Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

A general electrochemical strategy for α-Arylation of Enol Acetates Using Aryl Diazonium Salts

Pengcheng Zhou,[*ab†] Yunlong Liu,[a†] Yingli Xu, and Dong Wang [*a]

Key Laboratory of Textile Fiber and Products/Ministry of Education, Wuhan Textile University, Wuhan 430200, P. R. China;
State key laboratory of New Materials and Advanced Processing Technologies, Wuhan Textile University, Wuhan 430200, P. R. China;
E-mail: pczhou@wtu.edu.cn, wangdon08@126.com

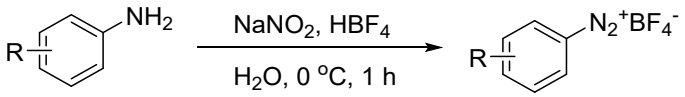
Table of Contents

1. General Information

The electrodes were purchased from Fanyuedianzi, Shanghai. Potentiostats (A-BF，SS-L303SPD) were purchased on JD.COM. Solvents were purchased from Sinopharm (China), in GR (or CCER). Purification of products was conducted by column chromatography on silica gel (200-300 mesh, for some cases 300-400 mesh were used, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (1H at 400 MHz, 13C at 100 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz). LC-MS spectra were recorded on SHIMADZU LC-MS 2020.

2. General Procedures

General Procedure A for the Synthesis of Aryl Diazonium Tetrafluoroborates



Compounds were prepared according to literature.[1] In a mixture of 5 mL of distilled water and 5 mL of 40% hydrofluoroboric acid was dissolved 10 mmol of the appropriate aniline. After the reaction mixture was cooled to 0 °C using an ice bath, a solution of sodium nitrite in distilled water (0.69 g in 1.5 mL) was added dropwise. The suspension was stirred for an additional 40 min and then filtered, and the resulting solid was redissolved in a minimum amount of acetone. Diethyl ether was added until precipitation of diazonium tetrafluoroborate, which was filtered, washed several times with diethyl ether, and dried under vacuum.

General Procedure B for the Synthesis of Enol Acetates. Compounds were prepared according to literature.[2] To a mixture of the ketone (50 mmol) and 2-propenyl acetate (250 mol) was added p-toluenesulfonic acid (3.6 mmol). The resulting mixture was refluxed overnight and afterward cooled to rt. The solvent was evaporated in vacuo. Diethyl ether (100 mL) was added, and the organic layer was subsequently washed with H_2O (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The resulting crude mixture was purified by column chromatography on SiO_2 (50% CH_2Cl_2 in hexane) for aromatic products and by fractionated distillation under reduced pressure for aliphatic products.

General Procedure C for the Electrocatalytic Arylation of Enol Acetates. In a single-necked flask (15 mL) equipped with a stir bar, aryl diazonium tetrafluoroborate (0.50 mmol), enol acetates (5.0 mmol), $LiClO_4$ (212 mg, 2.0 mmol) and MeCN/DMSO (v/v=5:1, 10 mL) were combined and added. The bottle was equipped with platinum plate electrode (10 ×10 mm^2) as the anode and RVC (reticulated vitreous carbon) plate electrode (10×10 mm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. When the reaction was finished, the solution was extracted with EtOAc and H_2O. The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (5:1).

General Procedure D for the One Pot Diazotization/Electrochemical Reaction

In a single-necked flask (15 mL) equipped with a stir bar, aryl amine (0.50 mmol) was dissolved in the MeCN (8.3 mL). The reaction mixture was cooled to 0 °C, then HBF_4 (50% in Et_2O, 0.525 mmol) and *t*BuONO (90%, 0.525 mmol) was added and the reaction mixture was stirred at 0 °C for 30 min. After that, $LiClO_4$ (2 mmol, 212 mg) and enol acetates (5 mmol) were dissolved in the DMSO (1.6 mL) and were added to the mixture. The bottle was equipped with platinum plate electrode (10 ×10 mm^2) as the anode and RVC (reticulated vitreous carbon) plate electrode (10×10 mm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. When the reaction was finished, the solution was extracted with EtOAc and H_2O. The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (5:1).

Procedure E for Gram Scale Synthesis: In a single-necked flask (250 mL) equipped with a stir bar, aryl diazonium tetrafluoroborate (10 mmol), isopropenyl acetate **2a** (100 mmol), $LiClO_4$ (4.24 g, 40 mmol) and MeCN/DMSO (v/v=5:1, 200 mL) were combined and added. The bottle was equipped with platinum plate electrode (30 ×30 mm^2) as the anode and RVC (reticulated vitreous carbon) plate electrode (30×30 mm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 90 mA under room temperature for 8 h. When the reaction was finished, the solution was extracted with EtOAc and H_2O. The combined organic layer was dried

with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (5:1).

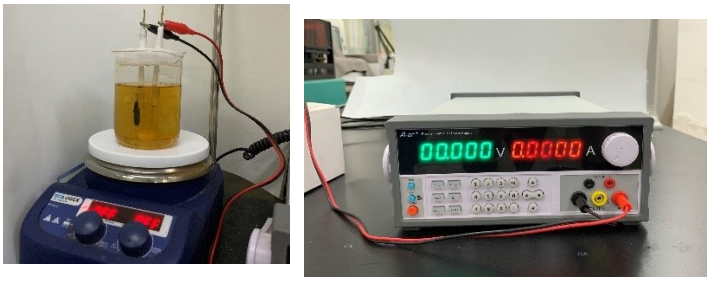
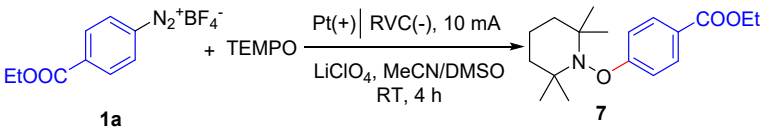


Fig. S1 Scale-up experiment equipment.

3. Preliminary mechanistic studies.

Procedure F：Reaction of 1a in the presence of TEMPO



In a single-necked flask (15 mL) equipped with a stir bar, 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**) (0.50 mmol), TEMPO (0.60 mmol), $LiClO_4$ (212 mg, 2.0 mmol) and MeCN/DMSO (v/v=5:1, 10 mL) were combined and added. The bottle was equipped with platinum plate electrode (10 ×10 mm^2) as the anode and RVC (reticulated vitreous carbon) plate electrode (10×10 mm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. When the reaction was finished, the solution was extracted with EtOAc and H_2O. The combined organic layer was dried with Na_2SO_4, filtered. The reaction mixture was analyzed by LC-MS. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (5:1). The pure product was analyzed by NMR.

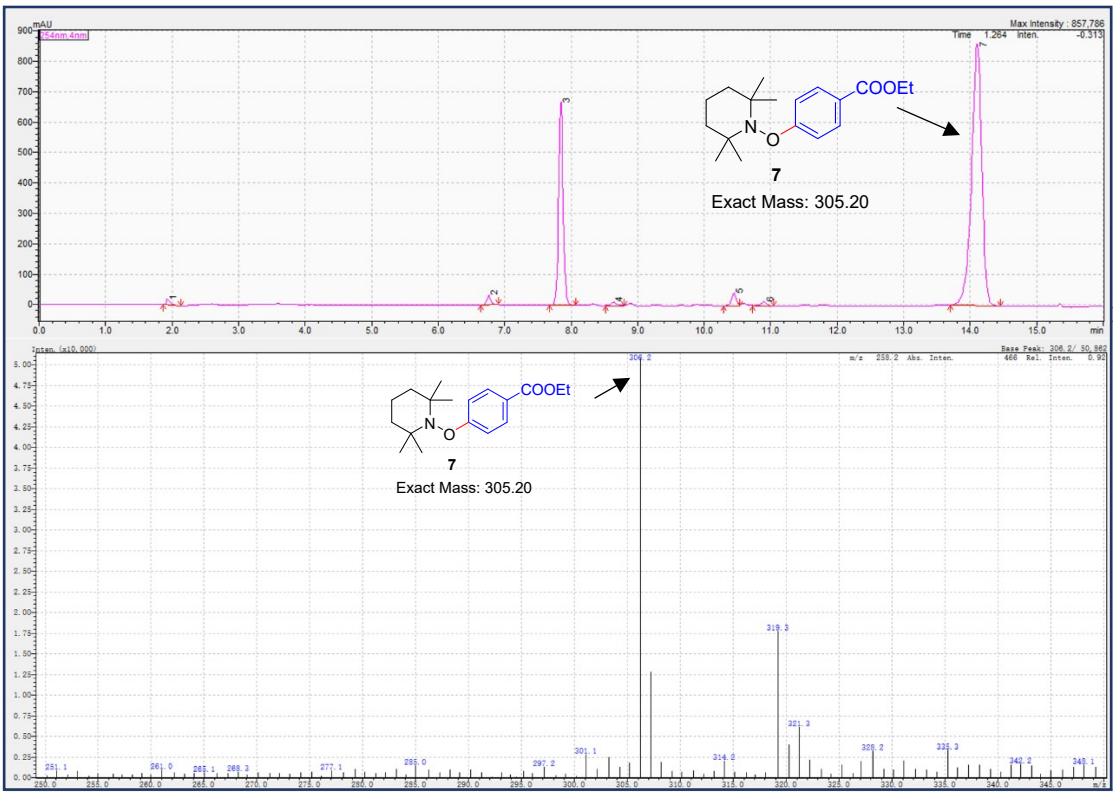
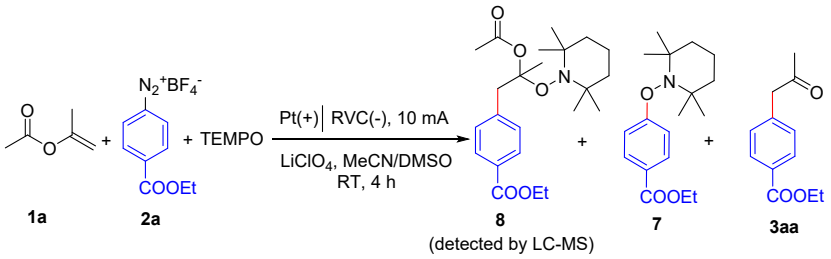


Fig. S2 LC-MS chart

Reaction of 1a with 2a in the presence of TEMPO



In a single-necked flask (15 mL) equipped with a stir bar, 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**) (0.50 mmol), isopropenyl acetate **2a** (5.0 mmol), TEMPO (0.60 mmol), $LiClO_4$ (2.0 mmol) and MeCN/DMSO (v/v=5:1, 10 mL) were combined and added. The bottle was equipped with platinum plate electrode (10 ×10 mm^2) as the anode and RVC (reticulated vitreous carbon) plate electrode (10×10 mm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. When the reaction was finished, the solution was extracted with EtOAc and H_2O. The combined organic layer was dried with Na_2SO_4, filtered. The reaction mixture was analyzed by LC-MS.

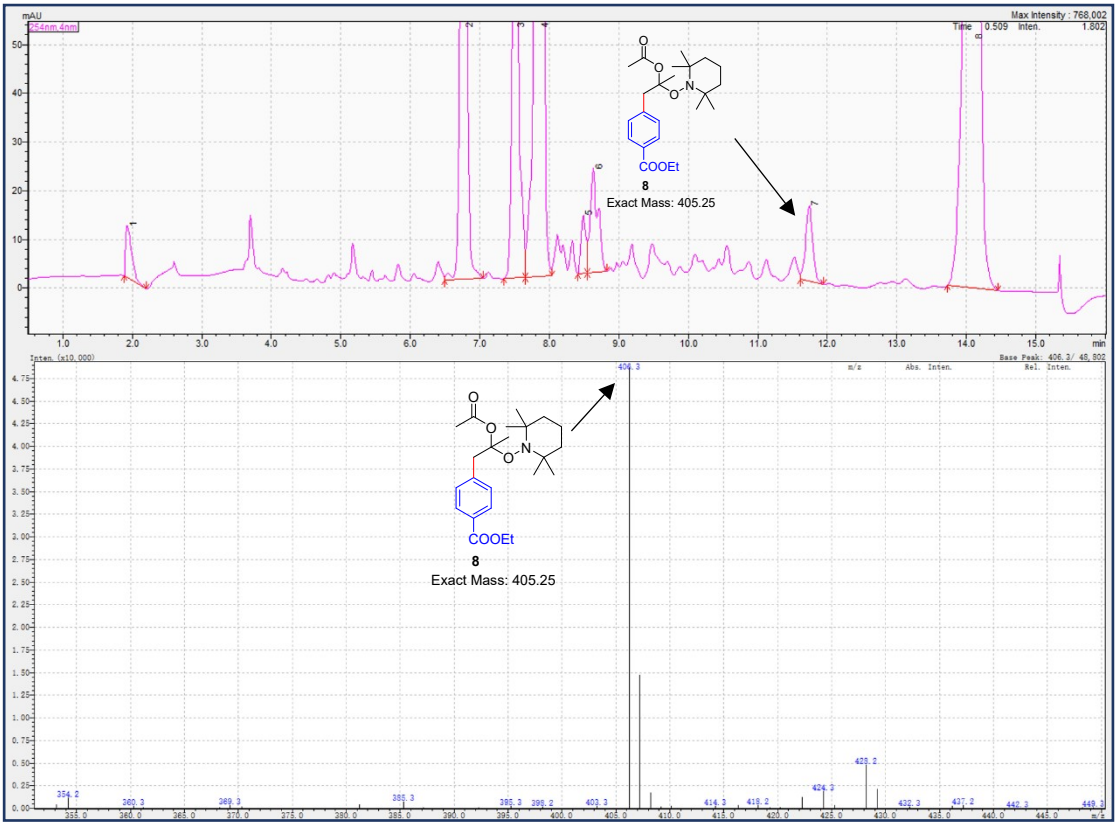
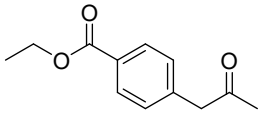


Fig. S3 LC-MS chart

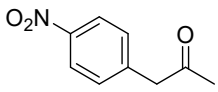
4. Characterization Data of Products.



3aa

ethyl 4-(2-oxopropyl)benzoate (3aa):

Synthesis carried out according to the General Procedure C, compound **3aa** was obtained in 87% yield as a yellow solid (89.7 mg, 0.44 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 3.76 (s, 2H), 2.17 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 166.3, 139.20, 130.0, 129.5, 129.4, 60.9, 50.8, 29.5, 14.3. IR (KBr) ν_{max} 2938, 1714, 1610, 1417, 1361, 1276, 1104, 1068, 864, 751 cm^{-1}. HRMS (ESI) calculated for $C_{12}H_{14}O_3$ $[M+H]^+$: 207.1016, found: 207.1021. These spectral data correspond to previously reported data.[3]

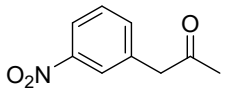


3ba

1-(4-nitrophenyl)propan-2-one (3ba):

Synthesis carried out according to the General Procedure C, compound **3ba** was obtained in 81% yield

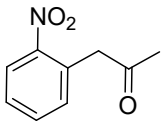
as a yellow solid (73.4 mg, 0.405 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 147.1, 141.4, 130.4, 123.7, 50.0, 29.8. IR (KBr) ν_{max} 3081, 2919, 2852, 1717, 1526, 1351, 732 cm^{-1}. HRMS (ESI) calculated for $C_9H_9NO_3$ $[M+H]^+$: 180.0655, found: 180.0659. These spectral data correspond to previously reported data.[3]



3ca

1-(3-nitrophenyl)propan-2-one (3ca):

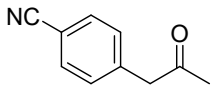
Synthesis carried out according to the General Procedure C, compound **3ca** was obtained in 73% yield as a yellow solid (65.3 mg, 0.365 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.10 (m, 1H), 8.06 (s, 1H), 7.56-7.46 (m, 2H), 3.85 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 147.4, 134.9, 134.8, 128.5, 123.5, 121.2, 48.7, 28.7. IR (KBr) ν_{max} 2922, 1713, 1523, 1348, 732 cm^{-1}. HRMS (ESI) calculated for $C_9H_9NO_3$ $[M+H]^+$: 180.0655, found: 180.0652. These spectral data correspond to previously reported data.[3]



3da

1-(2-nitrophenyl)propan-2-one (3da):

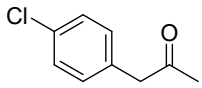
Synthesis carried out according to the General Procedure C, compound **3da** was obtained in 52% yield as a yellow solid (46.5 mg, 0.26 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48-7.42 (m, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 4.11 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 148.7, 133.6, 133.5, 130.4, 128.4, 125.2, 48.5, 29.9. IR (KBr) ν_{max} 2922, 1721, 1523, 1350, 1162, 732 cm^{-1}. HRMS (ESI) calculated for $C_9H_9NO_3$ $[M+H]^+$: 180.0655, found: 180.0651. These spectral data correspond to previously reported data.[3]



3ea

4-(2-oxopropyl)benzonitrile (3ea):

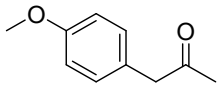
Synthesis carried out according to the General Procedure C, compound **3ea** was obtained in 95% yield as a yellow solid (75.6 mg, 0.475 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 139.5, 132.4, 130.4, 118.7, 111.1, 50.4, 29.7. IR (KBr) ν_{max} 3062, 3007, 2953, 2896, 2225, 1708, 1608, 1504, 1420, 1407, 1356, 1334, 1313, 1212, 1163, 1019 cm^{-1}. HRMS (ESI) calculated for $C_{10}H_9NO$ $[M+H]^+$: 160.0757, found: 160.0761. These spectral data correspond to previously reported data.[4]



3fa

1-(4-chlorophenyl)propan-2-one (3fa):

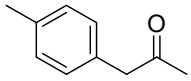
Synthesis carried out according to the General Procedure C, compound **3fa** was obtained in 36% yield as a yellow solid (30.2 mg, 0.18 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 3.68 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 133.0, 132.5, 130.8, 128.9, 50.1, 29.7. IR (KBr) ν_{max} 2917, 1714, 1597, 1490, 1410, 1356, 1323, 1284, 1225, 1192, 1159, 1086, 1016, 980, 832, 782 cm^{-1}. HRMS (ESI) calculated for C_9H_9ClO $[M+H]^+$: 169.0415, found: 169.0418. These spectral data correspond to previously reported data.[3]



3ga

1-(4-methoxyphenyl)propan-2-one (3ga):

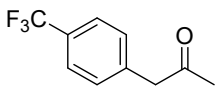
Synthesis carried out according to the General Procedure C, compound **3ga** was obtained in 28% yield as a yellow solid (23.1 mg, 0.14 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.63 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 158.7, 130.4, 126.3, 114.2, 55.3, 50.2, 29.7. IR (KBr) ν_{max} 2933, 2836, 1708, 1509, 1245, 1031, 833, 784 cm^{-1}. HRMS (ESI) calculated for $C_{10}H_{12}O_2$ $[M+H]^+$: 165.0910, found: 165.0913. These spectral data correspond to previously reported data.[3]



3ha

1-(p-tolyl)propan-2-one (3ha):

Synthesis carried out according to the General Procedure C, compound **3ha** was obtained in 31% yield as a yellow solid (23.1 mg, 0.156 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.66 (s, 2H), 2.34 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 136.7, 131.2, 129.5, 129.3, 50.7, 29.7, 21.1. IR (KBr) ν_{max} 3029, 2924, 2856, 1705, 1513, 1018, 818 cm^{-1}. HRMS (ESI) calculated for $C_{10}H_{12}O$ $[M+H]^+$: 149.0961, found:149.0958. These spectral data correspond to previously reported data.[3]

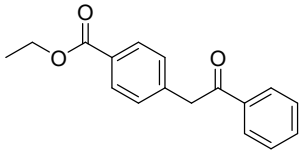


3ia

1-(4-(trifluoromethyl)phenyl)propan-2-one (3ia):

Synthesis carried out according to the General Procedure C, compound **3ia** was obtained in 63% yield as a yellow solid (63.6 mg, 0.315 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.78 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 138.1,

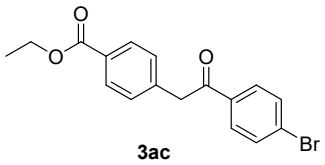
129.5 (q, J = 32 Hz),125.62 (q, J = 3.8 Hz), 124.1 (q, J = 271 Hz), 50.4, 29.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52. IR (KBr) ν_{max} 2921, 2853, 1722, 1511, 1459, 1325, 1269, 1065, 697 cm^{-1}. HRMS (ESI) calculated for $C_{10}H_9F_3O$ $[M+H]^+$: 203.0678, found: 203.0677. These spectral data correspond to previously reported data.[5]



3ab

ethyl 4-(2-oxo-2-phenylethyl)benzoate (3ab):

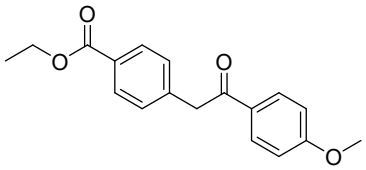
Synthesis carried out according to the General Procedure C, compound **3ab** was obtained in 88% yield as a yellow solid (117.9 mg, 0.44 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 4H), 7.59-7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.36 (dd, J = 13.2, 6.1 Hz, 4H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 166.4, 139.7, 136.5, 133.4, 129.9, 129.6, 129.3, 128.7, 128.6, 60.9, 45.4, 14.3. IR (KBr) ν_{max} 3055, 2983, 2884, 1706, 1682, 1610, 1449, 1104, 997, 753 cm^{-1}. HRMS (ESI) calculated for $C_{17}H_{16}O_3$ $[M+H]^+$: 269.1172, found: 269.1169. These spectral data correspond to previously reported data.[6]



3ac

ethyl 4-(2-(4-bromophenyl)-2-oxoethyl)benzoate (3ac):

Synthesis carried out according to the General Procedure C, compound **3ac** was obtained in 83% yield as a yellow solid (143.6 mg, 0.415 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.36 (dd, J = 14.2, 7.1 Hz, 2H), 4.30 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 166.3, 139.2, 135.1, 132.1, 131.9, 130.0, 130.0, 129.5, 128.6, 60.9, 45.4, 14.3. IR (KBr) ν_{max} 2978, 2928, 1714, 1683, 1583, 1395, 1279, 1072, 822, 756 cm^{-1}. HRMS (ESI) calculated for $C_{17}H_{15}BrO_3$ $[M+H]^+$: 347.0277 found: 347.0267.

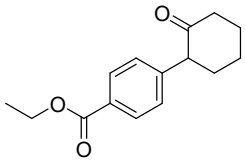


3ad

ethyl 4-(2-(4-methoxyphenyl)-2-oxoethyl)benzoate (3ad):

Synthesis carried out according to the General Procedure C, compound **3ad** was obtained in 74% yield as a yellow solid (110.3 mg, 0.37 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 11.9, 5.0 Hz, 4H), 7.33 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.28 (s, 2H), 3.86 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 166.4, 163.7, 140.2, 130.9, 129.9, 129.5, 129.1, 113.9, 60.9, 55.5, 45.2, 14.3. IR (KBr) ν_{max} 2982, 2921, 1755, 1703, 1675,

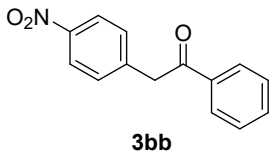
1602, 1578, 1510, 1465, 1421, 1367, 1317, 1278, 1257, 1224, 1204, 1176, 1111, 1030, 993, 831, 743 cm^{-1}. HRMS (ESI) calculated for $C_{18}H_{18}O_4$ $[M+H]^+$: 299.1278, found: 299.1274. These spectral data correspond to previously reported data.[7]



3ae

ethyl 4-(2-oxocyclohexyl)benzoate (3ae):

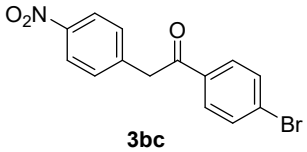
Synthesis carried out according to the General Procedure C, compound **3ae** was obtained in 62% yield as a yellow solid (76.3 mg, 0.31 mmol) after purification. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 3.67 (dd, J = 12.1, 5.3 Hz, 1H), 2.50 (dt, J = 12.1, 9.8 Hz, 2H), 2.35 – 2.23 (m, 1H), 2.21 – 2.13 (m, 1H), 2.03 (d, J = 10.1 Hz, 2H), 1.89 – 1.76 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 166.5, 143.9, 129.6, 129.2, 128.6, 60.8, 57.4, 42.2, 35.0, 29.7, 27.7, 25.3, 14.3. IR (KBr) ν_{max} 2921, 2853, 1714, 1612, 1453, 1365, 1277, 1180, 1108, 1022, 770 cm^{-1}. HRMS (ESI) calculated for $C_{15}H_{18}O_3$ $[M+H]^+$: 247.1329, found: 247.1331. These spectral data correspond to previously reported data.[8]



3bb

2-(4-nitrophenyl)-1-phenylethan-1-one (3bb):

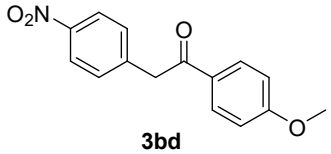
Synthesis carried out according to the General Procedure C, compound **3bb** was obtained in 85% yield as a yellow solid (102.5 mg, 0.425 mmol) after purification. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 4.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 147.1, 142.1, 136.2, 133.7, 130.6, 128.9, 128.4, 123.7, 44.9. IR (KBr) ν_{max} 2919, 2850, 1686, 1603, 1515, 1451, 1352, 1327, 1214, 856, 762, 734 cm^{-1}. HRMS (ESI) calculated for $C_{14}H_{11}NO_3$ $[M+H]^+$: 242.0812, found: 242.0809. These spectral data correspond to previously reported data.[9]



3bc

1-(4-bromophenyl)-2-(4-nitrophenyl)ethan-1-one (3bc):

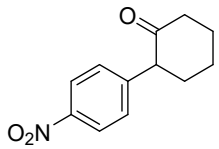
Synthesis carried out according to the General Procedure C, compound **3bc** was obtained in 86% yield as a yellow solid (137.2 mg, 0.43 mmol) after purification. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 4.37 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 147.2, 141.6, 134.9, 132.2, 130.6, 129.9, 129.0, 123.8, 44.9. IR (KBr) ν_{max} 2922, 2952, 1684, 1580, 1514, 1462, 1342, 1106, 1068, 816, 735 cm^{-1}. HRMS (ESI) calculated for $C_{14}H_{10}NO_3$ $[M+H]^+$: 319.9917, found: 319.9921. These spectral data correspond to previously reported data.[10]



3bd

1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (3bd):

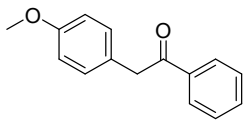
Synthesis carried out according to the General Procedure C, compound **3bd** was obtained in 71% yield as a yellow solid (96.2 mg, 0.355 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.9 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.35 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 164.0, 147.0, 142.5, 130.8, 130.5, 129.2, 123.7, 114.1, 55.5, 44.7. IR (KBr) ν_{max} 2958, 1606, 1509, 1291, 1248, 1174, 1108, 1033, 1008, 834, 691, 552 cm^{-1}. HRMS (ESI) calculated for $C_{15}H_{13}NO_4$ $[M+H]^+$: 272.0917, found: 272.0918. These spectral data correspond to previously reported data.[11]



3be

2-(4-nitrophenyl)cyclohexan-1-one (3be):

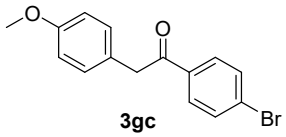
Synthesis carried out according to the General Procedure C, compound **3be** was obtained in 54% yield as a yellow solid (59.2 mg, 0.27 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 3.73 (dd, J = 12.5, 5.2 Hz, 1H), 2.62 – 2.43 (m, 2H), 2.35 – 2.16 (m, 2H), 2.08 – 1.93 (m, 2H), 1.92 – 1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 147.0, 146.3, 129.6, 123.5, 57.3, 42.2, 35.2, 27.7, 25.3. IR (KBr) ν_{max} 2933, 2859, 1711, 1601, 1518, 1346, 1122, 864, 754 cm^{-1}. HRMS (ESI) calculated for $C_{12}H_{13}NO_3$ $[M+H]^+$: 220.0968, found 220.0964. These spectral data correspond to previously reported data.[12]



3gb

2-(4-methoxyphenyl)-1-phenylethan-1-one (3gb):

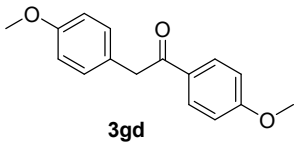
Synthesis carried out according to the General Procedure C, compound **3gb** was obtained in 33% yield as a yellow solid (37.3 mg, 0.165 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.23 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 158.6, 136.7, 133.0, 130.5, 128.6, 128.6, 126.6, 114.2, 55.2, 44.6. IR (KBr) ν_{max} 3063, 3000, 2835, 1689, 1511, 1174, 1034, 756 cm^{-1}. HRMS (ESI) calculated for $C_{15}H_{14}O_2$ $[M+H]^+$: 227.1067, found 227.1072. These spectral data correspond to previously reported data.[13]



3gc

1-(4-bromophenyl)-2-(4-methoxyphenyl)ethan-1-one (3gc):

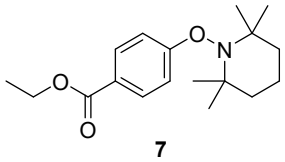
Synthesis carried out according to the General Procedure C, compound **3gc** was obtained in 28% yield as a yellow solid (42.6 mg, 0.14 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 4.20 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 158.6, 135.3, 132.0, 130.4, 130.2, 128.3, 126.1, 114.2, 55.3, 44.7. IR (KBr) ν_{max} 2922, 2852, 1684, 1580, 1515, 1462, 1343, 1201, 1106, 1068, 987, 816,734 cm^{-1}. HRMS (ESI) calculated for $C_{15}H_{13}BrO_2$ $[M+H]^+$: 305.0172, found 305.0169. These spectral data correspond to previously reported data.[7]



3gd

1,2-bis(4-methoxyphenyl)ethan-1-one (3gd):

Synthesis carried out according to the General Procedure C, compound **3gd** was obtained in 25% yield as a yellow solid (32.1 mg, 0.125 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.17 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 163.5, 158.5, 130.9, 130.4, 129.7, 127.0, 114.1, 113.8, 55.5, 55.2, 44.4. IR (KBr) ν_{max} 3035, 2918, 2846, 1681, 1604, 1513, 1460, 1251, 1177, 1106, 1031, 829, 781 cm^{-1}. HRMS (ESI) calculated for $C_{16}H_{16}O_3$ $[M+H]^+$: 257.1172, found 257.1168. These spectral data correspond to previously reported data.[14]



7

ethyl 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzoate (7):

Synthesis carried out according to the Procedure F, compound **7** was obtained in 66% yield as a white solid (101 mg, 0.33 mmol) after purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.1 Hz, 2H), 7.25 (d, J = 19.7 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 1.71-1.56 (m, 5H), 1.48 - 1.41 (m, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.24 (s, 6H), 1.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.6, 131.0, 122.3, 113.7, 60.6, 60.5, 39.7, 32.4, 20.5, 17.0, 14.5. IR (KBr) ν_{max} 2976, 2935, 1714, 1601, 1500, 1401, 1331, 1290, 1305, 1259, 1173, 1135, 1058, 1015, 809, 700, 682 cm^{-1}. HRMS (ESI) calculated for $C_{18}H_{27}NO_3$ $[M+H]^+$: 306.2064, found 306.2066. These spectral data correspond to previously reported data.[15]

5. References

[1] P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton and A. W. Timms, J. Chem. Soc., Perkin Trans. 2 2002, 2, 1135−1150.

[2] T. W. Liwosz and S. R. Chemler, J. Am. Chem. Soc., 2012, 134, 2020−2023.

[3] T. Hering, D. P. Hari, and B. König, J. Org. Chem., 2012, 77, 10347–10352.

[4] S. Inaba and D. R. Rieke, J. Org. Chem., 1985, 50, 1373-1381.

[5] C. Gabler, M. Korb and Schaarschmidt D., Adv. Synth. Catal., 2014, 356, 2979-2983.

[6] H.-Y. Wang., D. S. Mueller., R. M. Sachwani., R. Kapadia., H. N. Londino. and L. L. Anderson., J. Org. Chem., 2011, 76, 3203-3221.

[7] L.-Z. Yuan., D. Renko, I. Khelifi, O. Provot., J.-D. Brion, A. Hamze and M. Alami, Org. Lett. 2016, 18, 13, 3238–3241.

[8] MM. Hossain, A. Shaikh, J. Moutet and T. Gianetti, ChemRxiv, 2021, 1-23.

[9] P. Wan and S. Muralidharan, J. Am. Chem. Soc. 1988, 110, 4336–4345.

[10] D. Felipe-Blanco and J. C. Gonzalez-Gomez, Adv. Synth. Catal., 2018, 360, 14, 2773-2778

[11] E. Tatunashvili, B. Chan, P. E. Nashar and C. Mcerlean, Org Biomol Chem., 2020, 18, 9, 1812-1819.

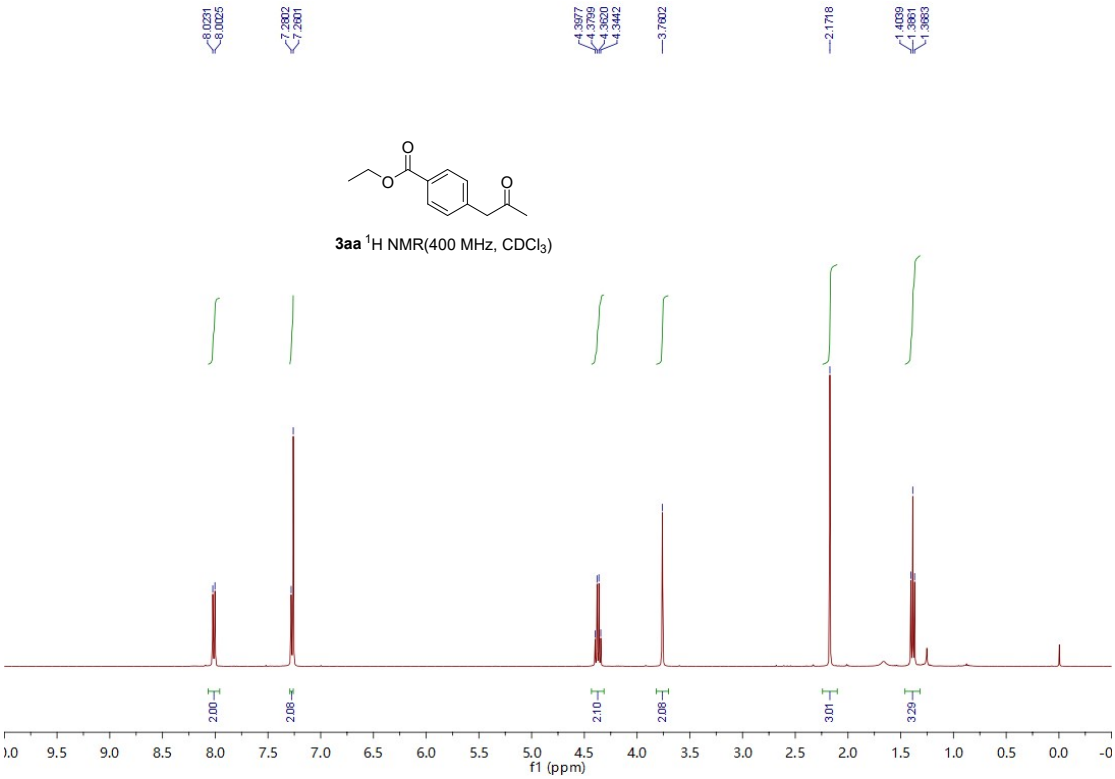
[12] A. A. N. D. Souza, N. S. Silva, A. V. Müller, A. S. Polo, T. J. Brocksom and K. T. D. Oliveira, J. Org. Chem., 2018, 83, 24, 15077–15086.

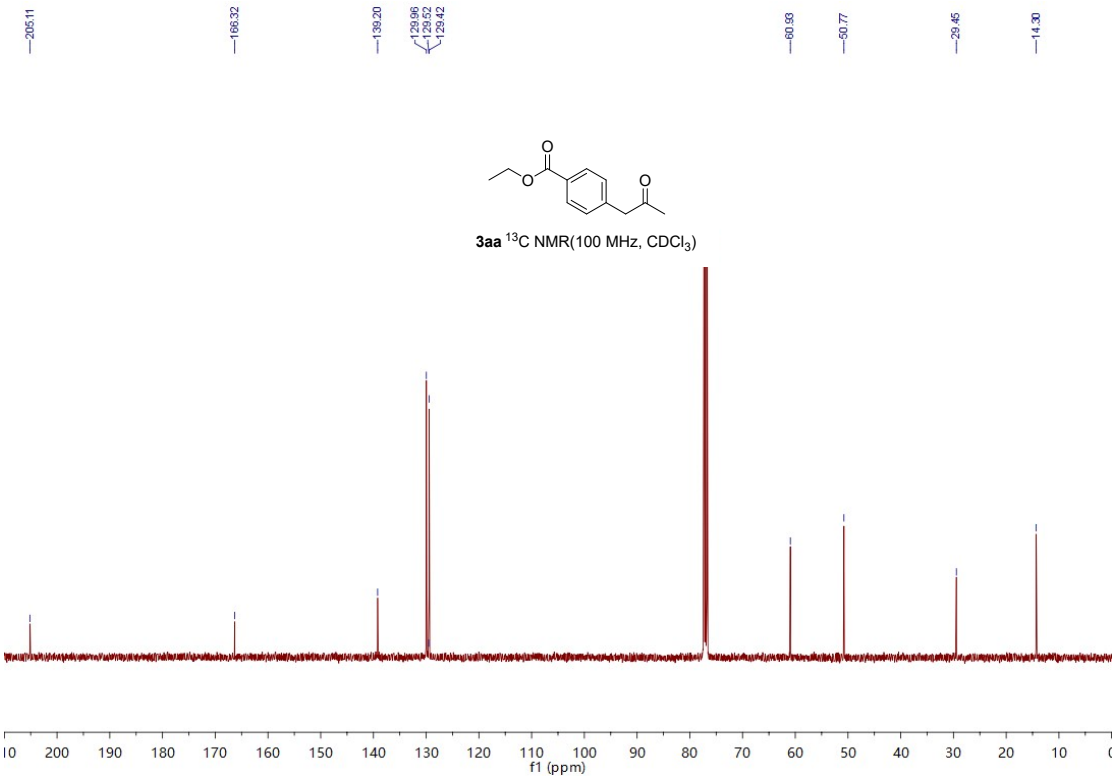
[13] P. E. Krach, A. Dewanji, T. Yuan and M. Rueping, Chem. Commun., 2020, 56, 6082-6085.

[14] C. Wang, L. Wu, W. Xu, F. He and Y. Chen, Org. Lett., 2020, 22, 6954–6959.

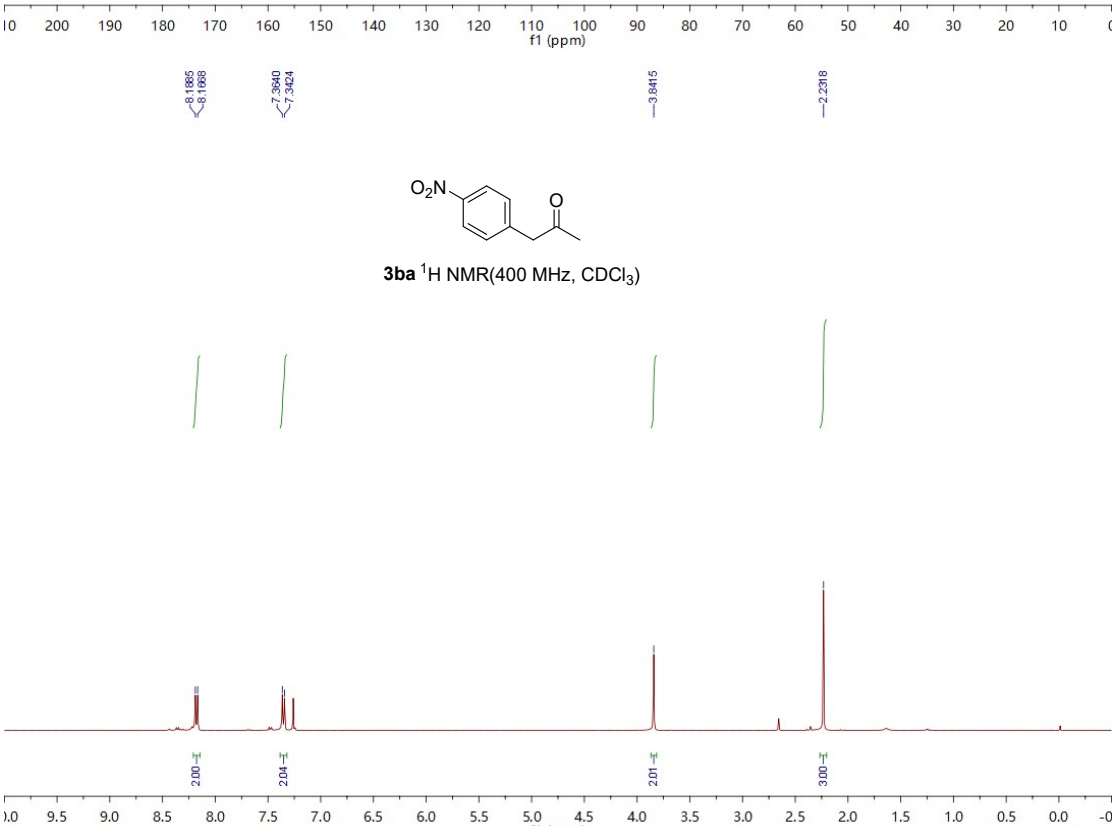
[15] D. Qiu, C. Lian, J. Mao, Y. Ding and S. Protti, Adv. Synth. Catal., 2019, 361, 22, 5239-5244.

6. Copy of ^{1}H and ^{13}C NMR Spectra of Products

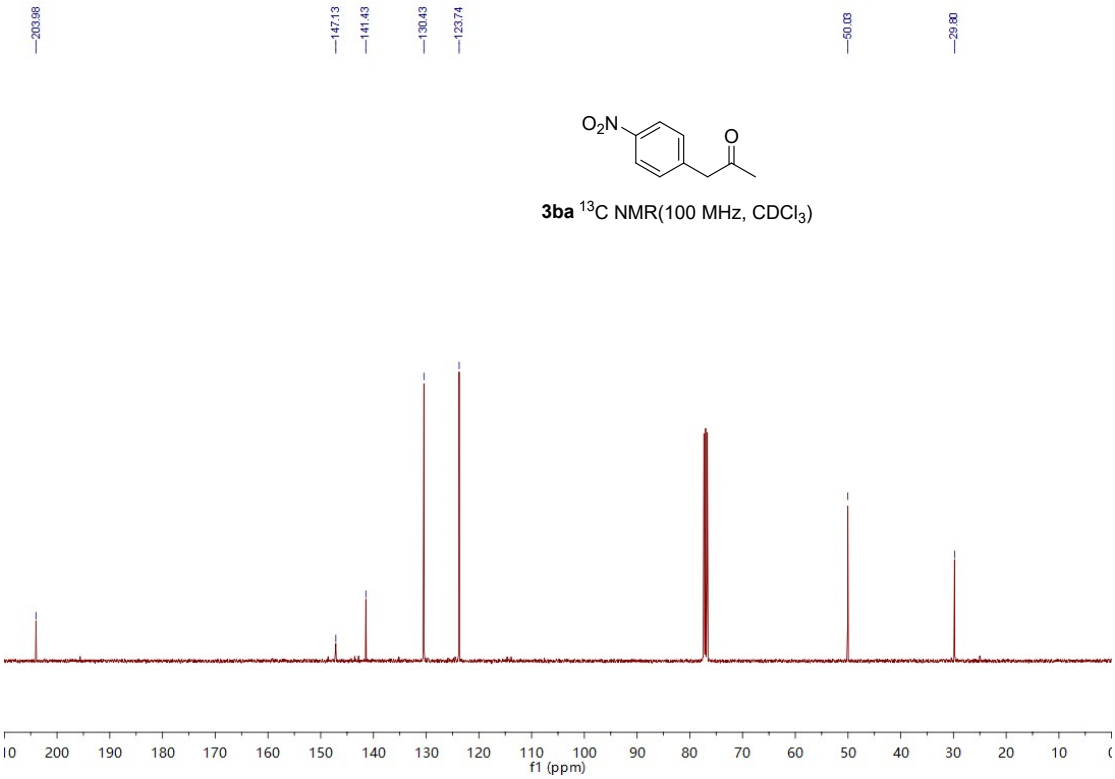




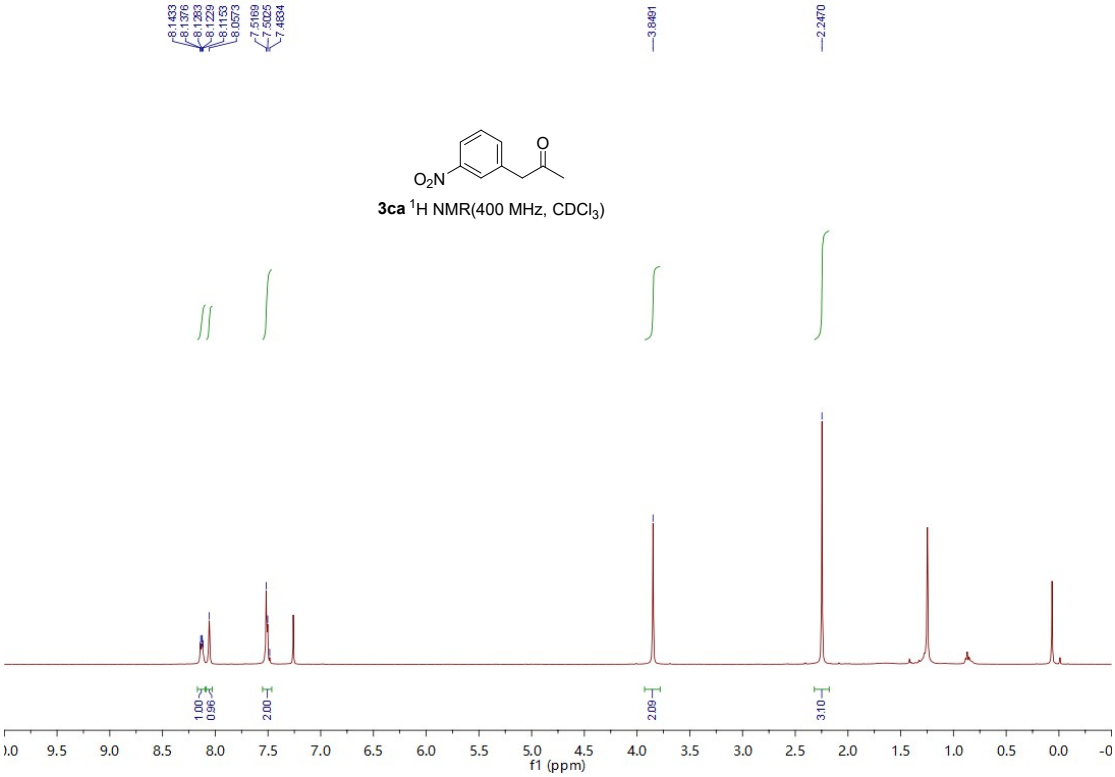
3aa ^{13}C NMR(100 MHz, $CDCl_3$)



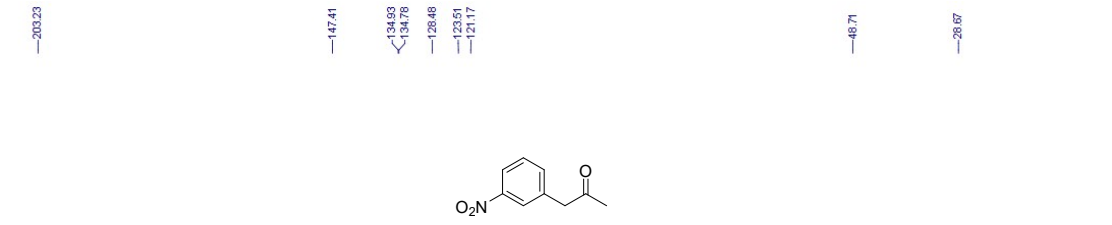
3ba ^{1}H NMR(400 MHz, $CDCl_3$)



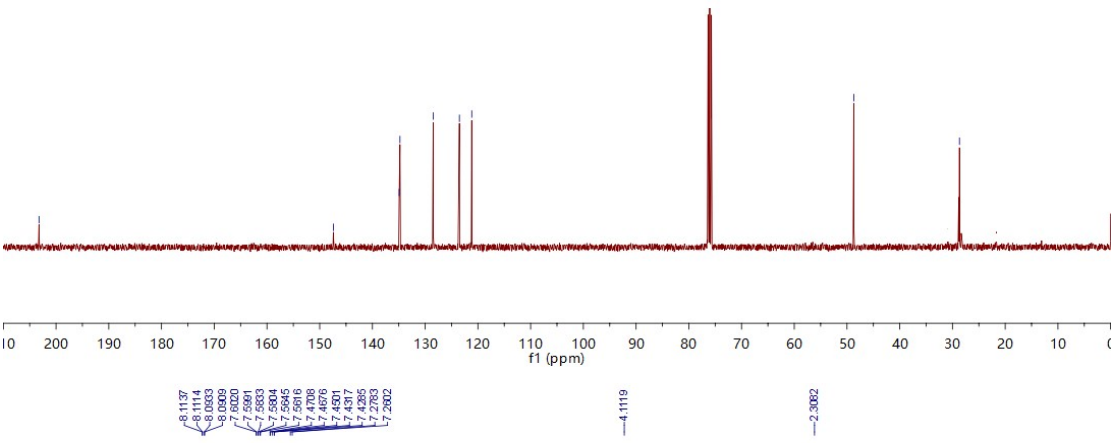
3ba ^{13}C NMR(100 MHz, $CDCl_3$)



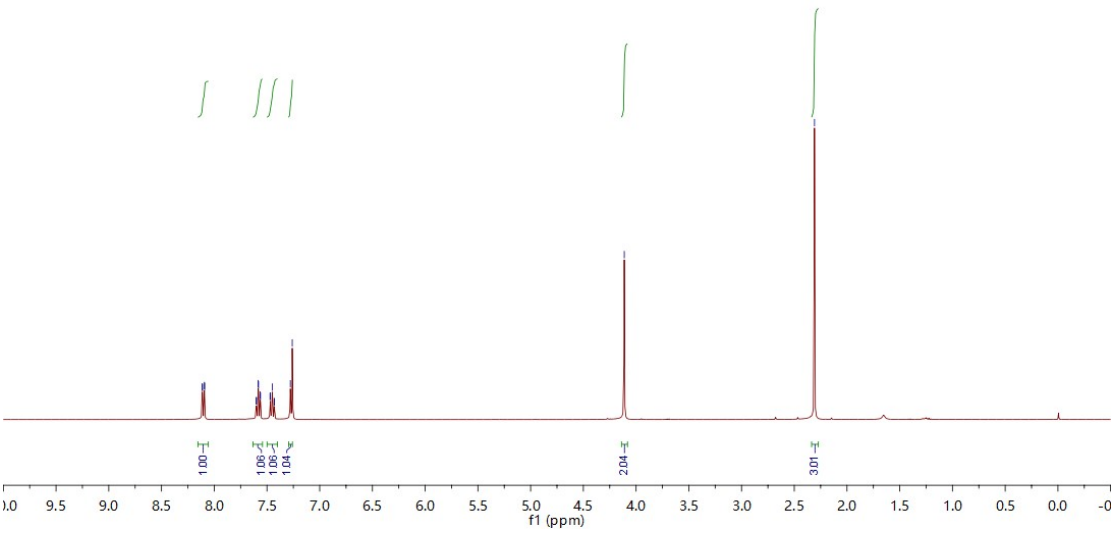
3ca ^{1}H NMR(400 MHz, $CDCl_3$)

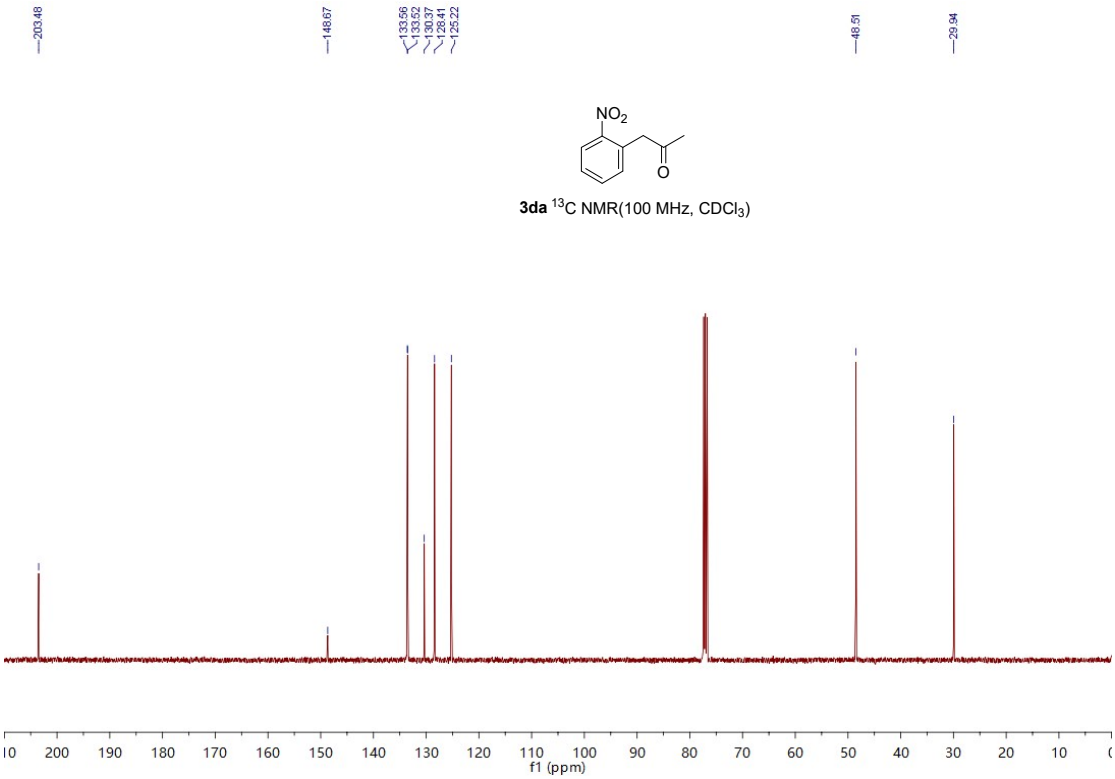


3ca ^{13}C NMR(100 MHz, $CDCl_3$)

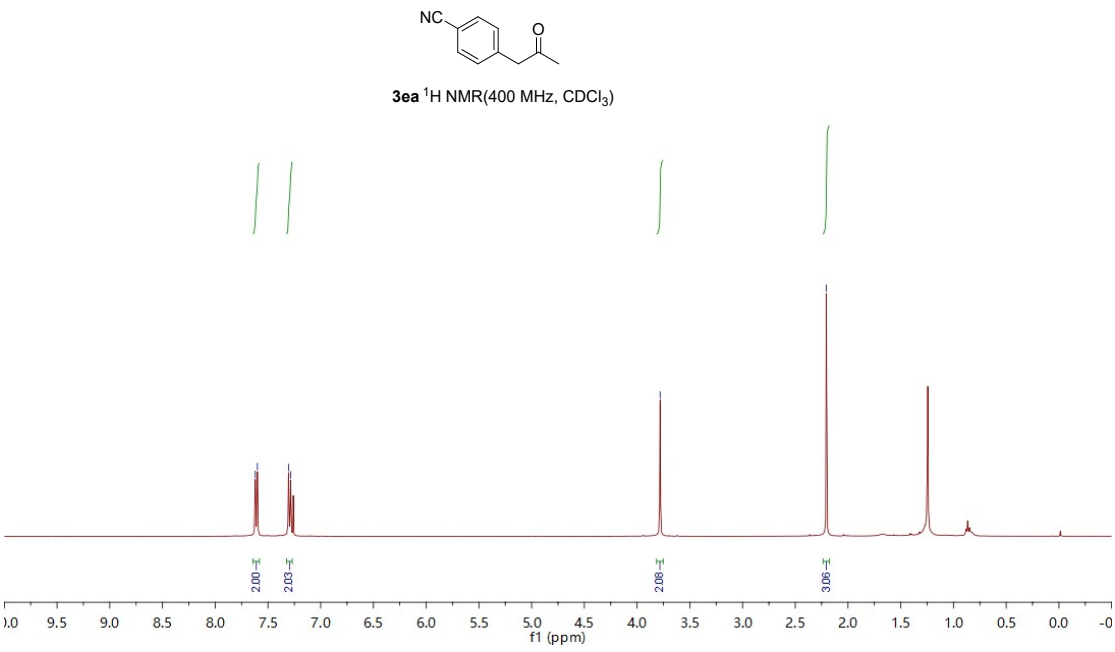


3da ^{1}H NMR(400 MHz, $CDCl_3$)

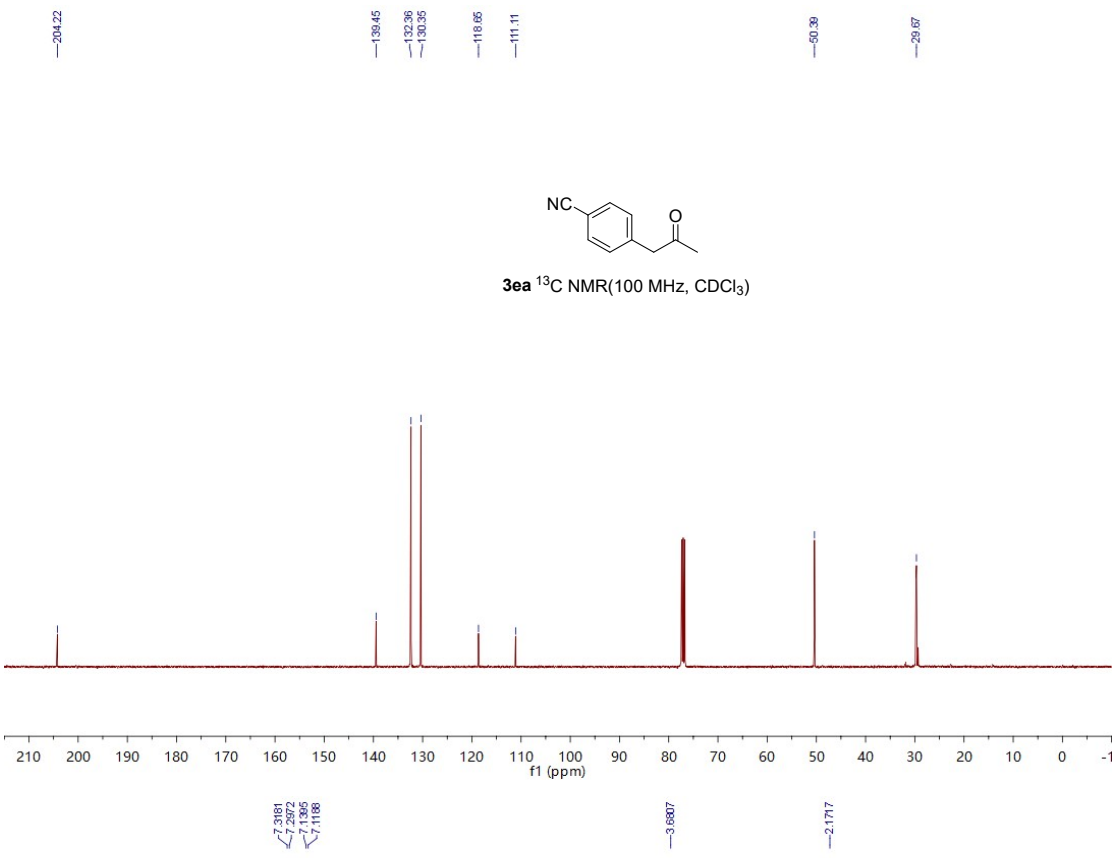




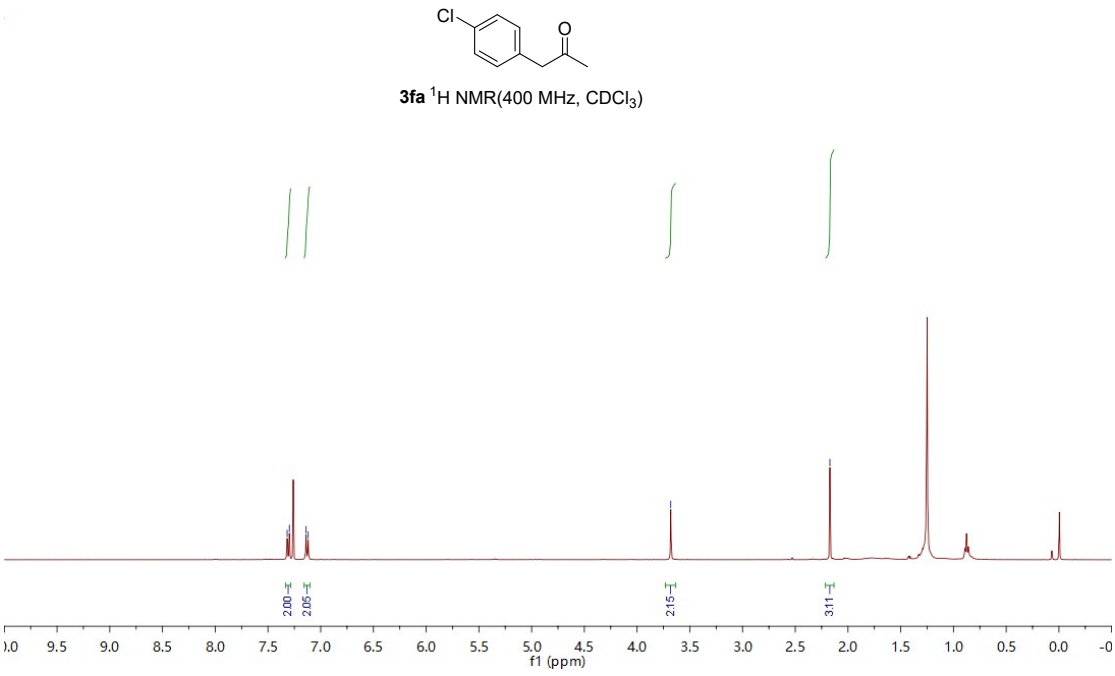
3da ^{13}C NMR(100 MHz, $CDCl_3$)



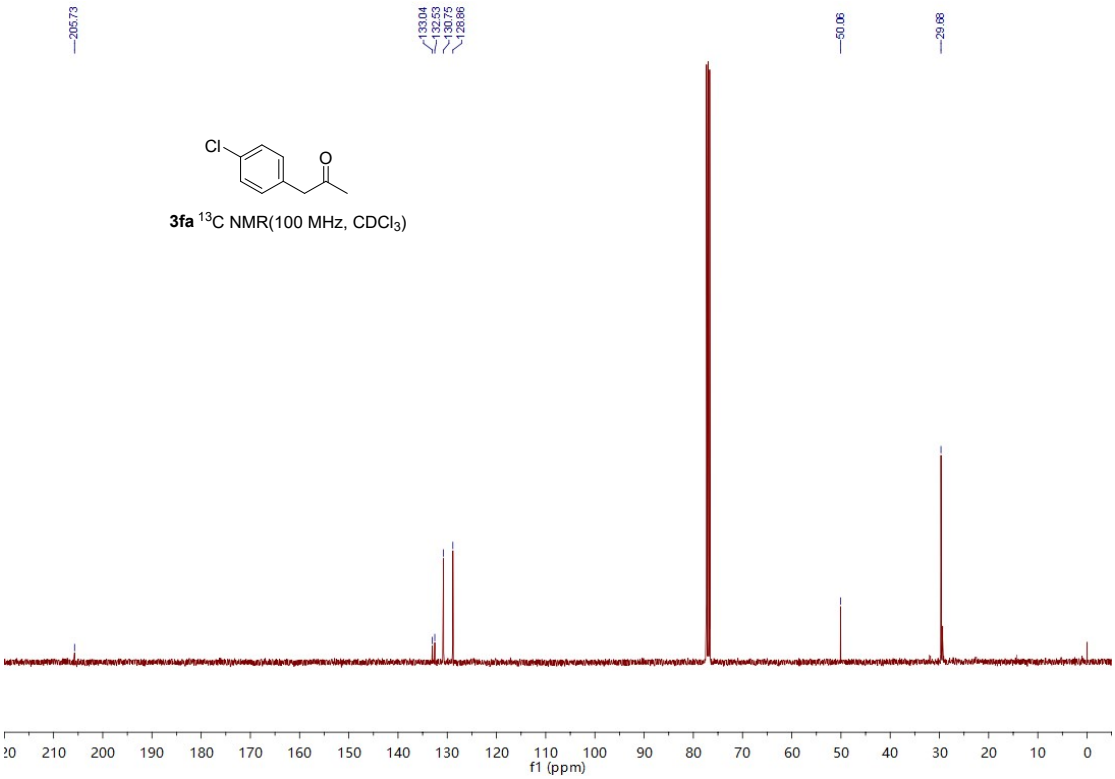
3ea ^{1}H NMR(400 MHz, $CDCl_3$)



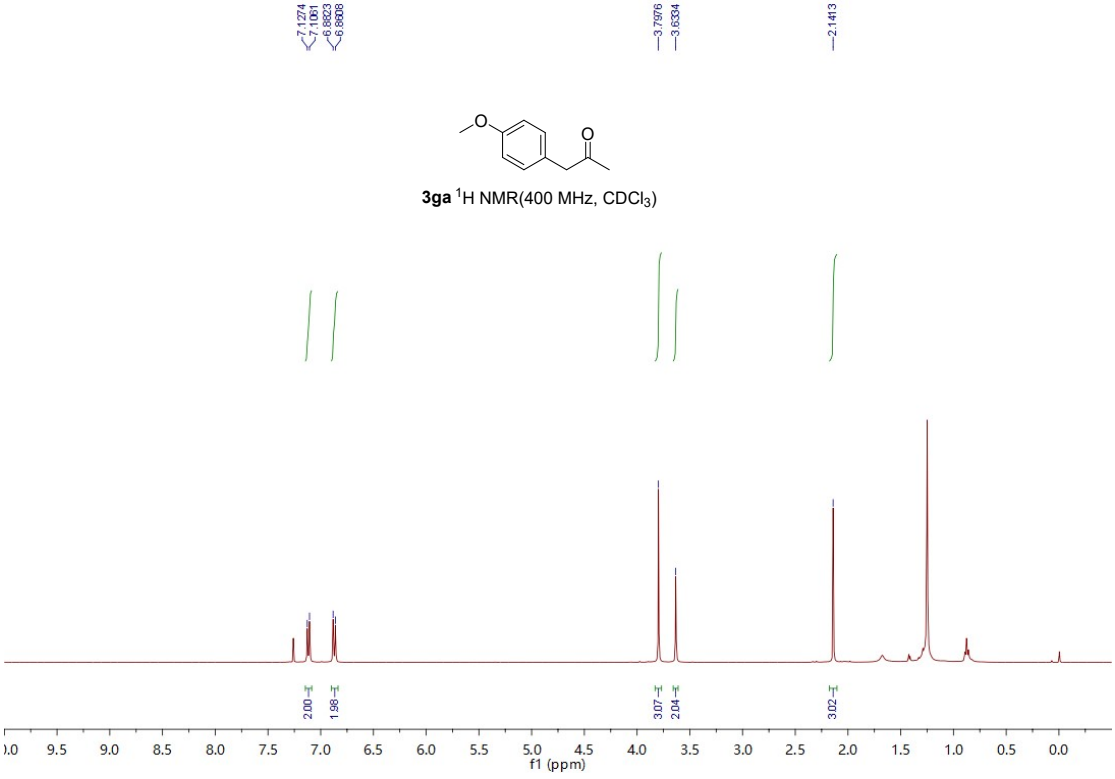
3ea ^{13}C NMR(100 MHz, $CDCl_3$)



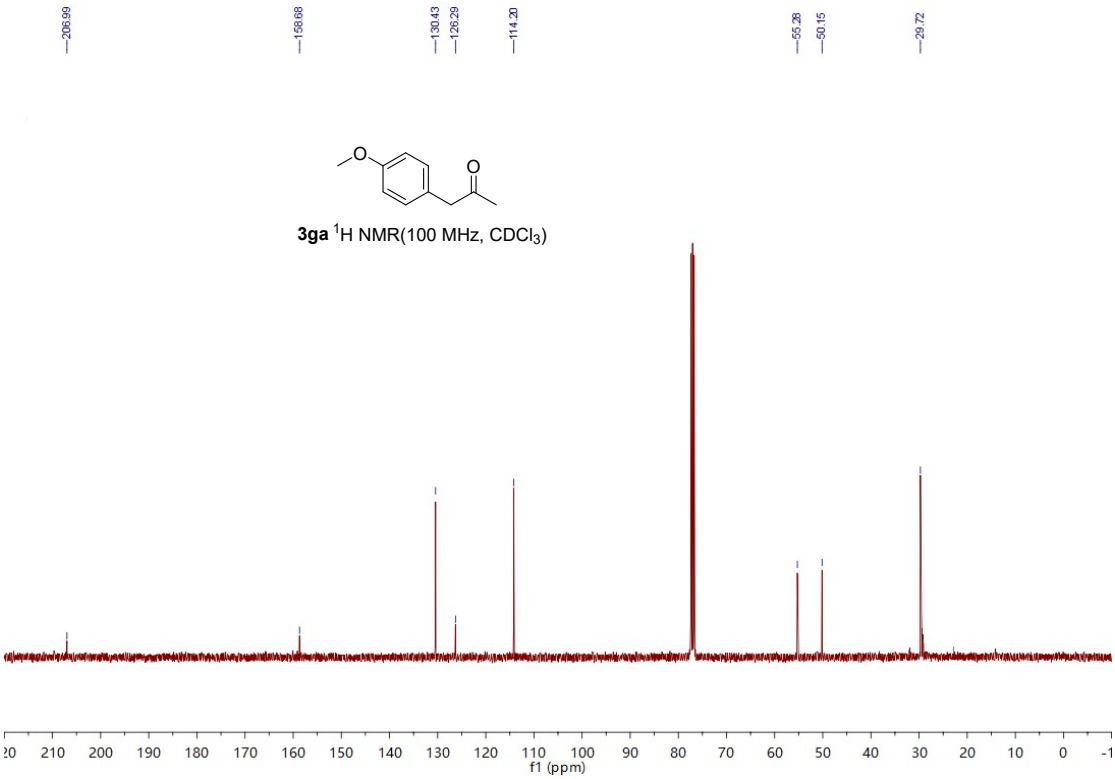
3fa ^{1}H NMR(400 MHz, $CDCl_3$)



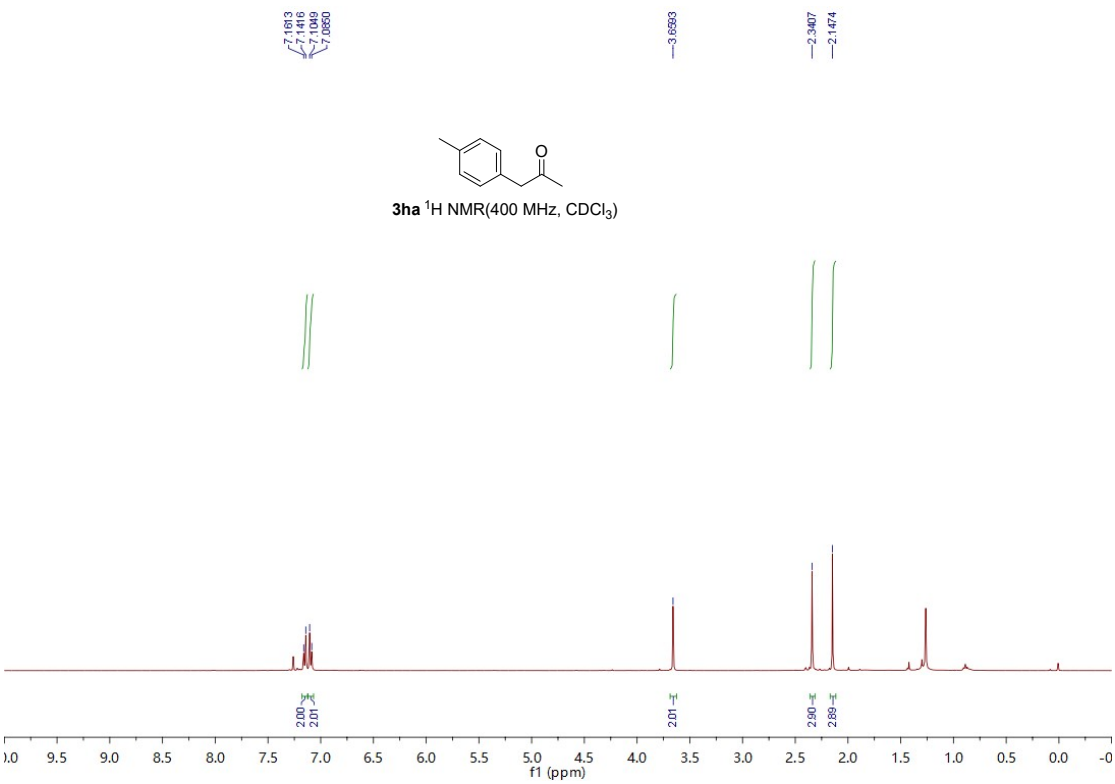
3fa ^{13}C NMR(100 MHz, $CDCl_3$)



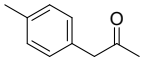
3ga ^{1}H NMR(400 MHz, $CDCl_3$)



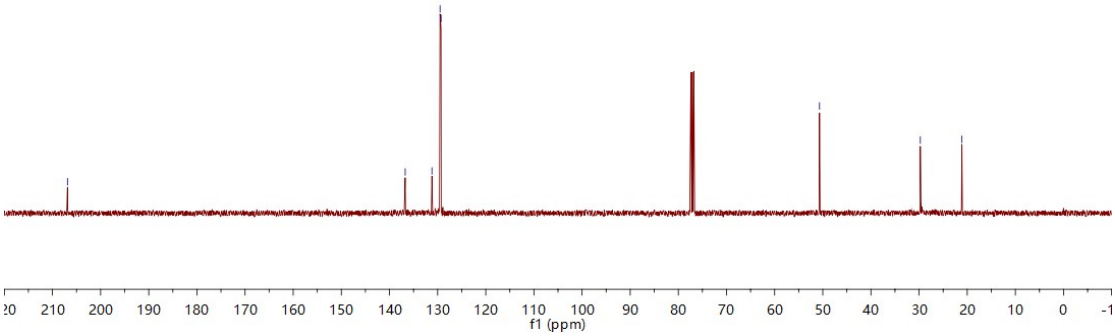
3ga ^{1}H NMR(100 MHz, $CDCl_3$)

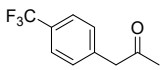


3ha ^{1}H NMR(400 MHz, $CDCl_3$)

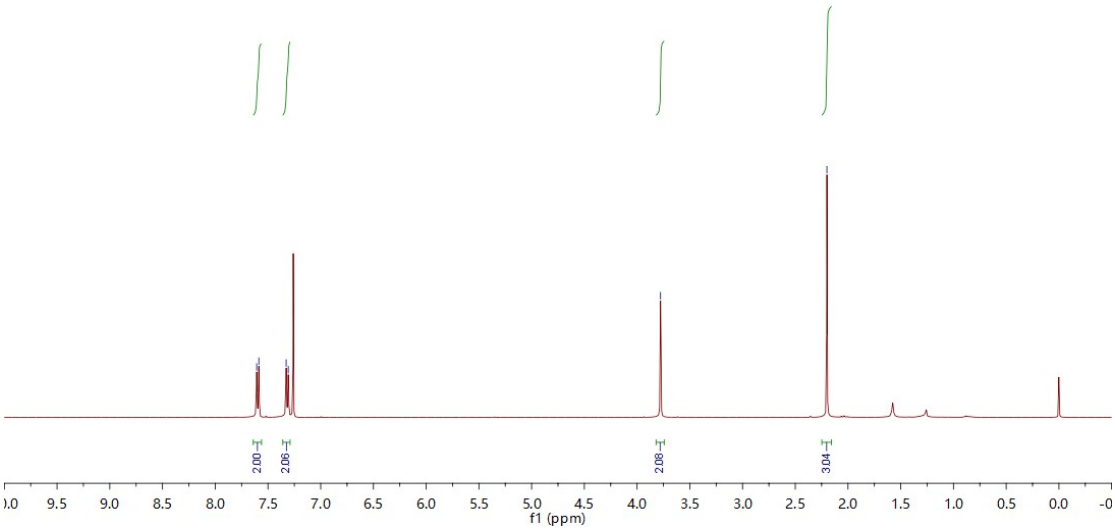


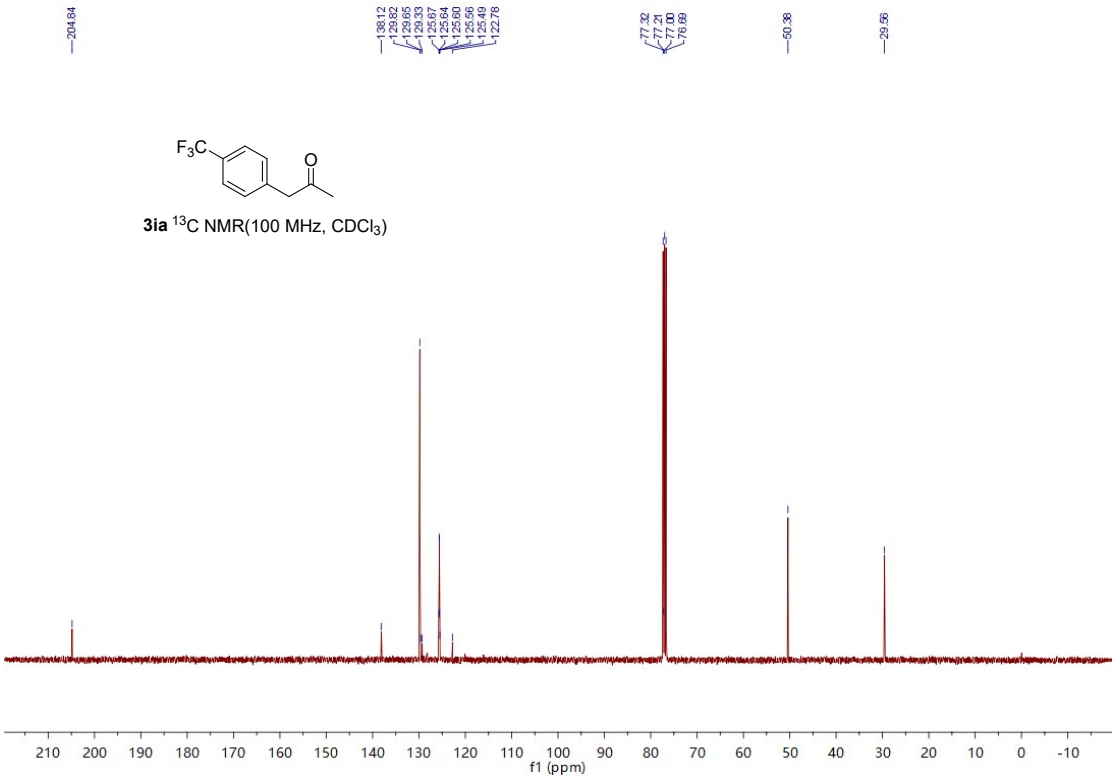
3ha ^{13}C NMR(100 MHz, $CDCl_3$)



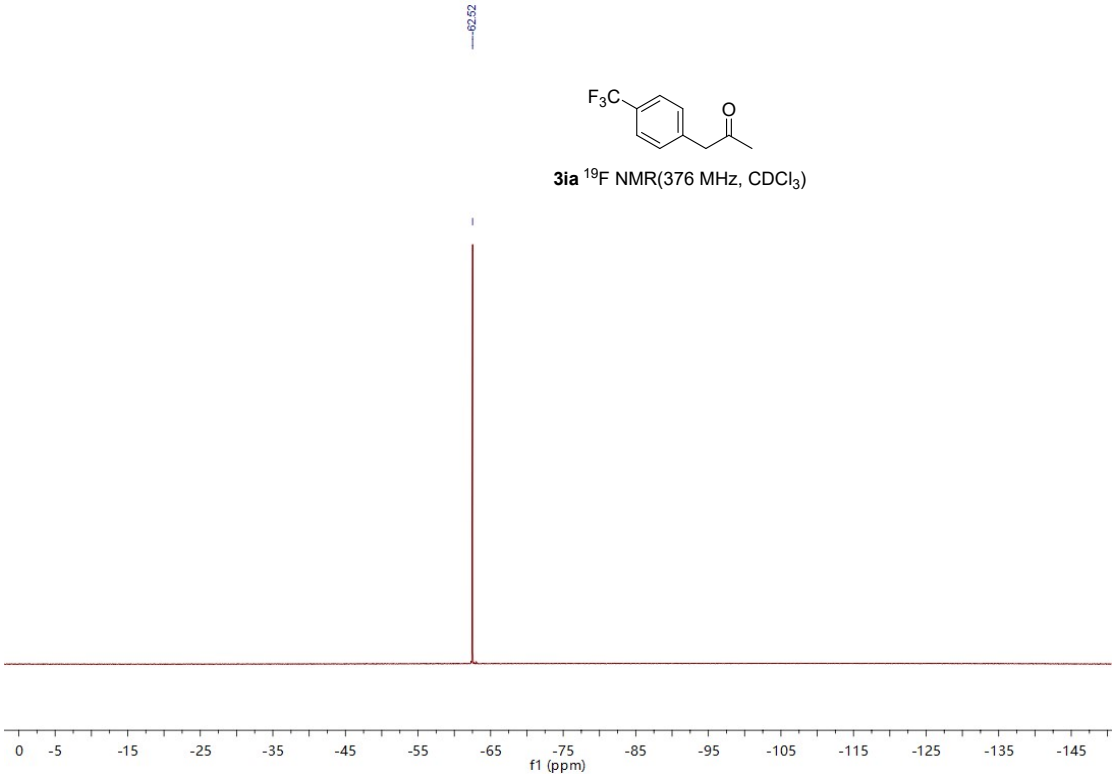


3ia ^{1}H NMR(400 MHz, $CDCl_3$)

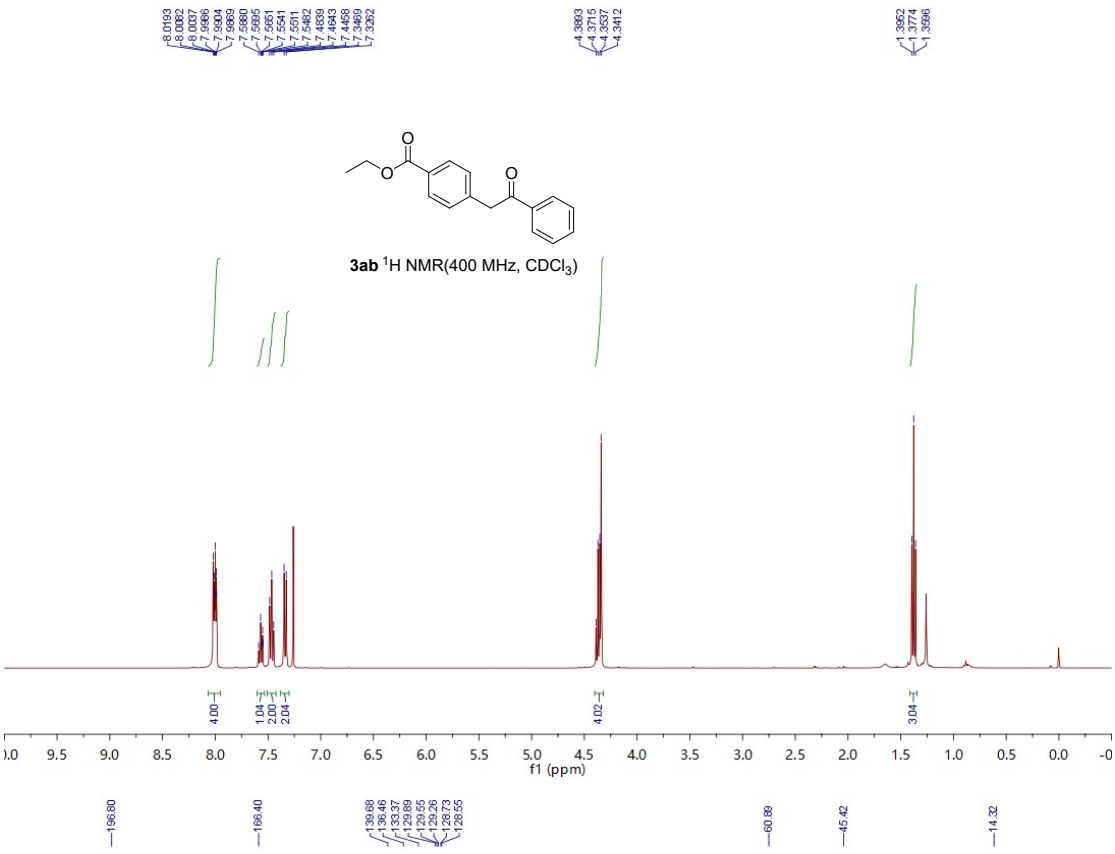




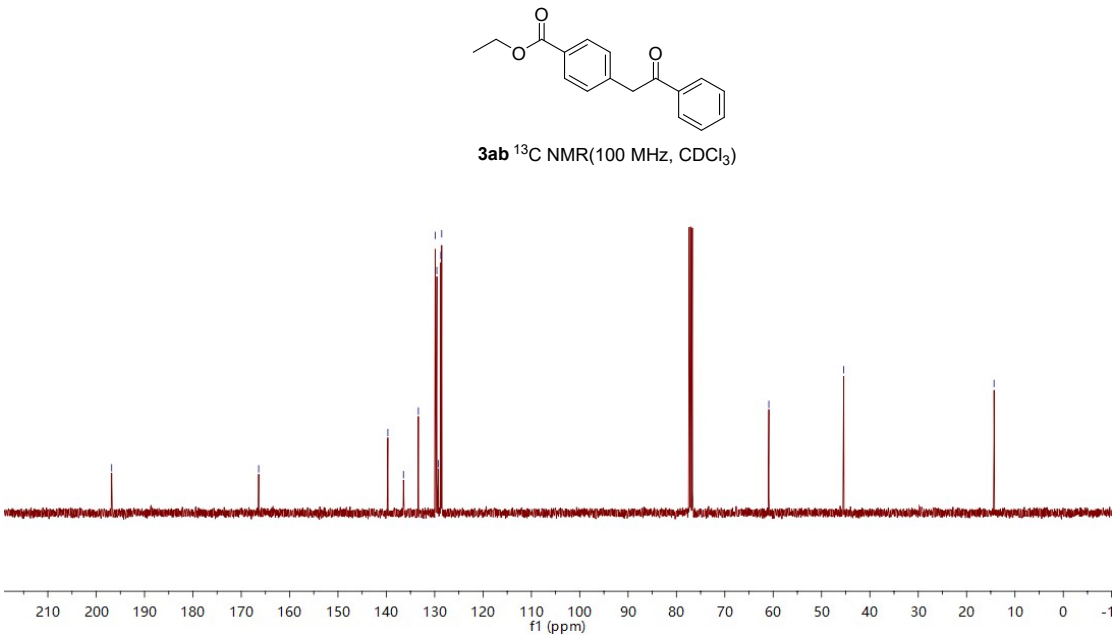
3ia ^{13}C NMR(100 MHz, $CDCl_3$)



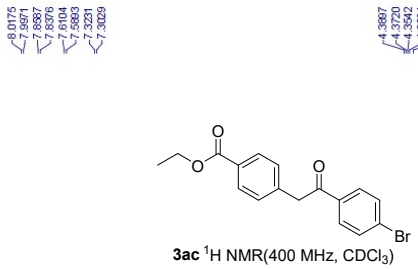
3ia ^{19}F NMR(376 MHz, $CDCl_3$)



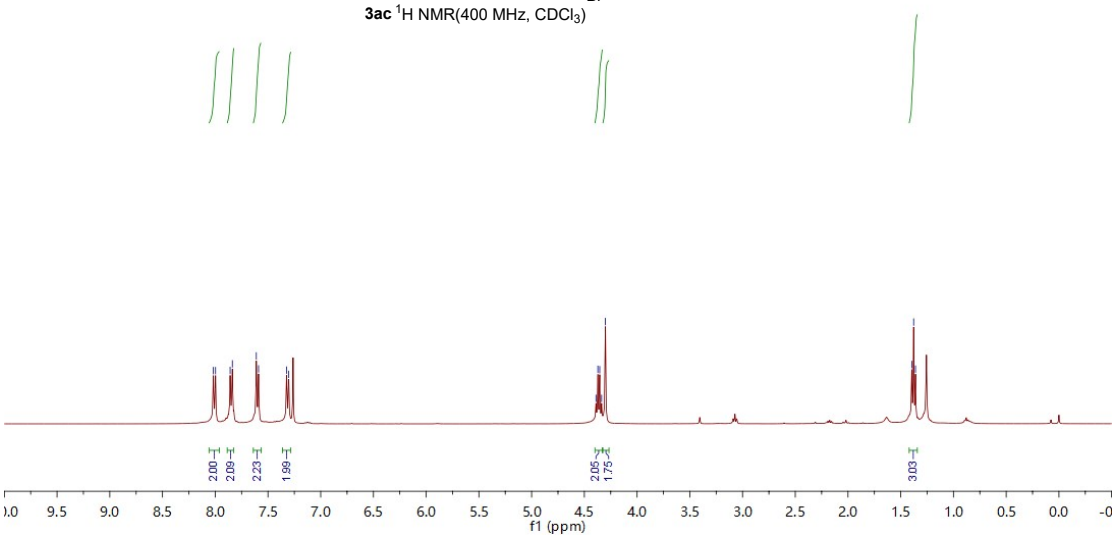
3ab ^{1}H NMR(400 MHz, $CDCl_3$)

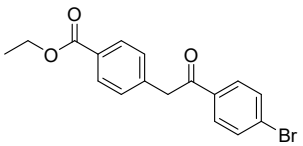


3ab ^{13}C NMR(100 MHz, $CDCl_3$)

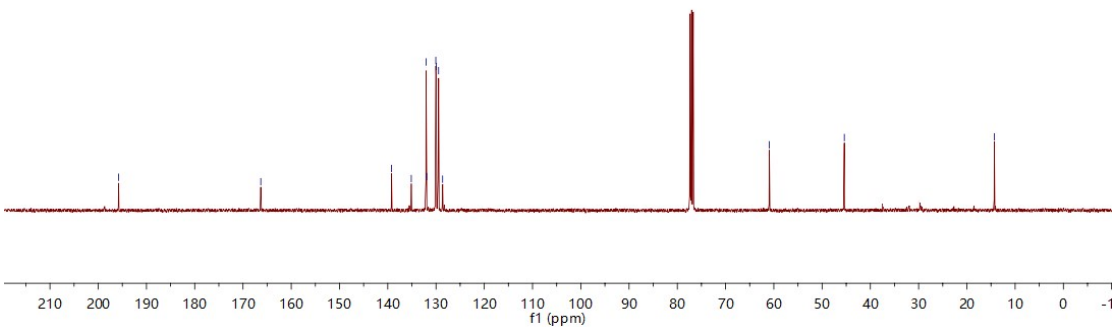


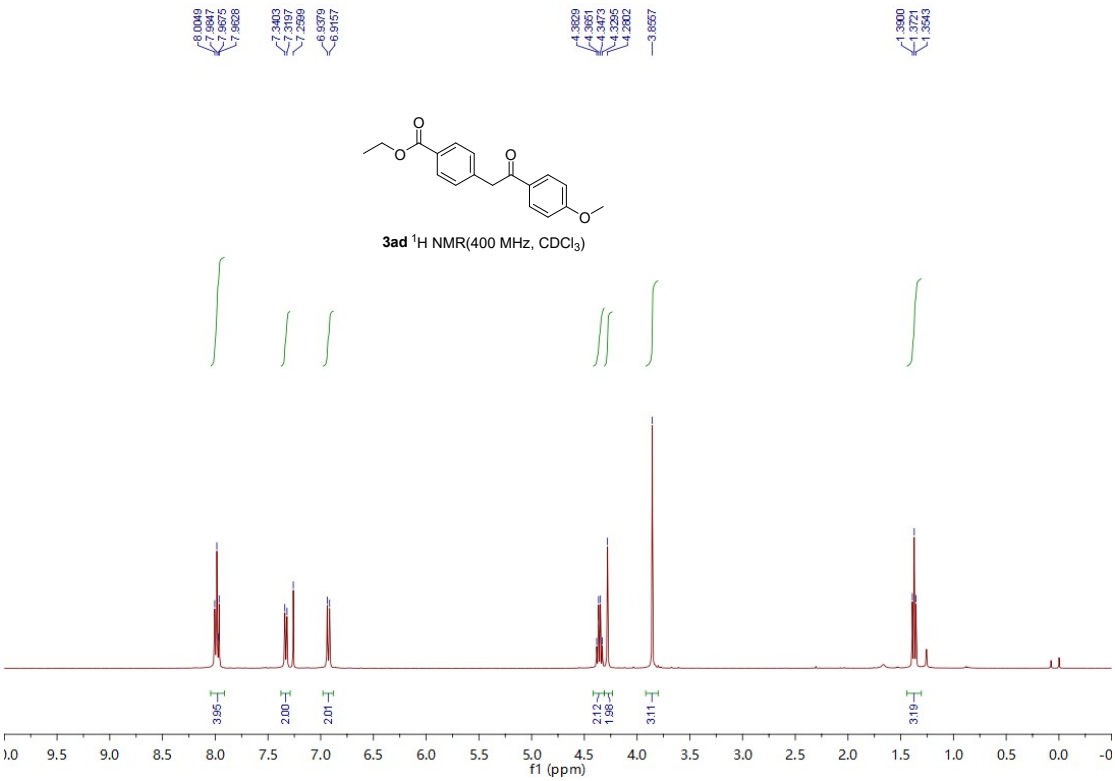
3ac ^{1}H NMR(400 MHz, $CDCl_3$)



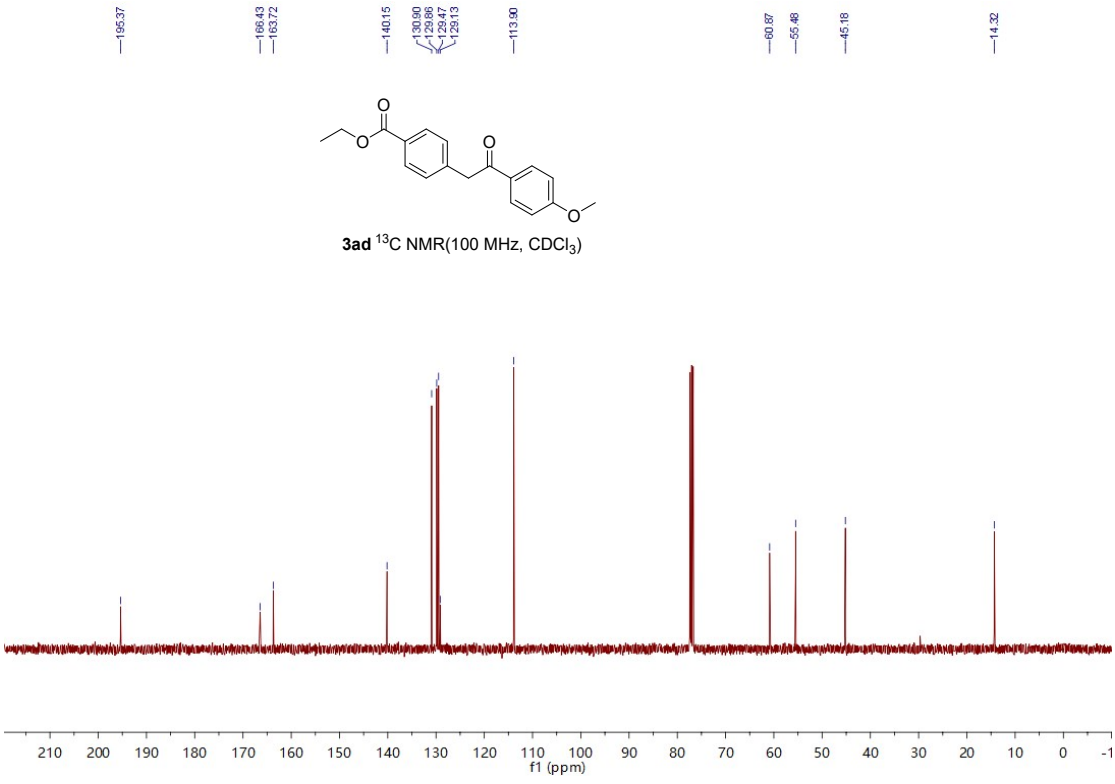


3ac ^{13}C NMR(100 MHz, $CDCl_3$)

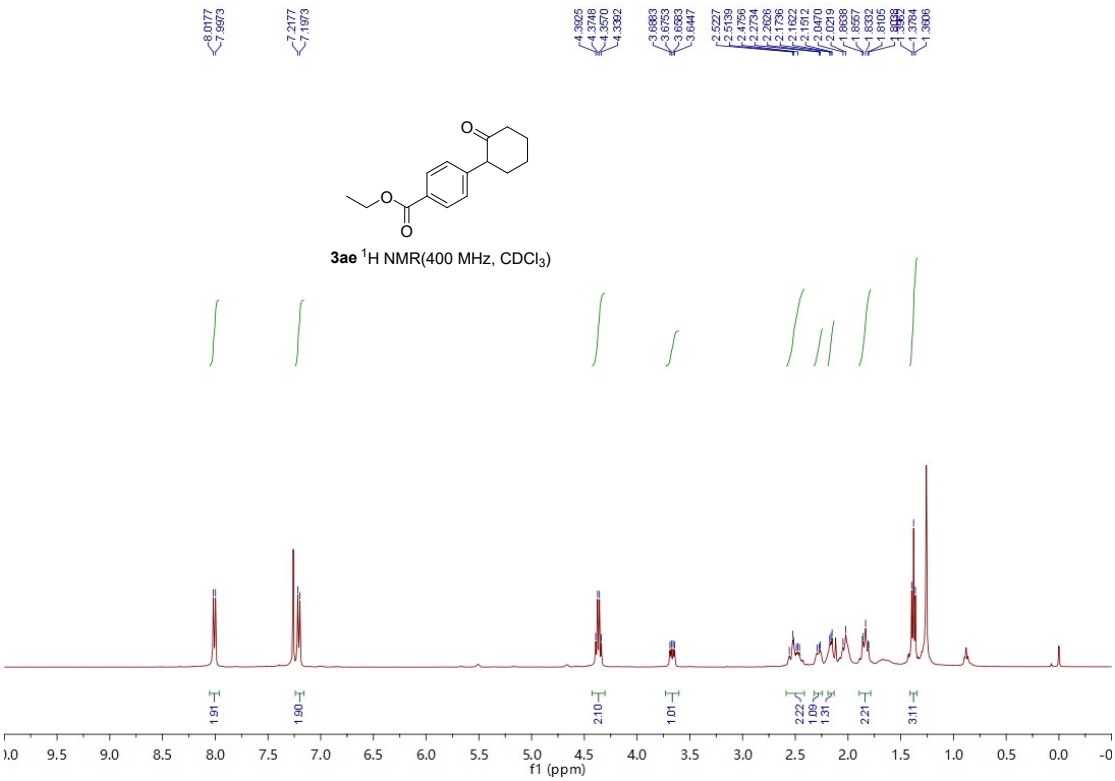




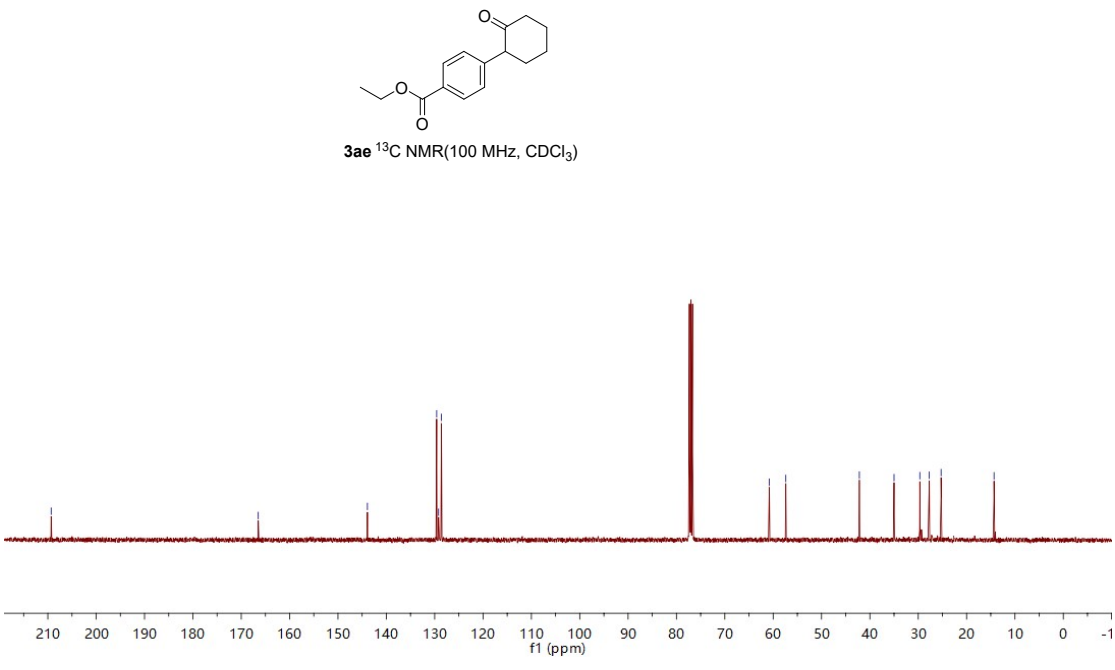
3ad ^{1}H NMR(400 MHz, $CDCl_3$)



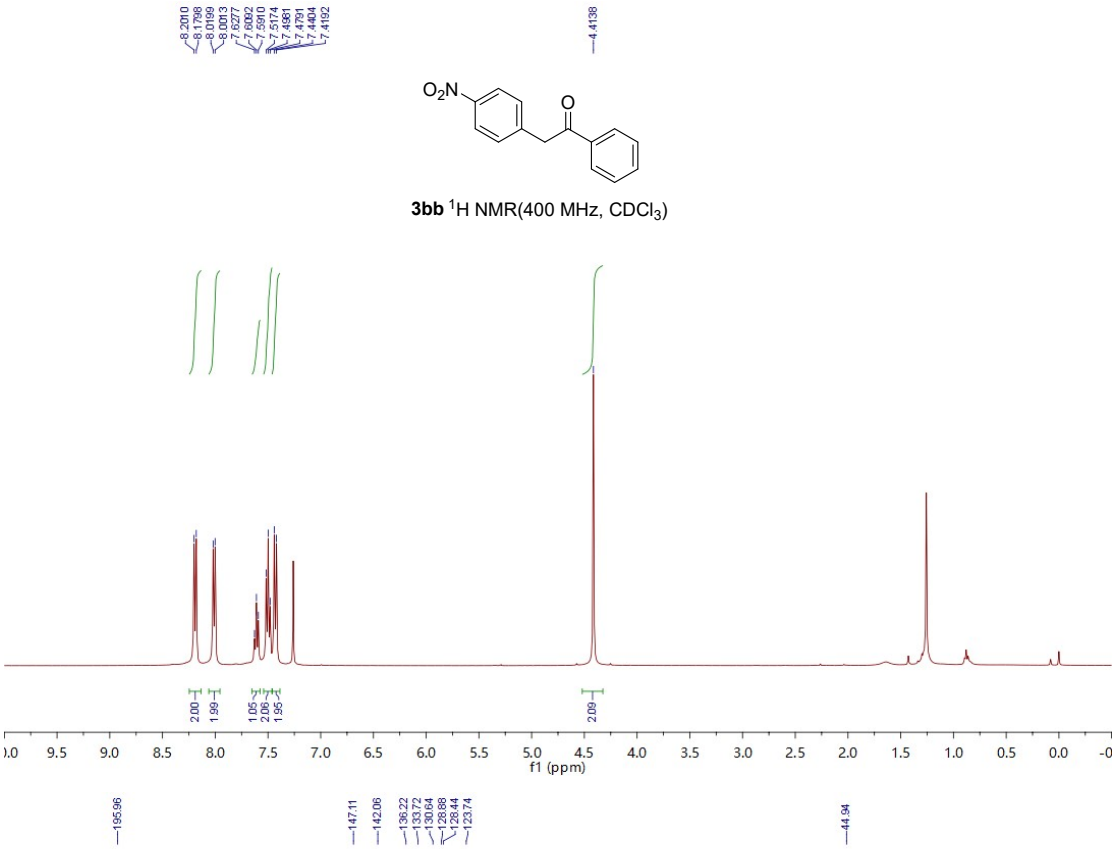
3ad ^{13}C NMR(100 MHz, $CDCl_3$)



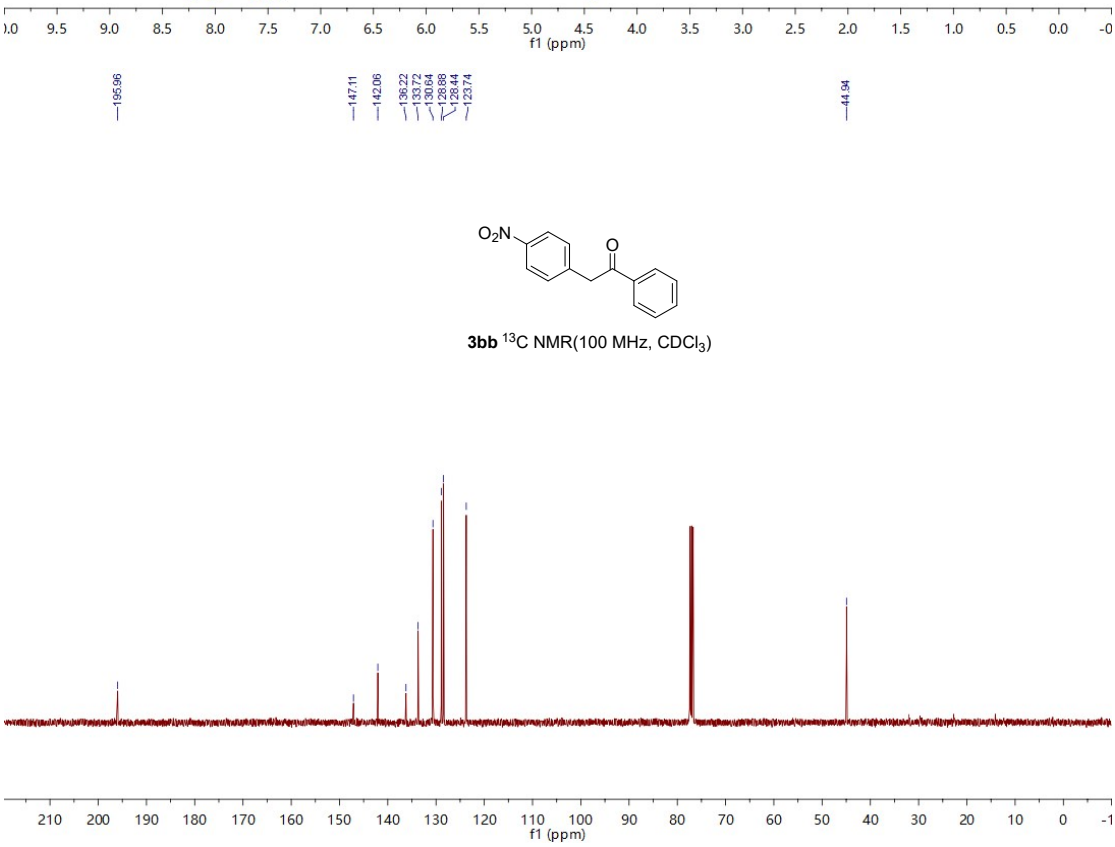
3ae ^{1}H NMR(400 MHz, $CDCl_3$)



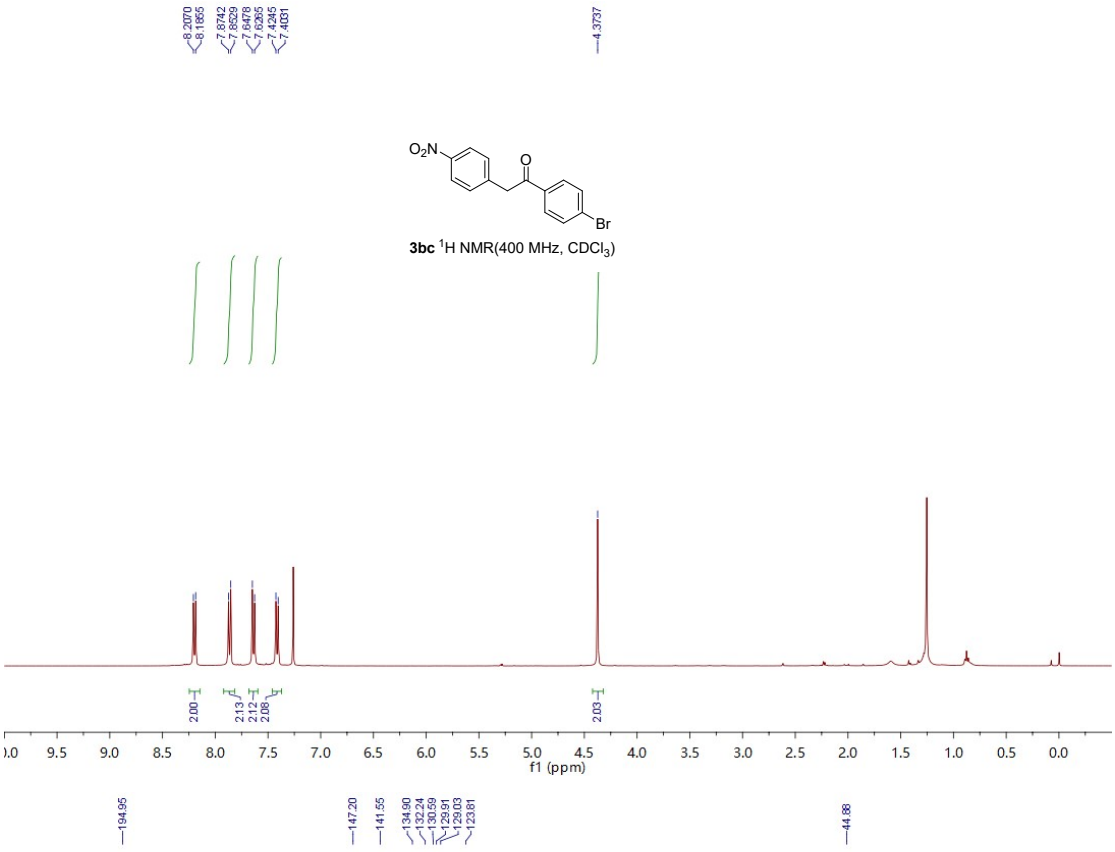
3ae ^{13}C NMR(100 MHz, $CDCl_3$)



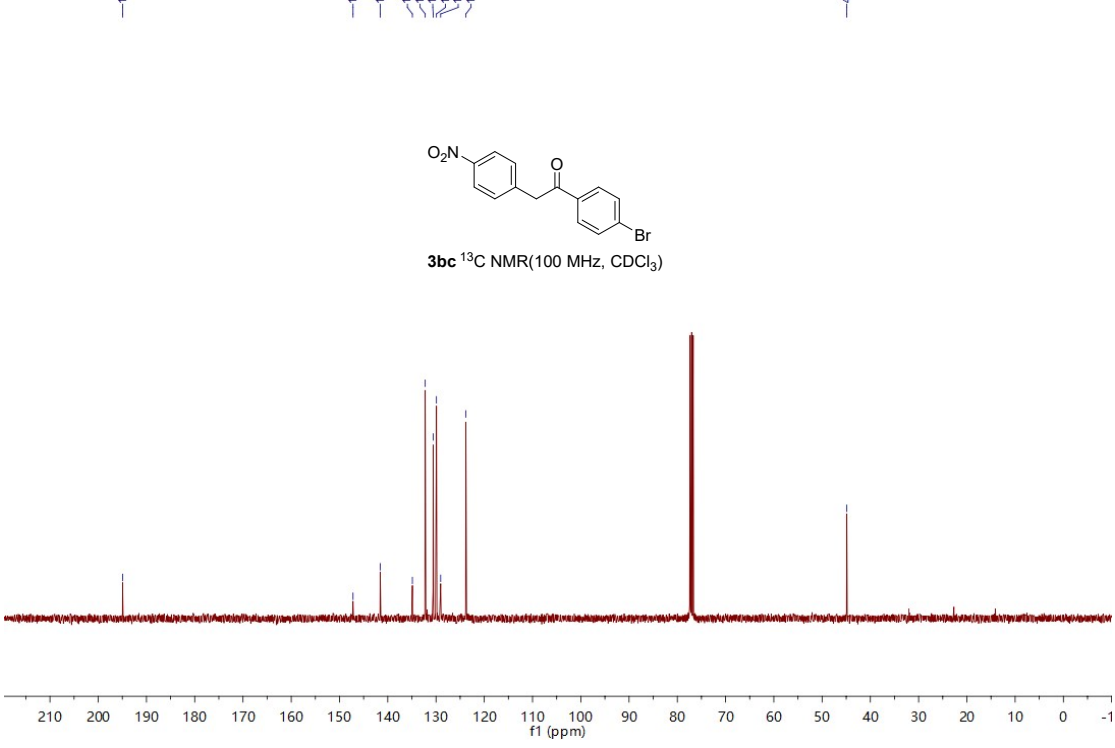
3bb ^{1}H NMR(400 MHz, $CDCl_3$)



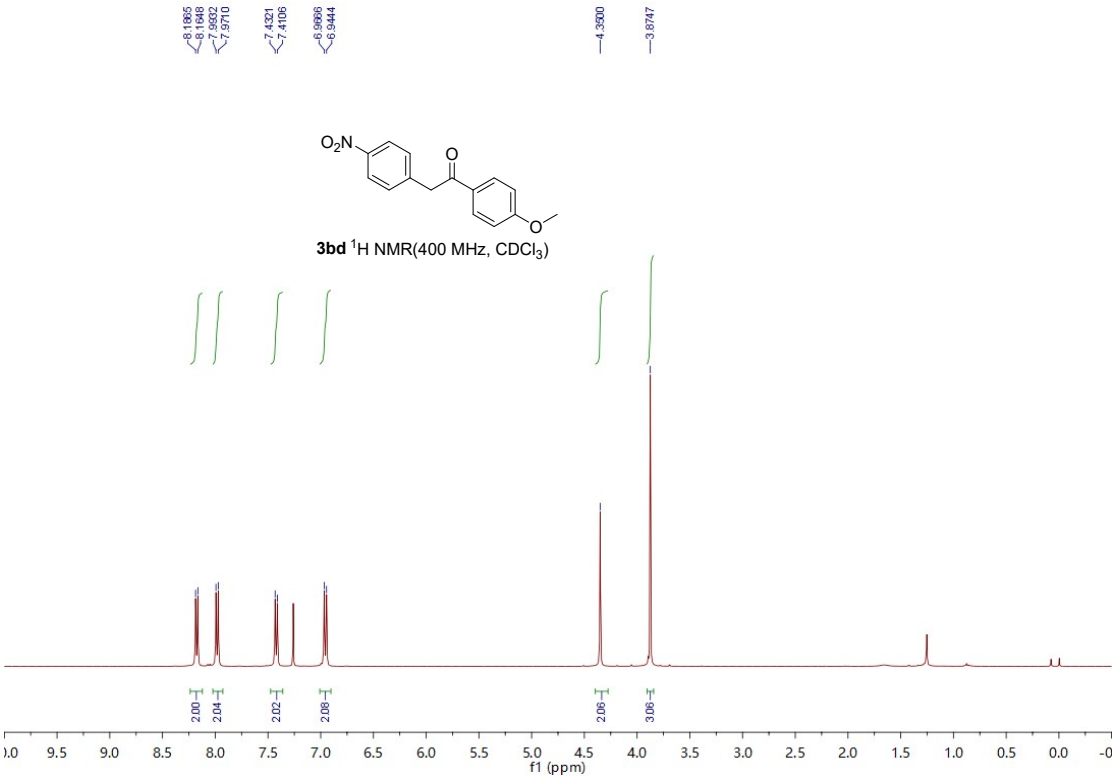
3bb ^{13}C NMR(100 MHz, $CDCl_3$)



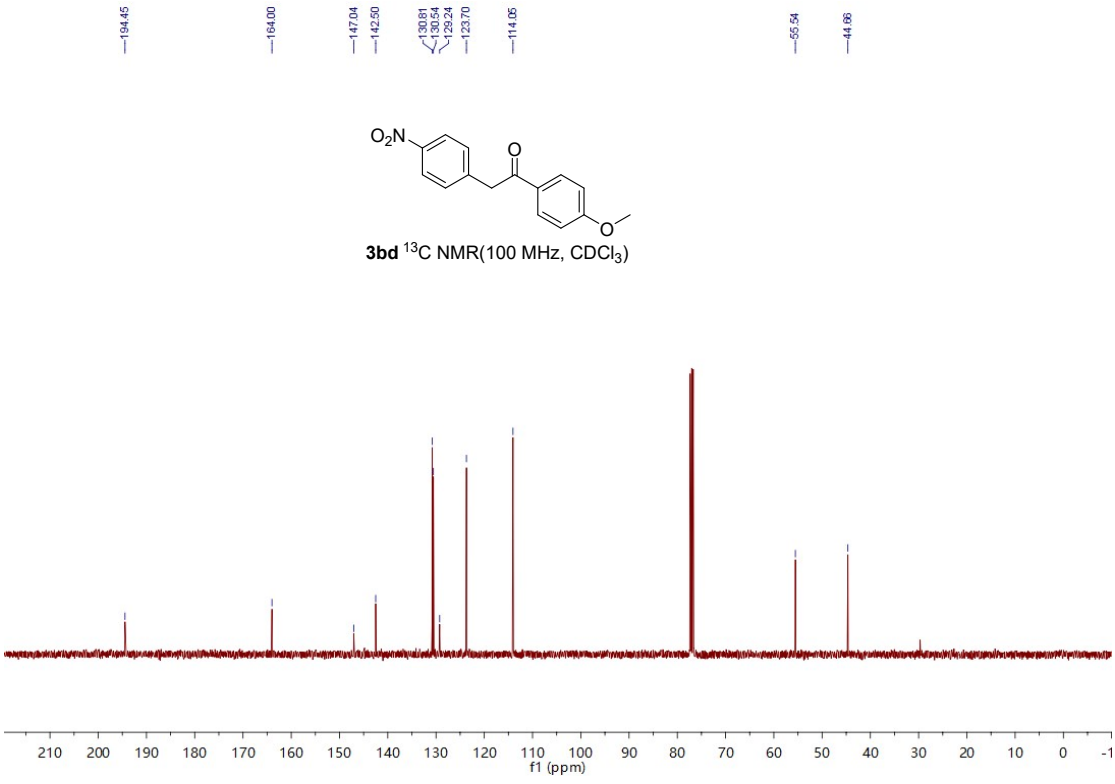
3bc ^{1}H NMR(400 MHz, $CDCl_3$)



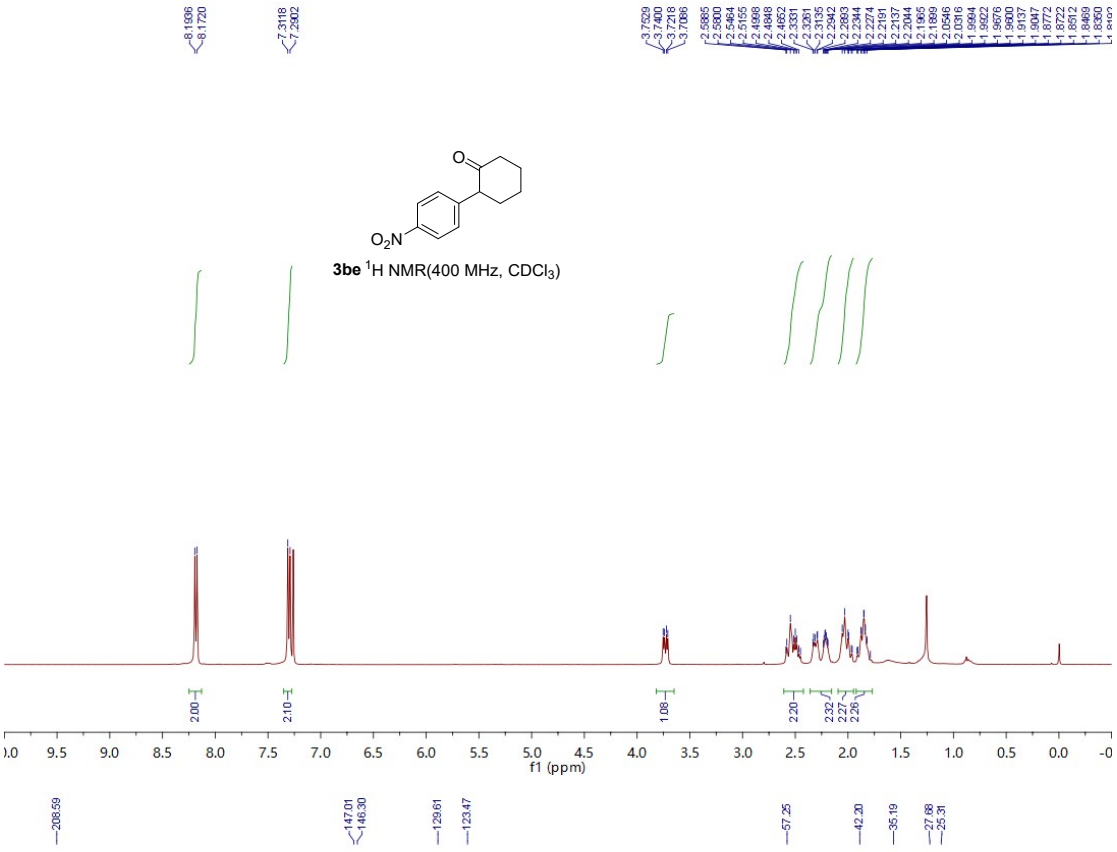
3bc ^{13}C NMR(100 MHz, $CDCl_3$)



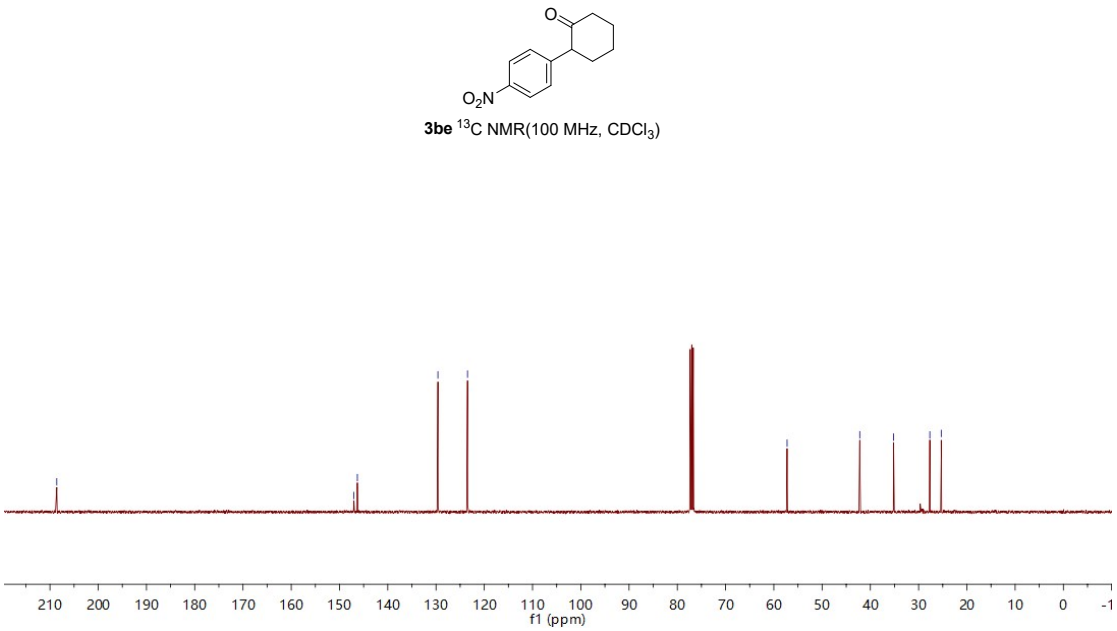
3bd ^{1}H NMR(400 MHz, $CDCl_3$)



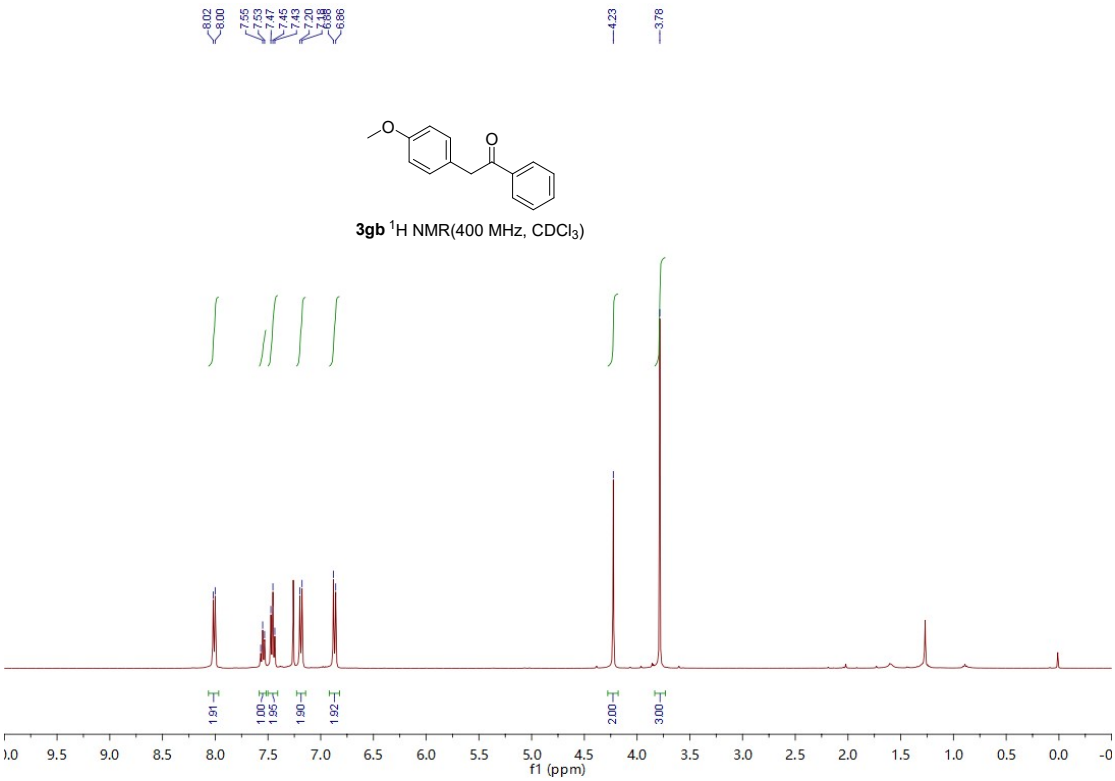
3bd ^{13}C NMR(100 MHz, $CDCl_3$)



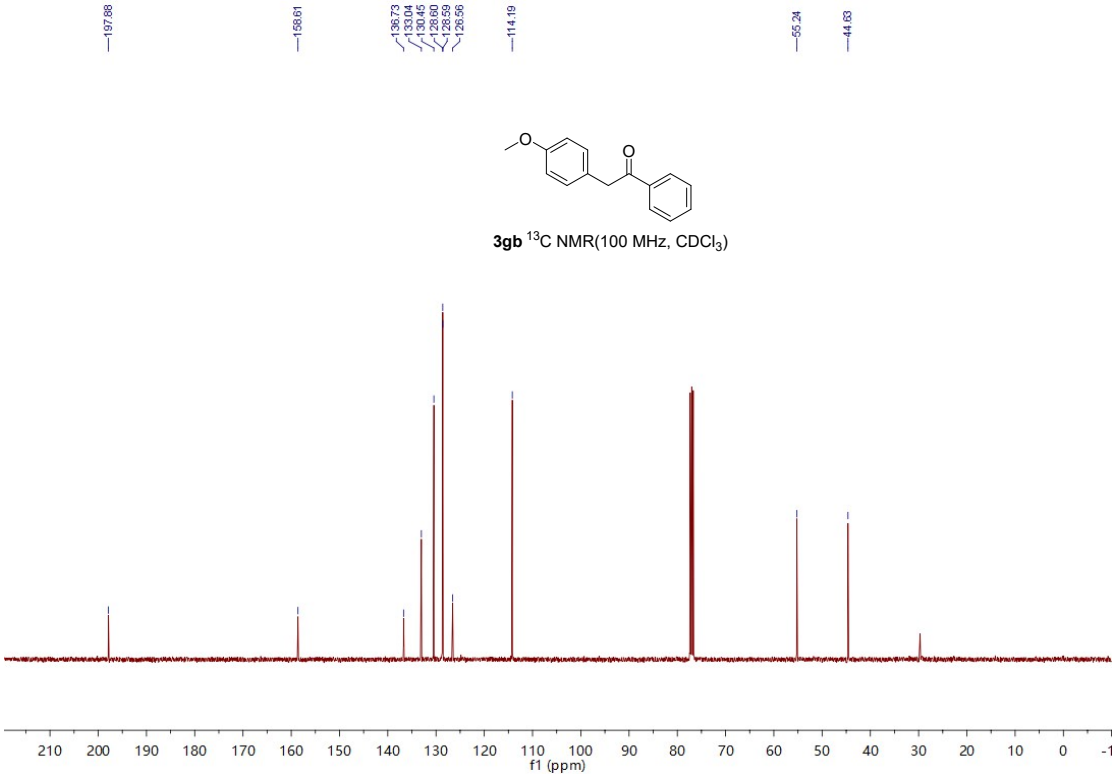
3be ^{1}H NMR(400 MHz, $CDCl_3$)



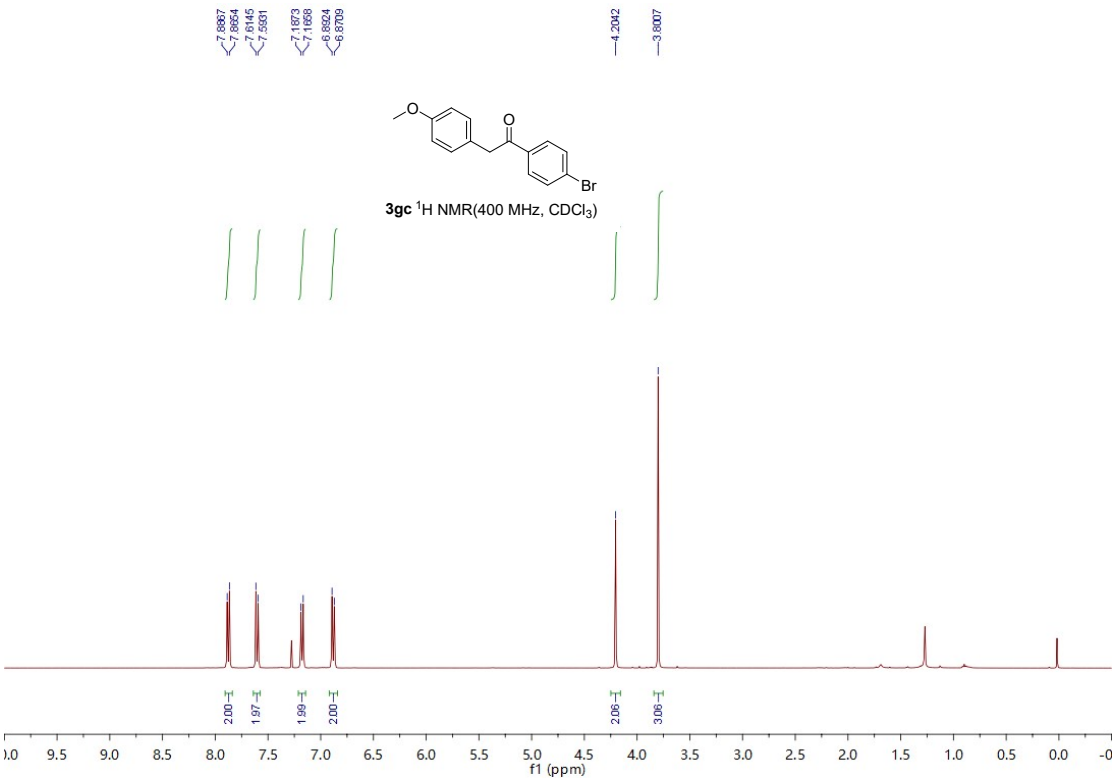
3be ^{13}C NMR(100 MHz, $CDCl_3$)



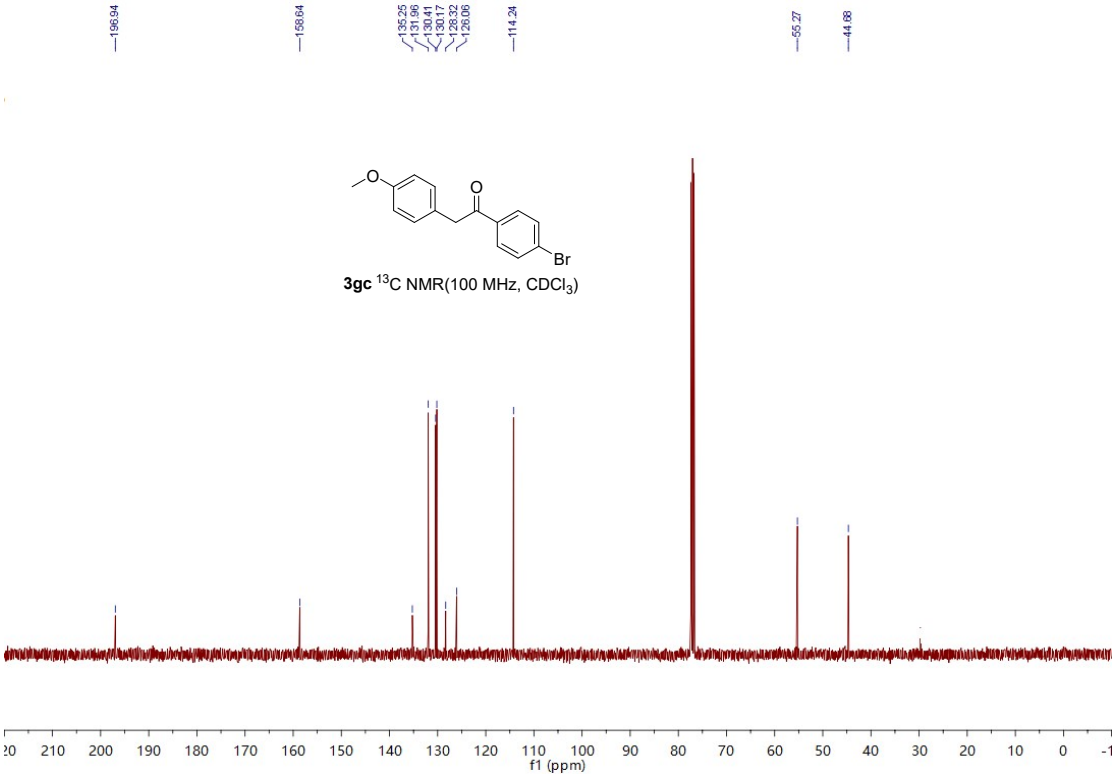
3gb ^{1}H NMR(400 MHz, $CDCl_3$)



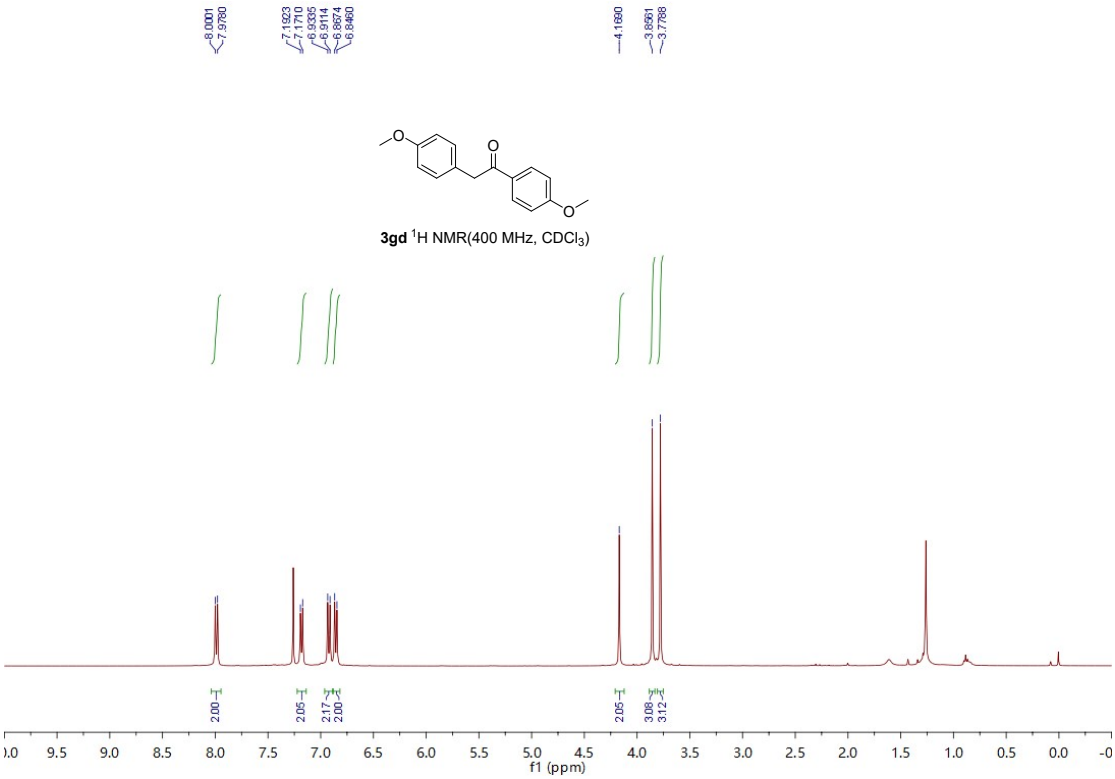
3gb ^{13}C NMR(100 MHz, $CDCl_3$)



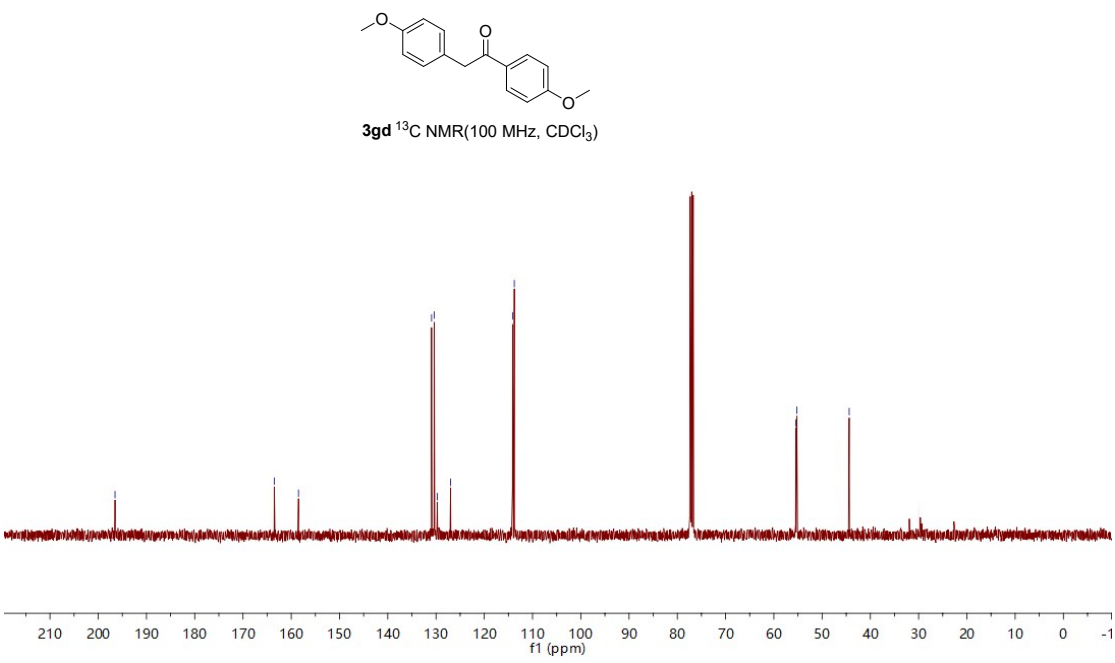
3gc ^{1}H NMR(400 MHz, $CDCl_3$)



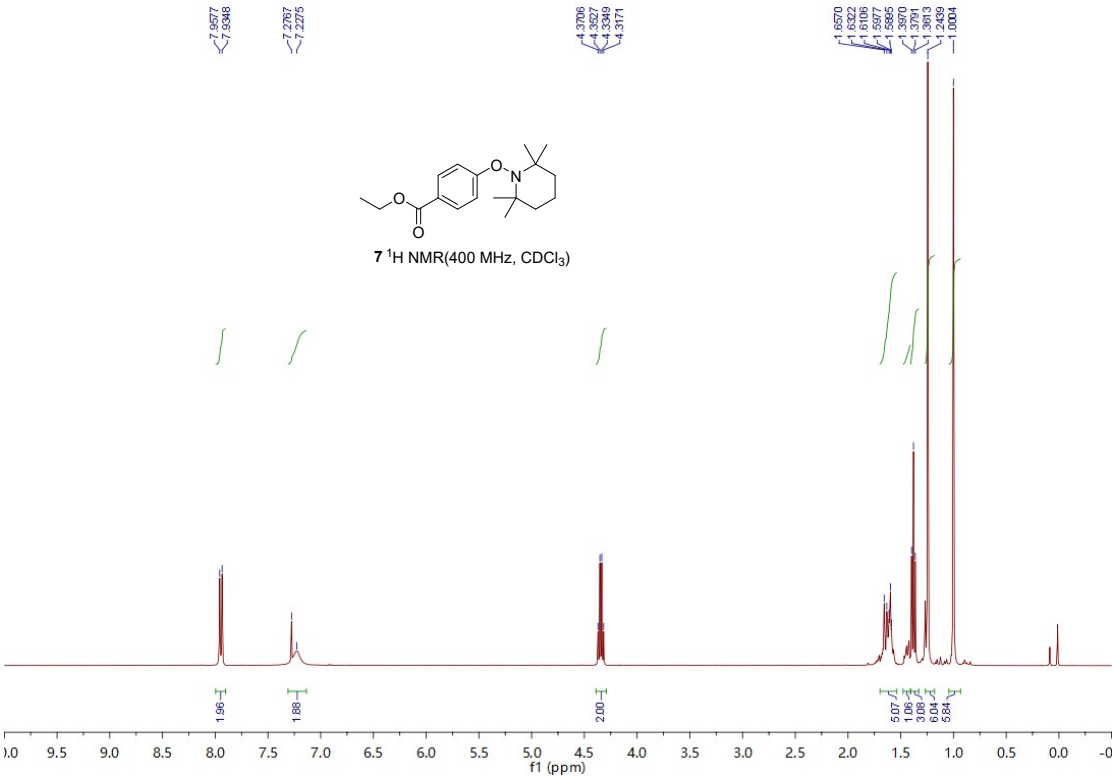
3gc ^{13}C NMR(100 MHz, $CDCl_3$)



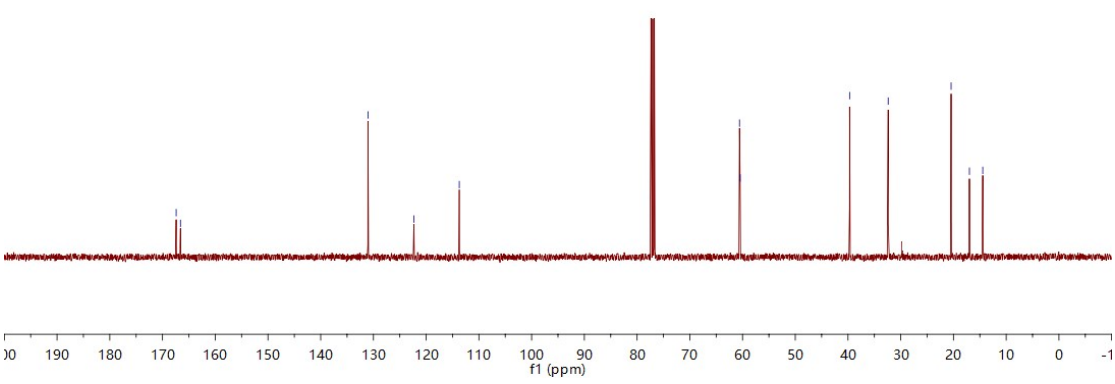
3gd ^{1}H NMR(400 MHz, $CDCl_3$)



3gd ^{13}C NMR(100 MHz, $CDCl_3$)



7 ^{1}H NMR(400 MHz, $CDCl_3$)



7 ^{13}C NMR(100 MHz, $CDCl_3$)