Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Synthesis of α-Amino Ketones through Aminations of Umpoled Enolates

Xiaowen Xia, Bocheng Chen, Xiaojun Zen*, Bo Xu*

Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China.

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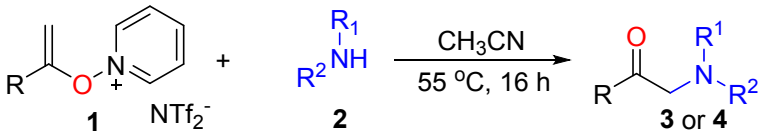
1. General

^{1}H NMR (400 MHz or 500 MHz) and ^{13}C NMR (100 MHz or 125 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (J), are reported in Hertz (Hz). GC analyses were performed using a Shimadzu GC-2010 ultra gas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler. Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates.

The N-alkenoxypyridinium salts **1** were prepared using published procedures. [1, 2-3]

2. General procedure for the preparation of α-amino ketones 3 or 4



To an oven-dried 10 mL Schlenk tube, N-alkenoxypyridinium **1** (0.2 mmol), amine **2** (0.6 mmol) and CH_3CN (1 mL) were introduced under argon atmosphere. The Schlenk tube was then sealed and was stirred at 55 °C until all the starting material **1** was consumed. After that, the reaction mixture was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were with Na_2SO_4 and filtered. The excess solvent in the filtrate was removed under reduced pressure and the residue was subjected to silica gel chromatography (hexanes / ethyl acetate: form 50 : 1 to 10 : 1) to afford the desired amination product **3** or **4**.

1-(Methyl(phenyl)amino)octan-2-one (**3a**). Light yellow oil, 67% (31.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 2H), 6.74 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.66 – 6.57 (m, 2H), 4.01 (s, 2H), 3.05 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.33 – 1.19 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.5, 148.9, 129.3, 117.2, 111.9, 62.8, 39.8, 39.5, 31.4, 23.1, 22.5, 13.9. IR ν (cm^{-1}): 2928, 1727, 1675, 1602, 1505, 1367, 695, 732. HRMS (ESI^{+}) calculated for $C_{14}H_{22}NO$ $(M + H)^{+}$: 220.1701 found $(M + H)^{+}$: 220.1695.

1,10-Bis (methyl(phenyl)amino) decane-2,9-dione (**3b**). Light yellow oil, 39% (29.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.15 (m, 4H), 6.73 (t, *J* = 7.3 Hz, 2H), 6.64 – 6.56 (m, 4H), 3.99 (s, 4H), 3.04 (s, 6H), 2.8 (t, *J* = 7.3 Hz, 4H), 1.60 – 1.47 (m, 4H), 1.25 – 1.20 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.4, 148.9, 129.3, 117.2, 111.9, 62.8, 39.8, 39.3, 28.9, 23.1. IR ν (cm^{-1}): 2927, 1713, 1667, 1595, 1496, 1351, 1116, 750, 696. HRMS (ESI^{+}) calculated for $C_{24}H_{33}N_2O_2$ (M + H)$^{+}$: 381.2542, found: 381.2535.

6-(Methyl(phenyl)amino)-5-oxohexanenitrile (**3c**). Light yellow oil, 62% (26.9 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 2H), 6.76 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.65 – 6.57 (m, 2H), 4.03 (s, 2H), 3.08 (s, 3H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.91 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.1, 148.6, 129.5, 119.2, 117.6, 111.9, 62.9, 39.9, 37.3, 18.9, 16.4. IR ν (cm^{-1}): 2944, 2244, 1725, 1668, 1600, 1507, 1360, 751, 694. HRMS (ESI^{+}) calculated for $C_{13}H_{17}N_2O$ (M + H)$^{+}$: 217.1341, found: 217.1334.

Methyl 2-isobutyryl-8-(methyl(phenyl) amino)-7-oxooctanoate (**3d**). Light yellow oil, 67% (46.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.16 (m, 2H), 6.73 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.64 – 6.50 (m, 2H), 4.00 (s, 2H), 3.69 (s, 3H), 3.59 (t, *J* = 7.2 Hz, 1H), 3.05 (s, 3H), 2.80 – 2.72 (m, 1H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.89 – 1.73 (m, 2H), 1.59 (p, *J* = 7.4 Hz, 2H), 1.29 – 1.18 (m, 2H), 1.1 (d, J = 7.2 Hz, 3H), 1.1 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 208.9, 170.2, 148.8, 129.3, 117.2, 111.9, 62.8, 56.6, 52.3, 40.6, 39.8, 38.9, 28.0, 27.0, 22.9, 18.3, 18.1. IR ν (cm^{-1}): 2950, 1743, 1713, 1672, 1602, 1508, 1438, 1263, 730, 695. HRMS (ESI^{+}) calculated for $C_{20}H_{30}NO_4$ (M + H)$^{+}$: 348.2175, found: 348.2167.

1-(Methyl(phenyl)amino)-7-(prop-1-en-1-yloxy)heptan-2-one (**3e**). Light yellow oil, 80% (44 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.17 (m, 2H), 6.73 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.65 – 6.56 (m, 2H), 5.97 – 5.83 (m, 1H), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.00 (s, 2H), 3.94 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 3.05 (s, 3H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.66 – 1.51 (m, 4H), 1.40 – 1.28 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.4, 148.8, 135.0, 129.3, 117.2, 116.8, 111.9, 71.8, 70.1, 62.8, 39.8, 39.4, 29.5, 25.8, 23.2. IR ν (cm^{-1}): 3055, 2940, 1732, 1674, 1595, 1497, 1265, 932, 733, 696. HRMS (ESI^{+}) calculated for $C_{17}H_{26}NO_2$ (M + H)$^{+}$: 276.1963, found: 276.1957.

7-(Benzyloxy)-1-(methyl(phenyl)amino)heptan-2-one (**3f**). Light yellow oil, 67% (43.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 5H), 7.26 – 7.15 (m, 2H), 6.73 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.64 – 6.55 (m, 2H), 4.47 (s, 2H), 3.99 (s, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.03 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.59 (p, *J* = 8.0, 7.6 Hz, 4H), 1.40 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.4, 148.9, 138.6, 129.3, 128.4, 127.7, 127.5, 117.2, 112.0, 72.9, 70.1, 62.8, 39.8, 39.4, 29.5, 25.9, 23.2. IR ν (cm^{-1}): 2942, 1732, 1669, 1597, 1496, 1269, 1093, 733, 698. HRMS (ESI^{+}) calculated for $C_{21}H_{28}NO_2$ (M + H)$^{+}$: 326.2120, found: 326.2113.

7-(Methyl(phenyl)amino)-6-oxoheptyl benzoate (**3g**). Light yellow oil, 53% (36 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.60 – 7.50 (m, 1H), 7.48 – 7.36 (m, 2H), 7.25 – 7.19 (m, 2H), 6.73 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.65 – 6.56 (m, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 4.00 (s, 2H), 3.05 (s, 3H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.47 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.2, 166.6, 148.8, 132.9, 130.4, 129.6, 129.3, 128.4, 117.3, 111.9, 64.8, 62.9, 39.8, 39.3, 28.6, 25.7, 22.9. IR ν (cm^{-1}): 2944, 1713, 1602, 1507, 1272, 1117, 731, 698. HRMS (ESI^{+}) calculated for $C_{21}H_{26}NO_3$ (M + H)$^{+}$: 340.1912, found: 340.1907.

7-(5-Bromo-2-fluorophenoxy)-1-(methyl(phenyl)amino)heptan-2-one (**3h**). Light yellow oil, 59% (48.1 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.17 (m, 2H), 7.04 (dd, *J* = 7.5, 2.3 Hz, 1H), 7.03 – 6.94 (m, 1H), 6.92 (dd, *J* = 10.7, 8.6 Hz, 1H), 6.74 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.65 – 6.56 (m, 2H), 4.01 (s, 2H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.05 (s, 3H), 2.46 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.72 (m, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.50 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 153.1, 150.6, 148.8, 147.9 (d, *J* = 11.6 Hz), 129.3, 123.6 (d, *J* = 6.7 Hz), 118.0 (d, *J* = 2.1 Hz), 117.4, 117.3, 117.2, 116.3 (d, *J* = 3.8 Hz), 111.9, 69.3, 62.9, 39.8, 39.3, 28.8, 25.5, 22.9. IR ν(cm^{-1}): 2947, 1726, 1602, 1498, 1258, 1202, 735, 693. HRMS (ESI$^+$) calculated for $C_{20}H_{24}BrFNO_2$ (M + H)$^+$: 408.0974, found: 408.0968.

7-(2,4-Dichlorophenoxy)-1-(methyl(phenyl) amino)heptan-2-one (**3i**). Light yellow oil, 65% (49.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 2.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.14 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.73 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.64 – 6.56 (m, 2H), 4.01 (s, 2H), 3.95 (t, *J* = 6.3 Hz, 2H), 3.05 (s, 3H), 2.46 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.53 – 1.40 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 153.4, 148.8, 129.9, 129.3, 127.5, 125.5, 123.7, 117.3, 114.0, 111.9, 69.1, 62.9, 39.8, 39.3, 28.8, 25.6, 22.9. IR ν(cm^{-1}): 2944, 1728, 1677, 1597, 1485, 1263, 729, 695. HRMS (ESI$^+$) calculated for $C_{20}H_{24}Cl_2NO_2$ (M + H)$^+$: 380.1184, found: 380.1177.

7-(Methyl(phenyl)amino)-6-oxoheptyl furan-2-carboxylate (**3j**). Light yellow oil, 64% (42.3 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 1H), 7.25 – 7.18 (m, 2H), 7.16 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.73 – 6.70 (m, 1H), 6.62 – 6.59 (m, 2H), 6.50 – 6.48 (m, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 4.00 (s, 2H), 3.05 (s, 3H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.68 – 1.59 (m, 2H), 1.45 – 1.34 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.2, 158.8, 148.8, 146.2, 144.8, 129.3, 117.8, 117.3, 111.9, 111.8, 64.7, 62.8, 39.8, 39.2, 28.5, 25.6, 22.9. IR ν(cm^{-1}): 2937, 1717, 1678, 1598, 1508, 1473, 1297, 1181, 1116, 734, 692. HRMS (ESI$^+$) calculated for $C_{19}H_{24}NO_4$ (M + H)$^+$: 330.1705 found (M + H)$^+$: 330.1698.

7-(Methyl(phenyl)amino)-6-oxoheptyl thiophene-2-carboxylate (**3k**). Light yellow oil, 65% (44.9 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.77 – 6.68 (m, 1H), 6.64 – 6.57 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 4.00 (s, 2H), 3.05 (s, 3H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.67 – 1.59 (m, 2H), 1.44 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.2, 162.3, 148.8, 133.9, 133.3, 132.3, 129.3, 127.8, 117.3, 111.9, 64.9, 62.9, 39.8, 39.3, 28.6, 25.6, 22.9. IR ν(cm^{-1}): 2943, 1702, 1599, 1506, 1418, 1259, 1094, 1074, 729, 695. HRMS (ESI$^+$) calculated for $C_{19}H_{24}NO_3S$ (M + H)$^+$: 346.1477 found: 346.1471.

7-(3-Acetyl-1H-indol-1-yl)-1-(methyl(phenyl)amino)heptan-2-one (**3l**). Light yellow oil, 58% (43.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 – 8.31 (m, 1H), 7.71 (s, 1H), 7.33 – 7.25 (m, 3H), 7.25 – 7.15 (m, 2H), 6.73 (td, *J* = 7.2, 1.0 Hz, 1H), 6.63 – 6.51 (m, 2H), 4.10 (t, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 3.02 (s, 3H), 2.51 (s, 3H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.83 – 1.79 (m, 2H), 1.60 – 1.57 (m, 2H), 1.31 – 1.22 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.2, 193.0, 148.8, 136.7, 134.9, 129.4, 126.4, 123.2, 122.7, 122.5, 117.3, 116.9, 111.9, 109.8, 62.9, 46.7, 39.8, 38.9, 29.6, 27.7, 26.3, 22.6. IR ν(cm^{-1}): 2932, 1719, 1637, 1601, 1526, 1506, 1389, 1208, 748, 690. HRMS (ESI$^+$) calculated for $C_{24}H_{29}N_2O_2$ (M + H)$^+$: 377.2229, found: 377.2223.

N,4-dimethyl-N-(7-(methyl(phenyl)amino)-6-oxoheptyl)benzenesulfonamide (**3m**). Light yellow oil, 67% (54 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.78 – 6.68 (m, 1H), 6.65 – 6.56 (m, 2H), 4.01 (s, 2H), 3.05 (s, 3H), 2.94 (t, *J* = 7.1 Hz,

2H), 2.66 (s, 3H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.65 – 1.54 (m, 2H), 1.53 – 1.44 (m, 2H), 1.37 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 148.8, 143.3, 134.5, 129.7, 129.3, 127.4, 117.2, 111.9, 62.8, 49.8, 39.8, 39.3, 34.6, 27.4, 26.1, 22.9, 21.5. IR ν (cm^{-1}): 2942, 1727, 1599, 1505, 1335, 1268, 1159, 729, 698. HRMS (ESI$^+$) calculated for $C_{22}H_{31}N_2O_3S$ (M + H)$^+$: 403.2055, found: 403.2048.

1-(Methyl(phenyl)amino)-7-tosylheptan-2-one (**3n**). colorless oil, 68% (50.9 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.74 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.62 – 6.53 (m, 2H), 3.97 (s, 2H), 3.03 (s, 3H), 3.02 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.42 (t, *J* = 6.4 Hz, 2H), 1.72 – 1.58 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.7, 148.7, 144.7, 136.1, 129.9, 129.4, 128.0, 117.4, 111.9, 62.9, 56.1, 39.8, 38.6, 22.3, 21.8, 21.7. IR ν (cm^{-1}): 2929, 1726, 1598, 1507, 1364, 1315, 1142, 732, 691. HRMS (ESI$^+$) calculated for $C_{20}H_{26}NO_3S$ (M + H)$^+$: 360.1633 found (M + H)$^+$: 360.1627.

2-(6-(Methyl(phenyl)amino)-5-oxohexyl)isoindoline-1,3-dione (**3o**). 62% (43.5 mg). Light yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.26 – 7.15 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.63 – 6.56 (m, 2H), 4.01 (s, 2H), 3.66 (t, *J* = 6.6 Hz, 2H), 3.05 (s, 3H), 2.49 (t, *J* = 6.8 Hz, 2H), 1.73 – 1.58 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.8, 168.4, 148.8, 133.9, 132.1, 129.3, 123.2, 117.2, 111.9, 62.8, 39.8, 38.6, 37.4, 27.9, 20.4. IR ν (cm^{-1}): 2939, 1769, 1707, 1601, 1499, 1398, 720, 695. HRMS (ESI$^+$) calculated for $C_{21}H_{23}N_2O_3$ (M + H)$^+$: 351.1708, found: 351.1702.

6-(Methyl(p-tolyl)amino)-5-oxohexanenitrile (**4a**). Light yellow oil, 62% (28.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 - 6.94 (m, 2H), 6.57 – 6.47 (m, 2H), 3.99 (s, 2H), 3.04 (s, 3H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 1.93 - 1.86 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.3, 146.6, 129.9, 126.8, 119.2, 112.3, 63.2, 40.1, 37.3, 20.2, 19.0, 16.4. IR ν (cm^{-1}): 2930, 2244, 1724, 1671, 1615, 1518, 1264, 731, 701. HRMS (ESI$^+$) calculated for $C_{14}H_{19}N_2O$ (M + H)$^+$: 231.1497, found: 231.1491.

6-((3-Chlorophenyl)(methyl)amino)-5-oxohexanenitrile (**4b**). Light yellow oil, 55% (27.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (t, *J* = 8.1 Hz, 1H), 6.76 – 6.66 (m, 1H), 6.58 (t, *J* = 2.3 Hz, 1H), 6.47 – 6.40 (m, 1H), 4.05 (s, 2H), 3.05 (s, 3H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.96 -1.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.7, 149.7, 135.3, 130.4, 119.1, 117.4, 112.0, 110.1, 62.4, 39.9, 37.3, 18.9, 16.4. IR ν (cm^{-1}): 2958, 2246, 1730, 1596, 1492, 1266, 988, 730, 704. HRMS (ESI$^+$) calculated for $C_{13}H_{16}ClN_2O$ (M + H)$^+$: 251.0951, found: 251.0944.

6-((2-Fluorophenyl)(methyl)amino)-5-oxohexanenitrile (**4c**). colorless oil, 64% (30 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 6.77 (m, 4H), 3.96 (s, 2H), 2.93 (s, 3H), 2.69 (t, *J* = 6.9 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.94 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.9, 154.2 (d, *J* = 242.4 Hz), 138.7 (d, *J* = 8.1 Hz), 124.6 (d, *J* = 3.3 Hz), 121.0 (d, *J* = 7.9 Hz), 119.2, 118.3 (d, *J* = 3.4 Hz), 116.3 (d, *J* = 21.2 Hz), 64.5 (d, *J* = 6.8 Hz), 40.8 (d, *J* = 1.2 Hz), 37.2, 19.1, 16.5. IR ν (cm^{-1}): 2973, 2246, 1717, 1612, 1505, 1264, 909, 733, 701. HRMS (ESI$^+$) calculated for $C_{13}H_{16}FN_2O$ (M + H)$^+$: 235.1246, found: 235.1240.

6-(Benzyl(phenyl)amino)-5-oxohexanenitrile (**4d**). Light yellow oil, 47% (27.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.33 (m , 2H), 7.30 – 7.13 (m, 5H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 – 6.54 (m, 2H), 4.62 (s, 2H), 4.07 (s, 2H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.92 - 1.85 (m, 2H). ^{13}C NMR

(101 MHz, Chloroform-*d*) δ 208.5, 148.4, 137.9, 129.5, 128.8, 127.4, 127.0, 119.1, 118.0, 112.6, 60.6, 55.9, 37.4, 19.0, 16.4. IR ν (cm^{-1}): 2987, 2253, 1732, 1597, 1505, 1267, 909, 727, 697. HRMS (ESI^+) calculated for $C_{19}H_{21}N_2O$ $(M + H)^+$: 293.1654, found: 293.1647.

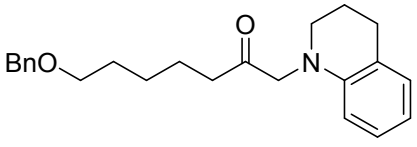
6-(Isopropyl(phenyl)amino)-5-oxohexanenitrile (**4e**). Light yellow oil, 34% (16.7 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.16 (m, 2H), 6.78 - 6.74 (m, 1H), 6.67 - 6.62 (m, 2H), 4.24 - 4.15 (m, 1H), 3.85 (s, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.92 - 1.85 (m, 2H), 1.18 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.3, 148.5, 129.5, 119.2, 118.1, 113.7, 54.6, 49.3, 36.8, 20.0, 19.1, 16.4. IR ν (cm^{-1}): 2978, 2246, 1711, 1596, 1501, 1264, 734, 699. HRMS (ESI^+) calculated for $C_{15}H_{21}N_2O$ $(M + H)^+$: 245.1654, found: 245.1647.

7-(Benzyloxy)-1-(methyl(m-tolyl)amino)heptan-2-one (**4f**). Light yellow oil, 57% (38.6 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.24 (m, 1H), 7.12 - 7.08 (m, 1H), 6.56 (d, *J* = 7.4 Hz, 1H), 6.42 -6.39 (m, 2H), 4.47 (s, 2H), 3.97 (s, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.02 (s, 3H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.29 (s, 3H), 1.63 - 1.55 (m, 4H), 1.40 – 1.30 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.7 148.9, 139.0, 138.6, 129.2, 128.4, 127.7, 127.5, 118.2, 112.8, 109.2, 72.9, 70.2, 62.9, 39.8, 39.4, 29.6, 25.9, 23.2, 21.9. IR ν (cm^{-1}): 2942, 1720, 1674, 1606, 1496, 1264, 1096, 911, 729, 700. HRMS (ESI^+) calculated for $C_{22}H_{30}NO_2$ $(M + H)^+$: 340.2276, found: 340.2270.

7-(Benzyloxy)-1-((4-fluorophenyl)(methyl)amino)heptan-2-one (**4g**). Light yellow oil, 77% (53 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 4H), 7.31 – 7.23 (m, 1H), 6.97 – 6.84 (m, 2H), 6.55 – 6.48 (m, 2H), 4.48 (s, 2H), 3.96 (s, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 2.99 (s, 3H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.53 (m, 4H), 1.40 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.9, 155.7 (d, *J* = 235.8 Hz), 145.6 (d, *J* = 1.8 Hz), 138.6, 128.4, 127.7, 127.6, 115.7 (d, *J* = 22.2 Hz), 113.1 (d, *J* = 7.4 Hz), 72.9, 70.1, 63.2, 40.2, 39.5, 29.5, 25.9 23.2. IR ν (cm^{-1}): 2937, 1728, 1675, 1510, 1267, 1229, 1105, 729, 700. HRMS (ESI^+) calculated for $C_{21}H_{27}FNO_2$ $(M + H)^+$: 344.2026, found: 344.2018.

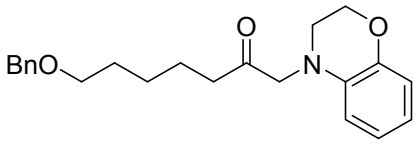
3-((7-(Benzyloxy)-2-oxoheptyl)(phenyl)amino)propanenitrile (**4h**). Light yellow oil, 33% (24 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 - 7.30 (m, 4H), 7.31 – 7.27 (m, 1H), 7.27 – 7.17 (m, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.56 – 6.47 (m, 2H), 4.49 (s, 2H), 4.15 (s, 2H), 3.72 (t, *J* = 7.0 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.54 (m, 4H), 1.44 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.3, 146.1, 138.6, 129.7, 128.4, 127.7, 127.6, 118.4, 112.3, 72.9, 70.1, 61.2, 48.4, 39.5, 29.5, 25.9, 23.3, 16.2. IR ν (cm^{-1}): 2939, 2252, 1723, 1599, 1505, 1264, 730, 700. HRMS (ESI^+) calculated for $C_{23}H_{29}N_2O_2$ $(M + H)^+$: 365.2229, found: 365.2221.

7-(Benzyloxy)-1-(cyclohexyl(phenyl)amino)heptan-2-one (**4i**). colorless oil, 36% (28.4 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.25 (m, 1H), 7.21 - 7.17 (m, 2H), 6.73 - 6.69 (m, 1H), 6.63 – 6.54 (m, 2H), 4.48 (s, 2H), 3.88 (s, 2H), 3.68 – 3.62 (m, 1H), 3.44 (t, *J* = 6.5 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.98 – 1.76 (m, 4H), 1.71 - 1.54 (m, 5H), 1.44 – 1.07 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.6, 148.6, 138.6, 129.3, 128.4, 127.6, 127.5, 117.3, 113.1, 72.9, 70.2, 57.7, 55.7, 38.8, 30.7, 29.5, 26.1, 25.9 25.8, 23.3. IR ν (cm^{-1}): 2929, 1708, 1601, 1503, 1264, 906, 730, 699. HRMS (ESI^+) calculated for $C_{26}H_{36}NO_2$ $(M + H)^+$: 394.2746, found: 394.2740.



7-(Benzyloxy)-1-(3,4-dihydroquinolin-1(2H)-yl)heptan-2-one (**4j**). Light yellow oil, 55% (38.6 mg). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 - 7.29 (m, 4H), 7.28 - 7.25 (m, 1H), 7.02 – 6.92 (m, 2H), 6.60 (t,

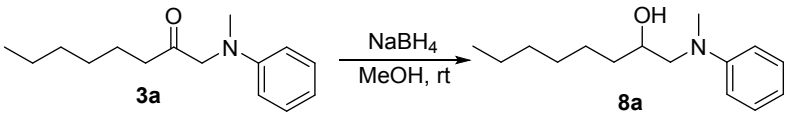
J = 7.3 Hz, 1H), 6.24 (d, *J* = 8.1 Hz, 1H), 4.48 (s, 2H), 3.90 (s, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.34 (t, *J* = 5.7 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.03 - 1.97 (m, 2H), 1.63 - 1.56 (m, 4H), 1.42 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.8, 144.9, 138.6, 129.3, 128.4, 127.7, 127.5, 127.2, 122.5, 116.8, 110.2, 72.9, 70.2, 61.8, 51.1, 39.4, 29.6, 27.9, 25.9, 23.2, 22.3. IR ν 2928, 1711, 1603, 1502, 1264, 1104, 911, 732, 697. HRMS (ESI$^+$) calculated for $C_{23}H_{30}NO_2$ (M + H)$^+$: 352.2276, found: 352.2269.



7-(Benzyloxy)-1-(2,3-dihydro-4H-benzo[b][1,4]oxazin-4-yl)heptan-2-one (**4k**). Light yellow oil, 40% (28.3 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 - 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 6.85 – 6.72 (m, 2H), 6.66 - 6.62 (m, 1H), 6.37 -6.33 (m, 1H), 4.48 (s, 2H), 4.32 – 4.21 (m, 2H), 3.93 (s, 2H), 3.45 (t, *J* = 6.5 Hz, 2H), 3.43 – 3.38 (m, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.66 – 1.54 (m, 4H), 1.41 - 1.35 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.2, 143.9, 138.6, 134.6, 128.4, 127.7, 127.5, 121.7, 118.4, 116.6, 111.5, 72.9, 70.1, 64.5, 60.8, 48.6, 39.7, 29.5, 25.9, 23.3. IR ν 2939, 1720, 1673, 1605, 1503, 1266, 1059, 729, 699. HRMS (ESI$^+$) calculated for $C_{22}H_{28}NO_3$ (M + H)$^+$: 354.2069 found (M + H)$^+$: 354.2062.

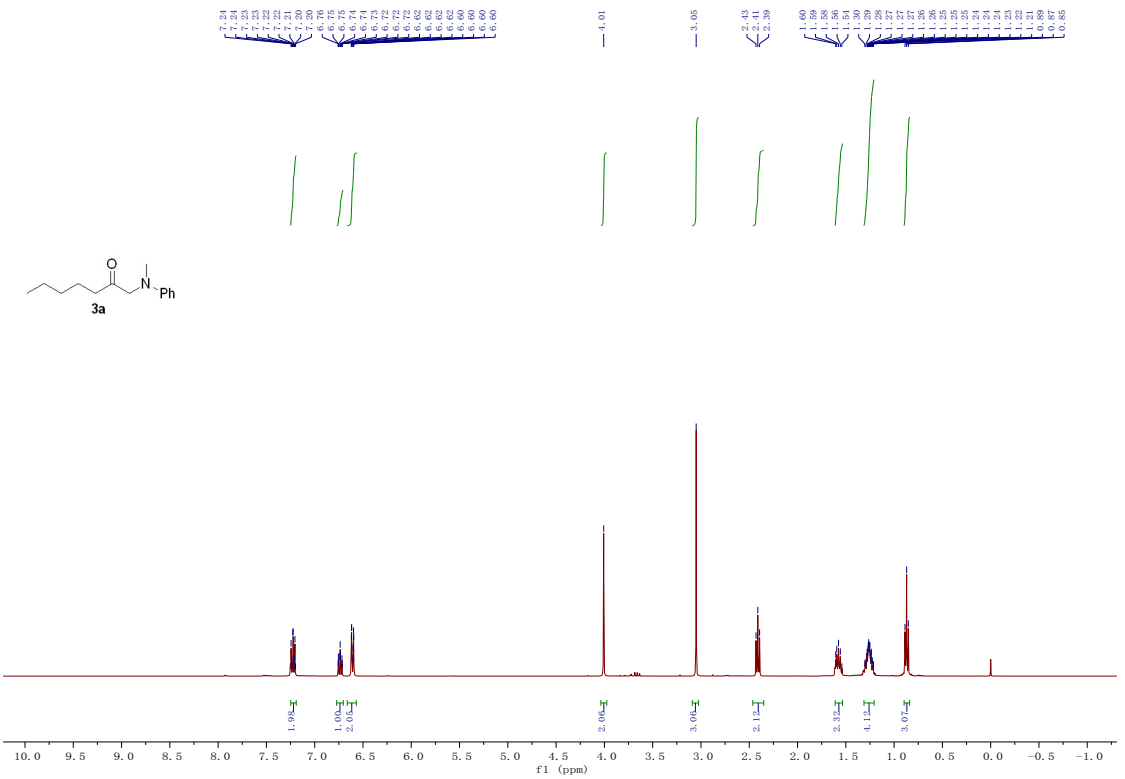
7-(Benzyloxy)-1-(1H-imidazol-1-yl)heptan-2-one (**4l**). Light yellow oil, 60% (34.3 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 - 8.42 (m, 1H), 8.39 – 8.33 (m, 1H), 7.47 - 7.44 (m, 1H), 7.28 -7.23 (m, 3H), 7.21 – 7.15 (m, 2H), 4.41 (s, 2H), 3.61 (s, 2H), 3.37 (t, *J* = 6.5 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 1.59 – 1.47 (m, 4H), 1.35 – 1.22 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.96, 149.3, 147.3, 137.5, 136.1, 128.9, 127.3, 126.6, 126.5, 122.5, 71.9, 69.1, 45.6, 41.4, 28.5, 24.7, 22.4. IR ν (cm^{-1}): 2940, 1714, 1576, 1479, 1425, 1266, 909, 729, 699. HRMS (ESI$^+$) calculated for $C_{17}H_{23}N_2O_2$ (M + H)$^+$: 287.1759, found: 287.1752.

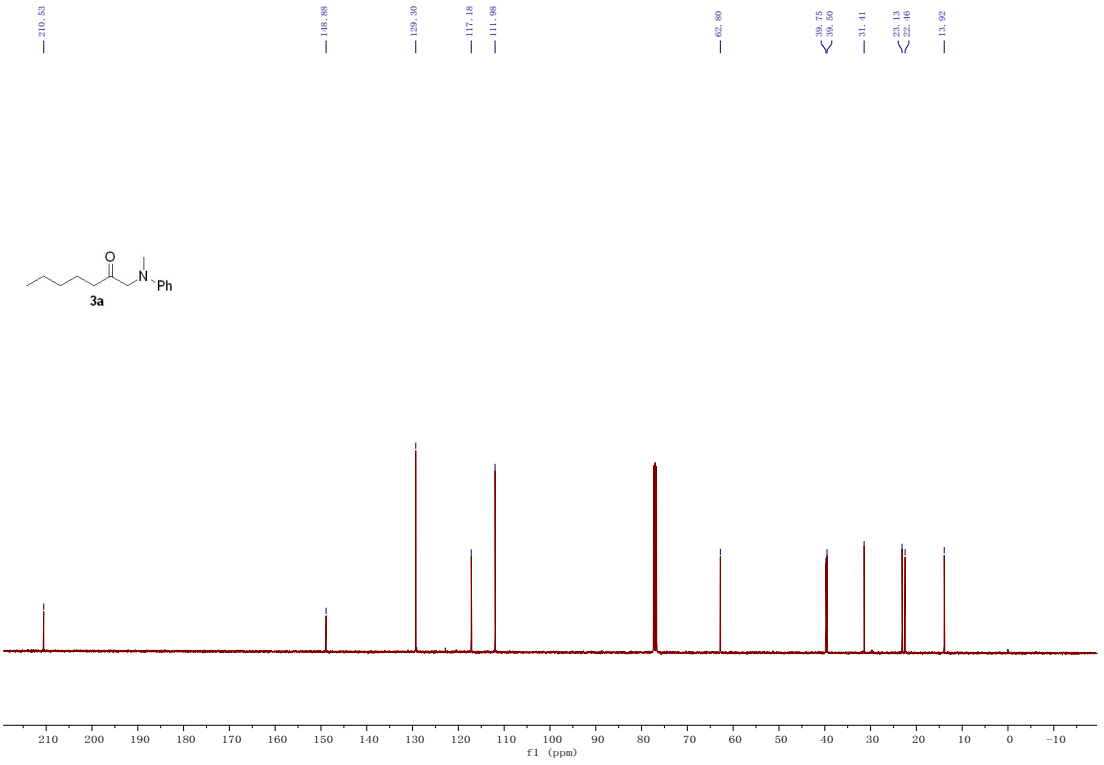
3. Further transformation of α-amino ketone

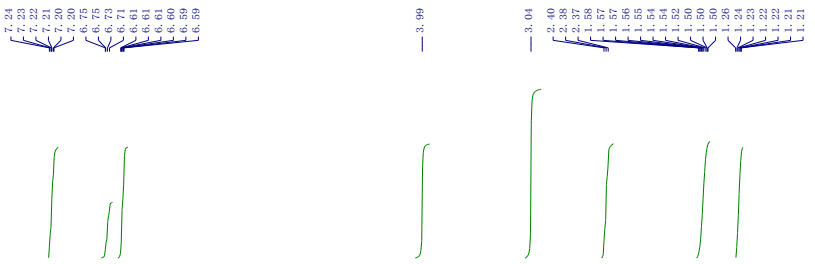


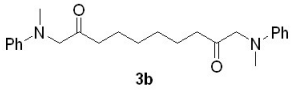
Under argon protection, a solution of α-amino ketone **3a** (0.2 mmol, 1 equiv) in MeOH (2 mL) and $NaBH_4$ (0.3 mmol, 1.5 equiv) were transferred into a glass reactor, the reaction mixture was stirred at room temperature until the total consumption of the starting material **3a**. After that, excess solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography to afford the desired product **8a** as a light-yellow oil in 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.19 (m, 2H), 6.83 - 6.77 (m, 2H), 6.78 - 6.73 (m, 1H), 3.93 - 3.86 (m, 1H), 3.28 - 3.15 (m , 2H), 2.94 (s, 3H), 2.26 (s, 1H), 1.55 - 1.42 (m, 3H), 1.43 – 1.21 (m, 7H), 0.93 – 0.85 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 129.2, 117.5, 113.4, 69.3, 60.7, 39.3, 34.6, 31.8, 29.5, 25.7, 22.6, 14.1. HRMS (ESI$^+$) calculated for $C_{15}H_{26}NO$ (M + H)$^+$: 235.1936, found: 235.1943.

4. Copies of NMR Spectra









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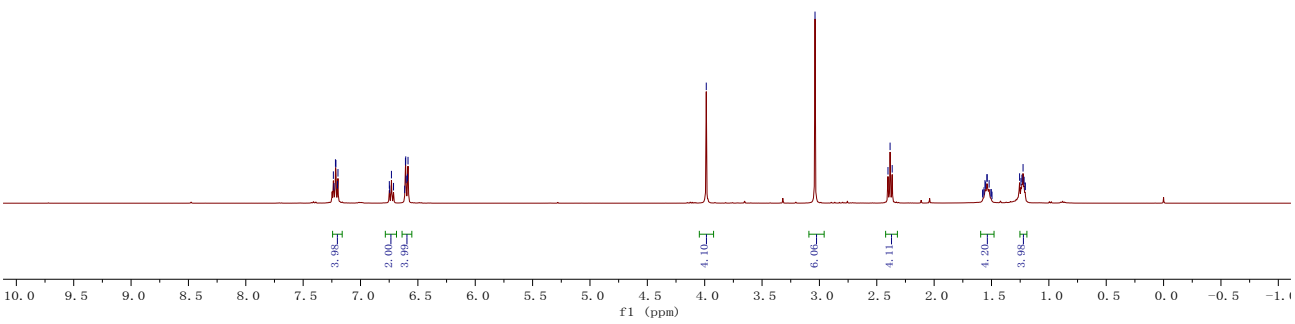

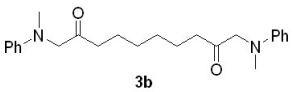

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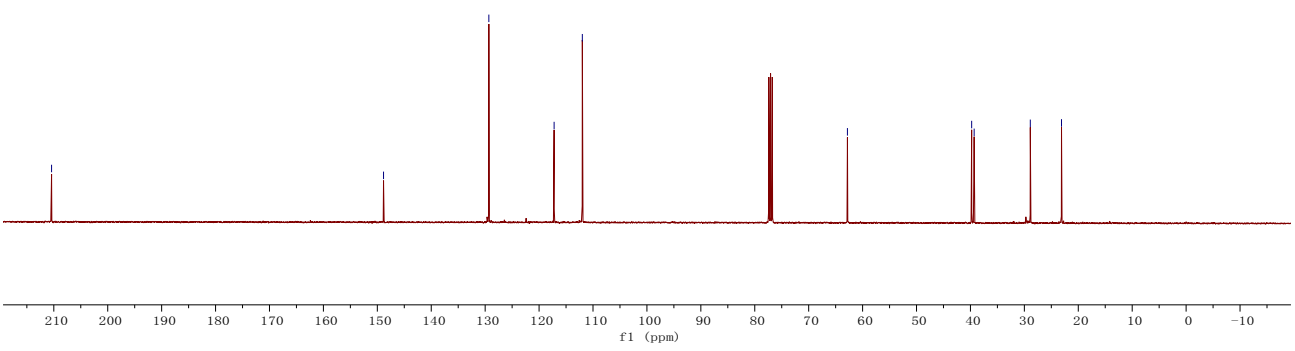

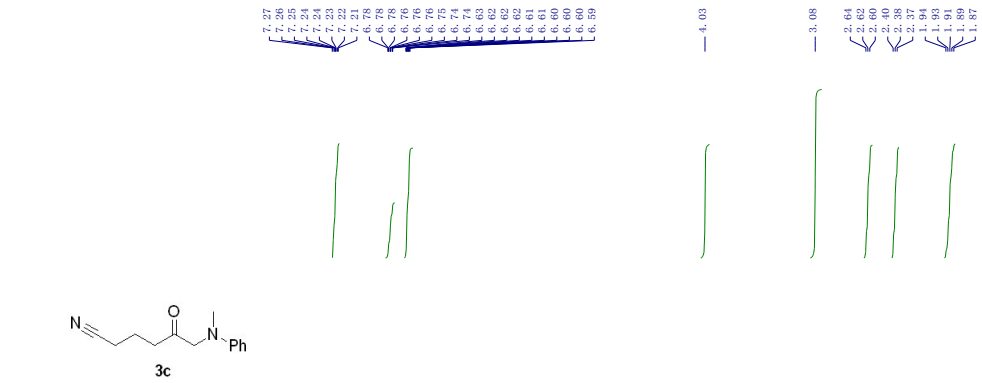
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2.62
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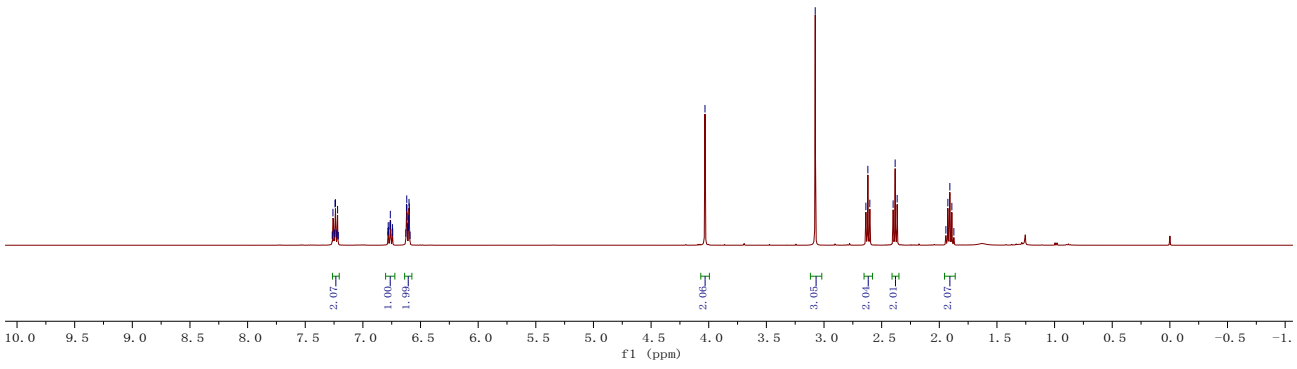
1.87

N
O
N
Ph

3c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5.0
4.5
4.0
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2.5
2.0
1.5
1.0
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−1.
f1 (ppm)


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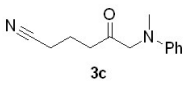
16.43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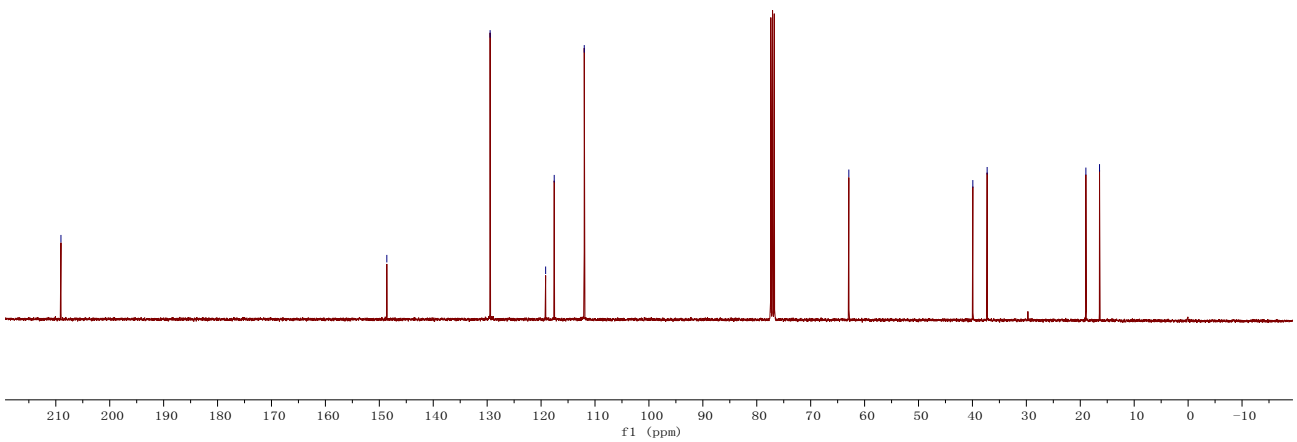
O
N
Ph

3c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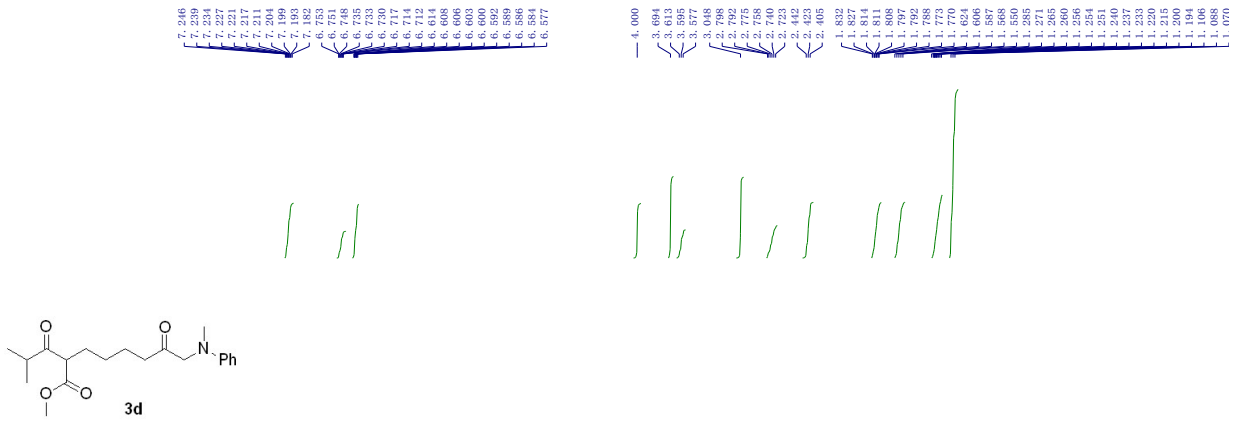
f1 (ppm)



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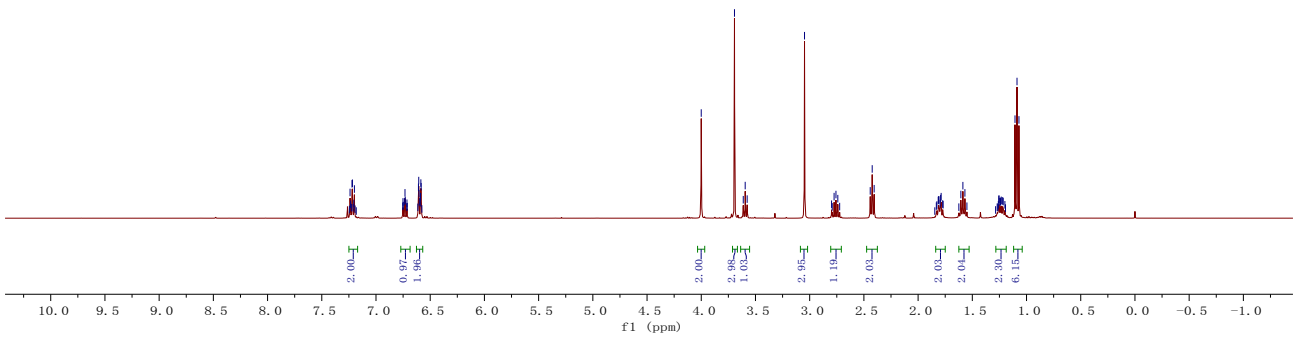

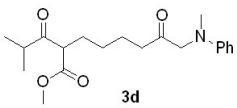

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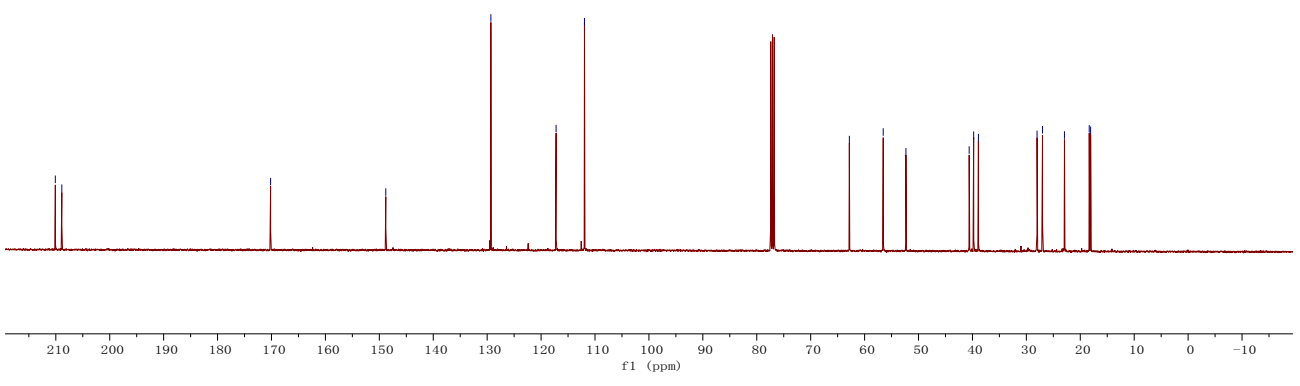

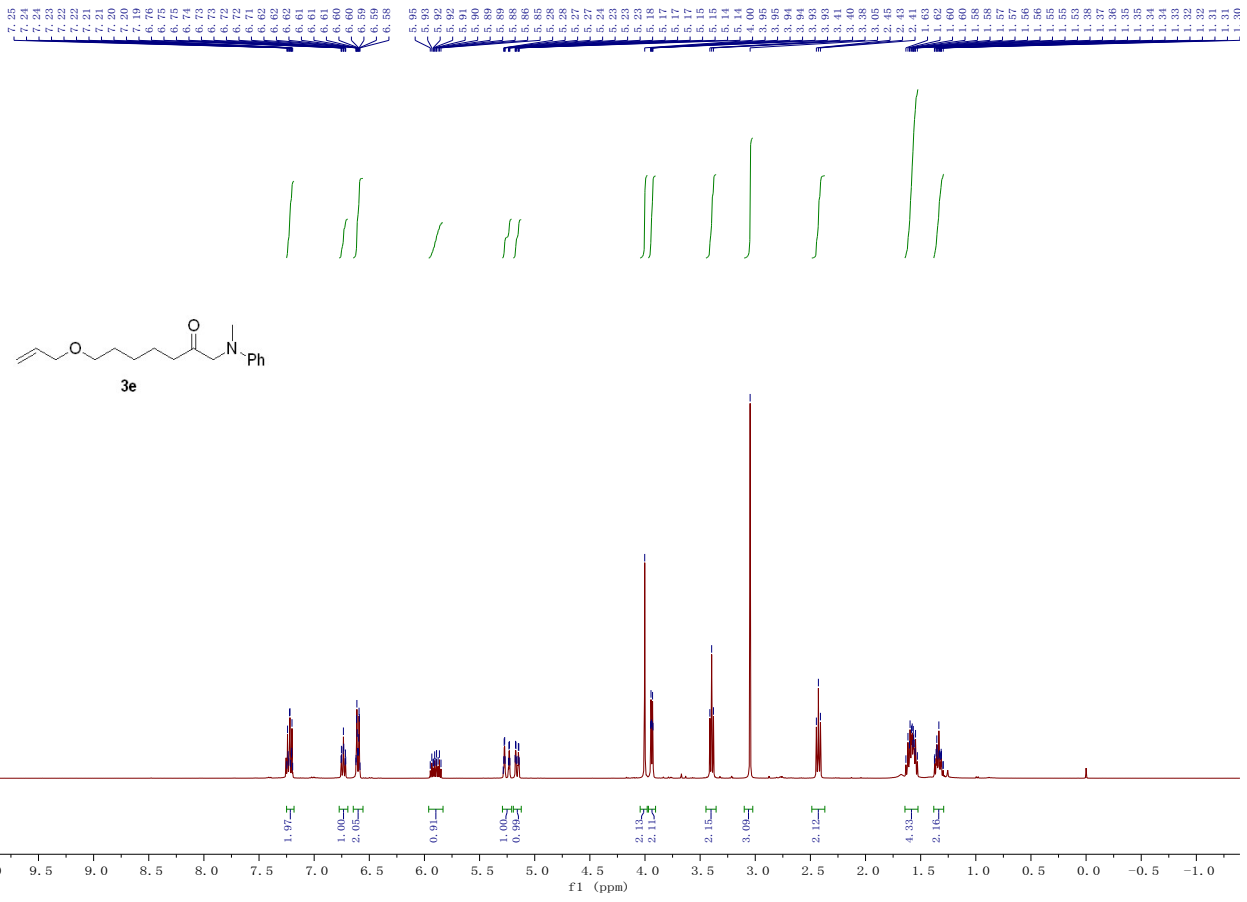
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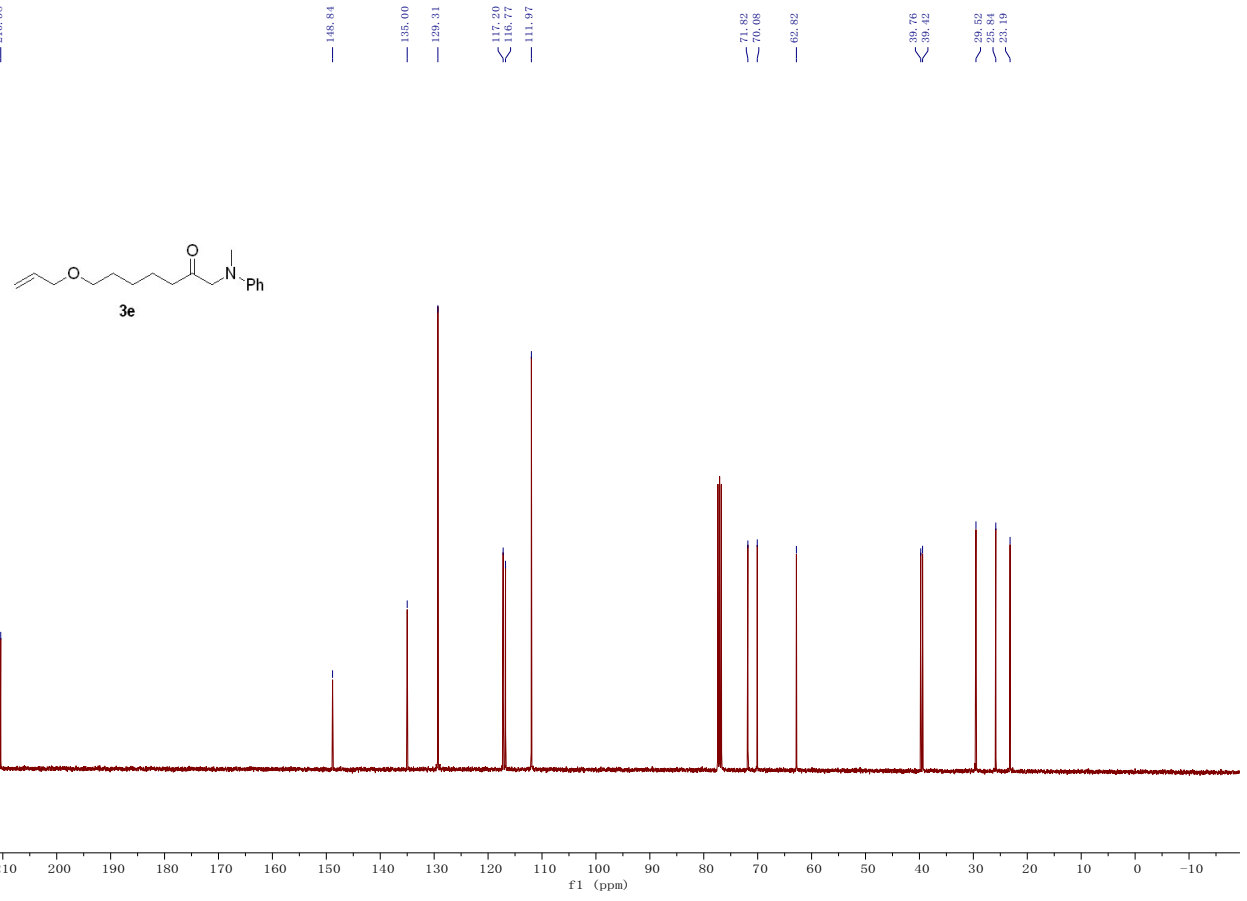
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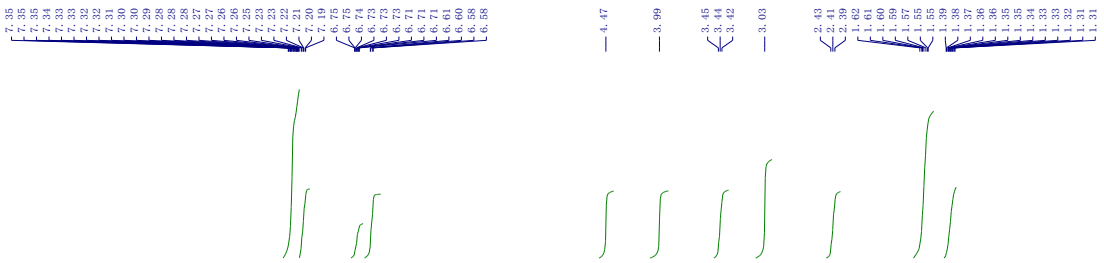
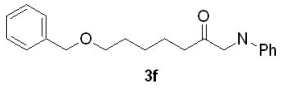
f1 (ppm)





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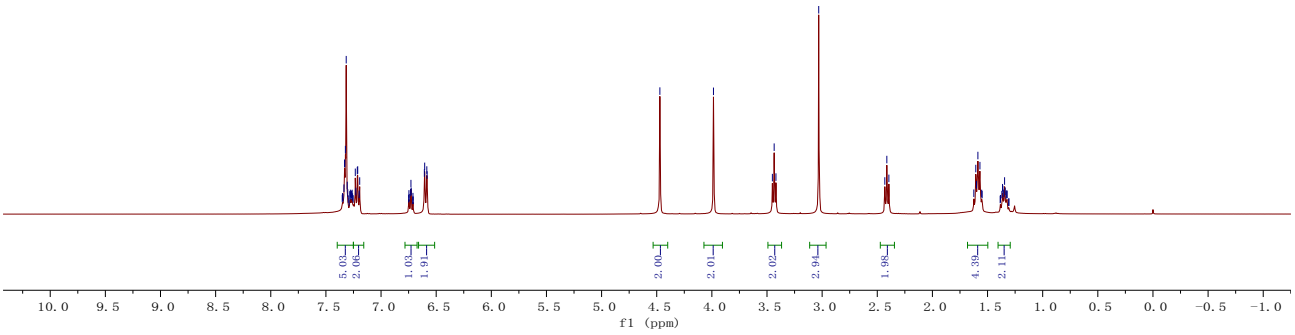

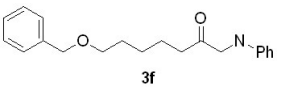

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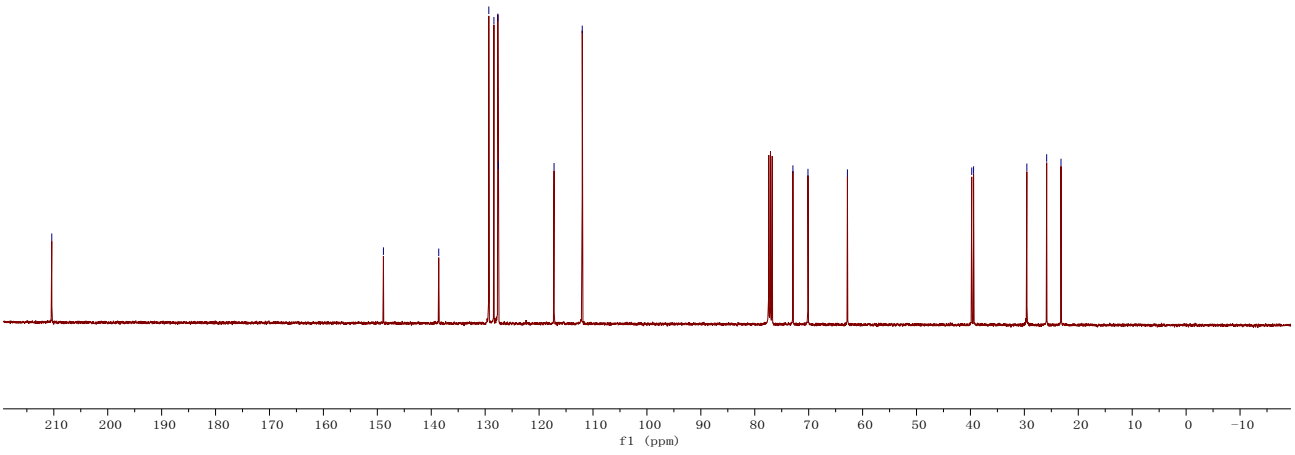

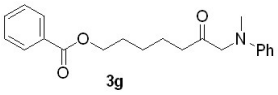

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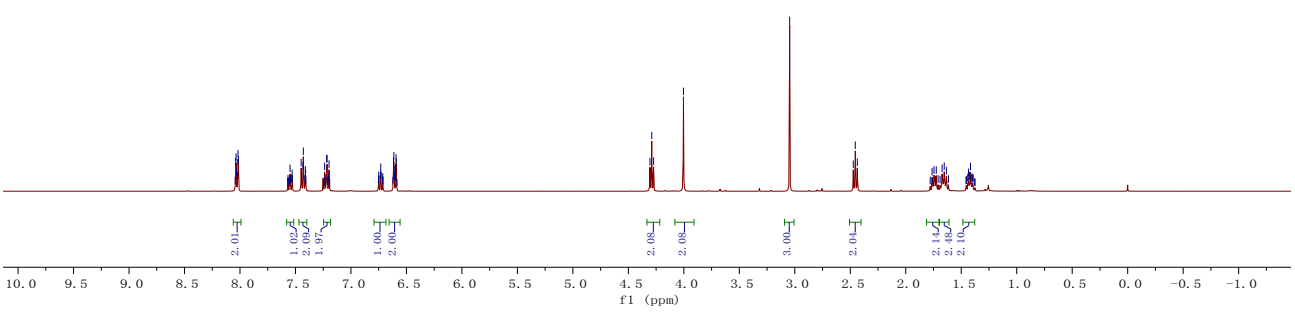
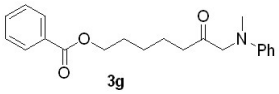
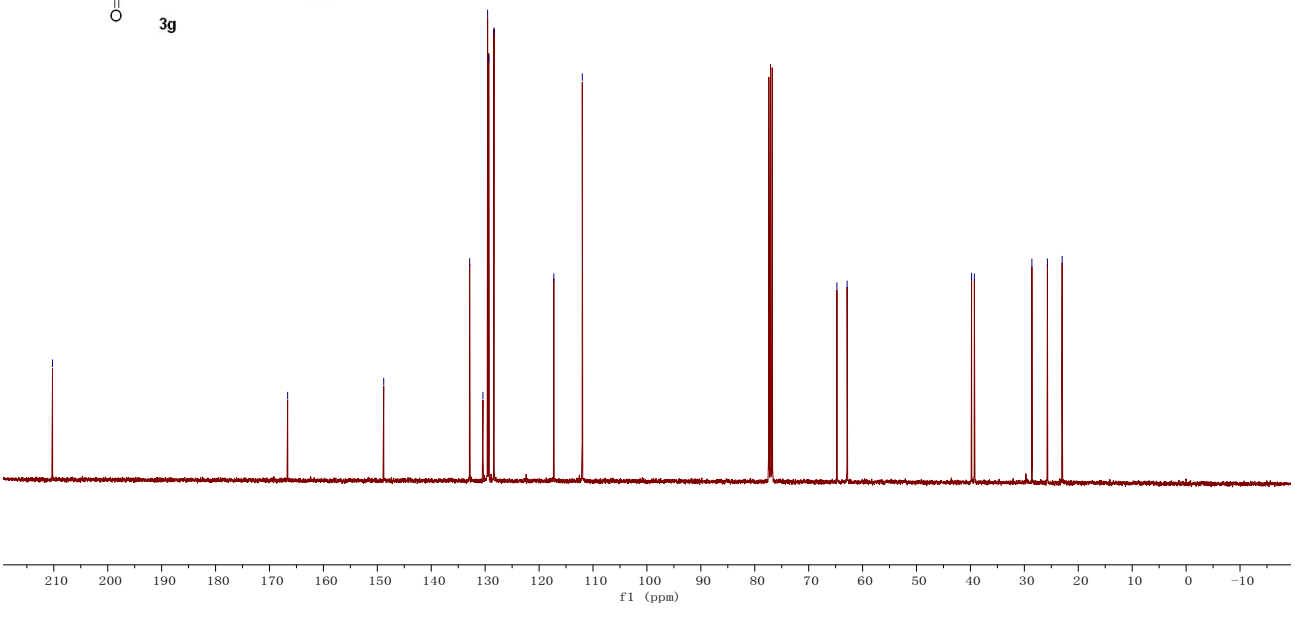
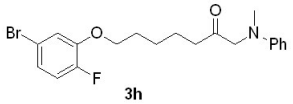


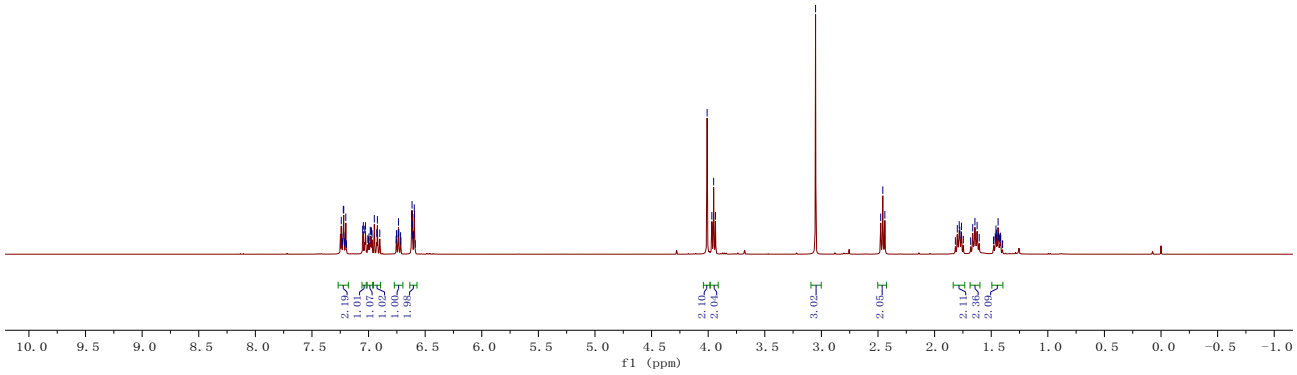


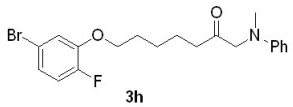
3g



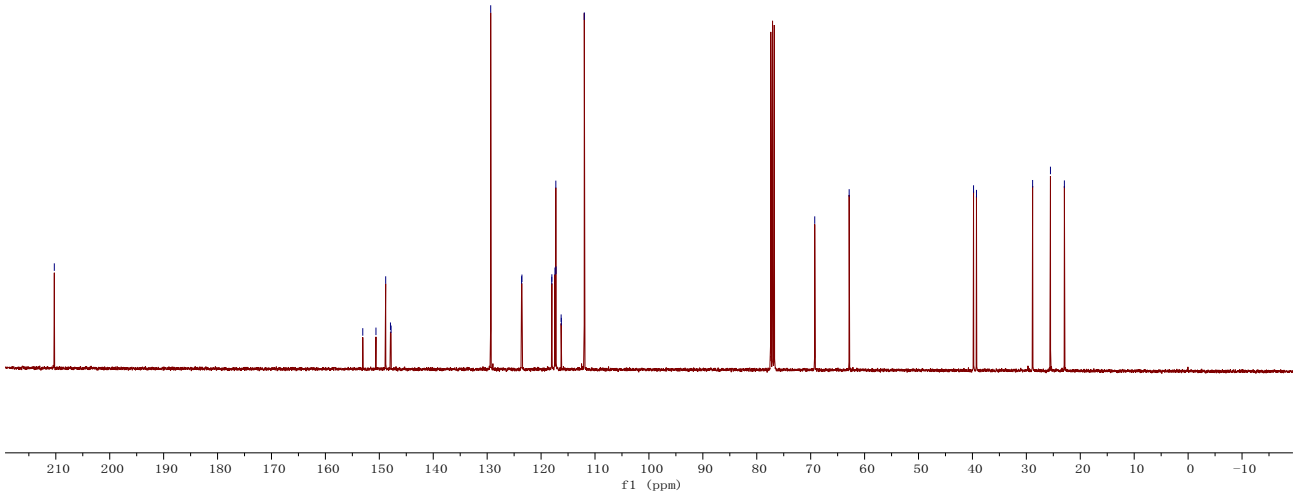

Br
O
O
N
Ph
F

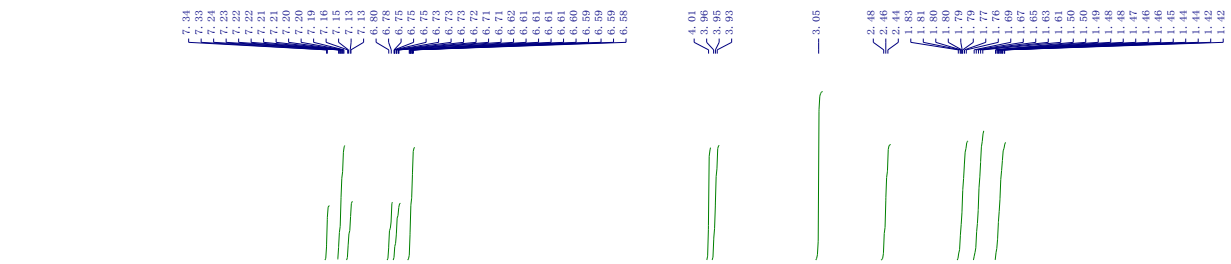
3h

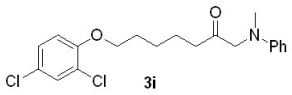

2.19
1.01
1.07
1.02
1.00
1.98
2.10
2.04
3.02
2.05
2.11
2.36
2.09
f1 (ppm)


Br
O
O
N
Ph
F

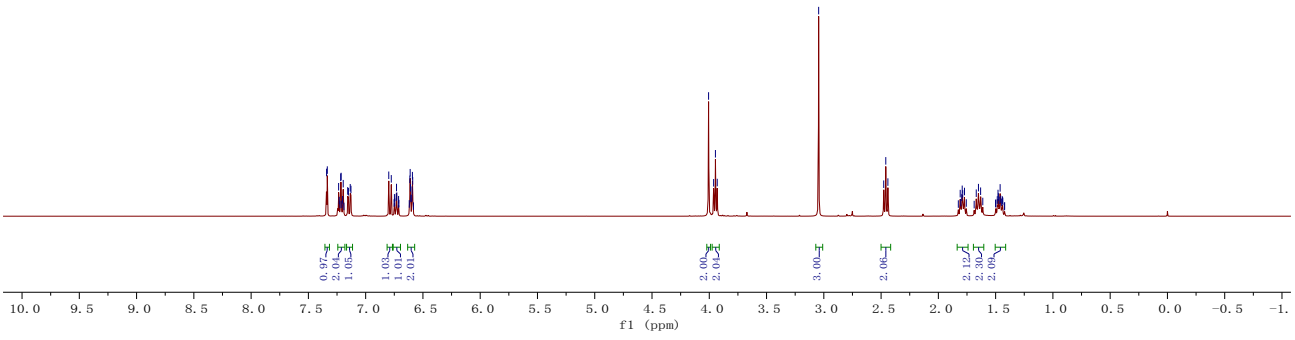
3h

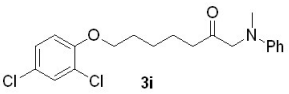

f1 (ppm)



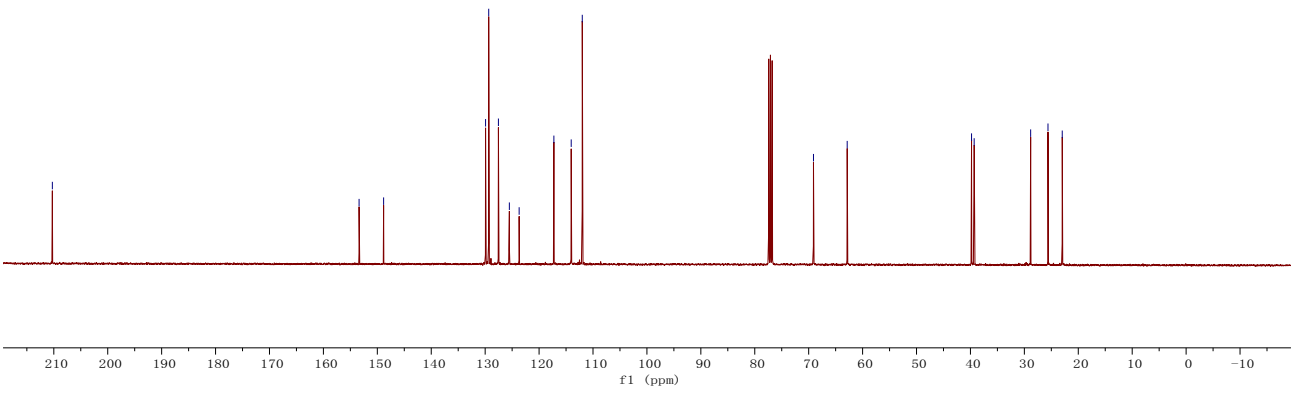


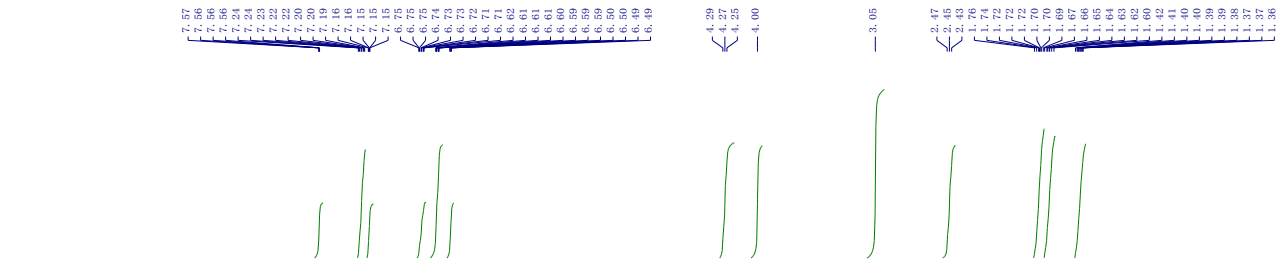
3i

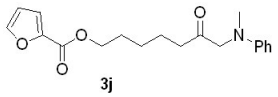




3i







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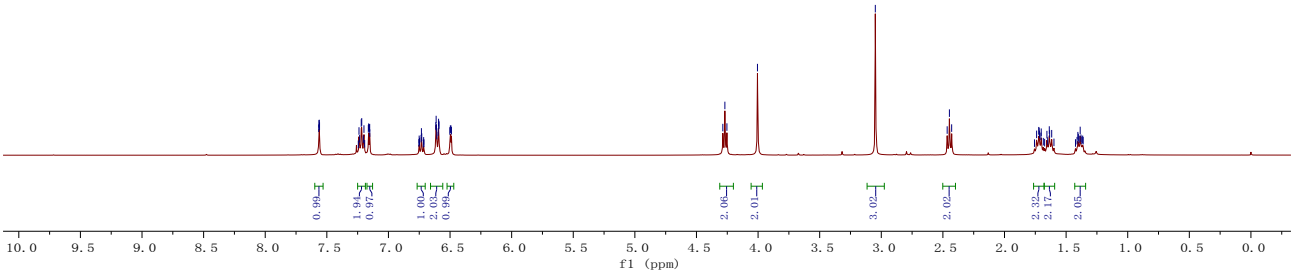

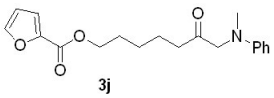

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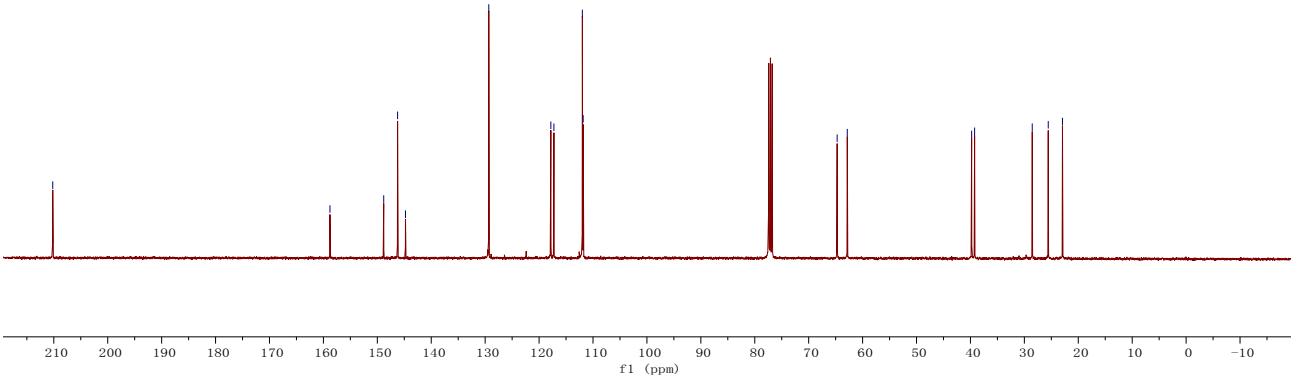
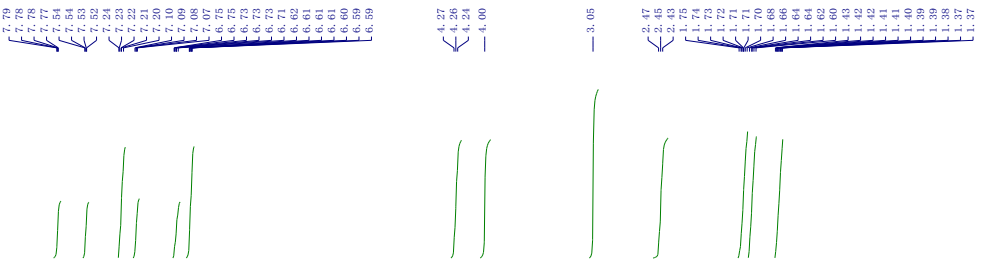
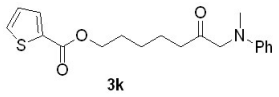
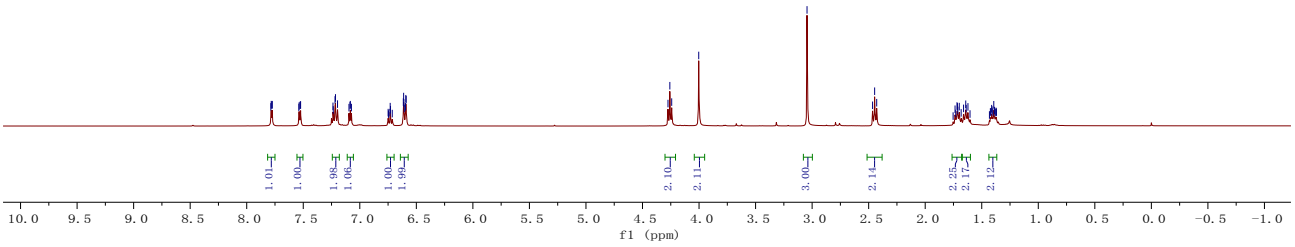
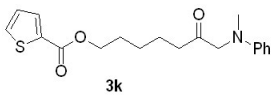




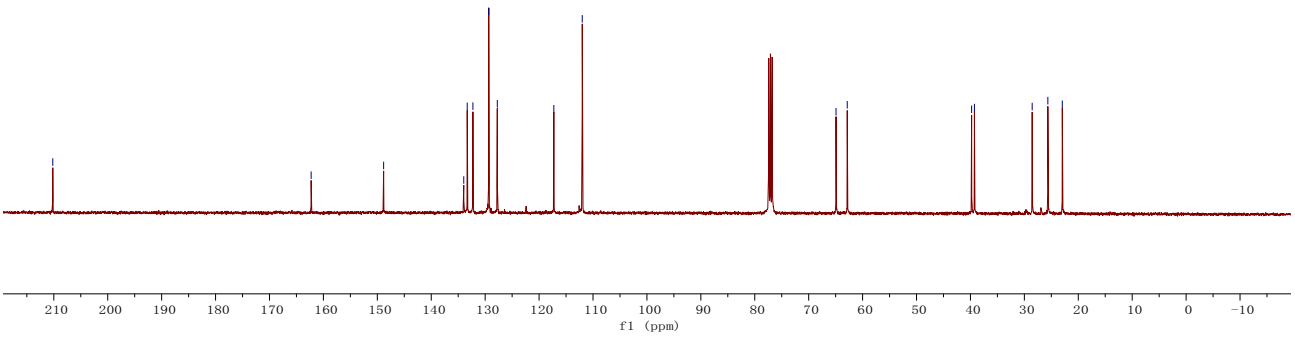


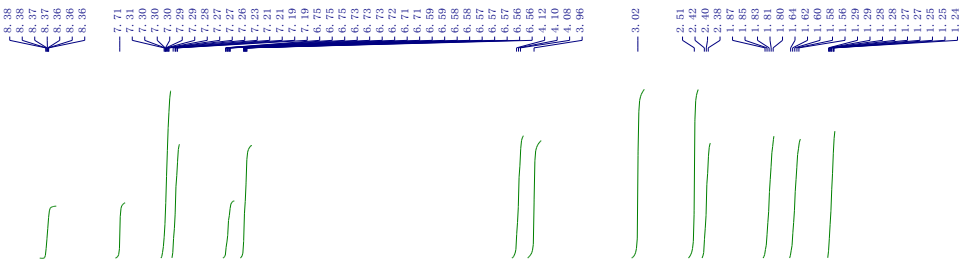
3k

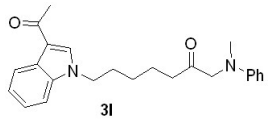




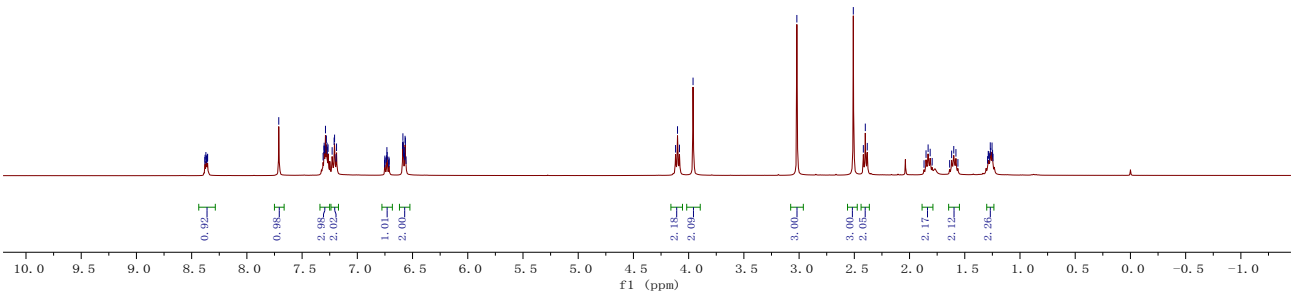
3k

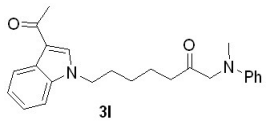




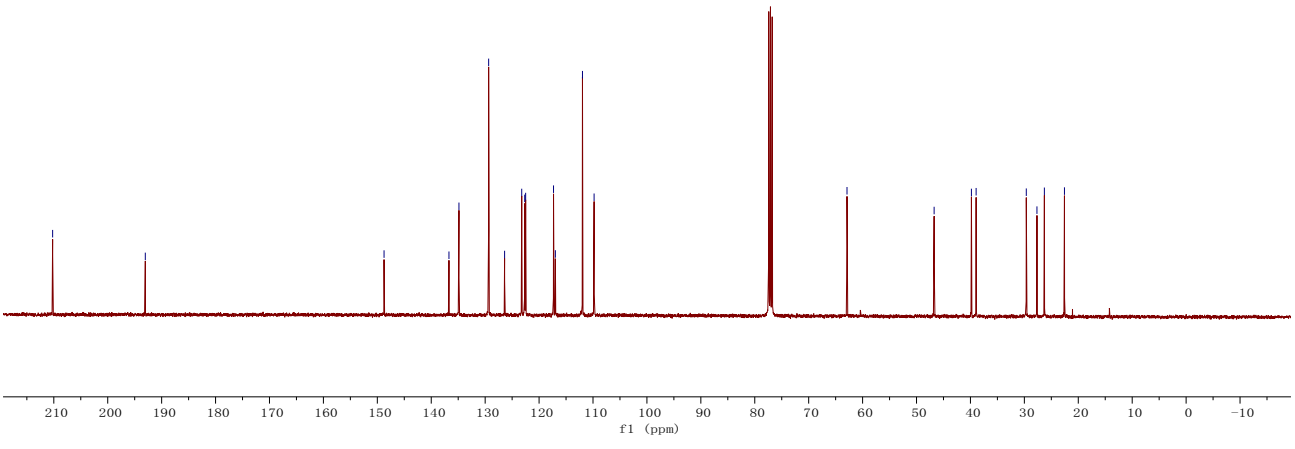


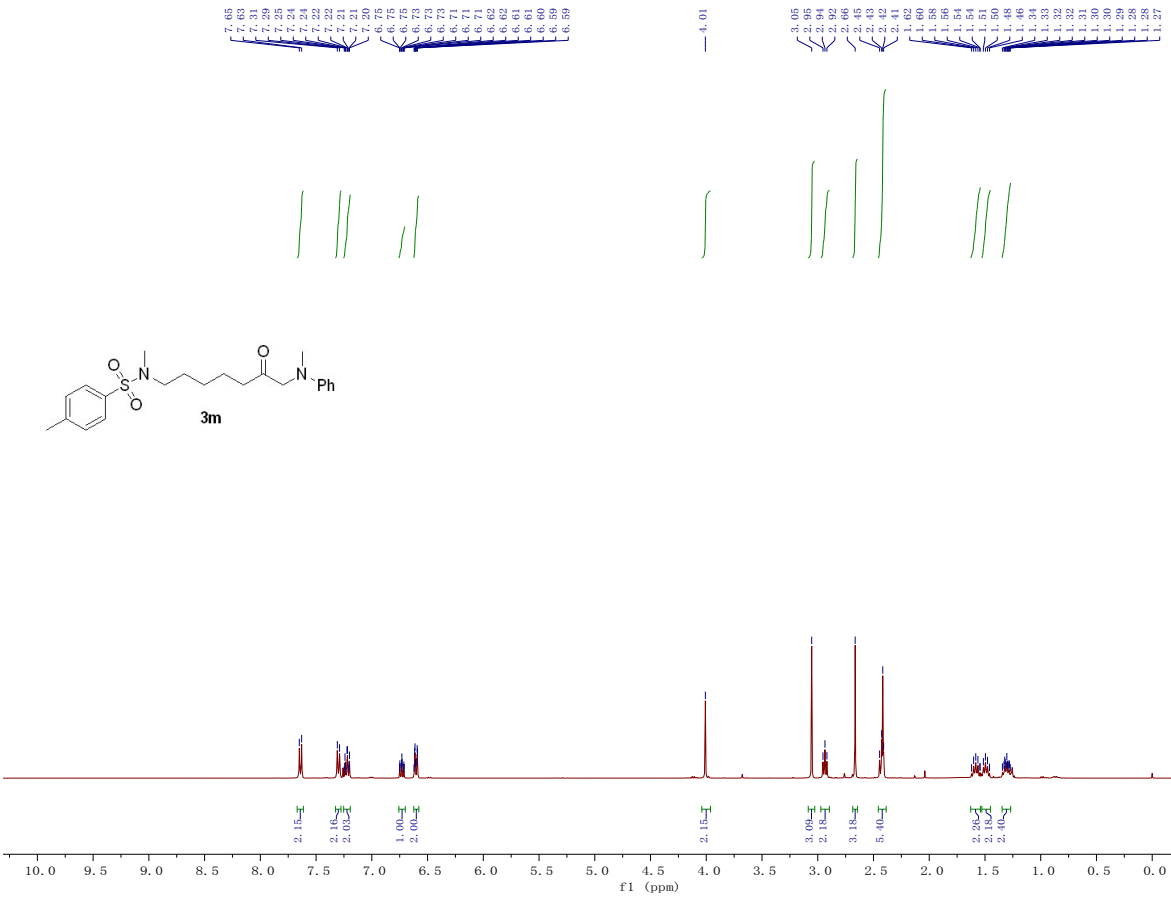
3l

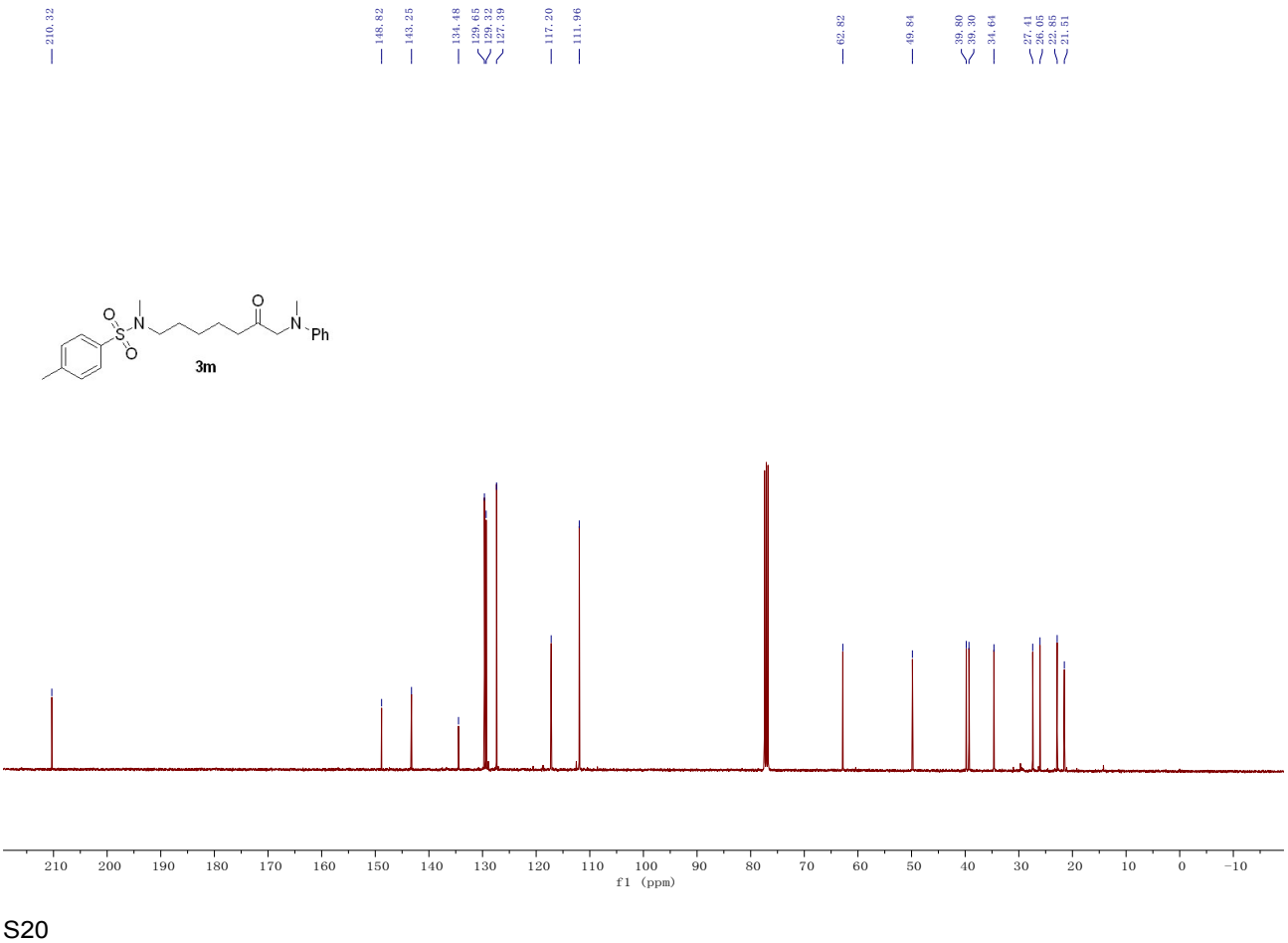


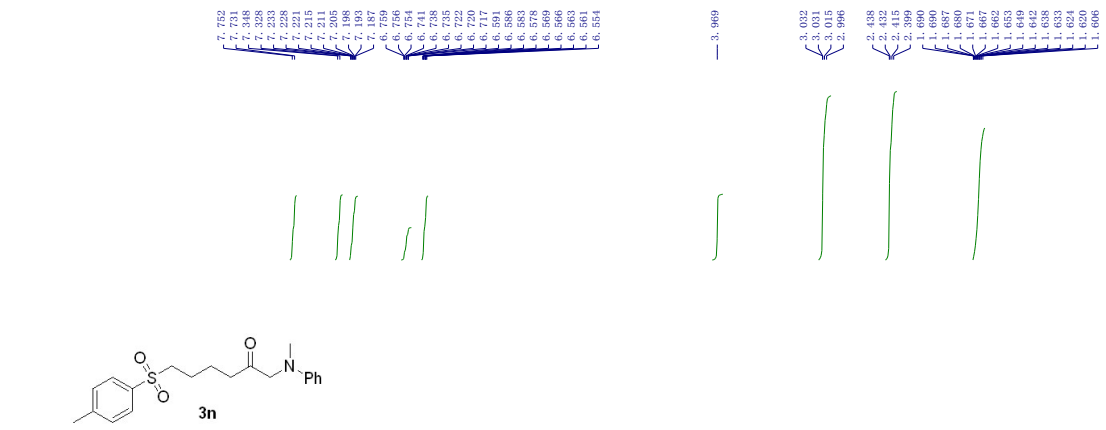


3l




7.65
7.63
7.31
7.29
7.25
7.24
7.22
7.21
7.20
6.75
6.73
6.71
6.62
6.61
6.60
6.59
4.01
3.05
2.95
2.94
2.92
2.66
2.45
2.43
2.42
2.41
1.62
1.60
1.58
1.56
1.54
1.51
1.50
1.48
1.46
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
3m
2.15
2.16
2.03
1.00
2.00
2.15
3.09
2.18
3.18
5.40
2.26
2.18
2.40
f1 (ppm)


210.32
148.82
143.25
134.48
129.65
129.32
127.39
117.20
111.96
62.82
49.84
39.80
39.30
34.64
27.41
26.05
22.85
21.51
3m
f1 (ppm)


7.752
7.731
7.348
7.328
7.233
7.228
7.221
7.215
7.211
7.205
7.198
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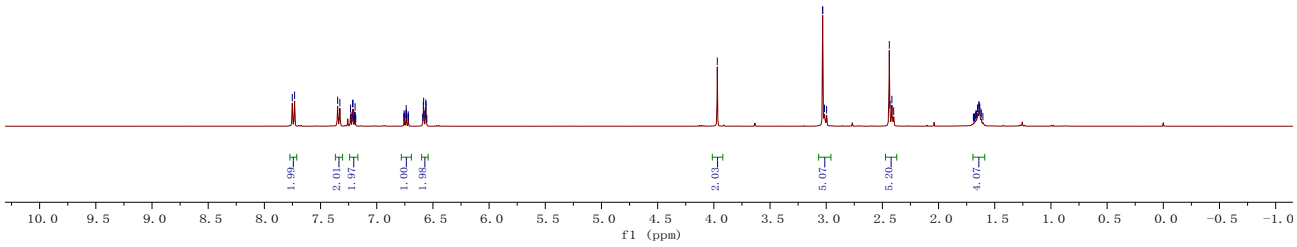
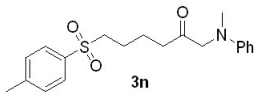
7.187
6.759
6.756
6.754
6.741
6.738
6.735
6.722
6.720
6.717
6.591
6.586
6.583
6.578
6.573
6.569
6.566
6.563
6.561
6.554
3.969
3.032
3.031
3.015
2.996
2.438
2.432
2.415
2.399
1.690
1.690
1.687
1.680
1.671
1.667
1.662
1.655
1.649
1.642
1.638
1.633
1.624
1.620
1.606

O
O
S
O
N
Ph

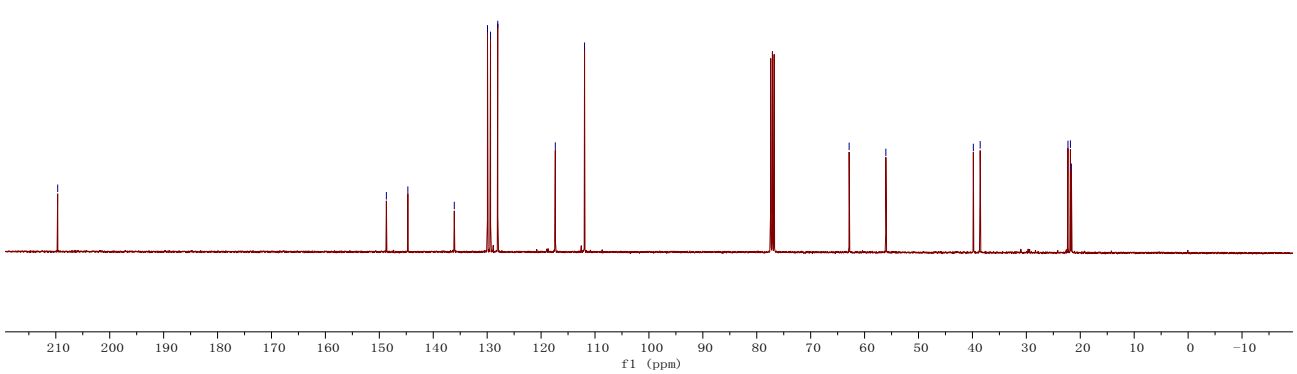
3n

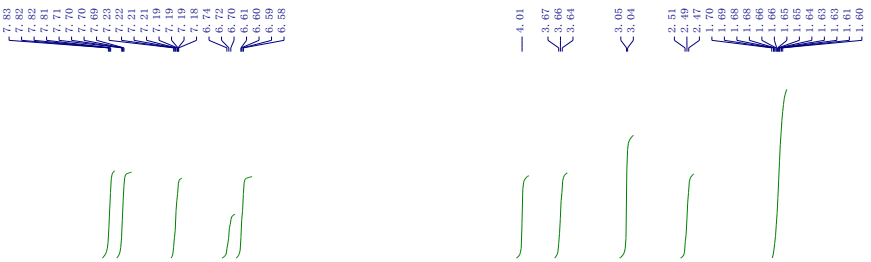

1.99
2.01
1.97
1.00
1.98
2.03
5.07
5.20
4.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

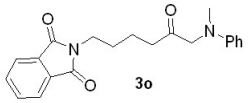

209.65
148.69
144.71
136.10
129.94
129.38
128.04
117.36
111.94
62.87
56.06
39.83
38.56
22.29
21.83
21.65


O
O
S
O
N
Ph

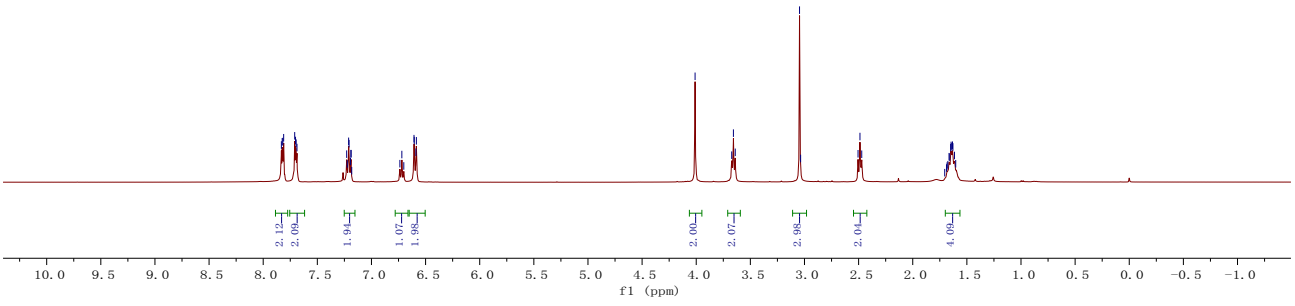
3n

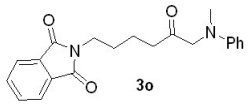

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



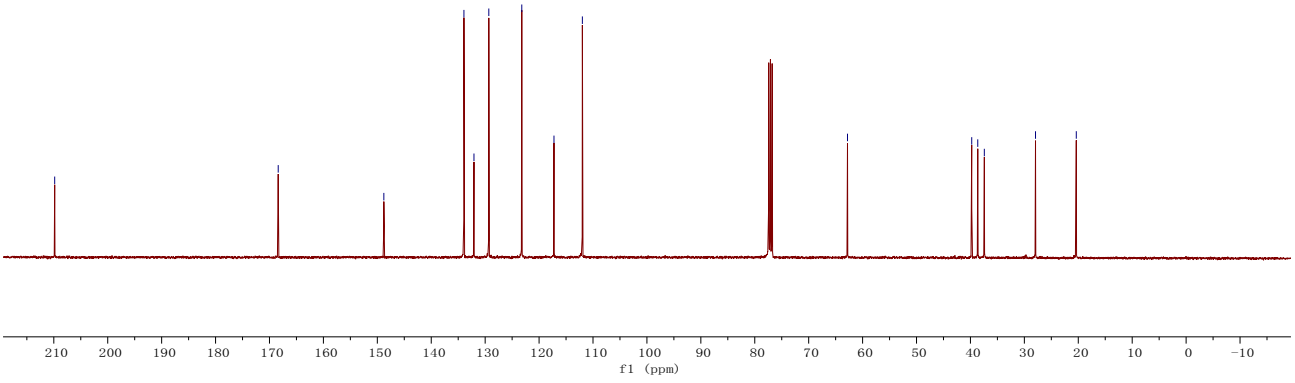


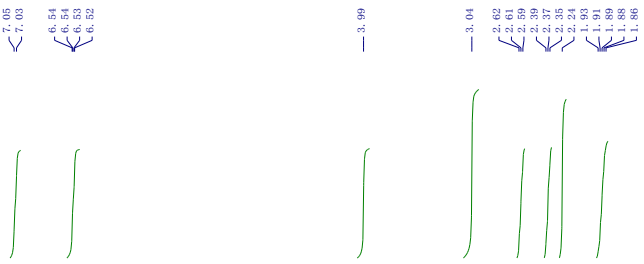
3o

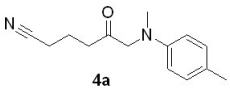




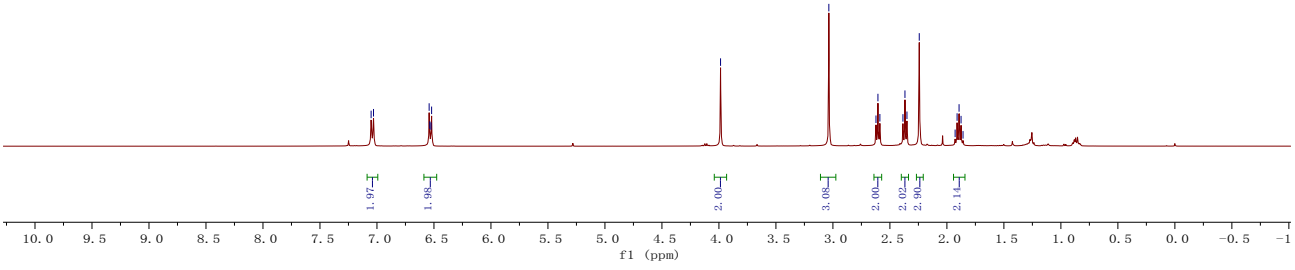
3o



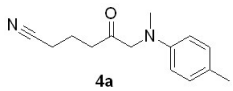

7.05
7.03
6.54
6.54
6.53
6.52
3.99
3.04
2.62
2.61
2.59
2.39
2.37
2.35
2.24
1.93
1.91
1.89
1.88
1.86



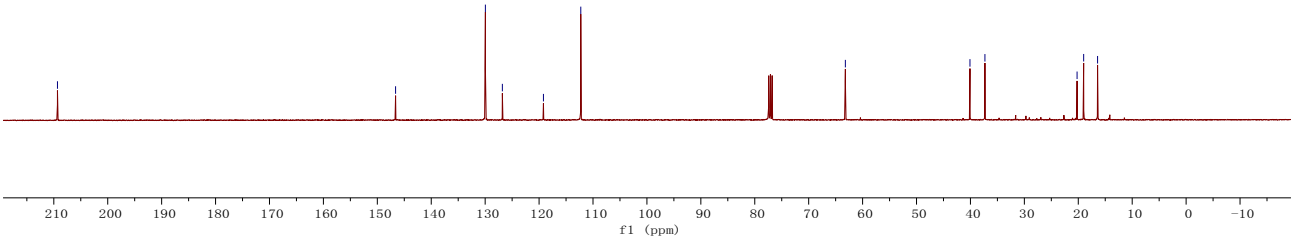
4a

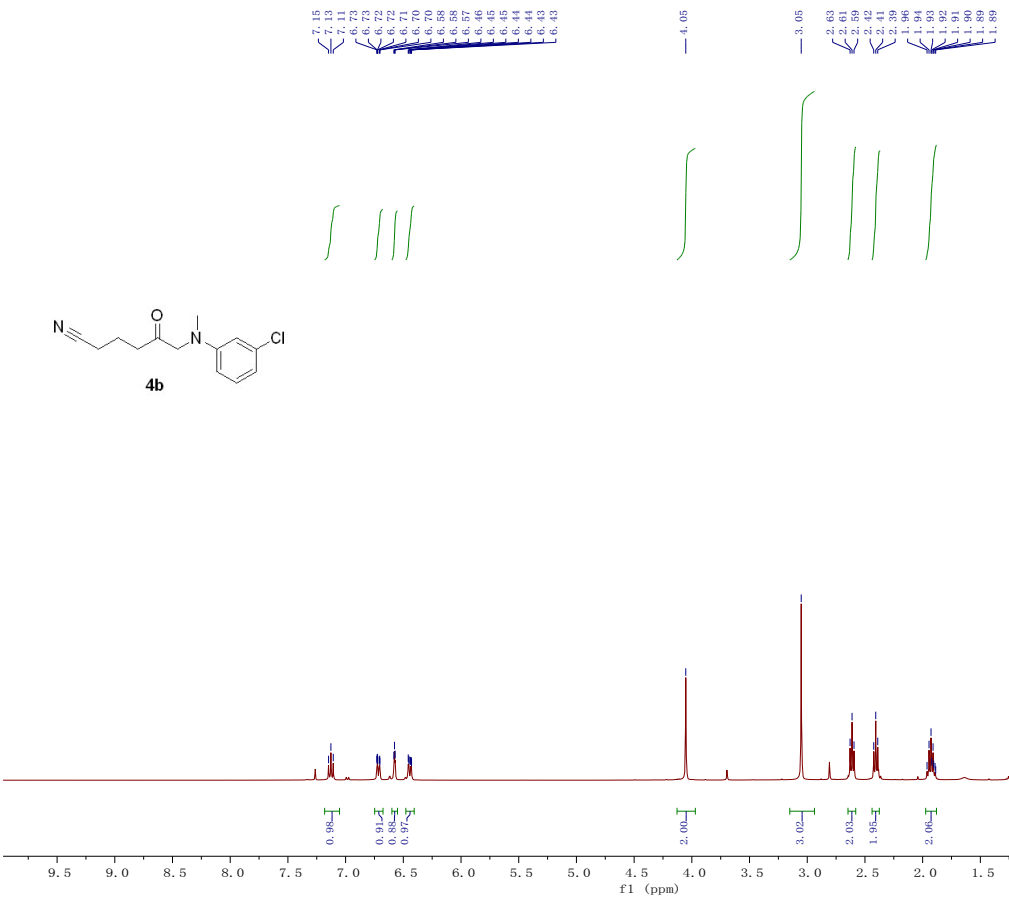

1.97
1.98
2.00
3.08
2.00
2.02
2.90
2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


209.32
146.61
129.96
126.81
119.19
112.27
63.20
40.09
37.31
20.22
19.00
16.42



4a


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)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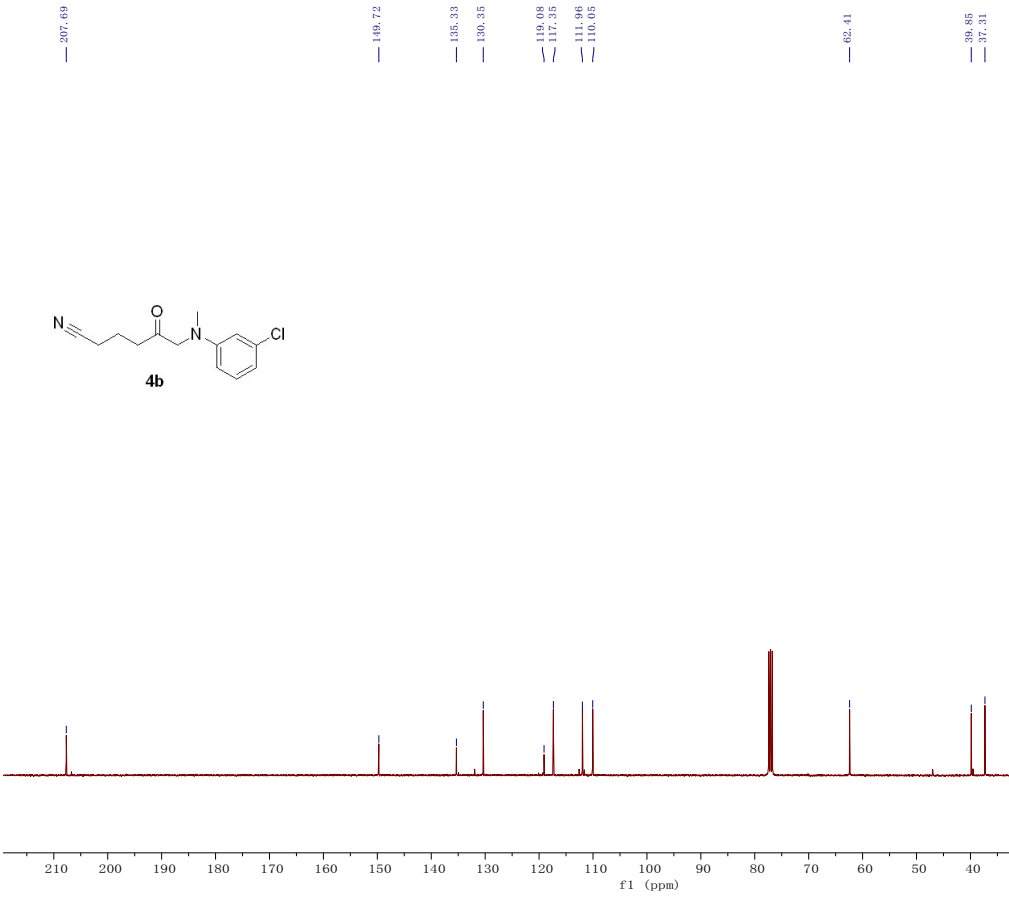
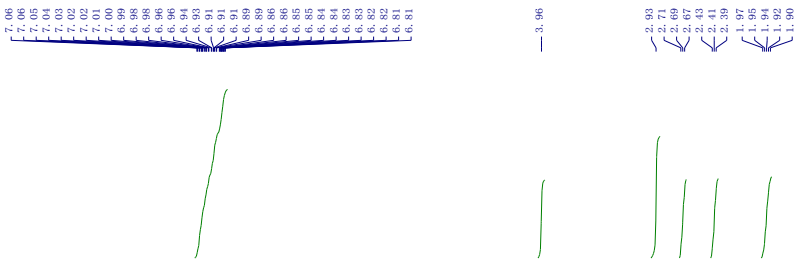
7.11
6.73
6.72
6.72
6.72
6.71
6.70
6.70
6.58
6.58
6.57
6.46
6.45
6.45
6.44
6.44
6.43
6.43
4.05
3.05
2.63
2.61
2.59
2.42
2.41
2.39
1.96
1.94
1.93
1.92
1.91
1.90
1.89
1.89
N
O
N
Cl
4b
0.98
0.91
0.88
0.97
2.00
3.02
2.03
1.96
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


207.69
149.72
135.33
130.35
119.08
117.35
111.96
110.05
62.41
39.85
37.31
18.91
16.42
N
O
N
Cl
4b
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)


7.06
7.06
7.05
7.04
7.03
7.02
7.02
7.01
7.00
6.99
6.98
6.98
6.96
6.96
6.94
6.93
6.91
6.91
6.89
6.89
6.86
6.86
6.85
6.84
6.84
6.83
6.82
6.82
6.81
6.81
3.96
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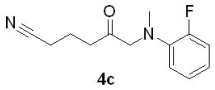
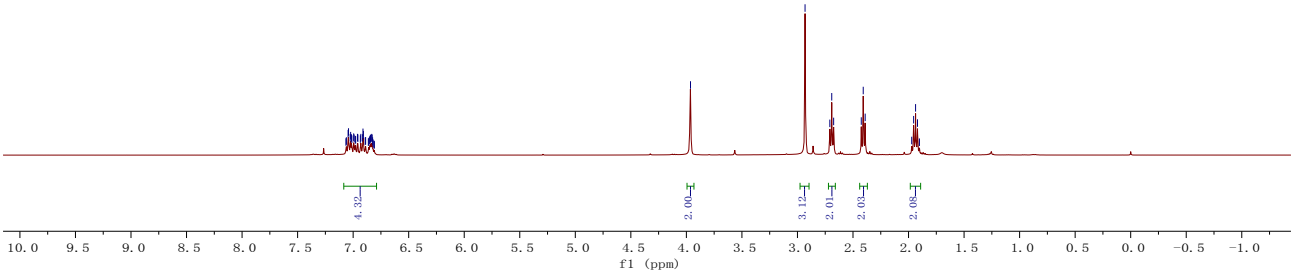
2.39
1.97
1.95
1.94
1.92
1.90


N
O
N
F

4c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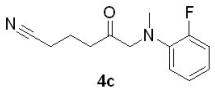
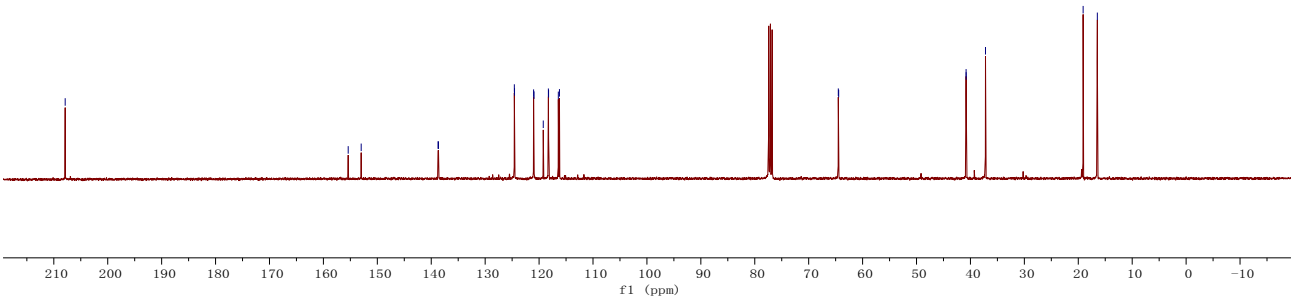
2.00
3.12
2.01
2.03
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


207.89
155.40
152.99
138.74
138.66
124.59
124.56
121.02
120.94
119.22
118.27
118.24
116.43
116.22
64.51
64.44
40.81
40.79
37.21
19.10
16.46


N
O
N
F

4c


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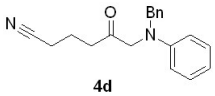
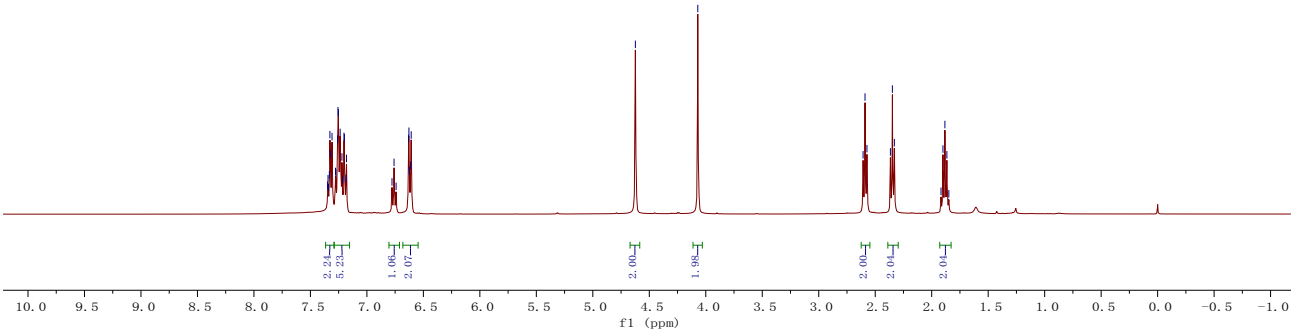
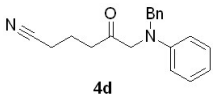
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

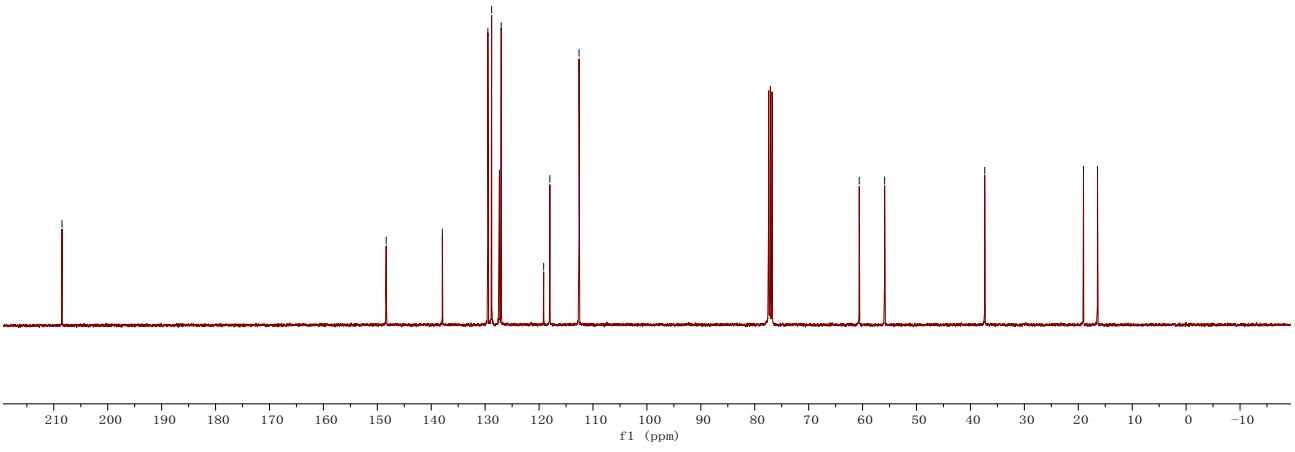


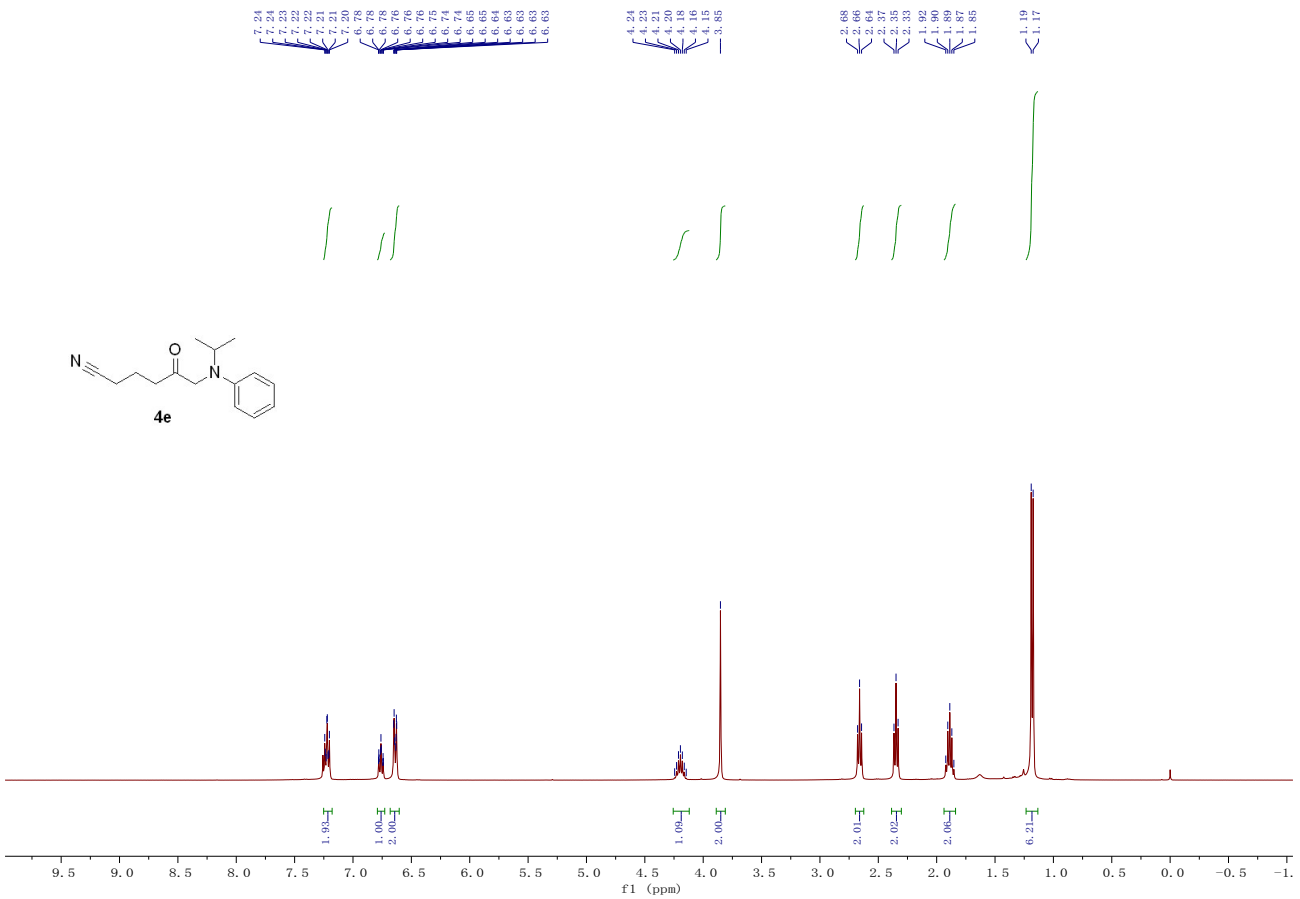
4d





4d

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7.24
7.23
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7.22
7.21
7.21
7.20
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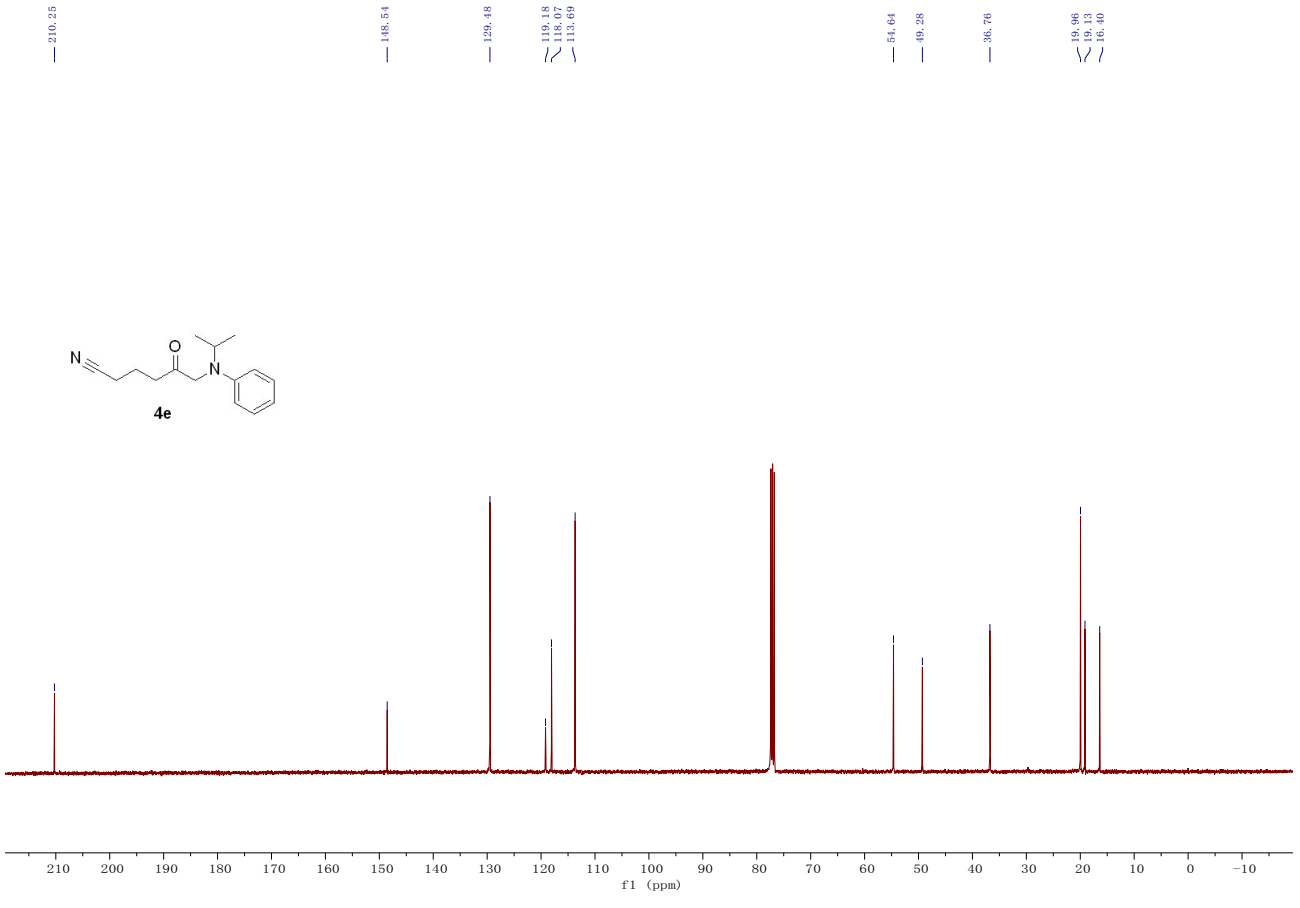
6.78
6.76
6.76
6.75
6.75
6.74
6.65
6.64
6.63
6.63
6.63
4.24
4.23
4.21
4.20
4.18
4.16
4.15
3.85
2.68
2.66
2.64
2.37
2.35
2.33
1.92
1.90
1.89
1.87
1.85
1.19
1.17
N
O
N
4e
1.93
1.00
2.00
1.09
2.00
2.01
2.02
2.06
6.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)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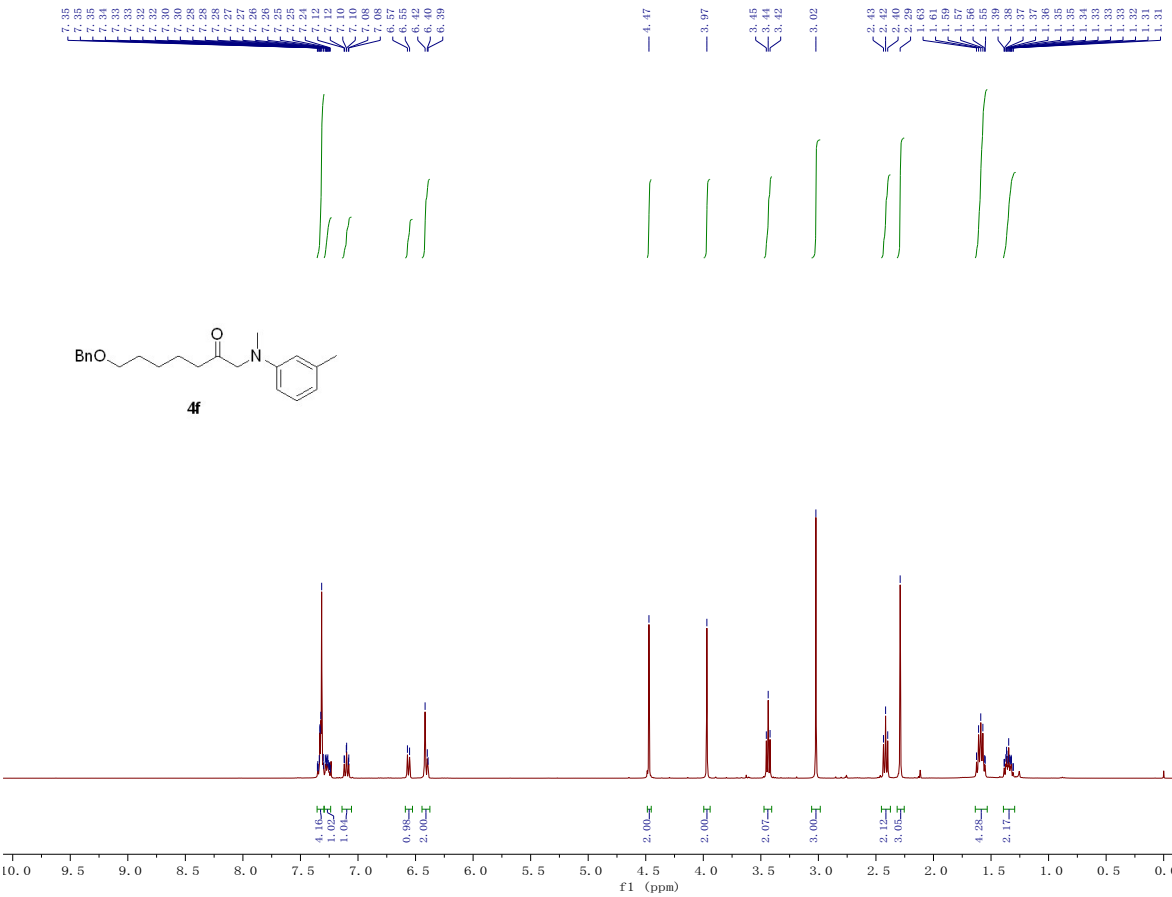
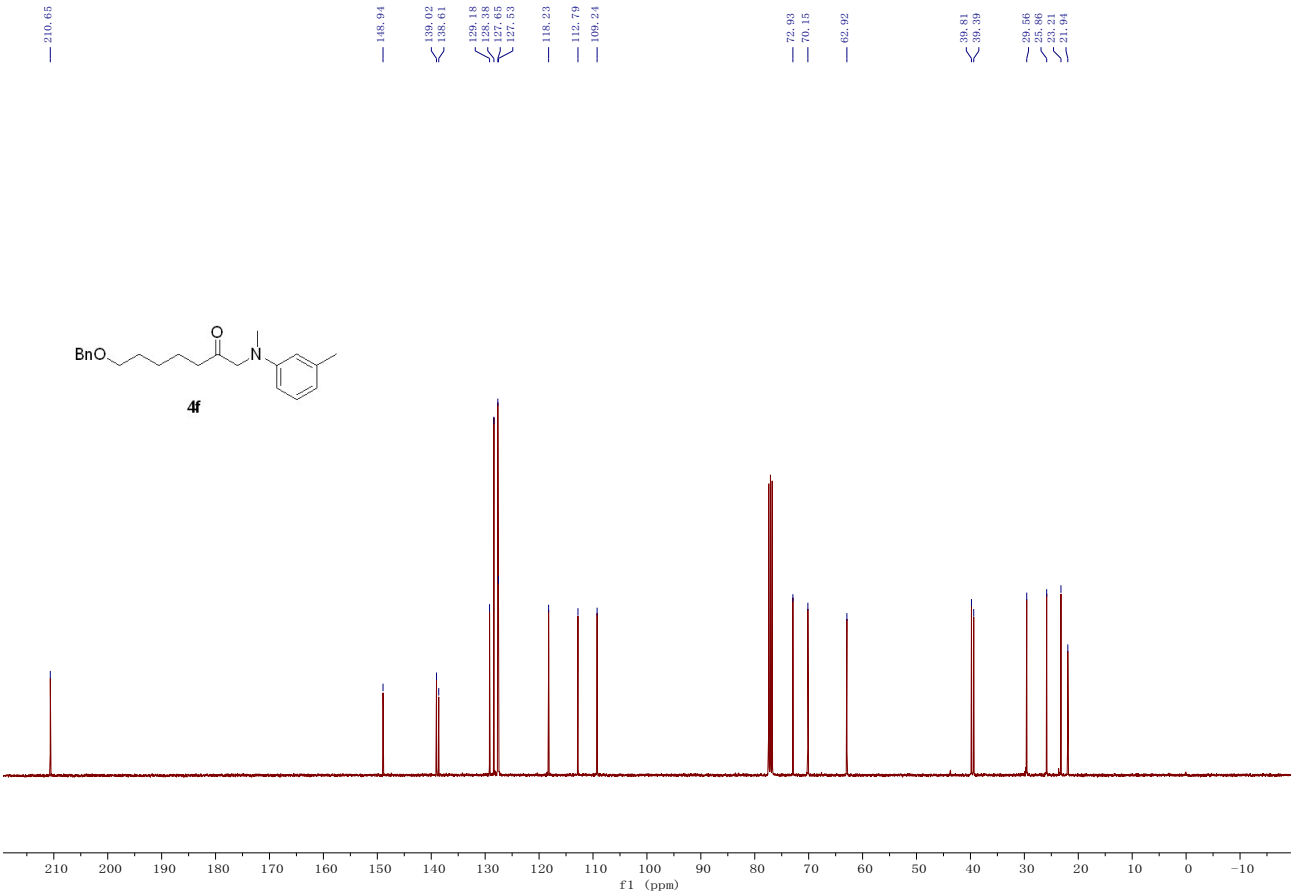
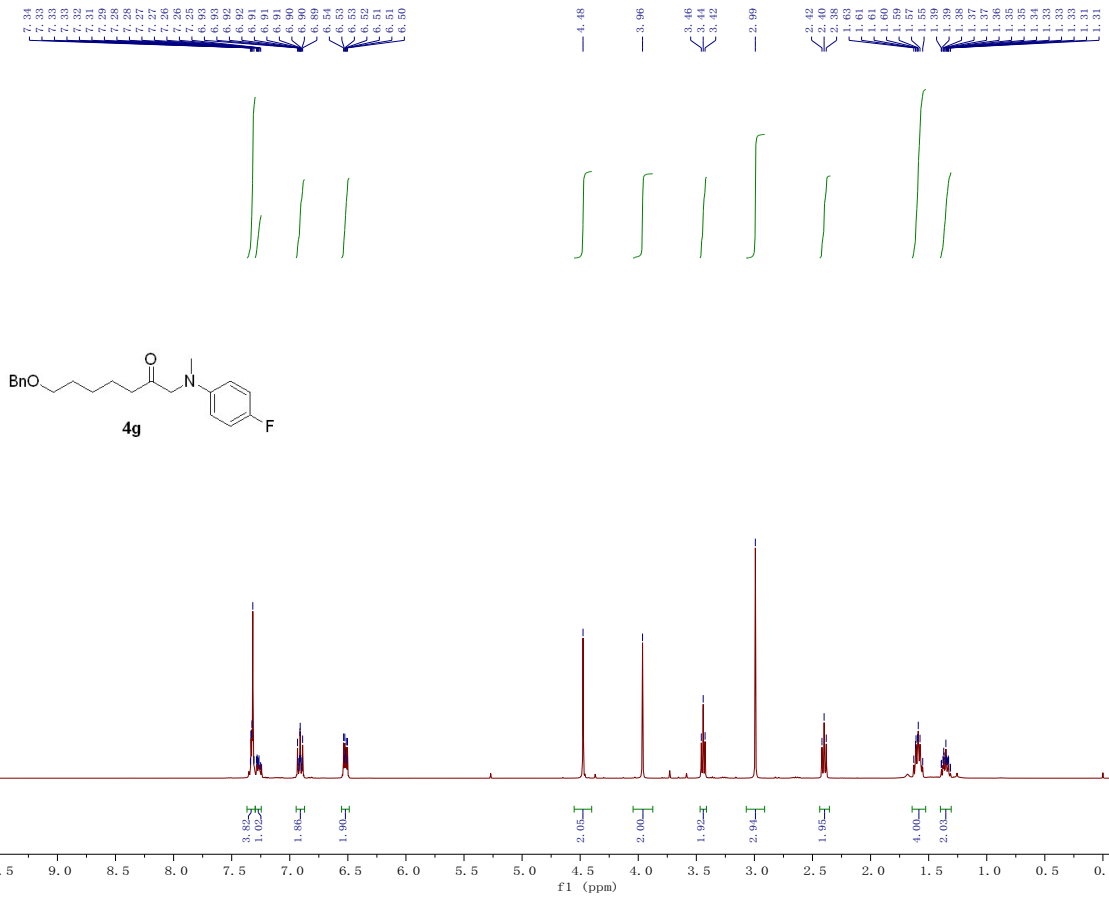
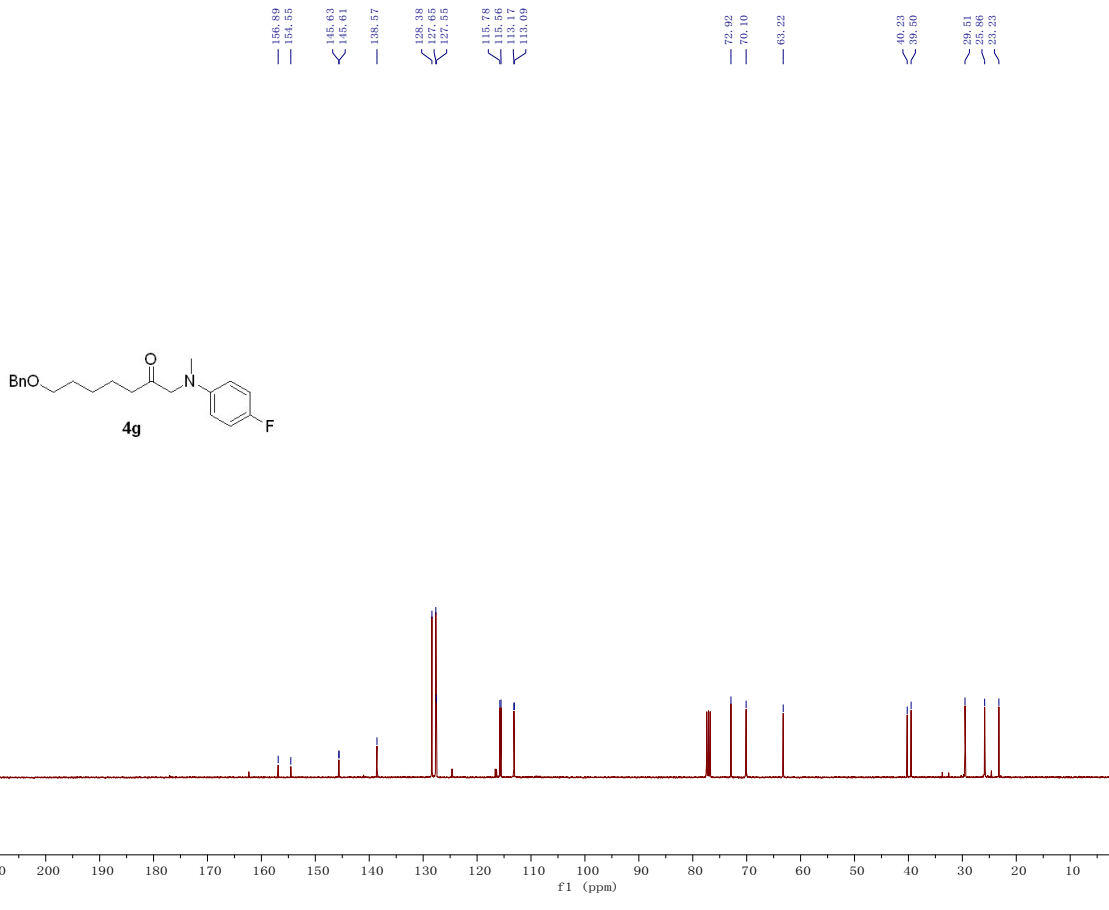
119.18
118.07
113.69
54.64
49.28
36.76
19.96
19.13
16.40
N
O
N
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


BnO
4f
f1 (ppm)


BnO
4f
f1 (ppm)


7.34
7.33
7.33
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.26
7.25
6.93
6.92
6.92
6.91
6.91
6.90
6.90
6.89
6.54
6.53
6.53
6.52
6.51
6.51
6.50
4.48
3.96
3.46
3.44
3.42
2.99
2.42
2.40
2.38
1.63
1.61
1.61
1.60
1.59
1.57
1.55
1.39
1.39
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.33
1.33
1.31
1.31
BnO
O
N
F
4g
3.82
1.02
1.86
1.90
2.05
2.00
1.92
2.94
1.95
4.00
2.03
f1 (ppm)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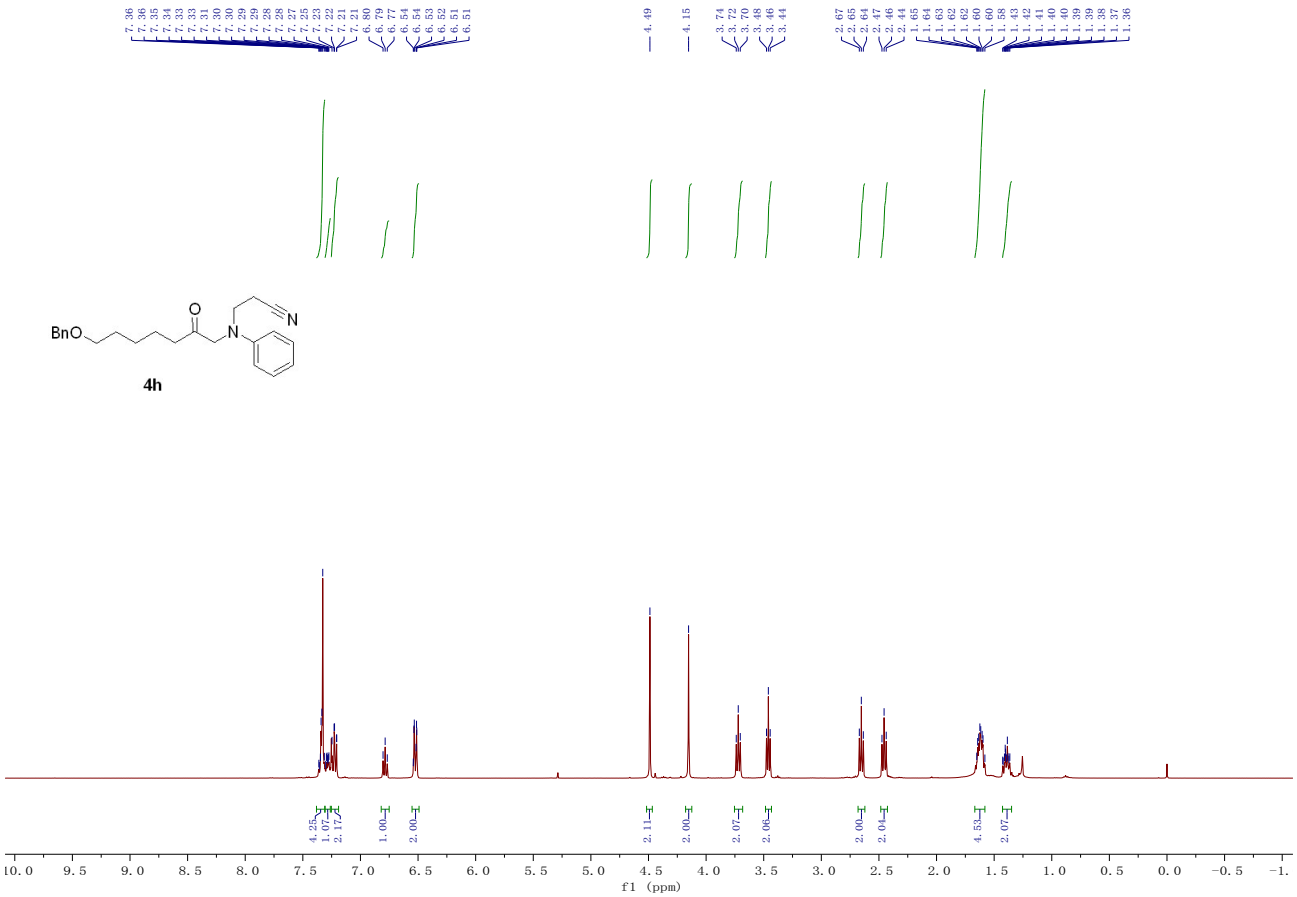
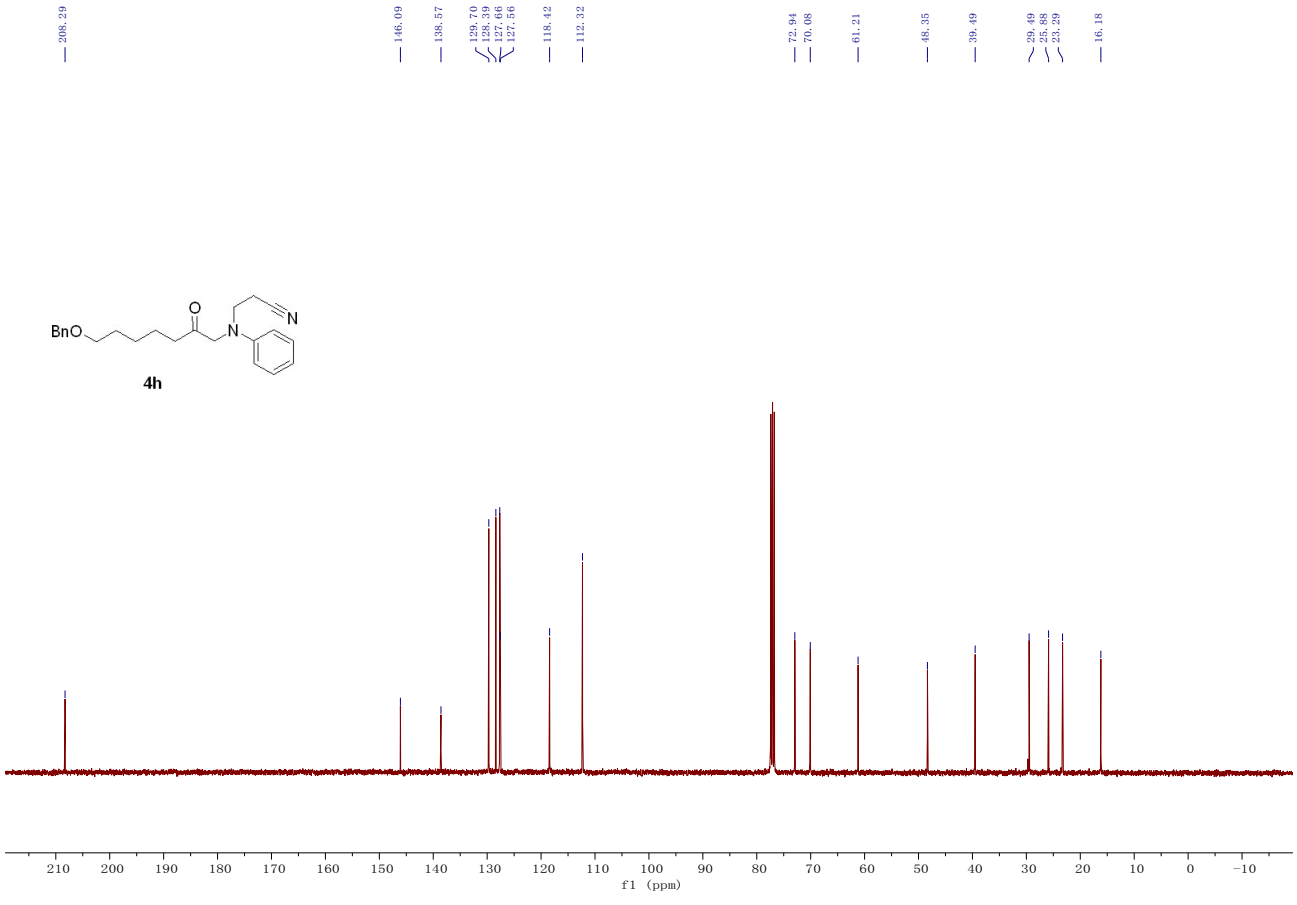
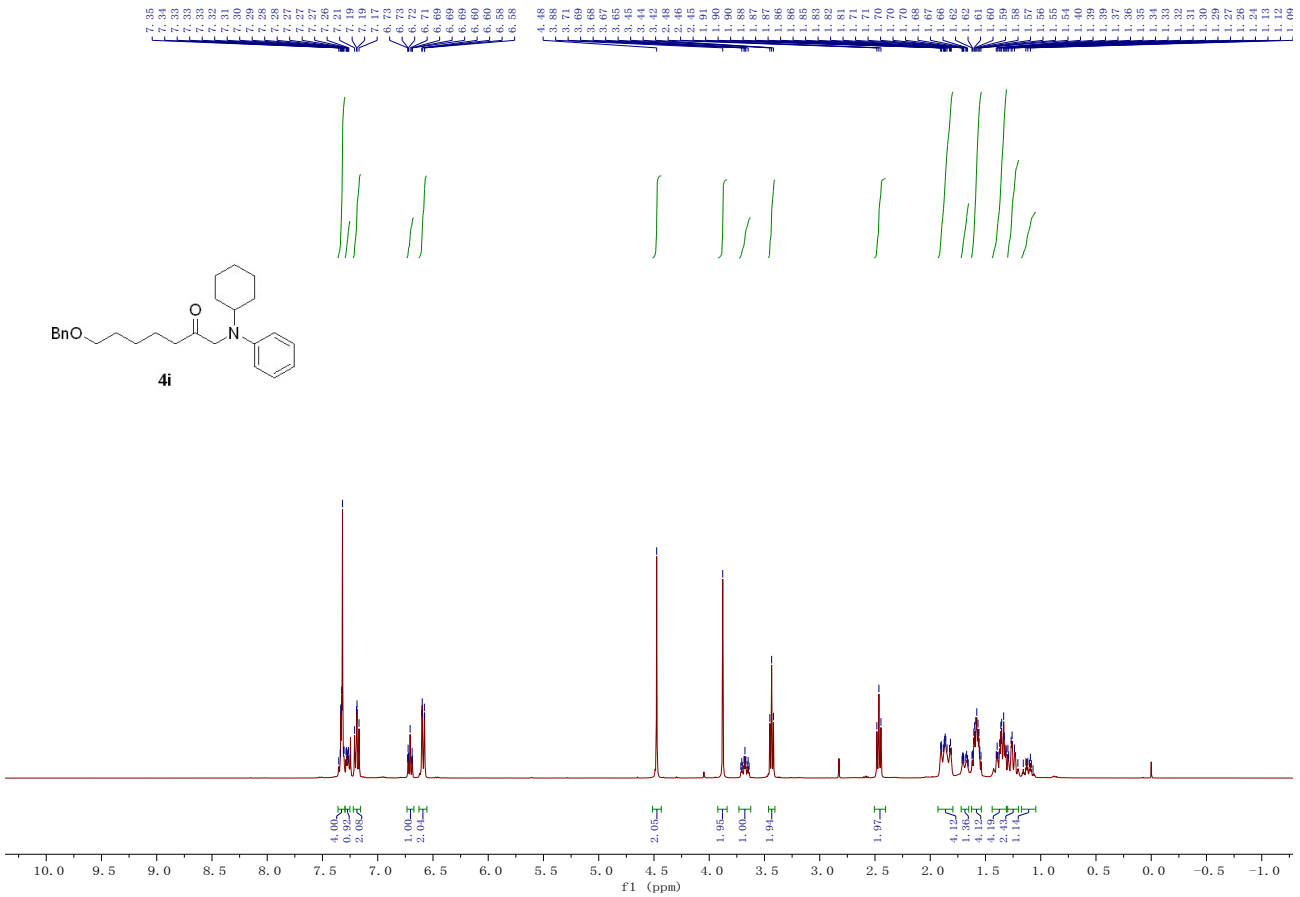
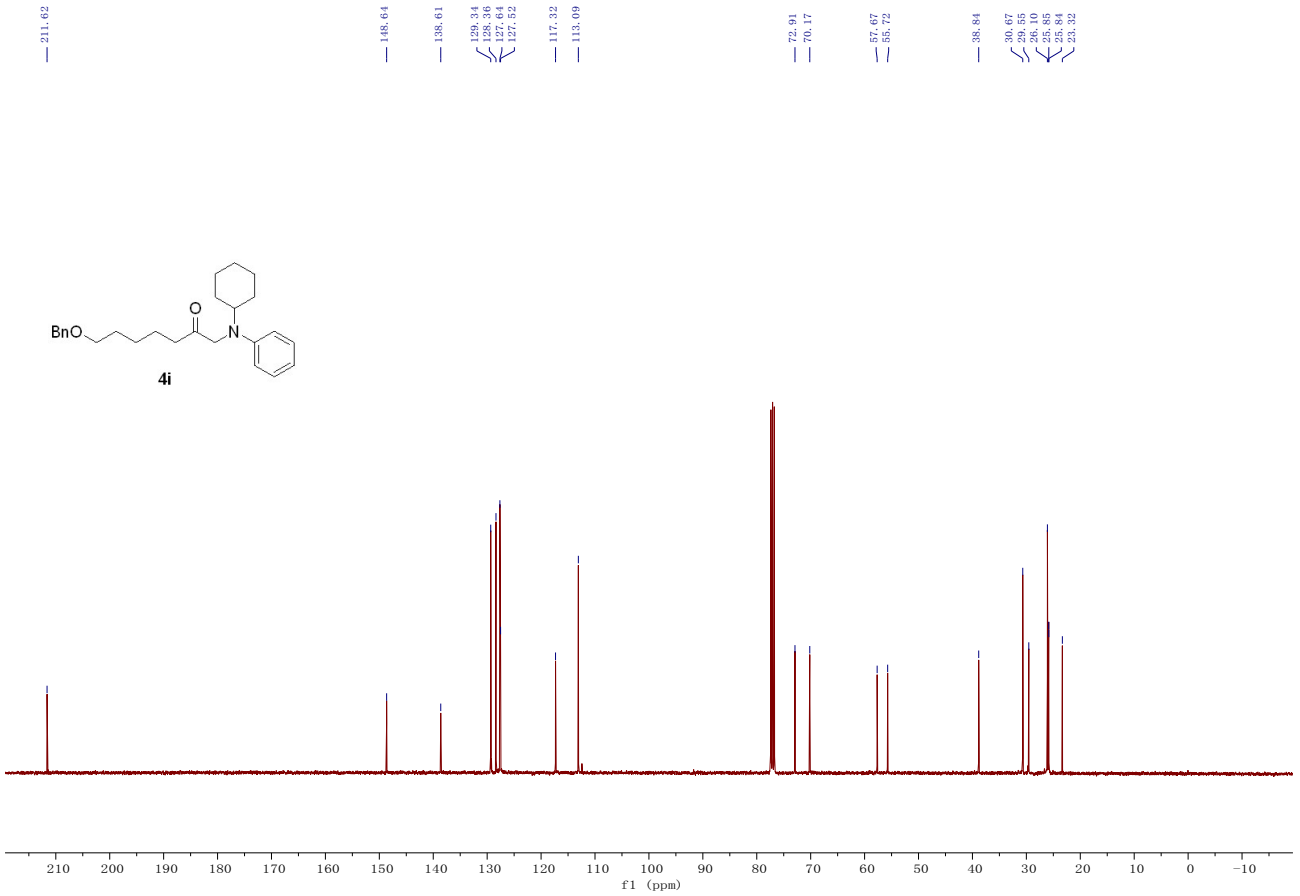
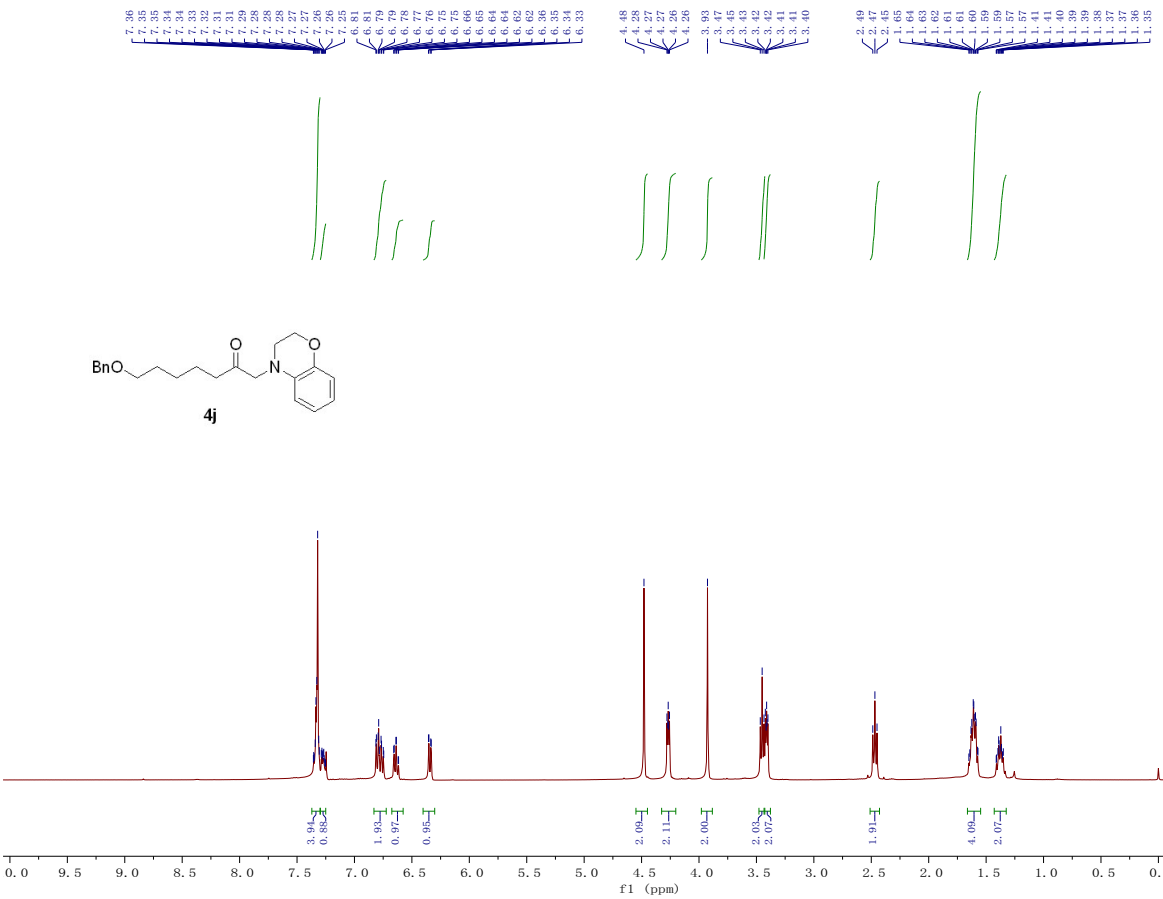
156.89
154.55
145.63
145.61
138.57
128.38
127.65
127.55
115.78
115.66
113.17
113.09
72.92
70.10
63.22
40.23
39.50
29.51
25.86
23.23
BnO
O
N
F
4g
f1 (ppm)

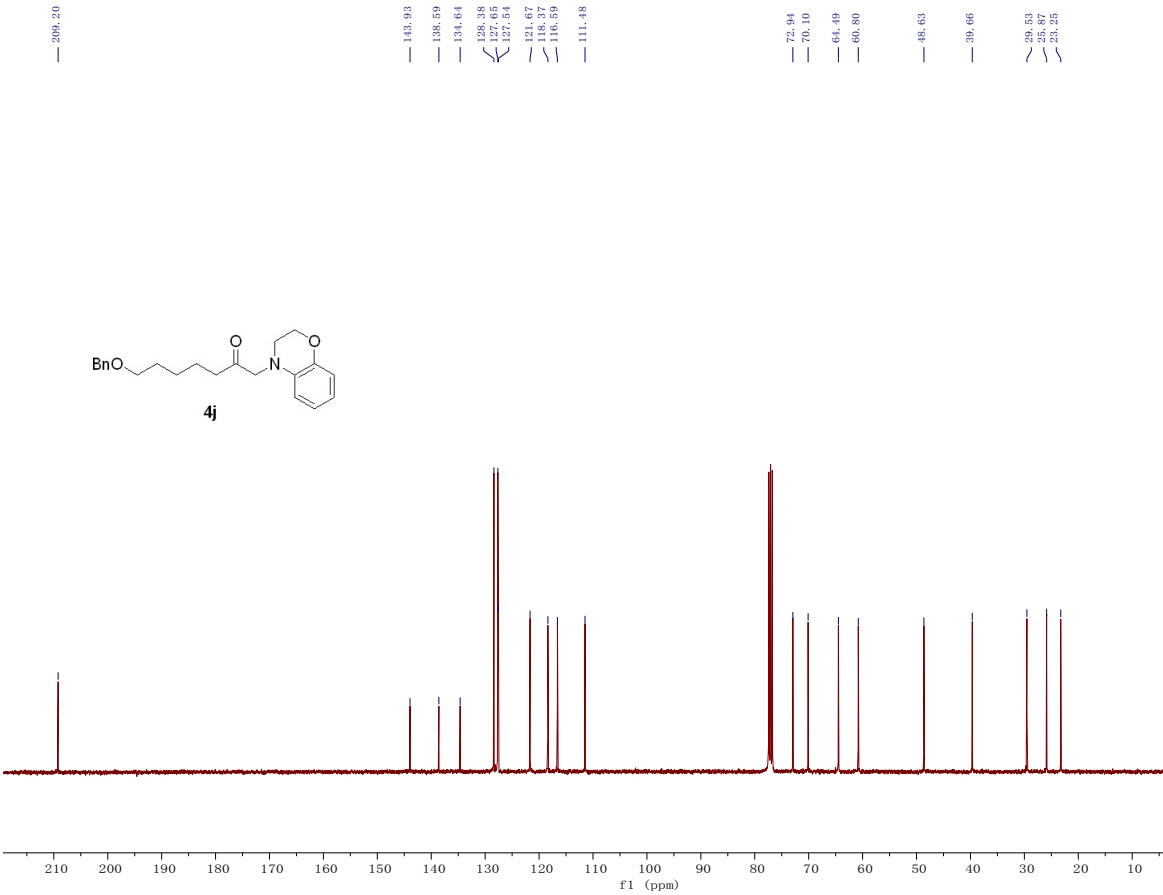

7.36
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.28
7.27
7.25
7.23
7.22
7.21
6.80
6.79
6.77
6.54
6.53
6.52
6.51
6.51
4.49
4.15
3.74
3.72
3.70
3.48
3.46
3.44
2.67
2.65
2.64
2.47
2.46
2.44
1.65
1.64
1.63
1.62
1.62
1.60
1.60
1.58
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.37
1.36
BnO
O
N
N
4h
4.25
1.07
2.17
1.00
2.00
2.11
2.00
2.07
2.06
2.00
2.04
4.53
2.07
f1 (ppm)

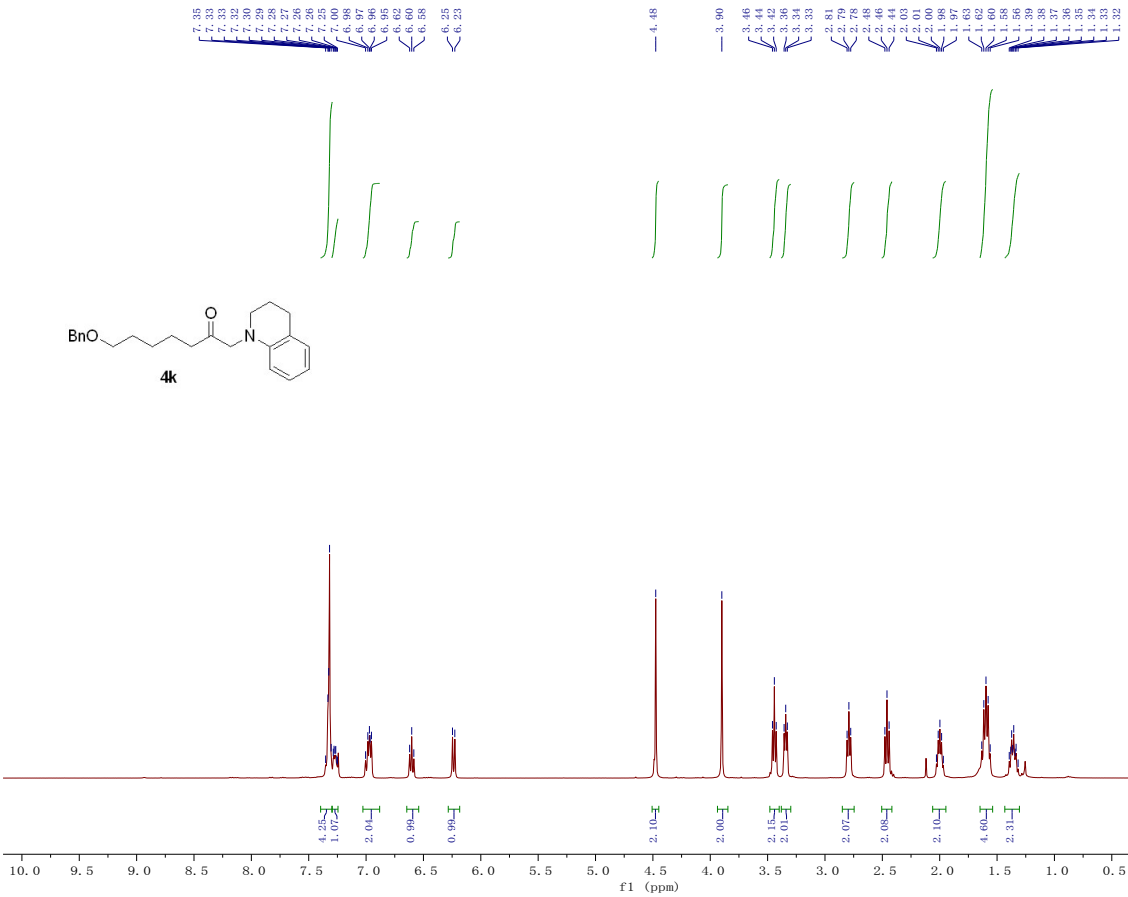

208.29
146.09
138.57
129.70
128.39
127.66
127.56
118.42
112.32
72.94
70.08
61.21
48.35
39.49
29.49
25.88
23.29
16.18
BnO
O
N
N
4h
f1 (ppm)


BnO
O
N
4i
f1 (ppm)


BnO
O
N
4i
f1 (ppm)


7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.25 6.81 6.79 6.79 6.78 6.77 6.76 6.75 6.66 6.65 6.64 6.64 6.62 6.62 6.36 6.35 6.34 6.33
4.48 4.28 4.27 4.27 4.26 4.26 3.93 3.47 3.45 3.43 3.42 3.42 3.41 3.41 3.40
2.49 2.47 2.45 1.65 1.64 1.63 1.62 1.61 1.61 1.61 1.60 1.59 1.59 1.57 1.57 1.44 1.41 1.40 1.39 1.39 1.38 1.37 1.37 1.36 1.35
BnO
O
N
O
4j
3.94 0.88 1.93 0.97 0.95 2.09 2.11 2.00 2.03 2.07 1.91 4.09 2.07
f1 (ppm)


209.20
143.93 138.59 134.64 128.38 127.65 127.54 121.67 118.37 116.59 111.48
72.94 70.10 64.49 60.80 48.63 39.66 29.53 25.87 23.25
BnO
O
N
O
4j
f1 (ppm)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7.33
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7.29
7.28
7.27
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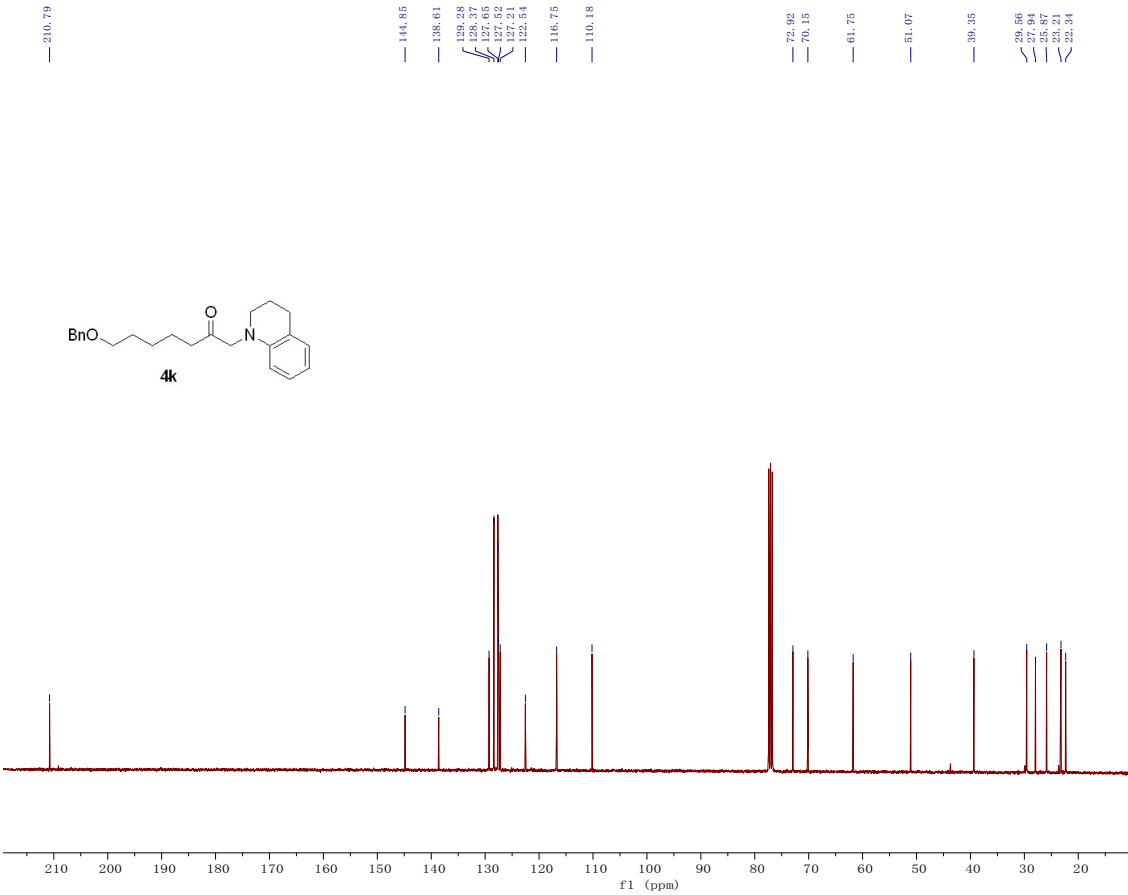
7.26
7.25
7.00
6.98
6.97
6.96
6.95
6.62
6.60
6.58
6.25
6.23
4.48
3.90
3.46
3.44
3.42
3.36
3.34
3.33
2.81
2.79
2.78
2.48
2.46
2.44
2.03
2.01
2.00
1.98
1.97
1.63
1.62
1.60
1.58
1.56
1.39
1.38
1.37
1.36
1.35
1.34
1.33
1.32
BnO
O
N
4k
4.25
1.07
2.04
0.99
0.99
2.10
2.00
2.15
2.01
2.07
2.08
2.10
4.60
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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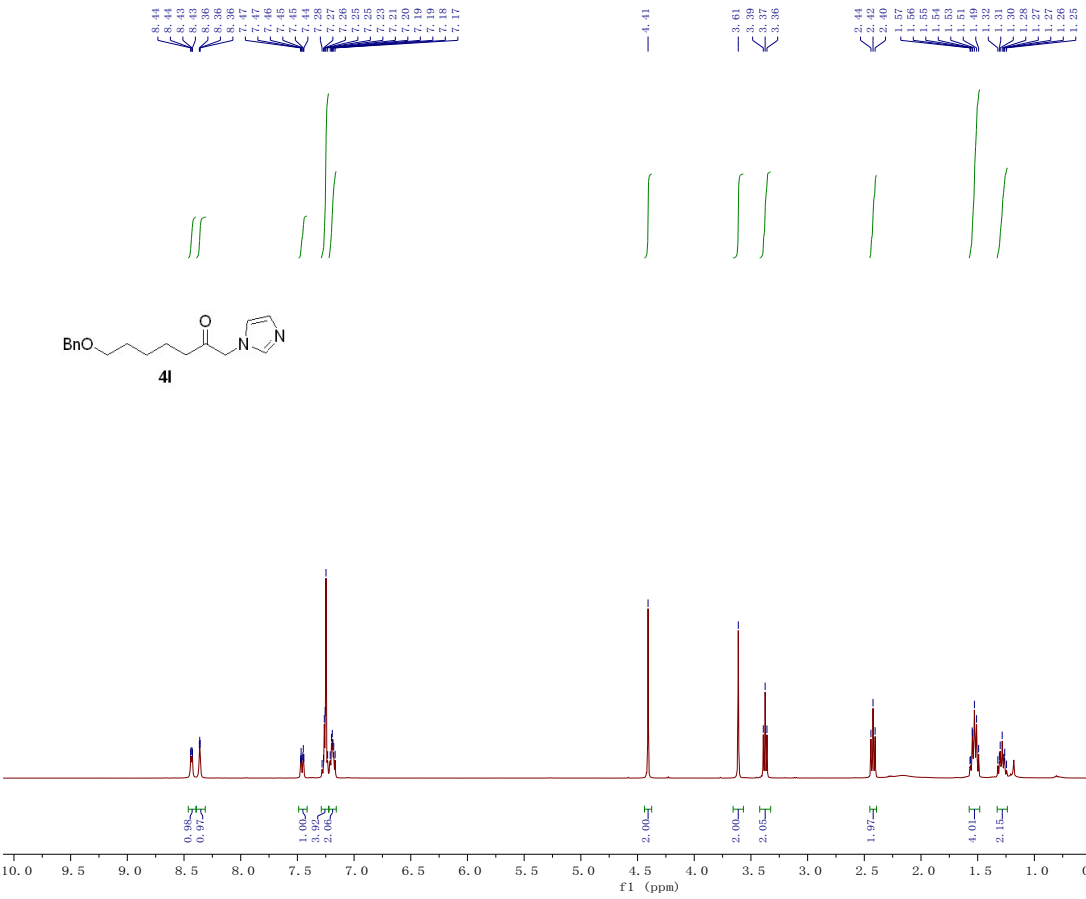
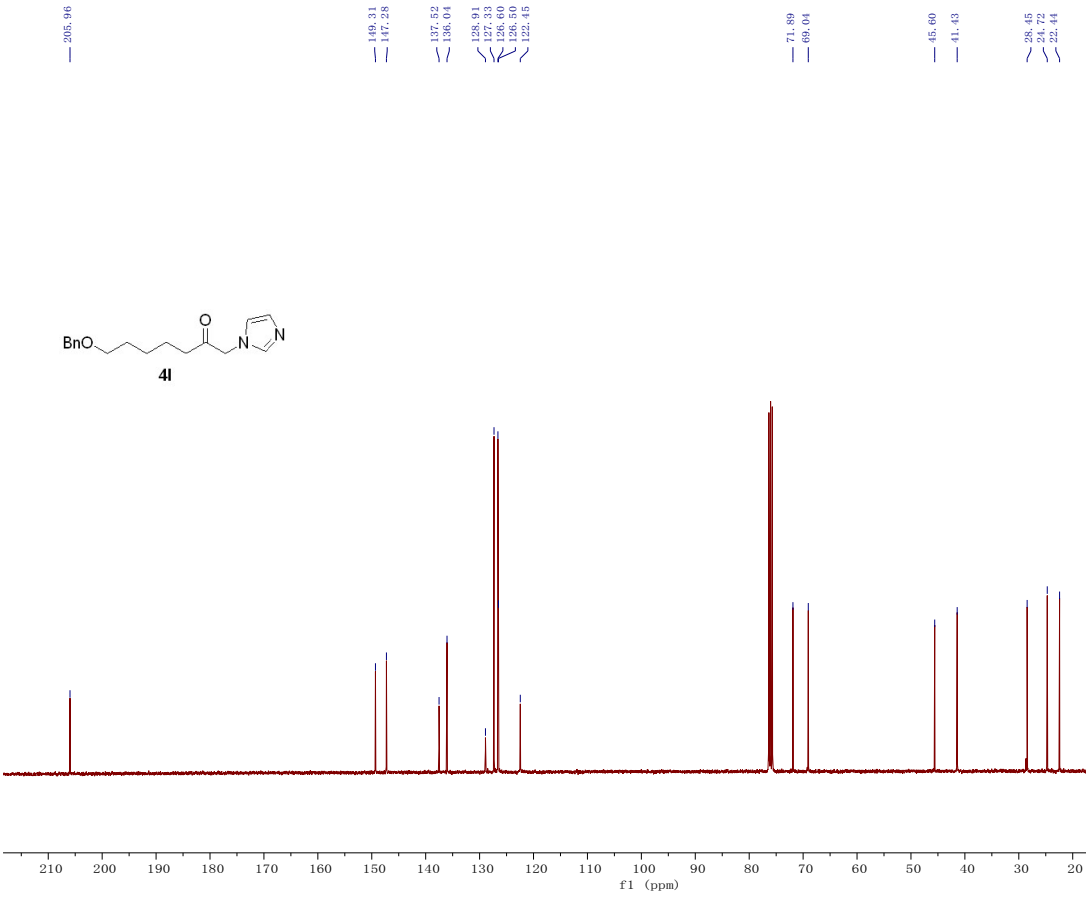
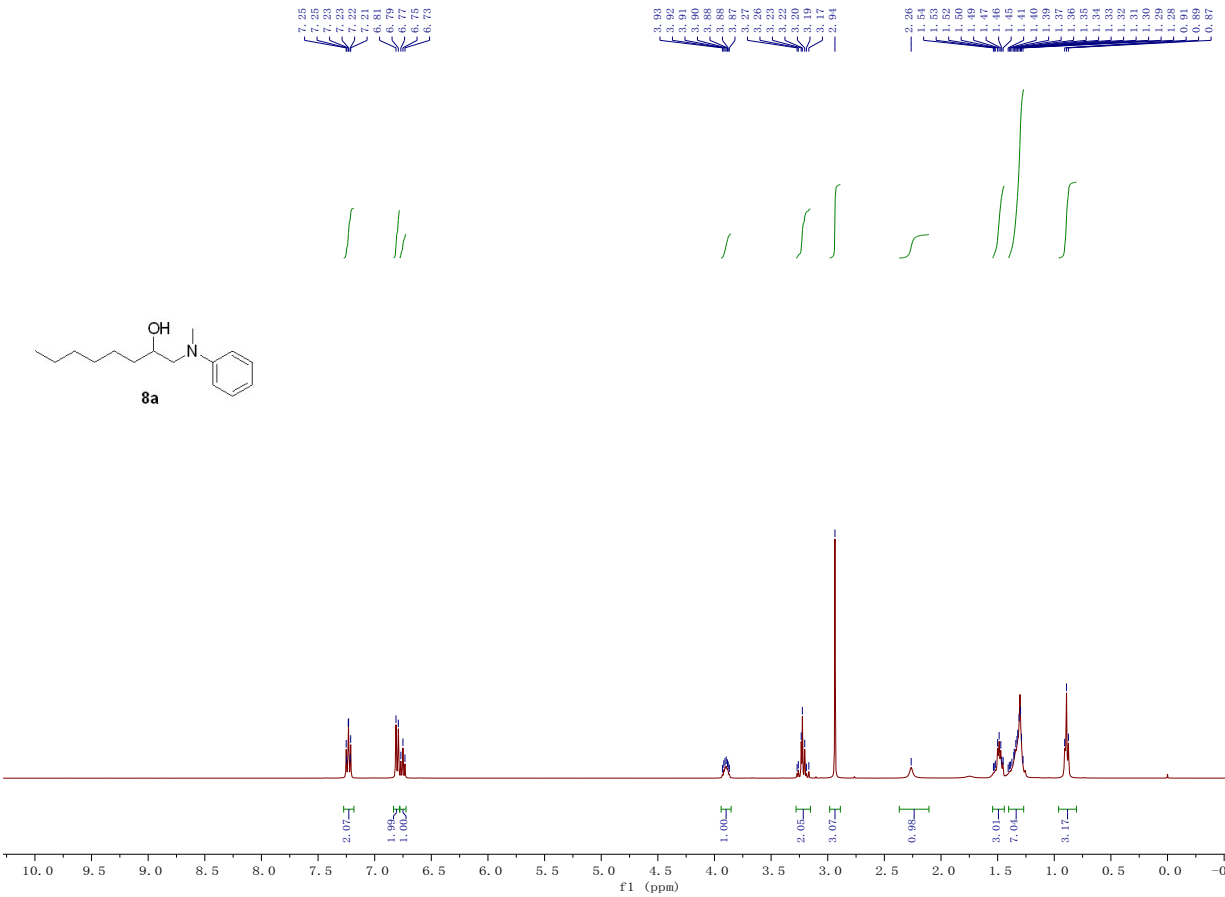
128.37
127.65
127.52
127.21
122.54
116.75
110.18
72.92
70.15
61.75
51.07
39.35
29.56
27.94
25.87
23.21
22.34
BnO
O
N
4k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.44
8.44
8.43
8.43
8.36
8.36
8.36
7.47
7.47
7.46
7.45
7.45
7.44
7.28
7.27
7.26
7.25
7.23
7.21
7.20
7.19
7.19
7.18
7.17
4.41
3.61
3.39
3.37
3.36
2.44
2.42
2.40
1.57
1.56
1.55
1.54
1.53
1.51
1.49
1.32
1.31
1.30
1.28
1.27
1.27
1.26
1.25
BnO
O
N
N
4l
0.98
0.97
1.00
3.92
2.06
2.00
2.00
2.05
1.97
4.01
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


205.96
149.31
147.28
137.52
136.04
128.91
127.33
126.60
126.50
122.45
71.89
69.04
45.60
41.43
28.45
24.72
22.44
BnO
O
N
N
4l
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)


7.25
7.25
7.23
7.23
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7.21
6.81
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6.77
6.75
6.73
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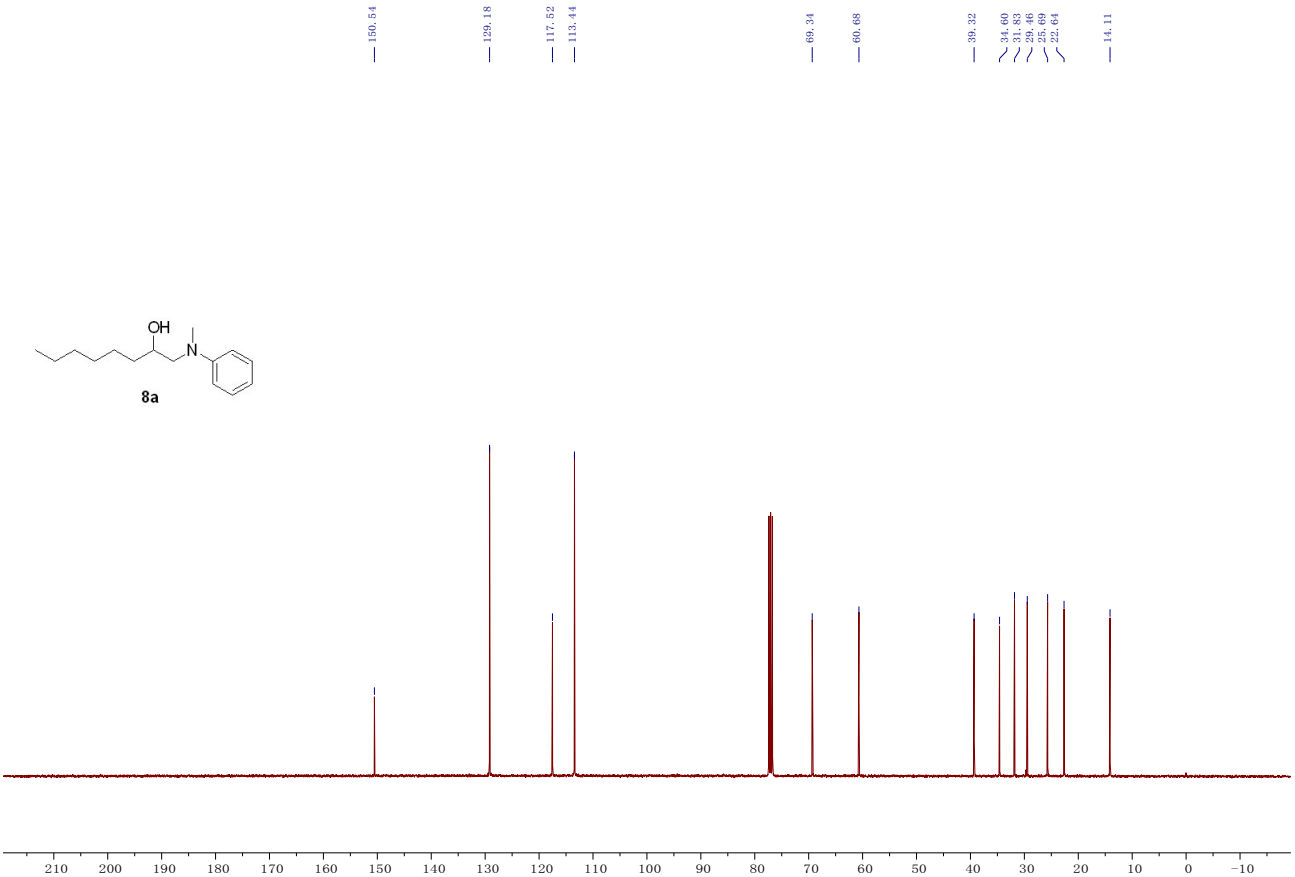
3.92
3.91
3.90
3.88
3.87
3.27
3.26
3.23
3.22
3.20
3.19
3.17
2.94
2.26
1.54
1.53
1.52
1.50
1.49
1.47
1.46
1.45
1.41
1.40
1.39
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
0.91
0.89
0.87
OH
N
8a
2.07
1.90
1.00
2.05
3.07
0.98
3.01
7.04
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)


150.54
129.18
117.52
113.44
69.34
60.68
39.32
34.60
31.83
29.46
25.69
22.64
14.11
OH
N
8a
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)

5. References

1. Xia, X.; Chen, B.; Zeng, X.; Xu, B., Synthesis of α-Trifluromethylthiolated and α-Thiocyanated Ketones Using Umpoled Enolates. *Adv. Synth. Catal.* **2018**, In press, DOI: 10.1002/adsc.201800968.

2. Xu, Z.; Zhai, R.; Liang, T.; Zhang, L., Efficient One-Pot Multifunctionalization of Alkynes en Route to alpha-Alkoxyketones, alpha-Thioketones, and alpha-Thio Thioketals by using an Umpolung Strategy. *Chem. Eur. J.* **2017,** *23* (57), 14133-14137.

3. Xu, Z.; Chen, H.; Wang, Z.; Ying, A.; Zhang, L., One-Pot Synthesis of Benzene-Fused Medium-Ring Ketones: Gold Catalysis-Enabled Enolate Umpolung Reactivity. *J Am Chem Soc* **2016,** *138* (17), 5515-8.

1. Xu, Z.; Zhai, R.; Liang, T.; Zhang, L., Efficient One-Pot Multifunctionalization of Alkynes en Route to alpha-Alkoxyketones, alpha-Thioketones, and alpha-Thio Thioketals by using an Umpolung Strategy. *Chem. Eur. J.* **2017,** *23* (57), 14133-14137.

2. Xu, Z.; Chen, H.; Wang, Z.; Ying, A.; Zhang, L., One-Pot Synthesis of Benzene-Fused Medium-Ring Ketones: Gold Catalysis-Enabled Enolate Umpolung Reactivity. *J Am Chem Soc* **2016,** *138* (17), 5515-8.