Supporting Information For

Thienylbenzotriazole Promoted Highly Active Gold Nanoparticles Supported on N-Doped Graphene as Efficient Catalysts in Water and Mechanism Exploration †

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Contents

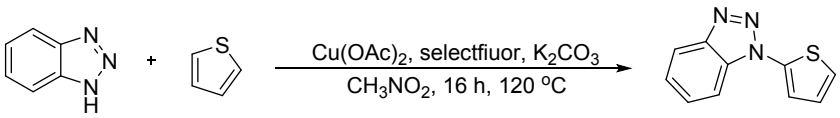
1. General methods and materials

All the reactions dealing with air were carried out in a high purity argon or nitrogen atmosphere using standard Schlenk techniques or glovebox techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 or 101 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm), DMSO (δ 2.50 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm), DMSO (δ 40.35 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ). IR spectra were recorded on total reflection Fourier infrared spectrometer (NICOLET 6700). The crystal structures were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer. TEM was recorded on a transmission electron microscope (JEM–2100, JEOL, Japan), operating at 200 kV. SEM image and EDS spectra was performed on a HITACHI S-4800 field-emission scanning electron microscope. XPS data were recorded with electron energy analyzer (ESCALAB 250Xi, Thermo Fisher Co, USA). TG analysis was carried out using a STA409 instrument in dry air at a heating rate of 10^{o}C/min from 50 to 800 ^{o}C.

2. Synthesis of catalyst TTA-Au-NG

2.1. Synthesis of gold (III) compound

2.1.1. Synthesis of thienylbenzotriazole ligand



L1

Thiophene (5.0 mmol), 1*H*-benzo[*d*][1,2,3]triazole (10.0 mmol), selectfluor (7.5 mmol), $Cu(OAc)_2$ (0.5mmol), and K_2CO_3 (10.0 mmol) were added to CH_3NO_2 (30 mL). The mixture was stirred at 120 ^{o}C for 16 h, the reaction mixture was added water and extracted with ethyl acetate three times. The combined organic phases was dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum. Finally, the residue was purified by flash column chromatography with ethyl acetate/ petroleum ether to give the desired product (**L1,** 90% yield).

2.1.2. Synthesis of gold(III) compound

The ligand (L1, 1.0 mmol) and KOH (1.0 mmol) were added to 50 mL Schlenk with EtOH (5 mL) under N_2 atmosphere, the mixture was stirred for 30 min at room temperature. Next, $KAuCl_4.2H_2O$ (1.0 mmol) solved in EtOH (5 mL) and added to above reaction. The resulting mixture was stirred overnight at room temperature, then the cloudy solution was filtered through a short pad of

celite. The clear solution was concentrated under vacuum. The yellow solid was dissolved with CH_2Cl_2 , the insoluble impurities was filtered through filter paper, The clear solution was concentrated under vacuum and then added dropwise to a flask containing petroleum ether. The precipitated solid was washed several times with diethyl ether, dried and filtered to afford the complex **TTA-Au.**

TTA-Au (yellow solid, 75% yield): ^{1}H NMR (400 MHz, DMSO) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.58 – 7.52 (m, 1H), 7.26 (dd, *J* = 5.0, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 145.93 (s), 137.18 (s), 132.44 (s), 129.79 (s), 127.36 (s), 125.65 (s), 124.77 (s), 120.33 (s), 120.31 (s), 111.39 (s).

2.2.1. Synthesis of Graphene oxide

The synthesis of graphene oxide is obtained by the modified Hummers method. Firstly, concentrated sulfuric acid (25 mL) was added to 100 mL conical flask under 90 ^{o}C, then potassium persulfate and phosphorus pentoxide poured into aboved liquid and stirred until the mixture dissolved completely. Next, the resulting mixture was cooled to 80 ^{o}C, 6 g of natural graphite powder was added and stirred for a while, then the mixture was cooled to room temperature and washed with 1 L of deionized water, and the resulting product was allowed to stand at room temperature overnight. After filtered, washed, dried, the above product (pre-oxidized graphite) was placed in a three-necked flask, and then a large amount of concentrated sulfuric acid and 30 g of potassium permanganate were slowly added, stirred untill dissolved completely under below 10 ^{o}C .The mixture was reacted in a water bath at 35 ^{o}C for 2 h, then deionized water was added for hydrolysis (initially, deionized water was slowly added, and this process was always carried out in an ice bath), and the temperature was controlled to below 50 ^{o}C, as the water added continuously, the activity of the reactants continued to decreased until the last added deionized water did not cause significant temperature changes. The solution was transferred to a large beaker, 1.4 L of deionized water was added, and the reaction was stirred for 2 h. Next, 25 mL of 30% hydrogen peroxide was added to the mixture, and a bright earthy yellow solution was obtained. Then the supernatant was removed, washed with a large amount of HCl solution, and then washed with a large amount of deionized water until the resulting solution was neutral. Finally, the resulting mixture solution was centrifuged to obtain a high concentration of graphene oxide.

2.2.2. Preparation of nitrogen-doped graphene

0.26 g of urea dissolved in 50 mL of methanol, then 0.6 g of grapheme oxide added to aboved solution under ultrasonication, the uniformly dispersed mixture was placed in a hydrothermal reactor under 150 ^{o}C for 12 h, the reaction product is taken out and dried, placed in a tube furnace, then passed through N_2, and calcined at 750 ^{o}C for 4 h. Finally, the product grinded for next step.

2.3. Synthesis of TTA-Au-NG

Nitrogen-doped graphene (500 mg) was dispersed in ethanol (50mL) under ultrasonication, gold(III) complex TTA-Au (25 mg) was dissolved in ethanol (5 mL), and added to above disperson liquid at 78 ^{o}C. After 12 hours later, cooling the reaction to room temperature. The composite (5 % loading, w/w) was collected by centrifugation, washed with ethanol for several times, followed by vacuum freeze-drying for 12 h.

3. Characterization of catalyst TTA-Au-NG

Fig.S1 showed SEM EDS image of TTA-Au-NG (a), and corresponding elemental mapping images of (b) C, (c) O, (d) S, (e) Au, which revealed gold nanoparticles was supported on nitrogen-doped graphene successfully.

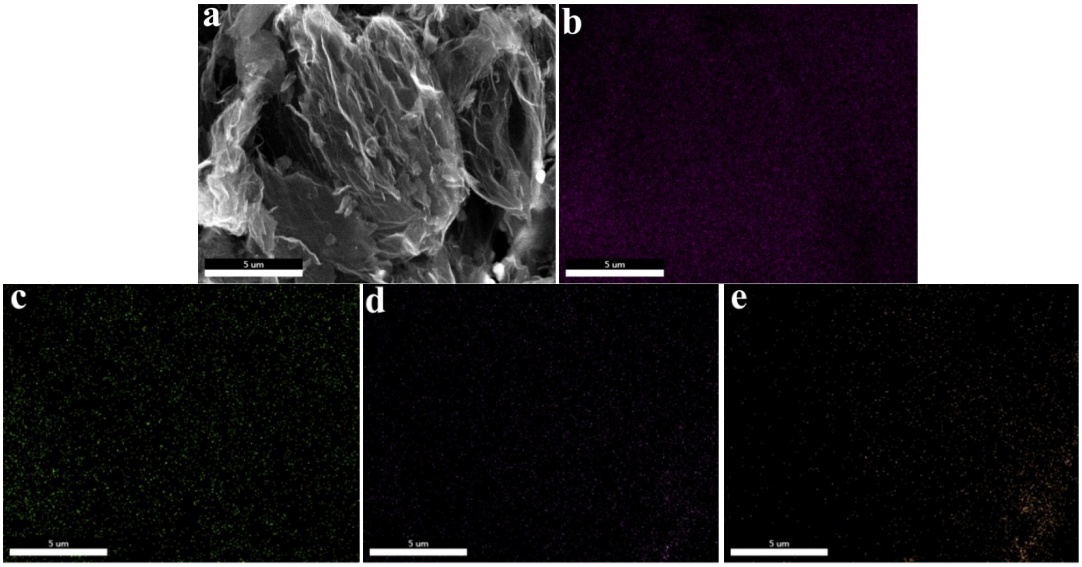


Fig.S1. SEM EDS image of TTA-Au-NG (a), and corresponding elemental mapping images of (b) C, (c) O, (d) S, (e) Au.

Fig.S2 showed SEM and TEM images of TTA-Au-NG after five runs, and Fig.S3 showed TG and DTG pattern of gold compound (TTA-Au). There was only a decrease in water composition before 140 ^{o}C, and the complex began to decompose after 140 ^{o}C.

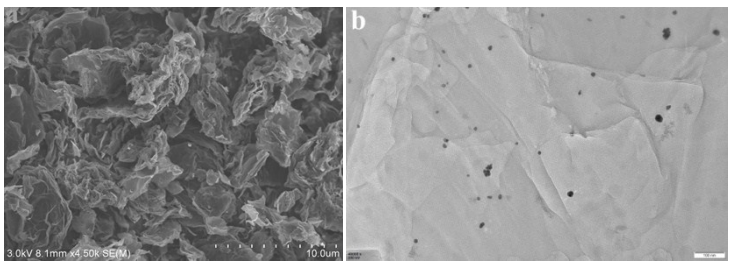


Fig.S2. SEM and TEM images of TTA-Au-NG after five runs

Fig.S4 showed XPS pattern of TTA-Au-NG. We could find the peaks at 87.9 and 84.2 eV were belonged to Au^0, the peaks of 284.8 and 532.6 eV were diffraction peaks of C 1s and O 1s respectively. In addition, the peaks of 398.3, 399.8 and 401.1 eV were diffraction peaks of N 1s.

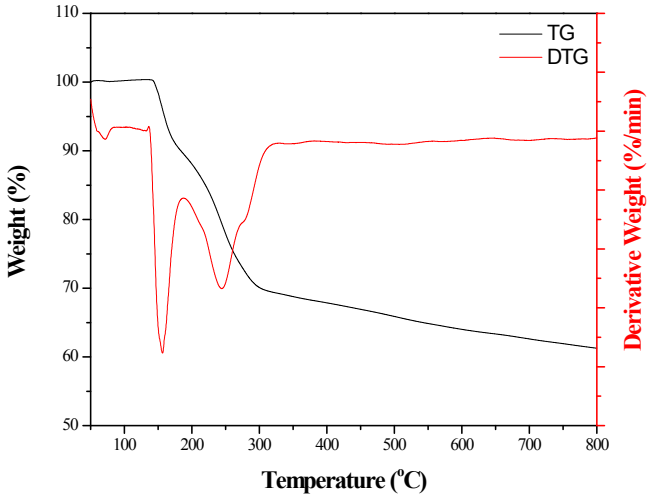


Fig.S3.TG and DTG pattern of gold compound (TTA-Au)

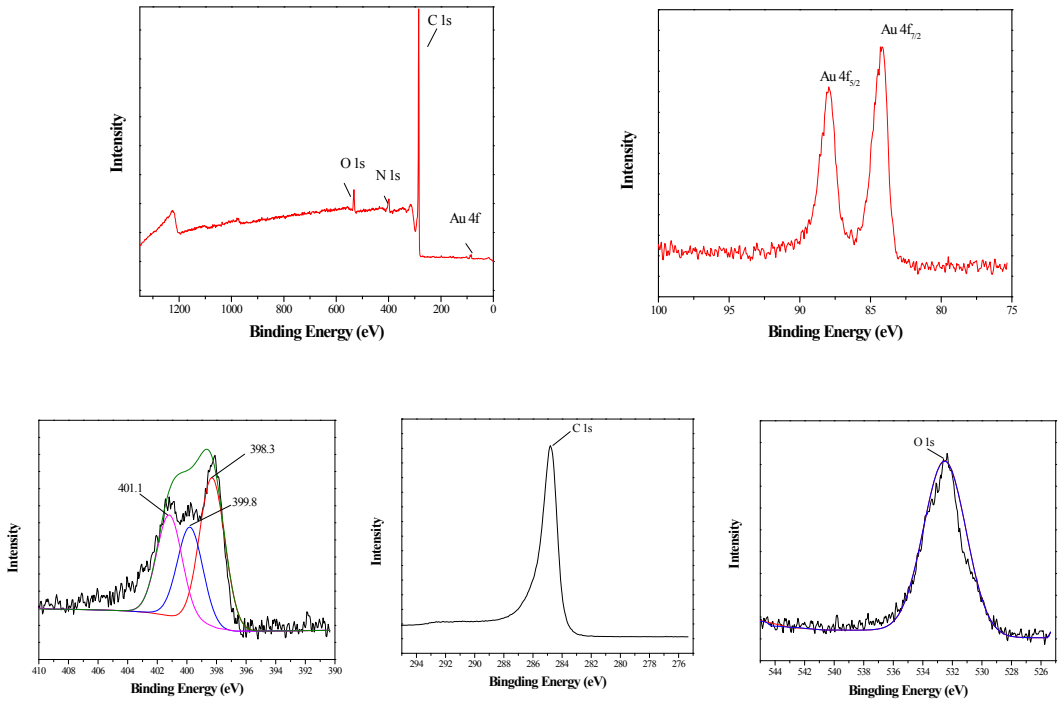


Fig.S4. XPS pattern of TTA-Au-NG

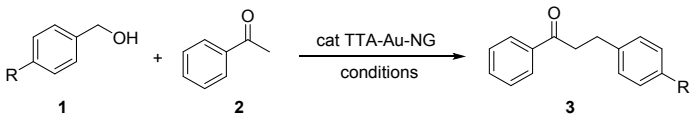
4. General procedure for 3

To 20 mL Schlenk tube was added TTA-Au-NG (5 wt%, 1.0 mol%), water (3.0 mL) and $AgNTf_2$ (0.05 eq.). Then **1** (1.0 mmol) and **2** (1.1 mmol) were added and the mixture was stirred at 100 ^oC for 12 h. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous $MgSO_4$ (or water was directly removed under reduced pressure). Then solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 20:1) afforded the compound **3**.

5. General procedure for 6

To 20 mL Schlenk tube was added TTA-Au-NG (5 wt%, 1.0 mol%), water (3.0 mL) and $AgNTf_2$ (0.05 eq.). Then **1** (1.0 mmol) and **5** (1.1 mmol) were added and the mixture was stirred at 90 ^oC for 12 h. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous $MgSO_4$ (or water was directly removed under reduced pressure). The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 20:1) afforded the compound **6**.

6. Hammett plot equation

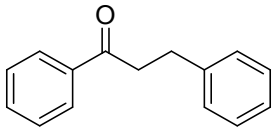


Experimental procedure: To 20 mL Schlenk tube was added TTA-Au-NG (5 wt%, 1.0 mol%), water (3.0 mL) and $AgNTf_2$ (0.05 eq.). Then **1** (1.0 mmol) and acetophenone (1.1 mmol) were added and the mixture was stirred at 100 ^{o} C for 1 h. After centrifugation and recovery the catalyst, the water mixture was extracted with EtOAc (3 x 10 mL). Next, the yield of product **3** was determined by GC.

R	H	Me	OMe	Cl
Yield	18 %	8 %	9 %	28 %

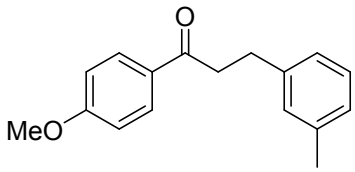
7. Compounds Characterization

1,3-diphenylpropan-1-one (3aa) [1]



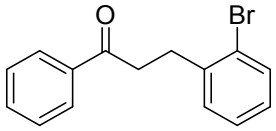
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.50 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.28 (m, 1H), 3.36 (dd, *J* = 8.5, 7.0 Hz, 2H), 3.19 – 3.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.20, 141.39, 136.98, 133.11, 128.68, 128.61, 128.52, 128.12, 126.22, 40.47, 30.22.

1-(4-methoxyphenyl)-3-(m-tolyl)propan-1-one (3ab) [2]



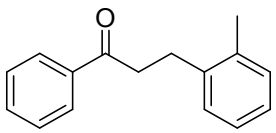
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 14.1, 9.3 Hz, 3H), 6.98 – 6.92 (m, 2H), 3.89 (s, 3H), 3.27 (dd, *J* = 8.8, 6.8 Hz, 2H), 3.11 – 2.99 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89, 163.46, 141.43, 138.08, 130.32, 130.05, 129.25, 128.43, 126.84, 125.40, 113.74, 55.46, 40.20, 30.31, 21.40.

3-(2-bromophenyl)-1-phenylpropan-1-one (3ac) [3]



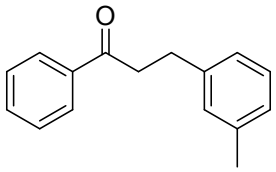
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.27 (td, *J* = 7.5, 1.1 Hz, 1H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 3.38 – 3.30 (m, 2H), 3.26 – 3.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.91 , 140.60 , 136.81 , 133.14 , 132.92 , 130.83 , 128.64 , 128.10 , 128.01 , 127.67 , 124.40 , 38.63 , 30.83 .

1-phenyl-3-(o-tolyl)propan-1-one (3ad) [4]



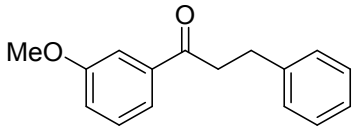
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 3.30 (dd, *J* = 9.0, 6.4 Hz, 2H), 3.11 (dd, *J* = 9.0, 6.7 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.38 , 139.42 , 136.91 , 136.02 , 133.11 , 130.38 , 128.77 , 128.66 , 128.08 , 126.36 , 126.21 , 39.14 , 27.56 , 19.38 .

1-phenyl-3-(m-tolyl)propan-1-one (3ae) [3]



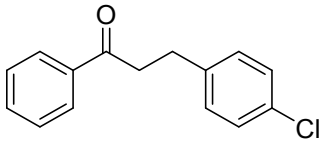
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 14.2, 9.4 Hz, 3H), 3.38 – 3.29 (m, 2H), 3.11 – 3.05 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.32 , 141.27 , 138.14 , 136.93 , 133.06 , 129.28 , 128.63 , 128.48 , 128.08 , 126.92 , 125.43 , 40.56 , 30.11 , 21.44 .

1-(3-methoxyphenyl)-3-phenylpropan-1-one (3af) [5]



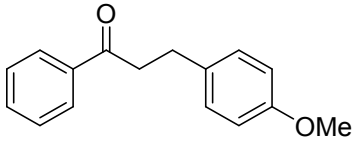
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 7.42 – 7.23 (m, 6H), 7.14 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.88 (s, 3H), 3.33 (t, *J* = 7.7 Hz, 2H), 3.11 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.04, 159.91, 141.32, 138.31, 129.61, 128.56, 128.46, 126.17, 120.70, 119.57, 112.36, 55.45, 40.56, 30.23.

3-(4-chlorophenyl)-1-phenylpropan-1-one (3ag) [3]



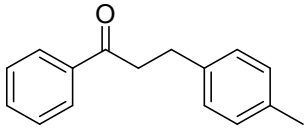
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.82 , 139.74, 136.79, 133.15, 131.89, 130.34, 129.82, 128.64, 128.01, 40.13, 29.40.

3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ah) [1]



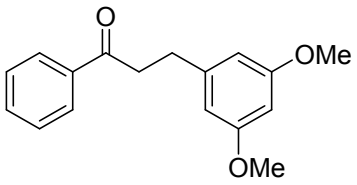
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.30 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.42, 158.03, 136.94, 133.34, 133.05, 129.38, 128.62, 128.06, 113.97, 55.30, 40.73, 29.31.

1-phenyl-3-(p-tolyl)propan-1-one (3ai) [3]



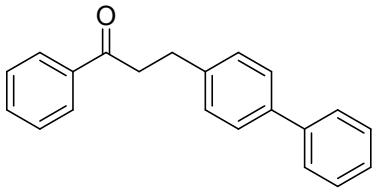
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.62 – 7.54 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.16 (q, *J* = 8.1 Hz, 4H), 3.40 – 3.19 (m, 2H), 3.15 – 2.97 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.37, 138.20, 136.91, 135.64, 133.04, 129.22, 128.61, 128.30, 128.06, 40.63, 29.74, 21.01.

3-(3,5-dimethoxyphenyl)-1-phenylpropan-1-one (3aj)



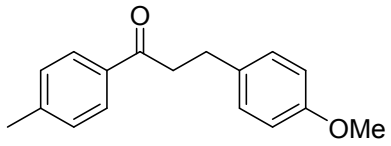
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.61 – 7.54 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 2.3 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 6H), 3.36 – 3.27 (m, 2H), 3.11 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.17, 160.94, 143.75, 136.89, 133.10, 128.64, 128.06, 106.52, 98.09, 55.28, 40.28, 30.46. HRMS (ESI) Calculated for $C_{17}H_{18}O_3$ $[M+H]^+$ 271.1334, found 271.1337.

3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one (3ak) [3]



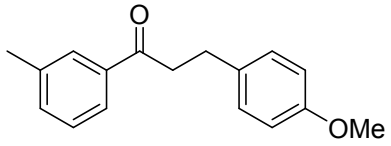
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.67 – 7.56 (m, 5H), 7.49 (dd, *J* = 17.5, 7.9 Hz, 4H), 7.41 – 7.33 (m, 3H), 3.39 (t, *J* = 7.6 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.21, 141.03, 140.47 , 139.18, 136.92, 133.15, 128.93, 128.80, 128.68, 128.11, 127.32, 127.17, 127.06, 40.41, 29.79.

3-(4-methoxyphenyl)-1-(p-tolyl)propan-1-one (3al) [1]



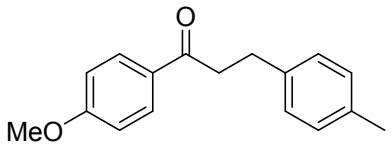
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.03, 158.04, 143.80, 134.51, 133.46, 129.40, 129.32, 128.22, 113.98, 55.27, 40.60, 29.42, 21.65.

3-(4-methoxyphenyl)-1-(m-tolyl)propan-1-one (3am)



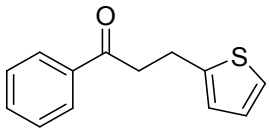
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 10.2 Hz, 2H), 7.37 (dd, *J* = 12.3, 4.8 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.29 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.59, 158.04, 138.39, 137.00, 133.82 , 133.43, 129.40, 128.63, 128.51, 125.30, 113.9. HRMS (ESI) Calculated for $C_{17}H_{18}O_2$ $[M+H]^+$ 255.1385, found 255.1387.

1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (3an) [6]



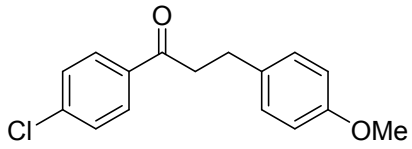
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.16 (q, *J* = 8.1 Hz, 4H), 7.00 – 6.89 (m, 2H), 3.89 (s, 3H), 3.30 – 3.21 (m, 2H), 3.11 – 2.94 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.96, 163.45, 138.39, 135.58, 130.33, 130.03, 129.21, 128.32, 113.74, 55.48, 40.31, 29.95, 21.03.

1-phenyl-3-(thiophen-2-yl)propan-1-one (3ao) [1]



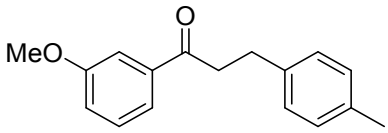
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.64 – 7.54 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.90 (dd, *J* = 3.4, 0.9 Hz, 1H), 3.43 – 3.37 (m, 2H), 3.37 – 3.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.59, 143.91, 136.79, 133.18, 128.66, 128.06, 126.88, 124.70, 123.40, 40.56, 24.25.

1-(4-chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (3ap) [7]



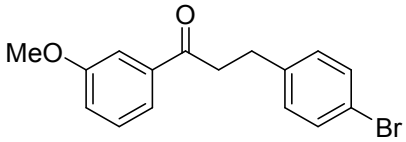
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.82 (m, 2H), 7.49 – 7.36 (m, 2H), 7.21 – 7.11 (m, 2H), 6.95 – 6.78 (m, 2H), 3.81 (s, 3H), 3.26 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.15, 158.08, 139.47, 135.24, 133.09, 129.48 , 129.36 , 128.92 , 114.00 , 55.29 , 40.69 , 29.23 .

1-(3-methoxyphenyl)-3-(p-tolyl)propan-1-one (3aq)



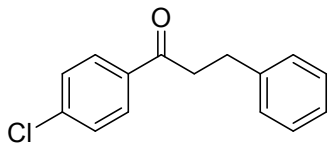
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.17 (ddd, *J* = 9.5, 4.4, 3.4 Hz, 5H), 3.89 (s, 3H), 3.32 (t, *J* = 7.7 Hz, 2H), 3.12 – 3.03 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.13 , 159.91 , 138.35 , 138.24 , 135.64 , 129.61 , 129.25 , 128.35 , 120.71 , 119.56 , 112.36 , 55.44 , 40.73 , 29.83 , 21.04 . HRMS (ESI) Calculated for $C_{17}H_{18}O_2$ $[M+H]^+$ 255.1385, found 255.1383.

3-(4-bromophenyl)-1-(3-methoxyphenyl)propan-1-one (3ar)



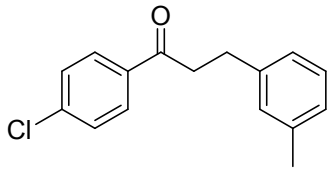
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.45 – 7.34 (m, 3H), 7.13 (dd, *J* = 12.8, 5.5 Hz, 3H), 3.86 (s, 3H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.59 , 159.91 , 140.28 , 138.16 , 131.56 , 130.77 , 130.26 , 129.64 , 120.63 , 119.62 , 112.35 , 55.45 , 40.15 , 29.51 . HRMS (ESI) Calculated for $C_{16}H_{15}BrO_2$ $[M+H]^+$ 319.0334, found 319.0336.

1-(4-chlorophenyl)-3-phenylpropan-1-one (3as) [3]



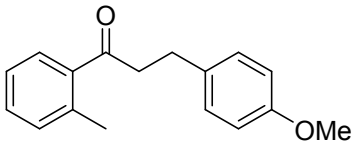
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 3.30 (t, *J* = 7.7 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.00 , 141.07 , 139.52 , 135.20 , 129.47 , 128.94 , 128.58 , 128.42 , 126.24 , 40.43 , 30.07 .

1-(4-chlorophenyl)-3-(m-tolyl)propan-1-one (3at)



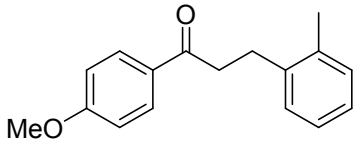
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.50 – 7.43 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.11 (dd, *J* = 13.6, 5.8 Hz, 3H), 3.34 – 3.25 (m, 2H), 3.11 – 3.05 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.99 , 141.08 , 139.47 , 138.17 , 135.26 , 129.52 , 129.29 , 128.94 , 128.54 , 127.03 , 125.46 , 40.52 , 30.04 , 21.47 . HRMS (ESI) Calculated for $C_{16}H_{15}ClO$ $[M+H]^+$ 259.0890, found 259.0892.

3-(4-methoxyphenyl)-1-(o-tolyl)propan-1-one (3au)



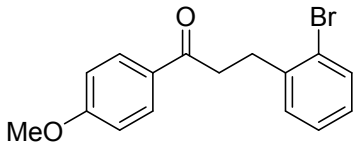
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.54 (m, 1H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.92 – 6.79 (m, 2H), 3.81 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.60, 158.02, 138.06, 138.02, 133.24, 131.93, 131.18, 129.35, 128.33, 125.65, 113.94, 55.28, 43.53, 29.50, 21.20. HRMS (ESI) Calculated for $C_{17}H_{18}O_2$ $[M+H]^+$ 255.1385, found 255.1383.

1-(4-methoxyphenyl)-3-(o-tolyl)propan-1-one (3av) [2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.26 – 7.15 (m, 4H), 7.02 – 6.92 (m, 2H), 3.90 (s, 3H), 3.31 – 3.17 (m, 2H), 3.13 – 3.01 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.97, 163.52 , 139.60 , 136.02 , 130.36 , 130.34 , 130.01 , 128.77 , 126.31 , 126.19 , 113.79 , 55.48 , 38.80 , 27.76 , 19.38 .

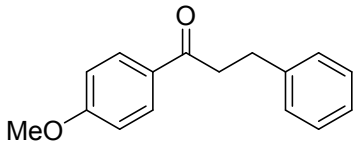
3-(2-bromophenyl)-1-(4-methoxyphenyl)propan-1-one (3aw) [6]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.26 (td, *J* = 7.5, 1.2 Hz, 1H), 7.10 (td, *J* = 7.7, 1.8 Hz, 1H), 6.98 – 6.89 (m, 2H), 3.88 (s, 3H),

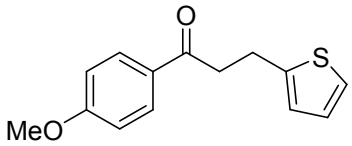
3.28 (m, 2H), 3.23 – 3.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.50, 163.53 , 140.76 , 132.88 , 130.80 , 130.36 , 129.93 , 127.94 , 127.64 , 124.39 , 113.77 , 55.47 , 38.28 , 31.04 .

1-(4-methoxyphenyl)-3-phenylpropan-1-one (3ax) [2]



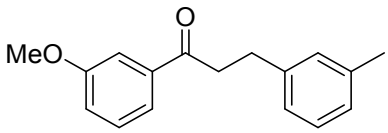
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.89 (m, 2H), 7.47 – 7.10 (m, 5H), 7.08 – 6.81 (m, 2H), 3.89 (s, 3H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.17 – 3.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.82 , 163.49 , 141.51 , 130.34 , 130.01 , 128.54 , 128.47 , 126.12 , 113.77 , 55.48 , 40.12 , 30.37 .

1-(4-methoxyphenyl)-3-(thiophen-2-yl)propan-1-one (3ay) [8]



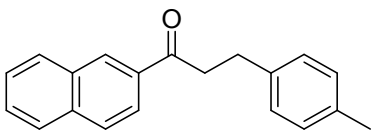
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.99 – 6.92 (m, 3H), 6.88 (dd, *J* = 3.3, 0.7 Hz, 1H), 3.88 (s, 3H), 3.32 (dt, *J* = 5.6, 2.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13 (s), 163.56 (s), 144.12 (s), 130.33 (s), 129.90 (s), 126.86 (s), 124.64 (s), 123.34 (s), 113.79 (s), 55.48 (s), 40.19 (s), 24.41 (s).

1-(3-methoxyphenyl)-3-(m-tolyl)propan-1-one (3az)



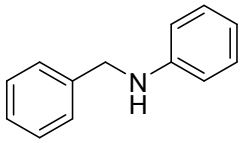
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.02 (m, 4H), 3.88 (s, 3H), 3.37 – 3.22 (m, 2H), 3.10 – 3.00 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.14 , 159.87 , 141.23 , 138.28 , 138.14 , 129.59 , 129.26 , 128.46 , 126.90 , 125.42 , 120.70 , 119.58 , 112.28 , 55.46 , 40.67 , 30.14 , 21.42. HRMS (ESI) Calculated for $C_{17}H_{18}O_2$ $[M+H]^+$ 255.1385, found 255.1387.

1-(naphthalen-2-yl)-3-(p-tolyl)propan-1-one (3ba) [9]



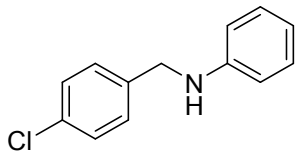
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 – 7.85 (m, 4H), 7.68 – 7.53 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.48 – 3.41 (m, 2H), 3.18 – 3.10 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.29 , 138.29 , 135.68 , 135.61 , 134.27 , 132.58 , 129.71 , 129.57 , 129.27 , 128.46 , 128.43 , 128.36 , 127.79 , 126.77 , 123.90 , 40.76 , 29.92 , 21.03 .

N-benzylaniline (6aa) [10]



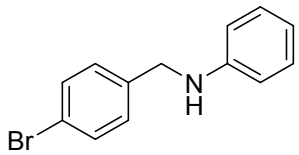
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 4H), 7.38 – 7.30 (m, 1H), 7.30 – 7.21 (m, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 4.39 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.22, 139.52, 129.33, 128.70, 127.58, 127.29, 117.65, 112.95, 48.40.

N-(4-chlorobenzyl)aniline (6ab) [10]



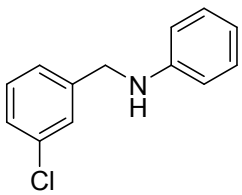
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 4H), 7.25 – 7.18 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 2H), 4.11 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.84, 138.03, 132.92 ,129.33 , 128.78, 128.74, 117.89, 112.97, 47.68.

N-(4-bromobenzyl)aniline (6ac) [10]



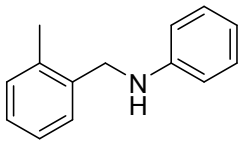
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.21 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.33 (s, 2H), 4.16 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.77, 138.54, 131.73, 129.33, 129.09, 120.97, 117.92, 112.99, 47.74.

N-(3-chlorobenzyl)aniline (6ad) [11]



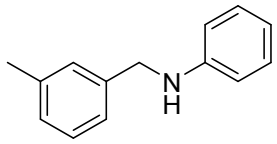
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.24 – 7.08 (m, 5H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.55 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.22 (s, 2H), 3.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95 , 141.96, 134.62, 130.05, 129.48, 127.54, 127.48, 125.56, 117.97, 113.05, 47.83.

N-(2-methylbenzyl)aniline (6ae) [10]



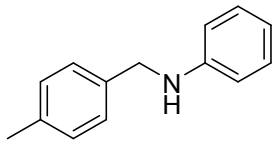
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.8 Hz, 1H), 7.32 – 7.18 (m, 5H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 2H), 4.32 (s, 2H), 3.93 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.29, 137.01, 136.38 , 130.45 , 129.31, 128.31 , 127.46 , 126.19 , 117.55 , 112.78 , 46.46 , 18.94 .

N-(3-methylbenzyl)aniline (6af) [12]



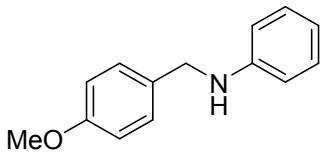
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.74 – 6.69 (m, 2H), 4.36 (s, 2H), 4.07 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.32 , 139.47 , 138.36, 129.33, 128.62, 128.38, 128.07, 124.68, 117.62, 112.96, 48.46, 21.49.

N-(4-methylbenzyl)aniline (6ag) [10]



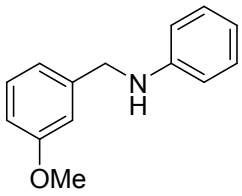
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3H), 7.22 – 7.16 (m, 3H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.31 (s, 2H), 4.13 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.10, 136.92, 136.27 , 129.32, 129.27, 117.64, 115.14, 112.98, 48.20, 21.11 .

N-(4-methoxybenzyl)aniline (6ah) [10]



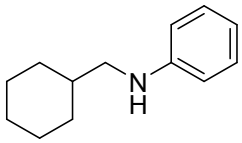
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.24 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 2H), 4.31 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95 , 148.26 , 131.49 , 129.30 , 128.86 , 117.59 , 114.11 , 112.95 , 55.34 , 47.88 .

N-(3-methoxybenzyl)aniline (6ai) [11]



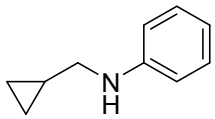
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.90 (dd, *J* = 8.3, 4.8 Hz, 2H), 6.78 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 4.23 (s, 2H), 3.98 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.06 , 148.31 , 141.38 , 129.79 , 129.40 , 119.85 , 117.68 , 113.16 , 113.01 , 112.75 , 55.30 , 48.39 .

N-(cyclohexylmethyl)aniline (6aj) [13]



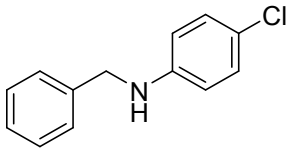
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 2H), 3.74 (s, 1H), 2.99 (d, *J* = 6.7 Hz, 2H), 1.86 (d, *J* = 13.0 Hz, 2H), 1.82 – 1.70 (m, 3H), 1.36 – 1.18 (m, 4H), 1.10 – 0.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 129.23, 116.93, 112.68, 50.65, 37.63, 31.35, 26.62, 26.01.

N-(cyclopropylmethyl)aniline (6ak) [13]



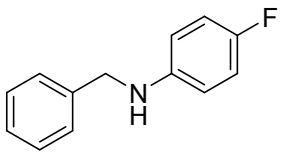
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.17 (s, 1H), 2.99 (d, *J* = 6.9 Hz, 2H), 1.18 – 1.07 (m, 1H), 0.65 – 0.52 (m, 2H), 0.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.13, 129.25, 117.65, 113.13, 49.35, 10.80, 3.48.

N-benzyl-4-chloroaniline (6al) [10]



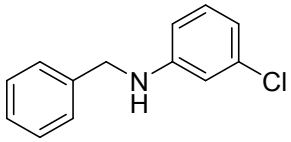
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.4 Hz, 4H), 7.36 – 7.30 (m, 1H), 7.18 – 7.12 (m, 2H), 6.64 – 6.49 (m, 2H), 4.34 (s, 2H), 4.14 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.65 , 138.95, 129.10, 128.73, 127.45, 127.41, 122.18, 113.99 , 48.40 .

N-benzyl-4-fluoroaniline (6am) [13]



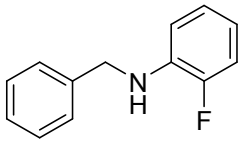
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.33 (m, 1H), 6.97 – 6.88 (m, 2H), 6.64 – 6.57 (m, 2H), 4.33 (s, 2H), 3.90 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.13 (s), 154.80 (s), 144.49 (d, *J* = 1.8 Hz), 139.26 (s), 128.70 (s), 127.44 (d, *J* = 18.3 Hz), 115.70 (d, *J* = 22.3 Hz), 113.74 (d, *J* = 7.4 Hz), 49.00 (s).

N-benzyl-3-chloroaniline (6an) [14]



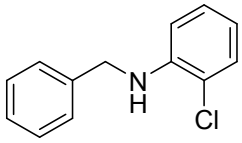
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 4H), 7.35 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.66 (t, *J* = 2.1 Hz, 1H), 6.54 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.35 (s, 2H), 4.17 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.28, 138.81, 135.08, 130.27, 128.79, 127.52 , 127.49, 117.48, 112.58, 111.20, 48.15 .

N-benzyl-2-fluoroaniline (6ao) [15]



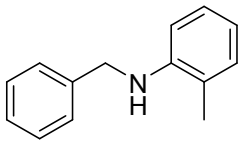
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 4H), 7.34 – 7.29 (m, 1H), 7.07 – 6.94 (m, 2H), 6.75 – 6.61 (m, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.97 (d, *J* = 245.7 Hz), 147.86 (s), 129.50 (d, *J* = 4.5 Hz), 129.34 (s), 128.85 (d, *J* = 8.1 Hz), 126.38 (d, *J* = 14.5 Hz), 124.25 (d, *J* = 3.5 Hz), 117.84 (s), 115.39 (d, *J* = 21.4 Hz), 113.02 (s), 41.91 (d, *J* = 4.3 Hz).

N-benzyl-2-chloroaniline (6ap) [10]



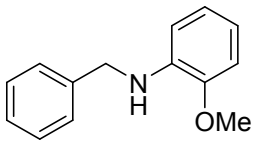
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.34 – 7.26 (m, 2H), 7.16 – 7.08 (m, 1H), 6.67 (t, *J* = 7.1 Hz, 2H), 4.80 (s, 1H), 4.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 138.70, 129.11, 128.72, 127.80, 127.37, 127.30, 119.18, 117.49, 111.59, 47.91.

N-benzyl-2-methylaniline (6aq) [10]



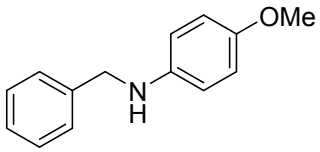
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 4H), 7.38 – 7.32 (m, 1H), 7.16 (dd, *J* = 12.7, 7.1 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.44 (s, 2H), 3.97 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.05, 139.51, 130.11, 128.69, 127.59, 127.29, 127.20, 122.00, 117.28, 110.09 , 48.39, 17.58.

N-benzyl-2-methoxyaniline (6ar) [16]



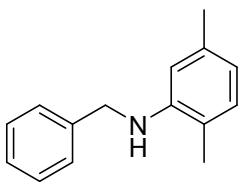
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 4H), 7.45 – 7.37 (m, 1H), 7.01 (td, *J* = 7.6, 1.4 Hz, 1H), 6.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.85 (td, *J* = 7.7, 1.5 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.80 (s, 1H), 4.49 (s, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.02, 139.86, 138.38, 128.77, 127.68, 127.29, 121.53, 116.84, 110.18, 109.66 , 55.55 , 48.21 .

N-benzyl-4-methoxyaniline (6as) [10]



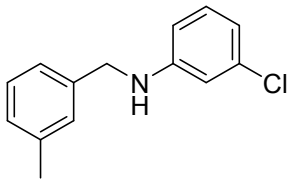
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 6.87 – 6.79 (m, 2H), 6.71 – 6.62 (m, 2H), 4.34 (s, 2H), 3.80 (s, 3H), 3.62 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.30, 142.54, 139.80, 128.66, 127.62, 127.23, 115.02, 114.22, 55.87, 49.31 .

N-benzyl-2,5-dimethylaniline (6at) [17]



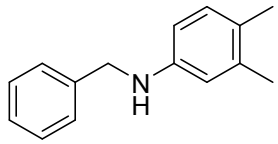
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 4H), 7.38 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.63 – 6.52 (m, 2H), 4.45 (s, 2H), 3.93 (s, 1H), 2.37 (s, 3H), 2.21 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.01, 139.64, 136.84, 130.01, 128.72, 127.71, 127.32, 119.07, 117.96, 110.98, 48.48, 21.63, 17.17.

3-chloro-N-(3-methylbenzyl)aniline (6au)



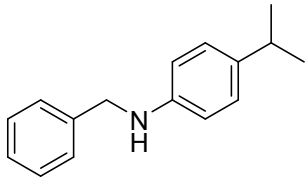
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 14.2, 6.3 Hz, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 2.0 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.35 (s, 2H), 4.15 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.49, 138.89, 138.54, 135.14, 130.37, 128.78, 128.40, 128.36, 124.71, 117.47, 112.69, 111.26, 48.22, 21.57. HRMS (ESI) Calculated for $C_{14}H_{14}ClN$ $[M+H]^+$ 232.0893, found 232.0895.

N-benzyl-3,4-dimethylaniline (6av).



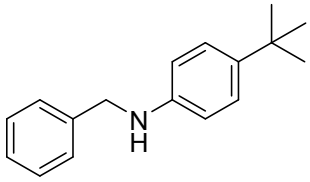
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H), 7.31 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 6.46 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.35 (s, 2H), 3.86 (s, 1H), 2.24 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.36, 139.78, 137.34, 130.33, 128.61, 127.56, 127.15, 125.66, 114.82, 110.35, 48.73, 20.06, 18.71. HRMS (ESI) Calculated for $C_{15}H_{17}N$ $[M+H]^+$ 212.1439, found 212.1437.

N-benzyl-4-isopropylaniline (6aw) [18]



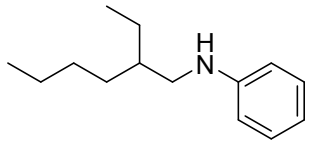
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.31 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.35 (s, 2H), 3.98 (s, 1H), 2.85 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.23, 139.69, 138.18, 128.62, 127.60 , 127.20, 127.14, 112.95, 48.74, 33.20, 24.26 .

N-benzyl-4-(tert-butyl)aniline (6ax) [8]



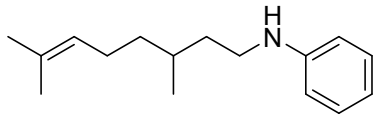
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 14.7, 7.5 Hz, 4H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.34 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.48, 140.73, 139.43, 128.61, 127.68, 127.25, 126.06, 112.90, 48.88, 33.90, 31.54.

N-(2-ethylhexyl)aniline (6ay) [19]



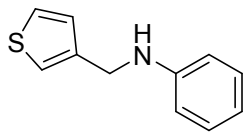
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.70 (s, 1H), 3.15 (d, *J* = 6.2 Hz, 2H), 1.70 (dt, *J* = 12.1, 6.0 Hz, 1H), 1.61 – 1.33 (m, 8H), 1.06 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.88, 129.31, 117.01, 112.73, 47.19, 39.26 , 31.47, 29.14, 24.64, 23.25, 14.22, 11.05.

N-(3,7-dimethyloct-6-en-1-yl)aniline (6az)



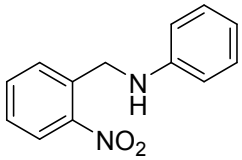
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.77 (dd, *J* = 8.5, 0.9 Hz, 2H), 5.40 – 5.24 (m, 1H), 3.67 (s, 1H), 3.28 (m, 2H), 2.37 – 2.09 (m, 2H), 1.91 (s, 3H), 1.86 – 1.71 (m, 5H), 1.67 – 1.52 (m, 2H), 1.50 – 1.36 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.74 , 131.31 , 129.35 , 124.93 , 117.21, 112.86, 42.09, 37.31, 36.89 , 30.63, 25.91, 25.70, 19.79, 17.84. HRMS (ESI) Calculated for $C_{16}H_{25}N$ $[M+H]^+$ 232.2065, found 232.2067.

N-(thiophen-3-ylmethyl)aniline (6ba) [20]



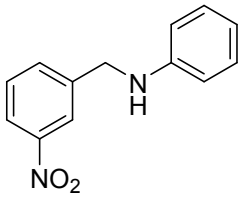
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.15 (dd, *J* = 4.9, 1.1 Hz, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 4.40 (s, 2H), 4.01 (s, 1H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.11, 140.57, 129.36, 127.25, 126.21, 121.80, 117.80, 113.04, 43.84.

N-(2-nitrobenzyl)aniline (6bb) [10]



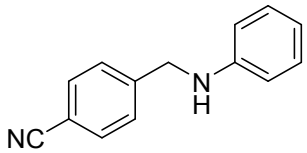
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.59 (td, *J* = 7.6, 1.1 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.19 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 4.76 (s, 2H), 4.38 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.30, 147.40, 135.68, 133.66, 129.81, 129.36, 127.99, 125.18, 118.06 , 112.93, 45.78.

N-(3-nitrobenzyl)aniline (6bc) [21]



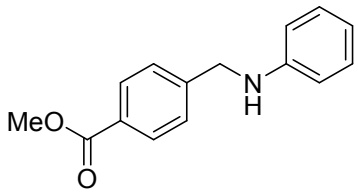
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.15 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.75 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.11 (m, 2H), 6.82 – 6.72 (m, 1H), 6.64 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.49 (s, 2H), 4.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.63, 147.33, 142.03, 133.24, 129.58, 129.40, 122.28, 122.09, 118.28, 113.03, 47.59.

4-((phenylamino)methyl)benzonitrile (6bd) [22]



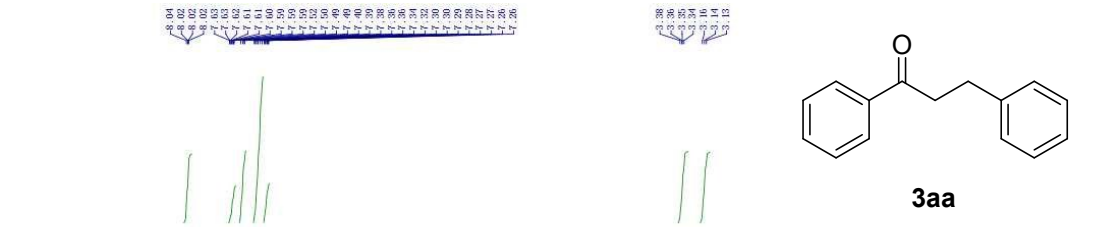
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.14 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.61 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.46 (s, 2H), 4.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.48 , 145.47, 132.46, 129.40, 127.75, 118.92, 118.14, 112.94, 110.94, 47.82.

methyl 4-((phenylamino)methyl)benzoate (6be) [22]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.14 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.65 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.43 (s, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 147.82, 145.06, 129.98, 129.34, 129.13, 127.19, 117.89, 112.98, 52.08, 48.02.

8. ^{1}H NMR and ^{13}C NMR Spectra



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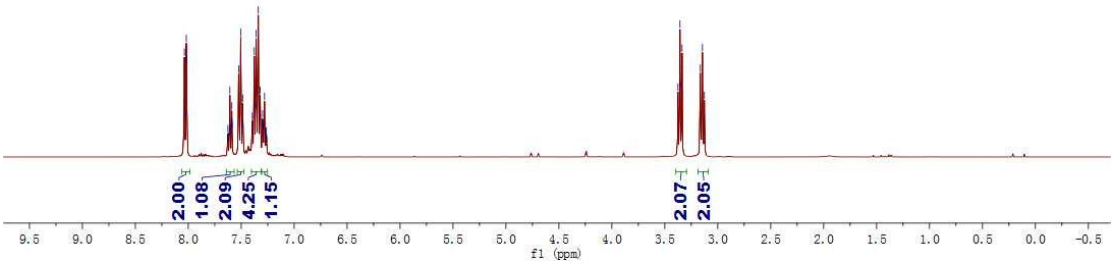

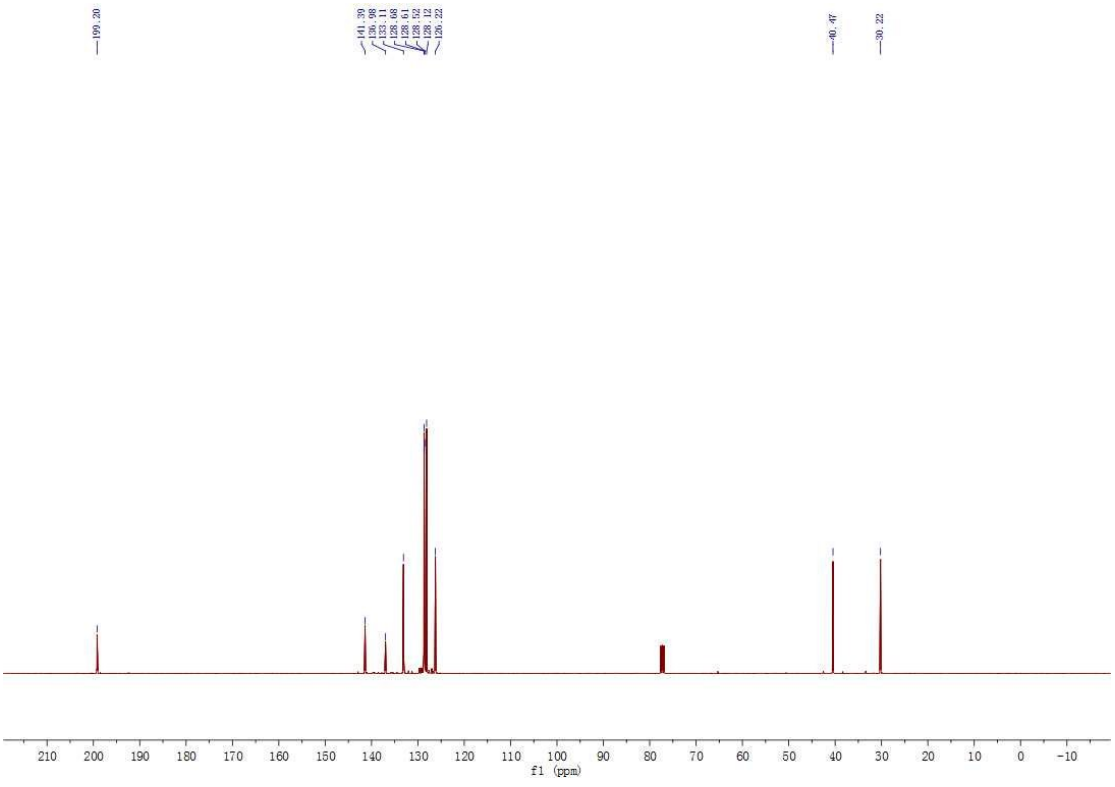

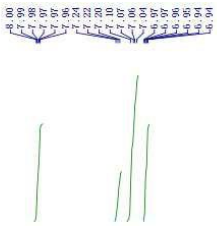

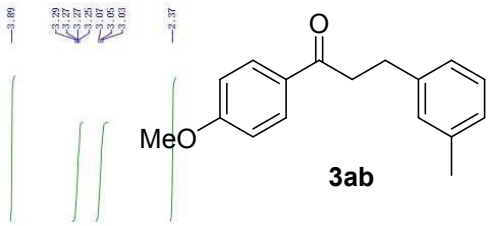

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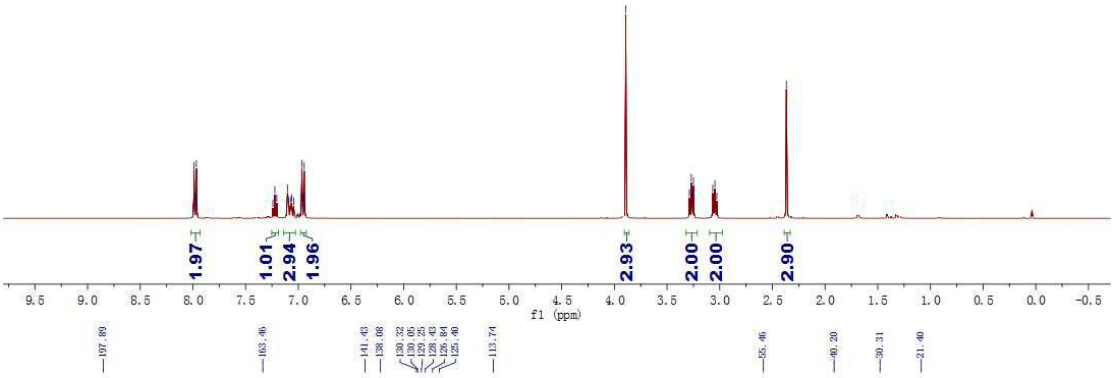

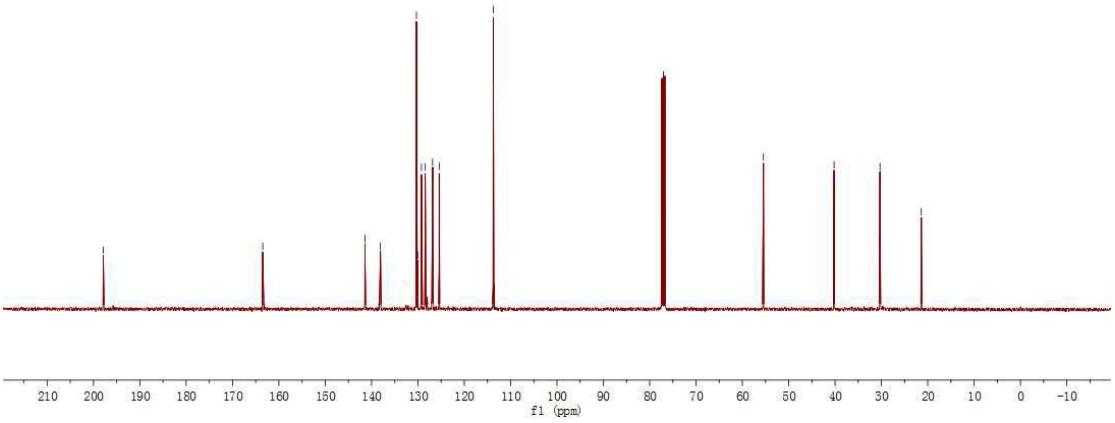

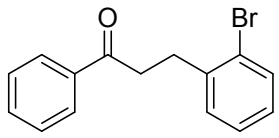

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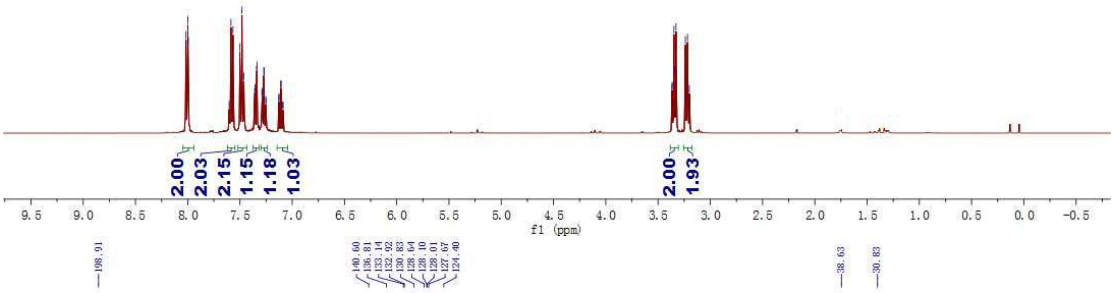

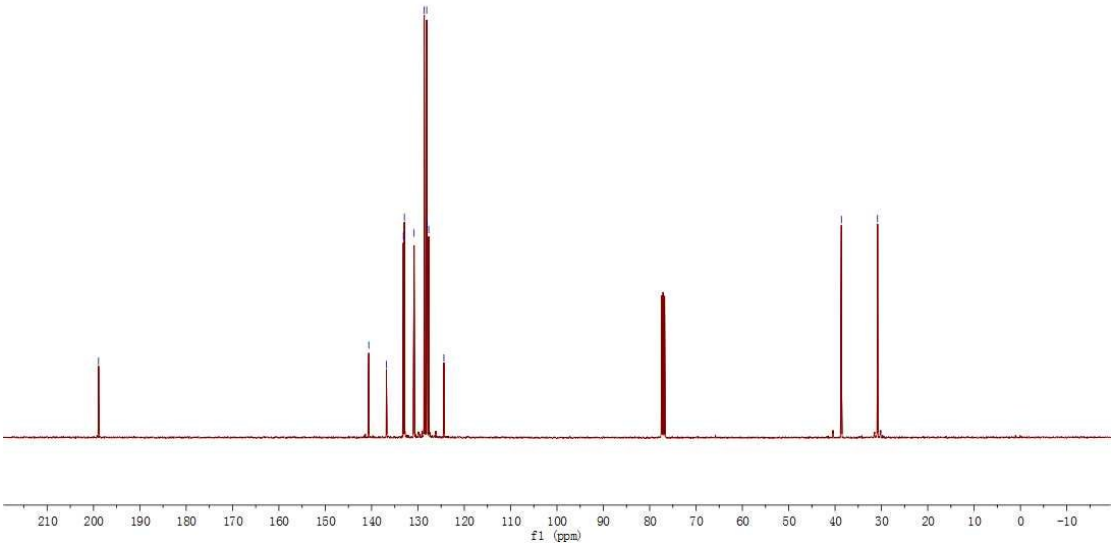

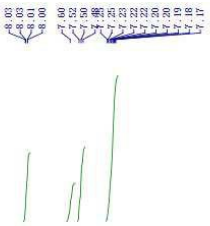

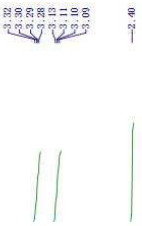

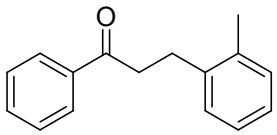

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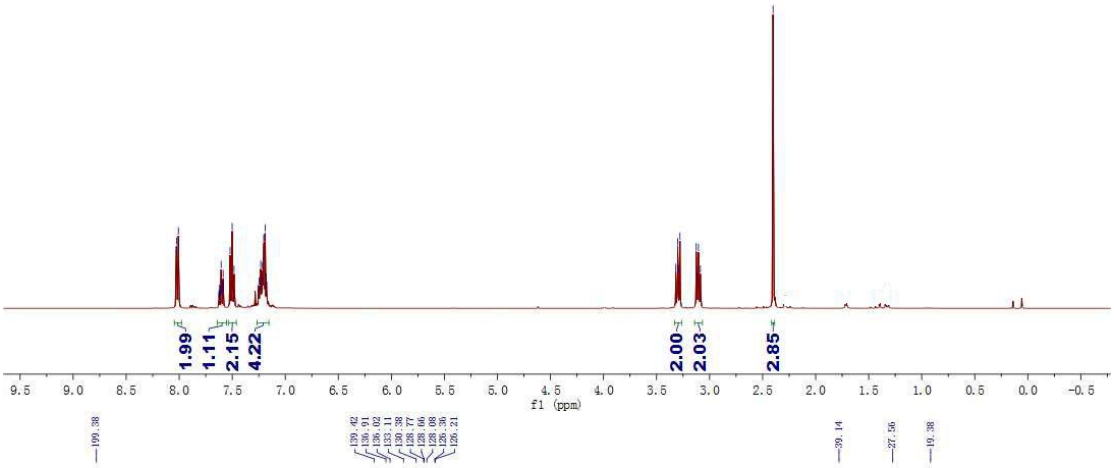

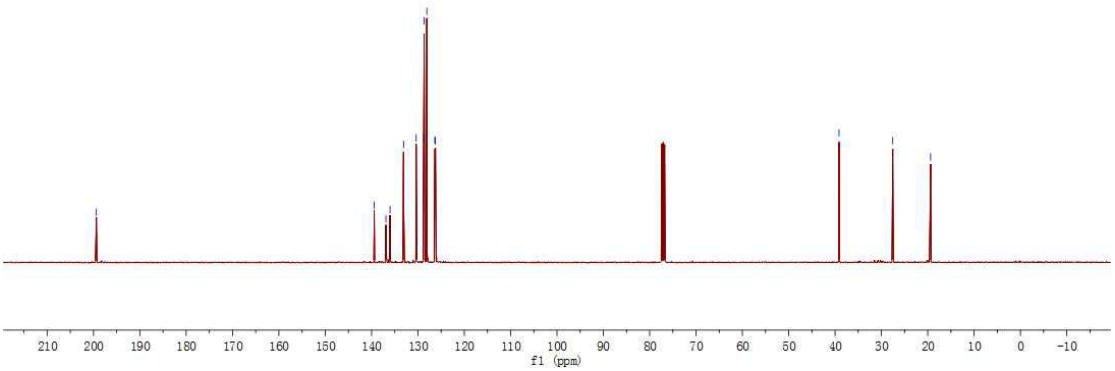

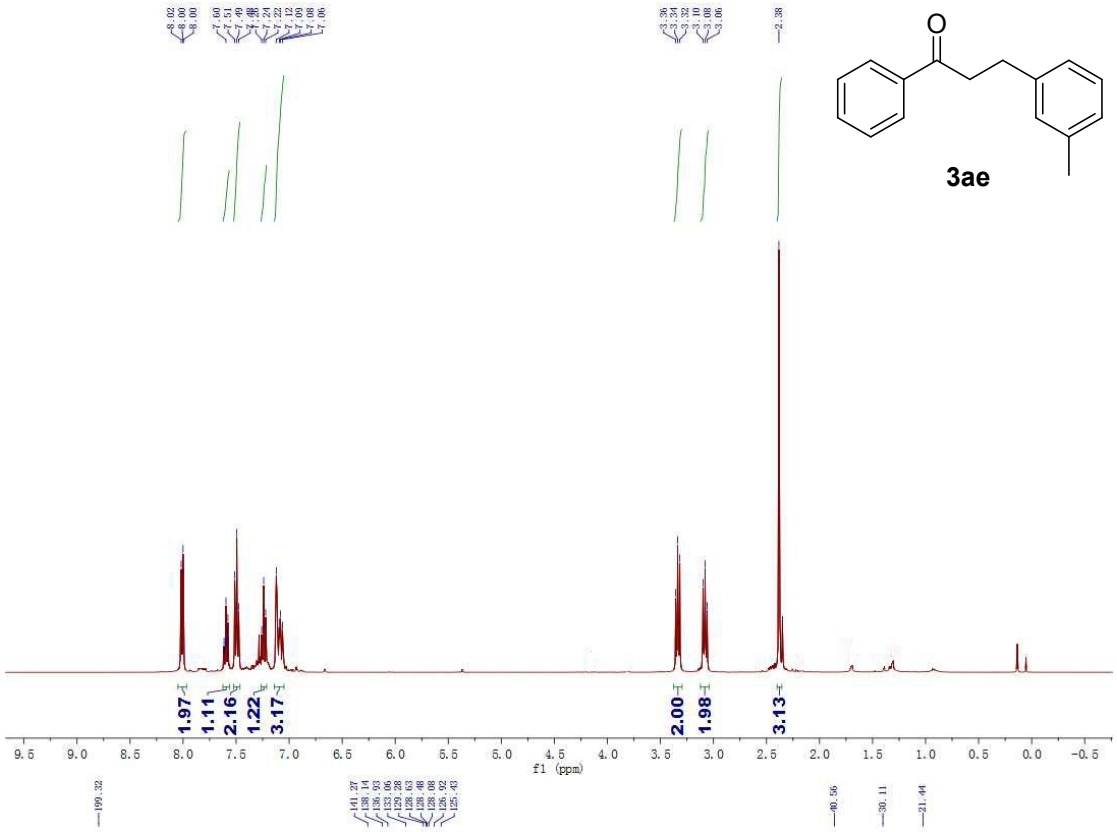
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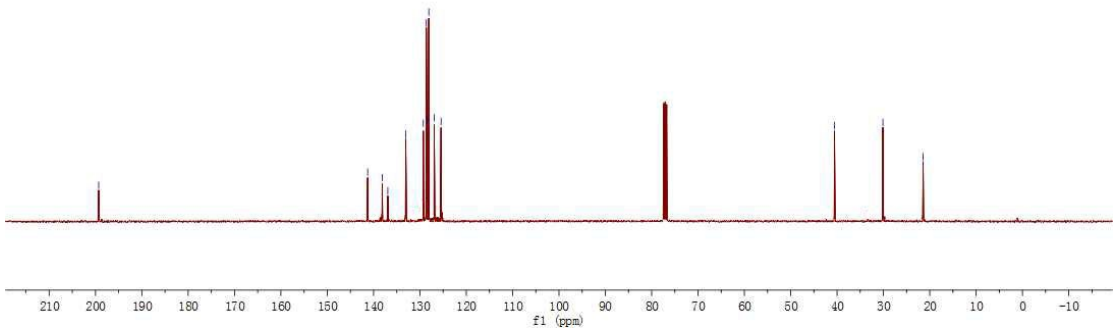
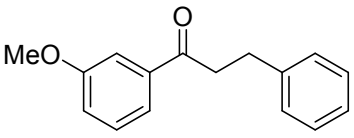
7.24
7.22
7.12
7.09
7.08
7.06
3.36
3.34
3.32
3.10
3.08
3.06
2.38
1.97
1.11
2.16
1.22
3.17
2.00
1.98
3.13
f1 (ppm)

3ae

199.32
141.27
138.14
136.65
133.06
129.28
128.63
128.48
126.98
126.92
125.43
40.56
30.11
21.44


f1 (ppm)



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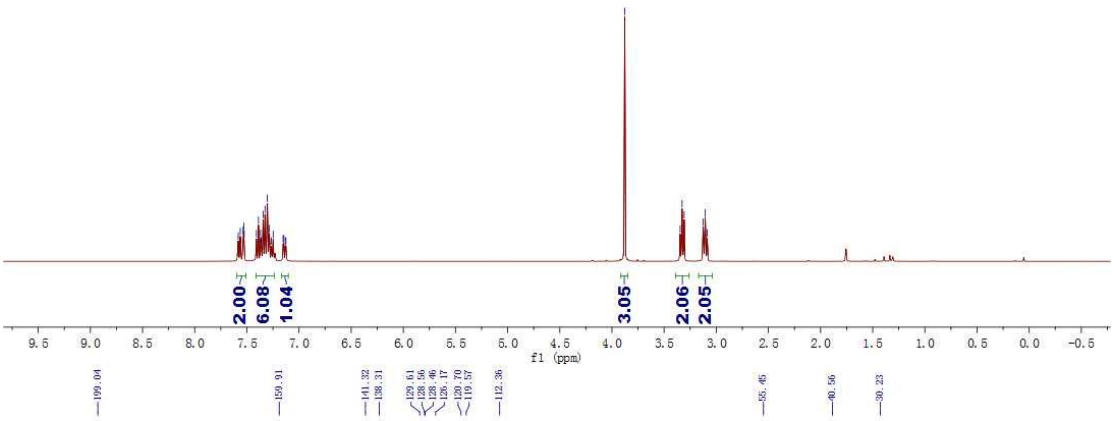

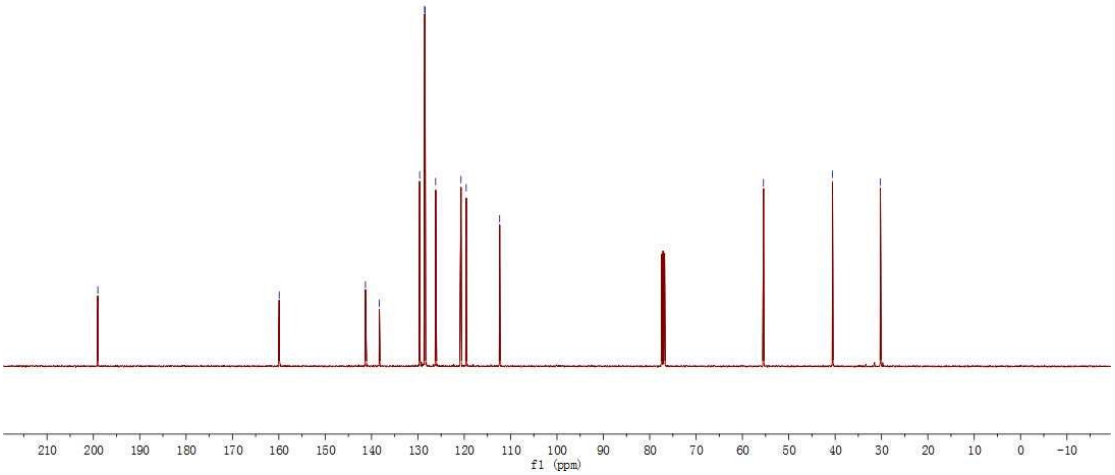

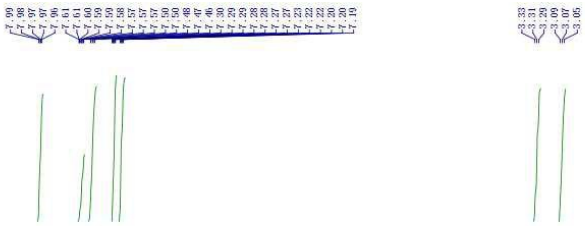

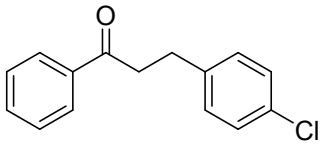

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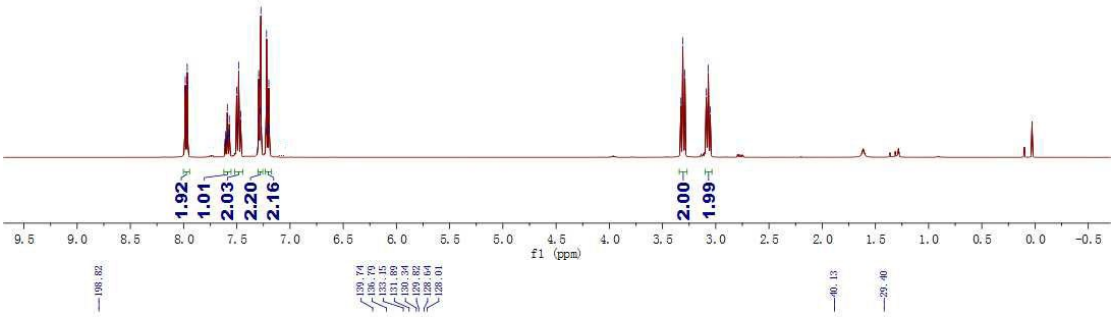

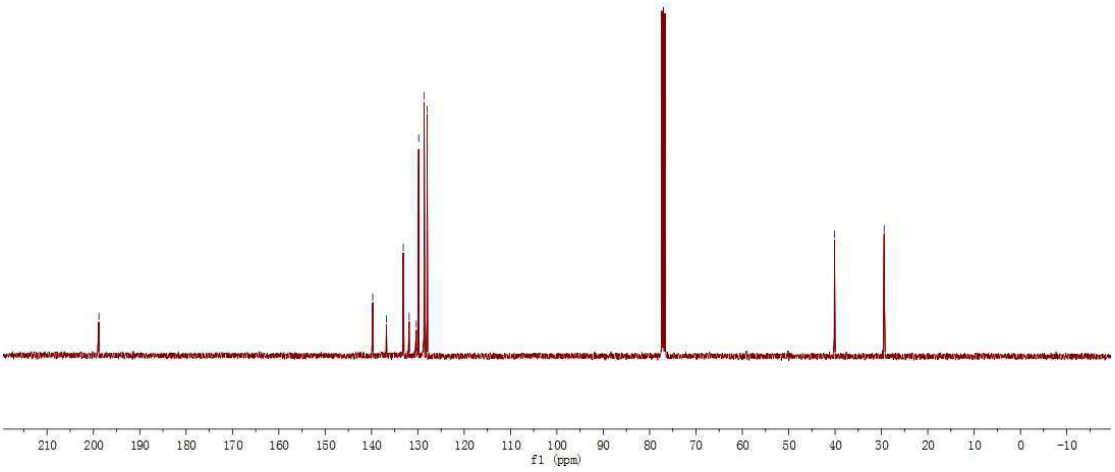

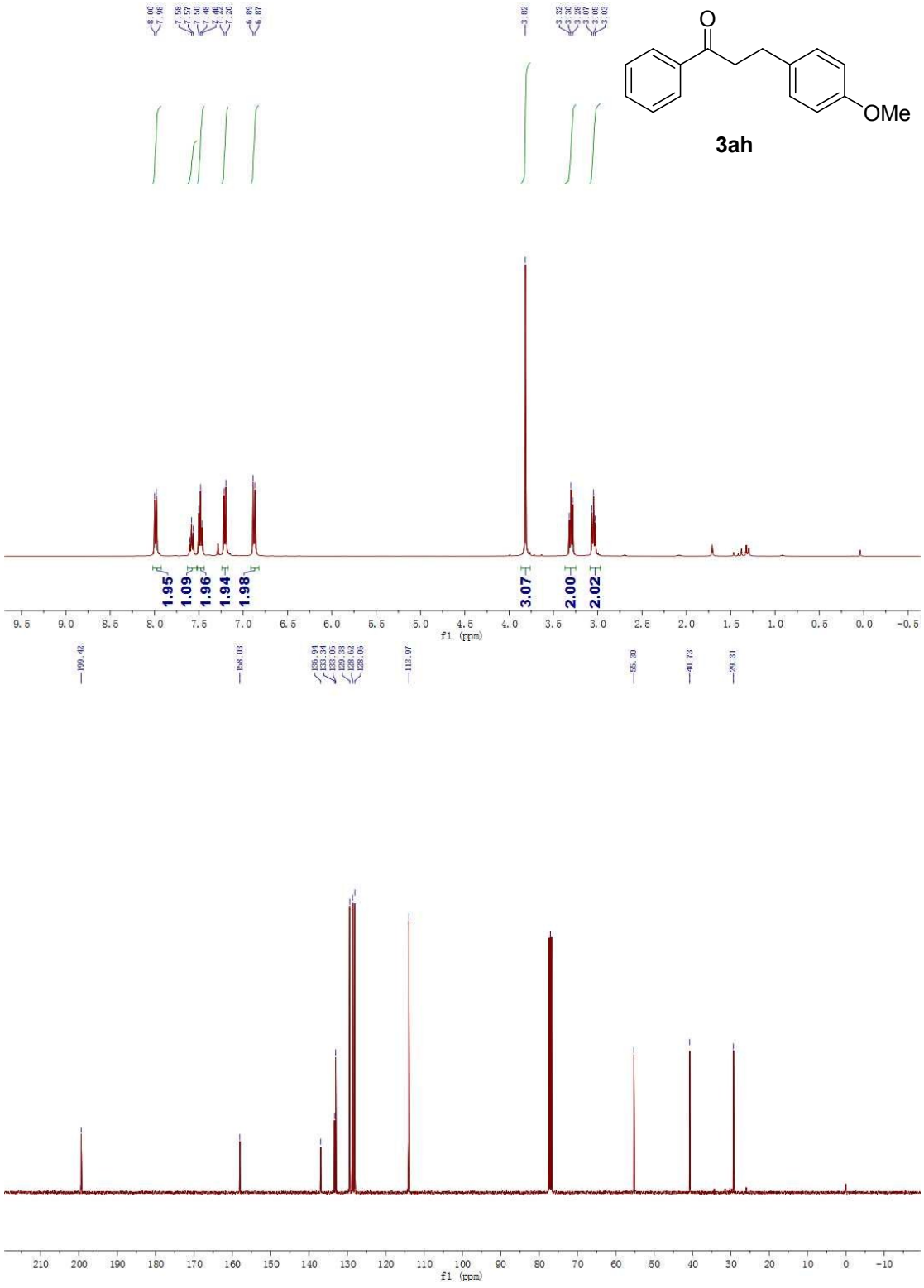
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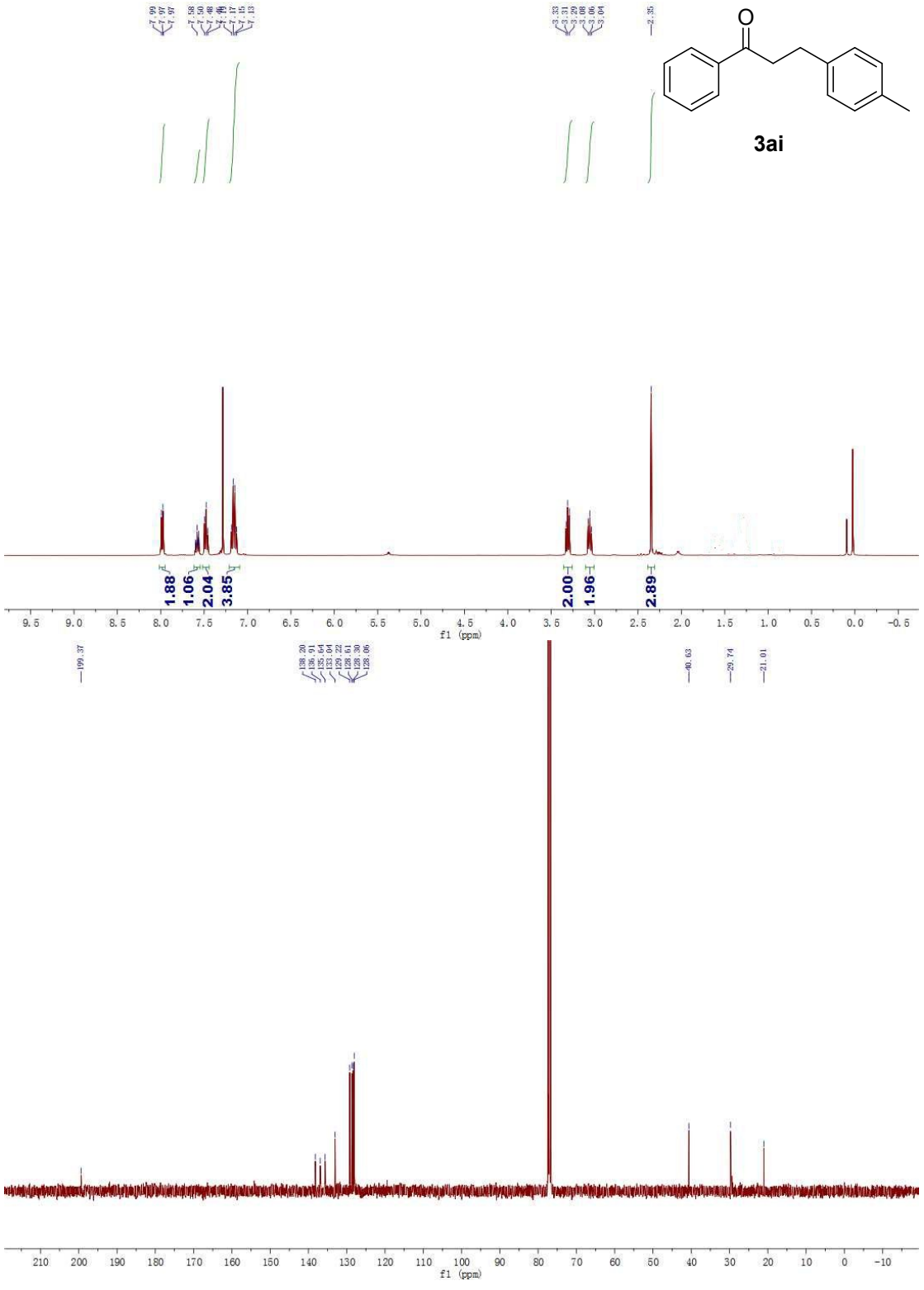
7.48
7.46
7.44
7.20
6.89
6.87
3.82
3.32
3.30
3.28
3.07
3.05
3.03
O
OMe
3ah
1.95
1.09
1.96
1.94
1.98
3.07
2.00
2.02
f1 (ppm)
199.42
158.03
136.94
133.94
133.05
129.38
128.62
128.06
113.97
55.30
40.73
29.31
f1 (ppm)


7.99
7.97
7.97
7.58
7.50
7.48
7.17
7.15
7.13
3.33
3.31
3.29
3.08
3.06
3.04
2.35
O
3ai
1.88
1.06
2.04
3.85
2.00
1.96
2.89
f1 (ppm)
199.37
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133.04
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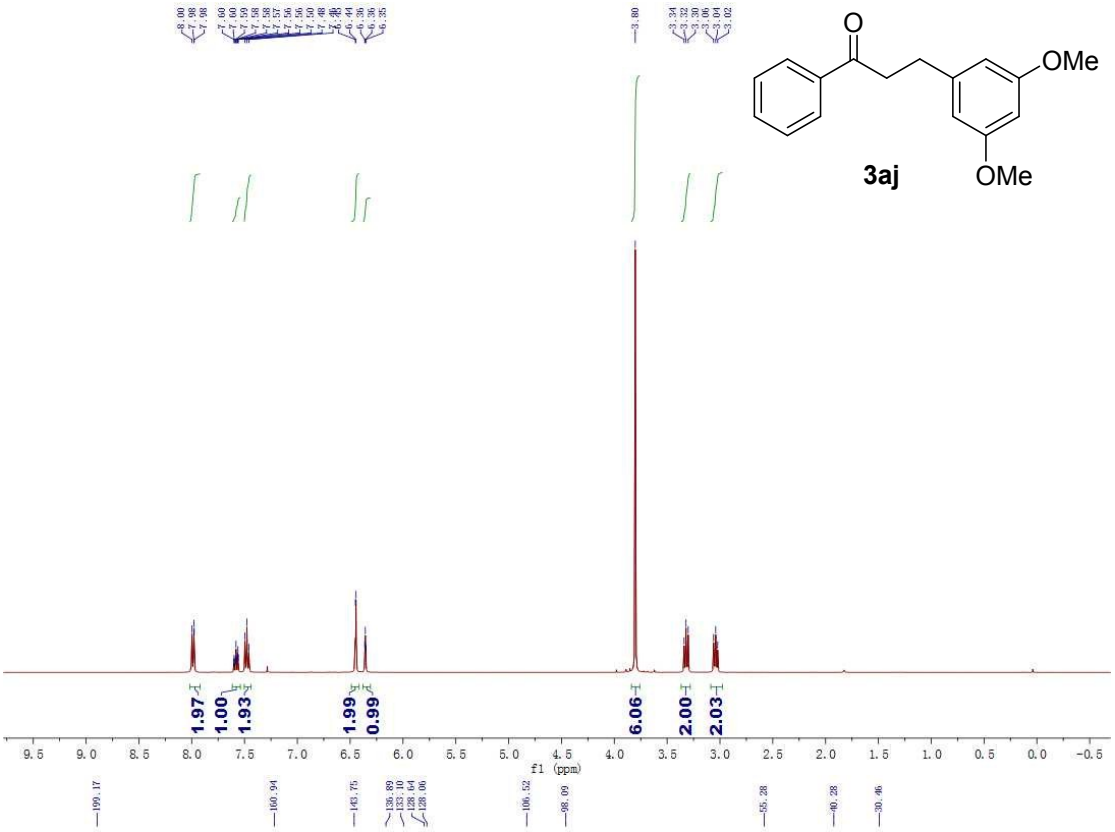
128.39
128.06
40.63
29.74
21.01
f1 (ppm)


O
OMe
OMe
3aj
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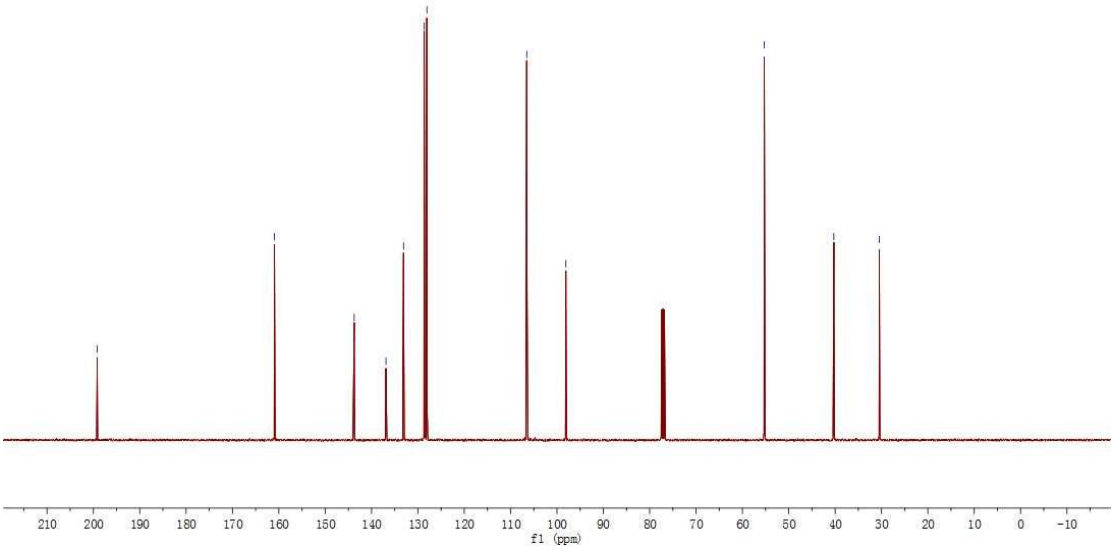
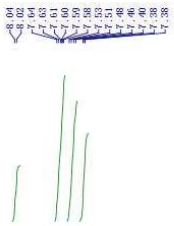
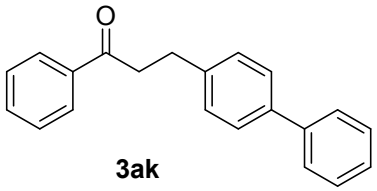
1.00
1.93
1.99
0.99
6.06
2.00
2.03
f1 (ppm)


f1 (ppm)





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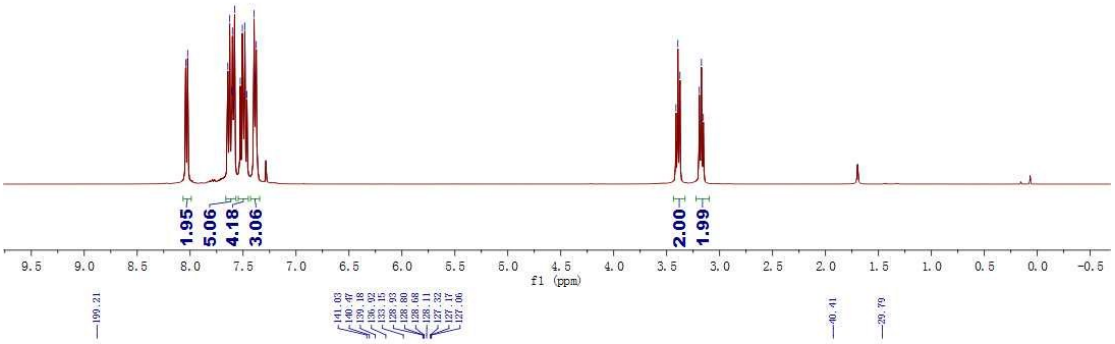

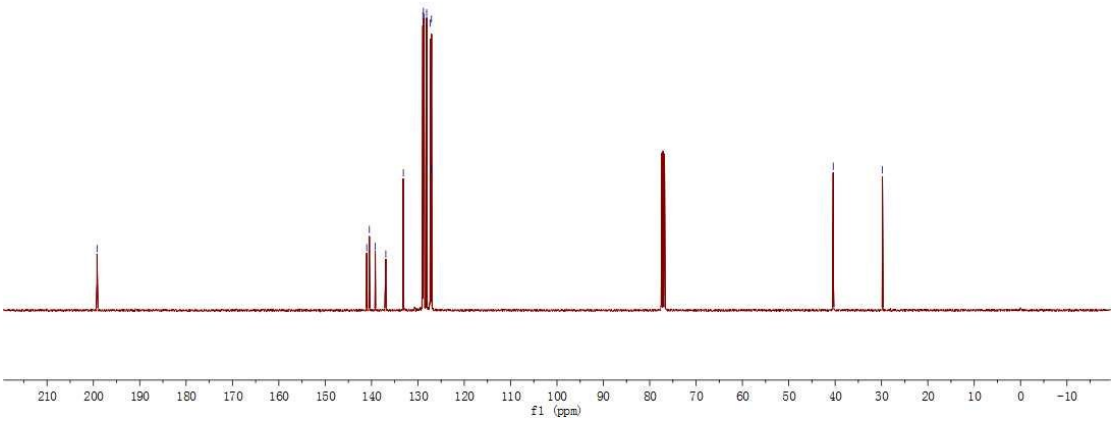

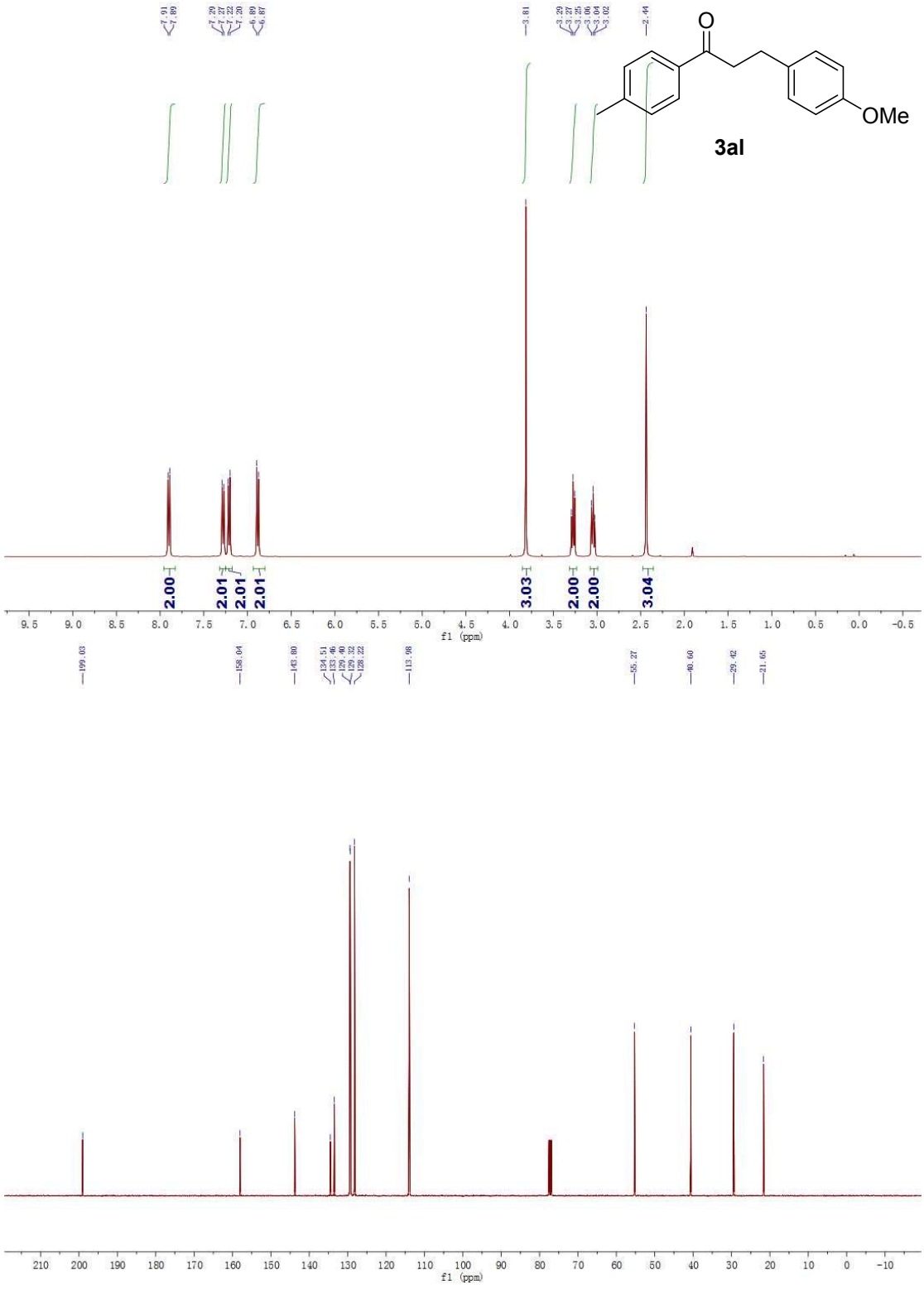
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7.27
7.22
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6.87
3.81
3.29
3.27
3.25
3.06
3.04
3.02
2.44
O
OMe
3al
2.00
2.01
2.01
2.01
3.03
2.00
2.00
3.04
f1 (ppm)
199.03
158.04
143.80
134.51
133.46
129.40
129.32
128.22
113.98
55.27
40.60
29.42
21.66
f1 (ppm)


7.81
7.78
7.39
7.37
7.35
7.22
7.20
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6.87
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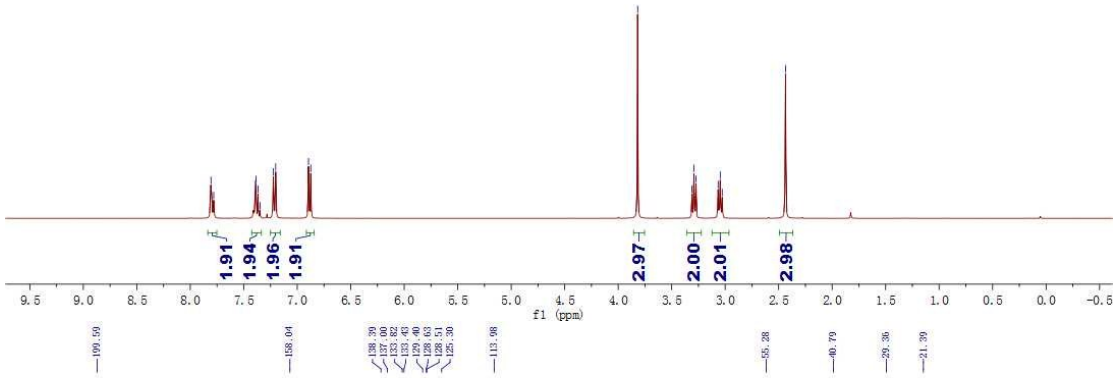
3.31
3.29
3.27
3.07
3.05
3.03
2.44
O
OMe

3am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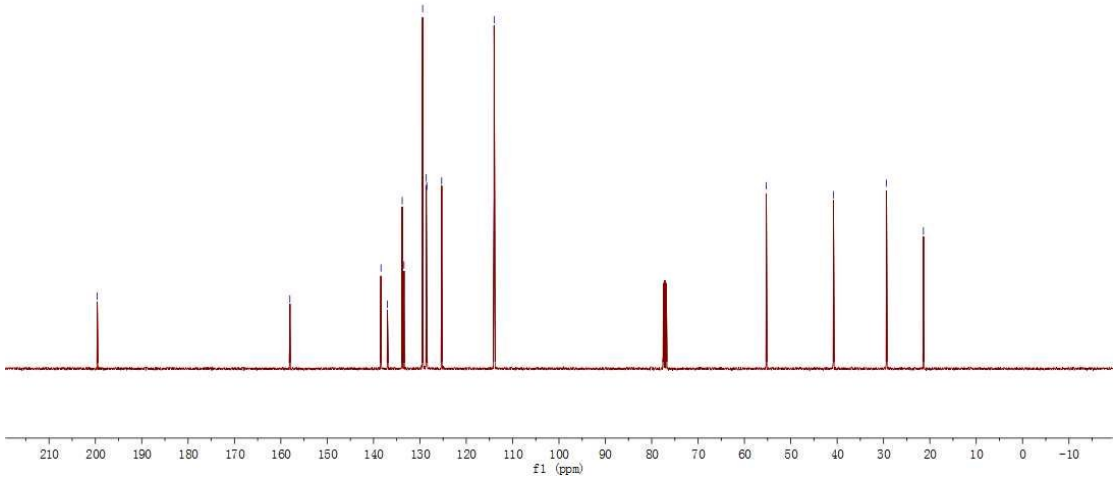
1.94
1.96
1.91
2.97
2.00
2.01
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
199.59
158.04
138.39
137.00
133.82
133.45
129.40
128.63
128.51
125.30
113.98
55.28
40.79
29.36
21.39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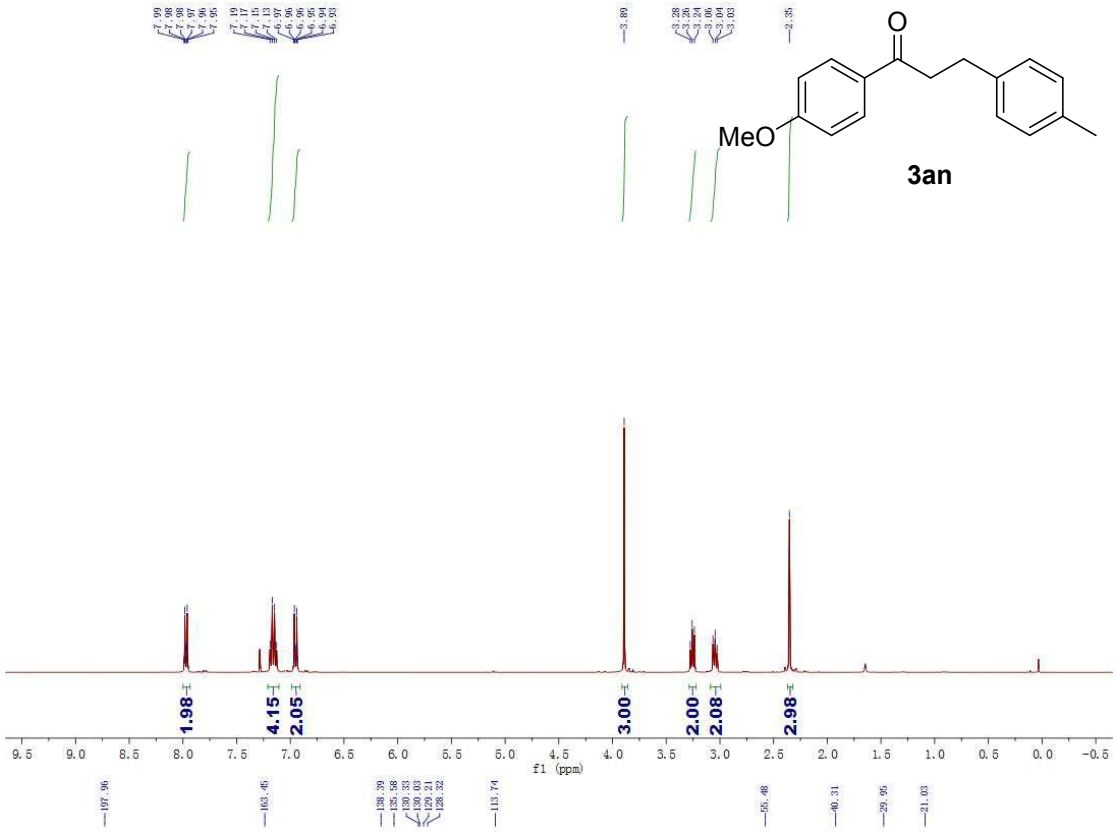
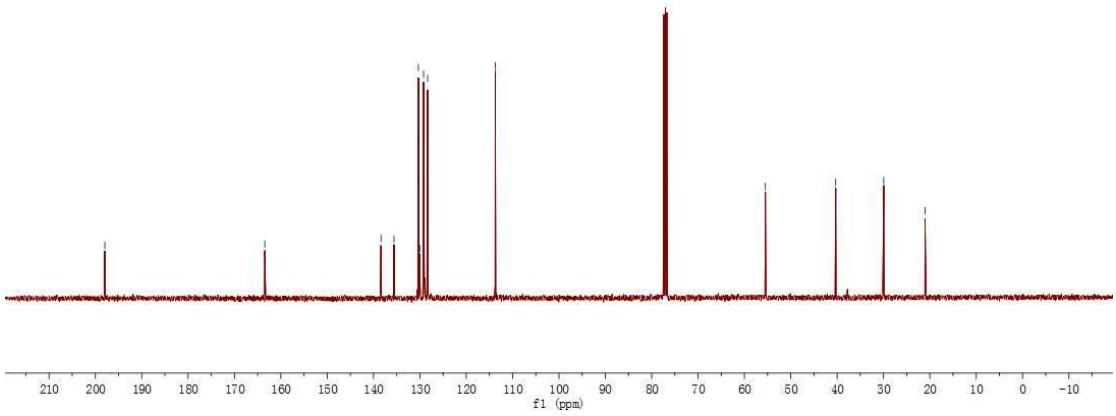
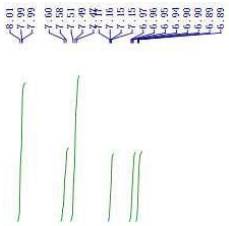
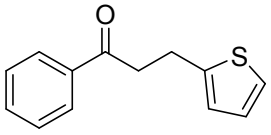
f1 (ppm)


MeO
O
3an
1.98
4.15
2.05
3.00
2.00
2.08
2.98
f1 (ppm)


f1 (ppm)





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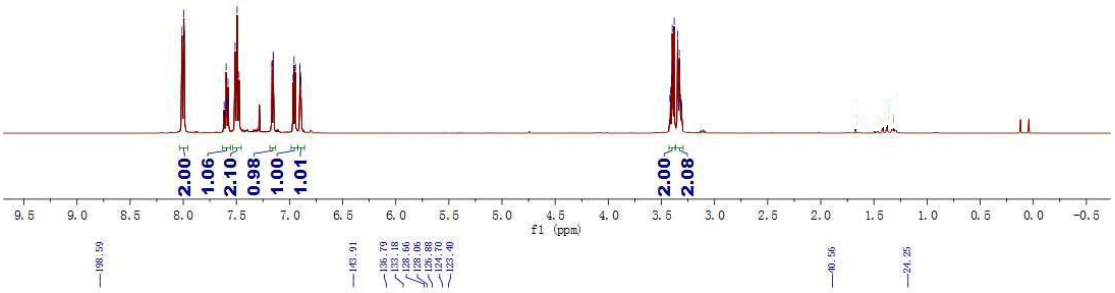

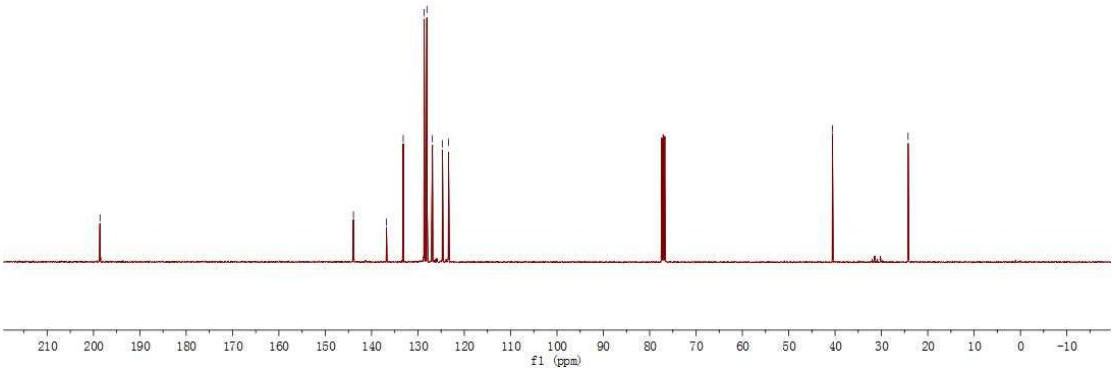

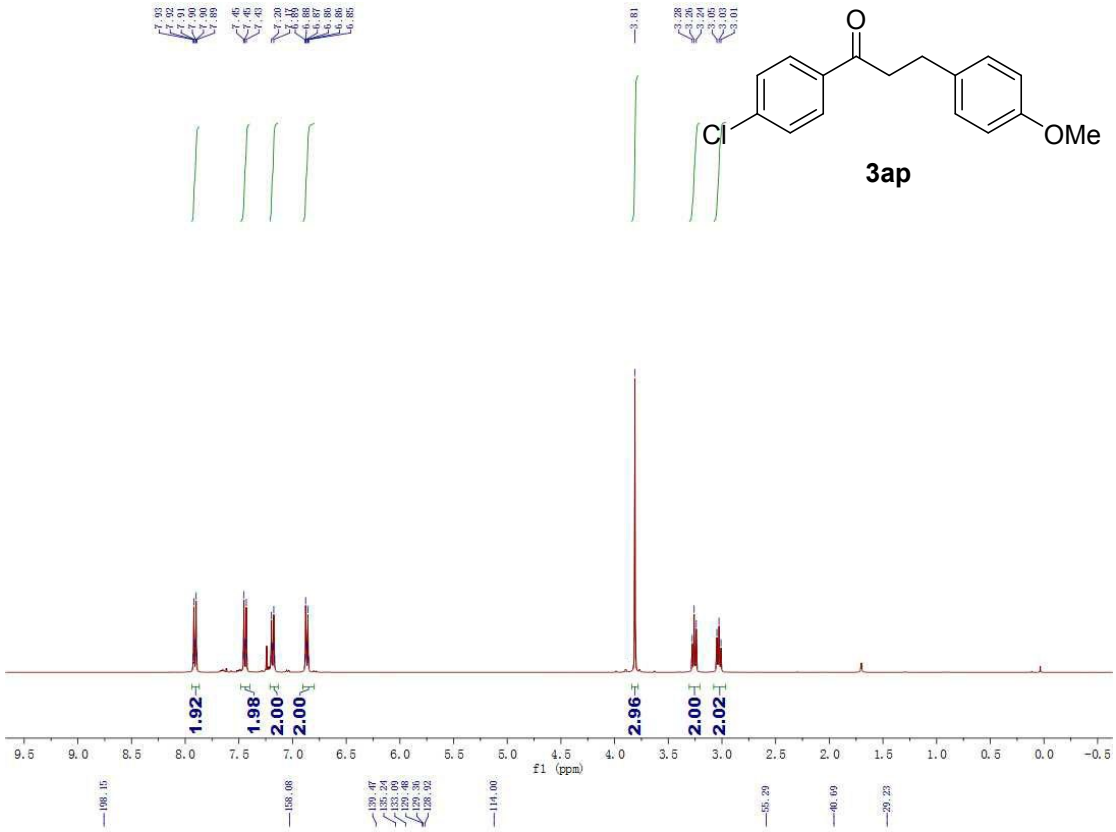
O
Cl
OMe
3ap
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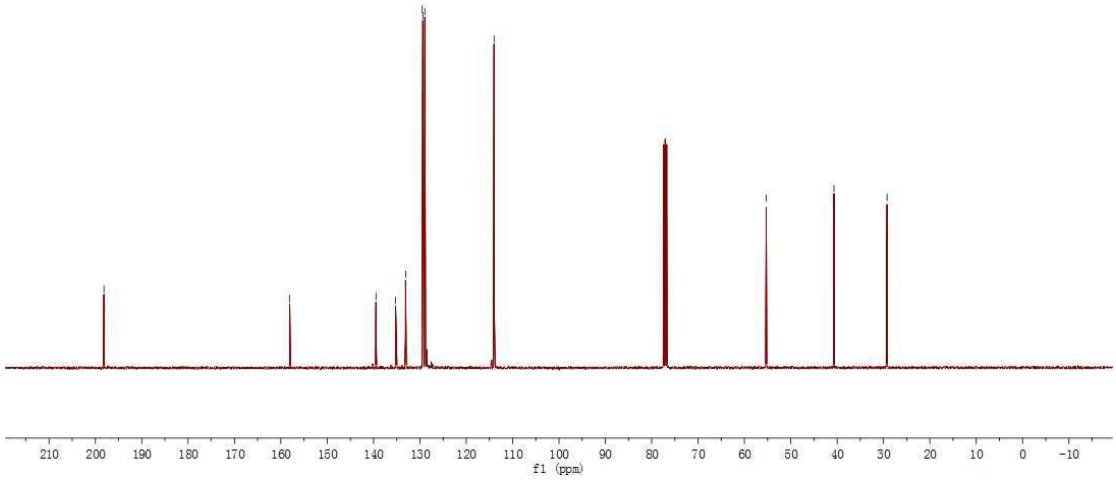
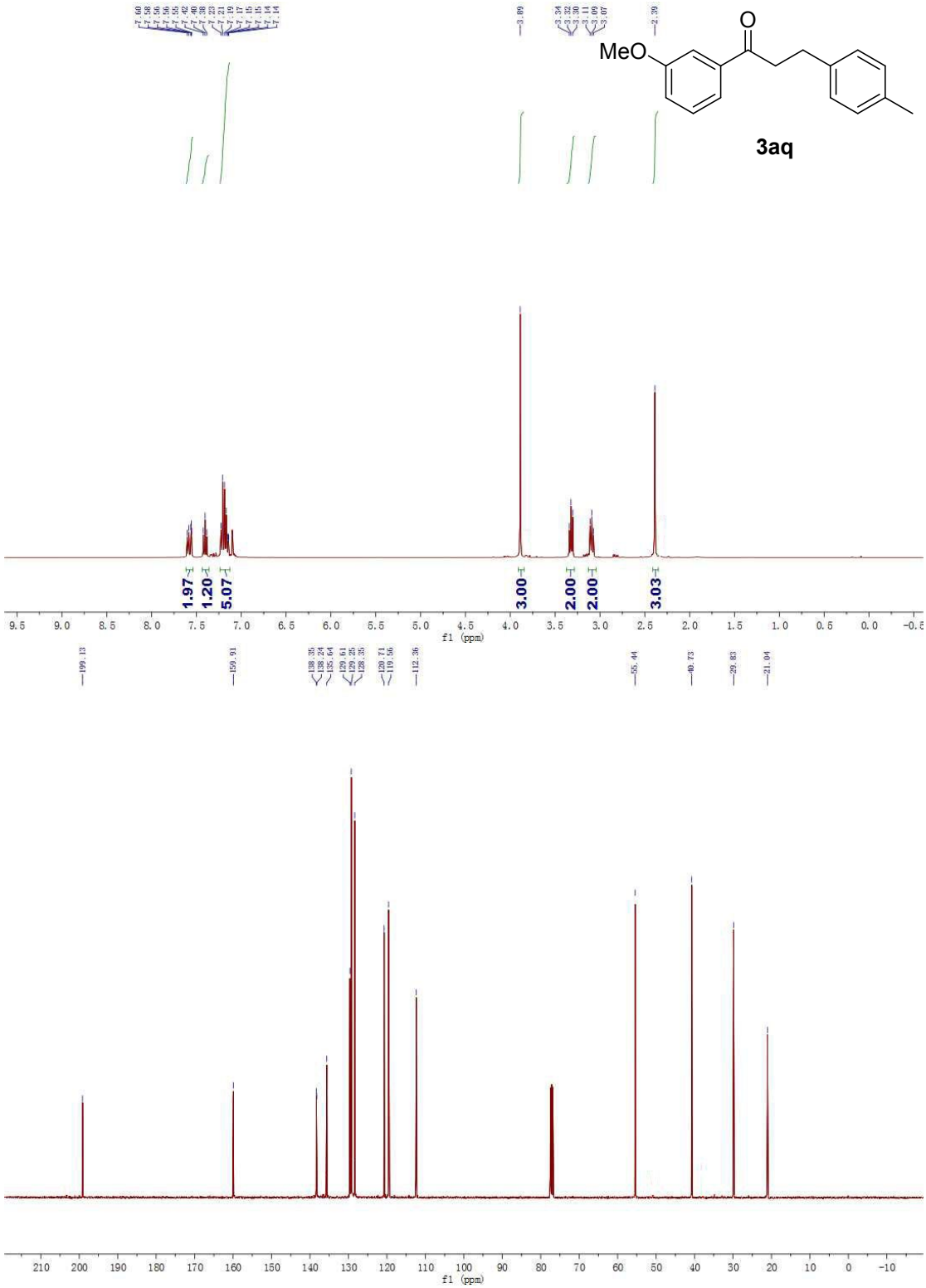
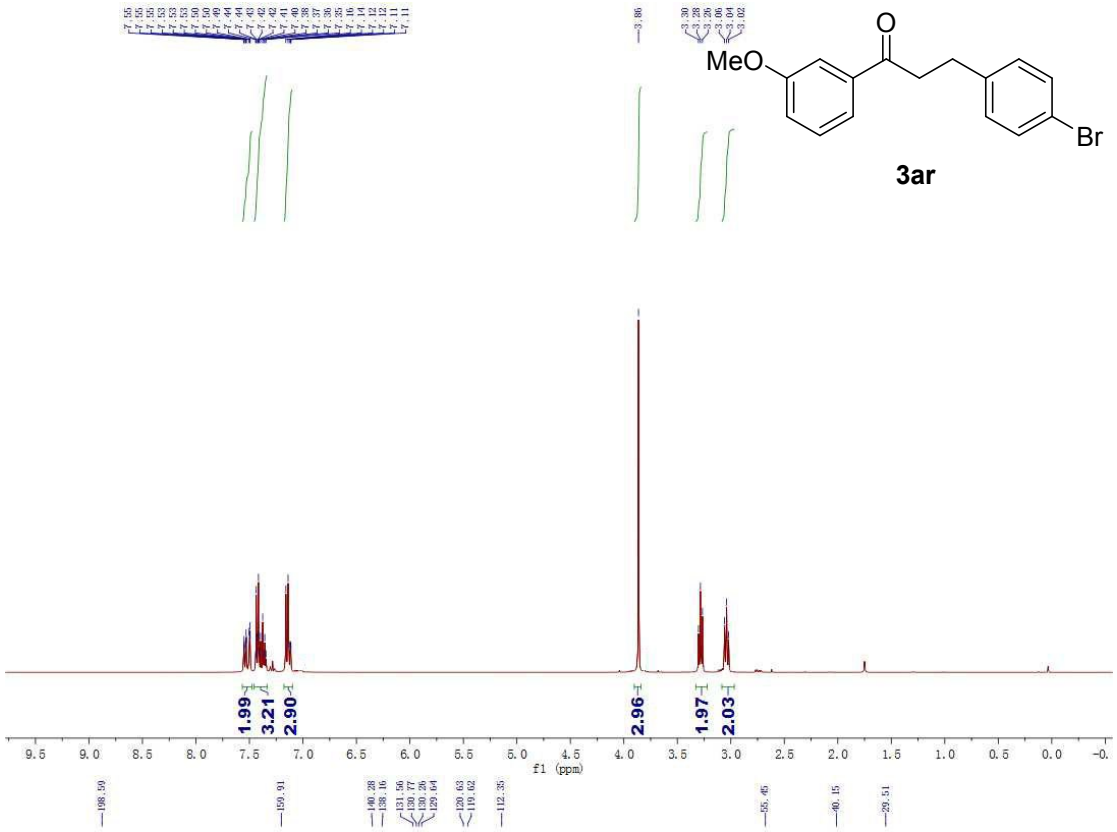
1.98
2.00
2.00
2.96
2.00
2.02
f1 (ppm)


f1 (ppm)


MeO
O
3aq
1.97
1.20
5.07
3.00
2.00
2.00
3.03
f1 (ppm)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Br
3ar
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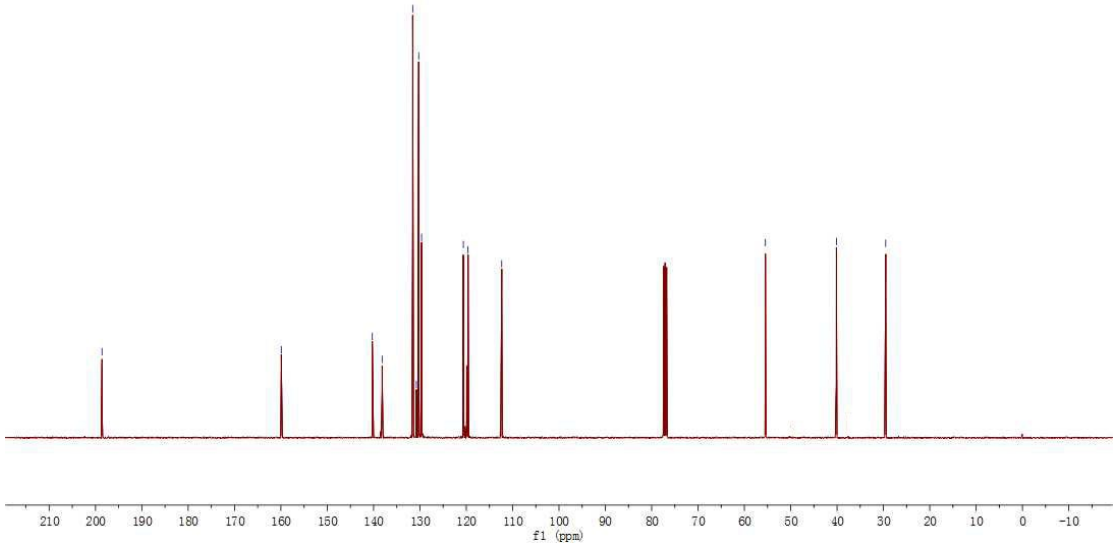
2.96
1.97
2.03
f1 (ppm)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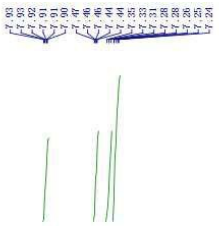
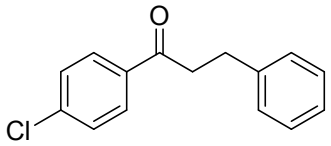
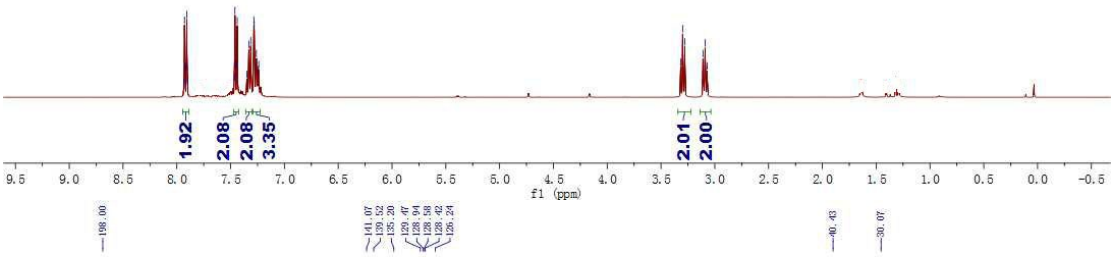
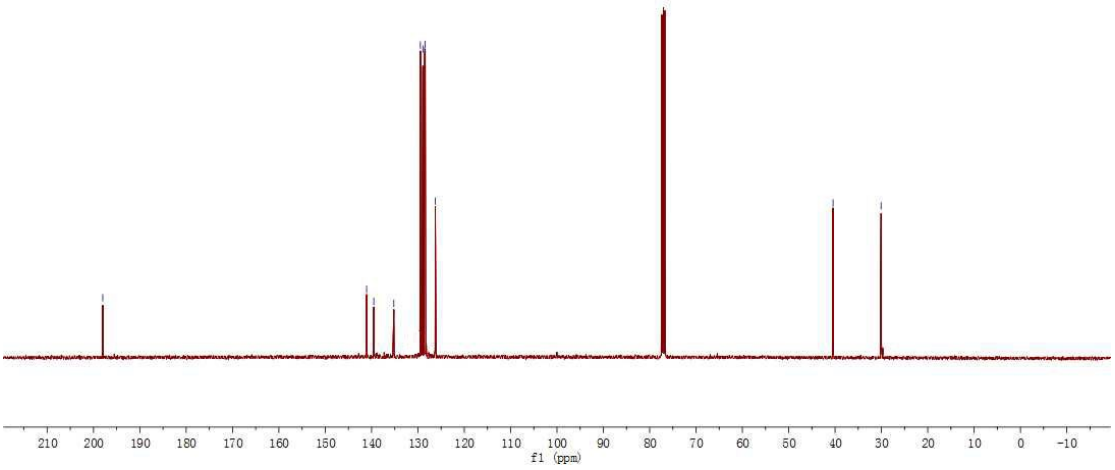
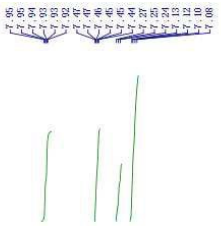


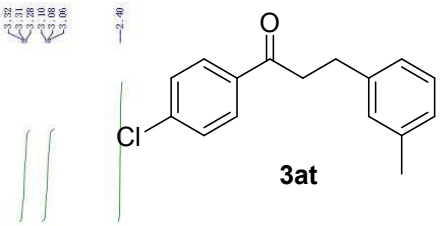


3as

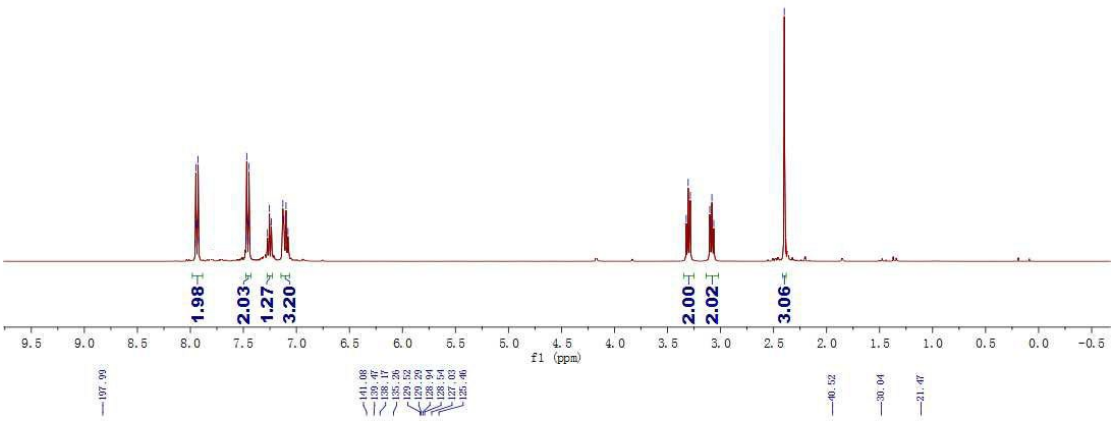


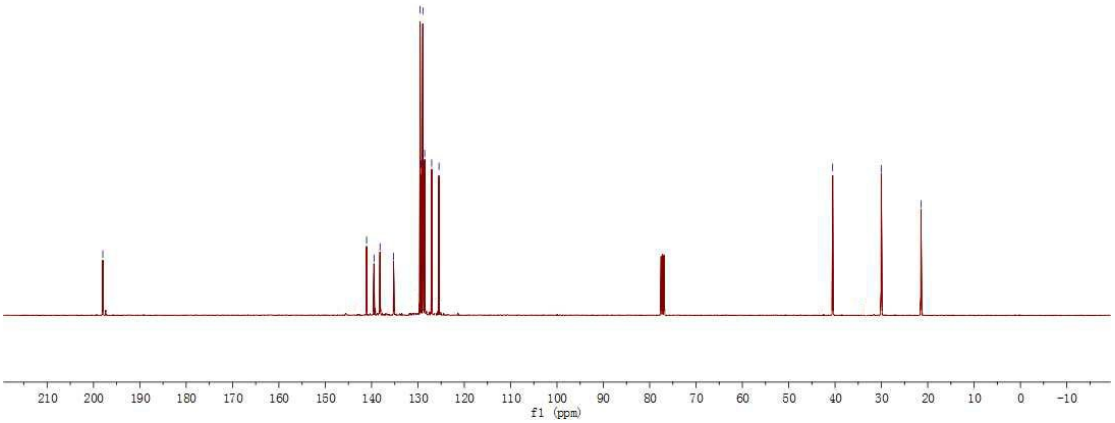


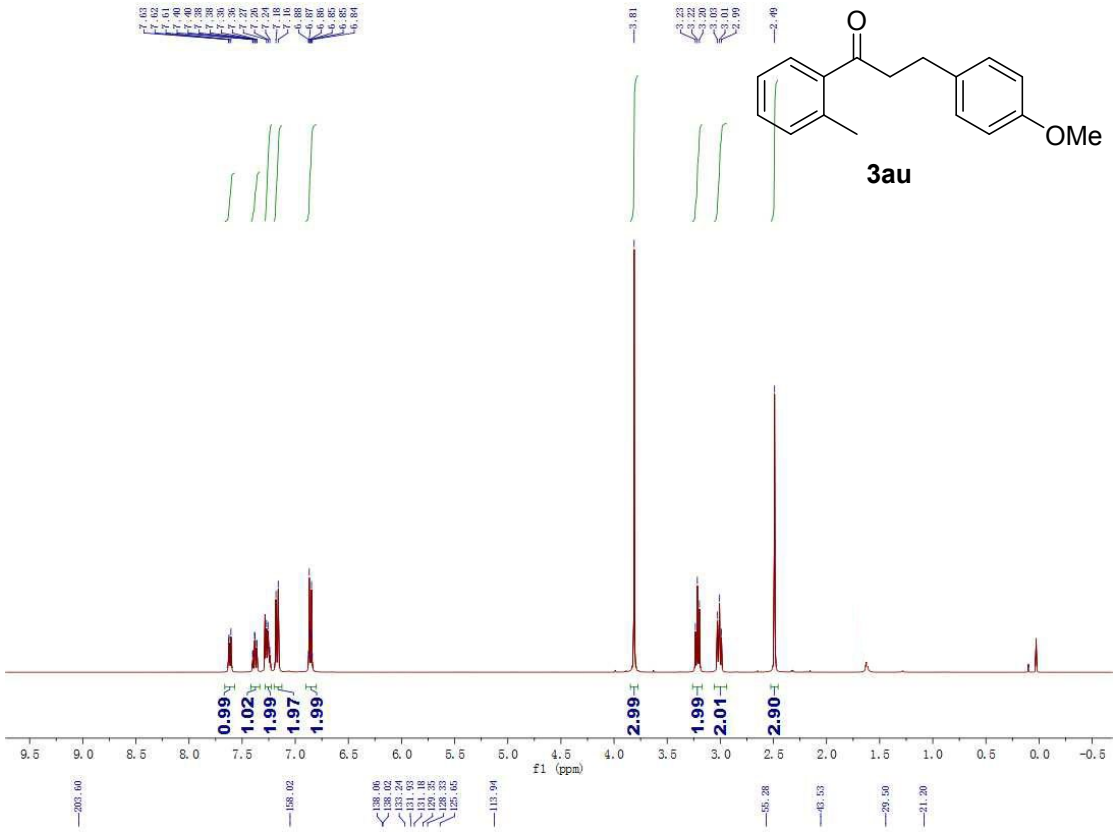




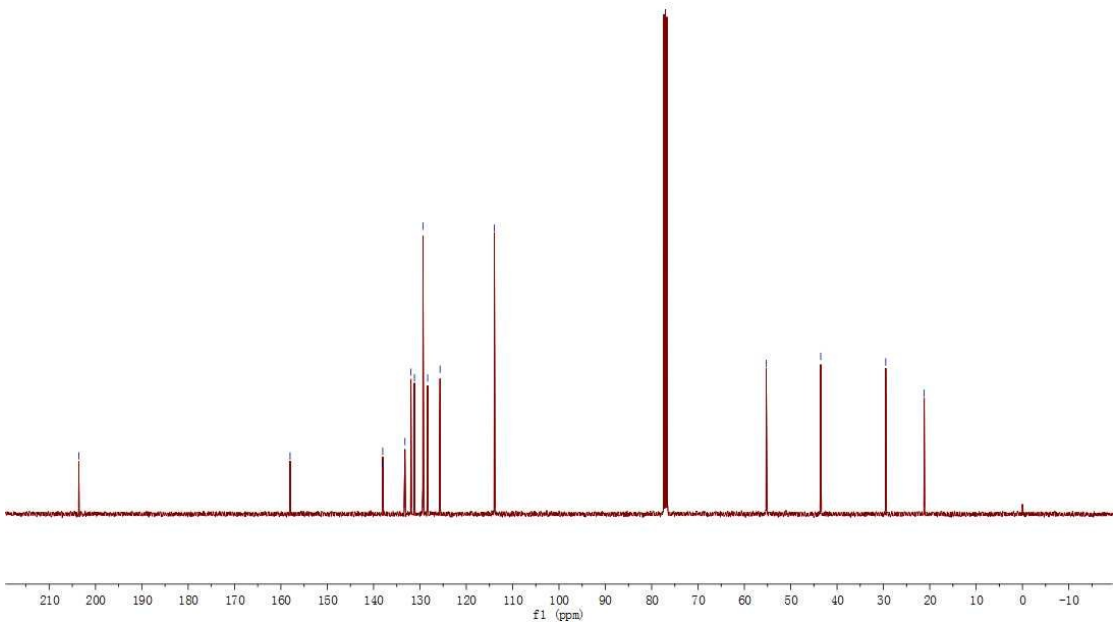
3at

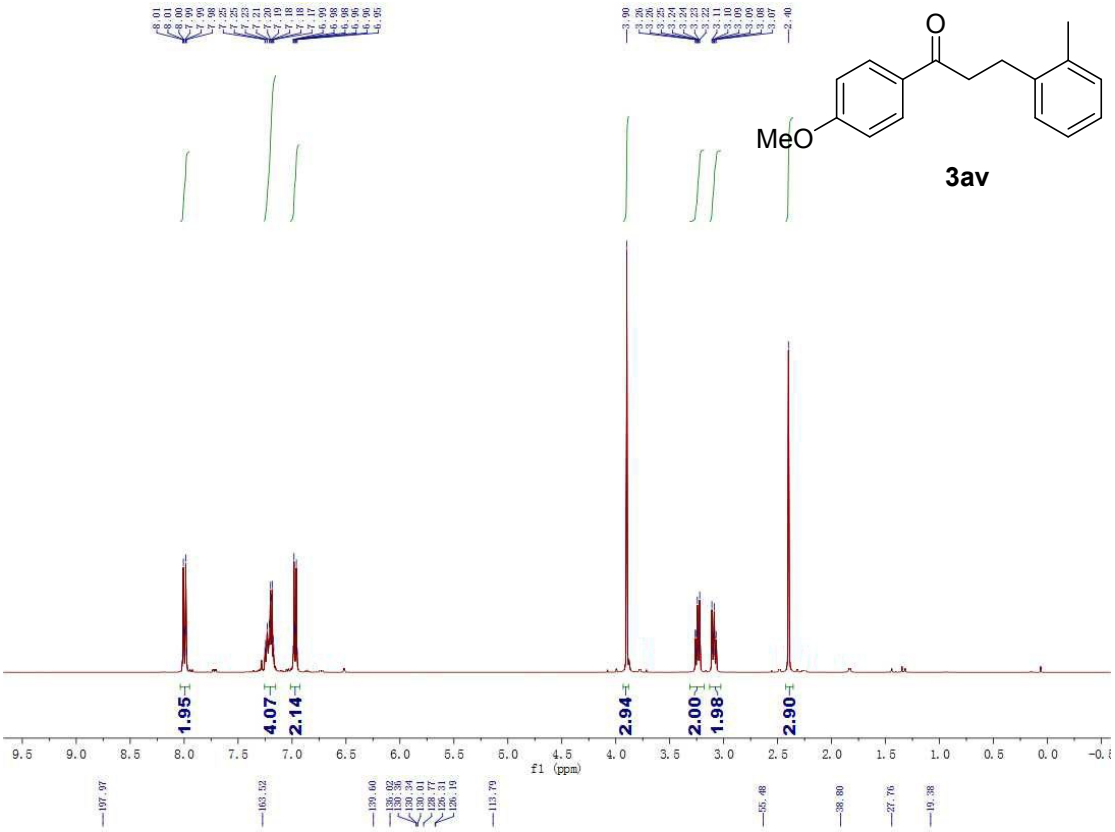


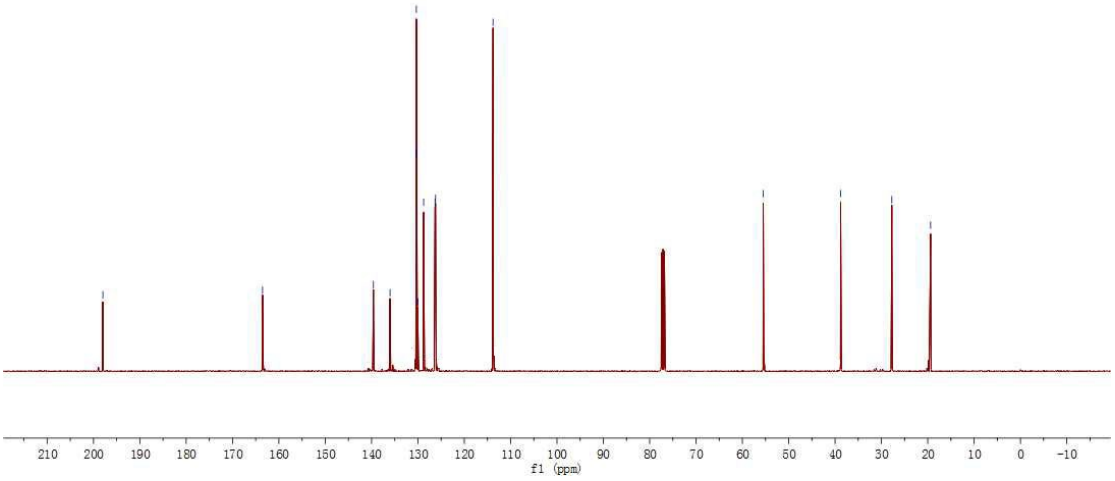


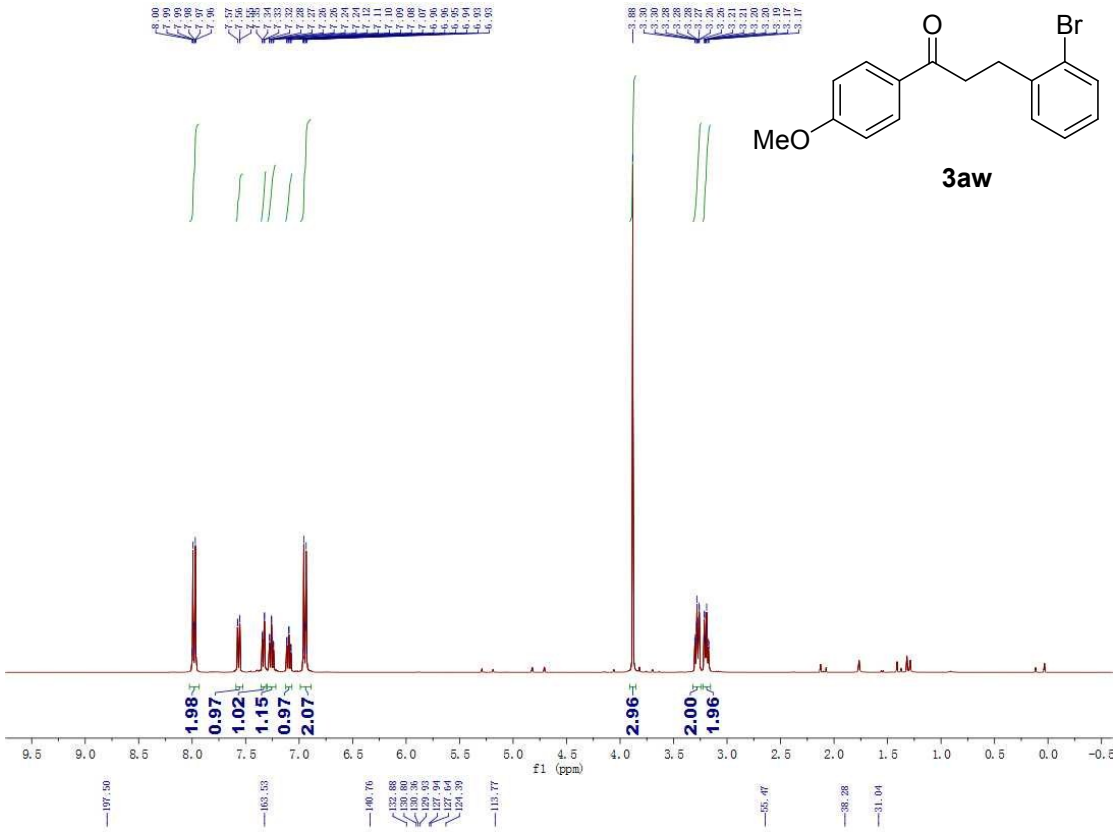

7.63
7.62
7.61
7.40
7.38
7.38
7.36
7.27
7.26
7.24
7.18
7.16
6.88
6.87
6.86
6.85
6.84
3.81
3.23
3.22
3.20
3.03
3.01
2.99
2.49
O
OMe
0.99
1.02
1.99
1.97
1.99
2.99
1.99
2.01
2.90
f1 (ppm)

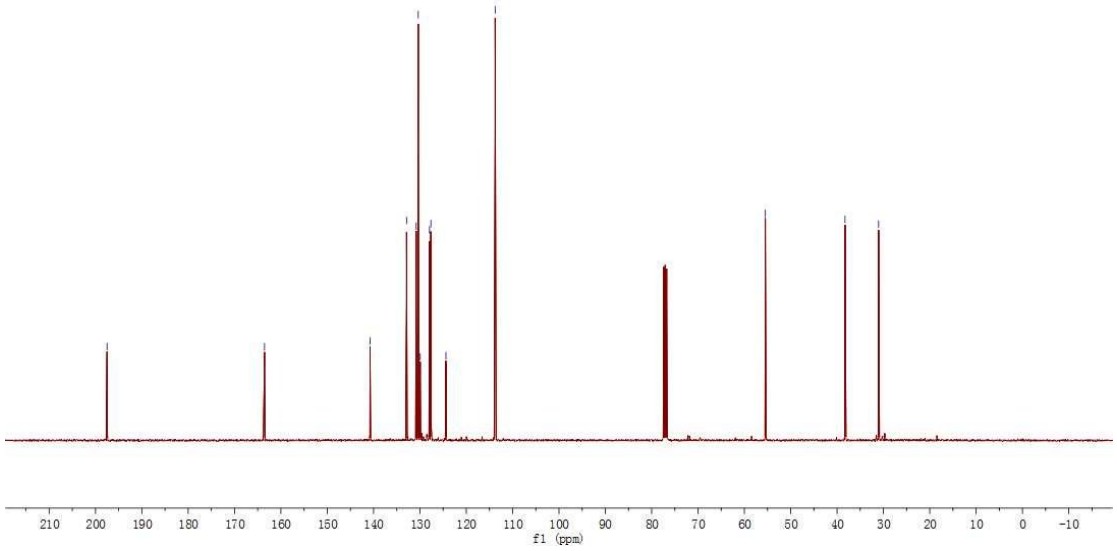
3au

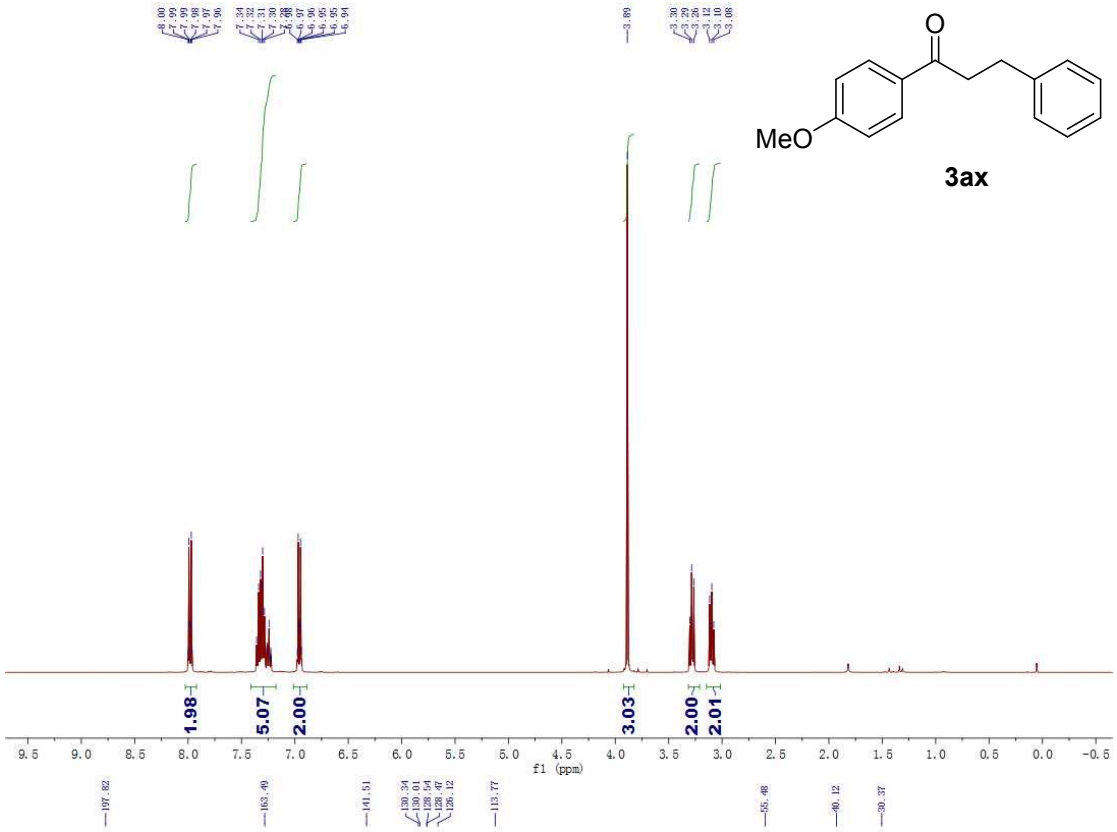

203.60
158.02
138.06
138.02
133.24
131.93
131.18
129.35
128.33
125.65
113.94
55.28
43.53
29.50
21.20
f1 (ppm)


MeO
O
3av
1.95
4.07
2.14
2.94
2.00
1.98
2.90
f1 (ppm)


f1 (ppm)

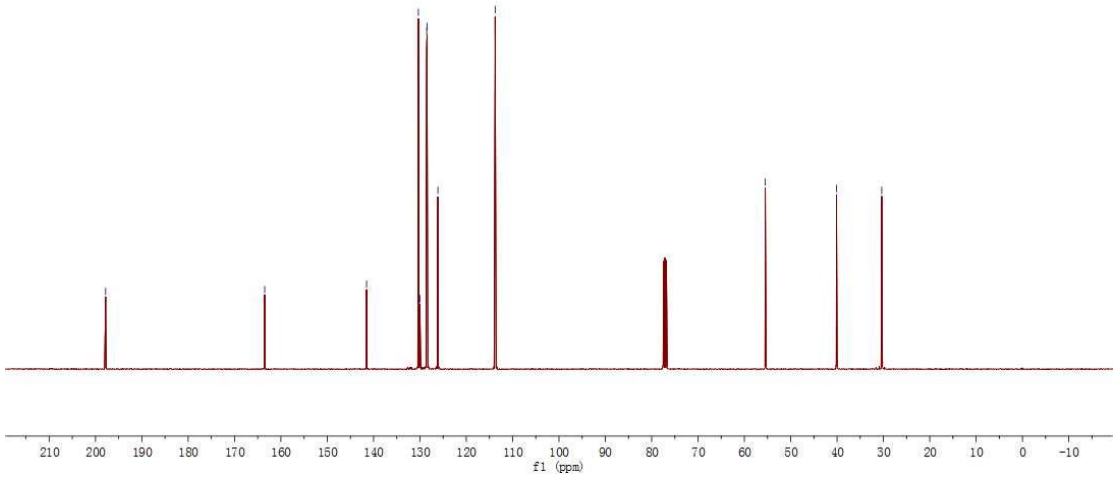

O
Br
MeO
3aw
1.98
0.97
1.02
1.15
0.97
2.07
2.96
2.00
1.96
f1 (ppm)

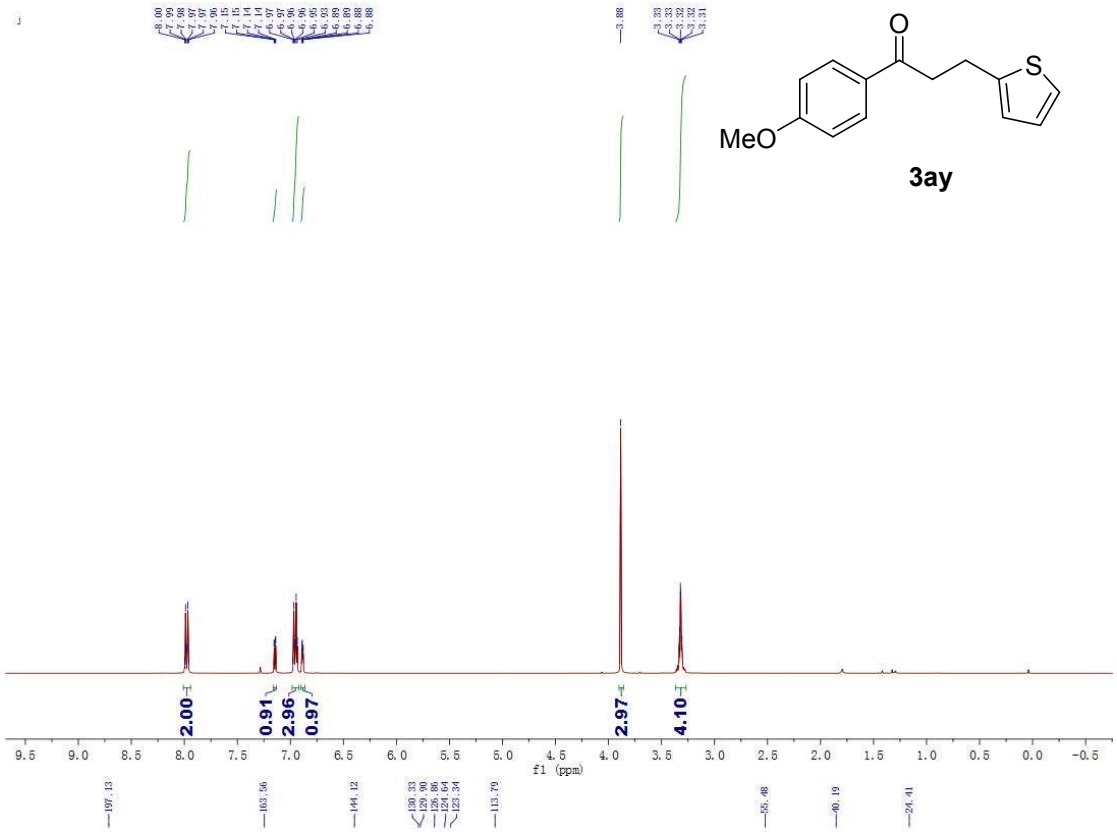

f1 (ppm)

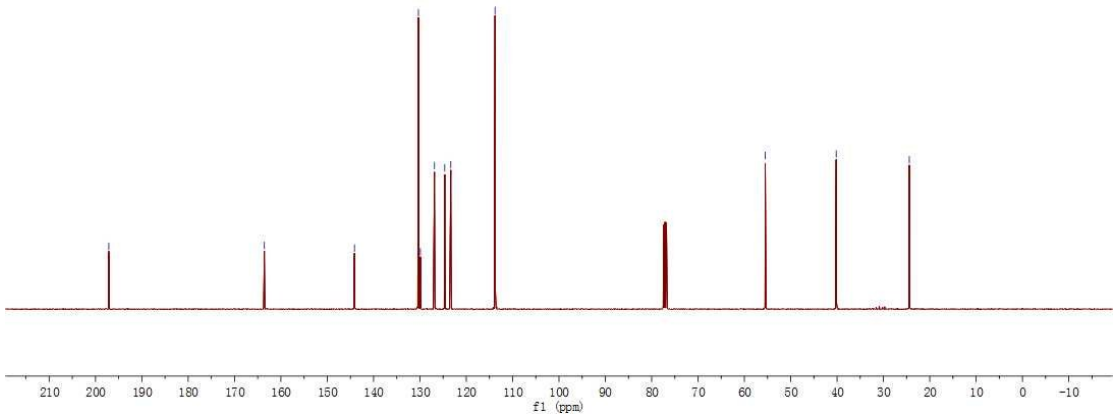

8.00
7.99
7.98
7.97
7.96
7.34
7.32
7.31
7.30
7.28
6.97
6.96
6.95
6.94
3.89
3.30
3.29
3.26
3.12
3.10
3.08
1.98
5.07
2.00
3.03
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

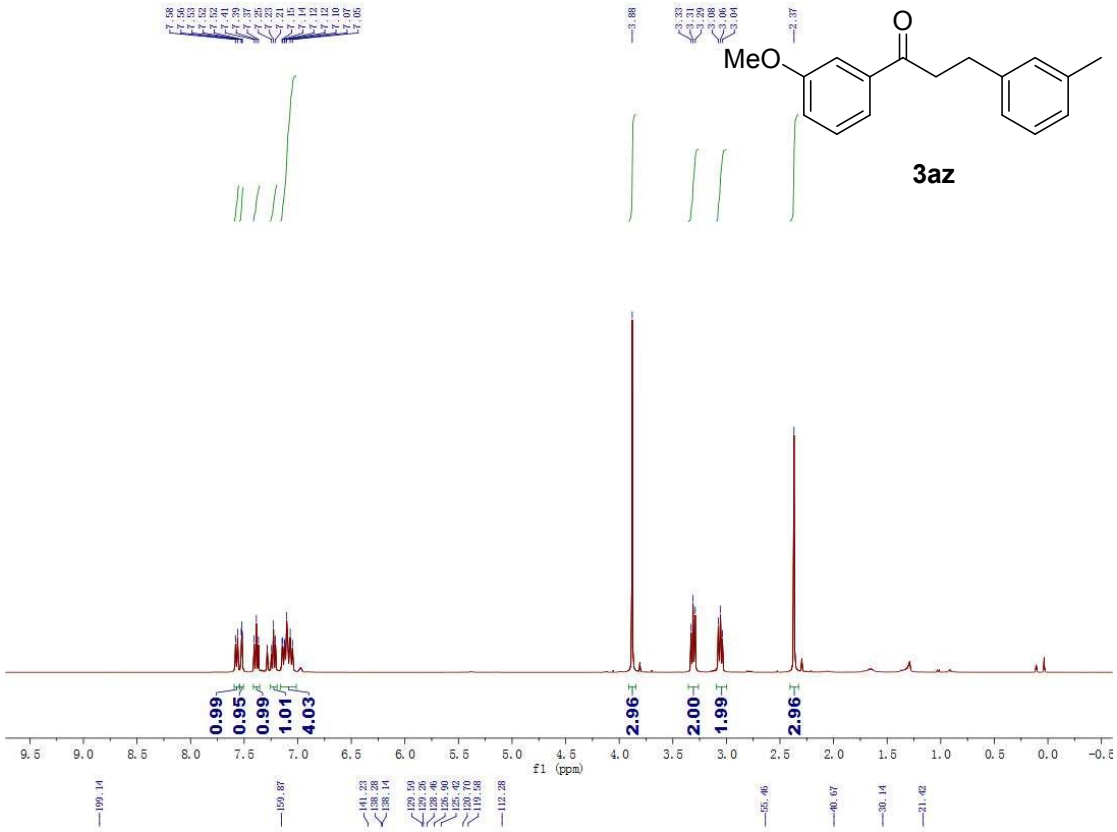
O
MeO

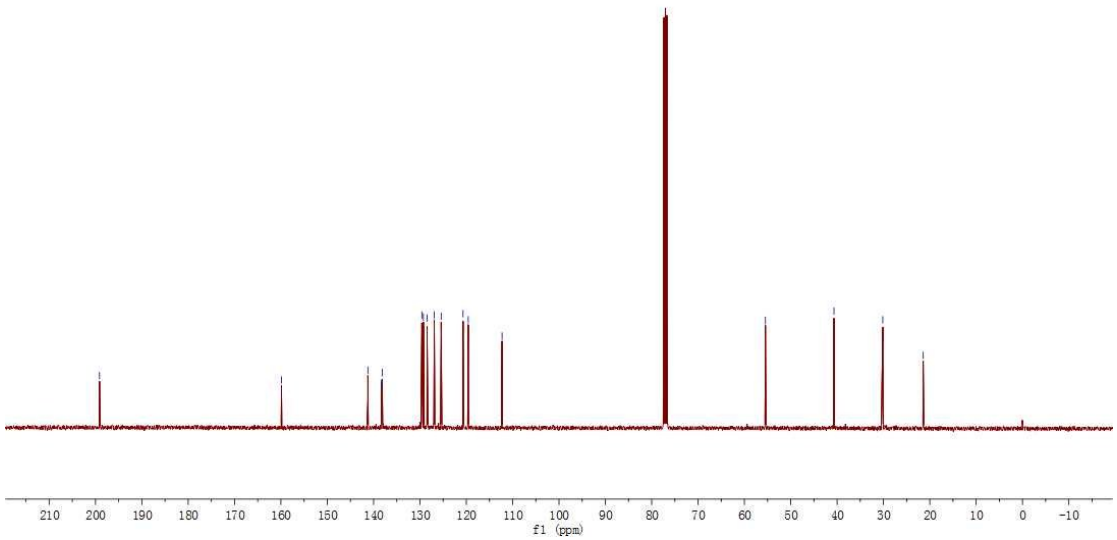
3ax

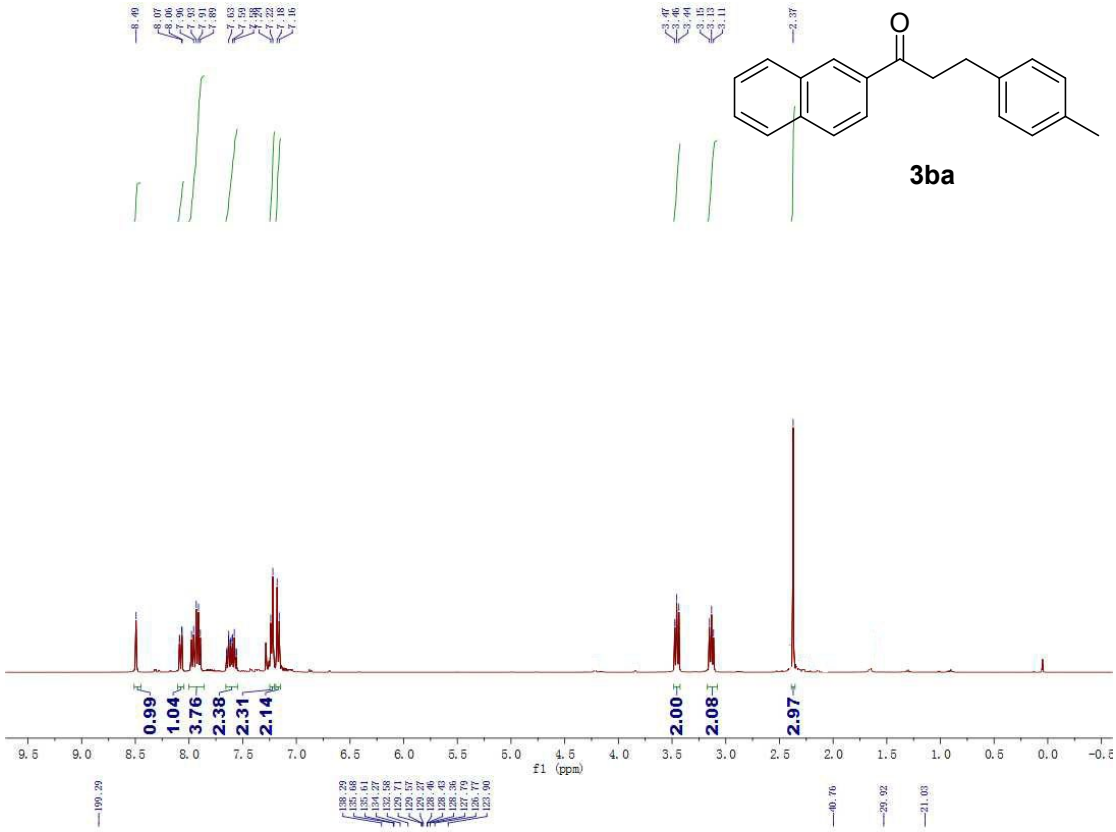

197.82
163.49
141.51
130.34
130.01
128.54
128.47
126.12
113.77
55.48
40.12
30.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

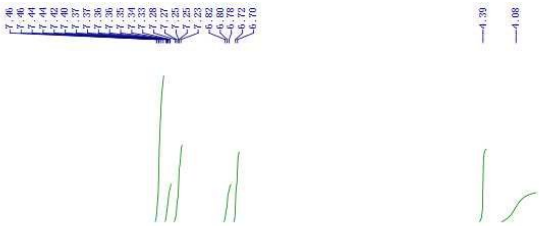

MeO
O
S
3ay
2.00
0.91
2.96
0.97
2.97
4.10
f1 (ppm)

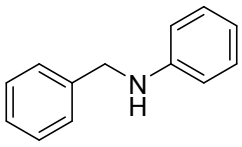

f1 (ppm)


MeO
O
3az
0.99
0.95
0.99
1.01
4.03
2.96
2.00
1.99
2.96
f1 (ppm)

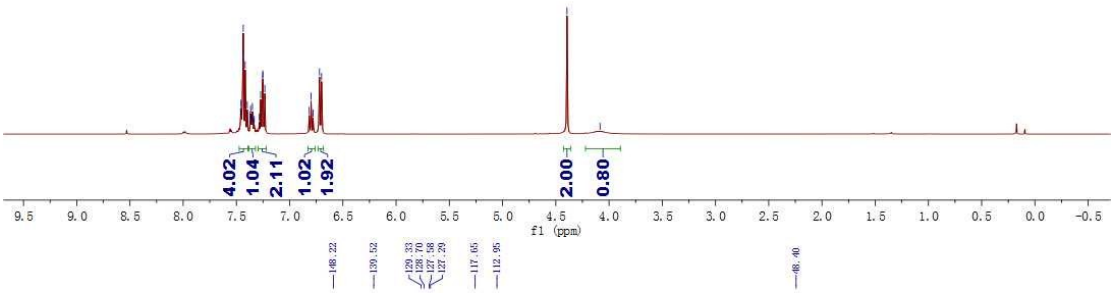

f1 (ppm)

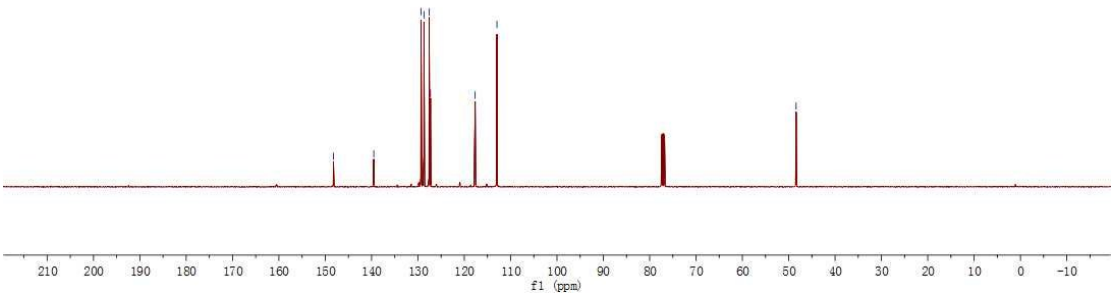

8.49
8.07
8.06
7.96
7.93
7.91
7.89
7.63
7.59
7.22
7.18
7.16
3.47
3.46
3.44
3.15
3.13
3.11
2.37
O
3ba
0.99
1.04
3.76
2.38
2.31
2.14
2.00
2.08
2.97
f1 (ppm)
199.29
138.29
135.68
135.01
134.27
132.58
129.71
129.57
128.97
128.46
128.43
128.36
127.79
126.77
125.99
40.76
29.92
21.03
f1 (ppm)

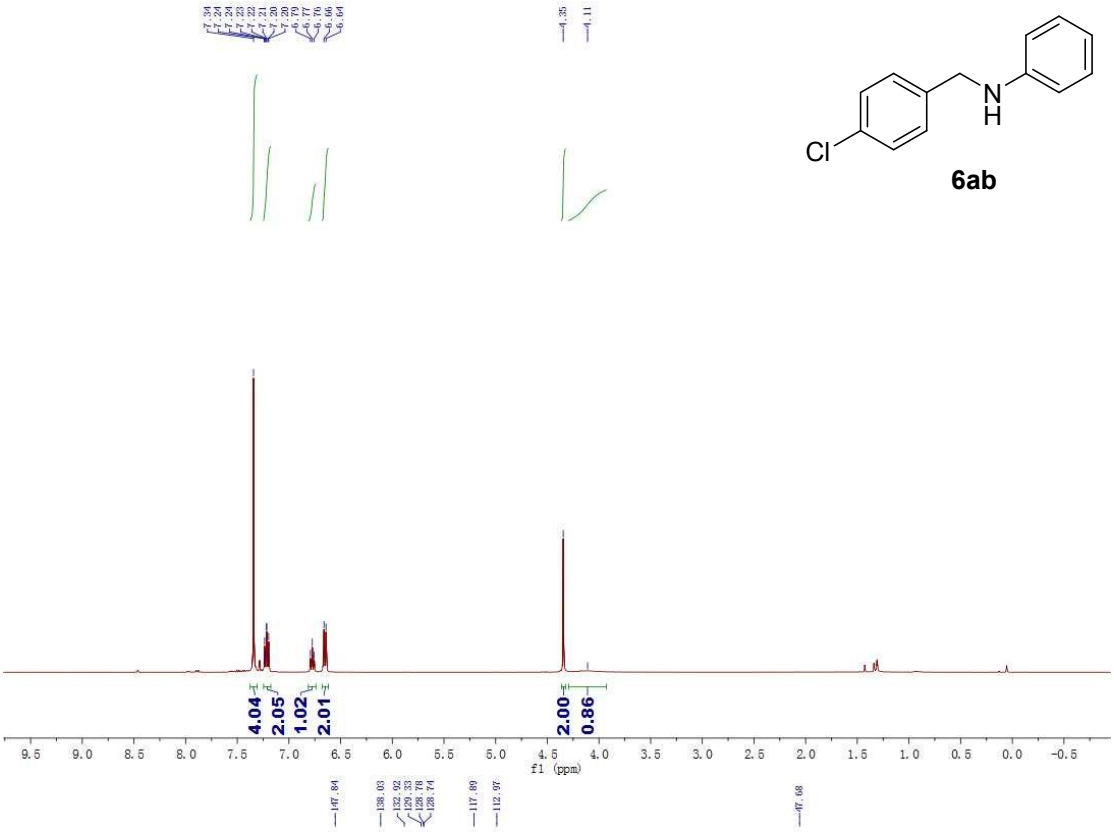




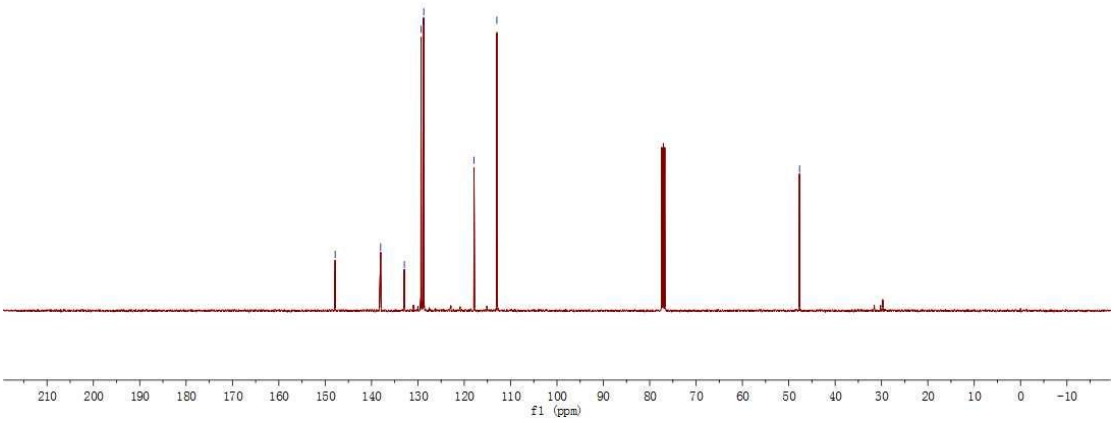
6aa

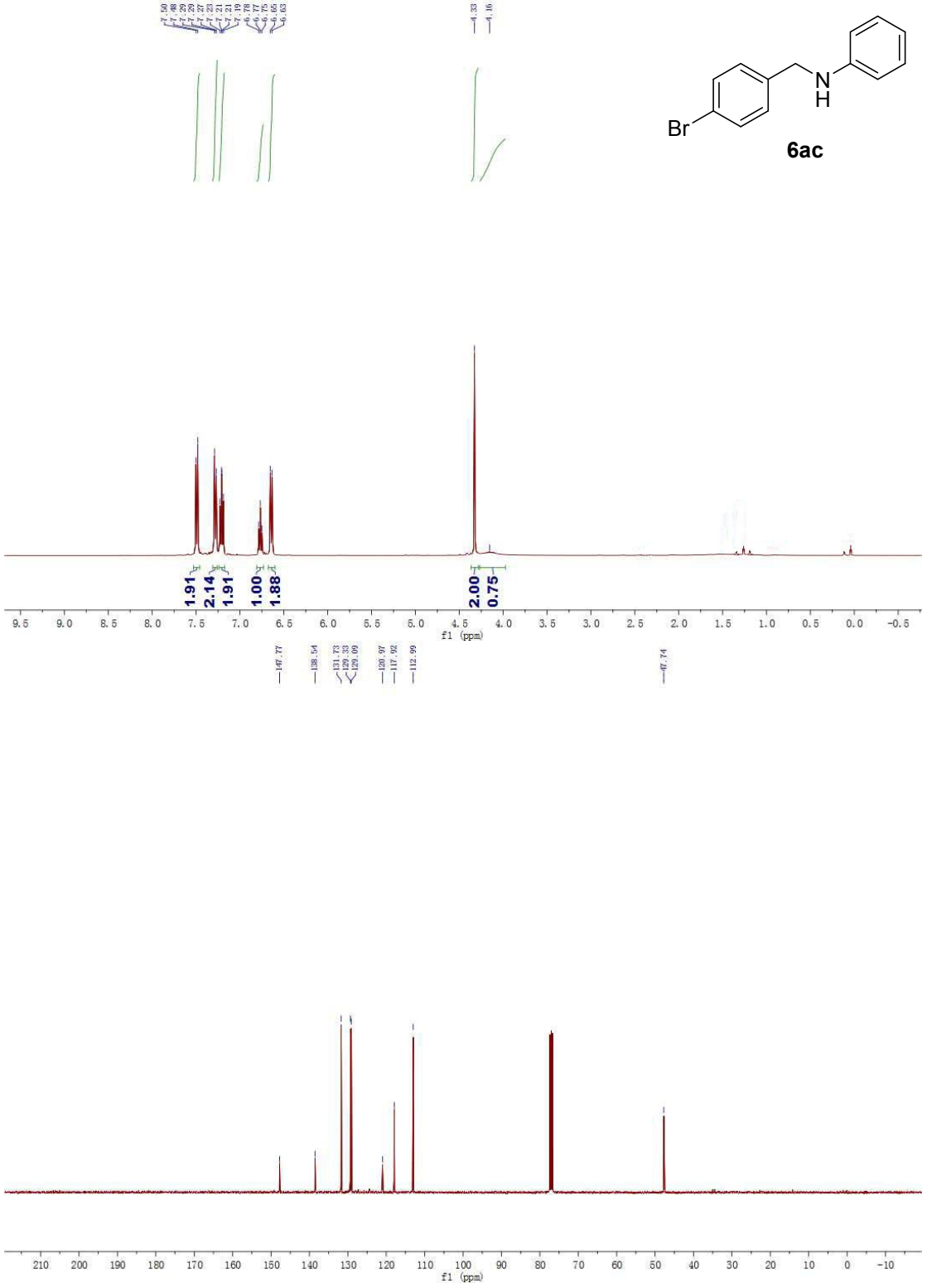


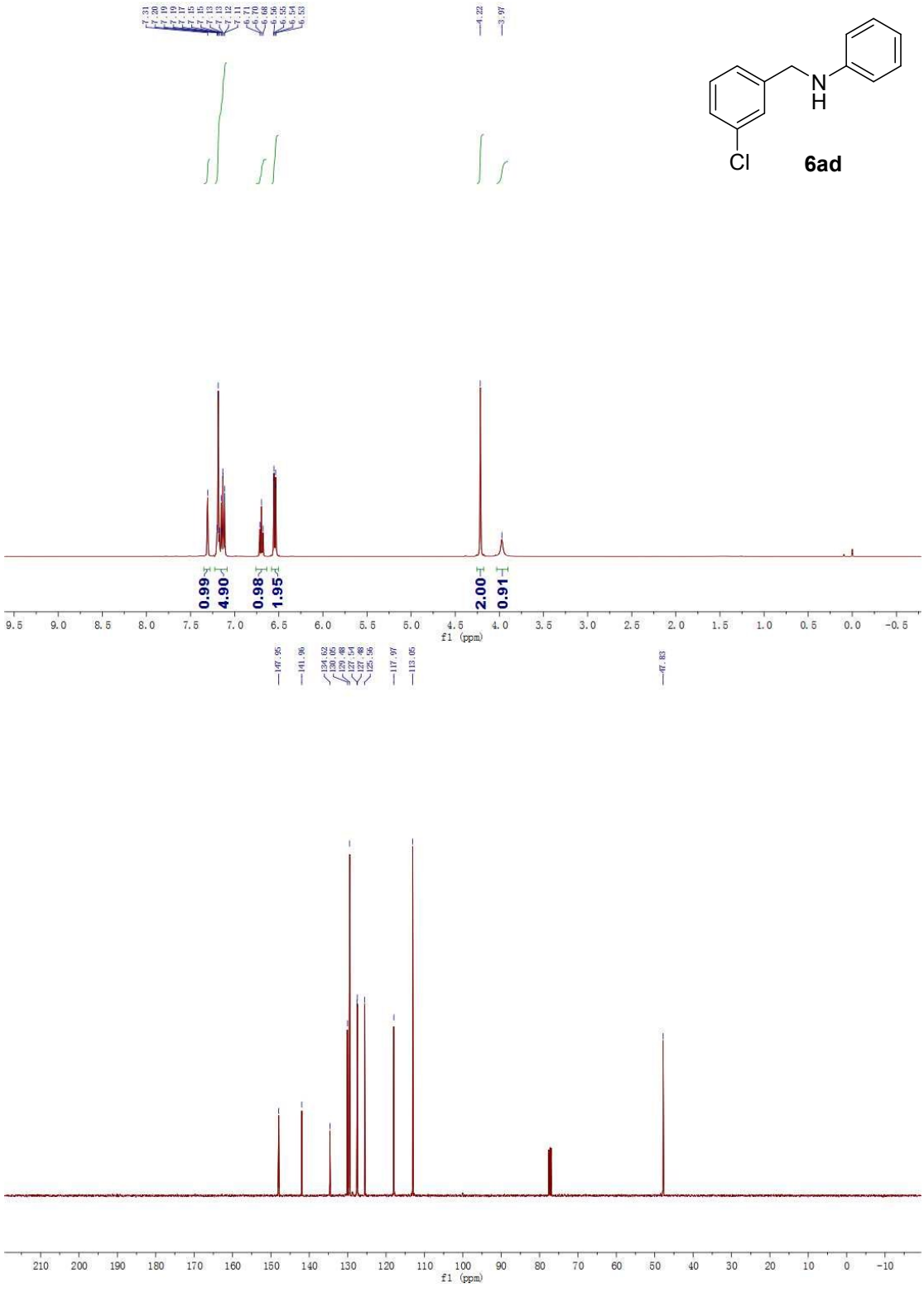


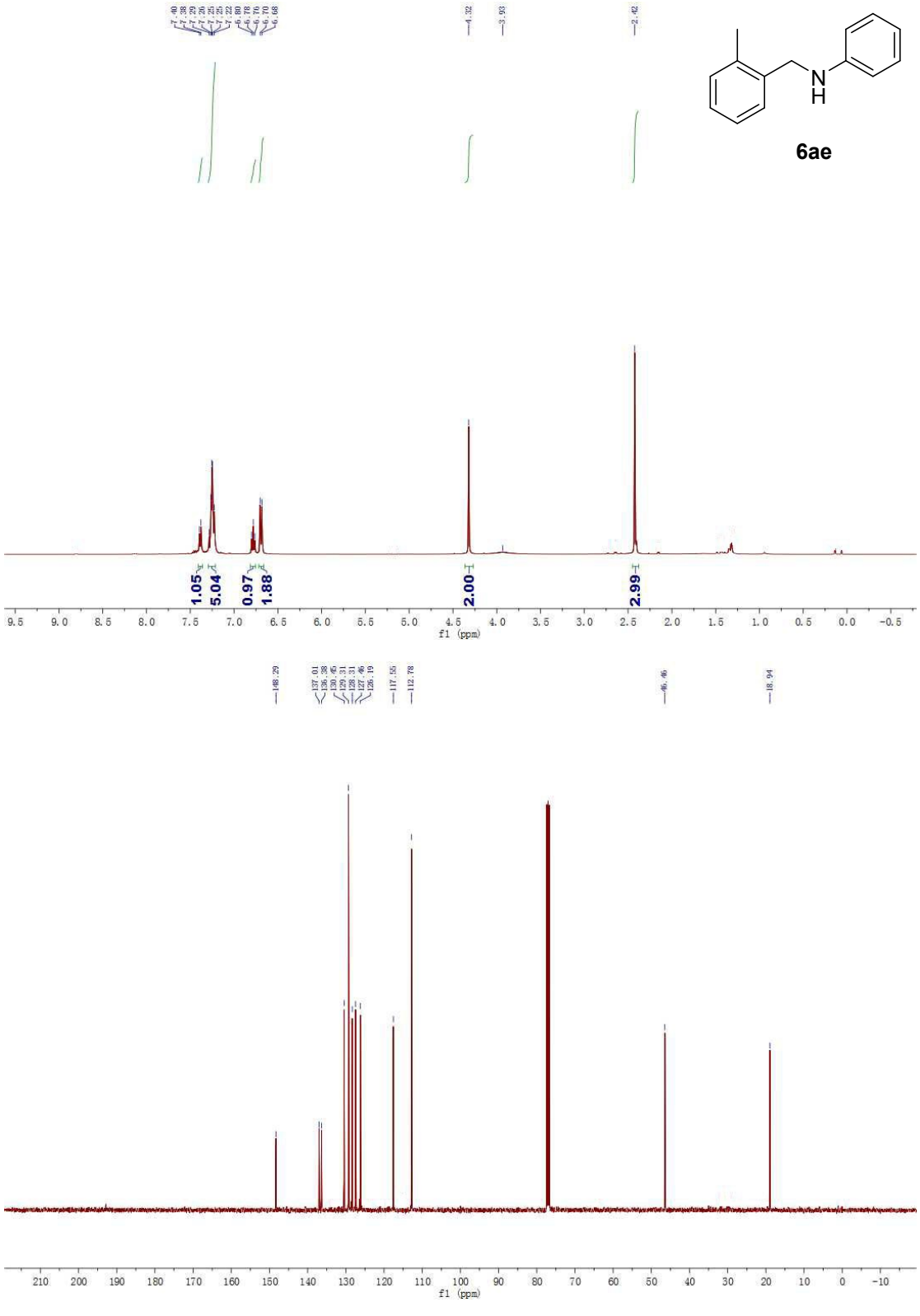


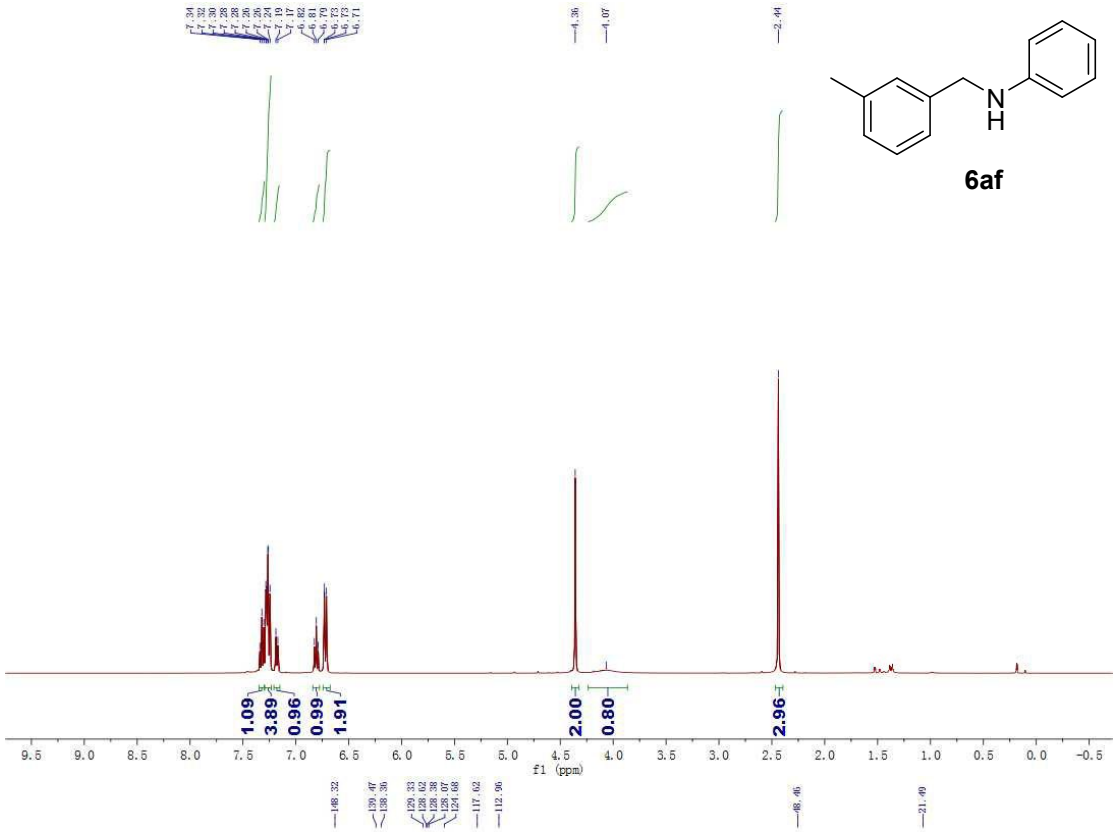
6ab



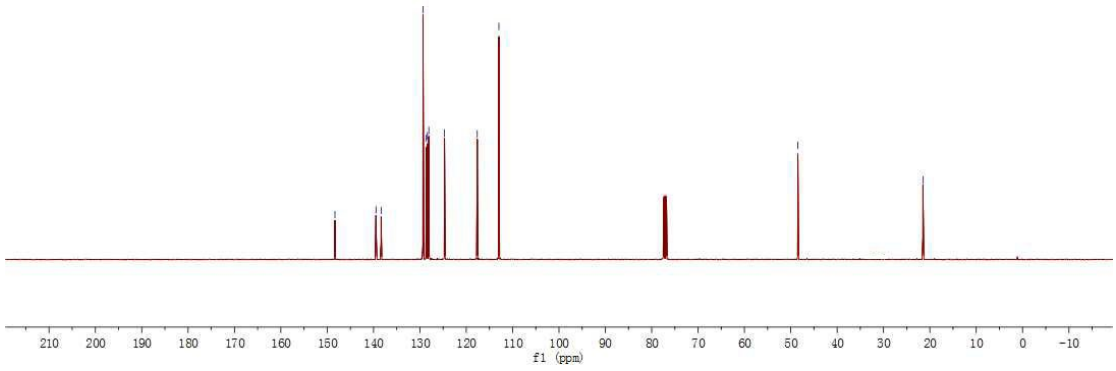

Br
N
H
6ac
1.91
2.14
1.91
1.00
1.88
2.00
0.75
f1 (ppm)

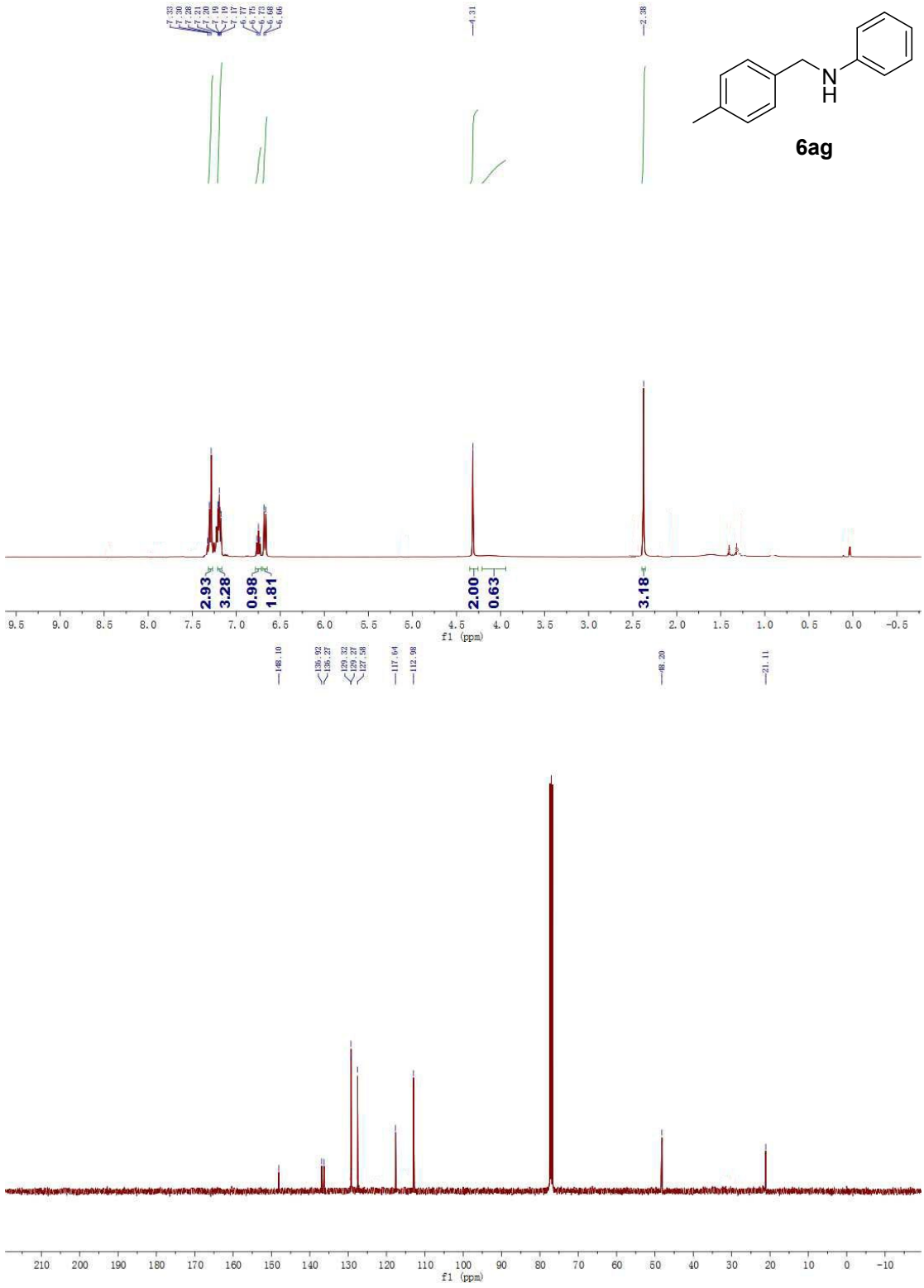

7.31
7.20
7.19
7.17
7.17
7.15
7.13
7.13
7.12
7.11
6.71
6.70
6.68
5.56
5.55
5.54
5.53
4.22
3.97
N
H
Cl
6ad
0.99
4.90
0.98
1.95
2.00
0.91
f1 (ppm)
147.95
141.96
134.62
130.05
129.48
127.54
127.48
125.56
117.97
113.05
47.83
f1 (ppm)

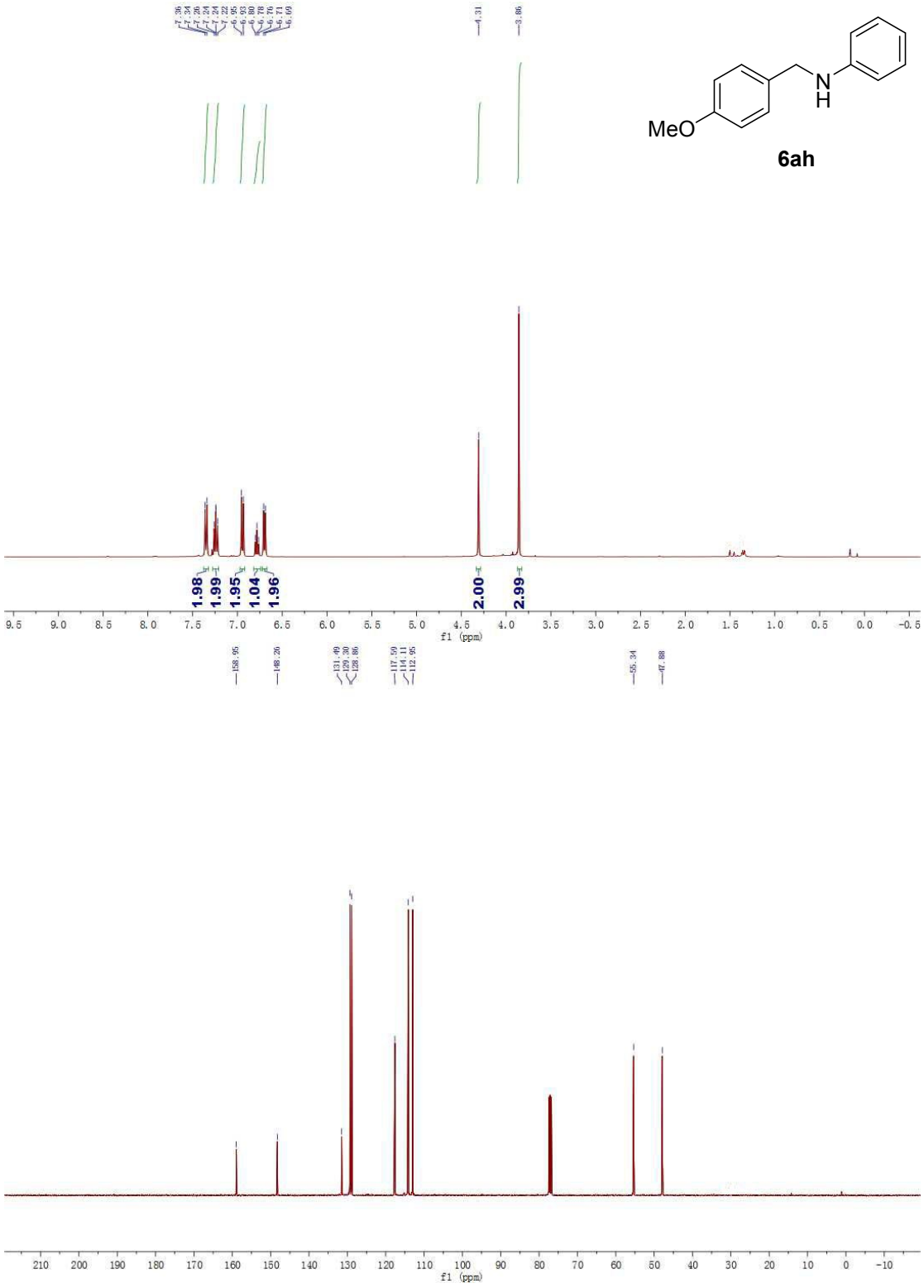

7.40
7.38
7.29
7.26
7.25
7.23
7.22
6.80
6.78
6.76
6.70
6.68
4.32
3.93
2.42
N
H
6ae
1.05
5.04
0.97
1.88
2.00
2.99
f1 (ppm)
148.29
137.01
136.38
130.45
129.31
128.31
127.46
126.19
117.55
112.78
46.46
18.94
f1 (ppm)

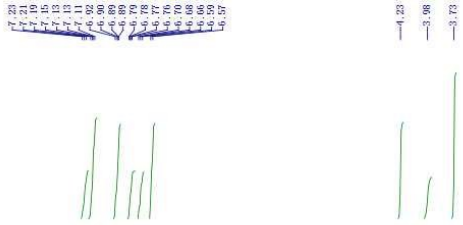

7.34
7.32
7.30
7.28
7.26
7.24
7.19
7.17
6.82
6.81
6.79
6.73
6.73
6.71
4.36
4.07
2.44
N
H
6af
1.09
3.89
0.96
0.99
1.91
2.00
0.80
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

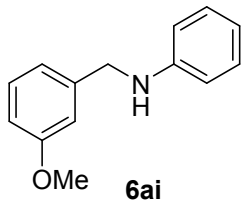
148.32
139.47
138.36
129.33
128.62
128.38
128.07
124.68
117.62
112.96
48.46
21.49


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

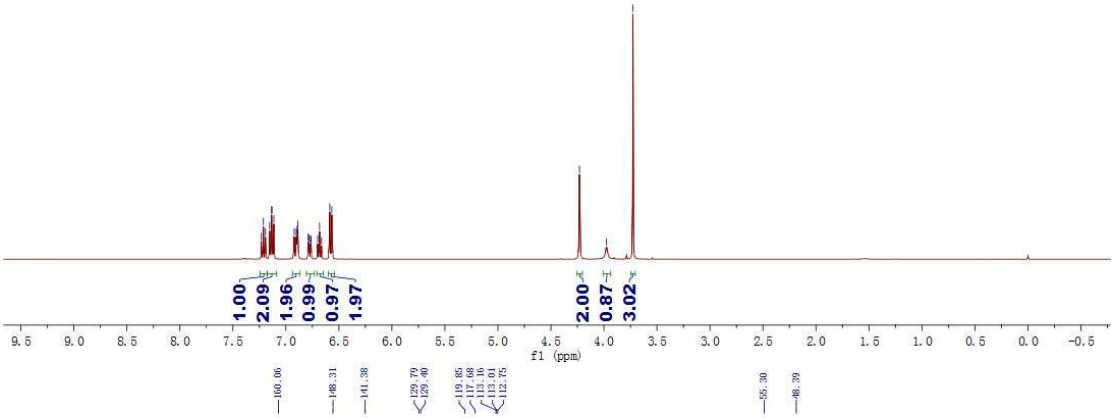

7.33
7.30
7.28
7.21
7.20
7.19
7.17
7.17
6.77
6.75
6.73
5.68
5.66
4.31
2.38
N
H
6ag
2.93
3.28
0.98
1.81
2.00
0.63
3.18
f1 (ppm)
148.10
136.92
136.27
129.32
129.27
127.58
117.64
112.98
48.20
21.11
f1 (ppm)

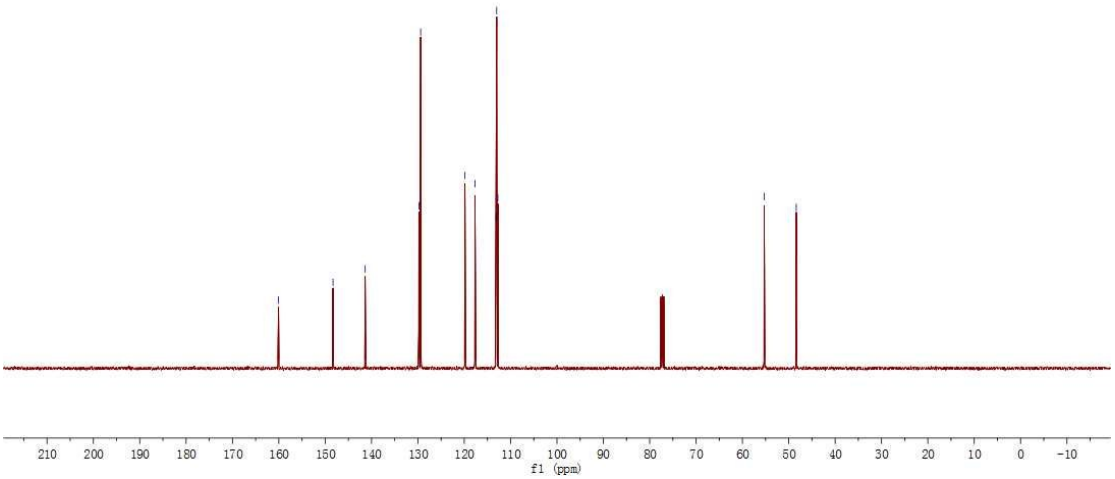

MeO
N
H
6ah
1.98
1.99
1.95
1.04
1.96
2.00
2.99
f1 (ppm)

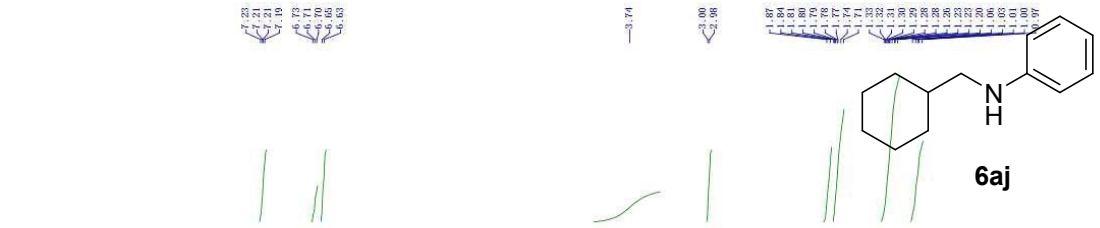




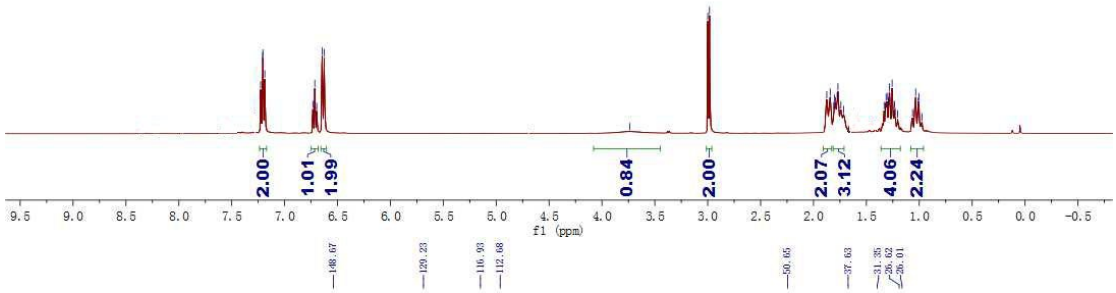
6ai

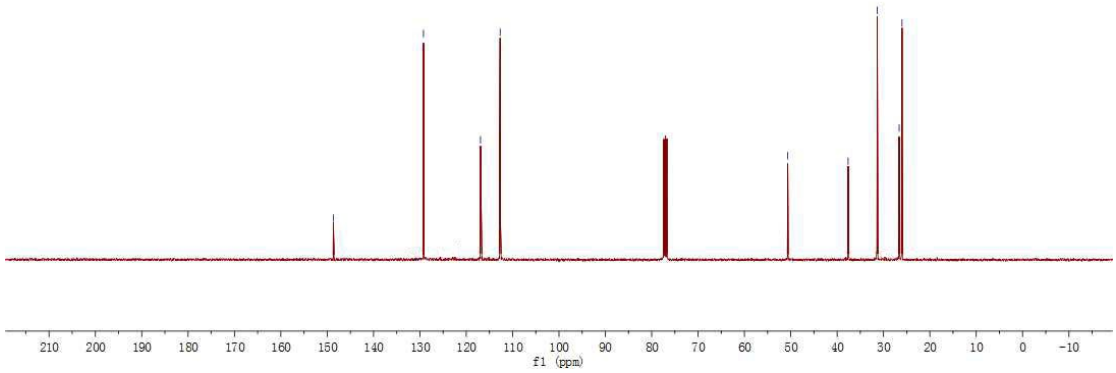


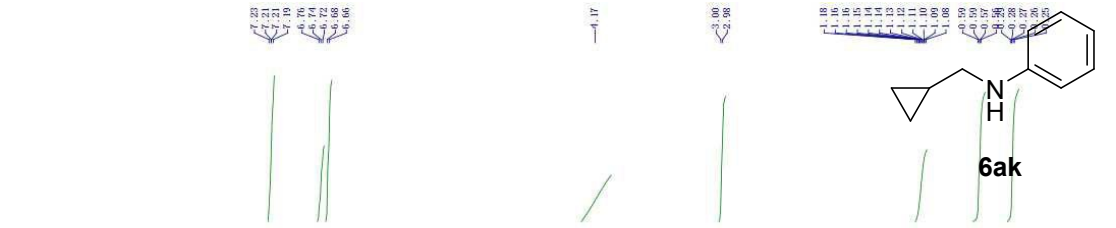


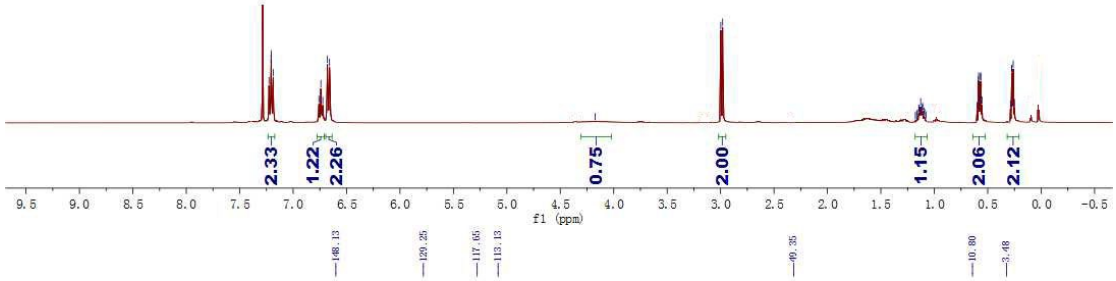


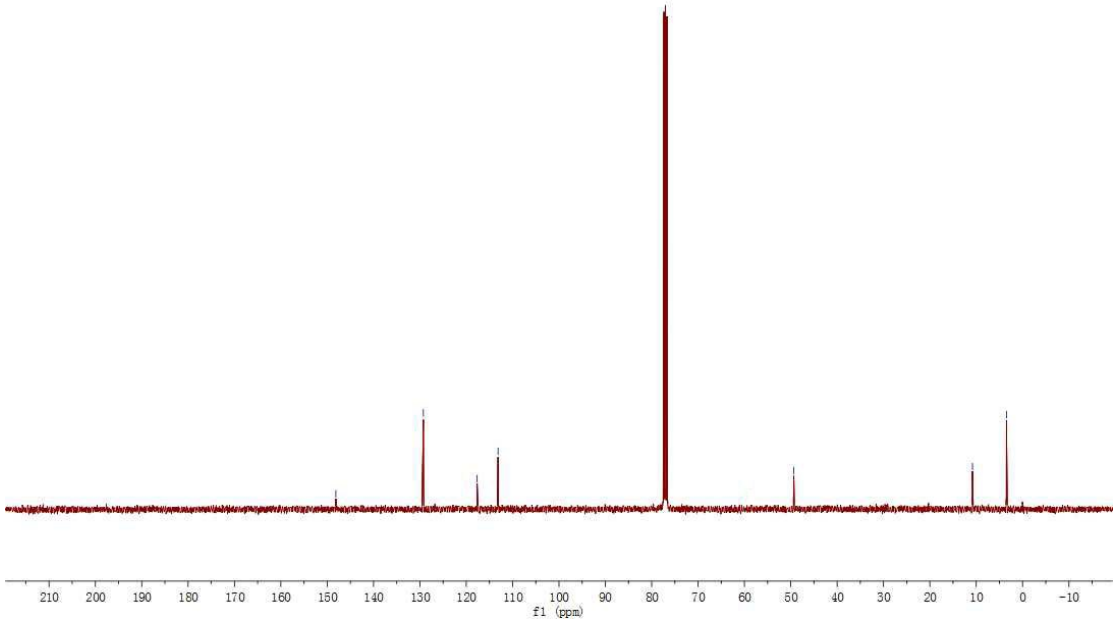
6aj

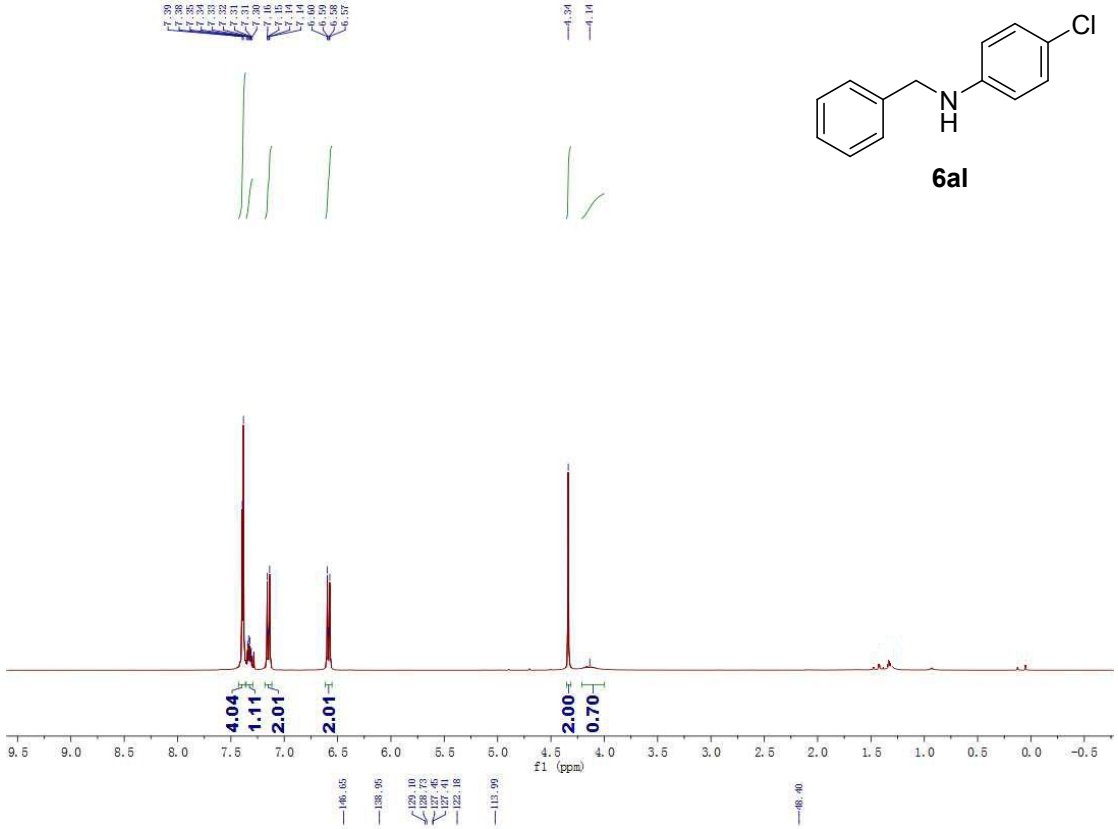




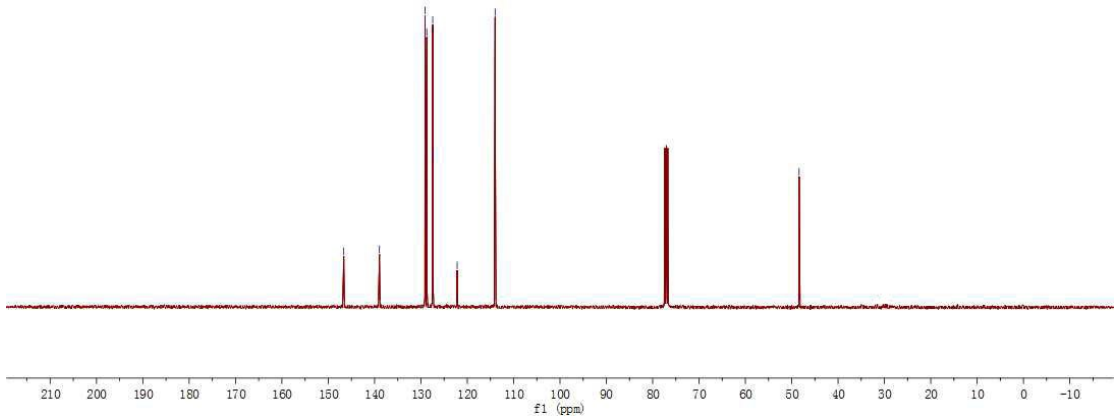

7.23
7.21
7.19
6.76
6.74
6.72
6.68
6.66
4.17
3.00
2.98
1.18
1.16
1.15
1.14
1.13
1.12
1.11
1.10
1.09
1.08
0.59
0.57
0.28
0.27
0.26
0.25
N
H
6ak

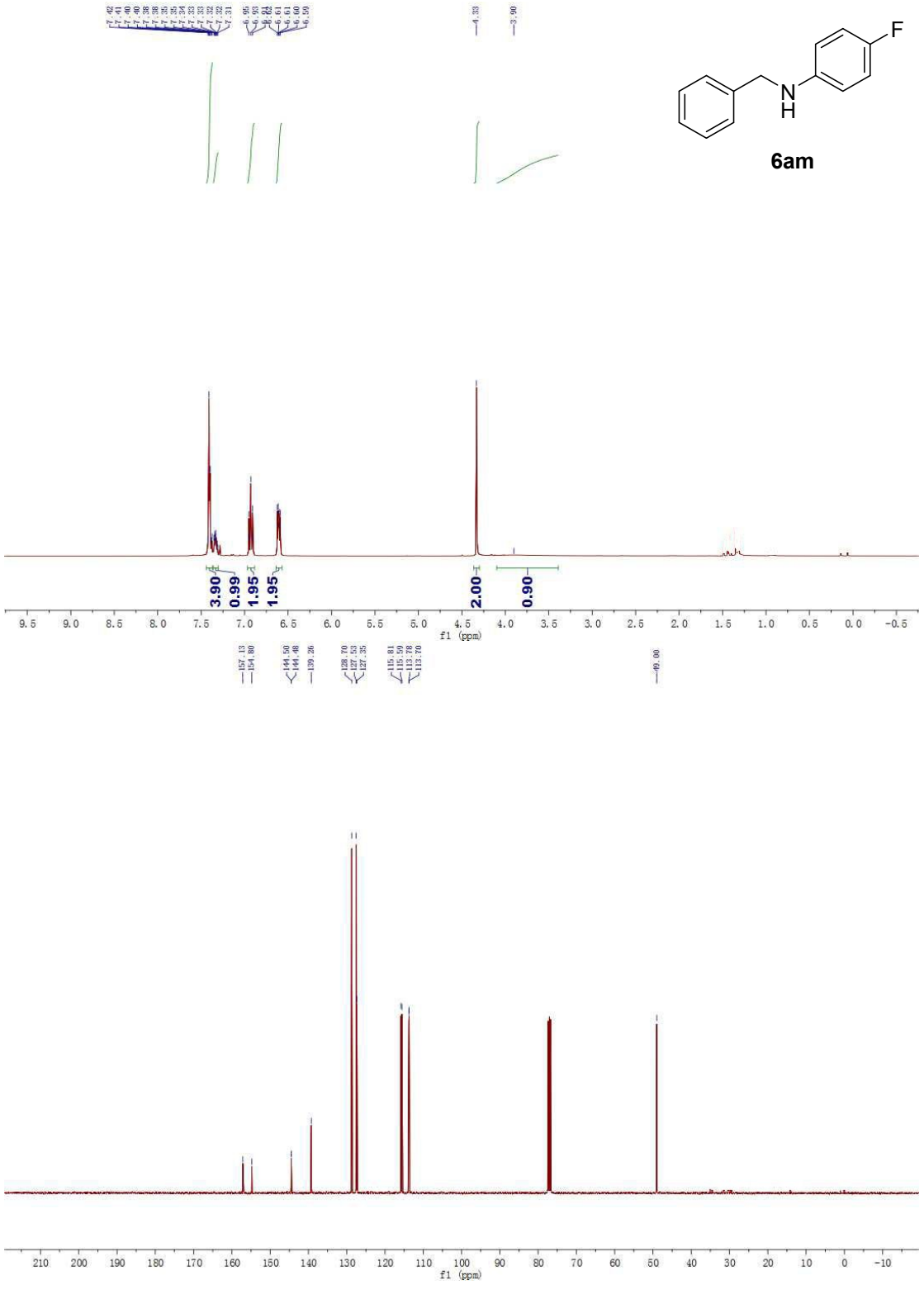

2.33
1.22
2.26
0.75
2.00
1.15
2.06
2.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
148.13
129.25
117.65
113.13
49.35
10.80
3.48


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



6al




F
N
H
6am
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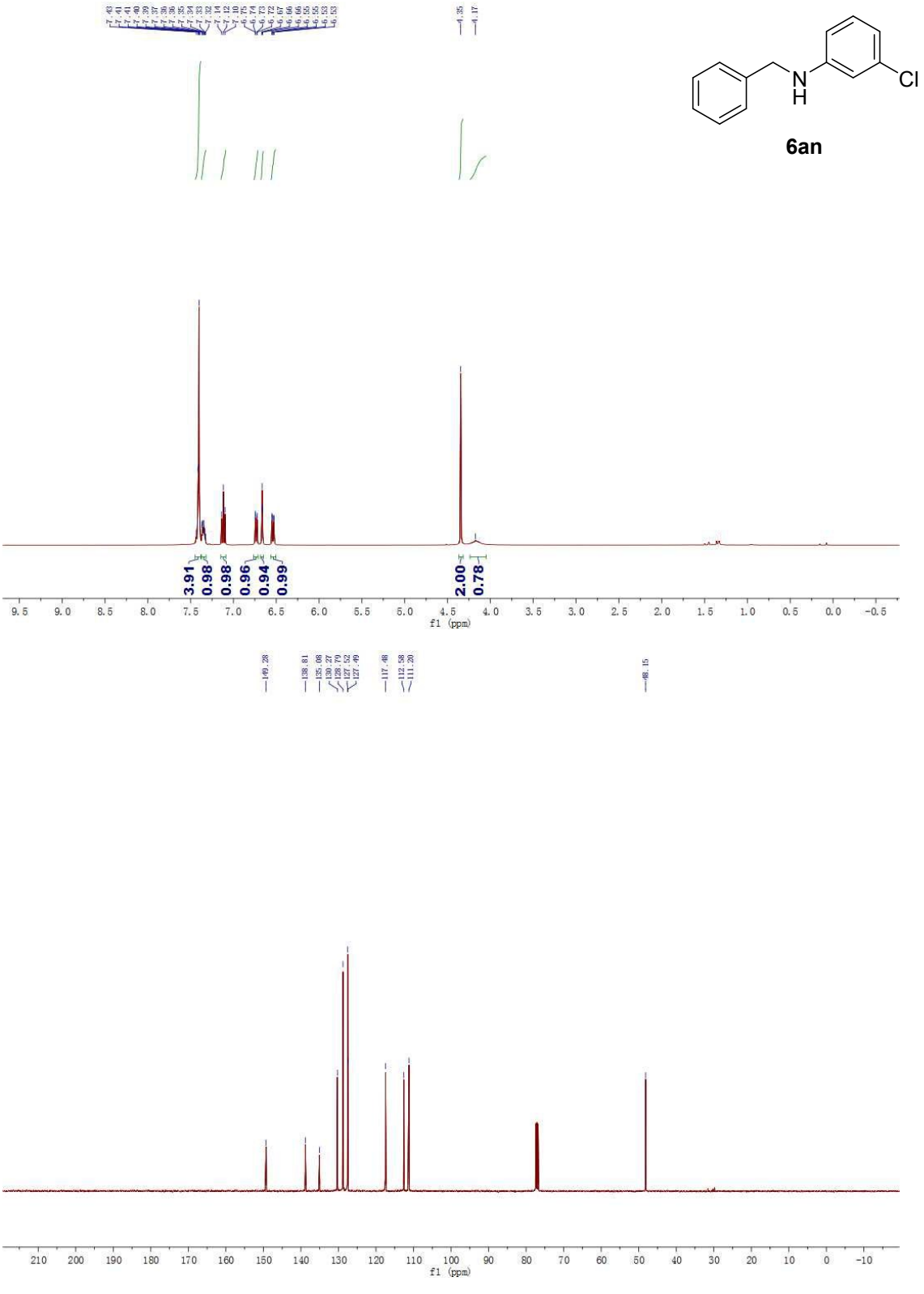
0.99
1.95
1.95
2.00
0.90
f1 (ppm)
f1 (ppm)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H
Cl
6an
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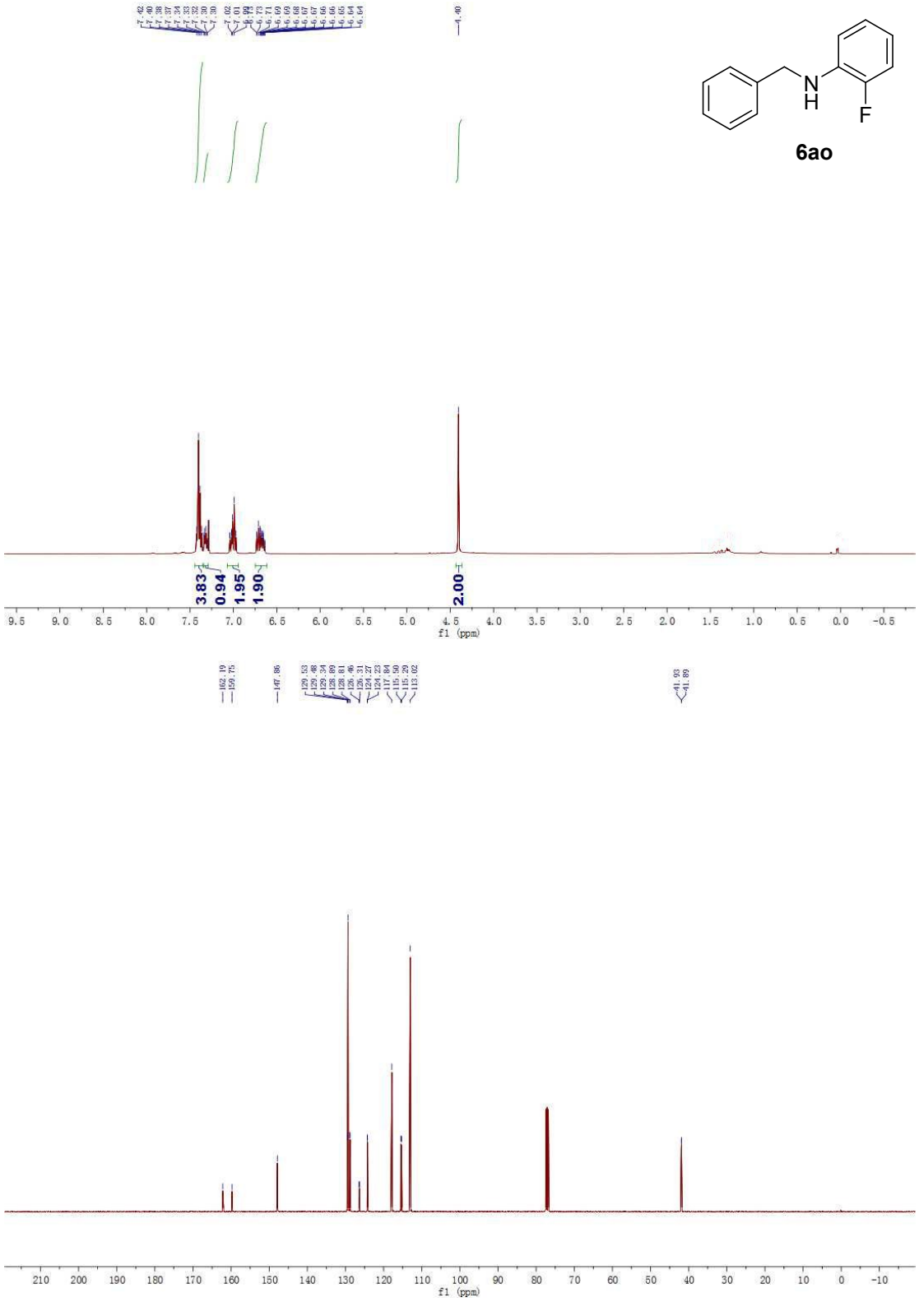
0.98
0.96
0.94
0.99
2.00
0.78
f1 (ppm)
f1 (ppm)



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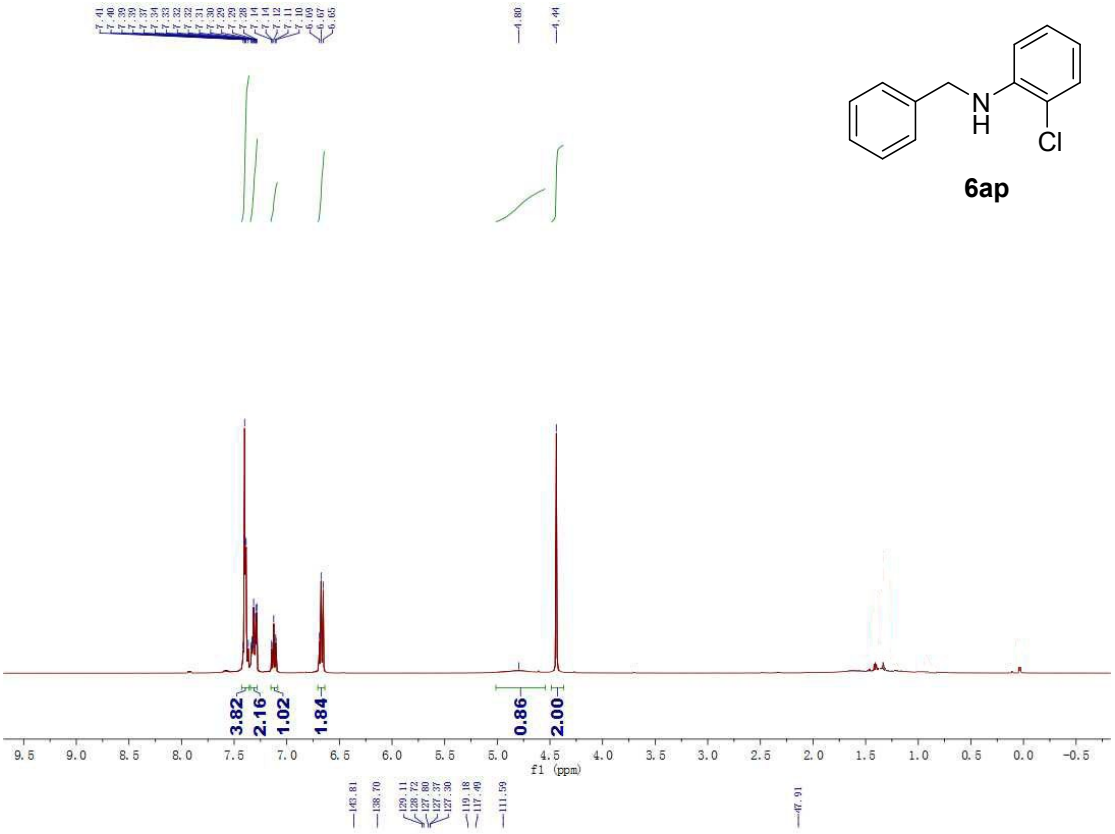

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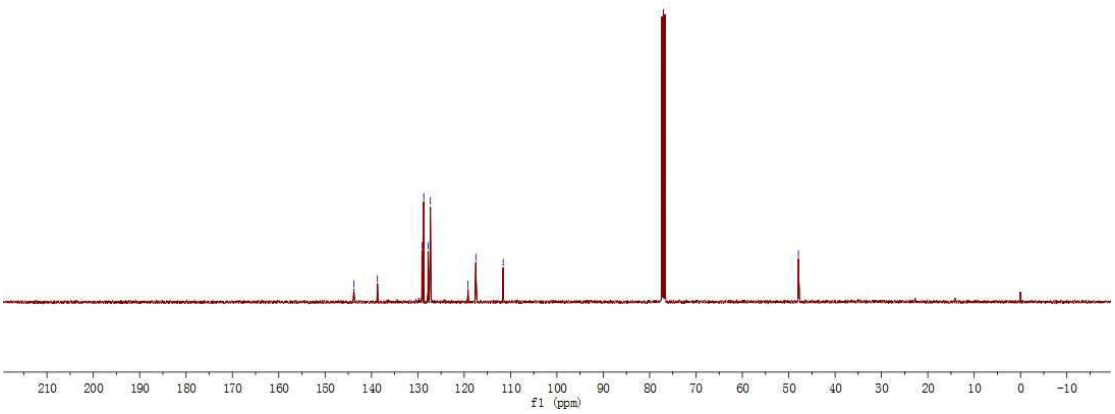

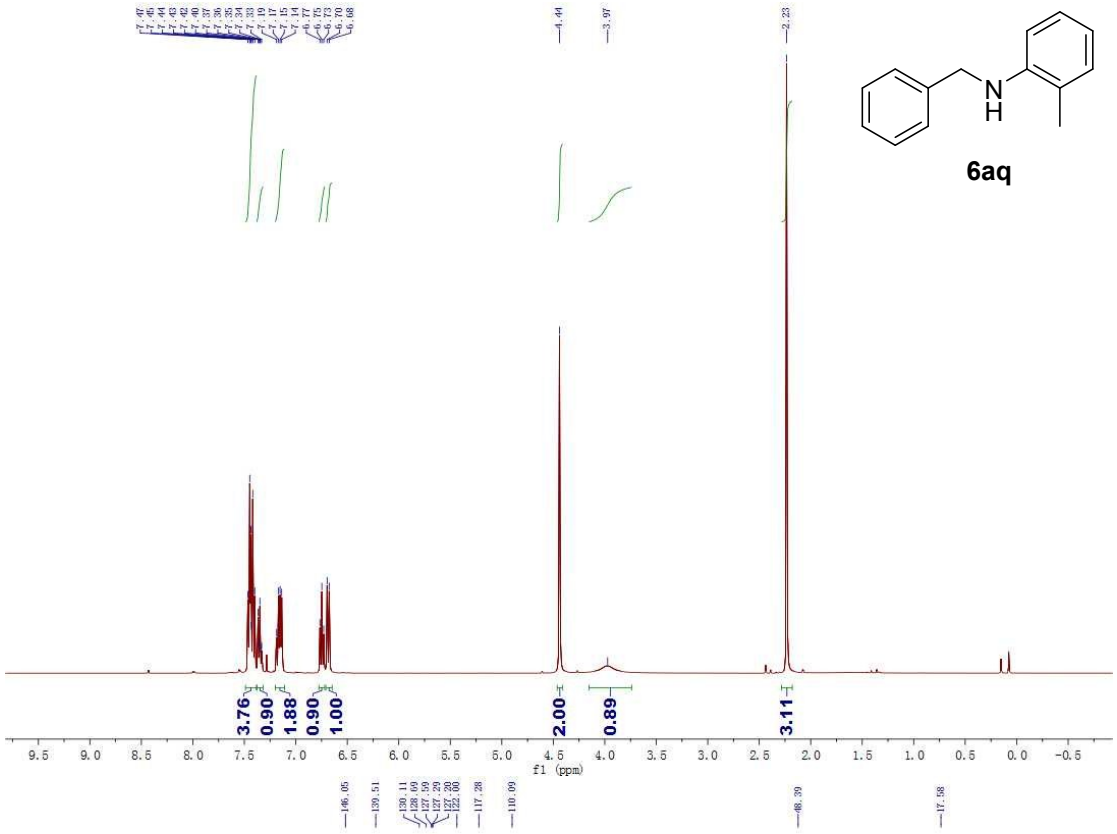
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7.34
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7.15
7.14
7.13
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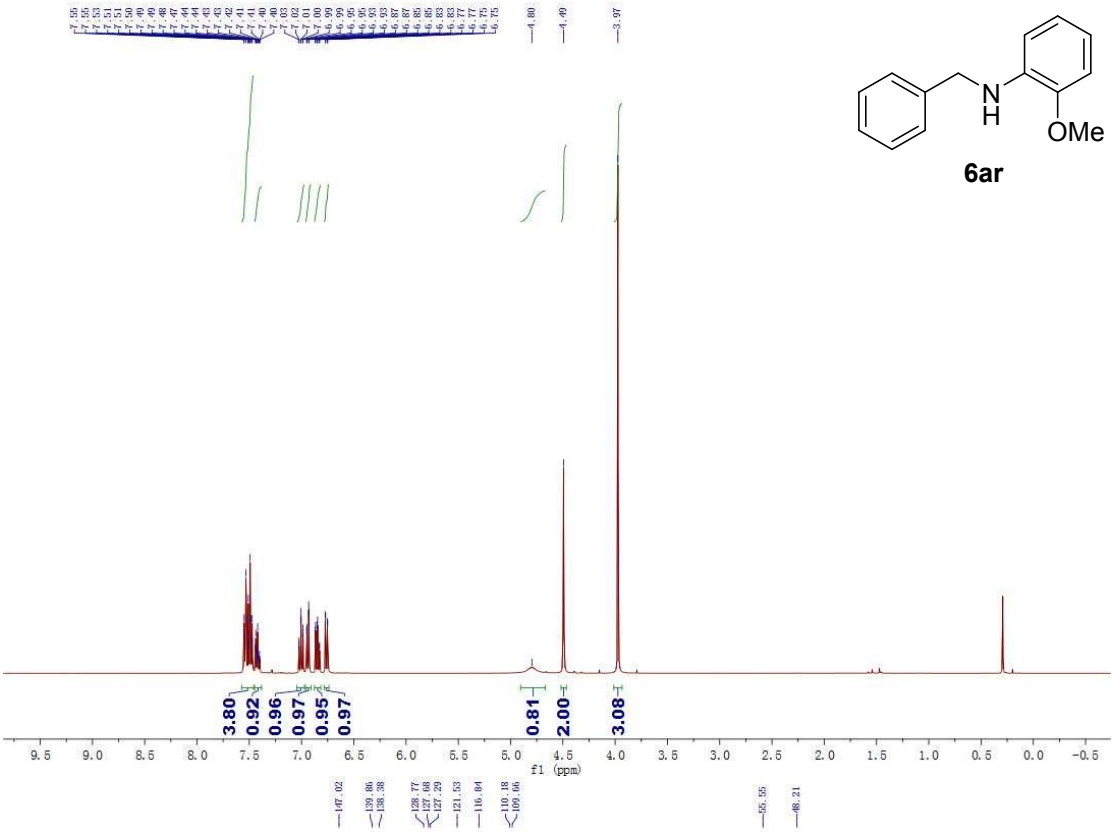
6.73
6.70
6.68
4.44
3.97
2.23
3.76
0.90
1.88
0.90
1.00
2.00
0.89
3.11
f1 (ppm)
146.05
139.51
130.11
128.69
127.59
127.29
122.03
117.28
110.09
48.39
17.58
f1 (ppm)

6aq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7.44
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7.42
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7.03
7.02
7.01
7.00
6.99
6.95
6.93
6.87
6.85
6.83
6.77
6.75
4.80
4.49
3.97
3.80
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0.96
0.97
0.95
0.97
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2.00
3.08
f1 (ppm)
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139.86
138.38
128.77
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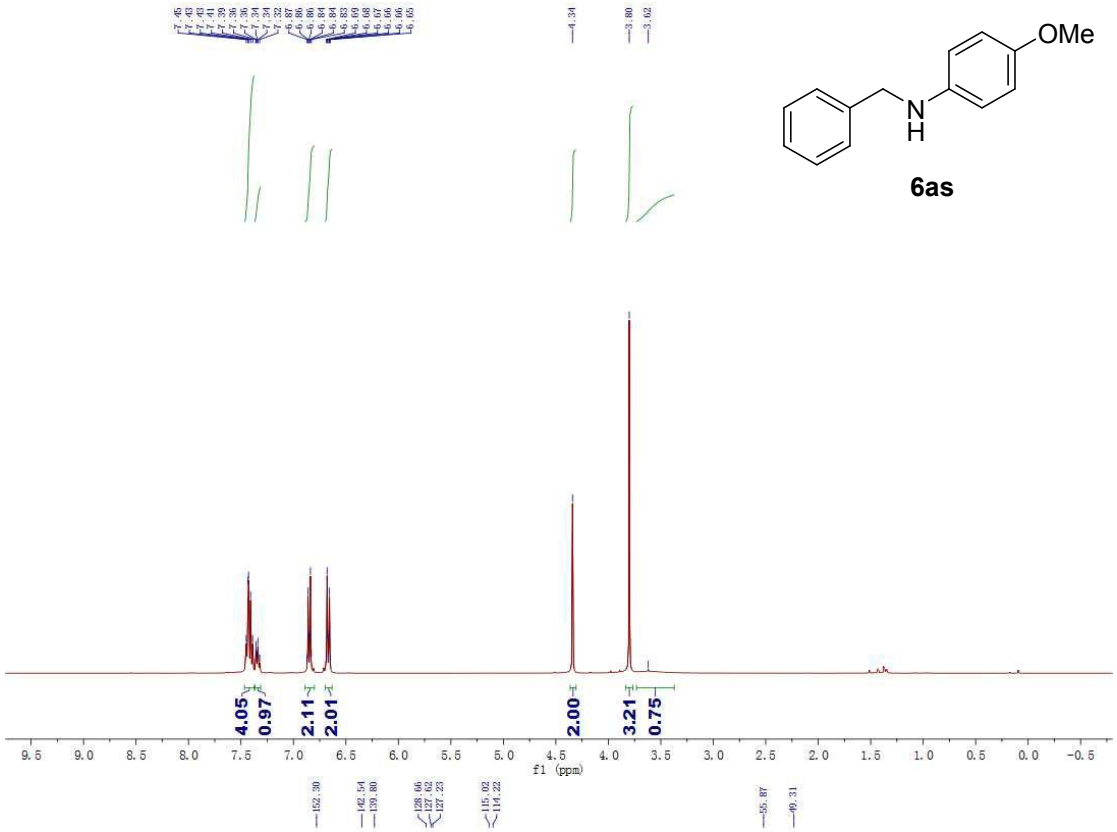
55.55
48.21
f1 (ppm)

N
H
OMe

6ar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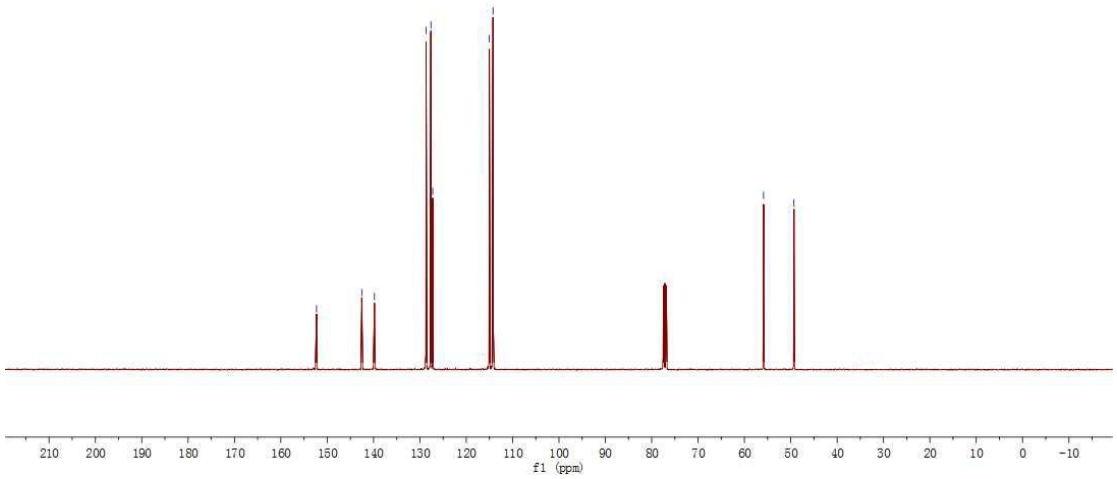
7.43
7.41
7.39
7.36
7.34
7.32
6.87
6.86
6.84
6.83
6.69
6.68
6.67
6.66
6.65
4.34
3.80
3.62
OMe
N
H
4.05
0.97
2.11
2.01
2.00
3.21
0.75
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

6as

152.30
142.54
139.80
128.66
127.62
127.23
115.02
114.22
55.87
49.31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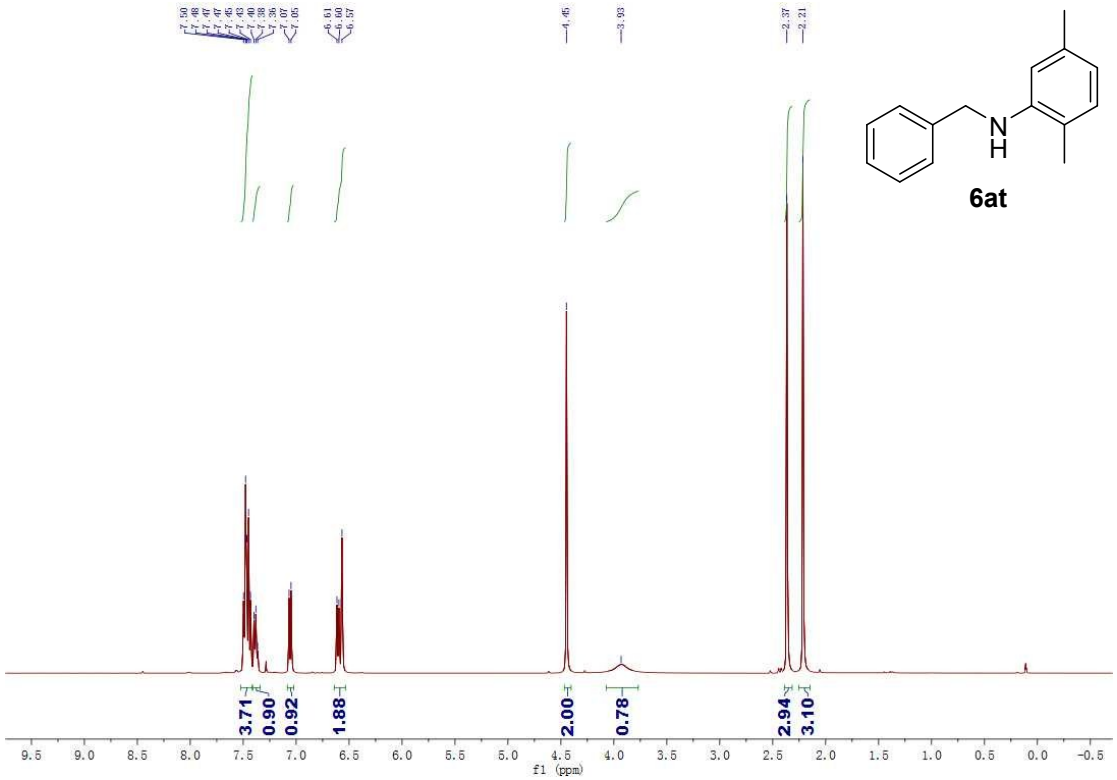
f1 (ppm)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7.38
7.36
7.07
7.05
6.61
6.60
6.57
4.45
3.93
2.37
2.21
3.71
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0.92
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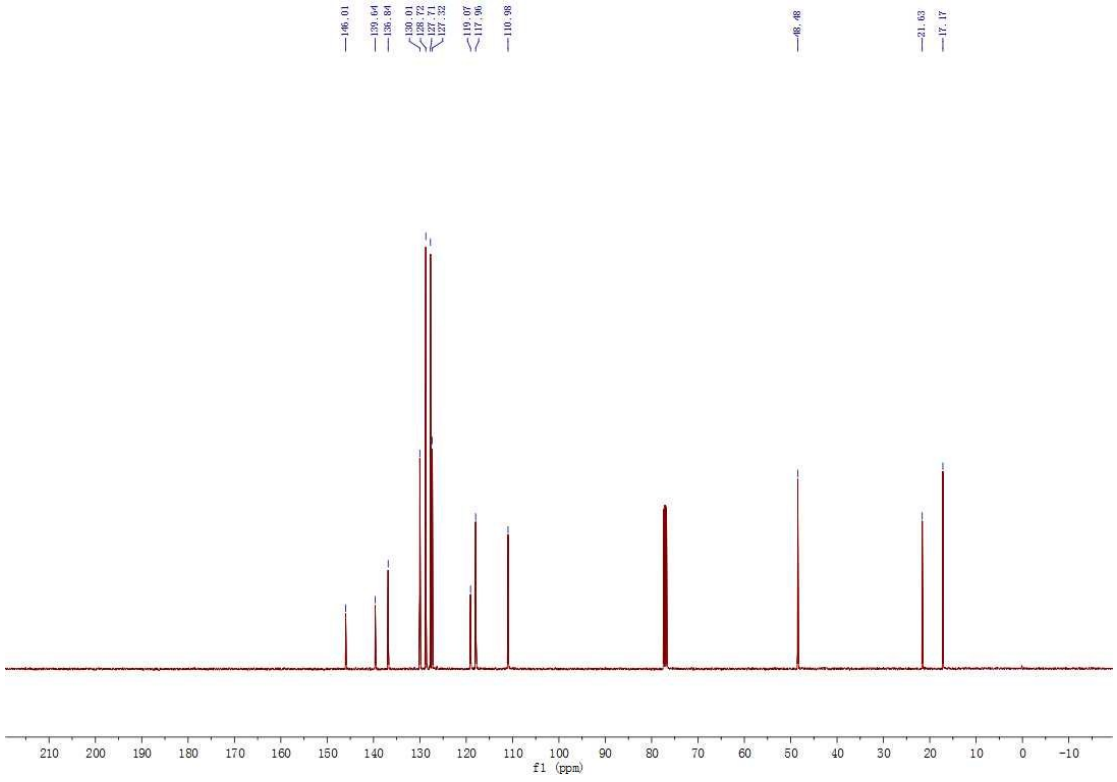
2.00
0.78
2.94
3.10
f1 (ppm)

N
H

6at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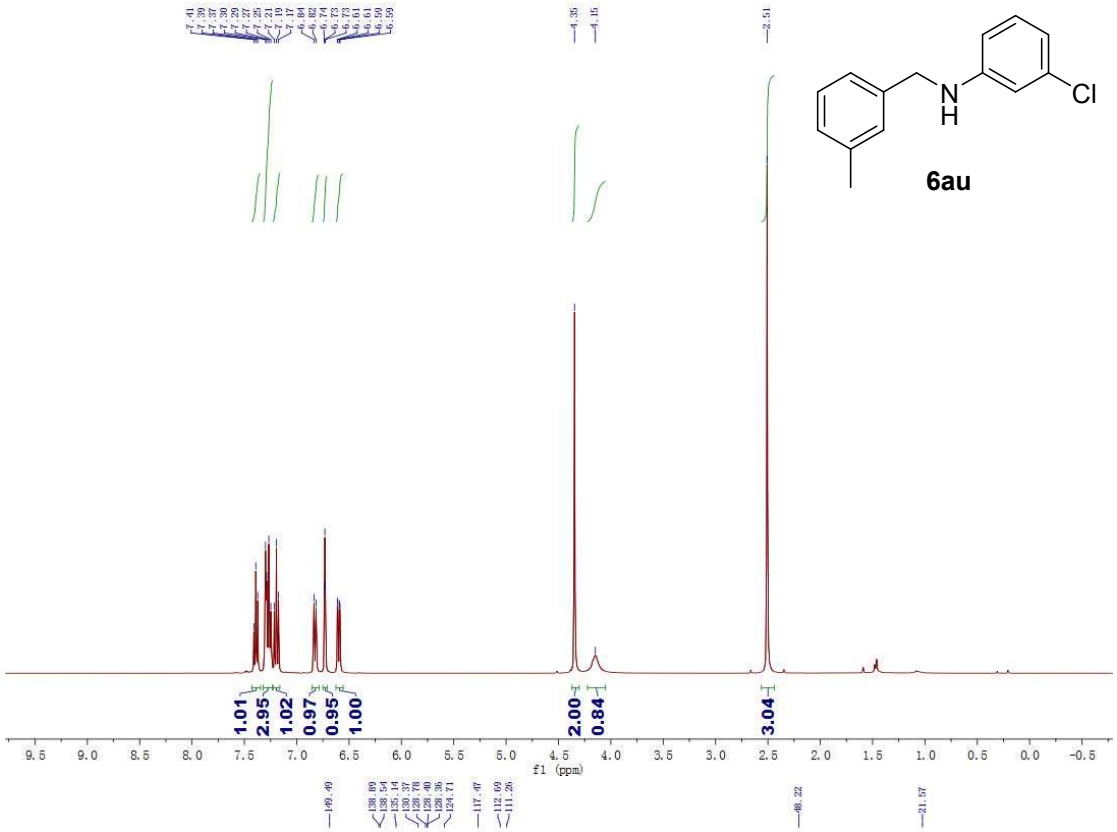
21.63
17.17
f1 (ppm)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7.17
6.84
6.82
6.74
6.73
6.61
6.61
6.59
6.59
4.35
4.15
2.51
N
H
Cl
6au
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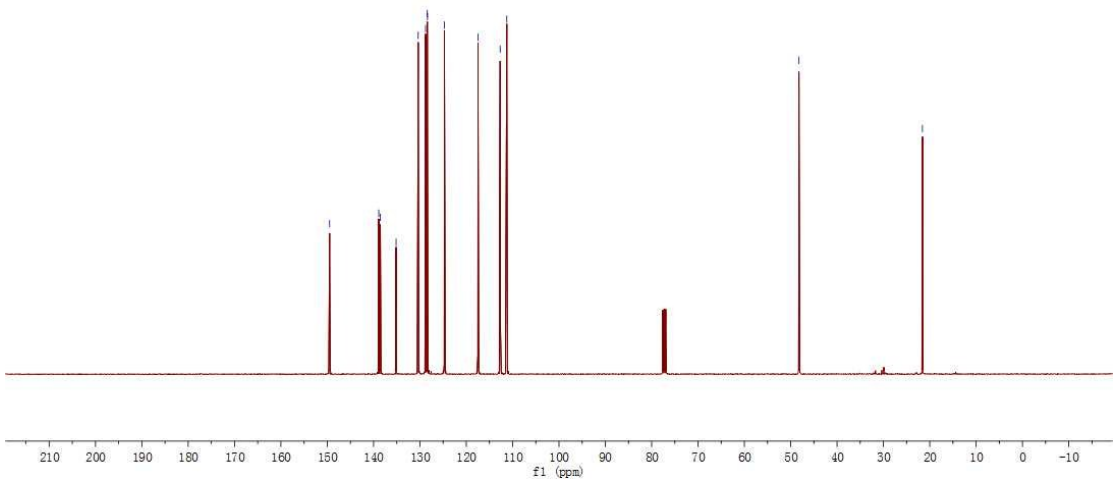
0.97
0.95
1.00
2.00
0.84
3.04
f1 (ppm)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111.26
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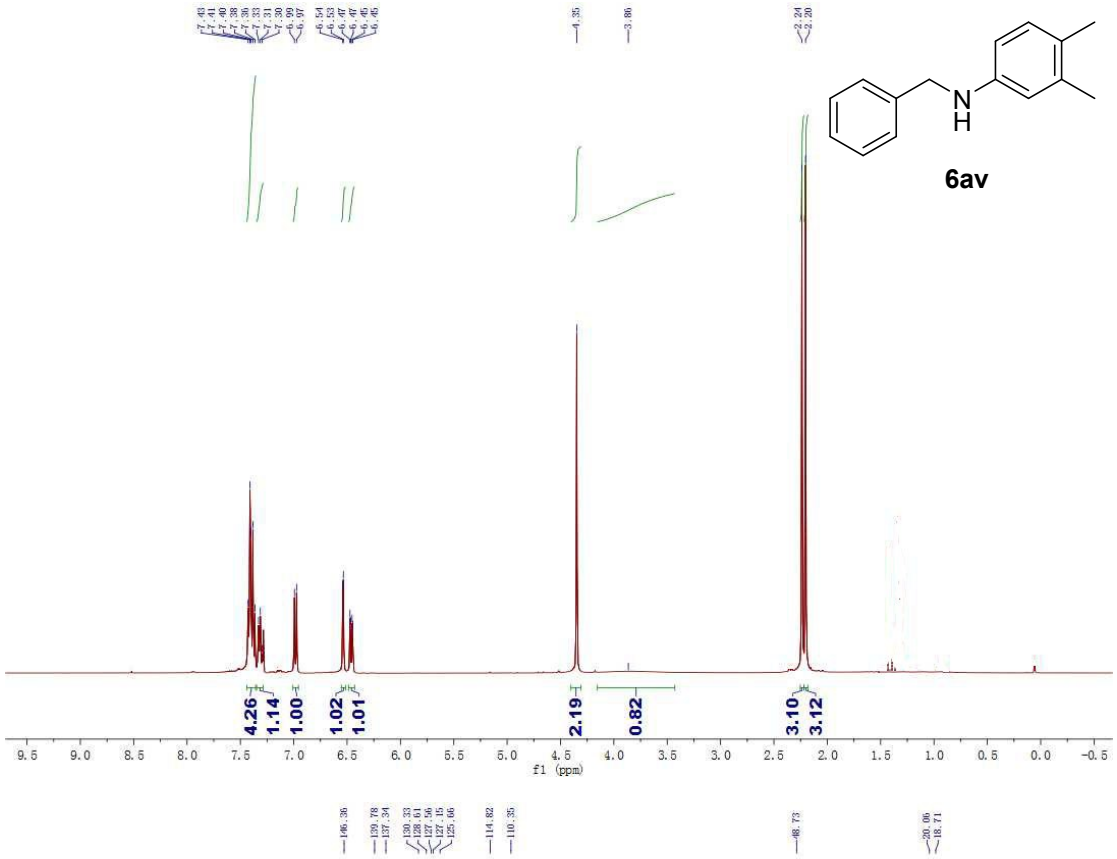
21.57
f1 (ppm)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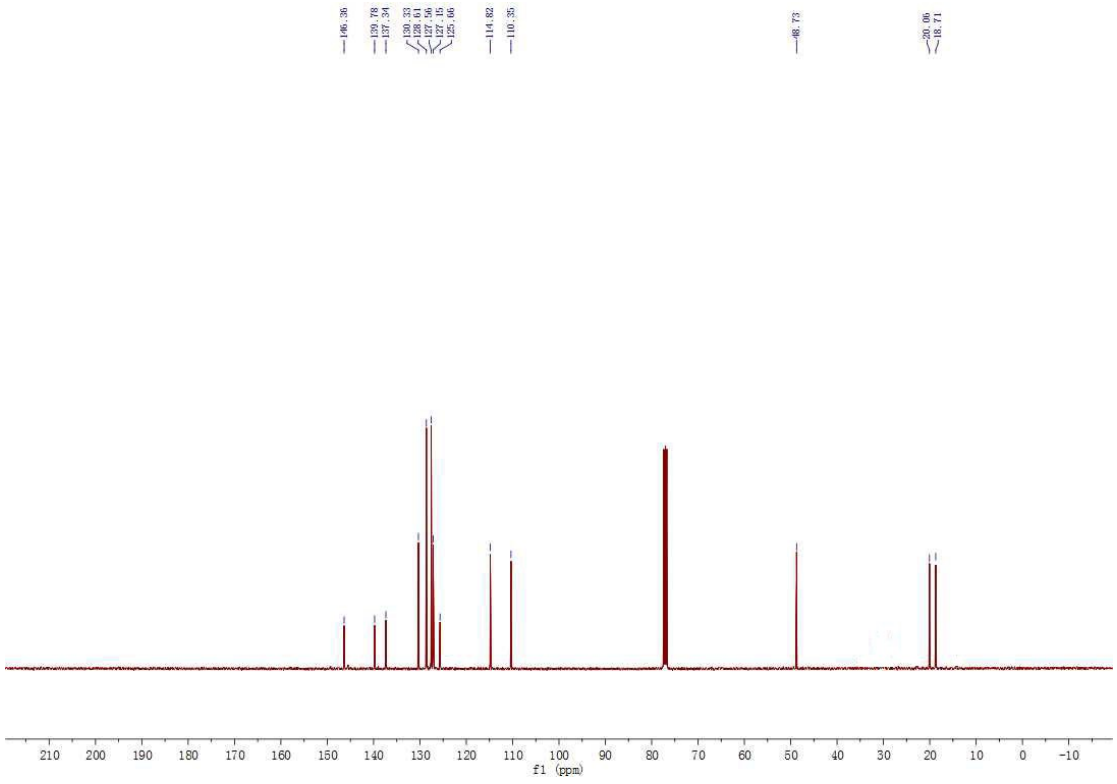
6.53
6.47
6.47
6.45
6.45
4.35
3.86
2.94
2.93
N
H
6av
4.26
1.14
1.00
1.02
1.01
2.19
0.82
3.10
3.12
f1 (ppm)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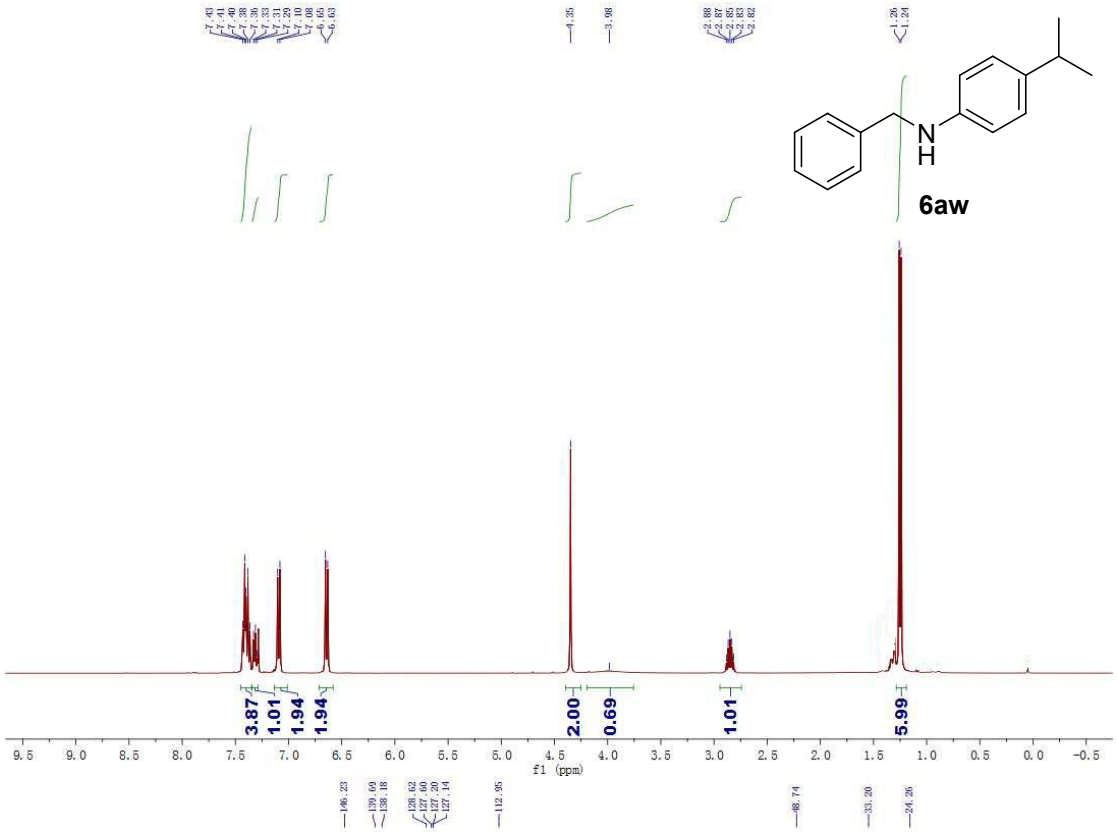
18.71
f1 (ppm)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6.63
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2.87
2.85
2.83
2.82
1.26
1.24
N
H
6aw
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1.01
1.94
1.94
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0.69
1.01
5.99
f1 (ppm)
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127.20
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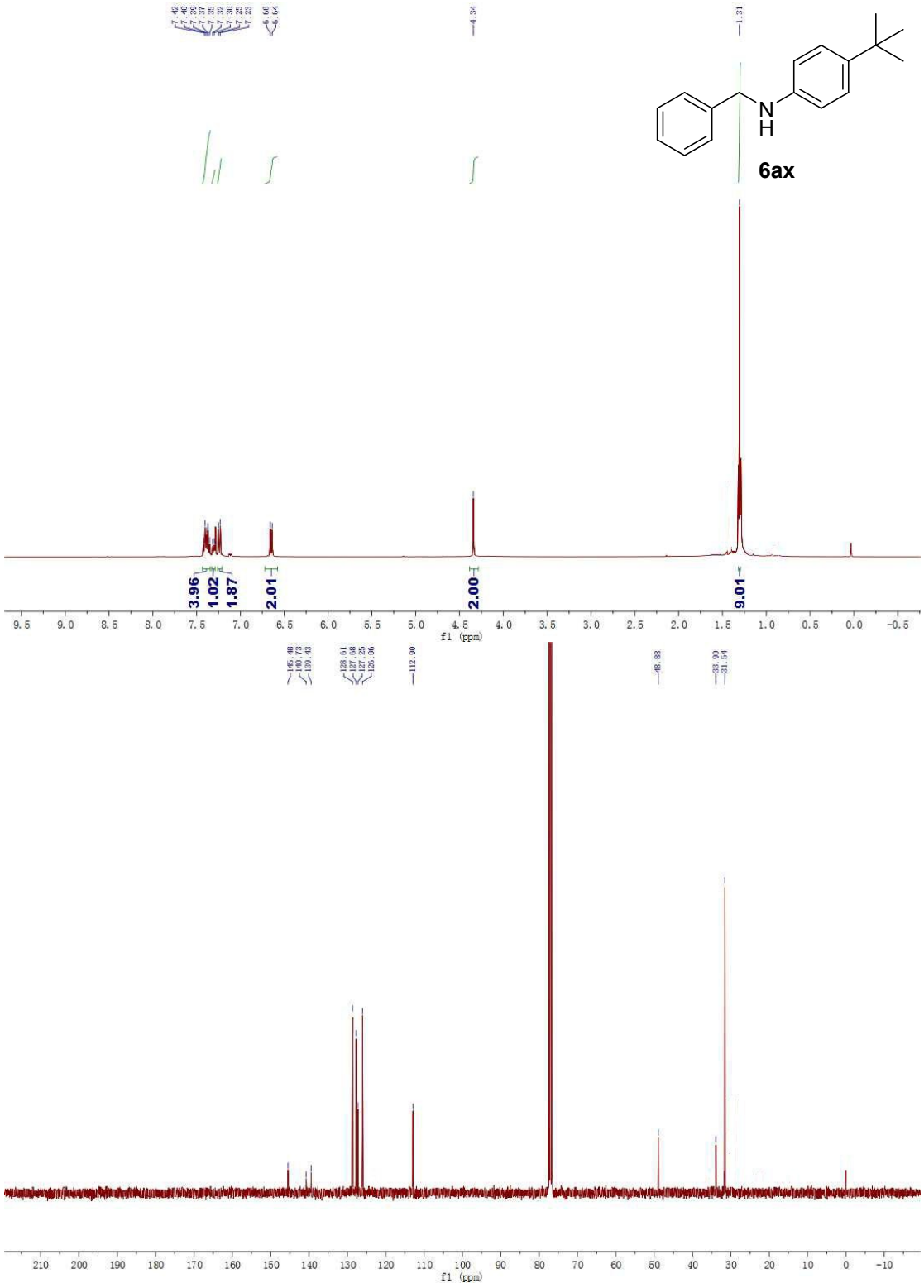
33.20
24.26
f1 (ppm)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6.64
4.34
1.31
N
H
6ax
3.96
1.02
1.87
2.01
2.00
9.01
f1 (ppm)
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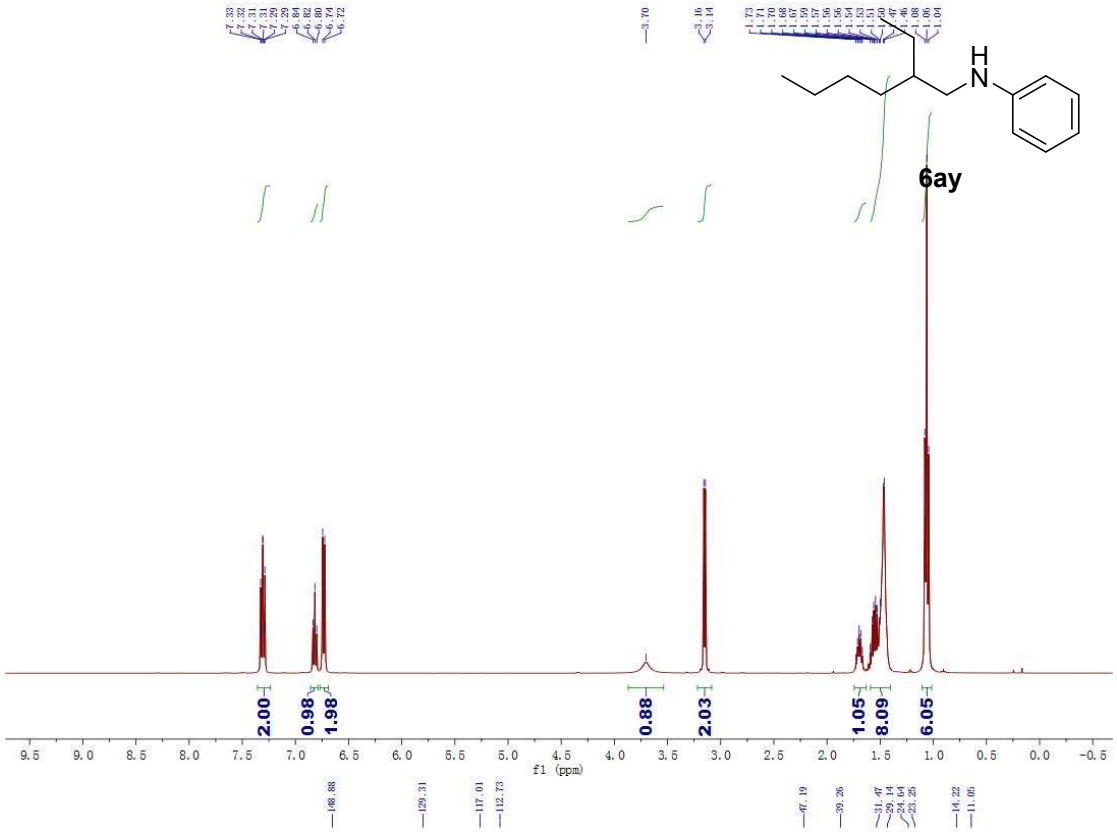
33.90
31.54
f1 (ppm)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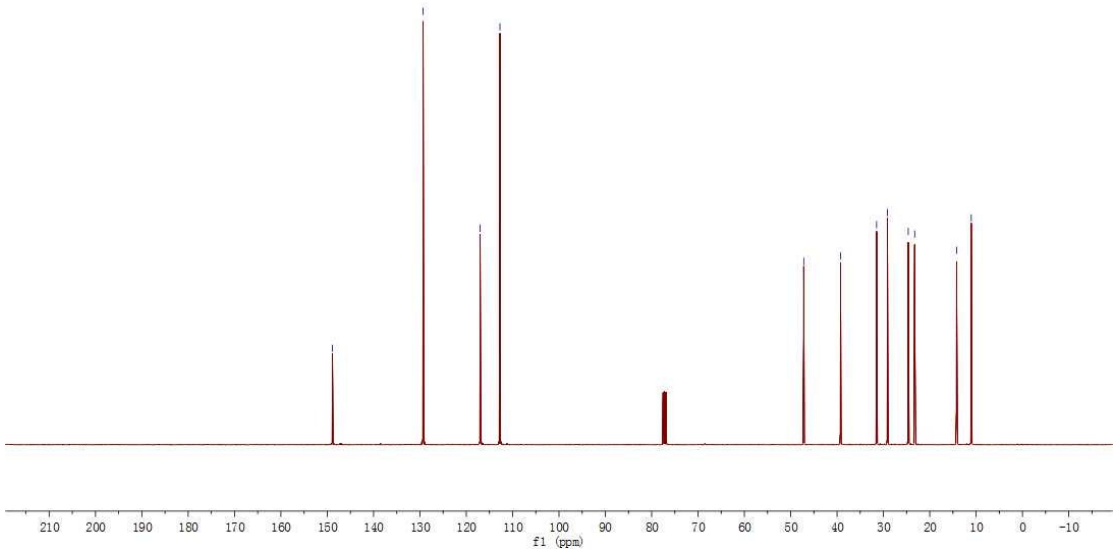
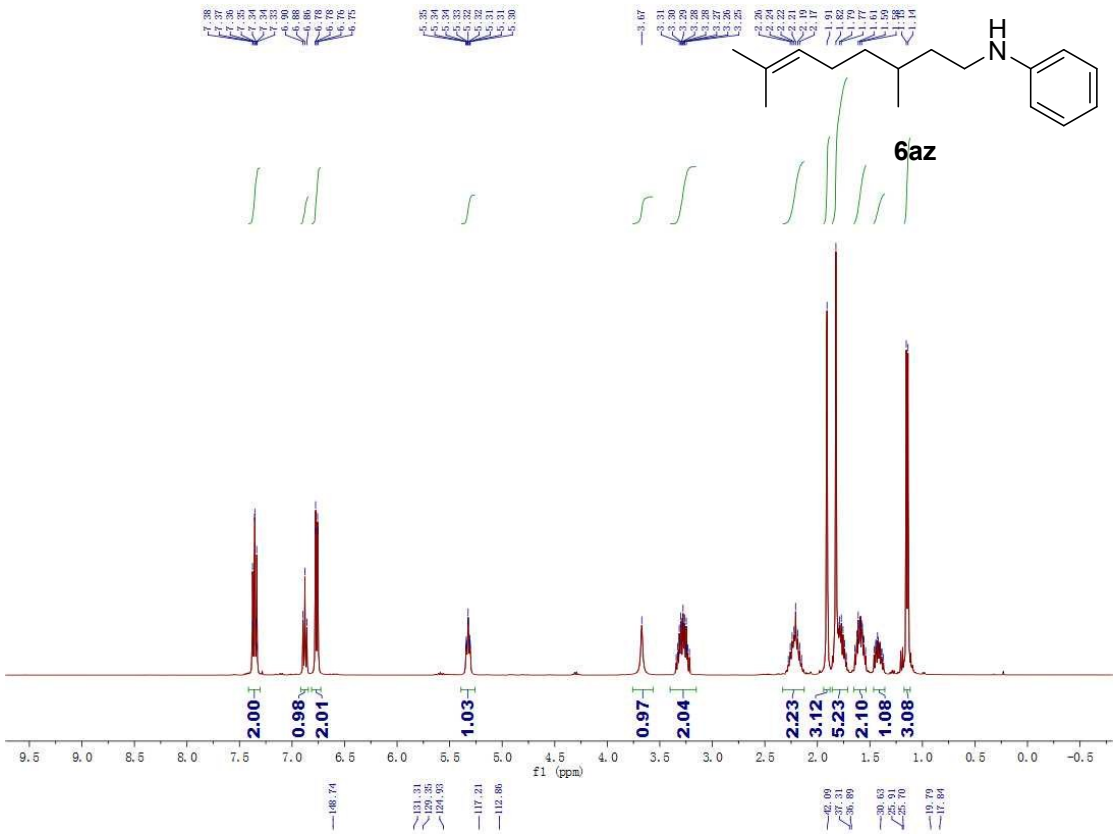
6.05
f1 (ppm)


f1 (ppm)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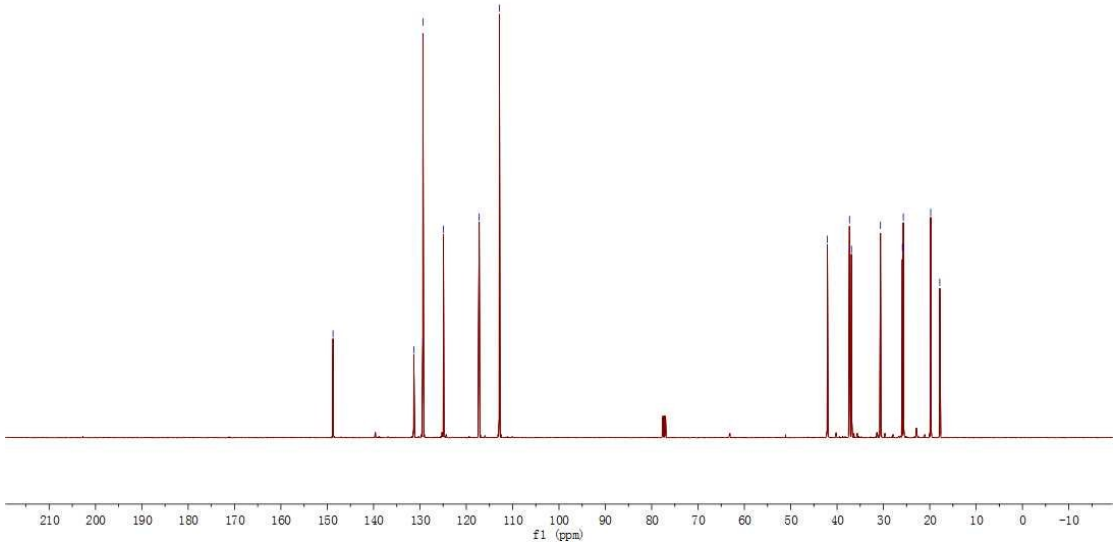
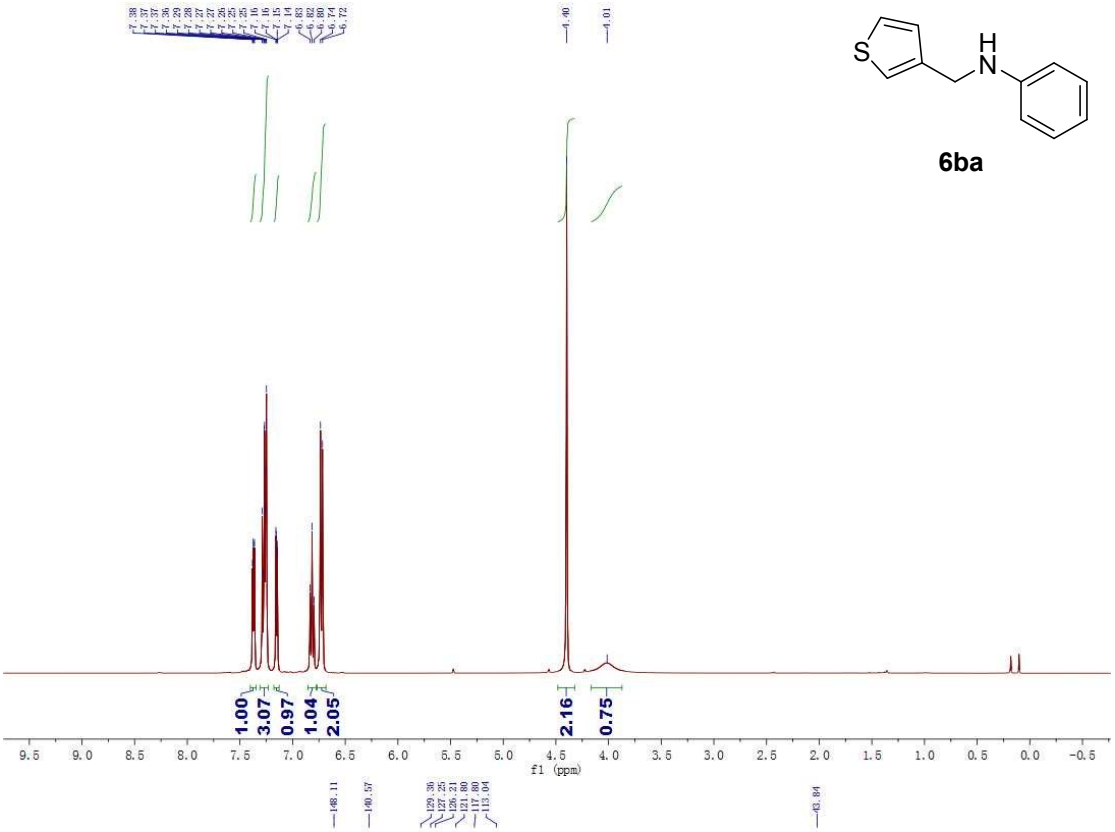
2.10
1.08
3.08
f1 (ppm)


f1 (ppm)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7.25
7.16
7.15
7.14
6.83
6.82
6.80
6.74
6.72
4.40
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1.00
3.07
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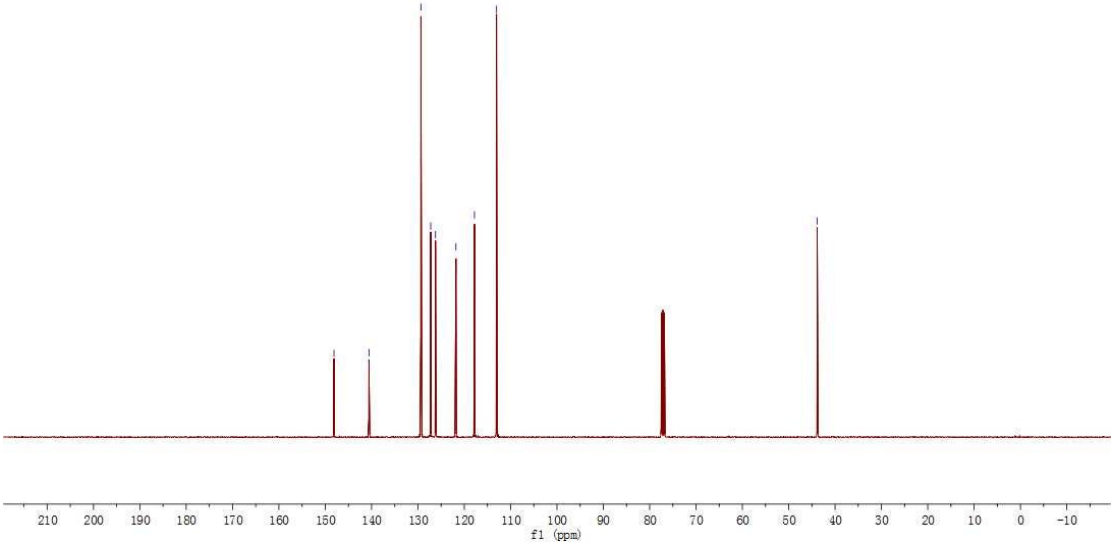
f1 (ppm)

6ba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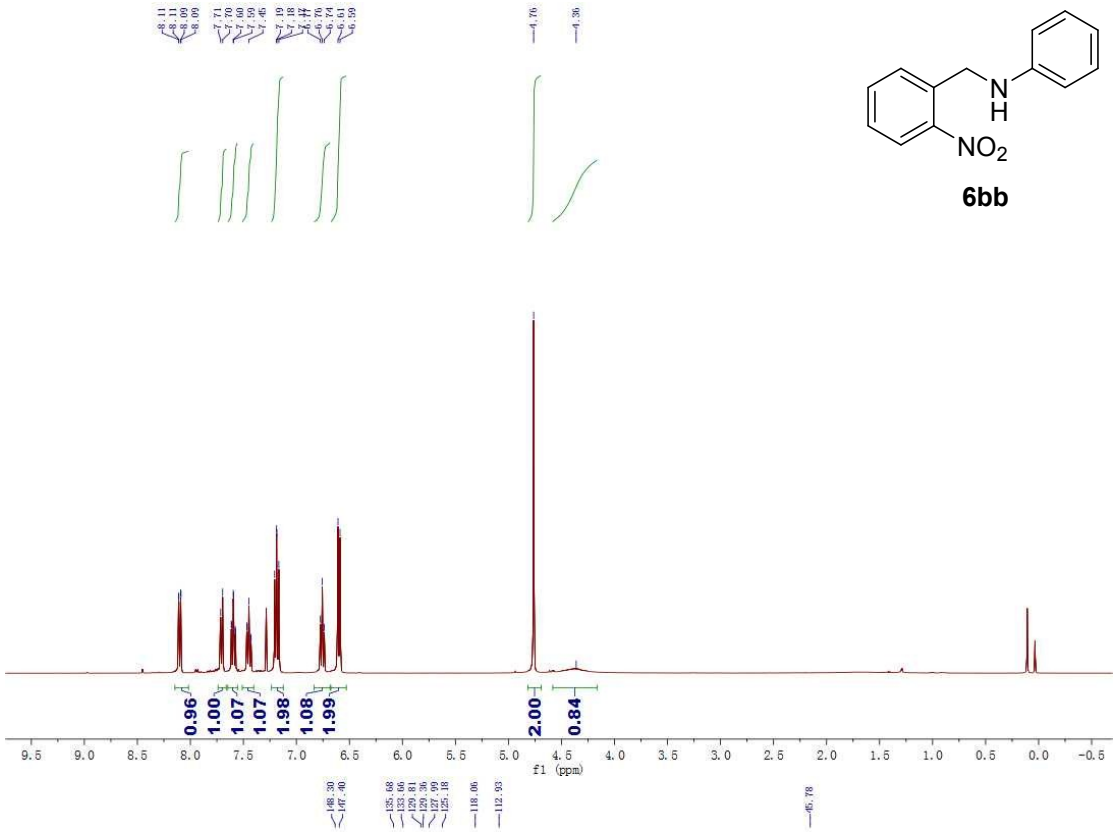
43.84
f1 (ppm)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8.11
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8.09
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7.69
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7.19
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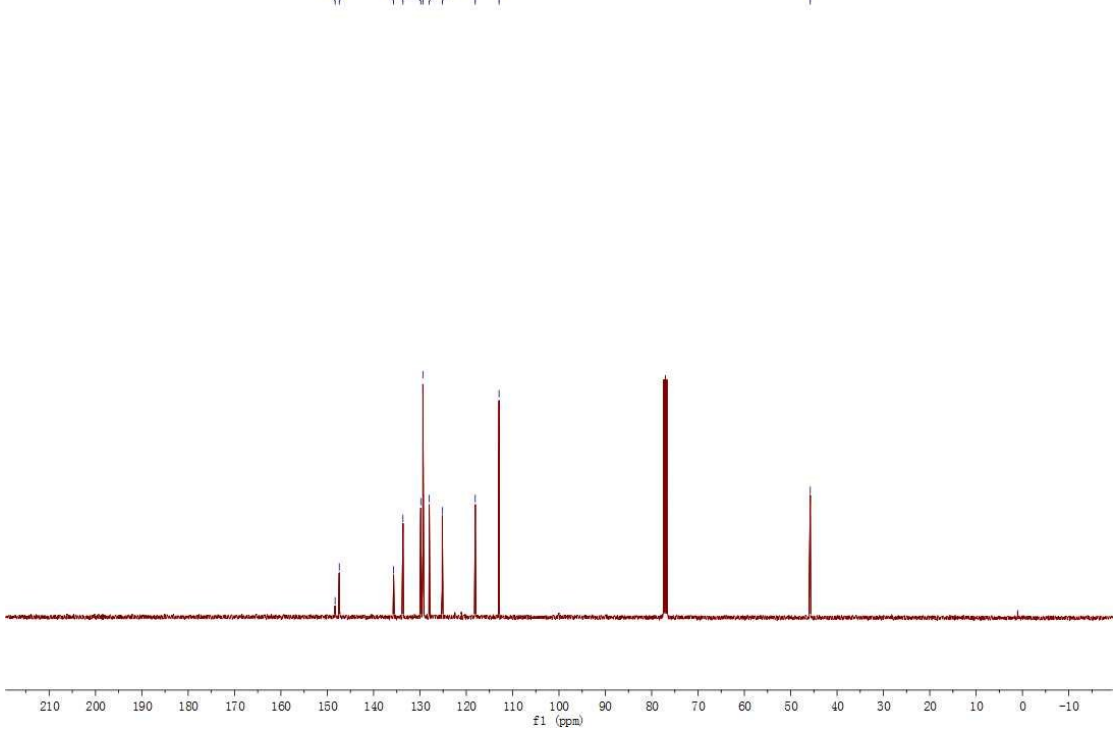
7.17
7.17
6.76
6.74
6.61
6.59
4.76
4.36
0.96
1.00
1.07
1.07
1.98
1.08
1.99
2.00
0.84
f1 (ppm)

N
H
NO2

6bb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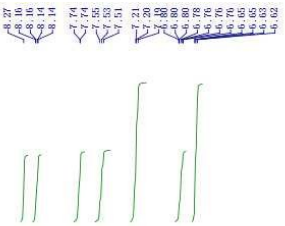
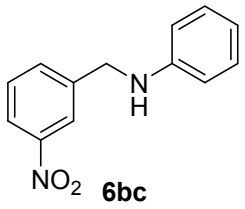
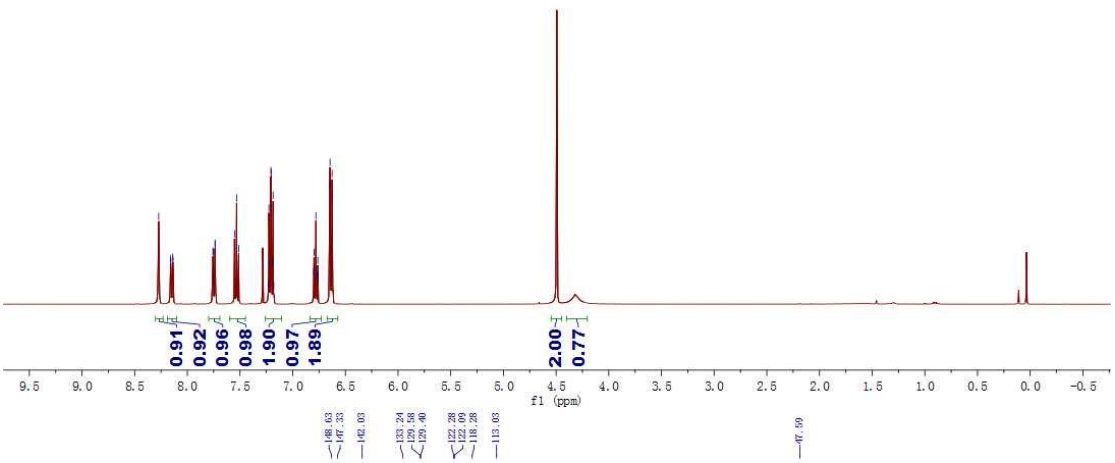
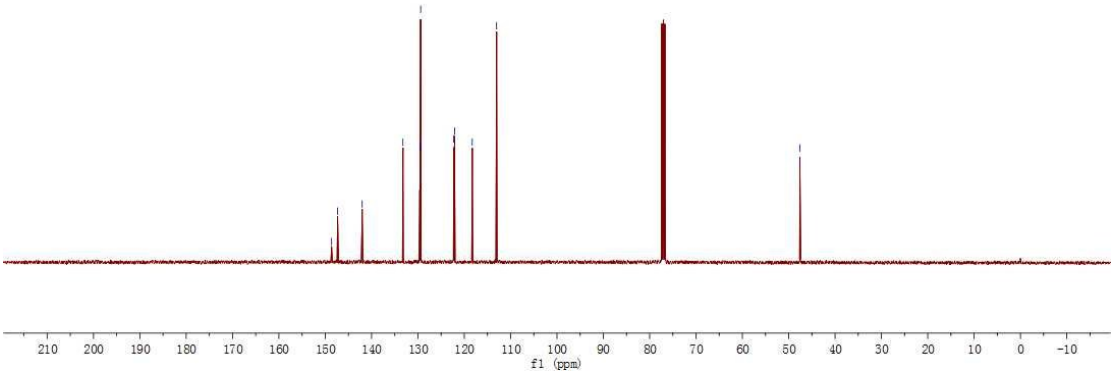
129.36
127.99
125.18
118.06
112.93
65.78
f1 (ppm)

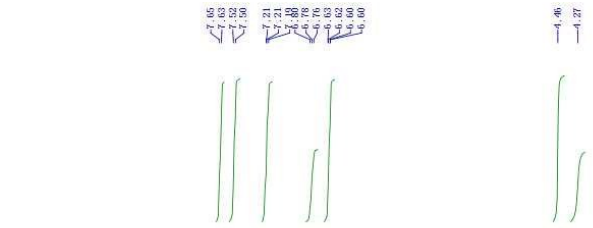


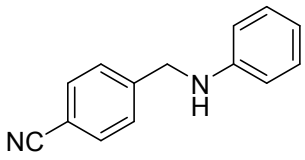


6bc

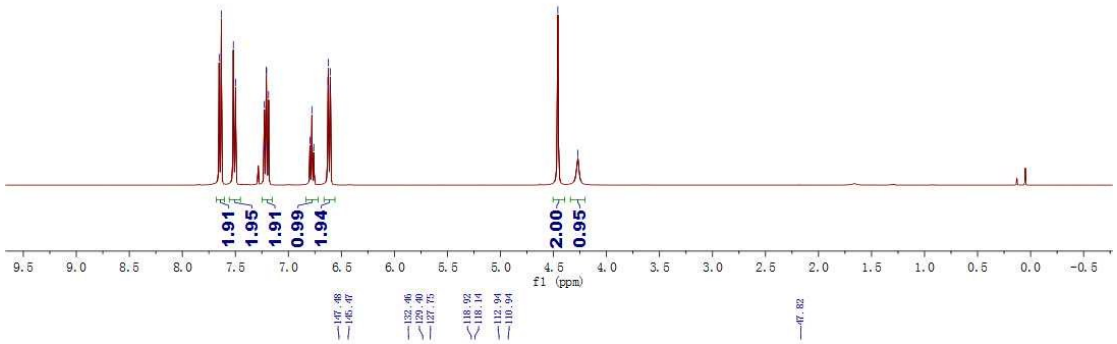


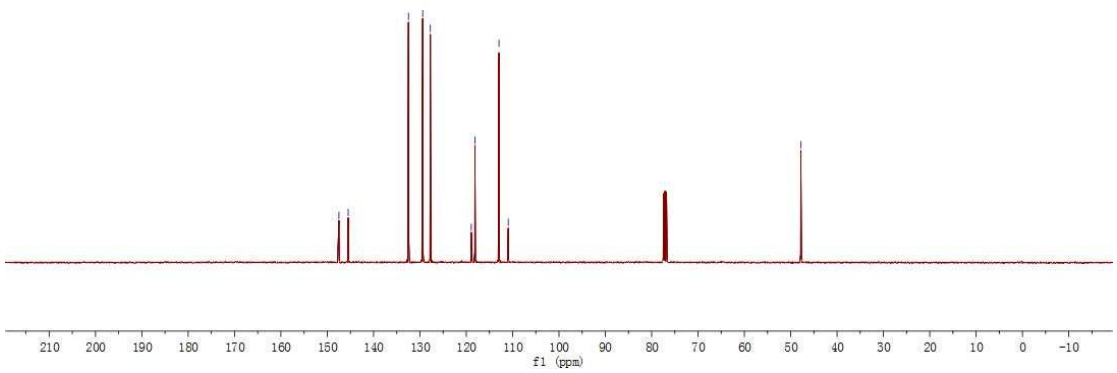


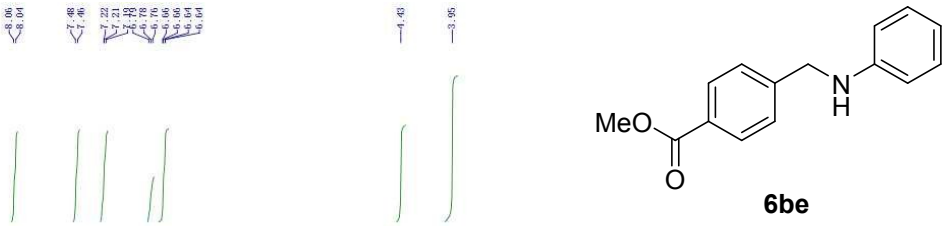




6bd



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8.04
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7.22
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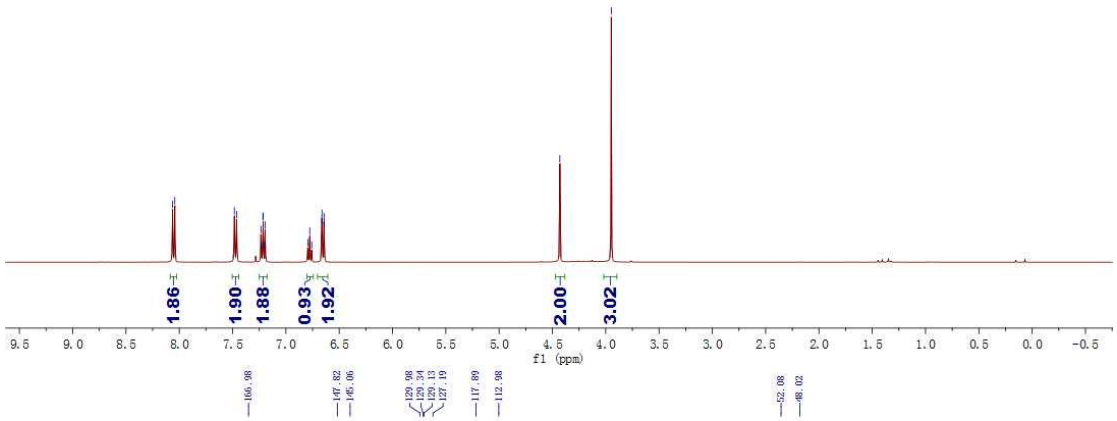
6.66
6.66
6.64
6.64
4.43
3.95
MeO
O
N
H

6be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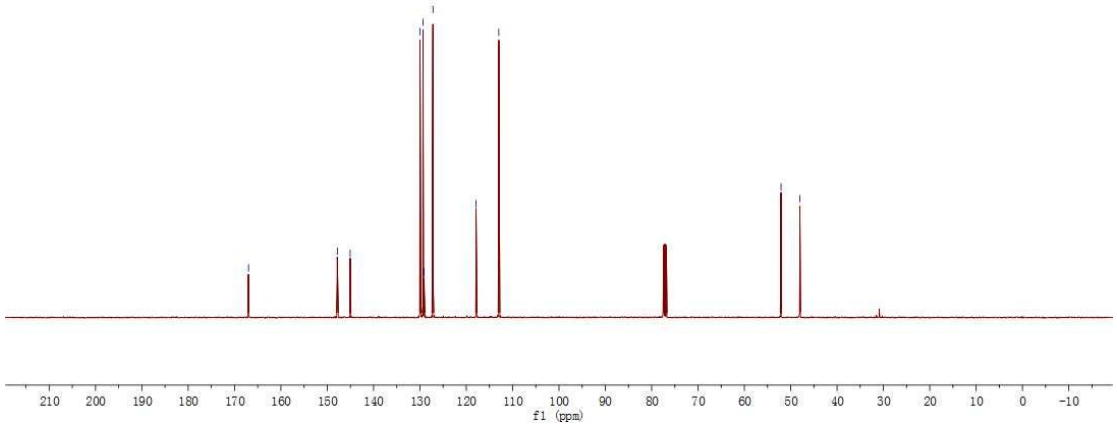
3.02
f1 (ppm)


166.98
147.82
145.66
129.98
129.34
129.15
127.19
117.89
112.98
52.08
46.02
f1 (ppm)

9. References

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[2] P. Colbon, J. Ruan, M. Purdie, K. Mulholland and J. Xiao, *Org. Lett*. 2011, **13**, 5456-5459.

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