Direct C(sp^3)-H acyloxylation of indolin-3-ones with carboxylic acids catalysed by KI

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Contents:

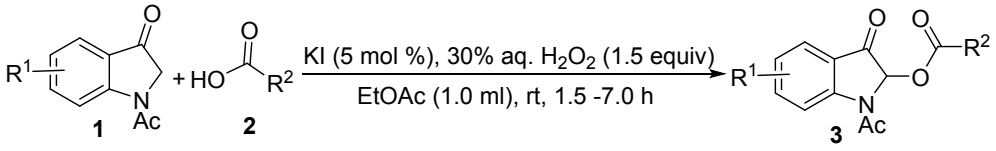
1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out utilizing silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR spectra were recorded on a Varain Mercury 400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *dd* = doublet), integration，coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. High resolution mass spectrometry (HRMS) were performed on a Thermofisher (Vanquish (UPLC)-Q-Exactive Plus) mass instrument (Orbitrap-ESI) and methanol was used to dissolve the sample.

2. Preparation of Substrates

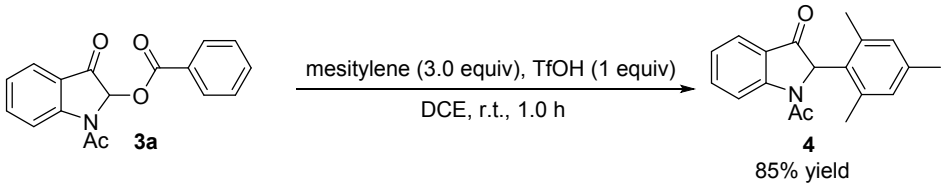
Indolin-3-ones **1** were prepared by following the publish procedures. [1-4]

3. General procedure for the KI-catalyzed direct C(sp^3)-H acyloxylation of nucleophilic indolin-3-ones with carboxylic acids



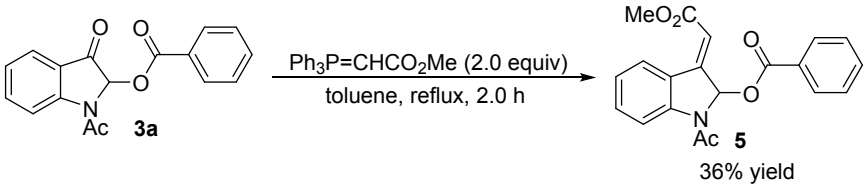
To a solution of indolin-3-ones **1** (0.20 mmol), benzoic acid **2**(0.60 mmol), and KI (5 mol %) in ethyl acetate (1.0 ml) was added 30% aq. H_2O_2(1.5 equiv) under stirring at room temperature. After the required period of time (as judged by TLC analysis). The resulting solution was concentrated under reduced pressure, and the crude product was directly purified by flash column chromatography on silica gel (200-300 mesh) (EtOAc/petroleum ether = 1/3) to give the desired acyloxylation products **3**.

4. General procedure for the synthesis of compound 4.



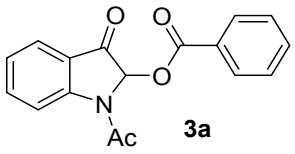
To a solution of indolin-3-one **3a** (0.4 mmol, 118 mg) and mesitylene (1.2 mmol, 0.16 in DCE (2.0 ml) was slowly added TfOH (0.4 mmol, 35 ul) under stirring at room temperature. After the reaction is complete (as judged by TLC analysis), the resulting solution was concentrated under reduced pressure, and the crude product was directly purified by flash column chromatography on silica gel (200-300 mesh) (EtOAc/petroleum ether = 1/5) to give a white solid **4** with 85% yield.

5. General procedure for the synthesis of compound 5.



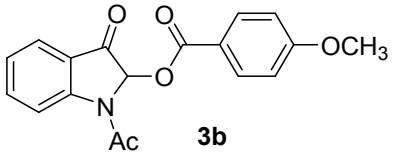
In a 10 ml round bottom flask, indolin-3-one **3a** (0.2 mmol, 59 mg), $Ph_3P{=}CHCO_2Me$ (0.4 mmol, 126 mg) and toluene (2.0 ml) was added and stirred at 110 ^oC for 2 hours (as judged by TLC analysis). Then, the reaction mixture was concentrated under reduced pressure, and the crude product was directly purified by flash column chromatography on silica gel (200-300 mesh) (EtOAc/petroleum ether = 1/10) to give a white solid **5** with 36% yield.

6. **Analytical data of compounds 3a-z, 3aa-3af, and 4 - 5.**



1-Acetyl-3-oxoindolin-2-yl benzoate (3a). White solid; Reaction time: 5 h; Yield: 89%; m. p.: 121-122 ^oC; IR (KBr): 3134, 3073, 1744, 1722, 1691, 1599, 1582, 1458, 1375, 1350, 1326, 1301, 1259, 1249, 1163, 1094, 1065, 1025, 977, 935, 838, 713, 687, 665, 606, 496 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ

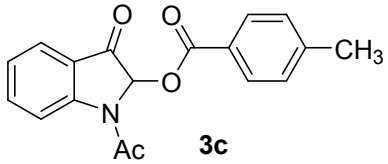
8.41 (d, *J* = 8.4 Hz, 1H), 8.03–7.93 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.56 – 7.51 (m, 1H), 7.40 – 7.34 (m, 2H), 7.21 – 7.15 (m, 1H), 6.51 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.4, 168.9, 164.5, 152.8, 137.9, 134.1, 130.1, 128.6, 127.9, 124.8, 124.4, 122.1, 118.1, 79.8, 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{14}NO_4$: 296.09174, found $[M+H]^+$: 296.09128.



3b

1-Acetyl-3-oxoindolin-2-yl 4-methoxybenzoate (3b).

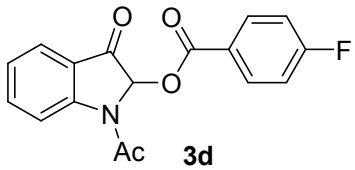
White solid; Reaction time: 5 h; Yield: 81%; m. p.: 148-149 °C; IR (KBr): 3018, 2974, 2844, 1729, 1715, 1697, 1605, 1591, 1581, 1508, 1464, 1423, 1383, 1350, 1302, 1276, 1266, 1255, 1188, 1168, 1147, 1097, 1044,1016, 1005, 968, 927, 882, 868, 845, 826, 806, 756, 700, 693, 673, 637, 622, 589, 562, 529, 502, 429 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.85 – 7.76 (m, 1H), 7.75 – 7.65 (m, 1H), 7.32 – 7.24 (m, 1H), 6.98 – 6.88 (m, 2H), 6.56 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 169.0, 164.3, 164.2, 152.9, 137.9, 132.4, 124.8, 124.4, 122.2, 120.1, 118.2, 114.0, 79.7, 55.5, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_5$: 326.10230, found$[M+H]^+$: 326.10216.



3c

1-Acetyl-3-oxoindolin-2-yl 4-methylbenzoate (3c).

White solid; Reaction time: 5 h; Yield: 84%; m. p.: 140-141 °C; IR (KBr): 2983, 2924, 2311,1745, 1725, 1685, 1608, 1464, 1382, 1353, 1304, 1271, 1245, 1180, 1165, 1149, 1084, 1057, 1018, 978, 932, 875, 842, 782, 751, 689, 671, 599, 564, 499, 474 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.76 (m, 1H), 7.74 – 7.68 (m, 1H), 7.32 – 7.22 (m, 3H), 6.58 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 168.9, 164.6, 152.8, 145.2, 137.9, 130.2, 129.4, 125.1, 124.8, 124.4, 122.2, 118.2, 79.7, 23.8, 21.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_4$: 310.10738, found $[M+H]^+$: 310.10715.

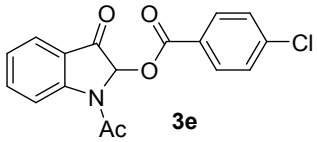


3d

1-Acetyl-3-oxoindolin-2-yl 4-fluorobenzoate (3d).

White solid; Reaction time: 6 h; Yield: 81%; m. p.: 123-124 °C; IR (KBr): 3073, 2922, 2852, 2316, 1938, 1739, 1679, 1604, 1507, 1465, 1386, 1358, 1326, 1312, 1273, 1248,

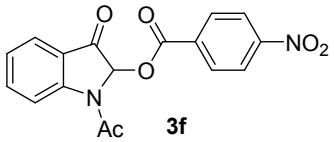
1233, 1190, 1174, 1152, 1104, 1091,1063, 1037, 1010, 978, 932, 881, 854, 815, 773, 758, 703, 686, 669, 619, 603, 563, 507, 492, 425 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.14 – 8.04 (m, 2H), 7.87 – 7.77 (m, 1H), 7.77 – 7.69 (m, 1H), 7.36 – 7.23 (m, 1H), 7.20 – 7.08 (m, 2H), 6.61 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.4, 168.8, 166.4 (d, J_{C-F} = 255.1 Hz), 163.6, 152.9, 138.1, 132.9 (d, J_{C-F} = 9.6 Hz), 124.9, 124.5, 124.2 (d, J_{C-F} = 3.1 Hz), 122.1, 118.2, 116.0 (d, J_{C-F} = 22.1 Hz), 79.9, 23.8; ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -102.78; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}FNO_4$: 314.08231, found $[M+H]^+$: 314.08201.



3e

1-Acetyl-3-oxoindolin-2-yl 4-chlorobenzoate (3e).

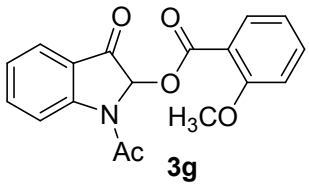
White solid; Reaction time: 6 h; Yield: 66%; m. p.: 162-163 °C; IR (KBr): 3445, 3354, 3077, 2956, 1740, 1685, 1607, 1590, 1489, 1462, 1434, 1385, 1353, 1330, 1309, 1270, 1256, 1173, 1151, 1093, 1065, 1034, 1011, 980, 932, 885, 849, 834, 770, 755, 704, 682, 590, 565, 525, 490, 475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.32–7.26 (m, 1H), 6.61 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.3, 168.8, 163.8, 152.9, 140.9, 138.1, 131.5, 129.1, 126.4, 125.0, 124.6, 122.1, 118.2, 79.9, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}ClNO_4$: 330.05276, found $[M+H]^+$: 330.05245.



3f

1-Acetyl-3-oxoindolin-2-yl 4-nitrobenzoate (3f).

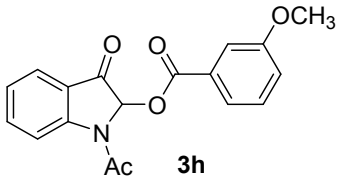
White solid; Reaction time: 7 h; Yield: 30%; m. p.: 211-212 °C; IR (KBr): 3116, 3079, 2923, 1742, 1732, 1721, 1683, 1609, 1595, 1530, 1464, 1386, 1356, 1325, 1307, 1268, 1243, 1190, 1171, 1151,1095,1058, 1010, 972, 932, 877, 851, 826, 780, 759, 755, 719, 699, 666, 609, 593, 565, 544, 506, 481cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.38 – 8.20 (m, 4H), 7.84 –7.70 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.68 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.8, 168.6, 162.9, 153.0, 151.1, 138.3, 133.4, 131.3, 125.1, 124.7, 123.8, 122.0, 118.2, 80.2, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}N_2O_6$: 341.07682, found $[M+H]^+$: 341.07696.



3g

1-Acetyl-3-oxoindolin-2-yl 2-methoxybenzoate (3g).

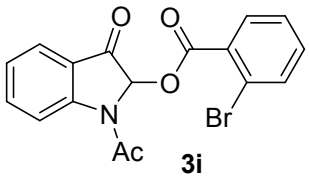
White solid; Reaction time: 3 h; Yield: 94%; m. p.: 105-106 °C; IR (KBr): 2991, 2954, 2845, 1738, 1717, 1696, 1602, 1594, 1492, 1472, 1460, 1437, 1388, 1361, 1351, 1306, 1291, 1263, 1242, 1184, 1166, 1143, 1122, 1091, 1037, 1016, 968, 930, 887, 858, 824, 809, 760, 710, 697, 679, 654, 597, 563, 548, 509, 460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 8.4 Hz, 1H), 7.89–7.86 (m, 1H), 7.81–7.77 (m, 1H), 7.74–7.67 (m, 1H), 7.58–7.50 (m, 1H), 7.26 (td, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.02–6.96 (m, 2H), 6.52 (s, 1H), 3.90 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 169.2, 163.7, 159.9, 152.8, 137.8, 135.0, 132.3, 124.7, 124.4, 122.3, 120.2, 118.2, 117.2, 112.0, 79.8, 55.9, 23.9; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_5$: 326.10230, found $[M+H]^+$: 326.10196.



3h

1-Acetyl-3-oxoindolin-2-yl 3-methoxybenzoate (3h).

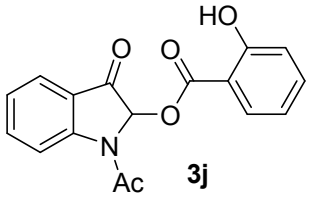
White solid; Reaction time: 5 h; Yield: 89%; m. p.: 124-125 °C; IR (KBr): 3130, 3085, 2997, 2963, 2937, 2835, 1739, 1724, 1684, 1610, 1583, 1486, 1464, 1435, 1387, 1359, 1315, 1290, 1276, 1258, 1216, 1166, 1144, 1089, 1040, 979, 935, 906, 889, 808, 774, 749, 685, 671, 604, 506, 422 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 8.4 Hz 1H), 7.82 – 7.78 (m, 1H), 7.75 – 7.69 (m, 1H), 7.67 – 7.63 (m, 1H), 7.56–7.53 (m, 1H), 7.37 (t, *J* = 8.0, 1H), 7.32 – 7.25 (m, 1H), 7.19 – 7.11 (m, 1H), 6.59 (s, 1H), 3.83 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.4, 168.9, 164.5, 159.6, 152.9, 138.0, 129.7, 129.1, 124.9, 124.5, 122.5, 122.2, 120.8, 118.2, 114.4, 79.9, 55.5, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_5$: 326.10230, found $[M+H]^+$: 326.10217.



3i

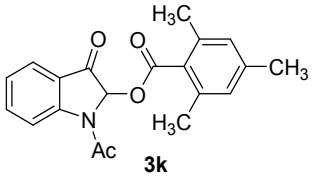
1-Acetyl-3-oxoindolin-2-yl 2-bromobenzoate (3i).

White solid; Reaction time: 6 h; Yield: 59%; m. p.: 92-93 °C; IR (KBr): 2968, 2918, 2849, 1738, 1722, 1694, 1605, 1590, 1465, 1429, 1383, 1349, 1312, 1303, 1276, 1236, 1152, 1081, 1039, 1018, 1004, 978, 956, 933, 872, 789, 779, 762, 736, 670, 641, 605, 595, 567, 505, 471 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 7.2 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.35 – 7.25 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.1, 168.9, 163.9, 153.0, 138.1, 134.7, 133.7, 131.9, 129.7, 127.3, 124.9, 124.6, 122.2, 122.0, 118.3, 79.8, 23.9; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}BrNO_4$: 374.00225, found $[M+H]^+$: 374.00198.



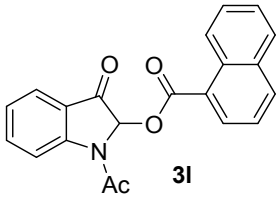
3j

1-Acetyl-3-oxoindolin-2-yl 2-hydroxybenzoate (3j). White solid; Reaction time: 5 h; Yield: 35%; m. p.: 143-144 ^{o}C; IR (KBr): 3314, 2985, 1743, 1697, 1689, 1608, 1586, 1483, 1463, 1381, 1348, 1315, 1308, 1286, 1261, 1244, 1184, 1160,1150, 1124, 1082, 1055, 1006, 976, 965, 930, 880, 866, 823, 780, 758, 695, 660, 610, 591, 566, 531, 502, 456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.51 (d, *J* = 5.6 Hz, 1H), 7.82 (t, *J* = 6.0 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.21(m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.9, 168.7, 168.1, 162.2, 152.9, 138.2, 137.1, 130.0, 125.0, 124.7, 122.0, 119.6, 118.2, 118.0, 110.6, 79.7, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{14}NO_5$: 312.08665, found $[M+H]^+$: 312.08644.



3k

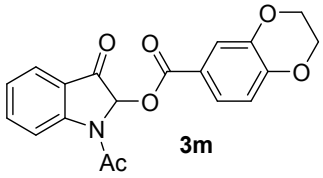
1-Acetyl-3-oxoindolin-2-yl 2,4,6-trimethylbenzoate (3k). White solid; Reaction time: 5 h; Yield: 76%; m. p.: 120-121 ^{o}C; IR (KBr): 3453, 2921, 2855, 1741, 1731, 1682, 1610, 1466, 1385, 1355, 1314, 1303, 1269, 1234, 1194, 1178, 1161, 1148, 1100, 1072, 1052, 970, 955, 931, 884, 854, 827, 776, 758, 699, 664, 613, 595, 566, 548, 522, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.73 – 7.68 (m, 1H), 7.65 – 7.58 (m, 1H), 7.22 – 7.16 (m, 1H), 6.77 (s, 2H), 6.54 (s, 1H), 2.35 (s, 3H), 2.26 (s, 6H), 2.20 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 191.5, 168.7, 168.1, 152.9, 140.5, 138.0, 135.9, 128.7, 128.1, 124.9, 124.5 , 122.2, 118.3, 79.9, 23.8, 21.1, 20.0; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{20}H_{20}NO_4$: 338.13869, found $[M+H]^+$: 338.13828.



3l

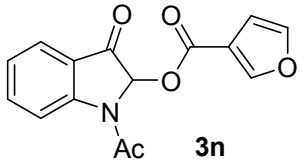
1-Acetyl-3-oxoindolin-2-yl 1-naphthoate (3l). White solid; Reaction time: 3 h; Yield: 65%; m. p.: 216-217 ^{o}C; IR (KBr): 2985, 2969, 1737, 1733, 1722, 1688, 1682, 1604, 1592, 1509, 1464, 1387,1355, 1330, 1305, 1277, 1241, 1228, 1186, 1169,1153, 1115, 1098, 1085, 1043, 992, 973, 933, 882, 807, 772, 760, 671, 652, 597, 565, 545, 530, 515, 504, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, *J* = 8.8 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 7.2, *J* = 1.2 Hz, 1H),

8.02 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.69 – 7.62 (m, 1H), 7.60 – 7.53 (m, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 1H), 7.25 – 7.19 (m, 1H), 6.64 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 168.9, 164.9, 153.0, 138.0, 135.0, 133.8, 131.5, 131.3, 128.7, 128.5, 126.6, 125.5, 124.7, 124.5, 124.4, 124.2, 122.2, 118.3, 79.7, 23.9; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{21}H_{16}NO_4$: 346.10738, found $[M+H]^+$: 346.10712.



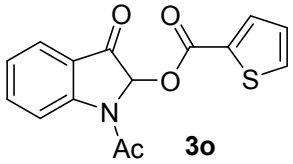
3m

1-Acetyl-3-oxoindolin-2-yl 2,3-dihydrobenzo[*b*][1,4]dioxine-5-carboxylate (3m). White solid; Reaction time: 2 h; Yield: 72%; m. p.: 149-150 °C; IR (KBr): 3119, 3015, 2980, 2927, 2875, 1742, 1718, 1699, 1694, 1684, 1607, 1587, 1505, 1464, 1431, 1386, 1382, 1351, 1334, 1325, 1312, 1294, 1266, 1215, 1182, 1165, 1151, 1125, 1082, 1058, 1046, 979, 944, 932, 913, 890, 816, 770, 756, 697, 665, 595, 563, 506, 475, 428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.78 – 7.69 (m, 1H), 7.63 – 7.55 (m, 2H), 7.34 – 7.26 (m, 1H), 6.95 – 6.89 (m, 1H), 6.56 (s, 1H), 4.38 – 4.25 (m, 4H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 169.0, 164.0, 152.8, 148.9, 143.3, 137.9, 124.8, 124.4, 124.2, 122.2, 120.9, 119.6, 118.2, 117.5, 79.8, 64.7, 64.0, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{19}H_{16}NO_6$: 354.09721, found $[M+H]^+$: 354.09695.



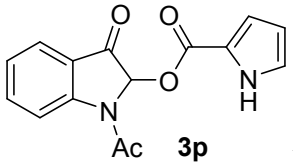
3n

1-Acetyl-3-oxoindolin-2-yl furan-3-carboxylate (3n). White solid; Reaction time: 6 h; Yield: 30%; m. p.: 152-153 °C; IR (KBr): 3137, 2963, 2924, 2851, 1738, 1732, 1674, 1606, 1575, 1505, 1463, 1435, 1386, 1358, 1319, 1285, 1262, 1190, 1163, 1136, 1081, 1036, 1009, 981, 963, 929, 873, 849, 802, 753, 666, 606, 596, 564, 500 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.02 (q, *J* = 0.8 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.68 – 7.61 (m, 1H), 7.42 – 7.38 (m, 1H), 7.25 – 7.18 (m, 1H), 6.70 (dd, *J* = 2.0 Hz, *J* = 0.8 Hz, 1H), 6.47 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.4, 168.9, 160.9, 152.9, 149.0, 144.3, 138.1, 124.9, 124.5, 122.1, 118.2, 117.4, 109.8, 79.3, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{15}H_{12}NO_5$: 286.07100, found $[M+H]^+$: 286.07080.



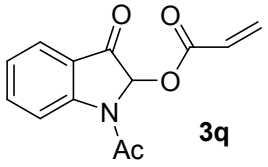
3o

1-Acetyl-3-oxoindolin-2-yl thiophene-3-carboxylate (3o). White solid; Reaction time: 6 h; Yield: 41%; m. p.: 126-127 ^{o}C; IR (KBr): 3122, 3103, 2924, 2852,1747, 1722, 1691, 1606, 1594, 1520, 1467, 1417, 1385, 1354, 1307, 1276, 1254, 1216, 1193, 1167,1153, 1087, 1053, 1029, 1018, 1006, 973, 930, 869, 775, 737, 653, 567, 546, 528, 482 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.75 – 7.69 (m, 1H), 7.68 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H), 7.30(td, J = 7.2 Hz, J = 0.8 Hz, 1H), 7.15 (dd, J = 4.8 Hz, J = 4.0 Hz, 1H), 6.51 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.3, 168.9, 160.1, 152.8, 138.0, 135.4, 134.6, 130.9, 128.2, 124.9, 124.5, 122.1, 118.2, 79.8, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{15}H_{12}NO_4S$: 302.04816, found $[M+H]^+$: 302.04804.



3p

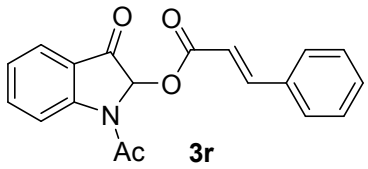
1-Acetyl-3-oxoindolin-2-yl-1H-pyrrole-3-carboxylate (3p). White solid; Reaction time: 5 h; Yield: 70%; m. p.: 99-101 ^{o}C; IR (KBr): 3304, 3128, 1733, 1705, 1677, 1606, 1552, 1468, 1406, 1386, 1360, 1320, 1294, 1270, 1153, 1121, 1081, 1065,1037, 1013, 978, 950, 930, 883, 841, 760, 749, 736, 666, 602, 565, 541, 509, 487 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.50 (d, J = 8.4 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.73 – 7.68 (m, 1H), 7.30 – 7.24 (m, 1H), 7.06 – 6.97 (m, 2H), 6.50 (s, 1H), 6.32 – 6.28 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 169.0, 158.7, 152.9, 138.0, 125.0, 124.8, 124.4, 122.1, 120.3, 118.2, 117.7, 111.2, 79.4, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{15}H_{13}N_2O_4$: 285.08698, found $[M+H]^+$: 285.08685.



3q

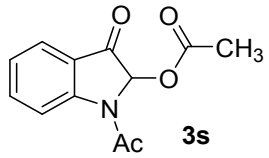
1-Acetyl-3-oxoindolin-2-yl acrylate (3q). White solid; Reaction time: 6 h; Yield: 84%; m. p.: 87-88 ^{o}C; IR (KBr): 3040, 2980, 1742, 1731, 1700, 1685, 1682, 1633, 1609, 1466, 1399, 1382, 1355, 1310, 1289, 1274, 1155, 1143, 1097, 1074, 990, 981, 976, 938, 877, 803, 768, 746, 704, 681, 654, 613, 594, 565, 543, 480 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.73 – 7.76 (m, 1H), 7.29 – 7.24 (m, 1H), 6.55 (dd, J = 17.2 Hz, J = 0.8 Hz, 1H), 6.46 (s, 1H), 6.19 (dd, J = 17.2 Hz, J = 14.8 Hz, 1H), 6.02 (dd, J = 14.8 Hz, J = 0.8

Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 M Hz, $CDCl_3$): δ 191.4, 168.8, 164.0, 152.9, 138.0, 134.1, 126.4, 124.8, 124.4, 122.0, 118.2, 79.4, 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{13}H_{12}NO_4$: 246.07608, found $[M+H]^+$: 246.07603.



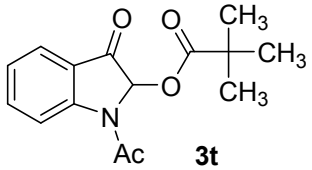
3r

1-Acetyl-3-oxoindolin-2-yl cinnamate (3r). White solid; Reaction time: 7 h; Yield: 79%; m. p.: 124-125 °C; IR (KBr): 3420, 3054, 2963, 1734,1723, 1679, 1630, 1605, 1589, 1498, 1464, 1449, 1386, 1353, 1304, 1270, 1222, 1164, 1149, 1083, 1037, 1022, 998, 941, 923, 866, 826, 794, 757, 705, 679, 664, 597, 563, 497, 481, 415 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 8.0 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.73 – 7.71 (m, 1H), 7.55 – 7.48 (m, 2H), 7.41 – 7.36 (m, 3H), 7.29 – 7.23 (m, 1H), 6.50 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 168.9, 164.9, 152.9, 148.1, 138.0, 133.6, 131.1, 129.0, 128.4, 124.8, 124.5, 122.1, 118.2, 115.4, 79.4, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{19}H_{16}NO_4$: 322.10378, found $[M+H]^+$: 322.10715.



3s

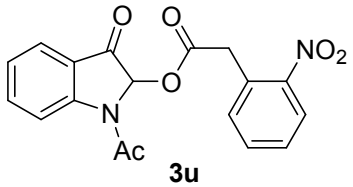
1-Acetyl-3-oxoindolin-2-yl acetate (3s). White solid; Reaction time: 5 h; Yield: 66%; m. p.: 90-91 °C; IR (KBr): 3126, 3011, 1759, 1725, 1695, 1607, 1592, 1465, 1433, 1387, 1349, 1304, 1271, 1241, 1215, 1186, 1171, 1155, 1099, 1072, 1017, 1007, 969, 957, 940, 915, 882, 826, 784, 764, 750, 701, 666, 642, 594, 564, 543, 526, 470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.0 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.71 – 7.65 (m, 1H), 7.25 (td, J = 0.8 Hz, J = 7.6 Hz, 1H), 6.37 (s, 1H), 2.31 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz,$CDCl_3$): δ 191.5, 168.9, 168.7, 152.8, 137.9, 124.8, 124.4, 122.0, 118.1, 79.3, 23.7, 20.5; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{12}H_{12}NO_4$: 234.07609, found $[M+H]^+$: 234.07585.



3t

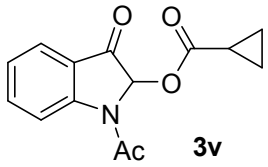
1-Acetyl-3-oxoindolin-2-yl pivalate (3t). White solid; Reaction time: 1.5 h; Yield: 88%; m. p.: 128-139 °C; IR (KBr): 2976, 2934, 2873, 1749, 1735, 1684, 1605, 1590, 1463, 1383, 1373, 1365, 1355, 1350, 1325, 1308, 1274, 1264, 1193, 1151, 1124, 1098, 1031, 1010, 979, 938, 825, 756, 705, 669, 610, 598, 583, 564, 549, 497, 420 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 8.4 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.72– 7.66 (m, 1H), 7.28– 7.15 (m, 1H), 6.31 (s, 1H), 2.31 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 176.5, 169.8, 152.7,

137.8, 124.8, 124.3, 122.1, 118.2, 79.6, 38.9, 26.8, 23.6; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{15}H_{18}NO_4$: 276.12303, found $[M+H]^+$: 276.12282.



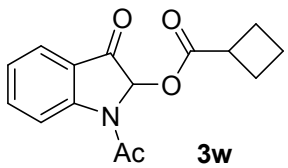
3u

1-Acetyl-3-oxoindolin-2-yl 2-(2-nitrophenyl)acetate (3u). White solid; Reaction time: 4 h; Yield: 63%; m. p.: 112-113 °C; IR (KBr): 3255, 2927, 2856, 1754, 1732, 1688, 1657, 1608, 1591, 1526, 1464, 1386, 1347, 1300, 1263, 1229, 1219, 1179, 1144, 1097,1075, 1006, 973, 927, 884, 877, 839, 818, 800, 768, 756, 723, 671, 655, 629, 590, 578, 561, 519, 495, 437 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.38 (s, 1H), 4.22 (d, *J* = 17.6, 1H), 4.02 (d, *J* = 17.2, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.4, 169.1, 168.6, 153.1, 148.3, 138.1, 134.0, 133.7, 129.2, 128.4, 125.5, 124.8, 124.4, 121.9, 118.3, 80.0, 39.6, 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{15}N_2O_6$: 355.09246, found $[M+H]^+$: 355.09201.



3v

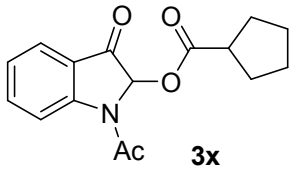
1-Acetyl-3-oxoindolin-2-yl cyclopropanecarboxylate (3v). White solid; Reaction time: 5 h; Yield: 69%; m. p.: 116-117 °C; IR (KBr): 3447, 3348, 3023, 2977, 1737, 1730, 1683, 1607, 1591, 1466, 1386, 1352, 1325,1296, 1277, 1232, 1151, 1134, 1098, 1035, 994, 946, 924, 880, 863, 821, 781, 768, 744, 704, 678, 649, 610, 591, 563, 542, 470 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.72 –7.64 (m, 1H), 7.29 – 7.23 (m, 1H), 6.34 (s, 1H), 2.33 (s, 3H), 1.76 – 1.69 (m, 1H), 1.17 – 1.05 (m, 2H), 1.04 – 0.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 173.2, 169.0, 152.9, 138.0, 124.9, 124.5, 122.2, 118.3, 79.5, 23.9, 12.7, 9.8, 9.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{14}H_{14}NO_4$: 260.09173, found $[M+H]^+$: 260.09158.



3w

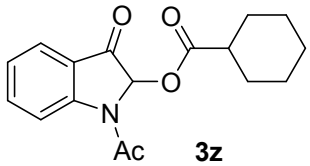
1-Acetyl-3-oxoindolin-2-yl cyclobutanecarboxylate (3w). White solid; Reaction time: 5 h; Yield: 78%; m. p.: 68-69 °C; IR (KBr): 3458, 2987,

2948, 2867, 1744, 1688, 1681, 1608, 1588, 1464, 1385, 1352, 1323, 1308, 1296, 1271, 1247, 1233, 1156, 1149, 1096, 1078, 1039, 1010, 978, 954, 928, 881, 827, 760, 702, 671, 604, 592, 542, 523, 470, 419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.60 (m, 2H), 7.30 – 7.22 (m, 1H), 6.33 (s, 1H), 3.31–3.21 (m, 1H), 2.42 – 2.18 (m, 7H), 2.09 – 1.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 173.4, 168.8, 152.7, 137.9, 124.7, 124.3, 122.1, 118.1, 79.4, 37.4, 25.0, 24.9, 23.6, 18.3; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{15}H_{16}NO_4$: 274.10738, found $[M+H]^+$: 274.10713.



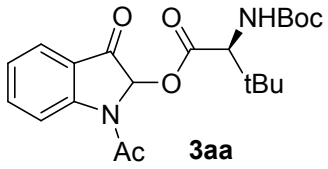
3x

1-Acetyl-3-oxoindolin-2-yl cyclopentanecarboxylate (3x). White solid; Reaction time: 2 h; Yield: 73%; m. p.: 75-76 °C; IR(KBr): 2958, 2870, 1751, 1734, 1683, 1606, 1588, 1463, 1383, 1350, 1327, 1309, 1298, 1270, 1234, 1193, 1133, 1098, 1082, 1067, 1038, 1011, 988, 980, 969, 929, 831, 760, 704, 671, 587, 566, 549, 523, 464 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.70 –7.65 (m, 1H), 7.63 – 7.57 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.24 (s, 1H), 2.83 – 2.73 (m, 1H), 2.40 (s, 3H), 1.92 – 1.71 (m, 4H), 1.69 – 1.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.8, 174.8, 169.0, 152.9, 138.0, 124.9, 124.4, 122.3, 118.3, 79.6, 43.3, 30.0, 29.9, 25.9, 25.8, 23.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{16}H_{18}NO_4$: 288.12303, found $[M+H]^+$: 288.12278.



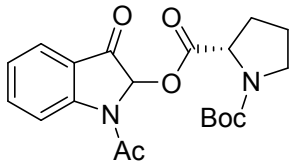
3z

1-Acetyl-3-oxoindolin-2-yl cyclohexanecarboxylate (3z). White solid; Reaction time: 3 h; Yield: 96%; m. p.: 92-93 °C; IR (KBr): 3457, 3363, 2929, 2854, 1741, 1691, 1607, 1589, 1463, 1384, 1352, 1322, 1311, 1291, 1268, 1194, 1150, 1126, 1095, 1075, 1036, 1021, 1010, 980, 957, 945, 923, 894, 828, 767, 757, 702, 667, 644, 592, 566, 532, 482, 419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 7.6 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.70 – 7.65 (m, 1H), 7.30 – 7.19 (m, 1H), 6.34 (s, 1H), 2.52 – 2.38 (m, 1H), 2.31 (s, 3H), 2.02 – 1.90 (m, 2H), 1.85 – 1.70 (m, 2H), 1.69 – 1.58 (m, 1H), 1.55 – 1.40 (m, 2H), 1.35 – 1.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.7, 174.0, 168.8, 152.7, 137.8, 124.7, 124.3, 122.1, 118.1, 79.3, 42.7, 28.6(28.65, 28.59), 25.4, 25.1(25.10, 25.09), 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$for $C_{17}H_{20}NO_4$: 302.13868, found $[M+H]^+$: 302.13847.



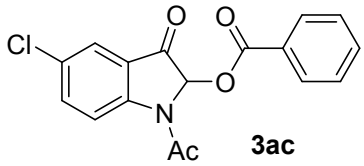
3aa

1-Acetyl-3-oxoindolin-2-yl (*2S*)-2-((tert-butoxycarbonyl)amino)-3,3-dimethylbutanoate (3aa). White solid; Reaction time: 3 h; Yield: 73%; dr = 1.2:1; m. p.: 69-71 °C; IR (KBr): 3373, 2975, 1758, 1742, 1738, 1694, 1609, 1593, 1511, 1503, 1466, 1435, 1384, 1369, 1351, 1302, 1266, 1250, 1205, 1170, 1152, 1128, 1098, 1062, 1034, 1008, 980, 937, 929, 912, 862, 825, 766, 755, 728, 701, 664, 595, 564, 545, 520, 460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 – 8.44 (m, 1H), 7.79 – 7.62 (m, 2H), 7.27 – 7.22 (m, 1H), 6.64 (s, 0.50H), 6.29 (s, 0.42H) (*minor diastereomer*), 4.13 (d, *J* = 8.8 Hz, 0.41H) (*minor diastereomer*), 4.08 (d, *J* = 9.2 Hz, 0.55H), 2.38 (s, 1.23H) (*minor diastereomer*), 2.32 (s, 1.60H), 1.44 (s, 5.24H), 1.41 (s, 3.80H) (*minor diastereomer*), 1.04 (s, 3.88H) (*minor diastereomer*), 1.03 (s, 5.34H); ^{13}C NMR (101 MHz,$CDCl_3$): δ 191.4, 191.3, 171.6, 169.9, 169.2, 169.1, 155.7, 155.5, 153.5, 152.9, 138.2, 138.0, 124.8, 124.7, 124.6, 124.3, 122.1, 121.7, 118.4, 118.2, 80.4, 80.3, 80.0, 79.1, 62.2, 61.9, 34.2 (34.23, 34.18), 28.2 (28.19, 28.18), 26.5 (26.50, 26.47), 23.9, 23.6; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{21}H_{29}N_2O_6$: 405.20201, found $[M+H]^+$: 405.20166.



3ab

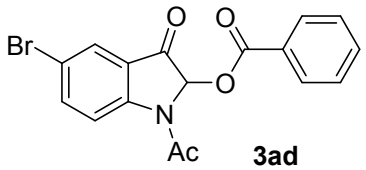
2-(1-Acetyl-3-oxoindolin-2-yl) 1-(tert-butyl) (*2S*)-pyrrolidine-1,2-diccarboxylate (3ab). White solid; Reaction time: 4 h; Yield: 48%; dr = 1.4:1; m. p.: 61-63 °C; IR (KBr): 2993, 2967, 2925, 1773, 1735, 1696, 1693, 1607, 1590, 1477, 1464, 1397, 1368, 1347, 1326, 1310, 1298, 1257, 1236, 1165, 1125, 1097, 1084, 1038, 1028, 1007, 984, 944, 919, 887, 855, 806, 765, 705, 678, 649, 596, 556, 544, 519, 457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 – 8.38 (m, 1H), 7.79 – 7.59 (m, 2H), 7.27 – 7.17 (m, 1H), 6.55 (s, 0.51H), 6.36 (s, 0.36H) (*minor diastereomer*), 4.39 – 4.28 (m, 1H), 3.60 – 3.30 (m, 2H), 2.37 (s, 1.68H), 2.37 (s, 1.32H) (*minor diastereomer*), 2.15 – 2.00 (m, 2H), 2.00 – 1.85 (m, 2H), 1.43 (s, 5.10H), 1.41 (s, 3.72H) (*minor diastereomer*); ^{13}C NMR (101 MHz, $CDCl_3$):δ 191.7, 191.1, 172.0, 171.2, 169.5, 168.6, 154.4, 153.5, 138.2, 138.1, 125.0, 124.7, 124.4, 121.7, 118.5, 80.6, 80.1, 79.6, 79.0, 58.5 (58.53, 58.48), 46.6, 46.3, 30.8, 29.7, 28.3, 28.2, 24.4, 23.8 (23.83, 23.76), 23.3; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{20}H_{25}N_2O_6$: 389.17071, found$[M+H]^+$: 389.17035.



3ac

1-Acetyl-5-chloro-3-oxoindolin-2-yl benzoate (3ac).

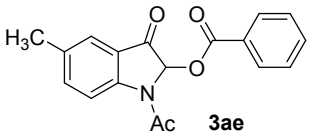
White solid; Reaction time: 5 h; Yield: 33%; m. p.: 153-154 ^{o}C; IR (KBr): 3130, 3082, 2922, 2851, 1736, 1717, 1682, 1601, 1585, 1470, 1451, 1379, 1354, 1322, 1304, 1280, 1247, 1165, 1106, 1099, 1070, 1061, 1037, 1025, 1008, 981, 935, 910, 851, 833, 779, 753, 716, 704, 608, 558, 493, 464 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.8 Hz, 1H), 8.04 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.47 (t, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.3, 168.8, 164.4, 151.1, 137.5, 134.4, 130.6, 130.2, 128.8, 127.7, 123.9, 123.6, 119.5, 80.1, 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}ClNO_4$: 330.05276, found $[M+H]^+$: 330.05258.



3ad

1-Acetyl-5-bromo-3-oxoindolin-2-yl benzoate (3ad).

White solid; Reaction time: 5 h; Yield: 48%; m. p.: 188-189 ^{o}C; IR (KBr): 3134, 3073, 2936, 1744, 1722, 1691, 1599, 1582, 1458, 1450, 1375, 1350, 1326, 1302, 1274, 1259, 1249, 1163, 1103, 1095, 1065, 1056, 1025, 1006, 977, 935, 899, 838, 802, 778, 751, 713, 687, 665, 606, 587, 556, 496 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.8 Hz, 1H), 8.08 – 8.02 (m, 2H), 7.90 (d, *J* = 2.4 Hz, 1H), 7.79 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.67–7.61 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.2, 168.8, 164.4, 151.5, 140.3, 134.4, 130.2, 128.8, 127.7, 127.0, 123.9, 119.8, 117.9, 80.0, 23.7; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{17}H_{13}BrNO_4$: 374.00225, found $[M+H]^+$: 374.00190.

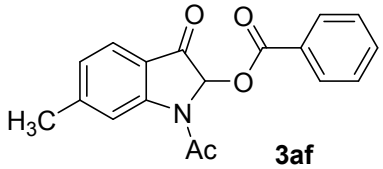


3ae

1-Acetyl-5-methyl-3-oxoindolin-2-yl benzoate (3ae).

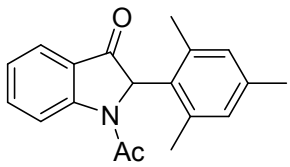
White solid; Reaction time: 5 h; Yield: 66%; m. p.: 145-146 ^{o}C; IR(KBr): 3076, 2956, 2914, 2314,1732, 1721, 1685, 1617, 1600, 1586, 1487, 1451, 1434, 1380, 1375, 1353, 1331, 1314, 1270, 1259, 1245, 1197, 1174, 1152, 1128, 1092, 1063, 1027, 1011, 980, 941, 877, 837, 794, 764, 729, 708, 642, 605, 565, 513, 500, 416 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 7.6 Hz, 1H), 8.11 – 7.98 (m, 2H), 7.67 – 7.57 (m, 2H), 7.56 – 7.51 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.58 (s, 1H), 2.41 (s, 3H), 2.34 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.5, 168.7, 164.6, 151.1, 139.0, 134.9, 134.2, 130.2, 128.7, 128.0, 124.2, 122.3, 118.0, 80.1, 23.7, 20.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_4$: 310.10738, found $[M+H]^+$: 310.10693.



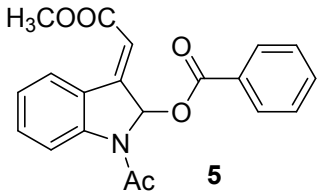
3af

1-Acetyl-6-methyl-3-oxoindolin-2-yl benzoate (3af). White solid; Reaction time: 5 h; Yield: 68%; m. p.: 189-190 °C; IR (KBr): 3072, 2960, 2920, 2855, 1736, 1677, 1606, 1449, 1434, 1387, 1353, 1328, 1315, 1269, 1253, 1238, 1178, 1135, 1096, 1061, 1020, 981, 948, 907, 888, 824, 798, 707, 691, 656, 610, 579, 511, 497, 428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.73 – 7.57 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 2.50 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.7, 168.9, 164.6, 153.3, 150.3, 134.2, 130.1, 128.7, 128.0, 126.1, 124.3, 119.9, 118.5, 80.2, 23.8, 22.9; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{18}H_{16}NO_4$: 310.10739, found $[M+H]^+$: 310.10720.



4

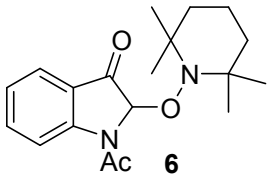
1-Acetyl-2-mesitylin dolin-3-one (4). White solid; Reaction time: 1 h; Yield: 85%; m. p.: 147-148 °C; IR (KBr): 3015, 2920, 2855, 1723, 1714, 1675, 1607, 1477, 1463, 1426, 1382, 1342, 1315, 1300, 1271, 1254, 1215, 1201, 1190, 1151, 1095, 1041, 1009, 925, 877, 865, 845, 804, 791, 764, 732, 679, 666, 588, 577, 556, 529, 511, 470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 5.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.29–7.24 (m, 1H), 6.96 (s, 1H), 6.76 (s, 1H), 5.66 (s, 1H), 2.55 (s, 3H), 2.26 (s, 3H), 1.96 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.1, 169.6, 153.5, 138.2, 137.4, 135.7, 131.3, 130.0, 129.3, 124.4, 124.2, 123.5, 118.7, 66.5, 24.1, 21.0, 20.8, 19.8; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{19}H_{20}NO_2$: 294.14886, found $[M+H]^+$: 294.14877.



5

1-Acetyl-3-(2-methoxy-2-oxoethylidene)indolin-2-yl benzoate (5). White solid; Reaction time: 2 h; Yield: 36%; m. p.: 118-119 °C; IR (KBr): 3072, 2949, 2851, 1716, 1686, 1641, 1591, 1463, 1438, 1390, 1358, 1335,

1316, 1287, 1262, 1213, 1187, 1172, 1092, 1068, 1025, 956, 933, 868, 797, 754, 711, 643, 599, 568, 541, 489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.0 Hz, 1H), 8.36 (s, 1H), 8.08 – 8.00 (m, 2H), 7.63 – 7.56 (m, 1H), 7.51 – 7.41 (m, 4H), 7.23 – 7.18 (m, 1H), 6.43 (s, 1H), 3.78 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 165.9, 165.7, 148.0, 146.6, 134.0, 133.1, 130.0, 128.8, 128.6, 128.5, 124.5, 123.5, 116.8, 116.4, 85.4, 51.7, 23.5; HRMS (Orbitrap-ESI) m/z: calculated $[M+Na]^+$ for $C_{20}H_{18}NNaO_5$: 374.09989, found $[M+Na]^+$: 374.09968.



6 **1-Acetyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)indolin-3-one (6).** White solid; Reaction time: 5 h; Yield: 15%; m. p.: 125 - 126 °C; IR (KBr): 3416, 2985, 2970, 2935, 2884, 2848, 1741, 1677, 1604, 1593, 1467, 1389, 1383, 1364, 1344, 1323, 1316, 1295, 1260, 1245, 1213, 1181, 1134, 1095, 1039, 1027, 1007, 986, 954, 921, 907, 878, 831, 799, 766, 713, 694, 665, 623, 598, 573, 519, 479 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.68 – 7.60 (m, 1H), 7.25 – 7.19 (m, 1H), 5.69 (s, 1H), 2.69 (s, 3H), 1.65 – 1.41 (m, 5H), 1.38 (s, 3H), 1.40 – 1.33 (m, 1H), 1.20 (s, 3H), 1.09 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.5, 170.3, 152.6, 137.2, 124.4, 124.3, 123.6, 119.3, 88.9, 61.9, 59.8, 39.9, 39.8, 32.6, 32.4, 25.2, 20.3, 20.2, 16.6; HRMS (Orbitrap-ESI) m/z: calculated $[M+H]^+$ for $C_{19}H_{27}N_2O_3$: 331.2016, found $[M+H]^+$: 331.2020.

References

1) Y. Z. Liu, J. Zhang, P. F. Xu and Y. C. Luo, *J. Org. Chem.* 2011, **76**, 7551–7555.

2) Y. Z. Liu, R. L. Chen and P. F. Xu, *J. Org. Chem.* 2011, **76**, 2884 – 2887.

3) W. S. Shun, L. Hong and R. Wang, *Chem. Eur. J.* 2011, **17**, 6030 – 6033.

4) J. Guo, Z. H. Lin, K. B. Chen, Y. Xie, A. S. C.Chan, J.Weng and L. Gui, *Org. Chem. Front.* 2017, **4**, 1400-1406.

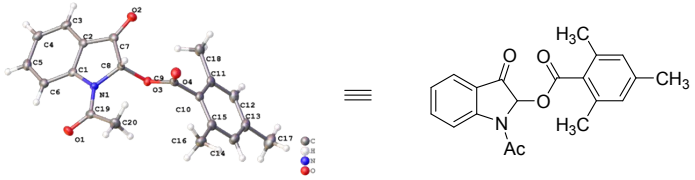
X-ray Crystallographic data of 3k (CCDC: 1939241)

The single crystals of compound **3k** for X-ray analysis was grown from the mixed solution of hexane and chloroform (V/V = 10/1). Compound **3k** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Mo Kα (λ = 0.71073). Data reduction was carried out with the diffractometer's software.[1] The structures were solved by direct methods using Olex2 software,[2] and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2014[3] using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition number: **CCDC 1939241** for compound **3k**. The thermal ellipsoid showing the atom-numbering of compound **3k** was drawn at the 30% probability level and H-atoms were shown as small arbitrary radii.

[1] Agilent Technologies, CrysAlisPRO, Version 1.171.36.28, **2013**.

[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J. *J. Appl. Cryst.* **2009**, *42*, 339.

[3] Kratzert, D.; Holstein, J. J.; Krossing, I. *J. Appl. Crystallogr.* **2015**, *48*, 933.



X-ray Crystal Structure of **3k**

Empirical formula	$C_{20}H_{19}NO_4$
Formula weight	337.36
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$

a/Å	8.4606(4)
b/Å	16.9137(8)
c/Å	35.129(3)
α/°	90
β/°	90.02(2)
γ/°	90
Volume/Å^3	5026.9(5)
Z	12
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.093
F(000)	2136.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.23 to 50
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -40 ≤ l ≤ 41
Reflections collected	24168
Independent reflections	8834 [R_{int} = 0.0370, R_{sigma} = 0.0464]
Data/restraints/parameters	8834/0/688
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1179
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1354
Largest diff. peak/hole / e Å^{-3}	0.30/-0.27

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell:	a=8.4606(4)	b=16.9137(8)	c=35.129(3)
	alpha=90	beta=90.02(2)	gamma=90

Temperature: 100 K

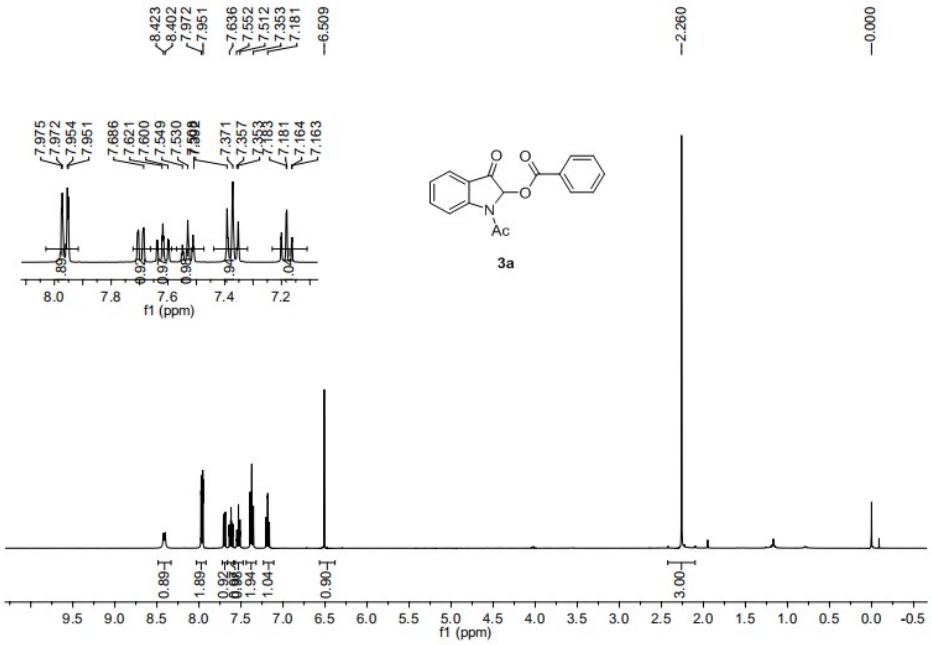
	Calculated	Reported
Volume	5027.0(5)	5026.9(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H19 N O4	C20 H19 N O4
Sum formula	C20 H19 N O4	C20 H19 N O4
Mr	337.36	337.36
Dx,g cm-3	1.337	1.337
Z	12	12
Mu (mm-1)	0.093	0.093
F000	2136.0	2136.0
F000’	2137.08	
h,k,lmax	10,20,41	10,20,41
Nref	8848	8834
Tmin,Tmax	0.988,0.990	0.718,1.000
Tmin’	0.988	

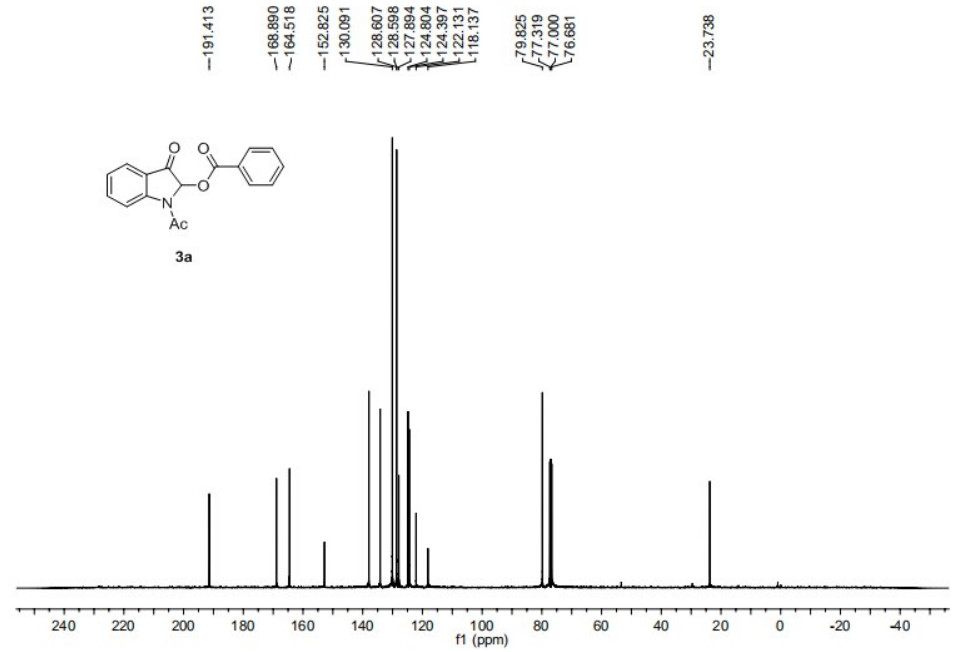
Correction method= # Reported T Limits: Tmin=0.718 Tmax=1.000

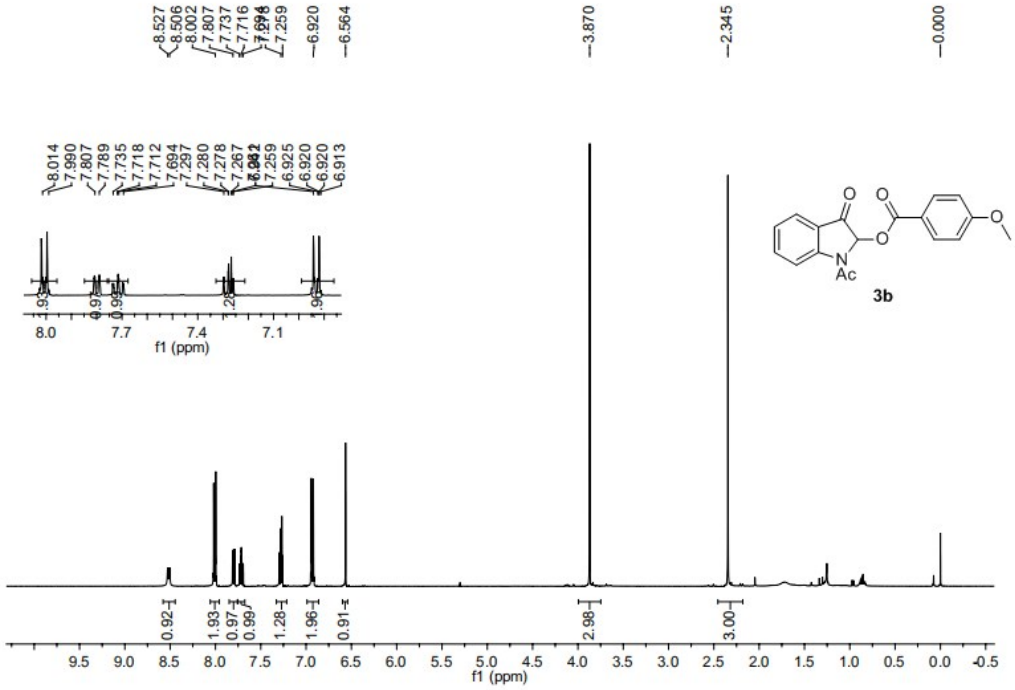
AbsCorr = MULTI-SCAN

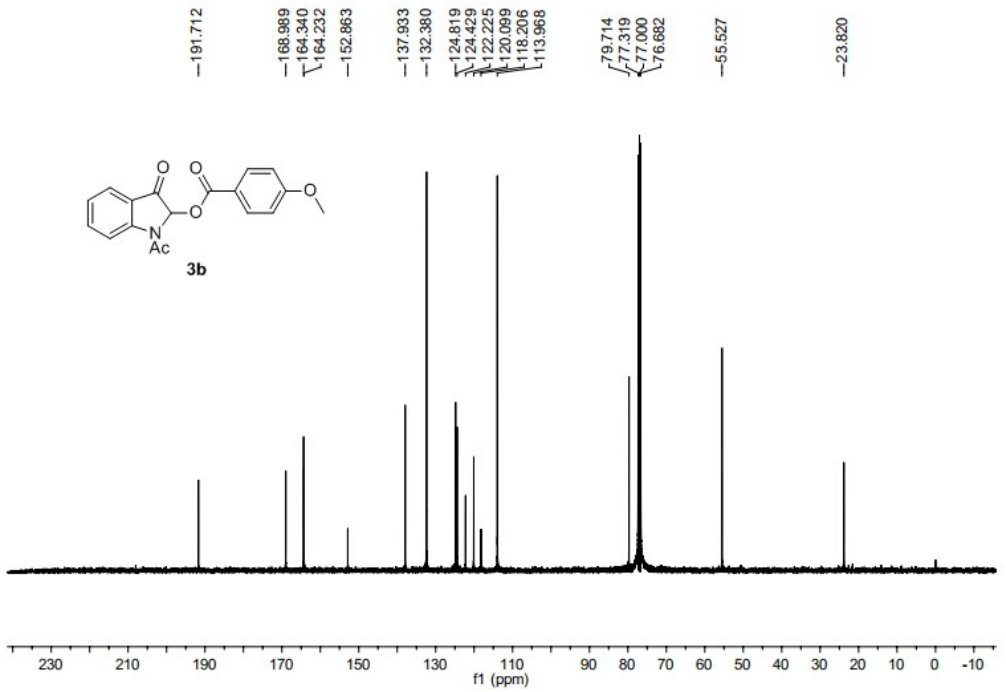
Data completeness= 0.998	Theta(max)= 25.000
R(reflections)= 0.0515(6349)	wR2(reflections)= 0.1354(8834)
S = 1.027	Npar= 688

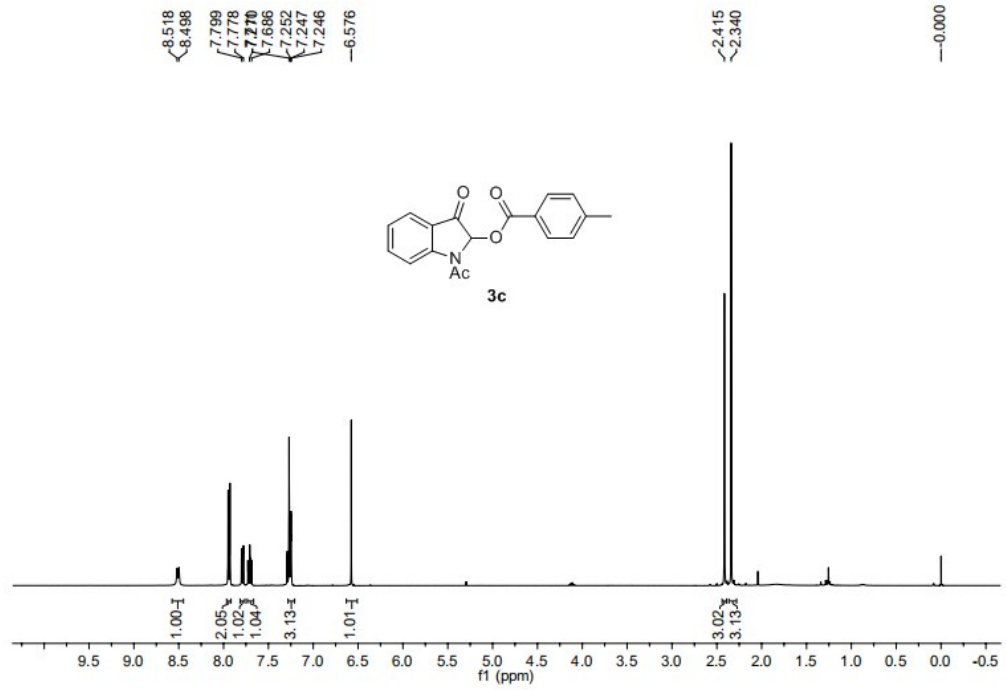
NMR spectrogram

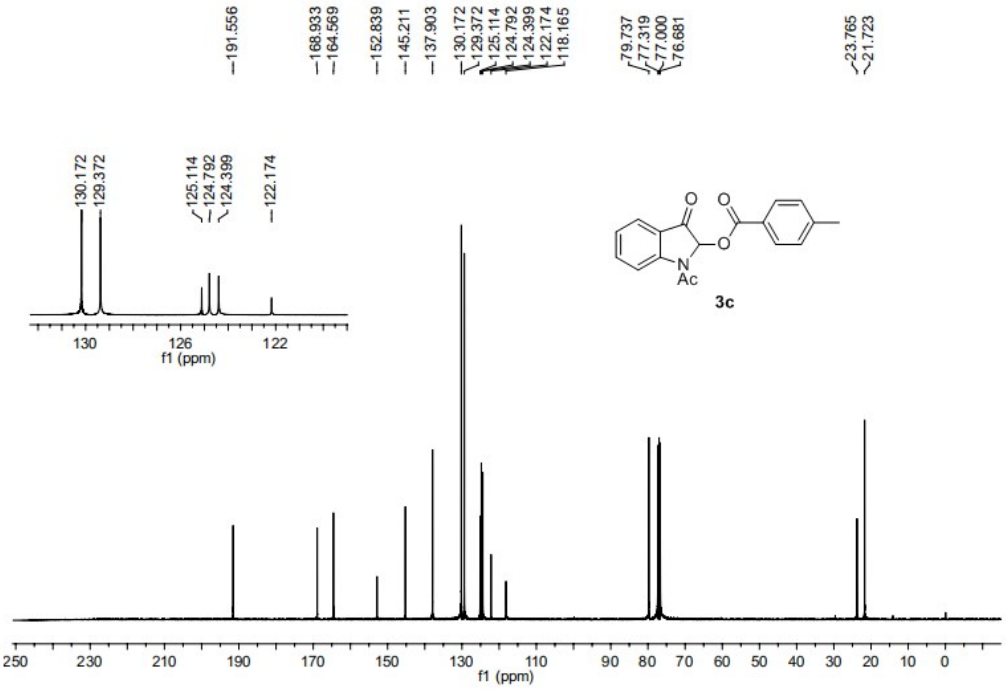


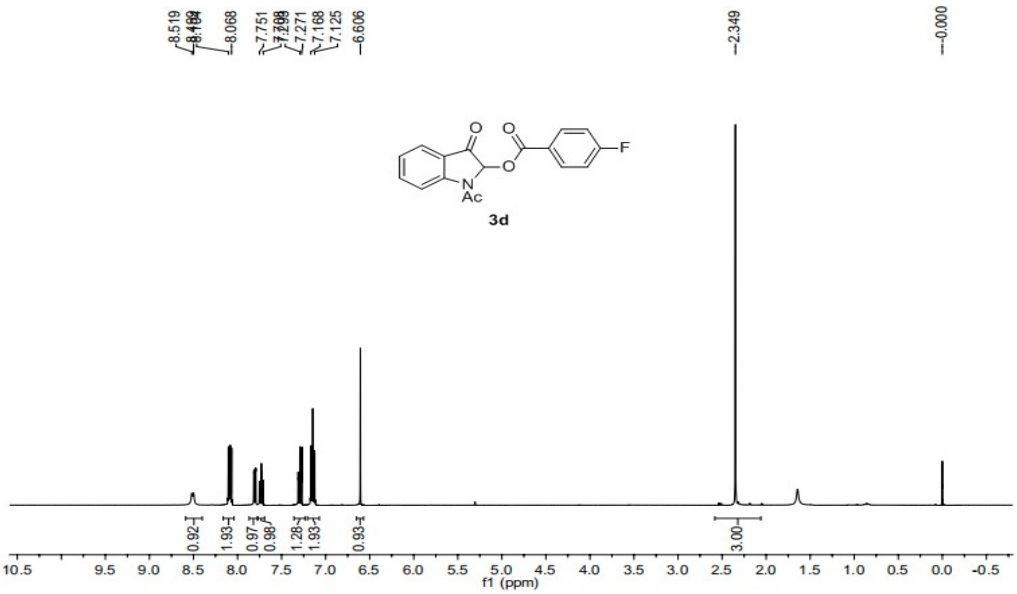


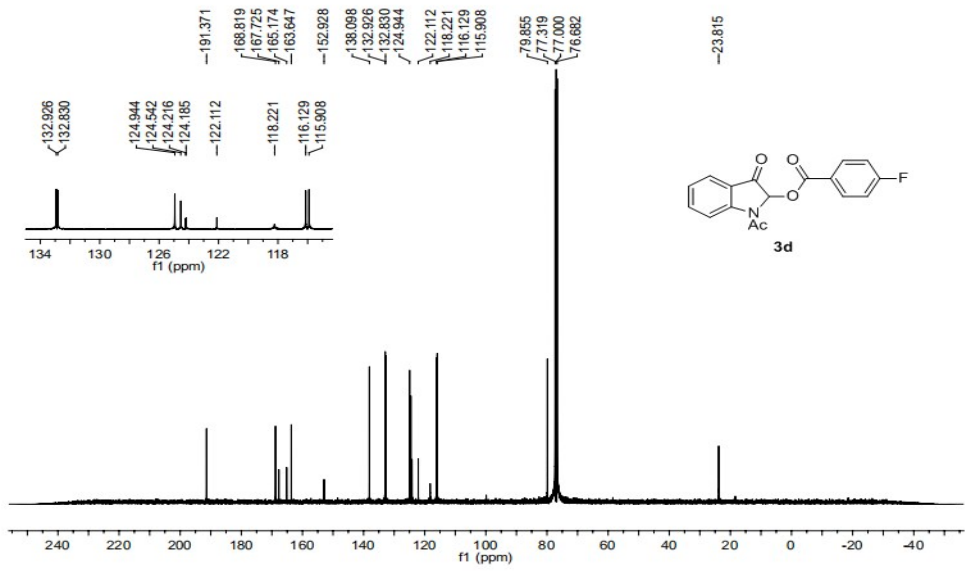

8.527
8.506
8.002
7.807
7.737
7.716
7.259
6.920
6.564
3.870
2.345
0.000
8.014
7.990
7.807
7.789
7.735
7.718
7.712
7.694
7.297
7.280
7.278
7.267
7.259
6.925
6.920
6.920
6.913
8.0
7.7
7.4
7.1
f1 (ppm)
O
O
O
N
Ac
3b
0.92
1.93
0.97
0.99
1.28
1.96
0.91
2.98
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

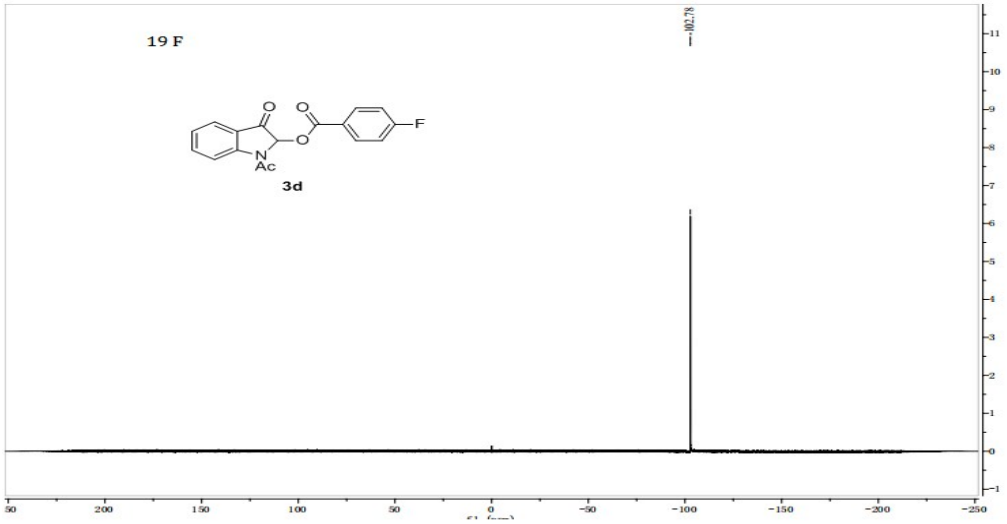

191.712
168.989
164.340
164.232
152.863
137.933
132.380
124.819
124.429
122.225
120.099
118.206
113.968
79.714
77.319
77.000
76.682
55.527
23.820
O
O
O
N
Ac
3b
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

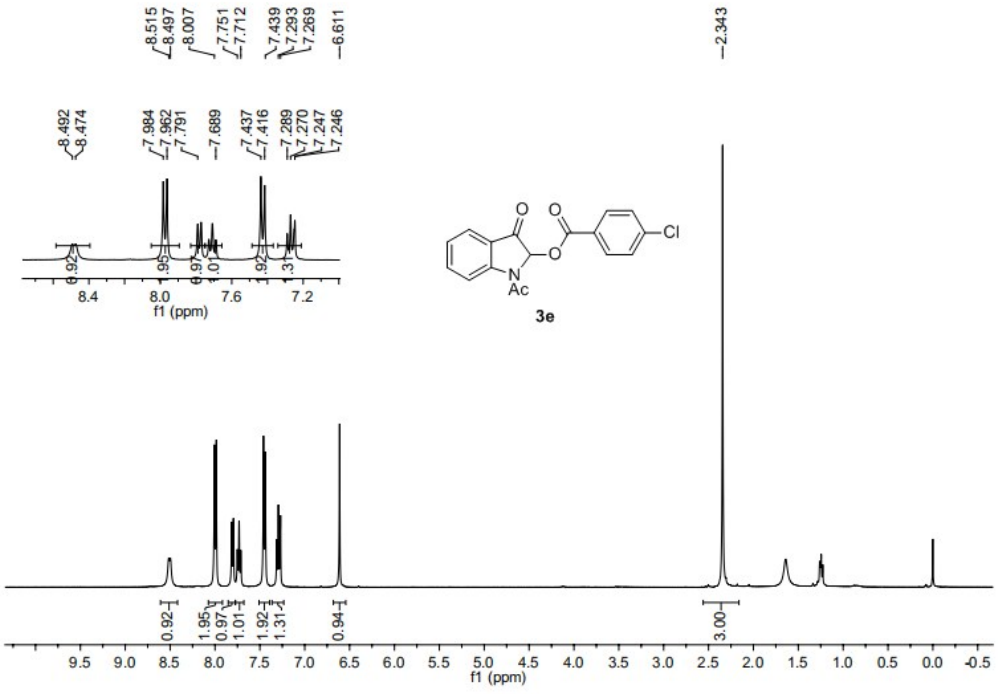

8.518
8.498
7.799
7.778
7.686
7.252
7.247
7.246
6.576
2.415
2.340
0.000
3c
1.00
2.05
1.02
1.04
3.13
1.01
3.02
3.13
f1 (ppm)

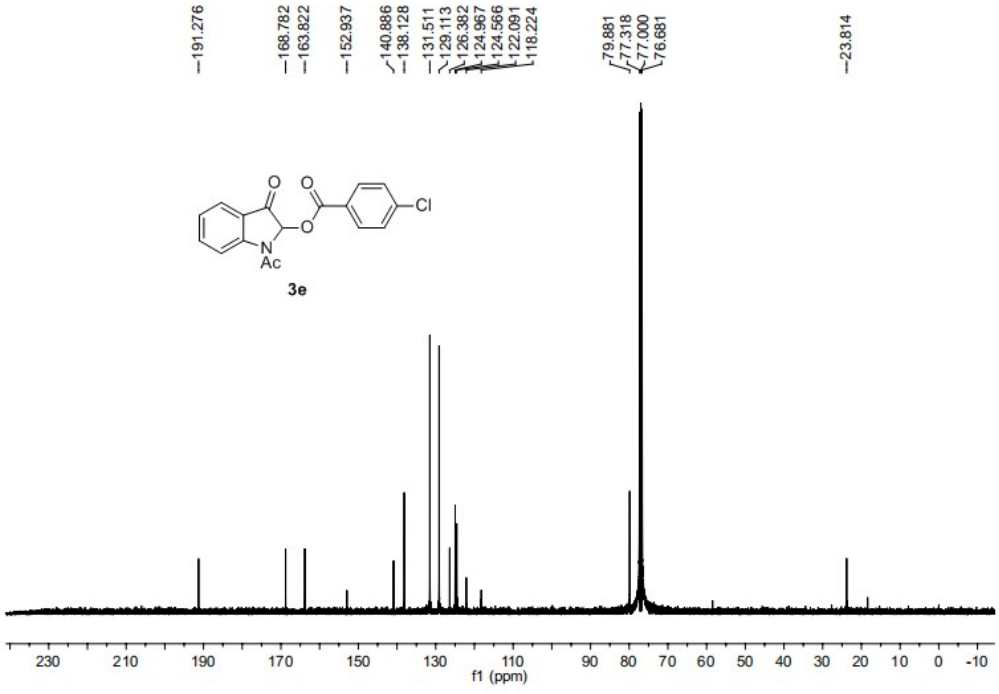

191.556
168.933
164.569
152.839
145.211
137.903
130.172
129.372
125.114
124.792
124.399
122.174
118.165
79.737
77.319
77.000
76.881
23.765
21.723
3c
f1 (ppm)

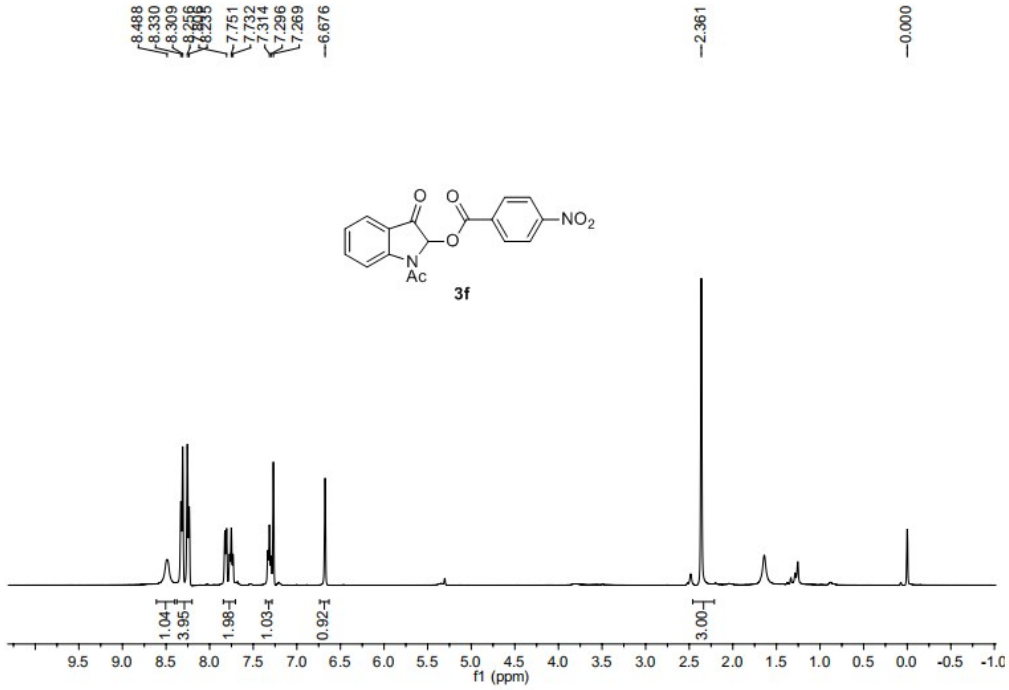

8.519
8.068
7.751
7.271
7.168
7.125
6.606
2.349
0.000
3d
0.92
1.93
0.97
0.98
1.28
1.93
0.93
3.00
f1 (ppm)

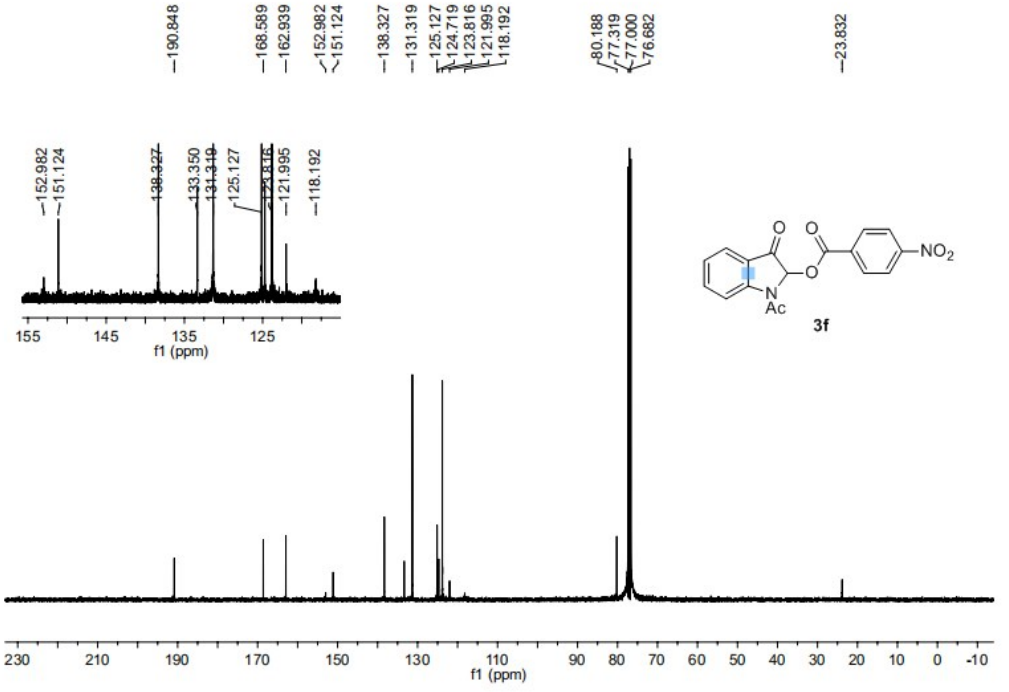

191.371
168.819
167.725
165.174
163.647
152.928
138.098
132.926
132.830
124.944
122.112
118.221
116.129
115.908
79.855
77.319
77.000
76.682
23.815
3d
f1 (ppm)

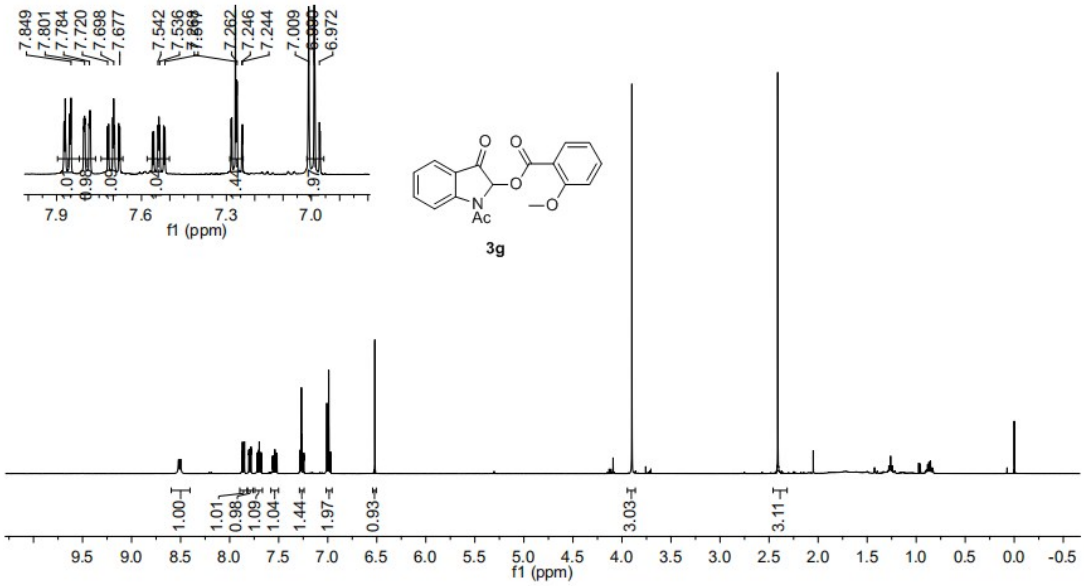

19 F
102.78
3d

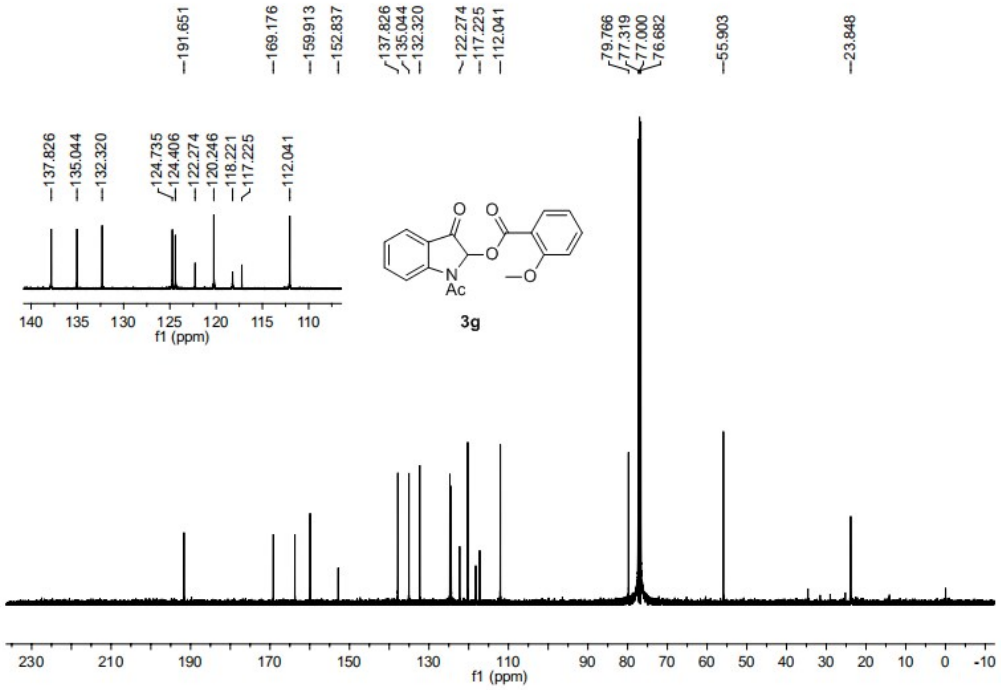

8.515
8.497
8.007
7.751
7.712
7.439
7.293
7.269
6.611
2.343
8.492
8.474
7.984
7.962
7.791
7.689
7.437
7.416
7.289
7.270
7.247
7.246
f1 (ppm)
3e
0.92
1.95
0.97
1.01
1.92
1.31
0.94
3.00
f1 (ppm)

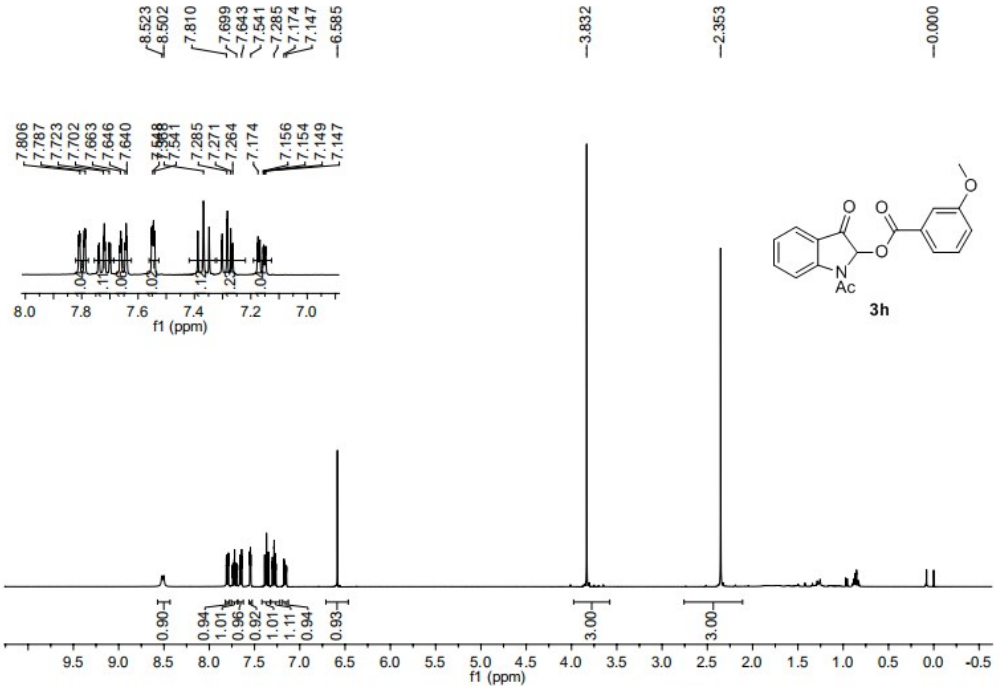

191.276
168.782
163.822
152.937
140.886
138.128
131.511
129.113
126.382
124.967
124.566
122.091
118.224
79.881
77.318
77.000
76.681
23.814
3e
f1 (ppm)

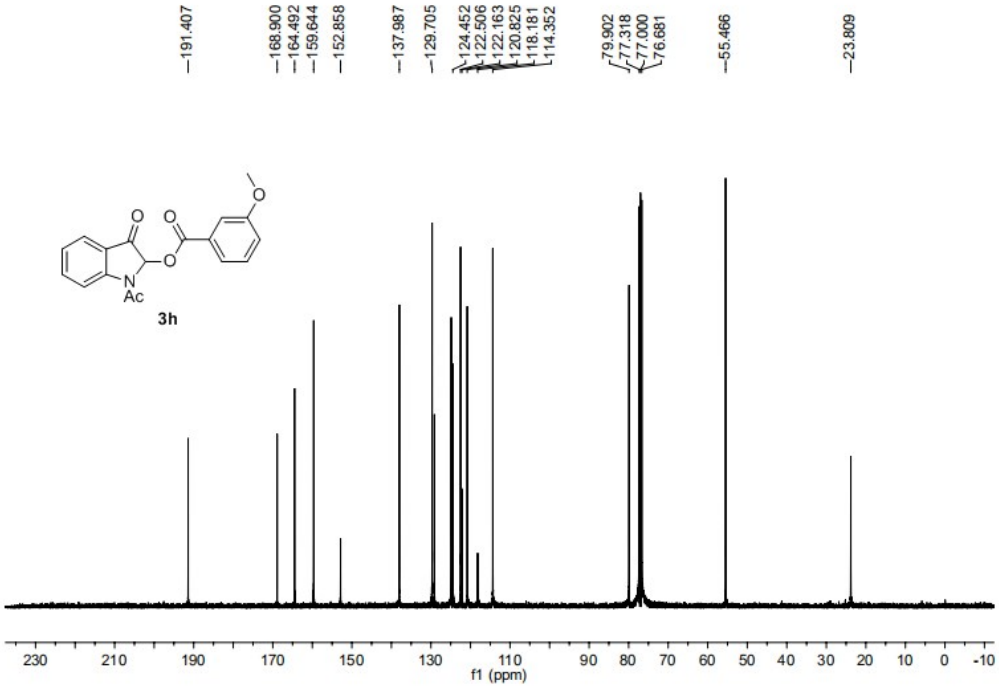

8.488
8.330
8.309
7.751
7.732
7.314
7.296
7.269
6.676
2.361
0.000
O
O
O
NO2
N
Ac
3f
1.04
3.95
1.98
1.03
0.92
3.00
f1 (ppm)

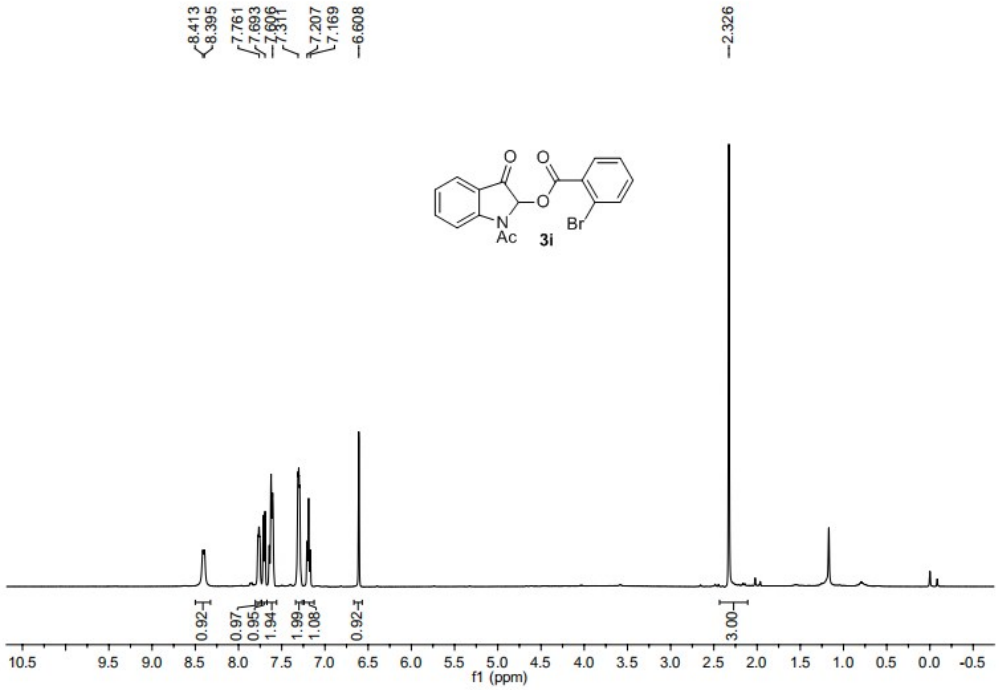

190.848
168.589
162.939
152.982
151.124
138.327
131.319
125.127
124.719
123.816
121.995
118.192
80.188
77.319
77.000
76.682
23.832
O
O
O
NO2
N
Ac
3f
f1 (ppm)

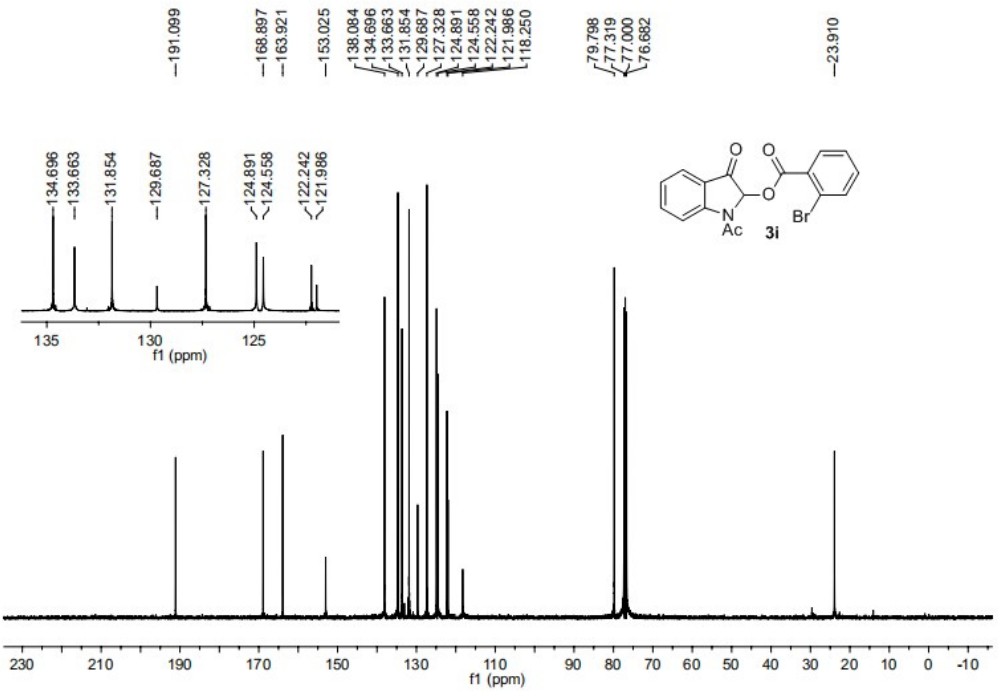

7.849
7.801
7.784
7.720
7.698
7.677
7.542
7.536
7.262
7.246
7.244
7.009
6.972
f1 (ppm)
3g
1.00
1.01
0.98
1.09
1.04
1.44
1.97
0.93
3.03
3.11
f1 (ppm)

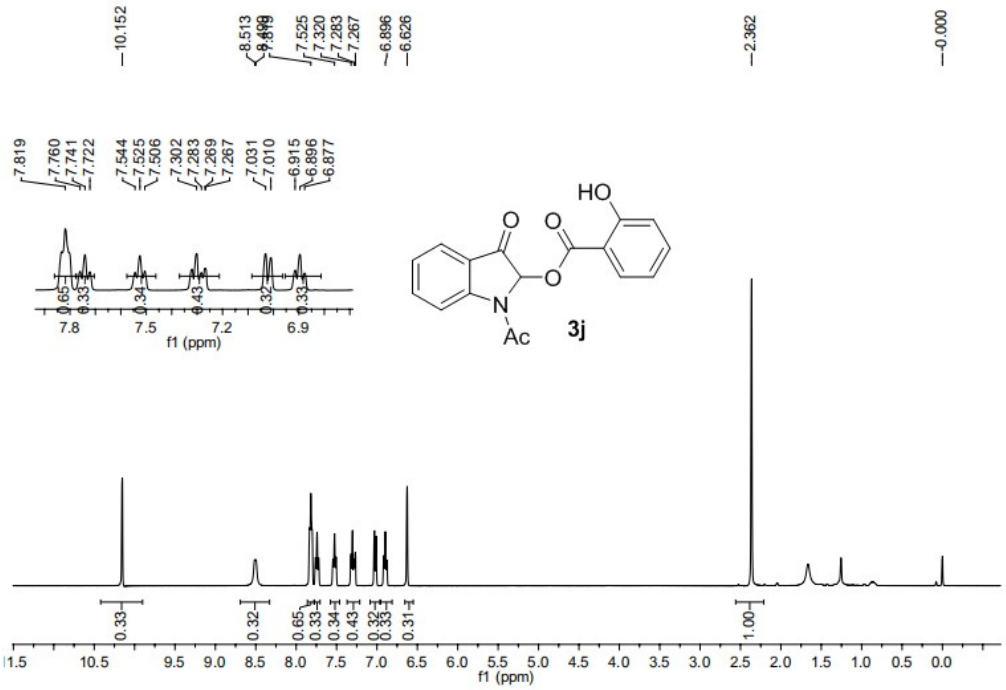

191.651
169.176
159.913
152.837
137.826
135.044
132.320
122.274
117.225
112.041
79.766
77.319
77.000
76.682
55.903
23.848
f1 (ppm)
3g
f1 (ppm)

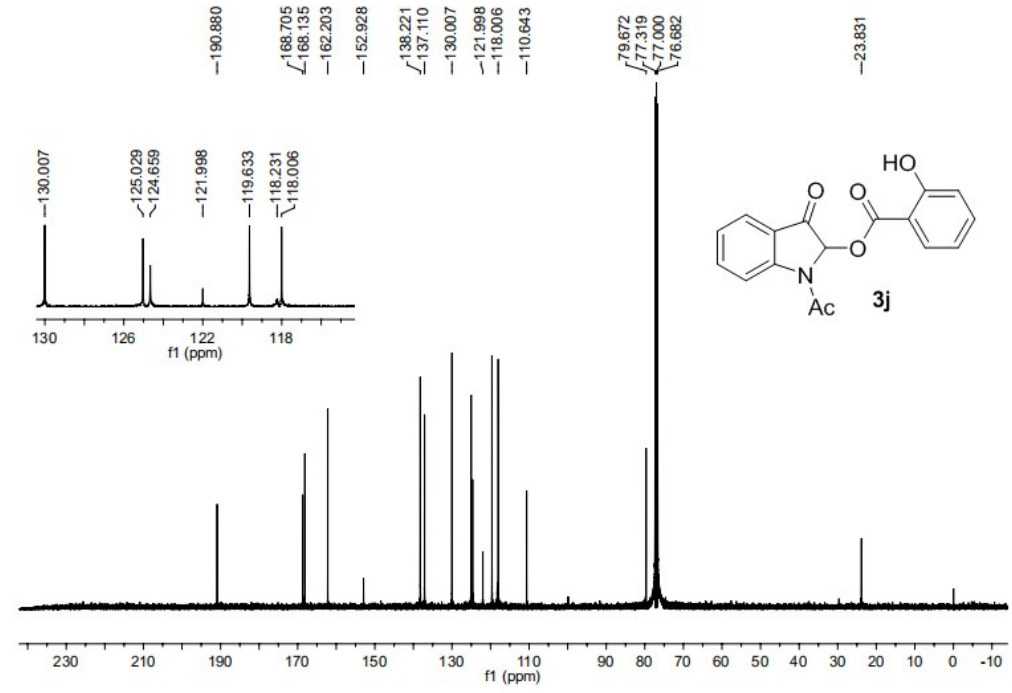

8.523
8.502
7.810
7.699
7.643
7.541
7.285
7.174
7.147
6.585
3.832
2.353
0.000
7.806
7.787
7.723
7.702
7.663
7.646
7.640
7.285
7.271
7.264
7.174
7.156
7.154
7.149
7.147
f1 (ppm)
3h
0.90
0.94
1.01
0.96
0.92
1.01
1.11
0.94
0.93
3.00
3.00
f1 (ppm)

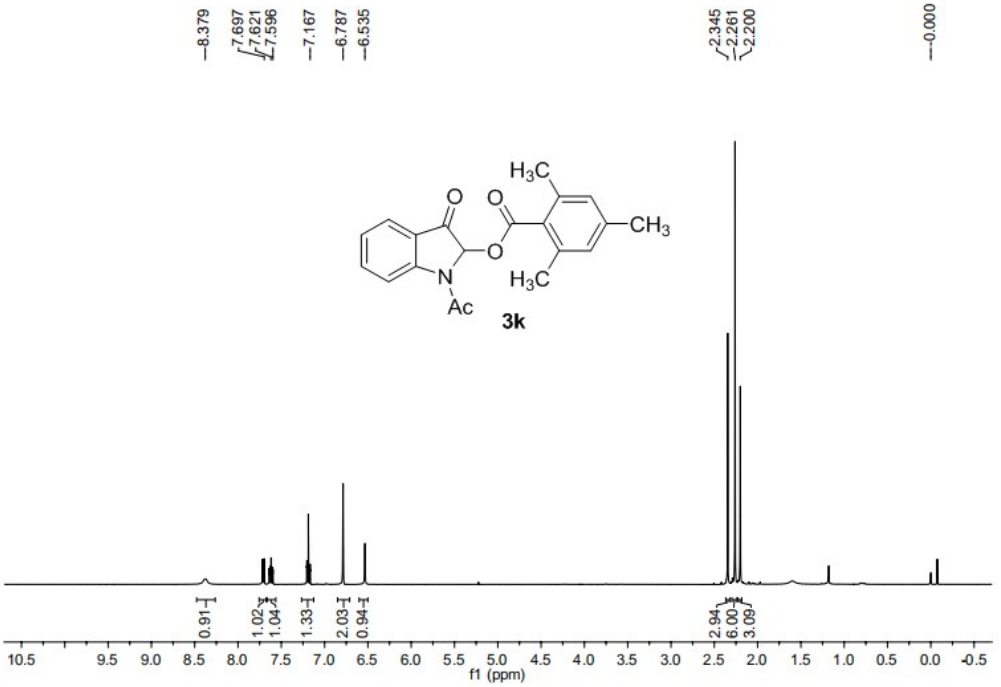

191.407
168.900
164.492
159.644
152.858
137.987
129.705
124.452
122.506
122.163
120.825
118.181
114.352
79.902
77.318
77.000
76.681
55.466
23.809
3h
f1 (ppm)

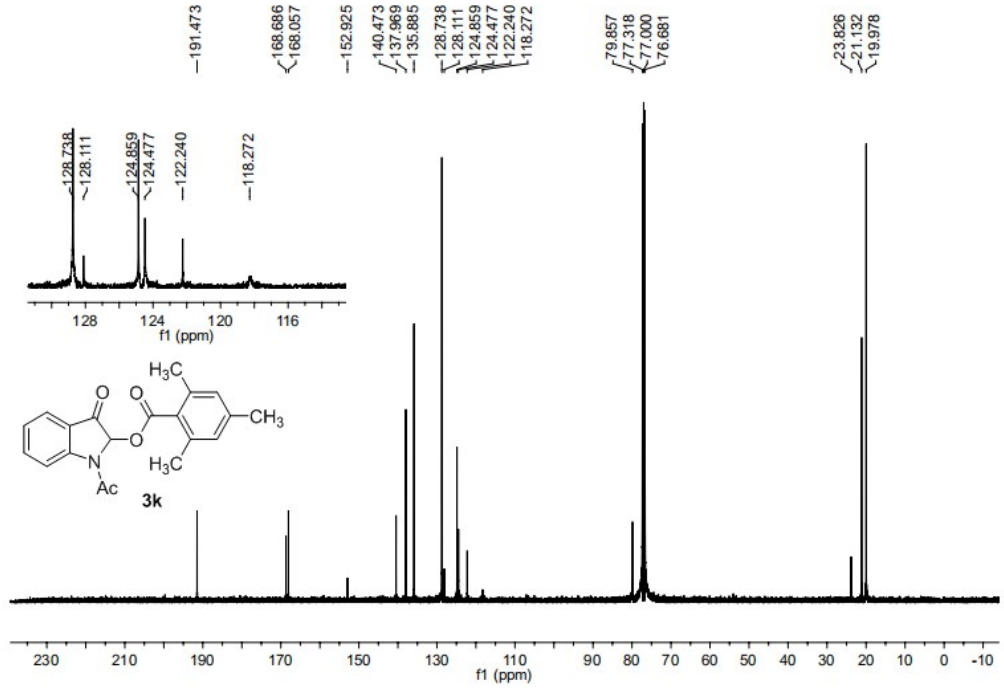

8.413
8.395
7.761
7.693
7.606
7.311
7.207
7.169
6.608
2.326
Ac
3i
Br
0.92
0.97
0.95
1.94
1.99
1.08
0.92
3.00
f1 (ppm)

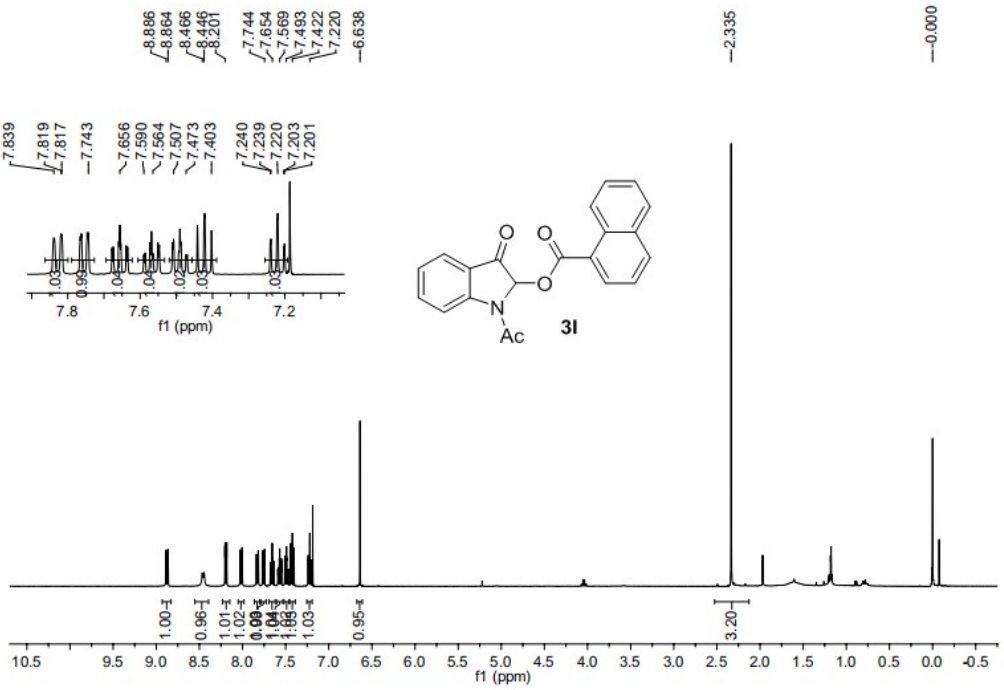

191.099
168.897
163.921
153.025
138.084
134.696
133.663
131.854
129.687
127.328
124.891
124.558
122.242
121.986
118.250
79.798
77.319
77.000
76.682
23.910
Ac
3i
Br
f1 (ppm)

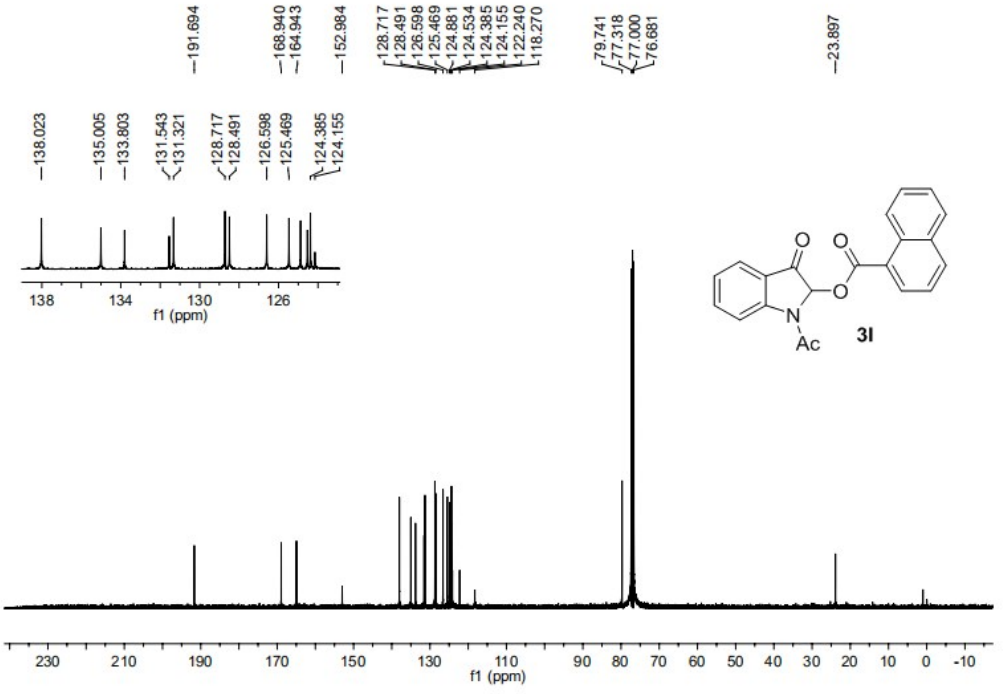

10.152
8.513
8.498
7.819
7.760
7.741
7.722
7.544
7.525
7.506
7.525
7.320
7.302
7.283
7.269
7.267
7.031
7.010
6.915
6.896
6.877
6.896
6.626
2.362
0.000
HO
O
O
O
N
Ac
3j
0.33
0.32
0.65
0.33
0.34
0.43
0.32
0.33
0.31
1.00
f1 (ppm)

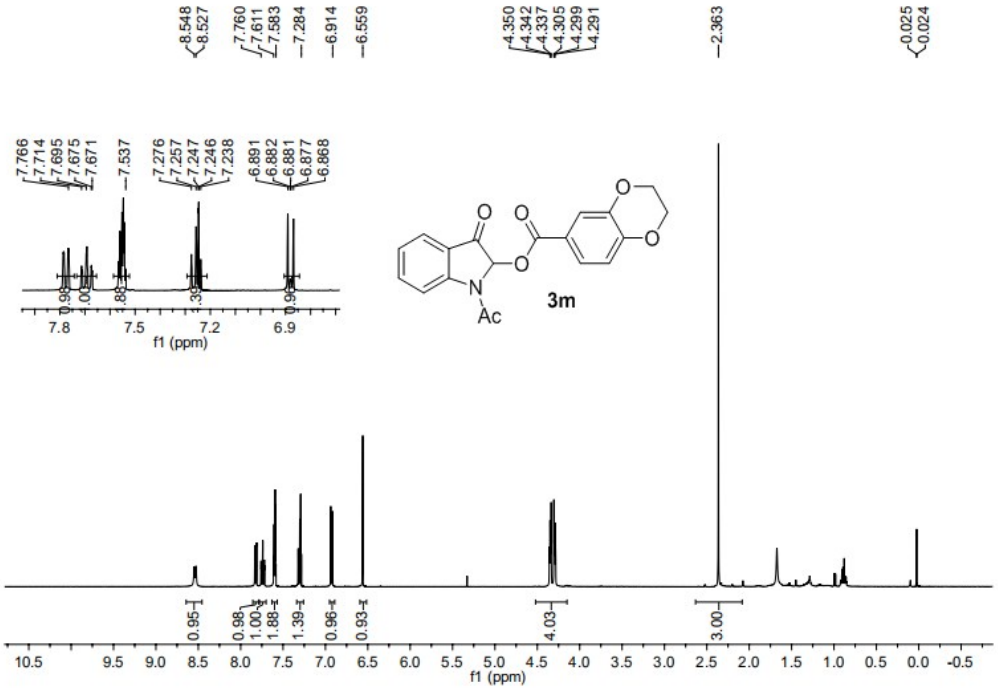

190.880
168.705
168.135
162.203
152.928
138.221
137.110
130.007
121.998
118.006
110.643
79.672
77.319
77.000
76.682
23.831
130.007
125.029
124.659
121.998
119.633
118.231
118.006
HO
O
O
O
N
Ac
3j
f1 (ppm)

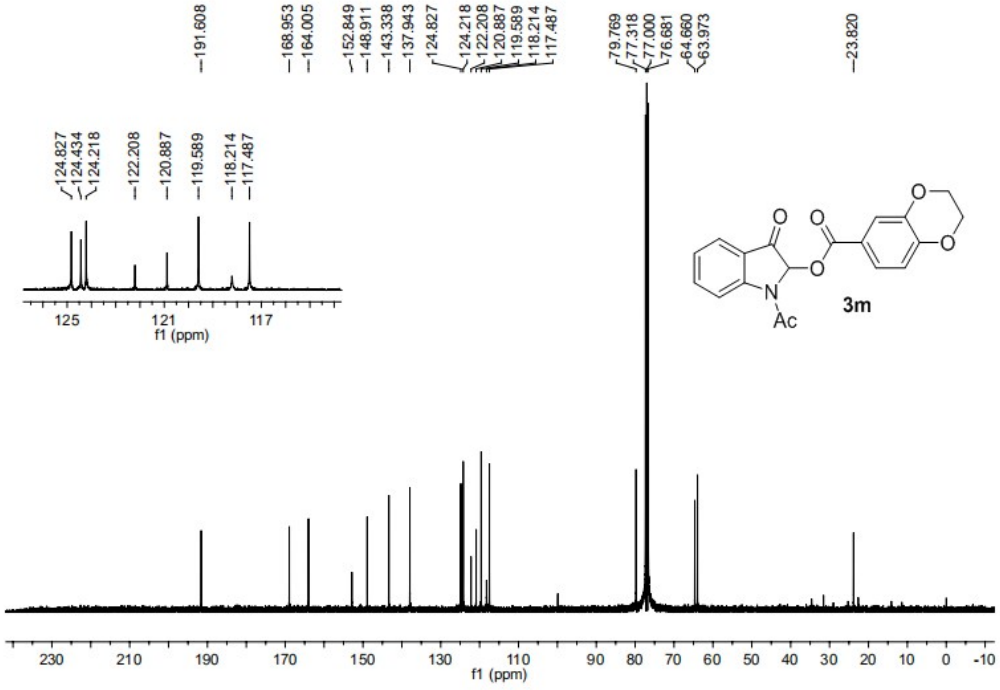

8.379
7.697
7.621
7.596
7.167
6.787
6.535
2.345
2.261
2.200
0.000
0.91
1.02
1.04
1.33
2.03
0.94
2.94
6.00
3.09
f1 (ppm)
3k

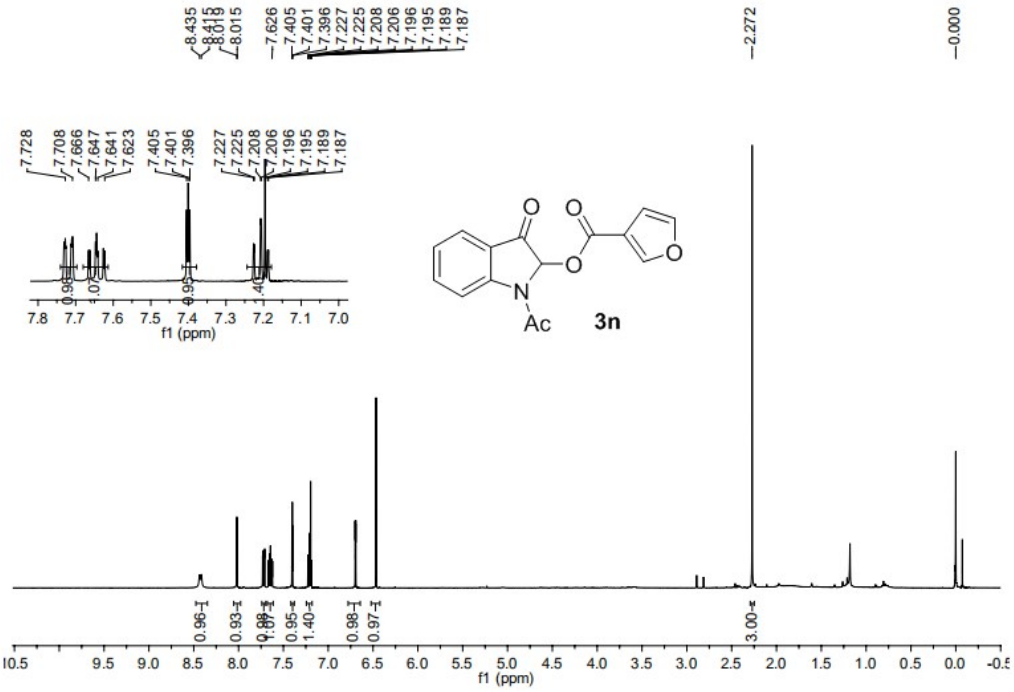

191.473
168.686
168.057
152.925
140.473
137.969
135.885
128.738
128.111
124.859
124.477
122.240
118.272
79.857
77.318
77.000
76.681
23.826
21.132
19.978
f1 (ppm)
3k

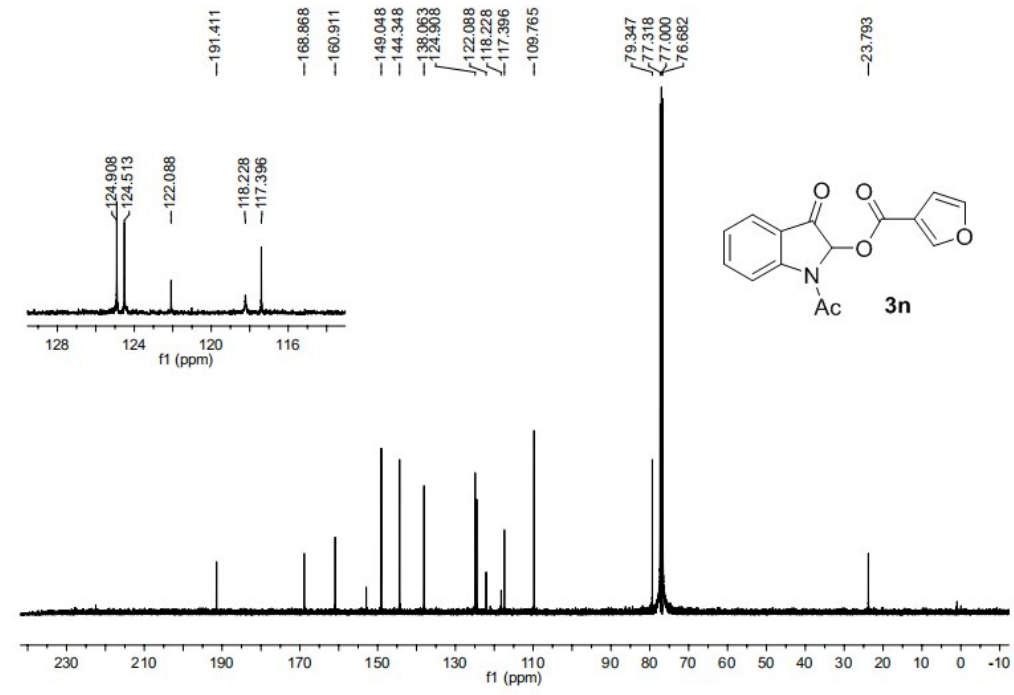

8.886
8.864
8.466
8.446
8.201
7.744
7.654
7.569
7.493
7.422
7.220
6.638
2.335
0.000
7.839
7.819
7.817
7.743
7.656
7.590
7.564
7.507
7.473
7.403
7.240
7.239
7.220
7.203
7.201
f1 (ppm)
O
O
O
N
Ac
3l
1.00
0.96
1.01
1.02
1.03
0.95
3.20
f1 (ppm)


191.694
168.940
164.943
152.984
128.717
128.491
126.598
125.469
124.881
124.534
124.385
124.155
122.240
118.270
79.741
77.318
77.000
76.681
23.897
138.023
135.005
133.803
131.543
131.321
128.717
128.491
126.598
125.469
124.385
124.155
f1 (ppm)
O
O
O
N
Ac
3l
f1 (ppm)


8.548
8.527
7.760
7.611
7.583
7.284
6.914
6.559
4.350
4.342
4.337
4.305
4.299
4.291
2.363
0.025
0.024
7.766
7.714
7.695
7.675
7.671
7.537
7.276
7.257
7.247
7.246
7.238
6.891
6.882
6.881
6.877
6.868
f1 (ppm)
3m
Ac
0.95
0.98
1.00
1.88
1.39
0.96
0.93
4.03
3.00
f1 (ppm)


191.608
168.953
164.005
152.849
148.911
143.338
137.943
124.827
124.218
122.208
120.887
119.589
118.214
117.487
79.769
77.318
77.000
76.681
64.660
63.973
23.820
124.827
124.434
124.218
122.208
120.887
119.589
118.214
117.487
f1 (ppm)
3m
Ac
f1 (ppm)


8.435
8.415
8.018
8.015
7.626
7.405
7.401
7.396
7.227
7.225
7.208
7.206
7.196
7.195
7.189
7.187
2.272
0.000
7.728
7.708
7.666
7.647
7.641
7.623
7.405
7.401
7.396
7.227
7.225
7.208
7.206
7.196
7.195
7.189
7.187
0.96
1.07
0.99
1.40
f1 (ppm)
O
O
O
N
Ac
3n
0.96
0.93
0.98
0.95
1.40
0.98
0.97
3.00
f1 (ppm)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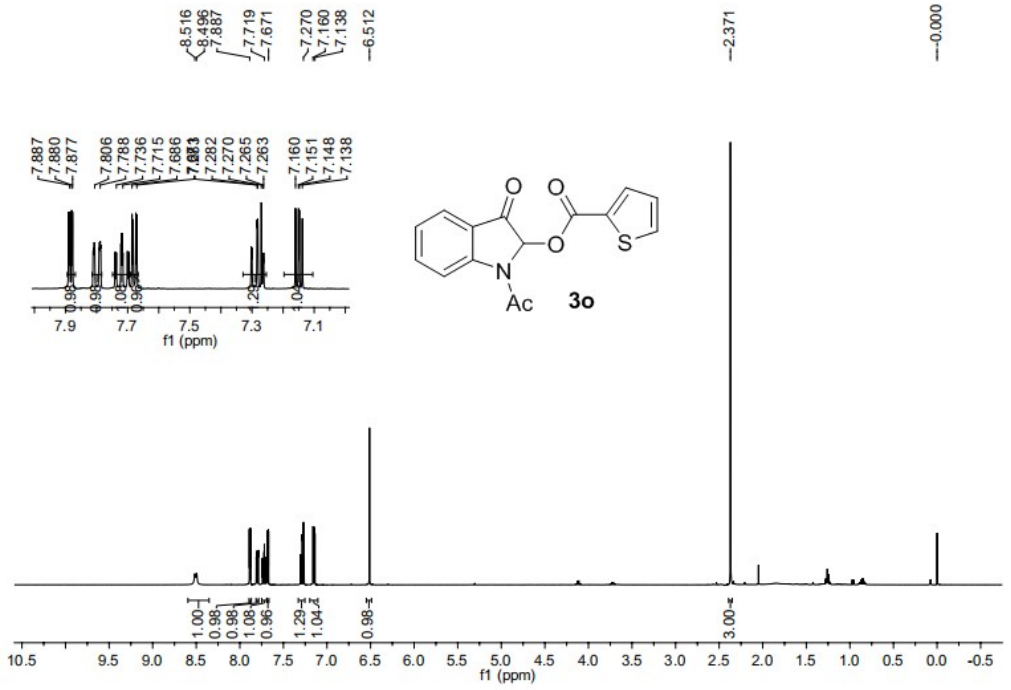
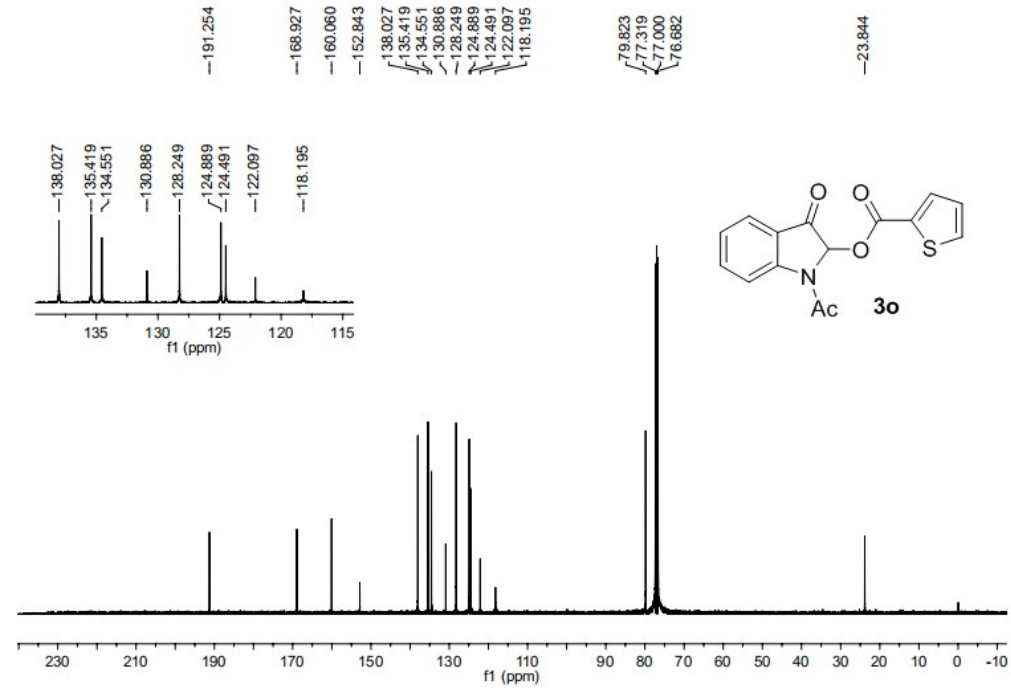
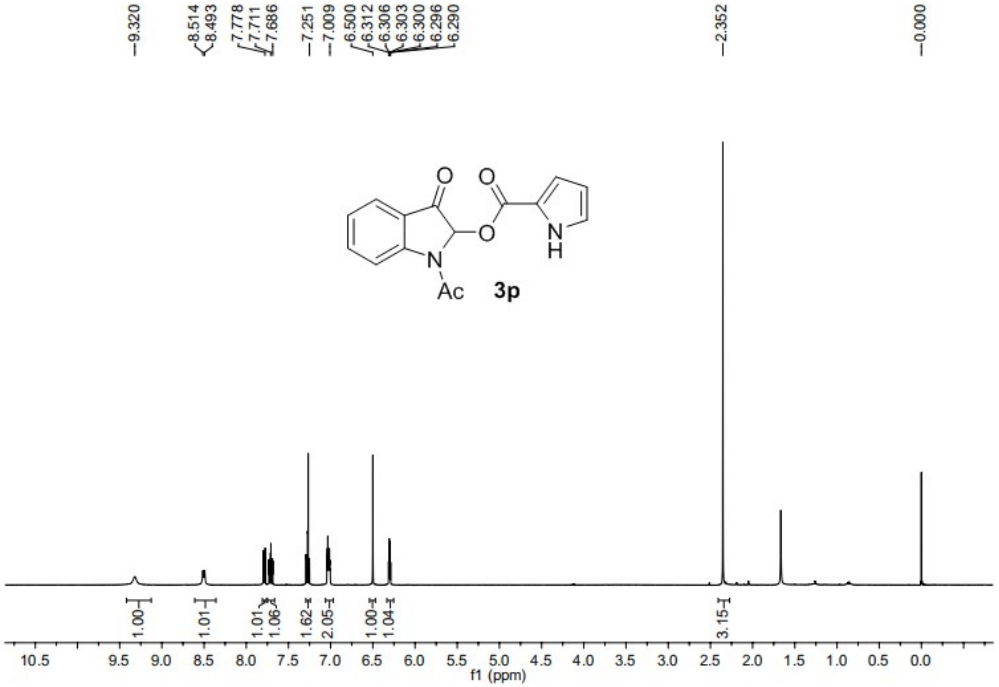
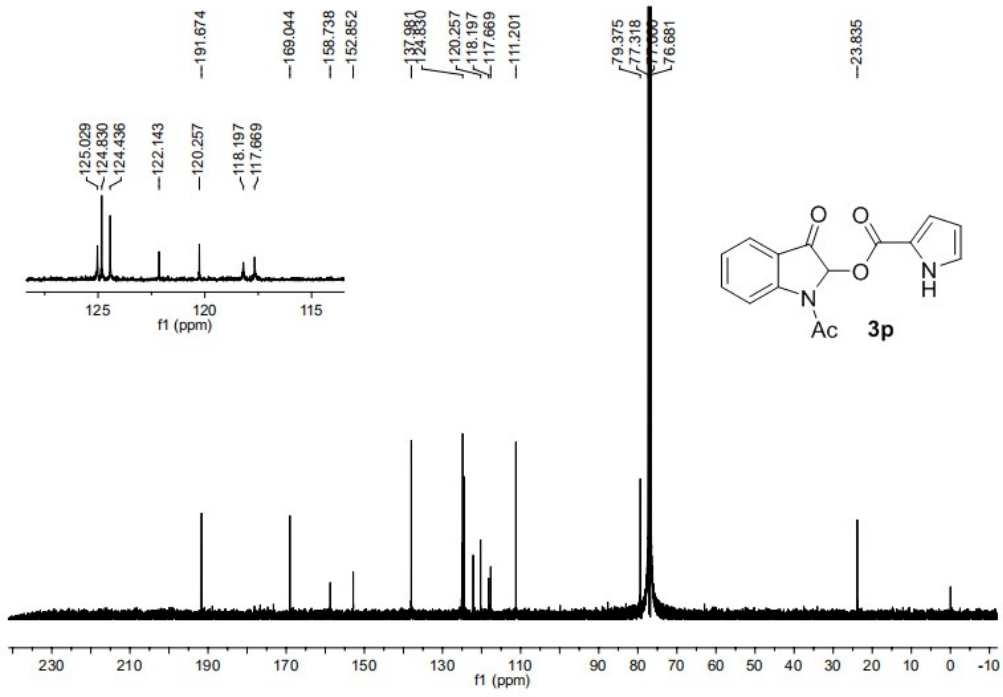
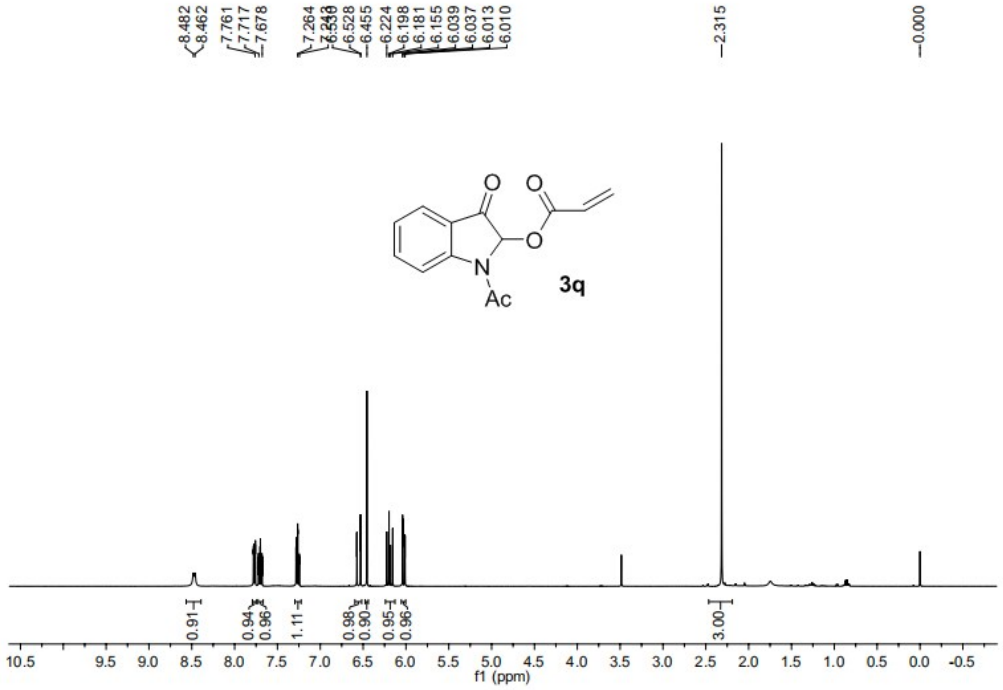
160.911
149.048
144.348
138.063
124.908
122.088
118.228
117.396
109.765
79.347
77.318
77.000
76.682
23.793
124.908
124.513
122.088
118.228
117.396
f1 (ppm)
O
O
O
O
N
Ac
3n
f1 (ppm)

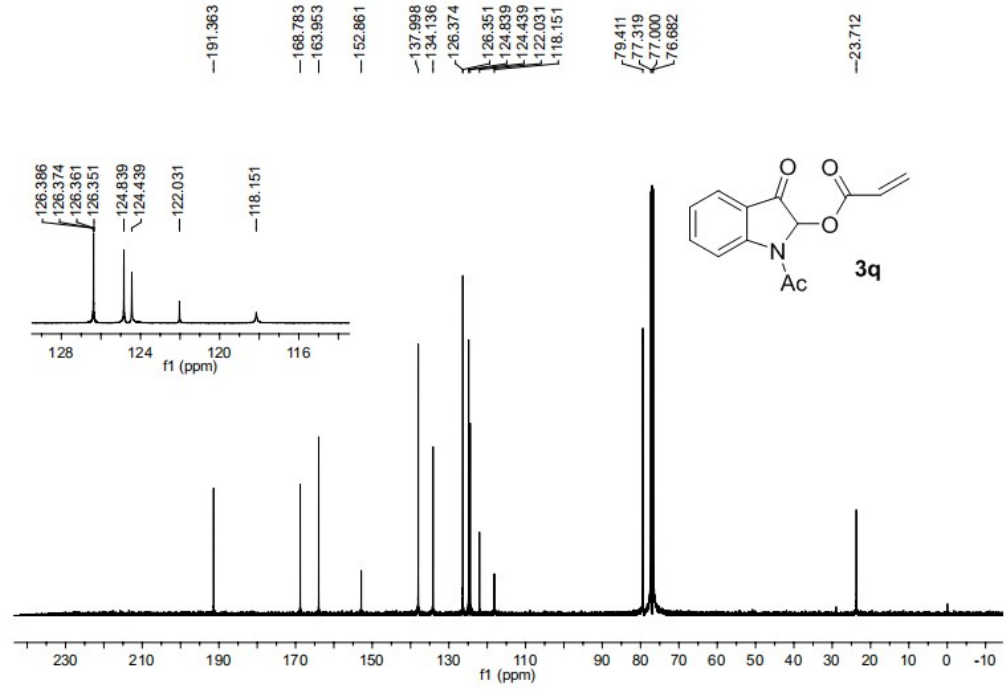

8.516
8.496
7.887
7.719
7.671
7.270
7.160
7.138
6.512
2.371
0.000
7.887
7.880
7.877
7.806
7.788
7.736
7.715
7.686
7.282
7.270
7.265
7.263
7.160
7.151
7.148
7.138
f1 (ppm)
3o
1.00
0.98
0.98
1.08
0.96
1.29
1.04
0.98
3.00
f1 (ppm)

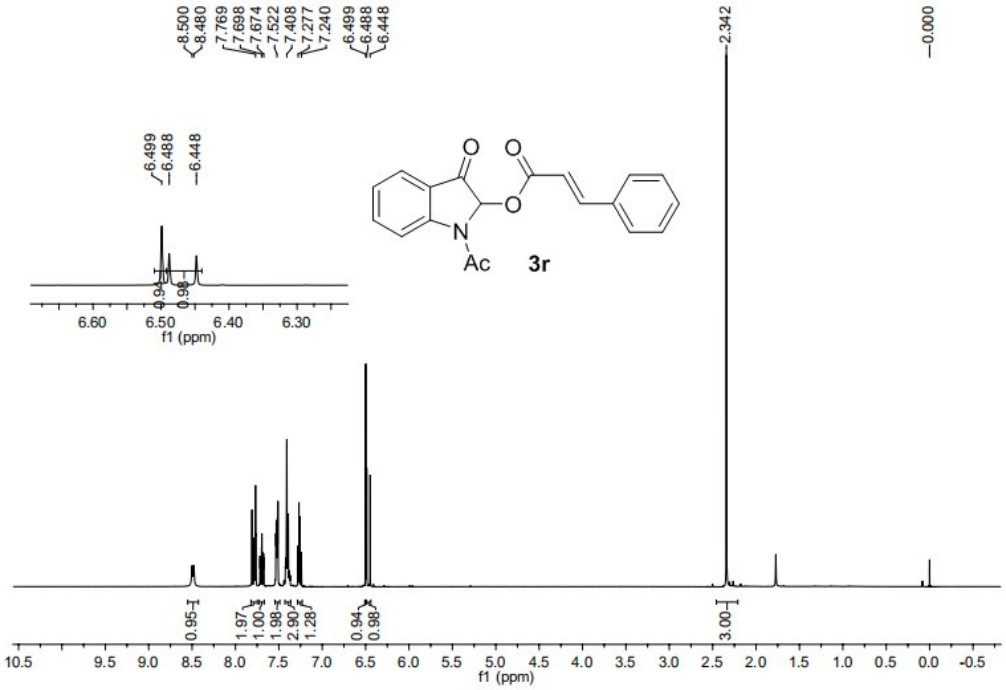

191.254
168.927
160.060
152.843
138.027
135.419
134.551
130.886
128.249
124.889
124.491
122.097
118.195
79.823
77.319
77.000
76.682
23.844
f1 (ppm)
3o
f1 (ppm)

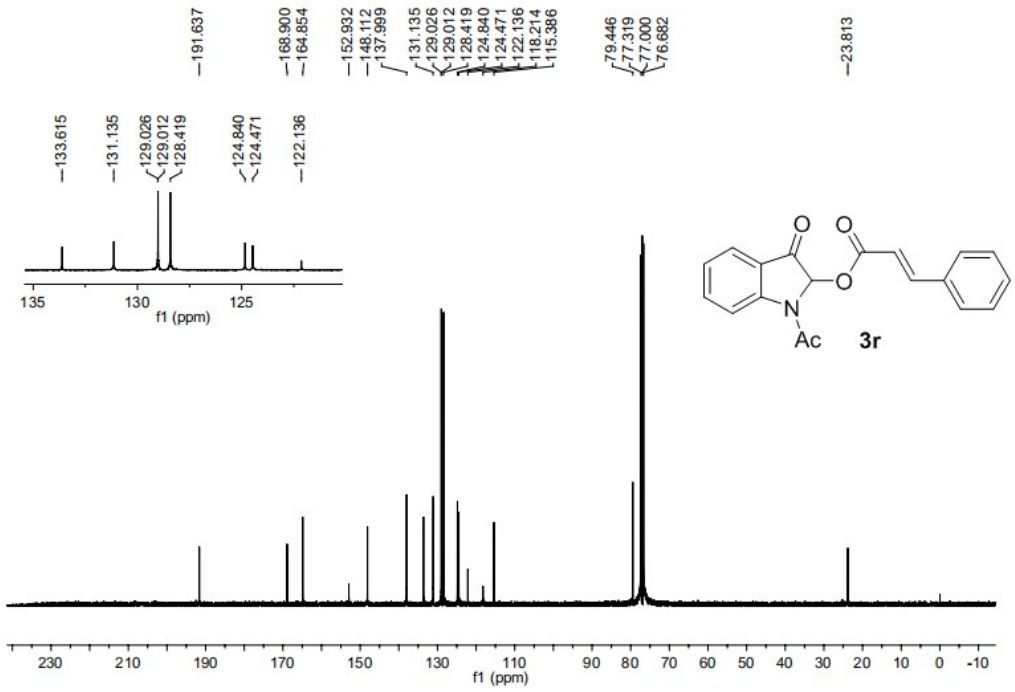

9.320
8.514
8.493
7.778
7.711
7.686
7.251
7.009
6.500
6.312
6.306
6.303
6.300
6.296
6.290
2.352
0.000
Ac
3p
1.00
1.01
1.01
1.06
1.62
2.05
1.00
1.04
3.15
f1 (ppm)

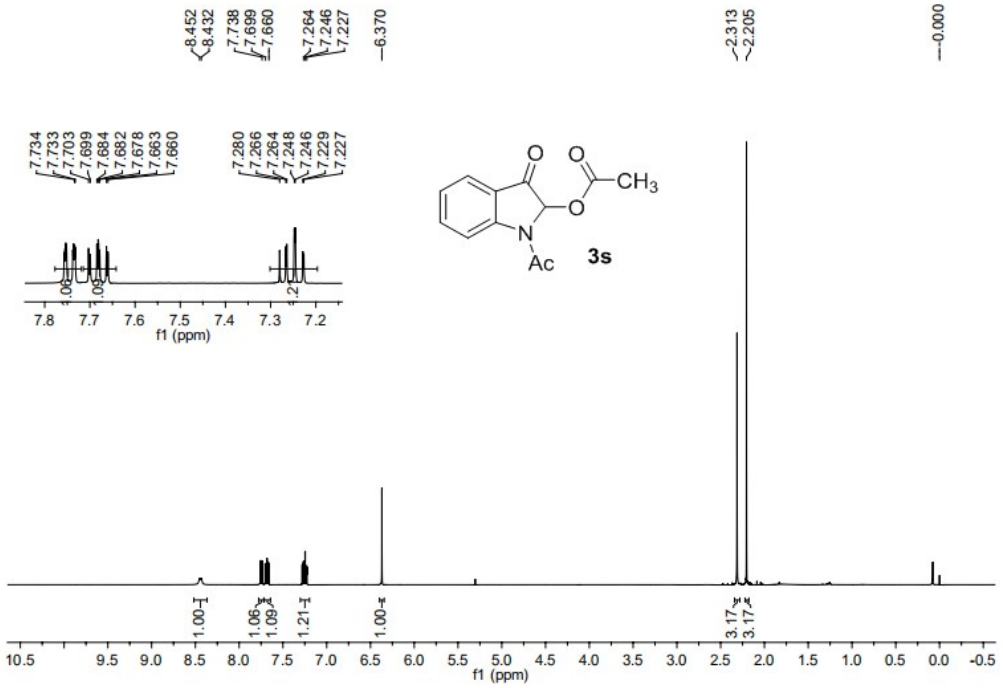

191.674
169.044
158.738
152.852
137.881
124.830
120.257
118.197
117.669
111.201
79.375
77.318
76.681
23.835
125.029
124.830
124.436
122.143
120.257
118.197
117.669
f1 (ppm)
Ac
3p
f1 (ppm)

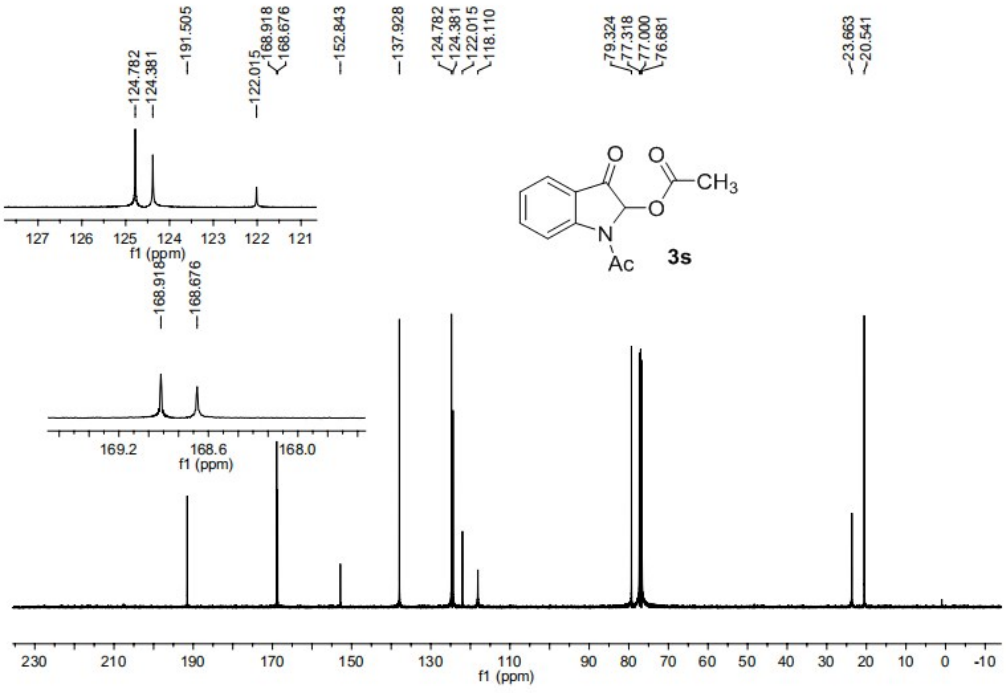

8.482
8.462
7.761
7.717
7.678
7.264
6.528
6.455
6.224
6.198
6.181
6.155
6.039
6.037
6.013
6.010
2.315
0.000
3q
0.91
0.94
0.96
1.11
0.98
0.90
0.95
0.96
3.00
f1 (ppm)


191.363
168.783
163.953
152.861
137.998
134.136
126.374
126.351
124.839
124.439
122.031
118.151
79.411
77.319
77.000
76.682
23.712
126.386
126.374
126.361
126.351
124.839
124.439
122.031
118.151
3q
f1 (ppm)


8.500
8.480
7.769
7.698
7.674
7.522
7.408
7.277
7.240
6.499
6.488
6.448
2.342
0.000
Ac
3r
f1 (ppm)


191.637
168.900
164.854
152.932
148.112
137.999
131.135
129.026
129.012
128.419
124.840
124.471
122.136
118.214
115.386
79.446
77.319
77.000
76.682
23.813
Ac
3r
f1 (ppm)


8.452
8.432
7.738
7.699
7.660
7.264
7.246
7.227
6.370
2.313
2.205
0.000
7.734
7.733
7.703
7.699
7.684
7.682
7.678
7.663
7.660
7.280
7.266
7.264
7.248
7.246
7.229
7.227
O
O
CH3
O
N
Ac
3s
1.00
1.06
1.09
1.21
1.00
3.17
3.17
f1 (ppm)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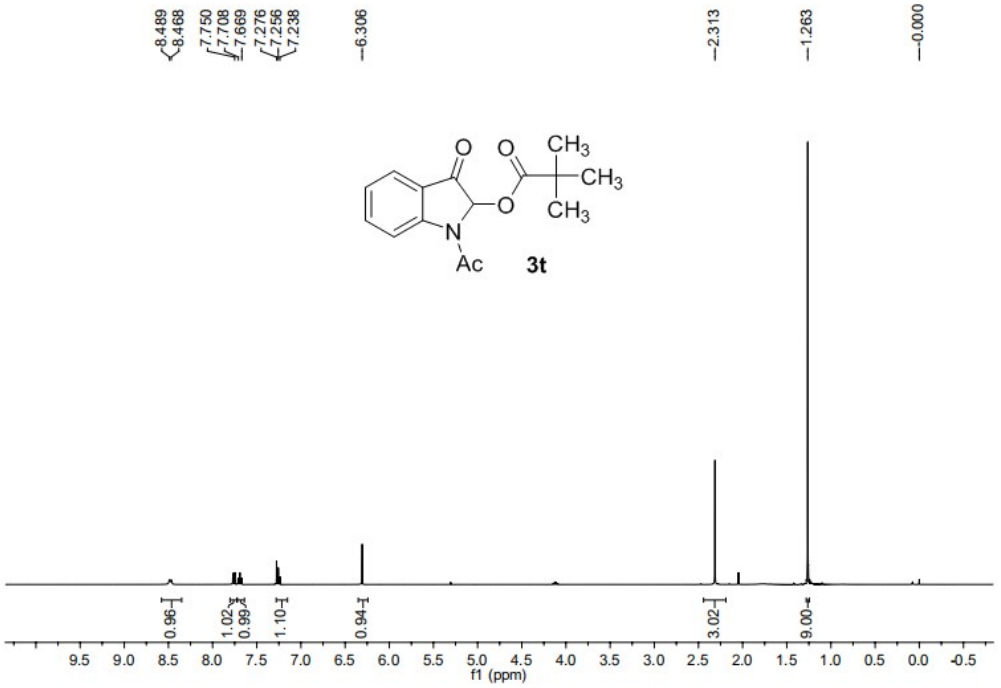
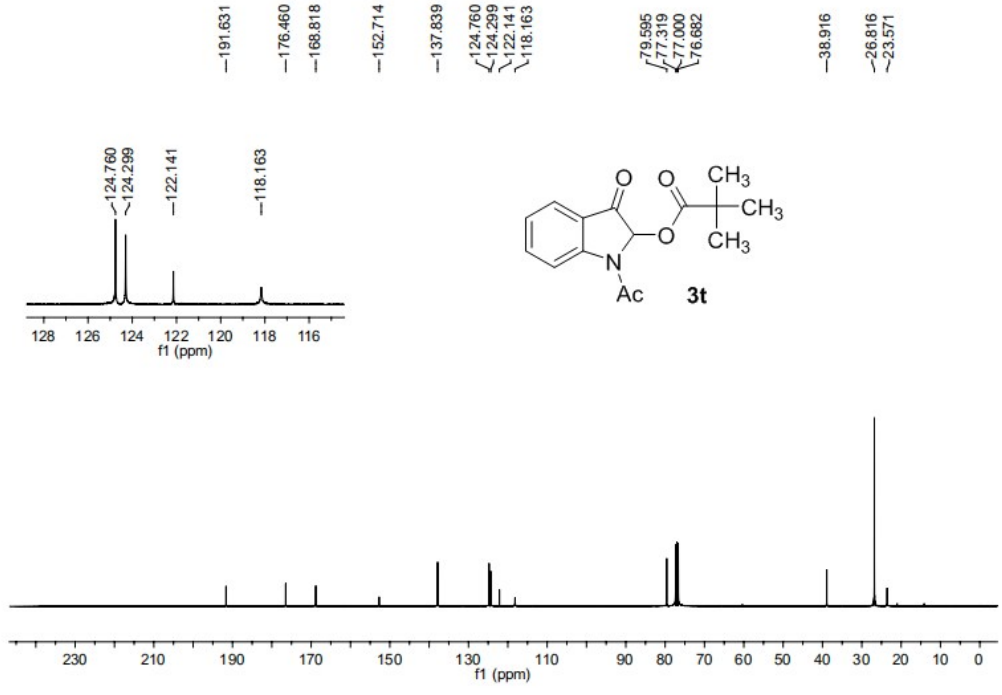
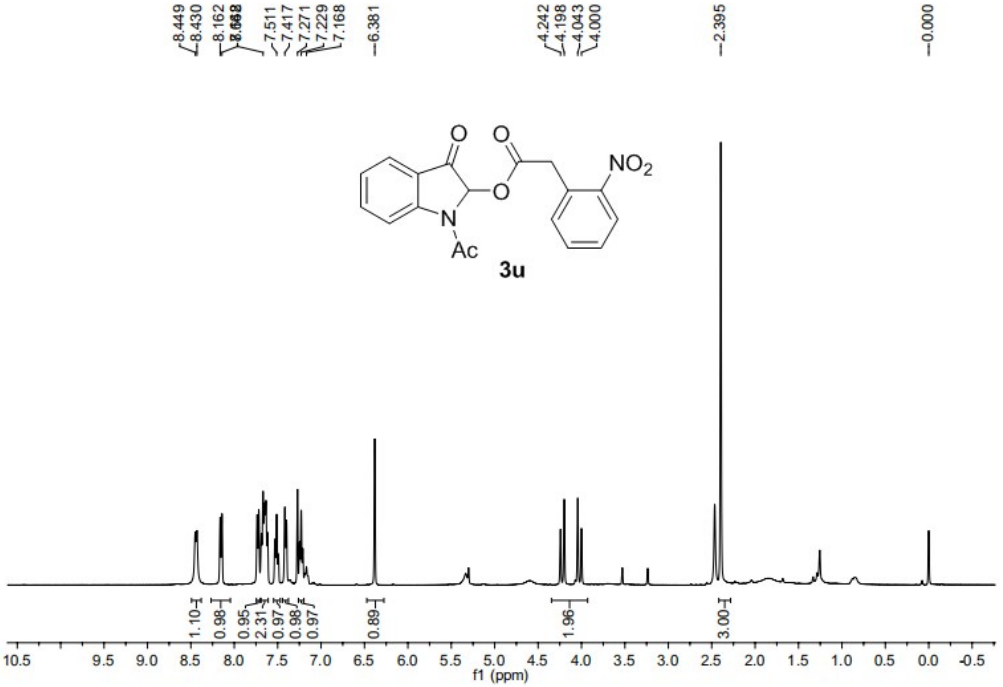
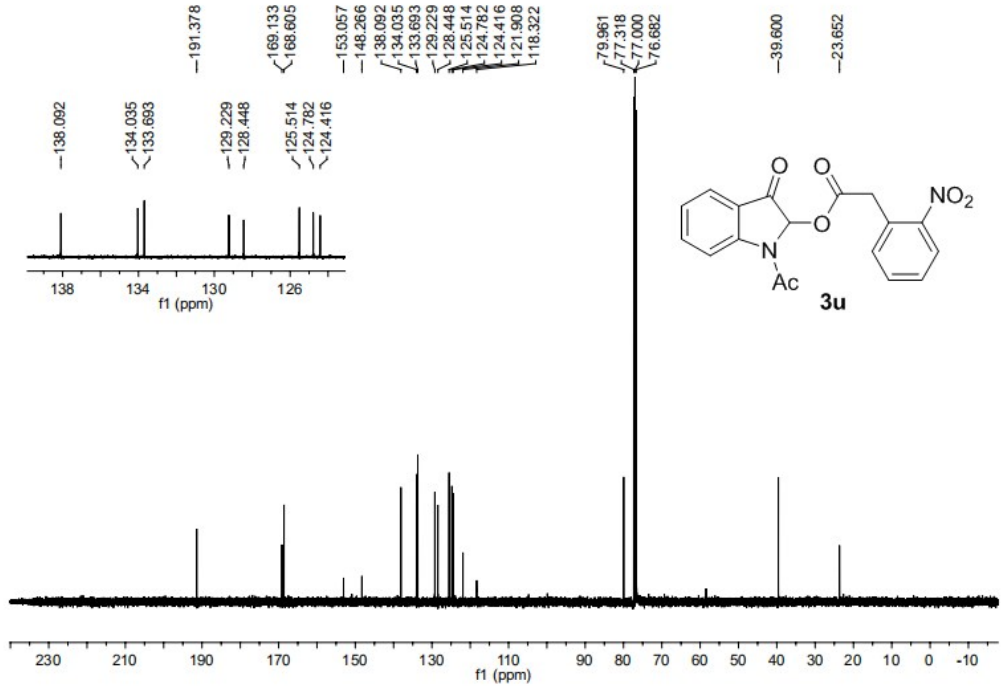
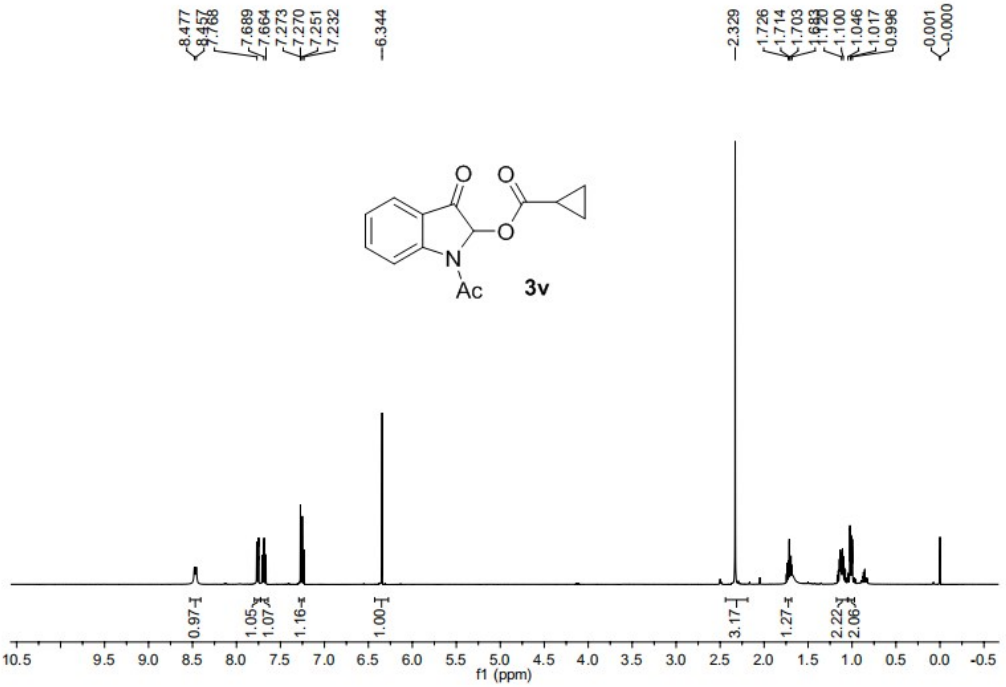
168.918
168.676
152.843
137.928
124.782
124.381
122.015
118.110
79.324
77.318
77.000
76.681
23.663
20.541
O
O
CH3
O
N
Ac
3s
f1 (ppm)

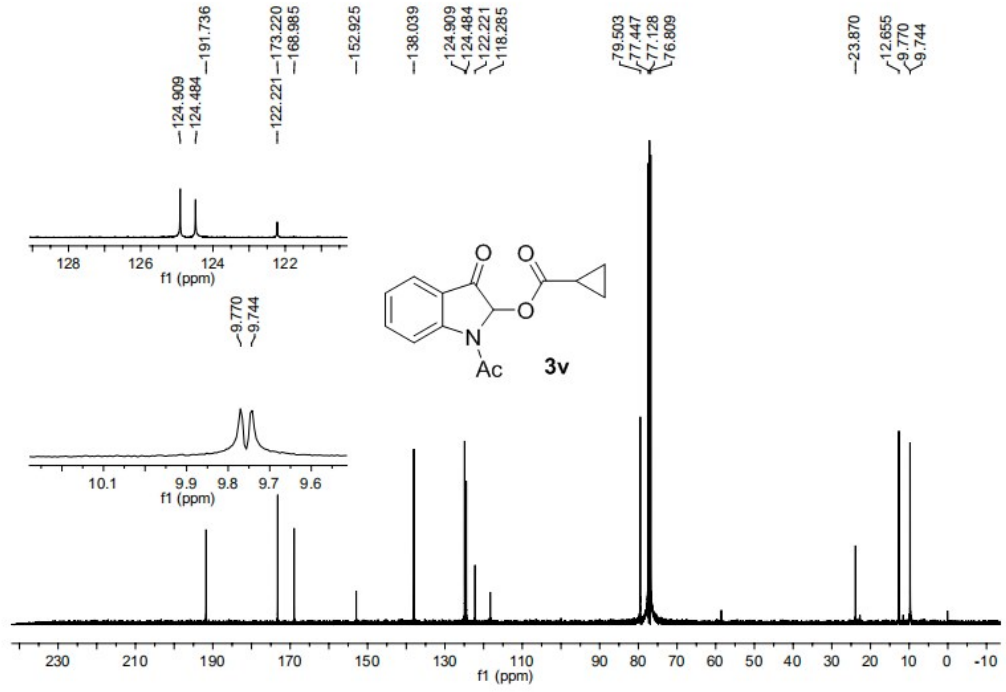

8.489
8.468
7.750
7.708
7.669
7.276
7.256
7.238
6.306
2.313
1.263
0.000
O
O
CH3
CH3
CH3
O
N
Ac
3t
0.96
1.02
0.99
1.10
0.94
3.02
9.00
f1 (ppm)

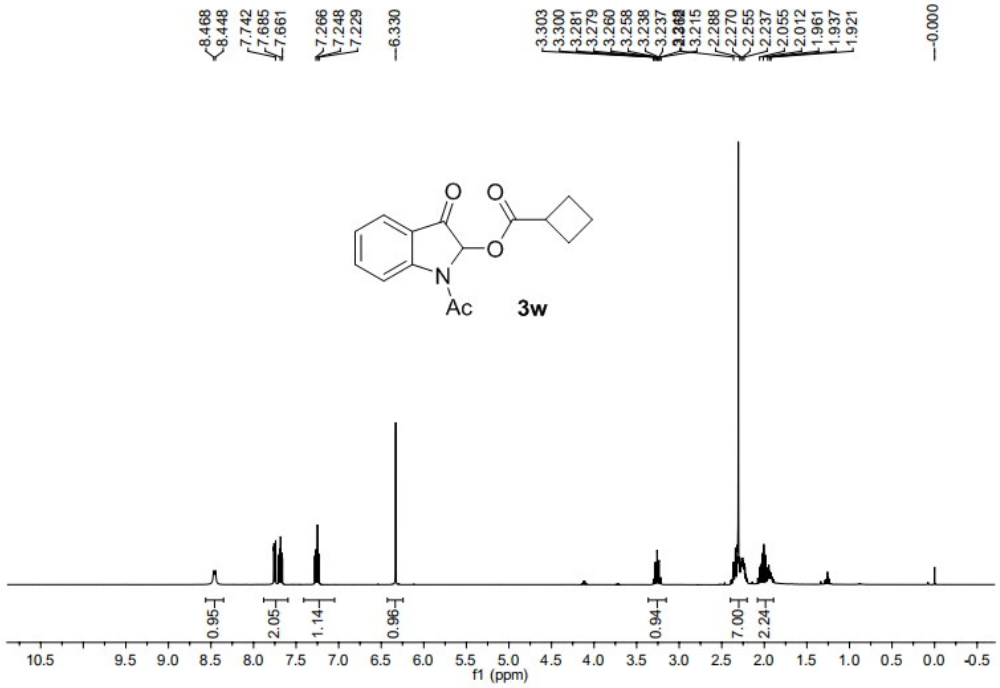

191.631
176.460
168.818
152.714
137.839
124.760
124.299
122.141
118.163
79.595
77.319
77.000
76.682
38.916
26.816
23.571
O
O
CH3
CH3
CH3
O
N
Ac
3t
f1 (ppm)

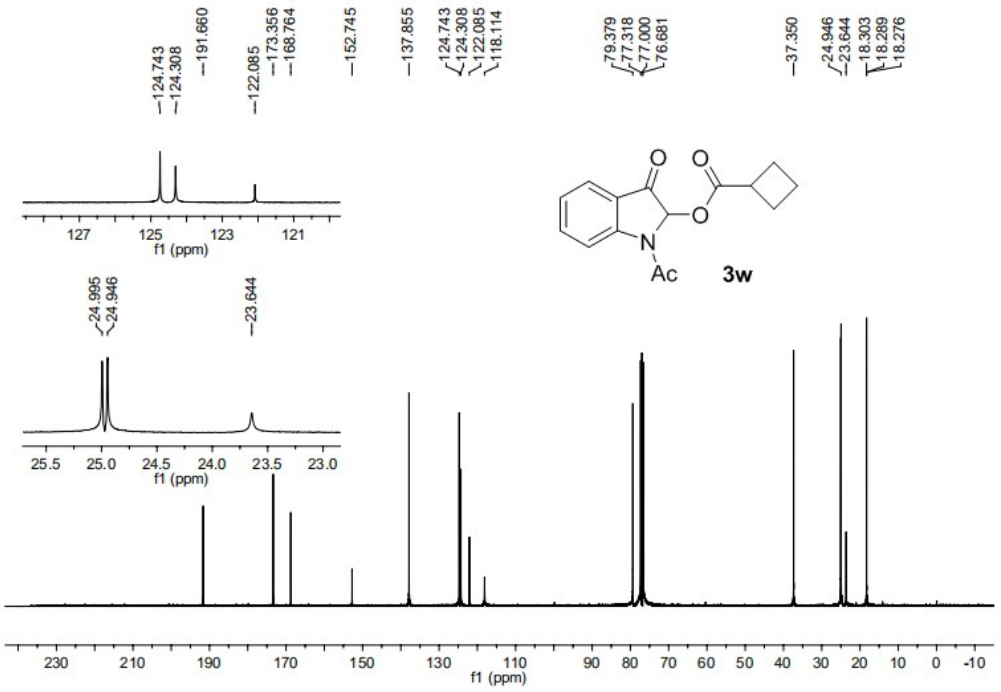

8.449
8.430
8.162
7.511
7.417
7.271
7.229
7.168
6.381
4.242
4.198
4.043
4.000
2.395
0.000
O
O
O
N
Ac
NO2
3u
1.10
0.98
0.95
2.31
0.97
0.98
0.97
0.89
1.96
3.00
f1 (ppm)

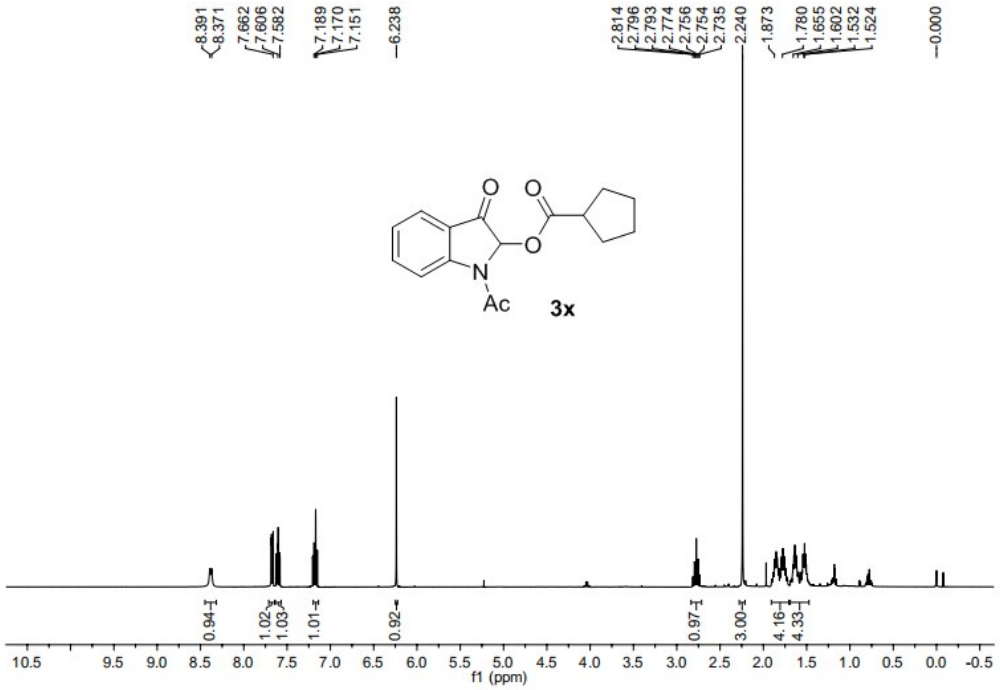

191.378
169.133
168.605
153.057
148.266
138.092
134.035
133.693
129.229
128.448
125.514
124.782
124.416
121.908
118.322
79.961
77.318
77.000
76.682
39.600
23.652
138.092
134.035
133.693
129.229
128.448
125.514
124.782
124.416
O
O
O
N
Ac
NO2
3u
f1 (ppm)

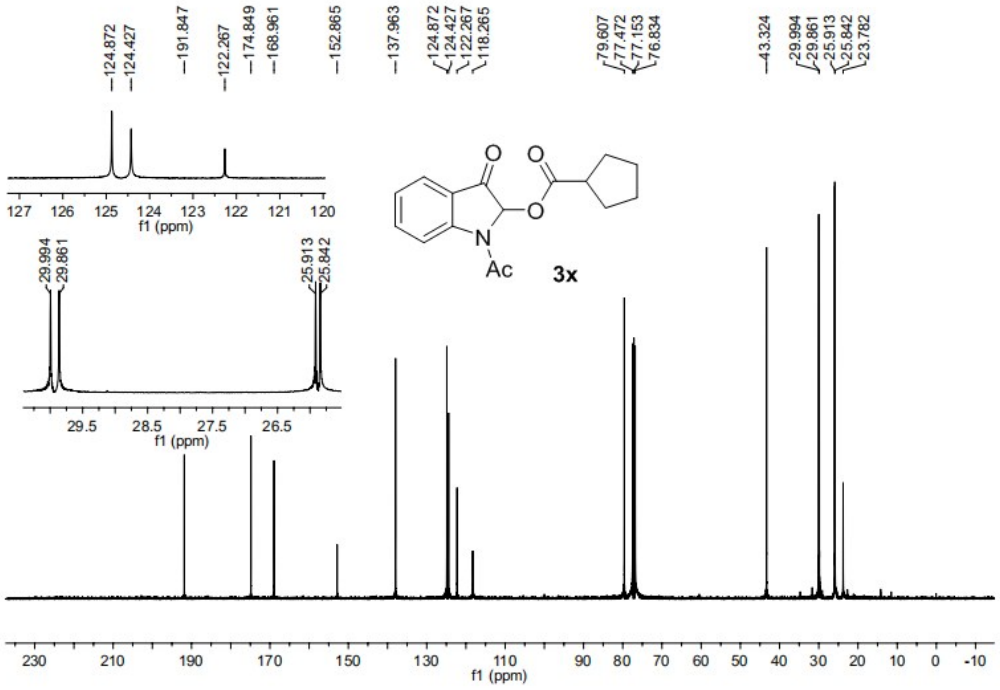

8.477
8.457
7.768
7.689
7.664
7.273
7.270
7.251
7.232
6.344
2.329
1.726
1.714
1.703
1.683
1.100
1.046
1.017
0.996
0.001
0.000
O
O
O
N
Ac
3v
0.97
1.05
1.07
1.16
1.00
3.17
1.27
2.22
2.06
f1 (ppm)

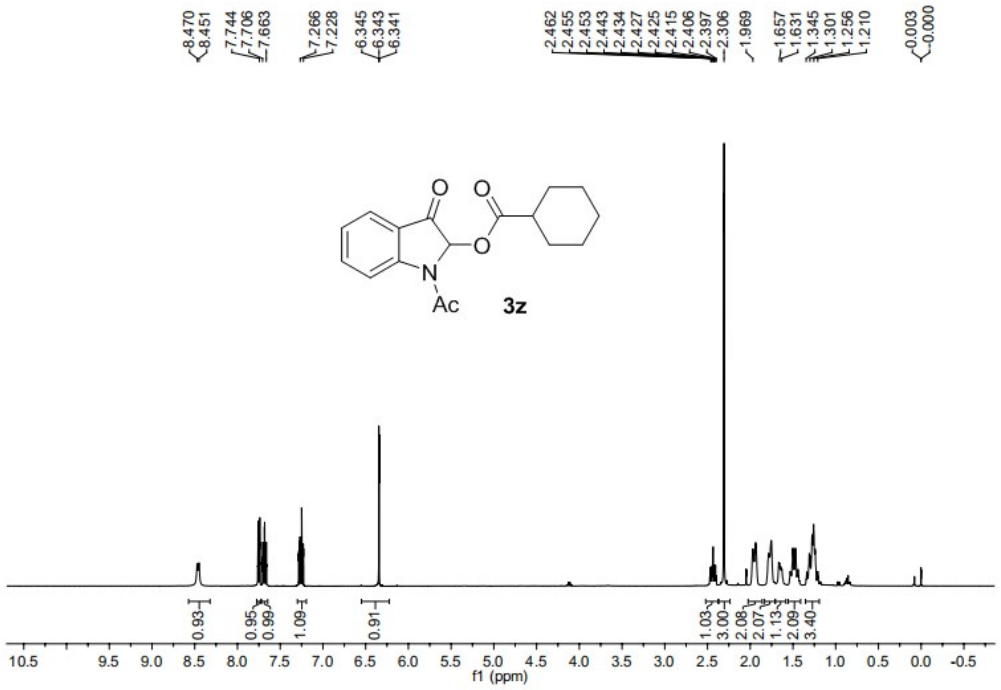

124.909
124.484
191.736
173.220
168.985
122.221
152.925
138.039
124.909
124.484
122.221
118.285
79.503
77.447
77.128
76.809
23.870
12.655
9.770
9.744
f1 (ppm)
O
O
O
N
Ac
3v

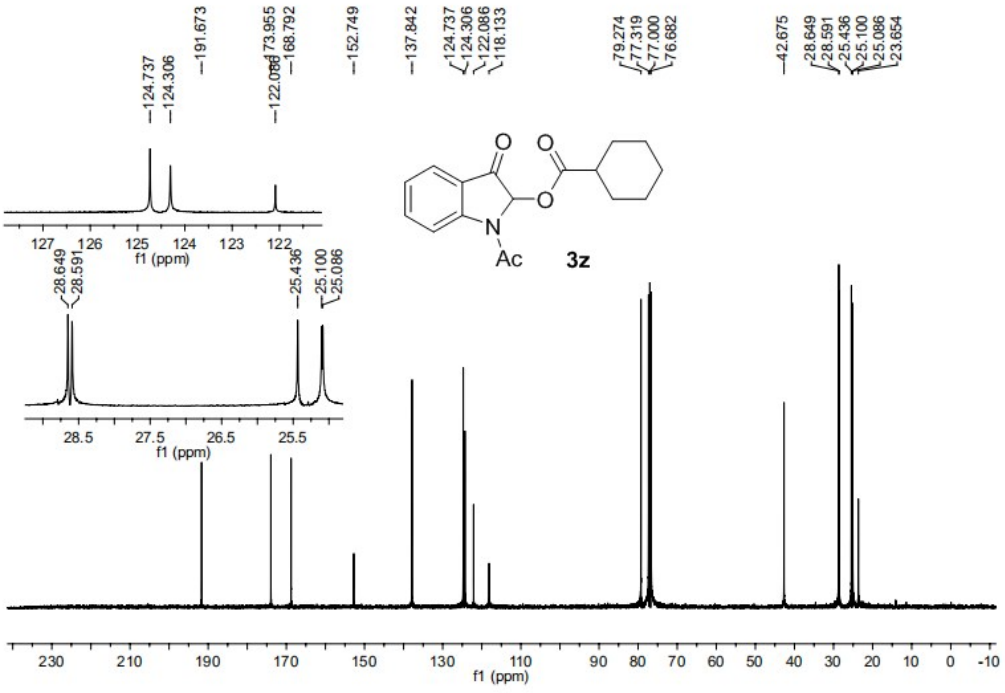

8.468
8.448
7.742
7.685
7.661
7.266
7.248
7.229
6.330
3.303
3.300
3.281
3.279
3.260
3.258
3.238
3.237
3.215
2.288
2.270
2.255
2.237
2.055
2.012
1.961
1.937
1.921
0.000
O
O
O
N
Ac
3w
0.95
2.05
1.14
0.96
0.94
7.00
2.24
f1 (ppm)

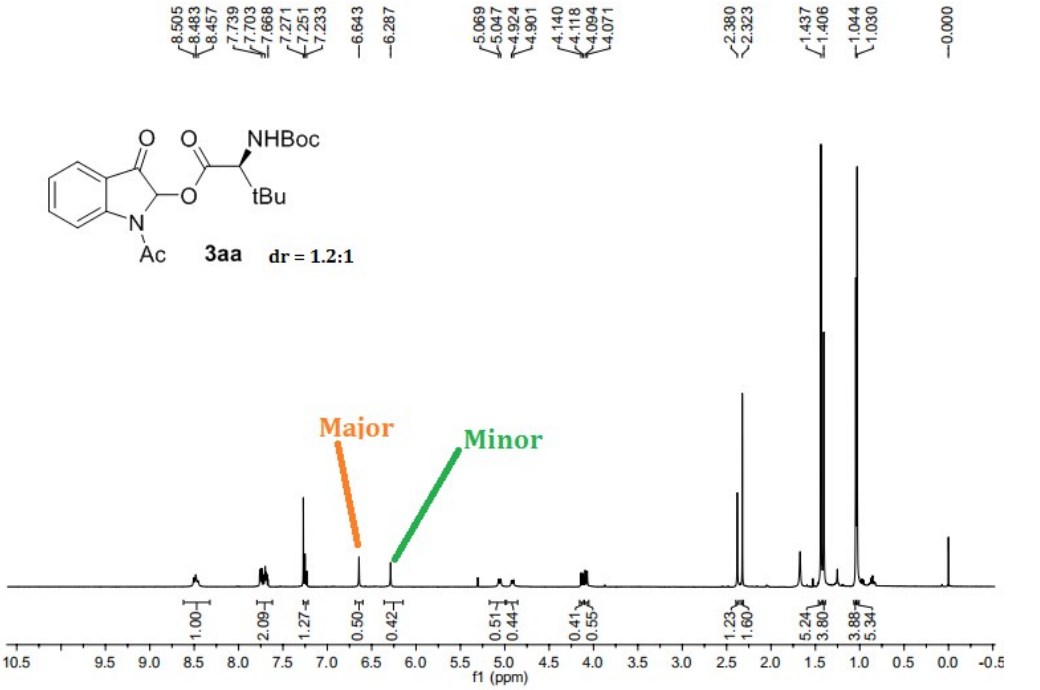

124.743
124.308
191.660
122.085
173.356
168.764
152.745
137.855
124.743
124.308
122.085
118.114
79.379
77.318
77.000
76.681
37.350
24.946
23.644
18.303
18.289
18.276
O
O
O
N
Ac
3w
24.995
24.946
23.644
f1 (ppm)
f1 (ppm)

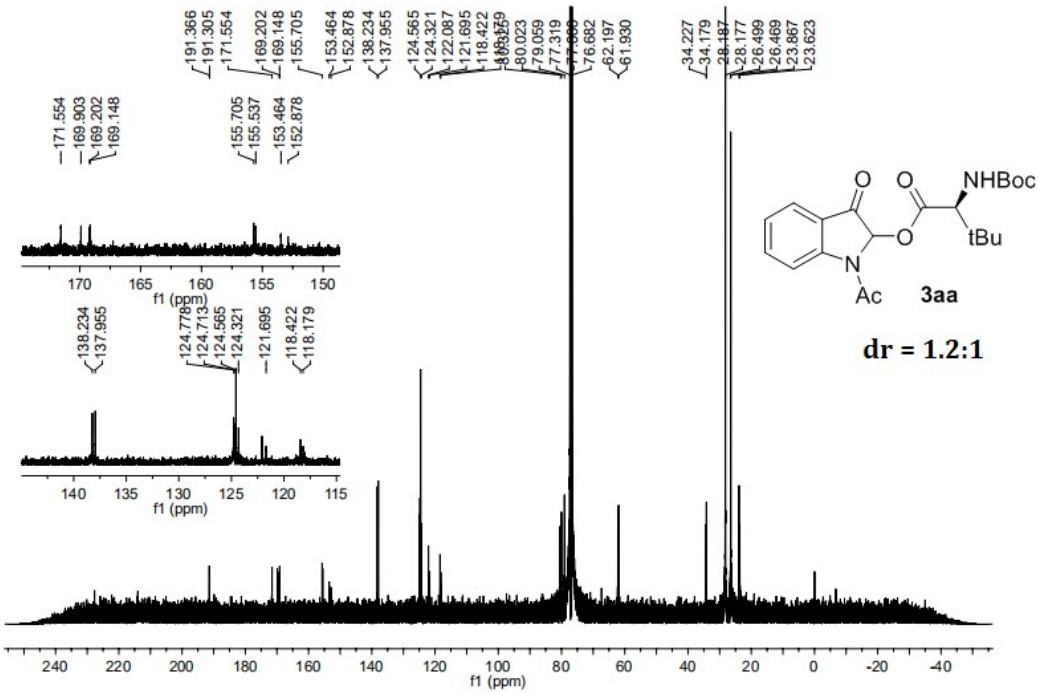

8.391
8.371
7.662
7.606
7.582
7.189
7.170
7.151
6.238
2.814
2.796
2.793
2.774
2.756
2.754
2.735
2.240
1.873
1.780
1.655
1.602
1.532
1.524
0.000
O
O
O
N
Ac
3x
0.94
1.02
1.03
1.01
0.92
0.97
3.00
4.16
4.33
f1 (ppm)

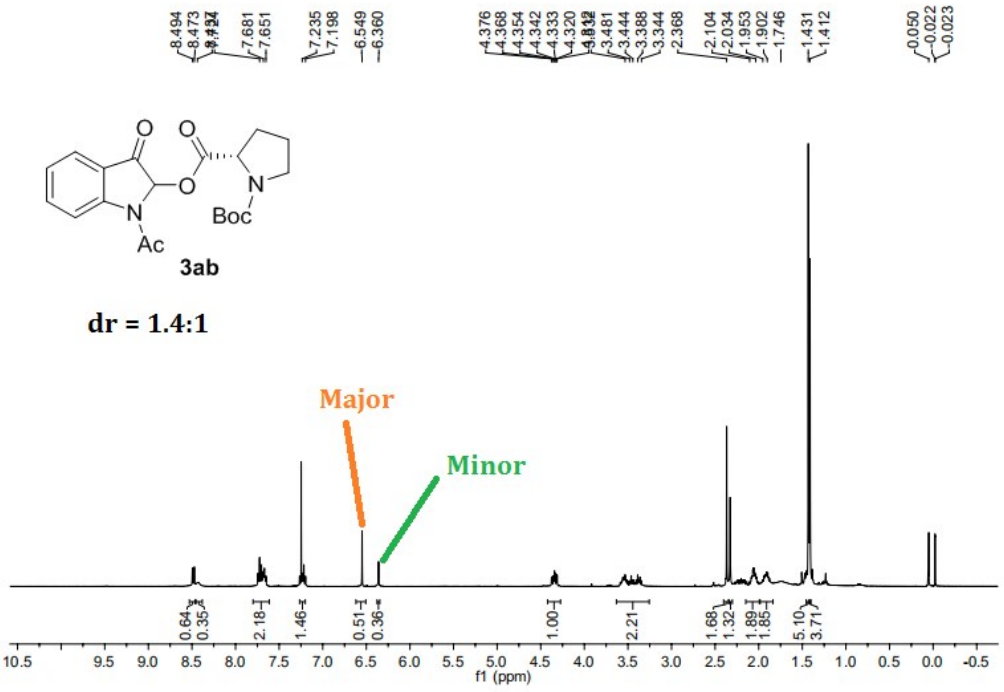

124.872
124.427
191.847
122.267
174.849
168.961
152.865
137.963
124.872
124.427
122.267
118.265
79.607
77.472
77.153
76.834
43.324
29.994
29.861
25.913
25.842
23.782
O
O
O
N
Ac
3x
f1 (ppm)
f1 (ppm)
f1 (ppm)

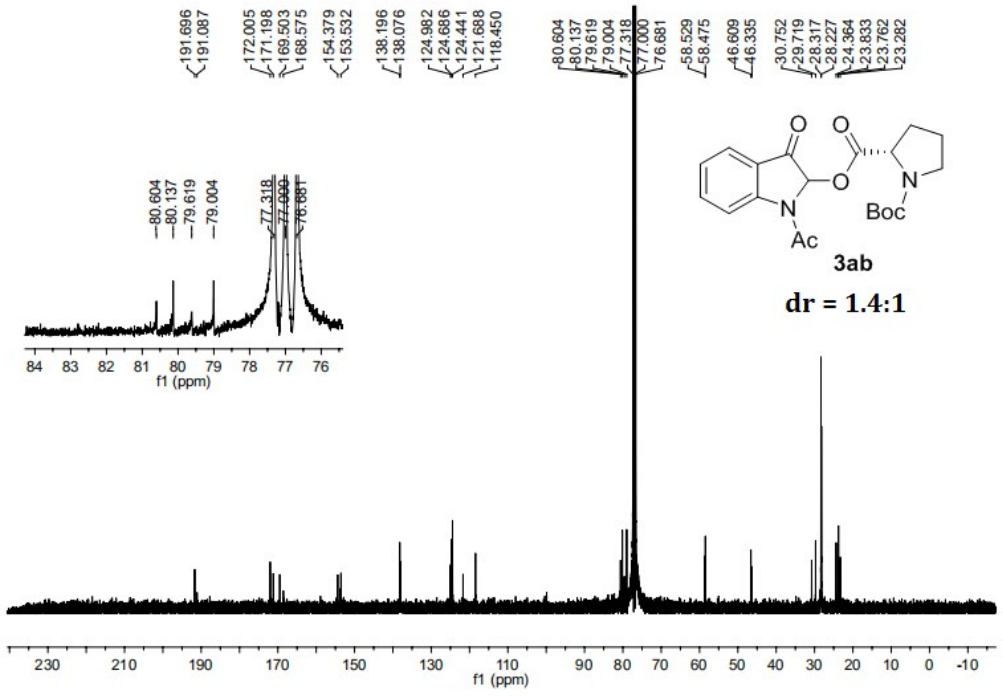

8.470
8.451
7.744
7.706
7.663
7.266
7.228
6.345
6.343
6.341
2.462
2.455
2.453
2.443
2.434
2.427
2.425
2.415
2.406
2.397
2.306
1.969
1.657
1.631
1.345
1.301
1.256
1.210
0.003
-0.000
O
O
O
N
Ac
3z
0.93
0.95
0.99
1.09
0.91
1.03
3.00
2.08
2.07
1.13
2.09
3.40
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

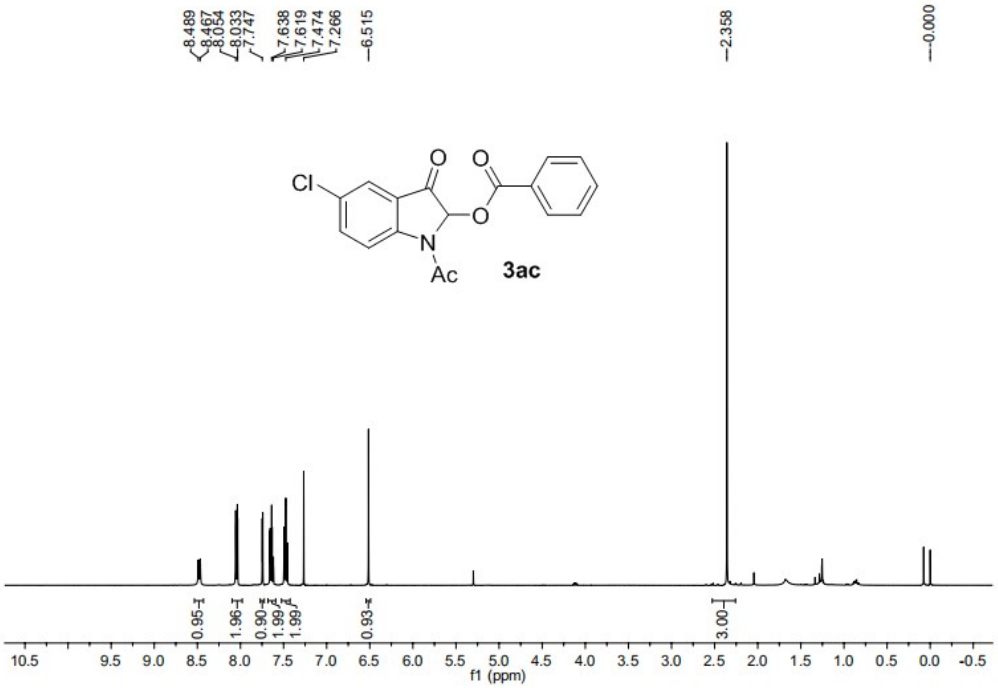

124.737
124.306
191.673
173.955
168.792
152.749
137.842
124.737
124.306
122.086
118.133
79.274
77.319
77.000
76.682
42.675
28.649
28.591
25.436
25.100
25.086
23.654
127
126
125
124
123
122
f1 (ppm)
28.5
27.5
26.5
25.5
f1 (ppm)
O
O
O
N
Ac
3z
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

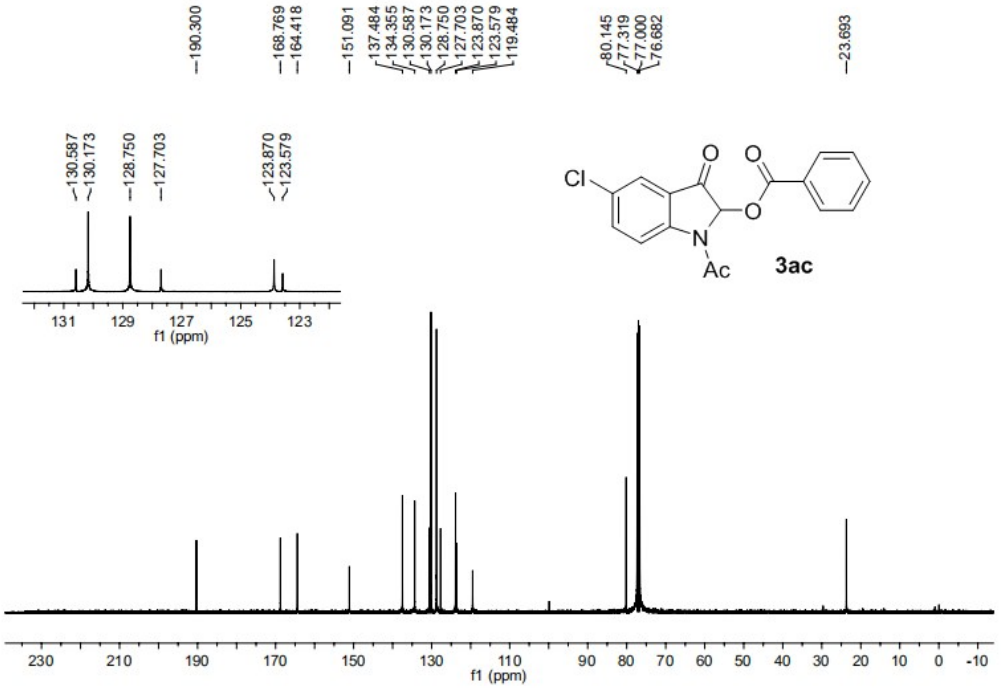

8.505
8.483
8.457
7.739
7.703
7.668
7.271
7.251
7.233
6.643
6.287
5.069
5.047
4.924
4.901
4.140
4.118
4.094
4.071
2.380
2.323
1.437
1.406
1.044
1.030
0.000
NHBoc
tBu
Ac
3aa
dr = 1.2:1
Major
Minor
1.00
2.09
1.27
0.50
0.42
0.51
0.44
0.41
0.55
1.23
1.60
5.24
3.80
3.88
5.34
f1 (ppm)

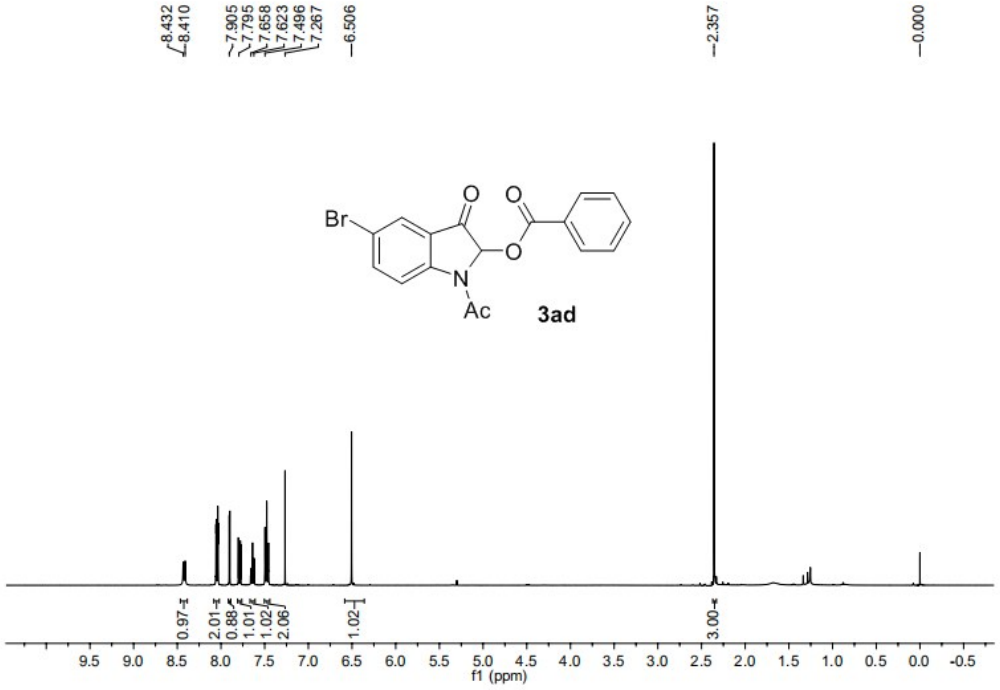

191.366
191.305
171.554
169.202
169.148
155.705
153.464
152.878
138.234
137.955
124.565
124.321
122.087
121.695
118.422
80.023
79.059
77.319
76.682
62.197
61.930
34.227
34.179
28.177
26.499
26.469
23.867
23.623
NHBoc
tBu
Ac
3aa
dr = 1.2:1
f1 (ppm)

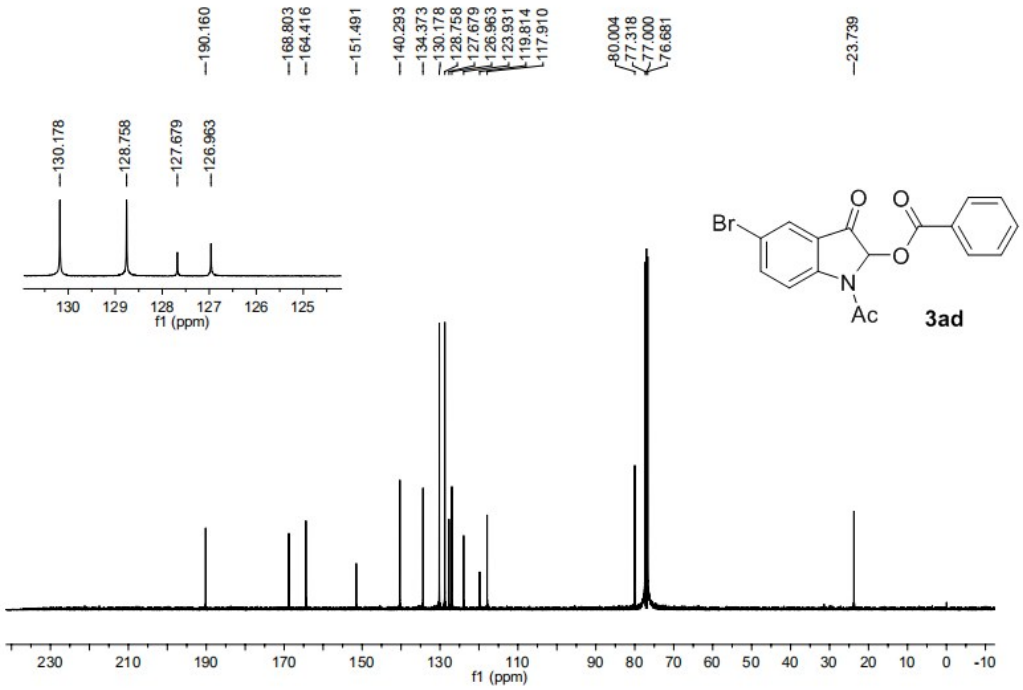

Major
Minor
3ab
dr = 1.4:1
f1 (ppm)

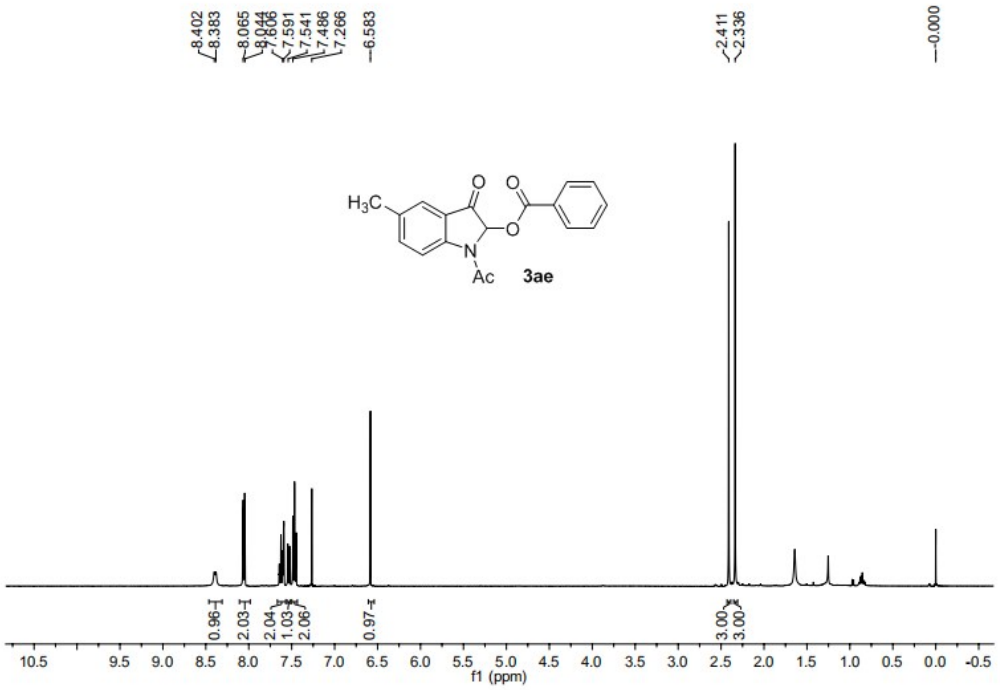

3ab
dr = 1.4:1
f1 (ppm)

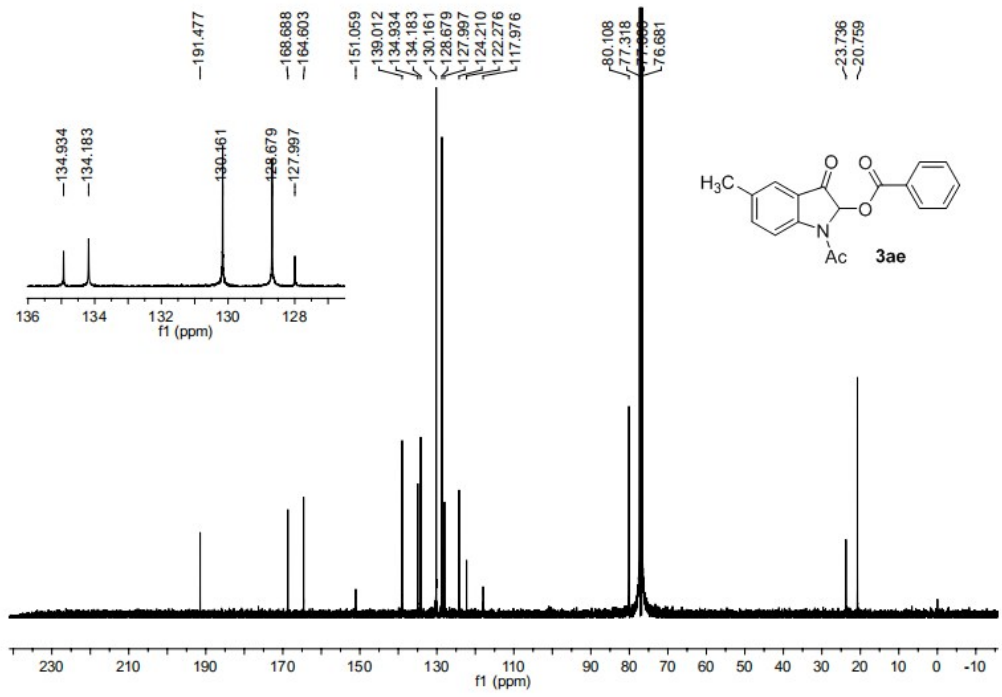

8.489
8.467
8.054
8.033
7.747
7.638
7.619
7.474
7.266
6.515
2.358
0.000
Cl
O
O
O
N
Ac
3ac
0.95
1.96
0.90
1.99
1.99
0.93
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

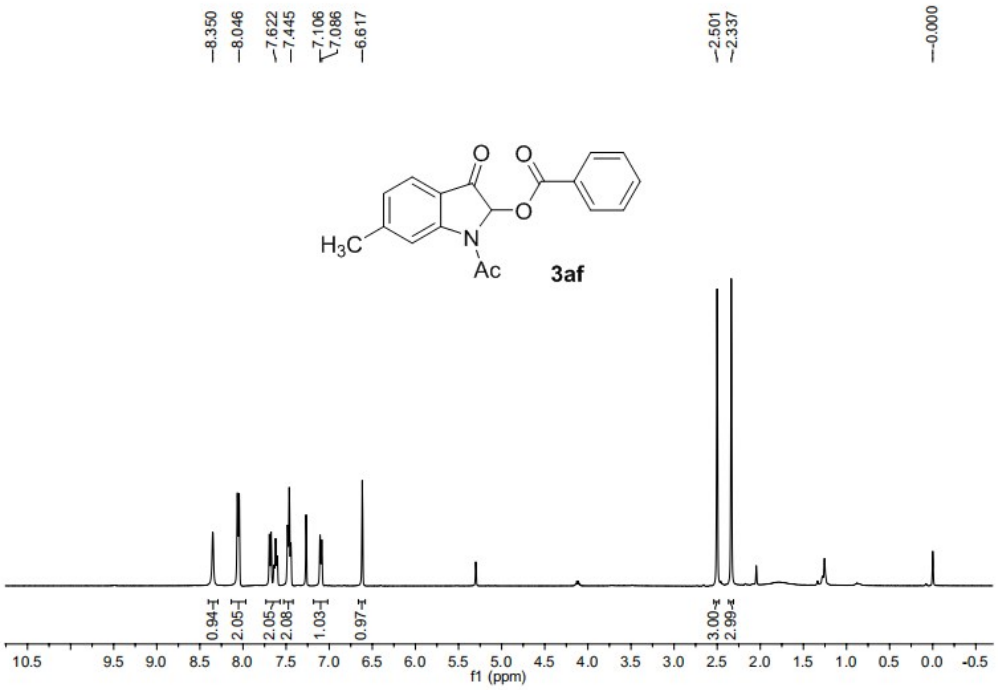

190.300
168.769
164.418
151.091
137.484
134.355
130.587
130.173
128.750
127.703
123.870
123.579
119.484
80.145
77.319
77.000
76.682
23.693
130.587
130.173
128.750
127.703
123.870
123.579
131 129 127 125 123
f1 (ppm)
Cl
O
O
O
N
Ac
3ac
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

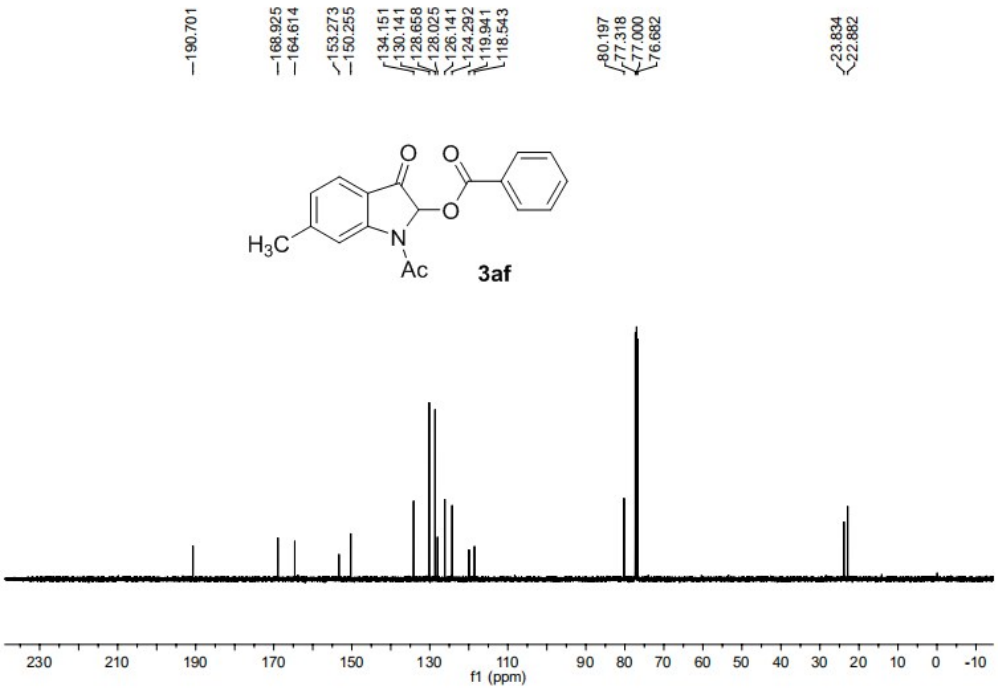

8.432
8.410
7.905
7.795
7.658
7.623
7.496
7.267
6.506
2.357
0.000
Br
O
O
O
N
Ac
3ad
0.97
2.01
0.88
1.01
1.02
2.06
1.02
3.00
f1 (ppm)

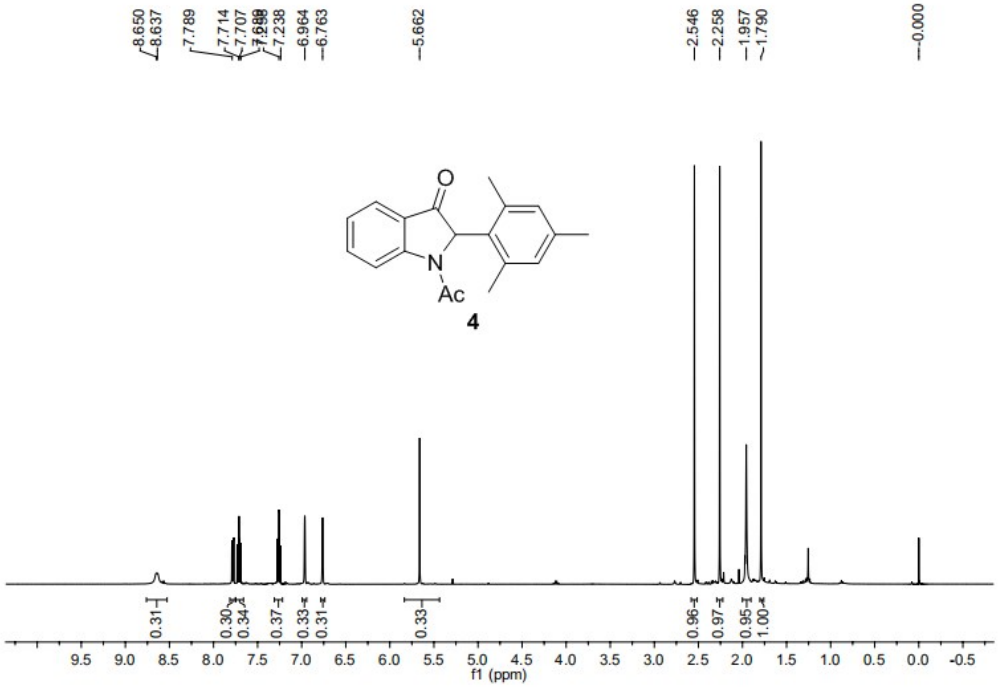

190.160
168.803
164.416
151.491
140.293
134.373
130.178
128.758
127.679
126.963
123.931
119.814
117.910
80.004
77.318
77.000
76.681
23.739
130.178
128.758
127.679
126.963
f1 (ppm)
Br
O
O
O
N
Ac
3ad
f1 (ppm)

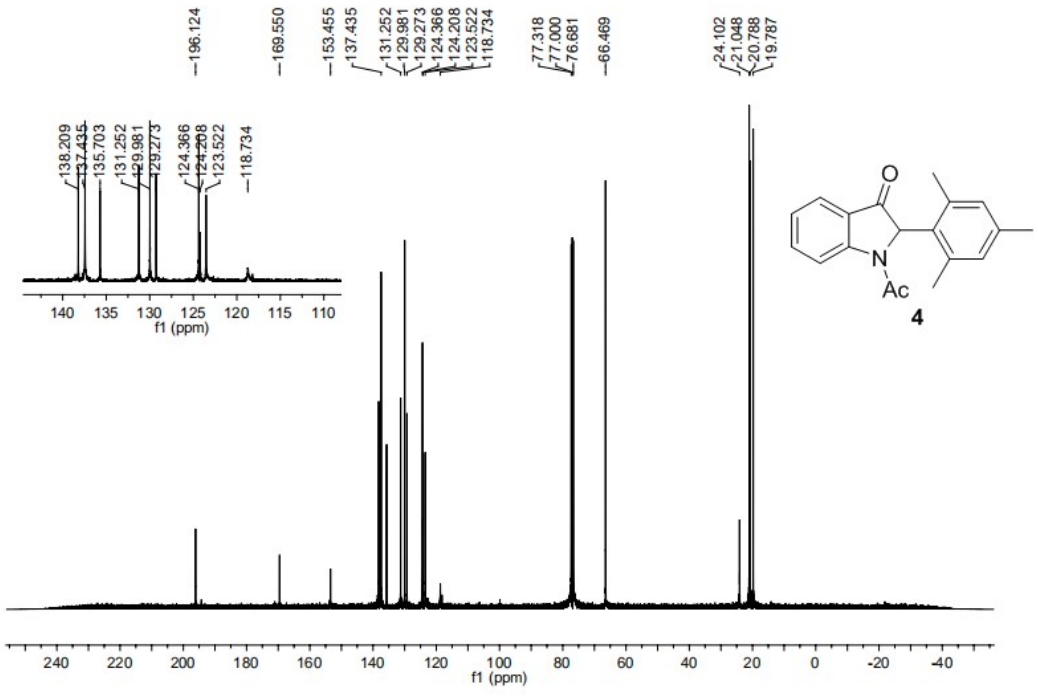

8.402
8.383
8.065
8.044
7.606
7.591
7.541
7.486
7.266
6.583
2.411
2.336
0.000
H3C
O
O
O
N
Ac
3ae
0.96
2.03
2.04
1.03
2.06
0.97
3.00
3.00
f1 (ppm)

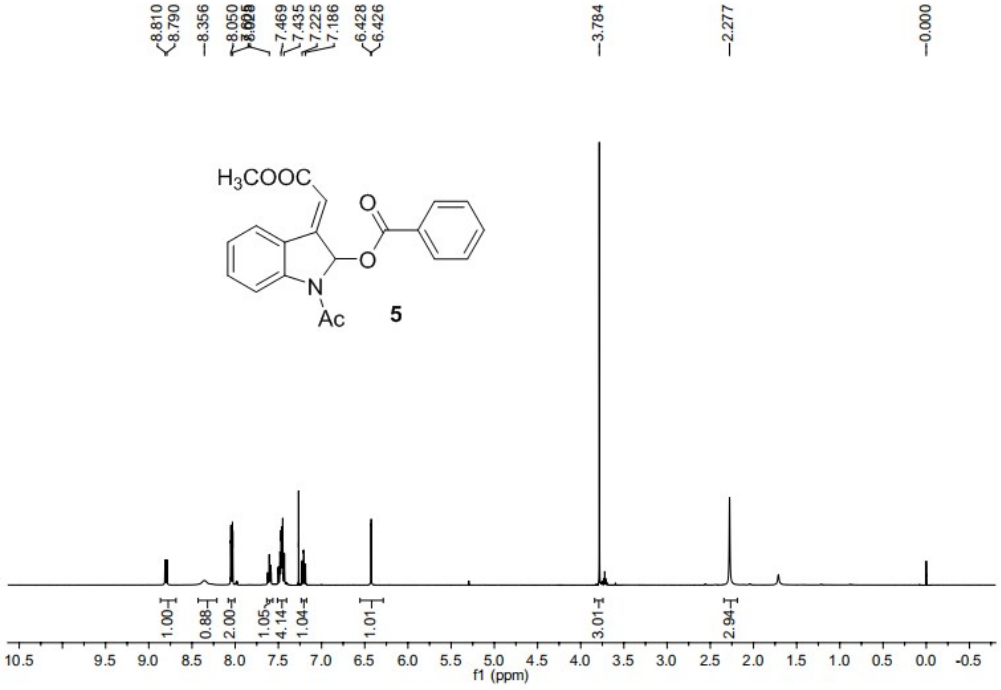

191.477
168.688
164.603
151.059
139.012
134.934
134.183
130.161
128.679
127.997
124.210
122.276
117.976
80.108
77.318
76.681
23.736
20.759
134.934
134.183
130.461
128.679
127.997
136
134
132
130
128
f1 (ppm)
H3C
O
O
O
N
Ac
3ae
f1 (ppm)

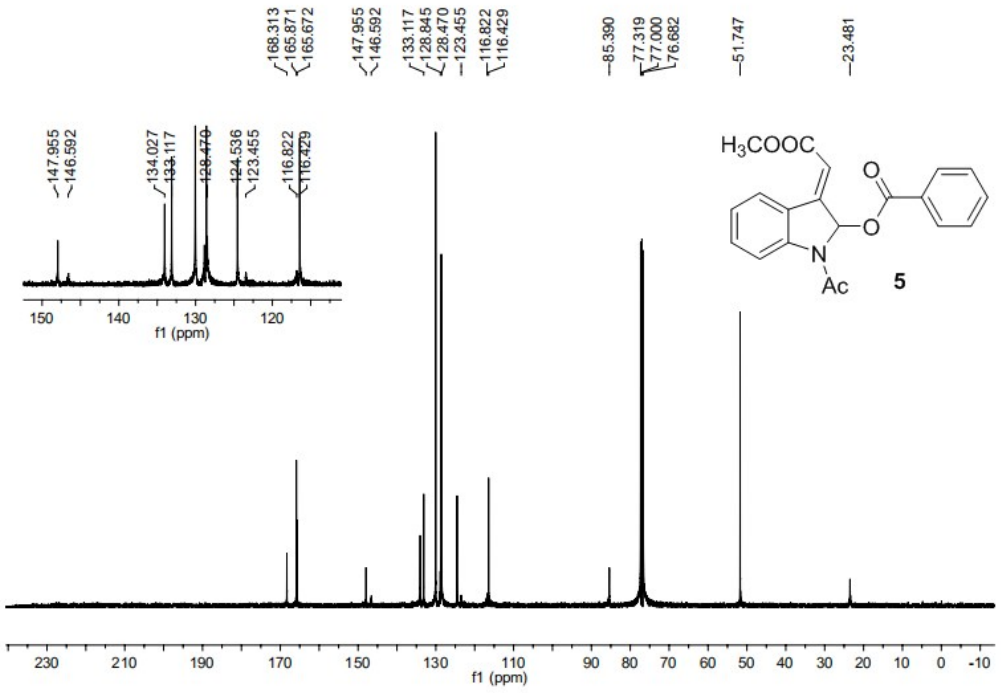

8.350
8.046
7.622
7.445
7.106
7.086
6.617
2.501
2.337
0.000
3af
0.94
2.05
2.05
2.08
1.03
0.97
3.00
2.99
f1 (ppm)

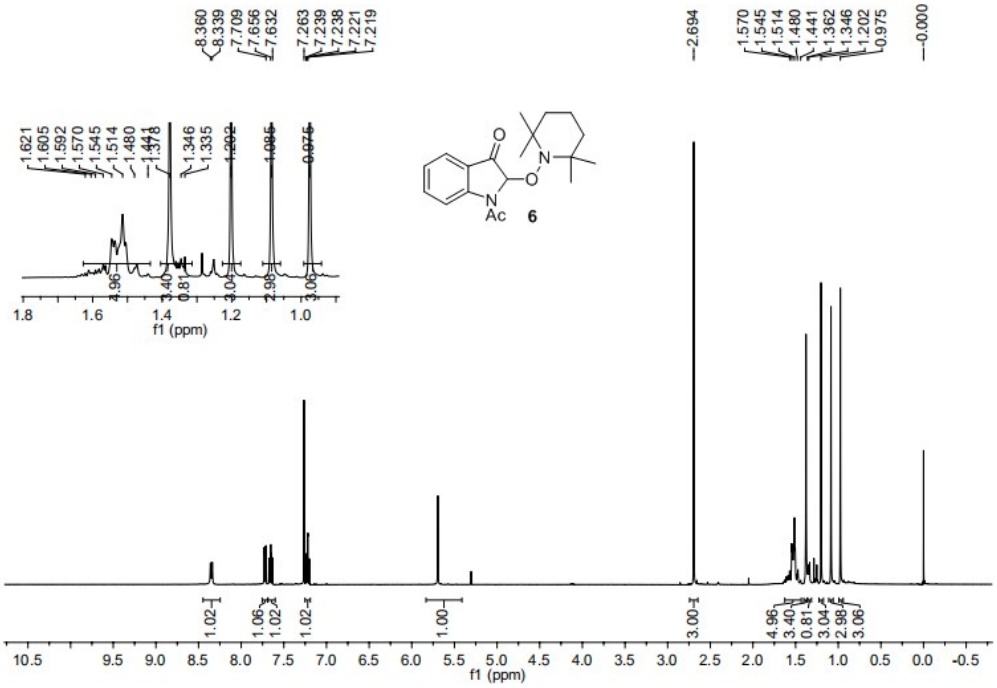

190.701
168.925
164.614
153.273
150.255
134.151
130.141
128.658
128.025
126.141
124.292
119.941
118.543
80.197
77.318
77.000
76.682
23.834
22.882
3af
f1 (ppm)

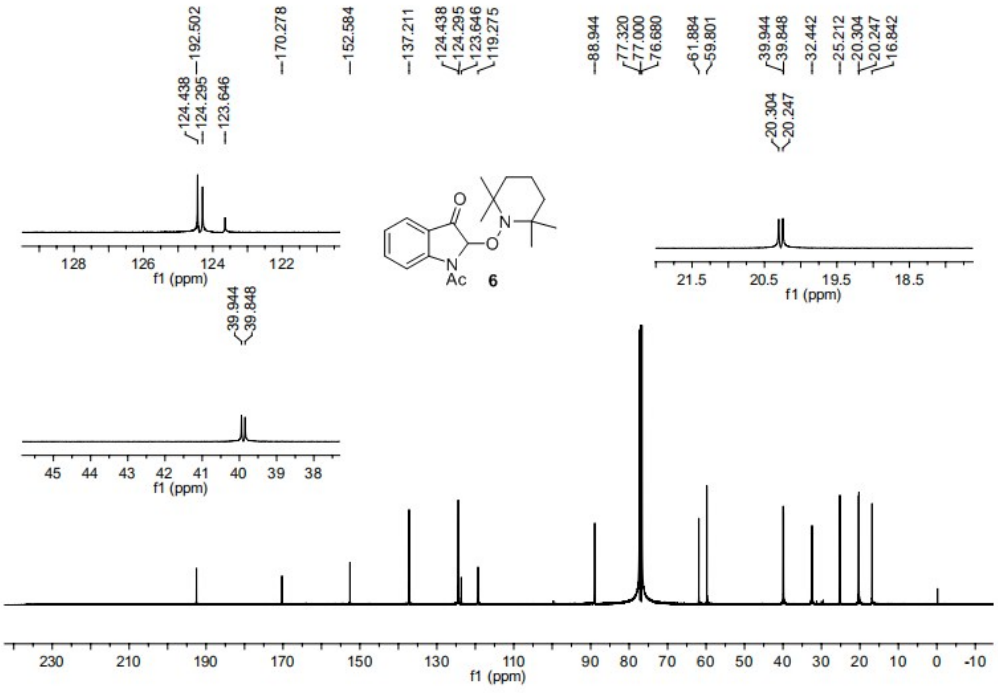

8.650
8.637
7.789
7.714
7.707
7.238
6.964
6.763
5.662
2.546
2.258
1.957
1.790
0.000
O
N
Ac
4
0.31
0.30
0.34
0.37
0.33
0.31
0.33
0.96
0.97
0.95
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

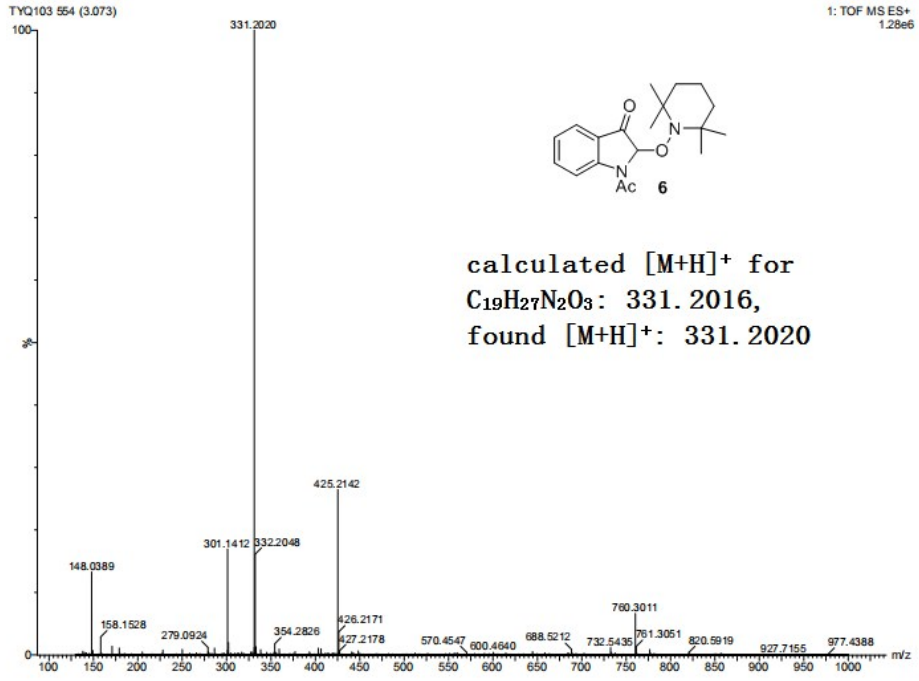

196.124
169.550
153.455
137.435
131.252
129.981
129.273
124.366
124.208
123.522
118.734
77.318
77.000
76.681
66.469
24.102
21.048
20.788
19.787
138.209
137.435
135.703
131.252
129.981
129.273
124.366
124.208
123.522
118.734
140 135 130 125 120 115 110
f1 (ppm)
O
N
Ac
4
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40
f1 (ppm)


8.810
8.790
8.356
8.050
7.469
7.435
7.225
7.186
6.428
6.426
3.784
2.277
0.000
H3COOC
O
O
N
Ac
5
1.00
0.88
2.00
1.05
4.14
1.04
1.01
3.01
2.94
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.313
165.871
165.672
147.955
146.592
133.117
128.845
128.470
123.455
116.822
116.429
85.390
77.319
77.000
76.682
51.747
23.481
147.955
146.592
134.027
133.117
128.470
124.536
123.455
116.822
116.429
150 140 130 120
f1 (ppm)
H3COOC
O
O
N
Ac
5
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.360
8.339
7.709
7.656
7.632
7.263
7.239
7.238
7.221
7.219
2.694
1.570
1.545
1.514
1.480
1.441
1.362
1.346
1.202
0.975
0.000
1.621
1.605
1.592
1.570
1.545
1.514
1.480
1.441
1.378
1.346
1.335
1.202
1.086
0.975
4.96
3.40
0.81
3.04
2.98
3.06
f1 (ppm)
O
N
O
N
Ac
6
1.02
1.06
1.02
1.02
1.00
3.00
4.96
3.40
0.81
3.04
2.98
3.06
f1 (ppm)


192.502
170.278
152.584
137.211
124.438
124.295
123.646
119.275
88.944
77.320
77.000
76.680
61.884
59.801
39.944
39.848
32.442
25.212
20.304
20.247
16.842
124.438
124.295
123.646
20.304
20.247
39.944
39.848
f1 (ppm)
O
N
O
N
Ac
6
f1 (ppm)
f1 (ppm)



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calculated $[M+H]^+$ for $C_{19}H_{27}N_2O_3$: 331.2016,
found $[M+H]^+$: 331.2020