

Supporting Information for

Rh(I)-catalyzed decarbonylative direct C2-olefination of indoles with vinyl carboxylic acids

Lingjuan Zhang, Ruiying Qiu, Xiao Xue, Yixiao Pan, Conghui Xu, Doudou Wang, Xinyu Wang, Lijin Xu* and Huanrong Li*

Department of chemistry, Renmin University of China, Beijing 100872, China.

Email: xulj@chem.ruc.edu.cn, hrli@ruc.edu.cn,

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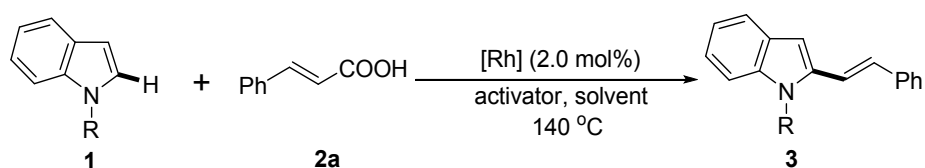
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1. General information:

Unless otherwise noted, all experiments were carried out under nitrogen atmosphere, and all commercially available chemicals were used as received from Aldrich, Acros or Strem without further purification. All organic solvents were dried using standard, published methods and were distilled before use. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^1H 400 MHz and ^{13}C 106 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. *N*-(2-pyrimidyl)-indoles (**1a,c-o**),¹⁻⁶ *N*-(2-pyridyl)-indole (**1b**),⁷ β,β -disubstituted acrylic acids (**2w** and **2x**)⁸ and tetra-substituted acrylic acid **4j**⁹ were prepared according to the previous reports. Cinnamic anhydride **11** was prepared from the parent acid using the known methods.¹⁰

2. Screening of reaction conditions

Table S1. Screening conditions for direct olefination of *N*-protected indoles with cinnamic acid **2a**^a



Entry	R	[Rh]	Solvent	Activator	Time(h)	Yield(%) ^b
1	2-pyrimidyl (1a)	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	95 (3aa)
2	2-pyridyl (1b)	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	40(3ba)
3	Me	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
4	Benzyl	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
5	Acetyl	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
6	Tosyl	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
7	Boc	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
8	Pivaloyl	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
9	PhCO	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
10	Me ₂ NCO	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
11	H	[Rh(CO) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	12	0
12	2-pyrimidyl (1a)	[Rh(COD) ₂][OTf]	toluene	(<i>t</i> BuCO) ₂ O	4	96(3aa)

13	2-pyrimidyl (1a)	[Rh(COD)Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	4	55(3aa)
14	2-pyrimidyl (1a)	[Rh(1,5-hexadiene)Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	4	52(3aa)
15	2-pyrimidyl (1a)	[Rh(C ₂ H ₄) ₂ Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	4	58(3aa)
16	2-pyrimidyl (1a)	[Rh(NBD)Cl] ₂	toluene	(<i>t</i> BuCO) ₂ O	4	54(3aa)
17	2-pyrimidyl (1a)	[Rh(PPh ₃) ₃ Cl]	toluene	(<i>t</i> BuCO) ₂ O	4	0
18	2-pyrimidyl (1a)	[Rh(acac)(C ₂ H ₄) ₂]	toluene	(<i>t</i> BuCO) ₂ O	4	24(3aa)
19	2-pyrimidyl (1a)	[Rh(acac)(CO) ₂]	toluene	(<i>t</i> BuCO) ₂ O	4	14(3aa)
20	2-pyrimidyl (1a)	[Rh(COD) ₂]BF ₄	toluene	(<i>t</i> BuCO) ₂ O	4	94(3aa)
21	2-pyrimidyl (1a)	[Rh(NBD) ₂]BF ₄	toluene	(<i>t</i> BuCO) ₂ O	4	36(3aa)
22	2-pyrimidyl (1a)	[RhCp*Cl ₂] ₂	toluene	(<i>t</i> BuCO) ₂ O	4	0
23	2-pyrimidyl (1a)	[Rh(COD) ₂]BF ₄	toluene	(<i>t</i> BuCO) ₂ O	1	86(3aa)
24	2-pyrimidyl (1a)	[Rh(COD)₂]OTf	toluene	(<i>t</i>BuCO)₂O	1	97(3aa)
25	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	PhCl	(<i>t</i> BuCO) ₂ O	1	87(3aa)
26	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	<i>p</i> -xylene	(<i>t</i> BuCO) ₂ O	1	49(3aa)
27	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	anisole	(<i>t</i> BuCO) ₂ O	1	81(3aa)
28	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	DMF	(<i>t</i> BuCO) ₂ O	1	45(3aa)
29	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	DMSO	(<i>t</i> BuCO) ₂ O	1	21(3aa)
30	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	decalin	(<i>t</i> BuCO) ₂ O	1	58(3aa)
31	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	Boc ₂ O	1	50(3aa)
32	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	Ac ₂ O	1	43(3aa)
33	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	<i>t</i> BuCOCl	1	29(3aa)
34	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(CF ₃ CO) ₂ O	1	0
35	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(MeOCO) ₂ O	1	0
36 ^c	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(<i>t</i> BuCO) ₂ O	1	34(3aa)
37 ^d	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(<i>t</i> BuCO) ₂ O	1	55(3aa)
38 ^e	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(<i>t</i> BuCO) ₂ O	1	43(3aa)
39 ^f	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(<i>t</i> BuCO) ₂ O	1	93(3aa)
40 ^g	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	(<i>t</i> BuCO) ₂ O	2	95(3aa)
41	2-pyrimidyl (1a)	none	toluene	(<i>t</i> BuCO) ₂ O	1	0

40	2-pyrimidyl (1a)	[Rh(COD) ₂]OTf	toluene	none	1	0
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^a Reaction Conditions: **1a** (0.5 mmol.), **2a** (0.5 mmol), [Rh] (2.0 mol%), activator (0.5 mmol), solvent (3.0 mL), 140 °C. ^b Isolated yield. ^c KI (50 mol%) was added. ^d Reaction temperature 120 °C. ^e [Rh(COD)₂]OTf (1.0 mol%) was used. ^f **2a** (1.5 mmol) and (tBuCO)₂O (1.5 mmol) were used, but no double (C2 and C7) olefination was observed. ^g **2a** (1.5 mmol), (tBuCO)₂O (1.5 mmol) and [Rh(COD)₂]OTf (5.0 mol%) were used, but still no double (C2 and C7) olefination was observed.

3. The general procedure for the direct C2-olefination of indoles

To an oven-dried pressure tube were sequentially added indole **1** (0.5 mmol), acrylic acid **2** (0.5 mmol), [Rh(COD)₂]OTf (4.68 mg, 2 mol%), (tBuCO)₂O (93 mg, 0.5 mmol) and anhydrous toluene (3.0 mL). After being degassed three times, the tube was heated and stirred vigorously at 140 °C for 1 h in the oil bath under nitrogen atmosphere. Then the tube was removed from the oil bath and cooled to room temperature. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

(E)-1-(pyrimidin-2-yl)-2-styryl-1H-indole (3aa), red oil; ¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 1H), 7.18~7.23 (m, 2H), 7.26~7.35 (m, 3H), 7.40 (t, *J* = 7.36 Hz, 2H), 7.55 (d, *J* = 7.44 Hz, 2H), 7.65~7.67 (m, 1H), 7.75 (d, *J* = 16.2 Hz, 1H), 8.36 (d, *J* = 8.24 Hz, 1H), 8.87 (d, *J* = 4.80 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.3, 114.1, 117.3, 120.4, 120.7, 122.4, 123.6, 126.7, 127.7, 128.7, 129.4, 129.7, 137.4, 137.5, 138.9, 158.2, 158.3; HRMS (ESI) calcd. for C₂₀H₁₆N₃[M+H]⁺: 298.1339, found: 298.1339.

(E)-1-(pyridin-2-yl)-2-styryl-1H-indole (3ba), red oil; ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 1H), 7.15 (d, *J* = 4.76 Hz, 2H), 7.23 (t, *J* = 3.84 Hz, 2H), 7.28~7.30 (m, 1H), 7.34~7.39 (m, 3H), 7.45 (d, *J* = 8.60 Hz, 3H), 7.54~7.56 (m, 1H), 7.67~7.70 (m, 1H), 7.92 (t, *J* = 7.52 Hz, 1H), 8.78 (d, *J* = 4.56 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ 102.4, 110.9, 118.4, 120.6, 121.4, 121.6, 122.1, 122.9, 126.5, 127.8, 128.7, 130.6, 137.2, 137.9, 138.1, 138.4, 149.7, 151.3; HRMS (ESI) calcd. for C₂₁H₁₇N₂[M+H]⁺: 297.1386, found: 297.1388.

(E)-4-methyl-1-(pyrimidin-2-yl)-2-styryl-1H-indole (3ca), grey solid, mp: 138.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.65 (s, 3H), 7.09 (d, *J* = 7.20 Hz, 1H), 7.11 (s, 1H), 7.18 (t, *J* = 4.76 Hz, 1H), 7.21~7.25 (m, 2H), 7.30 (t, *J* = 7.24 Hz, 1H), 7.40 (t, *J* = 7.52 Hz, 2H), 7.55 (d, *J* = 7.80 Hz, 2H), 7.75 (d, *J* = 16.16 Hz, 1H), 8.18 (d, *J* = 8.40 Hz, 1H), 8.86 (d, *J* = 4.76 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 18.7, 103.8, 111.6, 117.3, 120.8, 122.7, 123.7, 126.6, 127.6, 128.7, 129.1, 129.4, 129.8, 137.2, 137.6, 138.3, 158.2, 158.3; HRMS (ESI) calcd. for C₂₁H₁₈N₃[M+H]⁺: 312.1495, found: 312.1497.

(E)-5-Methyl-1-pyrimidin-2-yl-2-styryl-1H-indole (3da), red oil; ¹H NMR (400

MHz, CDCl₃) δ 2.58(s, 3H), 7.05(s, 1H), 7.09(t, *J*=4.76Hz, 1H), 7.21~7.27(m, 2H), 7.35(t, *J*=7.28Hz, 1H), 7.45(t, *J*=7.48Hz, 2H), 7.50(s, 1H), 7.60(d, *J*=7.64Hz, 2H), 7.85(d, *J*=16.16Hz, 1H), 8.35(d, *J*=8.52Hz, 1H), 8.82(d, *J*=4.76Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.5, 105.2, 114.1, 117.1, 120.3, 121.1, 125.2, 126.7, 127.7, 128.8, 129.4, 129.8, 131.8, 135.8, 137.7, 139.0, 158.3; HRMS (ESI) calcd. for C₂₁H₁₇N₃Na[M+Na]⁺: 334.1315, found: 334.1313.

(E)-6-Methyl-1-pyrimidin-2-yl-2-styryl-1H-indole (3ea), yellow solid, mp: 121.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.56(s, 3H), 7.03(s, 1H), 7.12(d, *J*=7.92Hz, 1H), 7.16~7.20(m, 2H), 7.30(t, *J*=7.28Hz, 1H), 7.40(t, *J*=7.44Hz, 2H), 7.55(dd, *J*=3.12, 8.12Hz, 3H), 7.72(d, *J*=16.20Hz, 1H), 8.16(s, 1H), 8.87(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 22.2, 105.3, 113.9, 117.2, 120.1, 120.8, 124.0, 126.6, 127.2, 127.5, 128.7, 129.1, 133.6, 137.7, 137.8, 138.3, 158.2, 158.3; HRMS (ESI) calcd. for C₂₁H₁₈N₃[M+H]⁺: 312.1495, found: 312.1493.

(E)-7-Methyl-1-pyrimidin-2-yl-2-styryl-1H-indole (3fa), red oil; ¹H NMR (400 MHz, CDCl₃) δ 2.00(s, 3H), 7.03~7.05(m, 2H), 7.16(t, *J*=7.32Hz, 3H), 7.25~7.29(m, 1H), 7.33~7.37(m, 3H), 7.42~7.44(m, 2H), 7.56(d, *J*=7.80Hz, 1H), 8.93(d, *J*=4.84Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 19.9, 102.9, 118.0, 118.6, 119.5, 121.9, 122.0, 125.9, 126.6, 127.8, 128.7, 129.8, 131.0, 137.2, 137.4, 139.5, 158.6, 158.9; HRMS (ESI) calcd. for C₂₁H₁₈N₃[M+H]⁺: 312.1495, found: 312.1499.

(E)-5-Methoxy-1-pyrimidin-2-yl-2-styryl-1H-indole (3ga), yellow solid, mp: 99.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.93(s, 3H), 6.97~7.00(m, 2H), 7.09~7.11(m, 2H), 7.19(d, *J*=16.20Hz, 1H), 7.28~7.33(m, 1H), 7.41(t, *J*=7.44Hz, 2H), 7.56(d, *J*=7.56Hz, 2H), 7.82(d, *J*=16.2Hz, 1H), 8.34(d, *J*=9.08Hz, 1H), 8.80(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 55.7, 102.3, 105.3, 112.9, 115.4, 117.0, 121.05, 126.7, 127.6, 128.7, 129.5, 130.2, 132.4, 137.6, 139.5, 155.8, 158.1, 158.2; HRMS (ESI) calcd. for C₂₁H₁₇N₃NaO[M+Na]⁺: 350.1264, found: 350.1258.

(E)-5-Chloro-1-pyrimidin-2-yl-2-styryl-1H-indole (3ha), Orange solid, mp: 106.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.94(s, 1H), 7.14~7.20(m, 2H), 7.26(dd, *J*=1.76, 8.84Hz, 1H), 7.32(t, *J*=7.20Hz, 1H), 7.41(t, *J*=7.44Hz, 2H), 7.53~7.59(m, 3H), 7.74(d, *J*=16.20Hz, 1H), 8.30(d, *J*=8.88Hz, 1H), 8.81(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 104.4, 115.5, 117.5, 119.7, 120.4, 123.5, 126.8, 127.8, 127.9, 128.8, 130.4, 130.6, 135.7, 137.3, 140.3, 157.9, 158.3; HRMS (ESI) calcd. for C₂₀H₁₄ClN₃Na[M+Na]⁺: 354.0768, found: 354.0772.

(E)-5-Bromo-1-pyrimidin-2-yl-2-styryl-1H-indole (3ia), brown solid, mp: 104 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.92(s, 1H), 7.13(t, *J*=4.80Hz, 1H), 7.18(d, *J*=16.16Hz, 1H), 7.33(t, *J*=7.32Hz, 1H), 7.38~7.43(m, 3H), 7.54(d, *J*=7.64Hz, 2H), 7.74(t, *J*=7.80Hz, 2H), 8.25(d, *J*=8.88Hz, 1H), 8.80(d, *J*=4.84Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 104.3, 115.6, 115.9, 117.6, 120.4, 122.7, 126.1, 126.8, 127.9, 128.8, 130.5, 131.2, 136.0, 137.3, 140.1, 157.8, 158.3; HRMS (ESI) calcd. for C₂₀H₁₅BrN₃[M+H]⁺: 376.0444, found: 376.0435.

(E)-5-Fluoro-1-pyrimidin-2-yl-2-styryl-1H-indole (3ja), yellow solid, mp: 120.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.99(s, 1H), 7.05~7.13(m, 2H), 7.20(d, *J*=16.20Hz, 1H), 7.29~7.35(m, 2H), 7.42(t, *J*=7.48Hz, 2H), 7.56(d, *J*=7.68Hz, 2H), 7.79(d, *J*=16.20Hz, 1H), 8.36(dd, *J*=4.64, 9.08Hz, 1H), 8.80(d, *J*=4.80Hz, 2H); ¹³C NMR

(100.6 MHz, CDCl₃) δ 104.9, 105.0, 105.2, 105.4, 111.2, 111.4, 115.4, 115.5, 117.4, 120.6, 126.8, 127.9, 128.8, 130.1, 130.3, 133.8, 137.4, 140.5, 157.9, 158.1, 158.3, 160.4; HRMS (ESI) calcd. for C₂₀H₁₅FN₃[M+H]⁺: 316.1245, found:316.1238.

(E)-5-Nitro-1-pyrimidin-2-yl-2-styryl-1H-indole (3ka), yellow solid, mp: 173.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.08(s, 1H), 7.21(d, *J*=16.24Hz, 1H), 7.31~7.34(m, 2H), 7.39(t, *J*=7.48Hz, 2H), 7.52(d, *J*=7.68Hz, 2H), 7.65(d, *J*=16.20Hz, 1H), 8.13(dd, *J*=1.88, 9.20Hz, 1H), 8.31(d, *J*=9.16Hz, 1H), 8.49(d, *J*=1.80Hz, 1H), 8.91(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.3, 114.1, 116.6, 118.5, 119.4, 126.8, 128.2, 128.8, 128.9, 131.9, 136.9, 140.1, 142.1, 143.4, 157.4, 158.4, 158.6; HRMS (ESI) calcd. for C₂₀H₁₅N₄O₂[M+H]⁺: 343.1190, found:343.1188.

(E)-1-Pyrimidin-2-yl-2-styryl-1H-indole-5-carboxylic acid methyl ester (3la), red oil; ¹H NMR (400 MHz, CDCl₃) δ 3.98(s, 3H), 7.07(s, 1H), 7.18(d, *J*=8.96Hz, 1H), 7.21(t, *J*=4.92Hz, 1H), 7.30(d, *J*=7.40Hz, 1H), 7.38(t, *J*=7.28Hz, 2H), 7.52(d, *J*=7.36Hz, 2H), 7.68(d, *J*=16.2Hz, 1H), 7.99(dd, *J*=1.68, 8.80Hz, 1H), 8.31(d, *J*=8.84Hz, 1H), 8.37(d, *J*=1.40Hz, 1H), 8.85(d, *J*=4.84Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 52.0, 105.5, 113.7, 117.9, 120.1, 122.8, 124.2, 124.7, 126.7, 127.9, 128.7, 129.0, 130.6, 137.2, 139.9, 140.3, 157.8, 158.4, 167.8; HRMS (ESI) calcd. for C₂₂H₁₇N₃NaO₂[M+Na]⁺: 378.1213, found: 378.1207.

(E)-3-Methyl-1-pyrimidin-2-yl-2-styryl-1H-indole (3ma), white solid, mp: 120.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.60(s, 3H), 6.85(d, *J*=16.44Hz, 1H), 7.12(t, *J*=4.76Hz, 1H), 7.28~7.44(m, 5H), 7.56~7.62(m, 3H), 7.67(d, *J*=7.48Hz, 1H), 8.38(d, *J*=8.08Hz, 1H), 8.82(d, *J*=4.76Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 10.7, 113.8, 115.7, 116.9, 118.9, 120.9, 122.0, 124.1, 126.5, 127.5, 128.7, 130.9, 131.4, 134.0, 136.6, 137.9, 158.2, 158.4; HRMS (ESI) calcd. for C₂₁H₁₈N₃[M+H]⁺: 312.1495, found:312.1484.

(E)-3-Phenyl-1-pyrimidin-2-yl-2-styryl-1H-indole (3na), red oil; ¹H NMR (400 MHz, CDCl₃) δ 6.45(d, *J*=16.52Hz, 1H), 7.21~7.24(m, 2H), 7.26~7.33(m, 5H), 7.35~7.40(m, 1H), 7.45(d, *J*=7.44Hz, 1H), 7.52~7.57(m, 3H), 7.63~7.68(m, 3H), 8.23(d, *J*=8.28Hz, 1H), 8.89(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 113.1, 117.8, 118.9, 119.7, 121.6, 122.4, 124.3, 126.4, 127.0, 127.6, 128.6, 128.7, 129.8, 130.6, 133.2, 133.7, 134.8, 137.3, 137.6, 158.5, 158.5; HRMS (ESI) calcd. for C₂₆H₂₀N₃[M+H]⁺: 374.1652, found:374.1657.

(E)-1-Pyrimidin-2-yl-2-styryl-1H-indole-3-carbonitrile (3oa), yellow solid, mp: 174.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.28~7.38(m, 6H), 7.52(dd, *J*=5.00, 12.68Hz, 3H), 7.67~7.75(m, 2H), 8.12~8.14(m, 1H), 8.89(dd, *J*=0.56, 4.84Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 88.2, 114.3, 116.5, 117.1, 119.1, 123.9, 125.3, 127.2, 128.2, 128.8, 129.0, 135.8, 136.0, 136.3, 144.5, 156.9, 158.4, 158.7; HRMS (ESI) calcd. for C₂₁H₁₄N₄Na[M+Na]⁺: 345.1111, found: 345.1107.

(E)-1-Pyrimidin-2-yl-2-(2-p-tolyl-vinyl)-1H-indole (3ab), colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 2.44(s, 3H), 7.08(s, 1H), 7.15(t, *J*=4.80Hz, 1H), 7.20~7.24(m, 3H), 7.28~7.38(m, 2H), 7.48(d, *J*=7.96Hz, 2H), 7.68~7.76(m, 2H), 8.38~8.40(d, *J*=8.12Hz, 1H), 8.86(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 21.4, 105.1, 114.1, 117.3, 119.7, 120.4, 122.4, 123.5, 126.6, 129.5, 129.5, 129.8, 134.8, 137.4, 137.6, 139.1, 158.2, 158.3; HRMS (ESI) calcd. for C₂₁H₁₈N₃[M+H]⁺: 312.1495,

found:312.1485.

(E)-2-[2-(4-Methoxy-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ac), red oil; ¹H NMR (400 MHz, CDCl₃) δ 3.86(s, 3H), 6.93(d, *J*=8.60Hz, 2H), 7.02(s, 1H), 7.14~7.19(m, 2H), 7.25~7.31(m, 2H), 7.48(d, *J*=8.56Hz, 2H), 7.59~7.66(m, 2H), 8.33(d, *J*=8.04Hz, 1H), 8.86(d, *J*=4.80Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 55.3, 104.7, 114.0, 114.1, 117.3, 118.5, 120.3, 122.3, 123.3, 127.9, 129.4, 129.5, 130.4, 137.3, 139.2, 158.2, 158.3, 159.4; HRMS (ESI) calcd. for C₂₁H₁₈N₃O[M+H]⁺: 328.1444, found:328.1448.

(E)-2-[2-(4-Chloro-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ad), colorless solid, mp: 103.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 7.12 (d, *J* = 16.16 Hz, 1H), 7.17 (t, *J* = 4.76 Hz, 1H), 7.27~7.36 (m, 4H), 7.44 (d, *J* = 8.40 Hz, 2H), 7.66 (d, *J* = 7.52 Hz, 1H), 7.72 (d, *J* = 16.16 Hz, 1H), 8.37 (d, *J* = 8.20 Hz, 1H), 8.84 (d, *J* = 4.80 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.6, 114.2, 117.3, 120.5, 121.3, 122.5, 123.8, 127.8, 128.2, 128.8, 129.4, 133.1, 136.1, 137.4, 138.5, 158.1, 158.3; HRMS (ESI) calcd. for C₂₀H₁₅ClN₃[M+H]⁺: 332.0949, found:332.0937.

(E)-2-[2-(4-Bromo-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ae), red oil; ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 1H), 7.10 (d, *J* = 16.20 Hz, 1H), 7.17 (t, *J* = 4.80 Hz, 1H), 7.26~7.30 (m, 1H), 7.31~7.38 (m, 3H), 7.49 (d, *J* = 8.36 Hz, 2H), 7.65 (d, *J* = 7.56 Hz, 1H), 7.73 (d, *J* = 16.16 Hz, 1H), 8.37 (d, *J* = 8.24 Hz, 1H), 8.84 (d, *J* = 4.80 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.7, 114.2, 117.3, 120.5, 121.3, 121.5, 122.5, 123.8, 128.1, 128.2, 129.4, 131.8, 136.5, 137.4, 138.5, 158.1, 158.3; HRMS (ESI) calcd. for C₂₀H₁₅BrN₃[M+H]⁺: 376.0444, found:376.0439.

(E)-2-[2-(4-Fluoro-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3af), red oil; ¹H NMR (400 MHz, CDCl₃) δ 7.04~7.18 (m, 5H), 7.27~7.35 (m, 2H), 7.49 (dd, *J* = 5.64, 8.36 Hz, 2H), 7.65 (s, 1H), 7.68 (d, *J* = 7.28 Hz, 1H), 8.37 (d, *J* = 8.16 Hz, 1H), 8.85 (d, *J* = 4.76 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.3, 114.2, 115.5, 115.7, 117.3, 120.4, 120.5, 122.4, 123.6, 128.1, 128.2, 128.4, 129.4, 133.8, 137.4, 138.7, 158.1, 158.3; HRMS (ESI) calcd. for C₂₀H₁₅FN₃[M+H]⁺: 316.1245, found:316.1238.

(E)-4-[2-(1-Pyrimidin-2-yl-1H-indol-2-yl)-vinyl]-phenol (3ag), orange solid, mp: 102.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 1H), 7.08 (d, *J* = 8.56 Hz, 2H), 7.16 (d, *J* = 16.28 Hz, 1H), 7.21 (t, *J* = 4.80 Hz, 1H), 7.24~7.27 (m, 1H), 7.28~7.33 (m, 1H), 7.52 (d, *J* = 8.56 Hz, 2H), 7.63~7.69 (m, 2H), 8.34 (d, *J* = 8.24Hz, 1H), 8.86 (d, *J* = 4.80 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 105.4, 114.1, 117.3, 120.4, 120.9, 121.7, 122.4, 123.6, 127.5, 128.7, 129.4, 135.1, 137.4, 138.7, 150.6, 158.1, 158.3; HRMS (ESI) calcd. for C₂₀H₁₆N₃O[M+H]⁺: 314.1288, found:314.1285.

(E)-1-Pyrimidin-2-yl-2-[2-(4-trifluoromethyl-phenyl)-vinyl]-1H-indole (3ah), colorless solid, mp: 98.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.08 (s, 1H), 7.15~7.20 (m, 2H), 7.29 (t, *J* = 7.56 Hz, 1H), 7.35 (t, *J* = 7.28 Hz, 1H), 7.58~7.67 (m, 5H), 7.83 (t, *J* = 16.16 Hz, 1H), 8.39 (d, *J* = 8.28 Hz, 1H), 8.86 (d, *J* = 4.80 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 106.2, 114.3, 117.3, 120.6, 122.6, 123.3, 124.0, 125.6, 125.6, 126.7, 127.7, 128.9, 129.3, 137.5, 138.1, 141.0, 158.1, 158.3; HRMS (ESI) calcd. for C₂₁H₁₄F₃N₃Na[M+Na]⁺: 388.1032, found: 388.1029.

(E)-2-[2-(4-Nitro-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ai), orange solid, mp: 217.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 1H), 7.20 (d, *J* = 16.28 Hz, 1H),

7.25~7.29 (m, 2H), 7.32~7.37 (m, 1H), 7.65 (dd, $J = 7.80, 13.56$ Hz, 3H), 7.94 (d, $J = 16.24$ Hz, 1H), 8.23 (d, $J = 8.80$ Hz, 2H), 8.38 (d, $J = 8.32$ Hz, 1H), 8.89 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 106.9, 114.4, 117.4, 120.8, 122.7, 124.2, 124.4, 125.4, 126.7, 126.9, 129.2, 137.6, 137.7, 144.1, 158.1, 158.4; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_4\text{NaO}_2[\text{M}+\text{Na}]^+$: 365.1009, found: 365.0997.

(E)-4-[2-(1-Pyrimidin-2-yl-1H-indol-2-yl)-vinyl]-benzoic acid methyl ester (3aj), yellow solid, mp: 117.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.95 (s, 3H), 7.08 (s, 1H), 7.16~7.20 (m, 2H), 7.27 (t, $J = 7.24$ Hz, 1H), 7.33 (t, $J = 7.24$ Hz, 1H), 7.55 (d, $J = 8.16$ Hz, 2H), 7.65 (d, $J = 7.60$ Hz, 1H), 7.86 (d, $J = 16.16$ Hz, 1H), 8.04 (d, $J = 8.12$ Hz, 2H), 8.37 (d, $J = 8.28$ Hz, 1H), 8.85 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 52.1, 106.1, 114.3, 117.3, 120.6, 122.5, 123.3, 124.0, 126.4, 128.2, 128.8, 129.3, 130.0, 137.5, 138.2, 142.0, 158.1, 158.3, 166.9; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2[\text{M}+\text{H}]^+$: 356.1394, found: 356.1388.

(E)-2-[2-(3-Methoxy-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ak), brown solid, mp: 90.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 3H), 6.88 (dd, $J = 2.20, 8.12$ Hz, 1H), 7.09 (d, $J = 11.12$ Hz, 2H), 7.14~7.21 (m, 3H), 7.28~7.36 (m, 3H), 7.68 (d, $J = 7.40$ Hz, 1H), 7.76 (d, $J = 16.12$ Hz, 1H), 8.38 (d, $J = 8.12$ Hz, 1H), 8.84 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 55.3, 105.4, 112.2, 113.1, 114.1, 117.3, 119.4, 120.4, 121.1, 122.4, 123.6, 129.4, 129.5, 129.7, 137.4, 138.8, 139.0, 158.1, 158.3, 159.9; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}[\text{M}+\text{H}]^+$: 328.1444, found: 328.1338.

(E)-2-[2-(3-Bromo-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3al), white solid, mp: 108.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (s, 1H), 7.08 (d, $J = 16.16$ Hz, 1H), 7.17 (t, $J = 4.80$ Hz, 1H), 7.23 (t, $J = 7.84$ Hz, 1H), 7.27~7.31 (m, 1H), 7.32~7.36 (m, 1H), 7.41 (d, $J = 7.88$ Hz, 2H), 7.65~7.67 (m, 2H), 7.73 (d, $J = 16.20$ Hz, 1H), 8.38 (d, $J = 8.28$ Hz, 1H), 8.84 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 105.9, 114.3, 117.3, 120.6, 122.2, 122.5, 122.9, 123.9, 125.4, 127.8, 129.3, 130.2, 130.4, 137.5, 138.3, 139.8, 158.0, 158.4; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{15}\text{BrN}_3[\text{M}+\text{H}]^+$: 376.0444, found: 376.0436.

(E)-2-[2-(2-Bromo-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3am), yellow solid, mp: 134.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.12~7.17 (m, 3H), 7.28~7.37 (m, 3H), 7.54 (d, $J = 16.12$ Hz, 1H), 7.63 (dd, $J = 0.80, 8.00$ Hz, 1H), 7.69 (d, $J = 7.72$ Hz, 2H), 7.75 (d, $J = 16.12$ Hz, 1H), 8.38 (d, $J = 8.20$ Hz, 1H), 8.84 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 106.3, 114.3, 117.3, 120.6, 122.5, 123.3, 123.9, 124.1, 126.8, 127.6, 128.0, 128.8, 129.4, 133.2, 137.2, 137.5, 138.4, 158.1, 158.3; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{15}\text{BrN}_3[\text{M}+\text{H}]^+$: 376.0444, found: 376.0434.

(E)-2-[2-(2-Chloro-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3an), brown solid, mp: 110.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.14~7.17 (m, 2H), 7.22 (t, $J = 7.44$ Hz, 1H), 7.26~7.36 (m, 3H), 7.44 (d, $J = 7.84$ Hz, 1H), 7.58 (d, $J = 16.2$ Hz, 1H), 7.69 (t, $J = 7.68$ Hz, 2H), 7.78 (d, $J = 16.2$ Hz, 1H), 8.38 (d, $J = 8.24$ Hz, 1H), 8.84 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 106.2, 114.2, 117.3, 120.6, 122.5, 123.2, 123.8, 125.3, 126.6, 126.9, 128.5, 129.4, 129.9, 133.4, 135.5, 137.5, 138.5, 158.1, 158.3; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{15}\text{ClN}_3[\text{M}+\text{H}]^+$: 332.0949, found: 332.0944.

(E)-1-Pyrimidin-2-yl-2-(2-o-tolyl-vinyl)-1H-indole (3ao), red oil; ^1H NMR (400 MHz, CDCl_3) δ 2.51 (s, 3H), 7.08 (s, 1H), 7.18 (t, $J = 4.8$ Hz, 1H), 7.24~7.27 (m, 3H),

7.29~7.31 (m, 1H), 7.32~7.36 (m, 1H), 7.42 (d, $J = 16.08$ Hz, 1H), 7.63~7.69 (m, 3H), 8.36 (d, $J = 8.12$ Hz, 1H), 8.86 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.0, 105.3, 114.1, 117.3, 120.4, 121.8, 122.4, 123.6, 125.6, 126.2, 127.4, 127.6, 129.5, 130.5, 135.9, 136.4, 137.4, 139.2, 158.2, 158.3; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_3[\text{M}+\text{H}]^+$: 312.1495, found:312.1491.

(E)-2-[2-(2,3-Dimethoxy-phenyl)-vinyl]-1-pyrimidin-2-yl-1H-indole (3ap), colorless solid, mp: 131.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.91(s, 6H), 6.86(dd, $J=1.08, 8.08\text{Hz}$, 1H), 7.08(t, $J=8.04\text{Hz}$, 1H), 7.12(s, 1H), 7.18(t, $J=4.84\text{Hz}$, 1H), 7.23~7.33 (m, 3H), 7.50 (d, $J = 16.4$ Hz, 1H), 7.65~7.67 (m, 1H), 7.81 (d, $J = 16.4$ Hz, 1H), 8.33 (d, $J = 8.16$ Hz, 1H), 8.85 (d, $J = 4.84$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 55.9, 61.1, 105.4, 111.4, 114.0, 117.3, 118.3, 120.4, 121.9, 122.3, 123.5, 124.0, 124.1, 129.5, 131.7, 137.4, 139.2, 147.0, 153.2, 158.2, 158.3; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_2[\text{M}+\text{H}]^+$: 358.1550, found:358.1551.

(E)-2-(2-Naphthalen-2-yl-vinyl)-1-pyrimidin-2-yl-1H-indole (3aq), yellow solid, mp: 76.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.13~7.16 (m, 2H), 7.28~7.40 (m, 3H), 7.49~7.55 (m, 2H), 7.71 (d, $J = 7.60$ Hz, 1H), 7.76 (d, $J = 8.68$ Hz, 1H), 7.85~7.92(m, 5H), 8.41 (d, $J = 8.20$ Hz, 1H), 8.86 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 105.4, 114.2, 117.3, 120.5, 121.1, 122.5, 123.7, 123.7, 126.0, 126.4, 126.8, 127.8, 128.1, 128.3, 129.5, 129.8, 133.1, 133.8, 135.1, 137.5, 139.0, 158.2, 158.3; HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{17}\text{N}_3\text{Na}[\text{M}+\text{Na}]^+$: 370.1315, found: 370.1306.

(E)-1-Pyrimidin-2-yl-2-(2-thiophen-2-yl-vinyl)-1H-indole (3ar), red oil; ^1H NMR (400 MHz, CDCl_3) δ 7.02~7.05 (m, 2H), 7.11 (d, $J = 3.36$ Hz, 1H), 7.18~7.33 (m, 5H), 7.62 (dd, $J = 7.48, 16.8$ Hz, 2H), 8.34 (d, $J = 8.16$ Hz, 1H), 8.86 (d, $J = 4.84$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 105.2, 114.1, 117.3, 120.3, 120.4, 122.4, 122.7, 123.6, 124.4, 126.2, 127.7, 129.4, 137.4, 138.4, 143.1, 158.1, 158.3; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{S}[\text{M}+\text{H}]^+$: 304.0903, found:304.0899

(E)-2-(2-Furan-2-yl-vinyl)-1-pyrimidin-2-yl-1H-indole (3as), red oil; ^1H NMR (400 MHz, CDCl_3) δ 6.40~6.46 (m, 2H), 7.00~7.03 (m, 2H), 7.16 (t, $J = 4.80$ Hz, 1H), 7.26~7.34 (m, 2H), 7.43 (s, 1H), 7.65 (dd, $J = 3.52, 11.24$ Hz, 2H), 8.32 (d, $J = 8.12$ Hz, 1H), 8.85 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 104.9, 109.0, 111.8, 113.9, 117.4, 117.4, 118.8, 120.4, 122.4, 123.6, 129.4, 137.5, 138.5, 142.2, 153.4, 158.0, 158.4; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}[\text{M}+\text{H}]^+$: 288.1131, found:288.1126.

(E)-2-(4-Phenyl-buta-1,3-dienyl)-1-pyrimidin-2-yl-1H-indole (3at), brown solid, mp: 126.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.73 (d, $J = 14.48$ Hz, 1H), 7.00~7.10 (m, 3H), 7.19 (t, $J = 4.80$ Hz, 1H), 7.25~7.32 (m, 3H), 7.34~7.39 (m, 3H), 7.49 (d, $J = 7.64$ Hz, 2H), 7.65 (d, $J = 7.48$ Hz, 1H), 8.31 (d, $J = 8.12$ Hz, 1H), 8.87 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 105.2, 113.9, 117.4, 120.4, 122.4, 123.6, 124.1, 126.7, 126.5, 127.6, 128.7, 129.5, 130.5, 132.8, 137.5, 138.6, 158.1, 158.4; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{Na}[\text{M}+\text{Na}]^+$: 346.1315, found: 346.1318.

(E)-3-(1-Pyrimidin-2-yl-1H-indol-2-yl)-acrylic acid ethyl ester (3au), red oil; ^1H NMR (400 MHz, CDCl_3) δ 1.36(t, $J=7.12\text{Hz}$, 3H), 4.29(q, $J=7.12\text{Hz}$, 2H), 6.50(d, $J=15.84\text{Hz}$, 1H), 7.15(s, 1H), 7.23(t, $J=4.92\text{Hz}$, 1H), 7.27~7.28(m, 1H), 7.36(td, $J=1.16, 7.24\text{Hz}$, 1H), 7.66(d, $J=7.80\text{Hz}$, 1H), 8.27(d, $J=15.88\text{Hz}$, 1H), 8.37(d,

$J=8.48\text{Hz}$, 1H), 8.87(d, $J=4.84\text{Hz}$, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.4, 60.5, 109.0, 114.4, 117.5, 117.9, 121.2, 122.7, 125.0, 128.8, 135.6, 136.4, 137.9, 157.7, 158.4, 167.1; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{NaO}_2[\text{M}+\text{Na}]^+$: 316.1056, found: 316.1060.

(*E/Z*)-2-(prop-1-enyl)-1-(pyrimidin-2-yl)-1H-indole (3av), red oil; ^1H NMR (400 MHz, CDCl_3): **E isomer**: δ 1.96 (dd, $J = 1.76, 6.76$ Hz, 3H), 6.30~6.39 (m, 1H), 6.82 (s, 1H), 6.91~6.95 (m, 1H), 7.17~7.19 (m, 1H), 7.22~7.28 (m, 2H), 7.58~7.61 (m, 1H), 8.24~8.26 (m, 1H), 8.85 (d, $J = 4.84$ Hz, 2H); **Z isomer**: δ 2.08 (dd, $J = 1.8, 7.08$ Hz, 3H), 5.90~5.98 (m, 1H), 6.77 (s, 1H), 6.77~6.79 (m, 1H), 7.17~7.19 (m, 1H), 7.22~7.28 (m, 2H), 7.63~7.65 (m, 1H), 8.26~8.27 (m, 1H), 8.84 (d, $J=4.64\text{Hz}$, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) **E isomer**: δ 18.9, 104.2, 113.7, 117.2, 120.1, 122.1, 122.9, 123.0, 127.6, 129.5, 136.9, 139.1, 158.1, 158.3; **Z isomer**: δ 15.5, 108.4, 113.7, 117.2, 120.3, 121.7, 122.0, 123.4, 127.1, 129.4, 136.1, 136.3, 158.1, 158.3; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_3[\text{M}+\text{H}]^+$: 236.1182, found: 236.1178.

(*E*)-2-(2-Methyl-propenyl)-1-pyrimidin-2-yl-1H-indole (3aw), colorless solid, mp: 68.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.00 (s, 3H), 2.06 (s, 3H), 6.60 (s, 1H), 6.67 (s, 1H), 7.15 (td, $J = 0.72, 4.68$ Hz, 1H), 7.23~7.31 (m, 2H), 7.64 (d, $J=7.32\text{Hz}$, 1H), 8.21 (d, $J = 7.80$ Hz, 1H), 8.83 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.5, 27.1, 107.5, 113.5, 117.2, 117.2, 120.1, 121.9, 123.0, 129.5, 136.3, 136.8, 137.4, 158.1, 158.2; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{Na}[\text{M}+\text{Na}]^+$: 272.1158, found: 272.1163.

(*E*)-2-(2,2-Diphenyl-vinyl)-1-pyrimidin-2-yl-1H-indole (3ax), white solid, mp: 92.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.14 (s, 1H), 7.13 (t, $J = 4.80$ Hz, 1H), 7.17~7.21 (m, 1H), 7.26~7.30 (m, 1H), 7.33~7.45 (m, 12H), 8.25 (dd, $J = 0.32, 8.32$ Hz, 1H), 8.81 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 109.0, 113.5, 117.3, 119.6, 120.6, 122.1, 123.6, 127.5, 127.8, 128.3, 128.7, 129.3, 130.4, 130.6, 136.6, 137.4, 140.7, 142.0, 143.1, 158.0, 158.3; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{19}\text{N}_3\text{Na}[\text{M}+\text{Na}]^+$: 396.1471, found: 396.1478.

2-Isopropenyl-1-pyrimidin-2-yl-1H-indole (5aa), red oil; ^1H NMR (400 MHz, CDCl_3) δ 2.00(s, 3H), 5.12~5.13 (m, 2H), 6.70 (s, 1H), 7.19 (t, $J = 4.80$ Hz, 1H), 7.23 (td, $J = 1.16, 7.68$ Hz, 1H), 7.26~7.30 (m, 1H), 7.61~7.63 (m, 1H), 8.16 (d, $J = 8.12$ Hz, 1H), 8.84 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 22.6, 107.4, 113.0, 114.9, 117.5, 120.6, 122.1, 123.5, 129.1, 137.8, 138.0, 142.3, 158.3; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_3[\text{M}+\text{H}]^+$: 236.1182, found: 236.1185.

2-(1-Phenyl-vinyl)-1-pyrimidin-2-yl-1H-indole (5ab), colorless solid, mp: 135.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.68 (s, 1H), 5.77 (s, 1H), 6.84 (t, $J = 4.80$ Hz, 1H), 6.97 (d, $J = 0.68$ Hz, 1H), 7.10~7.17 (m, 3H), 7.27~7.40 (m, 4H), 7.74 (d, $J = 7.52$ Hz, 1H), 8.30~8.32 (m, 1H), 8.52 (d, $J = 4.84$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 109.9, 113.6, 115.3, 116.8, 120.7, 122.2, 123.9, 126.8, 127.4, 128.0, 129.0, 137.3, 140.2, 140.5, 143.2, 157.3, 157.8; HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_3[\text{M}+\text{H}]^+$: 298.1339, found: 298.1335.

2-[1-(6-Methoxy-naphthalen-2-yl)-vinyl]-1-pyrimidin-2-yl-1H-indole (5ac), red oil; ^1H NMR (400 MHz, CDCl_3) δ 3.89 (s, 3H), 5.74 (d, $J = 14.84$ Hz, 2H), 6.73 (t, $J = 4.80$ Hz, 1H), 6.97 (s, 1H), 7.02 (s, 1H), 7.05 (dd, $J = 2.28, 9.0$ Hz, 1H), 7.31 (t, $J =$

7.44 Hz, 1H), 7.36 (t, $J = 7.16$ Hz, 1H), 7.47 (d, $J = 8.56$ Hz, 1H), 7.51~7.56 (m, 3H), 7.73 (d, $J = 7.56$ Hz, 1H), 8.29 (d, $J = 8.16$ Hz, 1H), 8.43 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 55.2, 105.5, 109.9, 113.7, 115.1, 116.8, 118.7, 120.7, 122.2, 123.8, 125.4, 125.7, 126.5, 128.4, 129.1, 129.7, 133.8, 135.8, 137.3, 140.4, 143.2, 157.4, 157.6; HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_3\text{O}[\text{M}+\text{H}]^+$: 378.1601, found: 378.1605.

2-(1-Benzyl-vinyl)-1-pyrimidin-2-yl-1H-indole (5ad), brown oil; ^1H NMR (400 MHz, CDCl_3) δ 3.63 (s, 2H), 5.09 (d, $J = 1.44$ Hz, 1H), 5.30 (t, $J = 0.56$ Hz, 1H), 6.62 (s, 1H), 7.17~7.34 (m, 8H), 7.60 (dd, $J = 0.76, 7.24$ Hz, 1H), 8.28 (dd, $J = 0.52, 8.16$ Hz, 1H), 8.86 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 42.7, 108.4, 113.5, 116.2, 117.5, 120.6, 122.1, 123.6, 126.2, 127.9, 128.3, 129.2, 137.7, 139.2, 141.3, 142.3, 157.8, 158.3; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_3[\text{M}+\text{H}]^+$: 312.1495, found: 312.1488.

(E)-3-(1-Pyrimidin-2-yl-1H-indol-2-yl)-but-2-enoic acid methyl ester (5ae), red oil; ^1H NMR (400 MHz, CDCl_3) δ 2.33 (d, $J = 1.20$ Hz, 3H), 3.77 (s, 3H), 6.16 (d, $J = 1.20$ Hz, 1H), 6.80 (s, 1H), 7.16 (td, $J = 0.76, 4.84$ Hz, 1H), 7.28 (d, $J = 7.44$ Hz, 1H), 7.33~7.37 (m, 1H), 7.64 (d, $J = 7.52$ Hz, 1H), 8.38 (dd, $J = 0.36, 8.24$ Hz, 1H), 8.79 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 20.0, 51.0, 109.6, 114.0, 116.9, 117.4, 121.1, 122.6, 124.6, 128.8, 138.3, 142.3, 150.4, 157.9, 158.3, 167.2; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{NaO}_2[\text{M}+\text{Na}]^+$: 316.1056, found: 316.1049.

(E)-2-(1-Methyl-propenyl)-1-pyrimidin-2-yl-1H-indole (5af), red oil; ^1H NMR (400 MHz, CDCl_3) δ 1.78~1.79 (m, 6H), 5.81~5.87 (m, 1H), 6.57 (s, 1H), 7.16 (t, $J = 4.84$ Hz, 1H), 7.21~7.27 (m, 2H), 7.57~7.59 (m, 1H), 8.17 (d, $J = 8.24$ Hz, 1H), 8.82 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.1, 16.9, 106.4, 113.1, 117.3, 120.3, 121.9, 123.1, 124.7, 129.3, 129.7, 137.5, 139.8, 144.5, 158.3; HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3[\text{M}+\text{H}]^+$: 250.1339, found: 250.1341.

(E)-2-(1-Methyl-2-phenyl-vinyl)-1-pyrimidin-2-yl-1H-indole (5ag),⁵ red oil; ^1H NMR (400 MHz, CDCl_3) δ 2.22 (d, $J = 0.96$ Hz, 3H), 6.78 (s, 1H), 6.85 (s, 1H), 7.12 (t, $J = 4.84$ Hz, 1H), 7.31~7.40 (m, 3H), 7.44~7.46 (m, 4H), 7.71 (d, $J = 7.76$ Hz, 1H), 8.34 (d, $J = 8.20$ Hz, 1H), 8.82 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 19.3, 107.4, 113.4, 117.5, 120.7, 122.3, 123.6, 126.7, 128.3, 129.2, 129.3, 129.4, 131.4, 138.0, 144.6, 158.2, 158.4; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_3[\text{M}+\text{H}]^+$: 312.1495, found: 312.1489.

(E)-2-[1-(3-Nitro-benzylidene)-propyl]-1-pyrimidin-2-yl-1H-indole (5ah), red oil; ^1H NMR (400 MHz, CDCl_3) δ 1.09 (t, $J = 7.48$ Hz, 3H), 2.55 (q, $J = 7.48$ Hz, 2H), 6.66 (s, 1H), 6.80 (s, 1H), 7.14 (t, $J = 4.80$ Hz, 1H), 7.27~7.38 (m, 2H), 7.52 (t, $J = 7.96$ Hz, 1H), 7.64 (d, $J = 7.68$ Hz, 1H), 7.68 (d, $J = 7.24$ Hz, 1H), 8.12 (dd, $J = 1.36, 8.16$ Hz, 1H), 8.23 (s, 1H), 8.37 (d, $J = 8.32$ Hz, 1H), 8.80 (d, $J = 4.84$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 13.1, 25.1, 108.6, 113.8, 117.4, 120.6, 121.4, 122.3, 123.4, 123.8, 126.2, 129.2, 134.8, 137.8, 139.4, 141.3, 141.7, 148.3, 157.9, 158.2; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{NaO}_2[\text{M}+\text{Na}]^+$: 393.1322, found: 393.1326.

(E)-3-Phenyl-2-(1-pyrimidin-2-yl-1H-indol-2-yl)-acrylonitrile (5ai), colorless solid, mp: 177.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.95 (s, 1H), 7.20 (t, $J = 4.68$ Hz, 1H), 7.28~7.34 (m, 1H), 7.40~7.51 (m, 5H), 7.69 (d, $J = 7.72$ Hz, 1H), 7.93 (d, $J = 6.52$ Hz,

2H), 8.51 (d, $J = 8.40$ Hz, 1H), 8.83 (d, $J = 4.76$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 106.1, 110.6, 114.6, 117.3, 117.8, 121.1, 122.8, 125.0, 128.6, 129.0, 129.3, 130.6, 133.8, 134.9, 137.7, 142.6, 157.5, 158.3; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_4[\text{M}+\text{H}]^+$: 323.1291, found: 323.1288.

2-(2-Methyl-1-phenyl-propenyl)-1-pyrimidin-2-yl-1H-indole (5aj), yellow solid, mp: 131.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.89 (s, 3H), 1.94 (s, 3H), 6.66 (s, 1H), 7.02 (t, $J = 4.80$ Hz, 1H), 7.05~7.09 (m, 1H), 7.13~7.15 (m, 4H), 7.21~7.27 (m, 2H), 7.63~7.65 (m, 1H), 8.11 (d, $J = 7.60$ Hz, 1H), 8.66 (d, $J = 4.80$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 22.2, 23.4, 108.8, 113.2, 117.0, 120.2, 121.7, 123.0, 126.0, 127.3, 129.1, 129.3, 130.1, 134.3, 136.5, 140.7, 141.1, 157.6, 157.9; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3[\text{M}+\text{H}]^+$: 326.1652, found: 326.1654.

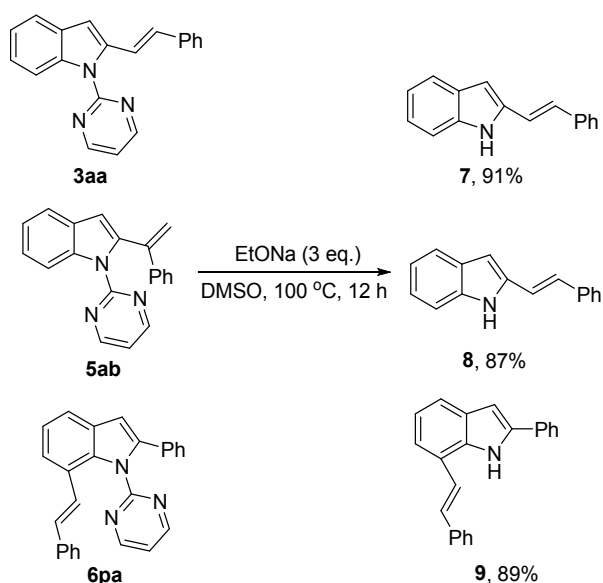
4. The general procedure for the direct C7-olefination of indoles

To an oven-dried pressure tube were sequentially added indole **1** (0.5 mmol), acrylic acid **2** (0.5 mmol), $[\text{Rh}(\text{COD})_2]\text{OTf}$ (11.71 mg, 5.0 mol%), $(t\text{BuCO})_2\text{O}$ (140.0 mg, 0.5 mmol) and anhydrous toluene (3.0 mL). After being degassed three times, the tube was heated and stirred vigorously at 140 °C for 2 h in an oil bath under nitrogen atmosphere. Then the tube was removed from the oil bath and cooled to room temperature. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product.

(E)-2-Phenyl-1-pyrimidin-2-yl-7-styryl-1H-indole (6pa), yellow solid, mp: 118.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.77 (s, 1H), 6.81 (d, $J = 24.96$ Hz, 2H), 7.15~7.17 (m, 3H), 7.27~7.30 (m, 6H), 7.37~7.43 (m, 4H), 7.69 (dd, $J = 0.96, 7.80$ Hz, 1H), 8.71 (d, $J = 4.88$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 105.6, 119.7, 120.5, 121.7, 122.3, 123.6, 126.0, 126.2, 127.3, 127.6, 128.2, 128.5, 129.0, 129.7, 129.8, 132.8, 136.4, 137.5, 142.3, 158.4, 159.9; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_3[\text{M}+\text{H}]^+$: 374.1652, found: 374.1655.

(E)-2-Methyl-1-pyrimidin-2-yl-7-styryl-1H-indole (6qa), colorless solid, mp: 159.8 °C ^1H NMR (400 MHz, CDCl_3) δ 2.46 (s, 3H), 6.48 (s, 1H), 6.57 (d, $J = 16.12$ Hz, 1H), 6.80 (d, $J = 16.12$ Hz, 1H), 7.10 (d, $J = 7.76$ Hz, 2H), 7.19~7.29 (m, 5H), 7.38 (d, $J = 7.40$ Hz, 1H), 7.53 (d, $J = 7.68$ Hz, 1H), 8.80 (d, $J = 4.84$ Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 14.2, 104.4, 118.8, 119.5, 121.4, 121.6, 122.9, 126.1, 126.5, 127.2, 128.5, 130.3, 135.1, 137.6, 138.3, 158.5, 159.0; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_3[\text{M}+\text{H}]^+$: 312.1495, found: 312.1497.

5. The general procedure for the deprotection of olefinated indoles



To an oven-dried pressure tube was added the olefinated indole (0.5 mmol), freshly prepared EtONa (1.5 mmol) and dry DMSO (3.0 mL). After being degassed by nitrogen for three times, the tube was heated and stirred vigorously at 100 °C for 12 h in an oil bath. Then the tube was removed from the oil bath and cooled to room temperature. The mixture was poured into 25 mL water and extracted with CH₂Cl₂ (20 mL × 3). The organic phase was dried by Na₂SO₄ and filtered. The filtrate was concentrated and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the unprotected indoles.

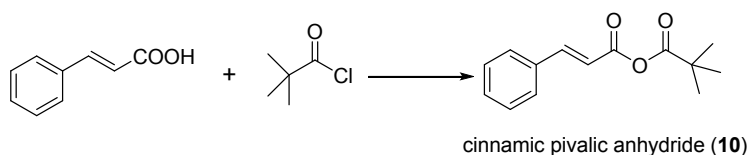
(E)-2-Styryl-1H-indole (7),¹¹ white solid, mp: 217.5 °C; ¹H NMR (400 MHz, d⁶-DMSO) δ 6.59 (s, 1H), 6.98 (t, *J* = 7.28 Hz, 1H), 7.11 (t, *J* = 7.44 Hz, 1H), 7.18~7.29 (m, 3H), 7.35~7.42 (m, 3H), 7.50 (d, *J* = 7.80 Hz, 1H), 7.57 (d, *J* = 7.56 Hz, 2H), 11.39 (s, 1H); ¹³C NMR (100.6 MHz, d⁶-DMSO) δ 103.5, 111.4, 119.7, 120.0, 120.5, 122.5, 126.6, 127.6, 128.0, 128.9, 129.3, 137.2, 137.4, 137.8; HRMS (ESI) calcd. for C₁₆H₁₄N[M+H]⁺: 220.1121, found: 220.1123.

2-(1-Phenyl-vinyl)-1H-indole (8),¹² yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 5.37 (s, 1H), 5.61 (s, 1H), 6.51 (s, 1H), 7.07~7.12 (m, 1H), 7.16~7.18 (m, 1H), 7.38~7.40 (m, 4H), 7.47~7.49 (m, 3H), 8.11 (br, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ 103.4, 110.8, 112.8, 120.2, 120.9, 122.8, 128.3, 128.4, 128.6, 128.7, 136.5, 137.9, 140.1, 141.7; HRMS (ESI) calcd. for C₁₆H₁₄N[M+H]⁺: 220.1121, found: 220.1124.

(E)-2-Phenyl-7-styryl-1H-indole (9), yellow solid, mp: 164.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.91 (d, *J* = 1.92 Hz, 1H), 7.18~7.25 (m, 2H), 7.35~7.52 (m, 8H), 7.63 (t, *J* = 7.76 Hz, 3H), 7.75 (d, *J* = 7.44 Hz, 2H), 8.60 (br, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ 100.6, 120.3, 120.5, 120.7, 121.4, 124.8, 125.3, 126.5, 127.8, 127.9, 128.8, 129.1, 129.9, 130.0, 132.3, 134.9, 137.5, 138.2; HRMS (ESI) calcd. for C₂₂H₁₈N[M+H]⁺: 296.1434, found: 296.1438.

6. The mechanistic study

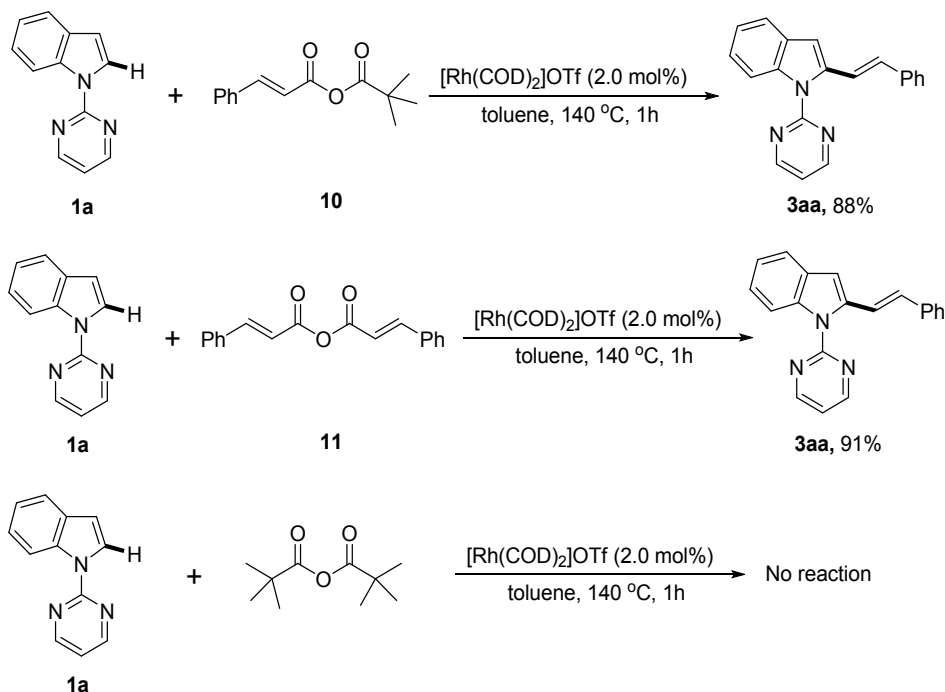
a)



Preparation of cinnamic pivalic anhydride (10): A solution of cinnamic acid (1.48 g, 10 mmol) was added dropwise distilled NEt_3 (1.01g, 10 mmol) in 20 mL of dry THF at $-15\text{ }^\circ\text{C}$, and then added trimethylacetyl chloride (1.21 g, 10 mmol) in 10 mL THF at $-15\text{ }^\circ\text{C}$. The reaction was monitored by TLC. When the acid disappeared, the reaction was poured into ice-cold saturated NaHCO_3 aqueous solution (20 mL). The organic layer was separated and the aqueous solution was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under vacuum to give cinnamic pivalic anhydride (2.11 g, 91%).

Cinnamic pivalic anhydride (10), colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 1.34 (s, 9H), 6.46 (d, $J = 15.92$ Hz, 1H), 7.41~7.45 (m, 3H), 7.55~7.58 (m, 2H), 7.77 (d, $J = 15.96$ Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 26.6, 40.0, 116.9, 128.6, 129.1, 131.3, 133.7, 148.4, 162.7, 174.1; HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_3[\text{M}+\text{H}]^+$: 233.1172, found: 233.1175.

b) the coupling reaction of anhydrides with **1a**:



General procedure for the reaction of anhydrides with 1a: To an oven-dried pressure tube were sequentially added **1a** (97.6 mg, 0.5 mmol), anhydride (0.5 mmol), $[\text{Rh}(\text{COD})_2]\text{OTf}$ (4.68 mg, 2.0 mol%) and anhydrous toluene (3.0 mL). The reaction mixture was degassed three times with nitrogen, and then heated and stirred vigorously at $140\text{ }^\circ\text{C}$ in an oil bath. After an appropriate reaction time, the tube was removed from the oil bath, and cooled to room temperature. The solvent was removed

and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure product **3aa**.

c) Procedure for the analysis of the gaseous products by GC-TCD:

To an oven-dried pressure tube were sequentially added indole **1a** (97.6 mg, 0.5 mmol), **2a** (74.1 mg, 0.5 mmol), $[\text{Rh}(\text{COD})_2]\text{OTf}$ (4.68 mg, 2.0 mol%), $(t\text{BuCO})_2\text{O}$ (93.1 mg, 0.5 mmol) and toluene (3.0 mL). After being degassed three times, the tube was heated and stirred vigorously at 140 °C for 1 h in an oil bath under argon atmosphere. After cooling, the reaction gas was analyzed by GC-TDC with argon as the carrier gas.

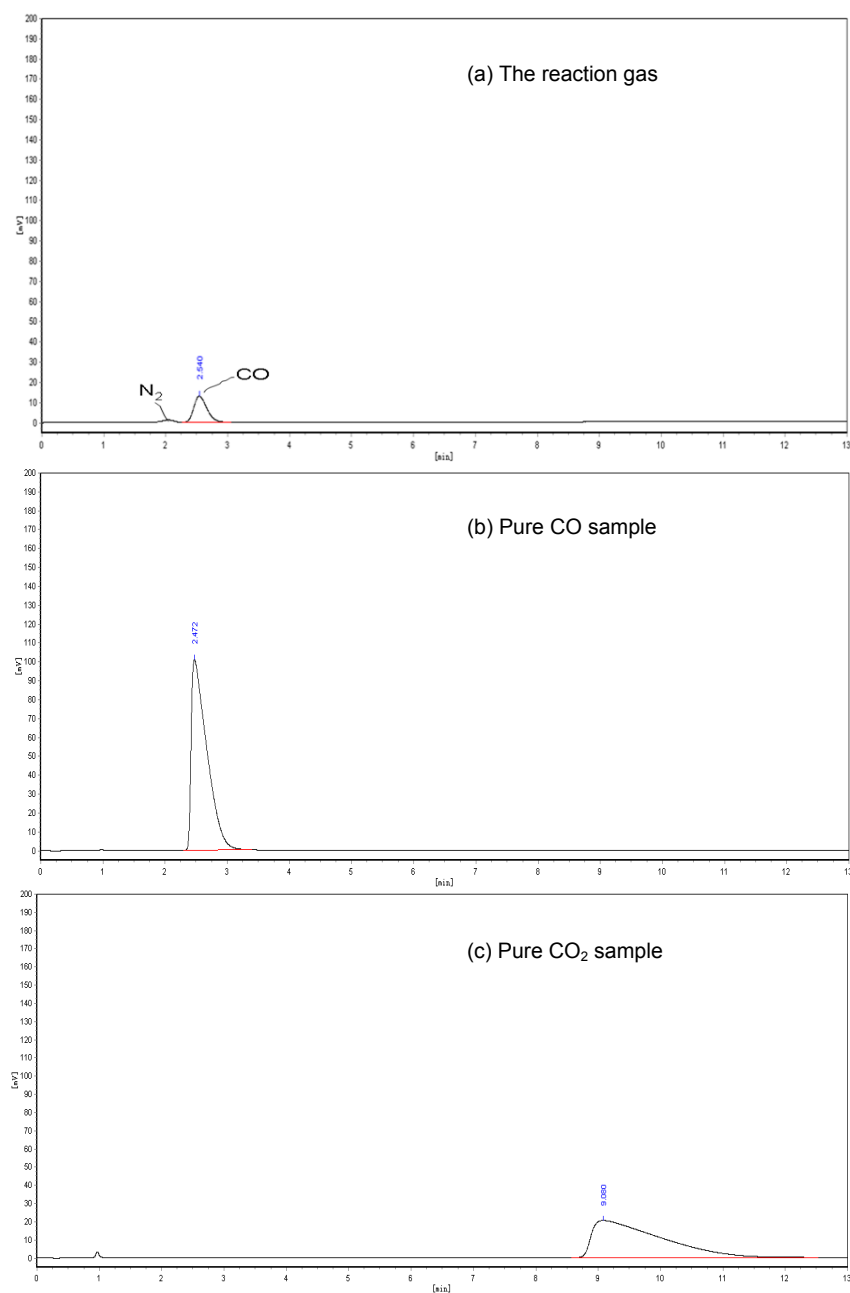
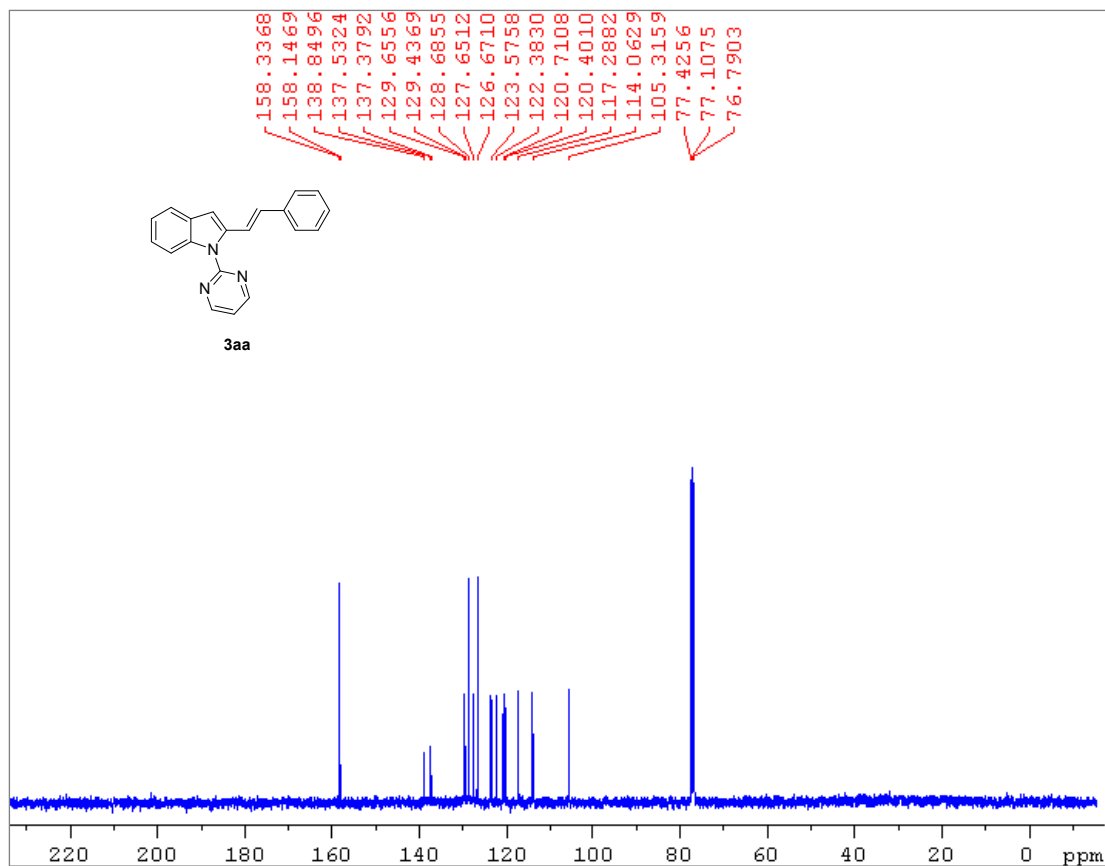
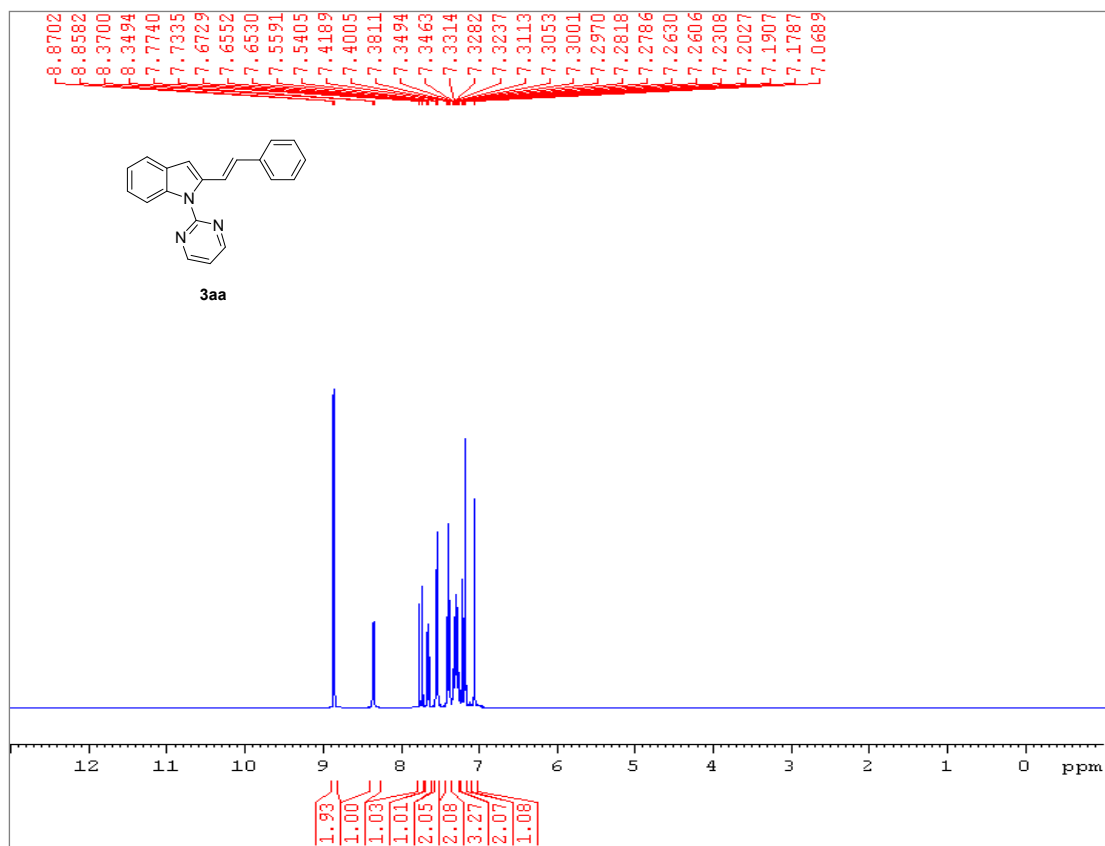


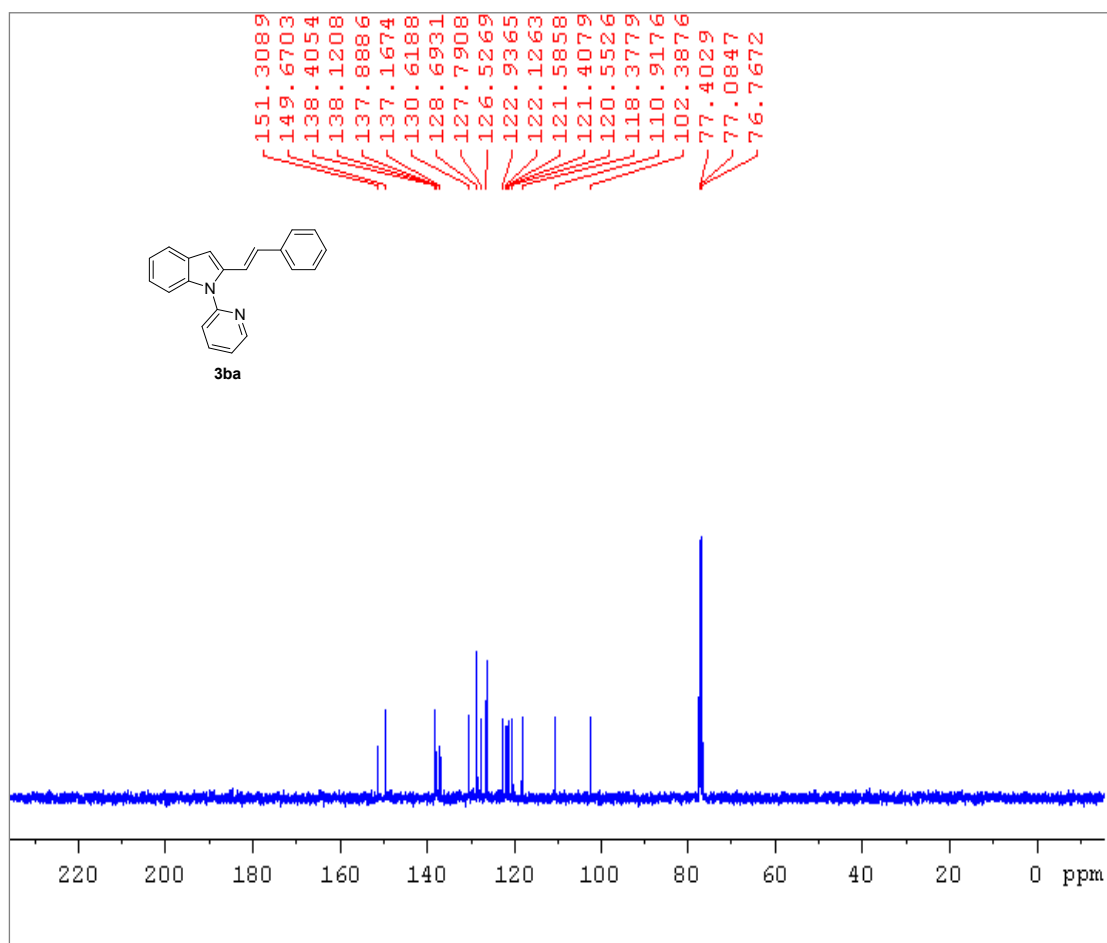
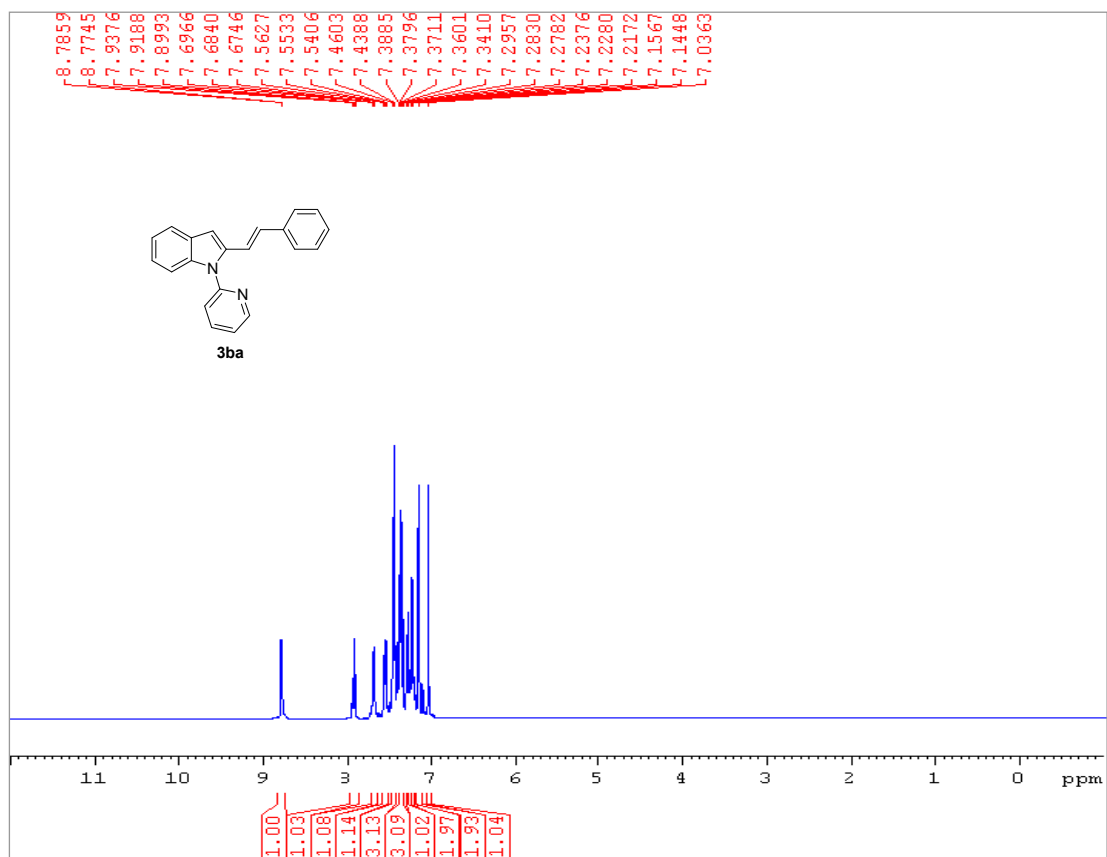
Figure S1. GC analysis indicated the existenc CO, and no CO₂ was produced.

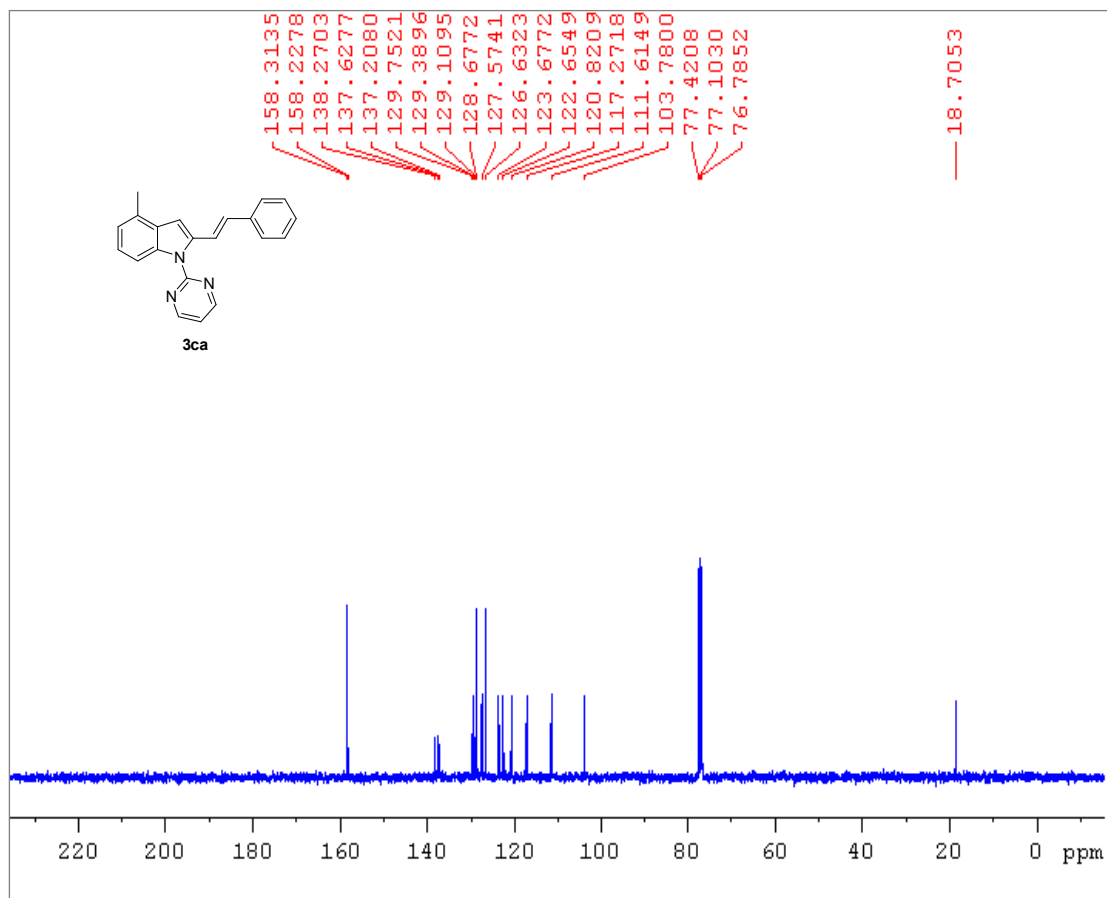
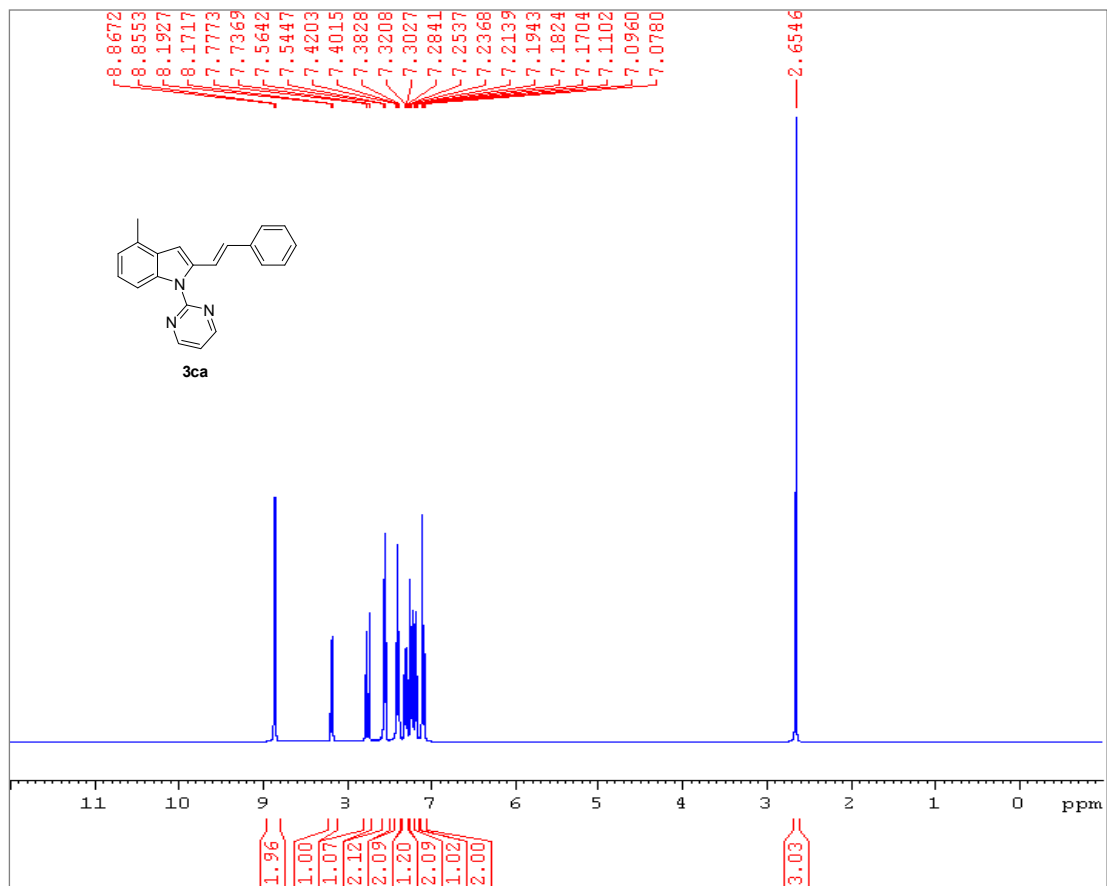
7. References:

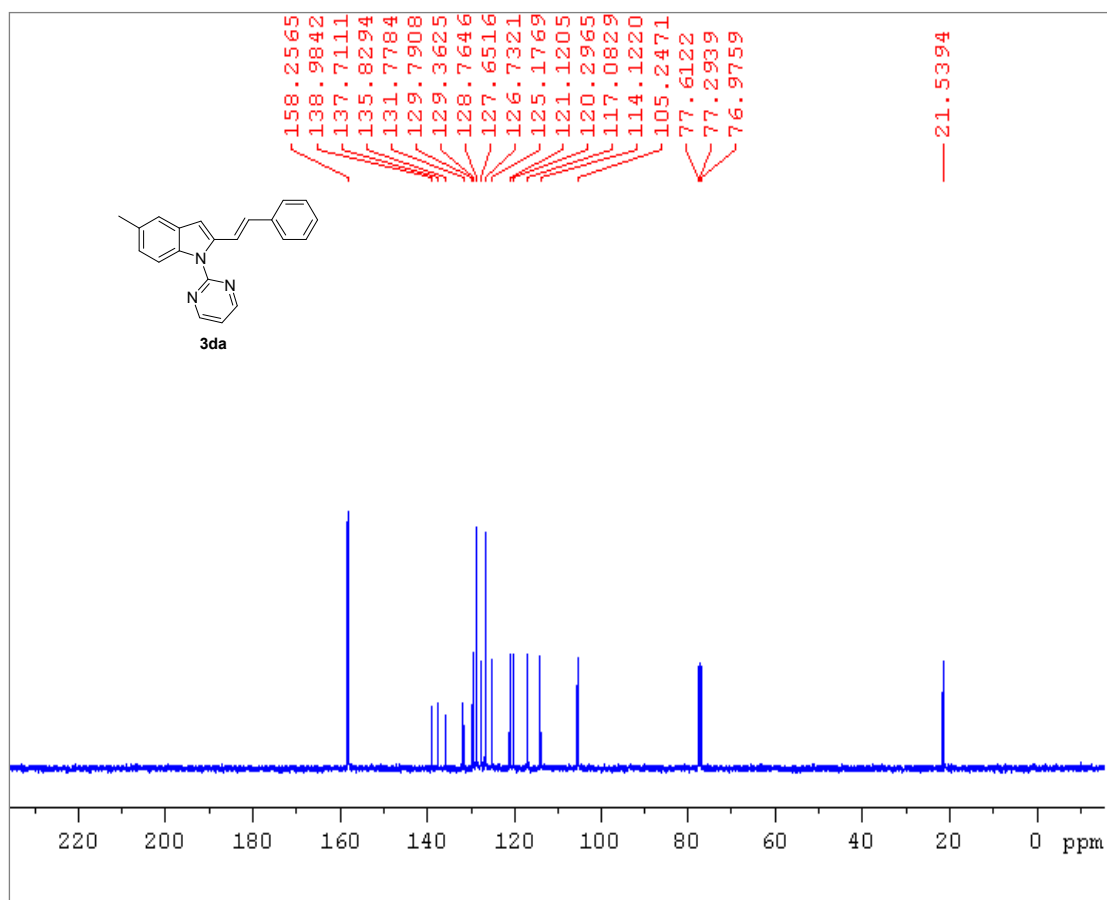
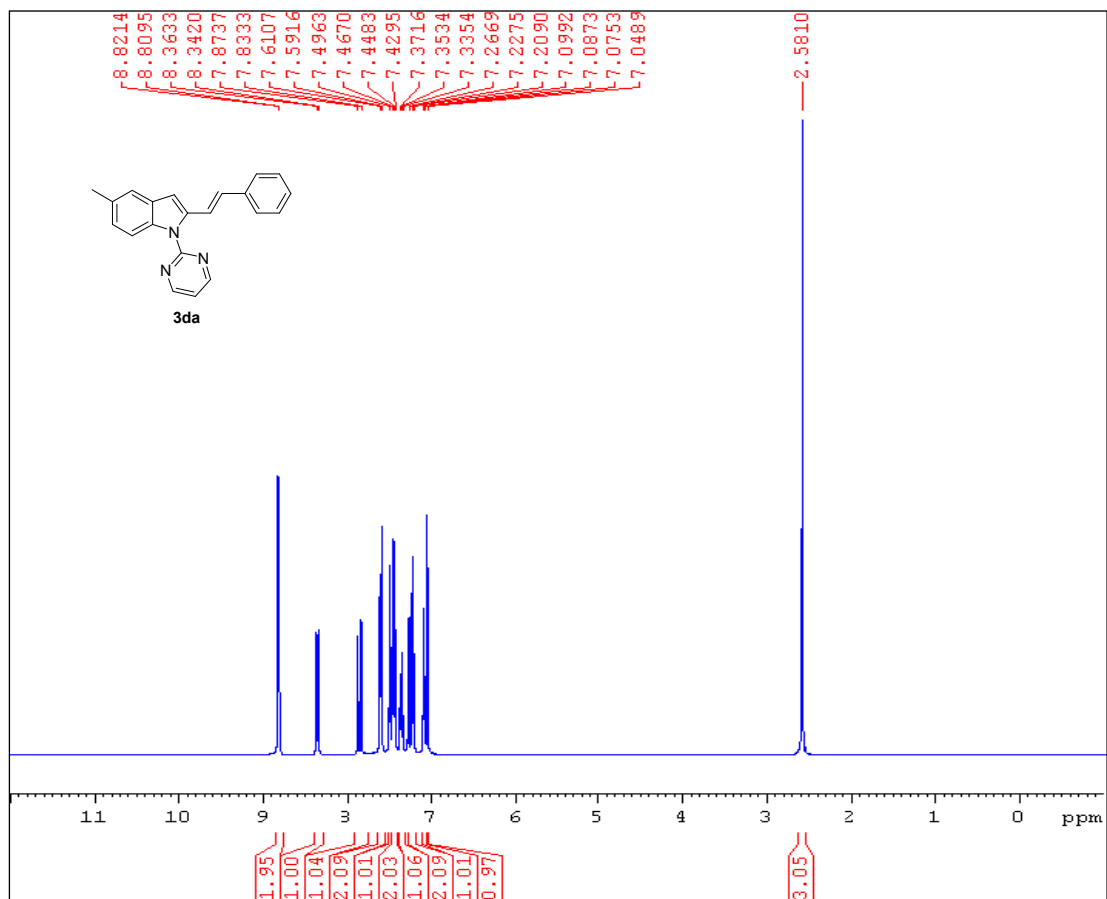
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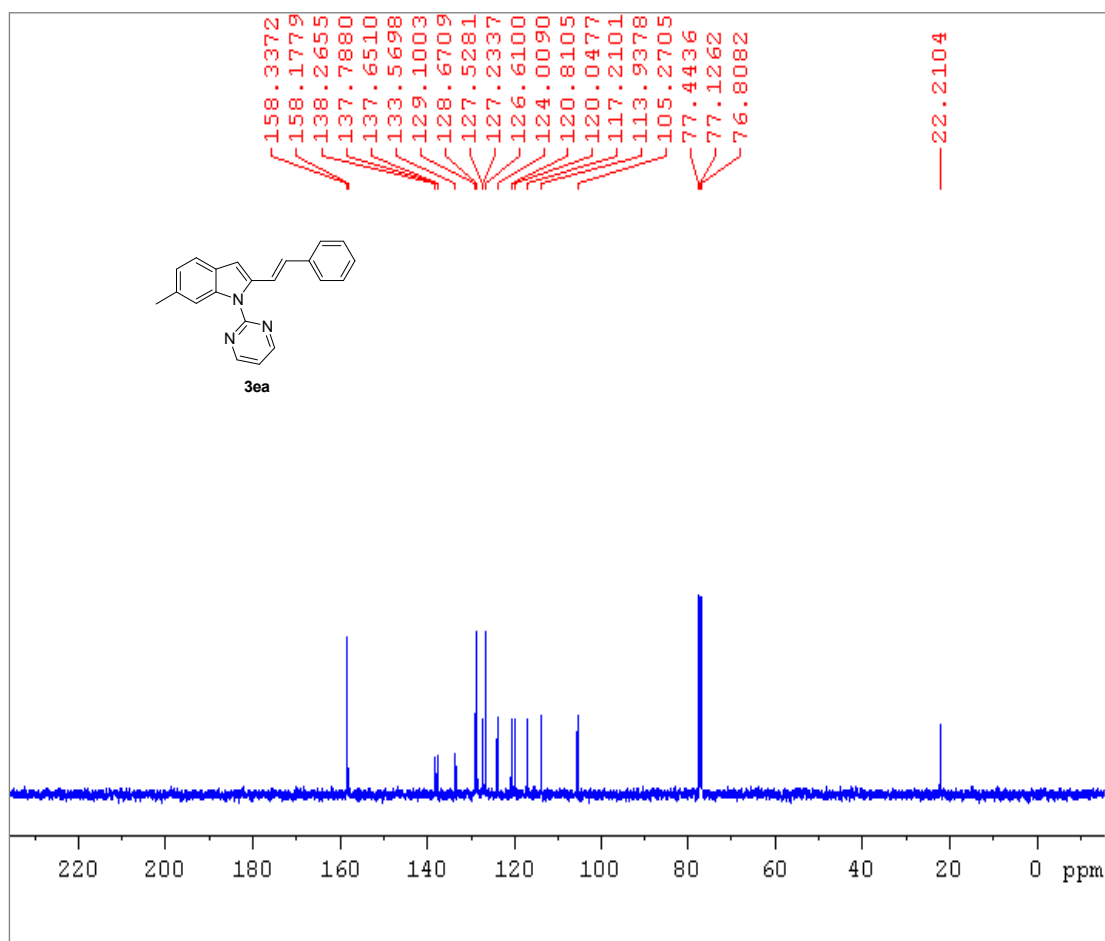
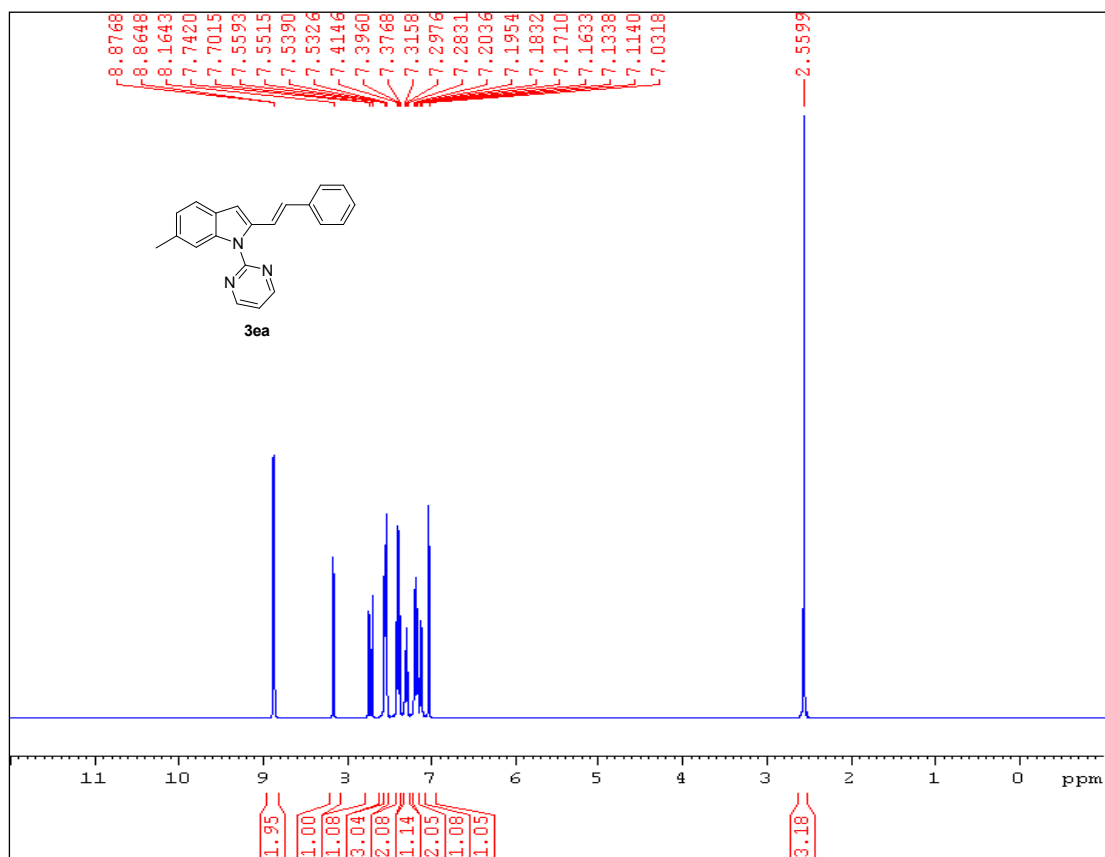
8. ^1H and ^{13}C NMR spectra of the olefinated indoles

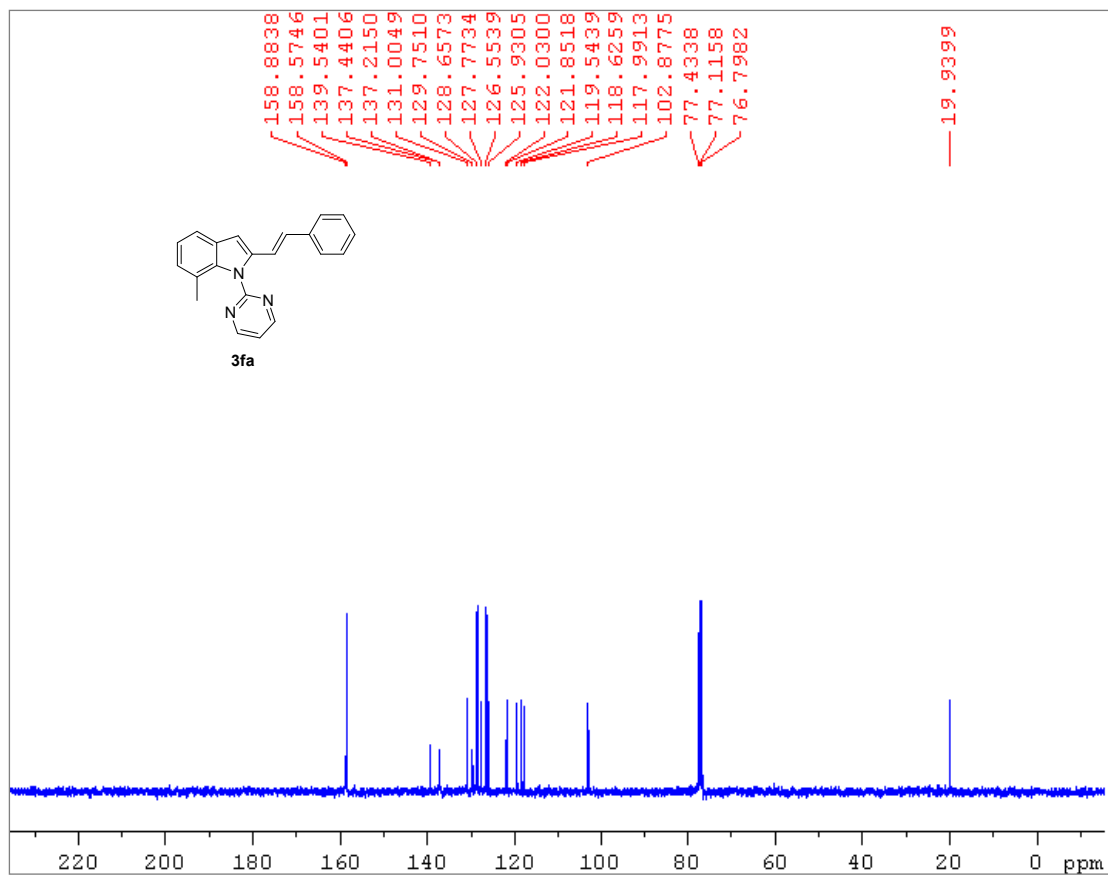
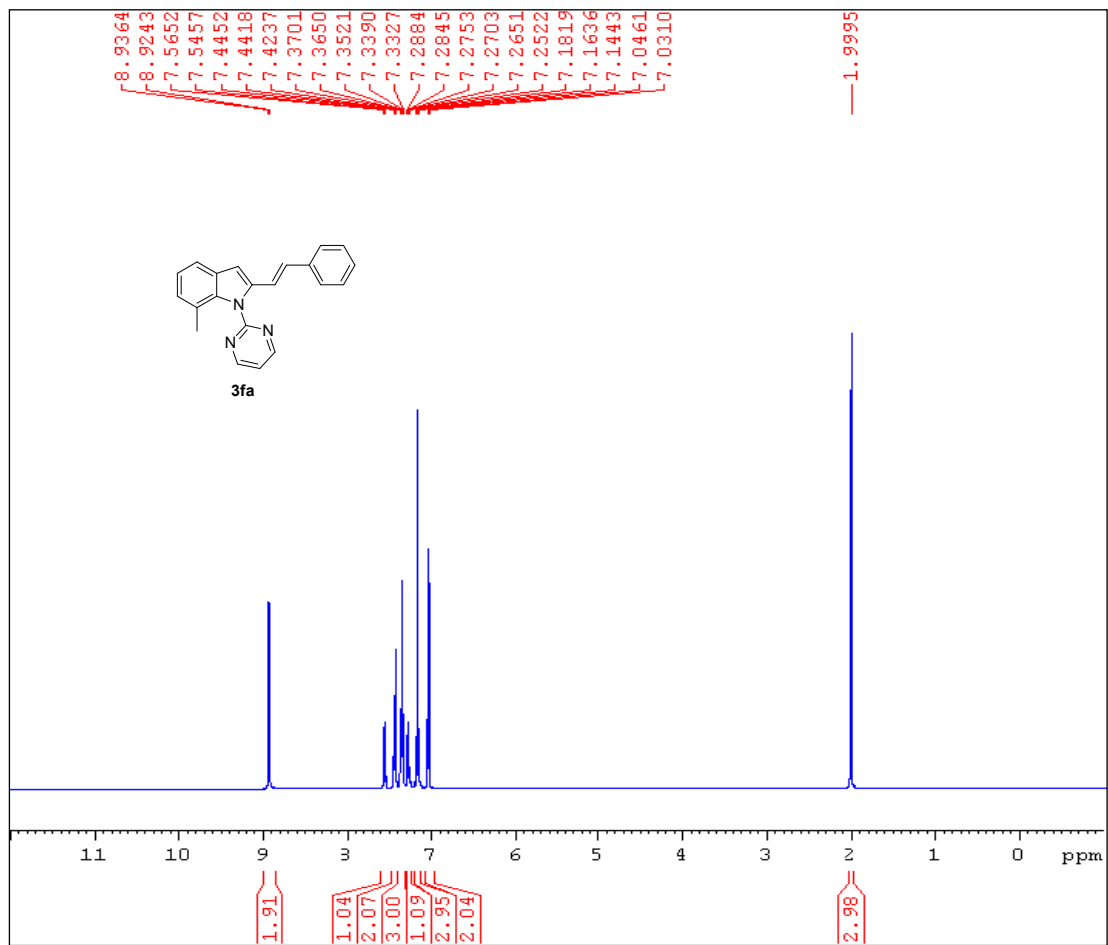


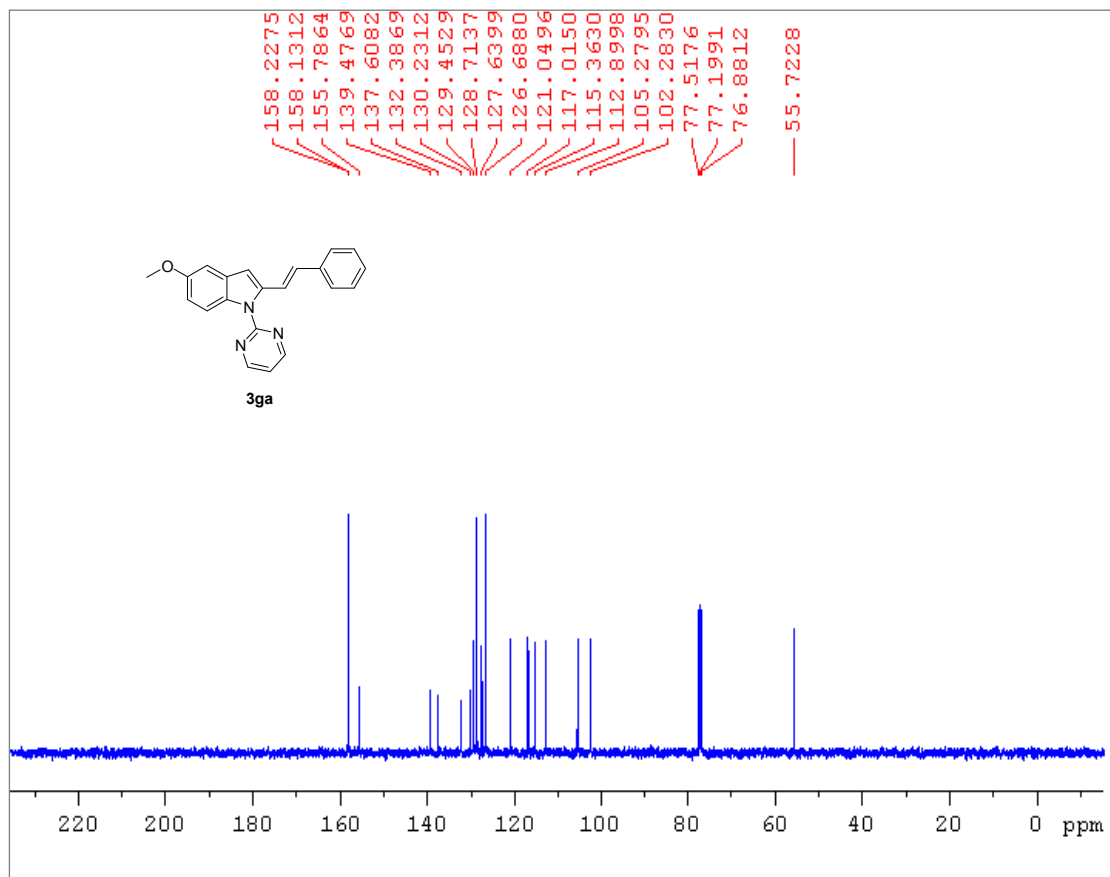
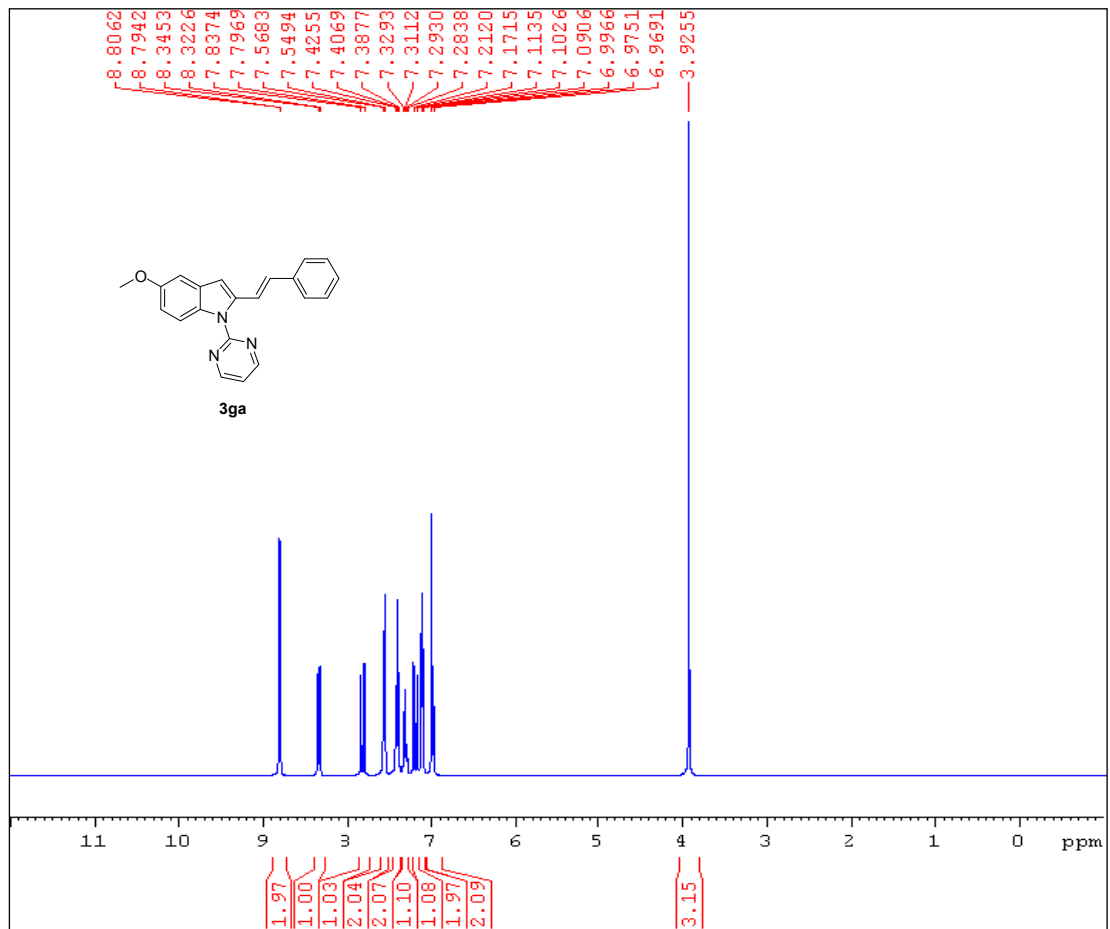


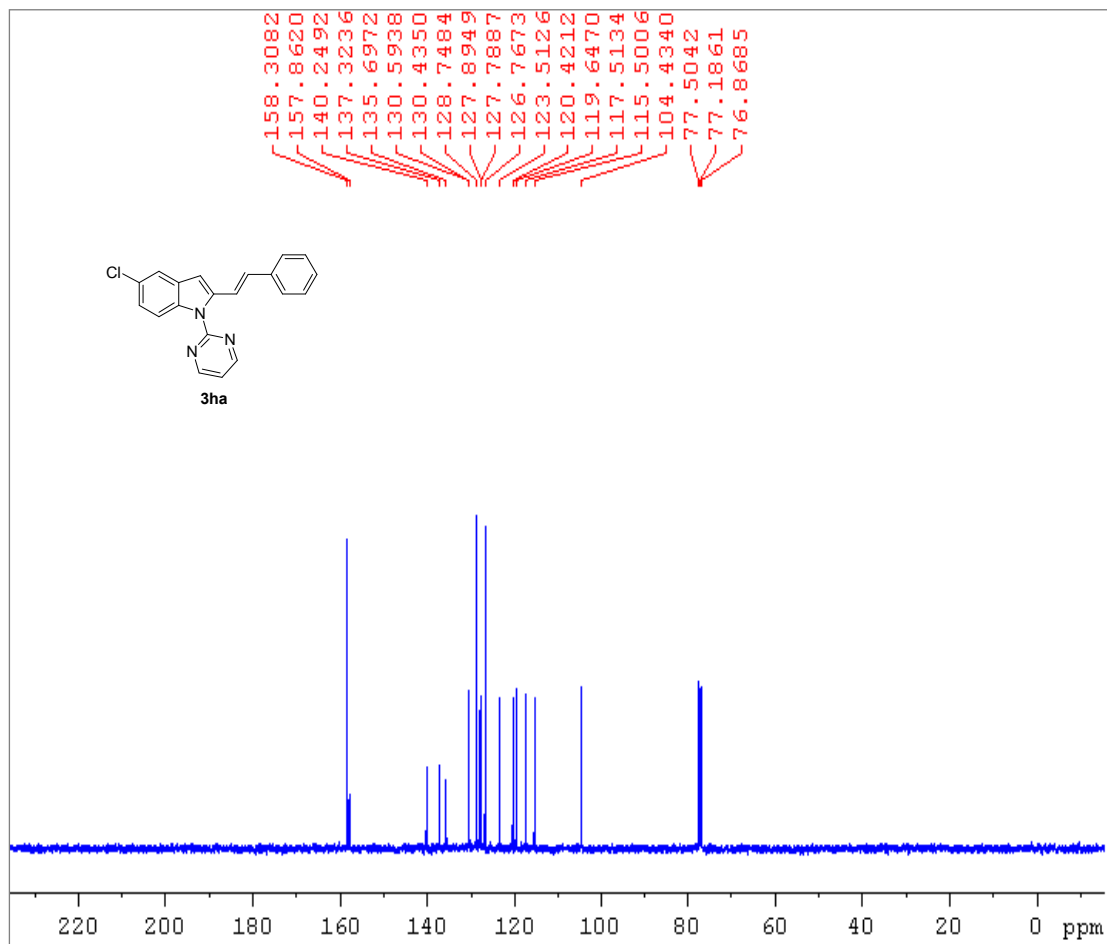
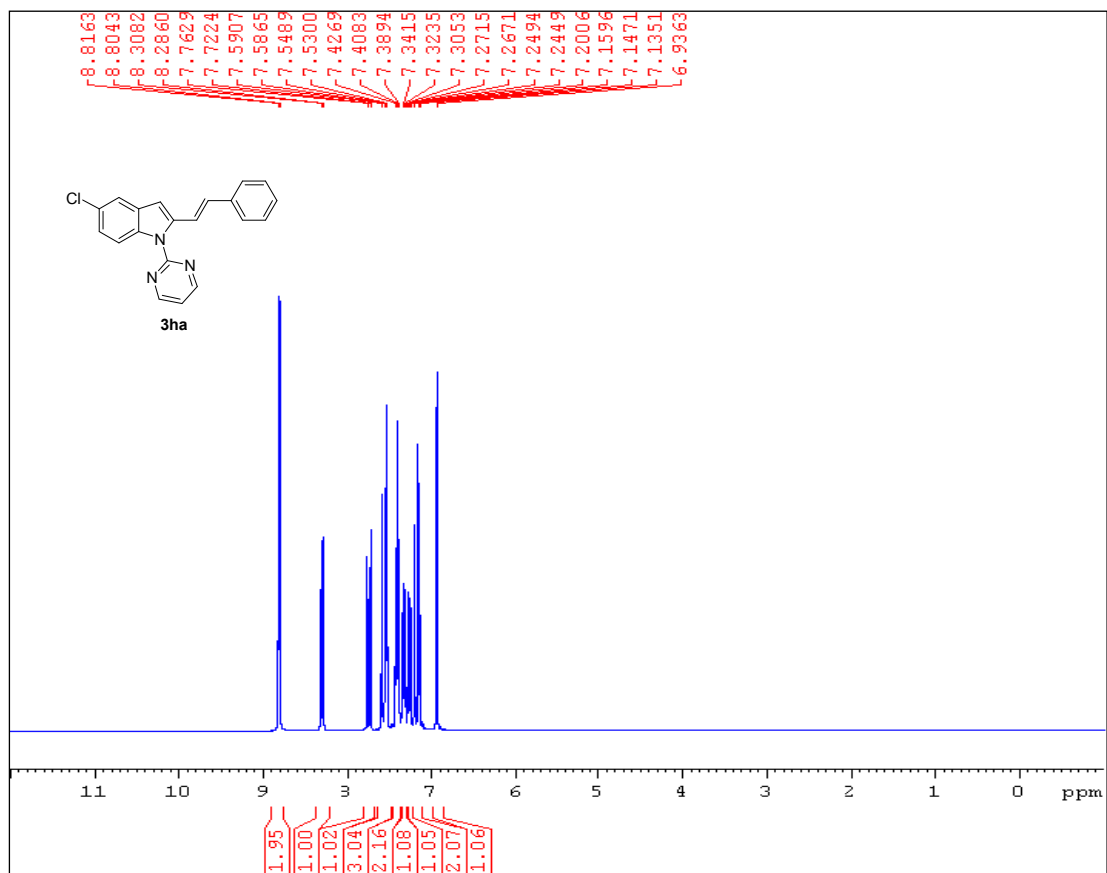


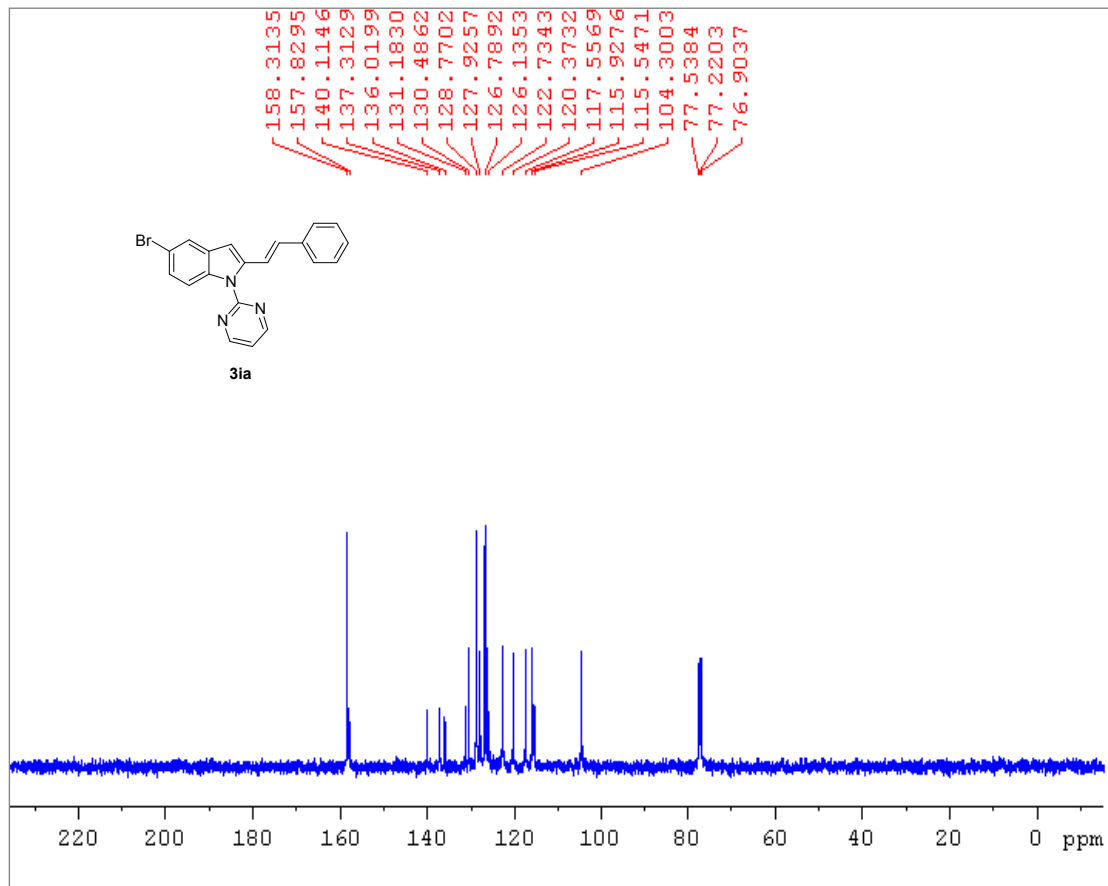
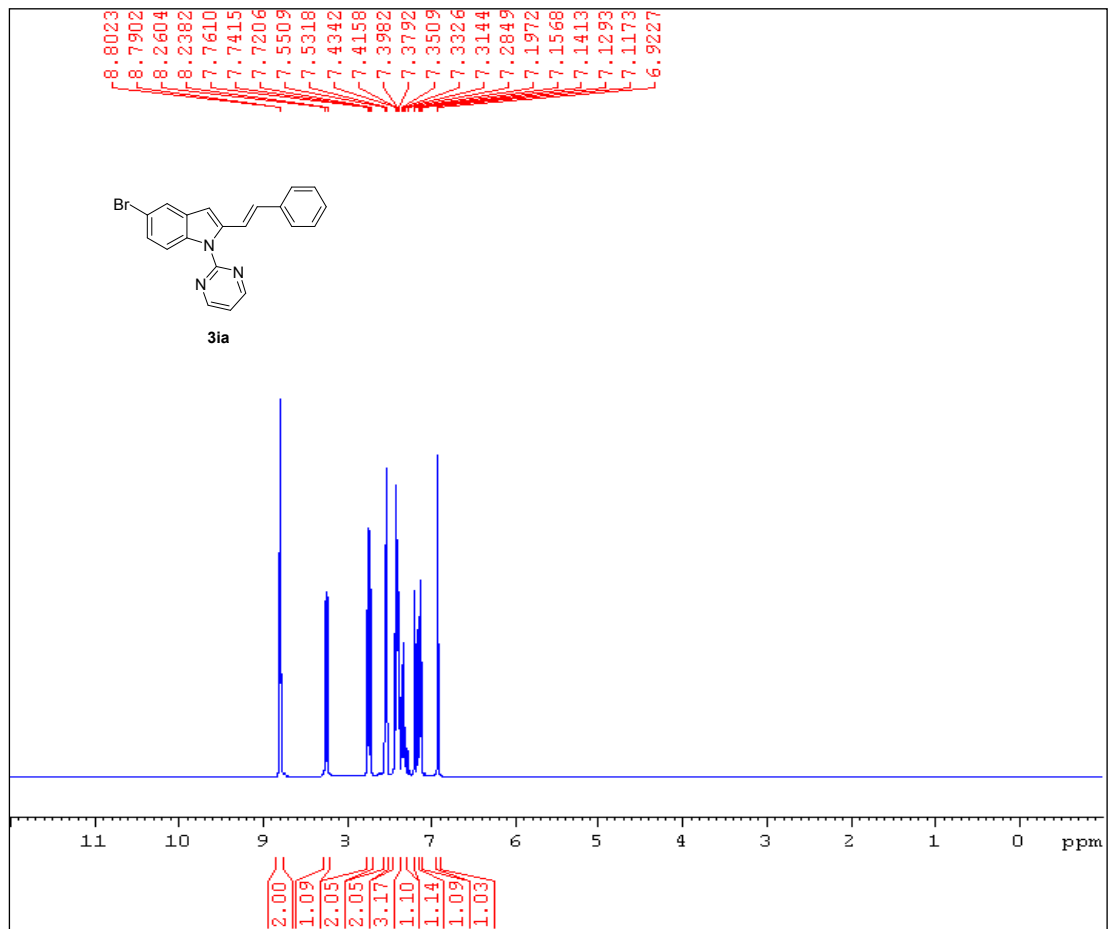


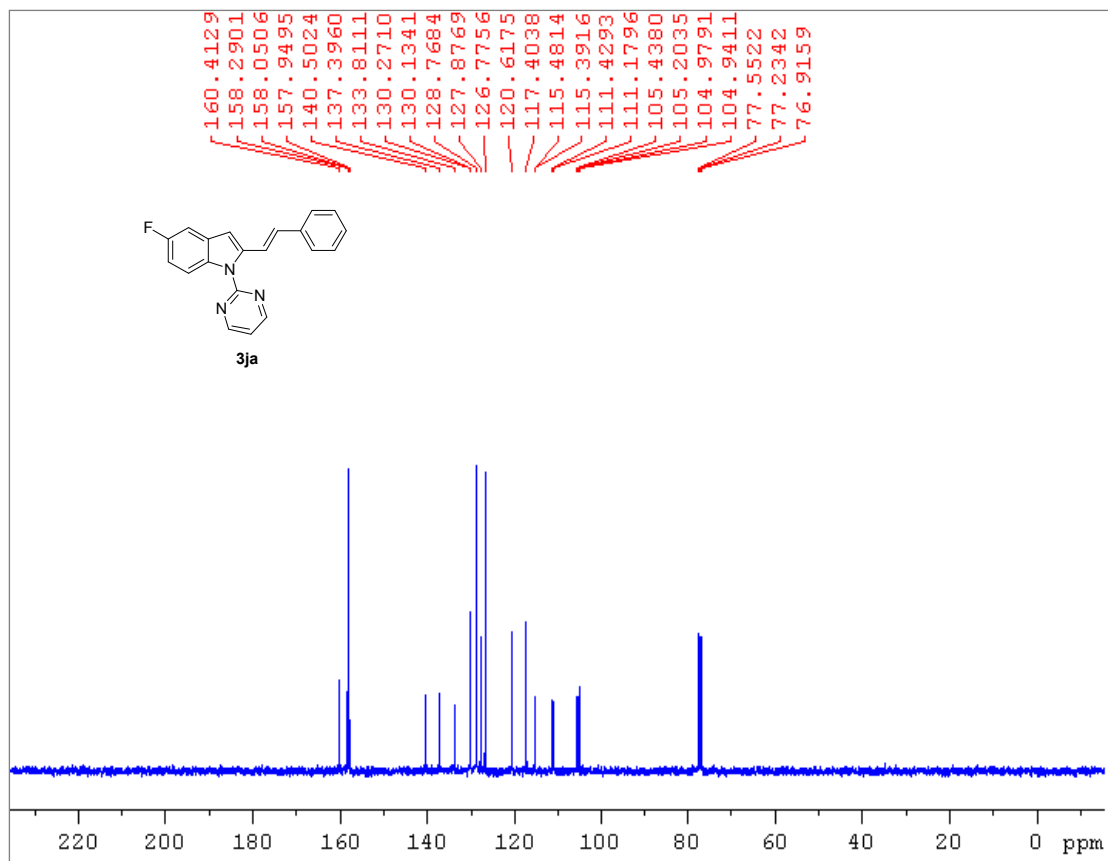
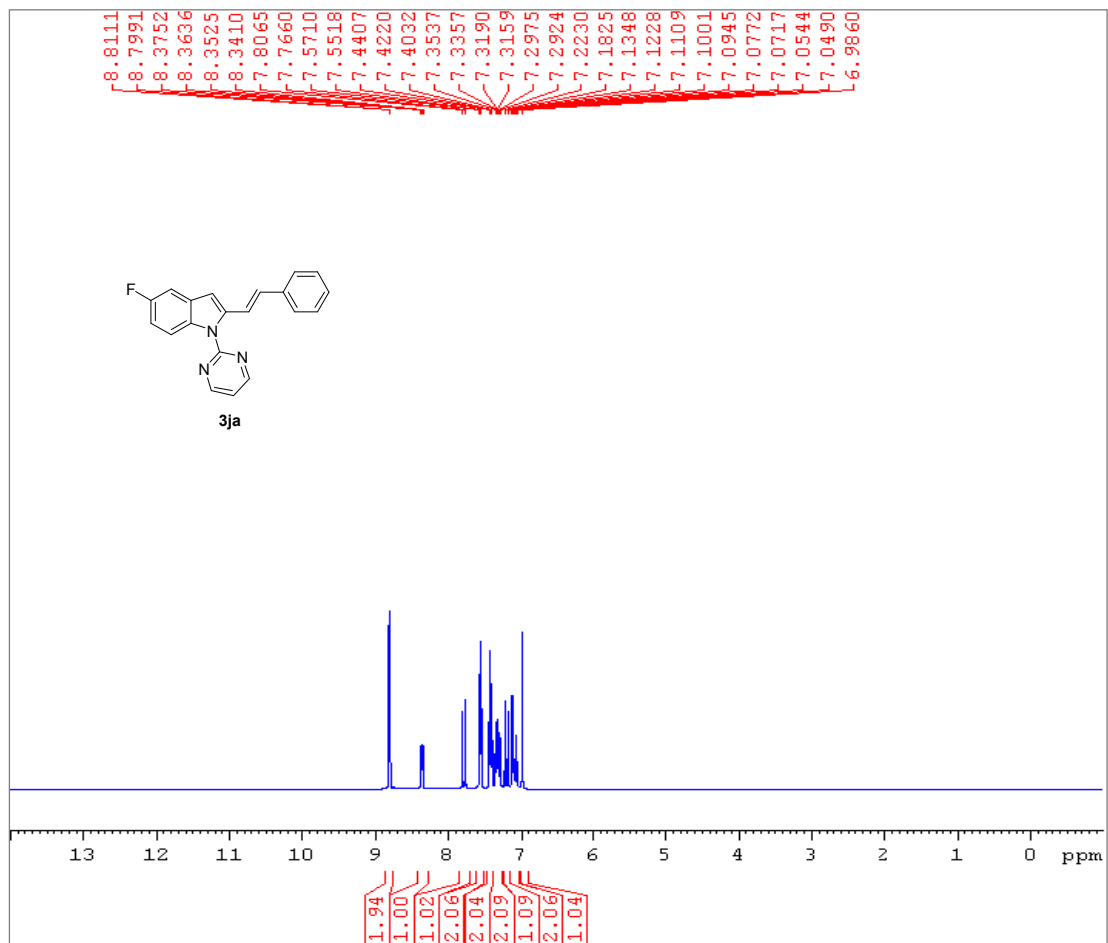


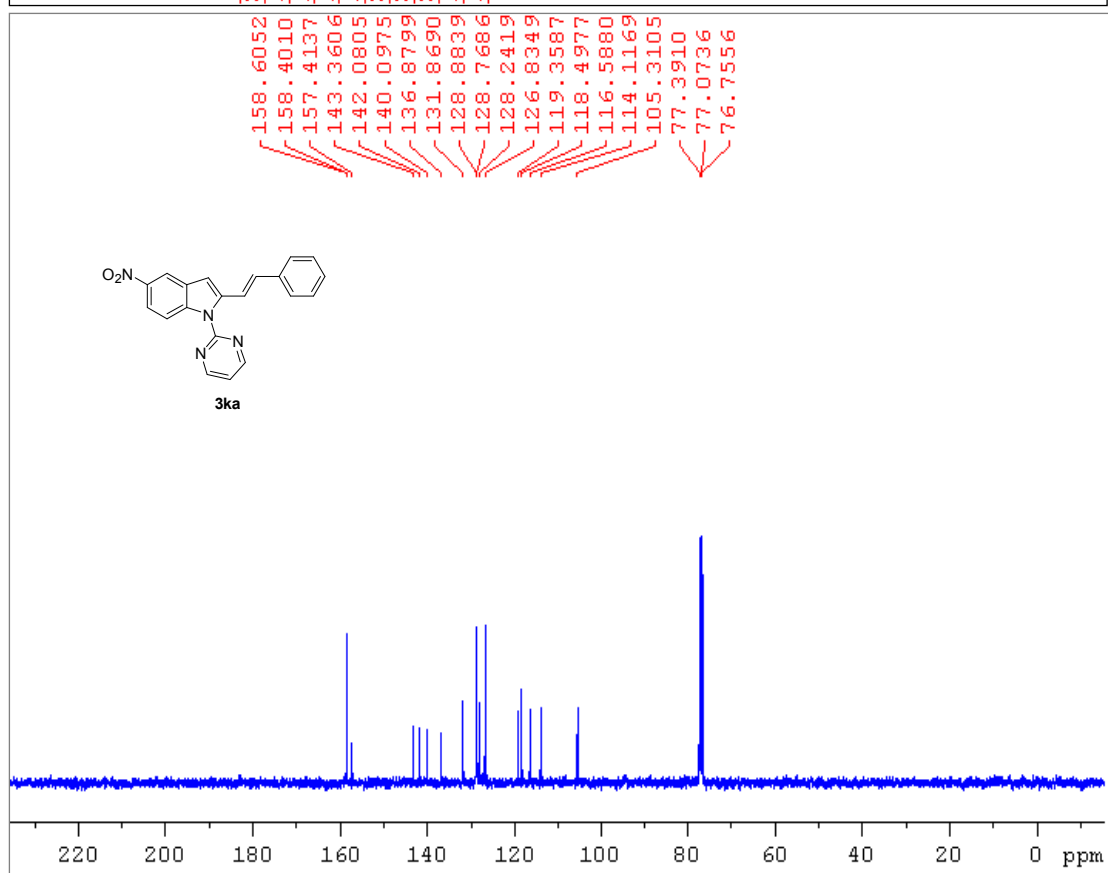
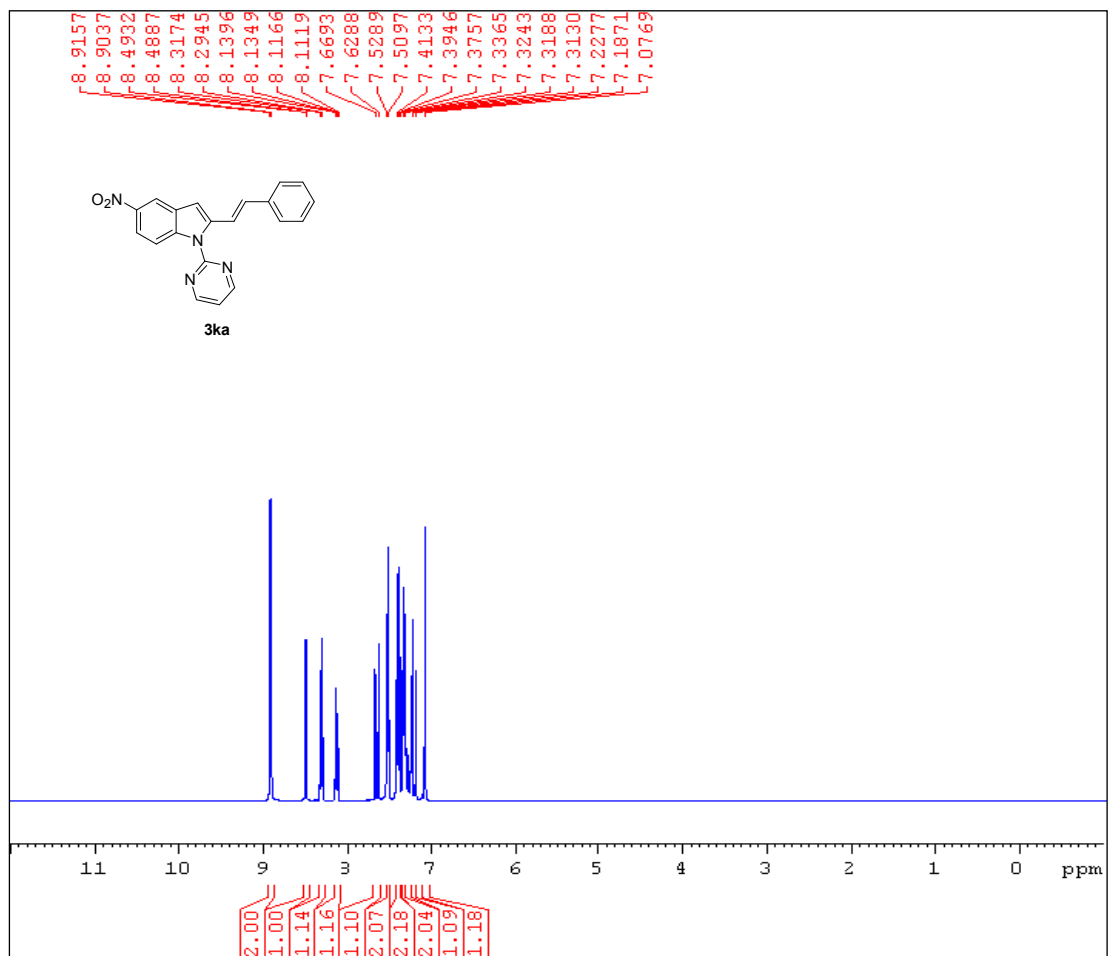


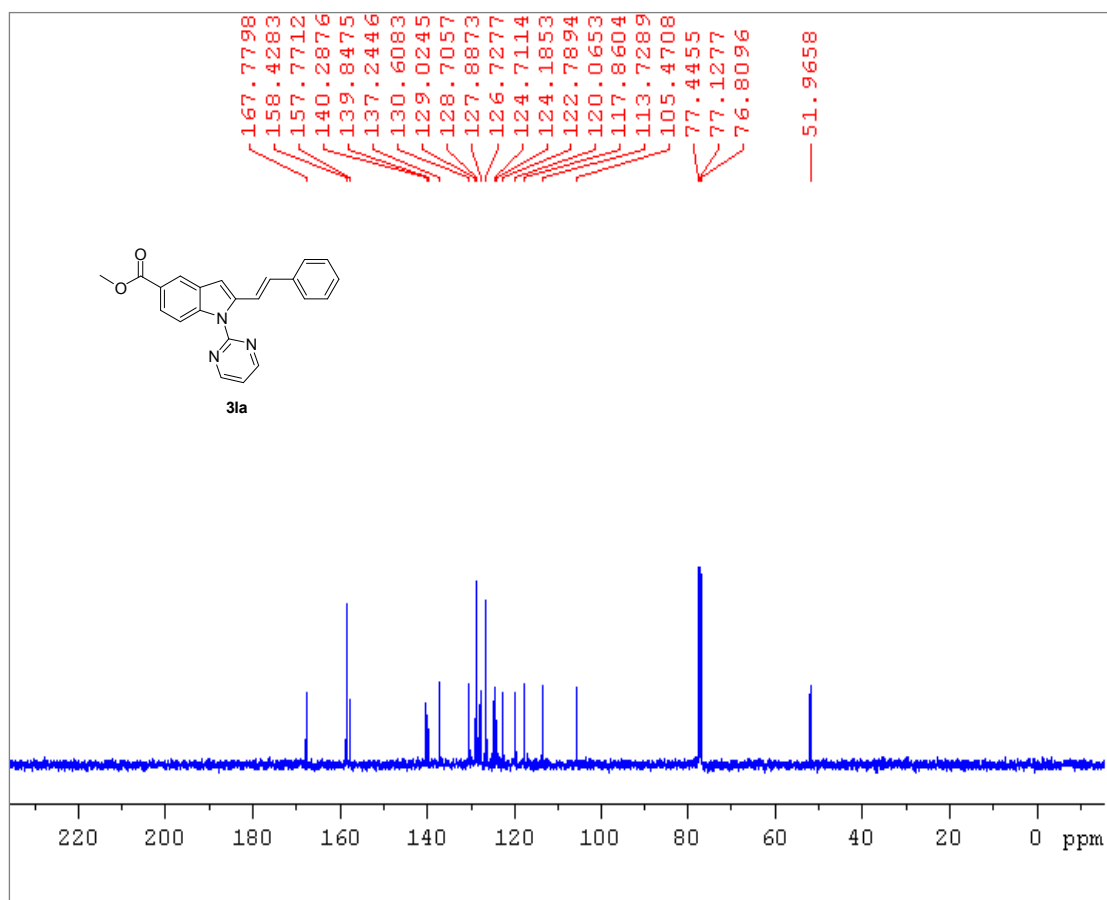
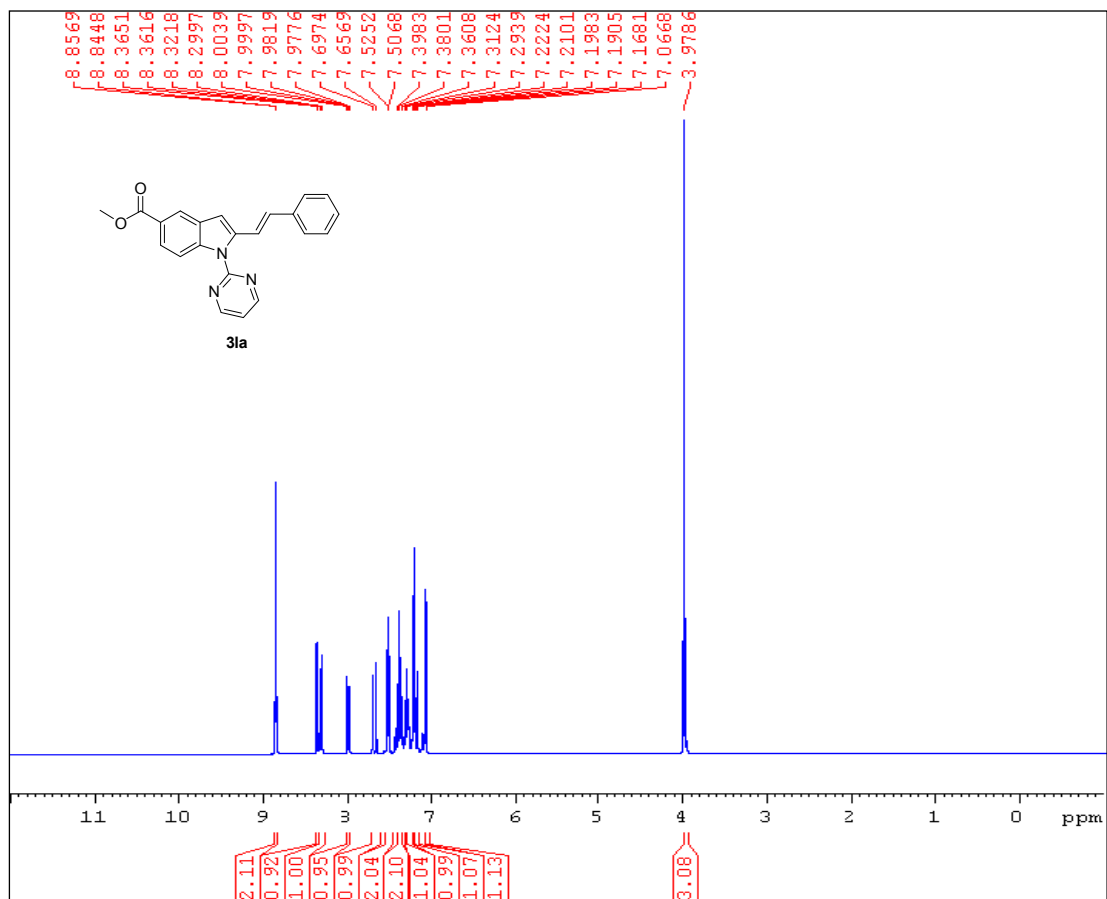


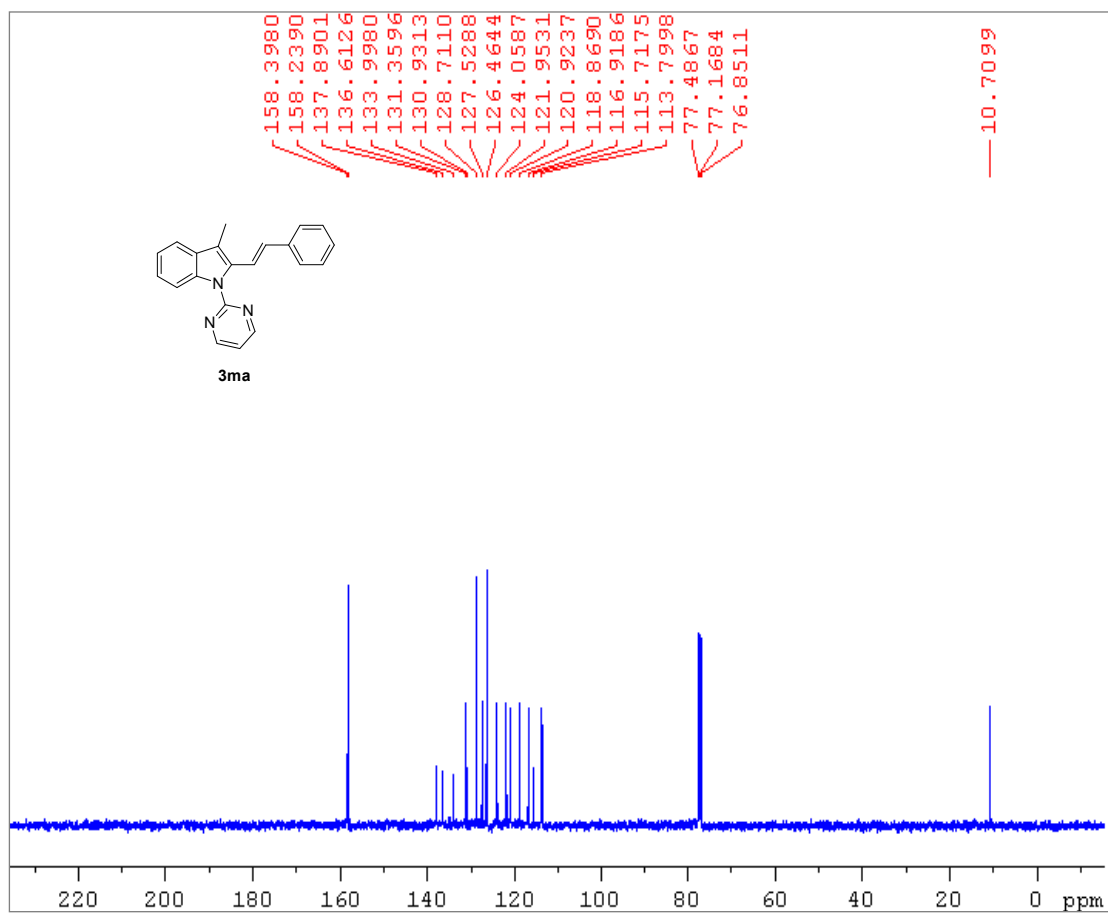
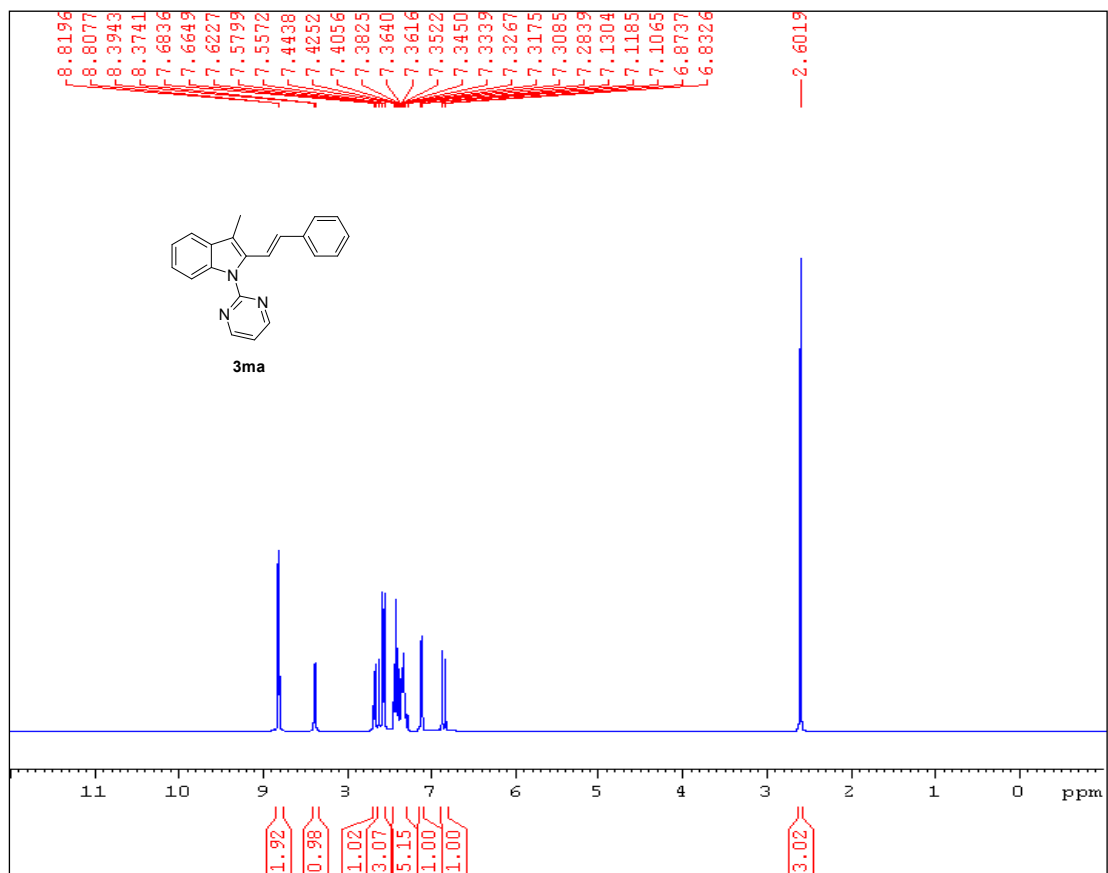


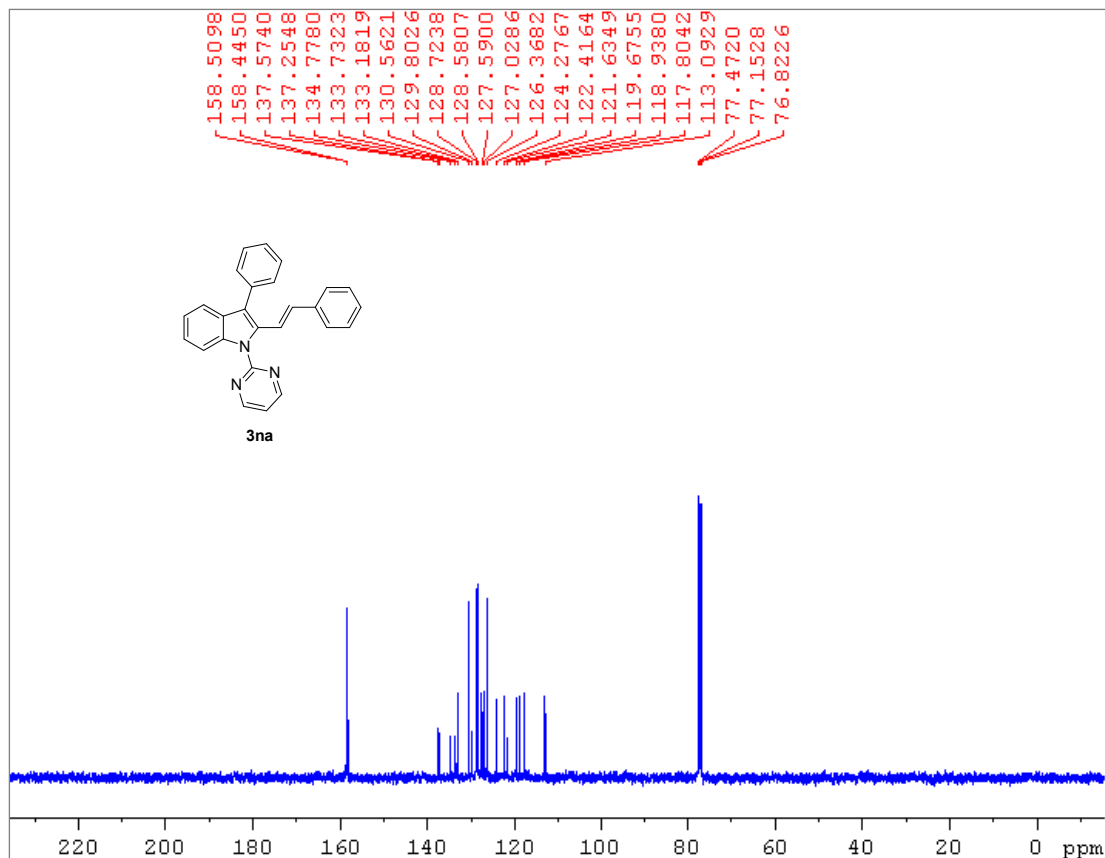
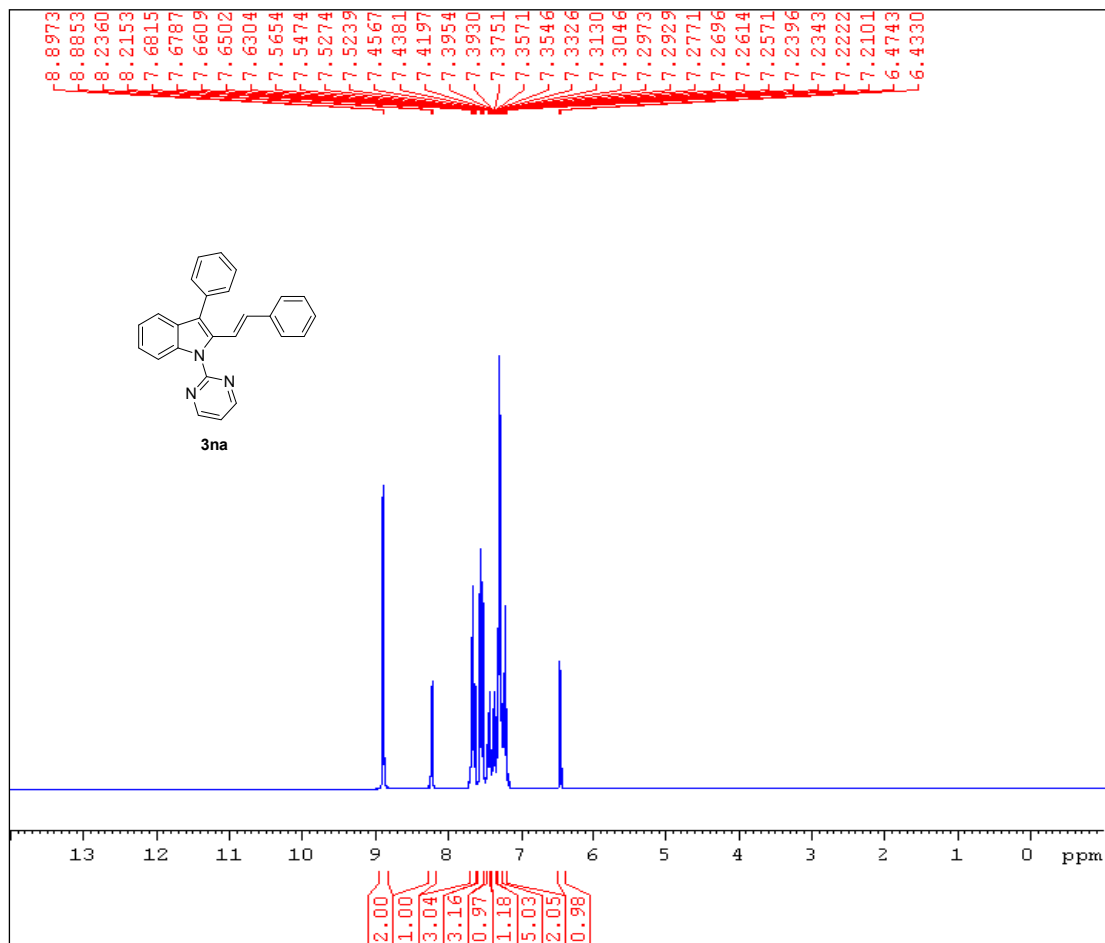


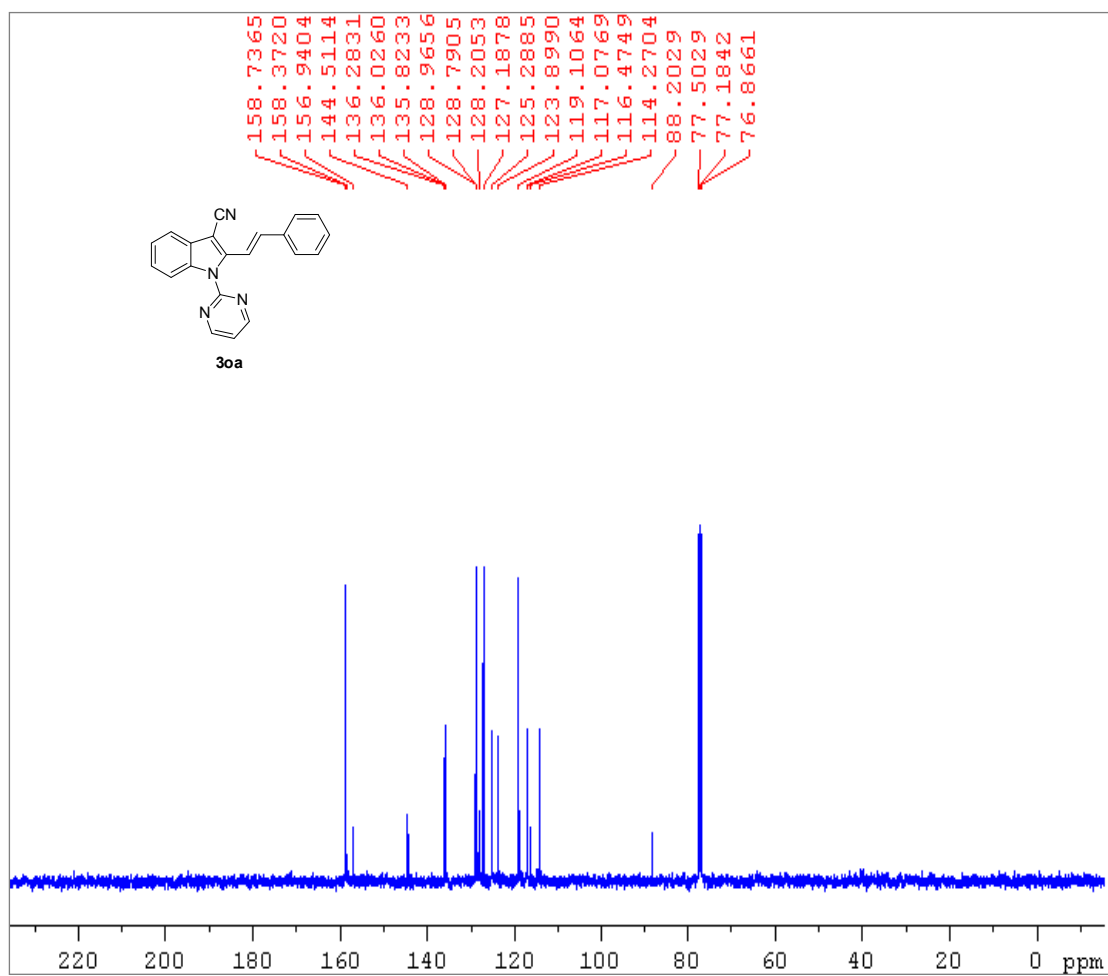
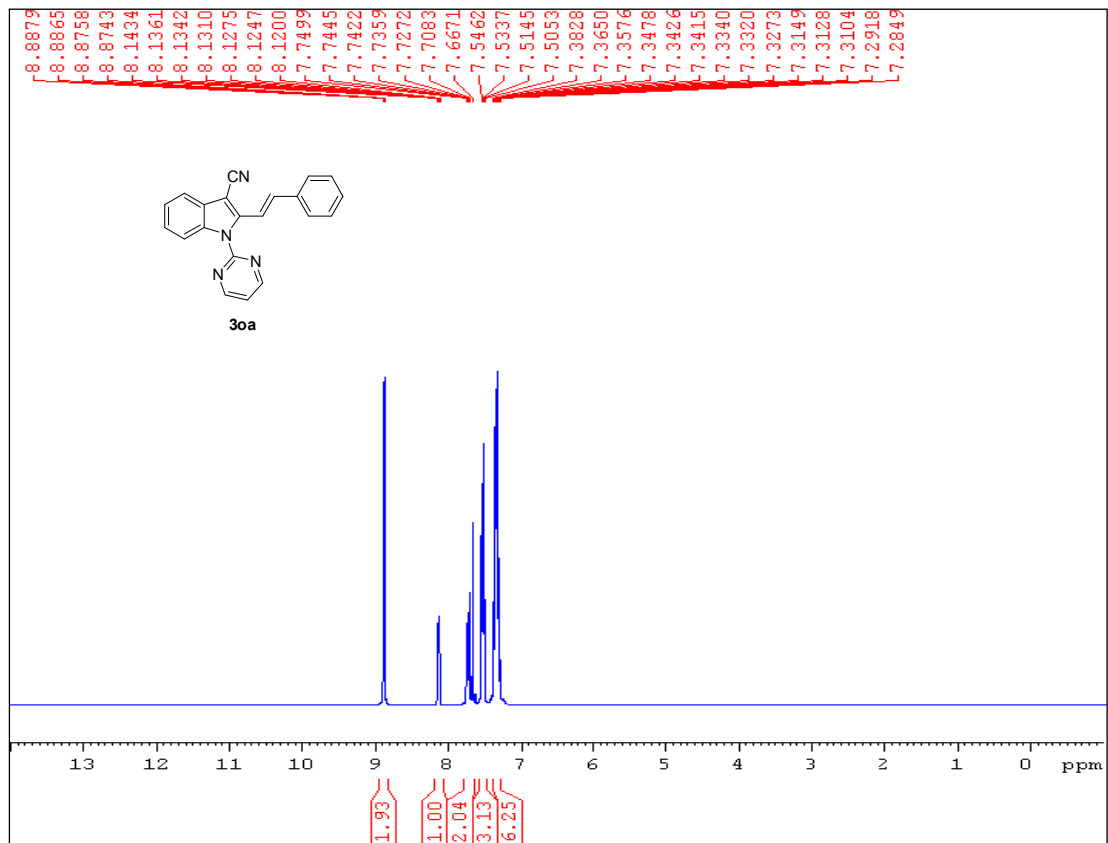


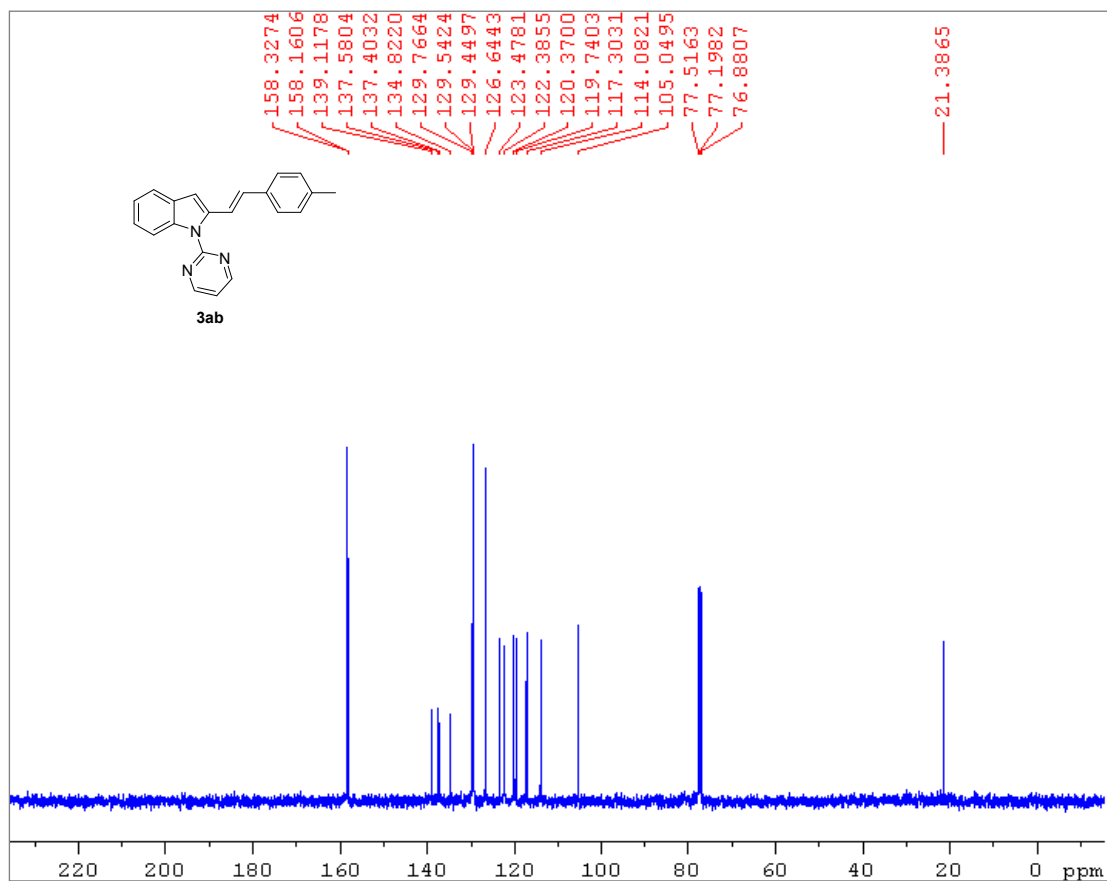
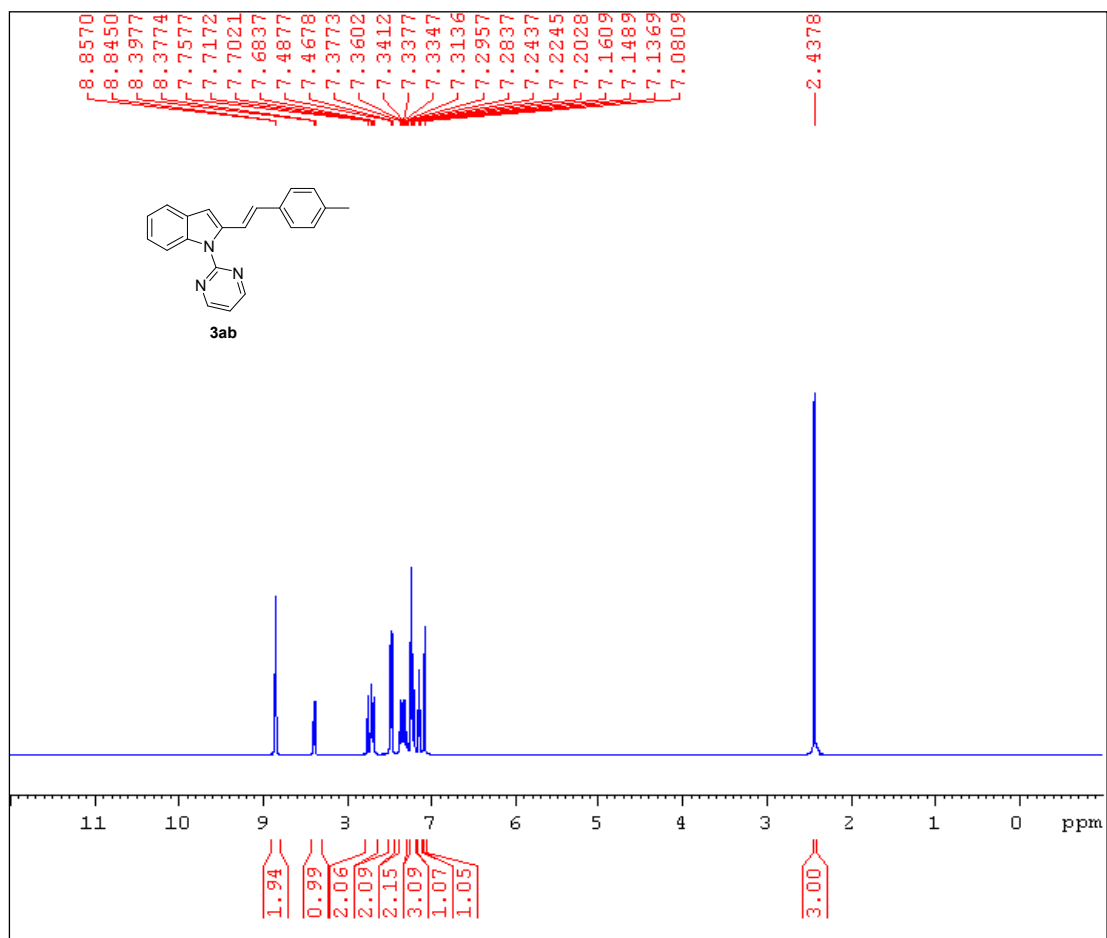


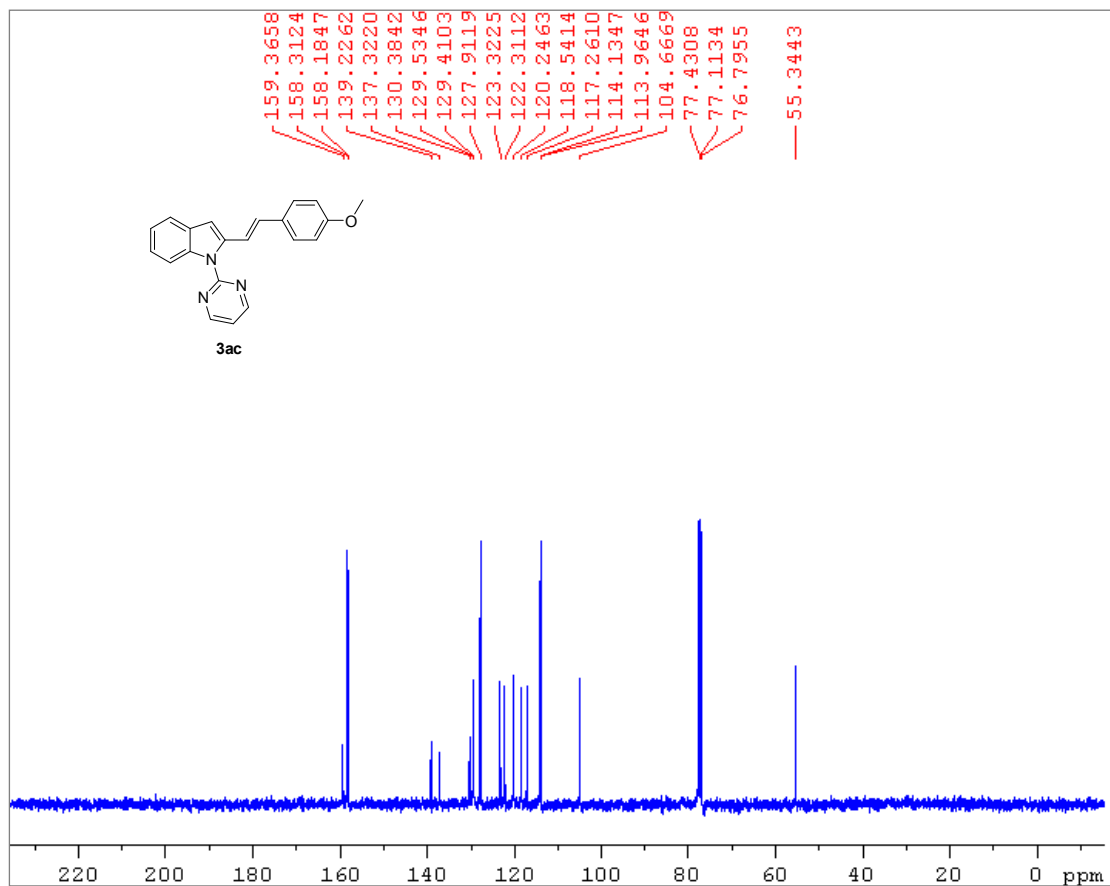
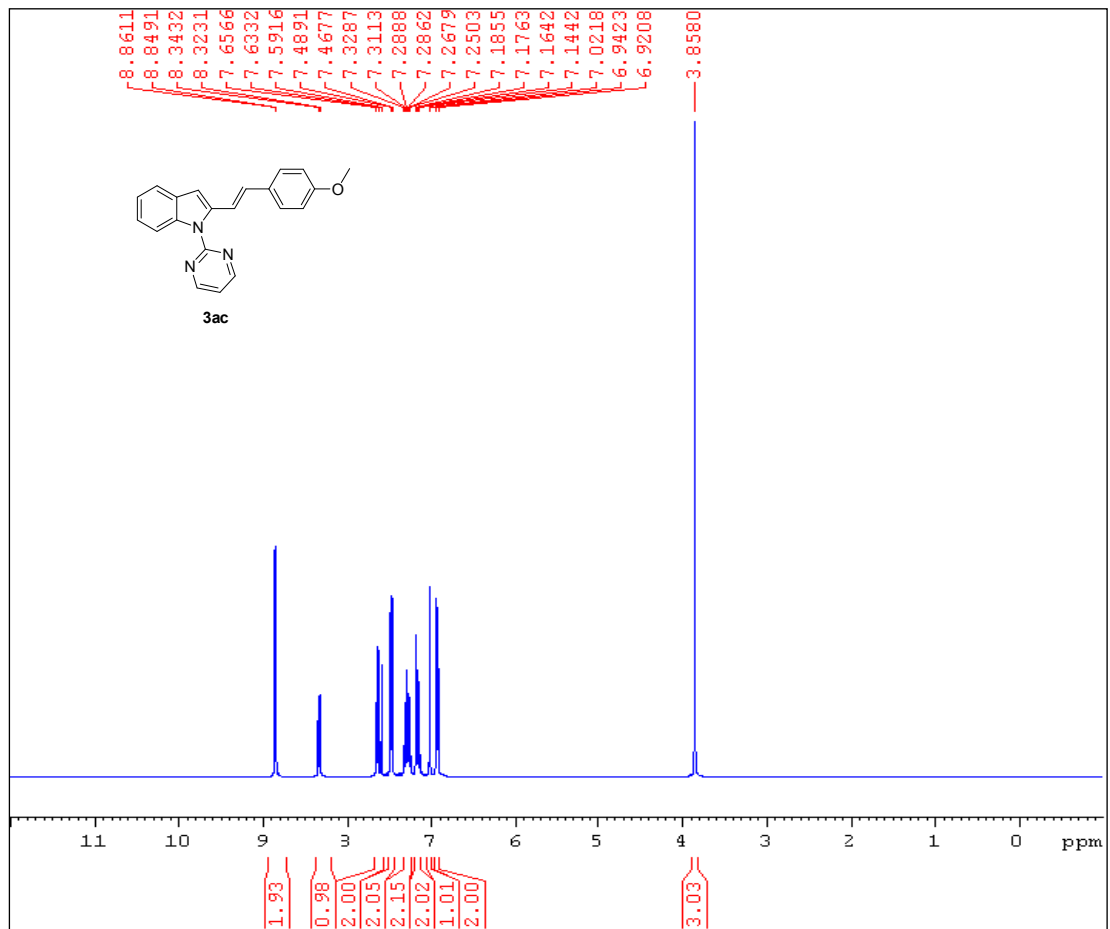


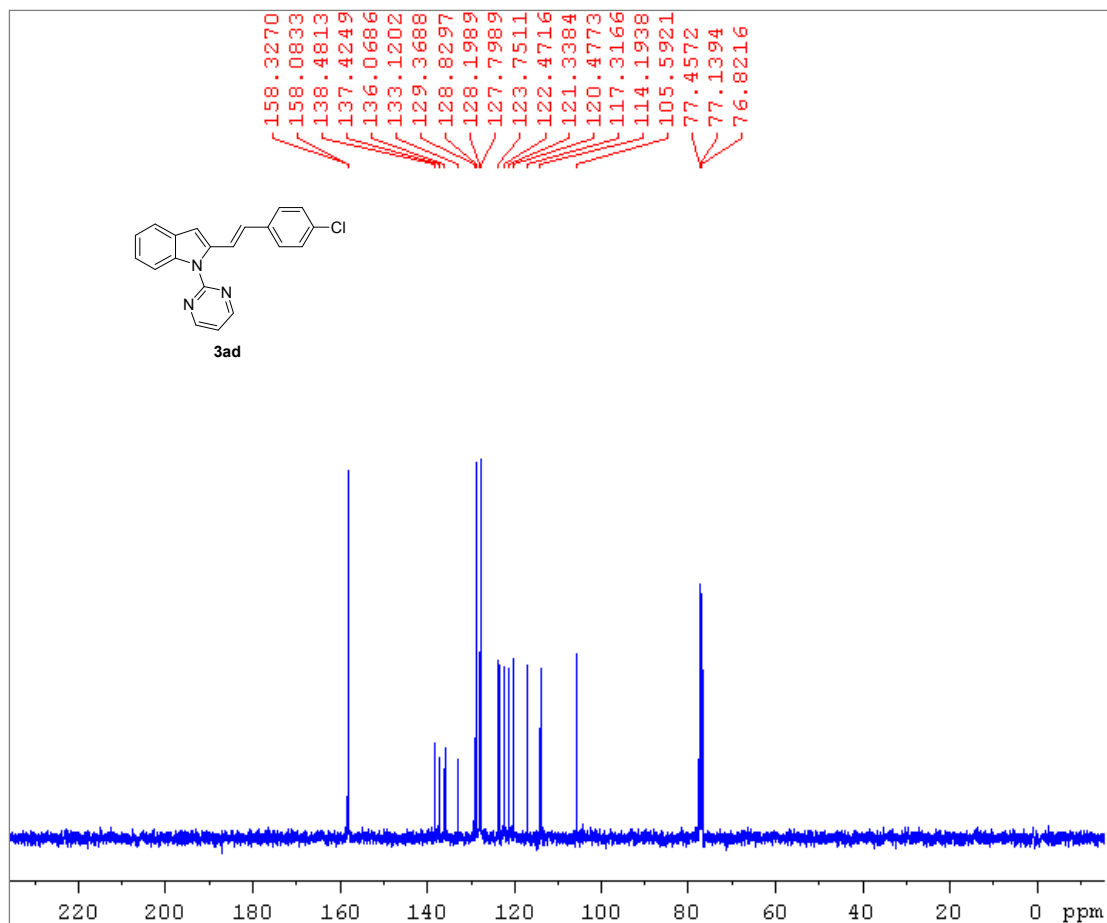
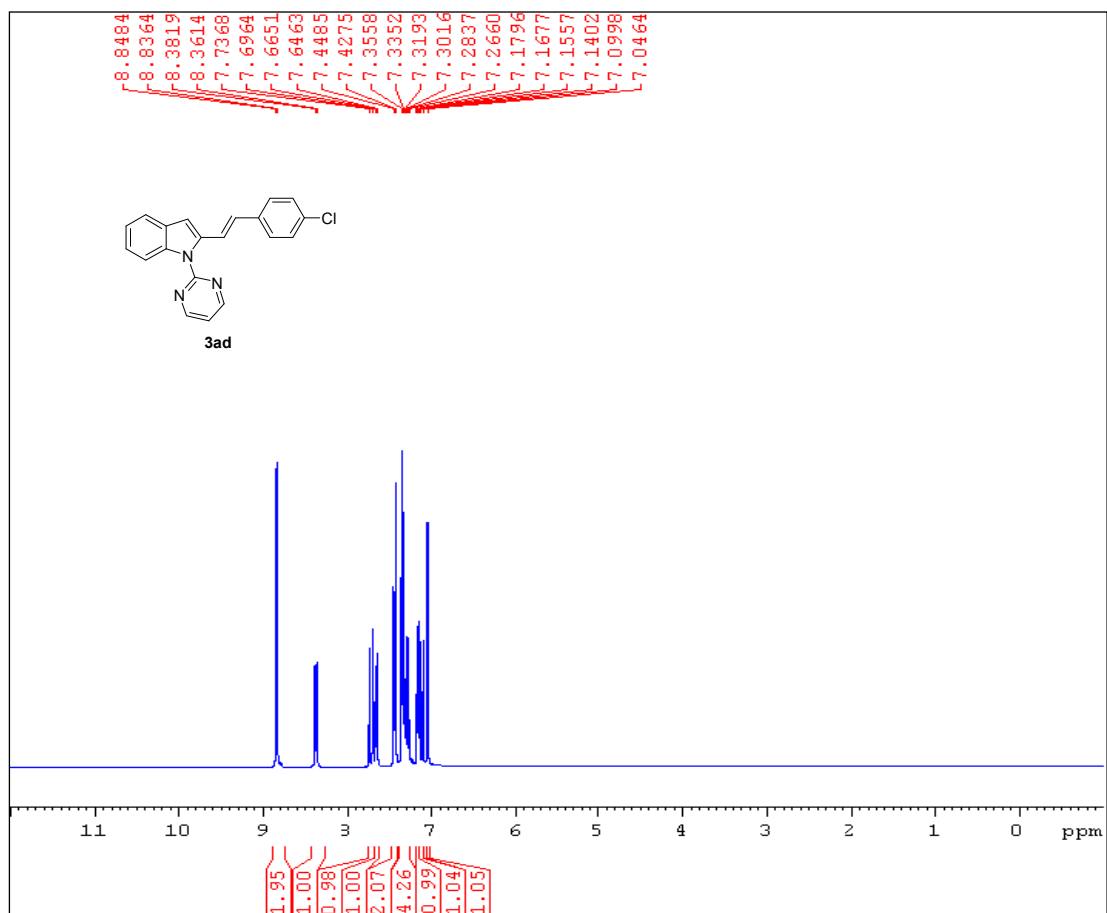


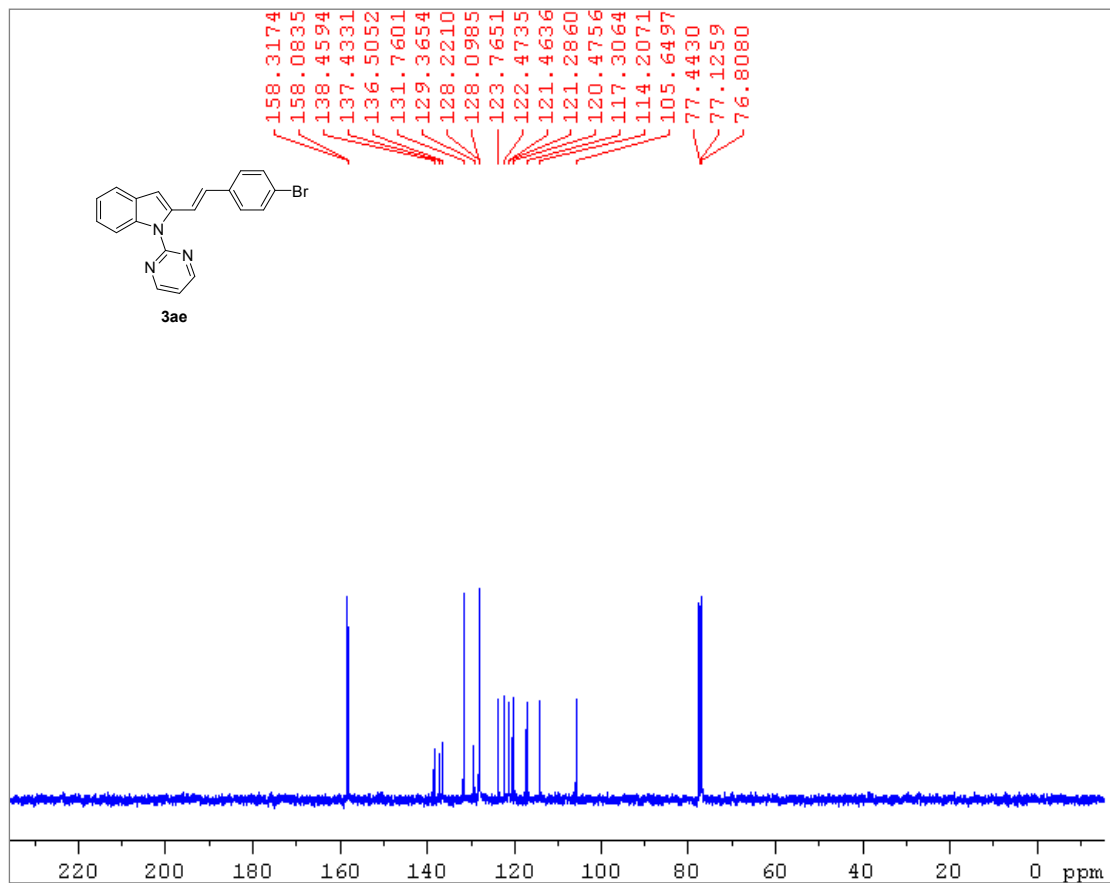
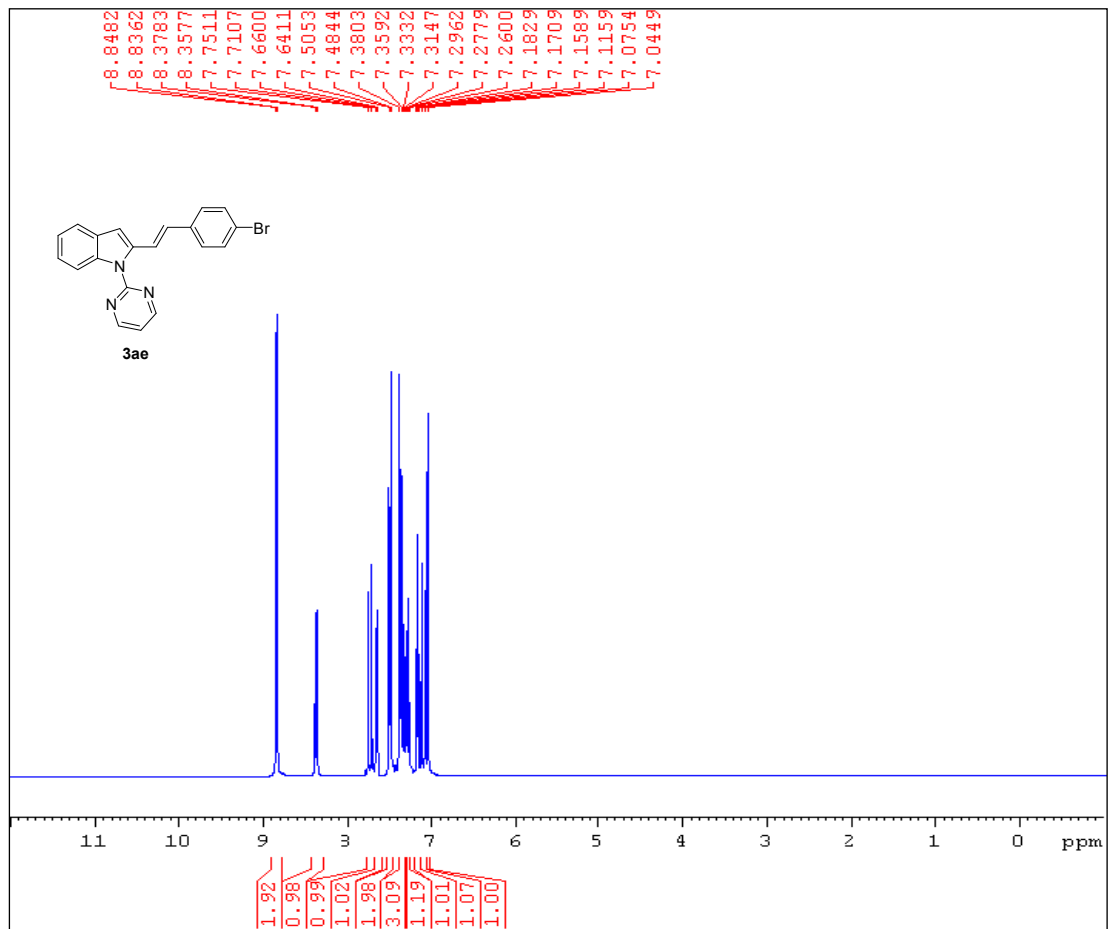


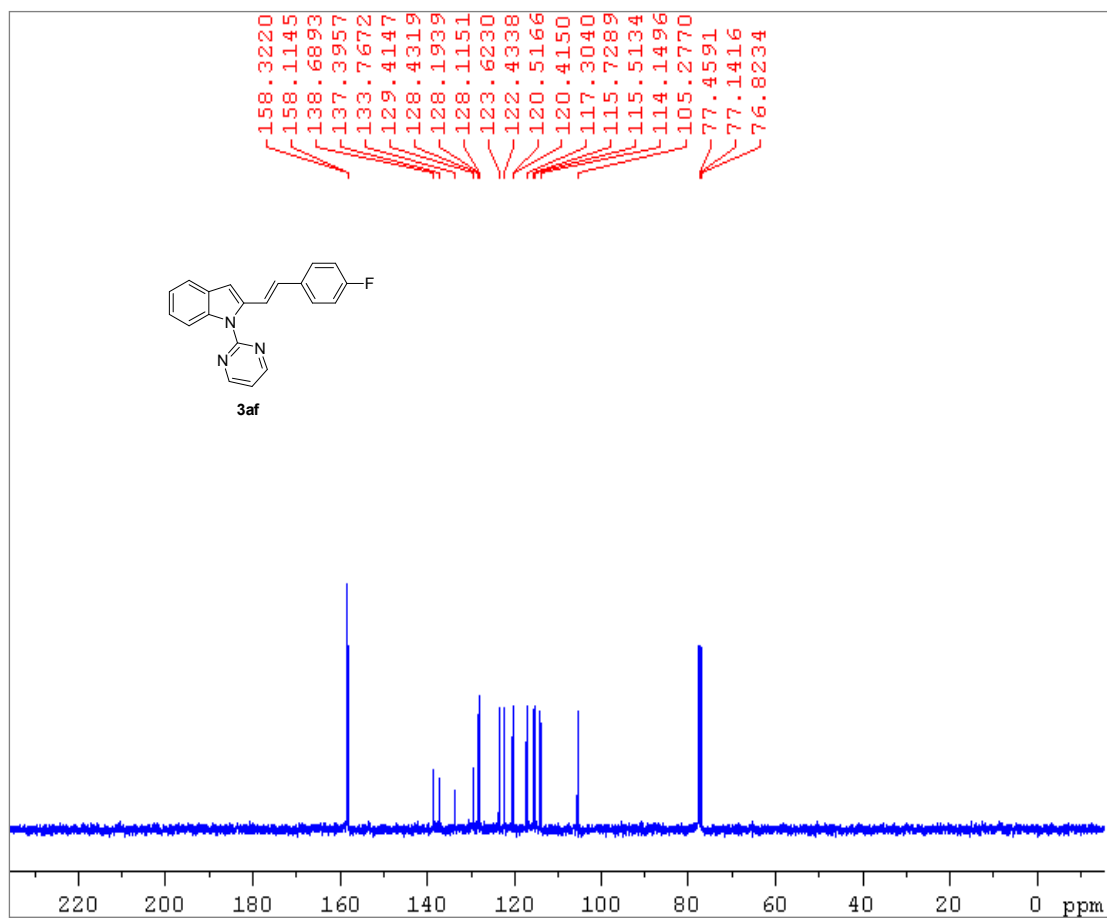
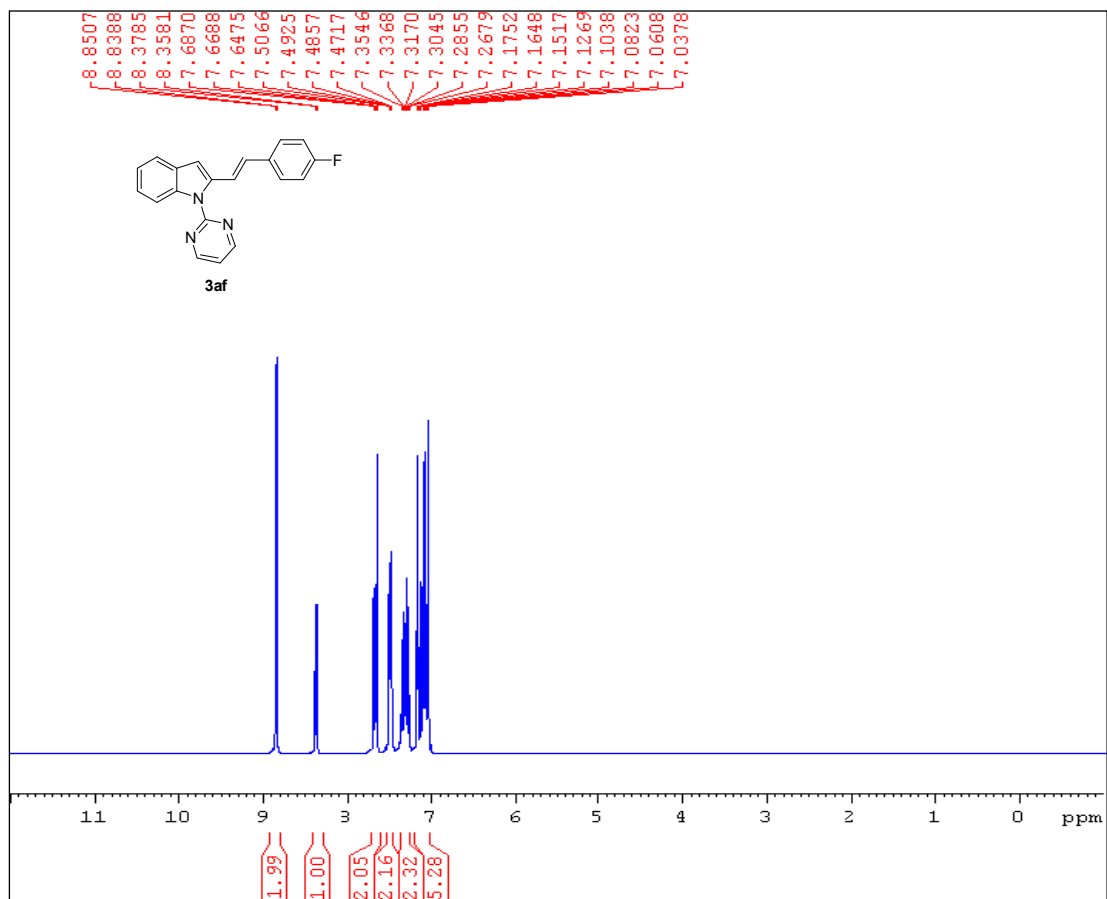


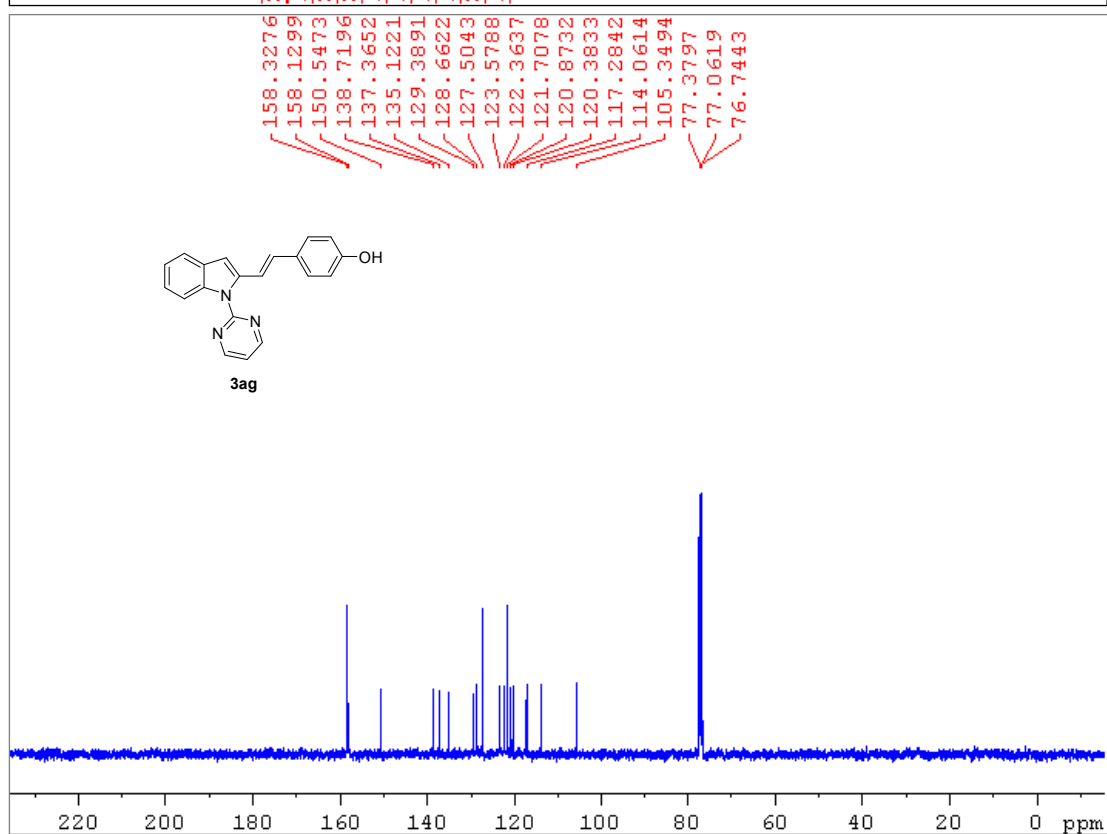
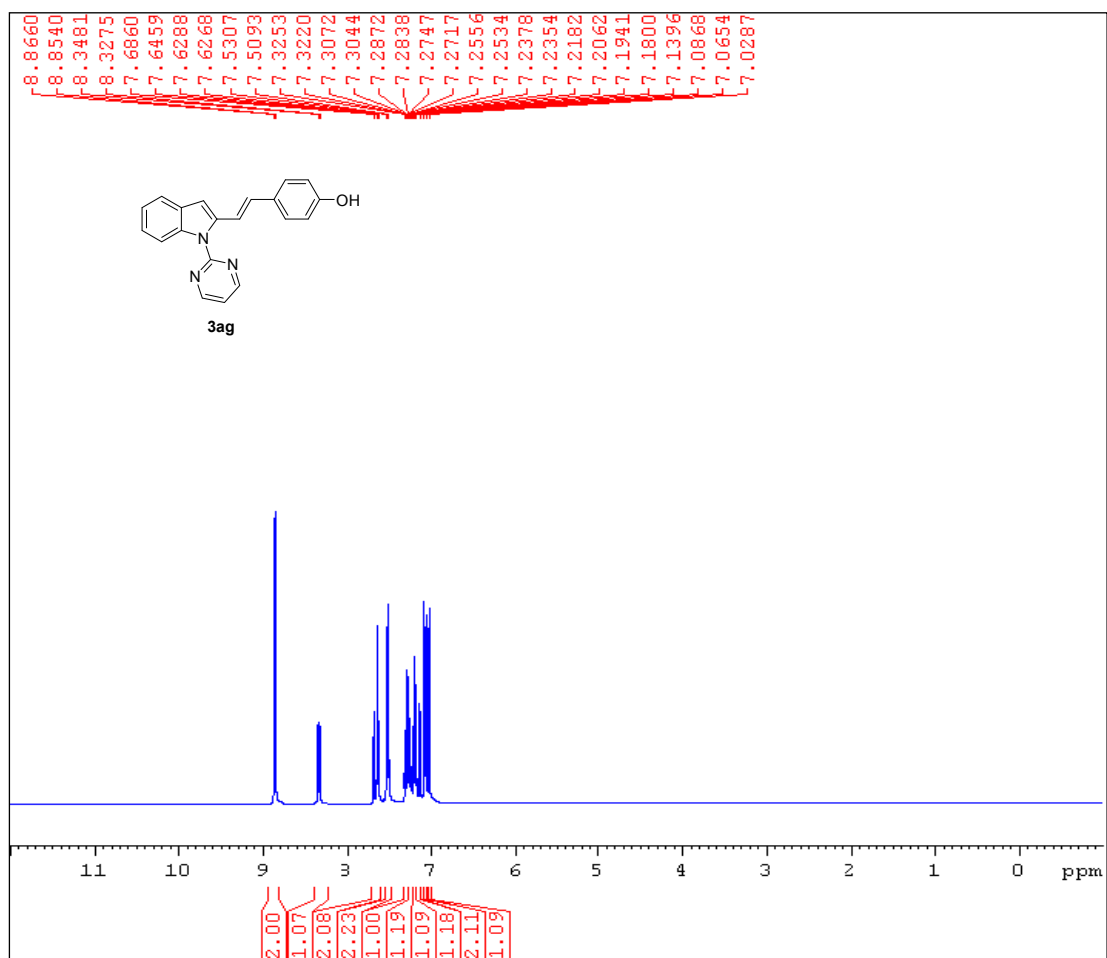


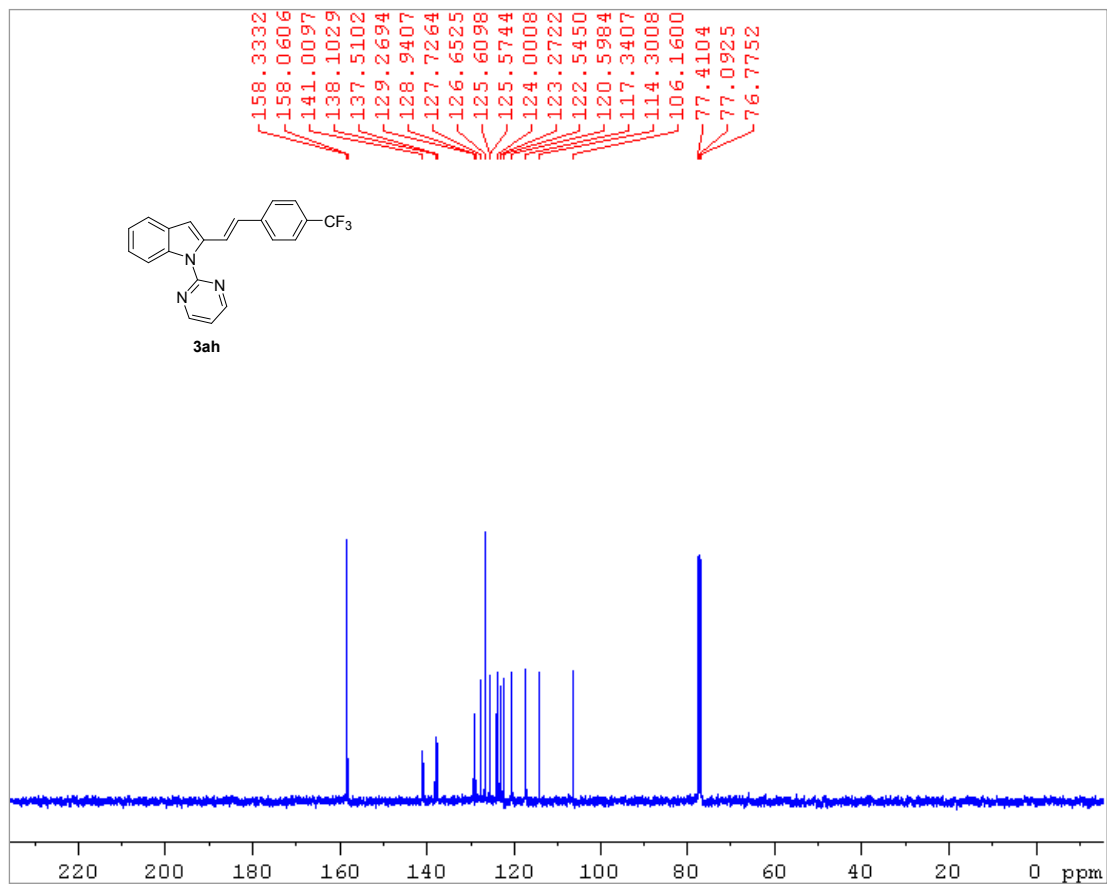
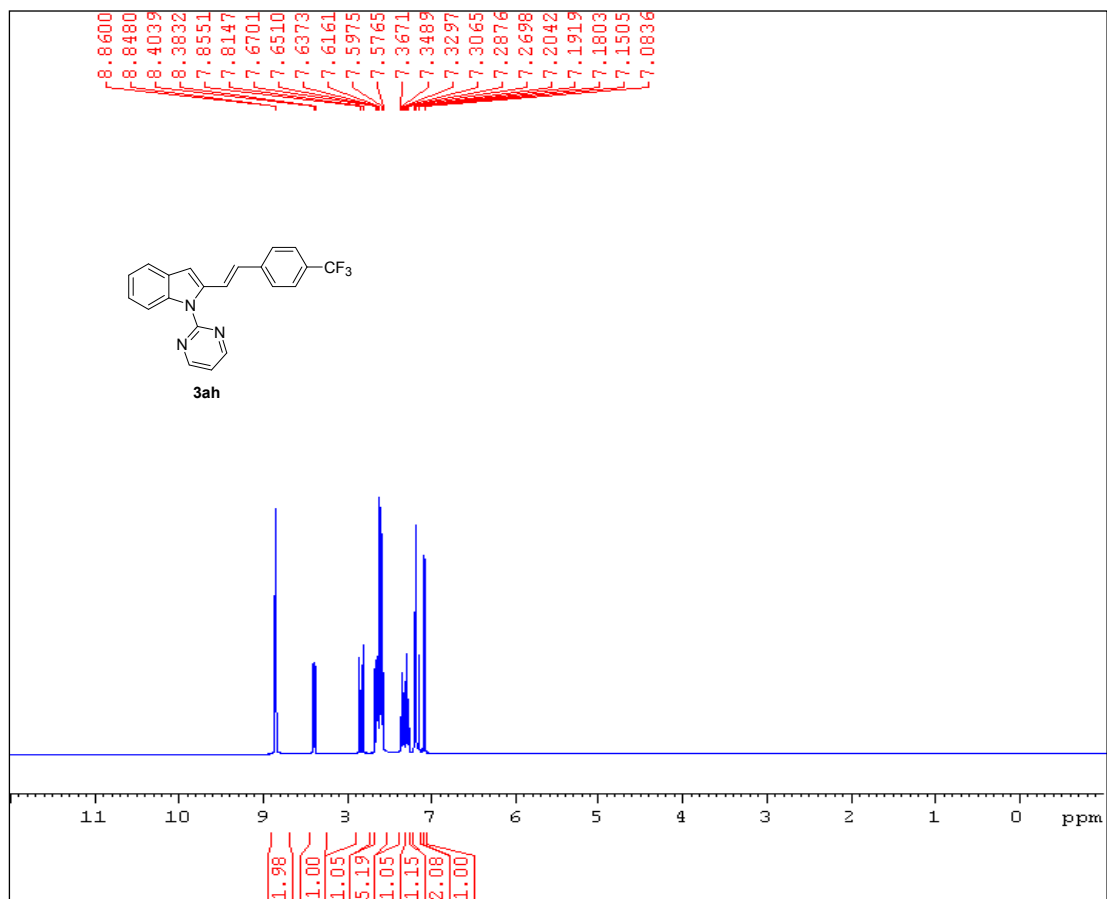


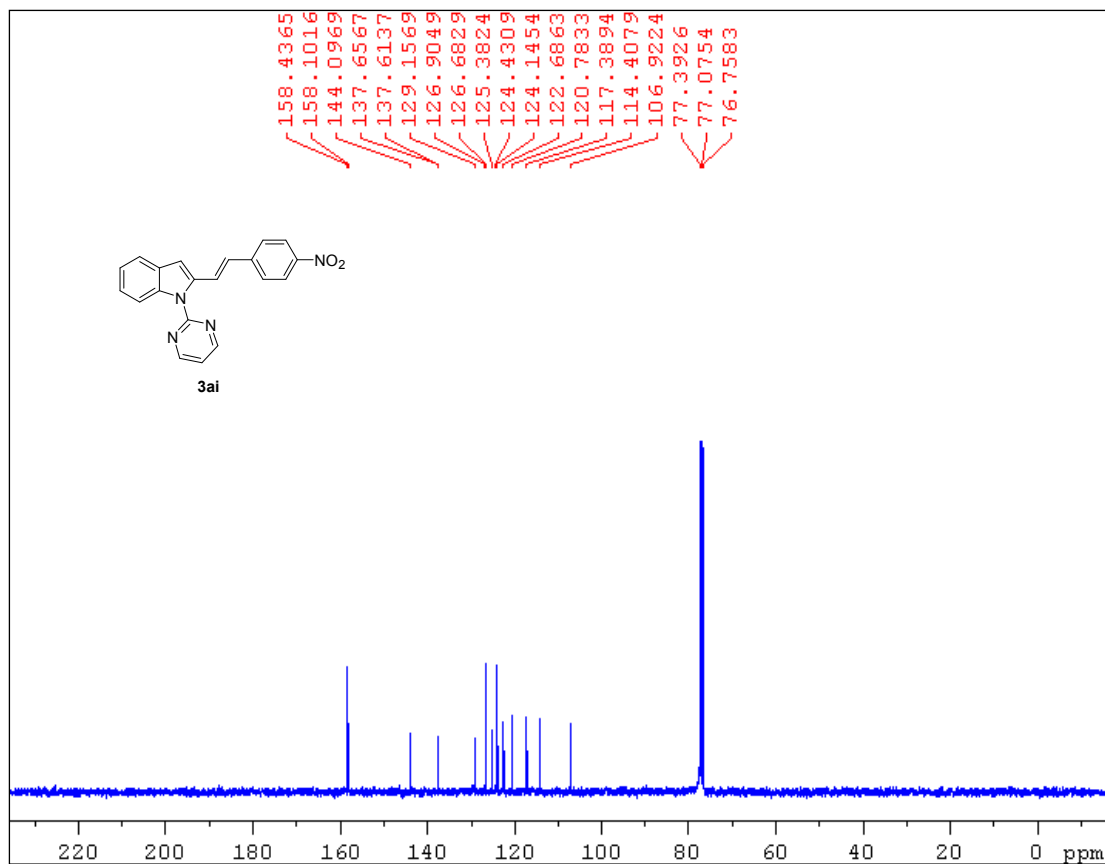
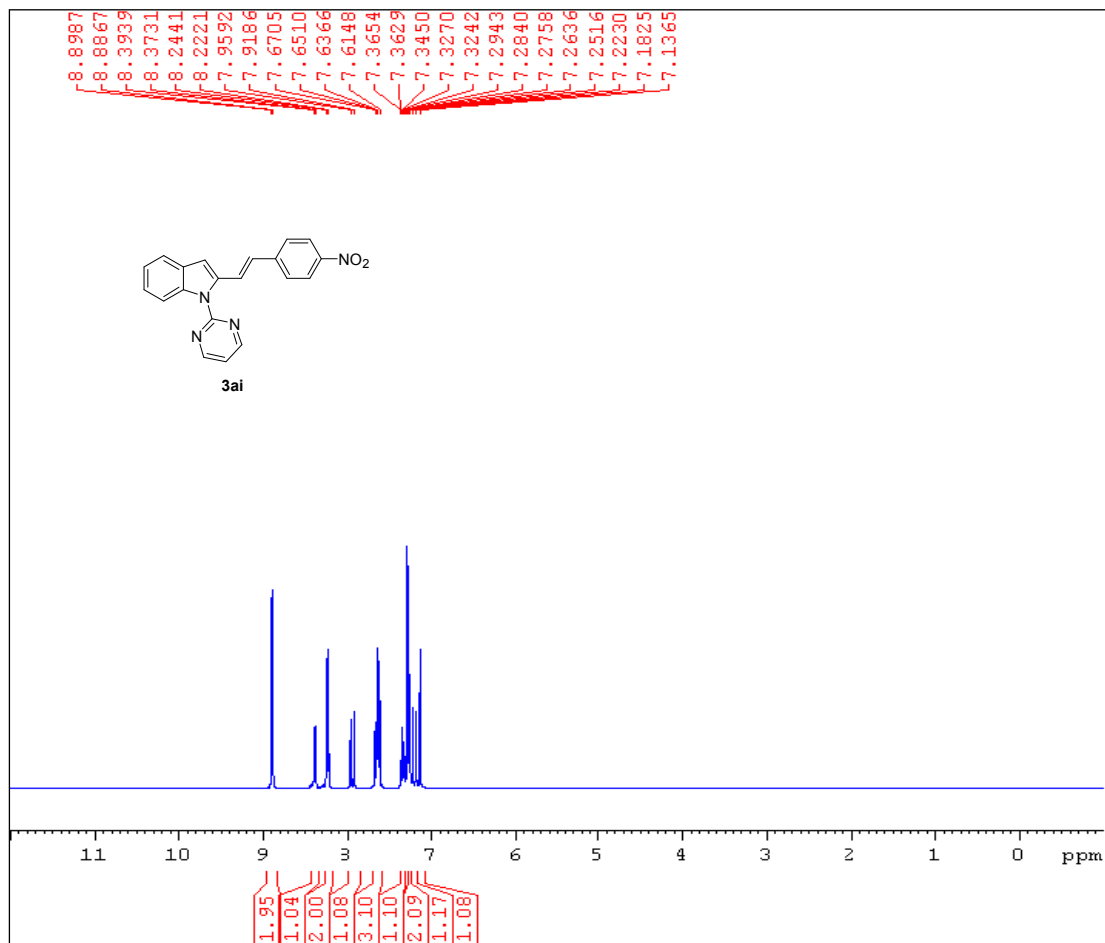


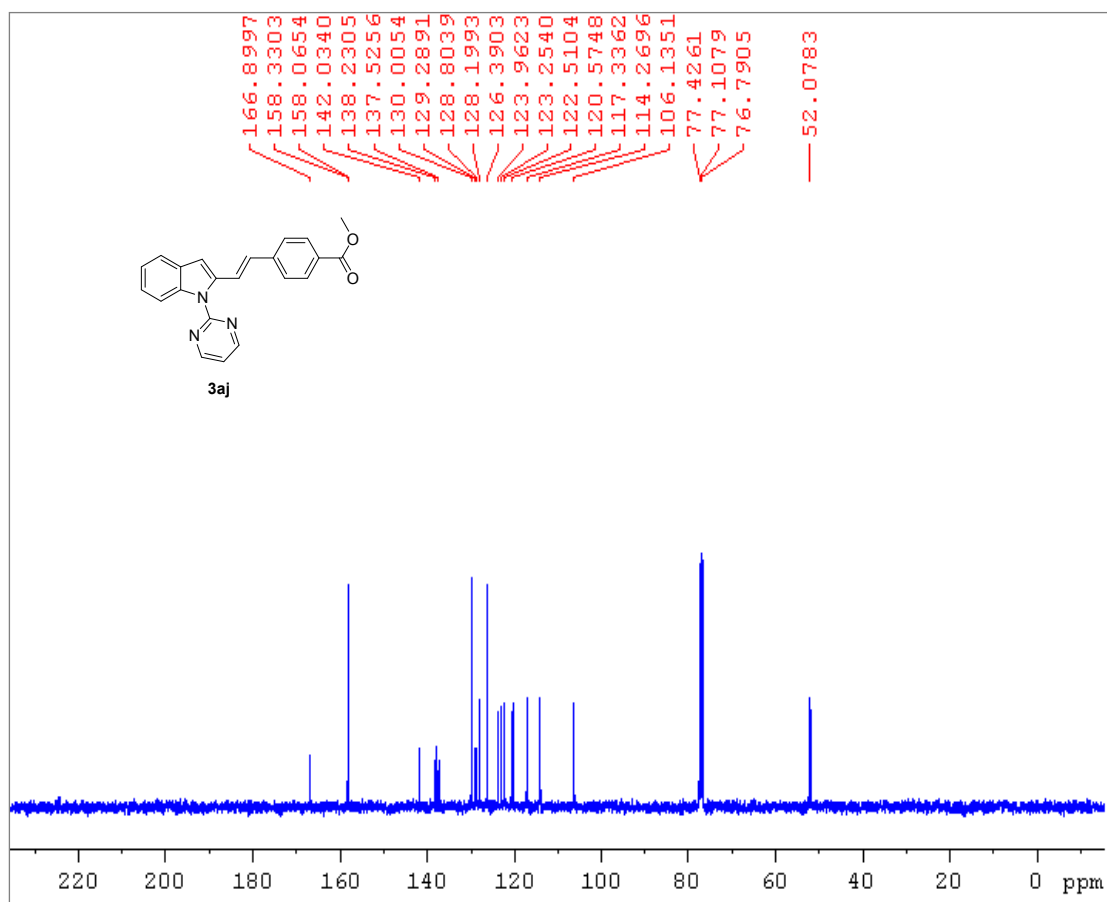
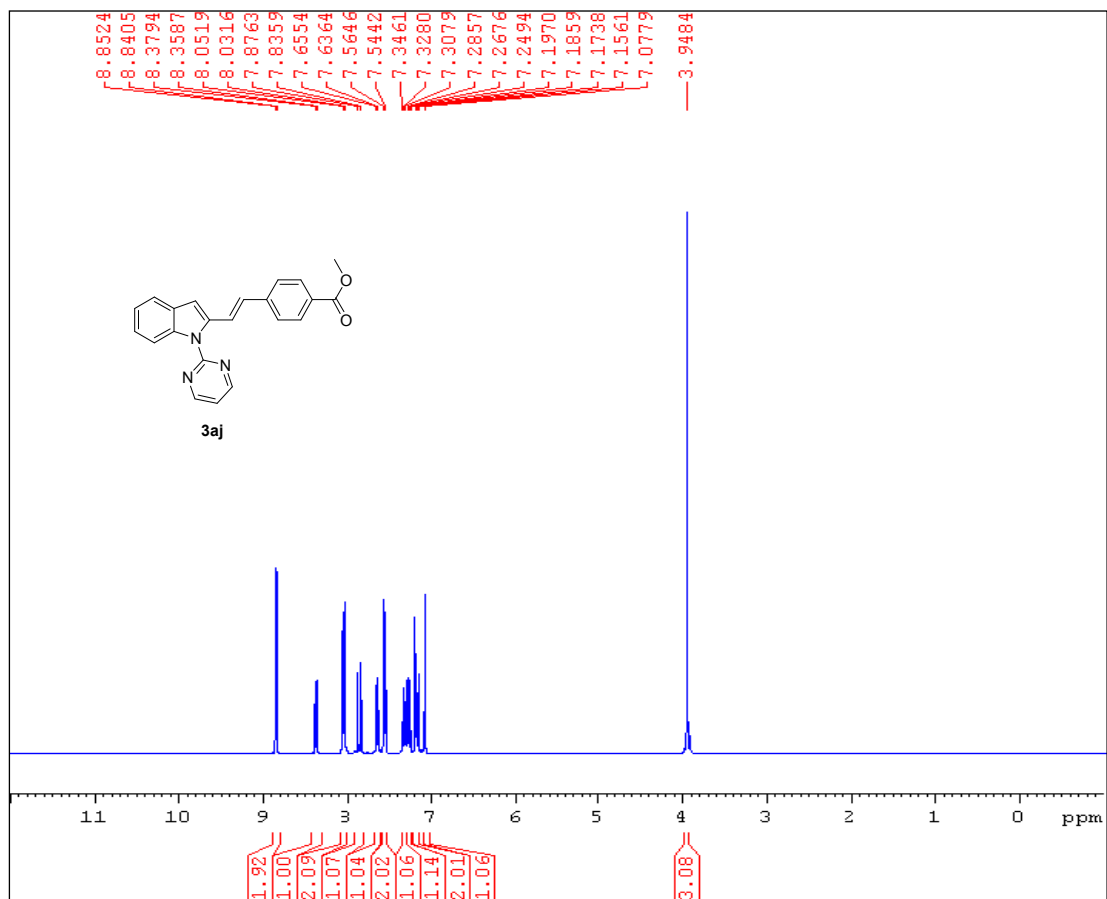


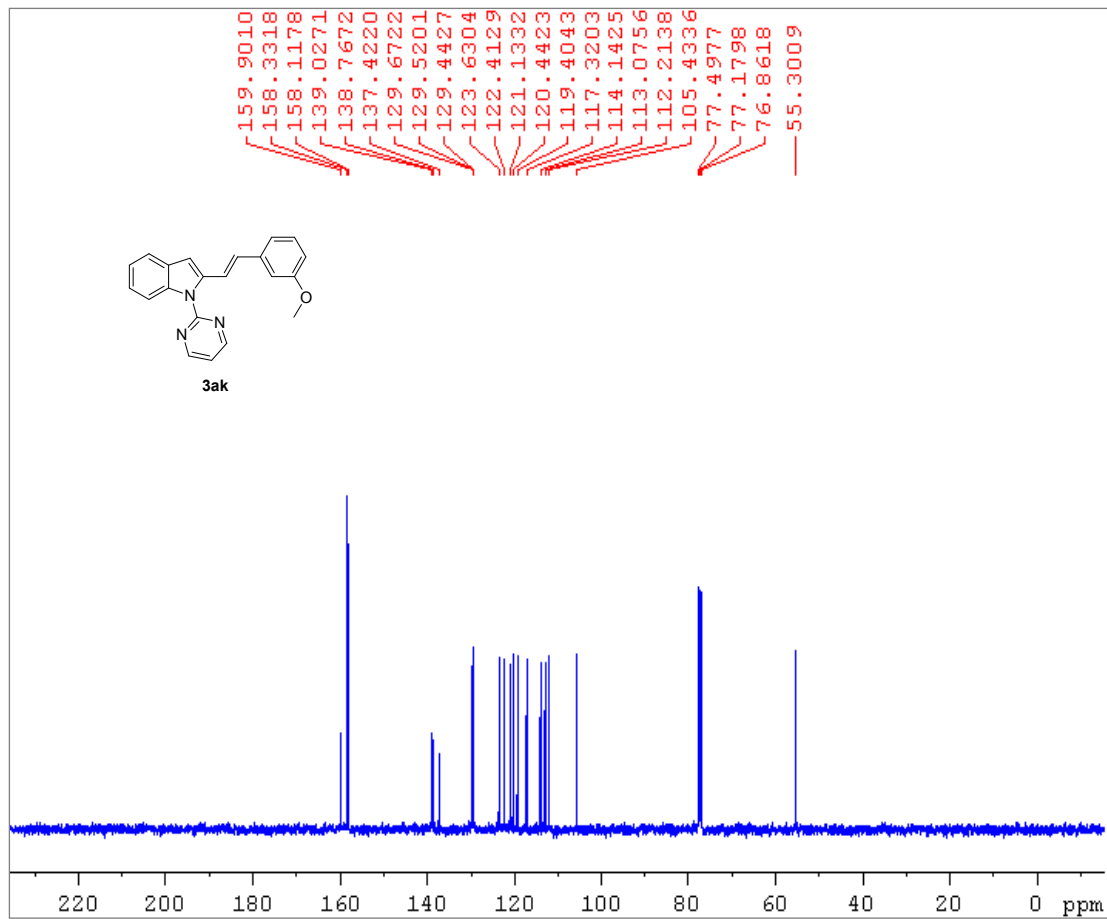
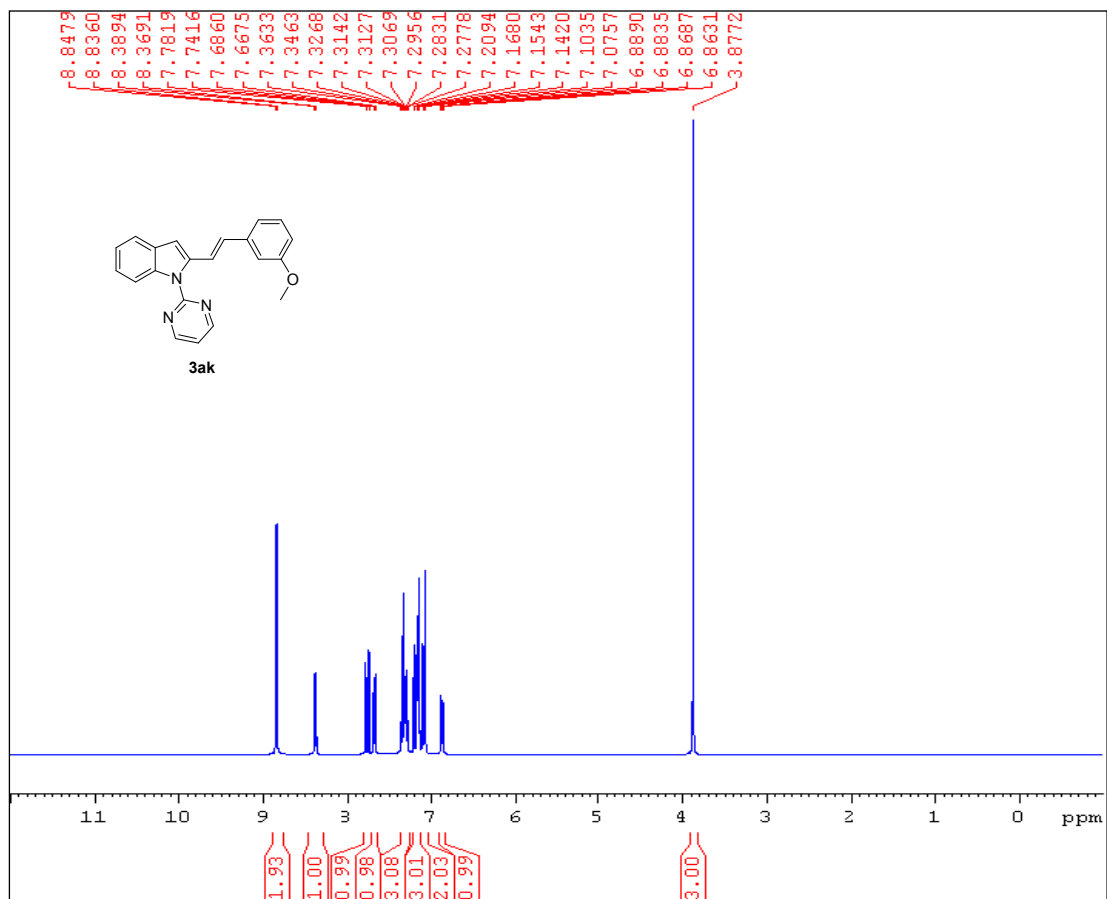


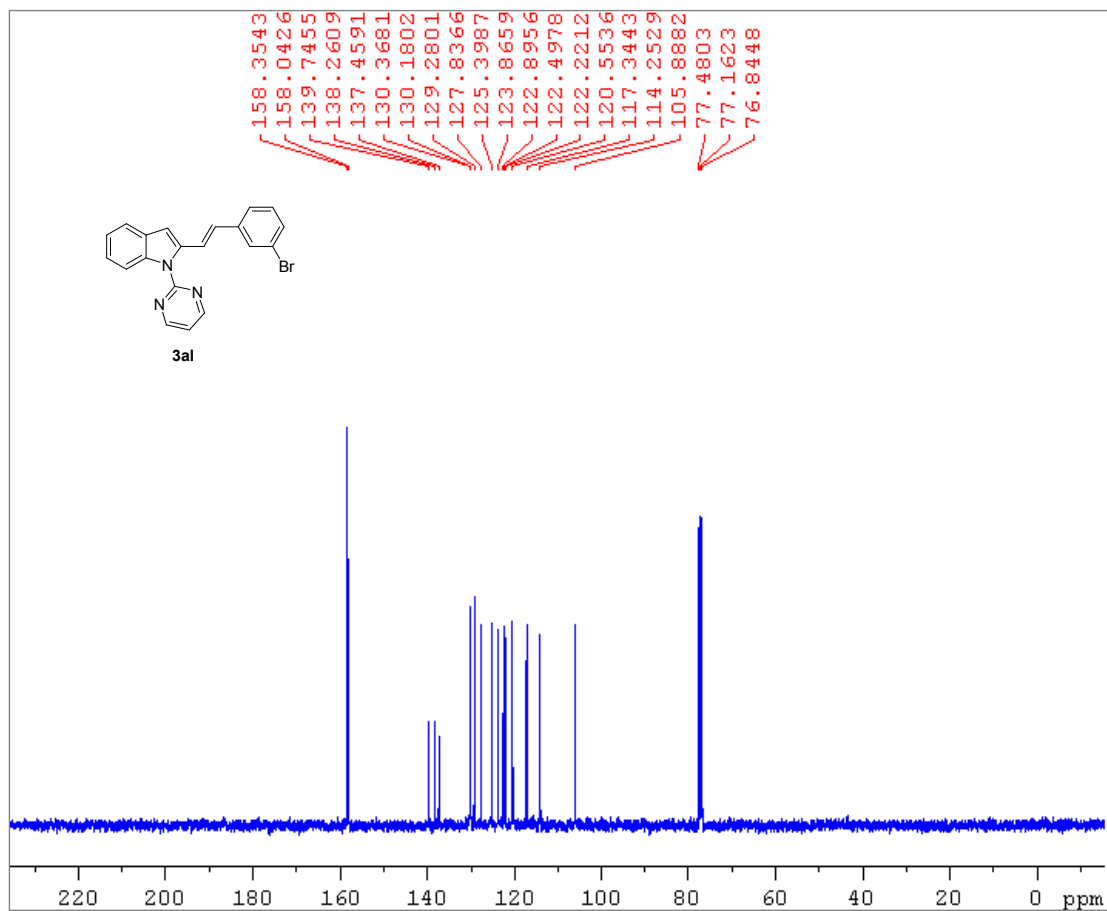
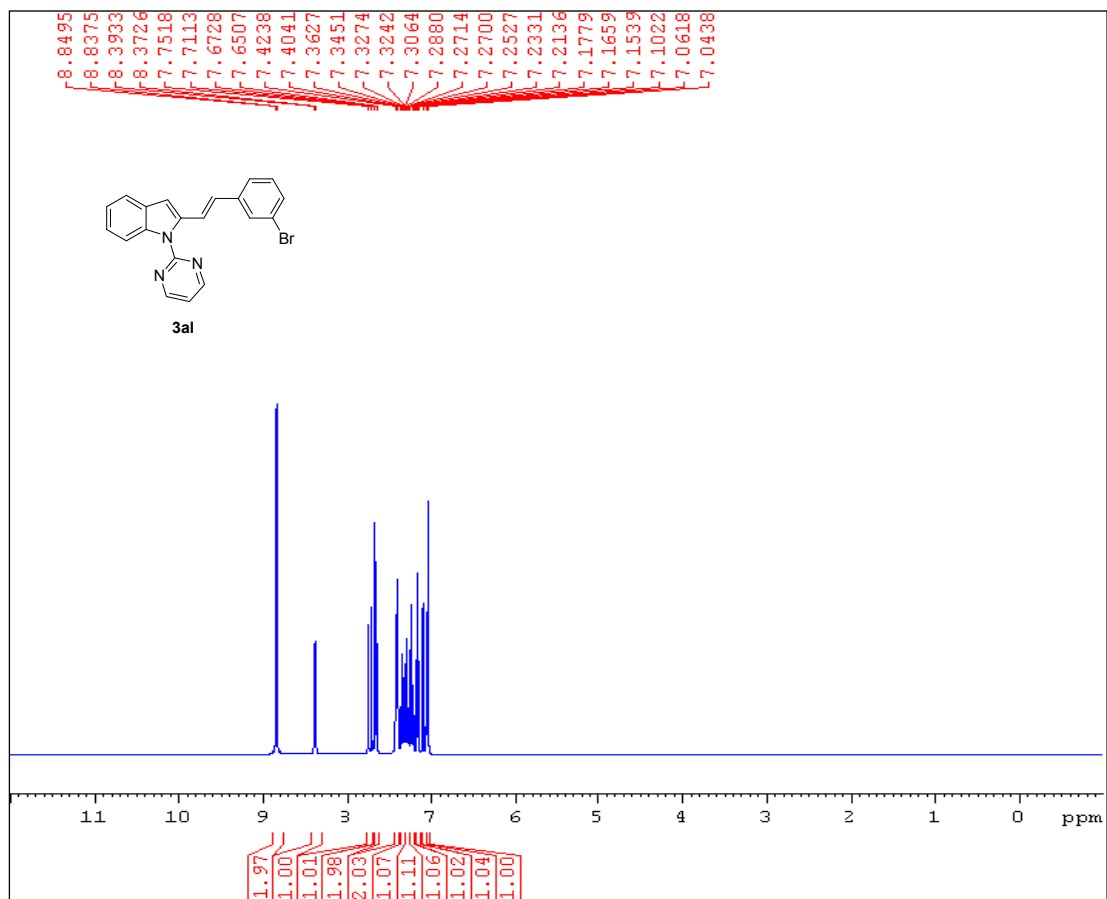


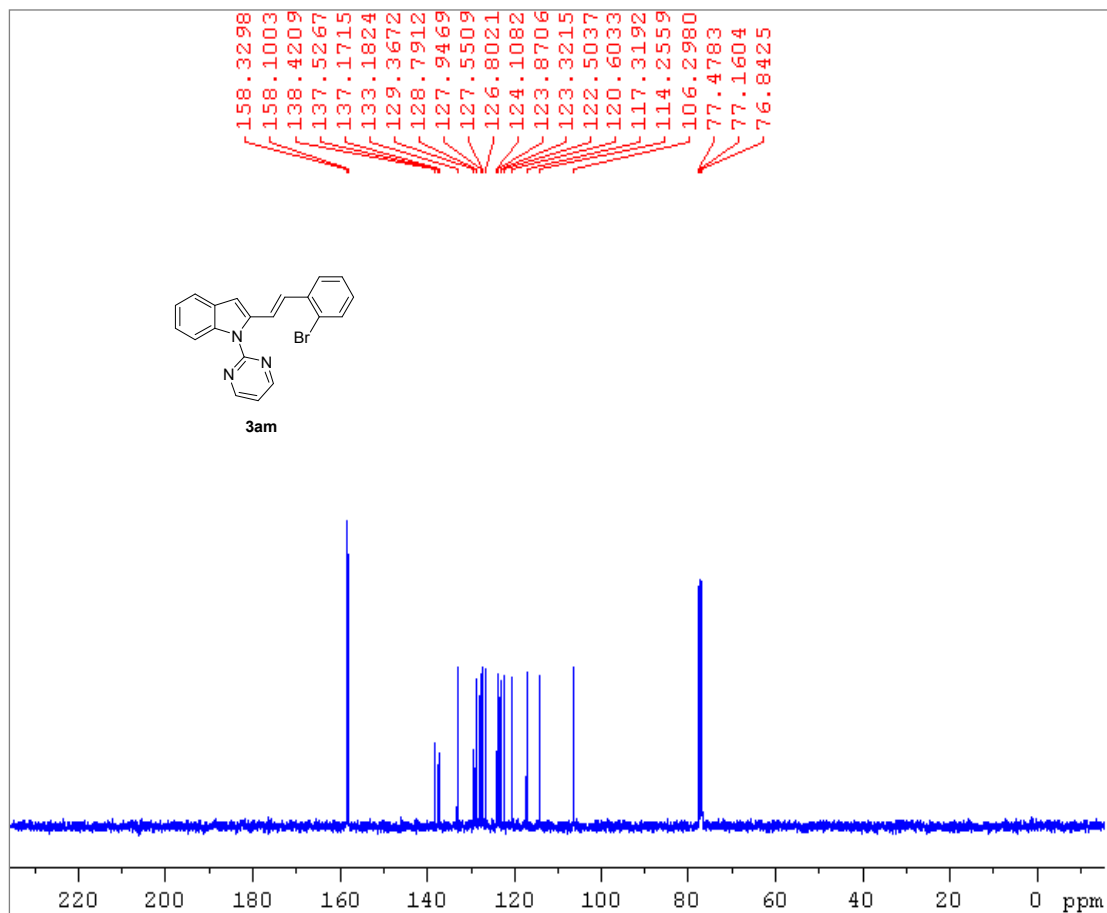
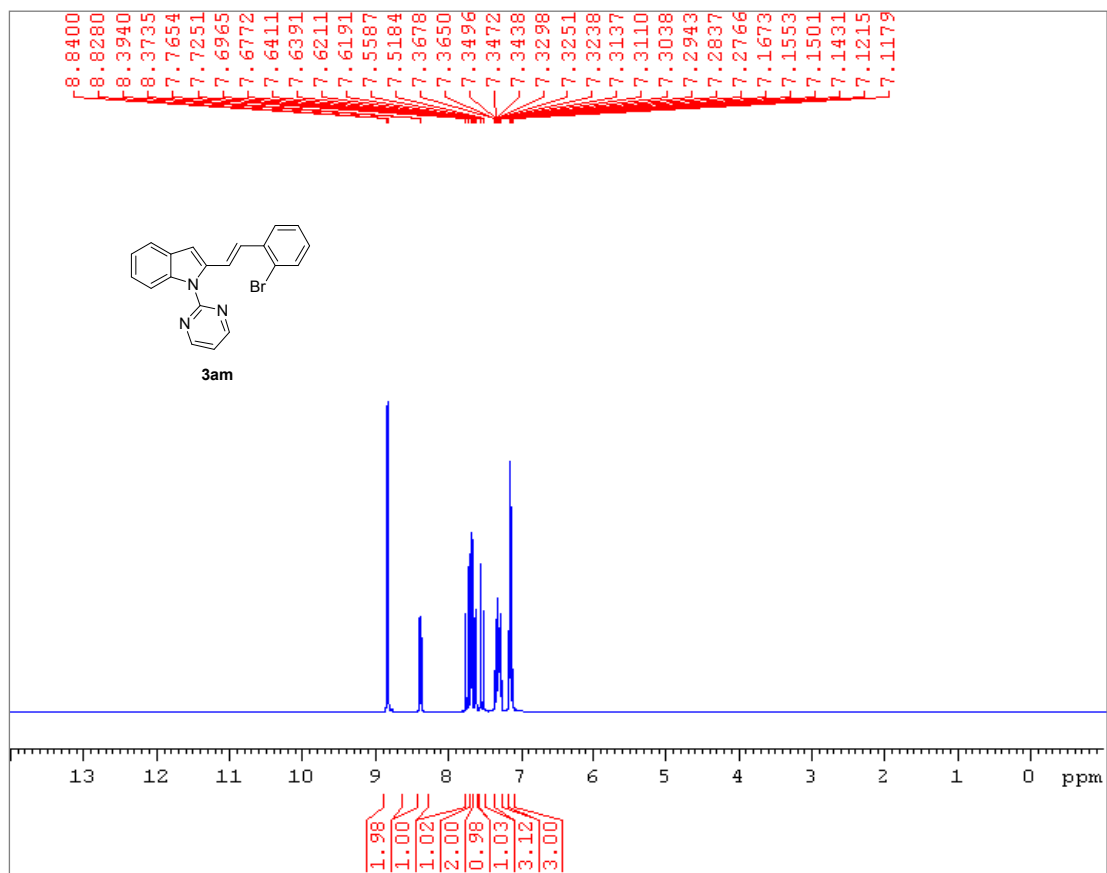


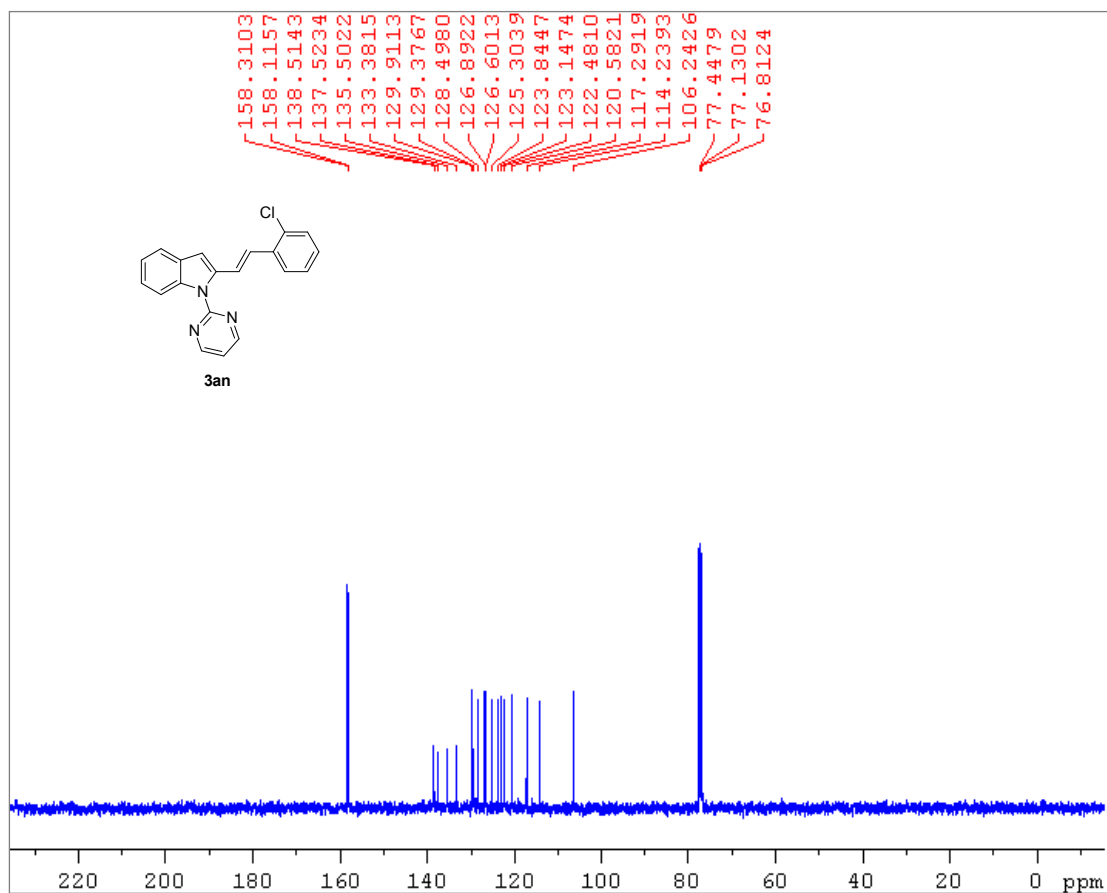
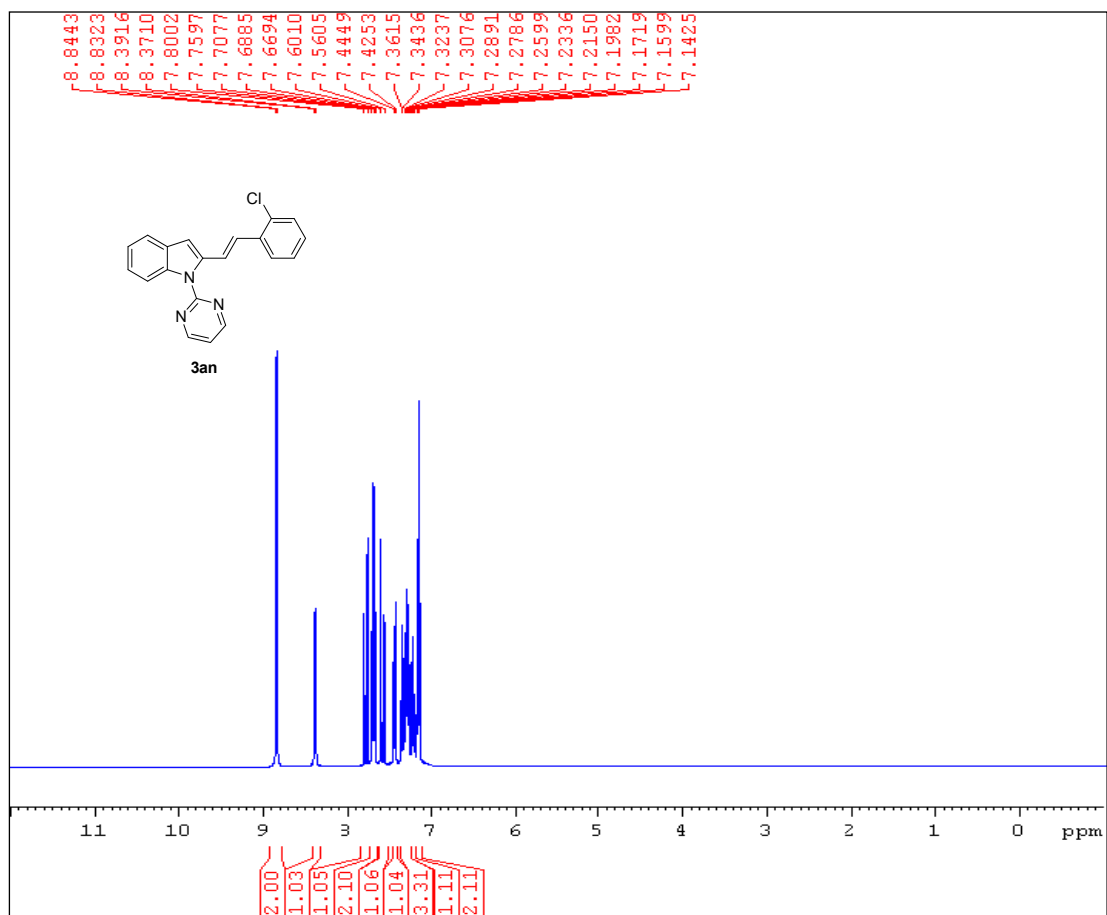


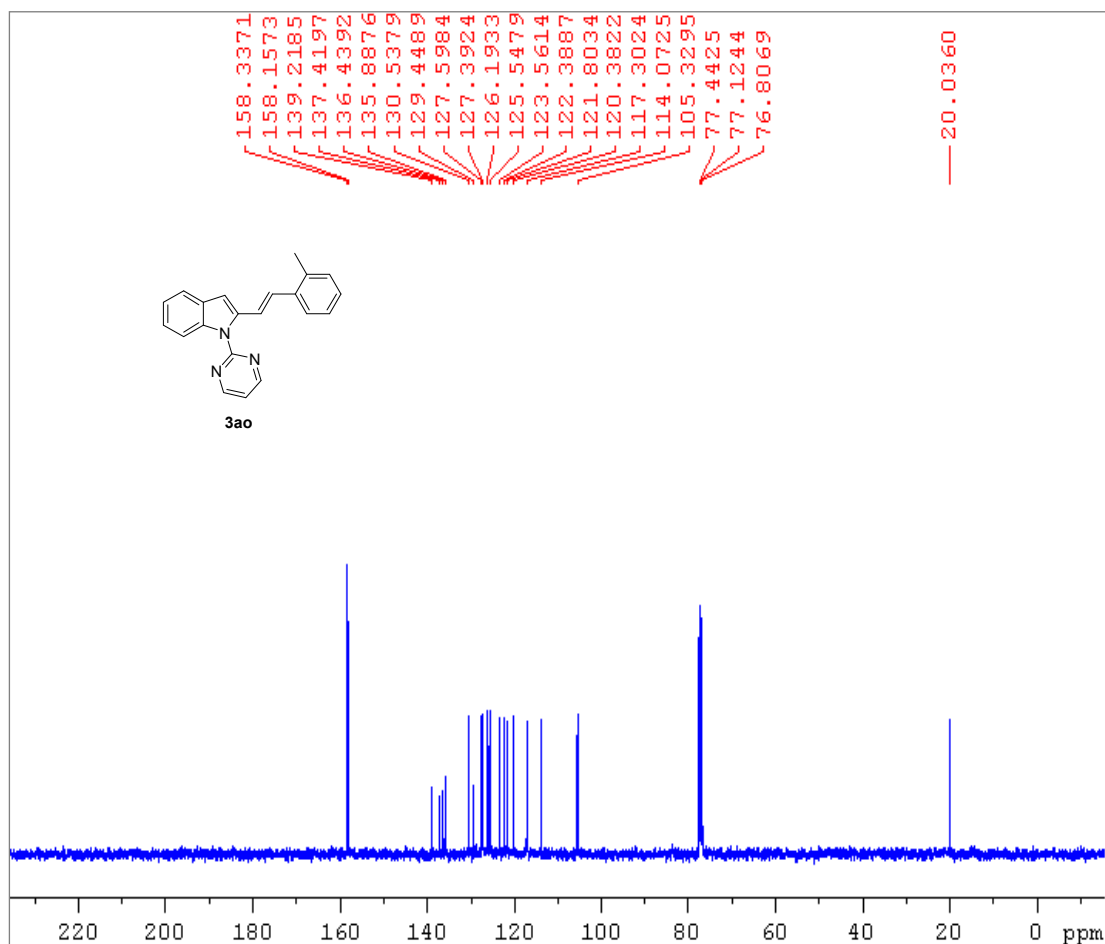
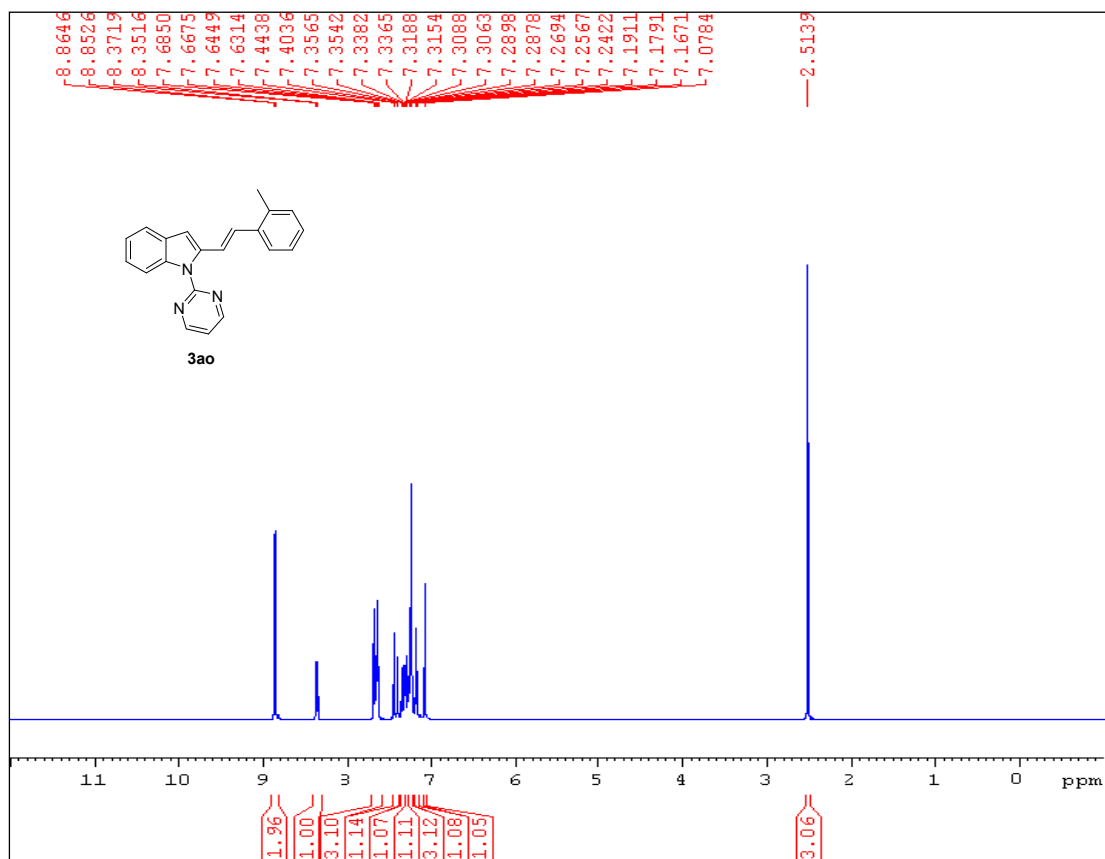


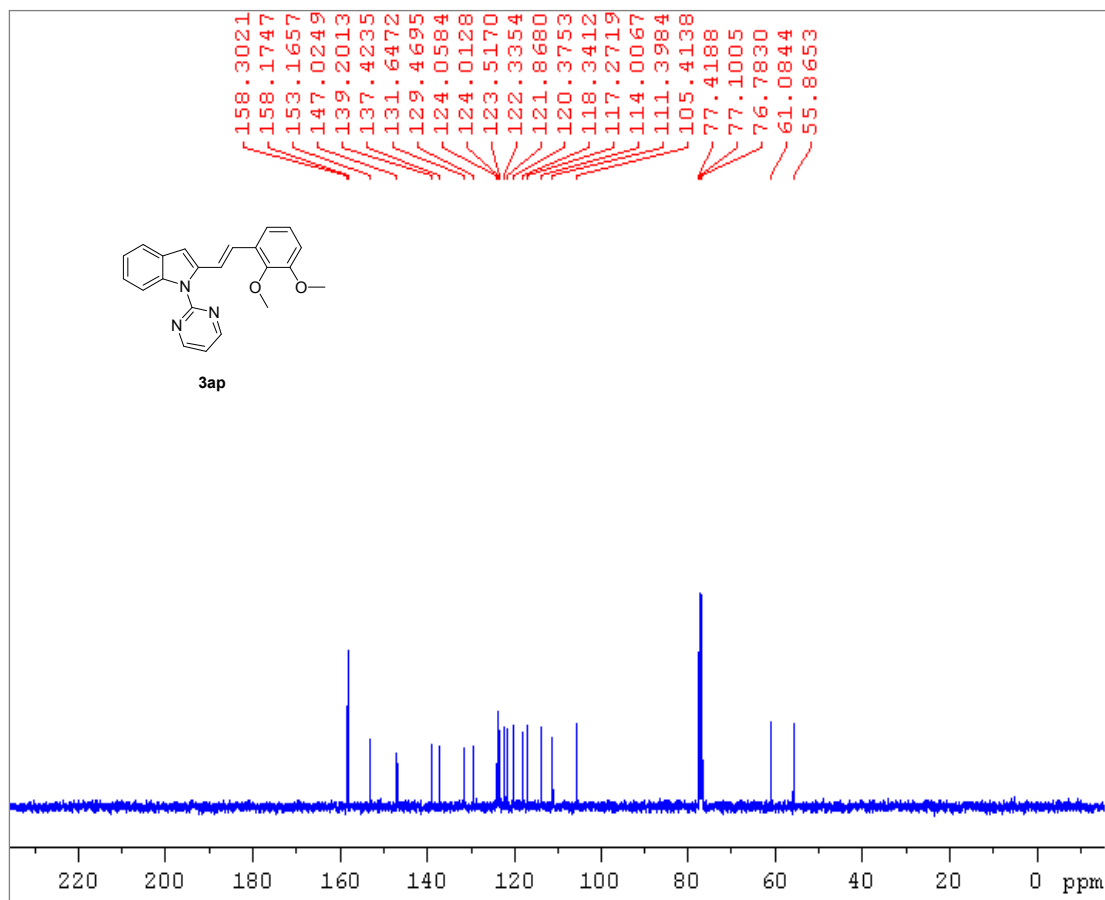
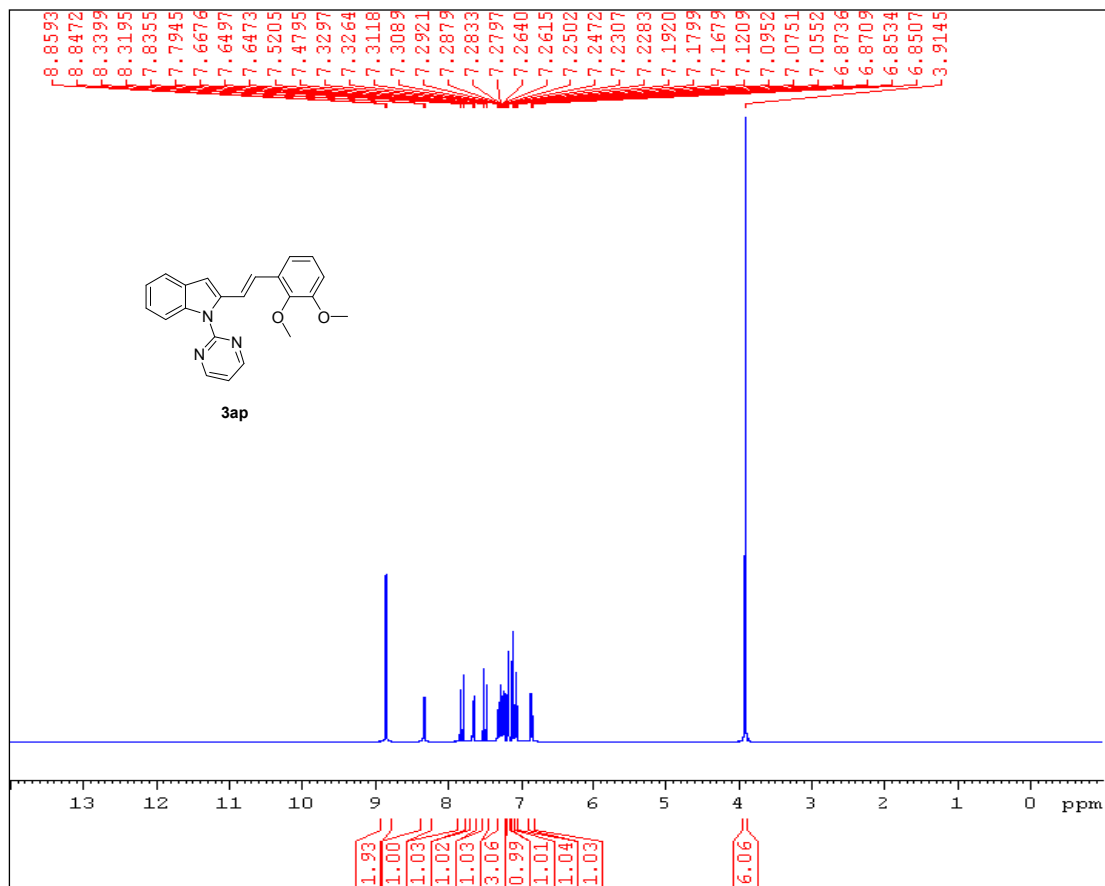


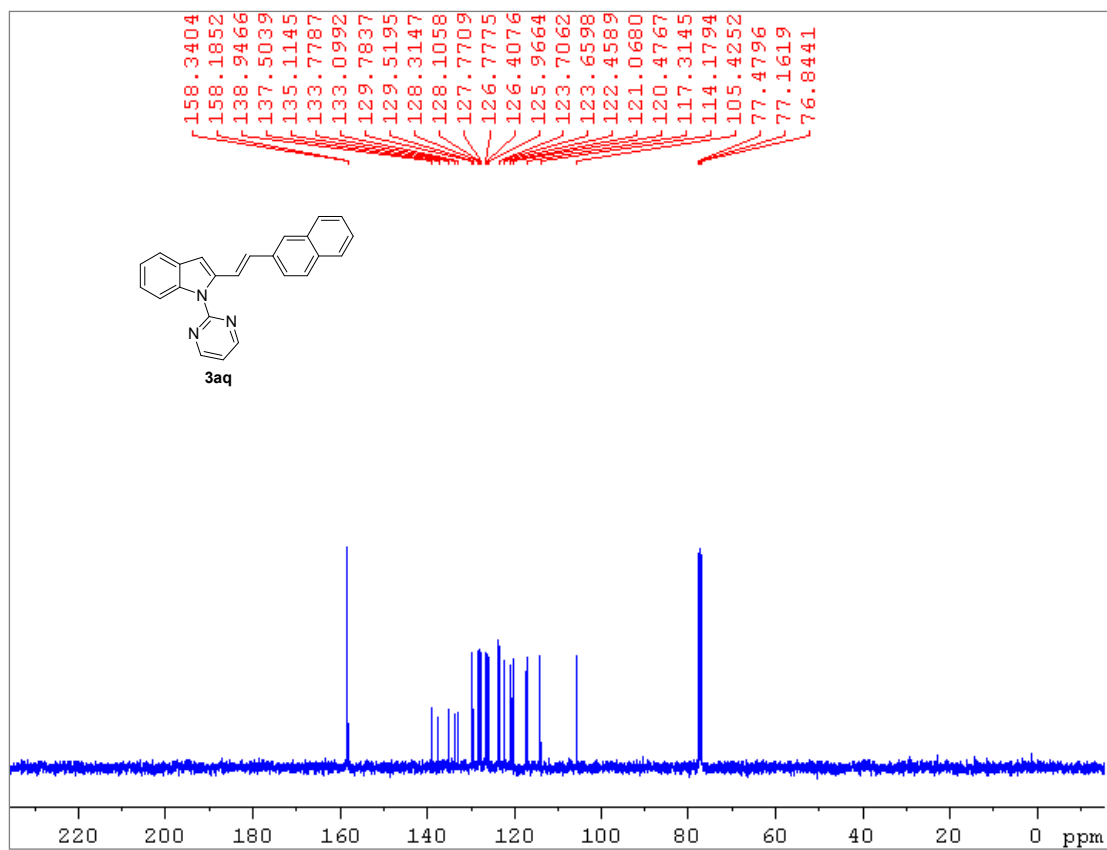
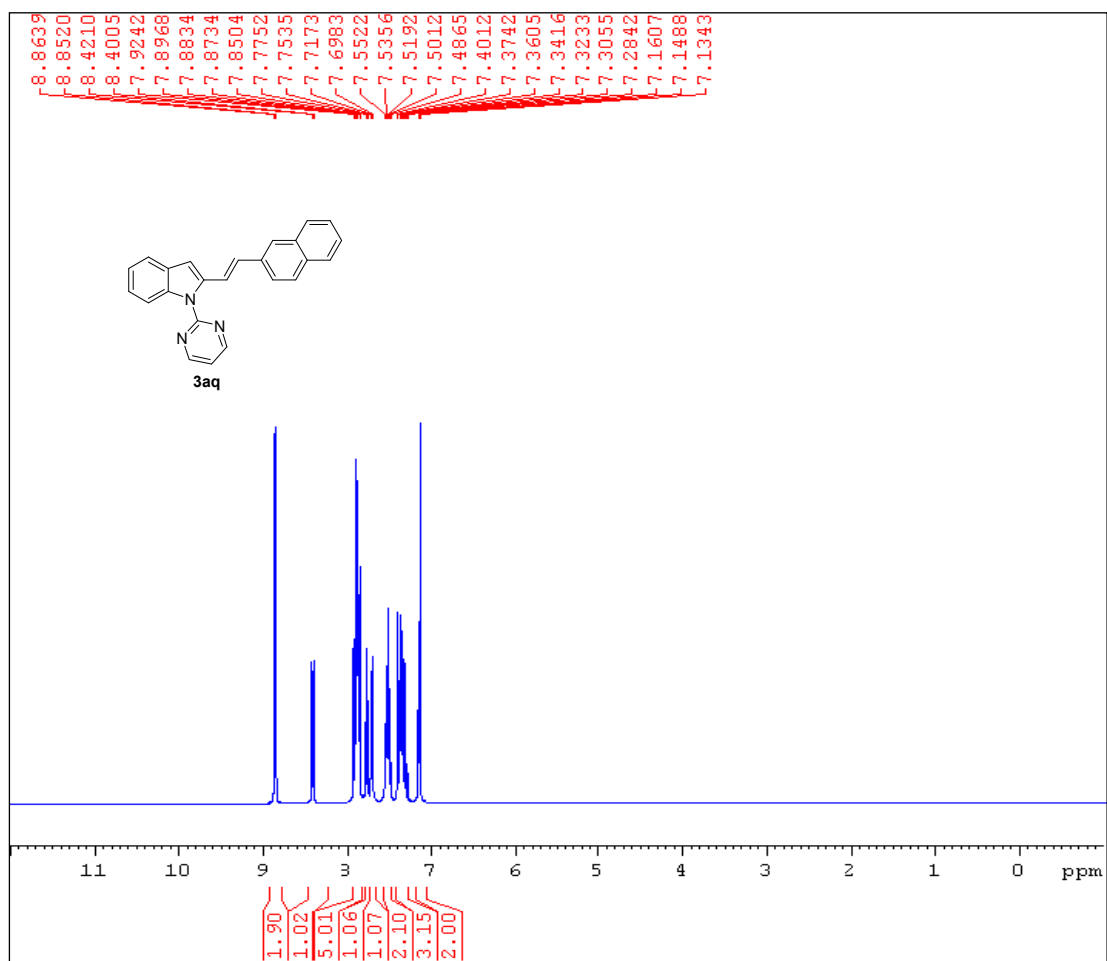


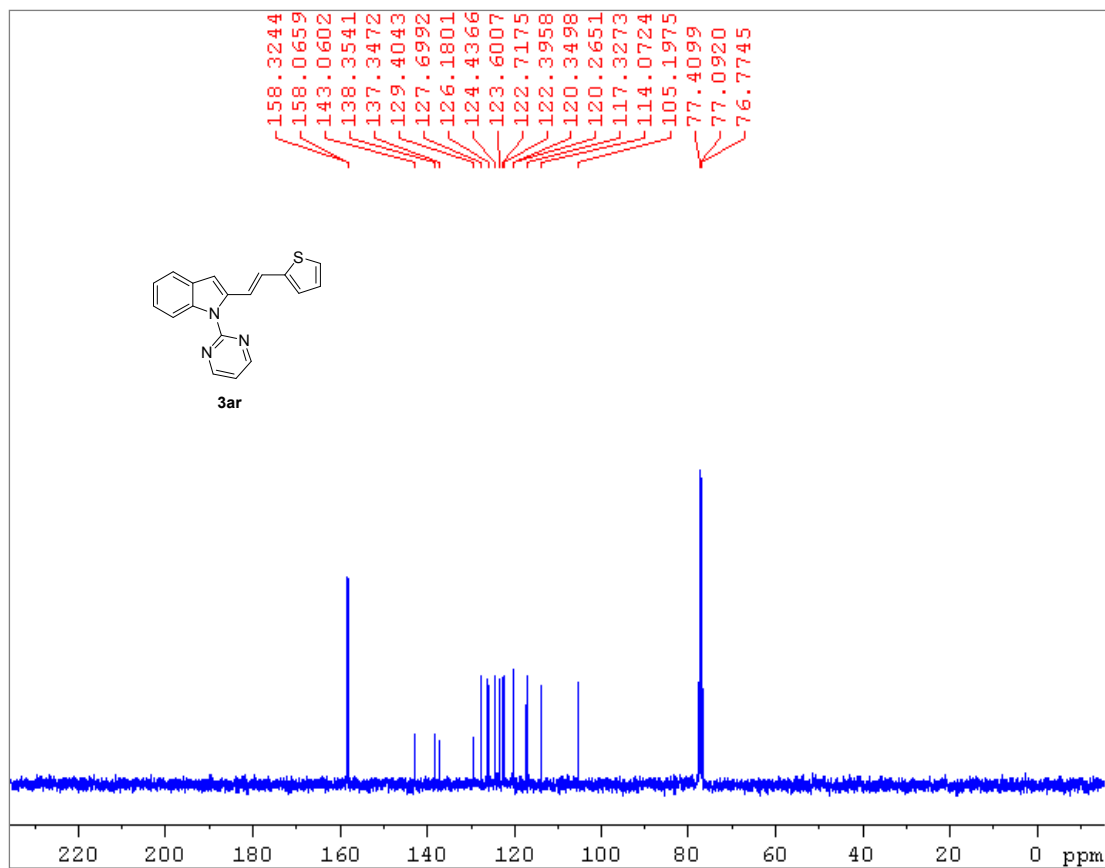
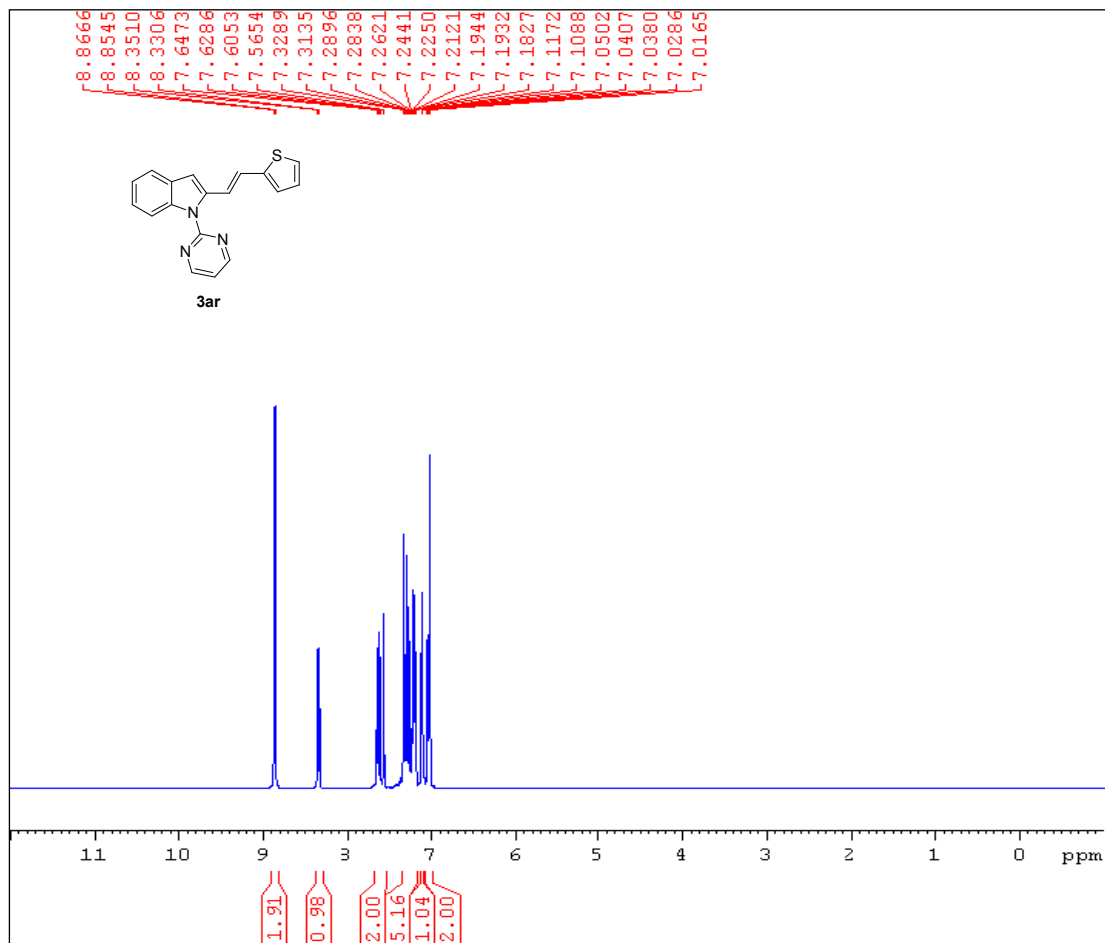


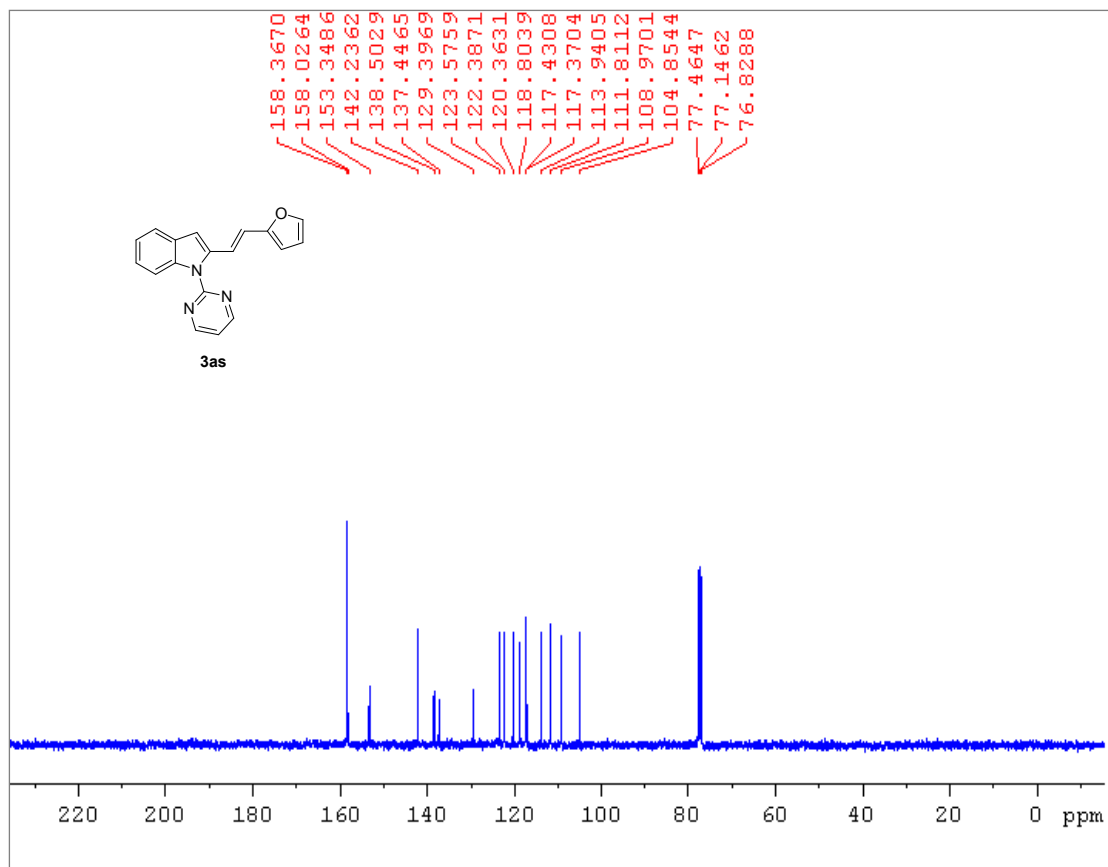
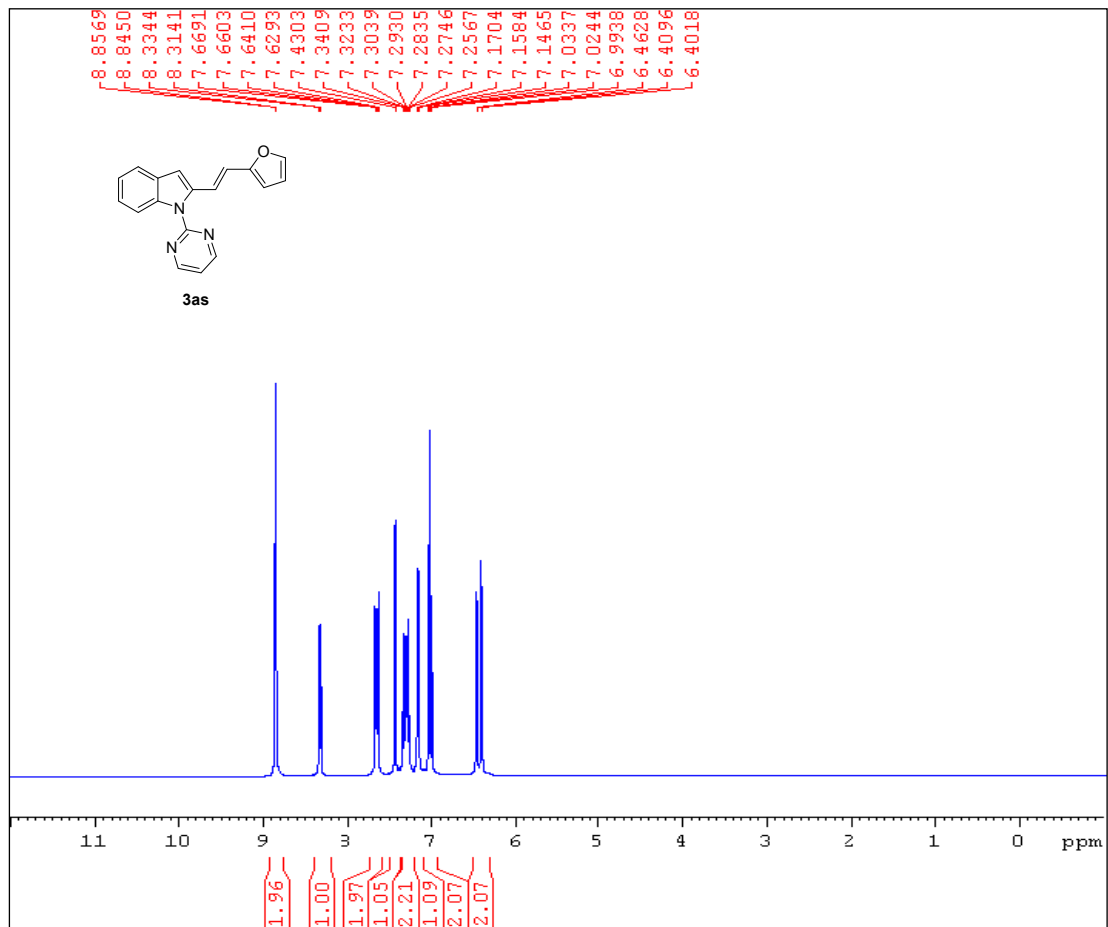


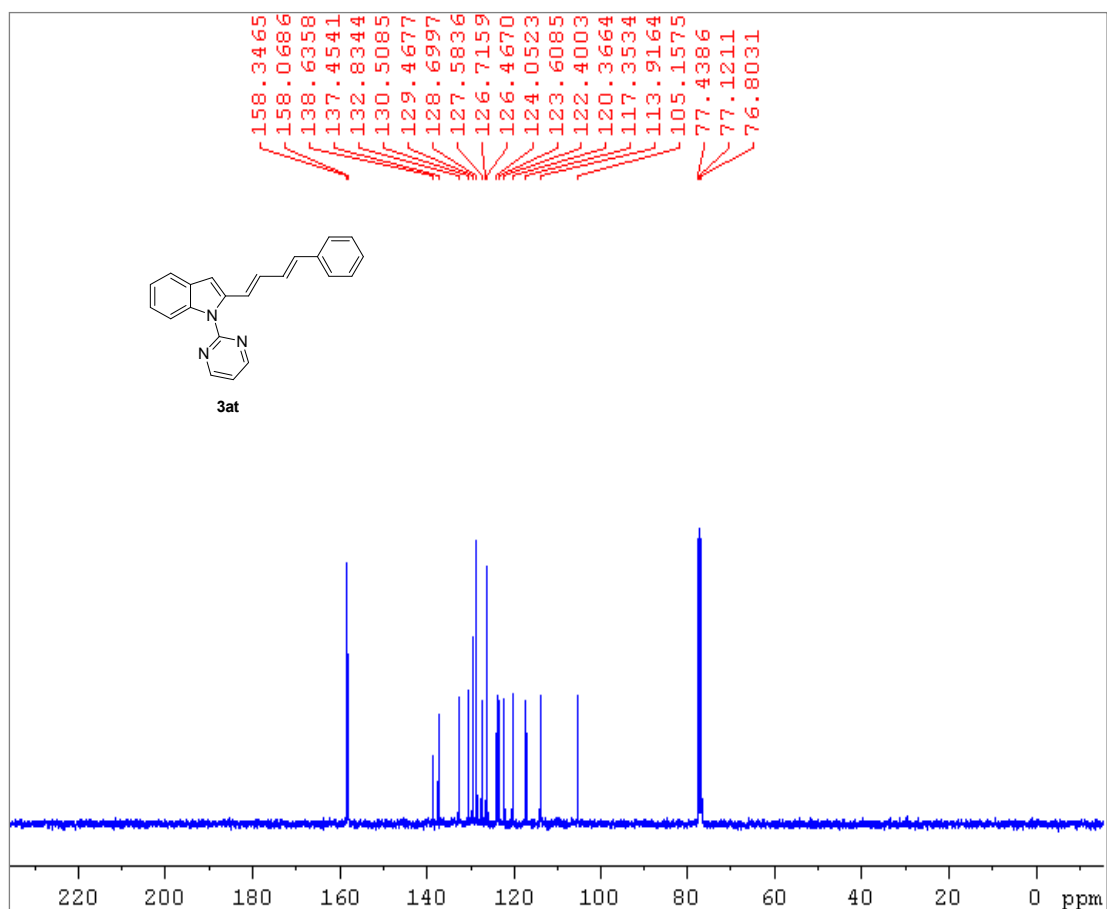
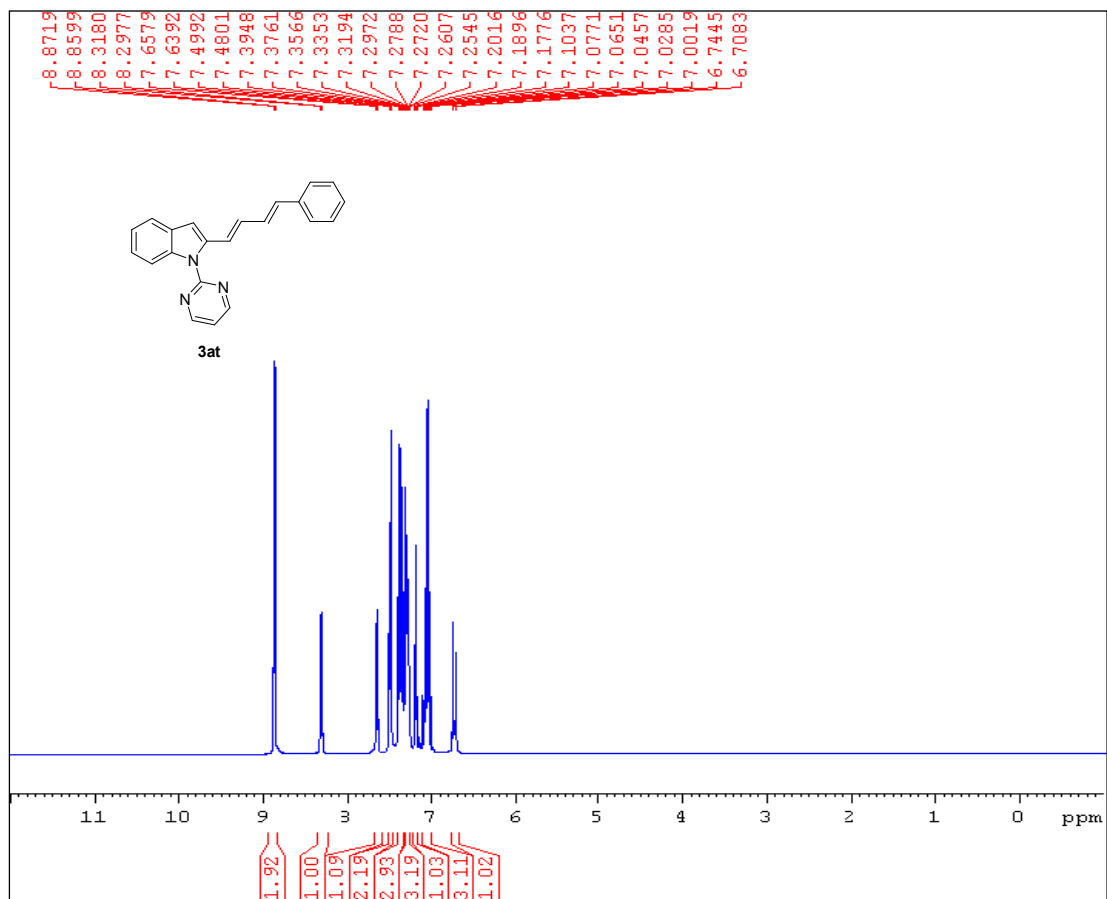


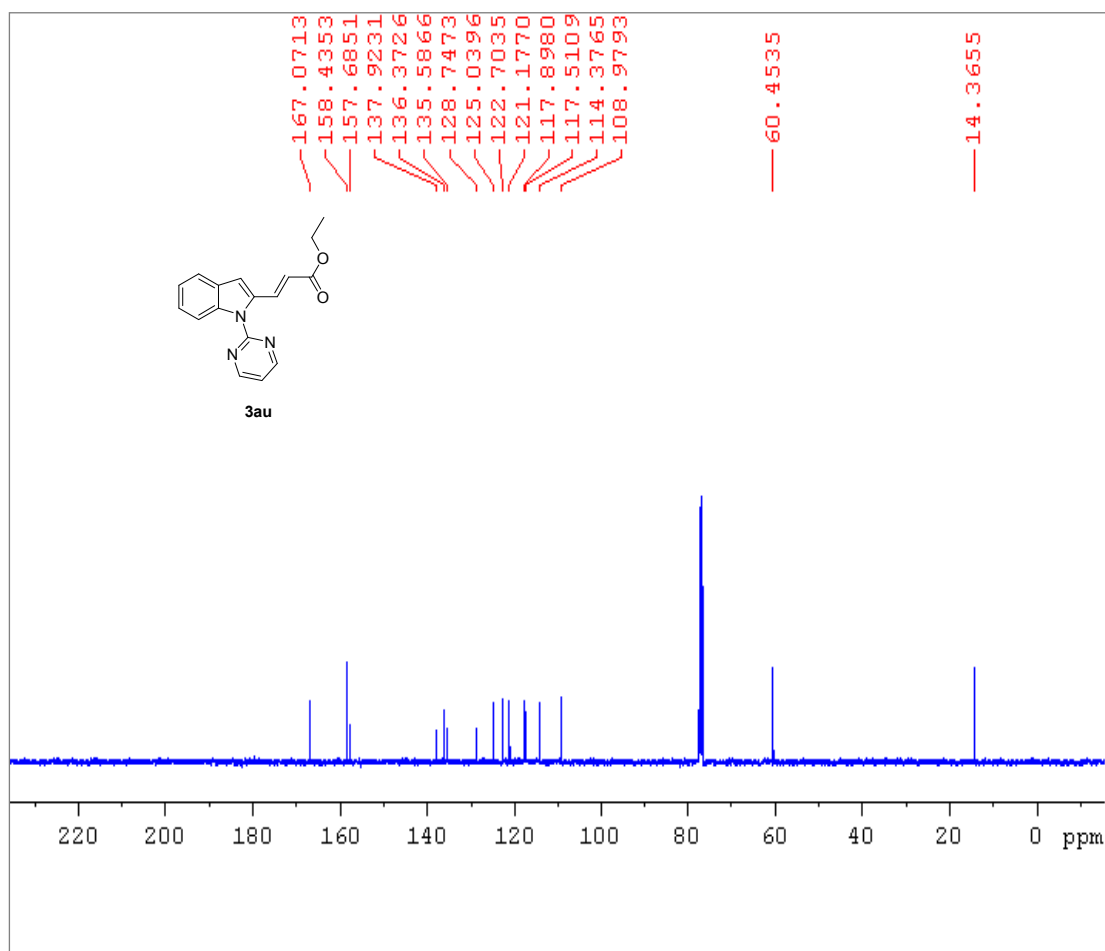
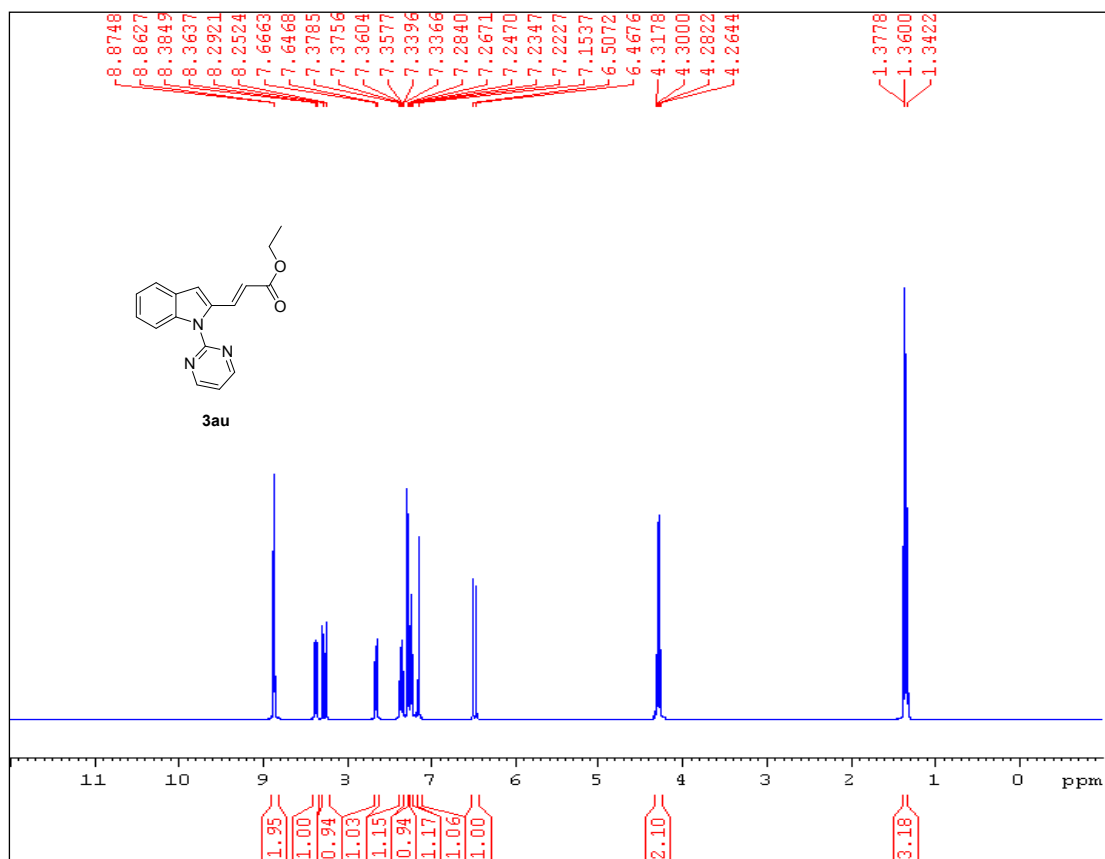


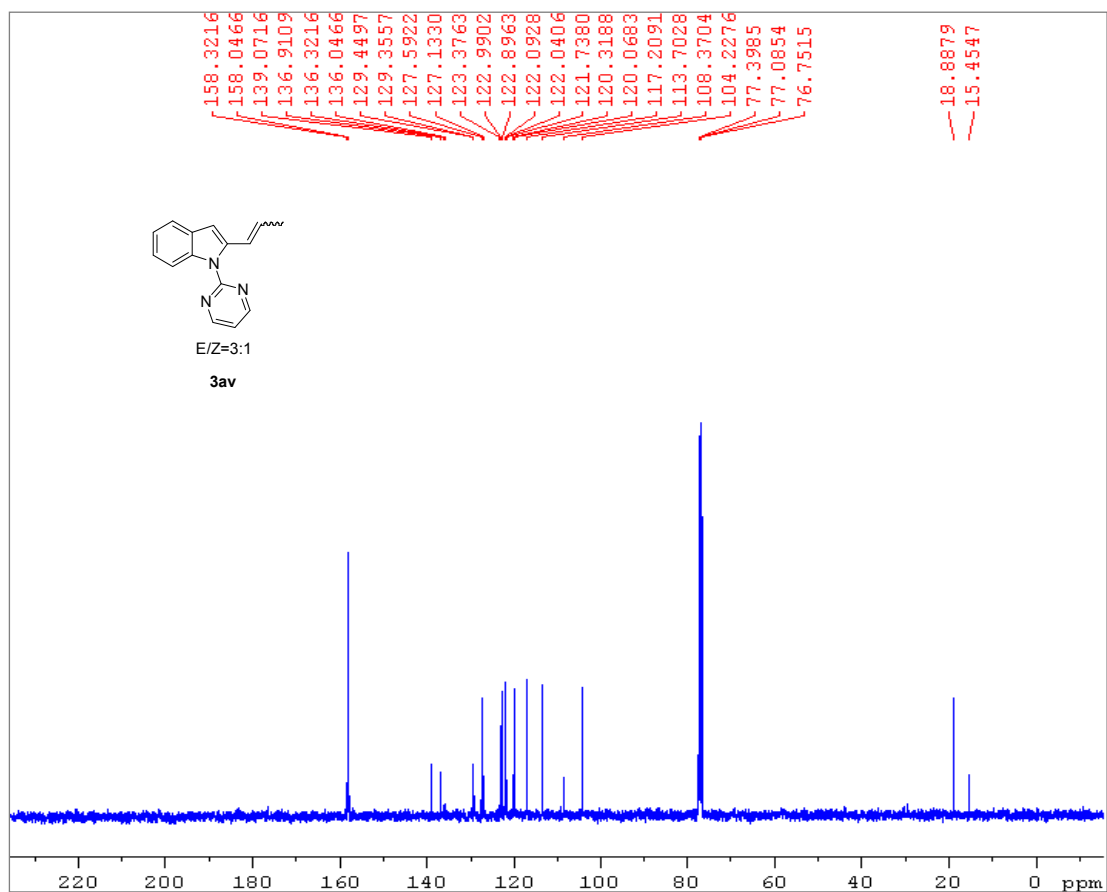
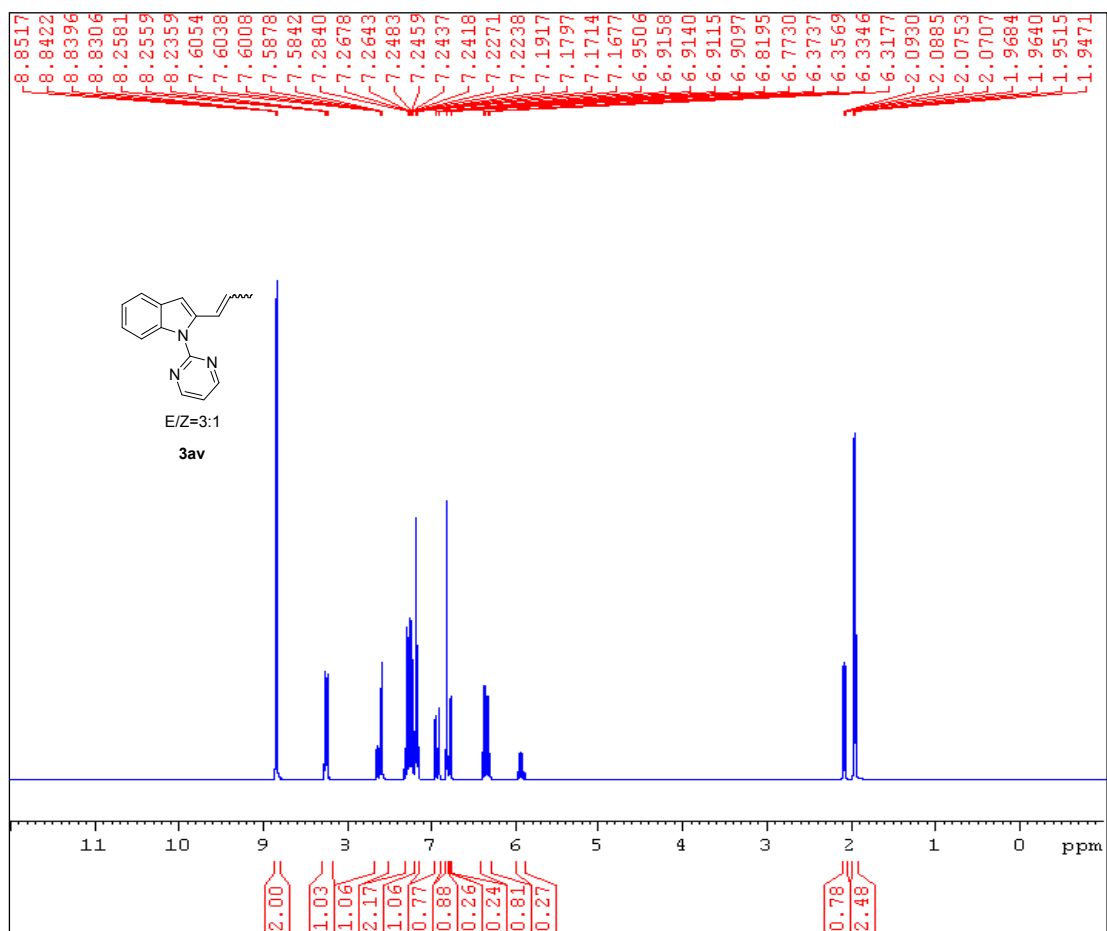


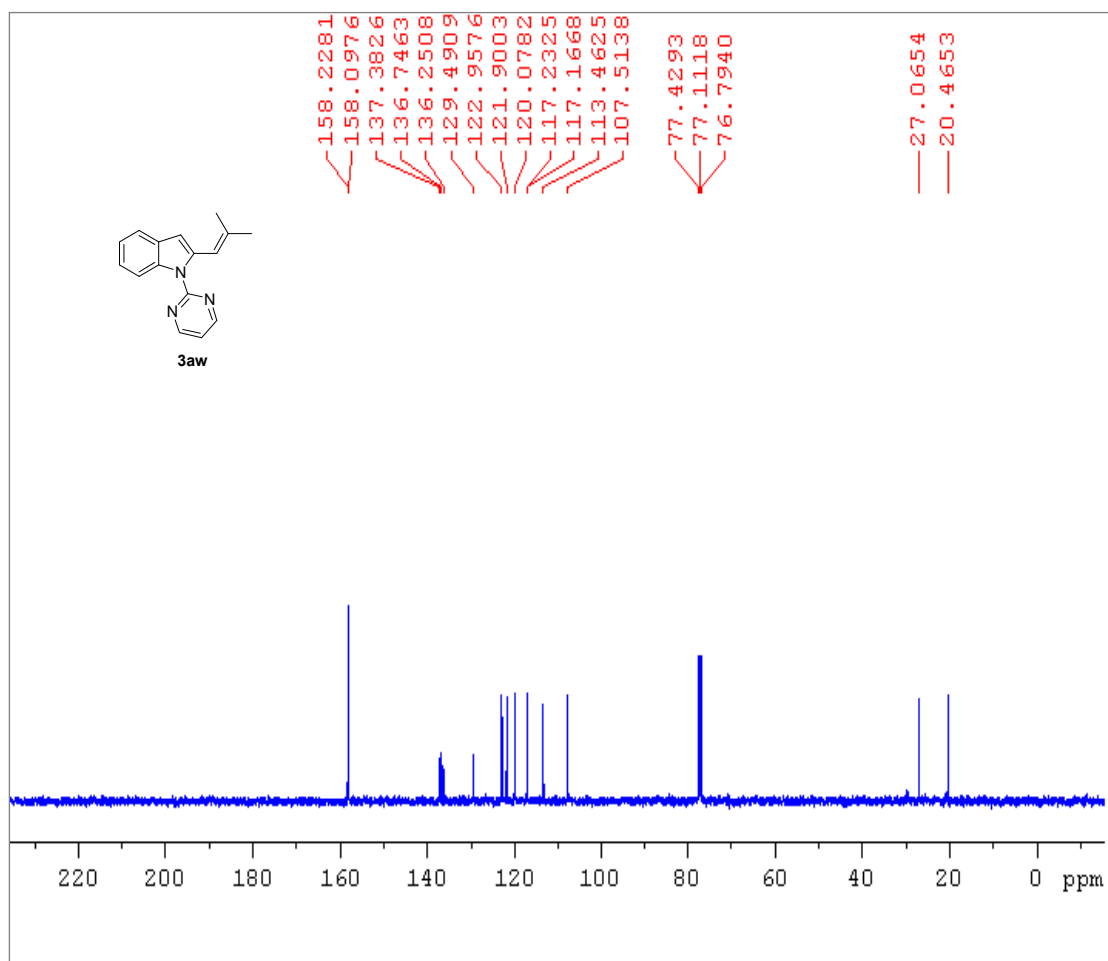
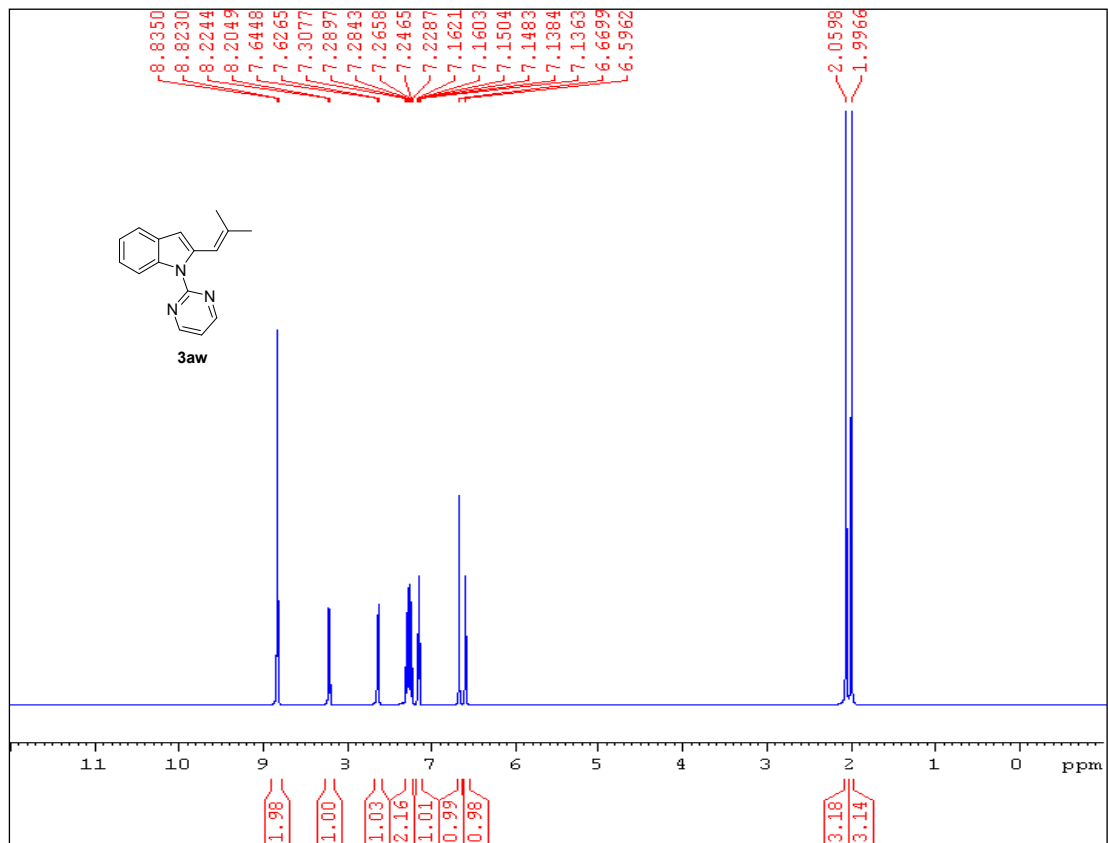


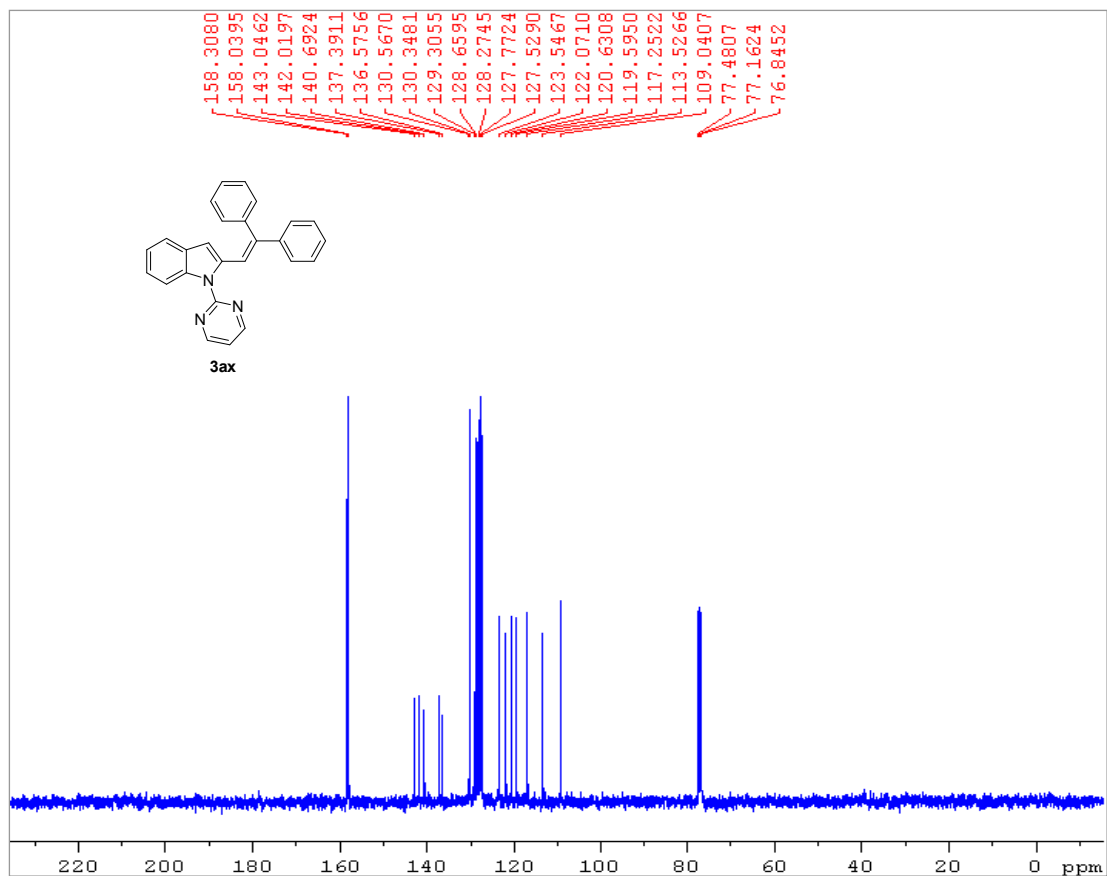
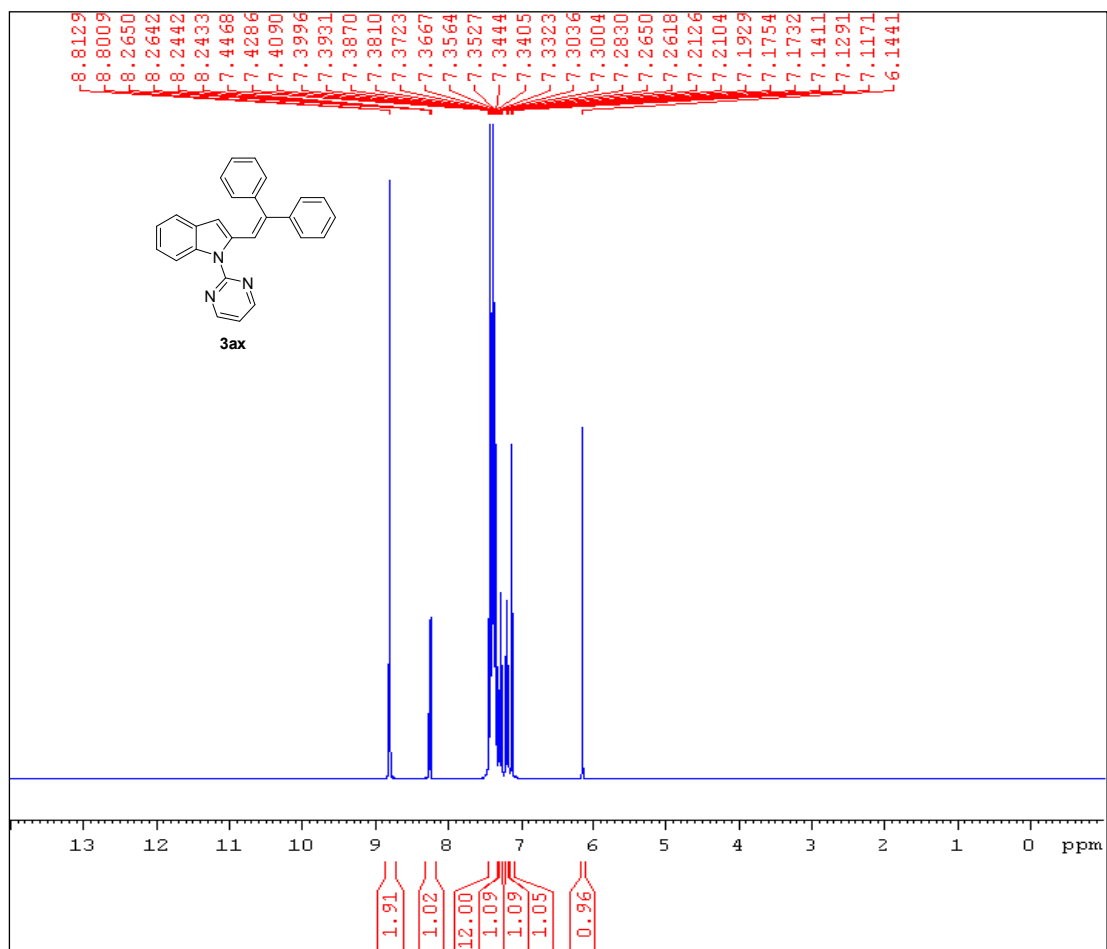


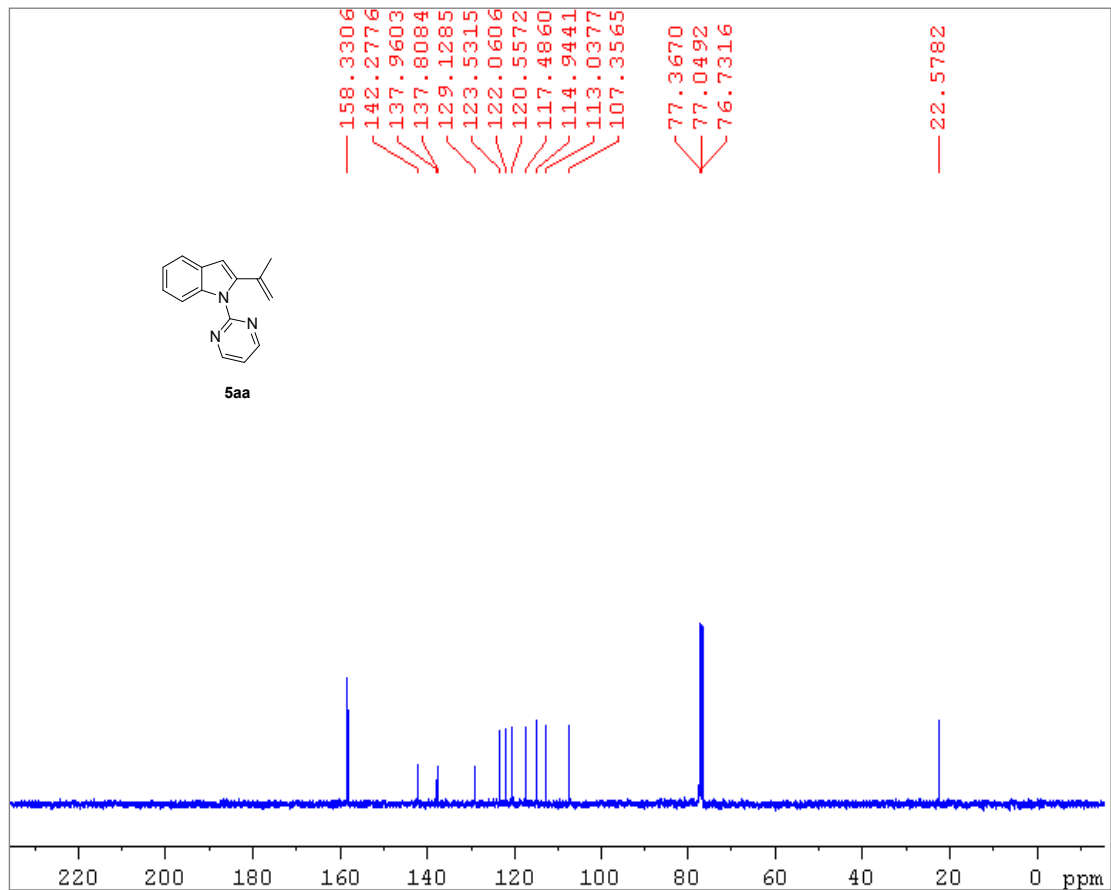
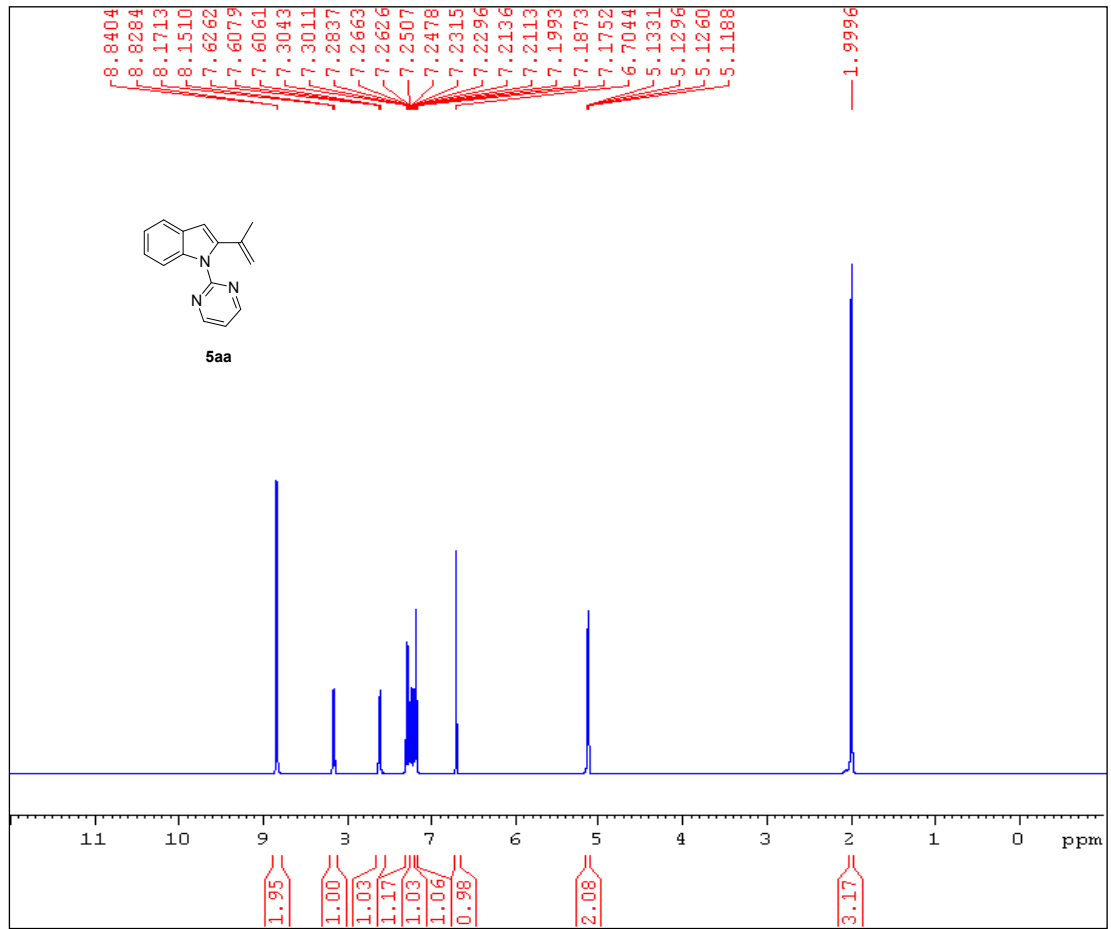


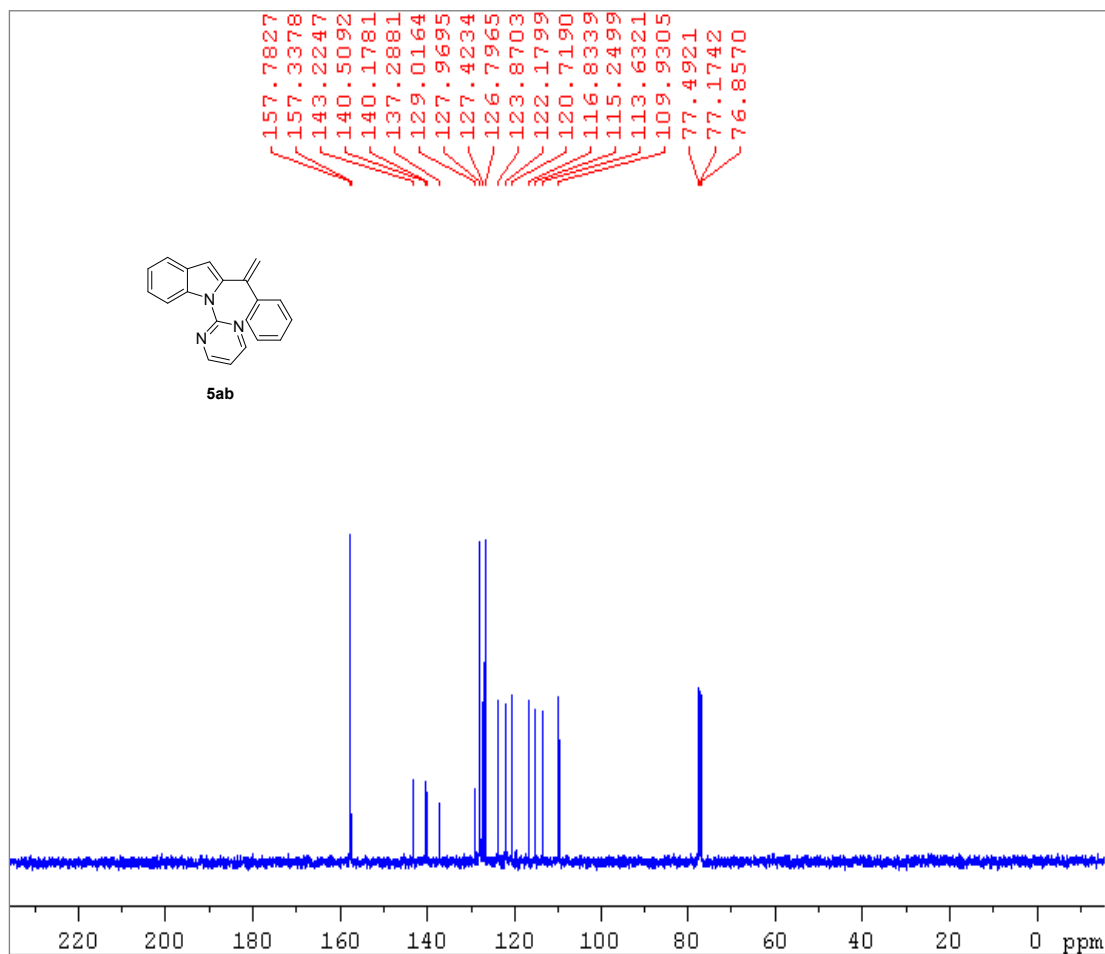
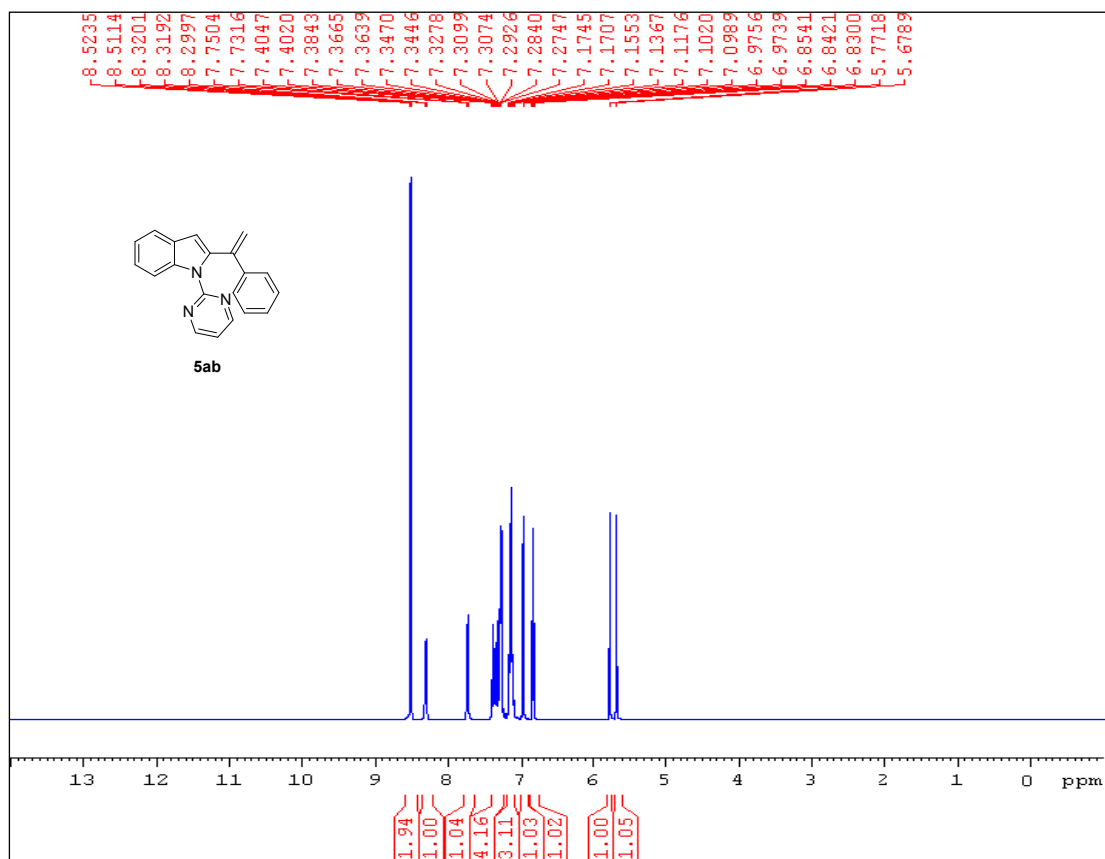


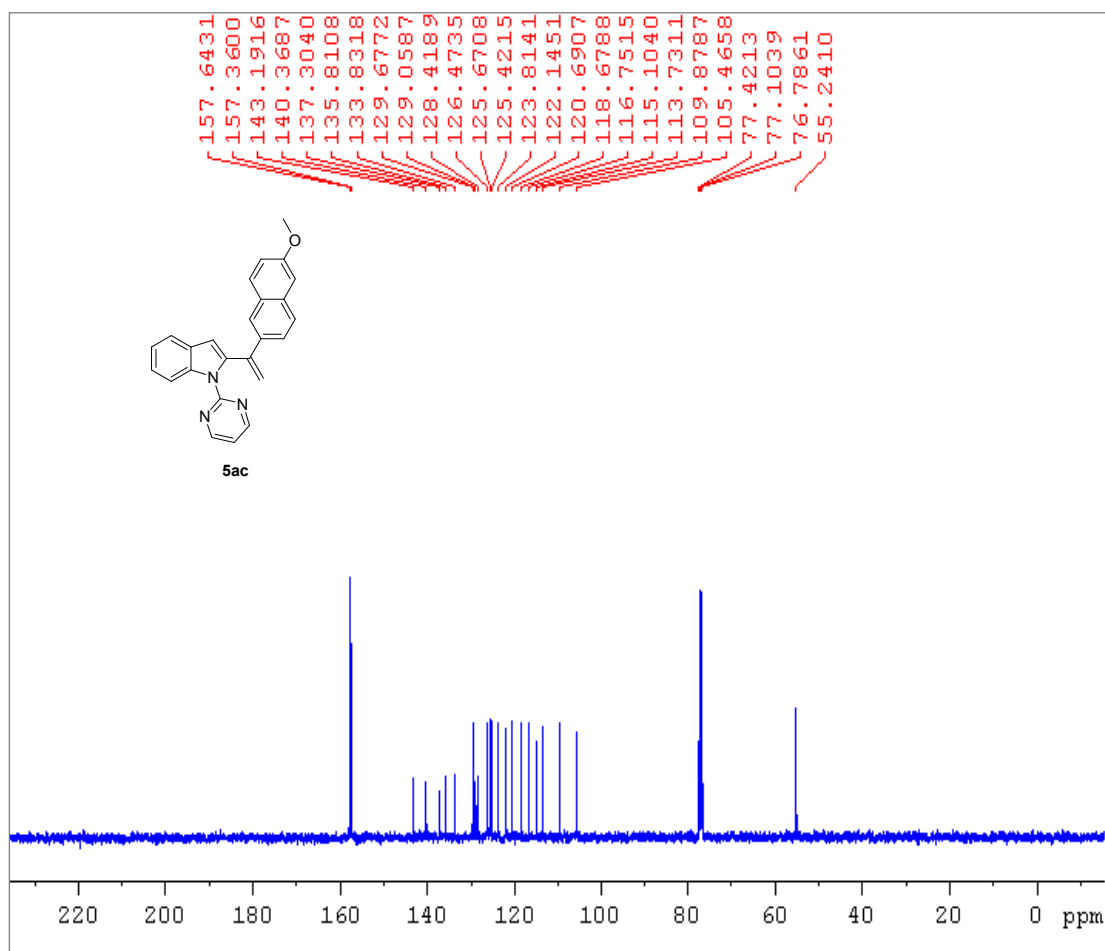
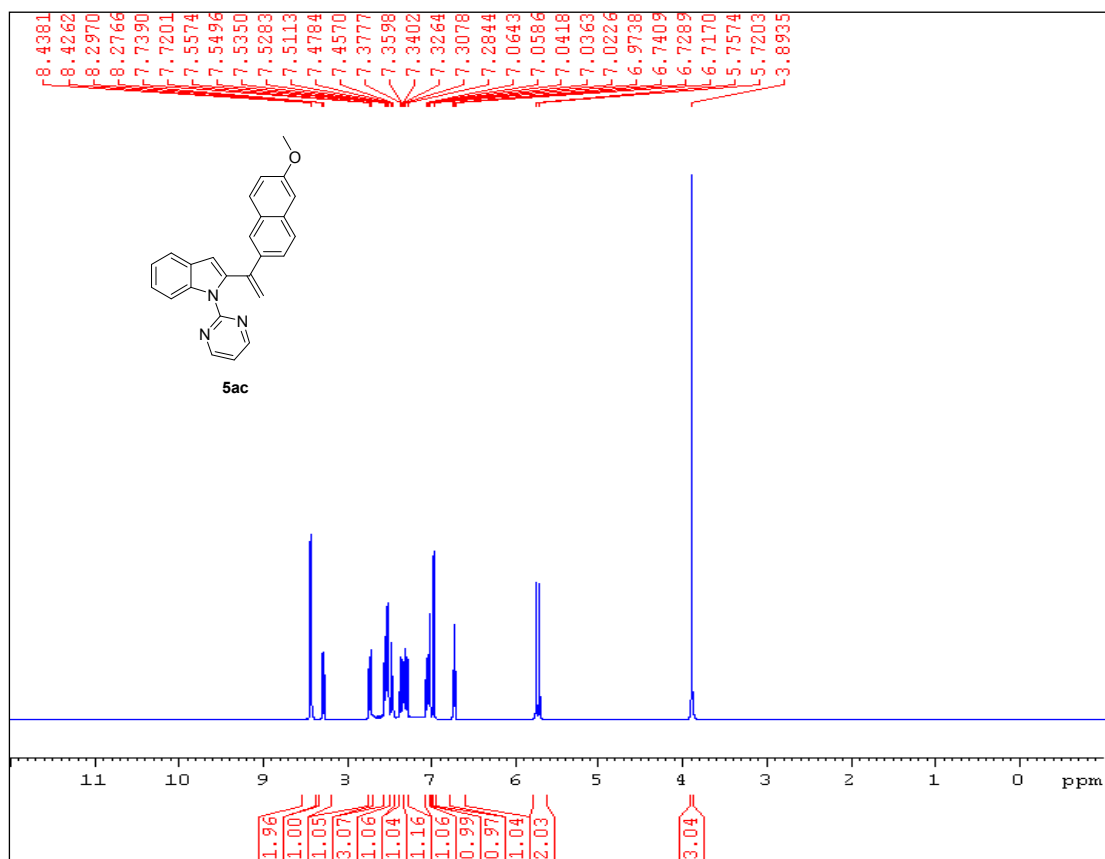


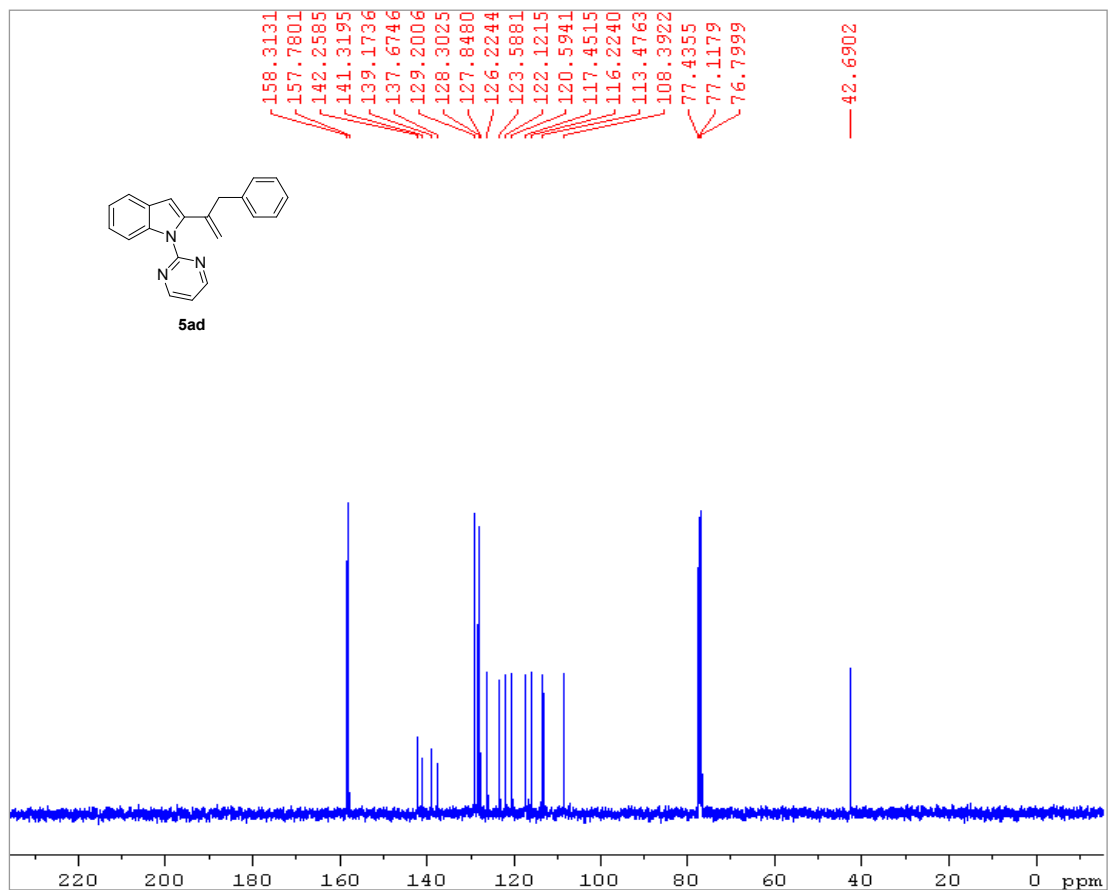
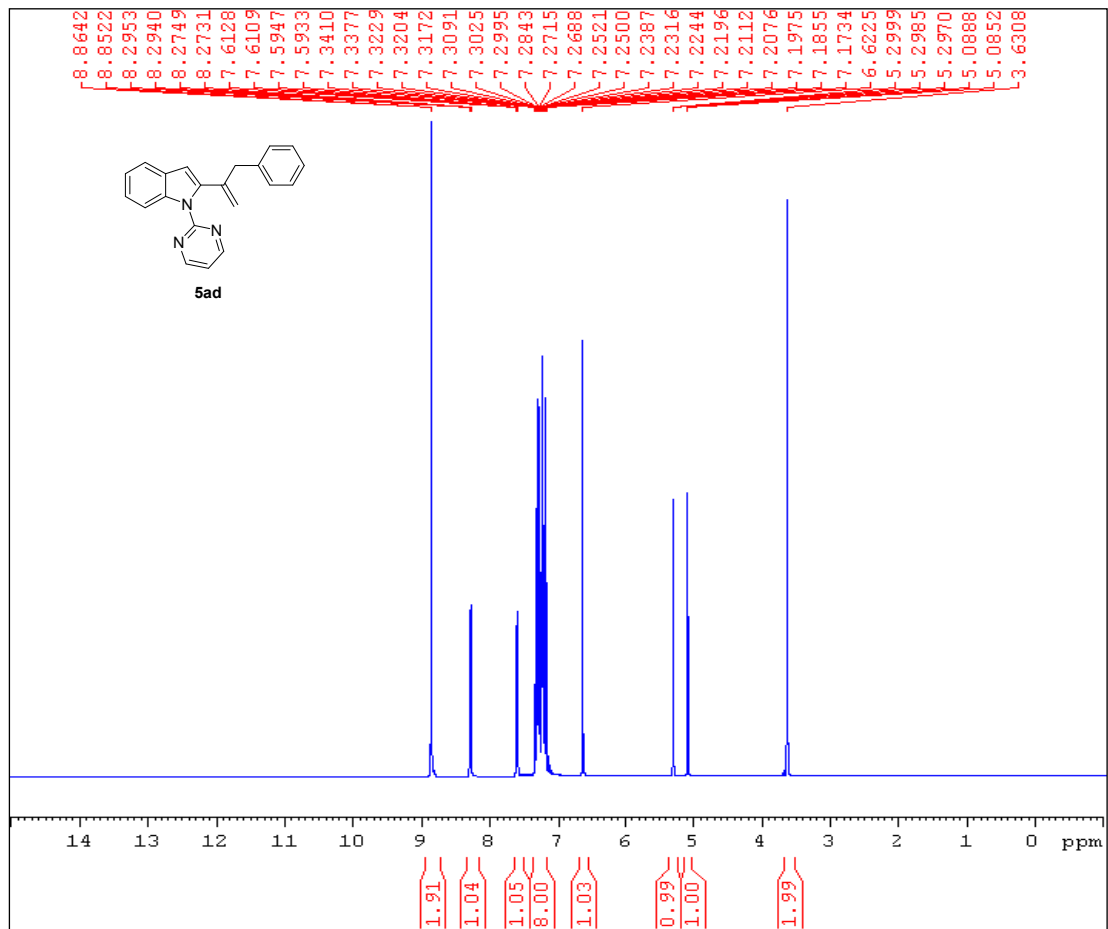


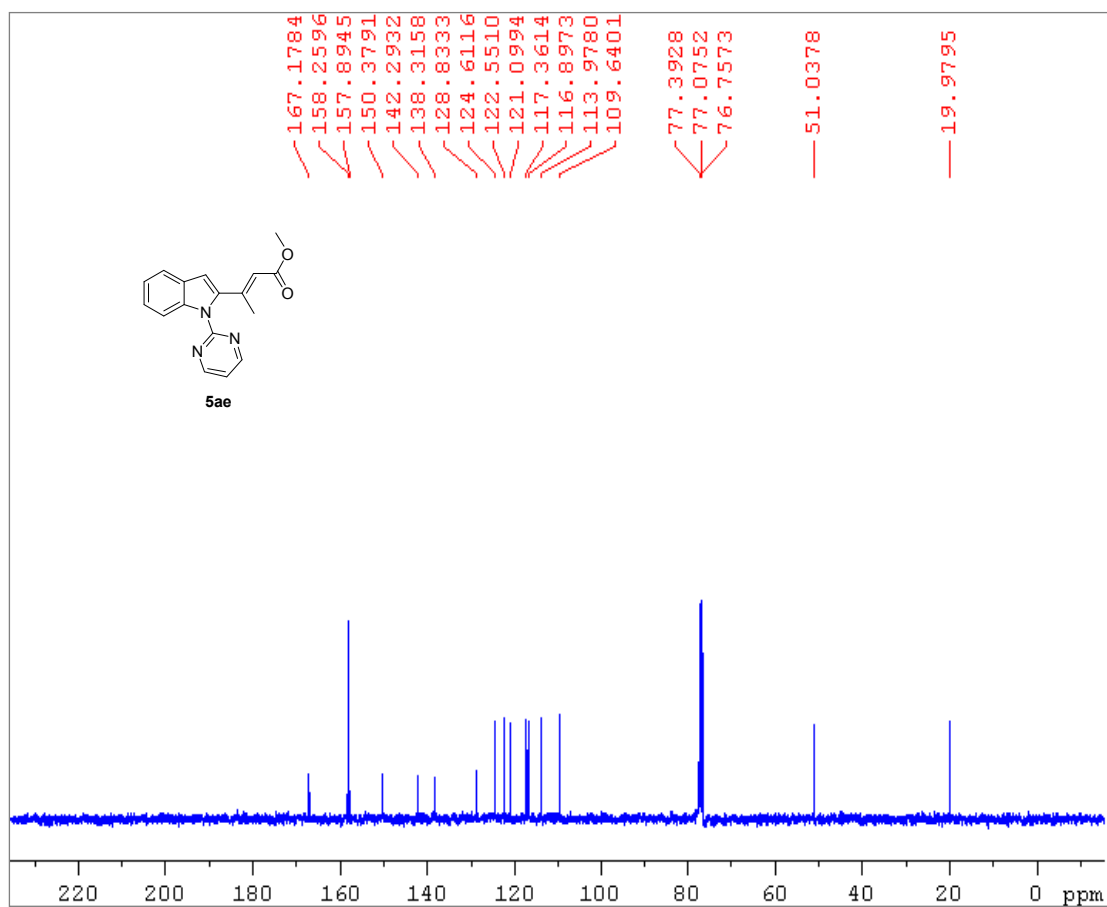
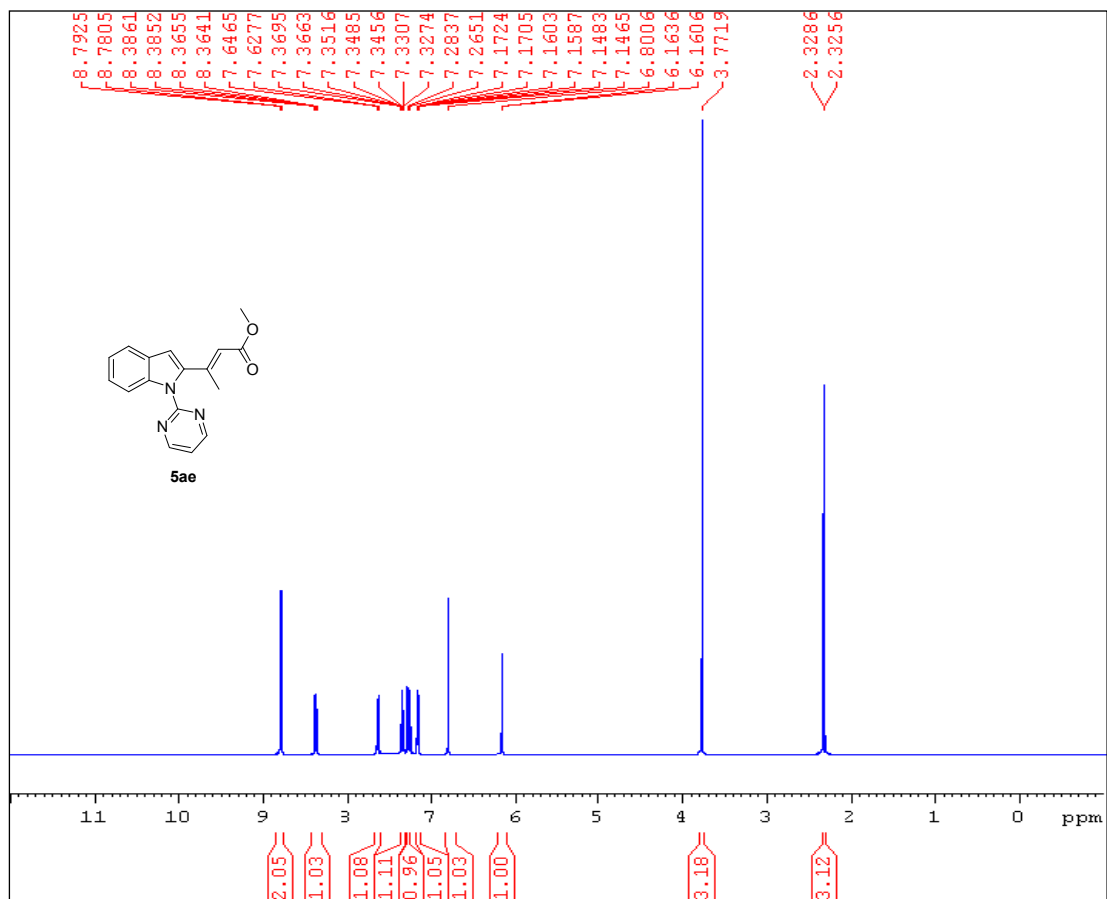


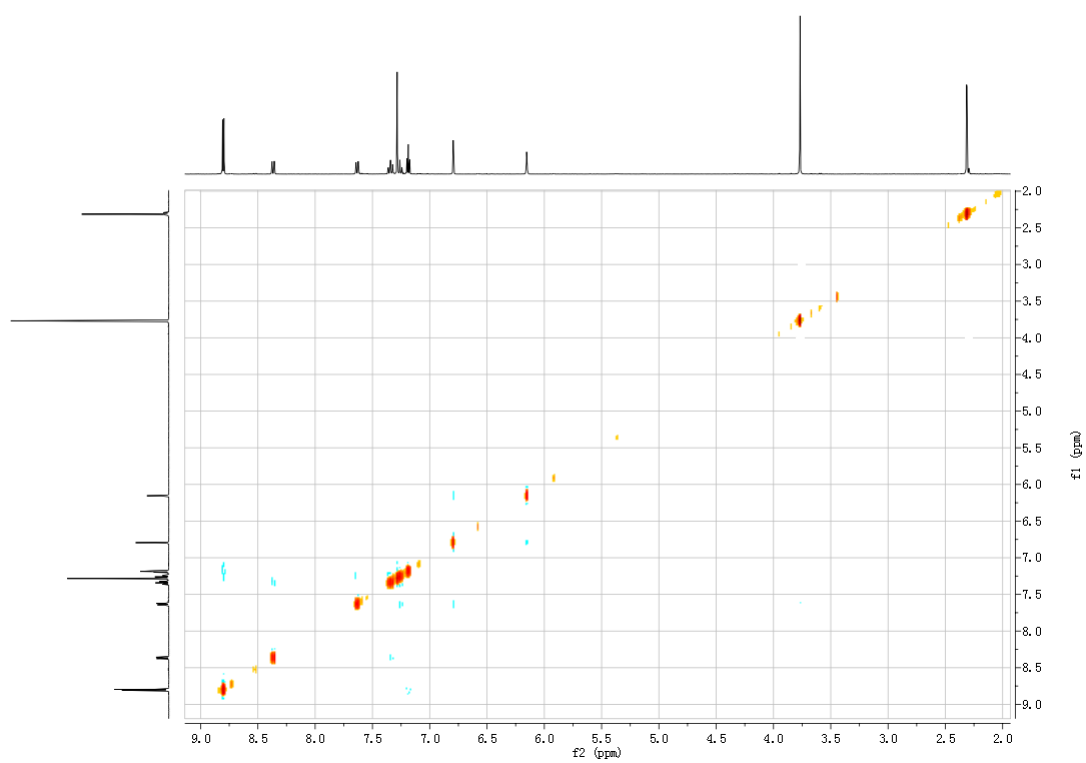
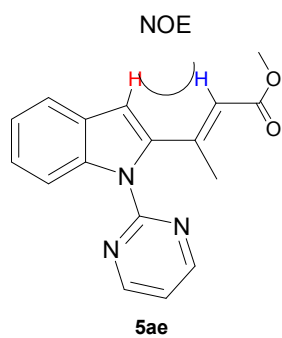


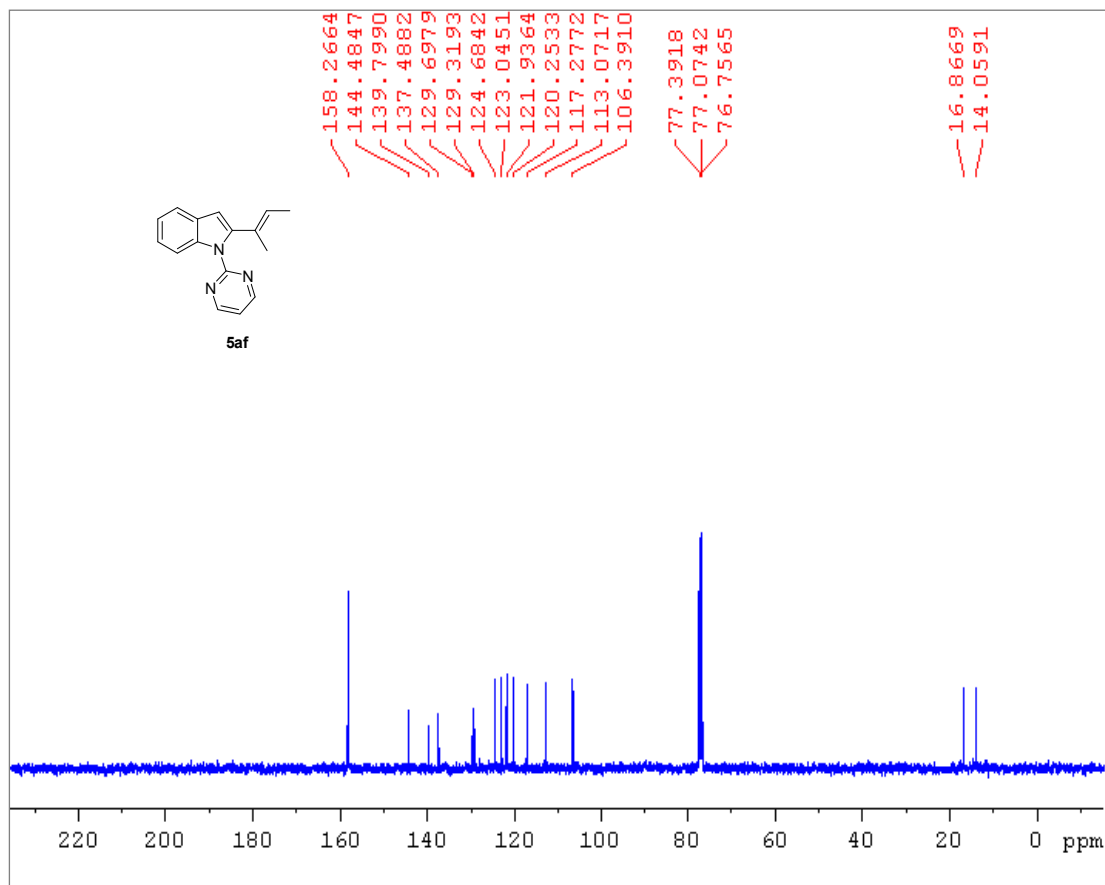
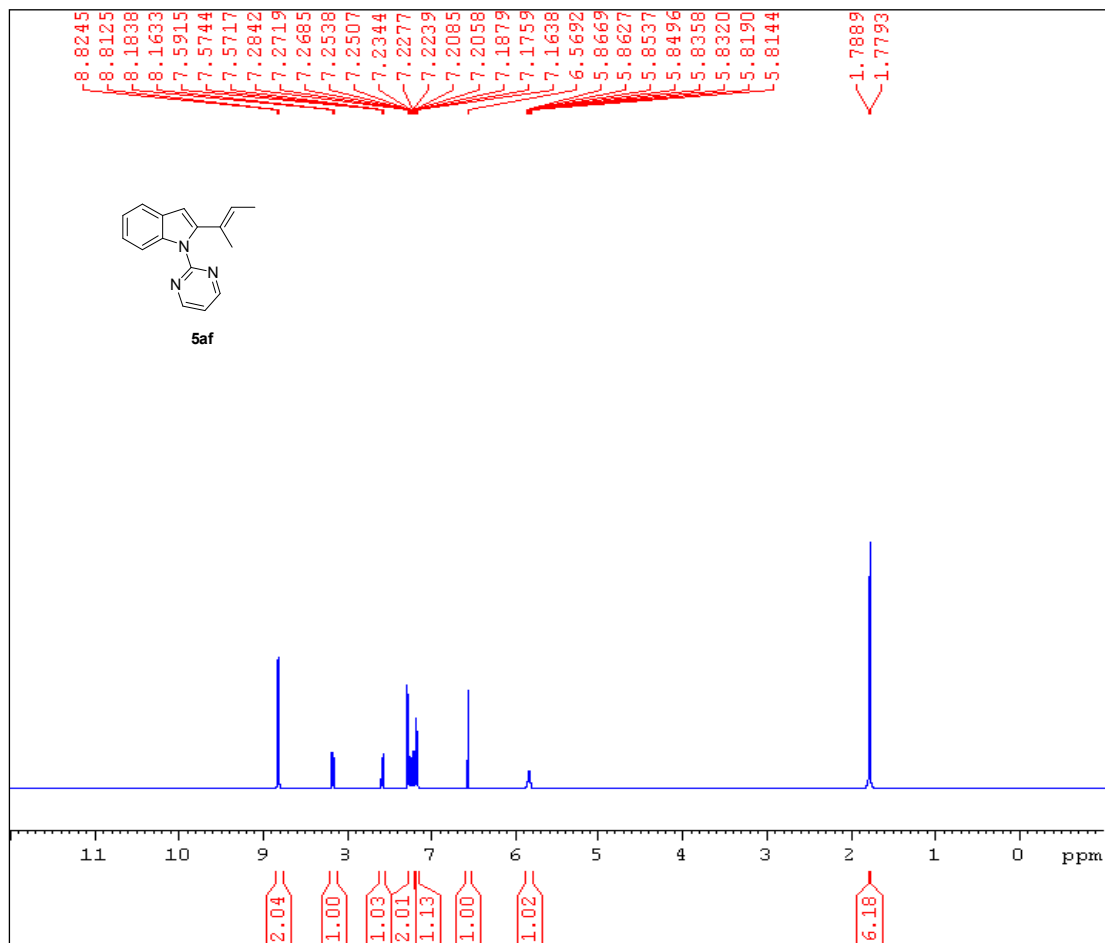


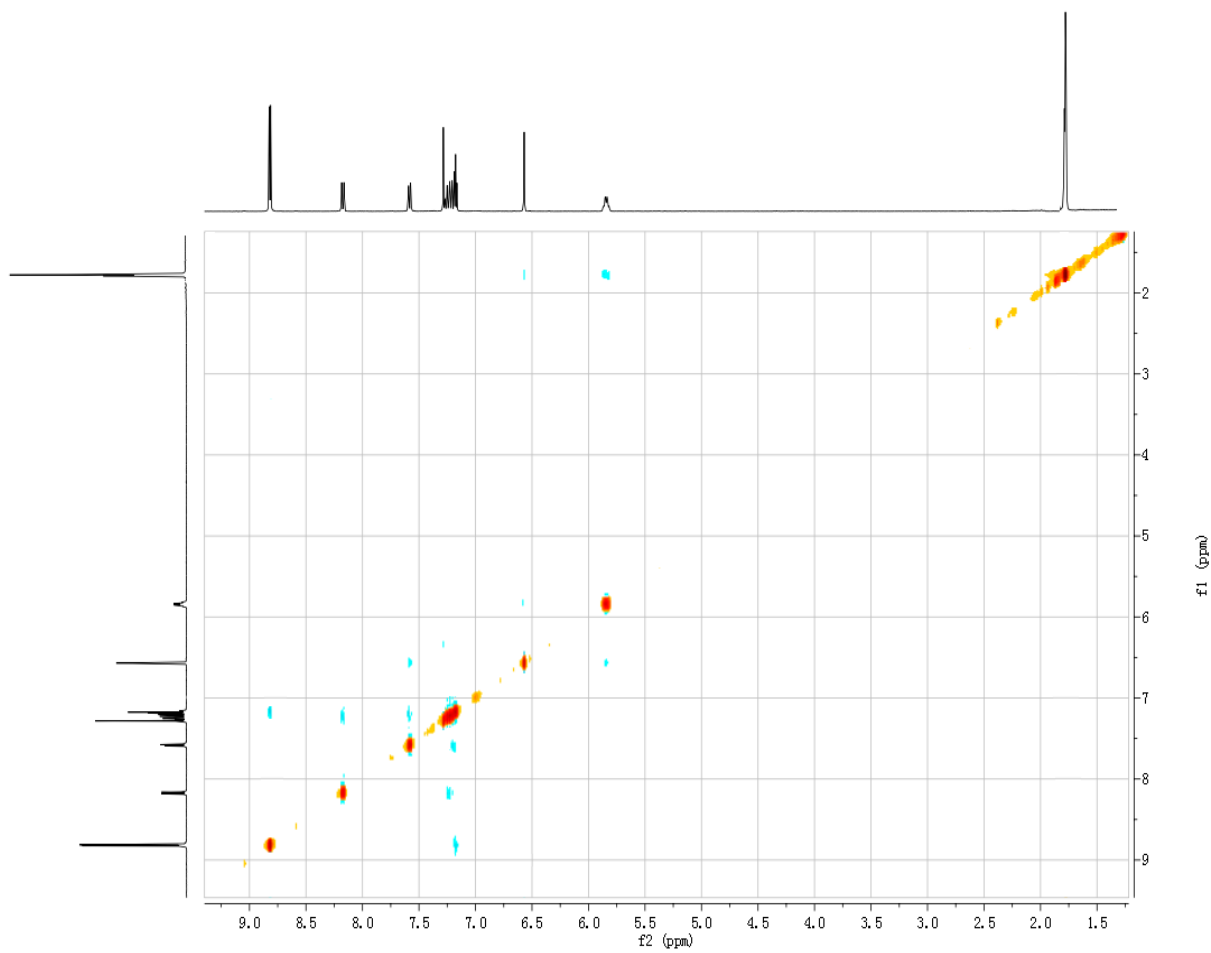
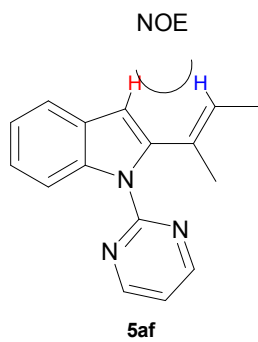


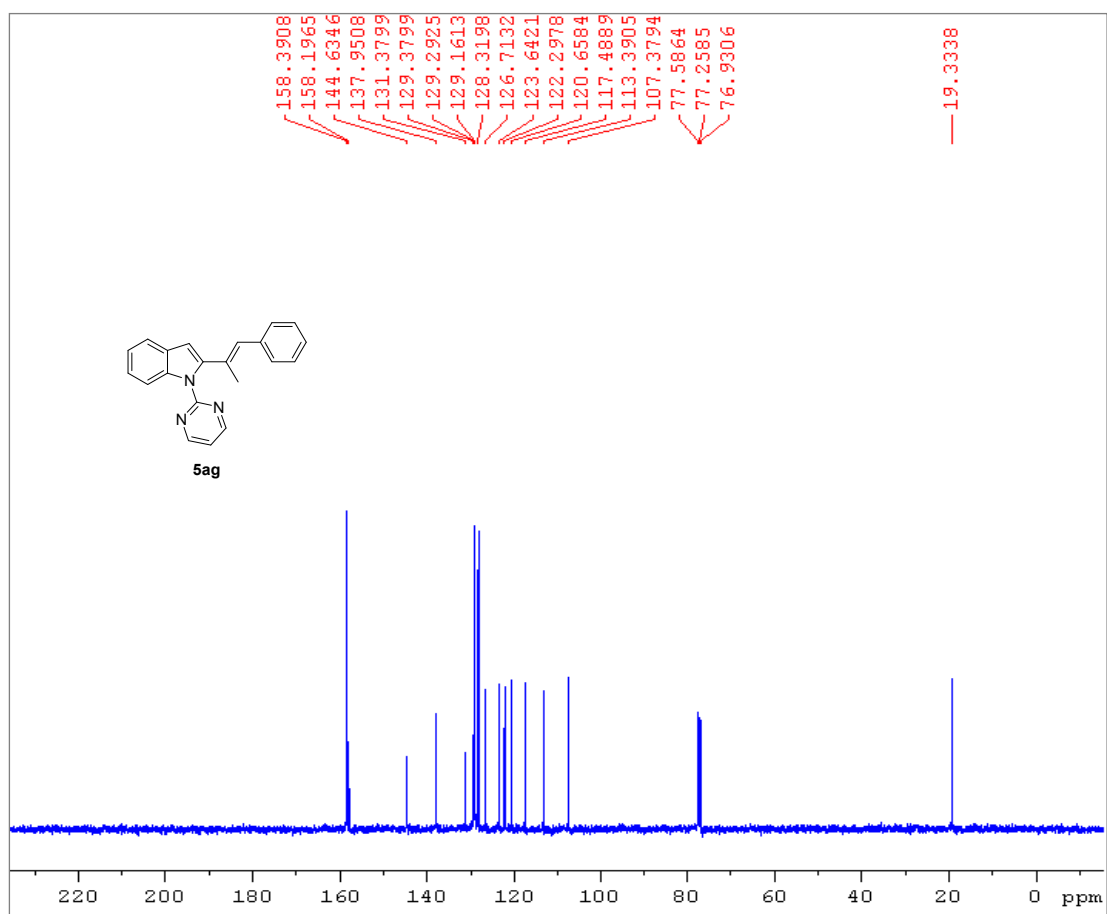
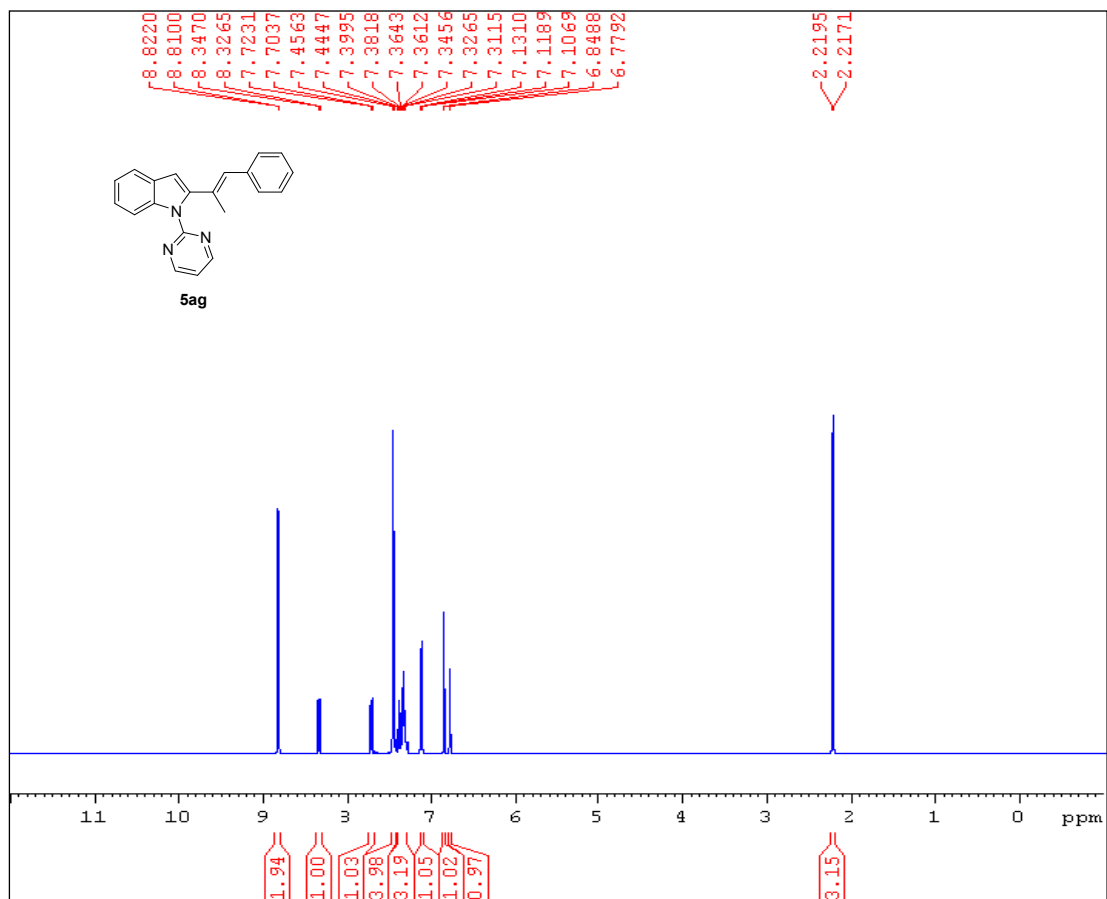


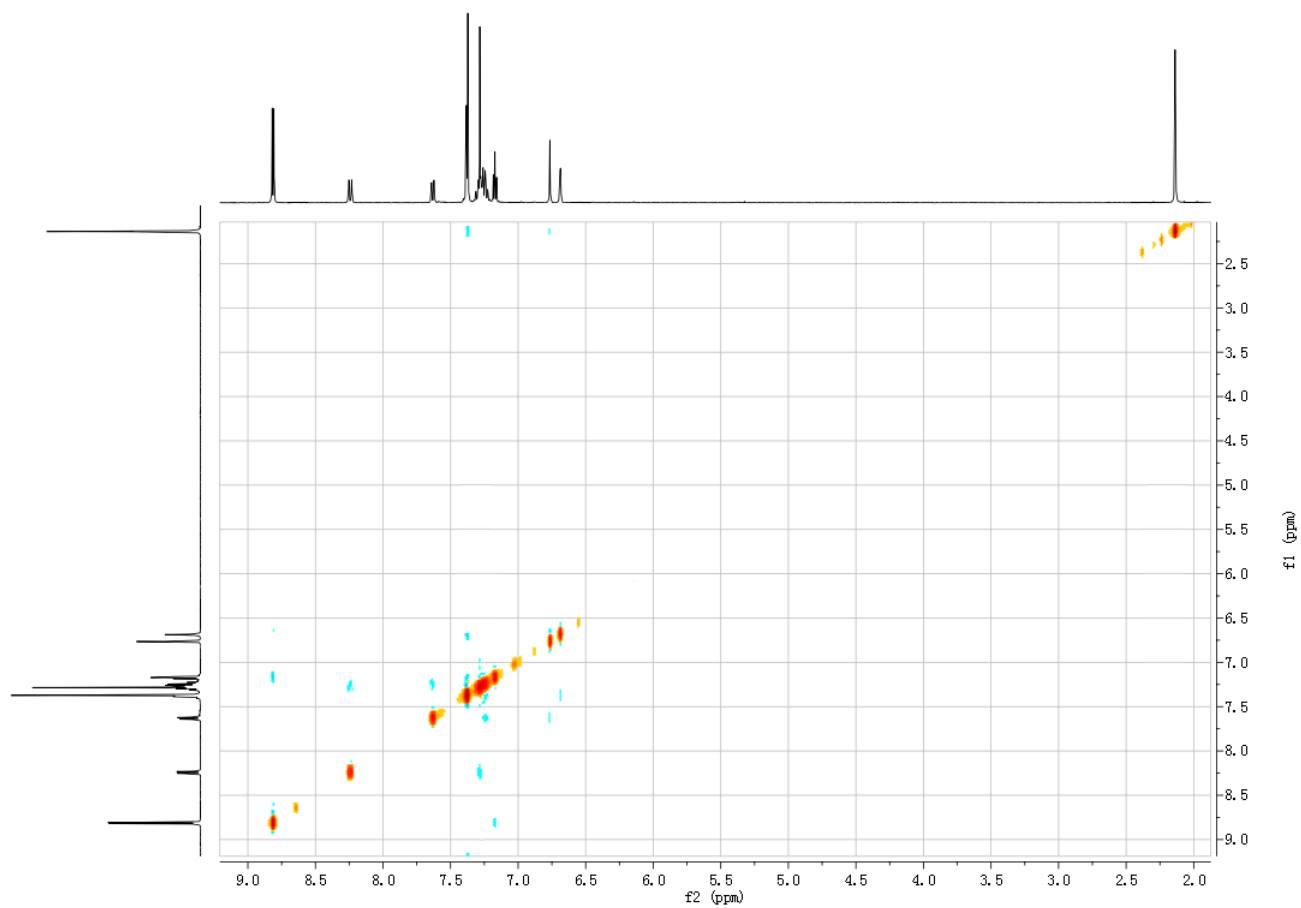
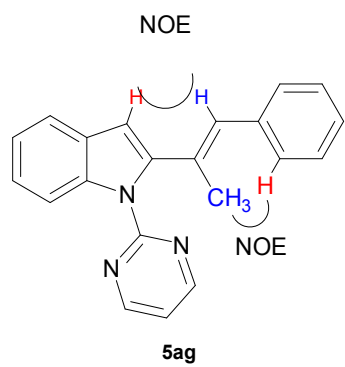


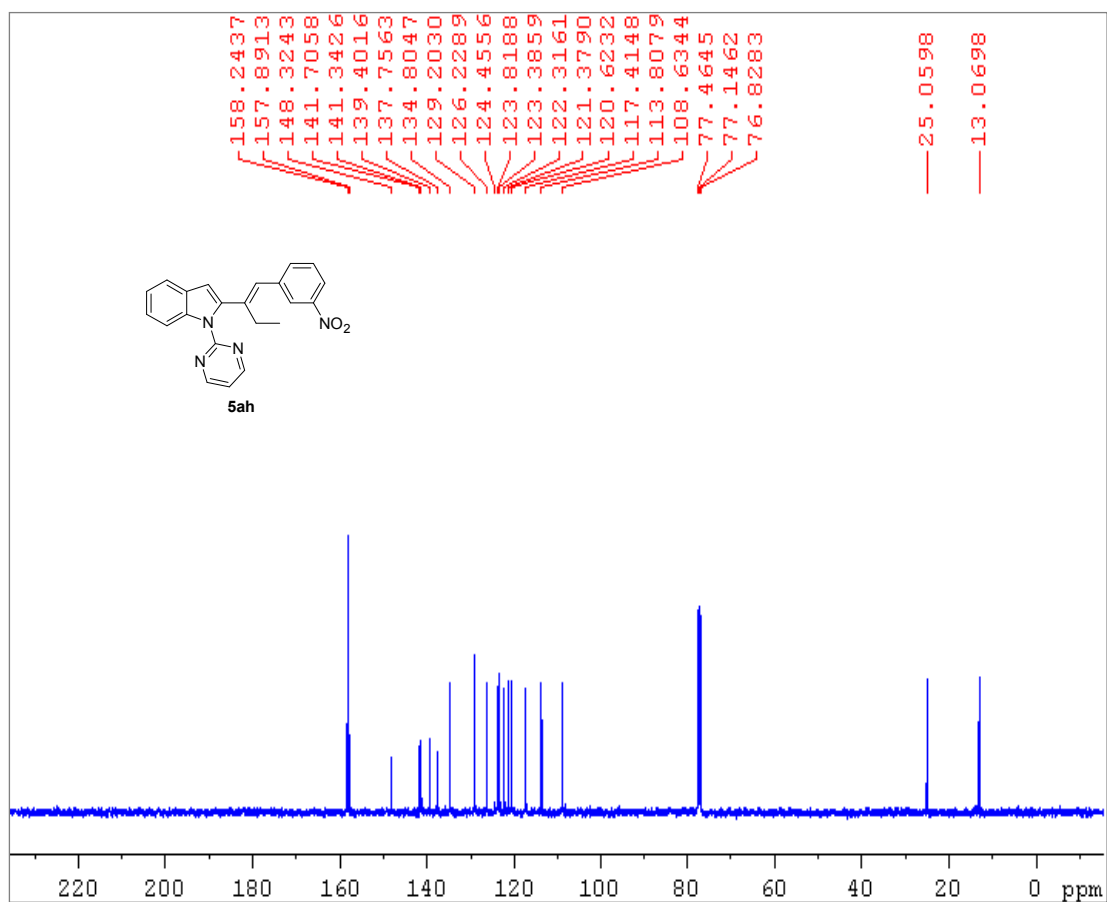
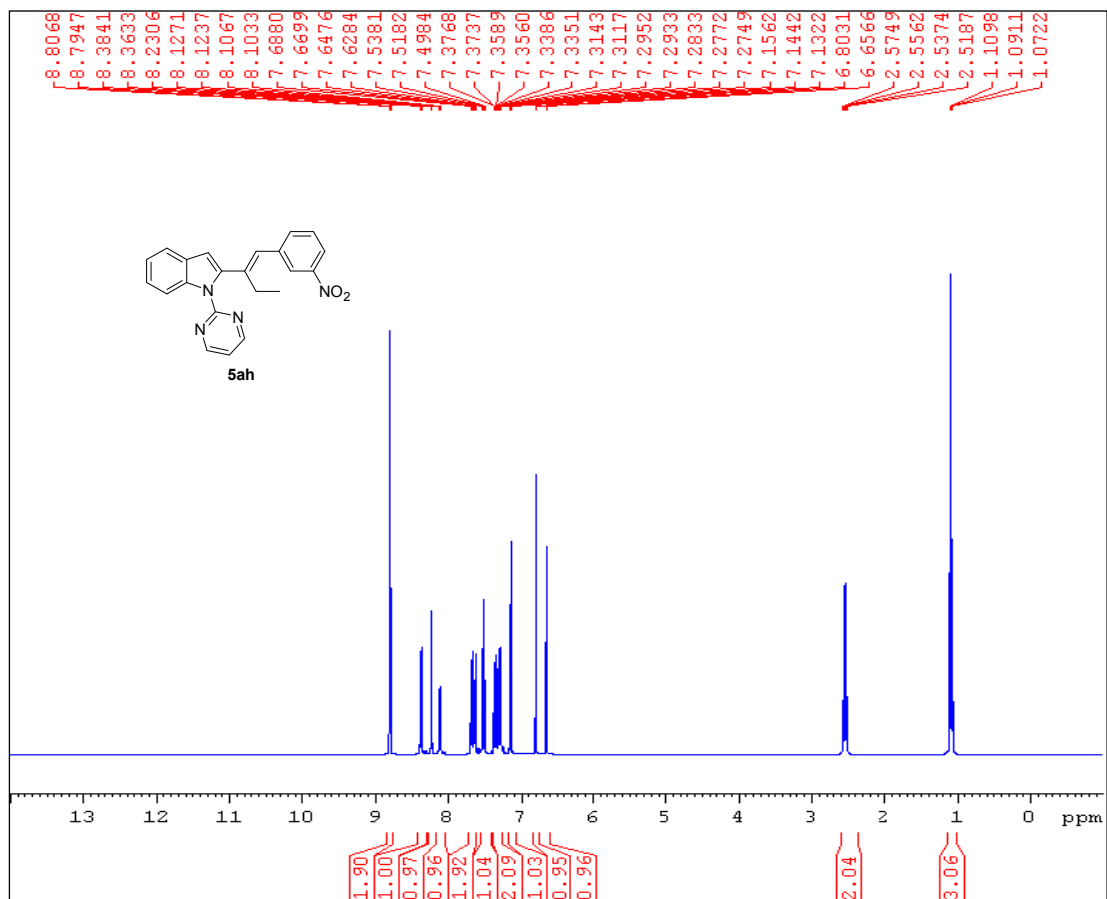


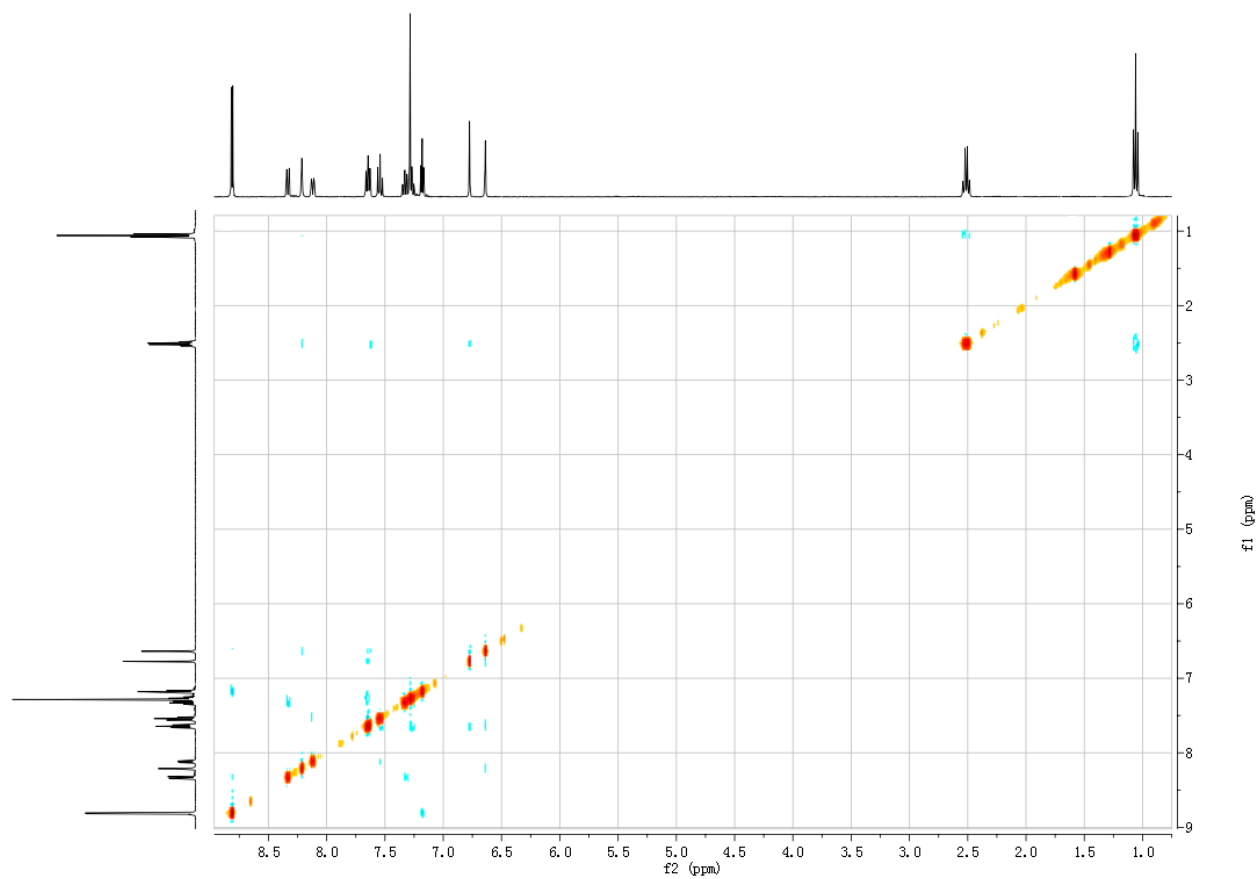
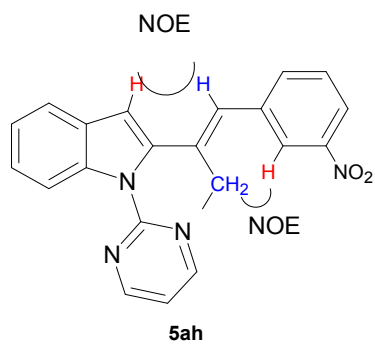


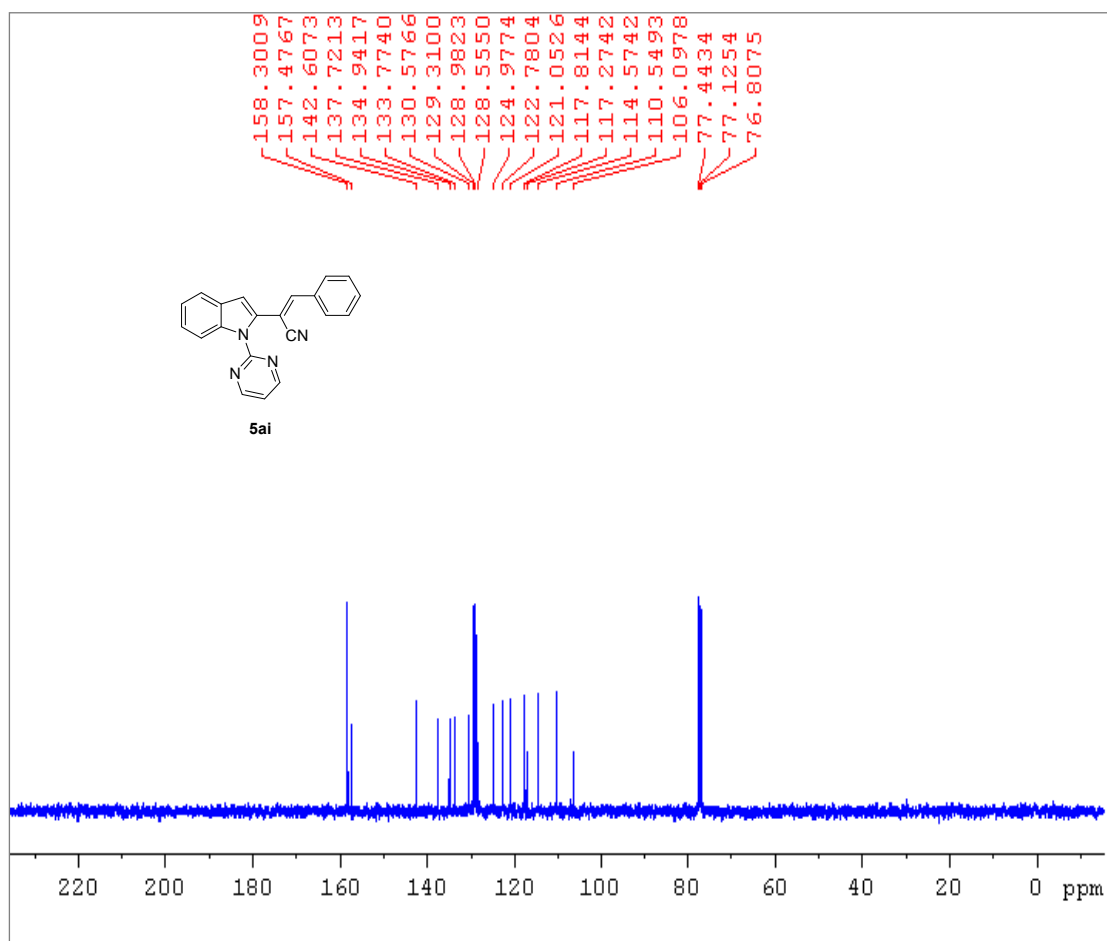
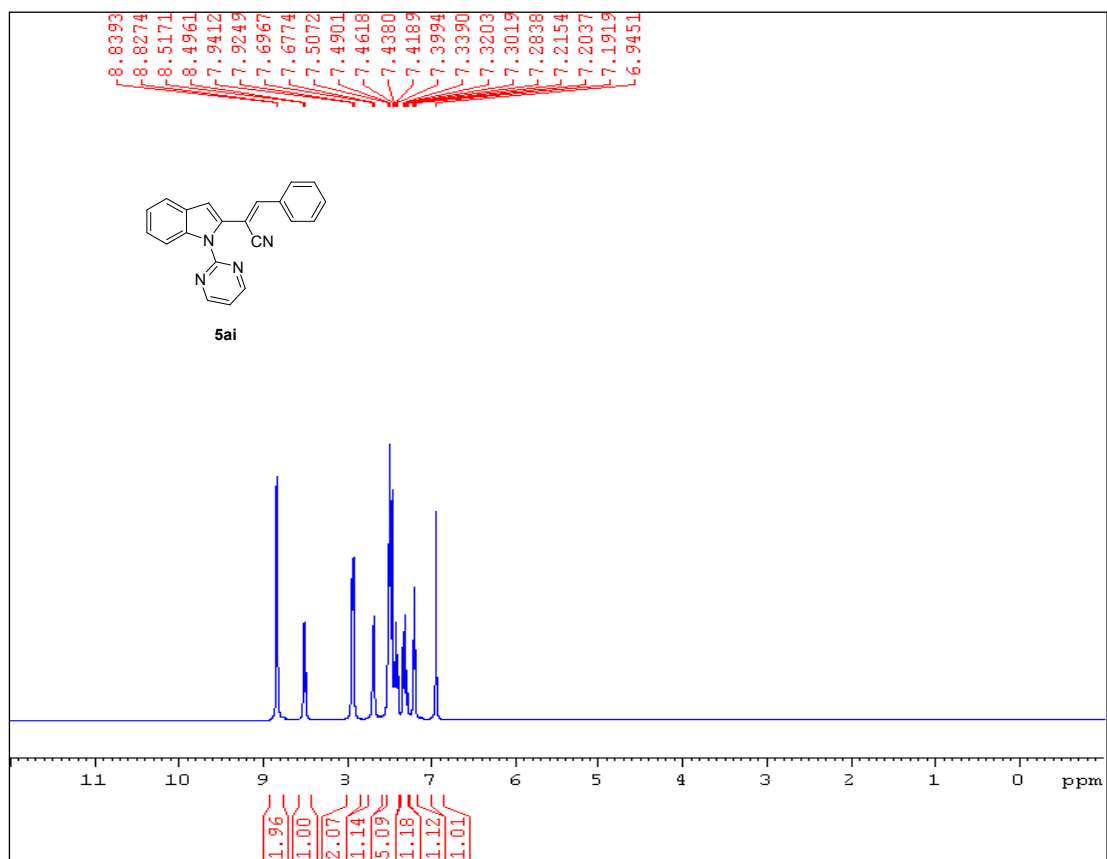












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