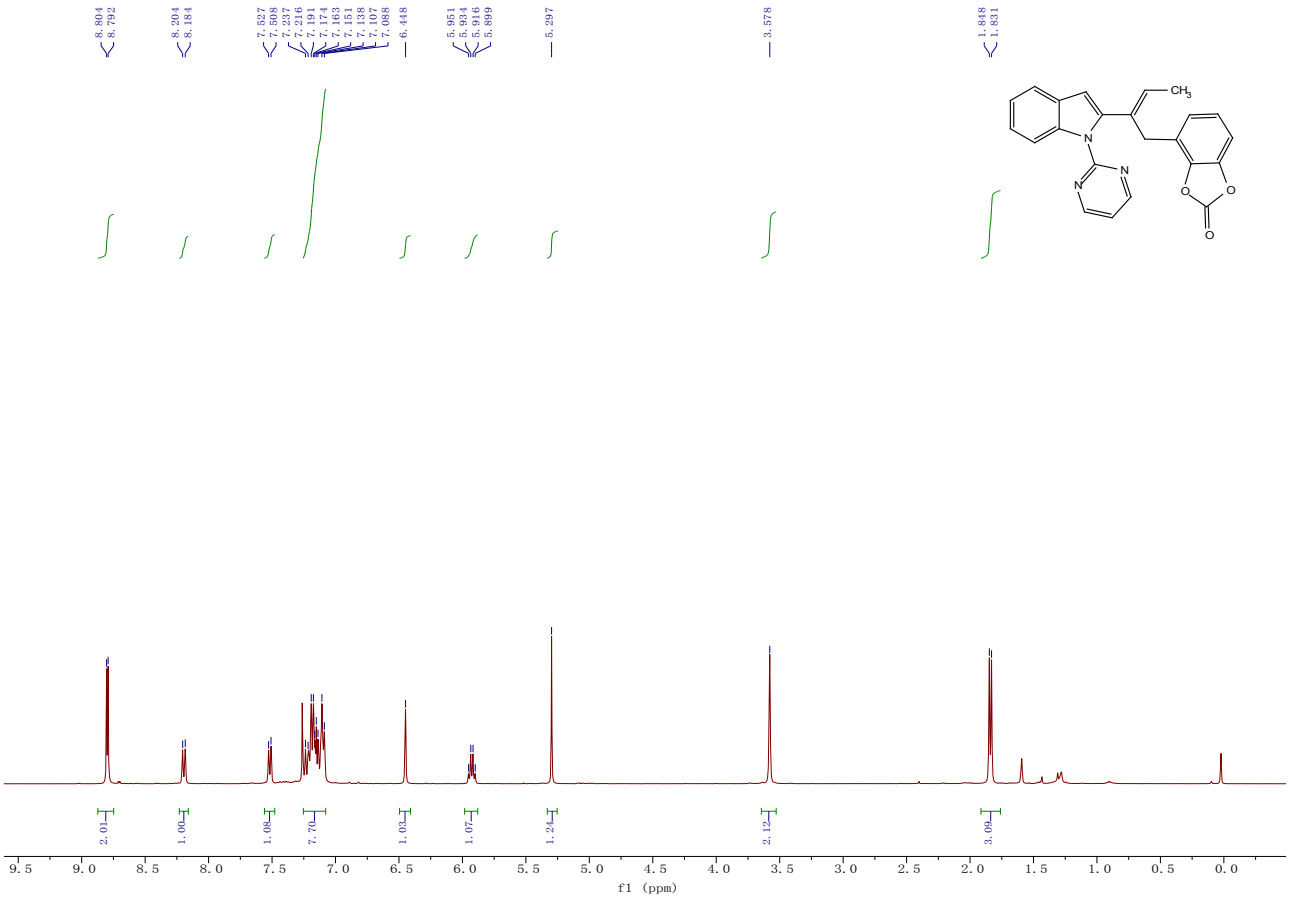
Compound 3am yellow oil (18.7 mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.74 (d, *J* = 7.0 Hz, 3H), 2.56 – 2.65 (m, 1H), 2.66 – 2.75 (m, 1H), 2.79 – 2.88 (m, 1H), 2.91 – 3.04 (m, 6H), 3.31 (dd, *J* = 119.5, 15.7 Hz, 3H), 5.90 (q, *J* = 6.8 Hz, 1H), 6.05 – 6.11 (m, 2H), 6.28 (d, *J* = 7.7 Hz, 1H), 6.33 – 6.40 (m, 3H), 6.43 – 6.47 (m, 2H), 7.12 – 7.23 (m, 4H), 7.47 – 7.53 (m, 1H), 8.12 – 8.17 (m, 1H), 8.86 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 33.4, 34.0, 34.9, 35.1, 35.3, 107.8, 113.2, 117.3, 120.3, 121.9, 123.1, 127.2, 128.0, 129.2, 130.2, 131.8, 132.6, 133.0, 133.2, 133.6, 134.4, 137.2, 137.9, 138.2, 139.1, 139.3, 139.4, 143.3, 158.3, 158.4. IR (neat) ν 3027, 2918, 2845, 1561, 1543, 1507, 1450, 1423, 1379, 1355, 1325, 1253, 1151, 1133, 1052 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{30}N_3$ requires (M^++H): 456.2434, Found: 456.2438.

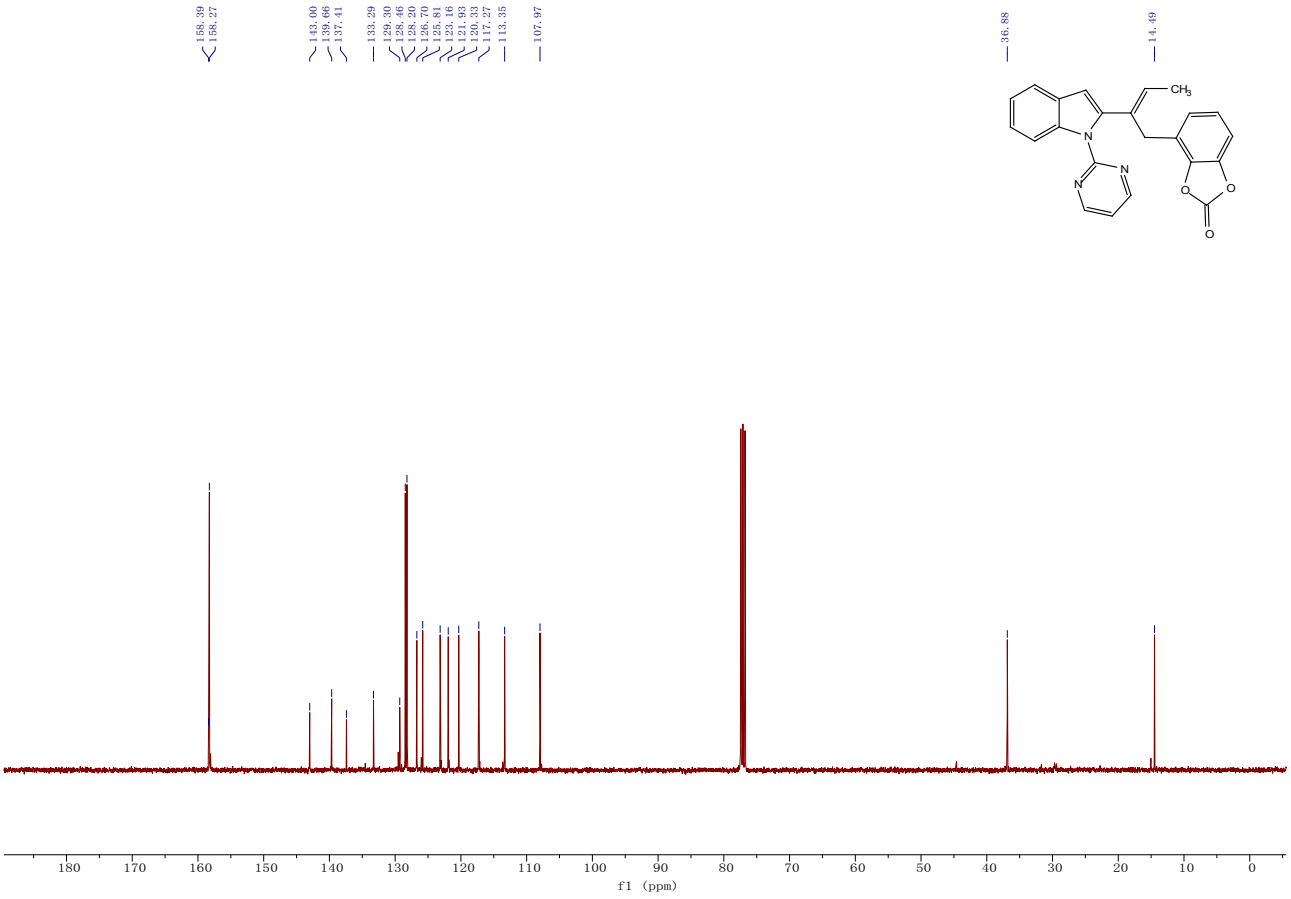

8.865
8.853
8.149
8.131
8.129
7.507
7.490
7.487
7.231
7.219
7.207
7.193
7.176
7.172
7.160
7.142
7.124
6.465
6.457
6.446
6.441
6.433
6.377
6.358
6.335
6.285
6.266
6.101
6.080
6.061
5.926
5.909
5.892
5.875
3.482
3.443
3.184
3.145
3.059
3.033
3.016
3.005
2.984
2.977
2.956
2.941
2.930
2.919
2.885
2.856
2.838
2.822
2.725
2.700
2.692
2.667
2.658
2.622
2.612
2.596
2.589
2.562
1.752
1.735
CH3
N
N
N
2.05
1.00
1.07
3.51
2.19
3.32
1.05
2.07
1.11
1.11
1.34
5.86
1.40
1.28
1.24
3.14
f1 (ppm)

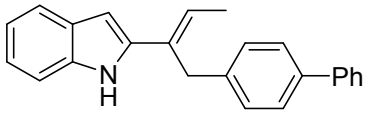

158.43
158.30
143.29
139.44
139.30
139.14
138.17
137.87
137.21
134.43
133.55
133.17
132.97
132.69
131.84
130.15
129.24
127.98
127.18
123.07
121.87
120.26
117.28
113.21
107.80
35.28
35.11
34.94
34.01
33.44
14.46
0.03
CH3
N
N
N
f1 (ppm)



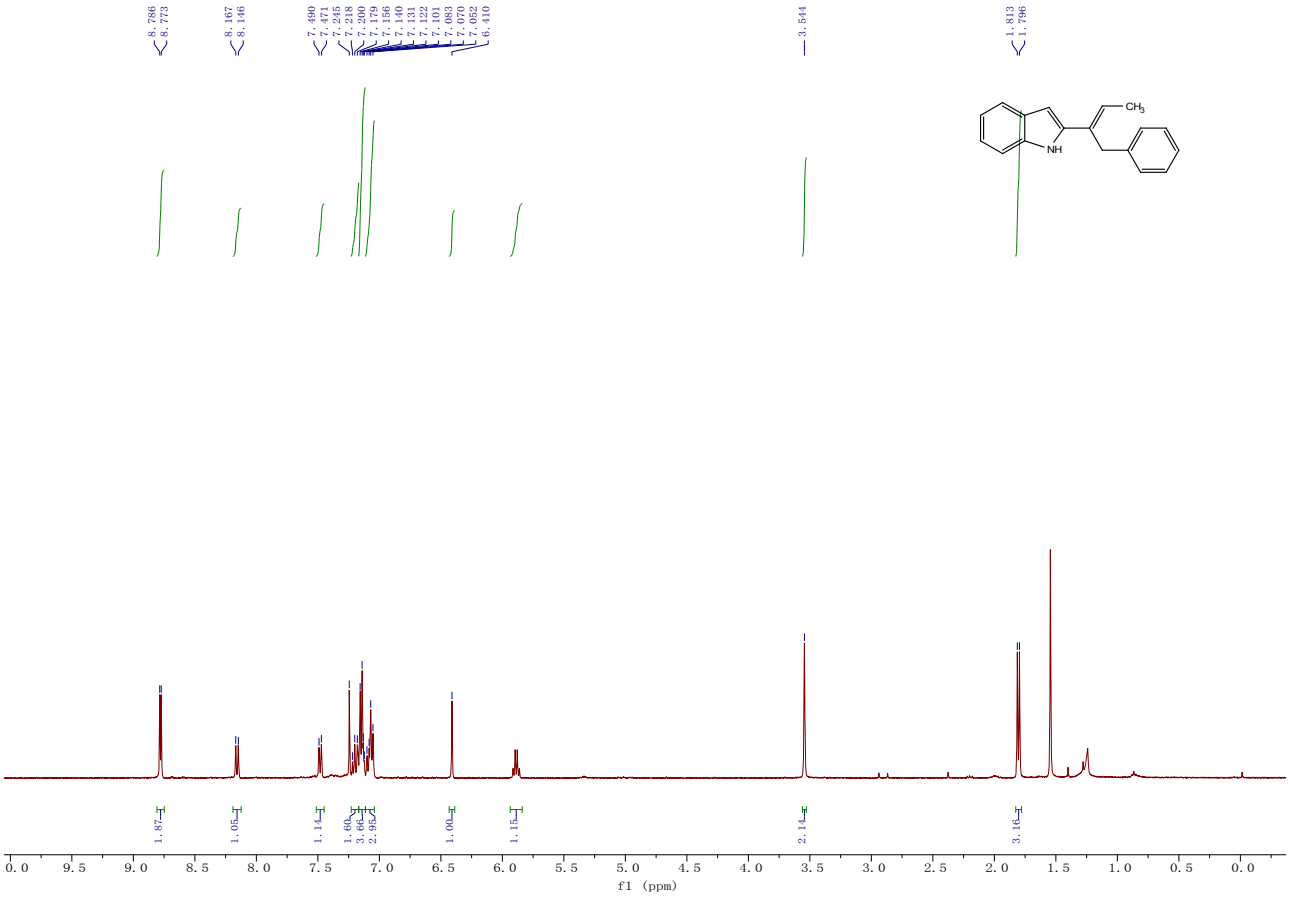
Compound 3ao: yellow oil (34.5 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 (d, *J* = 6.9 Hz, 3H), 3.58 (s, 2H), 5.30 (s, 1H), 5.93 (q, *J* = 6.9 Hz, 1H), 6.45 (s, 1H), 7.06 – 7.28 (m, 6H), 7.52 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.9, 108.0, 113.3, 117.3, 120.3, 121.9, 123.2, 125.8, 126.7, 128.2, 128.5, 129.3, 133.3, 137.4, 139.7, 143.0, 158.3, 158.4. IR (neat) ν 3033, 2923, 2850, 1653, 1561, 1507, 1451, 1427, 1383, 1347, 1321, 1226, 1182, 1123, 1038 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{18}N_3O_3$ requires (M^++H): 384.1343, Found: 384.1342.

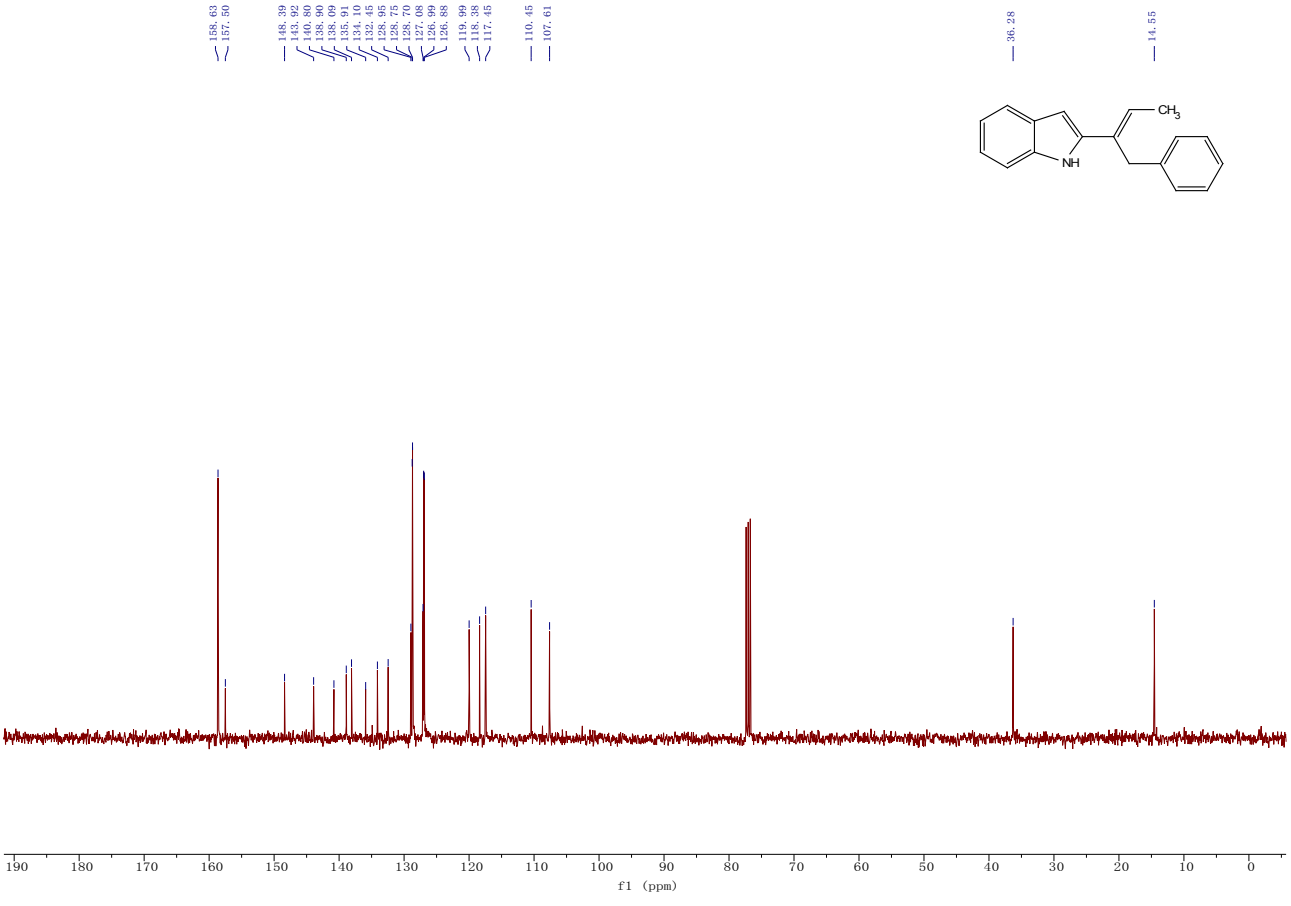


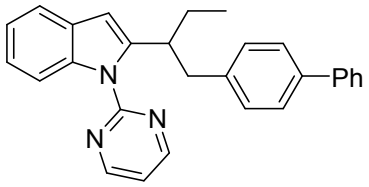




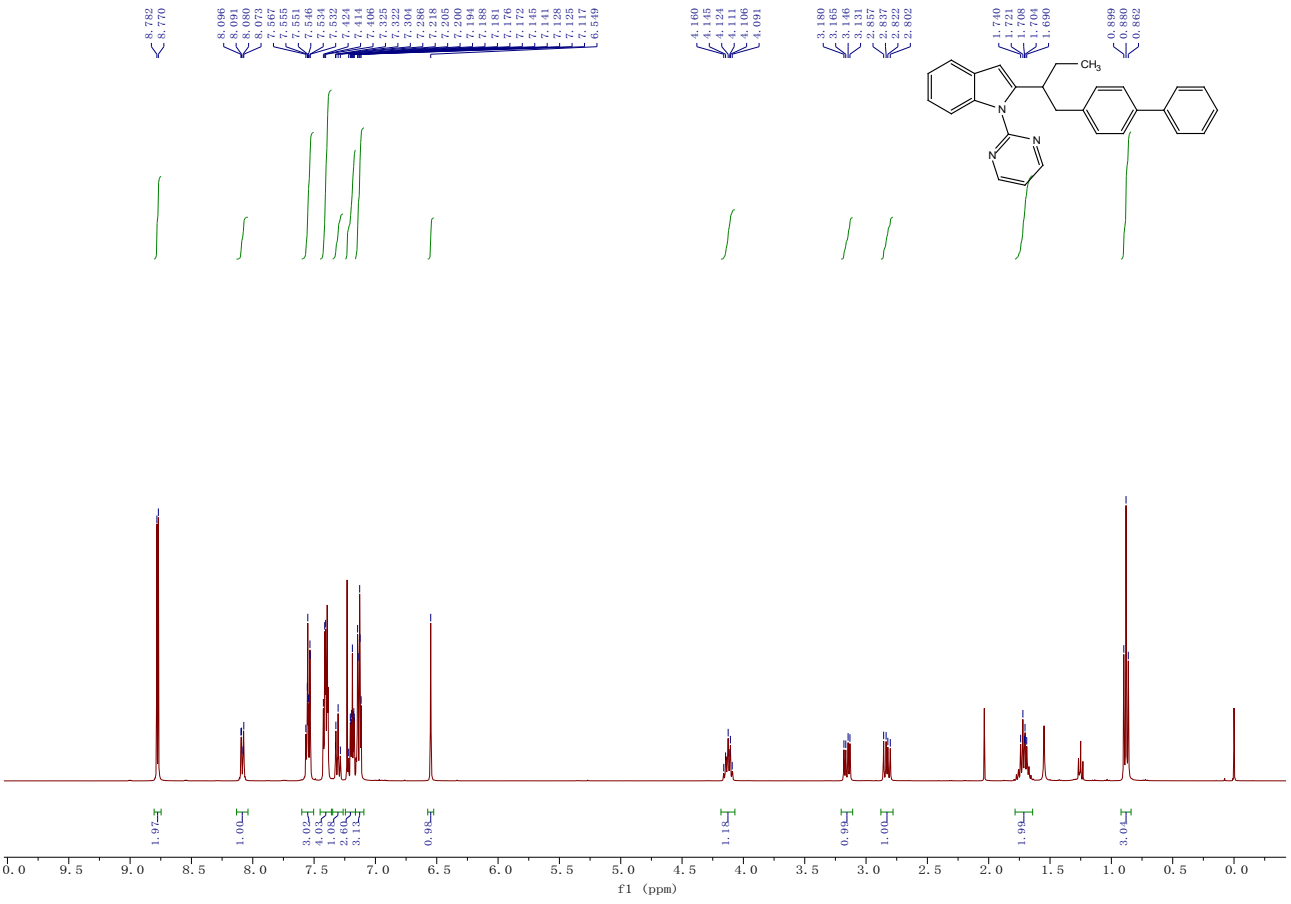
Compound 5: yellow oil (27.8 mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 (d, *J* = 6.9 Hz, 3H), 3.58 (s, 2H), 5.30 (s, 1H), 5.93 (q, *J* = 6.9 Hz, 1H), 6.45 (s, 1H), 7.06 – 7.28 (m, 5H), 7.52 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.80 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.9, 108.0, 113.3, 117.3, 120.3, 121.9, 123.2, 125.8, 126.7, 128.2, 128.5, 129.3, 133.3, 137.4, 139.7, 143.0, 158.3, 158.4. IR (neat) ν 3035, 2918, 2849, 1570, 1559, 1507, 1486, 1420, 1380, 1348, 1320, 1256, 1184, 1058, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}N$ requires (M^{+}+H): 247.1361, Found: 247.1361.

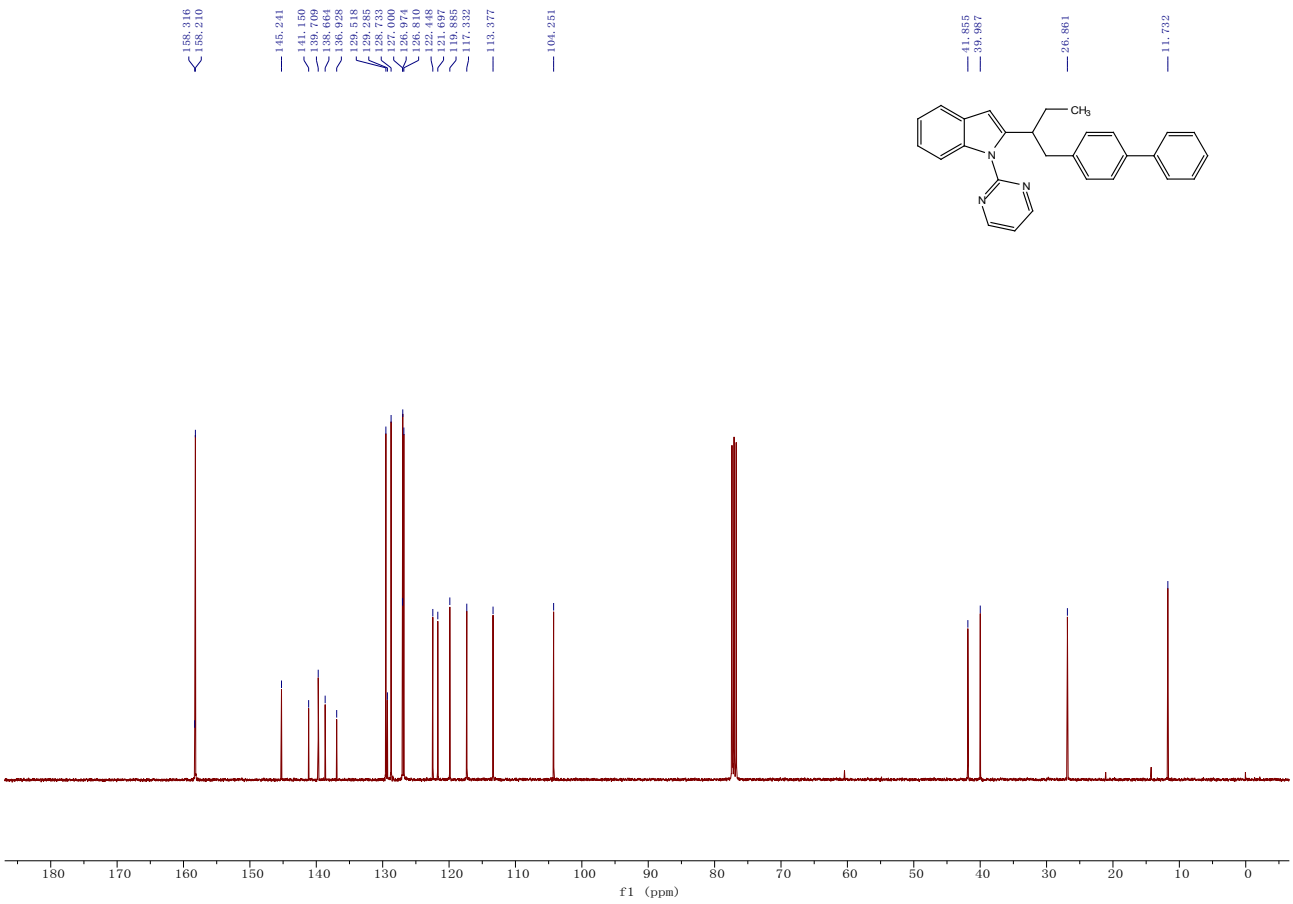

8.786
8.773
8.167
8.146
7.490
7.471
7.245
7.218
7.200
7.179
7.156
7.140
7.121
7.122
7.101
7.083
7.070
7.052
6.410
3.544
1.813
1.796
CH3
NH
1.87
1.05
1.14
1.60
3.66
2.95
1.00
1.15
2.14
3.16
f1 (ppm)

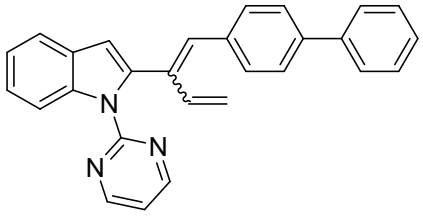

158.63
157.50
148.39
143.92
140.80
138.90
138.09
135.91
134.10
132.45
129.95
128.75
128.70
127.08
126.99
126.88
119.99
118.38
117.45
110.45
107.61
36.28
14.55
CH3
NH
f1 (ppm)



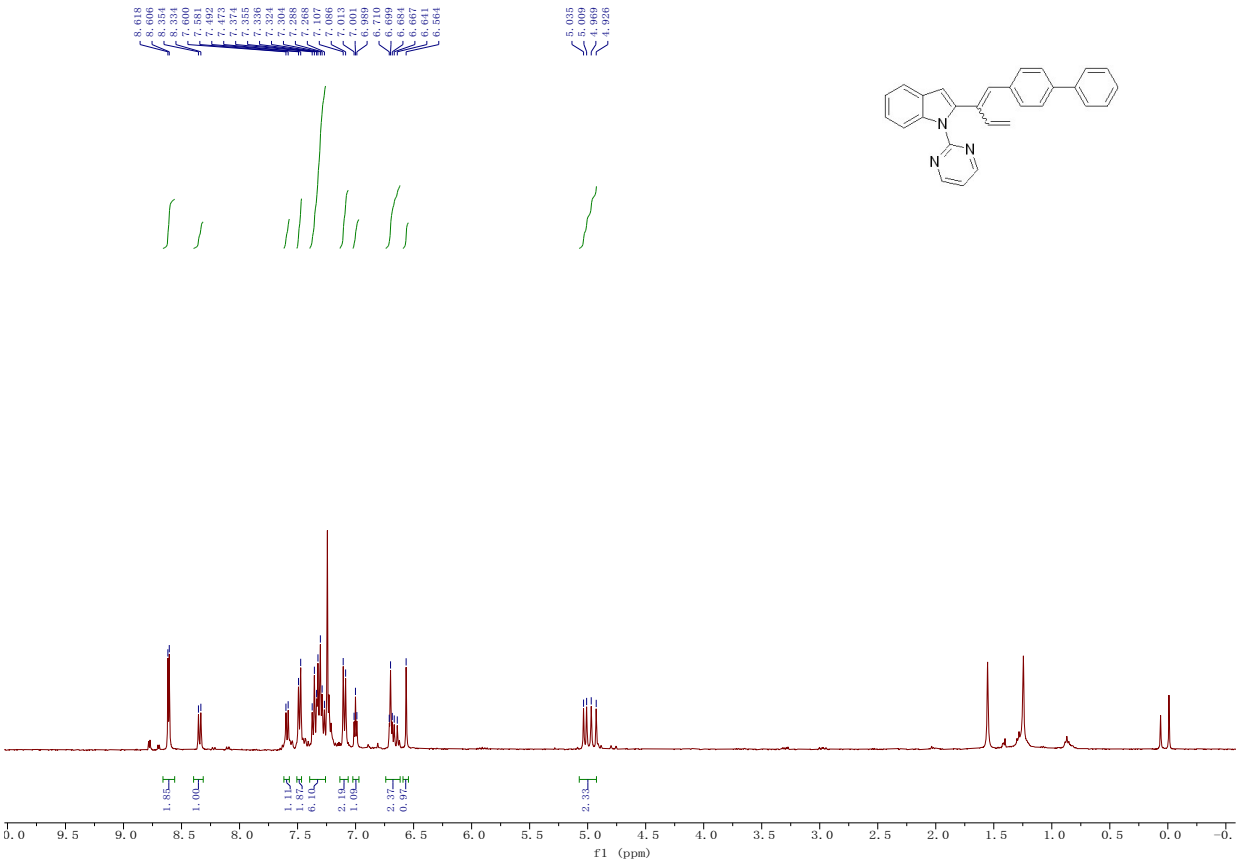
Compound 6: yellow oil (36.7 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.64 – 1.79 (m, 2H), 2.83 (dd, *J* = 13.6, 8.0 Hz, 1H), 3.16 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.07 – 4.18 (m, 1H), 6.55 (s, 1H), 7.09 – 7.16 (m, 3H), 7.16 – 7.25 (m, 3H), 7.26 – 7.35 (m, 1H), 7.36 – 7.45 (m, 4H), 7.50 – 7.60 (m, 3H), 8.09 (dd, *J* = 7.0, 2.3 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 14.5, 36.9, 108.0, 113.3, 117.3, 120.3, 121.9, 123.2, 125.8, 126.7, 128.2, 128.5, 129.3, 133.3, 137.4, 139.7, 143.0, 158.3, 158.4. IR (neat) ν 3039, 2917, 2850, 1559, 1507, 1451, 1422, 1385, 1345, 1323 1228, 1164, 1120, 1055 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{25}N_3$ requires (M^++H): 403.2048, Found: 403.2049.

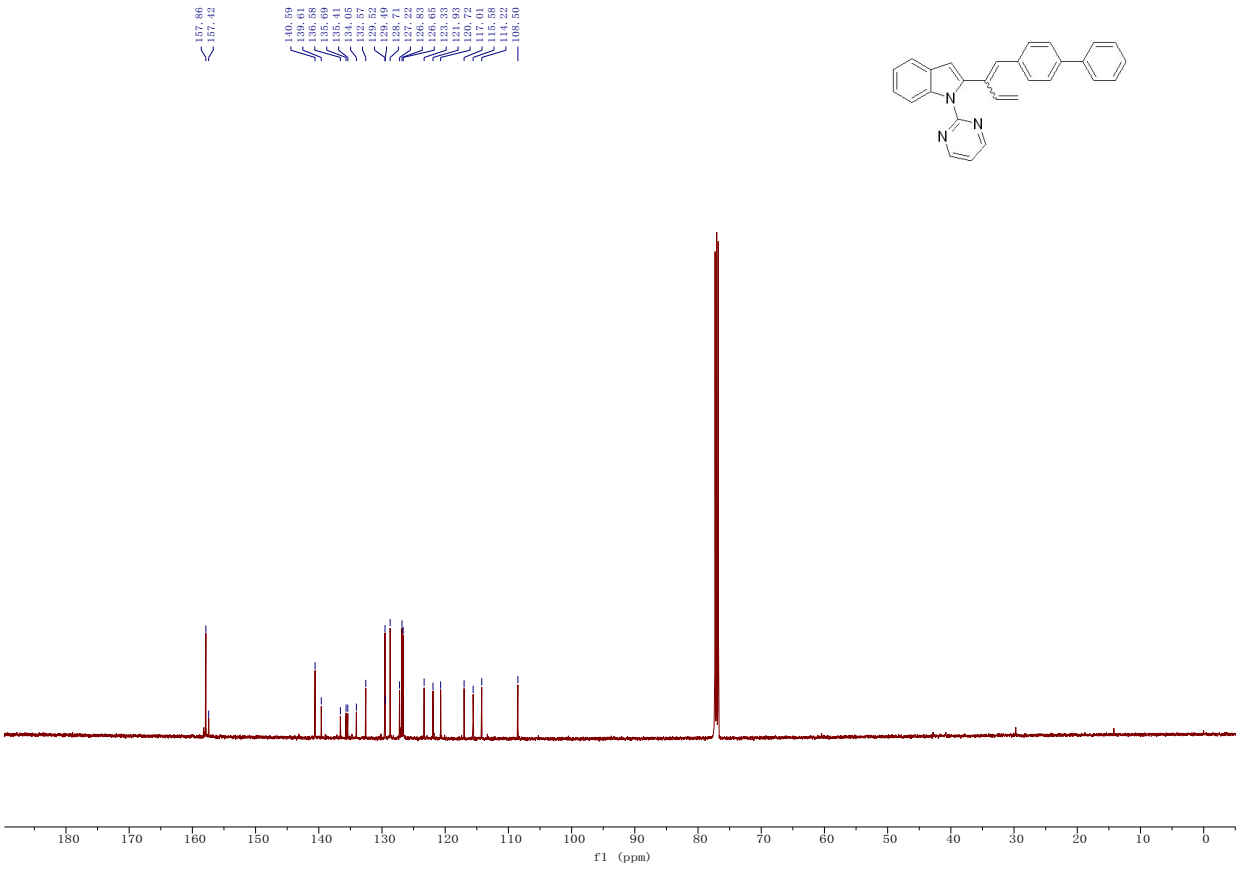




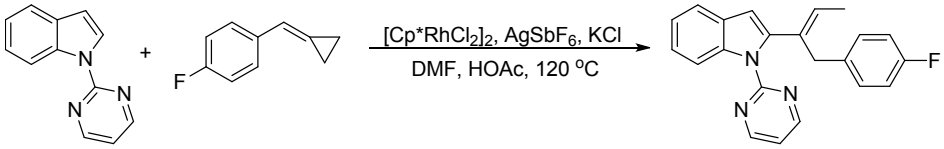


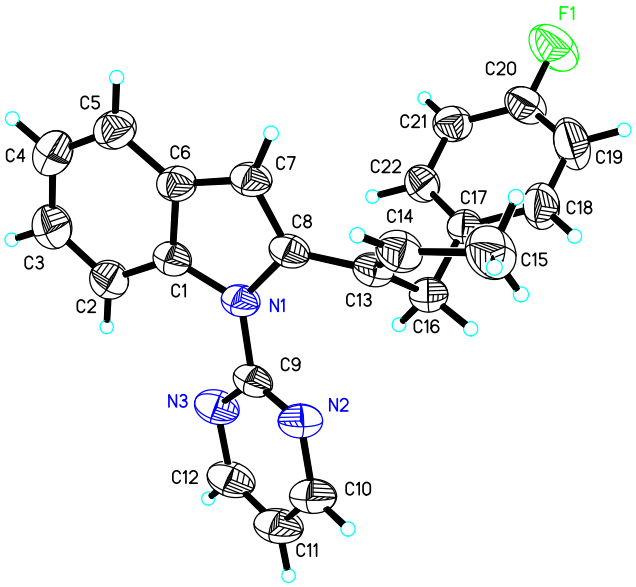
Compound 4aa: yellow oil (31.2 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.97 – 5.10 (m, 2H), 6.61 (s, 1H), 6.75 (d, *J* = 4.4 Hz, 1H), 7.05 (dd, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.43 (m, 6H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.5, 114.2, 115.6, 117.0, 120.7, 121.9, 123.3, 126.6, 126.8, 127.2, 128.7, 129.5, 129.5, 132.6, 134.1, 135.4, 135.7, 136.6, 139.6, 140.6, 157.4, 157.9. IR (neat) ν 3026, 2957, 2851, 1579, 1547, 1484, 1434, 1386, 1317, 1244, 1221, 1179, 1111, 1076, 1023, 1007 cm^{-1}. HRMS (ESI) Calcd. for $C_{28}H_{22}N_3$ requires (M^++H): 400.1808, Found: 400.1807.


8.618
8.606
8.554
8.334
7.600
7.581
7.492
7.473
7.374
7.355
7.336
7.324
7.304
7.288
7.268
7.107
7.096
7.013
7.001
6.989
6.710
6.699
6.684
6.667
6.641
6.564
5.035
5.009
4.969
4.926
1.85
1.00
1.11
1.87
6.10
2.19
1.09
2.37
0.97
2.33
f1 (ppm)

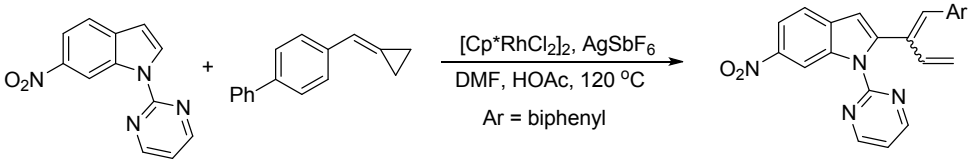

157.86
157.42
140.59
139.61
136.58
135.69
135.41
134.05
132.57
129.52
129.40
128.71
127.22
126.83
126.65
123.33
121.93
121.72
117.01
115.58
114.22
108.50
f1 (ppm)

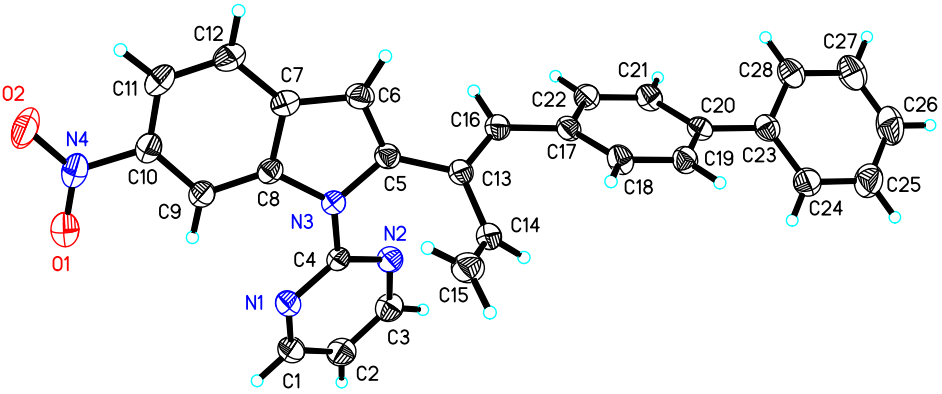
(E) X-ray Crystal Data





The crystal data of **3af** have been deposited in CCDC with number 1899061. Empirical formula: $C_{22}H_{18}FN_3$, Formula weight: 343.39, Crystal system: Monoclinic, Space group: P 21/c, Unit cell dimensions: a = 10.944(3) Å, α = 90°; b = 15.225(4) Å, β = 102.963(8)°; c = 22.273(7) Å, γ = 90°. Volume: 3616.6(17) $Å^3$, Z = 8, Density (calculated): 1.261 Mg/m^3, F(000) = 1440, Crystal size: 0.200 x 0.130 x 0.080 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0591, wR2 = 0.1286.





The crystal data of **4aa-NO_2 derivatives** have been deposited in CCDC with number 1878405. Empirical formula: $C_{28}H_{20}N_4O_2$, Formula weight: 444.48, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 7.8352(4) Å, α = 86.602(2)°; b = 11.9524(7) Å, β = 78.708(2)°; c = 12.5240(7) Å, γ = 75.444(2)°. Volume: 1113.18(11) $Å^3$, Z = 2, Density (calculated): 1.326 Mg/m^3, F(000) = 464, Crystal size: 0.180 x 0.150 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0414, wR2 = 0.1021.