Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Palladium-catalyzed C–H activation of anilides at room temperature: *ortho*-arylation and acetoxylation

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I. General remarks

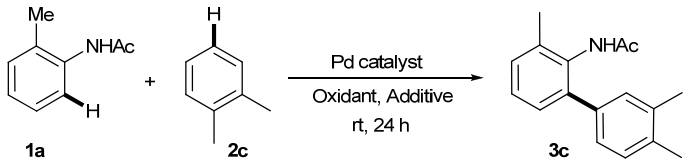
NMR spectra were obtained on a Bruker AV II-400 or a Varian Inova 400 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, TMS, acetone-d_6, methanol-d_4 or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; TMS: δ = 0.00 ppm; acetone-d_6: δ = 2.05 ppm; methanol-d_4: δ = 3.31 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$, acetone-d_6, methanol-d_4 or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; acetone-d_6: δ = 29.84, 206.26 ppm; methanol-d_4: δ = 49.00 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF Premier (ESI). Melting points were determined with XRC-1 instrument and are uncorrected.

All the reactions were carried out under an air atmosphere. Arenes, trifluoroacetic acid, $K_2S_2O_8$, $(NH_4)_2S_2O_8$, $Na_2S_2O_8$ and $Cu(OAc)_2$ were purchased from Chengdu Kelong Chemical Engineering Reagent (China) CO., Ltd. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Anilides were prepared according to the literature procedure from anilines.[1]

II. Optimization of the *ortho*-arylation reaction of anilides at room temperature

A Schlenk tube was charged with palladium species (0.05 mmol), oxidant (1.0 mmol, 2.0 equiv) and N-(*o*-tolyl)acetamide **1a** (0.5 mmol) under air. Additive and *o*-xylene **2c** were then added via syringes. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) to provide the desired product.

Table S1 Optimization of the palladium-catalyzed direct *ortho*-arylation of N-(*o*-tolyl)acetamide **1a**[a]



Entry	Palladium (mol%)	Oxidant (equiv)	Additive (equiv)	Yield (%)[b]
1	$Pd(OAc)_2$ (10)	$K_2S_2O_8$ (2)	TFA (20)	86
2	$Pd(OAc)_2$ (10)	$Na_2S_2O_8$ (2)	TFA (20)	80
3	**$Pd(OAc)_2$ (10)**	**$(NH_4)_2S_2O_8$ (2)**	**TFA (20)**	**95**
4	$Pd(OAc)_2$ (10)	Oxone (2)	TFA (20)	trace

5	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)	TFA (20)	trace[c]
6	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$ (2)	TFA (20)	16
7	$PdCl_2$ (10)	$(NH_4)_2S_2O_8$ (2)	TFA (20)	trace[c]
8	$Pd(TFA)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	TFA (20)	88
9	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	HOAc (20)	16
10	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	PivOH (20)	trace
11	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	HBF_4 (20)[d]	trace[c]
12	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	TFA (10)	63
13	$Pd(OAc)_2$ (5)	$(NH_4)_2S_2O_8$ (2)	TFA (20)	84
14[e]	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	TFA (20)	70
15	$Pd(OAc)_2$ (0)	$(NH_4)_2S_2O_8$ (2)	TFA (20)	0
16	$Pd(OAc)_2$ (10)	$(NH_4)_2S_2O_8$ (2)	TFA (0)	0

[a] Reaction conditions: 2-methyl acetanilide (0.5 mmol), *o*-xylene (10.0 mmol, 20.0 equiv), palladium species, additive, and oxidant (1.0 mmol, 2.0 equiv) at room temperature for 24 h under air. [b] Isolated yield. [c] Most of the starting materials were consumed. [d] 40% HBF_4 aqueous solution was used. [e] 10.0 equiv of *o*-xylene was used. TFA = Trifluoroacetic acid.

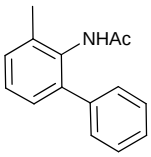
III. General procedure for the *ortho*-arylation reaction of anilides at room temperature

A Schlenk tube was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $(NH_4)_2S_2O_8$ (228.0 mg, 1.00 mmol) and anilide derivatives (0.5 mmol) under air. TFA (0.74 mL, 10.0 mmol) and arenes (10.0 mmol) were then added via syringes. After being stirred at room temperature for 24 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product.

IV. General procedure for the *ortho*-acetoxylation reaction of anilides at room temperature

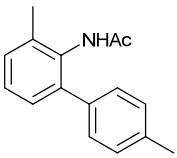
A Schlenk tube was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $(NH_4)_2S_2O_8$ (228.0 mg, 1.00 mmol) and anilide derivatives (0.5 mmol) under air. TFA (0.19 mL, 2.5 mmol) and HOAc (0.6 mL, 10.0 mmol) were then added via syringes. After being stirred at room temperature for 24 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product.

V. Characterization of the described substances



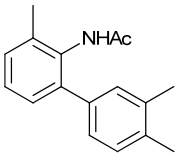
N-(3-Methyl-[1,1'-biphenyl]-2-yl)acetamide (3a)[2]

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3a** as a white solid (75.1 mg, 67% yield). M.p.: 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H), 2.31 (s, 3H), 6.65 (s, 1H), 7.17 (t, J = 4.8 Hz, 1H), 7.27 (d, J = 4.8 Hz, 1H), 7.32 (d, J = 7.6 Hz, 3H), 7.36 (d, J = 6.4 Hz, 1H), 7.39-7.43 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 23.1, 127.46, 127.53, 128.0, 128.4, 129.0, 130.2, 132.7, 136.9, 139.67, 139.73, 169.6 ppm. HRMS (ESI^+): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1232, found 226.1233.



N-(3,4'-Dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3b)

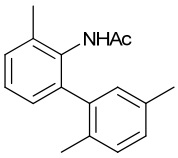
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v)) afforded **3b** as a white solid (94.5 mg, 79% yield). ^{1}H NMR (400 MHz, methanol-d_4): δ 1.93 (s, 3H), 2.26 (s, 3H), 2.36 (s, 3H), 7.14-7.26 (m, 7H) ppm. ^{13}C NMR (100 MHz, methanol-d_4): δ 18.5, 21.2, 22.2, 128.6, 129.1, 129.8, 130.5, 134.2, 137.9, 138.0, 138.4, 141.9, 172.6 ppm. HRMS (ESI^+): calcd for $C_{16}H_{17}NNaO$ $[M+Na]^+$ 262.1208, found 262.1214. The NMR data of **3b** were consistent with the compound obtained through the coupling reaction of N-(*o*-tolyl)acetamide and *p*-tolylboronic acid.[3]



N-(3,3',4'-Trimethyl-[1,1'-biphenyl]-2-yl)acetamide (3c)

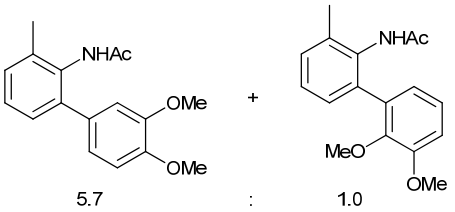
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3c** as a white solid (119.8 mg, 95% yield). M.p.: 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H), 2.28-2.31 (m, 9H), 6.64 (s, 1H), 7.06 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.10 (s, 1H), 7.15-7.18 (m, 2H), 7.24 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8, 19.6, 19.9, 23.2, 126.4, 127.4, 128.0, 129.7, 130.0, 130.2, 132.7, 135.9, 136.7, 136.8, 137.1, 139.4, 169.5 ppm. HRMS

(ESI$^+$): calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1545, found 254.1545.



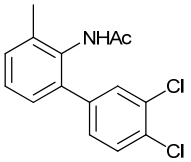
***N*-(2',3,5'-Trimethyl-[1,1'-biphenyl]-2-yl)acetamide (3d)**

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3d** as a white solid (92.9 mg, 73% yield). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H), 2.03 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 6.47 (s, 1H), 6.90 (s, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.20-7.27 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 19.5, 21.0, 23.2, 126.9, 127.6, 128.5, 128.7, 130.0, 130.1, 133.1, 133.3, 135.1, 136.3, 138.7, 138.8, 168.7 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1545, found 254.1546.



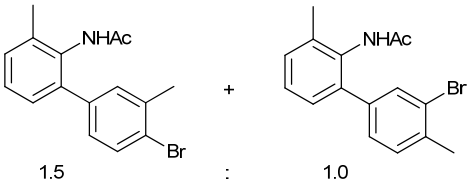
***N*-(3',4'-Dimethoxy-3-methyl-[1,1'-biphenyl]-2-yl)acetamide (3e) and *N*-(2',3'-dimethoxy-3-methyl-[1,1'-biphenyl]-2-yl)acetamide (3e')**

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded the mixture of **3e** and **3e'** as a white solid (107.2 mg, 70% yield). The ratio of **3e**/**3e'** was 5.7/1 as determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers): δ 2.02 (s, COC<u>H</u>$_3$, major + minor isomer), 2.30 (s, C<u>H</u>$_3$, major isomer), 2.33 (s, C<u>H</u>$_3$, minor isomer), 3.84 (s, OC<u>H</u>$_3$, major isomer), 3.86 (s, OC<u>H</u>$_3$, minor isomer), 3.90 (s, OC<u>H</u>$_3$, minor isomer), 3.91 (s, OC<u>H</u>$_3$, major isomer), 6.68 (br. s, N<u>H</u>Ac, major isomer), 6.75 (br. s, N<u>H</u>Ac, minor isomer), 6.84-6.92 (m), 7.17 (t, J = 4.8 Hz), 7.24-7.28 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18. 5, 18. 6, 20.2, 23.0, 55.75, 55.84, 111.0, 111.2, 112.1, 112.5, 121.0, 121.5, 127.4, 127.9, 128.2, 128.6, 129.78, 129.84, 131.6, 132.4, 132.8, 133.6, 136.7, 136.9, 139.5, 140.5, 148.3, 148.4, 148.5, 148.7, 169.5, 172.7 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$ 308.1263, found 308.1259.



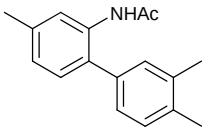
***N*-(3',4'-Dichloro-3-methyl-[1,1'-biphenyl]-2-yl)acetamide (3f)**

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3f** as a white solid (51.7 mg, 35% yield). M.p.: 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H), 2.30 (s, 3H), 6.59 (s, 1H), 7.14 (dd, J = 6.8 Hz, 2.4 Hz, 1H), 7.18 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.42 (d, J = 2.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 23.1, 127.8, 127.9, 128.4, 130.4, 130.8, 131.0, 131.8, 132.5, 132.6, 137.3, 137.8, 139.8, 169.5 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}Cl_2NNaO$ $[M+Na]^+$ 316.0272, found 316.0268.



***N*-(4'-Bromo-3,3'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3g)** and ***N*-(3'-bromo-3,4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3g')**

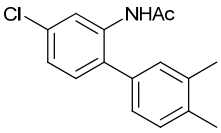
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded the mixture of **3g** and **3g'** as a white solid (49.1 mg, 31% yield). The ratio of **3g**/**3g'** was 1.5/1 as determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers): δ 2.02 (s, COC$\underline{H}_3$, major isomer), 2.03 (s, COC$\underline{H}_3$, minor isomer), 2.29 (s, C$\underline{H}_3$, major + minor isomer), 2.42 (s, C$\underline{H}_3$, major isomer), 2.43 (s, C$\underline{H}_3$, minor isomer), 6.62 (br. s, N$\underline{H}$Ac, major + minor isomer), 7.00 (d, J = 8.0 Hz, major isomer), 7.13-7.15 (m), 7.18 (s, major isomer) 7.23-7.30 (m), 7.50 (s, minor isomer), 7.54 (d, J = 8.4 Hz, major isomer) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 20.3, 22.7, 22.93, 22.95, 23.0, 124.1, 124.7, 127.6, 127.75, 127.82, 127.84, 130.3, 130.4, 130.6, 131.3, 132.2, 132.5, 132.6, 132.7, 136.9, 136.99, 137.02, 137.8, 138.2, 138.8, 139.98, 139.03, 169.55, 169.56 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{16}BrKNO$ $[M+K]^+$ 356.0052, found 356.0053.



***N*-(3',4,4'-Trimethyl-[1,1'-biphenyl]-2-yl)acetamide (3h)**

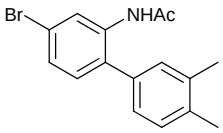
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3h** as a white solid (103.9 mg, 82% yield). M.p.: 58-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H), 2.315 (s, 3H), 2.323 (s, 3H), 2.40 (s, 3H), 6.97 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.10-7.12 (m, 2H), 7.19 (br. s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ 19.6, 19.9, 21.6, 24.7, 122.1, 125.2, 126.6, 129.5, 129.9, 130.3, 130.6, 134.6, 135.8, 136.3, 137.5, 138.2, 168.3 ppm. HRMS (ESI^+): calcd for $C_{17}H_{19}NNaO$ $[M+Na]^+$ 276.1364, found 276.1358.



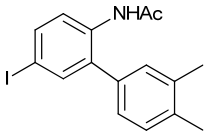
***N*-(4-Chloro-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3i)**

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3i** as a white solid (86.8 mg, 63% yield). M.p.: 66-68 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 7.06 (d, J = 7.6 Hz, 1H), 7.10-7.12 (m, 3H), 7.22 (br. s, 1H), 7.24 (d, J = 7.6 Hz, 1H), 8.42 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 20.0, 24.8, 121.0, 124.2, 126.5, 130.2, 130.5, 130.6, 131.0, 133.9, 134.6, 136.0, 137.0, 137.9, 168.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{16}ClNNaO$ $[M+Na]^+$ 296.0818, found 296.0818.



***N*-(4-Bromo-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3j)**

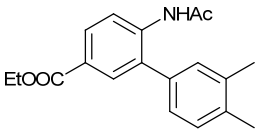
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3j** as a white solid (106.0 mg, 66% yield). M.p.: 88 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 7.09 (d, J = 7.6 Hz, 2H), 7.12 (s, 1H), 7.23 (br. s, 1H), 7.26-7.31 (m, 2H), 8.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 19.9, 24.8, 121.8, 123.8, 126.4, 127.1, 130.4, 130.5, 130.7, 131.3, 134.6, 136.1, 137.0, 137.9, 168.2 ppm. HRMS (ESI^+): calcd for $C_{16}H_{16}BrNNaO$ $[M+Na]^+$ 340.0313, found 340.0310.



***N*-(5-Iodo-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (3k)**

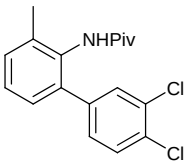
Purification via column chromatography on silica gel (DCM/EtOAc = 40/1, v/v) afforded **3k** as a white solid (80.6 mg, 44% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 7.06 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.18 (br. s, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.54 (s, 1H), 7.62 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 20.0,

24.8, 87.6, 122.9, 126.3, 130.4, 130.5, 134.0, 134.1, 134.8, 137.0, 137.2, 137.9, 138.6, 168.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{16}INNaO$ $[M+Na]^+$ 388.0174, found 388.0173.



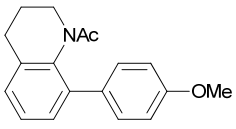
Ethyl 6-acetamido-3',4'-dimethyl-[1,1'-biphenyl]-3-carboxylate (3l)

Purification via column chromatography on silica gel (DCM/EtOAc = 40/1, v/v) afforded **3l** as a white solid (95.7 mg, 62% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, J = 7.2 Hz, 3H), 2.05 (s, 3H), 2.337 (s, 3H), 2.343 (s, 3H), 4.36 (q, J = 7.2 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.15 (s, 1H), 7.27 (d, J = 5.6 Hz, 1H), 7.42 (br. s, 1H), 7.90 (s, 1H), 8.02 (d, J = 8.8 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 19.6, 19.8, 24.8, 60.9, 120.0, 125.7, 126.4, 129.8, 130.50, 130.53, 131.4, 131.5, 134.6, 137.1, 137.9, 139.1, 166.2, 168.3 ppm. HRMS (ESI^+): calcd for $C_{19}H_{21}KNO_3$ $[M+K]^+$ 350.1159, found 350.1157.



***N*-(3',4'-Dichloro-3-methyl-[1,1'-biphenyl]-2-yl) pivalamide (3m)**

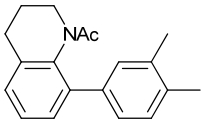
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 4/1, v/v) afforded **3m** as a white solid (51.7 mg, 31% yield). M.p.: 154-156 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (s, 9H), 2.24 (s, 3H), 6.82 (br. s, 1H), 7.13 (d, J = 6.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.23-7.26 (m, 2H), 7.41 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 27.6, 39.2, 127.6, 127.7, 128.6, 130.3, 130.86, 130.90, 131.6, 132.2, 132.8, 137.1, 137.8, 139.8, 177.0 ppm. HRMS (ESI^+): calcd for $C_{18}H_{20}Cl_2NO$ $[M+H]^+$ 336.0922, found 336.0925.



1-(8-(4-Methoxyphenyl)-3,4-dihydroquinolin-1(2*H*)-yl)ethanone (3n)[3]

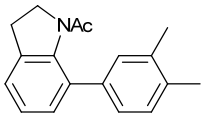
Purification via column chromatography on silica gel (petroleum ether/ether = 1/2, v/v)) afforded **3p** as a white solid (119.7 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 3H), 1.69-1.81 (m, 1H), 2.29-2.34 (m, 1H), 2.44-2.52 (m, 1H), 2.69-2.75 (m, 1H), 3.02-3.08 (m, 1H), 3.81 (s, 3H), 4.74-4.81 (m, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.23-7.29 (m, 4H) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ 21.9, 24.3, 26.8, 41.6, 55.2, 114.5, 126.3, 126.9, 128.5, 129.4, 131.3, 137.3, 137.5, 138.1, 159.0, 170.3 ppm.



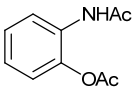
1-(8-(3,4-Dimethylphenyl)-3,4-dihydroquinolin-1(2*H*)-yl)ethanone (3o)[4]

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 4/1, v/v) afforded **3o** as a white solid (112.4 mg, 80% yield). M.p.: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 3H), 1.66-1.74 (m, 1H), 2.20 (s, 6H), 2.26 (s, 1H), 2.38-2.44 (m, 1H), 2.65-2.68 (m, 1H), 2.98-3.04 (m, 1H), 4.66-4.73 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.03 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H) 7.17-7.25 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 19.0, 21.0, 23.5, 26.0, 40.8, 124.7, 125.5, 125.9, 127.8, 128.5, 129.3, 135.0, 135.7, 136.2, 136.7, 137.0, 137.2, 169.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{21}NNaO$ $[M+Na]^+$ 302.1521, found 302.1518.



1-(7-(3,4-Dimethylphenyl)indolin-1-yl)ethanone (3p)

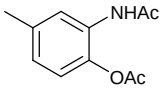
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 4/1, v/v) afforded **3p** as a white solid (112.1 mg, 84% yield). M.p.: 164-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (br. s, 3H), 2.28 (s, 6H), 3.02 (t, J = 6.8 Hz, 2H), 4.30 (s, 2H), 7.14-7.24 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 19.9, 22.7, 29.3, 50.6, 123.5, 124.8, 125.4, 128.5, 129.4, 130.4, 131.5, 135.7, 136.6, 137.4, 138.0, 140.3 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{19}NNaO$ $[M+Na]^+$ 288.1364, found 288.1369.



2-Acetamidophenyl acetate (4a)[5]

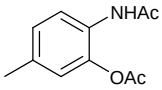
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4a** as a white solid (65.0 mg, 67% yield). M.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.37 (s, 3H), 7.13 (d, J = 4.0 Hz, 2H), 7.18 (br. s, 1H), 7.23 (dd, J = 8.4 Hz, 4.4 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 24.4, 122.2, 123.4, 125.0, 126.5, 129.8, 141.0, 168.6, 169.0 ppm. HRMS (ESI$^+$): calcd for $C_{10}H_{11}NNaO_3$ $[M+Na]^+$ 216.0637, found

216.0635.



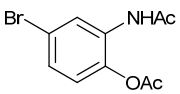
2-Acetamido-4-methylphenyl acetate (4b)[6]

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4b** as a white solid (78.0 mg, 75% yield). M.p.: 137-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.34 (s, 6H), 6.92 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.15 (br. s, 1H), 7.92 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 21.3, 24.6, 121.8, 123.8, 125.7, 129.3, 136.5, 138.8, 168.4, 169.2 ppm. HRMS (ESI^+): calcd for $C_{11}H_{13}NNaO_3$ $[M+Na]^+$ 230.0793, found 230.0789.



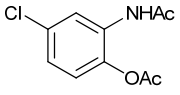
2-Acetamido-5-methylphenyl acetate (4c)[7]

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4c** as a white solid (52.9 mg, 51% yield). M.p.: 154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.32 (s, 3H), 2.35 (s, 3H), 6.93 (s, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.07 (br. s, 1H), 7.91 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 21.2, 24.5, 122.6, 123.7, 127.0, 127.3, 135.5, 141.2, 168.4, 169.1 ppm. HRMS (ESI^+): calcd for $C_{11}H_{13}NNaO_3$ $[M+Na]^+$ 230.0793, found 230.0794.



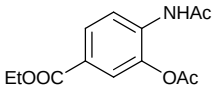
2-Acetamido-4-bromophenyl acetate (4d)

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4d** as a white solid (106.4 mg, 76% yield). M.p.: 171-172 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.09 (s, 3H), 2.30 (s, 3H), 7.11 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 8.18 (d, J = 2.0 Hz, 1H), 9.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 23.7, 117.6, 125.1, 125.4, 126.7, 132.3, 140.2, 168.90, 168.93 ppm. HRMS (ESI^+): calcd for $C_{10}H_{10}BrNNaO_3$ $[M+Na]^+$ 293.9742, found 293.9741.



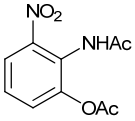
2-Acetamido-4-chlorophenyl acetate (4e)

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4e** as a white solid (82.7 mg, 73% yield). M.p.: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.36 (s, 3H), 7.06-7.10 (m, 2H), 7.20 (br. s, 1H), 8.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 24.8, 122.4, 123.1, 124.5, 130.8, 131.9, 138.6, 168.2, 168.5 ppm. HRMS (ESI$^+$): calcd for $C_{10}H_{10}ClNNaO_3$ $[M+Na]^+$ 250.0247, found 250.0249.



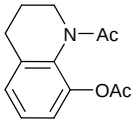
Ethyl 4-acetamido-3-acetoxybenzoate (4f)

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4f** as a white solid (77.2 mg, 58% yield). M.p.: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, J = 7.2 Hz, 3H), 2.21 (s, 3H), 2.39 (s, 3H), 4.35 (q, J = 7.2 Hz, 2H), 7.37 (s, 1H), 7.80 (d, J = 2.0 Hz, 1H), 7.91 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 8.39 (br. s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.2, 21.3, 23.9, 60.8, 122.2, 124.0, 125.0, 126.9, 135.4, 140.1, 164.8, 169.1, 169.2 ppm. HRMS (ESI$^+$): $C_{13}H_{15}NNaO_5$ $[M+Na]^+$ 288.0848, found 288.0851



2-Acetamido-3-nitrophenyl acetate (4g)

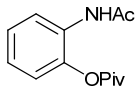
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4g** as a white solid (43.1 mg, 35% yield). M.p.: 181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.30 (s, 3H), 7.39 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.24 (br. s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 23.8, 122.5, 125.1, 126.3, 129.6, 144.6, 146.4, 168.1, 168.3 ppm. HRMS (ESI$^+$): calcd for $C_{10}H_{10}N_2NaO_5$ $[M+Na]^+$ 261.0487, found 261.0487.



1-Acetyl-1,2,3,4-tetrahydroquinolin-8-yl acetate (4h)

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **4h** as a white solid (86.9 mg, 74% yield). M.p.: 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73 (s, 1H), 2.03 (s, 3H), 2.20 (s, 1H), 2.26 (s, 3H), 2.55 (s, 1H), 2.72-2.76 (m, 1H), 2.89 (s, 1H), 4.56 (s, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 6.8 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100

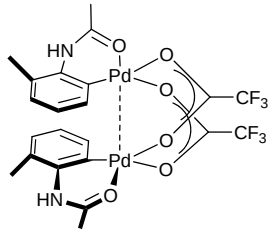
MHz, $CDCl_3$): δ 20.8, 21.7, 24.1, 26.3, 41.2, 120.7, 125.7, 126.9, 133.0, 137.8, 144.6, 168.6, 170.7 ppm. HRMS (ESI^+): calcd for $C_{13}H_{16}NO_3$ $[M+H]^+$ 234.1130, found 234.1132.



2-Acetamidophenyl pivalate (4i)

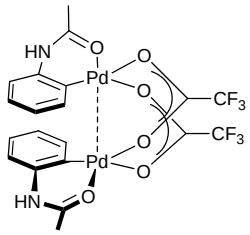
Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **4i** as a white solid (86.1 mg, 73% yield). M.p.: 85-87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 9H), 2.14 (s, 3H), 7.07 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 27.3, 39.5, 122.1, 123.4, 125.1, 126.5, 129.9, 141.2, 168.1, 176.4 ppm. HRMS (ESI^+): calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$ 236.1287, found 236.1288.

VI. The synthesis and characterization of bimetallic palladacycles 5a and 5b[8]



Bimetallic palladium complex 5a

To a 25 mL round-bottom flask was added *N*-(*o*-tolyl)acetamide (149.0 mg, 1.0 mmol), $Pd(OAc)_2$ (224.0 mg, 1.0 mmol), DCM (10 mL) and TFA (156.0 μL, 2.1 mmol) under air. After being stirred at room temperature for 8 h, the reaction mixture was diluted with 30 mL of EtOAc, filtered through a celite pad, and washed with 10 mL of EtOAc. The filtrate was collected and concentrated. The residue was recrystallized from EtOAc/hexane to give the palladium complex **5a** as a yellow solid (316 mg, 86% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 2.35 (s, 6H), 2.43 (s, 6H), 6.93 (t, J = 6.4 Hz, 2H), 7.01 (d, J = 6.4 Hz, 2H), 7.32 (br. s, 2H), 10.92 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.8, 21.2, 125.1, 125.8, 128.4, 130.6, 132.0, 159.2, 171.5 ppm. HRMS (ESI^+): calcd for $C_9H_{10}NOPd$ [monomer-TFA]$^+$ 253.9797, found 253.9796.



Bimetallic palladium complex 5b

Following the same procedure as complex **5a**. *N*-phenylacetamide (135.0 mg, 1.0 mmol) was used. Complex **5b** was obtained as a yellow solid (306 mg, 90% yield). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.46 (s, 6H), 6.86-6.90 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 10.49 (s, 2H) ppm. ^{13}C NMR (100 MHz, acetone-d_6): δ 20.2, 116.7, 123.8, 126.3, 131.9, 133.5, 167.9 ppm. HRMS (ESI^{+}): calcd for C_8H_8NOPd [monomer-TFA]$^{+}$ 239.9641, found 239.9633.

VII. The reaction of complex 5a with *o*-xylene

A Schlenk tube was charged with **5a** (73.7 mg, 0.1 mmol), TFA (296 μL, 4.0 mmol) and *o*-xylene (0.48 mL, 4.0 mmol) under air. After being stirred at room temperature for 24 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) to afford 46.4 mg of **3c** in 92% yield. No reaction happened if TFA was absent from the reaction mixture.

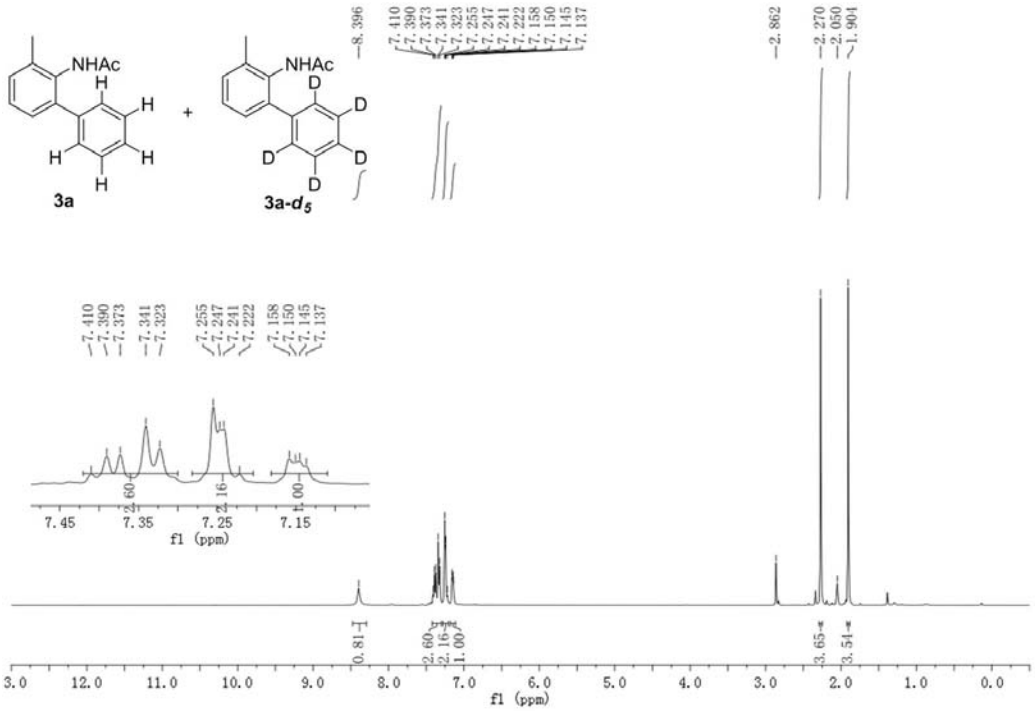
VIII. The acetoxylation of complex 5b

A Schlenk tube was charged with *N*-phenylacetamide (67.6 mg, 0.5 mmol), $(NH_4)_2S_2O_8$ (228.0 mg, 1.00 mmol), complex **5b** (17.0 mg, 0.025 mmol) and HOAc (0.6 mL, 10.0 mmol) under air. After being stirred at room temperature for 24 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) to afford 59.6 mg of **4a** in 62% yield. No reaction happened if $(NH_4)_2S_2O_8$ was absent from the reaction mixture.

IX. Intermolecular kinetic isotope effect

A Schlenk tube was charged with *N*-(*o*-tolyl)acetamide **1a** (75.0 mg, 0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and $(NH_4)_2S_2O_8$ (228.0 mg, 1.0 mmol) under air. TFA (0.74 mL, 10.0 mmol), benzene (0.45 mL, 5.0 mmol) and benzene-d_6 (0.45 mL, 5.0 mmol) were added via syringes. After being stirred at room temperature for 8 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) to afford **3a** and **3a-*d*$_5$** as an inseparable mixture (53.1 mg, 47% yield). The ratio of **3a**/**3a-*d*$_5$** was

2.6/2.4 (k_H/k_D = 1.1) as determined by ^{1}H NMR.



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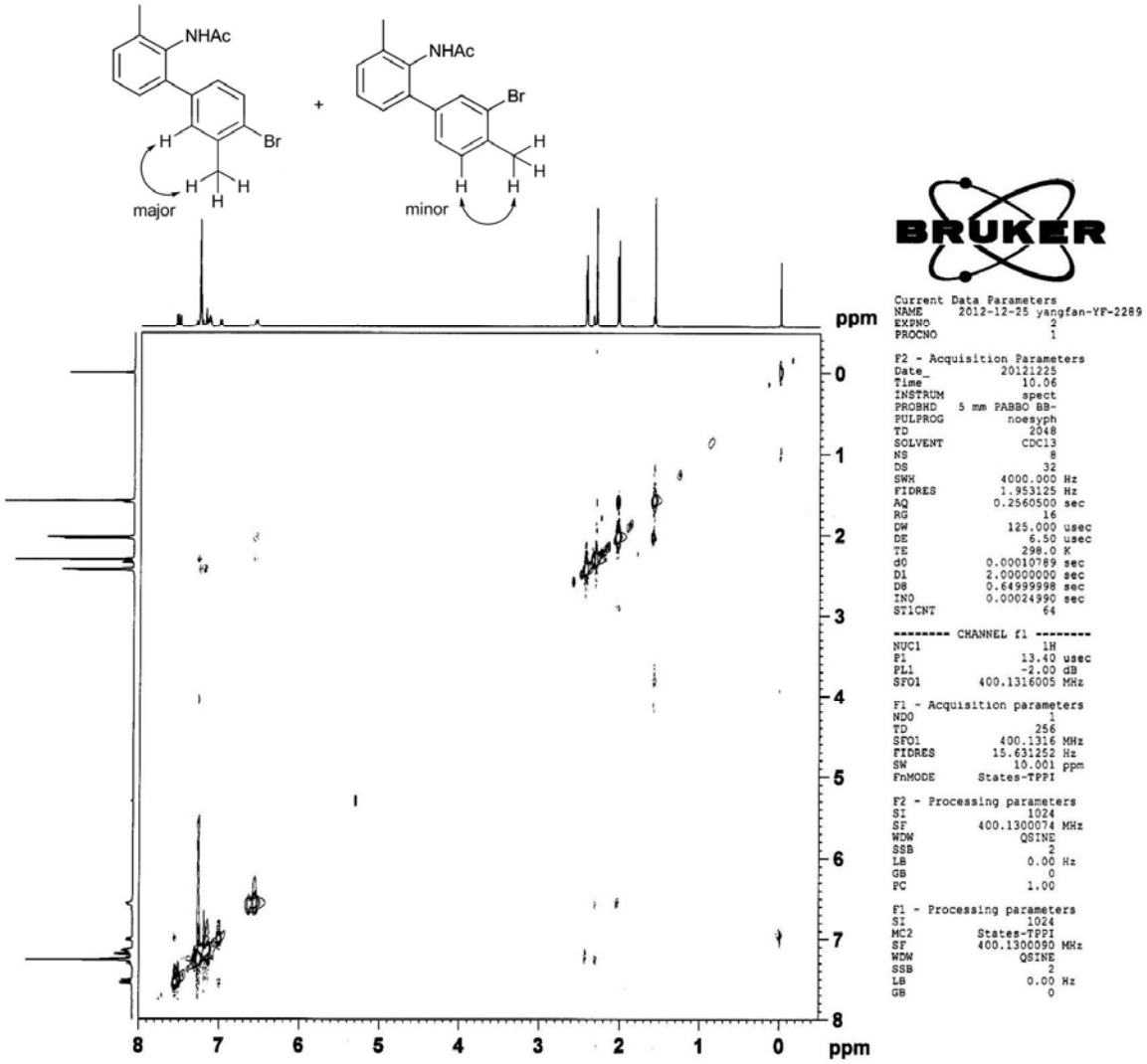
XI. ^{1}H-^{1}H NOESY spectrum of the mixture of 3g and 3g'



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Current Data Parameters
NAME        2012-12-25 yangfan-YF-2289
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20121225
Time              10.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         noesyph
TD                2048
SOLVENT           CDCl3
NS                   8
DS                  32
SWH           4000.000 Hz
FIDRES        1.953125 Hz
AQ            0.2560500 sec
RG                  16
DW             125.000 usec
DE               6.50 usec
TE              298.0 K
D0            0.00010789 sec
D1            2.00000000 sec
D8            0.64999998 sec
IN0           0.00024990 sec
ST1CNT              64

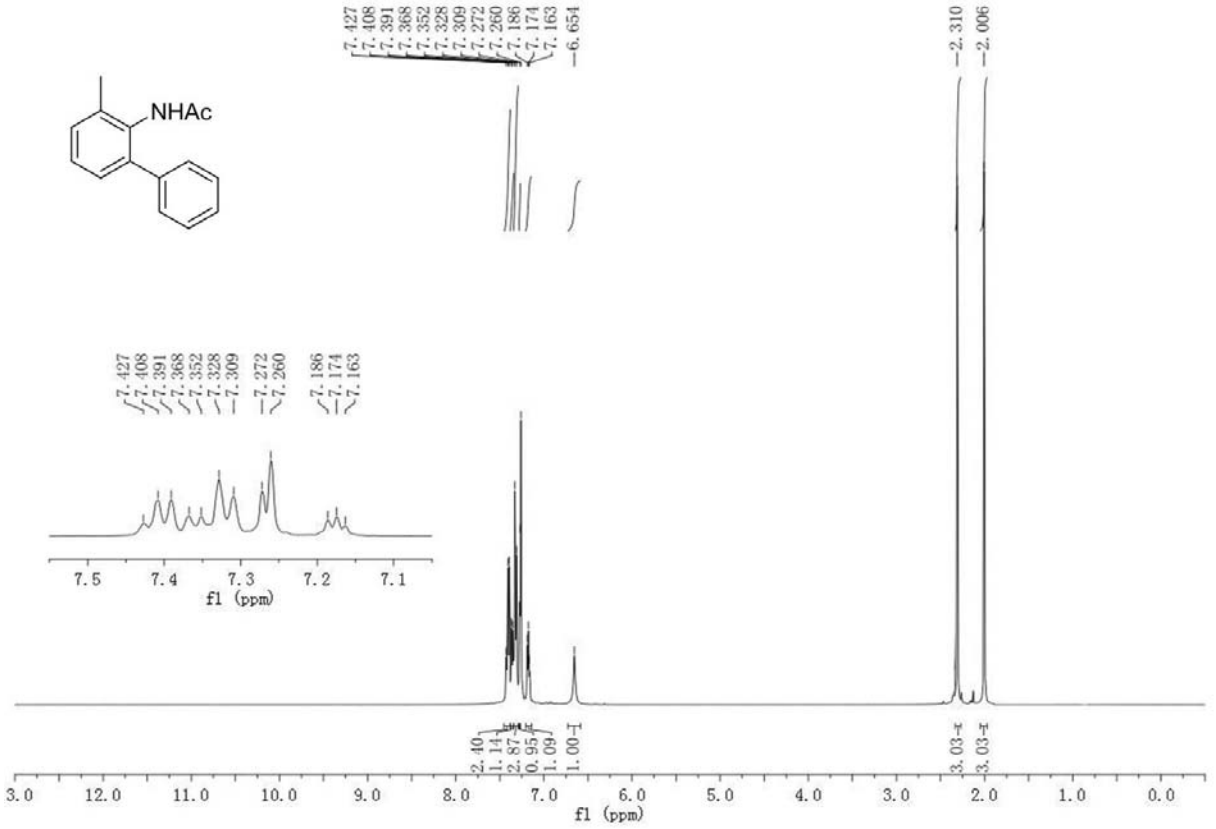
-------- CHANNEL f1 --------
NUC1                1H
P1                13.40 usec
PL1               -2.00 dB
SFO1        400.1316005 MHz

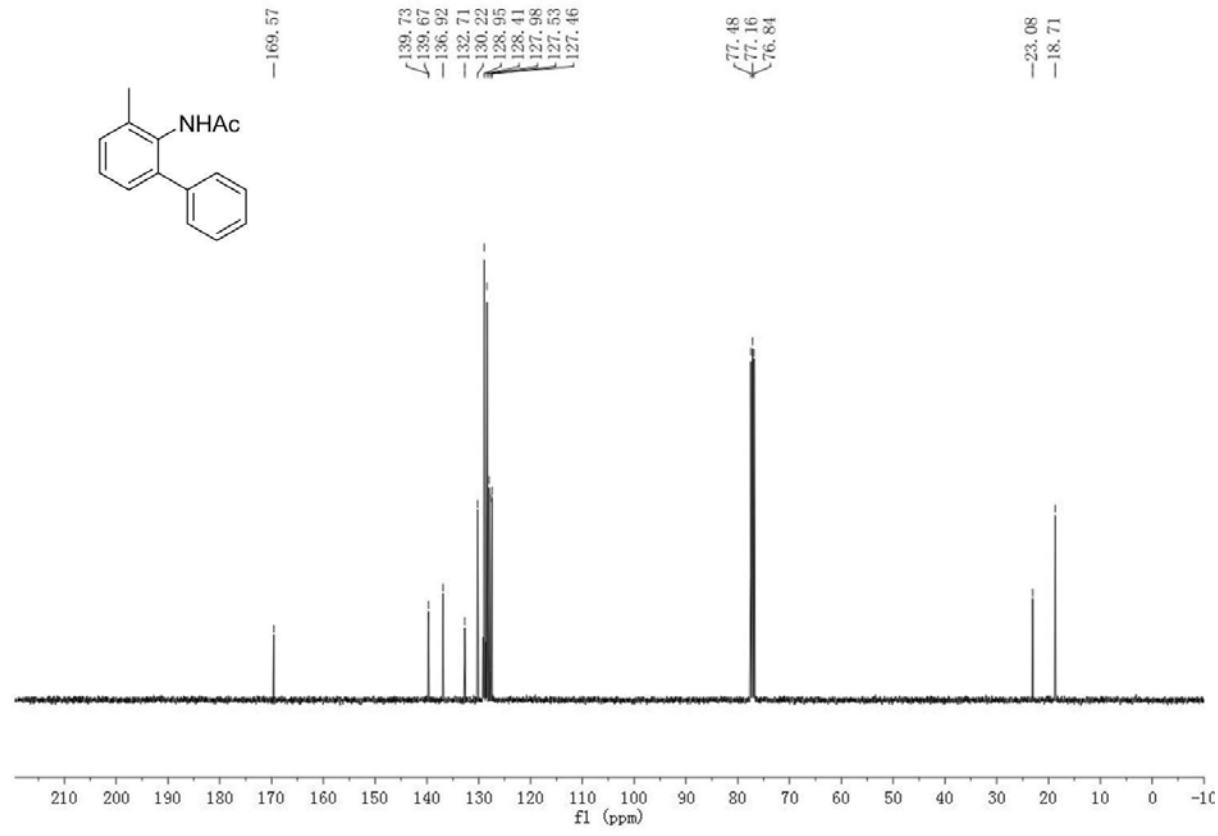
F1 - Acquisition parameters
ND0                 1
TD                256
SFO1        400.1316 MHz
FIDRES       15.631252 Hz
SW              10.001 ppm
FnMODE      States-TPPI

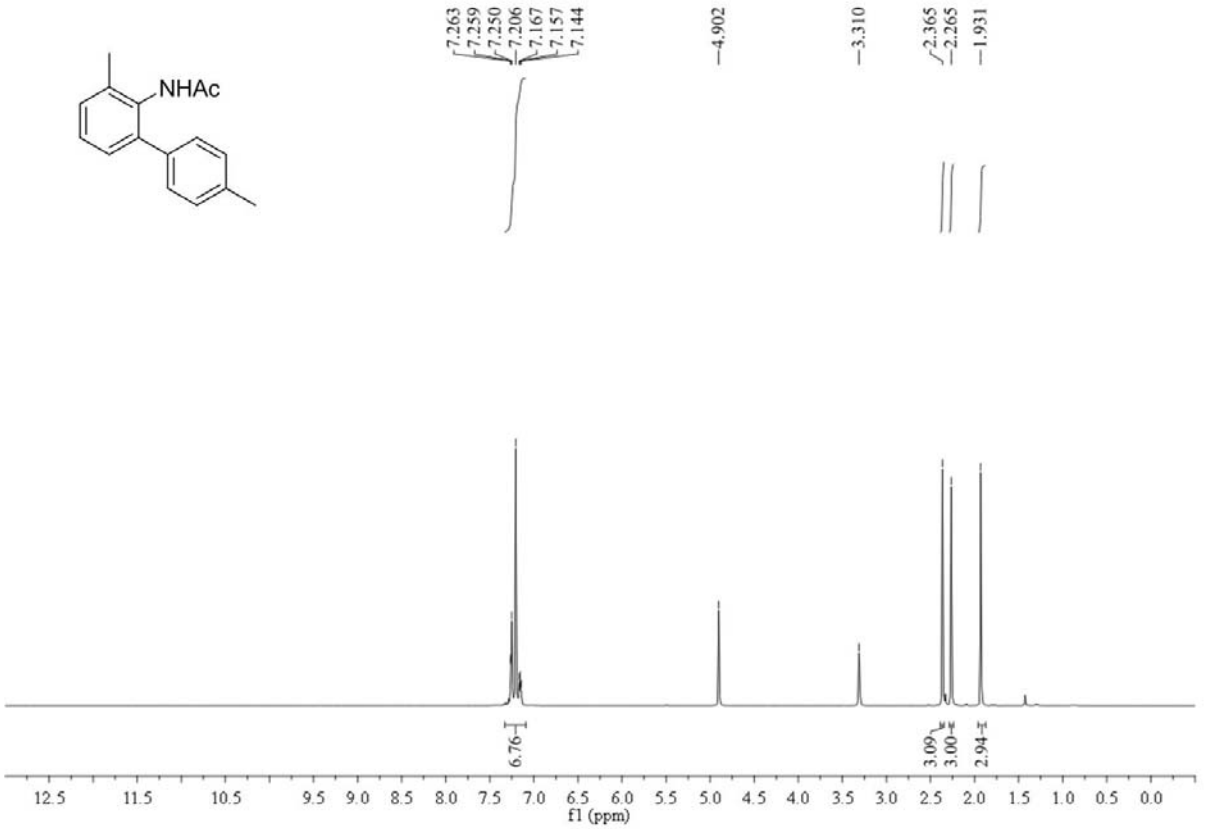
F2 - Processing parameters
SI                1024
SF          400.1300074 MHz
WDW               QSINE
SSB                 2
LB                0.00 Hz
GB                  0
PC                1.00

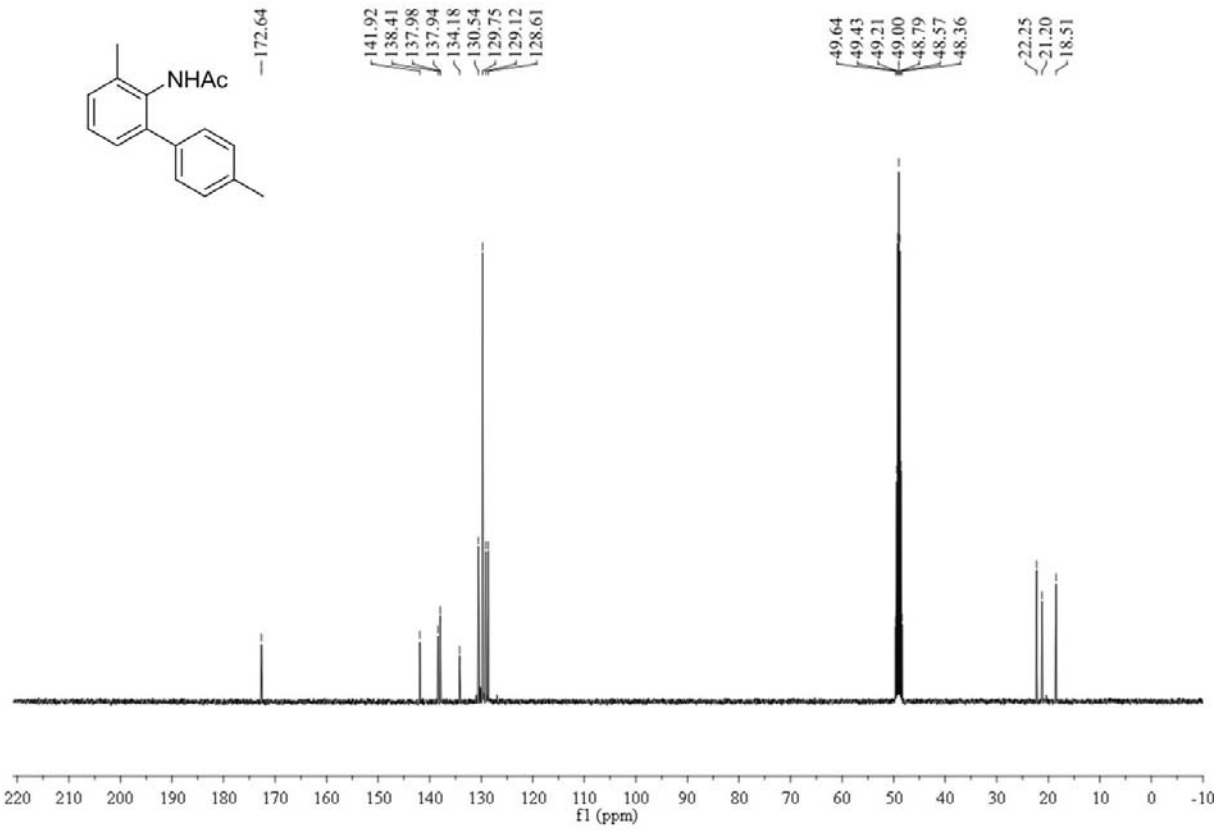
F1 - Processing parameters
SI                1024
MC2         States-TPPI
SF          400.1300090 MHz
WDW               QSINE
SSB                 2
LB                0.00 Hz
GB                  0
```

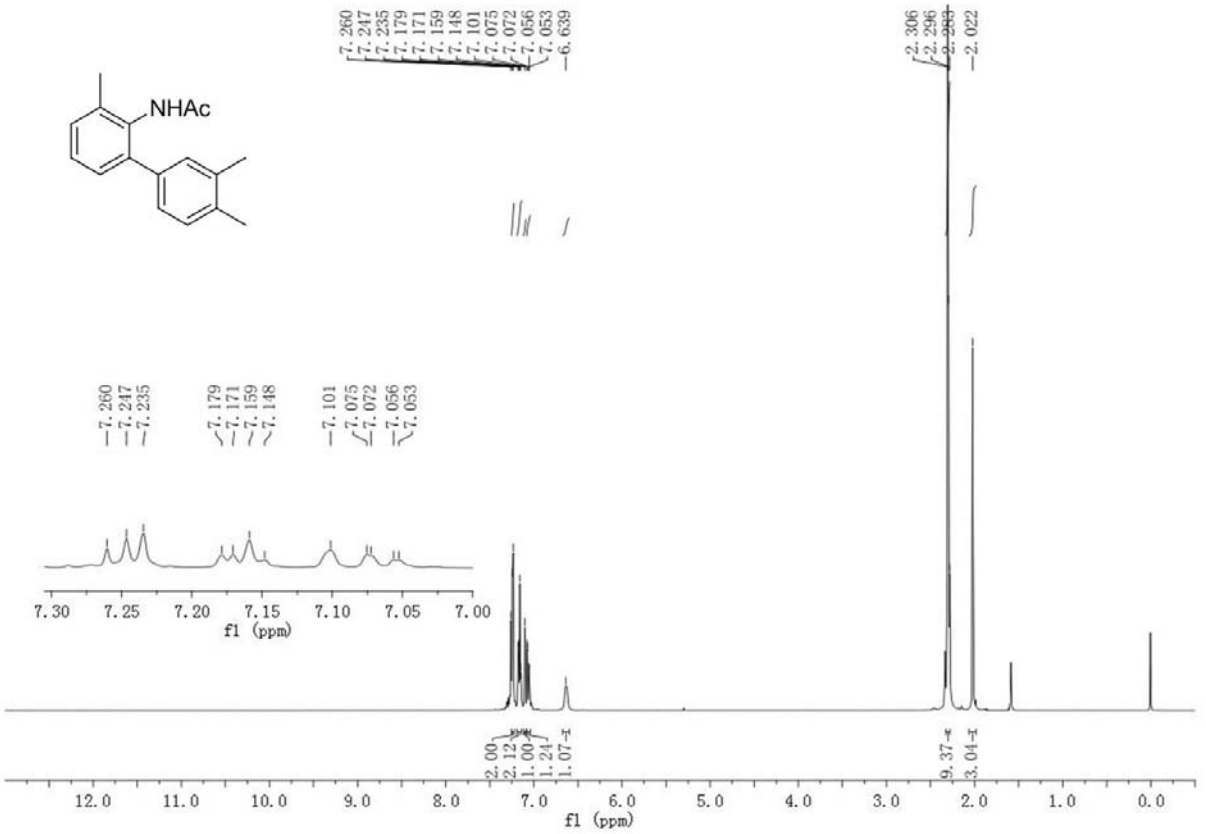
XII. Copies of ^{1}H and ^{13}C NMR spectra

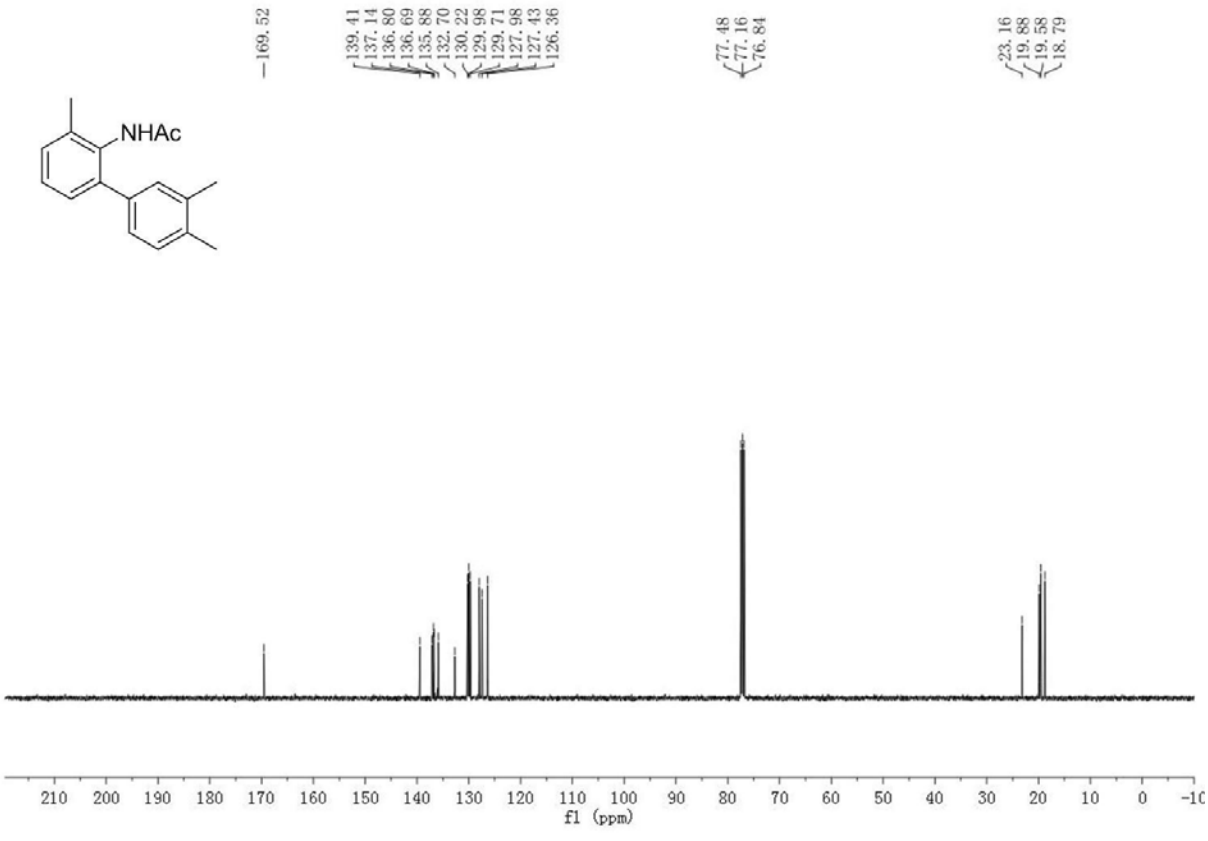





NHAc
7.263
7.259
7.250
7.206
7.167
7.157
7.144
4.902
3.310
2.365
2.265
1.931
6.76
3.09
3.00
2.94
f1 (ppm)


NHAc
172.64
141.92
138.41
137.98
137.94
134.18
130.54
129.75
129.12
128.61
49.64
49.43
49.21
49.00
48.79
48.57
48.36
22.25
21.20
18.51
f1 (ppm)


NHAc
7.260
7.247
7.235
7.179
7.171
7.159
7.148
7.101
7.075
7.072
7.056
7.053
6.639
2.306
2.296
2.283
2.022
f1 (ppm)
2.00
2.12
1.00
1.24
1.07
9.37
3.04


NHAc
169.52
139.41
137.14
136.80
136.69
135.88
132.70
130.22
129.98
129.71
127.98
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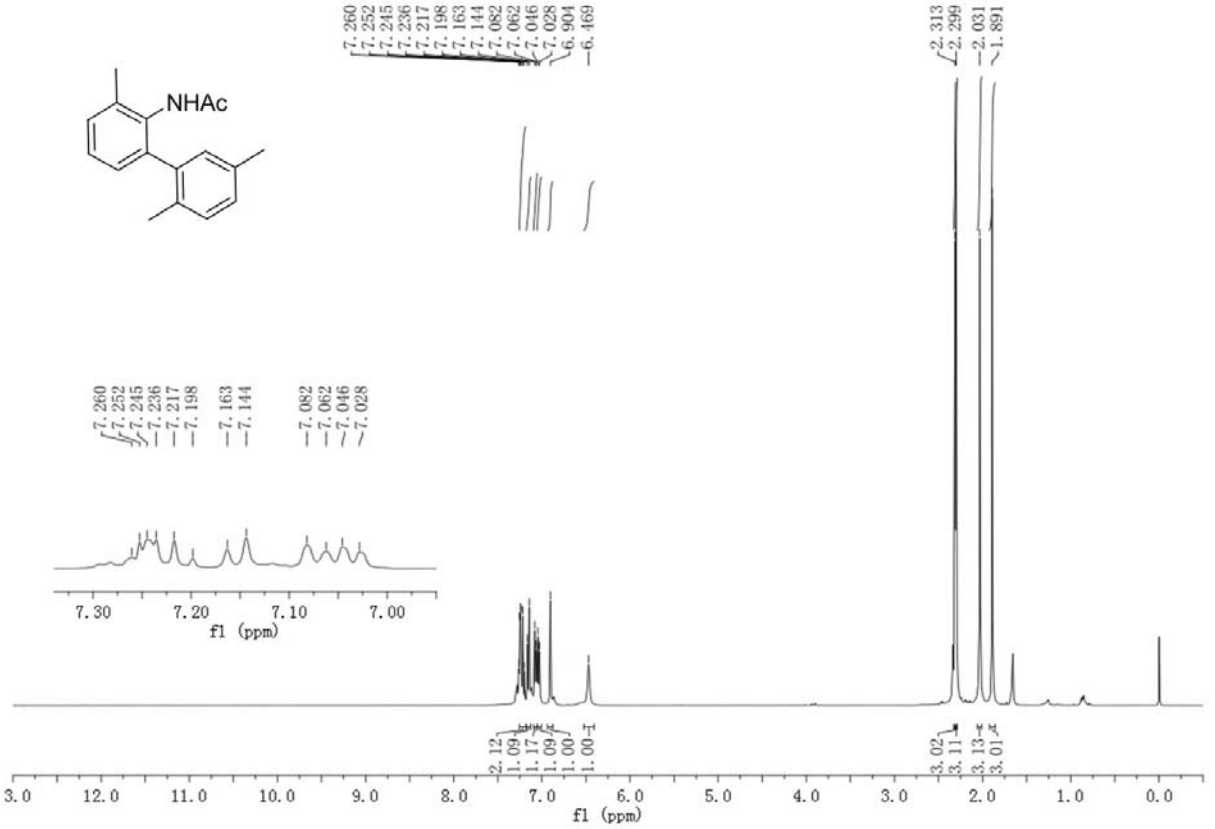
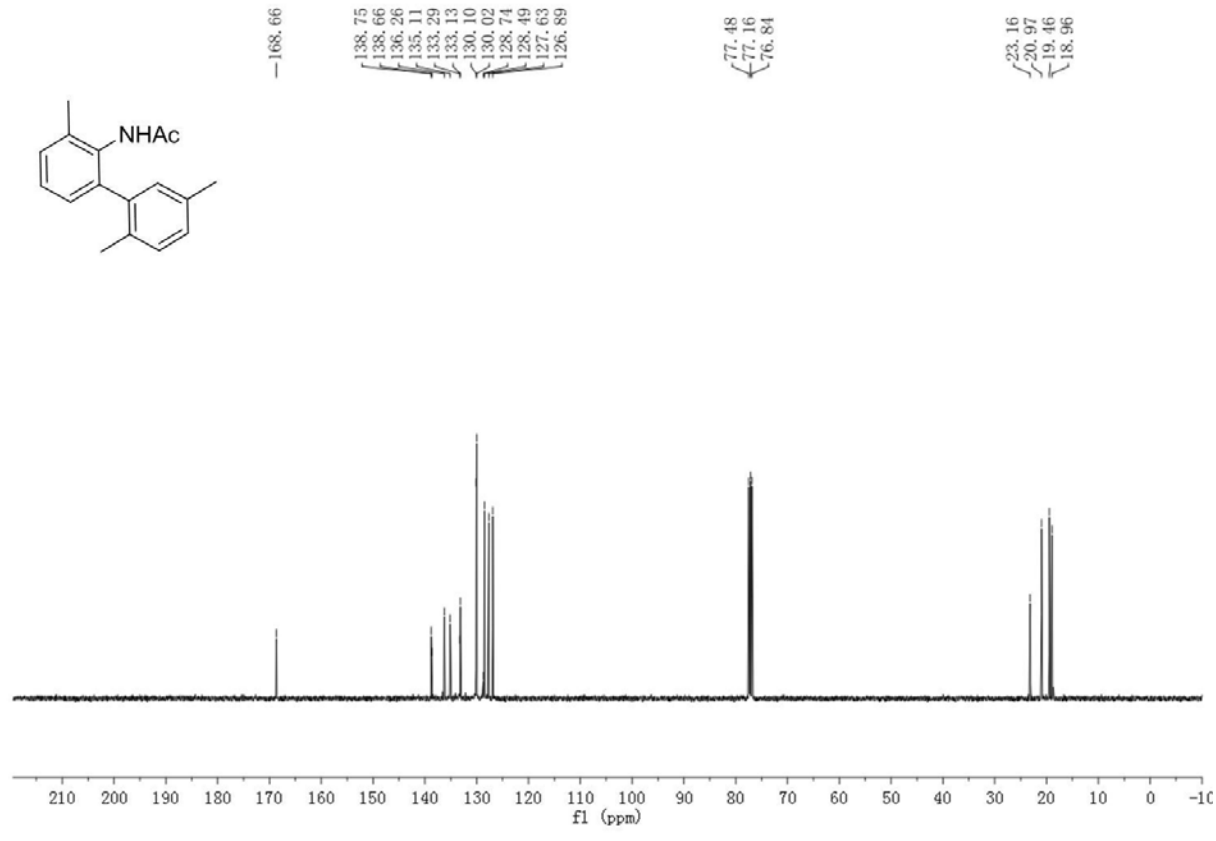
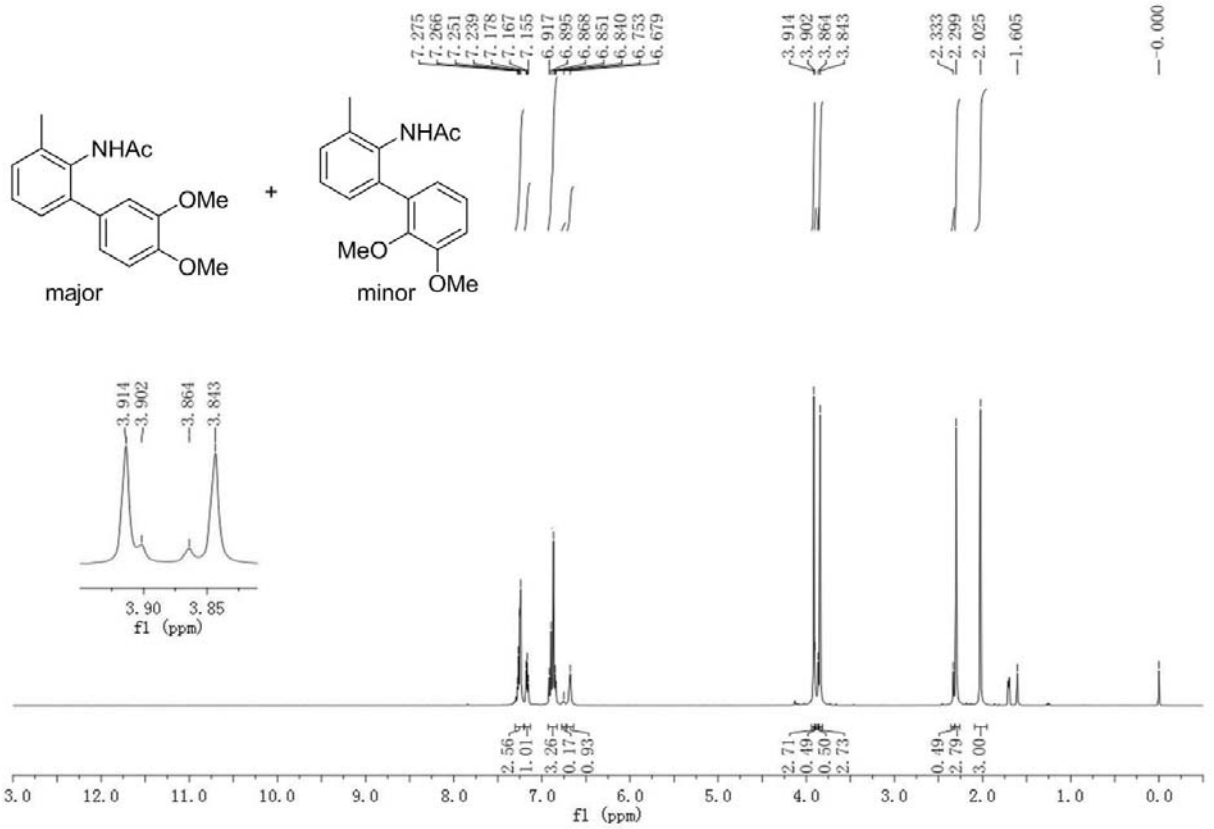
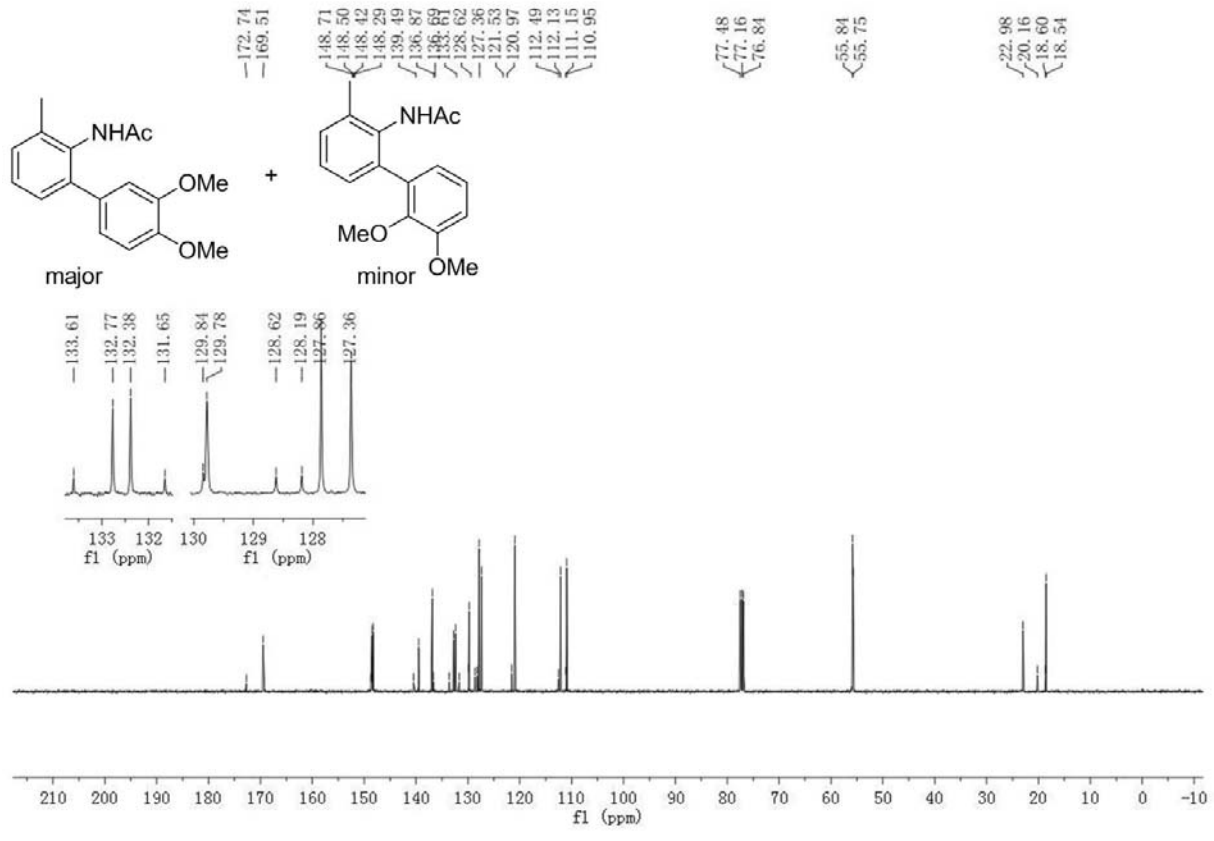
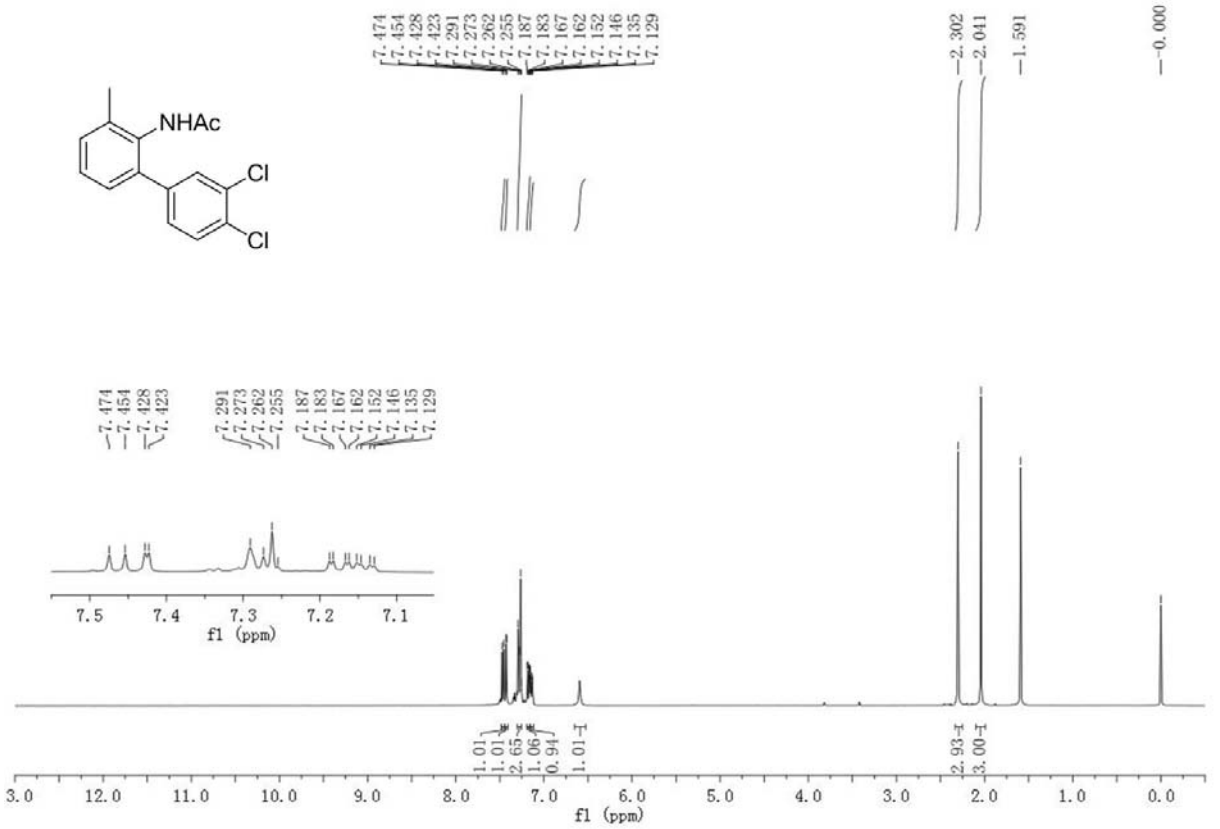
23.16
19.88
19.58
18.79
f1 (ppm)










NHAc
Cl
Cl
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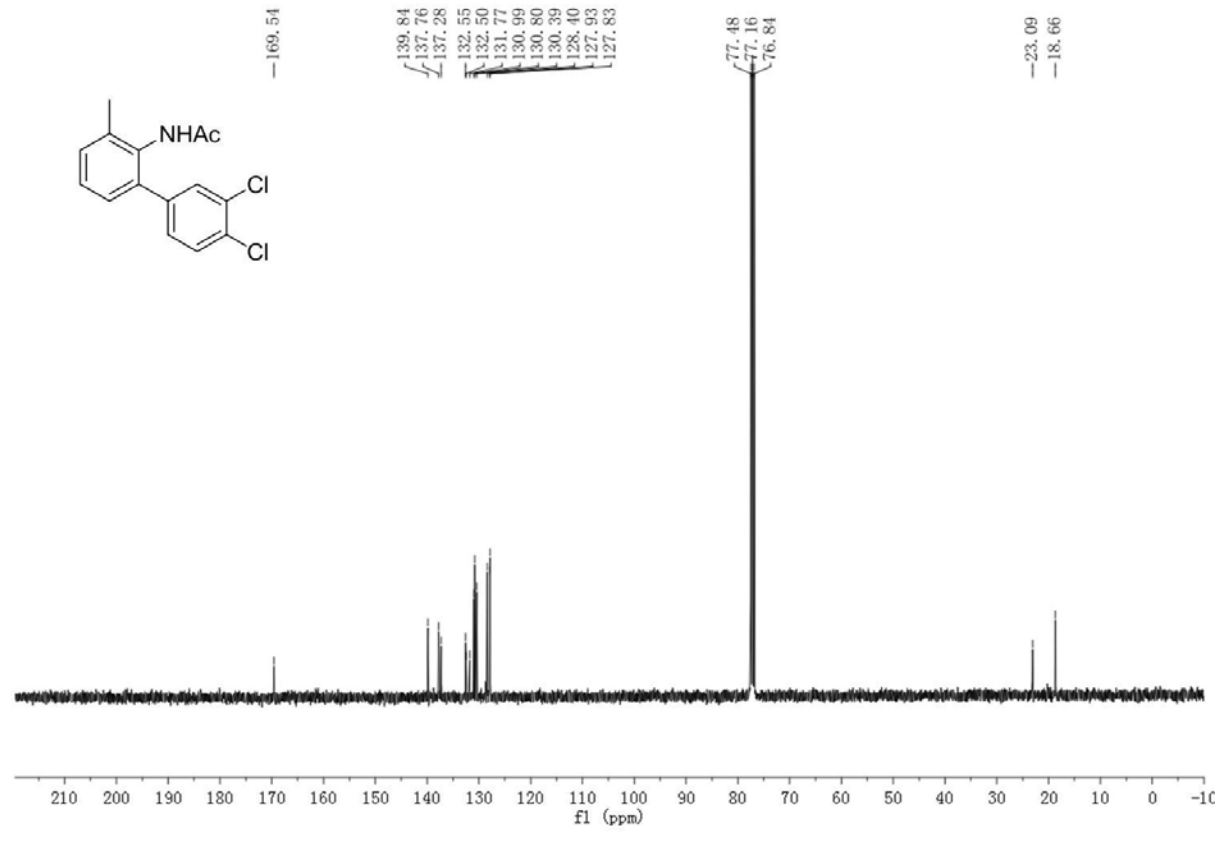
7.454
7.428
7.423
7.291
7.273
7.262
7.255
7.187
7.183
7.167
7.162
7.152
7.146
7.135
7.129
2.302
2.041
1.591
0.000
1.01
1.01
2.65
1.06
0.94
1.01
2.93
3.00
f1 (ppm)


NHAc
Cl
Cl
169.54
139.84
137.76
137.28
132.55
132.50
131.77
130.99
130.80
130.39
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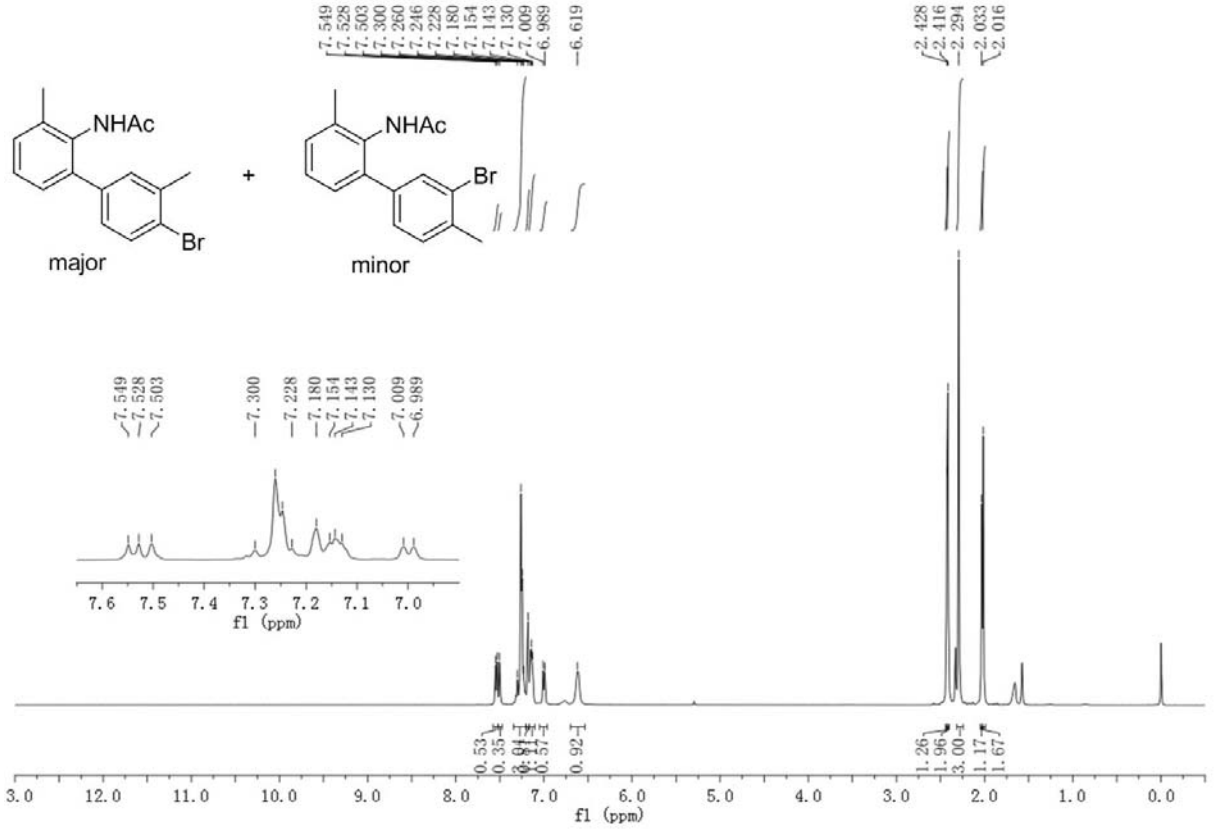
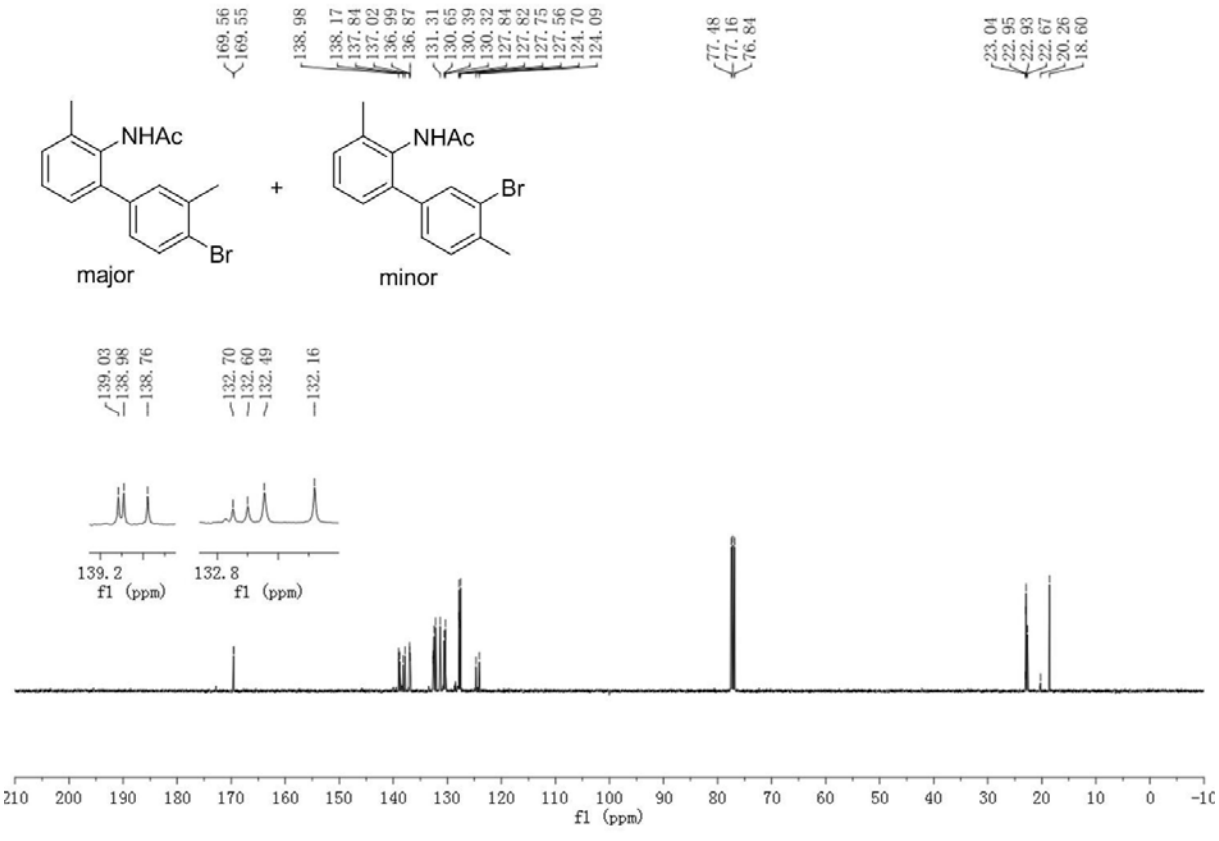
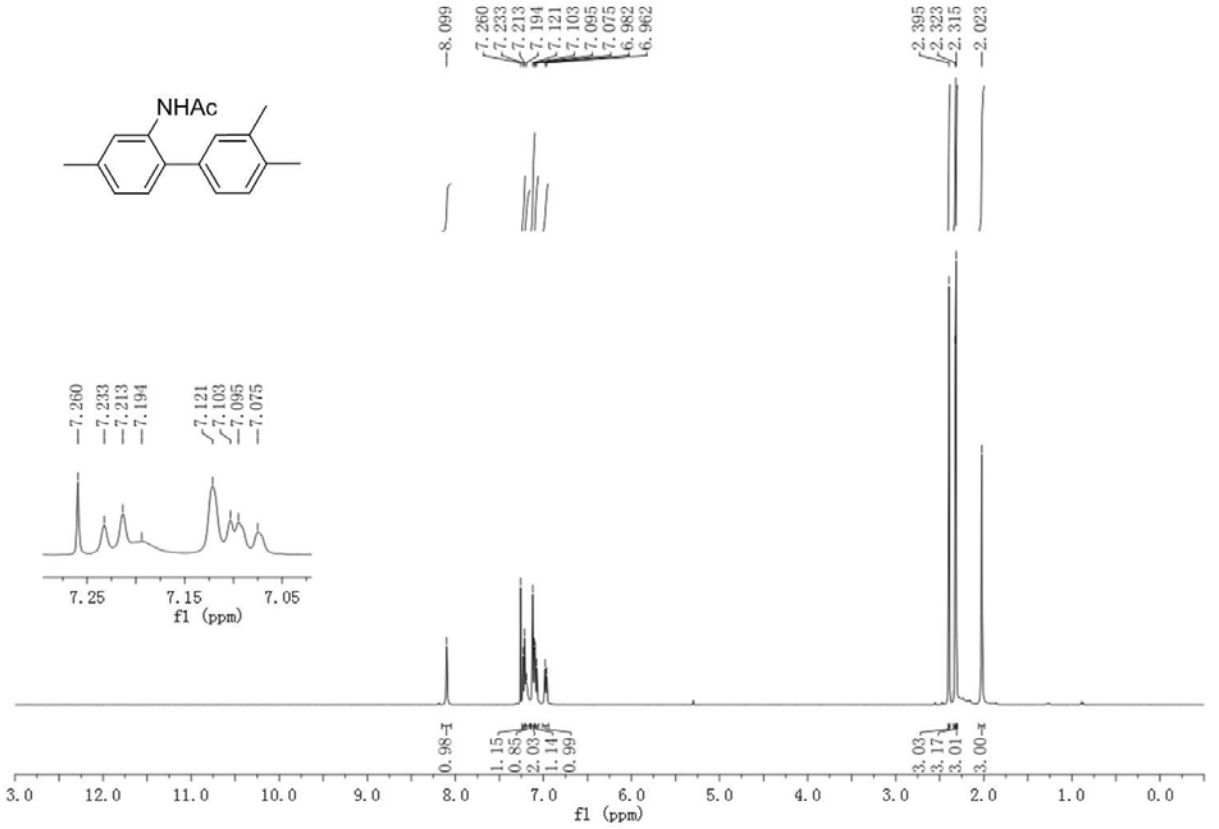
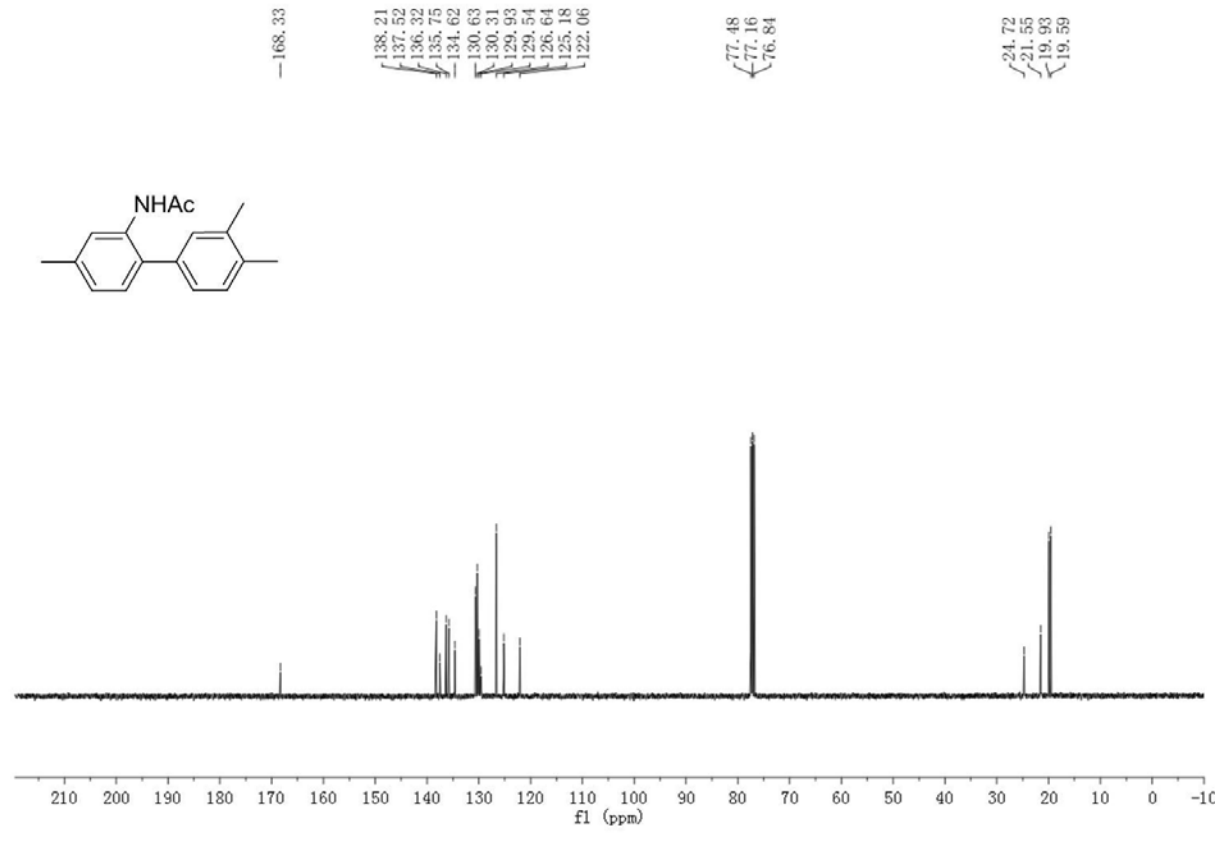
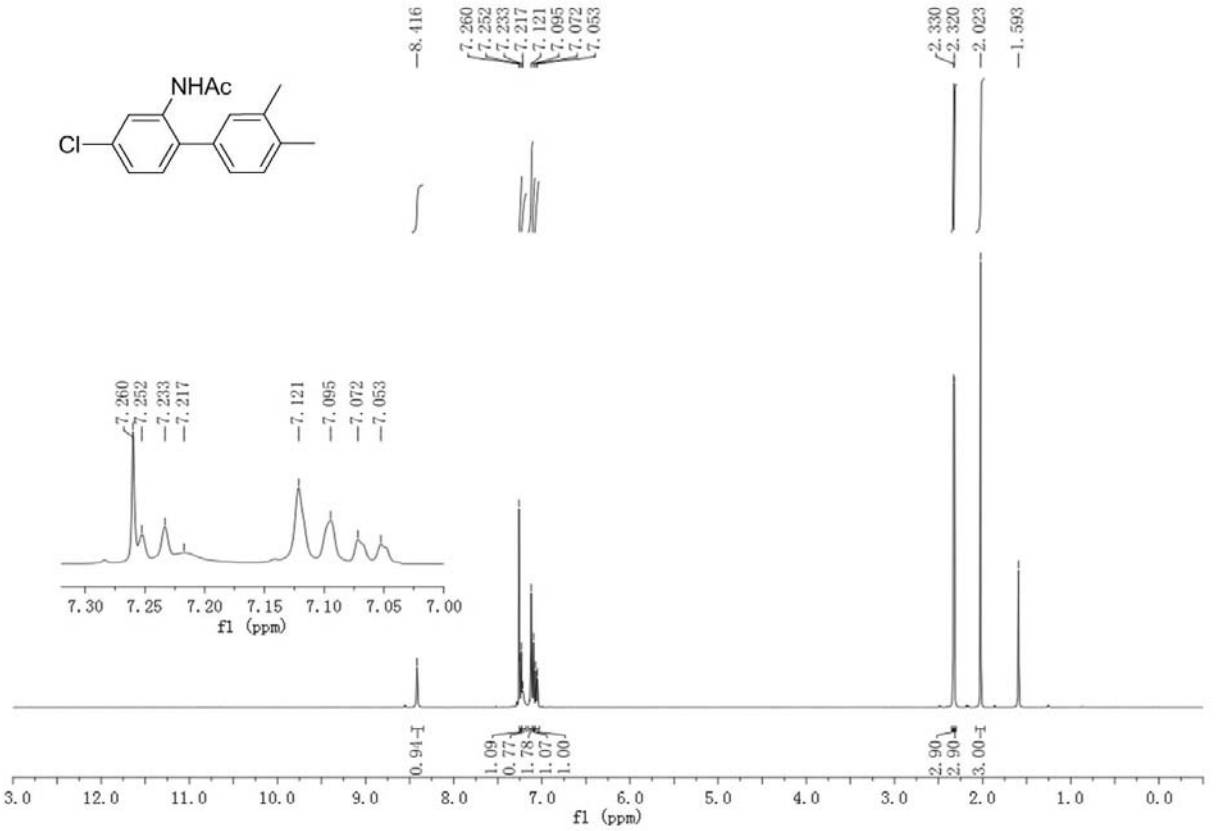
77.48
77.16
76.84
23.09
18.66
f1 (ppm)

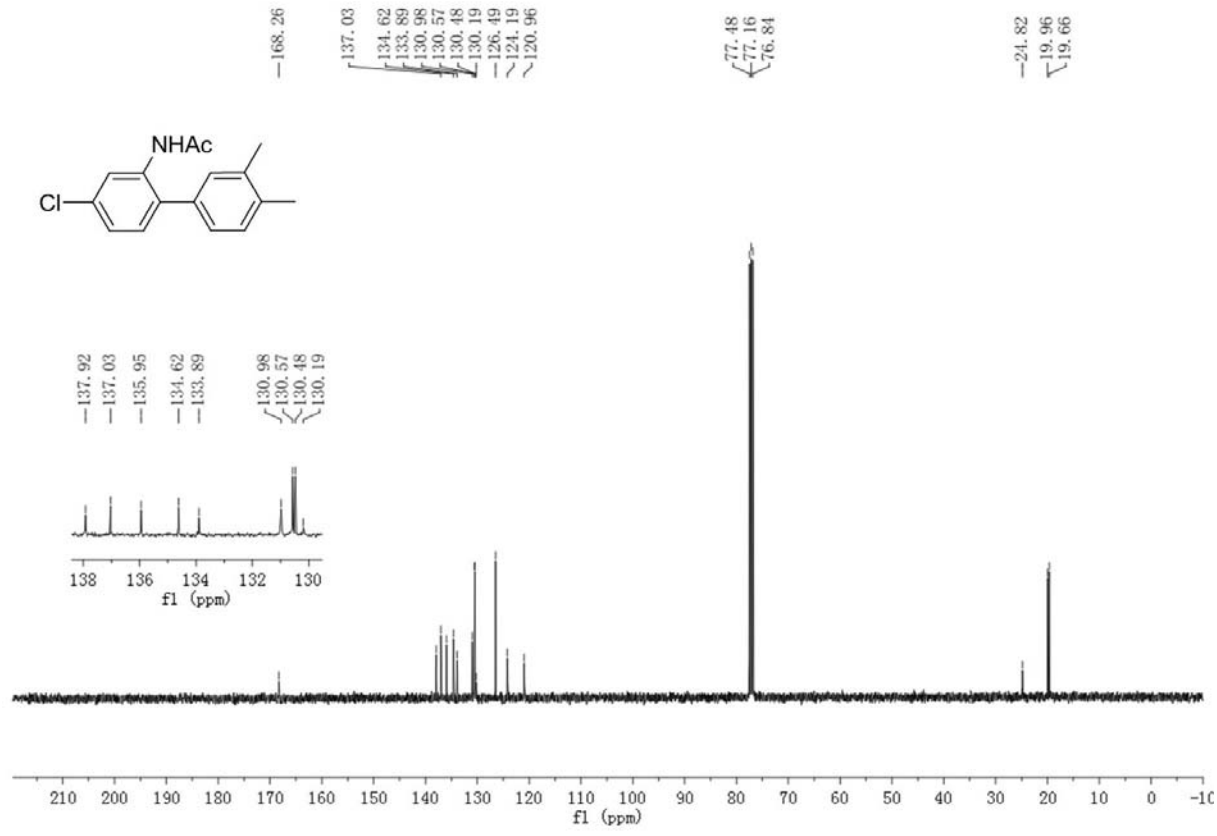


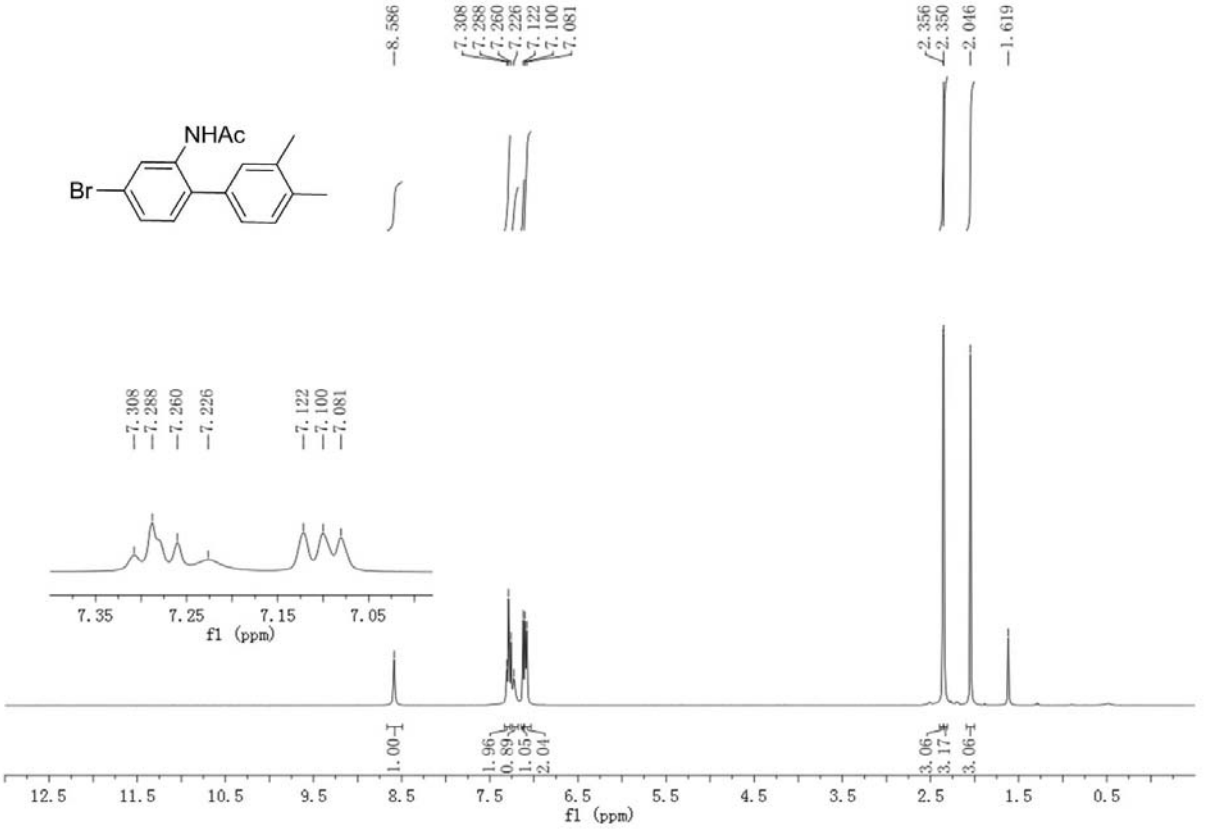








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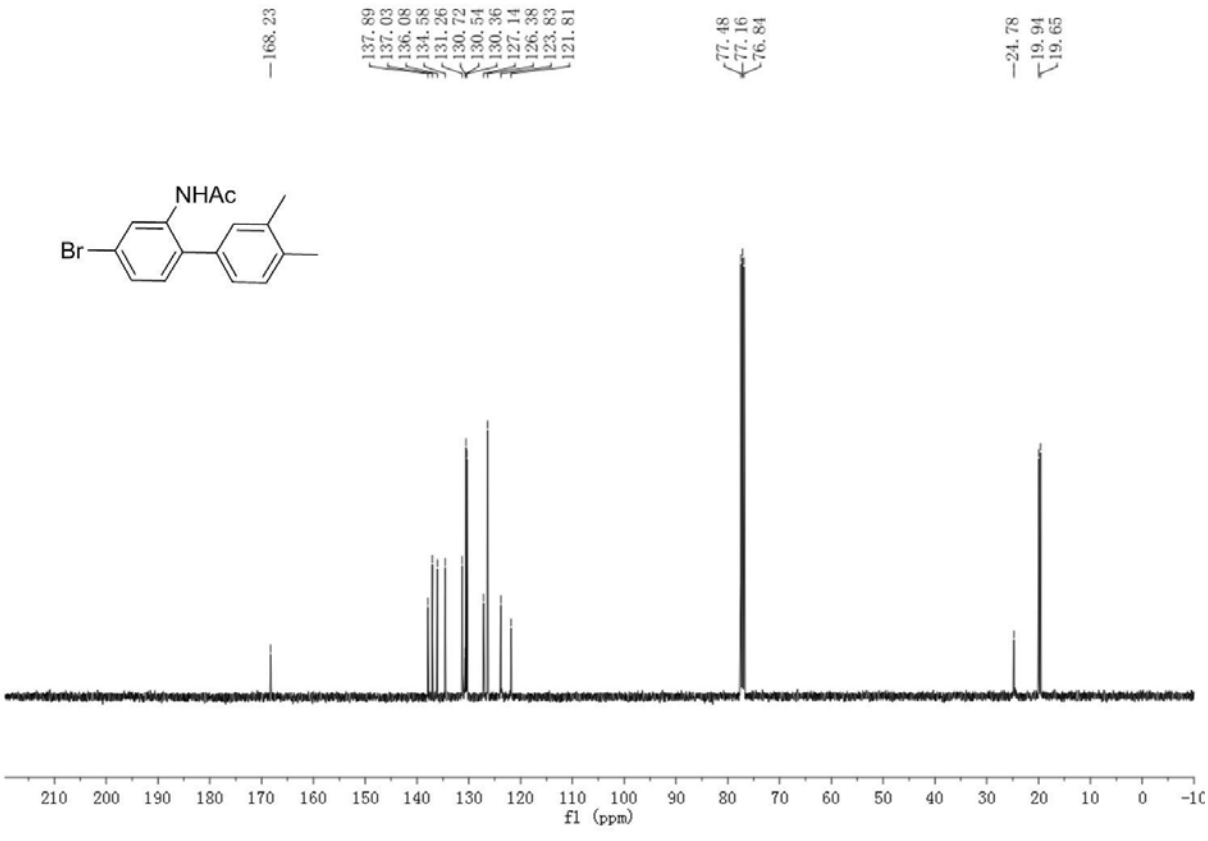
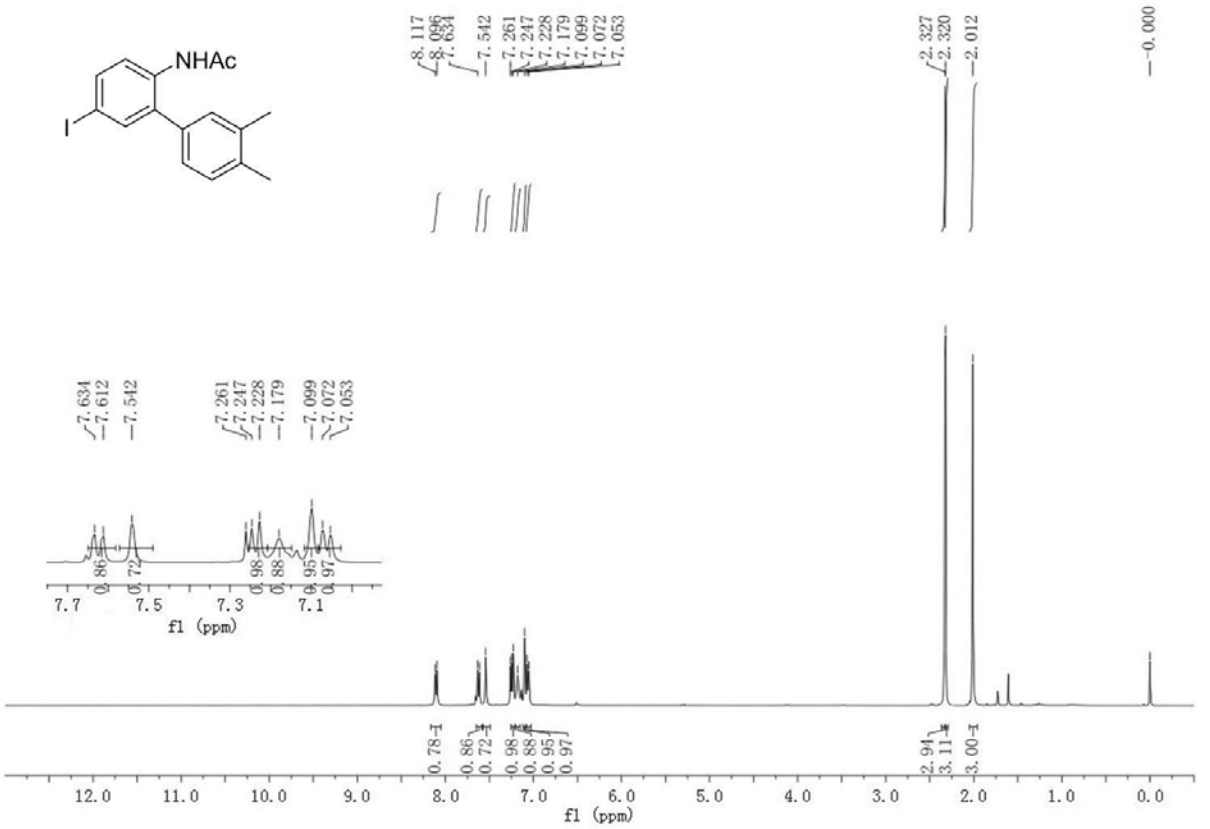
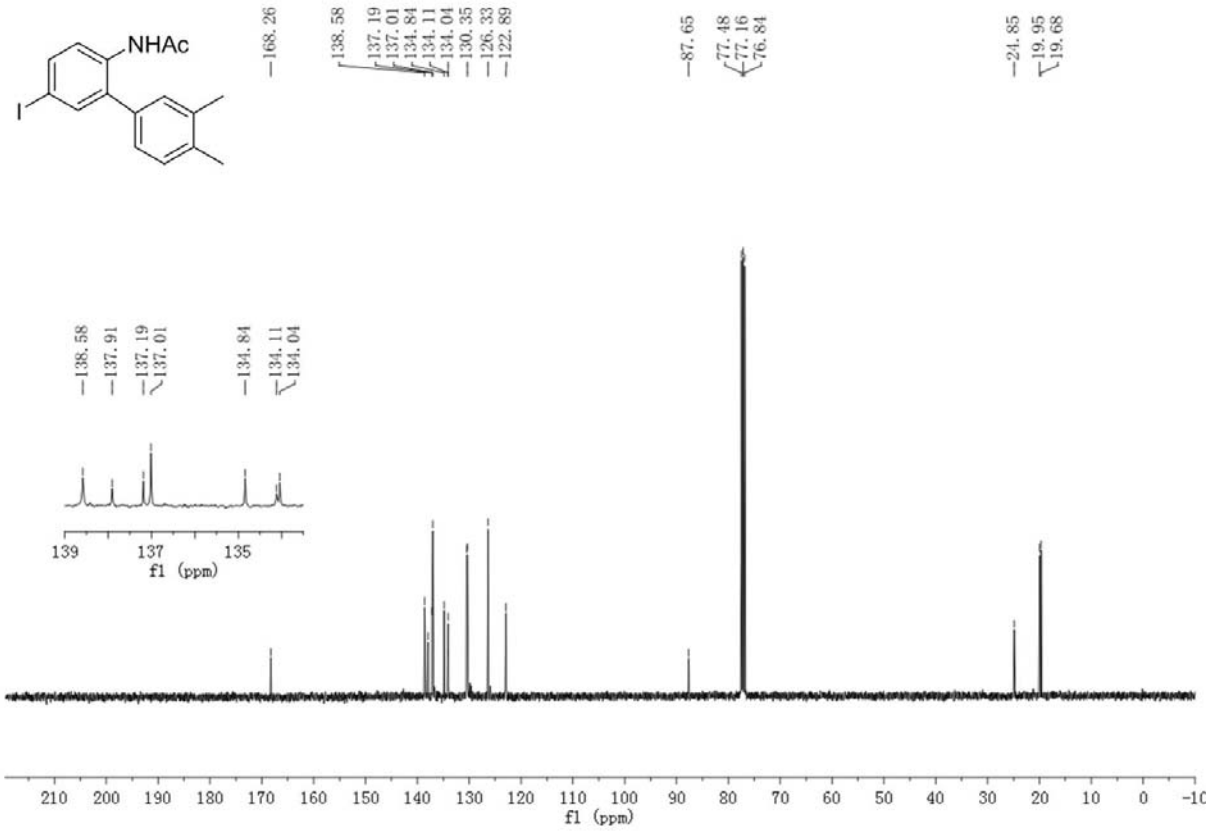
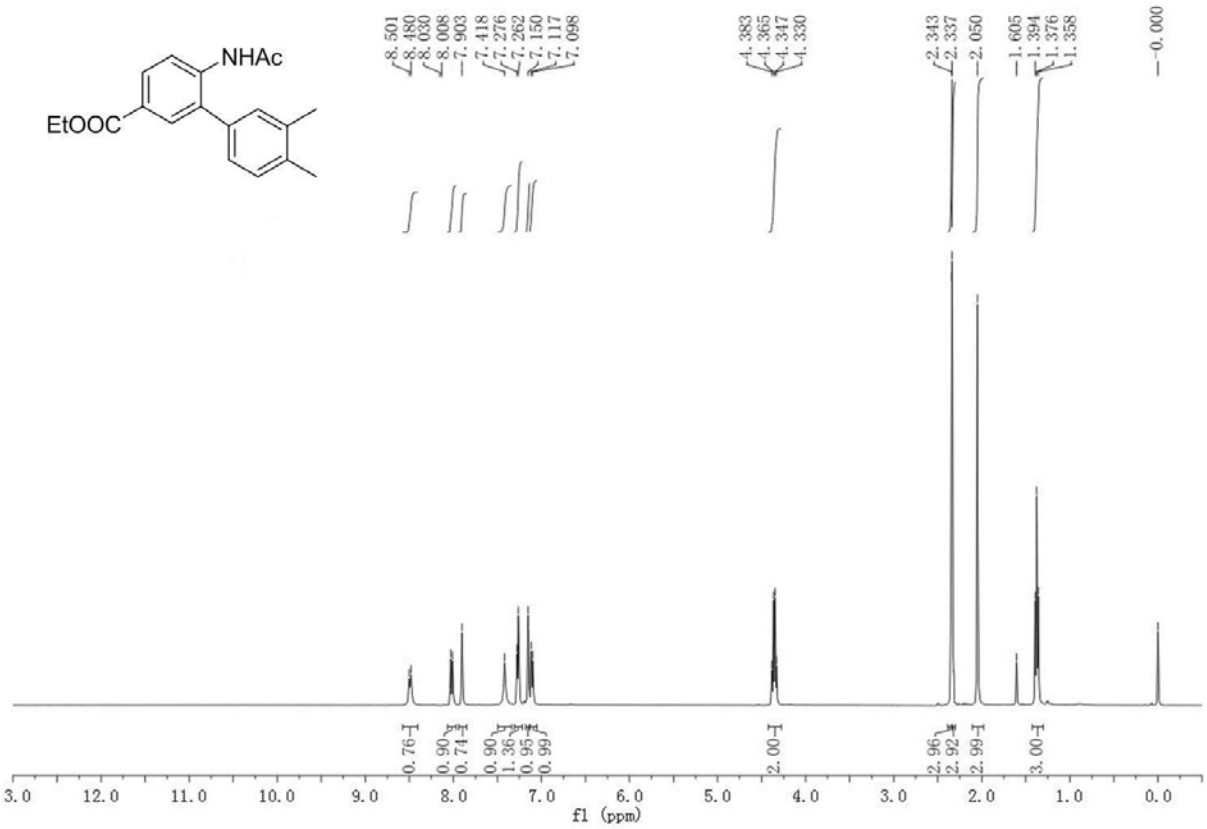
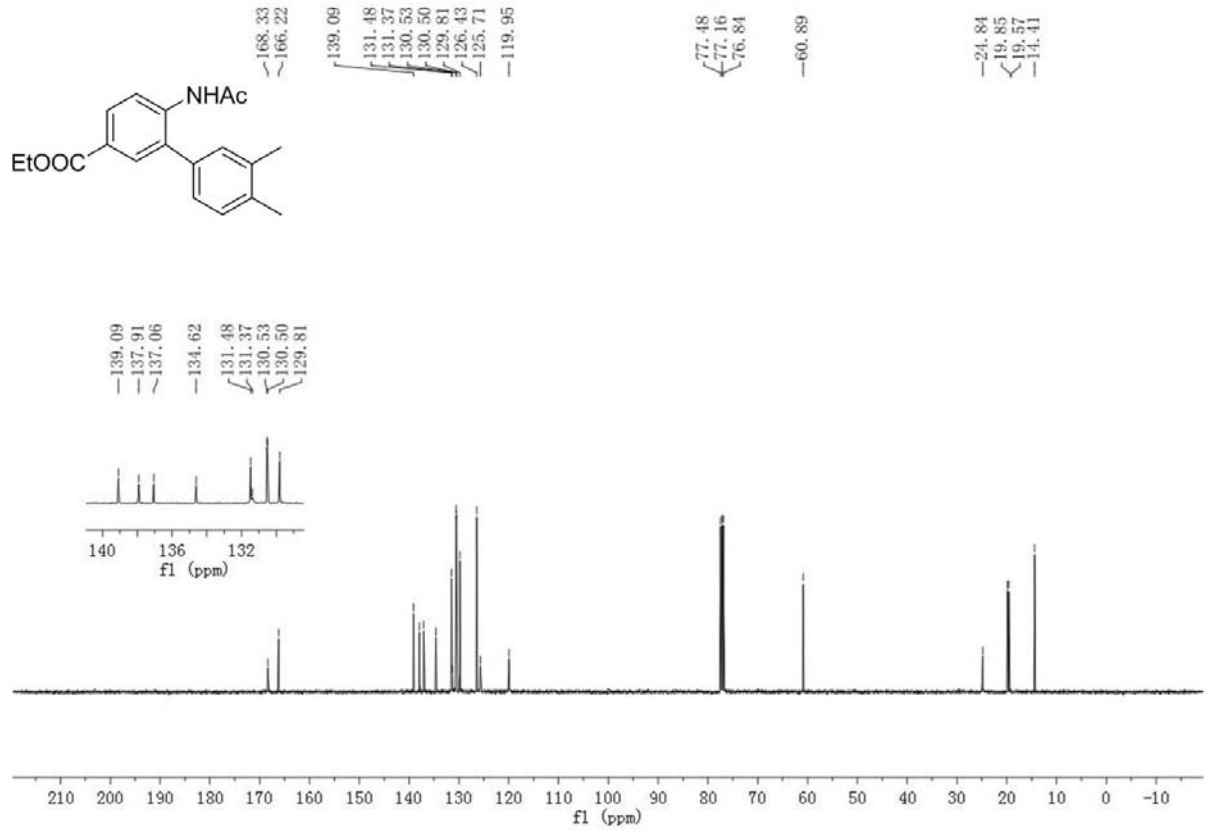
Br
8.586
7.308
7.288
7.260
7.226
7.122
7.100
7.081
2.356
2.350
2.046
1.619
1.00
1.96
0.89
1.05
2.04
3.06
3.17
3.06
f1 (ppm)

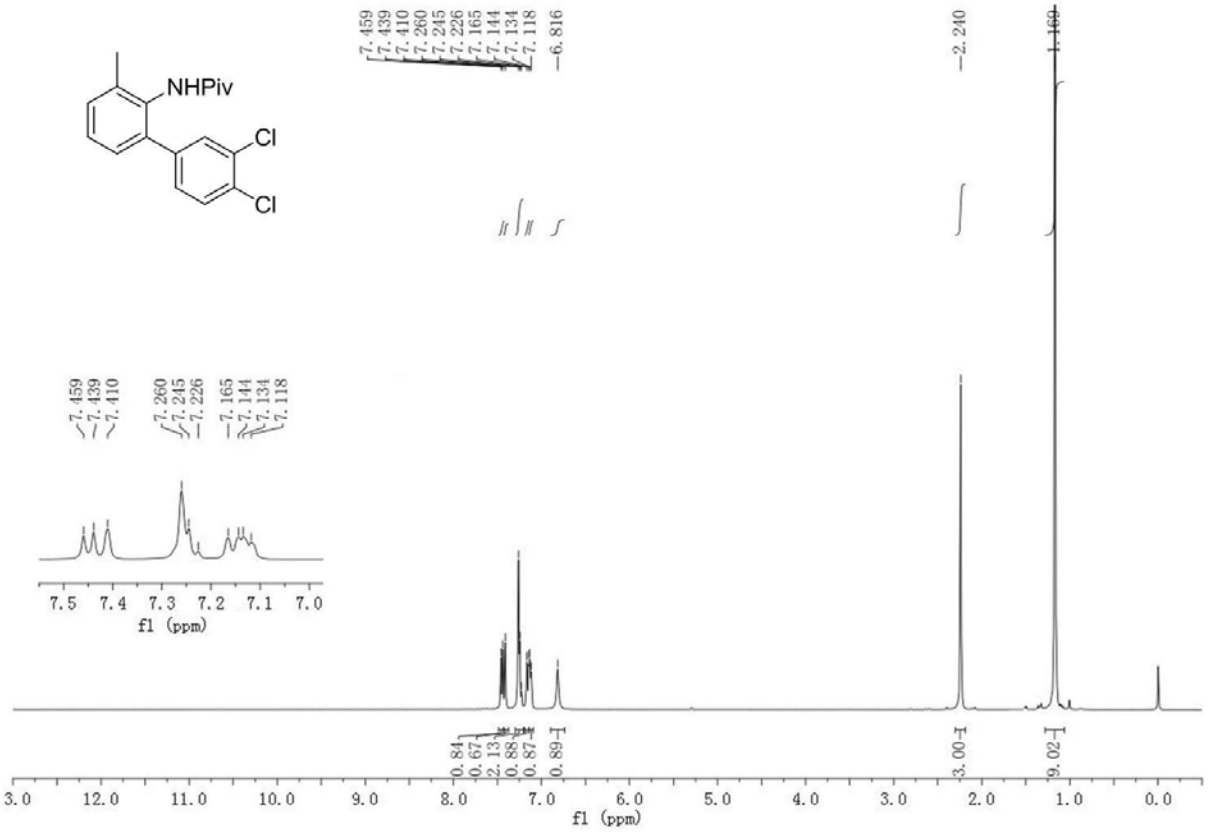

NHAc
Br
168.23
137.89
137.03
136.08
134.58
131.26
130.72
130.54
130.36
127.14
126.38
123.83
121.81
77.48
77.16
76.84
24.78
19.94
19.65
f1 (ppm)


NHAc
I
8.117
8.096
8.034
7.634
7.612
7.542
7.261
7.247
7.228
7.179
7.099
7.072
7.053
2.327
2.320
2.012
0.000
0.78
0.86
0.72
0.98
0.88
0.95
0.97
2.94
3.11
3.00
f1 (ppm)


NHAc
I
168.26
138.58
137.19
137.01
134.84
134.11
134.04
130.35
126.33
122.89
87.65
77.48
77.16
76.84
24.85
19.95
19.68
f1 (ppm)


NHAc
EtOOC
8.501
8.480
8.030
8.008
7.903
7.418
7.276
7.262
7.150
7.117
7.098
4.383
4.365
4.347
4.330
2.343
2.337
2.050
1.605
1.394
1.376
1.358
0.000
0.76
0.90
0.74
0.90
1.36
0.95
0.99
2.00
2.96
2.92
2.99
3.00
f1 (ppm)


NHAc
EtOOC
168.33
166.22
139.09
131.48
131.37
130.53
130.50
129.81
126.43
125.71
119.95
77.48
77.16
76.84
60.89
24.84
19.85
19.57
14.41
139.09
137.91
137.06
134.62
131.48
131.37
130.53
130.50
129.81
140
136
132
f1 (ppm)
f1 (ppm)


NHPiv
Cl
Cl
7.459
7.439
7.410
7.260
7.245
7.226
7.165
7.144
7.134
7.118
6.816
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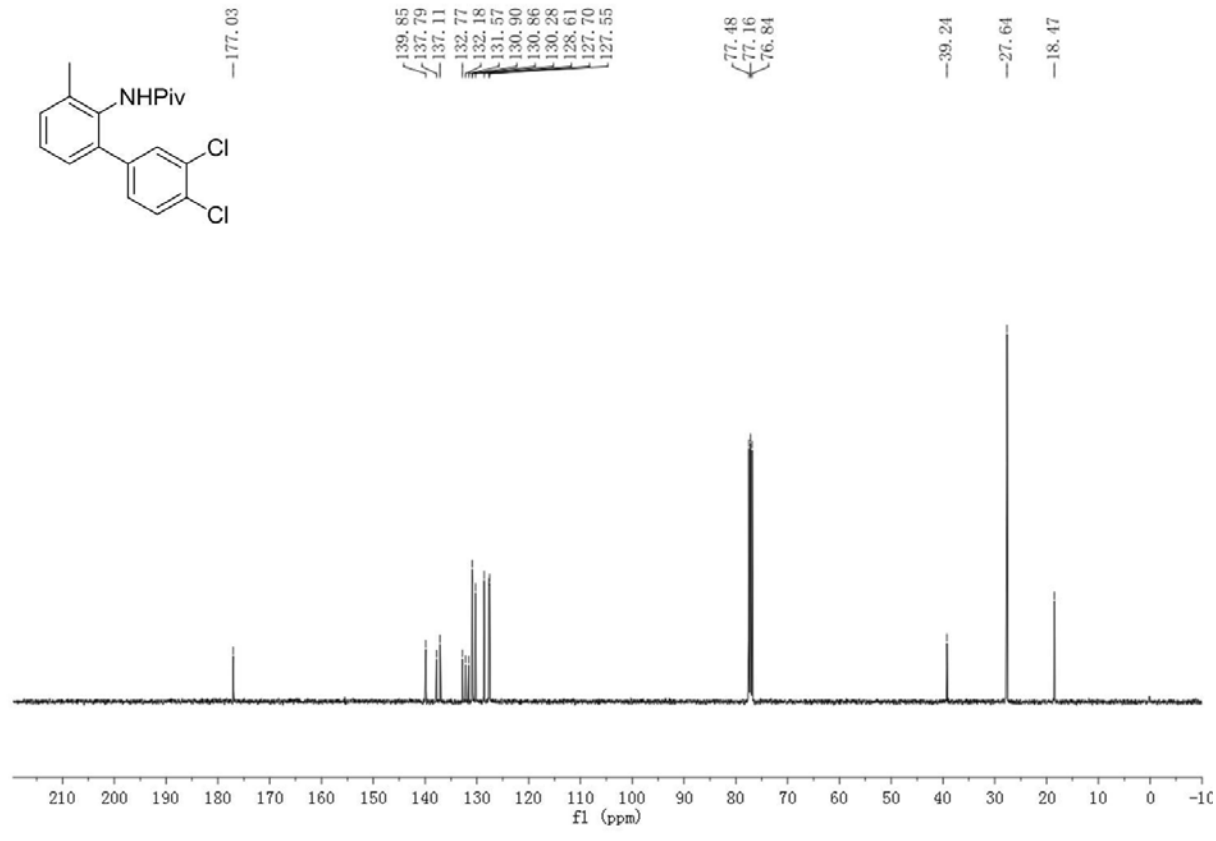
1.169
0.84
0.67
2.13
0.88
0.87
0.89
3.00
9.02
f1 (ppm)


NHPiv
Cl
Cl
177.03
139.85
137.79
137.11
132.77
132.18
131.57
130.90
130.86
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76.84
39.24
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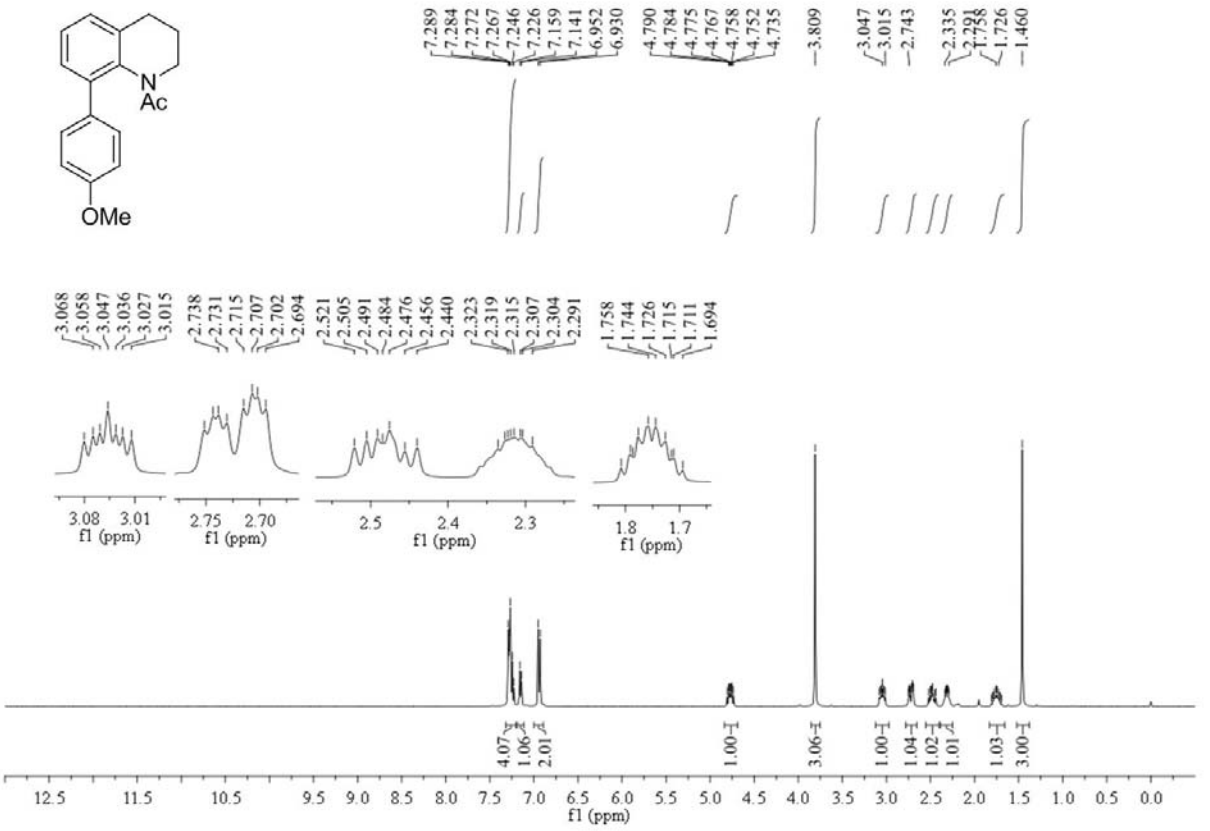
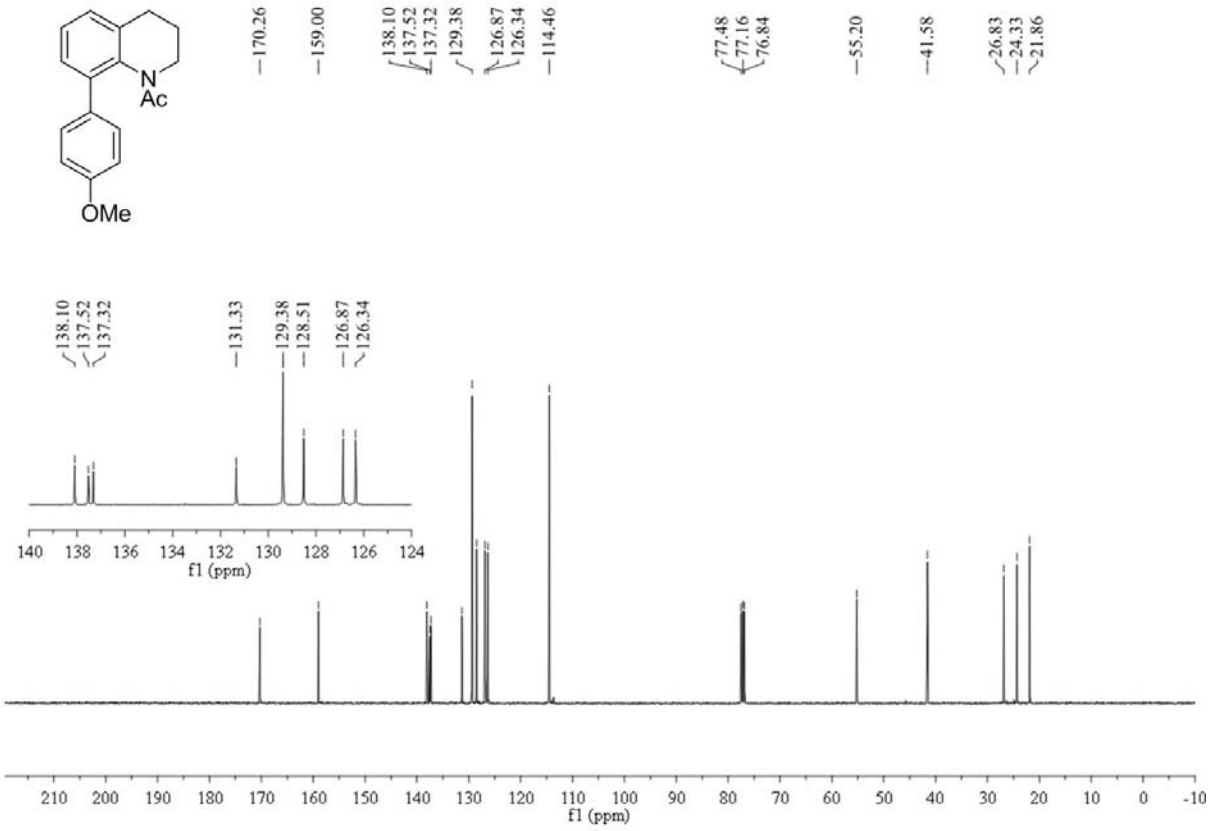
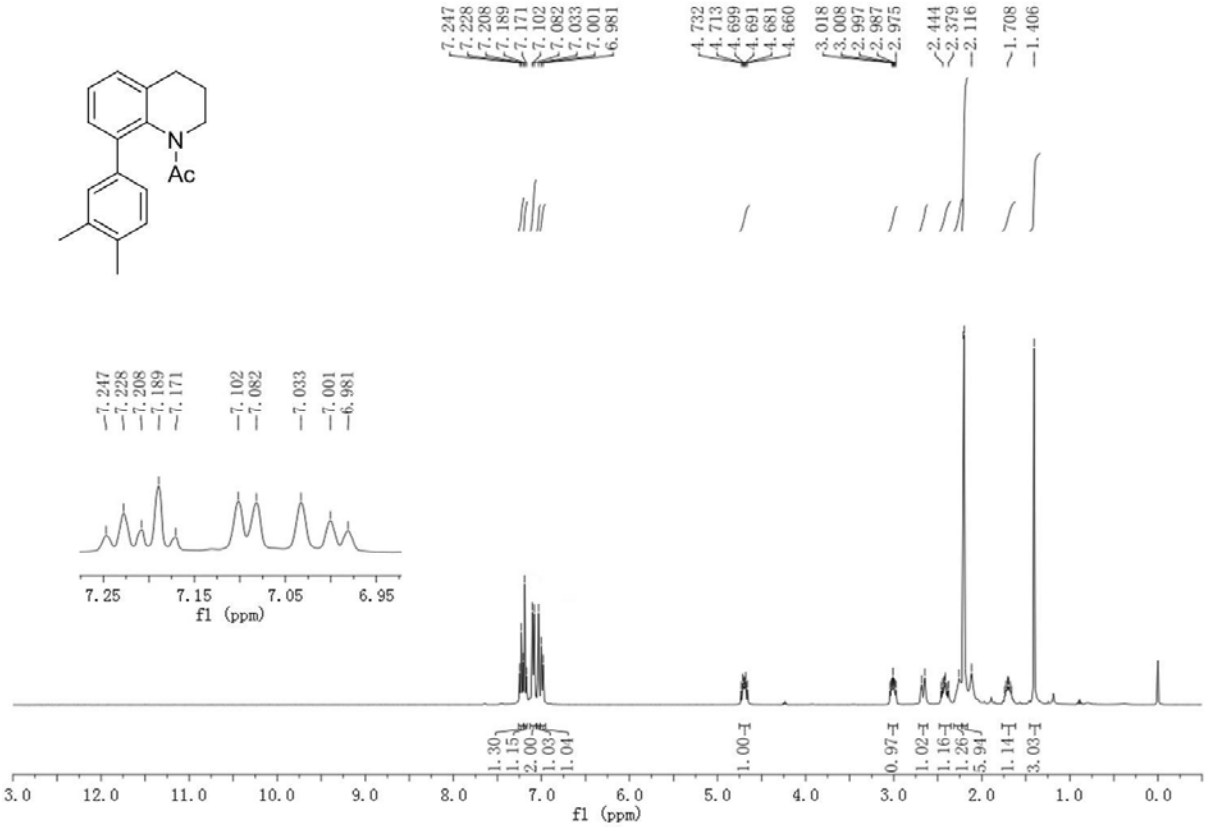
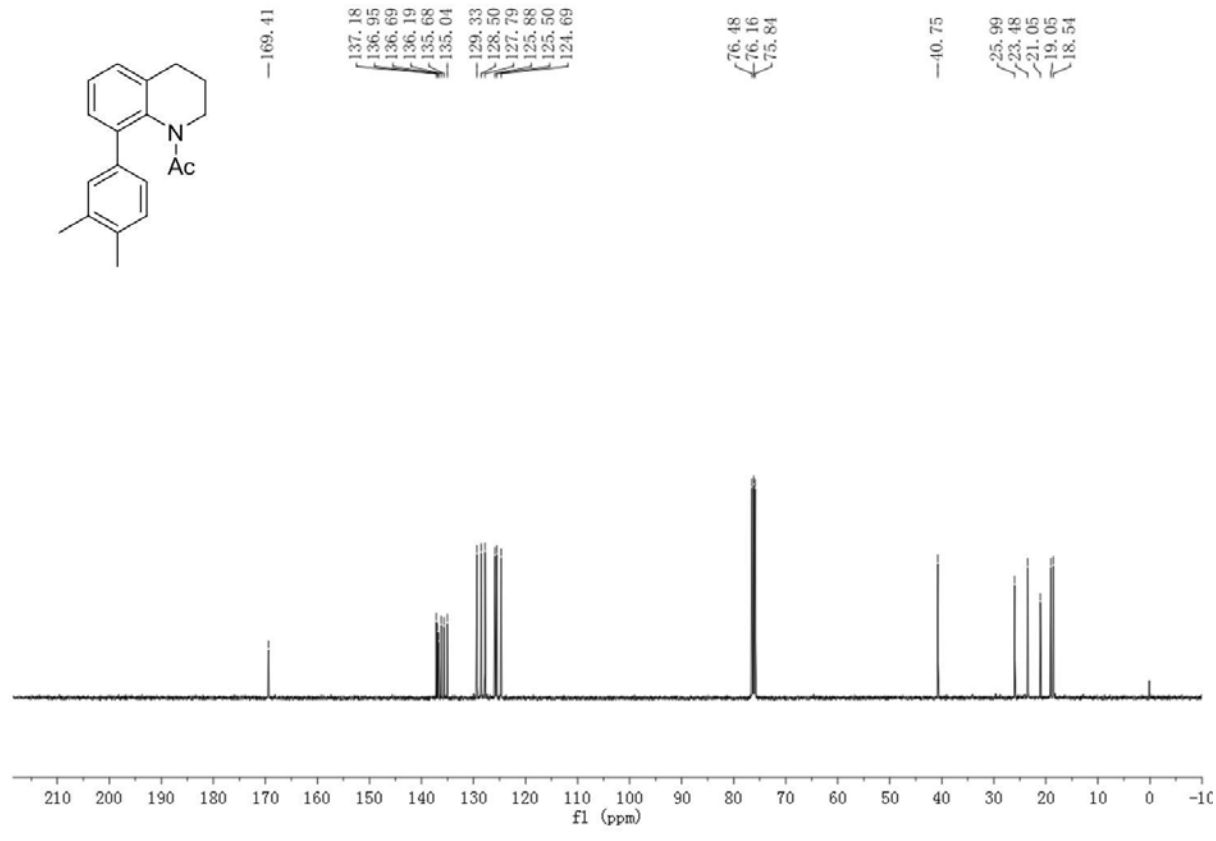
18.47
f1 (ppm)






N
Ac
7.247
7.228
7.208
7.189
7.171
7.102
7.082
7.033
7.001
6.981
4.732
4.713
4.699
4.691
4.681
4.660
3.018
3.008
2.997
2.987
2.975
2.444
2.379
2.116
1.708
1.406
f1 (ppm)
1.30
1.15
2.00
1.03
1.04
1.00
0.97
1.02
1.16
1.26
5.94
1.14
3.03


N
Ac
169.41
137.18
136.95
136.69
136.19
135.68
135.04
129.33
128.50
127.79
125.88
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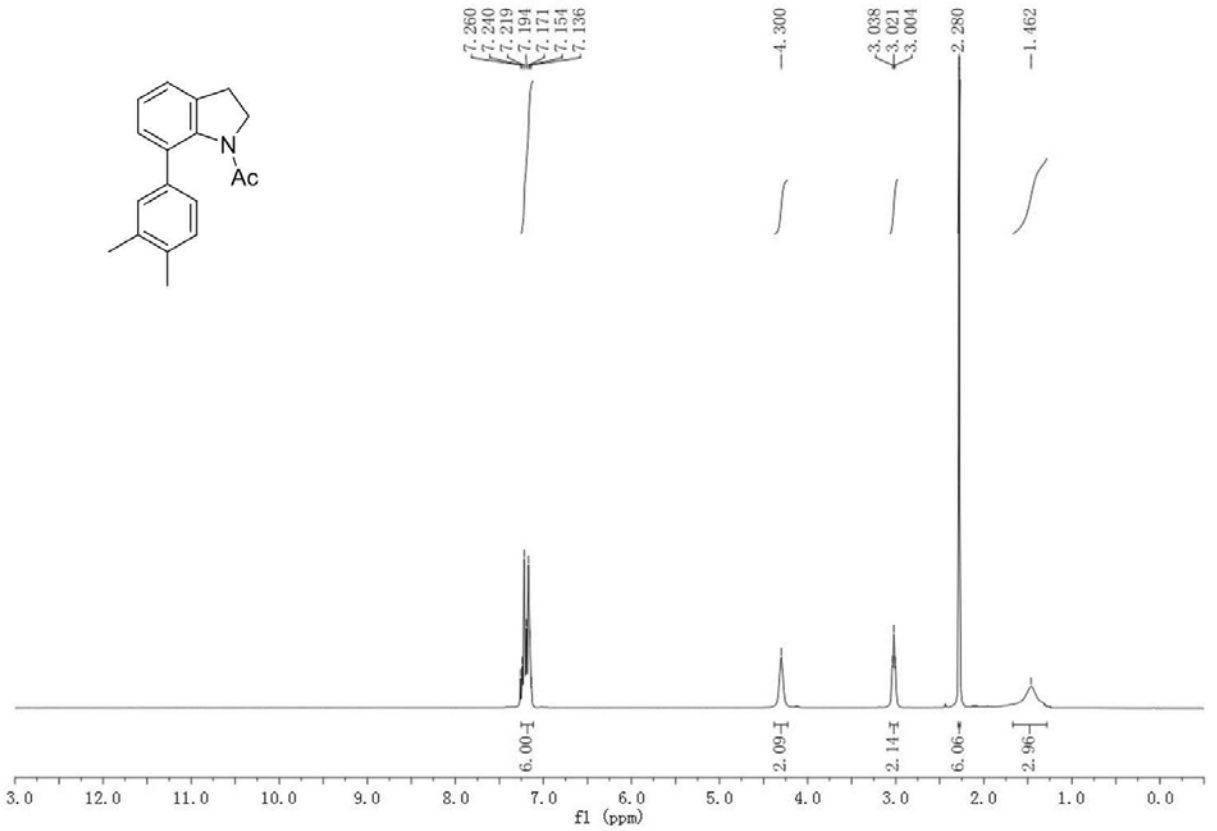
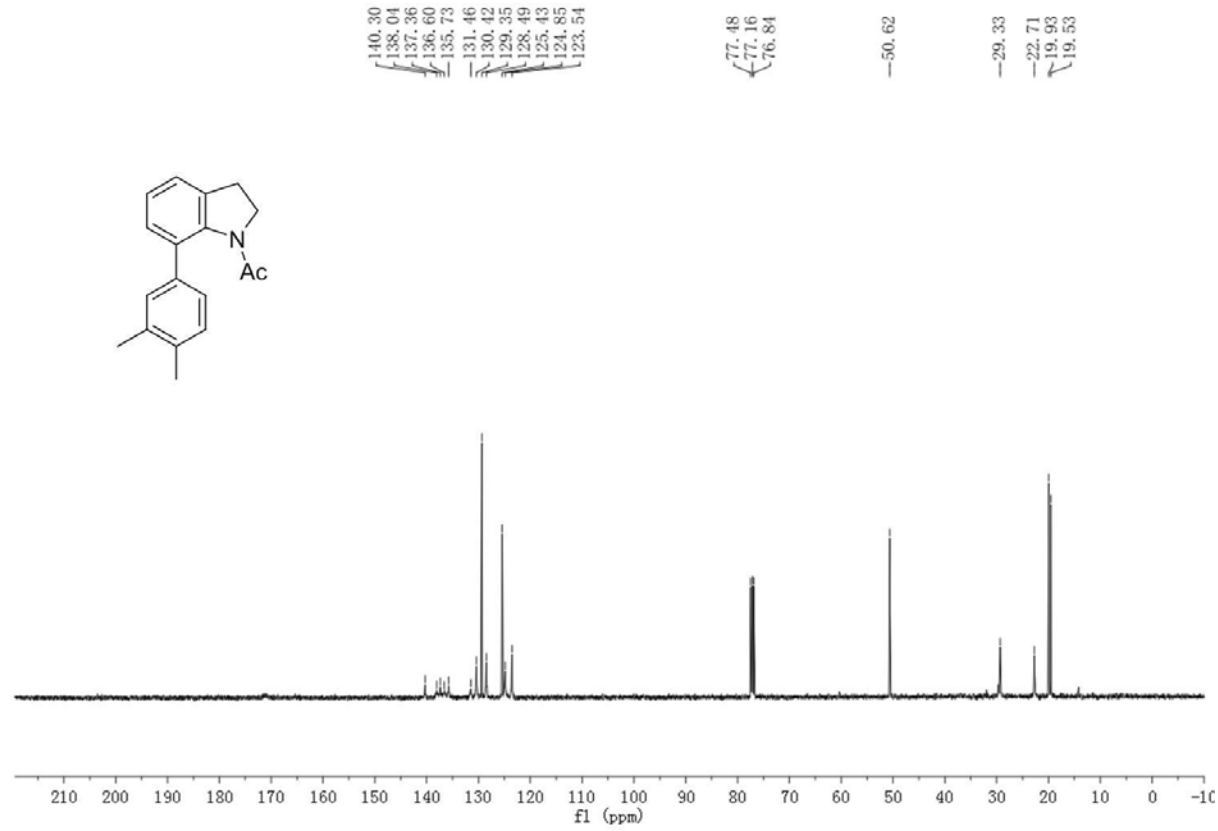
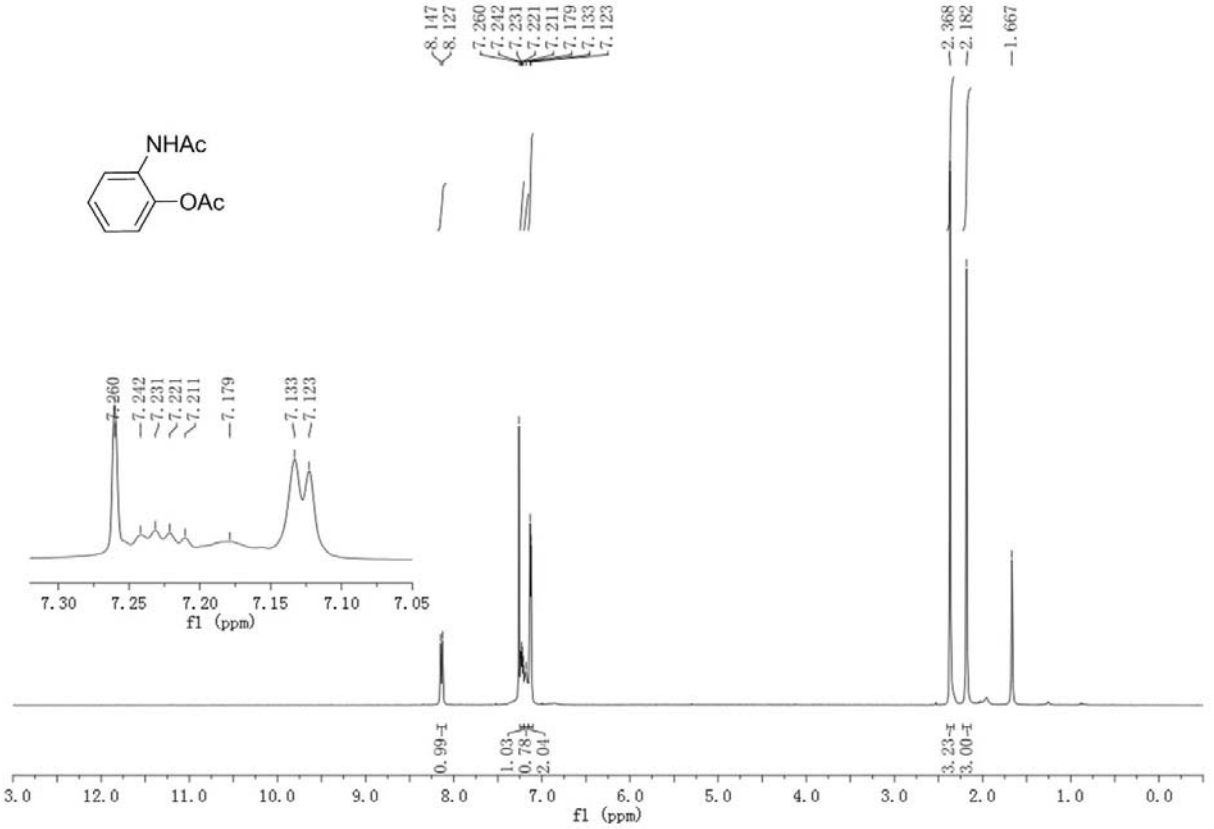
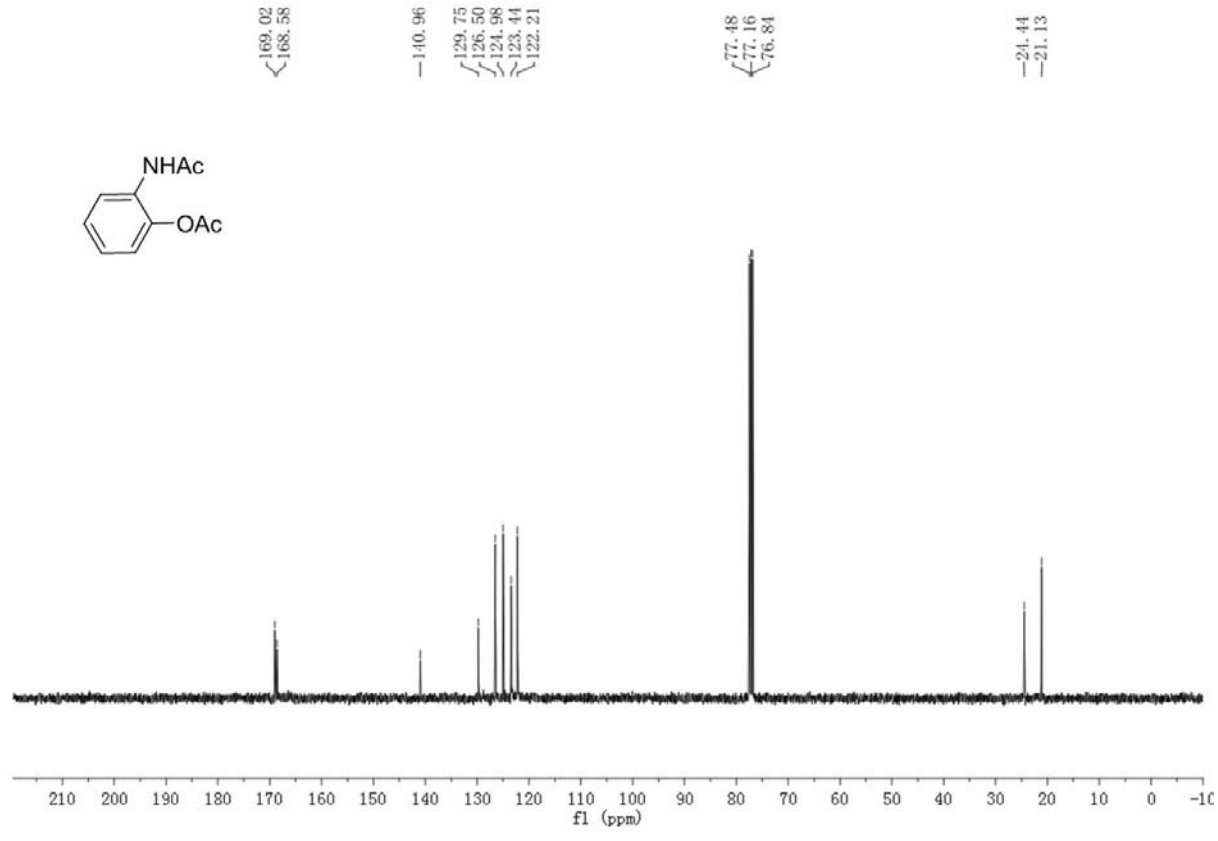
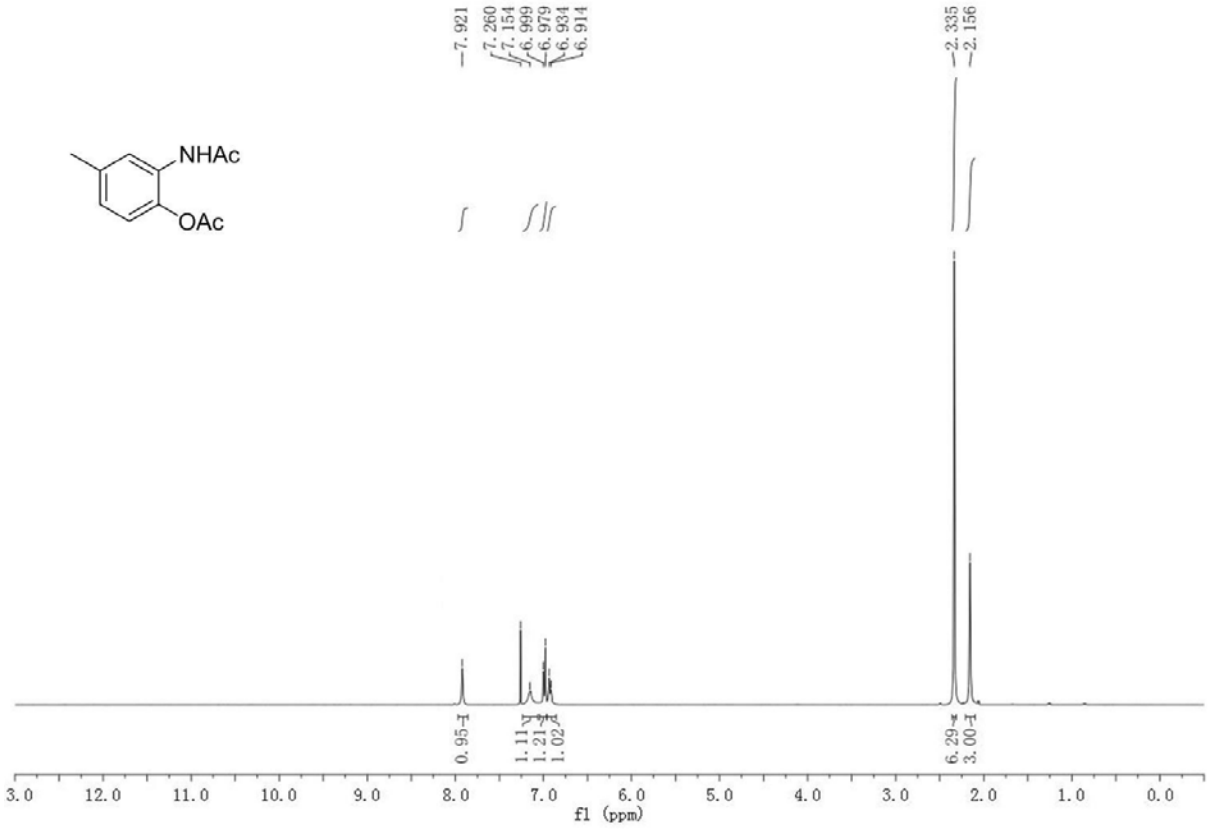
21.05
19.05
18.54
f1 (ppm)

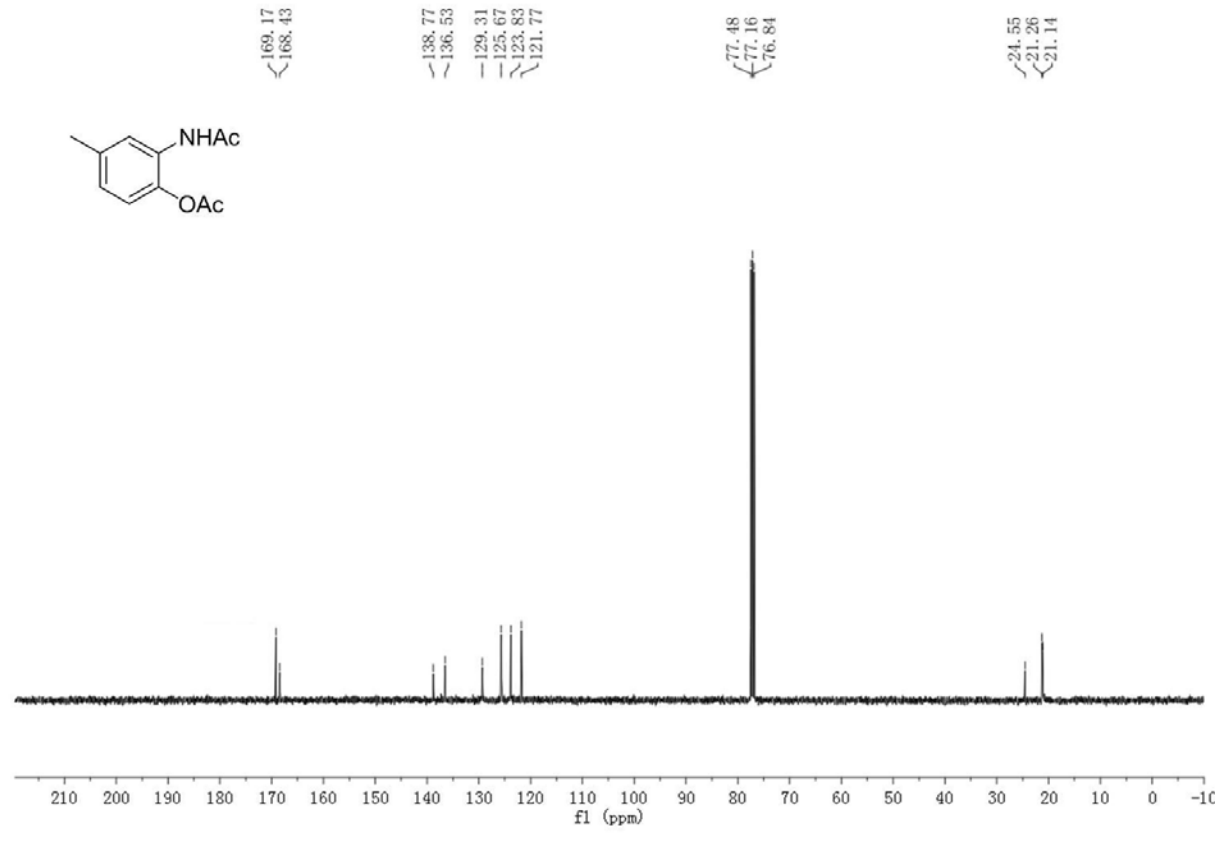


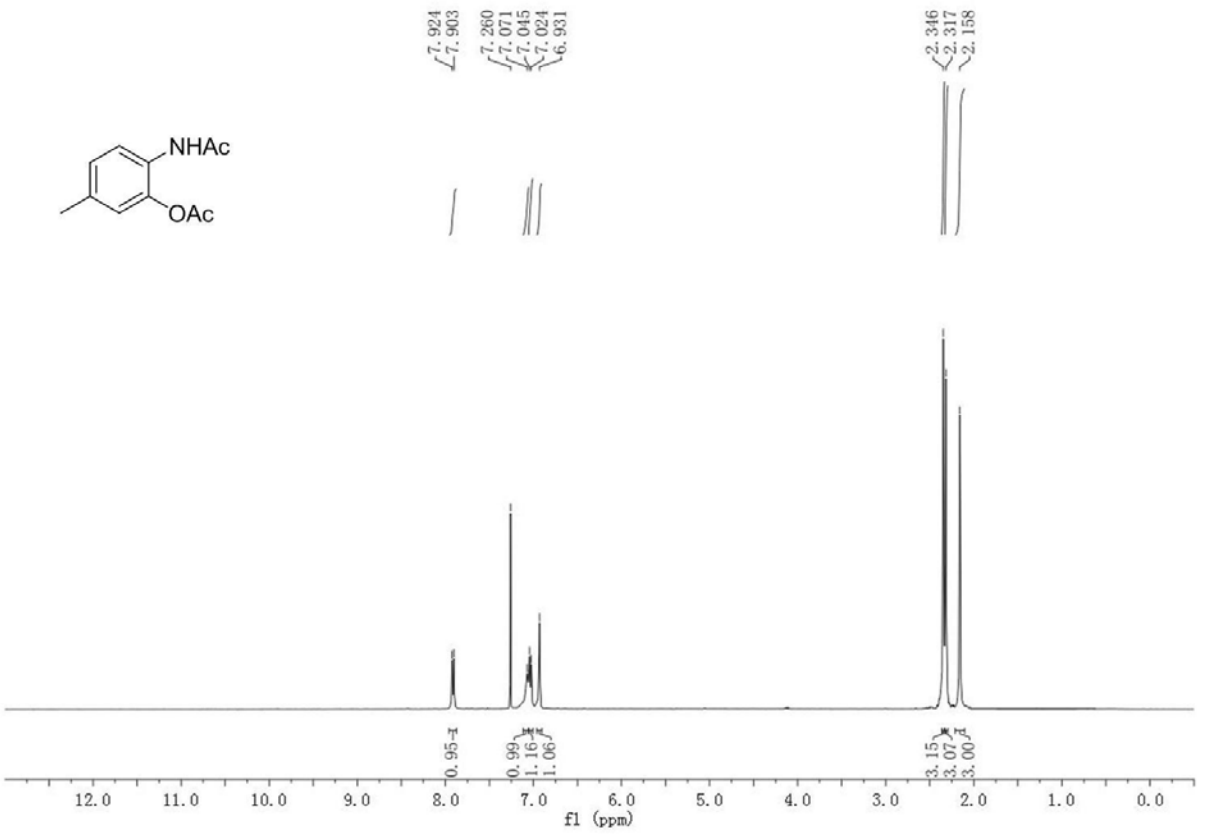


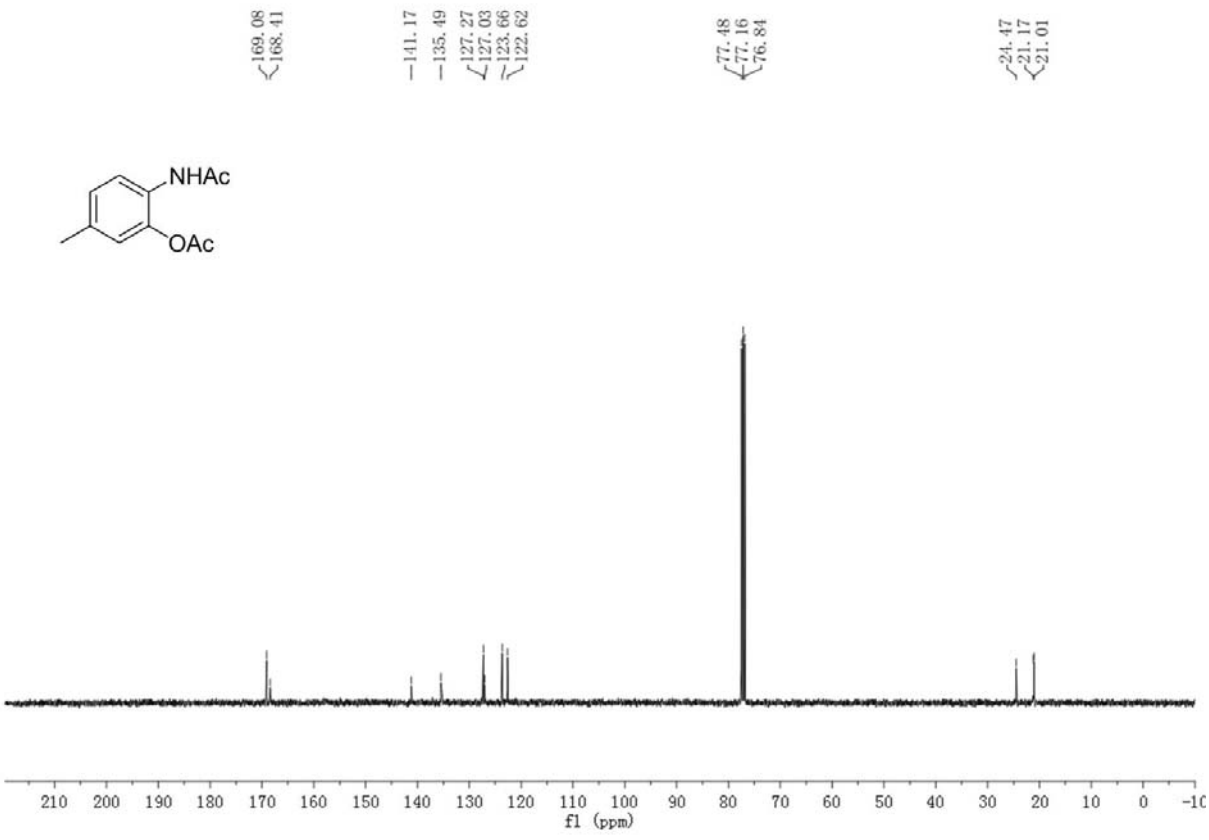


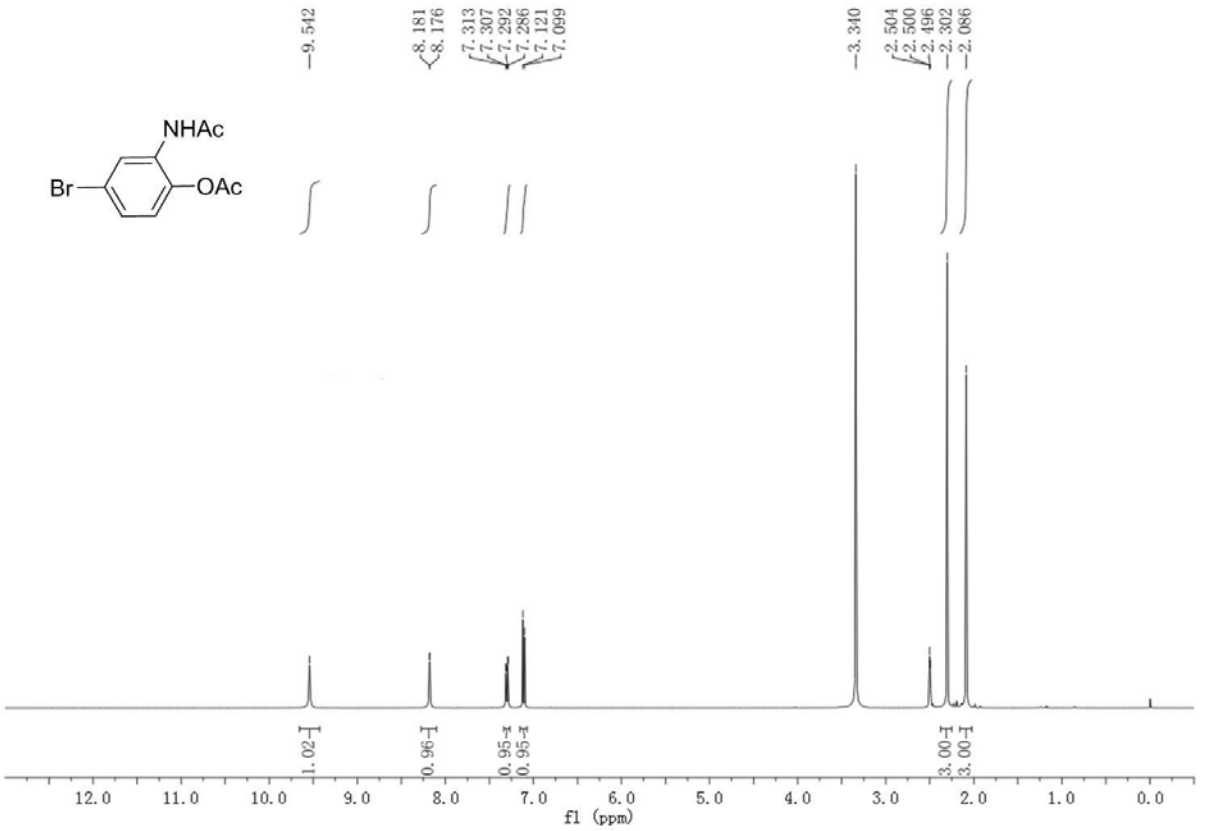


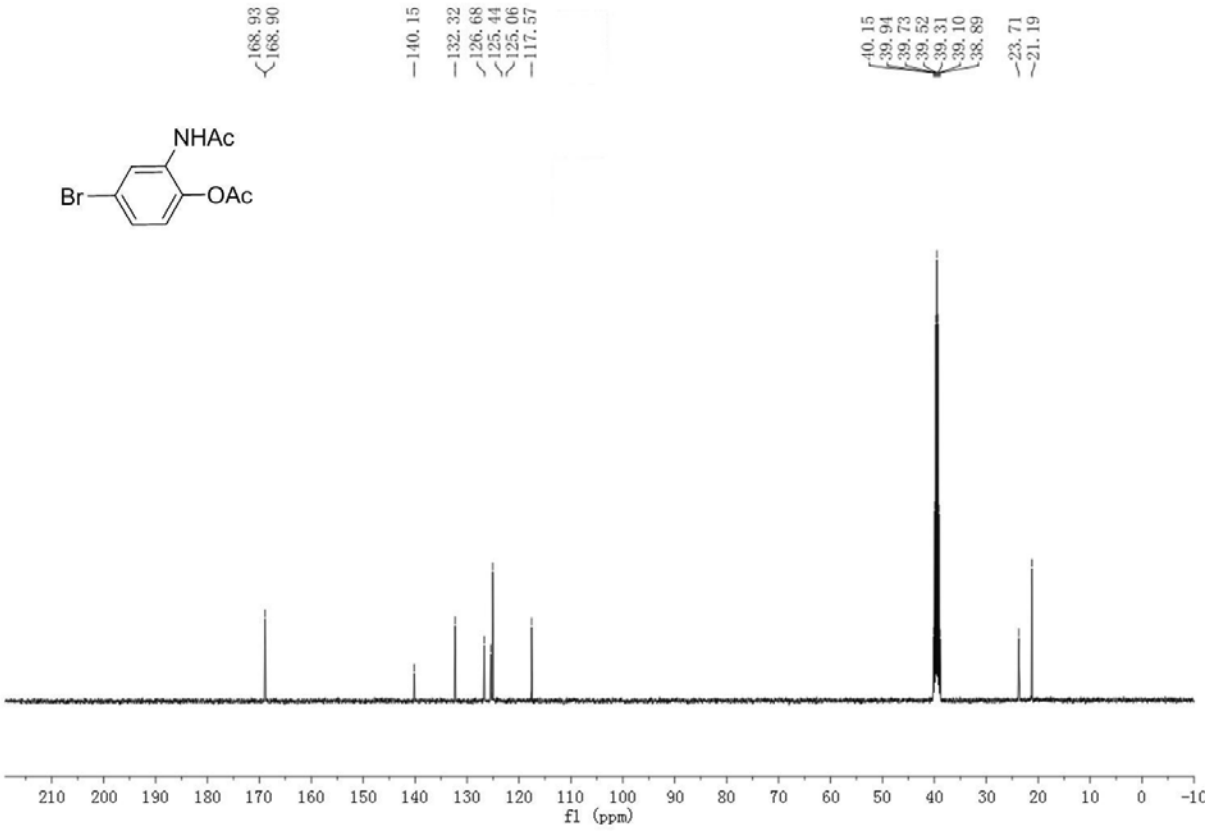


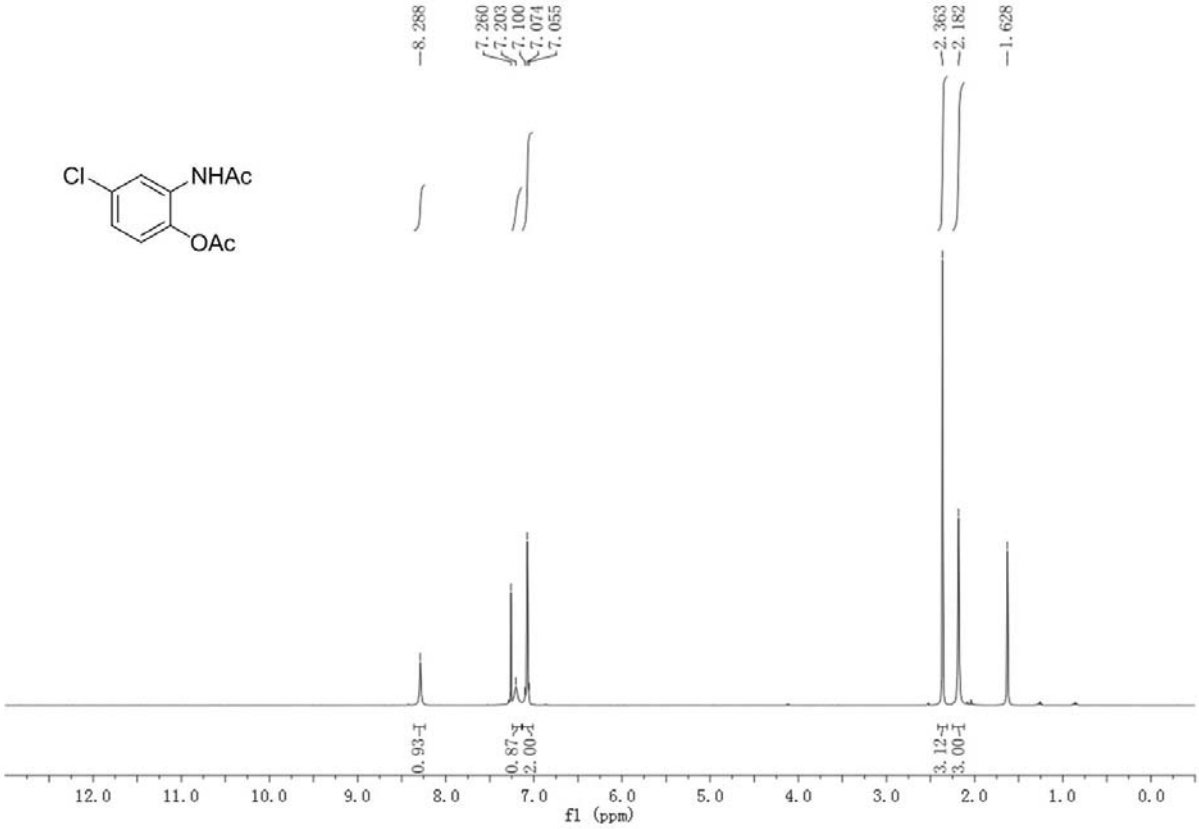


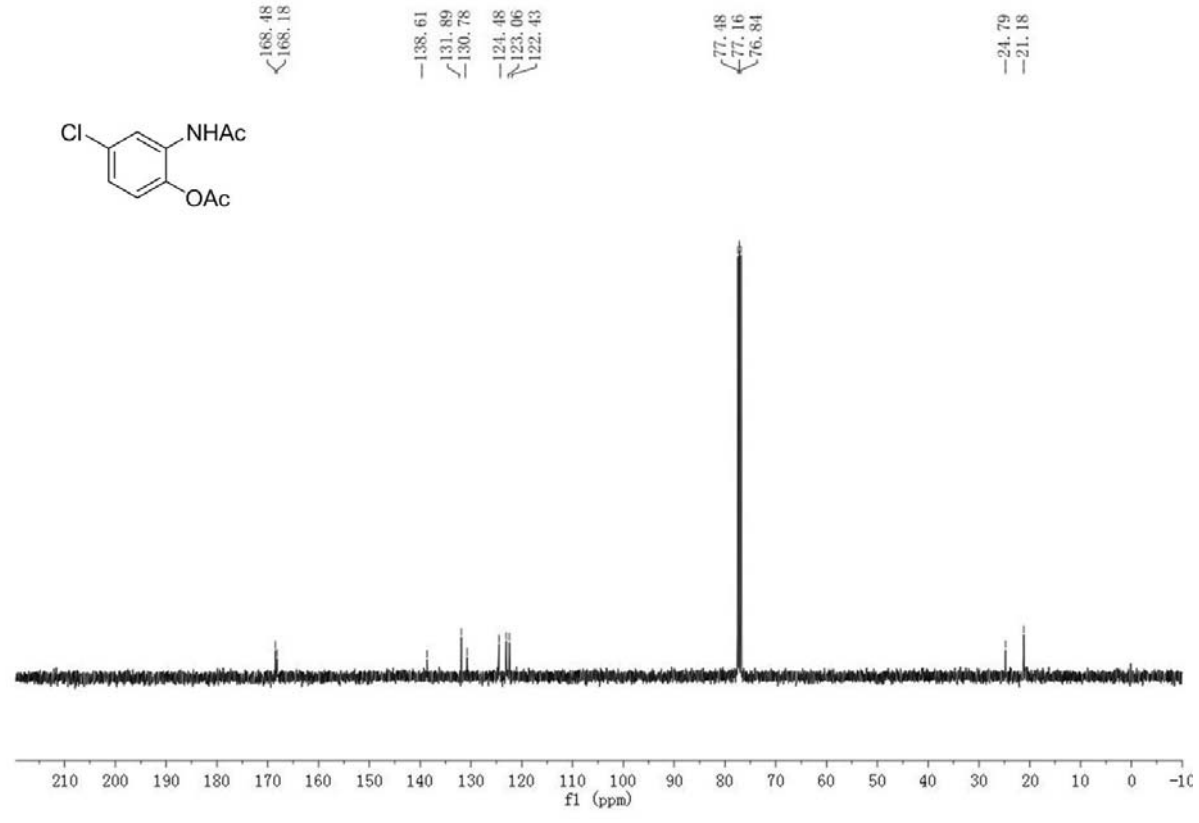


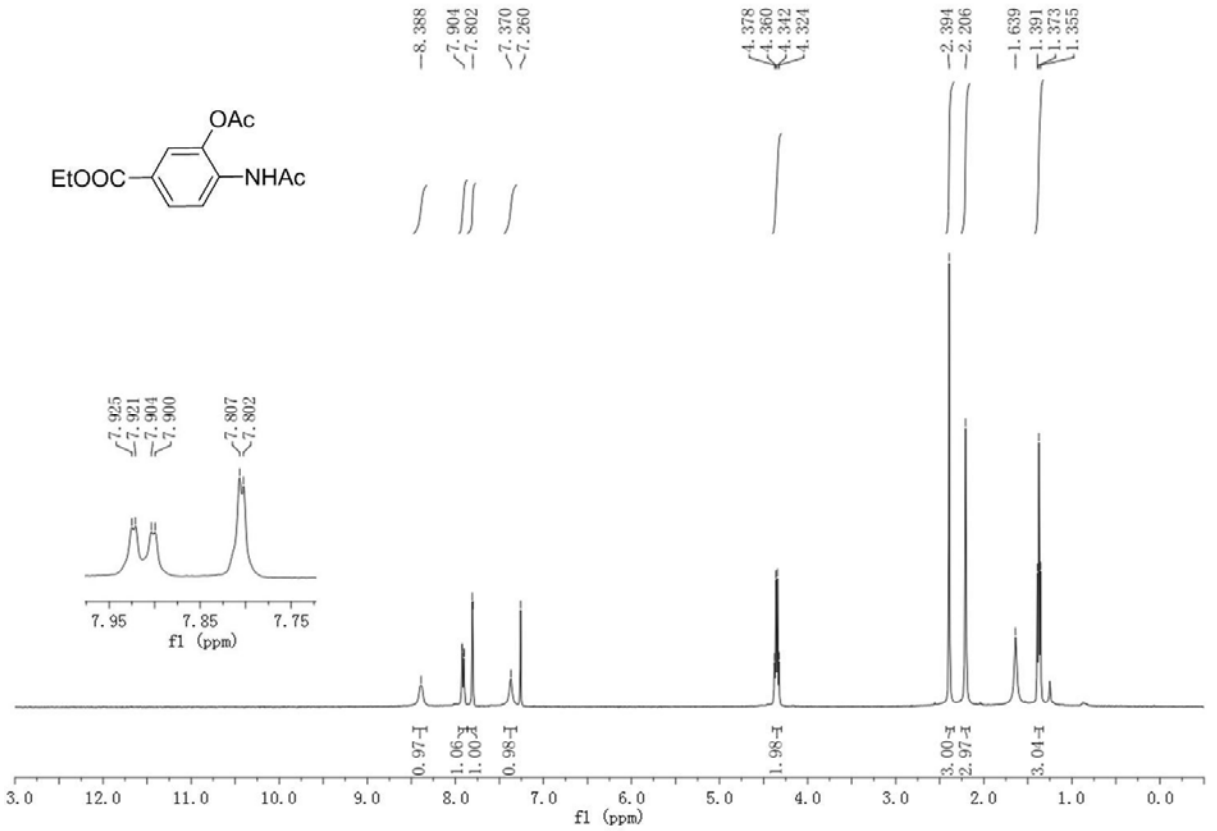


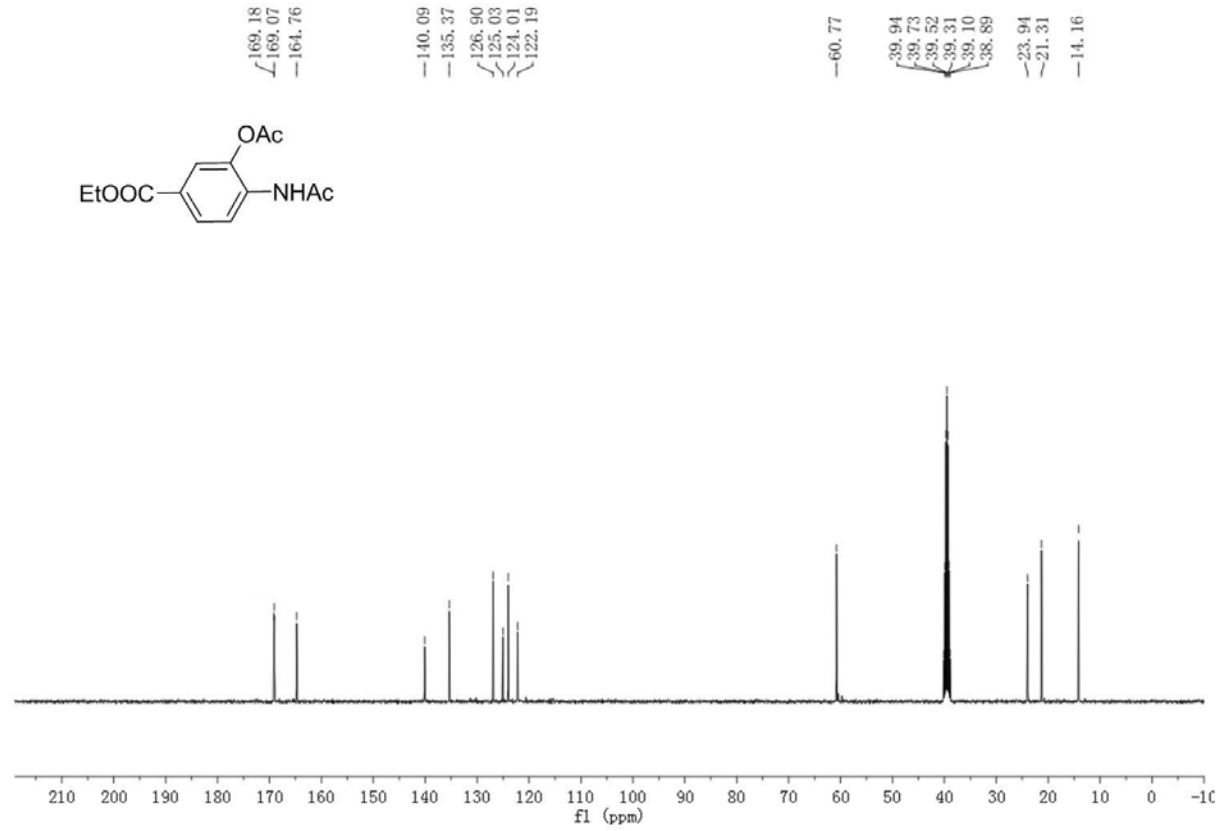


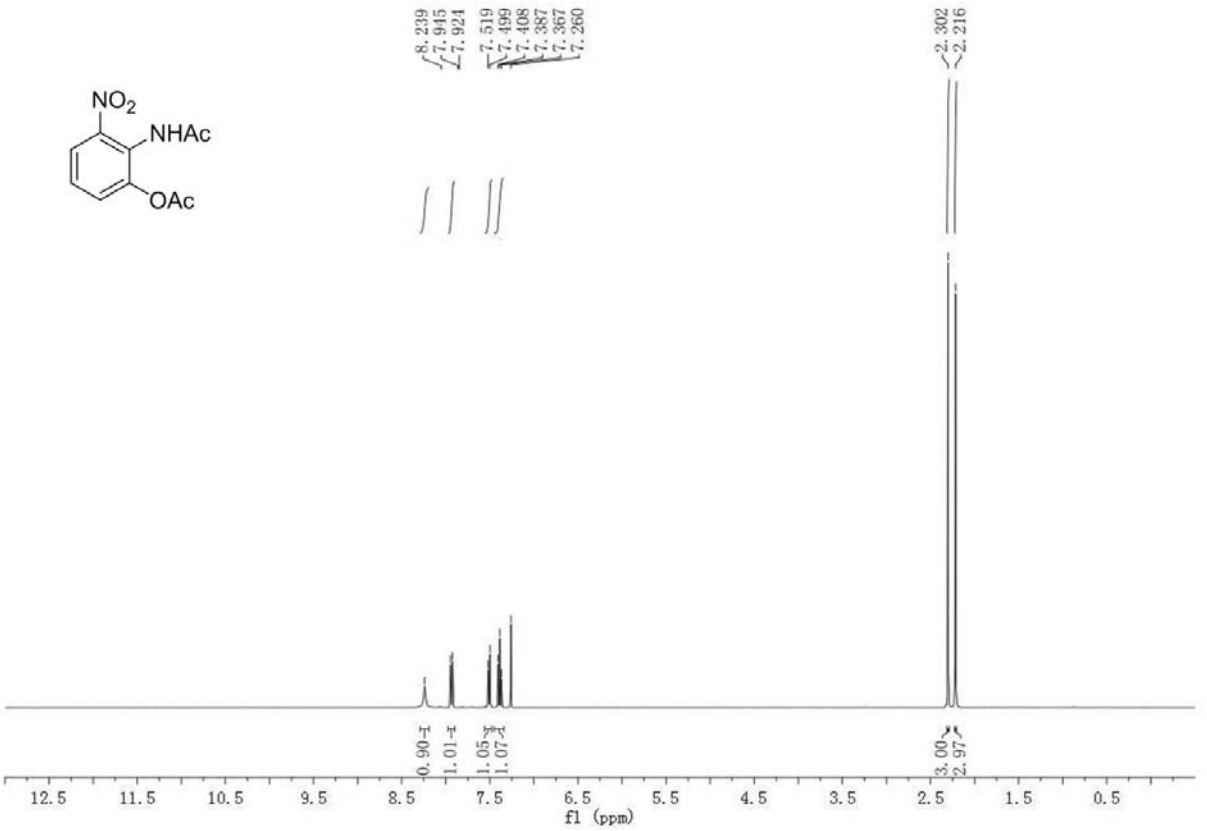


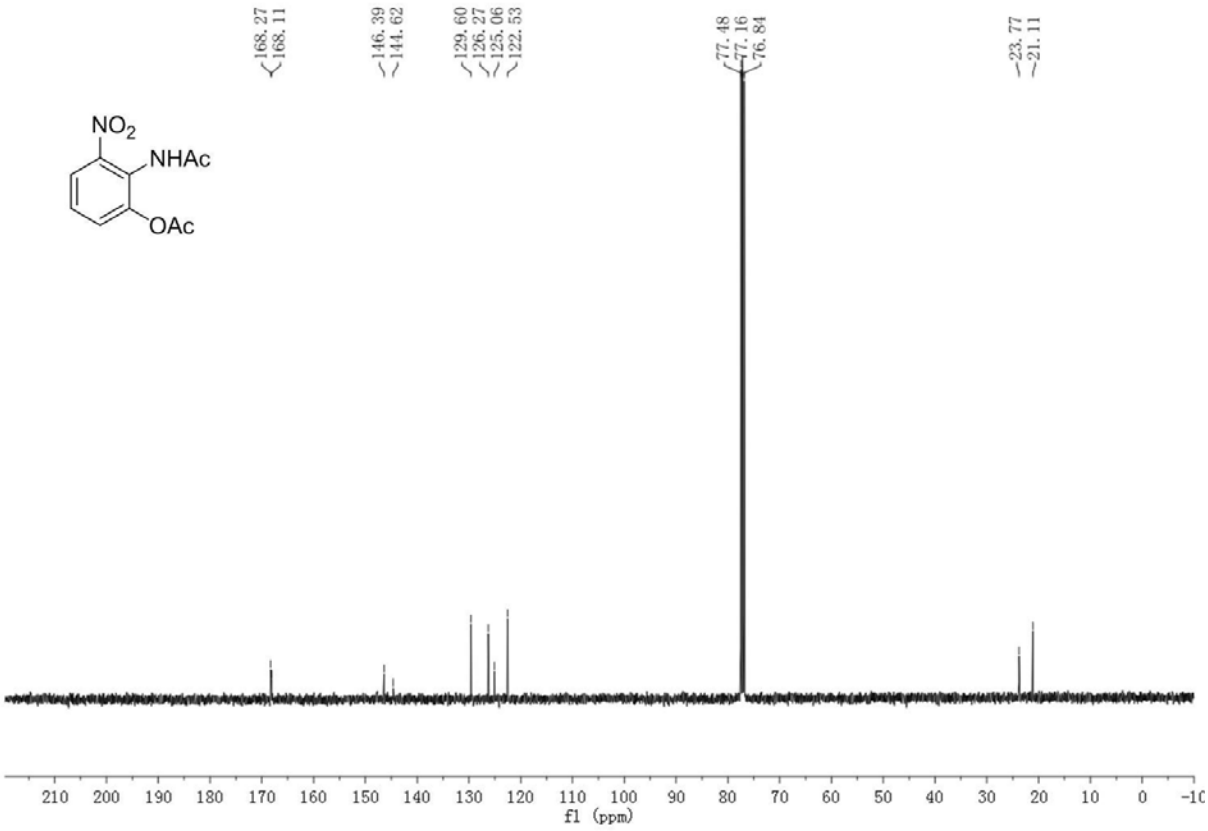


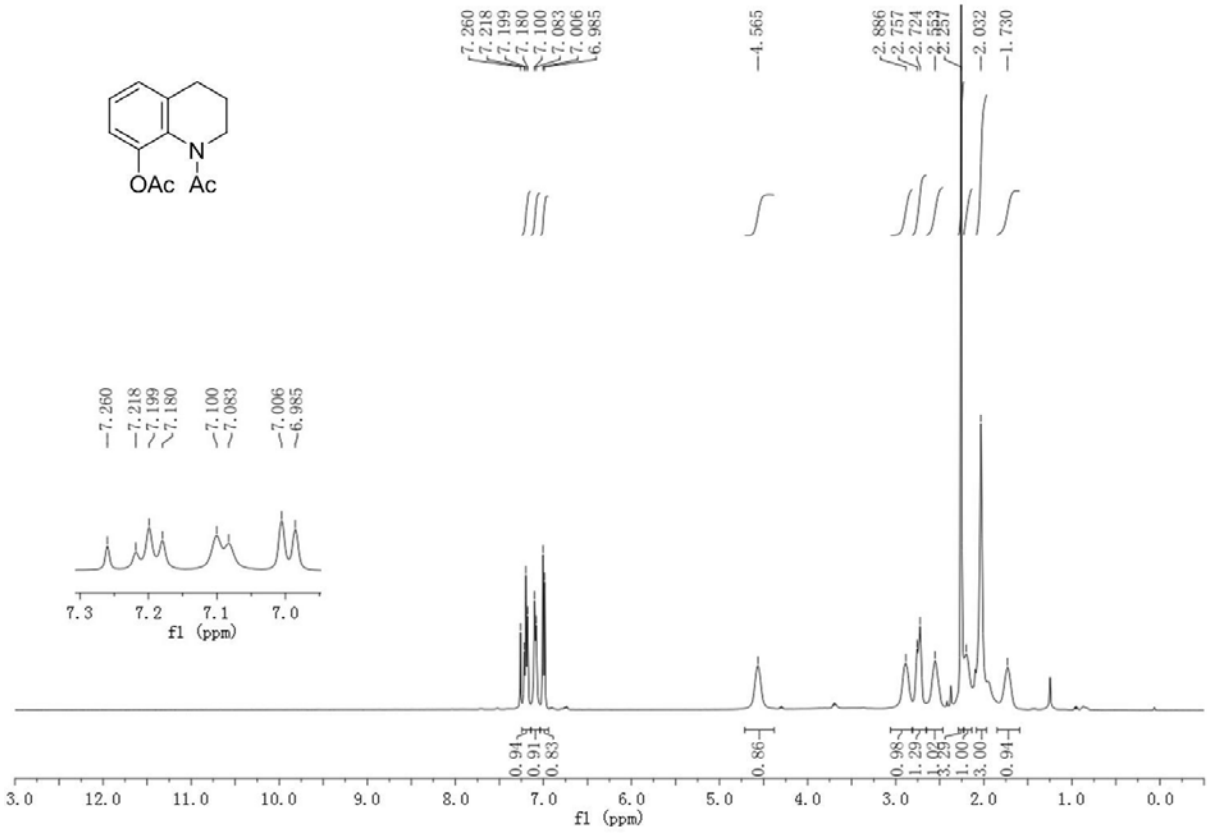


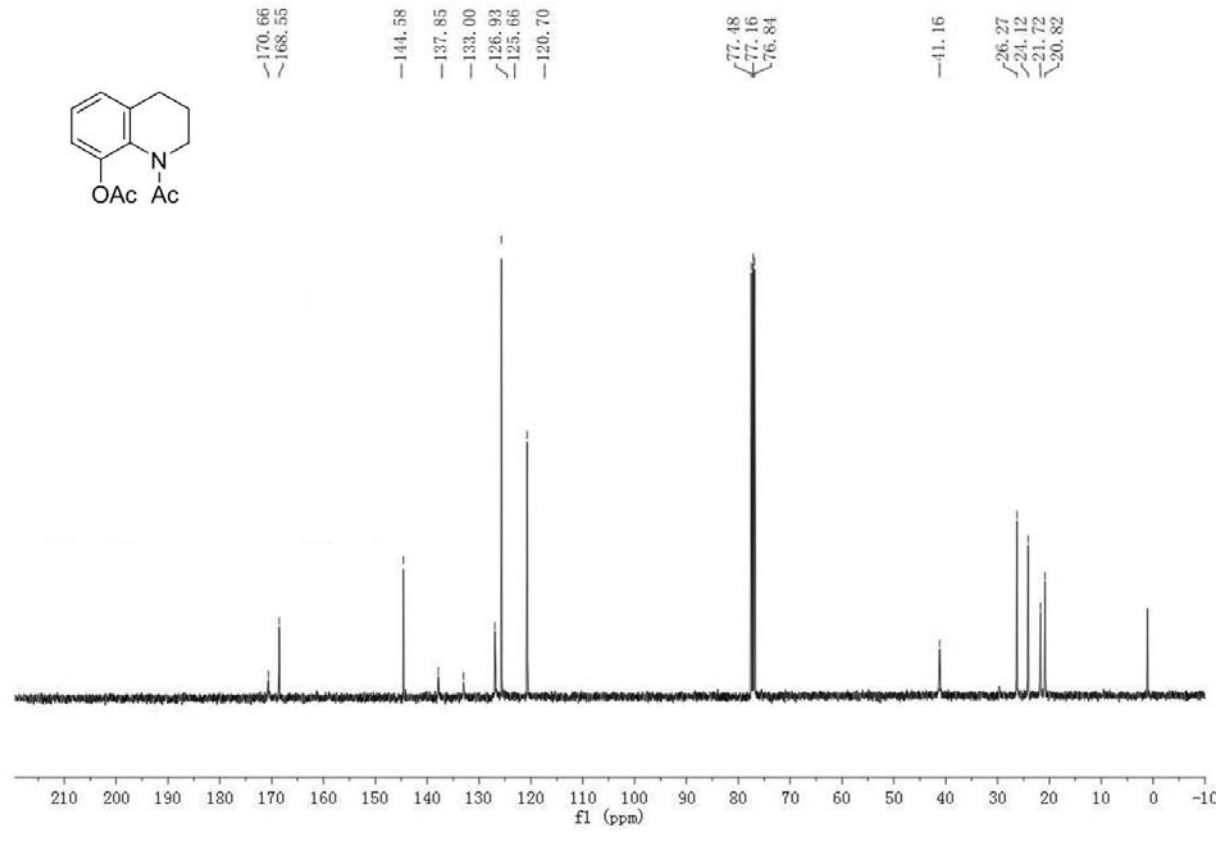

OAc
EtOOC
NHAc
8.388
7.904
7.802
7.370
7.260
4.378
4.360
4.342
4.324
2.394
2.206
1.639
1.391
1.373
1.355
7.925
7.921
7.904
7.900
7.807
7.802
7.95
7.85
7.75
f1 (ppm)
0.97
1.06
1.00
0.98
1.98
3.00
2.97
3.04
f1 (ppm)

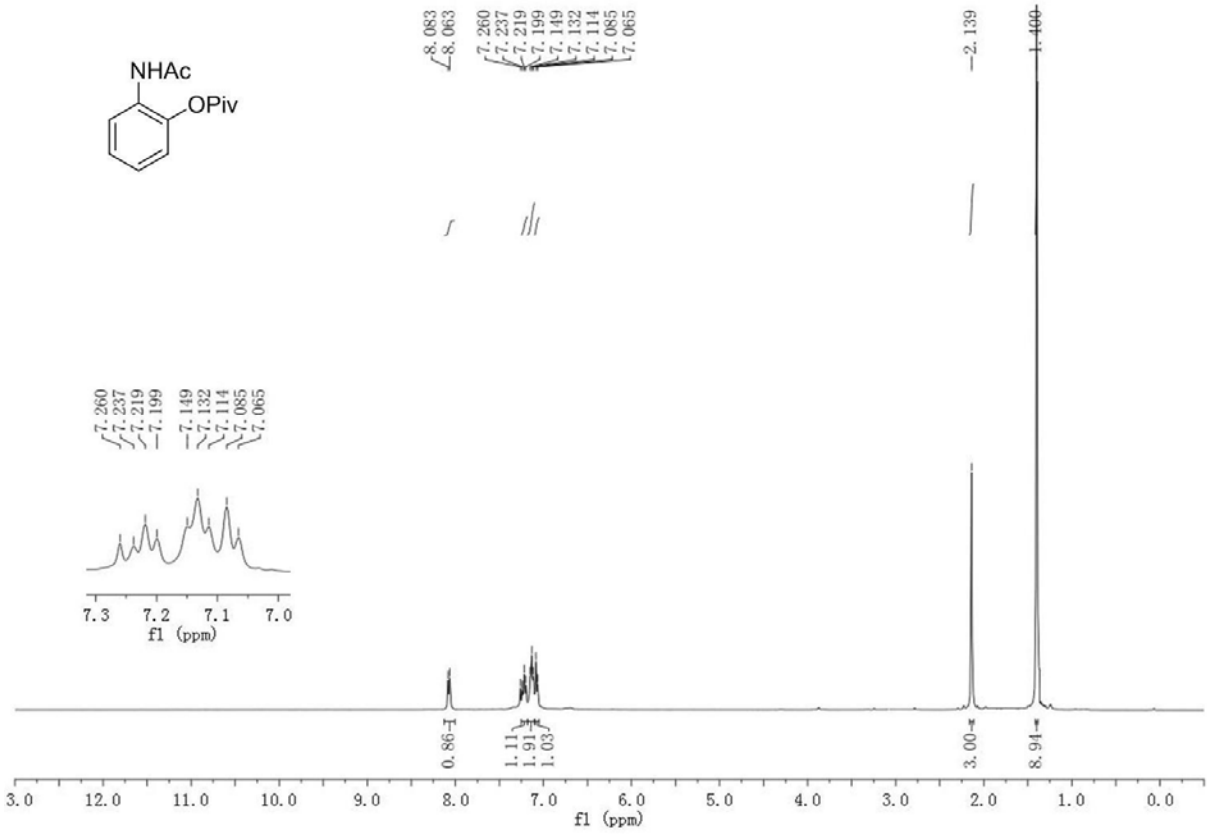

169.18
169.07
164.76
140.09
135.37
126.90
125.03
124.01
122.19
60.77
39.94
39.73
39.52
39.31
39.10
38.89
23.94
21.31
14.16
OAc
EtOOC
NHAc
f1 (ppm)

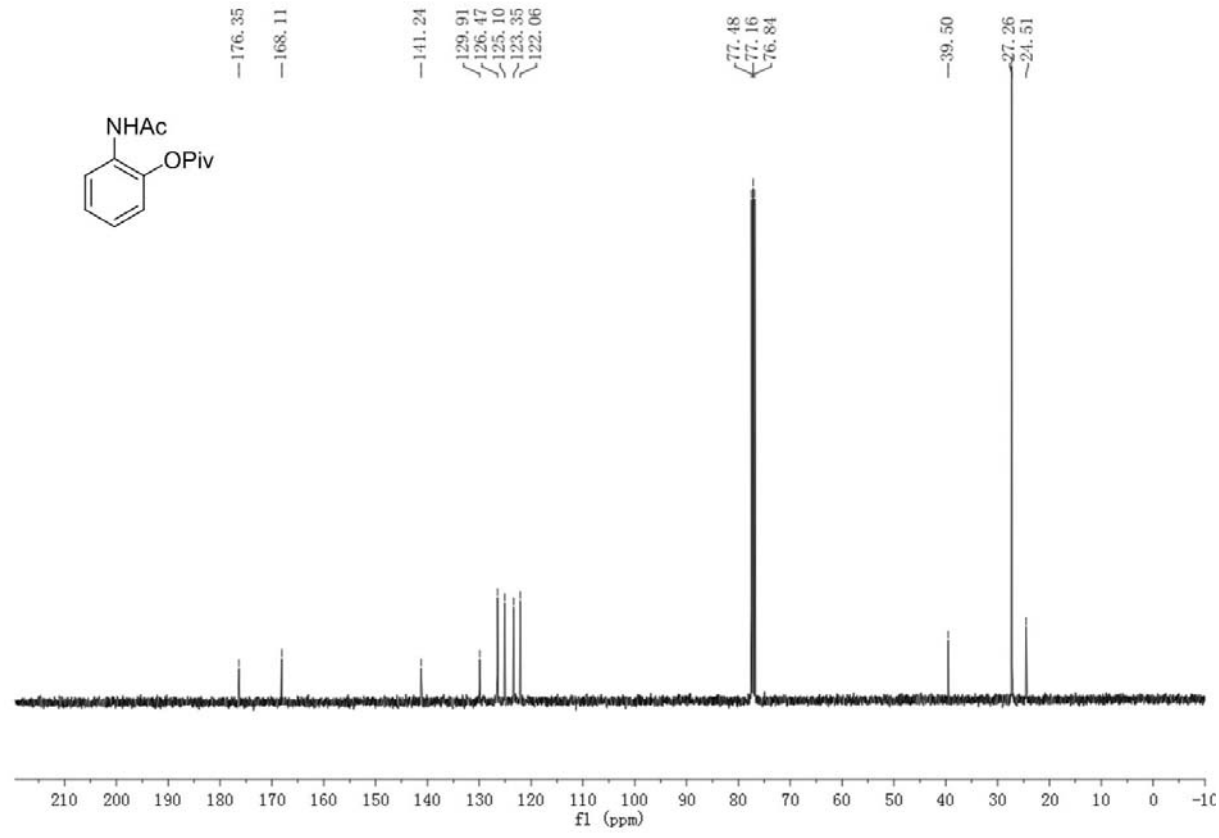


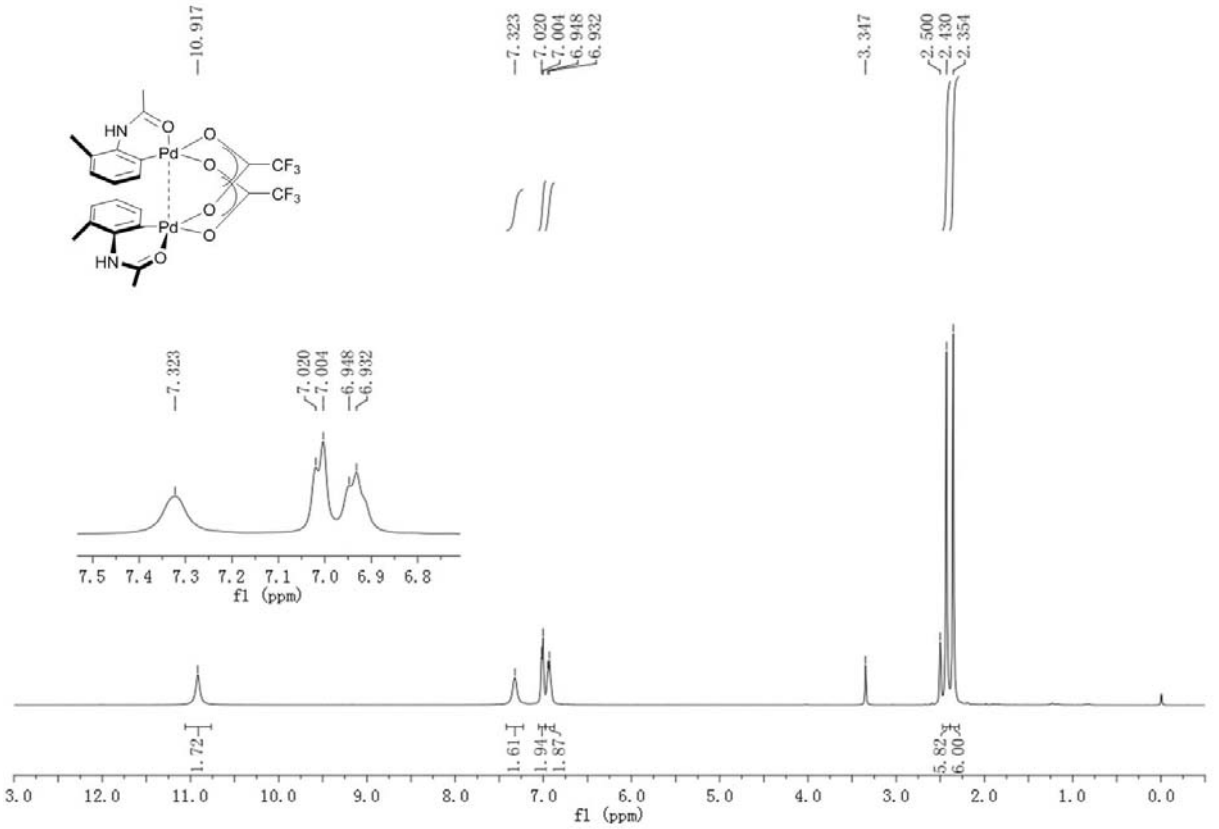


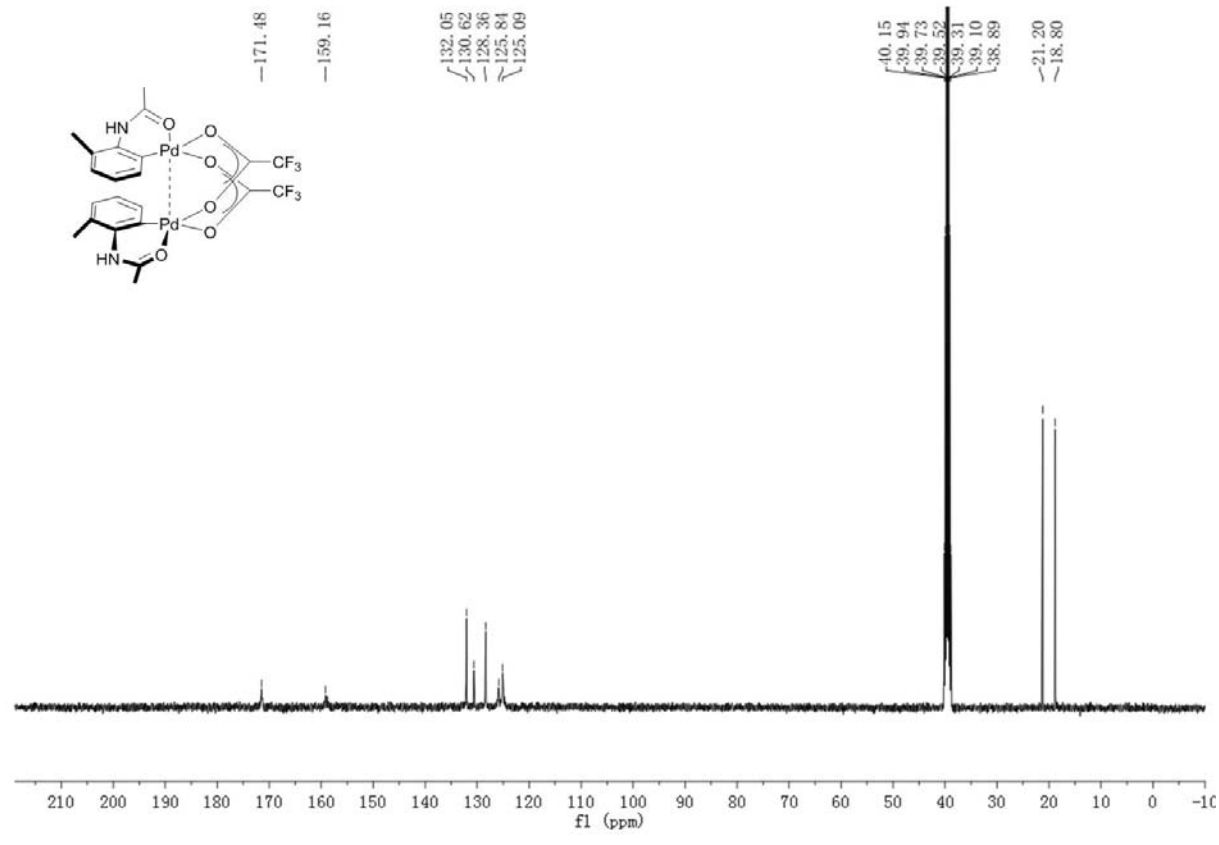

OAc Ac
7.260
7.218
7.199
7.180
7.100
7.083
7.006
6.985
4.565
2.886
2.757
2.724
2.553
2.257
2.032
1.730
f1 (ppm)
0.94
0.91
0.83
0.86
0.98
1.29
3.00
1.00
3.00
0.94


OAc Ac
170.66
168.55
144.58
137.85
133.00
126.93
125.66
120.70
77.48
77.16
76.84
41.16
26.27
24.12
21.72
20.82
f1 (ppm)


NHAc
OPiv
8.083
8.063
7.260
7.237
7.219
7.199
7.149
7.132
7.114
7.085
7.065
2.139
1.400
0.86
1.11
1.91
1.03
3.00
8.94
fl (ppm)


NHAc
OPiv
176.35
168.11
141.24
129.91
126.47
125.10
123.35
122.06
77.48
77.16
76.84
39.50
27.26
24.51
fl (ppm)


10.917
7.323
7.020
7.004
6.948
6.932
3.347
2.500
2.430
2.354
HN
O
Pd
O
O
CF3
CF3
O
O
Pd
HN
O
7.323
7.020
7.004
6.948
6.932
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.72
1.61
1.94
1.87
5.82
6.00
3.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


171.48
159.16
132.05
130.62
128.36
125.84
125.09
40.15
39.94
39.73
39.52
39.31
39.10
38.89
21.20
18.80
HN
O
Pd
O
O
CF3
CF3
O
O
Pd
HN
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)