Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Copper-catalyzed aerobic oxygenative cross dehydrogenative coupling of methyl ketones with *para*-C-H of primary anilines

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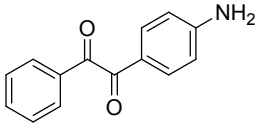
A. General information

Melting points were measured using a melting point instrument and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF254). All reagents were obtained from commercial suppliers and used without further purification.

B. General procedure for the coupling of methyl ketones and anilines

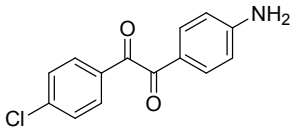
A 25 mL Schlenk tube was charged with CuI (0.015 mmol, 3 mg), methyl ketone **1** (0.3 mmol), and aniline derivative **2** (0.33 mmol) in DMSO (0.5 mL), and then boron fluoride etherate (0.06mmol, 8 μL) was added. The tube was equipped with an oxygen balloon, and the mixture was heated at 105 °C under magnetic stirring for 14 h. The reaction was then quenched with water, and the mixture was extracted with ethyl acetate (15 mL×3). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford the corresponding products **3**.

C. Characterization data of products



1-(4-aminophenyl)-2-phenylethane-1,2-dione (3aa)

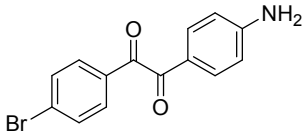
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 48.5 mg (72% yield) of the product as yellow solid. Mp 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 192.7, 153.1, 134.5, 133.4, 132.6, 129.8, 128.8, 122.9, 113.9. HRMS (ESI) for $C_{14}H_{11}NO_2$: $[M+Na]^+$ 248.0682, found 248.0681.



1-(4-aminophenyl)-2-(4-chlorophenyl)ethane-1,2-dione (3ba)

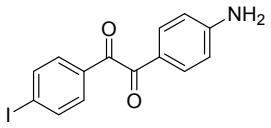
The titled compound was obtained through the general procedure with 1-(4-chlorophenyl)ethanone

(0.3 mmol, 46 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 50.5 mg (65% yield) of the product as yellow solid. Mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 191.9, 153.1, 141.1, 132.6, 131.8, 131.1, 129.2, 122.7, 113.9. HRMS (ESI) for $C_{14}H_{10}ClNO_2$: $[M+Na]^+$ 282.0292, found 282.0286.



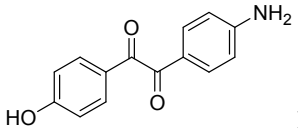
1-(4-aminophenyl)-2-(4-bromophenyl)ethane-1,2-dione (3ca)

The titled compound was obtained through the general procedure with 1-(4-bromophenyl)ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 42.0 mg (46% yield) of the product as yellow solid. Mp 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 191.9, 153.2, 132.6, 132.2, 132.1, 131.2, 130.0, 122.7, 113.9. HRMS (ESI) for $C_{14}H_{10}BrNO_2$: $[M+Na]^+$ 325.9787, found 325.9780.



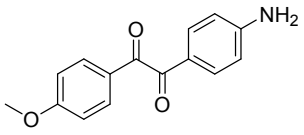
1-(4-aminophenyl)-2-(4-iodophenyl)ethane-1,2-dione (3da)

The titled compound was obtained through the general procedure with 1-(4-iodophenyl)ethanone (0.3 mmol, 74 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 70.3 mg (67% yield) of the product as yellow solid. Mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 191.9, 153.3, 138.1, 132.6, 130.9, 122.5, 113.9, 113.8, 103.1. HRMS (ESI) for $C_{14}H_{10}INO_2$: $[M+Na]^+$ 373.9648, found 373.9652.



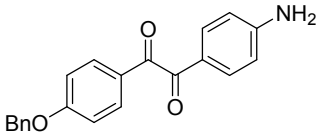
1-(4-aminophenyl)-2-(4-hydroxyphenyl)ethane-1,2-dione (3ea)

The titled compound was obtained through the general procedure with 1-(4-hydroxyphenyl)ethanone (0.3 mmol, 41 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=1/2, R_f = 0.25) afforded 33.3 mg (46% yield) of the product as yellow solid. Mp 172–174 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.73 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.51 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 194.4, 192.4, 163.5, 155.5, 132.1, 132.0, 124.7, 120.1, 115.9, 113.0. HRMS (ESI) for $C_{14}H_{11}NO_3$: $[M+Na]^+$ 264.0631, found 264.0633.



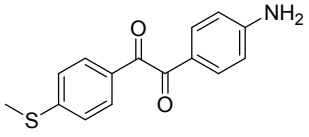
1-(4-aminophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (3fa)

The titled compound was obtained through the general procedure with 1-(4-methoxyphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.2) afforded 45.2 mg (59% yield) of the product as yellow solid. Mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.46 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 193.1, 164.6, 153.0, 132.5, 132.2, 126.5, 123.1, 114.1, 113.8, 55.5. HRMS (ESI) for $C_{15}H_{13}NO_3$: $[M+Na]^+$ 278.0788, found 278.0781.



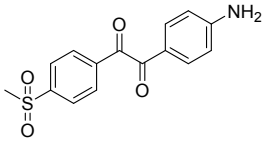
1-(4-aminophenyl)-2-(4-(benzyloxy)phenyl)ethane-1,2-dione (3ga)

The titled compound was obtained through the general procedure with 1-(4-benzyloxy phenyl)ethanone (0.3 mmol, 68 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 37.9 mg (38% yield) of the product as yellow solid. Mp 164–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.38 (dt, *J* = 12.8, 7.0 Hz, 5H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.13 (s, 2H), 4.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 193.0, 163.8, 152.8, 135.8, 132.6, 132.3, 128.7, 128.3, 127.4, 126.7, 123.3, 115.0, 113.9, 70.2. HRMS (ESI) for $C_{21}H_{17}NO_3$: $[M+Na]^+$ 354.1101, found 354.1097.



1-(4-aminophenyl)-2-(4-(methylthio)phenyl)ethane-1,2-dione (3ha)

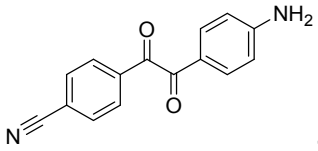
The titled compound was obtained through the general procedure with 1-(4-methylthio phenyl)ethanone (0.3 mmol, 50 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 49.5 mg (61% yield) of the product as yellow solid. Mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 4.47 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 192.7, 153.0, 148.2, 132.6, 130.1, 129.6, 124.9, 123.0, 113.8, 14.5. HRMS (ESI) for $C_{15}H_{13}NO_2S$: $[M+Na]^+$ 294.0559, found 294.0562.



1-(4-aminophenyl)-2-(4-(methylsulfonyl)phenyl)ethane-1,2-dione (3ia)

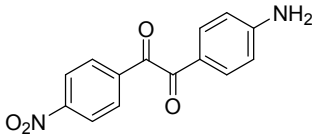
The titled compound was obtained through the general procedure with 1-(4-methylsulfonyl phenyl)ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 62.6 mg (69% yield) of the product as

yellow solid. Mp 156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.61 (s, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 190.9, 153.6, 145.0, 137.3, 132.7, 130.6, 127.8, 122.1, 113.9, 44.1. HRMS (ESI) for $C_{15}H_{13}NO_4S$: $[M+Na]^+$ 326.0457, found 326.0455.



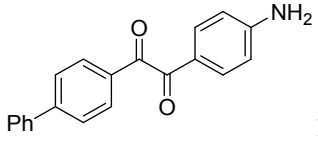
4-(2-(4-aminophenyl)-2-oxoacetyl)benzonitrile (3ja)

The titled compound was obtained through the general procedure with 4-acetylbenzonitrile (0.3 mmol, 44 mg), aniline (0.33 mmol, 31 mg). The reaction was performed for 4 h. The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.35) afforded 33.8 mg (45% yield) of the product as yellow solid. Mp 147–149 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.11 – 7.98 (m, 4H), 7.62 (d, *J* = 8.6 Hz, 2H), 6.78 – 6.58 (m, 4H). ^{13}C NMR (100 MHz, DMSO) δ 194.5, 190.3, 156.1, 136.0, 133.2, 132.5, 129.8, 119.2, 117.9, 116.5, 113.1. HRMS (ESI) for $C_{15}H_{10}N_2O_2$: $[M+Na]^+$ 273.0634, found 273.0633.



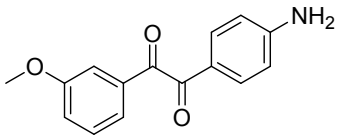
1-(4-aminophenyl)-2-(4-nitrophenyl)ethane-1,2-dione (3ka)

The titled compound was obtained through the general procedure with 1-(4-nitrophenyl)ethanone (0.3 mmol, 49 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 37.3 mg (46% yield) of the product as yellow solid. Mp 172–174 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 6.80 – 6.57 (m, 4H). ^{13}C NMR (100 MHz, DMSO) δ 194.2, 190.1, 156.1, 150.7, 137.4, 132.6, 130.7, 124.3, 119.1, 113.1. HRMS (ESI) for $C_{14}H_{10}N_2O_4$: $[M+Na]^+$ 293.0533, found 293.0538.



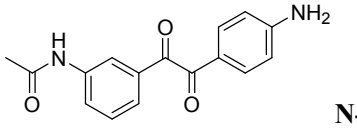
1-([1,1'-biphenyl]-4-yl)-2-(4-aminophenyl)ethane-1,2-dione (3la)

The titled compound was obtained through the general procedure with 1-([1,1'-biphenyl]-4-yl)ethanone (0.3 mmol, 59 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 45.0 mg (50% yield) of the product as yellow solid. Mp 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.45 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 192.7, 153.0, 147.1, 139.5, 132.6, 132.1, 130.4, 128.9, 128.5, 127.5, 127.3, 123.0, 113.9. HRMS (ESI) for $C_{20}H_{15}NO_2$: $[M+Na]^+$ 324.0995, found 324.0991.



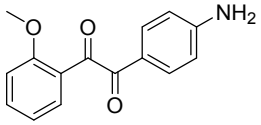
1-(4-aminophenyl)-2-(3-methoxyphenyl)ethane-1,2-dione (3ma)

The titled compound was obtained through the general procedure with 1-(3-methoxyl phenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 61.1 mg (80% yield) of the product as yellow solid. Mp 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.51 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 8.7 Hz, 2H), 4.53 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 192.6, 159.8, 153.2, 134.6, 132.5, 129.8, 123.0, 122.7, 121.3, 113.8, 112.9, 55.4. HRMS (ESI) for $C_{15}H_{13}NO_3$: $[M+Na]^+$ 278.0788, found 278.0792.



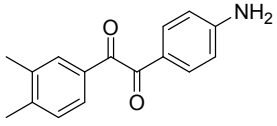
N-(3-(2-(4-aminophenyl)-2-oxoacetyl)phenyl)acetamide (3na)

The titled compound was obtained through the general procedure with *N*-(3-acetylphenyl) acetamide (0.3 mmol, 53 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=1/1, R_f = 0.2) afforded 43.2 mg (51% yield) of the product as yellow solid. Mp 176–178 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 8.14 (s, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.49 (m, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.61 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 195.9, 191.7, 168.7, 155.8, 140.0, 133.6, 132.2, 129.7, 124.9, 123.7, 119.7, 119.3, 113.1, 23.9. HRMS (ESI) for $C_{16}H_{14}N_2O_3$: $[M+Na]^+$ 305.0897, found 305.0897.



1-(4-aminophenyl)-2-(2-methoxyphenyl)ethane-1,2-dione (3oa)

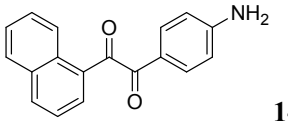
The titled compound was obtained through the general procedure with 1-(2-methoxyphenyl)ethanone (0.3 mmol, 45 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 45.1 mg (59% yield) of the product as yellow solid. Mp 141–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.30 (s, 2H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 192.2, 160.3, 152.0, 136.0, 131.9, 130.7, 124.2, 122.9, 121.3, 113.9, 112.4, 55.7. HRMS (ESI) for $C_{15}H_{13}NO_3$: $[M+Na]^+$ 278.0788, found 278.0795.



1-(4-aminophenyl)-2-(3,4-dimethylphenyl)ethane-1,2-dione (3pa)

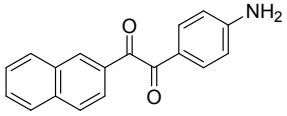
The titled compound was obtained through the general procedure with 1-(3,4-dimethylphenyl

phenyl)ethanone (0.3 mmol, 44 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 51.6 mg (68% yield) of the product as yellow solid. Mp 132–134 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.66 – 7.52 (m, 4H), 7.35 (d, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 8.6, 3.9 Hz, 2H), 6.56 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 195.8, 192.0, 155.6, 144.6, 137.5, 132.1, 131.0, 130.2, 129.8, 127.2, 119.8, 113.0, 19.8, 19.2. HRMS (ESI) for $C_{16}H_{15}NO_2$: $[M+Na]^+$ 276.0995, found 276.0996.



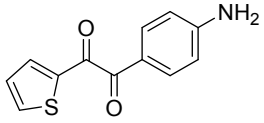
1-(4-aminophenyl)-2-(naphthalen-1-yl)ethane-1,2-dione (3qa)

The titled compound was obtained through the general procedure with 1-(naphthalen-1-yl)ethanone (0.3 mmol, 51 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 42.7 mg (52% yield) of the product as yellow solid. Mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.74 – 7067 (m, 1H), 7.62 – 7.57 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 192.9, 152.8, 135.5, 134.8, 134.0, 132.7, 130.9, 129.1, 128.7, 126.9, 125.9, 124.4, 123.3, 113.9. HRMS (ESI) for $C_{18}H_{13}NO_2$: $[M+Na]^+$ 298.0838, found 298.0837.



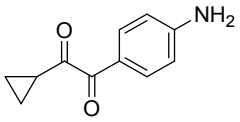
1-(4-aminophenyl)-2-(naphthalen-2-yl)ethane-1,2-dione (3ra)

The titled compound was obtained through the general procedure with 1-(naphthalen-2-yl)ethanone (0.3 mmol, 51 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 35.5 mg (43% yield) of the product as yellow solid. Mp 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 192.8, 153.1, 136.1, 133.3, 132.6, 132.3, 130.7, 129.8, 129.2, 128.9, 127.8, 126.9, 123.7, 122.9, 113.8. HRMS (ESI) for $C_{18}H_{13}NO_2$: $[M+Na]^+$ 298.0838, found 298.0842.



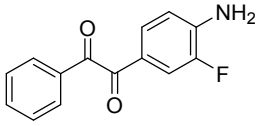
1-(4-aminophenyl)-2-(thiophen-2-yl)ethane-1,2-dione (3sa)

The titled compound was obtained through the general procedure with 1-(thiophen-2-yl)ethanone (0.3 mmol, 38 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 39.4 mg (57% yield) of the product as yellow solid. Mp 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.15 (t, *J* = 4.4 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 186.8, 153.0, 140.4, 136.4, 136.2, 133.0, 128.6, 122.6, 113.9. HRMS (ESI) for $C_{12}H_9NO_2S$: $[M+Na]^+$ 254.0246, found 254.0247.



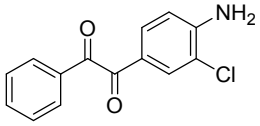
1-(4-aminophenyl)-2-cyclopropylethane-1,2-dione (3ta)

The titled compound was obtained through the general procedure with 1-cyclopropylethanone (0.3 mmol, 25 mg), aniline (0.33 mmol, 31 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.35) afforded 20.0 mg (35% yield) of the product as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 2H), 2.53 – 2.41 (m, 1H), 1.33 – 1.24 (m, 2H), 1.18 – 1.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 190.8, 152.6, 133.0, 122.2, 113.9, 18.8, 12.8. HRMS (ESI) for $C_{11}H_{11}NO_2$: $[M+Na]^+$ 212.0682, found 212.0679



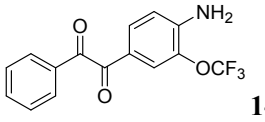
1-(4-amino-3-fluorophenyl)-2-phenylethane-1,2-dione (3ab)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-fluoroaniline (0.33 mmol, 37 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 56.8 mg (78% yield) of the product as yellow solid. Mp 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.48 (dd, *J* = 15.6, 7.8 Hz, 3H), 6.71 (t, *J* = 8.4 Hz, 1H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 192.1, 150.3, 141.9, 134.7, 133.1, 129.8, 128.9, 128.5, 122.9, 116.0, 115.1. HRMS (ESI) for $C_{14}H_{10}FNO_2$: $[M+Na]^+$ 266.0588, found 266.0580.



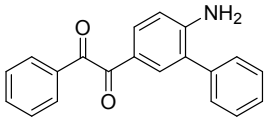
1-(4-amino-3-chlorophenyl)-2-phenylethane-1,2-dione (3ac)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-chloroaniline (0.33 mmol, 42 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 59.7 mg (77% yield) of the product as yellow solid. Mp 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 1H), 4.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 191.8, 149.1, 134.7, 133.0, 131.6, 130.5, 129.8, 128.9, 123.4, 118.5, 114.5. HRMS (ESI) for $C_{14}H_{10}ClNO_2$: $[M+Na]^+$ 282.0292, found 282.0289.



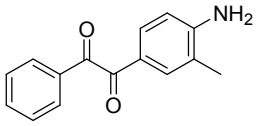
1-(4-amino-3-(trifluoromethoxy)phenyl)-2-phenylethane-1,2-dione (3ad)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-(trifluoromethoxy)aniline (0.33 mmol, 58 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 69.4 mg (75% yield) of the product as yellow solid. Mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.83 (s, 1H), 7.64 – 7.57 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 4.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 191.8, 145.8, 135.3, 134.8, 133.0, 130.9, 129.8, 128.9, 122.8, 120.7, 115.6, 115.3. HRMS (ESI) for $C_{15}H_{10}F_3NO_3$: $[M+Na]^+$ 332.0505, found 332.0511.



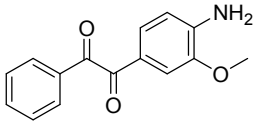
1-(6-amino-[1,1'-biphenyl]-3-yl)-2-phenylethane-1,2-dione (3ae)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), [1,1'-biphenyl]-2-amine (0.33 mmol, 56 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.35) afforded 40.7 mg (45% yield) of the product as yellow solid. Mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.83 – 7.72 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.36 (m, 7H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 192.8, 150.2, 137.5, 134.5, 133.4, 133.1, 131.5, 129.9, 129.1, 128.9, 128.8, 127.9, 126.7, 123.4, 114.6. HRMS (ESI) for $C_{20}H_{15}NO_2$: $[M+Na]^+$ 324.0995, found 324.0989.



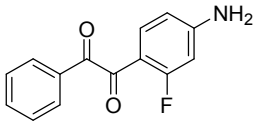
1-(4-amino-3-methylphenyl)-2-phenylethane-1,2-dione (3af)

The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), o-toluidine (0.33 mmol, 35 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 51.5 mg (72% yield) of the product as yellow solid. Mp 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.68 (s, 1H), 7.67 – 7.56 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 1H), 4.35 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 193.0, 151.4, 134.4, 133.5, 132.8, 130.6, 129.8, 128.8, 123.1, 121.3, 113.7, 17.0. HRMS (ESI) for $C_{15}H_{13}NO_2$: $[M+Na]^+$ 262.0838, found 262.0839.



1-(4-amino-3-methoxyphenyl)-2-phenylethane-1,2-dione (3ag)

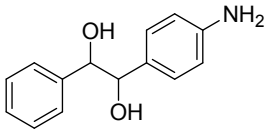
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 2-methoxyaniline (0.33 mmol, 41 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.25) afforded 38.4 mg (50% yield) of the product as yellow solid. Mp 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.32 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 4.34 (d, *J* = 167.0 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 192.9, 146.6, 143.8, 134.4, 133.6, 129.9, 128.8, 127.3, 123.2, 112.5, 109.4, 55.7. HRMS (ESI) for $C_{15}H_{13}NO_3$: $[M+Na]^+$ 278.0788, found 278.0793.



1-(4-amino-2-fluorophenyl)-2-phenylethane-1,2-dione (3ah)

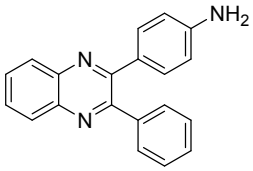
The titled compound was obtained through the general procedure with acetophenone (0.3 mmol, 36 mg), 3-fluoroaniline (0.33 mmol, 37 mg). The column chromatography on silica gel (petroleum ether/EtOAc=2/1, R_f = 0.3) afforded 43.7 mg (60% yield) of the product as yellow solid. Mp 117–

119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.86 – 7.76 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.45 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.18 (dd, *J* = 13.0, 2.1 Hz, 1H), 4.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 190.5, 165.3, 155.4, 134.3, 132.5, 132.4, 129.6, 128.8, 111.7, 111.0, 100.1. HRMS (ESI) for $C_{14}H_{10}FNO_2$: $[M+Na]^+$ 266.0588, found 266.0587.



1-(4-aminophenyl)-2-phenylethane-1,2-diol (7)

Reaction conditions: **3aa** (0.2 mmol), $NaBH_4$ (2 equiv), H_2O (2 equiv), THF (0.2 M), reflux, 0.5 h. The column chromatography on silica gel (petroleum ether/EtOAc=1/1, R_f = 0.3) afforded 38.8 mg (85% yield) of the product as light yellow solid (dr = 10:1, determined by NMR). Mp 192–194 °C. ^{1}H NMR of the main isomer (400 MHz, d_6-DMSO) δ 7.25–7.10 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 4.8 Hz, 1H), 4.85 (d, *J* = 4.8 Hz, 1H), 4.85 (br, 2H), 4.93 (t, *J* = 4.8 Hz, 1H) 4.39, (t, *J* = 4.8 Hz, 1H); ^{13}C NMR of the main isomer (100 MHz, d_6-DMSO) δ 147.2, 143.6, 130.4, 128.0, 127.4, 127.1, 126.4, 113.0, 77.2, 76.9. HRMS (ESI) for $C_{14}H_{15}NO_2$: $[M+H]^+$ 230.1176, found 230.1178.

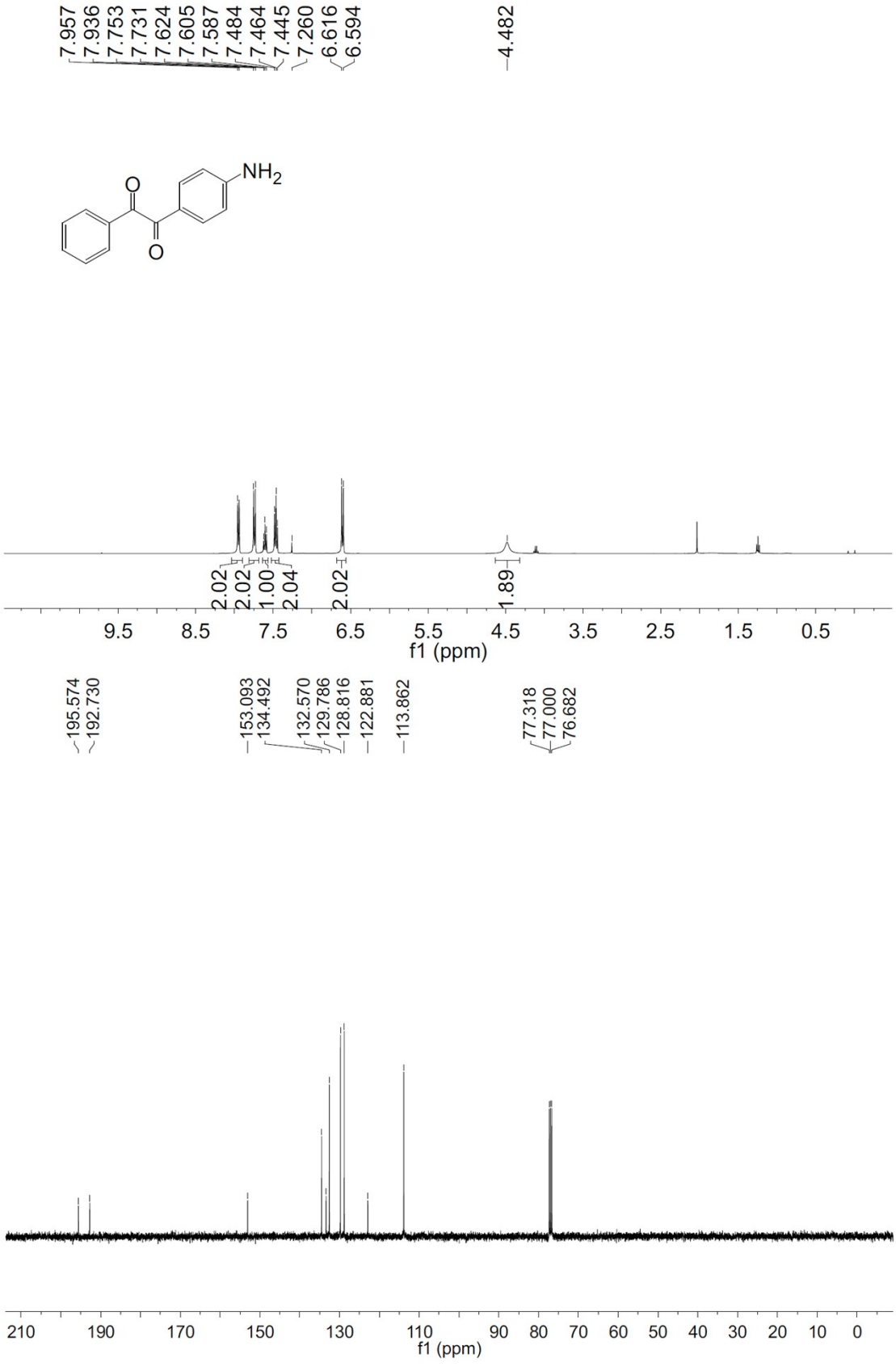


4-(3-phenylquinoxalin-2-yl)aniline (8)

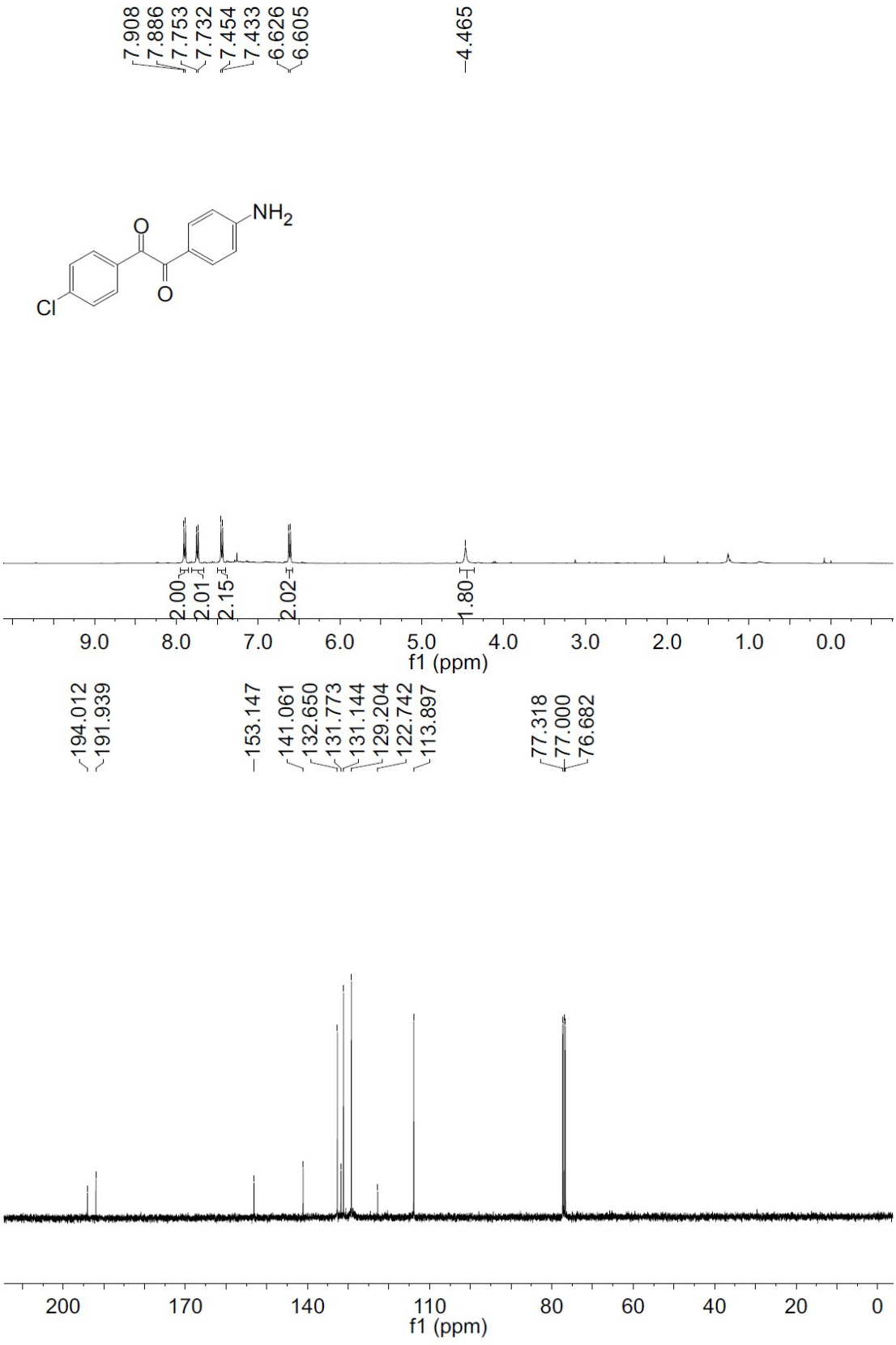
Reaction conditions: **3aa** (0.2 mmol), benzene-1,2-diamine (1.2 equiv), $FeCl_3$ (2 equiv), EtOH (0.2 M), 65 °C, 12 h. The column chromatography on silica gel (petroleum ether/EtOAc=3/1, R_f = 0.5) afforded 44.0 mg (74% yield) of the product as yellow solid. Mp 215–217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.12 (m, 2H), 7.76–7.69 (m, 2H), 7.58–7.55 (m, 2H), 7.37–7.34 (m, 5H), 6.60 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 153.3, 147.2, 141.3, 140.7, 139.6, 131.3, 129.7, 129.6, 129.2, 129.0, 128.9, 128.8, 128.6, 128.2, 114.5. HRMS (ESI) for $C_{20}H_{15}N_3$: $[M+H]^+$ 298.1339, found 298.1344.

D. ^{1}H NMR and ^{13}C NMR spectra of all products

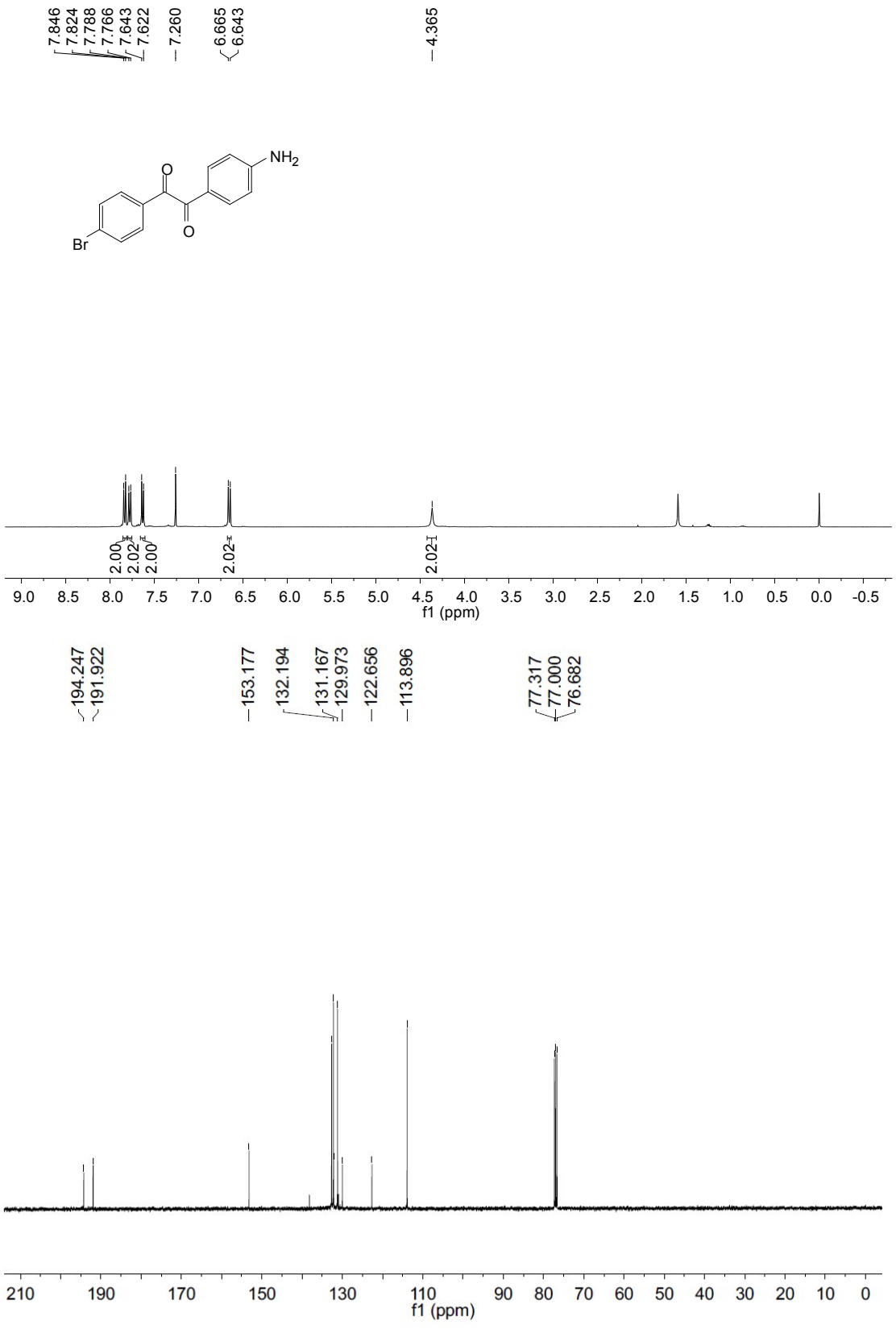
^{1}H NMR and ^{13}C NMR spectra of 3aa



^{1}H NMR and ^{13}C NMR spectra of 3ba



^{1}H NMR and ^{13}C NMR spectra of 3ca



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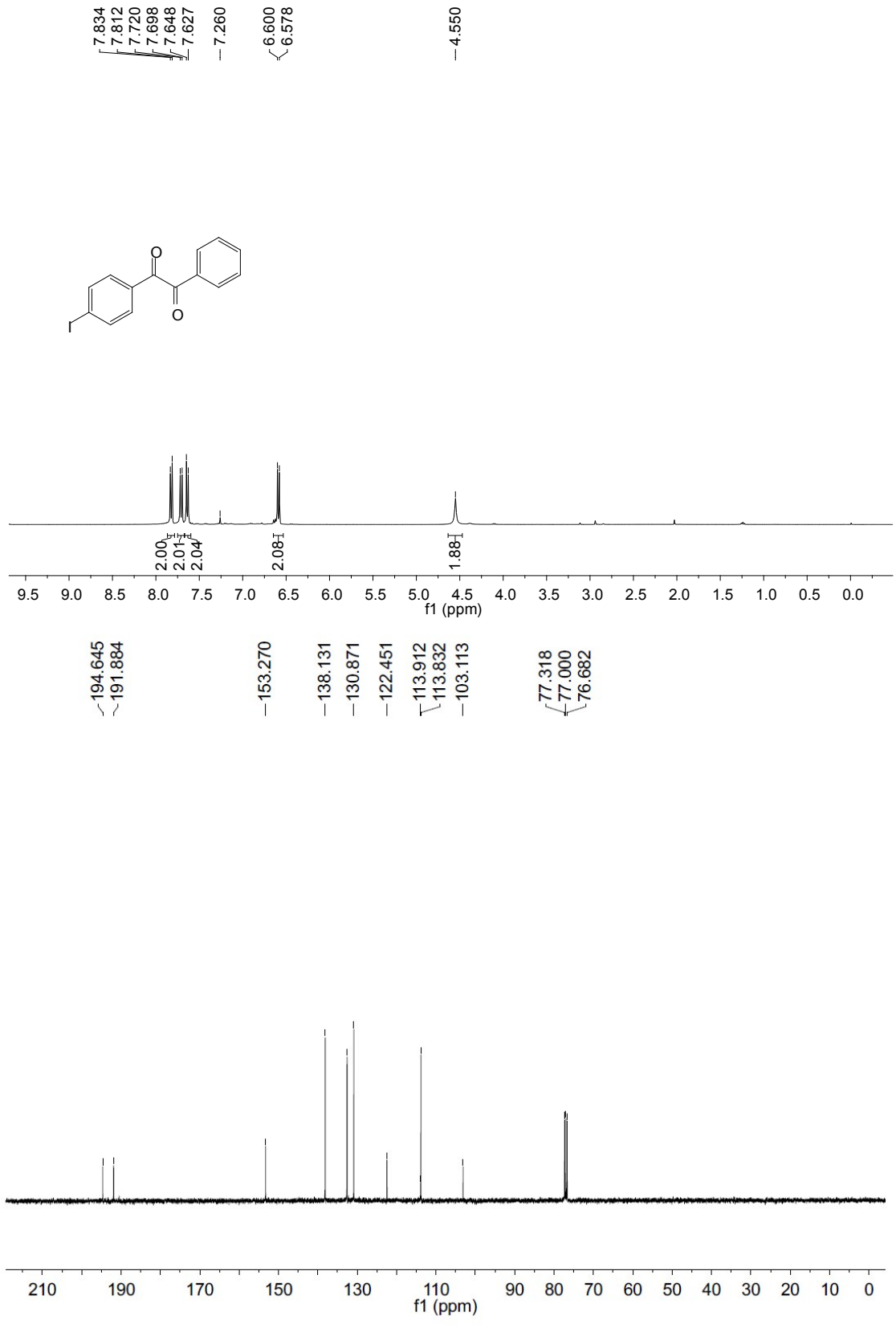

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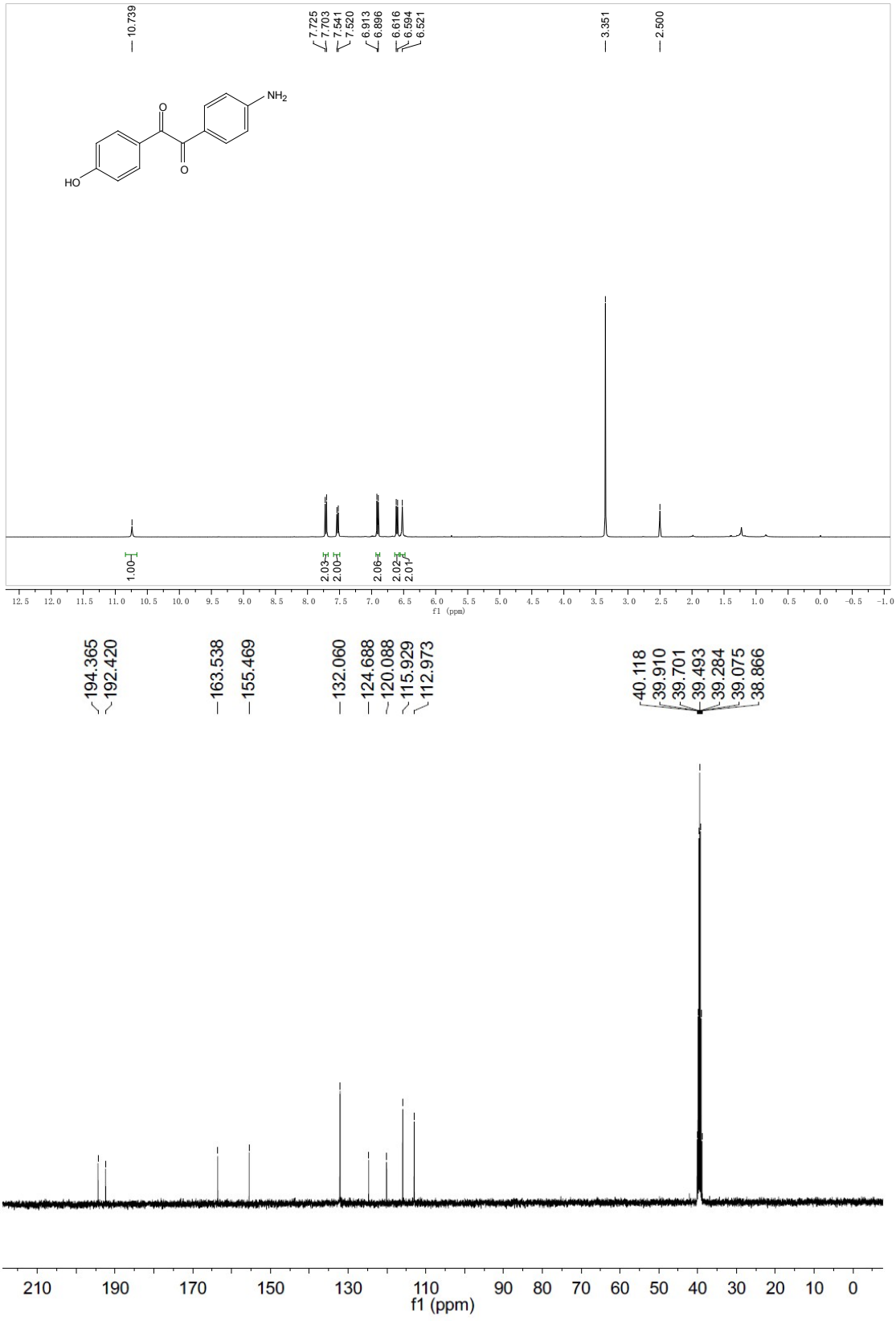
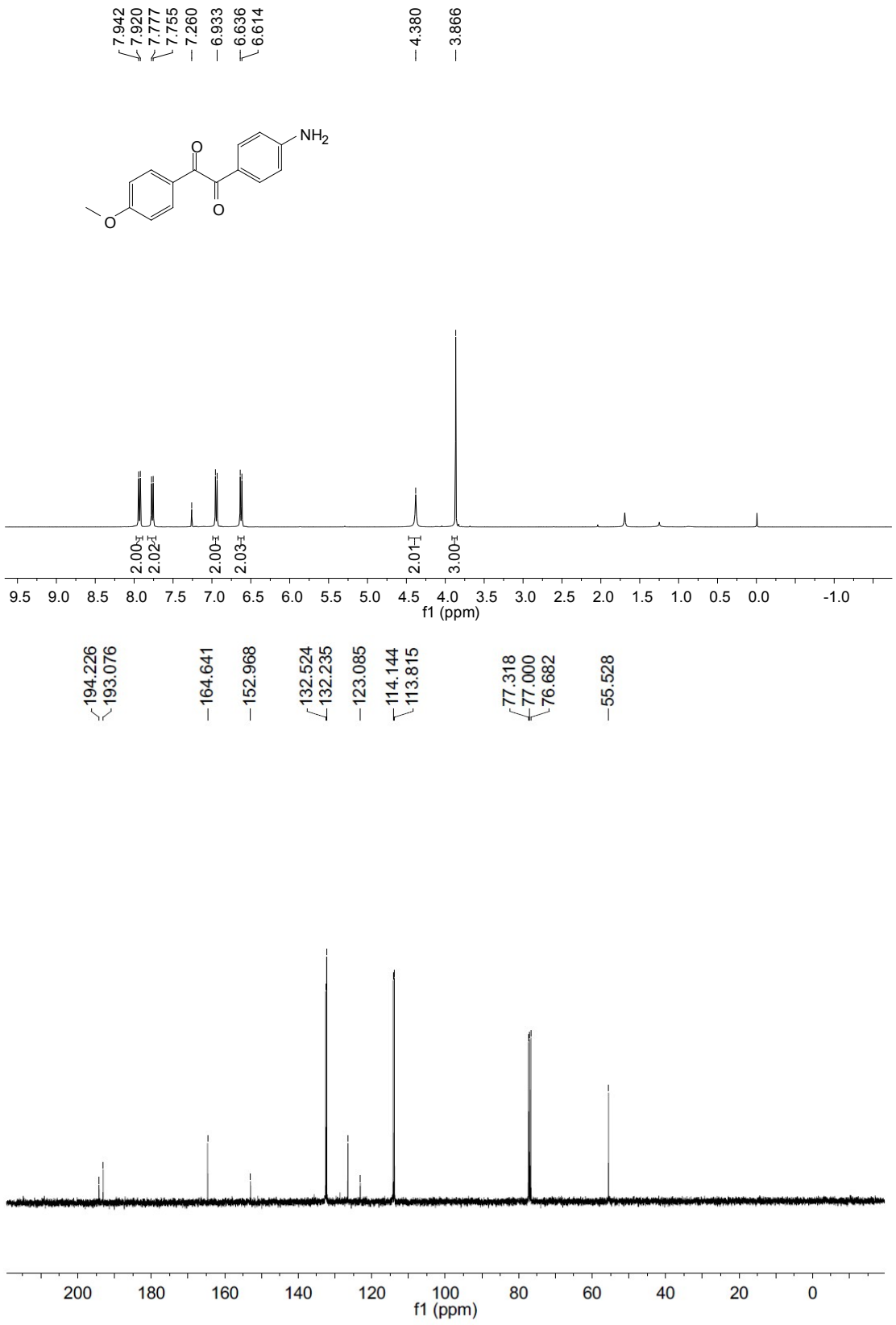
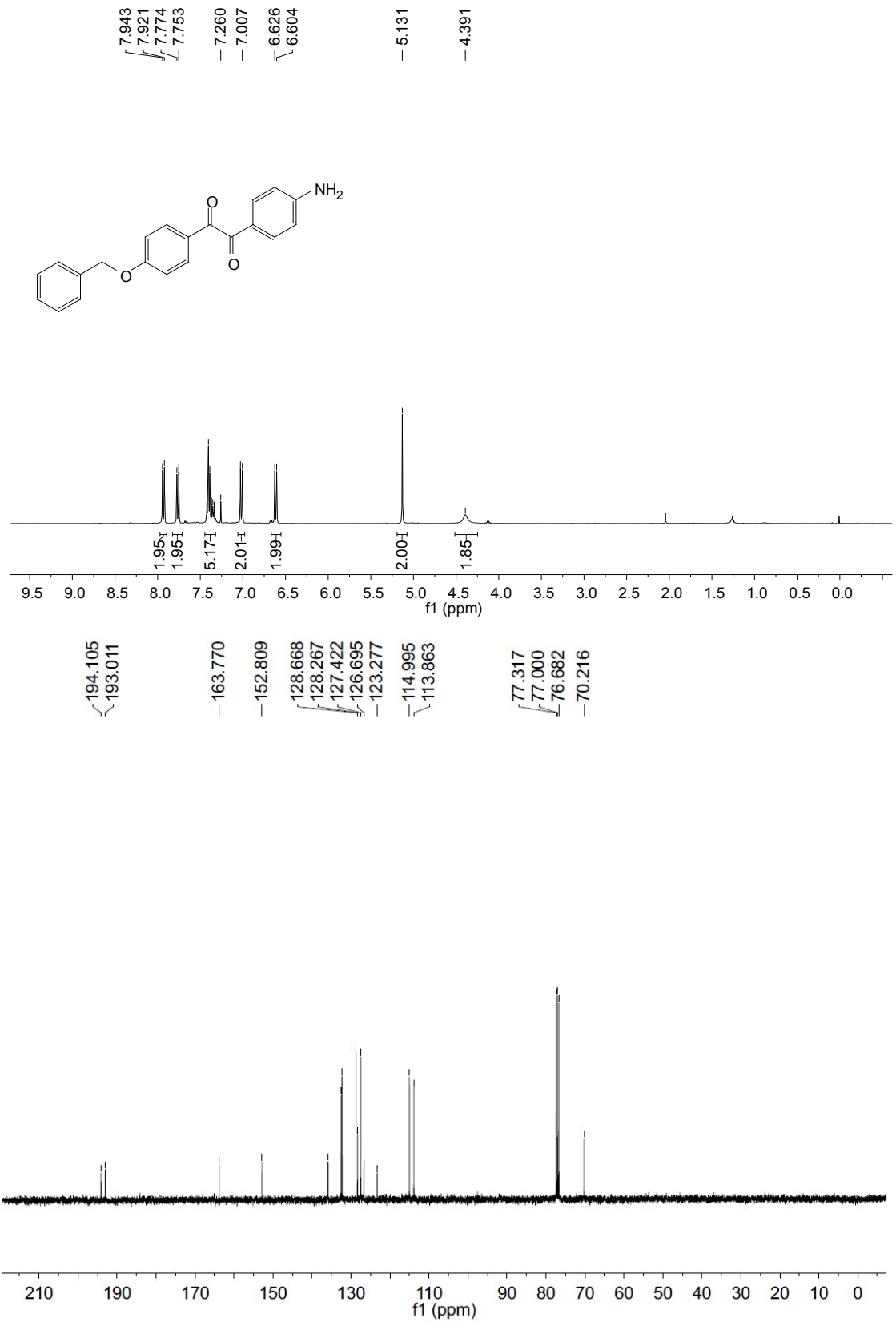


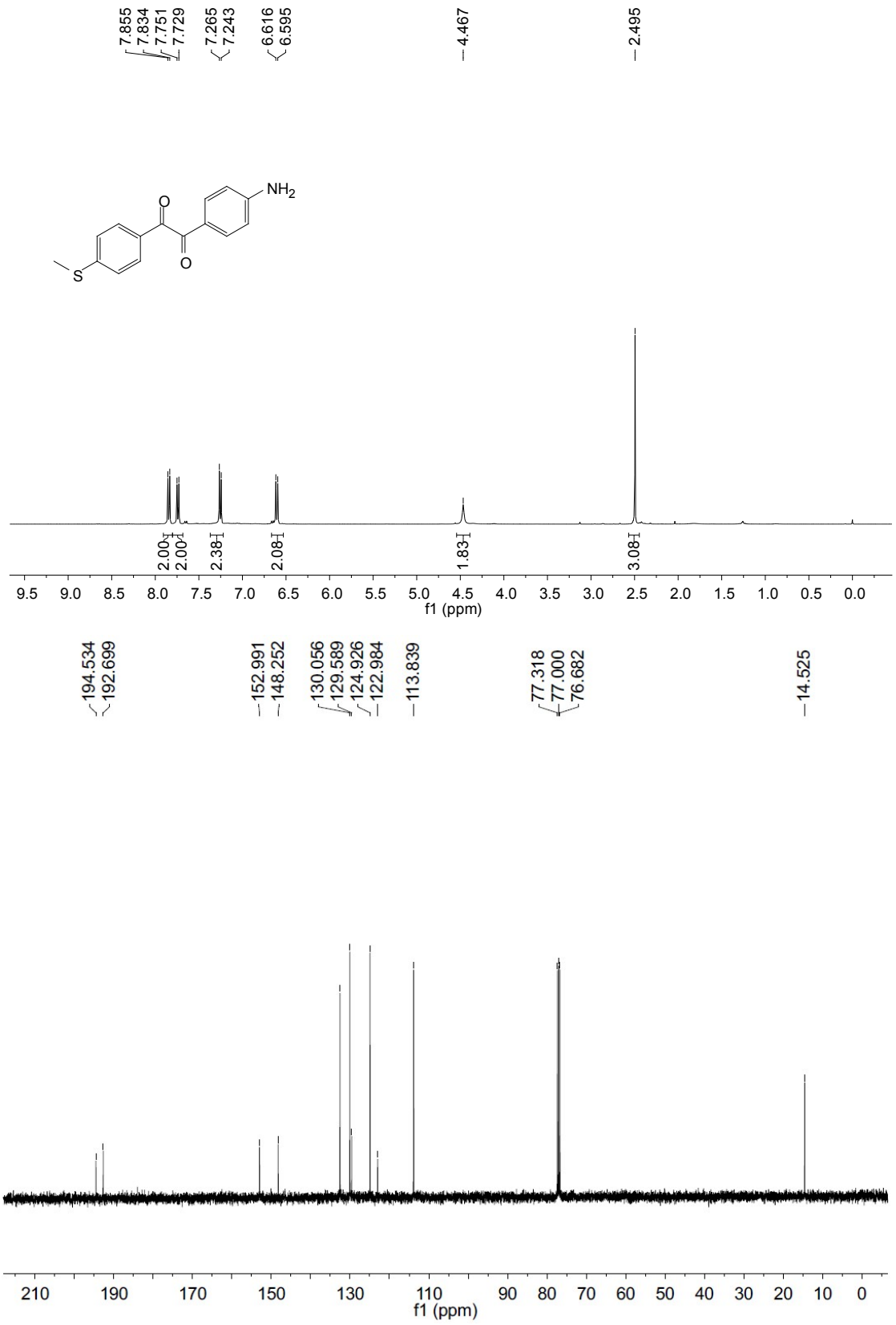
^{1}H NMR and ^{13}C NMR spectra of 3fa



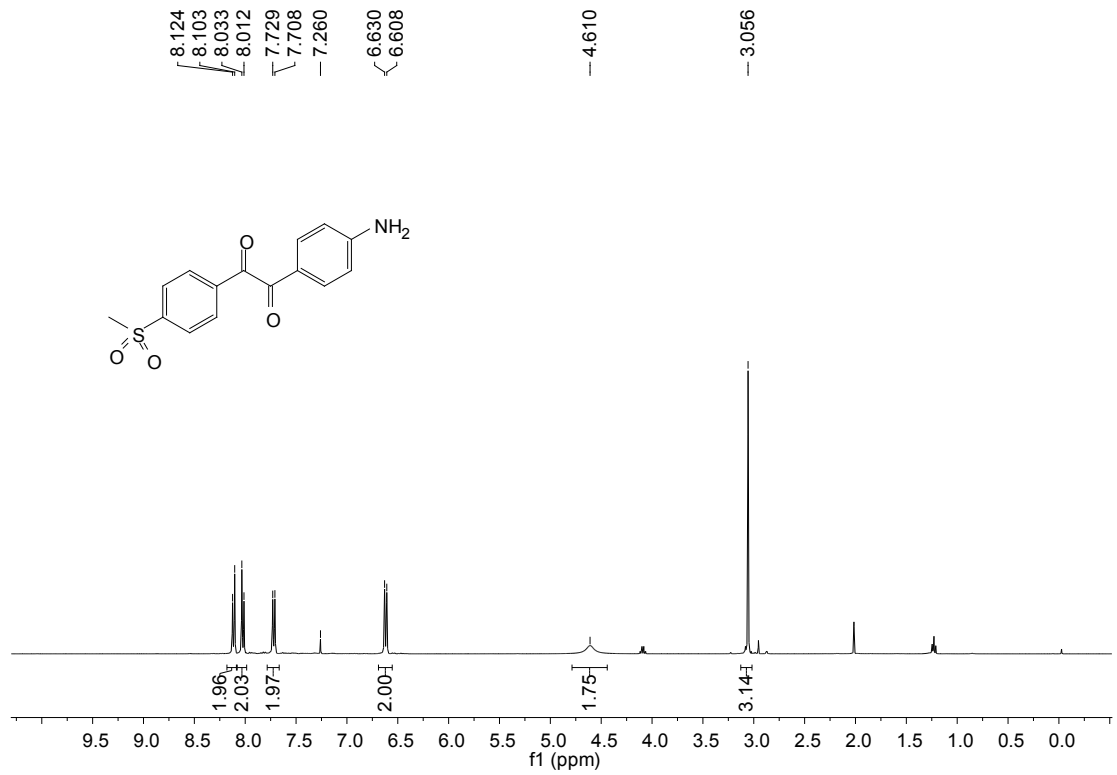
^{1}H NMR and ^{13}C NMR spectra of 3ga

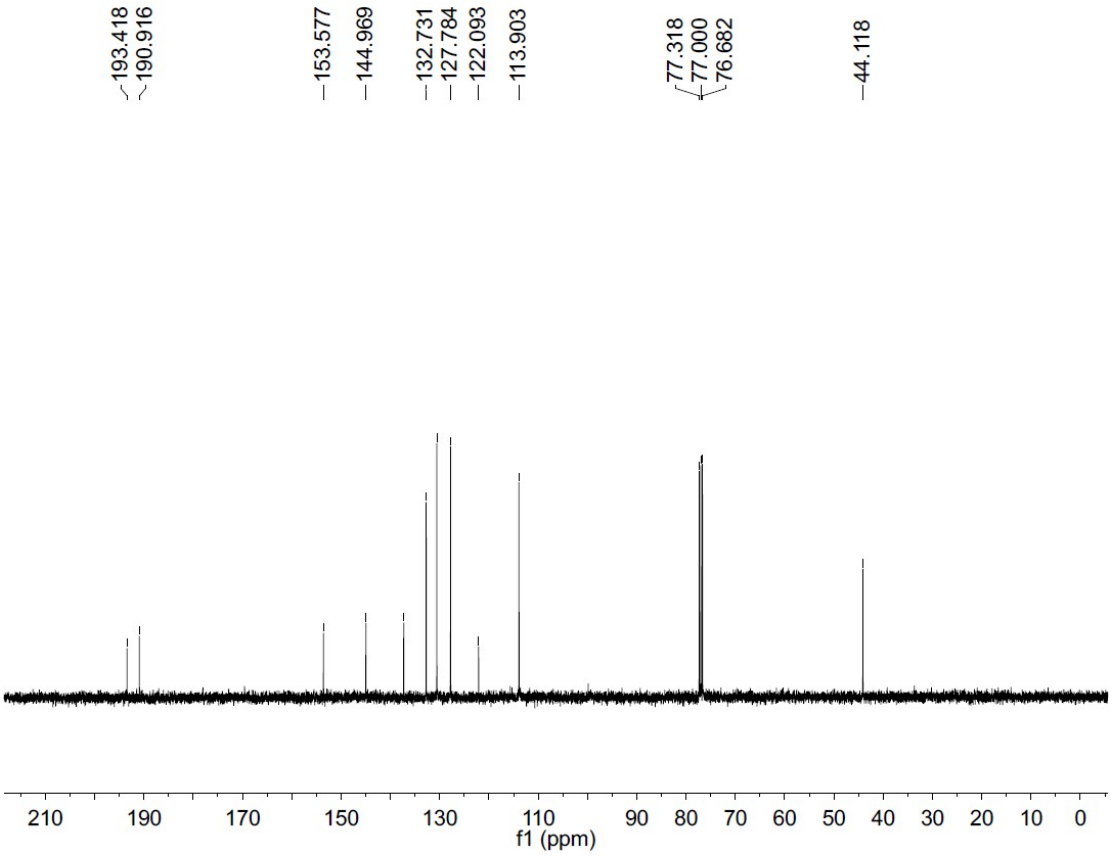


^{1}H NMR and ^{13}C NMR spectra of 3ha

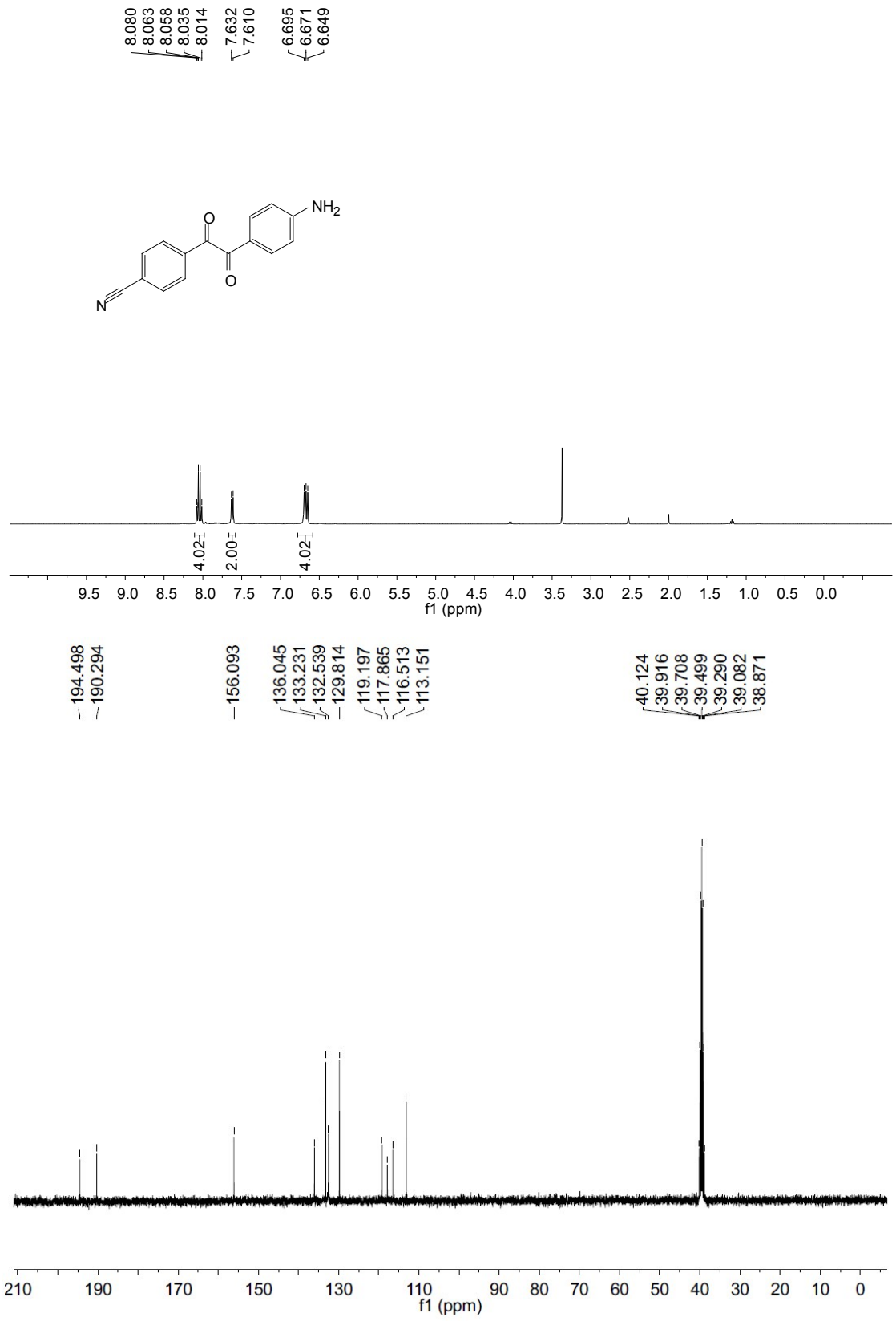


^{1}H NMR and ^{13}C NMR spectra of 3ia

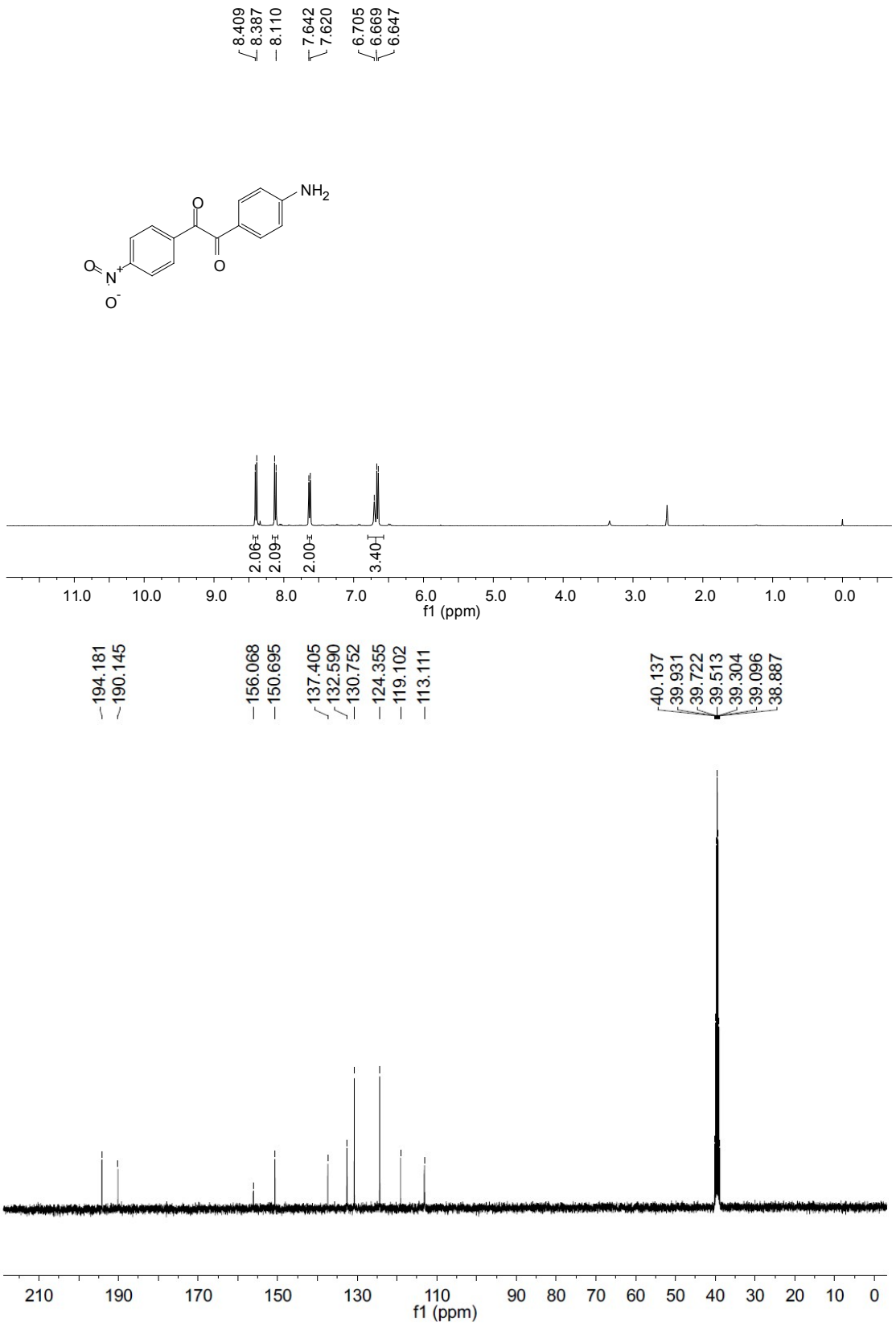




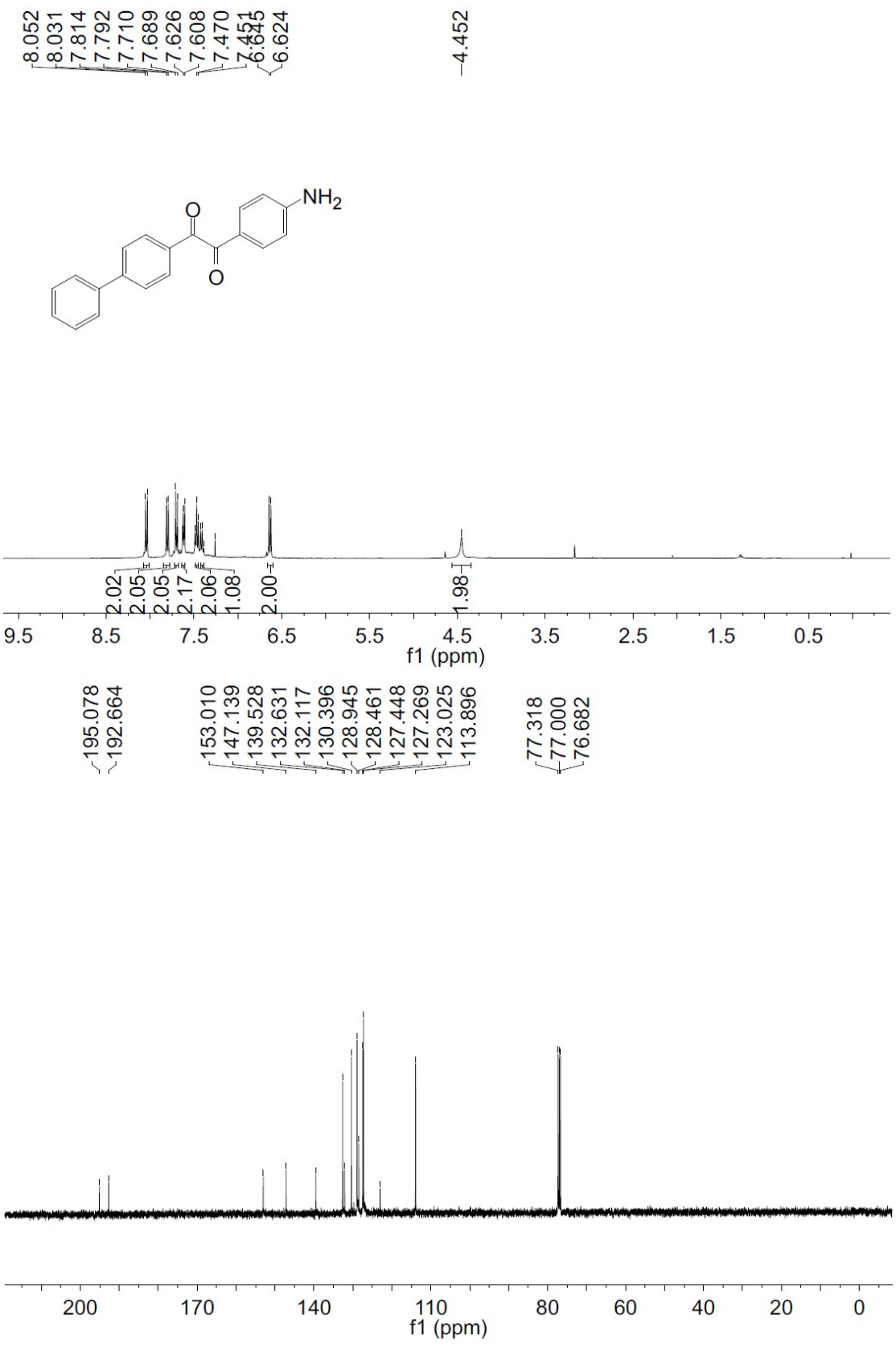
^{1}H NMR and ^{13}C NMR spectra of 3ja



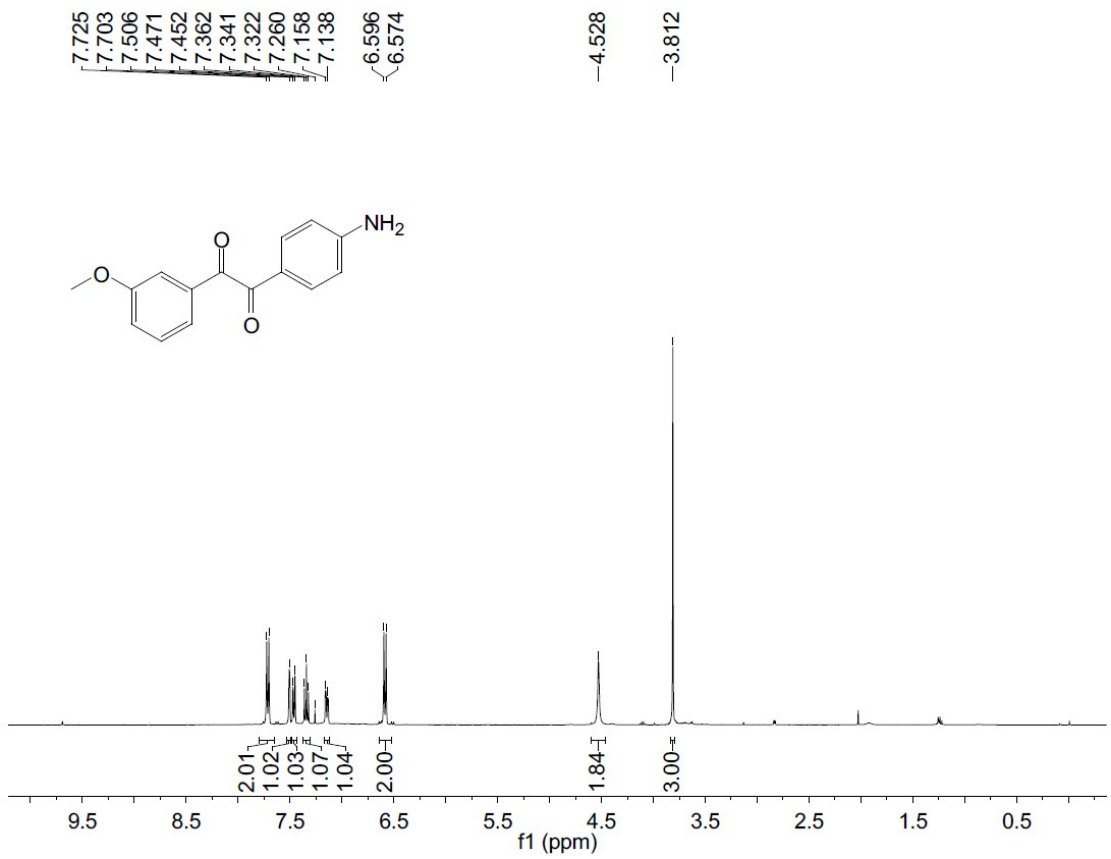
^{1}H NMR and ^{13}C NMR spectra of 3ka

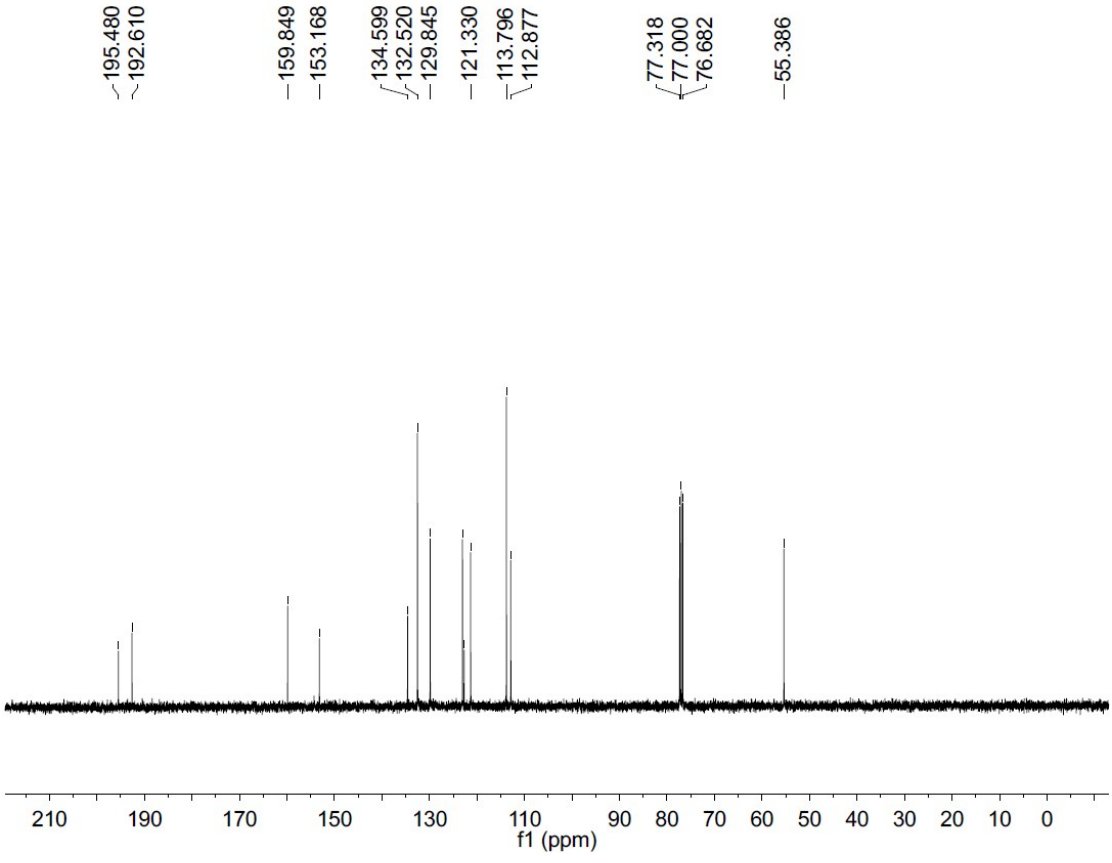


^{1}H NMR and ^{13}C NMR spectra of 3la

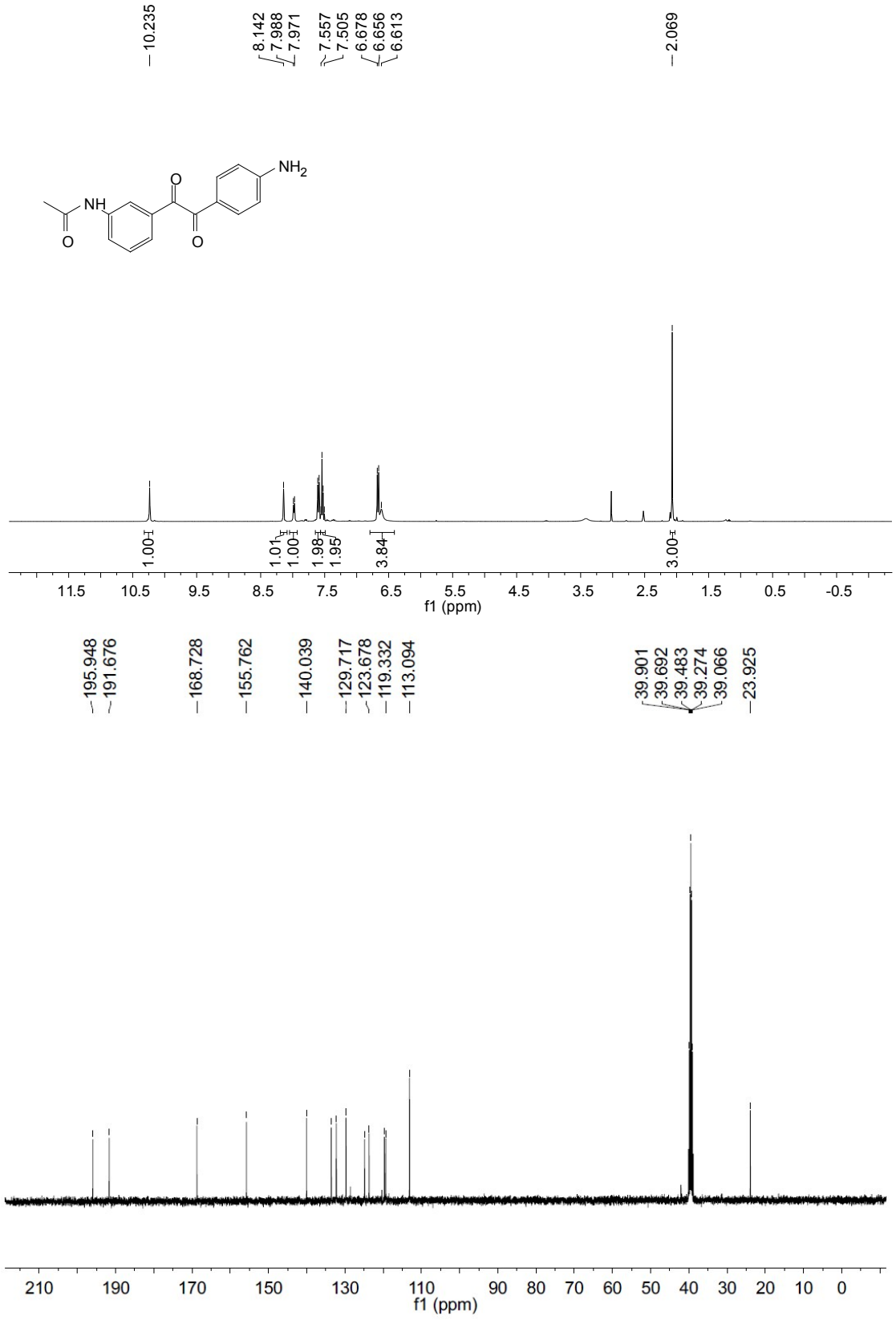


^{1}H NMR and ^{13}C NMR spectra of 3ma

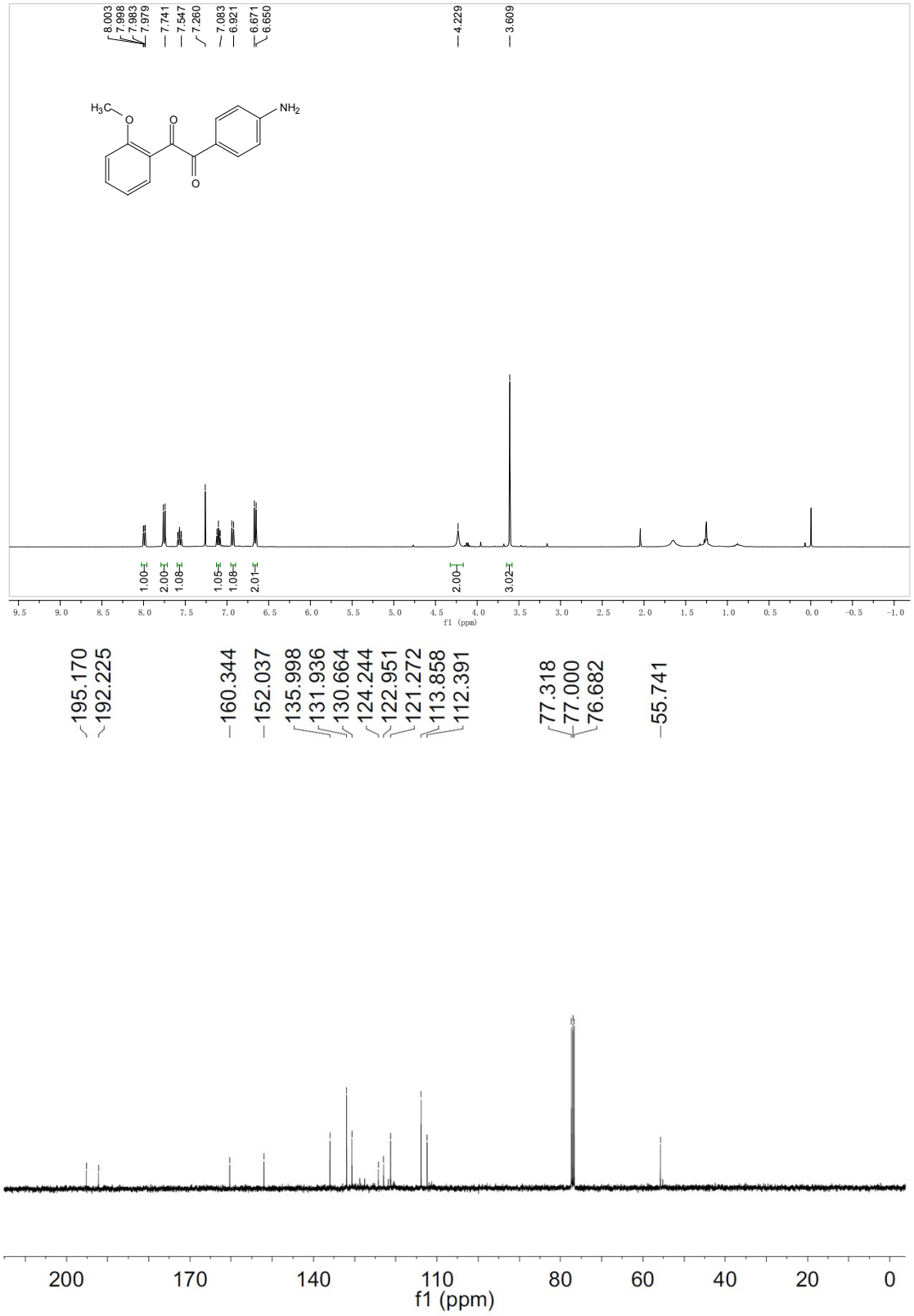

7.725
7.703
7.506
7.471
7.452
7.362
7.341
7.322
7.260
7.158
7.138
6.596
6.574
4.528
3.812
NH2
O
O
O
2.01
1.02
1.03
1.07
1.04
2.00
1.84
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


195.480
192.610
159.849
153.168
134.599
132.520
129.845
121.330
113.796
112.877
77.318
77.000
76.682
55.386
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

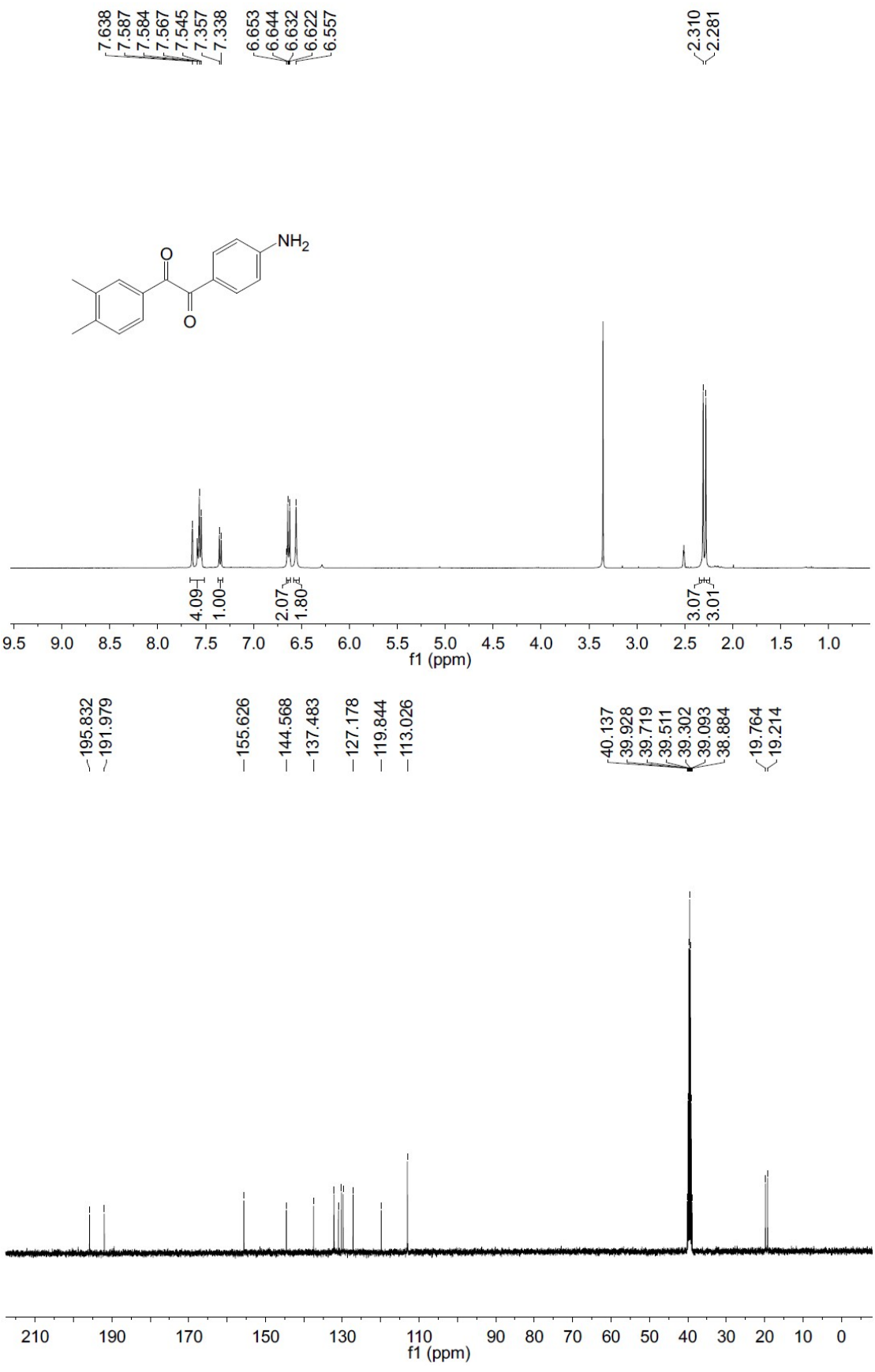
^{1}H NMR and ^{13}C NMR spectra of 3na



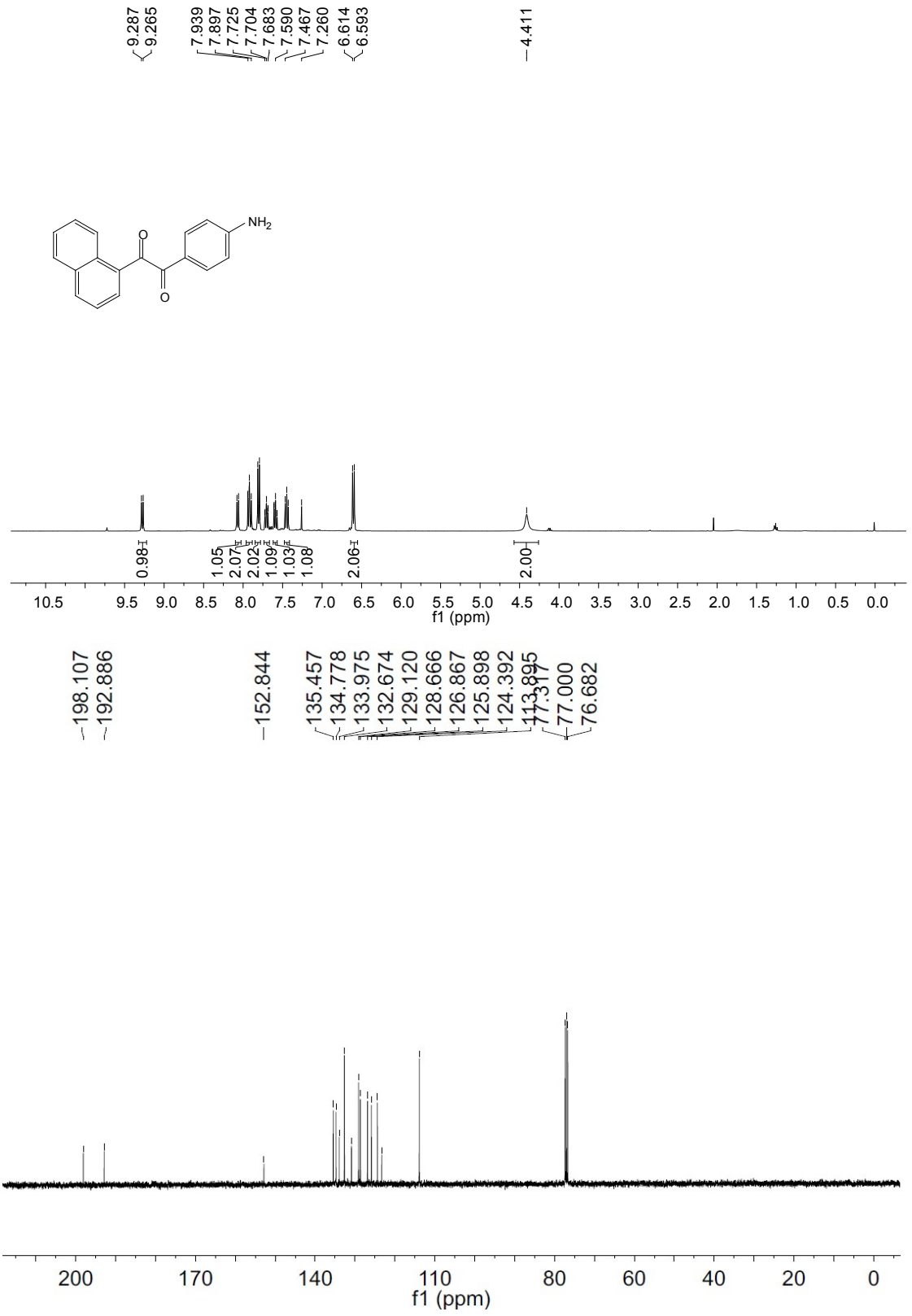
^{1}H NMR and ^{13}C NMR spectra of 3oa



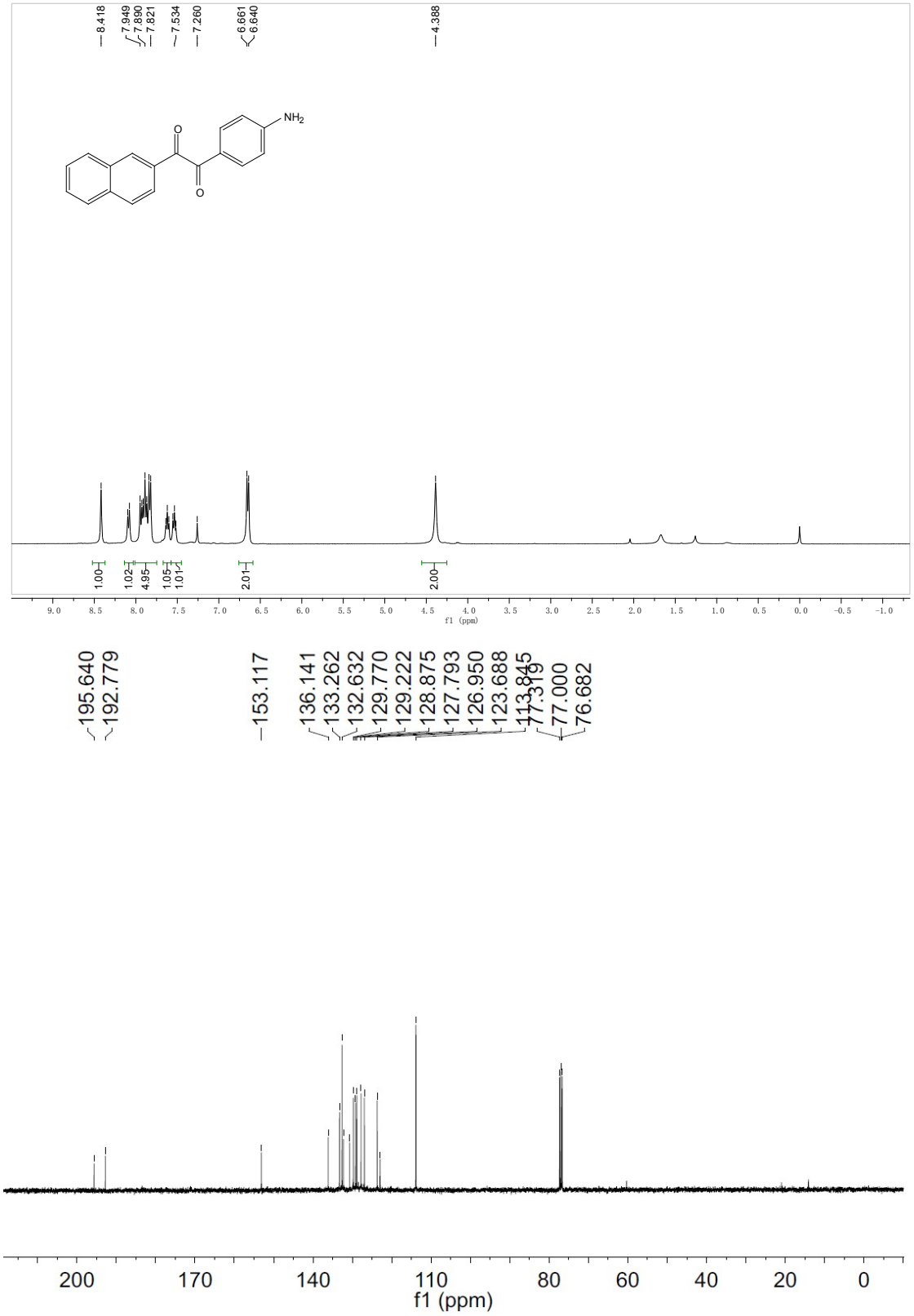
^{1}H NMR and ^{13}C NMR spectra of 3pa



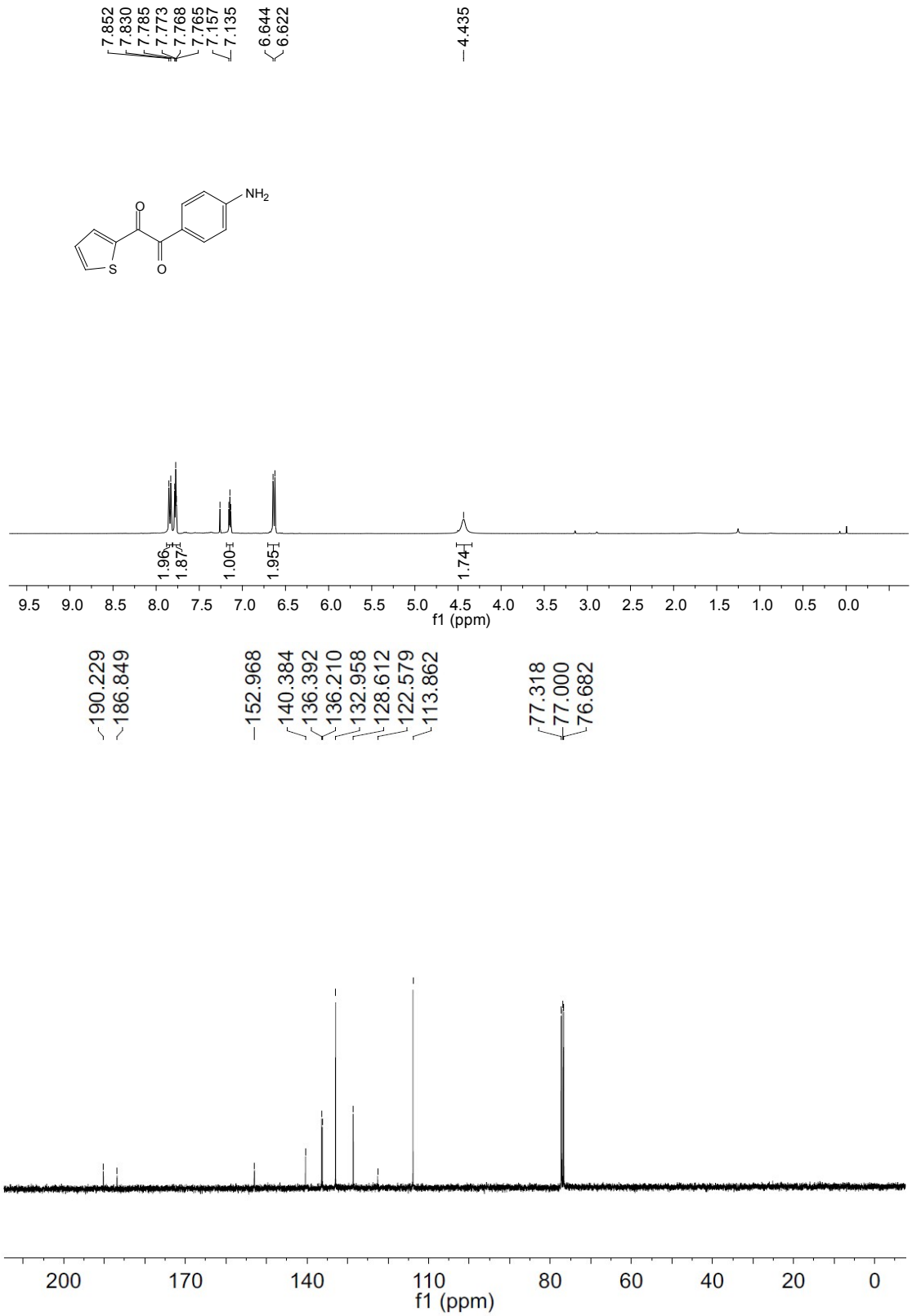
^{1}H NMR and ^{13}C NMR spectra of 3qa


9.287
9.265
7.939
7.897
7.725
7.704
7.683
7.590
7.467
7.260
6.614
6.593
4.411
NH2
O
O
0.98
1.05
2.07
2.02
1.09
1.03
1.08
2.06
2.00
10.5
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
f1 (ppm)
198.107
192.886
152.844
135.457
134.778
133.975
132.674
129.120
128.666
126.867
125.898
124.392
113.895
77.317
77.000
76.682
200
170
140
110
80
60
40
20
0
f1 (ppm)

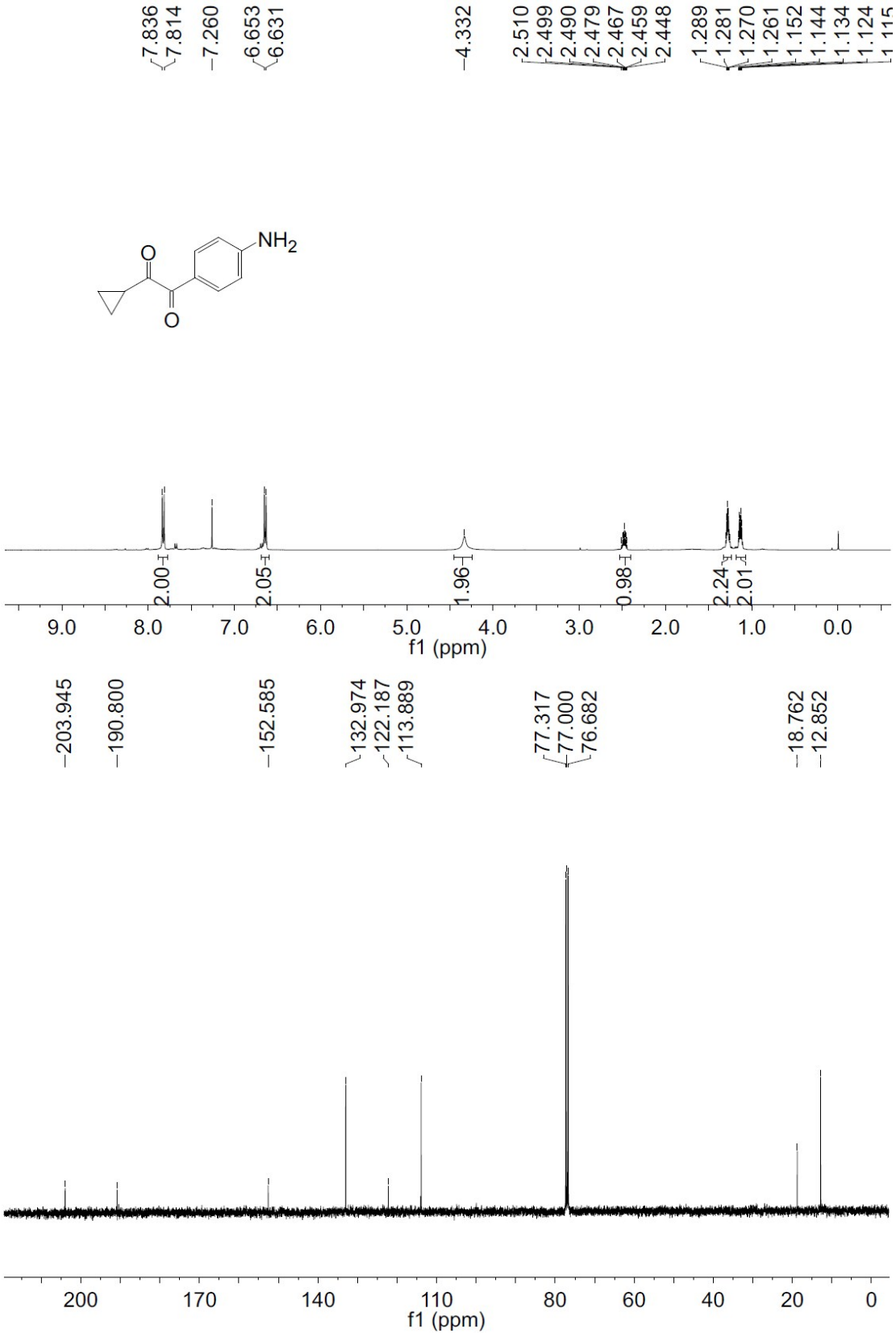
^{1}H NMR and ^{13}C NMR spectra of 3ra



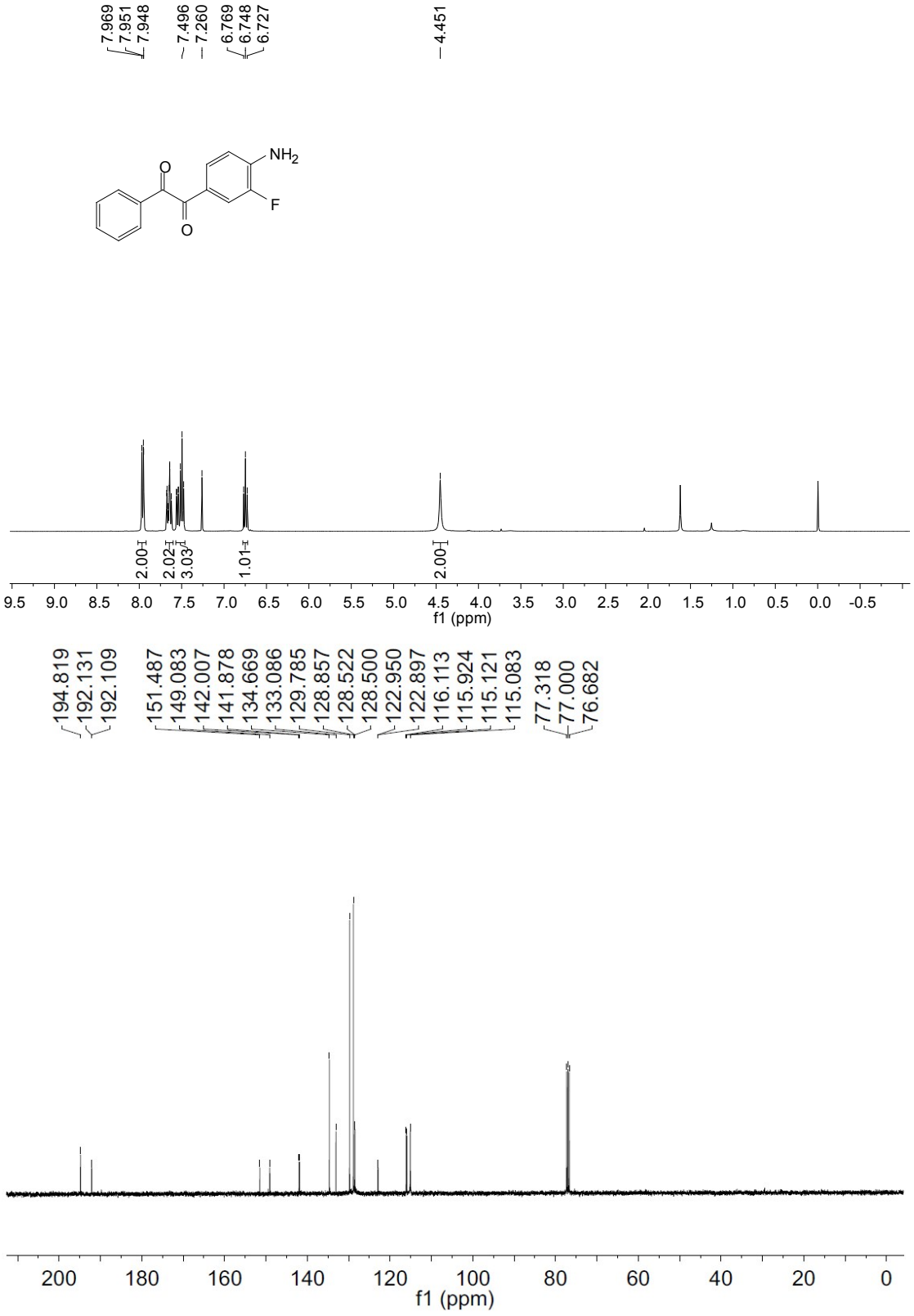
^{1}H NMR and ^{13}C NMR spectra of 3sa


7.852
7.830
7.785
7.773
7.768
7.765
7.157
7.135
6.644
6.622
4.435
NH2
O
O
S
1.96
1.87
1.00
1.95
1.74
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
f1 (ppm)
190.229
186.849
152.968
140.384
136.392
136.210
132.958
128.612
122.579
113.862
77.318
77.000
76.682
200 170 140 110 80 60 40 20 0
f1 (ppm)

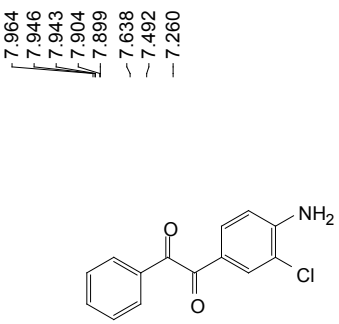
^{1}H NMR and ^{13}C NMR spectra of 3ta

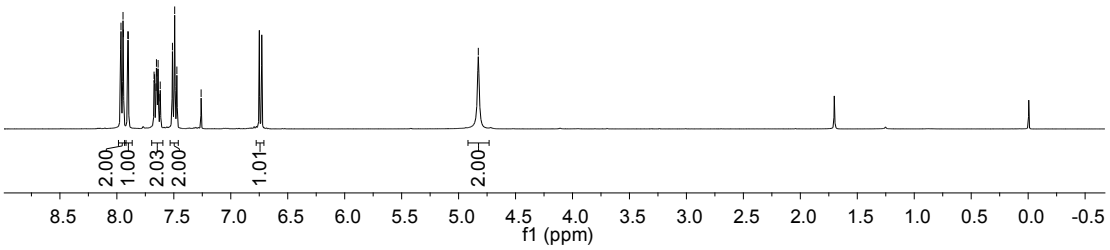


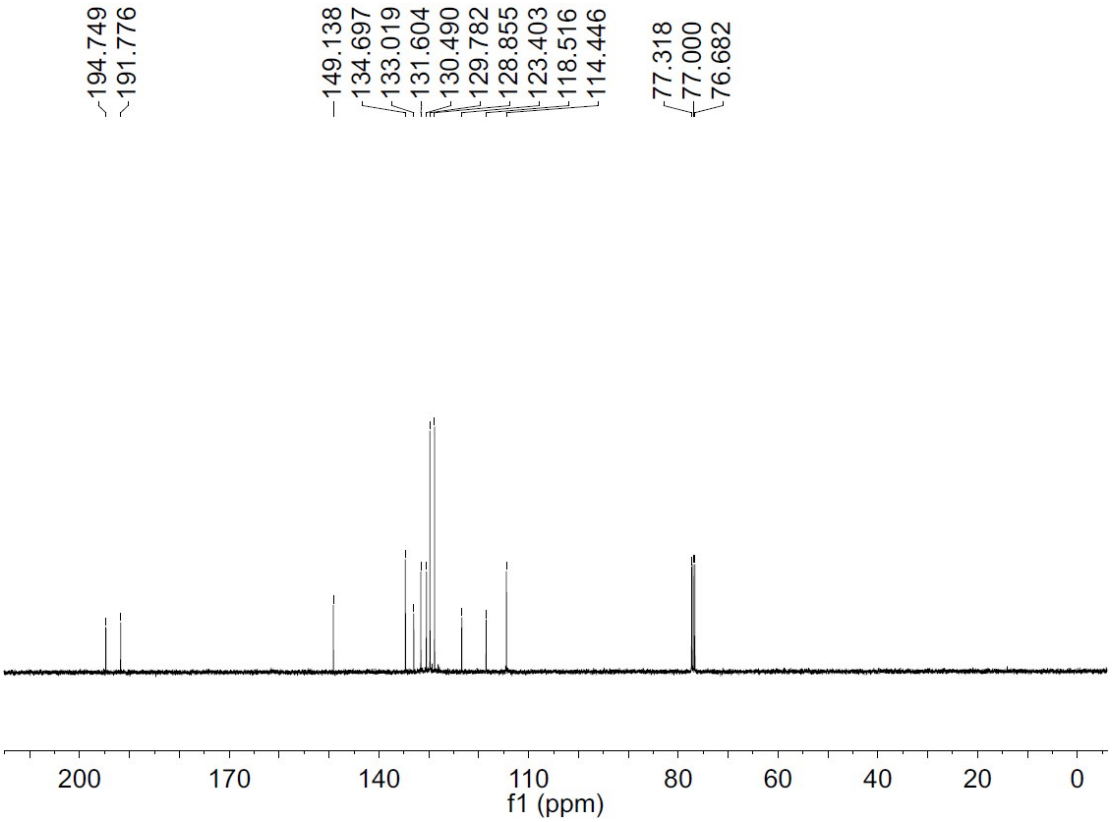
^{1}H NMR and ^{13}C NMR spectra of 3ab



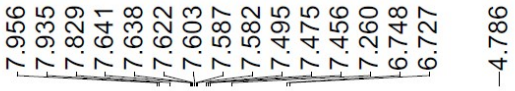
^{1}H NMR and ^{13}C NMR spectra of 3ac

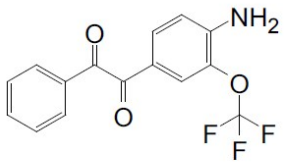

7.964
7.946
7.943
7.904
7.899
7.638
7.492
7.260
4.827
NH2
Cl
O
O

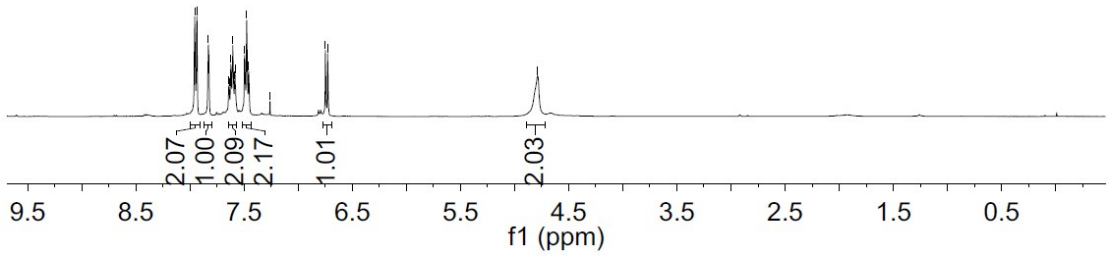

2.00
1.00
2.03
2.00
1.01
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

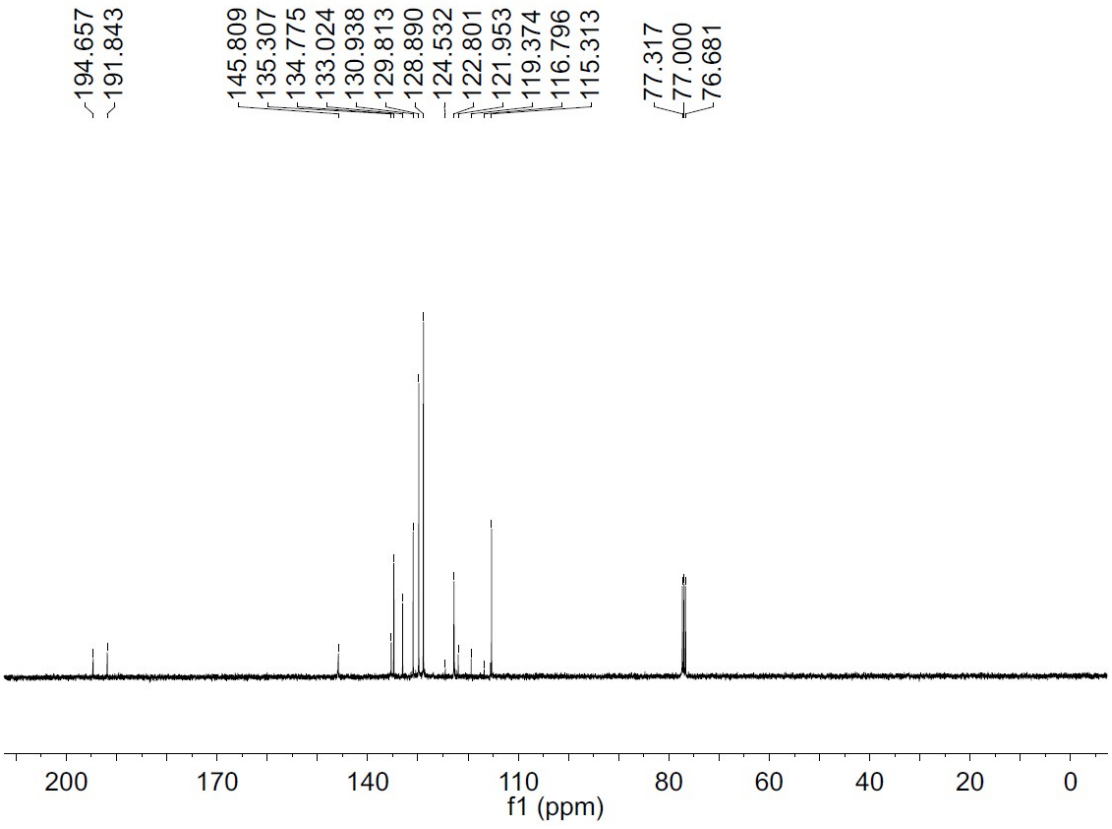

194.749
191.776
149.138
134.697
133.019
131.604
130.490
129.782
128.855
123.403
118.516
114.446
77.318
77.000
76.682
200 170 140 110 80 60 40 20 0
f1 (ppm)

^{1}H NMR and ^{13}C NMR spectra of 3ad

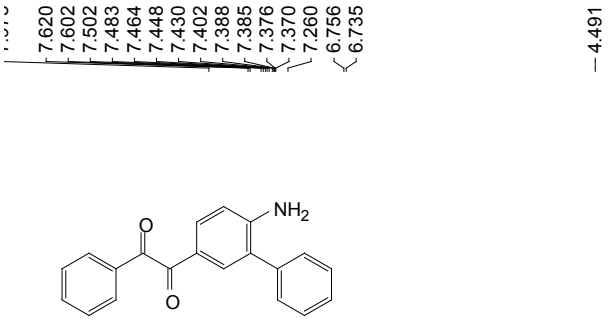


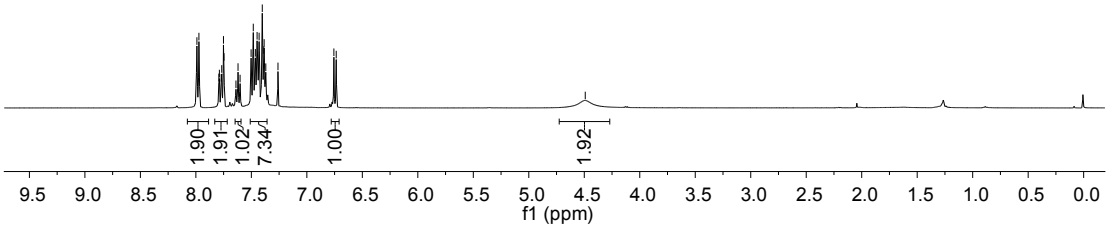


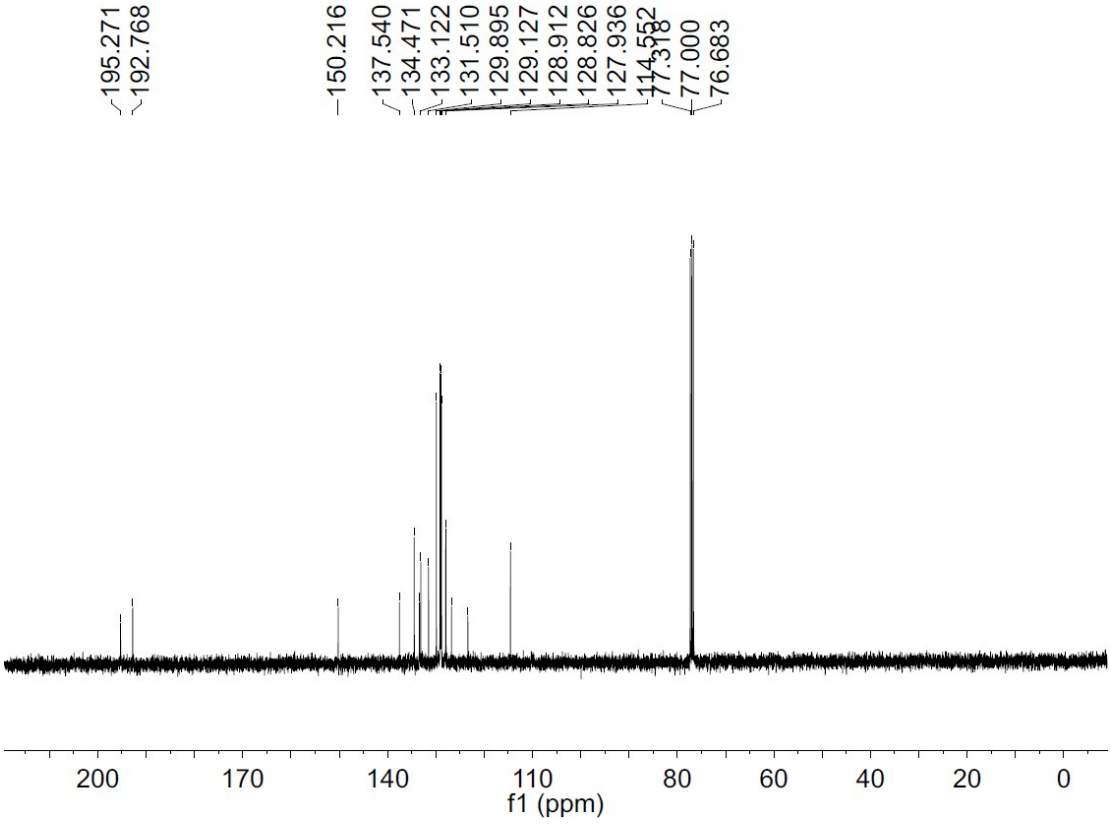




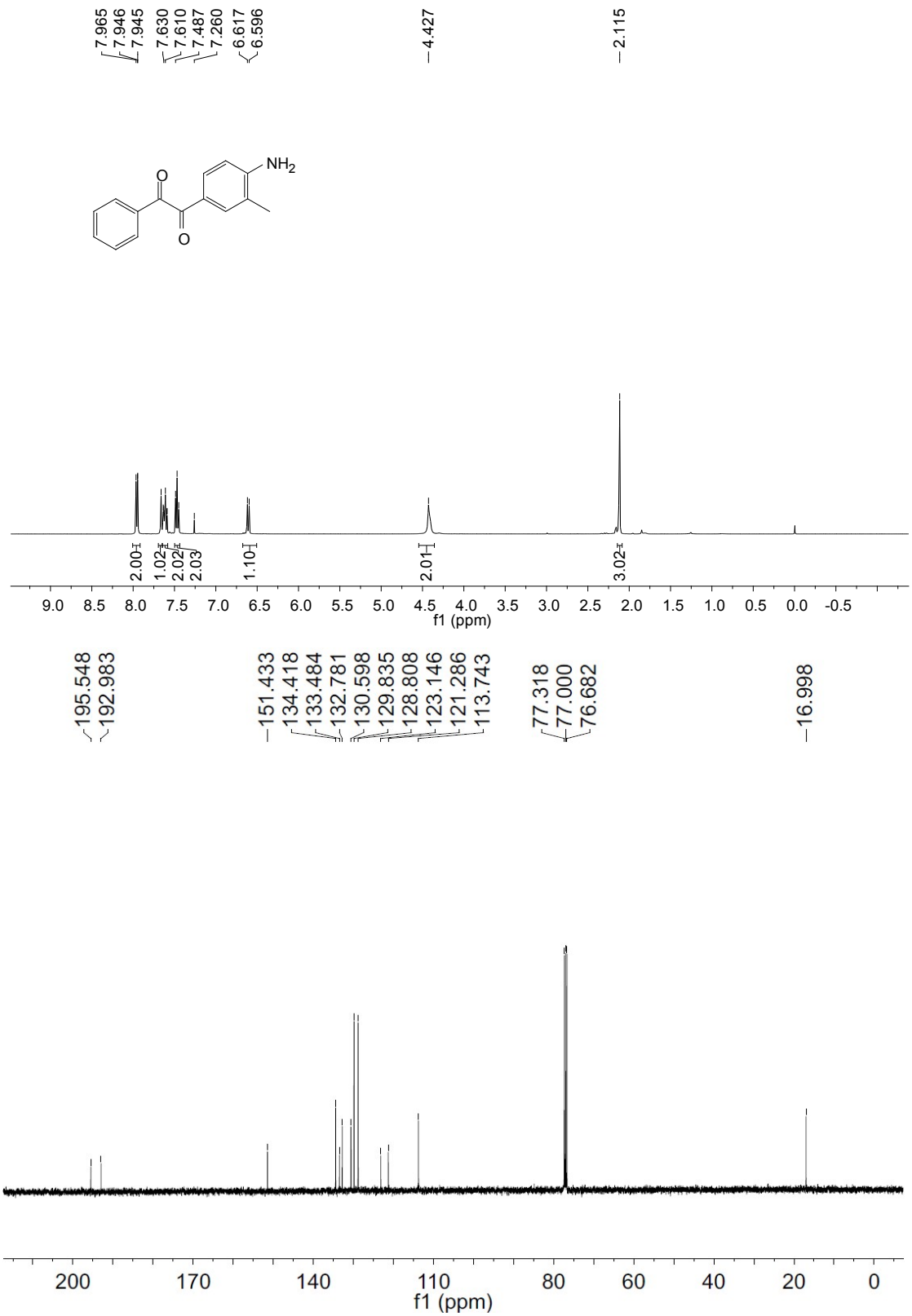
^{1}H NMR and ^{13}C NMR spectra of 3ae



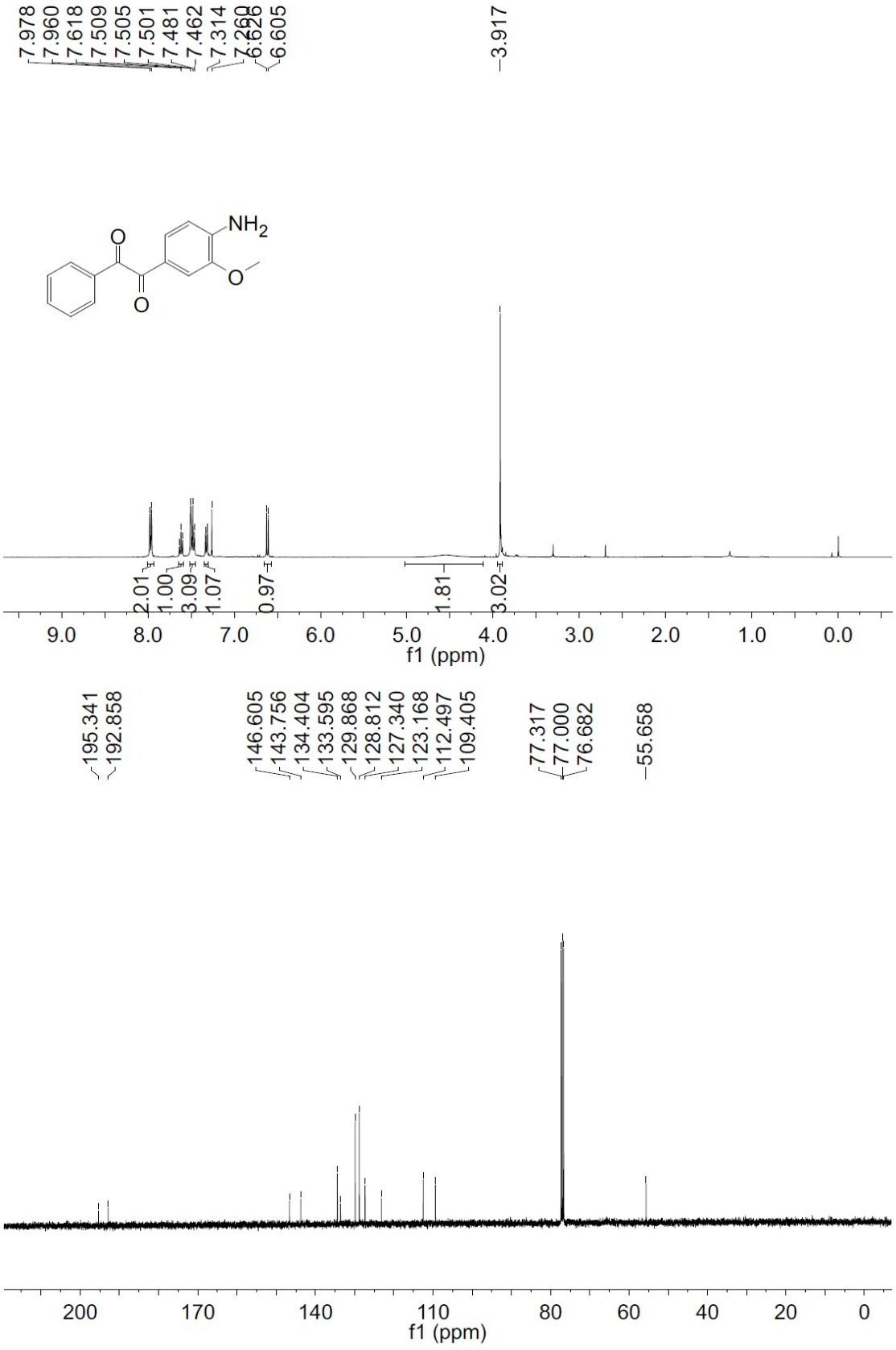




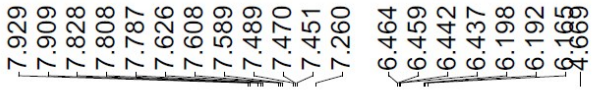
^{1}H NMR and ^{13}C NMR spectra of 3af

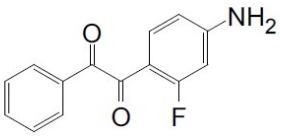

7.965
7.946
7.945
7.630
7.610
7.487
7.260
6.617
6.596
4.427
2.115
NH2
O
O
2.00
1.02
2.02
2.03
1.10
2.01
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
195.548
192.983
151.433
134.418
133.484
132.781
130.598
129.835
128.808
123.146
121.286
113.743
77.318
77.000
76.682
16.998
200 170 140 110 80 60 40 20 0
f1 (ppm)

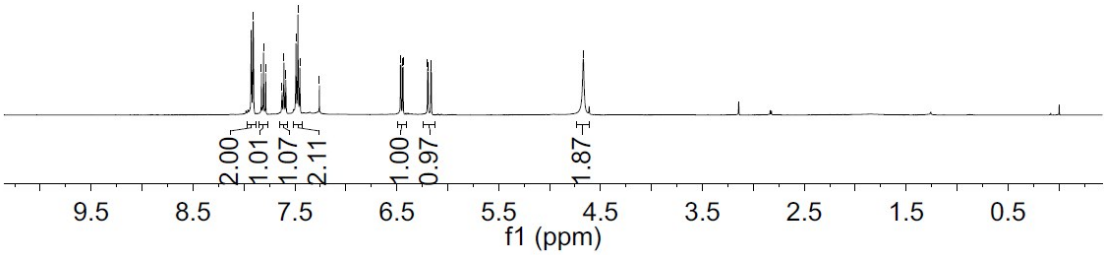
^{1}H NMR and ^{13}C NMR spectra of 3ag

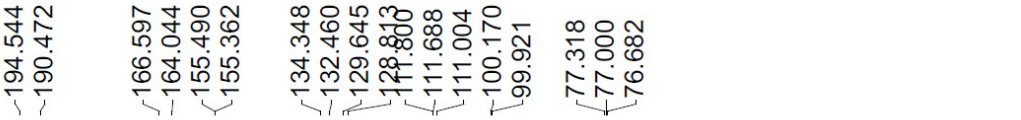


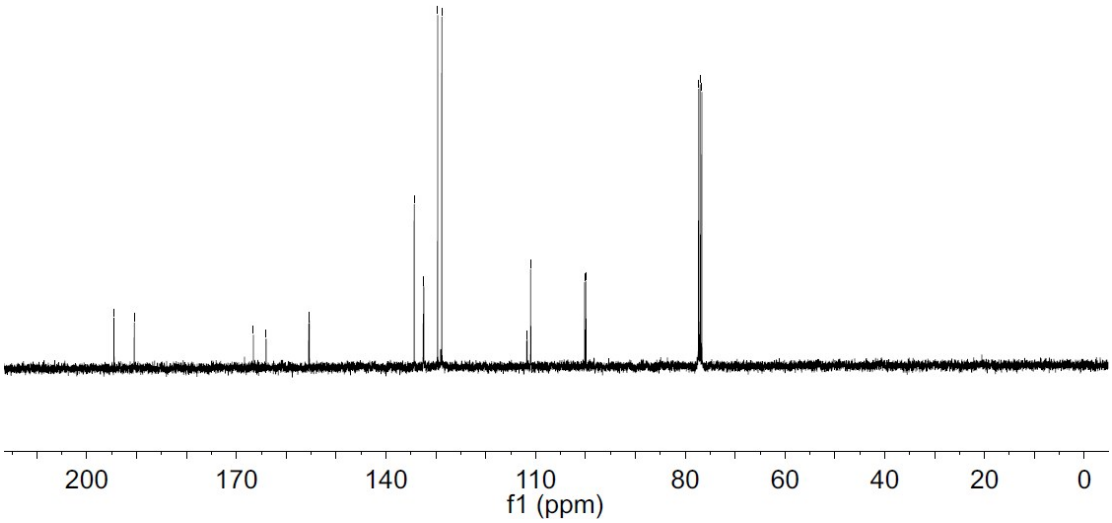
^{1}H NMR and ^{13}C NMR spectra of 3ah



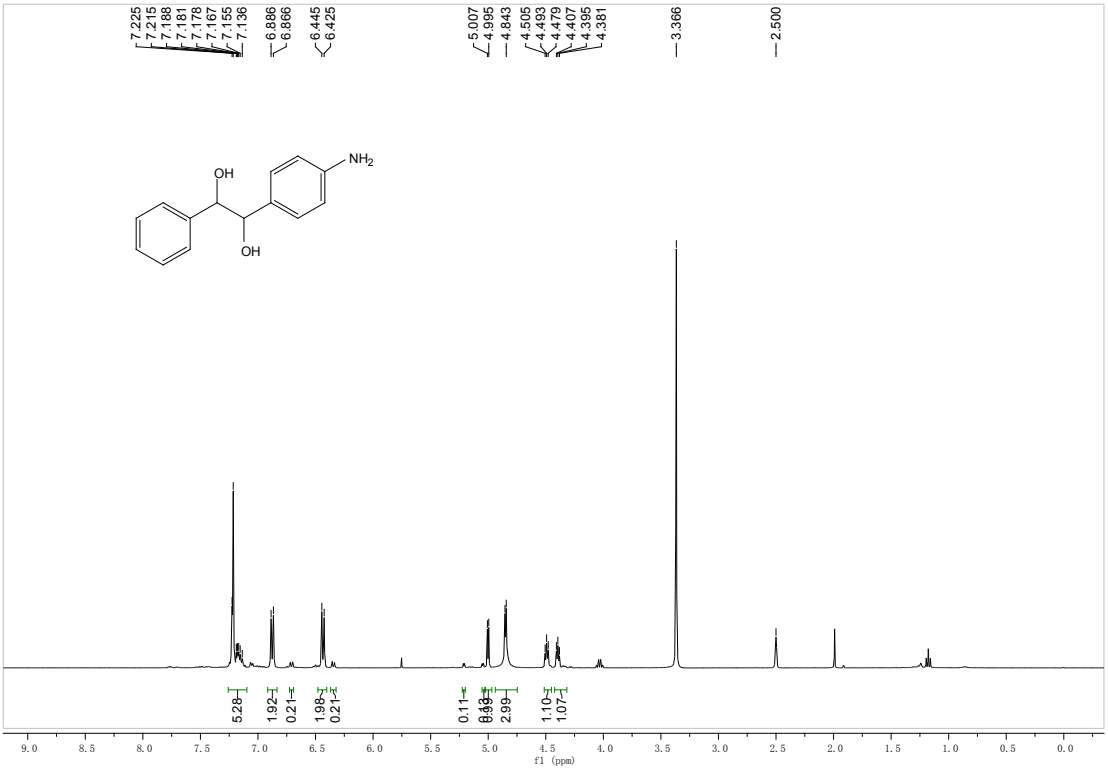


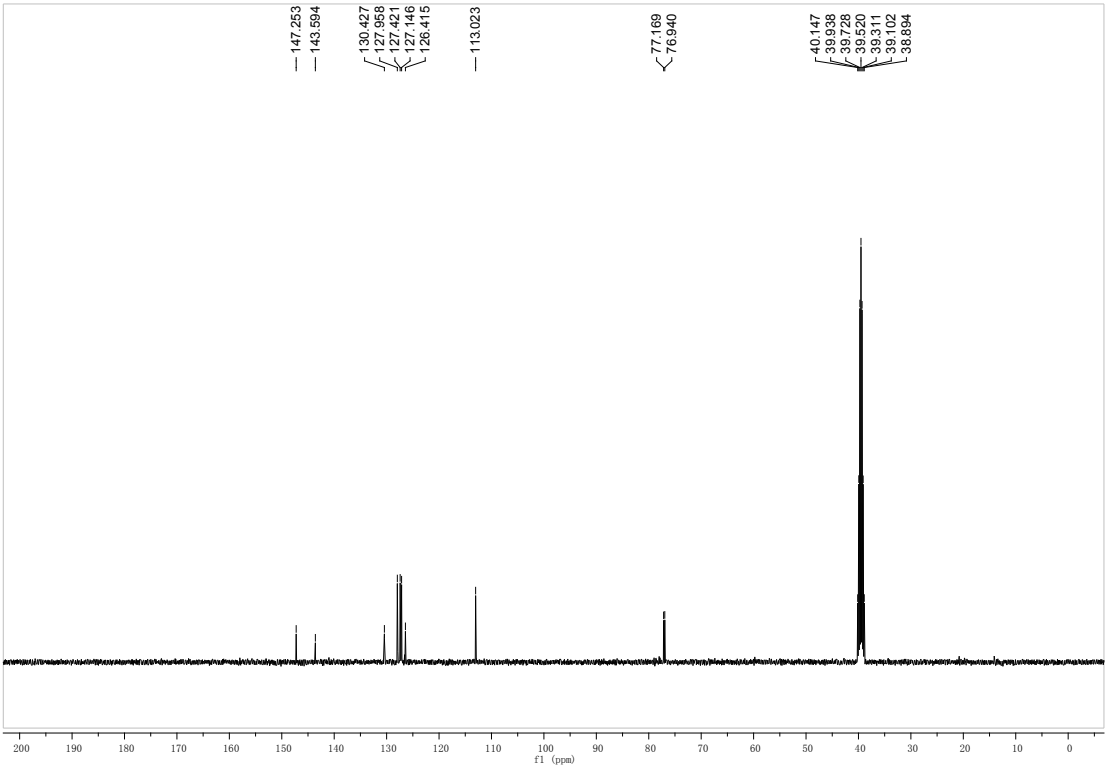




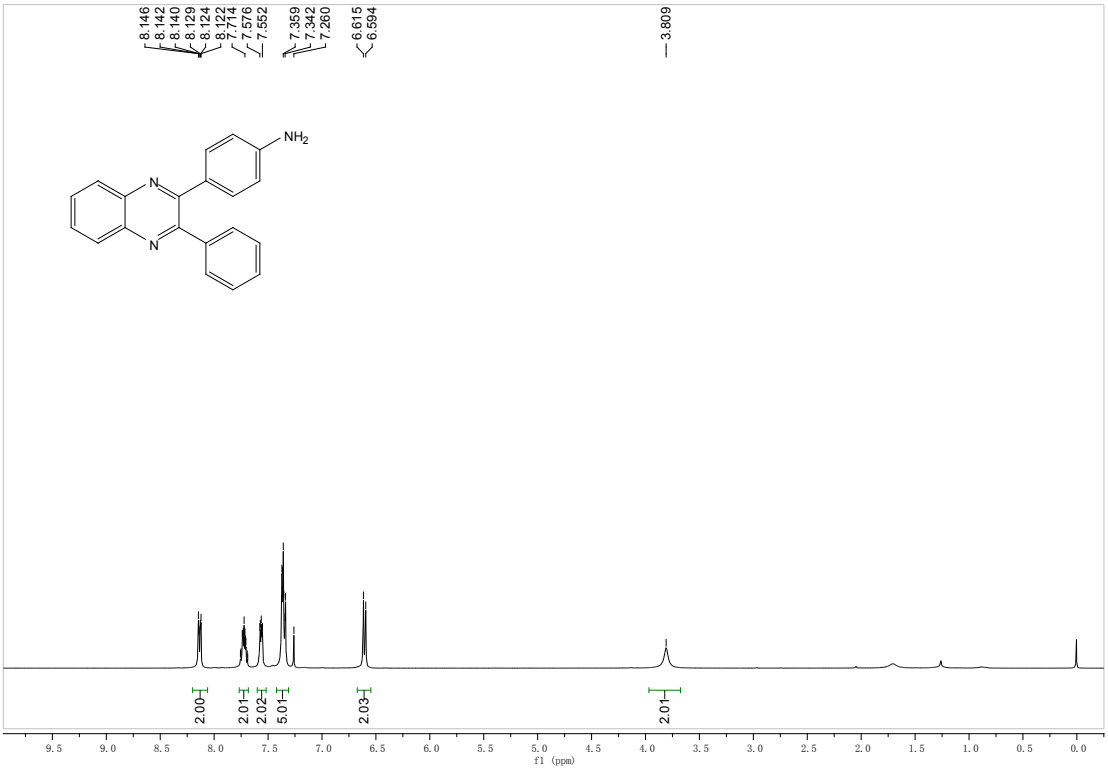


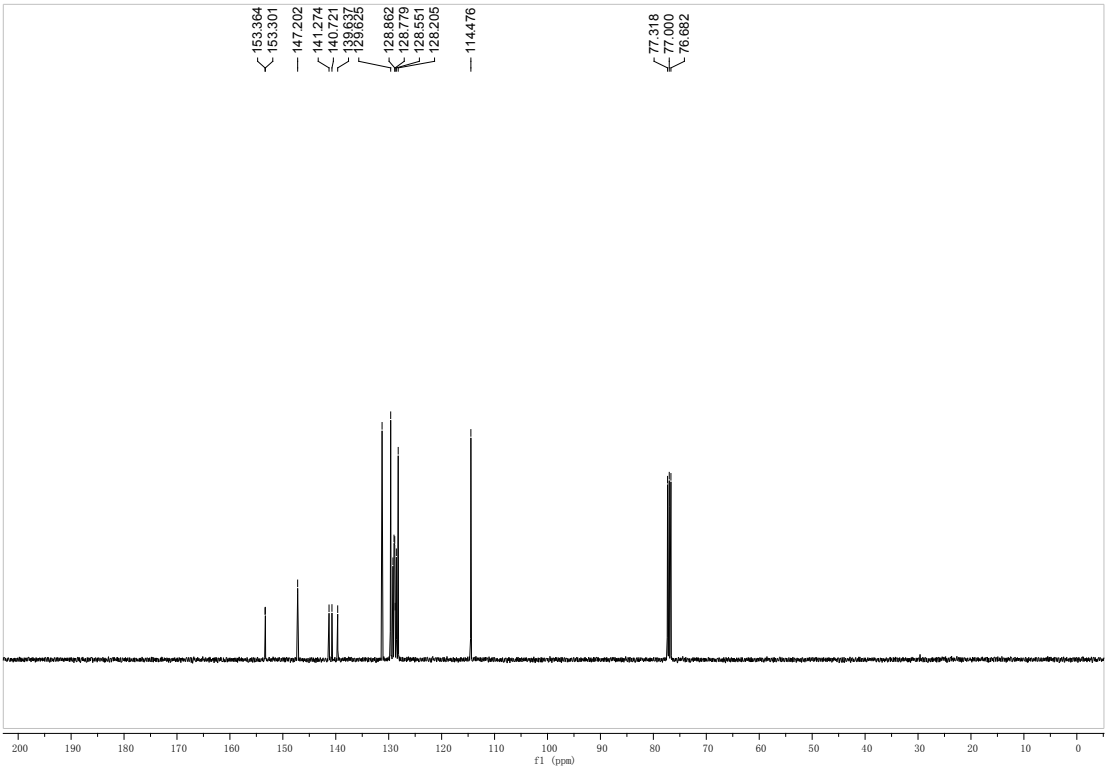
^{1}H NMR and ^{13}C NMR spectra of 7





^{1}H NMR and ^{13}C NMR spectra of 8


8.146
8.142
8.140
8.129
8.124
8.122
7.714
7.576
7.552
7.359
7.342
7.260
6.615
6.594
3.809
NH2
N
N
2.00
2.01
2.02
5.01
2.03
2.01
f1 (ppm)


153.364
153.301
147.202
141.274
140.721
139.637
129.625
128.862
128.779
128.551
128.205
114.476
77.318
77.000
76.682
f1 (ppm)