Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-Light Induced Divergent Dearomatization of Indole Derivatives: Controlled Access to Cyclobutane-Fused Polycycles and 2-Substituted Indolines

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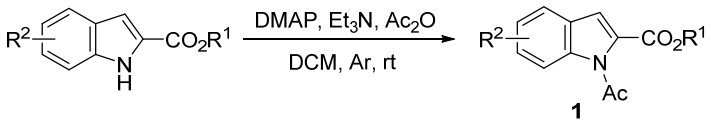
1. General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (600 MHz and 150 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The high resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS instrument or a High-Resolution LC-MS spectrometer Thermo Fisher Exactive. Melting points (M.p.) were determined in open capillaries without further correction.

2. General Procedure for the Synthesis of Substrates

Substrates **1a, 1b, 1i, 1o, 1q** were synthesized according to the literature procedures.[1] Solvents are commercially available from Alfa Aesar, and used without further purification.



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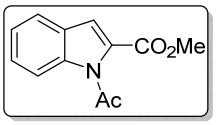
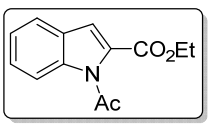
To a solution of *N*-unsubstituted indole derivatives (10 mmol) in DCE (40 mL) was added DMAP (1 mmol, 0.1 eq) at room temperature under argon. After stirring for 25 minutes, acetic anhydride (Ac_2O, 15 mmol, 1.5 eq) and triethylamine (Et_3N, 25 mmol, 2.5 eq) were added slowly, and then the reaction mixture was stirred at room temperature overnight. The mixture was quenched with H_2O, extracted with DCM, and dried over Na_2SO_4. After removal of Na_2SO_4 by filtration, the organic phase was concentrated *in vacuo* to give dark residue, which was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford the desired indole substrates **1a-1t**.

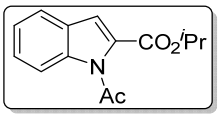


methyl 1-acetyl-1H-indole-2-carboxylate (1a), white solid, m.p. = 48-49 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.30 – 7.23 (m, 2H), 3.92 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** and **HRMS** data for the desired product were in agreement with the previously reported literature data[1].

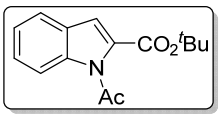


ethyl 1-acetyl-1H-indole-2-carboxylate (1b), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 1H), 7.32 – 7.24

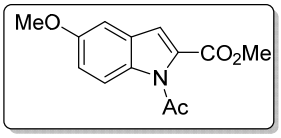
(m, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.61 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 161.6, 138.3, 129.7, 127.8, 127.1, 123.7, 122.3, 118.1, 115.1, 61.6, 27.1, 14.1. **IR** (thin film): ν_{max}/cm^{-1} = 2982, 2937, 1710, 1607, 1534, 1474, 1442, 1395, 1366, 1338, 1289, 1258, 1191, 1146, 1112, 1043, 1015, 988, 942, 906, 839, 806. **HRMS** data for the desired product were in agreement with the previously reported literature data [1].



isopropyl 1-acetyl-1H-indole-2-carboxylate (1c), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.43 (m, 1H), 7.32 – 7.23 (m, 2H), 5.32 – 5.18 (m, 1H), 2.61 (s, 3H), 1.39 (d, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 161.2, 138.3, 130.2, 127.7, 127.1, 123.7, 122.3, 117.9, 115.2, 69.4, 27.2, 21.7. **IR** (thin film): ν_{max}/cm^{-1} = 2981, 1709, 1608, 1535, 1473, 1443, 1367, 1291, 1258, 1197, 1146, 1102, 1039, 1000, 940, 917, 902, 861, 830. **HRMS (ESI)** calcd for $C_{14}H_{15}NO_3Na$ $[M+Na]^+$: 268.0944, Found: 268.0953.

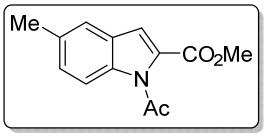


tert-butyl 1-acetyl-1H-indole-2-carboxylate (1d), white solid, m.p. = 36-39 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.4, 1.2 Hz, 1H), 7.60 (dt, J = 7.6, 1.2 Hz, 1H), 7.42 (m, 1H), 7.31 – 7.21 (m, 2H), 2.62 (s, 3H), 1.62 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 161.0, 138.2, 131.2, 127.5, 127.1, 123.6, 122.2, 117.4, 115.1, 82.6, 28.0, 27.2. **IR** (thin film): ν_{max}/cm^{-1} = 3005, 2980, 2934, 1704, 1608, 1535, 1474, 1442, 1366, 1292, 1264, 1218, 1197, 1160, 1141, 1034, 1000, 943, 867, 840. **HRMS (ESI)** calcd for $C_{15}H_{17}NO_3Na$ $[M+Na]^+$: 282.1101, Found: 282.1106.

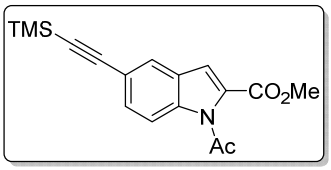


methyl 1-acetyl-5-methoxy-1H-indole-2-carboxylate (1e), white solid, m.p. = 91-92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.2 Hz, 1H), 7.23 (s, 1H), 7.09 – 6.99 (m, 2H), 3.93 (s, 3H), 3.84 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

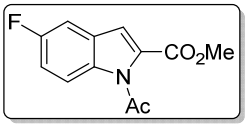
170.6, 162.0, 156.4, 133.4, 129.7, 127.8, 118.1, 117.5, 116.3, 103.6, 55.6, 52.4, 26.9. **IR** (thin film): ν_{max}/cm^{-1} = 3128, 3085, 3006, 2958, 2838, 2494, 2316, 1702, 1615, 1586, 1534, 1482, 1452, 1435, 1380, 1357, 1297, 1273, 1196, 1165, 1116, 1053, 1030, 955, 863, 830, 805. **HRMS (ESI)** calcd for $C_{13}H_{13}NO_4Na$ $[M+Na]^+$: 270.0737, Found: 270.0740.



methyl 1-acetyl-5-methyl-1H-indole-2-carboxylate (1f), white solid, m.p. = 32-33 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.38 (s, 1H), 7.28 – 7.22 (m, 2H), 3.93 (s, 3H), 2.59 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 162.1, 136.7, 133.3, 129.5, 129.3, 127.3, 122.0, 118.2, 114.8, 52.4, 27.0, 21.1. **IR** (thin film): ν_{max}/cm^{-1} = 2948, 2910, 1705, 1537, 1429, 1375, 1361, 1293, 1269, 1197, 1159, 1132, 1054, 1026, 958, 884, 861, 806. **HRMS (ESI)** calcd for $C_{13}H_{13}NO_3Na$ $[M+Na]^+$: 254.0788, Found: 254.0788.

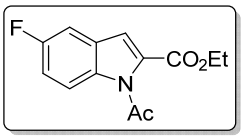


methyl 1-acetyl-5-((trimethylsilyl)ethynyl)-1H-indole-2-carboxylate (1g), yellow solid, m.p. = 109-110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.56 – 7.51 (m, 1H), 7.29 – 7.24 (m, 1H), 3.94 (s, 3H), 2.61 (s, 3H), 0.27 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 161.8, 137.9, 131.5, 130.1, 126.8, 126.2, 118.6, 117.7, 115.1, 104.8, 93.6, 52.6, 27.1, -0.03. **IR** (thin film): ν_{max}/cm^{-1} = 2953, 2899, 2147, 1708, 1607, 1564, 1540, 1454, 1436, 1369, 1334, 1294, 1205, 1163, 1053, 1020, 955, 908, 829. **HRMS (ESI)** calcd for $C_{17}H_{19}NO_3SiNa$ [M+Na]+: 336.1026, Found: 336.1024.

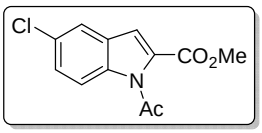


methyl 1-acetyl-5-fluoro-1H-indole-2-carboxylate (1h), white solid, m.p. = 96-97

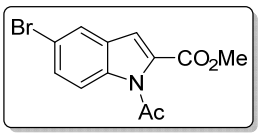
°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.18 (td, *J* = 9.2, 2.8 Hz, 1H), 3.95 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 161.8, 159.5 (d, *J* = 240.0 Hz), 134.8, 130.6, 127.8 (d, *J* = 10.0 Hz), 117.6 (d, *J* = 3.6 Hz), 116.7 (d, *J* = 9.6 Hz), 116.1 (d, *J* = 25.3 Hz), 107.3 (d, *J* = 23.5 Hz), 52.6, 27.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.92 ~ -118.98 (m, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 1710, 1586, 1533, 1463, 1433, 1381, 1354, 1303, 1285, 1262, 1191, 1161, 1118, 1103, 1051, 1020, 960, 948, 851. **HRMS (EI)** calcd for $C_{12}H_{10}NO_3F$ $[M]^+$: 235.0639, Found: 235.0632.



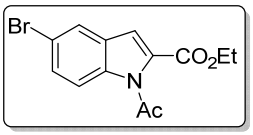
ethyl 1-acetyl-5-fluoro-1H-indole-2-carboxylate (1i), white solid, m.p. = 50-51 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.17 (td, *J* = 9.2, 2.8 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 161.4, 159.4 (d, *J* = 240.0 Hz), 134.8, 131.1, 127.7 (d, *J* = 10.0 Hz), 117.4 (d, *J* = 4.0 Hz), 116.6 (d, *J* = 9.0 Hz), 116.0 (d, *J* = 25.0 Hz), 107.2 (d, *J* = 24 Hz), 61.8, 27.0, 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.99 ~ -119.05 (m, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 2995, 1703, 1589, 1532, 1446, 1363, 1292, 1198, 1158, 1109, 1006, 953, 855. **HRMS** data for the desired product were in agreement with the previously reported literature data [1].



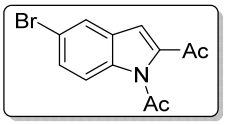
methyl 1-acetyl-5-chloro-1H-indole-2-carboxylate (1j), yellow solid, m.p. = 107-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.2 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (s, 1H), 3.95 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 161.7, 136.7, 130.4, 129.4, 128.12, 128.09, 121.7, 117.1, 116.5, 52.7, 27.0. **IR** (thin film): ν_{max}/cm^{-1} = 2955, 1707, 1570, 1527, 1429, 1382, 1361, 1339, 1298, 1279, 1261, 1197, 1128, 1066, 1051, 1031, 1016, 950, 915, 860, 818. **HRMS (EI)** calcd for $C_{12}H_{10}NO_3Cl$ $[M]^+$: 251.0344, Found: 251.0335.



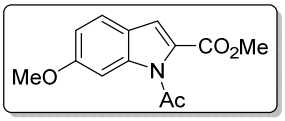
methyl 1-acetyl-5-bromo-1H-indole-2-carboxylate (1k), yellow solid, m.p. = 106-107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.23 (s, 1H), 3.95 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 161.7, 137.0, 130.7, 130.2, 128.6, 124.8, 116.9, 116.8, 52.7, 27.0. **IR** (thin film): ν_{max}/cm^{-1} = 3324, 3127, 3002, 2950, 2920, 2849, 2468, 2322, 1710, 1572, 1526, 1433, 1379, 1363, 1336, 1296, 1263, 1187, 1128, 1086, 1047, 1015, 951, 905, 871, 855. **HRMS (ESI)** calcd for $C_{12}H_{10}NO_3BrNa$ $[M+Na]^+$: 317.9736, Found: 317.9724.



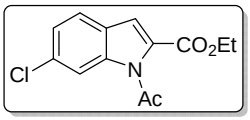
ethyl 1-acetyl-5-bromo-1H-indole-2-carboxylate (1l), white solid, m.p. = 72-73 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.22 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 161.2, 136.9, 130.6, 128.6, 124.7, 116.8, 116.7, 61.9, 27.1, 14.1. **IR** (thin film): ν_{max}/cm^{-1} = 3116, 2982, 2937, 1702, 1569, 1531, 1478, 1435, 1401, 1381, 1358, 1335, 1295, 1276, 1260, 1194, 1156, 1104, 1049, 1027, 999, 910, 881, 860. **HRMS (EI)** calcd for $C_{13}H_{12}NO_3Br$ $[M]^+$: 308.9995, Found: 308.9988.



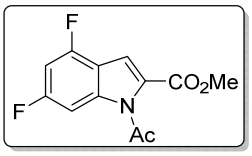
1,1'-(5-bromo-1H-indole-1,2-diyl)bis(ethan-1-one) (1m), yellow solid, m.p. = 130-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.26 (s, 1H), 2.63 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.0, 171.7, 138.2, 137.4, 131.4, 128.4, 125.1, 116.9, 116.7, 116.4, 27.6. **IR** (thin film): ν_{max}/cm^{-1} = 1711, 1667, 1569, 1521, 1437, 1364, 1345, 1297, 1262, 1198, 1170, 1124, 1056, 1034, 1018, 999, 951, 894, 820. **HRMS (EI)** calcd for $C_{12}H_{10}NO_2Br$ $[M]^+$: 278.9889, Found: 278.9883.



methyl 1-acetyl-6-methoxy-1H-indole-2-carboxylate (1n), white solid, m.p. = 98-99 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.31 (s, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 161.9, 160.8, 140.3, 127.8, 123.1, 120.6, 119.5, 114.3, 98.2, 55.6, 52.3, 27.3. **IR** (thin film): ν_{max}/cm^{-1} = 2994, 2964, 2940, 2831, 1705, 1611, 1531, 1490, 1424, 1378, 1360, 1316, 1284, 1220, 1199, 1114, 1051, 1025, 963, 936, 845, 831, 810. **HRMS (EI)** calcd for $C_{13}H_{13}NO_4$ $[M]^+$: 247.0839, Found: 247.0834.

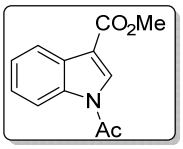


ethyl 1-acetyl-6-chloro-1H-indole-2-carboxylate (1o), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 1H), 7.24 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 161.3, 138.6, 133.9, 130.1, 125.4, 124.5, 123.0, 117.7, 115.4, 61.8, 27.1, 14.1. **IR** (thin film): ν_{max} (cm^{-1}) = 3129, 2983, 2938, 2901, 1703, 1601, 1532, 1457, 1419, 1394, 1365, 1338, 1298, 1274, 1243, 1189, 1113, 1068, 1042, 1025, 998, 946, 927, 857, 803. **HRMS** data for the desired product were in agreement with the previously reported literature data [1].

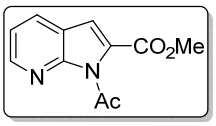


methyl 1-acetyl-4,6-difluoro-1H-indole-2-carboxylate (1p), yellow solid, m.p. = 113-114 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 1H), 7.39 – 7.37 (m, 1H), 6.77 (td, *J* = 9.6, 2.4 Hz, 1H), 3.95 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 162.9 (dd, *J* = 245.0, 12.0 Hz), 161.3, 156.1 (dd, *J* = 253.0, 15.0 Hz), 139.6 (dd, *J* = 16.0, 11.0 Hz), 129.3 (d, *J* = 4.0 Hz), 113.7, 113.0 (d, *J* = 22.0 Hz), 99.3 (dd, *J* = 28.0, 22.0 Hz), 98.7 (dd, *J* = 29.0, 5.0 Hz), 52.7, 27.0. **^{19}F NMR** (376 MHz,

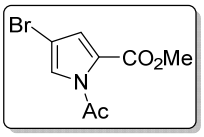
$CDCl_3$) δ -108.24 ~ -108.30 (m, 1F), -116.08 ~ -116.12 (m, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 3316, 3132, 3062, 1705, 1634, 1589, 1527, 1492, 1453, 1439, 1382, 1365, 1337, 1224, 1175, 1140, 1121, 1076, 1049, 1027, 1010, 986, 941, 843, 811. **HRMS (EI)** calcd for $C_{12}H_9NO_3F_2$ $[M]^+$: 253.0545, Found: 253.0537.



methyl 1-acetyl-1H-indole-3-carboxylate (1q), white solid, m.p. = 112-113 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 6.4, 2.0 Hz, 1H), 8.13 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.09 (s, 1H), 7.42 – 7.34 (m, 2H), 3.94 (s, 3H), 2.68 (s, 3H). **^{13}C NMR** and **HRMS** data for the desired product were in agreement with the previously reported literature data[1].



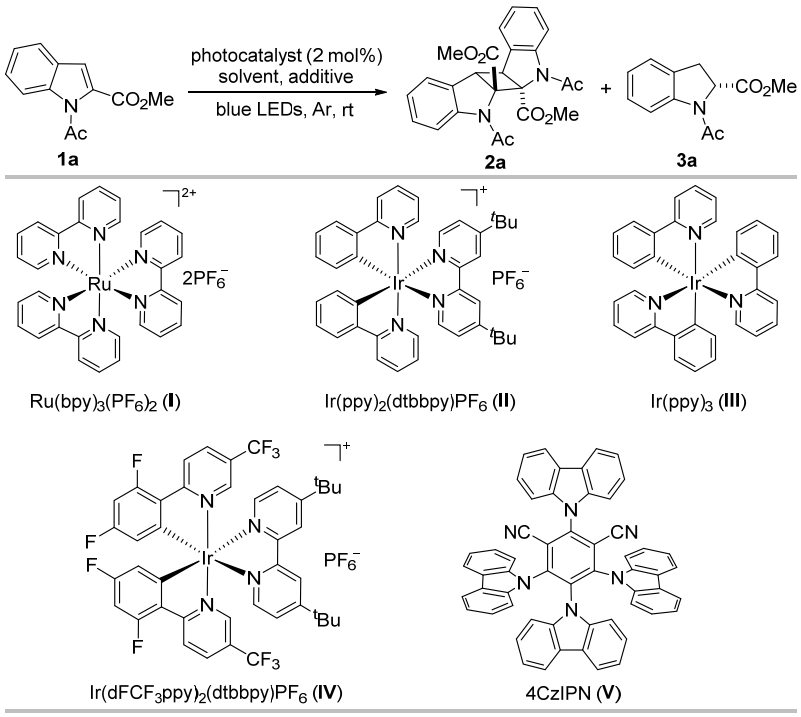
methyl 1-acetyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate (1r), yellow solid, m.p. = 50-51 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.04 (s, 1H), 3.93 (s, 3H), 3.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 162.6, 148.7, 146.3, 130.8, 130.7, 120.8, 119.2, 111.5, 52.7, 26.6. **IR** (thin film): ν_{max}/cm^{-1} = 3049, 2958, 1738, 1716, 1595, 1574, 1536, 1474, 1442, 1429, 1398, 1377, 1336, 1290, 1230, 1207, 1112, 1050, 997, 969, 911, 844. **HRMS (EI)** calcd for $C_{11}H_{10}N_2O_3$ $[M]^+$: 218.0686, Found: 218.0677.



methyl 1-acetyl-4-bromo-1H-pyrrole-2-carboxylate (1s), white solid, m.p. = 80-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.90 (s, 1H), 3.85 (s, 3H), 2.58 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 160.4, 125.1, 123.7, 99.8, 52.3, 24.4. **IR** (thin film): ν_{max}/cm^{-1} = 3145, 3045, 1701, 1679, 1595, 1579, 1544, 1473, 1425, 1401, 1377, 1351, 1328, 1300, 1236, 1203, 1188, 1099, 1040, 1013, 992, 937, 914, 831. **HRMS (DART)** calcd for $C_8H_9NO_3Br$ $[M+H]^+$: 245.9760, Found: 245.9759.

3. Detailed Screening of Reaction Conditions

Table 1. Optimization of the Reaction Conditions[a]



entry	photocatalyst	solvent	additive	yield (%) (**2a**)[b]	yield (%) (**3a**)[b]
1	**I**	CH_3CN	—	0	0
2	**II**	CH_3CN	—	47	0
3	**III**	CH_3CN	—	81(80)[c]	0
4	**IV**	CH_3CN	—	63	0
5	**V**	CH_3CN	—	26	10
6	**III**	CH_2Cl_2	—	54	0
7	**III**	acetone	—	70	0
8	**III**	DMSO	—	77	0
9	**III**	MeOH	—	trace	0
10	**III**	CH_3CN	$NaHCO_3$	72	0
11	**III**	CH_3CN	NEt_3	19	63
12	**III**	CH_3CN	DIPEA	trace	40
13[d]	**III**	CH_3CN	DIPEA	trace	75
14[e]	**III**	CH_3CN	DIPEA	trace	88(80)[c]
15[f]	—	CH_3CN	—	0	0

16[g]	**III**	CH_3CN	—	0	0

[a]Reaction conditions: A solution of **1a** (0.2 mmol), photocatalyst (2 mol%), and additive (2 equiv) in the indicated solvent (c = 0.1 M) was irradiated by 24W blue LEDs at room temperature under argon for 24 h. [b]Determined by ^1H NMR yield using CH_2Br_2 as an internal standard. [c]Isolated yield. [d]DIPEA (4 equiv) was used. [e]DIPEA (8 equiv) was used. [f]Without a photocatalyst. [g]Under dark. DIPEA = N,N-Diisopropylethylamine.

4. Single Crystal X-ray Structure Determination

X-Ray crystal structure of **2a** (The crystal was obtained by slow evaporation of the solution of DCM at 0 ºC) (CCDC 2039653):

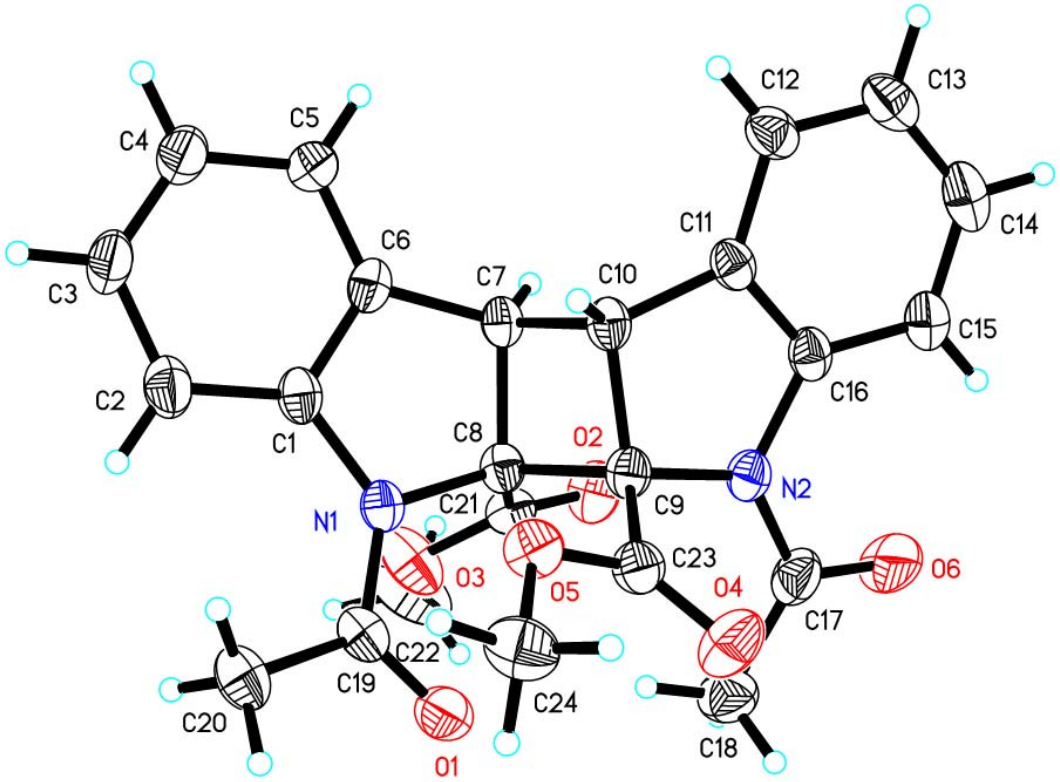


Figure S1. X-ray structure of **2a**

Table 1. Crystal data and structure refinement for d8v18928.

Identification code	d8v18928	
Empirical formula	C24 H22 N2 O6	
Formula weight	434.43	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 18.1971(18) Å	α= 90°.
	b = 12.7997(18) Å	β= 102.325(5)°.
	c = 9.1690(9) Å	γ = 90°.
Volume	2086.4(4) $Å^3$	
Z	4	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	912	
Crystal size	0.180 x 0.150 x 0.060 mm^3	
Theta range for data collection	2.291 to 25.497°.	
Index ranges	-22<=h<=22, -15<=k<=15, -11<=l<=11	
Reflections collected	13796	
Independent reflections	3806 [R(int) = 0.0588]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6118	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3806 / 2 / 294	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1740	
R indices (all data)	R1 = 0.0899, wR2 = 0.1956	
Absolute structure parameter	0.6(9)	
Extinction coefficient	0.012(2)	
Largest diff. peak and hole	0.256 and -0.242 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d8v18928. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4573(3)	933(4)	5370(6)	64(1)
O(2)	4808(3)	2660(5)	1889(5)	64(2)
O(3)	3811(3)	2007(5)	2584(5)	75(2)
O(4)	6389(3)	1725(5)	6773(6)	72(2)
O(5)	5449(3)	2413(4)	7666(5)	52(1)
O(6)	6755(4)	2204(5)	2708(9)	97(2)
N(1)	4169(3)	2585(4)	5368(5)	43(1)
N(2)	6099(3)	2940(4)	4274(6)	45(1)
C(1)	3730(4)	3455(5)	5680(7)	45(2)
C(2)	3105(4)	3487(7)	6298(9)	60(2)
C(3)	2768(5)	4462(7)	6402(10)	66(2)
C(4)	3052(4)	5348(7)	5945(9)	64(2)
C(5)	3664(4)	5318(6)	5272(9)	56(2)
C(6)	3998(4)	4370(5)	5147(7)	45(2)
C(7)	4657(3)	4119(5)	4489(7)	42(1)
C(8)	4681(4)	2909(5)	4423(7)	42(1)
C(9)	5551(4)	2946(5)	5240(7)	42(1)
C(10)	5453(4)	4135(5)	5544(7)	42(1)
C(11)	6055(4)	4657(5)	4969(7)	42(1)
C(12)	6258(4)	5722(6)	5064(8)	52(2)
C(13)	6836(4)	6034(7)	4408(9)	61(2)
C(14)	7214(4)	5317(7)	3702(9)	65(2)
C(15)	7009(4)	4277(6)	3598(8)	53(2)
C(16)	6417(3)	3962(6)	4228(7)	44(2)
C(17)	6298(4)	2089(7)	3505(9)	61(2)
C(18)	5936(5)	1062(7)	3594(10)	68(2)
C(19)	4187(4)	1571(6)	5858(7)	50(2)
C(20)	3758(5)	1263(7)	7014(9)	64(2)
C(21)	4458(4)	2492(5)	2827(7)	46(2)
C(22)	3510(8)	1657(9)	1050(9)	107(4)
C(23)	5845(4)	2261(6)	6608(7)	48(2)
C(24)	5635(5)	1754(7)	8976(8)	66(2)

Table 3. Bond lengths [Å] and angles [°] for d8v18928.

O(1)-C(19)	1.223(9)
O(2)-C(21)	1.194(8)
O(3)-C(21)	1.307(8)
O(3)-C(22)	1.466(10)
O(4)-C(23)	1.188(9)
O(5)-C(23)	1.340(8)
O(5)-C(24)	1.447(9)
O(6)-C(17)	1.228(9)
N(1)-C(19)	1.371(9)
N(1)-C(1)	1.434(9)
N(1)-C(8)	1.462(8)
N(2)-C(17)	1.388(9)
N(2)-C(16)	1.434(9)
N(2)-C(9)	1.468(8)
C(1)-C(2)	1.375(10)
C(1)-C(6)	1.396(10)
C(2)-C(3)	1.402(12)
C(2)-H(2)	0.9300
C(3)-C(4)	1.351(12)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(10)
C(4)-H(4)	0.9300
C(5)-C(6)	1.374(10)
C(5)-H(5)	0.9300
C(6)-C(7)	1.488(9)
C(7)-C(8)	1.550(10)
C(7)-C(10)	1.561(8)
C(7)-H(7)	0.9800
C(8)-C(21)	1.530(8)
C(8)-C(9)	1.600(8)
C(9)-C(23)	1.531(10)
C(9)-C(10)	1.564(10)
C(10)-C(11)	1.474(9)
C(10)-H(10)	0.9800
C(11)-C(16)	1.371(9)
C(11)-C(12)	1.411(10)

C(12)-C(13)	1.378(11)
C(12)-H(12)	0.9300
C(13)-C(14)	1.387(13)
C(13)-H(13)	0.9300
C(14)-C(15)	1.381(12)
C(14)-H(14)	0.9300
C(15)-C(16)	1.385(9)
C(15)-H(15)	0.9300
C(17)-C(18)	1.479(13)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-C(20)	1.499(10)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600

C(21)-O(3)-C(22)	116.5(7)
C(23)-O(5)-C(24)	116.7(6)
C(19)-N(1)-C(1)	130.2(5)
C(19)-N(1)-C(8)	119.3(5)
C(1)-N(1)-C(8)	110.5(5)
C(17)-N(2)-C(16)	123.4(5)
C(17)-N(2)-C(9)	126.5(6)
C(16)-N(2)-C(9)	110.1(5)
C(2)-C(1)-C(6)	120.0(7)
C(2)-C(1)-N(1)	130.6(7)
C(6)-C(1)-N(1)	109.3(5)
C(1)-C(2)-C(3)	117.8(7)
C(1)-C(2)-H(2)	121.1
C(3)-C(2)-H(2)	121.1
C(4)-C(3)-C(2)	121.6(7)

C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	120.9(8)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	118.3(7)
C(6)-C(5)-H(5)	120.8
C(4)-C(5)-H(5)	120.8
C(5)-C(6)-C(1)	121.2(6)
C(5)-C(6)-C(7)	129.4(6)
C(1)-C(6)-C(7)	109.4(6)
C(6)-C(7)-C(8)	105.3(5)
C(6)-C(7)-C(10)	117.8(5)
C(8)-C(7)-C(10)	90.3(5)
C(6)-C(7)-H(7)	113.6
C(8)-C(7)-H(7)	113.6
C(10)-C(7)-H(7)	113.6
N(1)-C(8)-C(21)	113.2(5)
N(1)-C(8)-C(7)	103.5(5)
C(21)-C(8)-C(7)	112.4(5)
N(1)-C(8)-C(9)	115.1(5)
C(21)-C(8)-C(9)	119.5(5)
C(7)-C(8)-C(9)	89.2(5)
N(2)-C(9)-C(23)	109.1(5)
N(2)-C(9)-C(10)	103.4(5)
C(23)-C(9)-C(10)	116.4(5)
N(2)-C(9)-C(8)	116.7(5)
C(23)-C(9)-C(8)	120.3(6)
C(10)-C(9)-C(8)	88.5(5)
C(11)-C(10)-C(7)	116.5(5)
C(11)-C(10)-C(9)	104.8(5)
C(7)-C(10)-C(9)	90.2(5)
C(11)-C(10)-H(10)	114.2
C(7)-C(10)-H(10)	114.2
C(9)-C(10)-H(10)	114.2
C(16)-C(11)-C(12)	120.7(6)
C(16)-C(11)-C(10)	110.9(6)
C(12)-C(11)-C(10)	128.4(6)

C(13)-C(12)-C(11)	117.9(7)
C(13)-C(12)-H(12)	121.1
C(11)-C(12)-H(12)	121.1
C(12)-C(13)-C(14)	120.8(8)
C(12)-C(13)-H(13)	119.6
C(14)-C(13)-H(13)	119.6
C(15)-C(14)-C(13)	121.1(7)
C(15)-C(14)-H(14)	119.4
C(13)-C(14)-H(14)	119.4
C(14)-C(15)-C(16)	118.3(8)
C(14)-C(15)-H(15)	120.8
C(16)-C(15)-H(15)	120.8
C(11)-C(16)-C(15)	121.1(7)
C(11)-C(16)-N(2)	109.7(5)
C(15)-C(16)-N(2)	129.2(6)
O(6)-C(17)-N(2)	119.5(8)
O(6)-C(17)-C(18)	120.4(7)
N(2)-C(17)-C(18)	120.1(6)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(1)-C(19)-N(1)	119.2(6)
O(1)-C(19)-C(20)	120.6(7)
N(1)-C(19)-C(20)	120.1(7)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(2)-C(21)-O(3)	124.3(6)
O(2)-C(21)-C(8)	123.5(6)
O(3)-C(21)-C(8)	112.0(5)
O(3)-C(22)-H(22A)	109.5
O(3)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5
O(3)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(4)-C(23)-O(5)	123.7(7)
O(4)-C(23)-C(9)	124.8(6)
O(5)-C(23)-C(9)	111.2(6)
O(5)-C(24)-H(24A)	109.5
O(5)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(5)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d8v18928. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	74(4)	54(3)	69(3)	0(2)	26(3)	-5(3)
O(2)	67(3)	87(4)	40(3)	-4(3)	18(3)	5(3)
O(3)	81(4)	96(4)	42(3)	-9(3)	-1(3)	-44(3)
O(4)	72(4)	82(4)	64(3)	13(3)	17(3)	29(3)
O(5)	62(3)	57(3)	38(2)	5(2)	13(2)	3(2)
O(6)	115(5)	74(4)	132(6)	1(4)	94(5)	19(4)
N(1)	40(3)	50(3)	40(3)	1(2)	13(2)	-2(2)
N(2)	43(3)	51(3)	44(3)	-1(2)	18(2)	2(2)
C(1)	41(4)	59(4)	37(3)	-1(3)	12(3)	-4(3)
C(2)	52(4)	70(5)	61(4)	-6(4)	25(4)	-8(4)
C(3)	49(4)	76(6)	80(5)	-9(4)	31(4)	3(4)
C(4)	52(5)	66(5)	77(5)	-13(4)	22(4)	2(4)
C(5)	51(4)	48(4)	70(5)	-6(3)	17(4)	1(3)
C(6)	38(4)	57(4)	42(3)	-5(3)	11(3)	3(3)
C(7)	37(3)	51(4)	40(3)	1(3)	12(3)	-2(3)
C(8)	41(3)	49(3)	35(3)	-5(3)	11(3)	-4(3)
C(9)	43(4)	50(4)	37(3)	0(3)	14(3)	1(3)
C(10)	39(3)	52(4)	36(3)	-2(3)	11(3)	-3(3)
C(11)	36(3)	49(4)	38(3)	4(3)	2(3)	-6(3)
C(12)	48(4)	51(4)	54(4)	0(3)	0(3)	-8(3)
C(13)	55(4)	59(5)	63(4)	13(4)	-4(4)	-15(4)
C(14)	44(4)	93(6)	57(4)	17(4)	8(4)	-15(4)
C(15)	41(4)	68(5)	49(4)	5(3)	11(3)	-2(3)
C(16)	35(4)	56(4)	40(3)	9(3)	5(3)	-1(3)
C(17)	57(5)	67(5)	64(5)	3(4)	28(4)	14(4)
C(18)	83(6)	57(5)	71(5)	-4(4)	29(4)	6(4)
C(19)	52(4)	54(4)	45(4)	0(3)	12(3)	-12(3)
C(20)	65(5)	73(5)	57(4)	6(4)	23(4)	-12(4)
C(21)	52(4)	46(4)	37(3)	-4(3)	7(3)	2(3)
C(22)	152(10)	108(8)	45(4)	-6(5)	-12(5)	-65(8)
C(23)	50(4)	49(4)	46(4)	2(3)	14(3)	0(3)
C(24)	90(6)	63(5)	47(4)	10(4)	15(4)	-4(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d8v18928.

	x	y	z	U(eq)
H(2)	2913	2882	6637	71
H(3)	2337	4498	6795	79
H(4)	2834	5988	6084	77
H(5)	3844	5925	4913	67
H(7)	4640	4456	3523	51
H(10)	5450	4301	6587	50
H(12)	6009	6199	5553	63
H(13)	6975	6734	4440	74
H(14)	7612	5541	3291	78
H(15)	7261	3799	3117	63
H(18A)	6300	580	4131	102
H(18B)	5745	801	2604	102
H(18C)	5530	1139	4103	102
H(20A)	3248	1098	6537	95
H(20B)	3760	1830	7700	95
H(20C)	3989	661	7548	95
H(22A)	3529	2222	371	160
H(22B)	2998	1435	955	160
H(22C)	3806	1084	818	160
H(24A)	5529	1039	8693	99
H(24B)	5341	1960	9680	99
H(24C)	6160	1827	9423	99

Table 6. Torsion angles [°] for d8v18928.

C(19)-N(1)-C(1)-C(2)	-14.7(12)
C(8)-N(1)-C(1)-C(2)	168.0(7)
C(19)-N(1)-C(1)-C(6)	169.5(6)
C(8)-N(1)-C(1)-C(6)	-7.7(7)
C(6)-C(1)-C(2)-C(3)	-1.5(10)
N(1)-C(1)-C(2)-C(3)	-176.9(7)
C(1)-C(2)-C(3)-C(4)	-1.5(12)
C(2)-C(3)-C(4)-C(5)	3.9(13)
C(3)-C(4)-C(5)-C(6)	-3.2(12)
C(4)-C(5)-C(6)-C(1)	0.2(11)
C(4)-C(5)-C(6)-C(7)	-179.7(6)
C(2)-C(1)-C(6)-C(5)	2.2(10)
N(1)-C(1)-C(6)-C(5)	178.4(7)
C(2)-C(1)-C(6)-C(7)	-178.0(6)
N(1)-C(1)-C(6)-C(7)	-1.7(7)
C(5)-C(6)-C(7)-C(8)	-170.5(7)
C(1)-C(6)-C(7)-C(8)	9.7(7)
C(5)-C(6)-C(7)-C(10)	90.8(9)
C(1)-C(6)-C(7)-C(10)	-89.0(7)
C(19)-N(1)-C(8)-C(21)	73.6(8)
C(1)-N(1)-C(8)-C(21)	-108.9(6)
C(19)-N(1)-C(8)-C(7)	-164.4(5)
C(1)-N(1)-C(8)-C(7)	13.2(6)
C(19)-N(1)-C(8)-C(9)	-68.9(7)
C(1)-N(1)-C(8)-C(9)	108.7(6)
C(6)-C(7)-C(8)-N(1)	-13.5(6)
C(10)-C(7)-C(8)-N(1)	105.5(5)
C(6)-C(7)-C(8)-C(21)	109.0(6)
C(10)-C(7)-C(8)-C(21)	-131.9(5)
C(6)-C(7)-C(8)-C(9)	-129.2(5)
C(10)-C(7)-C(8)-C(9)	-10.1(4)
C(17)-N(2)-C(9)-C(23)	65.7(8)
C(16)-N(2)-C(9)-C(23)	-114.0(6)
C(17)-N(2)-C(9)-C(10)	-169.9(6)
C(16)-N(2)-C(9)-C(10)	10.4(6)
C(17)-N(2)-C(9)-C(8)	-74.8(8)

C(16)-N(2)-C(9)-C(8)	105.5(6)
N(1)-C(8)-C(9)-N(2)	161.4(5)
C(21)-C(8)-C(9)-N(2)	21.5(9)
C(7)-C(8)-C(9)-N(2)	-94.1(6)
N(1)-C(8)-C(9)-C(23)	25.5(8)
C(21)-C(8)-C(9)-C(23)	-114.4(7)
C(7)-C(8)-C(9)-C(23)	130.0(6)
N(1)-C(8)-C(9)-C(10)	-94.4(6)
C(21)-C(8)-C(9)-C(10)	125.6(6)
C(7)-C(8)-C(9)-C(10)	10.1(4)
C(6)-C(7)-C(10)-C(11)	-135.4(6)
C(8)-C(7)-C(10)-C(11)	117.0(6)
C(6)-C(7)-C(10)-C(9)	117.9(6)
C(8)-C(7)-C(10)-C(9)	10.4(4)
N(2)-C(9)-C(10)-C(11)	-10.5(6)
C(23)-C(9)-C(10)-C(11)	109.1(6)
C(8)-C(9)-C(10)-C(11)	-127.6(5)
N(2)-C(9)-C(10)-C(7)	107.0(5)
C(23)-C(9)-C(10)-C(7)	-133.4(6)
C(8)-C(9)-C(10)-C(7)	-10.0(4)
C(7)-C(10)-C(11)-C(16)	-90.4(7)
C(9)-C(10)-C(11)-C(16)	7.3(7)
C(7)-C(10)-C(11)-C(12)	87.5(8)
C(9)-C(10)-C(11)-C(12)	-174.7(6)
C(16)-C(11)-C(12)-C(13)	-0.9(9)
C(10)-C(11)-C(12)-C(13)	-178.7(6)
C(11)-C(12)-C(13)-C(14)	-1.1(10)
C(12)-C(13)-C(14)-C(15)	1.8(11)
C(13)-C(14)-C(15)-C(16)	-0.5(11)
C(12)-C(11)-C(16)-C(15)	2.3(9)
C(10)-C(11)-C(16)-C(15)	-179.6(6)
C(12)-C(11)-C(16)-N(2)	-179.1(6)
C(10)-C(11)-C(16)-N(2)	-0.9(7)
C(14)-C(15)-C(16)-C(11)	-1.6(10)
C(14)-C(15)-C(16)-N(2)	-180.0(7)
C(17)-N(2)-C(16)-C(11)	173.8(6)
C(9)-N(2)-C(16)-C(11)	-6.5(7)
C(17)-N(2)-C(16)-C(15)	-7.6(10)

C(9)-N(2)-C(16)-C(15)	172.1(6)
C(16)-N(2)-C(17)-O(6)	-2.0(11)
C(9)-N(2)-C(17)-O(6)	178.3(8)
C(16)-N(2)-C(17)-C(18)	-179.2(7)
C(9)-N(2)-C(17)-C(18)	1.2(11)
C(1)-N(1)-C(19)-O(1)	175.3(6)
C(8)-N(1)-C(19)-O(1)	-7.7(9)
C(1)-N(1)-C(19)-C(20)	-6.7(10)
C(8)-N(1)-C(19)-C(20)	170.3(6)
C(22)-O(3)-C(21)-O(2)	0.0(12)
C(22)-O(3)-C(21)-C(8)	174.7(8)
N(1)-C(8)-C(21)-O(2)	-179.2(6)
C(7)-C(8)-C(21)-O(2)	63.9(9)
C(9)-C(8)-C(21)-O(2)	-38.6(10)
N(1)-C(8)-C(21)-O(3)	6.0(8)
C(7)-C(8)-C(21)-O(3)	-110.8(6)
C(9)-C(8)-C(21)-O(3)	146.6(6)
C(24)-O(5)-C(23)-O(4)	-10.0(11)
C(24)-O(5)-C(23)-C(9)	175.6(6)
N(2)-C(9)-C(23)-O(4)	-7.4(10)
C(10)-C(9)-C(23)-O(4)	-123.8(8)
C(8)-C(9)-C(23)-O(4)	131.4(8)
N(2)-C(9)-C(23)-O(5)	166.9(5)
C(10)-C(9)-C(23)-O(5)	50.5(8)
C(8)-C(9)-C(23)-O(5)	-54.3(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d8v18928 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(24)-H(24B)...O(2)#1	0.96	2.58	3.530(10)	168.2
C(18)-H(18C)...O(1)	0.96	2.31	3.249(11)	167.4
C(15)-H(15)...O(6)	0.93	2.24	2.785(10)	116.9
C(2)-H(2)...O(6)#2	0.93	2.51	3.137(10)	125.1

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 x-1/2,-y+1/2,z+1/2

X-Ray crystal structure of **3a** (The crystal was obtained by slow evaporation of the solution of DCM and PE at room temperature) (CCDC 2039654):

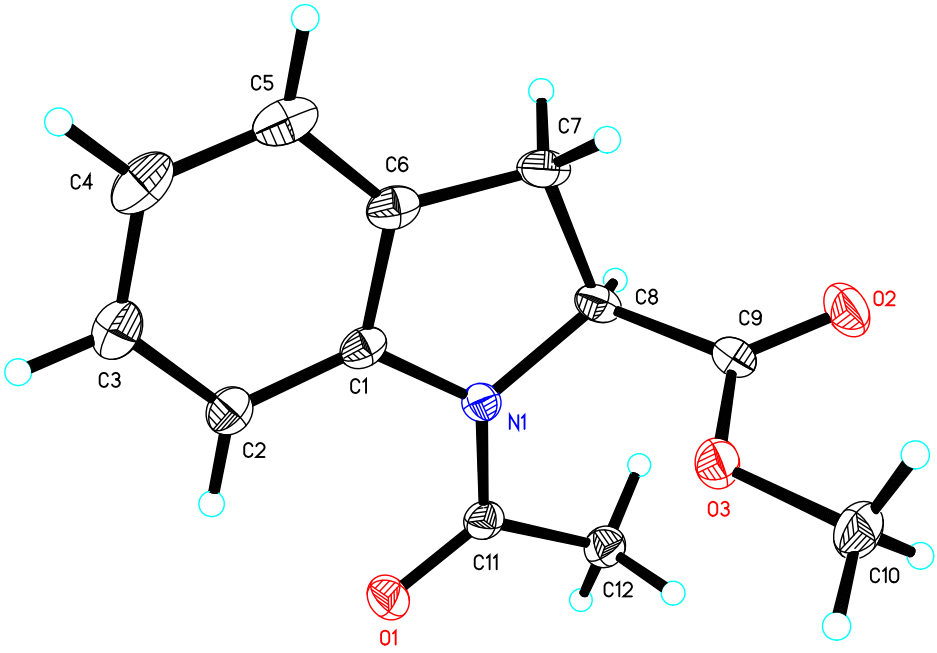


Figure S2. X-ray structure of **3a**

Table 1. Crystal data and structure refinement for d8v20173.

Identification code	d8v20173	
Empirical formula	C12 H13 N O3	
Formula weight	219.23	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 22.6211(9) Å	α= 90°.
	b = 4.8921(2) Å	β= 90°.
	c = 9.6732(3) Å	γ = 90°.
Volume	1070.48(7) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	464	
Crystal size	0.160 x 0.140 x 0.100 mm^3	
Theta range for data collection	4.166 to 25.959°.	
Index ranges	-27<=h<=23, -6<=k<=5, -11<=l<=10	
Reflections collected	4898	
Independent reflections	1810 [R(int) = 0.0233]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6534	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1810 / 1 / 148	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0692	
R indices (all data)	R1 = 0.0299, wR2 = 0.0715	
Absolute structure parameter	-0.2(5)	
Extinction coefficient	0.029(9)	
Largest diff. peak and hole	0.133 and -0.124 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d8v20173. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5006(1)	1694(3)	3900(2)	38(1)
O(2)	6776(1)	-311(3)	7422(2)	46(1)
O(3)	6175(1)	3201(3)	6974(2)	35(1)
N(1)	5988(1)	1648(3)	4338(2)	26(1)
C(1)	6168(1)	3632(4)	3356(2)	28(1)
C(2)	5823(1)	5219(4)	2484(2)	32(1)
C(3)	6111(1)	7016(5)	1597(2)	40(1)
C(4)	6724(1)	7235(5)	1589(3)	47(1)
C(5)	7060(1)	5645(5)	2471(3)	42(1)
C(6)	6782(1)	3847(4)	3357(2)	32(1)
C(7)	7048(1)	1959(5)	4407(2)	37(1)
C(8)	6506(1)	537(4)	5084(2)	29(1)
C(9)	6499(1)	1052(4)	6619(2)	28(1)
C(10)	6146(1)	3795(6)	8445(2)	43(1)
C(11)	5423(1)	706(4)	4532(2)	27(1)
C(12)	5336(1)	-1539(4)	5560(2)	34(1)

Table 3. Bond lengths [Å] and angles [°] for d8v20173.

O(1)-C(11)	1.223(2)
O(2)-C(9)	1.200(3)
O(3)-C(9)	1.326(2)
O(3)-C(10)	1.454(3)
N(1)-C(11)	1.372(2)
N(1)-C(1)	1.418(3)
N(1)-C(8)	1.479(2)
C(1)-C(2)	1.386(3)
C(1)-C(6)	1.392(3)
C(2)-C(3)	1.391(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.390(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.381(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.499(3)
C(7)-C(8)	1.554(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.507(3)
C(8)-H(8)	1.0000
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.495(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(9)-O(3)-C(10)	115.88(17)
C(11)-N(1)-C(1)	126.03(17)
C(11)-N(1)-C(8)	123.26(17)
C(1)-N(1)-C(8)	110.56(16)
C(2)-C(1)-C(6)	121.3(2)

C(2)-C(1)-N(1)	129.04(17)
C(6)-C(1)-N(1)	109.68(18)
C(1)-C(2)-C(3)	117.8(2)
C(1)-C(2)-H(2)	121.1
C(3)-C(2)-H(2)	121.1
C(4)-C(3)-C(2)	121.3(2)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	120.1(2)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.3(2)
C(6)-C(5)-H(5)	120.3
C(4)-C(5)-H(5)	120.3
C(5)-C(6)-C(1)	120.2(2)
C(5)-C(6)-C(7)	129.03(18)
C(1)-C(6)-C(7)	110.79(18)
C(6)-C(7)-C(8)	104.13(15)
C(6)-C(7)-H(7A)	110.9
C(8)-C(7)-H(7A)	110.9
C(6)-C(7)-H(7B)	110.9
C(8)-C(7)-H(7B)	110.9
H(7A)-C(7)-H(7B)	108.9
N(1)-C(8)-C(9)	114.25(16)
N(1)-C(8)-C(7)	104.77(17)
C(9)-C(8)-C(7)	110.41(17)
N(1)-C(8)-H(8)	109.1
C(9)-C(8)-H(8)	109.1
C(7)-C(8)-H(8)	109.1
O(2)-C(9)-O(3)	124.20(19)
O(2)-C(9)-C(8)	122.62(18)
O(3)-C(9)-C(8)	113.14(17)
O(3)-C(10)-H(10A)	109.5
O(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5

O(1)-C(11)-N(1)	121.2(2)
O(1)-C(11)-C(12)	121.44(18)
N(1)-C(11)-C(12)	117.38(17)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d8v20173. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	50(1)	37(1)	8(1)	-6(1)	-2(1)
O(2)	44(1)	52(1)	42(1)	3(1)	-11(1)	18(1)
O(3)	42(1)	37(1)	27(1)	-5(1)	-3(1)	13(1)
N(1)	23(1)	32(1)	24(1)	-2(1)	-1(1)	0(1)
C(1)	30(1)	29(1)	24(1)	-8(1)	4(1)	-5(1)
C(2)	36(1)	32(1)	28(1)	-4(1)	1(1)	-3(1)
C(3)	53(1)	34(1)	33(1)	-1(1)	5(1)	-4(1)
C(4)	60(2)	38(1)	43(2)	-2(1)	17(1)	-14(1)
C(5)	39(1)	43(1)	43(1)	-12(1)	14(1)	-10(1)
C(6)	31(1)	34(1)	31(1)	-13(1)	5(1)	-4(1)
C(7)	22(1)	52(1)	36(1)	-11(1)	2(1)	0(1)
C(8)	23(1)	30(1)	35(1)	-6(1)	-2(1)	4(1)
C(9)	22(1)	29(1)	33(1)	0(1)	-4(1)	2(1)
C(10)	52(1)	51(1)	27(1)	-8(1)	2(1)	7(1)
C(11)	27(1)	32(1)	23(1)	-5(1)	1(1)	0(1)
C(12)	31(1)	39(1)	31(1)	2(1)	1(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for d8v20173.

	x	y	z	U(eq)
H(2)	5404	5082	2492	38
H(3)	5885	8116	984	48
H(4)	6912	8479	976	57
H(5)	7479	5788	2466	50
H(7A)	7278	2992	5103	44
H(7B)	7310	603	3959	44
H(8)	6531	-1476	4914	35
H(10A)	5856	5247	8608	65
H(10B)	6535	4395	8770	65
H(10C)	6027	2145	8947	65
H(12A)	5301	-755	6488	51
H(12B)	5676	-2781	5530	51
H(12C)	4975	-2552	5335	51

Table 6. Torsion angles [°] for d8v20173.

C(11)-N(1)-C(1)-C(2)	6.6(3)
C(8)-N(1)-C(1)-C(2)	-177.6(2)
C(11)-N(1)-C(1)-C(6)	-173.46(19)
C(8)-N(1)-C(1)-C(6)	2.4(2)
C(6)-C(1)-C(2)-C(3)	0.7(3)
N(1)-C(1)-C(2)-C(3)	-179.37(19)
C(1)-C(2)-C(3)-C(4)	-0.4(3)
C(2)-C(3)-C(4)-C(5)	0.2(4)
C(3)-C(4)-C(5)-C(6)	-0.1(3)
C(4)-C(5)-C(6)-C(1)	0.3(3)
C(4)-C(5)-C(6)-C(7)	-179.2(2)
C(2)-C(1)-C(6)-C(5)	-0.6(3)
N(1)-C(1)-C(6)-C(5)	179.41(18)
C(2)-C(1)-C(6)-C(7)	178.96(19)
N(1)-C(1)-C(6)-C(7)	-1.0(2)
C(5)-C(6)-C(7)-C(8)	178.9(2)
C(1)-C(6)-C(7)-C(8)	-0.6(2)
C(11)-N(1)-C(8)-C(9)	-65.7(2)
C(1)-N(1)-C(8)-C(9)	118.31(19)
C(11)-N(1)-C(8)-C(7)	173.31(17)
C(1)-N(1)-C(8)-C(7)	-2.6(2)
C(6)-C(7)-C(8)-N(1)	1.9(2)
C(6)-C(7)-C(8)-C(9)	-121.53(18)
C(10)-O(3)-C(9)-O(2)	-2.8(3)
C(10)-O(3)-C(9)-C(8)	179.48(19)
N(1)-C(8)-C(9)-O(2)	157.98(19)
C(7)-C(8)-C(9)-O(2)	-84.2(3)
N(1)-C(8)-C(9)-O(3)	-24.3(3)
C(7)-C(8)-C(9)-O(3)	93.5(2)
C(1)-N(1)-C(11)-O(1)	-5.1(3)
C(8)-N(1)-C(11)-O(1)	179.55(19)
C(1)-N(1)-C(11)-C(12)	175.83(18)
C(8)-N(1)-C(11)-C(12)	0.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d8v20173 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12)-H(12A)...O(1)#1	0.98	2.48	3.323(3)	144.5
C(10)-H(10A)...O(1)#2	0.98	2.47	3.443(3)	170.0
C(7)-H(7B)...O(2)#3	0.99	2.58	3.463(3)	147.9
C(2)-H(2)...O(1)	0.95	2.33	2.875(3)	116.2

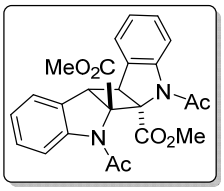
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z+1/2 #2 -x+1,-y+1,z+1/2 #3 -x+3/2,y,z-1/2

5. General Procedure for Visible-Light Induced Divergent Dearomatization of Indole Derivatives

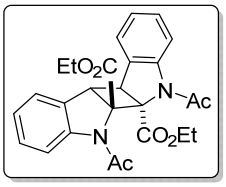
5.1 General Procedure for Visible-Light Induced Dimerization of Indole Derivatives

A flame-dried sealed tube were added indole derivative **1** (0.4 mmol, 1.0 equiv), $Ir(ppy)_3$ (5.3 mg, 0.008 mmol), and CH_3CN (4 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from two 24 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under argon atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatograph ($EtOAc/CH_2Cl_2$ = 8/1 to 4/1) to afford the desired product **2a-2k**, **2m**, **2n**. The analytical data of the products are summarized below.

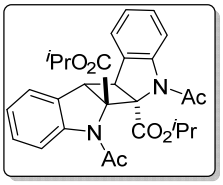


dimethyl-5,6-diacetyl-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2a), white solid, 24 hours, 35.7 mg, 80% yield, m.p. = 171-173 ^oC. **^1H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.26 (m, 4H), 7.20 – 7.04 (m, 3H), 4.06 (d, *J* = 5.2 Hz, 1H), 3.94 (d, *J* = 5.2 Hz, 1H), 3.65 (s, 6H), 2.58 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 169.7, 168.3, 167.2, 145.4, 142.5, 131.7, 129.1, 124.9, 124.0, 123.9, 122.9, 118.5, 114.1, 73.3, 72.4, 53.5, 53.0, 52.9, 50.9, 25.5, 24.8. **IR** (thin film): ν_{max}/cm^{-1} = 3016, 2920, 2850, 1735, 1658, 1602,

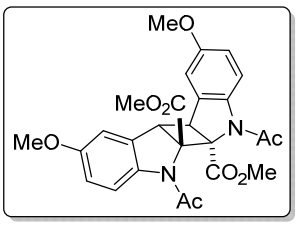
1473, 1374, 1326, 1241, 1197, 1097, 1005, 931, 858. **HRMS (ESI)** calcd for $C_{24}H_{22}N_2O_6Na$ $[M+Na]^+$: 457.1370, Found: 457.1368.



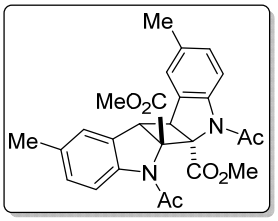
diethyl-5,6-diacetyl-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2b), yellow solid, 42 hours, 90.5 mg, 88% yield, m.p. = 182-183 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.25 (m, 4H), 7.21 – 7.03 (m, 3H), 4.25 – 4.08 (m, 2H), 4.11 – 3.99 (m, 3H), 3.93 (d, *J* = 5.2 Hz, 1H), 2.57 (s, 3H), 2.48 (s, 3H), 1.16 (dt, *J* = 14.8, 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 169.5, 168.0, 166.8, 145.5, 142.6, 131.6, 129.2, 129.0, 124.8, 124.0, 123.8, 122.8, 118.4, 114.0, 73.7, 72.7, 62.3, 62.1, 53.6, 51.0, 25.6, 25.1, 13.7. **IR** (thin film): ν_{max}/cm^{-1} = 2980, 2926, 1735, 1662, 1600, 1476, 1372, 1322, 1234, 1133, 1023, 954, 867, 812. **HRMS (ESI)** calcd for $C_{26}H_{26}N_2O_6Na$ $[M+Na]^+$: 485.1683, Found: 485.1684.



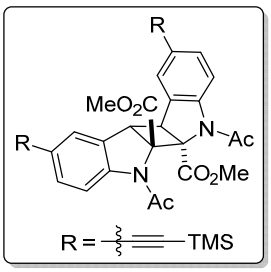
diisopropyl-5,6-diacetyl-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2c), yellow solid, 48 hours, 86.4 mg, 84% yield, m.p. = 155-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.28 (m, 4H), 7.22 – 7.04 (m, 3H), 5.03 – 4.88 (m, 2H), 3.99 (d, *J* = 4.8 Hz, 1H), 3.88 (d, *J* = 4.8 Hz, 1H), 2.56 (s, 3H), 2.49 (s, 3H), 1.14 (dt, *J* = 12.8, 6.2 Hz, 9H), 1.05 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 169.3, 167.5, 166.6, 145.6, 142.8, 131.7, 129.3, 128.9, 124.9, 123.7, 122.8, 118.3, 113.9, 73.7, 72.9, 70.1, 69.9, 54.1, 51.4, 25.5, 25.3, 21.4, 21.2. **IR** (thin film): ν_{max}/cm^{-1} = 2981, 2934, 1731, 1662, 1599, 1475, 1374, 1321, 1236, 1143, 1098, 1026, 981, 906, 829. **HRMS (ESI)** calcd for $C_{28}H_{31}N_2O_6$ $[M+H]^+$: 491.2177, Found: 491.2179.



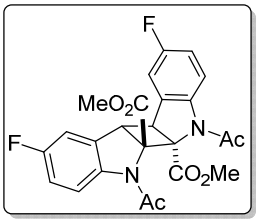
dimethyl-5,6-diacetyl-2,9-dimethoxy-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2d), white solid, 36 hours, 89.8 mg, 90% yield, m.p. = 210-212 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 9.0 Hz, 1H), 7.25 (s, 1H), 6.91 – 6.78 (m, 3H), 6.71 (d, *J* = 2.4 Hz, 1H), 4.03 (d, *J* = 5.6 Hz, 1H), 3.91 (d, *J* = 5.2 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.66 (s, 6H), 2.53 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 169.1, 168.3, 167.1, 156.5, 156.3, 139.2, 136.1, 133.1, 130.4, 119.2, 114.9, 113.5, 113.1, 110.8, 109.2, 73.5, 72.5, 55.7, 55.7, 53.2, 53.0, 52.9, 50.8, 25.2, 24.6. **IR** (thin film): ν_{max}/cm^{-1} = 3007, 2946, 2844, 1737, 1654, 1482, 1379, 1339, 1254, 1134, 1017, 935, 867, 804. **HRMS (ESI)** calcd for $C_{26}H_{26}N_2O_8Na$ $[M+Na]^+$: 517.1581, Found: 517.1574.



dimethyl-5,6-diacetyl-2,9-dimethyl-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2e), white solid, 48 hours, 86.1 mg, 92% yield, m.p. = 217-219 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.07 (m, 3H), 6.99 (s, 1H), 4.01 (d, *J* = 5.2 Hz, 1H), 3.89 (d, *J* = 5.2 Hz, 1H), 3.64 (s, 6H), 2.55 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 169.5, 168.4, 167.2, 143.2, 140.3, 133.9, 133.5, 131.9, 129.52, 129.45, 129.3, 125.4, 123.4, 118.2, 113.9, 73.4, 72.5, 53.5, 53.0, 52.9, 50.9, 25.4, 24.7, 20.8, 20.6. **IR** (thin film): ν_{max} (cm^{-1}) = 3007, 2946, 1741, 1658, 1484, 1435, 1377, 1336, 1215, 1150, 1111, 1013, 889, 813. **HRMS (ESI)** calcd for $C_{26}H_{27}N_2O_6$ $[M+H]^+$: 463.1864, Found: 463.1862.

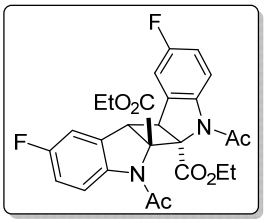


dimethyl-5,6-diacetyl-2,9-bis((trimethylsilyl)ethynyl)-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2f), yellow solid, 48 hours, 97.2 mg, 79% yield, m.p. = 263-265 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.33 (m, 3H), 7.28 (s, 2H), 3.97 (d, *J* = 5.2 Hz, 1H), 3.86 (d, *J* = 5.2 Hz, 1H), 3.63 (s, 6H), 2.55 (s, 3H), 2.40 (s, 3H), 0.27 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 169.6, 168.0, 166.8, 145.4, 142.3, 133.3, 133.1, 131.7, 129.1, 128.4, 126.5, 118.9, 118.5, 118.2, 113.8, 104.6, 103.7, 94.8, 93.7, 73.4, 72.7, 53.1, 50.4, 25.5, 24.7, -0.1. **IR** (thin film): ν_{max}/cm^{-1} = 3396, 2957, 2148, 1741, 1662, 1481, 1435, 1377, 1334, 1236, 1105, 1017, 841. **HRMS (ESI)** calcd for $C_{34}H_{39}N_2O_6Si_2$ $[M+H]^+$: 627.2341, Found: 627.2339.

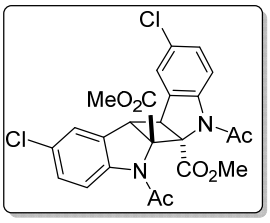


dimethyl-5,6-diacetyl-2,9-difluoro-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2g), yellow solid, 48 hours, 87.1 mg, 93% yield, m.p. = 228-229 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.12 – 6.93 (m, 3H), 6.87 (d, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 5.2 Hz, 1H), 3.94 (d, *J* = 5.6 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 2.55 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 169.3, 168.1, 166.9, 159.2 (d, *J* = 245.0 Hz), 159.1 (d, *J* = 241.0 Hz), 141.6, 138.7, 133.1 (d, *J* = 9.0 Hz), 130.3 (d, *J* = 245.0 Hz), 119.5 (d, *J* = 7.0 Hz), 115.5 (dd, *J* = 24.0, 18.0 Hz), 115.0 (d, *J* = 9.0 Hz), 114.9, 112.3 (d, *J* = 24.0 Hz), 110.1 (d, *J* = 24.0 Hz), 73.8, 72.8, 53.2, 53.1, 52.8, 50.3, 25.3, 24.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.57 ~ -118.70 (m, 1F), -118.71 ~ -118.90 (m, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 3014, 2948, 2323, 2103, 1741, 1666, 1612, 1479, 1441, 1376,

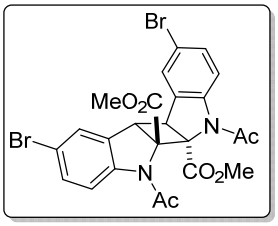
1333, 1244, 1212, 1119, 1013, 947, 873, 816. **HRMS (ESI)** calcd for $C_{24}H_{20}N_2O_6F_2Na$ $[M+Na]^+$: 493.1182, Found: 493.1174.



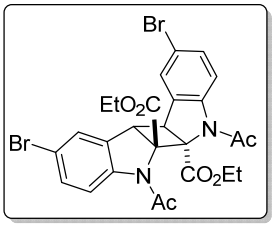
diethyl-5,6-diacetyl-2,9-difluoro-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2h), yellow solid, 48 hours, 83.1 mg, 83% yield, m.p. = 177-179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.10 – 6.94 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 1H), 4.25 – 4.12 (m, 2H), 4.13 – 4.01 (m, 3H), 3.92 (d, *J* = 5.2 Hz, 1H), 2.54 (s, 3H), 2.45 (s, 3H), 1.21 (t, *J* = 6.8 Hz, 3H), 1.16 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 169.2, 167.8, 166.5, 160.4, 158.0, 141.7, 138.9, 133.1 (d, *J* = 9.0 Hz), 130.4, 119.5 (d, *J* = 7.0 Hz), 115.6, 115.4 (d, *J* = 7.0 Hz), 115.2, 114.9 (d, *J* = 7.0 Hz), 112.3 (d, *J* = 23.0 Hz), 110.1 (d, *J* = 24.0 Hz), 74.2, 73.0, 62.6, 62.4, 53.0, 50.5, 25.4, 24.9, 13.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.69 ~ -119.04 (m, 2F). **IR** (thin film): ν_{max}/cm^{-1} = 2986, 1739, 1664, 1479, 1376, 1335, 1246, 1214, 1118, 1018, 949, 871, 816. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O_6F_2Na$ $[M+Na]^+$: 521.1495, Found: 521.1487.



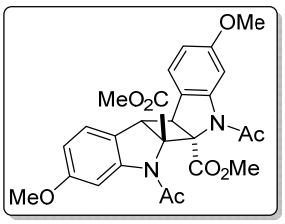
dimethyl-5,6-diacetyl-2,9-dichloro-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2i), yellow solid, 48 hours, 80.2 mg, 79% yield, m.p. = 237-239 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.8 Hz, 1H), 7.37 – 7.23 (m, 4H), 7.14 (s, 1H), 4.04 (d, *J* = 5.2 Hz, 1H), 3.92 (d, *J* = 5.2 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.55 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 169.5, 168.0, 166.8, 144.1, 141.2, 133.1, 130.5, 129.1, 128.6, 125.2, 123.1, 119.5, 115.0, 73.6, 72.7, 53.2, 53.1, 52.9, 50.3, 25.4, 24.7. **IR** (thin film): ν_{max}/cm^{-1} = 2953, 1726, 1668, 1471, 1374, 1328, 1249, 1200, 1011, 886, 816. **HRMS (ESI)** calcd for $C_{24}H_{20}N_2O_6Cl_2Na$ $[M+Na]^+$: 525.0591, Found: 525.0579.



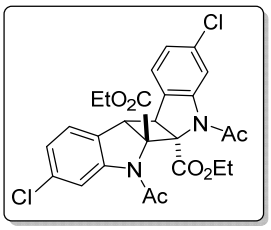
dimethyl-5,6-diacetyl-2,9-dibromo-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2j), yellow solid, 48 hours, 72.3 mg, 61% yield, m.p. = 233-234 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.28 (s, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 4.04 (d, *J* = 5.2 Hz, 1H), 3.93 (d, *J* = 5.2 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 169.5, 167.9, 166.7, 144.6, 141.7, 133.5, 132.1, 130.9, 128.0, 126.0, 120.0, 116.5, 116.0, 115.5, 73.5, 72.7, 53.2, 53.1, 52.9, 50.3, 25.4, 24.7. **IR** (thin film): ν_{max}/cm^{-1} = 2955, 2644, 2317, 1739, 1665, 1469, 1374, 1330, 1240, 1193, 1109, 1009, 890, 813. **HRMS (ESI)** calcd for $C_{24}H_{20}N_2O_6Br_2Na$ $[M+Na]^+$: 612.9580, Found: 612.9568.



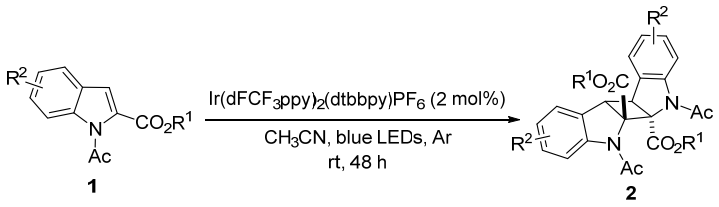
diethyl-5,6-diacetyl-2,9-dibromo-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2k), yellow solid, 48 hours, 78.5 mg, 63% yield, m.p. = 180-182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.37 (m, 3H), 7.29 (s, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 4.24 – 4.12 (m, 2H), 4.12 – 4.01 (m, 3H), 3.91 (d, *J* = 5.2 Hz, 1H), 2.53 (s, 3H), 2.43 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 169.3, 167.6, 166.4, 144.7, 141.9, 133.4, 132.0, 131.0, 128.0, 126.0, 119.9, 116.4, 116.0, 115.4, 73.9, 72.9, 62.6, 62.5, 53.0, 50.4, 25.5, 25.0, 13.7. **IR** (thin film): ν_{max}/cm^{-1} = 3063, 2983, 2932, 2245, 1724, 1661, 1469, 1372, 1330, 1250, 1197, 1104, 1016, 913, 872, 812. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O_6Br_2Na$ $[M+Na]^+$: 640.9893, Found: 640.9878.



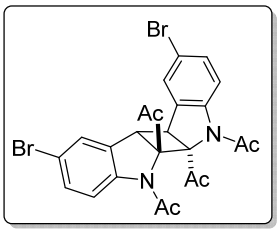
dimethyl-5,6-diacetyl-3,8-dimethoxy-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2m), white solid, 26 hours, 84.8 mg, 86% yield, m.p. = 227-229 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.19 – 6.89 (m, 3H), 6.63 (t, *J* = 8.8 Hz, 2H), 3.94 (d, *J* = 5.2 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 4H), 3.65 (s, 3H), 3.65 (s, 3H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 169.6, 168.4, 167.3, 160.6, 160.5, 146.8, 143.7, 125.2, 124.1, 123.1, 121.2, 110.3, 107.7, 104.1, 102.5, 73.9, 73.3, 55.7, 55.4, 53.4, 53.0, 52.8, 50.7, 25.4, 24.8. **IR** (thin film): ν_{max}/cm^{-1} = 2961, 2840, 1734, 1661, 1603, 1495, 1438, 1377, 1311, 1222, 1172, 1105, 1009, 932, 865, 811. **HRMS (ESI)** calcd for $C_{26}H_{27}N_2O_8$ $[M+H]^+$: 495.1762, Found: 495.1760.



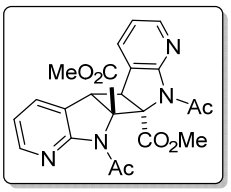
diethyl-5,6-diacetyl-3,8-dichloro-5,6,10b,10c-tetrahydrocyclobuta[1,2-b:4,3-b']diindole-5a,5b-dicarboxylate (2n), yellow solid, 48 hours, 77.7 mg, 72% yield, m.p. = 214-217 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.32 (s, 1H), 7.22 – 7.02 (m, 4H), 4.17 (s, 2H), 4.13 – 4.01 (m, 2H), 3.98 (s, 1H), 3.87 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H), 1.18 (t, *J* = 8.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 169.4, 167.6, 166.5, 146.5, 143.8, 135.0, 129.9, 127.4, 125.6, 123.9, 123.6, 118.8, 114.7, 74.1, 73.2, 62.6, 62.4, 53.2, 50.5, 25.6, 25.0, 13.7. **IR** (thin film): ν_{max}/cm^{-1} = 3099, 2946, 1740, 1663, 1596, 1474, 1373, 1324, 1237, 1199, 1146, 1103, 1018, 883, 827. **HRMS (ESI)** calcd for $C_{26}H_{24}N_2O_6Cl_2Na$ $[M+Na]^+$: 553.0904, Found: 553.0896.



A flame-dried sealed tube were added indole derivative **1** (0.4 mmol, 1.0 equiv), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (8.9 mg, 0.008 mmol), and CH_3CN (4 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from two 24 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under argon atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatograph ($EtOAc/CH_2Cl_2$ = 8/1) to afford the desired product **2l, 2o**. The analytical data of the products are summarized below.

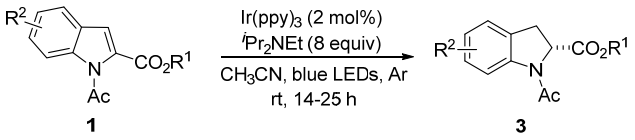


1,1',1'',1'''-(2,9-dibromo-10b,10c-dihydrocyclobuta[1,2-b:4,3-b']diindole-5,5a,5b,6-tetrayl)tetrakis(ethan-1-one) (2l), yellow solid, 48 hours, 51.4 mg, 46% yield, m.p. = 218-220 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.8 Hz, 1H), 7.52 – 7.34 (m, 4H), 7.25 (d, *J* = 9.2 Hz, 1H), 3.82 (d, *J* = 4.0 Hz, 1H), 3.75 (d, *J* = 4.0 Hz, 1H), 2.60 (s, 3H), 2.26 (s, 3H), 2.01 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.2, 198.7, 171.1, 169.7, 144.7, 141.5, 133.9, 132.6, 132.5, 131.2, 128.6, 126.6, 120.3, 116.6, 116.4, 115.6, 75.4, 75.0, 52.7, 48.9, 25.4, 24.8, 24.4, 24.0. **IR** (thin film): ν_{max}/cm^{-1} = 3128, 3081, 2922, 2323, 2110, 1723, 1663, 1471, 1430, 1374, 1328, 1258, 1184, 1079, 1028, 968, 900, 830. **HRMS (ESI)** calcd for $C_{24}H_{20}N_2O_4NaBr_2$ $[M+Na]^+$: 580.9682, Found: 580.9672.

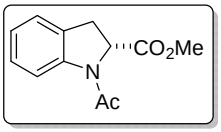


2o, white solid, 48 hours, 34.4 mg, 40% yield, m.p. = 260-262 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.54 (dd, *J* = 7.2, 1.6 Hz, 2H), 6.96 (dd, *J* = 7.2, 4.8 Hz, 2H), 3.81 (s, 2H), 3.58 (s, 6H), 2.79 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 167.7, 157.2, 148.1, 133.2, 123.9, 117.9, 69.7, 52.5, 48.5, 25.6. **IR** (thin film): ν_{max}/cm^{-1} = 2947, 1741, 1664, 1589, 1420, 1375, 1323, 1234, 1025, 898. **HRMS (ESI)** calcd for $C_{22}H_{20}N_4O_6Na$ $[M+Na]^+$: 459.1275, Found: 459.1275.

5.2 General Procedure for Visible-Light Induced Reduction of Indole Derivatives

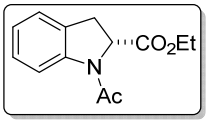


A flame-dried sealed tube were added indole derivative **1** (0.3 mmol, 1.0 equiv), $Ir(ppy)_3$ (3.9 mg, 0.006 mmol), N,N-diisopropylethylamine ($^iPr_2NEt$, 2.4 mmol), and CH_3CN (3 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from two 24 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under argon atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatograph (PE/EtOAc = 2/1) to afford the desired product **3**. The analytical data of the products are summarized below. Two rotamers were observed by NMR for all compounds except **3q** and **3r** at room temperature.

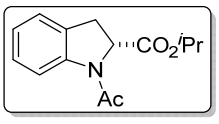


methyl 1-acetylindoline-2-carboxylate (3a), white solid, 24 hours, 35.5 mg, 80% yield, m.p. = 104-106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 and 7.17 (m, 3H), 7.02

(t, *J* = 7.6 Hz, 1H), 5.16 and 4.91 (a pair of d, *J* = 11.2 Hz, 1H), 3.76 and 3.73 (a pair of s, 3H), 3.61 and 3.47 (a pair of dd, *J* = 16.4, 11.2 Hz, 1H), 3.26 and 3.10 (a pair of d, *J* = 16.4 Hz, 1H), 2.48 and 2.16 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 168.8, 168.3, 142.5, 141.1, 130.7, 128.3, 127.8, 127.7, 125.6, 124.1, 123.9, 123.3, 117.2, 113.7, 61.2, 60.1, 52.8, 52.3, 33.4, 31.3, 24.4, 23.6. **^{1}H NMR** (600 MHz, DMSO-*d*$_6$, 110 °C) δ 7.86 (s, 1H), 7.24 – 7.16 (m, 2H), 7.04 – 6.99 (m, 1H), 5.18 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.72 (s, 3H), 3.59 (dd, *J* = 16.8, 11.4 Hz, 1H), 3.17 (d, *J* = 16.2 Hz, 1H), 2.19 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-*d*$_6$, 110 °C) δ 171.2, 167.8, 141.9, 129.1, 126.7, 124.1, 122.7, 115.0, 60.1, 51.7, 31.9, 22.8. **HRMS** data for the desired product were in agreement with the previously reported literature data[2].

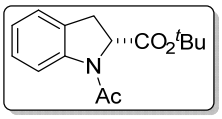


ethyl 1-acetylindoline-2-carboxylate (3b), white solid, 25 hours, 43.6 mg, 59% yield, m.p. = 58-60 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 and 7.28-7.13 (m, 3H), 7.06 – 6.97 (m, 1H), 5.13 and 4.88 (a pair of d, *J* = 11.2 Hz, 1H), 4.28 – 4.14 (m, 2H), 3.61 and 3.47 (a pair of dd, *J* = 16.8, 11.2 Hz, 1H), 3.25 and 3.08 (a pair of d, *J* = 16.4 Hz, 1H), 2.48 and 2.16 (a pair of s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 168.9, 168.3, 142.6, 141.2, 130.7, 128.3, 127.8, 127.7, 125.6, 124.1, 123.9, 123.3, 117.2, 113.7, 62.0, 61.3, 60.2, 33.5, 31.4, 24.5, 23.6, 14.0. **IR** (thin film): ν_{max}/cm^{-1} = 2982, 2929, 1725, 1660, 1596, 1474, 1397, 1333, 1273, 1198, 1020, 937, 873. **HRMS** data for the desired product were in agreement with the previously reported literature data[4].

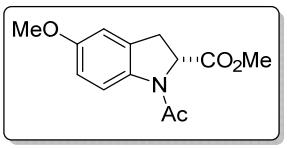


isopropyl 1-acetylindoline-2-carboxylate (3c), yellow solid, 19 hours, 41.5 mg, 56% yield, m.p. = 80-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 and 7.25 – 7.12 (m, 3H), 7.02 (t, *J* = 8.4 Hz, 1H), 5.11 – 4.85 (m, 2H), 3.61 and 3.47 (a pair of dd, *J* = 16.8, 11.2 Hz, 1H), 3.22 and 3.05 (a pair of dd, *J* = 16.8, 4.0 Hz, 1H), 2.48 and 2.16 (a pair of s, 3H), 1.26 and 1.23 (a pair of d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 168.8, 168.3, 142.7, 130.7, 128.3, 127.8, 125.6, 124.1, 123.8, 123.2, 117.2,

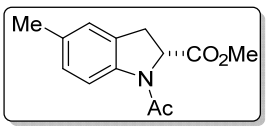
113.6, 69.7, 68.8, 61.4, 60.4, 33.4, 31.3, 29.6, 24.5, 23.6, 21.6. **IR** (thin film): ν_{max}/cm^{-1} = 3041, 2979, 2927, 2863, 1727, 1664, 1597, 1473, 1386, 1266, 1203, 1101, 1038, 1003, 936, 856, 822. **HRMS (ESI)** calcd for $C_{14}H_{17}NO_3Na$ $[M+Na]^+$: 270.1100, Found: 270.1099.



tert-butyl 1-acetylindoline-2-carboxylate (3d), white solid, 25 hours, 42.0 mg, 54% yield, m.p. = 102-105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 and 7.24 – 7.12 (m, 3H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.02 and 4.77 (a pair of d, *J* = 11.2 Hz, 1H), 3.59 and 3.45 (a pair of dd, *J* = 16.0, 11.2 Hz, 1H), 3.19 and 3.03 (a pair of d, *J* = 16.0 Hz, 1H), 2.48 and 2.16 (a pair of s, 3H), 1.46 (s, 9H). **^{13}C NMR** and **HRMS** data for the desired product were in agreement with the previously reported literature data[3].

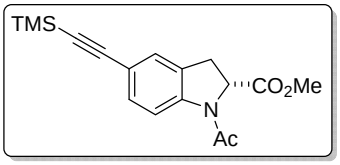


methyl 1-acetyl-5-methoxyindoline-2-carboxylate (3e), yellow solid, 14 hours, 50.8 mg, 69% yield, m.p. = 156-157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 and 7.09 (a pair of d, *J* = 8.8 Hz, 1H), 6.79 – 6.70 (m, 2H), 5.17 and 4.90 (a pair of dd, *J* = 10.8, 3.6 Hz, 1H), 3.77 and 3.73 (a pair of s, 3H), 3.76 (s, 3H), 3.59 and 3.45 (a pair of dd, *J* = 16.4, 10.8 Hz, 1H), 3.23 and 3.07 (a pair of dd, *J* = 16.4, 3.2 Hz, 1H), 2.44 and 2.14 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 168.2, 167.9, 156.4, 156.1, 136.2, 134.8, 132.4, 129.9, 117.8, 114.4, 112.5, 112.2, 111.7, 110.4, 61.5, 60.3, 55.6, 55.5, 52.9, 52.4, 33.5, 31.6, 24.1, 23.3. **IR** (thin film): ν_{max}/cm^{-1} = 3082, 3003, 2949, 2843, 1729, 1648, 1604, 1486, 1451, 1398, 1348, 1269, 1188, 1102, 1013, 922, 883, 816. **HRMS (ESI)** calcd for $C_{13}H_{15}NO_4Na$ $[M+Na]^+$: 272.0893, Found: 272.0891.

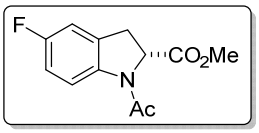


methyl 1-acetyl-5-methylindoline-2-carboxylate (3f), yellow solid, 19 hours, 40.1 mg, 57% yield, m.p. = 96-98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 and 7.09 – 6.94

(m, 3H), 5.15 and 4.89 (a pair of dd, *J* = 11.2, 3.6 Hz, 1H), 3.75 and 3.72 (a pair of s, 3H), 3.58 and 3.43 (a pair of dd, *J* = 16.0, 10.8 Hz, 1H), 3.22 and 3.05 (a pair of dd, *J* = 16.8, 3.2 Hz, 1H), 2.45 and 2.15 (a pair of s, 3H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 168.5, 168.2, 140.2, 138.9, 133.6, 133.1, 130.9, 128.4, 128.3, 128.1, 126.3, 124.8, 116.9, 113.5, 61.4, 60.2, 52.8, 52.4, 33.4, 31.4, 24.3, 23.5, 20.9, 20.6. **IR** (thin film): ν_{max}/cm^{-1} = 2918, 2857, 1731, 1657, 1485, 1434, 1389, 1343, 1265, 1202, 1004, 916, 816. **HRMS (ESI)** calcd for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.0944, Found: 256.0942.

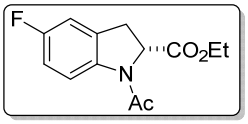


methyl 1-acetyl-5-((trimethylsilyl)ethynyl)indoline-2-carboxylate (3g), yellow solid, 19 hours, 66.2 mg, 74% yield, m.p. = 157-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 and 7.37 – 7.08 (m, 3H), 5.14 and 4.90 (a pair of d, *J* = 10.4 Hz, 1H), 3.76 and 3.73 (a pair of s, 3H), 3.56 and 3.43 (a pair of dd, *J* = 16.4, 11.2 Hz, 1H), 3.21 and 3.05 (a pair of d, *J* = 16.4 Hz, 1H), 2.46 and 2.15 (a pair of s, 3H), 0.23 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 168.8, 168.3, 142.6, 141.1, 132.1, 131.9, 130.9, 129.0, 128.5, 127.6, 118.4, 118.0, 116.8, 113.3, 104.9, 104.4, 93.9, 93.3, 61.4, 60.3, 52.9, 52.4, 33.1, 31.0, 29.6, 24.5, 23.6, -0.1. **IR** (thin film): ν_{max}/cm^{-1} = 2957, 2147, 1746, 1666, 1610, 1481, 1436, 1379, 1344, 1255, 1198, 1012, 925, 840. **HRMS (ESI)** calcd for $C_{17}H_{22}NO_3Si$ $[M+H]^+$: 316.1364, Found: 316.1354.

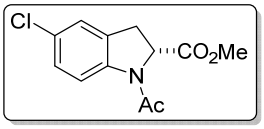


methyl 1-acetyl-5-fluoroindoline-2-carboxylate (3h), white solid, 17 hours, 49.5 mg, 70% yield, m.p. = 106-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 and 7.14 – 6.80 (m, 3H), 5.19 and 4.94 (a pair of dd, *J* = 10.8, 1.6 Hz, 1H), 3.78 and 3.73 (a pair of s, 3H), 3.60 and 3.46 (a pair of dd, *J* = 16.8, 10.8 Hz, 1H), 3.25 and 3.08 (a pair of dd, *J* = 16.0, 2.4 Hz, 1H), 2.45 and 2.15 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 168.5, 168.0, 159.3 (d, *J* = 241.0 Hz), 138.6, 137.4, 132.9 (d, *J* = 8.0 Hz), 130.3 (d, *J* = 9.0 Hz), 118.0 (d, *J* = 8.0 Hz), 114.3 (d, *J* = 9.0 Hz), 114.0 (d, *J* = 23.0

Hz), 113.0 (d, J = 25.0 Hz), 111.5 (d, J = 24.0 Hz), 61.5, 60.5, 52.9, 52.4, 33.2, 31.3, 24.1, 23.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.97 and -120.04 (a pair of s, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 3074, 2954, 2854, 1732, 1661, 1604, 1478, 1445, 1394, 1349, 1215, 1177, 1132, 1039, 1003, 932, 891, 823. **HRMS (ESI)** calcd for $C_{12}H_{12}NO_3FNa$ $[M+Na]^+$: 260.0693, Found: 260.0688.

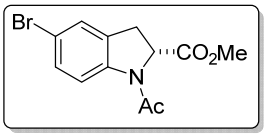


ethyl 1-acetyl-5-fluoroindoline-2-carboxylate (3i), yellow solid, 17 hours, 55.6 mg, 73% yield, m.p. = 103-104 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 and 7.14 – 6.81 (m, 3H), 5.16 and 4.91 (a pair of d, J = 10.0 Hz, 1H), 4.32 – 4.15 (m, 2H), 3.59 and 3.46 (a pair of dd, J = 16.4, 11.2 Hz, 1H), 3.23 and 3.06 (a pair of d, J = 16.4 Hz, 1H), 2.45 and 2.15 (a pair of s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.5, 167.9, 159.3 (d, J = 241.0 Hz), 138.7, 137.4, 132.93, 132.86, 130.4, 130.3, 117.9 (d, J = 7.0 Hz), 114.2 (d, J = 9.0 Hz), 113.9 (d, J = 23.0 Hz), 113.0 (d, J = 24.0 Hz), 111.4 (d, J = 24.0 Hz), 62.0, 61.5, 61.3, 60.5, 33.2, 31.3, 24.1, 23.3, 13.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.11 (q, J = 14.6 Hz) and -120.22 (1F). **IR** (thin film): ν_{max}/cm^{-1} = 3071, 2981, 1727, 1660, 1604, 1476, 1390, 1251, 1208, 1176, 1133, 1016, 932, 890, 818. **HRMS (ESI)** calcd for $C_{13}H_{14}NO_3FNa$ $[M+Na]^+$: 274.0850, Found: 274.0848.

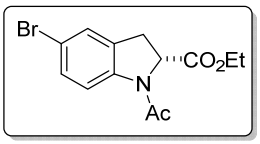


methyl 1-acetyl-5-chloroindoline-2-carboxylate (3j), yellow solid, 17 hours, 53.8 mg, 71% yield, m.p. = 128-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 and 7.22 – 7.06 (m, 3H), 5.16 and 4.92 (a pair of d, J = 10.0 Hz, 1H), 3.77 and 3.73 (a pair of s, 3H), 3.58 and 3.45 (a pair of dd, J = 16.4, 11.2 Hz, 1H), 3.23 and 3.07 (a pair of d, J = 16.4 Hz, 1H), 2.45 and 2.15 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 168.8, 168.1, 141.2, 139.9, 132.7, 130.3, 128.7, 128.5, 127.7, 125.8, 124.3, 118.0, 114.4, 61.4, 60.3, 52.9, 52.5, 33.1, 31.1, 24.3, 23.4. **IR** (thin film): ν_{max}/cm^{-1} = 3078, 2950, 2851, 2307, 2063, 1789, 1727, 1662, 1592, 1463, 1384, 1346, 1215, 1166, 1072,

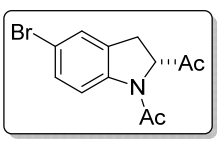
1001, 891, 824. **HRMS (ESI)** calcd for $C_{12}H_{12}NO_3ClNa$ $[M+Na]^+$: 276.0398, Found: 276.0395.



methyl 1-acetyl-5-bromoindoline-2-carboxylate (3k), yellow solid, 14 hours, 68.5 mg, 77% yield, m.p. = 120-122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 and 7.35 – 6.98 (m, 3H), 5.15 and 4.91 (a pair of d, *J* = 10.8 Hz, 1H), 3.76 and 3.73 (a pair of s, 3H), 3.58 and 3.45 (a pair of dd, *J* = 17.2, 12.4 Hz, 1H), 3.23 and 3.07 (a pair of d, *J* = 16.4 Hz, 1H), 2.44 and 2.14 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 168.8, 168.1, 141.7, 140.4, 133.1, 130.7, 128.7, 127.2, 118.5, 116.3, 114.9, 61.3, 60.3, 52.9, 52.4, 33.0, 31.1, 24.3, 23.4. **IR** (thin film): ν_{max}/m^{-1} = 3080, 2945, 1732, 1661, 1590, 1469, 1384, 1343, 1203, 1169, 1064, 1003, 931, 860, 817. **HRMS (ESI)** calcd for $C_{12}H_{12}NO_3BrNa$ $[M+Na]^+$: 319.9893, Found: 319.9887.

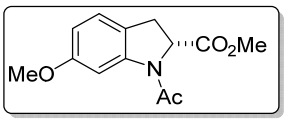


ethyl 1-acetyl-5-bromoindoline-2-carboxylate (3l), yellow solid, 14 hours, 76.3 mg, 81% yield, m.p. = 86-88 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 and 7.33 – 6.99 (m, 3H), 5.12 and 4.88 (a pair of d, *J* = 11.2 Hz, 1H), 4.30 – 4.14 (m, 2H), 3.58 and 3.45 (a pair of dd, *J* = 16.8, 11.6 Hz, 1H), 3.22 and 3.06 (a pair of d, *J* = 16.8 Hz, 1H), 2.44 and 2.14 (a pair of s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 168.8, 141.7, 130.7, 130.6, 128.6, 127.2, 118.4, 116.1, 114.8, 62.1, 61.3, 60.4, 33.0, 31.0, 24.3, 23.4, 14.0. **IR** (thin film): ν_{max}/cm^{-1} = 3081, 2983, 2929, 1717, 1665, 1592, 1466, 1380, 1336, 1238, 1205, 1168, 1120, 1016, 933, 863, 821. **HRMS (ESI)** calcd for $C_{13}H_{14}NO_3BrNa$ $[M+Na]^+$: 334.0049, Found: 334.0041.

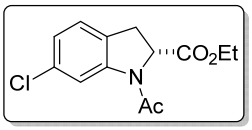


1,1'-(5-bromoindoline-1,2-diyl)bis(ethan-1-one) (3m), yellow solid, 16 hours, 32.9 mg, 39% yield, m.p. = 160-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 and 7.05 (a

pair of d, *J* = 8.8 Hz, 1H), 7.38 – 7.29 (m, 2H), 5.16 and 4.86 (a pair of dd, *J* = 11.6, 2.8 Hz, 1H), 3.64 and 3.39 (a pair of dd, *J* =16.8, 11.6 Hz, 1H), 3.06 and 3.00 (a pair of d, *J* = 17.2 Hz, 1H), 2.46 and 2.22 (a pair of s, 3H), 2.18 and 2.07 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.8, 204.6, 168.7, 168.3, 141.9, 140.5, 133.3, 131.1, 130.7, 130.4, 128.9, 127.4, 118.6, 116.5, 116.1, 115.1, 68.1, 66.4, 32.0, 29.8, 26.4, 25.1, 24.2, 23.7. **IR** (thin film): ν_{max}/cm^{-1} = 3063, 2993, 2852, 1714, 1645, 1469, 1380, 1255, 1146, 1033, 984, 930, 826. **HRMS (ESI)** calcd for $C_{12}H_{12}NO_2BrNa$ $[M+Na]^+$: 303.9944, Found: 303.9937.

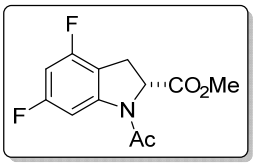


methyl 1-acetyl-6-methoxyindoline-2-carboxylate (3n), yellow solid, 14 hours, 23.5 mg, 32% yield, m.p. = 97-99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 and 7.12 – 6.53 (m, 3H), 5.16 and 4.92 (a pair of d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 3.77 and 3.73 (a pair of s, 3H), 3.55 and 3.40 (a pair of dd, *J* = 16.4, 11.2 Hz, 1H), 3.19 and 3.02 (a pair of d, *J* = 16.0 Hz, 1H), 2.47 and 2.16 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 168.9, 168.4, 159.6, 143.7, 142.2, 125.8, 124.3, 122.8, 120.1, 110.3, 107.3, 103.2, 102.0, 62.1, 60.9, 55.5, 52.9, 52.4, 32.8, 30.7, 29.6, 24.4, 23.7. **IR** (thin film): ν_{max}/cm^{-1} = 2947, 2845, 1728, 1658, 1600, 1495, 1443, 1402, 1338, 1278, 1196, 1094, 1016, 945, 895, 849, 806. **HRMS (ESI)** calcd for $C_{13}H_{15}NO_4Na$ $[M+Na]^+$: 272.0893, Found: 272.0890.

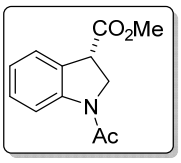


ethyl 1-acetyl-6-chloroindoline-2-carboxylate (3o), yellow solid, 25 hours, 52.0 mg, 65% yield, m.p. = 128-129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 and 7.23 – 6.96 (m, 3H), 5.14 and 4.91 (a pair of d, *J* = 10.4 Hz, 1H), 4.31 – 4.15 (m, 2H), 3.56 and 3.42 (a pair of dd, *J* = 16.8, 11.2 Hz, 1H), 3.21 and 3.04 (a pair of d, *J* = 16.4 Hz, 1H), 2.47 and 2.15 (a pair of s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.9, 168.1, 143.6, 133.4, 126.9, 126.3, 124.8, 123.8, 123.2, 117.5, 114.1, 62.1, 61.8, 61.4, 60.7, 33.0, 30.9, 24.5, 23.5, 14.0. **IR** (thin film): ν_{max}/cm^{-1} = 2985,

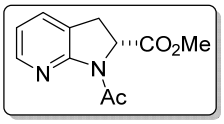
2924, 1725, 1658, 1594, 1474, 1397, 1273, 1202, 1137, 1069, 1023, 940, 862. **HRMS (ESI)** calcd for $C_{13}H_{14}NO_3ClNa$ $[M+Na]^+$: 290.0554, Found: 290.0555.



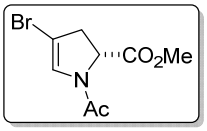
methyl 1-acetyl-4,6-difluoroindoline-2-carboxylate (3p), white solid, 25 hours, 49.3 mg, 65% yield, m.p. = 97-99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 and 6.79 – 6.45 (m, 2H), 5.19 and 4.99 (a pair of d, *J* = 10.8 Hz, 1H), 3.80 and 3.76 (a pair of s, 3H), 3.53 and 3.40 (a pair of dd, *J* = 16.0, 12.0 Hz, 1H), 3.29 and 3.09 (a pair of d, *J* = 16.4 Hz, 1H), 2.46 and 2.16 (a pair of s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 169.0, 168.2, 163.1 (dd, *J* = 243.0, 12.0 Hz), 157.8 (dd, *J* = 248.0, 15.0 Hz), 145.0, 110.2 (d, *J* = 24.0 Hz), 101.8, 101.5, 99.2, 98.9, 98.7, 98.2, 62.0, 61.0, 53.1, 52.6, 29.4, 27.1, 24.3, 23.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.21 and -109.53 (a pair of s, 1F), -113.55 and -115.79 (a pair of s, 1F). **IR** (thin film): ν_{max}/cm^{-1} = 3079, 2969, 1737, 1669, 1625, 1489, 1441, 1391, 1315, 1213, 1170, 1005, 975, 896, 842. **HRMS (ESI)** calcd for $C_{12}H_{11}NO_3F_2Na$ $[M+Na]^+$: 278.0599, Found: 278.0594.



methyl 1-acetylindoline-3-carboxylate (3q), yellow solid, 24 hours, 50.9 mg, 76% yield, m.p. = 120-121 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.22 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.50 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.28 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.14 (t, *J* = 10.4 Hz, 1H), 3.78 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 168.4, 142.4, 129.0, 127.6, 124.9, 123.6, 117.0, 52.7, 50.6, 45.1, 24.1. **IR** (thin film): ν_{max}/cm^{-1} = 2918, 1722, 1657, 1596, 1475, 1398, 1323, 1273, 1175, 1021, 930, 884, 848. **HRMS** data for the desired product were in agreement with the previously reported literature data[5].

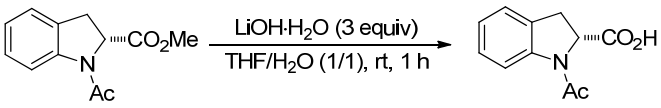


methyl 1-acetyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridine-2-carboxylate (3r), yellow oil, 25 hours, 42.0 mg, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 5.2 Hz, 1H), 7.45 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.91 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.07 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.75 (s, 3H), 3.43 (dd, *J* = 17.2, 11.6 Hz, 1H), 3.05 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 170.1, 155.4, 146.6, 133.3, 123.2, 118.2, 57.9, 52.5, 29.0, 24.6. **IR** (thin film): ν_{max}/cm^{-1} = 2951, 1745, 1660, 1593, 1422, 1376, 1322, 1236, 1197, 1009, 855. **HRMS (ESI)** calcd for $C_{11}H_{13}N_2O_3$ $[M+H]^+$: 221.0921, Found: 221.0916.



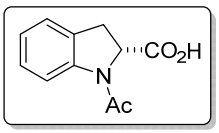
methyl 1-acetyl-4-bromo-2,3-dihydro-1H-pyrrole-2-carboxylate (3s), yellow oil, 17 hours, 40.1 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.99 and 5.96 (a pair of s, 1H), 5.13 – 5.09 and 5.07 – 5.04 (a pair of m, 1H), 4.55 – 4.33 (m, 2H), 3.78 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 168.3, 125.1, 124.0, 117.4, 67.1, 66.0, 58.3, 57.7, 53.0, 52.6, 21.6, 21.1. **IR** (thin film): ν_{max}/cm^{-1} = 3057, 2919, 2857, 1747, 1648, 1408, 1331, 1251, 1196, 1046, 997, 954, 863, 830. **HRMS (ESI)** calcd for $C_8H_{10}NO_3BrNa$ $[M+Na]^+$: 269.9736, Found: 269.9733.

6. Transformation of 3a



3a, 0.4 mmol **5**, 77% yield

A solution of compound 3a (87.7 mg, 0.4 mmol) in THF (1 mL) was slowly added to a solution of $LiOH·H_2O$ (50.4 mg, 1.2 mmol) in water (1 mL). The resulting mixture was vigorously stirred at room temperature for 1 h. THF was then evaporated under reduced pressure and the resulting aqueous solution was acidified with 2M HCl (pH = 6) until the amount of solid cristallized from the solvent. After filtration, product **5** was obtained as a white solid (63.3 mg, 77% yield).

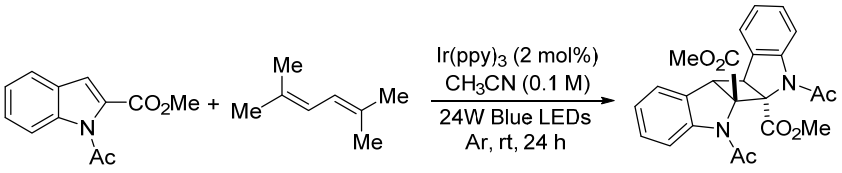


1-acetylindoline-2-carboxylic acid (5), white solid, 63.3 mg, 77% yield, m.p. = 177-178 °C. **^{1}H NMR** (600 MHz, DMSO-d_6, 110 °C) δ 7.88 (s, 1H), 7.22 – 7.12 (m, 2H), 6.97 (t, J = 4.8 Hz, 1H), 5.04 (dd, J = 7.2, 1.2 Hz, 1H), 3.55 (dd, J = 10.8, 7.6 Hz, 1H), 3.14 (d, J = 11.2 Hz, 1H), 2.15 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6, 110 °C) δ 172.1, 167.9, 142.1, 129.2, 126.6, 124.0, 122.6, 115.1, 60.3, 32.1, 22.8. **IR** (thin film): ν_{max}/cm^{-1} = 2801, 2670, 2502, 2118, 1720, 1615, 1576, 1480, 1406, 1322, 1209, 1093, 1034, 931, 834. **HRMS** data for the desired product were in agreement with the previously reported literature data[6].

7. Mechanistic Studies

7.1 Control Experiment with Triplet Quencher

2,5-Dimethylhexa-2,4-diene is known as a triplet quencher.[2] The model reaction **1a** → **2a** are significantly inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.



1a **4** **2a**, < 5% yield

Conclusion of this experiment: This experiment supports the involvement of excited triplet state intermediates.

7.2 Stern-Volmer Luminescence Quenching Studies

Stern-Volmer quenching experiments were conducted on a Hitachi F4600 Fluorescence Spectrophotometer. Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 2.0 × 10^{-5} M Ir(ppy)$_3$ and the appropriate amount of quencher in CH_3CN (for Tables S1 and S2) at room temperature. After

degassing with argon for 5 min, the emission spectra of the samples were collected. The solutions were irradiated at 340 nm and luminescence was measured at 550 nm (CH_3CN as the solvent). The data summarized in the tables are the phosphorescence intensity measured three times for each sample. The data illustrated in the graphs are the average of three experiments.

Table S1: Luminescence quenching data for $Ir(ppy)_3$ and **1a** in CH_3CN.

Vial	1	2	3	Average	I_0/I	[1a']
0	4115	3964	3918	3999	1.00	0
1	3875	3858	3717	3817	1.04	0.00004
2	3871	3845	3725	3814	1.05	0.00006
3	3929	3906	3776	3870	1.03	0.00008
4	3790	3741	3711	3747	1.07	0.0001
5	3662	3591	3570	3608	1.11	0.0002
6	3034	3011	2984	3010	1.32	0.0004

Table S2: Luminescence quenching data for $Ir(ppy)_3$ and DIPEA in CH_3CN.

Vial	1	2	3	Average	I_0/I	[2a]
0	4115	3964	3918	3999	1.00	0
1	3592	3650	3582	3608	1.11	0.00002
2	2998	2859	2732	2863	1.39	0.00004
3	3000	2908	2809	2906	1.38	0.00006
4	2581	2448	2371	2467	1.62	0.00008
5	2352	2290	2259	2300	1.73	0.0001
6	1880	1857	1839	1859	2.16	0.0002

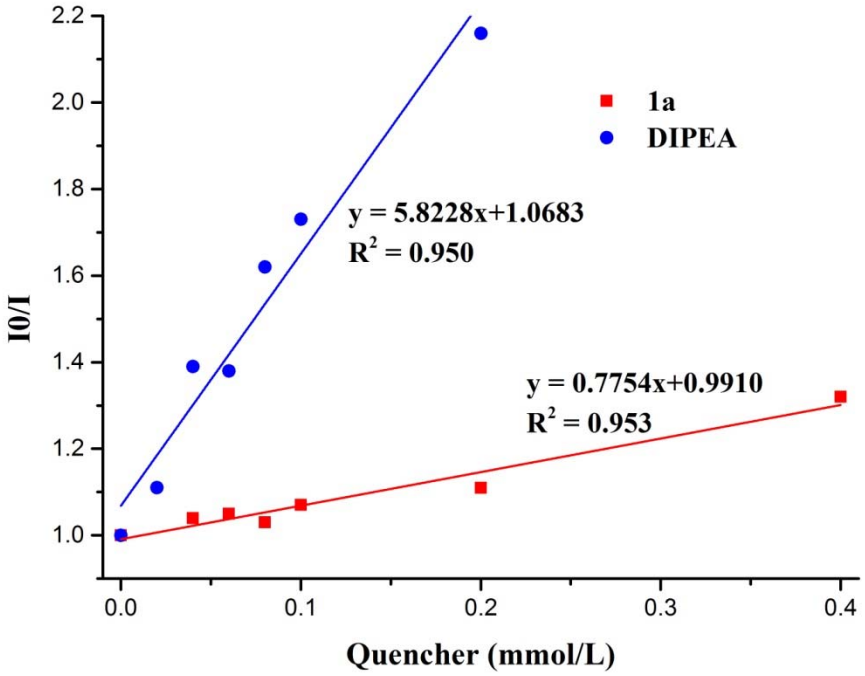


Figure S3: Luminescence quenching of $Ir(ppy)_3$ with varying concentrations of **1a** (blue) and DIPEA (red) in CH_3CN.

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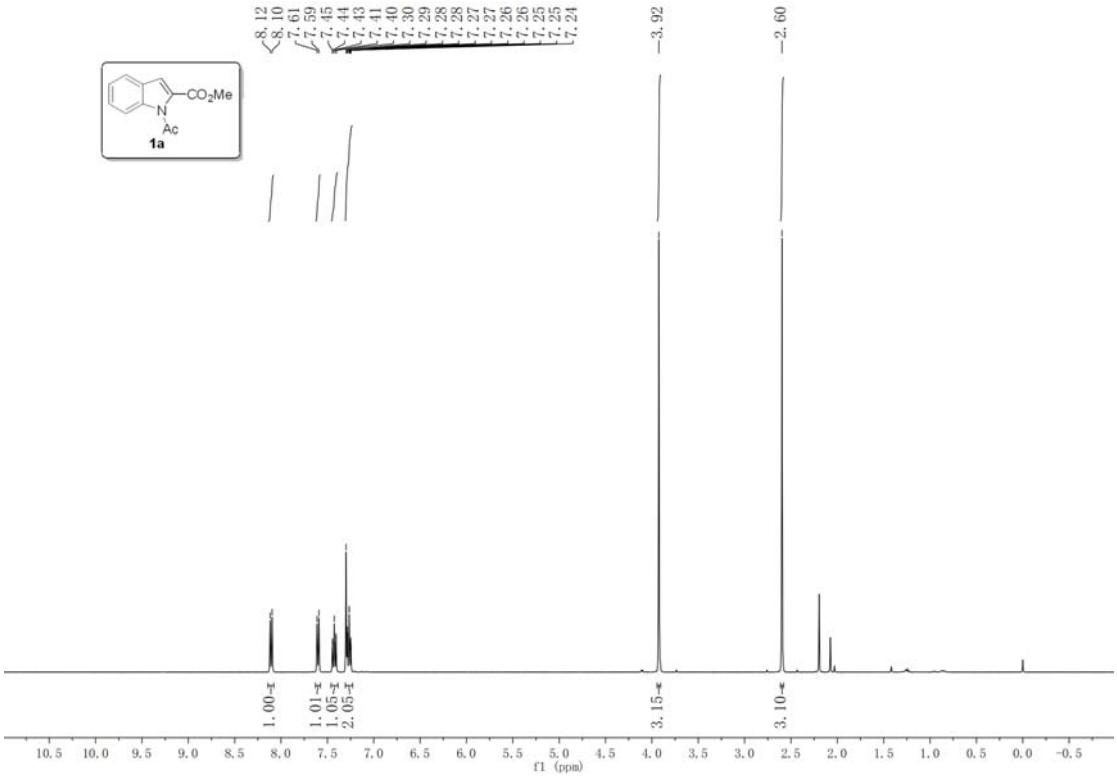
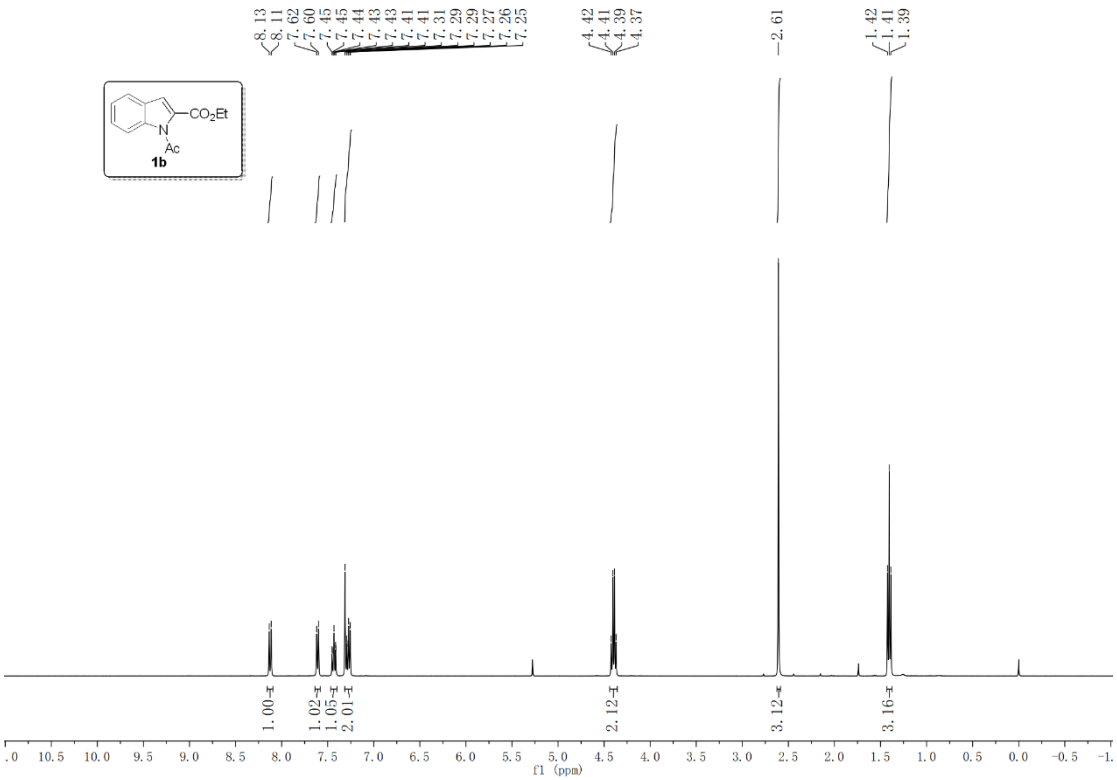
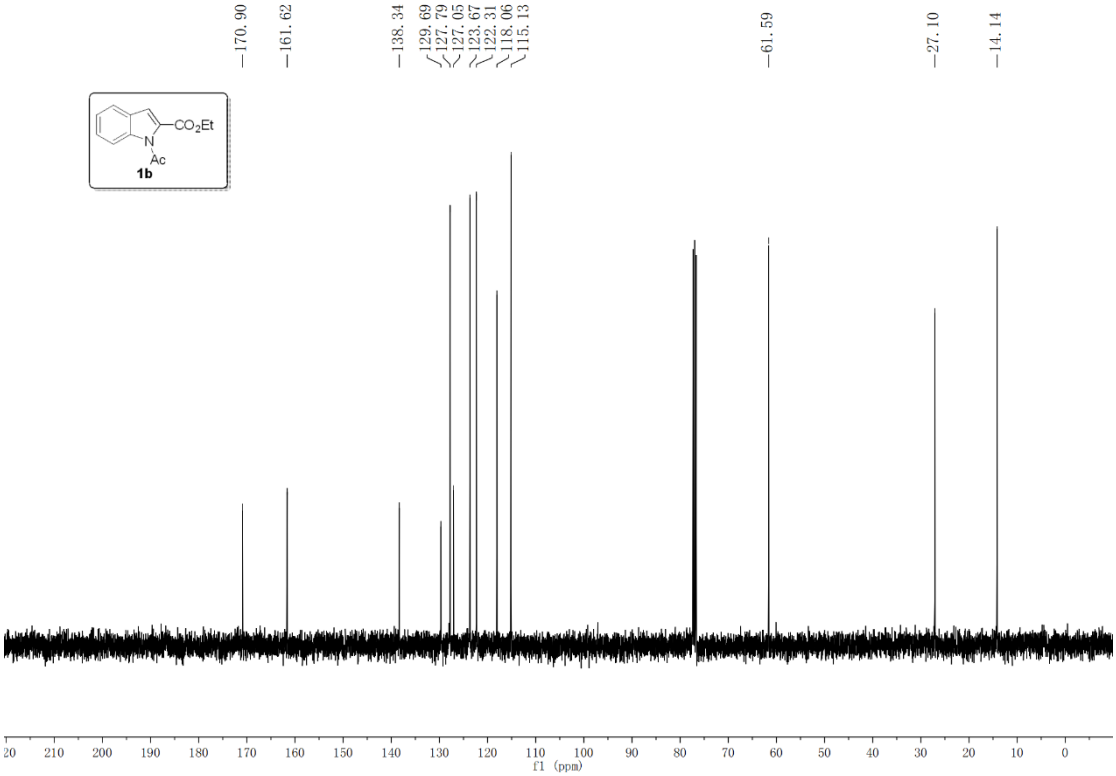
8. Copies of NMR Spectra



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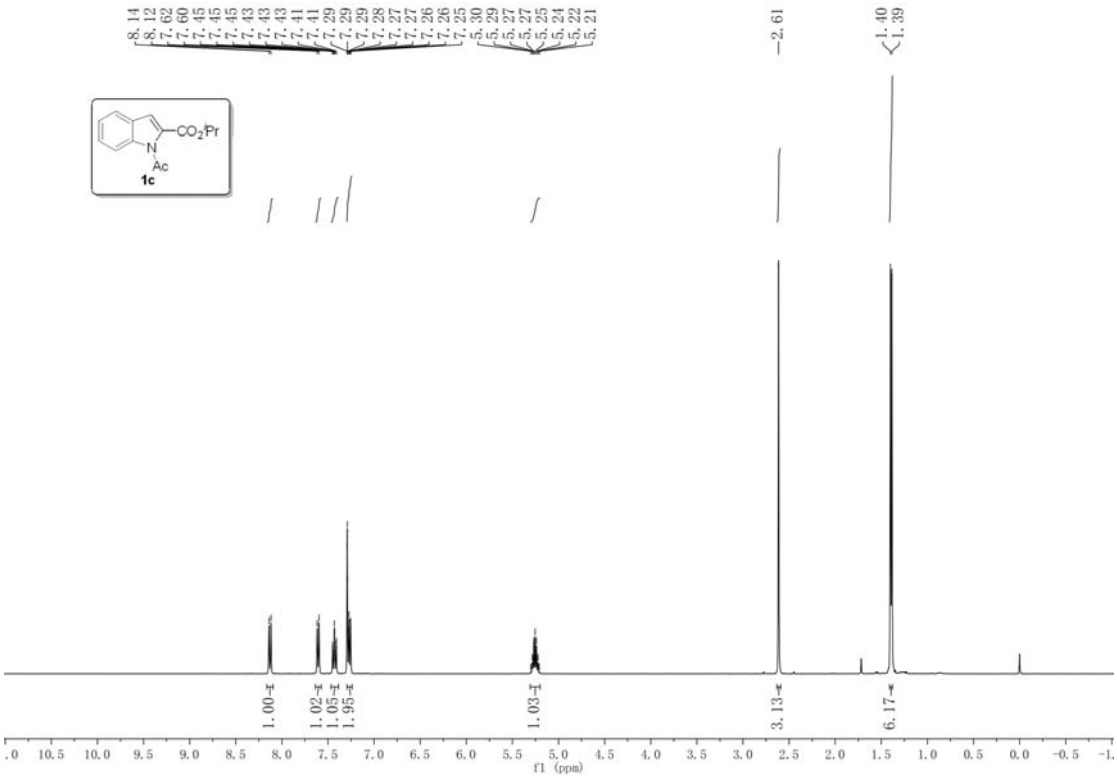
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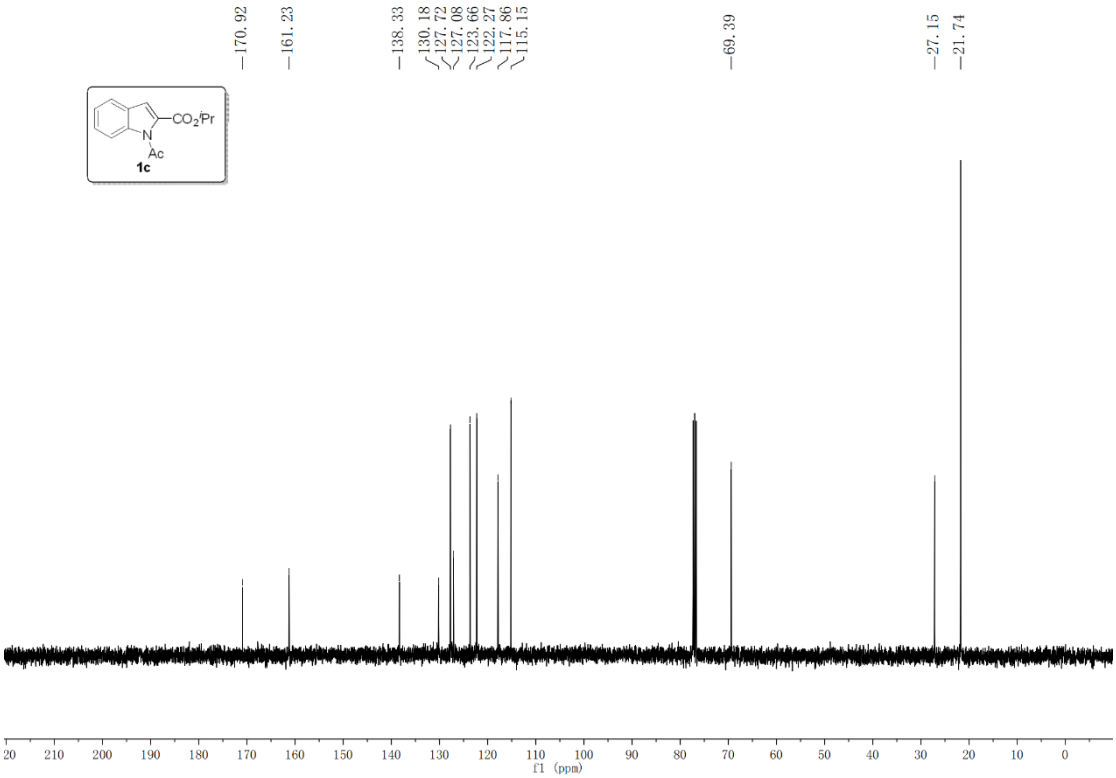
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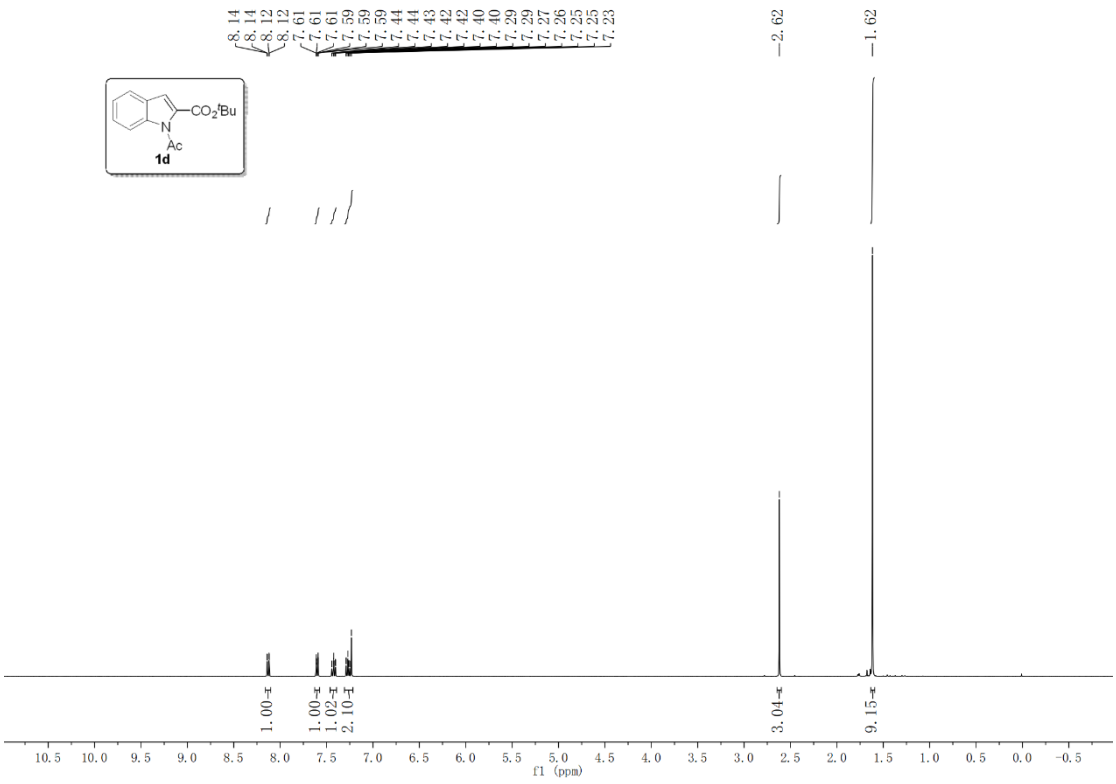
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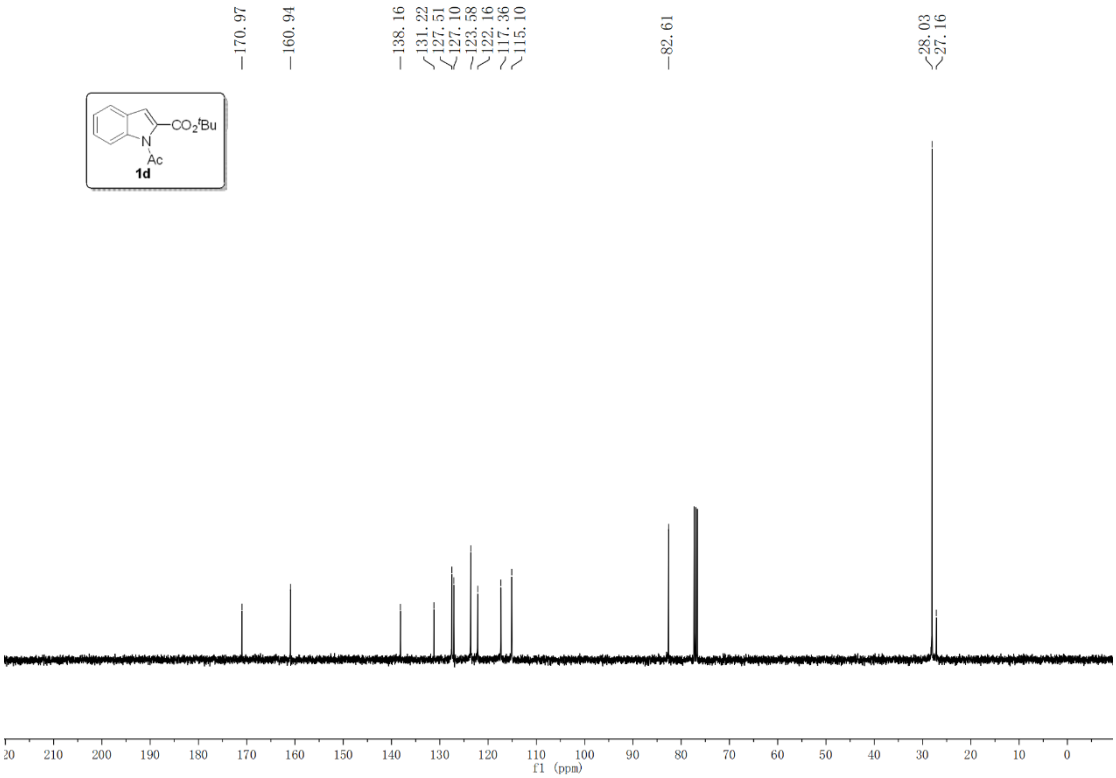
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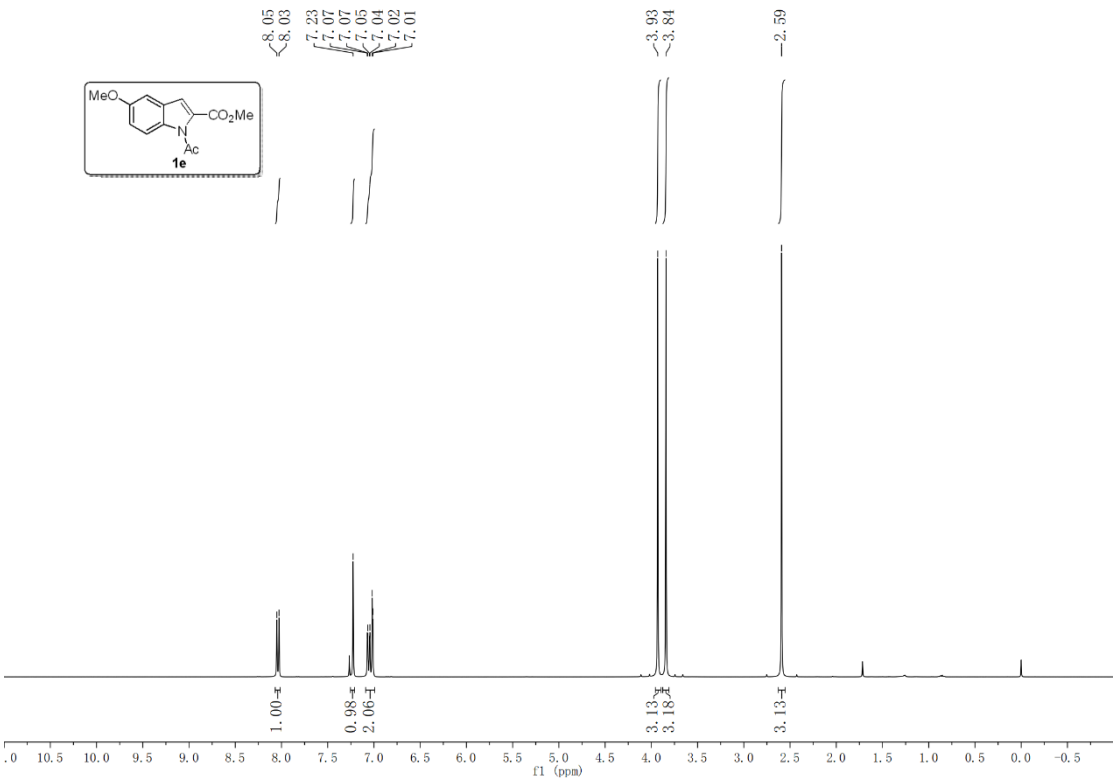
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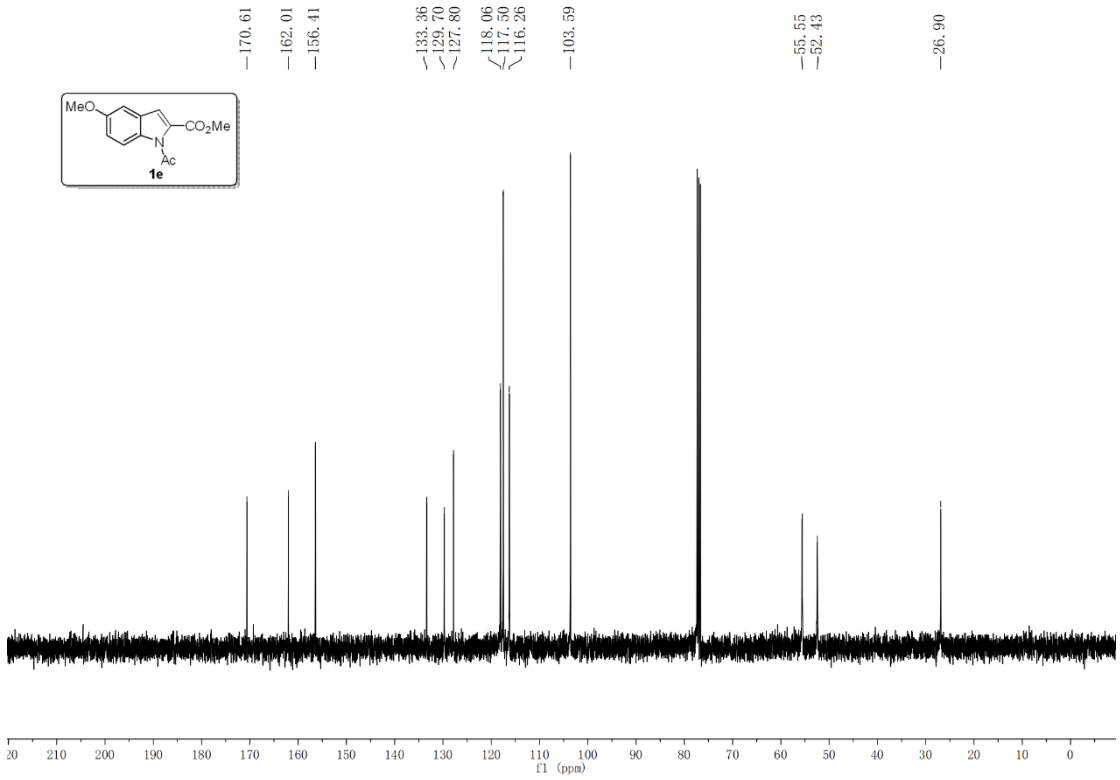
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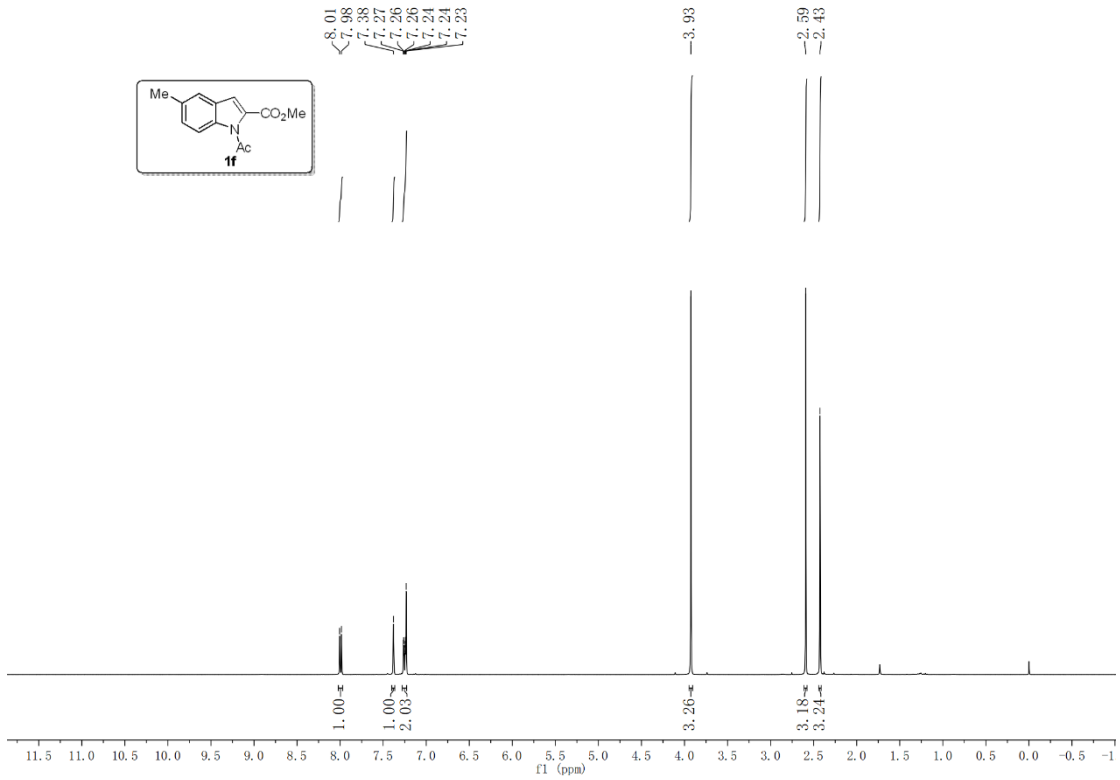
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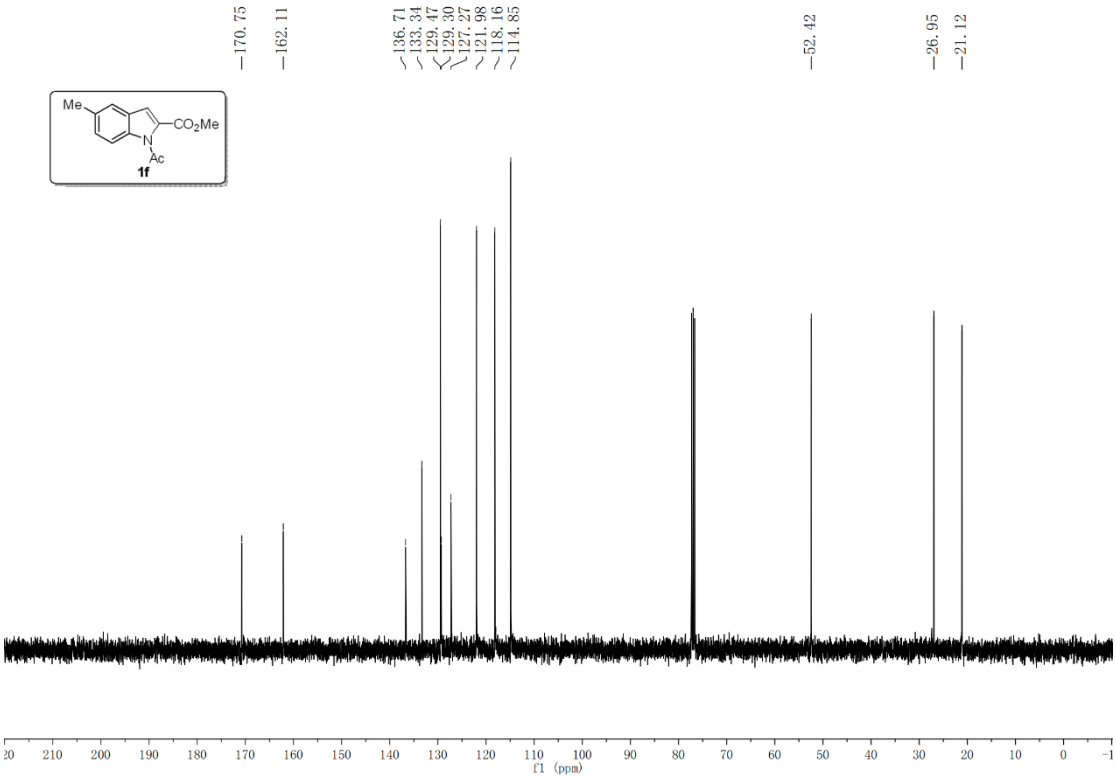
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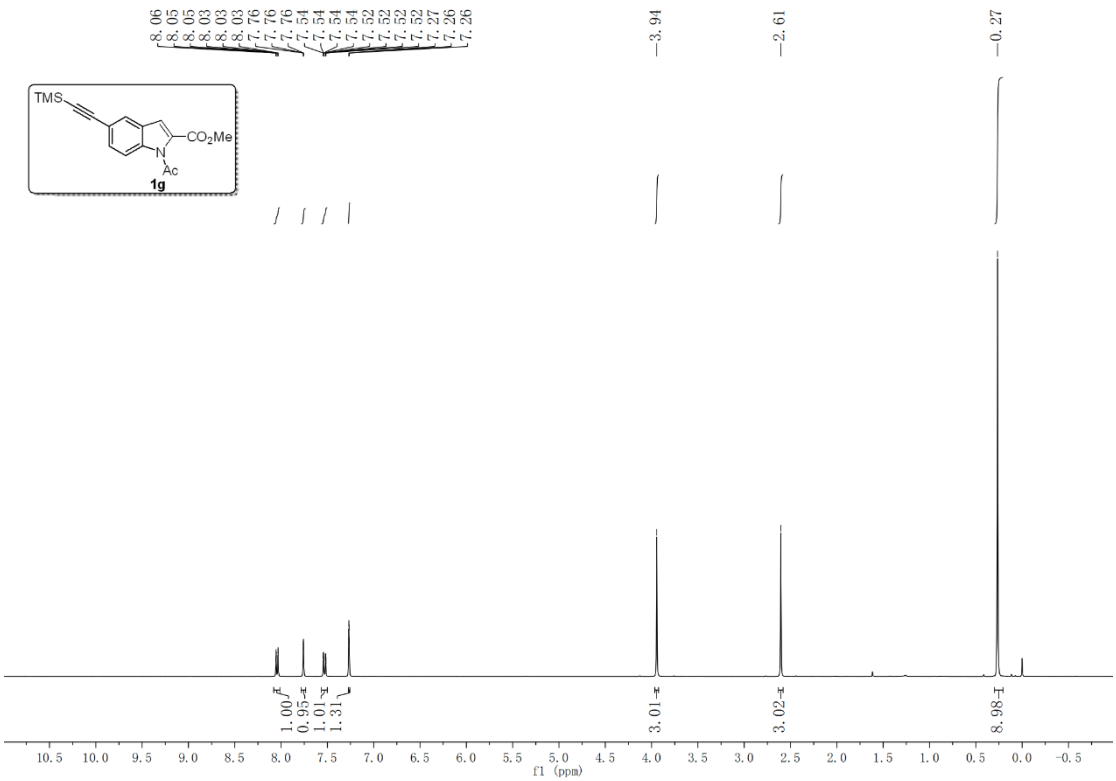
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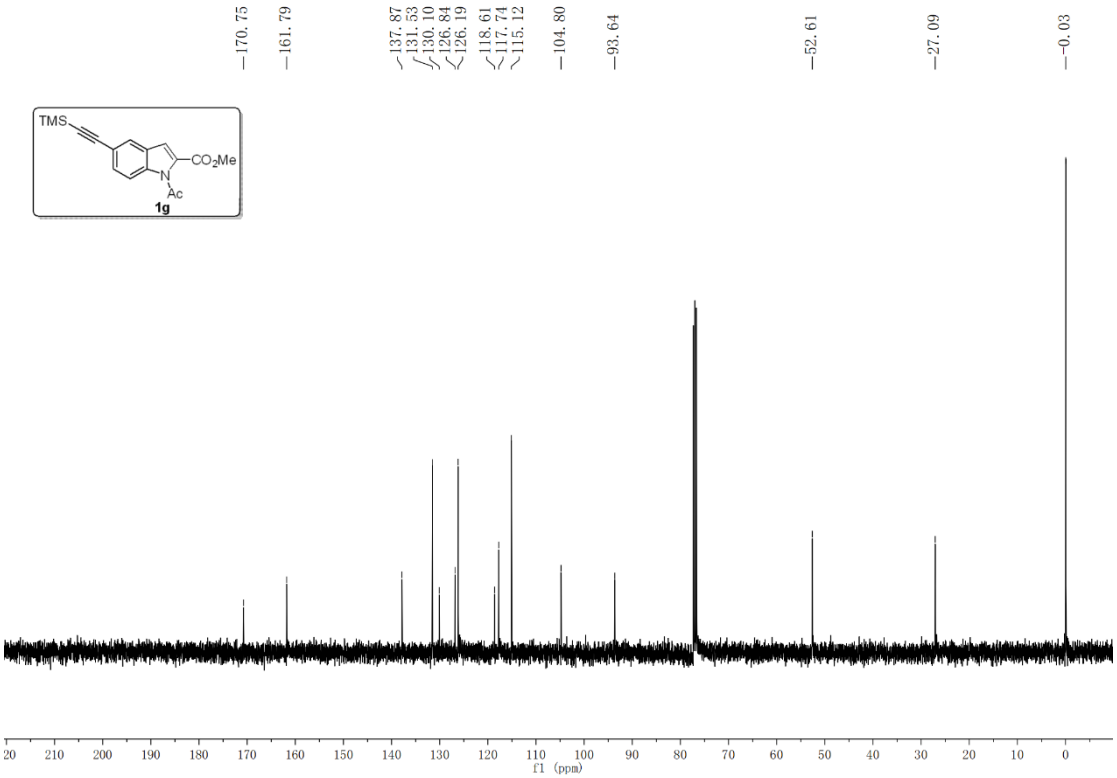
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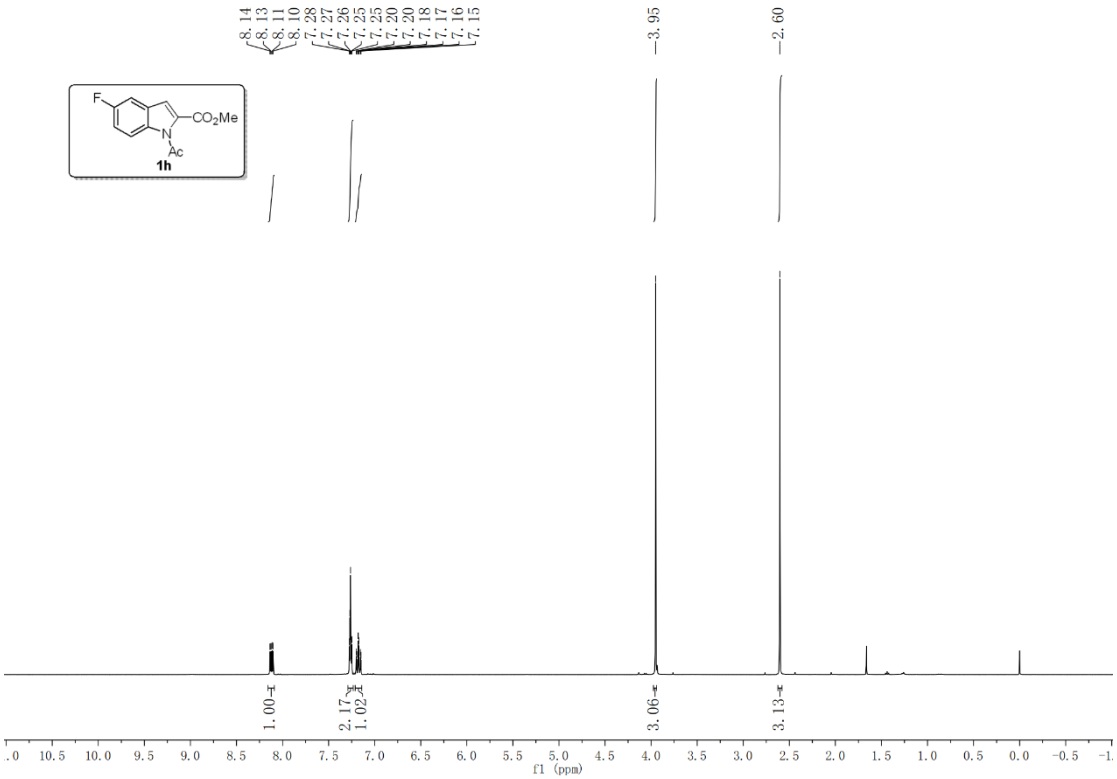
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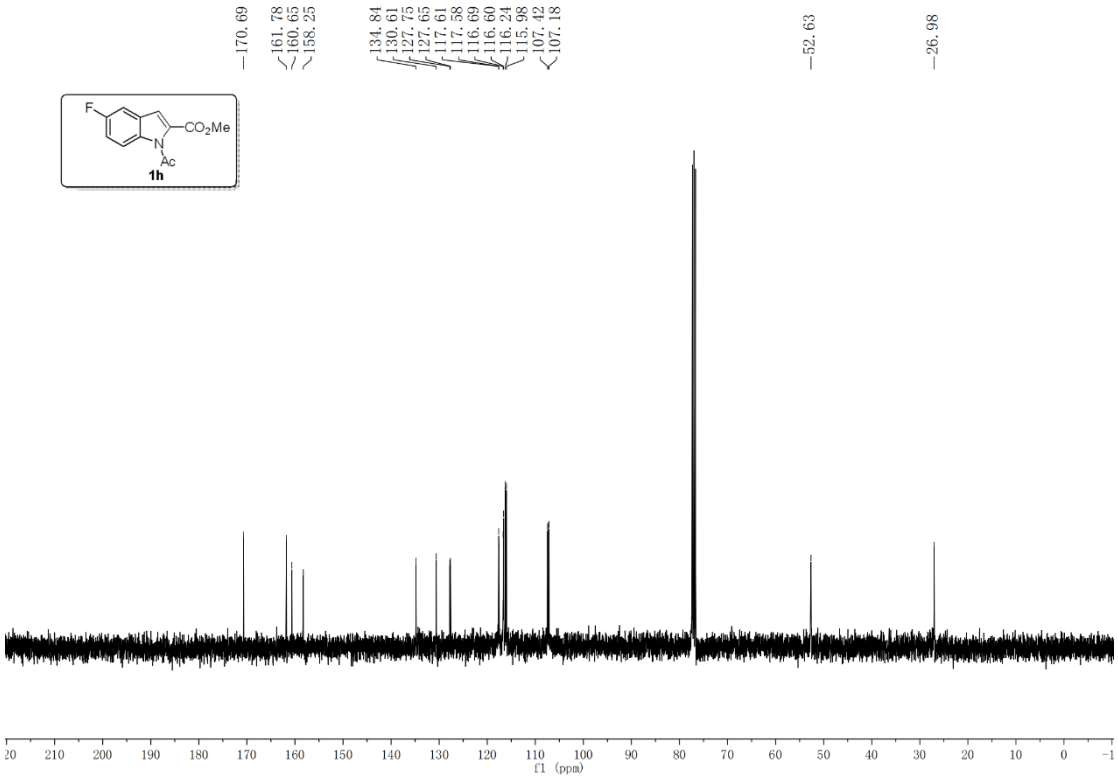
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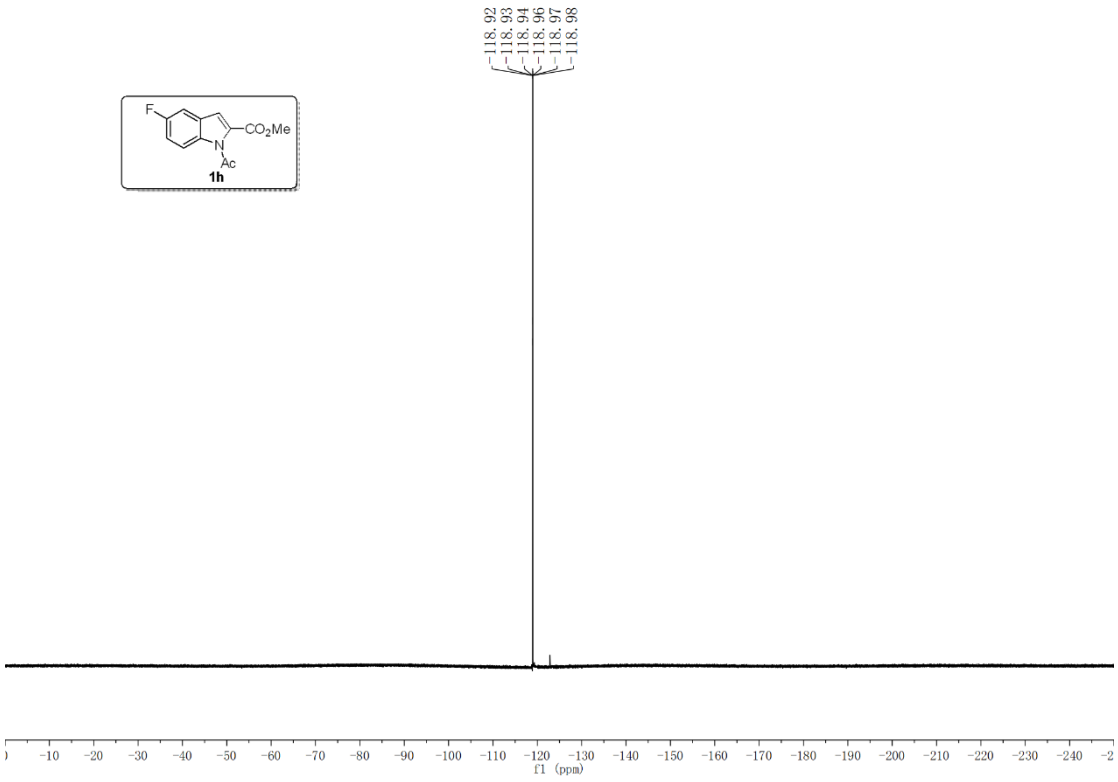
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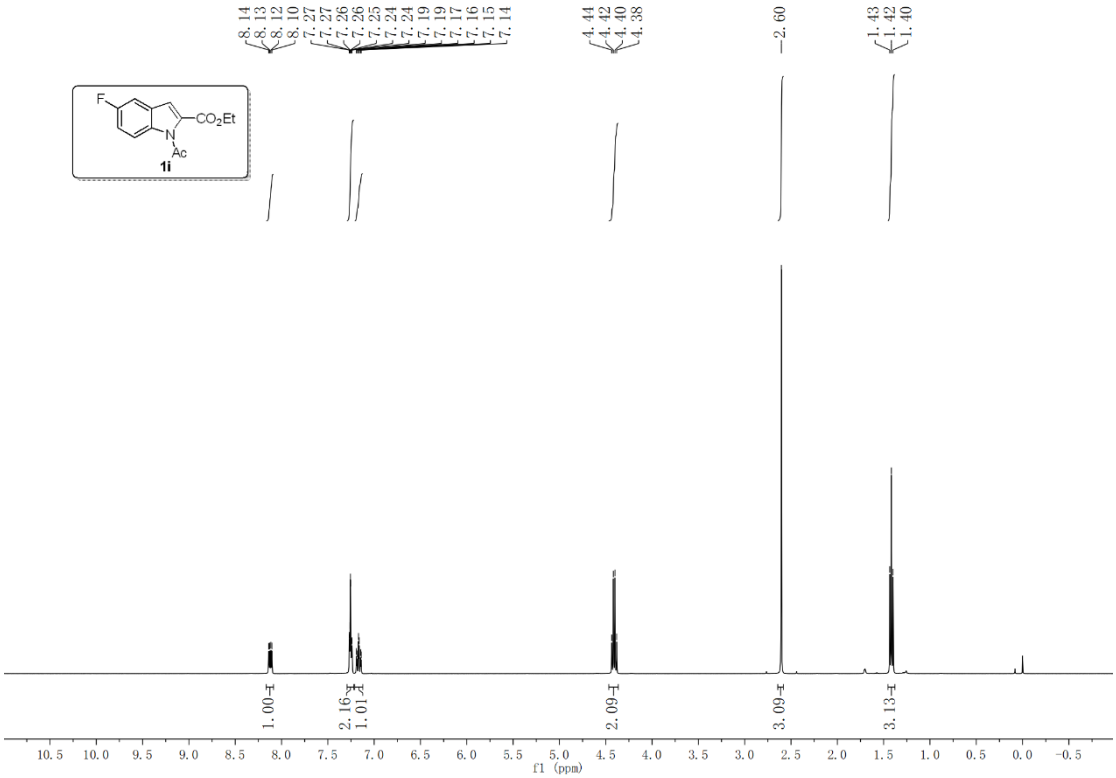
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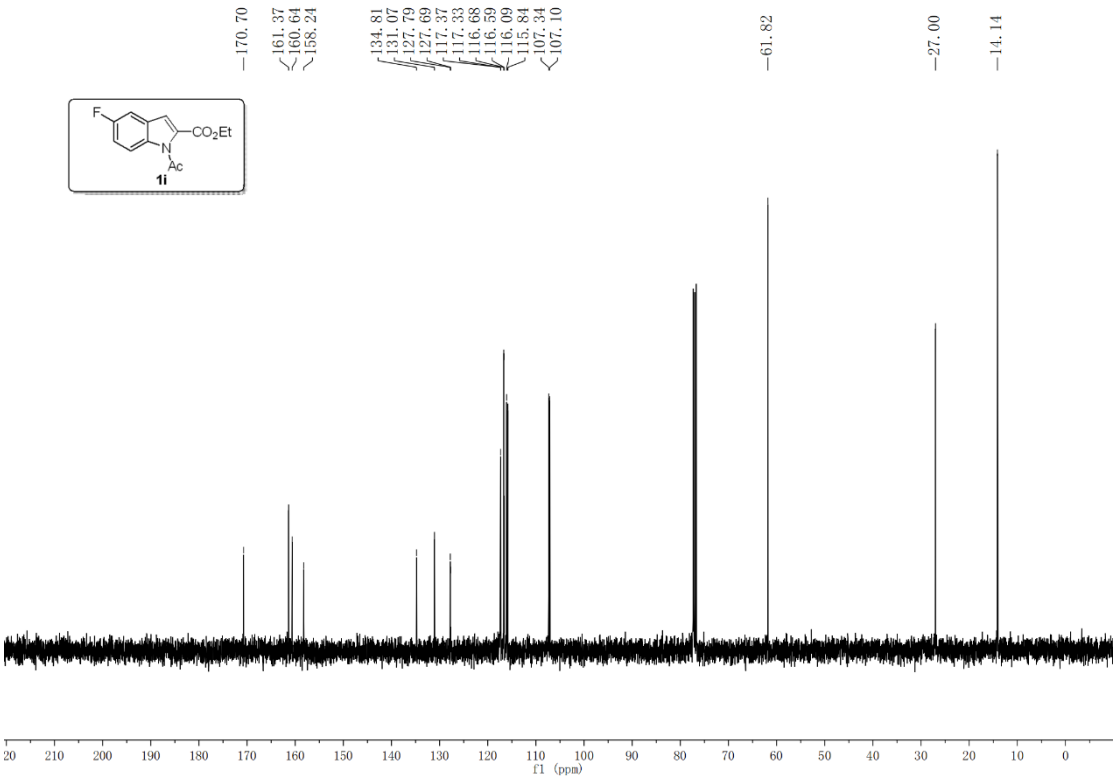
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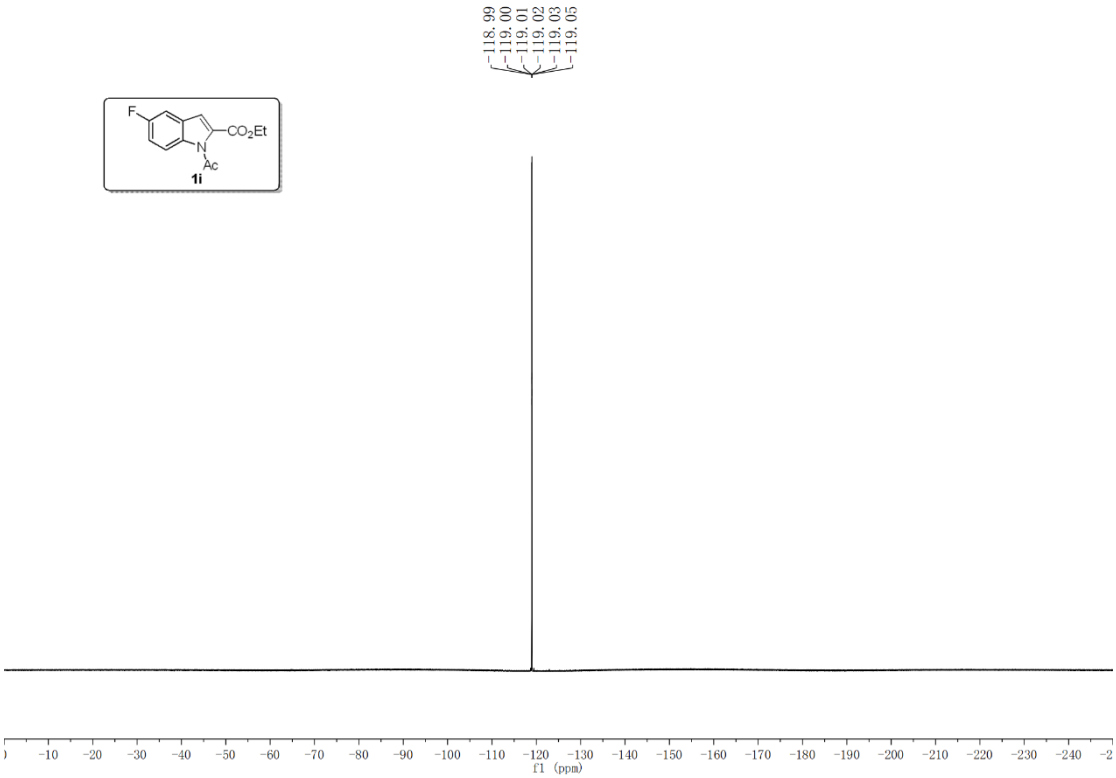
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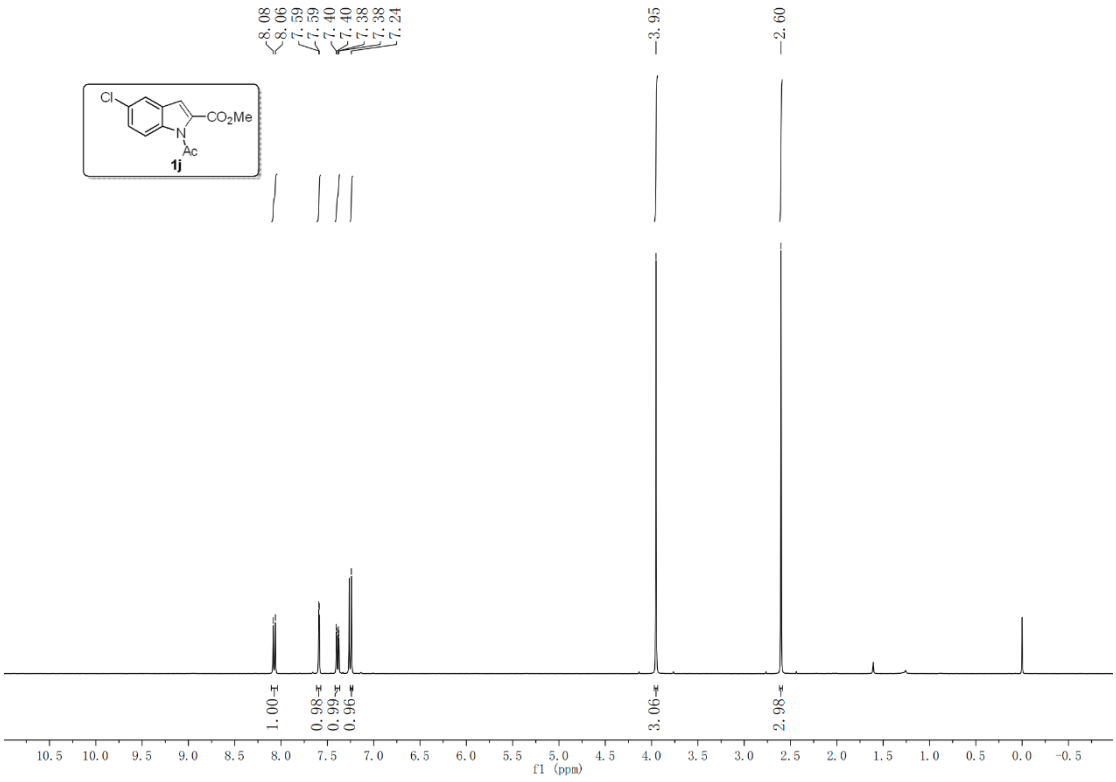
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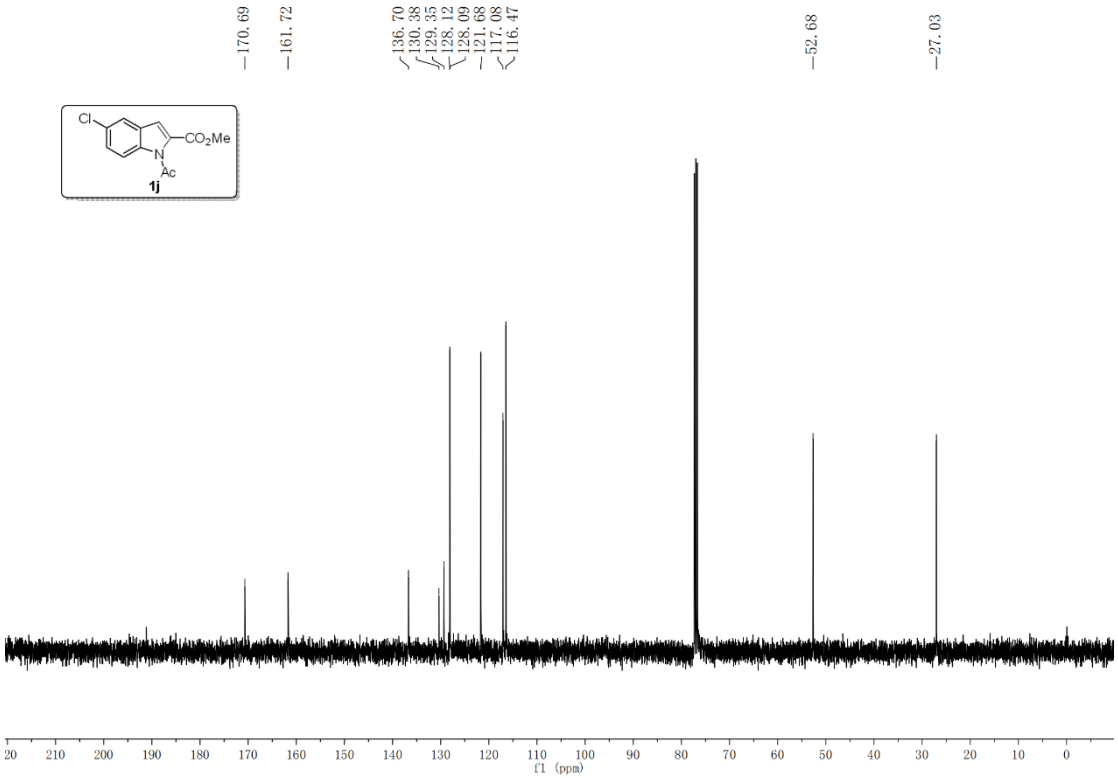
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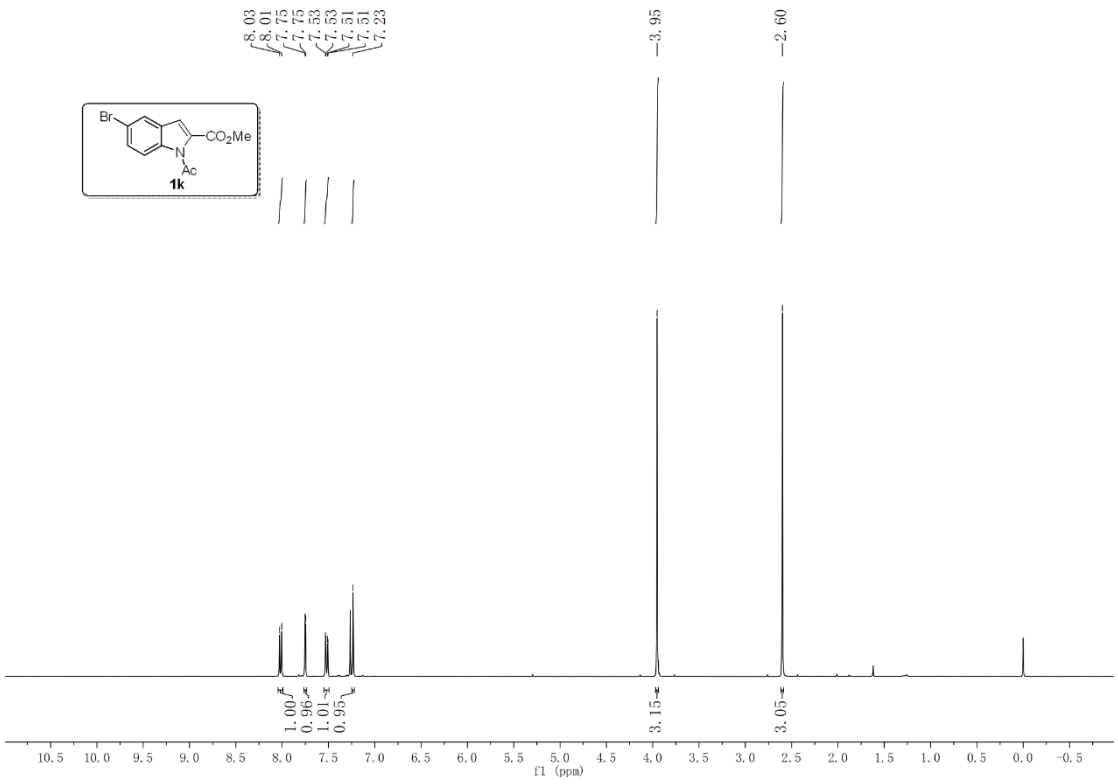
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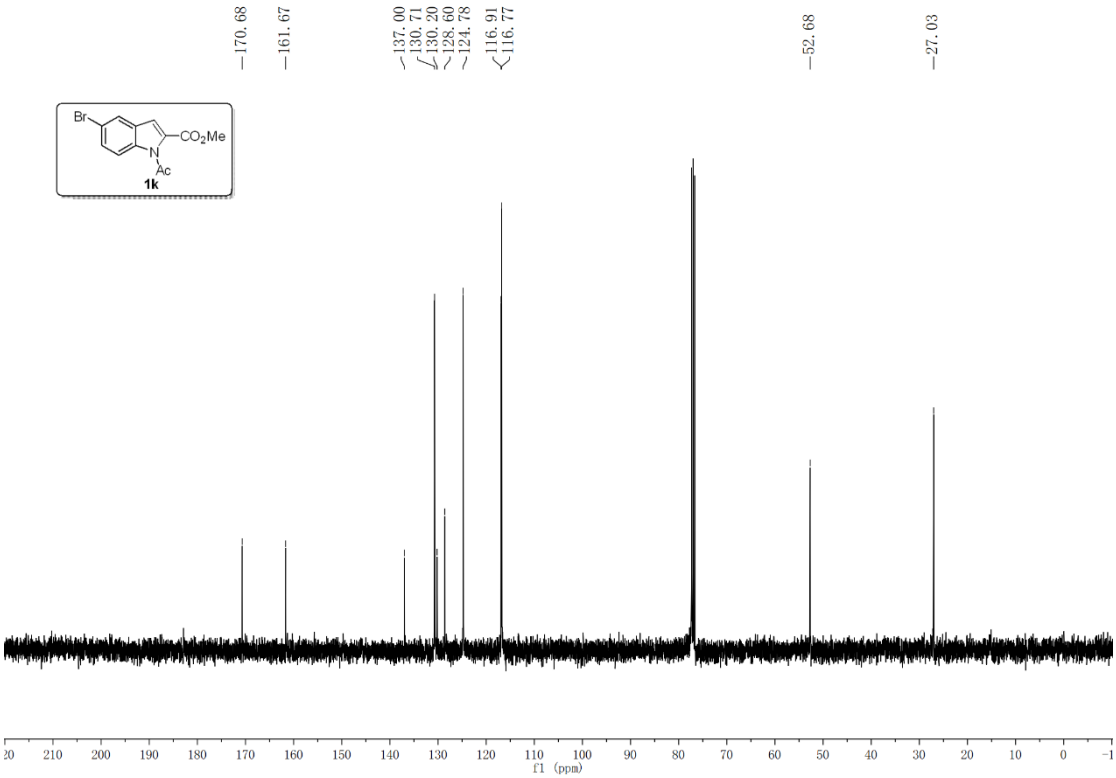
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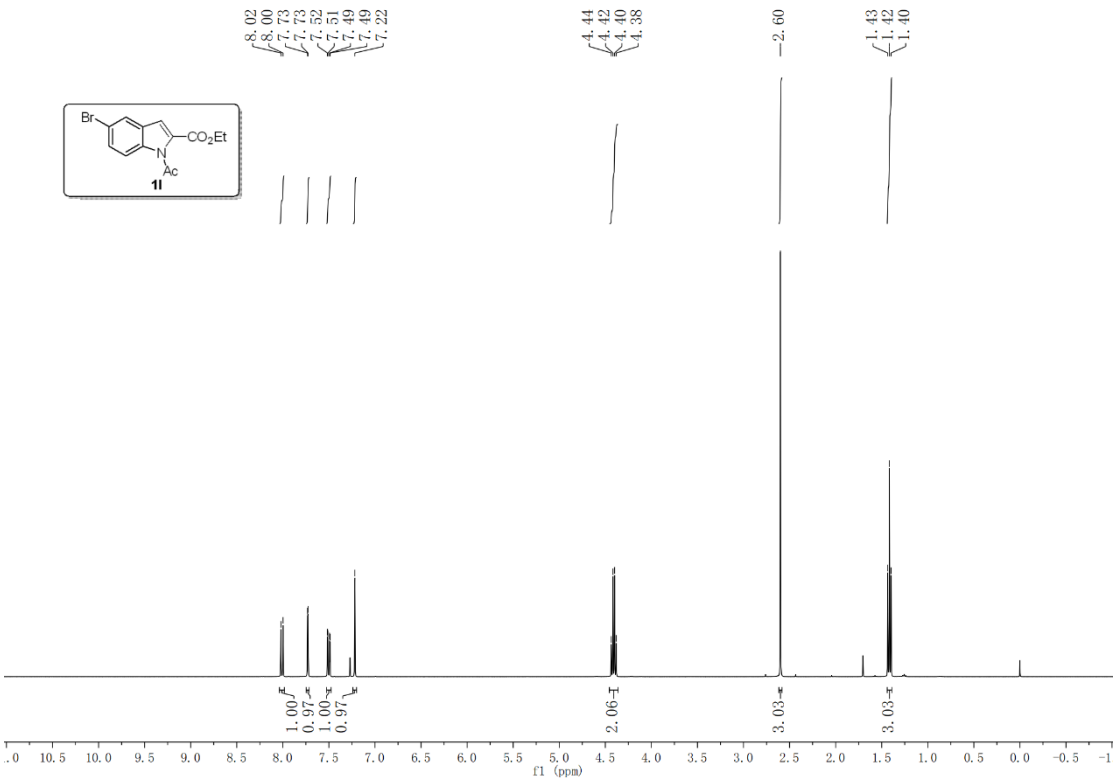
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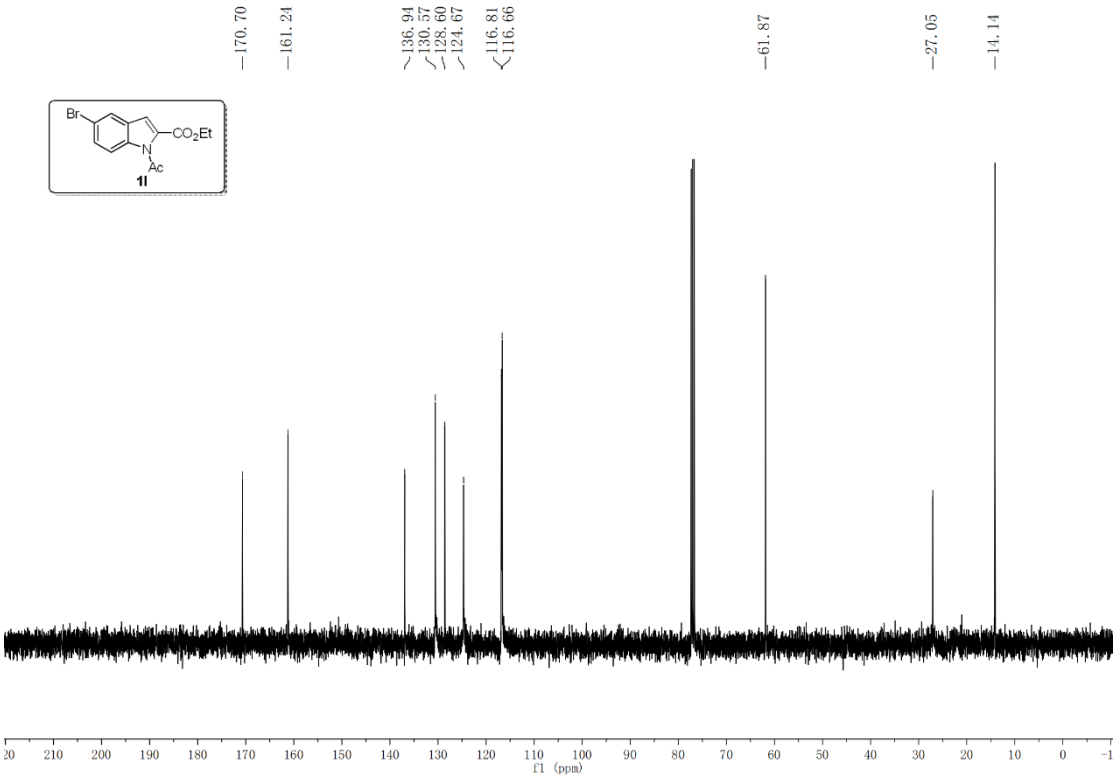
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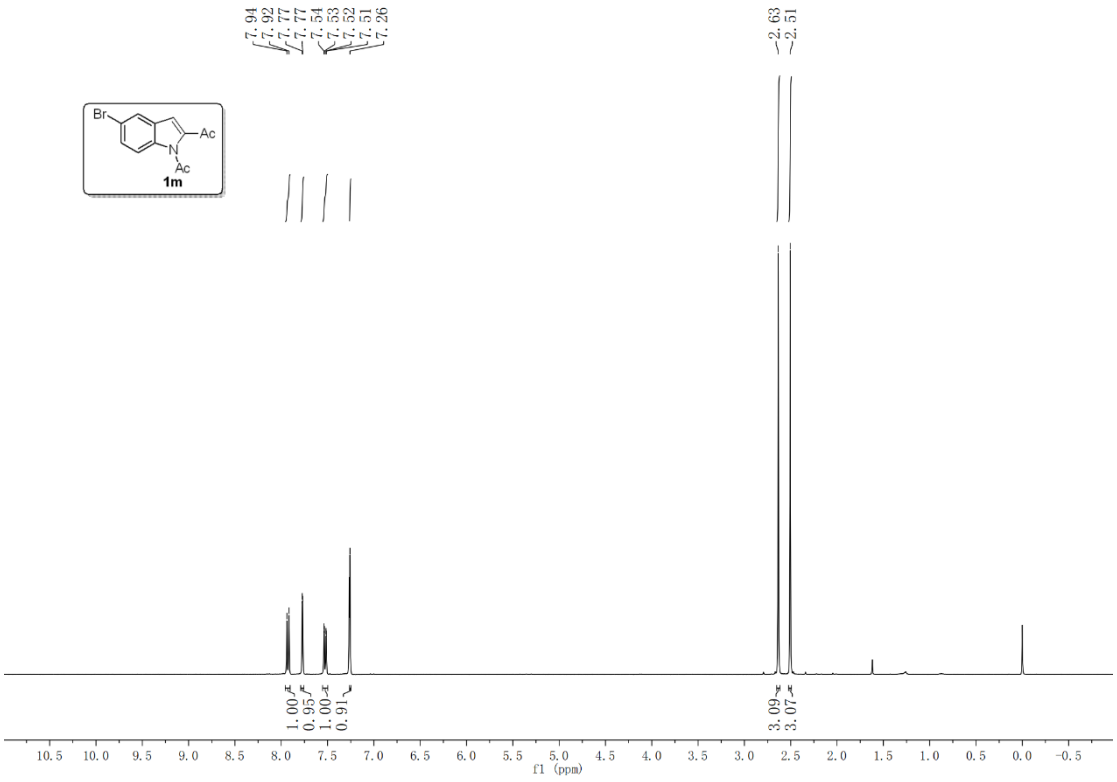
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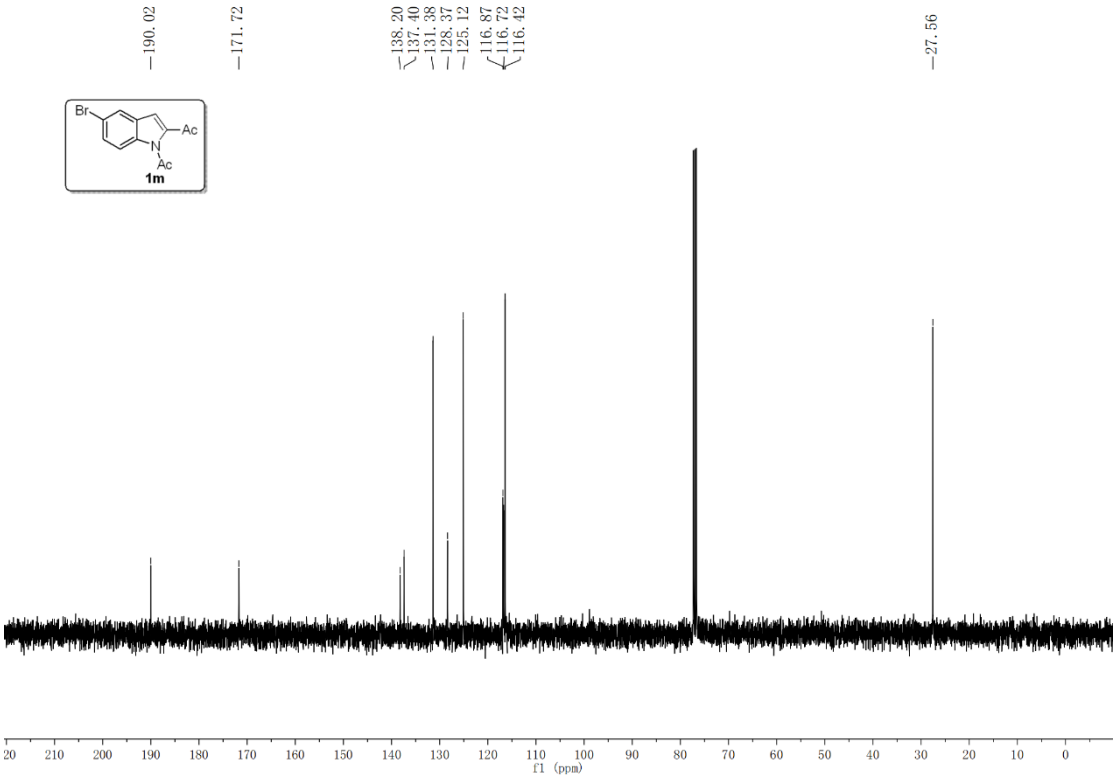
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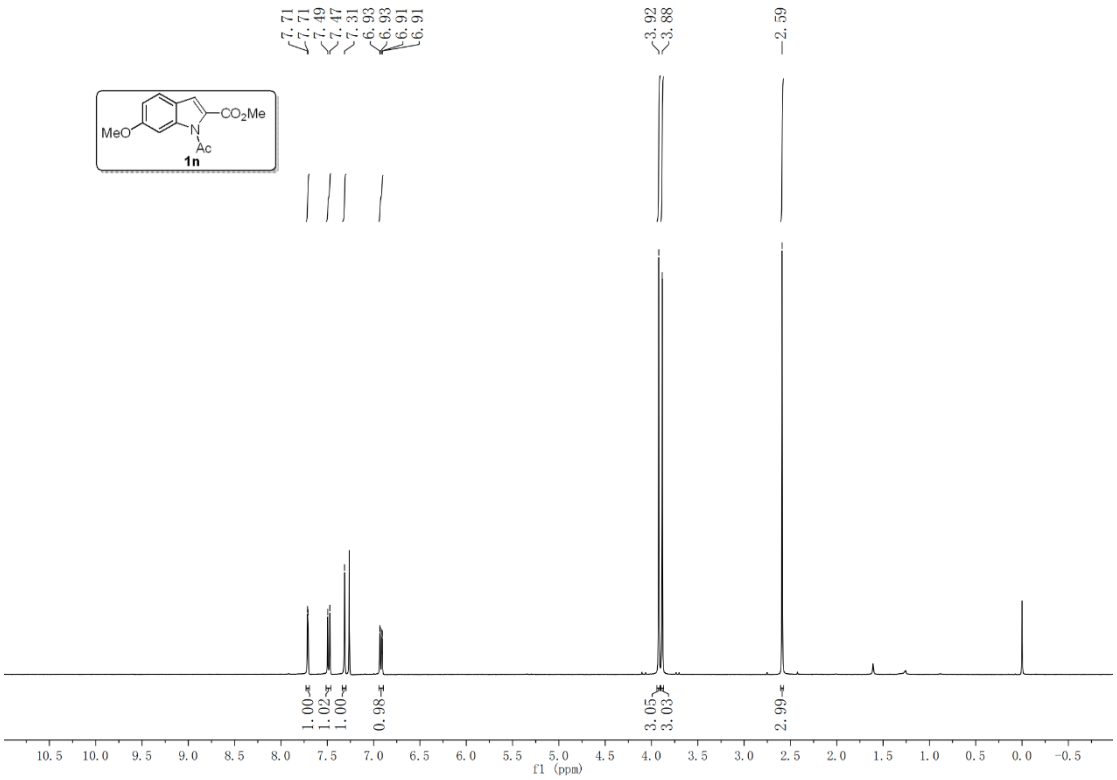
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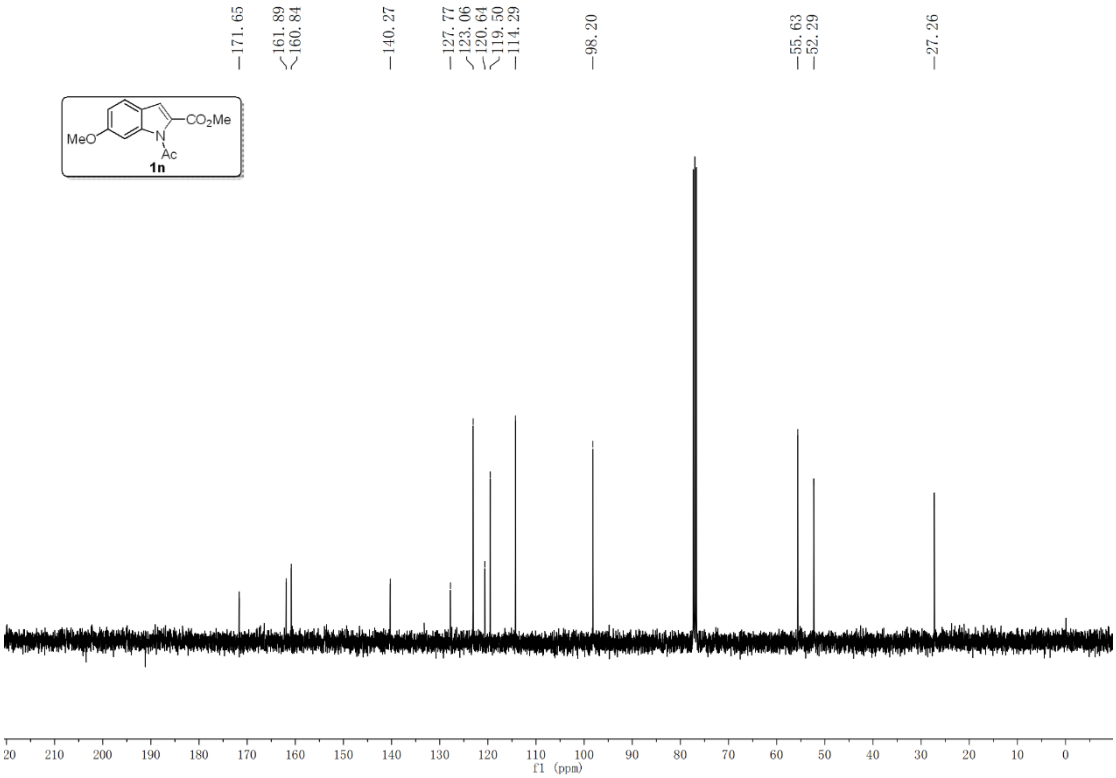
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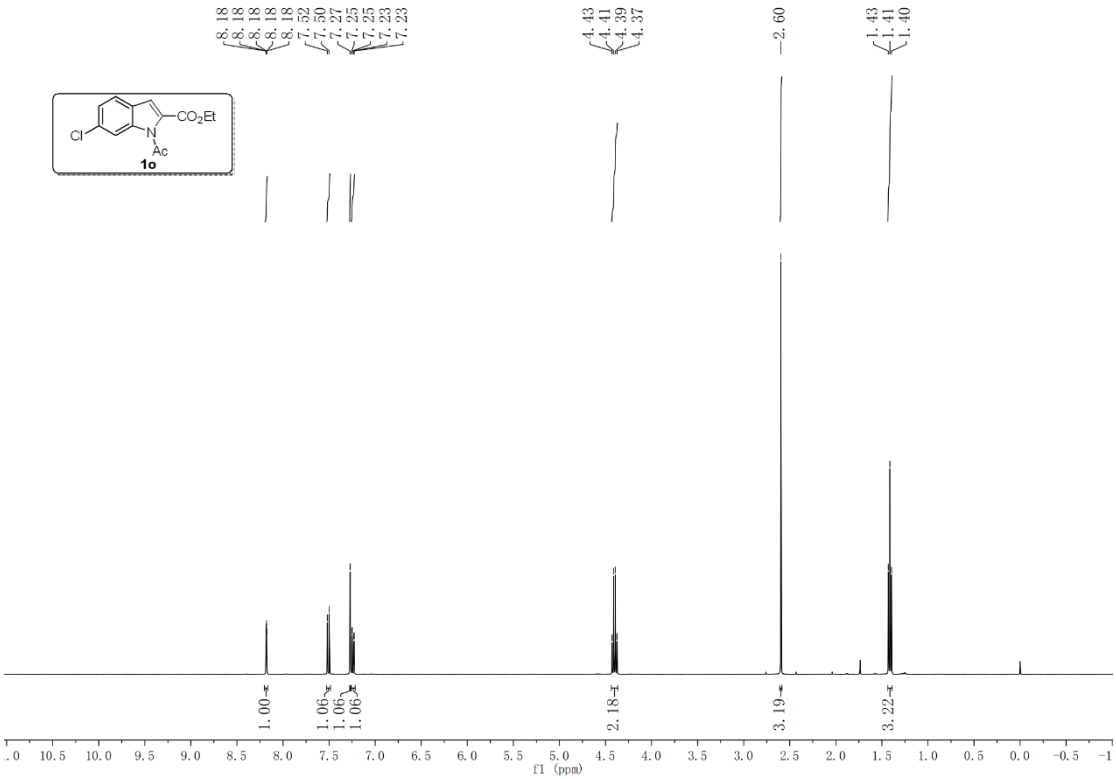
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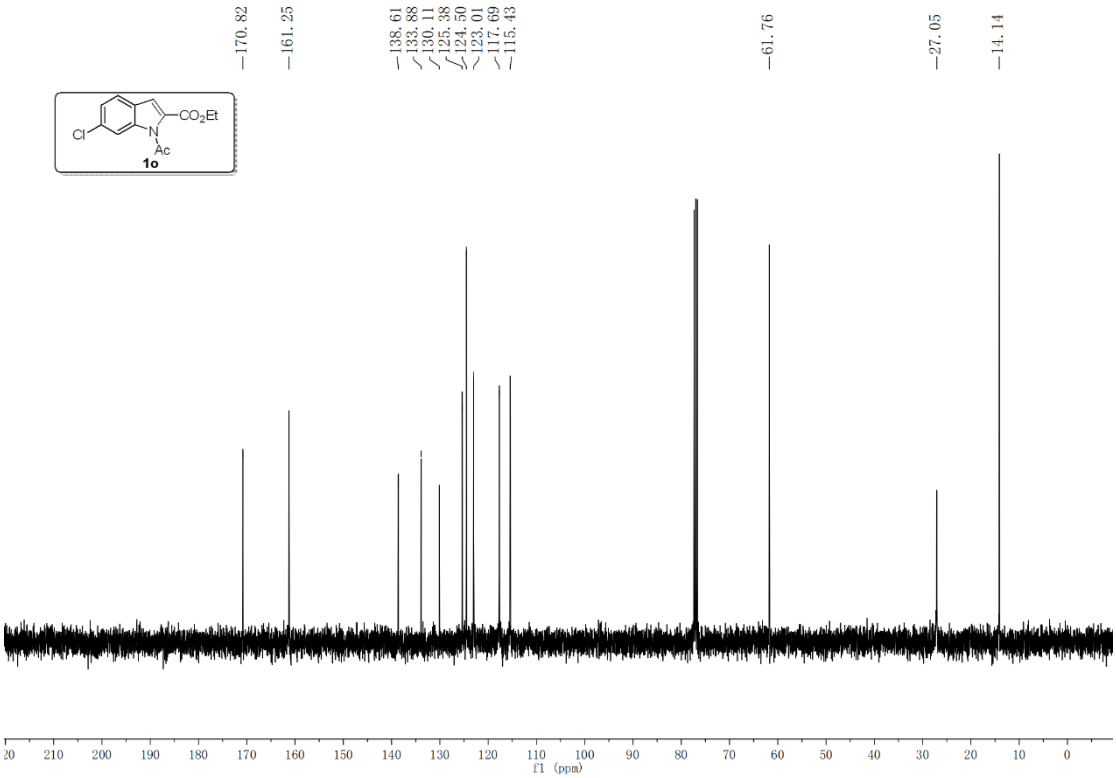
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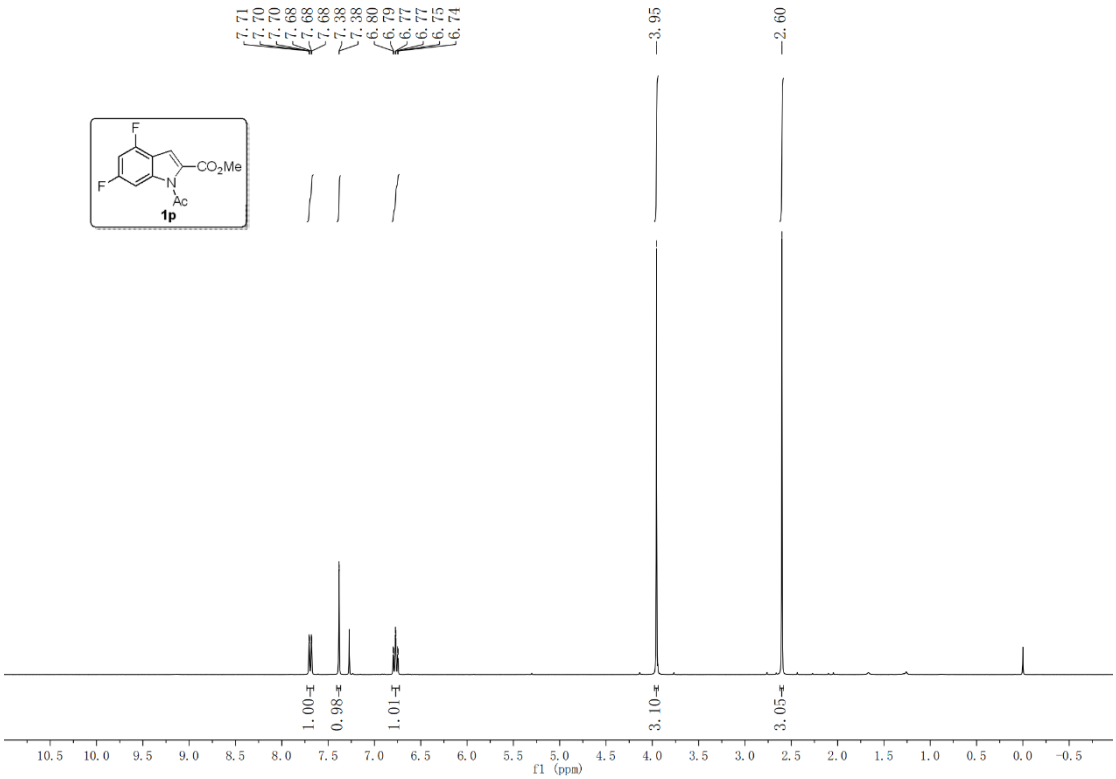
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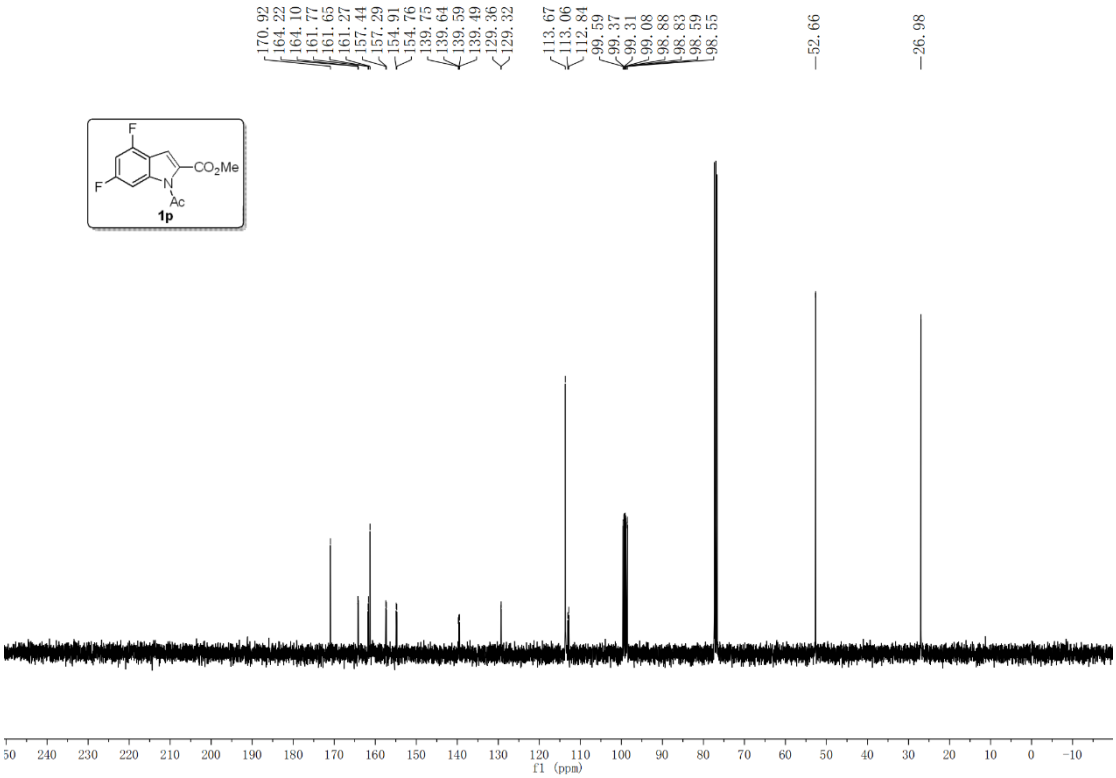
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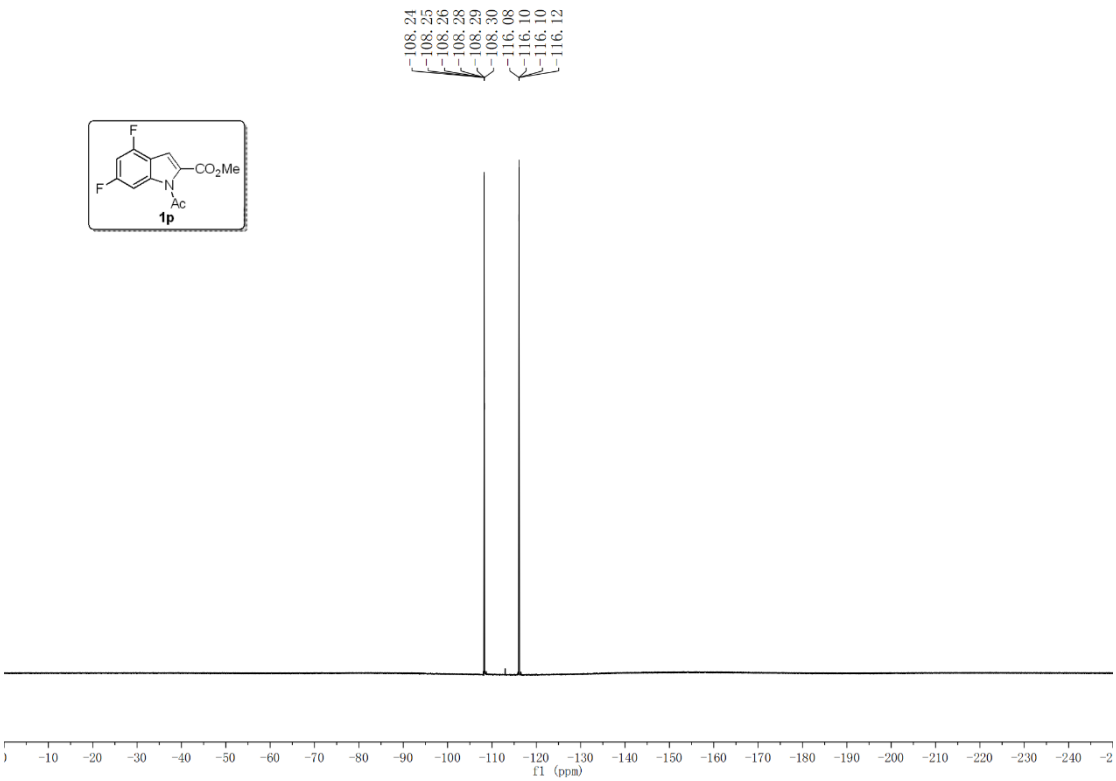
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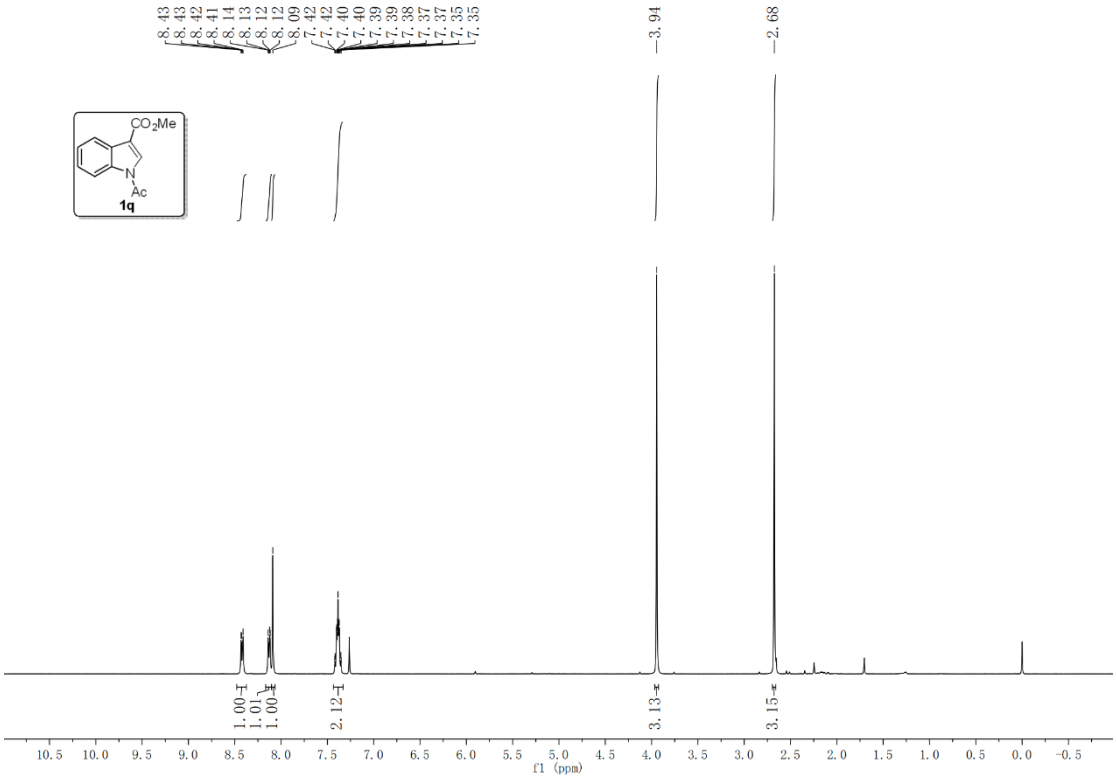
108.28
108.29
108.30
116.08
116.10
116.10
116.12
F
F
CO2Me
N
Ac
1p
f1 (ppm)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8.12
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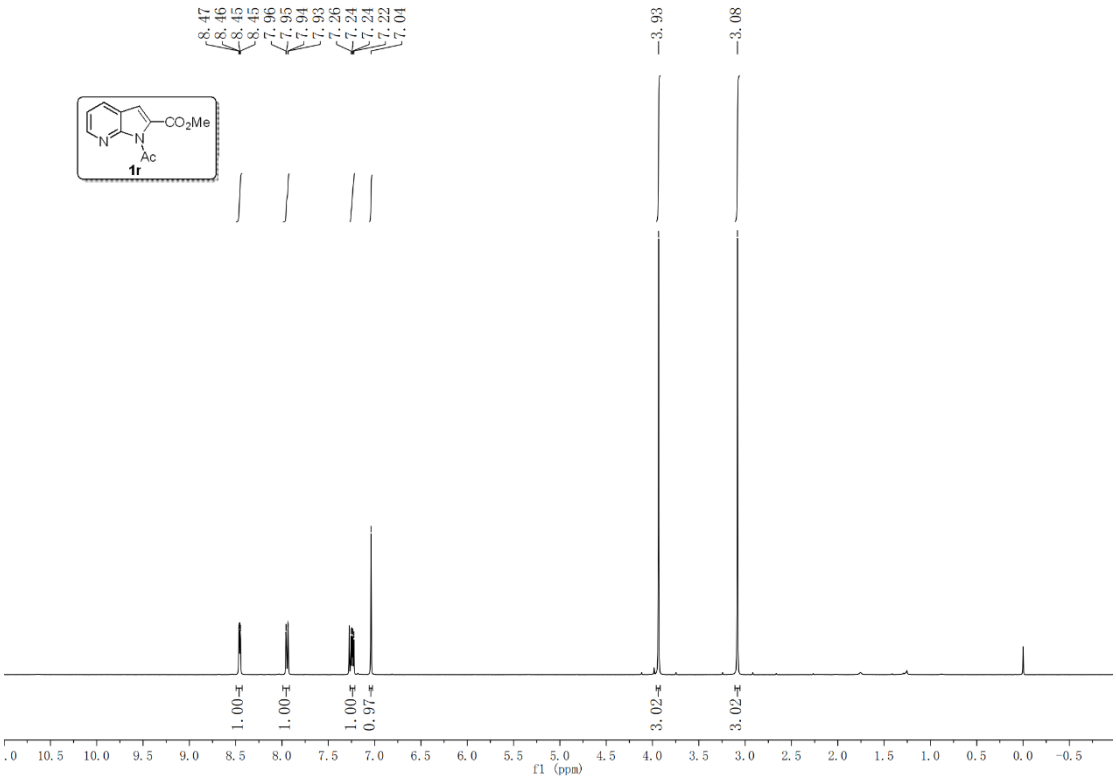
7.42
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.35
7.35
3.94
2.68
CO2Me
N
Ac
1q
1.00
1.01
1.00
2.12
3.13
3.15
f1 (ppm)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7.94
7.93
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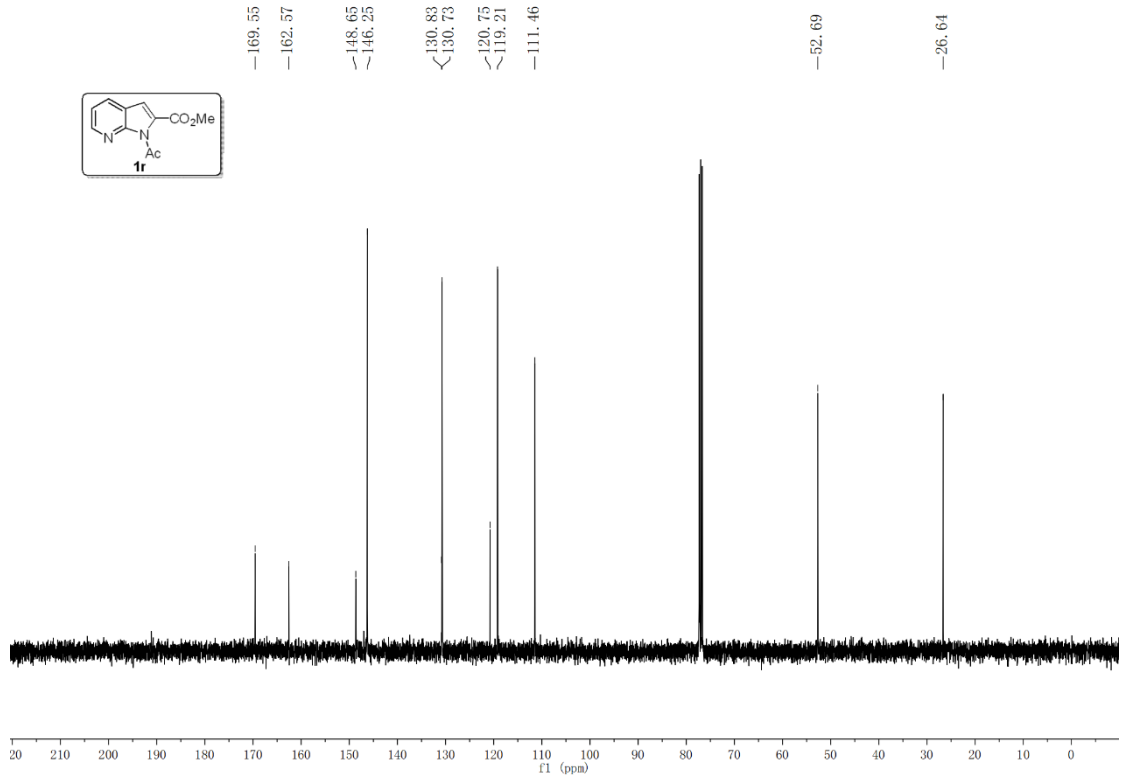
7.24
7.24
7.22
7.04
3.93
3.08
CO2Me
N
Ac
1r
1.00
1.00
1.00
0.97
3.02
3.02
f1 (ppm)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162.57
148.65
146.25
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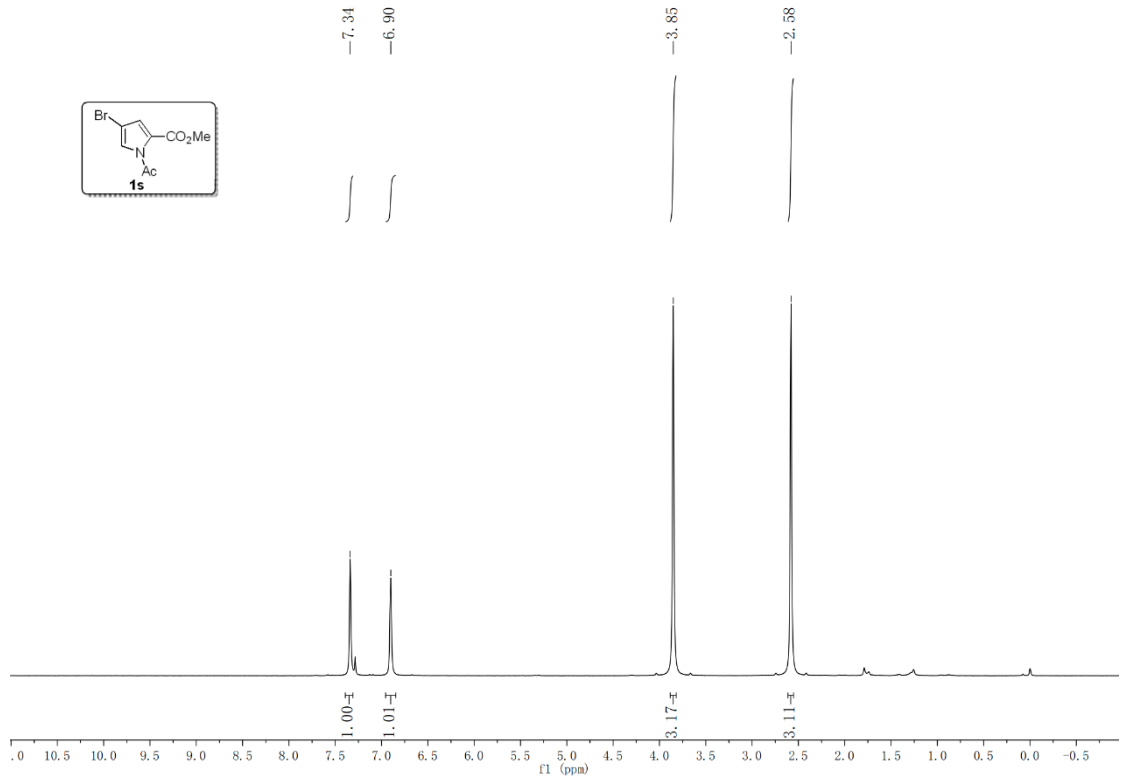
130.73
120.75
119.21
111.46
52.69
26.64
CO2Me
N
Ac
1r
f1 (ppm)


7.34
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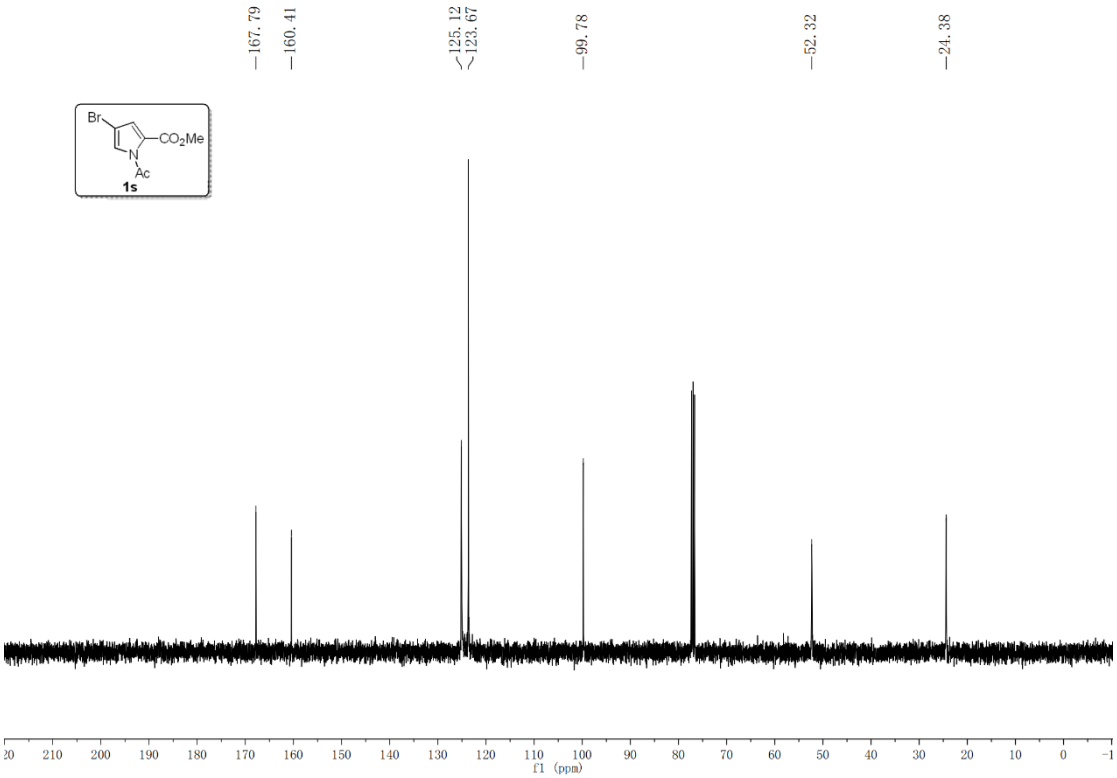
2.58
Br
CO2Me
N
Ac
1s
1.00
1.01
3.17
3.11
f1 (ppm)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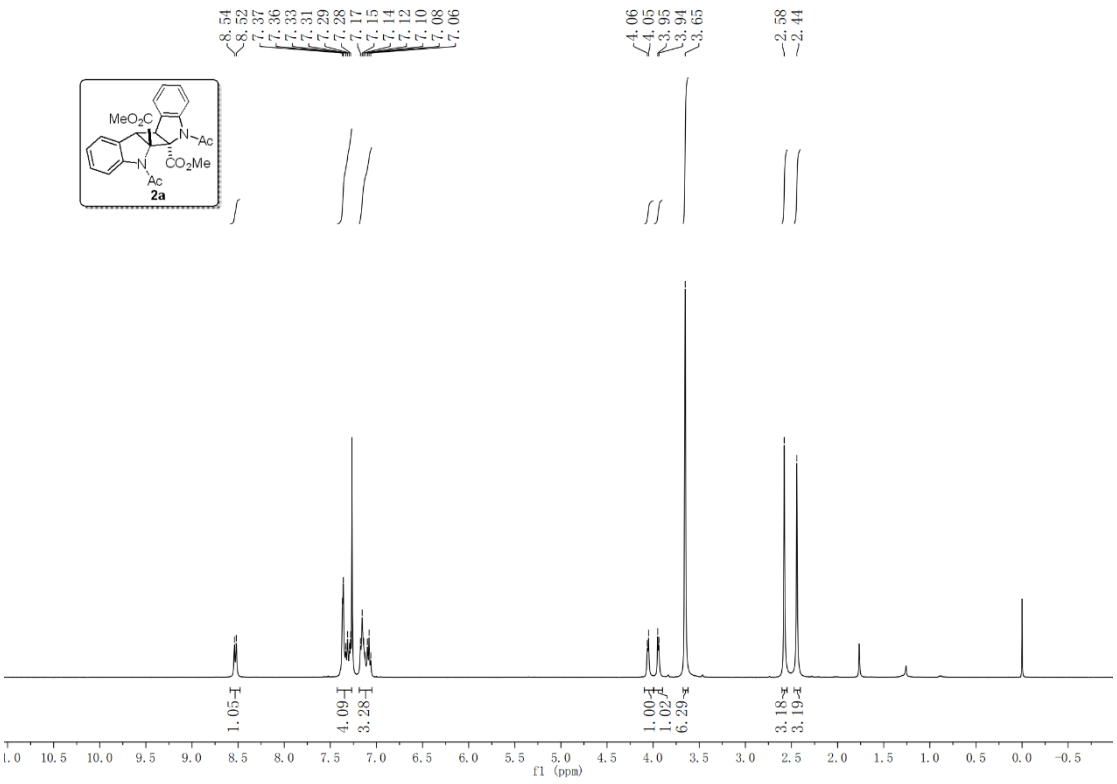
52.32
24.38
Br
CO2Me
N
Ac
1s
f1 (ppm)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8.52
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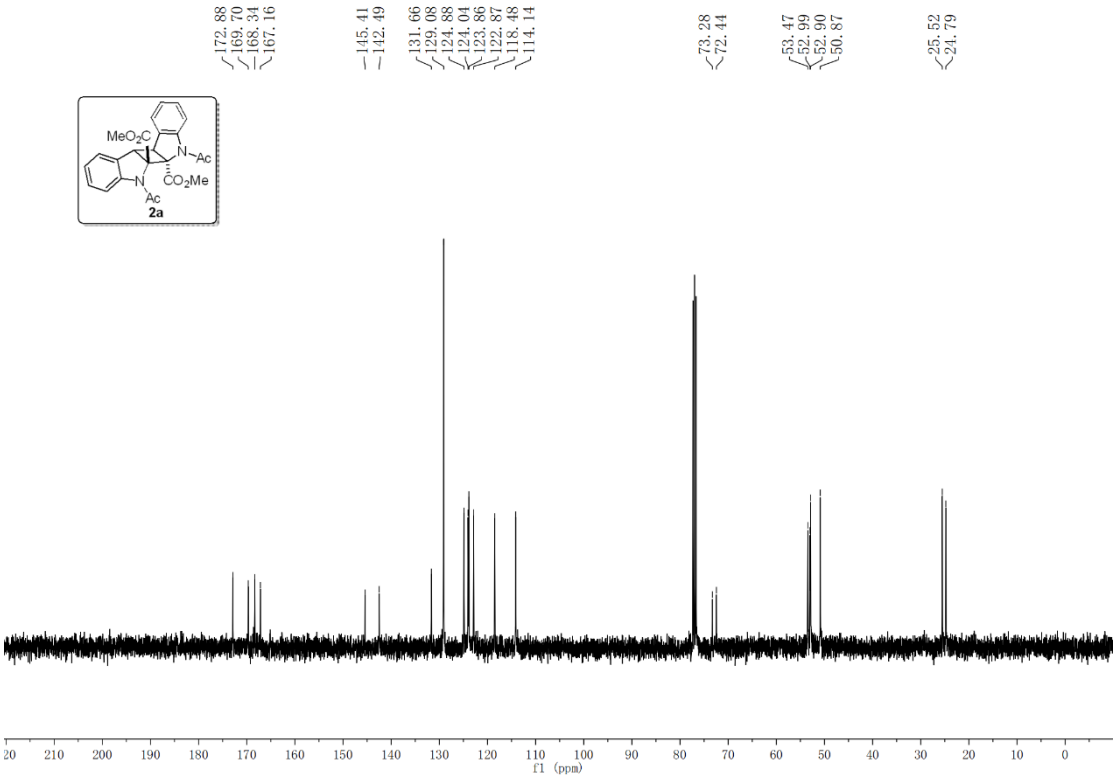
7.31
7.29
7.28
7.17
7.15
7.14
7.12
7.10
7.08
7.06
4.06
4.05
3.95
3.94
3.65
2.58
2.44
MeO2C
N
Ac
CO2Me
Ac
2a
1.05
4.09
3.28
1.00
1.02
6.29
3.18
3.19
f1 (ppm)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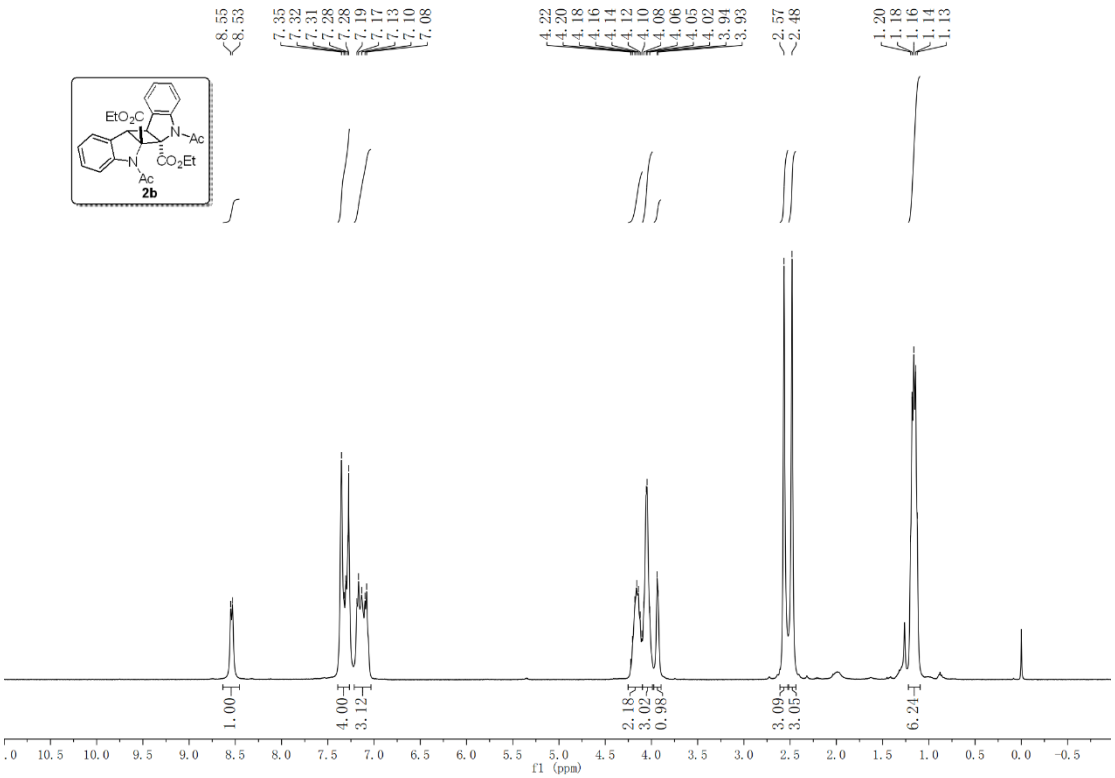
124.04
123.86
122.87
118.48
114.14
73.28
72.44
53.47
52.99
52.90
50.87
25.52
24.79
MeO2C
N
Ac
CO2Me
N
Ac
2a
f1 (ppm)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7.28
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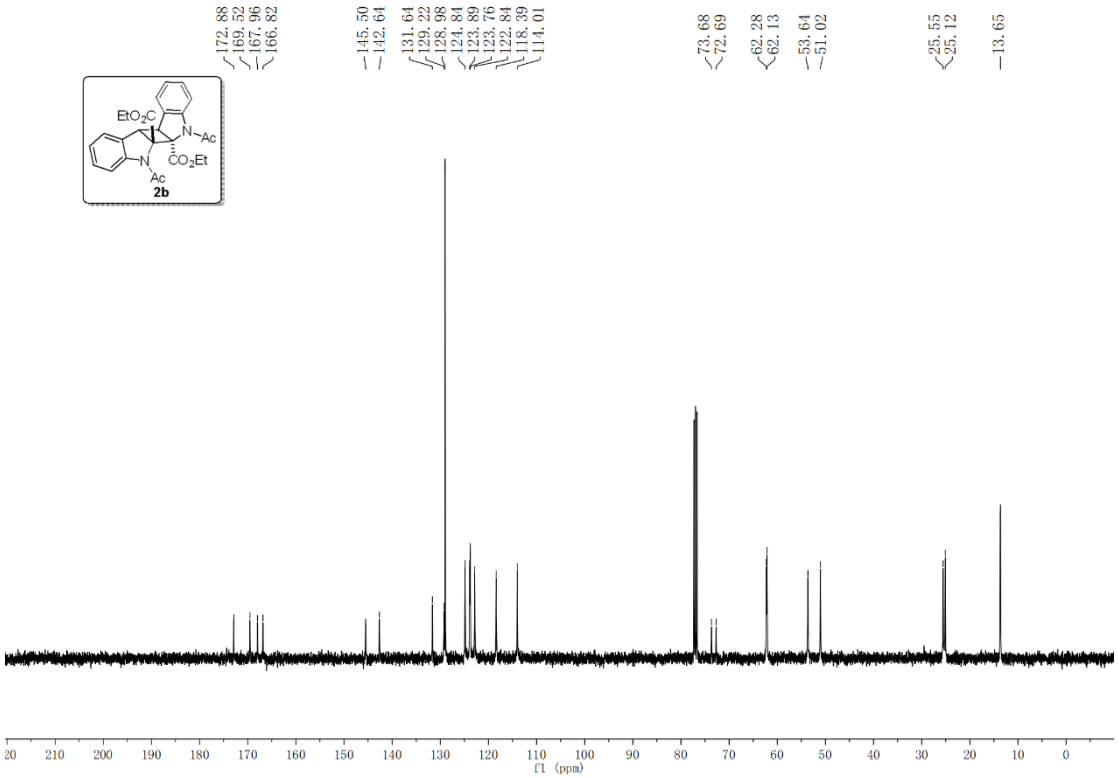
7.17
7.13
7.10
7.08
4.22
4.20
4.18
4.16
4.14
4.12
4.10
4.08
4.06
4.05
4.02
3.94
3.93
2.57
2.48
1.20
1.18
1.16
1.14
1.13
EtO2C
N
Ac
CO2Et
N
Ac
2b
1.00
4.00
3.12
2.18
3.02
0.98
3.09
3.05
6.24
f1 (ppm)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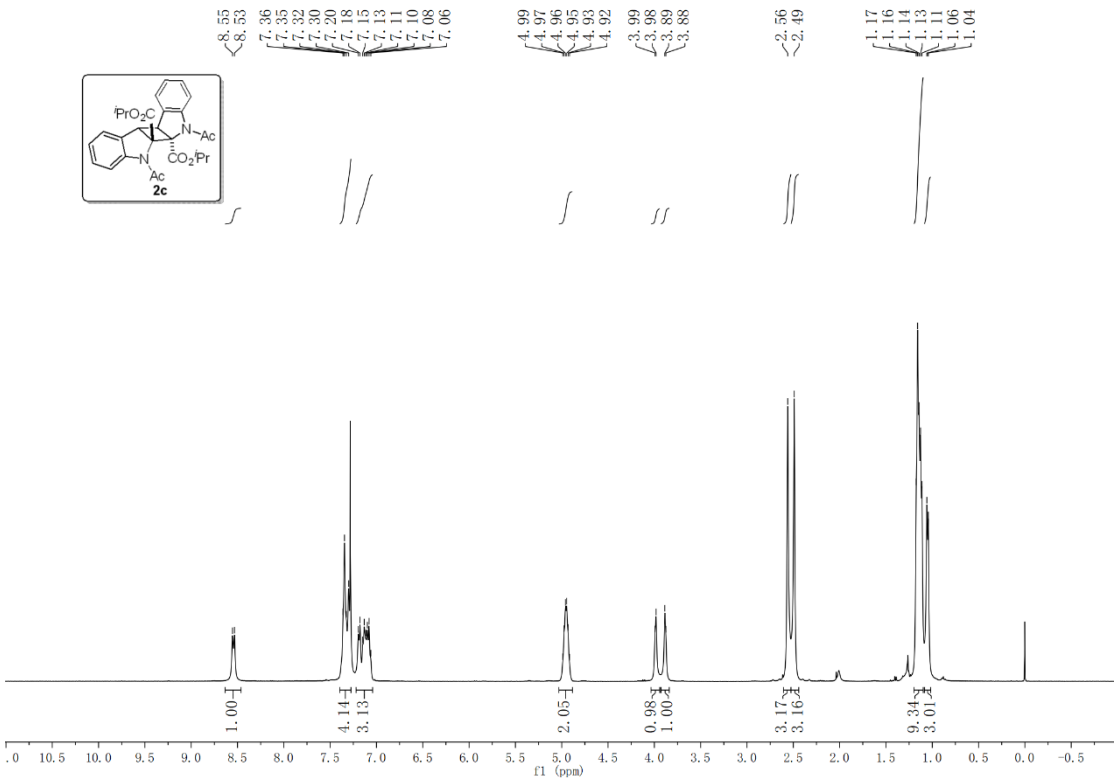
131.64
129.22
128.98
124.84
123.89
123.76
122.84
118.39
114.01
73.68
72.69
62.28
62.13
53.64
51.02
25.55
25.12
13.65
EtO2C
N
Ac
CO2Et
Ac
2b
f1 (ppm)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8.53
7.36
7.35
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7.20
7.18
7.15
7.13
7.11
7.10
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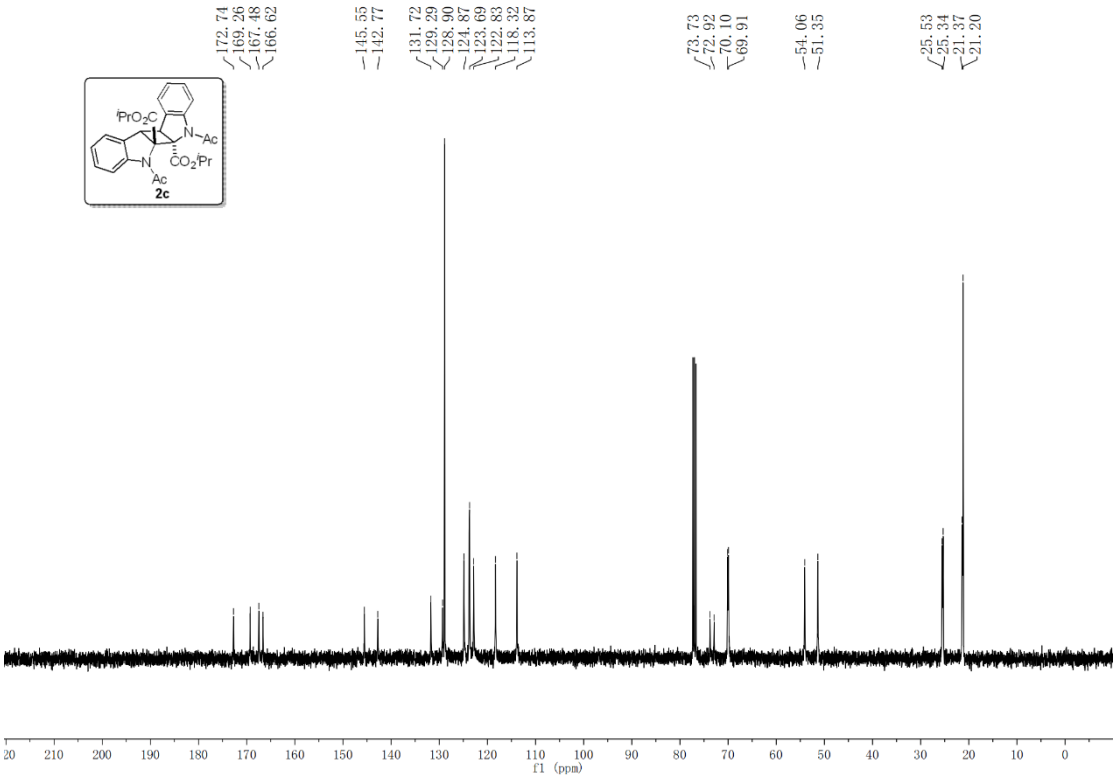
7.06
4.99
4.97
4.96
4.95
4.93
4.92
3.99
3.98
3.89
3.88
2.56
2.49
1.17
1.16
1.14
1.13
1.11
1.06
1.04
iPrO2C
N
Ac
CO2iPr
Ac
2c
1.00
4.14
3.13
2.05
0.98
1.00
3.17
3.16
9.34
3.01
f1 (ppm)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131.72
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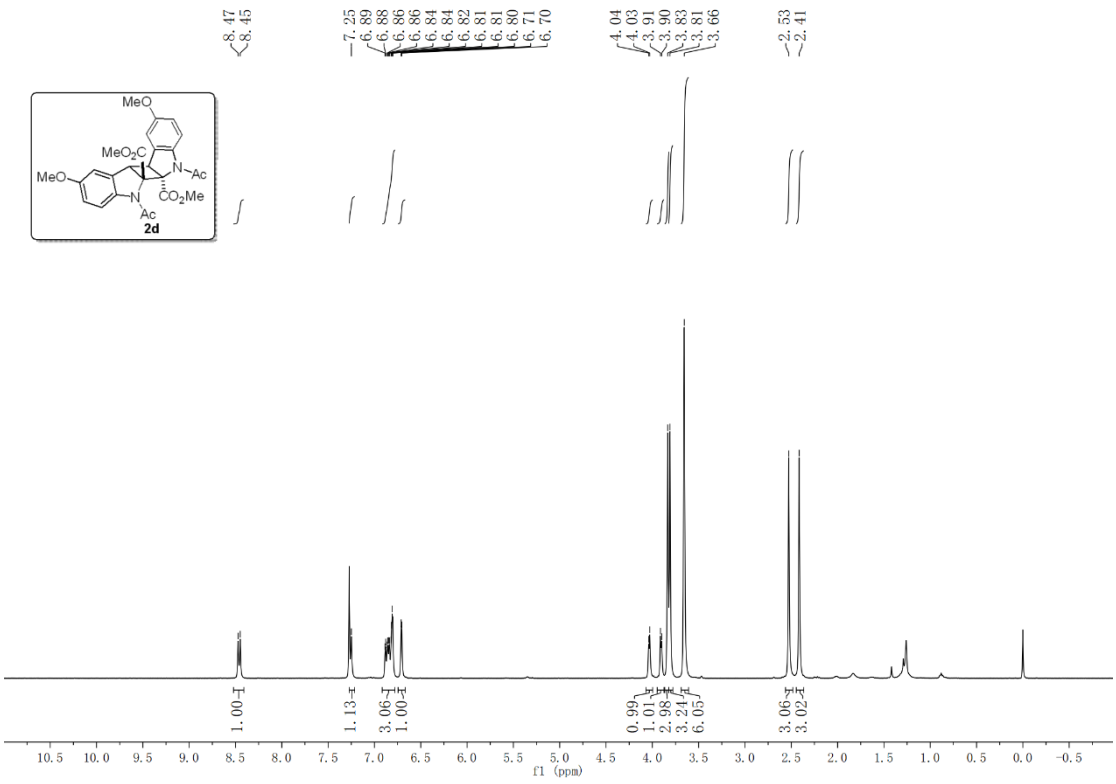
124.87
123.69
122.83
118.32
113.87
73.73
72.92
70.10
69.91
54.06
51.35
25.53
25.34
21.37
21.20
iPrO2C
N
Ac
CO2iPr
N
Ac
2c
f1 (ppm)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8.45
7.25
6.89
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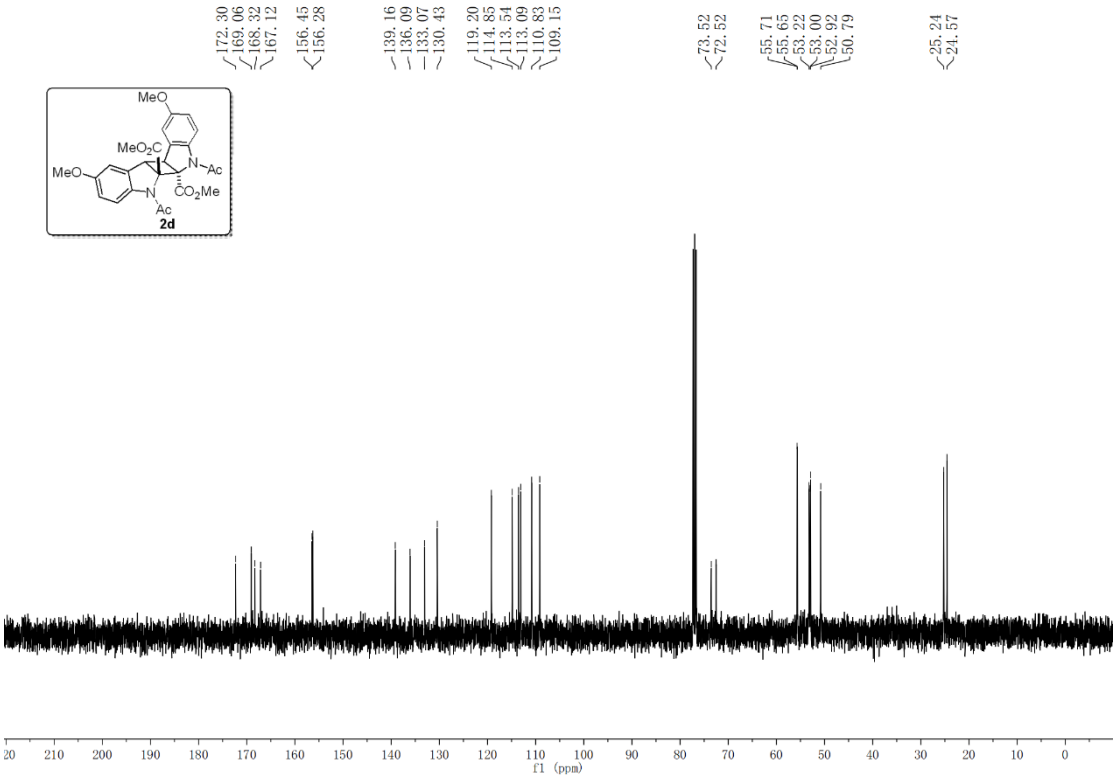
6.86
6.86
6.84
6.84
6.82
6.81
6.81
6.80
6.71
6.70
4.04
4.03
3.91
3.90
3.83
3.81
3.66
2.53
2.41
MeO
MeO2C
N
Ac
MeO
N
CO2Me
Ac
2d
1.00
1.13
3.06
1.00
0.99
1.01
2.98
3.24
6.05
3.06
3.02
f1 (ppm)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169.06
168.32
167.12
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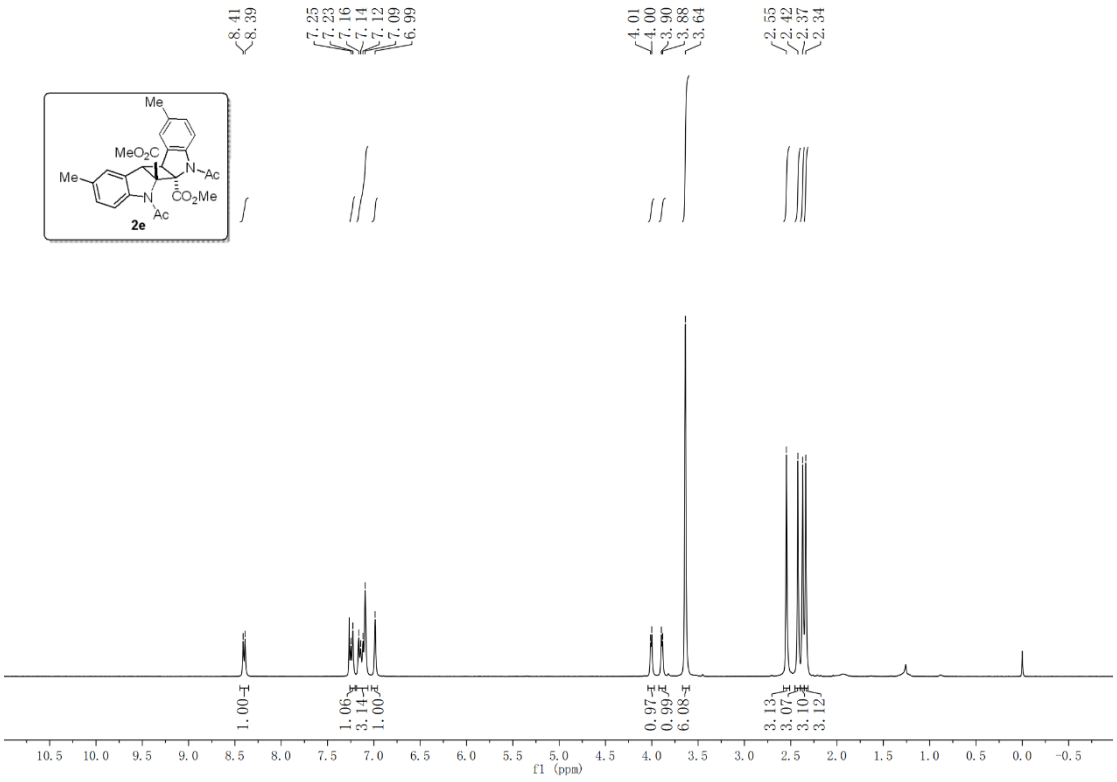
156.28
139.16
136.09
133.07
130.43
119.20
114.85
113.54
113.09
110.83
109.15
73.52
72.52
55.71
55.65
53.22
53.00
52.92
50.79
25.24
24.57
MeO
MeO2C
N
Ac
MeO
N
CO2Me
Ac
2d
f1 (ppm)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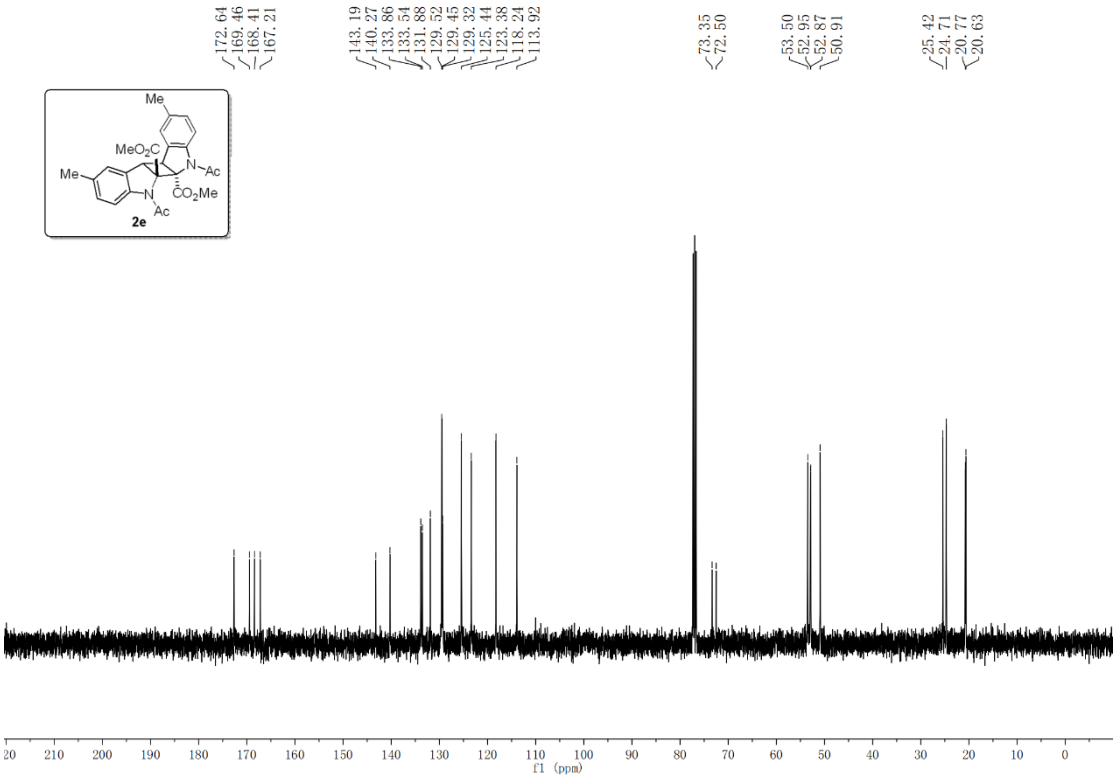
7.12
7.09
6.99
4.01
4.00
3.90
3.88
3.64
2.55
2.42
2.37
2.34
Me
MeO2C
N
Ac
Me
N
CO2Me
Ac
2e
1.00
1.06
3.14
1.00
0.97
0.99
6.08
3.13
3.07
3.10
3.12
f1 (ppm)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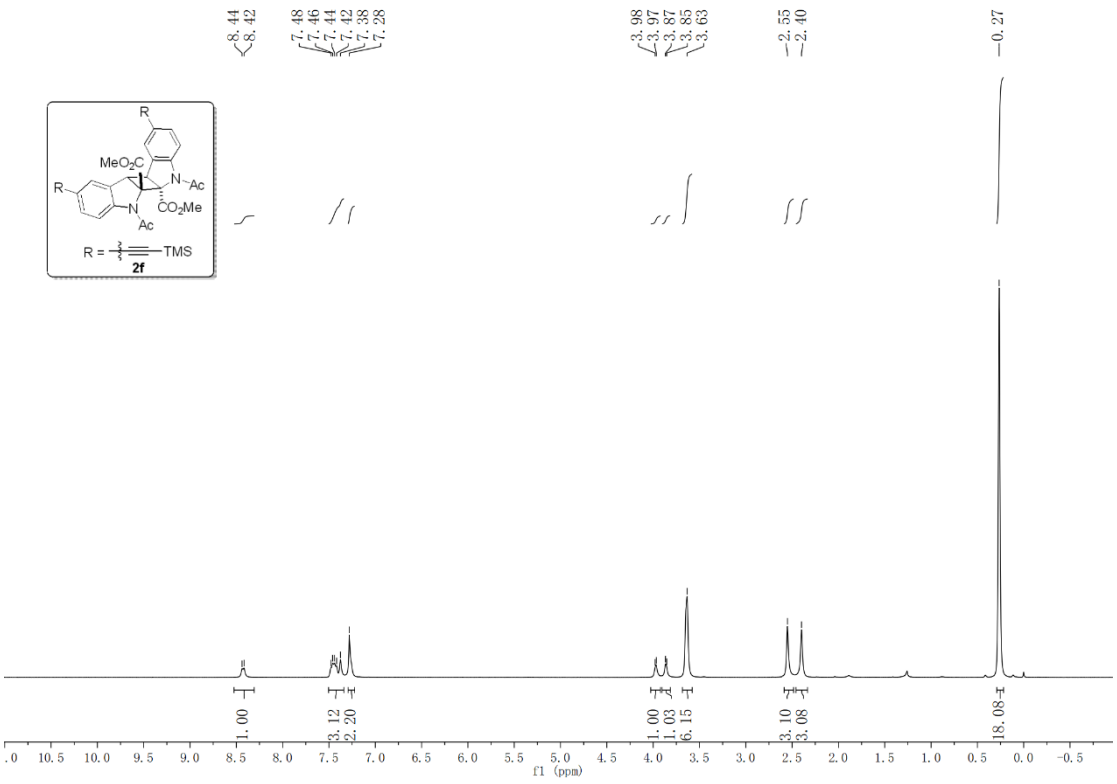
133.54
131.88
129.52
129.45
129.32
125.44
123.38
118.24
113.92
73.35
72.50
53.50
52.95
52.87
50.91
25.42
24.71
20.77
20.63
Me
MeO2C
N
Ac
Me
N
CO2Me
Ac
2e
f1 (ppm)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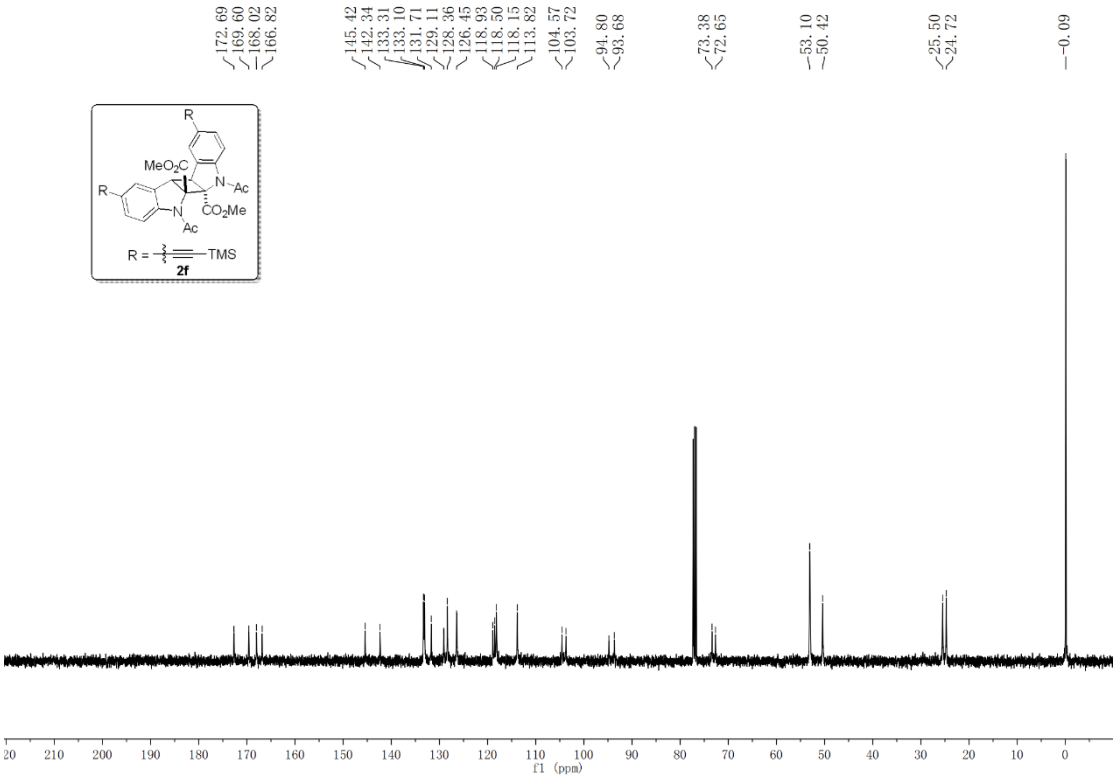
7.46
7.44
7.42
7.38
7.28
3.98
3.97
3.87
3.85
3.63
2.55
2.40
0.27
R
MeO2C
N
Ac
R
N
CO2Me
Ac
R = TMS
2f
1.00
3.12
2.20
1.00
1.03
6.15
3.10
3.08
18.08
f1 (ppm)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118.50
118.15
113.82
104.57
103.72
94.80
93.68
73.38
72.65
53.10
50.42
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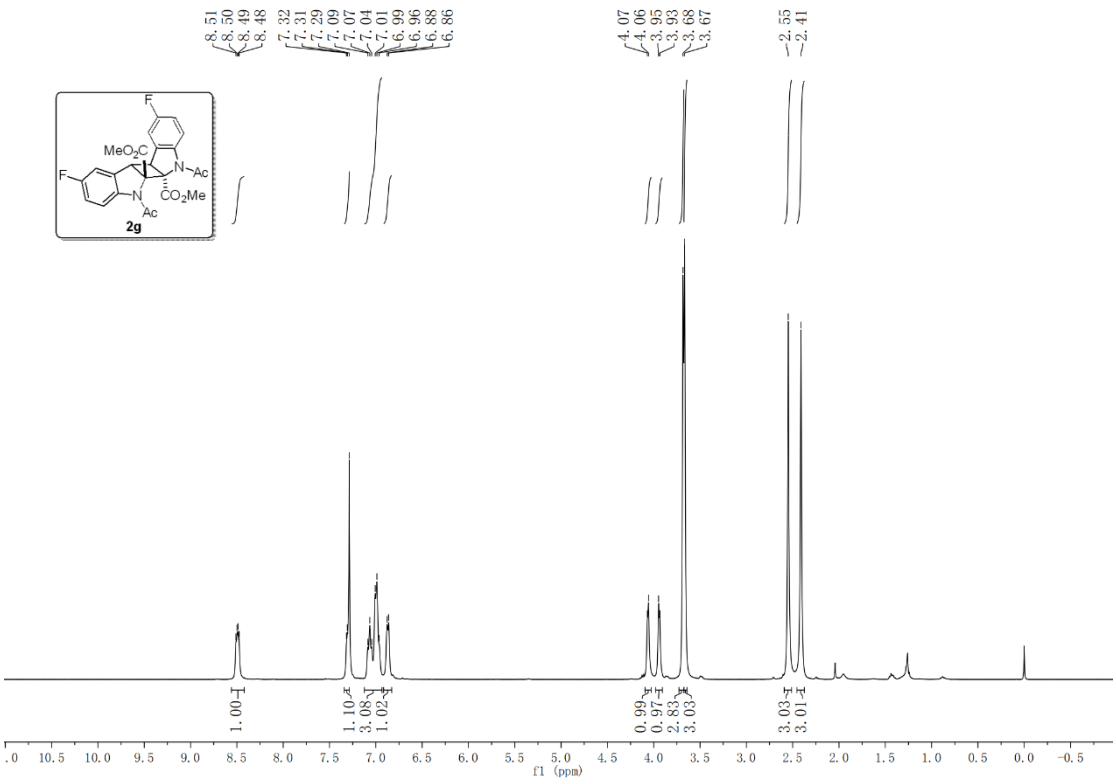
24.72
-0.09
MeO2C
N
Ac
R
CO2Me
Ac
R = TMS
2f
f1 (ppm)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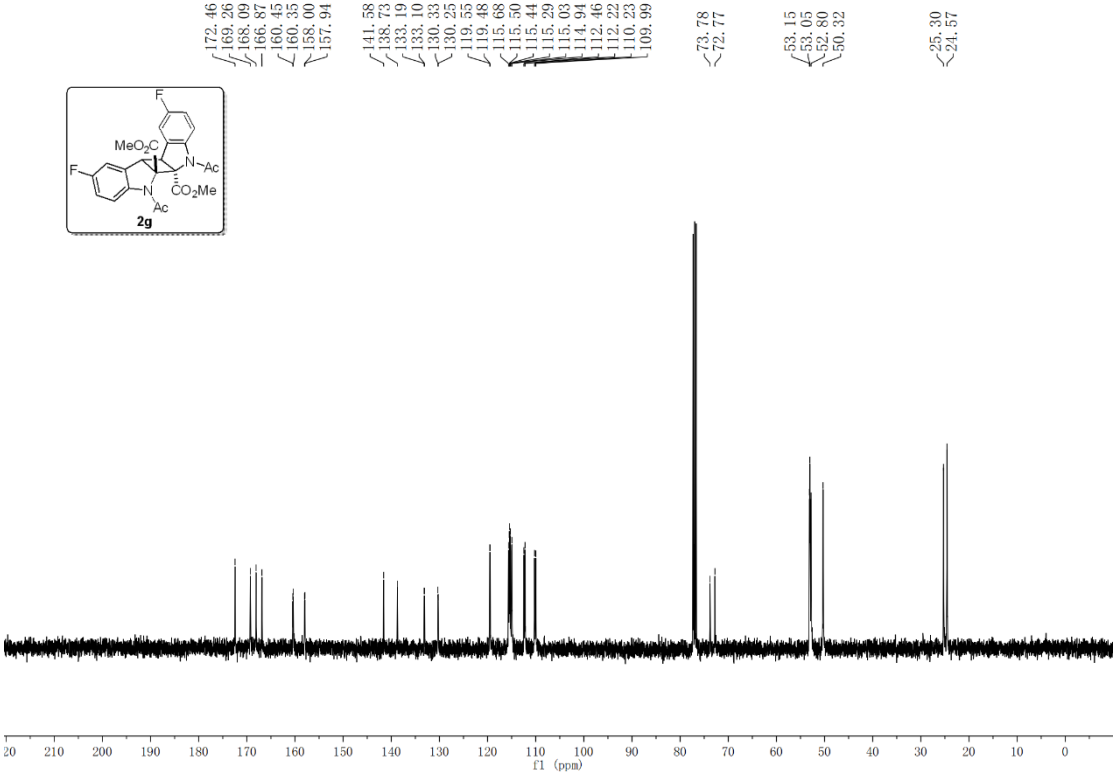
7.07
7.04
7.01
6.99
6.96
6.88
6.86
4.07
4.06
3.95
3.93
3.68
3.67
2.55
2.41
F
MeO2C
N
Ac
F
CO2Me
Ac
2g
1.00
1.10
3.08
1.02
0.99
0.97
2.83
3.03
3.03
3.01
f1 (ppm)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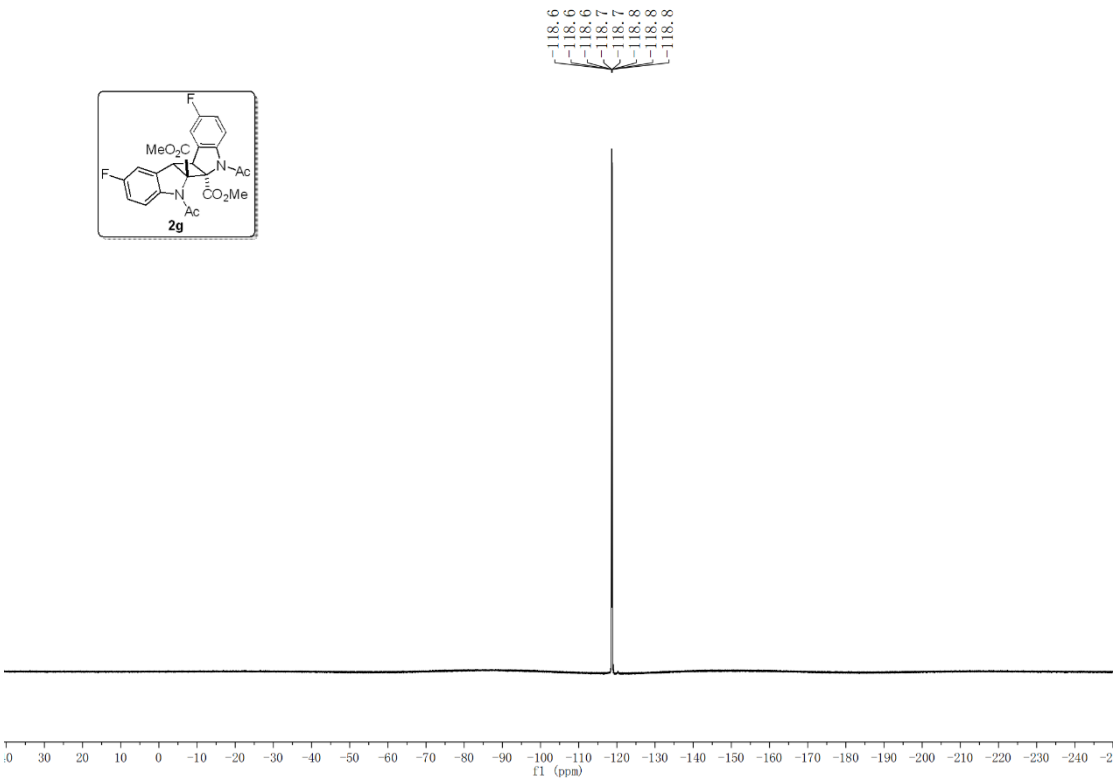
133.10
130.33
130.25
119.55
119.48
115.68
115.50
115.44
115.29
115.03
114.94
112.46
112.22
110.23
109.99
73.78
72.77
53.15
53.05
52.80
50.32
25.30
24.57
F
MeO2C
N
Ac
F
N
CO2Me
Ac
2g
f1 (ppm)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-118.6
-118.6
-118.7
-118.7
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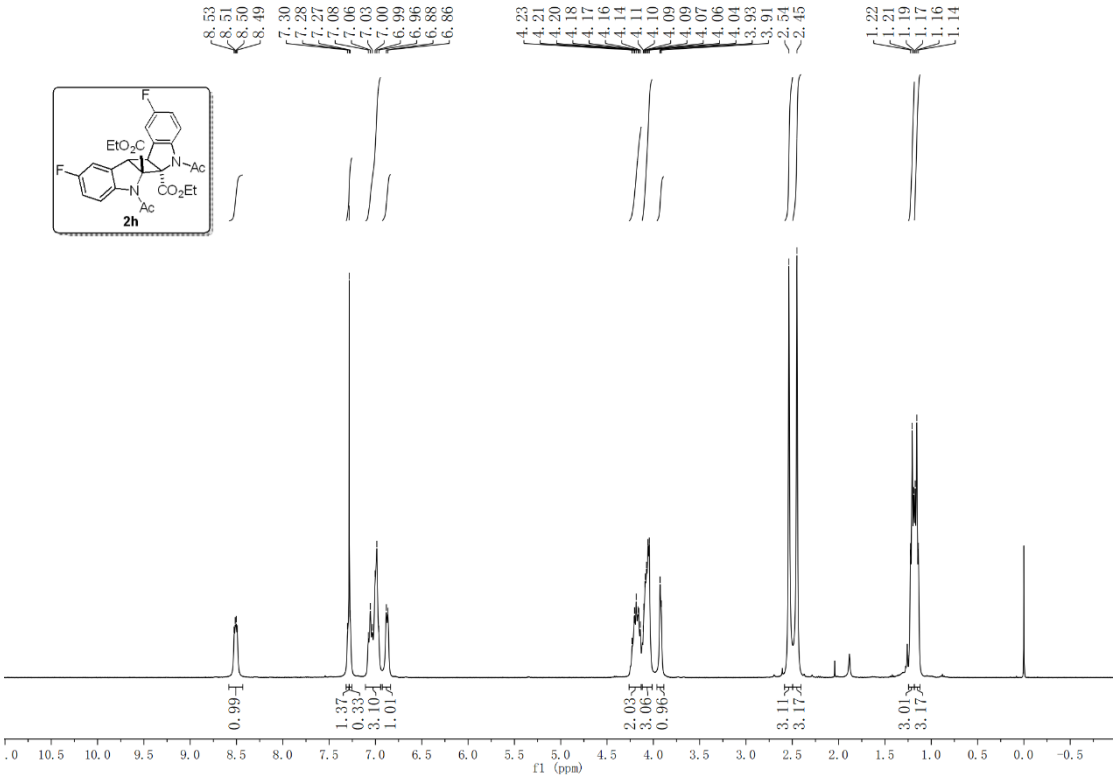
-118.8
-118.8
F
MeO2C
N
Ac
F
N
CO2Me
Ac
2g
f1 (ppm)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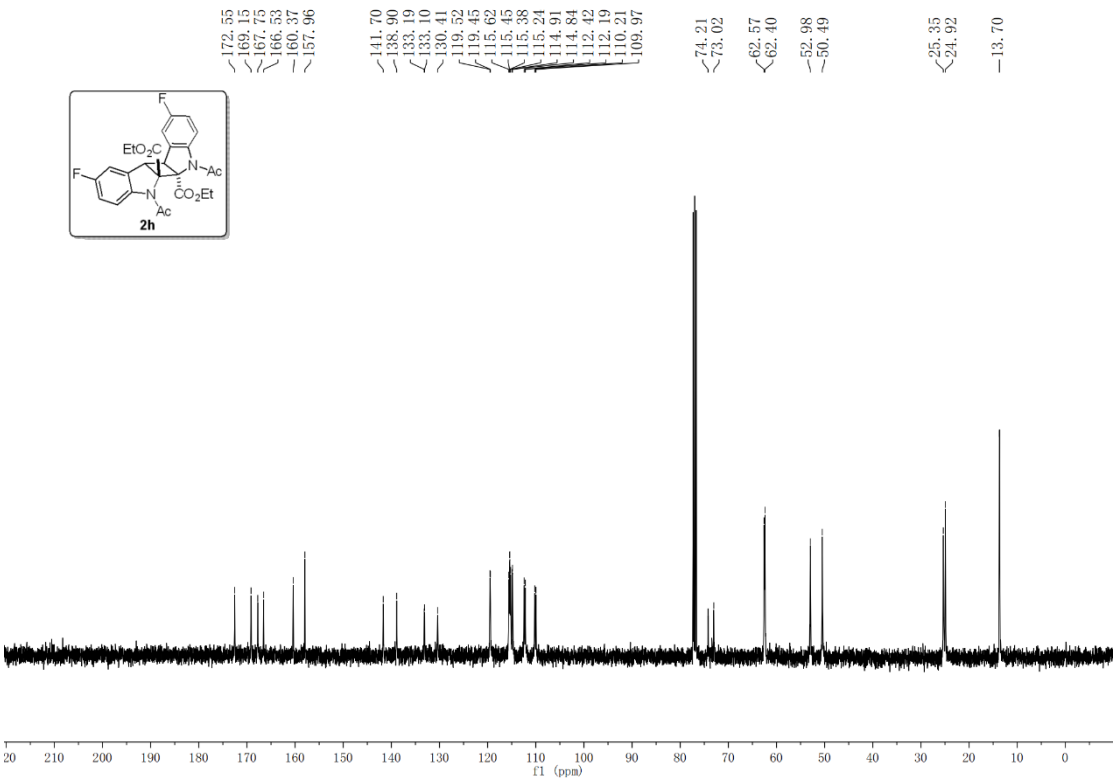
7.28
7.27
7.08
7.06
7.03
7.00
6.99
6.96
6.88
6.86
4.23
4.21
4.20
4.18
4.17
4.16
4.14
4.11
4.10
4.09
4.09
4.07
4.06
4.04
3.93
3.91
2.54
2.45
1.22
1.21
1.19
1.17
1.16
1.14
F
EtO2C
N
Ac
F
N
CO2Et
Ac
2h
0.99
1.37
0.33
3.10
1.01
2.03
3.06
0.96
3.11
3.17
3.01
3.17
f1 (ppm)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115.62
115.45
115.38
115.24
114.91
114.84
112.42
112.19
110.21
109.97
74.21
73.02
62.57
62.40
52.98
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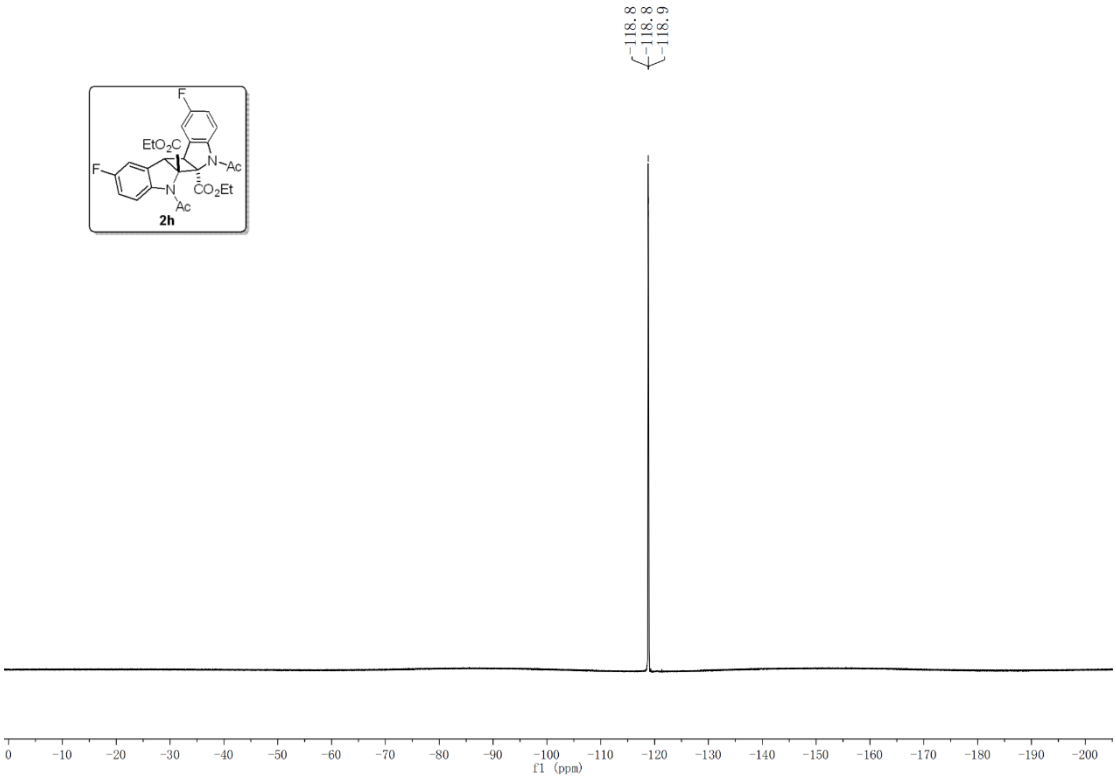
24.92
13.70
F
EtO2C
N
Ac
F
N
CO2Et
Ac
2h
f1 (ppm)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-118.9
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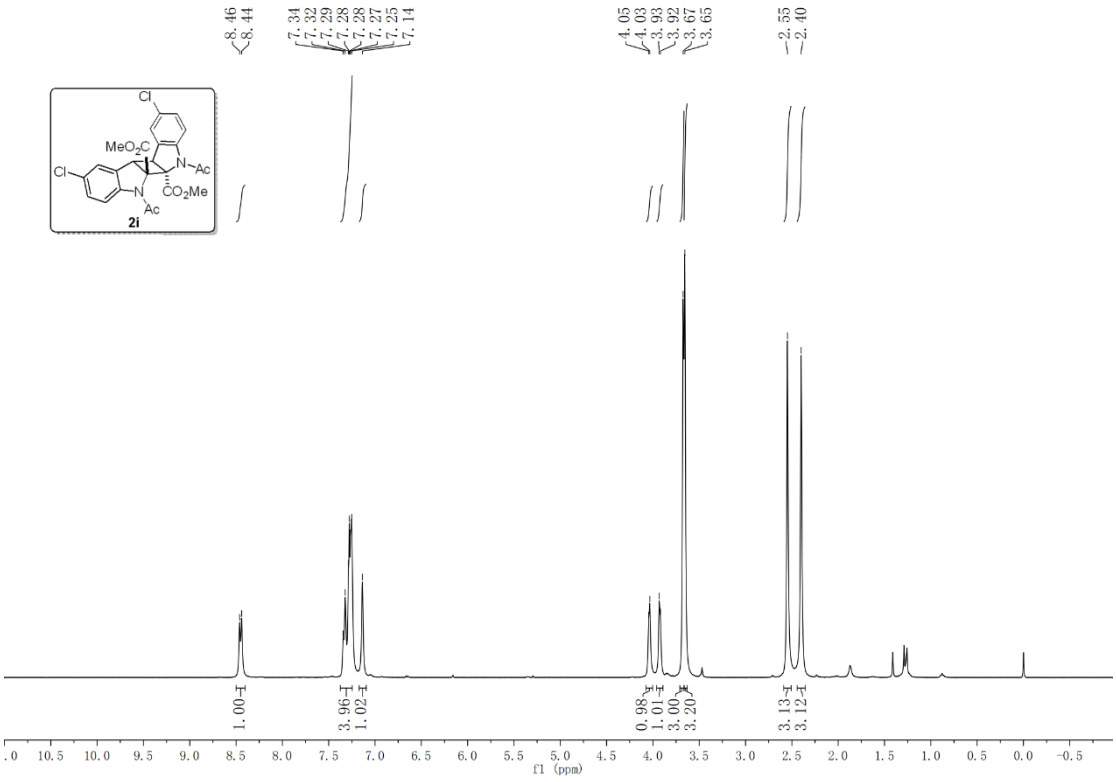
N
Ac
F
N
CO2Et
Ac
2h
f1 (ppm)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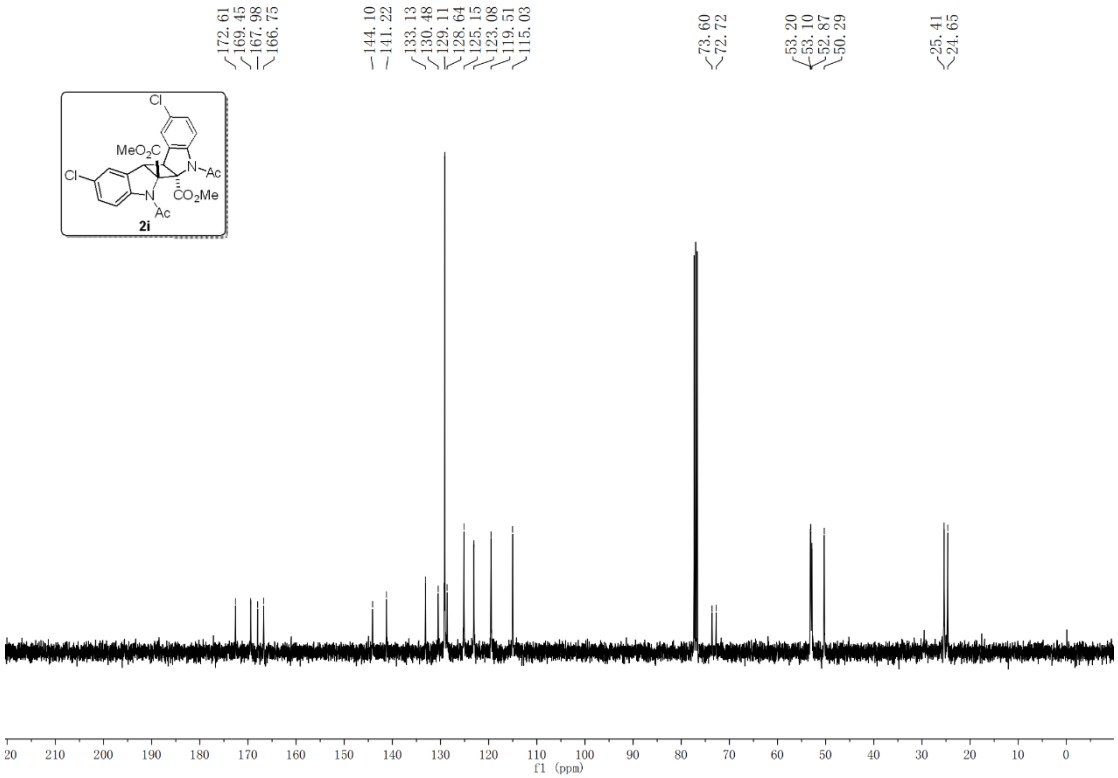
7.28
7.28
7.27
7.25
7.14
4.05
4.03
3.93
3.92
3.67
3.65
2.55
2.40
Cl
MeO2C
N
Ac
Cl
N
CO2Me
Ac
2i
1.00
3.96
1.02
0.98
1.01
3.00
3.20
3.13
3.12
f1 (ppm)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141.22
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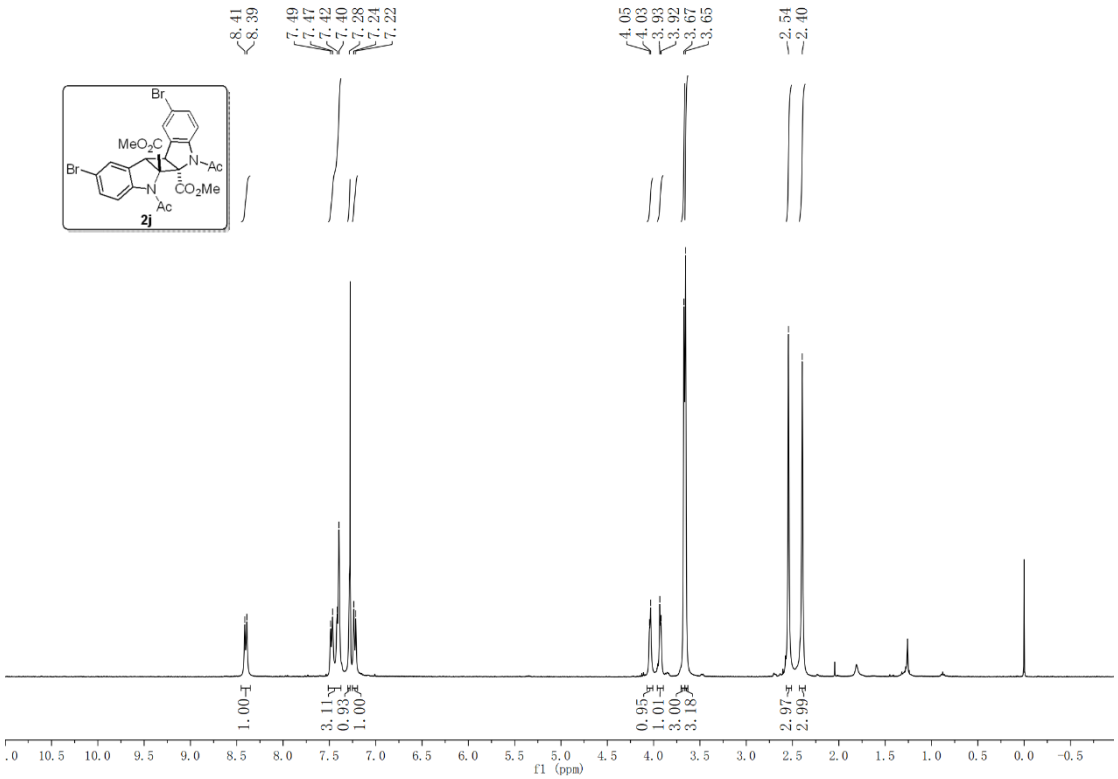
130.48
129.11
128.64
125.15
123.08
119.51
115.03
73.60
72.72
53.20
53.10
52.87
50.29
25.41
24.65
Cl
MeO2C
N
Ac
Cl
N
CO2Me
Ac
2i
f1 (ppm)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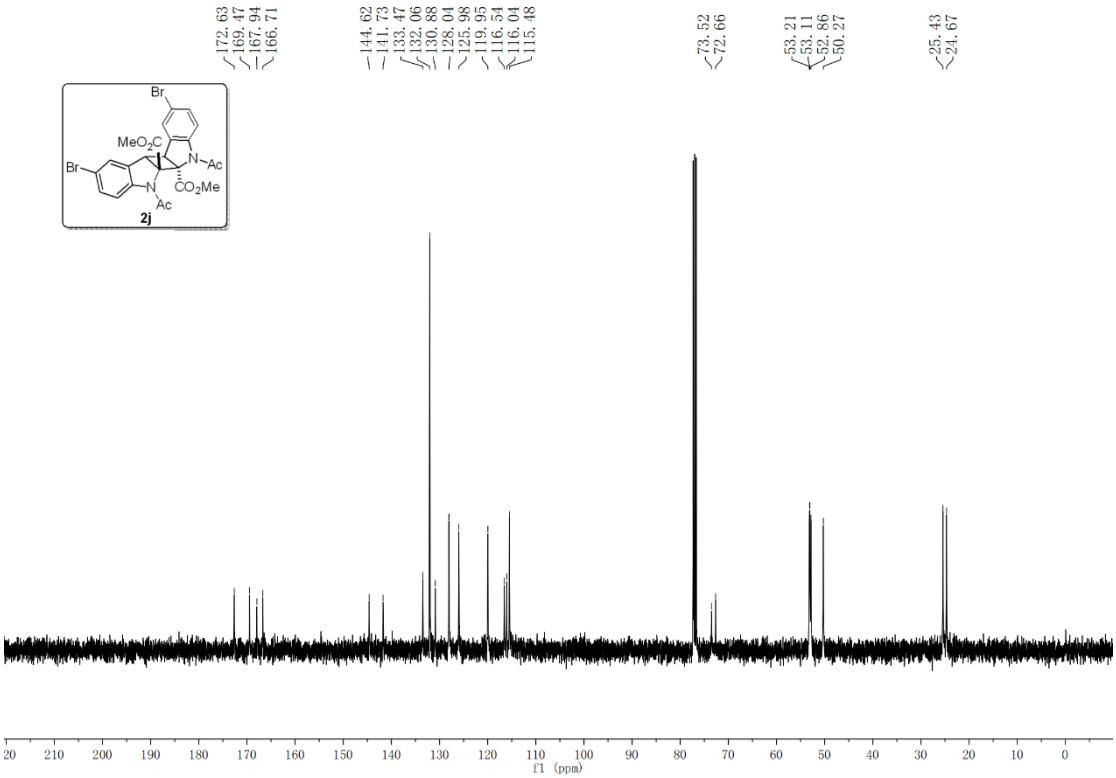
7.40
7.28
7.24
7.22
4.05
4.03
3.93
3.92
3.67
3.65
2.54
2.40
Br
MeO2C
N
Ac
Br
N
CO2Me
Ac
2j
1.00
3.11
0.93
1.00
0.95
1.01
3.00
3.18
2.97
2.99
f1 (ppm)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132.06
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128.04
125.98
119.95
116.54
116.04
115.48
73.52
72.66
53.21
53.11
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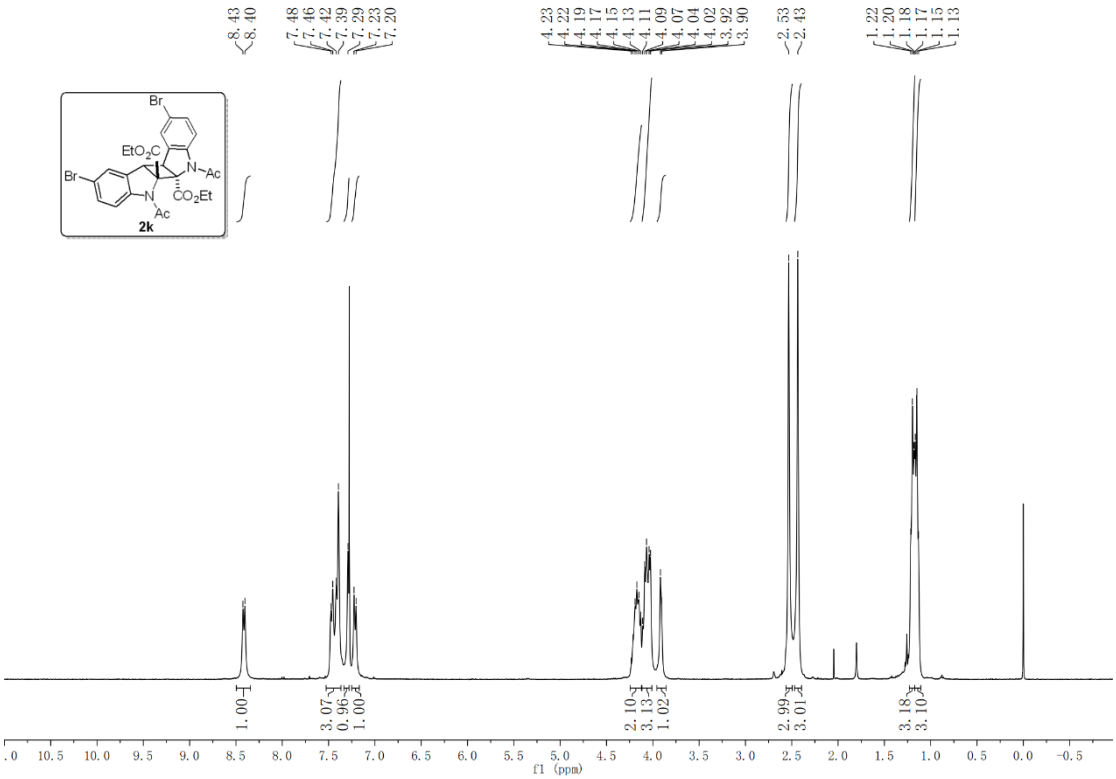
25.43
24.67
Br
MeO2C
N
Ac
Br
N
CO2Me
Ac
2j
f1 (ppm)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4.19
4.17
4.15
4.13
4.11
4.09
4.07
4.04
4.02
3.92
3.90
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2.43
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1.18
1.17
1.15
1.13
Br
EtO2C
N
Ac
Br
N
CO2Et
Ac
2k
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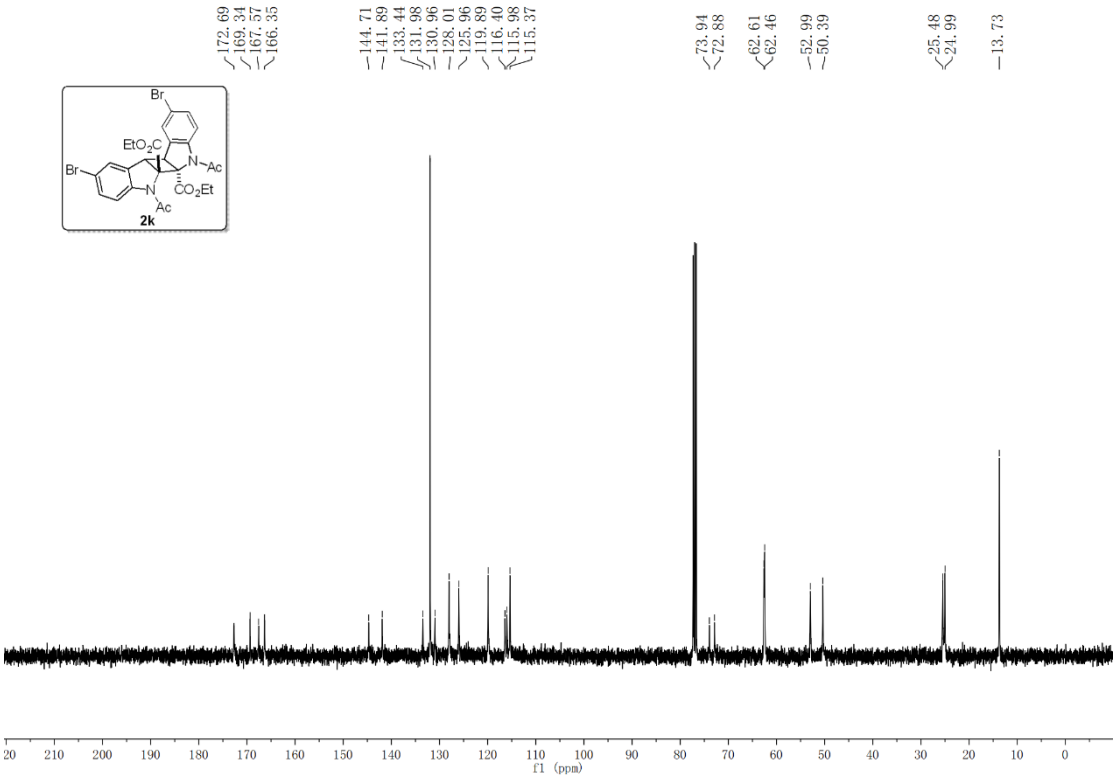
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73.94
72.88
62.61
62.46
52.99
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Ac
CO2Et
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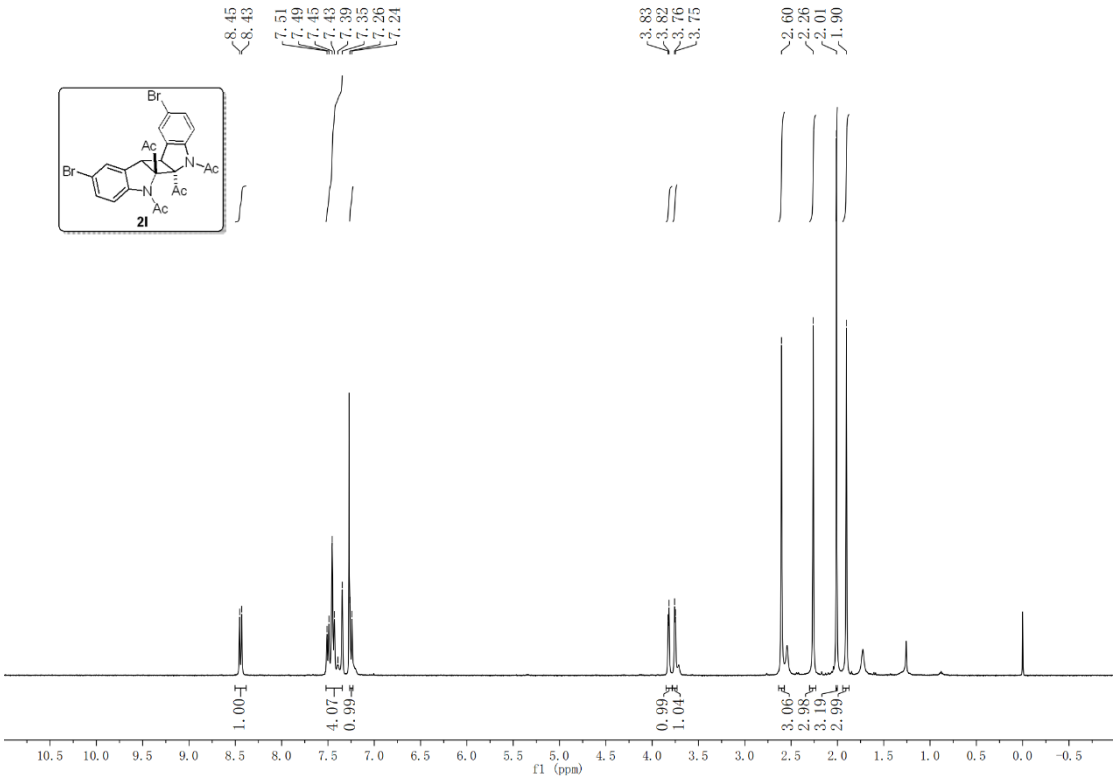
2k
f1 (ppm)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2.60
2.26
2.01
1.90
Br
Ac
N
Ac
Br
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0.99
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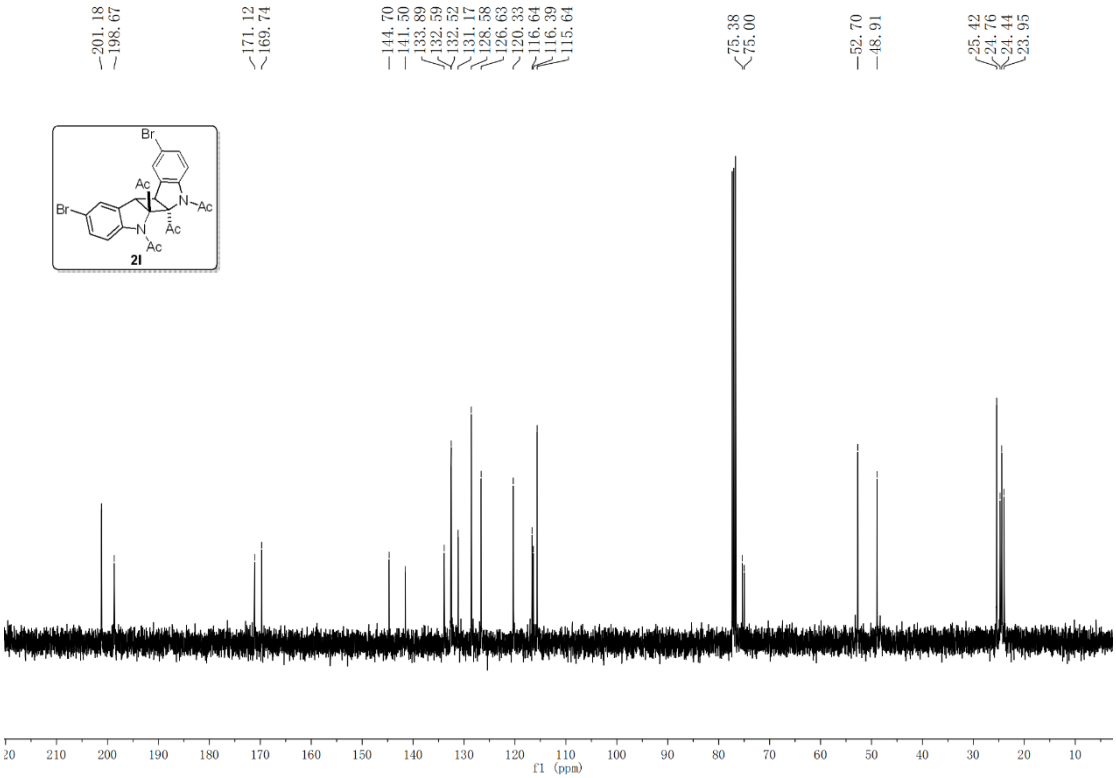
2.99
f1 (ppm)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75.38
75.00
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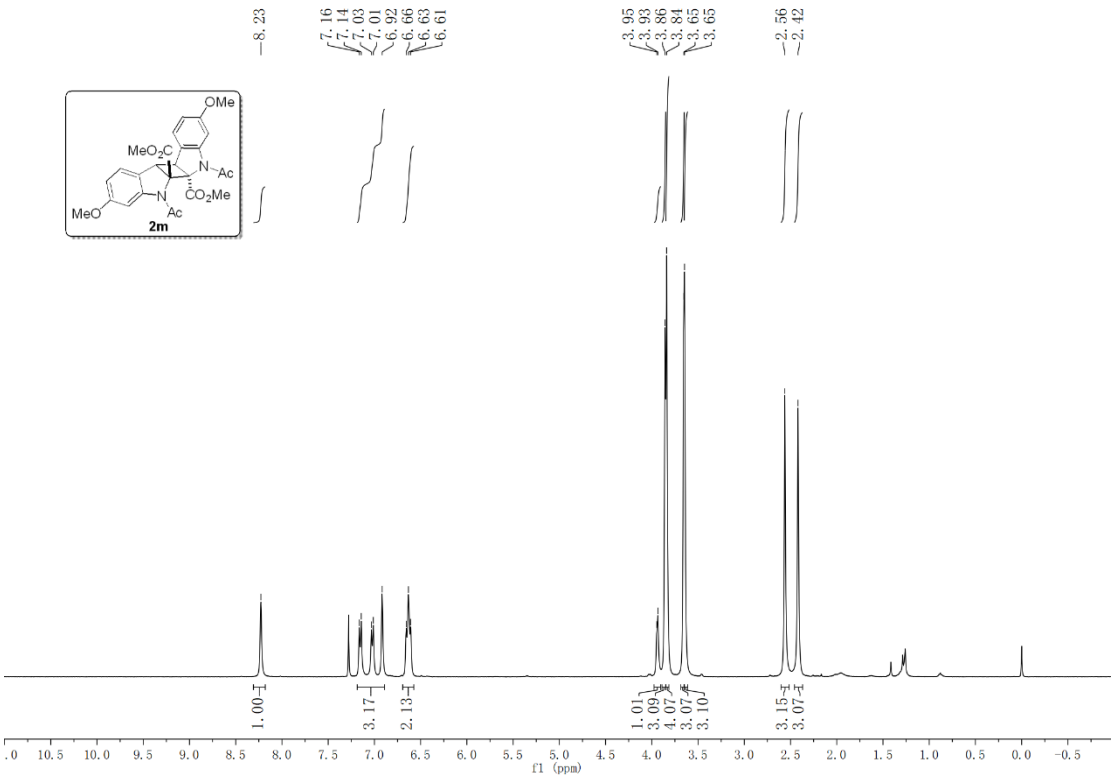
Ac
N
Ac
Br
N
Ac
2l
f1 (ppm)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3.84
3.65
3.65
2.56
2.42
OMe
MeO2C
N
Ac
CO2Me
MeO
N
Ac
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3.07
3.10
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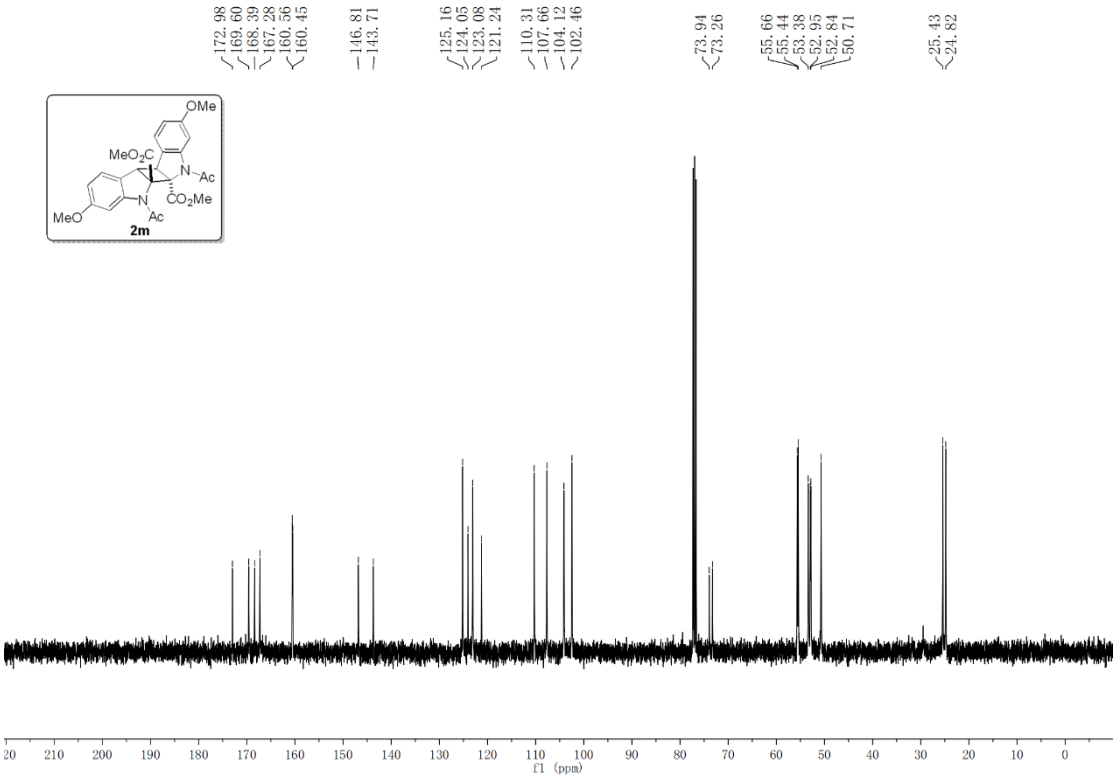
3.07
f1 (ppm)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104.12
102.46
73.94
73.26
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53.38
52.95
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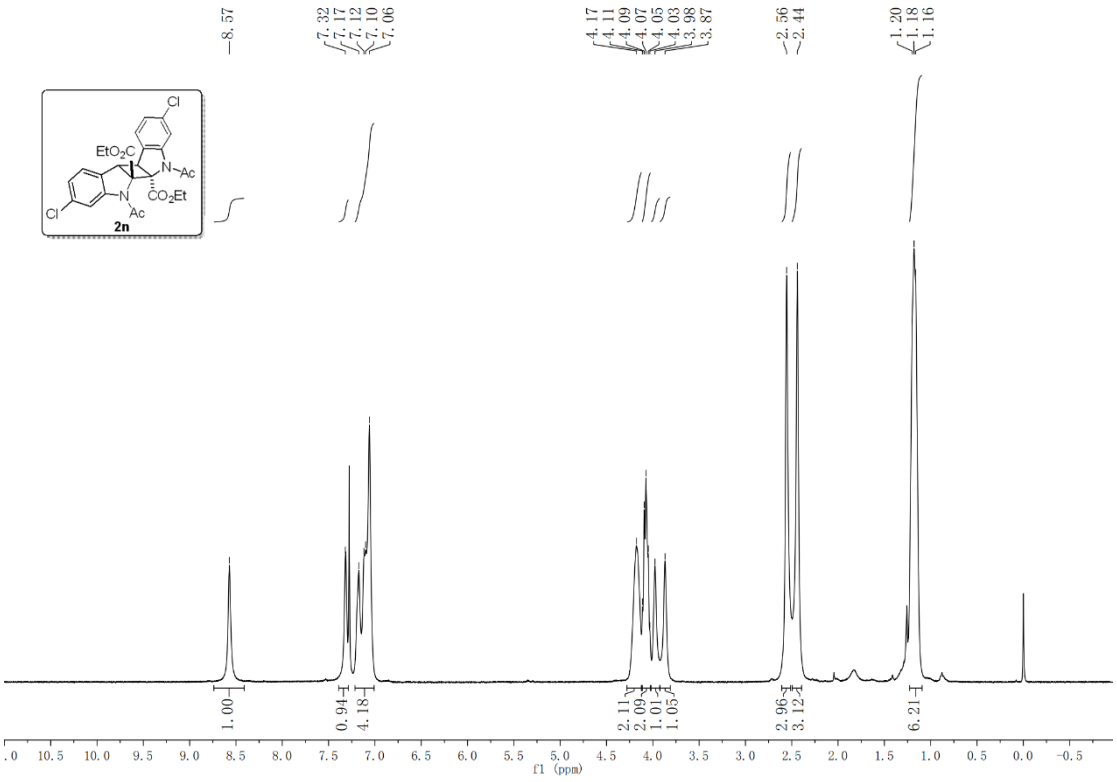
CO2Me
MeO
N
Ac
2m
f1 (ppm)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4.07
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2.56
2.44
1.20
1.18
1.16
Cl
EtO2C
N
Ac
CO2Et
N
Ac
Cl
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1.01
1.05
2.96
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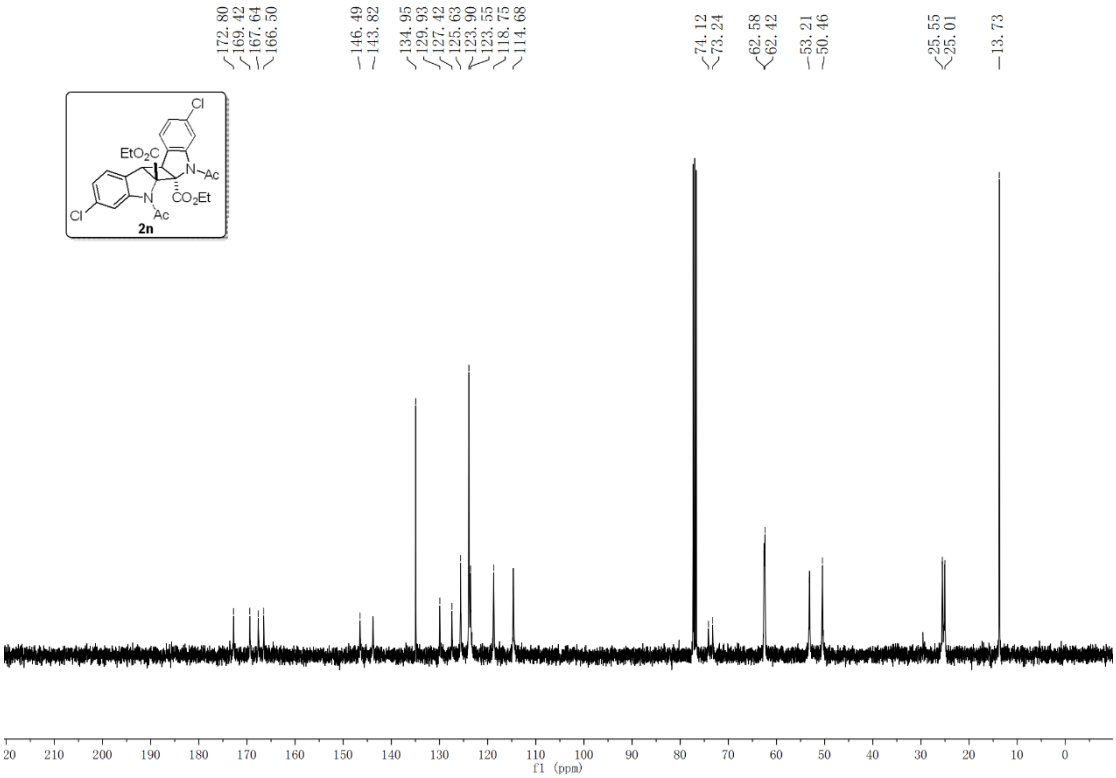
6.21
f1 (ppm)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114.68
74.12
73.24
62.58
62.42
53.21
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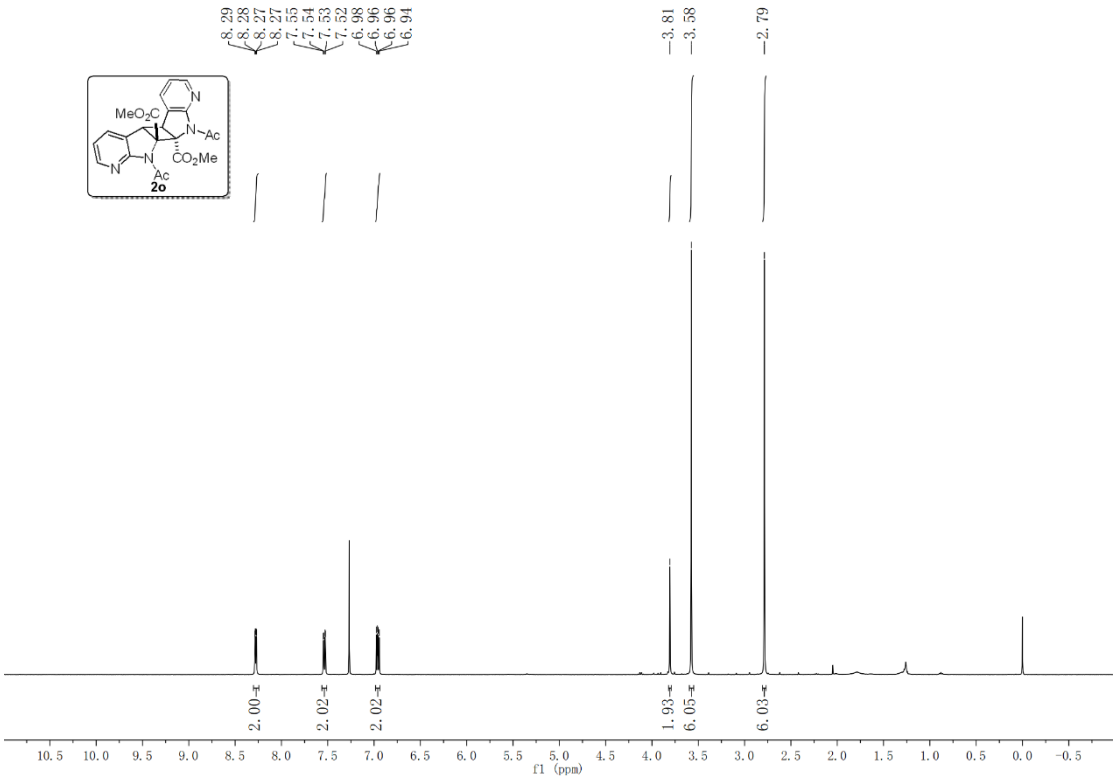
25.01
13.73
Cl
EtO2C
N
Ac
CO2Et
Cl
N
Ac
2n
f1 (ppm)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6.96
6.96
6.94
3.81
3.58
2.79
MeO2C
N
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N
Ac
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2.00
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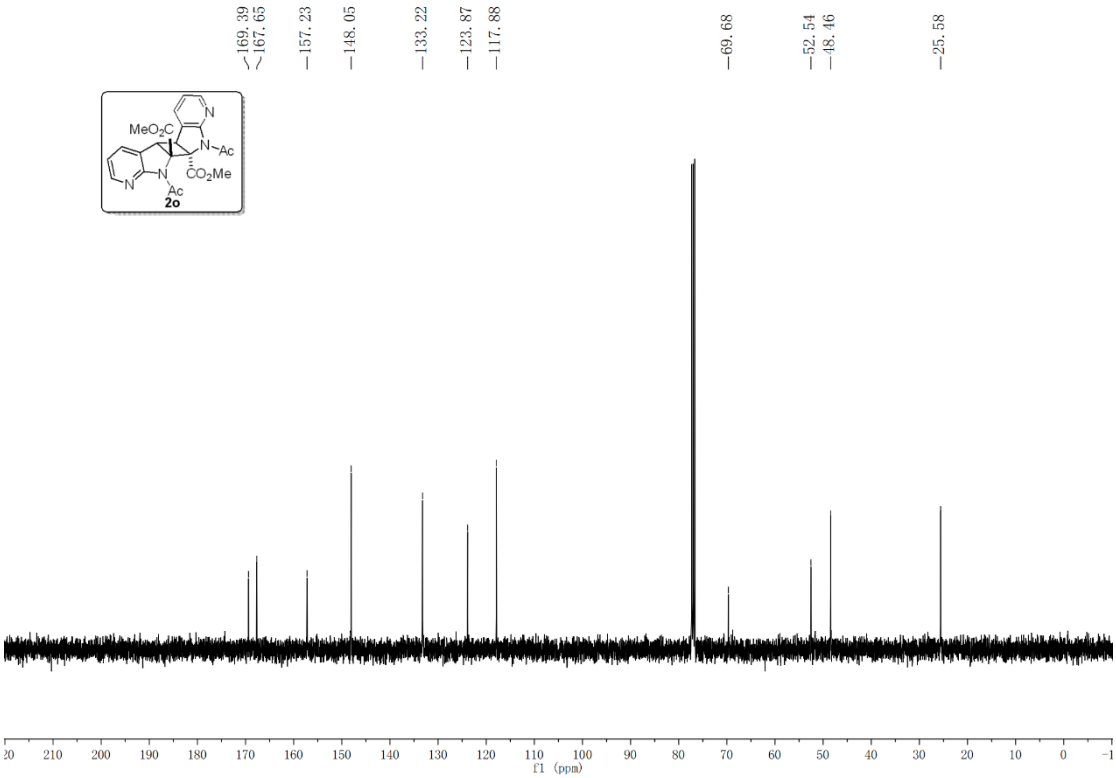
2.02
1.93
6.05
6.03
f1 (ppm)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25.58
MeO2C
N
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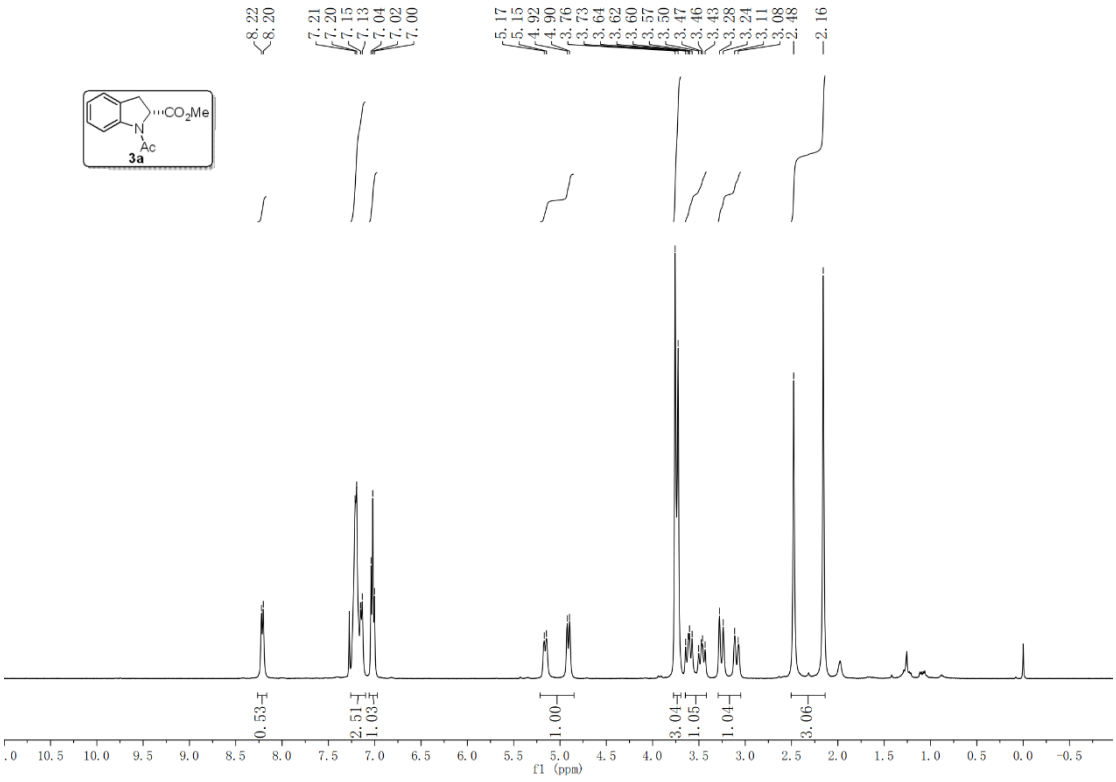
Ac
CO2Me
N
Ac
2o
f1 (ppm)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3.62
3.60
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3.47
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3.24
3.11
3.08
2.48
2.16
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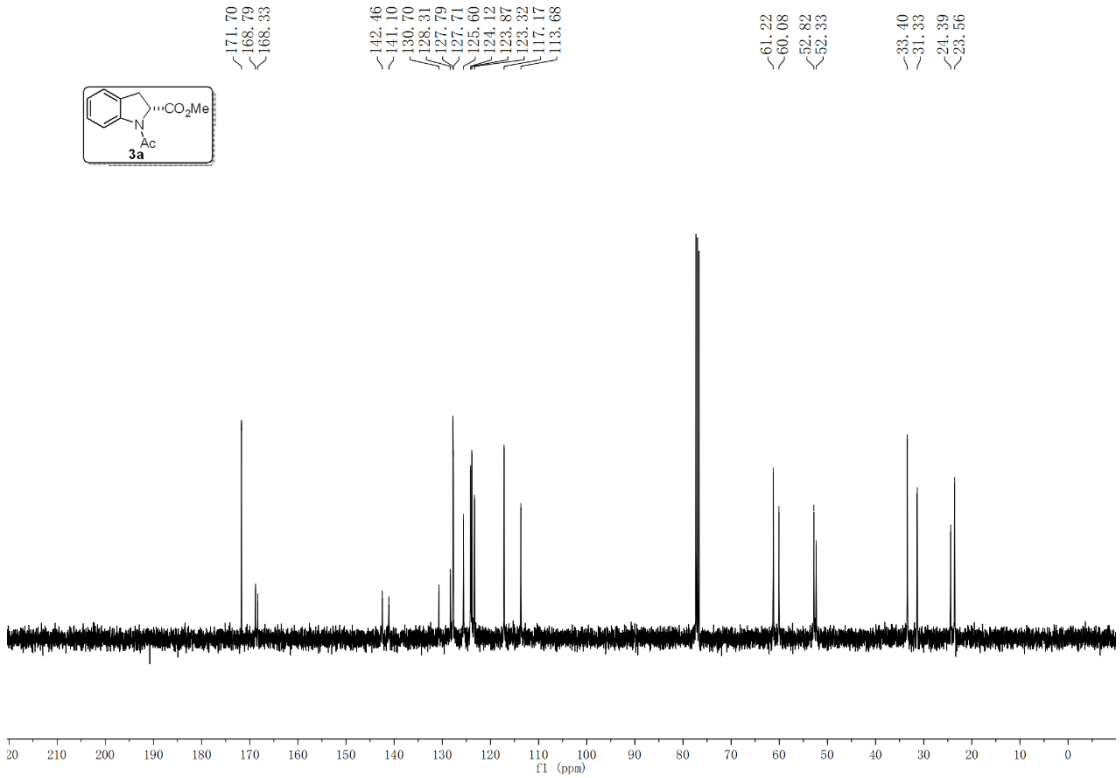
3.06
f1 (ppm)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123.32
117.17
113.68
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24.39
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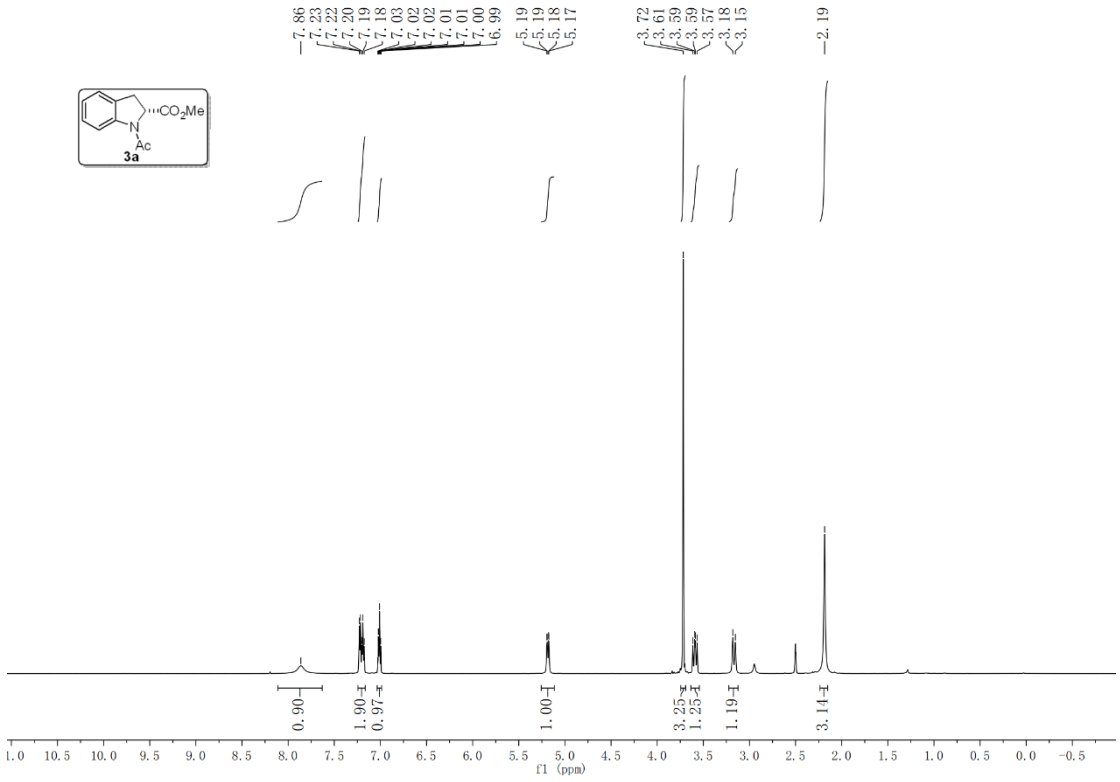
CO2Me
N
Ac
3a
f1 (ppm)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3.59
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3.15
2.19
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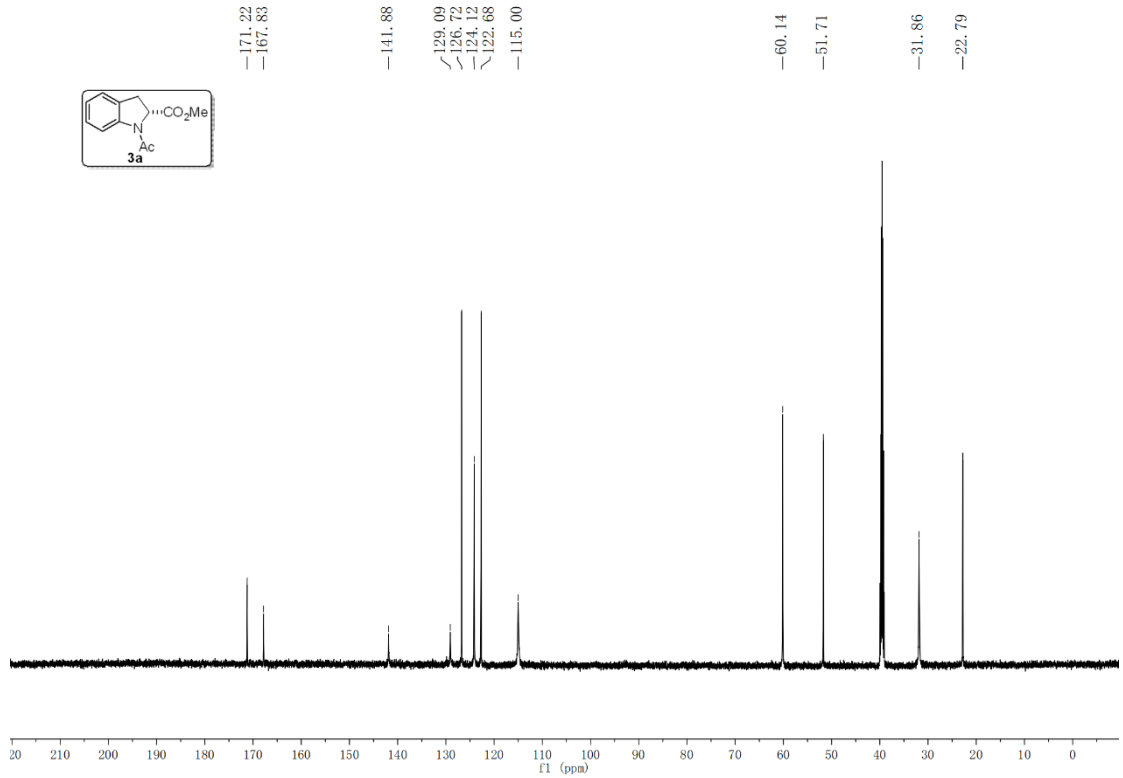
f1 (ppm)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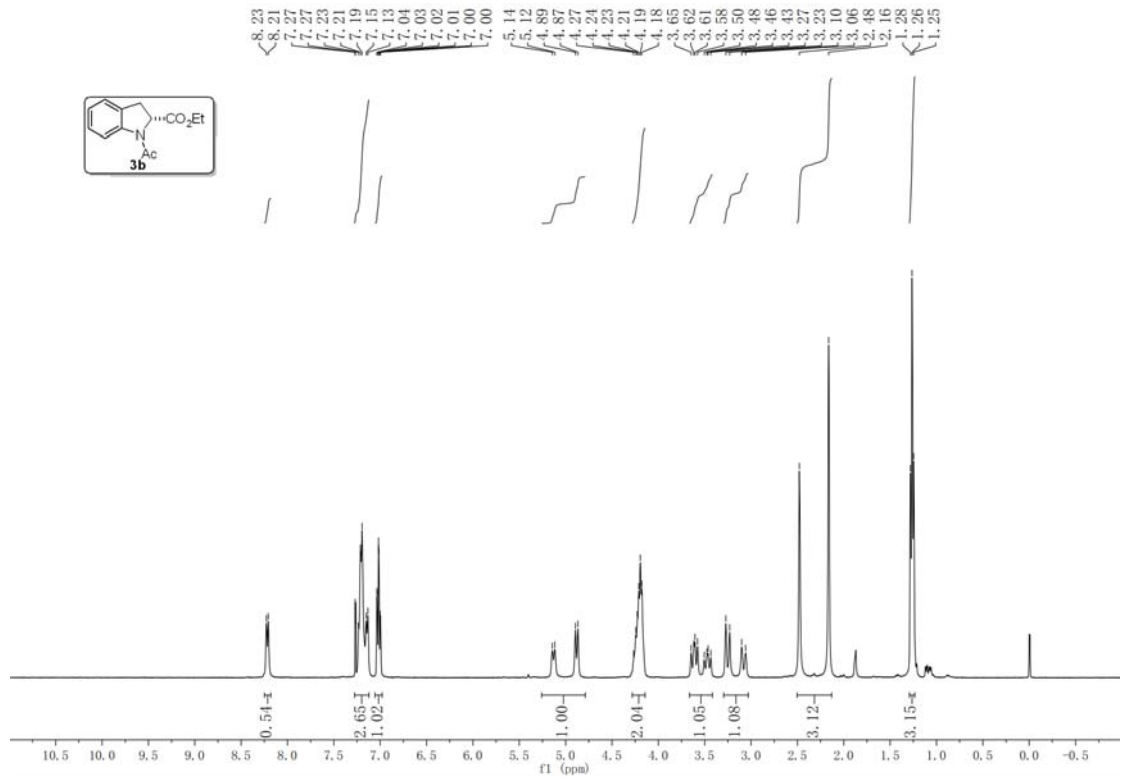
CO2Me
N
Ac
3a
f1 (ppm)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3.27
3.23
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3.06
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2.16
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1.26
1.25
CO2Et
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1.08
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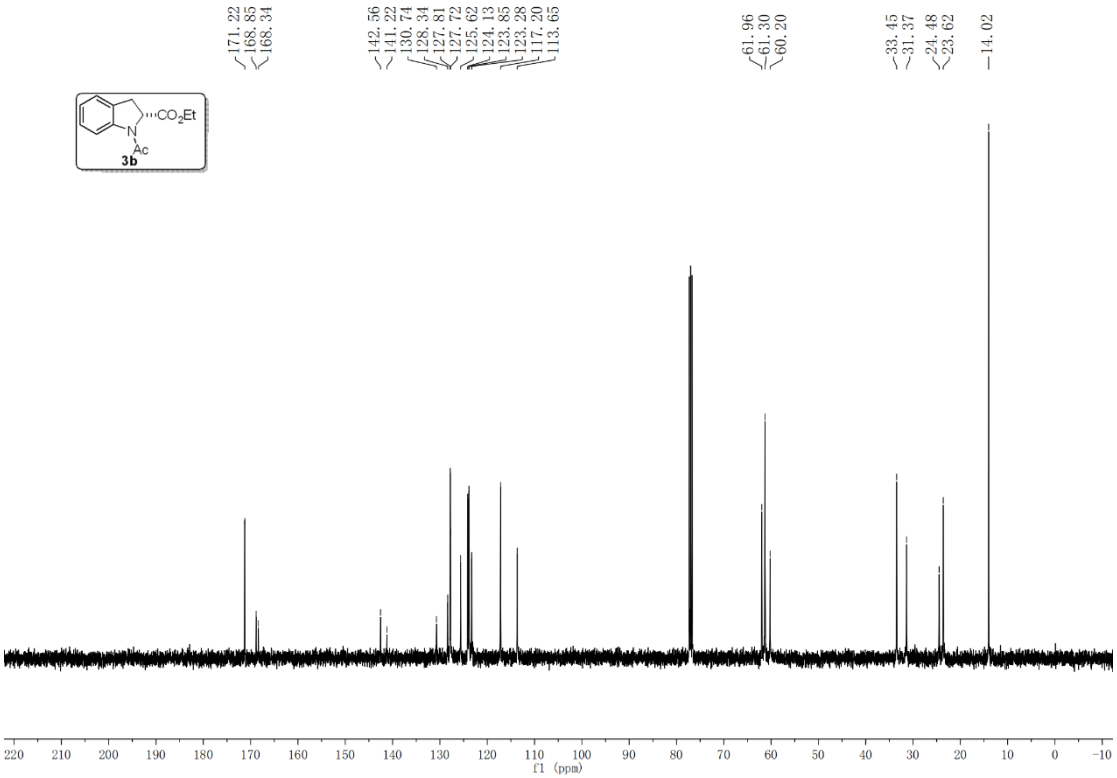
3.15
f1 (ppm)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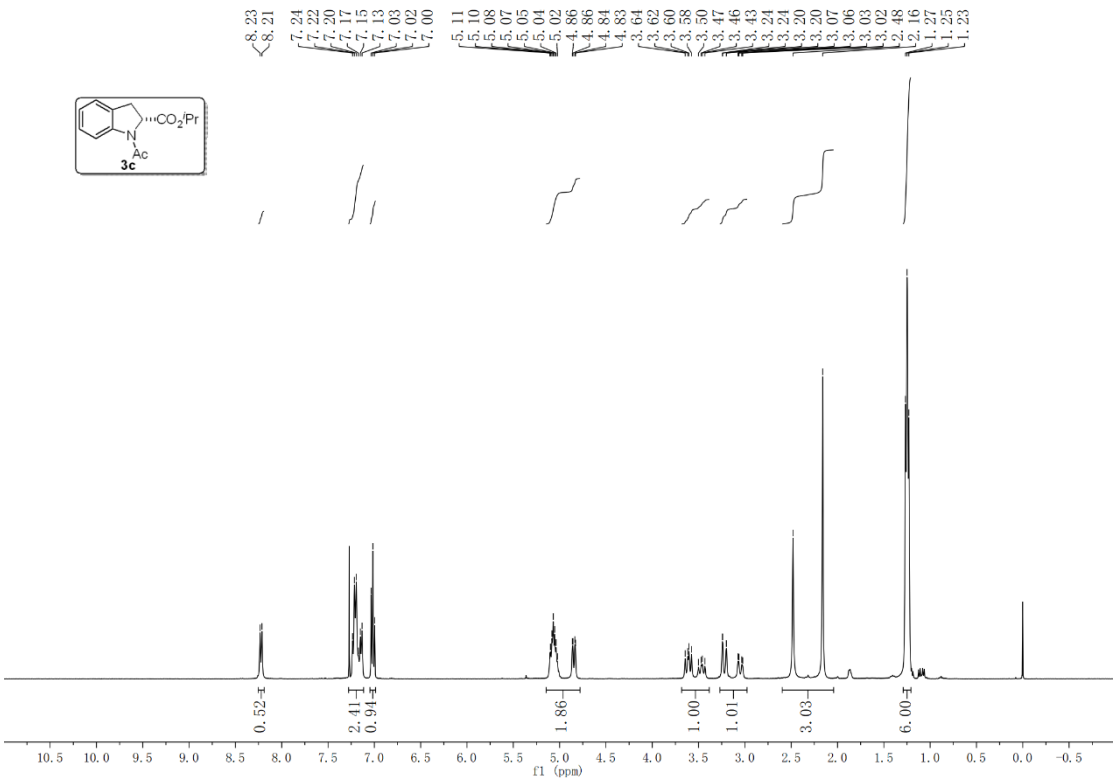
Ac
3b
f1 (ppm)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5.02
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3.03
3.02
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1.23
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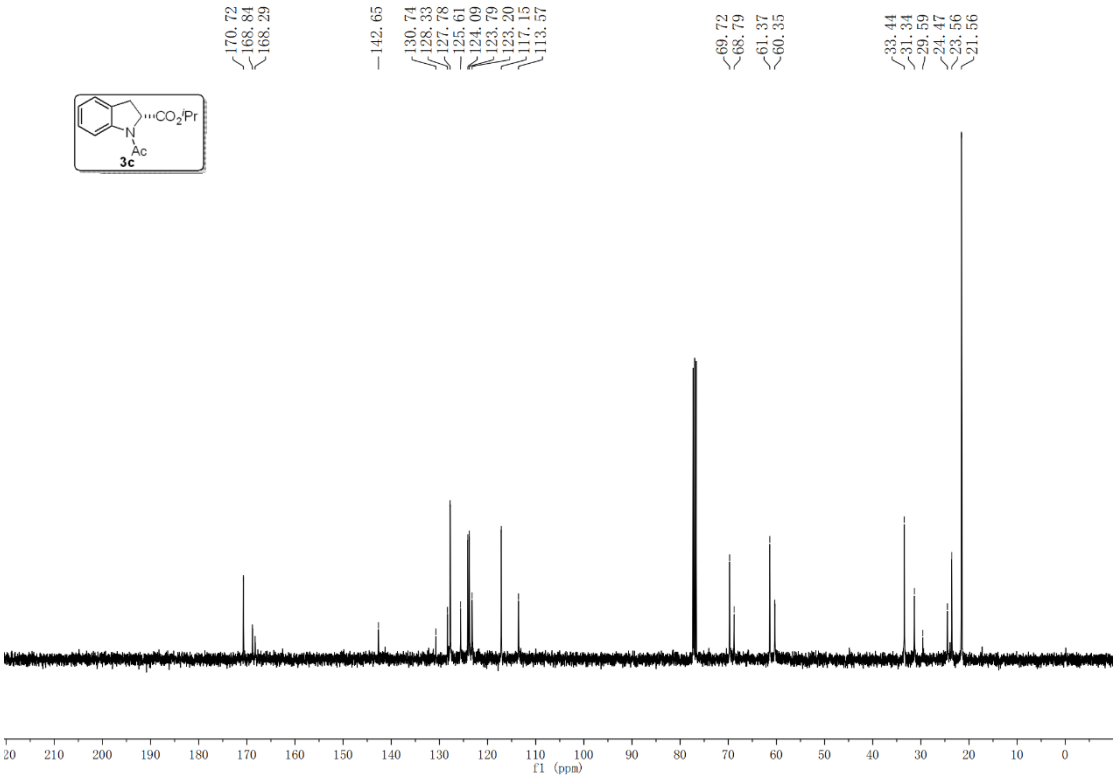
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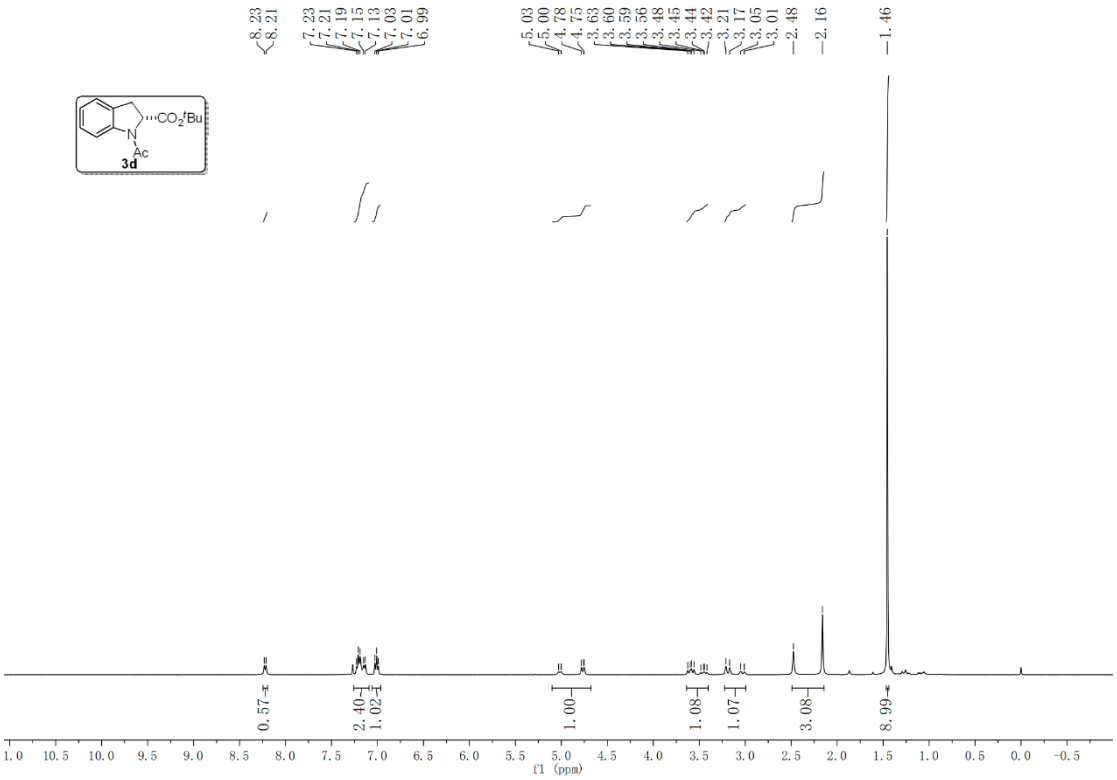
3c
f1 (ppm)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3.59
3.56
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3.21
3.17
3.05
3.01
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2.16
1.46
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1.07
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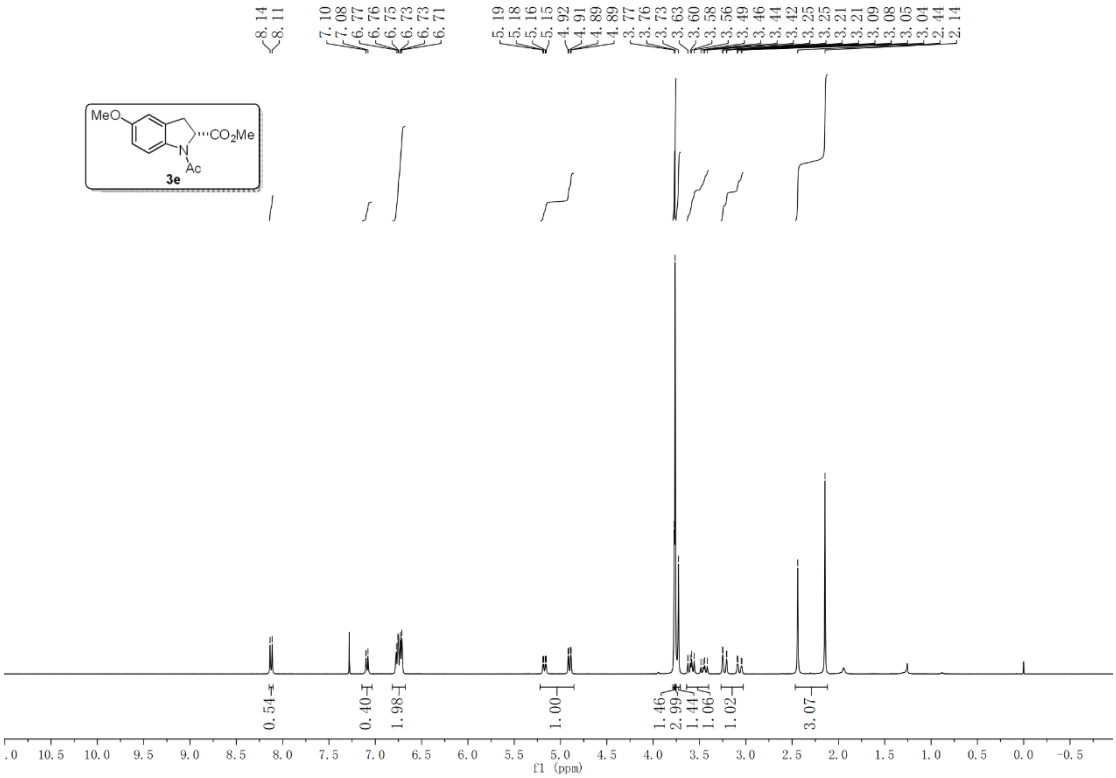
f1 (ppm)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3.63
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3.56
3.49
3.46
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3.42
3.25
3.25
3.21
3.21
3.09
3.08
3.05
3.04
2.44
2.14
MeO
CO2Me
N
Ac
3e
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1.06
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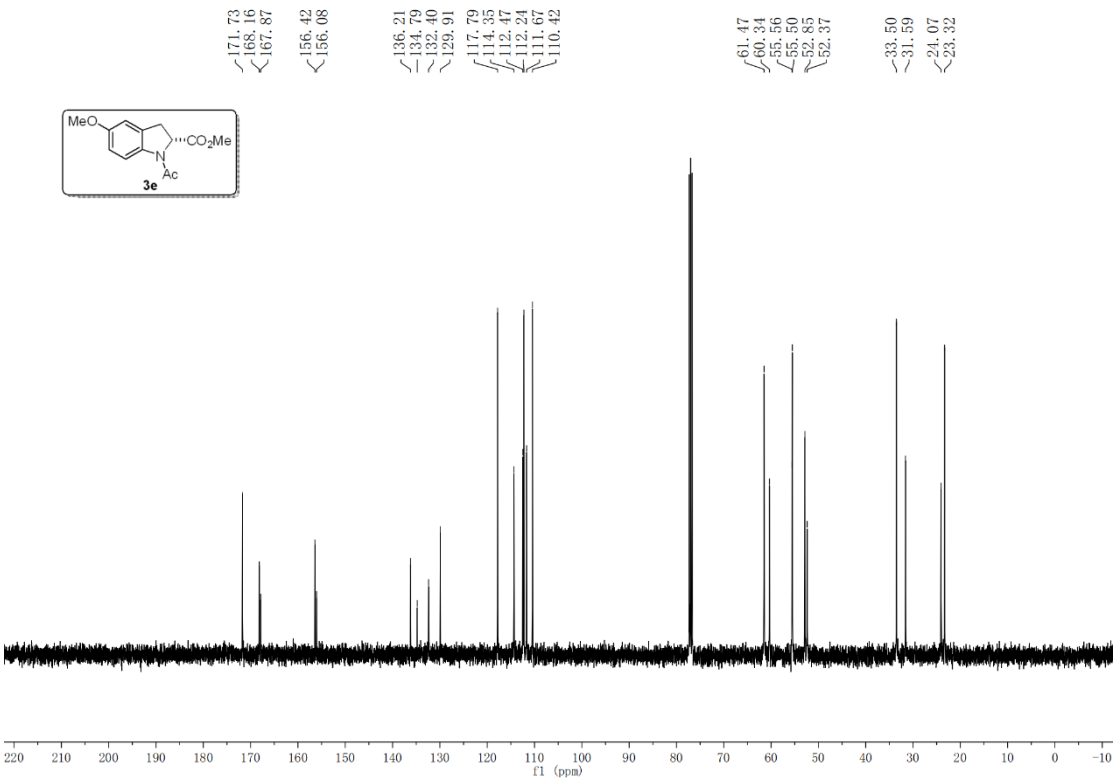
3.07
f1 (ppm)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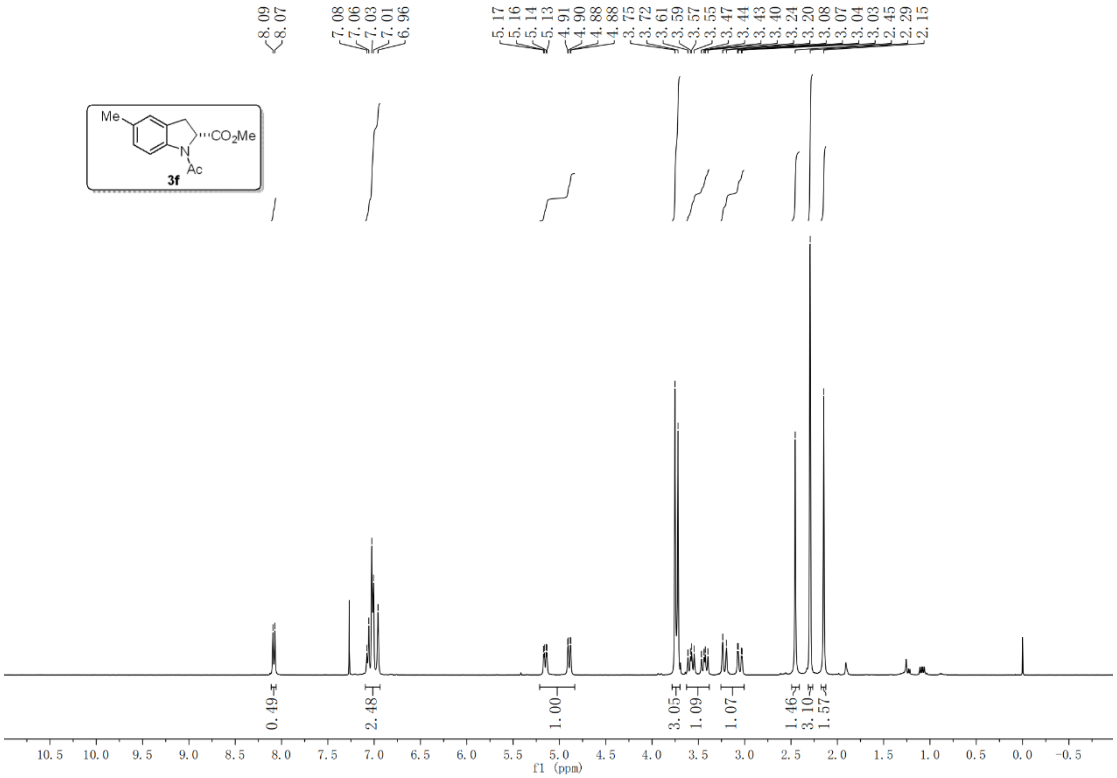
31.59
24.07
23.32
MeO
CO2Me
N
Ac
3e
f1 (ppm)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4.88
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3.57
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3.47
3.44
3.43
3.40
3.24
3.20
3.08
3.07
3.04
3.03
2.45
2.29
2.15
Me
CO2Me
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1.46
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1.57
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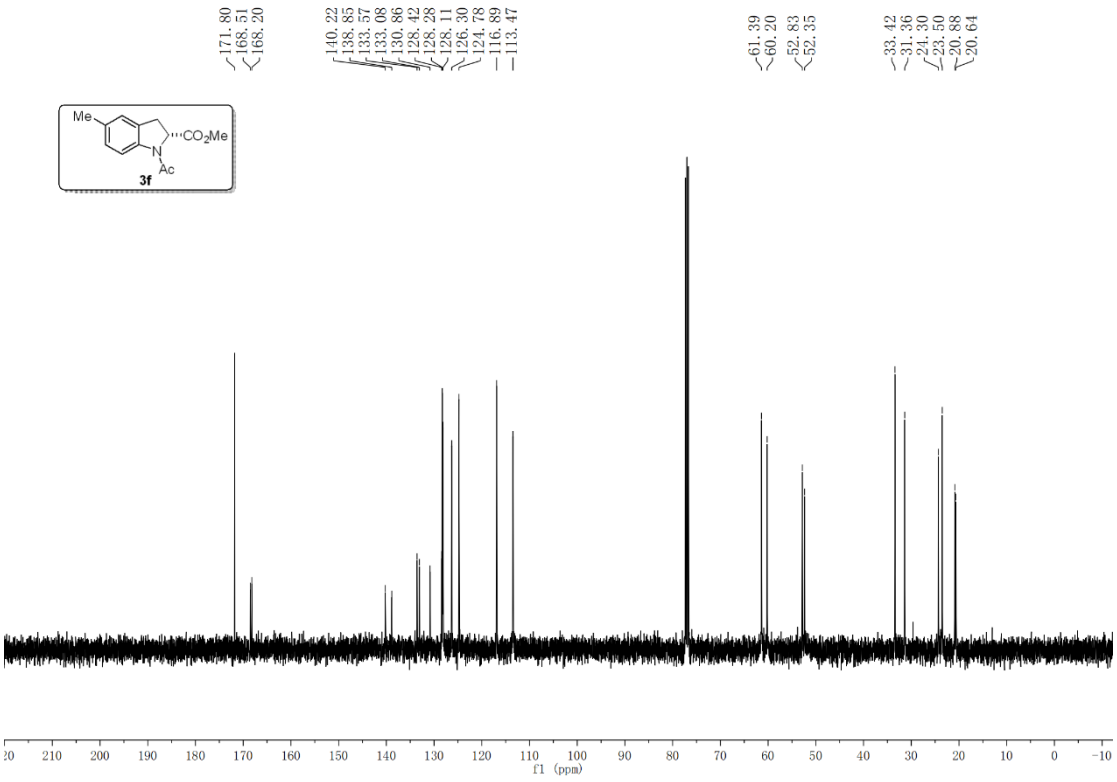
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113.47
61.39
60.20
52.83
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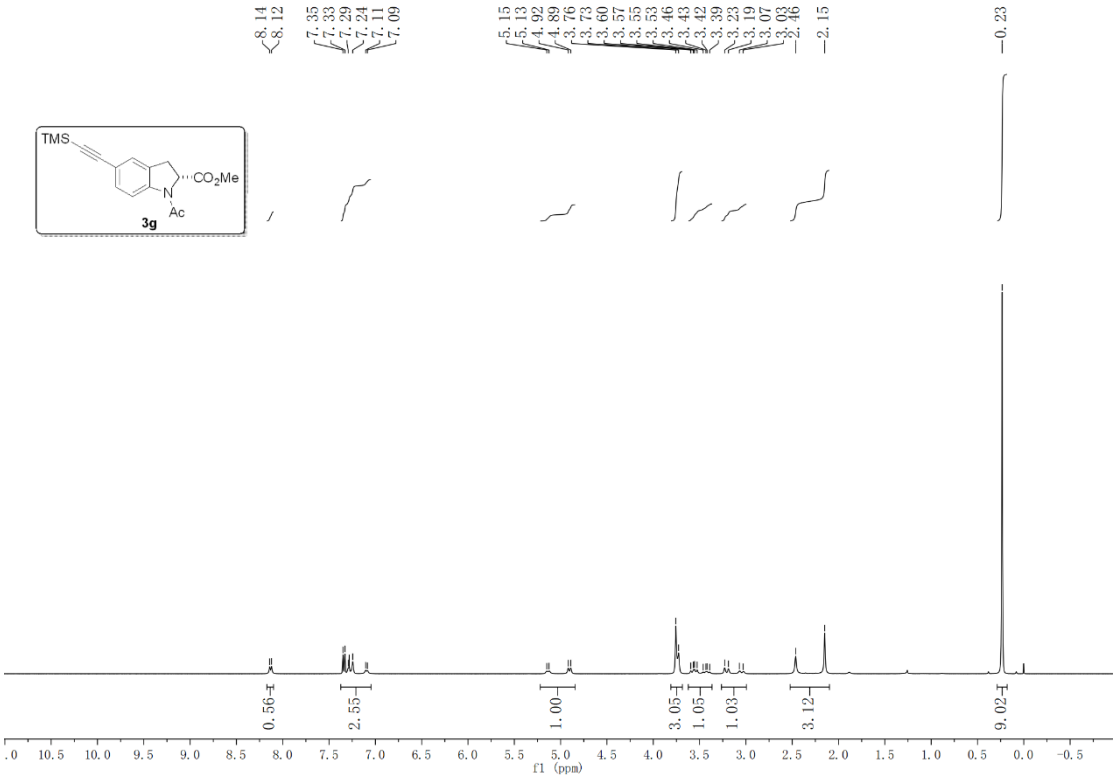
Me
CO2Me
N
Ac
3f
f1 (ppm)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5.13
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3.55
3.53
3.46
3.43
3.42
3.39
3.23
3.19
3.07
3.03
2.46
2.15
0.23
TMS
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1.03
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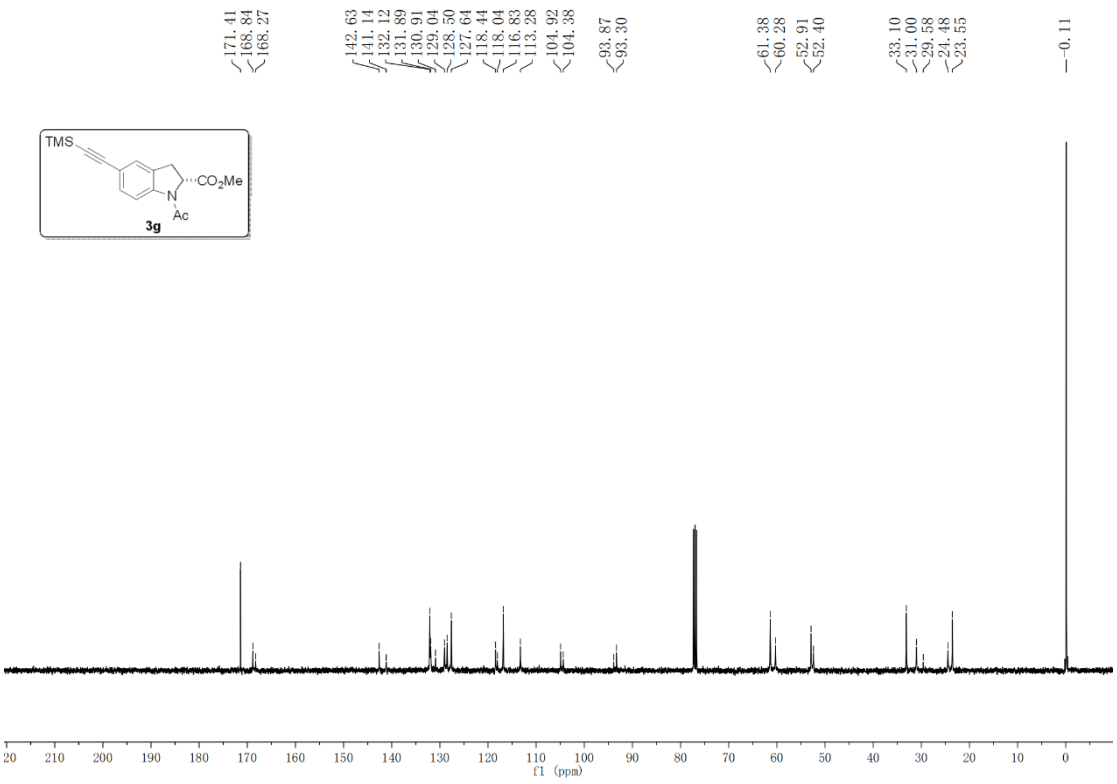
f1 (ppm)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93.87
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60.28
52.91
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23.55
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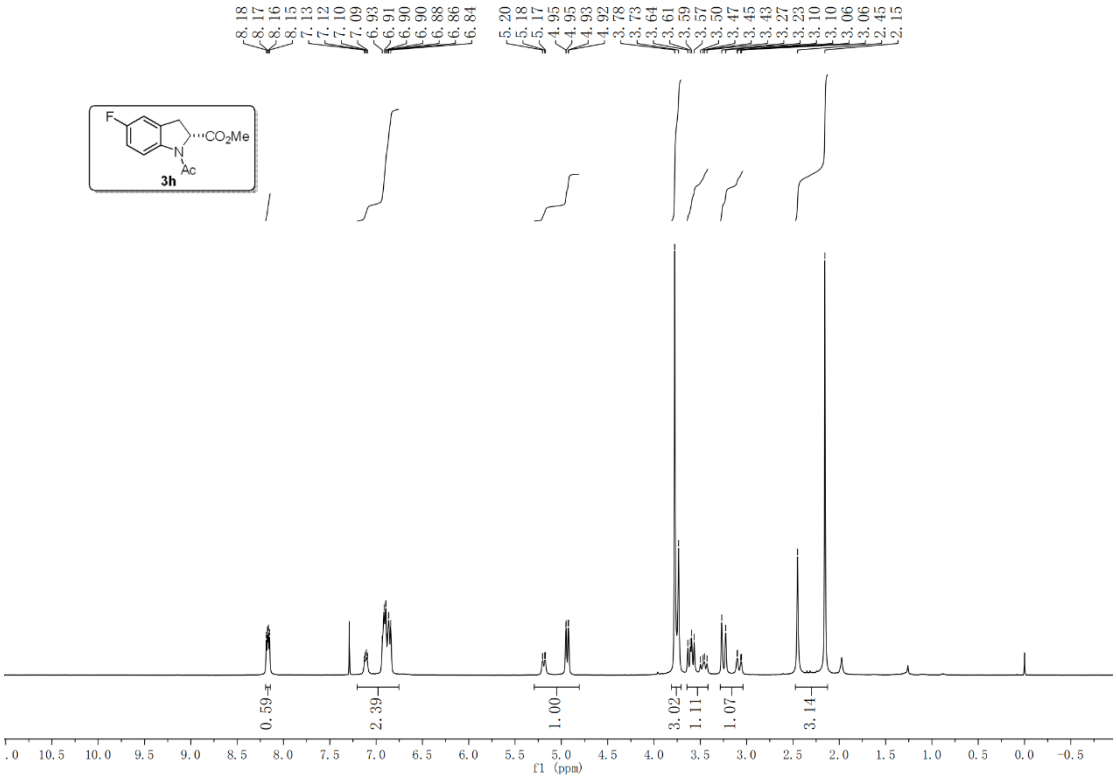
TMS
CO2Me
N
Ac
3g
f1 (ppm)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6.86
6.84
5.20
5.18
5.17
4.95
4.95
4.93
4.92
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3.57
3.50
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3.23
3.10
3.10
3.06
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2.15
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Ac
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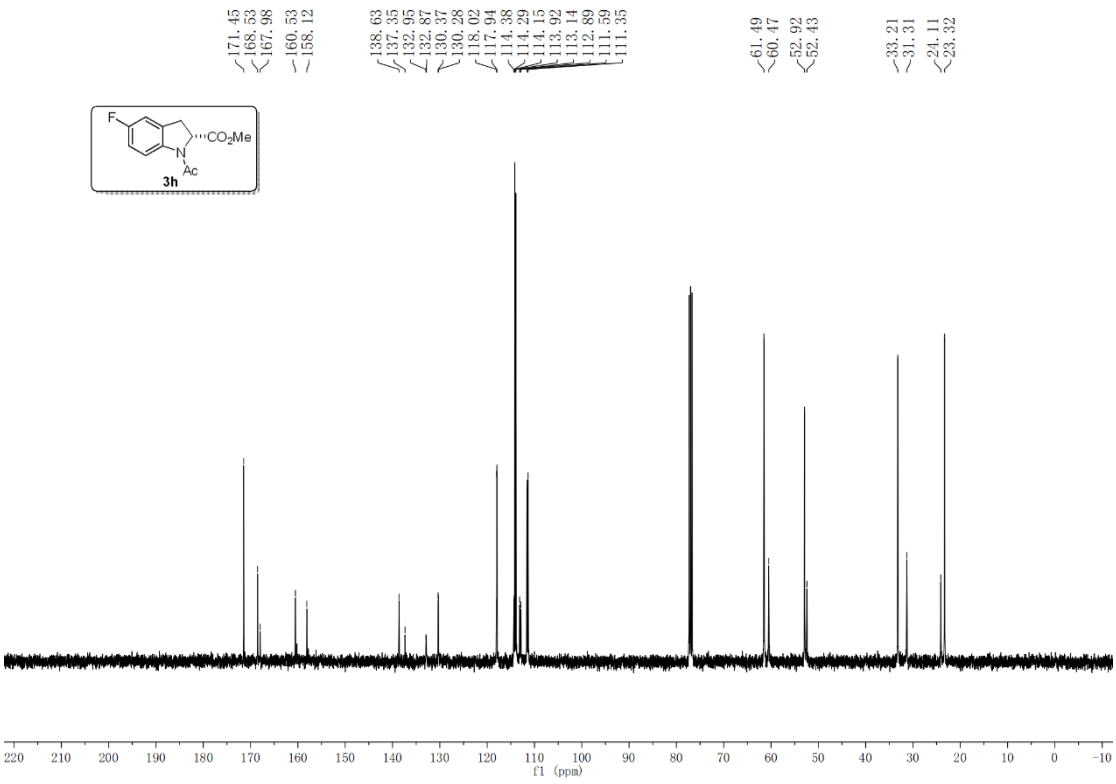
f1 (ppm)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158.12
138.63
137.35
132.95
132.87
130.37
130.28
118.02
117.94
114.38
114.29
114.15
113.92
113.14
112.89
111.59
111.35
61.49
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24.11
23.32
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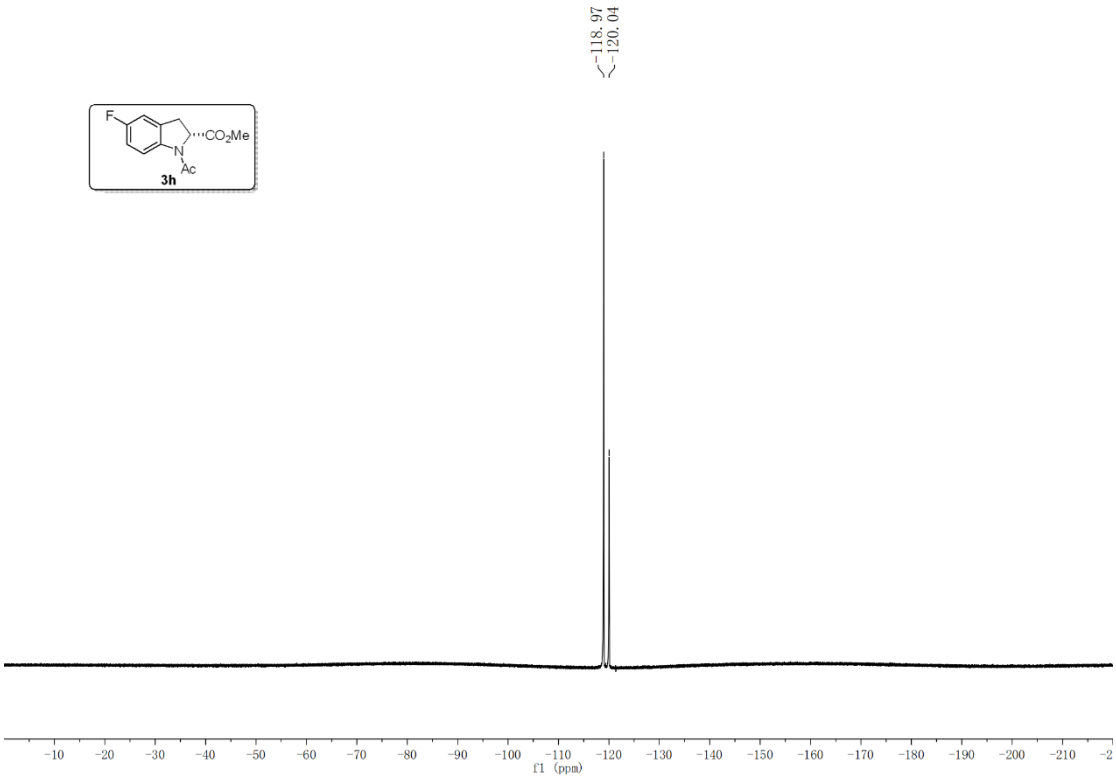
CO2Me
N
Ac
3h
f1 (ppm)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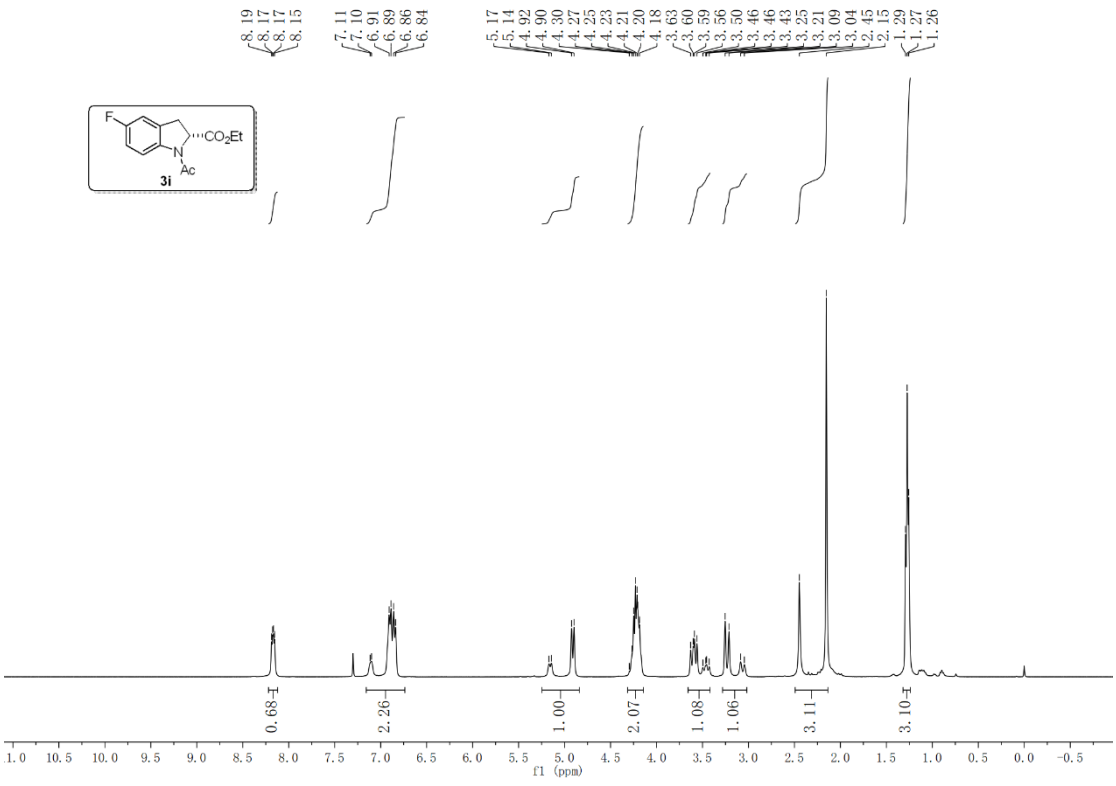
Ac
3h
f1 (ppm)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6.89
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6.84
5.17
5.14
4.92
4.90
4.30
4.27
4.25
4.23
4.21
4.20
4.18
3.63
3.60
3.59
3.56
3.50
3.46
3.46
3.43
3.25
3.21
3.09
3.04
2.45
2.15
1.29
1.27
1.26
F
CO2Et
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Ac
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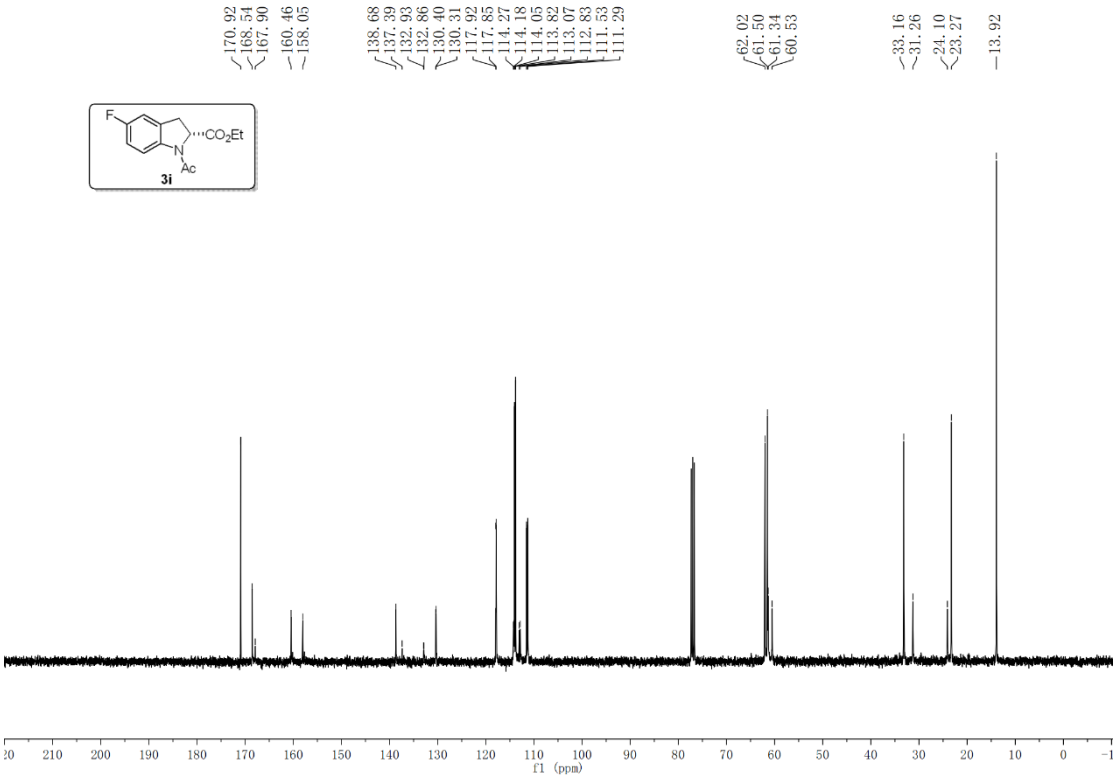
1.00
2.07
1.08
1.06
3.11
3.10
f1 (ppm)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117.85
114.27
114.18
114.05
113.82
113.07
112.83
111.53
111.29
62.02
61.50
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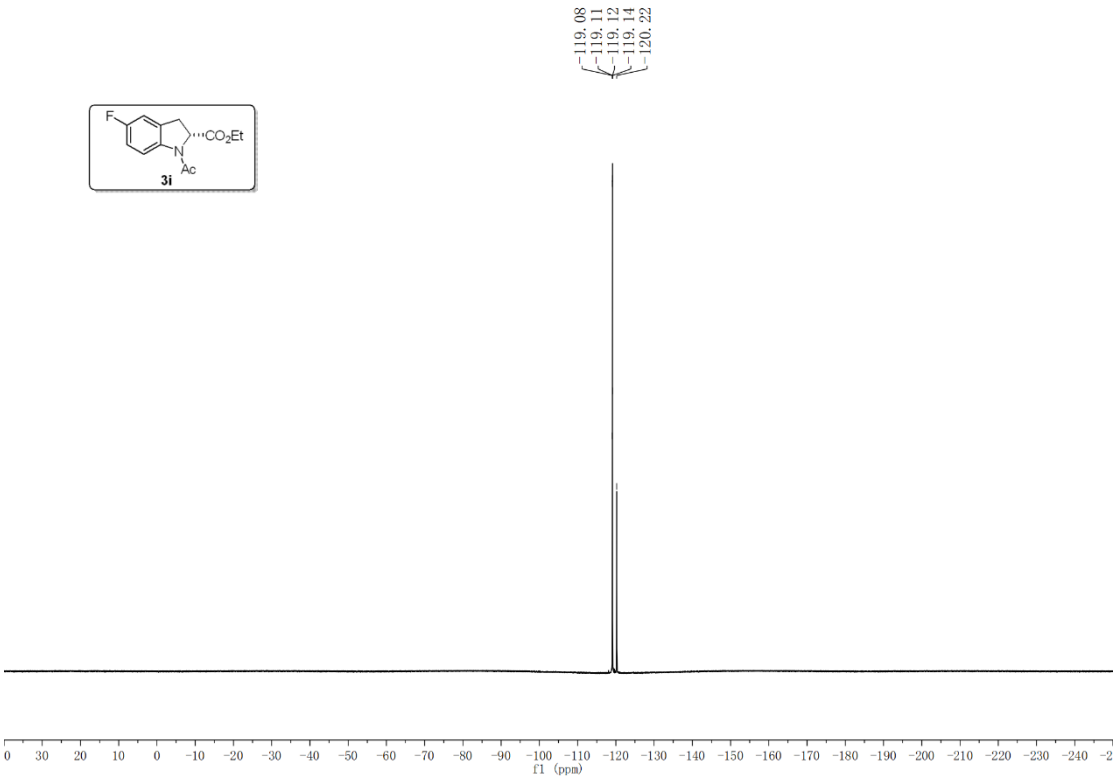
33.16
31.26
24.10
23.27
13.92
F
CO2Et
N
Ac
3i
f1 (ppm)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119.12
119.14
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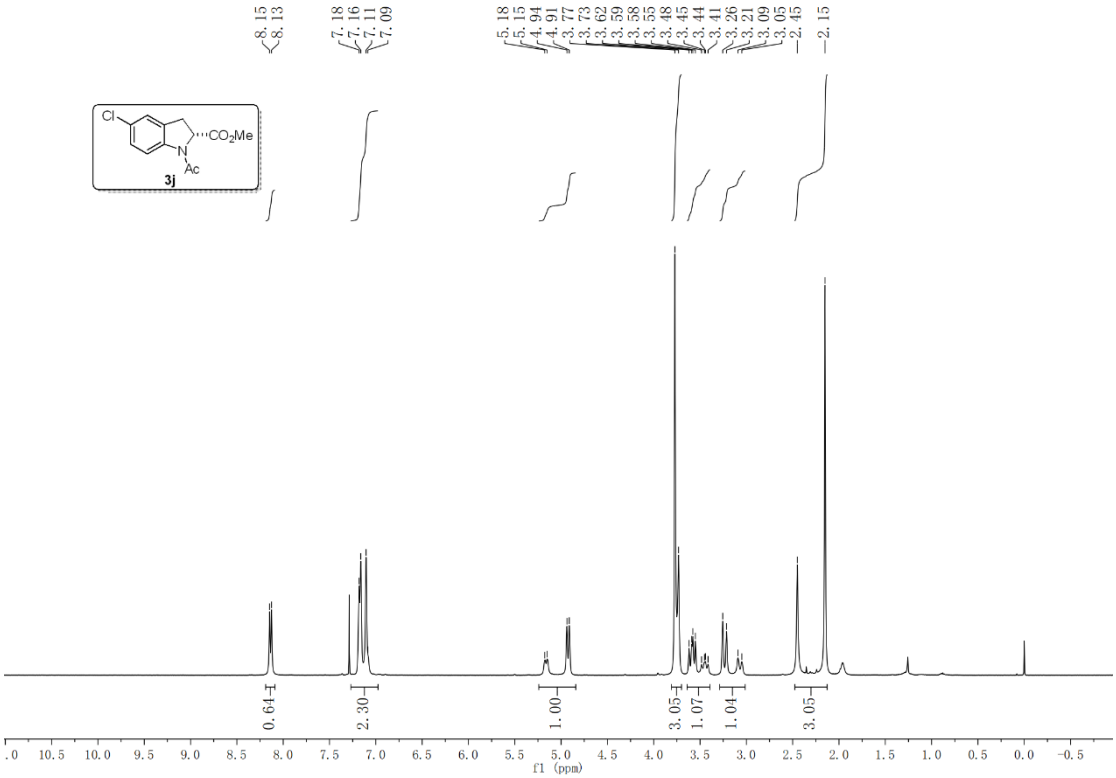
N
Ac
3i
f1 (ppm)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5.15
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4.91
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3.59
3.38
3.55
3.48
3.45
3.44
3.41
3.26
3.21
3.09
3.05
2.45
2.15
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Ac
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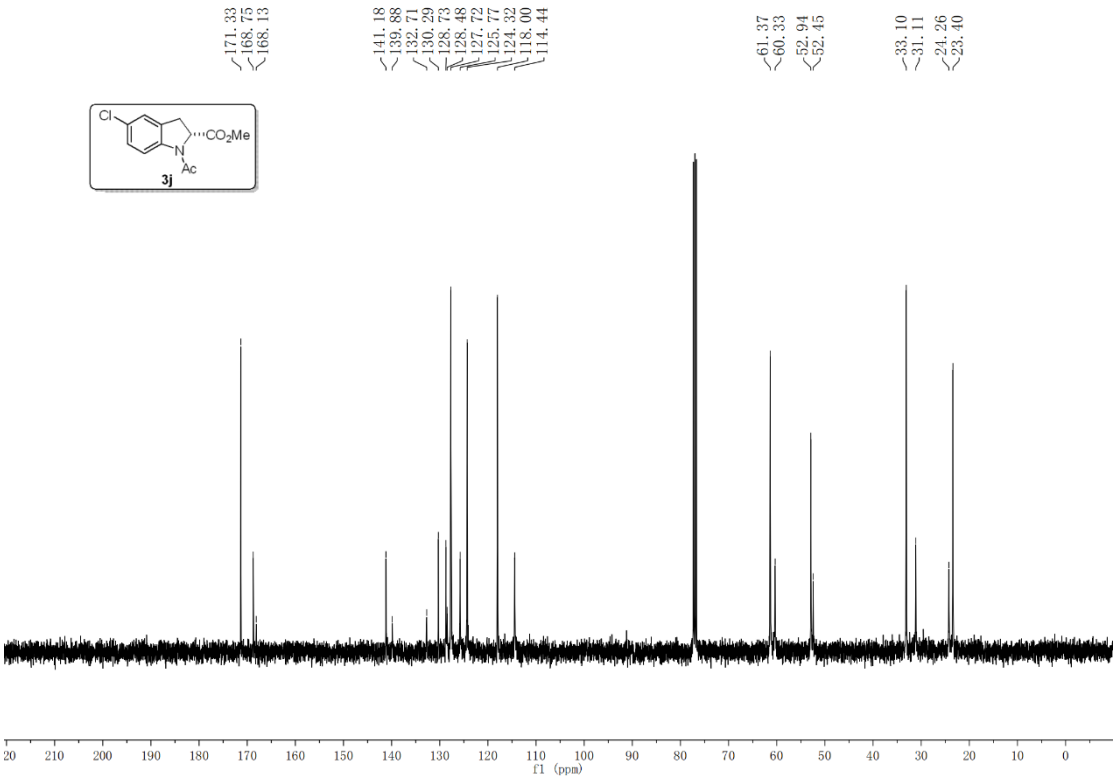
1.04
3.05
f1 (ppm)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114.44
61.37
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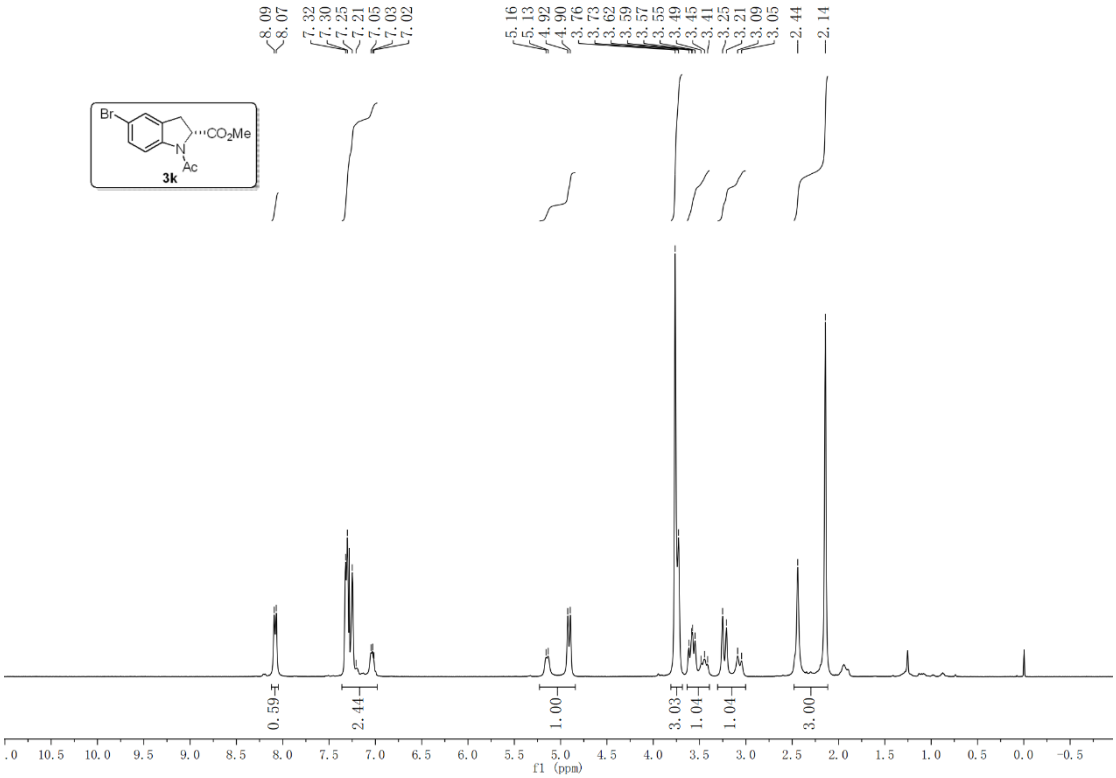
52.45
33.10
31.11
24.26
23.40
Cl
CO2Me
N
Ac
3j
f1 (ppm)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7.05
7.03
7.02
5.16
5.13
4.92
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3.76
3.73
3.62
3.59
3.57
3.55
3.49
3.45
3.41
3.25
3.21
3.09
3.05
2.44
2.14
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Ac
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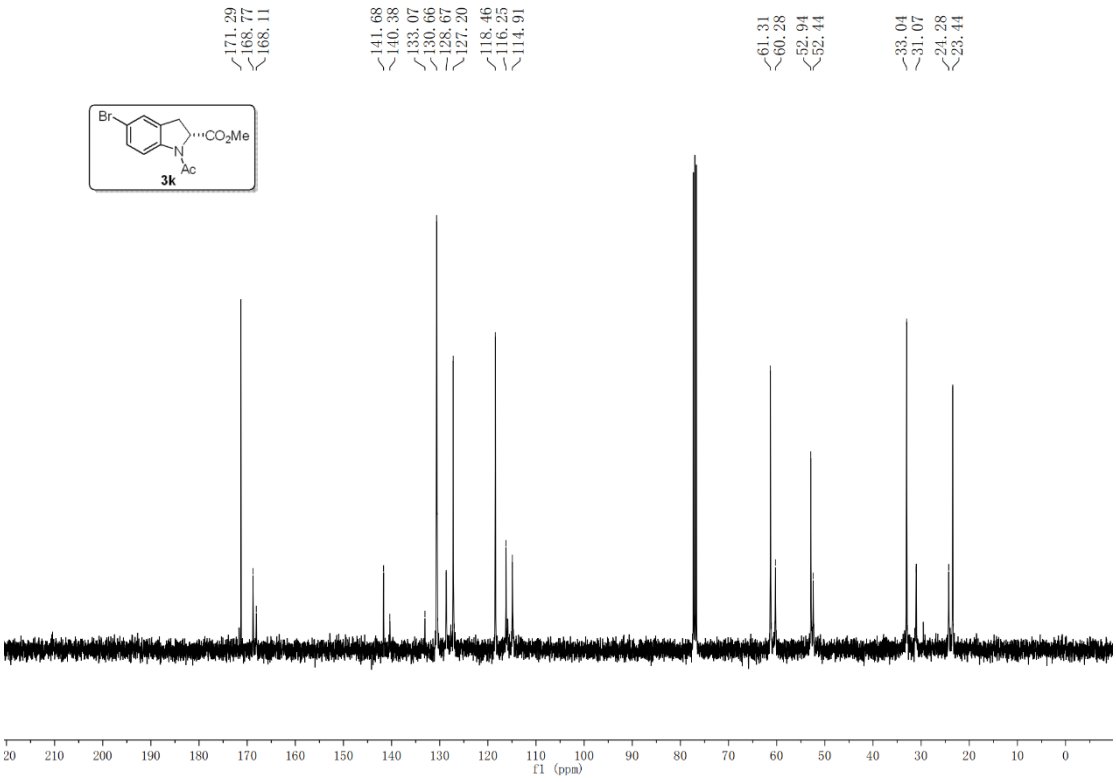
1.00
3.03
1.04
1.04
3.00
f1 (ppm)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118.46
116.25
114.91
61.31
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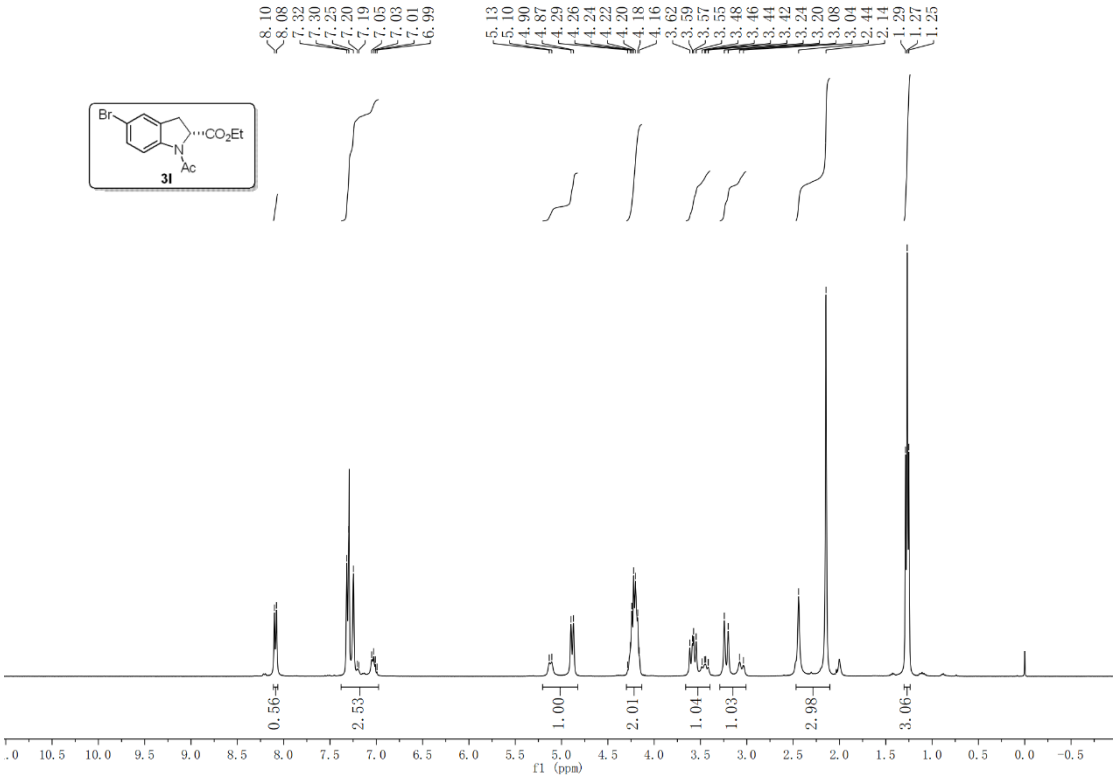
52.94
52.44
33.04
31.07
24.28
23.44
Br
CO2Me
N
Ac
3k
f1 (ppm)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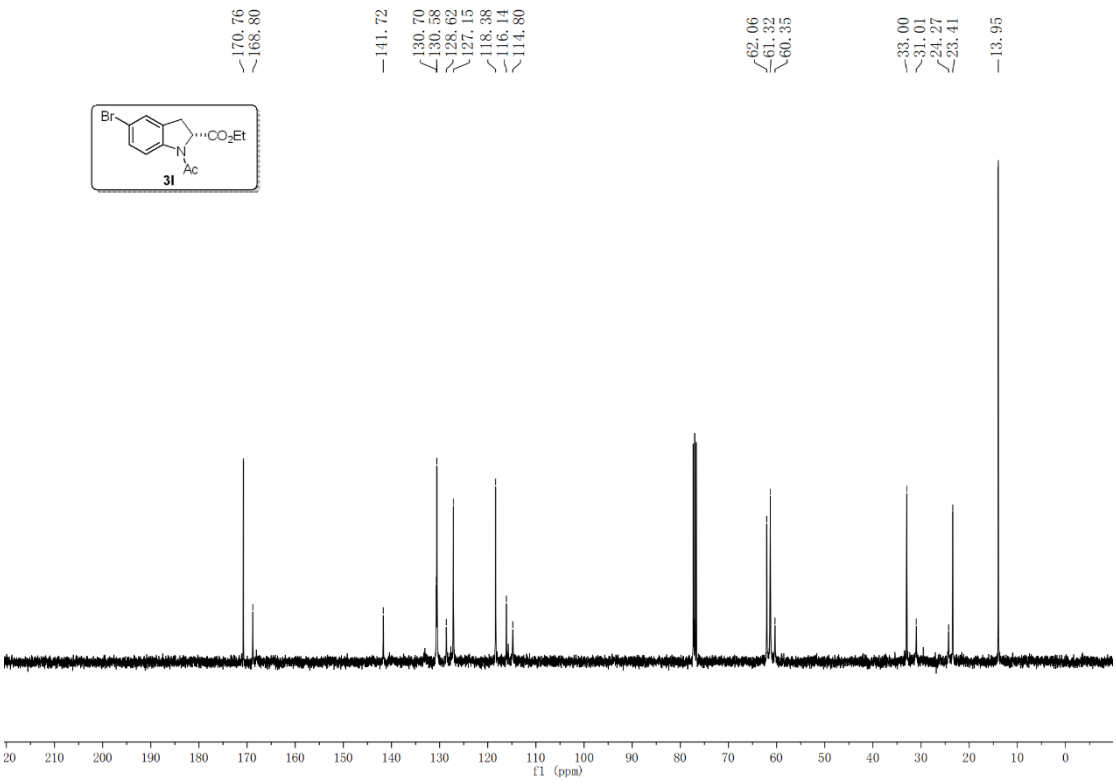
7.05
7.03
7.01
6.99
5.13
5.10
4.90
4.87
4.29
4.26
4.24
4.22
4.20
4.18
4.16
3.62
3.59
3.57
3.55
3.48
3.46
3.44
3.42
3.24
3.20
3.08
3.04
2.44
2.14
1.29
1.27
1.25
Br
CO2Et
N
Ac
3l
0.56
2.53
1.00
2.01
1.04
1.03
2.98
3.06
f1 (ppm)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118.38
116.14
114.80
62.06
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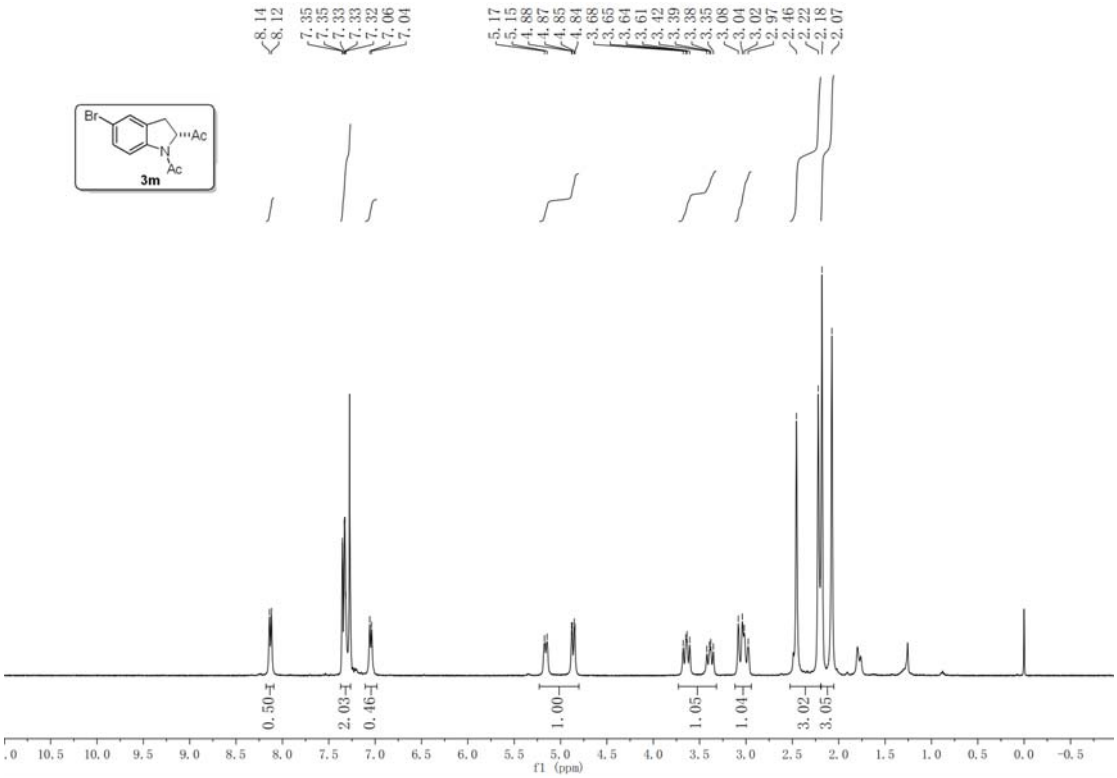
33.00
31.01
24.27
23.41
13.95
Br
CO2Et
N
Ac
3l
f1 (ppm)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7.33
7.32
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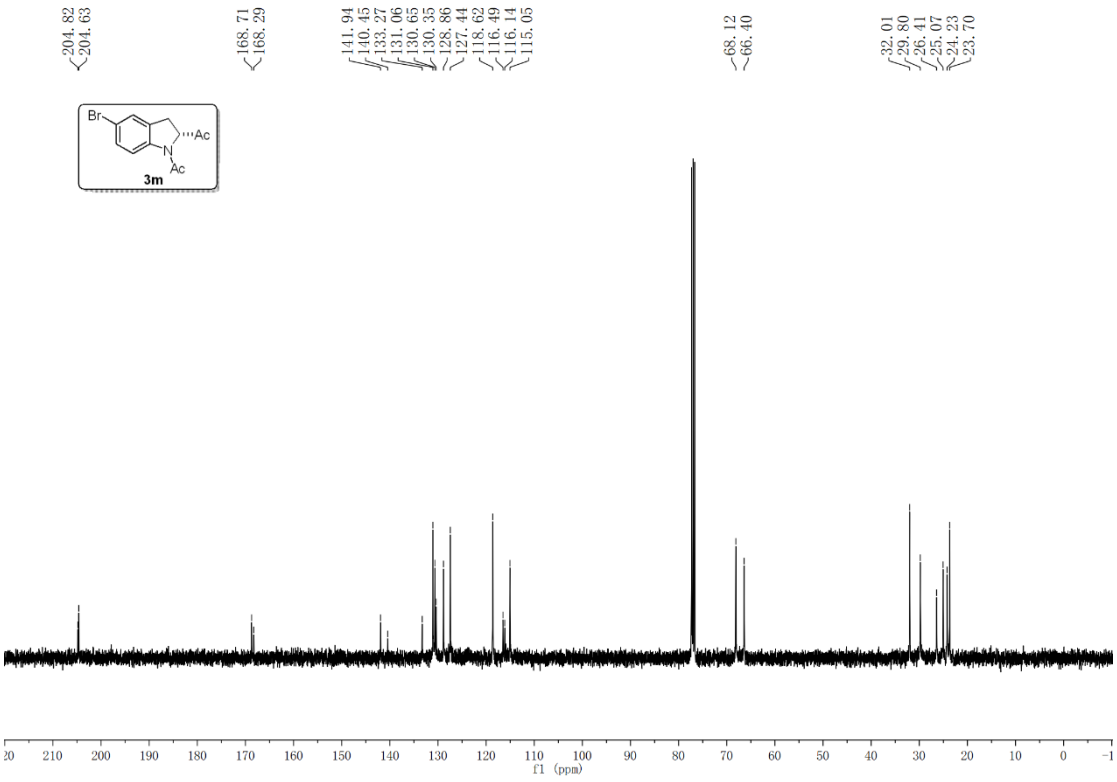
7.04
5.17
5.15
4.88
4.87
4.85
4.84
3.68
3.65
3.64
3.61
3.42
3.39
3.38
3.35
3.08
3.04
3.02
2.97
2.46
2.22
2.18
2.07
Br
Ac
N
Ac
3m
0.50
2.03
0.46
1.00
1.05
1.04
3.02
3.05
f1 (ppm)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131.06
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130.35
128.86
127.44
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116.49
116.14
115.05
68.12
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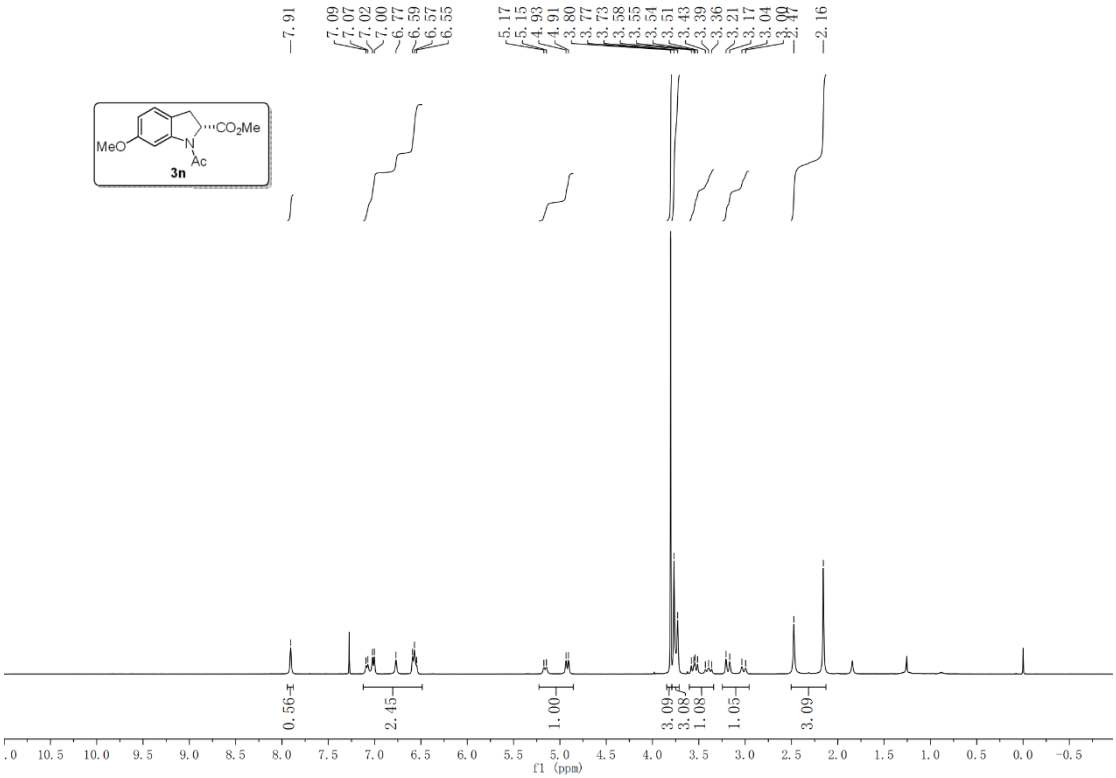
26.41
25.07
24.23
23.70
Br
Ac
N
Ac
3m
f1 (ppm)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6.55
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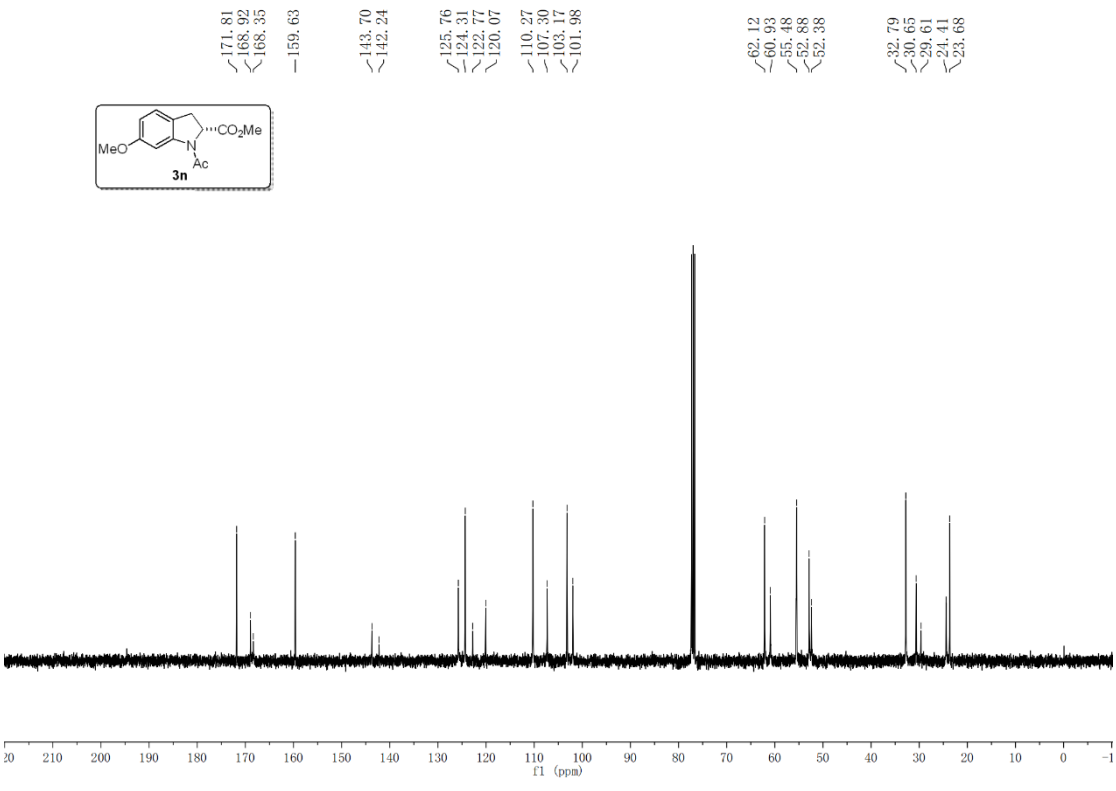
5.15
4.93
4.91
3.80
3.77
3.73
3.38
3.55
3.54
3.51
3.43
3.39
3.36
3.21
3.17
3.04
3.00
2.47
2.16
MeO
CO2Me
N
Ac
3n
0.56
2.45
1.00
3.09
3.08
1.08
1.05
3.09
f1 (ppm)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142.24
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120.07
110.27
107.30
103.17
101.98
62.12
60.93
55.48
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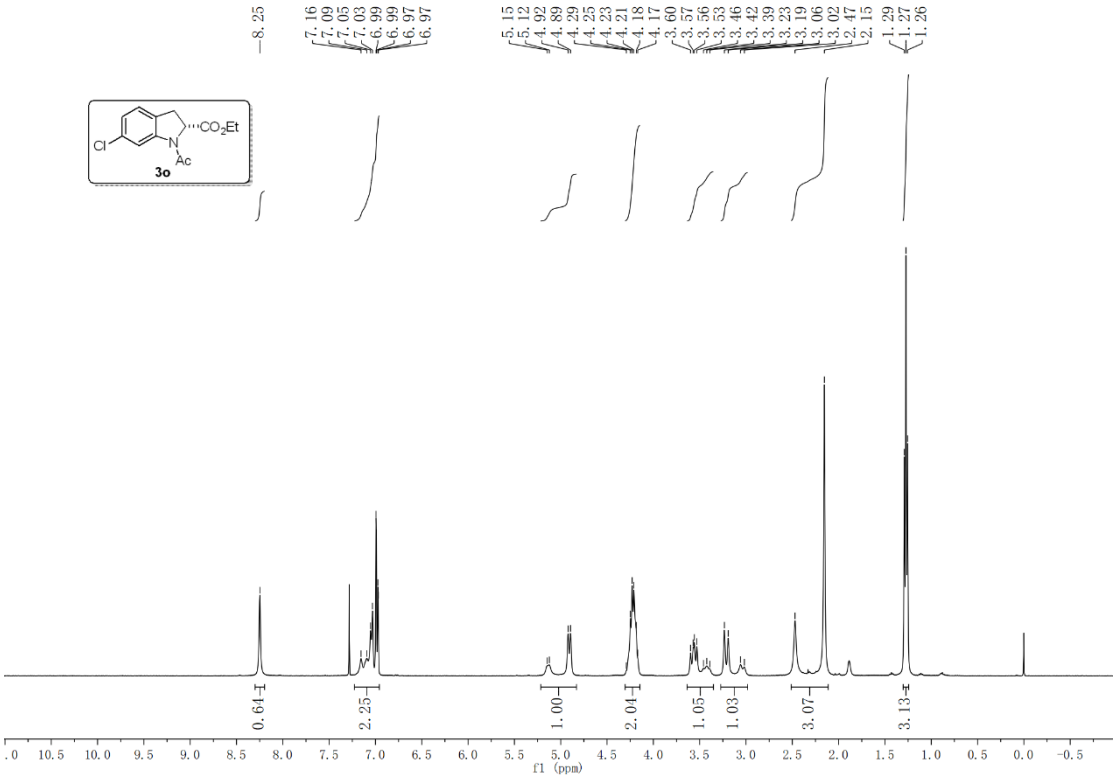
52.38
32.79
30.65
29.61
24.41
23.68
MeO
CO2Me
N
Ac
3n
f1 (ppm)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6.99
6.97
6.97
5.15
5.12
4.92
4.89
4.29
4.25
4.23
4.21
4.18
4.17
3.60
3.57
3.56
3.53
3.46
3.42
3.39
3.23
3.19
3.06
3.02
2.47
2.15
1.29
1.27
1.26
CO2Et
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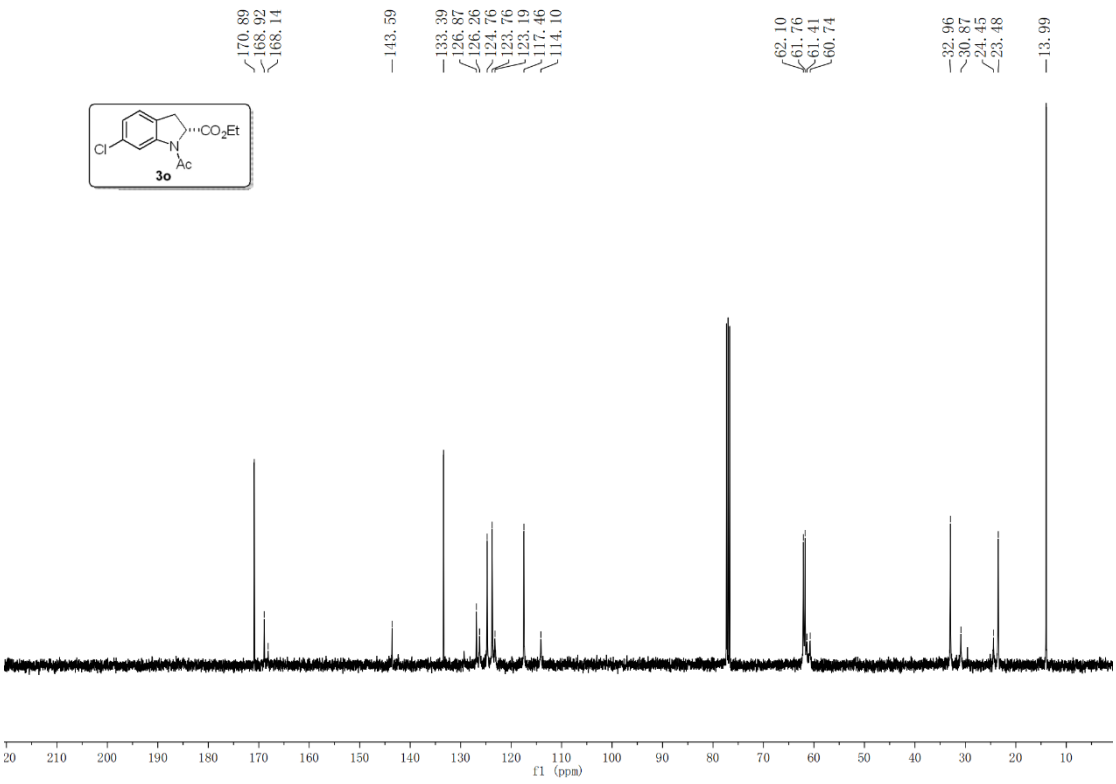
1.05
1.03
3.07
3.13
f1 (ppm)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124.76
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123.19
117.46
114.10
62.10
61.76
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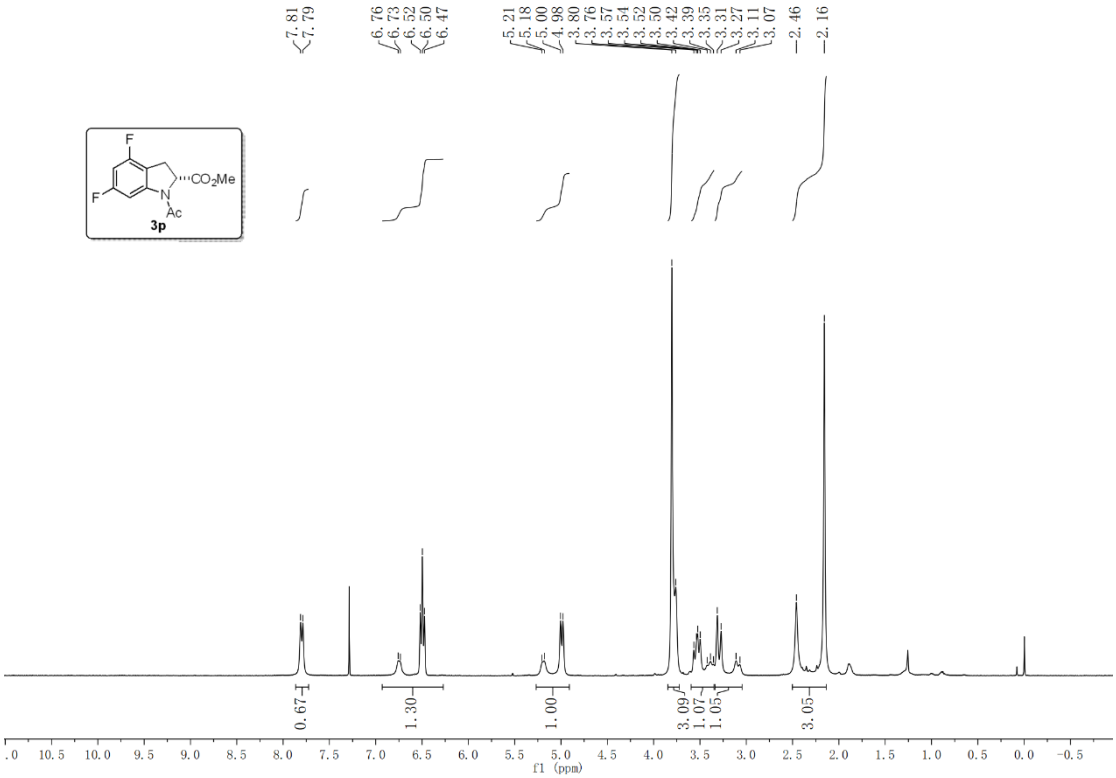
23.48
13.99
CO2Et
Cl
N
Ac
3o
f1 (ppm)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6.47
5.21
5.18
5.00
4.98
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3.57
3.54
3.52
3.50
3.42
3.39
3.35
3.31
3.27
3.11
3.07
2.46
2.16
F
F
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Ac
3p
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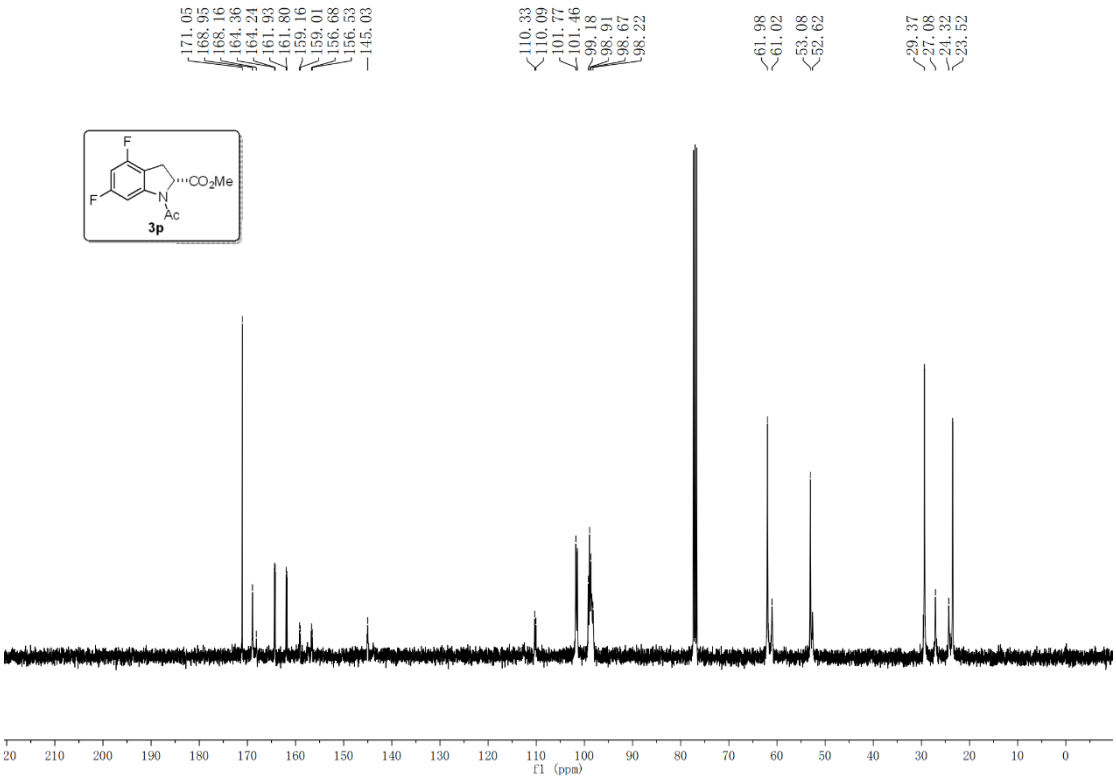
1.07
1.05
3.05
f1 (ppm)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156.53
145.03
110.33
110.09
101.77
101.46
99.18
98.91
98.67
98.22
61.98
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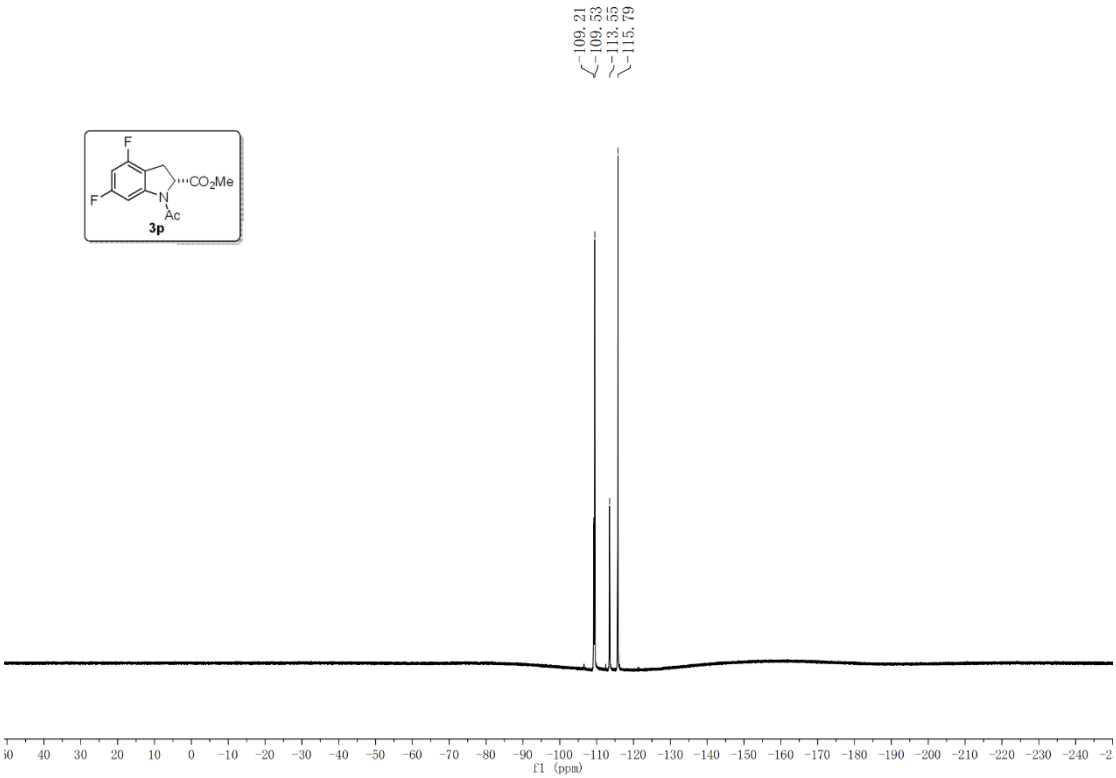
29.37
27.08
24.32
23.52
F
F
CO2Me
N
Ac
3p
f1 (ppm)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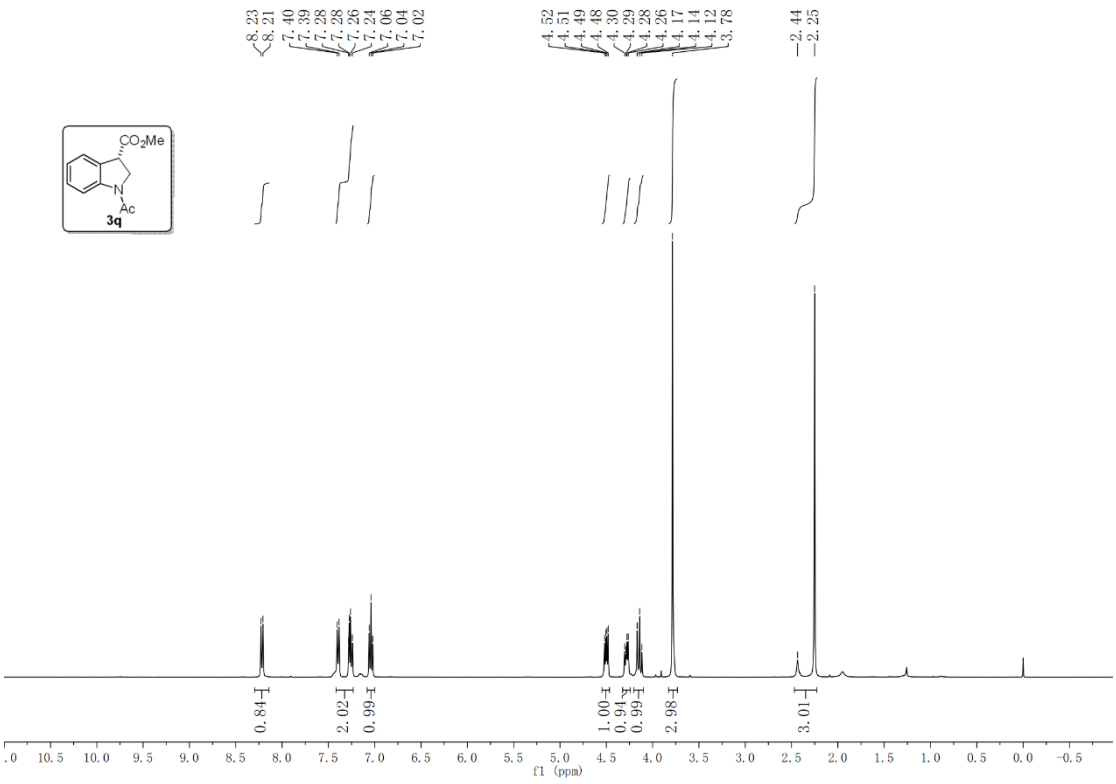
-115.79
F
F
CO2Me
N
Ac
3p
f1 (ppm)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7.24
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7.04
7.02
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4.51
4.49
4.48
4.30
4.29
4.28
4.26
4.17
4.14
4.12
3.78
2.44
2.25
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Ac
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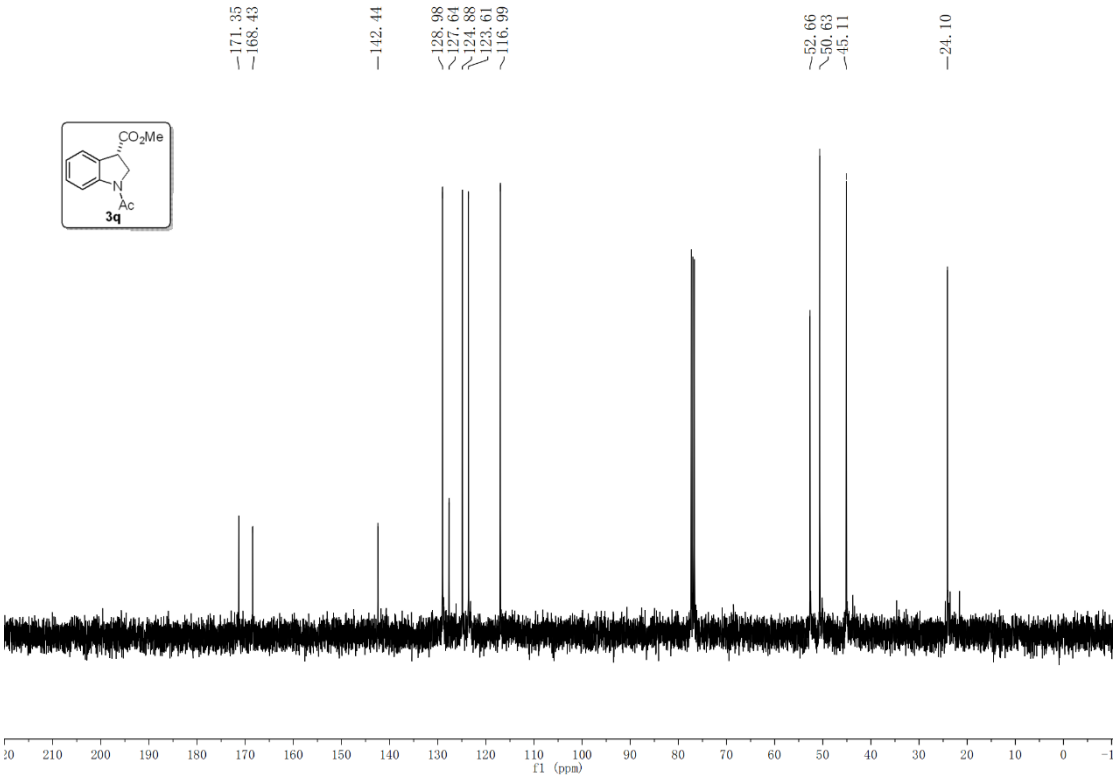
0.99
1.00
0.94
0.99
2.98
3.01
f1 (ppm)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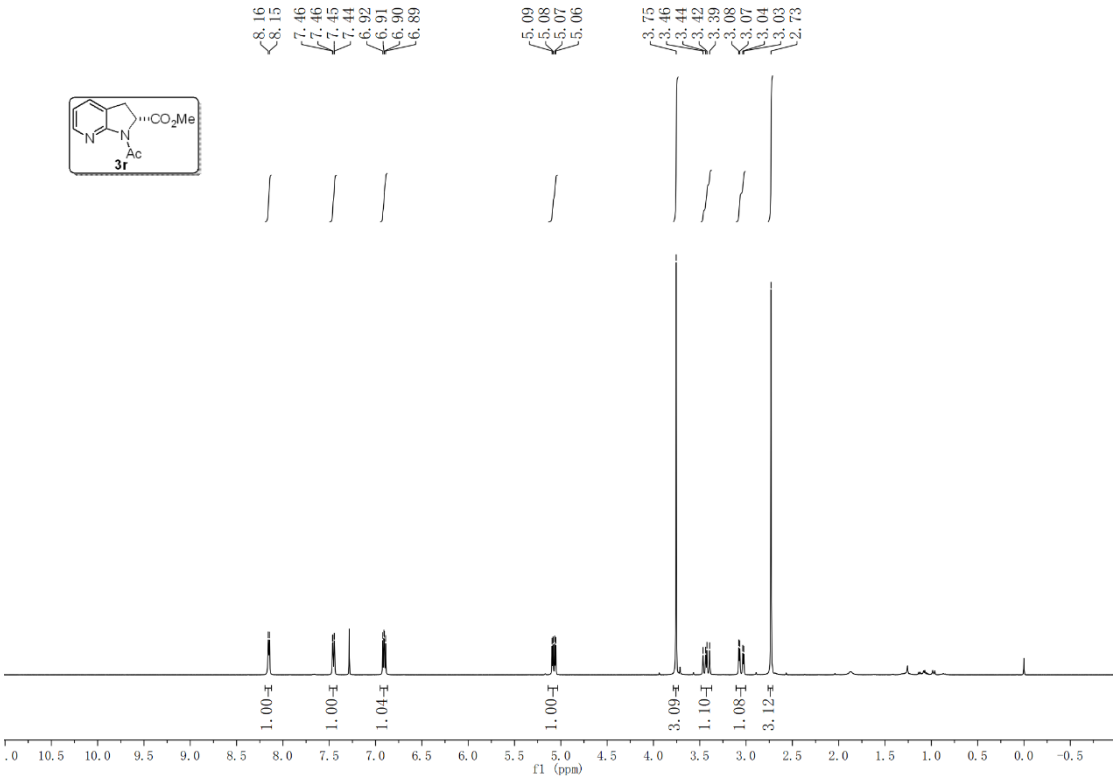
116.99
52.66
50.63
45.11
24.10
CO2Me
N
Ac
3q
f1 (ppm)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7.44
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6.91
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6.89
5.09
5.08
5.07
5.06
3.75
3.46
3.44
3.42
3.39
3.08
3.07
3.04
3.03
2.73
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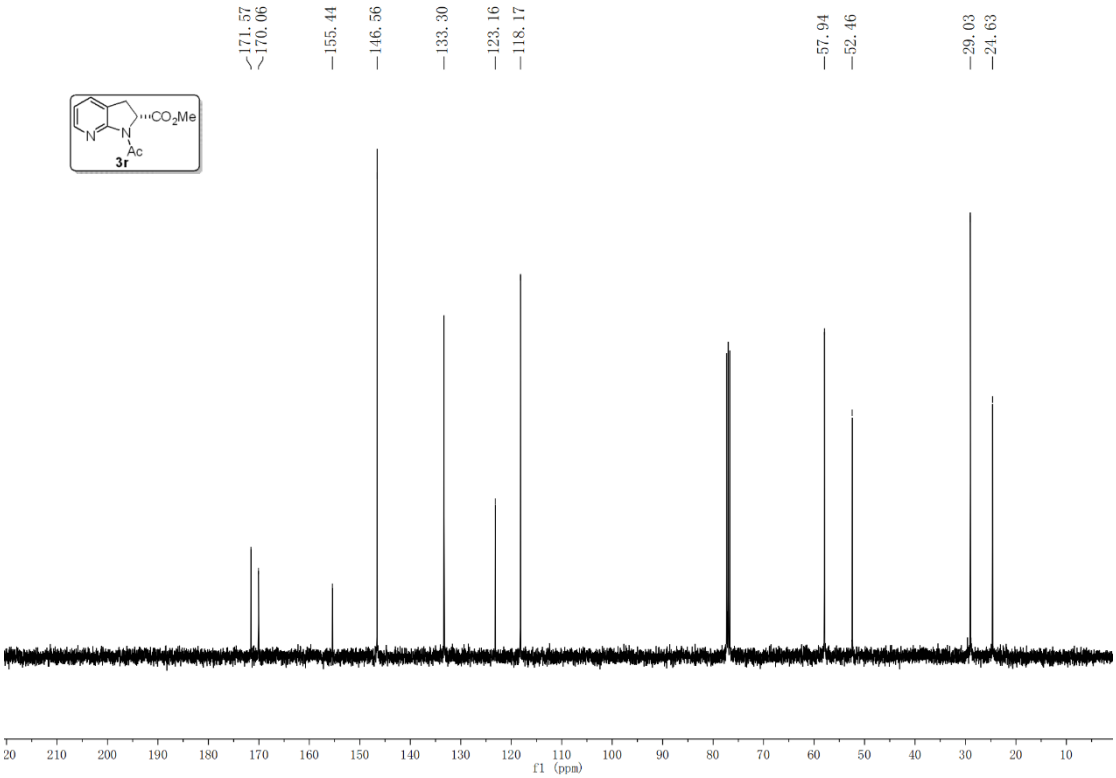
1.00
1.04
1.00
3.09
1.10
1.08
3.12
f1 (ppm)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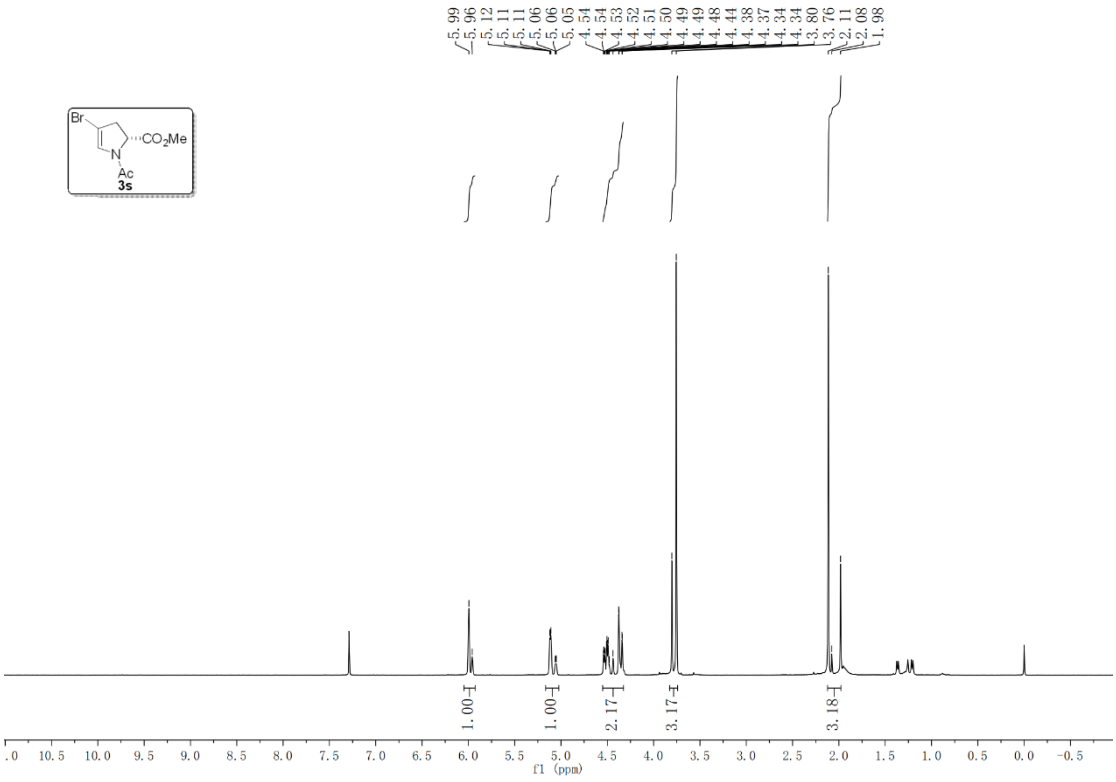
52.46
29.03
24.63
CO2Me
N
Ac
3r
f1 (ppm)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5.96
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5.06
5.06
5.05
4.54
4.54
4.53
4.52
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4.50
4.49
4.49
4.48
4.44
4.38
4.37
4.34
4.34
3.80
3.76
2.11
2.08
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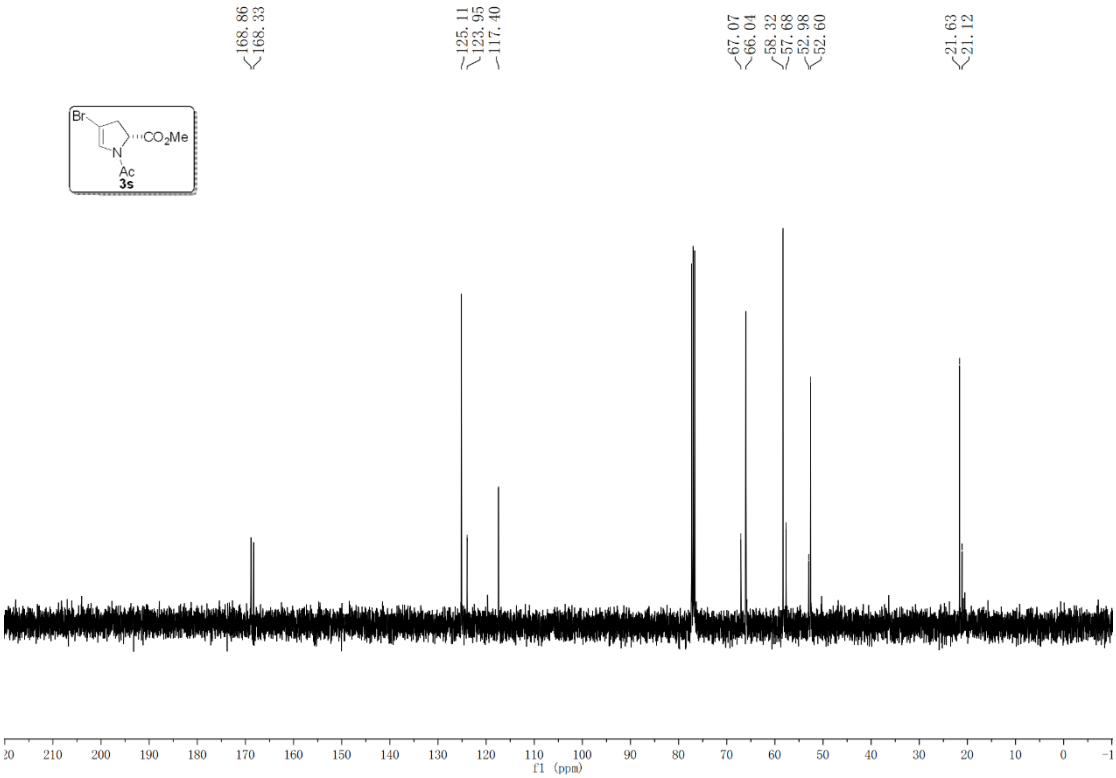
Br
CO2Me
N
Ac
3s
1.00
1.00
2.17
3.17
3.18
f1 (ppm)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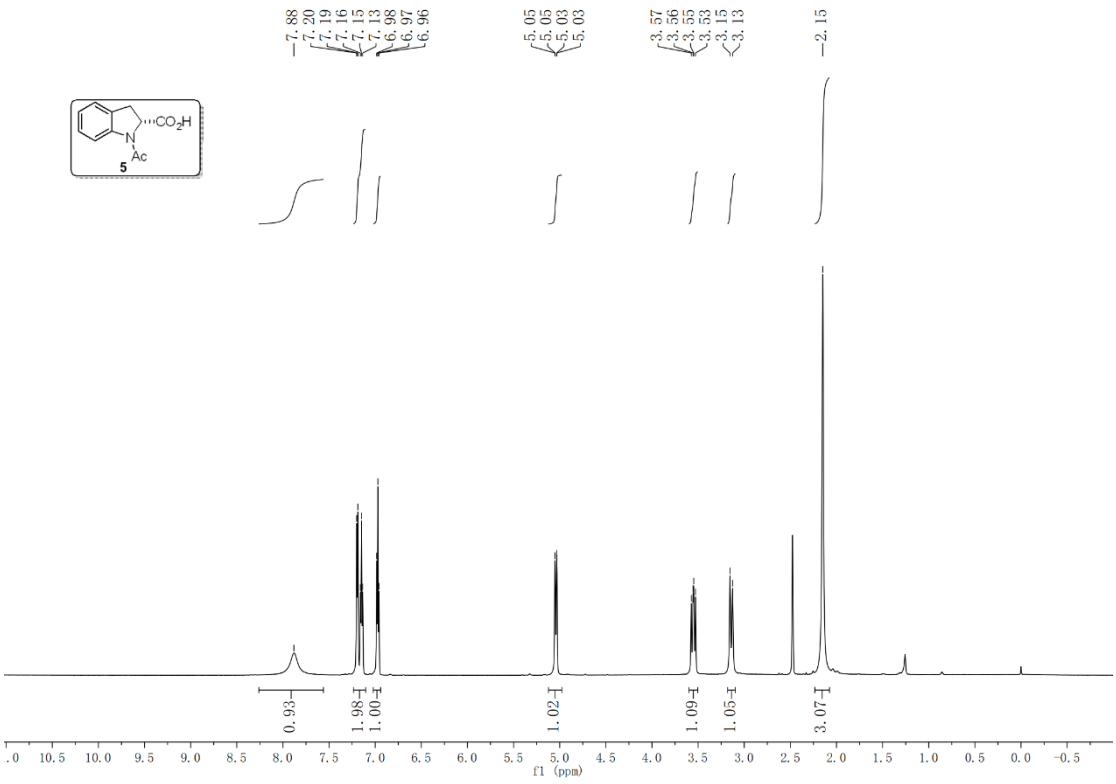
52.60
21.63
21.12
Br
CO2Me
N
Ac
3s
f1 (ppm)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6.98
6.97
6.96
5.05
5.05
5.03
5.03
3.57
3.56
3.55
3.53
3.15
3.13
2.15
CO2H
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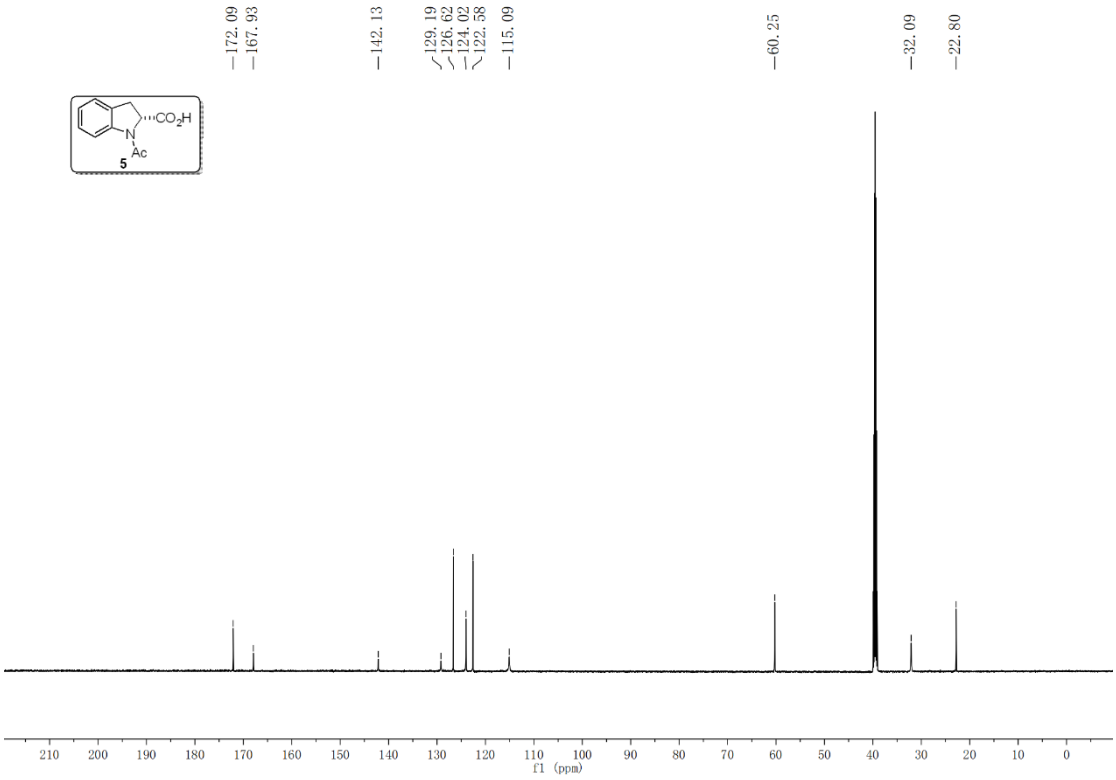
Ac
5
0.93
1.98
1.00
1.02
1.09
1.05
3.07
f1 (ppm)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167.93
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129.19
126.62
124.02
122.58
115.09
60.25
32.09
22.80
CO2H
N
Ac
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)