Supporting Information

Oxidative decarbonylative coupling of aliphatic aldehydes with methacryloyl benzamides to generate isoquinoline-1,3(2*H*,4*H*)-diones

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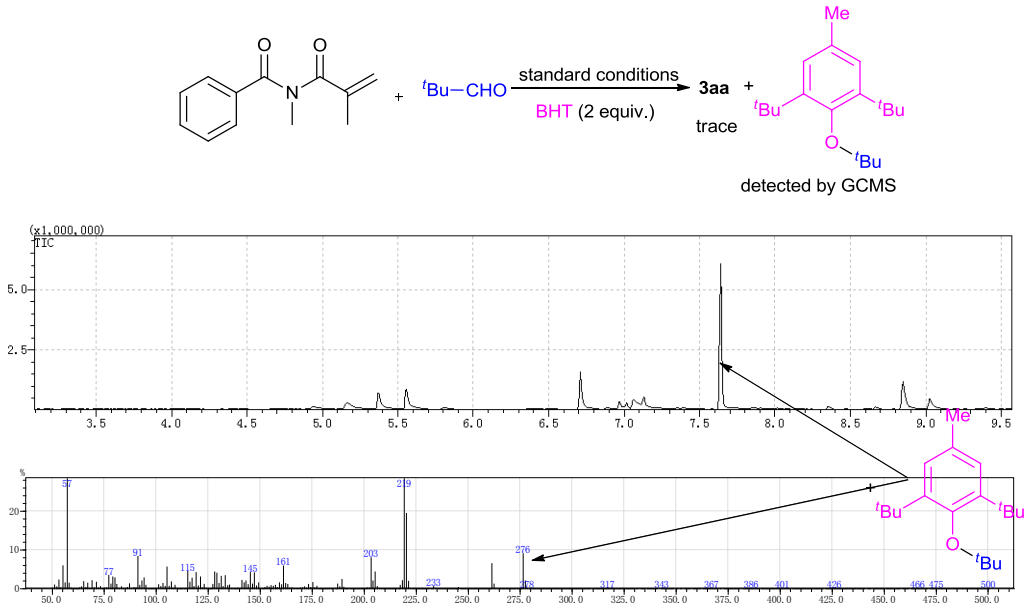
1. General experimental details

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 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 for the procedure for oxidative annulation of alkynoates with xanthates towards coumarins: Under N_2, the mixture of methacryloyl benzamide **1** (0.2 mmol), aliphatic aldehyde **2** (0.4 mmol), TBHP (0.4 mmol) and PhH (2 mL) were added into the sealed tube. The reaction mixture was vigorously stirred at 130 ^oC for 20 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products.

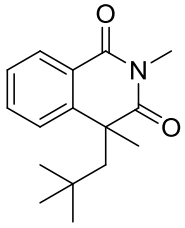
Mechanism Study

Standard Procedure + BHT (2.0 equiv)



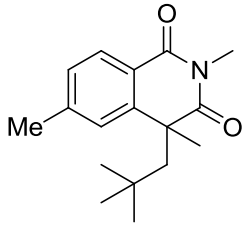
2. Characterization data of the products.

2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3aa)



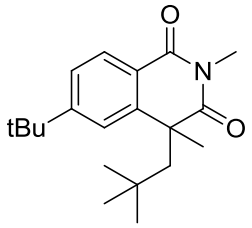
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.63-7.57 (m, 1H), 7.48-7.39 (m, 2H), 3.38 (s, 3H), 2.50 (d, *J* = 14.2 Hz, 1H), 2.50 (d, *J* = 14.2 Hz, 1H), 1.59 (s, 3H), 0.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.7, 164.5, 144.0, 133.3, 128.9, 127.2, 126.7, 124.3, 55.4, 45.9, 33.5, 31.9, 30.6, 27.2. IR (cm^{-1}): *v* 3021, 2954, 2922, 2852, 1671, 1653, 1495, 1466, 1365, 1298, 1255, 1057, 1016. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

2,4,6-trimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ba)



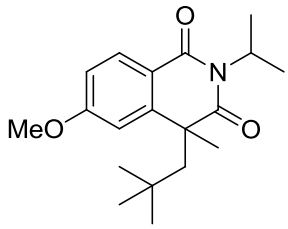
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.24-7.21 (m, 2H), 3.36 (s, 3H), 2.49 (d, *J* = 14.2 Hz, 1H), 2.44 (s, 3H), 1.99 (d, *J* = 14.2 Hz, 1H), 1.57 (s, 3H), 0.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.9, 164.5, 144.0, 143.9, 128.9, 128.3, 127.1, 121.8, 55.3, 45.9, 33.5, 31.9, 30.6, 27.1, 21.9. IR (cm^{-1}): *v* 3019, 2951, 2922, 1706, 1662, 1612, 1457, 1425, 1328, 1298, 1256, 1095, 1056. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1804.

6-(*tert*-butyl)-2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ca)



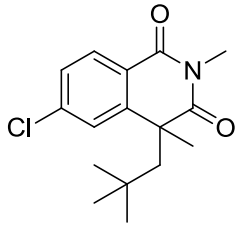
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d, *J* = 7.5 Hz, 1H), 7.46-7.43 (m, 2H), 3.37 (s, 3H), 2.53 (d, *J* = 14.2 Hz, 1H), 2.04 (d, *J* = 14.2 Hz, 1H), 1.59 (s, 3H), 1.35 (s, 9H), 0.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.1, 164.4, 156.8, 143.4, 128.7, 124.5, 123.6, 121.7, 55.2, 46.1, 35.2, 33.6, 31.8, 31.0, 30.6, 27.1. IR (cm^{-1}): *v* 3024, 2961, 2919, 2850, 1700, 1662, 1608, 1455, 1420, 1354, 1327, 1296, 1248, 1095, 1056. HRMS (ESI): *m/z* calcd for $C_{20}H_{30}NO_2$ $(M+H)^+$ 316.2271, found 316.2274.

2-isopropyl-6-methoxy-4-methyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3da)



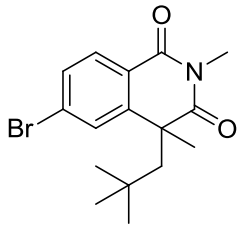
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d, *J* = 8.8 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 5.26-5.17 (m, 1H), 3.88 (s, 3H), 2.53 (d, *J* = 14.3 Hz, 1H), 1.95 (d, *J* = 14.3 Hz, 1H), 1.54 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.45 (d, *J* = 6.9 Hz, 3H), 0.59 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.7, 164.2, 163.3, 146.1, 131.2, 118.0, 113.3, 111.6, 55.5, 54.5, 46.5, 45.0, 34.2, 31.9, 30.9, 19.44, 19.40. IR (cm^{-1}): *v* 3020, 2963, 2927, 1705, 1661, 1604, 1499, 1458, 1420, 1347, 1321, 1262, 1229, 1092, 1034. HRMS (ESI): *m/z* calcd for $C_{19}H_{28}NO_3$ $(M+H)^+$ 318.2064, found 318.2062.

6-chloro-2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ea)



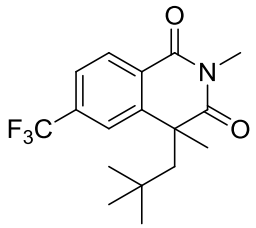
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.44-7.38 (m, 2H), 3.37 (s, 3H), 2.52 (d, *J* = 14.3 Hz, 1H), 1.98 (d, *J* = 14.3 Hz, 1H), 1.58 (s, 3H), 0.57 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.0, 163.6, 145.8, 140.0, 130.5, 127.9, 126.9, 122.8, 55.4, 46.0, 33.4, 31.9, 30.6, 27.3. IR (cm^{-1}): *v* 3021, 2956, 2920, 2850, 1708, 1663, 1598, 1458, 1428, 1356, 1328, 1297, 1092, 1057. HRMS (ESI): *m/z* calcd for $C_{16}H_{21}ClNO_2$ $(M+H)^+$ 294.1255, found 294.1257.

6-bromo-2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3fa)



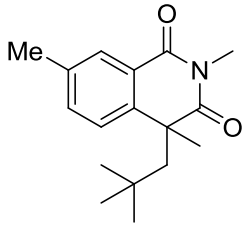
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.60-7.54 (m, 2H), 3.37 (s, 3H), 2.52 (d, *J* = 14.3 Hz, 1H), 1.98 (d, *J* = 14.3 Hz, 1H), 1.58 (s, 3H), 0.56 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 175.9, 163.7, 145.8, 130.8, 130.5, 129.9, 128.7, 123.2, 55.4, 45.9, 33.4, 31.9, 30.6, 27.3. IR (cm^{-1}): *v* 3070, 2962, 2939, 1708, 1663, 1592, 1574, 1457, 1426, 1355, 1328, 1297, 1250, 1096, 1057. HRMS (ESI): *m/z* calcd for $C_{16}H_{21}BrNO_2$ $(M+H)^+$ 338.0750, found 338.0756.

2,4-dimethyl-4-neopentyl-6-(trifluoromethyl)isoquinoline-1,3(2H,4H)-dione (3ga)



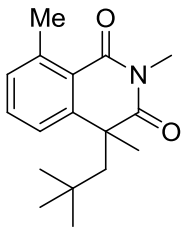
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.40 (d, *J* = 8.2 Hz, 1H), 7.71-7.66 (m, 2H), 3.40 (s, 3H), 2.57 (d, *J* = 14.4 Hz, 1H), 2.05 (d, *J* = 14.4 Hz, 1H), 1.62 (s, 3H), 0.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 175.9, 163.3, 144.8, 134.8 (q, J_{C-F} = 32.2 Hz), 129.8, 127.1, 124.1, 124.0, 123.98. 123.93, 123.89, 123.84, 123.4 (q, J_{C-F} = 271.5 Hz), 55.3, 46.1, 33.5, 31.9, 30.6, 27.4. ^{19}F NMR ($CDCl_3$, 282 MHz): δ -63.3. IR (cm^{-1}): *v* 3058, 2968, 2953, 2920, 1708, 1671, 1462, 1431, 1363, 1325, 1299, 1249, 1169, 1079, 1057. HRMS (ESI): *m/z* calcd for $C_{17}H_{21}F_3NO_2$ $(M+H)^+$ 328.1519, found 328.1523.

2,4,7-trimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ha)



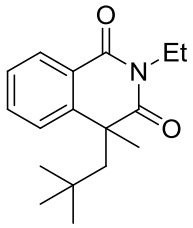
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.05 (s, 1H), 7.42-7.39 (m, 1H), 7.35-7.32 (m, 1H), 3.37 (s, 3H), 2.48 (d, *J* = 14.2 Hz, 1H), 2.43 (s, 3H), 2.00 (d, *J* = 14.2 Hz, 1H), 1.56 (s, 3H), 0.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.9, 164.6, 141.1, 137.1, 134.4, 128.8, 126.7, 124.0, 55.3, 45.7, 33.5, 31.9, 30.6, 27.2, 20.9. IR (cm^{-1}): *v* 3020, 2953, 2921, 2850, 1712, 1667, 1469, 1435, 1326, 1298, 1260, 1165, 1095. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1801.

2,4,8-trimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ia)



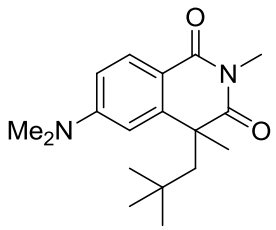
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (t, *J* = 7.6 Hz, 1H), 7.35-7.32 (m, 1H), 7.23-7.20 (m, 1H), 3.35 (s, 3H), 2.80 (s, 3H), 2.50 (d, *J* = 14.2 Hz, 1H), 2.01 (d, *J* = 14.2 Hz, 1H), 1.59 (s, 3H), 0.55 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.5, 165.0, 145.4, 142.5, 132.1, 131.2, 125.1, 122.7, 55.8, 45.9, 33.9, 31.9, 30.6, 27.2, 24.2. IR (cm^{-1}): *v* 3016, 2958, 2923, 1708, 1666, 1469, 1434, 1323, 1309, 1287, 1197, 1056. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1804.

2-ethyl-4-methyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ja)



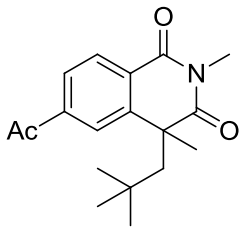
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.62-7.56 (m, 1H), 7.47-7.39 (m, 2H), 4.13-3.99 (m, 2H), 2.54 (d, *J* = 14.3 Hz, 1H), 2.03 (d, *J* = 14.3 Hz, 1H), 1.57 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.55 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.2, 164.0, 144.0, 133.2, 128.8, 127.2, 126.8, 124.3, 55.8, 46.0, 35.7, 33.9, 31.9, 30.8, 12.7. IR (cm^{-1}): *v* 3019, 2975, 2936, 2874, 1705, 1659, 1604, 1464, 1446, 1362, 1324, 1256, 1150, 1095. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1803.

6-(dimethylamino)-2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3ka)



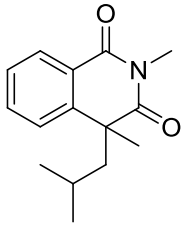
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.9 Hz, 1H), 6.70 (dd, *J* = 8.9, 2.2 Hz,1H), 6.54 (d, *J* = 2.1 Hz, 1H), 3.33 (s, 3H), 3.07 (s, 6H), 2.49 (d, *J* = 14.2 Hz, 1H), 1.99 (d, *J* = 14.2 Hz, 1H), 1.57 (s, 3H), 0.59 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.3, 164.4, 153.3, 145.6, 130.5, 112.4, 111.1, 108.1, 55.5, 46.2, 40.1, 33.9, 31.9, 30.7, 26.9. IR (cm^{-1}): *v* 3022, 2951, 2918, 2863, 1706, 1663, 1462, 1440, 1329, 1295, 1258, 1162, 1091. HRMS (ESI): *m/z* calcd for $C_{18}H_{27}N_2O_2$ $(M+H)^+$ 303.2067, found 303.2070.

6-acetyl-2,4-dimethyl-4-neopentylisoquinoline-1,3(2H,4H)-dione (3la)



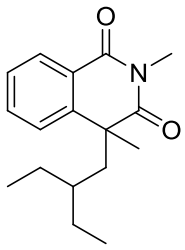
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 1.41H), 7.93 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.37 (s, 3H), 2.66 (s, 3H), 2.53 (d, *J* = 14.4 Hz, 1H), 2.09 (d, *J* = 14.2 Hz, 1H), 1.60 (s, 3H), 0.51 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.3, 176.2, 163.6, 144.4, 140.3, 129.5, 127.6, 126.8, 126.5, 55.2, 46.1, 33.5, 31.9, 30.7, 27.3, 26.9. IR (cm^{-1}): *v* 3018, 2955, 2857, 1710, 1667, 1458, 1325, 1291, 1253, 1160, 1089, 1054. HRMS (ESI): *m/z* calcd for $C_{18}H_{24}NO_3$ $(M+H)^+$ 302.1751, found 302.1755.

4-isobutyl-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (3ab)



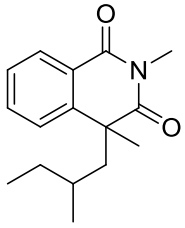
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.67-7.61 (m, 1H), 7.46-7.40 (m, 2H), 3.39 (s, 3H), 2.36-2.29 (q, 1H), 1.97-1.90 (q, 1H), 1.58 (s, 3H), 1.22-1.13 (m, 1H), 0.62 (d, *J* = 6.6 Hz, 3H), 0.60 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.9, 164.5, 143.8, 133.8, 128.8, 127.2, 126.6, 124.6, 50.9, 46.9, 31.6, 27.2, 25.5, 23.9, 22.3. IR (cm^{-1}): *v* 3021, 2957, 2927, 2870, 1713, 1669, 1606, 1466, 1417, 1362, 1308, 1212, 1084, 1051. HRMS (ESI): *m/z* calcd for $C_{15}H_{20}NO_2$ $(M+H)^+$ 246.1489, found 246.1491.

4-(2-ethylbutyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (3ac)



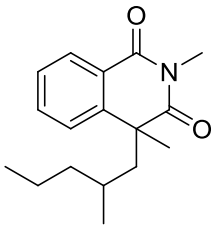
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.66-7.60 (m, 1H), 7.46-7.40 (m, 2H), 3.38 (s, 3H), 2.29-2.24 (q, 1H), 1.89-1.83 (q, 1H), 1.62 (s, 3H), 1.03-0.75 (m, 5H), 0.65 (t, *J* = 7.2 Hz, 3H), 0.56 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.9, 164.6, 143.8, 133.7, 128.7, 127.2, 125.8, 124.8, 46.9, 46.8, 37.2, 30.0, 27.1, 25.8, 25.3, 10.3, 10.2. IR (cm^{-1}): *v* 3022, 2960, 2925, 2874, 1714, 1670, 1606, 1466, 1417, 1362, 1324, 1298, 1210, 1051, 1033. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1805.

2,4-dimethyl-4-(2-methylbutyl)isoquinoline-1,3(2H,4H)-dione (3ad)



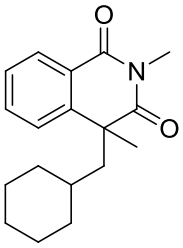
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.67-7.60 (m, 1H), 7.46-7.38 (m, 2H), 3.39 (s, 3H), 2.41-2.34 (m, 0.55H), 2.29-2.21 (m, 0.54H), 2.05-1.99 (m, 0.61H), 1.83-1.76 (m, 0.61H), 1.59 (d, *J* = 3.3 Hz, 3H), 1.10-0.88 (m, 3H), 0.72-0.65 (m, 3H), 0.56 (t, *J* = 6.4 Hz, 1.42H), 0.41 (d, *J* = 6.4 Hz, 1.58H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.0, 176.8, 164.6, 164.5, 144.0, 143.7, 133.8, 133.7, 128.8, 127.2, 127.1, 125.9, 125.7, 124.7, 124.6, 49.9, 48.7, 47.1, 46.7, 31.8, 31.6, 31.5, 30.7, 30.6, 29.6, 27.2, 27.1, 20.2, 18.9, 11.0, 10.9. IR (cm^{-1}): *v* 3016, 2958, 2921, 2851, 1713, 1669, 1605, 1466, 1418, 1363, 1297, 1212, 1051, 1032. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

2,4-dimethyl-4-(2-methylpentyl)isoquinoline-1,3(2H,4H)-dione (3ae)



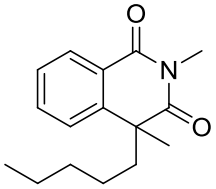
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (dd, *J* = 7.9, 3.1 Hz, 1H), 7.67-7.60 (m, 1H), 7.46-7.38 (m, 2H), 3.39 (s, 3H), 2.39-2.33 (m, 0.62H), 2.28-2.20 (m, 0.53H), 2.04-1.98 (m, 0.55H), 1.83-1.76 (m, 0.63H), 1.60 (d, *J* = 4.2 Hz, 3H), 1.17-0.82 (m, 6H), 0.74-0.66 (m, 3H), 0.56 (t, *J* = 6.3 Hz, 1.4H), 0.42 (d, *J* = 6.5 Hz, 1.6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.0, 176.8, 164.6, 164.5, 144.1, 143.7, 133.8, 133.7, 128.8, 127.2, 127.1, 125.9, 125.7, 124.7, 124.6, 50.4, 49.1, 47.1, 46.7, 40.3, 39.3, 31.4, 30.6, 29.9, 29.6, 27.2, 27.1, 20.7, 19.6, 19.5, 19.4, 14.1, 14.0. IR (cm^{-1}): *v* 3019, 2957, 2927, 2871, 1713, 1670, 1606, 1466, 1417, 1362, 1311, 1211, 1097, 1052. HRMS (ESI): *m/z* calcd for $C_{17}H_{24}NO_2$ $(M+H)^+$ 274.1802, found 274.1805.

4-(cyclohexylmethyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione[1] (3af)



^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.66-7.60 (m, 1H), 7.46-7.39 (m, 2H), 3.39 (s, 3H), 2.37-2.29 (dd, *J* = 14.0, 7.1 Hz, 1H), 1.93-1.87 (dd, *J* = 14.0, 4.3 Hz, 1H), 1.56 (s, 3H), 1.52-1.44 (m, 3H), 1.22-1.12 (m, 2H), 0.97-0.72 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.9, 164.5, 143.9, 133.8, 128.8, 127.2, 125.7, 124.5, 49.5, 46.6, 34.8, 34.3, 32.9, 31.7, 27.2, 26.03, 26.00, 25.9.

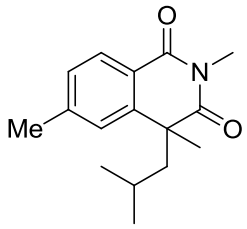
2,4-dimethyl-4-pentylisoquinoline-1,3(2H,4H)-dione (3ag)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.47-7.42 (m, 2H), 3.40 (s, 3H), 2.31-2.24 (m, 1H), 1.89-1.81 (m, 1H), 1.63 (s, 3H), 1.22-1.05 (m, 4H), 0.95-0.85 (m, 1H), 0.78-0.67 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.8, 164.6, 143.8, 133.9, 128.7, 127.2, 125.2, 124.9, 47.8, 43.4, 31.7, 29.1, 27.1, 24.8, 22.2, 13.9. IR (cm^{-1}): *v* 3018, 2955, 2921, 2851, 1715, 1670, 1633, 1467, 1418, 1362, 1324, 1051. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

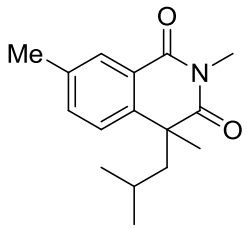
[1] P. Qian, B. Du, W. Jiao, H. Mei, J. Han and Y. Pan, *Beilstein J. Org. Chem*., 2016, **12**, 301.

4-isobutyl-2,4,6-trimethylisoquinoline-1,3(2H,4H)-dione (3bb)



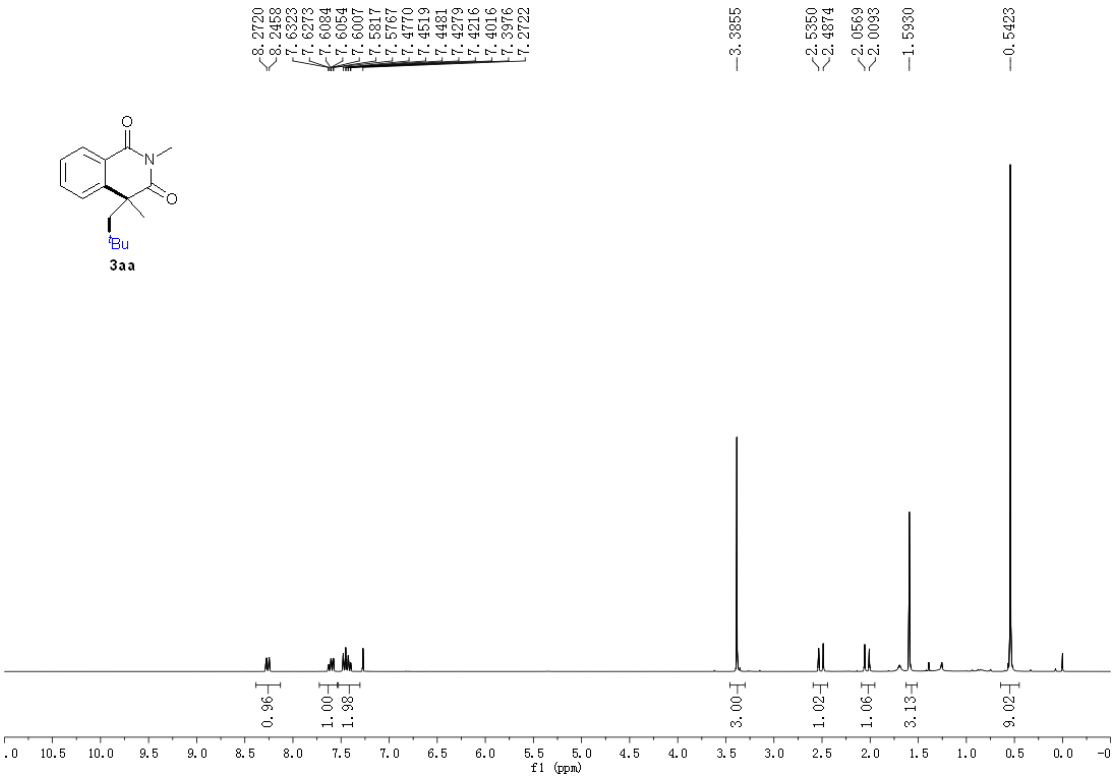
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.18 (s, 1H), 3.37 (s, 3H), 2.45 (s, 3H), 2.34-2.27 (q, 1H), 1.95-1.88 (q, 1H), 1.56 (s, 3H), 1.23-1.14 (m, 1H), 0.61 (t, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.0, 164.5, 144.6, 143.8, 128.9, 128.3, 126.1, 122.1, 50.9, 46.8, 31.6, 27.1, 25.5, 23.9, 22.3, 22.0. IR (cm^{-1}): *v* 3022, 2956, 2924, 1712, 1667, 1614, 1457, 1426, 1356, 1307, 1218, 1175, 1051. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1647.

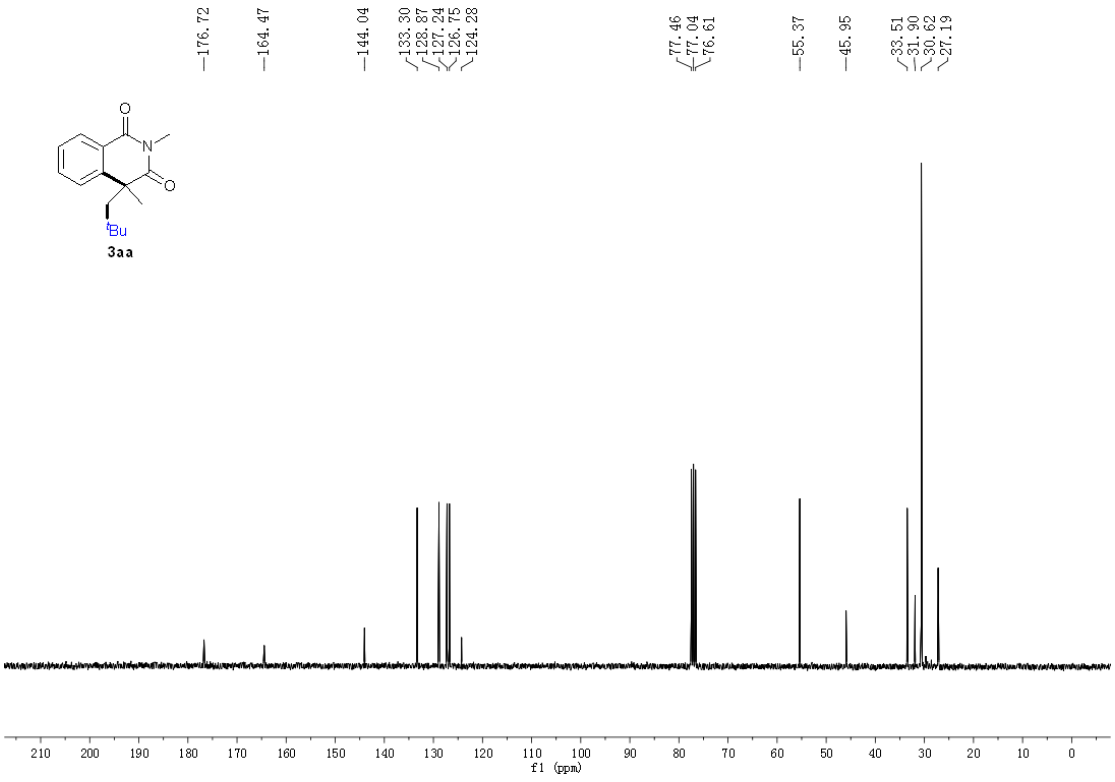
4-isobutyl-2,4,7-trimethylisoquinoline-1,3(2H,4H)-dione (3ib)

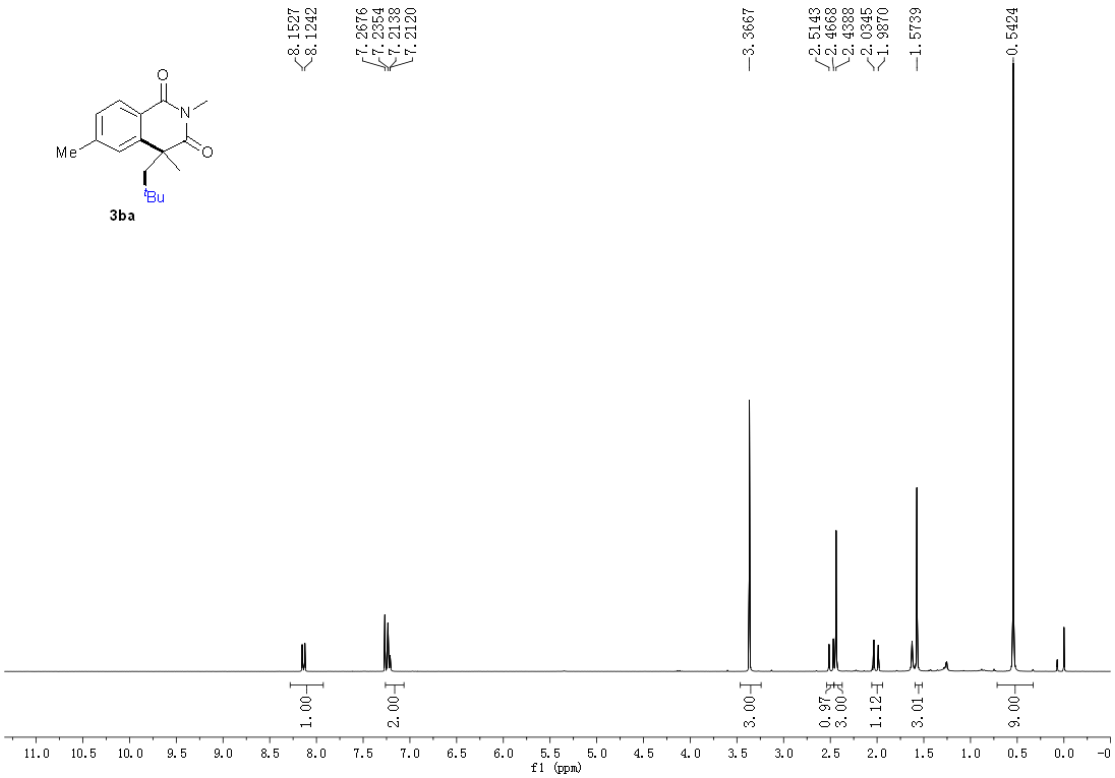


^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.05 (s, 1H), 7.46-7.42 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 3.37 (s, 3H), 2.43 (s, 3H), 2.34-2.26 (q, 1H), 1.94-1.88 (q, 1H), 1.55 (s, 3H), 1.21-1.12 (m, 1H), 0.60 (q, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.1, 164.7, 140.9, 137.0, 134.8, 128.8, 125.7, 124.4, 50.9, 46.6, 31.7, 27.2, 25.5, 23.9, 22.3, 20.9. IR (cm^{-1}): *v* 3019, 2956, 2923, 2851, 1712, 1668, 1617, 1455, 1434, 1352, 1308, 1165, 1084, 1050. HRMS (ESI): *m/z* calcd for $C_{16}H_{22}NO_2$ $(M+H)^+$ 260.1645, found 260.1646.

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



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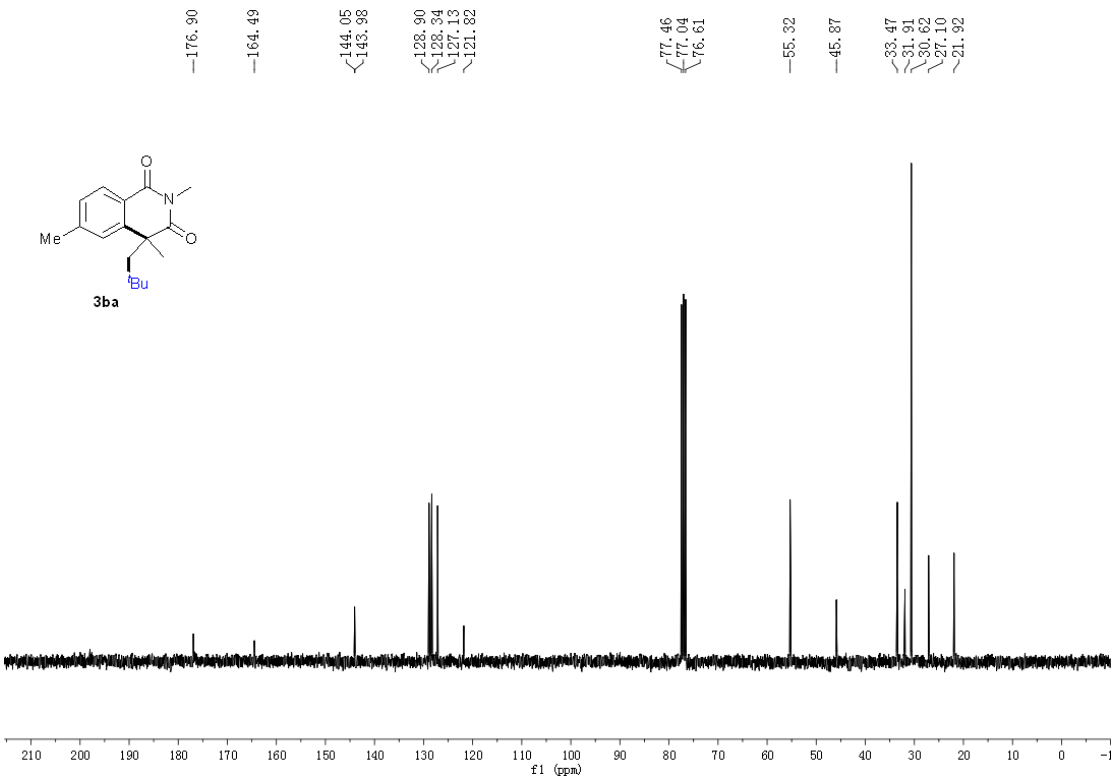
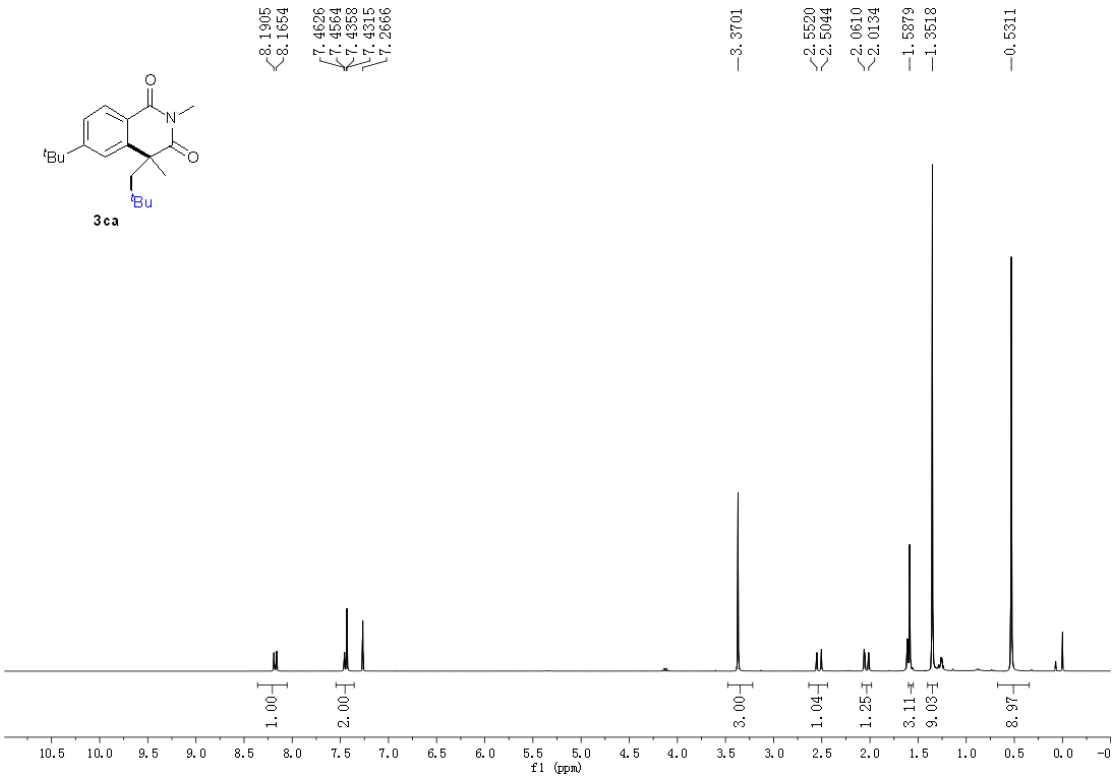
8.1242
7.2676
7.2354
7.2138
7.2120
3.3667
2.5143
2.4668
2.4388
2.0345
1.9870
1.5739
0.5424
Me
tBu
3ba
1.00
2.00
3.00
0.97
3.00
1.12
3.01
9.00
f1 (ppm)


176.90
164.49
144.05
143.98
128.90
128.34
127.13
121.82
77.46
77.04
76.61
55.32
45.87
33.47
31.91
30.62
27.10
21.92
Me
tBu
3ba
f1 (ppm)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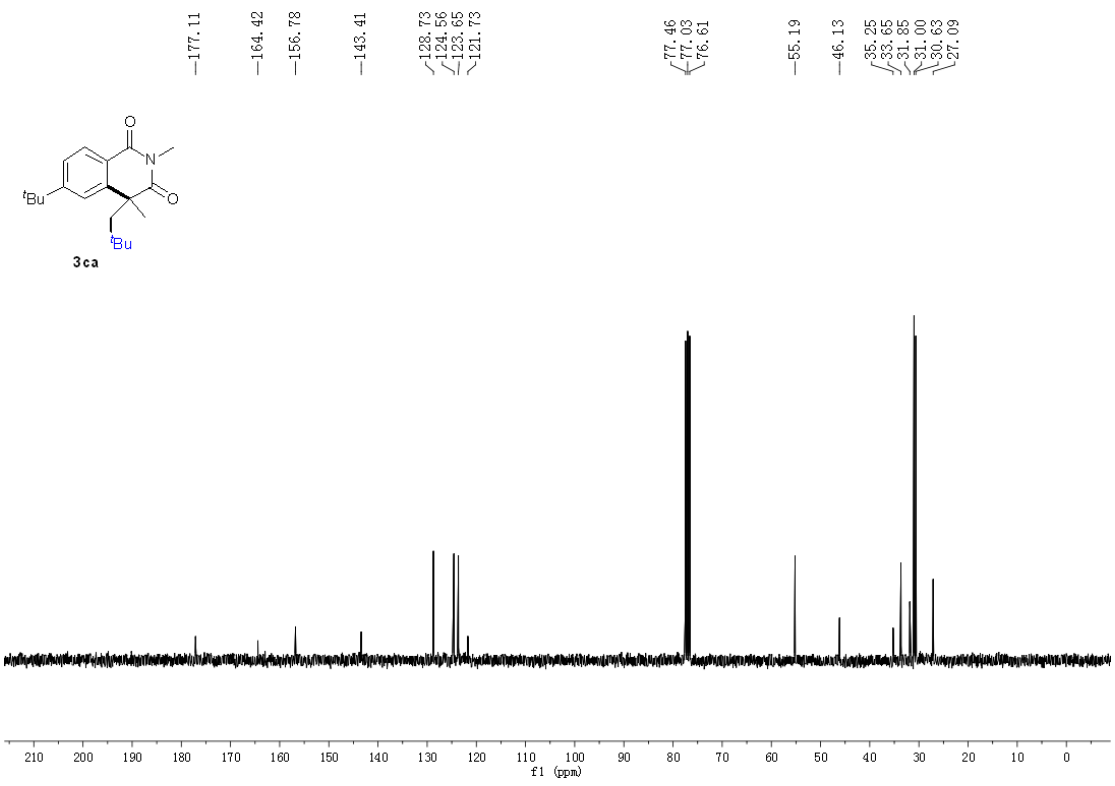
8.1654
7.4626
7.4564
7.4358
7.4315
7.2666
3.3701
2.5520
2.5044
2.0610
2.0134
1.5879
1.3618
0.5311
3ca
1.00
2.00
3.00
1.04
1.25
3.11
9.03
8.97
f1 (ppm)


177.11
164.42
156.78
143.41
128.73
124.56
123.65
121.73
77.46
77.03
76.61
55.19
46.13
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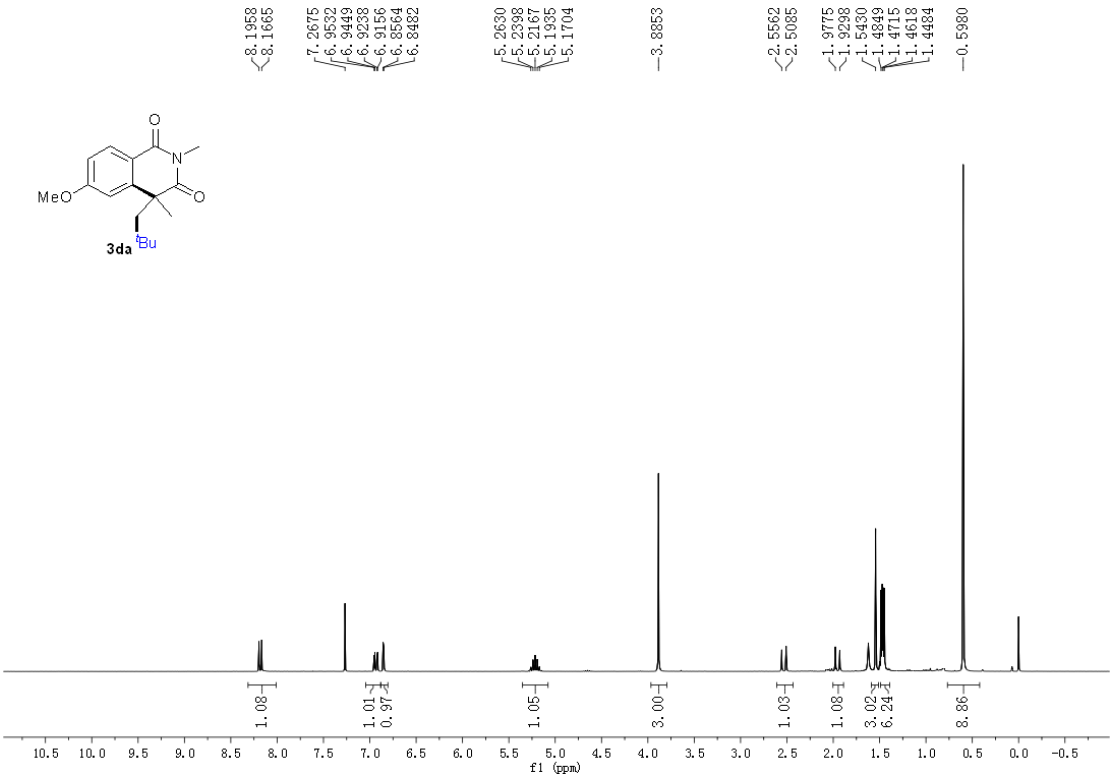
31.00
30.63
27.09
3ca
f1 (ppm)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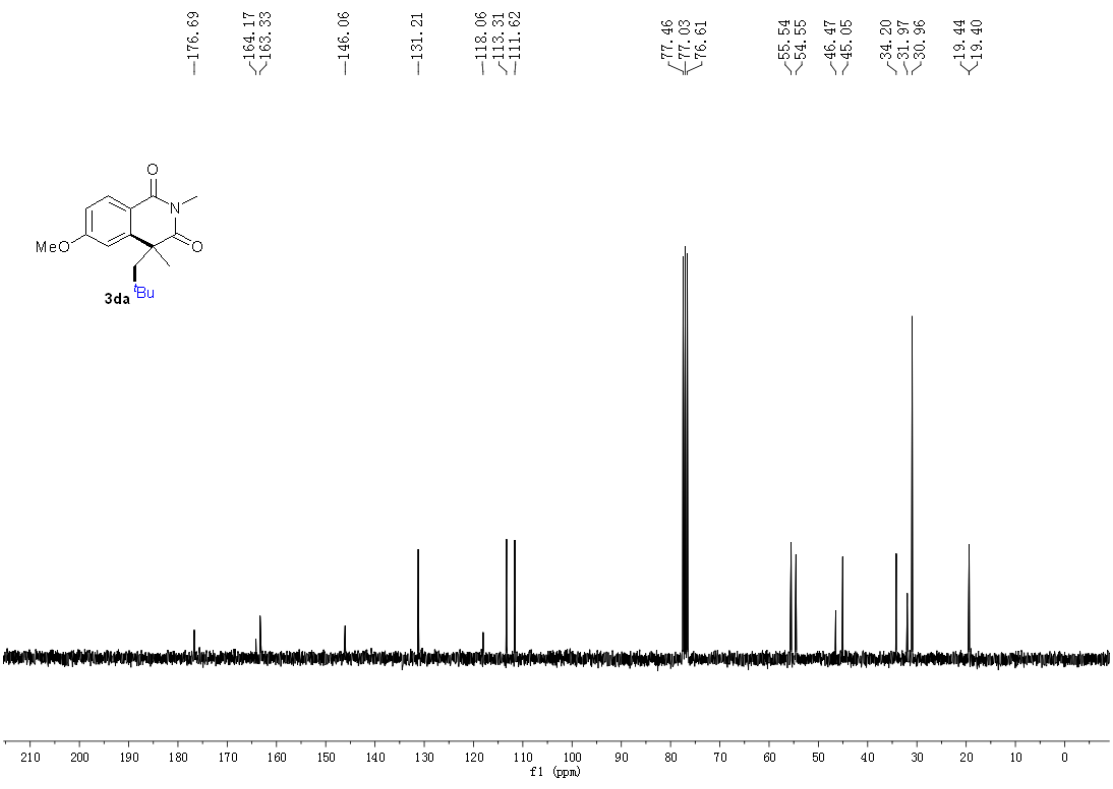
8.1665
7.2675
6.9532
6.9449
6.9238
6.9156
6.8564
6.8482
5.2630
5.2398
5.2167
5.1935
5.1704
3.8853
2.5562
2.5085
1.9775
1.9298
1.5430
1.4849
1.4715
1.4618
1.4484
0.5980
MeO
3da
tBu
1.08
1.01
0.97
1.05
3.00
1.03
1.08
3.02
6.24
8.86
f1 (ppm)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164.17
163.33
146.06
131.21
118.06
113.31
111.62
77.46
77.03
76.61
55.54
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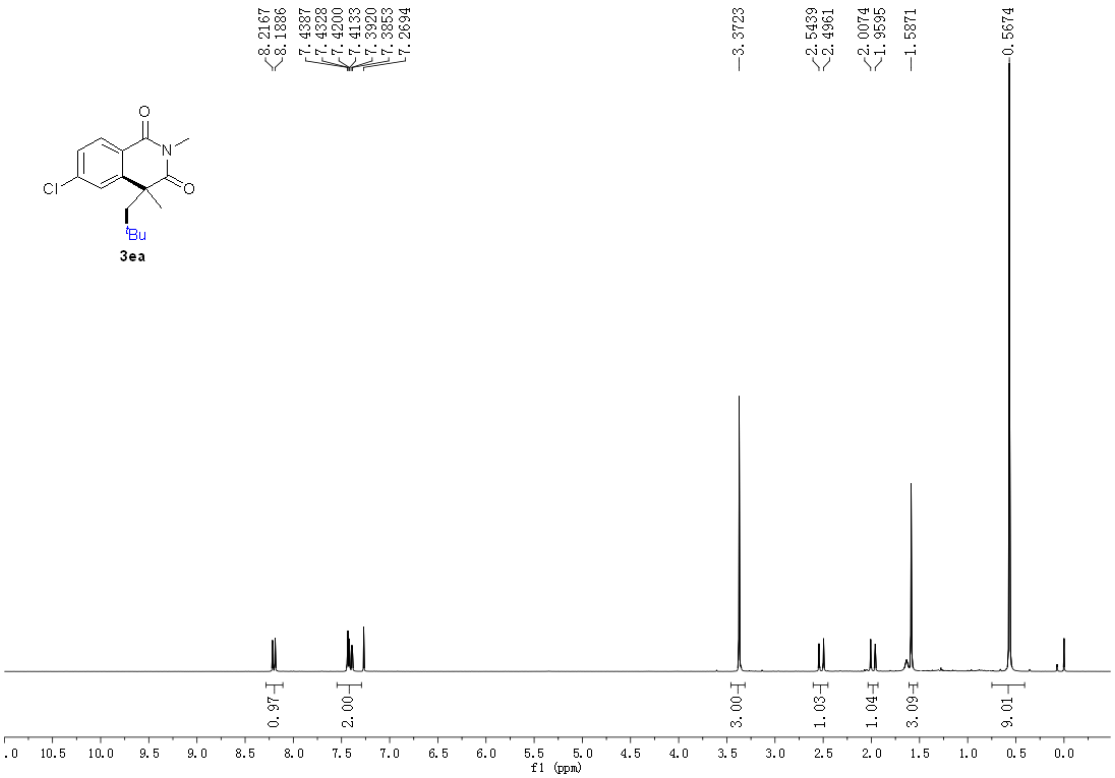
19.44
19.40
MeO
3da
tBu
f1 (ppm)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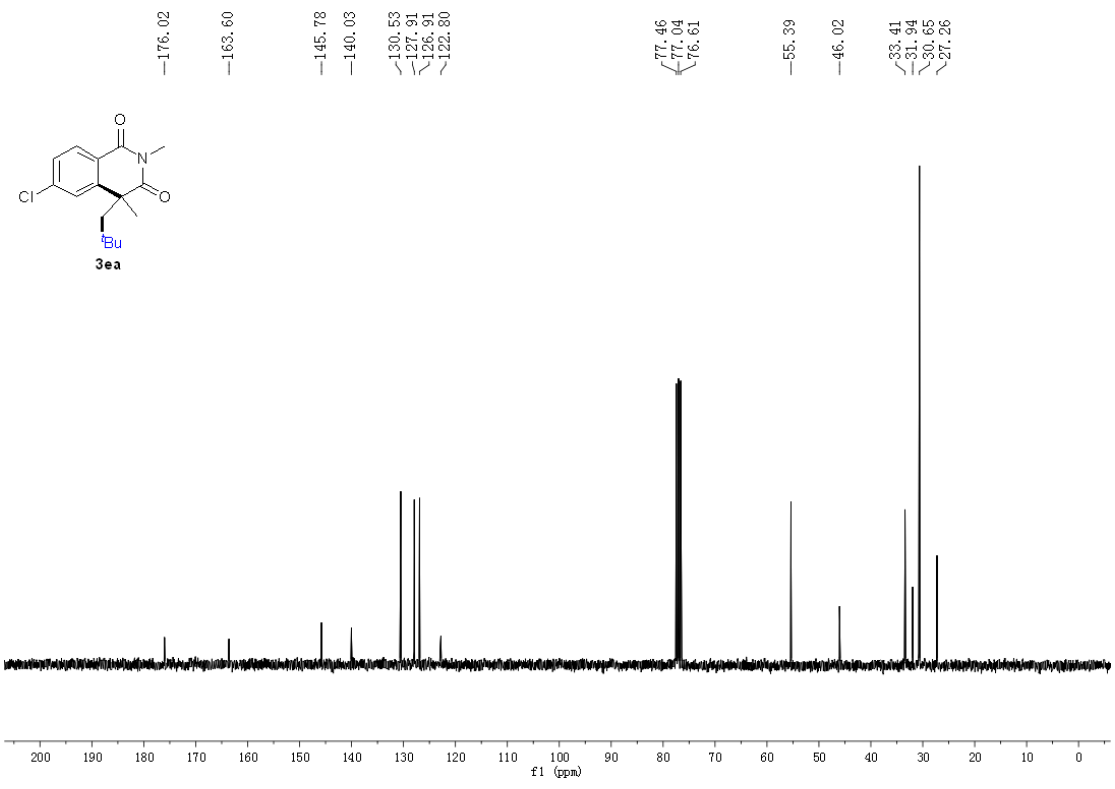
8.1886
7.4387
7.4328
7.4200
7.4133
7.3920
7.3853
7.2694
3.3723
2.5439
2.4961
2.0074
1.9595
1.5871
0.5674
0.97
2.00
3.00
1.03
1.04
3.09
9.01
f1 (ppm)
3ea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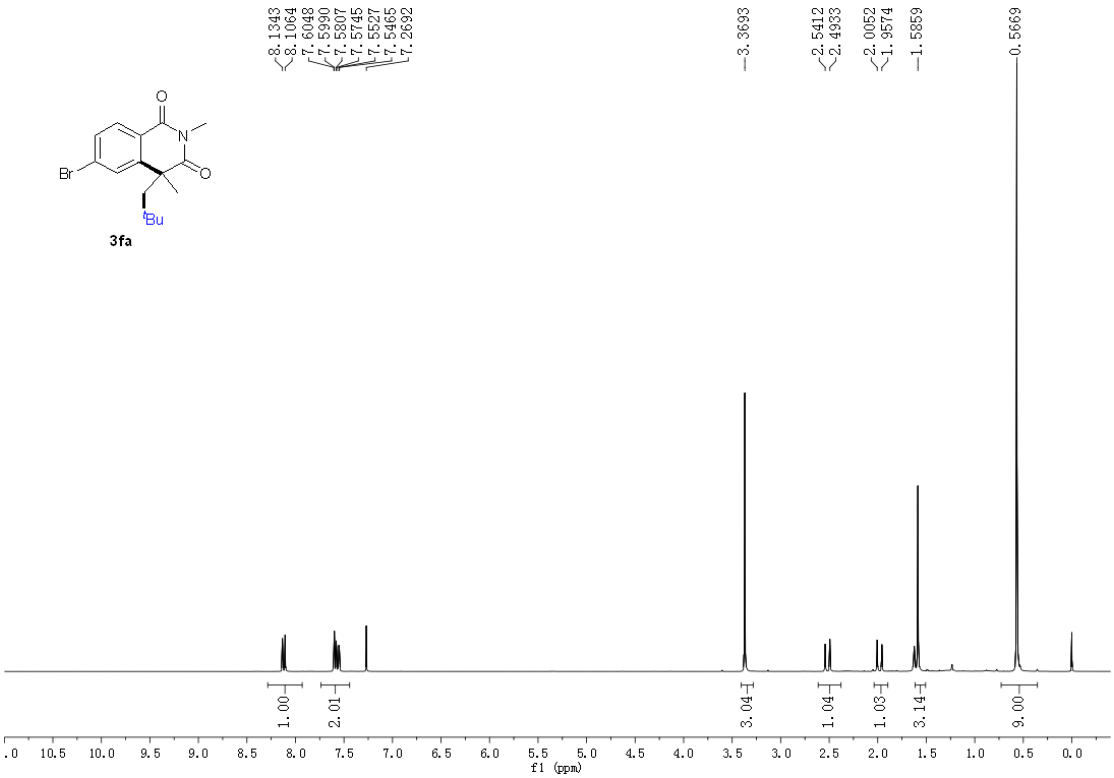
163.60
145.78
140.03
130.53
127.91
126.91
122.80
77.46
77.04
76.61
55.39
46.02
33.41
31.94
30.65
27.26
f1 (ppm)
3ea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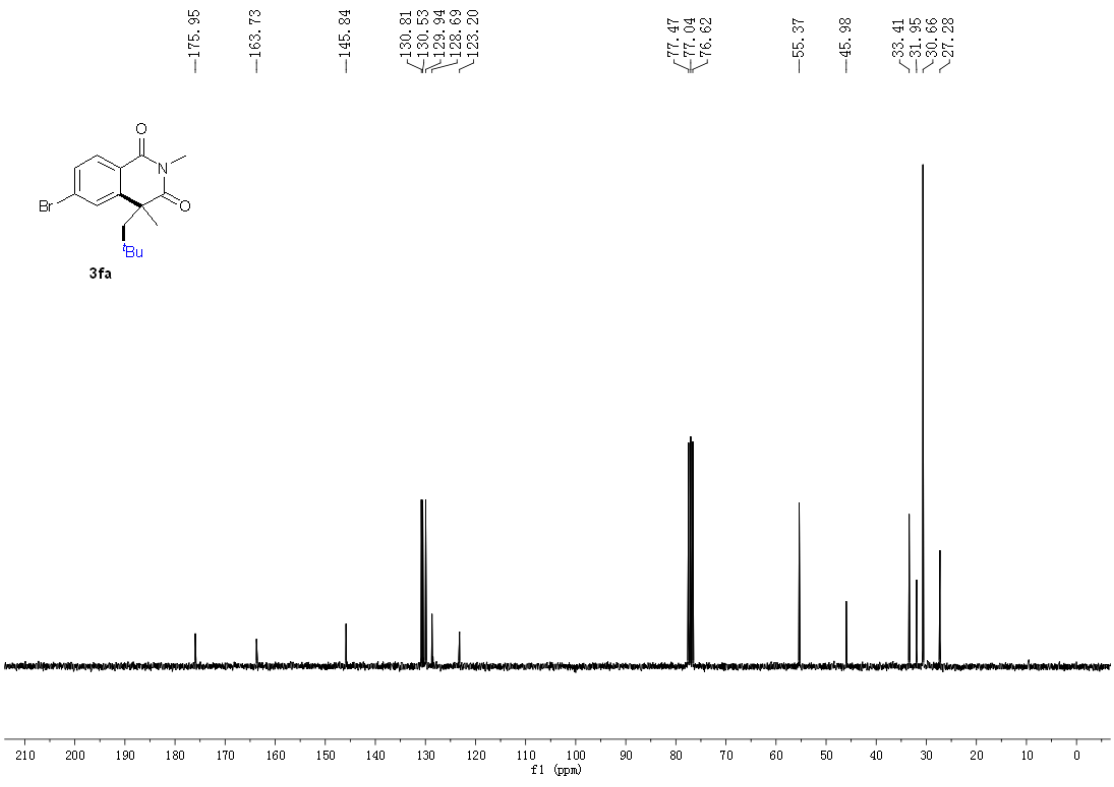
7.5807
7.5745
7.5527
7.5465
7.2692
3.3693
2.5412
2.4933
2.0052
1.9574
1.5859
0.5669
1.00
2.01
3.04
1.04
1.03
3.14
9.00
f1 (ppm)
Br
tBu
3fa


175.95
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130.53
129.94
128.69
123.20
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77.04
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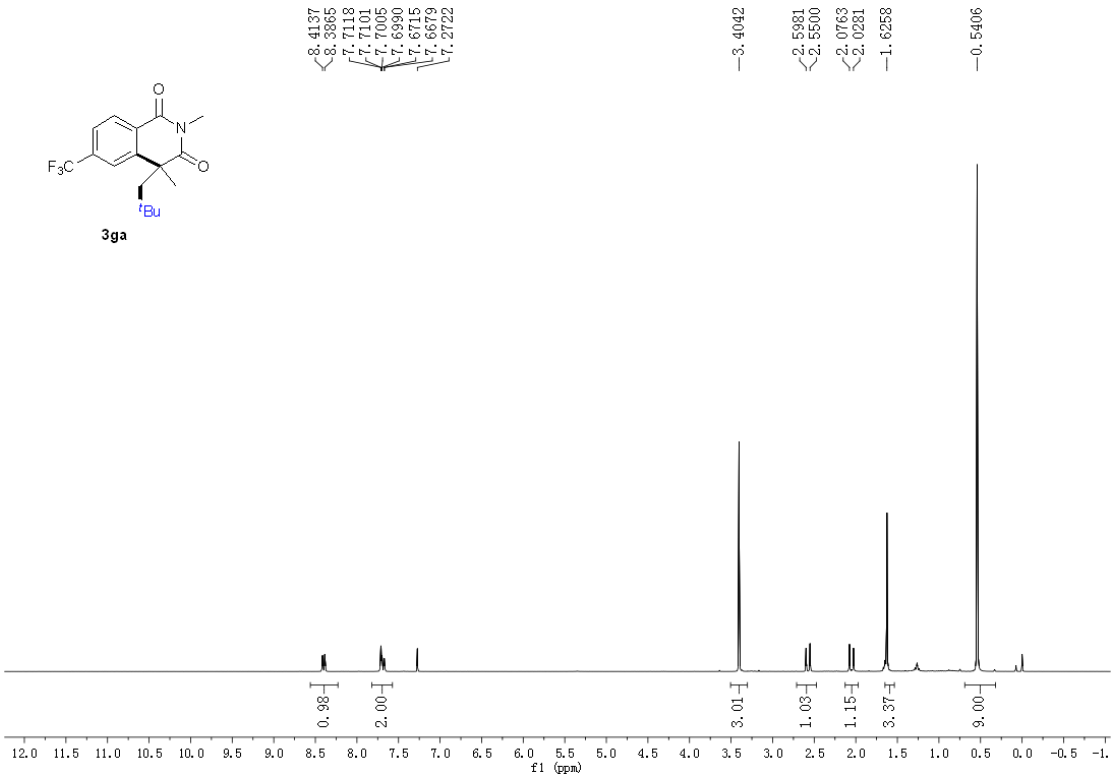
55.37
45.98
33.41
31.95
30.66
27.28
f1 (ppm)
Br
tBu
3fa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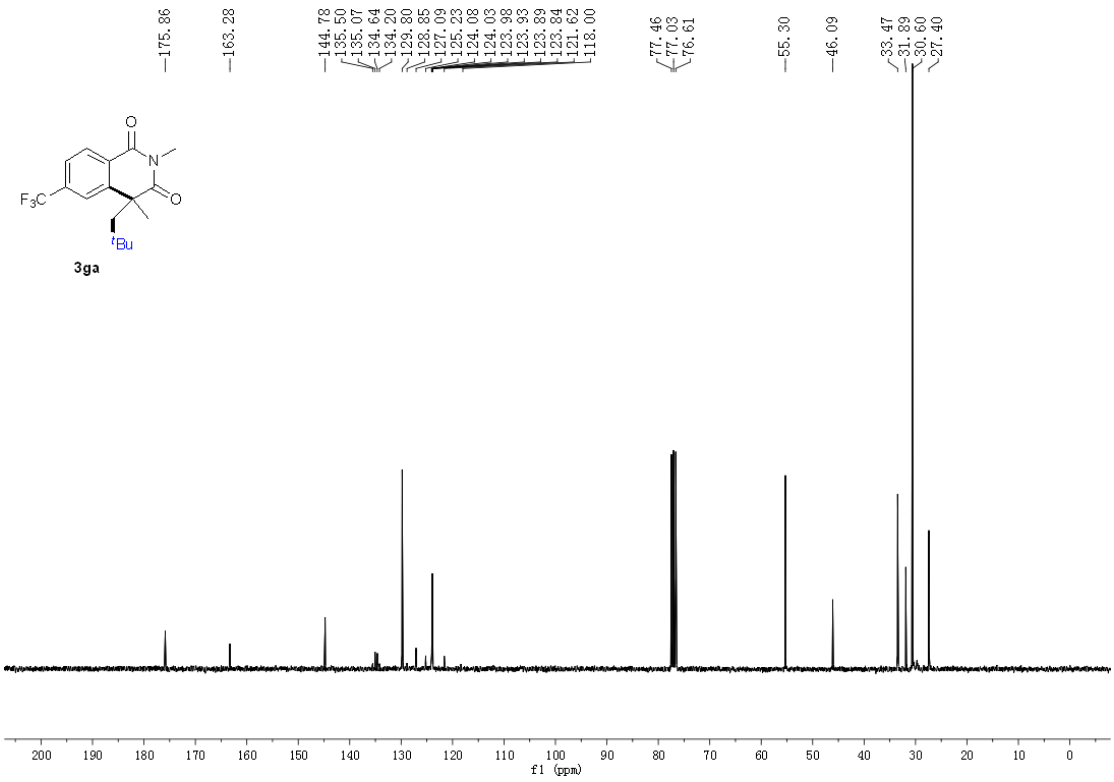
7.7005
7.6990
7.6715
7.6679
7.2722
3.4042
2.5981
2.5500
2.0763
2.0281
1.6258
0.5406
O
N
O
F3C
tBu
3ga
0.98
2.00
3.01
1.03
1.15
3.37
9.00
f1 (ppm)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163.28
144.78
135.50
135.07
134.64
134.20
129.80
128.85
127.09
125.23
124.08
124.03
123.98
123.93
123.89
123.84
121.62
118.00
77.46
77.03
76.61
55.30
46.09
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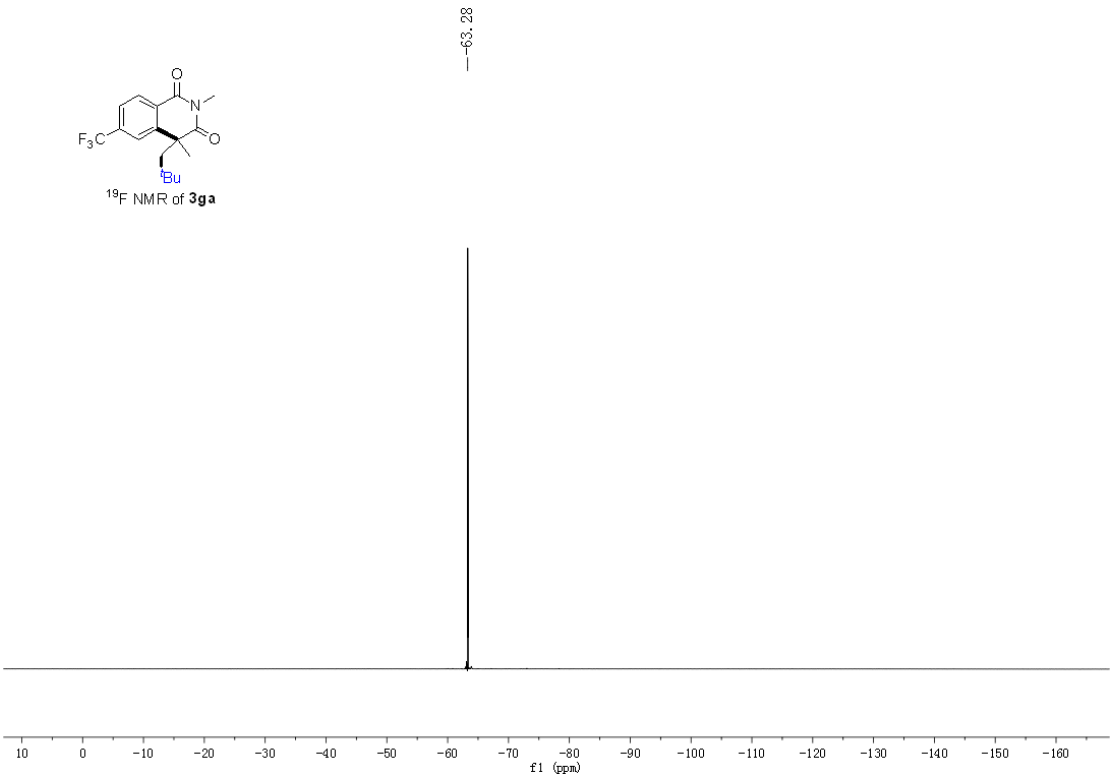
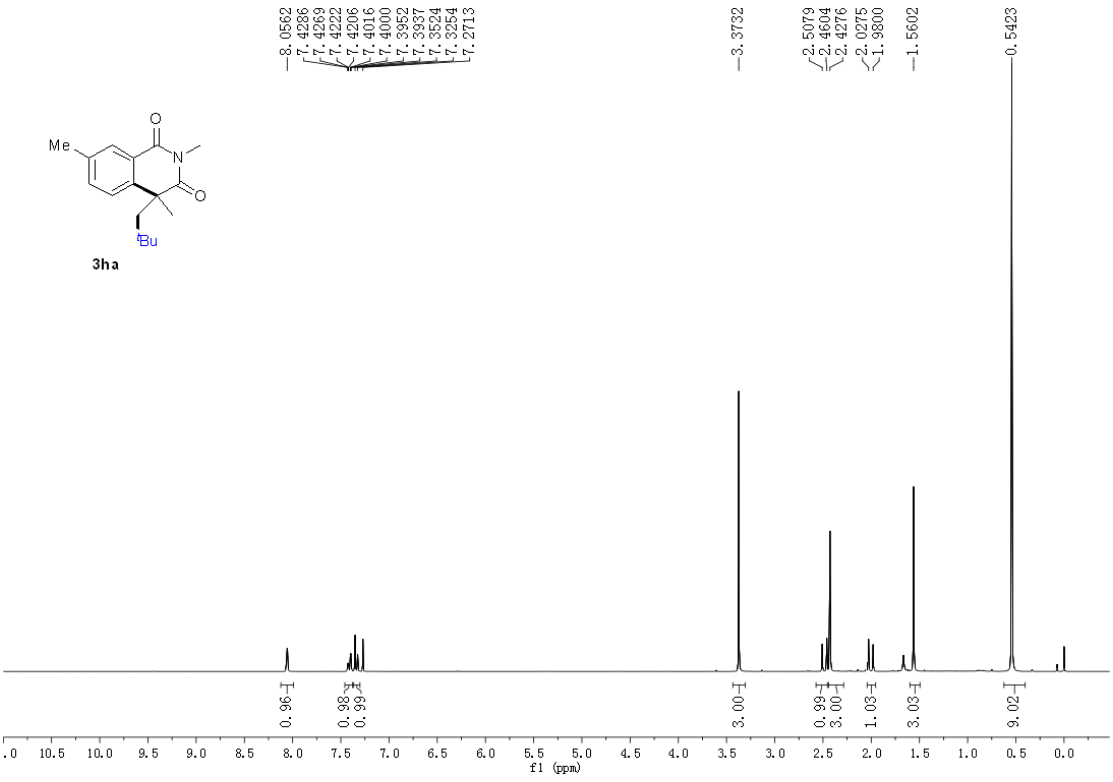
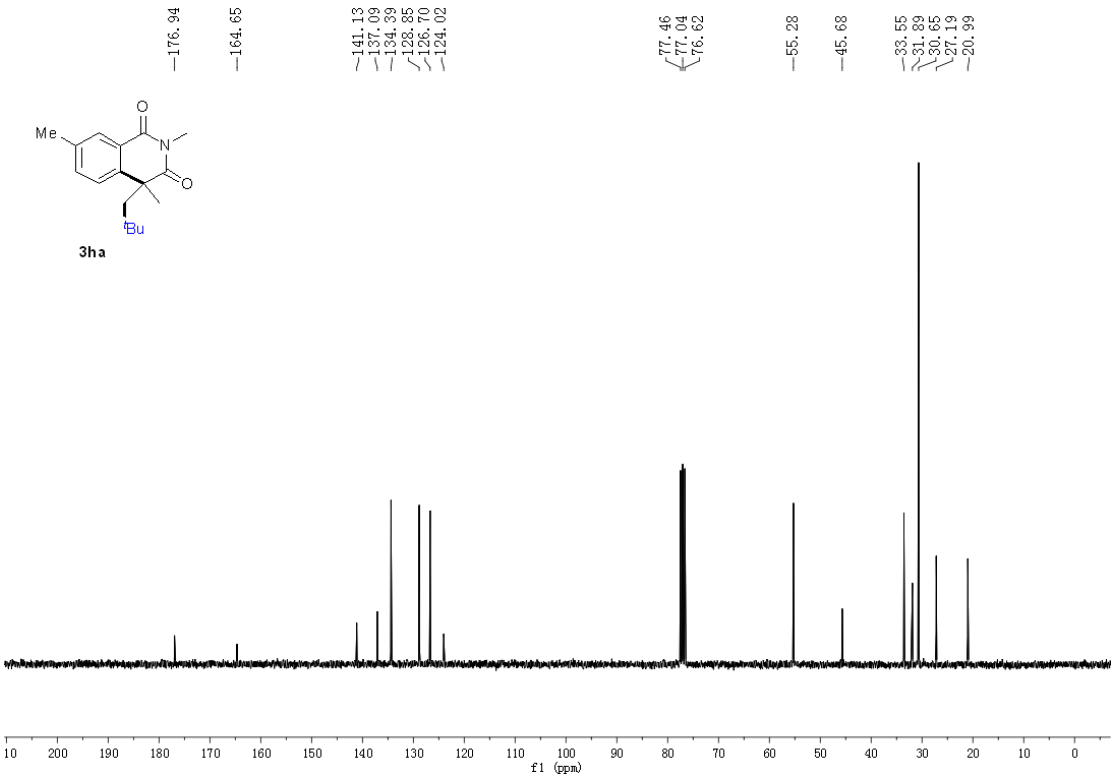
O
N
O
F3C
tBu
3ga
f1 (ppm)



^{19}F NMR of **3ga**



3ha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141.13
137.09
134.39
128.85
126.70
124.02
77.46
77.04
76.62
55.28
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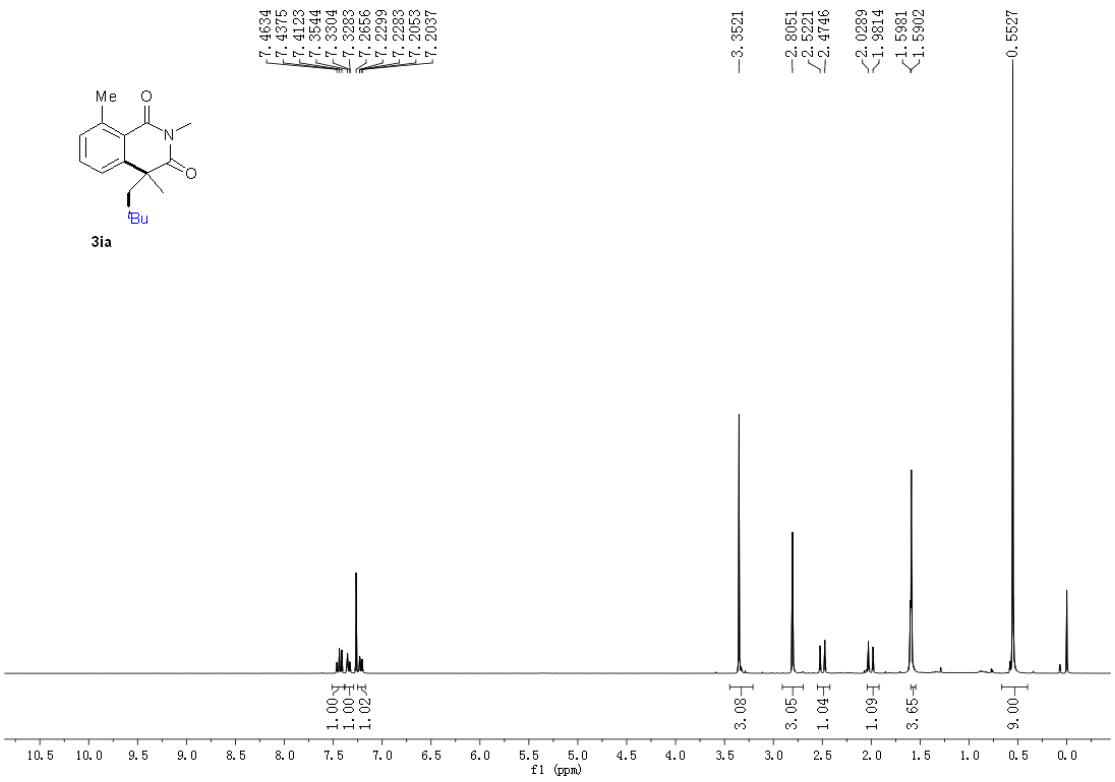
Me
O
N
O
tBu
3ha
f1 (ppm)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7.4123
7.3544
7.3304
7.3283
7.2656
7.2299
7.2283
7.2053
7.2037
3.3521
2.8051
2.5221
2.4746
2.0289
1.9814
1.5981
1.5902
0.5527
Me
O
N
O
tBu
3ia
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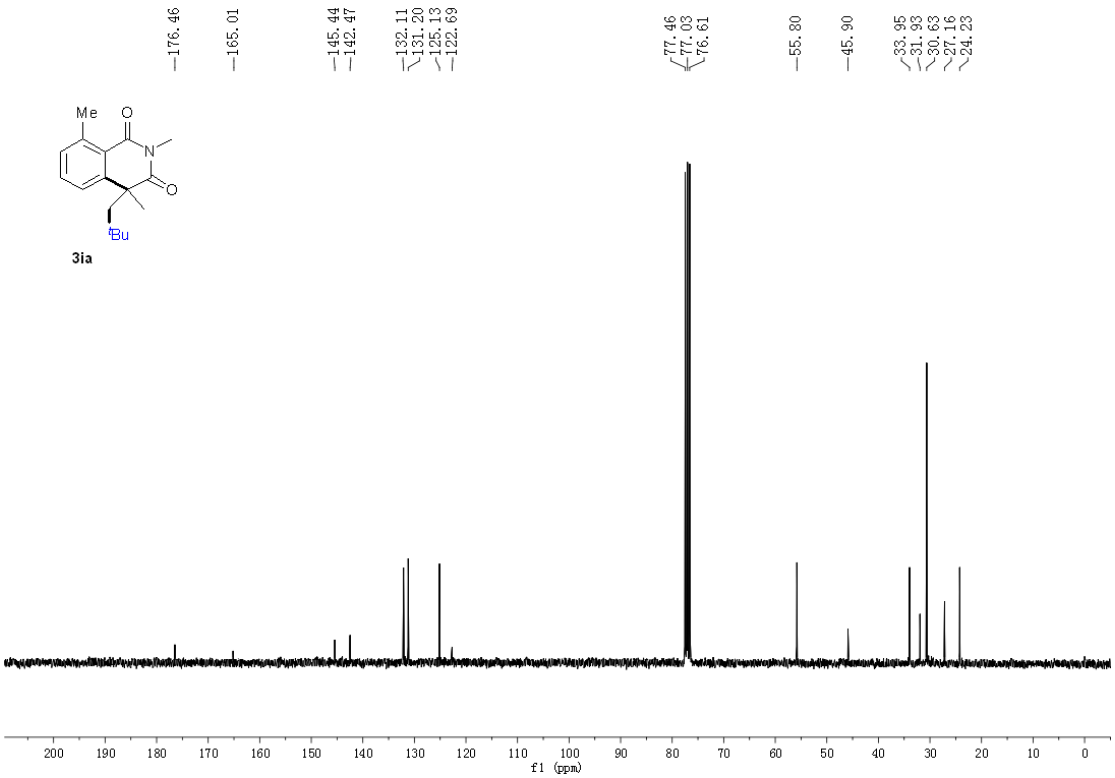
1.00
1.02
3.08
3.05
1.04
1.09
3.65
9.00
f1 (ppm)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142.47
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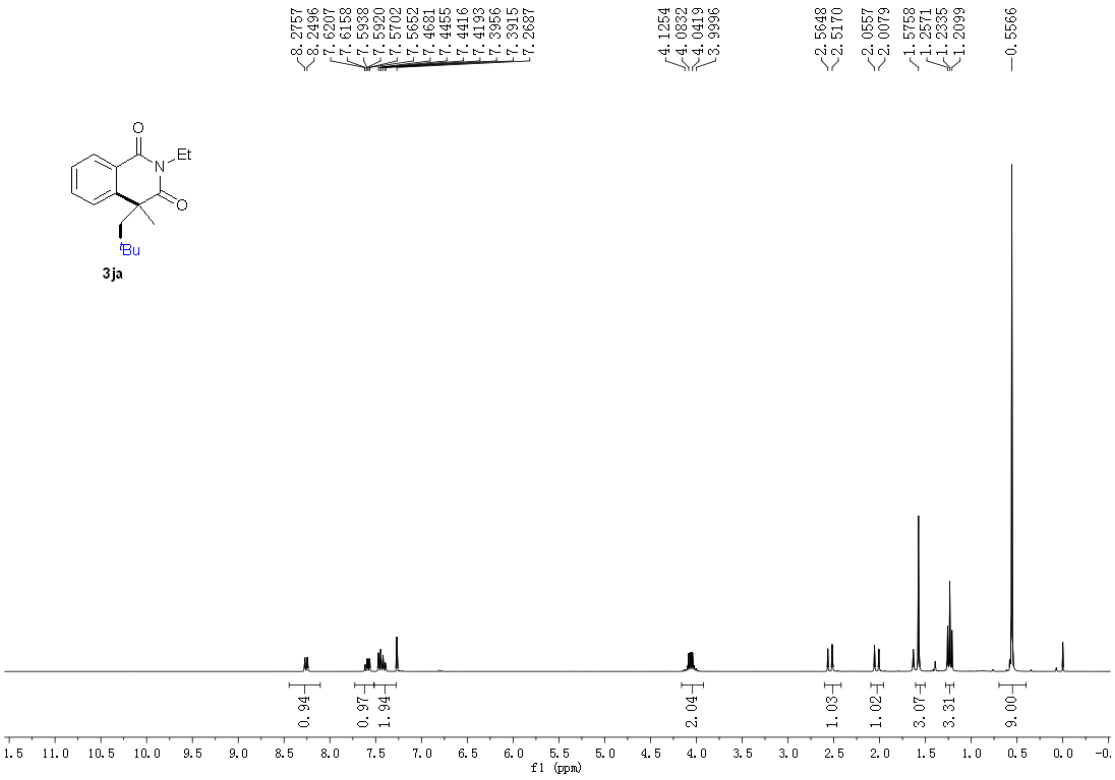
131.20
125.13
122.69
77.46
77.03
76.61
55.80
45.90
33.95
31.93
30.63
27.16
24.23
Me
O
N
O
tBu
3ia
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5702
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7.4455
7.4416
7.4193
7.3956
7.3915
7.2687
4.1254
4.0832
4.0419
3.9996
2.5648
2.5170
2.0557
2.0079
1.5758
1.2571
1.2335
1.2099
0.5566
O
N
Et
O
tBu
3ja
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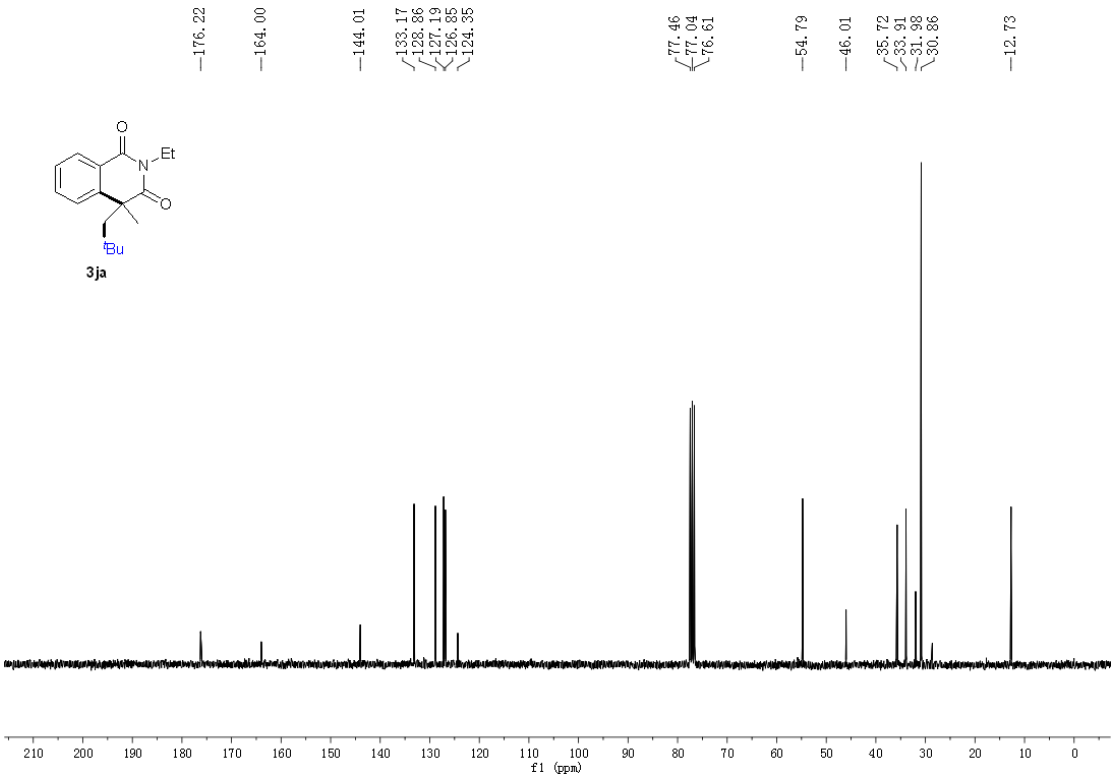
0.97
1.94
2.04
1.03
1.02
3.07
3.31
9.00
f1 (ppm)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124.35
77.46
77.04
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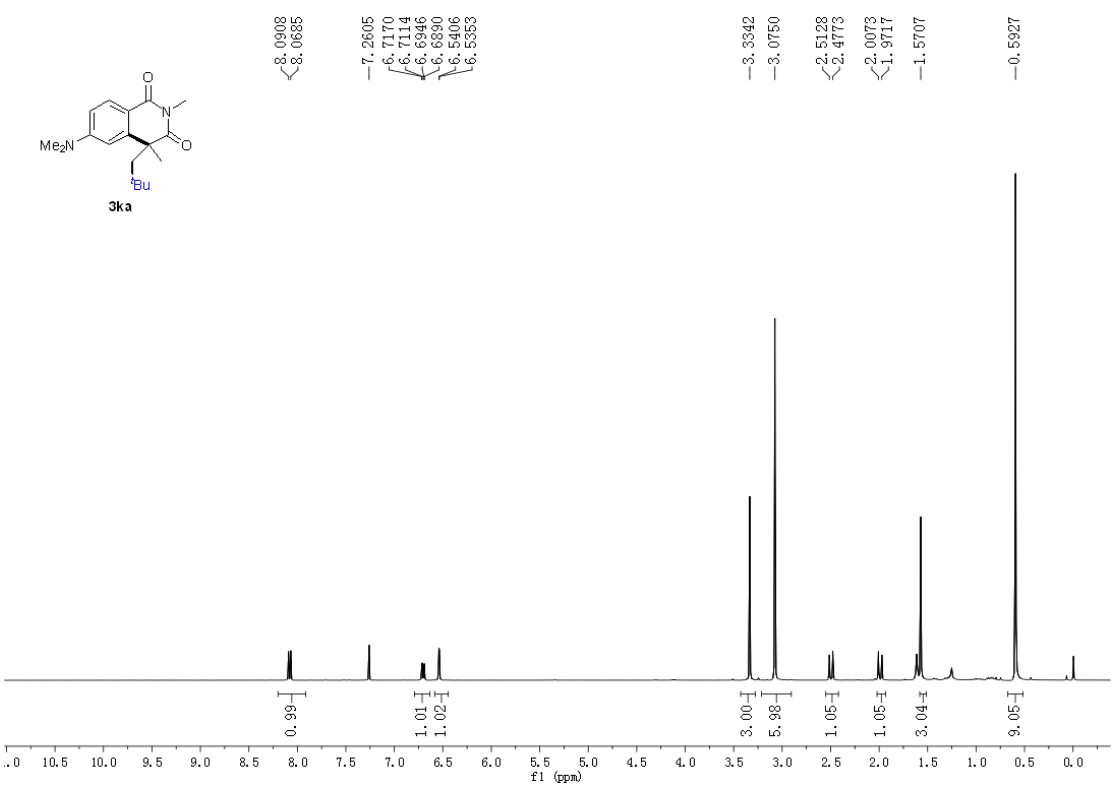
30.86
12.73
Et
tBu
3ja
f1 (ppm)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6.7170
6.7114
6.6946
6.6890
6.5406
6.5353
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3.0750
2.5128
2.4773
2.0073
1.9717
1.5707
0.5927
Me2N
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1.02
3.00
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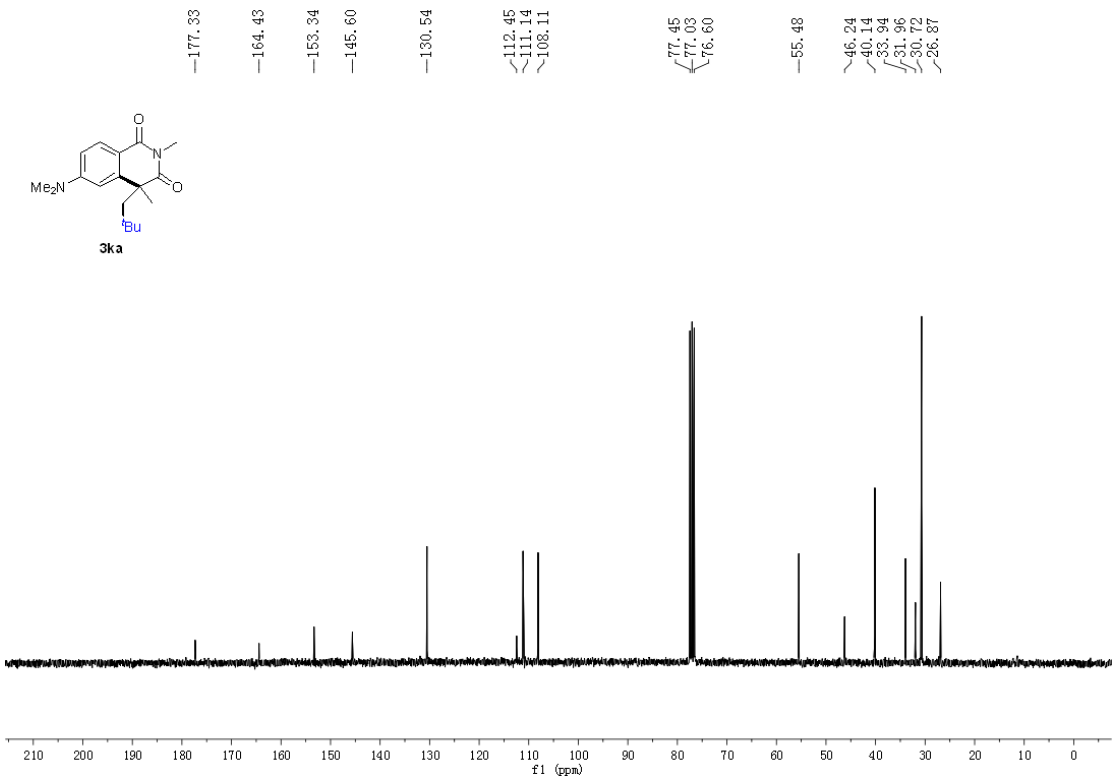
1.05
3.04
9.05
f1 (ppm)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130.54
112.45
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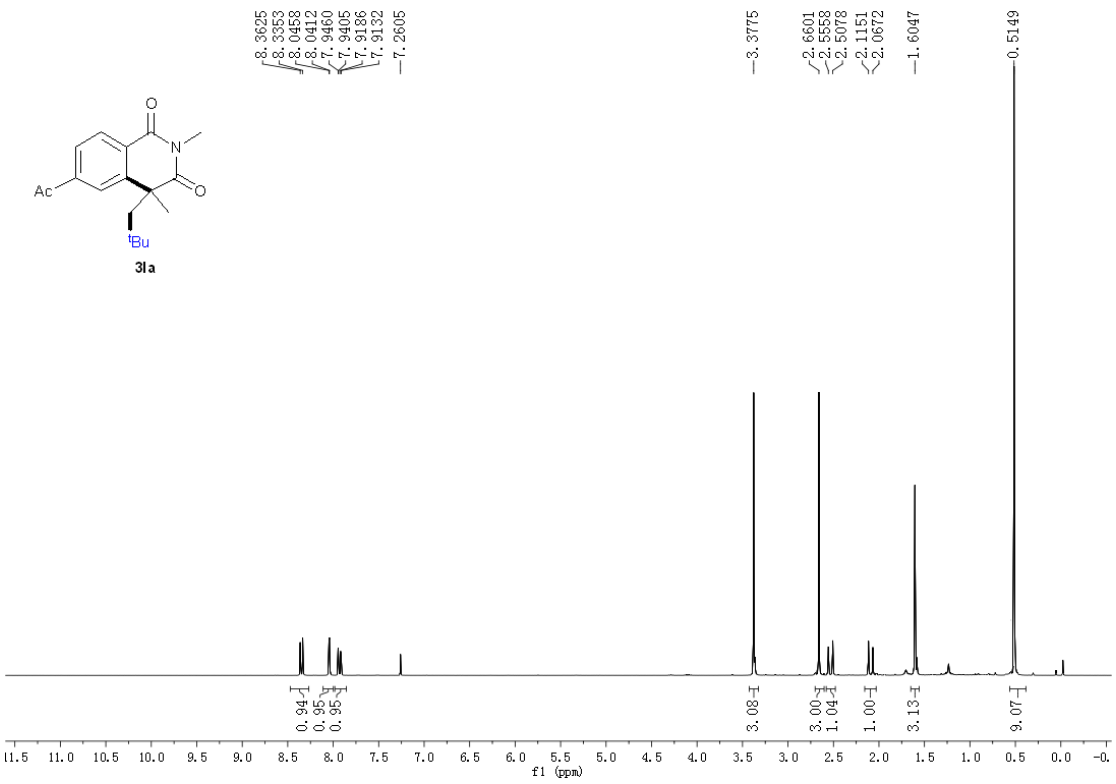
108.11
77.45
77.03
76.60
55.48
46.24
40.14
33.94
31.96
30.72
26.87
Me2N
tBu
3ka
f1 (ppm)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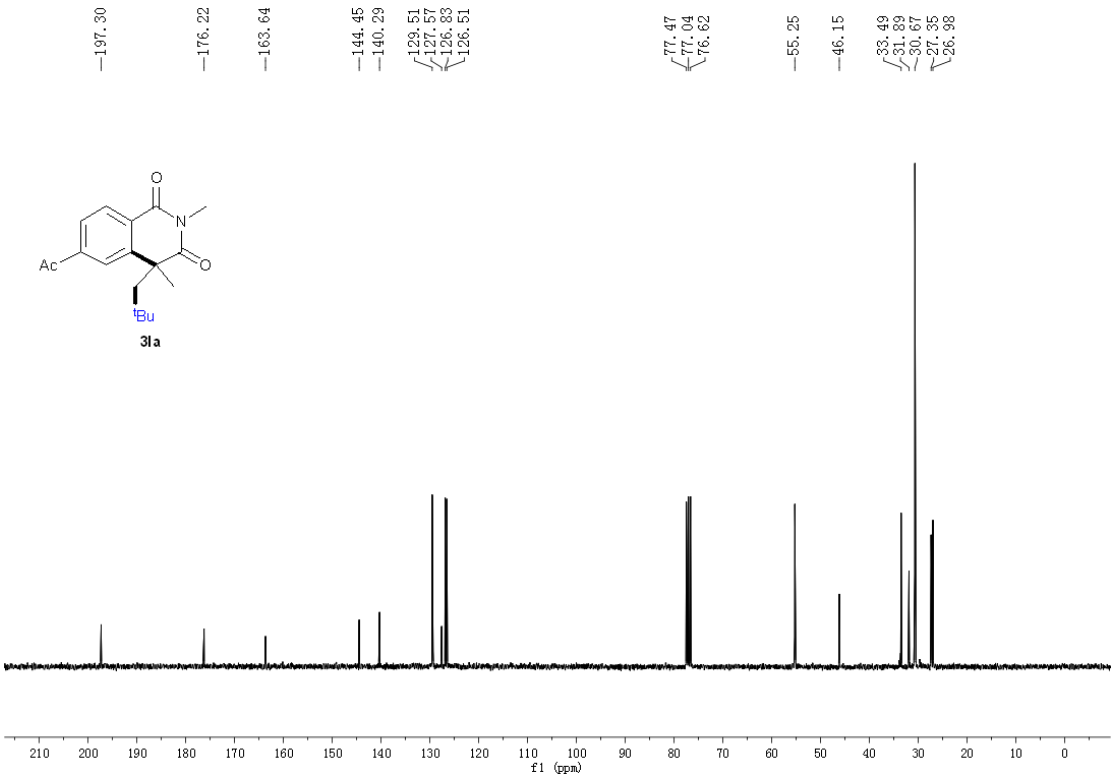
8.0458
8.0412
7.9460
7.9405
7.9186
7.9132
7.2605
3.3775
2.6601
2.5558
2.5078
2.1151
2.0672
1.6047
0.5149
Ac
tBu
3la
0.94
0.95
0.95
3.08
3.00
1.04
1.00
3.13
9.07
f1 (ppm)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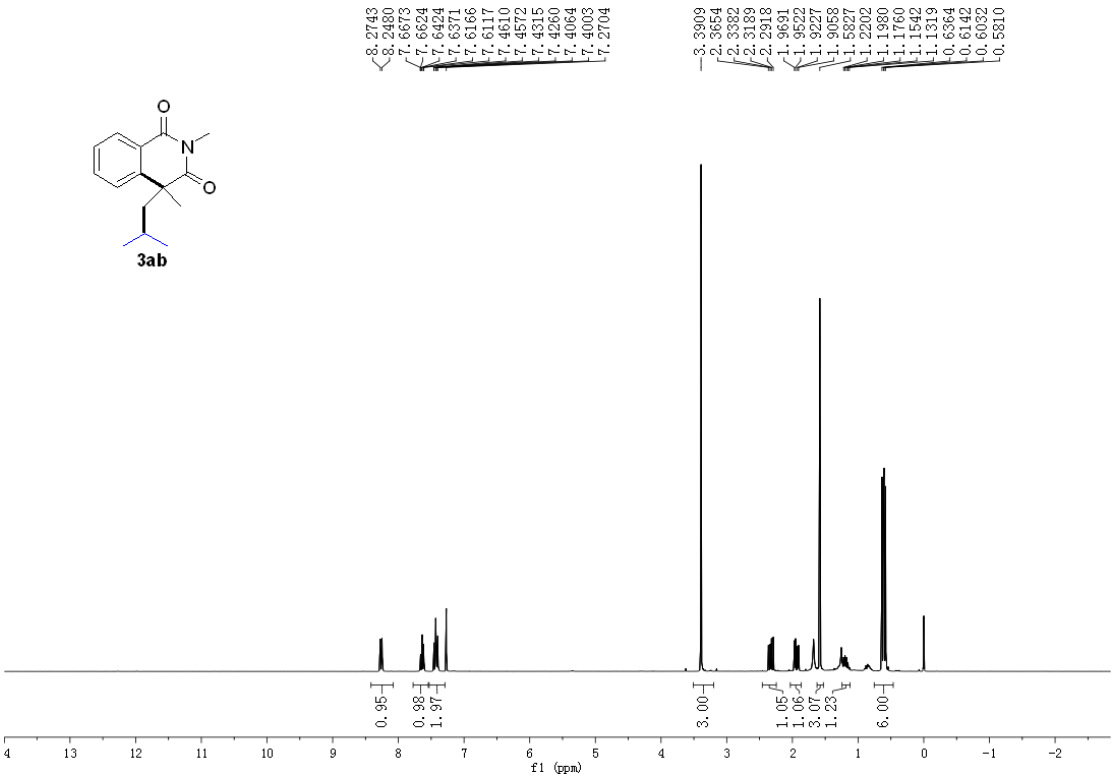
176.22
163.64
144.45
140.29
129.51
127.57
126.83
126.51
77.47
77.04
76.62
55.25
46.15
33.49
31.89
30.67
27.35
26.98
Ac
tBu
3la
f1 (ppm)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7.6673
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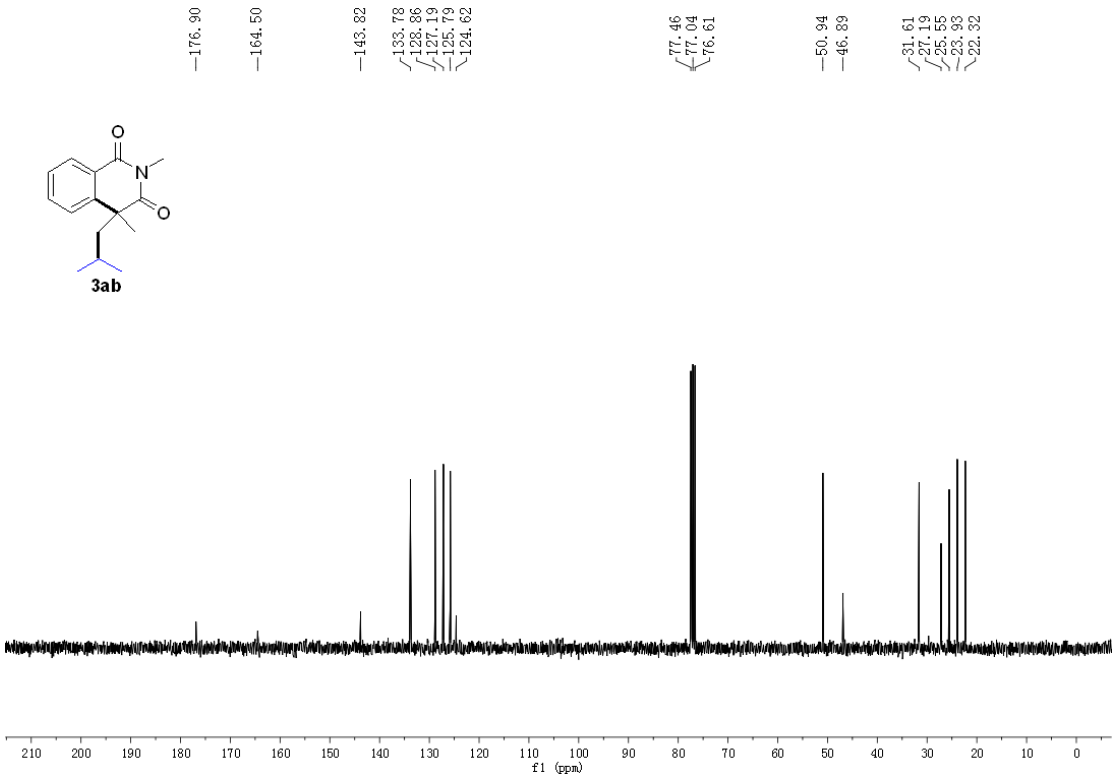
7.6424
7.6371
7.6166
7.6117
7.4610
7.4572
7.4315
7.4260
7.4064
7.4003
7.2704
3.3909
2.3654
2.3382
2.3189
2.2918
1.9691
1.9522
1.9227
1.9058
1.5827
1.2202
1.1980
1.1760
1.1542
1.1319
0.6364
0.6142
0.6032
0.5810
3ab
0.95
0.98
1.97
3.00
1.05
1.06
3.07
1.23
6.00
f1 (ppm)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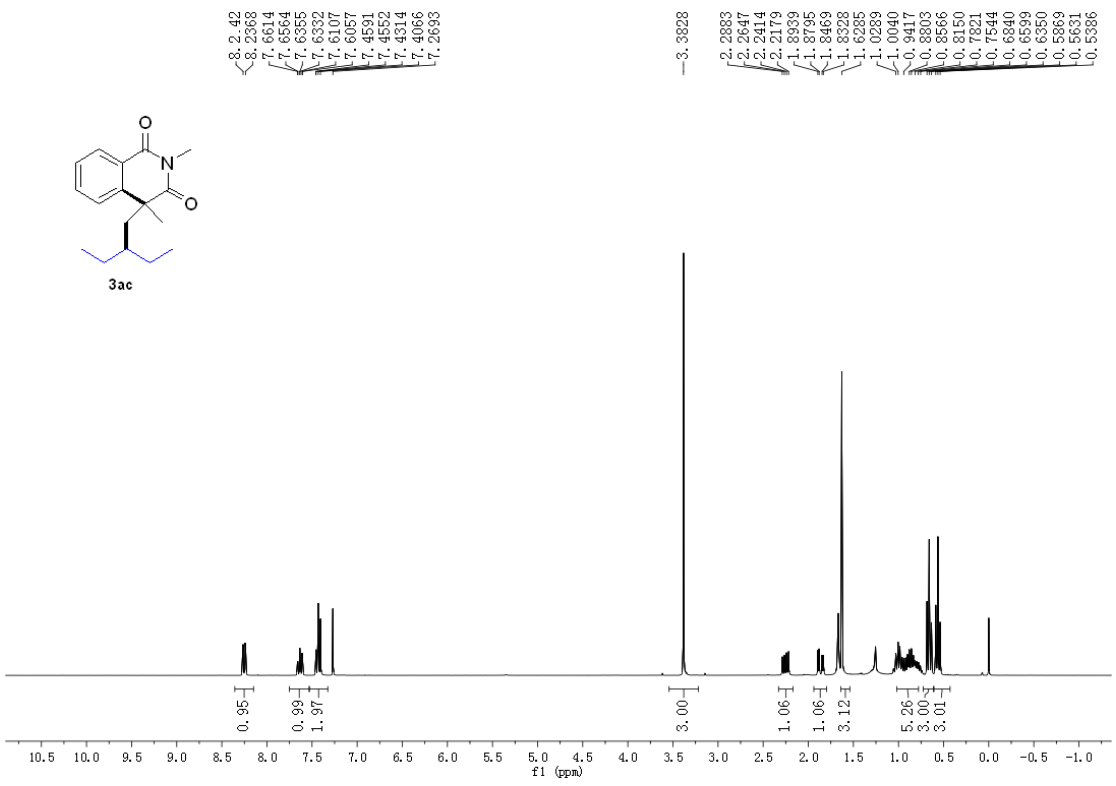
143.82
133.78
128.86
127.19
125.79
124.62
77.46
77.04
76.61
50.94
46.89
31.61
27.19
25.55
23.93
22.32
3ab
f1 (ppm)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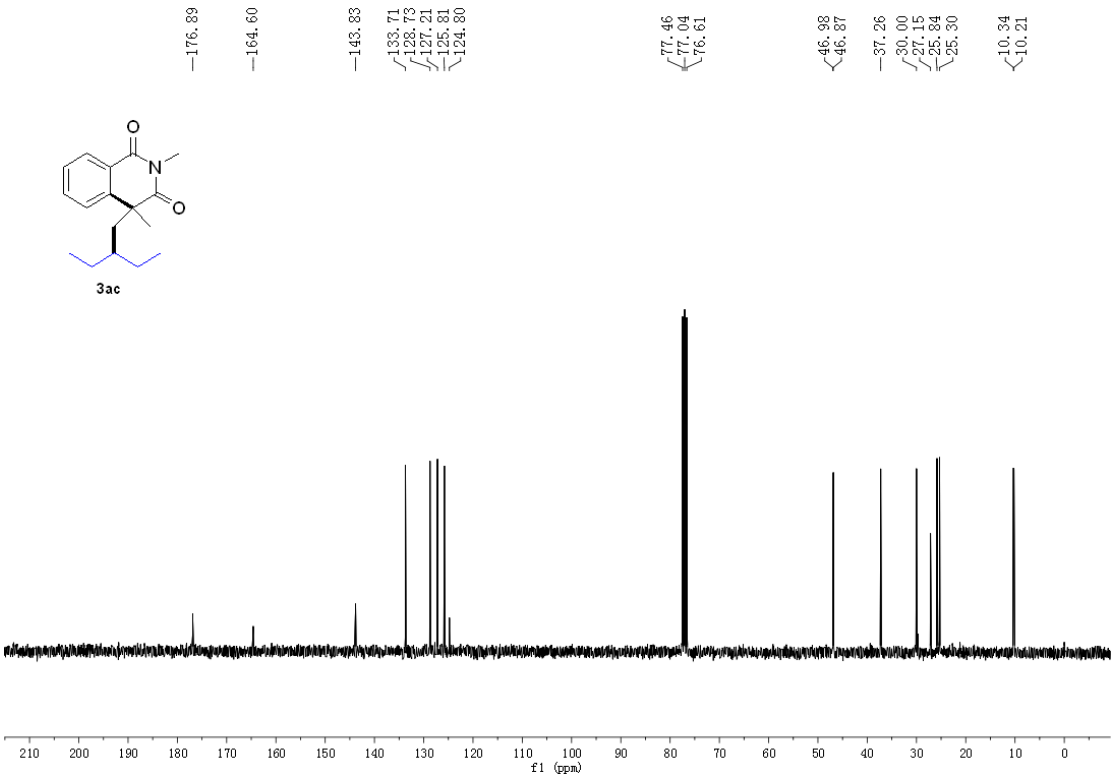
7.6355
7.6332
7.6107
7.6057
7.4591
7.4552
7.4314
7.4066
7.2693
3.3828
2.2883
2.2647
2.2414
2.2179
1.8939
1.8795
1.8469
1.8328
1.6285
1.0289
1.0040
0.9417
0.8803
0.8566
0.8150
0.7821
0.7544
0.6840
0.6599
0.6350
0.5869
0.5631
0.5386
3ac
0.95
0.99
1.97
3.00
1.06
1.06
3.12
5.26
3.00
3.01
f1 (ppm)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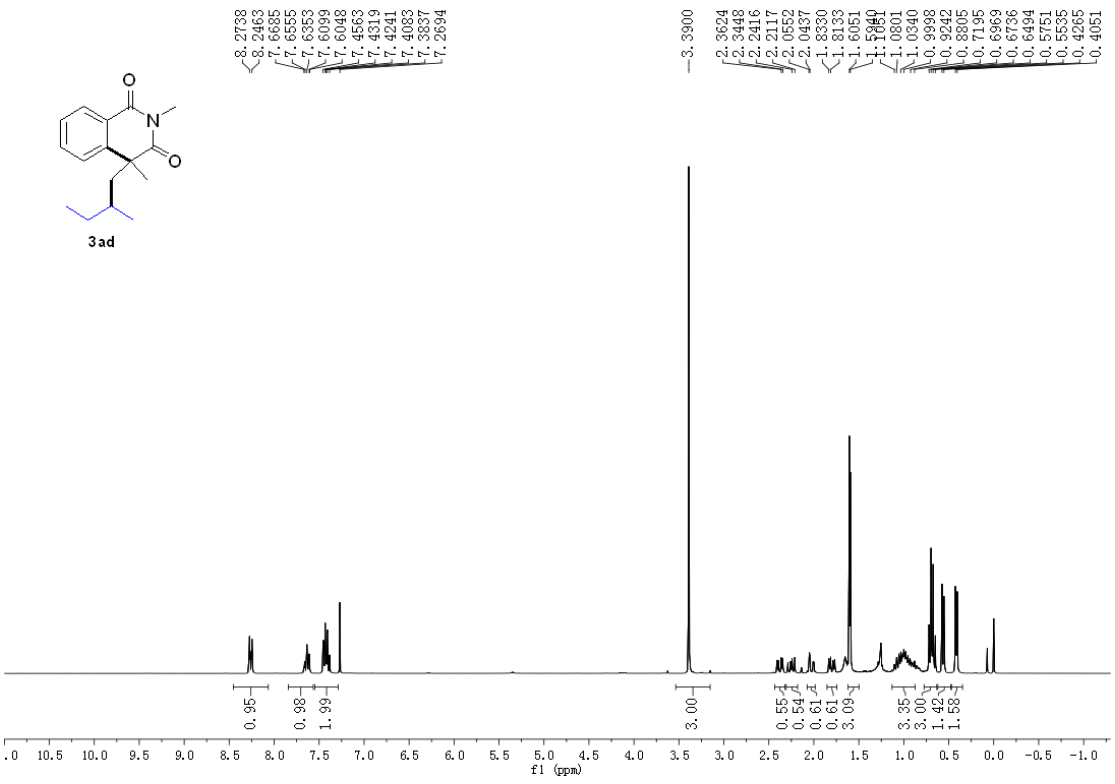
143.83
133.71
128.73
127.21
125.81
124.80
77.46
77.04
76.61
46.98
46.87
37.26
30.00
27.15
25.84
25.30
10.34
10.21
3ac
f1 (ppm)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7.6353
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7.6048
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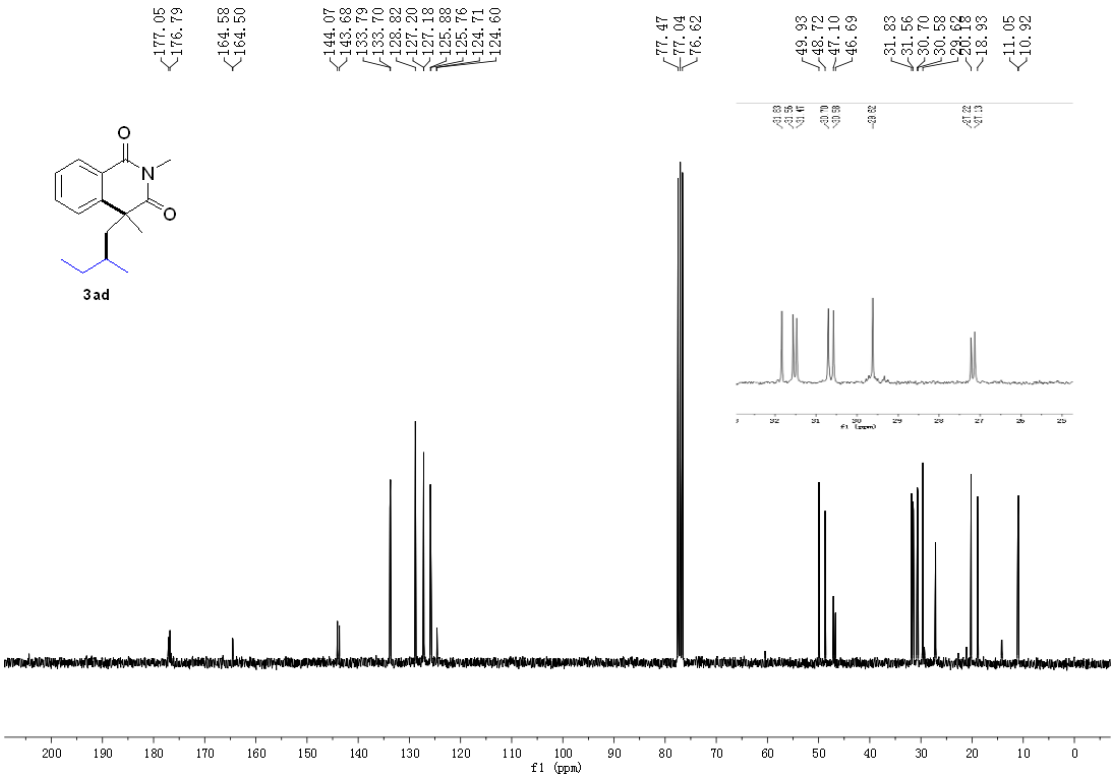
7.4319
7.4241
7.4083
7.3837
7.2694
3.3900
2.3624
2.3448
2.2416
2.2117
2.0552
2.0437
1.8330
1.8133
1.6051
1.0801
1.0340
0.9998
0.9242
0.8805
0.7195
0.6969
0.6736
0.6494
0.5751
0.5535
0.4265
0.4051
0.95
0.98
1.99
3.00
0.55
0.54
0.61
0.61
3.09
3.35
3.00
1.42
1.58
3ad
f1 (ppm)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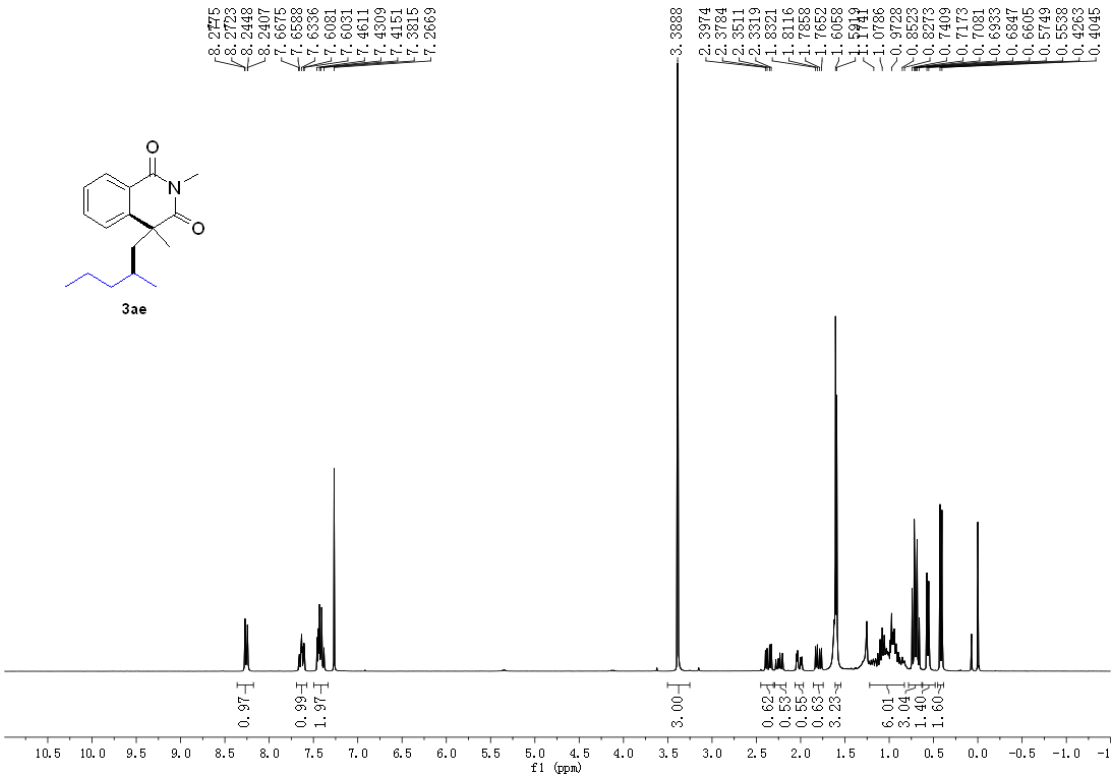
176.79
164.58
164.50
144.07
143.68
133.79
133.70
128.82
127.20
127.18
125.88
125.76
124.71
124.60
77.47
77.04
76.62
49.93
48.72
47.10
46.69
31.83
31.56
30.70
30.58
18.93
11.05
10.92
3ad
f1 (ppm)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8.2448
8.2407
7.6675
7.6588
7.6336
7.6081
7.6031
7.4611
7.4309
7.4151
7.3815
7.2669
3.3888
2.3974
2.3784
2.3511
2.3319
1.8321
1.8116
1.7858
1.7652
1.6058
1.5919
1.1741
1.0786
0.9728
0.8523
0.8273
0.7409
0.7173
0.7081
0.6933
0.6847
0.6605
0.5749
0.5538
0.4263
0.4045
0.97
0.99
1.97
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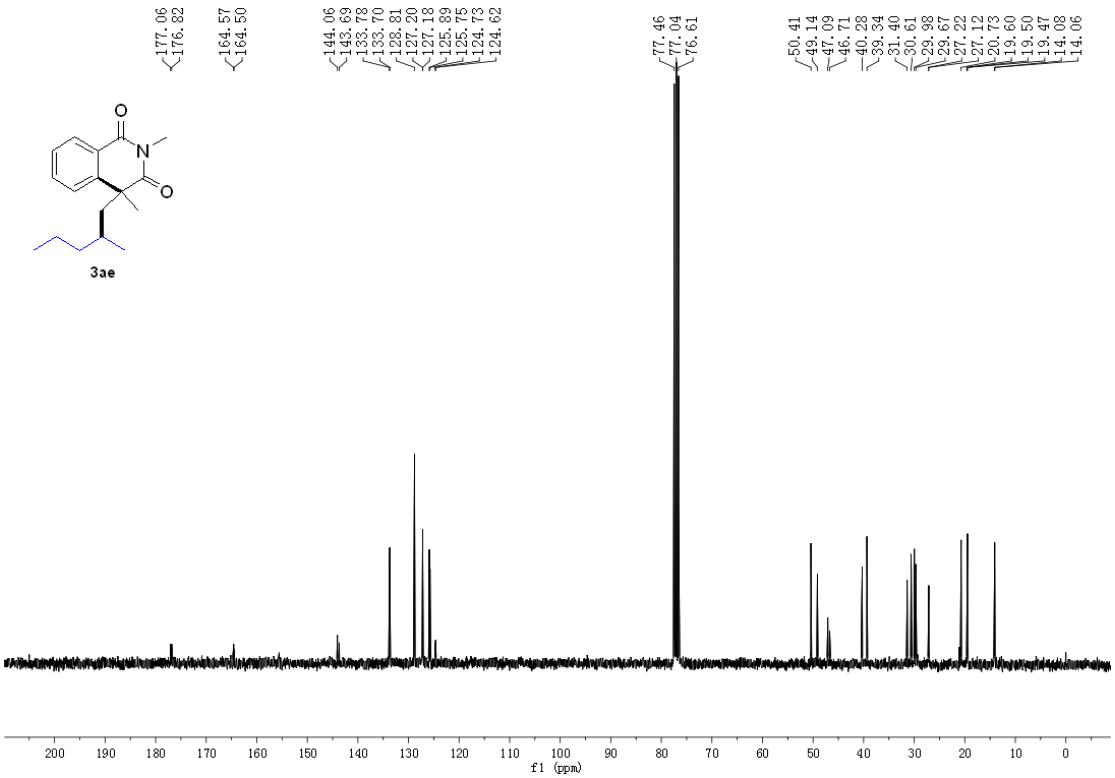
0.53
0.55
0.63
3.23
6.01
3.04
1.40
1.60
3ae
f1 (ppm)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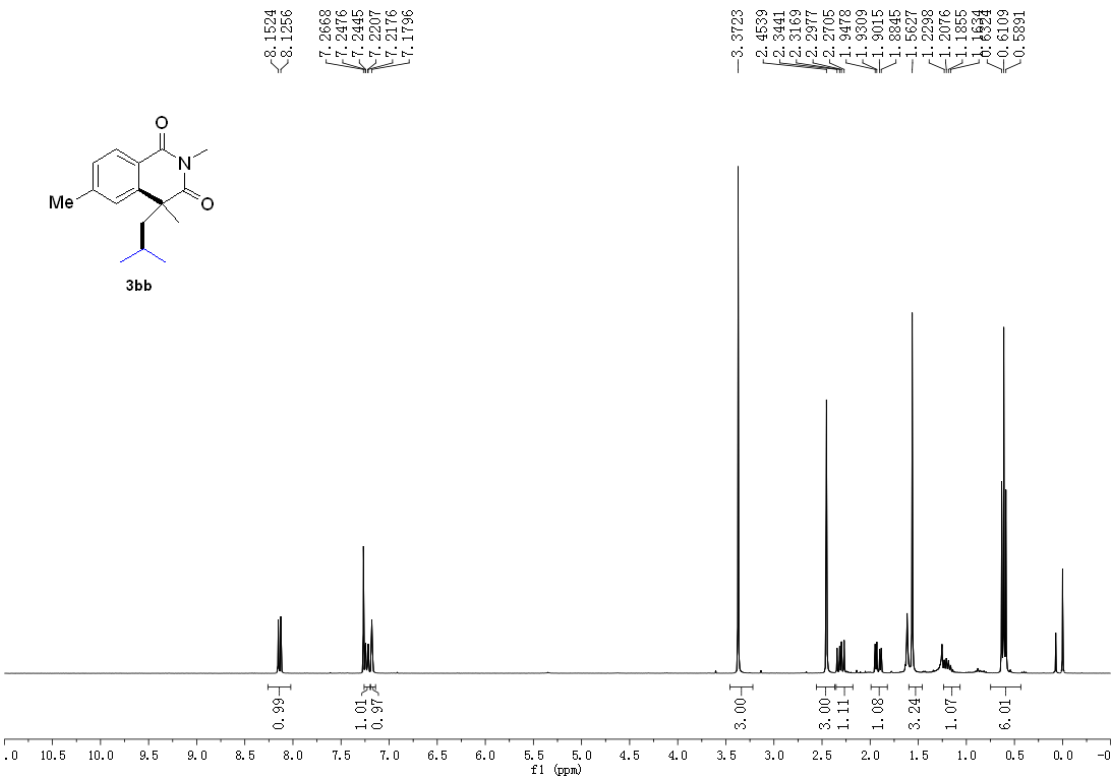
176.82
164.57
164.50
144.06
143.69
133.78
133.70
128.81
127.20
127.18
125.89
125.75
124.73
124.62
77.46
77.04
76.61
50.41
49.14
47.09
46.71
40.28
39.34
31.40
30.61
29.98
29.67
27.22
27.12
20.73
19.60
19.50
19.47
14.08
14.06
O
N
O
3ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2176
7.1796
3.3723
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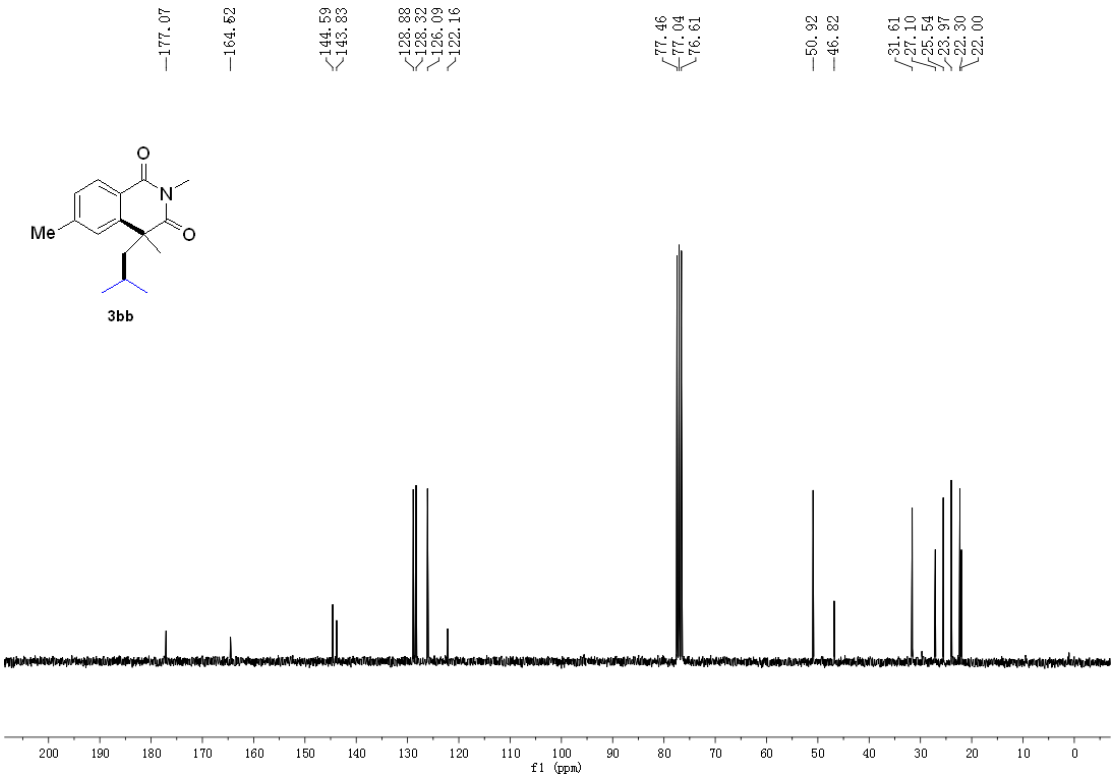
2.3441
2.3169
2.2977
2.2705
1.9478
1.9309
1.9015
1.8845
1.5627
1.2298
1.2076
1.1855
1.1634
0.6324
0.6109
0.5891
O
N
O
Me
3bb
0.99
1.01
0.97
3.00
3.00
1.11
1.08
3.24
1.07
6.01
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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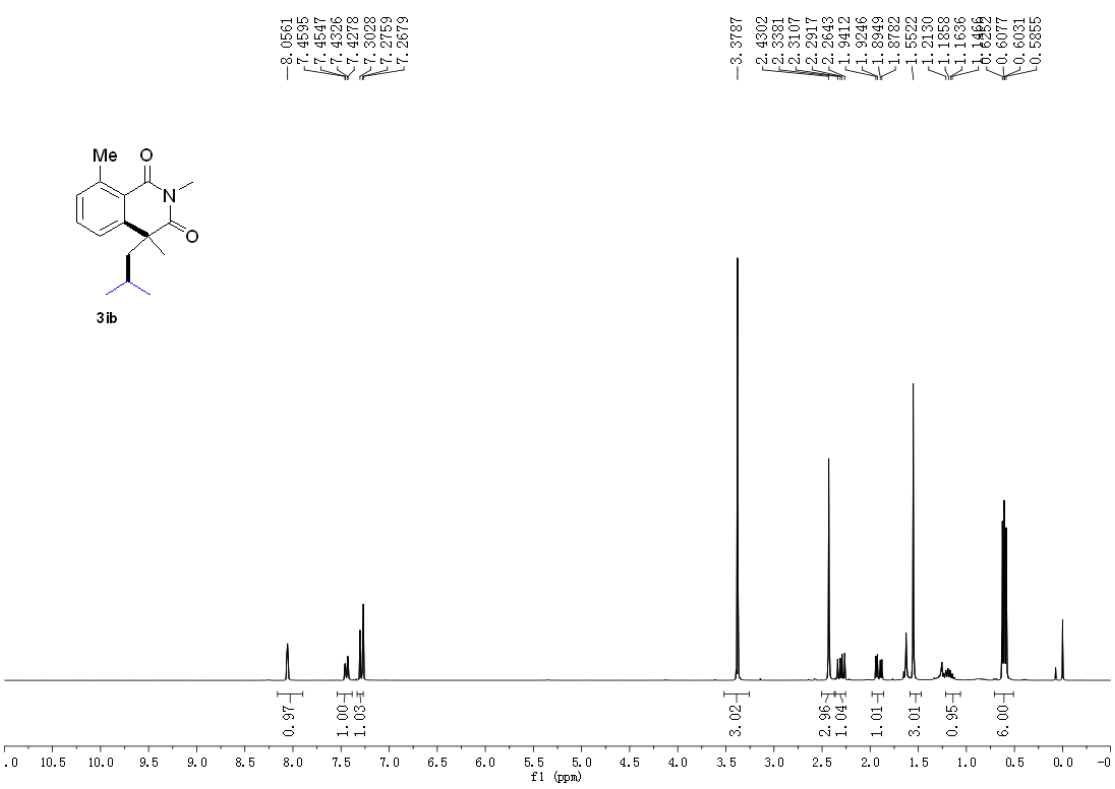
143.83
128.88
128.32
126.09
122.16
77.46
77.04
76.61
50.92
46.82
31.61
27.10
25.54
23.97
22.30
22.00
Me
O
N
O
3bb
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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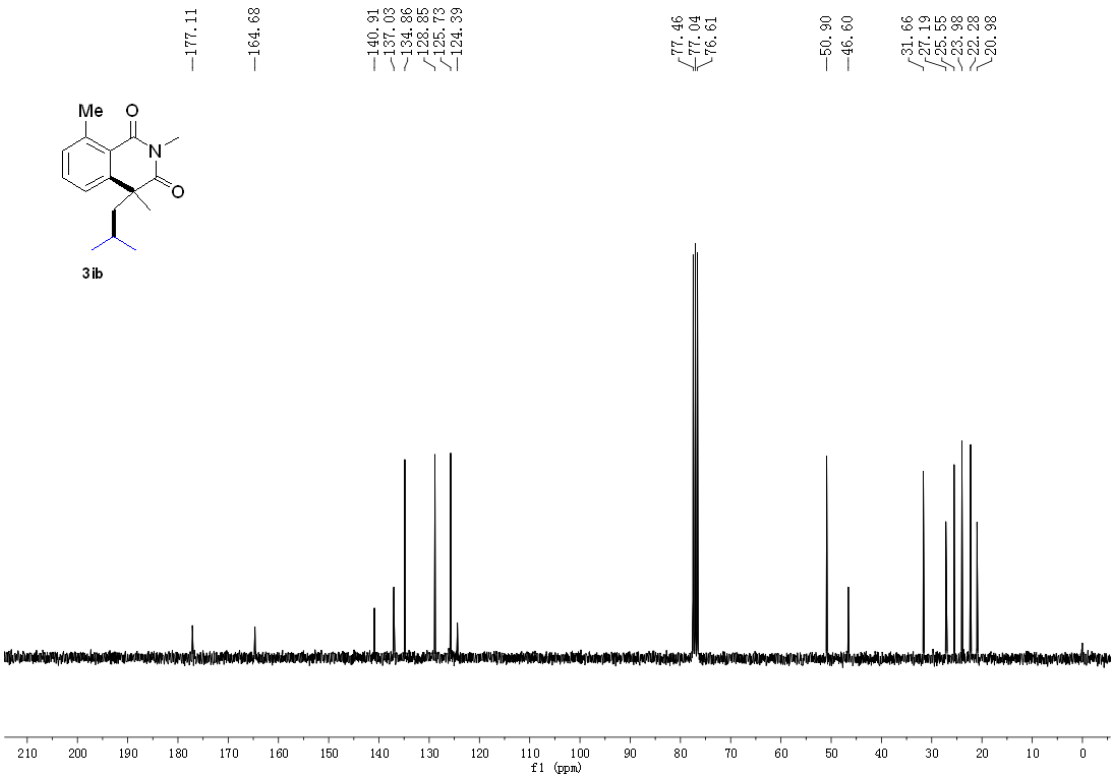
7.4547
7.4326
7.4278
7.3028
7.2759
7.2679
3.3787
2.4302
2.3381
2.3107
2.2917
2.2643
1.9412
1.9246
1.8949
1.8782
1.5522
1.2130
1.1858
1.1636
0.6077
0.6031
0.5855
Me
O
N
O
3ib
0.97
1.00
1.03
3.02
2.96
1.04
1.01
3.01
0.95
6.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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128.85
125.73
124.39
77.46
77.04
76.61
50.90
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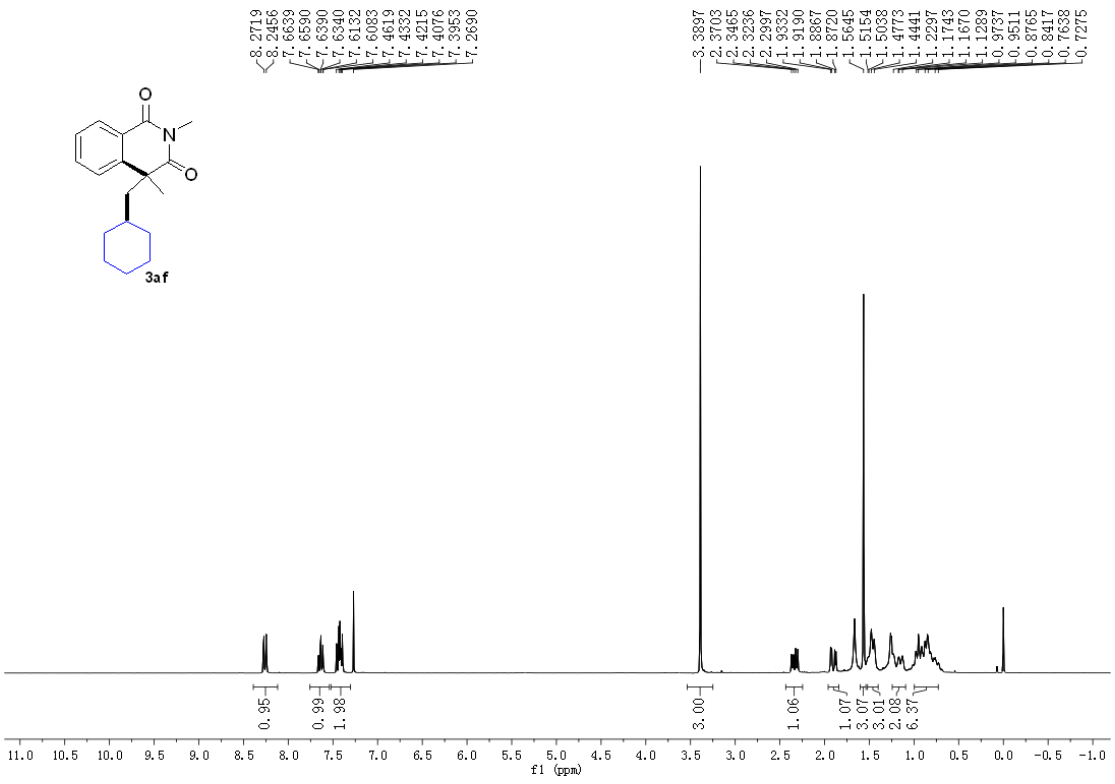
20.98
Me
O
N
O
3ib
f1 (ppm)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7.6132
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7.4619
7.4332
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7.4076
7.3953
7.2690
3.3897
2.3703
2.3465
2.3236
2.2997
1.9332
1.9190
1.8867
1.8720
1.5645
1.5154
1.5038
1.4773
1.4441
1.2297
1.1743
1.1670
1.1289
0.9737
0.9511
0.8765
0.8417
0.7638
0.7275
O
N
O
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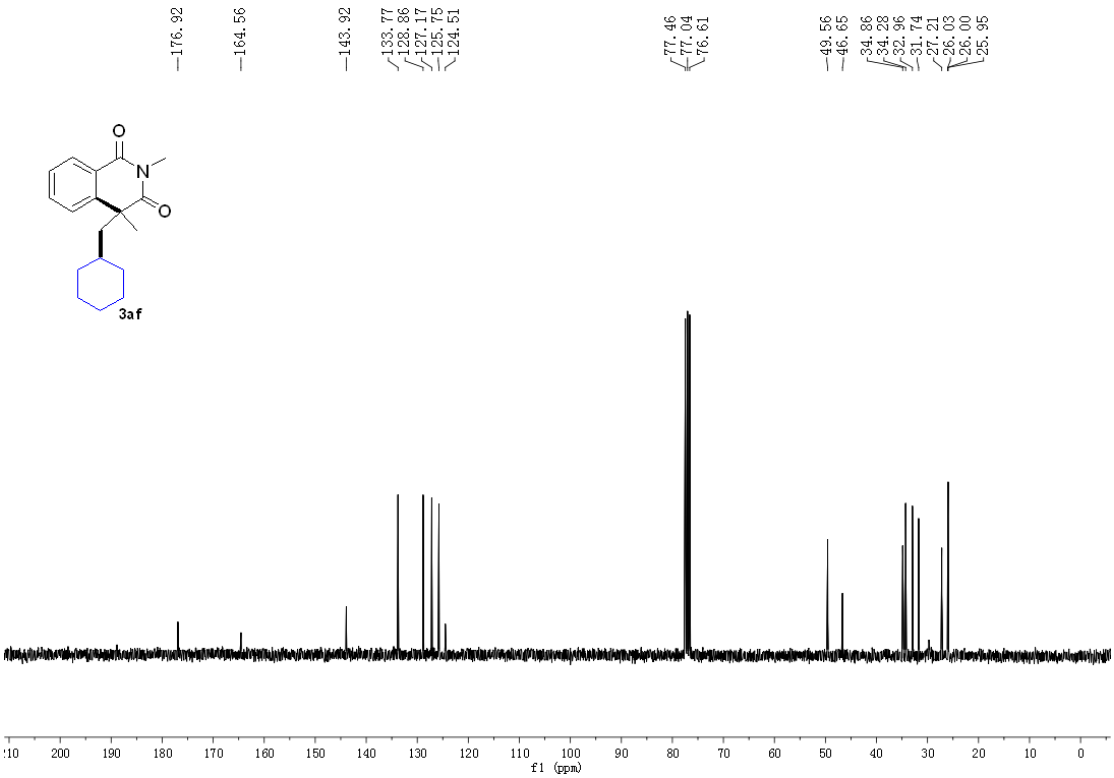
1.98
3.00
1.06
1.07
3.07
3.01
2.08
6.37
f1 (ppm)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128.86
127.17
125.75
124.51
77.46
77.04
76.61
49.56
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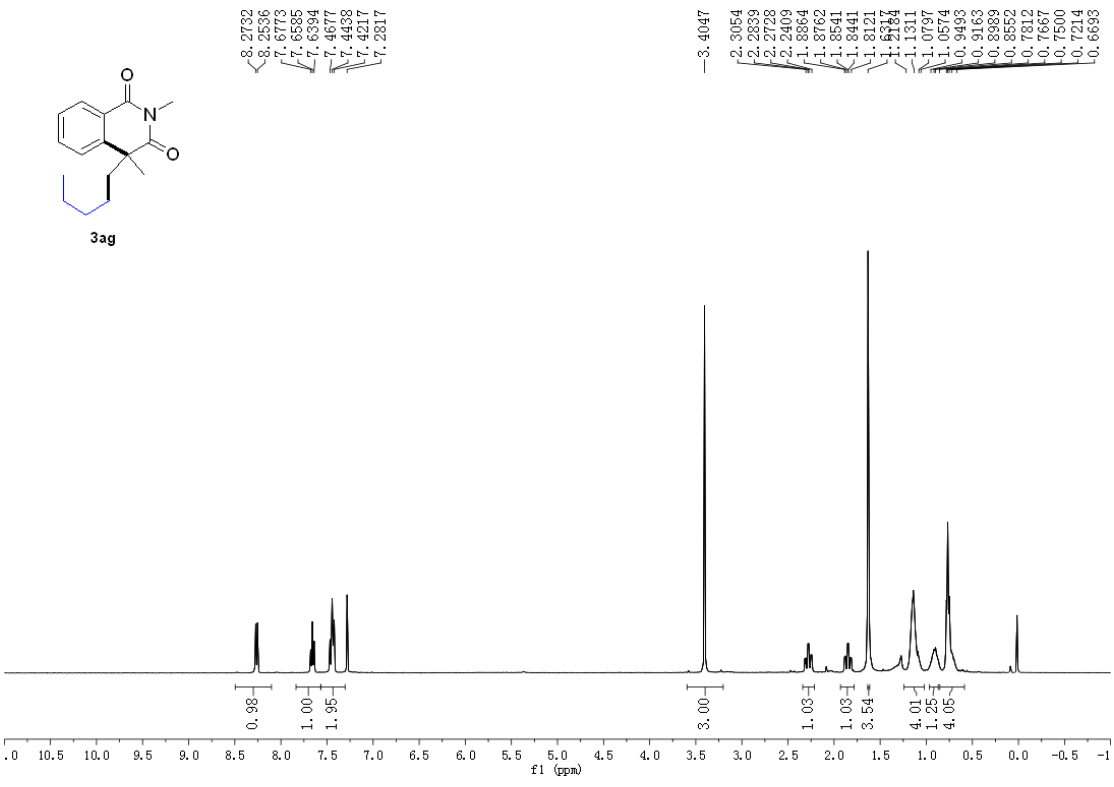
26.03
26.00
25.95
3af
f1 (ppm)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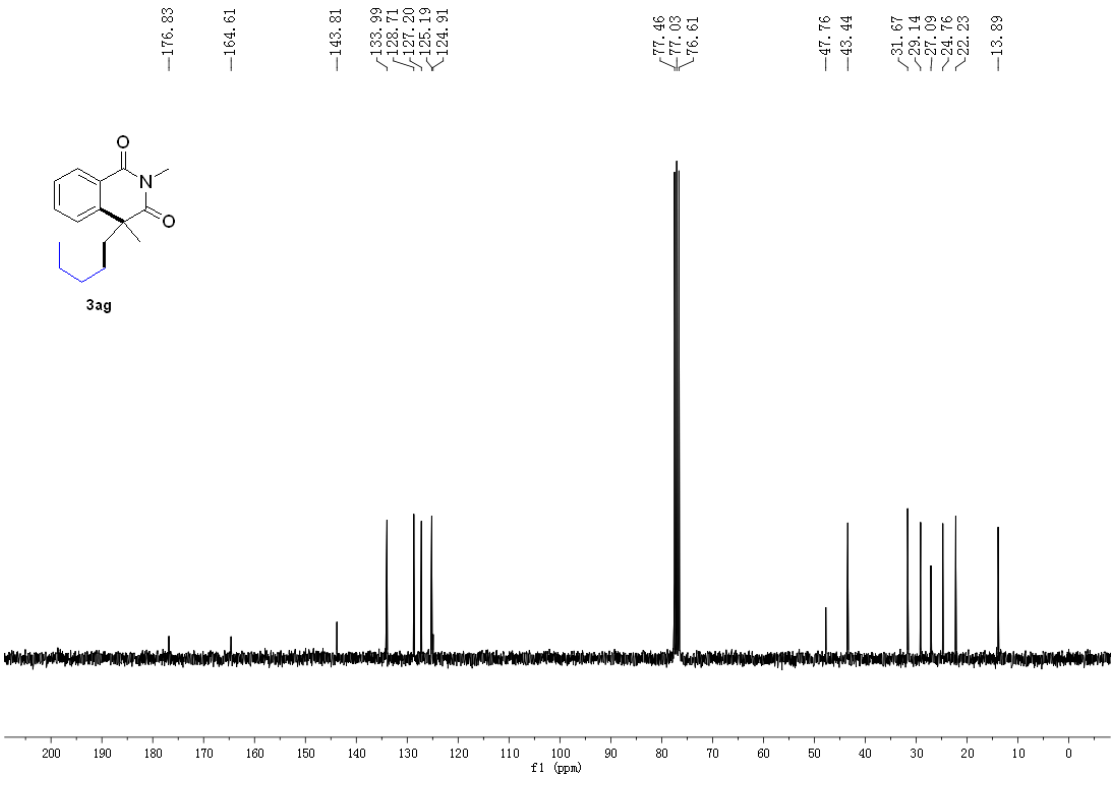
7.2817
3.4047
2.3054
2.2839
2.2728
2.2409
1.8864
1.8762
1.8541
1.8441
1.8121
1.1311
1.0797
1.0574
0.9493
0.9163
0.8989
0.8552
0.7812
0.7667
0.7500
0.7214
0.6693
3ag
0.98
1.00
1.95
3.00
1.03
1.03
3.54
4.01
1.25
4.05
f1 (ppm)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128.71
127.20
125.19
124.91
77.46
77.03
76.61
47.76
43.44
31.67
29.14
27.09
24.76
22.23
13.89
O
N
O
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)