Supporting Information for

Cross Couping of Thioether with Aryl Boroxines to Construct Biaryls via Rh Catalyzed C-S Activation

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General Experimental Section

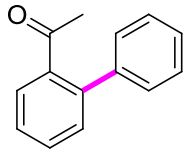
Analytic methods. All of the analytic methods: All of the analytic methods: GC, GC-MS, and HRMS were performed by State-Authorized Analytical Center at Peking University. The GC yields were obtained after amendment by standard curve, with *n*-dodecane as the internal standard. ^{1}H NMR and ^{13}C NMR data were obtained on Varian 400 M nuclear resource spectrometers, with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard (unless otherwise specified). Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR were recorded in ppm from tetramethylsilane using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm).

General preparation for chemicals. Palladium(II) acetate (trimer, Pd 45.9-48.4%) and Tetracarbonyldi-mu-chlorodirhodium(I) (Rh 50.1-52.9%) were purchased from Alfa Aesar. Arylboroxines were prepared by dehydration from corresponding aryl boronic acids refluxing in toluene. K_3PO_4 and boroxines were dried by heating (about 400 ^{o}C) under vacuum. The anhydrous tetrahydrofuran was prepared by refluxing with metal sodium.

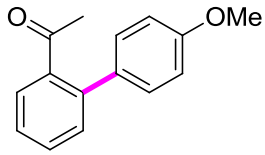
General Experimental Procedures for Rh-Catalyzed Cross-Coupling of Different Methyl(phenyl)sulfanes 1 with arylboroxines 2:

The reactions were carried out in Schlenk tubes, which were dried by heating under vacuum. Under air atmosphere, $[Rh(CO)_2Cl]_2$ (0.005 mmol, 1.9 mg), Ag_2CO_3 (0.30 mmol, 82.6 mg), and **1** (0.2 mmol) were added into a dried Schlenk tube. Then K_3PO_4 (0.3 mmol, 63.7 mg) and **2** (0.3 mmol) were added into tube in glove box under dry N_2 atmosphere. THF (1 ML) and DCE (0.5 ML) were added by syringe. The mixture was stirred under air atmosphere at 140 ^{o}C for 48 h (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The product **3** or **4** was further purified through flash chromatography on silica gel with petroleum ether and ethyl acetate (v/v = 50/1) as the eluent.

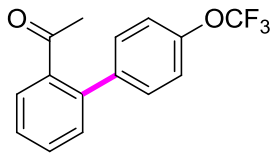
Characterization of Product in Details:



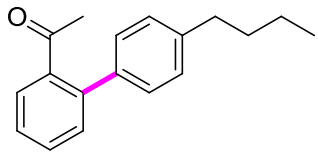
1-([1,1'-biphenyl]-2-yl)ethanone (3aa). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3aa** as light-yellow oil (30.3 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.47 (m, 2H), 7.47 – 7.37 (m, 5H), 7.37 – 7.32 (m, 2H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.95, 140.93, 140.75, 140.54, 130.74, 130.26, 128.88 (2C), 128.70 (2C), 127.91, 127.89, 127.47, 30.45. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{14}H_{13}O$ 197.0961; found 197.0962. Data consistent with that previously reported.[1]



1-(4'-methoxy-[1,1'-biphenyl]-2-yl)ethanone (3ab). According to the general procedure, the reaction mixture was stirred for 48 h to afford **3ab** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 15.0, 8.9, 1.5 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.19, 159.58, 140.93, 140.14, 133.03, 130.68, 130.17, 130.01(2C), 127.82, 127.06, 114.19(2C), 55.32, 30.44. Data consistent with that previously reported.[2]

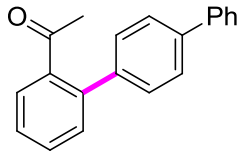


1-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)ethanone (3ac). According to the general procedure, the reaction mixture was stirred for 48 h to afford **3ac** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 3H), 7.28 (d, *J* = 8.9 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.00, 149.02, 140.62, 139.48, 139.08, 130.89, 130.37, 130.22(2C), 128.06, 127.89, 121.01(2C), 30.39.

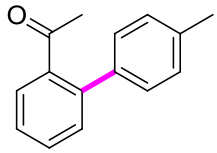


1-(4'-butyl-[1,1'-biphenyl]-2-yl)ethanone (3ad). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ad** as yellow oil (26.8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (td, *J* = 8.9, 1.3 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.23 (m, 4H), 2.70 – 2.62 (t, *J* = 7.9 Hz, 2H), 1.99 (s, 3H), 1.63 (ddd, *J* = 10.3, 7.2, 4.7 Hz, 2H), 1.38 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.95 (t, *J* =

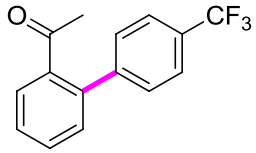
7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.23, 142.82, 140.98, 140.58, 137.95, 130.66, 130.19, 128.75 (3C), 127.80, 127.20, 35.33, 33.55, 30.43, 22.36, 13.96. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{18}H_{21}O$ 253.1587; found 253.1590.



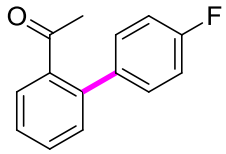
1-([1,1':4',1''-terphenyl]-2-yl)ethanone (3ae). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ae** as yellow oil (28.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.56 (m, 5H), 7.56 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 7.39 – 7.30 (m, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.84, 141.65, 141.27, 140.99, 140.53, 140.47, 130.81, 130.29, 129.17, 128.89 (2C), 127.96, 127.76, 127.68, 127.64, 127.62, 127.19 (2C), 126.67, 30.55. HRMS:*m/z*: $[M+H]^+$ calculated for $C_{20}H_{17}O$ 273.1240; found 273.1275. Data consistent with that previously reported.[3]



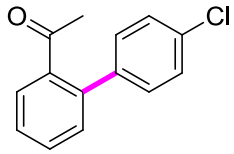
1-(4'-methyl-[1,1'-biphenyl]-2-yl)ethanone (3af). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3af** as yellow oil (29.5 mg, 66% yield) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (ddd, *J* = 9.5, 8.9, 4.6 Hz, 2H), 7.39 (dd, *J* = 11.9, 4.5 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 4H), 2.40 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.09, 139.89, 139.50, 136.78, 136.74, 129.65, 129.19, 128.39 (2C), 127.72 (2C), 126.80, 126.18, 76.32, 76.01, 75.69, 29.43, 20.17. HRMS:*m/z:* $[M+Na]^+$ calculated for $C_{15}H_{14}NaO$ 233.0937; found 233.0936. Data consistent with that previously reported.[4]



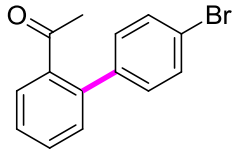
1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethanone (3ag). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ag** as yellow oil (32.1 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.62 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.37 (dd, *J* = 7.6, 1.0 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.50, 144.59, 140.37, 139.21, 131.03, 130.46, 130.08, 129.76, 129.14 (2C), 128.22 (d, *J* = 3.4 Hz), 125.53 (dd, *J* = 7.4, 3.7 Hz), 122.78 30.36. HRMS:*m/z:* $[M+H]^+$: calculated for $C_{15}H_{12}F_3O$ 265.0835, found 265.0837. Data consistent with that previously reported.[2]



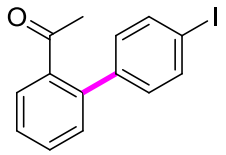
1-(4'-fluoro-[1,1'-biphenyl]-2-yl)ethanone (3ah). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ah** as yellow oil (32.5 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.47 (m, 2H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.15 – 7.09 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.17, 141.28, 138.90 (d, *J* = 36.6 Hz), 133.62, 131.93, 131.66, 130.84, 128.37 (d, *J* = 2.3 Hz), 128.32, 127.59 (2C, d, *J* = 45.2 Hz), 125.92 (2C, dd, *J* = 85.1, 40.4 Hz), 29.74. HRMS:*m/z:* $[M+Na]^+$: calculated for $C_{14}H_{11}FNaO$ 237.0686, found 237.0690. Data consistent with that previously reported.[2]



1-(4'-chloro-[1,1'-biphenyl]-2-yl)ethanone (3ai). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ai** as yellow oil (31.2 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.35 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.29 – 7.24 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.19, 140.63, 139.26 (2C), 134.11, 130.88, 130.27, 130.11 (2C), 128.87 (2C), 128.05, 127.80, 30.47. HRMS:*m/z*: $[M+H]^+$: calculated for $C_{14}H_{12}ClO$ 231.0571, found 231.0572. Data consistent with that previously reported.[7]

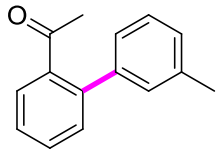


1-(4'-bromo-[1,1'-biphenyl]-2-yl)ethanone (3aj). According to the general procedure, the reaction mixture was stirred for 48h to afford compound **3aj** as yellow oil (30.4 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.52 (m, 3H), 7.51 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.23 – 7.18 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.13, 140.56, 139.74, 139.28, 131.82 (2C), 130.90, 130.43, 130.23 (2C), 128.08, 127.83, 122.26, 77.36, 77.05, 76.73, 30.49.

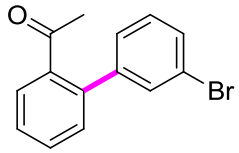


1-(4'-iodo-[1,1'-biphenyl]-2-yl)ethanone (3ak). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ak** as yellow oil (36.3 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 2H),

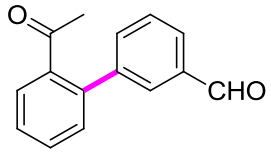
7.59 – 7.48 (m, 2H), 7.43 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.10 – 7.06 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.13, 140.50, 140.34, 139.37, 137.78 (2C), 130.65 (2C), 130.59 (2C, d, *J* = 36.4 Hz), 128.78 (d, *J* = 18.4 Hz), 127.97 (d, *J* = 26.2 Hz), 93.81, 30.50. HRMS:*m/z:* $[M+H]^+$: calculated for $C_{14}H_{12}IO$ 322.9927, found 322.9933.



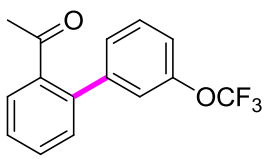
1-(3'-methyl-[1,1'-biphenyl]-2-yl)ethanone (3al). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3al** as yellow oil (25.3 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.46 (m, 2H), 7.43 – 7.36 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.11 (m, 2H), 2.40 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.06, 140.91, 140.72, 140.70, 138.40, 130.69, 130.21, 129.56, 128.66, 128.59, 127.85, 127.36, 126.04, 30.45, 21.43.



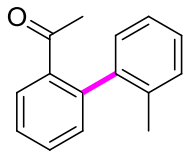
1-(3'-bromo-[1,1'-biphenyl]-2-yl)ethanone (3am). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3am** as yellow oil (30.8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.44 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.31 – 7.21 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.87, 142.91, 140.52, 139.01, 131.60, 130.93, 130.87, 130.33, 130.08, 128.13, 128.01, 127.66, 122.74, 30.45.



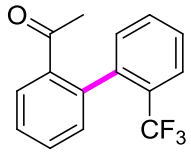
2'-acetyl-[1,1'-biphenyl]-3-carbaldehyde (3an). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3an** as yellow oil (21.7 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (td, *J* = 7.5, 1.2 Hz, 1H), 7.36 (t, *J* = 5.5 Hz, 3H), 7.27 (d, *J* = 9.8 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.03, 149.02, 140.62, 139.47, 139.08, 130.90, 130.37, 130.21 (2C), 128.06, 127.89, 121.76, 121.01, 119.20, 30.40. HRMS:*m/z*: $[M+H]^+$: calculated for $C_{15}H_{14}NaO_4$ 281.0784, found 281.0788.



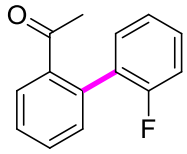
1-(3'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)ethanone (3ao). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ao** as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (dd, *J* = 11.0, 5.0 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.28 – 7.23 (m, 2H), 7.22 (s, 1H), 2.10 (s, 3H).



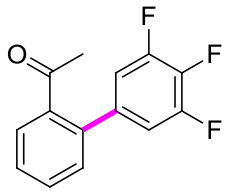
1-(2'-methyl-[1,1'-biphenyl]-2-yl)ethanone (3ap). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ap** as yellow oil (27.0 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.33 – 7.17 (m, 4H), 7.12 (d, *J* = 7.4 Hz, 1H), 2.13 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.09, 140.77, 140.50, 140.20, 135.59, 130.88, 130.67, 130.24, 129.53, 128.19, 128.00, 127.39, 125.85, 29.77, 20.12. HRMS:*m/z*: $[M+H]^+$: calculated for $C_{15}H_{15}O$ 211.1117, found 211.1120. Data consistent with that previously reported.[5]



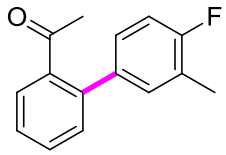
1-(2'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethanone (3aq). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3aq** as yellow oil (30.8 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.60 (m, 3H), 7.57 – 7.44 (m, 4H), 7.38 (dd, *J* = 7.5, 0.9 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.39, 141.69, 140.38, 139.14, 132.26, 131.06, 130.52, 129.02, 128.29, 128.15, 125.48, 125.44, 125.41, 125.37, 125.33, 124.52, 124.48, 124.44, 122.62, 30.29.



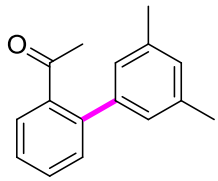
1-(2'-fluoro-[1,1'-biphenyl]-2-yl)ethanone (3ar). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ar** as yellow oil (35.6 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.54 (td, *J* = 7.5, 1.3 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.26 (m, 3H), 7.21 (td, *J* = 7.5, 0.9 Hz, 1H), 7.14 – 7.06 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.15, 160.40, 157.96, 140.19, 134.28, 132.32, 131.41, 131.11, 131.06, 131.03, 129.69, 129.61, 128.71, 128.55, 128.02, 128.01, 124.91, 124.48, 124.44, 123.39, 115.68, 115.46, 29.08. HRMS: *m/z*: $[M+H]^+$: calculated for $C_{14}H_{12}FO$ 215.0867, found 215.0864.



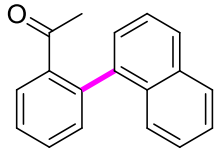
1-(3',4',5'-trifluoro-[1,1'-biphenyl]-2-yl)ethanone (3as). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3as** as yellow oil (29.0 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.31 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.99 – 6.89 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.72, 152.38, 152.33, 152.24, 149.88, 149.84, 149.78, 140.75, 139.93, 138.24, 137.71, 137.01, 136.96, 131.16, 130.38, 128.49, 128.37, 113.16, 113.10, 113.00, 112.94, 30.18.



1-(4'-fluoro-3'-methyl-[1,1'-biphenyl]-2-yl)ethanone (3at). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3at** as yellow oil (32.6 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.46 (m, 2H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.16 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.11 (ddd, *J* = 7.4, 5.0, 2.2 Hz, 1H), 7.05 (t, *J* = 8.8 Hz, 1H), 2.05 (s, 3H). HRMS: *m/z*: $[M+H]^+$: calculated for $C_{15}H_{14}FO$ 229.1023, found 229.1026.

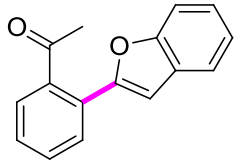


1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)ethanone (3au). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3au** as yellow oil (30.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.45 (m, 2H), 7.42 – 7.33 (m, 2H), 7.03 (s, 1H), 6.96 (s, 2H), 2.35 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.18, 140.88, 140.85, 140.70, 138.26 (2C), 130.64, 130.16, 129.54, 127.81, 127.25, 126.76 (2C), 30.45, 21.29 (2C). HRMS: *m/z*: $[M+H]^+$: calculated for $C_{16}H_{17}O$ 225.1274, found 225.1276.

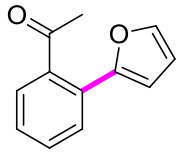


1-(2-(naphthalen-1-yl)phenyl)ethanone (3av). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3av** as yellow oil (45.8 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 8.1, 4.4 Hz, 2H), 7.77 – 7.73 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.56 (td, *J* = 7.4, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.4, 4.1 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.33 (dd, *J* = 7.0, 1.0 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.14, 141.29, 139.10, 138.74,

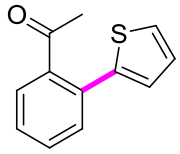
133.64, 131.94, 131.67, 130.86, 128.40, 128.37, 128.34, 127.83, 127.38, 126.60, 126.12, 125.68, 125.35, 29.75. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{18}H_{15}O$ 247.1117, found 247.1121. Data consistent with that previously reported.[6]



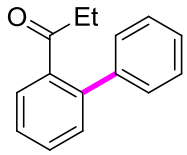
1-(2-(benzofuran-2-yl)phenyl)ethanone (3aw). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3aw** as yellow oil (27.2 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.57 – 7.41 (m, 4H), 7.34 – 7.23 (m, 2H), 6.95 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.39, 155.18, 154.27, 140.40, 130.43, 128.96, 128.87, 128.52, 127.98, 127.32, 124.83, 123.26, 121.26, 111.35, 105.01, 30.06. HRMS:*m/z*: $[M+H]^+$ calculated for $C_{16}H_{13}O_2$ 237.0910, found 237.0912. Data consistent with that previously reported.[7]



1-(2-(furan-2-yl)phenyl)ethanone (3ax). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ax** as yellow oil (24.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dtd, *J* = 5.7, 3.5, 1.3 Hz, 3H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.23 – 7.19 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.18, 140.55, 139.73, 139.28, 131.83, 130.91, 130.43, 130.23, 128.08, 127.83, 122.26, 30.50.

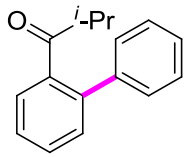


1-(2-(thiophen-2-yl)phenyl)ethanone (3ay). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **3ay** as yellow oil (27.8 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 6.7, 4.7 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.08 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.00 (dd, *J* = 3.5, 1.1 Hz, 1H), 2.15 (s, 3H). HRMS: *m/z*: $[M+H]^+$: calculated for $C_{12}H_{11}OS$ 203.0525, found 203.0526.

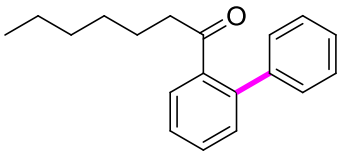


1-([1,1'-biphenyl]-2-yl)propan-1-one (4a). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4a** as yellow oil (25.0 mg, 60% yield). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.80, 140.73,

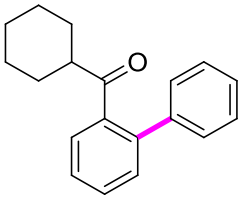
140.61, 139.66, 130.16, 129.99, 128.83 (2C), 128.69 (2C), 128.00, 127.78, 127.35, 40.23, 18.64. HRMS: *m/z*: $[M+H]^+$: calculated for $C_{15}H_{15}O$ 211.1117, found 211.1123. Data consistent with that previously reported.[8]



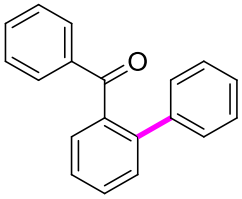
1-([1,1'-biphenyl]-2-yl)-2-methylpropan-1-one (4b). According to the general procedure, the reaction mixture was stirred for 48 to afford **4b** compound as yellow oil (33.8 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.30 (m, 9H), 2.42 (dt, *J* = 13.7, 6.9 Hz, 1H), 0.87 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.79, 140.72, 140.61, 139.66, 130.15, 129.98, 128.83 (2C), 128.68 (2C), 128.00, 127.77, 127.34, 40.22, 18.63. HRMS: *m/z*: $[M+H]^+$: calculated for $C_{16}H_{17}O$ 225.1274, found 225.1276. Data consistent with that previously reported.[9]



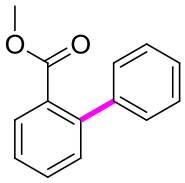
1-([1,1'-biphenyl]-2-yl)heptan-1-one (4c). According to the general procedure, the reaction mixture was stirred for 48 h to afford **4c** compound as yellow oil (34.2 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.36 (m, 7H), 7.36 – 7.30 (m, 2H), 2.15 – 2.05 (m, 1H), 1.64 – 1.54 (m, 3H), 1.49 (dd, *J* = 14.3, 1.4 Hz, 3H), 1.30 – 1.15 (m, 3H), 1.07 (d, *J* = 12.6 Hz, 1H), 0.97 – 0.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.76, 140.79, 140.70, 139.79, 130.11, 129.91, 128.88 (2C), 128.62 (2C), 127.95, 127.73, 127.31, 77.30, 77.04, 76.79, 50.26, 28.96, 25.73 (2C), 25.64 (2C). HRMS: *m/z*: $[M+H]^+$: calculated for $C_{19}H_{21}O$ 265.1587, found 265.1594.



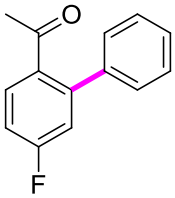
[1,1'-biphenyl]-2-yl(cyclohexyl)methanone (4d). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4d** as yellow oil (30.7 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 1H), 7.45 – 7.35 (m, 6H), 7.35 – 7.30 (m, 2H), 2.10 (tt, *J* = 11.4, 3.3 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.49 (d, *J* = 12.8 Hz, 3H), 1.29 – 1.16 (m, 2H), 1.14 – 1.00 (m, 1H), 0.93 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.71, 140.80, 140.70, 139.79, 130.09, 129.90, 128.87 (2C), 128.60 (2C), 127.94, 127.72, 127.30, 50.25, 28.95 (2C), 25.72, 25.64 (2C). Data consistent with that previously reported.[10]



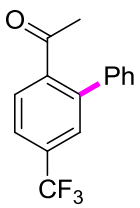
[1,1'-biphenyl]-2-yl(phenyl)methanone (4e). According to the general procedure, the reaction mixture was stirred for 48 h to afford **4e** as yellow oil (29.4 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.61 (m, 2H), 7.60 – 7.54 (m, 1H), 7.54 – 7.42 (m, 3H), 7.43 – 7.35 (m, 1H), 7.30 – 7.22 (m, 4H), 7.22 – 7.10 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.81, 141.17, 140.19, 138.99, 137.41, 132.82, 130.38, 130.08, 129.91 (2C), 129.02, 128.79, 128.26 (2C), 128.08 (2C), 127.34, 127.08. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{19}H_{15}O$ 259.1117, found 259.1122. Data consistent with that previously reported.[11]



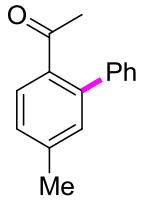
methyl [1,1'-biphenyl]-2-carboxylate (4f). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4f** as yellow oil (33.0 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.39 (dddd, *J* = 15.7, 7.2, 4.3, 1.9 Hz, 5H), 7.32 (dd, *J* = 5.2, 3.0 Hz, 2H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.17, 142.49, 141.33, 131.25, 130.89, 130.71, 129.78, 128.32 (2C), 128.04 (2C), 127.23, 127.16, 51.93. Data consistent with that previously reported.[12]



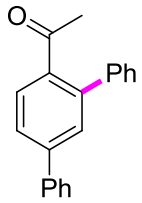
1-(5-fluoro-[1,1'-biphenyl]-2-yl)ethanone (4**g**). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound 4**g** as yellow oil (24.8 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.33 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.25 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 2.53 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.33, 142.87, 141.60, 140.68, 136.89, 128.90, 128.79 (2C), 128.69 (2C), 128.08, 127.10, 124.26, 30.28, 15.05. . HRMS: *m/z*: $[M+H]^+$ calculated for $C_{19}H_{15}O$ 259.1117, found 259.1122.



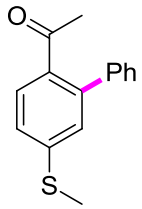
1-(5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethanone (**4h**). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4h** as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, *J* = 7.8 Hz, 3H), 7.50 – 7.43 (m, 3H), 7.38 – 7.34 (m, 2H), 2.01 (s, 3H). HRMS: *m/z*: $[M+H]^+$ calculated for $C_{15}H_{12}F_3O$ 265.08348, found 265.08359. Data consistent with that previously reported.[9]



1-(5-methyl-[1,1'-biphenyl]-2-yl)ethanone (**4i**). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4i** as yellow oil (26.7 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.35 – 7.31 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.19 (s, 1H), 2.42 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.28, 140.82, 140.72, 137.77, 137.39, 131.46, 130.21, 128.88 (2C), 128.65 (2C), 128.37, 127.69, 30.49, 20.98. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{15}H_{15}O$ 211.11174, found 211.11189.



1-([1,1':3',1''-terphenyl]-4'-yl)ethanone (**4j**). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4j** as yellow oil (39.3 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddd, *J* = 14.3, 9.9, 4.6 Hz, 5H), 7.50 – 7.36 (m, 8H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.27, 143.67, 141.34, 140.89, 139.91, 139.43, 129.13, 128.96 (2C), 128.91 (2C), 128.81, 128.74 (2C), 128.09, 128.02, 127.29 (2C), 126.06, 30.44. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{20}H_{17}O$ 273.12738, found 273.12778. Data consistent with that previously reported.[13]



1-(5-(methylthio)-[1,1'-biphenyl]-2-yl)ethanone (**4k**). According to the general procedure, the reaction mixture was stirred for 48 h to afford compound **4k** as yellow oil (36.0 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.35 – 7.31 (m, 2H), 7.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (d, *J* = 1.9 Hz, 1H), 2.52 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.31,

142.87, 141.60, 140.69, 136.90, 128.89, 128.79 (2C), 128.68 (2C), 128.07, 127.11, 124.28, 30.26, 15.05. HRMS: *m/z*: $[M+H]^+$ calculated for $C_{15}H_{15}OS$ 243.08381, found 243.08346.

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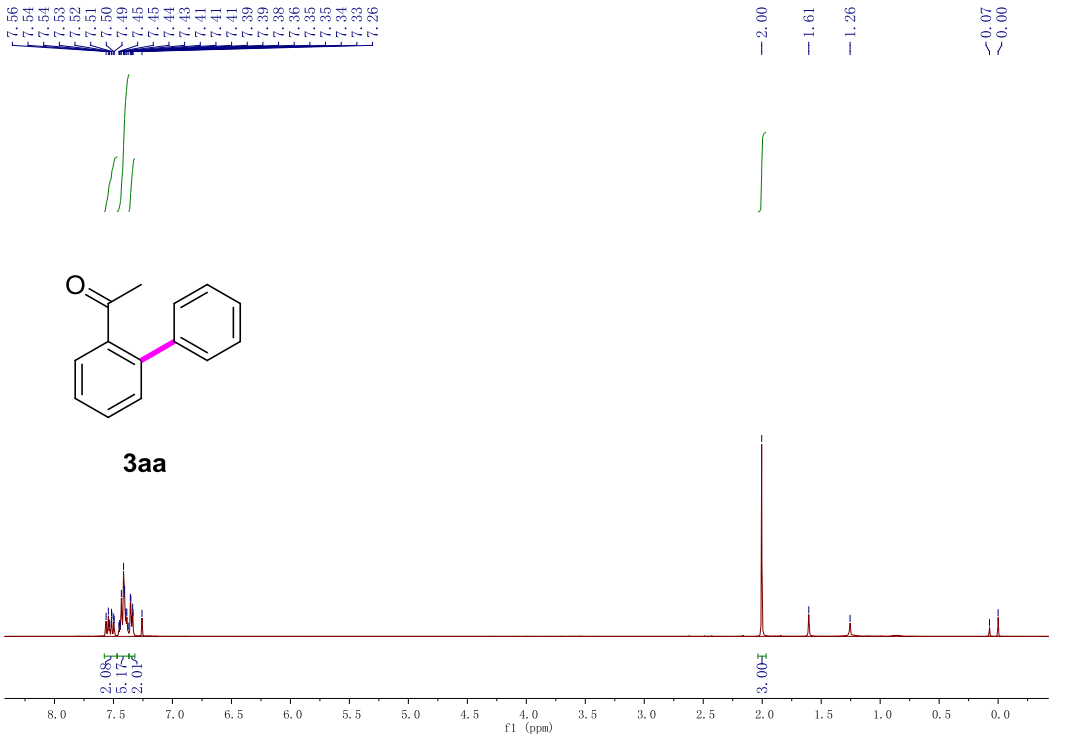

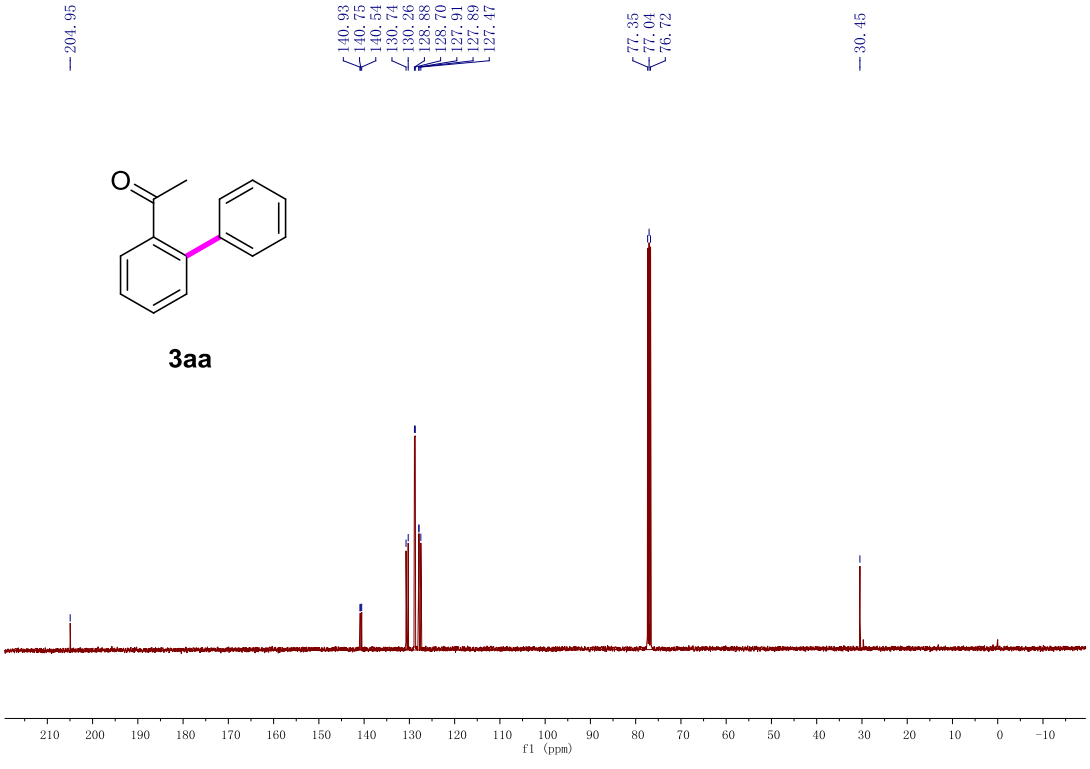

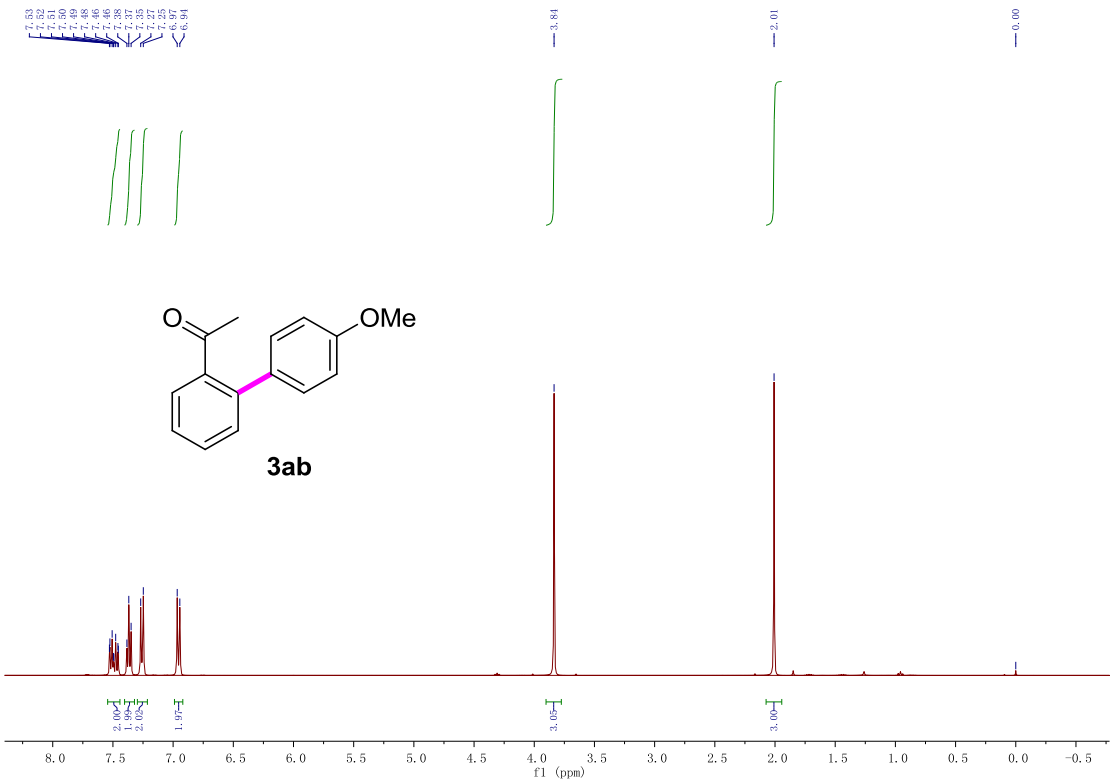

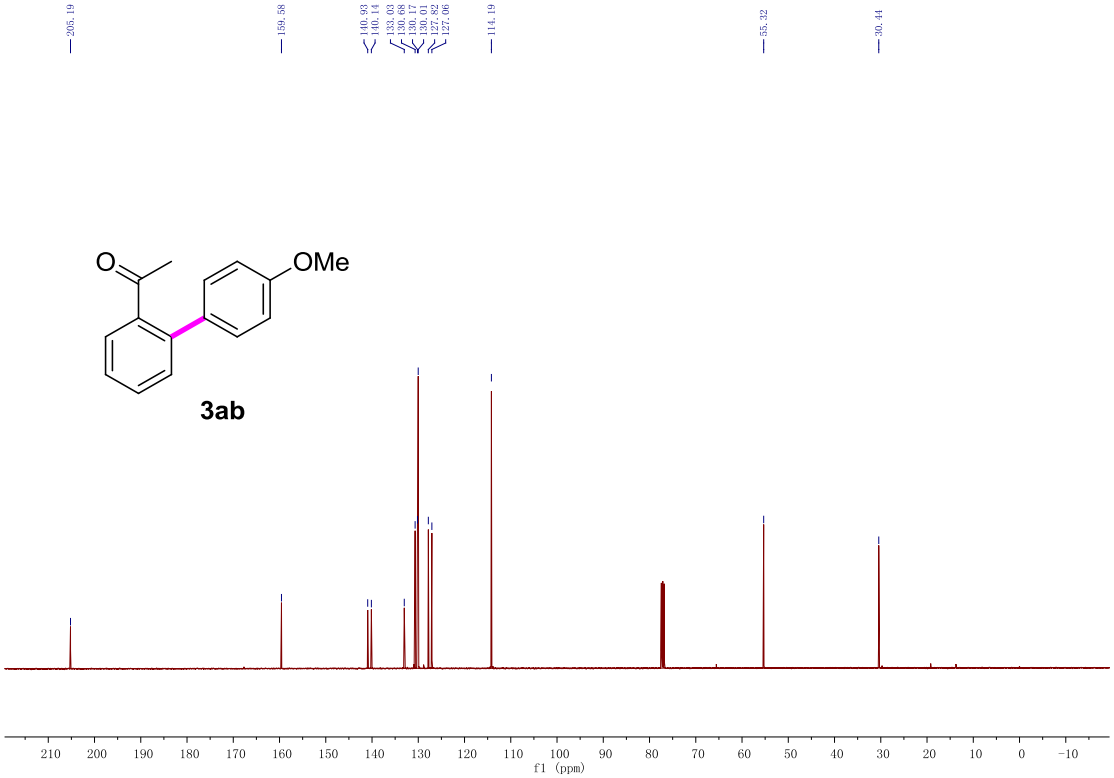

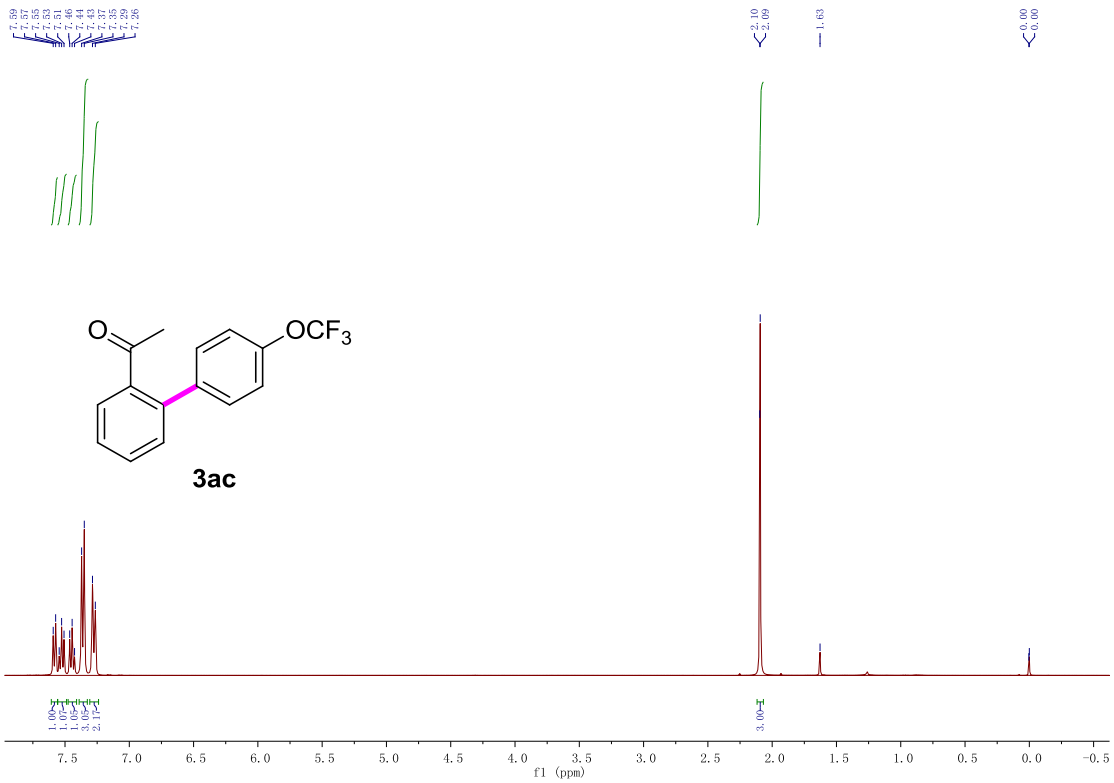

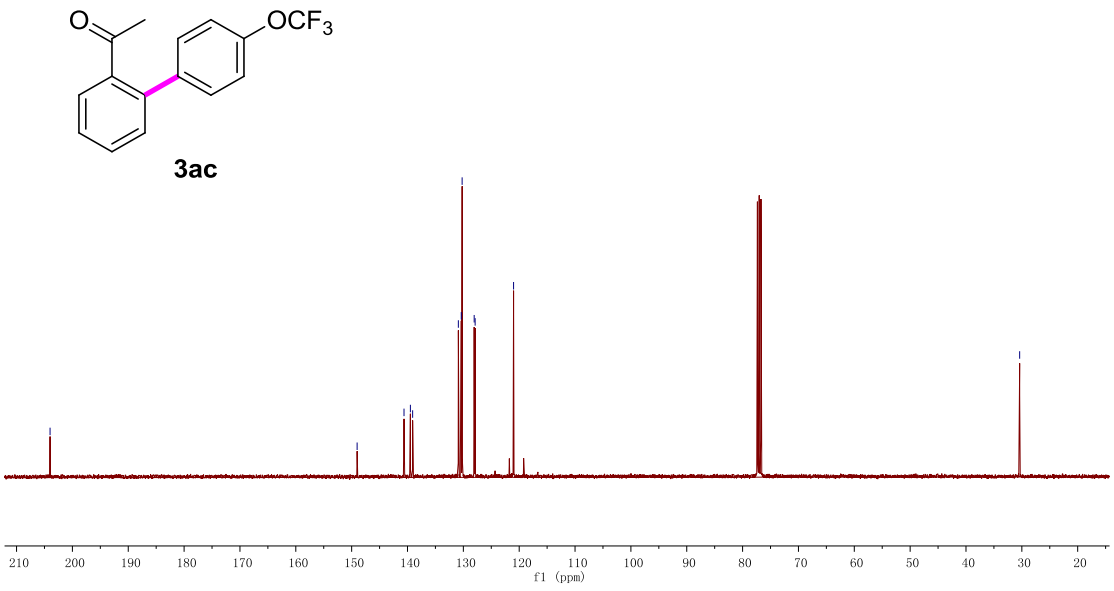

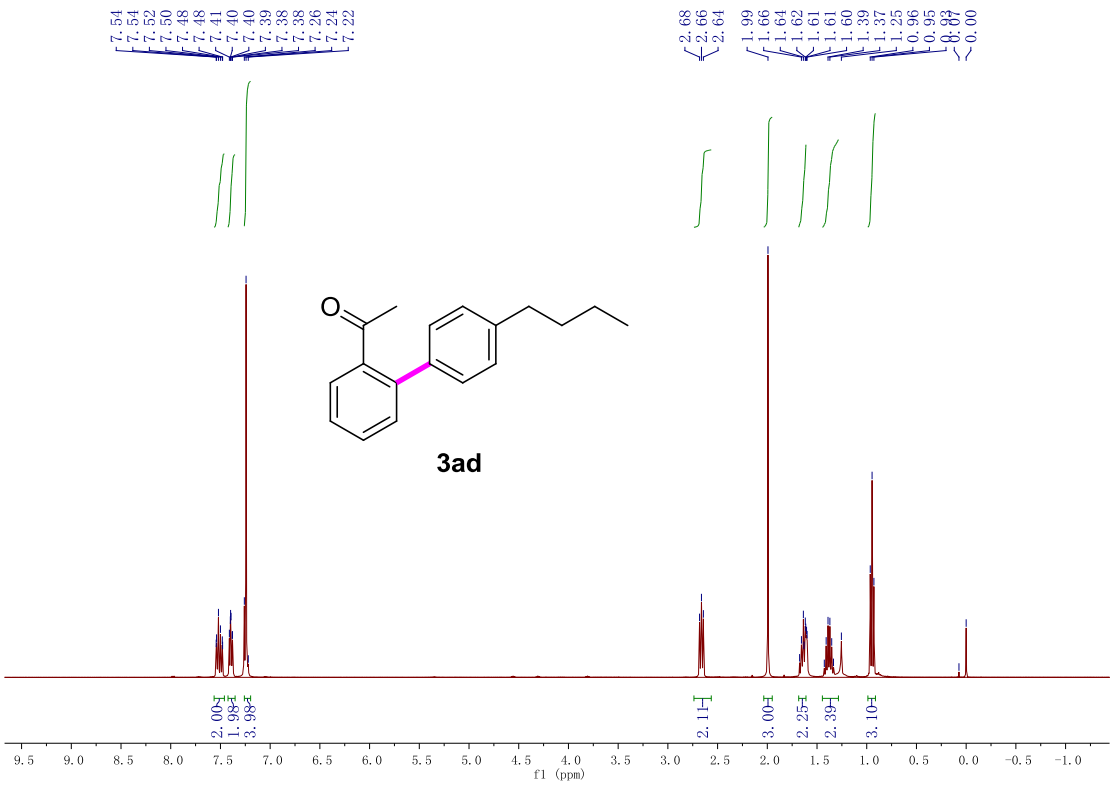

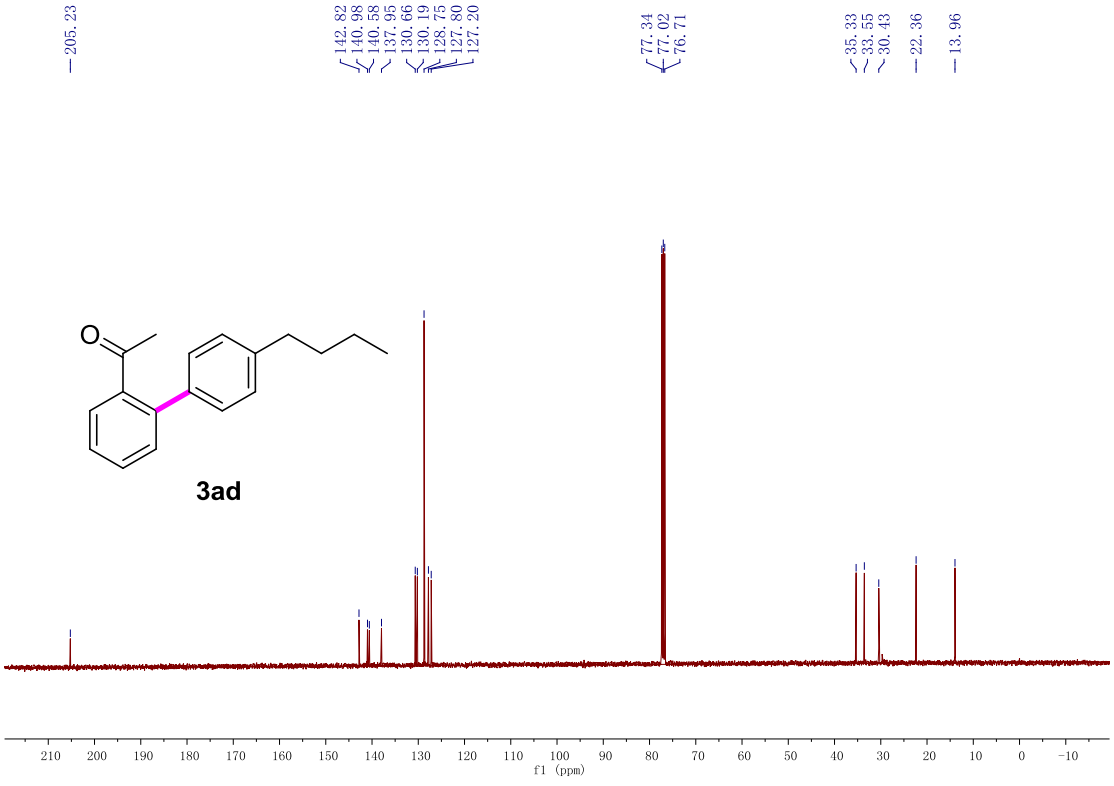

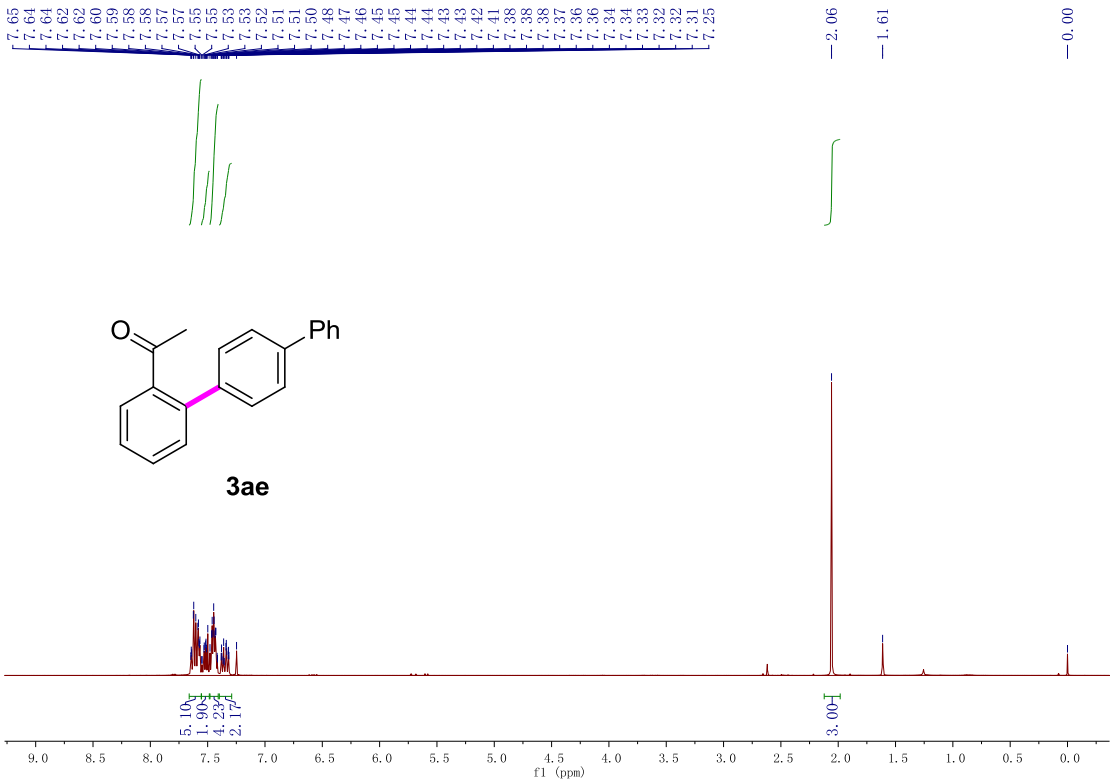

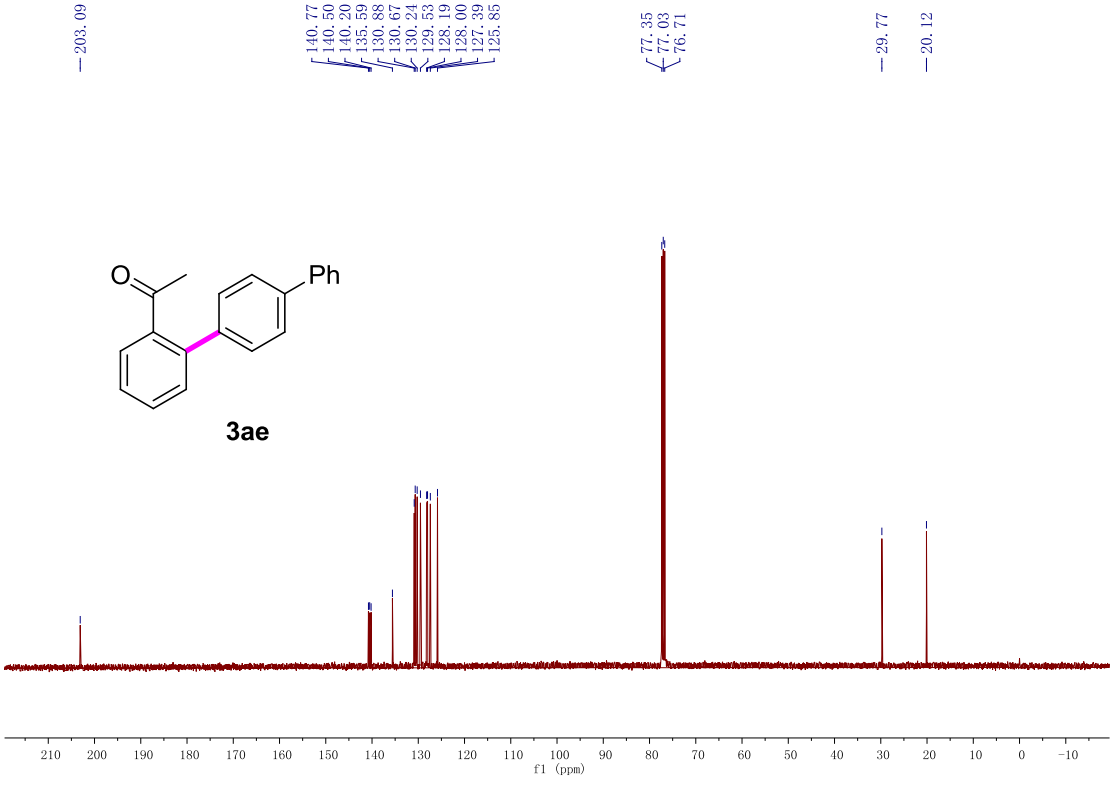

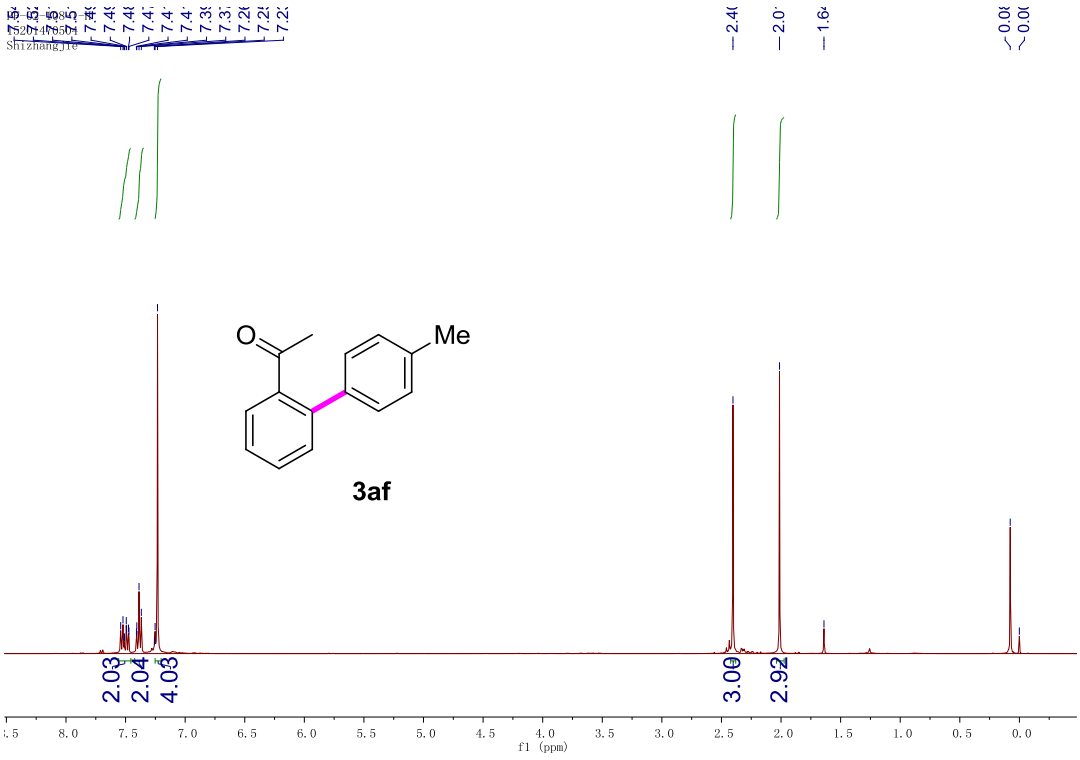
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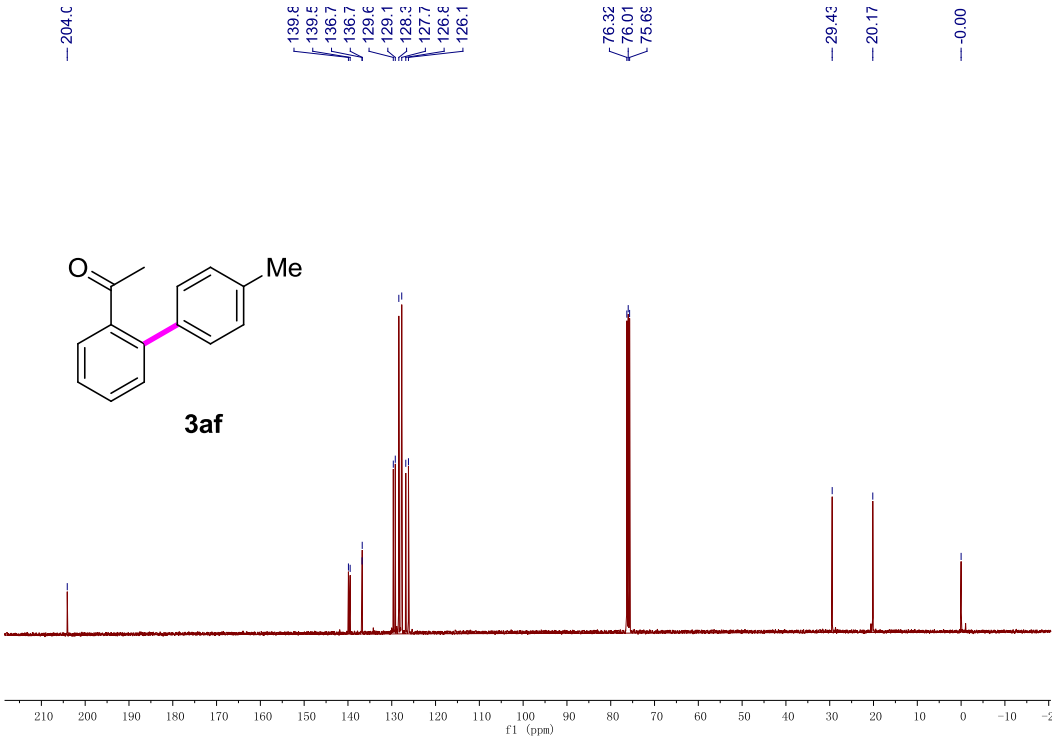
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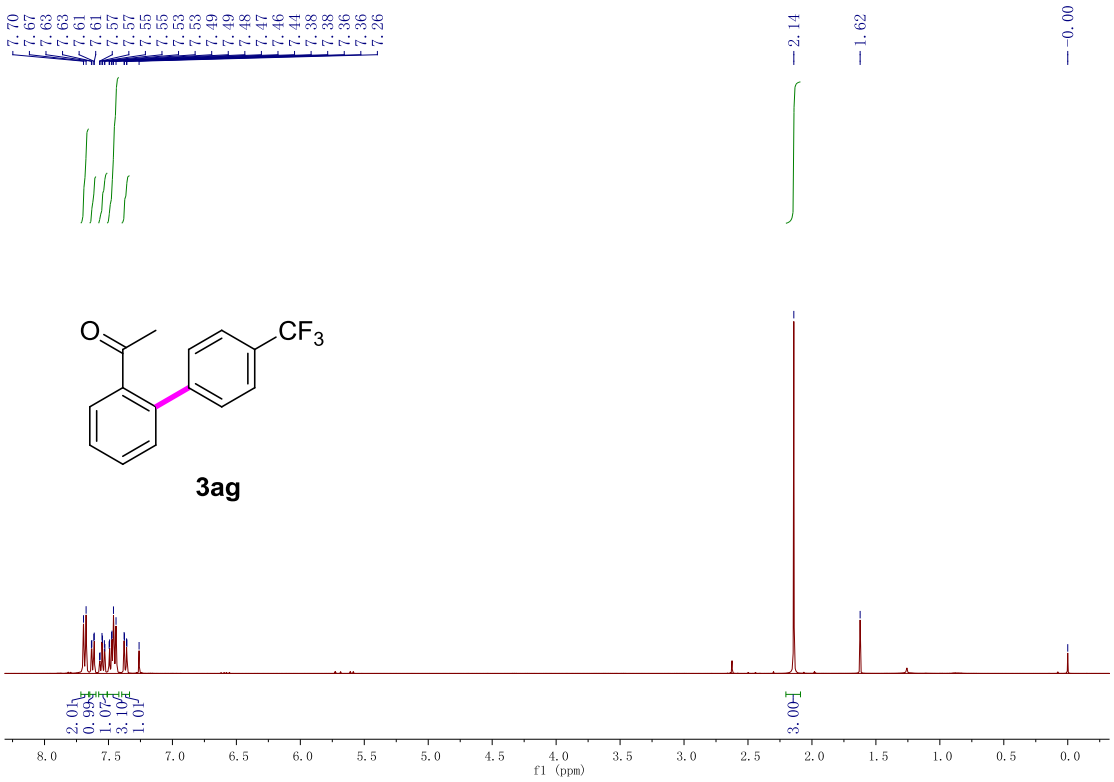

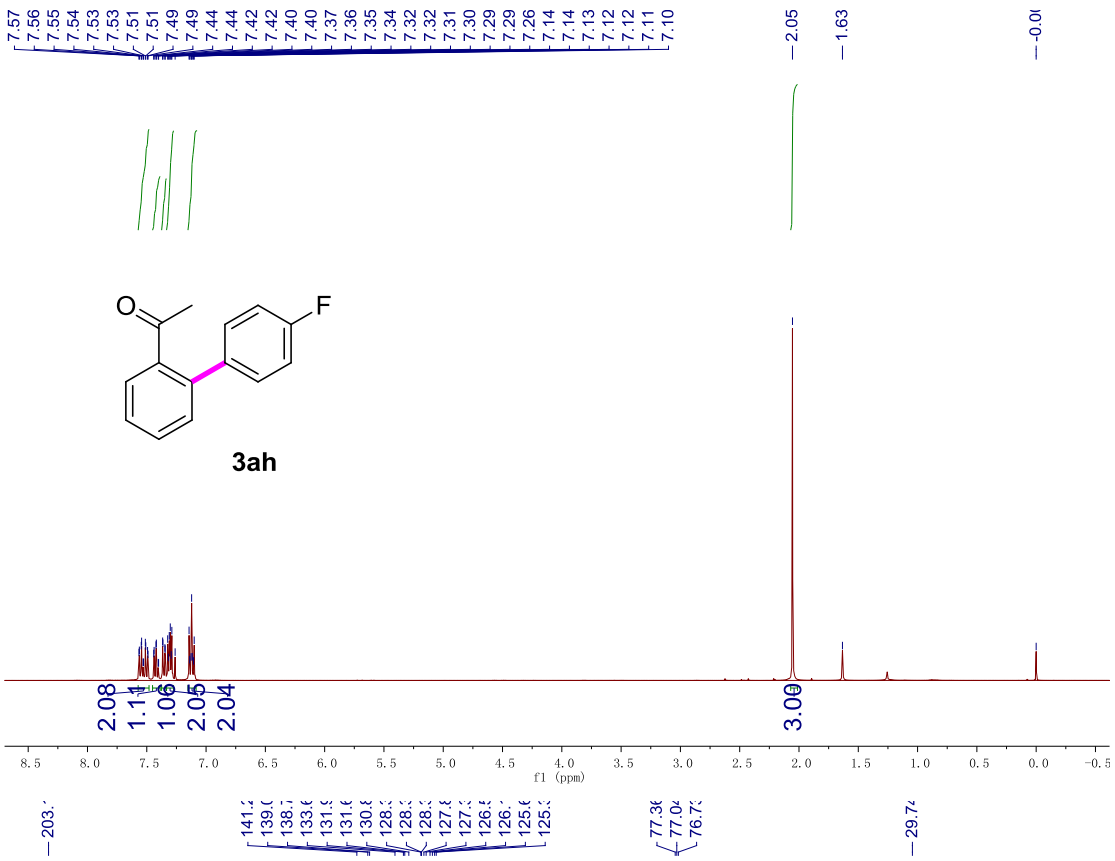

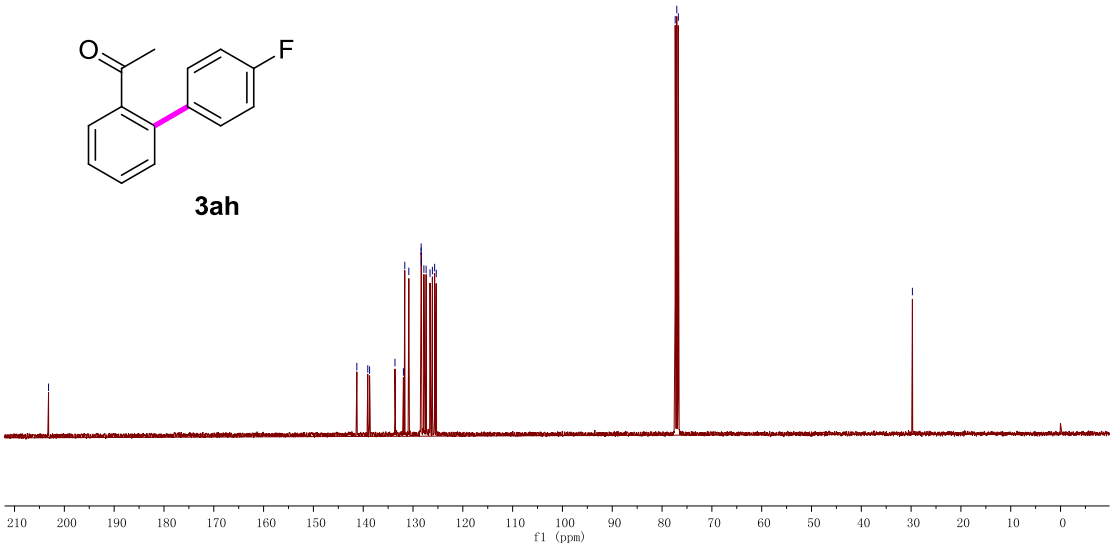

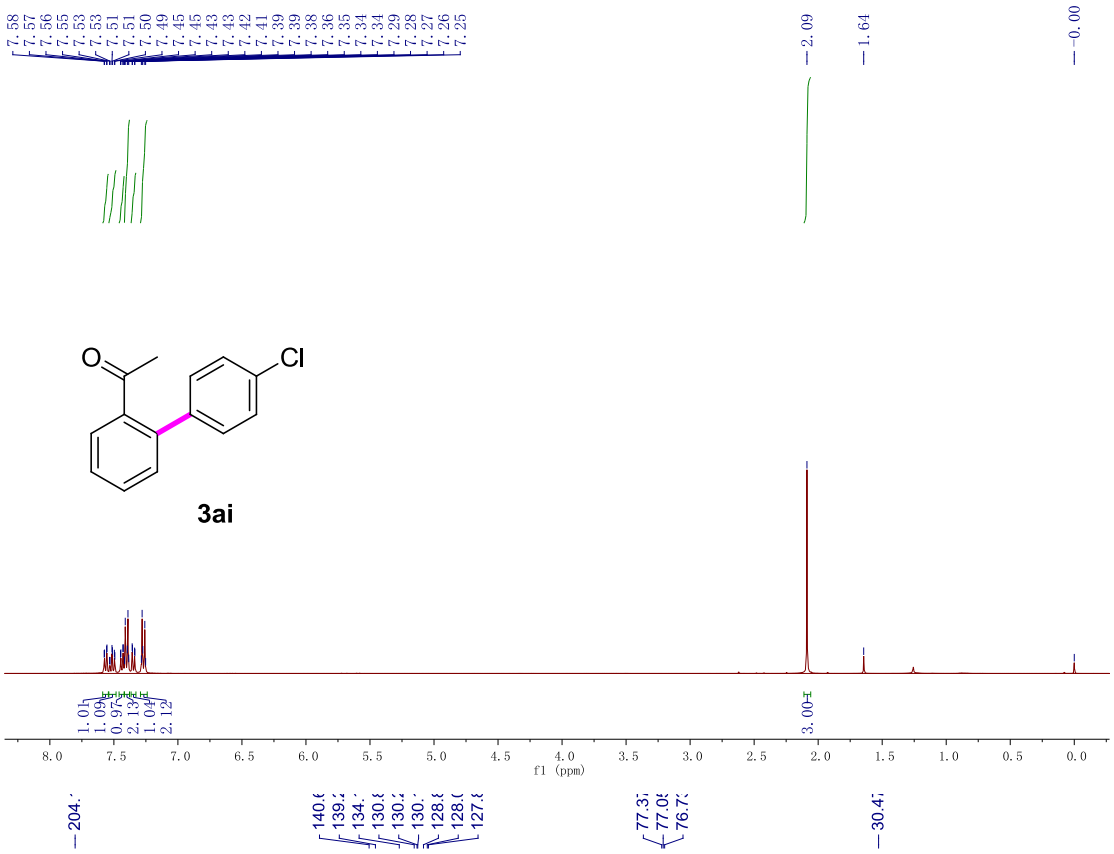

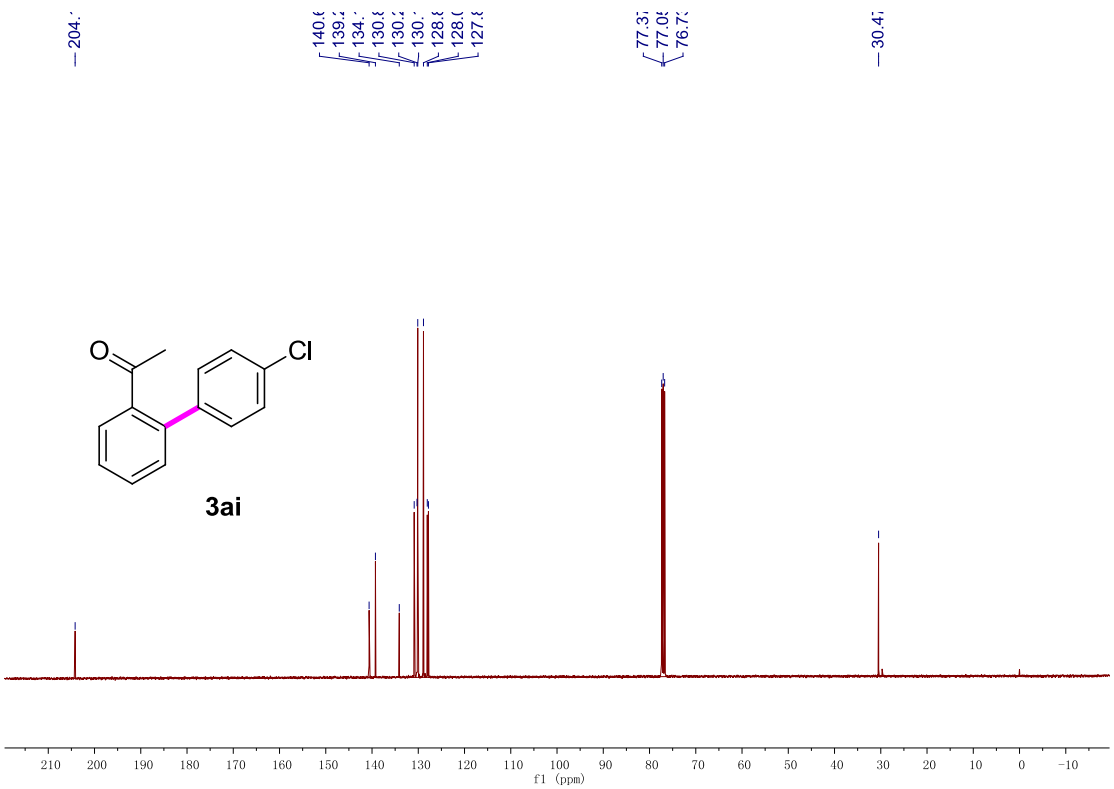

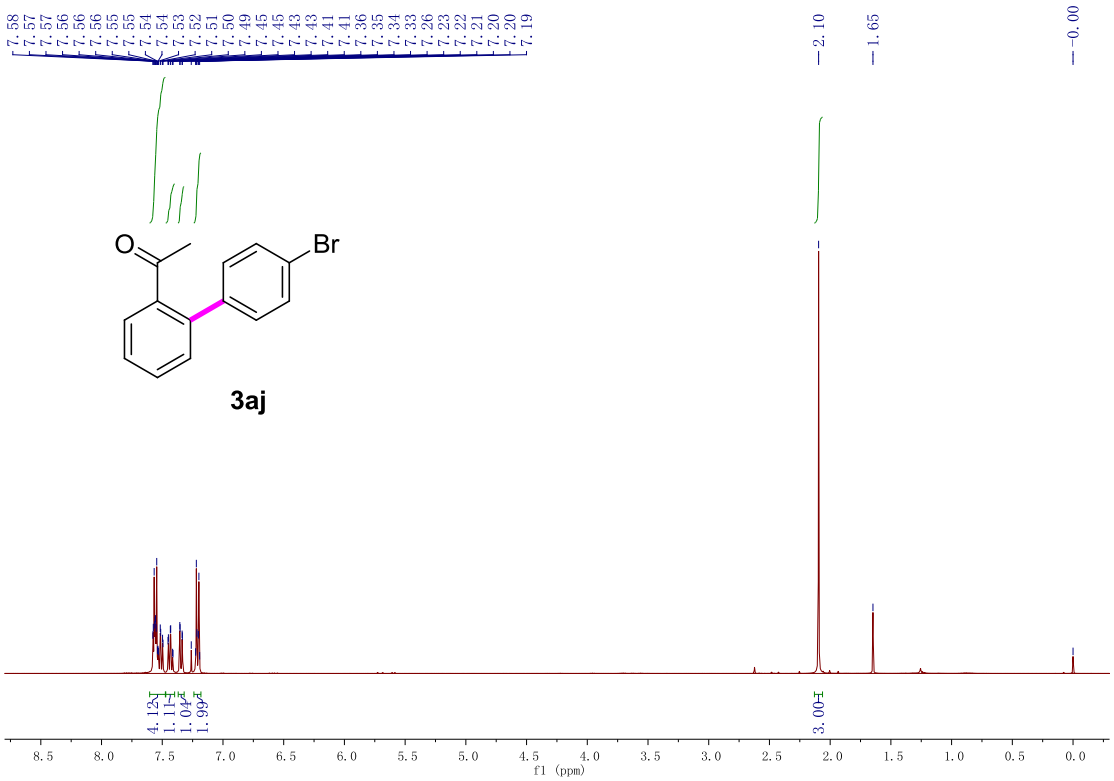

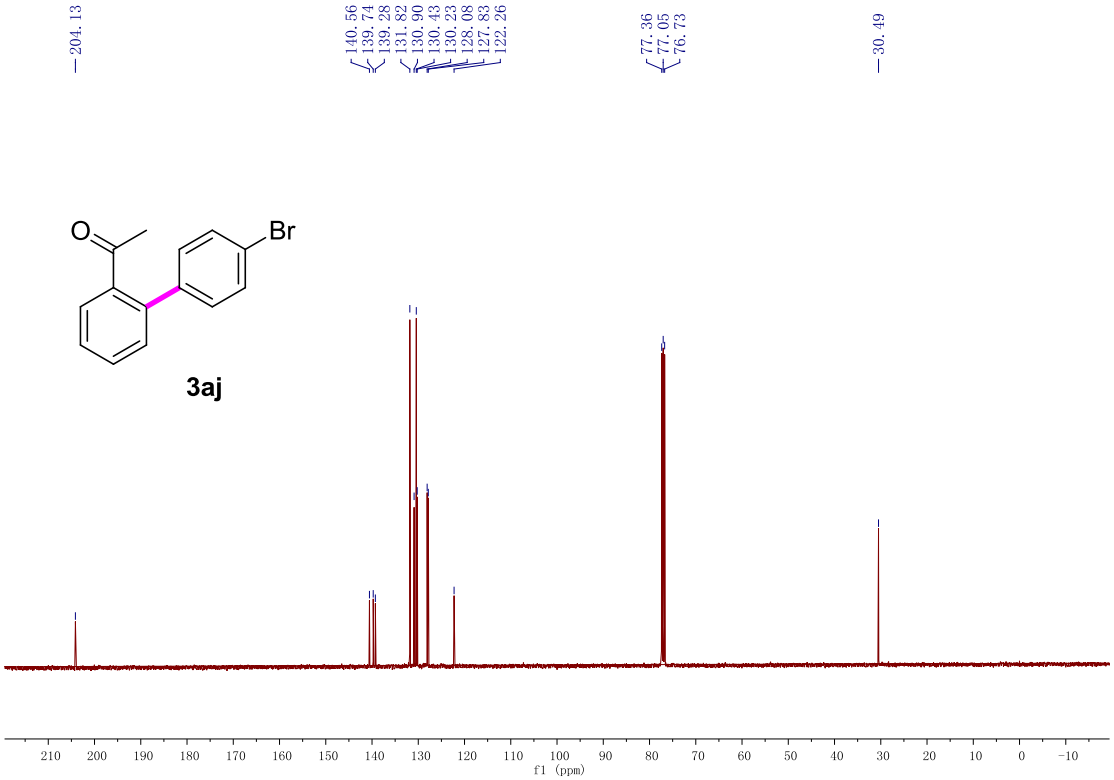

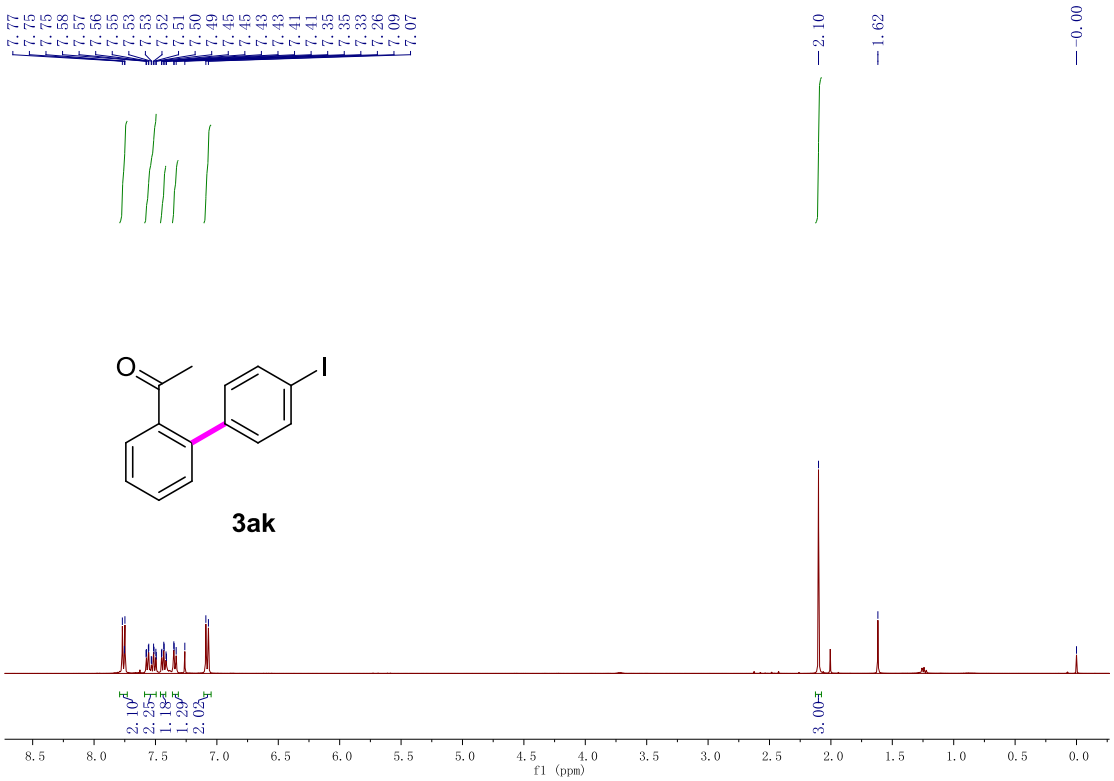
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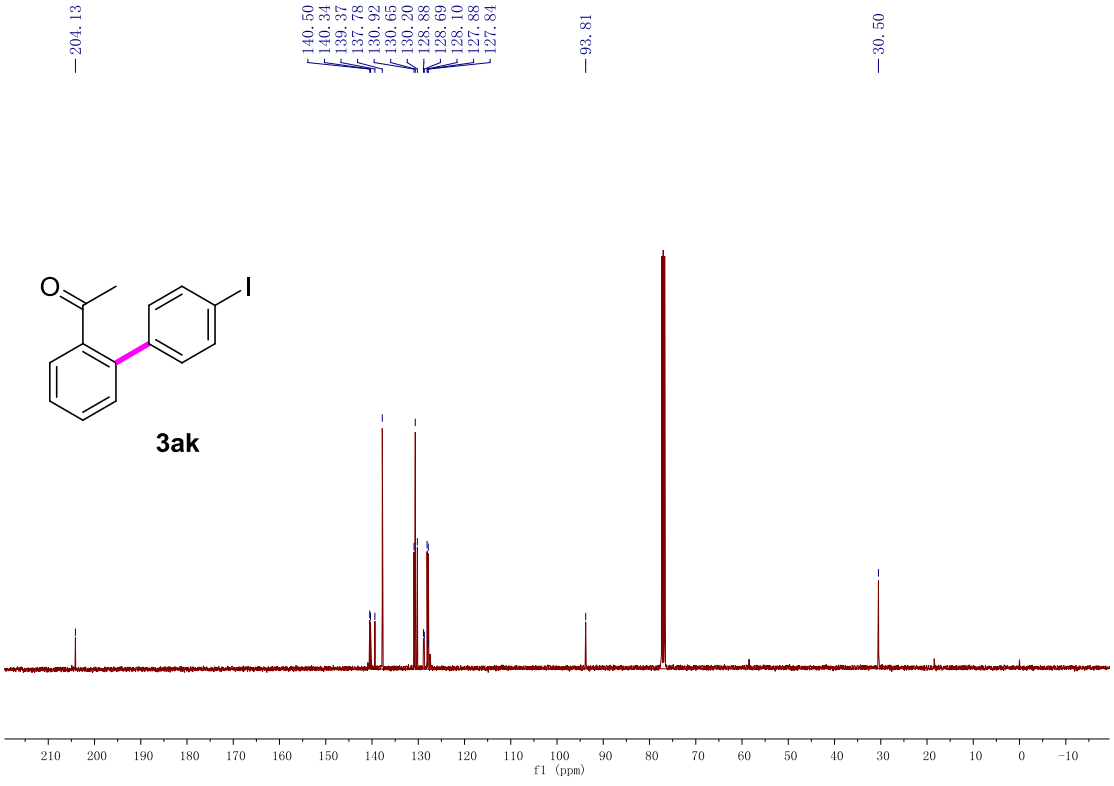
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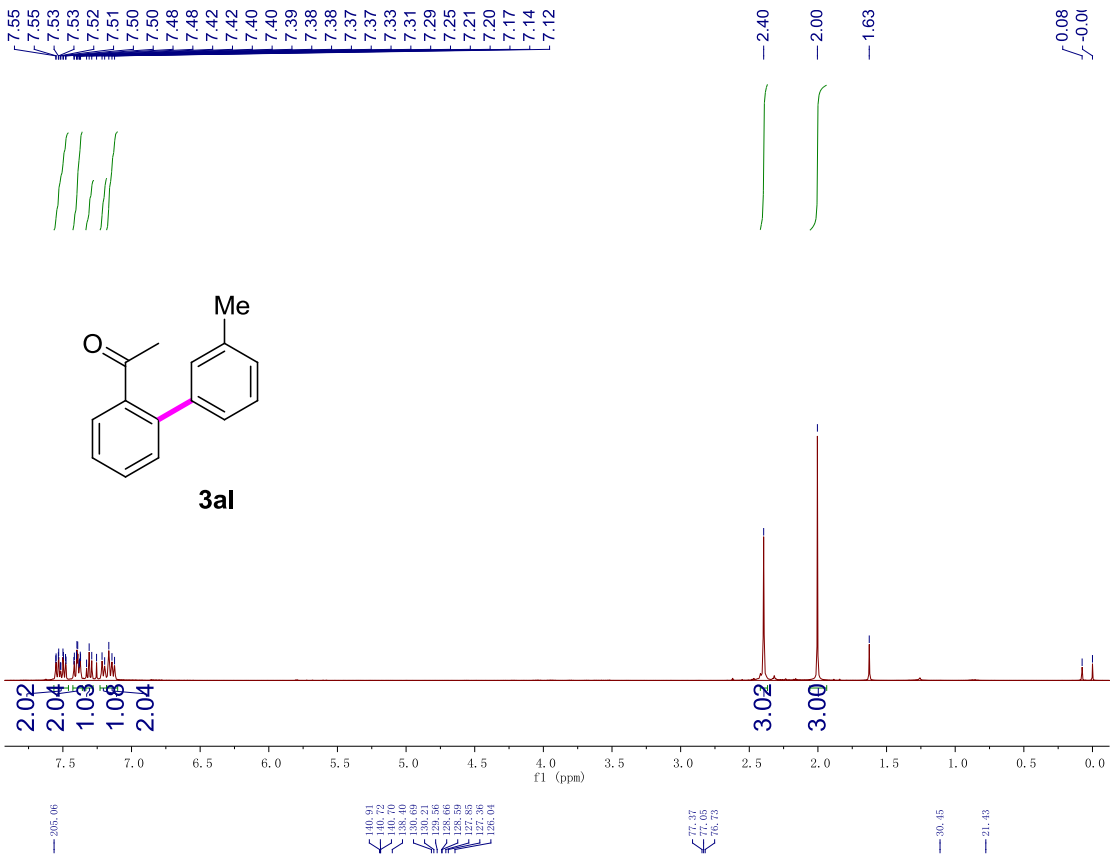

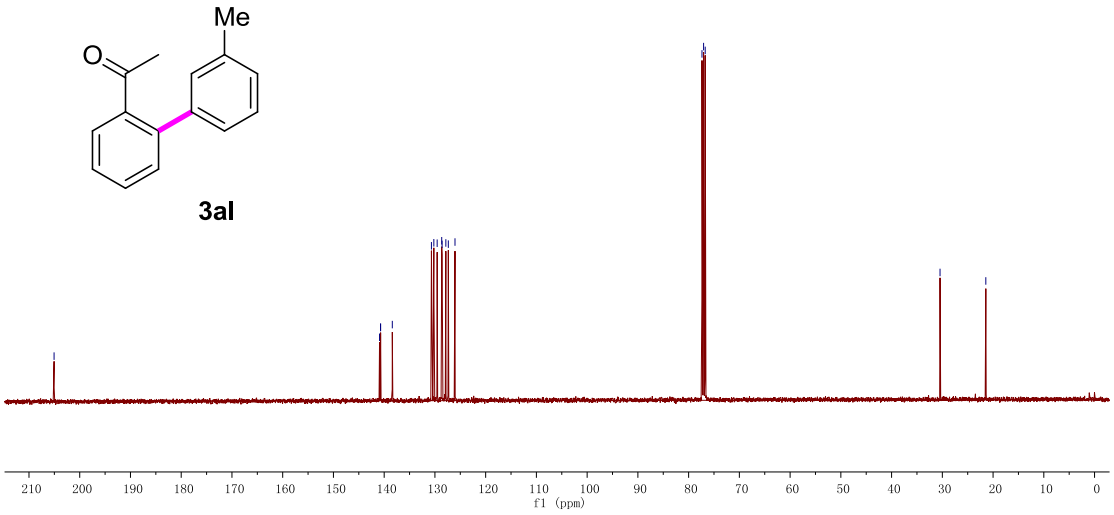

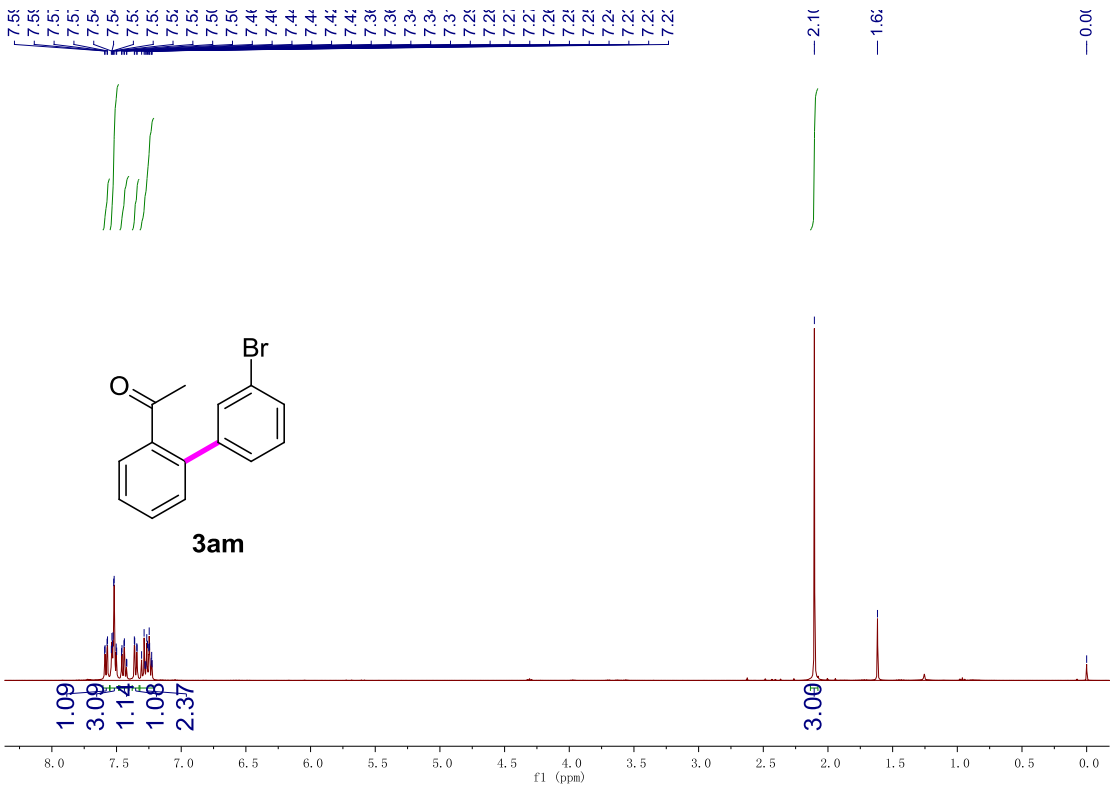

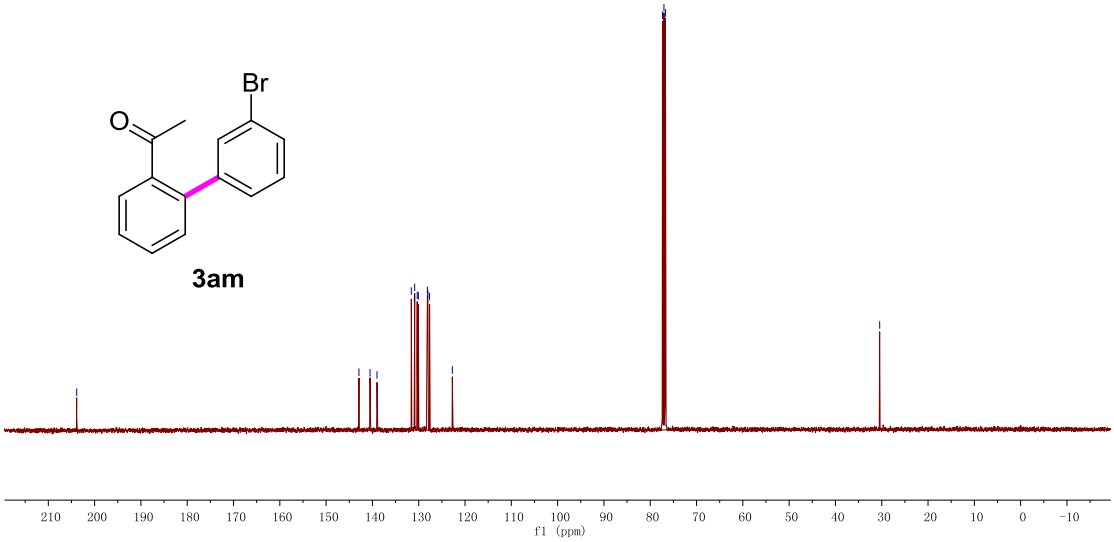

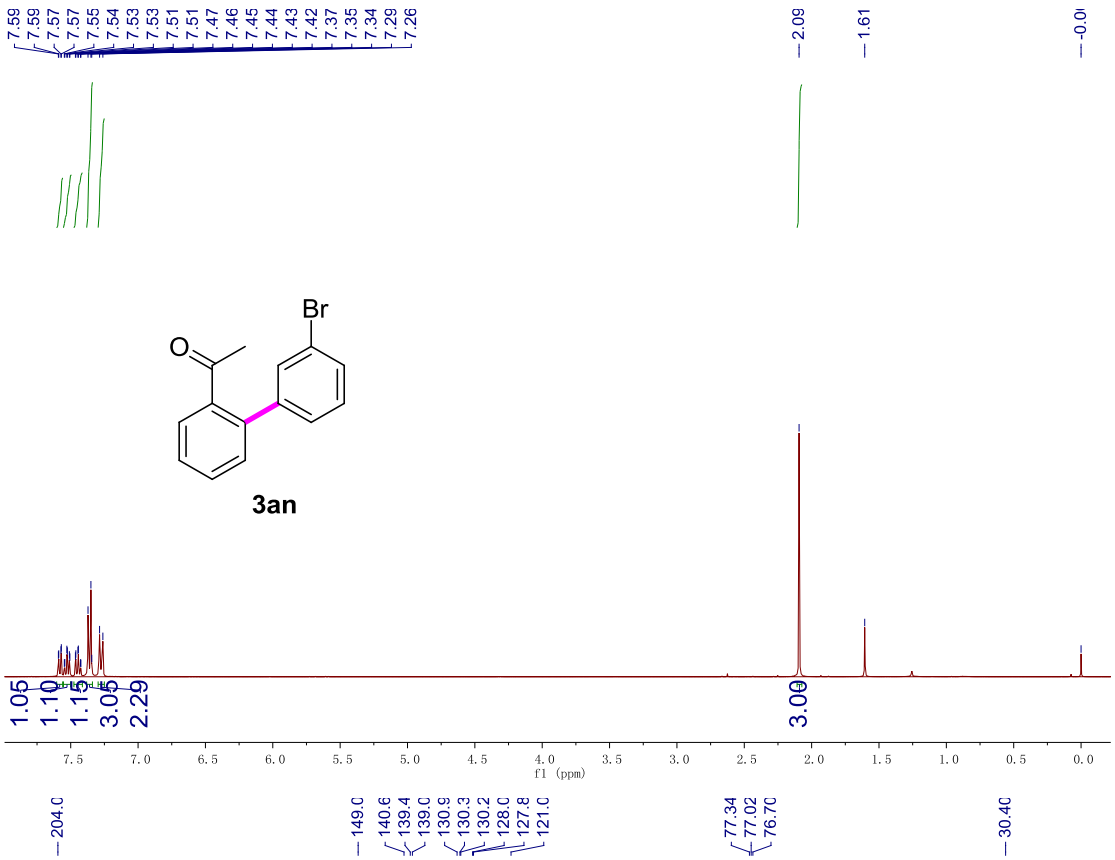

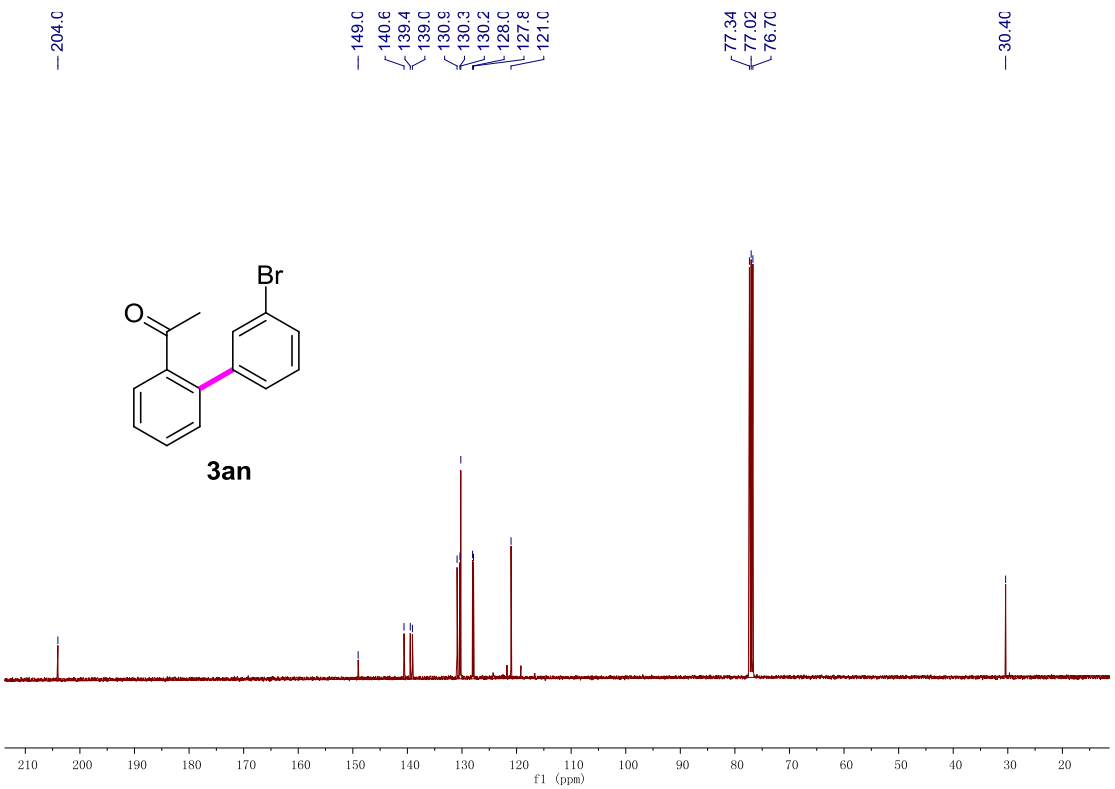

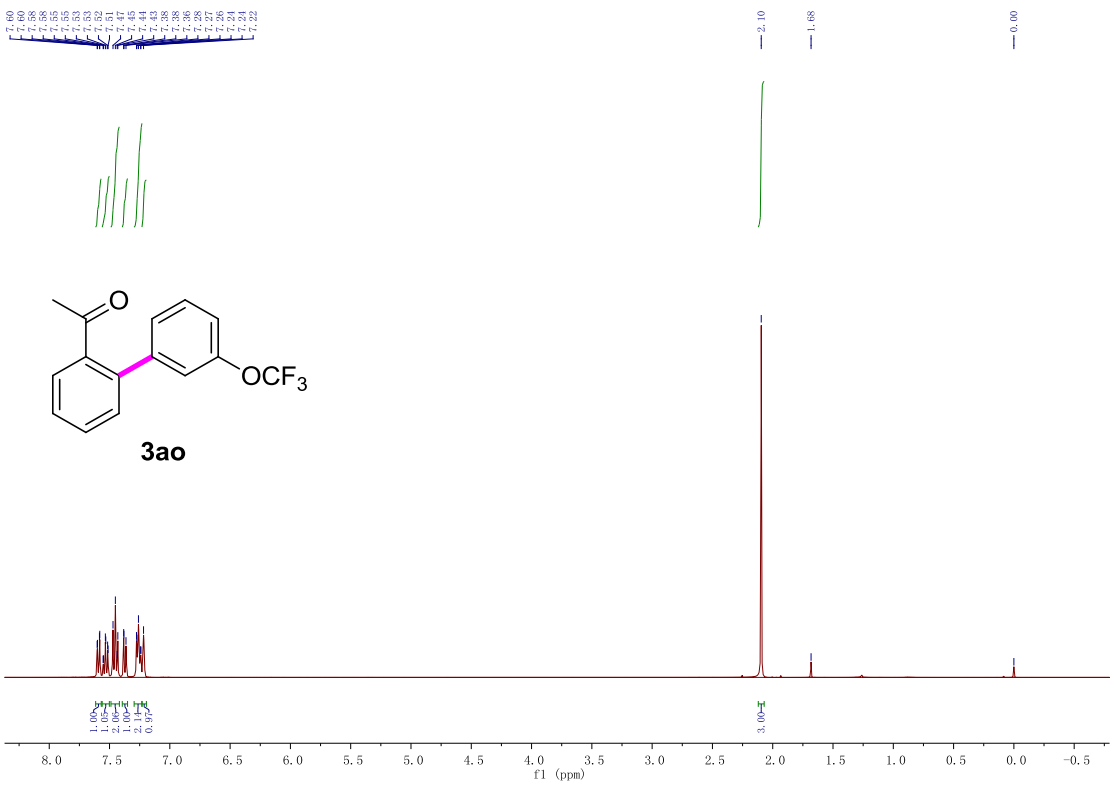

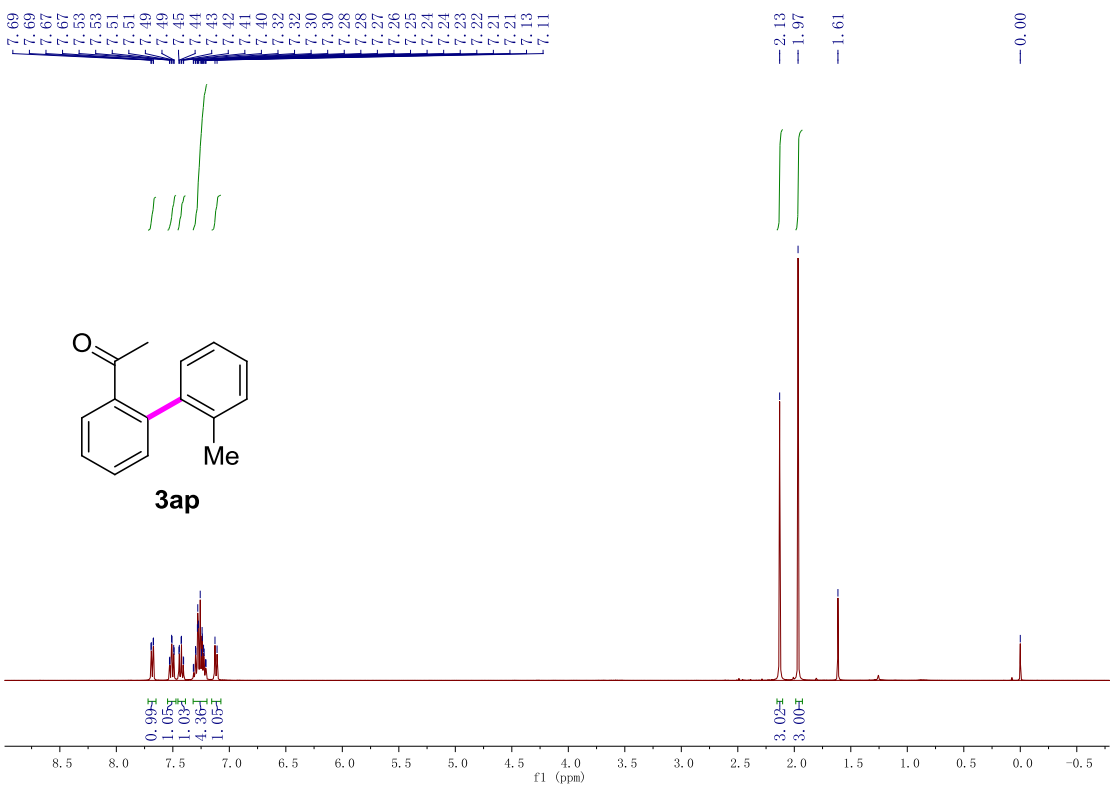

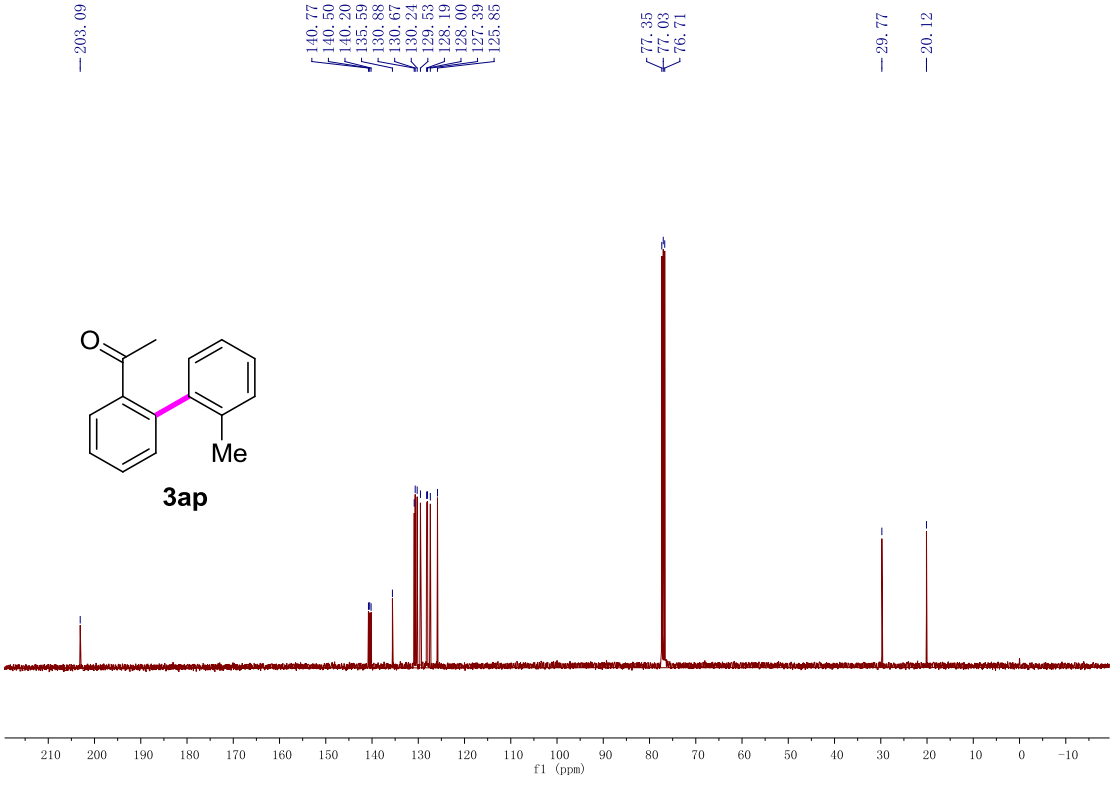

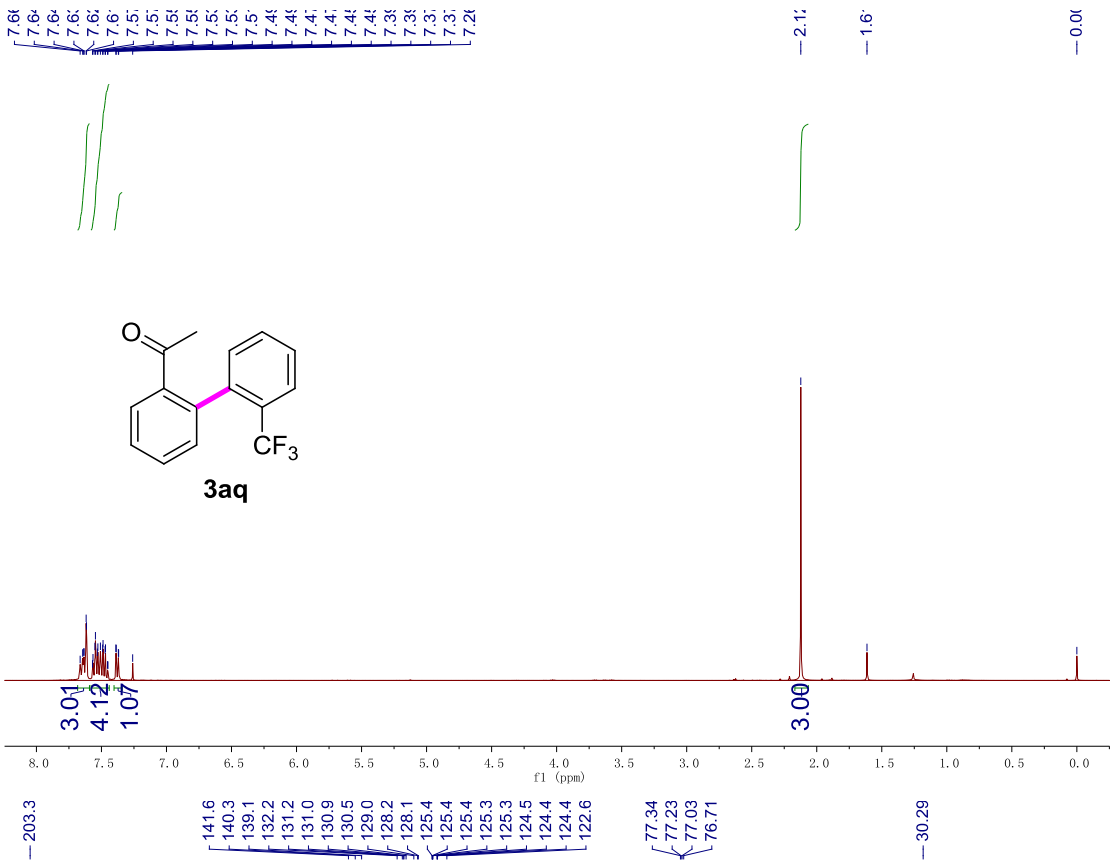
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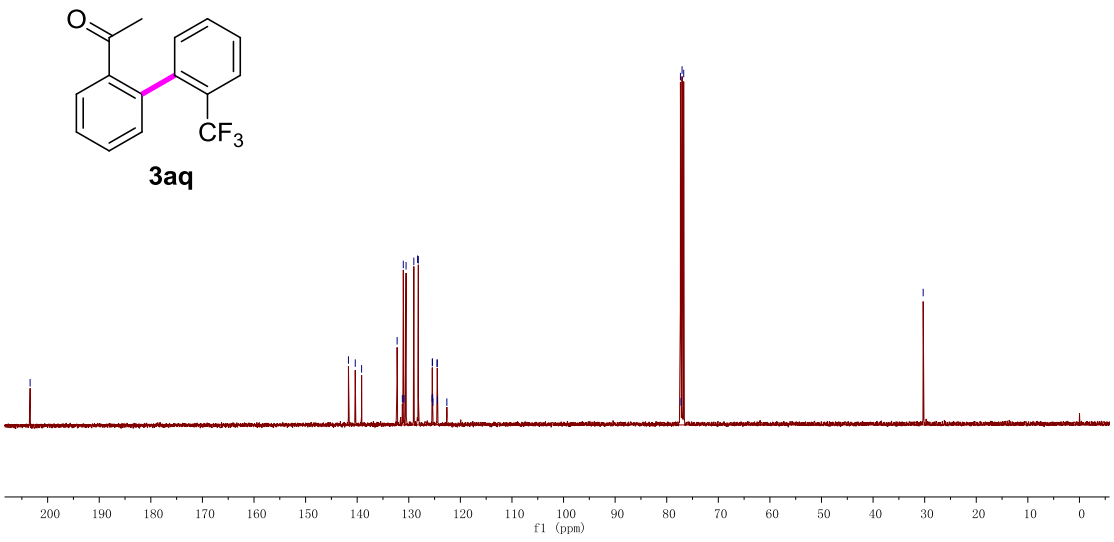
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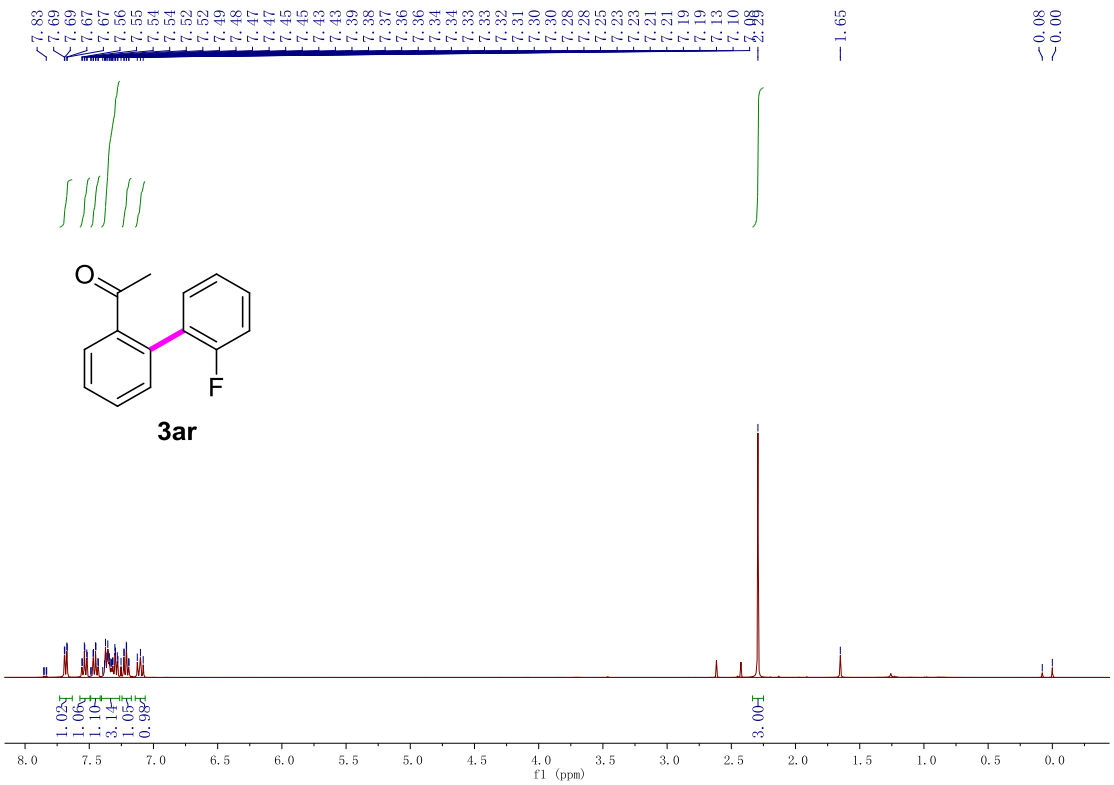

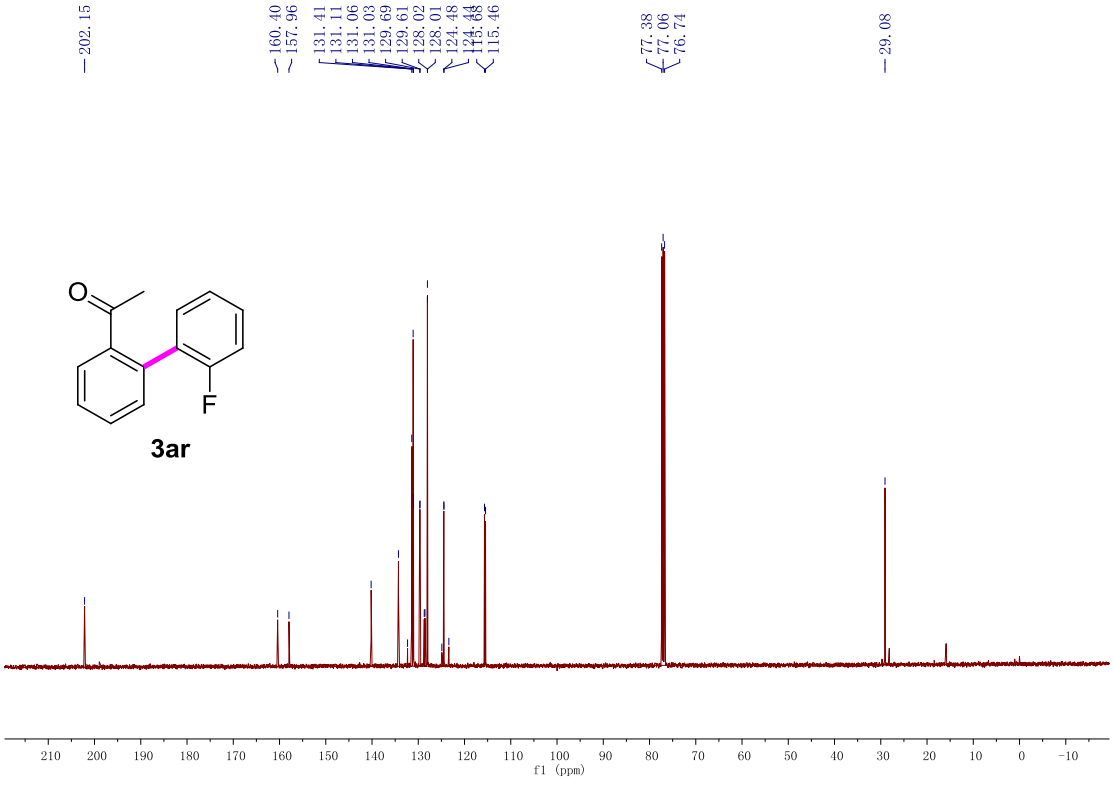

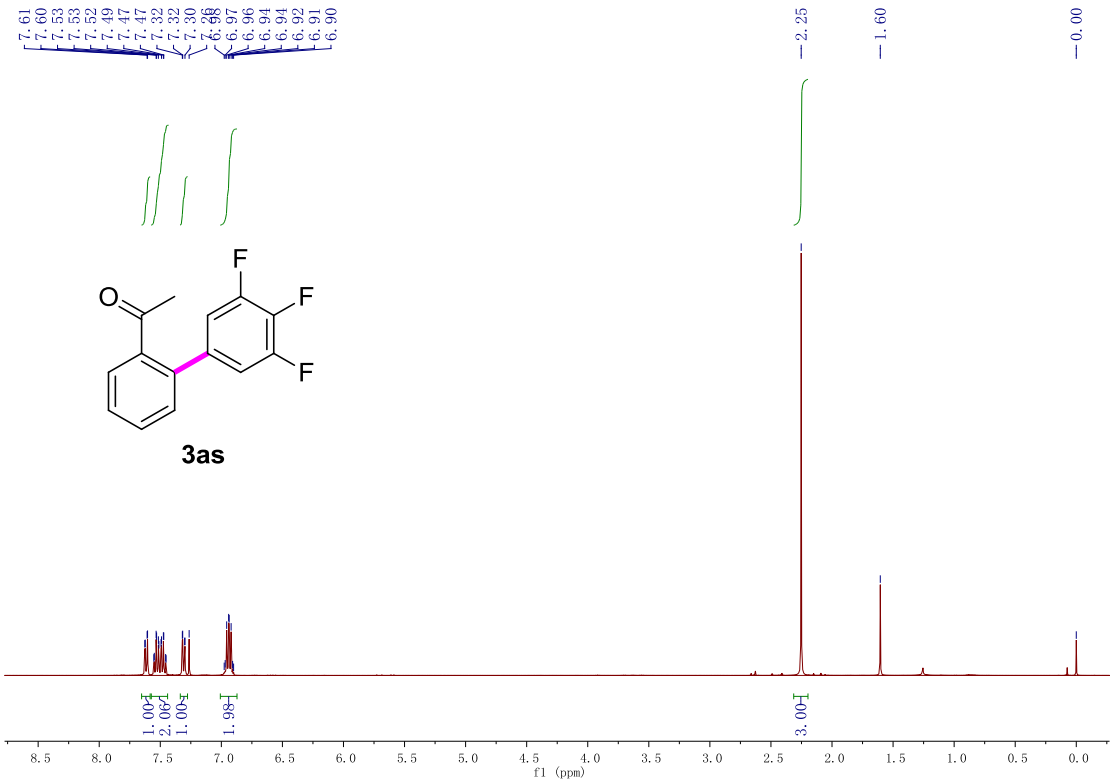

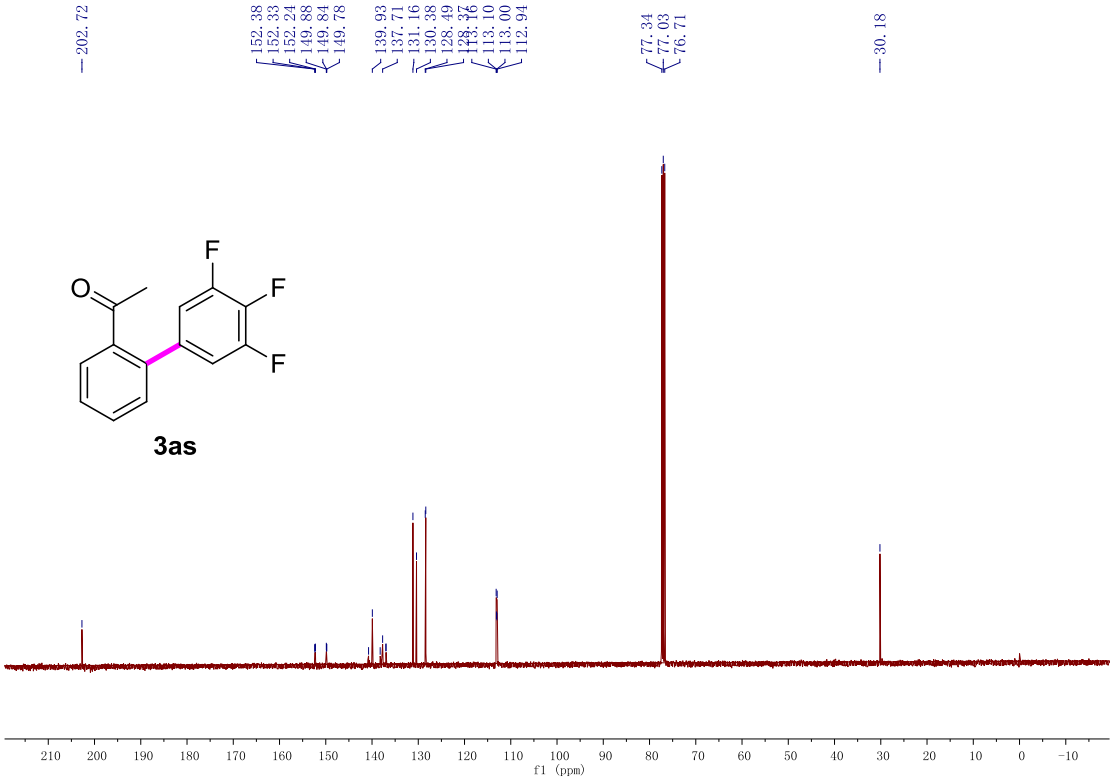

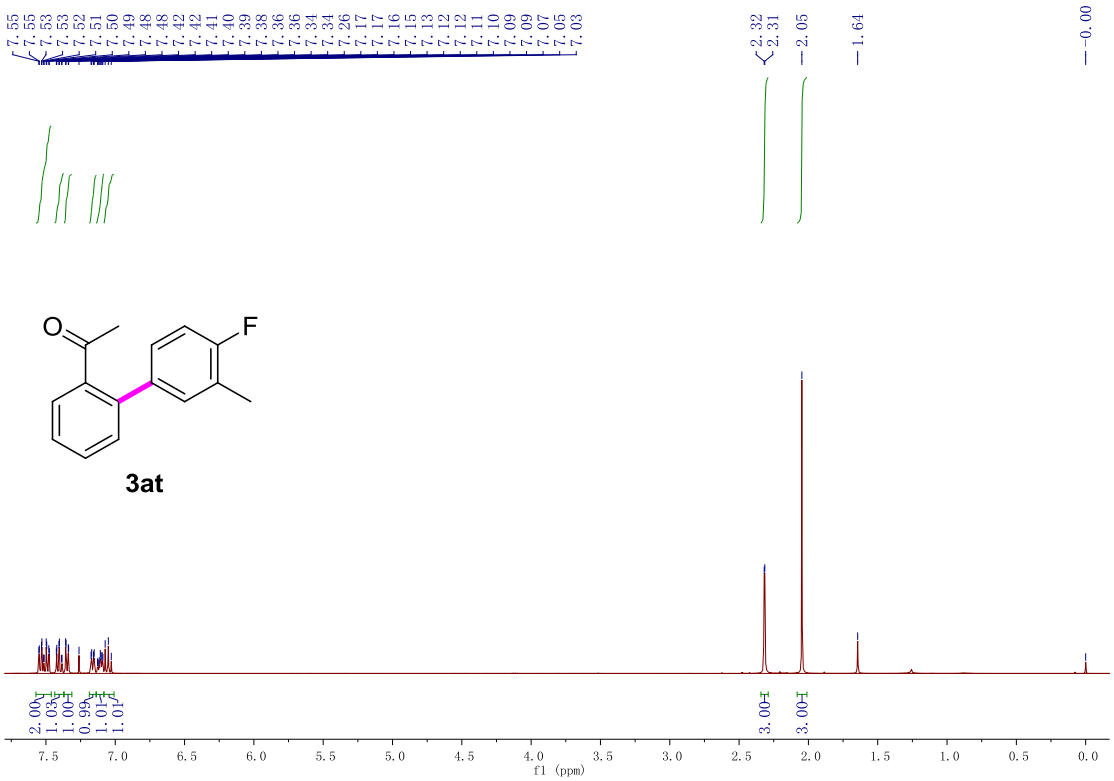
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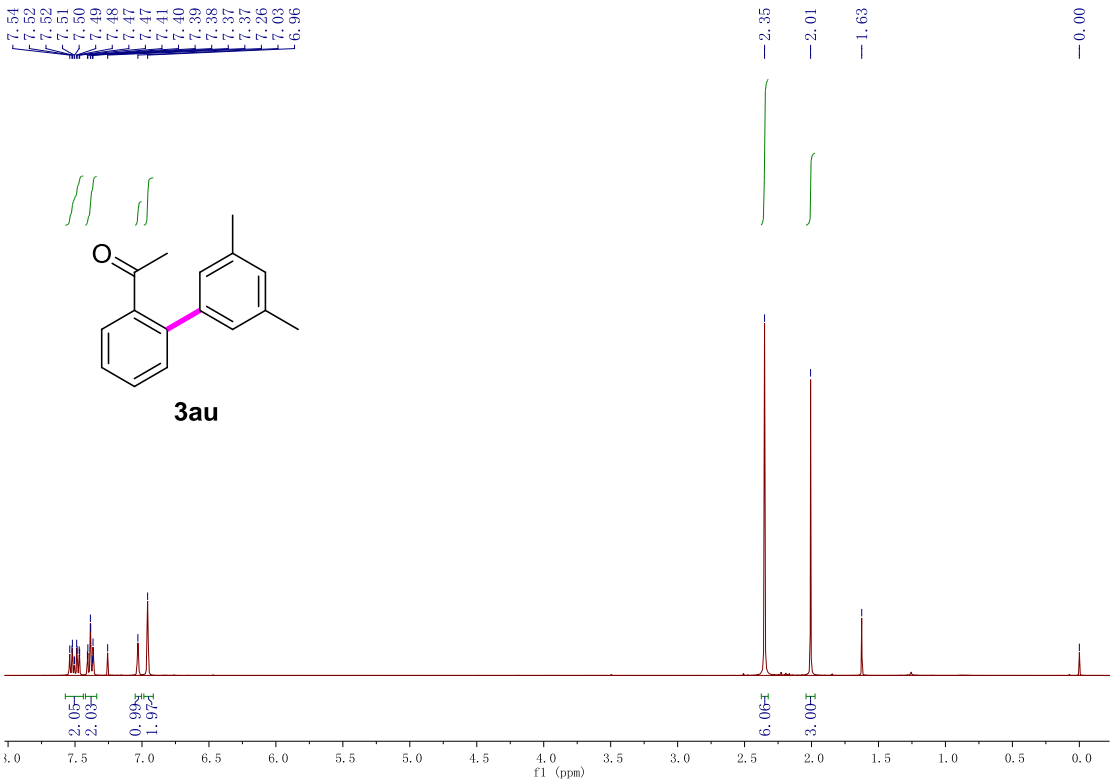
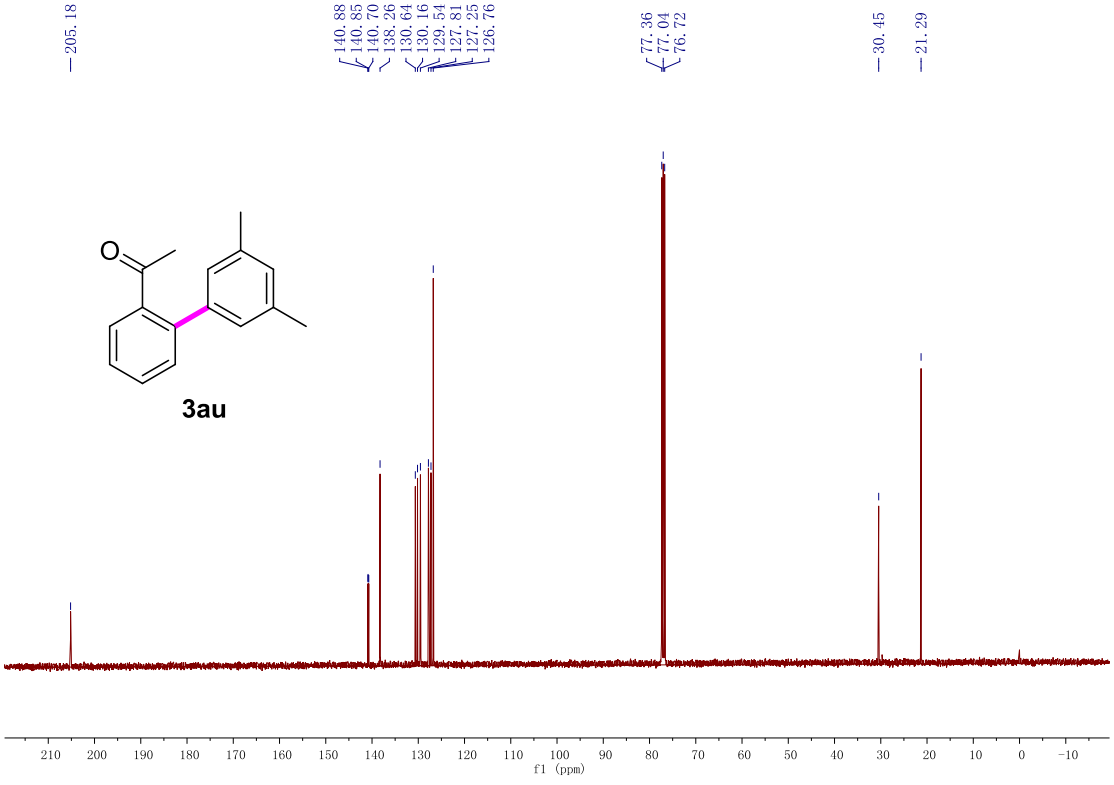
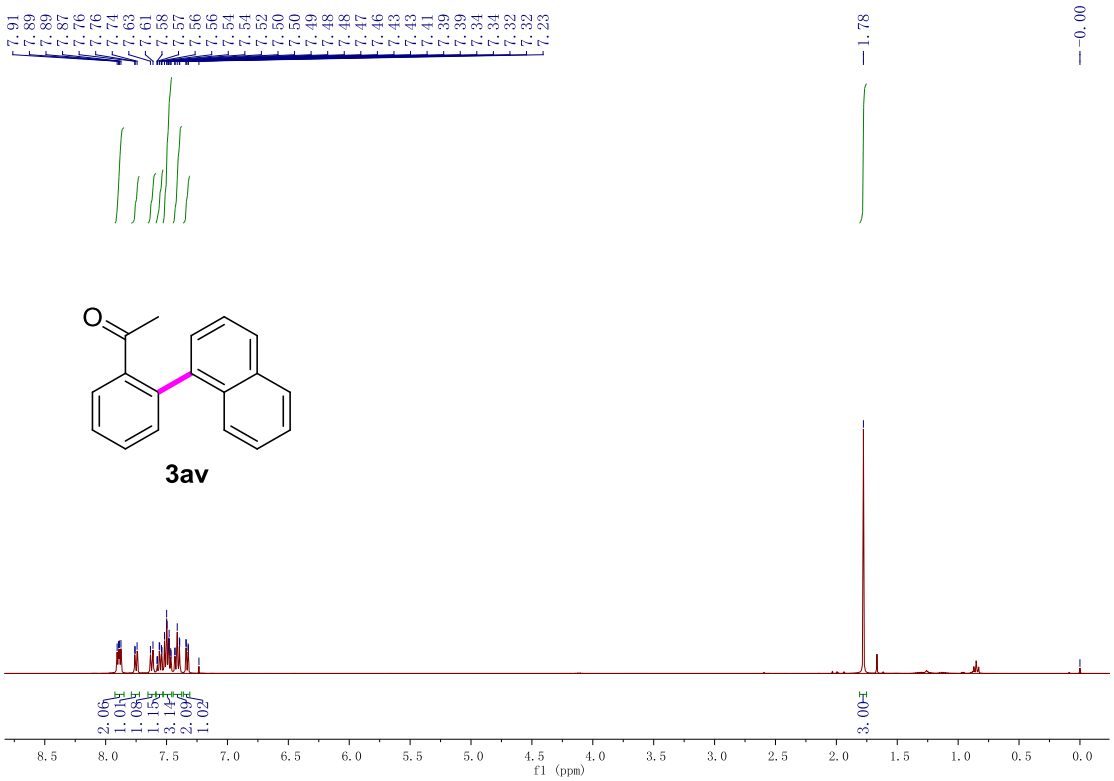
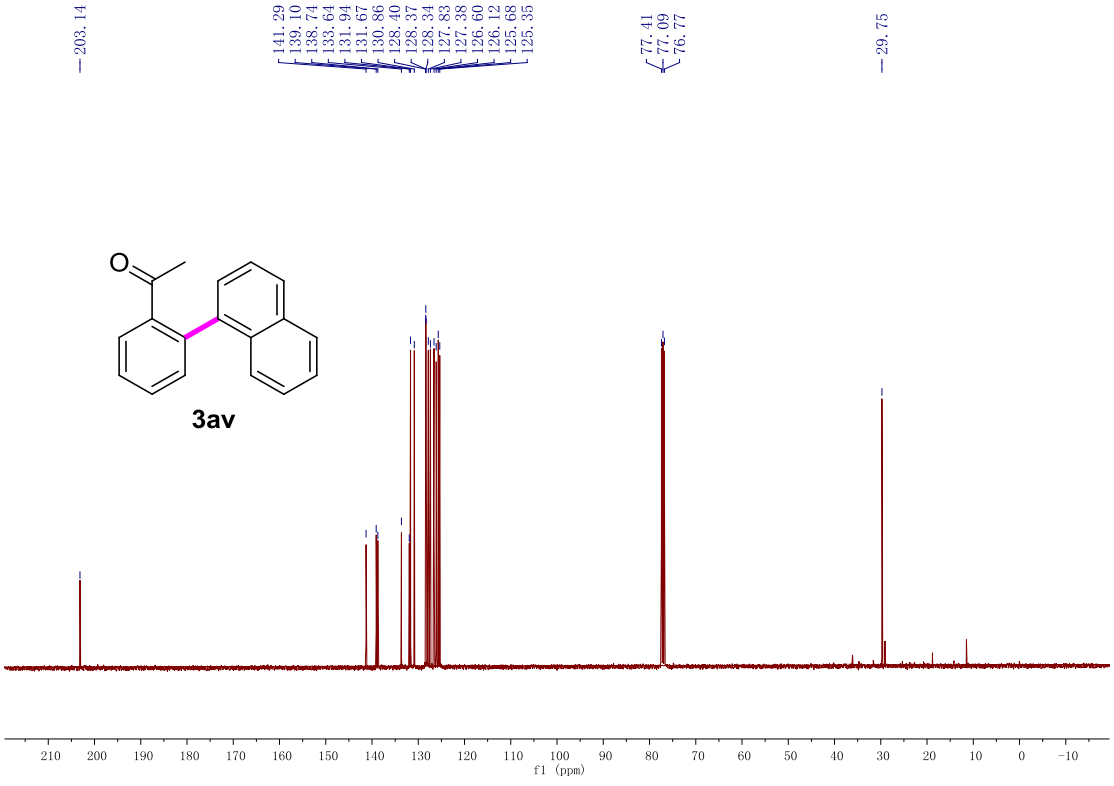
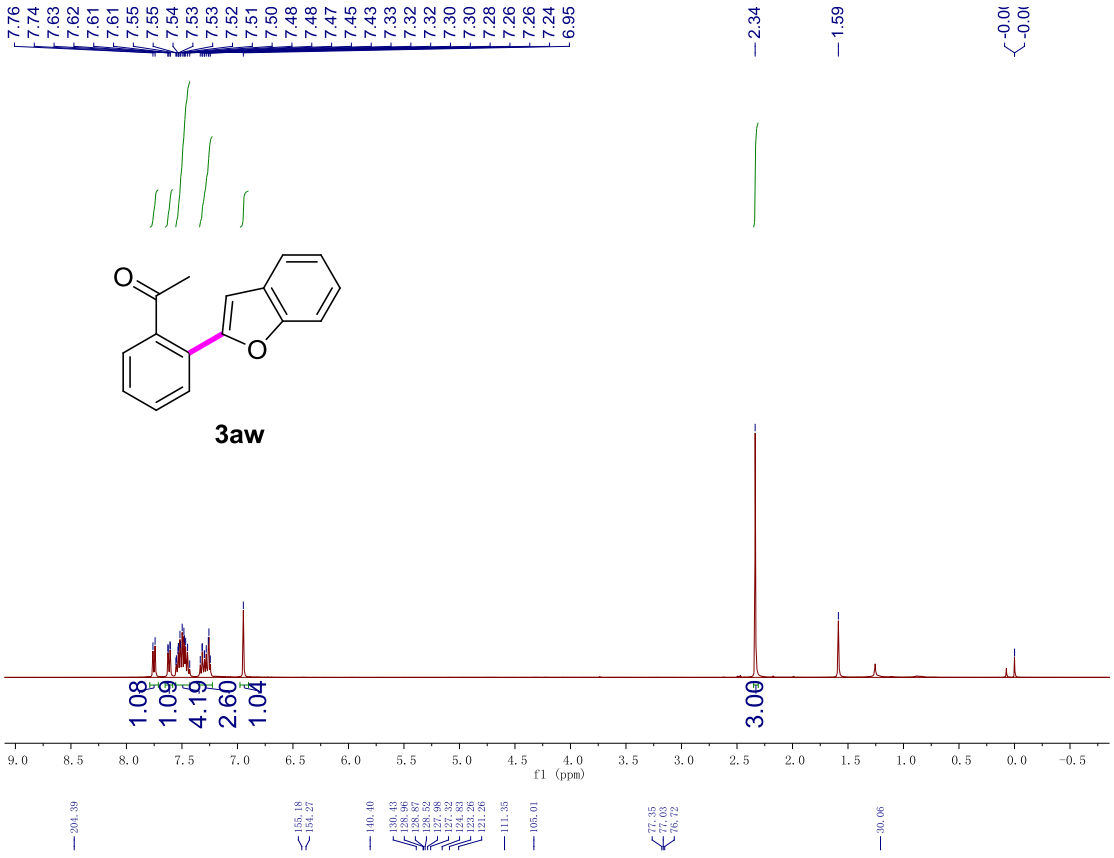
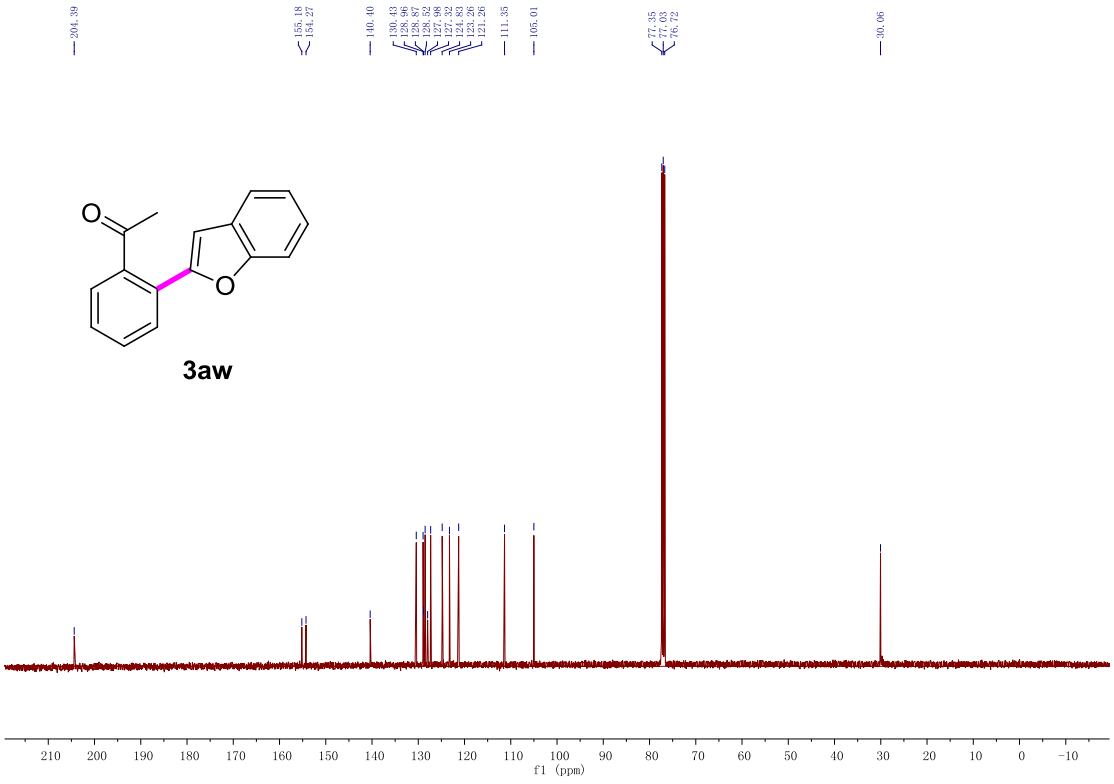


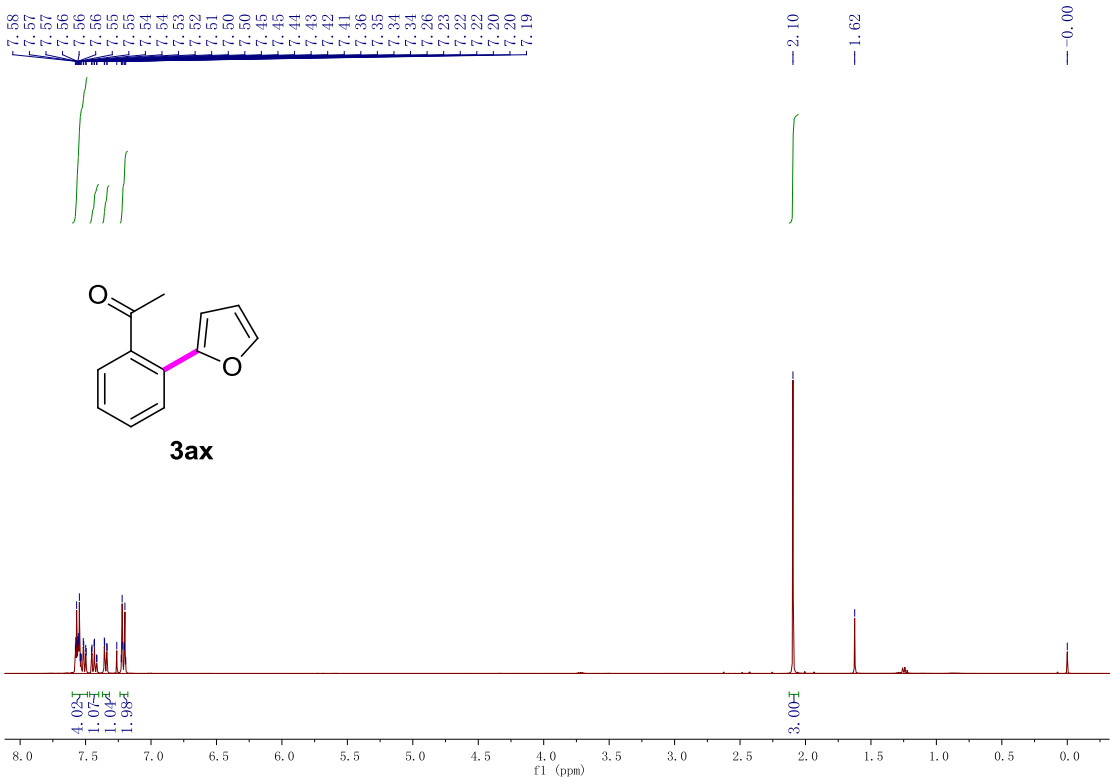


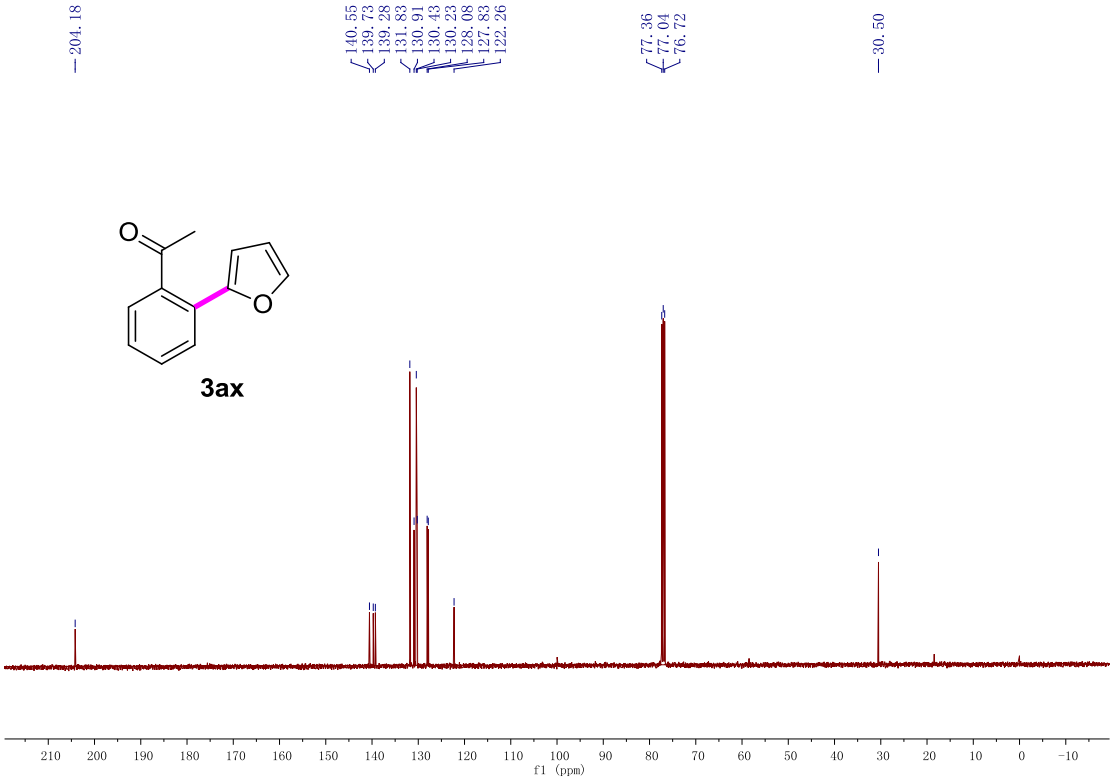


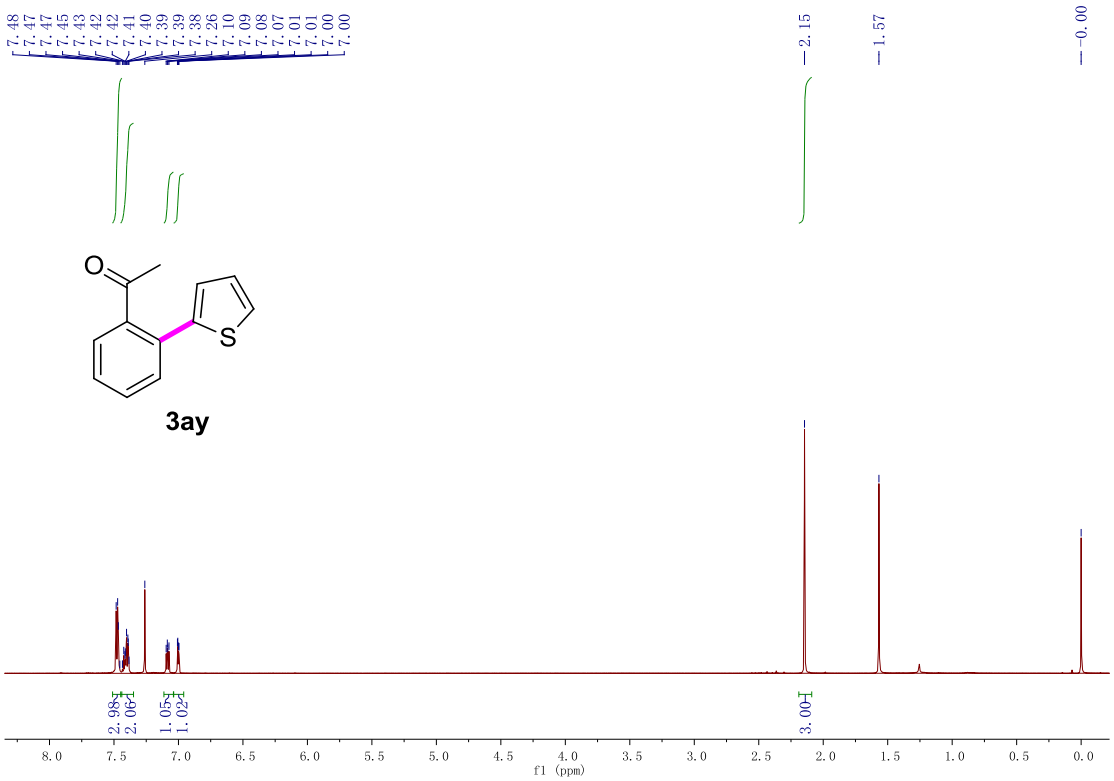


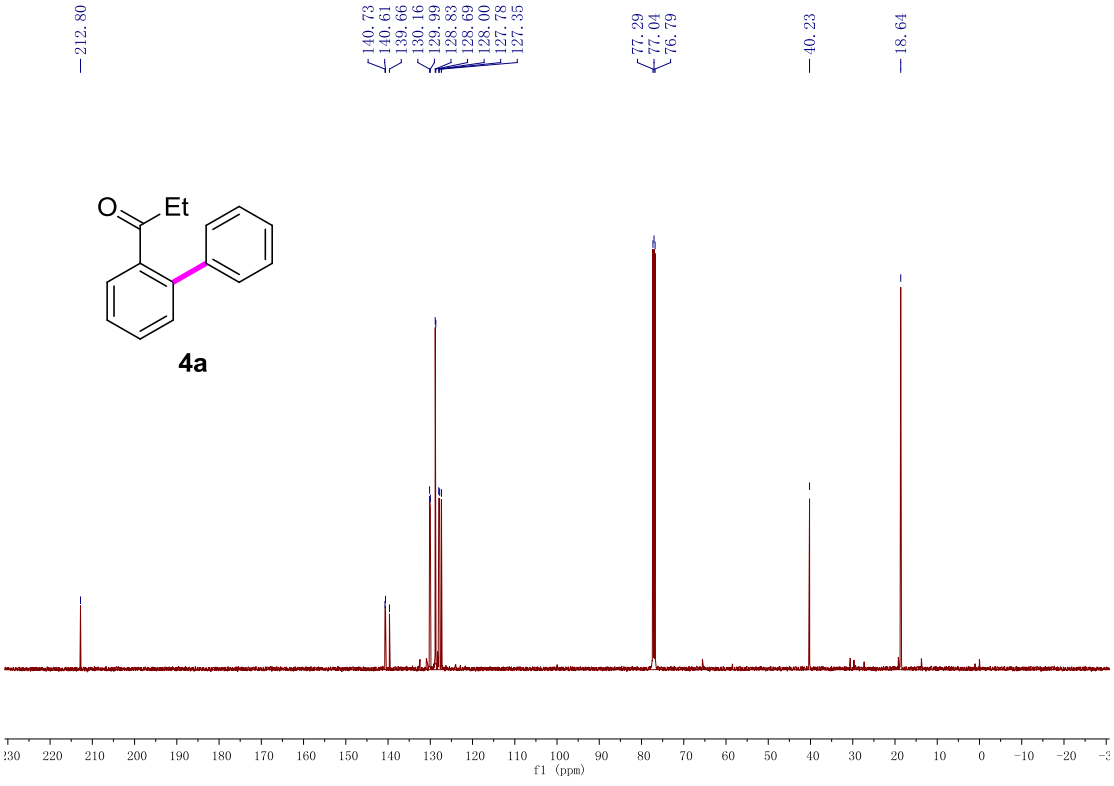


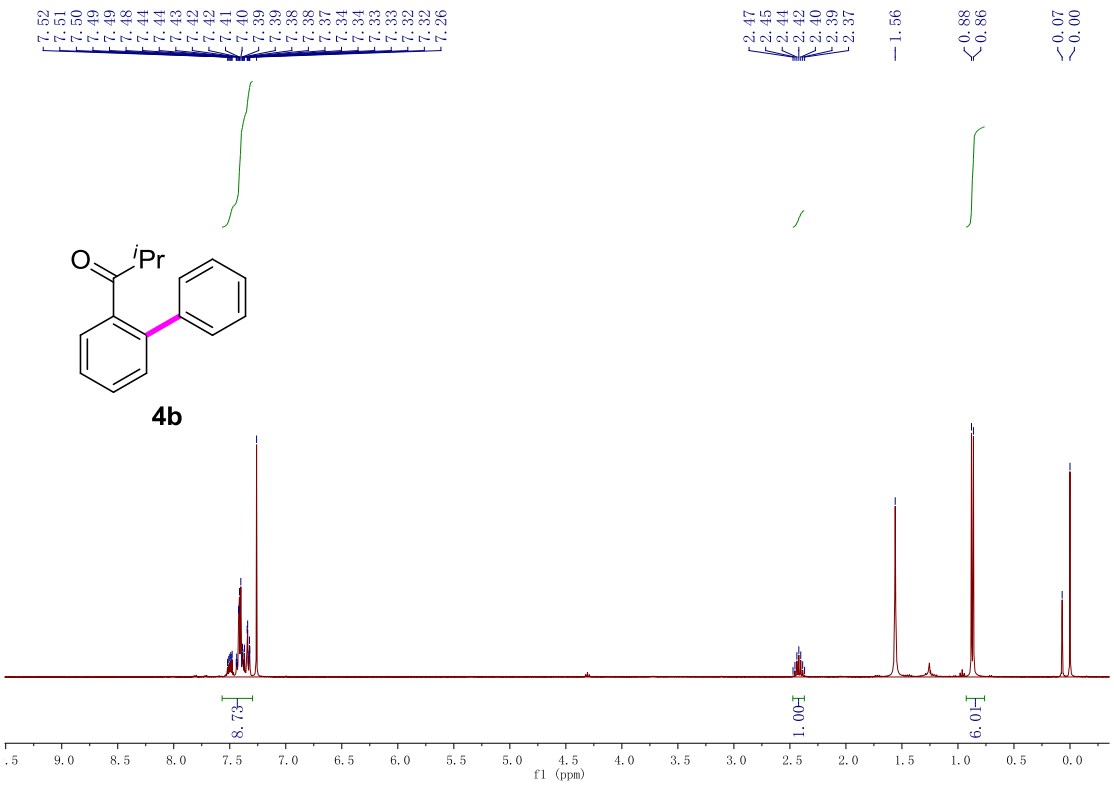


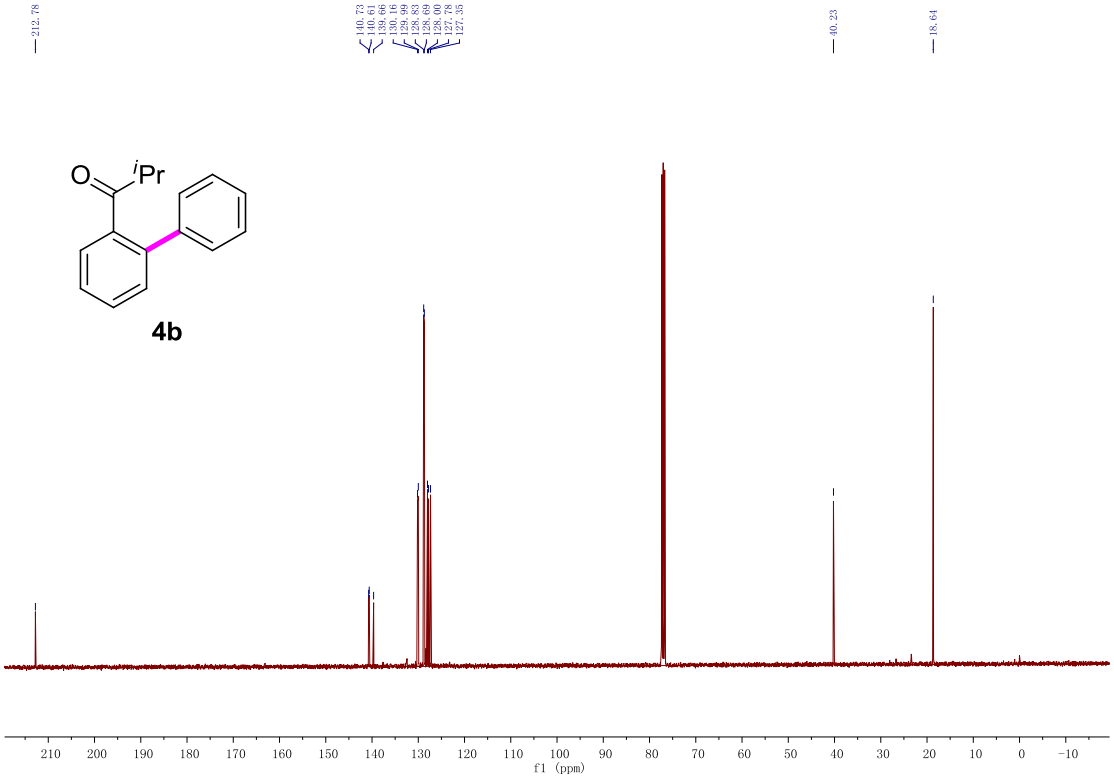


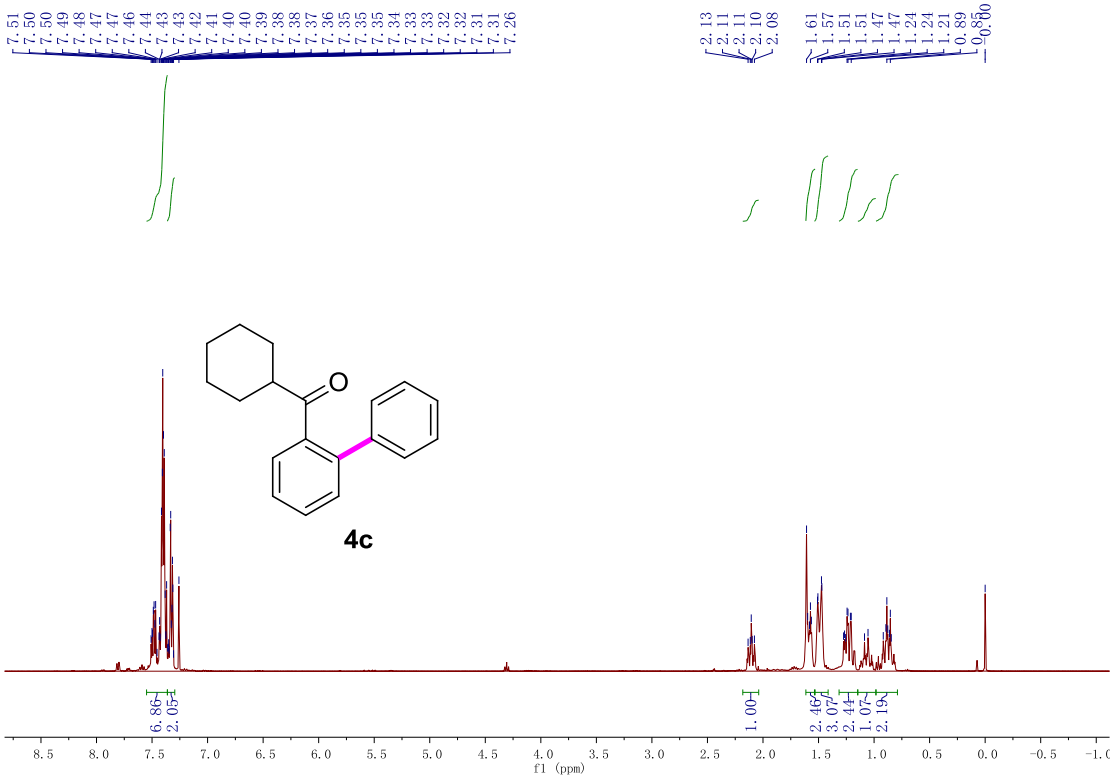


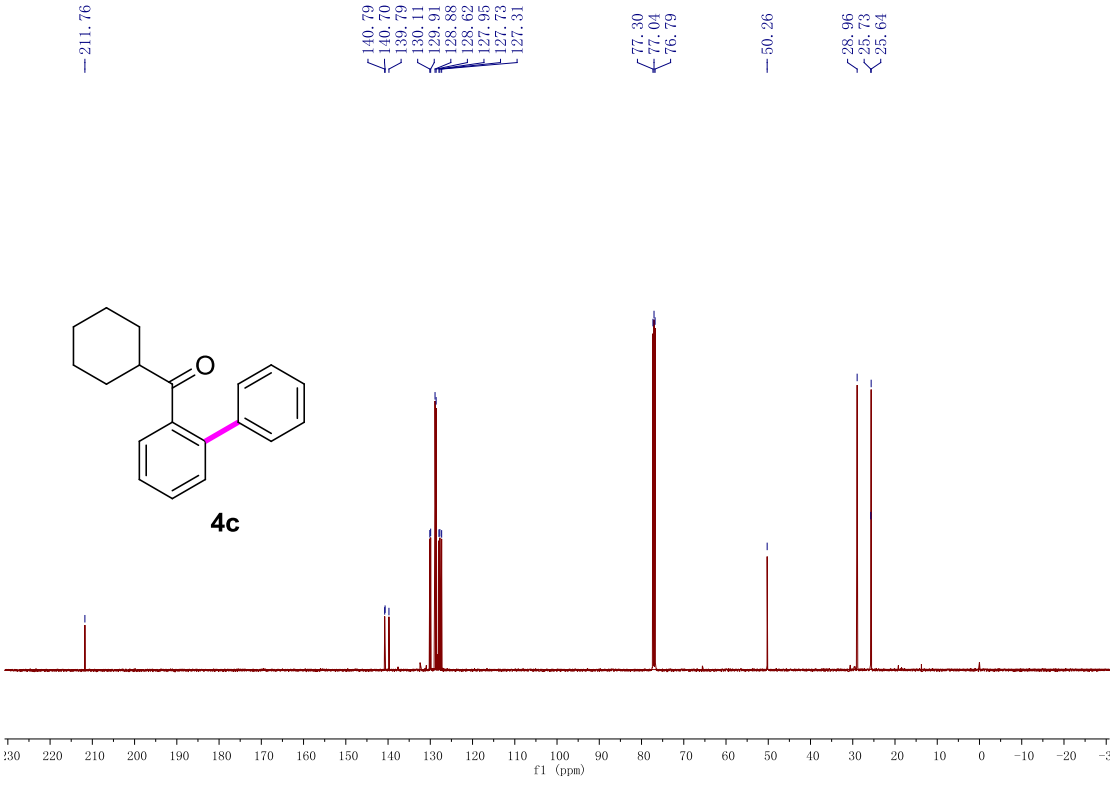


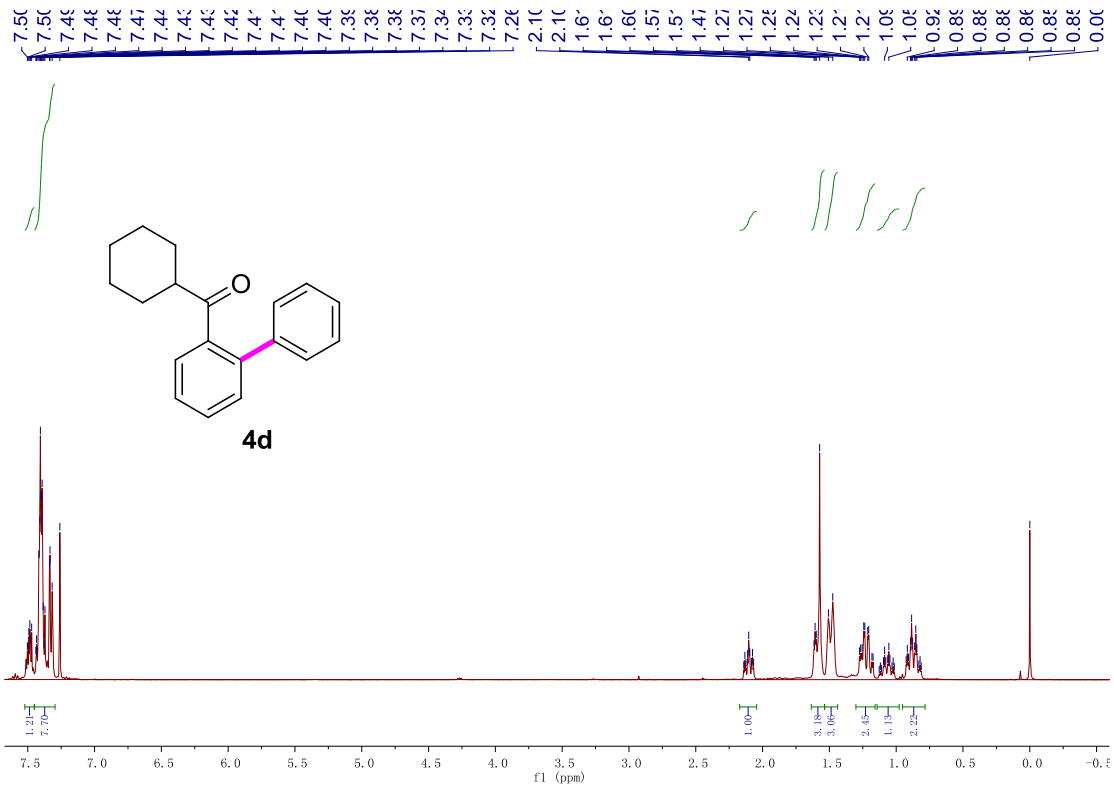


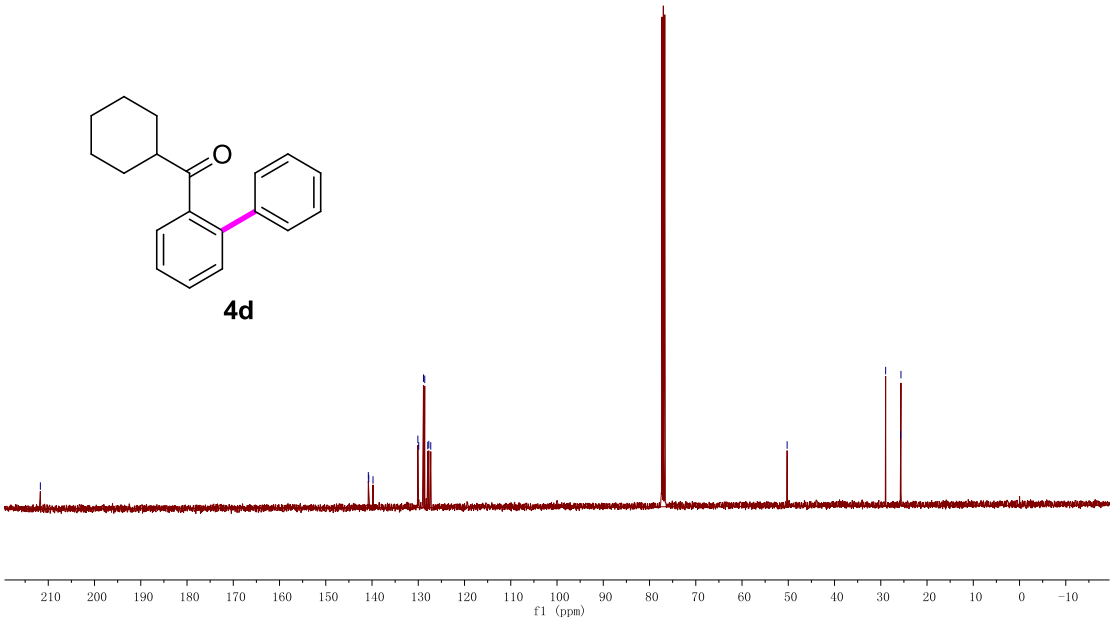


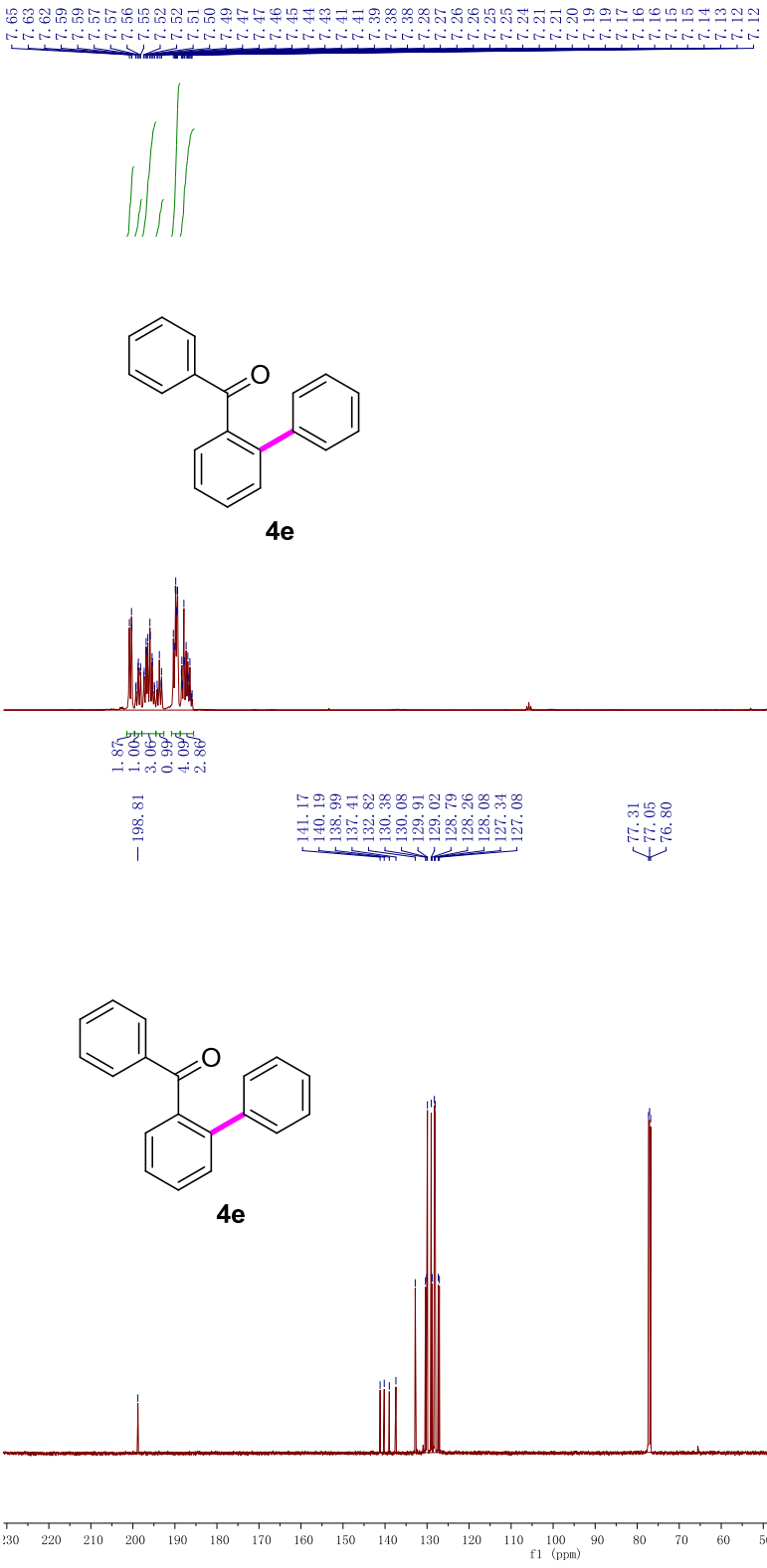


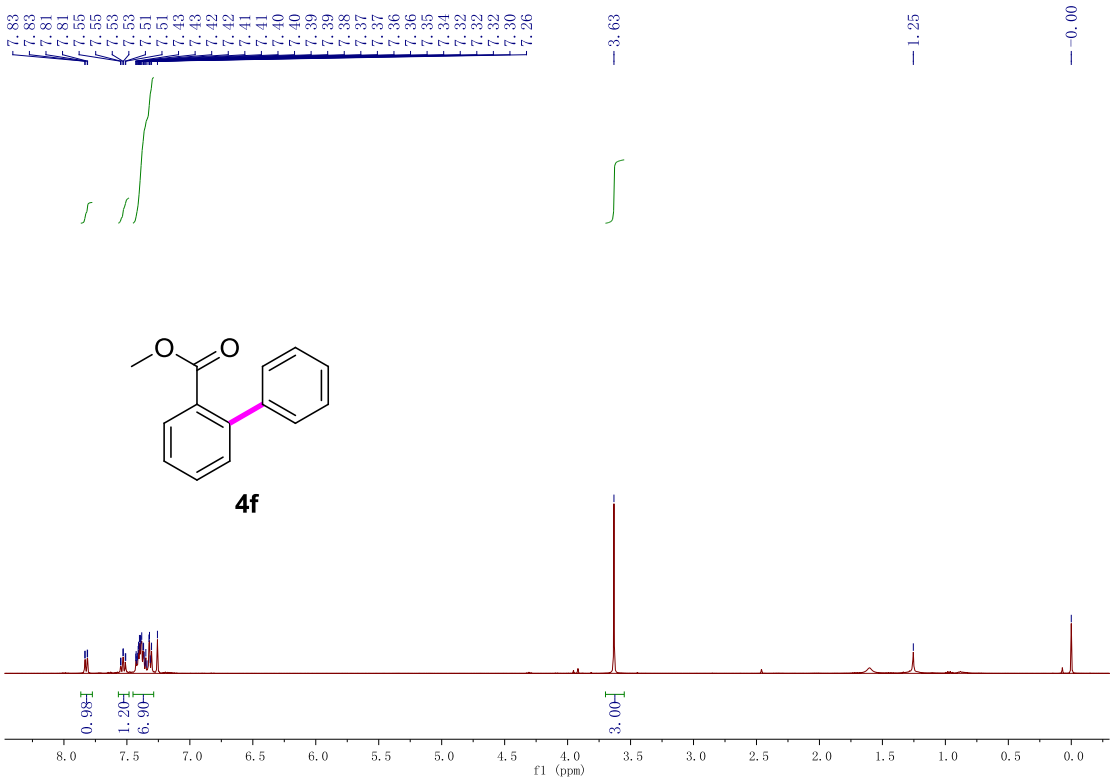


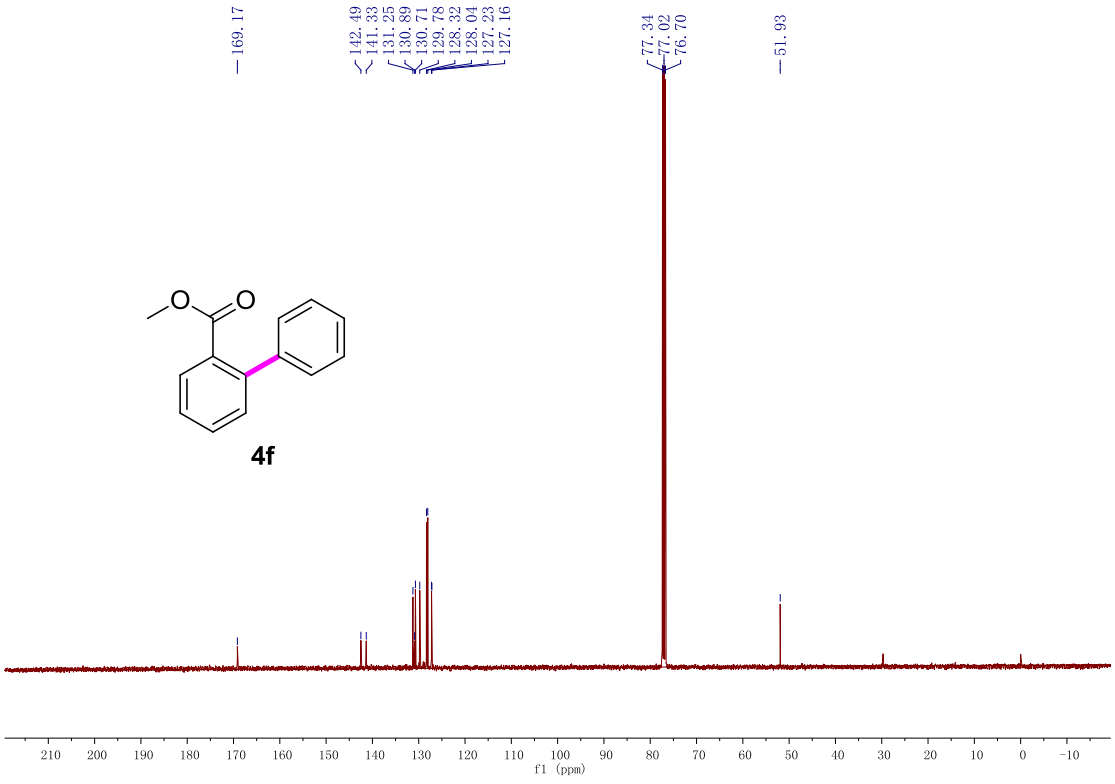


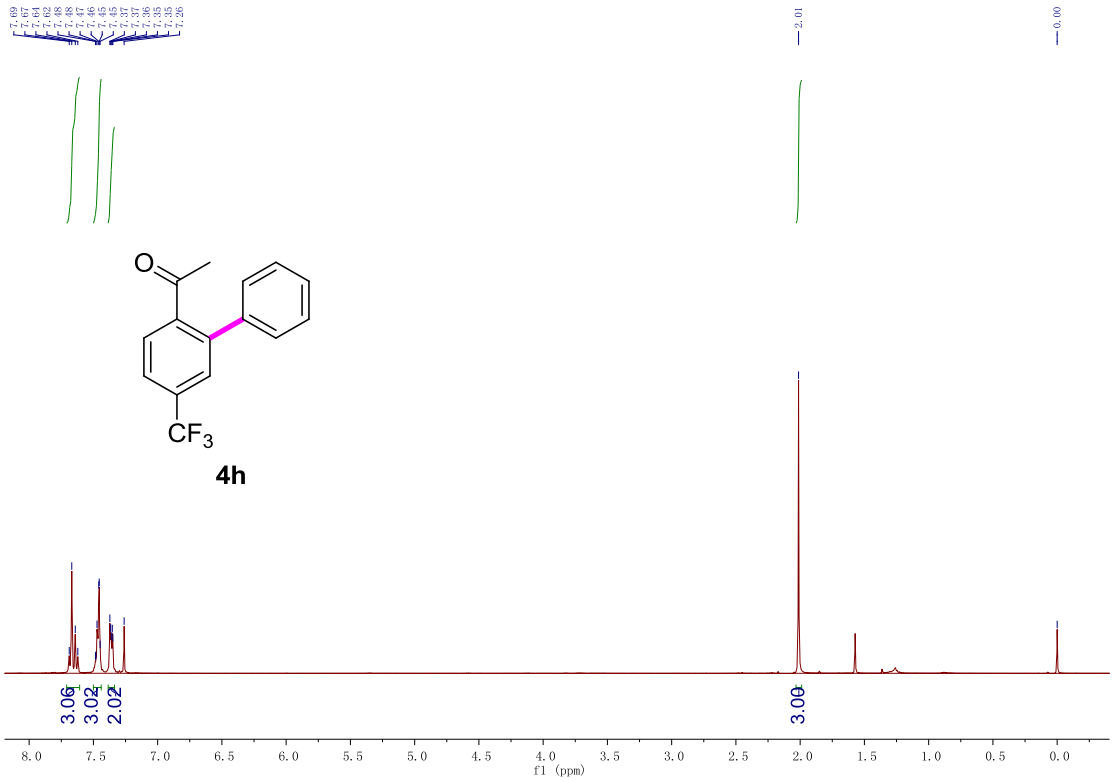


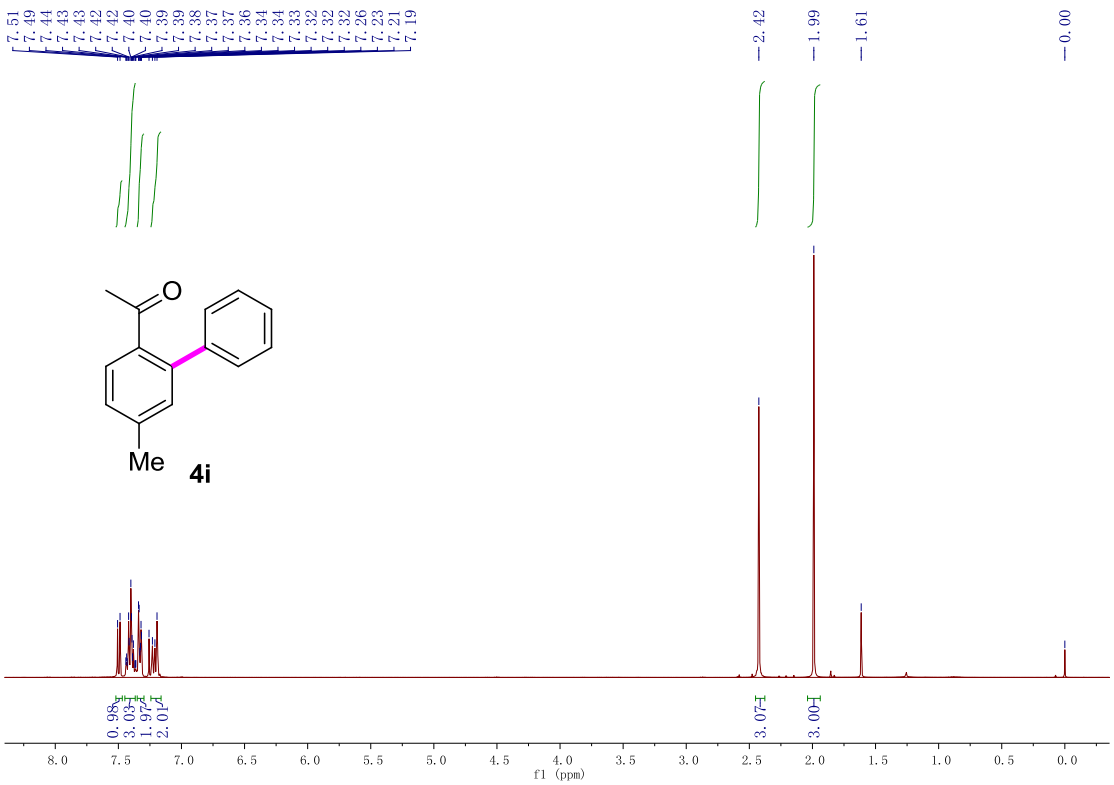


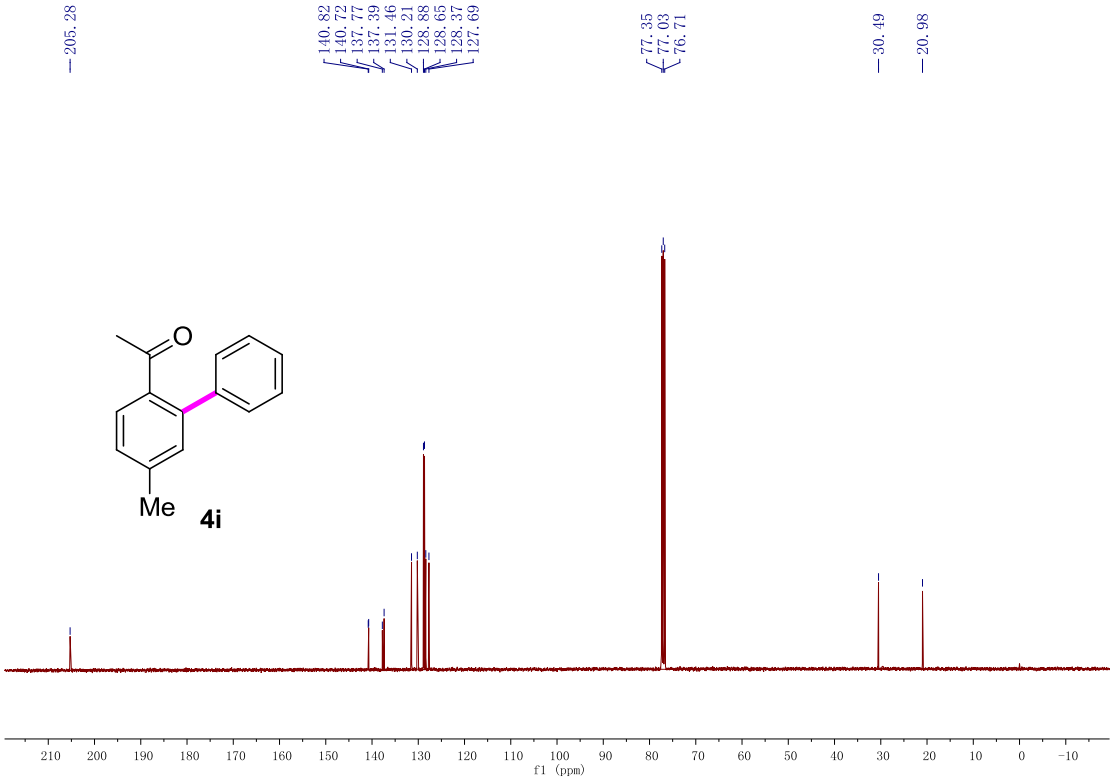

7.65 7.63 7.62 7.59 7.59 7.57 7.57 7.56 7.55 7.52 7.52 7.51 7.50 7.49 7.47 7.47 7.46 7.45 7.44 7.43 7.41 7.41 7.39 7.38 7.38 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.21 7.21 7.20 7.19 7.19 7.17 7.16 7.16 7.15 7.14 7.13 7.12 7.12
O
4e
1.87 1.00 3.06 0.99 4.09 2.80
198.81
141.17 140.19 138.99 137.41 132.82 130.38 130.08 129.91 129.02 128.79 128.26 128.08 127.34 127.08
77.31 77.05 76.80
O
4e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

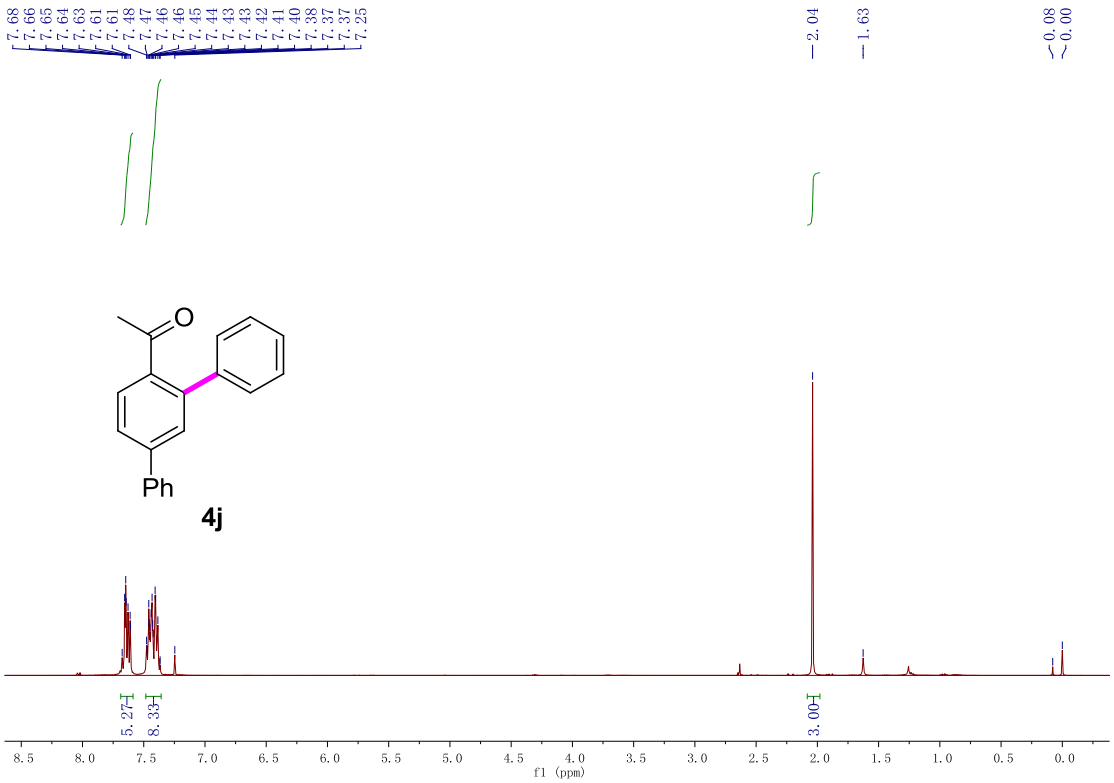


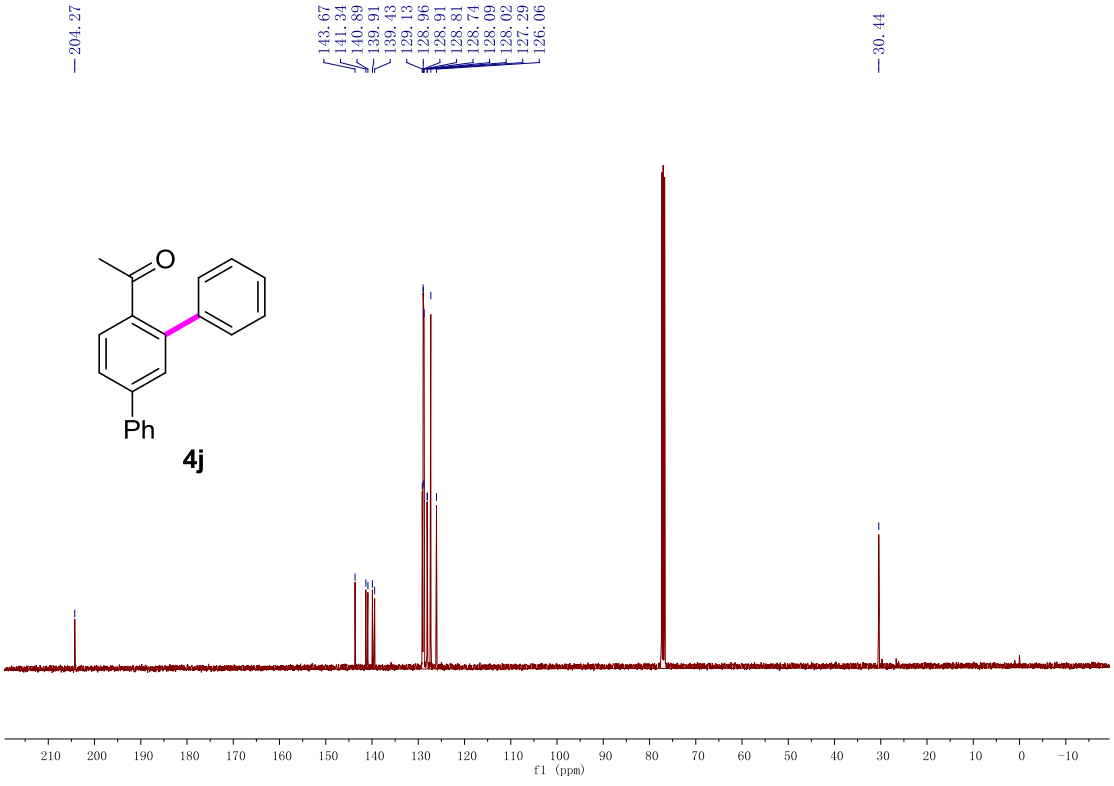


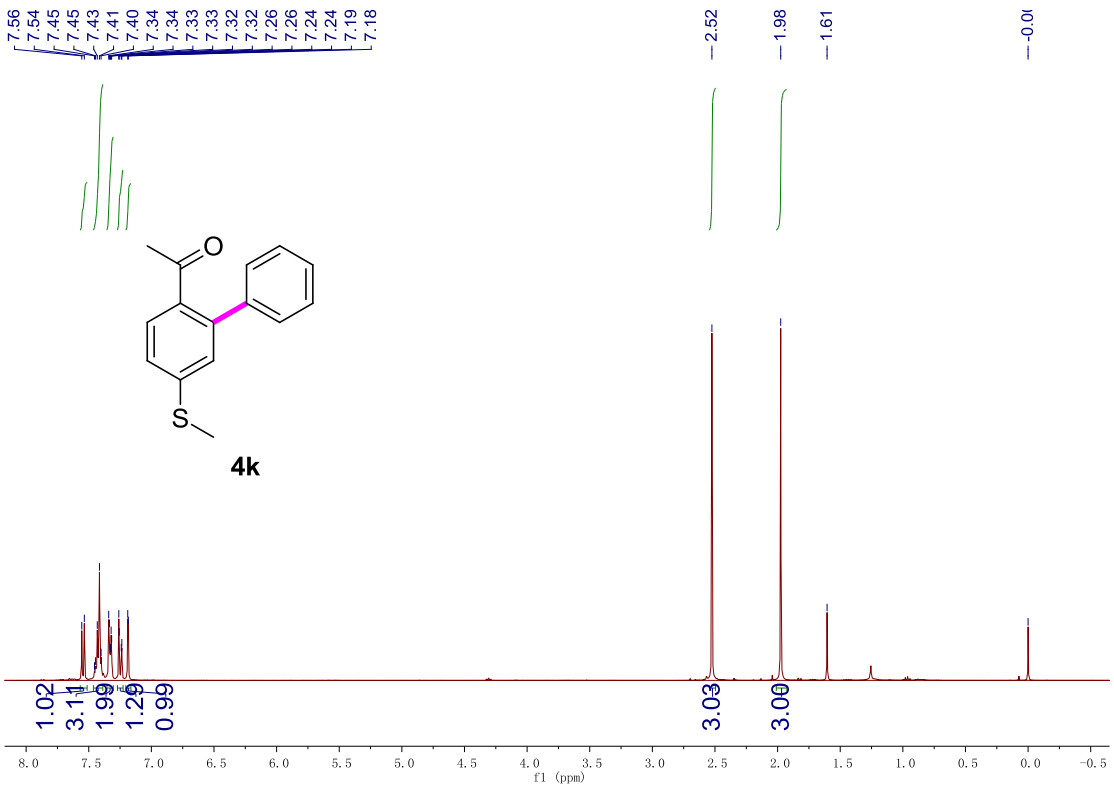


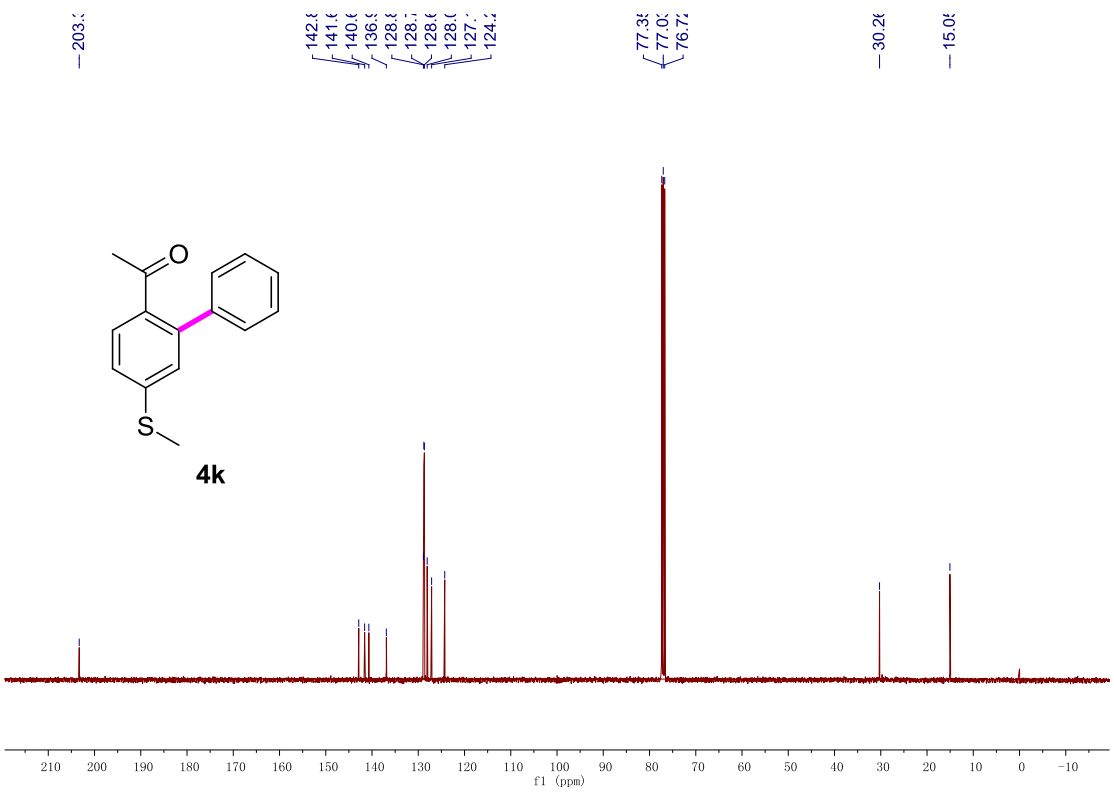









7.56
7.54
7.45
7.45
7.43
7.41
7.40
7.34
7.34
7.33
7.33
7.32
7.32
7.26
7.26
7.24
7.24
7.19
7.18
2.52
1.98
1.61
-0.0
O
S
4k
1.02
3.11
1.99
1.29
0.99
3.03
3.00
f1 (ppm)


203.
142.
141.
140.
136.
128.
128.
128.
128.
127.
124.
77.3
77.0
76.7
30.2
15.0
O
S
4k
f1 (ppm)