Supporting Information

Selective synthesis of pyrrolo[1,2-*a*]azepines or 4,6-dicarbonyl indoles via tandem reactions of alkynones with pyrrole derivatives

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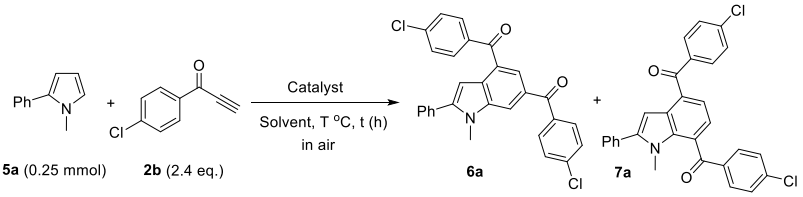
General Methods. All reactions were carried out in air except noted. Anhydrous DCE were prepared by distillation from CaH_2. Anhydrous toluene, THF and 1,4-dioxane were distilled from sodium and benzophenone. MeOH were prepared by distillation from Mg and I_2. Unless noted, all commercial reagents were used without further purification. The silica gel was purchased from Huanghai Chemical Co. Ltd. and Qingdao Haiyang Chemical Co. Ltd.. Column chromatographic purification of products was carried out using silica gel (300-400 mesh). NMR spectra were recorded at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) respectively, referenced to tetramethylsilane (δ = 0.00 ppm) and the residual solvent peak (δ = 77.00 ppm) in $CDCl_3$ or $(CD_3)_2SO$ (containing 0.03% TMS) solutions. *J* values are in hertz. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers.

Table S1. Optimization of the reaction conditions[a]



5a (0.25 mmol) **2b** (2.4 eq.) **6a** **7a**

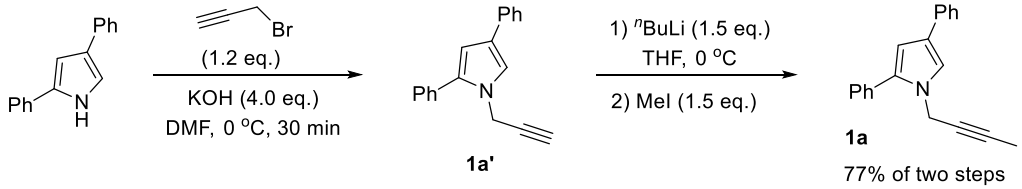
Entry	Catalyst	Solvent	T_1 (°C), t_1 (h or d)	Yield of **6a**+**7a** (%)	**6a**/**7a**
1	$CoCl_2$ (0.2 eq.)	PhMe	100 °C, 24 h	64	1/2
2	$ZnCl_2$ (0.2 eq.)	PhMe	100 °C, 5 h	60	3/1
3	$ZnCl_2$ (0.2 eq.)	PhMe	60 °C, 18 h	76	4/1
4	ZnI_2 (0.2 eq.)	PhMe	60 °C, 5 h	74%	2/1
5	$(CH_3)_3CO_2H$ (1.0 eq.)	PhMe	60 °C, 24 h	trace	-
6	$AlCl_3$ (0.2 eq.)	PhMe	60 °C, 2 d	messy	-
7	$FeCl_3$ (0.2 eq.)	PhMe	60 °C, 2 d	messy	-
8	100-200 mesh silica gel	PhMe	60 °C, 4 d	71	13/1
9	100-200 mesh silica gel	PhMe	100 °C, 15 h	70	7/1
10	200-300 mesh silica gel	PhMe	60 °C, 4 d	72	12/1
11	**300-400 mesh silica gel (A)**	**PhMe**	**60 °C, 4 d**	**74**	**13/1**
12	**A**	PhF	60 °C, 3 d	59	10/1
13	**A**	PhCl	60 °C, 3 d	76	11/1
14	**A**	DCE	60 °C, 3 d	69	4/1
15	**A**	EtOAc	60 °C, 3 d	ND	-
16	**A**	THF	60 °C, 3 d	ND	-
17	**A**	MeOH	60 °C, 4 d	41	> 20/1
18	**A**	AcOH	60 °C, 4 d	42	17/1
19[b]	**A**	PhMe	60 °C, 5 d	69	13/1

[a] The reactions were carried out with silica gel (300 mg) in air unless otherwise stated. Isolated yield. The ratio of **6/7** was determined by ^{1}H NMR. ND = no desired product. 300-400 mesh silica gel = **A**. [b] 150 mg silica gel was used.

The reaction of 1-methyl-2-phenyl-1H-pyrrole (**5a**) and 1-(4-chlorophenyl) prop-2-yn-1-one (**2b**) was selected as a model case to screen the experimental conditions. Firstly, the reaction of **5a** with **2b** was carried out using $CoCl_2$ (20 mol %) as the catalyst in toluene at 100 °C. However, **6a** and **7a** were isolated in 64% total yield with a ratio of 1:2 (Table S1, entry 1). Structural identification of **6a** and **7a** was

carried out by X-ray crystallography. 0.2 Equiv of $ZnCl_2$ did not result in a better yield for the target product, although the ratio was improved to 3:1 (entry 2). When the reaction was carried out at 60 °C, **6a** and **7a** was obtained in 76% yield with a ratio of 4:1 (entry 3). Other catalysts such as ZnI_2, $(CH_3)_3CO_2H$, $AlCl_3$ or $FeCl_3$ didn't give better results (entries 4-7). Accidentally, we found there was transformation tendency with **5a** and **2b** on the silica gel plate. So, we chose silica gel (300 mg) as the promoter for further investigations (entries 8-19). To our delight, when the reaction was carried out at 60 °C with 100-200 mesh silica gel in air, the ratio was improved significantly to 13:1 (**6a**:**7a**) with a total yield of 71% (entry 8). Increasing the temperature to 100 °C resulted in a lower ratio (entry 9, 7:1). Furtherly, we found 100-200, 200-300 or 300-400 mesh silica gel provided similar results at 60 °C (entries 8, 10 and 11). Then, we screened the solvents with 300-400 mesh silica gel (entries 12-18). Although an excellent ratio could be detected with MeOH as the solvent, the yield was too poor to be accepted (entry 17, 41%, >20:1). We also used the mixed solvent of MeOH and PhMe, but no significant improvement was obtained. When the amount of silica gel was decreased to 150 mg, the reaction time was further increased (entry 19). So, we examined the substrate scope using 300-400 mesh silica gel in combination with toluene as the solvent at 60 °C in air (entry 11).

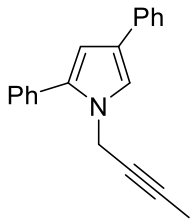
Synthesis and characterization of 1



Under nitrogen, to a 100 mL Schlenk tube were added 2,4-diphenyl pyrrole[1] (1.44 g, 6.55 mmol), KOH (1.50 g, 26.2 mmol) and DMF (35 mL). After the mixture was cooled to 0 °C, propargyl bromide (678 uL, 7.86 mmol) was added. The mixture was slowly warmed to room temperature. About 30 min latter，after full conversion of 2,4-diphenyl pyrrole by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (80 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/dichloromethane = 15/1-10/1 as the eluent afforded the intermediate propargyl pyrrole intermediate **1a'** with an 86% yield.

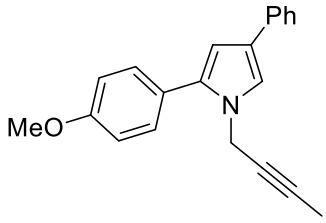
To a solution of the propargyl pyrrole intermediate **1a'** (1.40 g, 5.44 mmol) in anhydrous THF (50 mL) in Schlenk tube was added n-BuLi (2.5 M in THF, 3.7 mL, 8.16 mmol) at 0 °C. 2 h latter, MeI (580 uL, 8.16 mmol) was added dropwise at 0 °C under nitrogen. About 1 h latter，after full conversion of propargyl pyrrole intermediate by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (100 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica

gel with petroleum ether/dichloromethane = 20/1 as the eluent afforded the substrate propargyl pyrrole **1a**.



1-(but-2-yn-1-yl)-2,4-diphenyl-1H-pyrrole (**1a**)

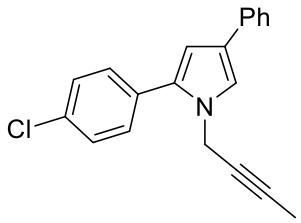
White solid, 77% yield of two steps, mp 86-88 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.46 (m, 4H), 7.46-7.40 (m, 2H), 7.80-7.30 (m, 3H), 7.25 (s, 1H), 7.21-7.14 (m, 1H), 6.52 (s, 1H), 4.63 (s, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.73, 135.45, 132,84, 128.99, 128.81, 128.78, 127.45, 125.76, 125.25, 125.08, 119.03, 106.85, 81.37, 74.35, 37.14, 3.32; HRMS (ESI) calcd for $C_{20}H_{18}N$ $[M+H]^+$: 272.1434, found 272.1430.



1-(but-2-yn-1-yl)-2-(4-methoxyphenyl)-4-phenyl-1H-pyrrole (1b)

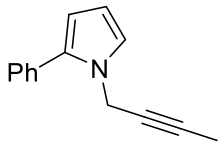
White solid, 57% yield of two steps, mp 96-98 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37-7.29 (m, 2H), 7.21 (s, 1H), 7.20-7.13 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.45 (s, 1H), 4.59 (s, 2H), 3.85 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.37, 135.87, 135.22, 130.40, 128.79,

125.68, 125.38, 125.24, 124.93, 118.40, 114.14, 106.31, 81.22, 74.46, 55.21, 36.99, 3.30; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539, found 302.1542.



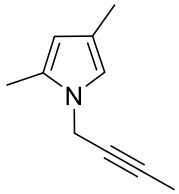
1-(but-2-yn-1-yl)-2-(4-chlorophenyl)-4-phenyl-1H-pyrrole (1c)

Yellowish solid, 50% yield of two steps, mp 119-121 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.48-7.30 (m, 6H), 7.28-7.14 (m, 2H), 6.51 (s, 1H), 4.60 (d, *J* = 2.0 Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.54, 134.18, 133.46, 131.32, 130.15, 129.00, 128.85, 125.90, 125.27, 119.47, 107.22, 81.63, 74.18, 37.20, 3.29; HRMS (ESI) calcd for $C_{20}H_{17}ClN$ $[M+H]^+$: 306.1044, found 306.1046.



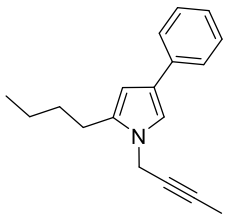
1-(but-2-yn-1-yl)-2-phenyl-1H-pyrrole (1d)

Yellowish oil, 64% yield of two steps; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.28 (m, 5H), 6.95 (s, 1H), 6.26 (s, 1H), 6.22 (s, 1H), 4.61 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.46, 133.19, 129.00, 128.68, 127.17, 122.32, 108.85, 108.61, 81.05, 74.56, 36.95, 3.25; HRMS (ESI) calcd for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found 196.1119.



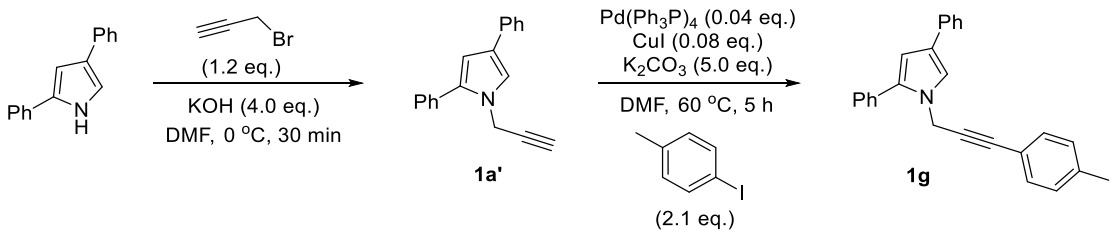
1-(but-2-yn-1-yl)-2,4-dimethyl-1H-pyrrole (1e)

Yellowish oil, 28% yield of two steps;^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H), 2.05 (s, 3H), 2.22 (s, 3H), 4.44 (s, 2H), 5.73 (s, 1H), 6.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.19, 11.37, 11.48, 35.98, 74.05, 80.38, 108.76, 117.69, 128.48, 143.60; HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$: 148.1121, found 148.1120.



1-(but-2-yn-1-yl)-2-butyl-4-phenyl-1H-pyrrole (1f)

Yellowish oil, 36% yield of two steps;^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J = 7.2 Hz, 3H), 1.40-1.50 (m, 2H), 1.62-1.70 (m, 2H), 1.84 (s, 3H), 2.60 (t, J = 8.0 Hz, 2H), 4.54 (s, 2H), 6.22 (s, 1H), 7.01 (s, 1H), 7.10-7.16(m, 1H), 7.27-7.33 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.24, 13.66, 22.28, 25.57, 30.64, 36.30, 73.76, 81.05, 104.34, 116.70, 123.77, 125.08, 125.31, 128.69, 134.56, 136.22; HRMS (ESI) calcd for $C_{18}H_{22}N$ $[M+H]^+$: 252.1747, found 252.1747.



The first step was the same as that of **1a'**.

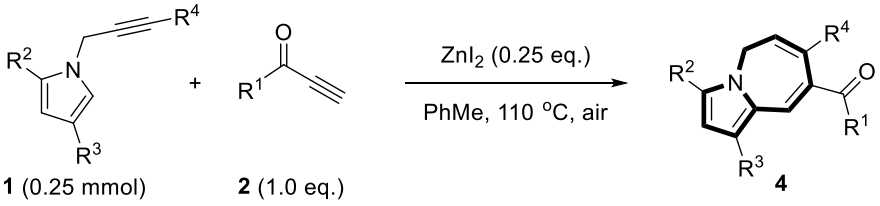
Under an atmosphere of N_2, to a 25 mL Schlenk tube were added propargyl pyrrole intermediate **1a'** (257.3 mg, 1 mmol), K_2CO_3 (691.1 mg, 5 mmol), Pd $(Ph_3P)_4$, CuI (15.2 mg, 0.08 mmol), 4-methyl iodobenzene (457.9 mg, 2.1 mmol) and DMF (4 mL). Then, the mixture was heated to 60 °C. About 4.5 h latter, after full conversion of propargyl pyrrole intermediate **1a'** by TLC analysis, the resulting mixture was cooled to room temperature and quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (30 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/dichloromethane = 50/1 as the eluent afforded the intermediate propargyl pyrrole **1g** with an 64% yield.

2,4-diphenyl-1-(3-(p-tolyl)prop-2-yn-1-yl)-1H-pyrrole (1g)

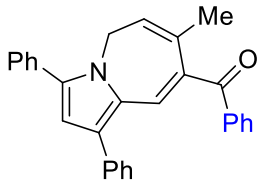
Yellow oil, 64%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.52 (m, 4H), 7.47-7.42 (m, 2H), 7.37-7.30 (m, 6H), 7.20-7.15 (m, 1H), 7.14-7.09 (m, 2H), 6.55 (d, *J* = 1.6 Hz, 1H), 4.90 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.07, 135.70, 135.63, 132.86, 131.91, 129.31, 129.11, 128.84, 128.83, 127.55, 125.82, 125.29,

125.20, 119.44, 119.16, 107.07, 85.31, 83.49, 37.69, 21.22; HRMS (ESI) calcd for $C_{26}H_{22}N$ $[M+H]^+$: 348.1747, found 348.1749.

Synthesis and characterization of 4



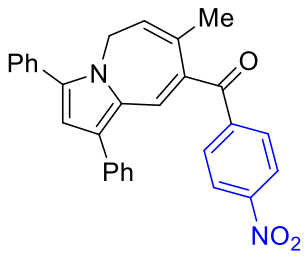
In air, to a solution of the corresponding propargyl pyrrole **1** (0.25 mmol) and alkynone **2** (0.25 mmol) in anhydrous PhMe (2.5 mL) in Schlenk tube was added ZnI_2 (20.0 mg, 0.063 mmol). Then, the reaction temperature was increased to 110 °C. After the corresponding reaction time (see Figure 2 in the text), the solution was cooled to room temperature and concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 40/1-5/1 as the eluent afforded **4**.



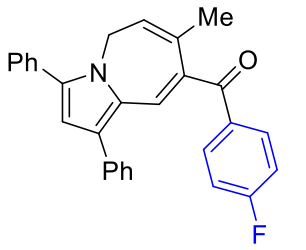
(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(phenyl)methanone (4a)

Yellow solid, 90% yield (91 mg), mp 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.55-7.42 (m, 8H), 7.42-7.32 (m, 4H), 7.28-7.23 (m, 1H), 6.55 (s, 1H), 6.05 (t, *J* = 6.8 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.11, 140.97, 138.73, 136.51, 135.36,

132.64, 132.12, 131.50, 129.88, 129.76, 129.16, 129.06, 128.69, 128.62, 128.44, 128.28, 128.08, 126.82, 124.87, 110.99, 42.95, 20.79; HRMS (ESI) calcd for $C_{29}H_{23}NNaO$ $[M+Na]^+$: 424.1672, found 424.1670.

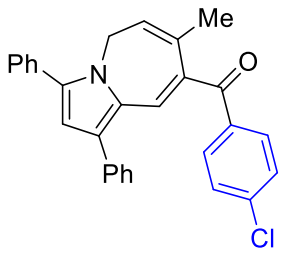


(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(4-nitrophenyl)methanone (**4b**): Red solid, 87% yield (97 mg), mp 194-196 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.55-7.45 (m, 4H), 7.45-7.34 (m, 5H), 7.33-7.26 (m, 2H), 6.55 (s, 1H), 6.07 (t, *J* = 6.8 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.79, 149.96, 144.58, 140.41, 137.65, 135.02, 133.90, 133.52, 131.76, 131.43, 130.33, 129.13, 129.03, 128.75, 128.46, 128.39, 128.31, 127.32, 125.23, 123.81, 111.44, 42.93, 20.95; HRMS (ESI) calcd for $C_{29}H_{23}N_2O_3$ $[M+H]^+$: 447.1703, found 447.1708.

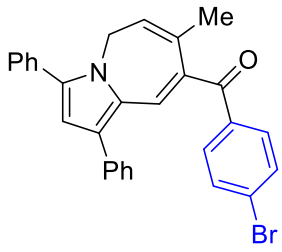


(4-fluorophenyl)(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4c**): Yellow solid, 91% yield (95 mg), mp 72-74 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02-7.82 (m, 2H), 7.54-7.43 (m, 6H), 7.43-7.34 (m, 3H), 7.33-7.26 (m, 2H), 7.20-7.11(m, 2H), 6.55 (s, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 2H), 1.98

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.46, 165.73 (d, J_{C-F} = 253.7 Hz), 140.81, 136.62, 135.34, 135.01, 134.91 (d, J_{C-F} = 2.7 Hz), 132.26 (d, J_{C-F} = 9.1 Hz), 132.06, 131.22, 130.04, 129.11, 129.08, 128.72, 128.46, 128.28, 128.13, 126.95, 124.89, 115.71 (d, J_{C-F} = 21.9 Hz), 111.09, 42.95, 20.79; HRMS (ESI) calcd for $C_{29}H_{23}FNO$ $[M+H]^+$: 420.1758, found 420.1758.

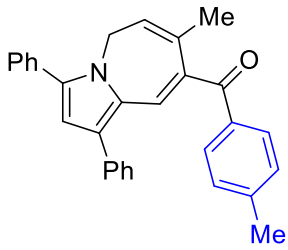


(4-chlorophenyl)(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4d**): Yellow solid, 91% yield (99 mg), mp 162-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.67-7.32 (m, 11H), 7.32-7.21 (m, 2H), 6.55 (s, 1H), 6.04 (t, *J* = 6.4 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.60, 140.75, 138.97, 137.06, 136.75, 135.27, 134.80, 132.02, 131.55, 131.10, 130.23, 129.08, 128.94, 128.73, 128.45, 128.27, 128.15, 127.00, 124.92, 111.13, 42.94, 20.82; HRMS (ESI) calcd for $C_{29}H_{23}ClNO$ $[M+H]^+$: 436.1463, found 436.1461.



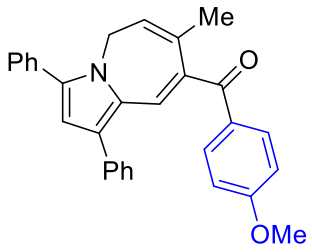
(4-bromophenyl)(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanon

e (**4e**): Yellow solid, 95% yield (114 mg), mp 170-172 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.53-7.35 (m, 9H), 7.34-7.26 (m, 2H), 6.56 (s, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.77, 140.74, 137.51, 136.79, 135.26, 134.75, 132.00, 131.94, 131.63, 131.23, 130.28, 129.08, 128.75, 128.45, 128.28, 128.17, 127.53, 127.02, 124.94, 111.14, 42.94, 20.84; HRMS (ESI) calcd for $C_{29}H_{23}BrNO$ $[M+H]^+$: 480.0958, found 480.0953.

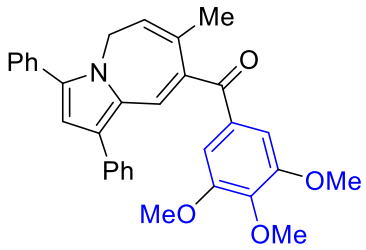


(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(p-tolyl)methanone (**4f**)

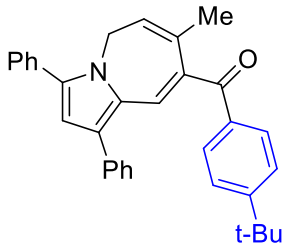
Yellow solid, 83% yield (86 mg), mp 165-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.59-7.43 (m, 6H), 7.43-7.35 (m, 3H), 7.35-7.26 (m, 4H), 6.55 (s, 1H), 6.03 (t, *J* = 6.8 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.78, 143.53, 141.06, 136.26, 135.88, 135.69, 135.44, 132.19, 130.73, 129.98, 129.52, 129.34, 129.18, 129.05, 128.69, 128.45, 128.28, 128.02, 126.75, 124.74, 110.93, 42.95, 21.42, 20.77; HRMS (ESI) calcd for $C_{30}H_{25}NNaO$ $[M+Na]^+$: 438.1828, found 438.1836.



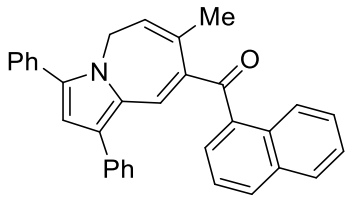
(4-methoxyphenyl)(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4g**): Yellow solid, 71% yield (77 mg), mp 180-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.55-7.44 (m, 6H), 7.43-7.34 (m, 3H), 7.32-7.24 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 6.03 (t, *J* = 6.4 Hz, 1H), 4.41 (d, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.77, 163.62, 141.08, 136.06, 135.77, 135.50, 132.22, 132.15, 131.08, 129.91, 129.25, 129.04, 128.69, 128.47, 128.25, 127.97, 126.72, 124.61, 113.83, 110.90, 55.39, 42.96, 20.74; HRMS (ESI) calcd for $C_{30}H_{25}NNaO_2$ $[M+Na]^+$: 454.1777, found 454.1785.



(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(3,4,5-trimethoxyphenyl)methanone (**4h**): Yellow solid, 73% yield (90 mg), mp 75-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.43 (m, 6H), 7.42-7.33 (m, 4H), 7.29-7.23 (m, 1H), 7.14 (s, 2H), 6.56 (s, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 3.85 (s, 6H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.32, 153.34, 142.28, 140.91, 136.41, 135.36, 135.18, 133.82, 132.04, 130.35, 129.49, 129.07, 128.72, 128.36, 128.23, 128.11, 126.93, 124.66, 111.12, 107.10, 60.88, 56.06, 43.04, 20.79; HRMS (ESI) calcd for $C_{32}H_{29}NNaO_4$ $[M+Na]^+$: 514.1989, found 514.1993.

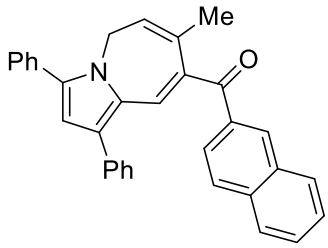


(4-(tert-butyl)phenyl)(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)metha none (**4i**): Yellow solid, 87% yield (100 mg), mp 180-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.58-7.43 (m, 8H), 7.41-7.33 (m, 3H), 7.30 (s, 1H), 7.27-7.22 (m, 1H), 6.55 (s, 1H), 6.04 (t, *J* = 6.4 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 2H), 2.00 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.97, 156.47, 141.03, 136.29, 135.90, 135.65, 135.42, 132.16, 130.83, 129.83, 129.52, 129.28, 129.05, 128.63, 128.48, 128.25, 128.02, 126.70, 125.58, 124.72, 110.91, 42.97, 34.88, 30.92, 20.76; HRMS (ESI) calcd for $C_{33}H_{31}NNaO$ $[M+Na]^+$: 480.2298, found 480.2302.

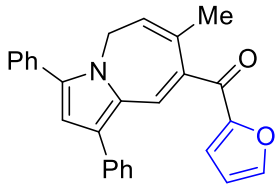


(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(naphthalen-1-yl)methanon e (**4j**): Yellow solid, 81% yield (91 mg), mp 91-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.20 (m, 1H), 8.02-7.85 (m, 2H), 7.77 (d, *J* = 6.8 Hz, 1H), 7.60-7.42 (m, 7H), 7.42-7.32 (m, 1H), 7.27-7.23 (m, 1H), 7.16-6.97 (m, 5H), 6.51 (s, 1H), 6.11 (t, *J* = 7.2 Hz, 1H), 4.38 (d, *J* = 7.2 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.66, 140.87, 137.66, 137.21, 136.67, 134.71, 134.05, 131.96, 131.45, 131.17, 130.55, 129.08, 128.81, 128.51, 128.31, 128.21, 128.05, 127.87, 127.41, 126.64, 126.60, 125.78, 125.14, 124.87, 110.96, 42.88, 21.04; HRMS (ESI) calcd for

$C_{33}H_{25}NNaO$ $[M+Na]^+$: 474.1828, found 474.1835.



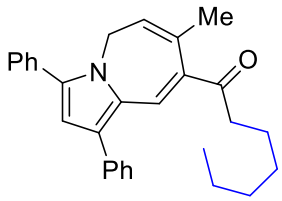
(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(naphthalen-2-yl)methanon e (**4k**): Yellow solid, 94% yield (106 mg), mp 87-89 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.06-7.88 (m, 4H), 7.68-7.60 (m, 2H), 7.59-7.43 (m, 7H), 7.43-7.35 (m, 2H), 7.25-7.20 (m, 1H), 7.18-7.09 (m, 1H), 6.56 (s, 2H), 6.09 (t, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 7.2 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.18, 141.02, 136.51, 135.92, 135.65, 135.62, 135.33, 132.66, 132.14, 131.43, 131.16, 129.79, 129.52, 129.17, 129.08, 128.78, 128.68, 128.49, 128.33, 128.28, 128.15, 128.10, 127.05, 126.71, 125.68, 125.02, 111.07, 43.02, 20.79; HRMS (ESI) calcd for $C_{33}H_{25}NNaO$ $[M+Na]^+$: 474.1828, found 474.1840.



furan-2-yl(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (4l)

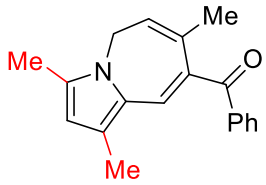
Yellow solid, 84% yield (81 mg), mp 158-160 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.52-7.37 (m, 7H), 7.34-7.28 (m, 1H), 7.28-7.24 (m, 1H), 6.56 (s, 1H), 6.02 (t, *J* = 6.8 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.05, 153.04, 146.85, 140.48, 136.48, 135.52, 134.63, 132.12, 130.27, 129.85, 129.23, 129.06, 128.68, 128.29, 128.07,

126.89, 124.91, 119.30, 112.35, 111.03, 42.89, 20.74; HRMS (ESI) calcd for $C_{27}H_{21}NNaO_2$ $[M+Na]^+$: 414.1464, found 414.1469.



1-(7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)heptan-1-one (**4m**)

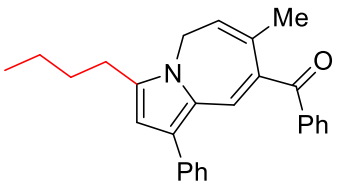
Yellow oil, 83% yield (68 mg, scale: 0.2 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.55-7.42 (m, 8H), 7.41-7.36 (m, 1H), 7.36-7.31 (m, 1H), 6.56 (s, 1H), 5.97 (t, *J* = 7.2 Hz, 1H), 4.28 (d, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.04 (s, 3H), 1.75-1.62 (m, 2H), 1.40-1.26 (m, 6H), 0.93-0.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.10, 140.75, 136.61, 136.14, 135.53, 132.10, 130.00, 129.69, 129.05, 128.86, 128.44, 128.35, 128.08, 126.90, 124.85, 110.76, 42.67, 38.83, 31.45, 28.89, 25.20, 22.27, 21.25, 13.76; HRMS (ESI) calcd for $C_{29}H_{32}NO$ $[M+H]^+$: 410.2478, found 410.2479.



phenyl(1,3,7-trimethyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4n**)

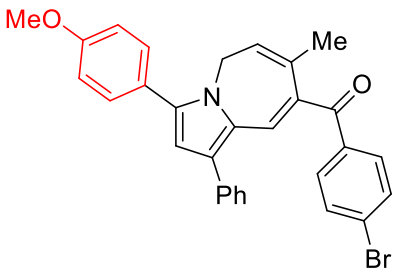
Yellow solid, 53% yield (37 mg), mp 102-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.87 (s, 3H), 2.08 (s, 3H), 2.24 (s, 2H), 4.21 (d, *J* = 7.2 Hz, 2H), 5.78 (t, *J* = 6.8 Hz, 1H), 5.93 (s, 1H), 7.26 (s, 1H), 7.29 (s, 1H), 7.44-7.50 (m, 2H), 7.53-7.59 (m, 1H), 7.86 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 10.96, 11.75, 21.30, 41.44, 111.73, 121.49, 124.32, 127.73, 128.54, 129.71, 130.53, 131.25, 131.62, 132.29, 139.36,

140.29, 198.01; HRMS (ESI) calcd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1541.



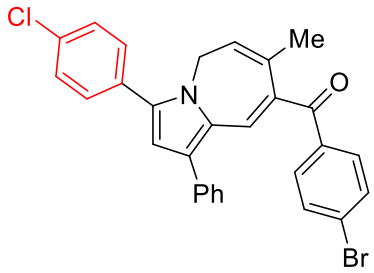
(3-butyl-7-methyl-1-phenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(phenyl)methanone (4o)

Yellow oil, 76% yield (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.2 Hz, 3H), 1.40-1.49 (m, 2H), 1.63-1.70 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 4.27 (d, J = 7.2 Hz, 2H), 5.90 (t, J = 6.8 Hz, 1H), 6.27 (s, 1H), 7.18-7.24 (m, 1H), 7.28-7.42 (m, 5H), 7.44-7.49 (m, 2H), 7.50-7.56 (m, 1H), 7.89 (d, J = 6.8Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.60, 20.87, 22.23, 25.92, 30.30, 41.44, 108.90, 122.95, 126.51, 126.73, 128.36, 128.54, 128.57, 129.10, 129.66, 132.05, 132.40, 134.16, 135.61, 136.49, 138.95, 140.83, 198.25; HRMS (ESI) calcd for $C_{27}H_{28}NO$ $[M+H]^+$: 382.2165, found 382.2161.

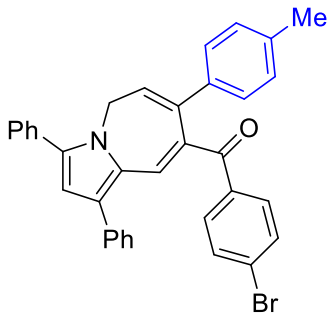


(4-bromophenyl)(3-(4-methoxyphenyl)-7-methyl-1-phenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4p**): Yellow solid, 85% yield (87 mg, scale: 0.2 mmol), mp 170-172 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.49-7.36 (m, 6H), 7.34-7.27 (m, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H),

6.01 (t, *J* = 6.8 Hz, 1H), 4.37 (d, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.81, 159.86, 140.77, 137.64, 136.76, 135.35, 134.31, 131.92, 131.87, 131.23, 130.33, 129.65, 128.74, 128.65, 128.45, 127.44, 126.98, 124.74, 124.45, 114.48, 110.73, 55.30, 42.90, 20.88; HRMS (ESI) calcd for $C_{30}H_{25}BrNO_2$ $[M+H]^+$: 510.1063, found 510.1056.

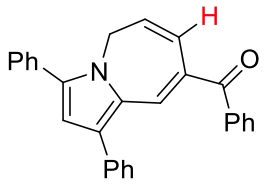


(4-bromophenyl)(3-(4-chlorophenyl)-7-methyl-1-phenyl-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4q**): Yellow solid, 83% yield (86 mg, scale: 0.2 mmol), mp 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51-7.35 (m, 8H), 7.34-7.27 (m, 2H), 6.53 (s, 1H), 6.02 (t, *J* = 6.4 Hz, 1H), 4.36 (d, *J* = 7.2 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.67, 140.90, 137.39, 135.40, 135.08, 134.12, 131.97, 131.34, 131.22, 130.46, 130.24, 129.44, 129.36, 128.79, 128.43, 127.65, 127.12, 124.75, 111.28, 42.94, 20.82; HRMS (ESI) calcd for $C_{29}H_{22}BrClNO$ $[M+H]^+$: 514.0568, found 514.0567.



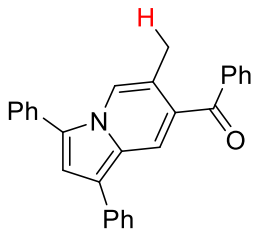
(4-bromophenyl)(1,3-diphenyl-7-(p-tolyl)-5H-pyrrolo[1,2-a]azepin-8-yl)methanone (**4s**): Yellow solid, 56% yield (62 mg, scale: 0.2 mmol), mp 188-190 ºC; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.68-7.30 (m, 14H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.61 (s, 1H), 6.27 (t, *J* = 7.2 Hz, 1H), 4.57 (d, *J* = 7.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.21, 146.18, 137.89, 137.82, 137.53, 137.18, 135.27, 133.53, 132.91, 131.99, 131.55, 130.80, 129.60, 129.33, 129.10, 128.87, 128.57, 128.25, 127.47, 127.14, 126.94, 124.29, 111.42, 43.14, 20.84; HRMS (ESI) calcd for $C_{35}H_{27}BrNO$ $[M+H]^+$: 556.1271, found 556.1270.



(1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl)(phenyl)methanone (4u)

Yellow solid, 27% yiled (26 mg), mp 133-135 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.60 (s, 1H), 7.55-7.45 (m, 5H), 7.45-7.30 (m, 7H), 7.26-7.23 (m, 1H), 7.02 (d, *J* = 10.4 Hz, 1H), 6.58 (s, 1H), 6.20-6.05 (m, 1H), 4.53 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.68, 138.86, 137.65, 135.22, 134.40, 132.31, 131.79, 131.71, 131.29, 130.52, 130.36, 129.40, 129.09, 128.73, 128.67, 128.41, 128.39, 127.05, 124.91, 112.29, 43.29; HRMS (ESI) calcd for $C_{28}H_{22}NO$ $[M+H]^+$: 388.1696, found 388.1694.

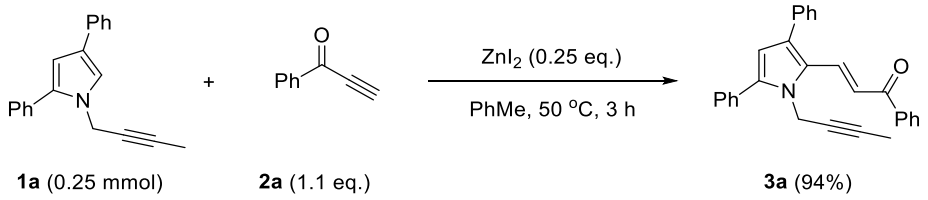


(6-methyl-1,3-diphenylindolizin-7-yl)(phenyl)methanone (4u')

Yellow solid, 38% yield (37 mg), mp 144-146 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.92 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.60-7.32

(m, 10H), 7.28-7.20 (m, 1H), 7.07 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.50, 138.68, 135.62, 132.91, 131.82, 130.27, 129.39, 129.11, 128.63, 128.55, 128.15, 127.81, 127.72, 126.29, 123.27, 121.42, 120.05, 120.01, 115.05, 17.69; HRMS (ESI) calcd for $C_{28}H_{22}NO$ $[M+H]^+$: 388.1696, found 388.1690.

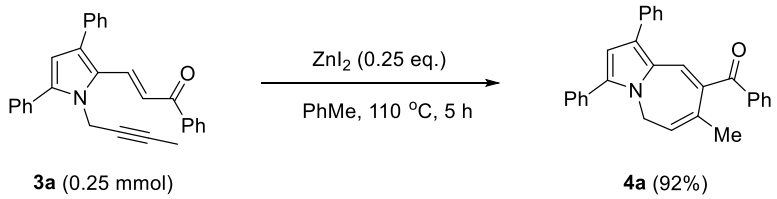
Control experiments



1a (0.25 mmol) **2a** (1.1 eq.) **3a** (94%)

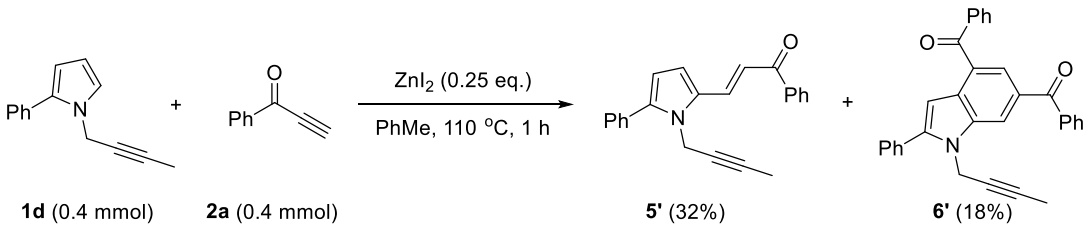
In air, to a solution of propargyl pyrrole **1a** (0.25 mmol) and alkynone **2a** (0.25 mmol) in anhydrous PhMe (2.5 mL) in Schlenk tube was added ZnI_2 (20.0 mg, 0.063 mmol). Then, the reaction temperature was increased to 50 °C. After 3 hours, the solution was concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/DCM = 2/1 as the eluent afforded **3a**.

(E)-3-(1-(but-2-yn-1-yl)-3,5-diphenyl-1H-pyrrol-2-yl)-1-phenylprop-2-en-1-one (**3a**): Yellow solid, 94% yield (94 mg), mp 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-7.88 (m, 3H), 7.79-7.61 (m, 3H), 7.55-7.41 (m, 10H), 7.38-7.32 (m, 1H), 6.45 (s, 1H), 4.73 (s, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.10, 141.10, 139.12, 136.02, 133.68, 132.81, 132.54, 131.97, 129.50, 129.15, 129.06, 128.87, 128.67, 128.49, 128.30, 127.34, 118.07, 111.90, 82.56, 75.56, 37.02, 3.49; HRMS (ESI) calcd for $C_{29}H_{23}NNaO$ $[M+Na]^+$: 424.1672, found 424.1677.



3a (0.25 mmol) **4a** (92%)

Under air atmosphere, to a solution of **3a** (0.25 mmol) in anhydrous PhMe (2.5 mL) in Schlenk tube was added ZnI_2 (20.0 mg, 0.063 mmol). Then, the reaction temperature was increased to 110 °C. After 5 hours, the solution was concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/DCM = 3/1-2/1 as the eluent afforded **4a**.



1d (0.4 mmol) **2a** (0.4 mmol) **5'** (32%) **6'** (18%)

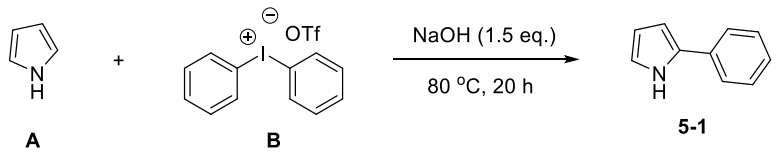
Under air atmosphere, to a solution of the propargyl pyrrole **1d** (78.1 mg, 0.4 mmol) and alkynone **2a** (52.0 mg, 0.4 mmol) in anhydrous PhMe (6 mL) in Schlenk tube was added ZnI_2 (32.0 mg, 0.25 equiv). Then, the reaction temperature was increased to 110 °C. About 1 hour, after full conversion of alkynone **2a** by TLC analysis, the solution was concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/ ethyl acetate = 20/1-10/1 as the eluent to afford **5' and 6'**.

5': yellow oil, 32% yield (41.6 mg); ^{1}H NMR (400 MHz, $CDCL_3$): δ 8.05 (d, J = 7.2 Hz, 2H), 7.99 (d, J = 15.2 Hz, 1H), 7.60-7.42 (m, 8H), 7.41-7.34 (m, 1H), 6.92 (d, J = 3.6 Hz, 1H), 6.35 (d, J = 3.6 Hz, 1H), 4.71 (s, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz,

$CDCL_3$): δ 190.36, 140.50, 139.12, 133.11, 132.52, 132.10, 131.70, 129.03, 128.96, 128.70, 128.49, 128.23, 117.37, 113.87, 111.12, 82.09, 74.52, 35.17, 3.36; HRMS (ESI) calcd for $C_{23}H_{20}NO$ $[M+H]^+$: 326.1539, found 326.1536.

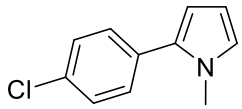
6': yellow oil, 18% yield (32.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.98 (s, 1H), 7.93-7.75 (m, 4H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.60-7.40 (m, 9H), 7.09 (s, 1H), 4.89 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.17, 196.70, 147.04, 138.73, 138.56, 138.03, 132.60, 132.36, 131.46, 131.17, 130.27, 129.55, 129.25, 129.09, 128.73, 128.49, 128.40, 127.07, 116.95, 103.74, 81.68, 73.57, 34.62, 3.28; HRMS (ESI) calcd for $C_{32}H_{23}NNaO_2$ $[M+Na]^+$: 476.1621, found 476.1623.

Synthesis and characterization of 5



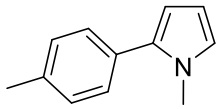
Under an atmosphere of N_2, to a 100 mL Schlenk tube were added pyrrole **A** (50 mL), **B** (12.91 g, 30 mmol)[2], and NaOH (1.8 g, 45 mmol). Then, the mixture was heated to 80 °C. About 10 h latter, after full conversion of **B** by TLC analysis, the resulting mixture was cooled to room temperature and quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (80 mL). The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 50/1/10 as the eluent afforded the intermediate 2-phenyl pyrrole **5-1**[3] with a 70% yield. ^1H NMR (400 MHz,

$CDCL_3$): δ 8.42 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 2H), 7.24-7.15 (m, 1H), 6.90-6.80 (m, 1H), 6.55-6.45 (m, 1H), 6.35-6.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCL_3$): δ 133.02, 132.37, 129.11, 126.41, 124.05, 118.99, 110.26, 106.07.



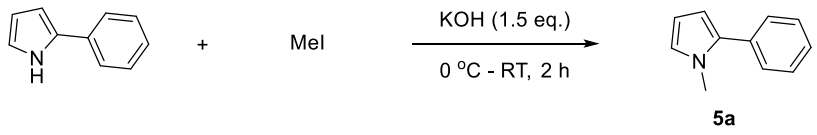
2-(4-chlorophenyl)-1-methyl-1H-pyrrole (5b)[4]

Yellow oil, 68% yield (reacted with *N*-Me pyrrole); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.28 (m, 4H), 6.72 (s, 1H), 6.30-6.10 (m, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.59, 132.92, 132.02, 130.00, 128.78, 124.25, 109.12, 108.06, 34.84.



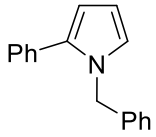
1-methyl-2-(p-tolyl)-1H-pyrrole (5c)[4]

Yellow oil, 51% yield (reacted with *N*-Me pyrrole); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.70 (s, 1H), 6.19 (d, *J* = 2.0 Hz, 2H), 3.65 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.76, 134.88, 130.70, 129.27, 128.84, 123.50, 108.41, 107.76, 34.76, 20.88.



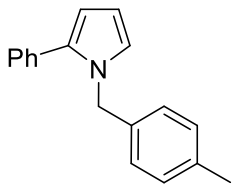
Under an atmosphere of N_2, to a 100 mL Schlenk tube were added 2-phenyl pyrrole (897.1 mg, 6.26 mmol), KOH (1.76 g, 31.3 mmol), DMF (30 mL) and MeI (507 uL, 8.14 mmol) at room temperature. About 30 min latter，after full conversion of 2-phenyl pyrrole by TLC analysis, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (50 mL).

The organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel with petroleum ether/dichloromethane = 40/1 as the eluent afforded **5a** with an 89% yield. **1-methyl-2-phenyl-1H-pyrrole (5a)**[3] white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.29 (m, 5H), 6.76 (s, 1H), 6.40-6.20 (m, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.82, 133.56, 128.83, 128.54, 126.90, 123.81, 108.73, 107.85, 34.80.



1-benzyl-2-phenyl-1H-pyrrole (**5d**)[5]

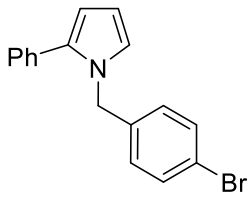
Using the synthetic method of **5a** (Benzyl bromide was used in place of MeI). **5d**: Yellow oil, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.20 (m, 8H), 7.01 (d, J = 7.2 Hz, 2H), 6.75 (s, 1H), 6.28 (d, J = 2.0 Hz, 2H), 5.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.10, 135.23, 133.51, 129.11, 128.89, 128.59, 127.52, 127.19, 126.67, 123.08, 109.00, 108.61, 50.51.



1-(4-methylbenzyl)-2-phenyl-1H-pyrrole (**5e**)

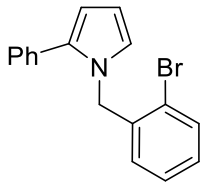
Using the synthetic method of **5a** (Corresponding benzyl bromide was used in place of MeI). **5e**: Yellowish oil, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.24 (m, 5H), 7.10 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.73 (s, 1H), 6.27 (d, J = 1.6

Hz, 2H), 5.11 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.23, 136.01, 135.18, 133.54, 129.56, 129.08, 128.58, 127.13, 126.66, 123.01, 108.88, 108.52, 50.26, 20.79; HRMS (ESI) calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$: 270.1253, found 270.1258.



1-(4-bromobenzyl)-2-phenyl-1H-pyrrole (**5f**)

Using the synthetic method of **5a** (Corresponding benzyl bromide was used in place of MeI). **5f**: Yellowish oil, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.4 Hz, 2H), 7.36-1.25 (m, 5H), 6.85 (d, J = 8.4 Hz, 2H), 6.73 (s, 1H), 6.28 (s, 2H), 5.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.13, 135.19, 133.31, 132.00, 129.07, 128.66, 128.33, 127.33, 122.95, 121.38, 109.27, 108.90, 49.97; HRMS (ESI) calcd for $C_{17}H_{14}BrNNa$ $[M+Na]^+$: 334.0202, found 334.0207.

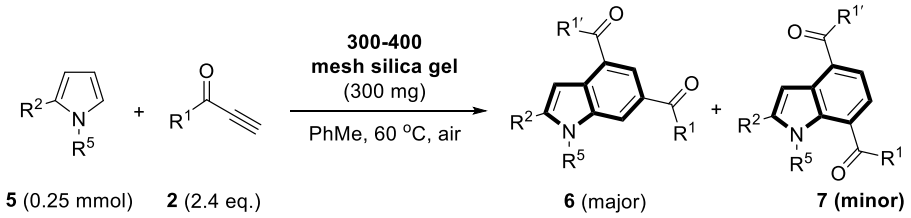


1-(2-bromobenzyl)-2-phenyl-1H-pyrrole (**5g**)

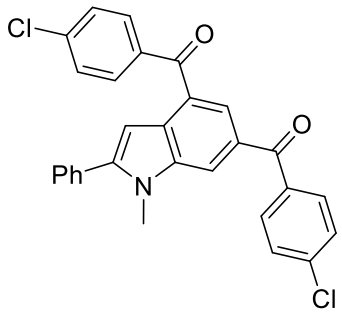
Using the synthetic method of **5a** (Corresponding benzyl bromide was used in place of MeI). **5g**: White solid, 70% yield, mp 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.0 Hz, 1H), 7.29-7.15 (m, 6H), 7.15-7.00 (m, 1H), 6.72 (s, 1H), 6.64 (d, J = 7.6 Hz, 1H), 6.32 (s, 2H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.48,

135.20, 133.14, 132.74, 129.02, 128.71, 128.68, 128.14, 128.07, 127.22, 123.21, 121.79, 109.24, 108.97, 50.92; HRMS (ESI) calcd for $C_{17}H_{14}BrNNa$ $[M+Na]^+$: 334.0202, found 334.0200.

Synthesis and characterization of 6 and 7



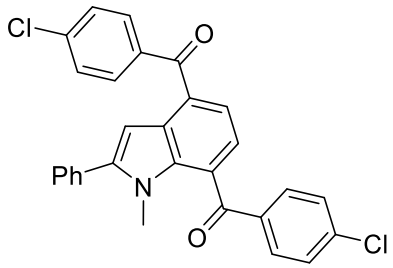
In air, to a solution of the corresponding pyrrole **5** (0.25 mmol) and alkynone **2** (0.6 mmol, 2.4 equiv) in anhydrous PhMe (5 mL) in Schlenk tube was added 300-400 mesh silica gel (300 mg). Then, the reaction temperature was increased to 60 °C. After the corresponding reaction time (see Figure 3 in the text), the solution was cooled to room temperature and concentrated carefully under reduced pressure directly. To determine the ratio of product, the residue was first dissolved in $CDCl_3$, and some samples were taken for NMR analysis. Then the sample for analysis and the rest mixture were recombined for column chromatographic purification using petroleum ether/ethyl acetate (from 30/1 to 10/1) as the eluent to give the **6** and **7**.



(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis((4-chlorophenyl)methanone) (6a)

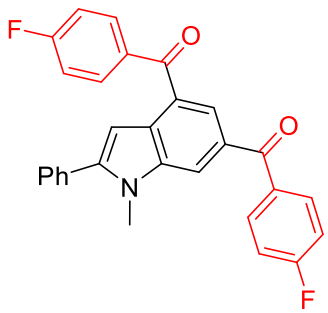
74% (total yield of **6a and 7a**).

6a： yellow solid, mp 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.87 (s, 1H), 7.85-7.71 (m, 4H), 7.58-7.41 (m, 9H), 7.01 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.89, 195.51, 148.19, 139.20, 138.95, 138.87, 136.97, 136.83, 131.66, 131.56, 130.93, 129.70, 129.65, 129.26, 129.02, 128.90, 128.36, 126.17, 116.32, 103.43, 31.46; HRMS (ESI) calcd for $C_{29}H_{20}Cl_2NO_2$ $[M+H]^+$: 484.0866, found 484.0853.



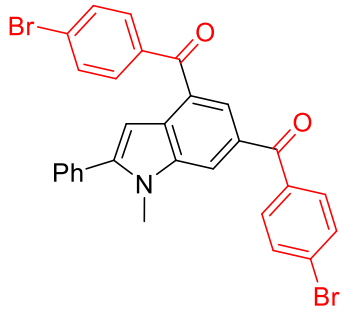
(1-methyl-2-phenyl-1H-indole-4,7-diyl)bis((4-chlorophenyl)methanone) (7a)

Yellow solid, mp 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.57-7.38 (m, 10H), 7.28-7.24 (m, 1H), 6.97 (s, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.09, 195.46, 146.45, 140.69, 139.27, 137.04, 136.90, 136.15, 132.21, 131.80, 131.40, 129.80, 129.44, 129.29, 128.86, 126.71, 122.33, 122.26, 103.09, 35.07; HRMS (ESI) calcd for $C_{29}H_{20}Cl_2NO_2$ $[M+H]^+$: 484.0866, found 484.0863.



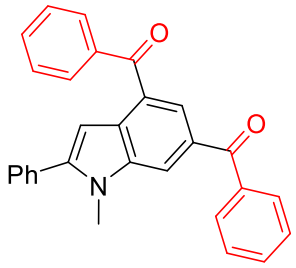
(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis((4-fluorophenyl)methanone) (6b)

71% (79 mg, **6b** and **7b**, 11/1). **6b：** yellow solid, mp 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.94-7.82 (m, 5H), 7.59-7.45 (m, 5H), 7.21-7.09 (m, 4H), 6.99 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.68, 195.37, 165.79 (d, J_{C-F} = 254.0 Hz), 165.56 (d, J_{C-F} = 253.7 Hz), 147.98, 138.95, 134.82 (d, J_{C-F} = 16.3 Hz), 134.79 (d, J_{C-F} = 16.6 Hz), 132.83 (d, J_{C-F} = 9.2 Hz), 132.70 (d, J_{C-F} = 9.1 Hz), 131.63, 130.86, 129.90, 129.63, 129.20, 128.99, 128.50, 126.12, 116.13, 115.63 (d, J_{C-F} = 21.3 Hz), 103.33, 31.43; HRMS (ESI) calcd for $C_{29}H_{20}F_2NO_2$ $[M+H]^+$: 452.1457, found 452.1456.



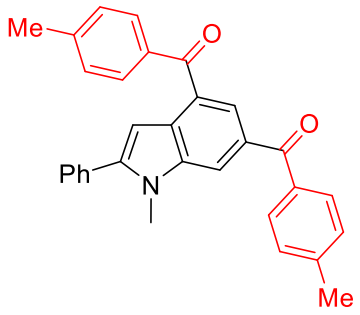
(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis((4-bromophenyl)methanone) (6c)

73% (105 mg, **6c** and **7c**, 12/1). **6c：** yellow solid, mp 225-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.87 (s, 1H), 7.82-7.35 (m, 13H), 7.01 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.05, 195.64, 148.23, 138.93, 137.39, 137.25, 131.89, 131.77, 131.67, 131.57, 130.93, 129.64, 129.26, 129.01, 128.29, 127.80, 127.40, 126.18, 116.36, 103.43, 31.46; HRMS (EI) calcd for $C_{29}H_{19}Br_2NO_2$ $[M]^+$: 570.9783, found 570.9785.



(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6d)

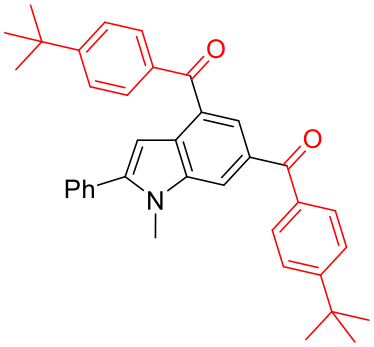
80% (82 mg, **6d** and **7d**, 13/1). **6d**： yellow solid, mp 44-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.95 (s, 1H), 7.90-7.72 (m, 4H), 7.62-7.35 (m, 11H), 7.08 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.25, 196.79, 147.88, 138.99, 138.76, 138.57, 132.56, 132.29, 131.74, 130.91, 130.22, 130.13, 129.94, 129.61, 129.07, 128.92, 128.44, 126.92, 116.25, 103.49, 31.39; HRMS (ESI) calcd for $C_{29}H_{22}NO_2$ $[M+H]^+$: 416.1645, found 416.1643.



(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis(p-tolylmethanone) (6e)

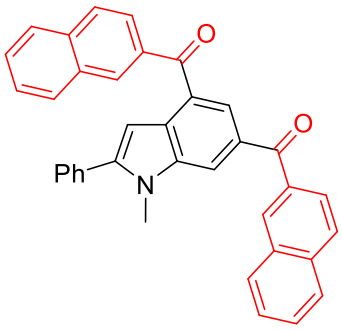
74% (82 mg, **6e** and **7e**, 11/1). **6e**： yellow solid, mp 222-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.92 (s, 1H), 7.85-7.66 (m, 4H), 7.65-7.37 (m, 5H), 7.34-7.21 (m, 4H), 7.02 (s, 1H), 3.87 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.04, 196.73, 147.46, 143.47, 143.11, 138.93, 135.99, 135.84, 131.86, 130.72, 130.53, 130.46, 130.38, 129.64, 129.39, 129.20, 129.17, 129.00, 128.91,

126.26, 115.93, 103.34, 31.39, 21.36; HRMS (ESI) calcd for $C_{31}H_{26}NO_2$ $[M+H]^+$: 444.1958, found 444.1958.



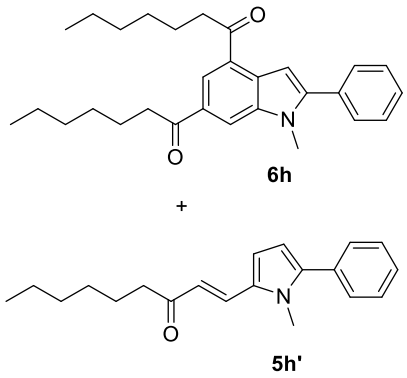
(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis((4-(tert-butyl)phenyl)methanone) (6f)

67% (88 mg, **6f** and **7f**, 9/1). **6f**： yellow solid mp 79-81 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.96 (s, 1H), 7.91-7.70 (m, 4H), 7.65-7.30 (m, 9H), 7.11 (s, 1H), 3.89 (s, 3H), 1.37 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.94, 196.56, 156.36, 156.11, 147.63, 139.05, 136.02, 135.83, 131.91, 130.81, 130.37, 130.30, 130.25, 129.65, 129.01, 128.93, 128.67, 126.83, 125.41, 115.95, 103.47, 34.86, 31.44, 30.92; HRMS (ESI) calcd for $C_{37}H_{38}NO_2$ $[M+H]^+$: 528.2897, found 528.2894.



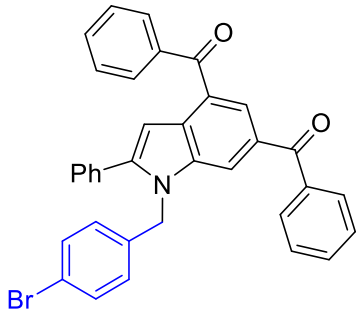
(1-methyl-2-phenyl-1H-indole-4,6-diyl)bis(naphthalen-2-ylmethanone) (6g)

81% (104 mg, **6g** and **7g**, 11/1). **6g**： orange solid, mp 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 10.0 Hz, 2H), 8.25 (s, 1H), 8.05 (s, 1H), 8.03-7.75 (m, 8H), 7.68-7.35 (m, 9H), 7.11 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.27, 196.97, 147.89, 139.11, 136.01, 135.88, 135.52, 135.32, 132.56, 132.51, 132.06, 131.80, 131.65, 131.00, 130.44, 129.68, 129.56, 129.11, 128.96, 128.88, 128.45, 128.42, 128.35, 128.00, 126.95, 126.85, 126.67, 126.17, 125.99, 116.22, 103.48, 31.49; HRMS (ESI) calcd for $C_{37}H_{26}NO_2$ $[M+H]^+$: 516.1958, found 516.1955.



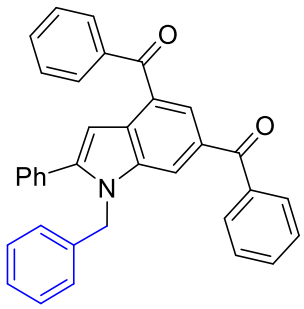
54% (58 mg, **6h** and **5h'**, 1/1), yellow oil; **6h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.23 (s, 1H), 7.70-7.27 (m, 6H), 3.87 (s, 3H), 3.25-3.00 (m, 4H), 1.75-1.60 (m, 4H), 1.50-1.25 (m, 12H), 1.00-0.75 (m, 6H); **5h'**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (d, *J* = 3.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.30 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.80-1.75 (m, 2H) other peaks are overlapped with the signals of **6h**; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.24, 200.76, 200.46, 148.35, 140.52, 139.41, 132.48, 131.82, 131.30, 130.50, 129.99, 129.61, 129.20, 129.05, 128.92, 128.77, 128.40, 127.97, 122.86, 120.85, 114.59, 112.35, 110.95, 104.35, 41.60, 39.45, 38.47, 32.07, 31.50, 31.44, 31.30, 28.89, 28.83, 24.50, 24.41, 22.28, 22.26, 13.75; **6h**:

HRMS (ESI) calcd for $C_{29}H_{38}NO_2$ $[M+H]^+$: 432.2897, found 432.2896; **5h'**: HRMS (ESI) calcd for $C_{20}H_{26}NO$ $[M+H]^+$: 296.2009, found 296.2010.



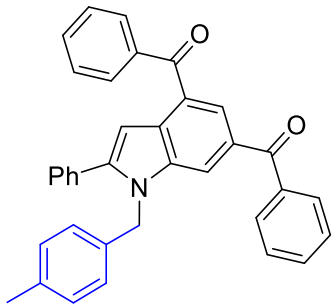
(1-(4-bromobenzyl)-2-phenyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6i)

69% (98 mg, **6i** and **7i**, 11/1). **6i**: yellow solid, mp 63-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.93-7.83 (m, 3H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.60-7.37 (m, 13H), 7.20 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.25, 196.41, 147.89, 138.61, 138.18, 138.01, 136.44, 132.71, 132.34, 131.54, 131.29, 130.31, 130.17, 129.42, 129.37, 129.11, 128.95, 128.55, 128.41, 127.93, 127.05, 121.73, 117.33, 104.31, 47.31; HRMS (ESI) calcd for $C_{35}H_{25}BrNO_2$ $[M+H]^+$: 570.1063, found 570.1057.



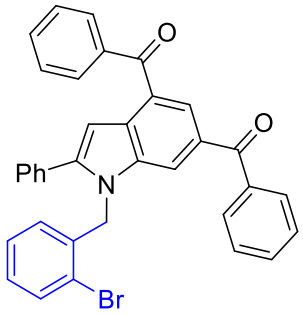
(1-benzyl-2-phenyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6j)

74% (91 mg, **6j** and **7j**, 10/1). **6j**：yellow solid, mp 39-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.95-7.81 (m, 3H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.60-7.26 (m, 14H), 7.21 (s, 1H), 7.08-6.90 (m, 2H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.30, 196.37, 148.03, 138.70, 138.22, 138.14, 137.40, 132.62, 132.23, 131.71, 131.22, 130.29, 130.16, 129.98, 129.47, 129.23, 129.16, 129.01, 128.83, 128.51, 128.36, 127.82, 126.96, 126.17, 117.65, 104.10, 47.82; HRMS (ESI) calcd for $C_{35}H_{26}NO_2$ $[M+H]^+$: 492.1958, found 492.1954.



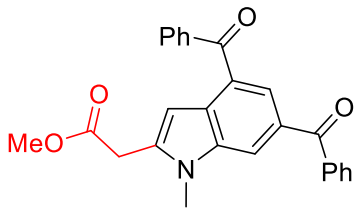
(1-(4-methylbenzyl)-2-phenyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6k)

69% (88 mg, **6k** and **7k**, 13/1). **6k**：yellow solid, mp 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.94-7.83 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.60-7.32 (m, 11H), 7.19 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.45 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.35, 196.44, 148.06, 138.75, 138.30, 138.20, 137.52, 134.37, 132.62, 132.23, 131.79, 131.24, 130.31, 130.22, 129.95, 129.83, 129.50, 129.21, 129.01, 128.77, 128.52, 128.34, 126.97, 126.13, 117.71, 104.03, 47.65, 20.82; HRMS (ESI) calcd for $C_{36}H_{28}NO_2$ $[M+H]^+$: 506.2115, found 506.2112.



(1-(2-bromobenzyl)-2-phenyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6l)

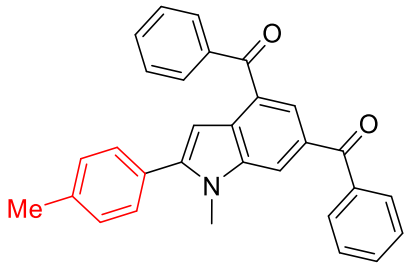
71% (102 mg, **6l** and **7l**, 12/1). **6l**： yellow solid, mp 164-166 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.87 (s, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.64-7.55 (m, 2H), 7.54-7.31 (m, 10H), 7.24 (s, 1H), 7.21-7.11 (m, 2H), 6.61 (d, J = 6.4 Hz, 1H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.25, 196.42, 147.99, 138.67, 138.30, 138.22, 136.45, 133.28, 132.71, 132.37, 131.40, 131.22, 130.39, 130.33, 130.18, 129.37, 129.23, 129.14, 128.89, 128.55, 128.40, 128.24, 127.40, 127.22, 121.84, 117.05, 104.32, 48.34; HRMS (ESI) calcd for $C_{35}H_{25}BrNO_2$ $[M+H]^+$: 570.1063, found 570.1061.



methyl 2-(4,6-dibenzoyl-1-methyl-1H-indol-2-yl)acetate (6m)

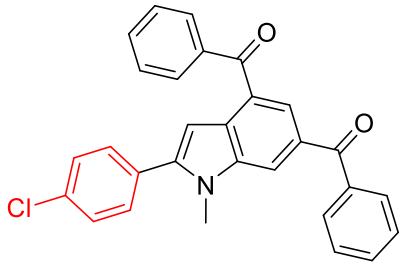
71% (102 mg, **6m** and **7m**, >20/1). **6m**： yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.83 (s, 3H), 3.92 (s, 2H), 6.94 (s, 1H), 7.43-7.50 (m, 4H), 7.53-7.60 (m, 2H), 7.79-7.85 (m, 4H), 7.89 (s, 1H), 8.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.17, 33.04, 52.44, 104.00, 115.85, 126.62, 128.36, 128.44, 129.94, 130.14, 130.21,

130.48, 132.34, 132.56, 138.30, 138.49, 138.70, 139.26, 169.92, 196.86, 197.21; HRMS (ESI) calcd for $C_{26}H_{22}NO_4$ $[M+H]^+$: 412.1543, found 412.1543.



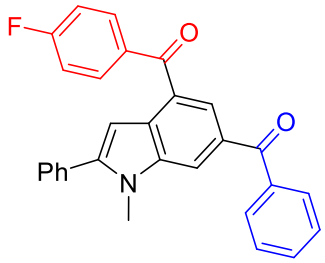
(1-methyl-2-(p-tolyl)-1H-indole-4,6-diyl)bis(phenylmethanone) (6n)

70% (75 mg, **6n** and **7n**, 17/1). **6n**： yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.94 (s, 1H), 7.90-7.78 (m, 4H), 7.61-7.54 (m, 2H), 7.51-7.41 (m, 6H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.05 (s, 1H), 3.87 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.33, 196.87, 148.15, 139.26, 139.00, 138.83, 138.66, 132.56, 132.29, 131.05, 130.25, 130.16, 129.78, 129.68, 129.54, 128.84, 128.46, 128.31, 126.99, 116.20, 103.24, 31.40, 21.08; HRMS (ESI) calcd for $C_{30}H_{24}NO_2$ $[M+H]^+$: 430.1802, found 430.1801.

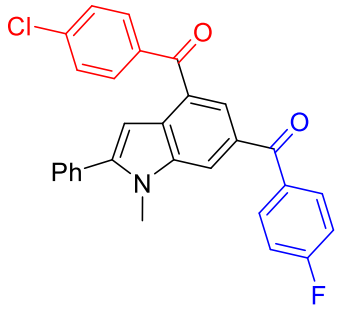


(2-(4-chlorophenyl)-1-methyl-1H-indole-4,6-diyl)bis(phenylmethanone) (6o)

76% (86 mg, **6o** and **7o**, 9/1). **6o：** yellow solid, mp 171-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.94 (s, 1H), 7.90-7.78 (m, 4H), 7.61-7.42 (m, 10H), 7.08 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.22, 196.78, 146.47, 139.08, 138.67, 138.49, 135.37, 132.66, 132.40, 130.84, 130.25, 130.16, 129.27, 128.49, 126.99, 116.30, 103.78, 31.42; HRMS (ESI) calcd for $C_{29}H_{21}ClNO_2$ $[M+H]^+$: 450.1255, found 450.1252.



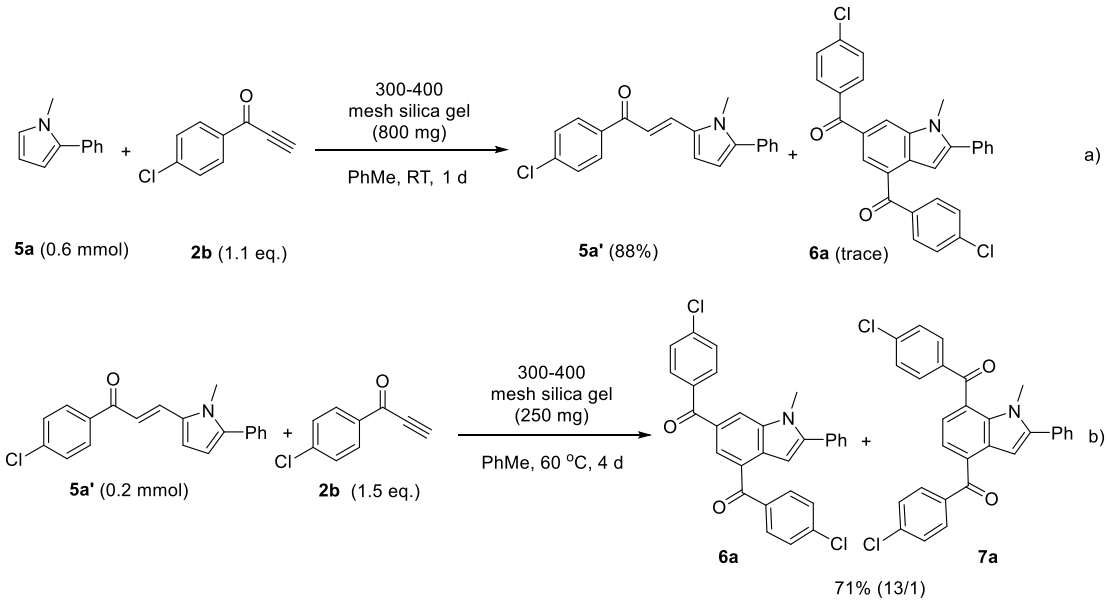
After the complete conversion of **5a** and **2a** (1:1) with 300-400 mesh silica gel at room temperature, 1.1 equiv of 1-(4-fluorophenyl)prop-2-yn-1-one (**2c**) was added and the reaction was heated to 60 °C for another 4 days. (scale: 0.25 mmol) **(6-benzoyl-1-methyl-2-phenyl-1H-indol-4-yl)(4-fluorophenyl)methanone (6p):** yellow solid, 58% yield of **6p** (63 mg), mp 222-224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.00-7.87 (m, 3H), 7.84 (d, J = 7.2 Hz, 2H), 7.62-7.43 (m, 8H), 7.20-7.09 (m, 2H), 7.02 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.81, 195.74, 165.74 (d, $J_{C\text{-}F}$ = 253.9 Hz), 147.94, 138.76 (d, $J_{C\text{-}F}$ = 40.5 Hz), 134.95, 132.84 (d, $J_{C\text{-}F}$ = 9.1 Hz), 132.39, 131.69, 130.84, 130.13, 130.00, 129.63, 129.15, 128.97, 128.50, 128.35, 126.51, 116.34, 115.59 (d, $J_{C\text{-}F}$ = 21.8 Hz), 103.34, 31.43; HRMS (ESI) calcd for $C_{29}H_{21}FNO_2$ $[M+H]^+$: 434.1551, found 434.1550.



The conjugate addition intermediate, which was isolated after complete conversion of **5a** and 1-(4-fluorophenyl)prop-2-yn-1-one (**2c**) (1:1) at room temperature (24 h), was used for the subsequent reaction with **2b** (that with *p*-ClPh group, 1.1 eq.) using 300-400 mesh silica gel as the catalyst at 60 ºC. (scale: 0.25 mmol)

(4-(4-chlorobenzoyl)-1-methyl-2-phenyl-1H-indol-6-yl)(4-fluorophenyl)metha none (6q): yellow solid, 54% yield of **6q** (63 mg), mp 61-63 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.95 (m, 5H), 7.60-7.38 (m, 7H), 7.22-7.10 (m, 2H), 7.01 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.94, 195.36, 165.60 (d, $J_{C\text{-}F}$ = 253.7 Hz), 148.10, 139.07 (d, $J_{C\text{-}F}$ = 19.3 Hz), 137.00, 134.71, 132.72 (d, $J_{C\text{-}F}$ = 9.0 Hz), 131.66, 130.84, 129.93, 129.65, 129.23, 129.01, 128.88, 128.25, 126.27, 116.29, 115.66 (d, $J_{C\text{-}F}$ = 21.9 Hz), 103.39, 31.45; HRMS (ESI) calcd for $C_{29}H_{20}ClFNO_2$ $[M+H]^+$: 468.1161, found 468.1157.

Control reactions:



(a) In air, to a solution of propargyl pyrrole **5a** (0.6 mmol) and alkynone **2b** (1.1 equiv) in anhydrous PhMe (15 mL) in Schlenk tube was added 300-400 mesh silica gel (800 mg) at room temperature. After 24 hours, the solution was added petroleum ether (5 mL) and purified directly by flash chromatography on silica gel with petroleum ether/ethyl acetate/DCM = 30/2/3 as the eluent afforded **5a'**. Yellow solid, 88% yield, mp 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 14.8 Hz, 1H), 7.53-7.36 (m, 7H), 7.31 (d, *J* = 15.2 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.35 (d, *J* = 3.6 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.81, 141.23, 138.89, 137.46, 133.38, 132.33, 131.98, 129.85, 129.25, 129.02, 128.84, 128.18, 115.88, 113.05, 111.42, 32.10; HRMS (ESI) calcd for $C_{20}H_{16}ClNNaO$ $[M+Na]^+$: 344.0813, found 344.0818.

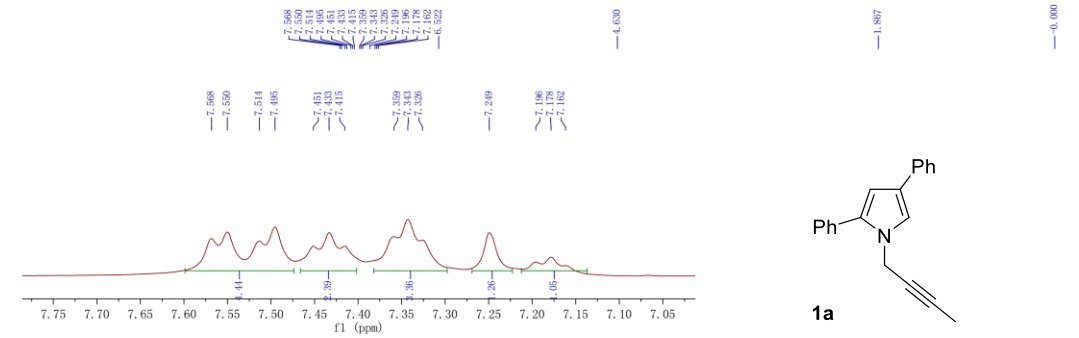
(b) In air, to a solution of **5a'** (64.4 mg, 0.2 mmol) and **2b** (36.2 mg, 0.22 mmol) in anhydrous PhMe (5 mL) in Schlenk tube was added 300-400 mesh silica gel (250

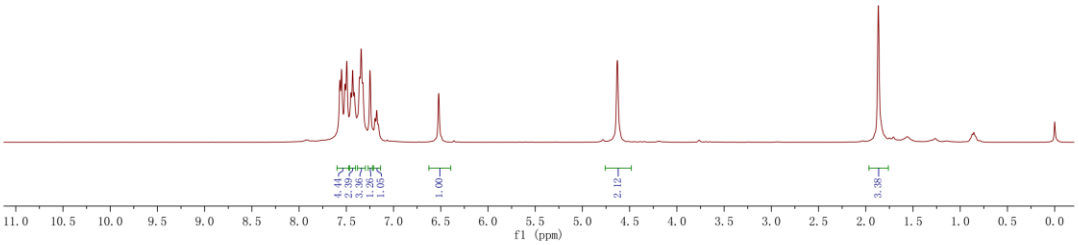
mg). Then, the reaction temperature was increased to 60 ºC. After 4 days, the solution was concentrated under reduced pressure directly. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 25/1-125/8 as the eluent to afford **6a** and **7a** (68.8 mg, 71%, 13/1).

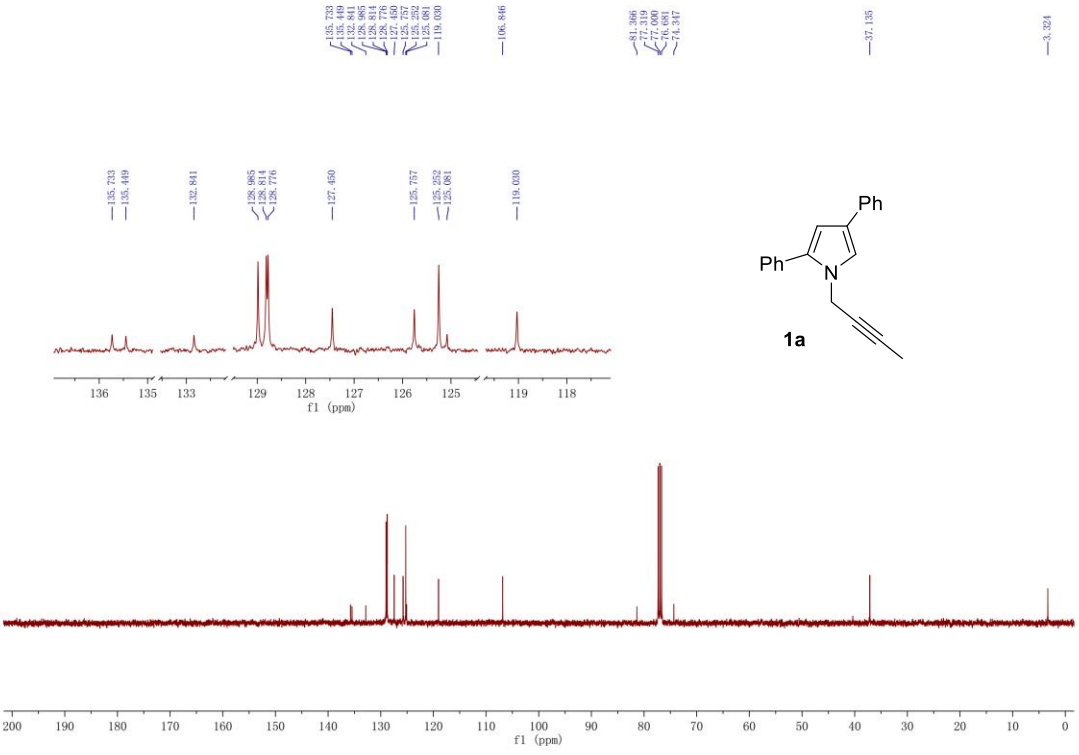
References

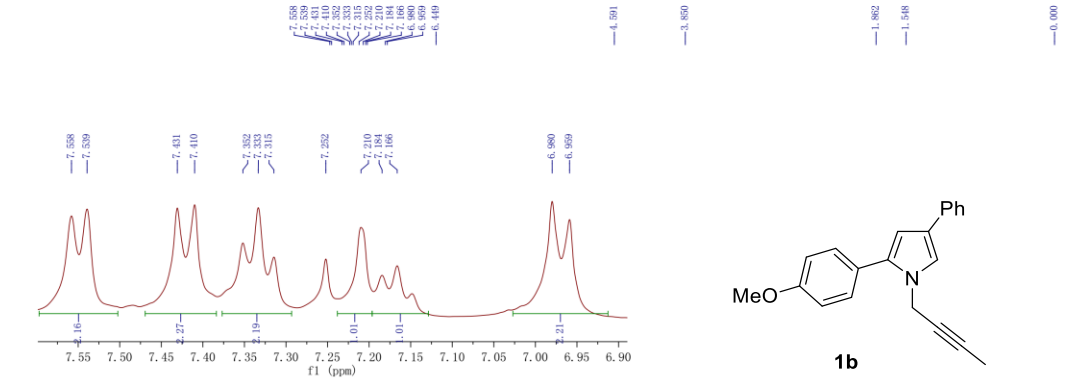
1. X. Li, X. Xie, Y. Liu, *J. Org. Chem.*, 2016, **81**, 3688.
2. (a) M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.*, 2007, **349**, 2610; (b) M. Bielawski, D. Aili, B. Olofsson, *J. Org. Chem.*, 2008, **73**, 4602.
3. J. Wen, R.-Y. Zhang, S.-Y. Chen, J. Zhang, X.-Q. Yu, *J. Org. Chem.*, 2012, **77**, 766.
4. Y.-X. Liu, D. Xue, J.-D. Wang, C.-J. Zhao, Q.-Z. Zou, C. Wang, J. Xiao, *Synlett*, 2013, **24**, 507.
5. J. Yang, S. Liu, J.-F. Zheng, J. Zhou, *Eur. J. Org. Chem.*, 2012, 6248.

NMR spectra of new compounds (1)





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6.449
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3.850
1.862
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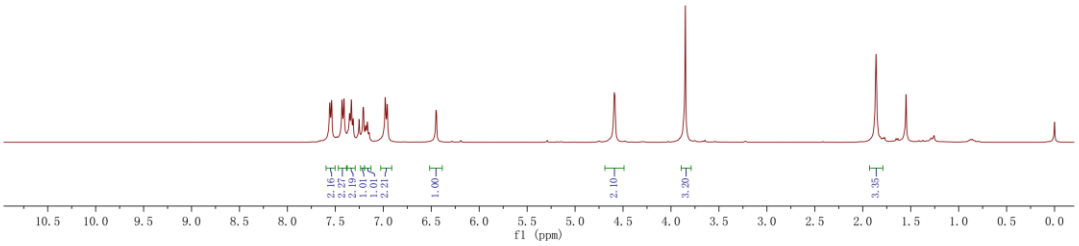
1.01
1.01
2.21
f1 (ppm)

Ph
MeO
N

1b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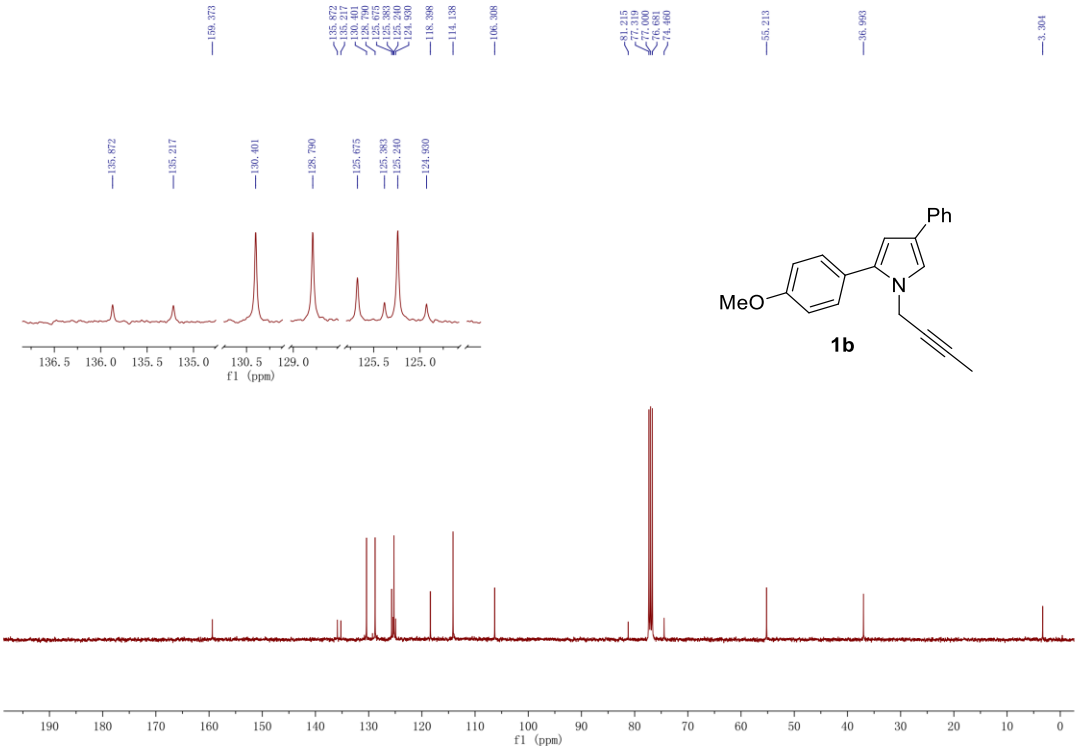
f1 (ppm)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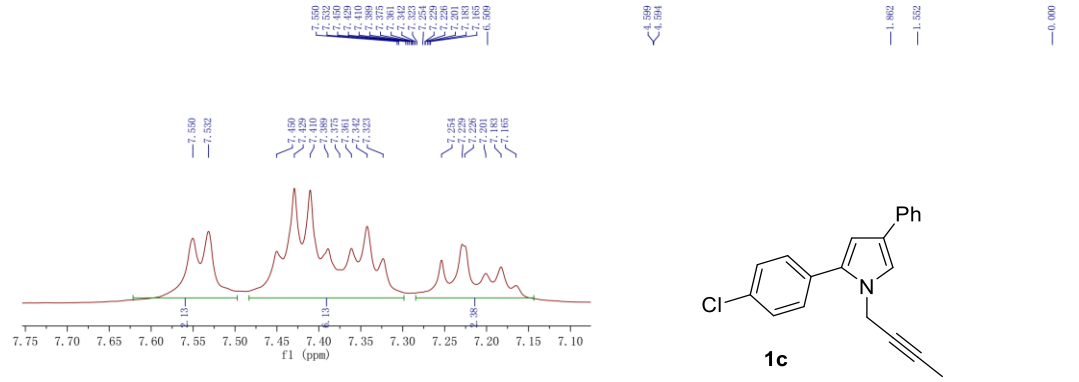
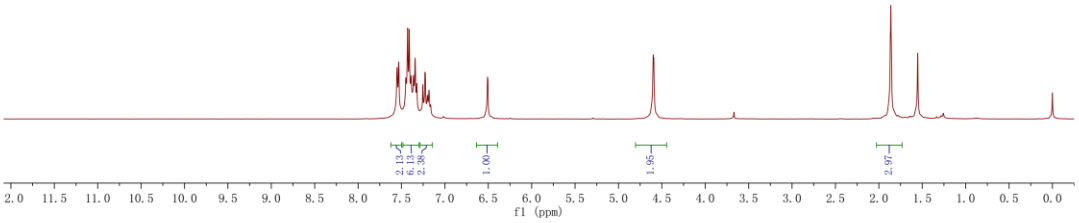
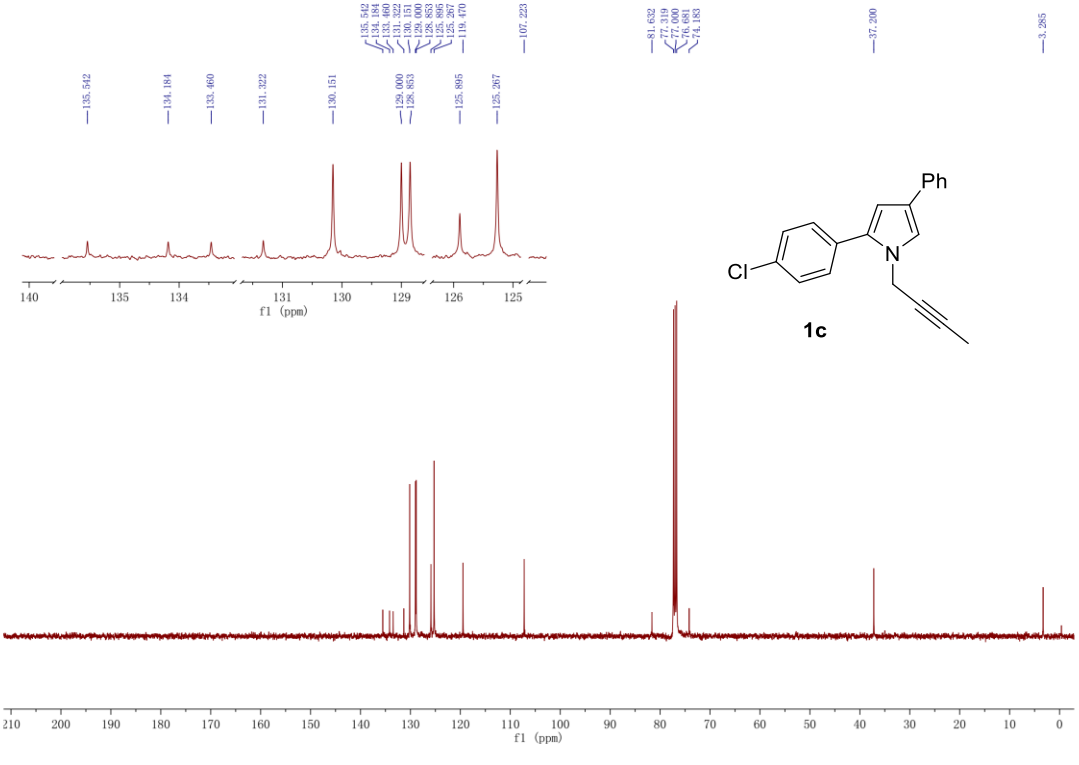
f1 (ppm)

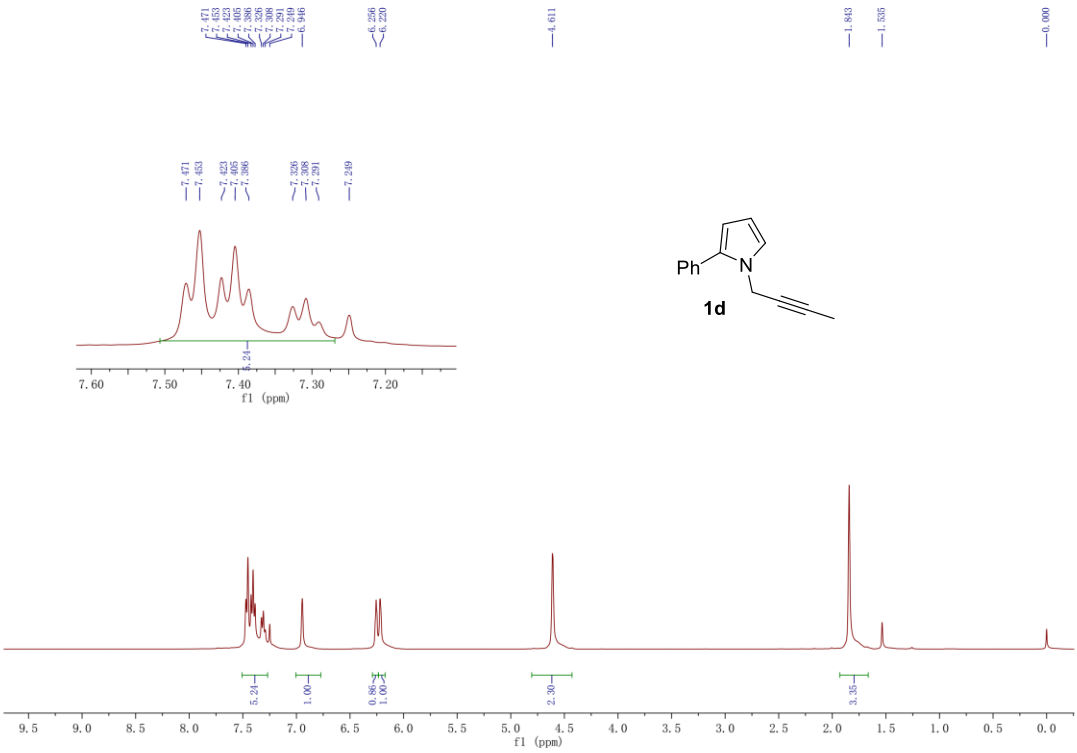
Ph
MeO
N

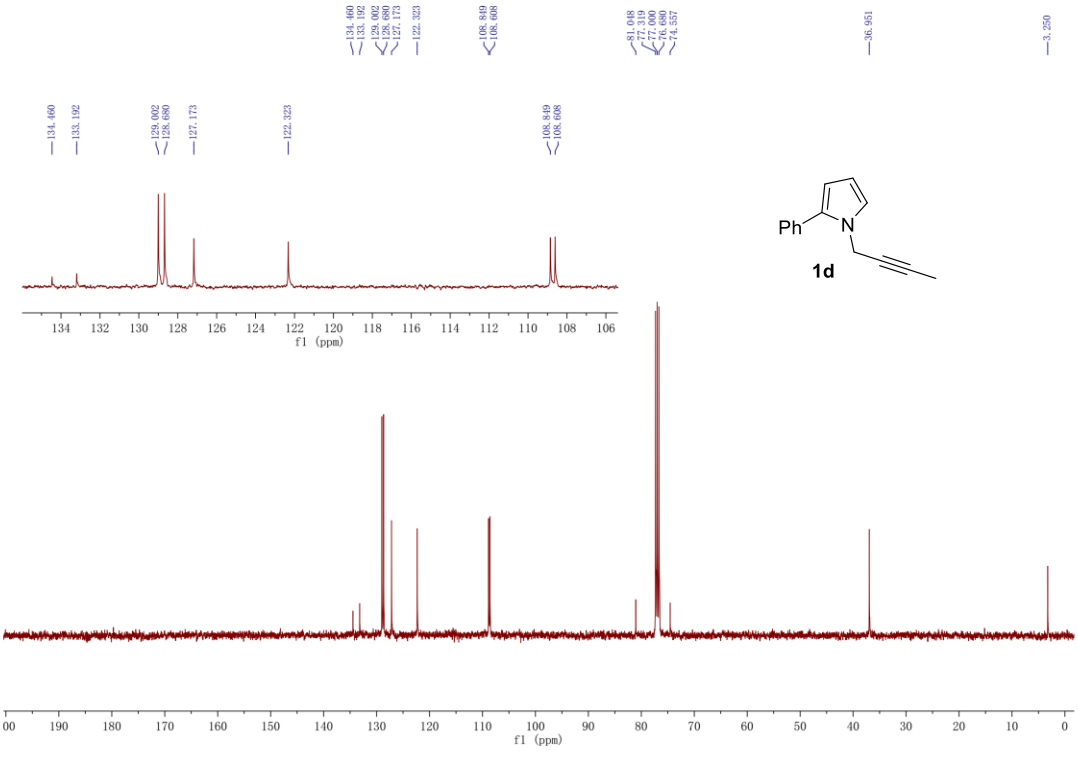
1b

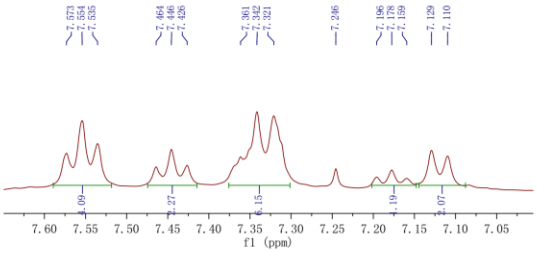

7.550
7.532
7.490
7.429
7.410
7.389
7.375
7.361
7.342
7.323
7.254
7.229
7.201
7.183
7.165
6.909
4.599
4.594
1.862
1.552
0.000
2.13
6.13
2.38
f1 (ppm)
Ph
Cl
N
1c

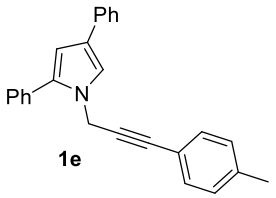

2.13
6.13
2.38
1.00
1.95
2.97
f1 (ppm)

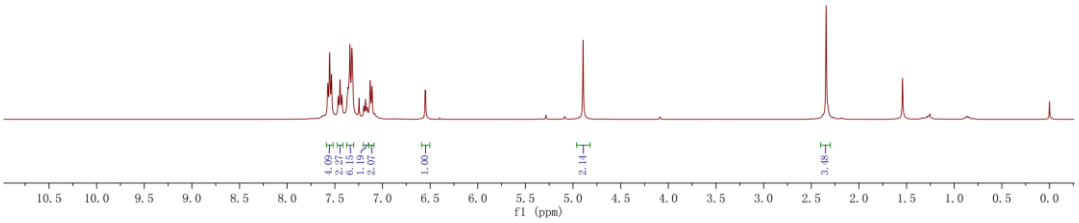

135.542
134.184
133.460
131.322
130.151
129.000
128.853
125.895
125.267
119.470
107.223
81.632
77.319
77.000
76.681
74.183
37.200
3.285
f1 (ppm)
Ph
Cl
N
1c

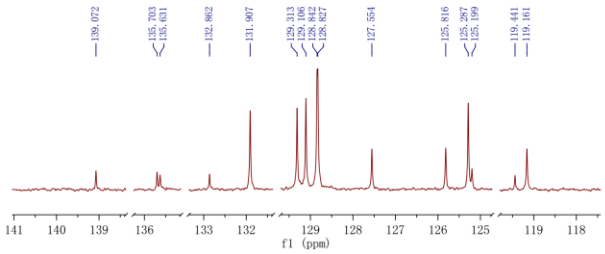

7.471
7.453
7.423
7.405
7.396
7.326
7.308
7.291
7.249
6.946
6.256
6.220
4.611
1.843
1.535
0.000
5.24
7.60
7.50
7.40
7.30
7.20
f1 (ppm)
Ph
N
1d
5.24
1.00
0.86
1.00
2.30
3.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

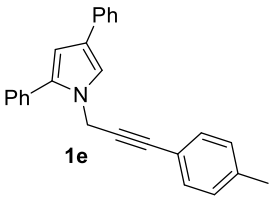

134.460
133.192
129.602
128.680
127.173
122.323
108.849
108.608
81.048
77.314
77.000
76.680
74.557
36.961
3.250
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
f1 (ppm)
Ph
N
1d
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

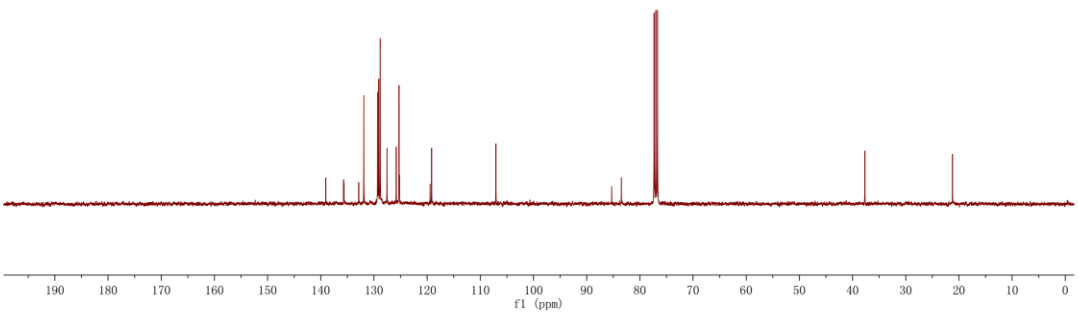


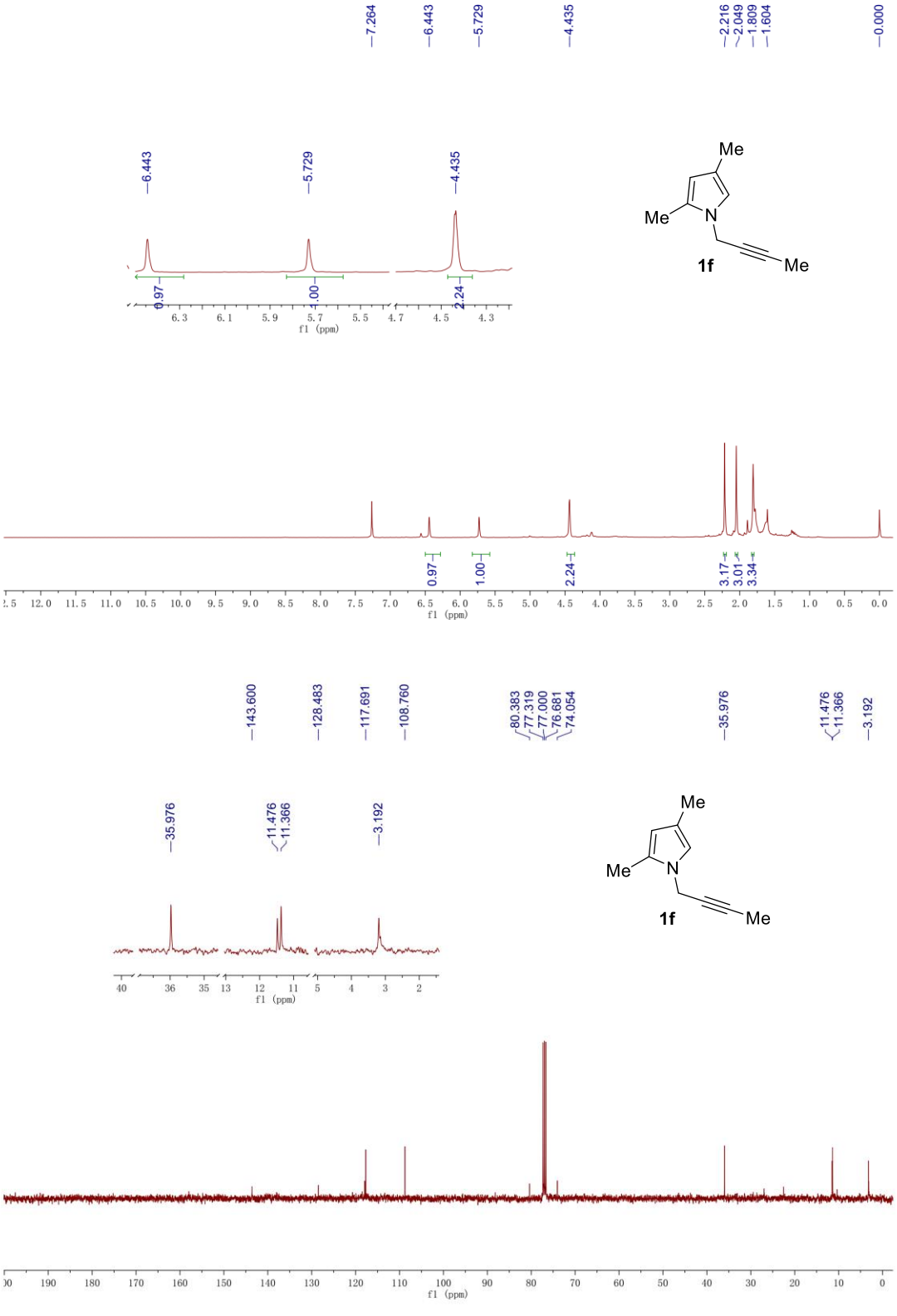

Ph
Ph
N
1e

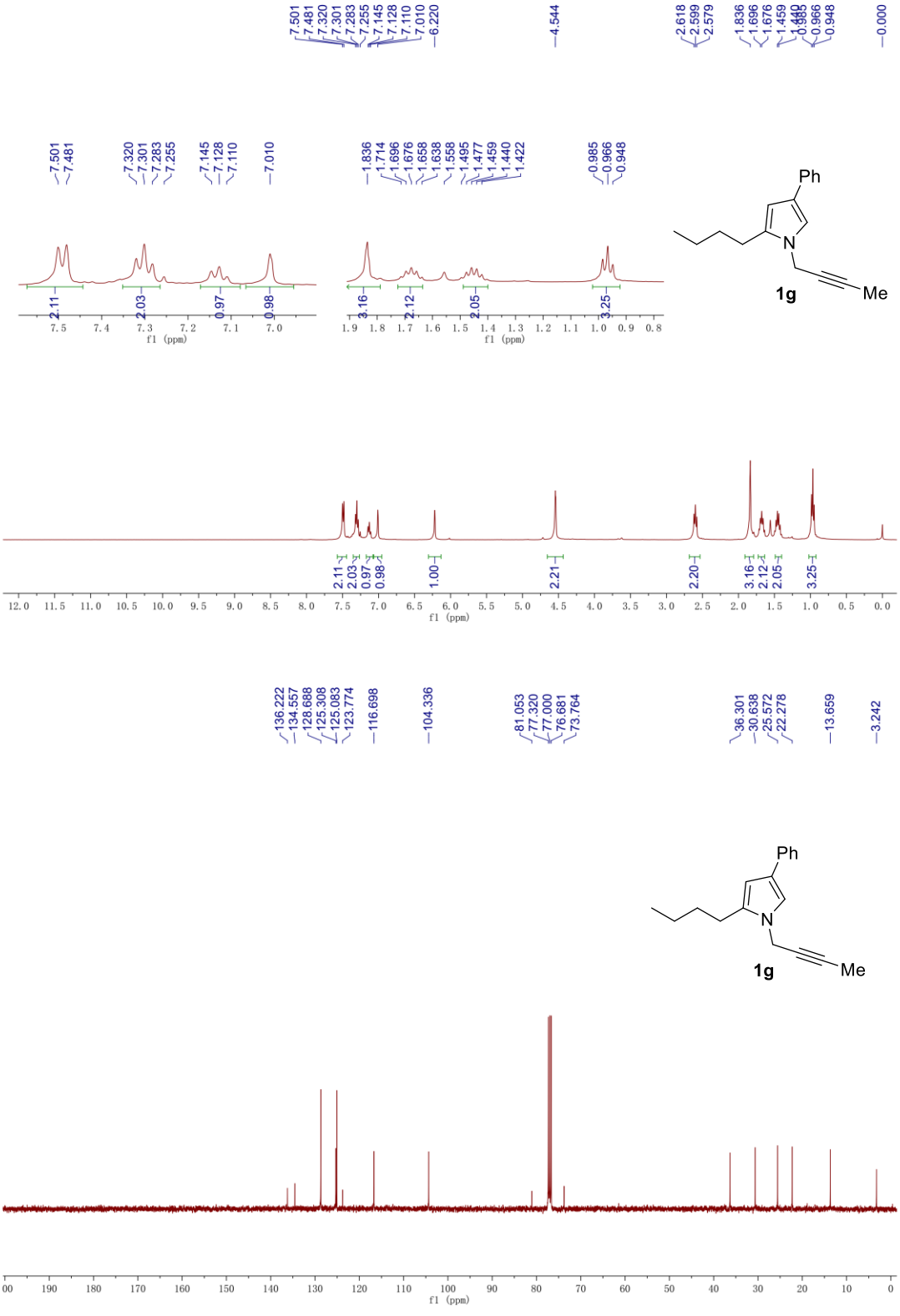




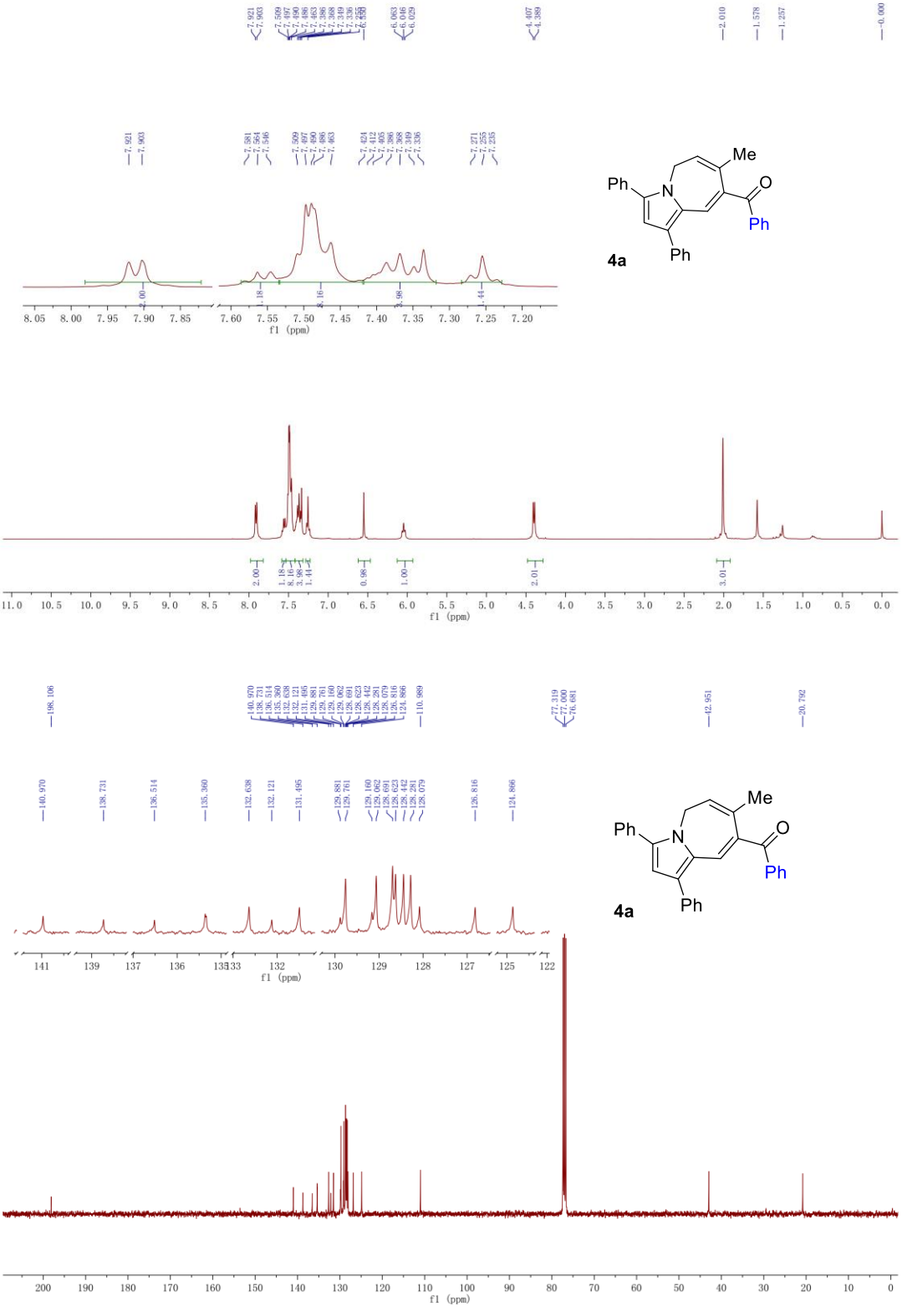

Ph
Ph
N
1e

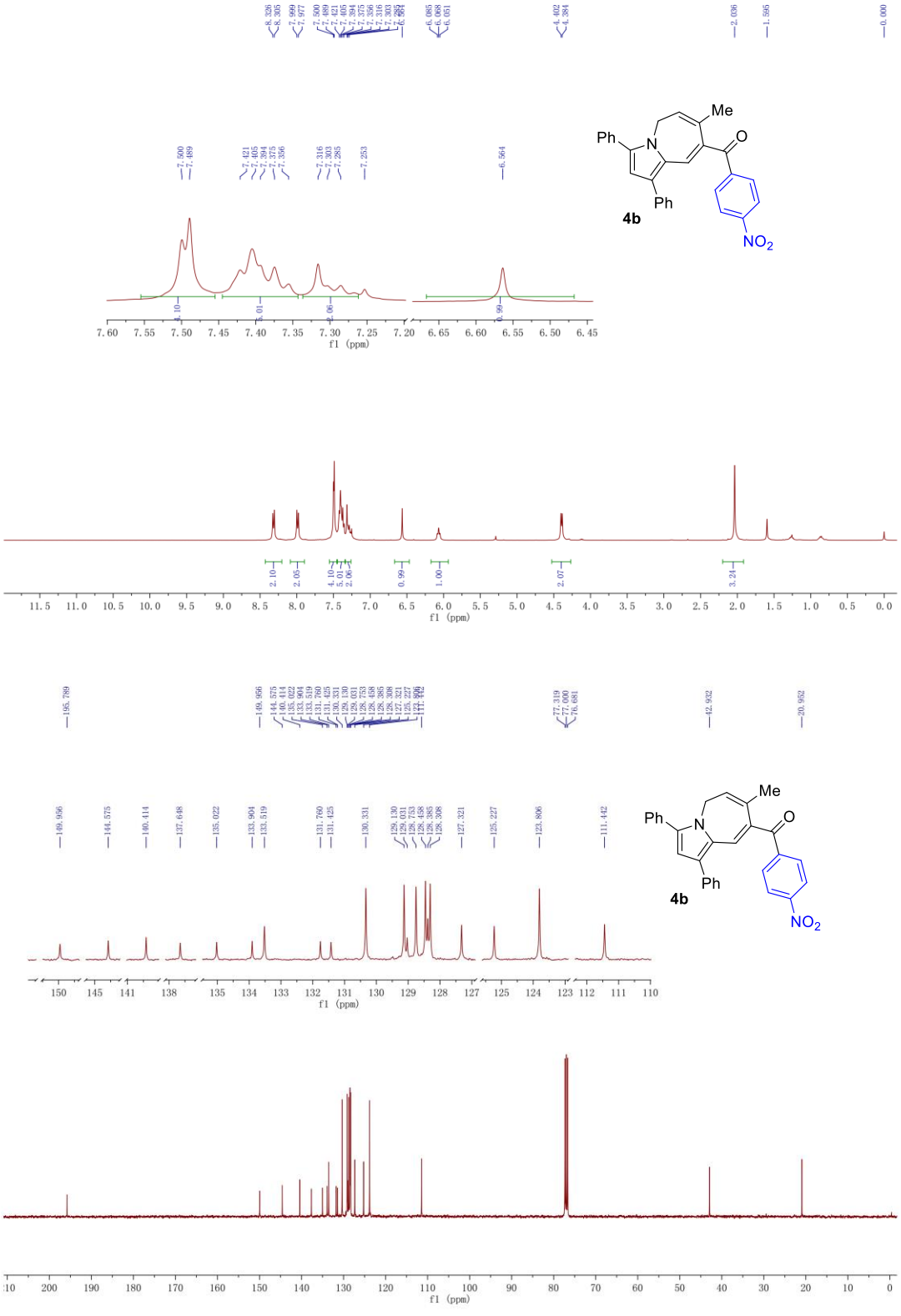


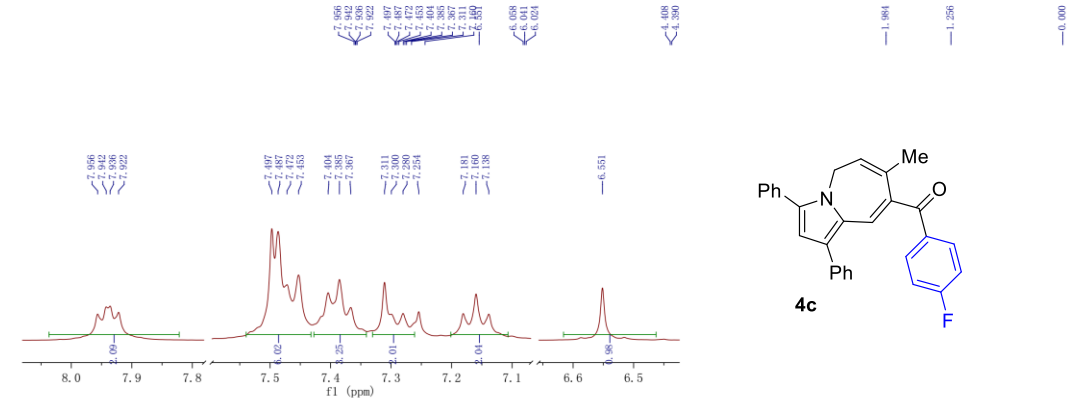

7.264
6.443
5.729
4.435
2.216
2.049
1.809
1.604
0.000
Me
Me
N
Me
1f
0.97
1.00
2.24
3.17
3.01
3.34
f1 (ppm)
143.600
128.483
117.691
108.760
80.383
77.319
77.000
76.681
74.054
35.976
11.476
11.366
3.192

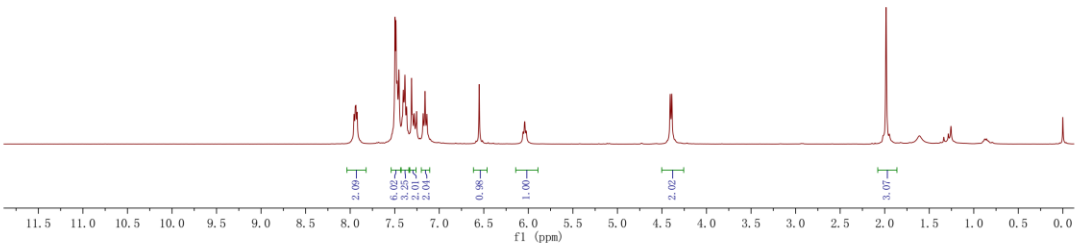


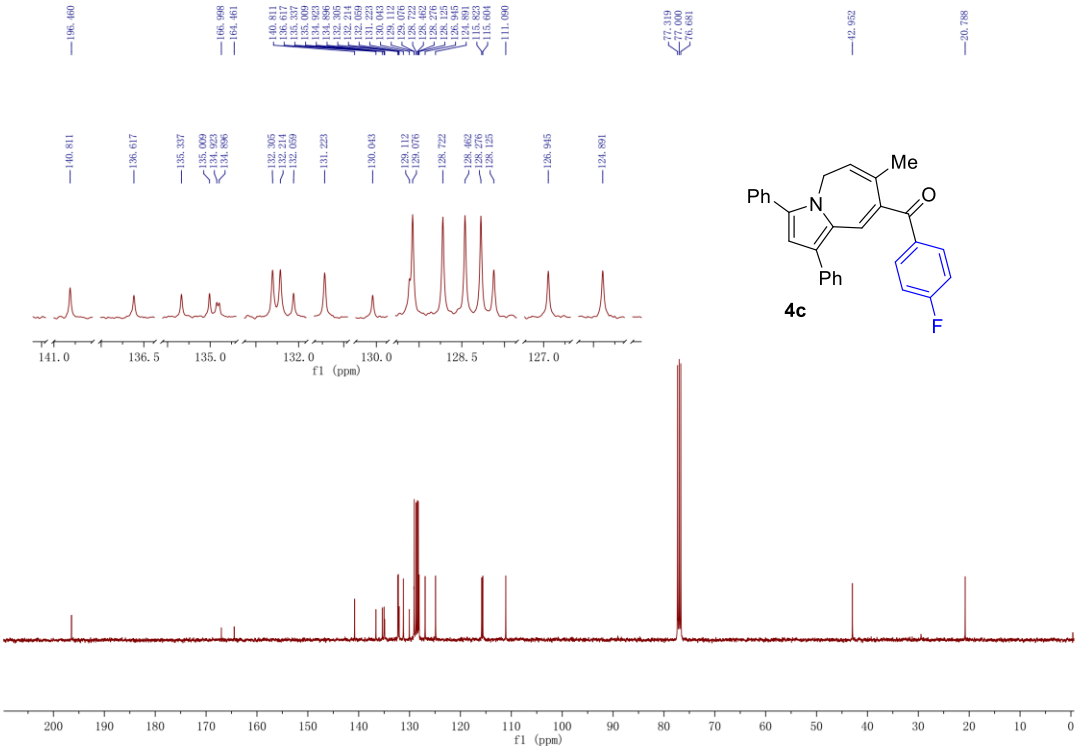
NMR spectra of new compounds (4)

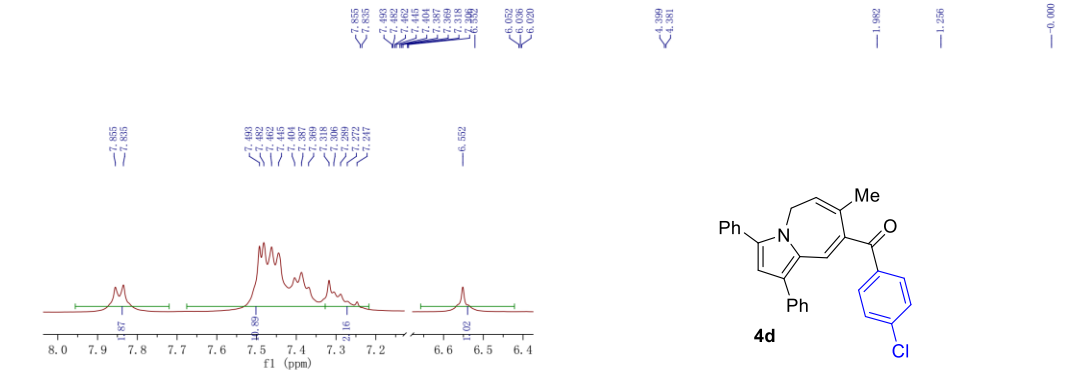

Me
Ph
N
O
Ph
Ph
4a
f1 (ppm)

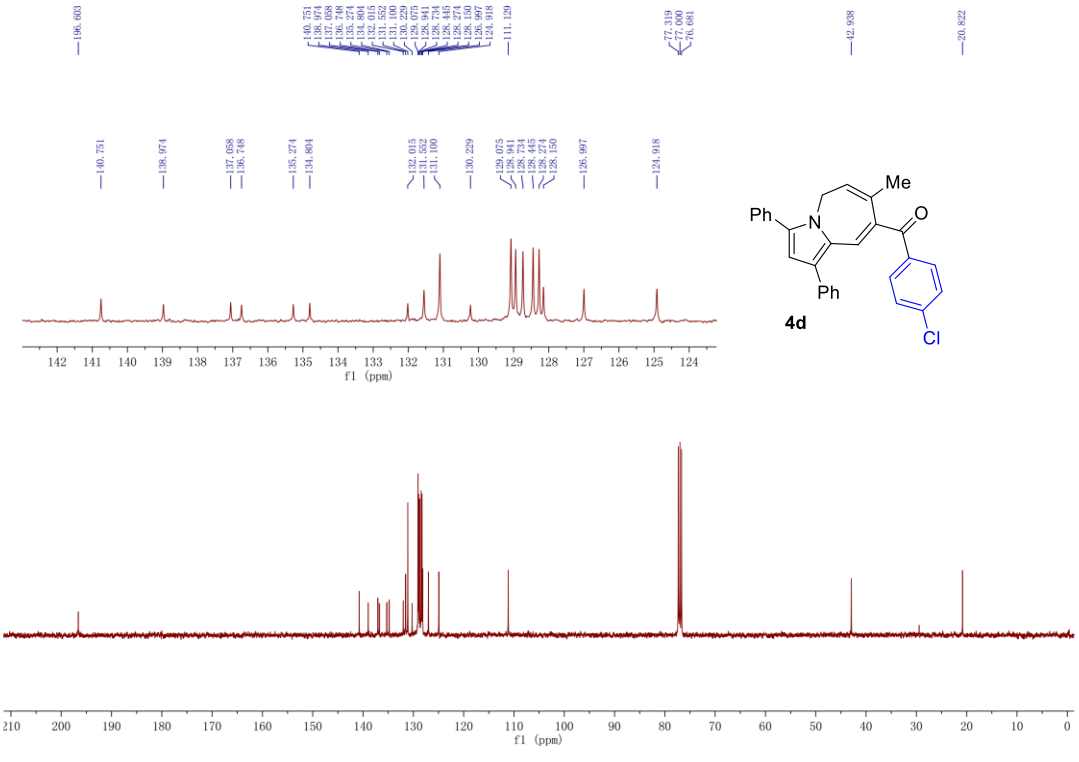

Me
Ph
N
O
Ph
NO2
4b
f1 (ppm)

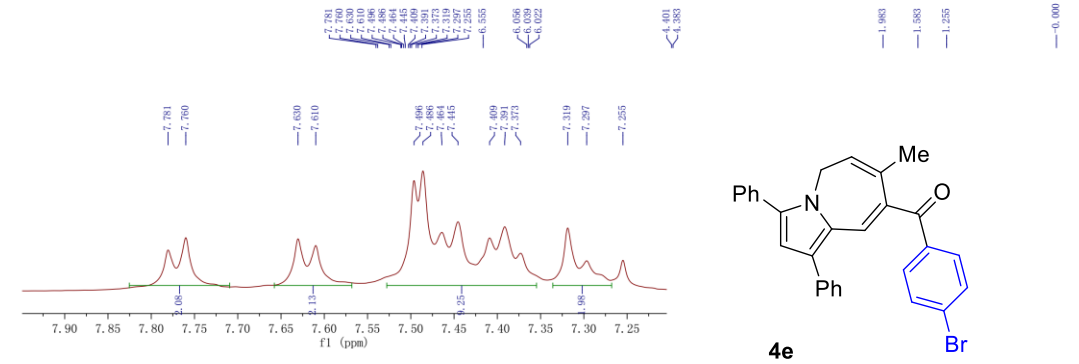

Me
Ph
N
O
Ph
F
4c
f1 (ppm)

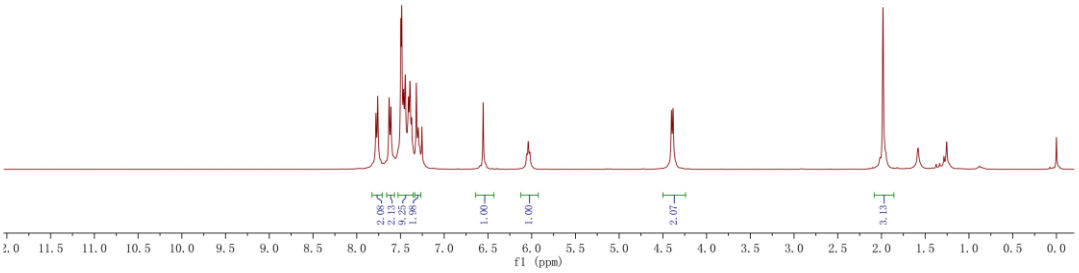

f1 (ppm)

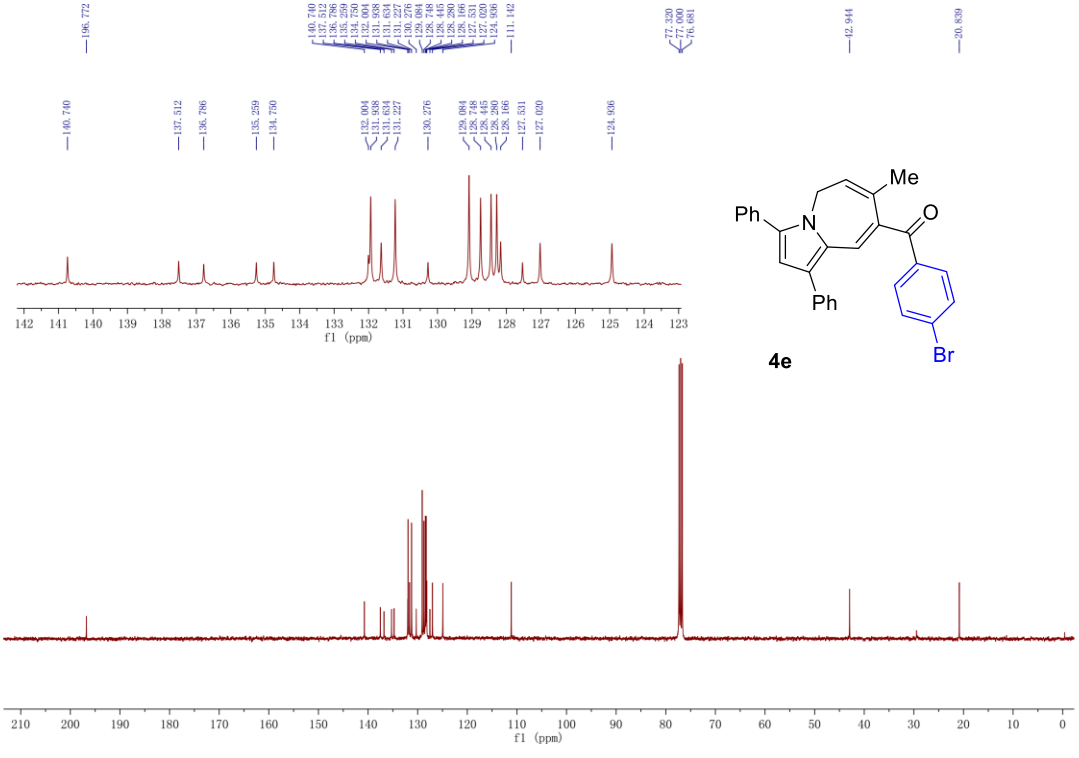

Me
Ph
N
O
Ph
F
4c
f1 (ppm)
f1 (ppm)

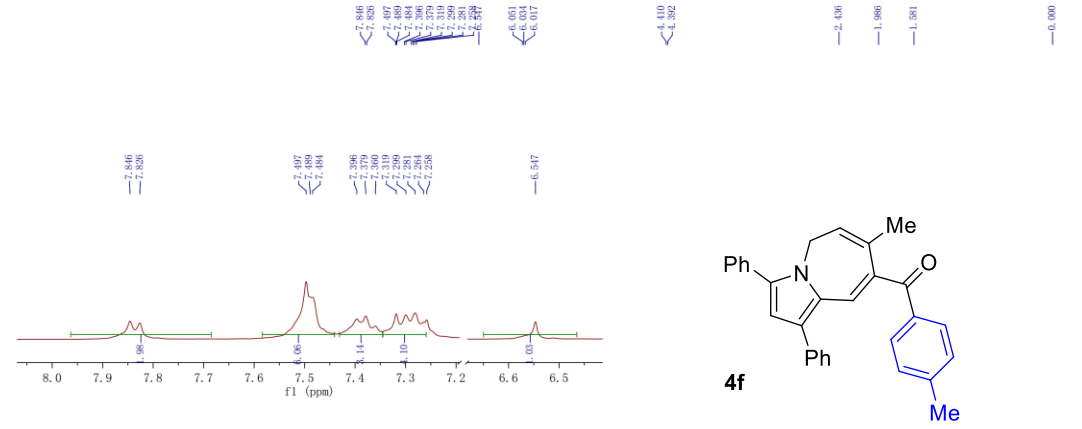

7.855
7.835
7.493
7.482
7.462
7.445
7.404
7.397
7.389
7.318
7.306
7.289
7.272
7.247
6.552
6.052
6.036
6.020
4.399
4.381
1.982
1.256
0.000
1.87
10.89
2.16
1.02
1.00
1.95
2.91
f1 (ppm)
Me
Ph
N
O
Ph
Cl
4d

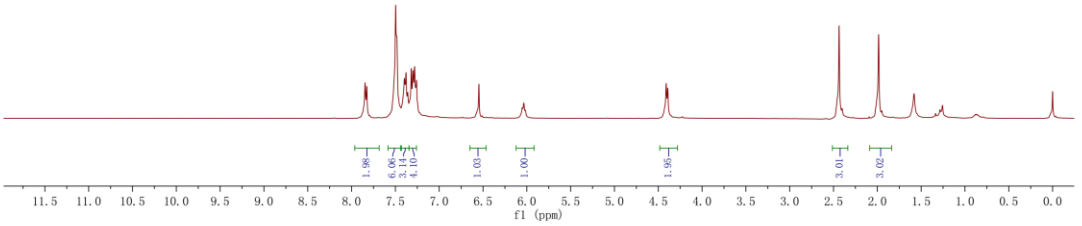

196.603
140.751
138.974
137.658
136.748
135.274
134.804
132.015
131.552
131.100
130.229
129.075
128.941
128.734
128.445
128.274
128.150
126.997
124.918
111.129
77.319
77.000
76.681
42.938
20.822
f1 (ppm)
Me
Ph
N
O
Ph
Cl
4d

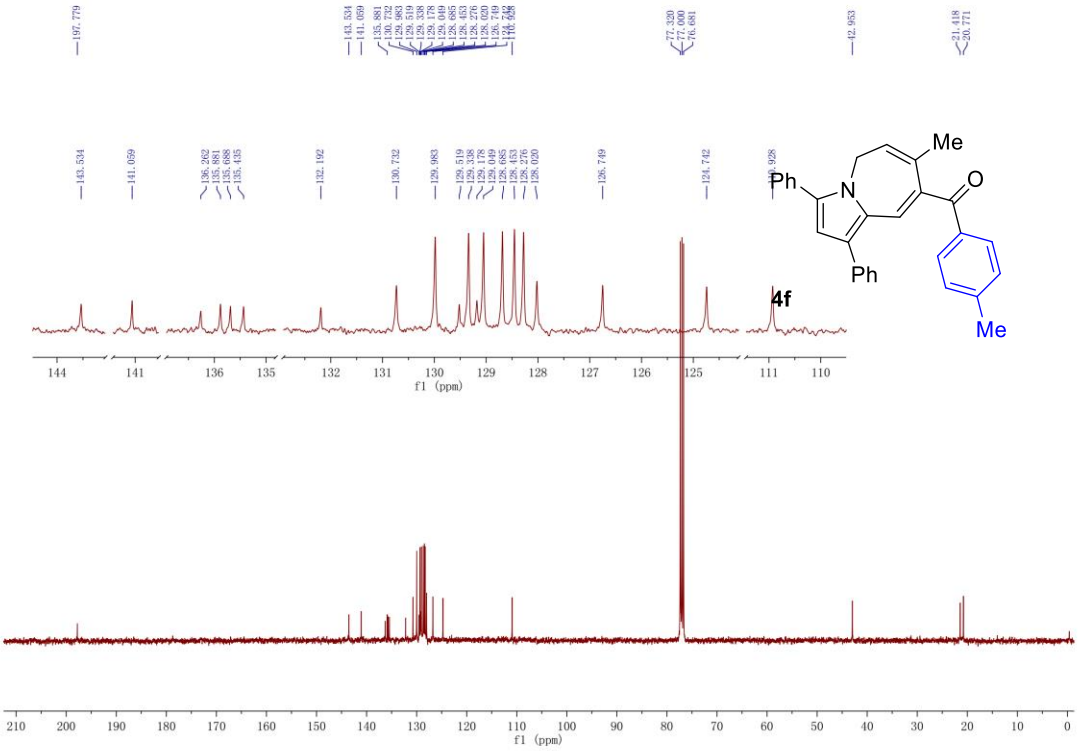

Me
Ph
N
O
Ph
Br
4e

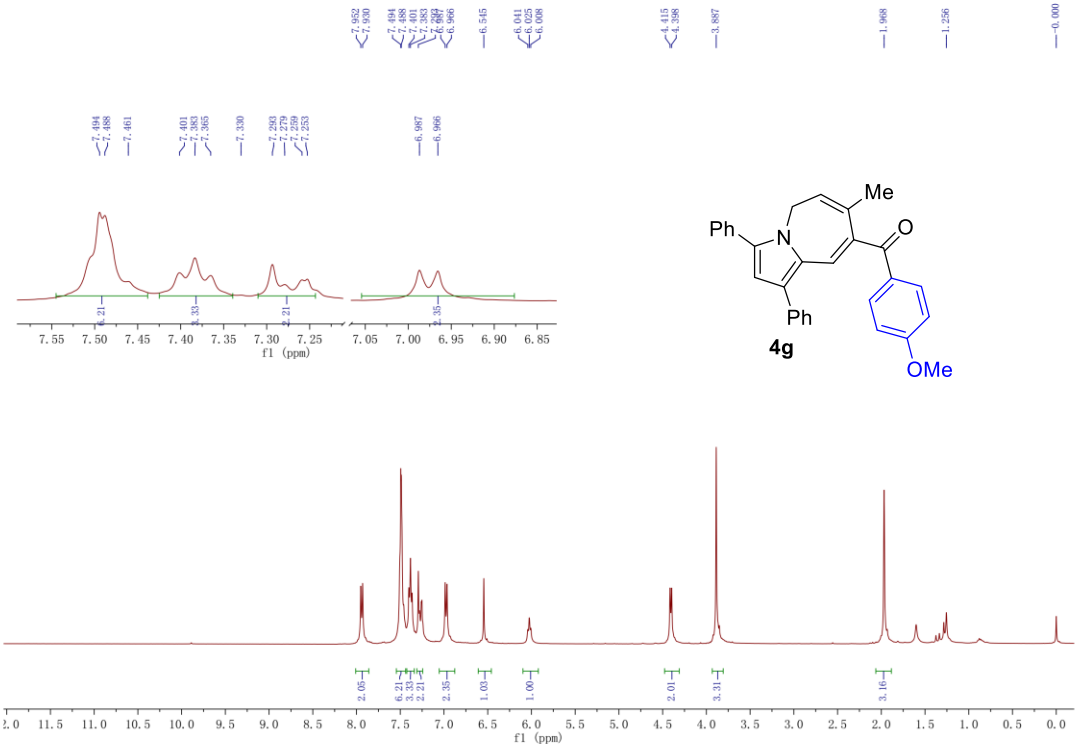


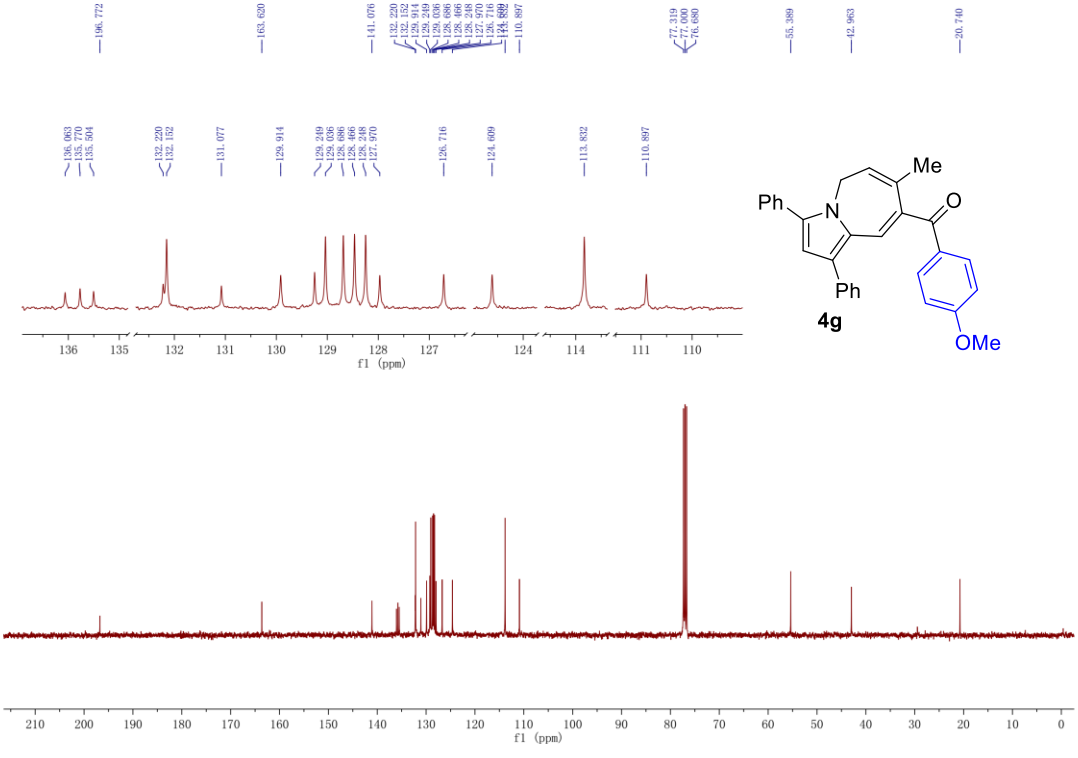

Me
Ph
N
O
Ph
Br
4e

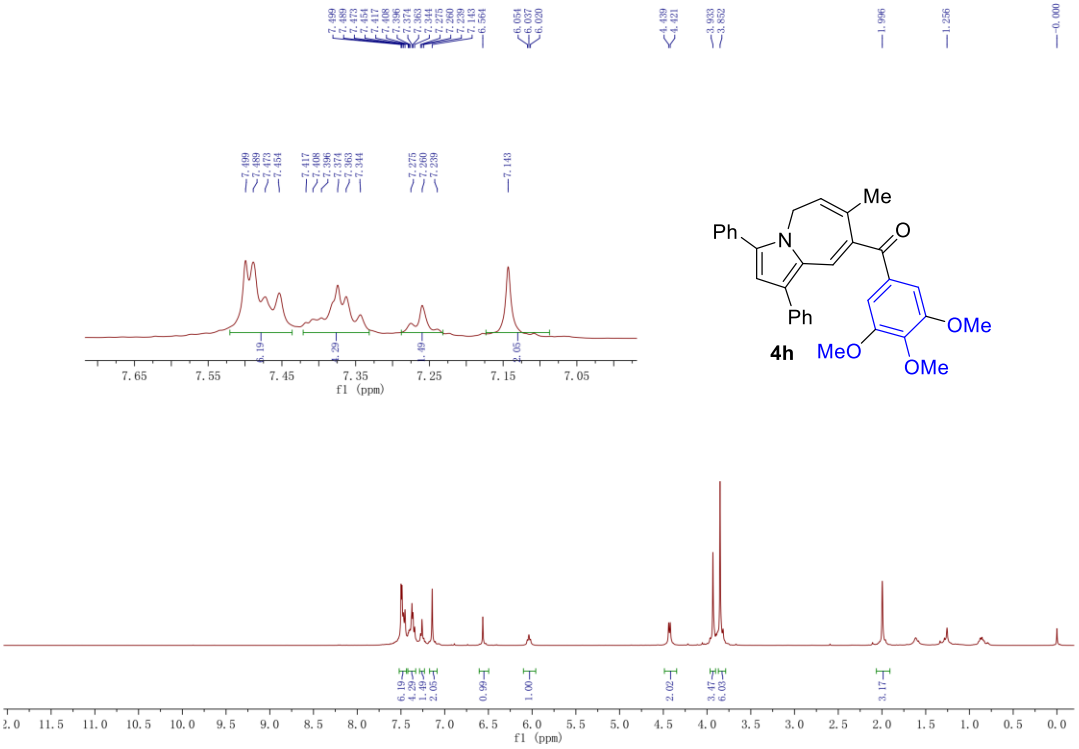

Me
Ph
N
O
Ph
Me
4f

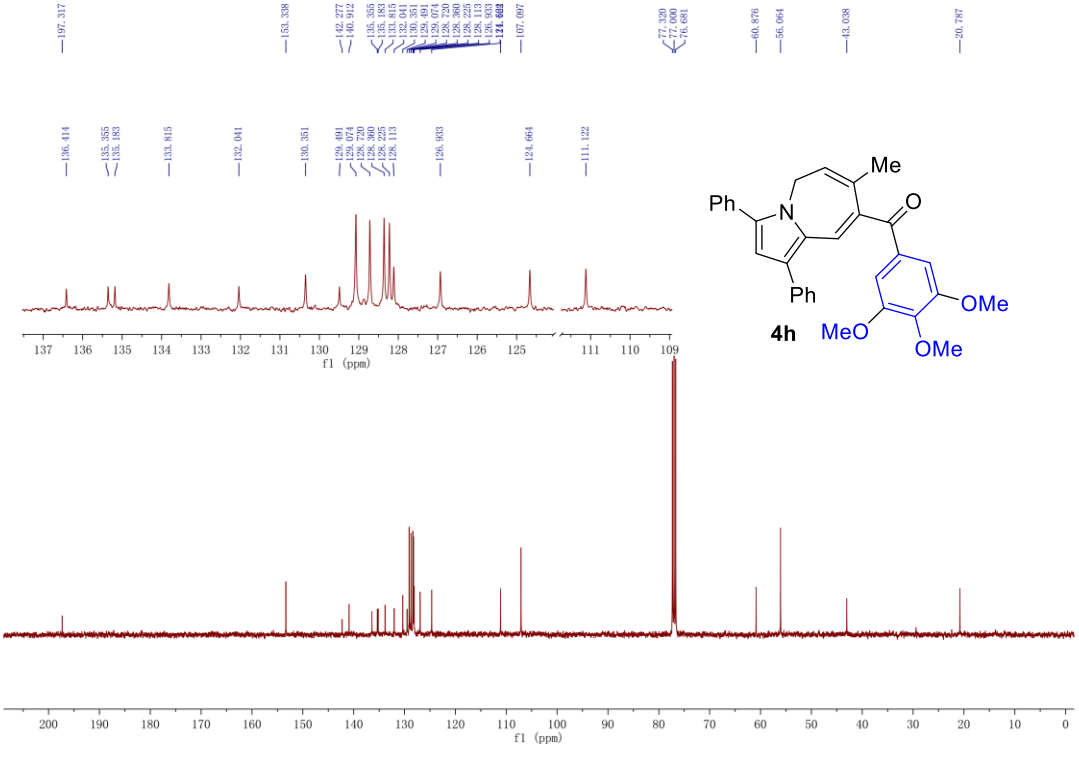


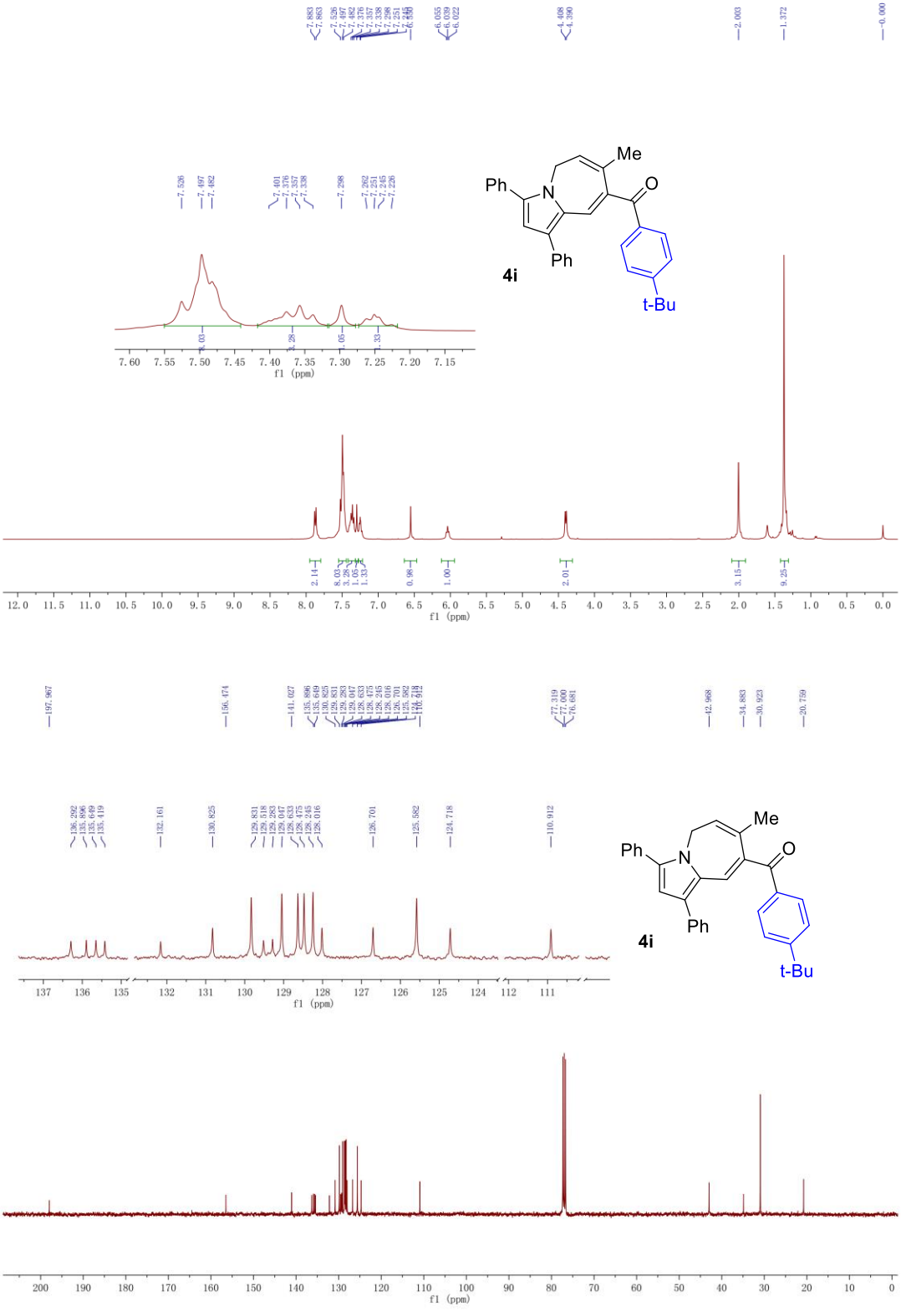

Me
Ph
N
O
Ph
Me
4f

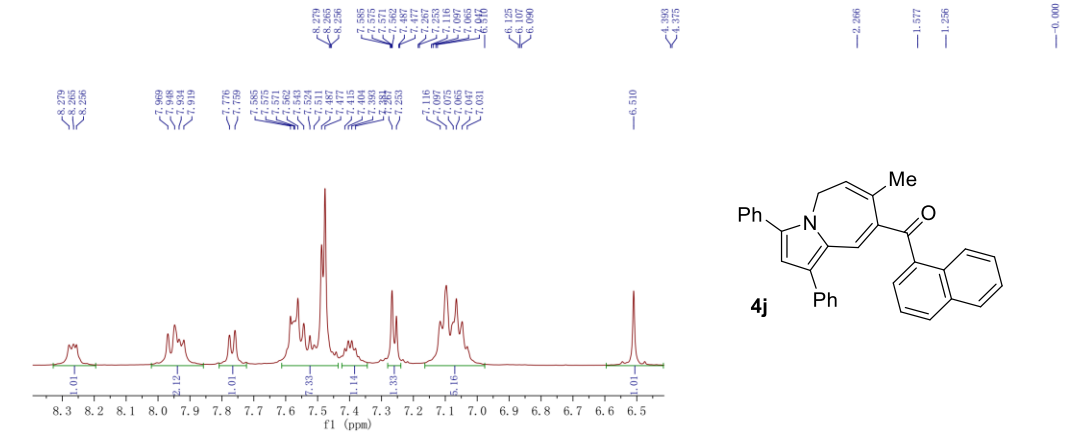

Me
Ph
N
O
Ph
4g
OMe
f1 (ppm)

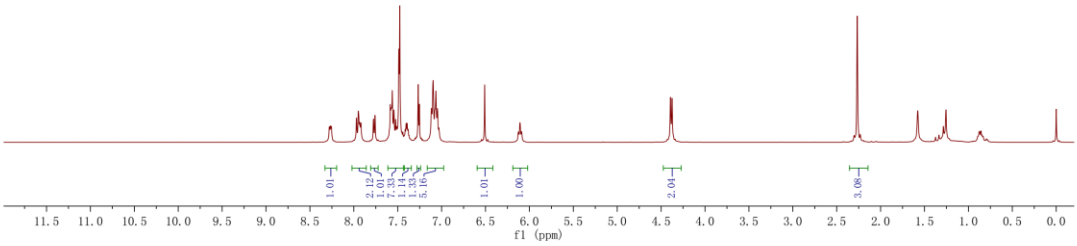

Me
Ph
N
O
Ph
4g
OMe
f1 (ppm)

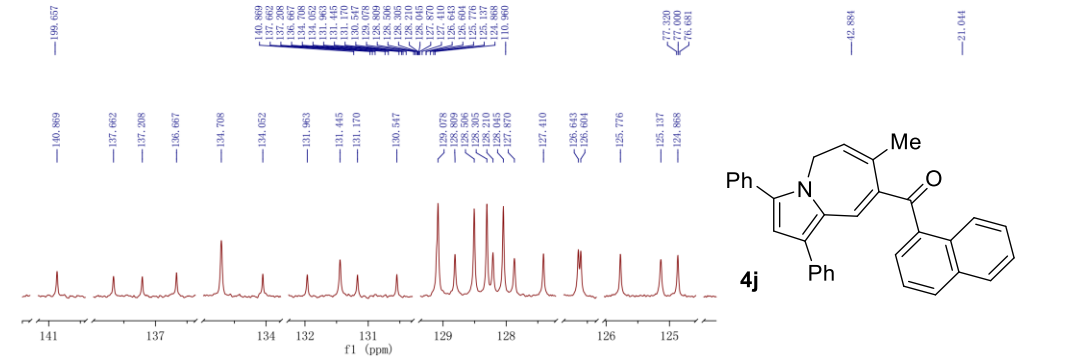

4h
Me
Ph
N
O
Ph
OMe
MeO
OMe
f1 (ppm)

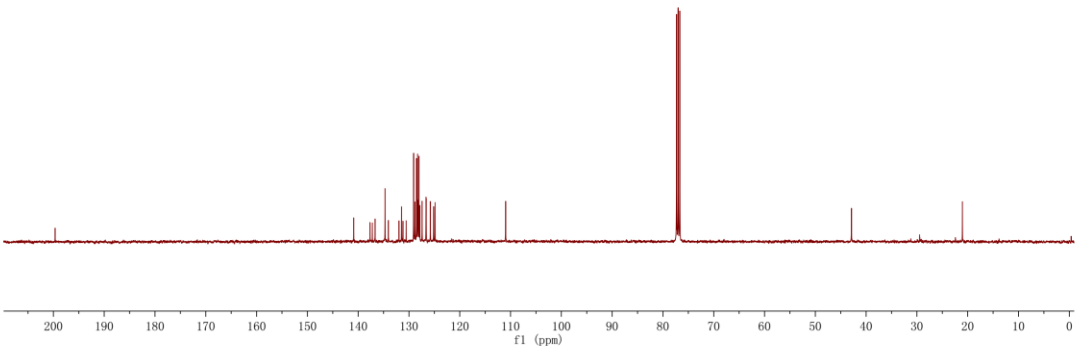

4h
Me
Ph
N
O
Ph
OMe
MeO
OMe
f1 (ppm)

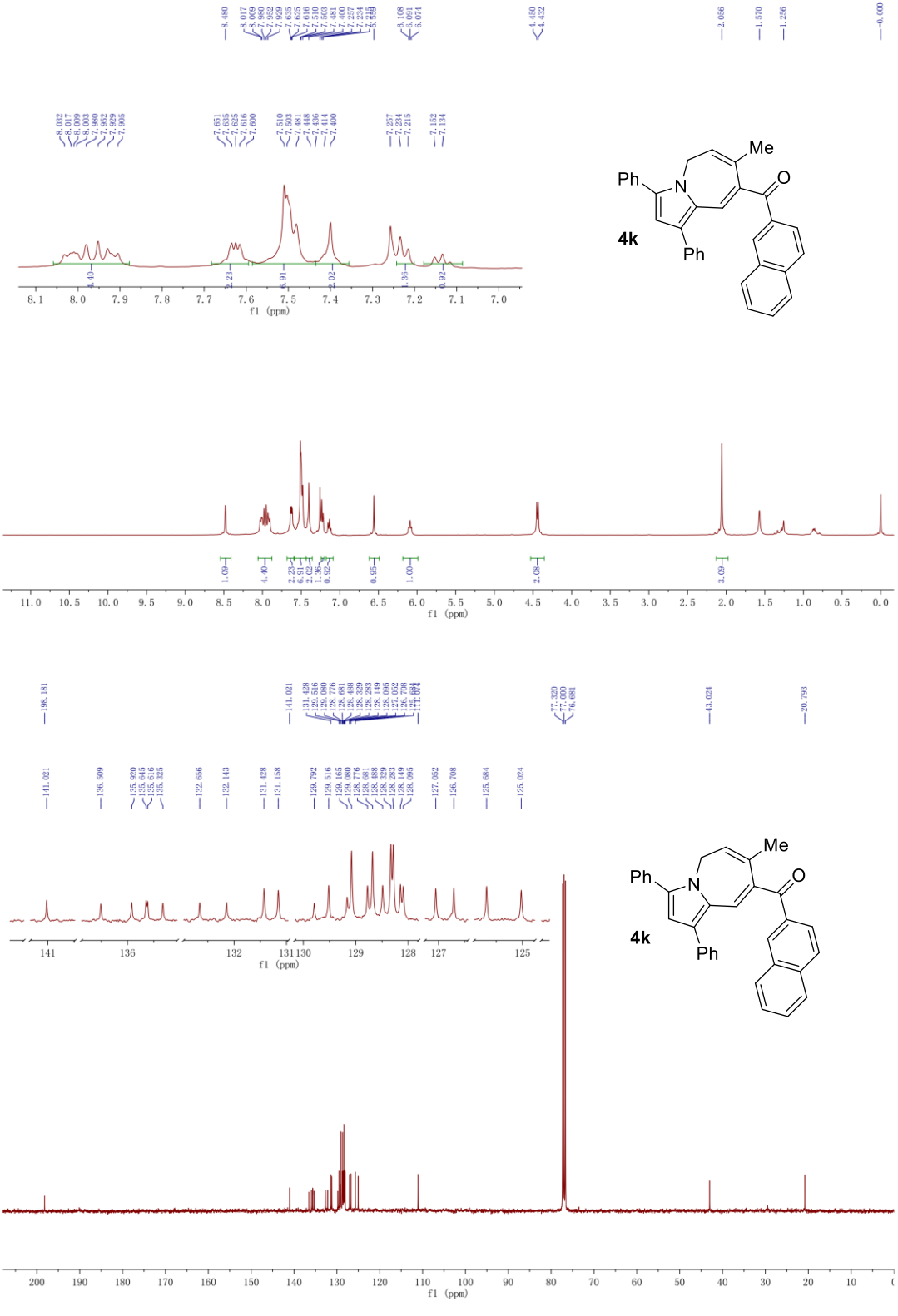

Me
Ph
N
O
Ph
t-Bu
4i
f1 (ppm)

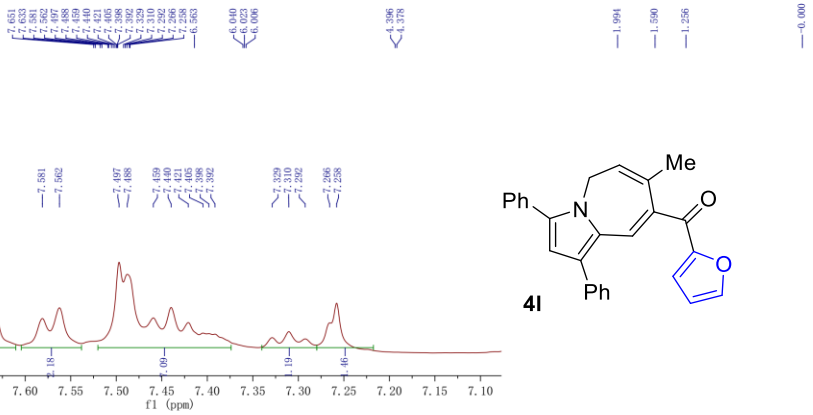

Me
Ph
N
O
Ph
4j

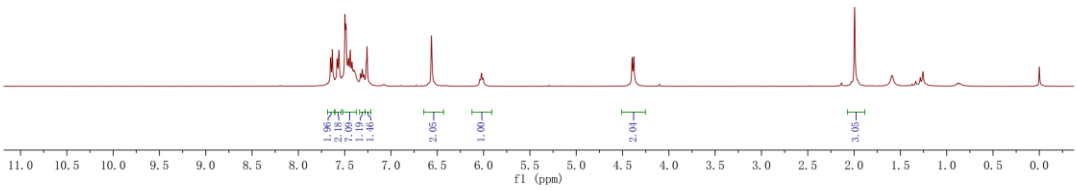


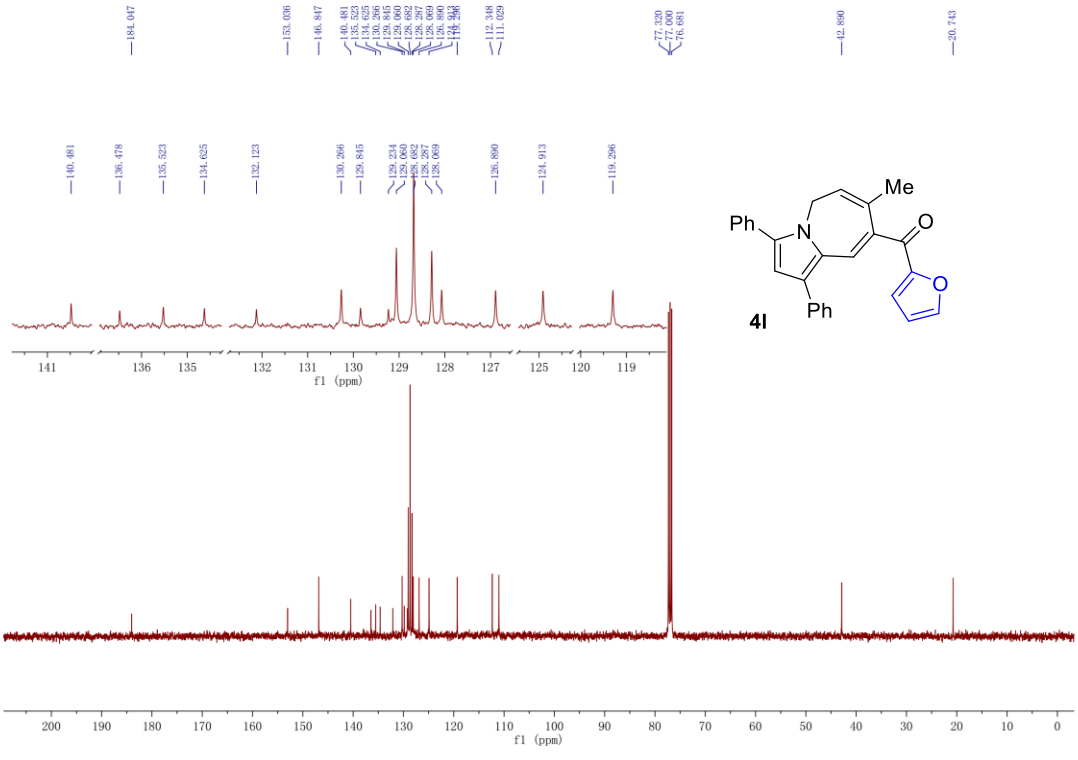

Me
Ph
N
O
Ph
4j

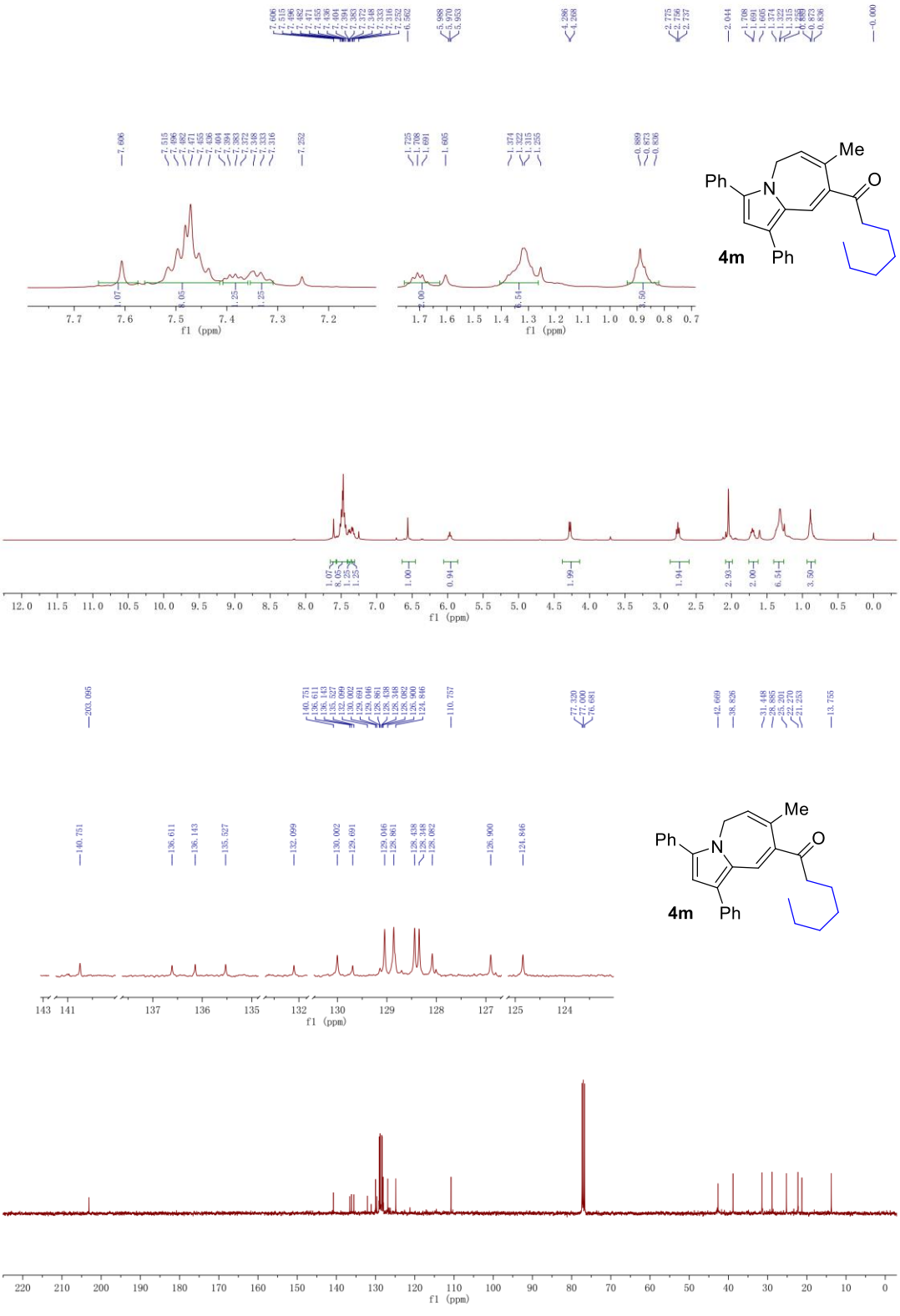


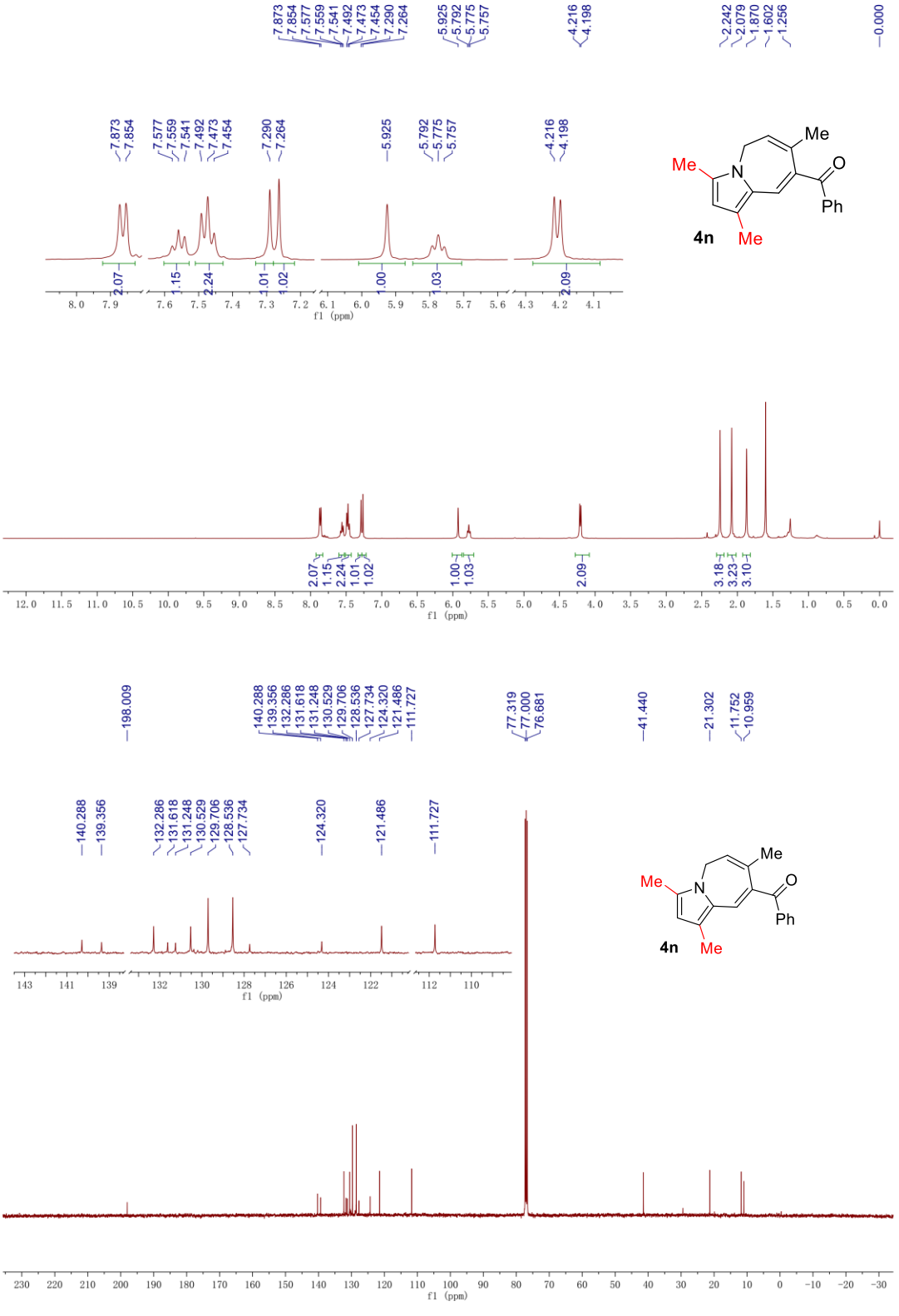

Me
Ph
N
O
Ph
4k
f1 (ppm)

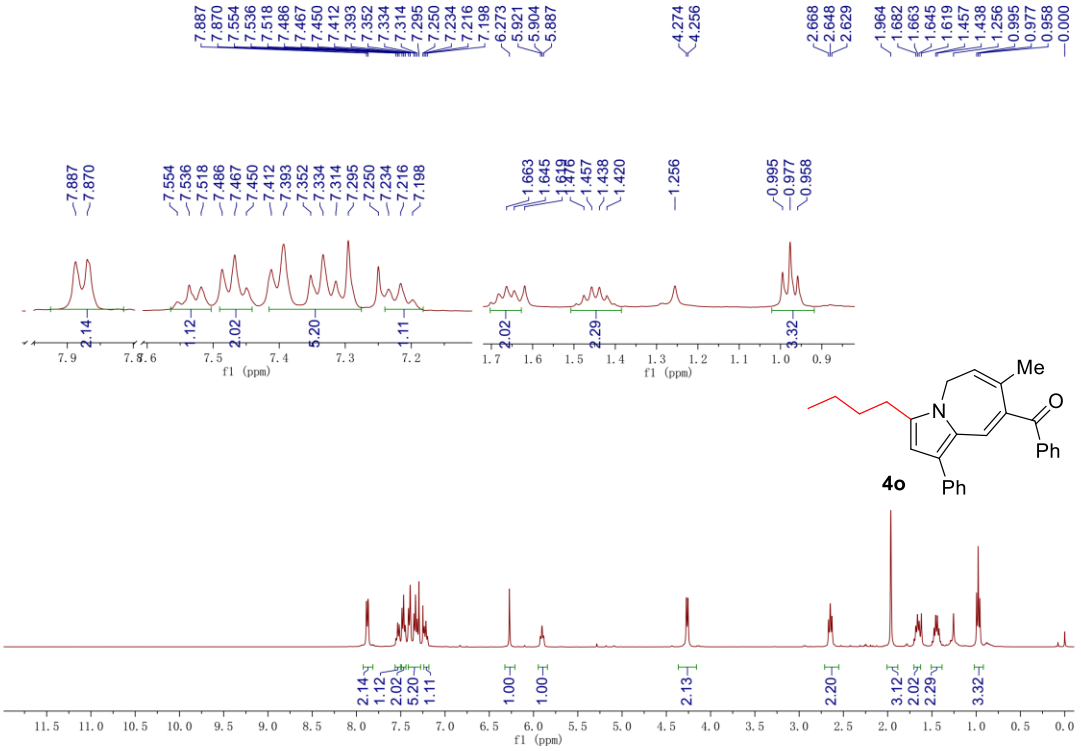

Me
Ph
N
O
O
Ph
4l

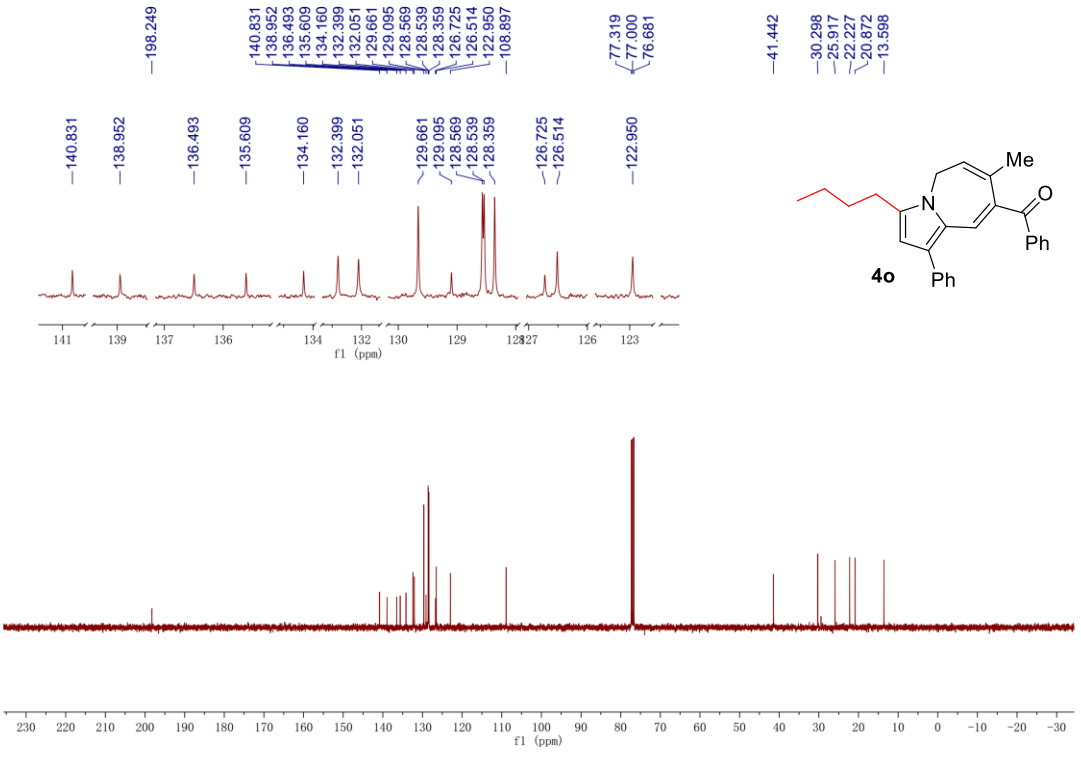


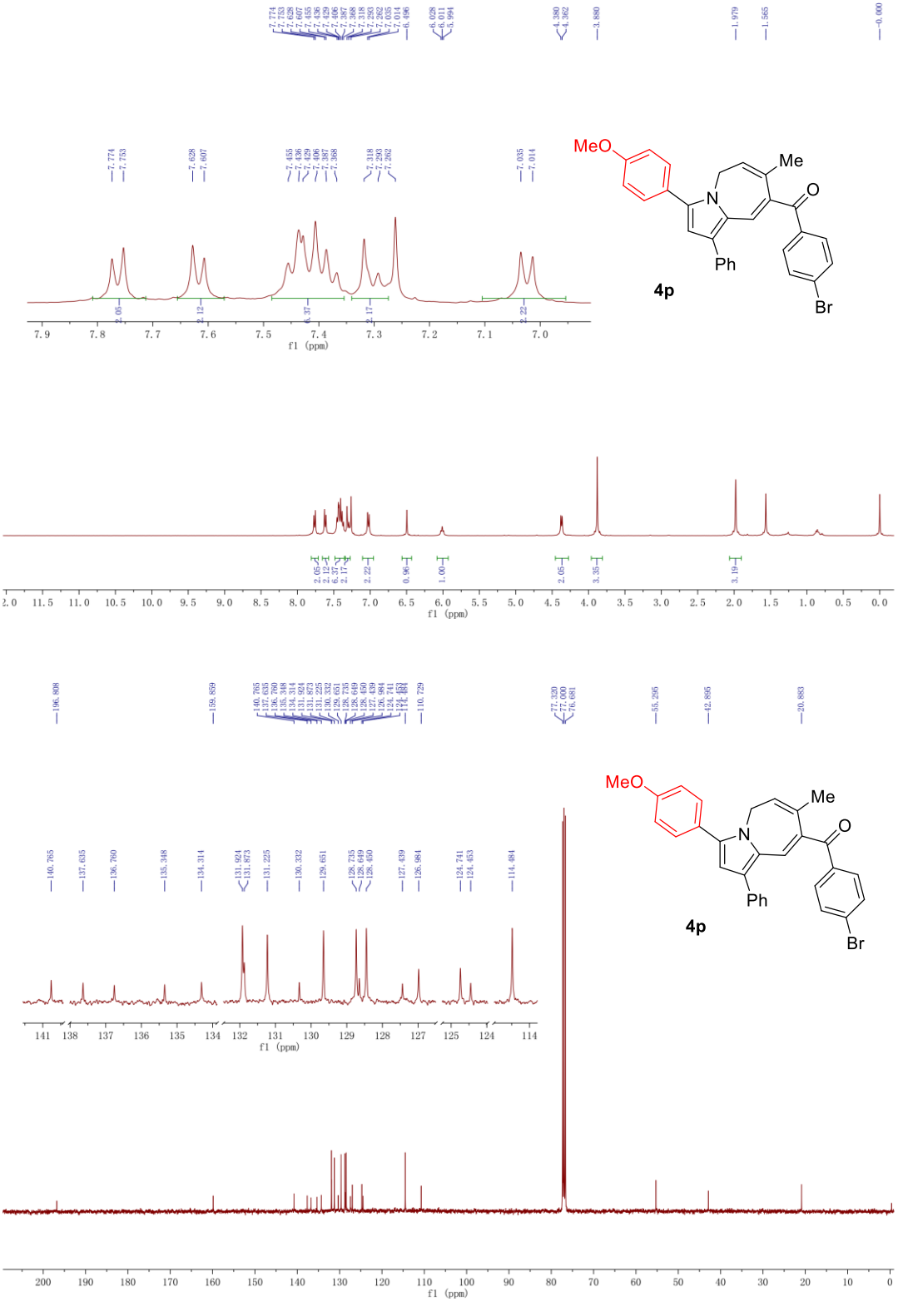

Me
Ph
N
O
O
Ph
4l

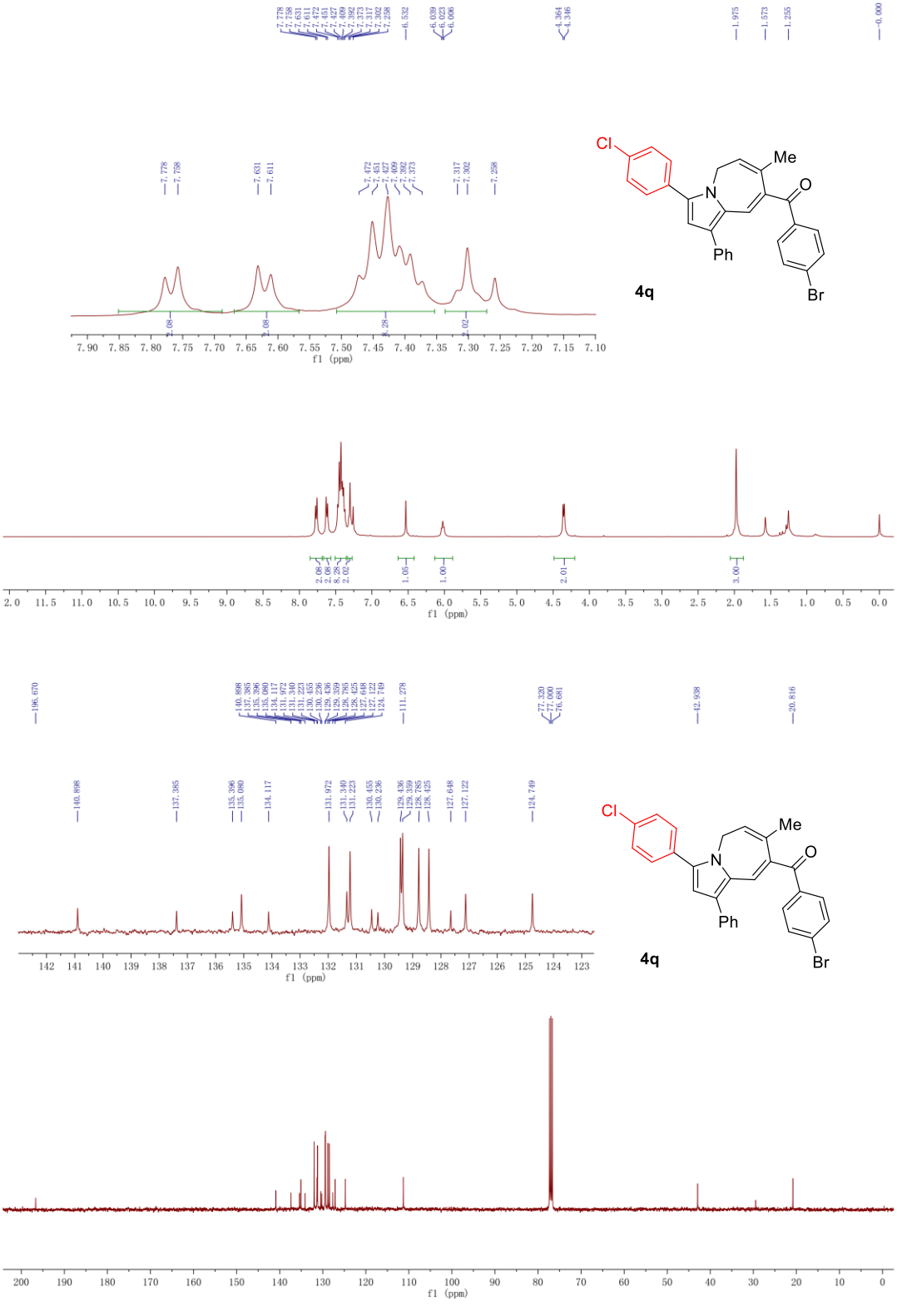

Me
Ph
N
O
4m
Ph
f1 (ppm)

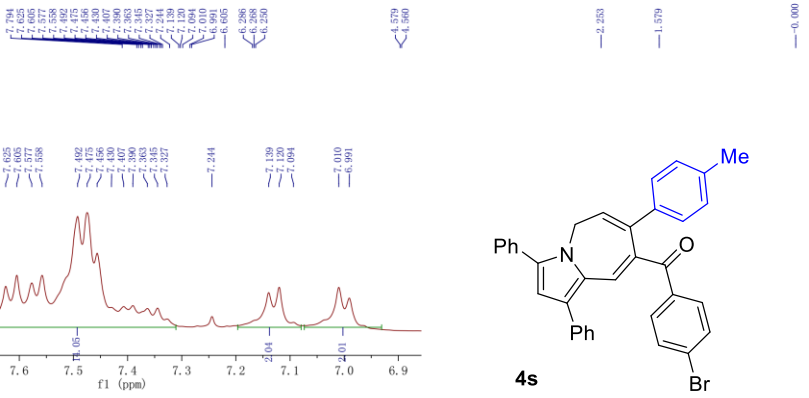

7.873
7.854
7.577
7.559
7.541
7.492
7.473
7.454
7.290
7.264
5.925
5.792
5.775
5.757
4.216
4.198
2.242
2.079
1.870
1.602
1.256
0.000
Me
Me
N
O
Ph
4n
Me
2.07
1.15
2.24
1.01
1.02
1.00
1.03
2.09
3.18
3.23
3.10
f1 (ppm)
198.009
140.288
139.356
132.286
131.618
131.248
130.529
129.706
128.536
127.734
124.320
121.486
111.727
77.319
77.000
76.681
41.440
21.302
11.752
10.959

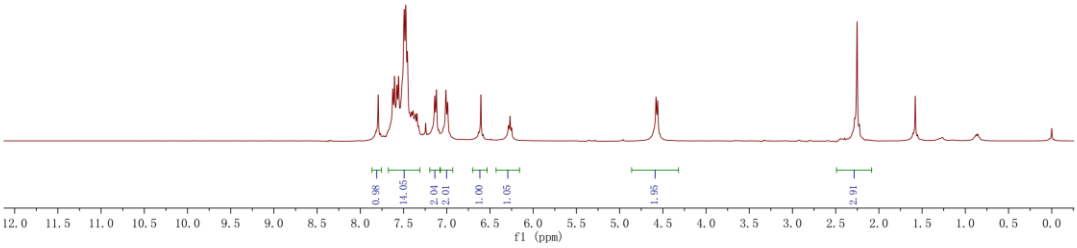

7.887
7.870
7.554
7.536
7.518
7.486
7.467
7.450
7.412
7.393
7.352
7.334
7.314
7.295
7.250
7.234
7.216
7.198
6.273
5.921
5.904
5.887
4.274
4.256
2.668
2.648
2.629
1.964
1.682
1.663
1.645
1.619
1.457
1.438
1.256
0.995
0.977
0.958
0.000
f1 (ppm)
Me
O
N
Ph
Ph
4o

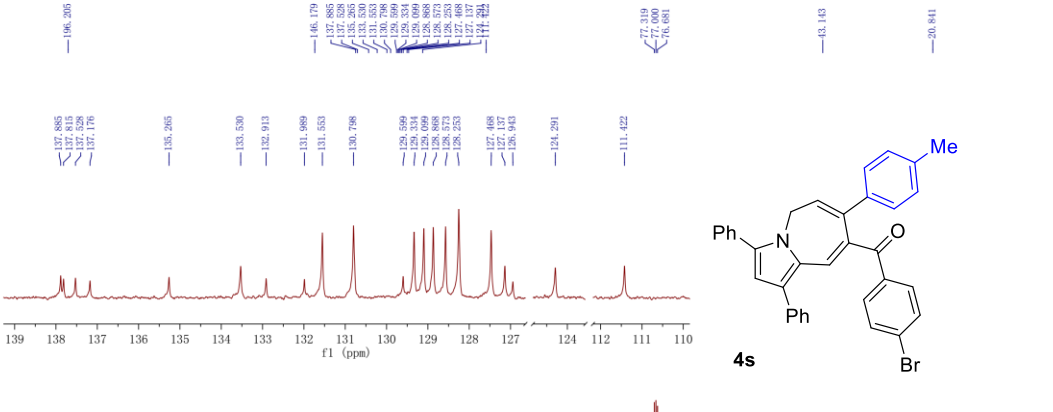

198.249
140.831
138.952
136.493
135.609
134.160
132.399
132.051
129.661
129.095
128.569
128.539
128.359
126.725
126.514
122.950
108.897
77.319
77.000
76.681
41.442
30.298
25.917
22.227
20.872
13.598
f1 (ppm)
Me
O
N
Ph
Ph
4o

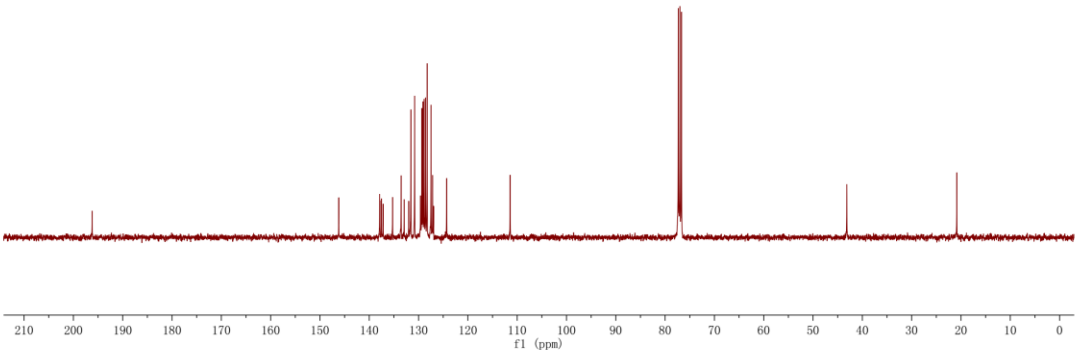

MeO
Me
O
N
Ph
Br
4p
f1 (ppm)

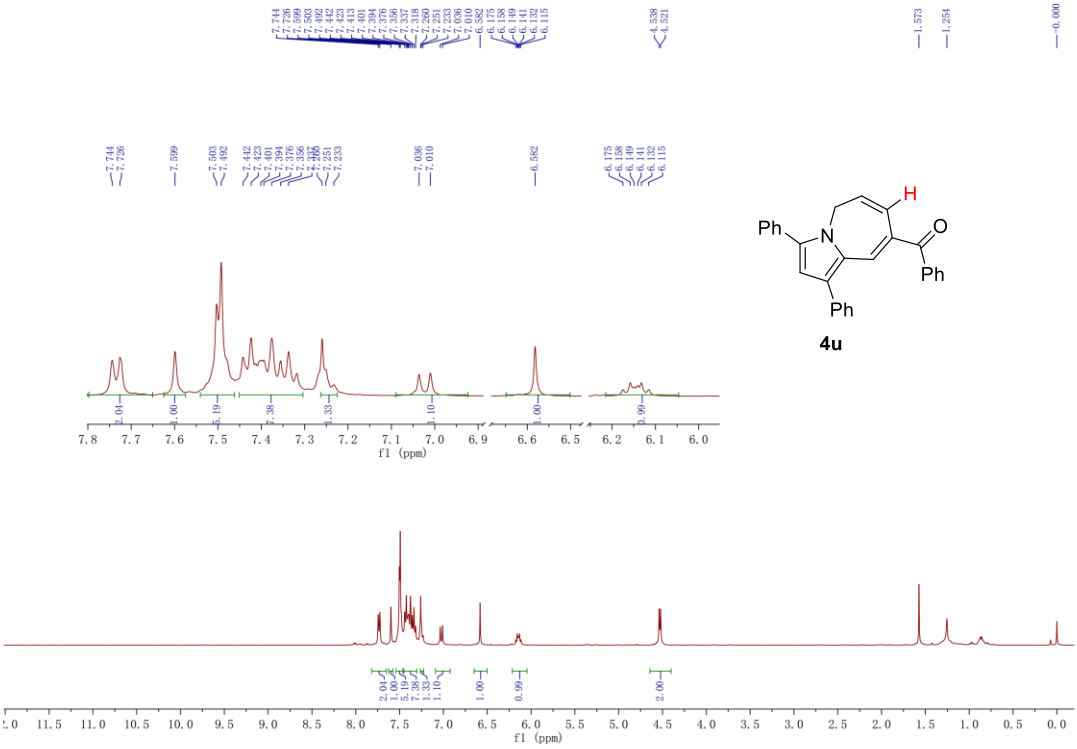

Cl
Me
N
O
Ph
Br
4q
f1 (ppm)

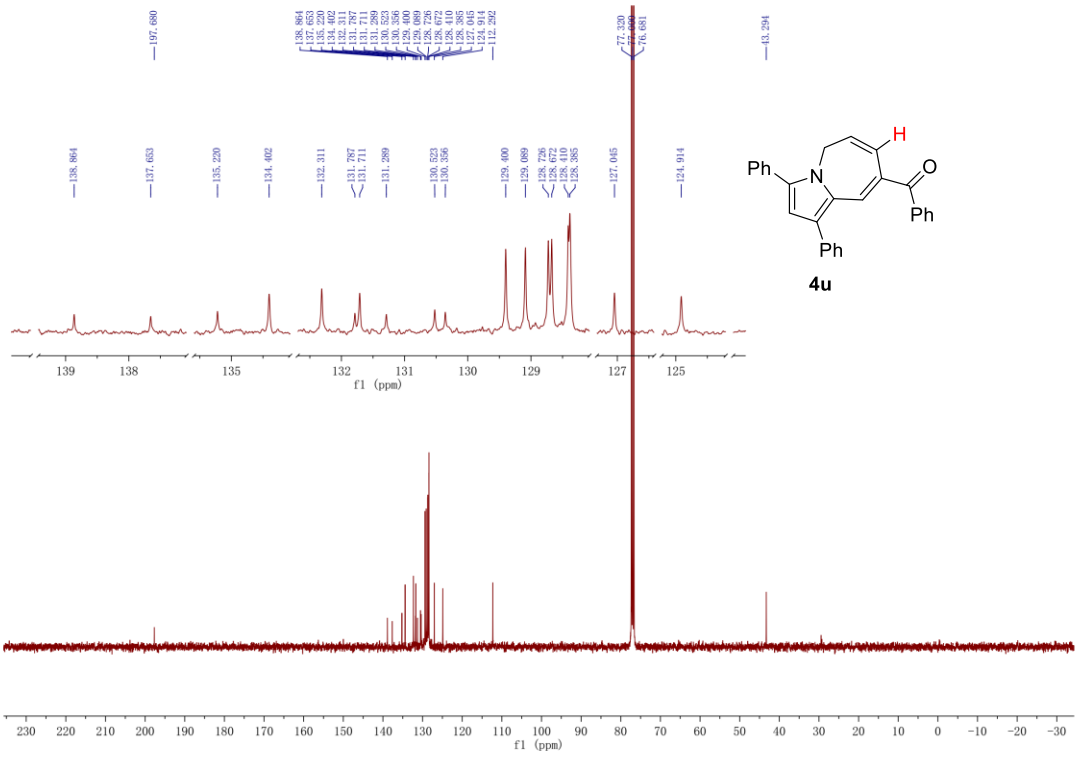

Me
Ph
N
O
Ph
Br
4s

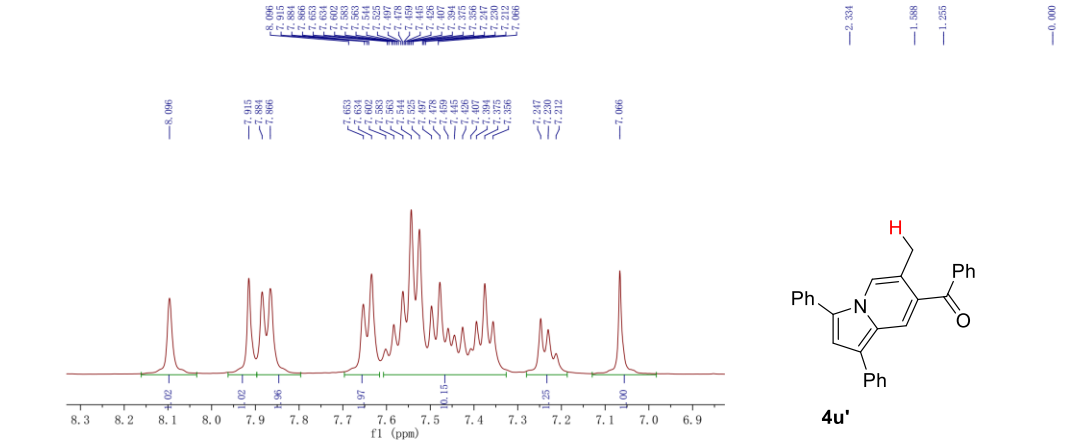


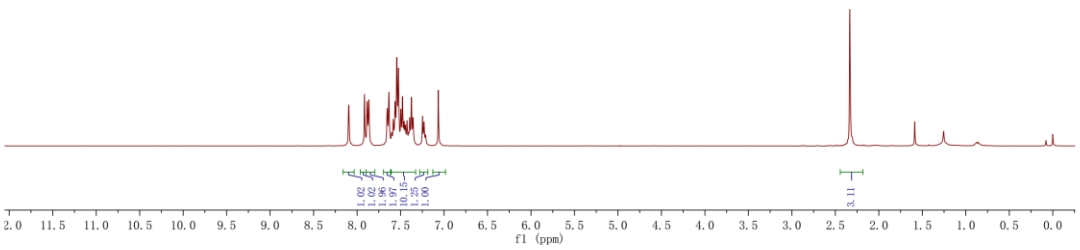

Me
Ph
N
O
Ph
Br
4s

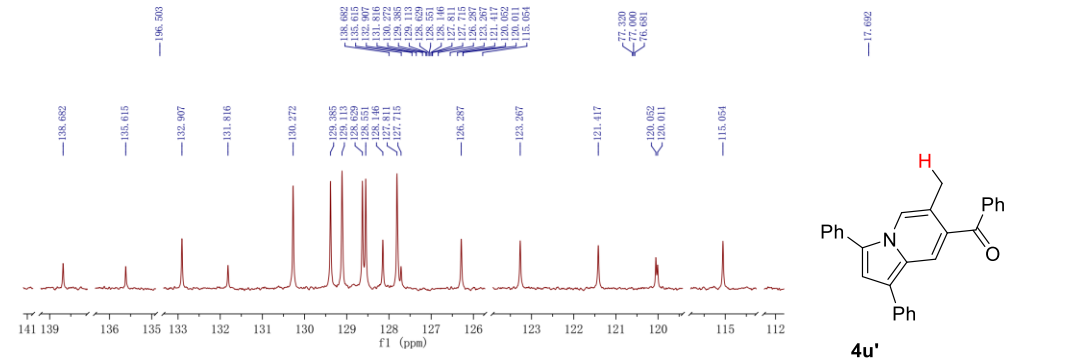


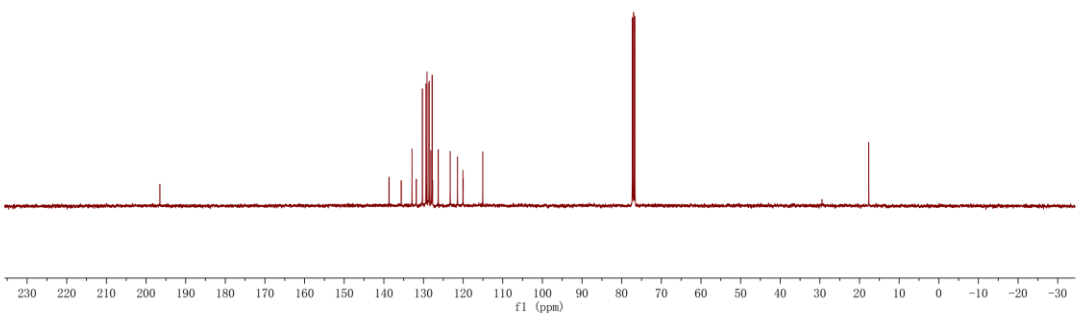

7.744
7.736
7.599
7.503
7.492
7.442
7.423
7.401
7.394
7.376
7.356
7.337
7.260
7.251
7.233
7.096
7.010
6.582
6.175
6.158
6.149
6.141
6.132
6.115
4.538
4.521
1.573
1.254
0.000
H
Ph
N
O
Ph
Ph
4u
f1 (ppm)


197.680
138.864
137.653
135.220
134.402
132.311
131.787
131.711
131.289
130.523
130.356
129.400
129.089
128.726
128.672
128.410
128.385
127.045
124.914
112.292
77.320
77.000
76.681
13.294
H
Ph
N
O
Ph
Ph
4u
f1 (ppm)





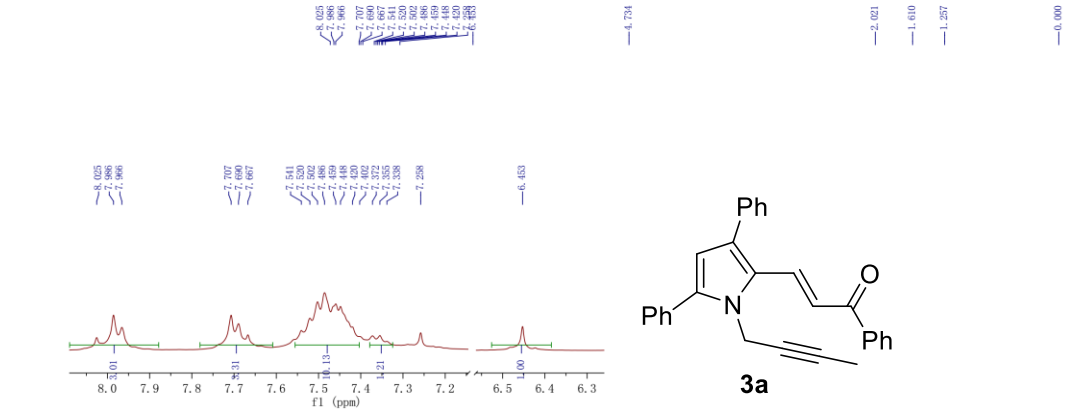


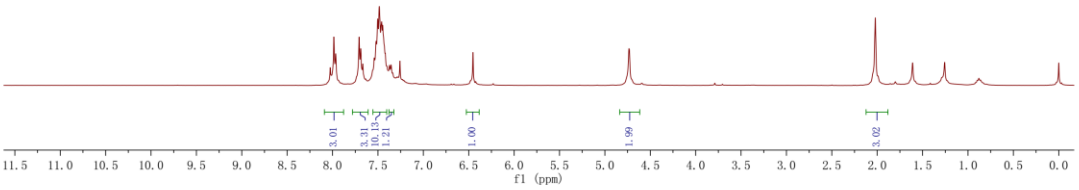


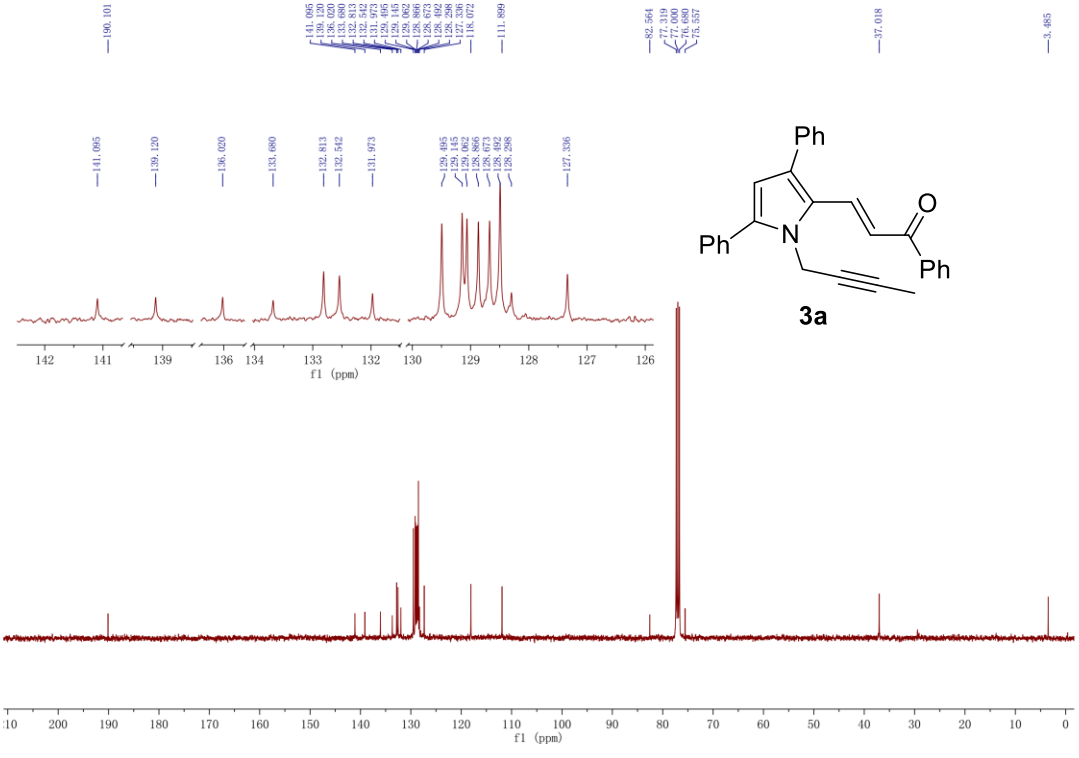
4u'

4u'

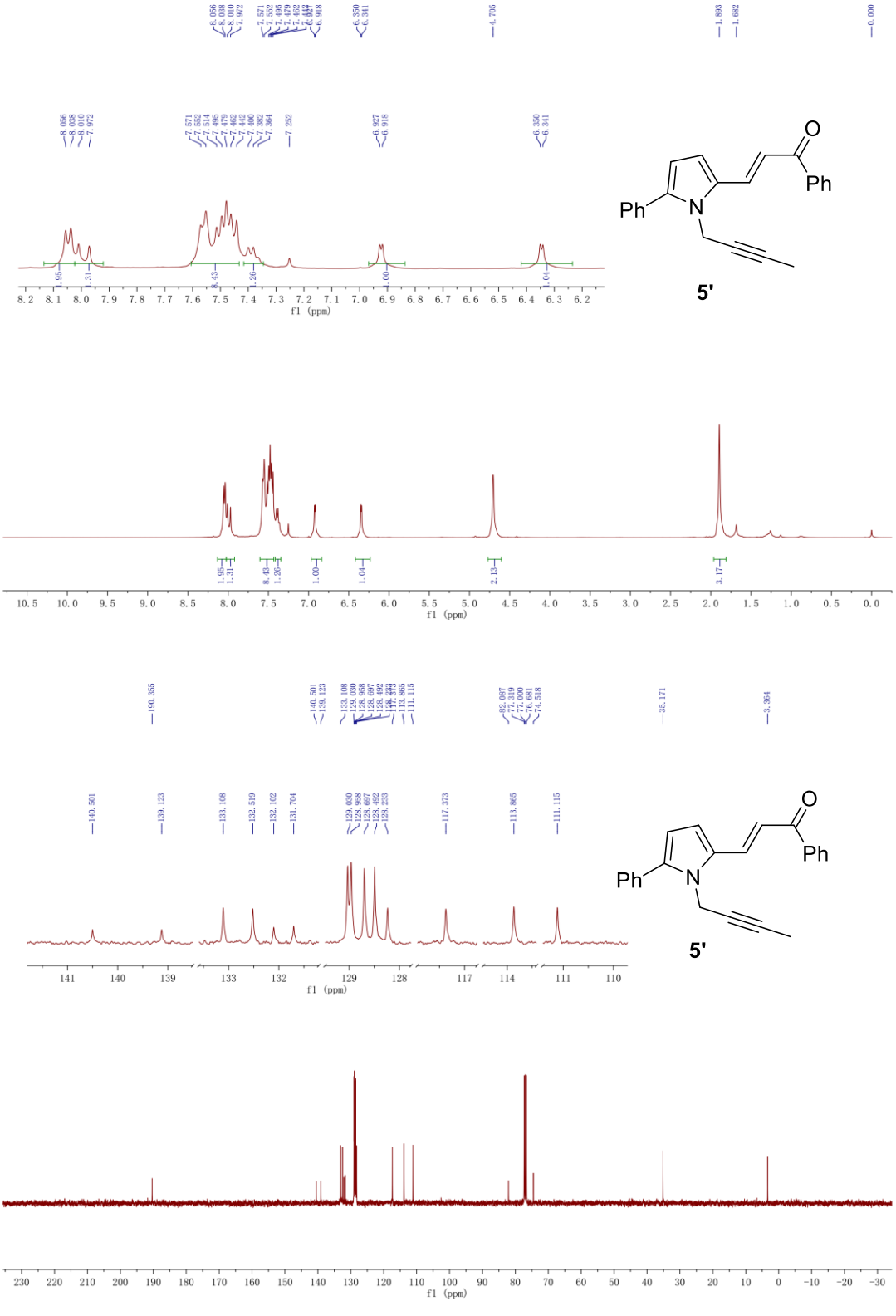
NMR spectra of new compounds (3a)



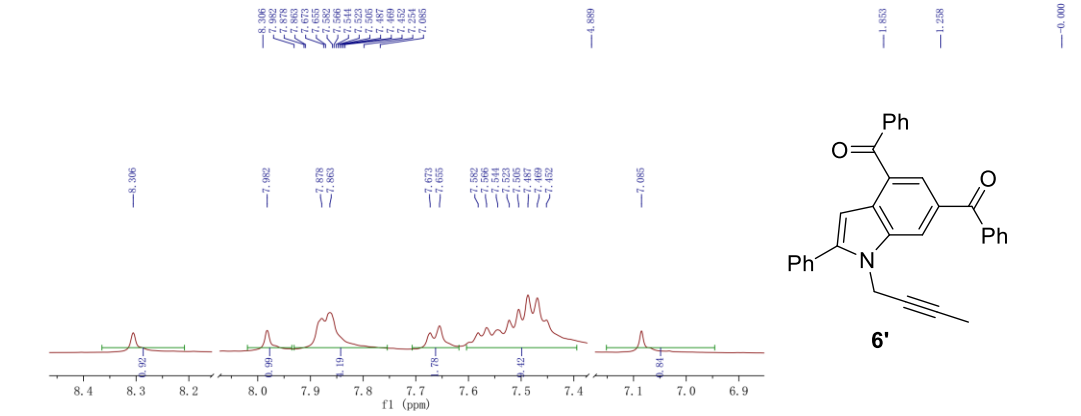




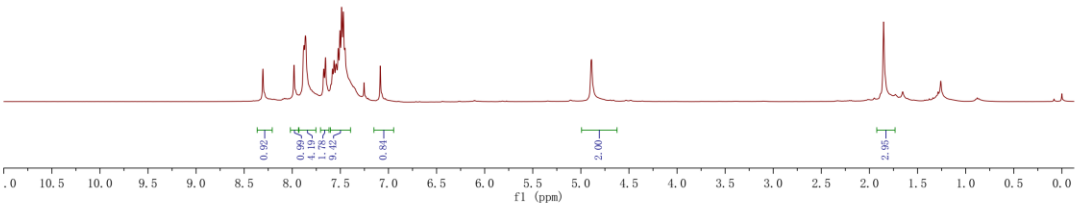
NMR spectra of new compounds (5')

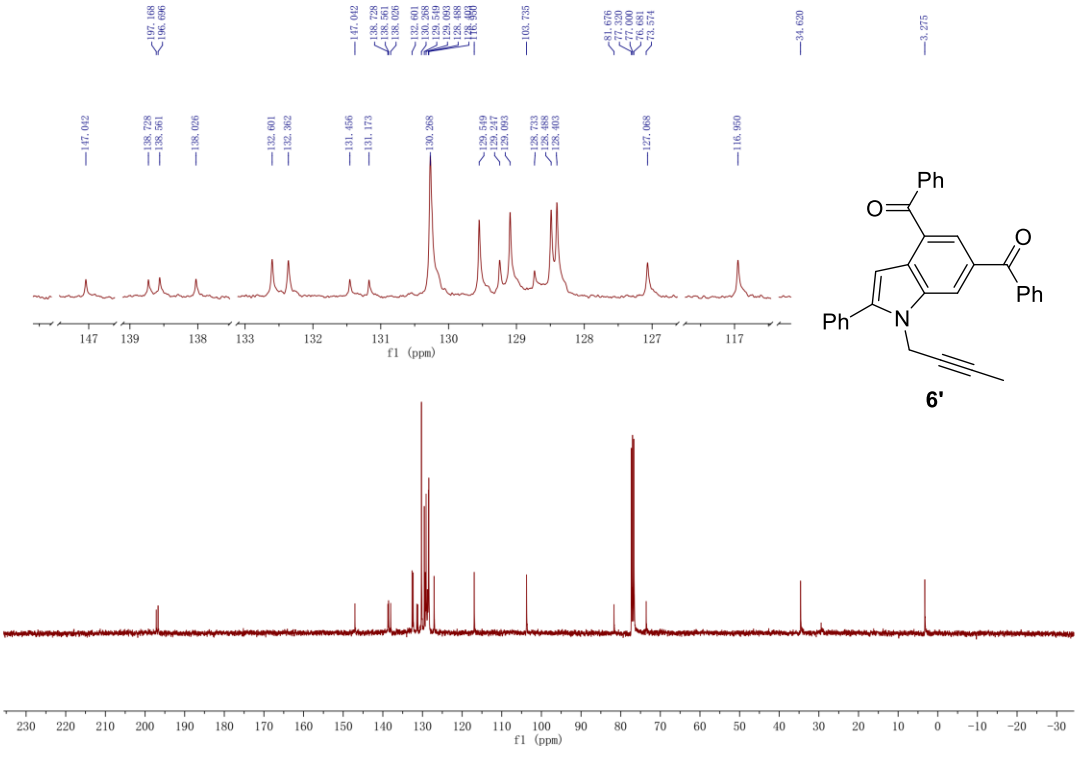


NMR spectra of new compounds (6')



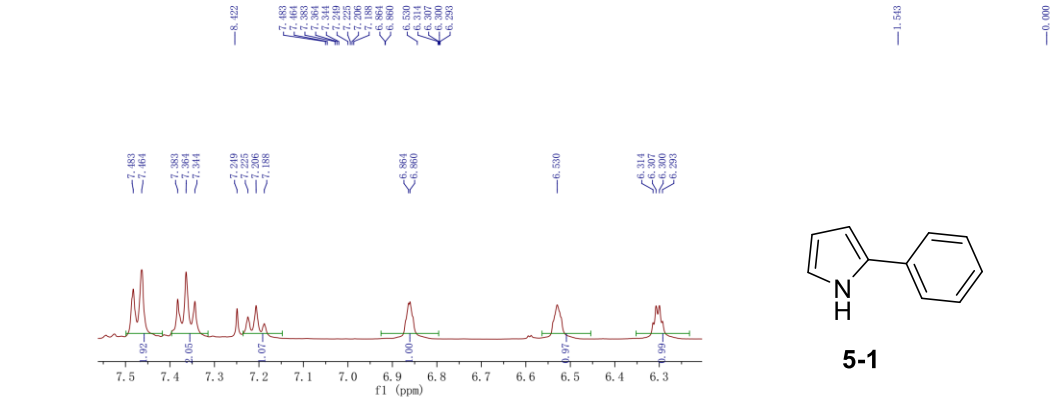
6'



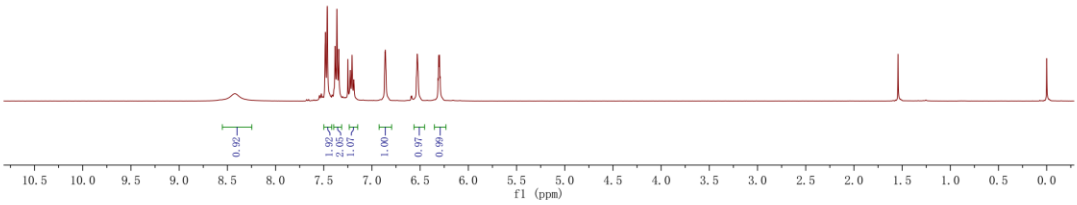


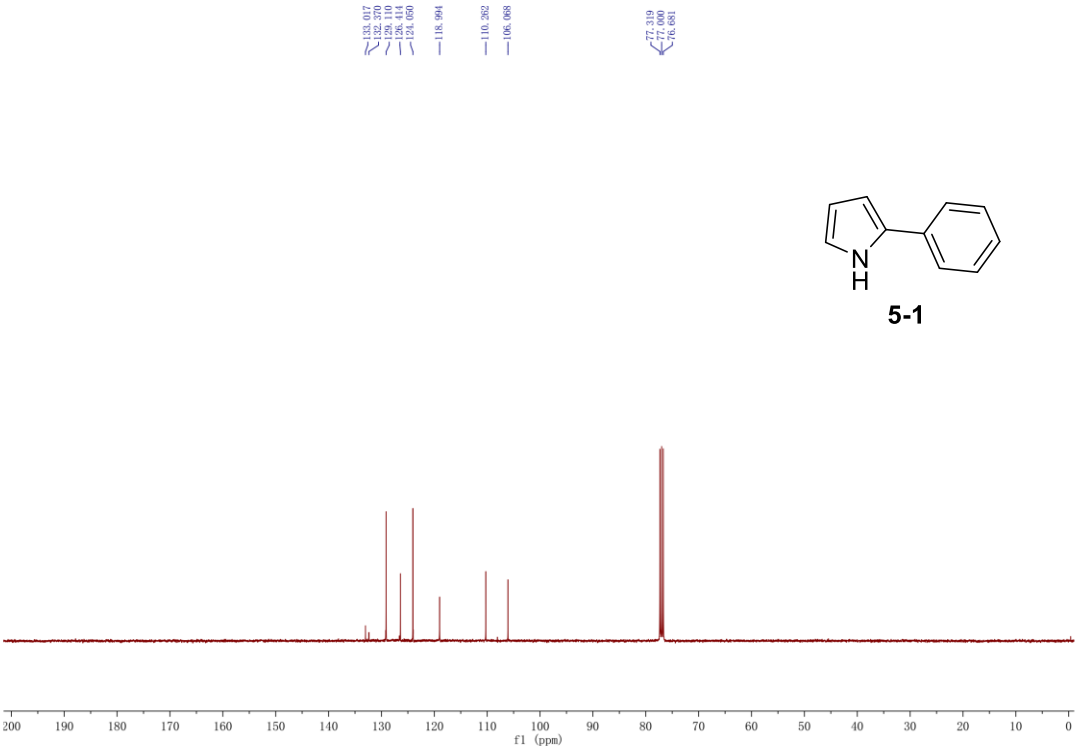
6'

NMR spectra of new compounds (5)

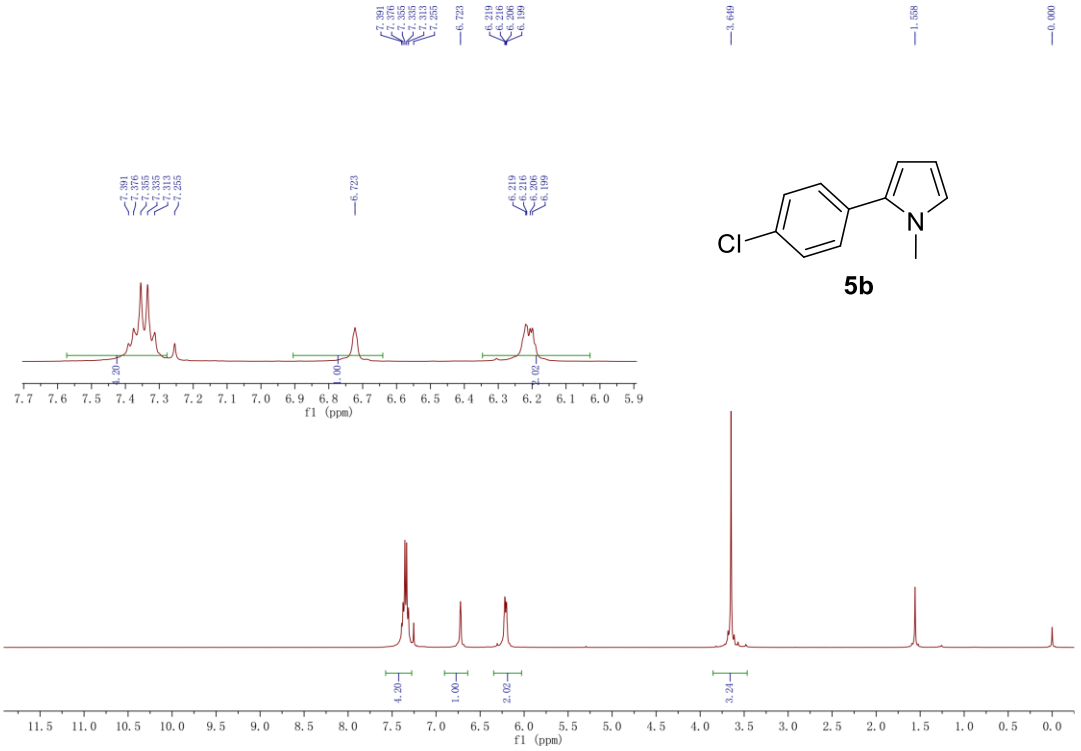

8.422
7.483
7.464
7.383
7.364
7.344
7.249
7.225
7.206
7.188
6.864
6.860
6.530
6.314
6.307
6.300
6.293
1.543
0.000
1.92
2.05
1.07
1.00
0.97
0.99
f1 (ppm)

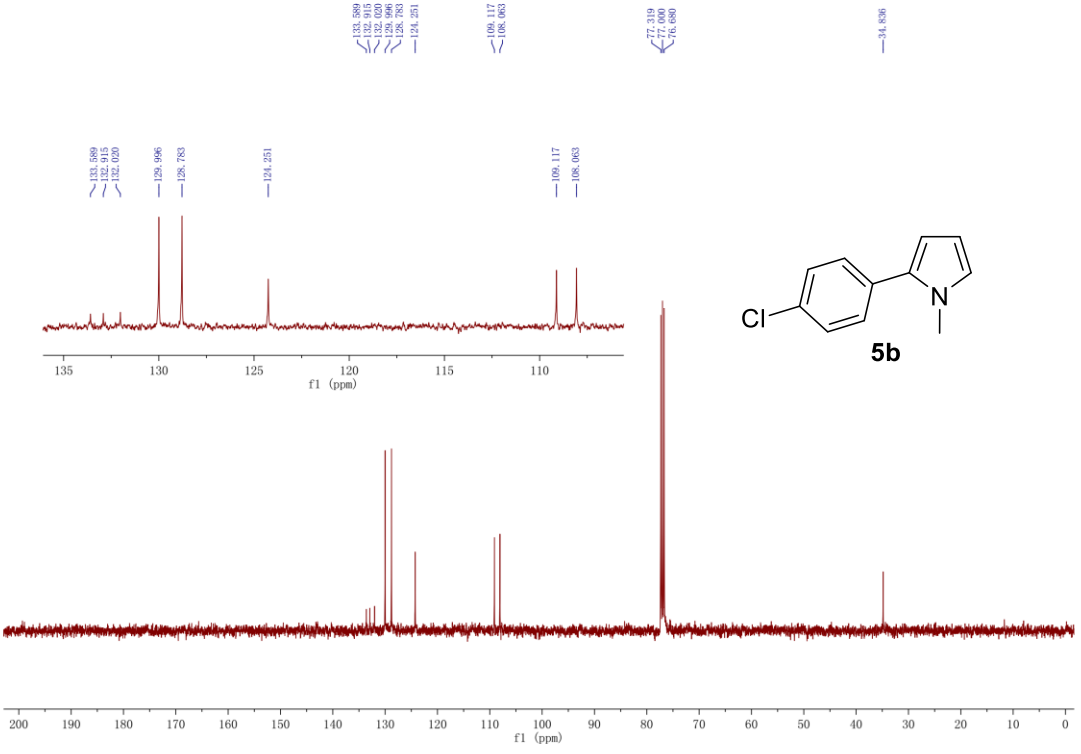
5-1

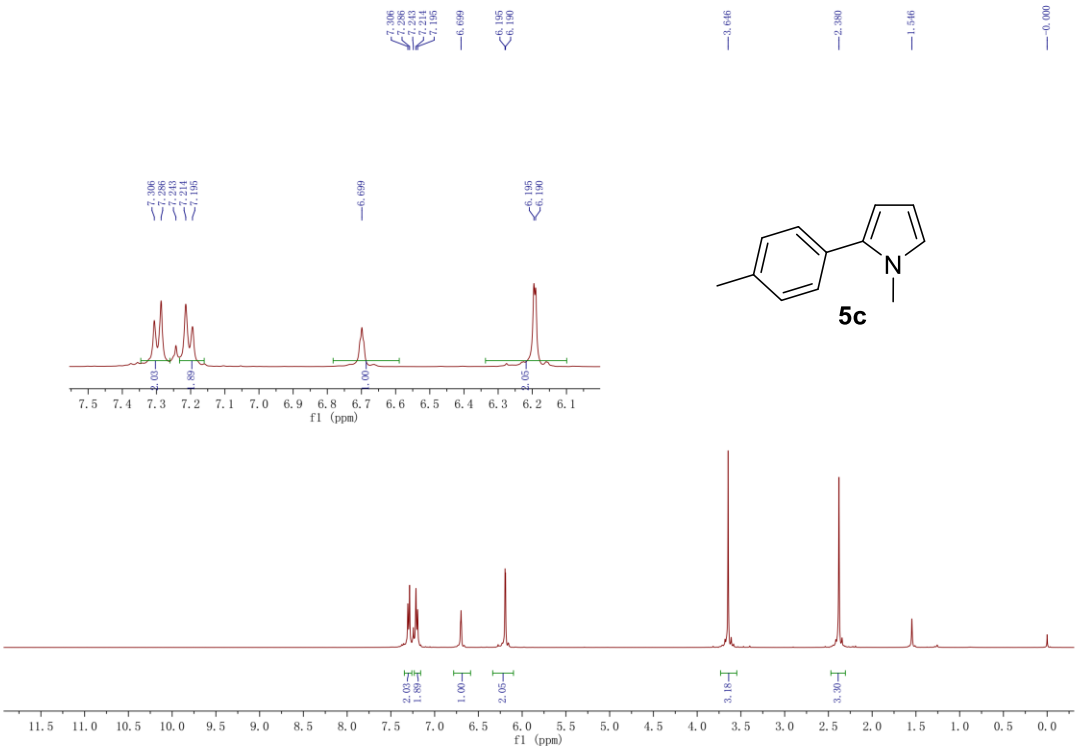

0.92
1.92
2.05
1.07
1.00
0.97
0.99
f1 (ppm)


133.017
132.370
129.110
126.414
124.050
118.994
110.382
106.068
77.319
77.000
76.681
f1 (ppm)

5-1

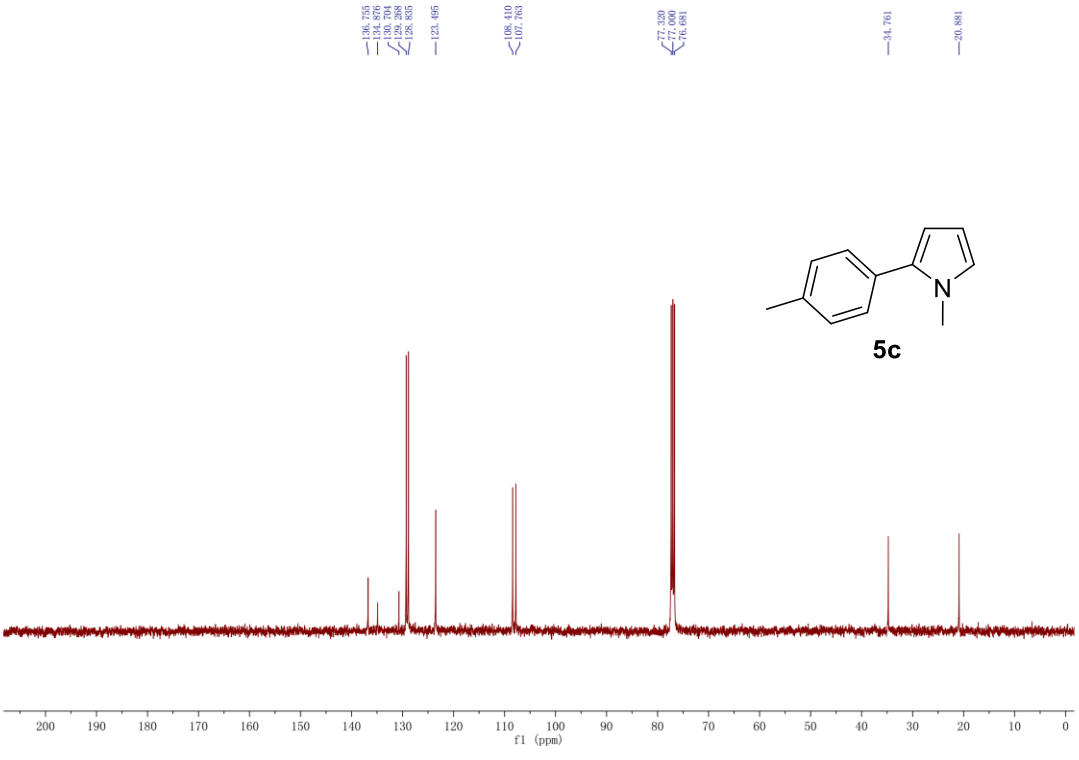

7.391
7.376
7.355
7.335
7.313
7.255
6.723
6.219
6.216
6.206
6.199
3.649
1.558
0.000
Cl
N
5b
4.20
1.00
2.02
3.24
f1 (ppm)


133.589
132.915
132.020
129.996
128.783
124.251
109.117
108.063
77.319
77.000
76.680
34.836
Cl
N
5b
f1 (ppm)


7.306
7.286
7.243
7.214
7.195
6.699
6.195
6.190
3.646
2.380
1.546
0.000
2.03
1.89
1.00
2.05
3.18
3.30
f1 (ppm)

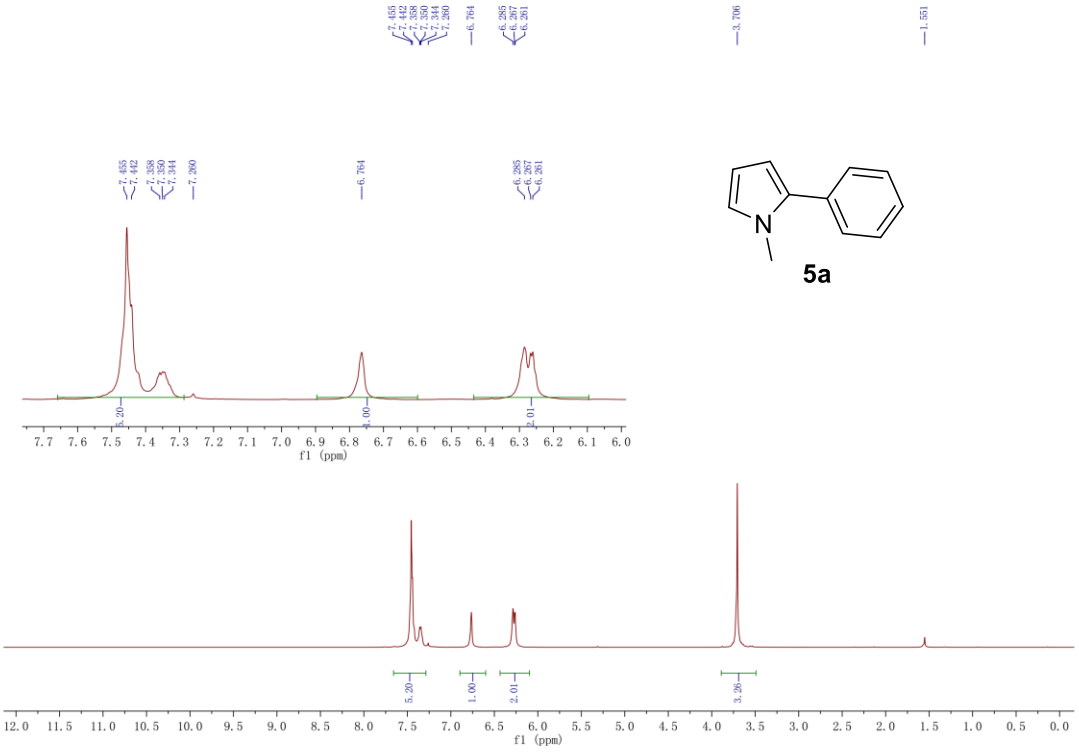
N

5c

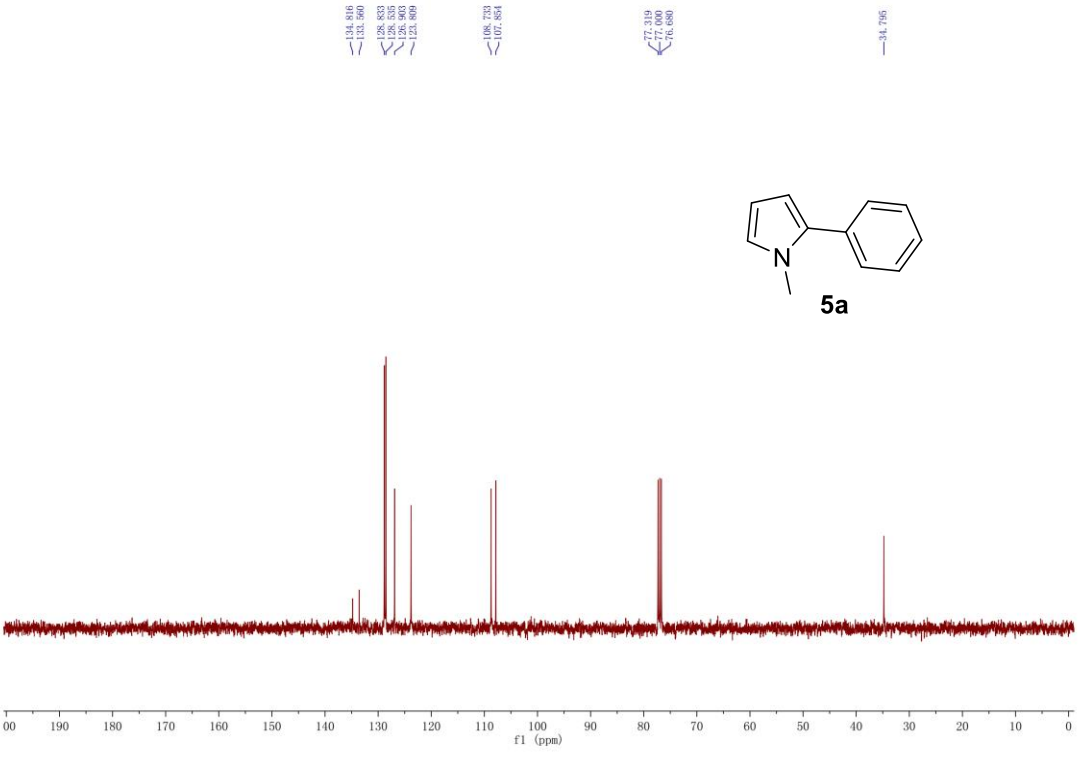

136.755
134.876
130.701
129.288
128.855
123.495
108.410
107.763
77.320
77.000
76.681
34.761
20.881
f1 (ppm)

N

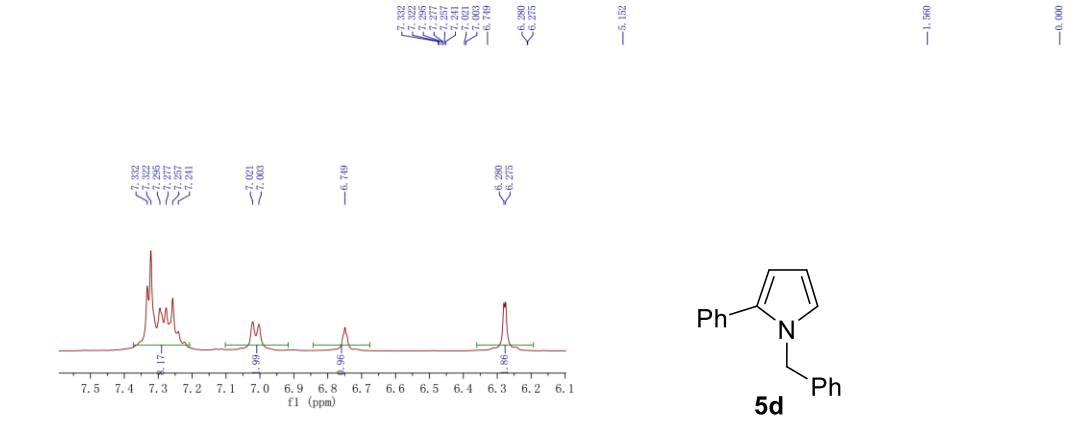
5c

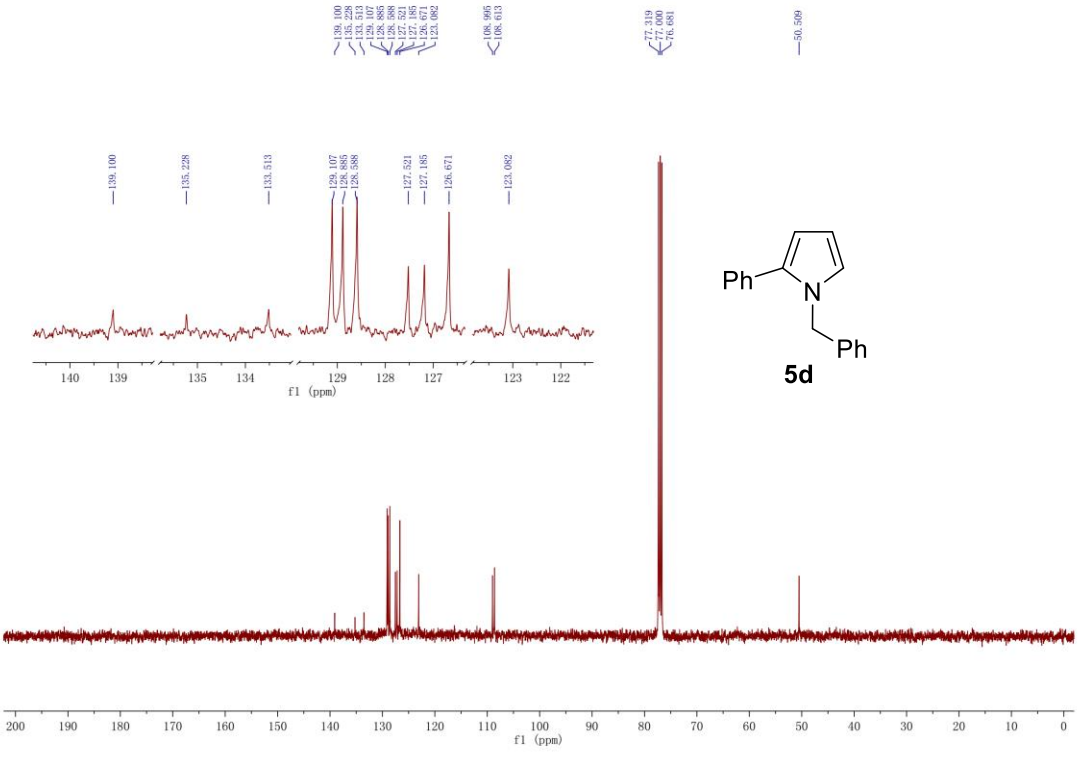

7.455
7.442
7.358
7.350
7.344
7.260
6.764
6.285
6.267
6.261
3.706
1.551
5.20
1.00
2.01
3.26
f1 (ppm)

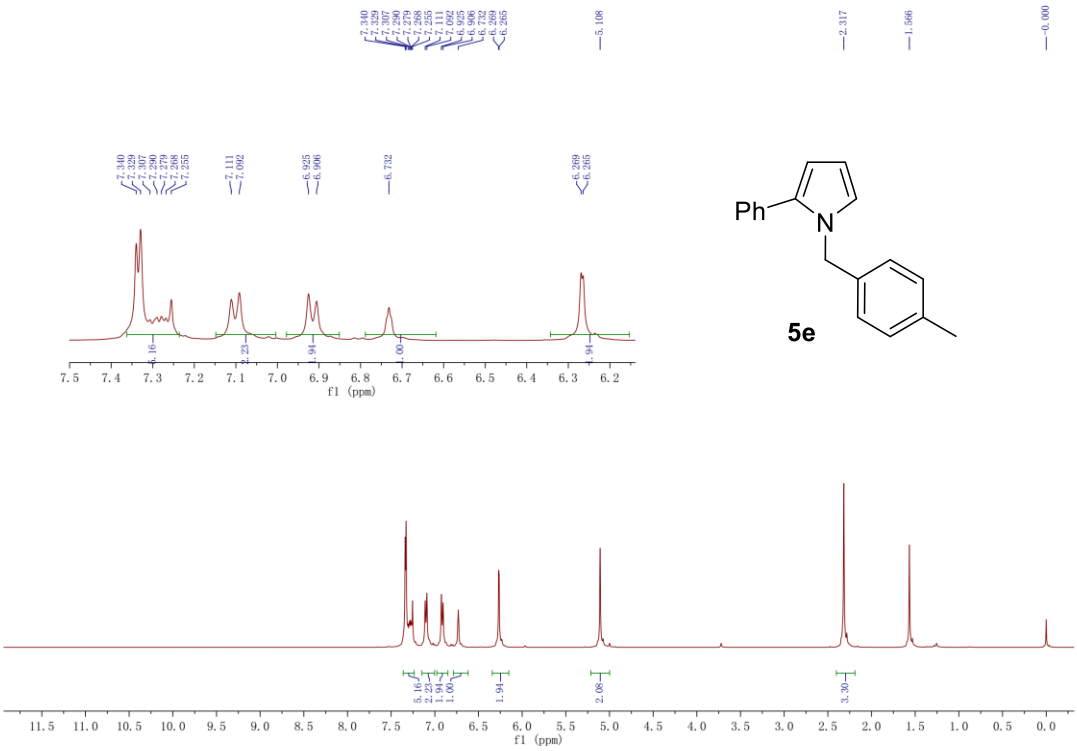
5a

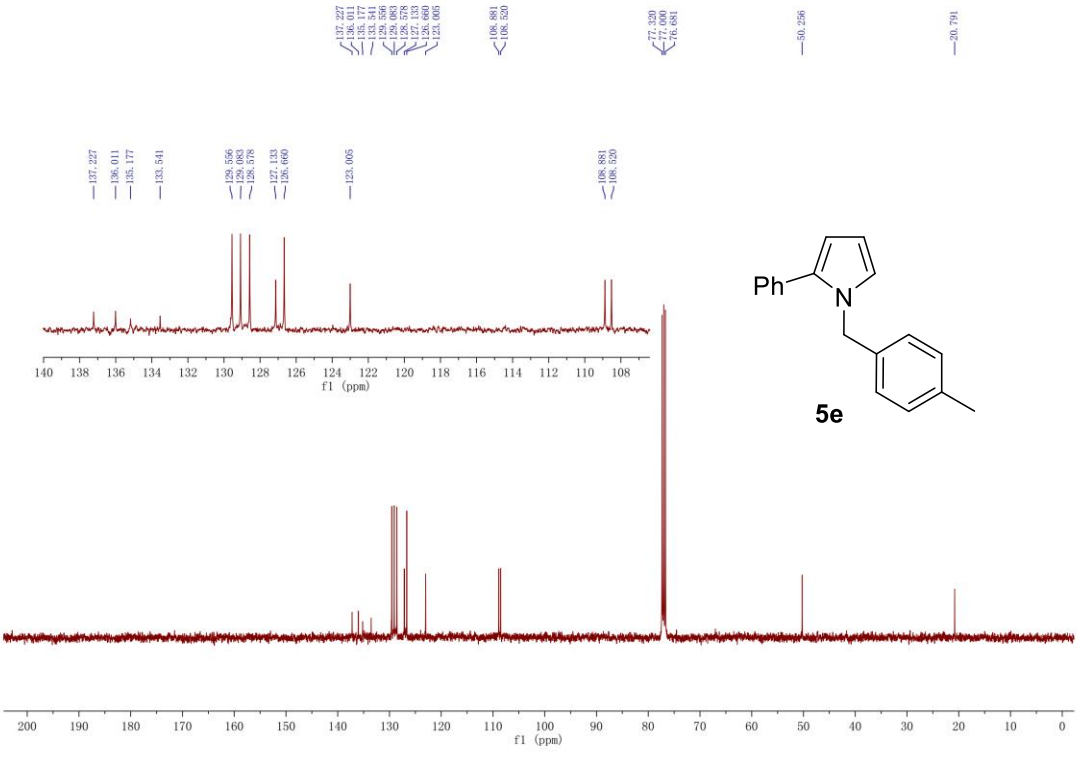

134.816
133.560
128.833
128.535
126.905
123.899
108.733
107.854
77.319
77.000
76.680
34.795
f1 (ppm)

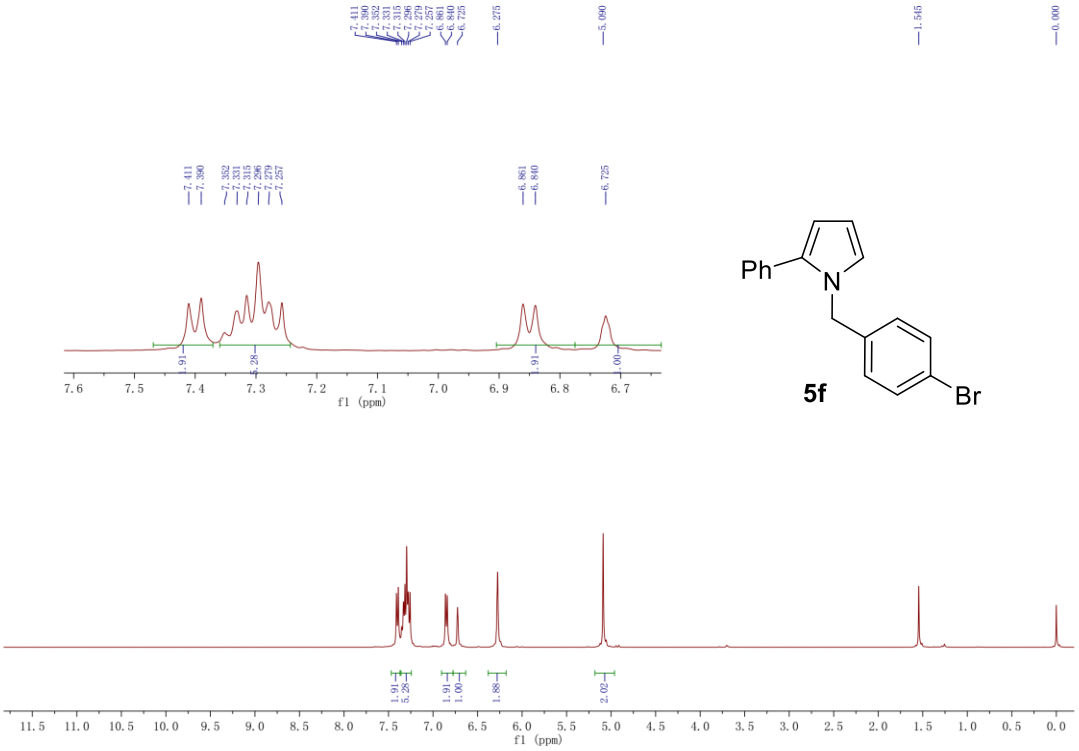
5a

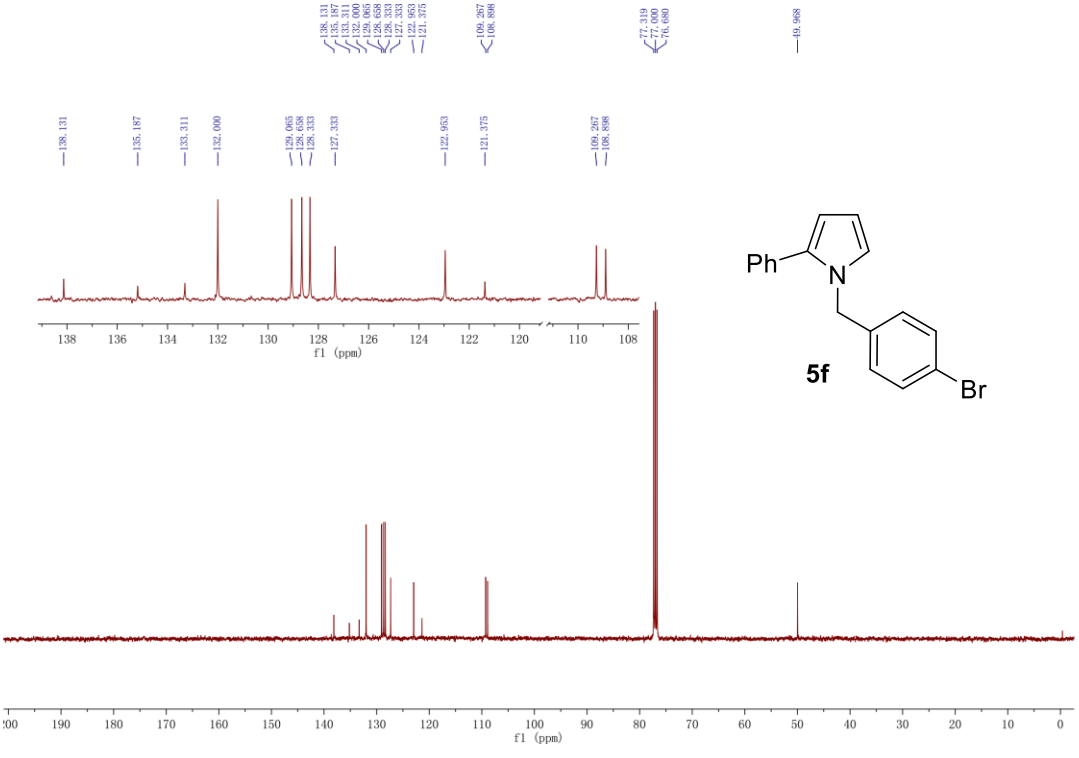

7.332
7.322
7.295
7.277
7.257
7.241
7.021
7.003
6.749
6.280
6.275
5.152
1.560
0.000
8.17
1.99
0.96
1.86
2.00
f1 (ppm)
Ph
N
Ph
5d

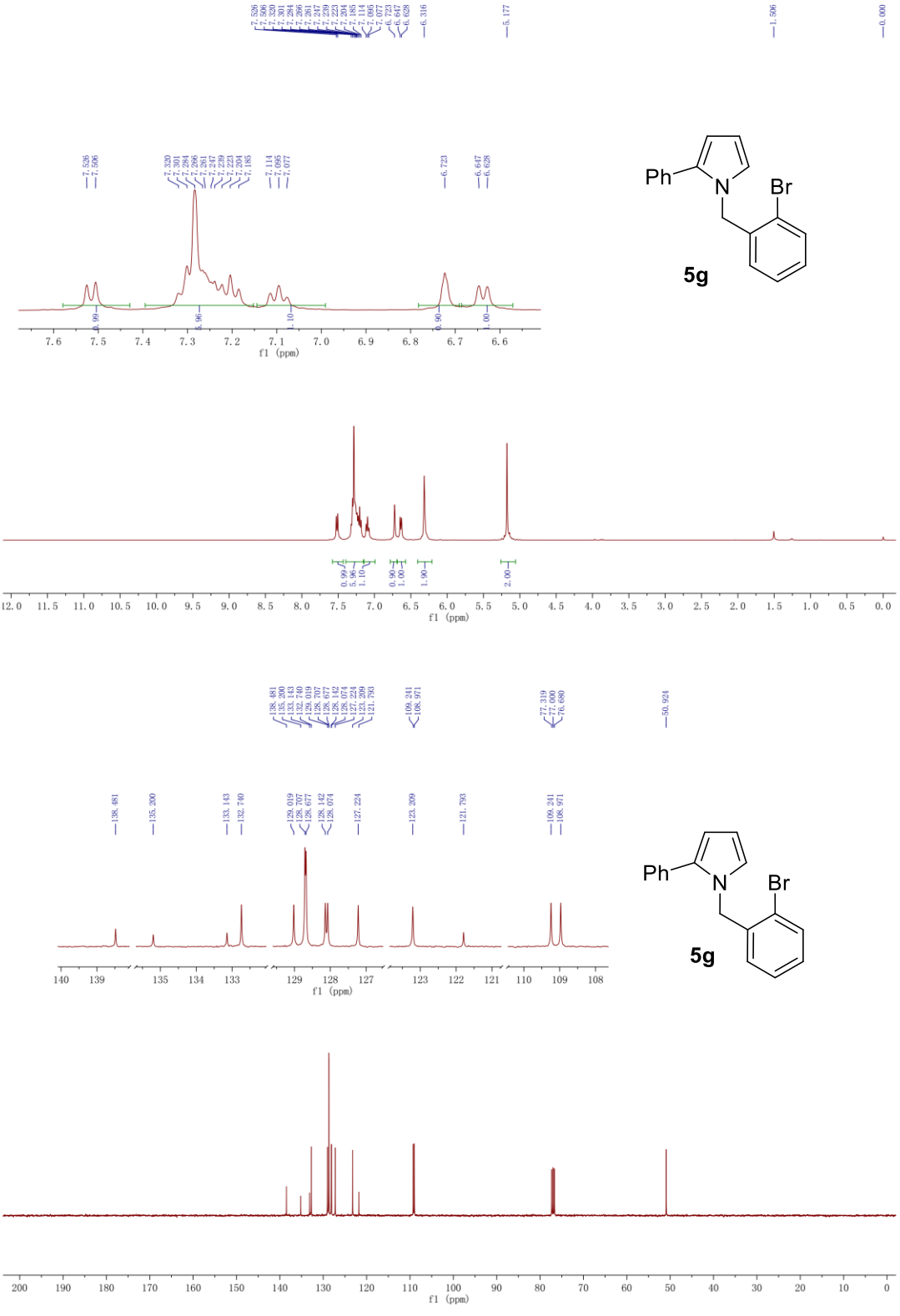

139.100
135.228
133.513
129.107
128.885
128.588
127.521
127.185
126.671
123.082
108.905
108.613
77.319
77.000
76.681
50.569
f1 (ppm)
Ph
N
Ph
5d


Ph
N
5e
f1 (ppm)

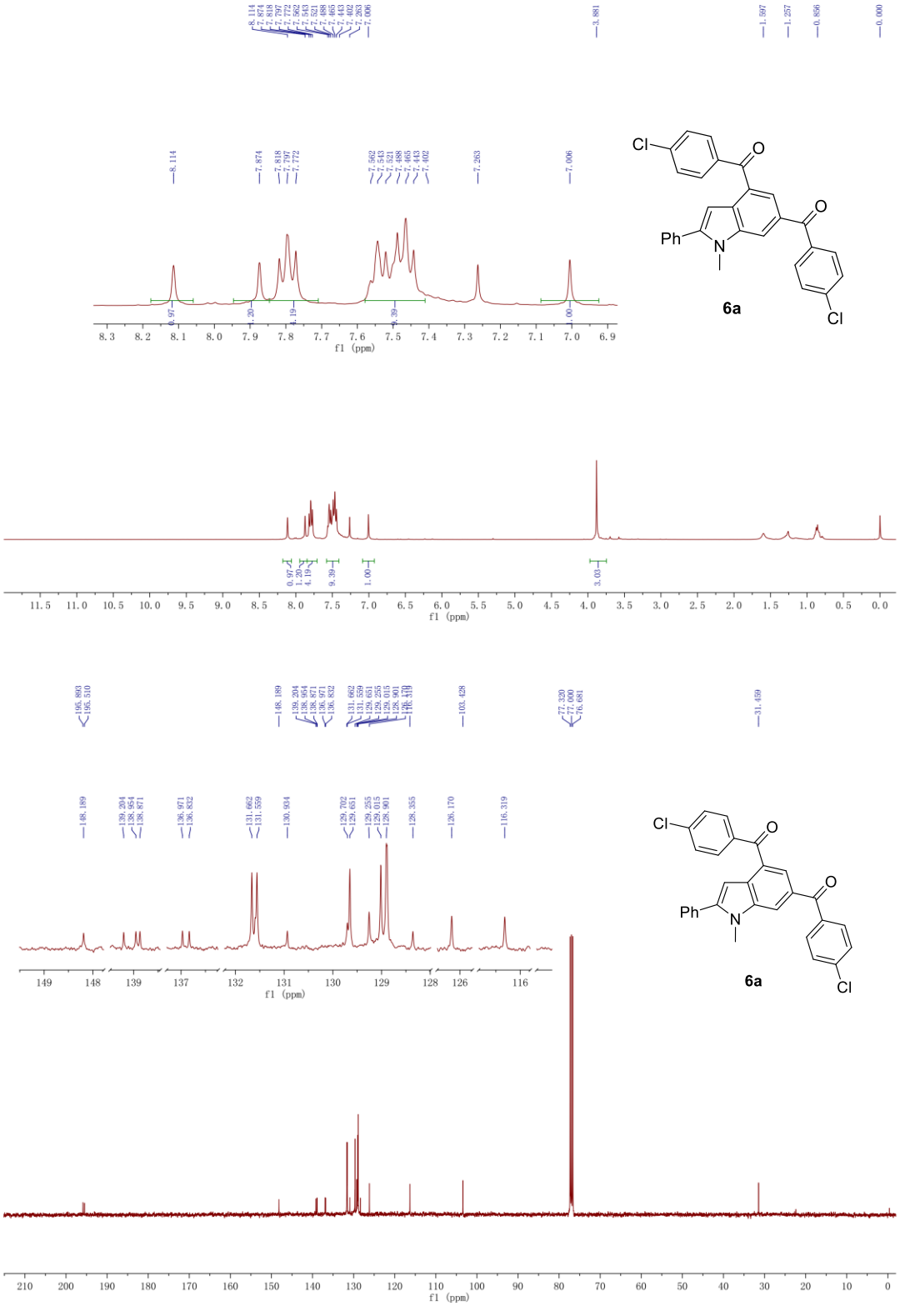

Ph
N
5e
f1 (ppm)

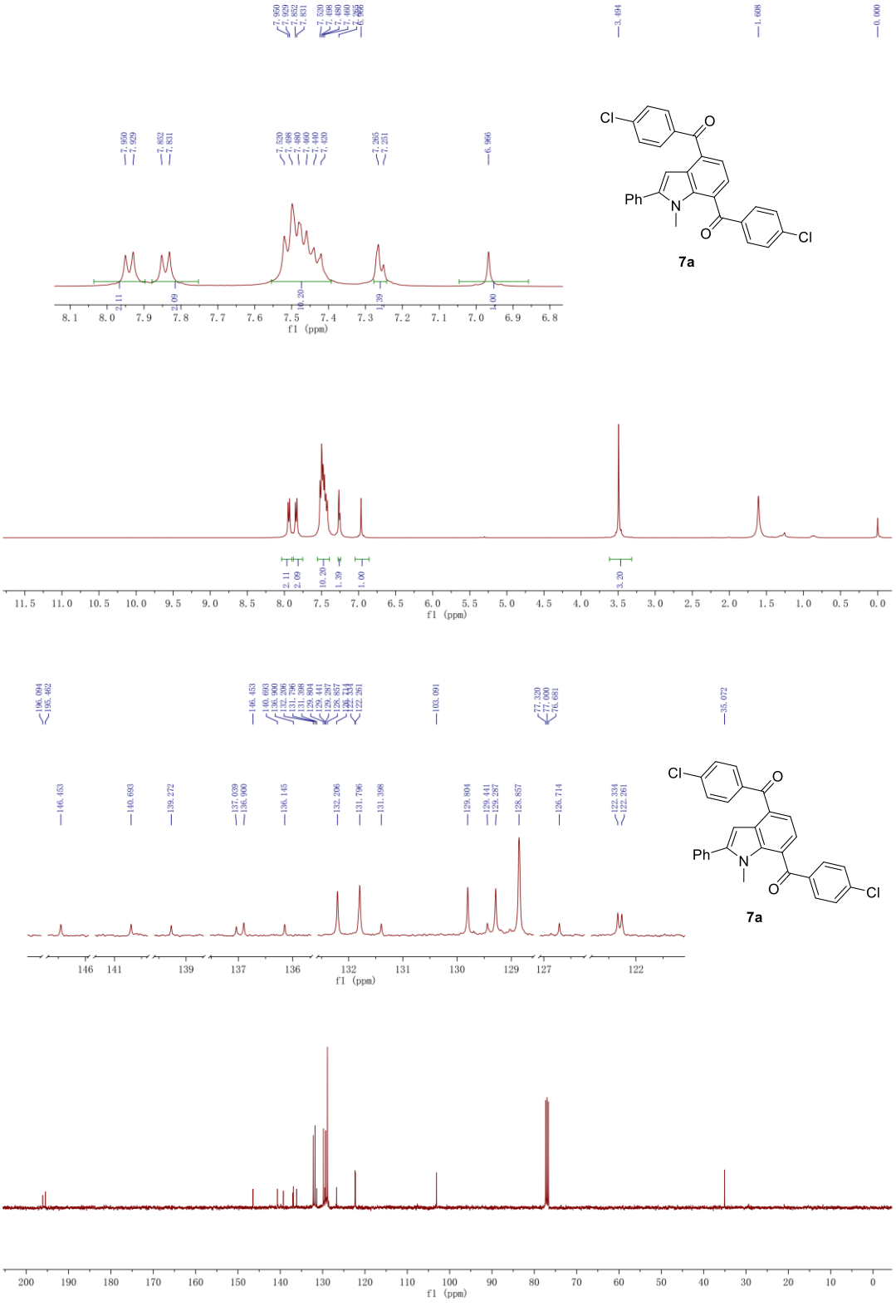

7.411
7.390
7.352
7.331
7.315
7.296
7.279
7.257
6.861
6.840
6.725
6.275
5.090
1.545
0.000
Ph
N
Br
5f
f1 (ppm)

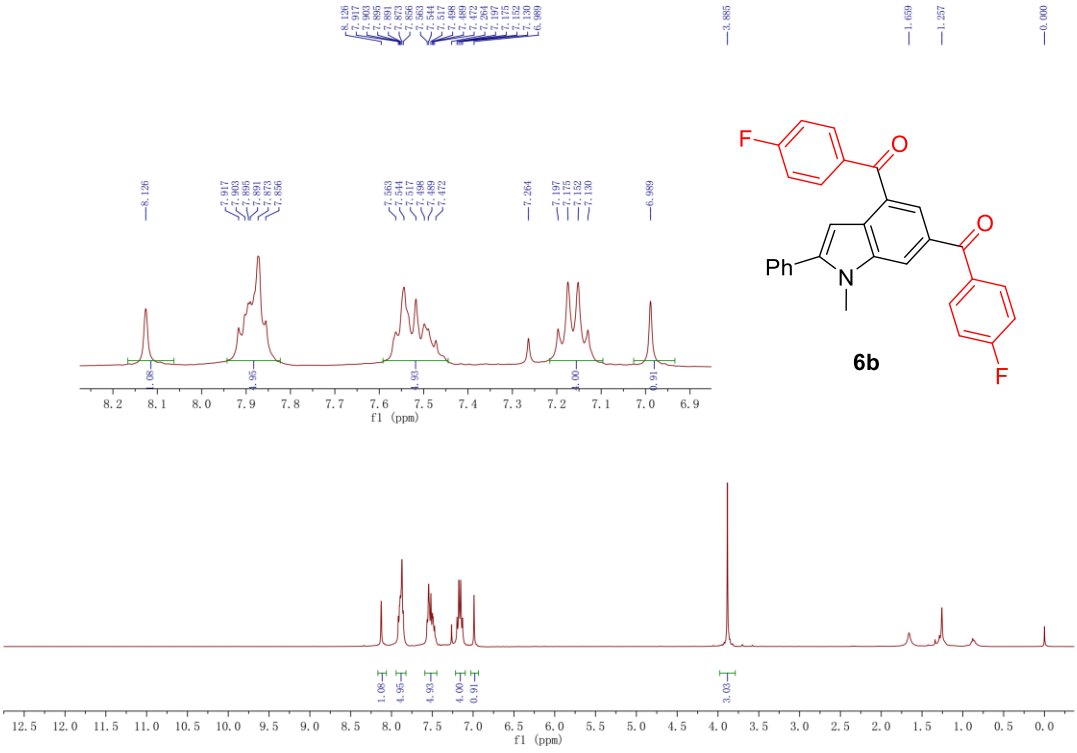

138.131
135.187
133.311
132.000
129.065
128.658
128.333
127.333
122.953
121.375
109.267
108.898
77.319
77.000
76.680
49.968
Ph
N
Br
5f
f1 (ppm)

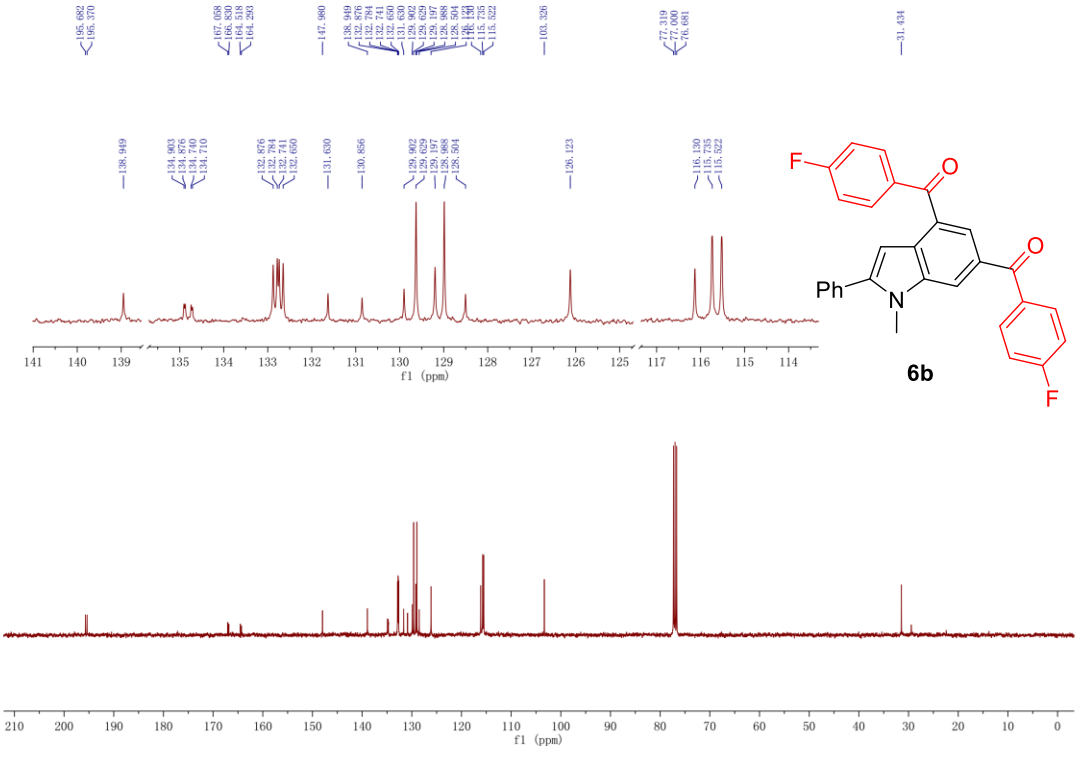


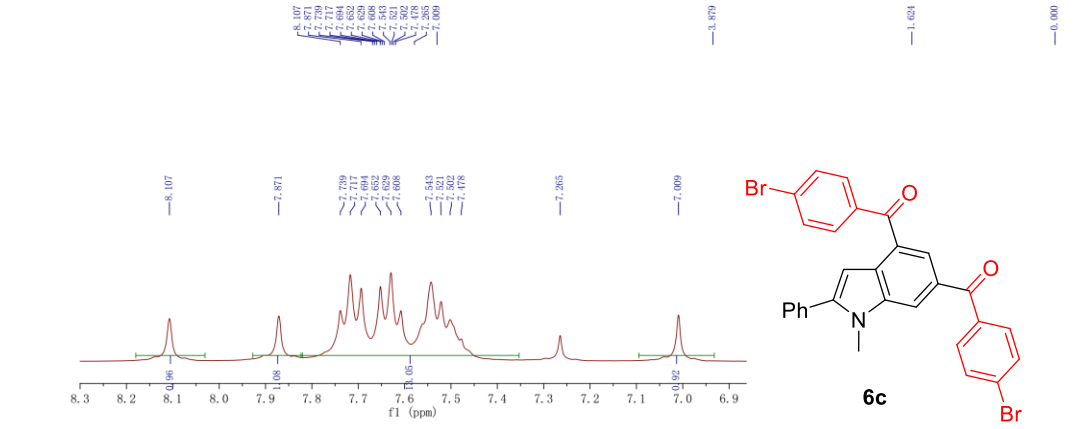
NMR spectra of new compounds (6 and 7a)

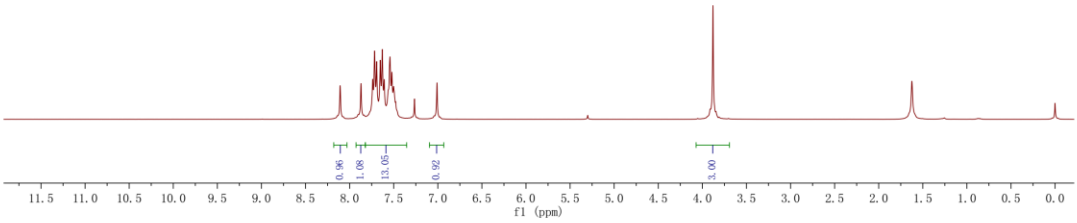

8.114
7.874
7.818
7.797
7.772
7.562
7.543
7.521
7.488
7.465
7.443
7.402
7.283
7.006
3.881
1.597
1.257
0.856
0.000
Cl
O
O
Ph
N
6a
Cl
f1 (ppm)
195.883
195.510
148.189
139.204
138.954
138.871
136.971
136.832
131.662
131.559
130.934
129.702
129.651
129.255
129.015
128.901
128.355
126.170
116.319
103.428
77.320
77.000
76.681
31.459

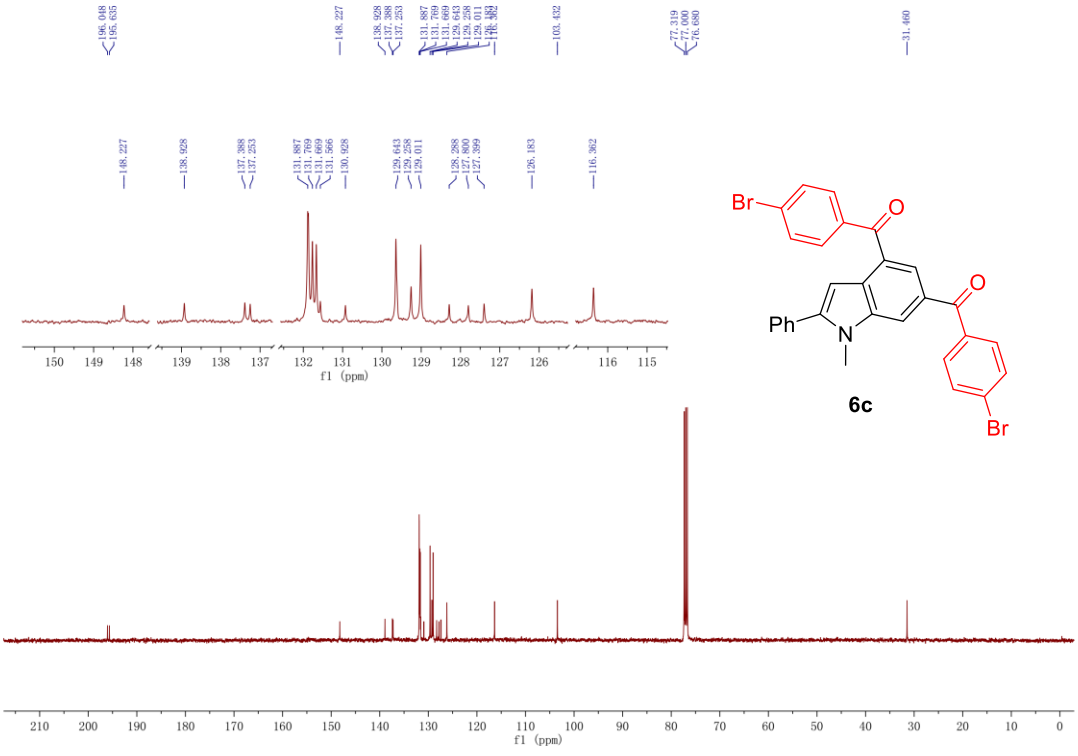

7.950
7.929
7.852
7.831
7.520
7.498
7.480
7.460
7.440
7.420
7.265
7.251
6.966
3.494
1.608
0.000
2.11
2.09
10.20
1.39
1.00
3.20
f1 (ppm)
Cl
O
Ph
N
O
Cl
7a
196.094
195.462
146.453
140.693
139.272
137.039
136.900
136.145
132.206
131.796
131.398
129.804
129.441
129.287
128.857
126.714
122.334
122.261
103.091
77.320
77.000
76.681
35.072


8.126
7.917
7.903
7.895
7.891
7.873
7.856
7.563
7.544
7.517
7.498
7.489
7.472
7.364
7.197
7.175
7.152
7.130
6.989
3.885
1.639
1.257
0.000
F
O
O
Ph
N
F
6b
1.08
1.95
4.93
4.00
0.91
3.03
f1 (ppm)


195.682
195.370
167.058
166.830
164.518
164.280
147.980
138.949
132.876
132.784
132.741
132.650
131.630
130.856
129.902
129.629
129.197
128.968
128.504
126.123
116.130
115.735
115.522
103.326
77.319
77.000
76.681
31.434
F
O
O
Ph
N
F
6b
f1 (ppm)


8.107
7.871
7.739
7.717
7.694
7.652
7.629
7.608
7.543
7.521
7.502
7.478
7.265
7.009
3.879
1.624
0.000
0.96
1.08
13.05
0.92
f1 (ppm)
Br
O
Ph
N
O
Br
6c


0.96
1.08
13.05
0.92
3.00
f1 (ppm)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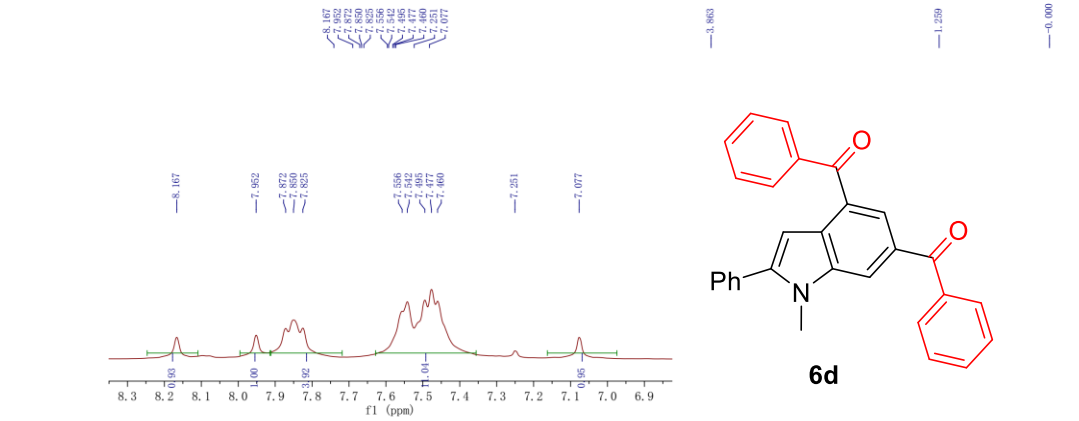
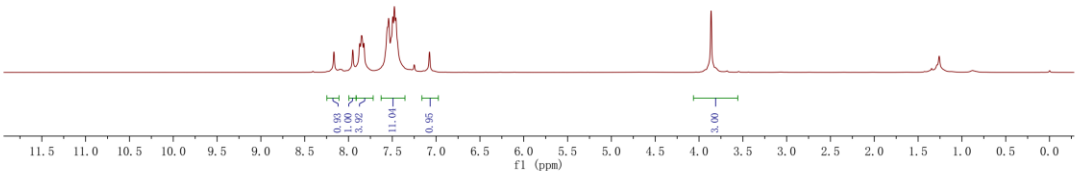
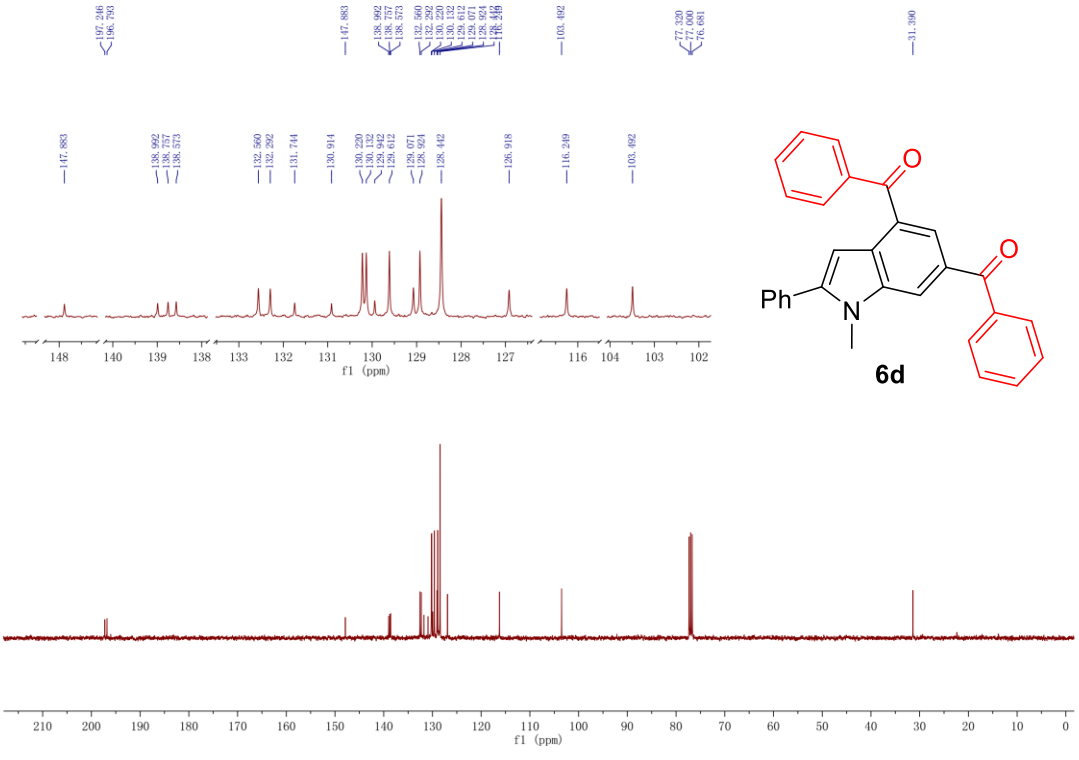
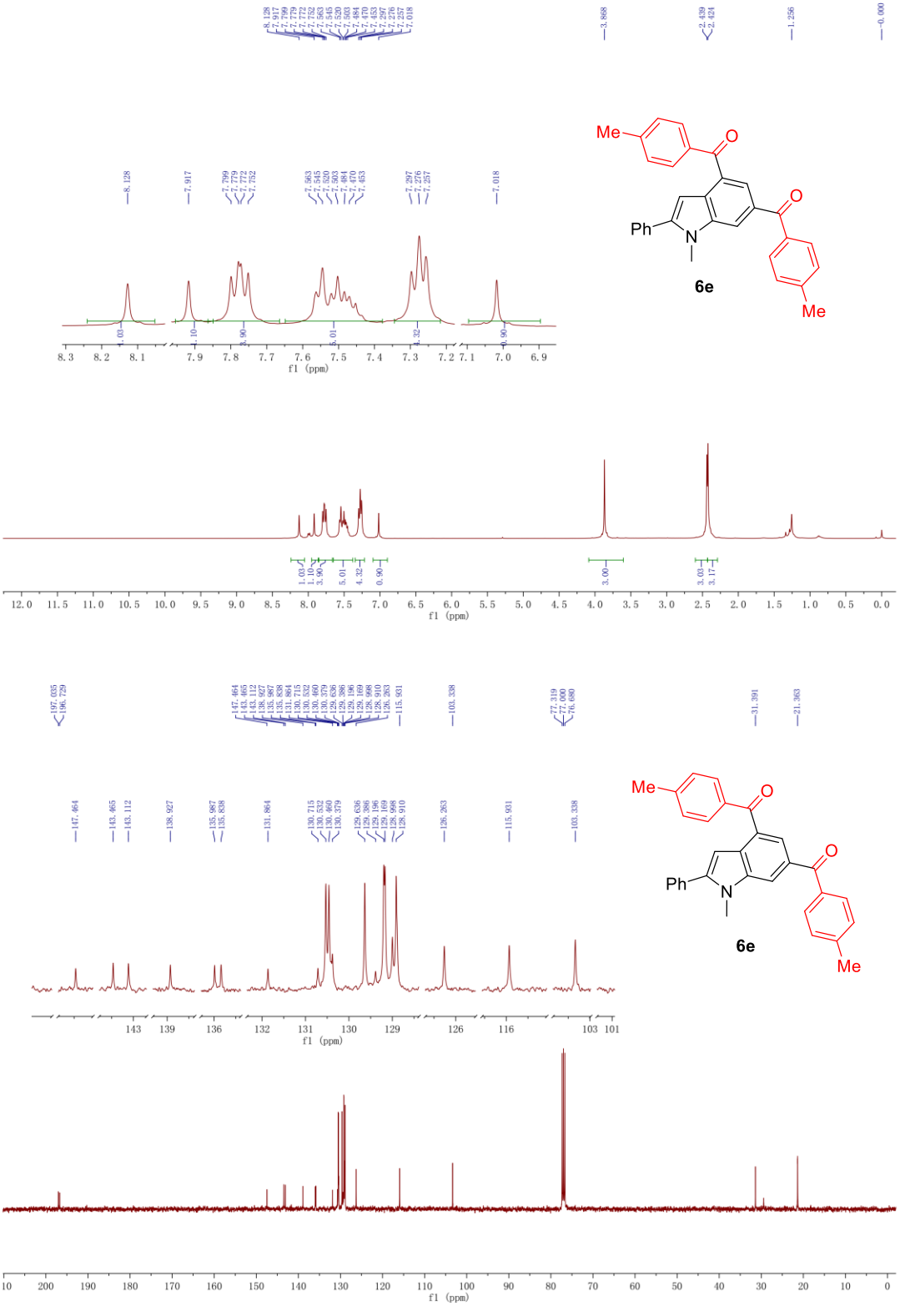
195.635
148.227
138.928
137.388
137.253
131.887
131.769
131.649
131.566
130.928
129.643
129.258
129.011
128.288
127.800
127.399
126.183
116.362
103.432
77.319
77.000
76.680
31.460
f1 (ppm)
Br
O
Ph
N
O
Br
6c

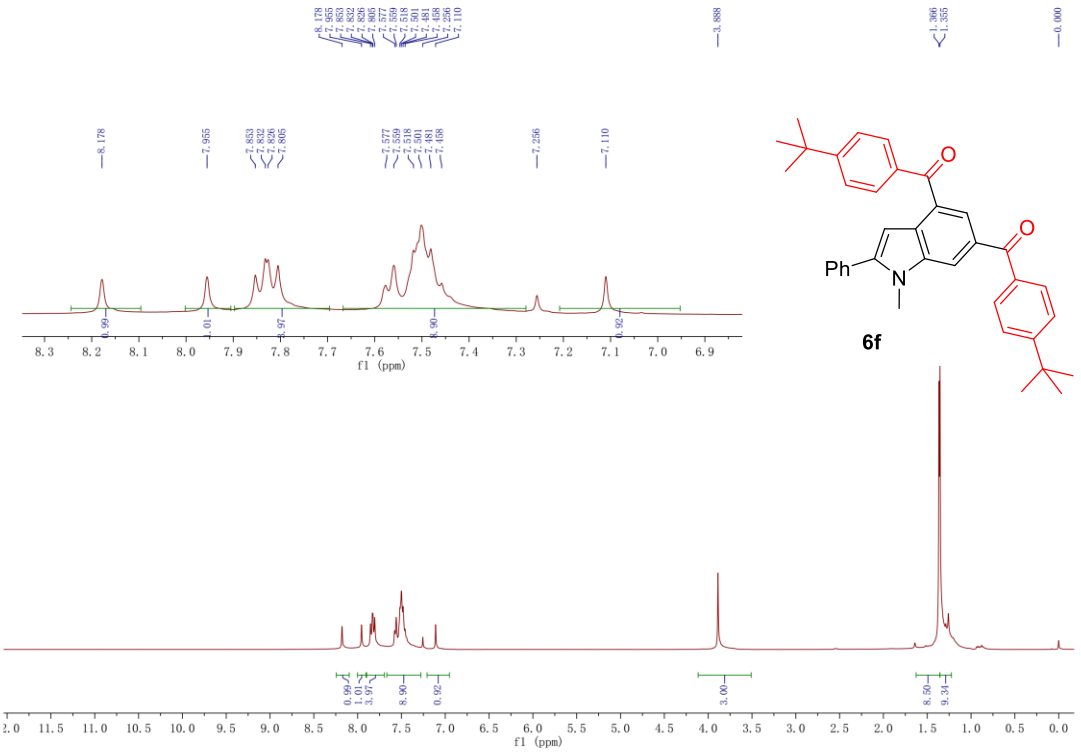

8.167
7.952
7.872
7.850
7.825
7.556
7.542
7.496
7.477
7.460
7.251
7.077
3.863
1.259
0.000
0.93
1.00
3.92
11.04
0.95
3.00
f1 (ppm)
Ph
N
O
O
6d


0.93
1.00
3.92
11.04
0.95
3.00
f1 (ppm)


197.246
196.793
147.883
138.992
138.757
138.573
132.560
132.292
130.914
130.220
130.132
129.942
129.612
129.071
128.924
128.442
126.918
116.249
103.492
77.320
77.000
76.681
31.390
f1 (ppm)
Ph
N
O
O
6d


Me
O
O
Ph
N
6e
Me
f1 (ppm)

Me
O
O
Ph
N
6e
Me
f1 (ppm)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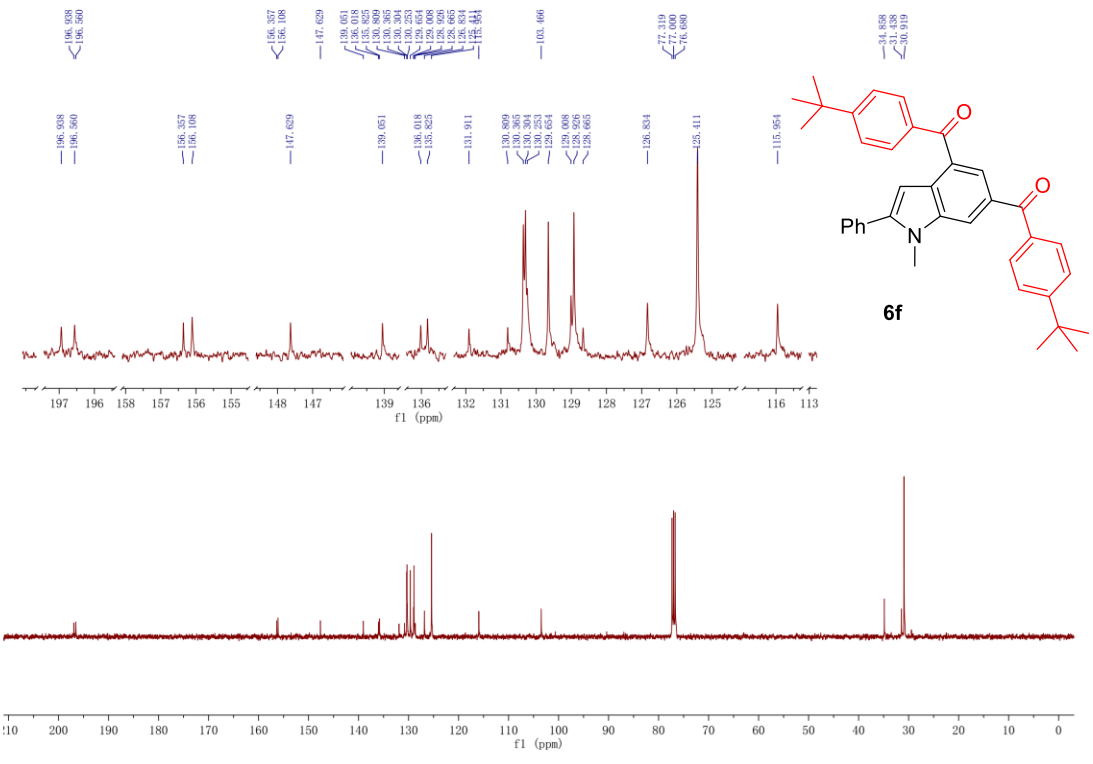
7.955
7.853
7.832
7.826
7.805
7.577
7.559
7.518
7.501
7.481
7.458
7.256
7.110
3.888
1.366
1.355
0.000
f1 (ppm)
6f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196.560
156.357
156.108
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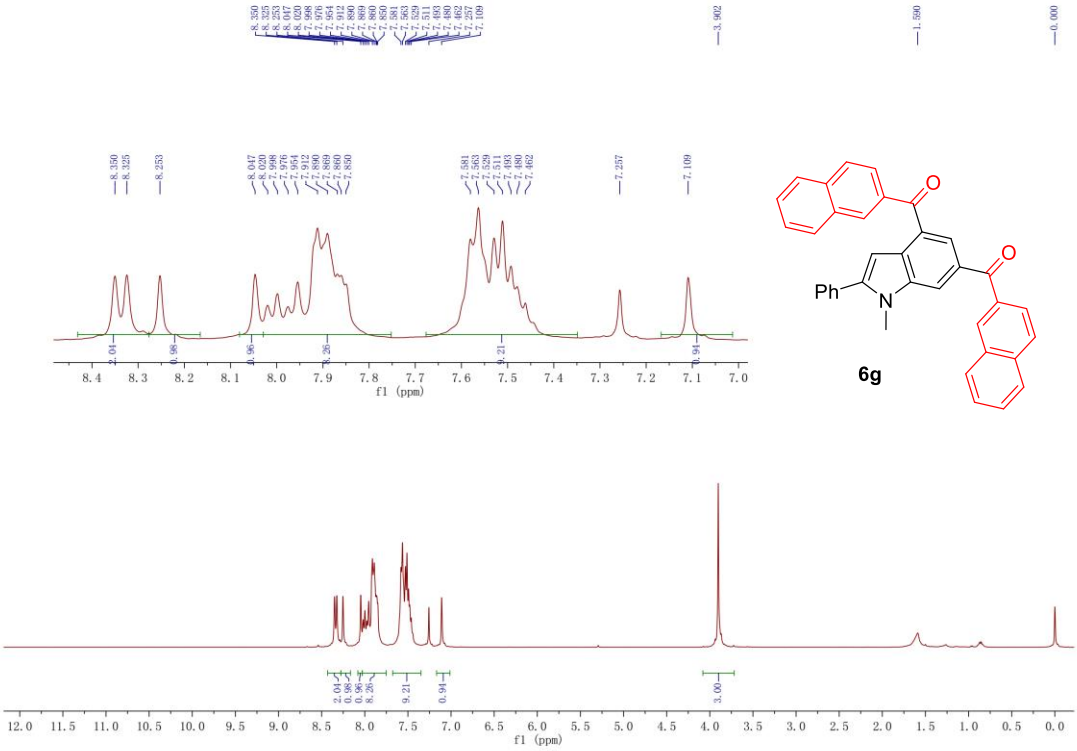
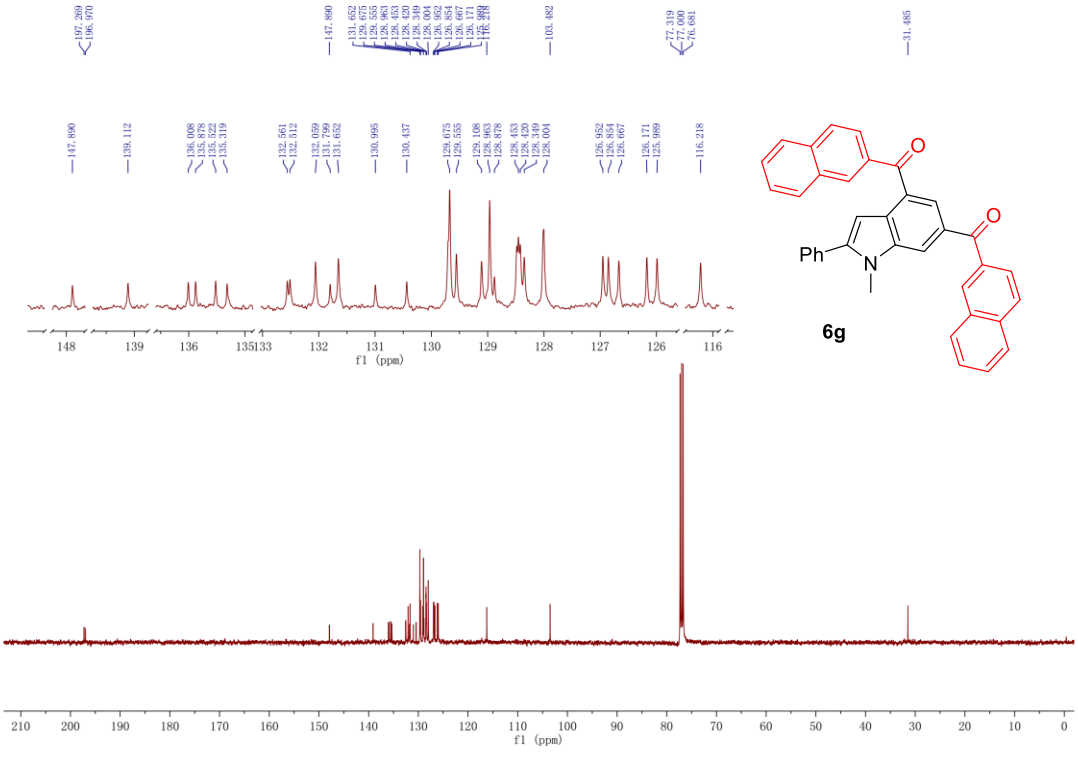
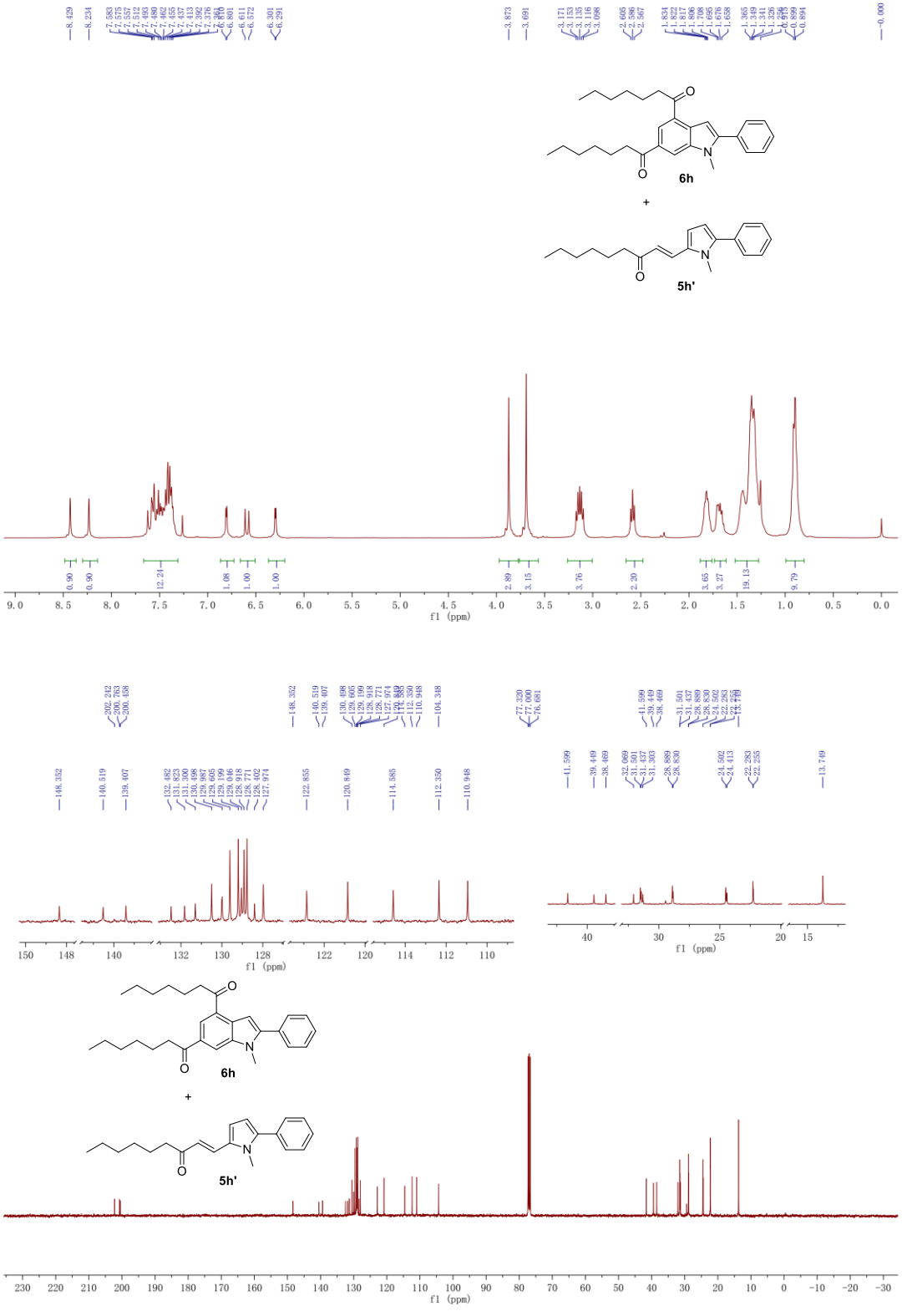
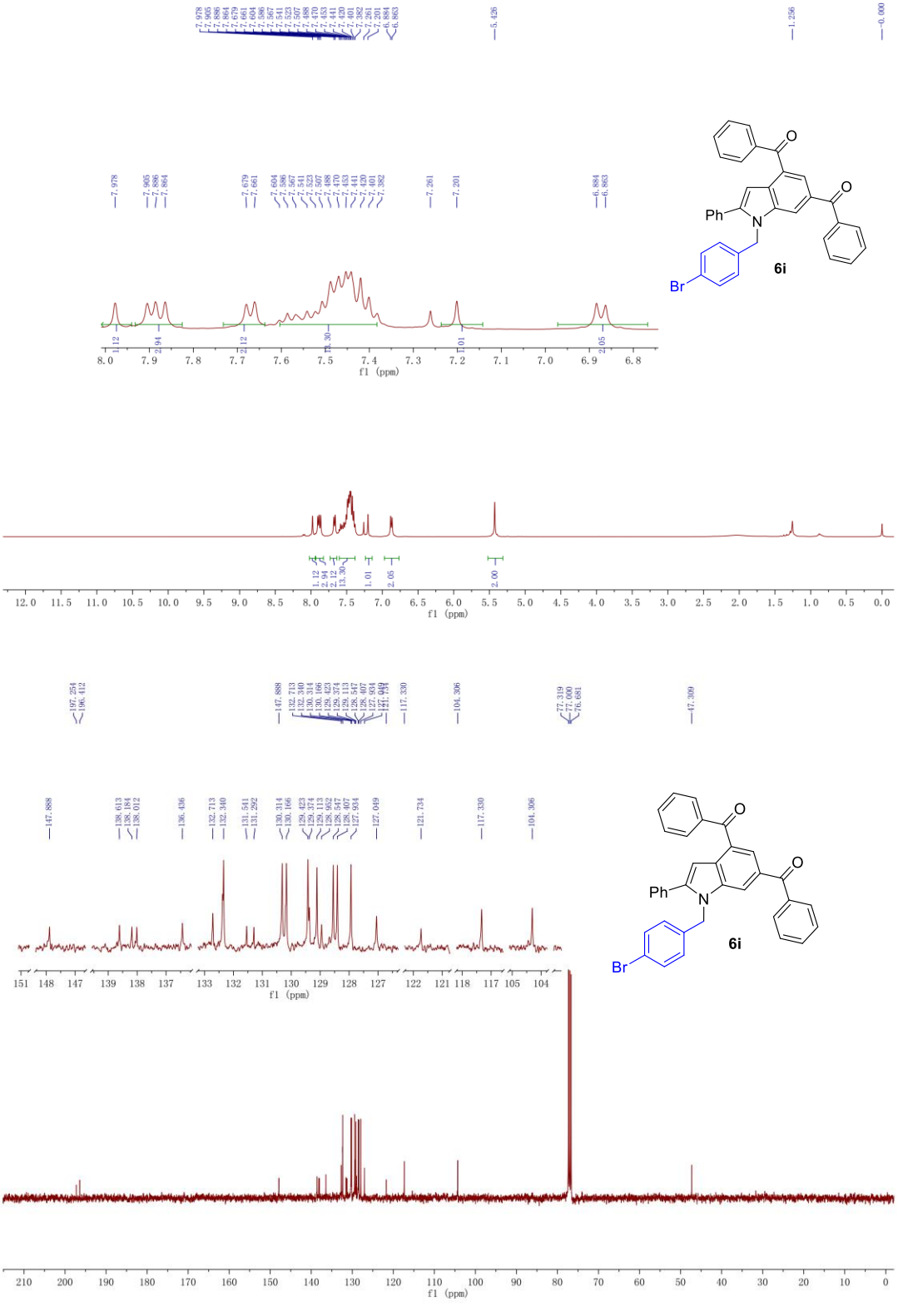
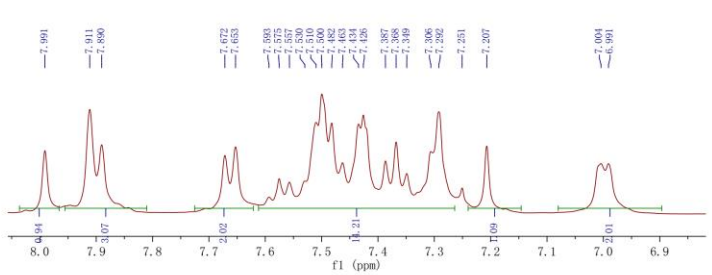
136.018
135.825
131.911
130.809
130.305
130.304
130.253
129.654
129.008
128.926
128.665
126.834
125.411
115.954
103.466
77.319
77.000
76.680
34.858
31.438
30.919
f1 (ppm)
6f

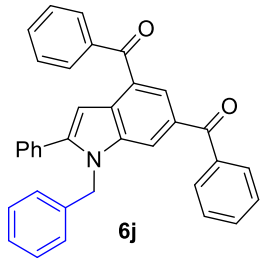

f1 (ppm)
6g


f1 (ppm)
6g

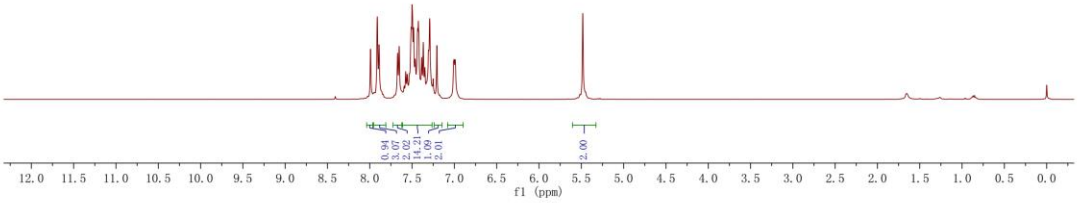

6h
+
5h'
f1 (ppm)

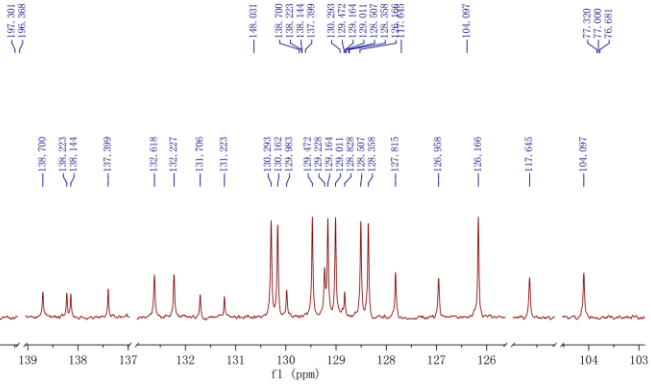

7.978
7.965
7.886
7.884
7.679
7.661
7.604
7.586
7.567
7.541
7.533
7.507
7.488
7.470
7.453
7.441
7.420
7.401
7.382
7.361
7.201
6.884
6.863
5.426
1.256
0.000
Ph
N
O
O
Br
6i
f1 (ppm)
197.254
196.412
147.888
132.713
132.340
130.314
130.166
129.423
129.374
129.113
128.962
128.947
128.547
128.407
127.934
127.049
121.734
117.330
104.306
77.319
77.000
76.681
47.309
f1 (ppm)

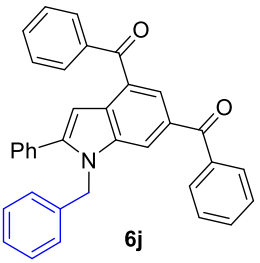




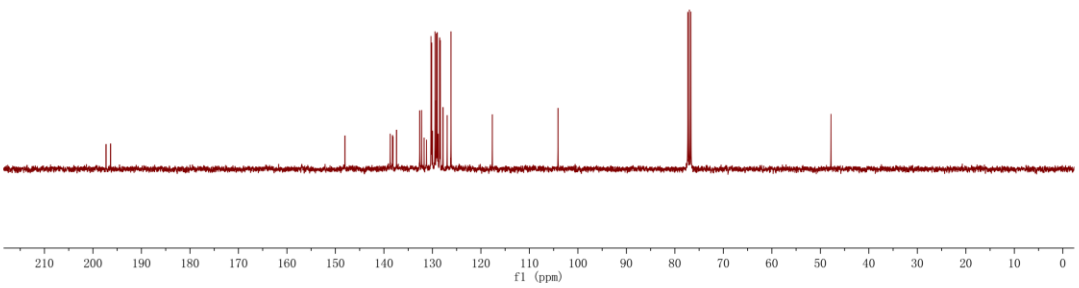
6j

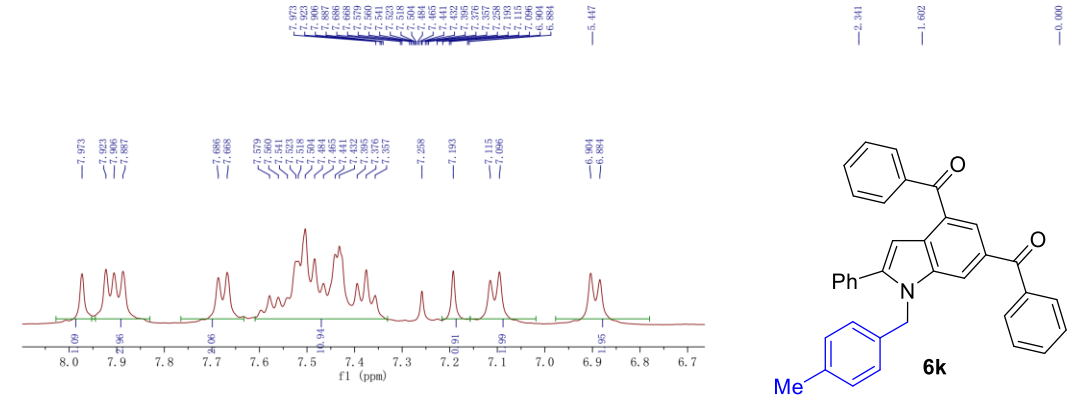






6j

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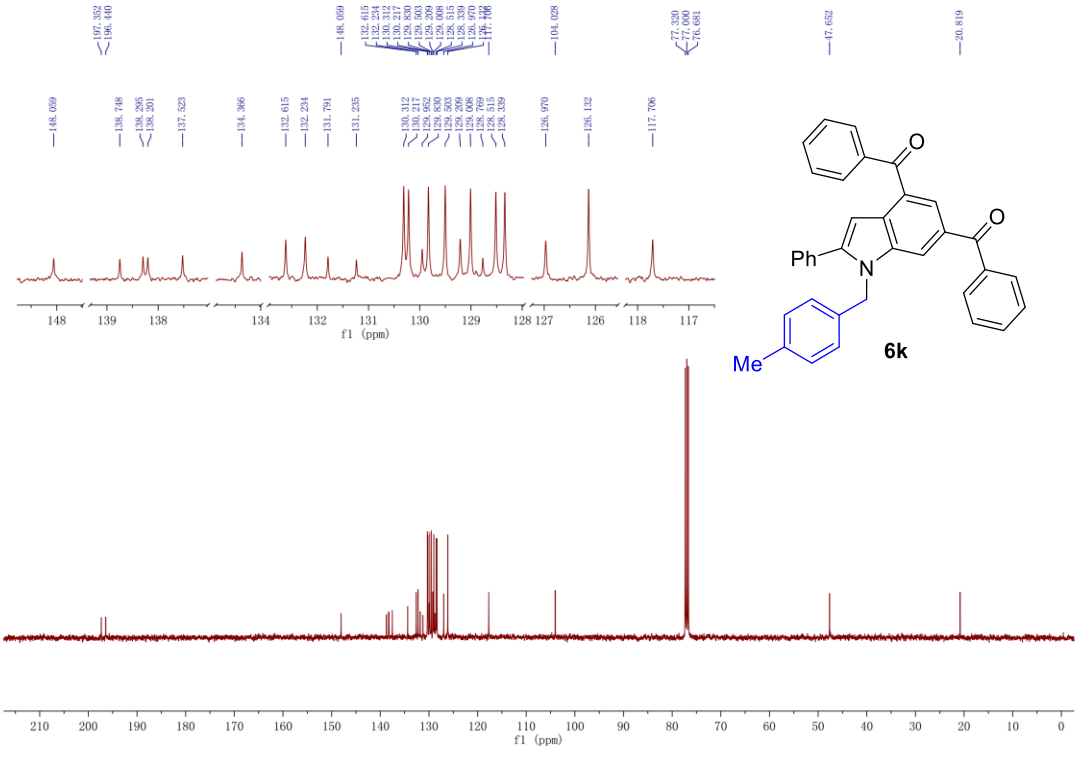
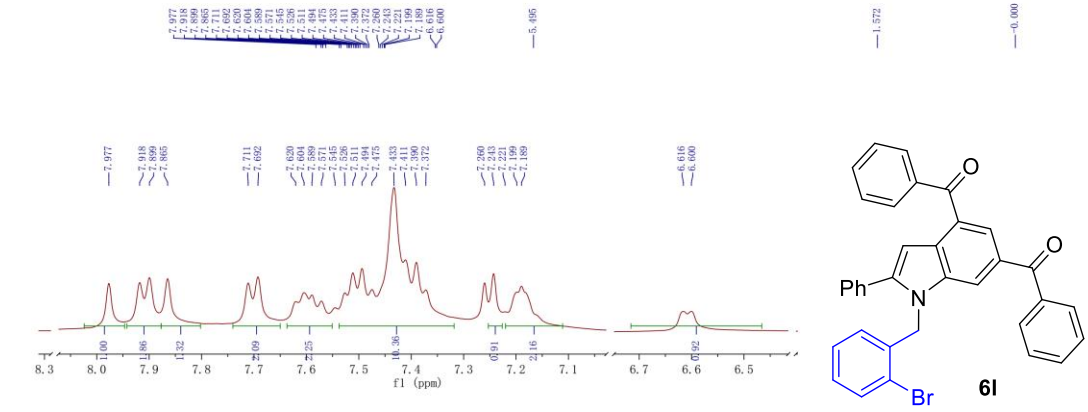
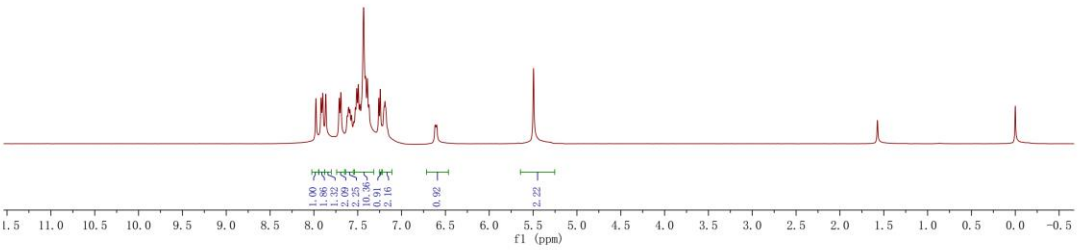
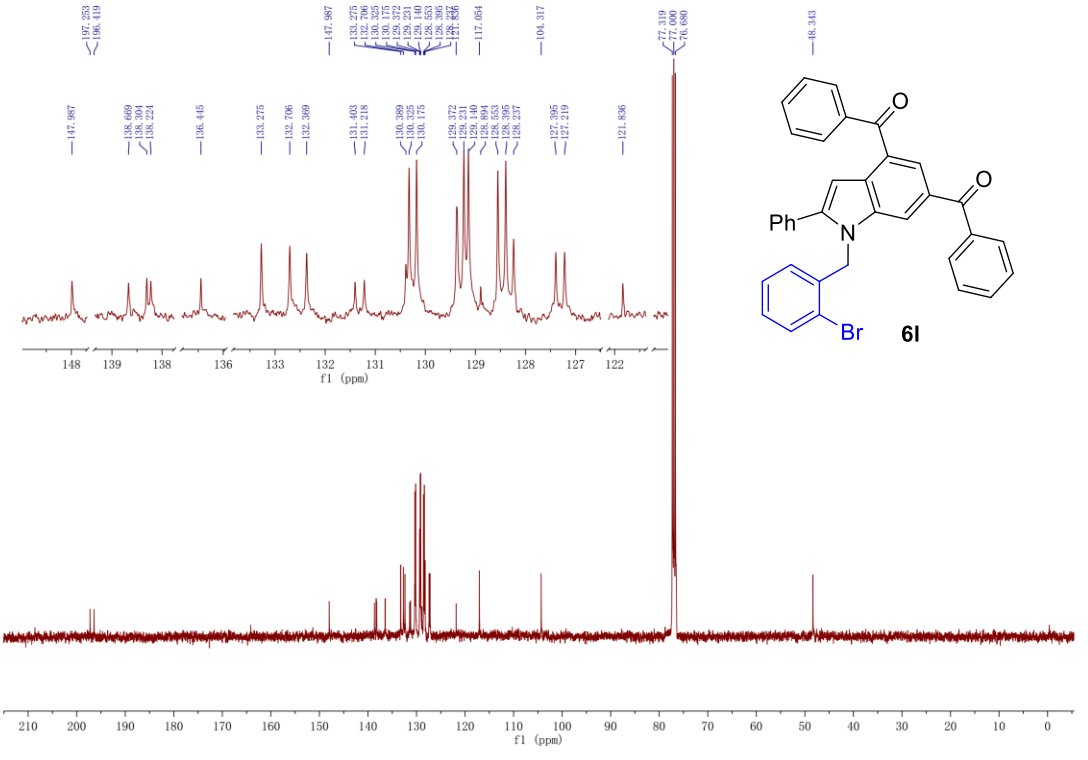
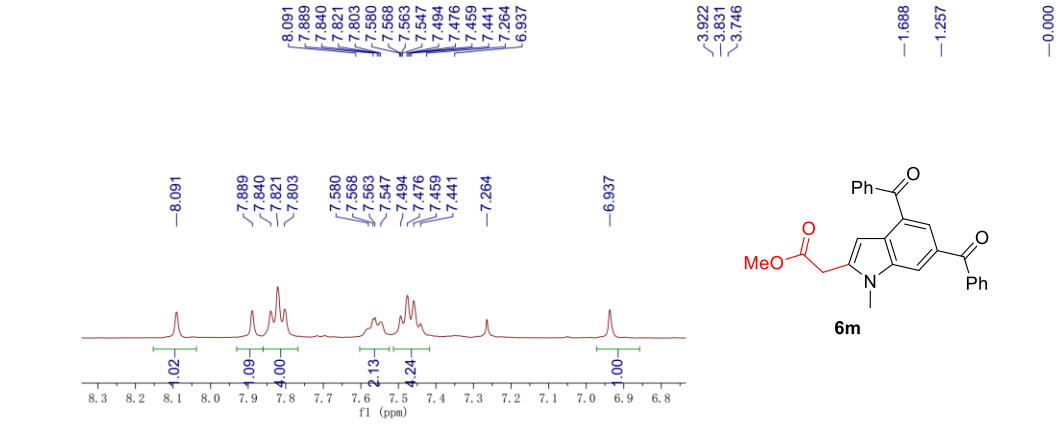
7.906
7.887
7.686
7.668
7.579
7.560
7.541
7.533
7.518
7.504
7.484
7.465
7.441
7.432
7.395
7.376
7.357
7.258
7.193
7.115
7.096
6.904
6.884
5.447
2.341
1.602
0.000
1.09
2.96
2.06
10.94
0.91
1.99
1.95
1.93
3.00
f1 (ppm)
Ph
N
O
O
Me
6k


197.332
196.440
148.069
132.615
132.234
131.791
131.235
130.312
130.217
129.952
129.830
129.503
129.008
128.769
128.515
128.339
126.970
126.132
117.706
104.028
77.320
77.000
76.681
47.652
20.819
f1 (ppm)
Ph
N
O
O
Me
6k


7.977
7.918
7.899
7.865
7.711
7.692
7.620
7.604
7.589
7.571
7.545
7.536
7.511
7.494
7.475
7.433
7.411
7.390
7.372
7.260
7.243
7.221
7.199
7.189
6.616
6.600
5.495
1.572
0.000
1.00
1.86
1.32
2.09
2.25
10.36
0.91
2.16
0.92
2.22
0.92
f1 (ppm)
O
O
Ph
N
Br
6l


1.00
1.86
1.32
2.09
2.25
10.36
0.91
2.16
0.92
2.22
f1 (ppm)


197.553
196.419
147.987
133.275
132.706
132.369
130.389
130.225
130.175
129.372
129.231
129.140
128.553
128.395
128.237
127.395
127.219
121.836
117.054
104.317
77.319
77.000
76.680
48.343
O
O
Ph
N
Br
6l
f1 (ppm)
f1 (ppm)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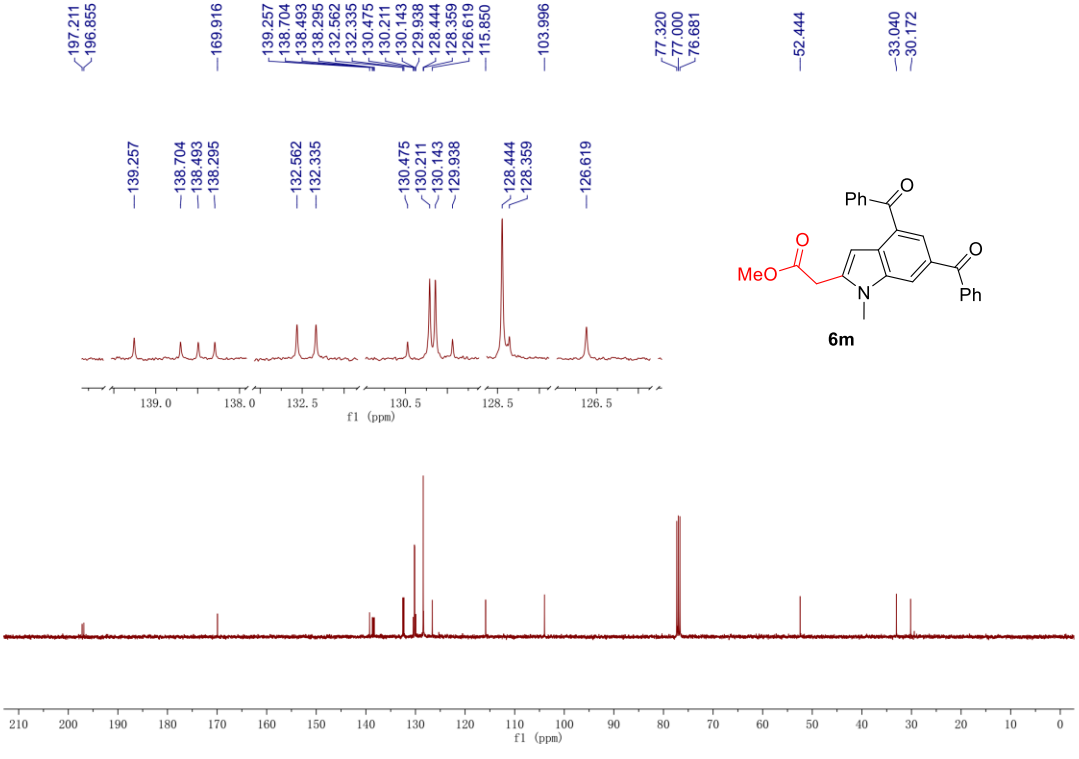
7.840
7.821
7.803
7.580
7.568
7.563
7.547
7.494
7.476
7.459
7.441
7.264
6.937
3.922
3.831
3.746
1.688
1.257
0.000
1.02
1.09
4.00
2.13
4.24
1.00
2.00
3.04
3.02
f1 (ppm)
Ph
O
MeO
N
6m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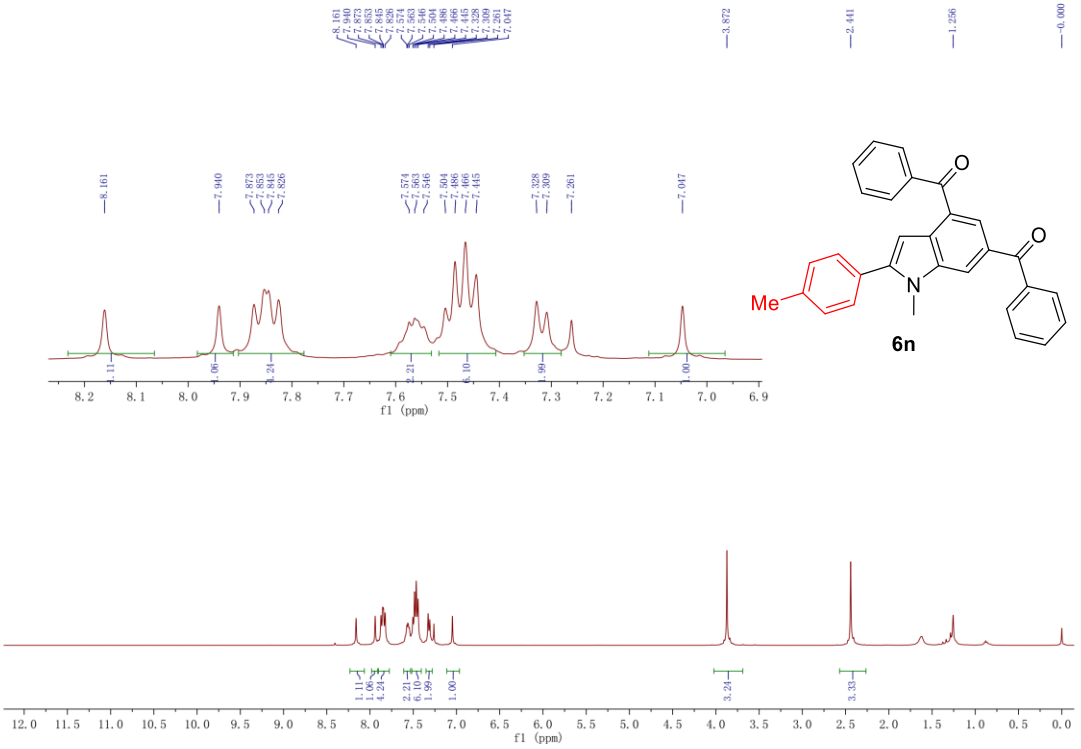
138.704
138.493
138.295
132.562
132.335
130.475
130.211
130.143
129.938
128.444
128.359
126.619
115.850
103.996
77.320
77.000
76.681
52.444
33.040
30.172
f1 (ppm)
Ph
O
MeO
N
6m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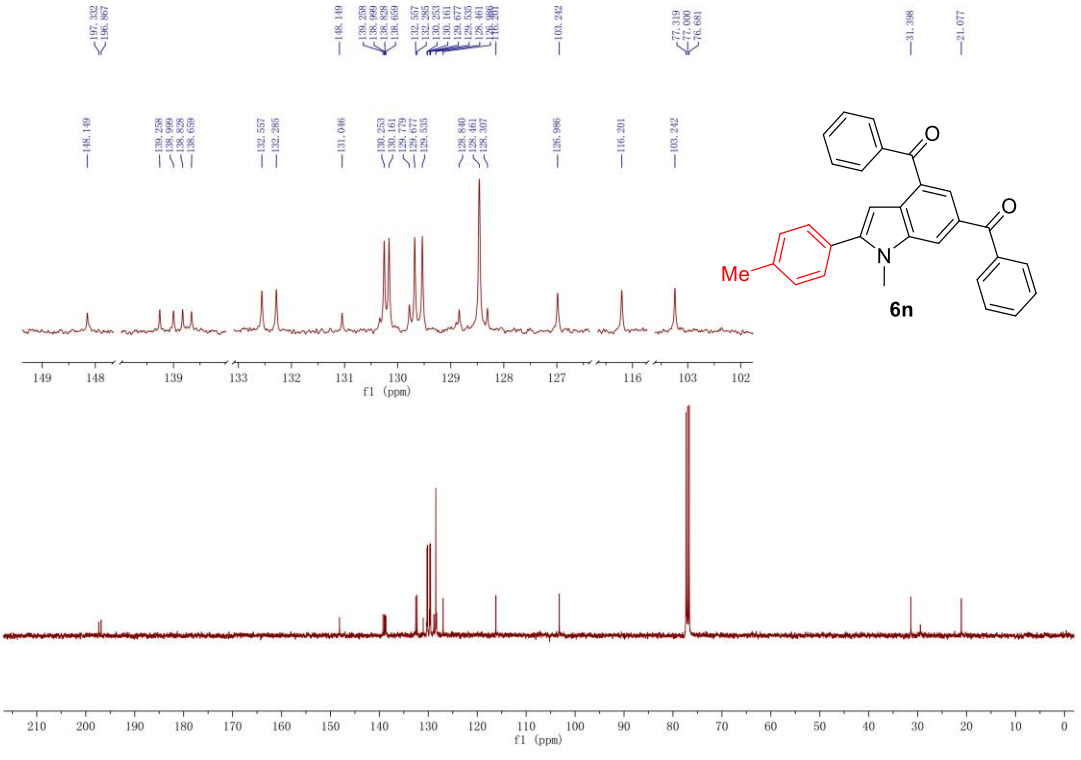
7.563
7.546
7.504
7.486
7.466
7.445
7.328
7.309
7.261
7.047
3.872
2.441
1.256
0.000
f1 (ppm)
Me
N
O
O
6n

f1 (ppm)


197.332
196.867
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139.258
138.999
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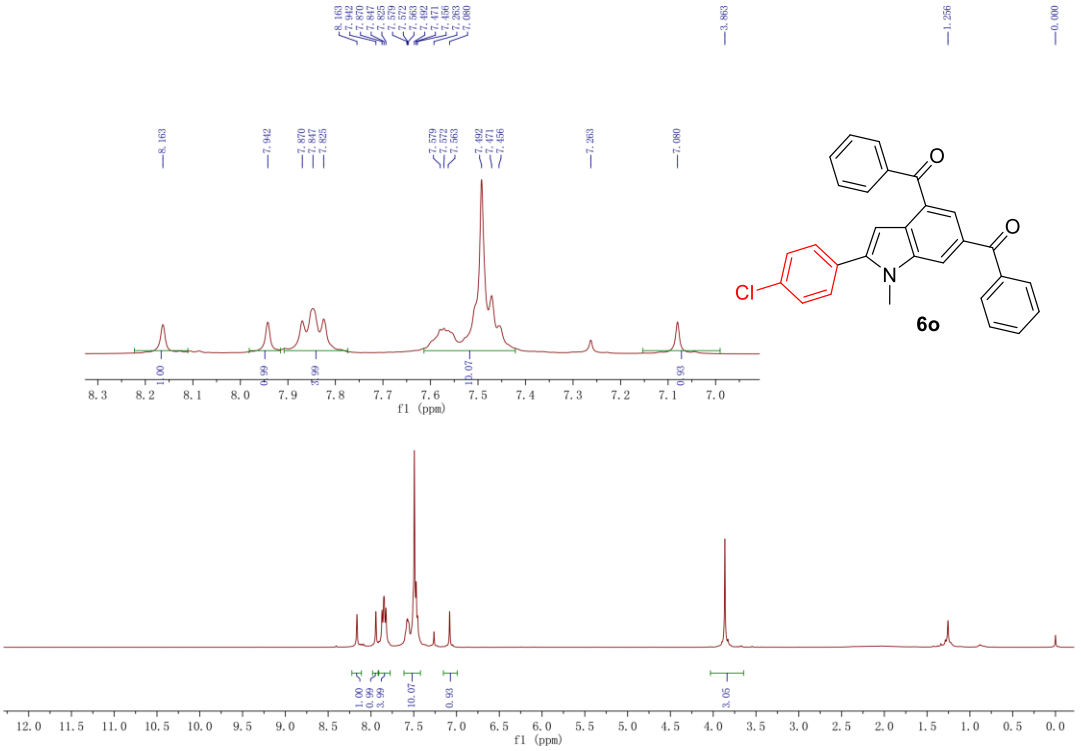
138.659
132.557
132.285
131.046
130.253
130.161
129.879
129.677
129.535
128.840
128.461
128.307
126.986
116.201
103.242
77.319
77.000
76.681
31.398
21.077
f1 (ppm)
Me
N
O
O
6n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7.825
7.579
7.572
7.563
7.492
7.471
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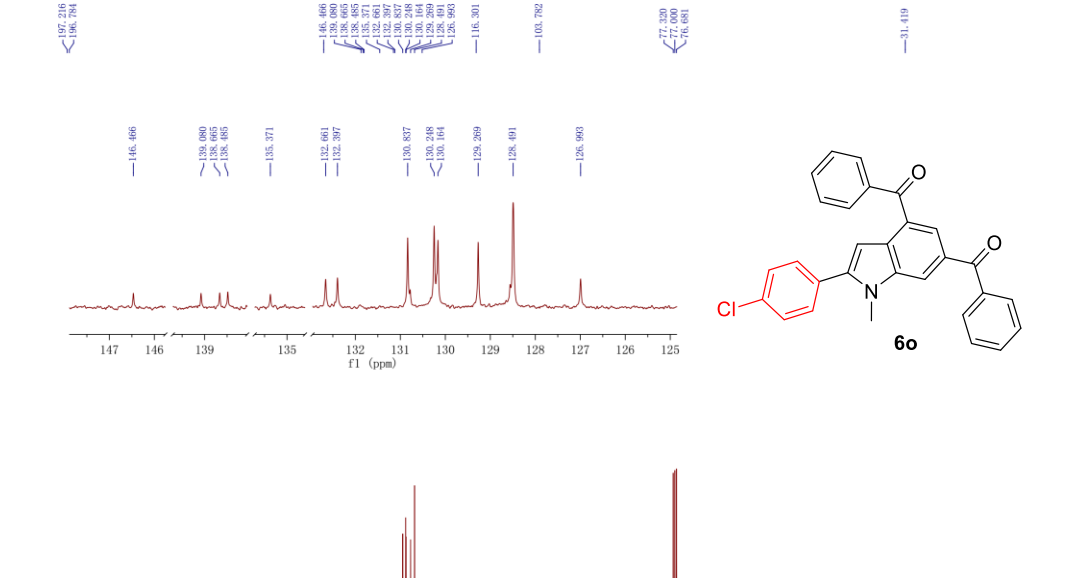
7.263
7.080
3.863
1.256
0.000
Cl
N
O
O
6o
f1 (ppm)


f1 (ppm)

197.216
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146.466
139.080
138.665
138.485
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132.661
132.397
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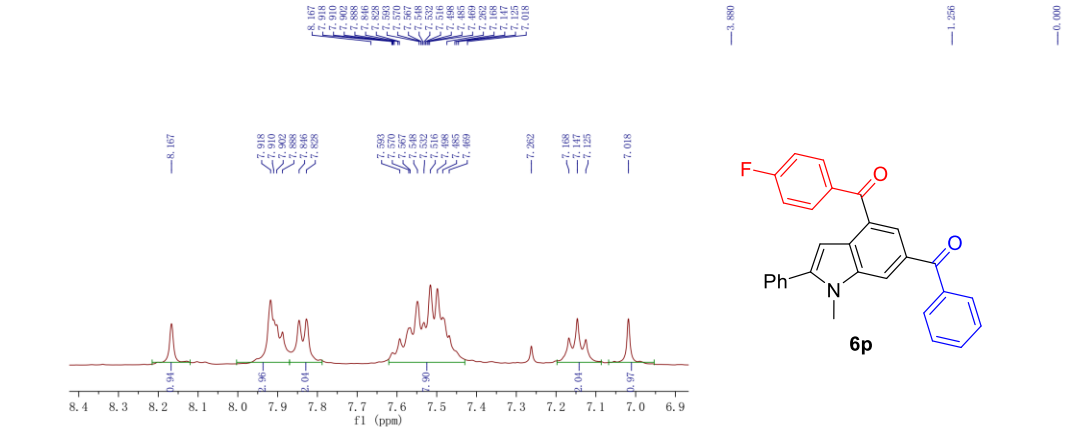
130.248
130.164
129.289
128.491
126.993
116.301
103.782
77.320
77.000
76.681
31.419
Cl
N
O
O
6o
f1 (ppm)


8.167
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7.902
7.888
7.846
7.828
7.593
7.570
7.567
7.548
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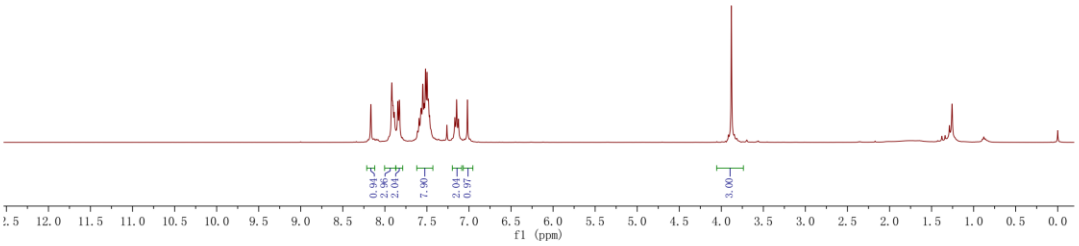
7.516
7.498
7.485
7.469
7.262
7.168
7.147
7.125
7.018
3.880
1.256
0.000
0.94
2.96
2.04
7.90
2.04
0.97
f1 (ppm)

F
O
O
Ph
N

6p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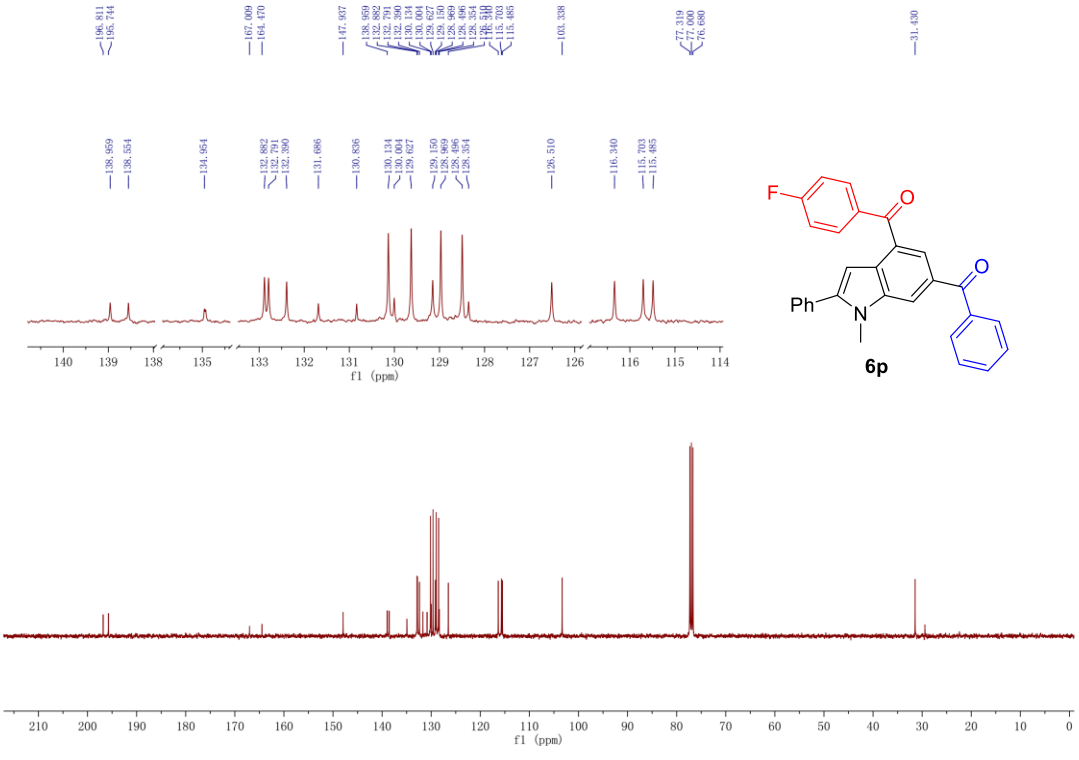
2.96
2.04
7.90
2.04
0.97
3.00
f1 (ppm)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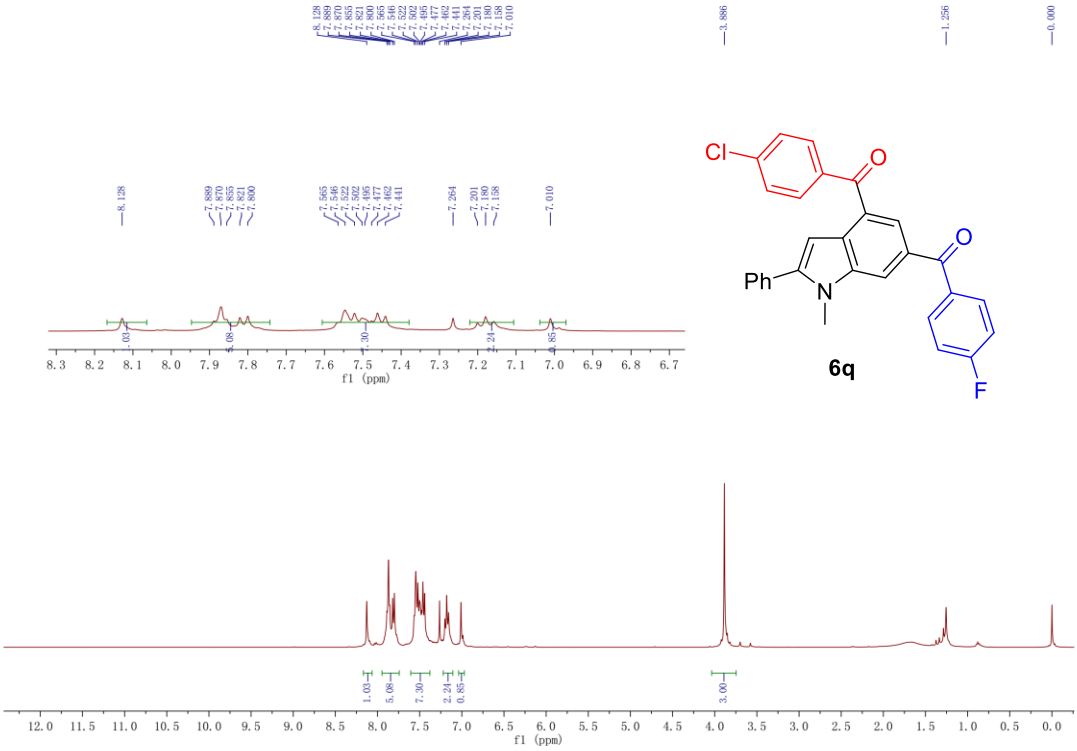
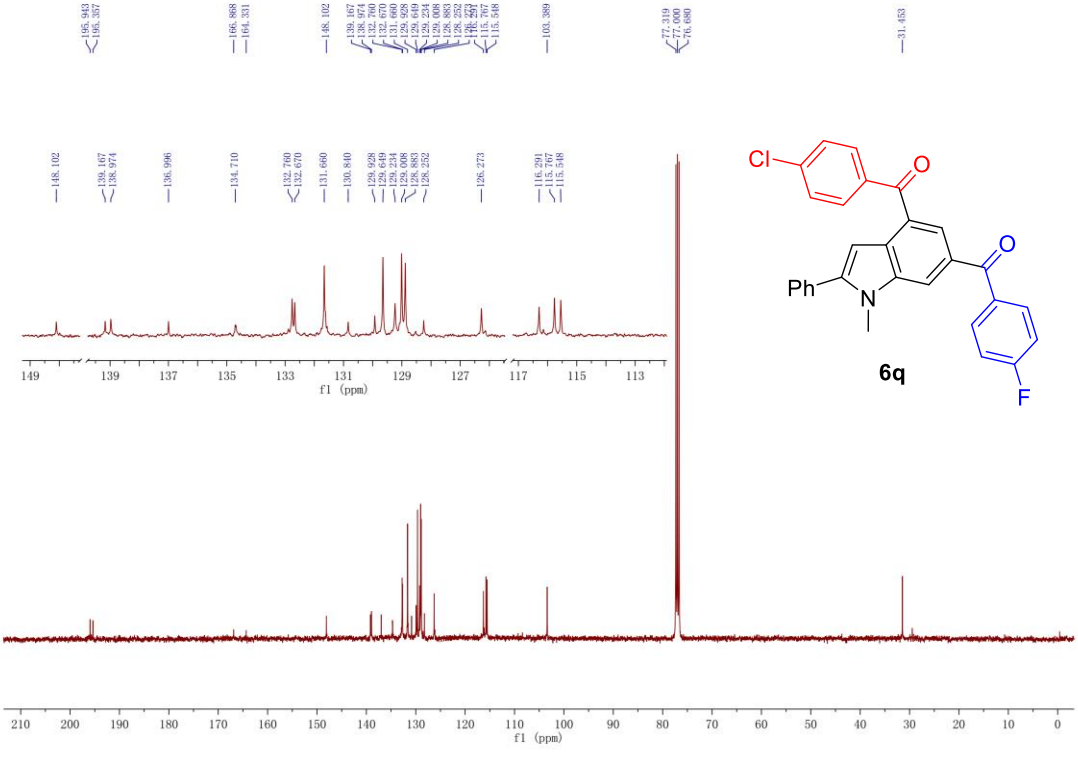
167.009
164.470
147.937
138.959
132.882
132.791
132.390
130.134
130.004
129.627
129.150
128.969
128.496
128.354
126.510
116.340
115.703
115.485
103.338
77.319
77.000
76.680
31.430
f1 (ppm)

F
O
O
Ph
N

6p


8.128
7.889
7.870
7.855
7.821
7.800
7.565
7.546
7.522
7.502
7.495
7.477
7.462
7.441
7.264
7.201
7.160
7.138
7.010
3.886
1.256
0.000
1.03
5.08
7.30
2.24
0.85
3.00
f1 (ppm)
Cl
O
Ph
N
O
F
6q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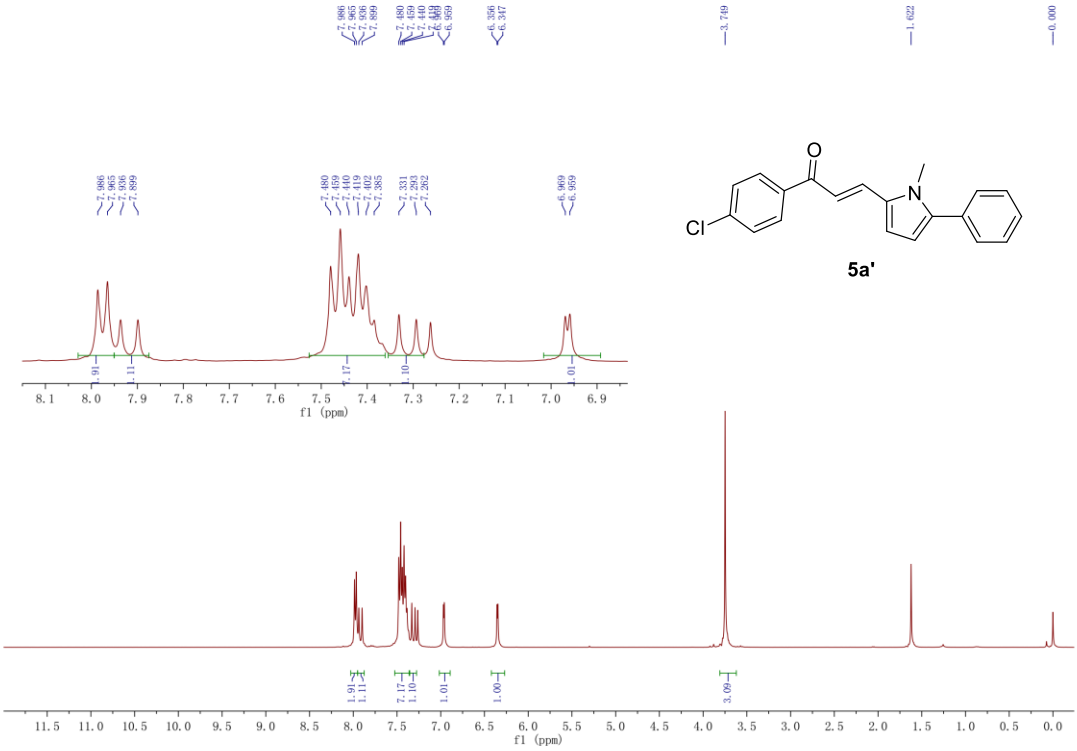
166.888
164.331
148.102
139.167
138.974
136.996
134.710
132.760
132.670
131.660
130.840
129.928
129.649
129.234
129.008
128.885
128.252
126.273
116.291
115.767
115.548
103.389
77.319
77.000
76.680
31.453
f1 (ppm)
Cl
O
Ph
N
O
F
6q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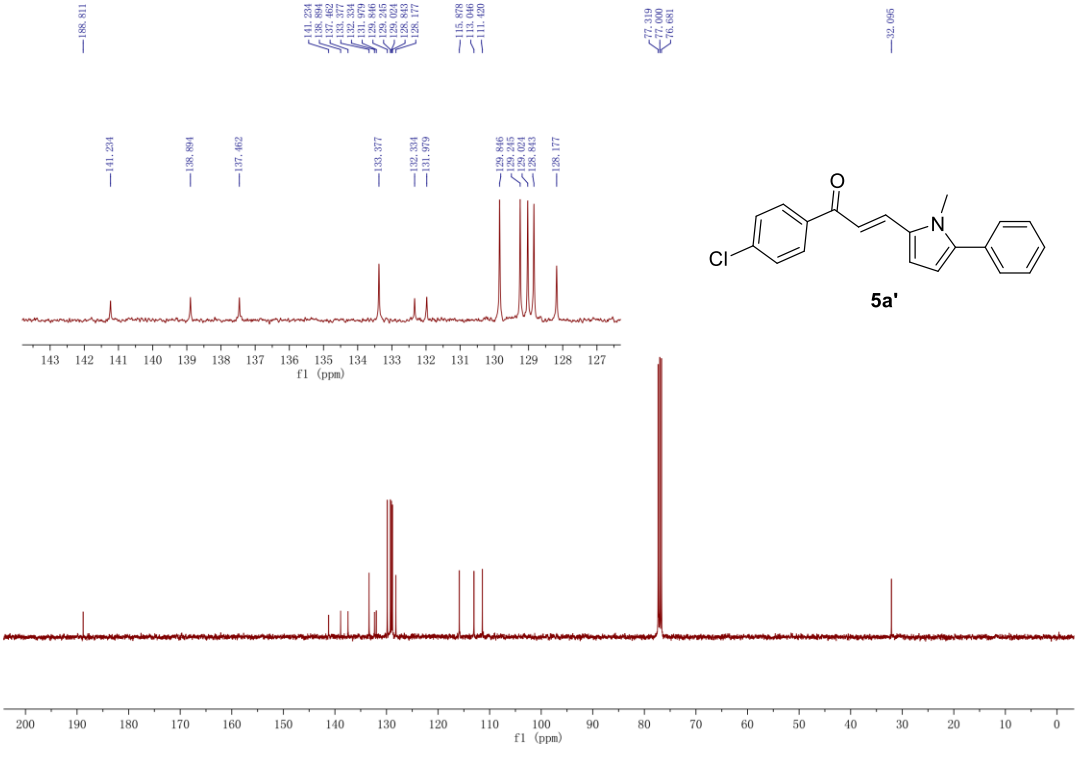
7.936
7.899
7.480
7.459
7.440
7.419
7.402
7.385
7.331
7.293
7.262
6.969
6.959
6.356
6.347
3.749
1.622
0.000
f1 (ppm)
1.91
1.11
7.17
1.10
1.01
1.00
3.09
O
N
Cl
5a'


188.811
141.234
138.894
137.462
133.377
132.334
131.979
129.846
129.245
129.024
128.843
128.177
115.878
113.046
111.420
77.319
77.000
76.681
32.095
f1 (ppm)
O
N
Cl
5a'

X-ray crystal structure of 4b:

X-ray ORTEP illustration of (7-methyl-1,3-diphenyl-5H-pyrrolo[1,2-a]azepin-8-yl) (4-nitrophenyl)methanone (**4b**) (50% probability ellipsoids)

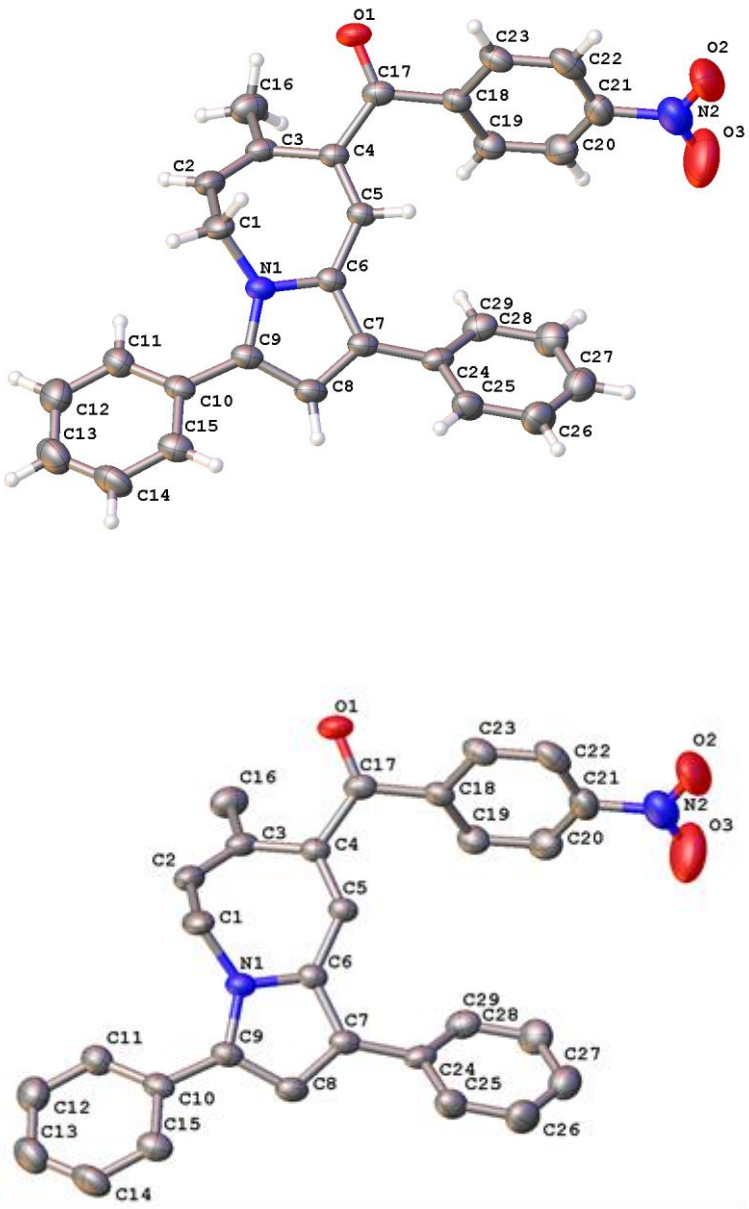


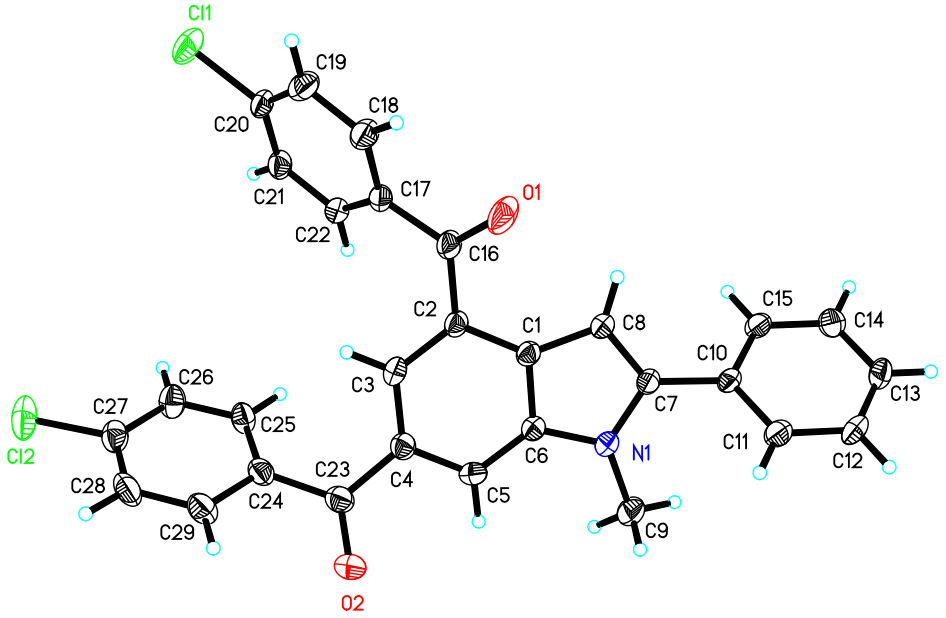
Table 1. Crystal data and structure refinement for mo_dm16500_0m (**4b**).

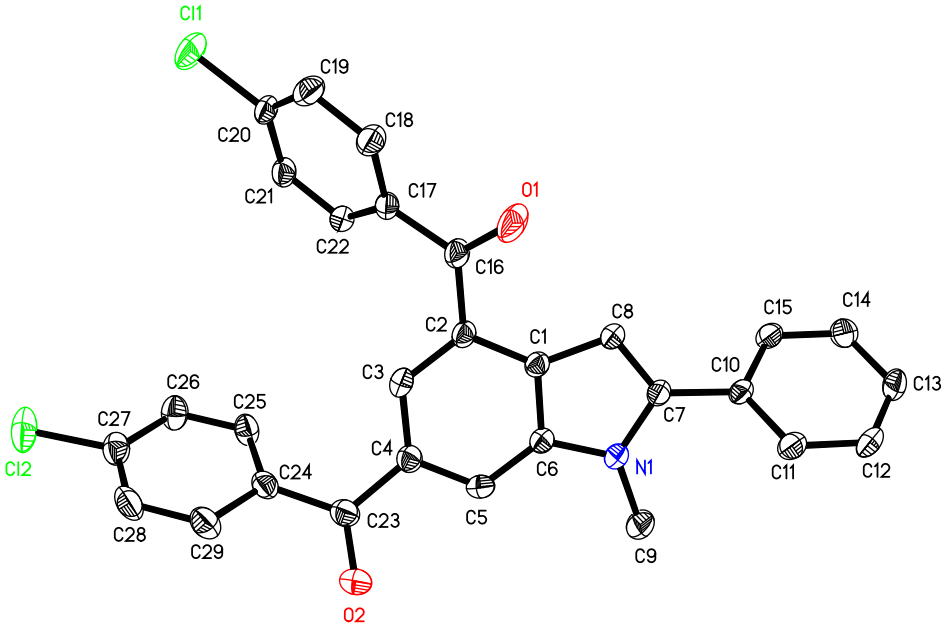
Identification code	mo_dm16500_0m	
Empirical formula	$C_{29}H_{22}N_2O_3$	
Formula weight	446.49	

Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.396(3) Å	α= 81.864(6)°.
	b = 12.966(4) Å	β= 89.495(5)°.
	c = 16.944(5) Å	γ = 89.905(5)°.
Volume	2260.9(12) $Å^3$	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	936	
Crystal size	0.22 x 0.18 x 0.15 mm^3	
Theta range for data collection	1.587 to 25.500°.	
Index ranges	-12<=h<=12, -15<=k<=15, -20<=l<=20	
Reflections collected	15906	
Independent reflections	8408 [R(int) = 0.0577]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6128	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8408 / 0 / 616	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0724, wR2 = 0.1784	
R indices (all data)	R1 = 0.1584, wR2 = 0.2253	
Extinction coefficient	0.0118(18)	
Largest diff. peak and hole	0.287 and -0.246 $e.Å^{-3}$	

X-ray crystal structure of 6a:

X-ray ORTEP illustration of (1-methyl-2-phenyl-1H-indole-4,6-diyl)bis((4-chloro phenyl)methanone)(4-nitrophenyl)methanone (**6a**) (50% probability ellipsoids)





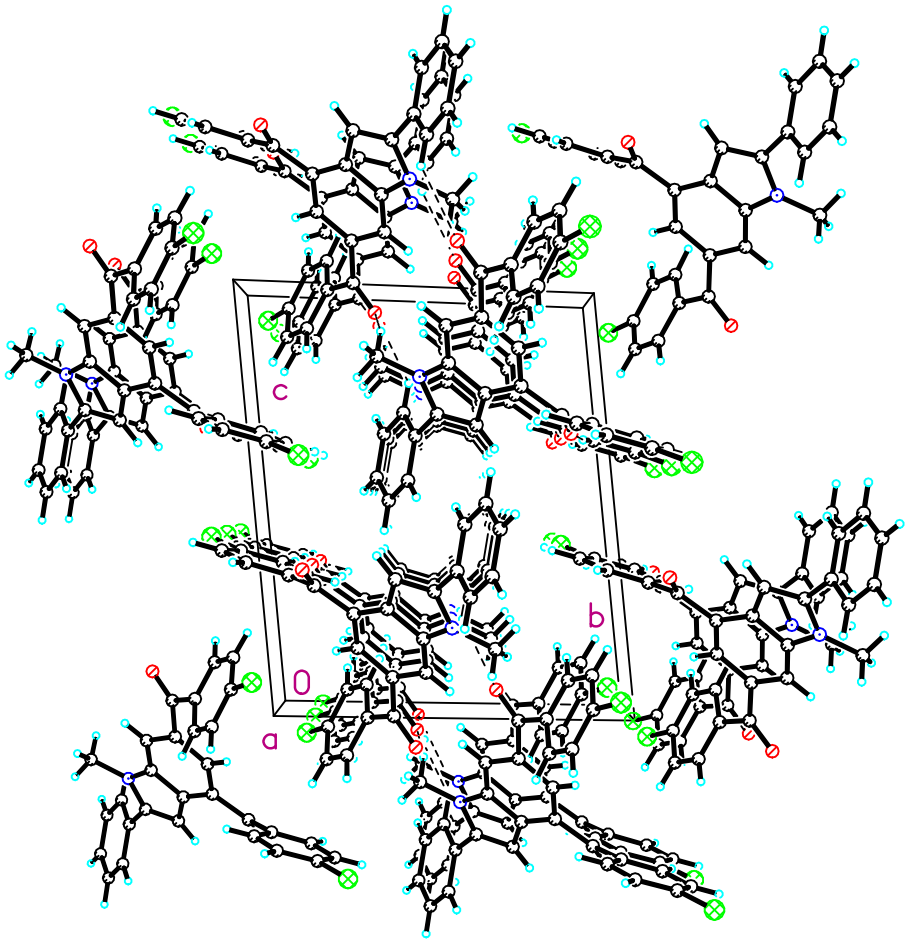


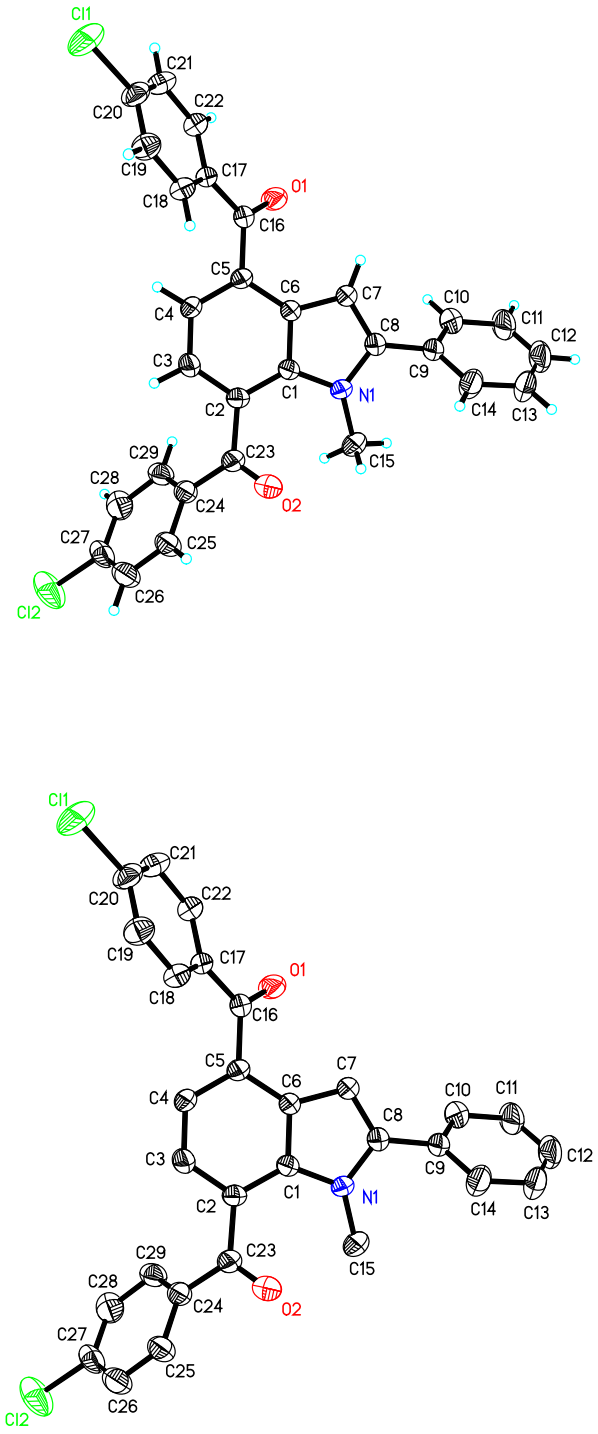
Table 1. Crystal data and structure refinement for cd16305 (**6a**).

Identification code	cd16305	

Empirical formula	$C_{29}H_{19}Cl_2NO_2$	
Formula weight	484.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6783(13) Å	α= 96.491(4)°.
	b = 11.4349(19) Å	β= 91.287(4)°.
	c = 13.505(2) Å	γ = 100.696(4)°.
Volume	1156.6(3) $Å^3$	
Z	2	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	0.309 mm^{-1}	
F(000)	500	
Crystal size	0.180 x 0.110 x 0.050 mm^3	
Theta range for data collection	1.825 to 24.999°.	
Index ranges	-9<=h<=8, -13<=k<=13, -16<=l<=15	
Reflections collected	6443	
Independent reflections	4052 [R(int) = 0.0317]	
Completeness to theta = 25.242°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5740	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4052 / 0 / 308	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1458	
R indices (all data)	R1 = 0.0984, wR2 = 0.1607	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.219 and -0.201 $e.Å^{-3}$	

X-ray crystal structure of 7a:

X-ray ORTEP illustration of (1-methyl-2-phenyl-1H-indole-4,7-diyl)bis((4-chloro phenyl)methanone) (**7a**) (50% probability ellipsoids)



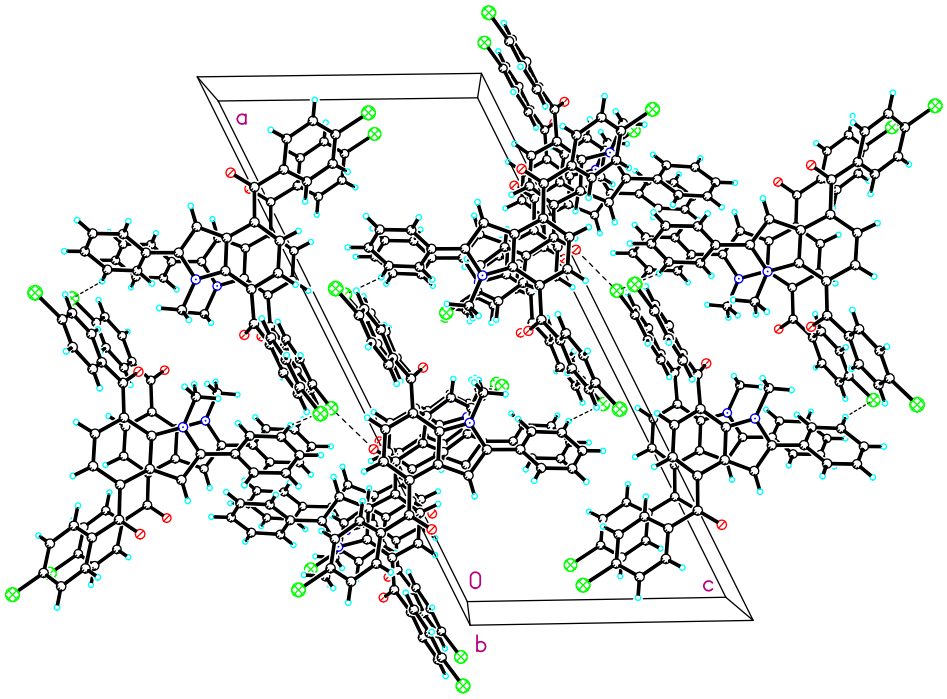


Table 1. Crystal data and structure refinement for cd16445 (**7a**).

Identification code	cd16445	
Empirical formula	$C_{29}H_{19}Cl_2NO_2$	
Formula weight	484.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 26.413(4) Å	α= 90°.
	b = 8.3862(13) Å	β= 115.572(3)°.
	c = 12.2342(18) Å	γ = 90°.
Volume	2444.5(6) $Å^3$	
Z	4	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.292 mm^{-1}	
F(000)	1000	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	1.898 to 25.495°.	
Index ranges	-31<=h<=31, -10<=k<=10,	

	-13<=l<=14	
Reflections collected	7073	
Independent reflections	4266 [R(int) = 0.0334]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6426	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4266 / 1 / 308	
Goodness-of-fit on F^2	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1364	
R indices (all data)	R1 = 0.0832, wR2 = 0.1542	
Absolute structure parameter	-0.09(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.316 and -0.201 e.$Å^{-3}$	