Rh(III)-Catalyzed *ortho* Oxidative Alkylation of Unactivated Arenes with Allylic Alcohols

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Electronic Supplementary Information

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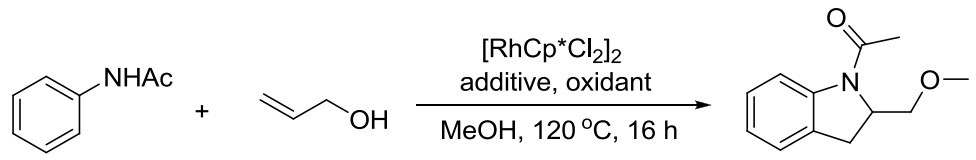
A. General method and Screening reaction conditions

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer.

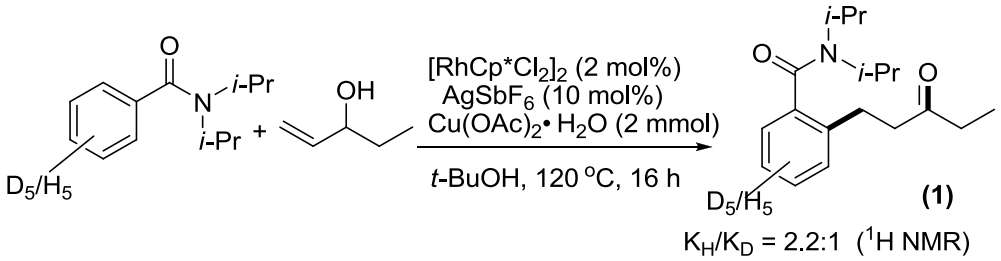
Table 1. Screening Conditions for Carboamination of Olefins with Acetanilides[a]



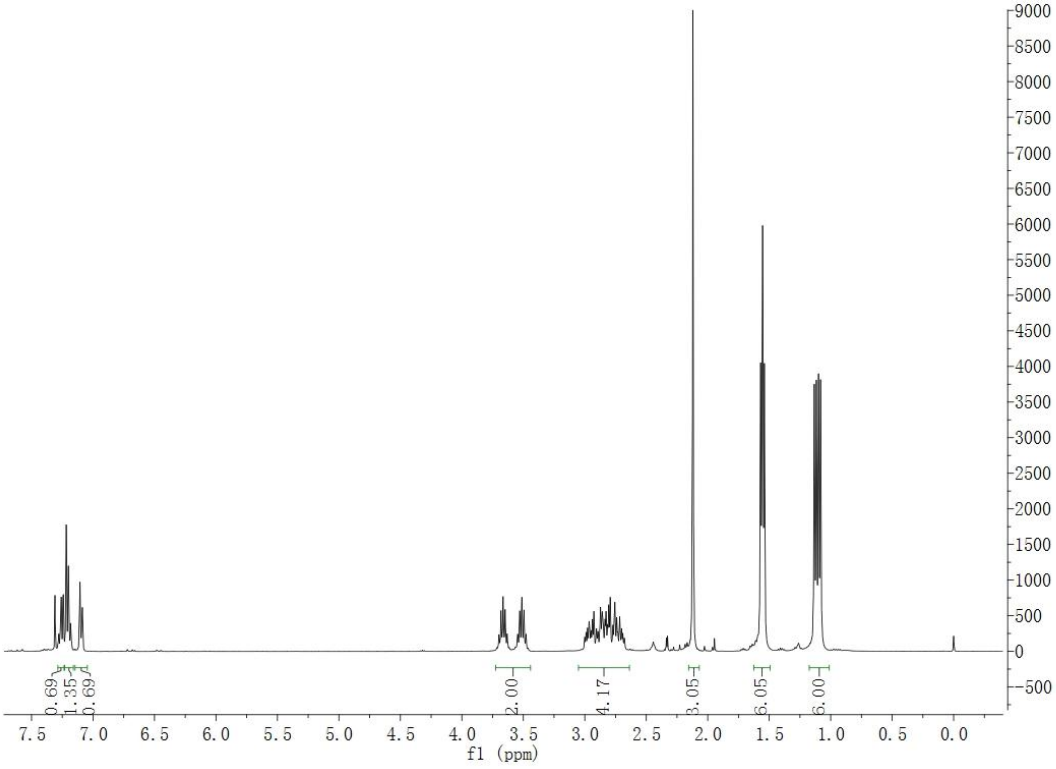
1a' **4a**

entry	additive (mol %)	oxidant (equiv)	solvent	yield[b] (%)
1	$AgSbF_6$ (10)	None	MeOH	<5
2	None	$Cu(OAc)_2$ (2)	MeOH	<5
3	$AgSbF_6$ (10)	$Cu(OAc)_2$ (2)	MeOH	63 (55)
4	$AgSbF_6$ (10)	Ag_2CO_3 (2)	MeOH	19
5	$AgSbF_6$ (7.5)	$Cu(OAc)_2{\cdot}H_2O$ (2)	MeOH	63 (55)
6	$AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (2)	MeOH	66 (57)
7	$AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (3)	MeOH	63
8	$AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (1)/Ag_2CO_3 (1)	MeOH	55
9[c]	$AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (2)	MeOH	58
10[d]	$AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (2)	MeOH	47

[a] The reactions were carried out at 120 °C using **4a** (0.3 mmol), allyl alcohol (0.33 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), MeOH 2 mL for 16 h. [b] Determined by GC. Number in parentheses is isolated yield. [c] 140 °C. [d] 100 °C



A kinetic isotope effect (KIE) of $k_H/k_D \approx 2.2$ was observed (eq 1).

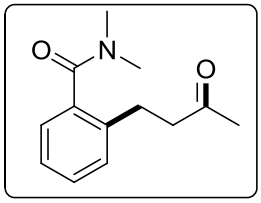


B. General procedure for substrate 1a-1ag

To a Schlenk tube were added N,N-dimethylbenzamide (1 mmol), but-3-en-2-ol (1.2 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2 \cdot H_2O$ (2 mmol) and *t*-BuOH 5 mL at 120 ^oC stirred for overnight. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and wash with $NaHCO_3$. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired product.

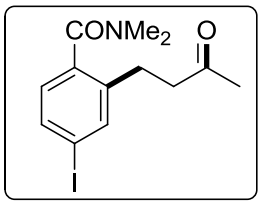
C. Analytical data for 3a-ag, 4a-f

N,N-dimethyl-2-(3-oxobutyl)benzamide (3a)



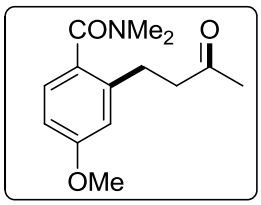
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 - 7.28 (m, 1H), 7.24 - 7.21 (m, 2H), 7.16 - 7.14 (m, 1H), 3.12 (s, 3H), 2.83 - 2.81 (m, 7H) , 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 171.1, 137.2, 136.3, 129.3, 128.8, 126.2, 125.9, 44.7, 38.5, 34.5, 29.7, 27.0 ppm; IR *v* (neat, cm^{-1}) 2933, 2361, 1765, 1636, 1765, 1393, 1163, 753; MS (EI, 70 eV) m/z (%): 219 (M+, 8.5), 176 (100.0), 131 (61.1), 103 (20.8), 77 (18.9). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.23; H, 7.80; N, 6.38.

4-iodo-N,N-dimethyl-2-(3-oxobutyl)benzamide (3b)



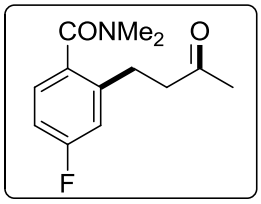
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 - 7.55 (m, 2H), 6.90 (d, *J* = 7.6, 1H), 3.10 (s, 3H), 2.86 - 2.69 (m, 7H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.2, 170.2, 139.8, 138.4, 135.9, 135.3, 127.6, 94.7, 44.5, 38.6, 34.6, 29.8, 26.7 ppm; IR *v* (neat, cm^{-1}) 2930, 1714, 1635, 1582, 1448, 1394, 1262, 1060, 916, 826; MS (EI, 70 eV) *m/z* (%): 345 (M^+, 9.8), 302 (98.0), 257 (55.0), 175 (20.9), 130 (67.6), 102 (100.0), 77 (65.0). Anal. Calcd for $C_{13}H_{16}INO_2$: C, 45.23; H, 4.67; N, 4.06. Found: C, 45.23; H, 4.66; N, 4.08.

4-methoxy-N,N-dimethyl-2-(3-oxobutyl)benzamide (3c)



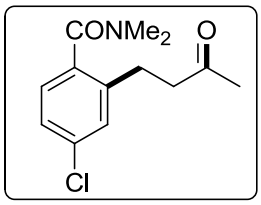
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 - 7.08 (m, 1H), 6.76 - 6.74 (m, 2H), 3.80 (s, 3H), 3.10 (s, 3H), 2.85-2.80 (m,7H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.8, 171.3, 159.9, 139.5, 128.9, 127.6, 115.0, 111.5, 55.2, 44.9, 38.8, 34.7, 29.8, 27.4 ppm; IR *v* (neat, cm^{-1}) 3740, 2936, 2361, 1714, 1633, 1392, 1244, 1162, 1054; MS (EI, 70 eV) *m/z* (%): 249 (M^+, 7.0), 206 (35.9), 161 (100.0), 131 (16.2), 91 (35.3), 72 (24.3). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.44; H, 7.67; N, 5.60.

4-fluoro-N,N-dimethyl-2-(3-oxobutyl)benzamide (3d)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 - 7.13 (m, 1H), 6.97 - 6.90 (m, 2H), 3.12 (s, 3H), 2.84 - 2.81 (m, 7H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.09, 170.03, 139.59, 134.78, 134.49, 129.44, 127.31, 126.38, 44.29, 38.53, 34.53, 29.68, 26.72 ppm; IR *v* (neat, cm^{-1}) 2991, 2361, 1765, 1715, 1637, 1392, 1243, 1098, 1060, 831; MS (EI, 70 eV) *m/z* (%): 237 (M^+, 8.0), 194 (88.8), 149 (100.0), 121 (31.9), 72 (45.5). Anal. Calcd for $C_{13}H_{16}FNO_2$: C, 65.81; H, 6.80; N, 5.90. Found: C, 65.80; H, 6.78; N, 5.89.

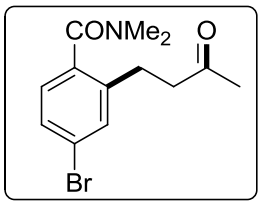
4-chloro-N,N-dimethyl-2-(3-oxobutyl)benzamide (3e)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 - 7.20 (m, 2H), 7.11- 7.10 (m, 1H), 3.11 (s, 3H), 2.84 - 2.80 (m, 7H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 170.0, 139.6, 134.8, 134.5, 129.4, 127.3, 126.4, 44.3, 38.5, 34.5, 29.7, 26.7 ppm; IR *v* (neat, cm^{-1}) 2937, 2361, 1765, 1716, 1637, 1395, 1242, 1160, 1062, 828, 581; MS (EI, 70 eV) *m/z* (%): 253 (M^+, 11.0), 210 (100.0), 165 (72.3), 131 (14.5), 89 (21.8), 72 (49.4). Anal. Calcd for $C_{13}H_{16}ClNO_2$: C, 61.54; H, 6.36; N, 5.52. Found: C, 61.55; H, 6.38; N,

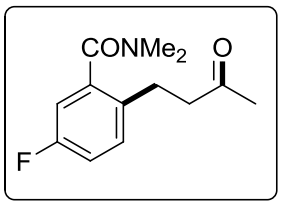
5.53.

4-bromo-N,N-dimethyl-2-(3-oxobutyl)benzamide (3f)



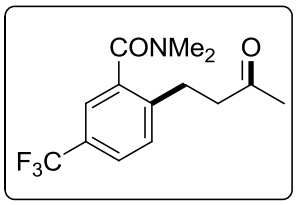
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.34 (m, 2H), 7.04 (d, *J*=8.1, 1H), 3.11 (s, 3H), 2.87 – 2.73 (m, 7H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.04, 170.00, 139.80, 135.23, 132.35, 129.29, 127.49, 122.68, 44.32, 38.51, 34.51, 29.67, 26.67 ppm; IR *v* (neat, cm^{-1}) 2930, 1714, 1636, 1587, 1394, 1265, 1088, 1063, 917, 827; MS (EI, 70 eV) *m/z* (%): 297 (M^+, 9.5), 254 (100.0), 211 (56.2), 183 (11.0), 130 (43.7), 102 (75.6), 89 (34.2) 77 (25.8), 72 (60.6). Anal. Calcd for $C_{13}H_{16}BrNO_2$: C, 52.36; H, 5.41; N, 4.70. Found: C, 52.35; H, 5.42; N, 4.73.

5-fluoro-N,N-dimethyl-2-(3-oxobutyl)benzamide (3g)



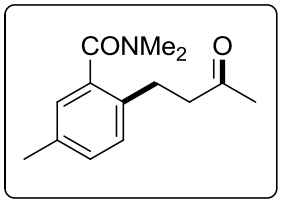
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 - 7.20 (m, 1H), 7.04 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 3.12 (s, 3H), 2.84 - 2.79 (m, 7H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.32, 169.52, 169.49, 162.44, 159.99, 138.65, 138.61, 127.94, 127.85, 124.98, 124.81, 121.59, 121.55, 115.67, 115.44, 43.39, 38.57, 34.49, 29.47, 20.80, 20.77 ppm; IR *v* (neat, cm^{-1}) 2933, 2361, 1765, 1751, 1639, 1456, 1395, 1244, 1053, 799, 751; MS (EI, 70 eV) *m/z* (%): 237 (M^+, 18.1), 149 (100.0), 121 (42.2), 101 (52.9), 96 (20.3), 75 (40.1). Anal. Calcd for $C_{13}H_{16}FNO_2$: C, 65.81; H, 6.80; N, 5.90. Found: C, 65.82; H, 6.81; N, 5.88.

N,N-dimethyl-2-(3-oxobutyl)-5-(trifluoromethyl)benzamide (3h)



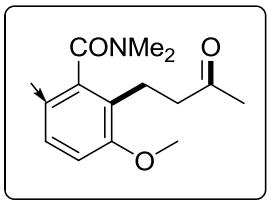
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 - 7.37 (m, 3H), 3.14 (s, 3H), 2.93 - 2.75 (m, 7H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.1, 169.6, 141.8, 137.1, 130.2, 125.8, 125.7, 123.1, 123.1, 44.3, 38.7, 34.7, 29.8, 27.0 ppm; IR *v* (neat, cm^{-1}) 2937, 1765, 1713, 1640, 1513, 1399, 1330, 1246, 1166, 1124, 1085, 841; MS (EI, 70 eV) m/z (%): 287 (M+, 5.4), 244 (100.0), 199 (68.1), 151 (32.8), 103 (14.2), 77 (17.5). Anal. Calcd for $C_{14}H_{16}F_3NO_2$: C, 58.53; H, 5.61; N, 4.88. Found: C, 58.52; H, 5.62; N, 4.89.

N,N,5-trimethyl-2-(3-oxobutyl)benzamide (3i)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 – 7.10 (m, 2H), 6.97 (s, 1H), 3.11 (s, 3H), 2.84 - 2.77 (m, 7H), 2.31 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 171.1, 136.1, 135.7, 133.9, 129.4, 129.1, 126.2, 44.7, 38.4, 34.3, 29.6, 26.4, 20.6 ppm; IR *v* (neat, cm^{-1}) 2928, 2362, 1714, 1636, 1498, 1392, 1243, 1167, 1068, 817, 649; MS (EI, 70 eV) *m/z* (%): 233 (M^+, 7.5), 190 (93.6), 145 (100.0), 117 (33.8), 91 (36.4), 77 (30.4). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.06; H, 8.20; N, 5.99.

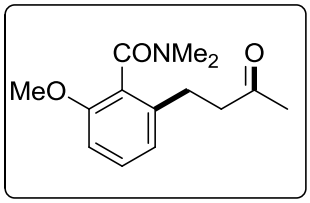
3-methoxy-N,N-dimethyl-2-(3-oxobutyl)benzamide (3j)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (t, *J* = 7.9 Hz, 0.66H), 7.14 (d, *J* = 8.5 Hz, 0.32H), 6.89 – 6.81 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 0.64H), 6.70 (d, *J* = 2.2 Hz, 0.31H), 3.82 (s, 2H), 3.78 (s, 1H), 3.11 (s, 0.92H), 3.10 (s, 1.85H), 2.85 (s, 0.91H), 2.82 (s, 1.91H), 2.76 – 2.41 (m, 4H), 2.13 (s, 1.87H), 2.12 (s, 0.91H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.72, 208.10, 170.91, 170.89, 157.92, 157.71, 137.87, 137.30, 130.65, 129.08, 127.56, 125.71, 117.83, 114.79, 111.19, 110.46, 55.34, 55.32, 45.02, 43.42,

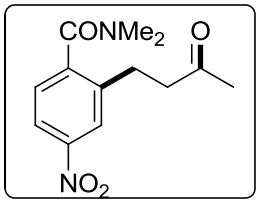
38.69, 38.62, 34.57, 34.53, 29.88, 29.63, 26.25, 21.94 ppm; IR *v* (neat, cm^{-1}) 2992, 2361, 1765, 1712, 1636, 1461, 1387, 1244, 1057, 792; MS (EI, 70 eV) *m/z* (%): 249 (M^+, 14.0), 206 (100.0), 161 (94.2), 131 (29.5), 91 (74.6), 77 (41.6). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.46; H, 7.68; N, 5.63.

2-methoxy-N,N-dimethyl-6-(3-oxobutyl)benzamide (3k)



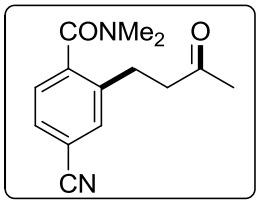
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (t, *J* = 8.0, 1H), 6.81 (d, *J* = 7.7, 1H), 6.76 (d, *J* = 8.3, 1H), 3.80 (s, 3H), 3.12 (s, 3H), 2.95-2.84 (m, 2H), 2.80 (s, 3H), 2.72 - 2.61 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.0, 168.9, 155.3, 138.9, 129.6, 125.9, 121.5, 108.5, 55.6, 44.9, 37.7, 34.4, 29.8, 27.1 ppm; IR *v* (neat, cm^{-1}) 2993, 1765, 171, 1635, 1468, 1376, 1243, 1058, 767; MS (EI, 70 eV) *m/z* (%): 249 (M^+, 3.2), 206 (34.4), 161 (100.0), 133 (19.4), 105 (20.1), 77 (20.2). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.45; H, 7.66; N, 5.61.

N,N-dimethyl-4-nitro-2-(3-oxobutyl)benzamide (3l)



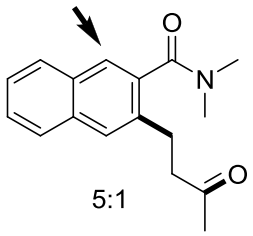
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 - 8.09 (m, 2H), 7.35 (d, *J* = 8.3, 1H), 3.15 (s, 3H), 2.93 -2.83 (m, 7H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.7, 169.0, 148.0, 142.7, 139.8, 127.1, 124.4, 121.6, 43.9, 38.5, 34.7, 29.8, 26.8 ppm; IR *v* (neat, cm^{-1}) 2991, 1765, 1716, 1639, 1523, 1349, 1243, 1060, 846, 741; MS (EI, 70 eV) *m/z* (%): 264 (M^+, 17.0), 221 (84.0), 207 (76.0), 191 (46.4), 176 (60.6) 103 (95.3), 89 (39.2), 77 (24.8). Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.09; H, 6.11; N, 10.59.

4-cyano-N,N-dimethyl-2-(3-oxobutyl)benzamide (3m)



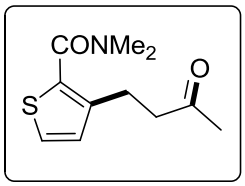
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 2.9, 1H), 7.53 (d, *J* = 1.4, 1H), 7.27 - 7.28 (m, 1H), 3.13 (s, 3H), 2.81-2.83 (m, 7H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.8, 169.2, 141.0, 139.2, 133.2, 130.1, 126.8, 118.1, 112.9, 44.0, 38.5, 34.7, 29.8, 26.6 ppm; IR *v* (neat, cm^{-1}) 2932, 2230, 1766, 1715, 1638, 1398, 1244, 1063,842; MS (EI, 70 eV) *m/z* (%): 244 (M^+, 6.0), 243 (6.9), 201 (100), 156 (58.0), 128 (21.5), 116 (8.7), 101 (16.7), 77 (12.1). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.85; H, 6.61; N, 11.47.

N,N-dimethyl-3-(3-oxobutyl)-2-naphthamide (3n)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 - 7.75 (m, 2H), 7.69 - 7.66 (m, 2H), 7.49 - 7.43 (m, 2H), 3.17 (s, 3H), 3.97 - 2.86 (m, 7H), 2.16 (s, 0.5H), 2.14 (s, 2.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.8, 171.1, 135.0, 135.0, 133.4, 131.5, 128.1, 127.7, 127.3, 126.7, 126.1, 125.4, 44.8, 38.8, 34.7, 29.9, 27.3 ppm; IR *v* (neat, cm^{-1}) 2993, 1765, 1712, 1633, 1496, 1389, 1243, 1119, 1052; MS (EI, 70 eV) *m/z* (%): 269 (M^+, 18.6), 226 (93.6), 181 (100.0), 153 (4.1), 72 (25.9). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.81; H, 7.10; N, 5.23.

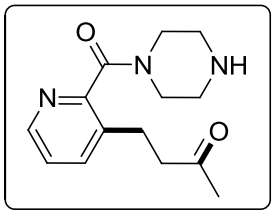
N,N-dimethyl-3-(3-oxobutyl)thiophene-2-carboxamide (3o)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (s, 1H), 6.86 (d, *J* = 5.0, 1H), 3.06 (s, 6H), 2.87 (t, *J* = 7.2, 2H), 2.77 (t, *J* = 7.1, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 165.7, 140.7, 130.8, 128.4, 125.8, 44.1, 36.9, 29.9, 23.0 ppm; MS (EI, 70 eV)

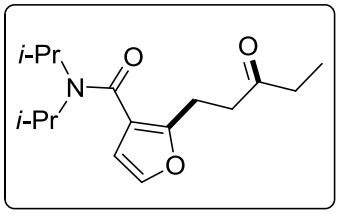
m/z (%): 225 (M^+, 9.1), 182 (79.6), 137 (100.0), 109 (17.4), 72 (36.8). Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22. Found: C, 58.65; H, 6.72; N, 6.21.

4-(2-(piperazine-1-carbonyl)pyridin-3-yl)butan-2-one (3p)



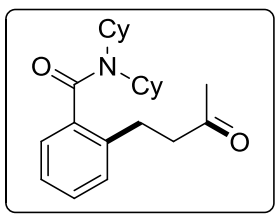
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 0.7 Hz, 1H), 7.00 (d, *J* = 3.4 Hz, 1H), 6.48 (dd, *J* = 3.3, 1.7 Hz, 1H), 3.81 (s, 4H), 2.73 – 2.70 (m, 2H), 2.67 – 2.64 (m, 2H), 2.55 – 2.50 (m, 4H), 2.33 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.44, 159.04, 147.88, 143.71, 143.67, 116.42, 111.27, 53.32, 53.12, 53.05, 52.96, 52.49, 41.05, 30.14; MS (EI, 70 eV) *m/z* (%): 261 (M^+, 10.4), 219 (17.5), 176 (45.8), 132 (100), 78 (7.6). Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; , 16.08. Found: C, 64.33; H,7.32; N, 16.07.

N,N-diisopropyl-2-(3-oxopentyl)furan-3-carboxamide (3q)



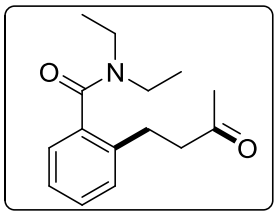
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 1.6, 1H), 6.31 (d, *J* = 1.6, 1H), 3.47 - 4.07 (m, 2H), 2.87 (t, *J* = 7.2, 2H), 2.74 (t, *J* = 7.3, 2H), 2.42 (q, *J* = 7.3, 2H), 1.26 - 1.53 (m, 12H), 1.02 - 1.06 (t, *J* = 9.4, 5.3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.7, 161.3, 144.9, 140.9, 127.6, 112.9, 42.5, 35.8, 20.9, 19.4, 7.7; IR *v* (neat, cm^{-1}) 2977, 2937, 1743, 1625, 1444, 1373, 1333, 1242, 1109, 1047, 774, 610; MS (EI, 70 eV) *m/z* (%): 279 (M^+, 2.5), 236 (27.4), 179 (59.2), 135 (100.0), 84 (29.8). Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.78; H, 9.01; N, 5.03.

N,N-dicyclohexyl-2-(3-oxobutyl)benzamide (3r)



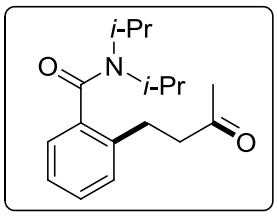
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 - 7.16 (m, 3H), 7.08 - 7.06 (m, 1H), 3.19 - 3.13 (m, 1H), 3.07 - 2.98 (m, 1H), 2.78 - 2.62 (m, 4H), 2.12 (s, 3H), 1.83 (s, 2H), 1.68 - 1.64 (m, 8H), 1.51 - 1.41 (m, 4H), 1.36 - 1.17 (m, 3H), 1.03 - 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 207.9, 170.5, 138.3, 136.7, 129.4, 128.2, 126.0, 124.7, 59.6, 55.8, 45.1, 31.3, 31.1, 29.8, 29.8, 29.8, 27.2, 26.5, 26.5, 25.5, 25.4, 25.2, 24.9; IR *v* (neat, cm^{-1}) 2929, 2855, 2361, 1751, 1629, 1433, 1364, 1313, 1245, 752; MS (EI, 70 eV) *m/z* (%): 355 (M^+, 5.2), 175 (100.0), 148 (34.2), 98 (21.0), 55 (66.0). Anal. Calcd for $C_{23}H_{33}NO_2$: C, 77.70; H, 9.36; N, 3.94. Found: C, 77.71; H, 9.33; N, 3.96.

N,N-diisopropyl-2-(3-oxobutyl)benzamide (3s)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.27 (m, 1H), 7.22 (t, *J* = 6.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 3.56 (m, 2H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.78 (s, 4H), 2.12 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.67, 170.53, 137.15, 136.74, 129.42, 128.77, 126.17, 125.55, 44.86, 42.85, 38.78, 29.77, 27.10, 13.87, 12.68; IR *v* (neat, cm^{-1}) 2974, 2935, 2362, 1715, 1630, 1428, 1366, 1289, 1162, 1083, 755, 630; MS (EI, 70 eV) *m/z* (%): 247 (M^+, 19.6), 246 (45.3), 204 (100.0), 175 (54.6), 131 (19.4), 103 (21.1), 103 (21.1), 77 (16.8). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.85; H, 8.54; N, 5.68.

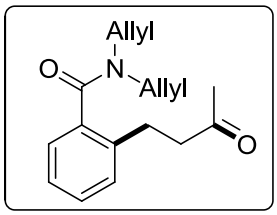
N,N-diisopropyl-2-(3-oxobutyl)benzamide (3t)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 - 7.18 (m, 3H), 7.11 - 7.09 (m, 1H), 3.70-3.63 (m, 1H), 3.54 - 3.47 (m, 1H), 3.01 - 2.67 (m, 4H), 2.12 (s, 3H), 1.55 (t, *J* = 6.3, 6H), 1.11 (q, *J* = 13.5, 6.7, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.0., 170.3, 138.3, 137.0, 129.5, 128.3, 126.2, 124.9, 50.8, 45.7, 45.2, 29.9, 27.2, 20.8, 20.6, 20.5, 20.4

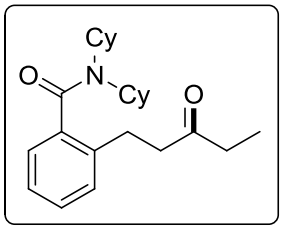
ppm; IR *v* (neat, cm^{-1}) 2972, 1765, 1715, 1628, 1441, 1371, 1336, 1243, 1160, 1055, 756, 615; MS (EI, 70 eV) m/z (%): 275 (M+, 5.8), 232 (19.5), 175 (100.0), 131 (34.2), 103 (20.0), 77 (16.8). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.12; H, 9.16; N, 5.07.

N,N-diallyl-2-(3-oxobutyl)benzamide (3u)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 - 7.28 (m, 1H), 7.23 - 7.17 (m, 3H), 5.92 - 2.82 (m, 1H), 5.69 - 5.60 (m, 1H), 5.26 - 5.07 (m, 4H), 4.43 (s, 1H), 3.88 (s, 1H), 3.70 (d, *J* = 5.4, 2H), 2.82 (s, 4H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 171.0, 137.5, 136.1, 132.7, 132.5, 129.5, 129.1, 126.2, 125.8, 118.1, 118.0, 50.5, 46.3, 45.0, 29.9, 27.3 ppm; IR *v* (neat, cm^{-1}) 2991, 1765, 1715, 1635, 1374, 1244, 1055, 927; MS (EI, 70 eV) *m/z* (%): 271 (M^+, 2.0), 228 (44.3), 175 (100.0), 131 (77.3), 103 (43.4), 91 (30.8), 77 (45.6). Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.24; H, 7.83; N, 5.17.

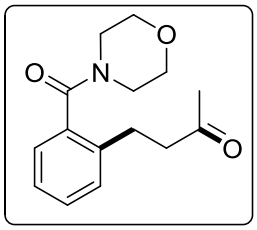
N,N-dicyclohexyl-2-(3-oxopentyl)benzamide (3v)



1H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 7.4 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 3.15 (dd, *J* = 13.4, 10.2 Hz, 1H), 3.06 – 3.02 (m, 1H), 2.92 - 2.83 (m, 2H), 2.81 – 2.75 (m, 1H), 2.71 – 2.61 (m, 3H), 2.43 – 2.36 (m, 2H), 1.83 (s, 2H), 1.69 – 1.63 (m, 7H), 1.51 – 1.43 (m, 3H), 1.27 (s, 3H), 1.05 – 0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.83, 170.67, 138.48, 136.99, 129.51, 128.28, 126.15, 124.79, 59.75, 55.96, 43.89, 35.93, 31.38, 31.22, 29.89, 27.39, 26.68, 26.61, 25.67, 25.56, 25.30, 25.08, 7.76; IR *v* (neat, cm^{-1}) 3742, 2929, 2855, 1765, 1714, 1629, 1433, 1366, 1313, 1244, 1125, 1055, 896, 753, 604; MS (EI, 70 eV) *m/z* (%): 369 (M^+, 5.0),

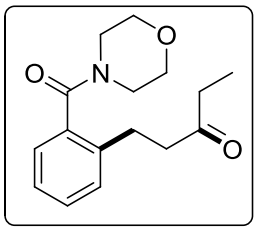
312 (4.0), 284 (11.0), 230 (78.2), 189 (100.0), 148 (34.7), 131 (23.6), 98 (20.4), 77 (9.0), 57 (78.3). Anal. Calcd for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; N, 3.79. Found: C, 78.02; H, 9.54; N, 3.78.

4-(2-(morpholine-4-carbonyl)phenyl)butan-2-one (3w)



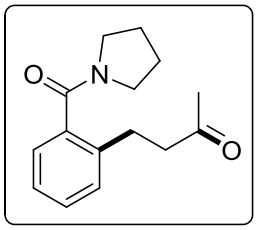
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 - 7.30 (m, 1H), 7.25 - 7.22 (m, 2H), 7.16 - 7.14 (m, 1H), 3.80 - 3.77 (m, 4H), 3.59 (t, *J* = 4.6, 2H), 3.25 (m, 2H), 2.90 - 2.76 (m, 4H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.5, 169.7, 137.6, 135.3, 129.5, 129.2, 126.3, 125.9, 66.7, 47.3, 44.7, 41.8, 29.8, 26.9 ppm; IR *v* (neat, cm^{-1}) 2965, 2855, 2362, 1765, 1713, 1634, 1428, 1364, 1250, 1114, 1016, 754, 558; MS (EI, 70 eV) *m/z* (%): 261 (M^+, 8.5), 218 (22.0), 175 (34.4), 103 (40.2), 91 (28.2), 77 (50.5). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.96; H, 7.32; N, 5.35.

1-(2-(morpholine-4-carbonyl)phenyl)pentan-3-one (3w')



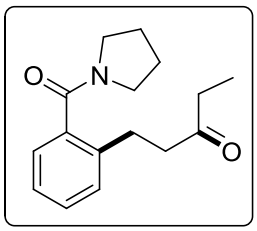
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 - 7.29 (m, 2H), 7.23 - 7.21 (m, 1H), 7.16 - 7.14 (m, 1H), 3.80 - 3.77 (m, 4H), 3.59 (t, *J* = 4.8 Hz, 2H), 3.25 (d, *J* = 3.2 Hz 2H), 2.92 - 2.74 (m, 4H), 2.44 – 2.39 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.3, 169.8, 137.9, 135.5, 129.6, 129.3, 126.4, 126.1, 66.9, 47.5, 43.5, 42.0, 35.9, 27.2, 7.7; IR *v* (neat, cm^{-1}) 2982, 2361, 1745, 1713, 1636, 1427, 1373, 1244, 1113, 1050, 1015, 771; MS (EI, 70 eV) *m/z* (%): 275 (M^+, 13.1), 218 (84.5), 189 (37.1), 131 (84.0), 103 (35.8), 77 (27.9). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.78; H, 7.71; N, 5.08.

4-(2-(pyrrolidine-1-carbonyl)phenyl)butan-2-one (3x)



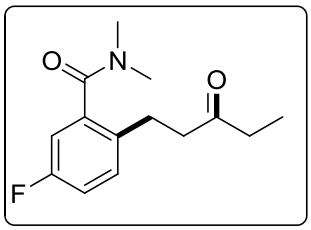
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 - 7.27 (m, 1H), 7.24 - 7.18 (m, 3H), 3.64 (t, *J* = 7.0, 2H), 3.15 (t, *J* = 6.7, 2H), 2.83 (s, 4H), 2.12 (s, 3H), 2.00 - 1.93 (m, 2H), 1.90 - 1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 207.7, 169.4, 137.4, 137.0, 129.4, 128.8, 126.2, 125.7, 48.5, 45.2, 44.9, 29.7, 27.1, 25.8, 24.4 ppm; IR *v* (neat, cm^{-1}) 2984, 2362, 1750, 1628, 1421, 1373, 1242, 1049, 753, 608; MS (EI, 70 eV) *m/z* (%): 245 (M^+, 7.0), 202 (100.0), 131 (79.5), 103 (35.4), 77 (44.5). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.45; H, 7.80; N, 5.69.

1-(2-(pyrrolidine-1-carbonyl)phenyl)pentan-3-one (3x')



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.26 (m, 1H), 7.23 – 7.18 (m, 3H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.82 (td, *J* = 10.0, 3.5 Hz, 4H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.98 – 1.95 (m, 2H), 1.89 – 1.85 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.66, 169.63, 137.65, 137.38, 129.57, 129.00, 126.31, 125.87, 48.64, 45.39, 43.73, 35.88, 27.38, 25.97, 24.56, 7.72; IR *v* (neat, cm^{-1}) 3741, 2973, 2878, 2361, 1711, 1629, 1420, 1243, 755, 655; MS (EI, 70 eV) *m/z* (%): 259 (M^+, 7.0), 202 (100.0), 131 (23.9), 103 (27.7), 77 (20.1), 57 (44.5). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.11; H, 8.18; N, 5.43.

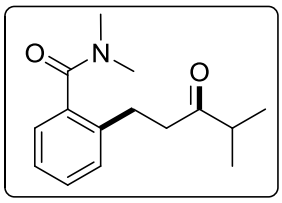
5-fluoro-N,N-dimethyl-2-(3-oxopentyl)benzamide (3y)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.19 (m, 1H), 7.03 (t, *J* = 8.8 Hz, 1H), 6.96 (d,

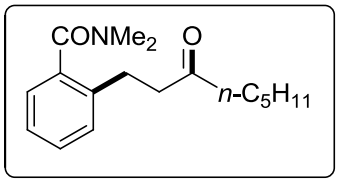
J = 7.5 Hz, 1H), 3.11 (s, 3H), 2.84 (s, 3H), 2.76 (s, 4H), 2.42 (q, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.24, 169.68, 165.34, 162.62, 160.17, 138.84, 138.80, 128.06, 127.98, 125.29, 125.12, 121.73, 121.70, 115.82, 115.60, 42.19, 38.72, 35.66, 34.67, 21.03, 21.01, 7.74; IR *v* (neat, cm^{-1}) 2938, 1765, 1713, 1639, 1503, 1456, 1396, 1244, 1114, 1061, 802; MS (EI, 70 eV) *m/z* (%): 251 (M^+, 11.3), 194 (100.0), 149 (60.6), 121 (23.0), 101 (26.0), 57 (81.4). Anal. Calcd for $C_{14}H_{18}FNO_2$: C, 66.91; H, 7.22; N, 5.57. Found: C, 66.89; H, 7.23; N, 5.56.

N,N-dimethyl-2-(4-methyl-3-oxopentyl)benzamide (3z)



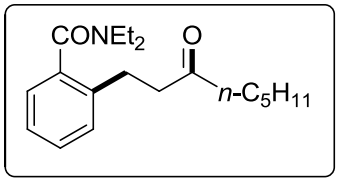
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 - 7.27 (m, 1H), 7.25 - 7.19 (m, 2H), 7.14 - 7.17 (m, 1H), 3.12 (s, 3H), 2.81 - 2.83 (m, 7H), 2.53 - 2.60 (m, 1H), 1.07 (d, *J* = 6.9, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.9, 171.3, 137.7, 136.5, 129.5, 129.0, 126.3, 126.0, 41.6, 40.9, 38.7, 34.6, 27.3, 18.1 ppm; IR *v* (neat, cm^{-1}) 2968, 1765, 1708, 1634, 1456, 1389, 1243, 1062, 753, 636; MS (EI, 70 eV) *m/z* (%): 247 (M^+, 5.7), 204 (18.4), 176 (100), 131 (86.6), 117 (20.1), 103 (42.4), 77 (27.7). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.86; H, 8.55; N, 5.67.

N,N-dimethyl-2-(3-oxooctyl)benzamide (3aa)



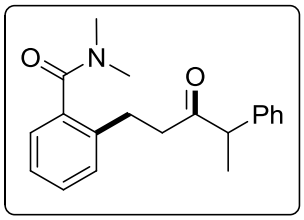
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 - 7.27 (m, 1H), 7.24 - 7.20 (m, 2H), 7.16 - 7.14 (m, 1H), 3.12 (s, 3H), 2.83 - 2.79 (m, 7H), 2.37 (t, *J* = 7.5, 2H), 1.59 - 1.52 (m, 2H), 1.33 - 1.21 (m, 4H), 0.88 (t, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.3, 171.2, 137.5, 136.5, 129.5, 128.9, 126.3, 126.0, 43.9, 42.8, 38.6, 34.6, 31.3, 27.2, 23.4, 22.4, 13.8 ppm; IR *v* (neat, cm^{-1}) 2990, 2360, 1745, 1637, 1377, 1243, 1057, 752; MS (EI, 70 eV) *m/z* (%): 275 (M^+, 2.5), 219 (21.8), 176 (100.0), 131 (52.3), 103 (31.8), 71 (31.1). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.17; H, 9.15; N, 5.07.

N,N-diethyl-2-(3-oxooctyl)benzamide (3ab)



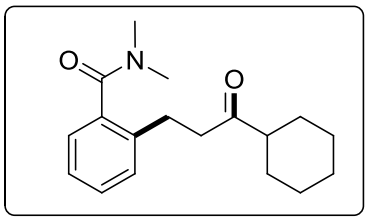
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (t, *J* = 6.7 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.15 (m, 1H), 3.74 – 3.38 (m, 2H), 3.12 (q, *J* = 7.0 Hz, 2H), 2.80 (d, *J* = 29.0 Hz, 4H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.57 – 1.54 (m, 2H), 1.30 – 1.22 (m, 7H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.31, 170.57, 137.39, 136.95, 129.52, 128.78, 126.22, 125.65, 44.04, 42.87, 42.83, 38.80, 31.37, 27.27, 23.48, 22.40, 13.96, 13.88, 12.79; IR *v* (neat, cm^{-1}) 2933, 1713, 1633, 1427, 1375, 1289, 1077, 755, 631; MS (EI, 70 eV) *m/z* (%): 303 (M^+, 1.8), 247 (22.1), 204 (100.0), 131 (47.5), 103 (35.8), 71 (28.4). Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.20; H, 9.64; N, 4.64.

N,N-dimethyl-2-(3-oxo-4-phenylpentyl)benzamide (3ac)



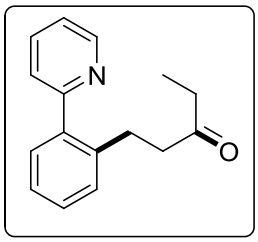
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 - 7.27 (m, 2H), 7.16 - 7.25 (m, 5H), 7.09 - 7.11 (m, 2H), 3.73 (q, *J* = 6.9, 1H), 3.05 (s, 3H), 2.81 - 2.63 (m, 7H), 1.37 (d, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 209.7, 171.1, 140.5, 137.3, 136.4, 128.8, 127.8, 127.1, 126.2, 125.9, 52.9, 42.1, 38.6, 34.5, 27.2, 17.3 ppm; IR *v* (neat, cm^{-1}) 2931, 1765, 1711, 1634, 1498, 1450, 1390, 1244, 1066, 756, 702, 637; MS (EI, 70 eV) *m/z* (%): 309 (M^+, 1.0), 204 (98.7), 176 (33.4), 131 (100.0), 103 (99.8), 91 (55.4), 77 (73.6). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.66; H, 7.51; N, 4.53.

2-(3-cyclohexyl-3-oxopropyl)-N,N-dimethylbenzamide (3ad)



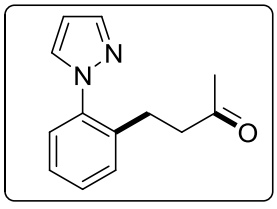
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 - 7.28 (m, 1H), 7.20 - 7.24 (m, 2H), 7.14 - 7.16 (m, 1H), 3.12 (s, 3H), 2.80 - 2.83 (m, 7H), 2.35 - 2.25 (m, 1H), 1.80 - 1.83 (m, 2H), 1.78 - 1.72 (m, 2H), 1.63 - 1.66 (m, 1H), 1.20 - 1.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.2, 171.2, 137.6, 136.5, 129.4, 128.9, 126.3, 126.0, 50.7, 41.8, 38.6, 34.6, 28.3, 27.1, 25.8, 25.6 ppm; IR *v* (neat, cm^{-1}) 2928, 2854, 2361, 1705, 1635, 1503, 1447, 1393, 1265, 1068; MS (EI, 70 eV) *m/z* (%): 287 (M^+, 8.3), 204 (15.2), 176 (100.0), 131 (47.8), 83 (40.6). Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.23; H, 8.75; N, 4.88.

1-(2-(pyridin-2-yl)phenyl)pentan-3-one (3ae)



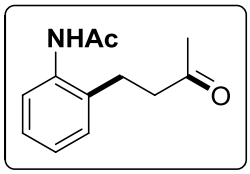
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 4.1 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.24 (m, 5H), 3.00 – 2.94 (m, 2H), 2.67 – 2.63 (m, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl^3$) δ = 210.94, 160.00, 149.06, 140.33, 139.27, 136.43, 129.90, 129.83, 128.54, 126.28, 124.02, 121.83, 44.01, 35.86, 27.60, 7.78; IR *v* (neat, cm^{-1}) 3848, 2990, 2356, 1764, 1375, 1243, 1055, 752, 631; MS (EI, 70 eV) *m/z* (%): 239 (M^+, 1.0), 210 (1.0), 182 (100), 167 (75.4), 152 (4.1), 139 (5.2), 115 (2.8), 91 (6.6), 78 (5.2). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.82. Found: C, 80.31; H, 7.16; N,5.84.

4-(2-(1H-pyrazol-1-yl)phenyl)butan-2-one (3af)



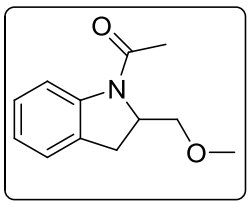
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 1.3 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 6.44 (t, *J* = 2.0 Hz, 1H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl^3$) δ = 207.80, 140.40, 139.72, 137.25, 130.70, 130.61, 128.79, 127.05, 126.56, 106.48, 44.39, 29.82, 25.90; IR *v* (neat, cm^{-1}) 3789, 2988, 2359, 1763, 1713, 1512, 1367, 1243, 1049, 938, 759; MS (EI, 70 eV) *m/z* (%): 214 (M^+, 3.0), 171 (100.0), 156 (17.2), 144 (10.8), 130 (10.7), 103 (12.4), 77 (13.7). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.65; H, 7.05; N, 12.28.

N-(2-(3-oxobutyl)phenyl)acetamide (3ag)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 4.1 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.24 (m, 5H), 3.00 – 2.94 (m, 2H), 2.67 – 2.63 (m, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl^3$) δ = 210.94, 160.00, 149.06, 140.33, 139.27, 136.43, 129.90, 129.83, 128.54, 126.28, 124.02, 121.83, 44.01, 35.86, 27.60, 7.78; MS (EI, 70 eV) *m/z* (%): 205 (M^+, 20.2), 187 (12.7), 162 (53.4), 144 (37.8), 120 (100), 106 (73.9), 93 (19.1), 77 (17.8). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.22; H, 7.80; N, 6.39.

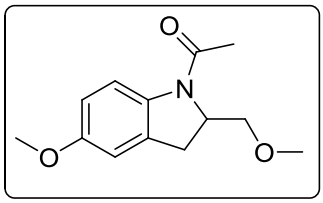
1-(2-(methoxymethyl)indolin-1-yl)ethanone (4a)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.14 (m, 4H), 6.03 (s, 1H), 3.33 (m, 3H), 2.73 – 2.65 (m, 1H), 2.58 – 2.49 (m, 1H), 2.44 – 2.38 (m, 1H), 2.17 (s, 3H), 1.83 – 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.96, 136.94, 127.92, 126.48, 126.09, 125.73, 99.99, 81.96, 55.27, 30.86, 24.29, 23.21; IR *v* (neat, cm^{-1}) 2991, 1765, 1659, 1491, 1375, 1243, 1057, 759; MS (EI, 70 eV) *m/z* (%): 205 (M^+, 7.7), 190 (7.5), 163

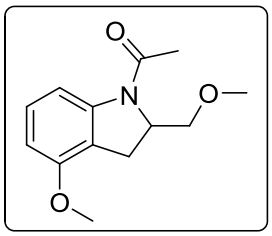
(10.5), 148 (11.1), 130 (100), 118 (18.8), 103 (13.8), 91 (11.6), 77 (31.3). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.23; H, 7.37; N, 6.84.

1-(5-methoxy-2-(methoxymethyl)indolin-1-yl)ethanone (4b)



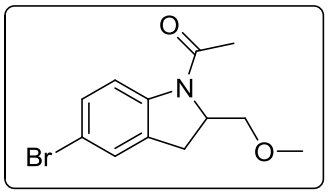
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 – 6.97 (m, 1H), 6.79 – 6.74 (m, 2H), 6.28 -5.80 (s, 1H), 3.80 (s, 3H), 3.32 (s, 3H), 2.72 – 2.58 (m, 1H), 2.47 (dd, *J* = 25.8, 10.0 Hz, 2H), 2.14 (s, 3H), 1.82 – 1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.18, 157.73, 135.98, 126.70, 113.03, 111.90, 81.90, 55.43, 55.25, 31.03, 24.88, 23.07; IR *v* (neat, cm^{-1}) 2989, 1763, 1663, 1501, 1373, 1243, 1052, 914, 741, 603; MS (EI, 70 eV) m/z (%): 235 (M+, 14), 203 (8), 193 (9), 178 (8), 161 (100), 146 (27.7), 130 (15), 131 (61.1), 103 (20.8), 77 (18.9). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.37; H, 7.27; N, 5.96.

1-(4-methoxy-2-(methoxymethyl)indolin-1-yl)ethanone (4c)



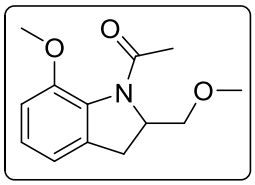
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (t, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 6.8 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.00 (s, 1H), 3.84 (s, 3H), 3.31 (s, 3H), 2.91 – 2.83 (m, 1H), 2.45 – 2.38 (m, 1H), 2.25 – 2.17 (m, 4H), 1.99 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.95, 156.70, 137.34, 126.26, 121.36, 117.99, 107.33, 81.52, 55.53, 55.29, 29.27, 23.56, 17.46; IR *v* (neat, cm^{-1}) 2989, 2362, 1766, 1663, 1590, 1471, 1371, 1244, 1059, 913, 744; MS (EI, 70 eV) m/z (%): 235 (M+, 15.2), 220 (10), 203 (9), 193 (8), 178 (15.7), 160 (100), 145 (26), 130 (21), 117 (20), 104 (10), 89 (12), 77 (13.5). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.34; H, 7.26; N, 5.96.

1-(5-bromo-2-(methoxymethyl)indolin-1-yl)ethanone (4d)



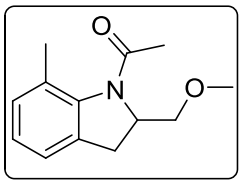
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.34 (m, 2H), 7.18 -7.10 (m, 1H), 5.95 (s, 1H), 3.31 (s, 3H), 2.75 – 2.67 (m, 1H), 2.60 – 2.52 (m, 1H), 2.33 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.18 (s, 3H), 1.92 -1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.54, 135.82, 131.03, 129.48, 127.13, 119.11, 81.91, 55.26, 30.15, 23.93, 23.23; IR *v* (neat, cm^{-1}) 2990, 1764, 1666, 1484, 1373, 1308, 1243, 914, 744; MS (EI, 70 eV) m/z (%): 285 (M+, 7), 283(7), 241 (11), 210 (81), 130 (100), 117 (23), 102 (17), 89 (10), 77 (20). Anal. Calcd for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97; N, 4.93. Found: C, 50.74; H, 4.96; N, 4.94.

1-(7-methoxy-2-(methoxymethyl)indolin-1-yl)ethanone (4e)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.9 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 2H), 6.11 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.87 (s, 3H), 3.37 (s, 3H), 2.55 (dddd, *J* = 14.3, 7.9, 5.5, 2.9 Hz, 2H), 2.41 – 2.28 (m, 1H), 1.99 (s, 3H), 1.54 (tt, *J* = 12.5, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.45, 154.18, 138.14, 127.51, 126.31, 119.33, 110.07, 82.17, 55.51, 55.31, 32.72, 25.51, 21.88; IR *v* (neat, cm^{-1}) 2991, 1765, 1665, 1480, 1375, 1243, 1056; MS (EI, 70 eV) m/z (%): 235 (M+, 10), 220 (4), 193 (14), 160 (100.0), 145 (17), 130 (29), 103 (20.8), 117 (23), 91 (14), 77 (15). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.36; H, 7.25 N, 5.97.

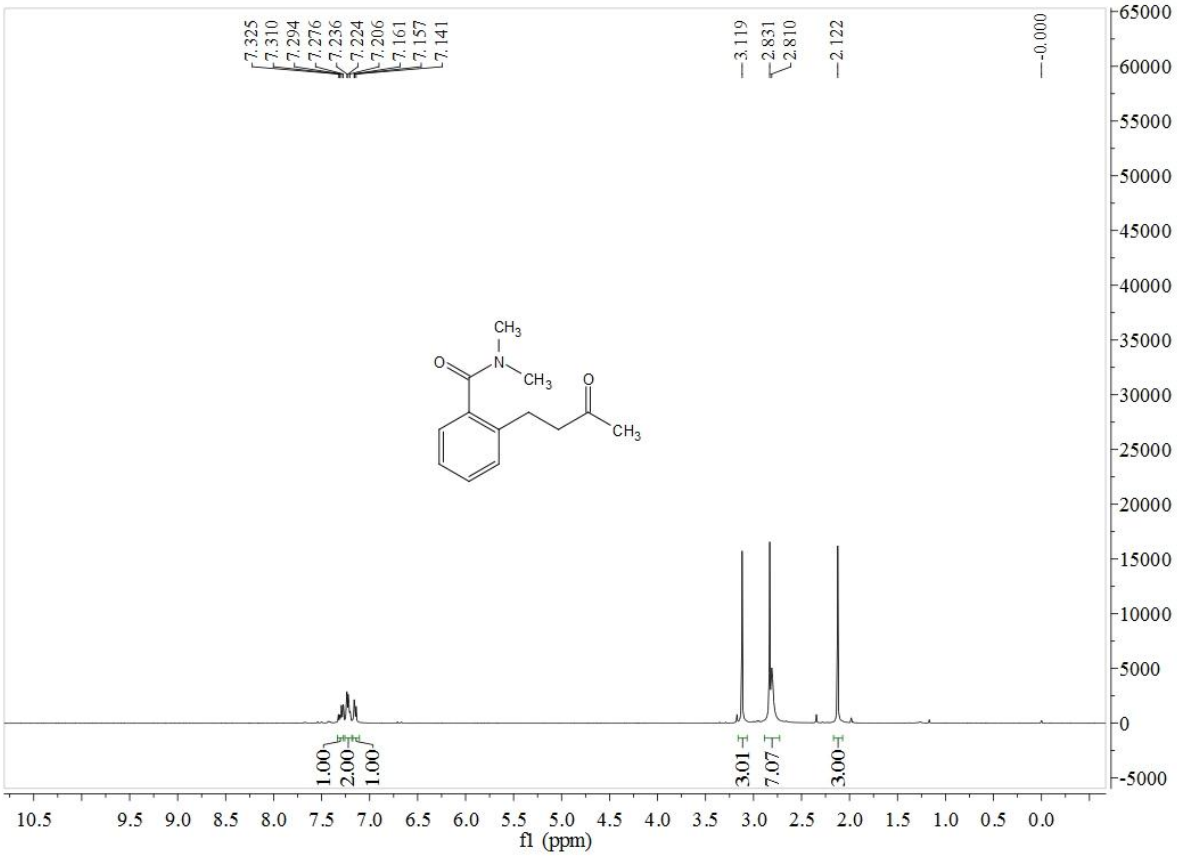
1-(2-(methoxymethyl)-7-methylindolin-1-yl)ethanone (4f)

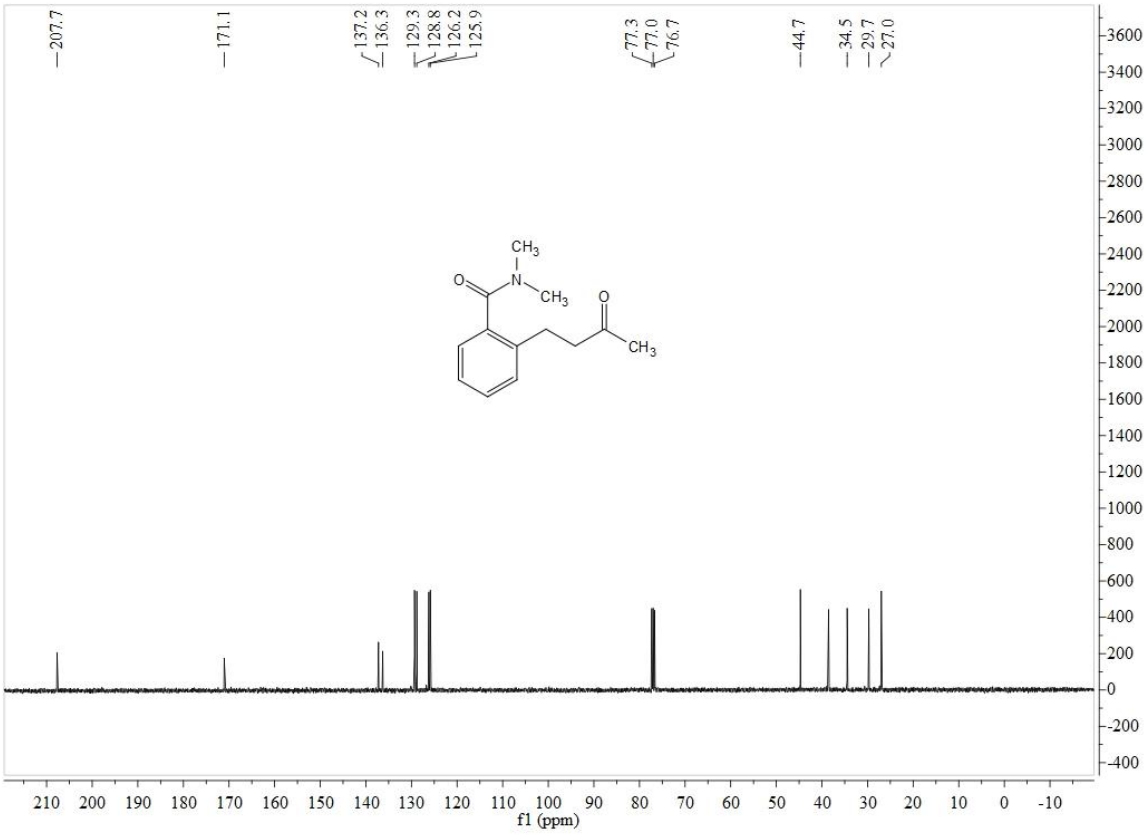


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 – 7.11 (m, 2H), 7.07 – 7. 5 (m, 1H), 6.13 (dd, *J* = 8.2, 5.8 Hz, 1H), 3.45 (s, 3H), 2.60 – 2.56 (m, 1H), 2.48 (ddd, *J* = 14.2, 4.6, 2.5 Hz,

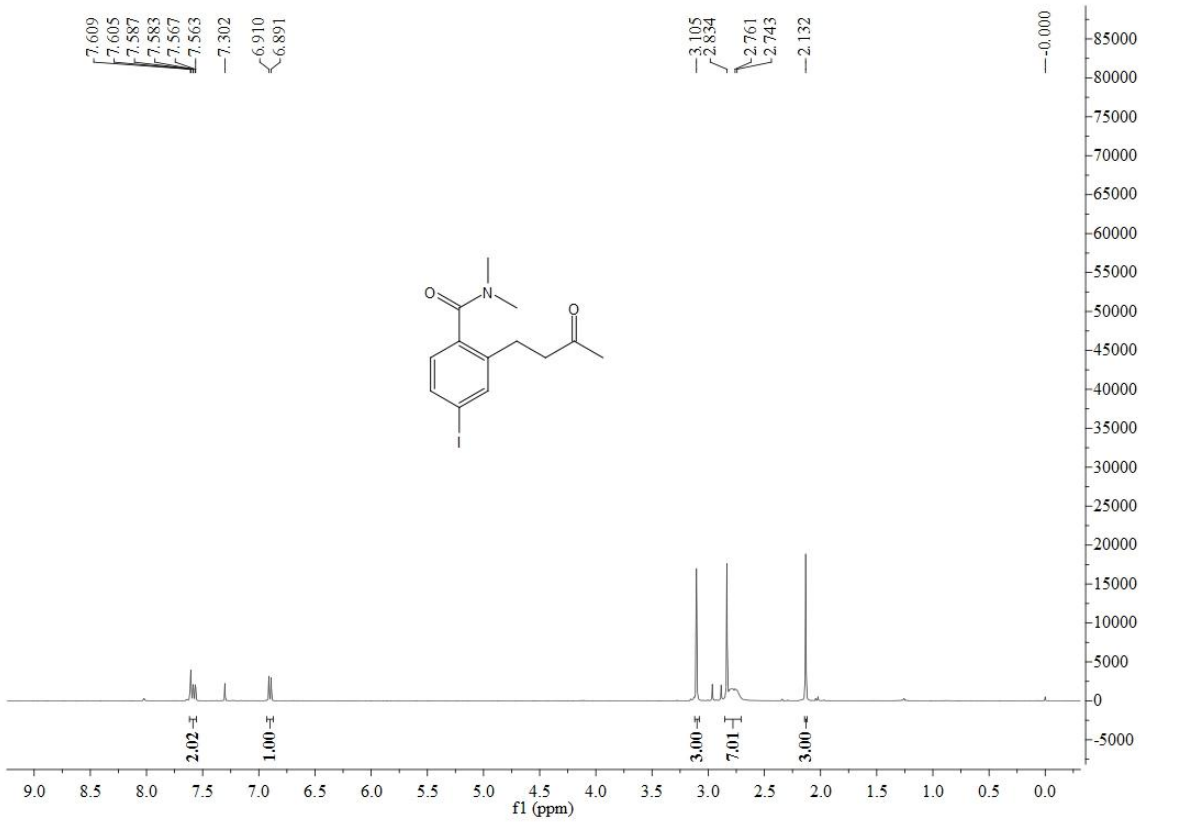
1H), 2.31 (s, 3H), 2.25 (dd, *J* = 14.0, 4.9 Hz, 1H), 1.90 (s, 3H), 1.48 – 1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.36, 137.91, 136.85, 134.42, 129.29, 126.95, 124.61, 83.90, 56.02, 32.90, 26.08, 21.89, 17.52; IR *v* (neat, cm^{-1}) 2992, 1765, 1377, 1243, 1056; MS (EI, 70 eV) m/z (%): 219 (M+, 3), 177 (4), 162 (6), 145 (100), 130 (23), 115 (23), 103 (9), 91 (25), 77 (17). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.22; H, 7.28; N, 6.41.

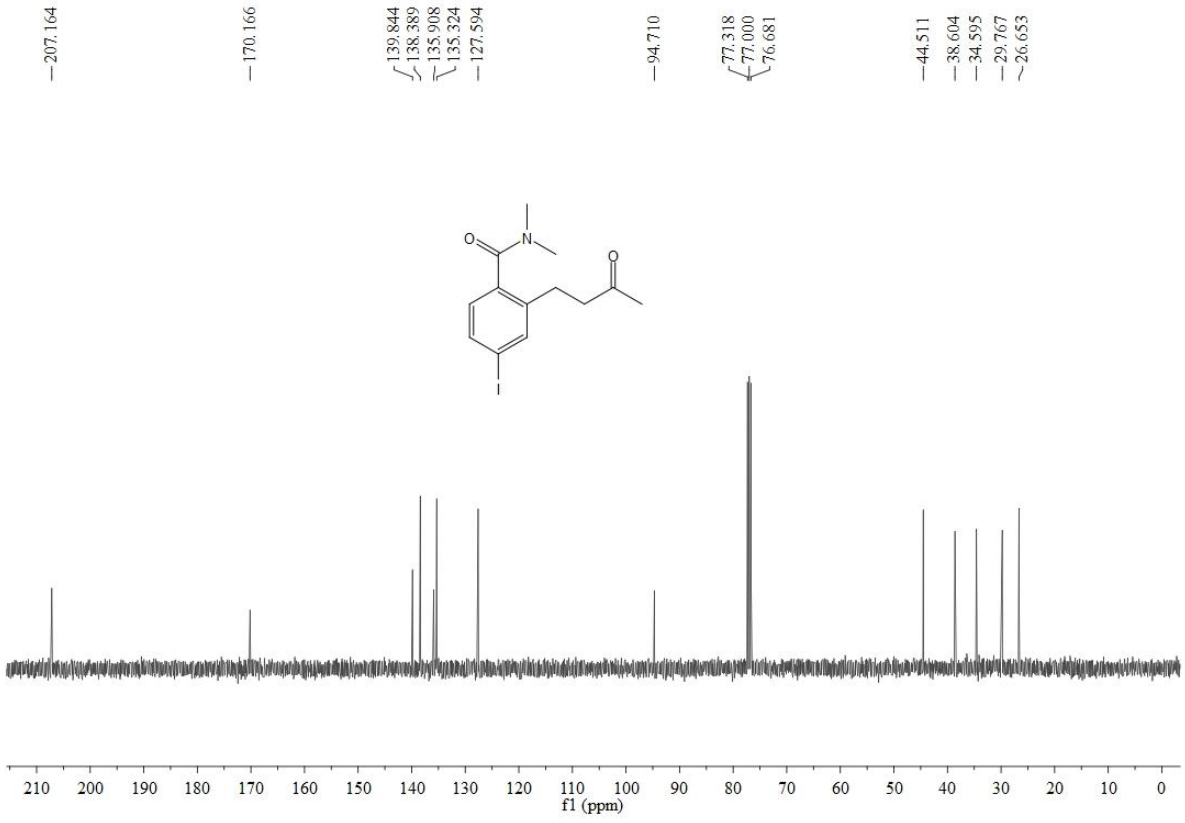
3a


7.325
7.310
7.294
7.276
7.236
7.224
7.206
7.161
7.157
7.141
3.119
2.831
2.810
2.122
-0.000
1.00
2.00
1.00
3.01
7.07
3.00
f1 (ppm)

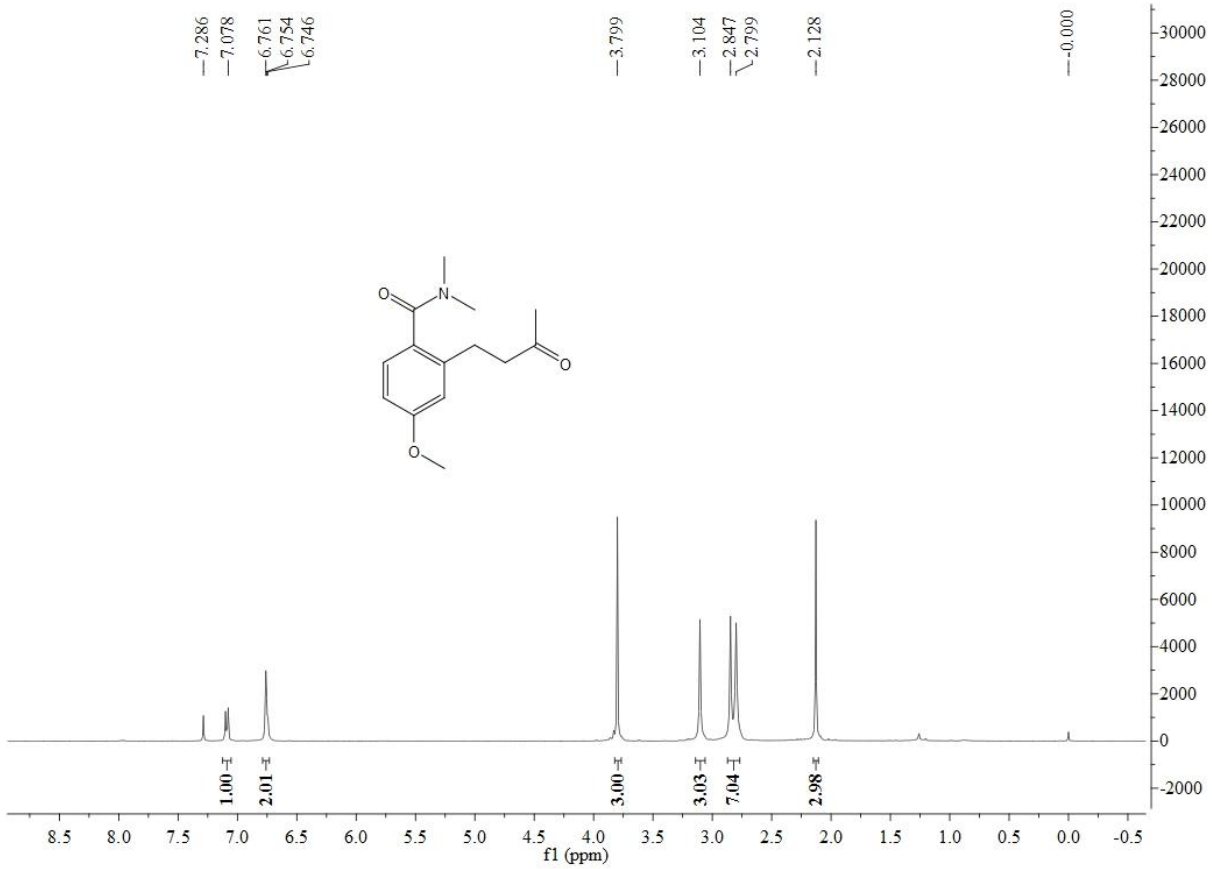

207.7
171.1
137.2
136.3
129.3
128.8
126.2
125.9
77.3
77.0
76.7
44.7
34.5
29.7
27.0
f1 (ppm)

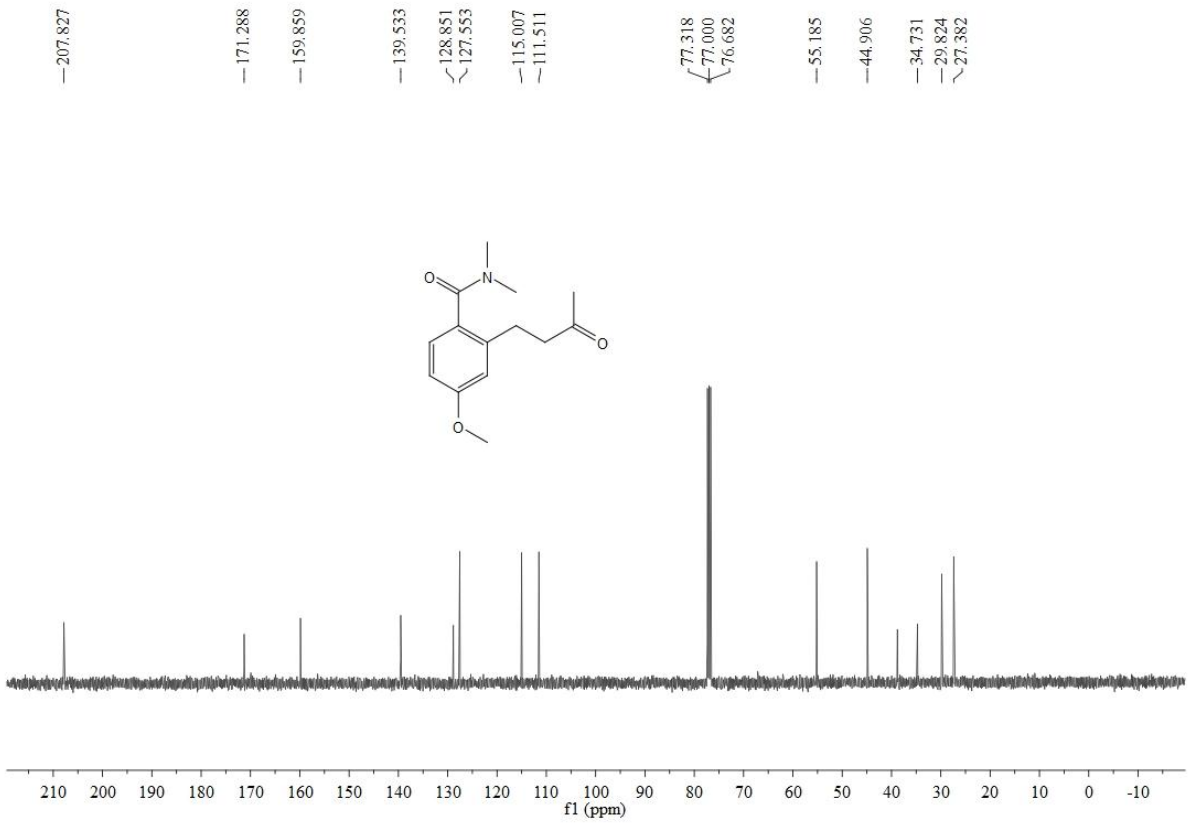
3b





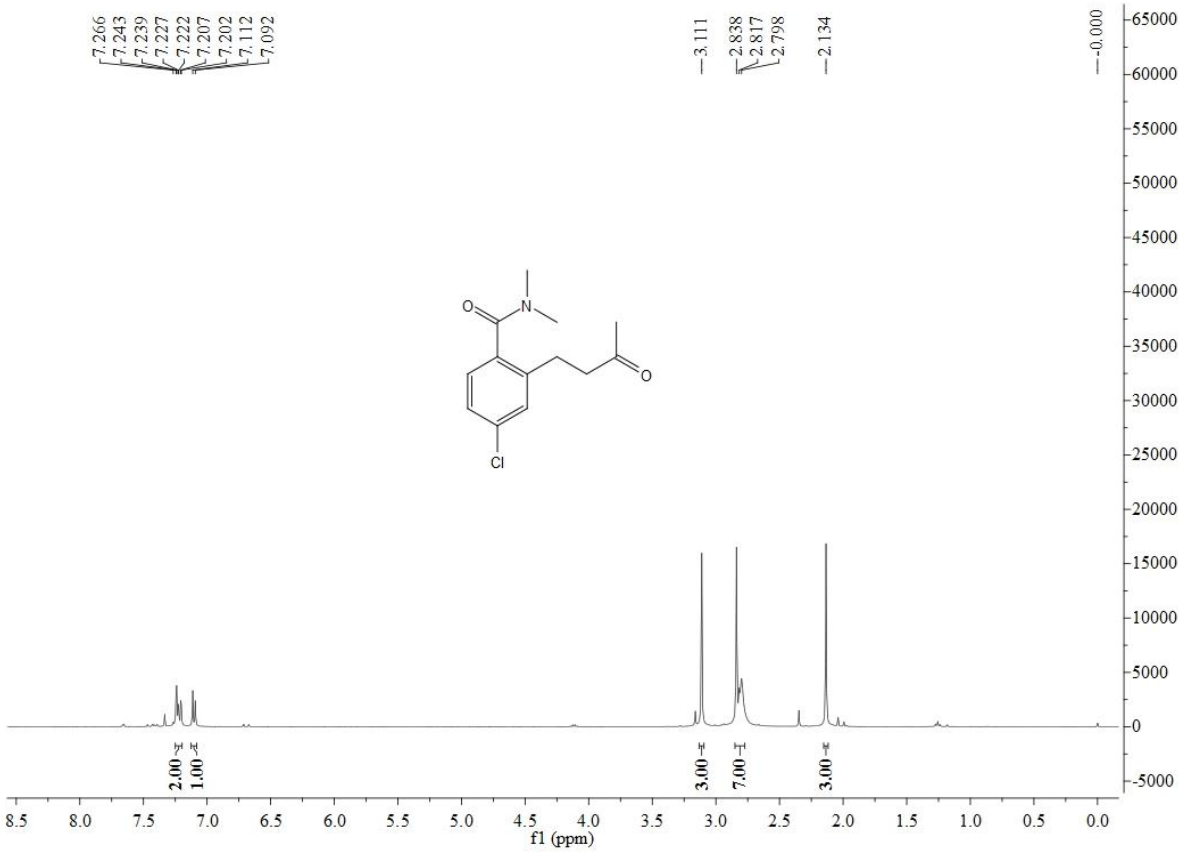
3c

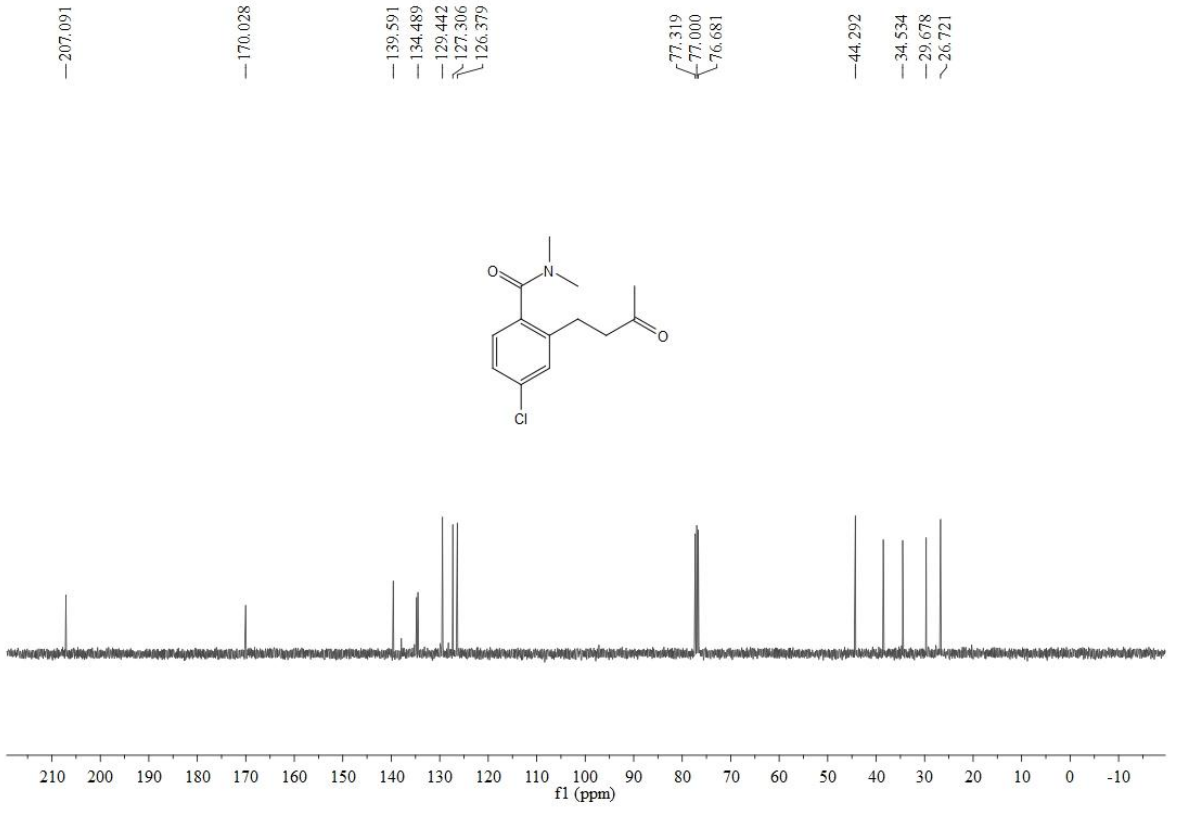




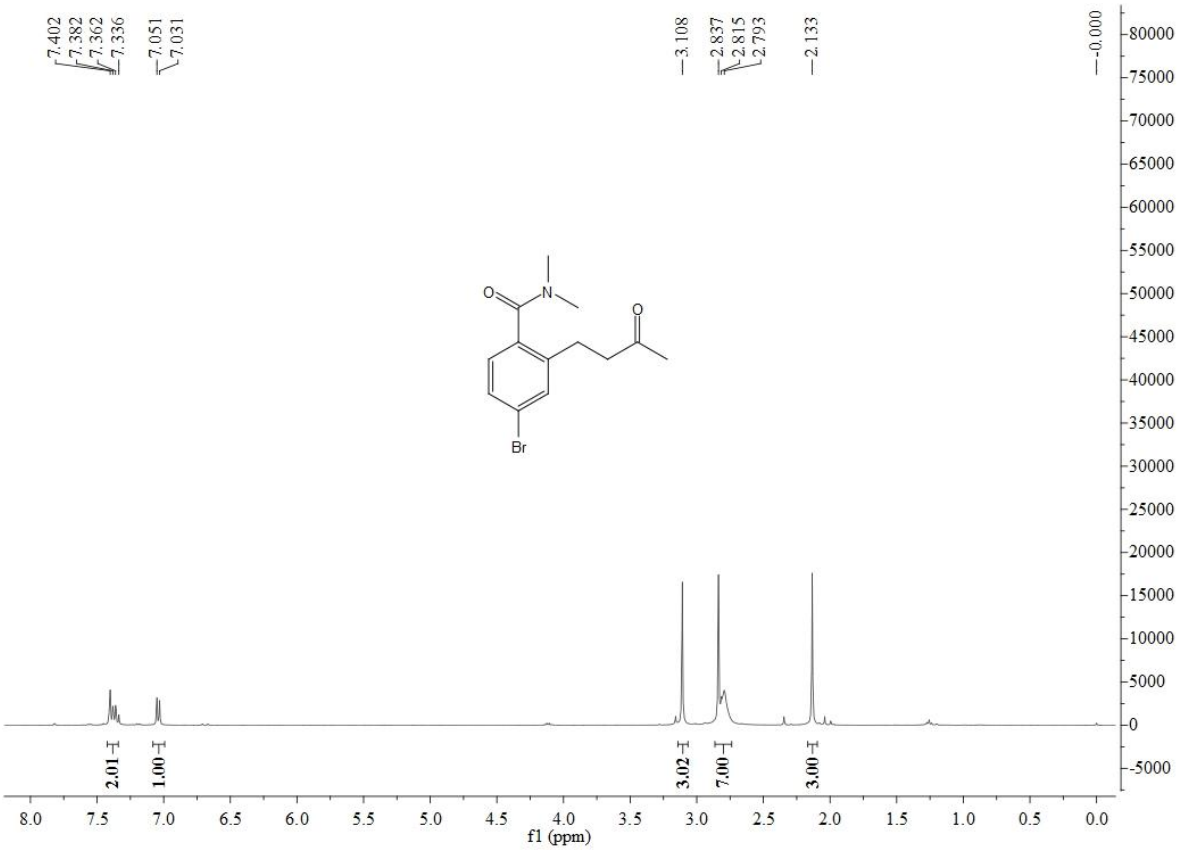
3d

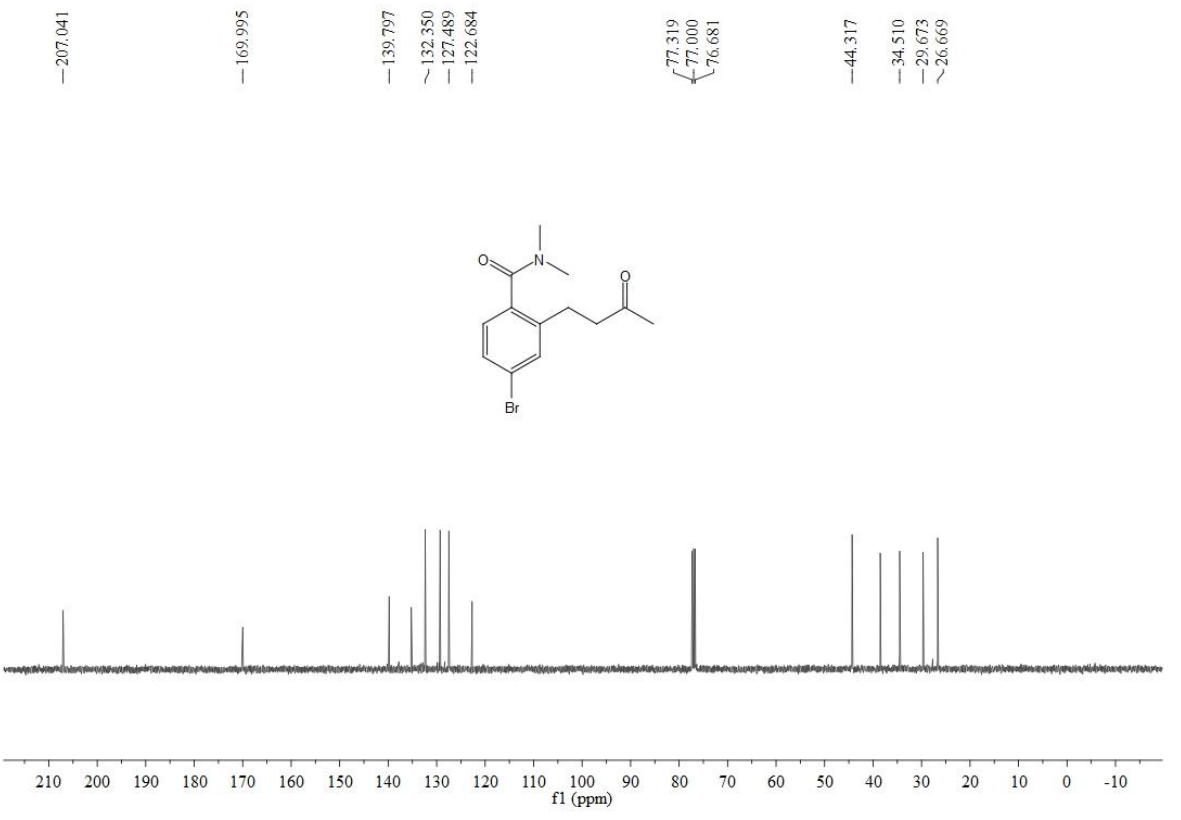
3e



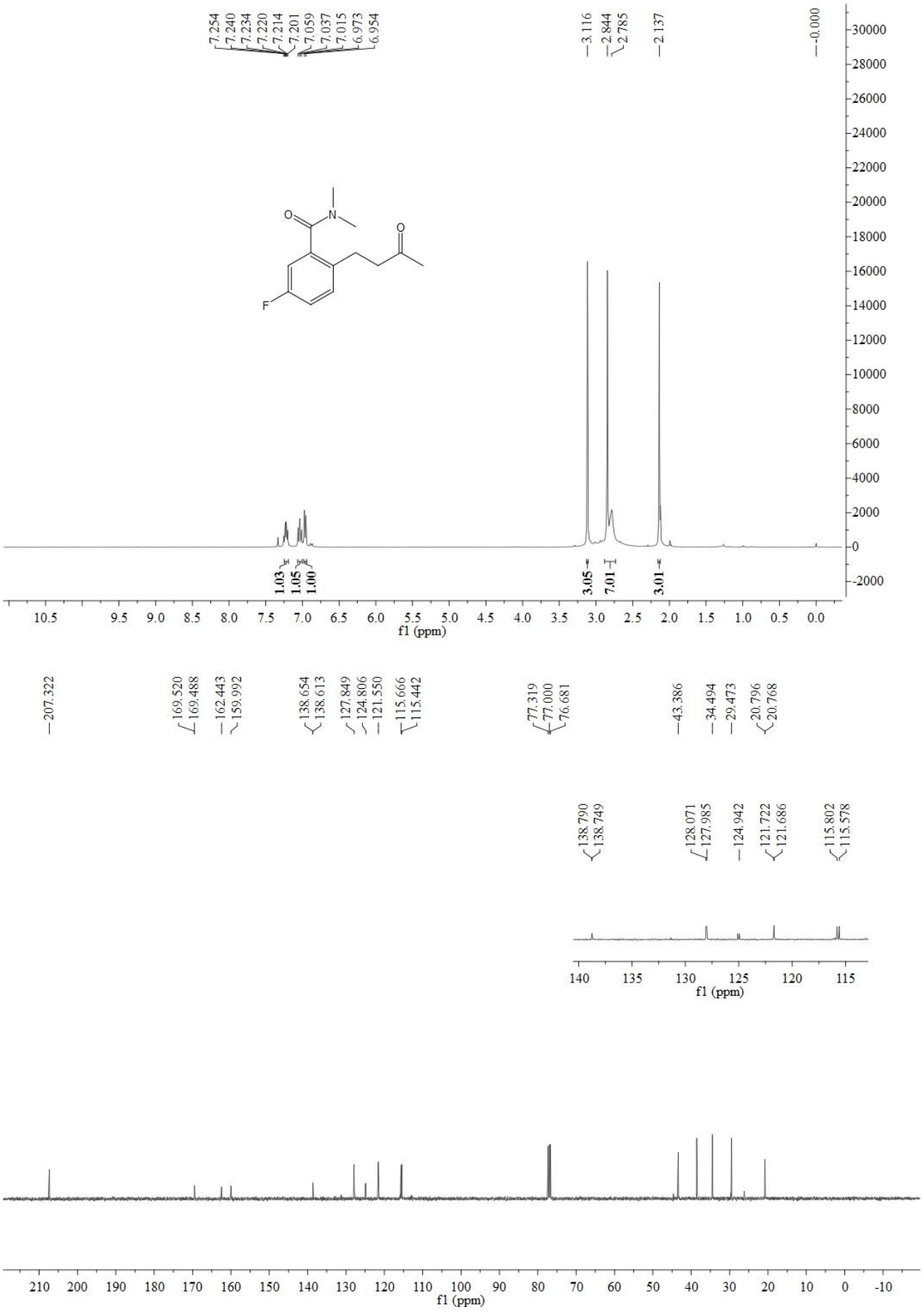


3f

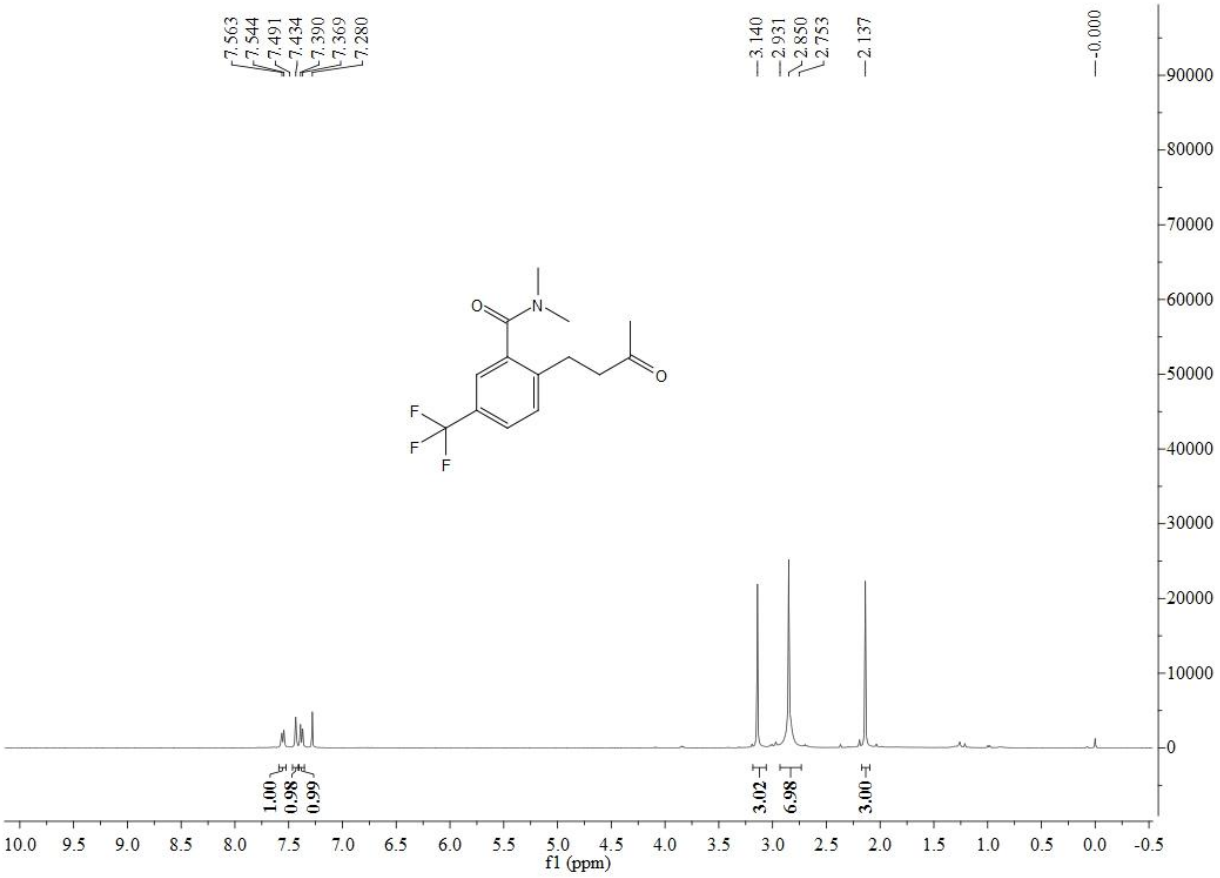


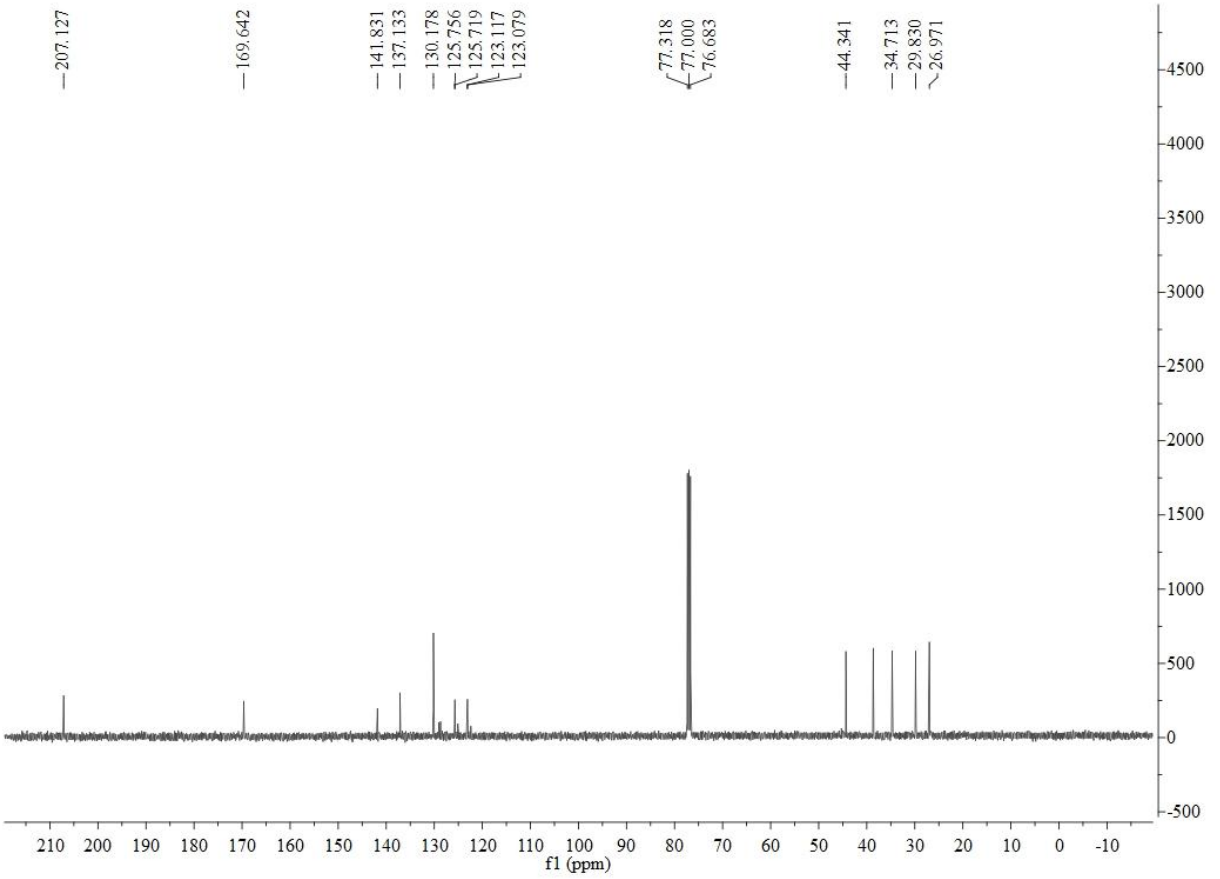


3g



3h





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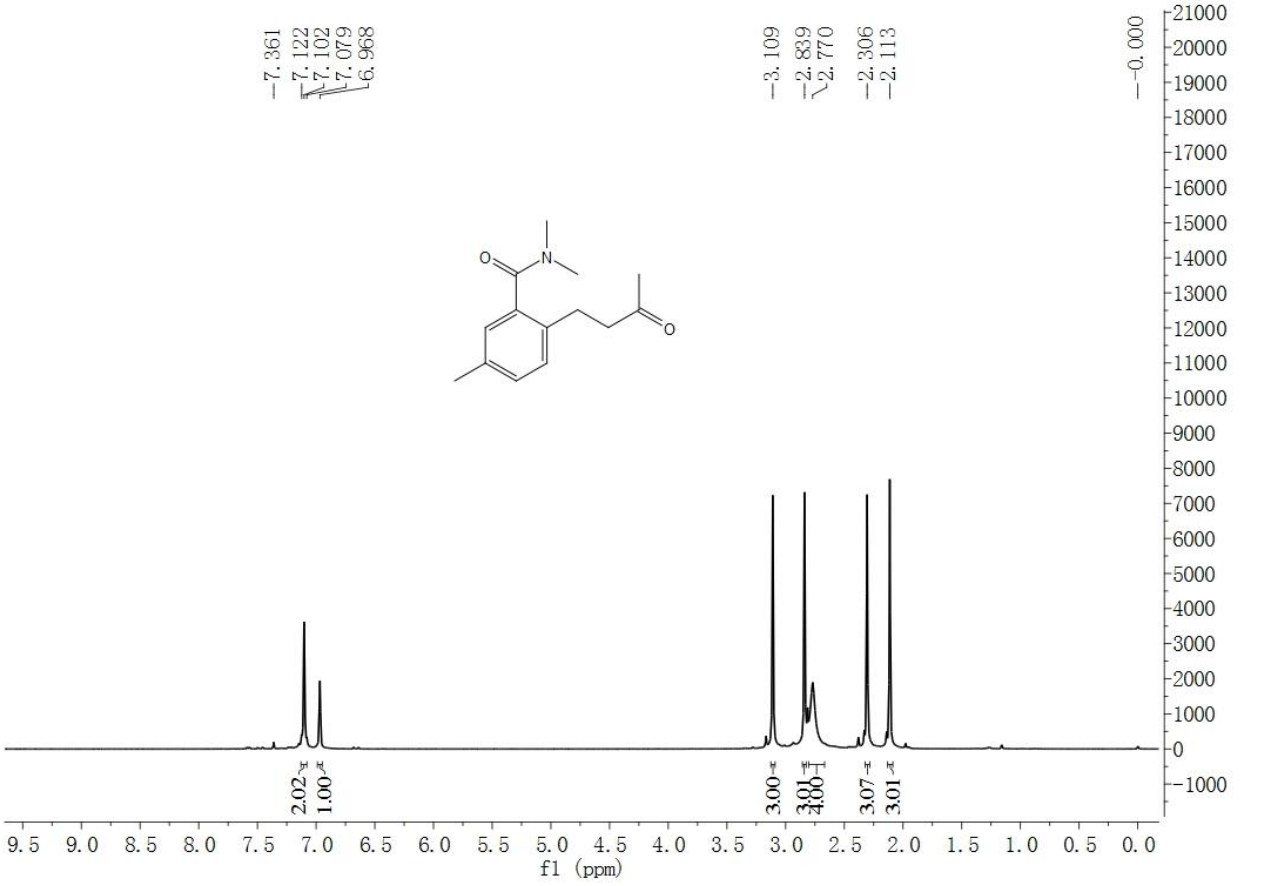

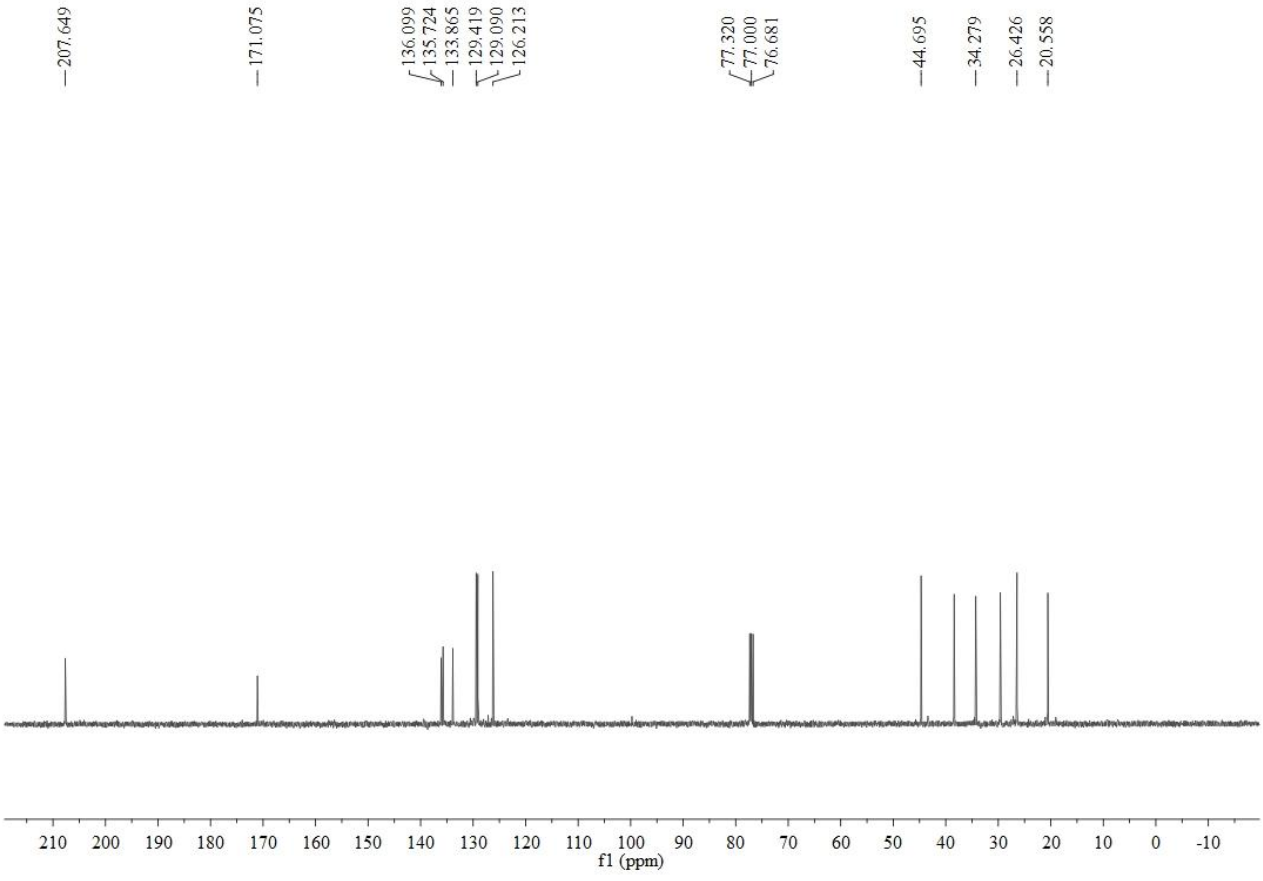

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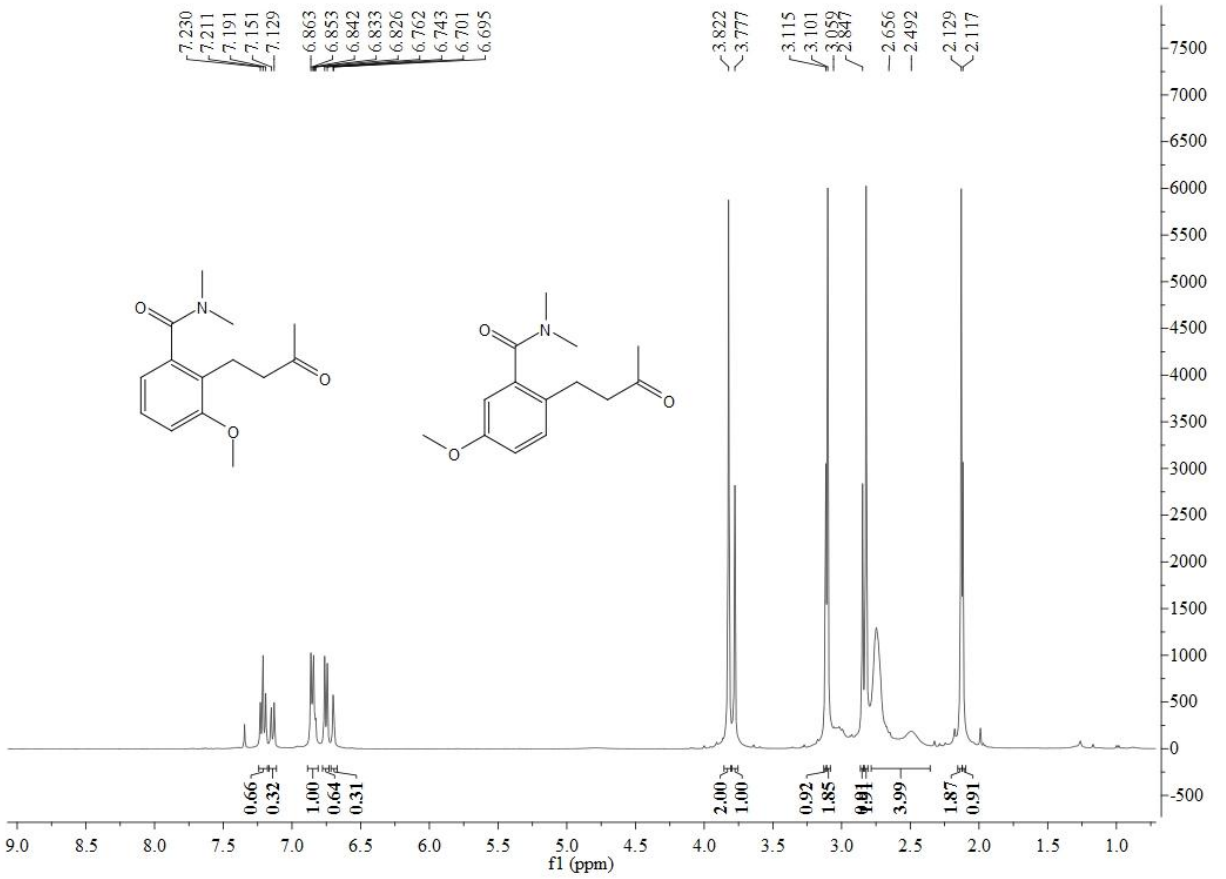

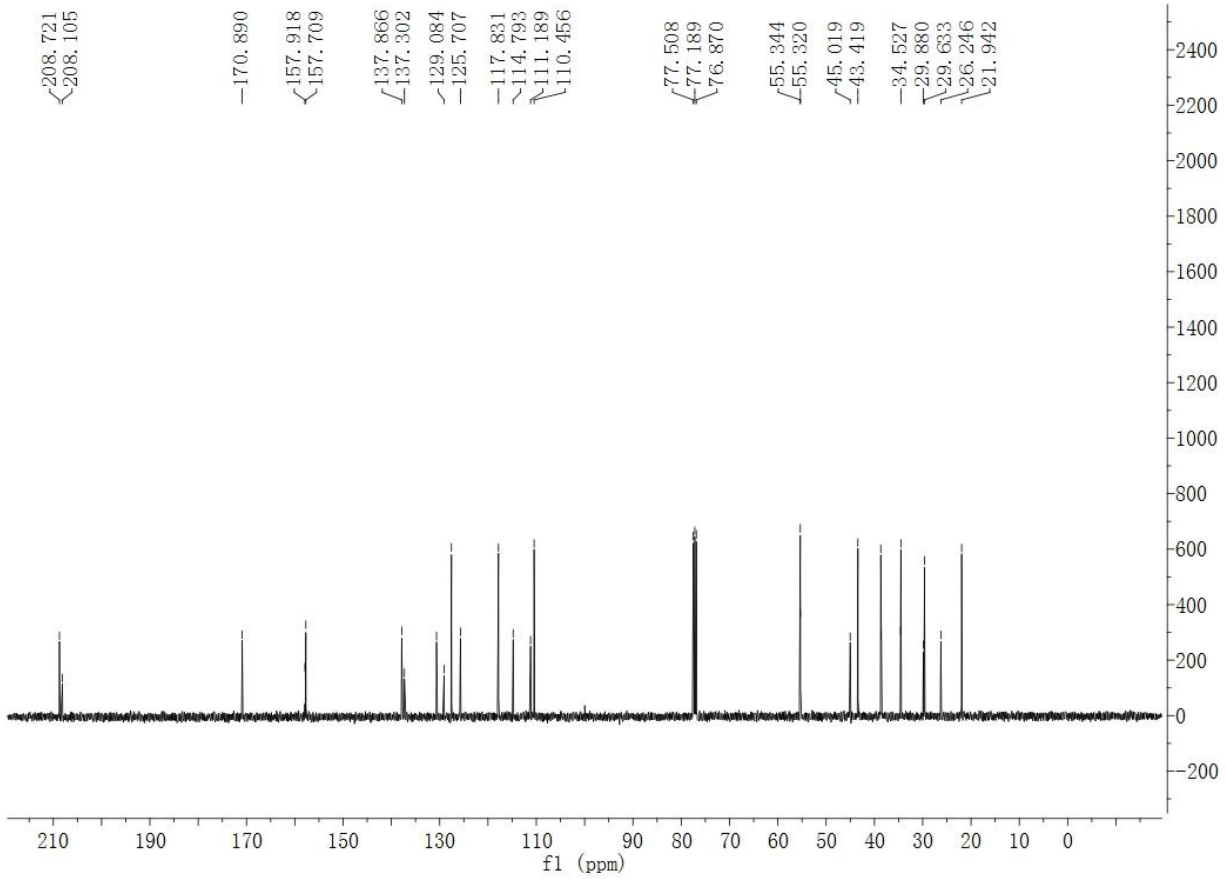

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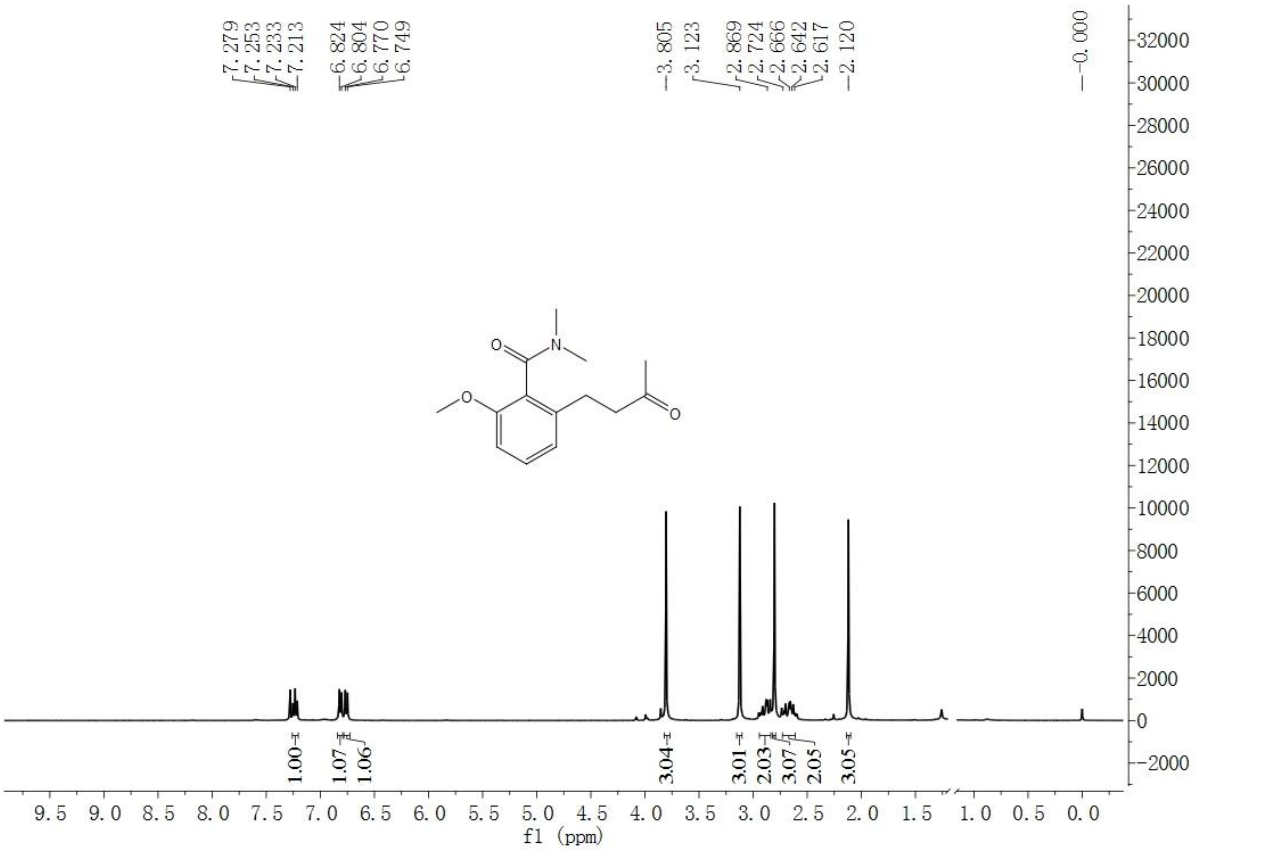

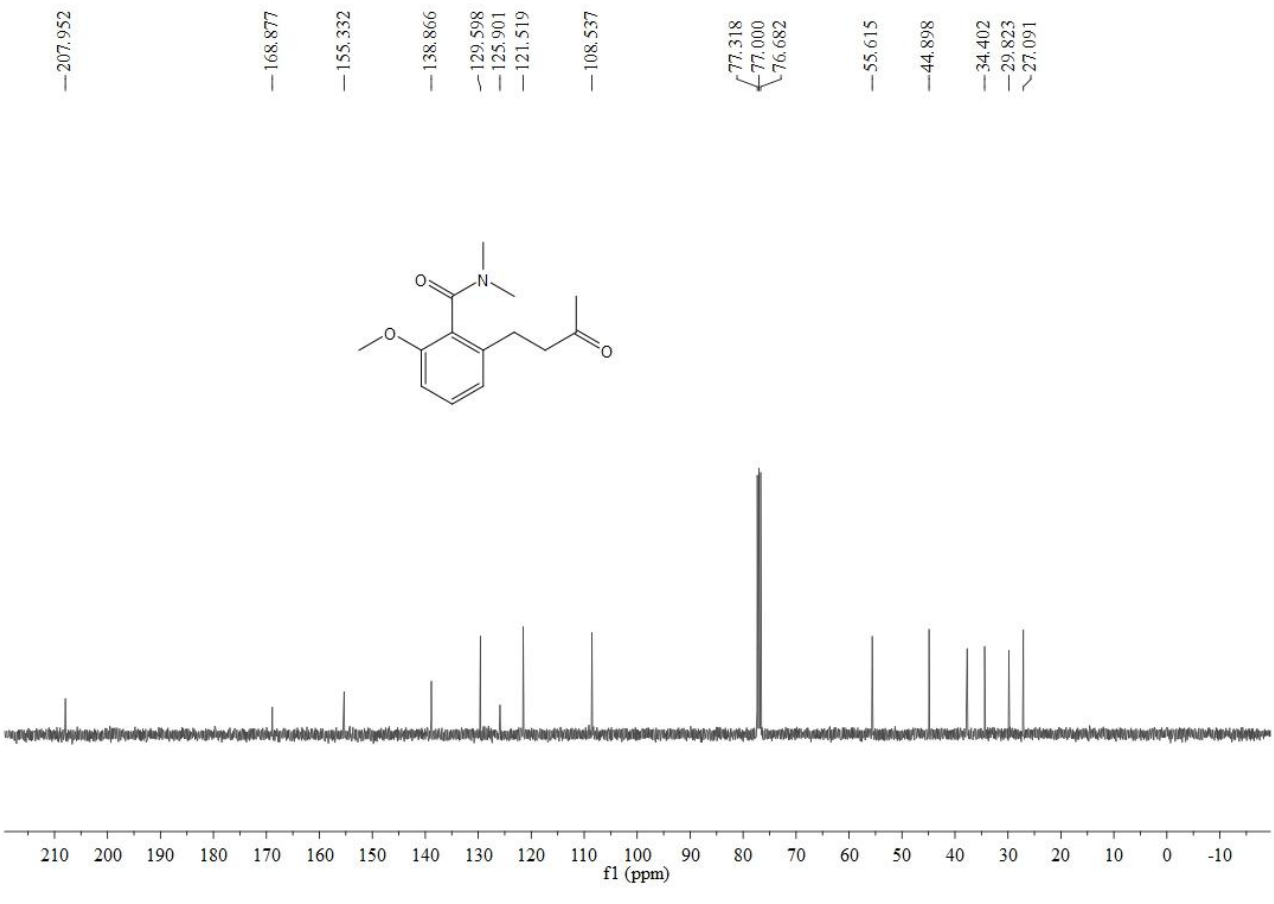

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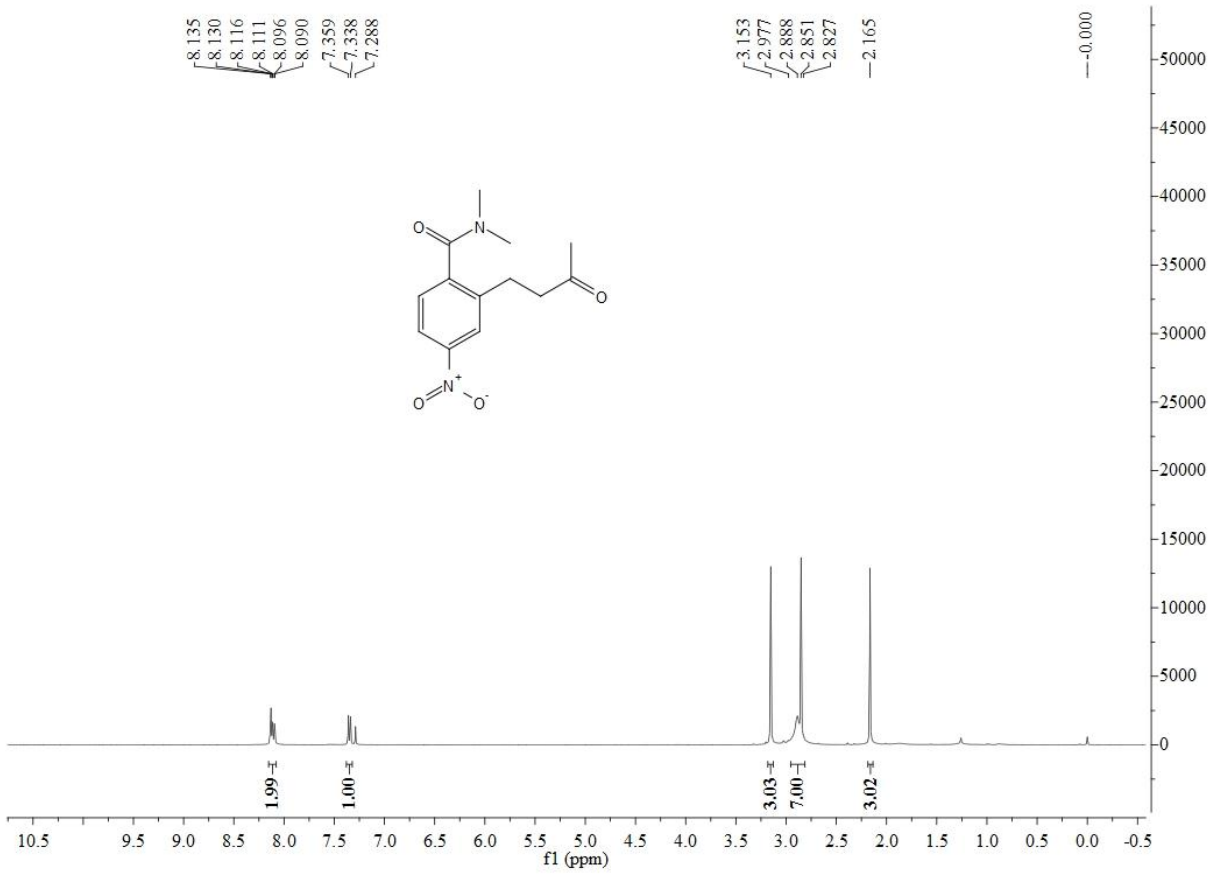
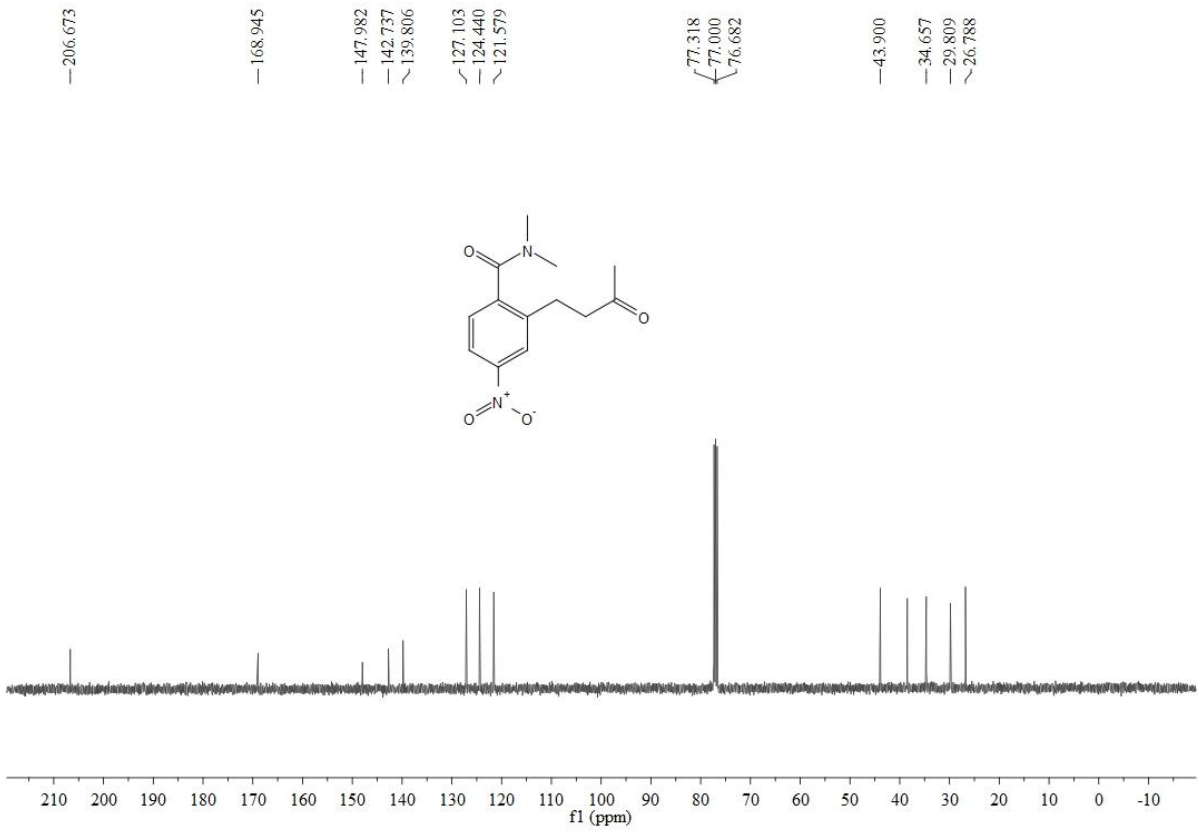
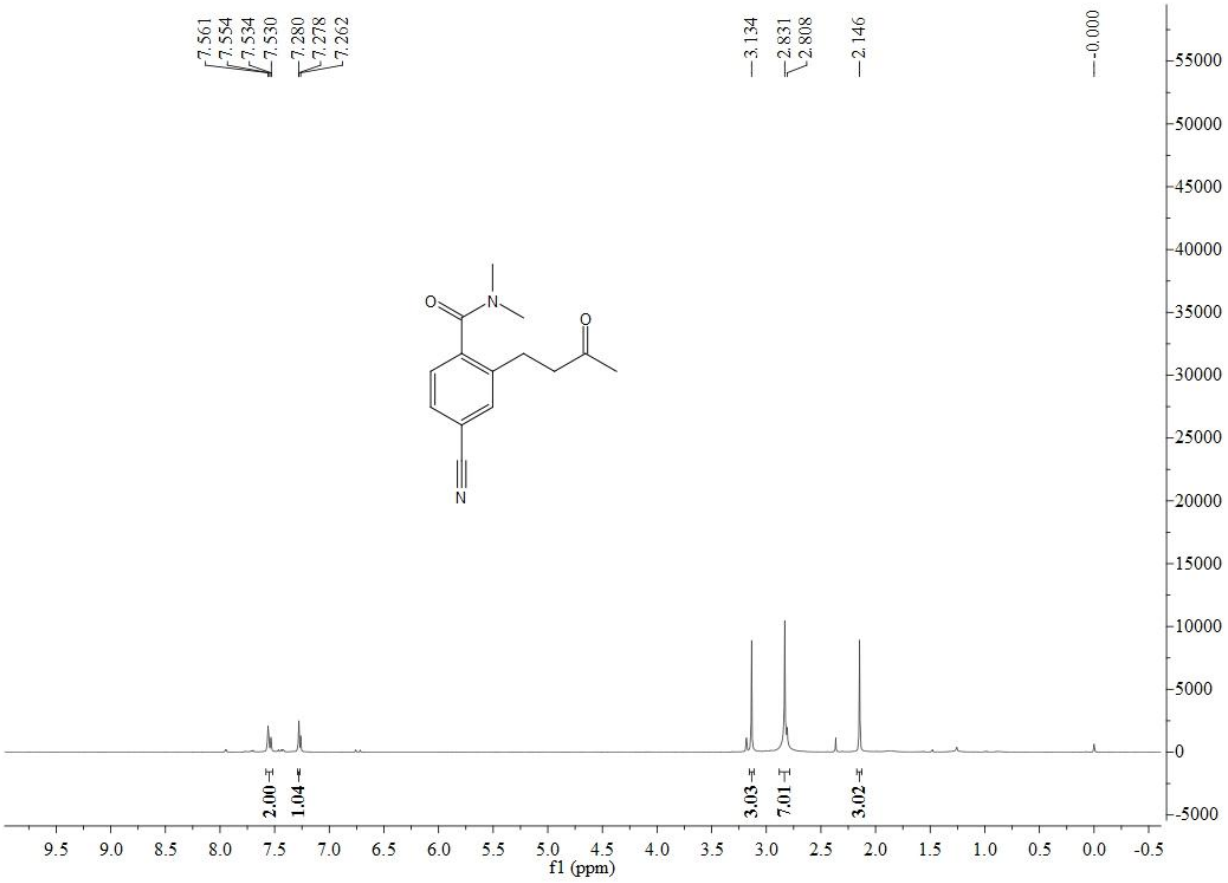
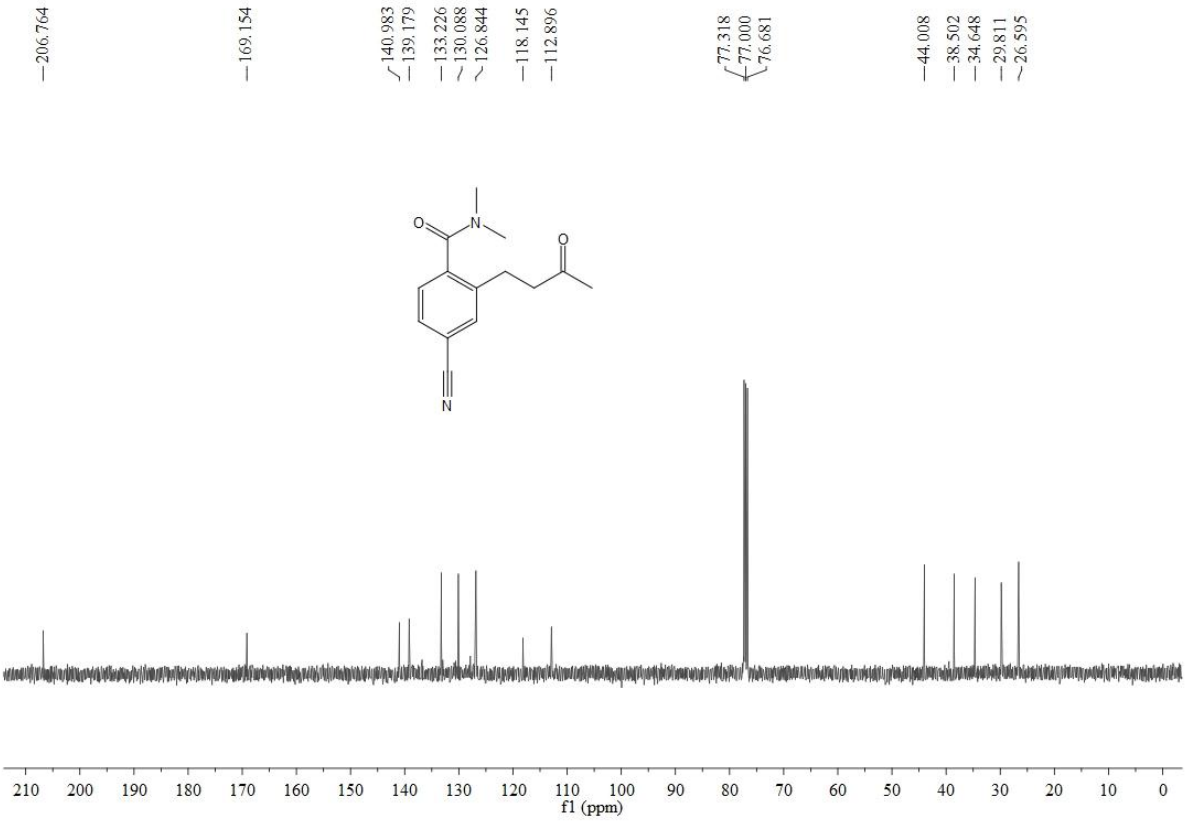




3m





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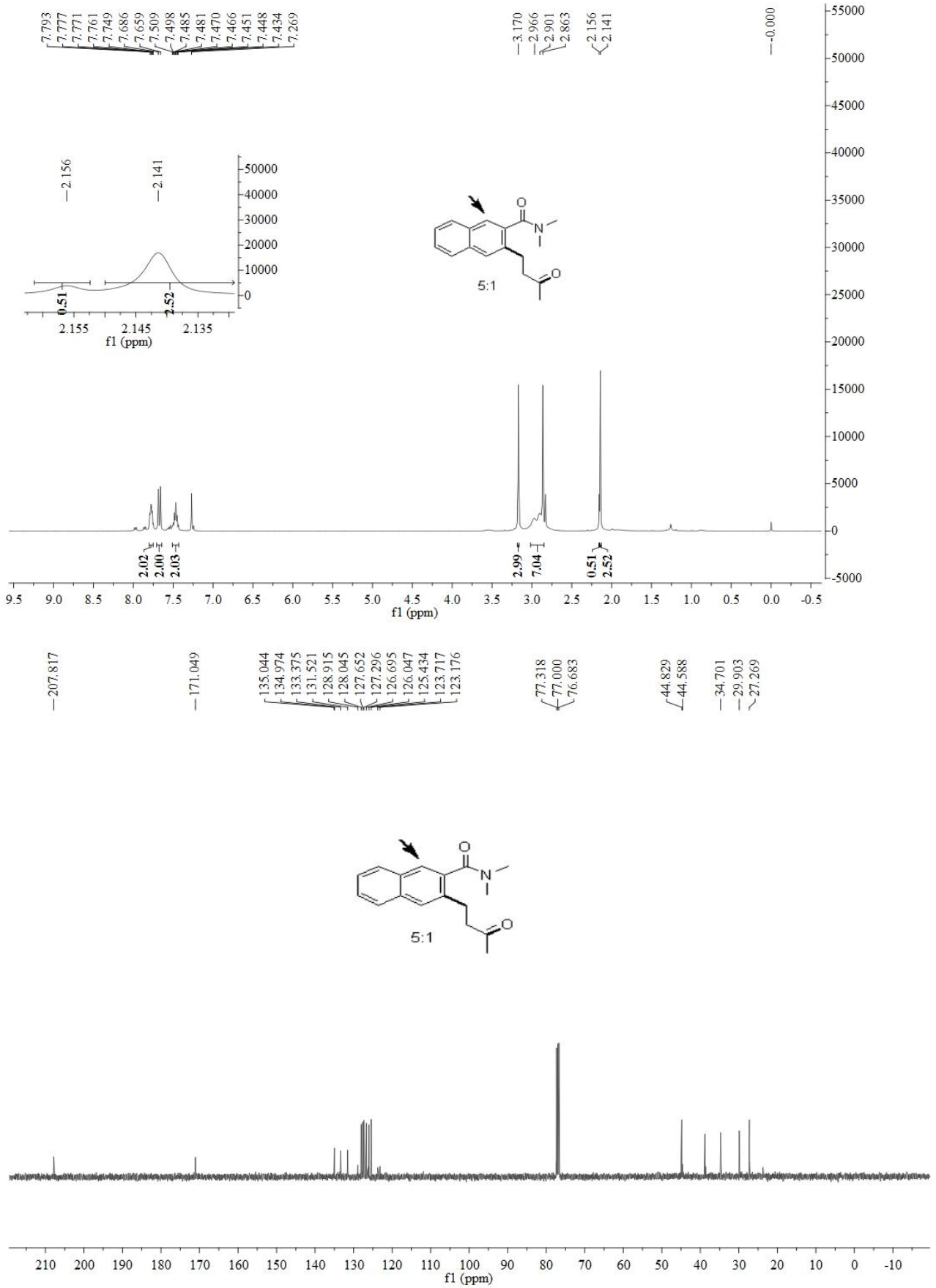

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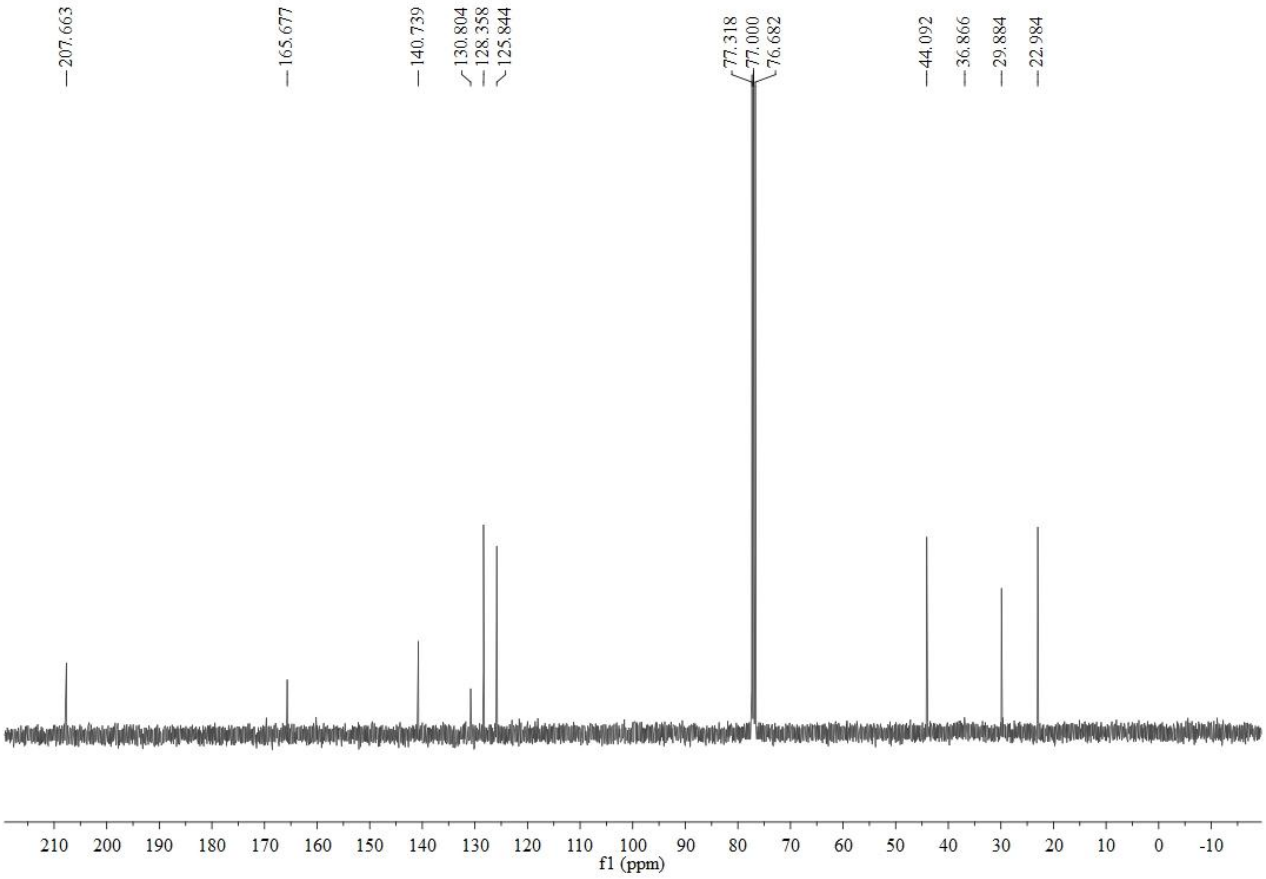

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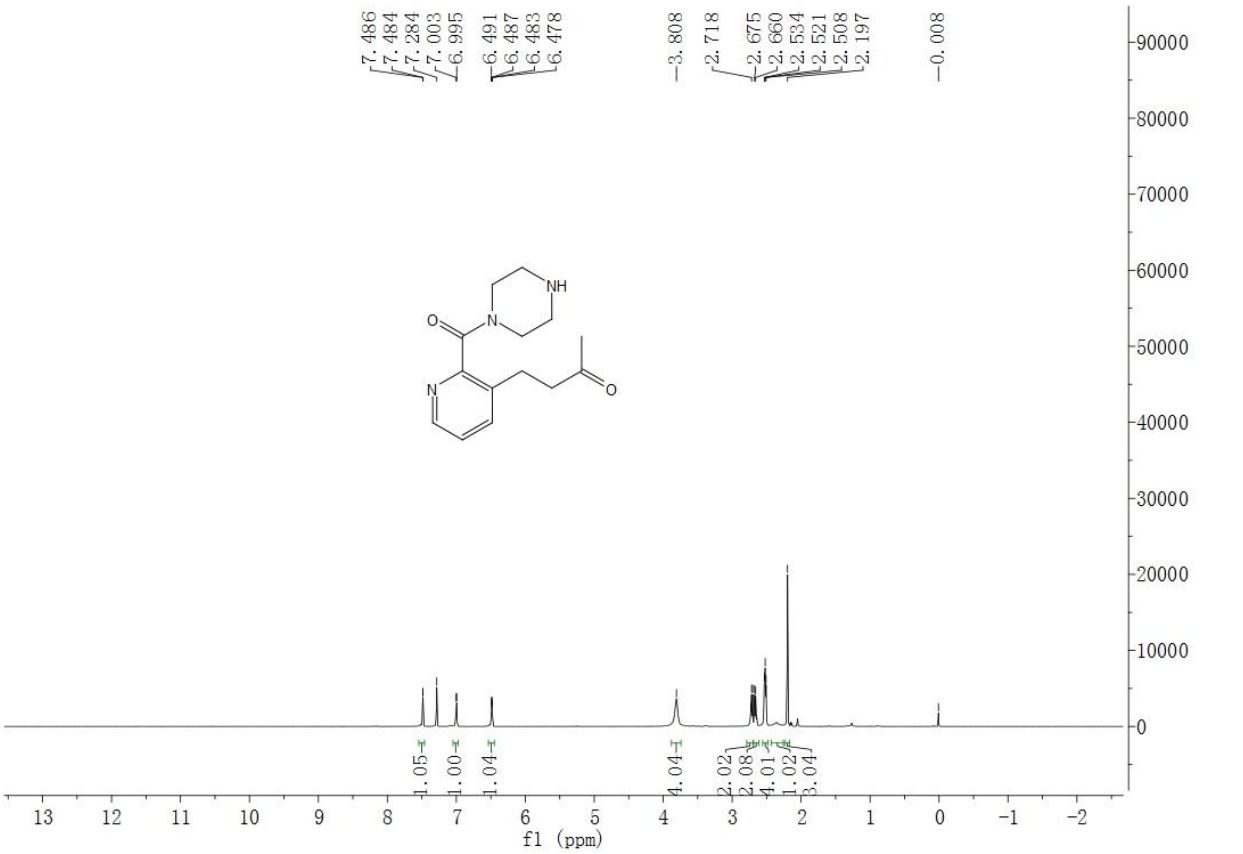
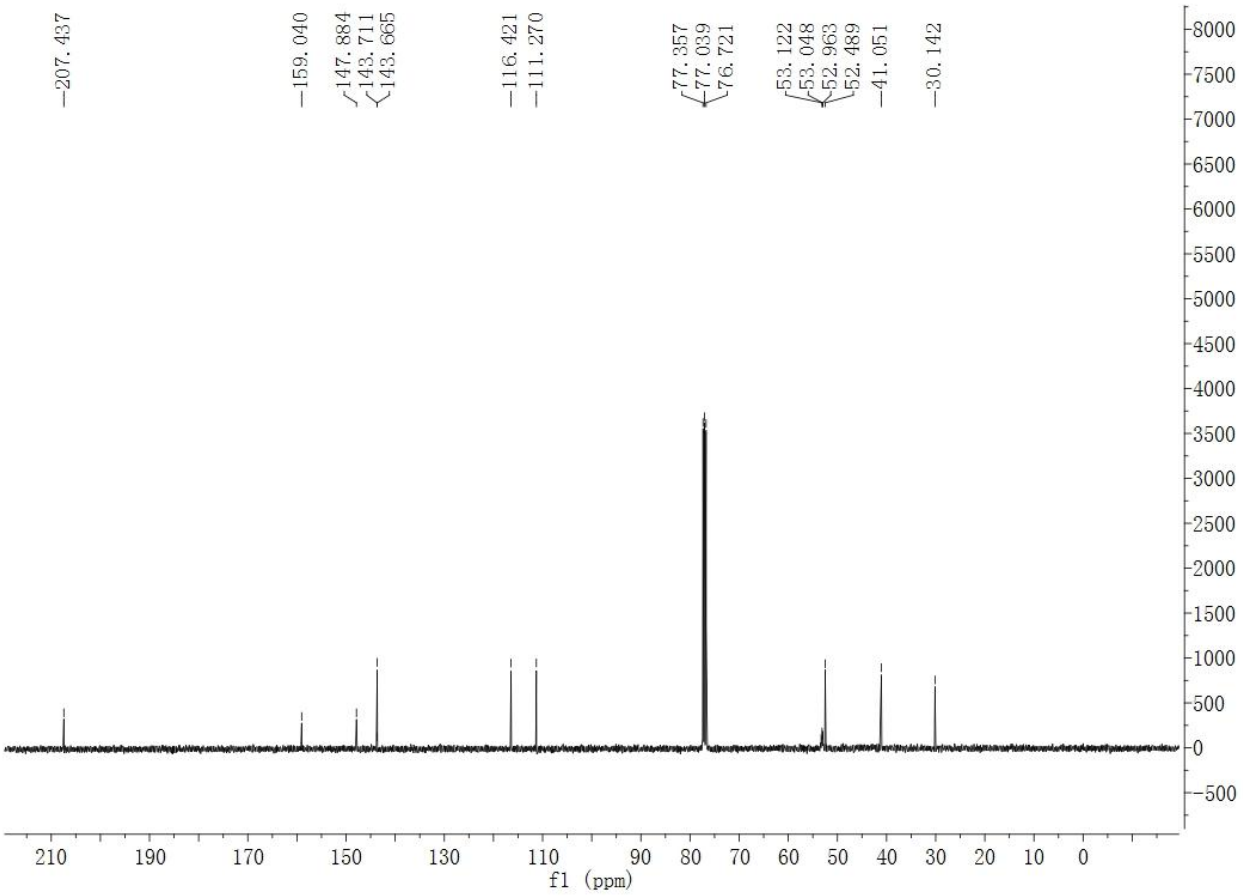
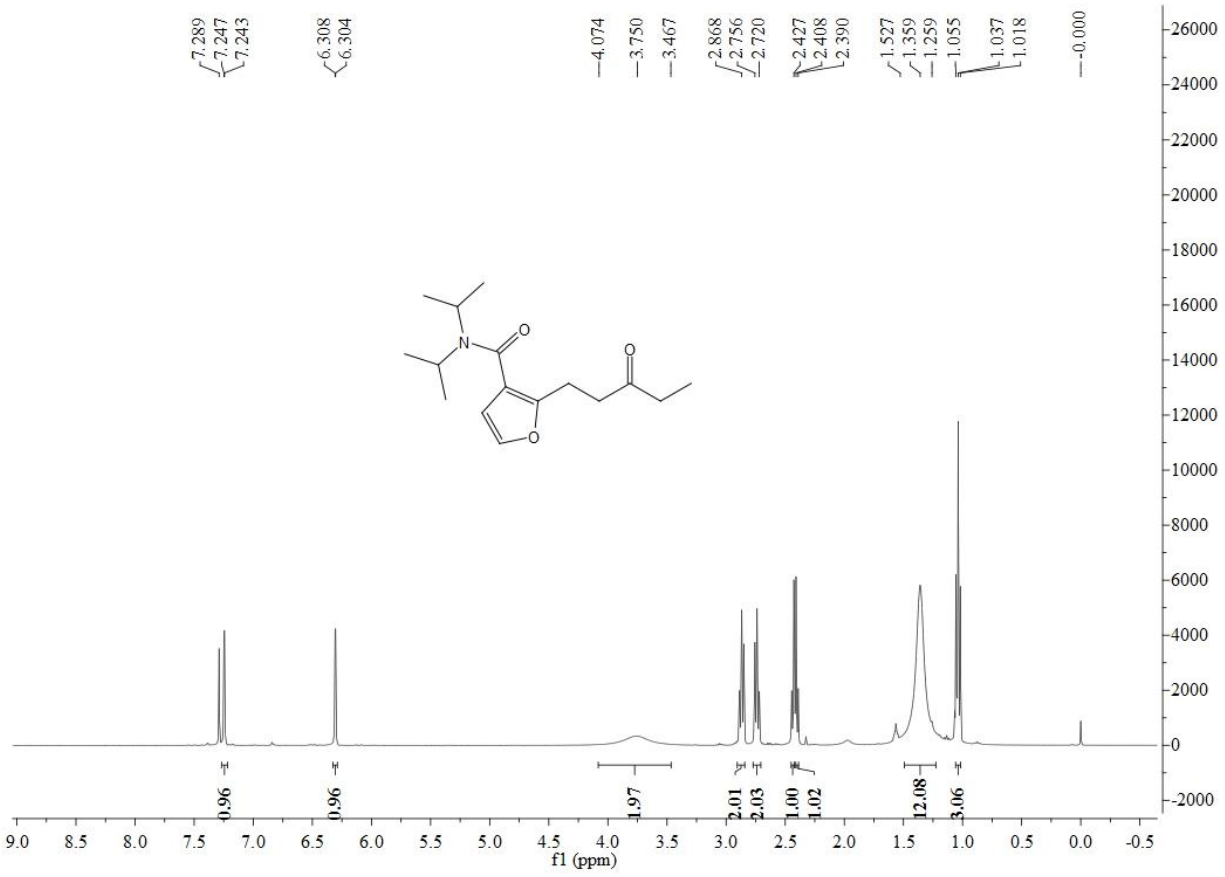
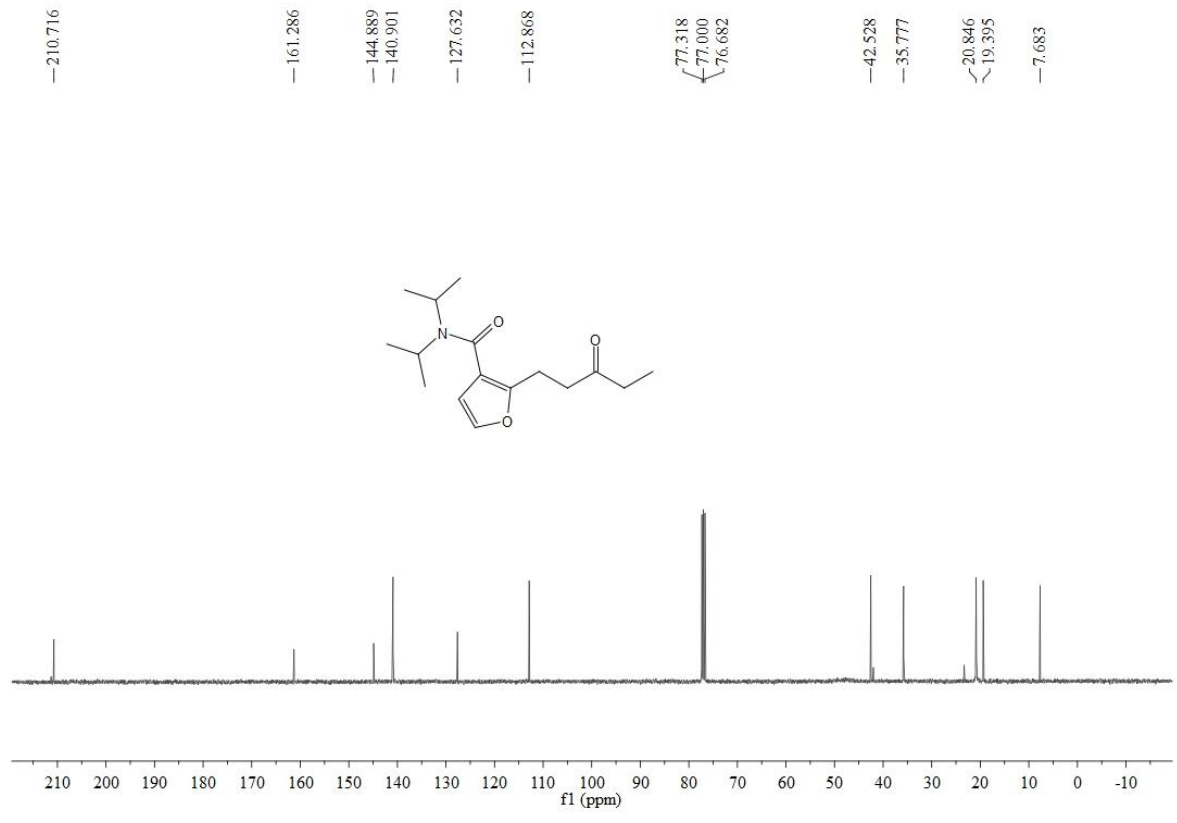




3q





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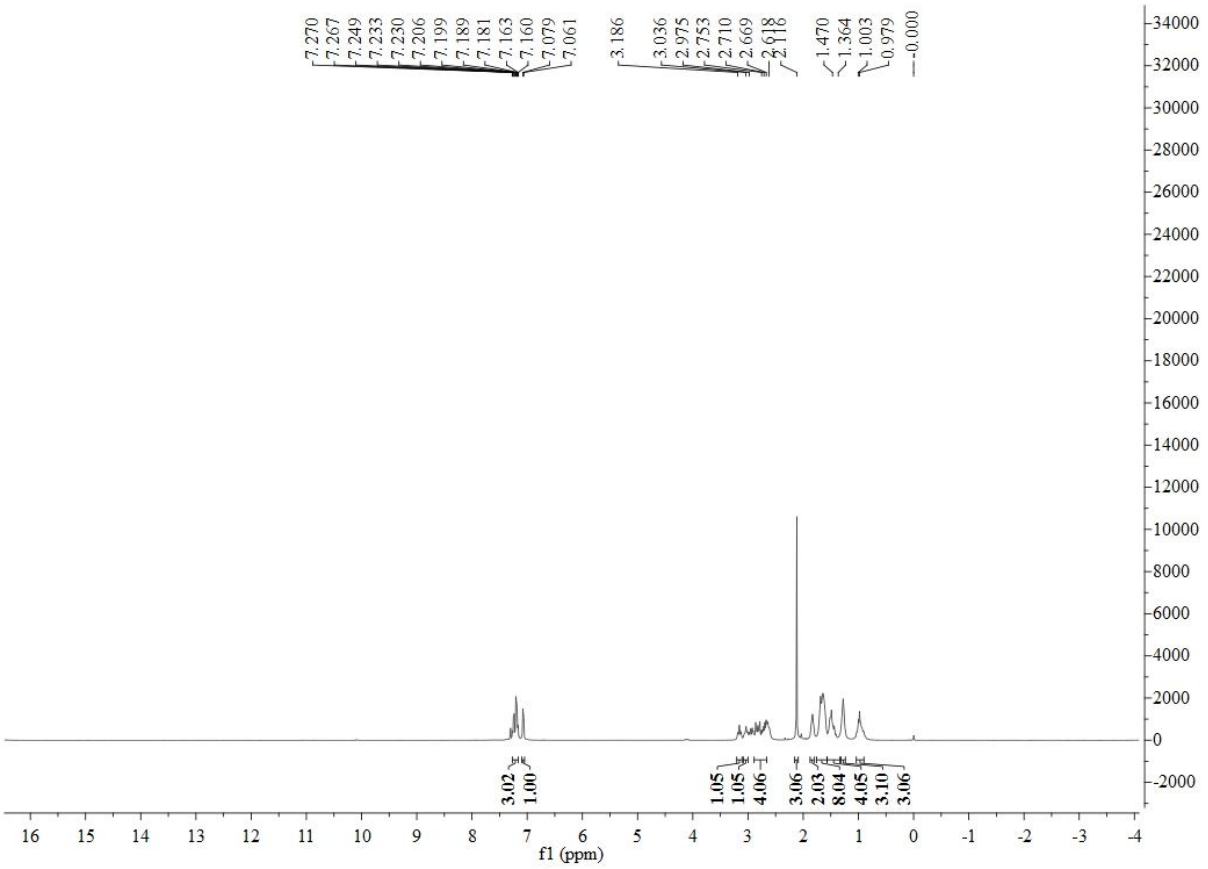
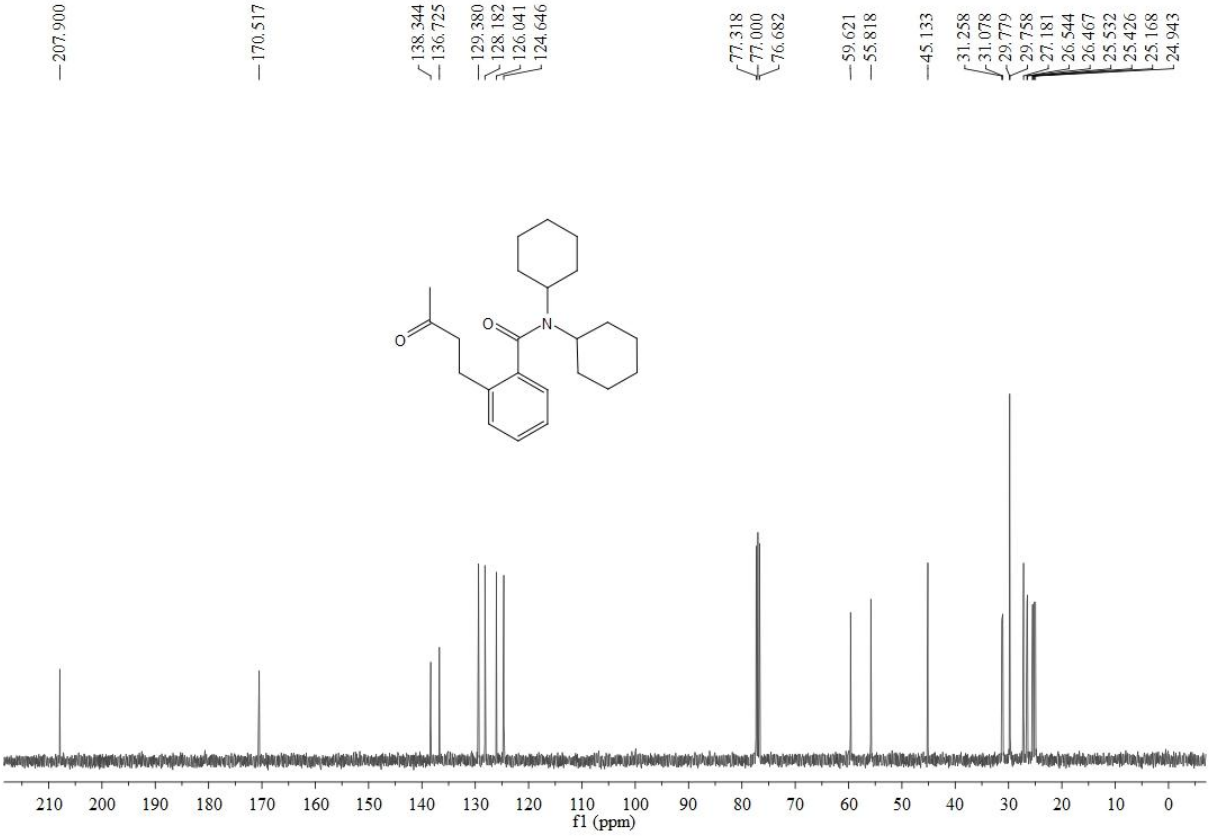
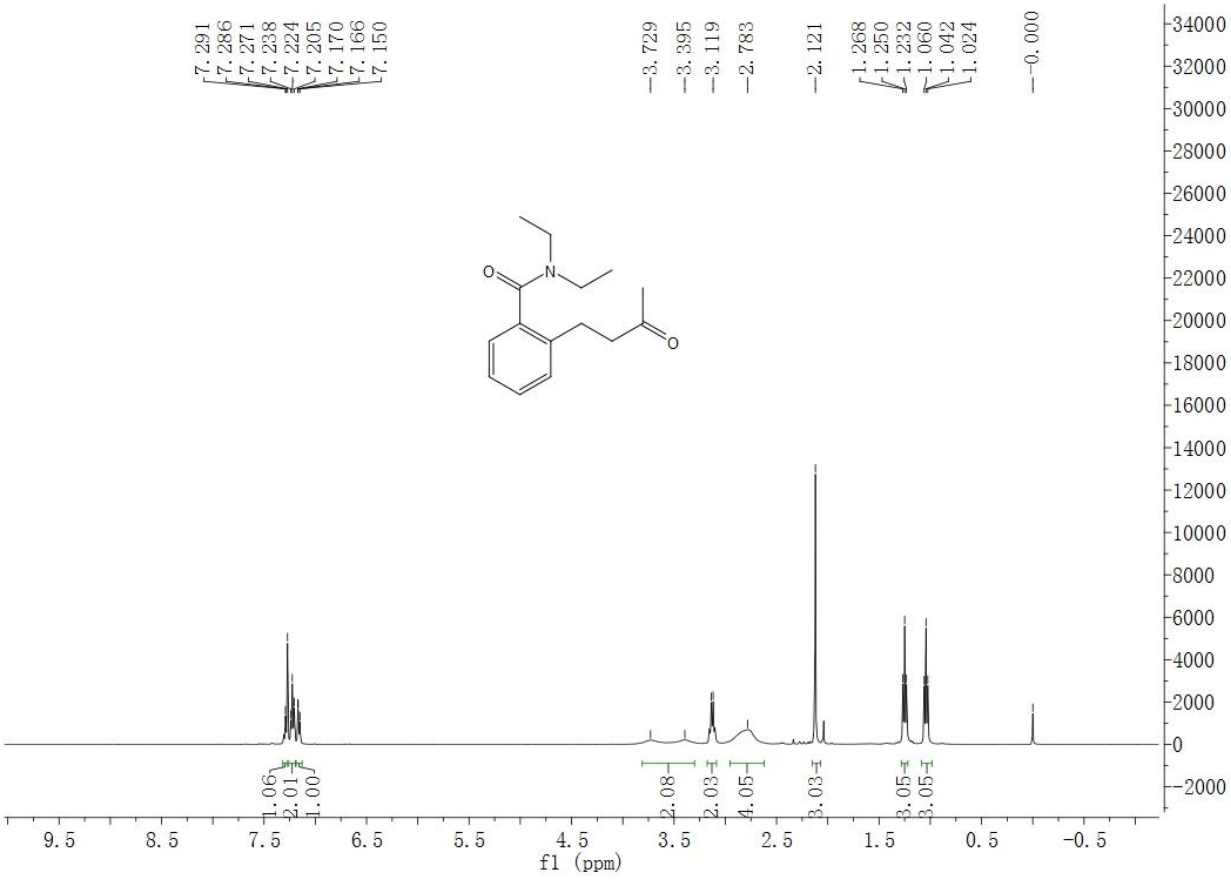
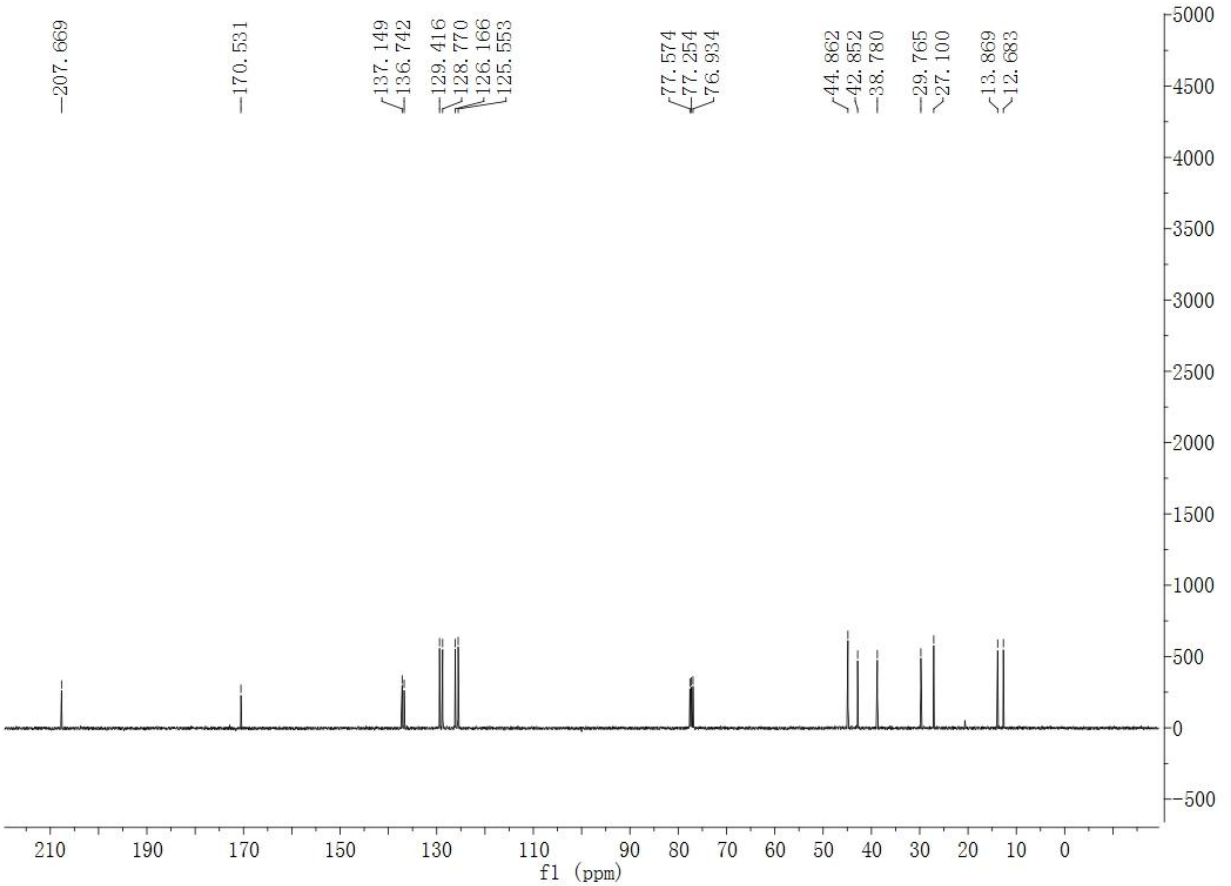




3s


7.291
7.286
7.271
7.238
7.224
7.205
7.170
7.166
7.150
3.729
3.395
3.119
2.783
2.121
1.268
1.250
1.232
1.060
1.042
1.024
0.000
1.06
2.01
1.00
2.08
2.03
4.05
3.03
3.05
3.05
f1 (ppm)


207.669
170.531
137.149
136.742
129.416
128.770
126.166
125.553
77.574
77.254
76.934
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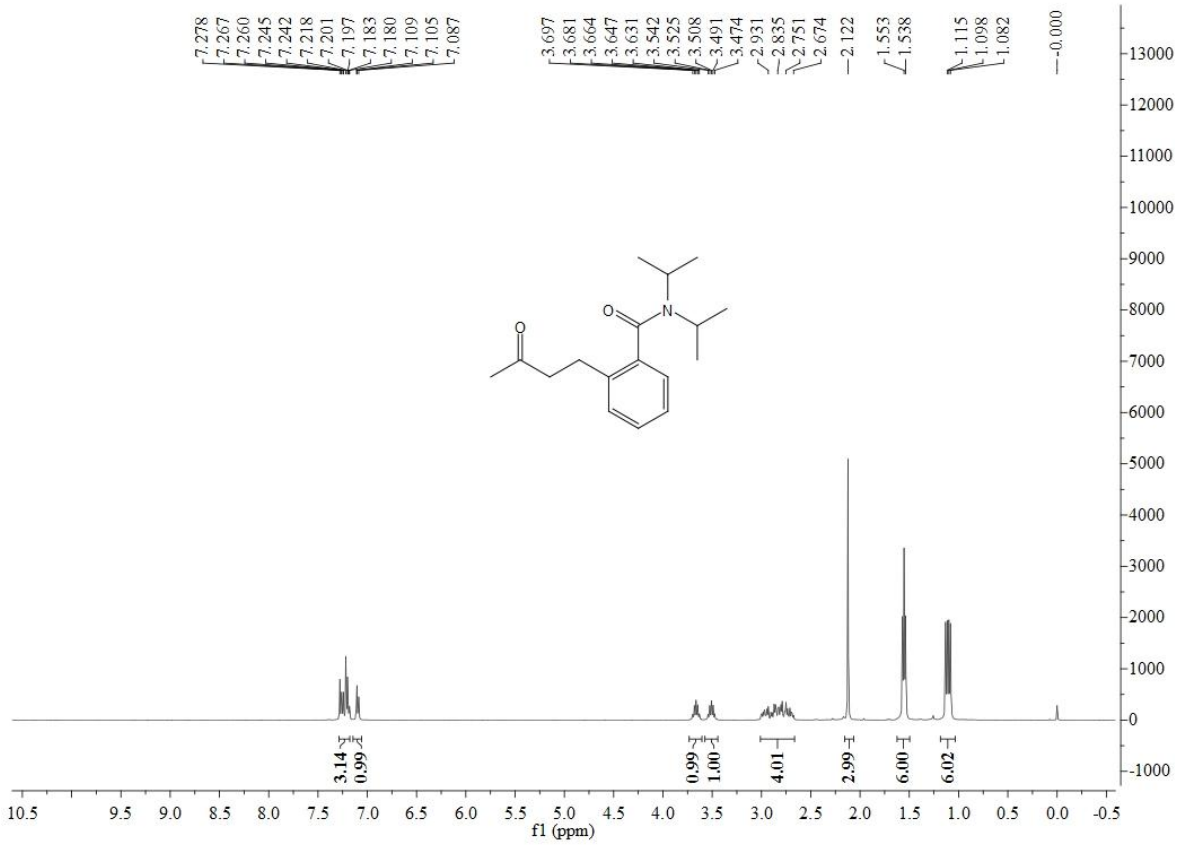
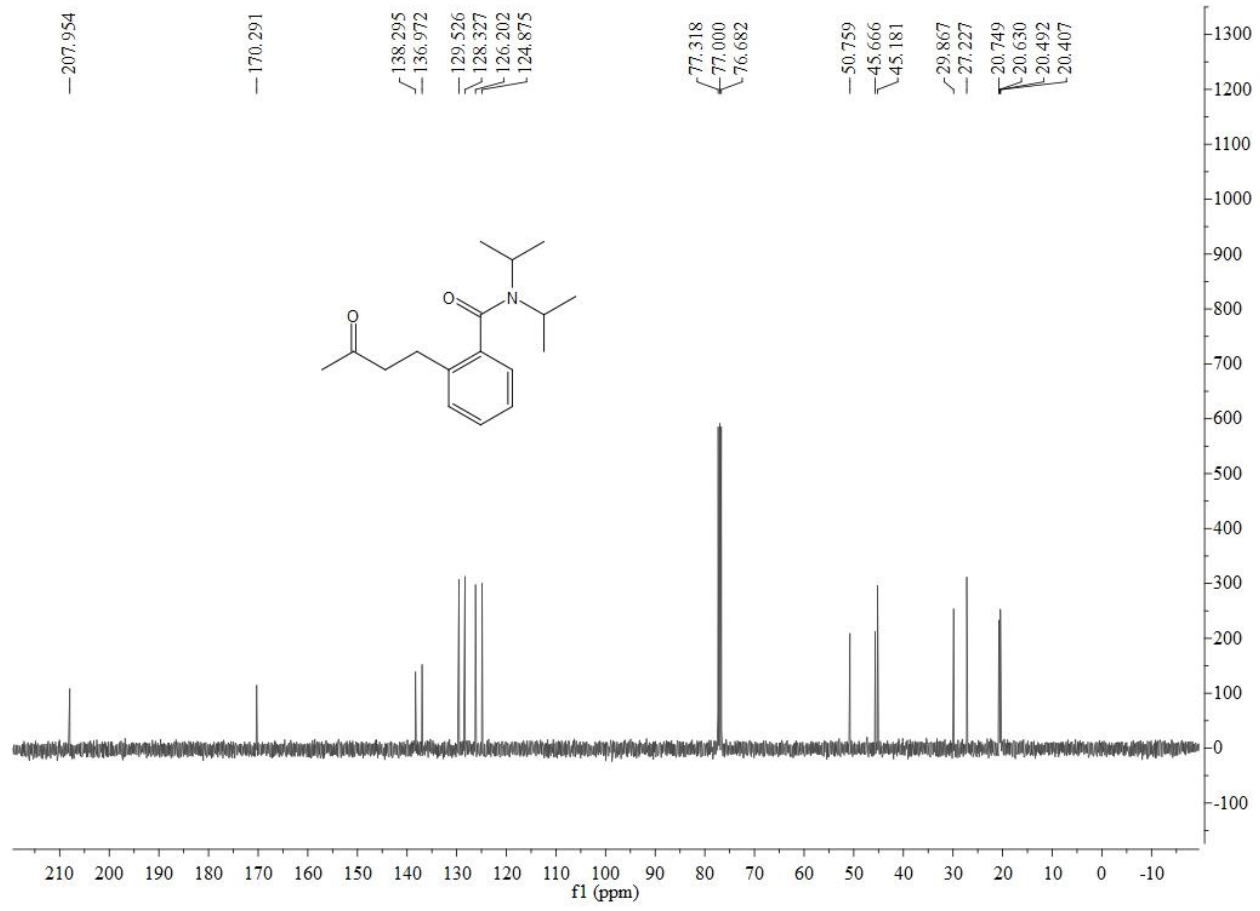
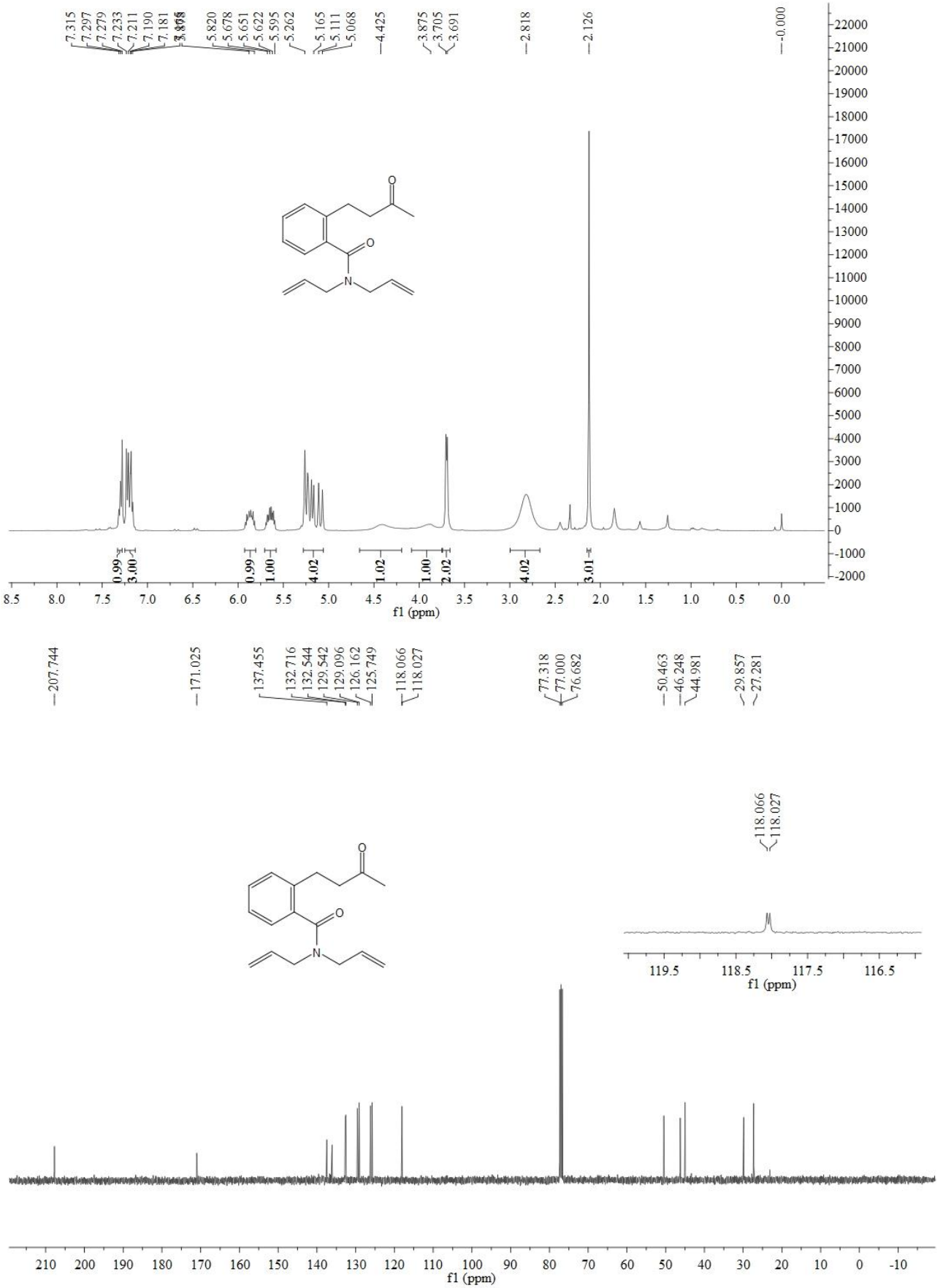
42.852
38.780
29.765
27.100
13.869
12.683
f1 (ppm)

3t

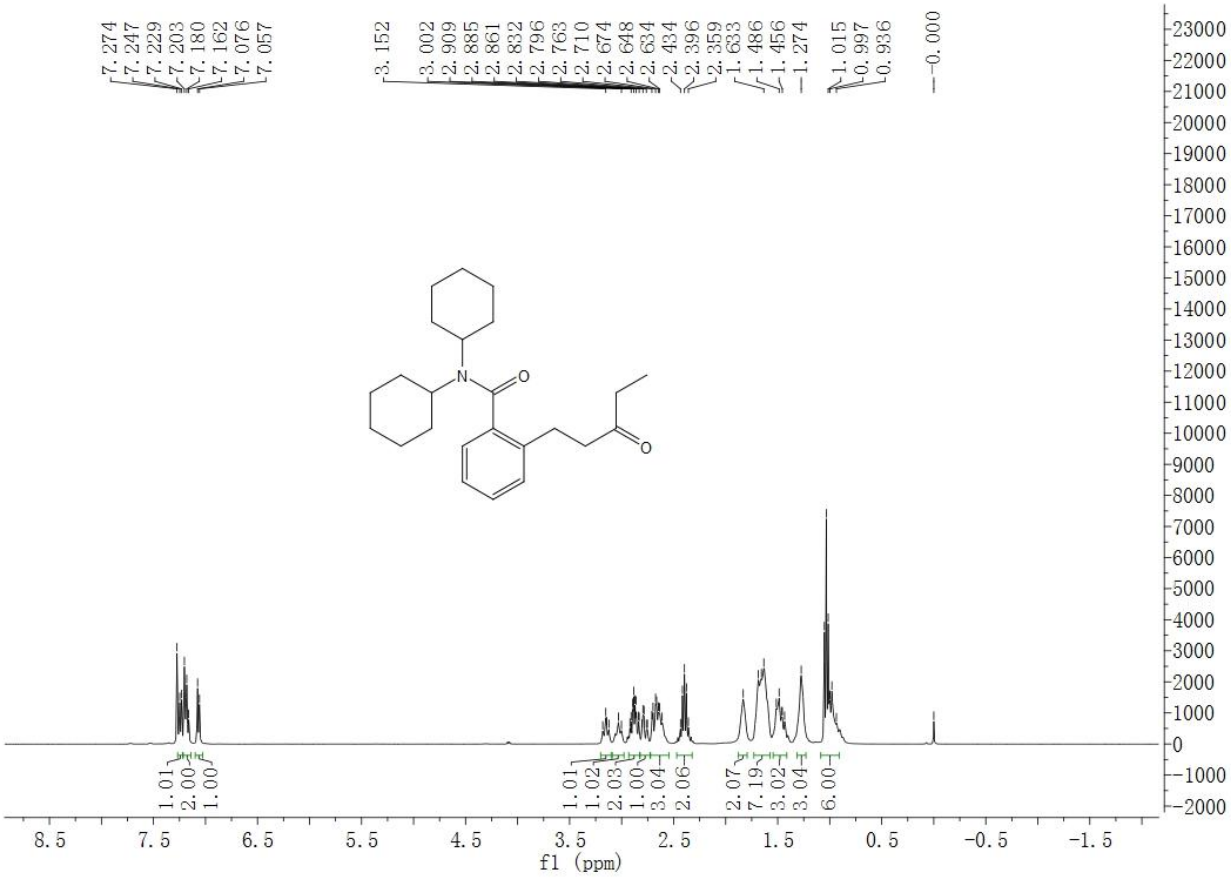


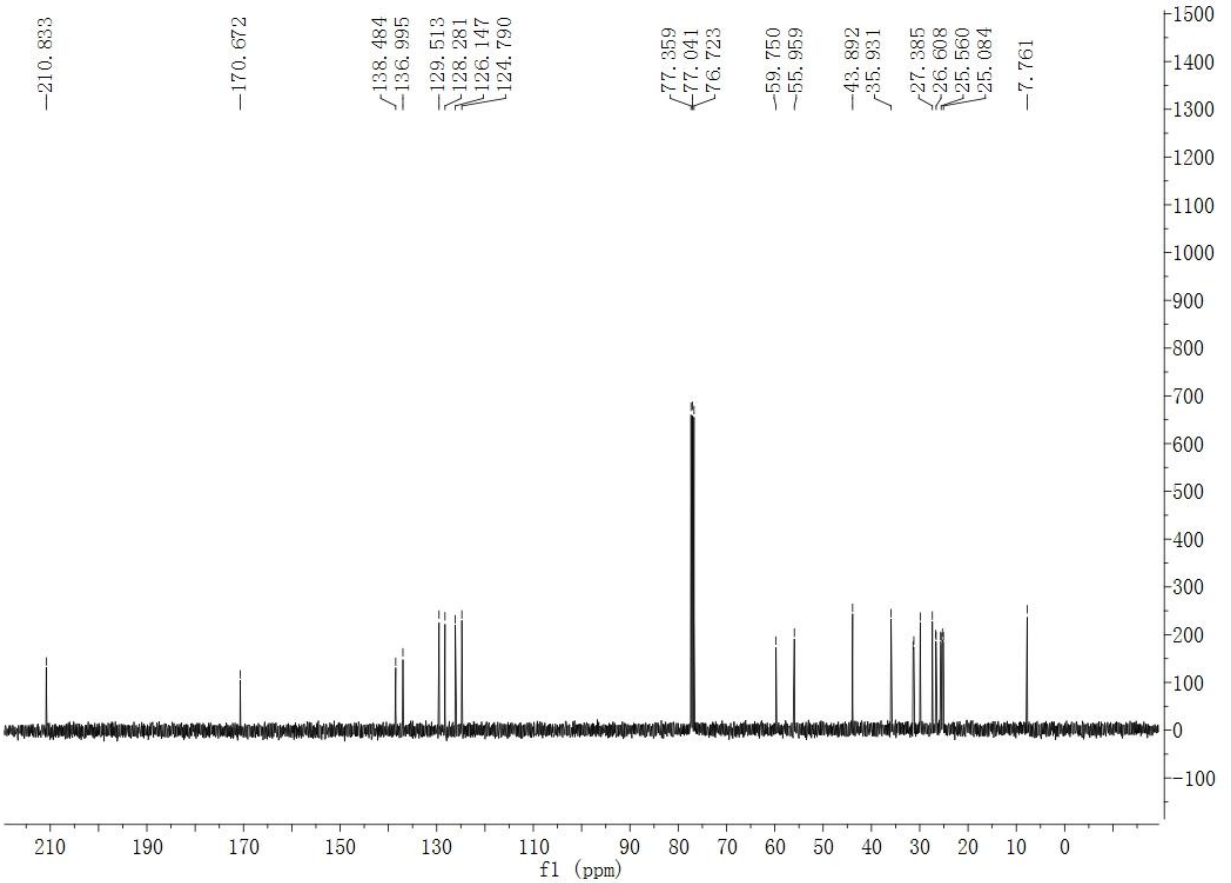


3u



3v


7.274
7.247
7.229
7.203
7.180
7.162
7.076
7.057
3.152
3.002
2.909
2.885
2.861
2.832
2.796
2.763
2.710
2.674
2.648
2.634
2.434
2.396
2.359
1.633
1.486
1.456
1.274
1.015
0.997
0.936
0.000
N
O
O
1.01
2.00
1.00
1.01
1.02
2.03
1.00
3.04
2.06
2.07
7.19
3.02
3.04
6.00
f1 (ppm)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129.513
128.281
126.147
124.790
77.359
77.041
76.723
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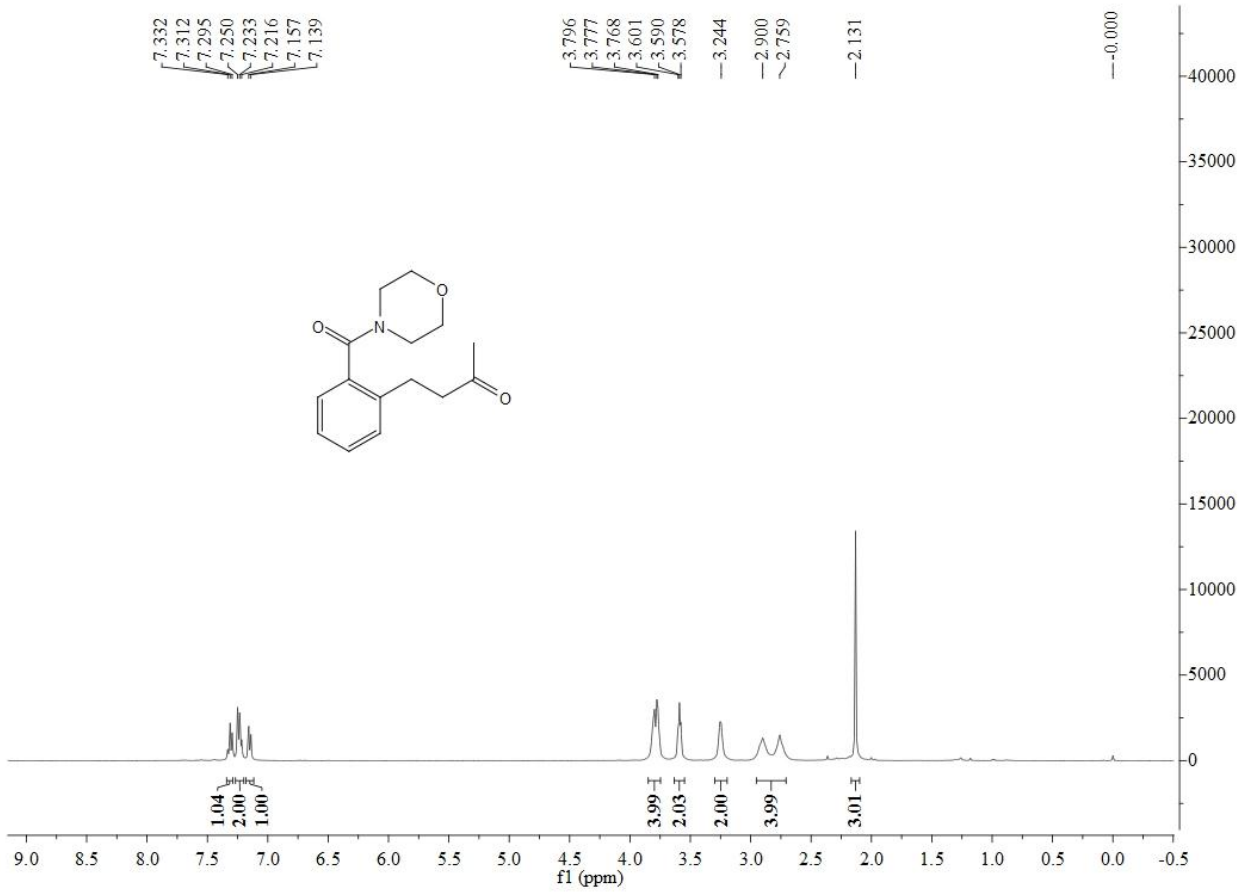
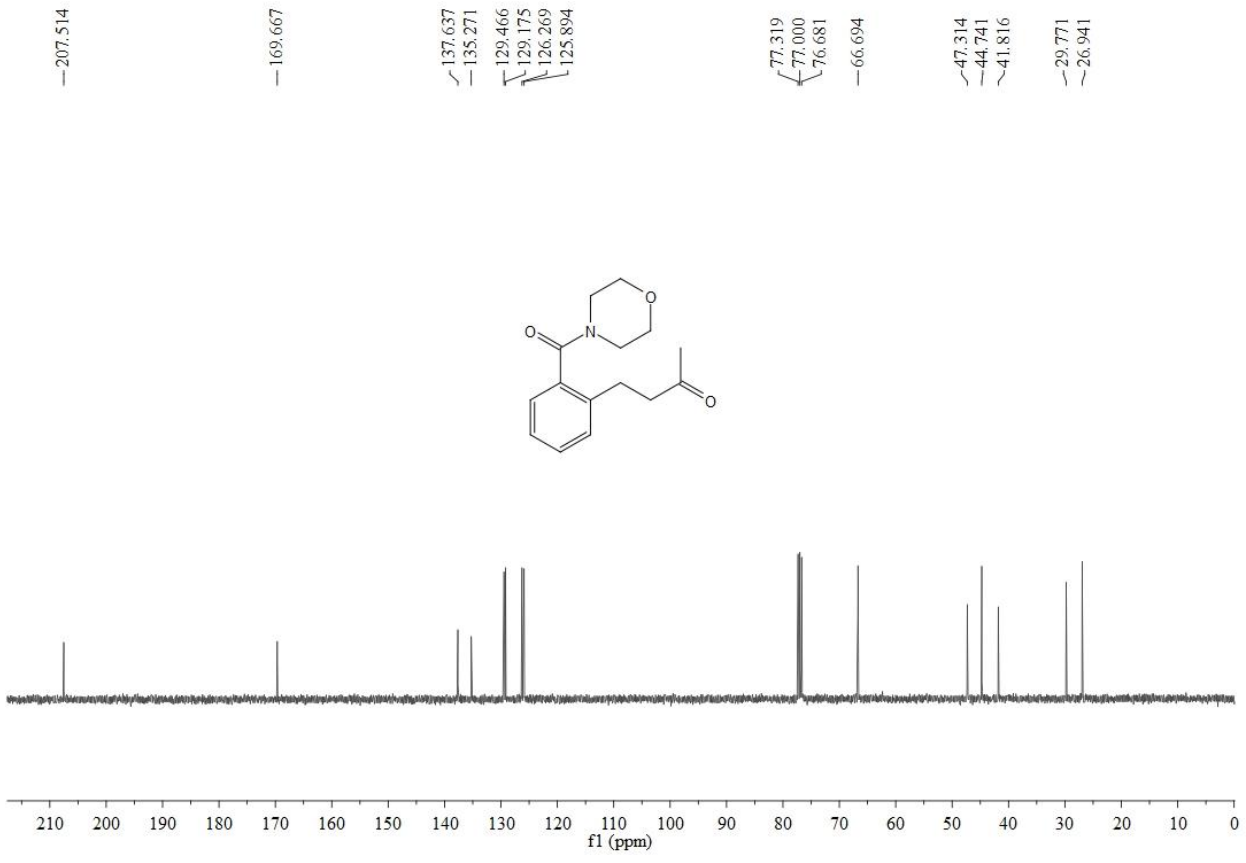
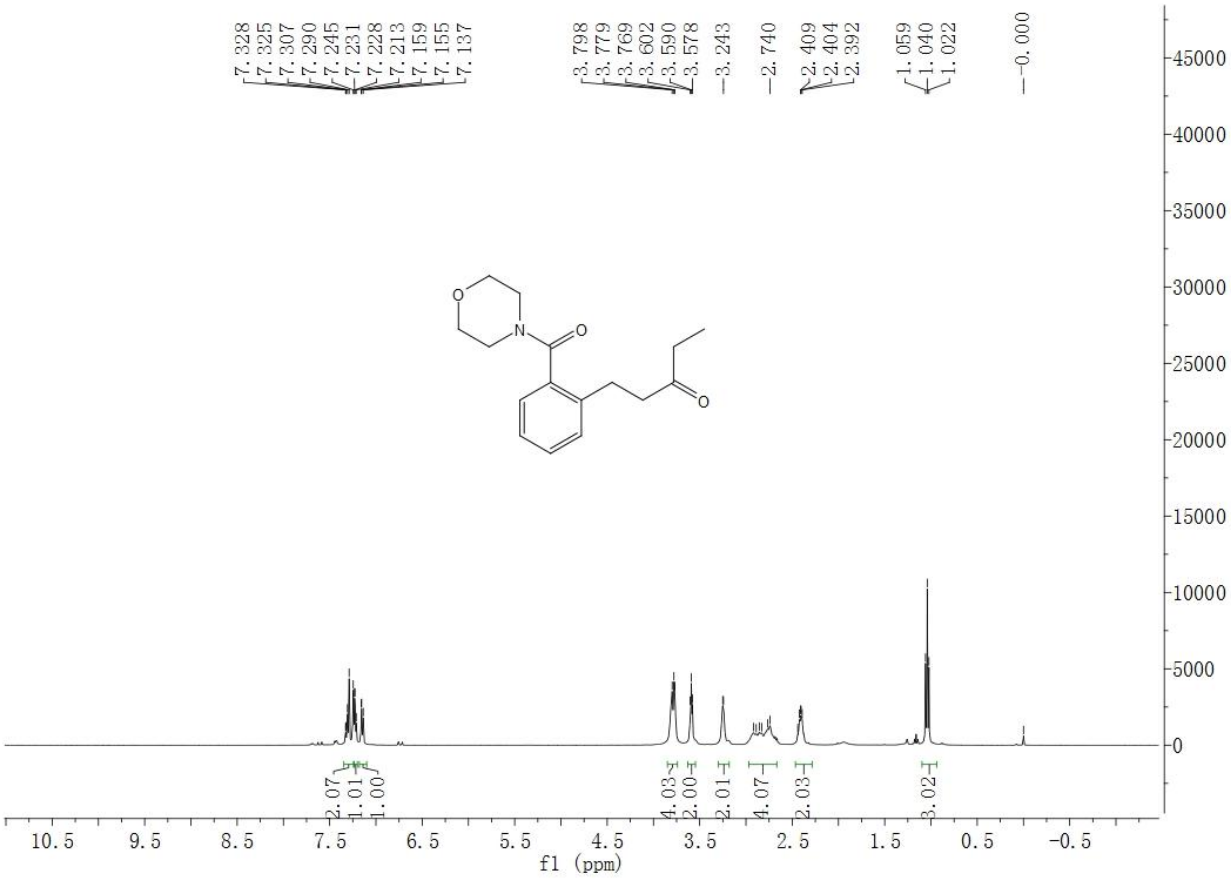
43.892
35.931
27.385
26.608
25.560
25.084
7.761
f1 (ppm)

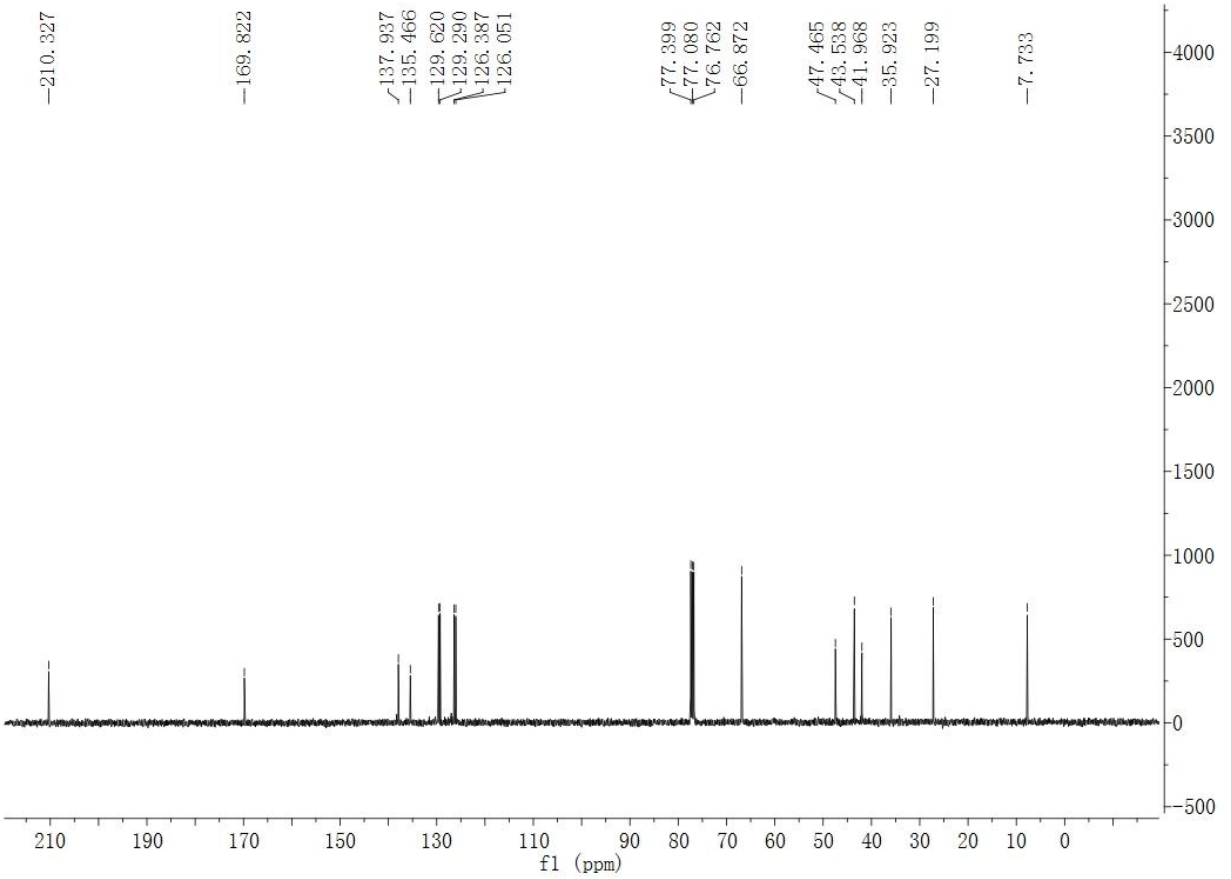
3w



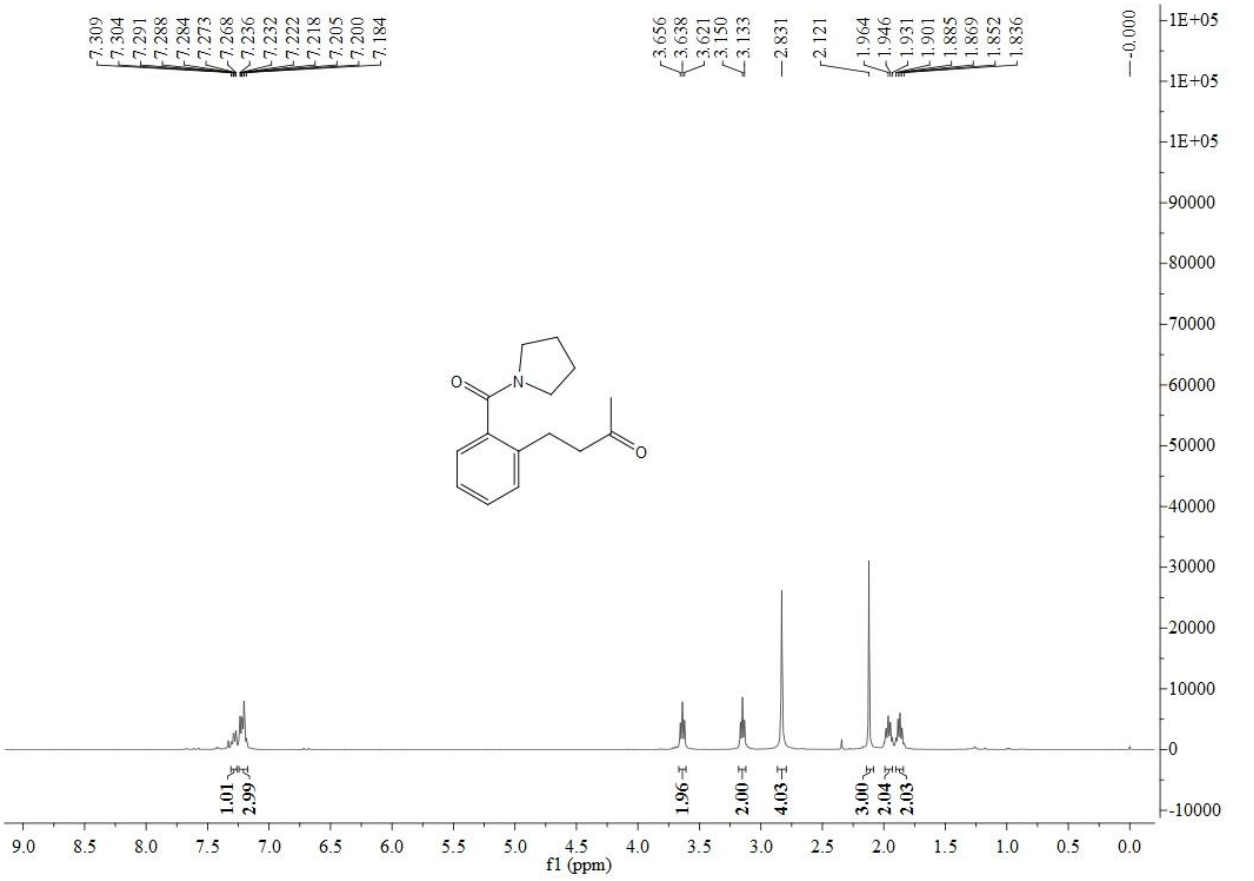


3w'





3x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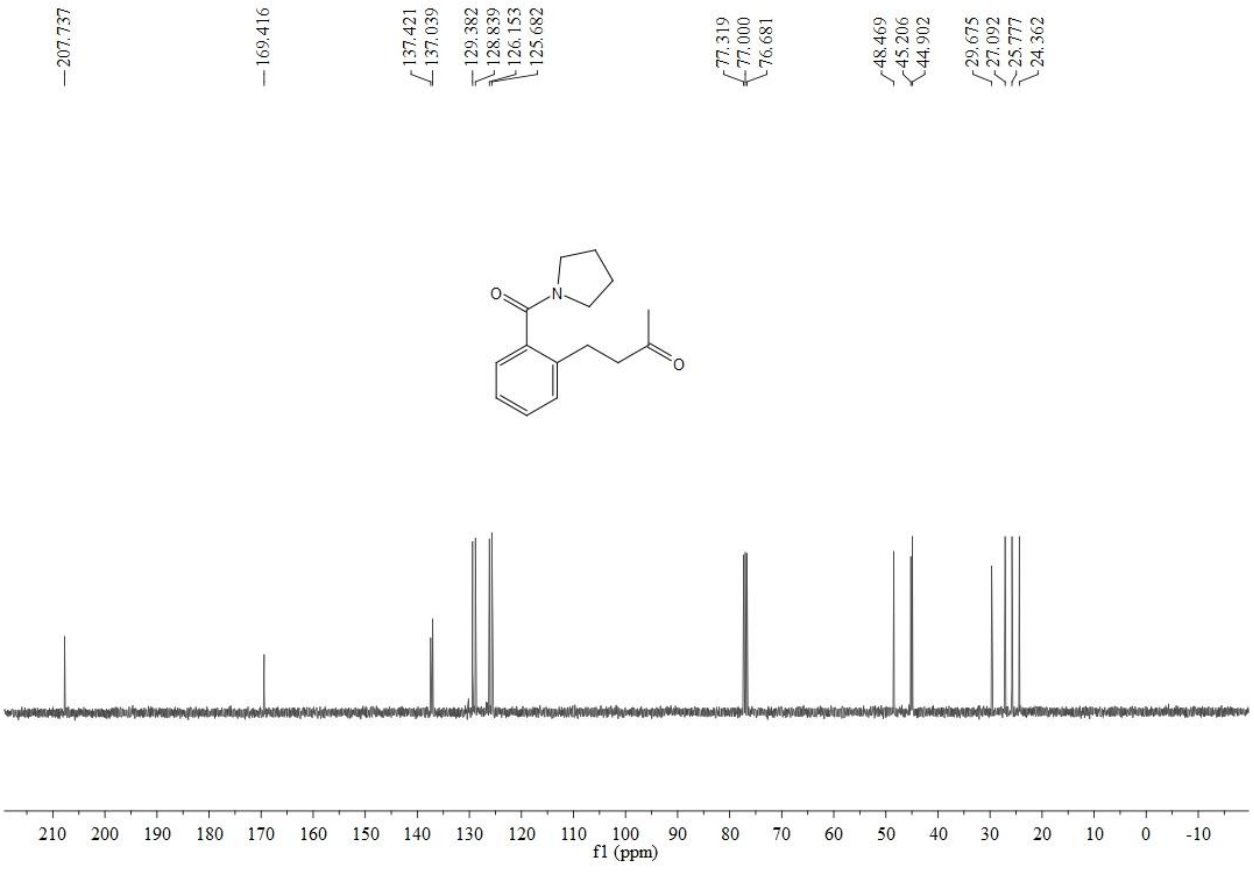
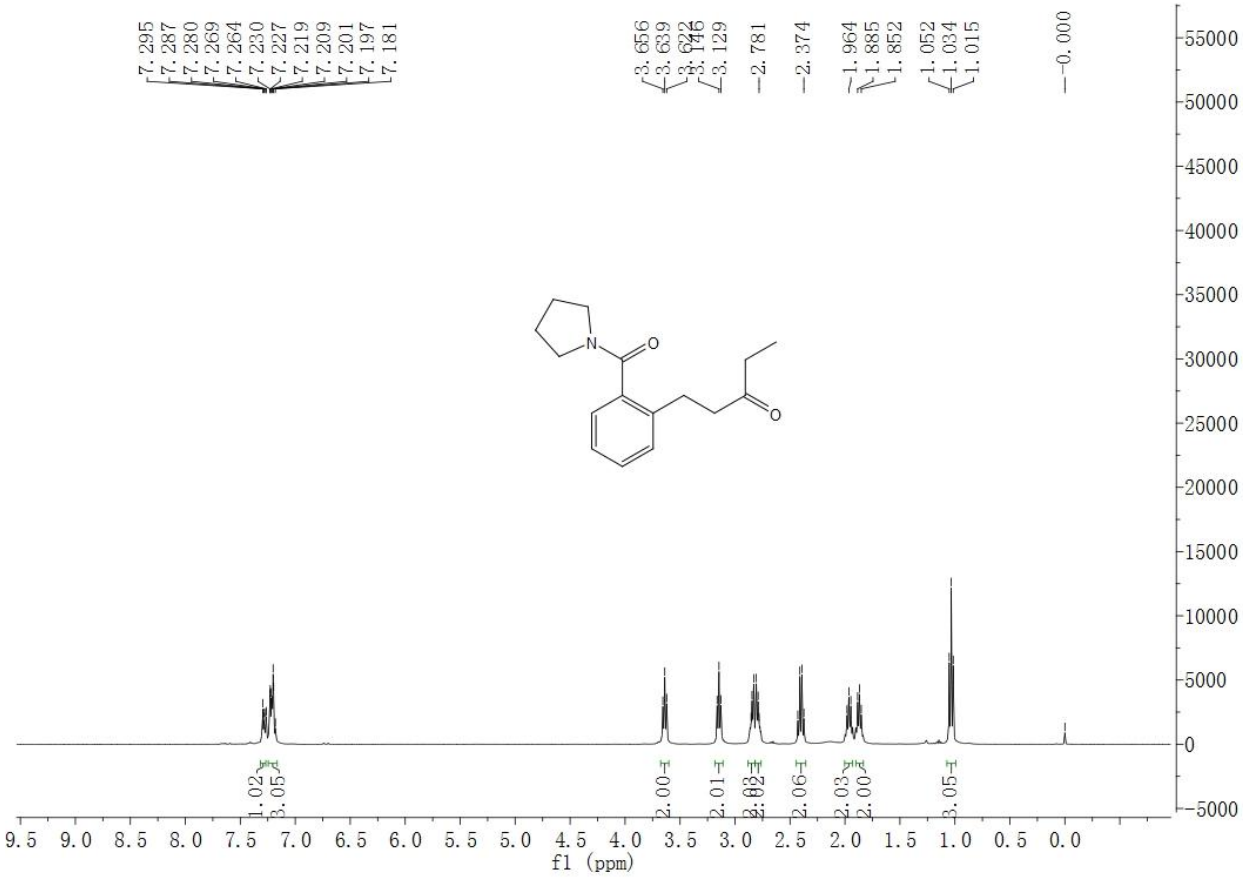
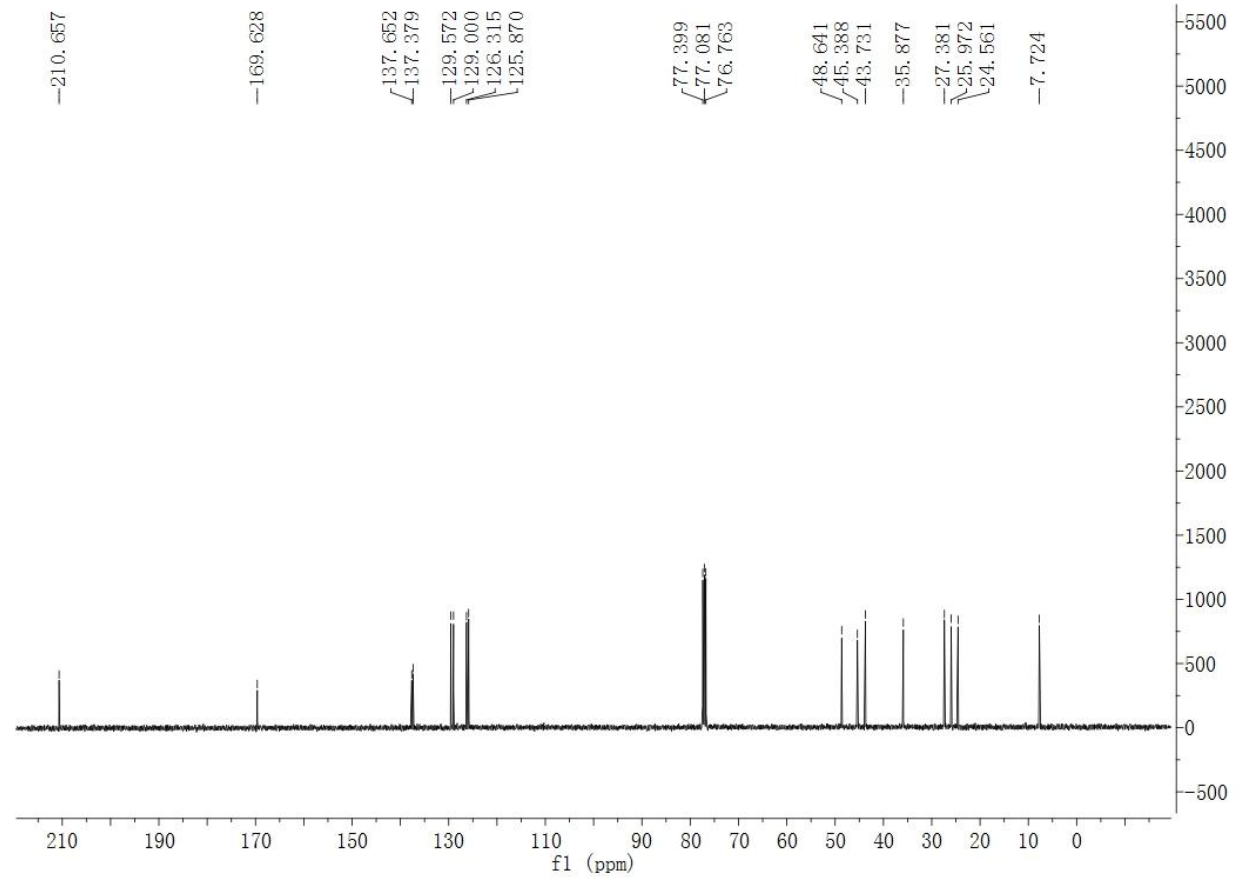
7.304
7.291
7.288
7.284
7.273
7.268
7.236
7.232
7.222
7.218
7.205
7.200
7.184
3.656
3.638
3.621
3.150
3.133
2.831
2.121
1.964
1.946
1.931
1.901
1.885
1.869
1.852
1.836
-0.000
1.01
2.99
1.96
2.00
4.03
3.00
2.04
2.03
f1 (ppm)

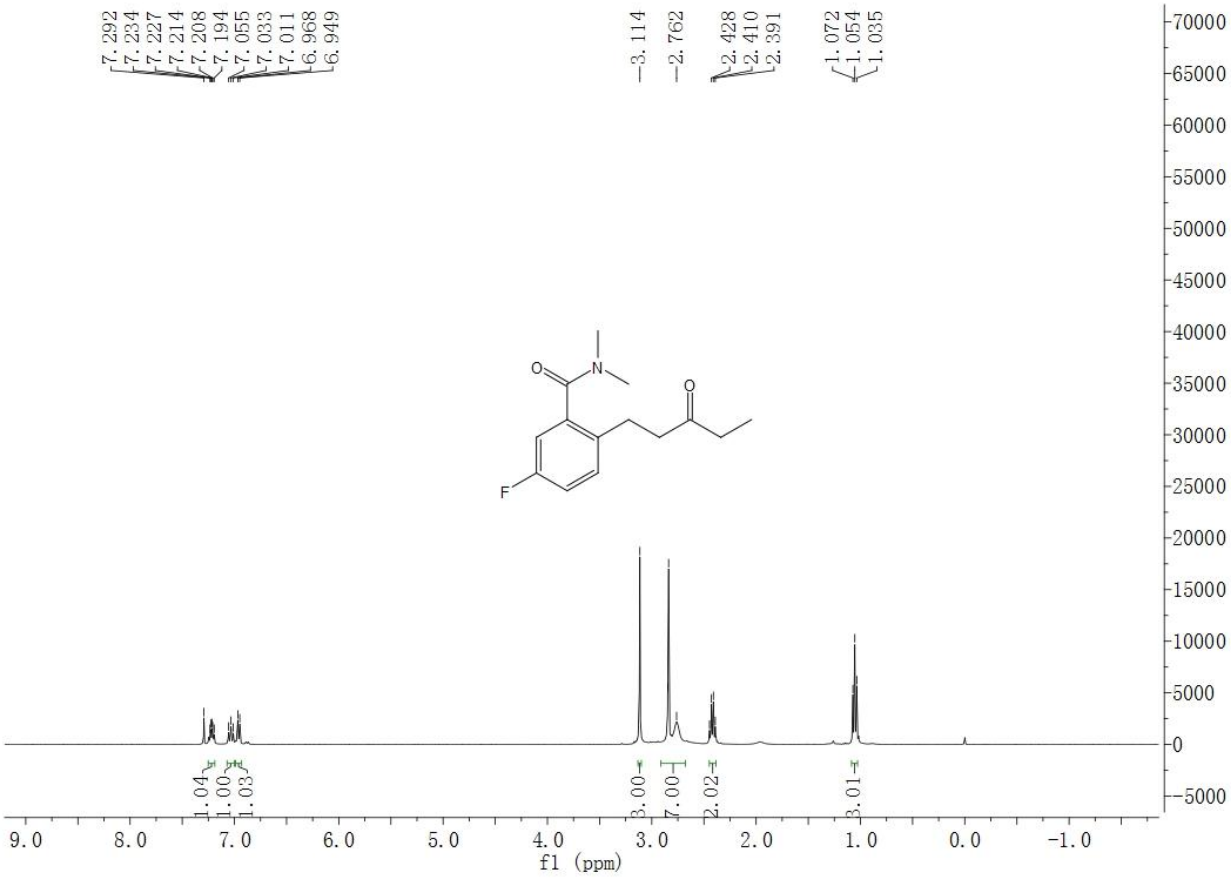

207.737
169.416
137.421
137.039
129.382
128.839
126.153
125.682
77.319
77.000
76.681
48.469
45.206
44.902
29.675
27.092
25.777
24.362
f1 (ppm)

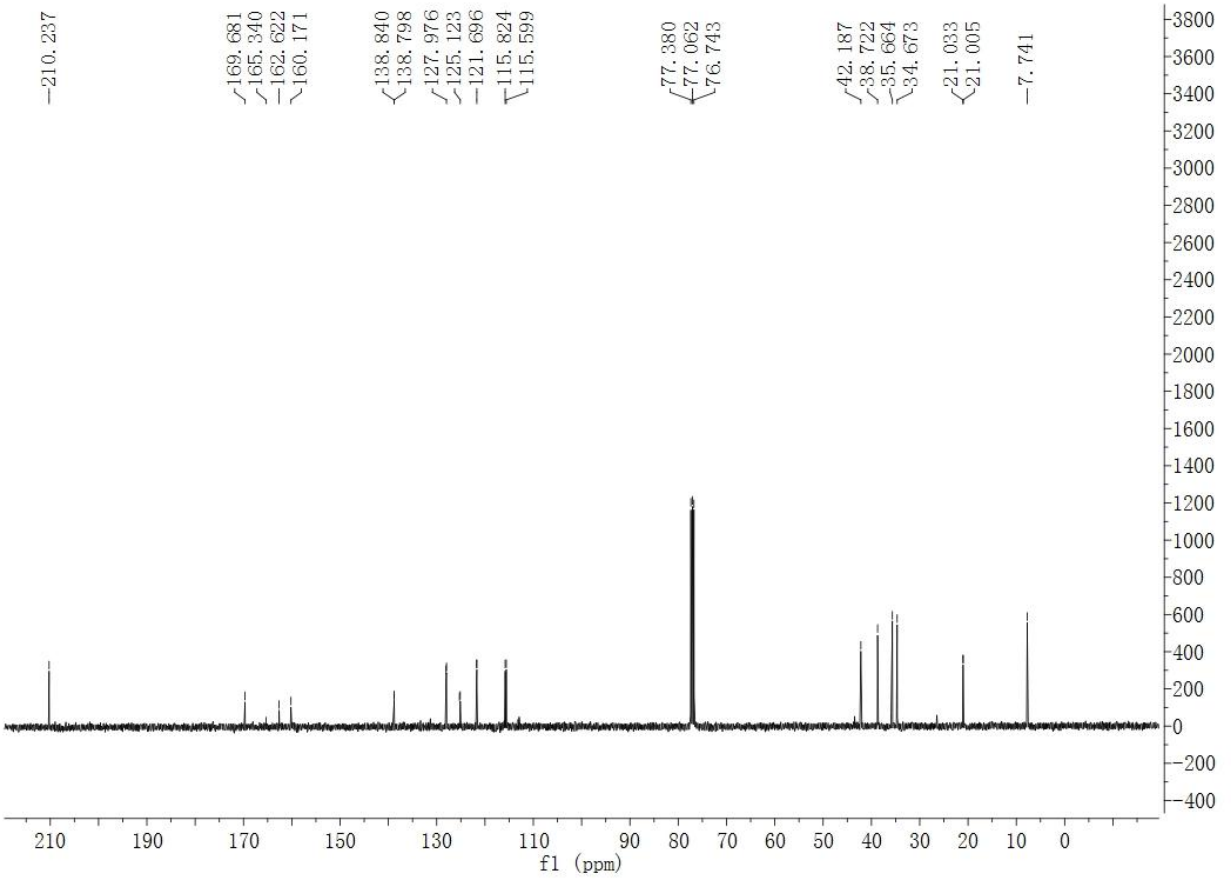
3x'



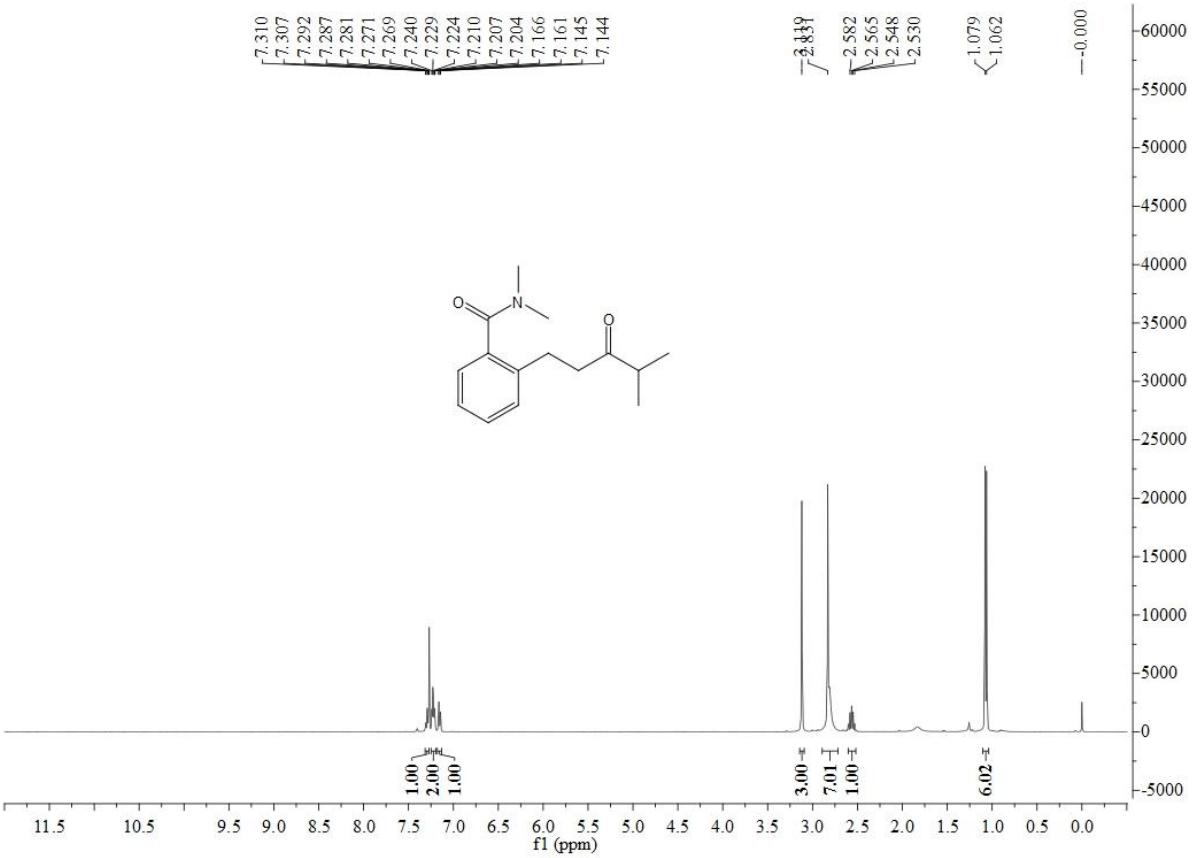


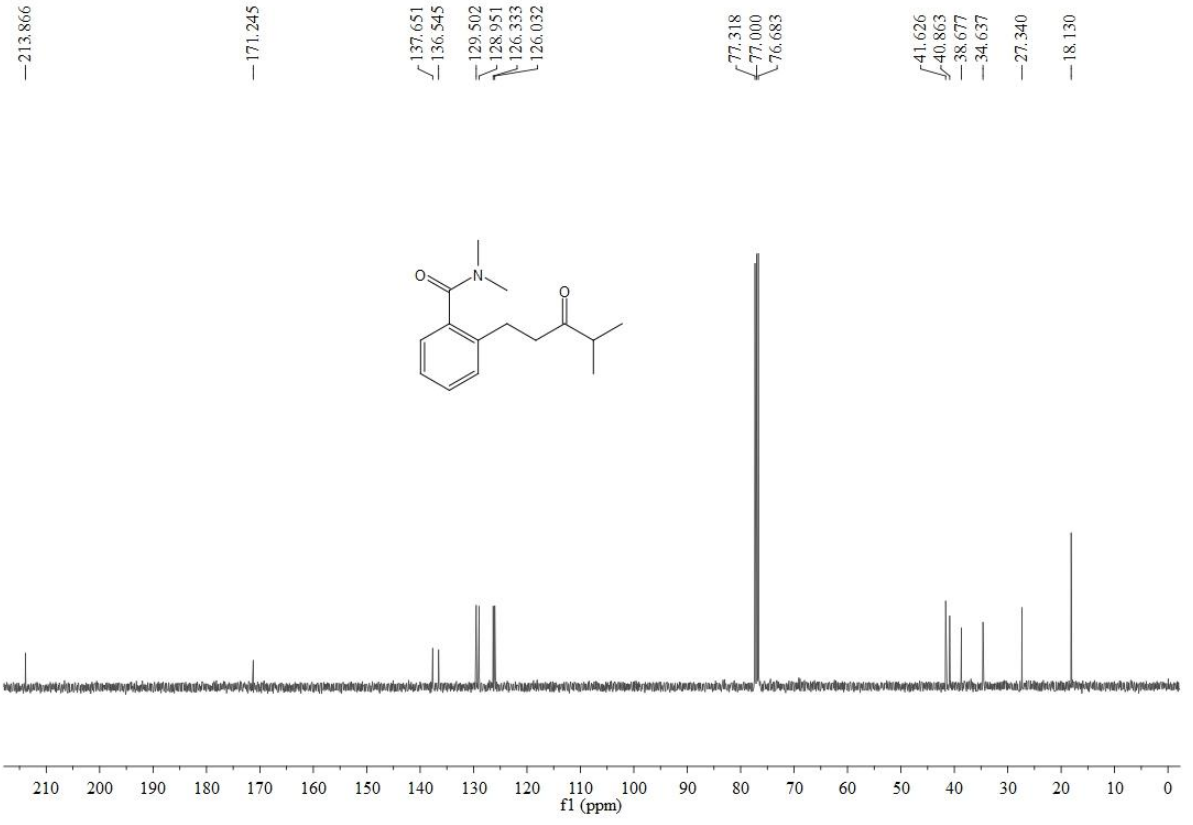
3y



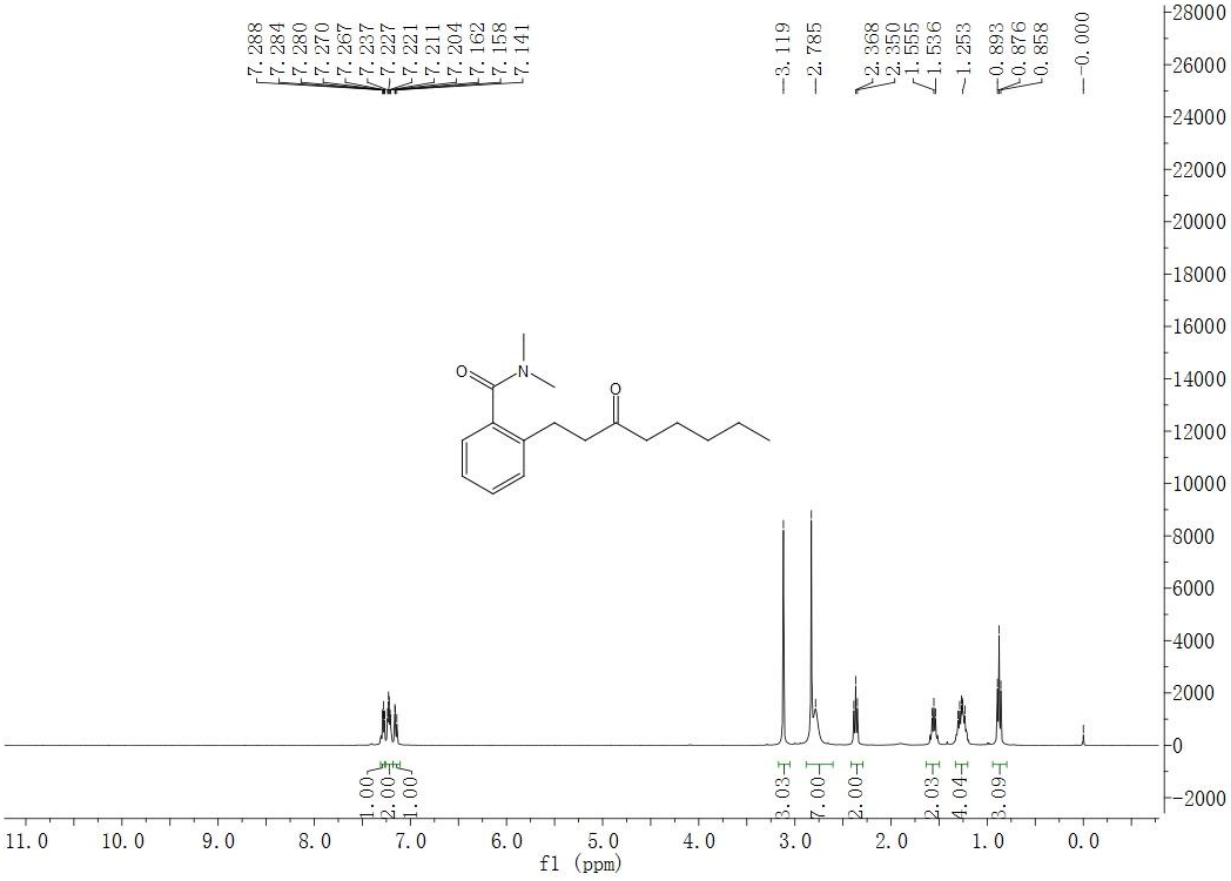


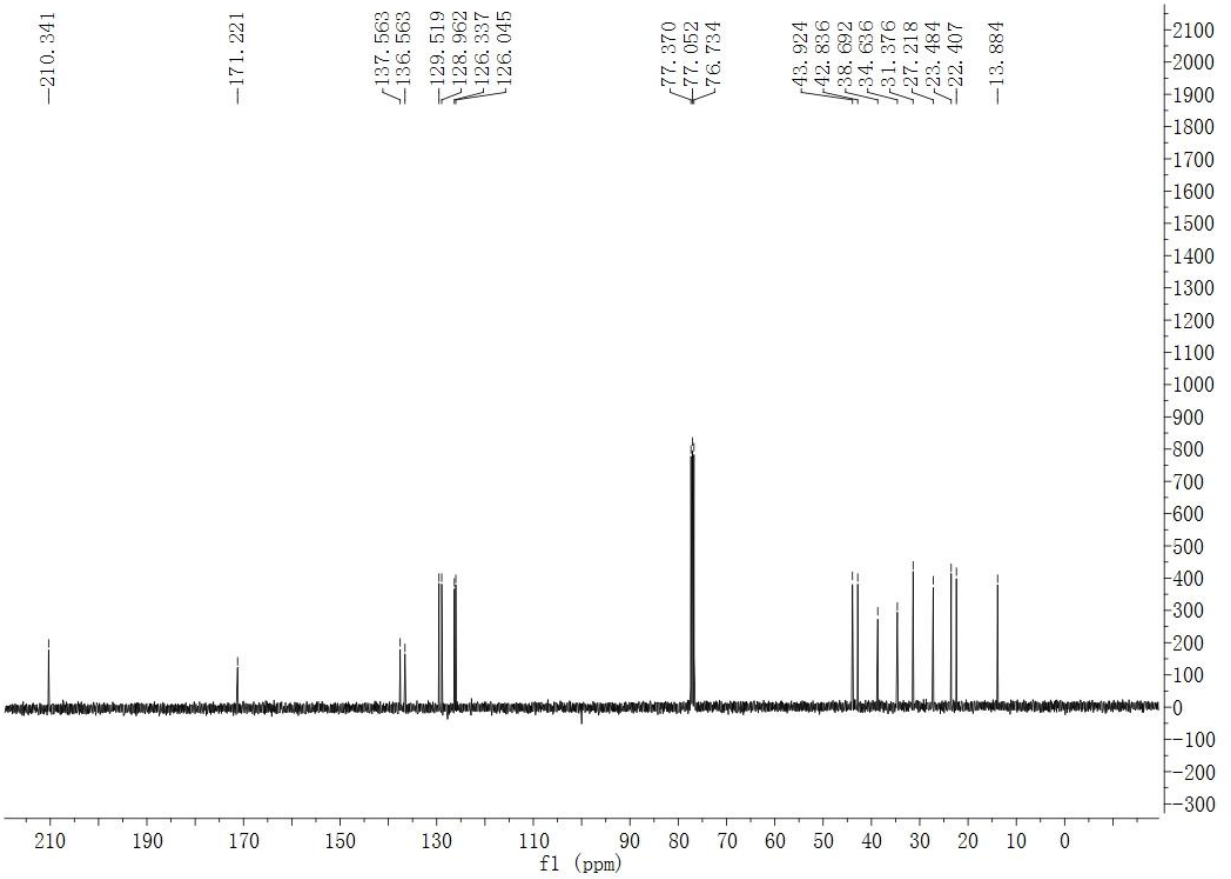
3z



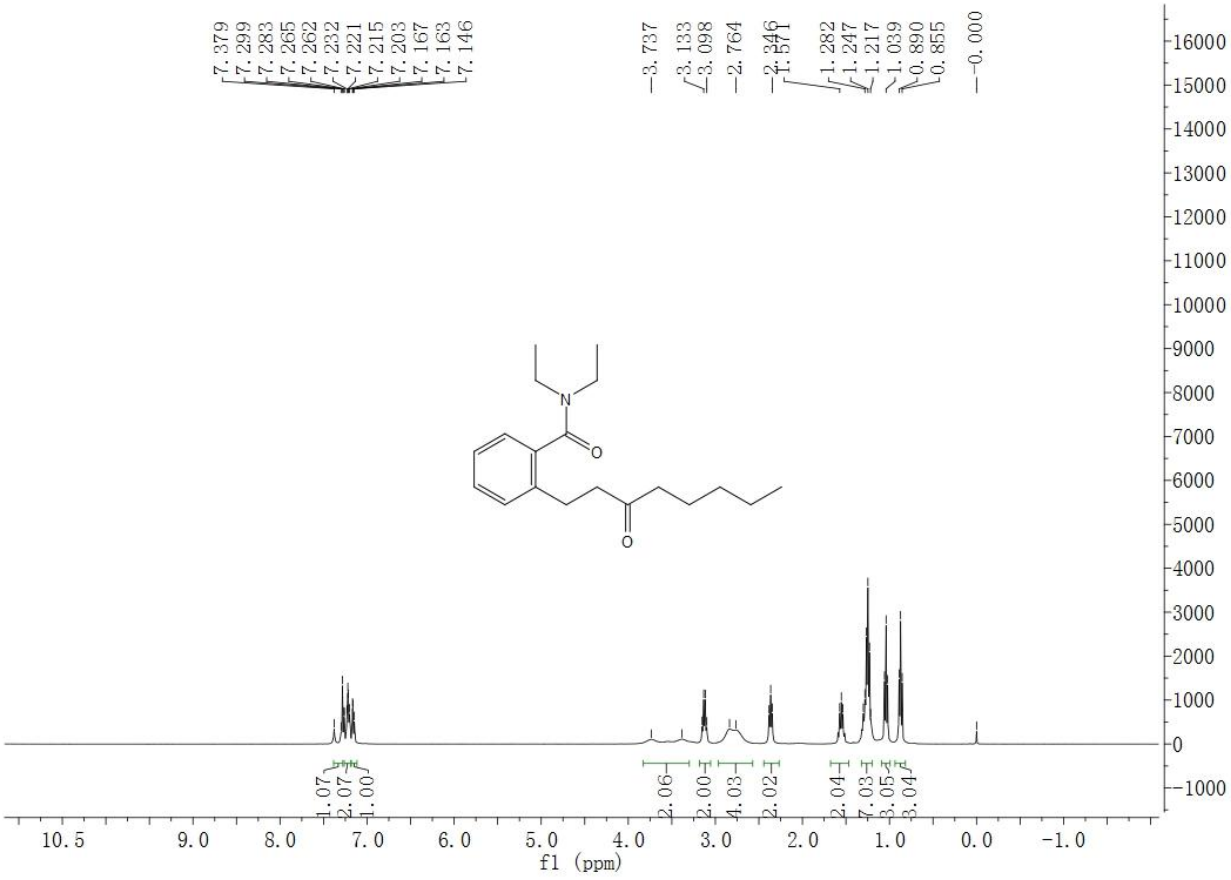


3aa





3ab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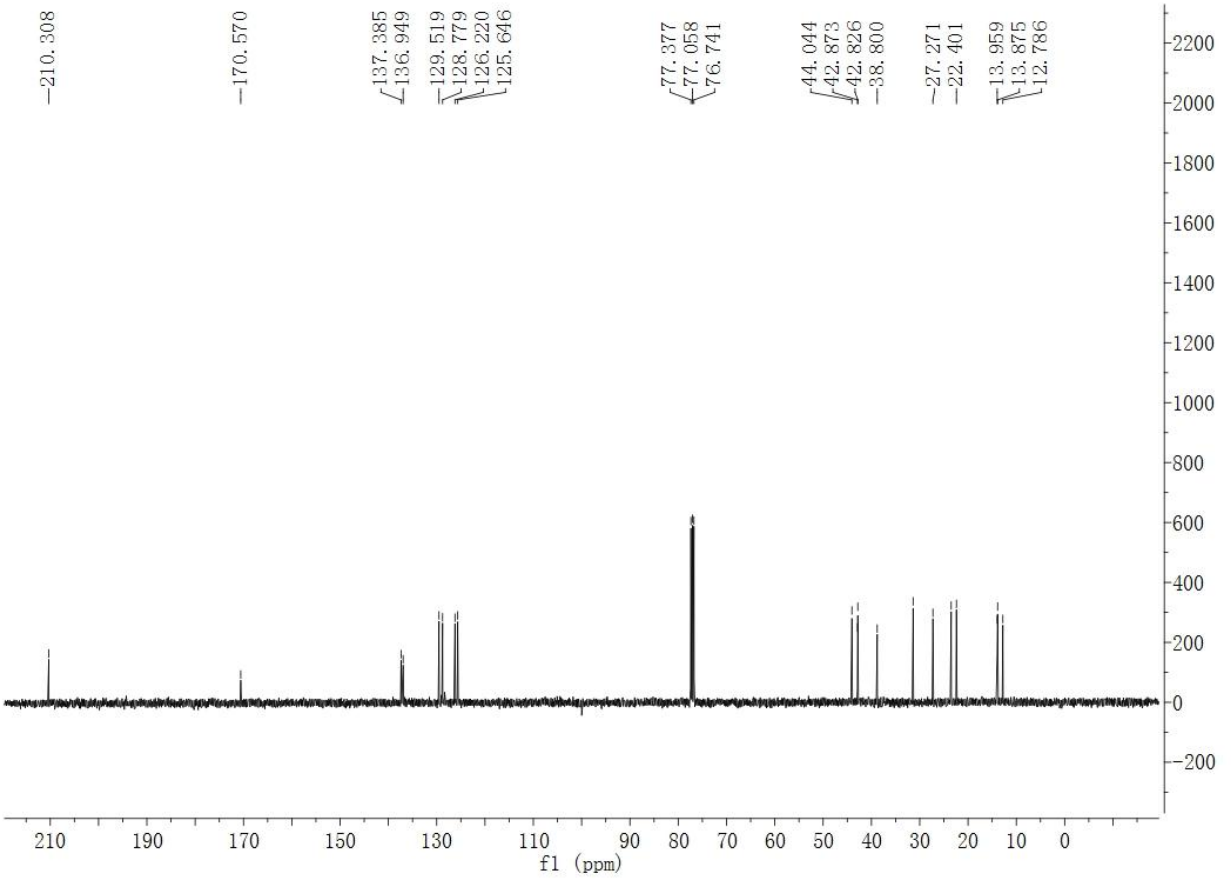
7.299
7.283
7.265
7.262
7.232
7.221
7.215
7.203
7.167
7.163
7.146
3.737
3.133
3.098
2.764
2.346
1.571
1.282
1.247
1.217
1.039
0.890
0.855
0.000
N
O
O
1.07
2.07
1.00
2.06
2.00
4.03
2.02
2.04
7.03
3.05
3.04
f1 (ppm)


210.308
170.570
137.385
136.949
129.519
128.779
126.220
125.646
77.377
77.058
76.741
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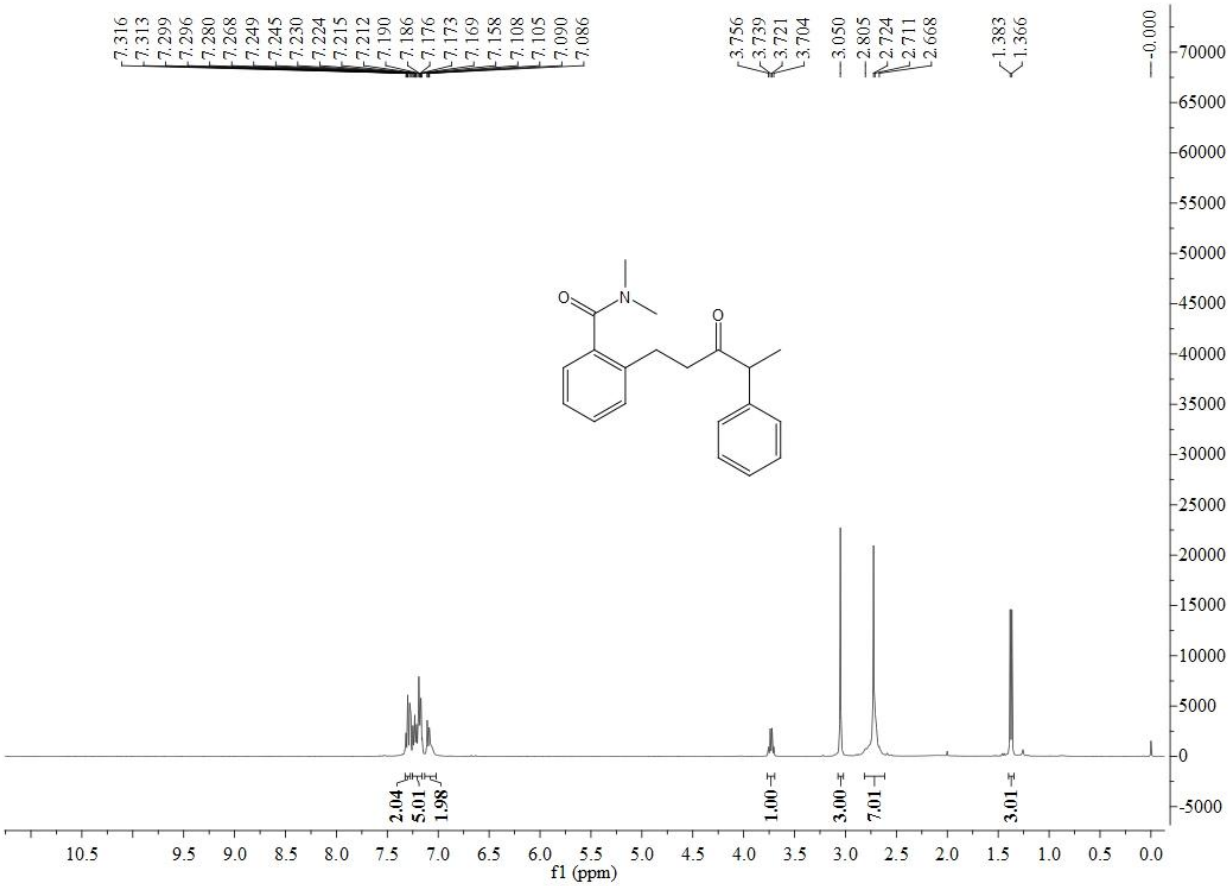
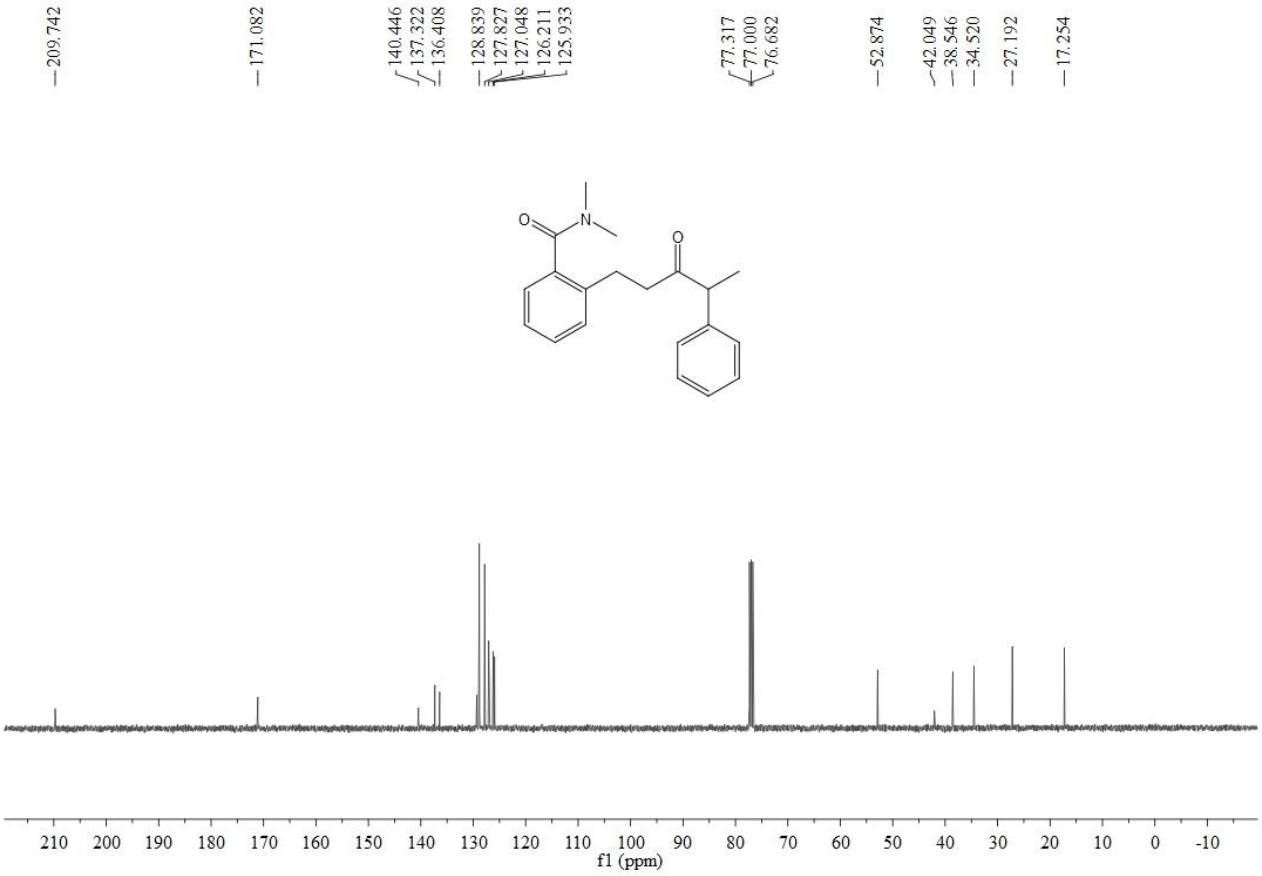
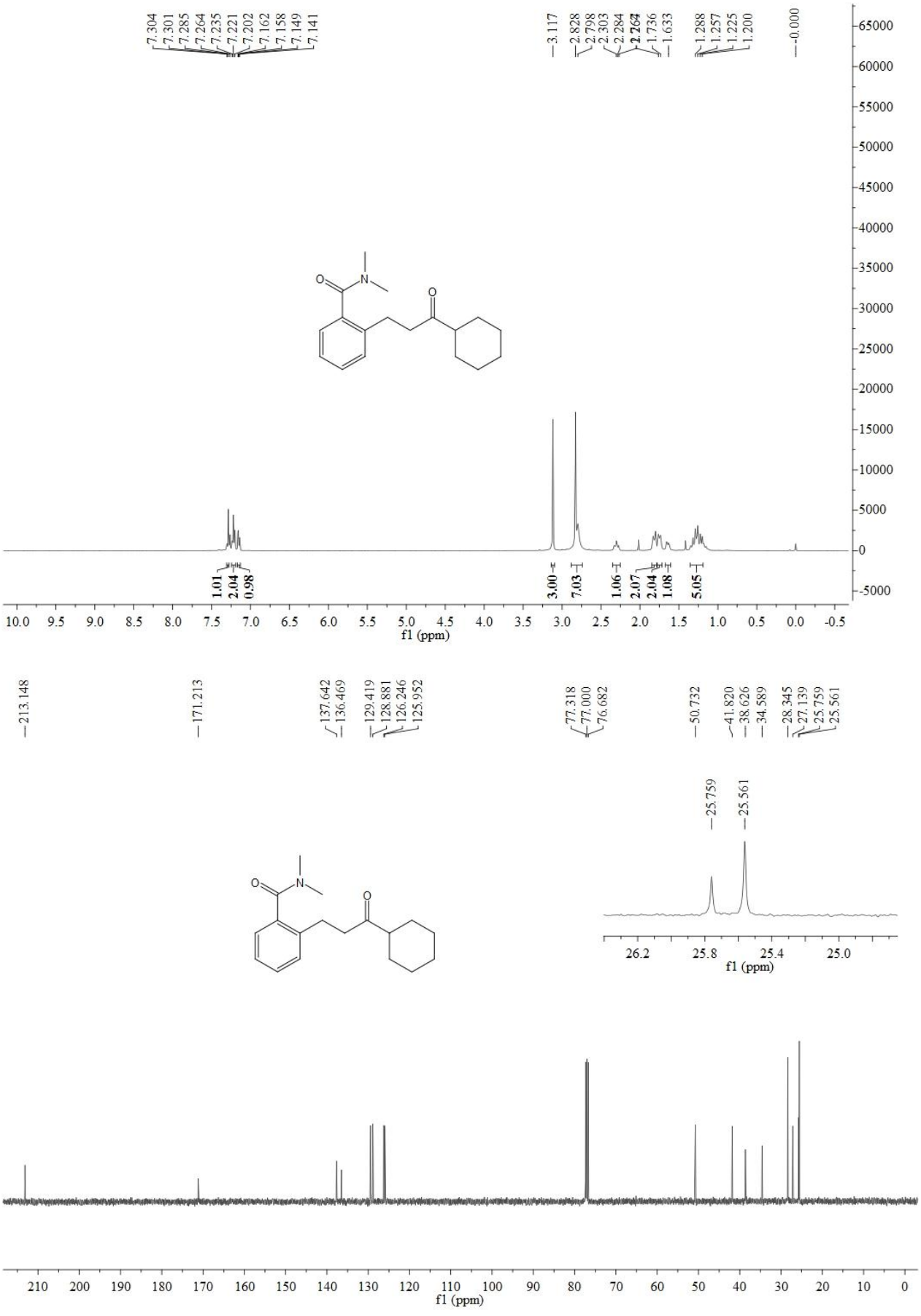
22.401
13.959
13.875
12.786
f1 (ppm)

3ac

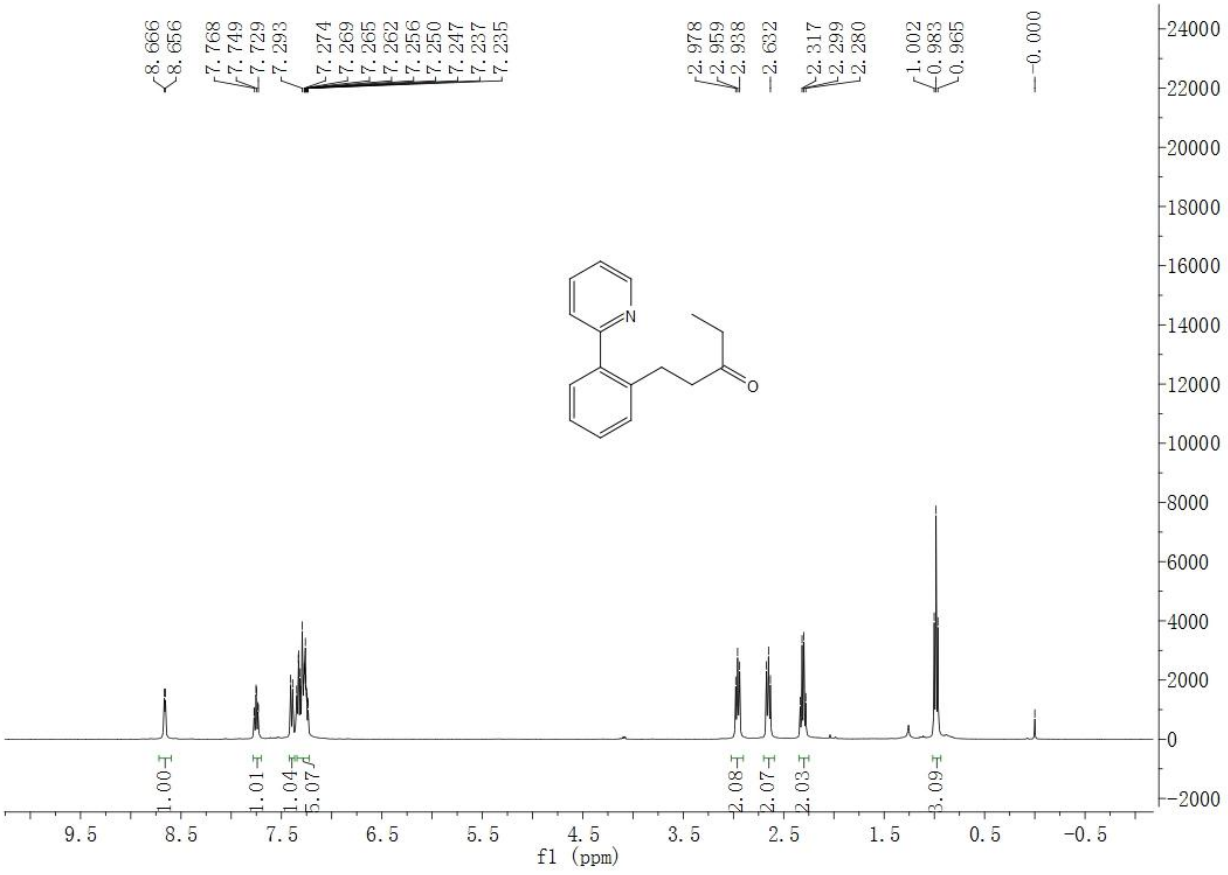


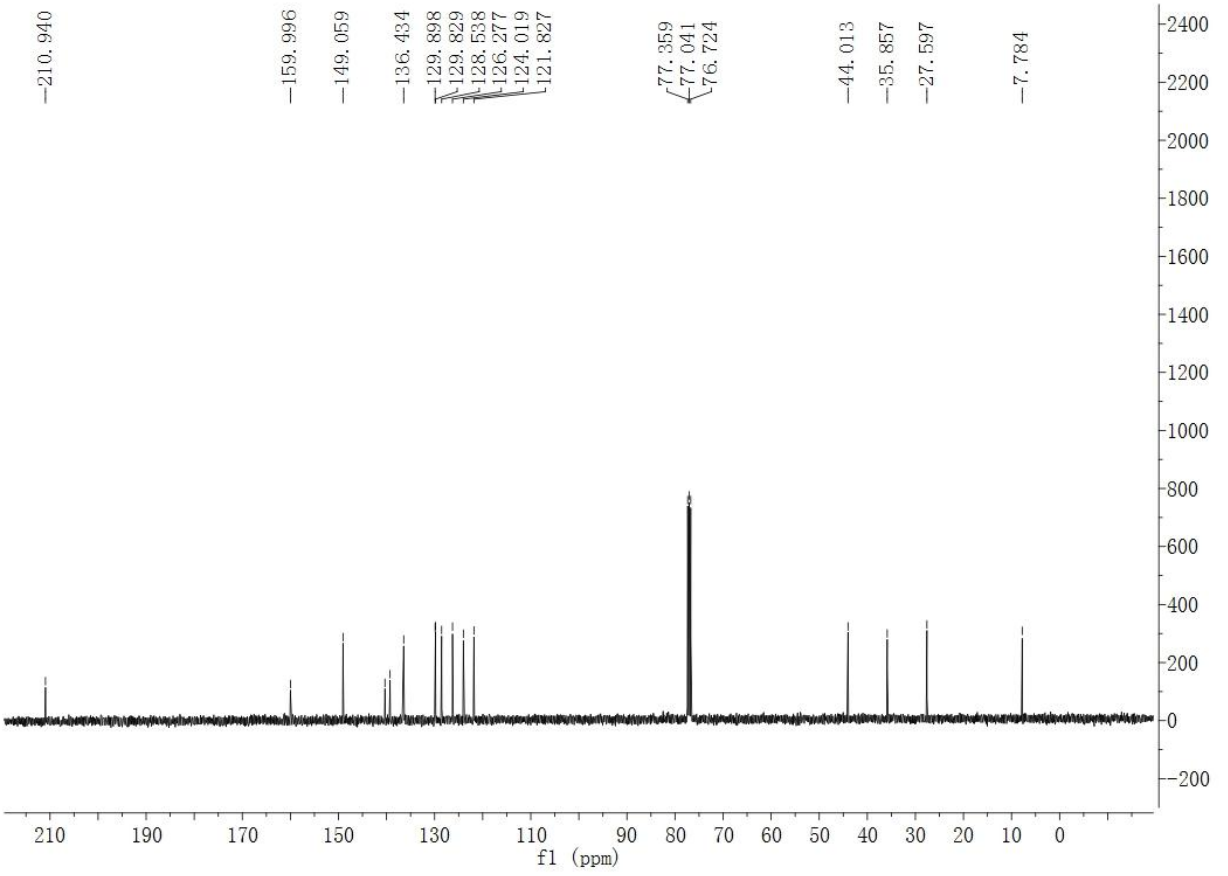


3ad

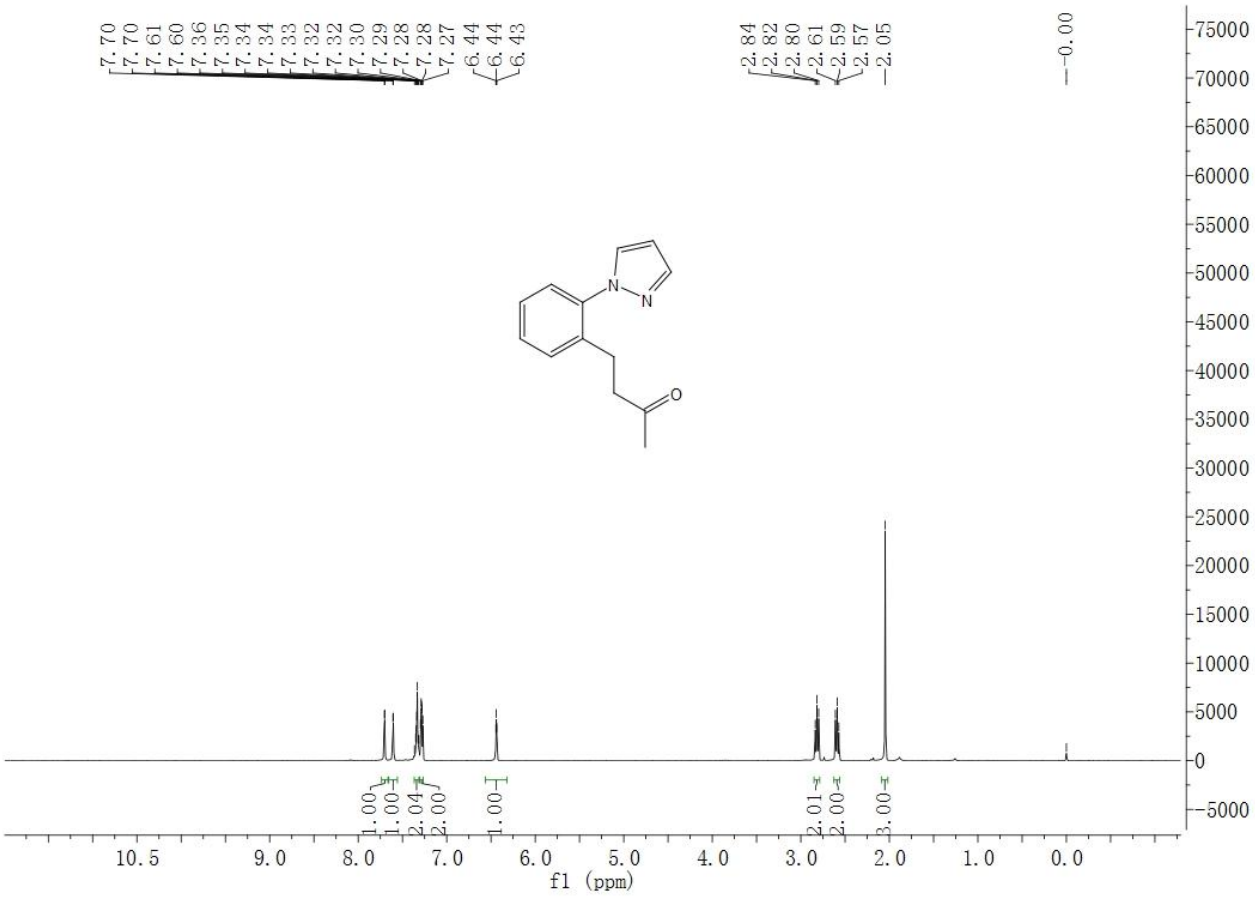


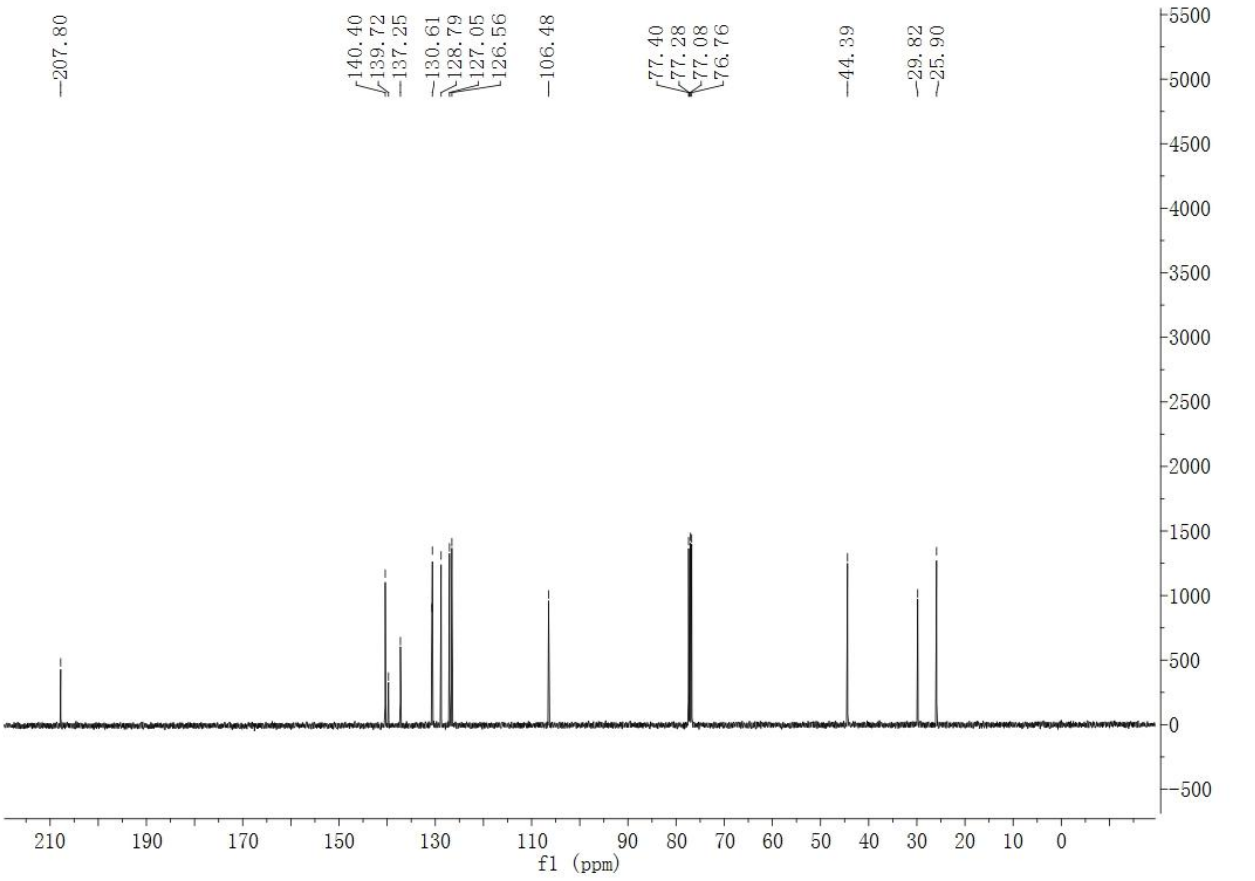
3ae



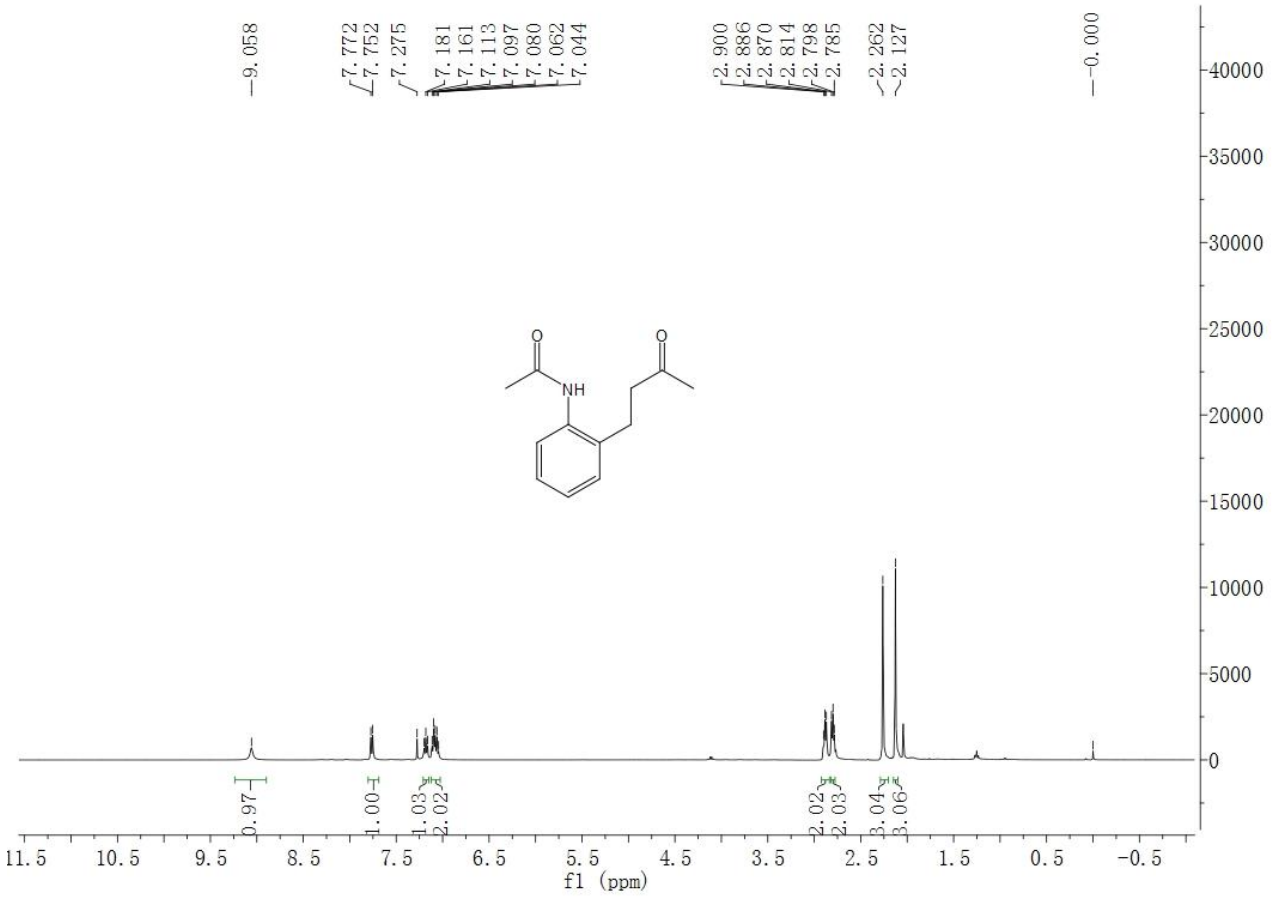


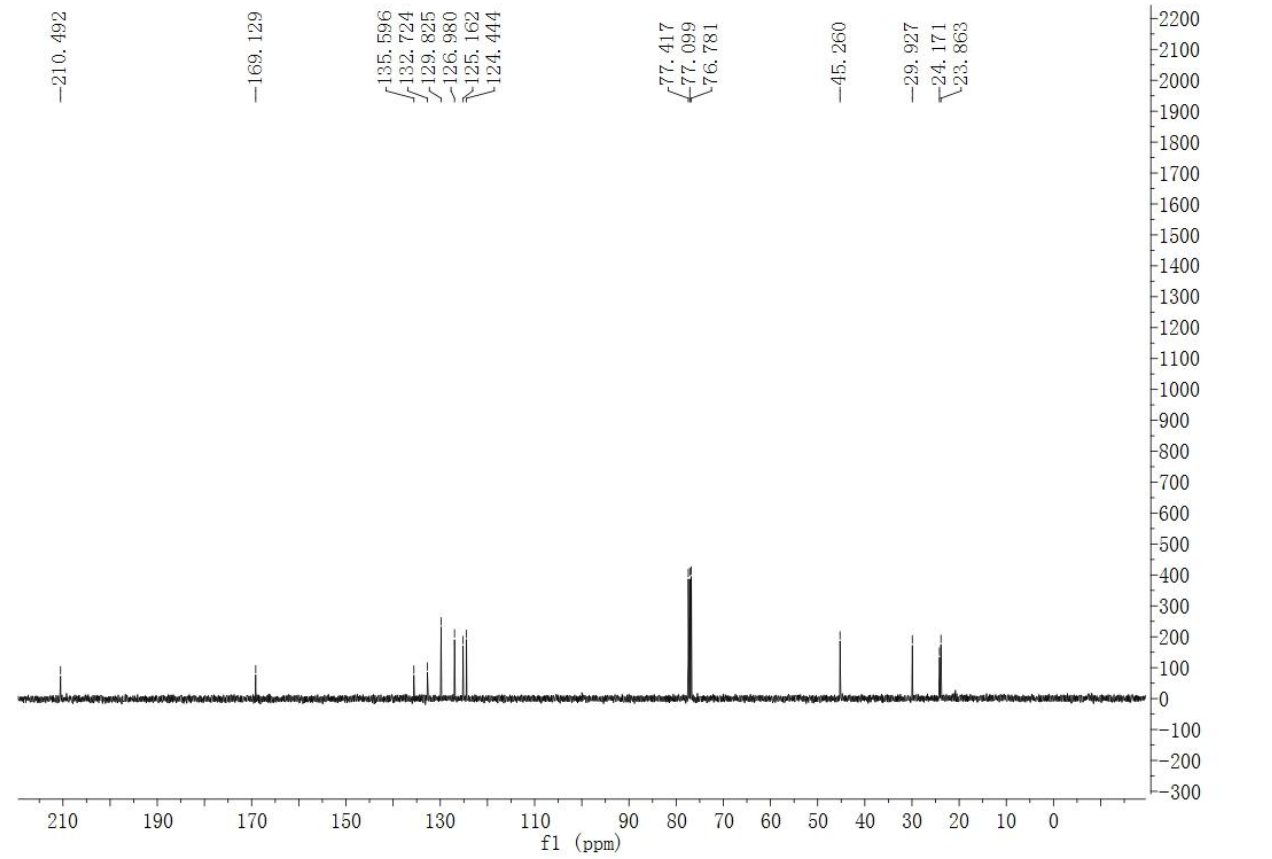
3af



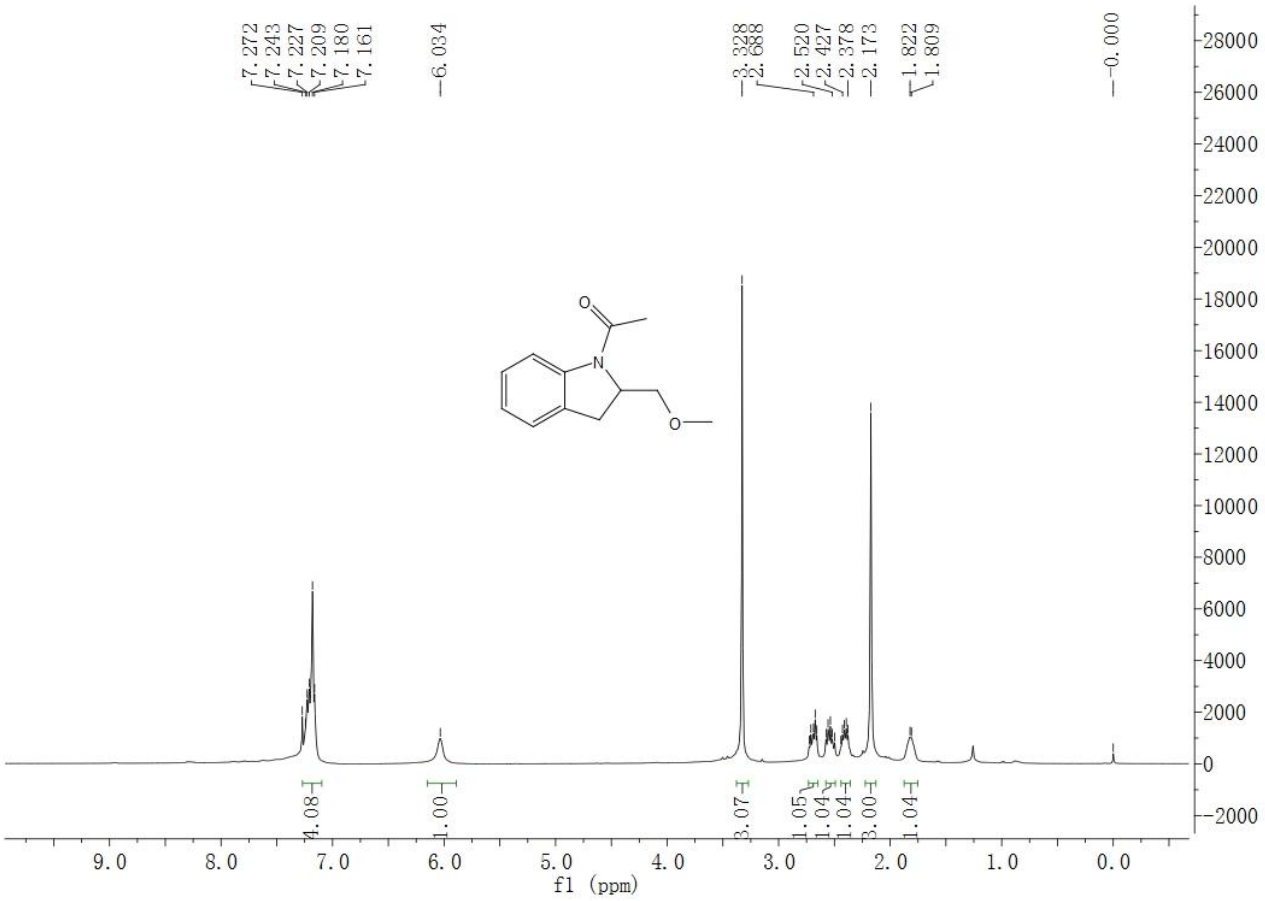


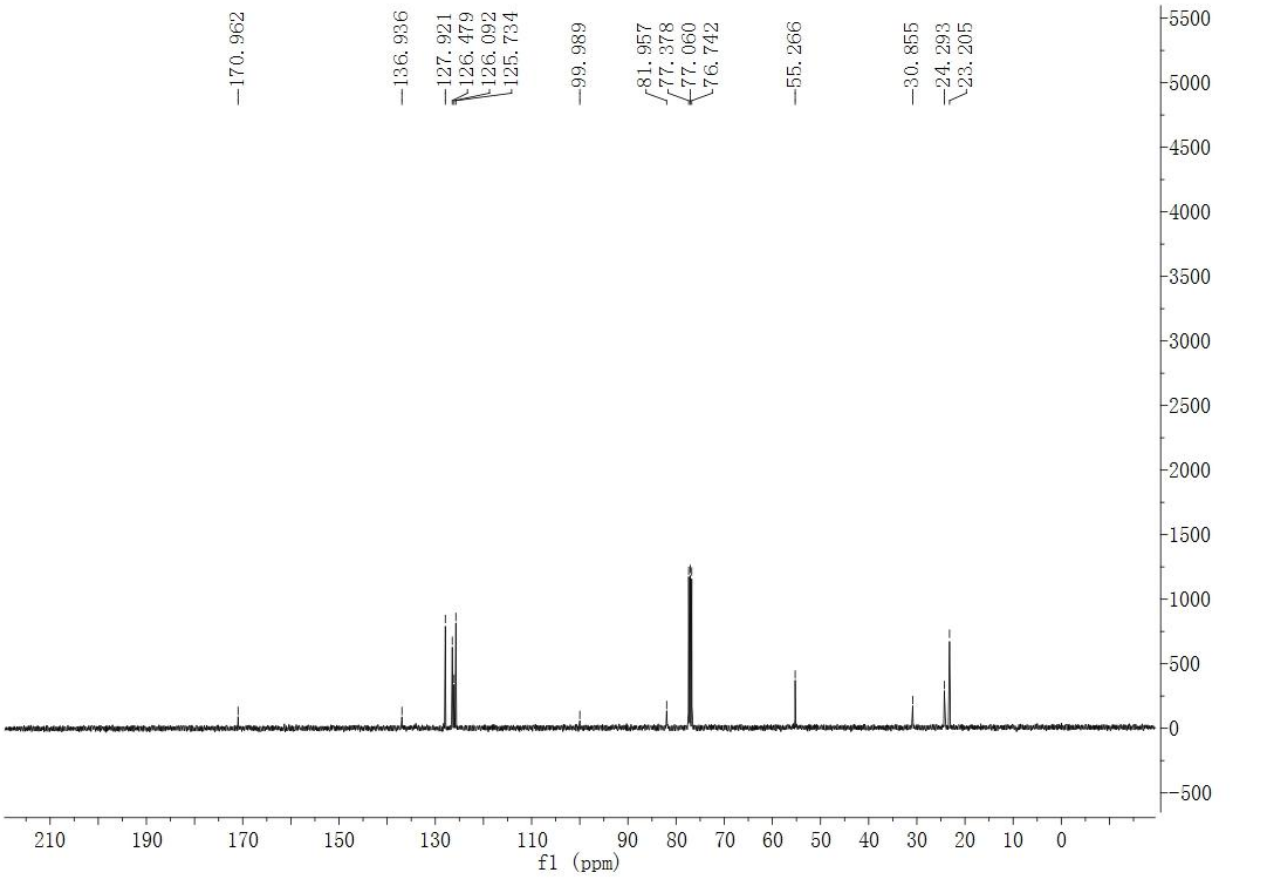
3ag



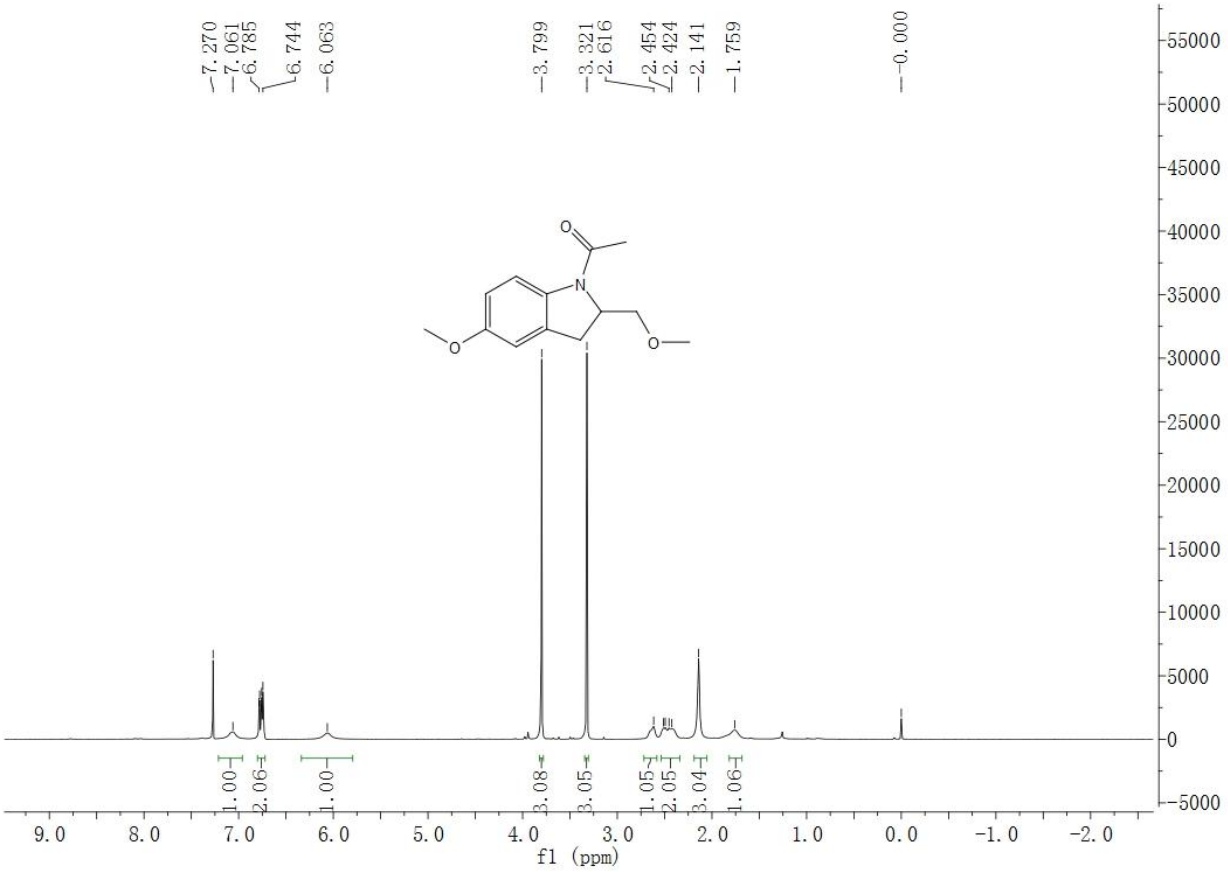


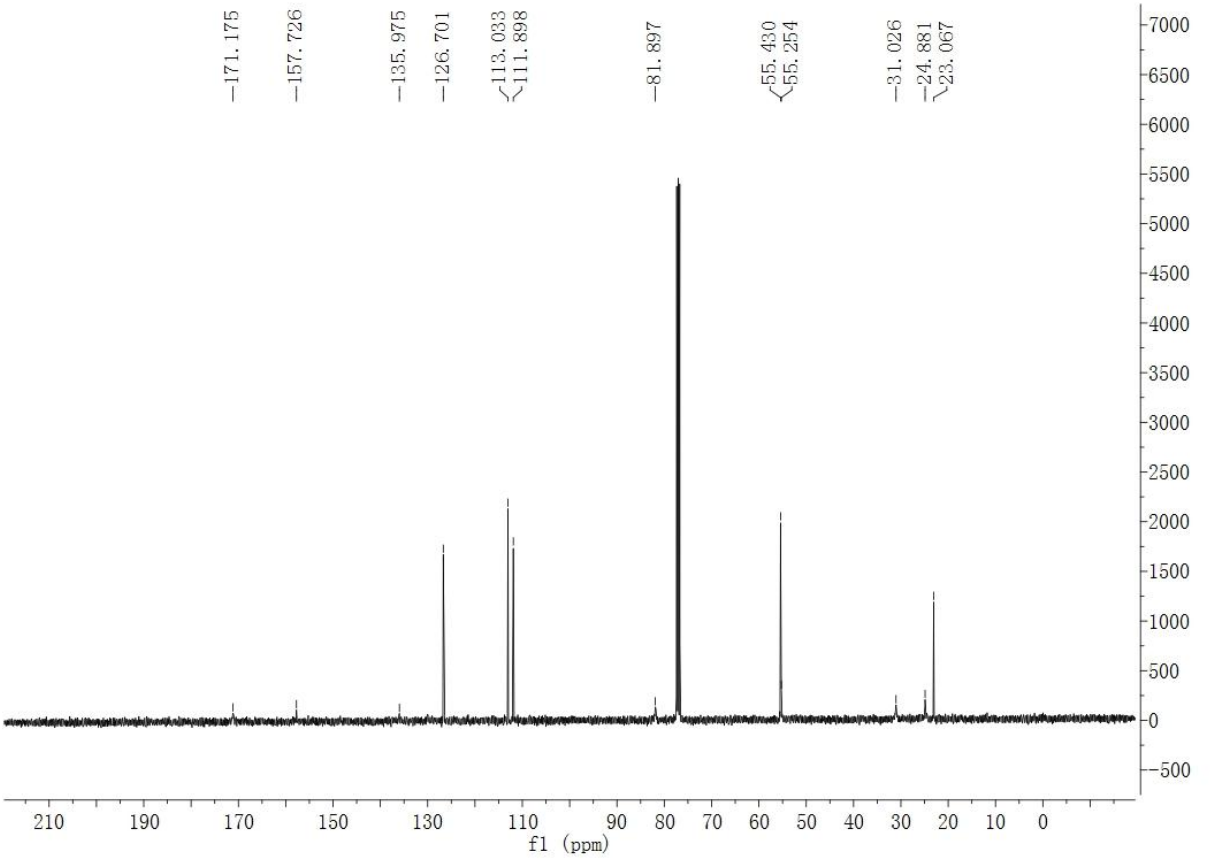
4a


7.272
7.243
7.227
7.209
7.180
7.161
6.034
3.328
2.688
2.520
2.427
2.378
2.173
1.822
1.809
0.000
O
N
O
4.08
1.00
3.07
1.05
1.04
1.04
3.00
1.04
f1 (ppm)

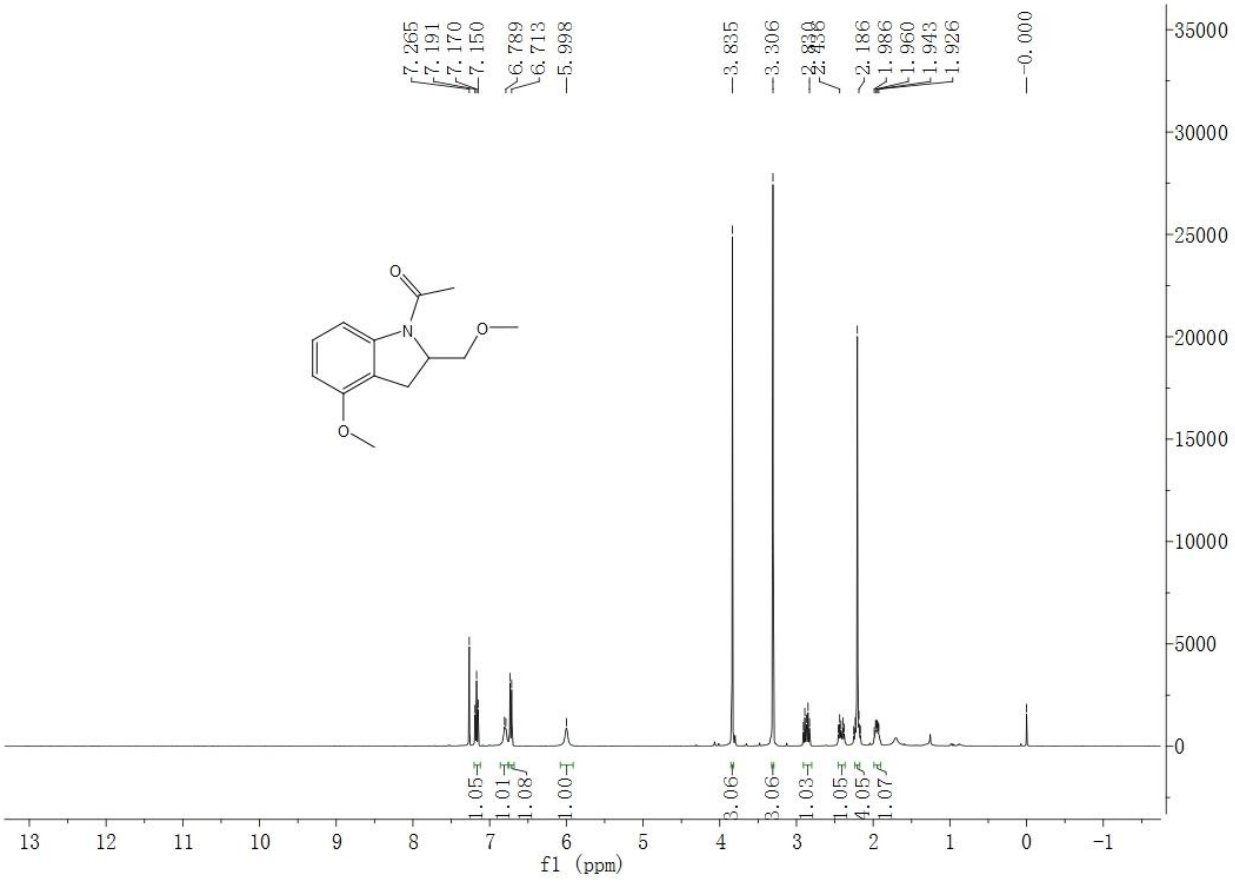

170.962
136.936
127.921
126.479
126.092
125.734
99.989
81.957
77.378
77.060
76.742
55.266
30.855
24.293
23.205
f1 (ppm)

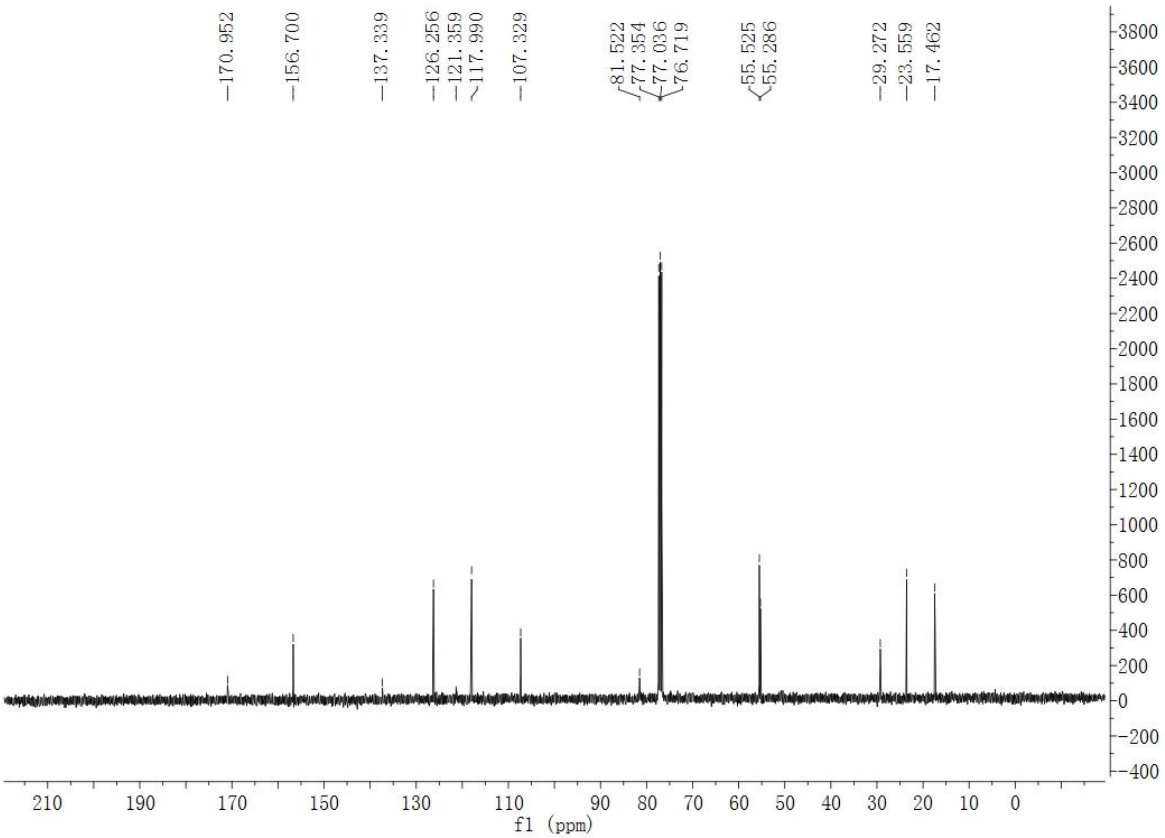
4b



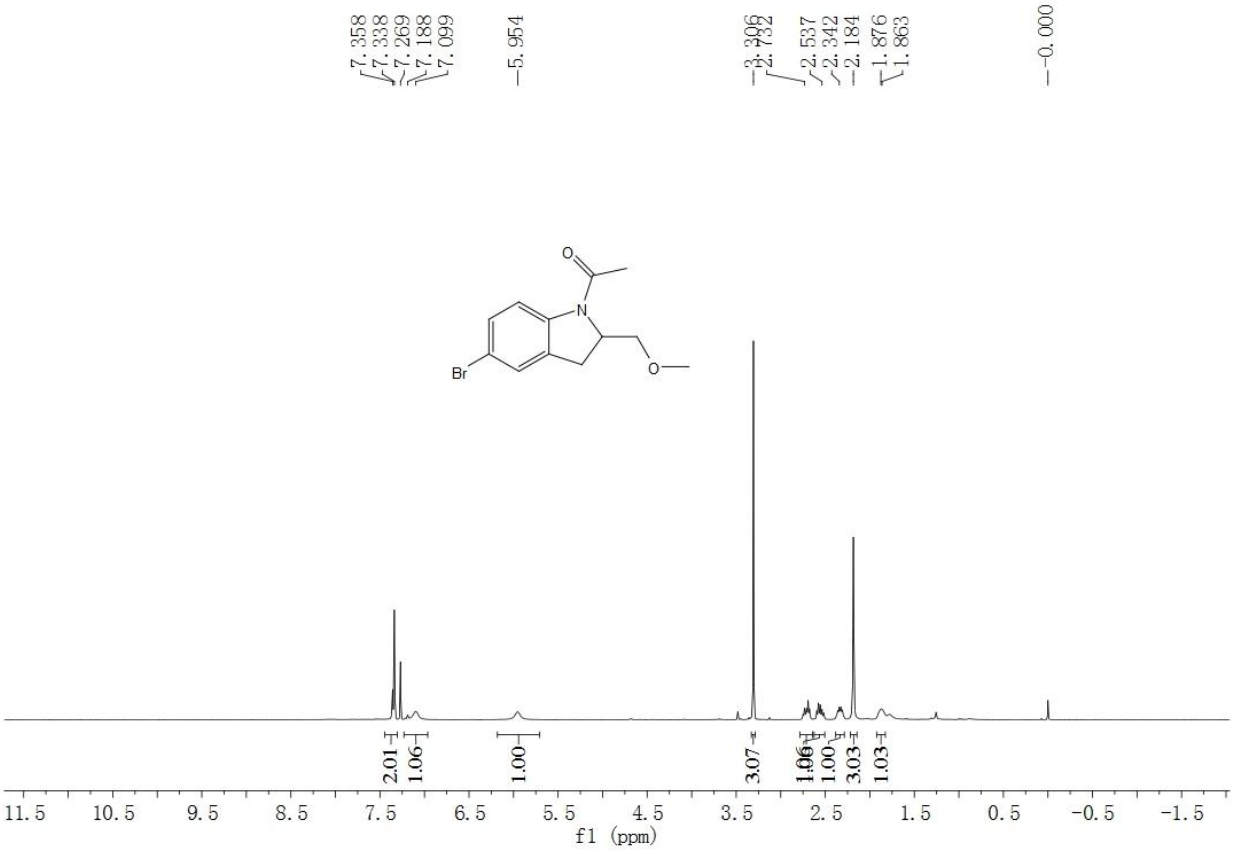


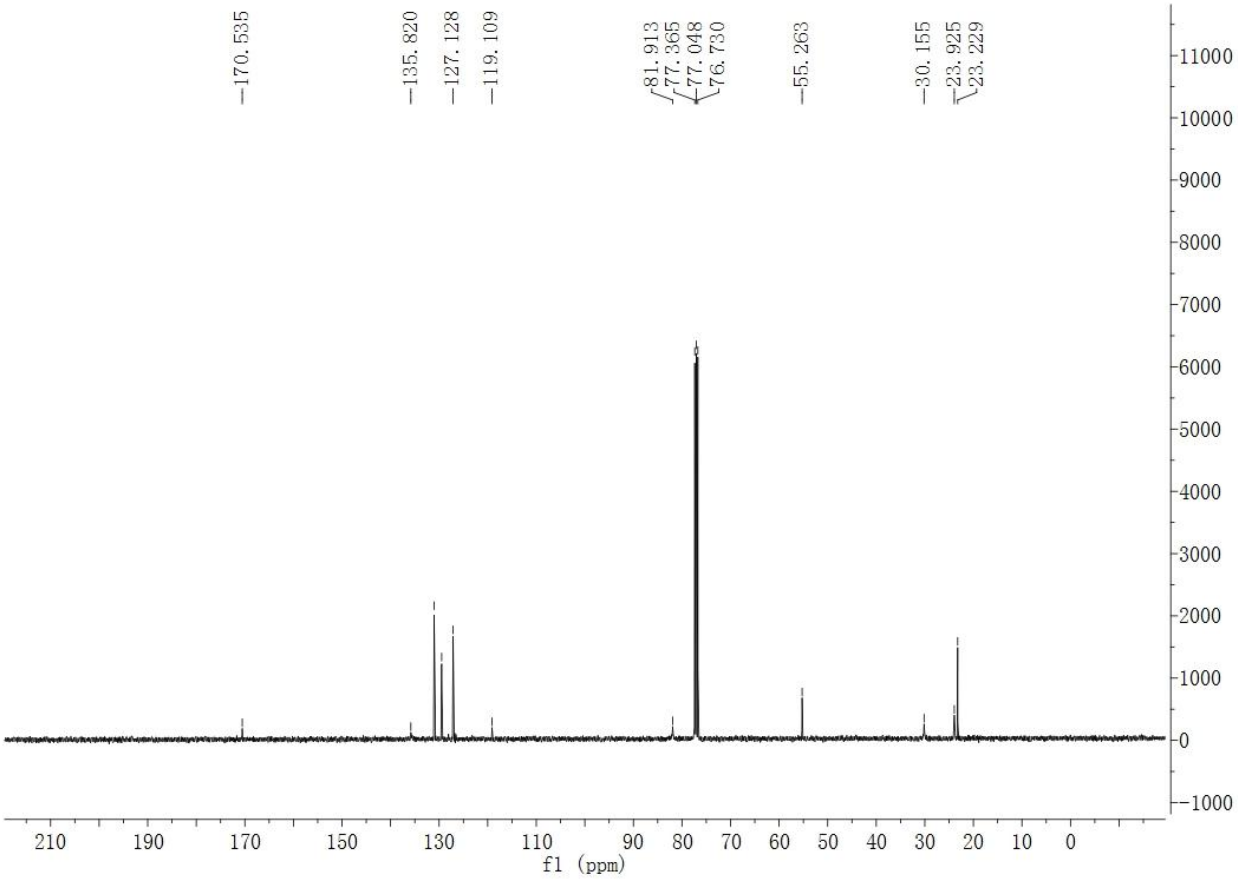
4c


7.265
7.191
7.170
7.150
6.789
6.713
5.998
3.835
3.306
2.186
1.986
1.960
1.943
1.926
0.000
1.05
1.01
1.08
1.00
3.06
3.06
1.03
1.05
4.05
1.07
f1 (ppm)

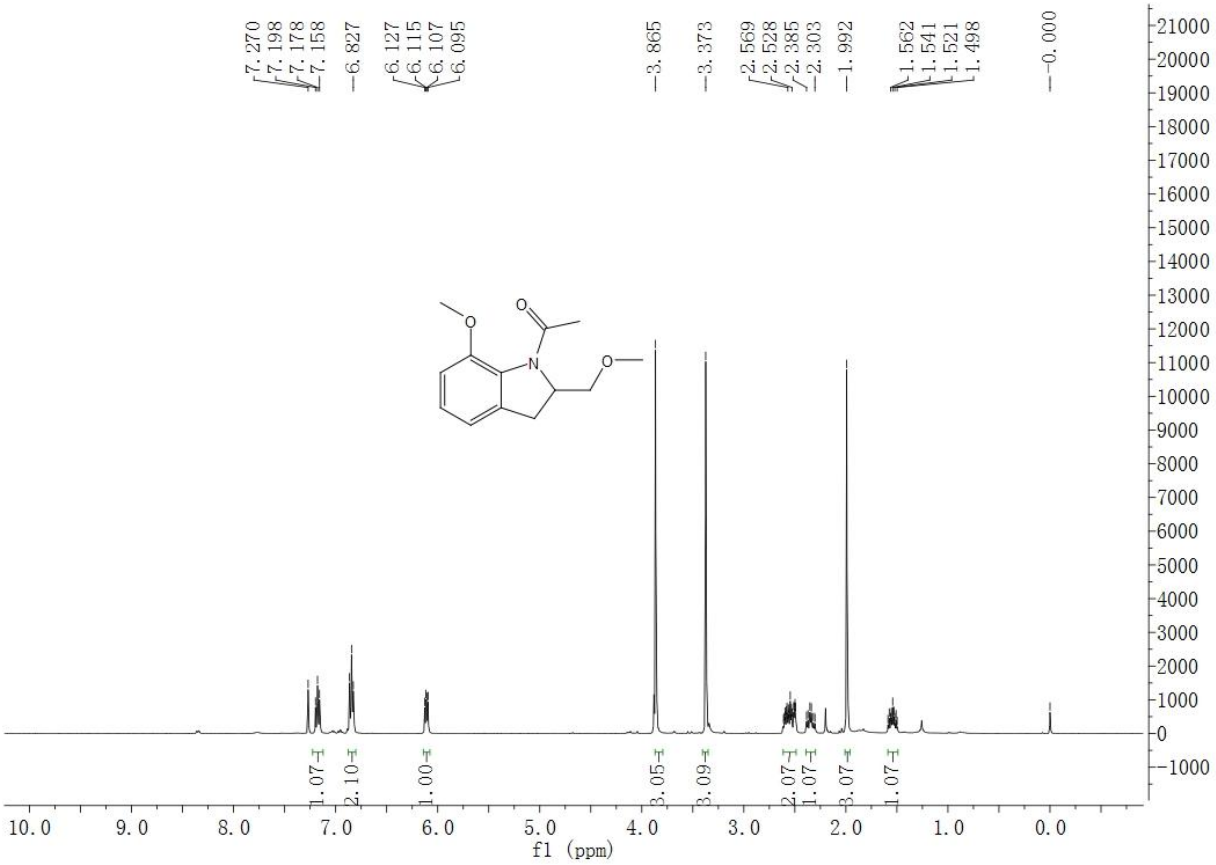

170.952
156.700
137.339
126.256
121.359
117.990
107.329
81.522
77.354
77.036
76.719
55.525
55.286
29.272
23.559
17.462
f1 (ppm)

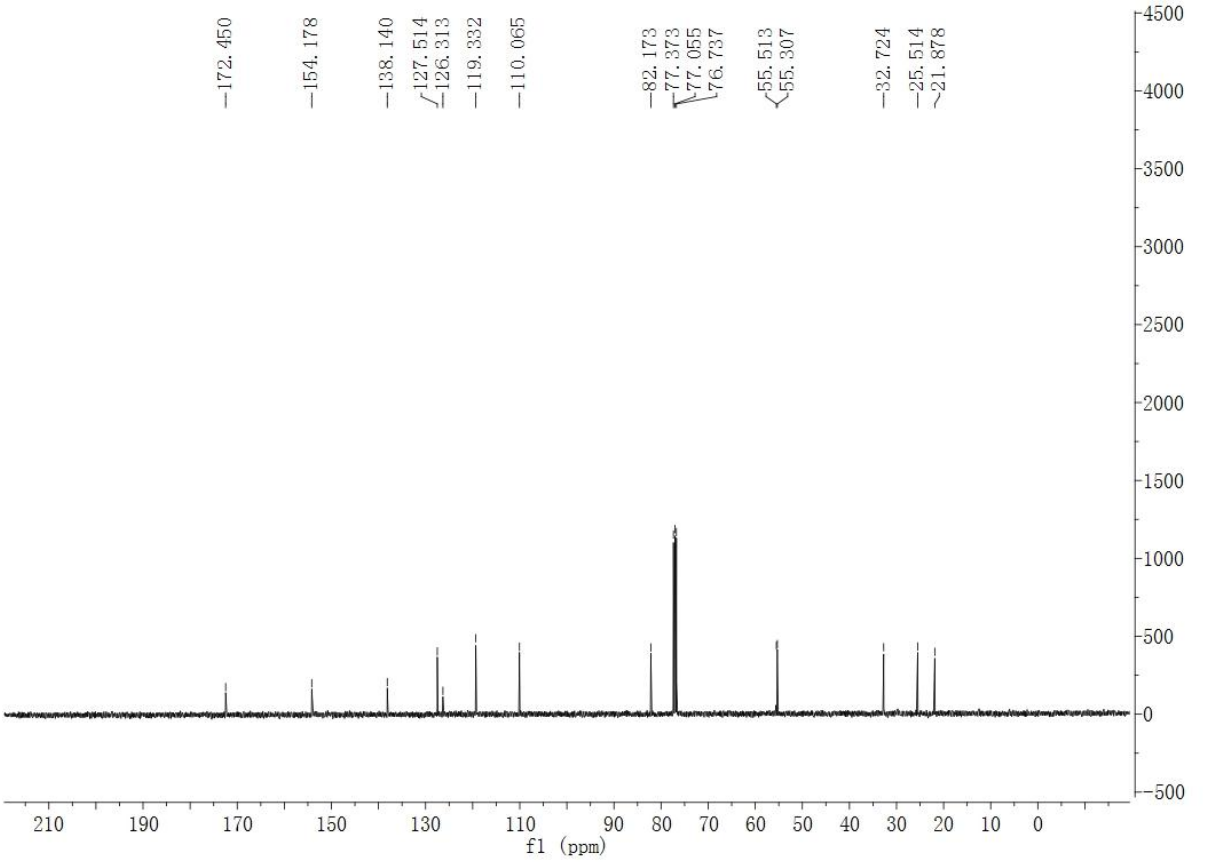
4d


7.358
7.338
7.269
7.188
7.099
5.954
3.396
3.382
2.732
2.537
2.342
2.184
1.876
1.863
0.000
O
N
Br
O
2.01
1.06
1.00
3.07
1.06
1.00
3.03
1.03
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)


170.535
135.820
127.128
119.109
81.913
77.365
77.048
76.730
55.263
30.155
23.925
23.229
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4e


7.270
7.198
7.178
7.158
6.827
6.127
6.115
6.107
6.095
3.865
3.373
2.569
2.528
2.385
2.303
1.992
1.562
1.541
1.521
1.498
0.000
1.07
2.10
1.00
3.05
3.09
2.07
1.07
3.07
1.07
f1 (ppm)


172.450
154.178
138.140
127.514
126.313
119.332
110.065
82.173
77.373
77.055
76.737
55.513
55.307
32.724
25.514
21.878
f1 (ppm)

4f