Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel-Catalyzed Regioselective C–H Oxygenation: New Routes for Versatile C–O Bond Formation

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1. General information

All compounds are characterized by ^{1}H NMR, ^{13}C NMR and MS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413:30 m × 320 μm × 0.25 μm, H, FID detection). GC-MS data was recorded on a 5975C Mass Selective Detector,coupled with a 7890A Gas Chromatograph (Agilent Technologies).

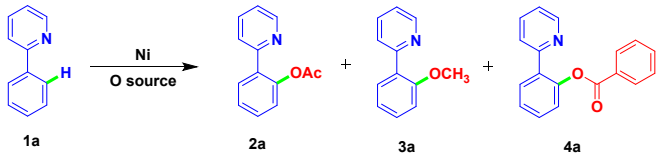
2. General procedure

General procedure for C-H oxygenation of chelating arenes with iodobenzene diacetate: To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (30 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **2a**.

General procedure for C-H oxygenation of chelating arenes with alcohols: To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (30 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **3a**.

General procedure for C-H oxygenation of chelating arenes with benzoic acids: To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and PhCOOH (91.6 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (30 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **4a**.

Table S1. Optimization of the reaction conditions[a]

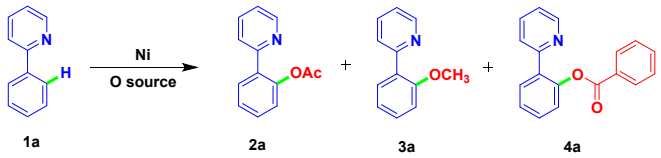


1a 2a 3a 4a

Entry	Cat.	O source	Additive	Solvent	**2a/3a/4a**(%)[b]
1	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	$Cu(OAc)_2$	CH_3CN	trace/23/0
2	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	AgOAc	CH_3CN	0/26/0
3	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	AgO_2CCF_3	CH_3CN	0/41/0
4	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	Ag_2CO_3	CH_3CN	0/13/0
5	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	AgOPiv	CH_3CN	0/34/0
6	$Ni(acac)_2$/ $MePh_2P$	CH_3OH[c]	Ag_2O	CH_3CN	0/17/0

[a]Reaction condition: **1a** (0.5 mmol), cat.(0.1 mmol), ligand (0.1 mmol), O source (0.75 mmol), additive (0.75 mmol), solvent (2 mL), 115 °C, 24 h. [b]Isolated yield. [c](5.0 mmol).

Table S2. Optimization of the reaction conditions[a]



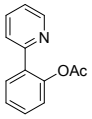
1a 2a 3a 4a

Entry	Cat.	O source	Additive	Solvent	**2a/3a/4a**(%)[b]
1	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	CH_3OH	0/38/0
2	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	CH_3CN	0/0/<5
3	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	PhCl	0/0/37
4	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	NMP	0/0/49
5[f]	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	NMP	0/0/60
6[d,f]	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	AgO_2CCF_3	NMP	0/0/67
7[d,f]	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	-	NMP	0/0/68
8[f,h]	$Ni(acac)_2$/ $MePh_2P$	PhCOOH	-	NMP	0/0/65

[a]Reaction condition: **1a** (0.5 mmol), cat.(0.1 mmol), ligand (0.1 mmol), O source (0.75 mmol), additive (0.75 mmol), solvent (2 mL), 115 °C, 24 h. [b]Isolated yield. [d]130 °C. [e]100°C. [f]O_2 atmosphere. [g]Ar atmosphere. [h]145°C

3. Characterization data

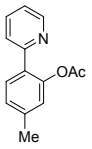
2-(pyridin-2-yl)phenyl acetate (2a)



Formula: $C_{13}H_{11}NO_2$
Mass: 213

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2a** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (80.9 mg, 76%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.8 – 8.7 (m, 1H), 7.8 – 7.7 (m, 2H), 7.6 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.5 (td, *J* = 7.7, 1.7 Hz, 1H), 7.4 (td, *J* = 7.5, 1.2 Hz, 1H), 7.3 – 7.3 (m, 1H), 7.2 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.2 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 154.9, 148.6, 147.1, 135.3, 132.2, 129.8, 128.7, 125.4, 122.6, 122.3, 121.2, 20.0. GC-MS (EI) *m/z*: 213.

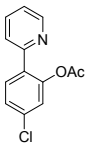
5-methyl-2-(pyridin-2-yl)phenyl acetate (2b)



Formula: $C_{14}H_{13}NO_2$
Mass: 227

To a mixture of 2-(p-tolyl)pyridine (84.5 mg, 0.5 mmol) **1b**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2b** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (73.8 mg, 65%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 – 8.69 (m, 1H), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.6, 154.8, 148.4, 146.9, 139.3, 135.4, 129.6, 129.0, 126.3, 122.7, 122.6, 121.0, 20.2, 20.0. GC-MS (EI) *m/z*: 227.

5-chloro-2-(pyridin-2-yl)phenyl acetate (2c)

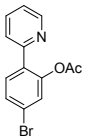


Formula: $C_{13}H_{10}ClNO_2$
Mass: 247

To a mixture of 2-(4-chlorophenyl)pyridine (94.5 mg, 0.5 mmol) **1c**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following

the general procedure, **2c** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (95.1 mg, 77%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 – 8.51 (m, 1H), 7.89 (d, *J* = 1.7 Hz, 2H), 7.75 – 7.72 (m, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.9, 156.1, 144.8, 137.0, 135.7, 130.7, 126.0, 122.8, 120.8, 118.1, 117.6, 116.4, 19.9. GC-MS (EI) *m/z*: 247.

5-bromo-2-(pyridin-2-yl)phenyl acetate (2d)

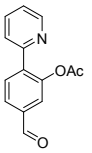


Formula: $C_{13}H_{10}BrNO_2$

Mass: 291

To a mixture of 2-(4-bromophenyl)pyridine (116.5 mg, 0.5 mmol) **1d**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2d** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (101.9 mg, 70%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 4.8 Hz, 1H), 7.94 – 7.84 (m, 1H), 7.78 (tt, *J* = 7.8, 1.7 Hz, 1H), 7.63 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.52 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.39 (s, 1H), 7.30 (td, *J* = 5.1, 4.5, 3.0 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.9, 153.8, 148.7, 147.5, 144.9, 135.5, 130.9, 128.6, 125.6, 122.5, 121.5, 118.0, 19.9. GC-MS (EI) *m/z*: 291.

5-formyl-2-(pyridin-2-yl)phenyl acetate (2e)

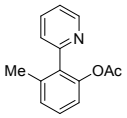


Formula: $C_{14}H_{11}NO_3$

Mass: 241

To a mixture of 4-(pyridin-2-yl)benzaldehyde (91.5 mg, 0.5 mmol) **1e**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2e** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (86.8 mg, 72%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 8.73 (d, *J* = 4.8 Hz, 1H), 7.88 (q, *J* = 8.0 Hz, 2H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.69 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 7.6, 4.9 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.9, 169.1, 154.5, 149.8, 148.7, 138.7, 137.4, 136.6, 131.7, 127.4, 124.3, 123.9, 123.0, 20.9. GC-MS (EI) *m/z*: 241.

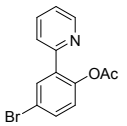
3-methyl-2-(pyridin-2-yl)phenyl acetate (2f)



Formula: $C_{14}H_{13}NO_2$
Mass: 227

To a mixture of 2-(o-tolyl)pyridine (84.5 mg, 0.5 mmol) **1f**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2f** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (78.3 mg, 69%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 – 8.47 (m, 1H), 7.62 – 7.54 (m, 1H), 7.43 (td, *J* = 7.7, 2.0 Hz, 1H), 7.35 (ddd, *J* = 20.0, 7.5, 1.6 Hz, 2H), 7.20 (dd, *J* = 7.9, 4.8 Hz, 2H), 2.20 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 155.4, 148.2, 146.6, 138.1, 133.3, 132.4, 130.5, 129.4, 125.9, 122.7, 122.6, 20.6, 19.1. GC-MS (EI) *m/z*: 227.

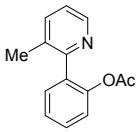
4-bromo-2-(pyridin-2-yl)phenyl acetate (2g)



Formula: $C_{13}H_{10}BrNO_2$
Mass: 291

To a mixture of 2-(3-bromophenyl)pyridine (116.5 mg, 0.5 mmol) **1g**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2g** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (88.8 mg, 61%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 7.98 – 7.86 (m, 2H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.03 (m, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.1, 145.0, 137.1, 135.8, 133.1, 132.7, 131.7, 127.7, 124.0, 121.2, 119.5, 118.2, 19.9. GC-MS (EI) *m/z*: 291.

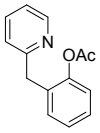
2-(3-methylpyridin-2-yl)phenyl acetate (2h)



Formula: $C_{14}H_{13}NO_2$
Mass: 227

To a mixture of 3-methyl-2-phenylpyridine (84.5 mg, 0.5 mmol) **1h**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2h** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (85.1 mg, 75%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.35 – 7.25 (m, 3H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 2.15 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.5, 155.8, 149.5, 148.4, 138.2, 136.2, 133.5, 128.9, 128.0, 124.8, 122.2, 120.0, 20.6, 19.9. GC-MS (EI) *m/z*: 227.

2-(pyridin-2-ylmethyl)phenyl acetate (2i)

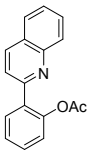


Formula: $C_{14}H_{13}NO_2$

Mass: 227

To a mixture of 2-benzylpyridine (84.5 mg, 0.5 mmol) **1i**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2i** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (79.5 mg, 70%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.60 – 8.55 (m, 1H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (td, *J* = 7.4, 1.3 Hz, 1H), 7.18 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.10 (dd, *J* = 15.5, 8.1 Hz, 2H), 4.17 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.2, 158.7, 148.2, 147.8, 136.0, 130.3, 130.2, 127.0, 125.3, 122.1, 121.7, 120.5, 38.1, 19.9. GC-MS (EI) *m/z*: 227.

2-(quinolin-2-yl)phenyl acetate (2j)

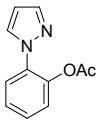


Formula: $C_{17}H_{13}NO_2$

Mass: 263

To a mixture of 2-phenylquinoline (102.5 mg, 0.5 mmol) **1j**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2j** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (96.0 mg, 73%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.84 (ddd, *J* = 15.1, 7.9, 1.6 Hz, 2H), 7.74 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.48 (td, *J* = 7.7, 1.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.5, 148.4, 136.4, 132.1, 131.2, 130.1, 127.5, 127.0, 126.7, 126.5, 123.4, 121.6, 100.0, 21.1. GC-MS (EI) *m/z*: 263.

2-(1H-pyrazol-1-yl)phenyl acetate (2k)



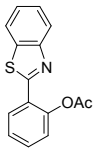
Formula: $C_{11}H_{10}N_2O_2$

Mass: 202

To a mixture of 1-phenyl-1H-pyrazole (72.0 mg, 0.5 mmol) **1k**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general

procedure, **2k** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (66.7 mg, 66%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 2H), 7.65 (dd, *J* = 7.6, 2.2 Hz, 1H), 7.41 (ddd, *J* = 9.7, 7.5, 1.9 Hz, 2H), 7.26 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.48 (t, *J* = 2.3 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4, 140.0, 129.2, 127.6, 127.4, 125.8, 124.7, 123.1, 123.0, 106.0, 19.8. GC-MS (EI) *m/z*: 202.

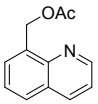
2-(benzo[d]thiazol-2-yl)phenyl acetate (2l)



Formula: $C_{15}H_{11}NO_2S$
Mass: 269

To a mixture of 2-phenylbenzo[d]thiazole (105.5 mg, 0.5 mmol) **1l**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2l** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (95.5 mg, 71%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 (t, *J* = 3.6 Hz, 1H), 7.95 (t, *J* = 2.9 Hz, 1H), 7.83 (dd, *J* = 8.2, 2.9 Hz, 1H), 7.74 (m, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.25 (d, *J* = 3.9 Hz, 1H), 6.90 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.87 (d, *J* = 3.1 Hz, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.1, 153.5, 148.4, 134.9, 132.7, 131.5, 129.8, 124.1, 121.2, 112.5, 112.2, 54.9. GC-MS (EI) *m/z*: 269.

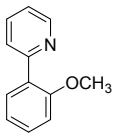
quinolin-8-ylmethyl acetate (2n)



Formula: $C_{12}H_{11}NO_2$
Mass: 201

To a mixture of 8-methylquinoline (71.5 mg, 0.5 mmol) **1n**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and $PhI(OAc)_2$ (483.2 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CN=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in air. Following the general procedure, **2n** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (78.4 mg, 78%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.95 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.78 (ddd, *J* = 13.6, 7.7, 1.4 Hz, 2H), 7.54 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.86 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.0, 149.9, 146.1, 136.3, 134.2, 128.8, 128.2, 128.2, 126.2, 121.3, 62.8, 21.2. GC-MS (EI) *m/z*: 201.

2-(2-methoxyphenyl)pyridine (3a)

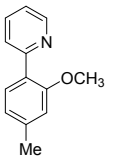


Formula: $C_{12}H_{11}NO$

Mass: 185

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3a** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (74.9 mg, 81%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 4.9 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.82 – 7.71 (m, 2H), 7.42 (td, *J* = 8.0, 1.8 Hz, 1H), 7.26 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.9, 155.0, 148.2, 134.9, 130.2, 129.9, 129.1, 124.2, 120.7, 120.1, 110.5, 54.7. GC-MS (EI) *m/z*: 185.

2-(2-methoxy-4-methylphenyl)pyridine (3b)

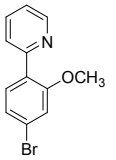


Formula: $C_{13}H_{13}NO$

Mass: 199

To a mixture of 2-(p-tolyl)pyridine (84.5 mg, 0.5 mmol) **1b**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3b** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (69.7 mg, 70%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.26 – 7.16 (m, 1H), 6.96 – 6.90 (m, 1H), 6.85 (s, 1H), 3.88 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.9, 155.1, 148.2, 139.3, 134.8, 130.0, 125.2, 124.1, 120.8, 120.5, 111.3, 54.6, 20.7. GC-MS (EI) *m/z*: 199.

2-(4-bromo-2-methoxyphenyl)pyridine (3c)



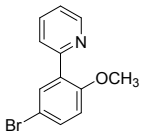
Formula: $C_{12}H_{10}BrNO$

Mass: 263

To a mixture of 2-(4-bromophenyl)pyridine (116.5 mg, 0.5 mmol) **1d**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3c** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (111.8 mg, 85%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.77 – 8.69 (m, 1H), 7.93 – 7.82 (m, 1H), 7.75 (td, *J* = 7.7, 1.9

Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.18 (d, *J* = 1.8 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.5, 148.3, 135.1, 131.3, 130.9, 127.5, 124.1, 123.2, 122.6, 121.1, 114.0, 55.0. GC-MS (EI) *m/z*: 263.

2-(5-bromo-2-methoxyphenyl)pyridine (3d)

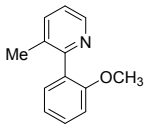


Formula: $C_{12}H_{10}BrNO$

Mass: 263

To a mixture of 2-(3-bromophenyl)pyridine (116.5 mg, 0.5 mmol) **1g**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3d** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (96.0 mg, 73%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.45 (d, *J* = 1.2 Hz, 1H), 7.30 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.9, 148.5, 134.3, 130.5, 129.4, 126.7, 125.4, 124.4, 122.8, 122.4, 120.4, 20.7. GC-MS (EI) *m/z*: 263.

2-(2-methoxyphenyl)-3-methylpyridine (3e)

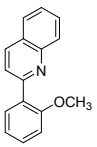


Formula: $C_{13}H_{13}NO$

Mass: 199

To a mixture of 3-methyl-2-phenylpyridine (84.5 mg, 0.5 mmol) **1h**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3e** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (77.6 mg, 78%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 5.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 7.23 (td, *J* = 5.0, 2.4 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.8, 155.6, 145.9, 145.4, 136.6, 131.9, 129.5, 128.6, 121.3, 119.8, 109.9, 54.5, 18.0. GC-MS (EI) *m/z*:199.

2-(2-methoxyphenyl)quinoline (3f)



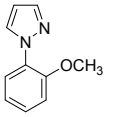
Formula: $C_{16}H_{13}NO$

Mass: 235

To a mixture of 2-phenylquinoline (102.5 mg, 0.5 mmol) **1j**, $Ni(acac)_2$ (25.7 mg, 0.1

mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3f** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (76.4 mg, 65%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.85 (td, *J* = 8.9, 8.2, 1.6 Hz, 2H), 7.71 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.9, 7.5, 1.8 Hz, 1H), 7.14 (td, *J* = 7.4, 1.0 Hz, 1H), 7.04 (dd, *J* = 8.3, 0.9 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.2, 157.1, 135.3, 131.5, 130.4, 129.6, 129.3, 127.4, 127.1, 126.3, 123.5, 121.3, 111.5, 55.7. GC-MS (EI) *m/z*: 235.

1-(2-methoxyphenyl)-1H-pyrazole (3g)

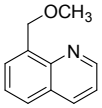


Formula: $C_{10}H_{10}N_2O$

Mass: 174

To a mixture of 1-phenyl-1H-pyrazole (72.0 mg, 0.5 mmol) **1k**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3g** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (68.7 mg, 79%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 10.8, 2.1 Hz, 2H), 7.65 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.26 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.48 (t, *J* = 2.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.8, 142.4, 140.0, 129.2, 127.4, 125.8, 124.7, 123.0, 106.0, 19.8. GC-MS (EI) *m/z*: 174.

8-(methoxymethyl)quinoline (3j)

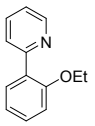


Formula: $C_{11}H_{11}NO$

Mass: 173

To a mixture of 8-methylquinoline (71.5 mg, 0.5 mmol) **1n**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3j** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (74.4 mg, 86%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.92 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.20 (s, 2H), 3.57 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.6, 145.9, 136.5, 136.3, 128.1, 127.5, 127.2, 126.4, 121.0, 70.8, 58.9. GC-MS (EI) *m/z*: 173.

2-(2-ethoxyphenyl)pyridine (3k)

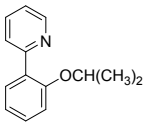


Formula: $C_{13}H_{13}NO$

Mass: 199

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (CH_3CH_2OH=2.0 mL). The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3k** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (76.6 mg, 77%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.9 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.84 (dt, *J* = 8.1, 2.5 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 4.13 (dd, *J* = 7.0, 3.0 Hz, 2H), 1.42 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.4, 155.0, 148.2, 134.7, 130.2, 129.0, 128.0, 124.3, 120.6, 120.1, 111.7, 63.2, 13.8. GC-MS (EI) *m/z*: 199.

2-(2-isopropoxyphenyl)pyridine (3l)

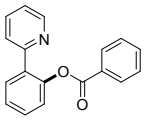


Formula: $C_{14}H_{15}NO$

Mass: 213

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and additive AgO_2CCF_3 (165.7 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent [$(CH_3)_2CHOH$=2.0 mL]. The reaction mixture was stirred at 115 °C for 24 h in O_2. Following the general procedure, **3l** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (79.9 mg, 75%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.3 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 4.56 (hept, *J* = 6.0 Hz, 1H), 1.33 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.0, 154.3, 147.9, 134.8, 130.4, 129.0, 124.6, 124.5, 120.6, 120.2, 113.9, 70.2, 21.1. GC-MS (EI) *m/z*: 213.

2-(pyridin-2-yl)phenyl benzoate (4a)



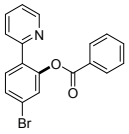
Formula: $C_{18}H_{13}NO_2$

Mass: 275

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and PhCOOH (91.6 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4a** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (93.5 mg, 68%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 6.9 Hz, 2H), 7.82 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.52 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.33 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.25 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*)

δ 171.3, 149.1, 148.3, 136.8, 133.6, 133.5, 131.0, 130.2, 130.2, 130.0, 128.5, 128.5, 126.5, 124.1, 123.4, 122.4. GC-MS (EI) *m/z*: 275.

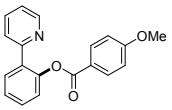
5-bromo-2-(pyridin-2-yl)phenyl benzoate (4b)



Formula: $C_{18}H_{12}BrNO_2$
Mass: 353

To a mixture of 2-(4-bromophenyl)pyridine (116.5 mg, 0.5 mmol) **1d**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and PhCOOH (91.6 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4b** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (111.2 mg, 63%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.24 – 7.09 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.8, 164.3, 149.7, 133.8, 133.6, 133.6, 130.2, 129.5, 128.9, 128.5, 128.5, 128.4, 127.2, 125.5, 124.3, 123.0. GC-MS (EI) *m/z*: 353.

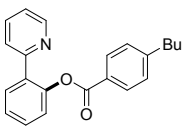
2-(pyridin-2-yl)phenyl 4-methoxybenzoate (4c)



Formula: $C_{19}H_{15}NO_3$
Mass: 305

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and 4-methoxybenzoic acid (76.0 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4c** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (101.0 mg, 66%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 1.1 Hz, 2H), 7.79 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.68 (td, *J* = 7.8, 1.8 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.49 (td, *J* = 7.8, 1.7 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.23 (t, *J* = 6.2 Hz, 1H), 6.94 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.1, 164.8, 164.0, 163.9, 149.0, 148.4, 132.4, 132.3, 131.0, 130.1, 126.3, 123.5, 122.4, 121.9, 113.8, 113.7, 55.5. GC-MS (EI) *m/z*: 305.

2-(pyridin-2-yl)phenyl 4-butylbenzoate (4d)

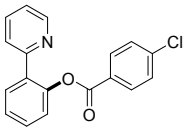


Formula: $C_{22}H_{21}NO_2$
Mass: 331

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and 4-butylbenzoic

acid (80.1 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4d** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (110.9 mg, 67%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 4.9 Hz, 1H), 8.03 (d, *J* = 3.0 Hz, 2H), 7.80 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 3H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.24 – 7.19 (m, 1H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.3, 165.1, 157.3, 149.3, 148.3, 136.6, 131.0, 130.1, 130.1, 129.9, 126.4, 125.5, 125.5, 124.1, 123.4, 122.3, 35.2, 31.1. GC-MS (EI) *m/z*: 331.

2-(pyridin-2-yl)phenyl 4-chlorobenzoate (4e)

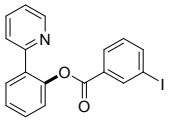


Formula: $C_{18}H_{12}ClNO_2$

Mass: 309

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, Ni(acac)$_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and 4-chlorobenzoic acid (117.0 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4e** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (89.6 mg, 58%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.63 – 8.57 (m, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.77 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.31 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.22 (t, *J* = 6.3 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.3, 157.3, 156.7, 148.1, 140.1, 131.6, 131.5, 131.0, 130.1, 128.9, 127.9, 126.6, 123.9, 123.3, 122.4, 113.9. GC-MS (EI) *m/z*: 309.

2-(pyridin-2-yl)phenyl 3-iodobenzoate (4f)

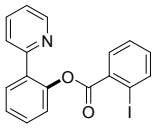


Formula: $C_{18}H_{12}INO_2$

Mass: 401

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, Ni(acac)$_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and 3-iodobenzoic acid (185.9 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4f** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (120.3 mg, 60%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.24 (t, *J* = 1.7 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.89 (dt, *J* = 7.9, 1.4 Hz, 2H), 7.78 – 7.70 (m, 1H), 7.60 (t, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.1, 160.0, 159.6, 152.1, 149.2, 142.5, 138.9, 132.4, 130.7, 130.2, 129.3, 127.7, 125.7, 123.2, 120.8, 116.5, 102.6, 93.8. GC-MS (EI) *m/z*: 401.

2-(pyridin-2-yl)phenyl 2-iodobenzoate (4g)

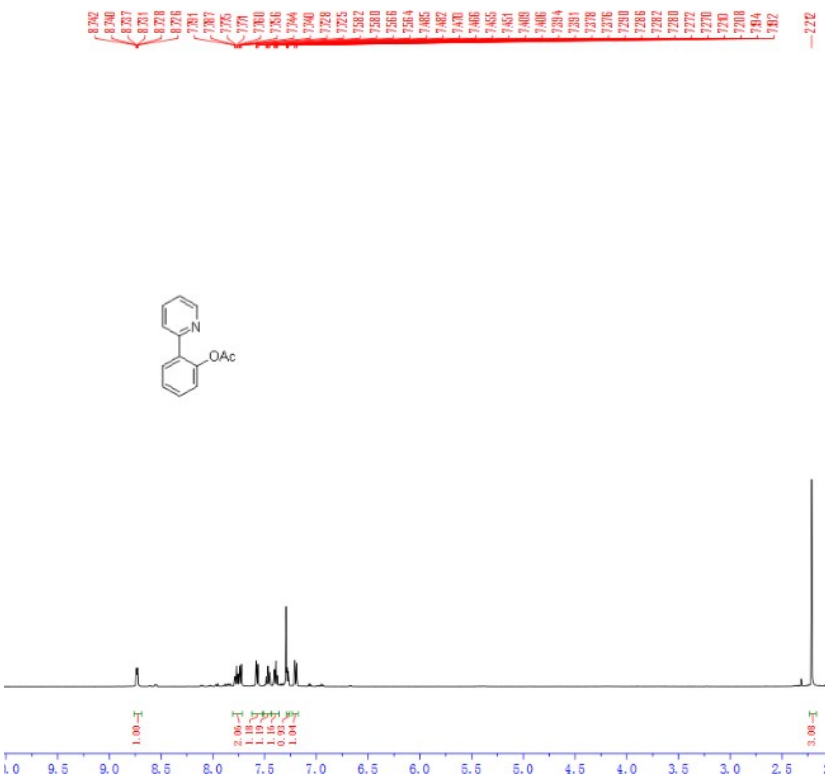


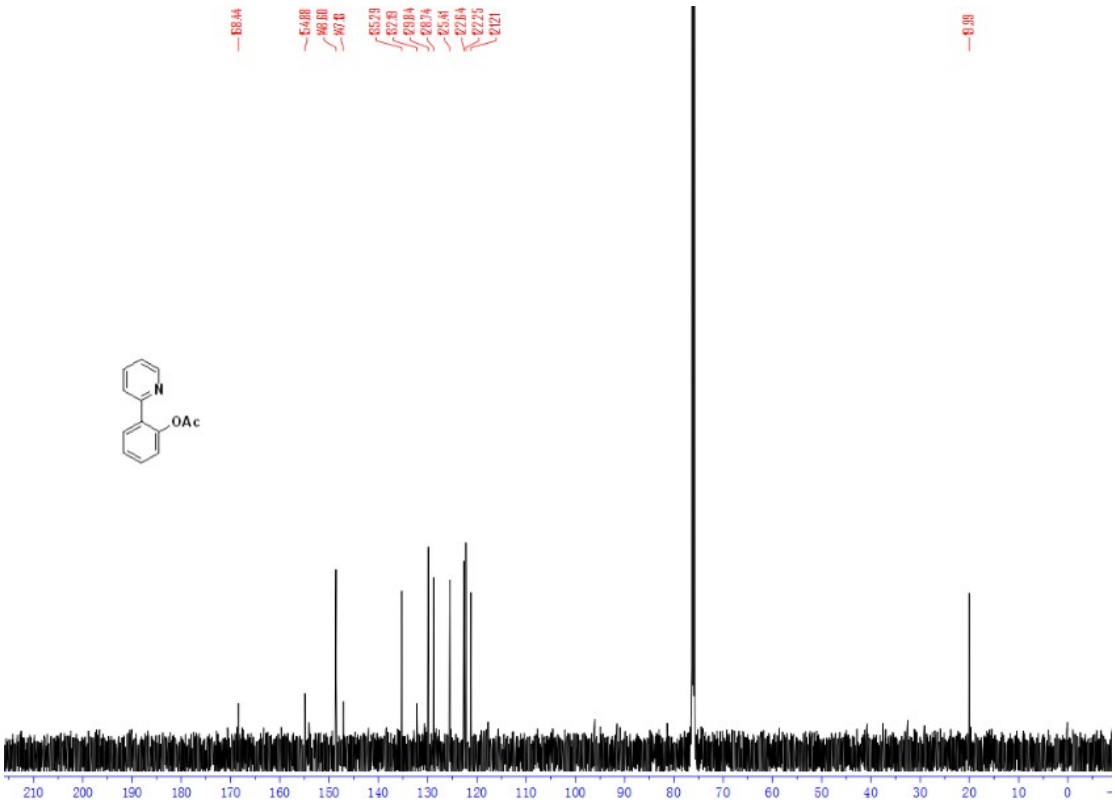
Formula: $C_{18}H_{12}INO_2$

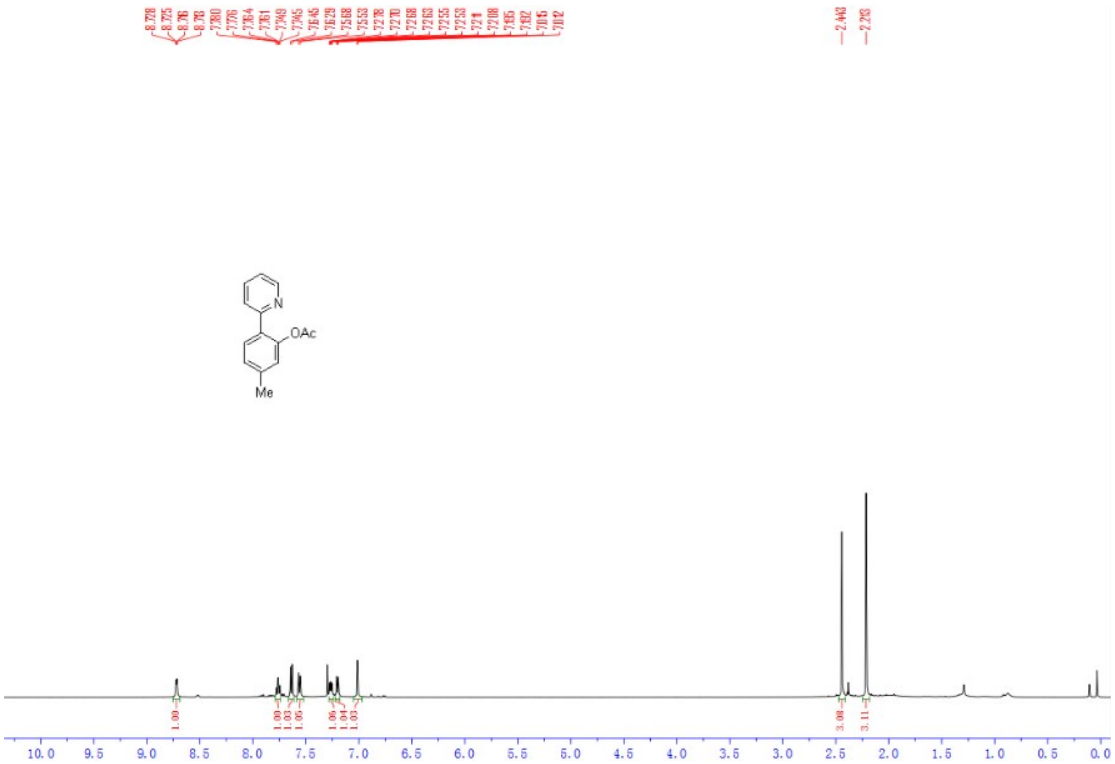
Mass: 401

To a mixture of 2-phenylpyridine (77.5 mg, 0.5 mmol) **1a**, $Ni(acac)_2$ (25.7 mg, 0.1 mmol, 20 mol %), ligand $MePh_2P$ (20.0 mg, 0.1 mmol, 20 mol %), and 2-iodobenzoic acid (185.9 mg, 0.75 mmol, 1.5 equiv) in a reaction tube was added solvent (NMP=2.0 mL). The reaction mixture was stirred at 130 °C for 24 h in O_2. Following the general procedure, **4g** was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) as a white solid (110.3 mg, 55%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 – 8.66 (m, 1H), 8.51 (d, *J* = 5.0 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.91 – 7.82 (m, 1H), 7.76 (dd, *J* = 13.8, 7.5 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.0, 157.9, 157.4, 149.4, 145.9, 139.1, 137.8, 137.1, 131.5, 129.1, 128.8, 127.0, 126.1, 122.2, 121.5, 120.7, 119.1, 118.7. GC-MS (EI) *m/z*: 401.

4. NMR spectra



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7.230
7.208
7.163
7.155
7.150
7.108
7.035
7.032
7.015
7.012
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2.293
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OAc
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1.09
1.03
1.05
1.06
1.04
1.03
3.08
3.11
10.0
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9.0
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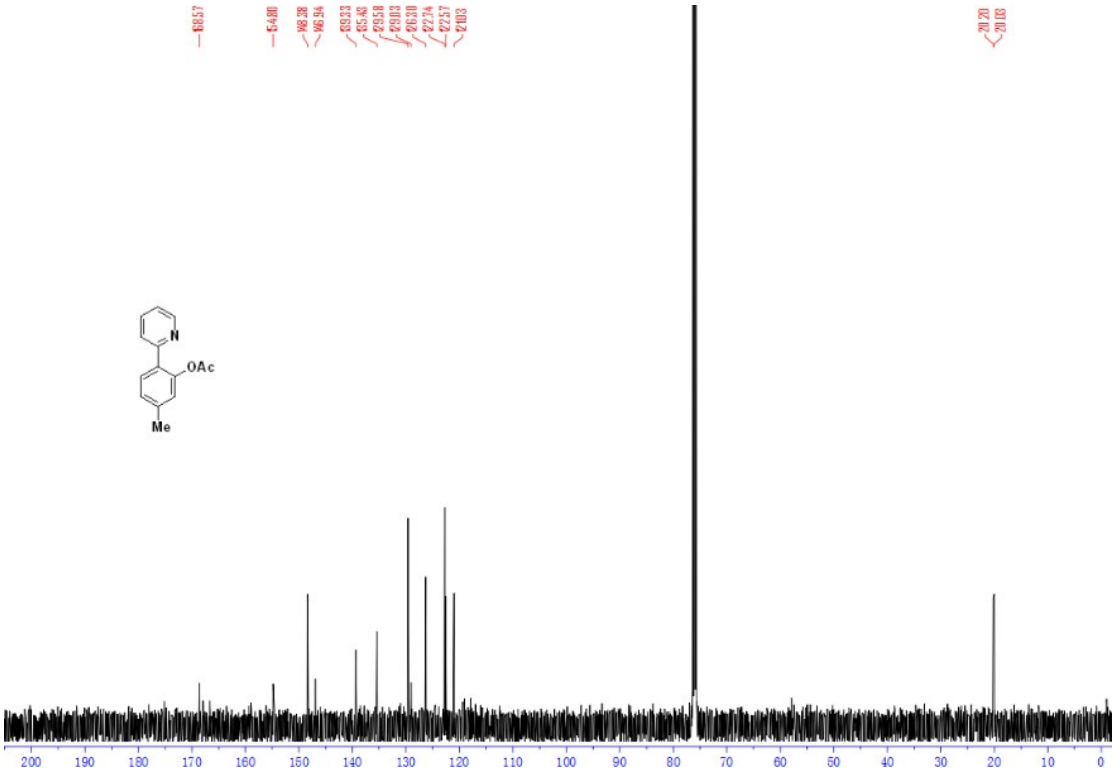
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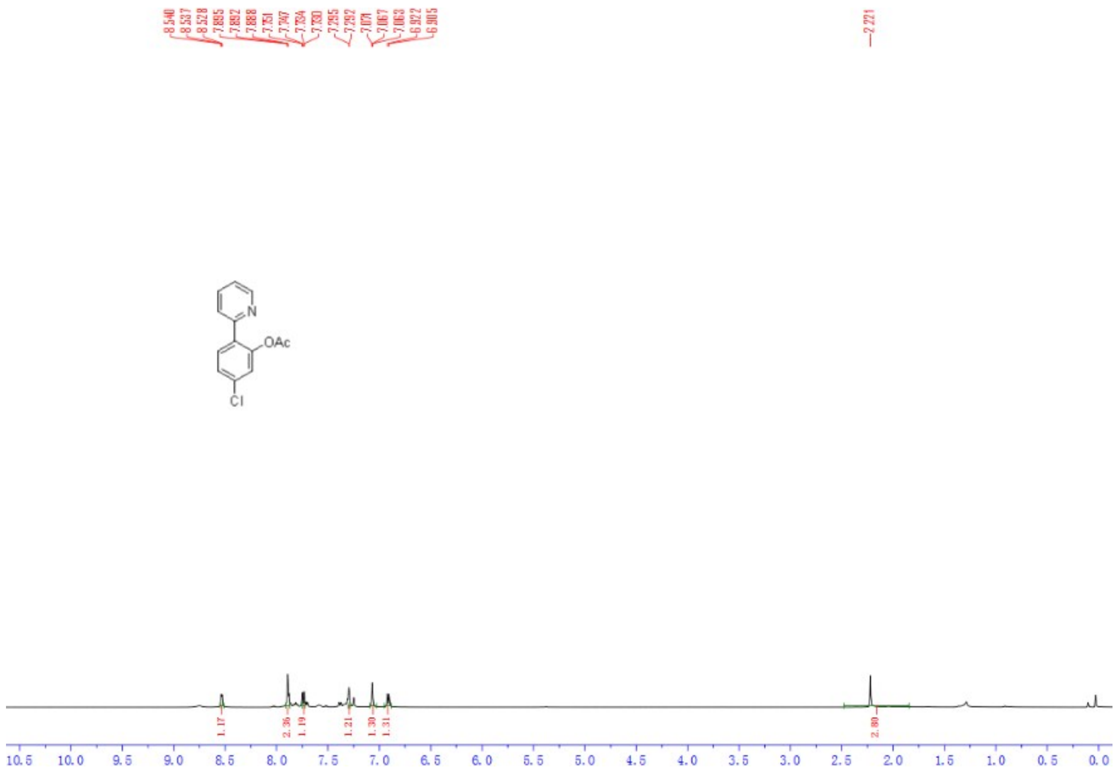
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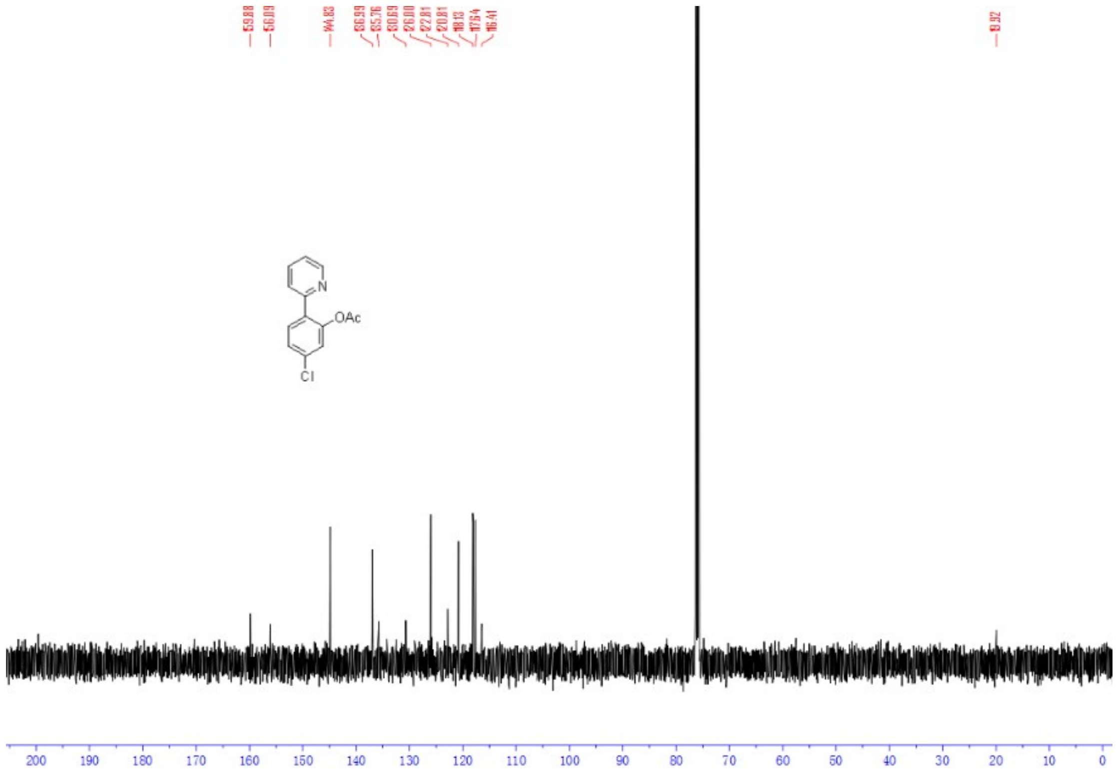
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Cl
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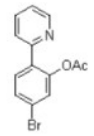
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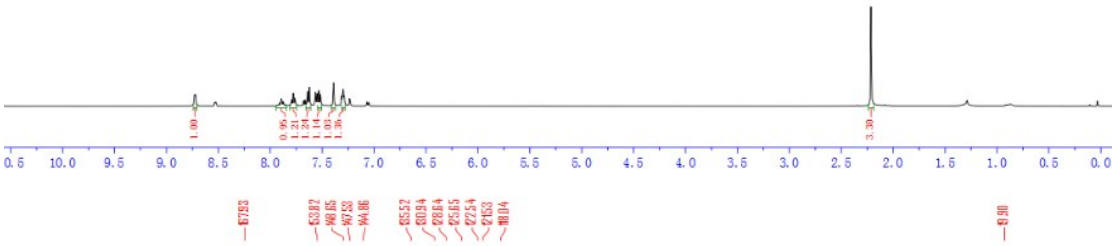
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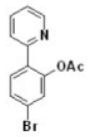
1.36
3.39
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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OAc
Br

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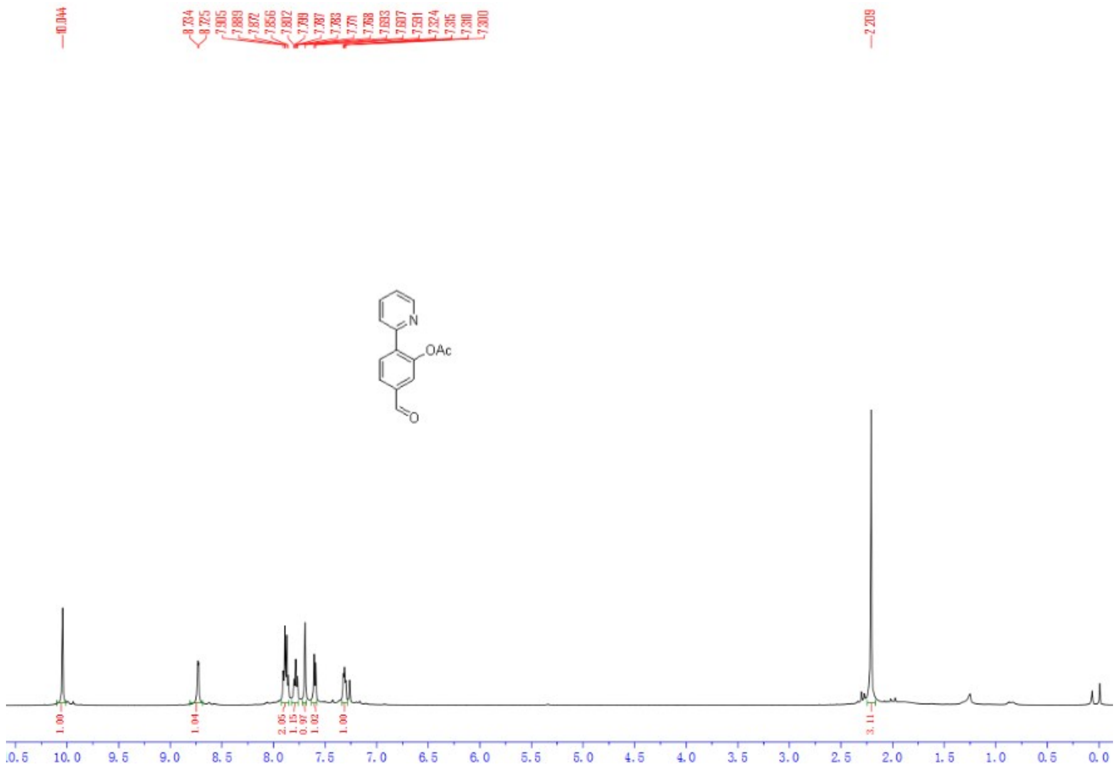

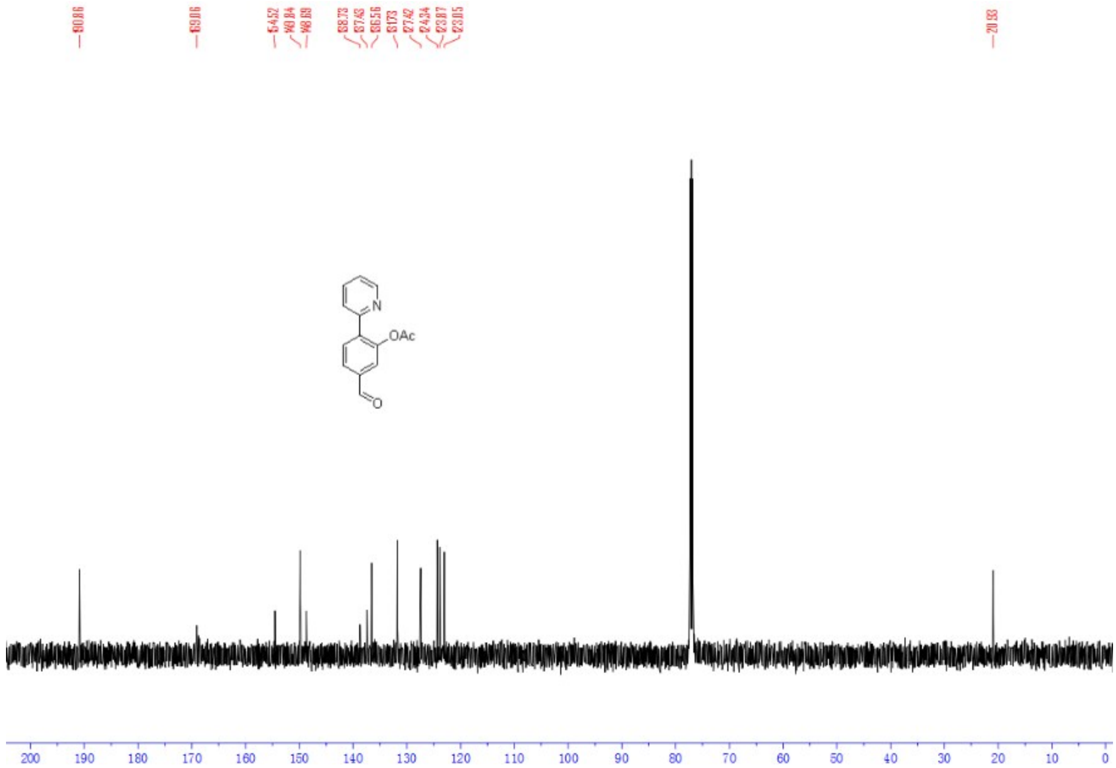

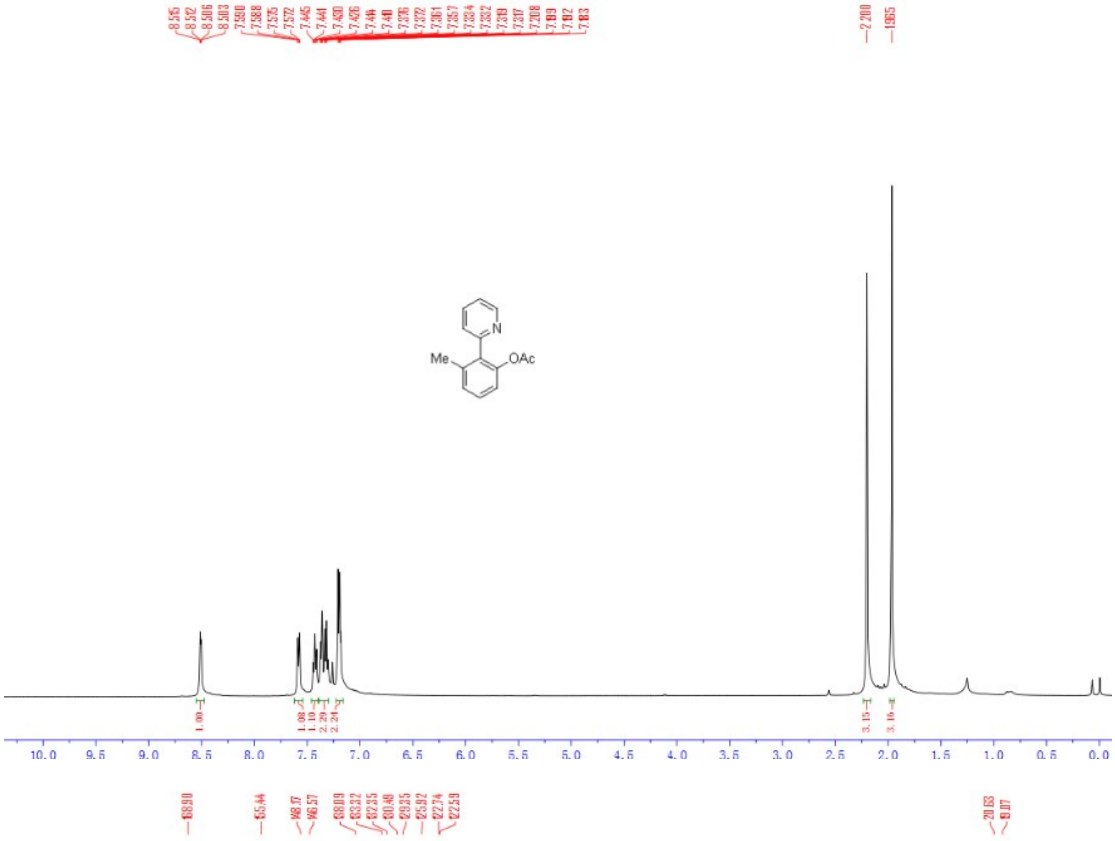
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7.308
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7.192
7.183
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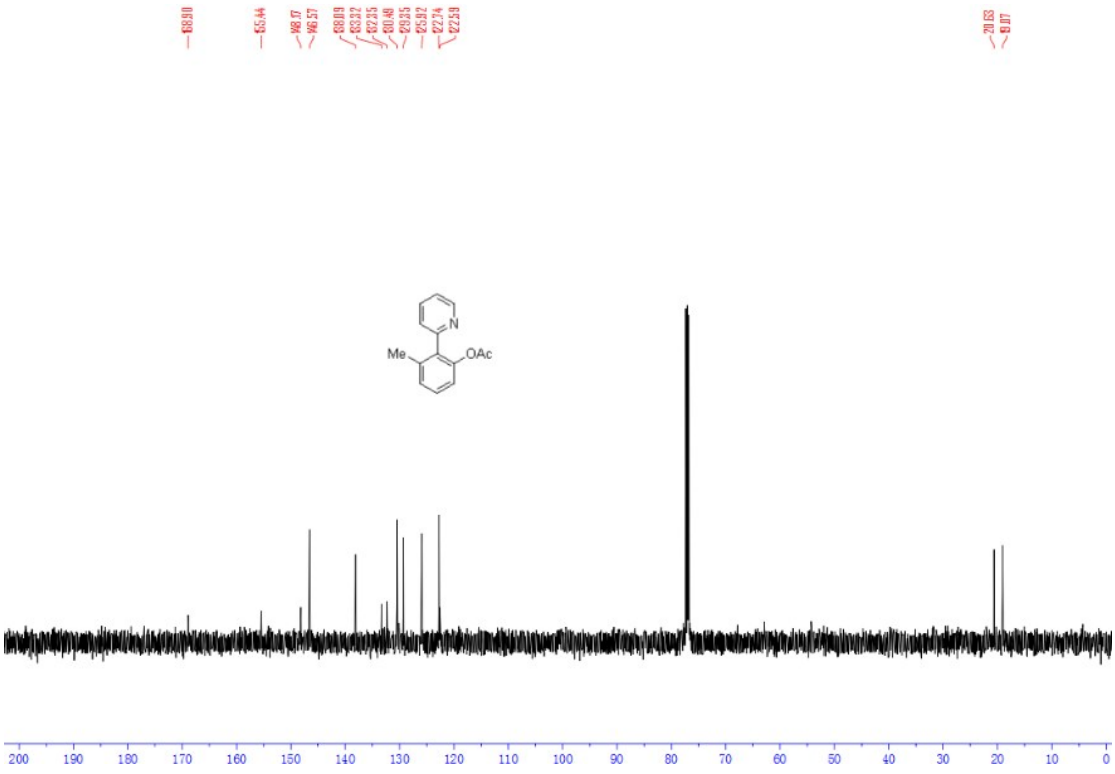
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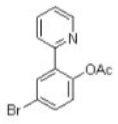
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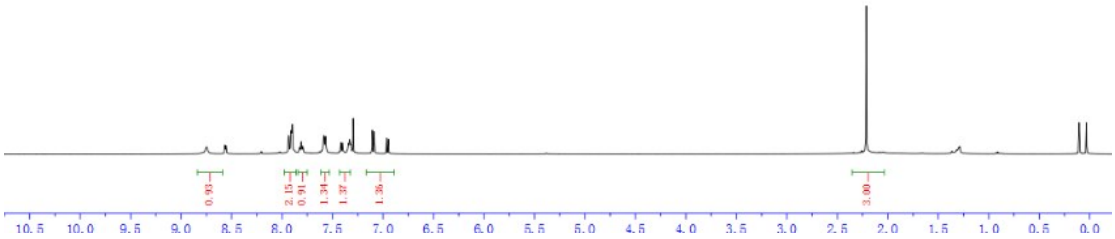
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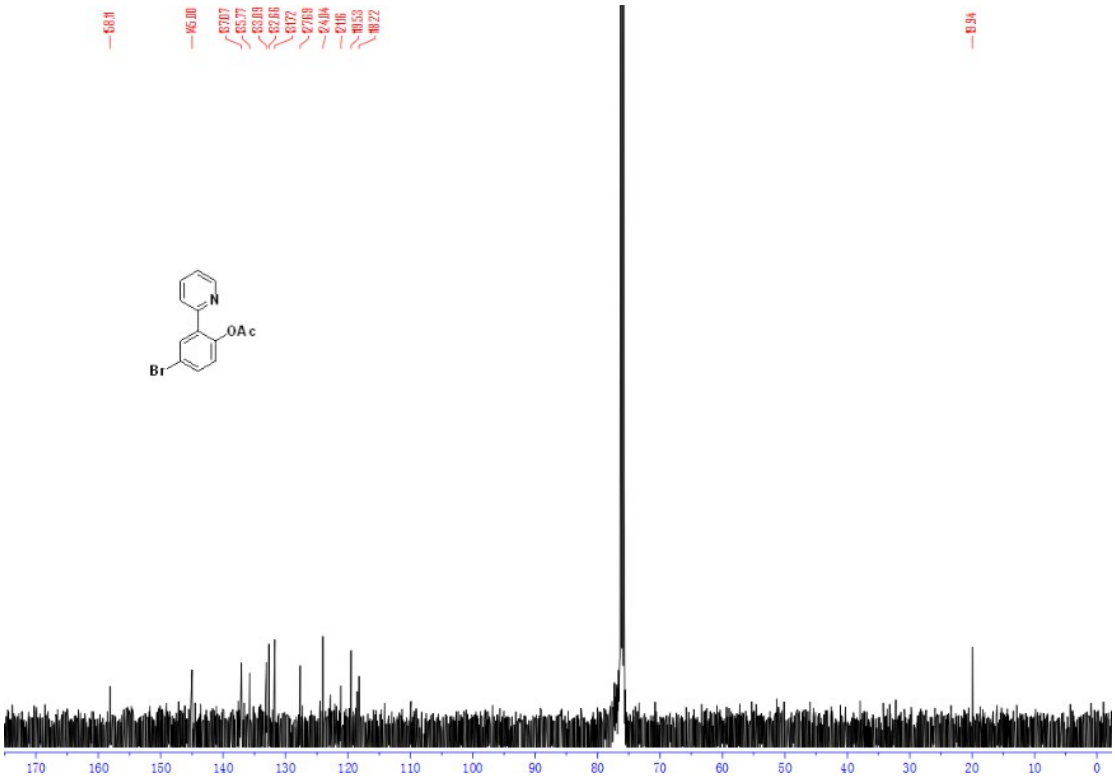
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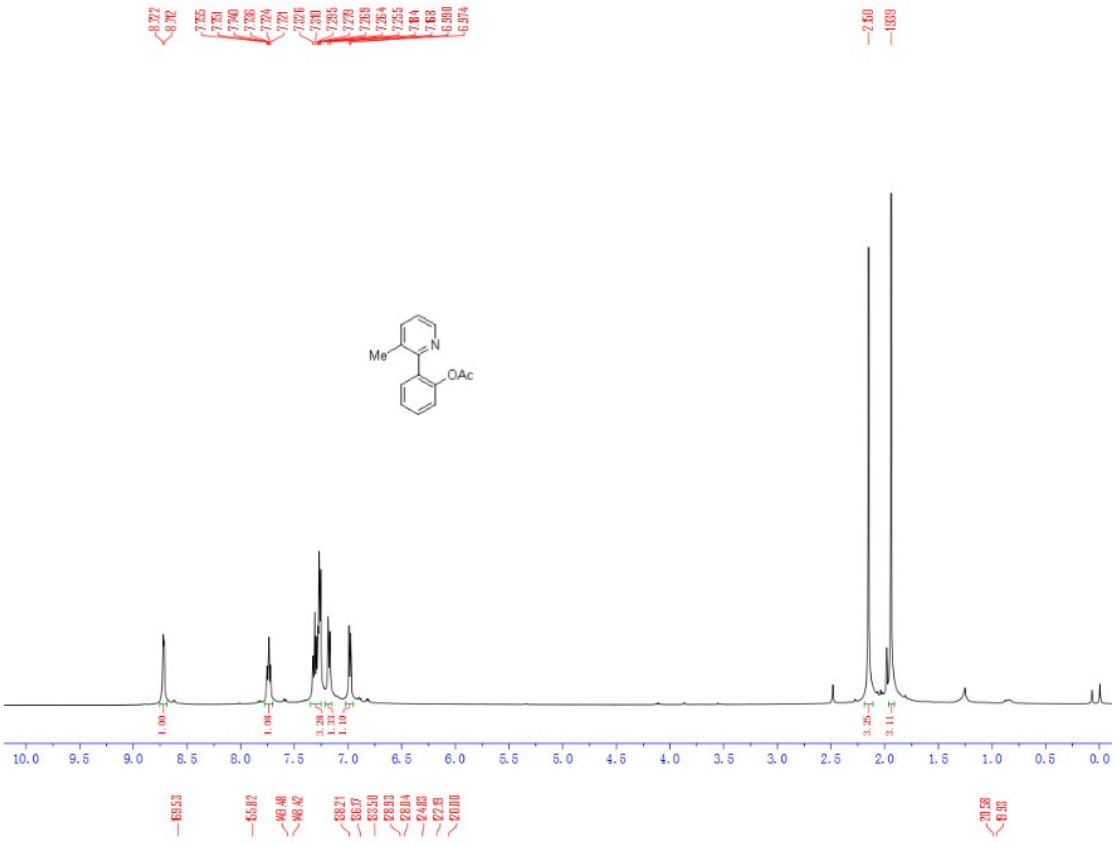
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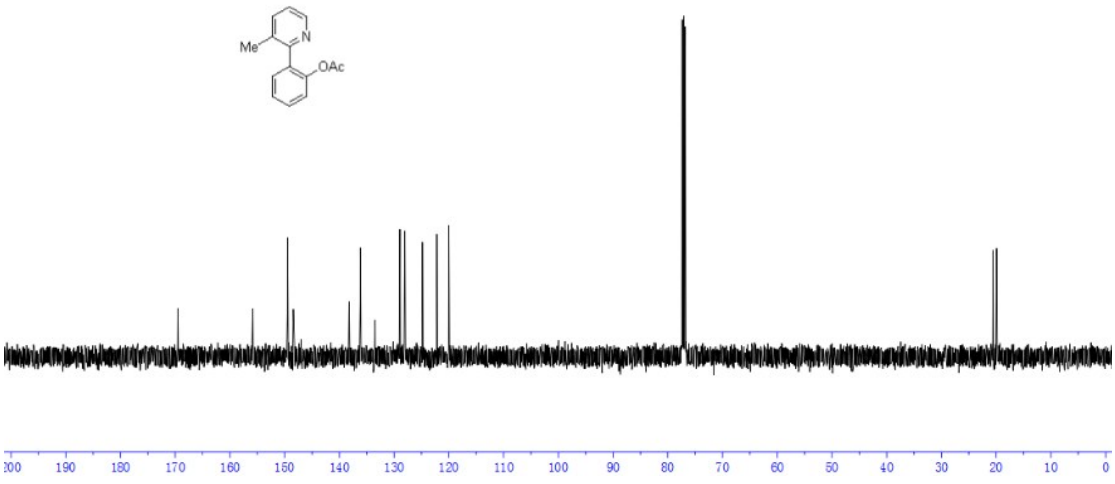
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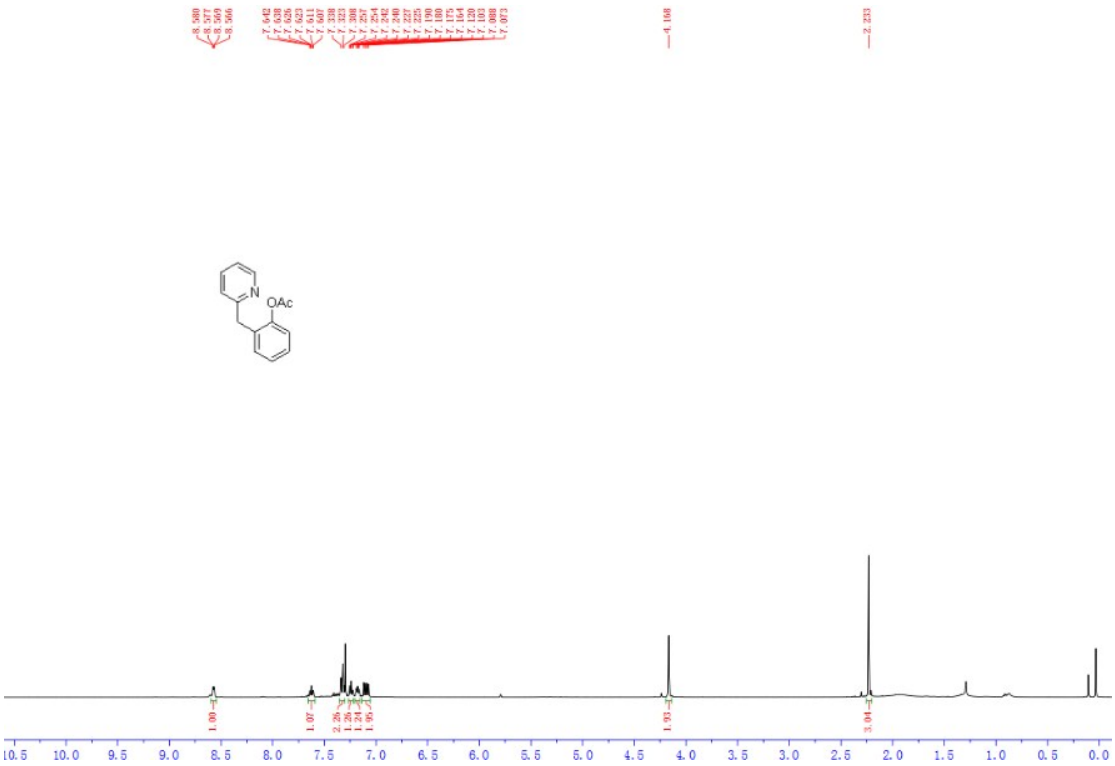
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2.233
OAc
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2.26
1.26
1.24
1.05
1.93
3.04
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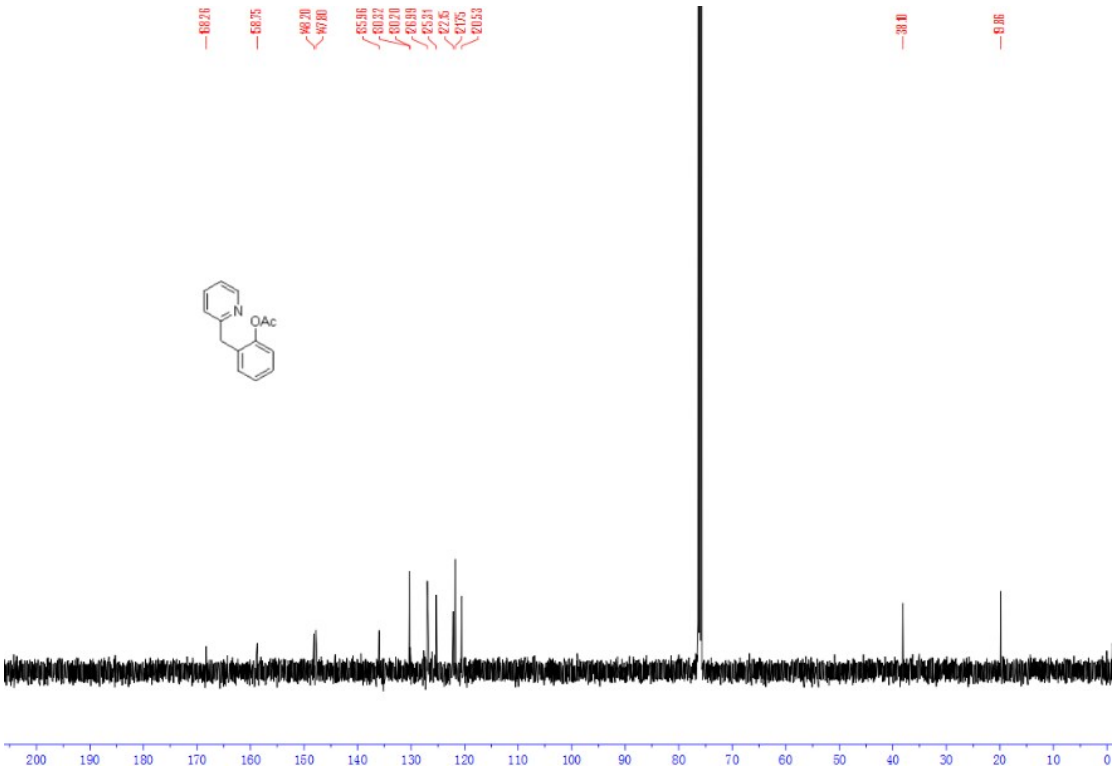
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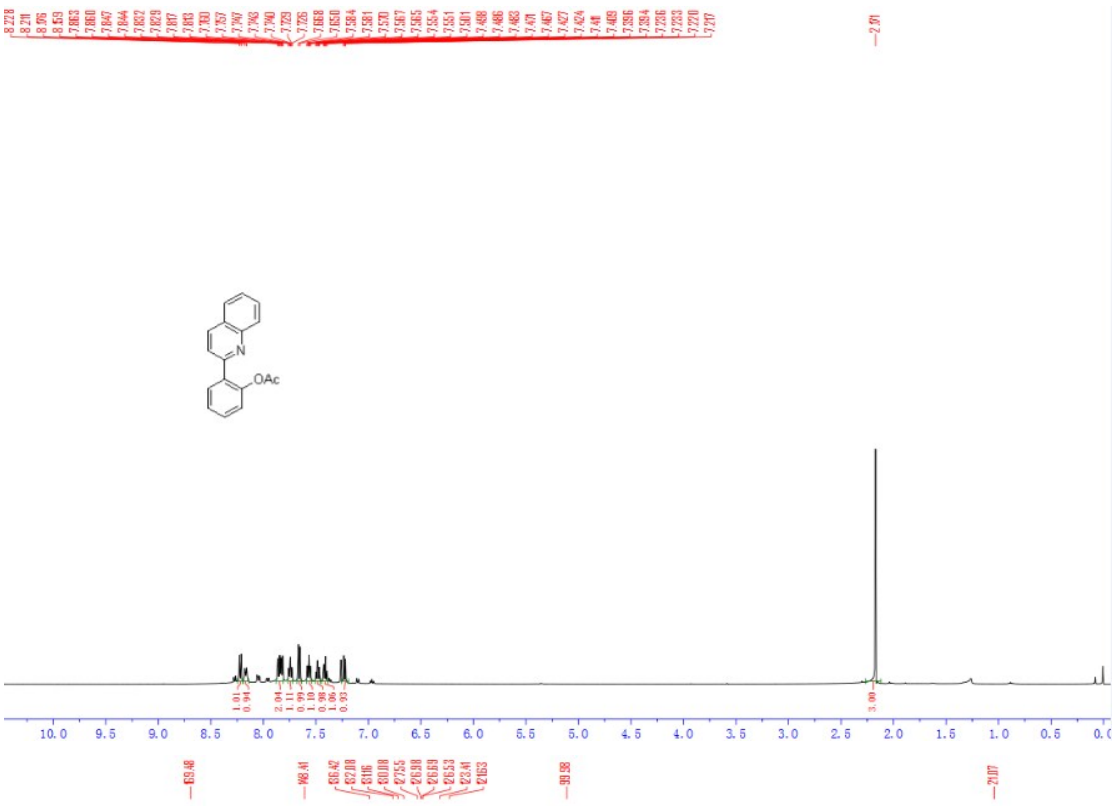
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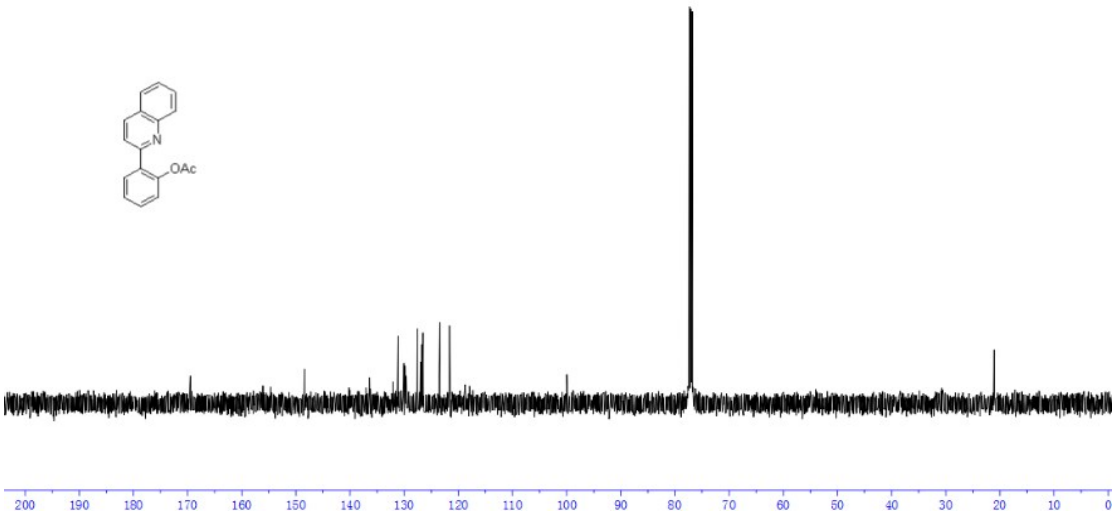
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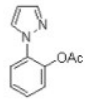
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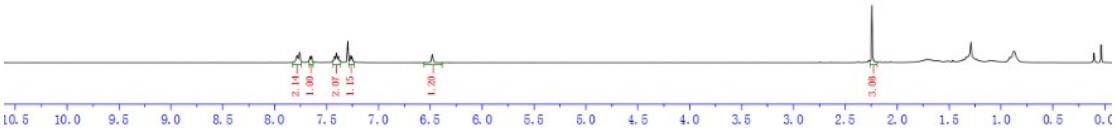
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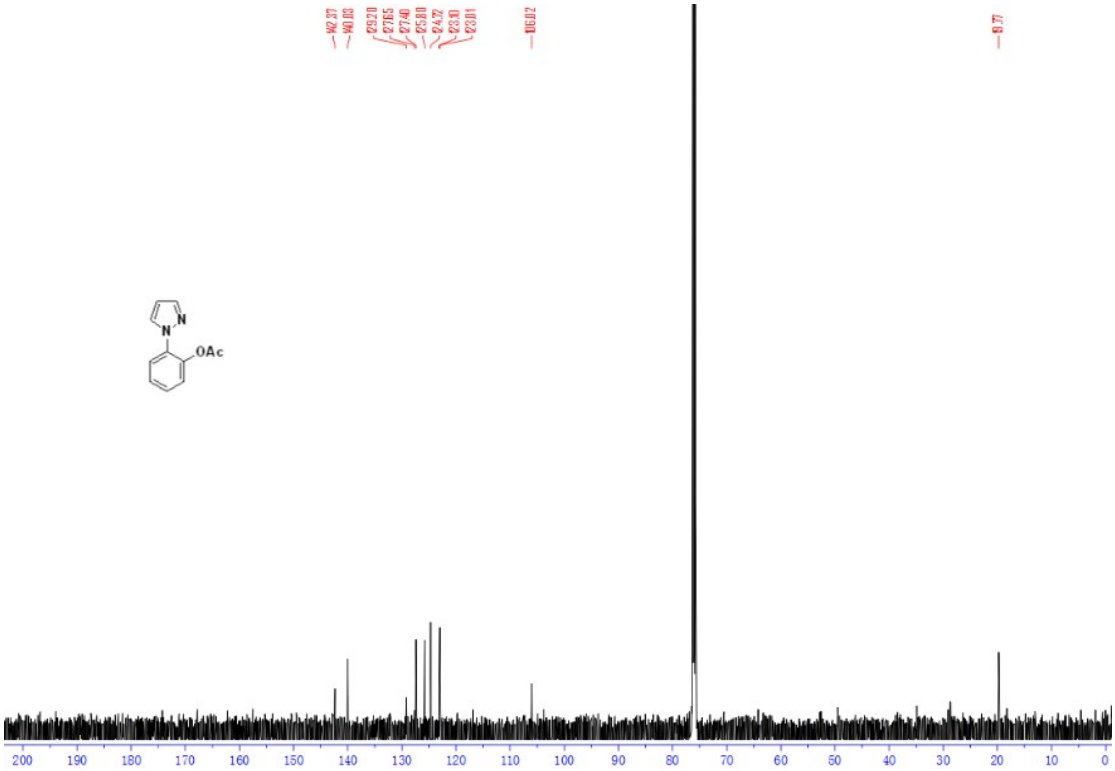
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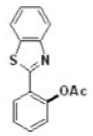
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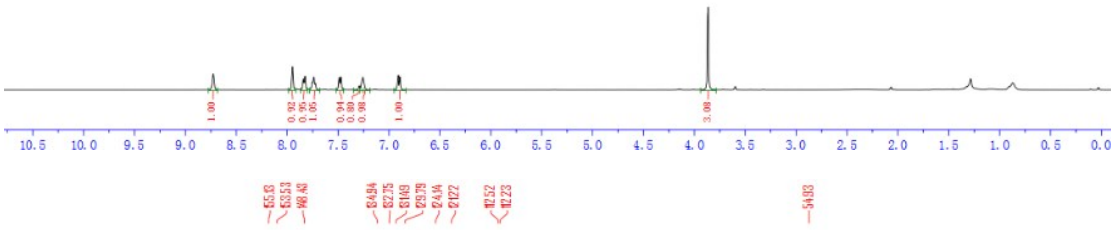
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1.00
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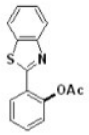
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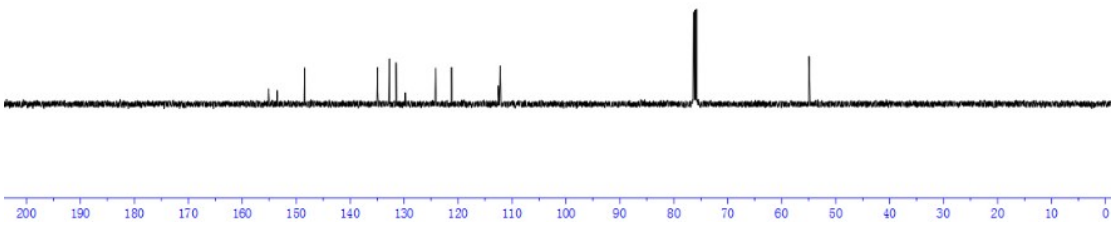
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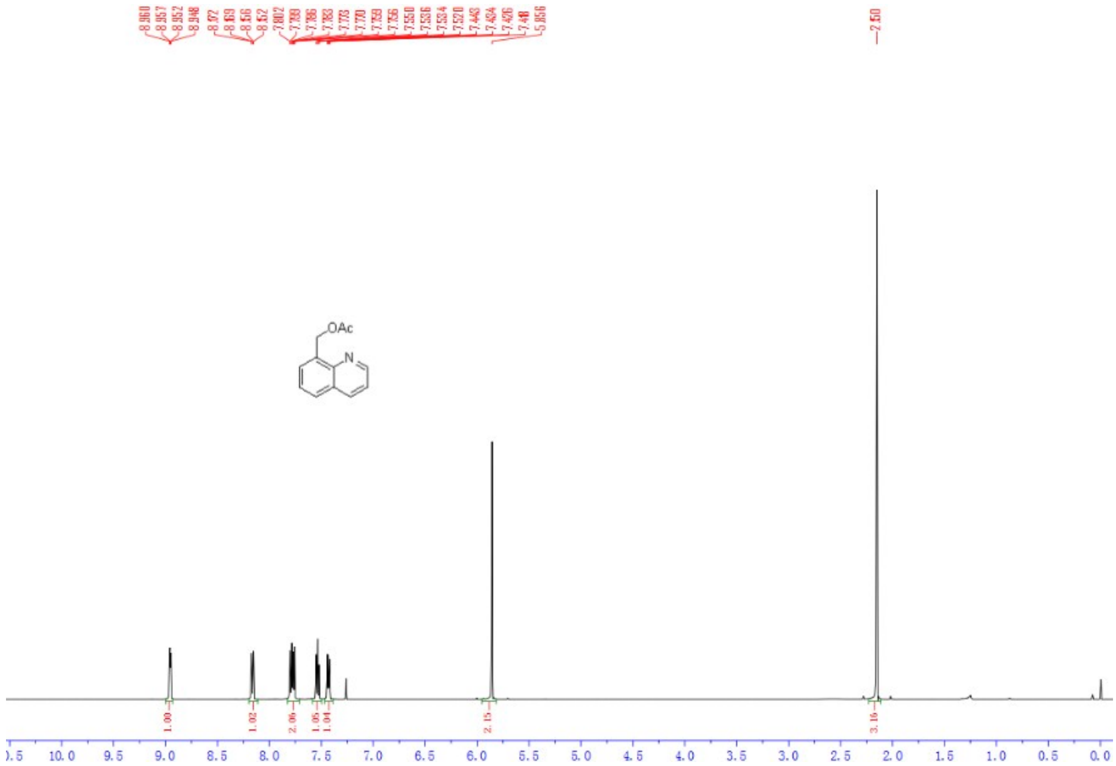

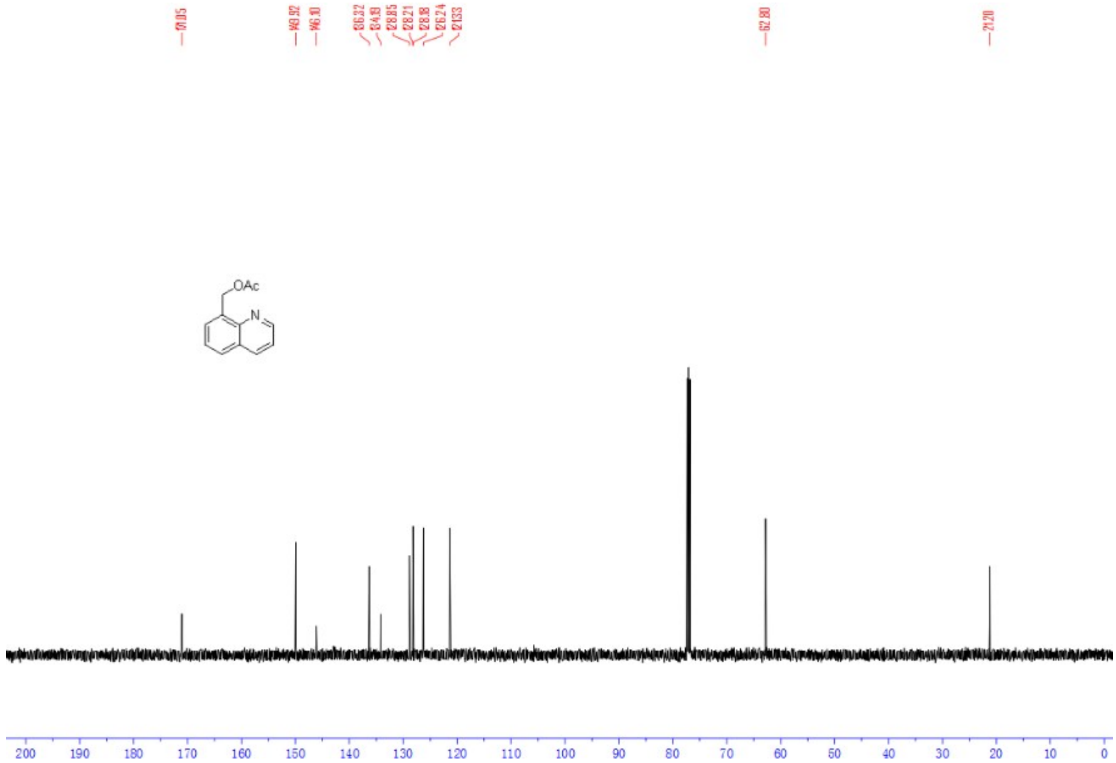

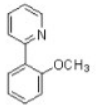

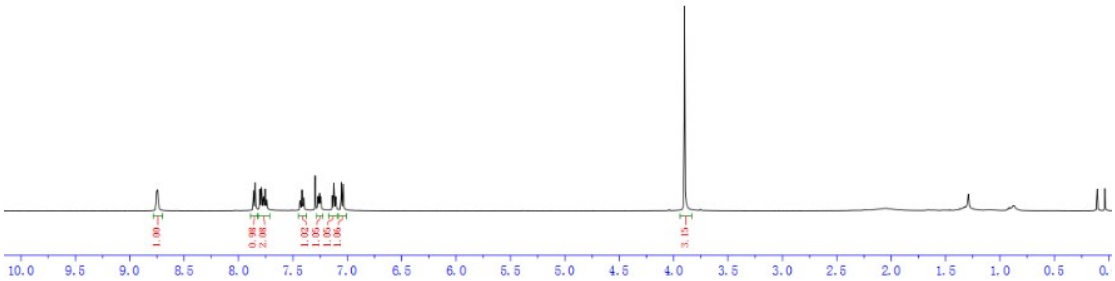

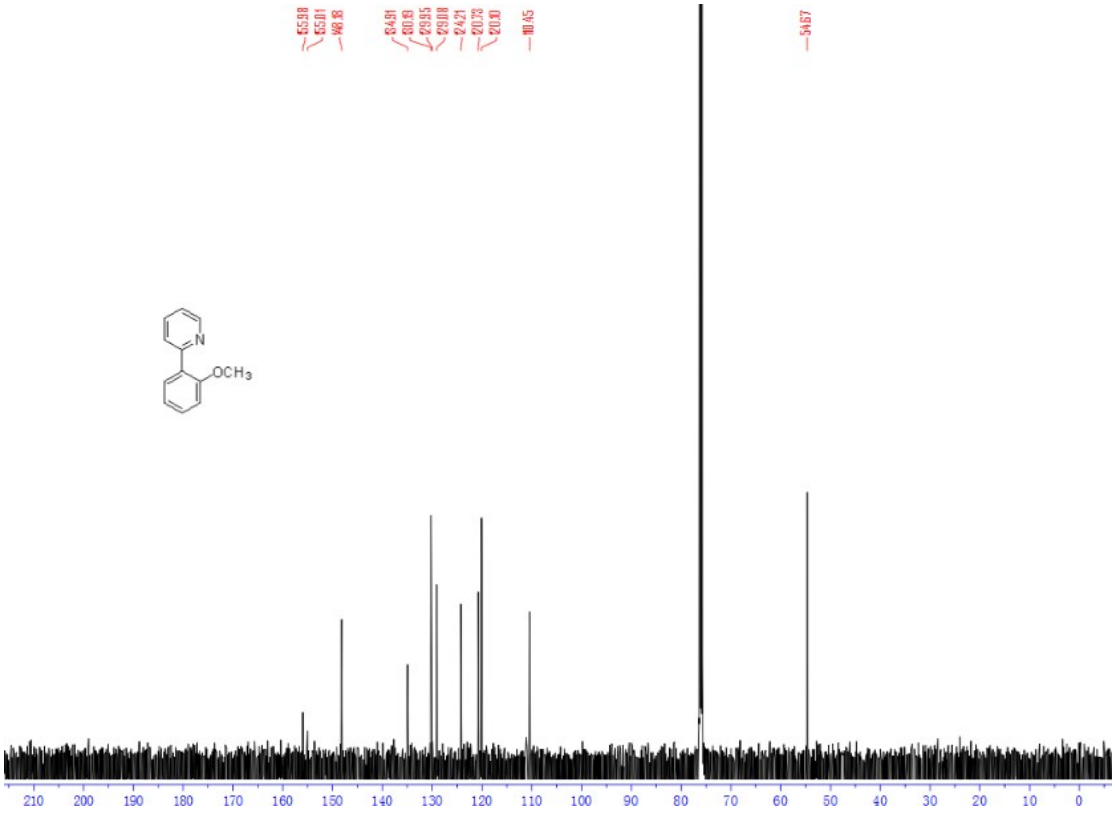


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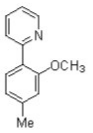
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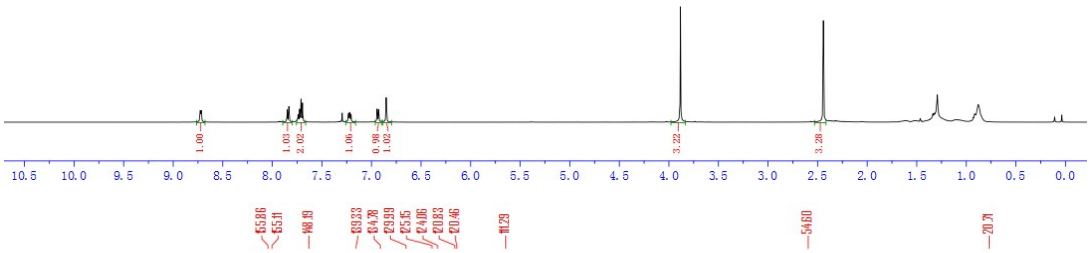
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3.0
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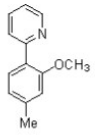
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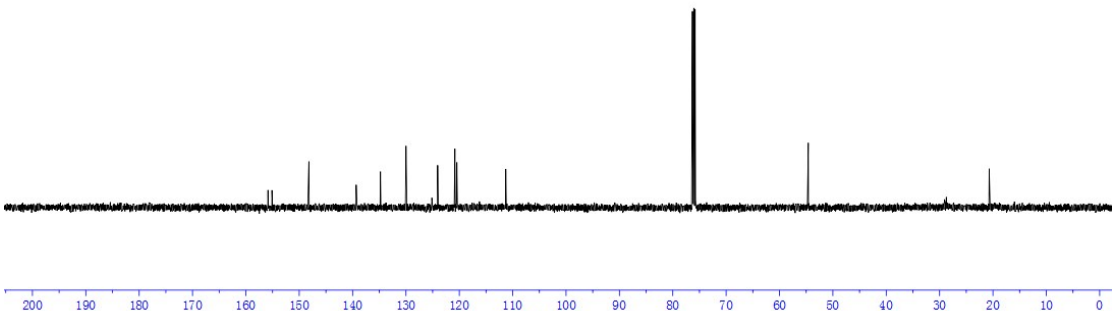
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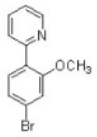
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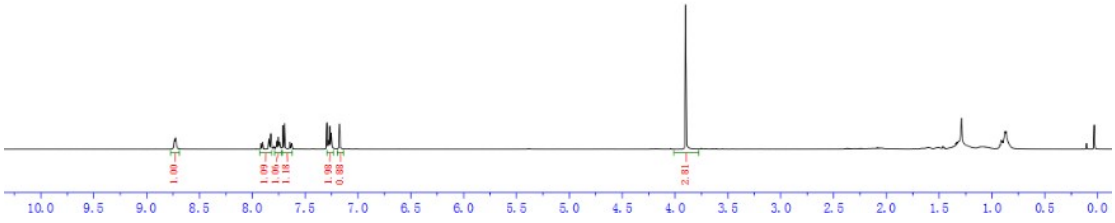
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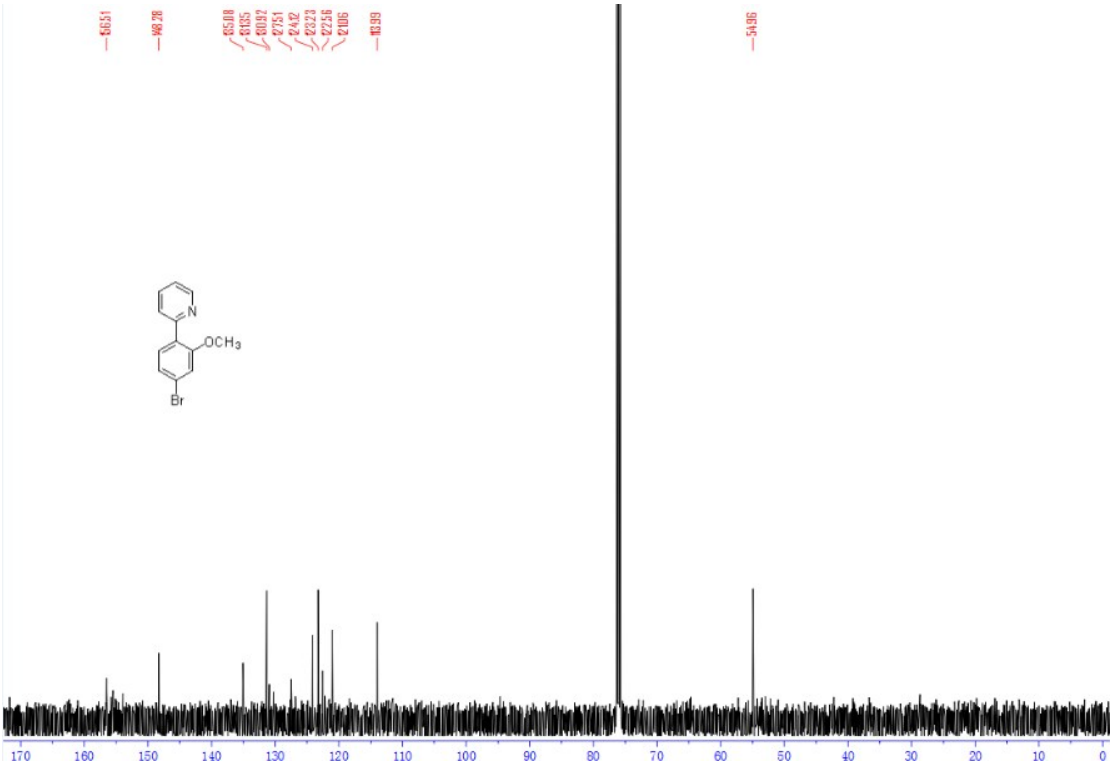
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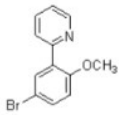
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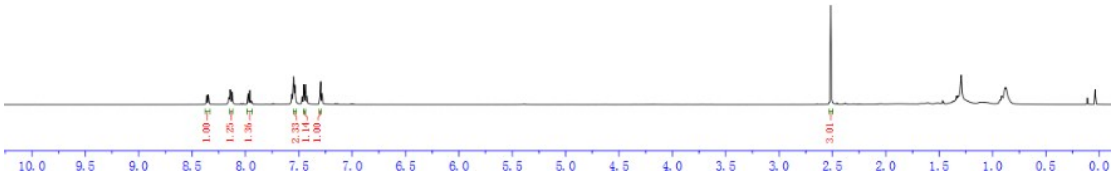
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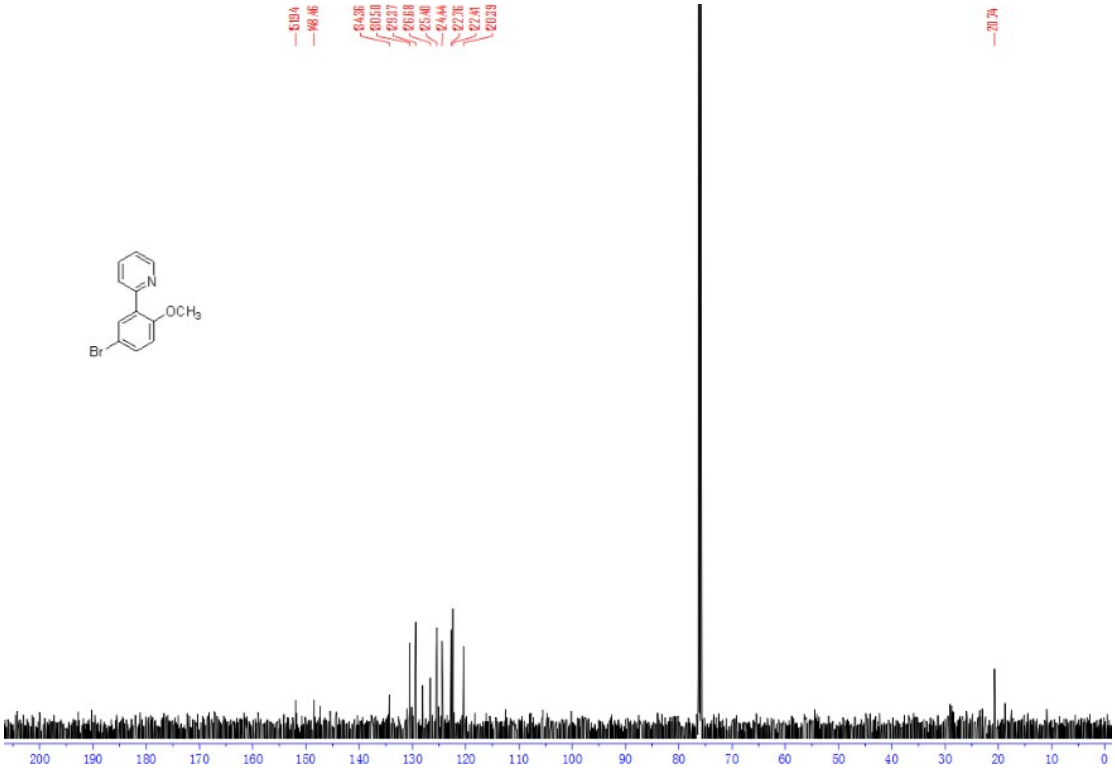
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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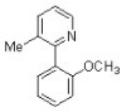
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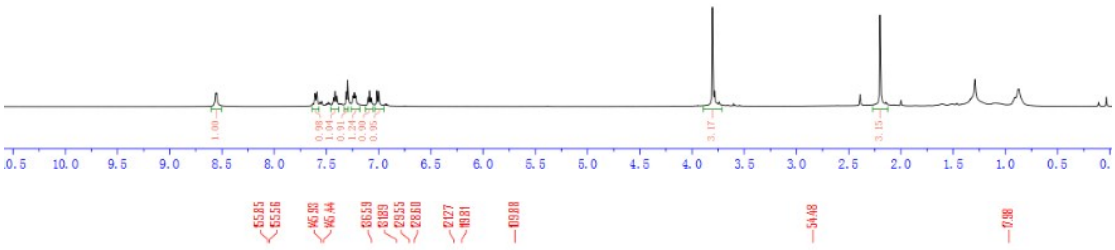

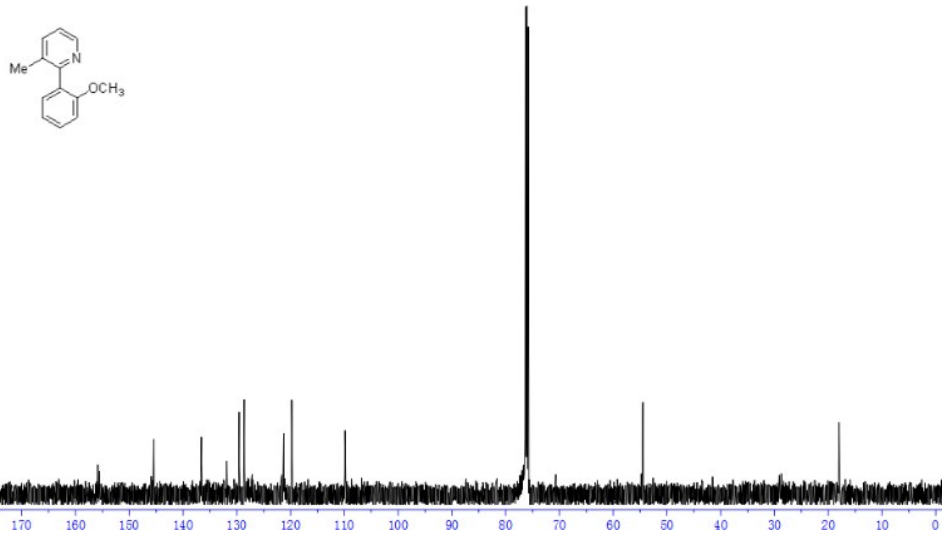
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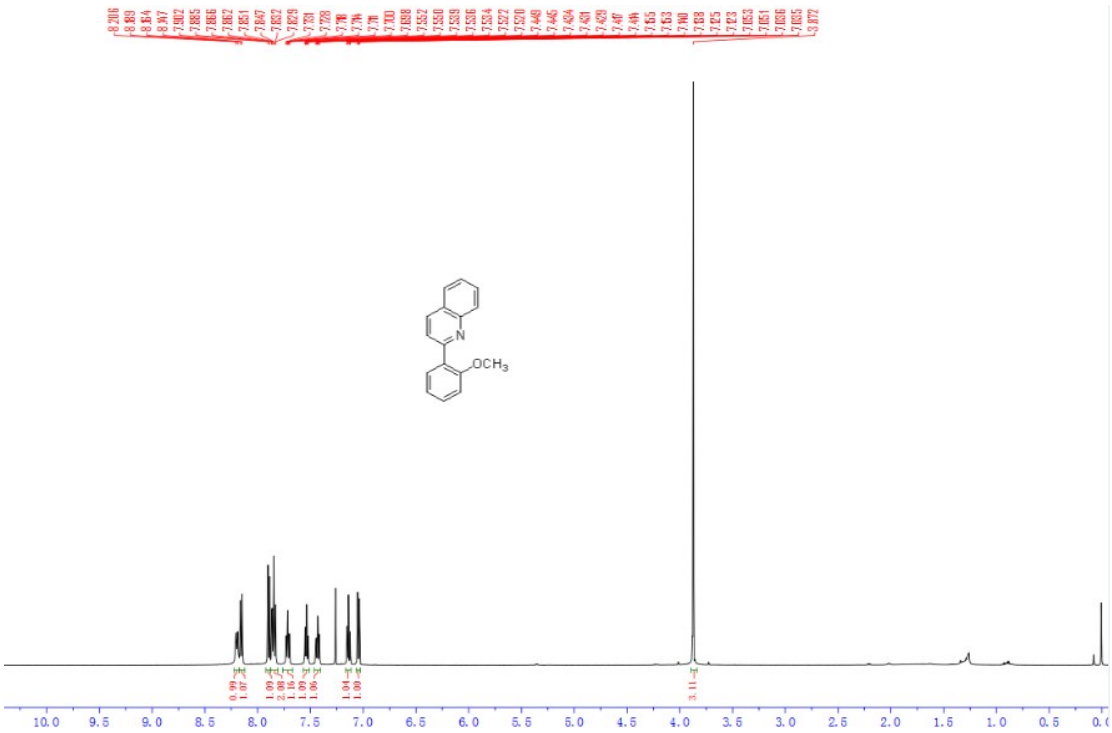
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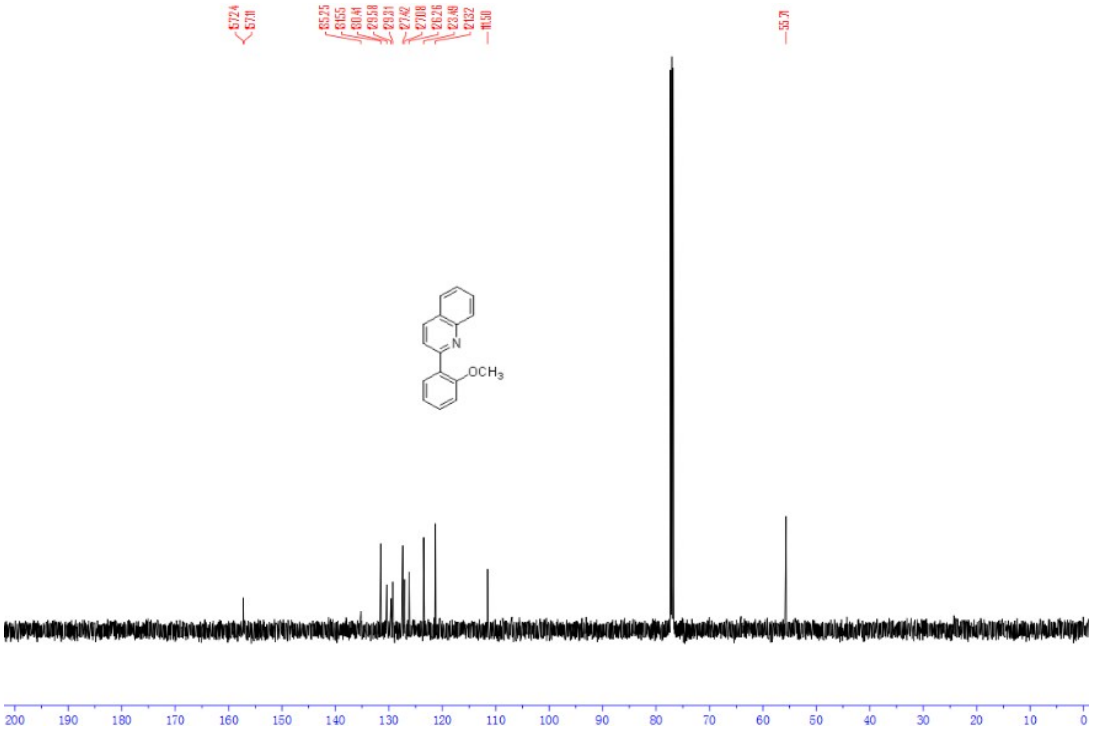
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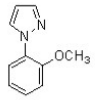
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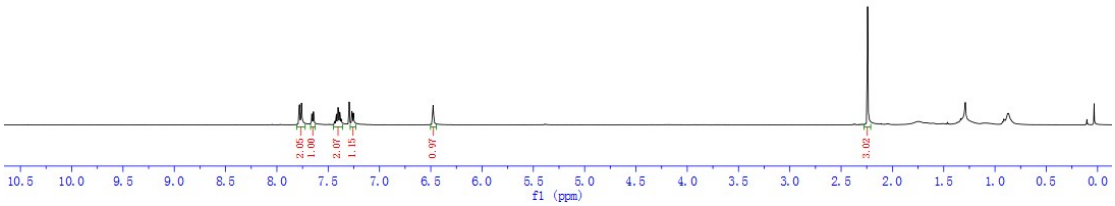
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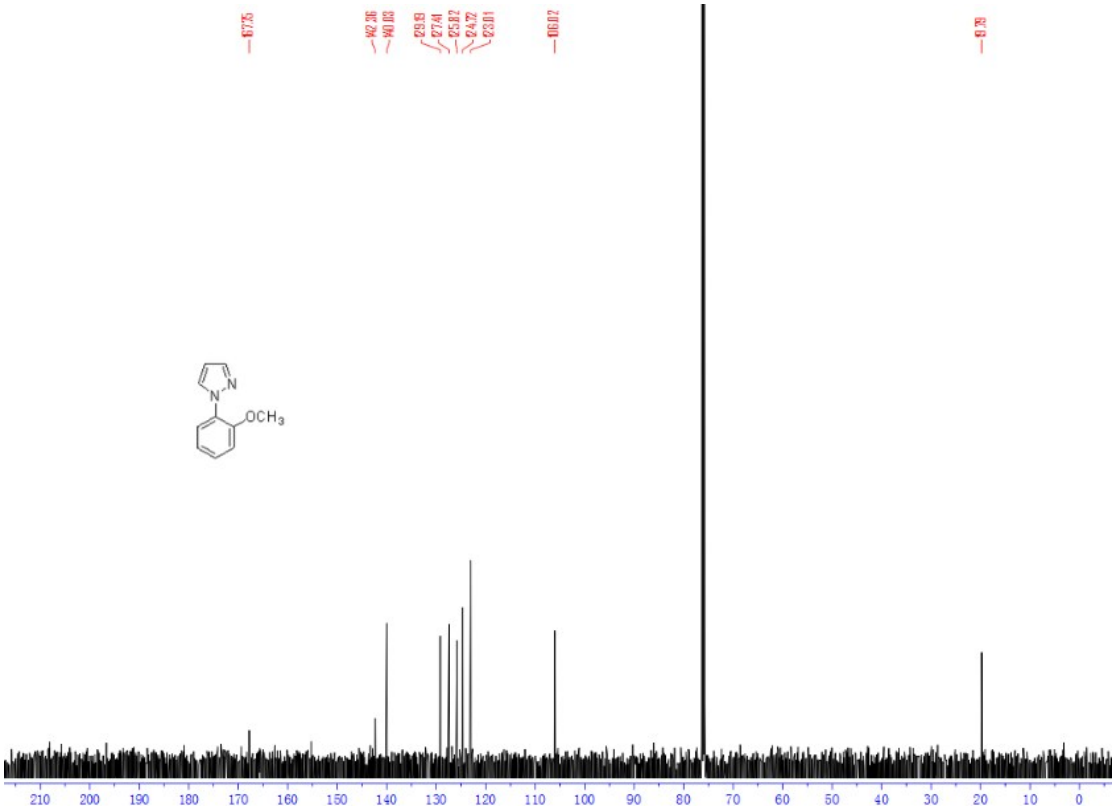
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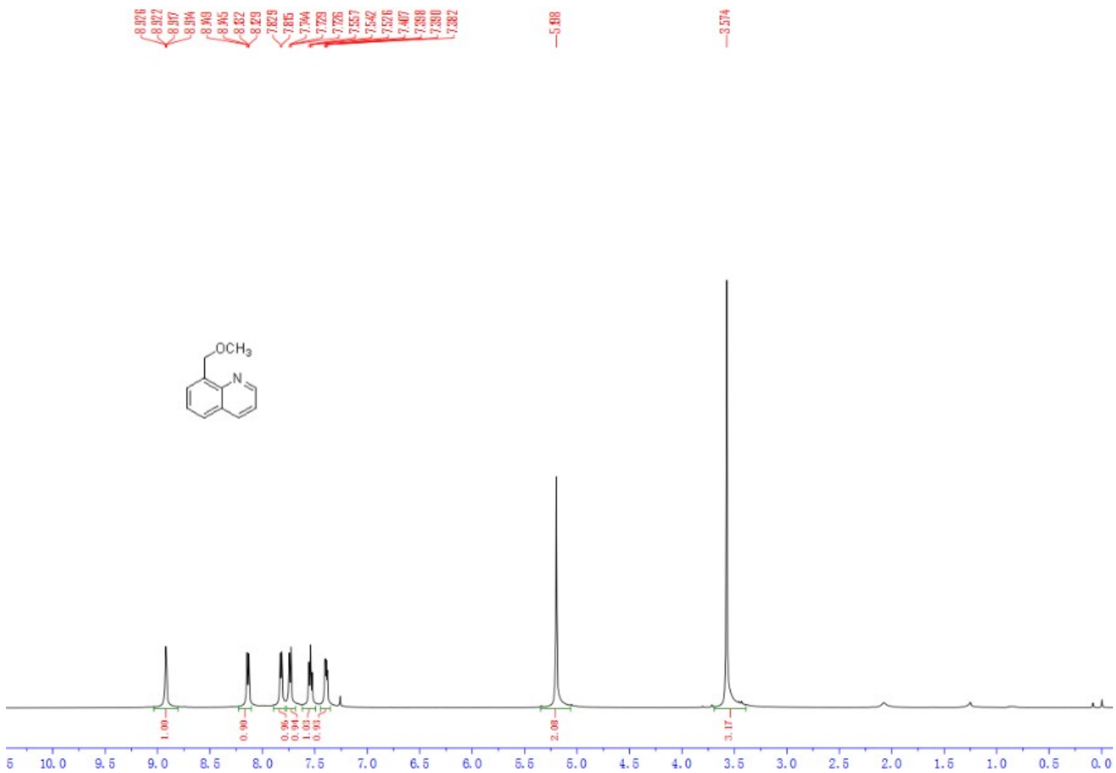

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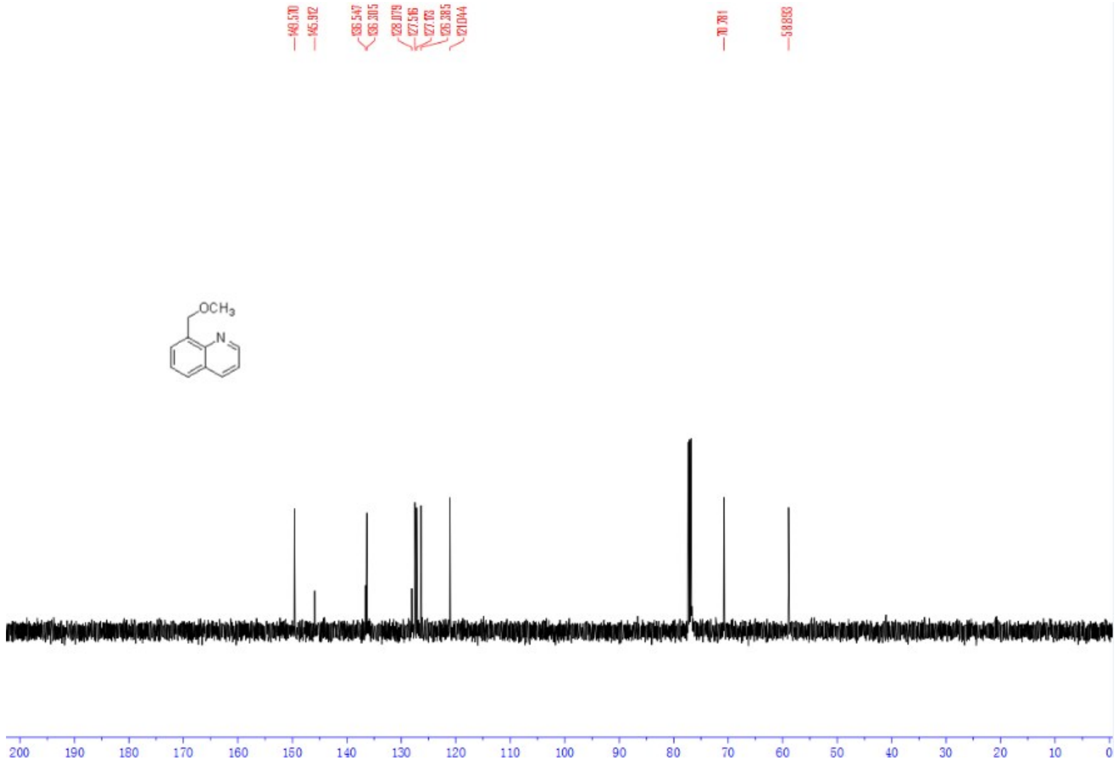

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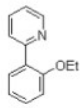
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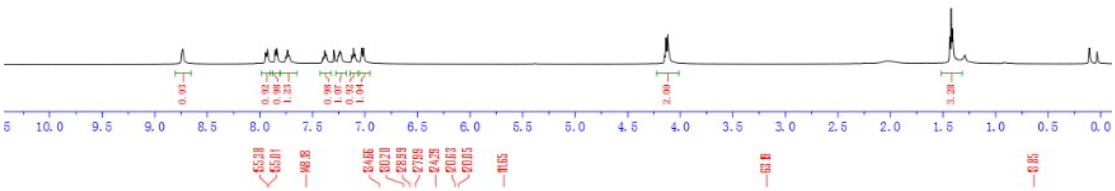

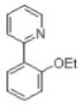
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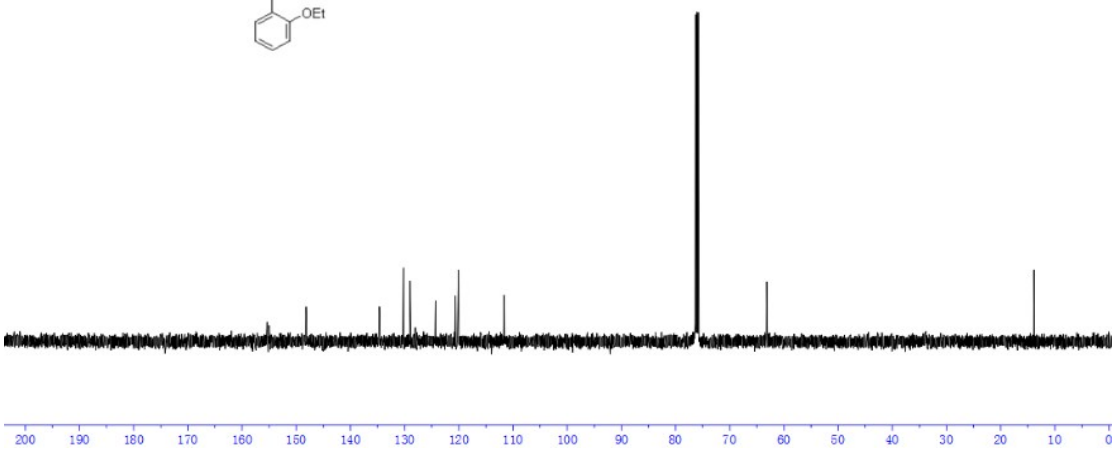

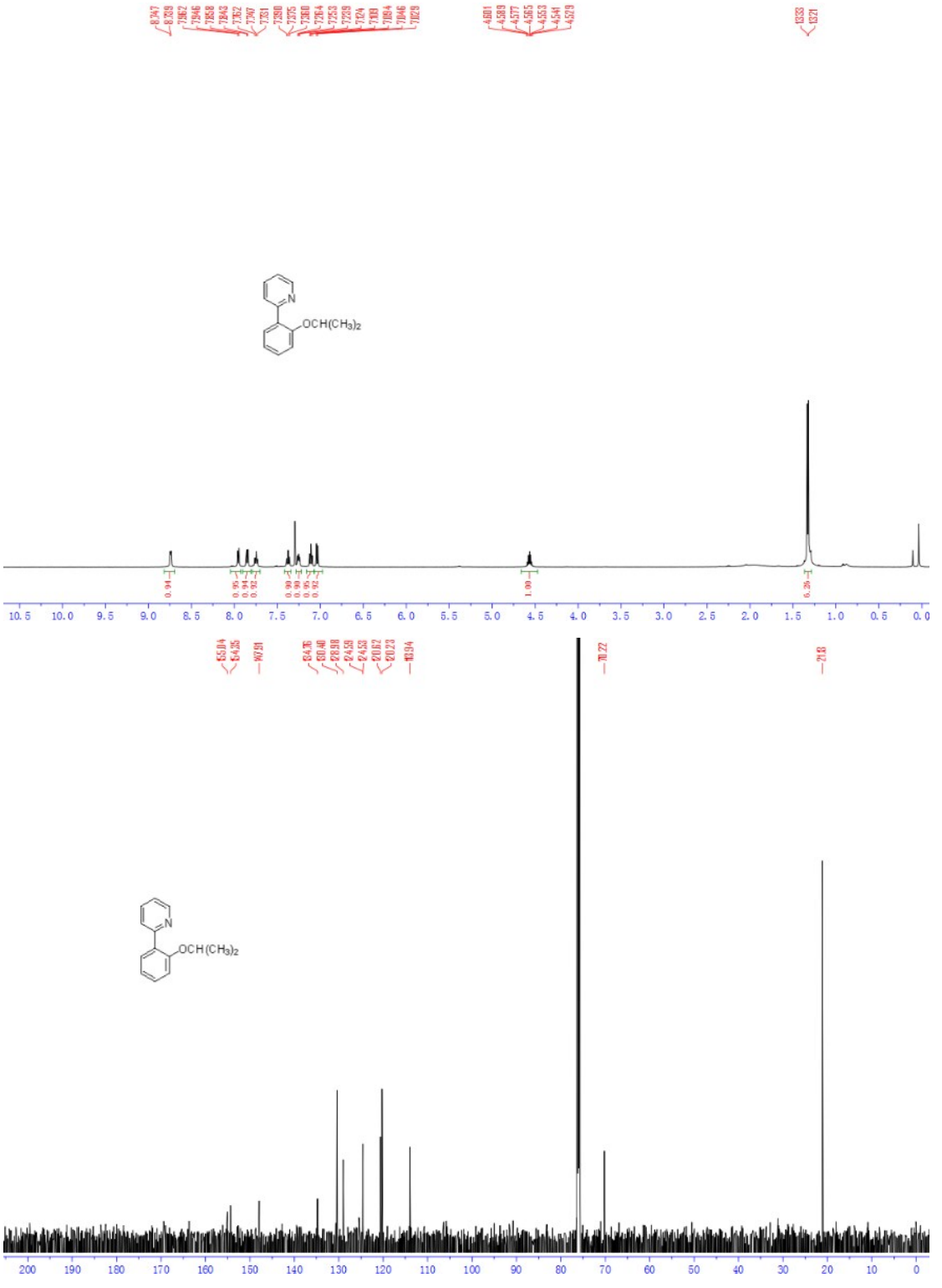
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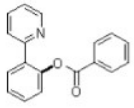

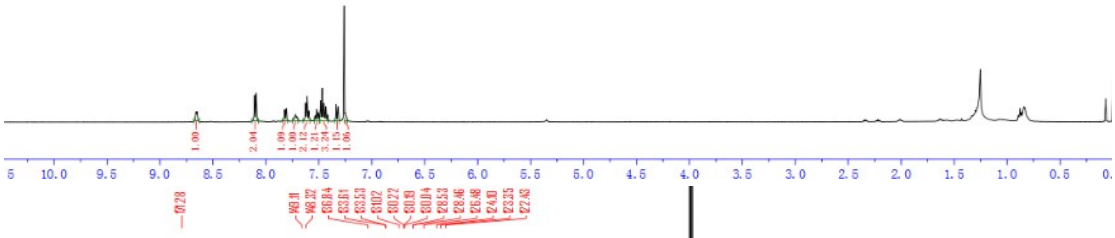

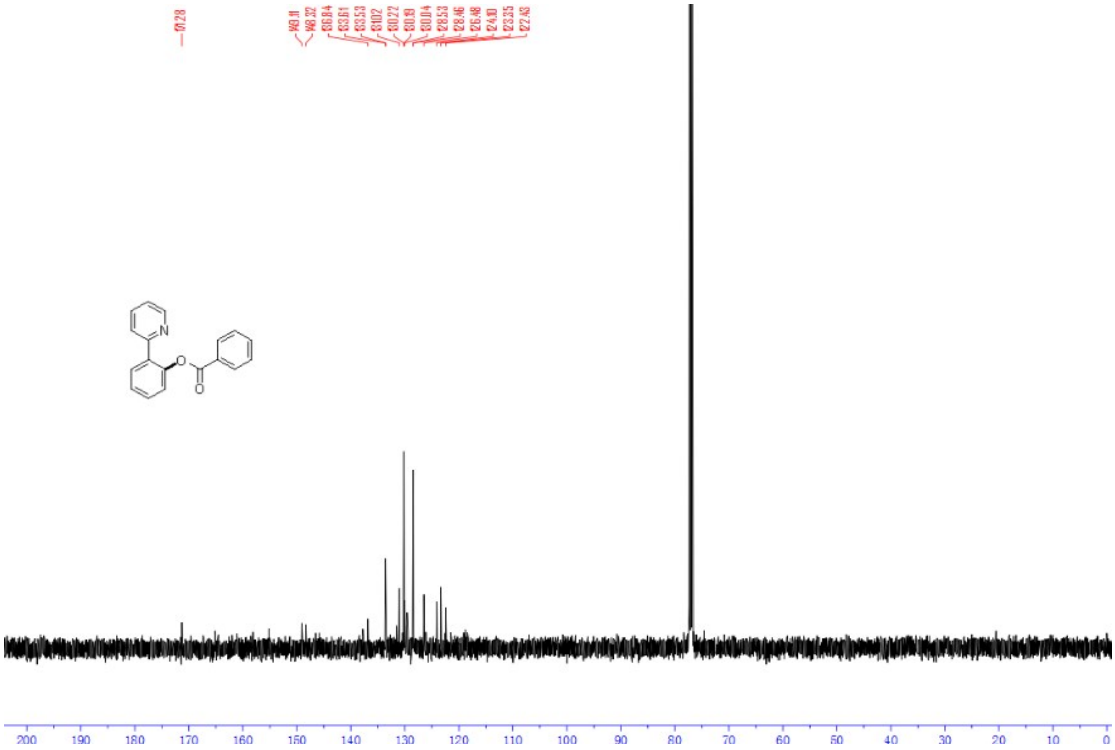

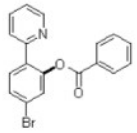

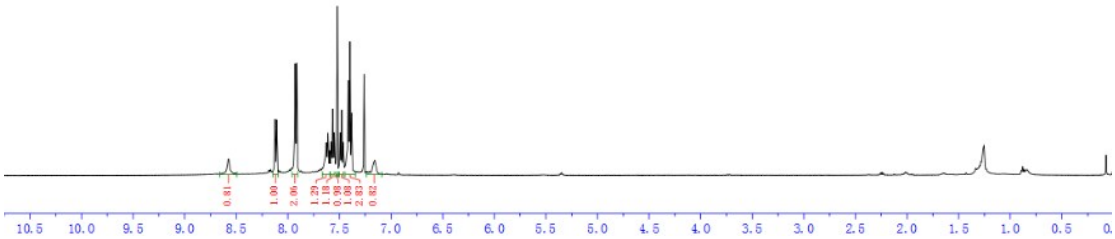

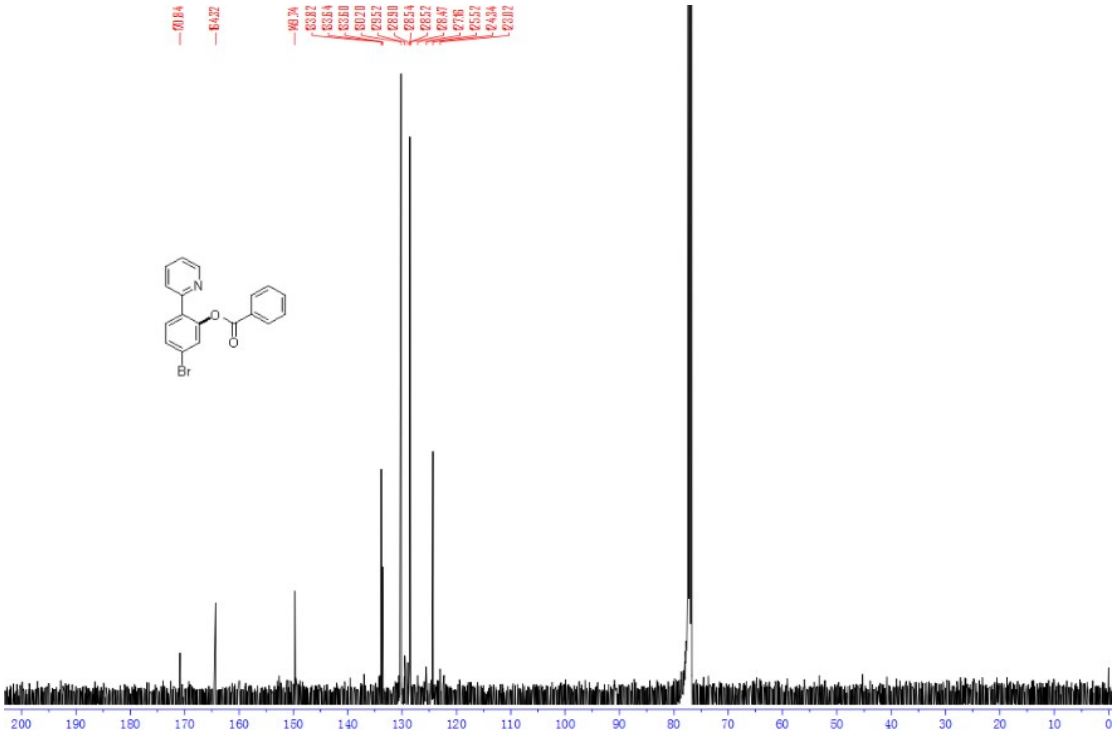

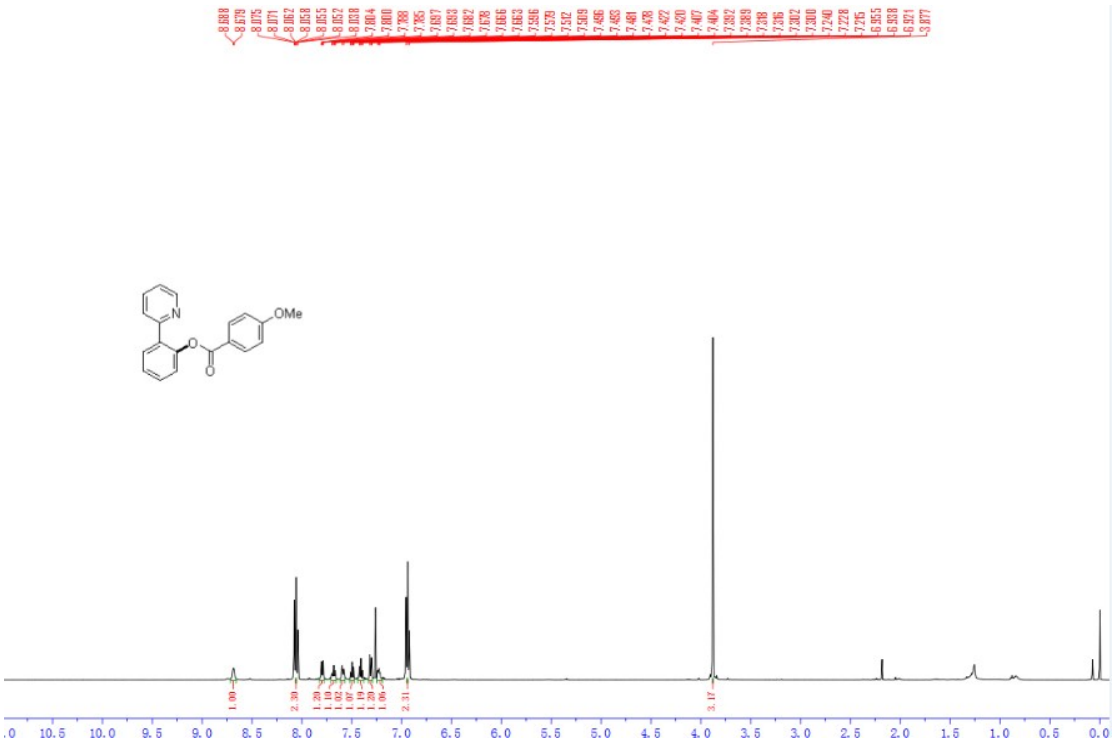
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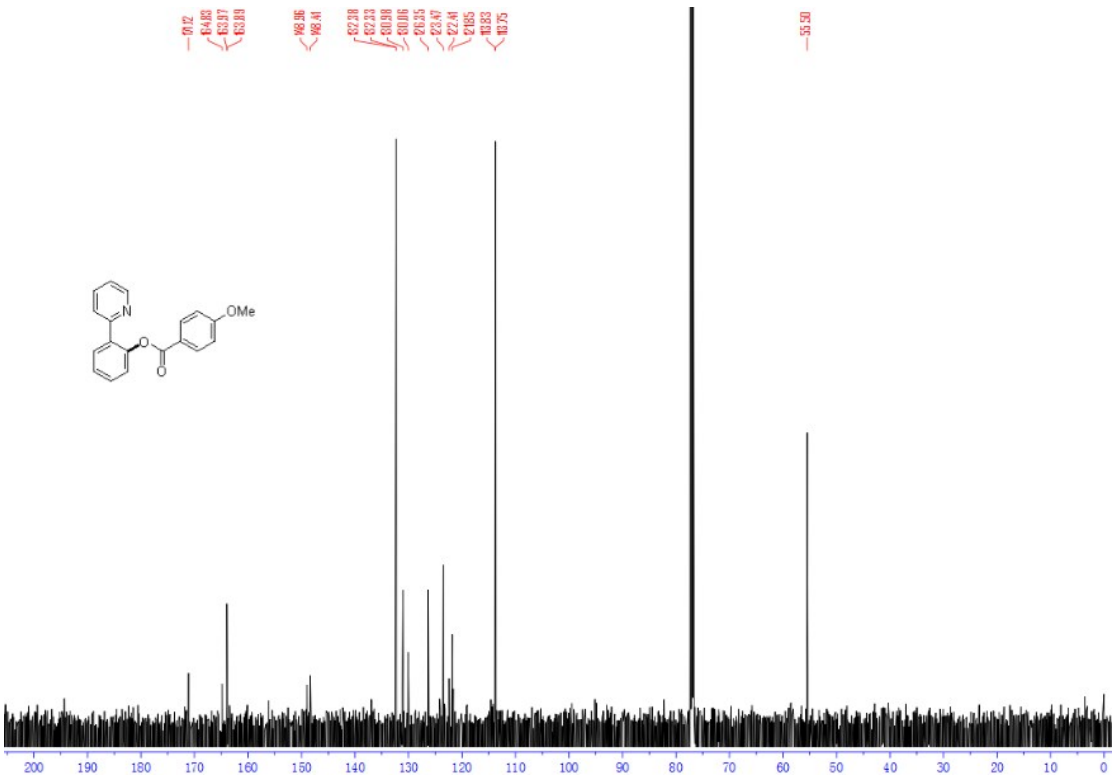
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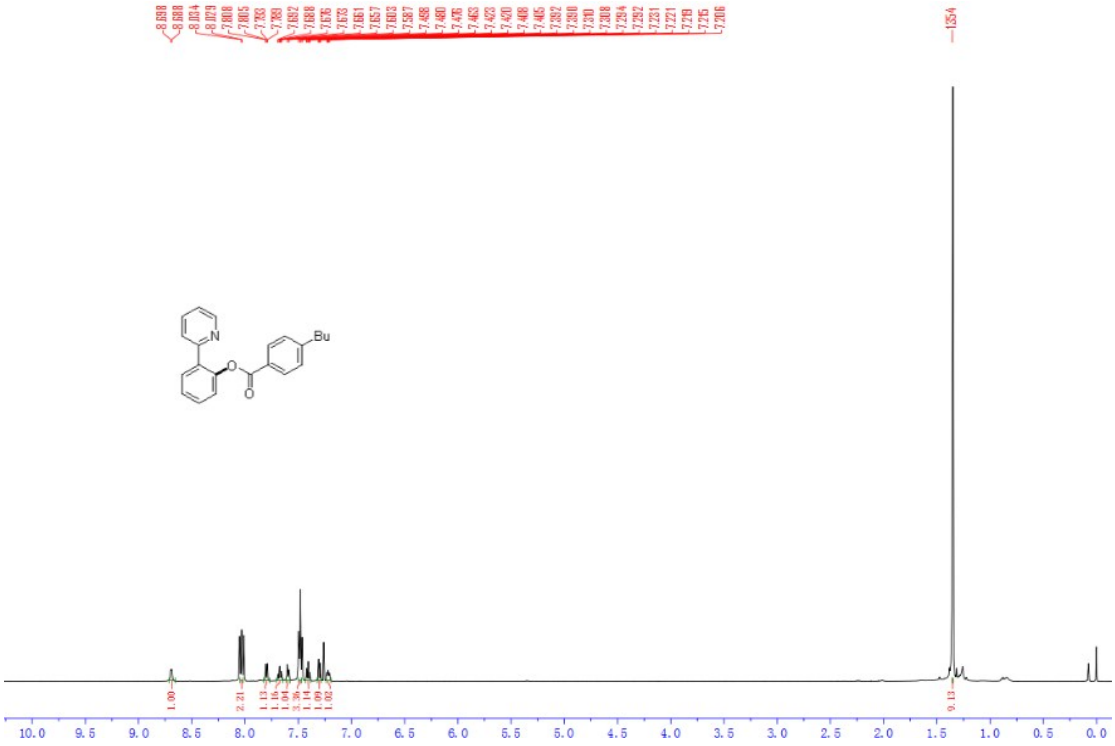
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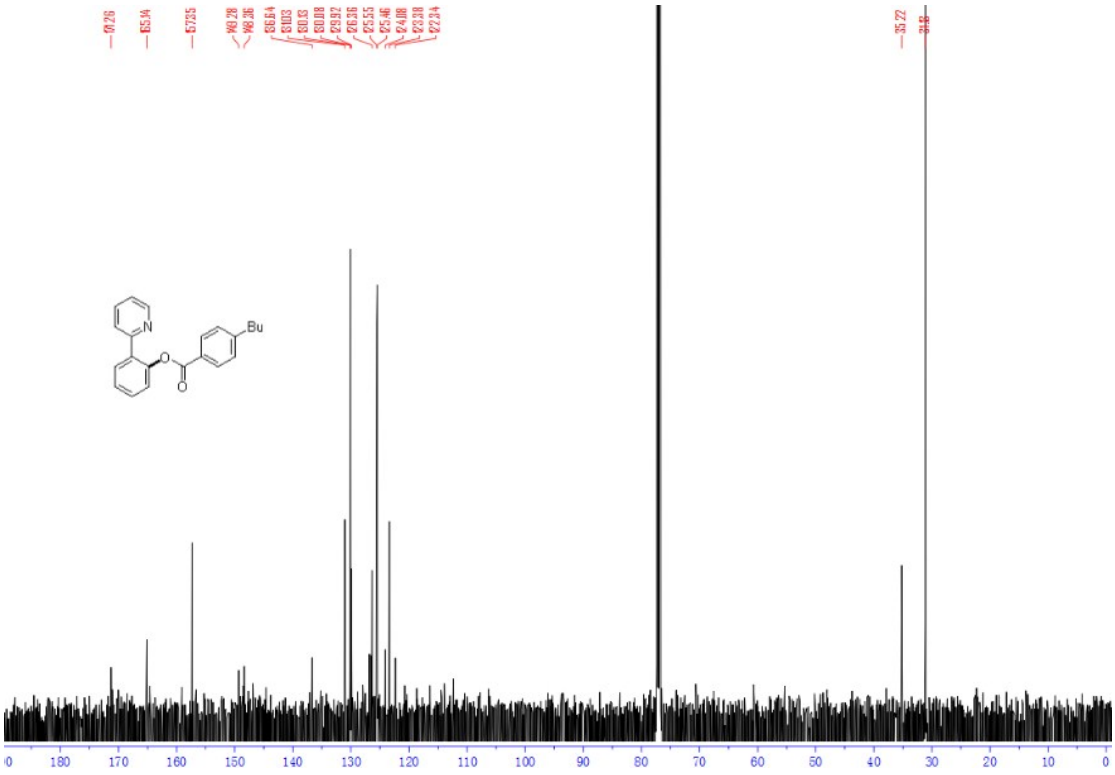
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