Supporting Information

Efficient synthesis of highly substituted pyrroles through a $Pd(OCOCF_3)_2$-catalyzed cascade reaction of 2-alkenal-1,3-dicarbonyl compounds with primary amines

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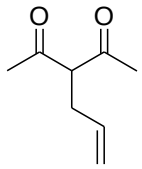
General information

The reagents (chemicals) were purchased from commercial sources, and used without further purification. Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). All products were characterized by their NMR and MS SPECTRA. ^{1}H and ^{13}C NMR spectra were recorded in deuterchloroform ($CDCl_3$) on a 400MHz instrument. Chemical shifts were reported in parts per million (ppm,δ) downfield from tetramethylsilane. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiple (m), and broad (br). Low-and high-resolution mass spectra (LRMS and HRMS) were measured on spectrometer.

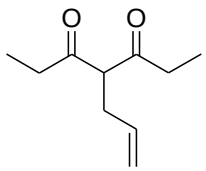
General procedures for the substrates preparation

3-allylpentane-2,4-dione (**S1**)
4-allylheptane-3,5-dione (**S2**)
2-allyl-1-phenylbutane-1,3-dione (**S3**)
ethyl 2-acetylpent-4-enoate (**S4**)
3-cinnamylpentane-2,4-dione (**S5**)
2-(2-d-allyl)-1-phenylbutane-1,3-dione (**S6**)



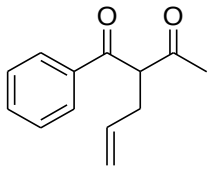
3-Allylpentane-2,4-dione (S1)

Under a nitrogen atmosphere, acetyl acetone (100 mmol) were dissolved in anhydrous acetone (100 mL) and anhydrous potassium carbonate (120 mmol, 1.2 eq.) was added. After stirring the solution at room temperature for 15min.the allyl bromide (120 mmol, 1.2 eq.) was added slowly and the reaction mixture was refluxed overnight at 80 °C. Acetyl acetone was completely consumed monitored by TLC. The reaction mixture was filtered and the filtrate was collected, then evaporated to dryness, the residue was purified by column silica gel (hexane/EtOAc, v/v, 40/1), 90% isolated yield. The spectroscopic data were in accordance with those reported in literature.[1]



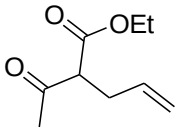
4-Allylheptane-3,5-dione (S2)

4-Allylheptane-3,5-dione (**S2**) was prepared similarly to the **S1**. And the spectroscopic data were in accordance with those reported in literature.[2]



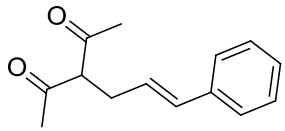
2-Allyl-1-phenylbutane-1,3-dione (S3)

1-Phenyl-1,3-butanedione (4.86g, 30 mmol) was dissolved in 20 mL anhydrous DMF, followed by added Sodium hydride (864 mg, 36 mmol, 1.2 eq) at 0 °C, stirred for 30 min. Allyl bromide (36 mmol, 4.4 g, 1.2 eq) was added slowly over a period of 30 min at 0 °C, then stirred overnight at room temperature. Complete reaction was observed by thin layer chromatography. 100 mL water was added to the reaction mixture, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), the organic layer was washed with brine and dried with Na_2SO_4, and the solvents were evaporated. The residue was purified by column chromatography (hexane/EtOAc; v/v, 60/1 then 20/1) giving the product (4.8 g, 80%) as a colorless oil. The spectroscopic data were in accordance with those reported in literature.[2]



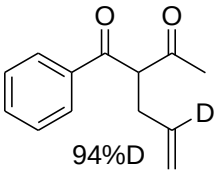
Ethyl 2-acetylpent-4-enoate (S4)

This compound was synthesized according to (**S3**). The spectroscopic data were in accordance with those reported in literature.[3]



***trans*-3-Cinnamylpentane-2,4-dione (S5)**

trans-3-Cinnamylpentane-2,4-dione (S5) was prepared similarly to the **S1**. And the spectroscopic data were in accordance with those reported in literature.[4]



2-(2-D-Allyl)-1-phenylbutane-1,3-dione (S6)

2-Allyl-1-phenylbutane-1,3-dione (648 mg, 4 mmol) and 2-deuteriated allyl alcohol[5] (354mg, 6 mmol) were suspended in water (10 mL) at rt under argon, then 1-adamantanecarboxylic acid (0.4 mmol) and $Pd(PPh_3)_4$ (0.2 mmol) were added. The solution was heated to 8 °C in an oil bath and stirred for 45 min. After the mixture was cooled to rt, water (15 mL) and brine (15 mL) were added. The organic materials were extracted with ethyl acetate, dried over sodium sulfate, and concentrated under vacuum. The crude was purified by silica gel to give the target compound (552 mg,

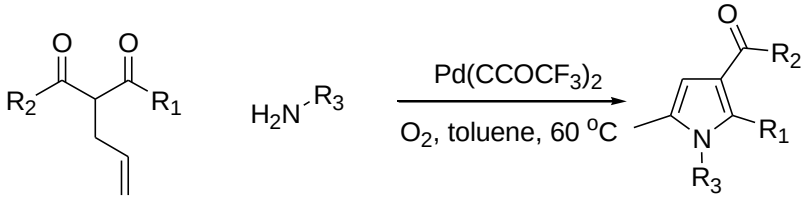
68% yield).[6] ^{1}HNMR: (400 MHz, $CDCl_3$) keto/enol (20:1) δ 17.06 (s, 0.03H), 7.98-7.96 (d, 2H, *J* =8.0 Hz), 7.60-7.56 (t, 1H, *J* = 8.0 Hz), 7.50-7.46 (t, 2H, *J* = 8.0 Hz), 5.07 (s, 1H), 5.01 (s, 1H), 4.56-4.52 (t, 1H, *J* = 8.0 Hz), 3.03 (m, 0.09H), 2.73-2.71 (m, 2H), 2.23 (s, 0.15H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.32, 197.82, 138.21, 135.94, 135.72, 130.81, 130.65, 118.96, 64.71, 34.92, 29.93 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{13}O_2H_{13}DNa$ 226.0954, found: 226.0959.

Table S1. Optimization of reaction conditions.

entry[a]	solvent	catalyst	oxidant	yield (%)[b]
1	toluene	$Pd(OAc)_2$	air	45
2	CH_3CN	$Pd(OAc)_2$	air	23
3	THF	$Pd(OAc)_2$	air	25
4	DMF	$Pd(OAc)_2$	air	32
5	$ClCH_2CH_2Cl$	$Pd(OAc)_2$	air	40
6	DMA	$Pd(OAc)_2$	air	18
7	DMSO	$Pd(OAc)_2$	air	12
8	xylenes	$Pd(OAc)_2$	air	50
9	xylenes	$Pd(OAc)_2$	$Cu(OAc)_2$	21
10	xylenes	$Pd(OAc)_2$	AgOAc	trace
11	xylenes	$Pd(OAc)_2$	O_2	58
12	xylenes	$PdCl_2$	O_2	28
13	xylenes	$PdCl_2(PPh_3)_2$	O_2	14
14	xylenes	$PdCl_2(CH_3CN)_2$	O_2	trace
15	xylenes	$Pd(PPh_3)_4$	O_2	17
16[c]	xylenes	$Pd(OCOCF_3)_2$	O_2	82
17[d]	toluene	$Pd(OCOCF_3)_2$	O_2	86
18[e]	toluene	$Pd(OCOCF_3)_2$	O_2	85
19[f]	toluene	$Pd(OCOCF_3)_2$	O_2	88

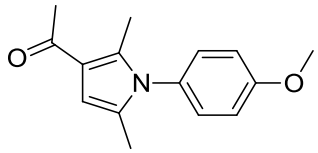
[a] A solution of **1a** (1.2 mmol) and **1b** (0.6 mmol) with catalyst (0.12 mmol) in the solvent (2 mL) was stirred at 60 °C for 16 h;. [b] Isolated yield; [c] The reaction time is 2 h; [d] The reaction time is 1.5 h; [e]10 mol% Catalyst was used with the reaction time of 9 h; [f] 5 mol% catalyst was used with the reaction time of 16 h.

General procedures for the synthesis of substituted pyrrole derivatives



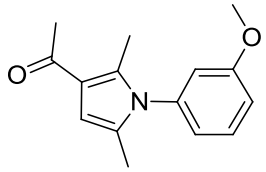
S1, S2, S3, S4, S5, S6

All the reactions were carried out under aerobic atmosphere. To a solution of α-allyl diketones (1.2 mmol), and amines (0.6 mmol) in dry toluene (2 mL) was added $Pd(OCOCF_3)_2$ (0.03 mmol, 0.05 eq.). The reaction mixture with O_2 balloon was stirred at 60 °C overnight. The amines were completely consumed monitored by TLC. The mixture was filtered through celite, washed with methanol, the filtration was concentrated, and the residue was purified by column chromatography, hexane/EtOAc (v/v, 20/1 then 10/1) as eluent, giving the desired pyrrole products as an oil.



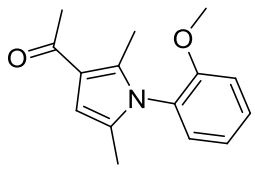
1-(1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4a

Isolated yield 88%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.06 (m, 2H), 6.98-6.96 (m, 2H), 6.26 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H), 1.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.92, 159.55, 136.28, 130.29, 129.04, 128.94, 120.29, 114.92, 108.00, 55.68, 28.71, 13.01, 12.92 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{17}NNaO_2$: 266.1157, found: 266.1151.



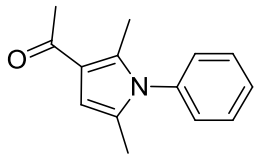
1-(1-(3-Methoxyphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4b

Isolated yield 86%, brown oil, ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.41-7.37 (t, 1H, J = 8 Hz), 7.01-6.98 (dd, 1H, J_1 = 4 Hz, J_2 = 8 Hz), 6.77-6.75 (d, 1H, J = 8 Hz), 6.70-6.69 (t, 1H , J = 4 Hz), 6.31 (s, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.06, 160.24, 138.38, 135.76, 130.08, 128.58, 120.38, 120.23, 114.24, 113.78, 107.89, 55.44, 28.60, 12.88, 12.58 ppm. HRMS(ESI) calcd for $[M+Na]^+$ $C_{15}H_{17}NNaO_2$: 266.1157, found: 266.1170.



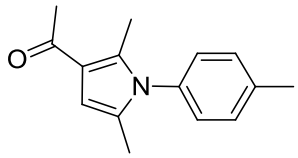
1-(1-(2-Methoxyphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4c

Isolated yield 70%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.45 (m, 1H), 7.14-7.06 (m, 3H), 6.36 (s, 1H), 3.80 (s, 3H), 2.44 (s, 3H), 2.28 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.06, 155.50, 136.50, 130.35, 129.76, 128.90, 125.85, 120.85, 120.30, 112.09, 107.64, 55.72, 28.63, 12.58, 12.27 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{17}NNaO_2$: 266.1157, found: 266.1163.



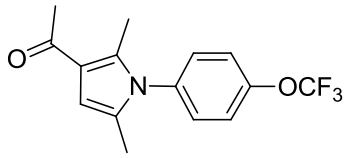
1-(2,5-Dimethyl-1-phenyl-1H-pyrrol-3-yl)ethanone 4d

Isolated yield 77%, an oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.42 (m, 3H), 7.17-7.15 (m, 2H), 6.32 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.99, 137.24, 135.69, 129.33, 128.56, 128.53, 127.94, 120.33, 107.88, 28.55, 12.85, 12.58 ppm. HRMS (ESI) calcd for $C_{14}H_{15}NO$, 213.1154; found, 213.1144.



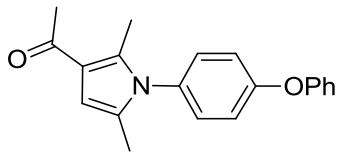
1-(2,5-Dimethyl-1-p-tolyl-1H-pyrrol-3-yl)ethanone 4e

Isolated yield 82%, brown oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.05-7.02 (m, 2H), 6.30 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.98, 138.53, 135.84, 134.57, 129.93, 128.62, 127.63, 120.22, 107.73, 28.51, 21.08, 12.84, 12.57 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{17}NNaO$: 250.1208, found: 250.1187.



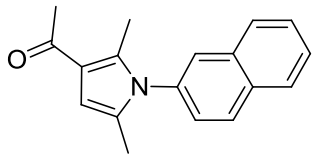
1-(2,5-Dimethyl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrrol-3-yl)ethanone 4f

Isolated yield 81%, an oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (d, 2H,*J* = 8 Hz), 7.26-7.20 (m, 2H), 6.33 (s, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.11, 149.08, 135.83, 135.68, 129.66, 128.58, 121.83, 121.41, 120.75, 119.36, 108.34, 28.69, 12.98, 12.69 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{15}H_{14}F_3NNaO_2$: 320.0874, found: 320.0888.



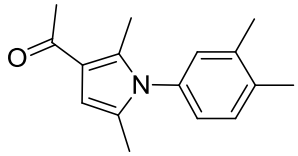
1-(2,5-Dimethyl-1-(4-phenoxyphenyl)-1H-pyrrol-3-yl)ethanone 4g

Isolated yield 84%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.36 (m, 2H), 7.19-7.05 (m, 7H), 6.32 (s, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.04, 157.88, 156.12, 135.98, 131.93, 130.07, 129.37, 128.83, 124.29, 120.46, 119.78, 118.69, 107.98, 28.67, 13.01, 12.74 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{20}H_{19}NNaO_2$: 328.1313, found: 328.1304.



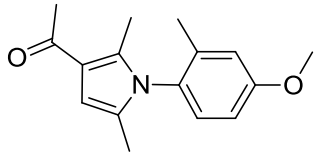
1-(2,5-Dimethyl-1-(naphthalen-2-yl)-1H-pyrrol-3-yl)ethanone 4h

Isolated yield 84%, yellow oil, ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.97-7.92 (m, 2H), 7.89-7.87 (m, 1H), 7.68-7.67 (m., 1H), 7.60-7.56 (m, 2H), 7.27-7.24 (dd, 1H, J_1 = 4 Hz, J_2 = 8 Hz), 6.38 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ 195.00, 135.88, 134.63, 133.14, 132.70, 129.38, 128.74, 127.90, 127.76, 126.95, 126.74, 125.53, 120.44, 108.00, 28.57, 12.95, 12.66 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{18}H_{17}NNaO$: 286.1208, found: 286.1190.



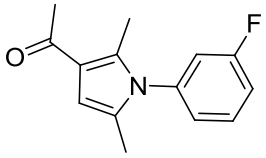
1-(1-(3,4-dimethylphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4i

Isolated yield 85%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.21 (m, 1H), 6.93-6.87 (m, 2H), 6.30 (s, 1H), 2.41 (s, 3H), 2.32 (s, 3H), 2.30 (s, 6H), 1.97(s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ 195.00, 137.94, 137.28, 135.94, 134.98, 130.45, 128.88, 128.73, 125.23, 120.28, 107.77, 28.63, 19.85, 19.52, 12.96, 12.70 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{19}NNaO$: 264.1364, found : 264.1360.



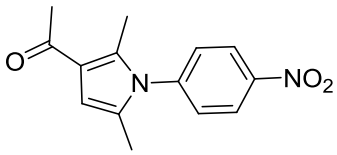
1-(1-(4-Methoxy-2-methylphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4j

Isolated yield 74%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.014-6.997 (d, 1H, J = 6.8 Hz), 6.863-6.858 (d, 1H, J = 2 Hz), 6.831-6.808 (dd, 1H, J_1 = 2 Hz, J_2 = 6.8 Hz), 6.32 (s, 1H), 3.84 (s, 3H), 2.41 (s, 3H), 2.22 (s, 3H), 1.89 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.05, 159.72, 137.66, 135.81, 129.25, 129.16, 128.43, 120.34, 116.02, 112.10, 107.72, 55.41, 28.54, 17.38, 12.54, 12.30 ppm. HRMS(ESI) calcd for $[M+Na]^+$ $C_{16}H_{19}NNaO_2$: 280.1313, found: 280.1290.



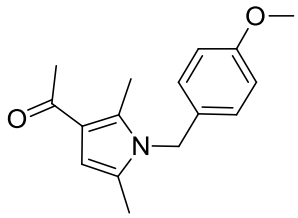
1-(1-(3-Fluorophenyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4k

Catalyst with 20 mmol% was used, isolated yield 50%, ^{1}H NMR (500 MHz, $CDCl_3$) 7.51-7.46 (m, 1H), 7.21-7.17 (dt, 1H, J = 10.0 Hz), 7.00-6.99 (d, 1H, J = 5.0 Hz), 6.94-6.92 (dt, 1H, J_1 = 10.0 Hz, J_2 = 5.0 Hz), 6.33 (s, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.00 (s, 3H) ppm, ^{13}C NMR (125 MHz, $CDCl_3$) 195.00, 163.69, 161.71, 138.74, 138.67, 135.48, 130.64, 130.57, 128.39, 123.96, 123.94, 120.58, 115.92, 115.76, 115.68, 115.51, 108.20, 28.58, 12.76, 12.52 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{14}FNONa$: 254.0957, found: 254.0956.



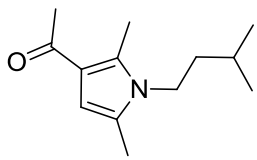
1-(2,5-dimethyl-1-(4-nitrophenyl)-1H-pyrrol-3-yl)ethanone 4l

Catalyst with 20 mmol% was used, isolated yield 40%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40-8.38 (d, 2H, J = 10.0 Hz), 7.42-7.40 (d, 2H, J = 10.0 Hz), 6.37 (s, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (125 MHz,$CDCl_3$) 195.00, 147.46, 142.96, 135.08, 129.10, 128.18, 124.79, 121.20, 109.05, 28.67, 12.85, 12.67 ppm; HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{14}N_2O_3Na$: 281.0902, found: 281.0903.



1-(1-(4-Methoxybenzyl)-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4m

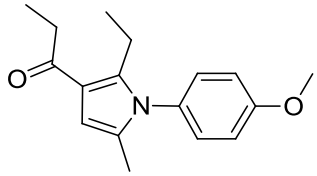
Isolated yield 91%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84-6.80 (m, 4H), 6.27 (s, 1H), 4.95 (s, 2H), 3.75 (s, 3H), 2.48 (s, 3H), 2.38 (s, 3H), 2.12 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.90, 158.73, 134.94, 128.56, 127.67, 126.63, 120.03, 114.11, 108.23, 55.10, 45.93, 28.44, 12.06, 11.66 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{19}NNaO_2$: 280.1313, found: 280.1331.



1-(1-Isopentyl-2,5-dimethyl-1H-pyrrol-3-yl)ethanone 4n

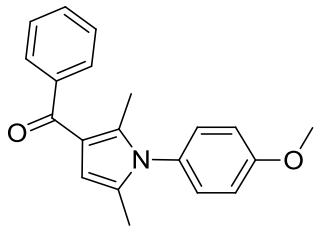
Isolated yield 90%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (s, 1H), 3.74-3.70 (t, 2H, J = 8 Hz), 2.52 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H), 1.70-1.60 (m, 1H), 1.49-1.43

(m, 2H), 0.96-0.95 (d, 6H, *J* = 4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.82, 134.38, 127.01, 119.88, 108.18, 41.92, 39.45, 28.46, 26.27, 22.45, 12.15, 11.74 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{13}H_{21}NNaO$: 230.1521, found: 230.1508.



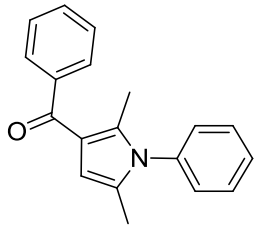
1-(2-Ethyl-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)propan-1-one 4o

Isolated yield 83%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.09 (m, 2H), 7.00-6.96 (m, 2H), 6.30 (s, 1H), 3.87 (s, 3H), 2.82-2.77 (q, 2H, *J* = 8 Hz), 2.75-2.69 (q, 2H, *J* = 8 Hz), 1.95 (s, 3H), 1.20-1.16 (t, 3H, *J* = 8 Hz), 1.01-0.97 (t, 3H, *J* = 8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.58, 159.51, 142.34, 129.96, 129.23, 128.75, 118.83, 114.38, 107.06, 55.47, 33.43, 19.65, 14.01, 12.58, 8.56 ppm. HRMS(ESI) calcd for $[M+Na]^+$ $C_{17}H_{21}NNaO_2$: 294.1470, found: 294.1494.



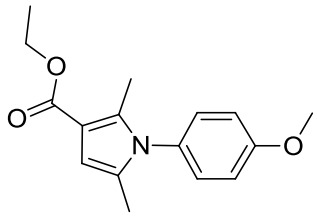
(1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrol-3-yl)(phenyl)methanone 4p

Isolated yield 78%, an oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.51-7.42 (m, 3H), 7.16-7.12 (m, 2H), 7.02-6.98 (m, 2H), 6.18 (s. 1H), 3.86 (s, 3H), 2.33 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.30, 159.44, 140.88, 137.67, 130.80, 129.98, 128.93, 128.92, 128.63, 127.83, 119.25, 114.48, 109.55, 55.42, 12.97, 12.56 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{20}H_{19}NNaO_2$: 328.1313, found: 328.1298.



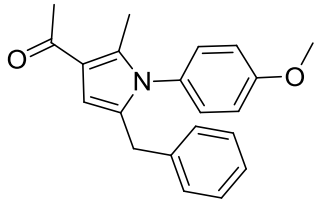
(2,5-Dimethyl-1-phenyl-1H-pyrrol-3-yl)(phenyl)methanone 4q

Isolated yield 75%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2H), 7.54-7.43 (m, 6H), 7.27-7.21 (m, 2H), 6.21 (s, 1H), 2.34 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.31, 140.85, 137.37, 137.30, 130.86, 129.37, 128.94, 128.59, 128.33, 127.96, 127.85, 119.46, 109.81, 13.00, 12.60 ppm. HRMS (ESI) calcd for $[M+Na]^+$ $C_{19}H_{17}NNaO$: 298.1208, found: 298.1222.



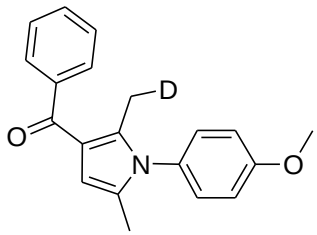
Ethyl 1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole-3-carboxylate 4r

Isolated yield 85%, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09-7.07 (d, 2H, *J* = 8 Hz), 6.99-6.97 (d, 2H, *J* = 8 Hz), 6.34 (s, 1H), 4.29-4.24 (q, 2H, *J* = 8 Hz), 3.85 (s, 3H), 2.27 (s, 3H), 1.95 (s, 3H), 1.36-1.32 (t, 3H, *J* = 8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.68, 159.33, 136.43, 130.27, 129.05, 128.91, 114.39, 111.04, 107.07, 59.12, 55.39, 14.49, 12.54, 12.26 ppm. HRMS(ESI) calcd for $[M+Na]^+$ $C_{16}H_{19}NNaO_3$: 296.1236, found: 296.1238.



1-(5-Benzyl-1-(4-methoxyphenyl)-2-methyl-1H-pyrrol-3-yl)ethanone 4s

Isolated yield 60%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 3H), 6.97-6.88 (m, 6H), 6.31 (s, 1H), 3.85 (s, 3H), 3.67 (s, 2H), 2.43 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ 195.29, 159.64, 138.93, 136.53, 132.54, 132.24, 129.35, 128.59, 128.25, 126.18, 120.42, 114.37, 108.81, 55.54, 33.20, 28.62, 12.84. HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{22}NO_2$: 320.1651, found: 320.1677.



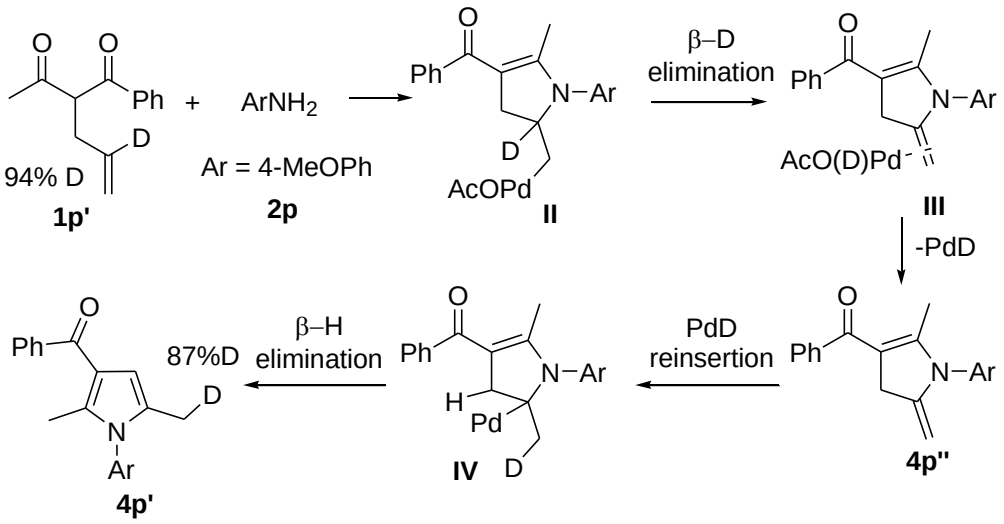
(1-(4-Methoxyphenyl)-2-D,5-dimethyl-1H-pyrrol-3-yl)(phenyl)methanone 4p'

87% D, ^{1}H NMR: (400 MHz,$CDCl_3$) δ7.83-7.82 (m, 2H), 7.50-7.73 (m, 3H), 7.16-7.13 (m, 2H), 7.03-6.99 (m 2H), 6.18 (s, 1H), 3.87 (s, 3H), 2.33 (s, 3H), 1.98 (s, 0.04H), 1.96 (m, 1.6 H); ^{13}C NMR (100 MHz,$CDCl_3$): δ194.13, 161.44, 142.90, 139.70, 132.82, 132.02, 130.95, 130.61, 129.85, 121.31, 116.49, 111.56, 57.45, 14.99, 14.57, 14.54-14.15 (t, *J* = 20.0 Hz). HRMS (ESI) cacld for $[M+Na]^+$ $C_{20}H_{18}DNO_2Na$: 329.1376, found: 329.1379.

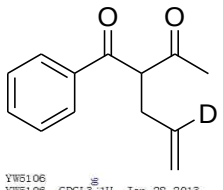
Deuterated experiment study

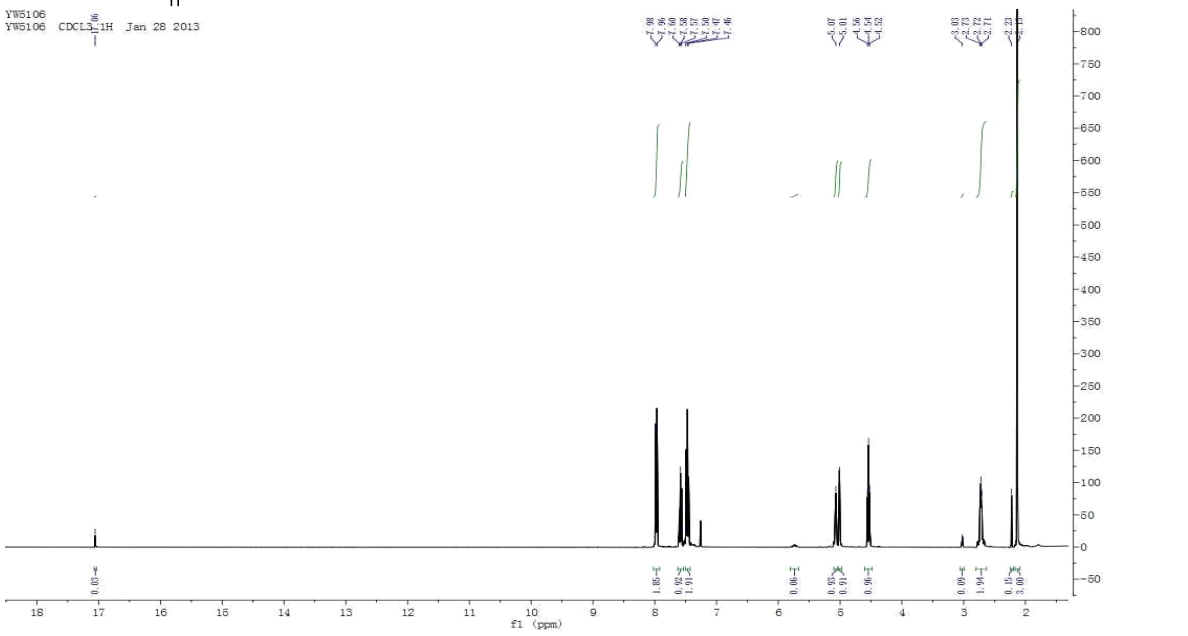
To investigate the mechanism of palladium-catalyzed cascade Wacker-type reactions, we designed and prepared the deuterated 2-allyl-1-phenylbutane-1,3-dione

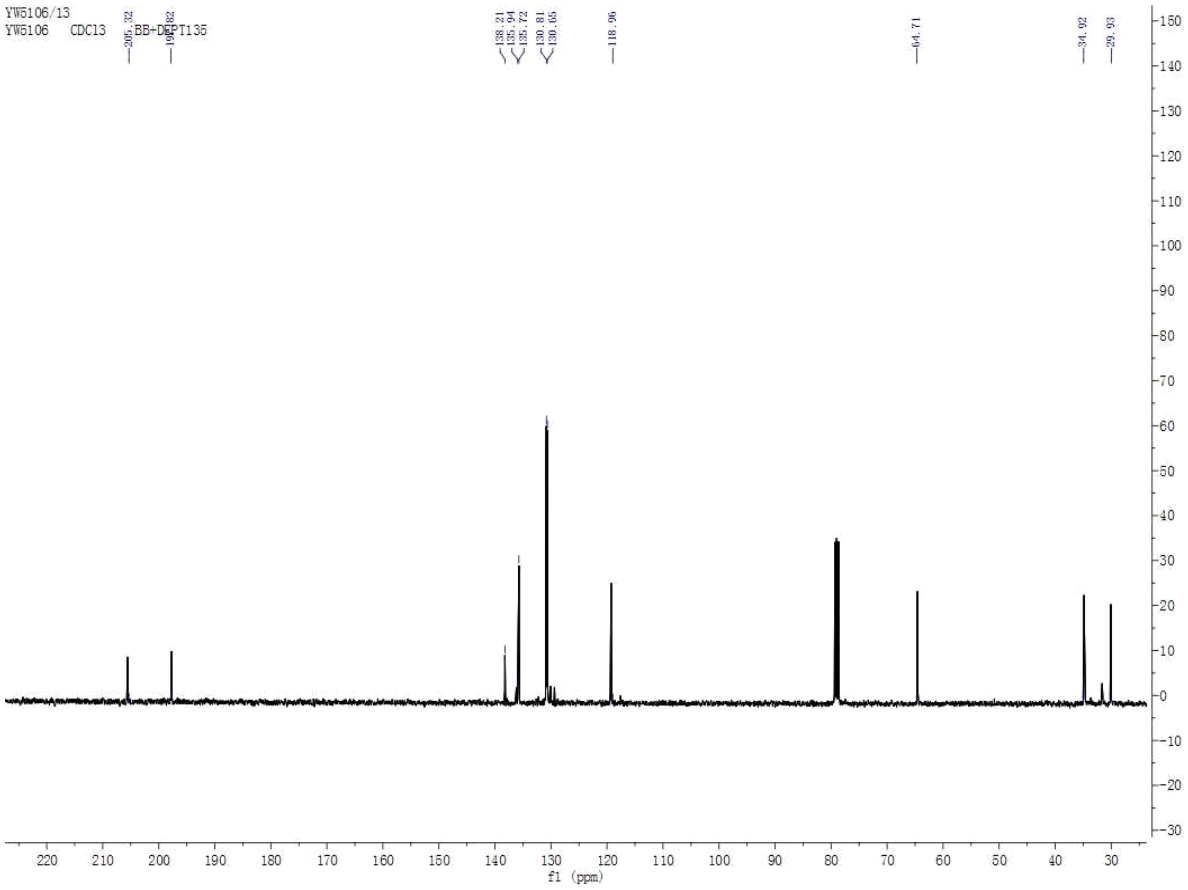
(**1p'**, 94% D), the final result shows that the product 4**p'** has 87% D, which indicates that the Pd-D reinsertion does happen (Scheme S1).

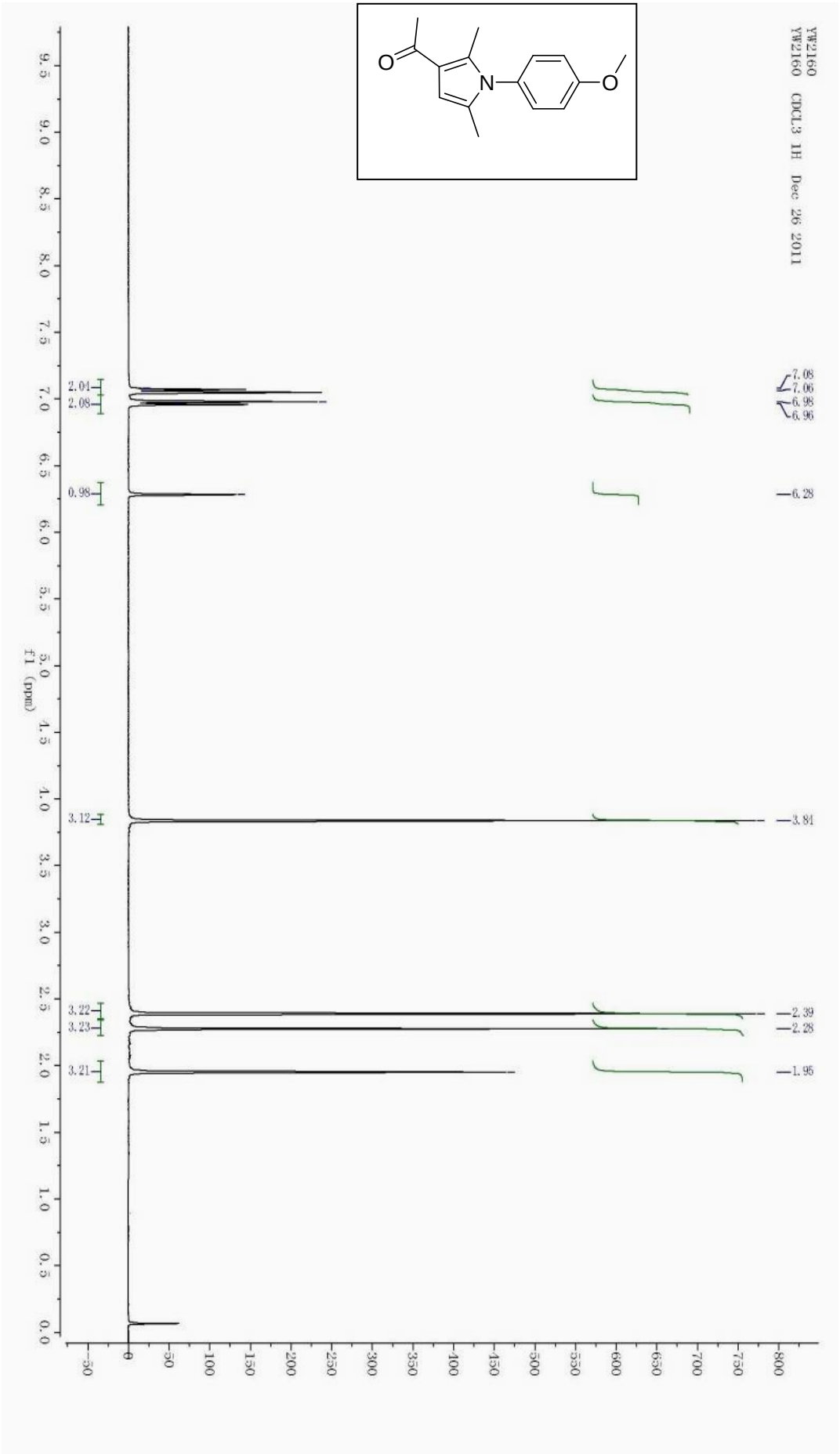


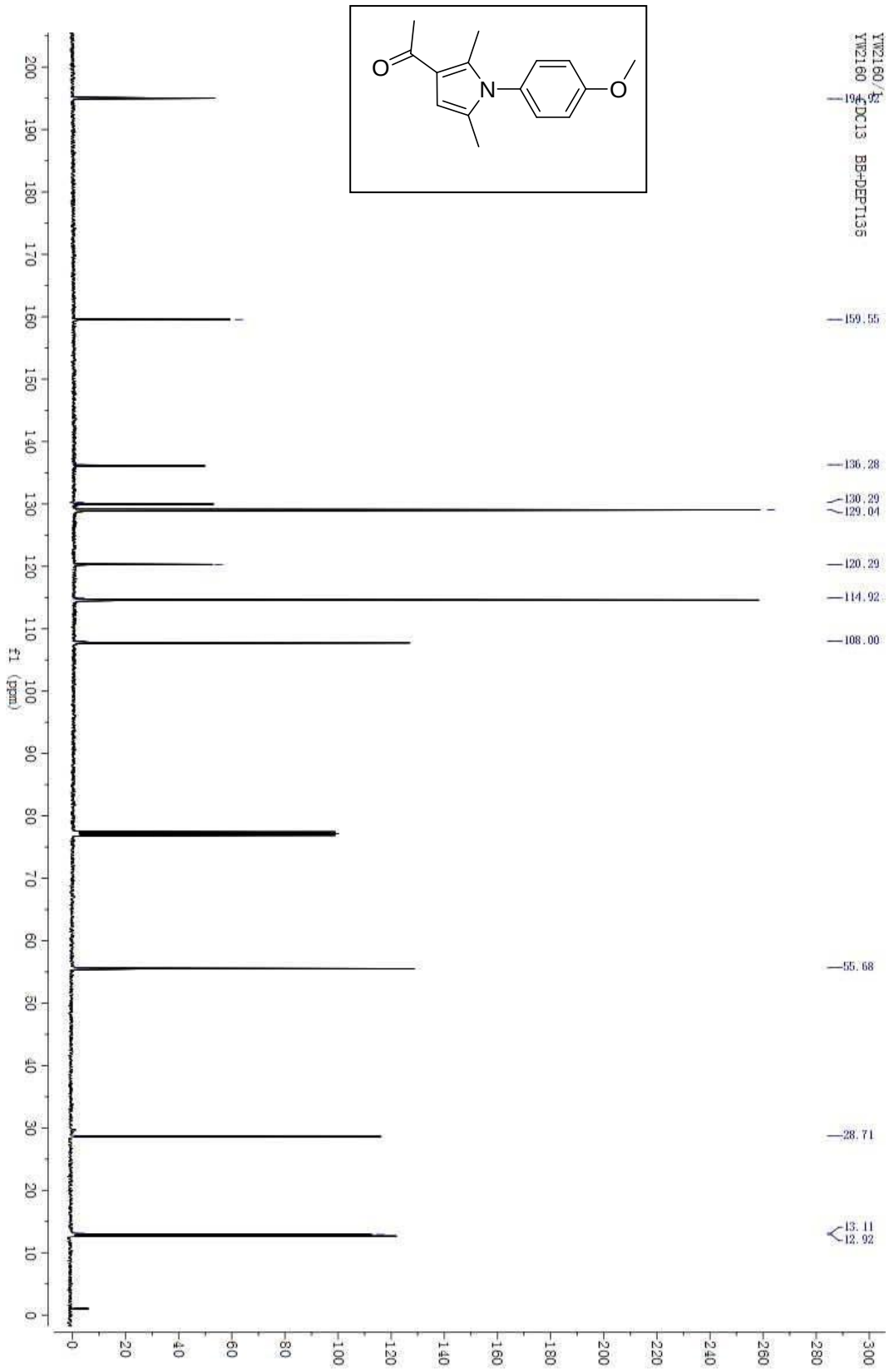
Scheme S1. Deuterium mechanism study.

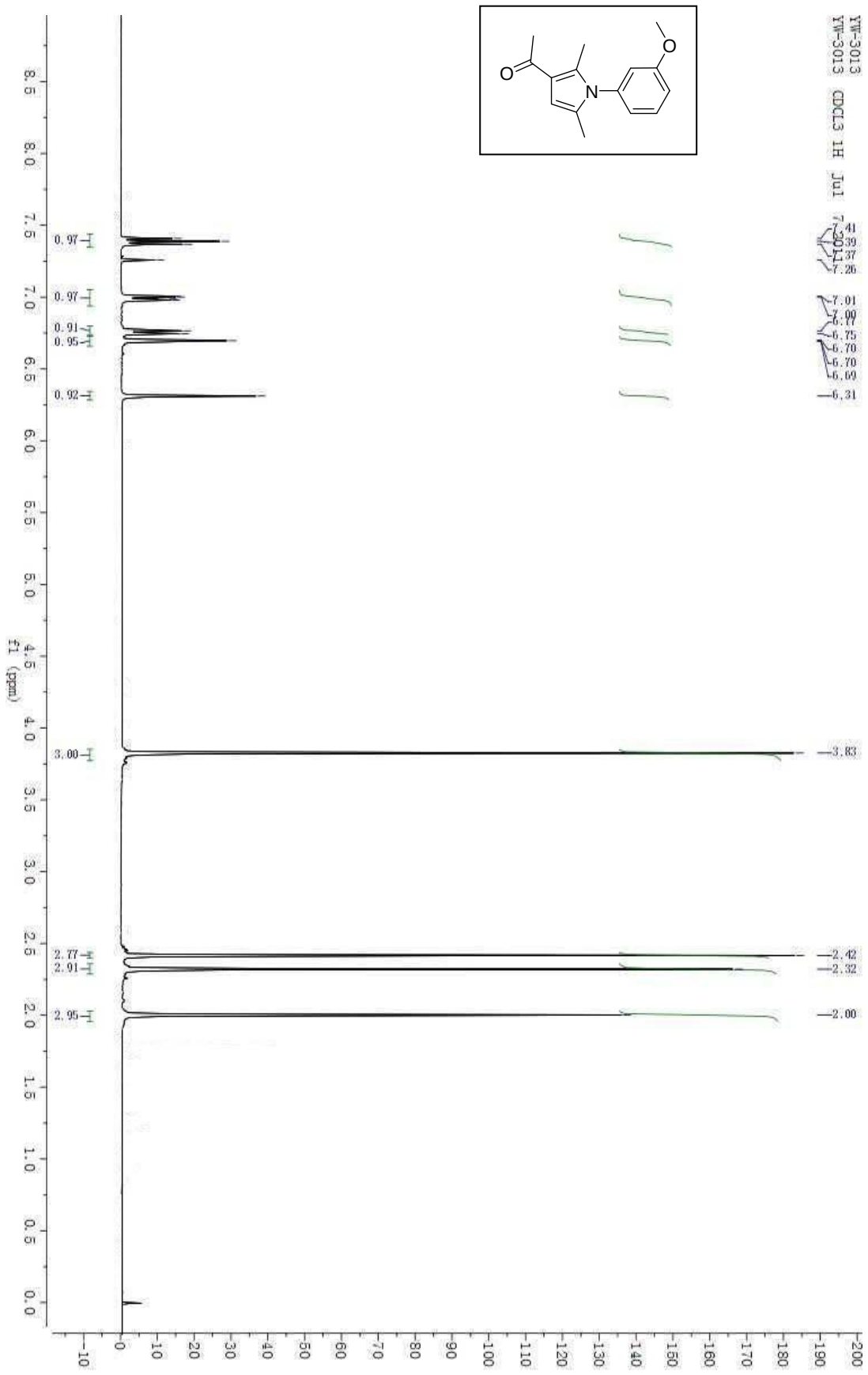


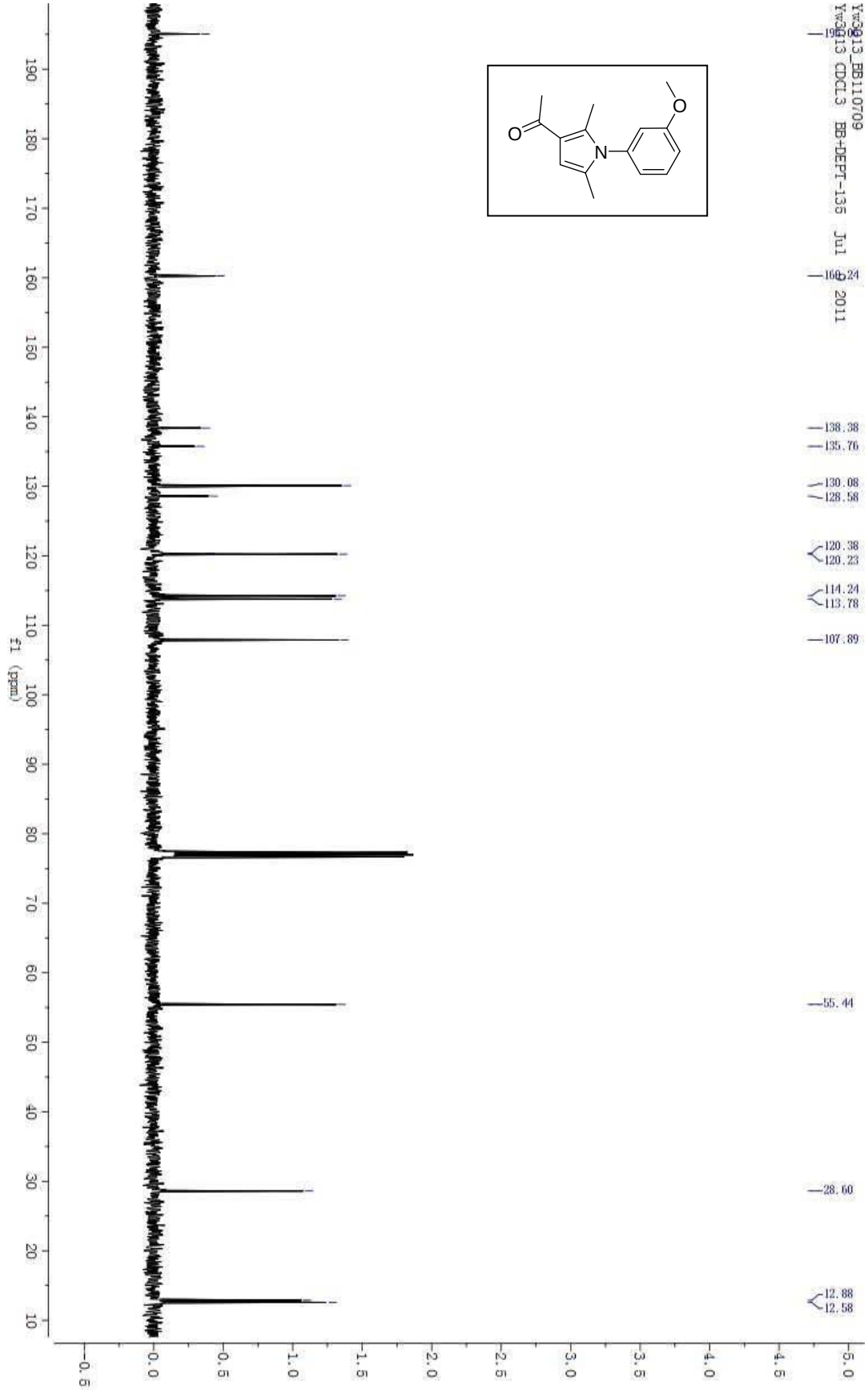








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Yw3013 CDCL3 BB-DEPT-135 Jul 6 2011
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O
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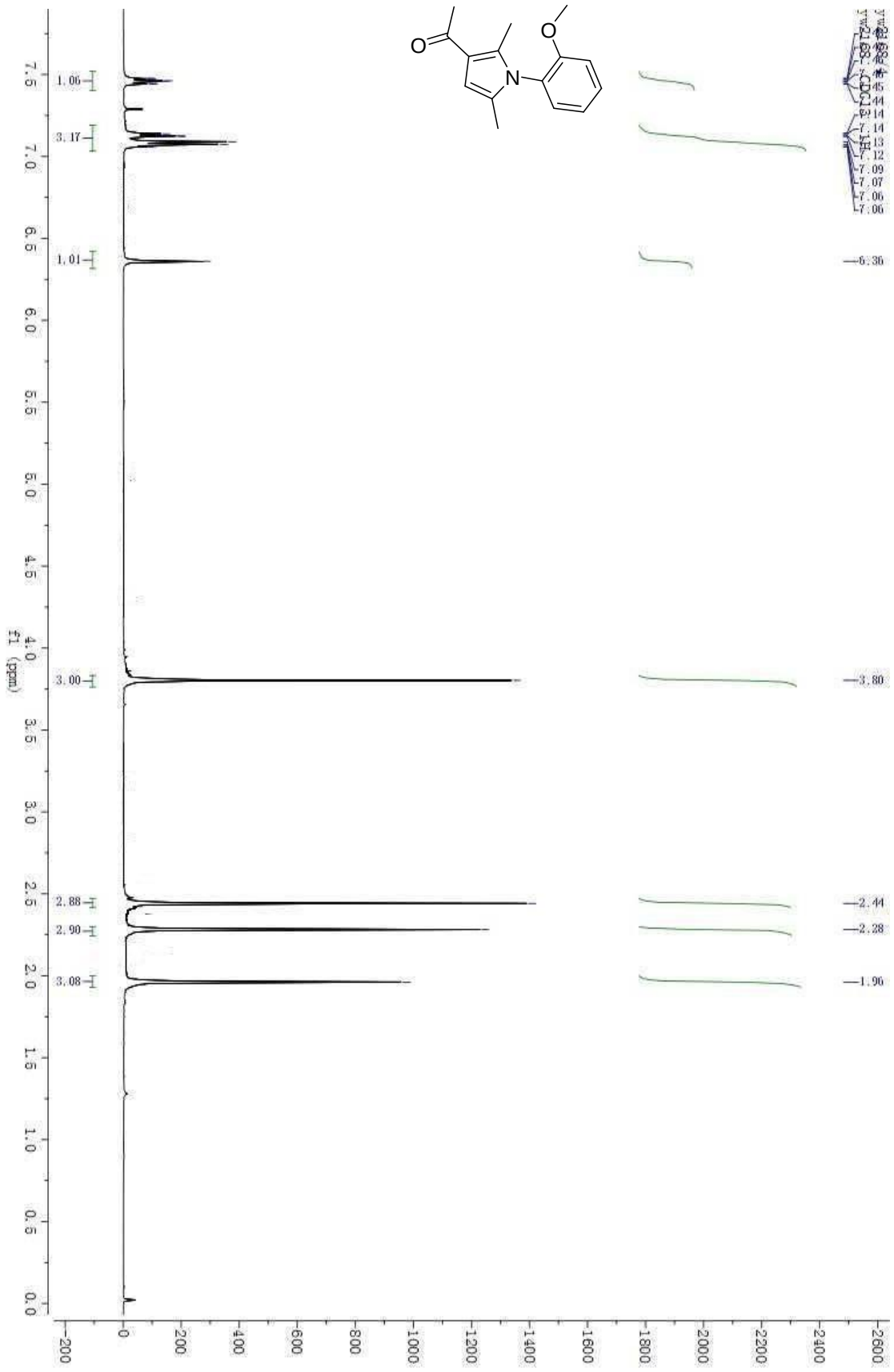
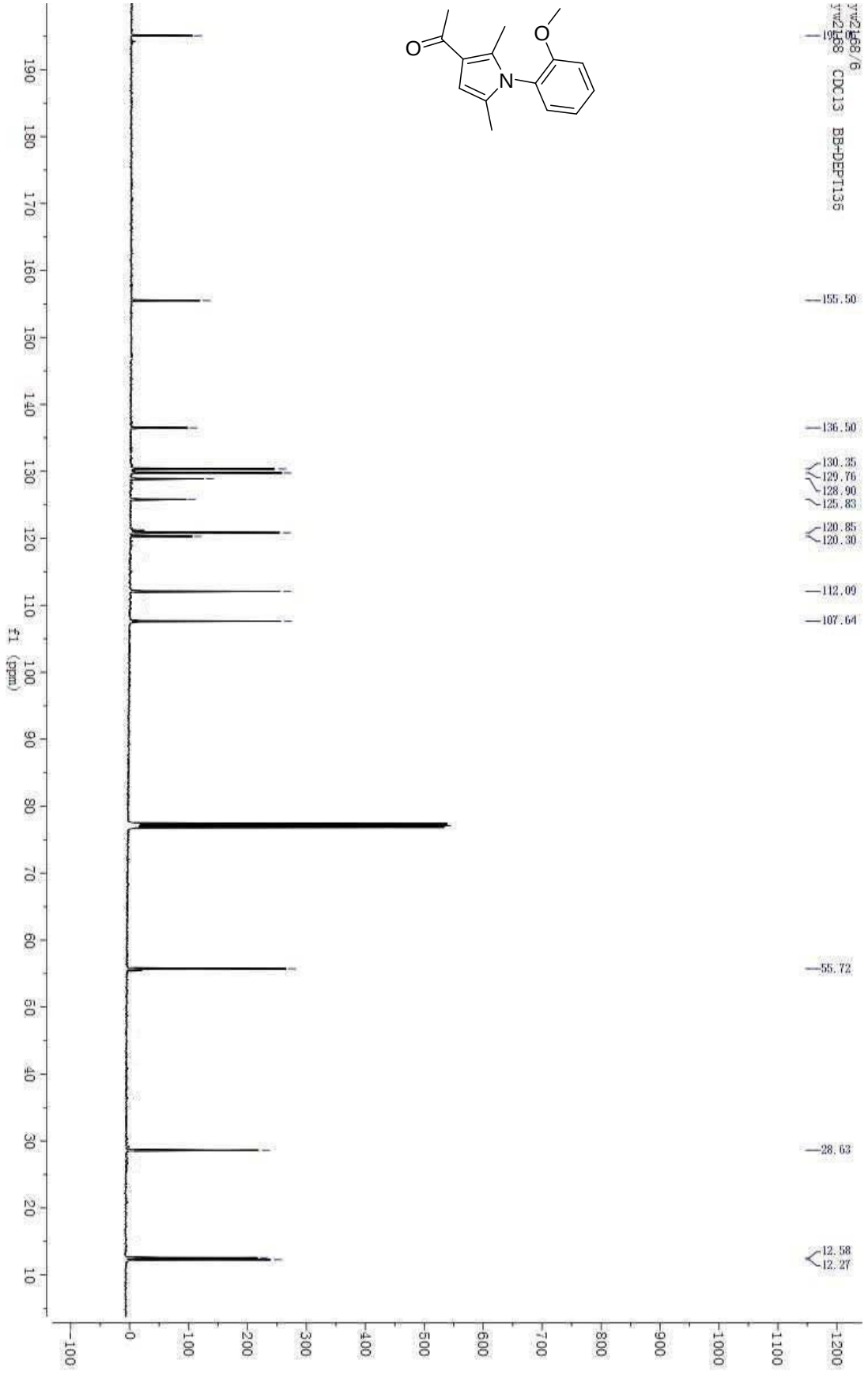
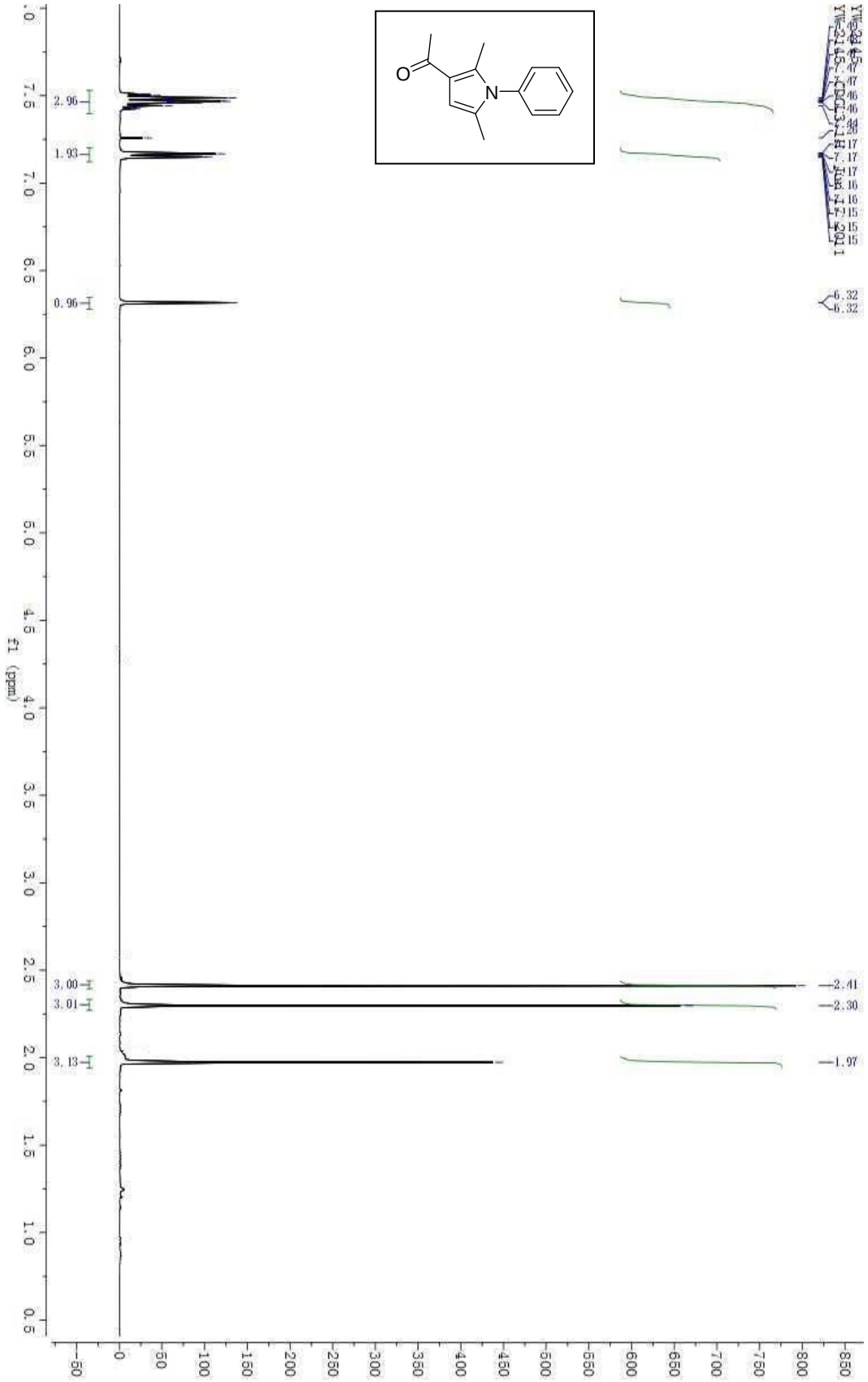
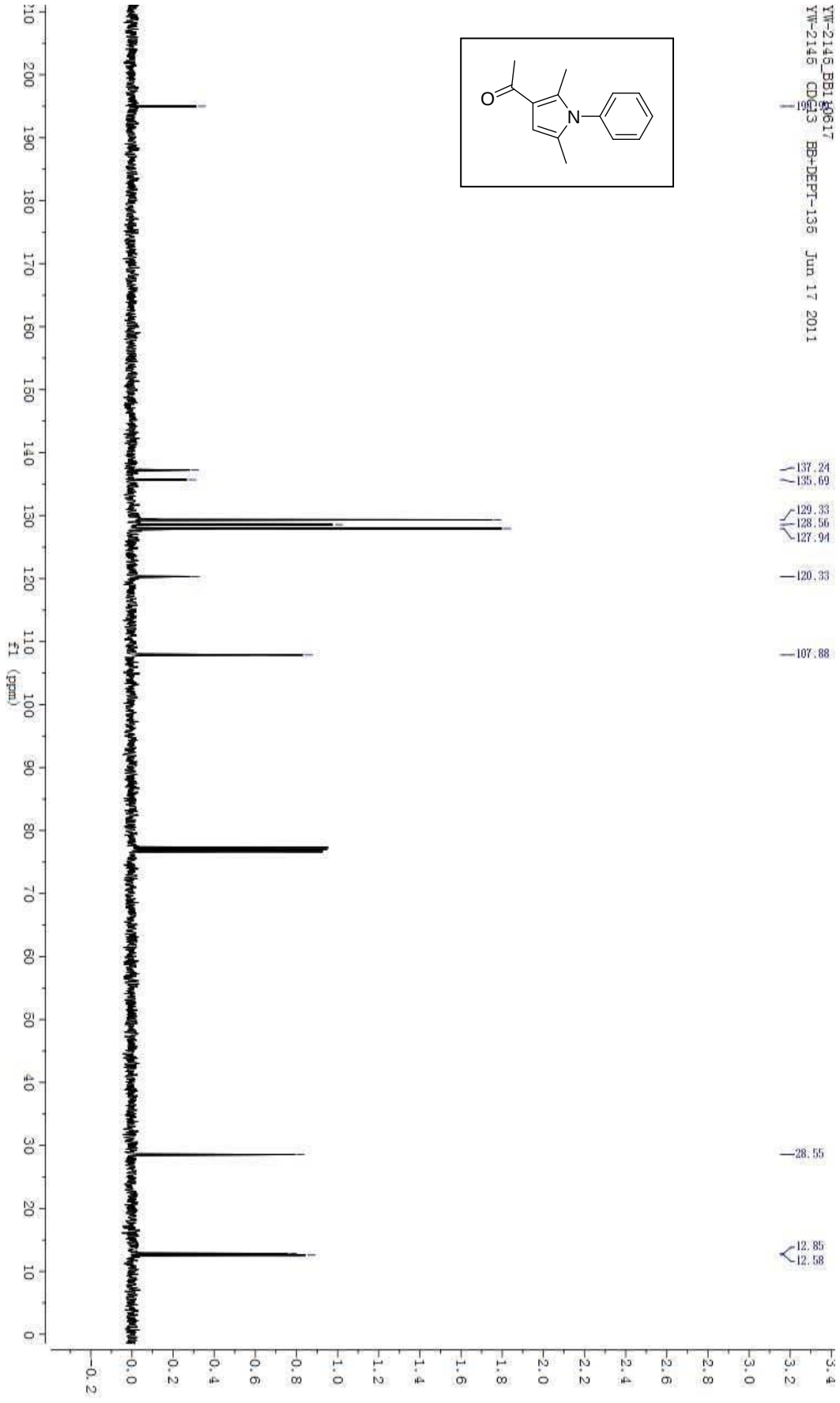
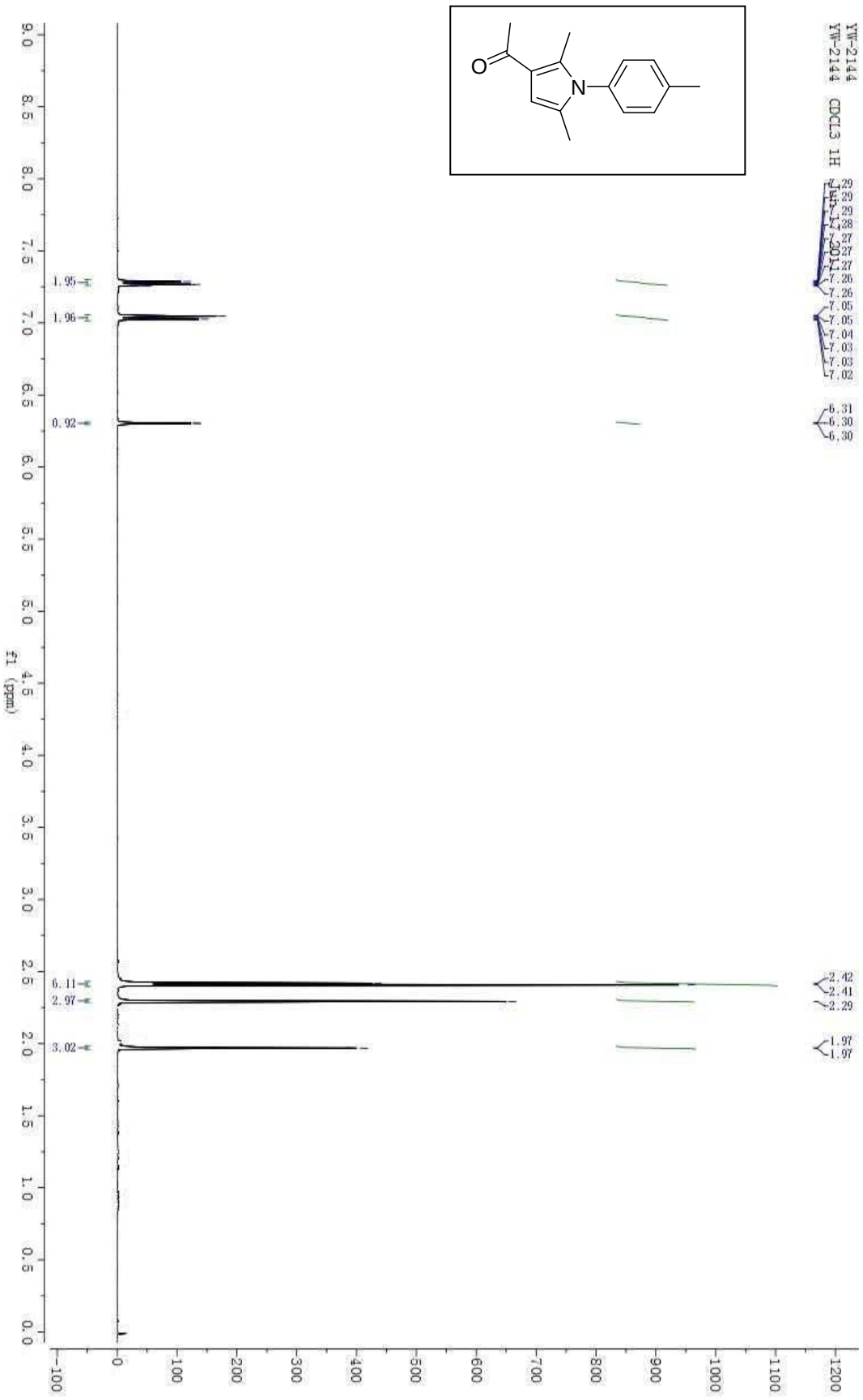
f1 (ppm)







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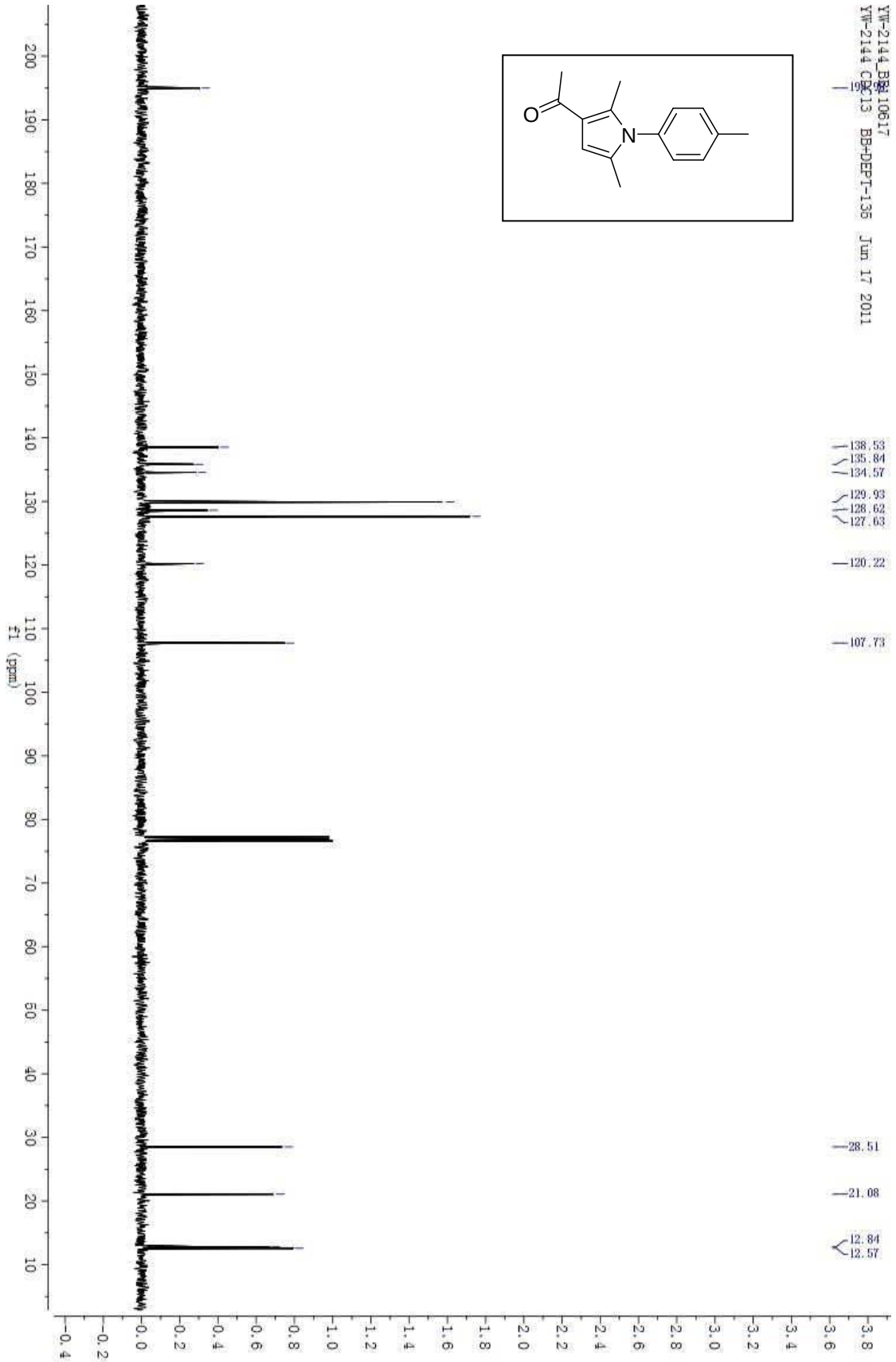
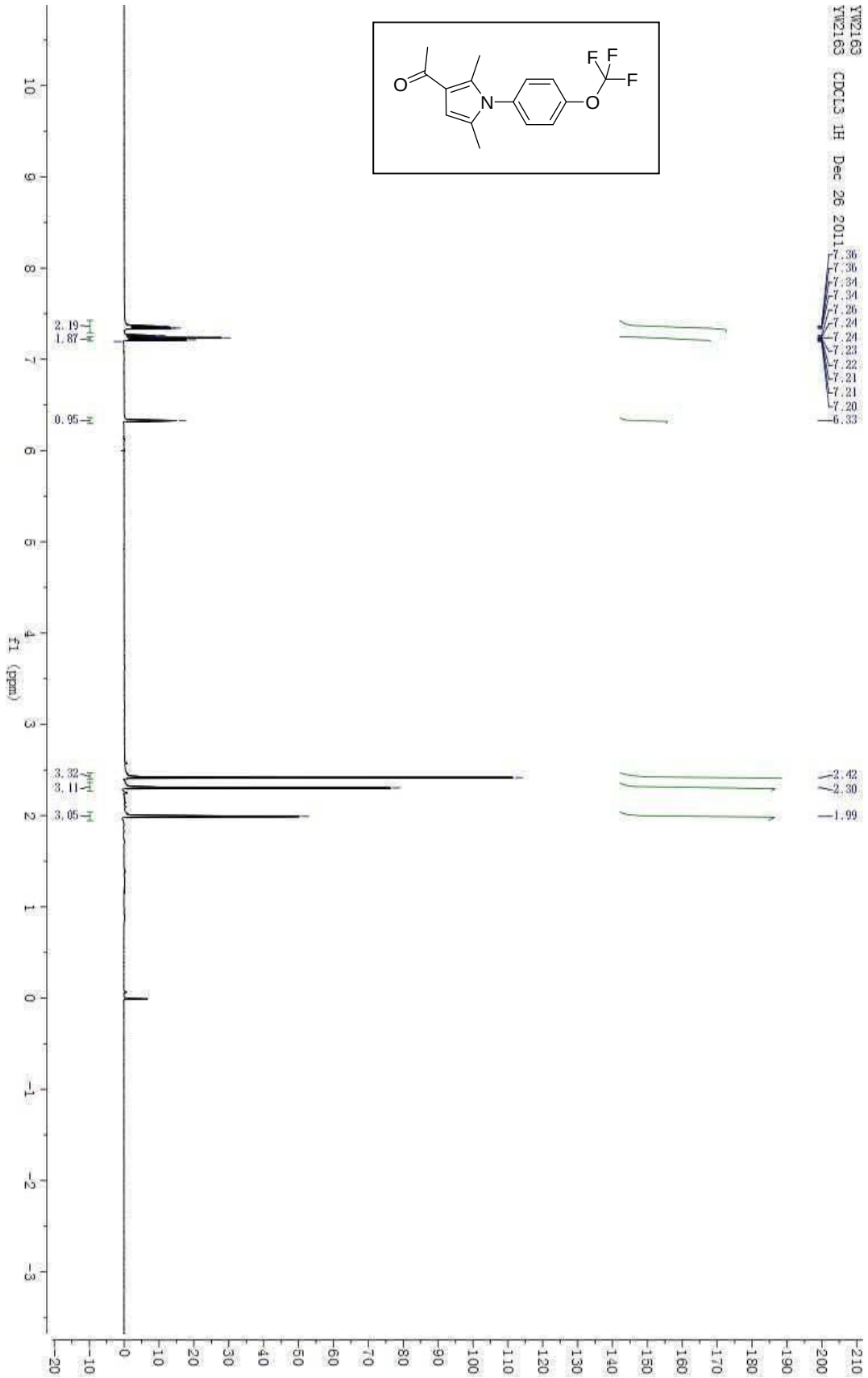
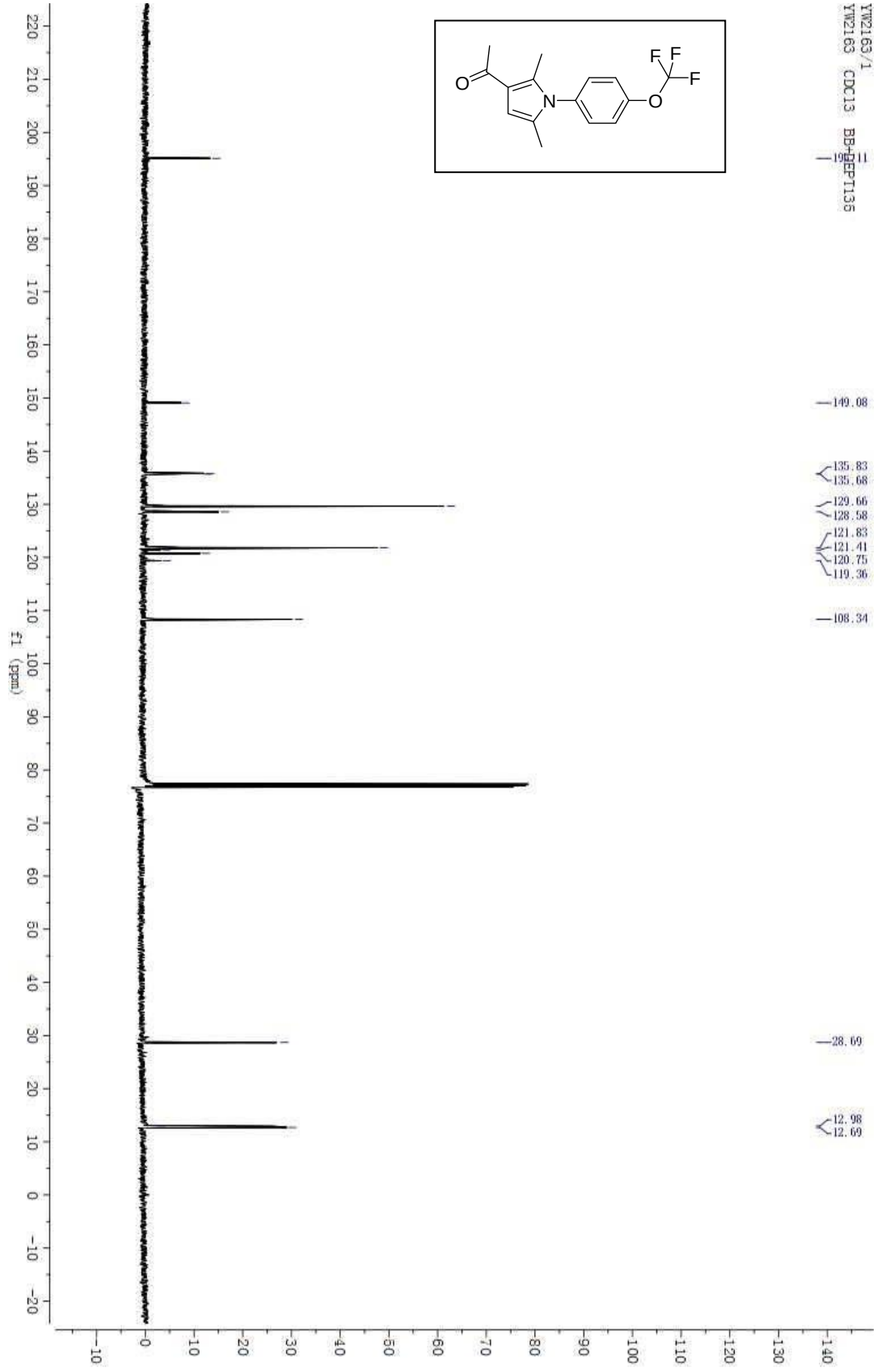
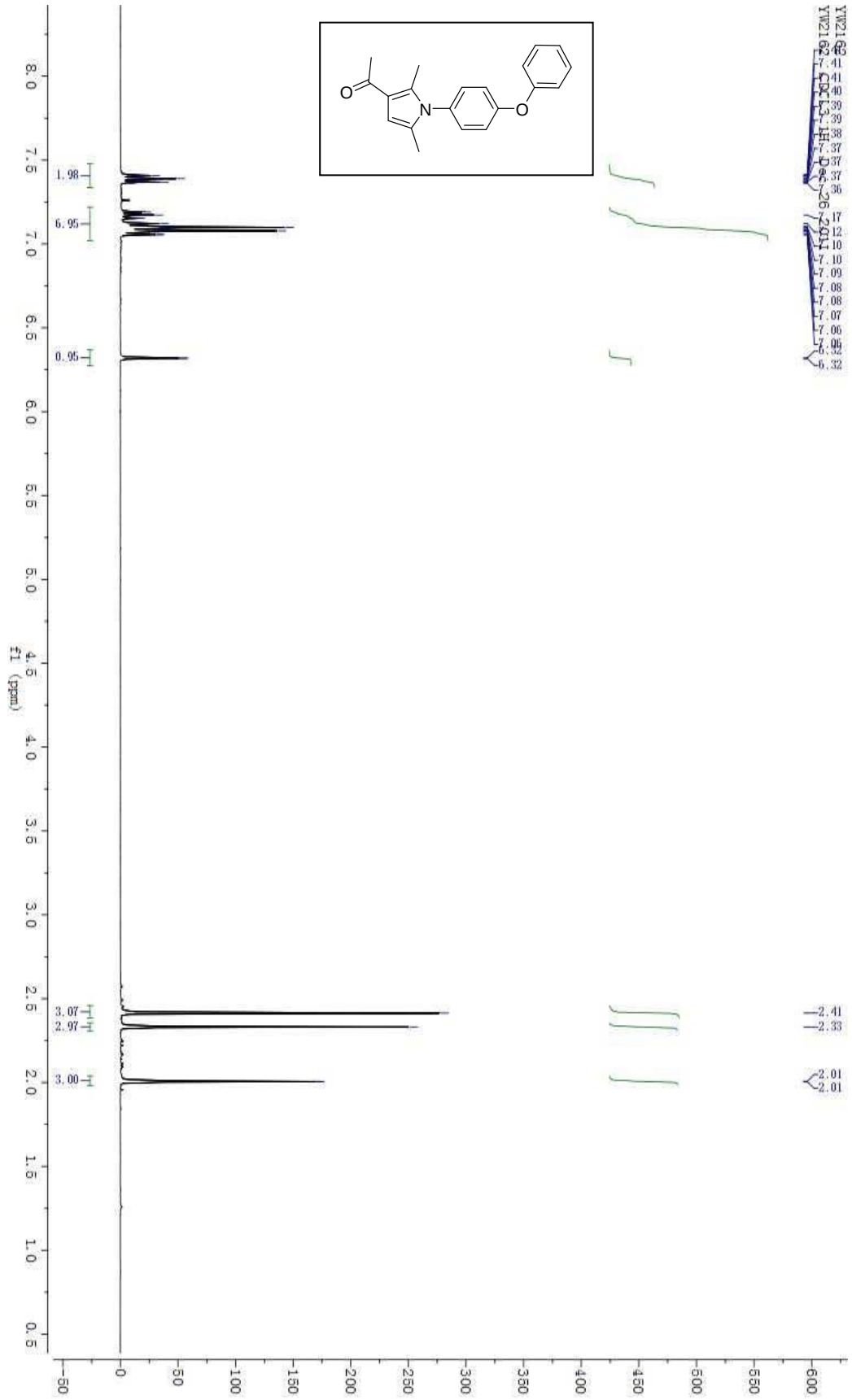
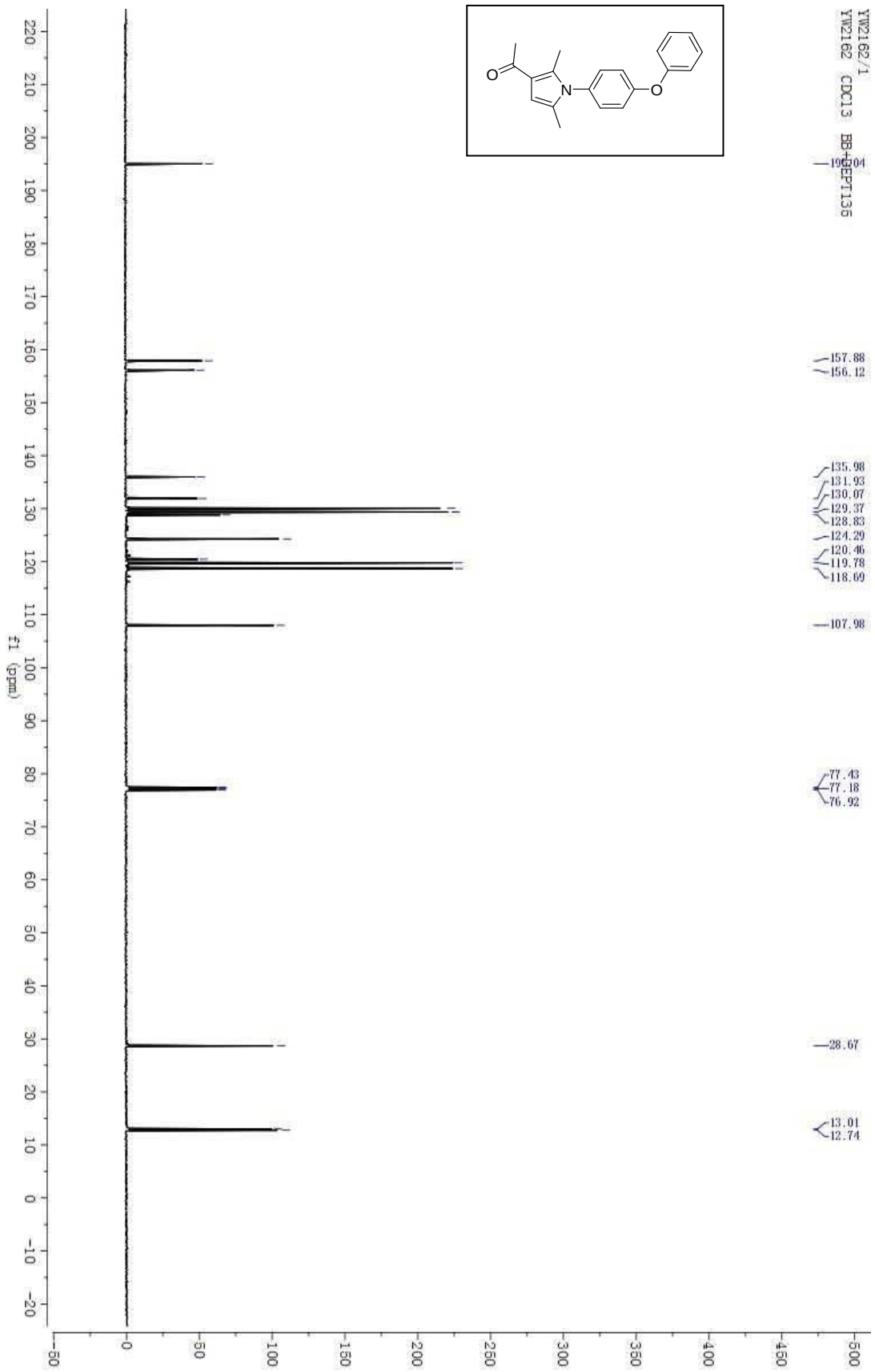
f1 (ppm)

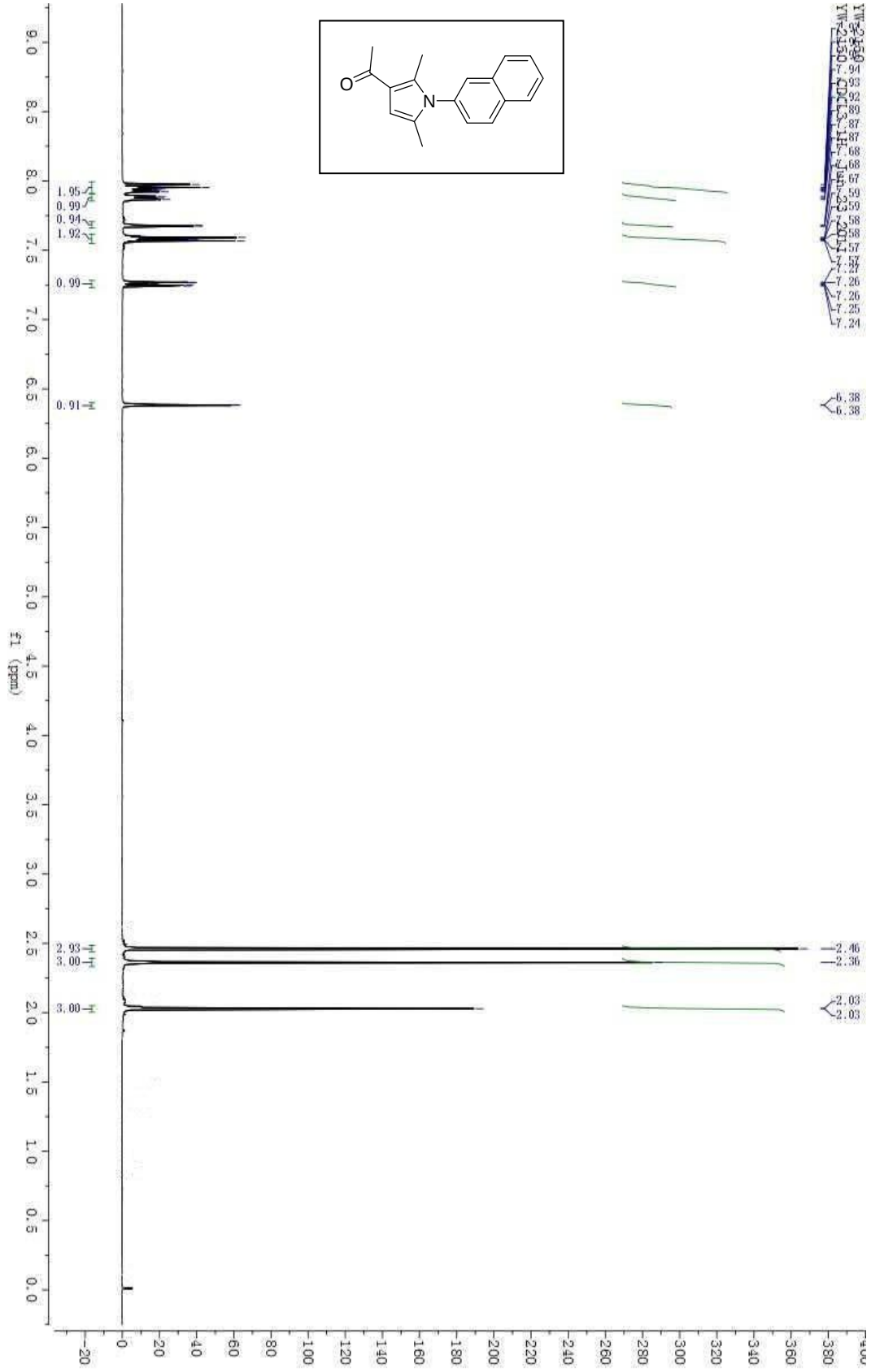


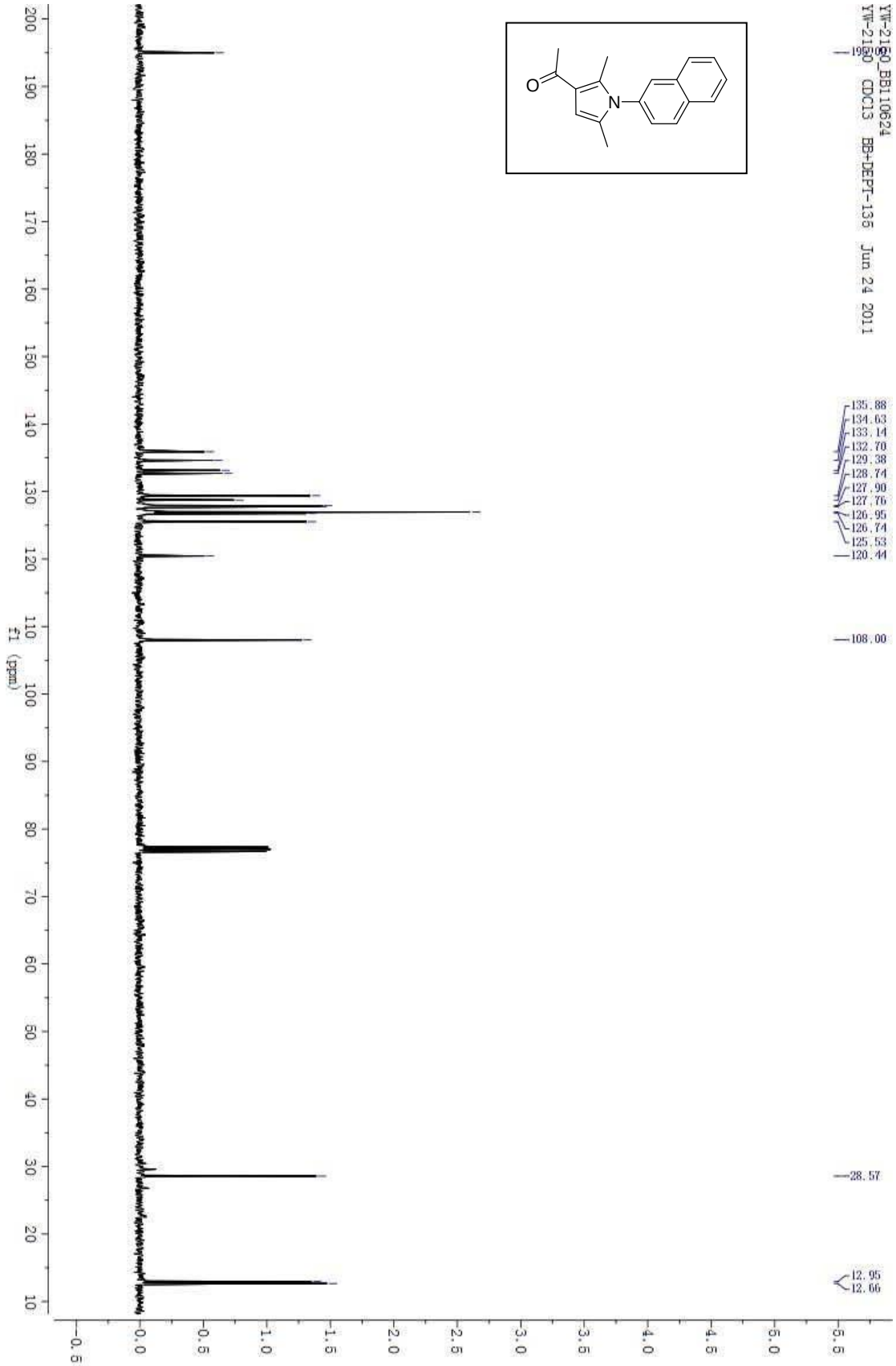


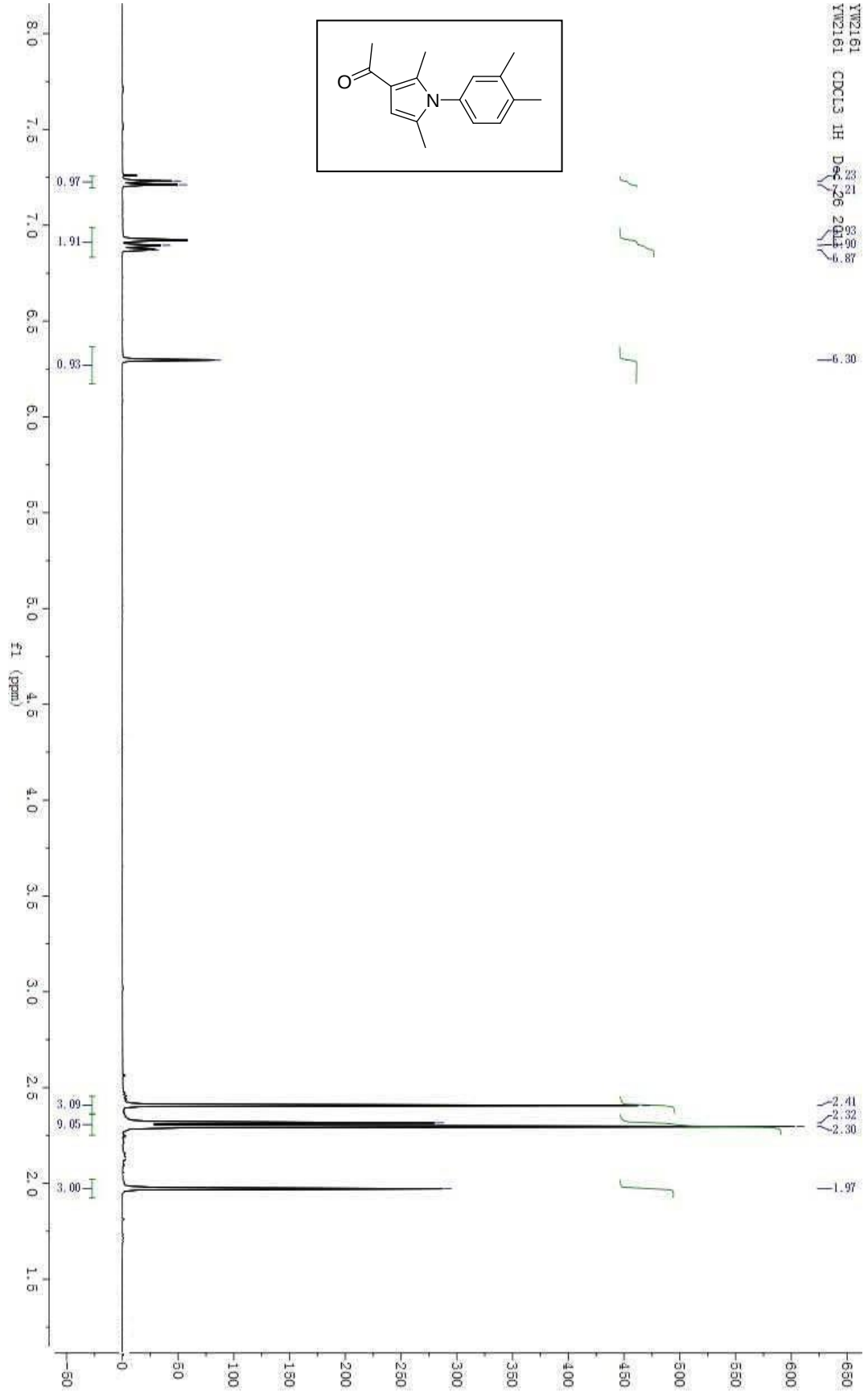


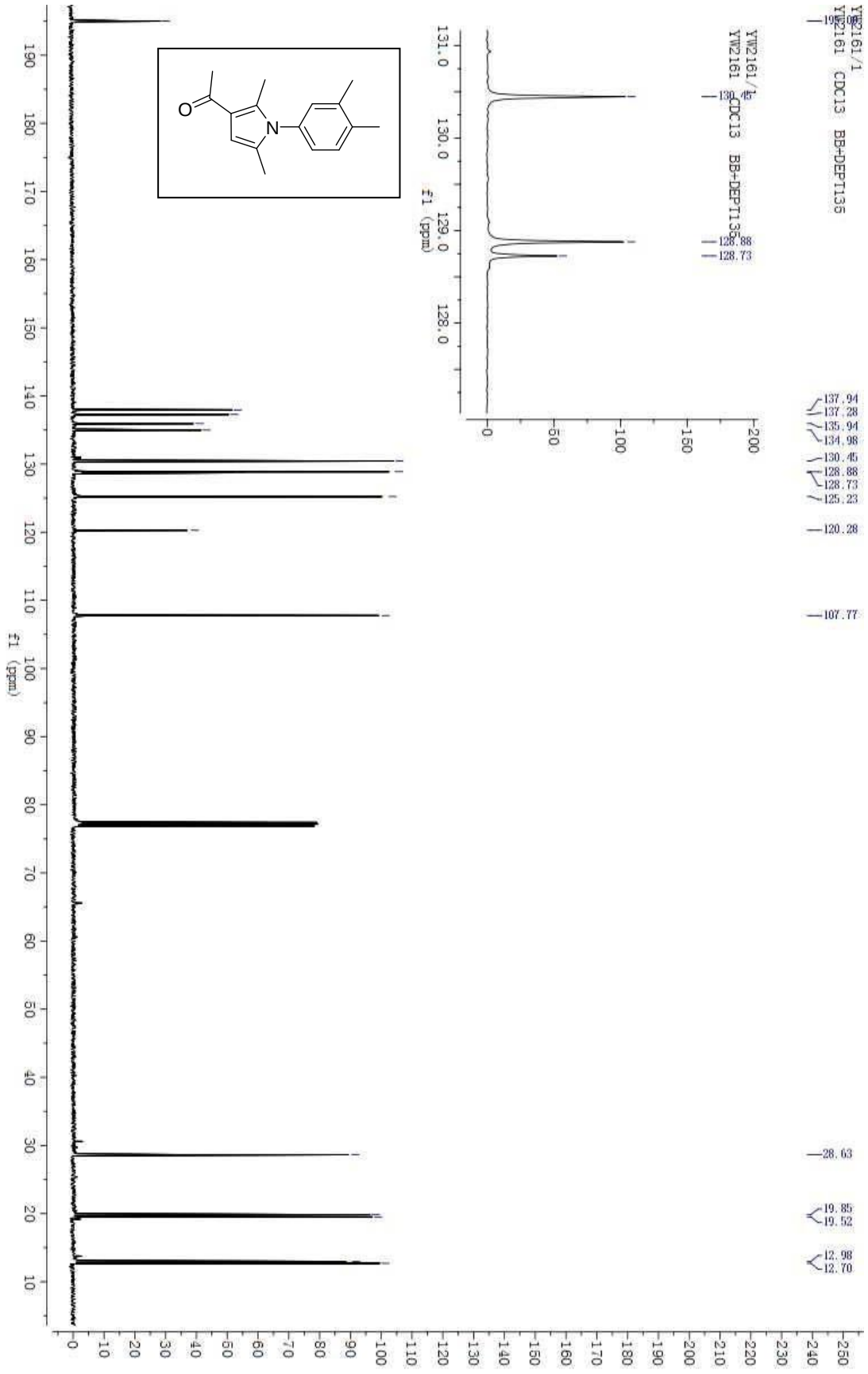








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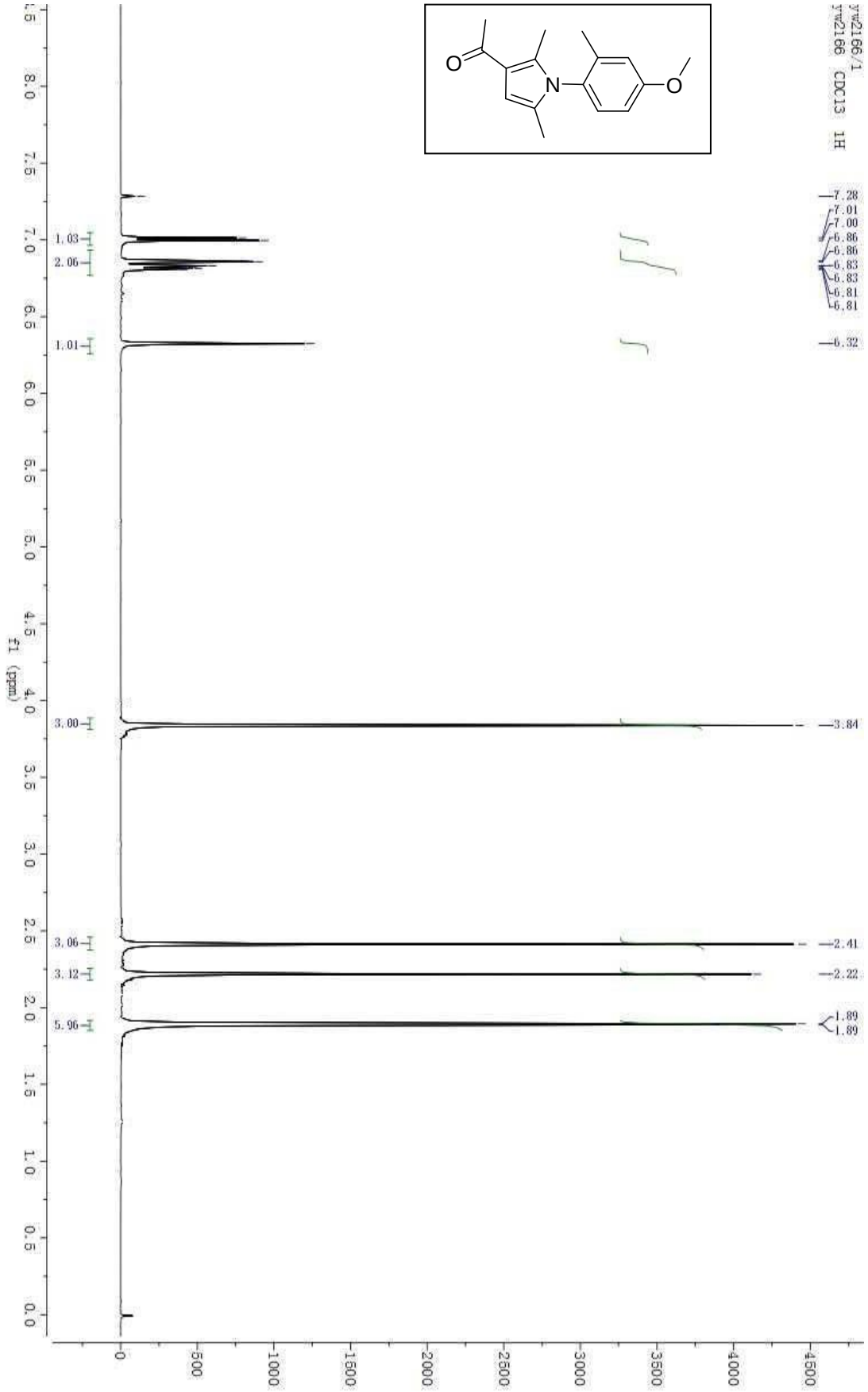
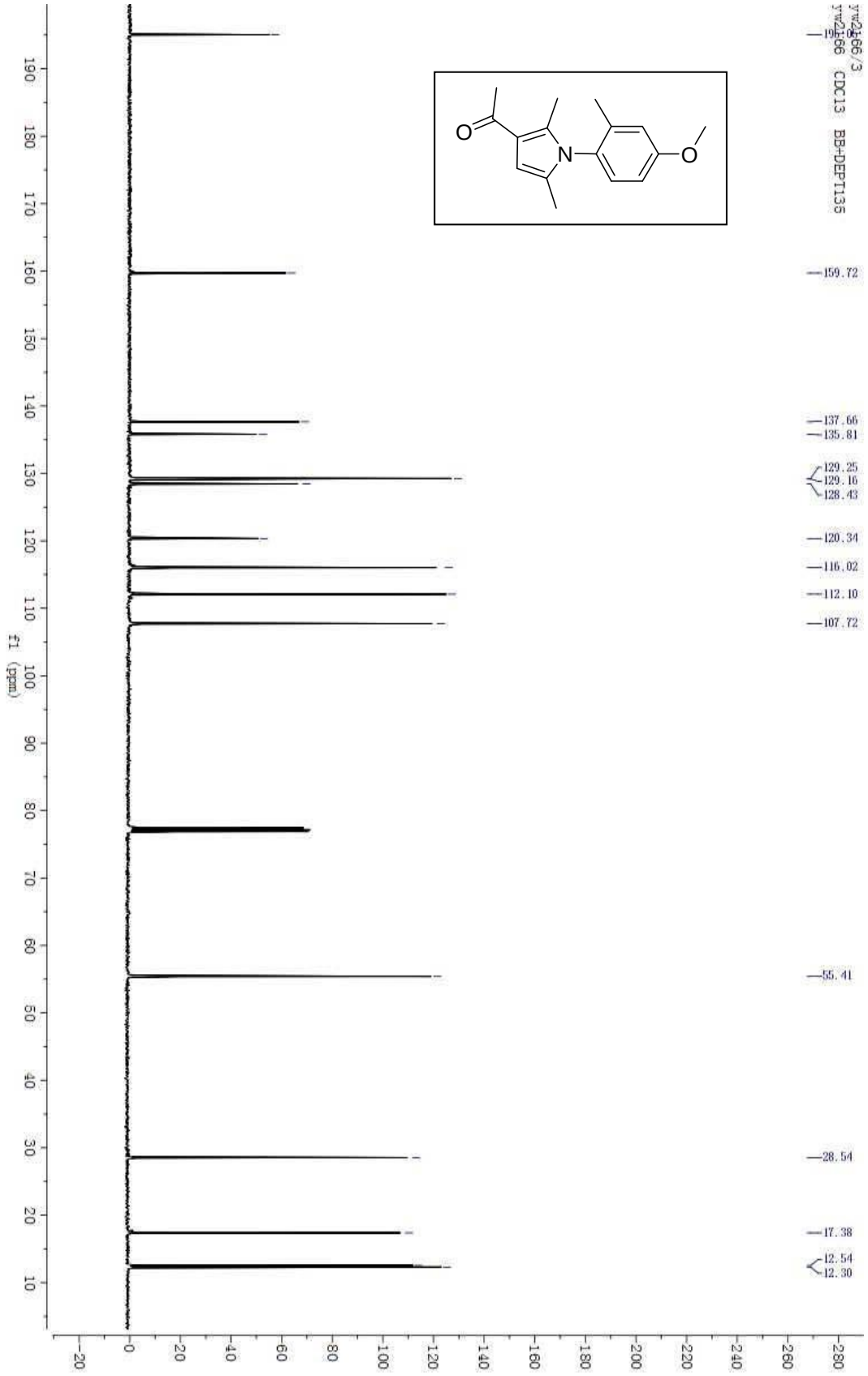
f1 (ppm)

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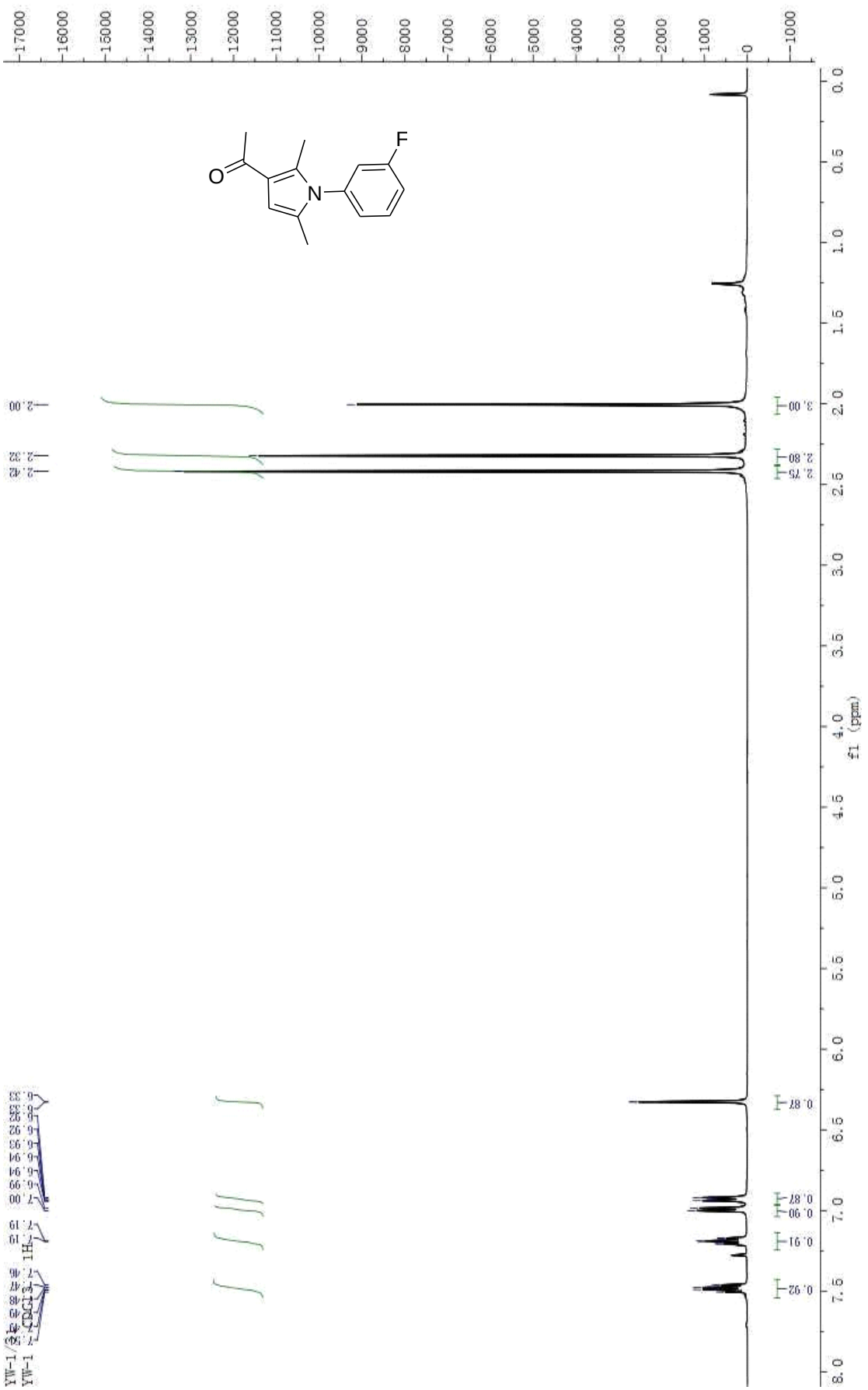
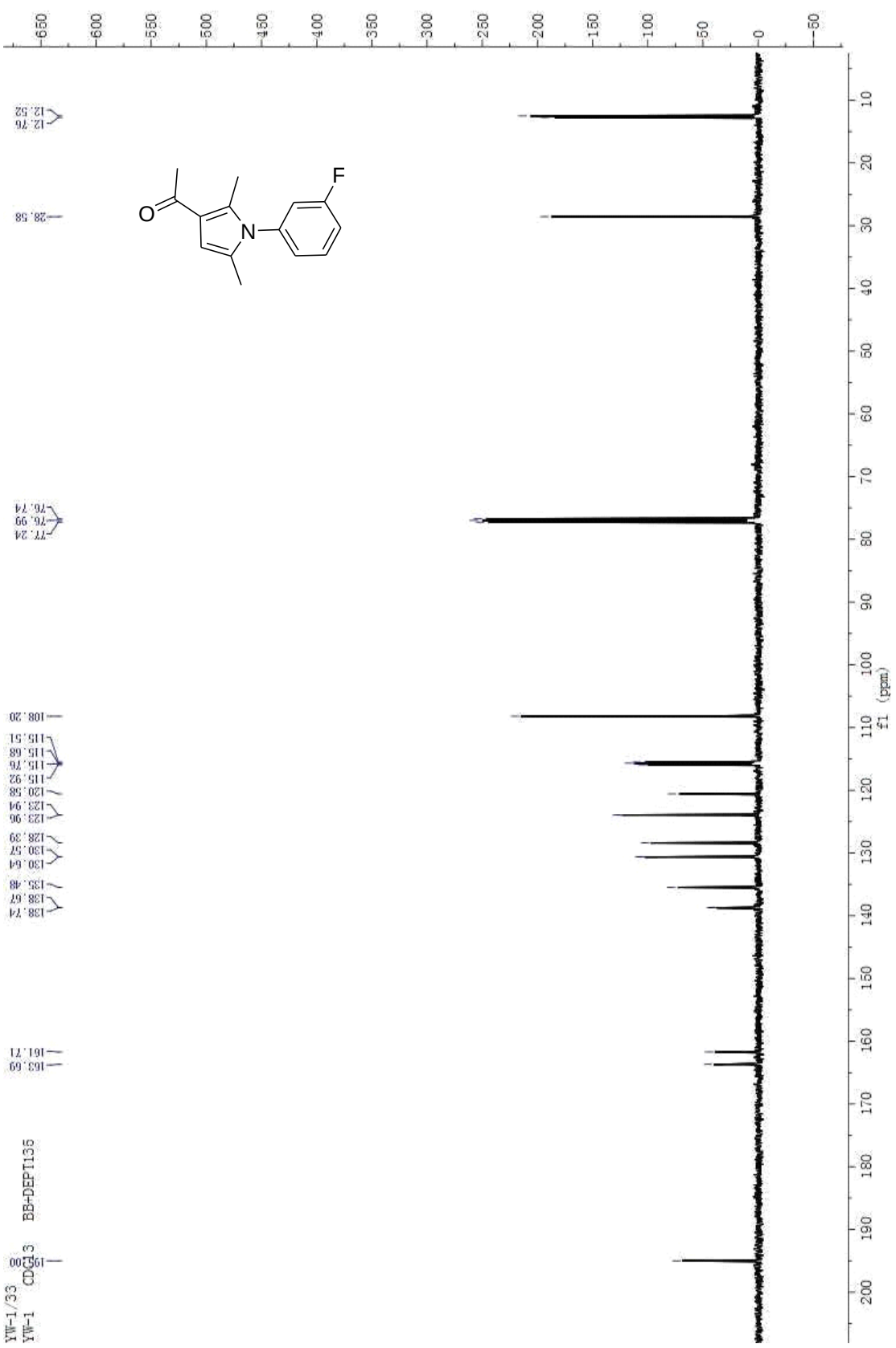
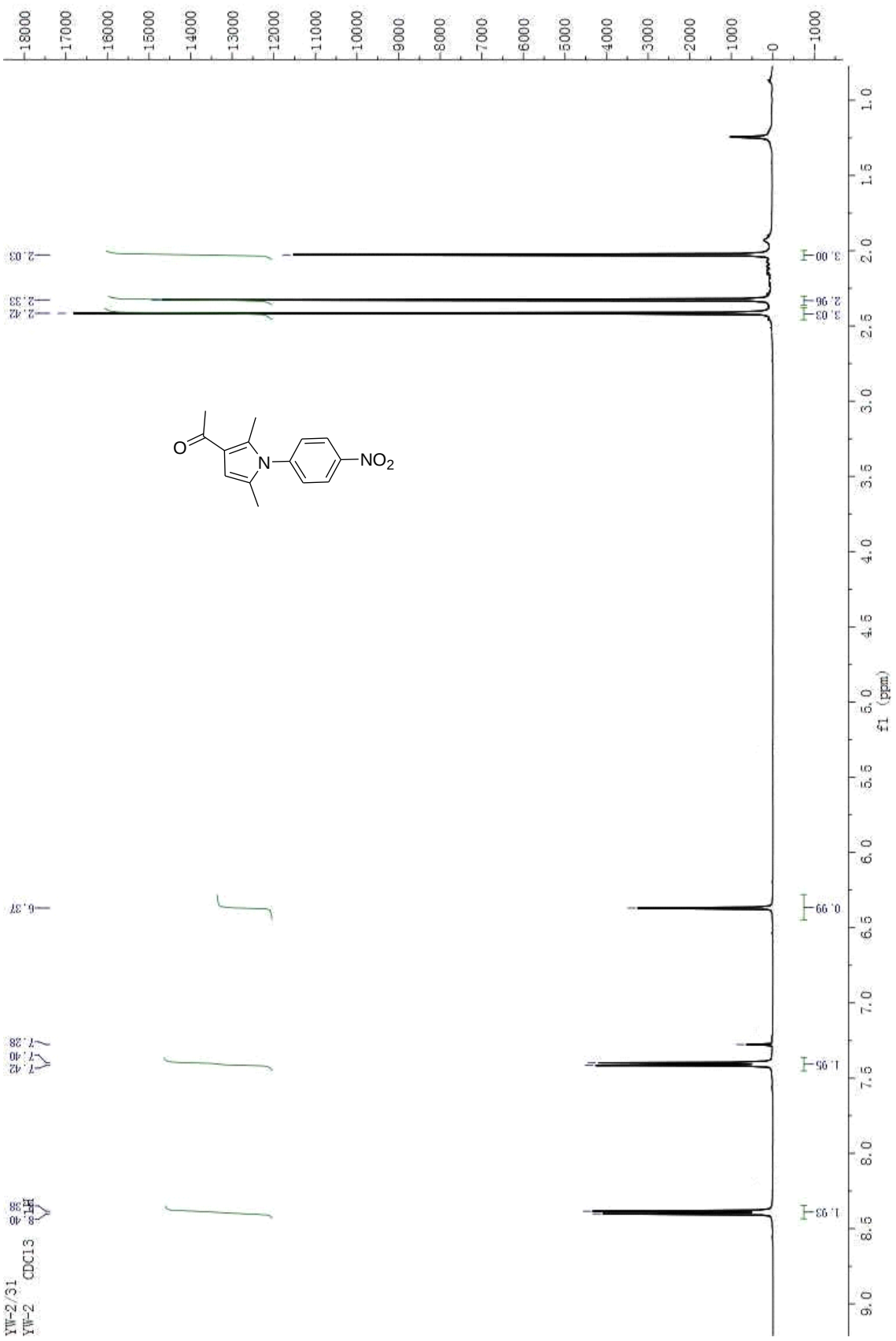
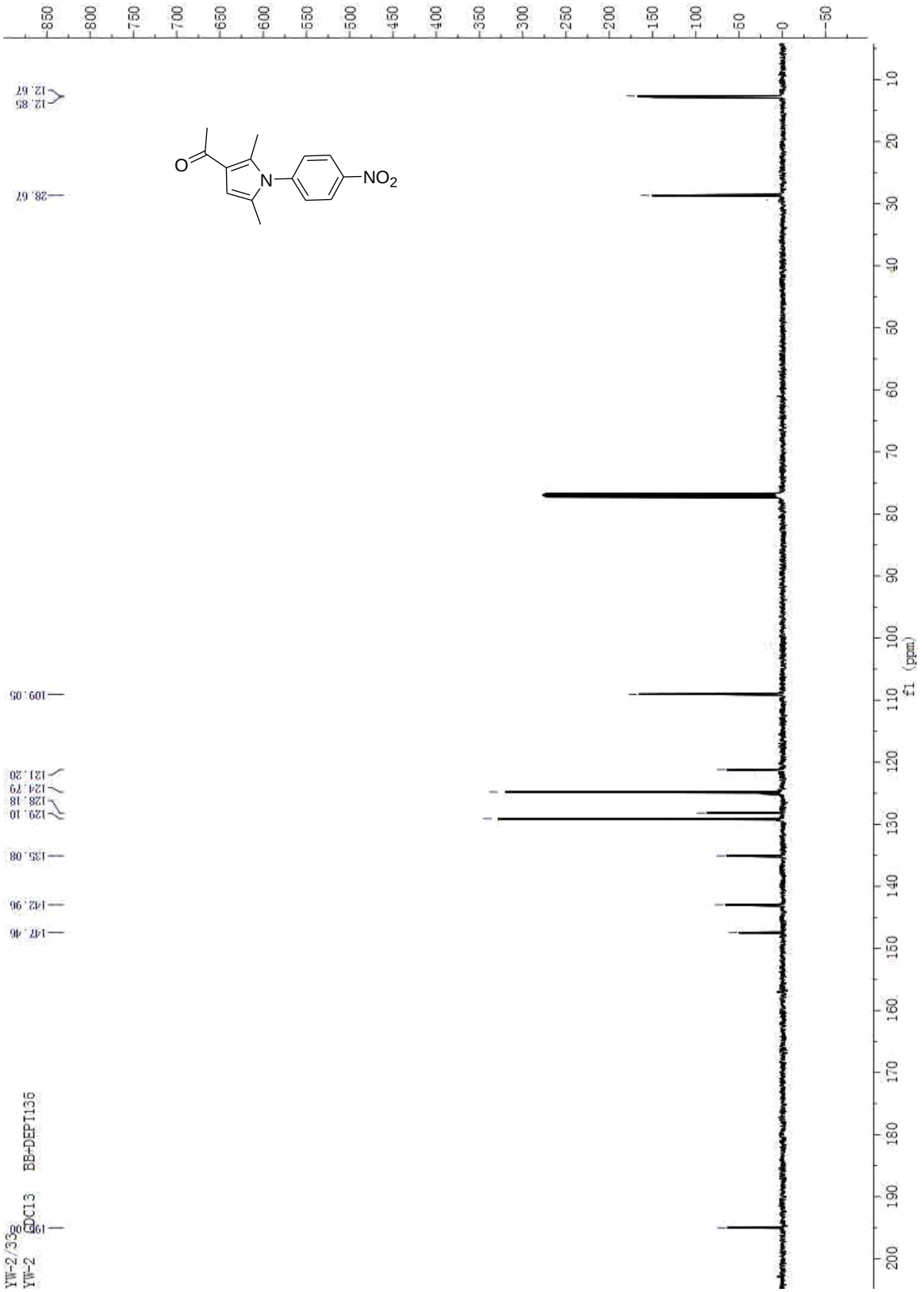
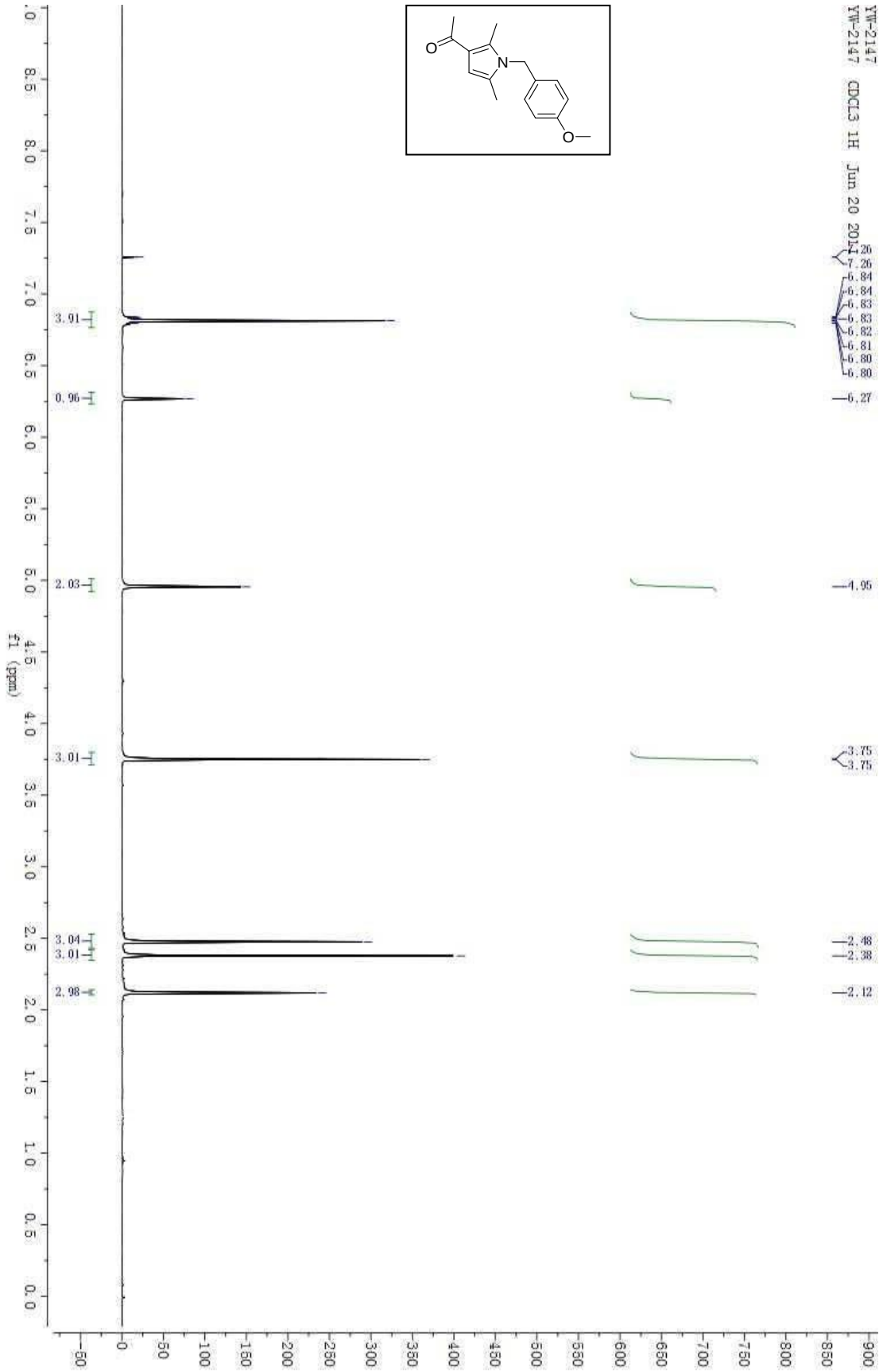
12.30
f1 (ppm)

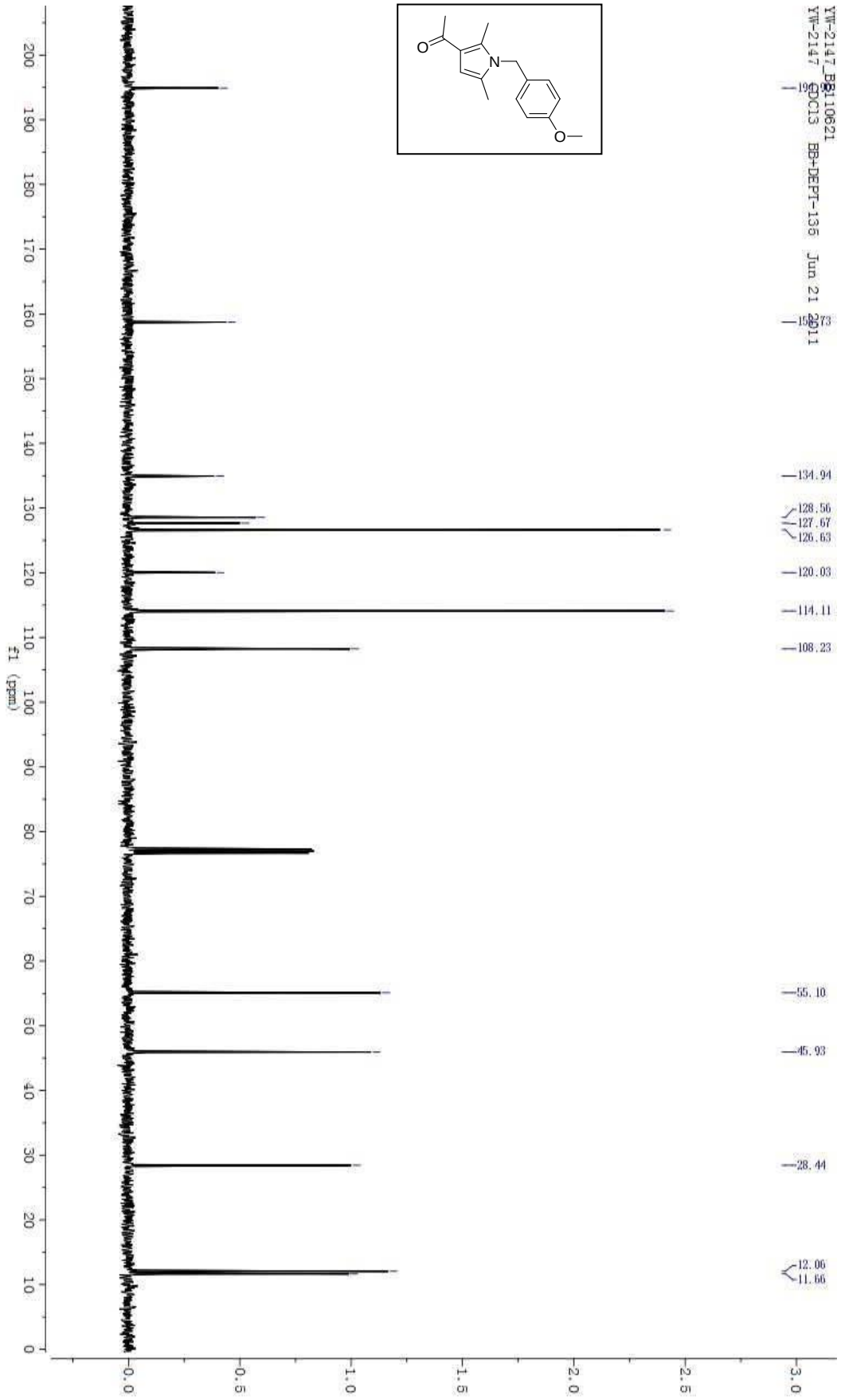








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YW-2147 CDCl3 BB+DEPT-135 Jun 21 2011
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N
O
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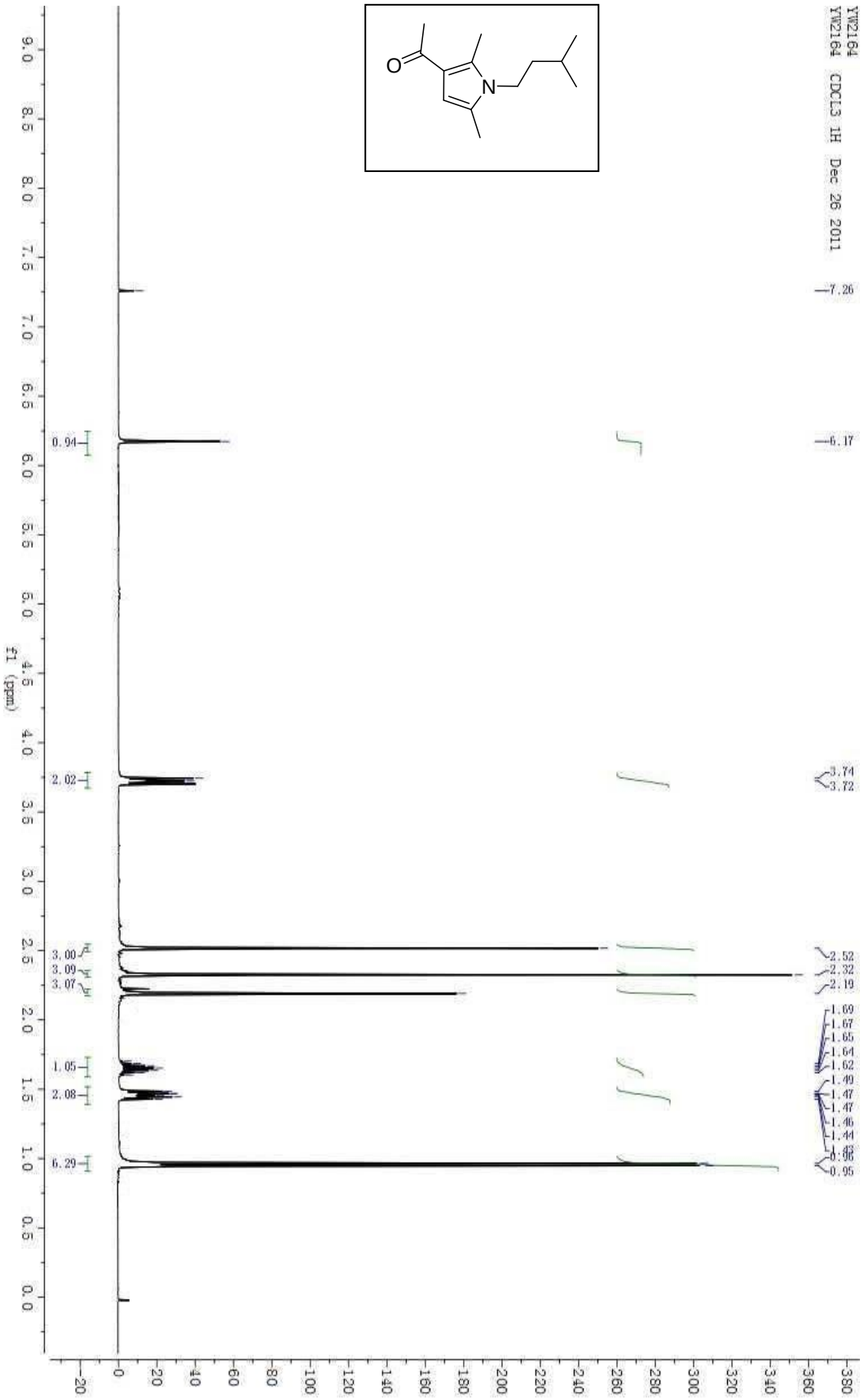
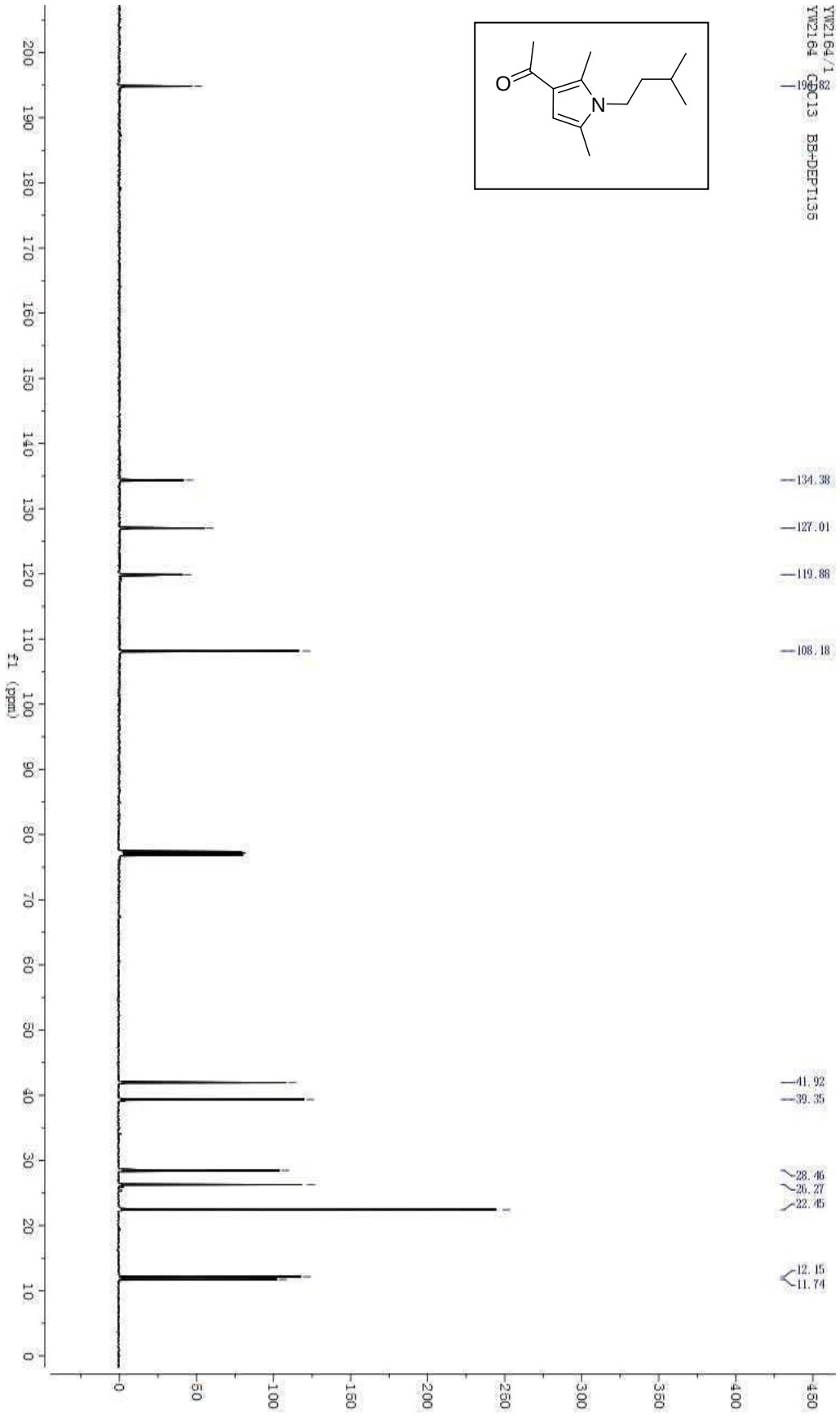
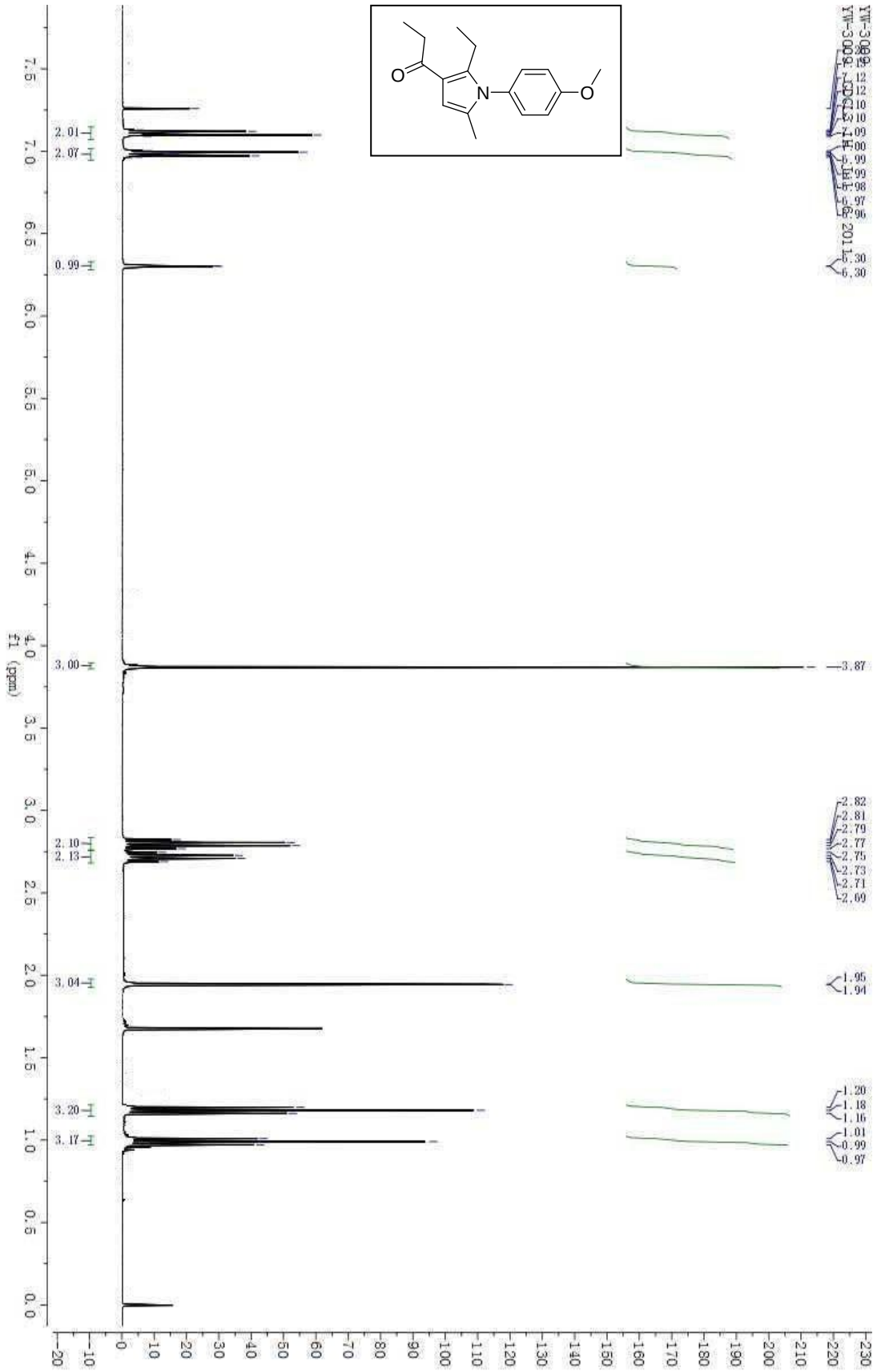
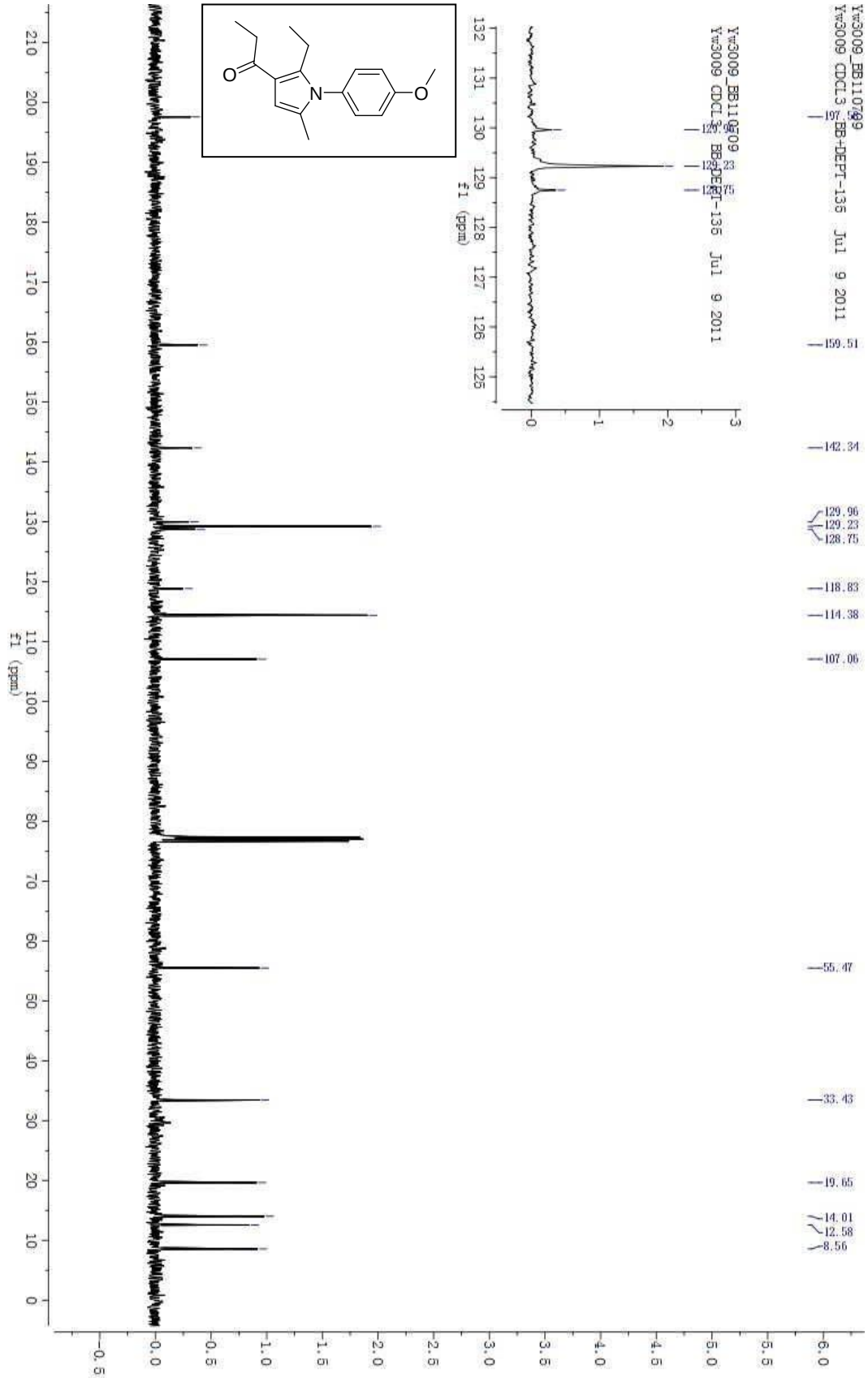
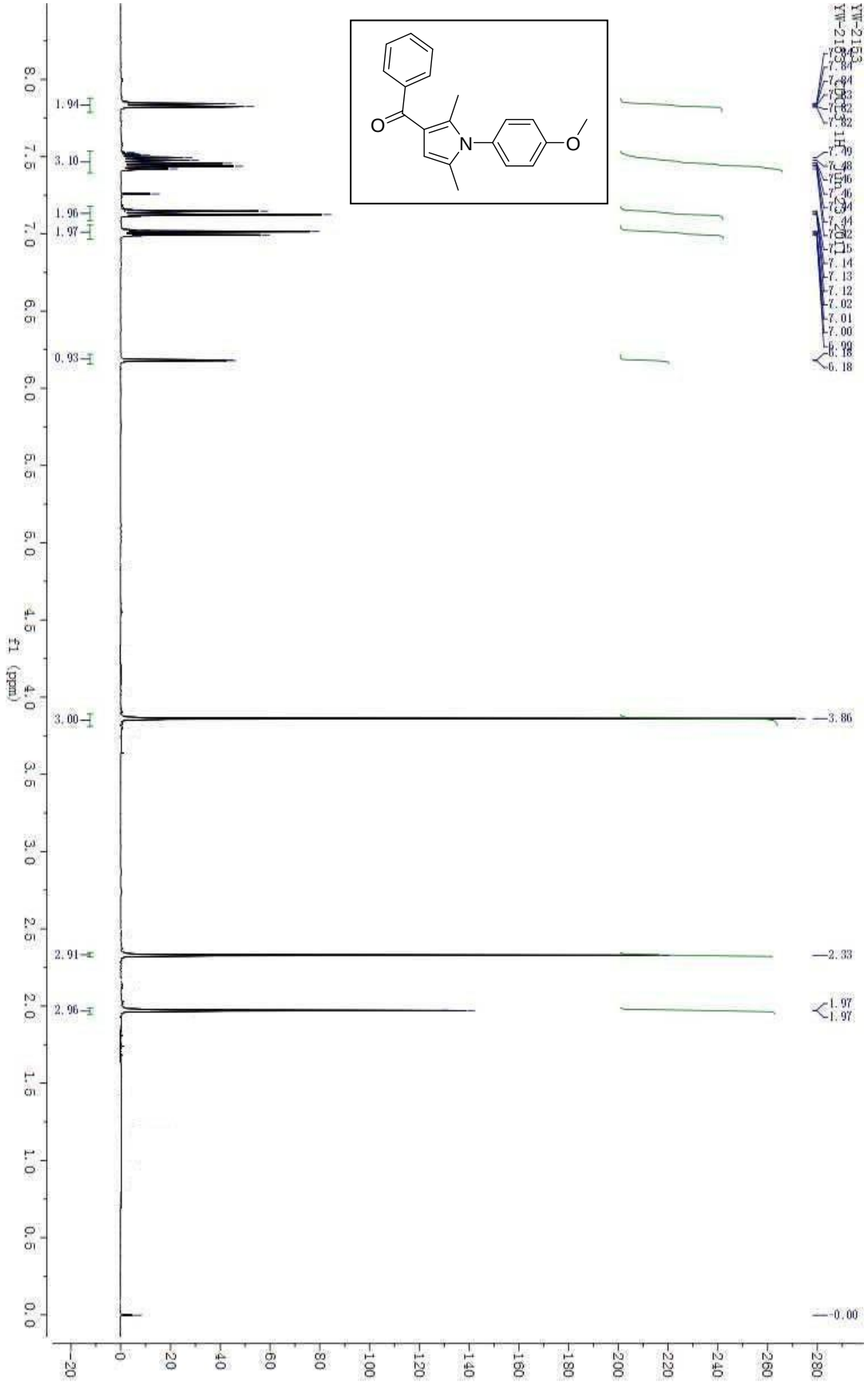
134.94
128.56
127.67
126.63
120.03
114.11
108.23
55.10
45.93
28.44
12.06
11.66

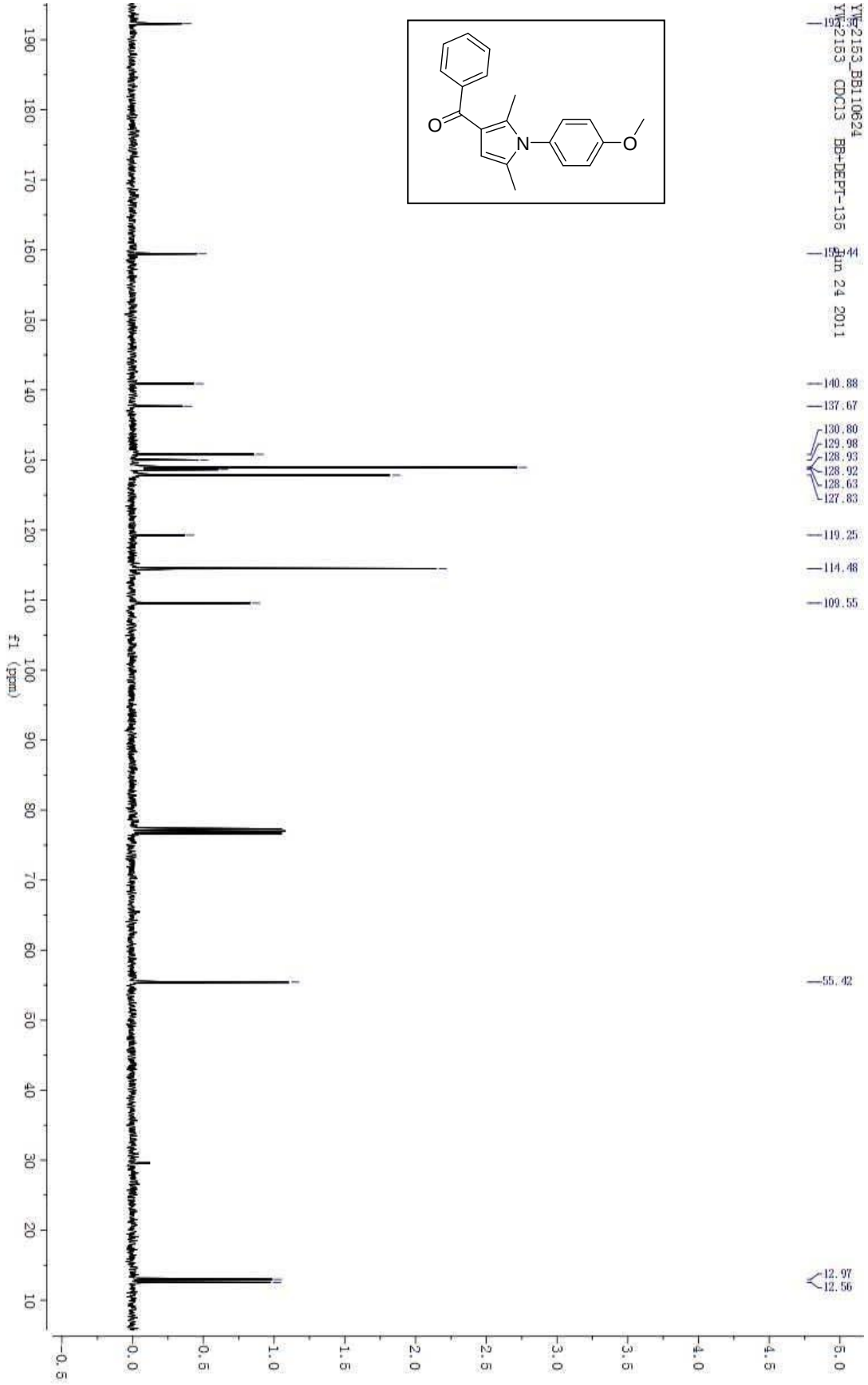


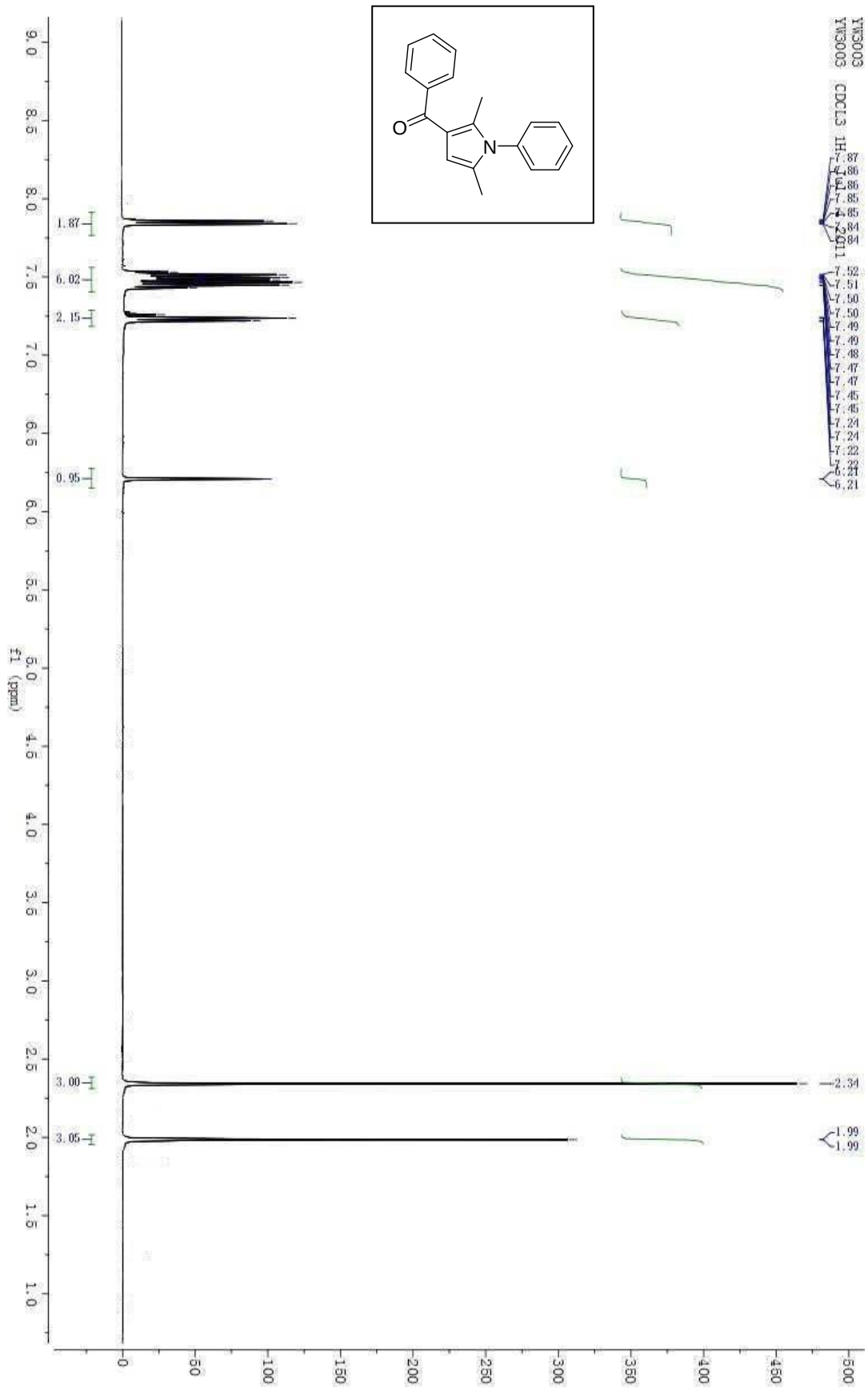


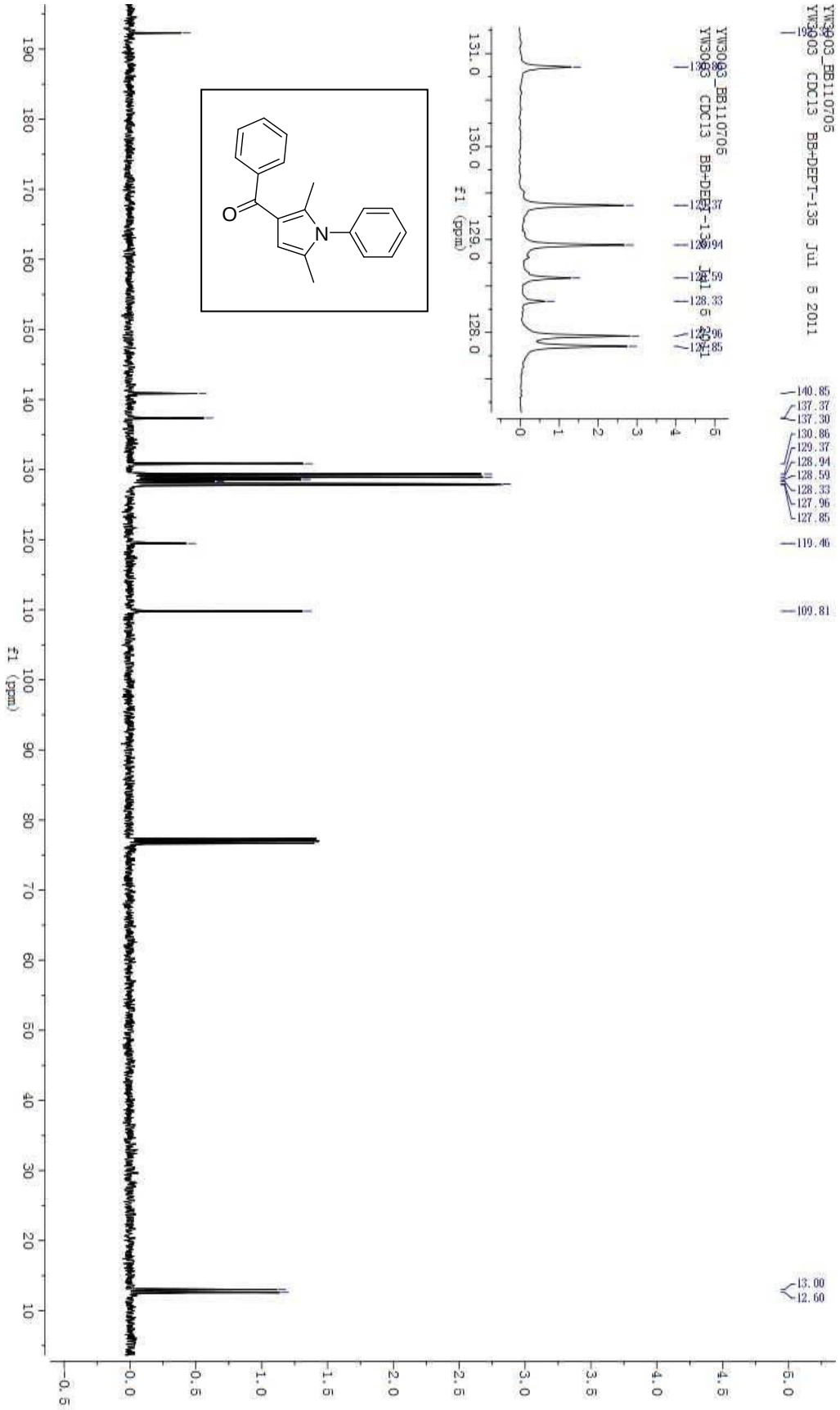


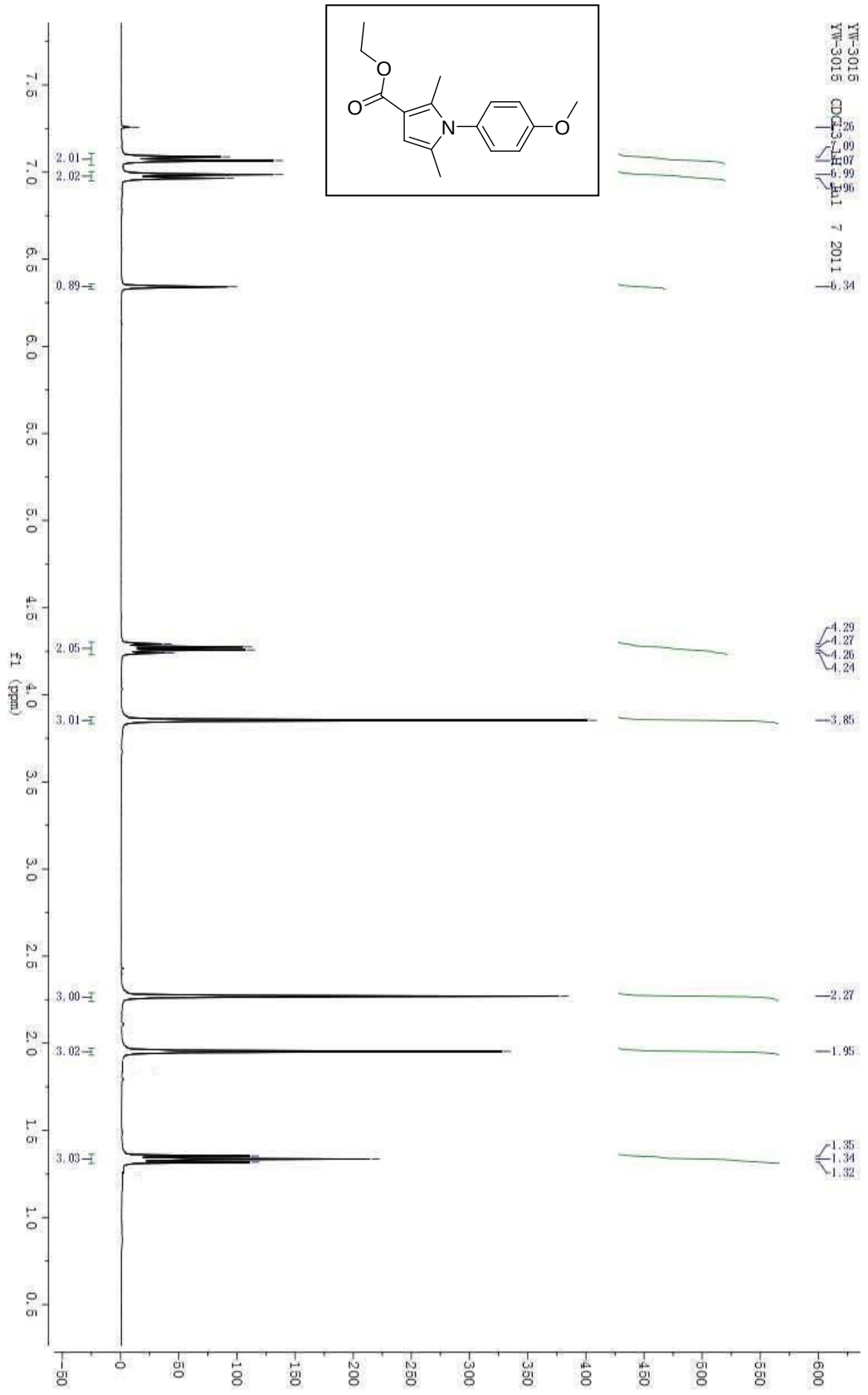


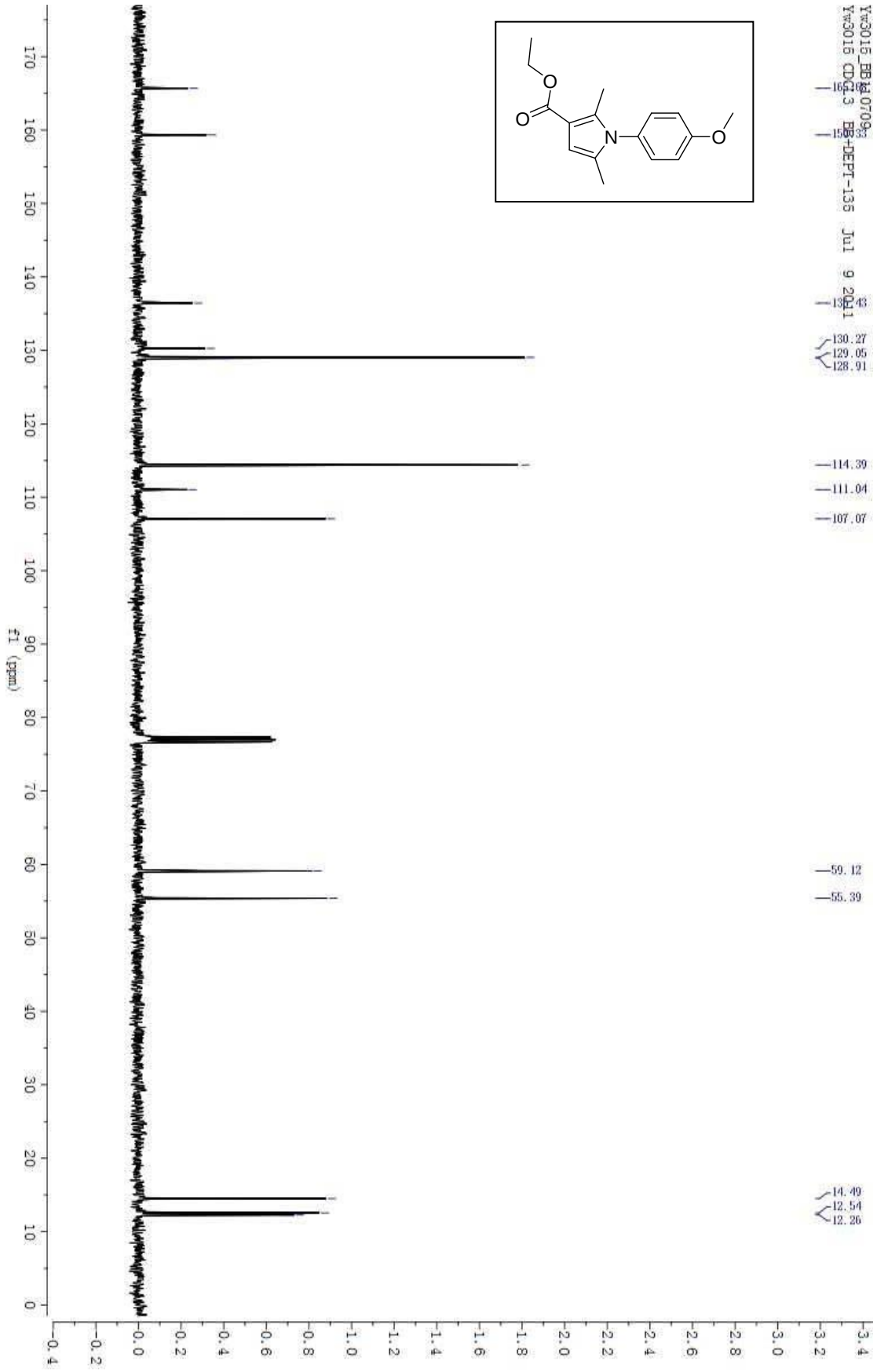


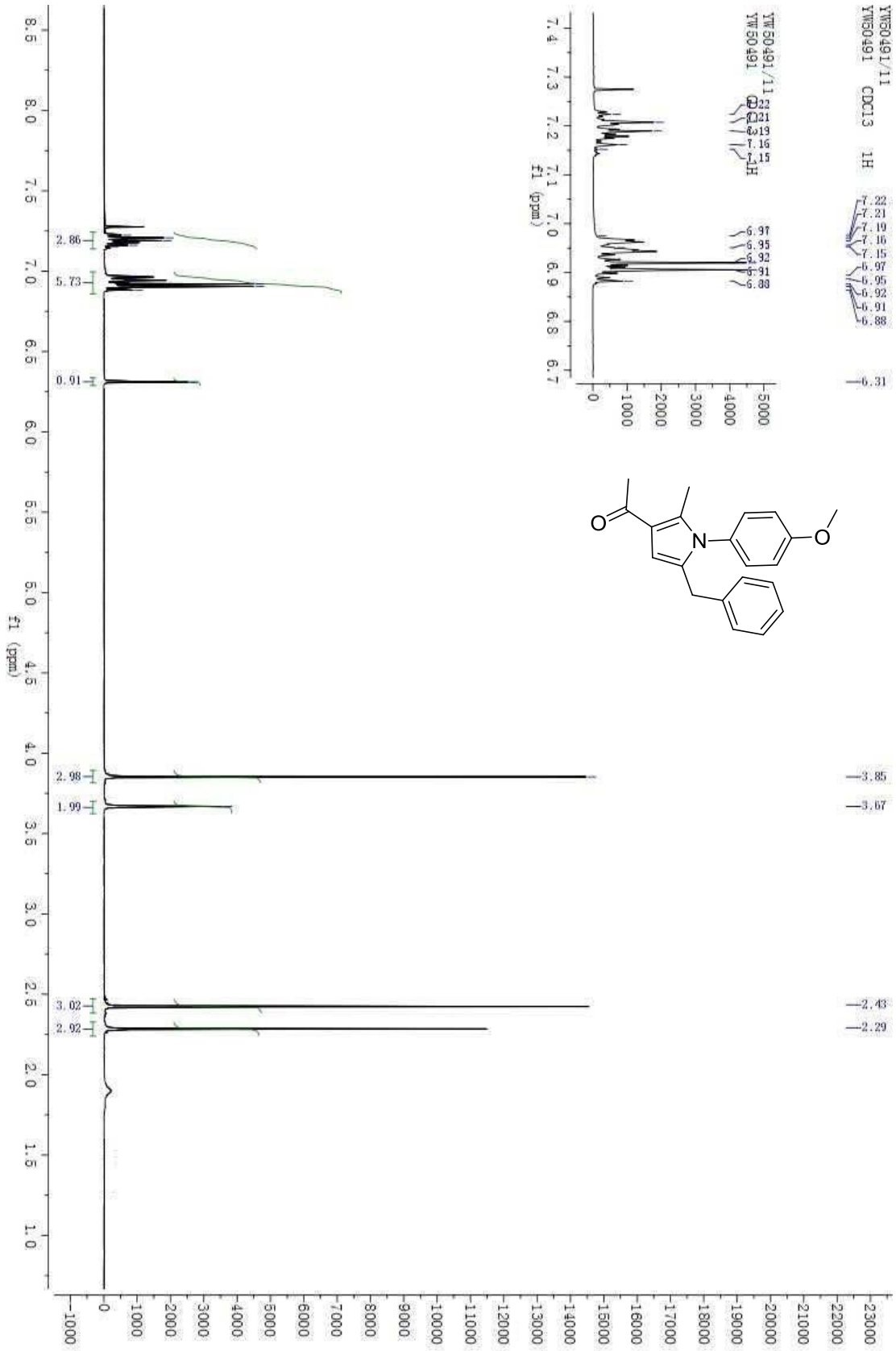


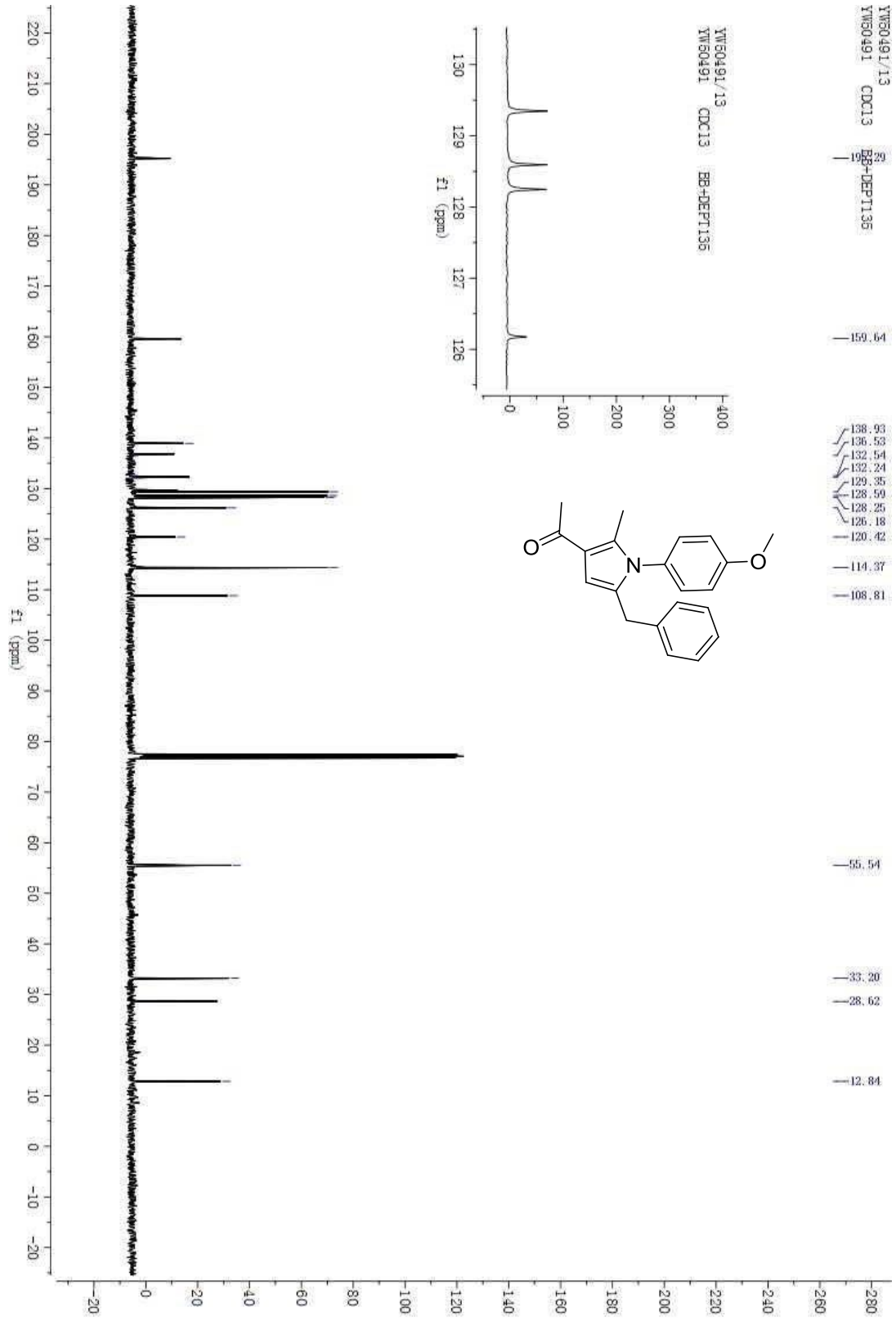




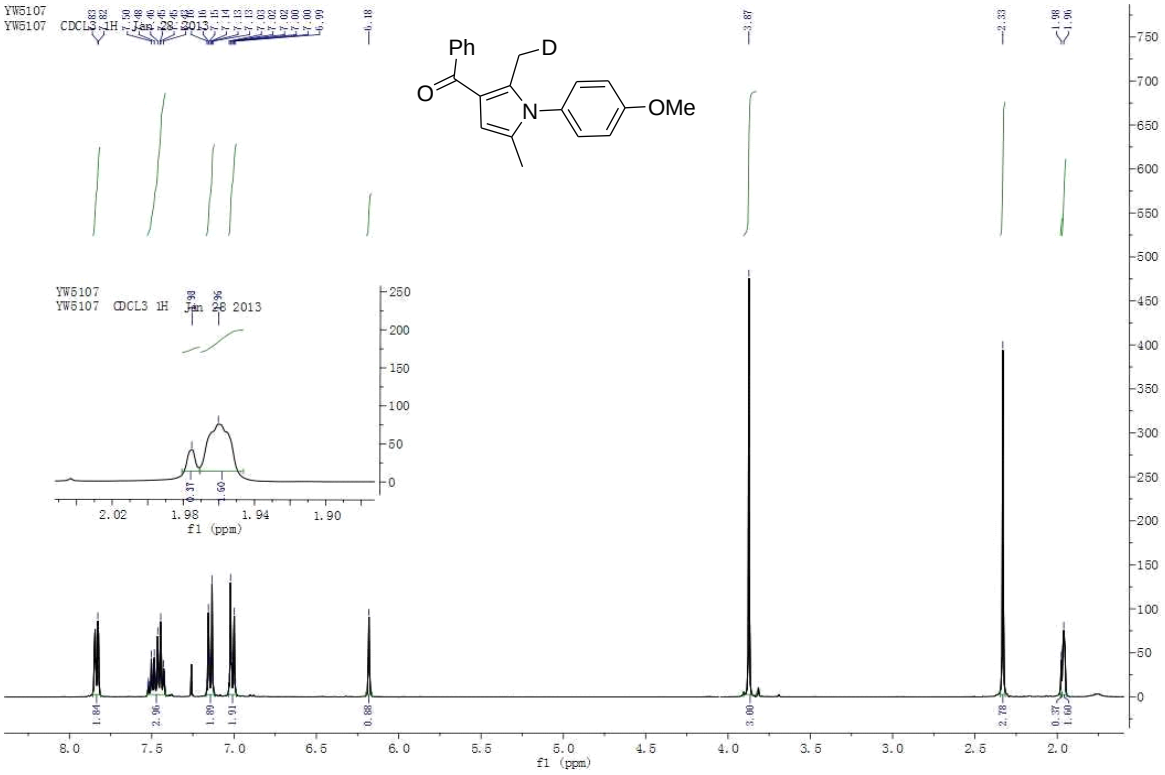



Yw3016_BB-H-0709-3
Yw3016 CDCl3 BB-DEPT-135 Jul 9 2011
O
O
N
O
130.27
129.05
128.91
114.39
111.04
107.07
59.12
55.39
14.49
12.54
12.26
f1 (ppm)

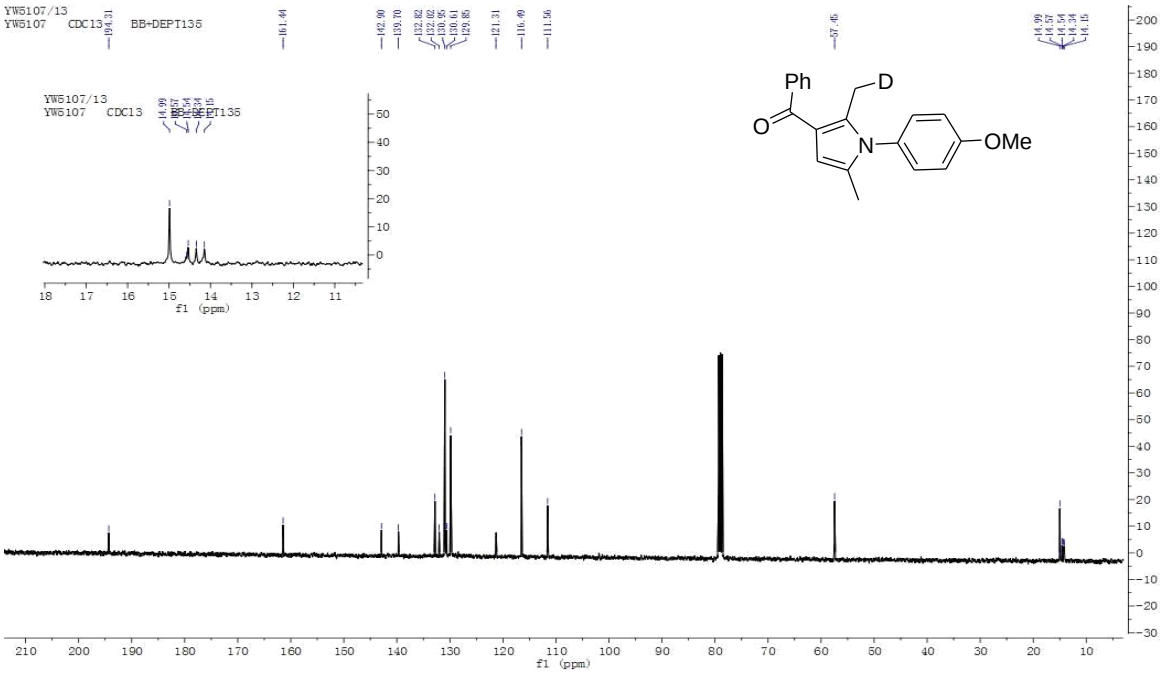

YW50491/11
YW50491 CDCl3 1H
7.22
7.21
7.19
7.16
7.15
6.97
6.95
6.92
6.91
6.88
6.31
3.85
3.67
2.43
2.29
2.86
5.73
0.91
2.98
1.99
3.02
2.92
f1 (ppm)
O
N
O


YW50491/13
YW50491 CDCl3 BB-DEPT135
159.64
138.93
136.53
132.54
132.24
129.35
128.59
128.25
126.18
120.42
114.37
108.81
55.54
33.20
28.62
12.84
f1 (ppm)
O
N
O

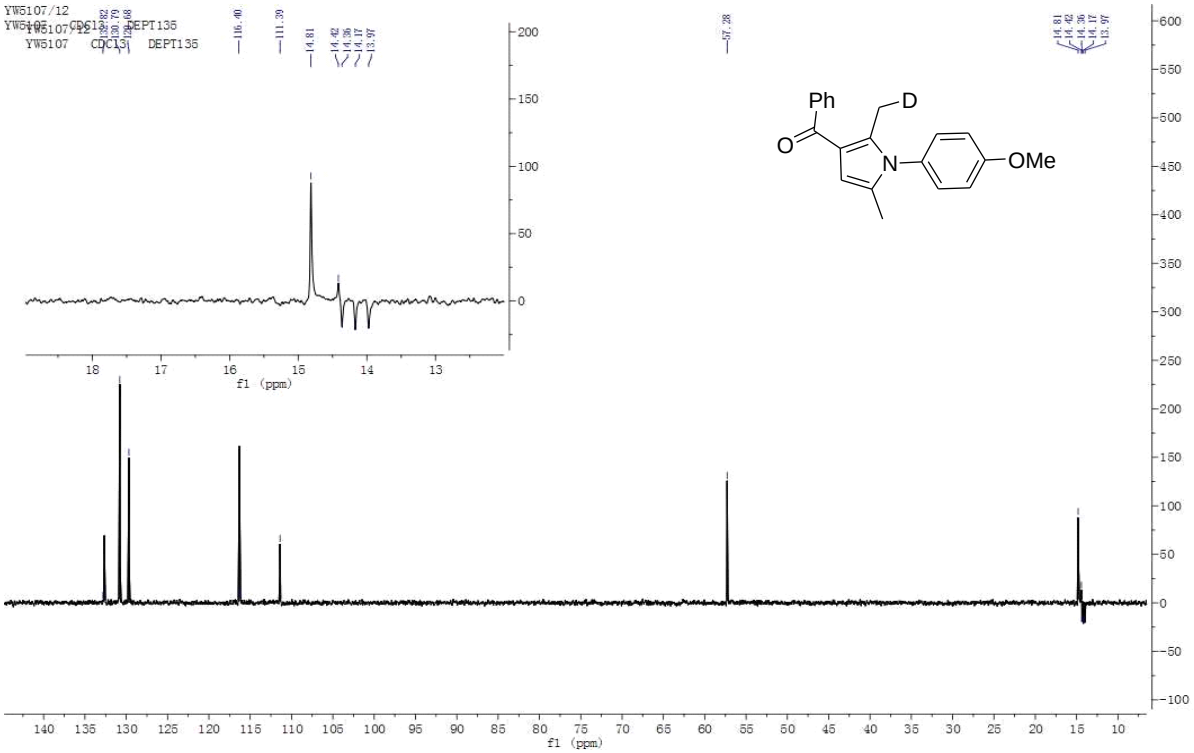
^{1}H NMR



^{13}C NMR



DEPT



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