Supporting Information

Metal-free oxidative radical cascade addition/oxobutylation of unactivated alkenes with acetone towards 3-(3-oxobutyl)indolines

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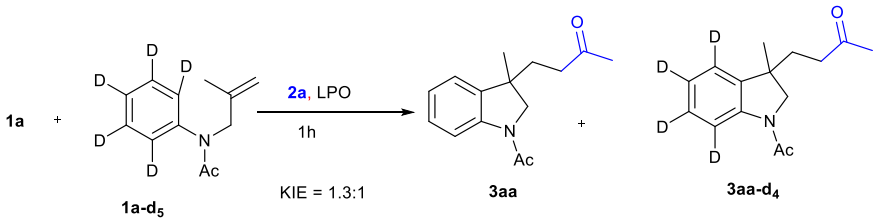
1. General experimental details

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300, 400 or 600 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

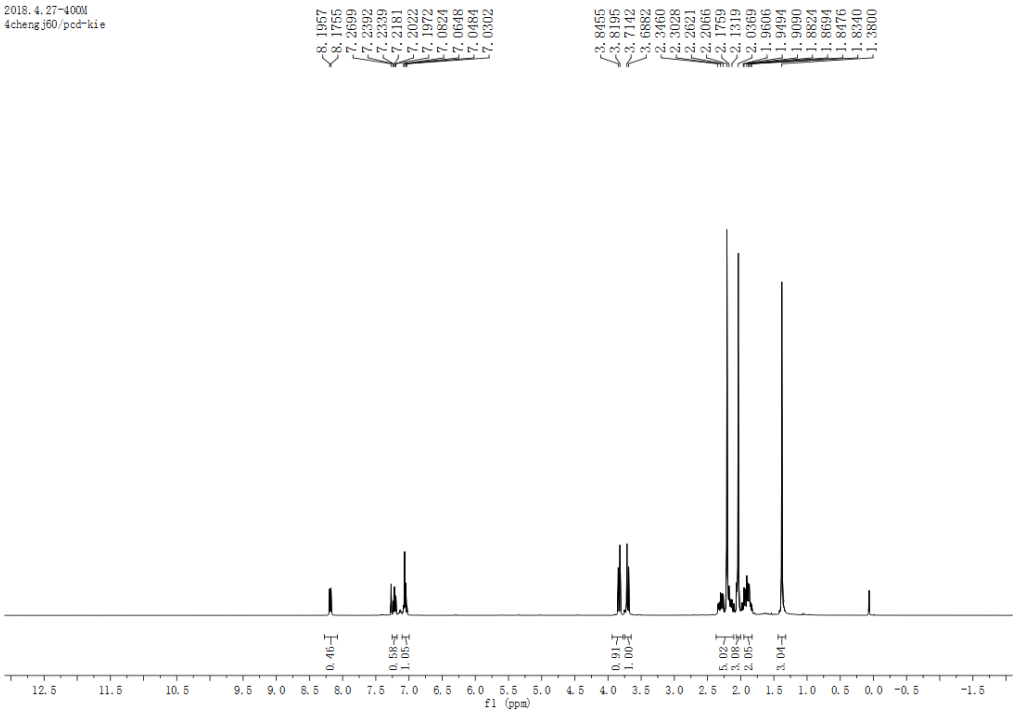
Experimental procedure: Under N_2, the mixture of **1** (0.2 mmol), **2** (1 mL) and LPO (0.4 mmol) were added into the tube and sealed. The mixture was stirred at 100 ^oC for 12 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product **3**.

2. Mechanism Studies

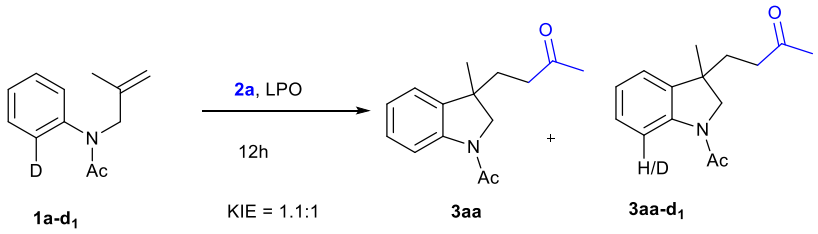
Intermolecular competition experiment with isotopically labeled 1a-d_5



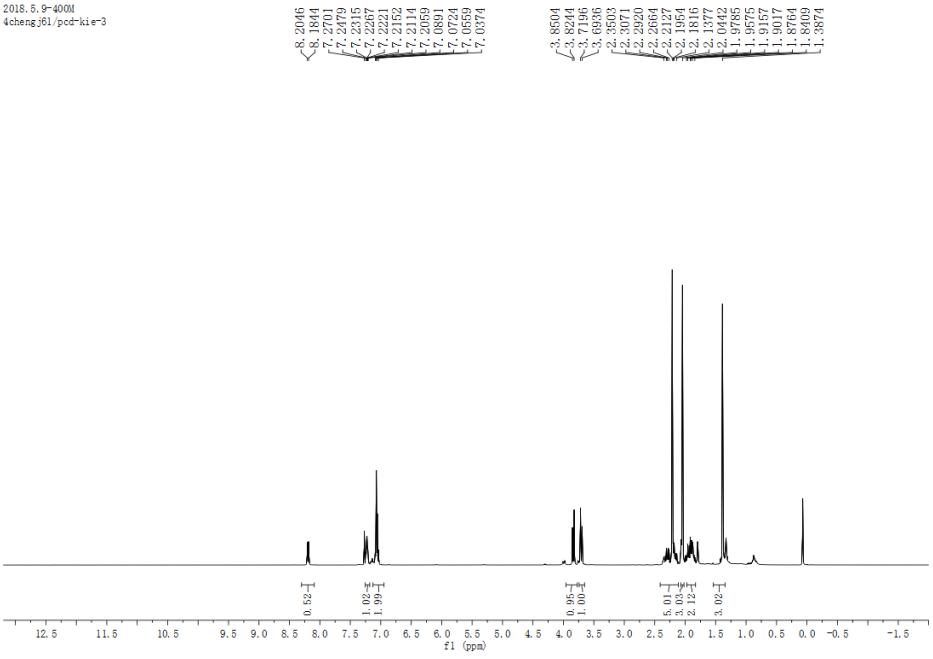
Under N_2, the mixture of **1a** (18.9 mg, 0.1 mmol), **1a-d_5** (19.4 mg, 0.1 mmol), **2a** (1 mL) and LPO (0.4 mmol) were added into the tube and sealed. The mixture was stirred at 100 ^oC for 1 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **3aa** and **3aa-d_4** in 32% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.18 (d, *J* = 8.1 Hz, 0.46H), 7.24-7.19 (m, 0.58H), 7.08-7.03 (m, 1H), 3.83 (d, *J* = 10.4 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 2.35-2.13 (m, 5H), 2.04 (s, 3H), 1.96-1.83 (m, 2H), 1.38 (s, 3H).



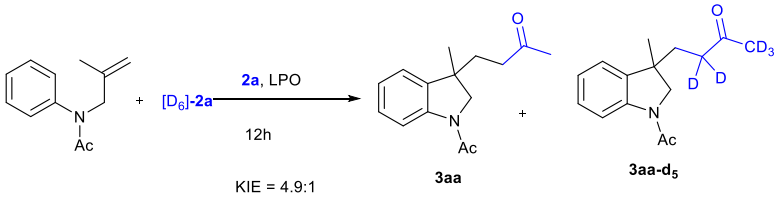
Intramolecular competition experiment isotopically labeled [D_1]-1a



Under N_2, the mixture of **1a-d$_1$** (38.0 mg, 0.2 mmol), **2a** (1 mL) and LPO (0.4 mmol) were added into the tube and sealed. The mixture was stirred at 100 ^{o}C for 12 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **3aa** and **3aa-d$_1$** in 76% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, *J* = 8.1 Hz, 0.52H), 7.25-7.20 (m, 1H), 7.09-7.04 (m, 2H), 3.84 (d, *J* = 10.4 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 2.35-2.14 (m, 5H), 2.04 (s, 3H), 1.97-1.84 (m, 2H), 1.39 (s, 3H).

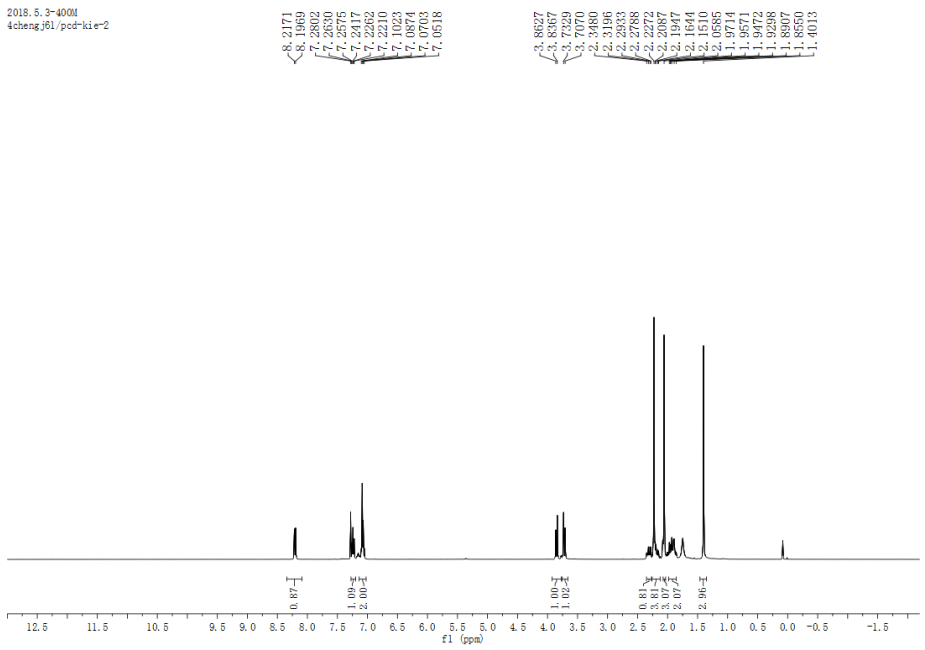


The KIE studies on solvent (competition reaction):



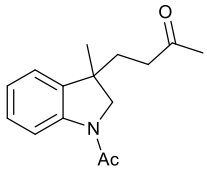
Under N_2, the mixture of **1a** (37.8 mg, 0.2 mmol), LPO (0.4 mmol), **2a** (0.5 mL) and **[d$_6$]-2a** (0.5 mL) were added into the tube and sealed. The mixture was stirred at 100 ^{o}C for 12 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **3aa** and **3aa-d$_5$** in 73% yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.26-7.22 (m, 1H), 7.09-7.05 (m, 2H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.72 (d, *J* = 10.4 Hz, 1H), 2.35-2.28 (m, 0.81H), 2.23-2.15 (m, 3.81H), 2.06 (s, 3H), 1.97-1.85 (m, 2H), 1.40 (s, 3H).



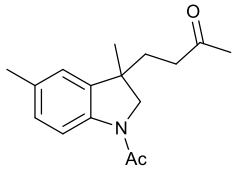
3. Characterization data of the products

4-(1-acetyl-3-methylindolin-3-yl)butan-2-one (3aa)



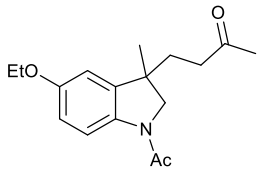
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.25-7.21 (m, 1H), 7.09-7.04 (m, 2H), 3.84 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 2.35-2.14 (m, 5H), 2.05 (s, 3H), 1.96-1.84 (m, 2H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.1, 168.7, 142.3, 137.6, 128.1, 123.9, 122.4, 116.9, 61.2, 42.9, 38.9, 34.9, 30.1, 27.3, 24.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NO_2$ $(M+H)^+$ 246.1489, found 246.1491.

4-(1-acetyl-3,5-dimethylindolin-3-yl)butan-2-one (3ba)



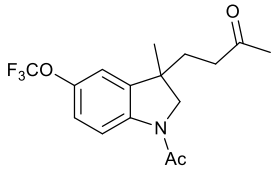
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.88 (s, 1H), 3.83 (d, *J* = 10.4 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 1H), 2.36-2.27 (m, 4H), 2.22-2.14 (m, 4H), 2.07 (s, 3H), 1.99-1.83 (m, 2H), 1.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.2, 168.3, 140.0, 137.7, 133.6, 128.6, 122.9, 116.7, 61.3, 42.9, 38.9, 34.9, 30.1, 27.3, 24.2, 21.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

4-(1-acetyl-5-ethoxy-3-methylindolin-3-yl)butan-2-one (3ca)



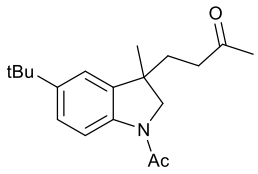
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.04 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 2H), 3.81 (d, *J* = 10.4 Hz, 1H), 3.68 (d, *J* = 10.4 Hz, 1H), 2.32-2.27 (m, 1H), 2.20-2.15 (m, 4H), 2.04 (s, 3H), 1.96-1.90 (m, 1H), 1.87-1.81 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.0, 167.8, 155.9, 139.2, 136.0, 117.6, 112.8, 109.5, 63.8, 61.3, 43.0, 38.8, 34.8, 30.1, 27.2, 23.9, 14.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{24}NO_3$ $(M+H)^+$ 290.1751, found 290.1753.

4-(1-acetyl-3-methyl-5-(trifluoromethoxy)indolin-3-yl)butan-2-one (3da)



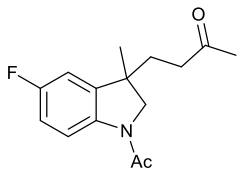
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.09-7.08 (m, 1H), 6.93 (s, 1H), 3.89 (d, *J* = 10.3 Hz, 1H), 3.76 (d, *J* = 10.3 Hz, 1H), 2.35-2.29 (m, 1H), 2.25-2.17 (m, 4H), 2.08 (s, 3H), 2.00-1.95 (m, 1H), 1.90-1.86 (m, 1H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.5, 168.7, 145.3, 140.9, 139.6, 120.9, 120.5 (q, J_{C-F} = 255.0 Hz), 117.6, 115.7, 61.4, 43.1, 38.6, 34.6, 30.1, 26.9, 24.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_3NO_3$ $(M+H)^+$ 330.1312, found 330.1316.

4-(1-acetyl-5-(tert-butyl)-3-methylindolin-3-yl)butan-2-one (3ea)



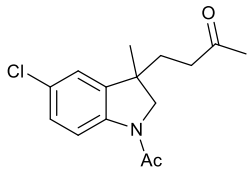
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.71 (d, *J* = 10.3 Hz, 1H), 2.34-2.29 (m, 1H), 2.24-2.17 (m, 4H), 2.04 (s, 3H), 1.98-1.88 (m, 2H), 1.40 (s, 3H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.1, 168.3, 147.2, 139.9, 137.3, 124.9, 119.0, 116.3, 61.4, 43.1, 38.9, 34.9, 34.5, 31.5, 30.1, 27.2, 24.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}NO_2$ $(M+H)^+$ 302.2115, found 302.2117.

4-(1-acetyl-5-fluoro-3-methylindolin-3-yl)butan-2-one (3fa)



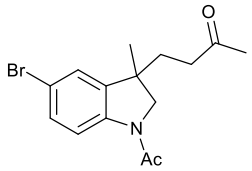
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18-8.15 (m, 1H), 6.94-6.88 (m, 1H), 6.79-6.76 (m, 1H), 3.87 (d, *J* = 10.4 Hz, 1H), 3.73 (d, *J* = 10.4 Hz, 1H), 2.36-2.28 (m, 1H), 2.24-2.16 (m, 4H), 2.07 (s, 3H), 2.00-1.93 (m, 1H), 1.89-1.83 (m, 1H), 1.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.7, 168.4, 159.6 (d, J_{C-F} = 241.3 Hz), 139.8 (d, J_{C-F} = 7.1 Hz), 138.3 (d, J_{C-F} = 1.9 Hz), 117.9 (d, J_{C-F} = 8.0 Hz), 114.4 (d, J_{C-F} = 22.6 Hz), 109.7 (d, J_{C-F} = 23.7 Hz), 61.3, 43.0 (d, J_{C-F} = 1.7 Hz), 38.7, 34.6, 30.1, 27.1, 24.0. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}FNO_2$ $(M+H)^+$ 264.1394, found 264.1393.

4-(1-acetyl-5-chloro-3-methylindolin-3-yl)butan-2-one (3ga)



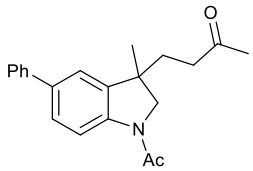
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.04 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.88 (d, *J* = 1.9 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 2.35-2.27 (m, 1H), 2.24-2.15 (m, 4H), 2.07 (s, 3H), 1.98-1.91 (m, 1H), 1.88-1.80 (m, 1H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.7, 168.7, 140.9, 139.7, 128.8, 128.1, 122.7, 117.9, 61.2, 43.0, 38.7, 34.7, 30.1, 27.2, 24.1. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}ClNO_2$ $(M+H)^+$ 280.1099, found 280.1102.

4-(1-acetyl-5-bromo-3-methylindolin-3-yl)butan-2-one (3ha)



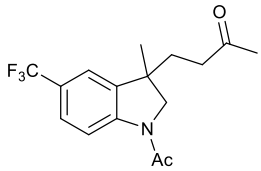
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.35-7.33 (m, 1H), 7.18 (d, *J* = 1.9 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.72 (d, *J* = 10.4 Hz, 1H), 2.34-2.27 (m, 1H), 2.24-2.18 (m, 4H), 2.08 (s, 3H), 1.99-1.94 (m, 1H), 1.88-1.83 (m, 1H), 1.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.6, 168.7, 141.4, 140.1, 131.0, 125.5, 118.4, 116.3, 61.2, 43.1, 38.7, 34.7, 30.1, 27.2, 24.1. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}BrNO_2$ $(M+H)^+$ 324.0594, found 324.0597.

4-(1-acetyl-3-methyl-5-phenylindolin-3-yl)butan-2-one (3ia)



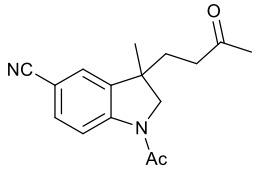
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.58-7.56 (m, 2H), 7.49-7.41 (m, 3H), 7.36-7.29 (m, 2H), 3.89 (d, *J* = 10.4 Hz, 1H), 3.76 (d, *J* = 10.4 Hz, 1H), 2.39-2.31 (m, 1H), 2.28-2.20 (m, 4H), 2.05 (s, 3H), 2.01-1.90 (m, 2H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.2, 168.8, 141.9, 140.9, 138.5, 137.3, 128.9, 127.3, 127.2, 127.0, 121.1, 117.3, 61.6, 43.2, 39.0, 35.0, 30.3, 27.5, 24.4. HRMS (ESI) *m/z* calcd for $C_{21}H_{24}NO_2$ $(M+H)^+$ 322.1802, found 322.1803.

4-(1-acetyl-3-methyl-5-(trifluoromethyl)indolin-3-yl)butan-2-one (3ja)



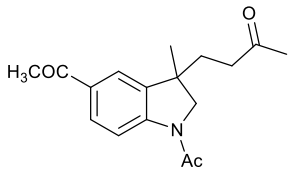
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.31 (s, 1H), 3.91 (d, *J* = 10.3 Hz, 1H), 3.77 (d, *J* = 10.3 Hz, 1H), 2.35-2.29 (m, 1H), 2.24-2.17 (m, 4H), 2.08 (s, 3H), 2.03-1.98 (m, 1H), 1.92-1.87 (m, 1H), 1.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.6, 169.2, 145.0, 138.5, 126.1, 125.9 (q, J_{C-F} = 3.6 Hz), 124.1 (q, J_{C-F} = 249.4 Hz), 119.4 (q, J_{C-F} = 3.3 Hz), 116.7, 61.3, 42.9, 38.7, 34.7, 30.1, 27.1, 24.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_3NO_2$ $(M+H)^+$ 314.1362, found 314.1360.

1-acetyl-3-methyl-3-(3-oxobutyl)indoline-5-carbonitrile (3ka)



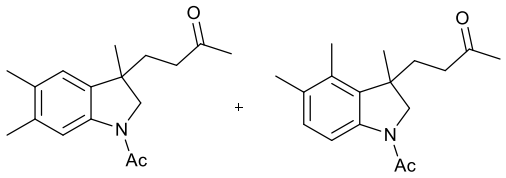
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.33 (s, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.76 (d, *J* = 10.4 Hz, 1H), 2.35-2.16 (m, 5H), 2.08 (s, 3H), 2.01-1.94 (m, 1H), 1.91-1.83 (m, 1H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.3, 169.5, 145.8, 139.0, 133.2, 126.2, 119.2, 117.2, 106.7, 61.2, 42.9, 38.6, 34.5, 30.1, 27.0, 24.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}N_2O_2$ $(M+H)^+$ 271.1441, found 271.1442.

1,1'-(3-methyl-3-(3-oxobutyl)indoline-1,5-diyl)bis(ethan-1-one) (3la)



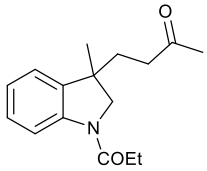
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.85-7.82 (m, 1H), 7.72 (s, 1H), 3.89 (d, *J* = 10.4 Hz, 1H), 3.75 (d, *J* = 10.4 Hz, 1H), 2.57 (s, 3H), 2.33-2.15 (m, 5H), 2.05 (s, 3H), 1.98-1.84 (m, 2H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.8, 197.3, 169.5, 146.4, 138.6, 130.4, 122.4, 116.3, 114.2, 61.7, 42.9, 38.9, 34.8, 30.2, 27.3, 26.7, 24.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NO_3$ $(M+H)^+$ 288.1594, found 288.1596.

4-(1-acetyl-3,5,6-trimethylindolin-3-yl)butan-2-one(3ma) and 4-(1-acetyl-3,4,5-trimethylindolin-3-yl)butan-2-one (3m'a)



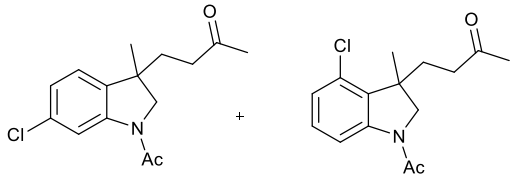
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 0.55H), 6.81 (s, 0.49H), 3.81-3.76 (m, 1H), 3.67-3.63 (m, 1H), 2.33-2.13 (m, 11H), 2.04-2.01 (m, 3H), 1.95-1.79 (m, 2H), 1.47 (s, 1.57H), 1.35 (s, 1.42H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 208.3, 208.2, 168.3, 168.2, 141.2, 140.4, 136.4, 135.1, 133.8, 133.1, 132.6, 132.1, 129.6, 123.3, 117.9, 114.3, 61.9, 61.4, 44.1, 42.7, 39.1, 38.9, 34.9, 33.3, 30.2, 30.1, 27.4, 27.3, 24.3, 24.2, 20.1, 19.8, 19.7, 14.9. MS (EI): 273, 231, 202, 160, 144.

4-(3-methyl-1-propionylindolin-3-yl)butan-2-one (3na)



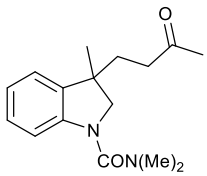
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.09-7.05 (m, 2H), 3.84 (d, *J* = 10.3 Hz, 1H), 3.70 (d, *J* = 10.3 Hz, 1H), 2.47-2.42 (m, 2H), 2.31-2.29 (m, 1H), 2.21-2.16 (m, 1H), 2.05 (s, 3H), 1.98-1.87 (m, 2H), 1.39 (s, 3H), 1.25 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.0, 171.9, 142.6, 137.5, 128.2, 123.8, 122.3, 116.9, 60.2, 42.9, 38.9, 34.9, 30.1, 29.2, 27.3, 8.7. HRMS (ESI) *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

4-(1-acetyl-6-chloro-3-methylindolin-3-yl)butan-2-one (3oa) and 4-(1-acetyl-4-chloro-3-methylindolin-3-yl)butan-2-one(3oa')



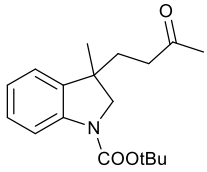
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23-8.18 (m, 1H), 7.19-7.15 (m, 0.73H), 7.04-6.98 (m, 1.27H), 3.86-3.84 (m, 1H), 3.74-3.69 (m, 1H), 2.44-2.18 (m, 5H), 2.07-2.06 (m, 3H), 1.99-1.82 (m, 2H), 1.54 (s, 2.23H), 1.37 (s, 0.83H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 208.0, 207.8, 168.8, 144.4, 143.2, 136.2, 133.6, 132.8, 130.1, 129.6, 125.3, 123.9, 123.1, 117.2, 115.5, 61.4, 61.2, 44.8, 42.7, 39.2, 38.8, 34.7, 32.0, 30.13, 30.10, 27.3, 26.3, 24.4, 24.2. MS (EI): 279, 237, 208, 166, 131.

N,N,3-trimethyl-3-(3-oxobutyl)indoline-1-carboxamide (3pa)



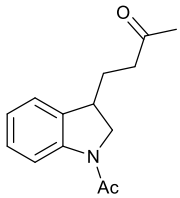
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.14 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.92-6.89 (m, 2H), 3.66-3.60 (m, 2H), 2.92 (s, 6H), 2.43-2.37 (m, 1H), 2.32-2.26 (m, 1H), 2.05 (s, 3H), 1.93-1.82 (m, 2H), 1.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.3, 159.9, 143.6, 137.8, 127.5, 122.7, 121.6, 113.5, 62.0, 42.3, 39.1, 38.1, 33.6, 29.9, 25.5. HRMS (ESI) *m/z* calcd for $C_{16}H_{23}N_2O_2$ $(M+H)^+$ 275.1754, found 275.1752.

<u>*tert*-butyl 3-methyl-3-(3-oxobutyl)indoline-1-carboxylate</u> (3qa)



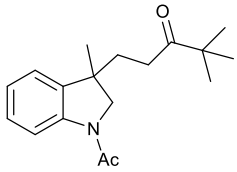
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (s, 0.52H), 7.46 (s, 0.36H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 3.78-3.76 (m, 1H), 3.64-3.61 (m, 1H), 2.39-2.35 (m, 1H), 2.21-2.13 (m, 1H), 2.06 (s, 3H), 1.89 (t, *J* = 7.8 Hz, 2H), 1.58 (s, 9H), 1.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.3, 152.5, 142.4, 137.2, 127.9, 122.5, 114.7, 80.7, 59.8, 42.2, 39.0, 35.0, 30.1, 28.5, 27.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{26}NO_3$ $(M+H)^+$ 304.1907, found 304.1910.

<u>4-(1-acetylindolin-3-yl)butan-2-one</u> (3ra)[1]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (t, *J* = 8.1 Hz, 1H), 7.24-7.16 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.14 (t, *J* = 9.9 Hz, 1H), 3.69-3.66 (m, 1H), 3.47-3.41 (m, 1H), 2.51-2.44 (m, 2H), 2.23 (s, 3H), 2.15 (s, 3H), 2.11-2.02 (m, 1H), 1.93-1.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.1, 168.8, 142.8, 134.1, 128.3, 124.1, 123.8, 117.1, 54.9, 40.2, 39.2, 30.2, 28.8, 24.4.

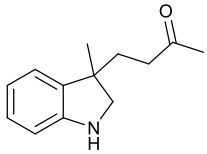
<u>1-(1-acetyl-3-methylindolin-3-yl)-4,4-dimethylpentan-3-one</u> (3ab)



[1] S. Z. Tasker and T. F. Jamison, *J. Am. Chem. Soc*., 2015, **137**, 9531.

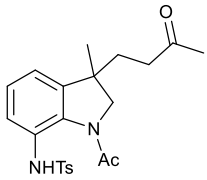
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (t, *J* = 8.1 Hz, 1H), 7.25-7.21 (m, 1H), 7.10-7.05 (m, 2H), 3.88 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 2.35-2.27 (m, 2H), 2.23 (s, 3H), 1.96-1.86 (m, 2H), 1.39 (s, 3H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 215.4, 168.7, 142.3, 137.8, 128.1, 123.9, 122.3, 117.0, 61.2, 44.3, 43.2, 35.1, 31.7, 27.5, 26.4, 24.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{26}NO_2$ $(M+H)^+$ 288.1958, found 288.1961.

4-(3-methylindolin-3-yl)butan-2-one (4)



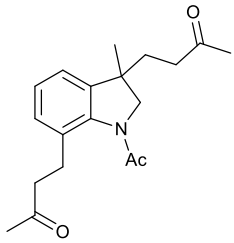
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 3.38-3.29 (m, 3H), 2.54-2.45 (m, 1H), 2.33-2.23 (m, 1H), 2.08 (s, 3H), 1.95-1.82 (m, 2H), 1.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 209.2, 150.9, 135.8, 127.8, 122.8, 118.8, 109.7, 59.4, 44.6, 39.5, 30.1, 26.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NO$ $(M+H)^+$ 204.1383, found 204.1382.

N-(1-acetyl-3-methyl-3-(3-oxobutyl)indolin-7-yl)-4-methylbenzenesulfonamide (5)



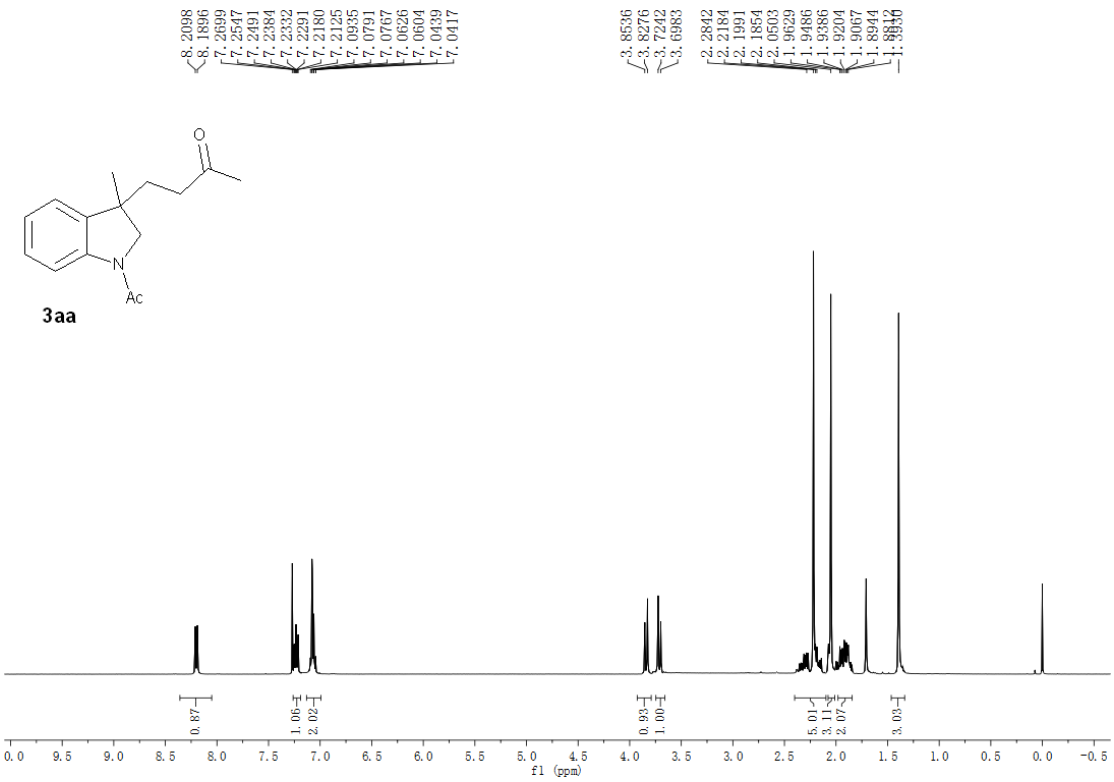
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.66 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.21-7.16 (m, 3H), 6.92 (d, *J* = 7.4, 0.9 Hz, 1H), 3.50 (d, *J* = 10.4 Hz, 1H), 3.17 (d, *J* = 10.4 Hz, 1H), 2.39 (s, 3H), 2.22-2.18 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.88-1.71 (m, 2H), 1.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.8, 169.1, 143.2, 141.4, 137.6, 134.9, 129.2, 127.2, 127.1, 126.6, 126.2, 120.4, 63.0, 43.1, 38.7, 33.1, 30.2, 25.4, 24.2, 21.6. HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_2O_4S$ $(M+H)^+$ 415.1686, found 415.1690.

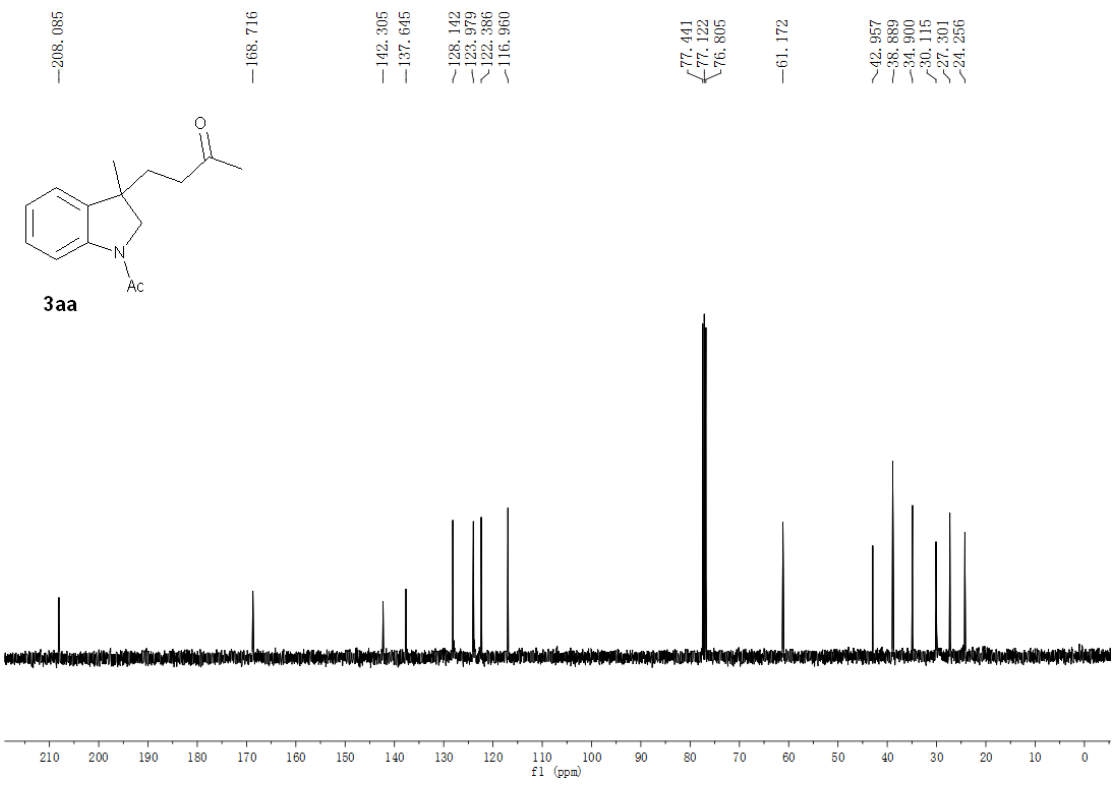
4,4'-(1-acetyl-3-methylindoline-3,7-diyl)bis(butan-2-one) (6)

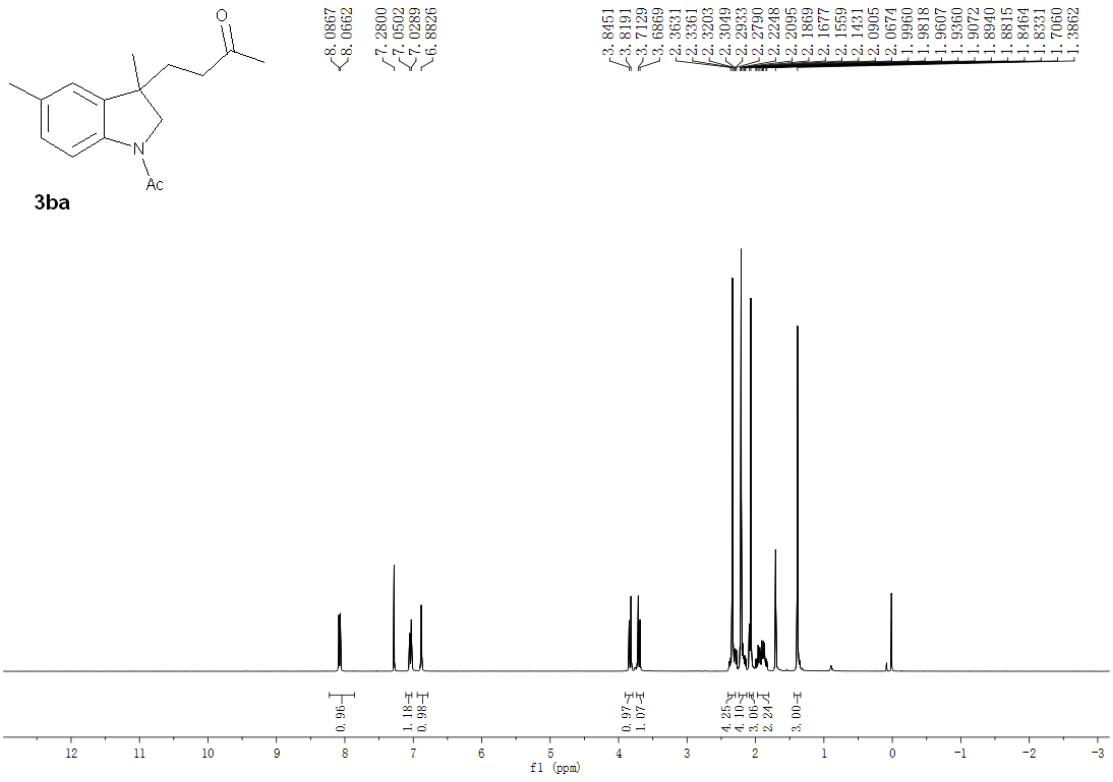


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10-7.04 (m, 2H), 6.94-6.92 (m, 1H), 3.84 (d, *J* = 10.1 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 2.91-2.74 (m, 4H), 2.35-2.30 (m, 2H), 2.24 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 1.92-1.76 (m, 2H), 1.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.8, 208.0, 169.0, 141.2, 140.4, 132.0, 128.8, 125.8, 120.2, 63.1, 43.9, 43.5, 38.8, 32.5, 30.0, 29.8, 27.7, 24.4, 23.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{26}NO_3$ $(M+H)^+$ 316.1907, found 316.1909.

4. Copies of ^{1}H NMR and ^{13}C NMR spectra of the products



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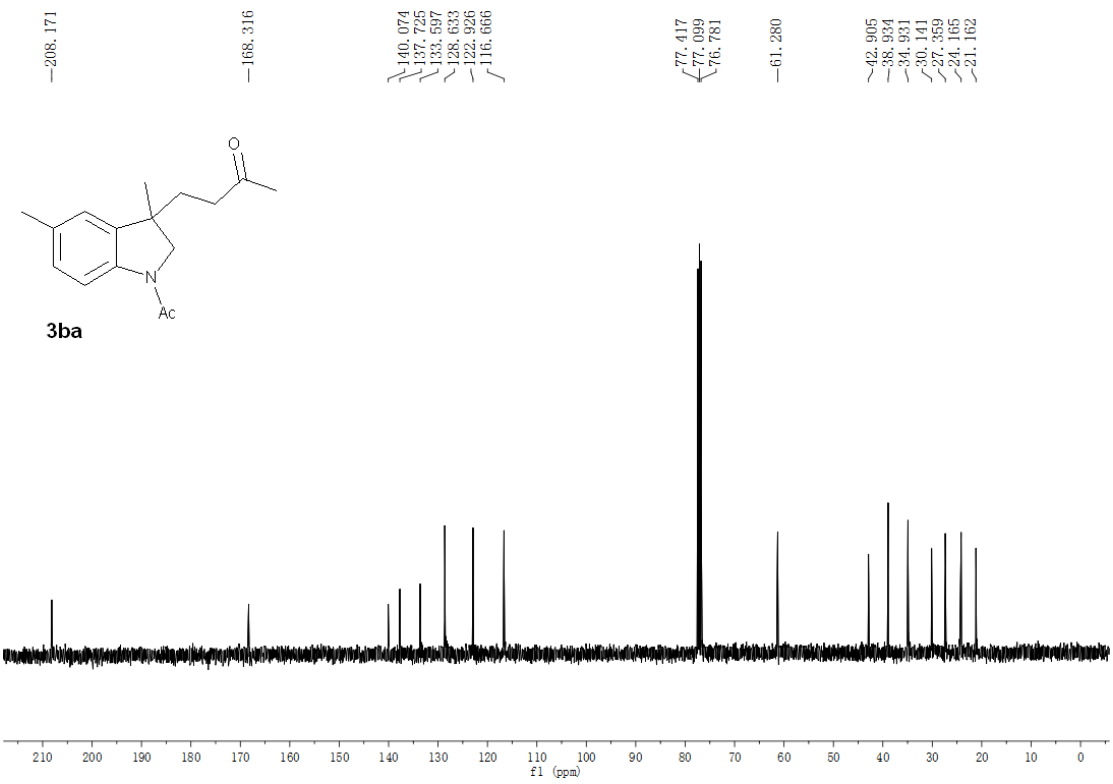
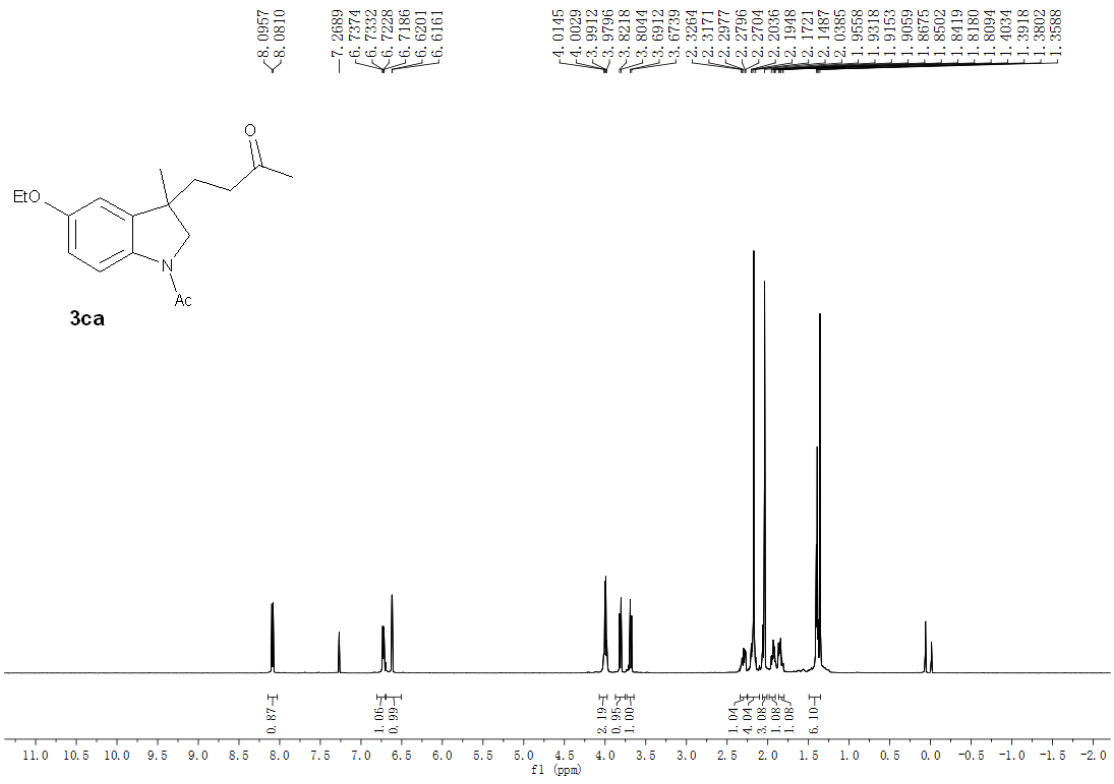
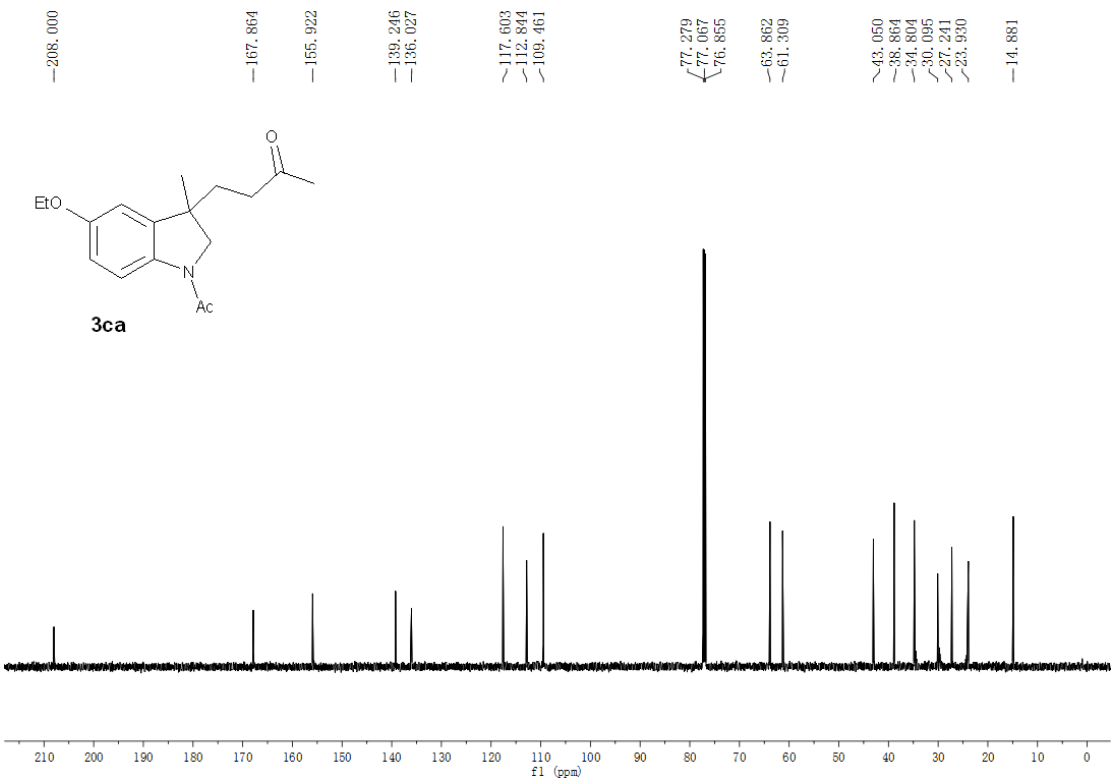
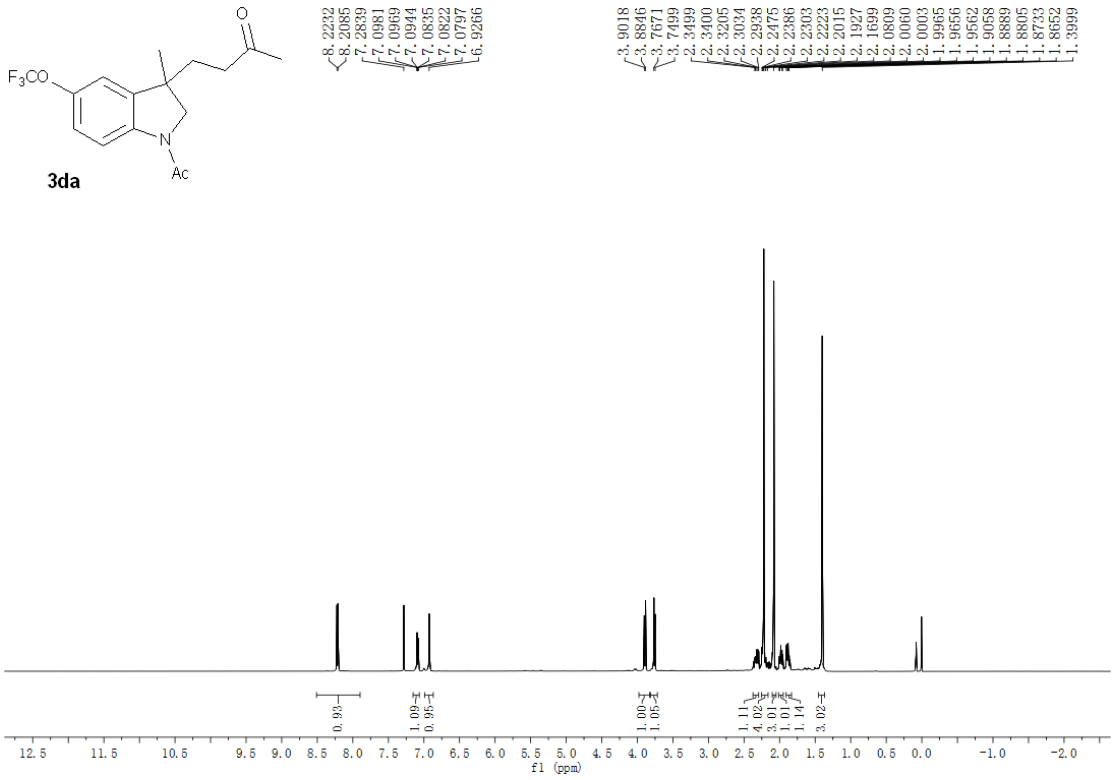
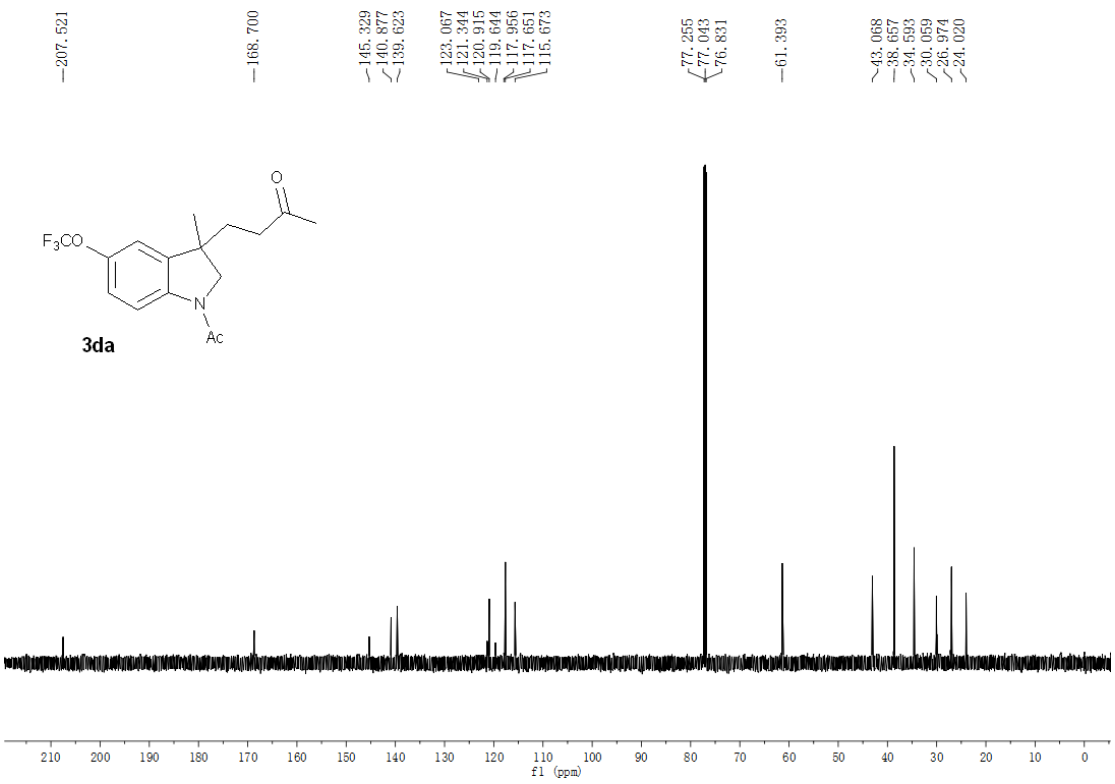
7.2800
7.0502
7.0289
6.8826
3.8451
3.8191
3.7129
3.6869
2.3631
2.3361
2.3203
2.3049
2.2933
2.2790
2.2248
2.2095
2.1869
2.1677
2.1559
2.1431
2.0905
2.0674
1.9960
1.9818
1.9607
1.9360
1.9072
1.8940
1.8815
1.8464
1.8331
1.7060
1.3862
O
N
Ac
3ba
0.96
1.18
0.98
0.97
1.07
4.25
4.10
3.06
2.24
3.00
f1 (ppm)


208.171
168.316
140.074
137.725
133.597
128.633
122.926
116.666
77.417
77.099
76.781
61.280
42.905
38.934
34.931
30.141
27.359
24.165
21.162
O
N
Ac
3ba
f1 (ppm)


8.0957
8.0810
7.2689
6.7374
6.7332
6.7228
6.7186
6.6201
6.6161
4.0145
4.0029
3.9912
3.9796
3.8218
3.8044
3.6912
3.6739
2.3264
2.3171
2.2977
2.2796
2.2704
2.2036
2.1948
2.1721
2.1487
2.0385
1.9558
1.9318
1.9153
1.9059
1.8675
1.8502
1.8419
1.8180
1.8094
1.4034
1.3918
1.3802
1.3588
EtO
O
N
Ac
3ca
0.87
1.06
0.99
2.19
0.95
1.00
1.04
4.04
3.08
1.08
1.08
6.10
f1 (ppm)


208.000
167.864
155.922
139.246
136.027
117.603
112.844
109.461
77.279
77.067
76.855
63.862
61.309
43.050
38.864
34.804
30.095
27.241
23.930
14.881
EtO
O
N
Ac
3ca
f1 (ppm)


F3CO
O
N
Ac
3da
8.2232
8.2085
7.2839
7.0981
7.0969
7.0944
7.0835
7.0822
7.0797
6.9266
3.9018
3.8846
3.7671
3.7499
2.3499
2.3400
2.3205
2.3034
2.2938
2.2475
2.2386
2.2303
2.2223
2.2015
2.1927
2.1699
2.0809
2.0060
2.0003
1.9965
1.9656
1.9562
1.9058
1.8889
1.8805
1.8733
1.8652
1.3999
0.93
1.09
0.95
1.00
1.05
1.11
4.02
3.01
1.14
3.02
f1 (ppm)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168.700
145.329
140.877
139.623
123.067
121.344
120.915
119.644
117.956
117.651
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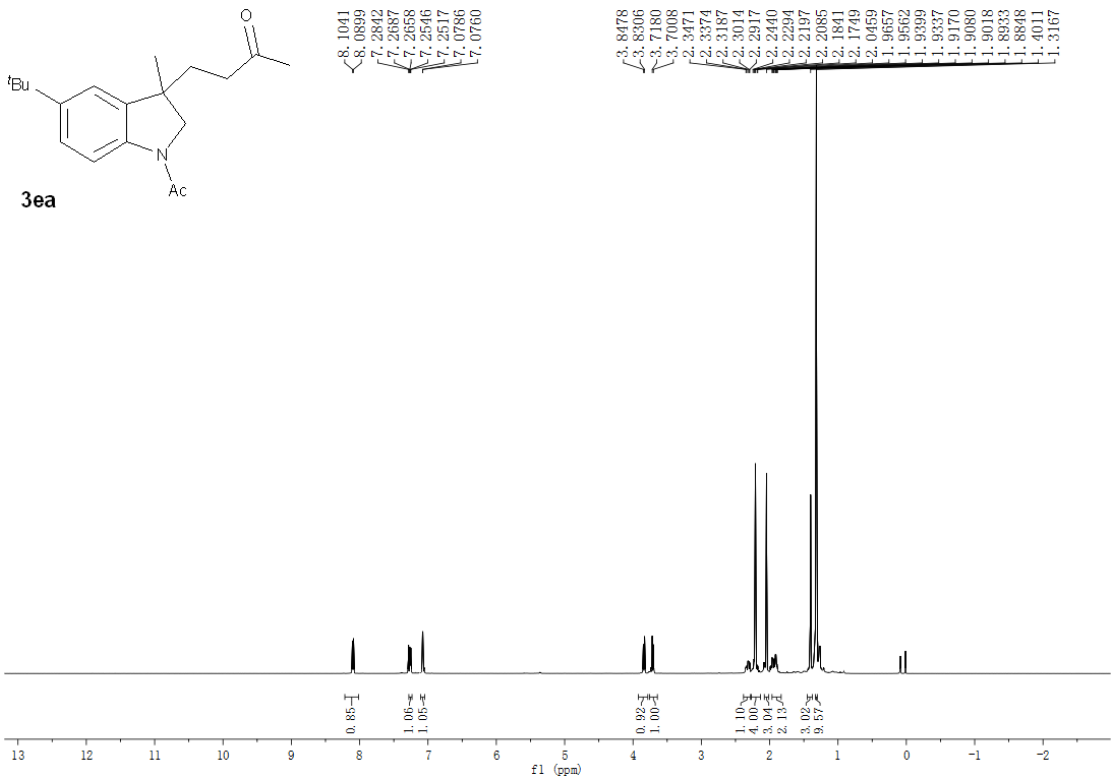
77.255
77.043
76.831
61.393
43.068
38.657
34.593
30.059
26.974
24.020
F3CO
O
N
Ac
3da
f1 (ppm)


tBu
N
Ac
O
3ea
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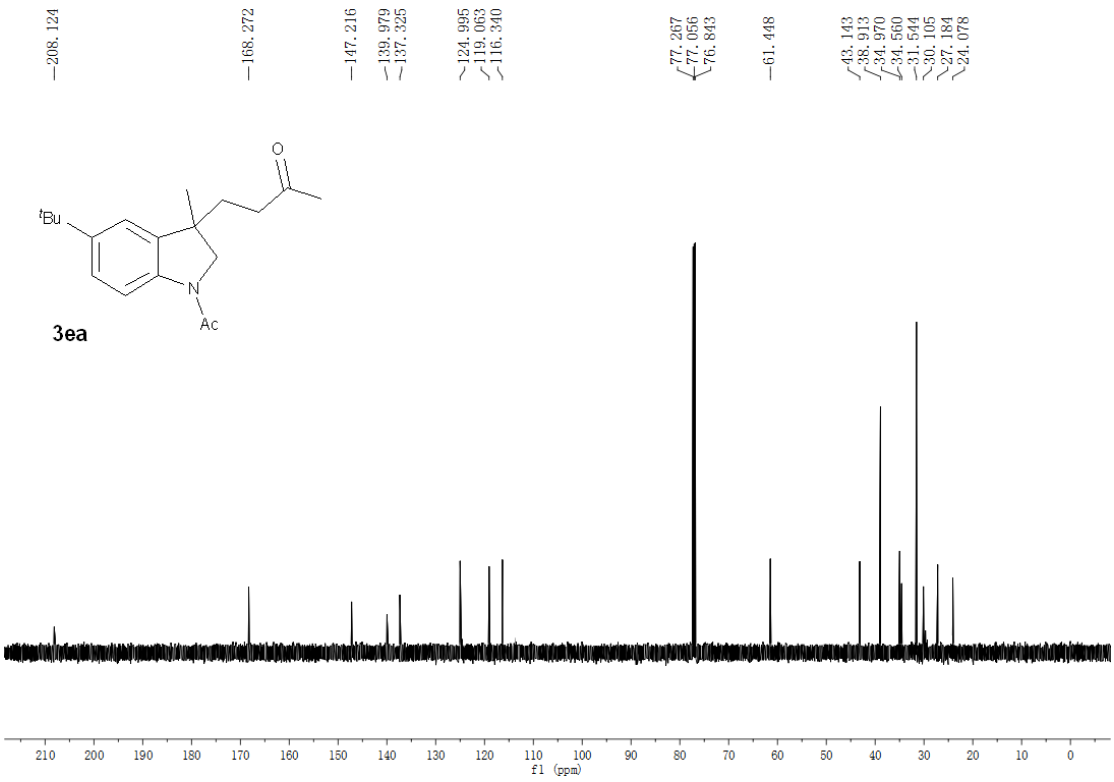
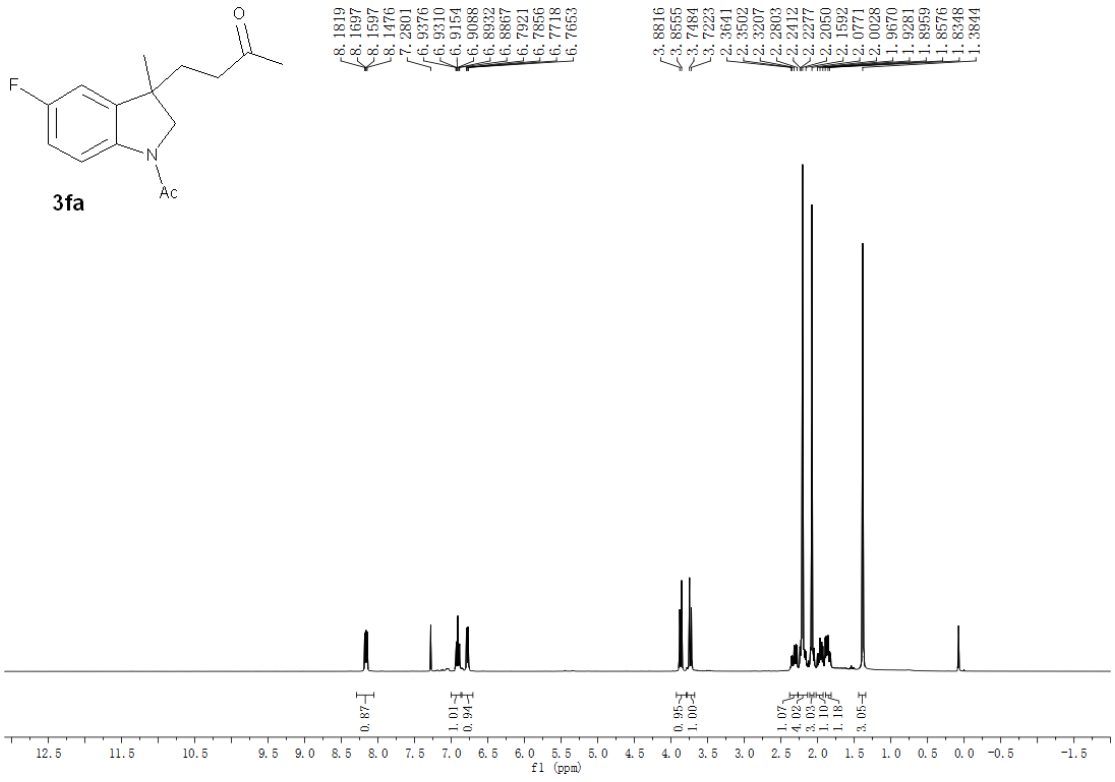
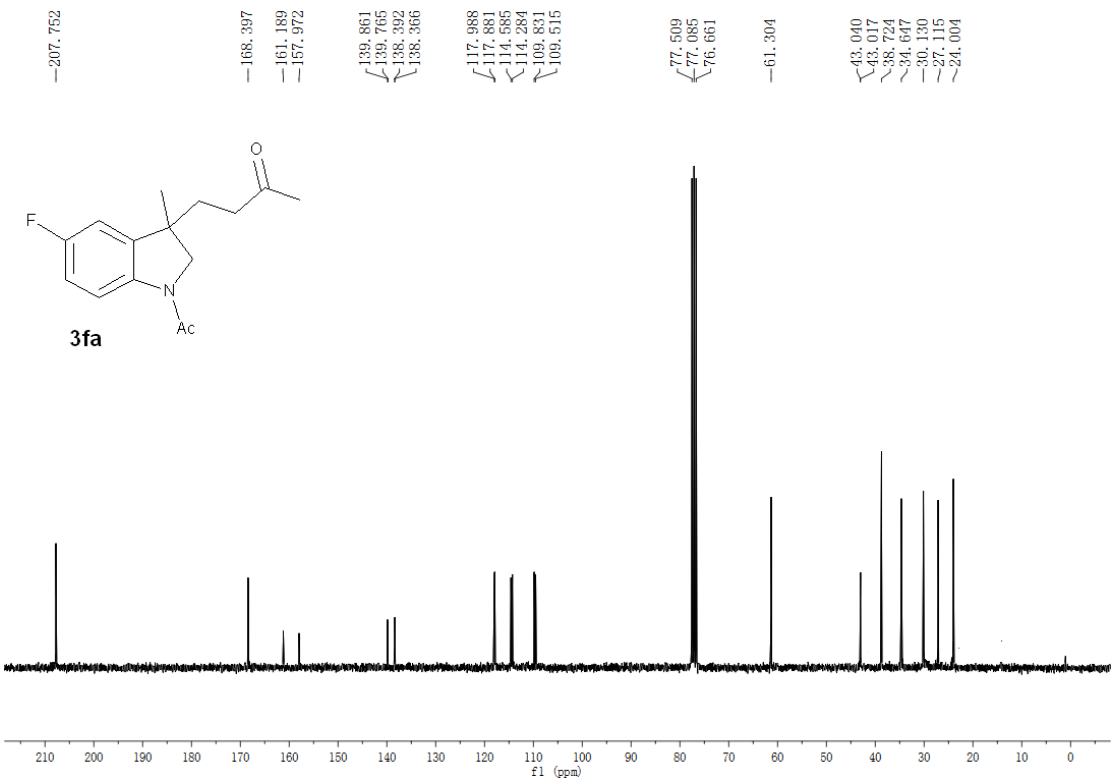
8.0899
7.2842
7.2687
7.2658
7.2546
7.2517
7.0786
7.0760
3.8478
3.8306
3.7180
3.7008
3.3471
2.3374
2.3187
2.3014
2.2917
2.2440
2.2294
2.2197
2.2085
2.1841
2.1749
2.0459
1.9657
1.9562
1.9399
1.9337
1.9170
1.9080
1.9018
1.8933
1.8848
1.4011
1.3167
0.85
1.06
1.05
0.92
1.00
1.10
4.00
3.04
2.13
3.02
9.57
f1 (ppm)


208.124
168.272
147.216
139.979
137.325
124.995
119.063
116.340
77.267
77.056
76.843
61.448
43.143
38.913
34.970
34.560
31.544
30.105
27.184
24.078
tBu
N
Ac
O
3ea
f1 (ppm)


3fa
8.1819
8.1697
8.1597
8.1476
7.2801
6.9376
6.9310
6.9154
6.9088
6.8932
6.8867
6.7921
6.7856
6.7718
6.7653
3.8816
3.8555
3.7484
3.7223
2.3641
2.3502
2.3207
2.2803
2.2412
2.2277
2.2050
2.1592
2.0771
2.0028
1.9670
1.9281
1.8959
1.8576
1.8348
1.3844
0.87
1.01
0.94
0.95
1.00
1.07
4.02
3.03
1.10
1.18
3.05
f1 (ppm)


3fa
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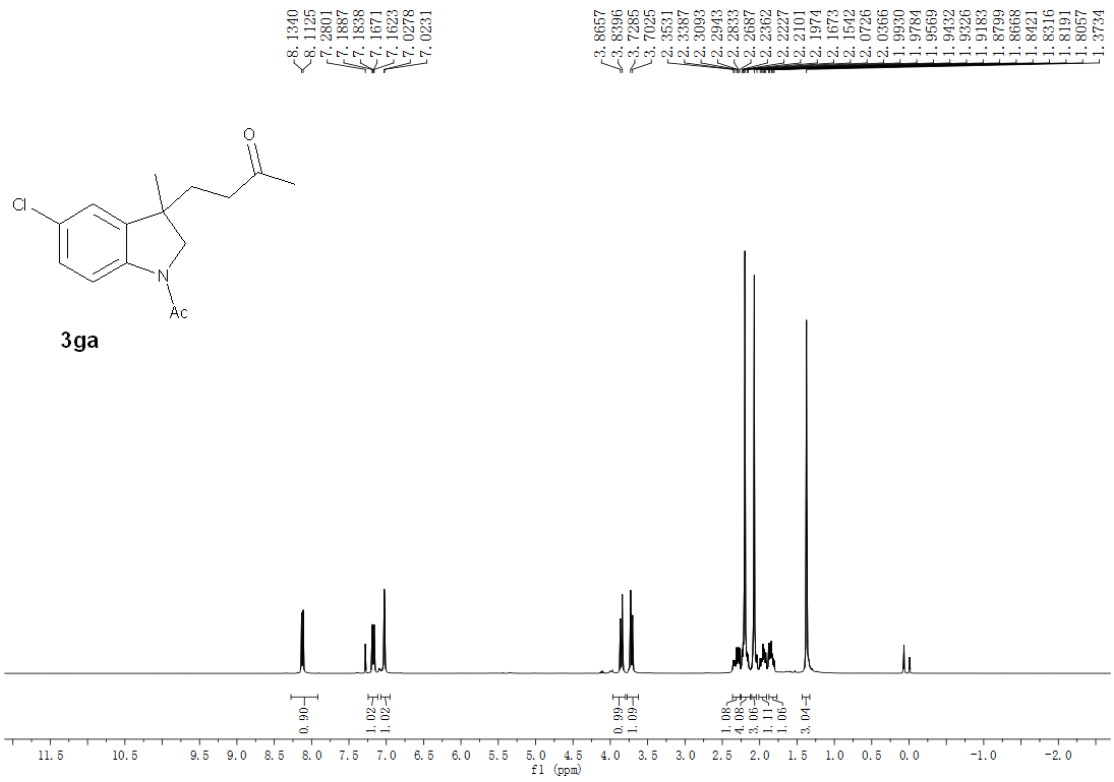
161.189
157.972
139.861
139.765
138.392
138.366
117.988
117.881
114.585
114.284
109.831
109.515
77.509
77.085
76.661
61.304
43.040
43.017
38.724
34.647
30.130
27.115
24.004
f1 (ppm)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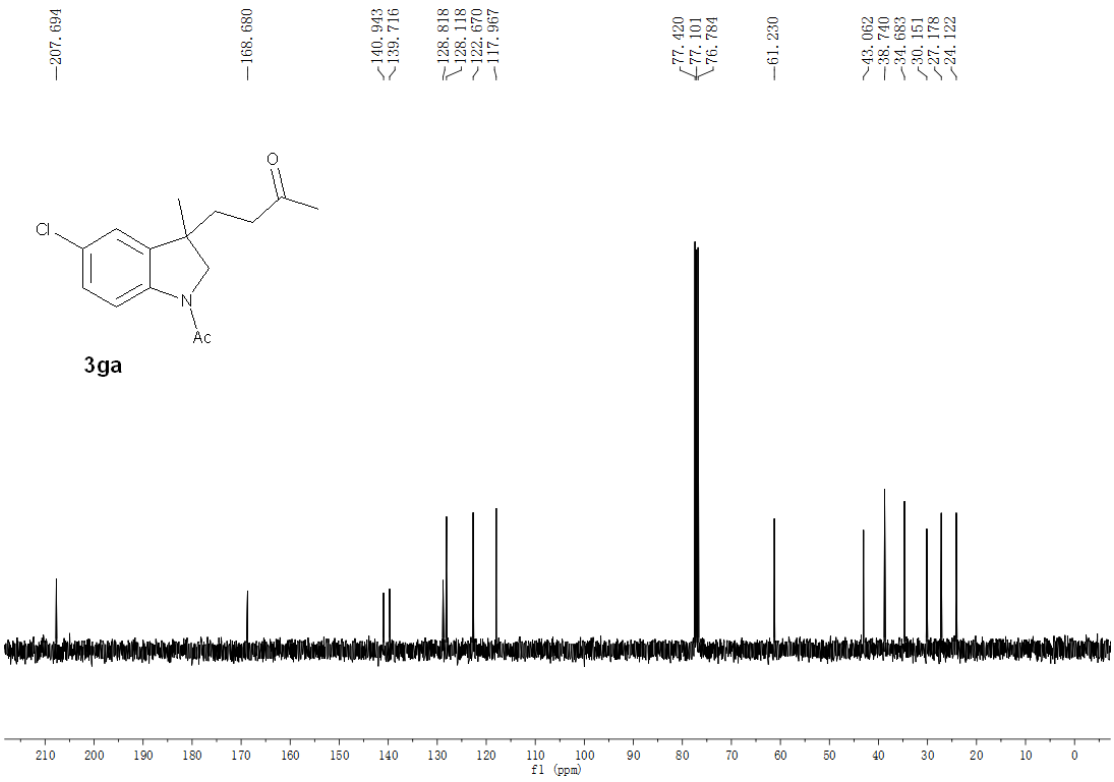
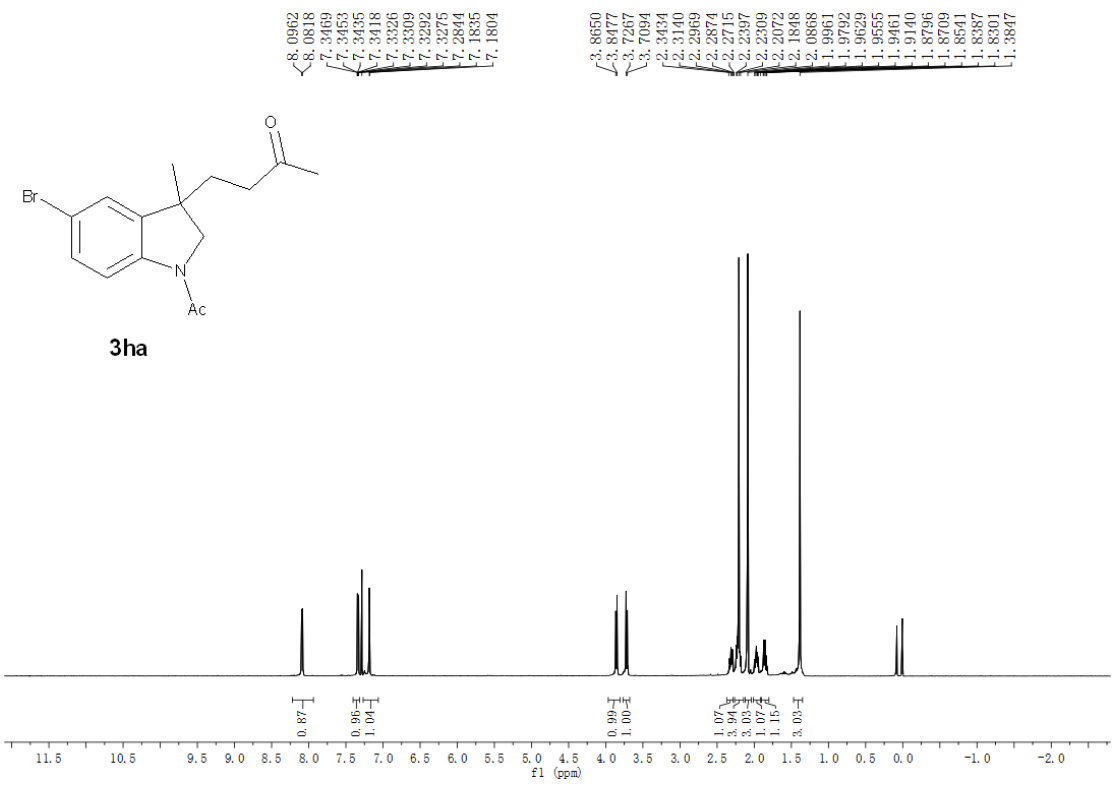
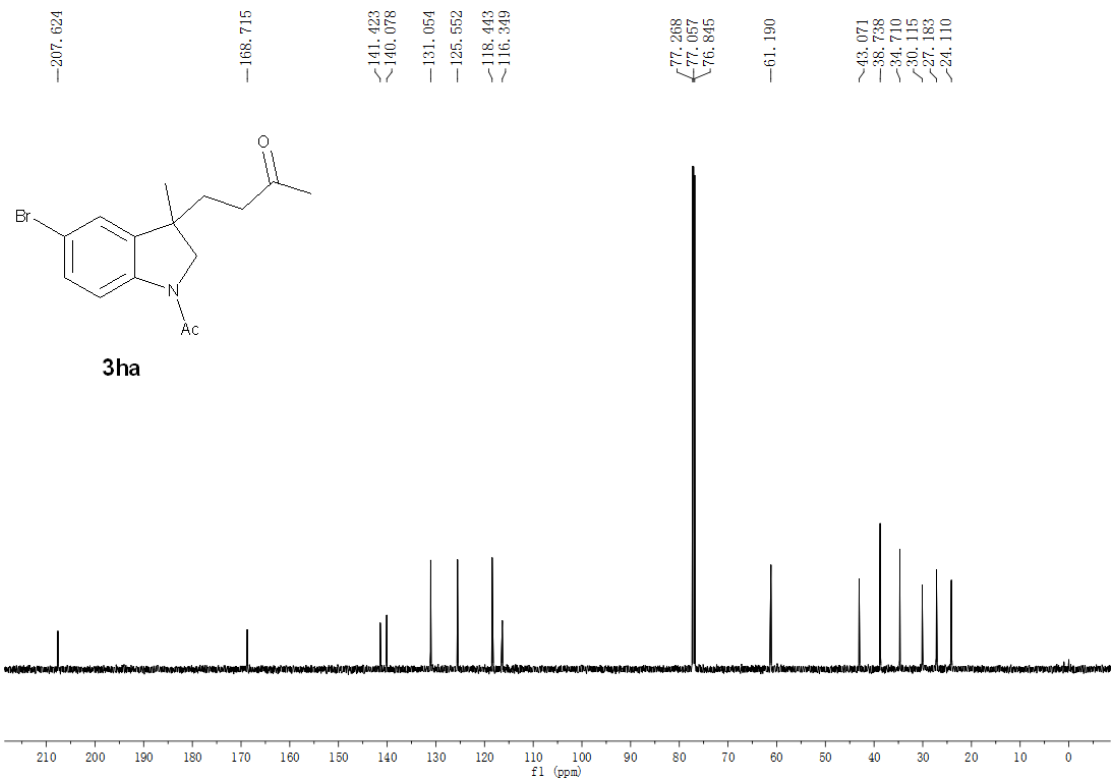
7.2801
7.1887
7.1838
7.1671
7.1623
7.0278
7.0231
3.8657
3.8396
3.7285
3.7025
2.3531
2.3387
2.3093
2.2943
2.2833
2.2687
2.2362
2.2227
2.2101
2.1974
2.1673
2.1542
2.0726
2.0366
1.9930
1.9784
1.9569
1.9432
1.9326
1.9183
1.8799
1.8668
1.8421
1.8316
1.8191
1.8057
1.3734
Cl
O
N
Ac
3ga
0.90
1.02
1.02
0.99
1.09
1.08
4.08
3.06
1.11
1.06
3.04
f1 (ppm)


207.694
168.680
140.943
139.716
128.818
128.118
122.670
117.967
77.420
77.101
76.784
61.230
43.062
38.740
34.683
30.151
27.178
24.122
Cl
O
N
Ac
3ga
f1 (ppm)


8.0962
8.0818
7.3469
7.3453
7.3435
7.3418
7.3326
7.3309
7.3292
7.3275
7.2844
7.1835
7.1804
3.8650
3.8477
3.7267
3.7094
2.3434
2.3140
2.2969
2.2874
2.2715
2.2397
2.2309
2.2072
2.1848
2.0868
1.9961
1.9792
1.9629
1.9555
1.9461
1.9140
1.8796
1.8709
1.8541
1.8387
1.8301
1.3847
Br
O
N
Ac
3ha
0.87
0.96
1.04
0.99
1.00
1.07
3.94
3.03
1.07
1.15
3.03
f1 (ppm)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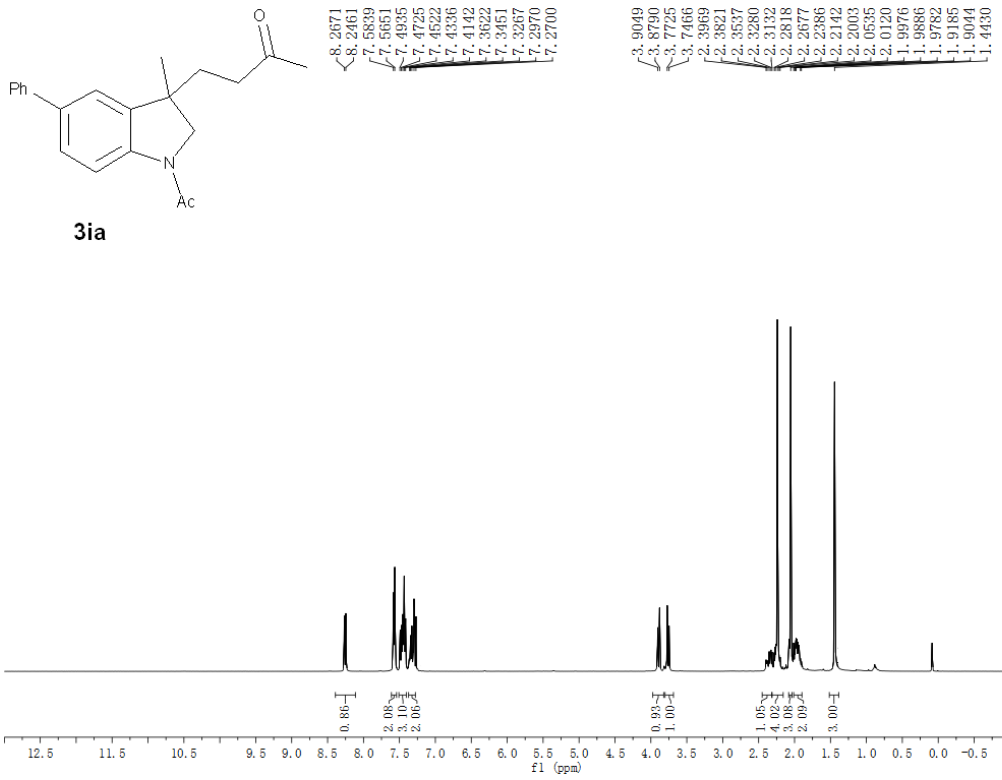
141.423
140.078
131.054
125.552
118.443
116.349
77.268
77.057
76.845
61.190
43.071
38.738
34.710
30.115
27.183
24.110
Br
O
N
Ac
3ha
f1 (ppm)

Ph
N
Ac
O

3ia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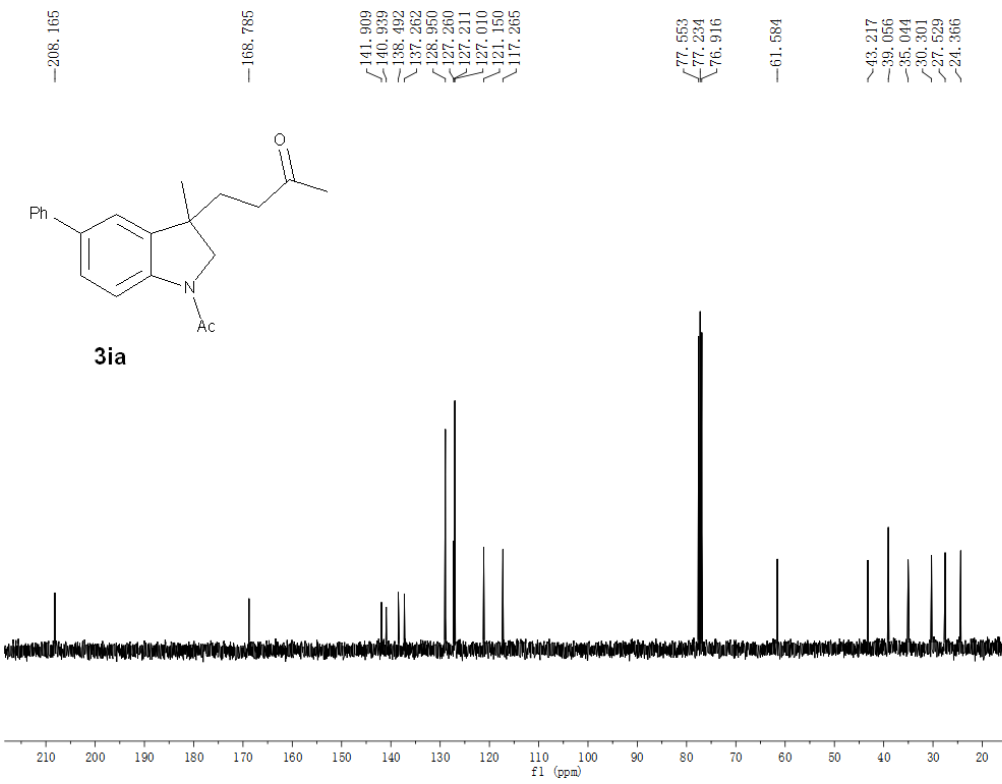
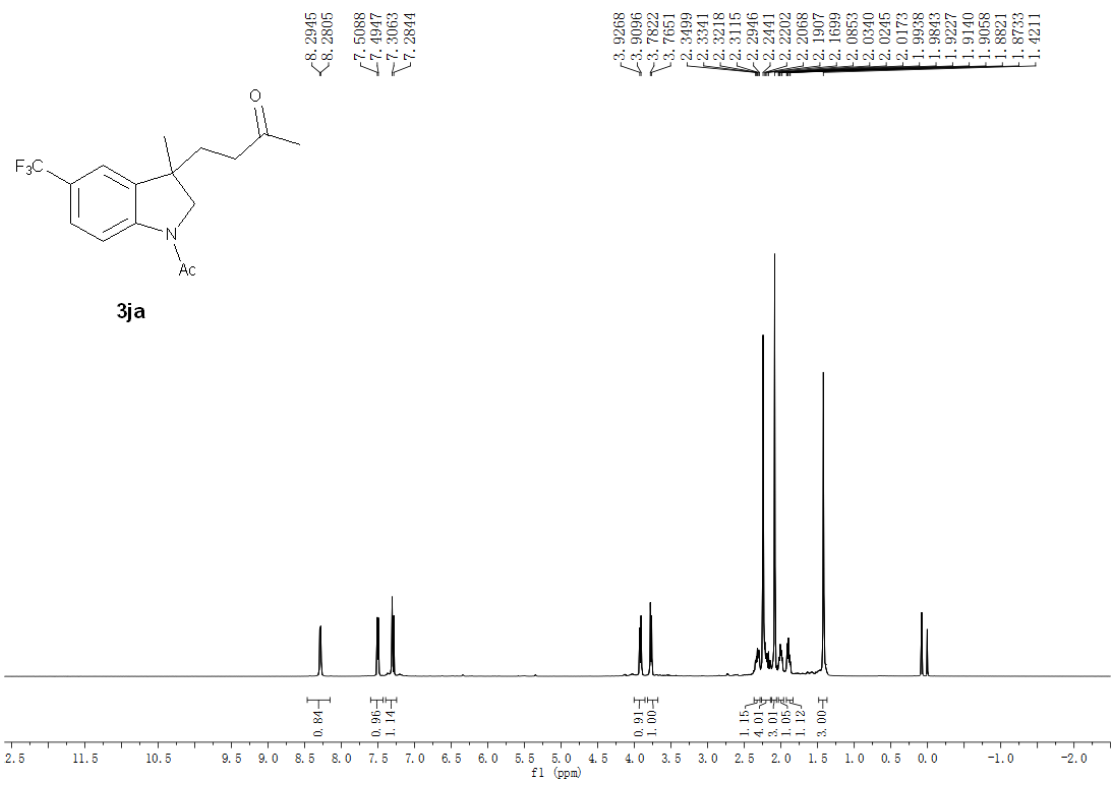
8.2461
7.5839
7.5651
7.4935
7.4725
7.4522
7.4336
7.4142
7.3622
7.3451
7.3267
7.2970
7.2700
3.9049
3.8790
3.7725
3.7466
2.3969
2.3821
2.3537
2.3280
2.3132
2.2818
2.2677
2.2386
2.2142
2.2003
2.0535
2.0120
1.9976
1.9886
1.9782
1.9185
1.9044
1.4430
0.86
2.08
3.10
2.06
0.93
1.00
1.05
4.02
3.08
2.09
3.00
f1 (ppm)

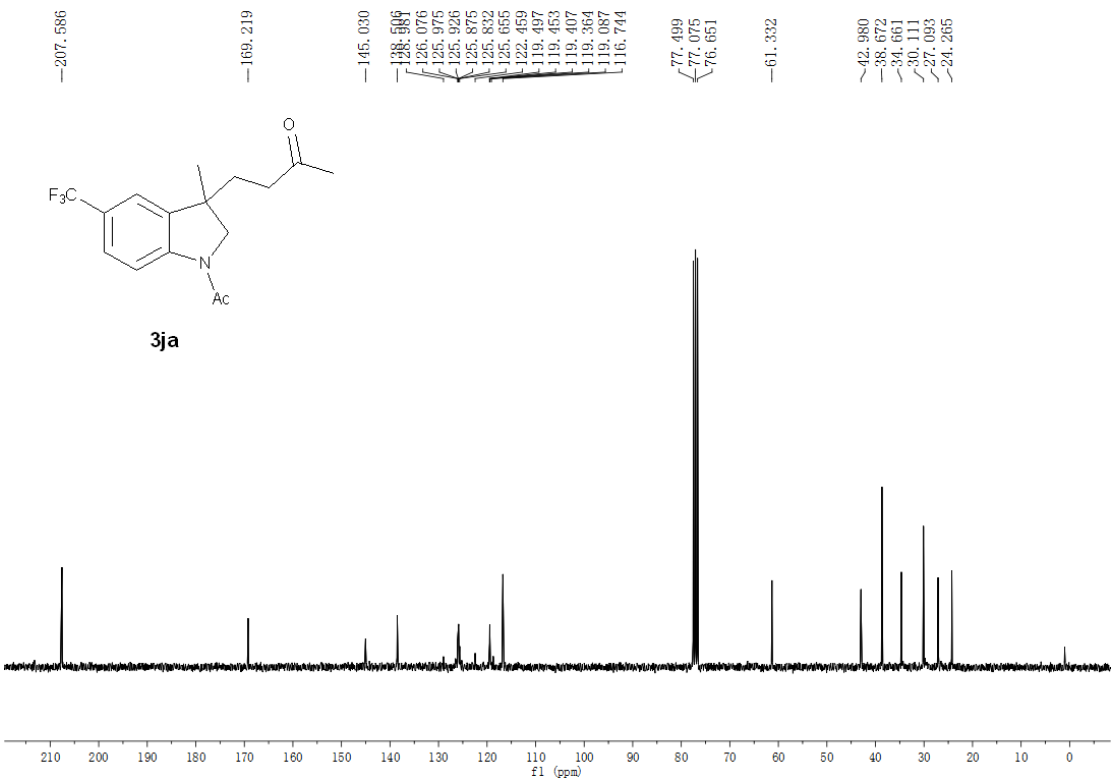

208.165
168.785
141.909
140.939
138.492
137.262
128.950
127.260
127.211
127.010
121.150
117.265
77.553
77.234
76.916
61.584
43.217
39.056
35.044
30.301
27.529
24.366
f1 (ppm)

Ph
N
Ac
O

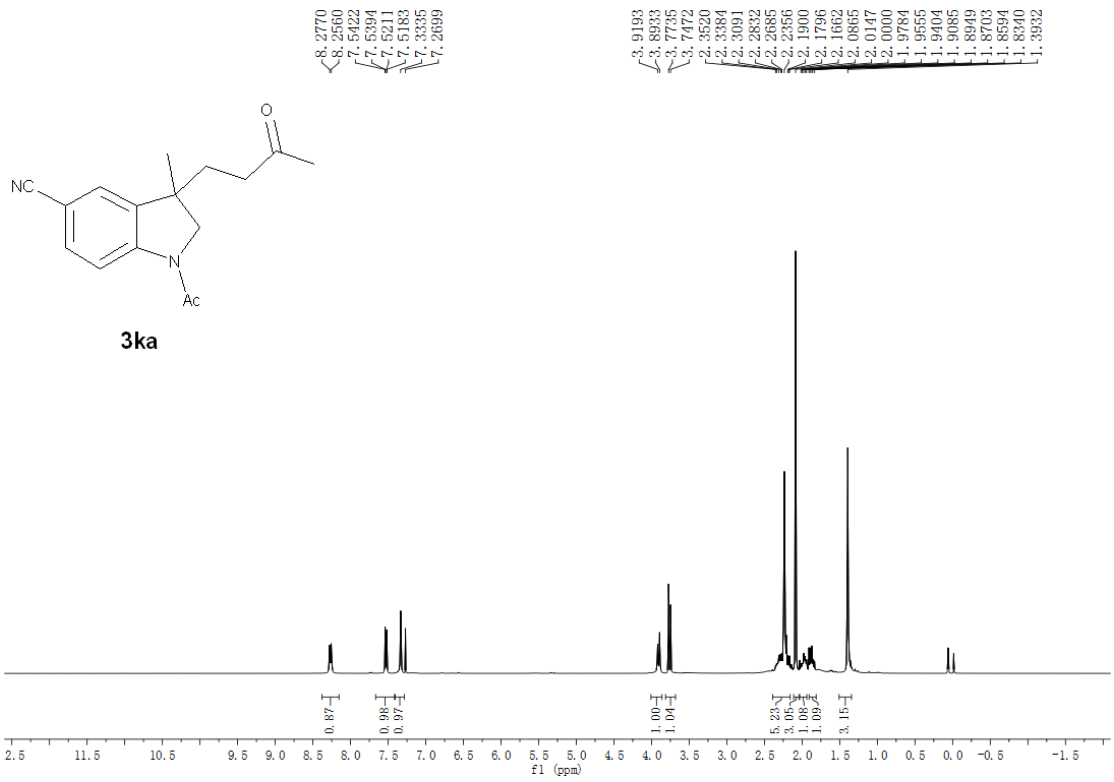
3ia

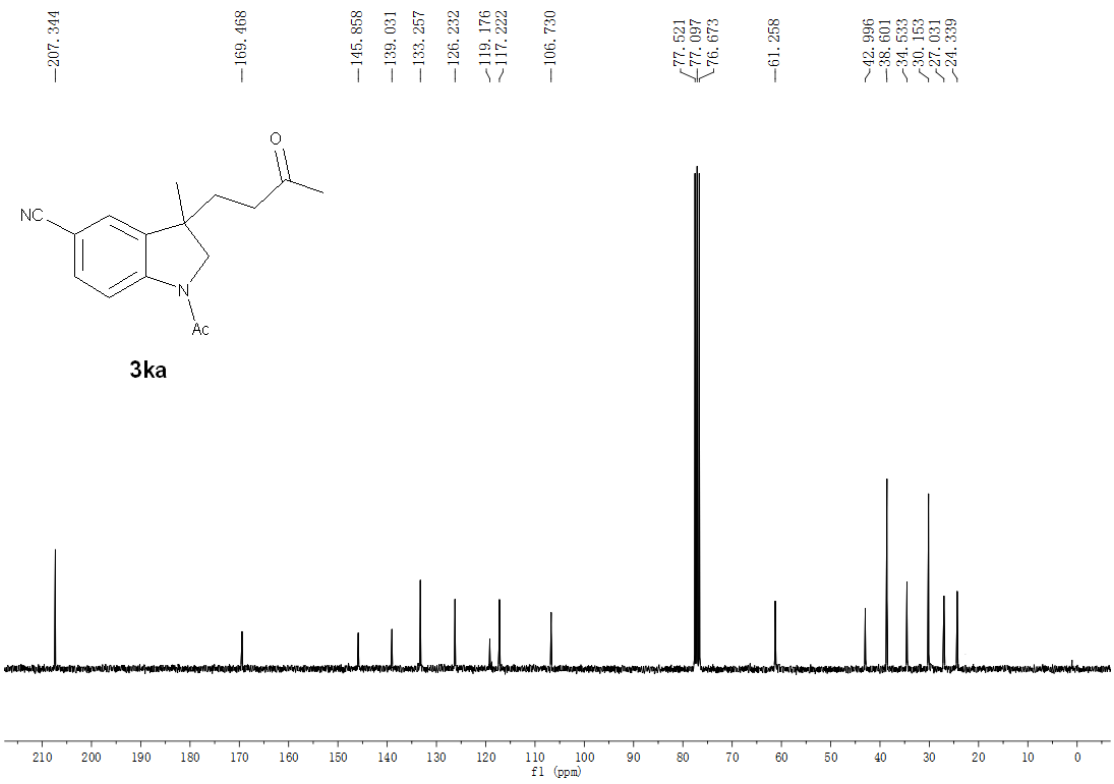

8.2945
8.2805
7.5088
7.4947
7.3063
7.2844
3.9268
3.9096
3.7822
3.7651
2.3499
2.3341
2.3218
2.3115
2.2946
2.2441
2.2202
2.2068
2.1907
2.1699
2.0853
2.0340
2.0245
2.0173
1.9938
1.9843
1.9227
1.9140
1.9058
1.8821
1.8733
1.4211
O
F3C
N
Ac
0.84
0.96
1.14
0.91
1.00
1.15
4.01
3.01
1.05
1.12
3.00
f1 (ppm)

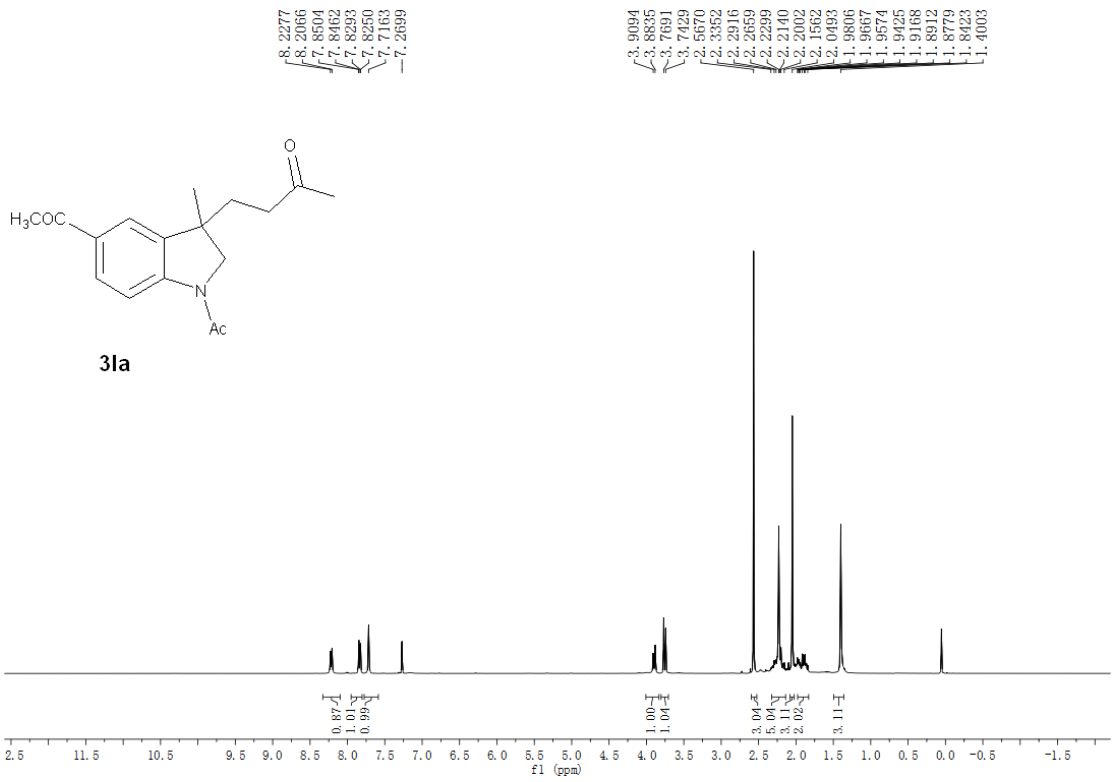
3ja

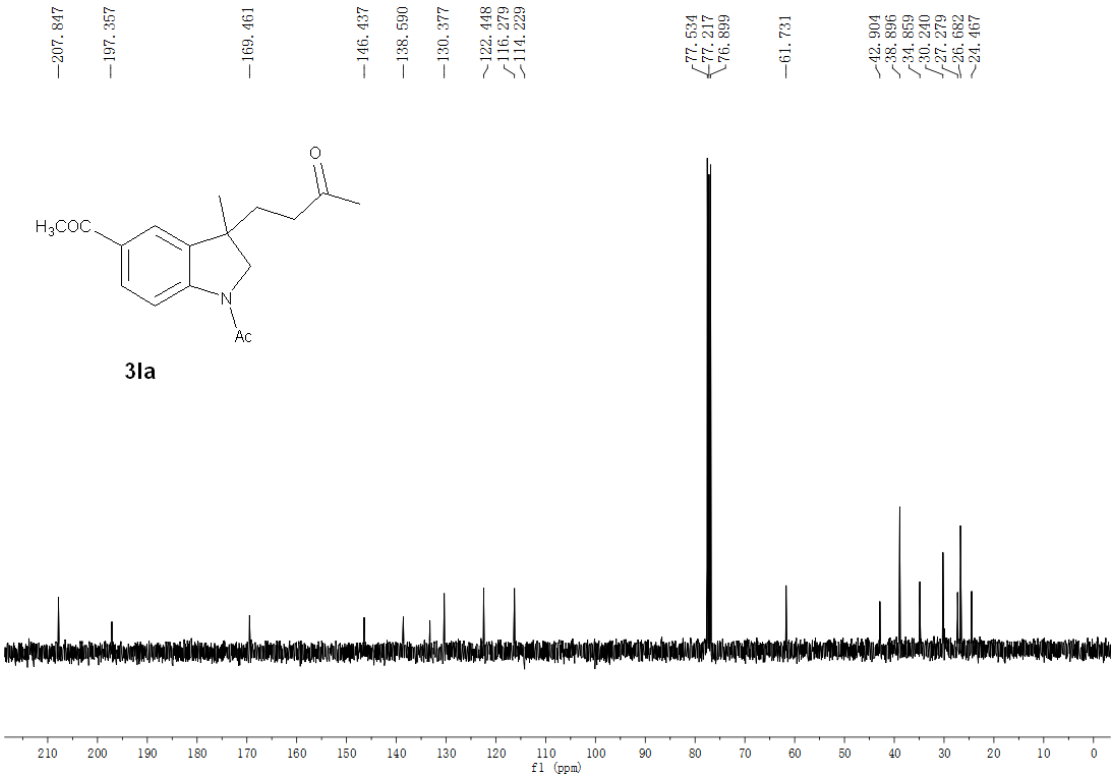

207.586
169.219
145.030
138.506
138.385
126.076
125.975
125.926
125.875
125.832
125.655
122.459
119.497
119.453
119.407
119.364
119.087
116.744
77.499
77.075
76.651
61.332
42.980
38.672
34.661
30.111
27.093
24.265
O
F3C
N
Ac
f1 (ppm)

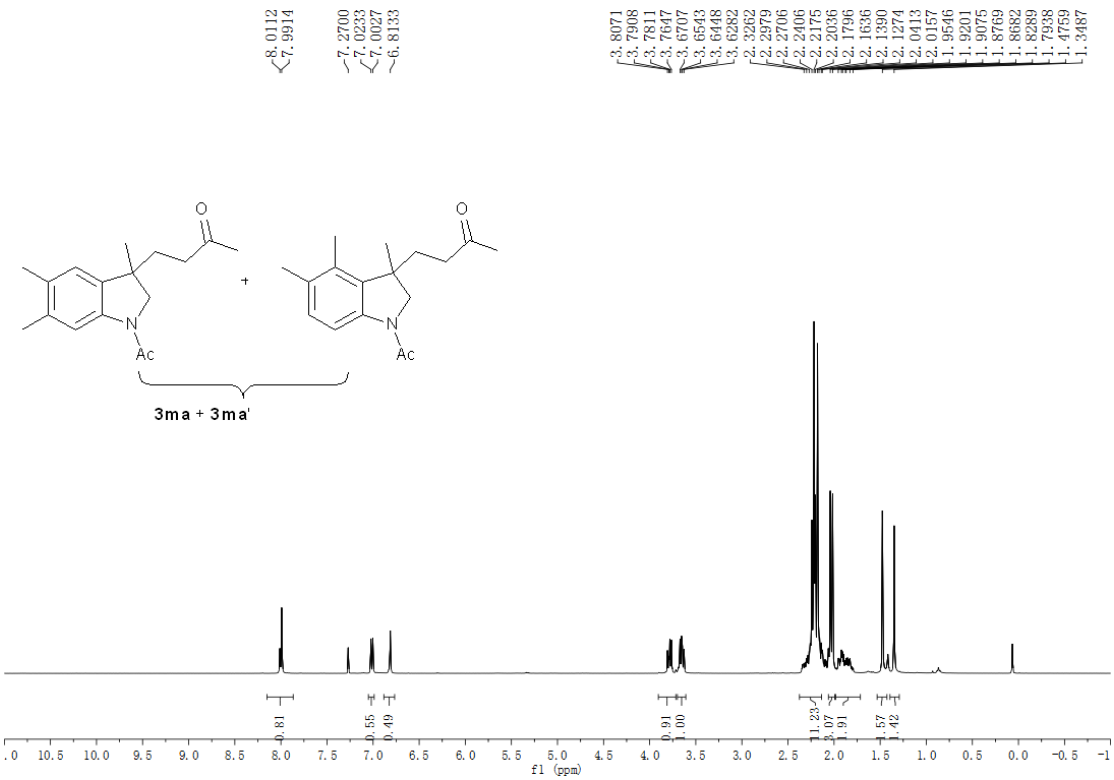
3ja

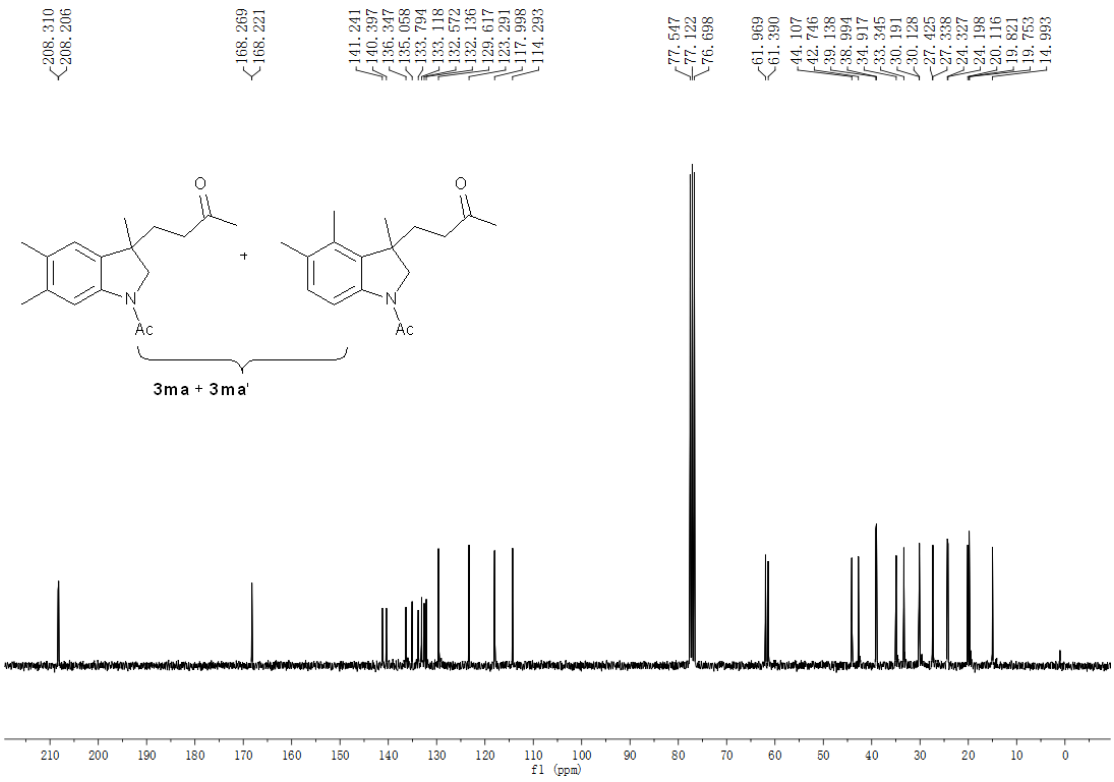

8.2770
8.2560
7.5422
7.5394
7.5211
7.5183
7.3335
7.2699
3.9193
3.8933
3.7735
3.7472
2.3520
2.3384
2.3091
2.2832
2.2685
2.2356
2.1900
2.1796
2.1662
2.0865
2.0147
2.0000
1.9784
1.9555
1.9404
1.9085
1.8949
1.8703
1.8594
1.8340
1.3932
NC
O
N
Ac
3ka
0.87
0.98
0.97
1.00
1.04
5.23
3.05
1.08
1.09
3.15
f1 (ppm)


207.344
169.468
145.858
139.031
133.257
126.232
119.176
117.222
106.730
77.521
77.097
76.673
61.258
42.996
38.601
34.533
30.153
27.031
24.339
NC
O
N
Ac
3ka
f1 (ppm)


8.2277
8.2066
7.8504
7.8462
7.8293
7.8250
7.7163
7.2699
3.9094
3.8835
3.7691
3.7429
2.5670
2.3352
2.2916
2.2659
2.2299
2.2140
2.2002
2.1562
2.0493
1.9806
1.9667
1.9574
1.9425
1.9168
1.8912
1.8779
1.8423
1.4003
H3COC
O
N
Ac
3Ia
0.87
1.01
0.99
1.00
1.04
3.04
5.04
3.11
2.02
3.11
f1 (ppm)

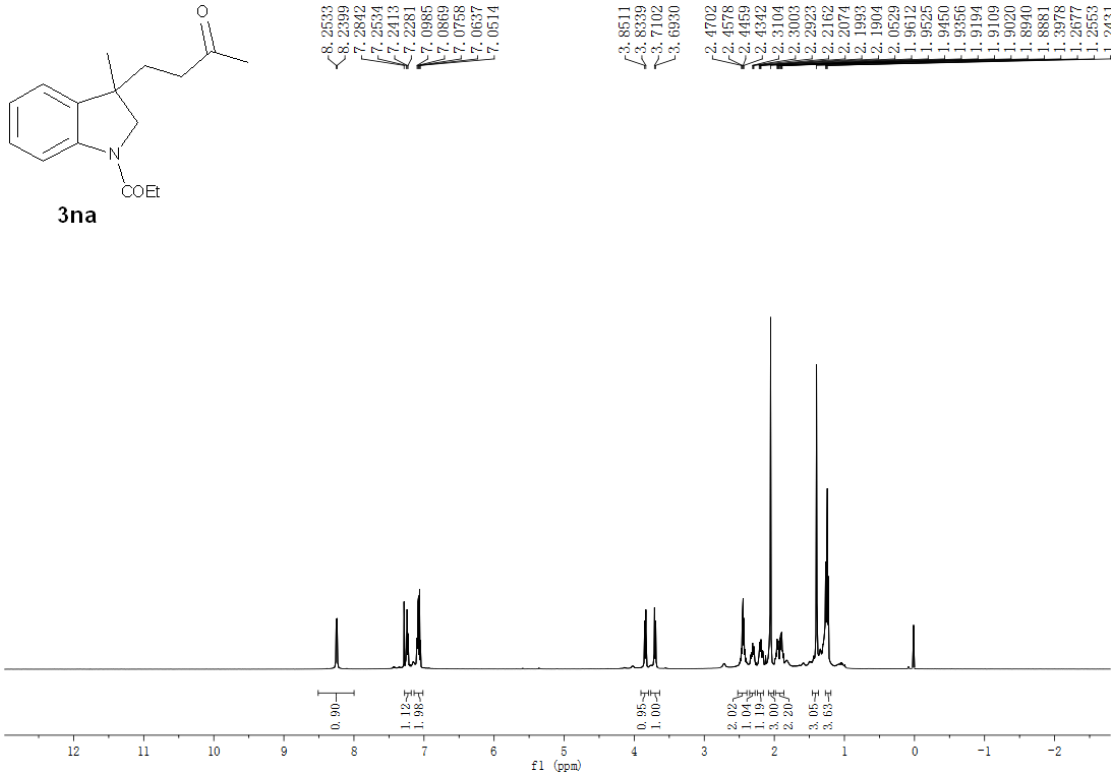

207.847
197.357
169.461
146.437
138.590
130.377
122.448
116.279
114.229
77.534
77.217
76.899
61.731
42.904
38.896
34.859
30.240
27.279
26.682
24.467
H3COC
O
N
Ac
3Ia
f1 (ppm)

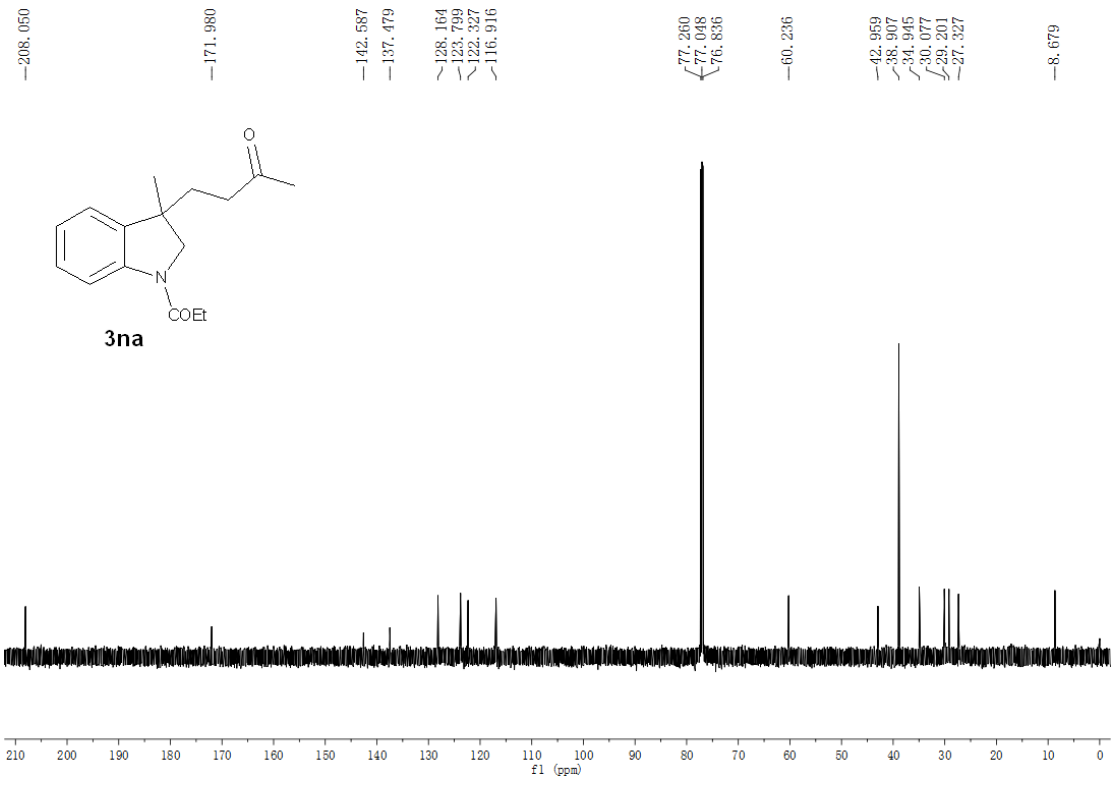

8.0112
7.9914
7.2700
7.0233
7.0027
6.8133
3.8071
3.7908
3.7811
3.7647
3.6707
3.6543
3.6448
3.6282
2.3262
2.2979
2.2706
2.2406
2.2175
2.2036
2.1796
2.1636
2.1390
2.1274
2.0413
2.0157
1.9546
1.9201
1.9075
1.8769
1.8682
1.8289
1.7938
1.4759
1.3487
O
N
Ac
+
3ma + 3ma'
0.81
0.55
0.49
0.91
1.00
11.23
5.07
1.91
1.57
1.42
f1 (ppm)


208.310
208.206
168.269
168.221
141.241
140.397
136.347
135.058
133.794
133.118
132.572
132.136
129.617
123.291
117.998
114.293
77.547
77.122
76.698
61.969
61.390
44.107
42.746
39.138
38.994
34.917
33.345
30.191
30.128
27.425
27.338
24.327
24.198
20.116
19.821
19.753
14.993
O
N
Ac
+
3ma + 3ma'
f1 (ppm)

O
N
COEt

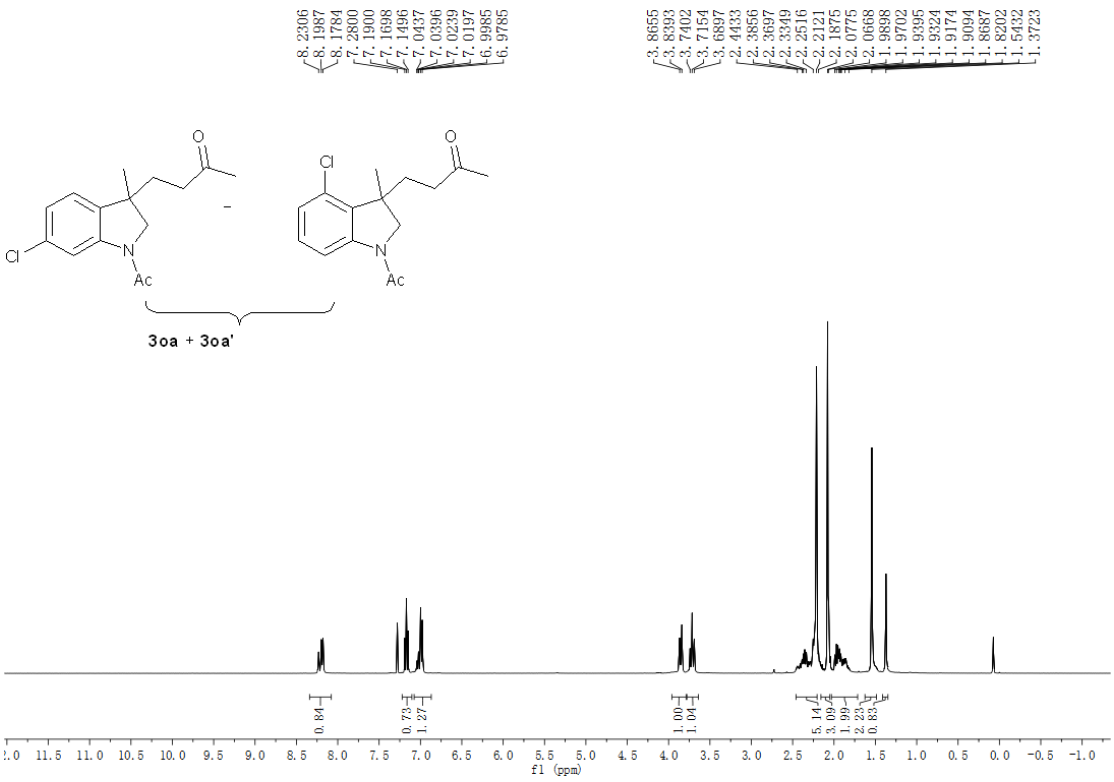
3na

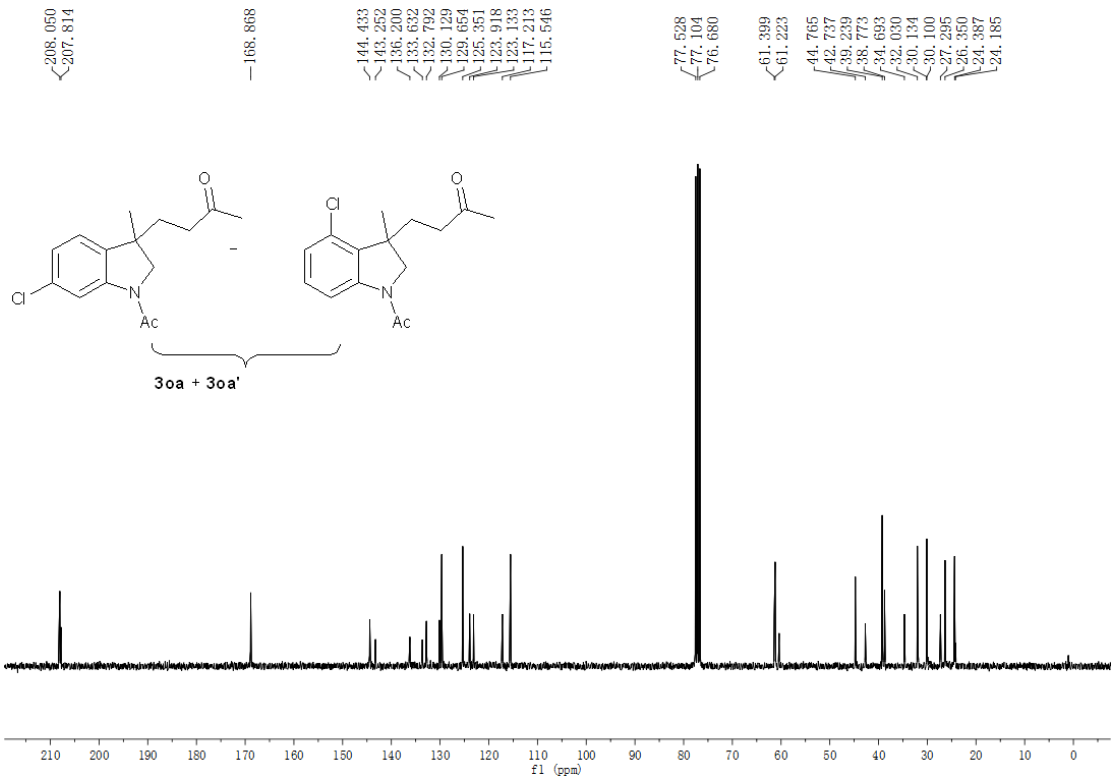

8.2533
8.2399
7.2842
7.2534
7.2413
7.2281
7.0985
7.0869
7.0758
7.0637
7.0514
3.8511
3.8339
3.7102
3.6930
2.4702
2.4578
2.4459
2.4342
2.3104
2.3003
2.2923
2.2162
2.2074
2.1993
2.1904
2.0529
1.9612
1.9525
1.9450
1.9356
1.9194
1.9109
1.9020
1.8940
1.8881
1.3978
1.2677
1.2553
0.90
1.12
1.98
0.95
1.00
2.02
1.04
1.19
3.00
2.20
3.05
3.63
f1 (ppm)


208.050
171.980
142.587
137.479
128.164
123.799
122.327
116.916
77.260
77.048
76.836
60.236
42.959
38.907
34.945
30.077
29.201
27.327
8.679
f1 (ppm)

O
N
COEt

3na


8.2306
8.1987
8.1784
7.2800
7.1900
7.1698
7.1496
7.0437
7.0396
7.0239
7.0197
6.9985
6.9785
3.8655
3.8393
3.7402
3.7154
3.6897
2.4433
2.3856
2.3697
2.3349
2.2516
2.2121
2.1875
2.0775
2.0668
1.9898
1.9702
1.9395
1.9324
1.9174
1.9094
1.8687
1.8202
1.5432
1.3723
Cl
O
N
Ac
3oa + 3oa'
0.84
0.73
1.27
1.00
1.04
5.14
3.09
1.99
2.23
0.83
f1 (ppm)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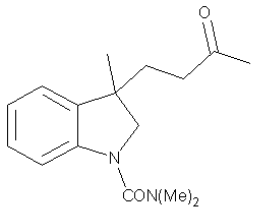
207.814
168.868
144.433
143.252
136.200
133.632
132.792
130.129
129.654
125.351
123.918
123.133
117.213
115.546
77.528
77.104
76.680
61.399
61.223
44.765
42.737
39.239
38.773
34.693
32.030
30.134
30.100
27.295
26.350
24.387
24.185
Cl
O
N
Ac
3oa + 3oa'
f1 (ppm)



7.2711
7.1552
7.1424
7.1298
7.0520
7.0400
6.9171
6.9036
6.8909

3.6589
3.6419
3.6202
3.6103
3.6031
2.9213
2.4341
2.4251
2.4061
2.3967
2.3871
2.3785
2.3164
2.3081
2.2984
2.2798
2.2622
2.1226
2.0623
2.0547
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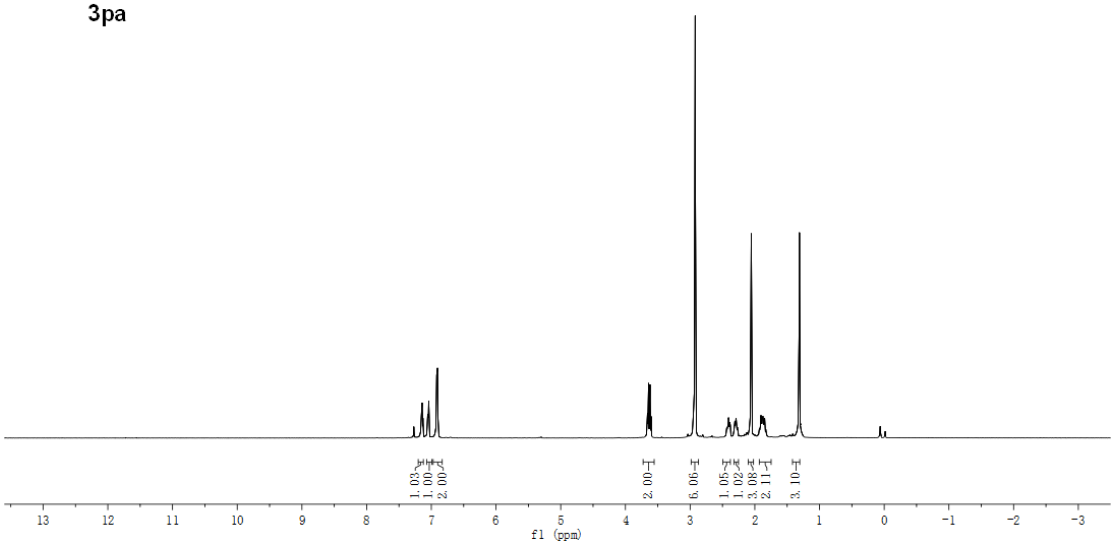
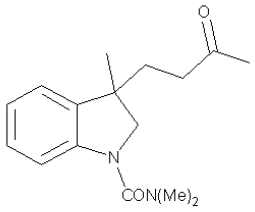
1.9047
1.8770
1.8728
1.8638
1.8477
1.8306
1.8234
1.3107

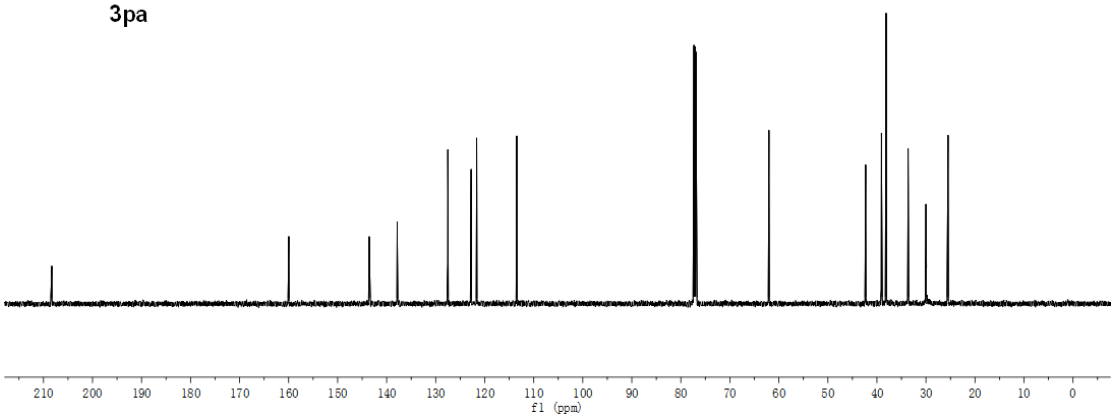
3pa

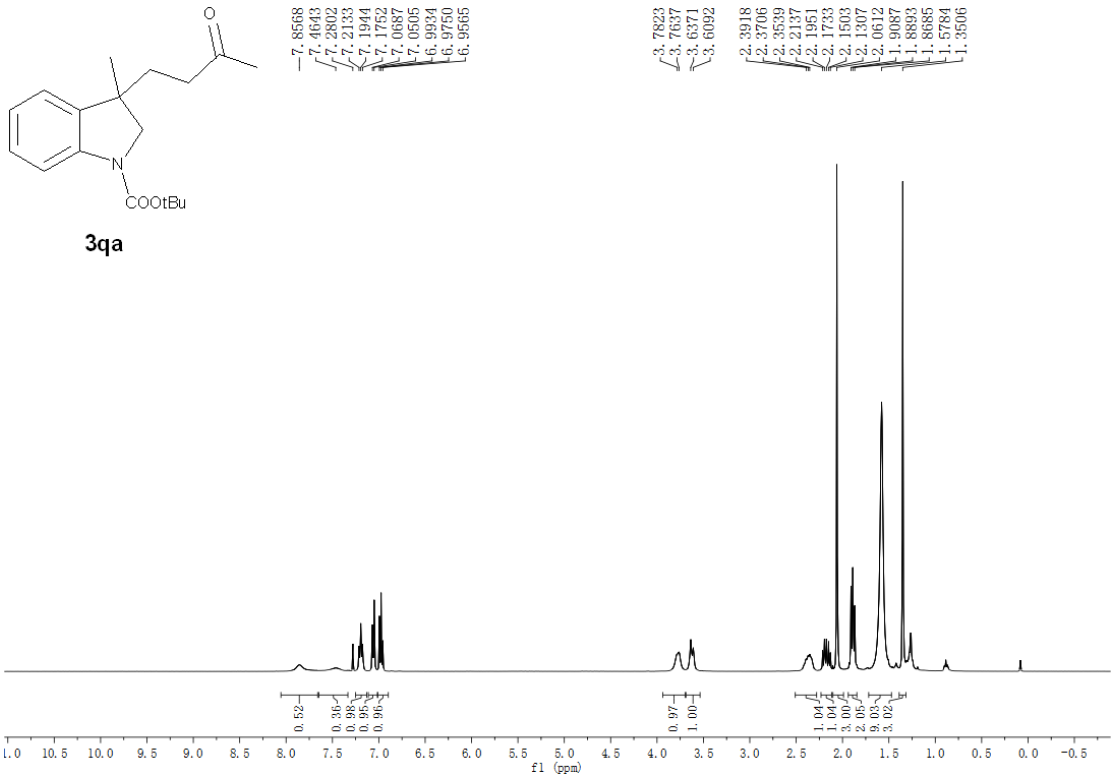


208.300
159.968
143.571
137.857
127.513
122.757
121.636
113.465
77.316
77.104
76.892
62.035
42.306
39.084
38.130
33.630
29.989
25.500



3pa

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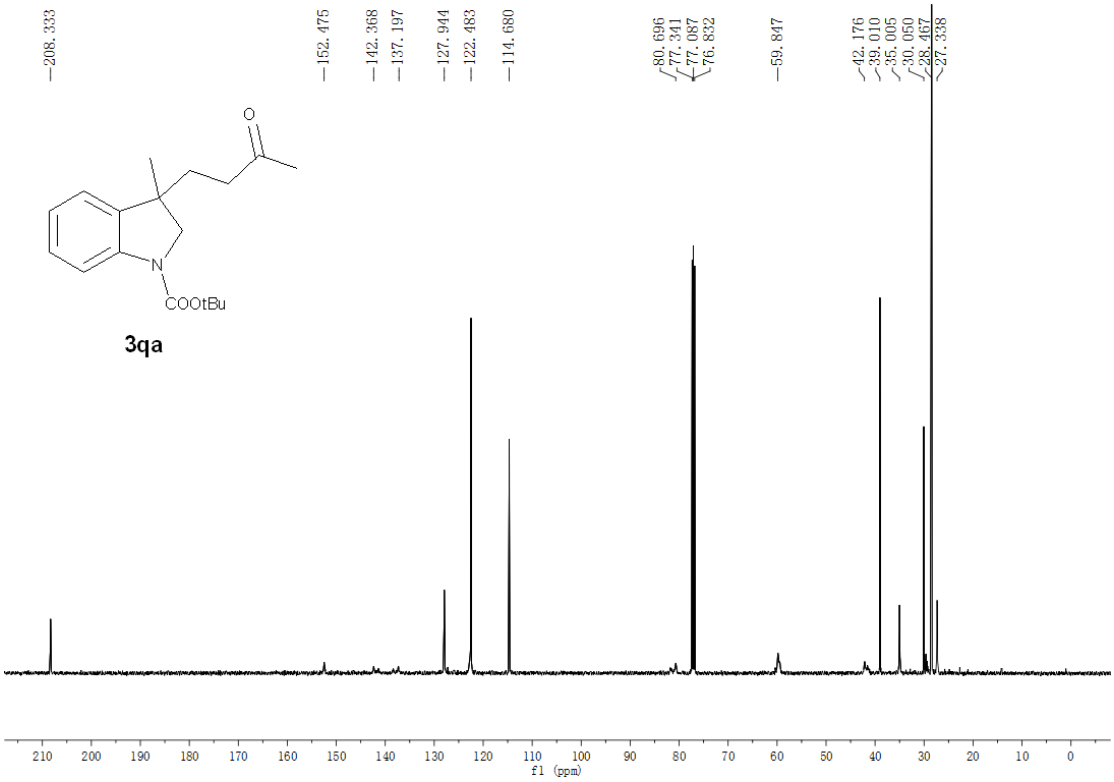
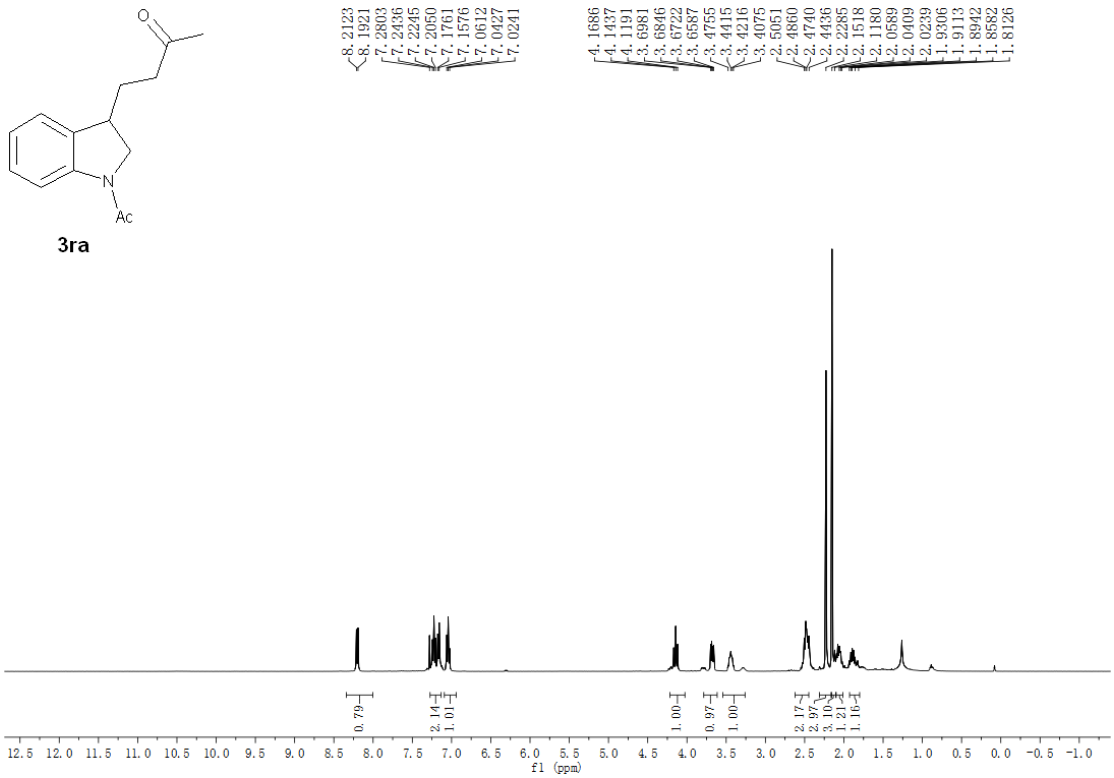
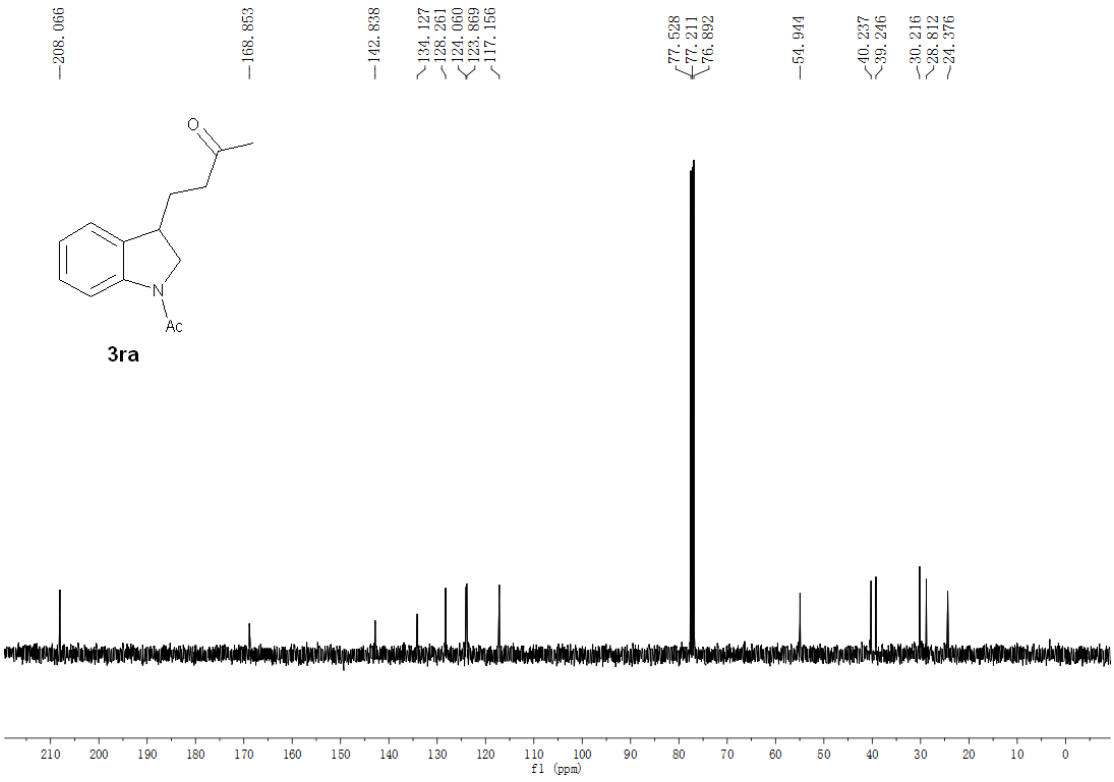
7.2802
7.2133
7.1944
7.1752
7.0687
7.0505
6.9934
6.9750
6.9565
3.7823
3.7637
3.6371
3.6092
2.3918
2.3706
2.3539
2.2137
2.1951
2.1733
2.1503
2.1307
2.0612
1.9087
1.8893
1.8685
1.5784
1.3506
O
N
COOtBu
0.52
0.36
0.98
0.95
0.96
0.97
1.00
1.04
1.04
3.00
2.05
9.03
3.02
f1 (ppm)

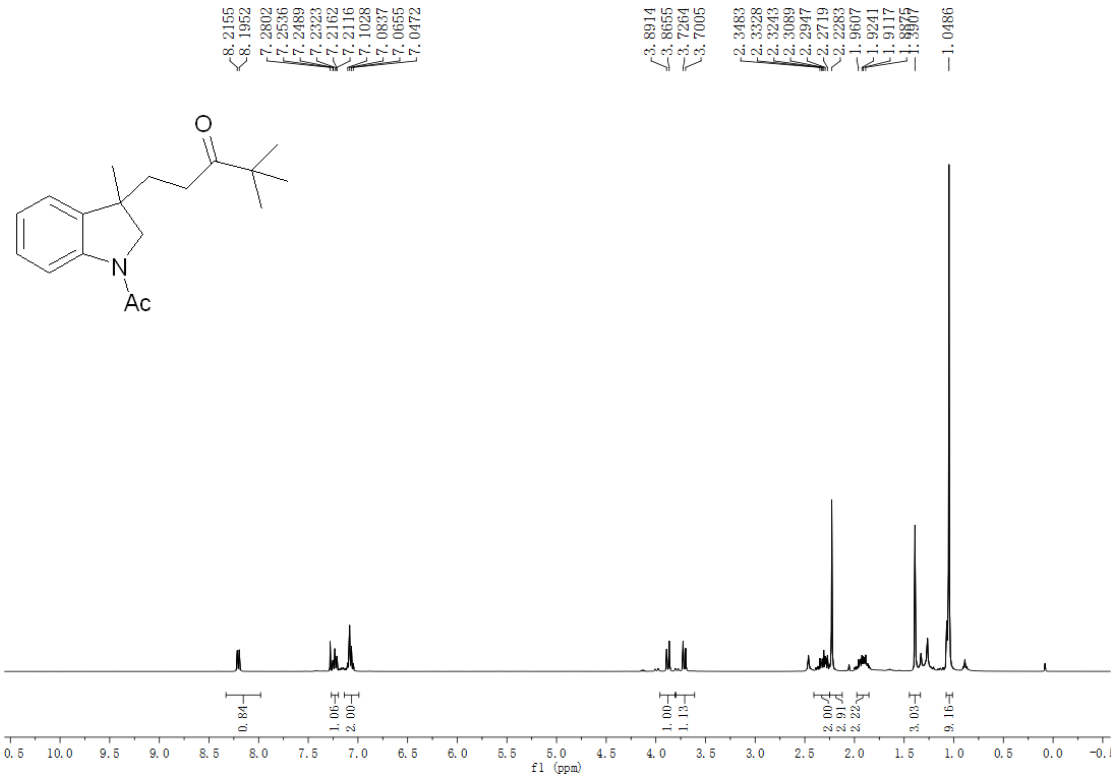
3qa


208.333
152.475
142.368
137.197
127.944
122.483
114.680
80.696
77.341
77.087
76.832
59.847
42.176
39.010
35.005
30.050
28.467
27.338
O
N
COOtBu
f1 (ppm)

3qa


8.2123
8.1921
7.2803
7.2436
7.2245
7.2050
7.1761
7.1576
7.0612
7.0427
7.0241
4.1686
4.1437
4.1191
3.6981
3.6846
3.6722
3.6587
3.4755
3.4415
3.4216
3.4075
2.5051
2.4860
2.4740
2.4436
2.2285
2.1518
2.1180
2.0589
2.0409
2.0239
1.9306
1.9113
1.8942
1.8582
1.8126
O
N
Ac
3ra
0.79
2.14
1.01
1.00
0.97
1.00
2.17
2.97
3.10
1.21
1.16
12.5 12.0 11.5 11.0 10.5 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)


208.066
168.853
142.838
134.127
128.261
124.060
123.869
117.156
77.528
77.211
76.892
54.944
40.237
39.246
30.216
28.812
24.376
O
N
Ac
3ra
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.2155
8.1952
7.2802
7.2536
7.2489
7.2323
7.2162
7.2116
7.1028
7.0837
7.0655
7.0472
3.8914
3.8655
3.7264
3.7005
2.3483
2.3328
2.3243
2.3089
2.2947
2.2719
2.2283
1.9607
1.9241
1.9117
1.3907
1.0486
O
N
Ac
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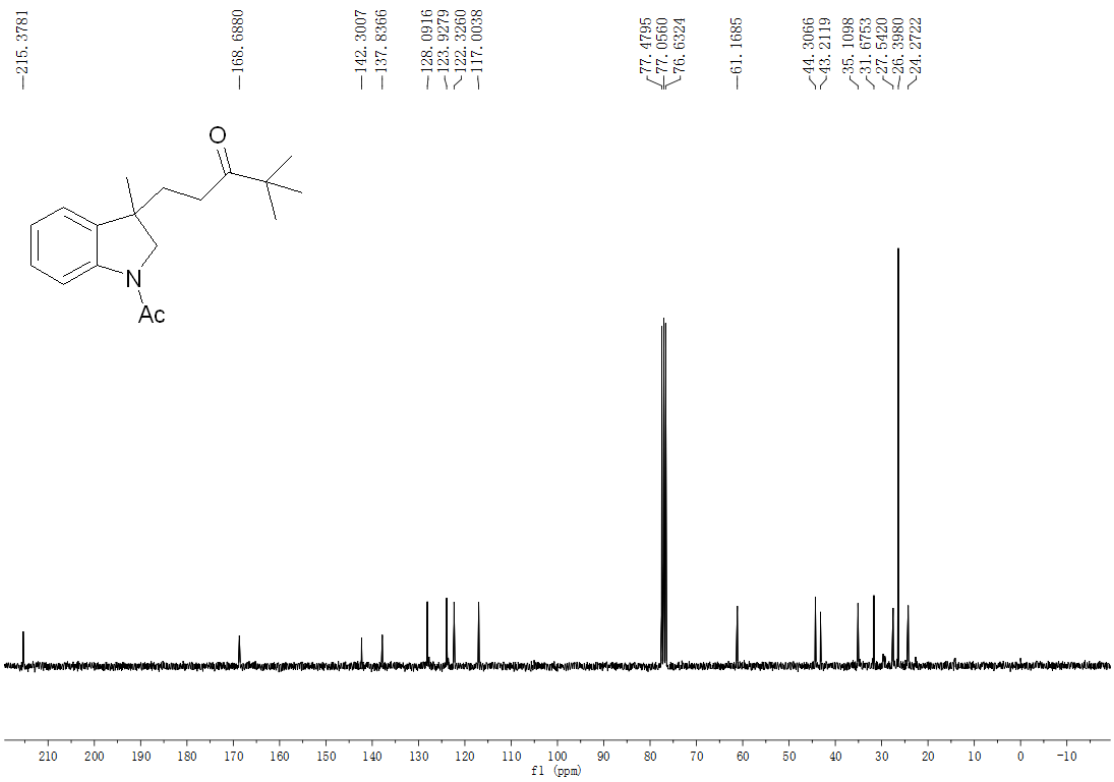
1.00
1.13
2.00
2.01
2.22
3.03
9.16
f1 (ppm)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142.3007
137.8366
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77.0560
76.6324
61.1685
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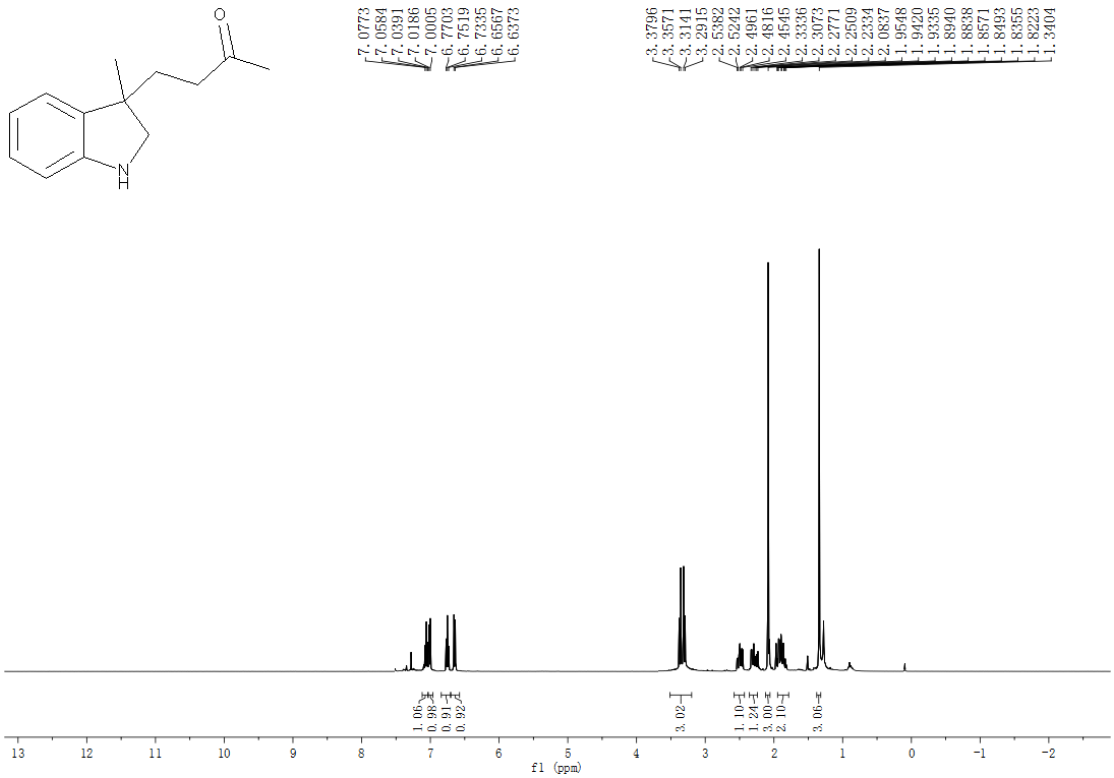
35.1098
31.6753
27.5420
26.3980
24.2722
O
N
Ac
f1 (ppm)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7.0005
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6.7519
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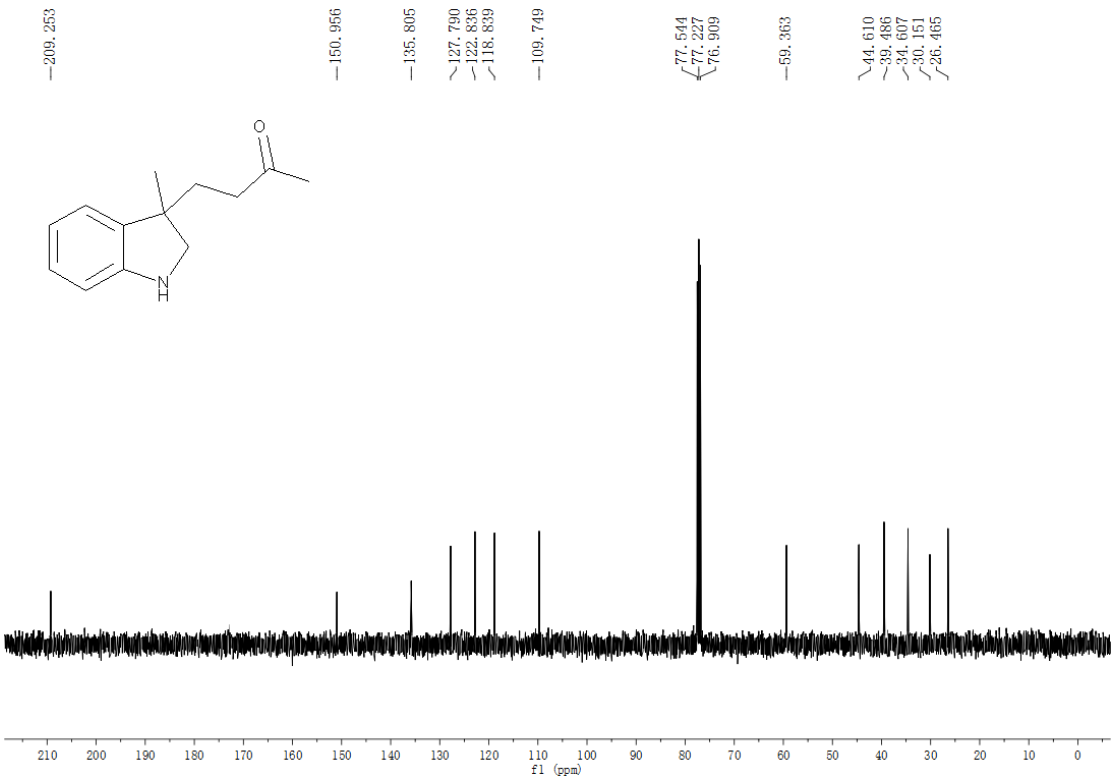
6.6567
6.6373
3.3796
3.3571
3.3141
3.2915
2.5382
2.5242
2.4961
2.4816
2.4545
2.3336
2.3073
2.2771
2.2509
2.2334
2.0837
1.9548
1.9420
1.9335
1.8940
1.8838
1.8571
1.8493
1.8355
1.8223
1.3404
1.06
0.98
0.91
0.92
3.02
1.10
1.24
3.00
2.10
3.06
f1 (ppm)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150.956
135.805
127.790
122.836
118.839
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77.227
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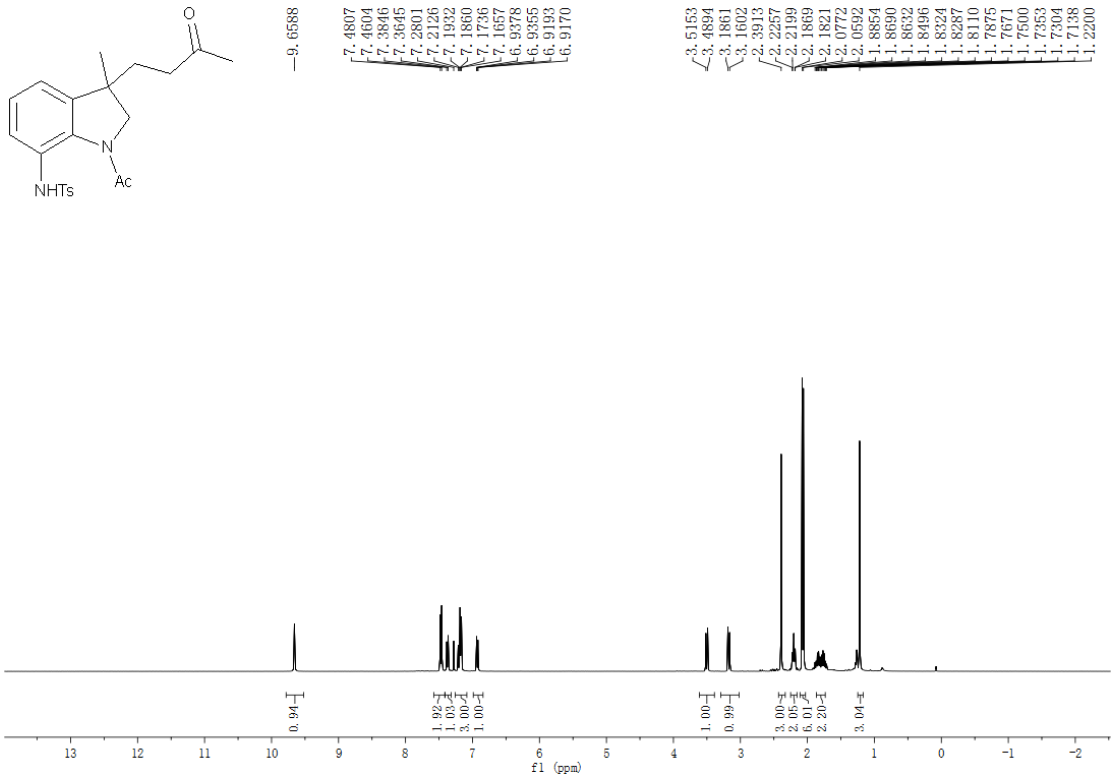
44.610
39.486
34.607
30.151
26.465
f1 (ppm)


O
N
Ac
NHTs
9.6588
7.4807
7.4604
7.3846
7.3645
7.2801
7.2126
7.1932
7.1860
7.1736
7.1657
6.9378
6.9355
6.9193
6.9170
3.5153
3.4894
3.1861
3.1602
2.3913
2.2257
2.2199
2.1869
2.1821
2.0772
2.0592
1.8854
1.8690
1.8632
1.8496
1.8324
1.8287
1.8110
1.7875
1.7671
1.7500
1.7353
1.7304
1.7138
1.2200
0.94
1.92
1.03
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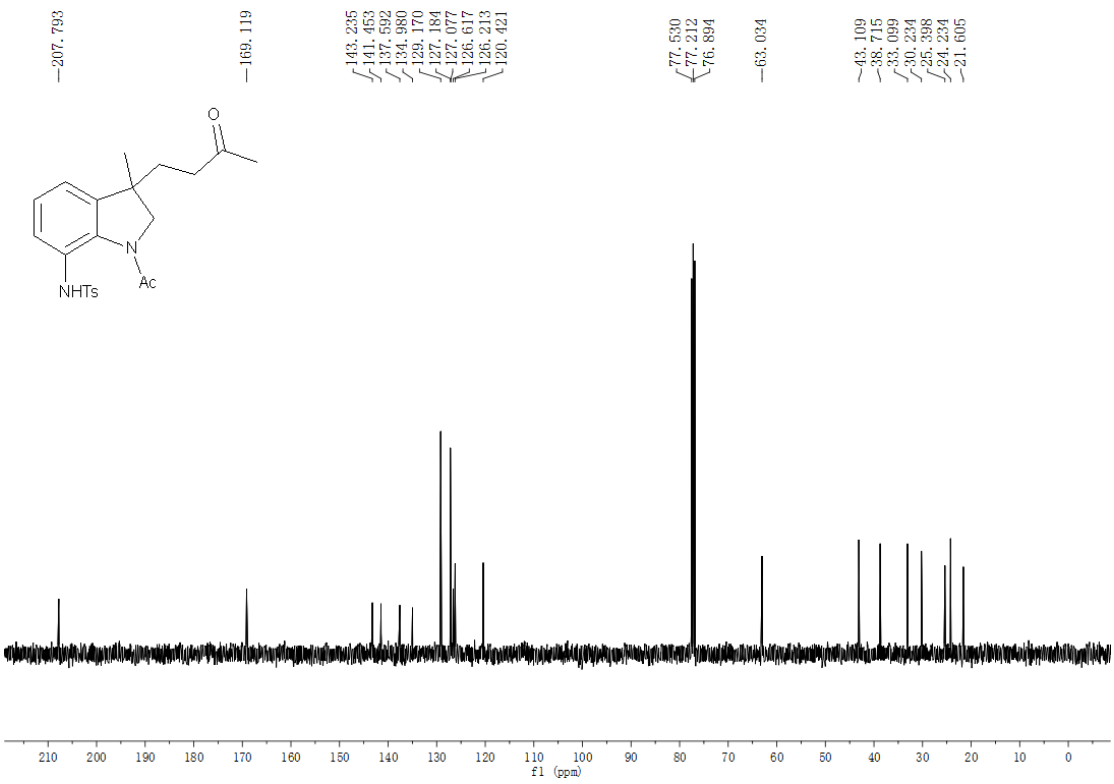
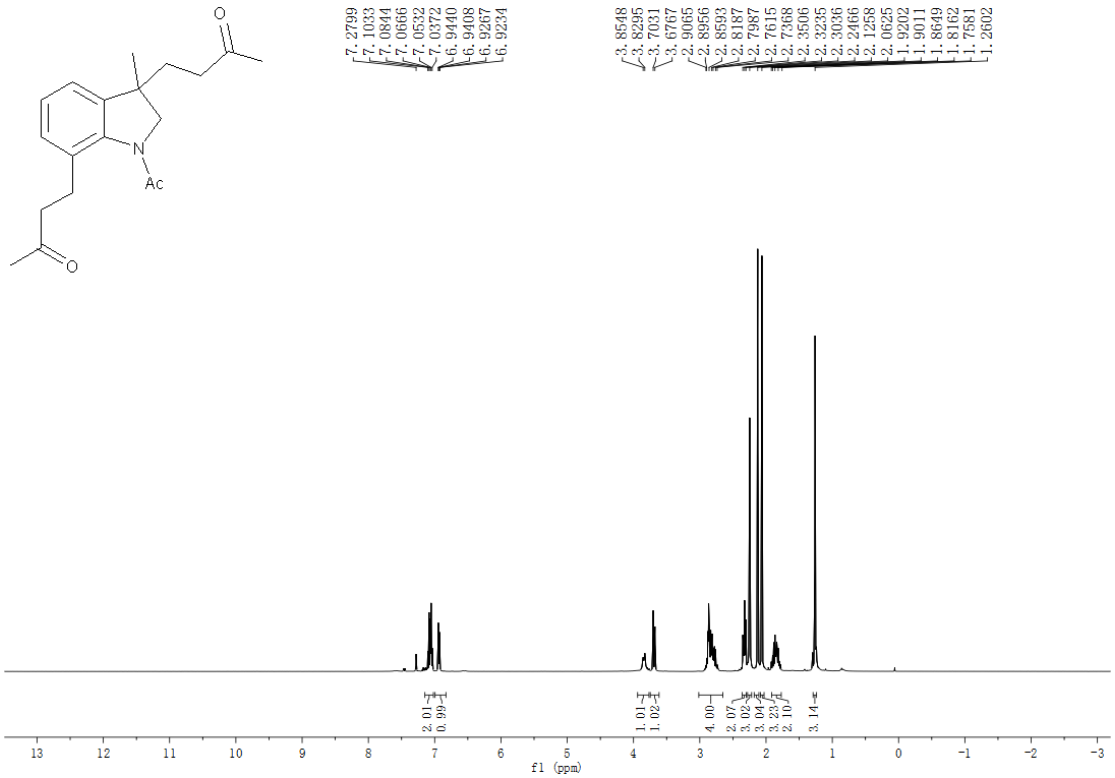
1.00
1.00
0.99
3.00
2.05
6.01
2.20
3.04
f1 (ppm)


O
N
Ac
NHTs
207.793
169.119
143.235
141.453
137.592
134.980
129.170
127.184
127.077
126.617
126.213
120.421
77.530
77.212
76.894
63.034
43.109
38.715
33.099
30.234
25.398
24.234
21.605
f1 (ppm)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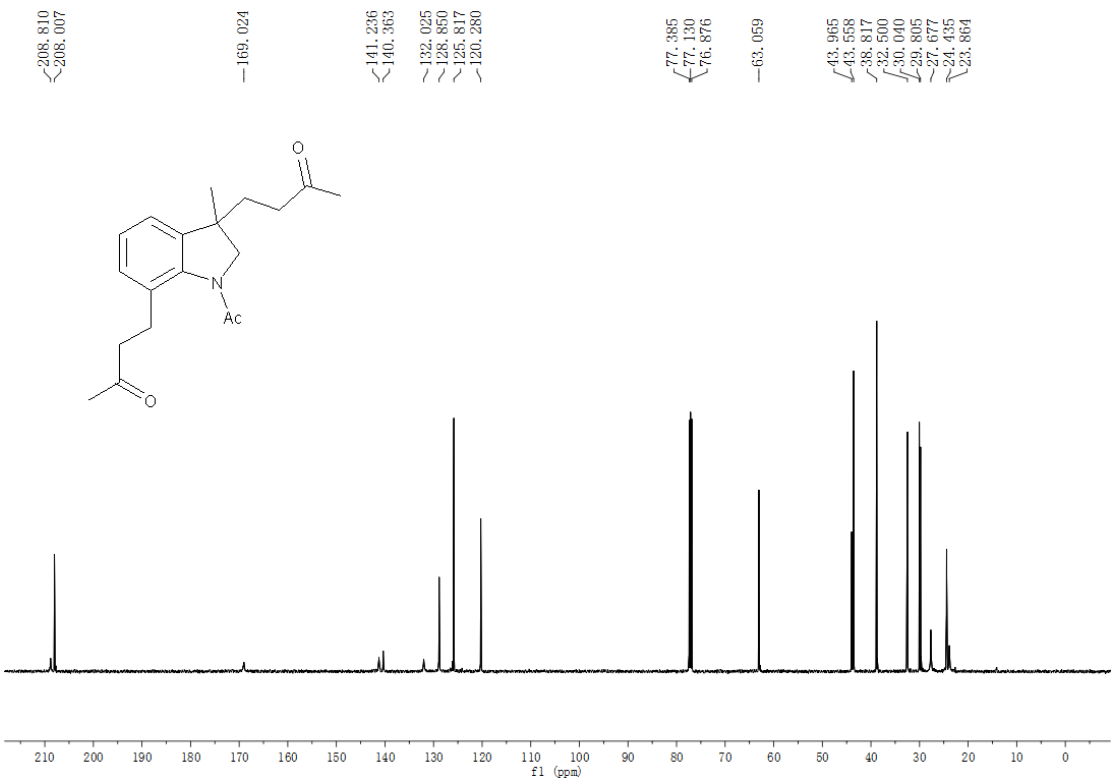
7.1033
7.0844
7.0666
7.0532
7.0372
6.9440
6.9408
6.9267
6.9234
3.8548
3.8295
3.7031
3.6767
2.9065
2.8956
2.8593
2.8187
2.7987
2.7615
2.7368
2.3506
2.3235
2.3036
2.2466
2.1258
2.0625
1.9202
1.9011
1.8649
1.8162
1.7581
1.2602
Ac
O
O
2.01
0.99
1.01
1.02
4.00
2.07
3.02
3.23
2.10
3.14
f1 (ppm)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208.007
169.024
141.236
140.363
132.025
128.850
125.817
120.280
77.385
77.130
76.876
63.059
43.965
43.558
38.817
32.500
30.040
29.805
27.677
24.435
23.864
Ac
O
O
f1 (ppm)