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Electronic Supplementary Information

Direct and Site-Selective Pd(II)-Catalyzed C-7 Arylation of Indoline with Arylsilanes

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Ⅰ. General Informations

Analytical methods: Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 300, 400 and 500 NMR spectrometers. Chemical shifts ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublets of doublets); dddd (doublet of doublets of doublets of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as d in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet). High resolution mass spectral analysis (HRMS) was performed on Water XVEO G2 Q-TOF (Waters Corporation). Infrared spectra were recorded on a Nicolet IS50 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}).

Materials: All commercial available reagents were used without further purification unless otherwise noted. It must be point out that tetrahydrofuran was dried by sodium and distilled until the diphenylmethanone turned blue. All substituted indoline[1-3], arylsilanes[4] were prepared according to the known methods. In addition, column chromatography was performed using 200-300 mesh silica gels.

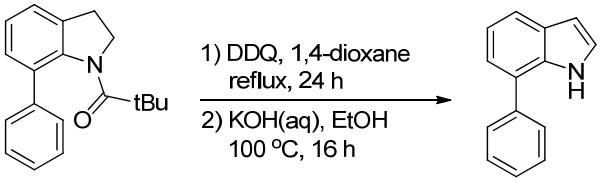
Ⅱ. Experimental Procedures

1. General procedure for Pd(II)-catalyzed C-7 arylation of indoline with arylsilanes

To a septum capped 15 mL of dried sealed tube with a magnetic stirring bar were added 1-(indolin-1-yl)-2,2-dimethylpropan-1-one (**1a**, 0.2 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), AgF (50 mg, 0.4 mmol), $Cu(OTf)_2$ (145 mg, 0.4 mmol) and 4 mL fresh distilled THF, followed by addition of trimethoxy(phenyl)silane (**2a,** 75 μL, 0.4 mmol) by microsyringe. The sealed tube was screw capped and heated to 40 ^oC for 48 h (oil bath). After completed, the reaction was cooled to room temperature, and then the mixture was diluted with 10 mL water. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate) to provide pure product **3ab.**

2. General experimental procedure for the transformation of C7-arylated indoline 3ab to the corresponding indole 5a[5,6]

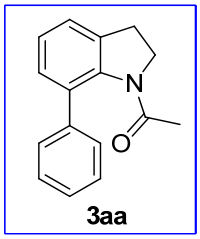
To a septum capped 15 mL of dried sealed tube with a magnetic stirring bar were added 2,2-dimethyl-1-(7-phenylindolin-1-yl)propan-1-one(**3ab**, 0.2 mmol), DDQ (0.4 mmol) and 1,4-Dioxane (1 ml). The sealed tube was screw capped and heated to 135 ^oC for 24 h. After the reaction completed, the resulting mixture was filtered over a short silica column and washed by ethyl acetate. The filtrate was evaporated to dryness to the crude intermediate product. Then, crude intermediate product was dissolved in 2 ml ethanol, and 1 ml saturated KOH solution was added. And the reaction mixture was allowed to stir for 16 h at 100 ^oC. After completed, then the reaction mixture was diluted with ethyl acetate (3 mL) and neutralized with saturated NH_4Cl solution to pH 7. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (Petroleum ether /EtOAc = 15:1) to afford **5a** in 84% yield.



3ab **5a**, 84%

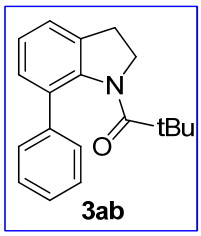
III. Spectroscopic Data for Arylated Products.

1-(7-phenylindolin-1-yl)ethanone **(3aa)**[7]



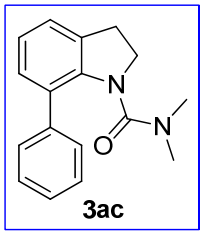
The product **3aa** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.20) to give product as a white solid (43.2 mg, 91 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 7.26 – 7.19 (m, 1H), 7.16 (td, *J* = 7.4, 6.7, 1.6 Hz, 2H), 7.13 – 7.05 (m, 1H), 4.21 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.3, 129.1, 127.4, 127.2, 125.4, 123.8, 50.6, 29.3, 22.5.

2,2-dimethyl-1-(7-phenylindolin-1-yl)propan-1-one (3ab)



The product **3ab** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1, Rf = 0.35) to give product as a white solid(phenyltriethyloxysilane, 53.1 mg, 95 % yield. phenyltrimethoxysilane, 51.3 mg, 92 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 4H), 7.20 – 7.09 (m, 3H), 7.08 – 7.02 (m, 1H), 4.09 (t, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 1.08 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 141.8, 141.4, 134.5, 133.0, 128.5, 128.2, 126.5, 124.9, 123.1, 50.5, 39.7, 31.1, 27.9. IR (KBr disk): 2982, 2965, 2926, 1654, 1353, 1320, 1188, 918, 758, 698, 587 cm^{-1}. **HRMS (ESI)** calcd for $C_{19}H_{21}NO\ Na^+$ $[M + Na]^+$ 302.1521, found 302.1520.

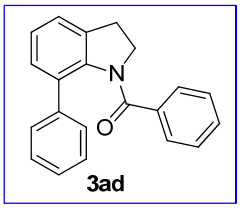
N,N-dimethyl-7-phenylindoline-1-carboxamide (3ac)[8]



The product **3ac** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 3:1, Rf = 0.24) to give product as a white solid (29.3 mg, 55 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.39 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.29 (tt, *J* = 6.6, 1.4 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.01 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H),

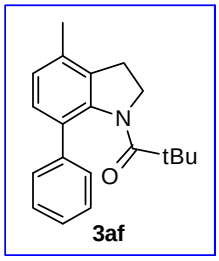
2.58 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 142.3, 140.3, 133.6, 129.1, 129.0, 128.2, 127.0, 126.7, 123.6, 122.9, 51.8, 36.8, 29.7.

phenyl(7-phenylindolin-1-yl)methanone (3ad)



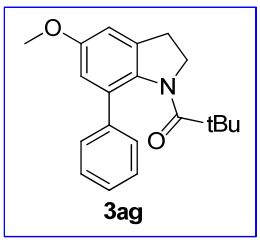
The product **3ad** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 3:1, Rf = 0.24) to give product as a white solid (55.7 mg, 90 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (m, *J* = 25.6, 18.3, 11.7, 7.4 Hz, 13H), 4.17 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 140.4, 135.7, 135.1, 132.0, 130.3, 129.1, 128.5, 127.9, 127.8, 126.7, 126.5, 125.2, 123.6, 52.5, 29.8. **IR** (KBr disk): 3057, 3032, 2946, 2886, 1661, 1470, 1362, 1331, 1132, 1071, 1022, 873, 761 cm^{-1}. **HRMS (ESI)** calcd for $C_{21}H_{17}NO\ Na^+$ $[M + Na]^+$ 322.1206 found 322.1203

2,2-dimethyl-1-(4-methyl-7-phenylindolin-1-yl)propan-1-one(3af)



The product **3af** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.33) to give product as a white solid (55.1 mg, 94 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 4H), 7.13 (ddt, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.90 – 6.84 (m, 1H), 4.08 (t, *J* = 7.5 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.4, 141.5, 141.4, 133.2, 132.5, 130.5, 128.6, 128.2, 126.6, 126.2, 125.9, 50.3, 39.7, 29.8, 28.0, 18.5. **IR** (KBr disk): 3055, 3026, 2962, 1650, 1483, 1400, 1320, 1158, 1011, 911, 889, 817, 766, 700 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO\ Na^+$ $[M + Na]^+$ 316.1677, found 316.1675.

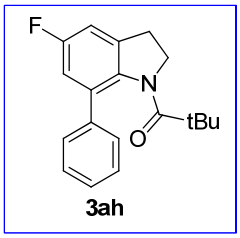
1-(5-methoxy-7-phenylindolin-1-yl)-2,2-dimethylpropan-1-one(3ag)



The product **3ag** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 3:1, Rf = 0.24) to give product as a white solid (57.7 mg, 93 % yield). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.35 – 7.23 (m, 4H), 7.19 – 7.11 (m, 1H), 6.71 – 6.66 (m, 2H), 4.08 (t, *J* = 7.4 Hz, 2H), 3.72 (s, 3H), 2.97 (t, *J* = 7.4 Hz, 2H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.0, 157.5, 141.3, 136.1, 135.2, 133.6, 128.2, 126.6, 126.5, 113.5, 109.3, 55.7, 50.8, 39.6, 31.4, 28.0. **IR** (KBr disk) 3064, 2963, 1660, 1610, 1465, 1325, 1228, 1163, 1076, 1033, 911, 846, 763, 701, 650. **HRMS (ESI)** calcd for $C_{20}H_{23}NO_2$ Na^+ $[M + Na]^+$ 332.1626, found 332.1623.

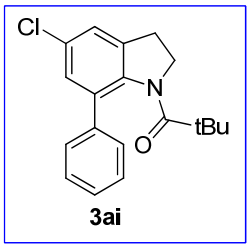
1-(5-fluoro-7-phenylindolin-1-yl)-2,2-dimethylpropan-1-one(3ah)



3ah

The product **3ah** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.37) to give product as a white solid (41.6 mg, 70 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.18 (dq, *J* = 6.7, 3.2, 2.6 Hz, 1H), 6.89 – 6.77 (m, 2H), 4.11 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3, 160.5 (d, *J* = 242.8 Hz),140.4 (d, *J* = 1.7 Hz), 137.8 (d, *J* = 2.2 Hz), 136.5 (d, *J* = 9.0 Hz), 134.2 (d, *J* = 8.3 Hz), 128.4, 127.0, 126.4, 114.9 (d, *J* = 23.7 Hz), 110.2 (d, *J* = 23.8 Hz), 50.8, 39.7, 31.3 (d, *J* = 2.2 Hz), 28.0. **IR** (KBr disk): 3032, 2965, 1654, 1597, 1460, 1413, 1321, 1187, 1162, 1080, 911, 866, 767, 698 cm^{-1}. **HRMS (ESI)** calcd for $C_{19}H_{20}FNONa^+$ $[M + Na]^+$ 320.1427, found 320.1424.

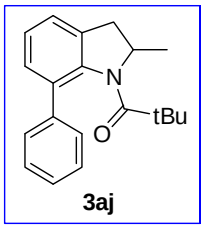
1-(5-chloro-7-phenylindolin-1-yl)-2,2-dimethylpropan-1-one(3ai)



3ai

The product **3ai** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.24) to give product as a white solid (43.8 mg, 70 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.4 Hz, 4H), 7.22 – 7.16 (m, 1H), 7.14 – 7.07 (m, 2H), 4.11 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3, 140.6, 140.2, 136.5, 134.1, 130.0, 128.4, 128.4, 127.1, 126.4, 123.2, 50.7, 39.8, 31.0, 27.9. **IR** (KBr disk): 3071, 2965, 1655, 1573, 1455, 1404, 1343, 1318, 1181, 1077, 901, 856, 770, 700 cm^{-1}. **HRMS (ESI)** calcd for $C_{19}H_{20}ClNO$ Na^+ $[M + Na]^+$ 336.1131, found 336.1133.

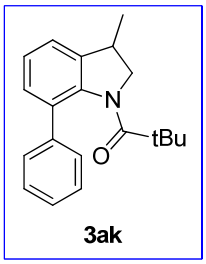
2,2-dimethyl-1-(2-methyl-7-phenylindolin-1-yl)propan-1-one (3aj)



3aj

The product **3aj** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.30) to give product as a white solid (53.7 mg, 91 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.27 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.12 – 7.06 (m, 1H), 4.67 (p, *J* = 6.5 Hz, 1H), 3.32 – 3.16 (m, 1H), 2.52 (d, *J* = 14.9 Hz, 1H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3, 141.2, 140.9, 134.8, 134.3, 128.2, 128.1, 126.6, 126.5, 125.4, 123.8, 57.0, 40.1, 38.4, 28.5, 20.6. **IR** (KBr disk): 2958, 1651, 1456, 1349, 1320, 1205, 1176, 993, 752, 695 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO$ Na^+ $[M + Na]^+$ 316.1677, found 316.1675.

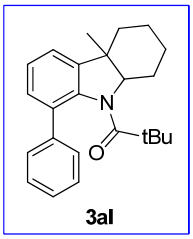
2,2-dimethyl-1-(3-methyl-7-phenylindolin-1-yl)propan-1-one(3ak)



3ak

The product **3ak** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.30) to give product as a white solid (56.3 mg, 96 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.27 – 7.14 (m, 4H), 4.31 (dd, *J* = 10.2, 7.6 Hz, 1H), 3.71 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.39 (h, *J* = 7.0 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.15 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 141.5, 141.4, 139.7, 132.9, 128.7, 128.2, 126.5, 126.5, 125.1, 121.8, 58.2, 39.6, 37.6, 28.0, 18.1. **IR** (KBr disk): 3064, 2962, 2930, 1653, 1454, 1427, 1347, 1212, 1177, 1010, 960, 798, 755, 698, 611 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO$ Na^+ $[M + Na]^+$ 316.1677, found 316.1678.

2,2-dimethyl-1-(4a-methyl-8-phenyl-2,3,4,4a-tetrahydro-1H-carbazol-9(9aH)-yl)propan-1-one(3al)

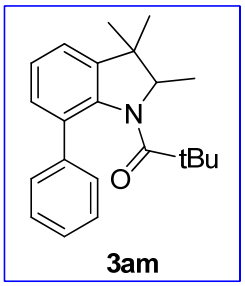


3al

The product **3al** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 30:1, Rf = 0.41) to give product as a white solid (34.7 mg, 50 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 – 7.09 (m, 3H), 7.00 (dd, *J* = 6.4, 2.3

Hz, 1H), 4.01 (dd, *J* = 10.7, 5.9 Hz, 1H), 2.33 – 2.18 (m, 2H), 1.62 – 1.48 (m, 3H), 1.40 (tdd, *J* = 13.7, 10.7, 3.7 Hz, 1H), 1.16 (ddt, *J* = 14.3, 11.9, 2.7 Hz, 2H), 1.08 (s, 9H), 1.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 141.7, 141.4, 141.1, 135.1, 128.1, 128.1, 126.6, 126.5, 125.6, 120.2, 68.9, 46.9, 40.2, 33.2, 29.5, 29.0, 28.6, 23.8, 22.1. **IR** (KBr disk): 3054, 2923, 2853, 1650, 1450, 1423, 1324, 1168, 1075, 1029, 914, 856, 756, 699, 580 cm^{-1}. **HRMS (ESI)** calcd for $C_{24}H_{29}NO\ Na^+$ $[M + Na]^+$ 370.2147, found 370.2146.

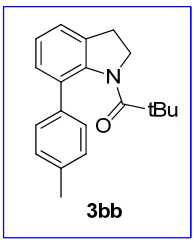
2,2-dimethyl-1-(2,3,3-trimethyl-7-phenylindolin-1-yl)propan-1-one(3am)



3am

The product **3am**was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.37) to give product as a white solid (20.1 mg, 31 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.27 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.02 (dd, *J* = 6.9, 1.8 Hz, 1H), 4.18 (q, *J* = 6.5 Hz, 1H), 1.50 (s, 2H), 1.28 (d, *J* = 4.3 Hz, 4H), 1.26 (s, 1H), 1.08 (d, *J* = 1.9 Hz, 11H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 143.0, 141.0, 140.3, 134.6, 128.2, 126.7, 126.6, 125.7, 120.8, 100.0, 67.8, 46.2, 40.3, 29.0, 28.7, 20.5, 16.4. **IR** (KBr disk): 2964, 1651, 1453, 1425, 1378, 1322, 1200, 1087, 755, 697 cm^{-1}. **HRMS (ESI)** calcd for $C_{22}H_{27}NO\ Na^+$ $[M + Na]^+$ 344.1990, found 344.1989.

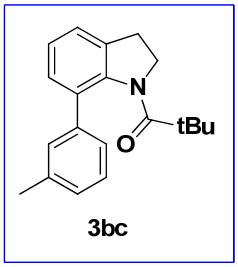
2,2-dimethyl-1-(7-(p-tolyl)indolin-1-yl)propan-1-one(3bb)



3bb

The product **3bb** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.30) to give product as a white solid (51.2 mg, 87 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.14 – 7.01 (m, 5H), 4.09 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.26 (s, 3H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 141.8, 138.5, 136.1, 134.6, 133.0, 129.0, 128.6, 126.4, 124.9, 122.9, 50.6, 39.7, 31.1, 28.0, 21.2. **IR** (KBr disk): 2966, 2922, 1662, 1470, 1443, 1395, 1351, 1100, 911, 828, 781, 752, 570 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO\ Na^+$ $[M + Na]^+$ 316.1677, found 316.1676.

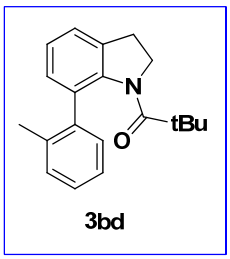
2,2-dimethyl-1-(7-(m-tolyl)indolin-1-yl)propan-1-one(3bc)



3bc

The product **3bc** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.30) to give product as a white solid (51.1 mg, 87 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.08 – 7.01 (m, 1H), 4.17 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 1.17 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 141.8, 141.3, 137.4, 134.5, 133.0, 128.6, 128.3, 127.3, 127.1, 124.9, 123.6, 123.0, 50.5, 39.7, 31.1, 27.9, 21.5. **IR** (KBr disk): 2968, 1654, 1588, 1470, 1396, 1316, 1186, 1100, 1013, 912, 833, 778 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO\ Na^+$ $[M + Na]^+$ 316.1677, found 316.1675.

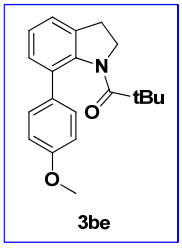
2,2-dimethyl-1-(7-(o-tolyl)indolin-1-yl)propan-1-one(3bd)



3bd

The product **3bd** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.33) to give product as a white solid (35.8 mg, 61 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.07 (m, 7H), 4.12 (td, *J* = 7.7, 2.9 Hz, 2H), 3.14 (dt, *J* = 12.4, 7.5 Hz, 2H), 2.29 (s, 3H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 142.6, 140.6, 134.8, 134.2, 132.7, 130.0, 129.1, 128.4, 126.6, 125.4, 124.3, 123.0, 50.6, 39.8, 31.2, 28.0, 19.9. **IR** (KBr disk): 2983, 2963, 1658, 1471, 1424, 1364, 1318, 1161, 1097, 915, 763, 726 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO\ Na^+$ $[M + Na]^+$ 316.1677, found 316.1678.

1-(7-(4-methoxyphenyl)indolin-1-yl)-2,2-dimethylpropan-1-one(3be)

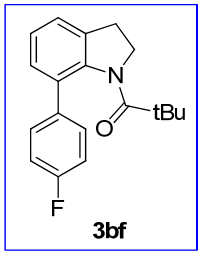


3be

The product **3be** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 5:1, Rf = 0.30) to give product as a white solid (30 mg, 48 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.20 – 7.09 (m, 3H), 6.93 – 6.86 (m, 2H), 4.17 (t, *J* = 7.5 Hz,

2H), 3.81 (s, 3H), 3.08 (t, J = 7.5 Hz, 2H), 1.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 158.3, 141.7, 134.6, 134.0, 132.6, 128.5, 127.5, 124.9, 122.7, 113.7, 55.2, 50.6, 39.7, 31.1, 28.1. **IR** (KBr disk): 2966, 1659, 1612, 1515, 1470, 1246, 1165, 1099, 1033, 912, 835, 782, 754 cm^{-1}. **HRMS (ESI)** calcd for $C_{20}H_{23}NO_2\ Na^+$ $[M + Na]^+$ 332.1626, found 332.1623.

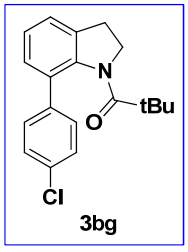
1-(7-(4-fluorophenyl)indolin-1-yl)-2,2-dimethylpropan-1-one(3bf)



3bf

The product **3bf** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.34) to give product as a white solid (30.4 mg, 51 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.15 – 7.03 (m, 3H), 7.00 – 6.93 (m, 2H), 4.11 (t, J = 7.5 Hz, 2H), 3.03 (t, J = 7.5 Hz, 2H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.33, 161.71 (d, J = 245.0 Hz), 141.87, 137.56 (d, J = 3.4 Hz), 134.73, 132.13, 128.53, 128.14 (d, J = 8.0 Hz), 125.06, 123.31, 115.15 (d, J = 21.3 Hz), 50.64, 39.76, 31.14, 28.04. **IR** (KBr disk): 3068, 2967, 1653, 1512, 1472, 1349, 1320, 1208, 1162, 916, 849, 775, 755 cm^{-1}. **HRMS (ESI)** calcd for $C_{19}H_{20}FNONa^+$ $[M + Na]^+$ 320.1427, found 320.1423.

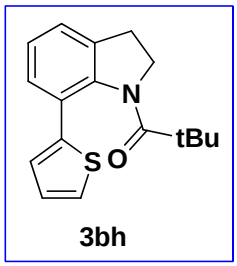
1-(7-(4-chlorophenyl)indolin-1-yl)-2,2-dimethylpropan-1-one(3bg)



3bg

The product **3bg** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.34) to give product as a white solid (45.2 mg, 72 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.23 – 7.10 (m, 3H), 4.18 (t, J = 7.5 Hz, 2H), 3.10 (t, J = 7.5 Hz, 2H), 1.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 141.7, 140.0, 134.7, 132.3, 131.8, 128.4, 128.4, 127.8, 125.1, 123.5, 50.6, 39.7, 31.0, 28.0. **IR** (KBr disk): 2968, 1654, 1470, 1396, 1316, 1186, 1099, 1013, 912, 833, 778 cm^{-1}. **HRMS (ESI)** calcd for $C_{19}H_{20}ClNONa^+$ $[M + Na]^+$ 336.1131, found 336.1128.

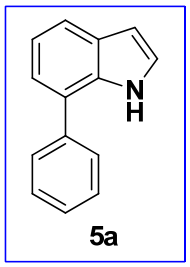
2,2-dimethyl-1-(7-(thiophen-2-yl)indolin-1-yl)propan-1-one(3bh)



3bh

The product **3bh** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.23) to give product as a brown solid (12.0 mg, 21 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.19 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.21 (t, *J* = 7.5 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 142.8, 142.1, 135.0, 128.5, 126.9, 126.4, 125.0, 124.1, 124.0, 123.4, 50.8, 39.8, 31.2, 28.1. **IR** (KBr disk): 2966, 2927, 1656, 1445, 1396, 1428, 1326, 1183, 1152, 1088, 908, 777, 700 cm^{-1}. **HRMS (ESI)** calcd for $C_{17}H_{19}NOSNa^{+}$ $[M + Na]^{+}$ 308.1085, found 308.1082.

7-phenyl-1H-indole(5a)[9]



5a

The product **5a** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1, Rf = 0.41) to give product as a colorless oil liquid (32.5 mg, 84 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.67 – 7.58 (m, 3H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.22 – 7.18 (m, 2H), 7.14 (dd, *J* = 3.2, 2.5 Hz, 1H), 6.60 (dd, *J* = 3.2, 2.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 133.6, 129.10, 128.2, 127.4, 125.5, 124.3, 121.8, 120.3, 120.0, 103.0.

IV. References

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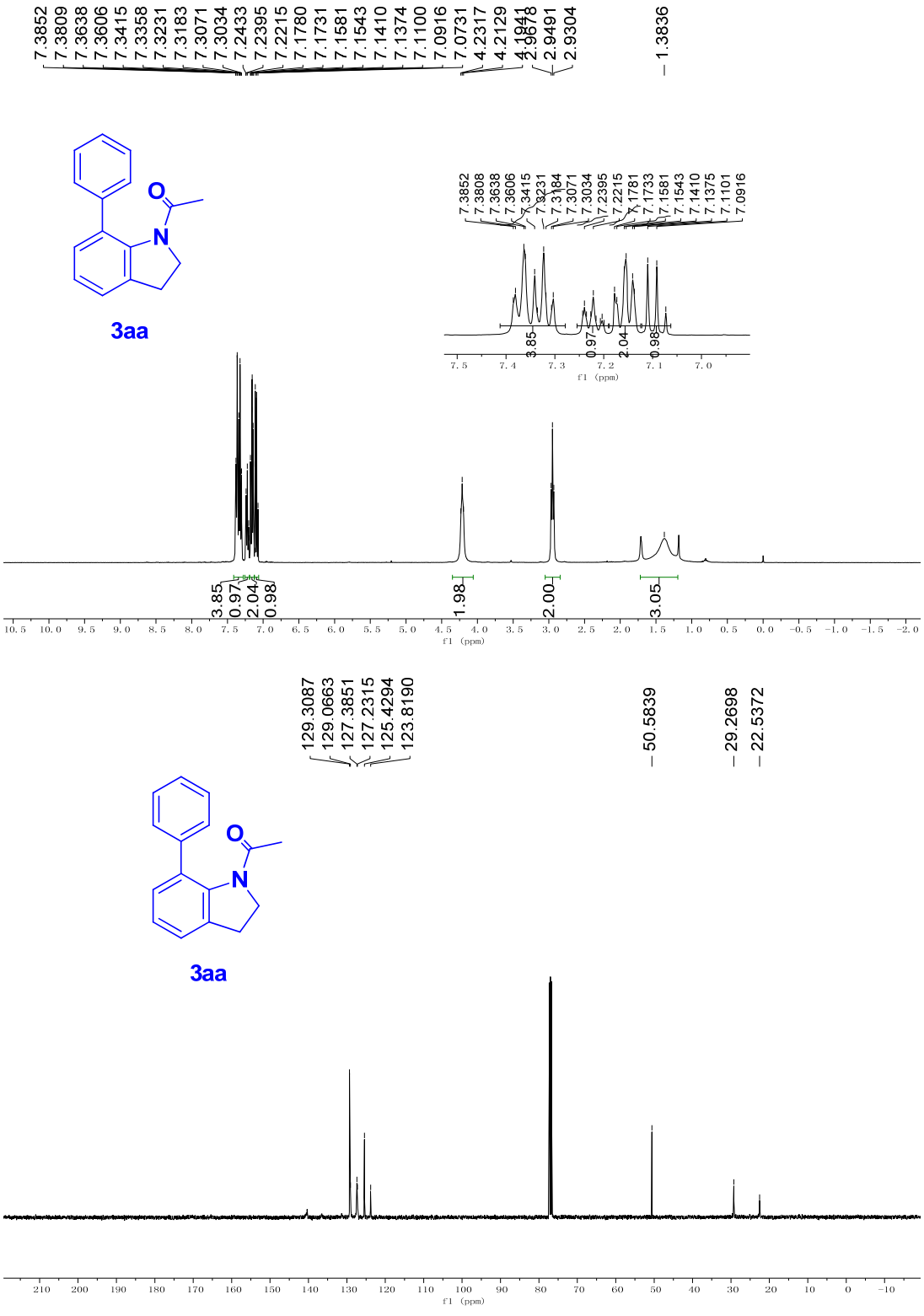
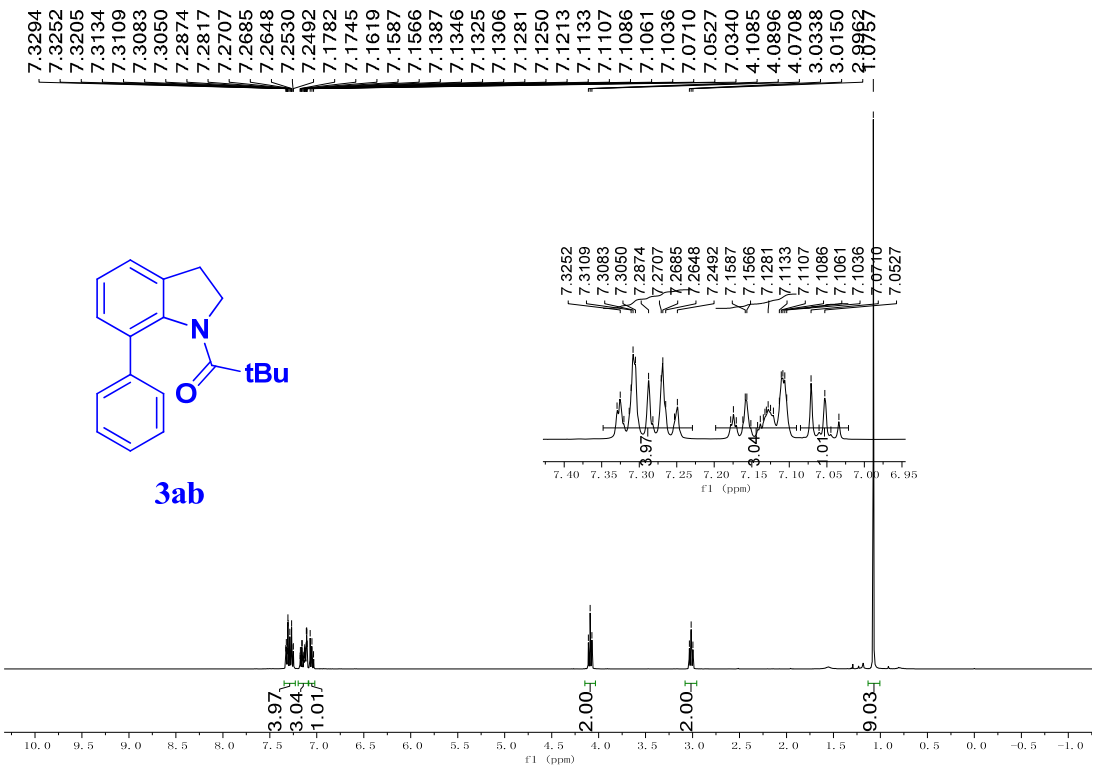
V. NMR Spectra

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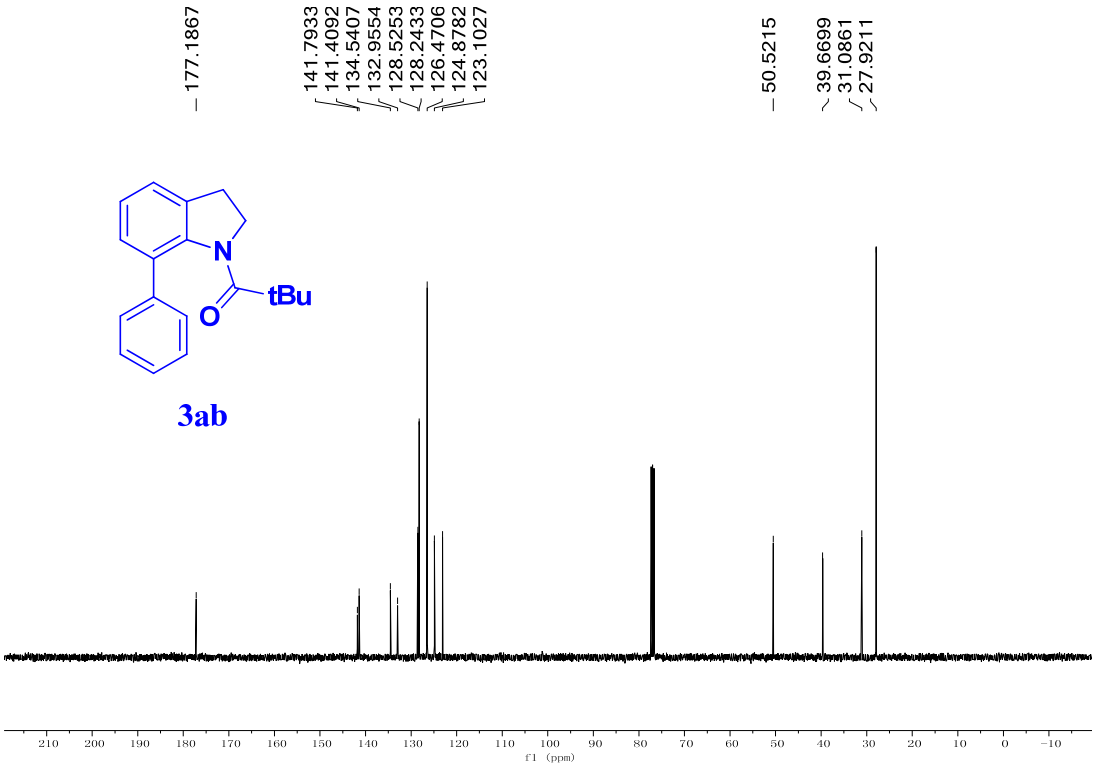
f1 (ppm)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tBu
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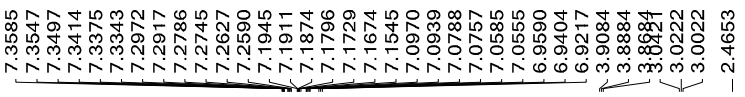
f1 (ppm)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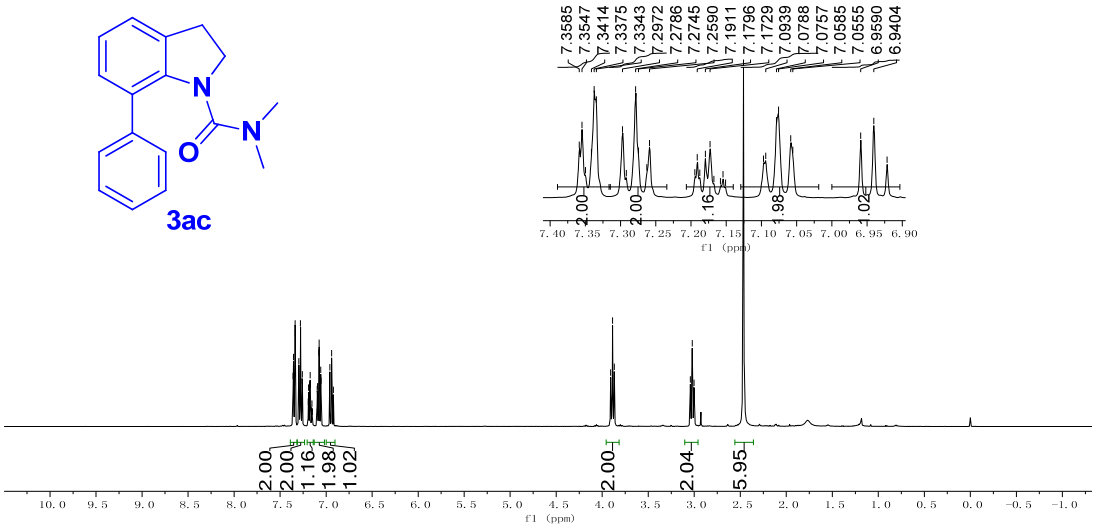
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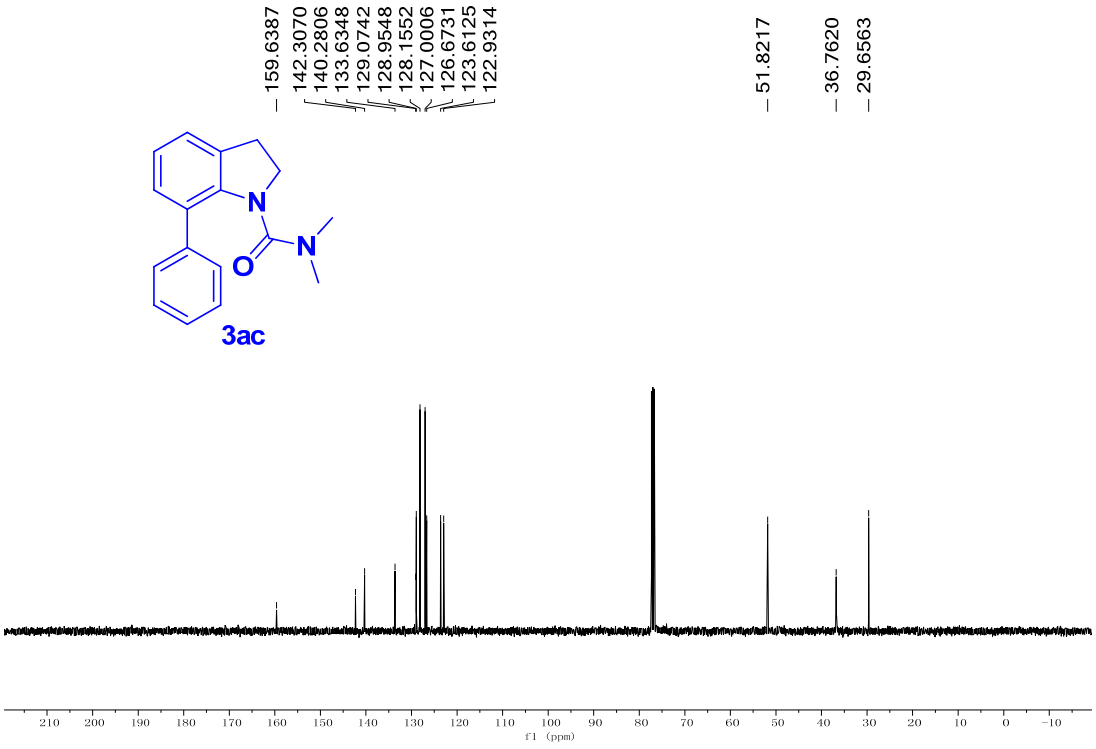
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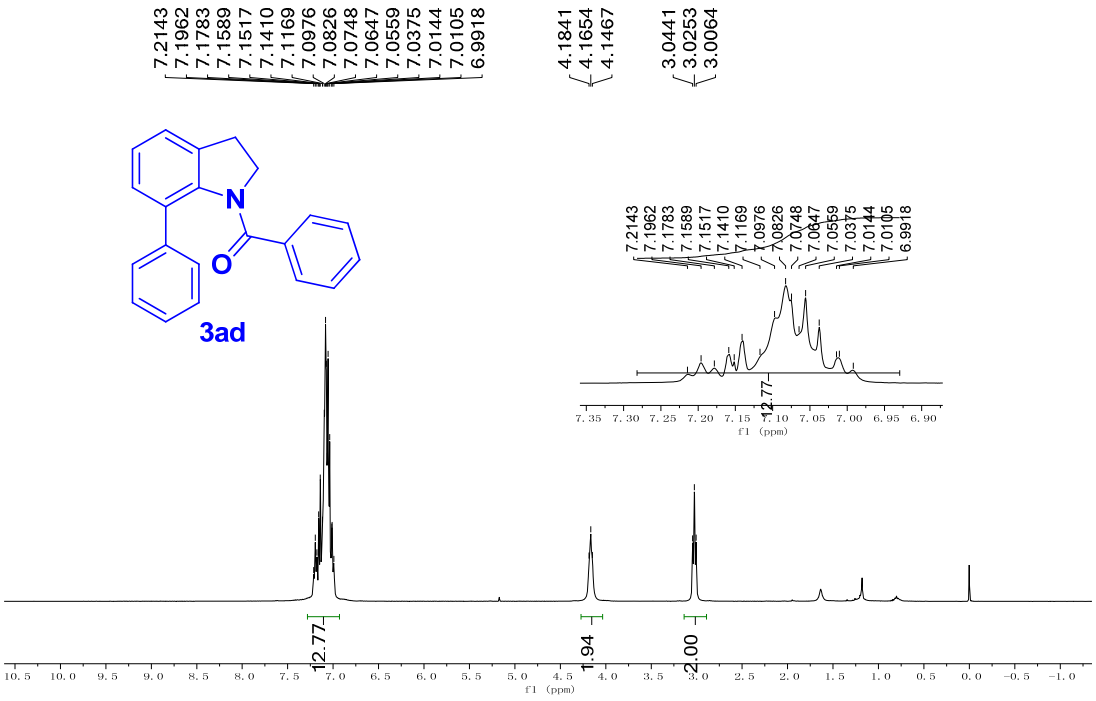
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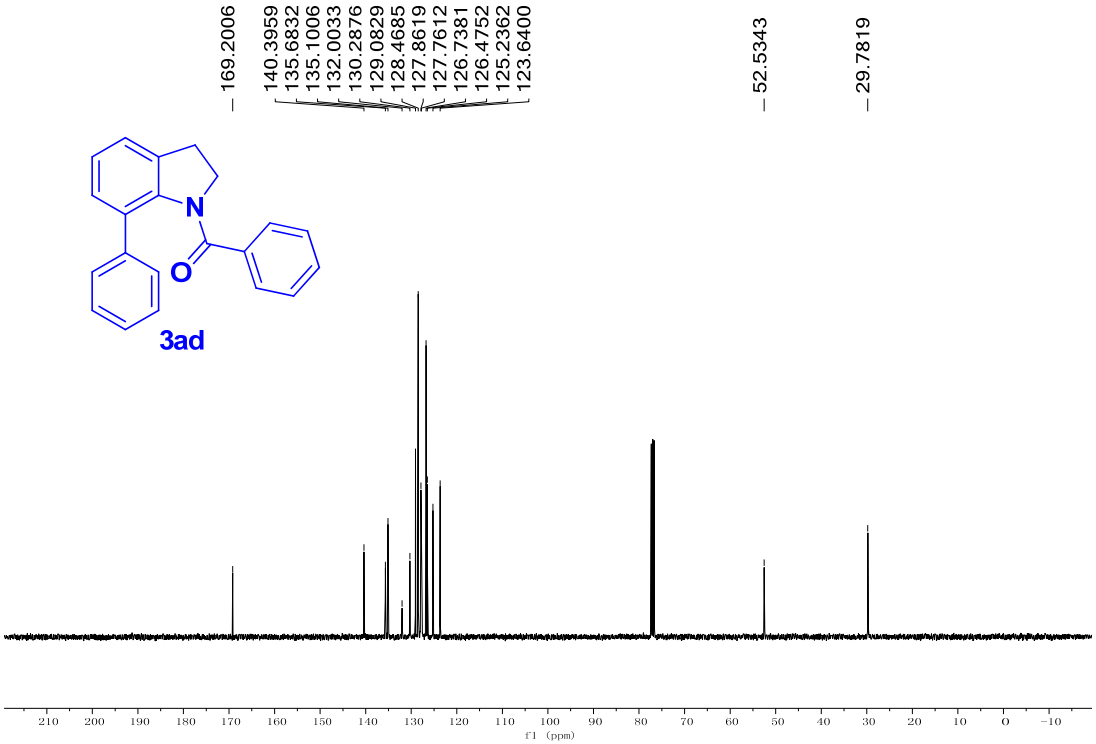
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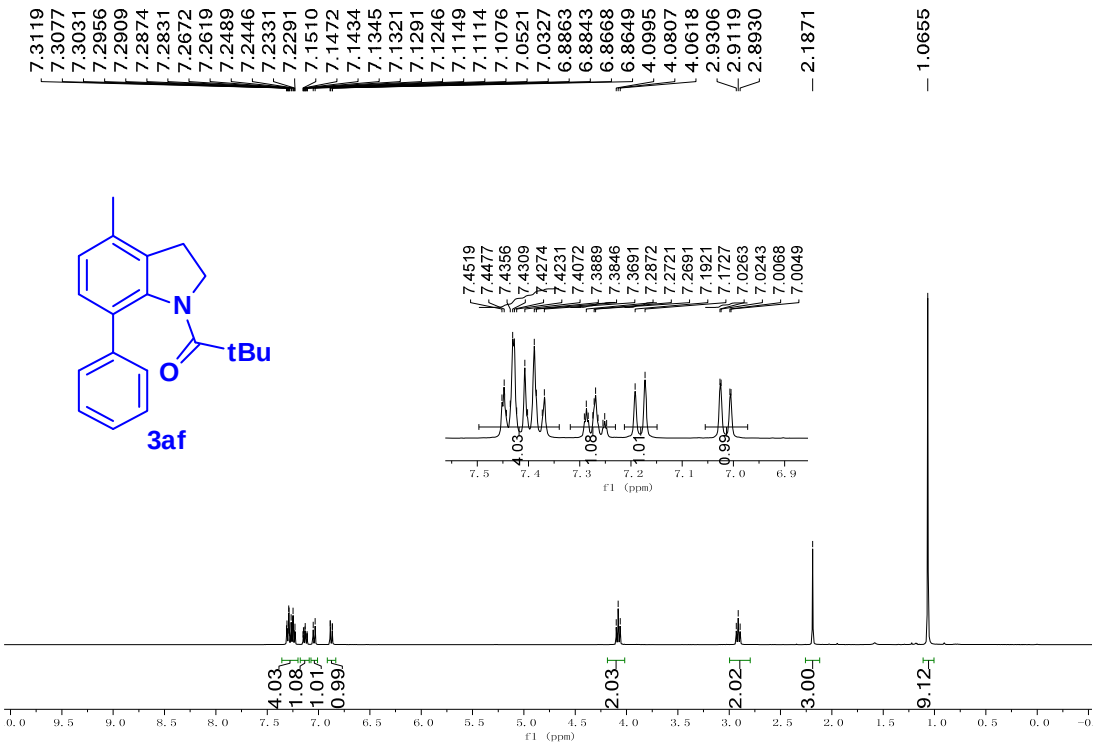
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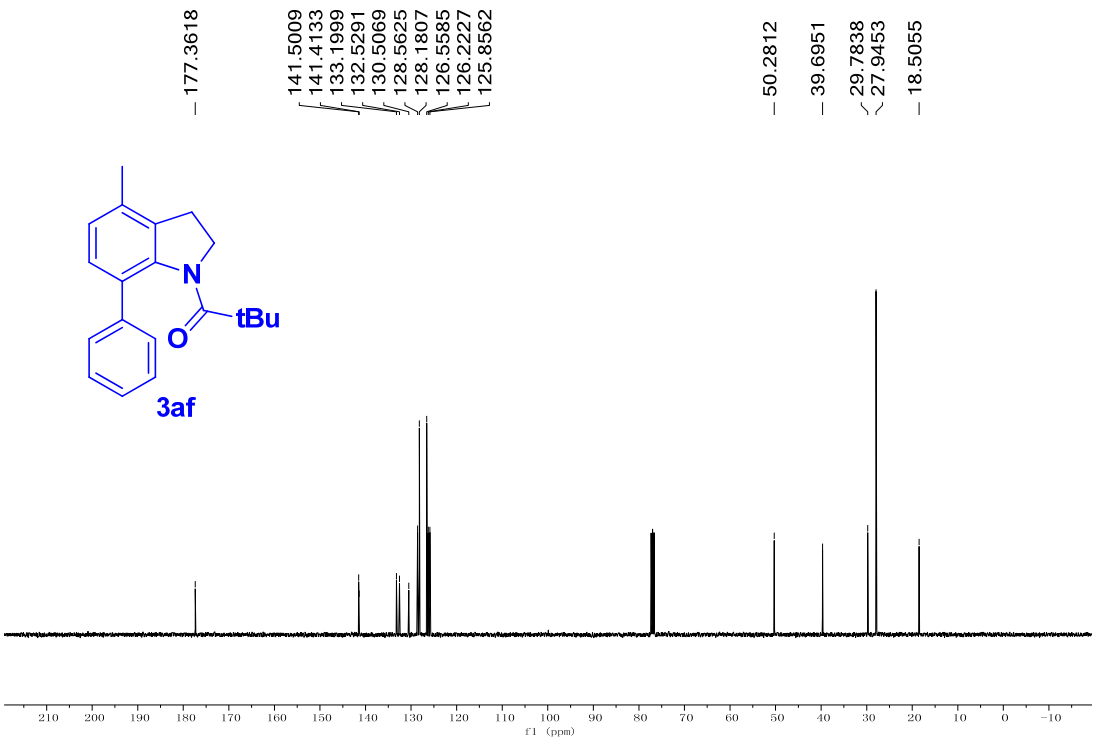
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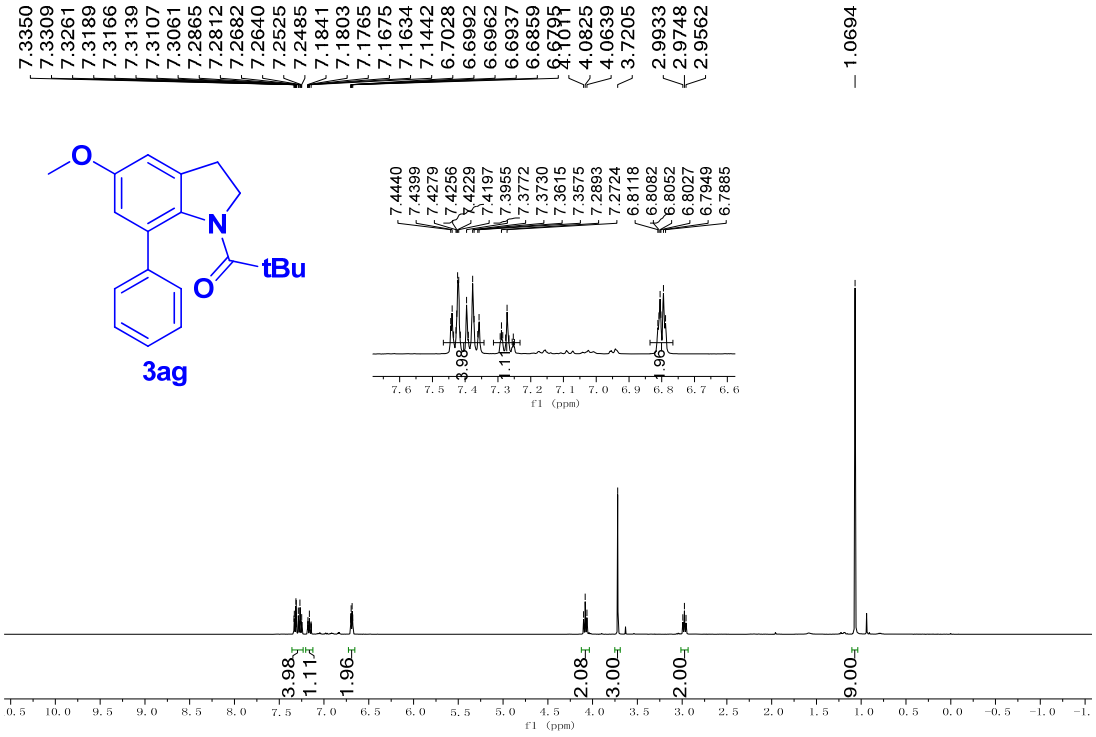
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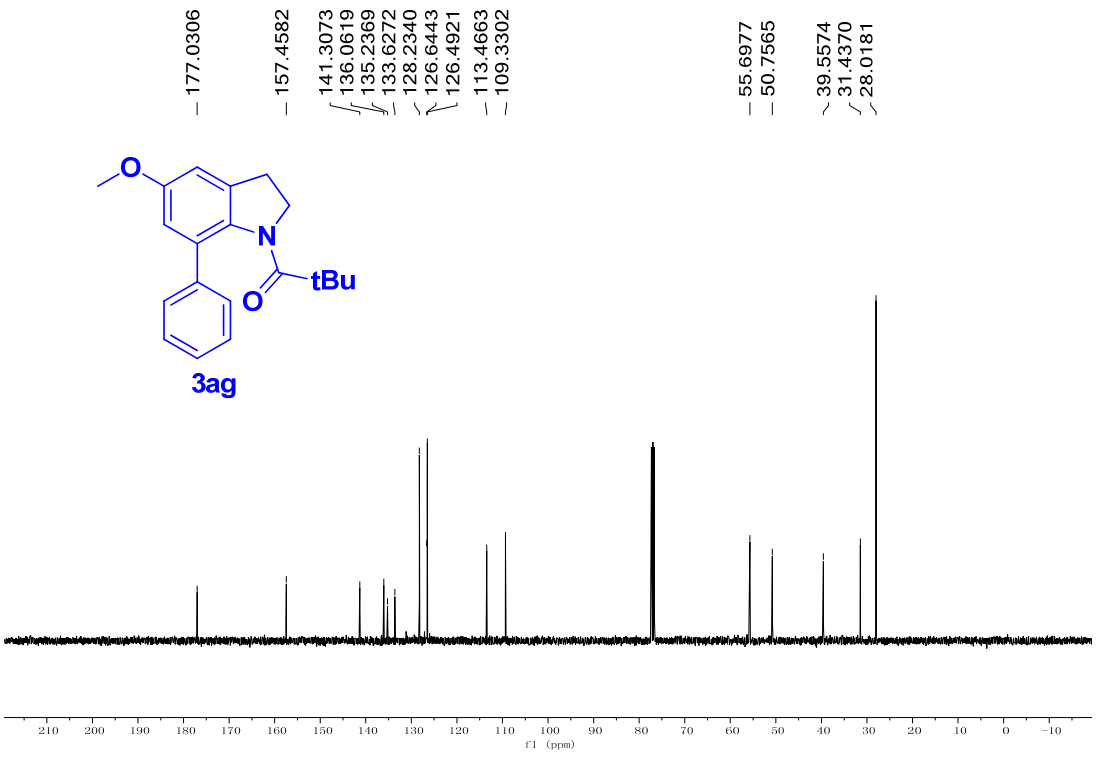
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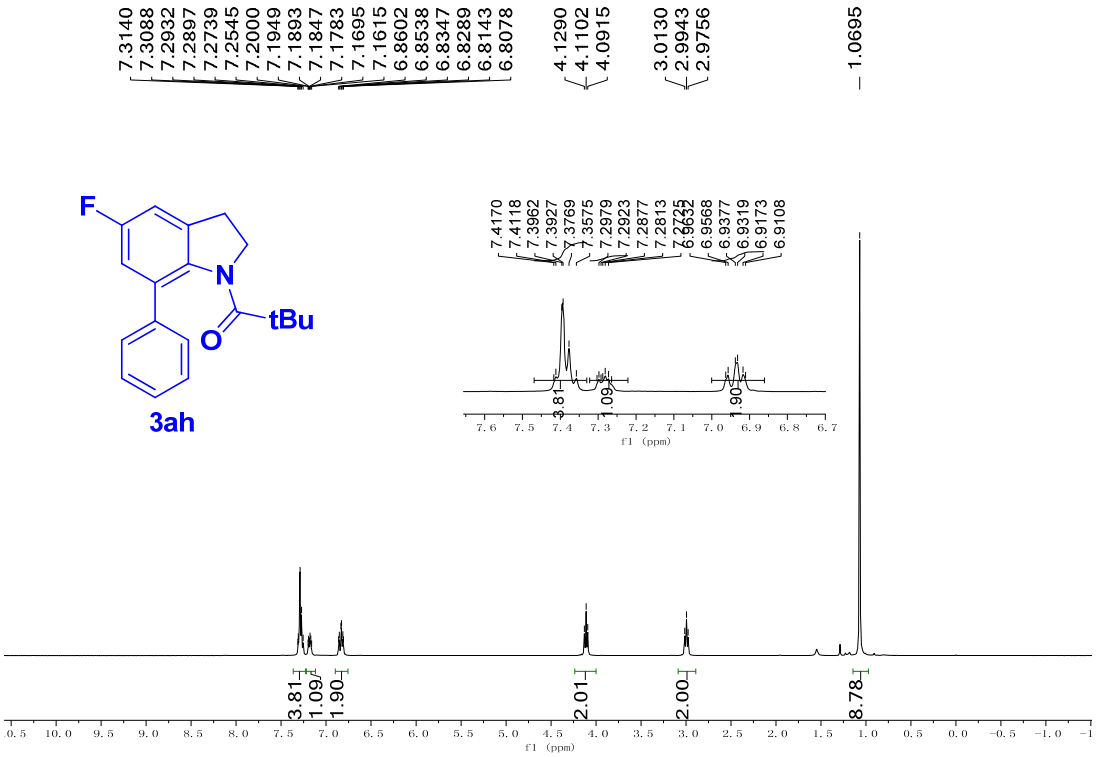
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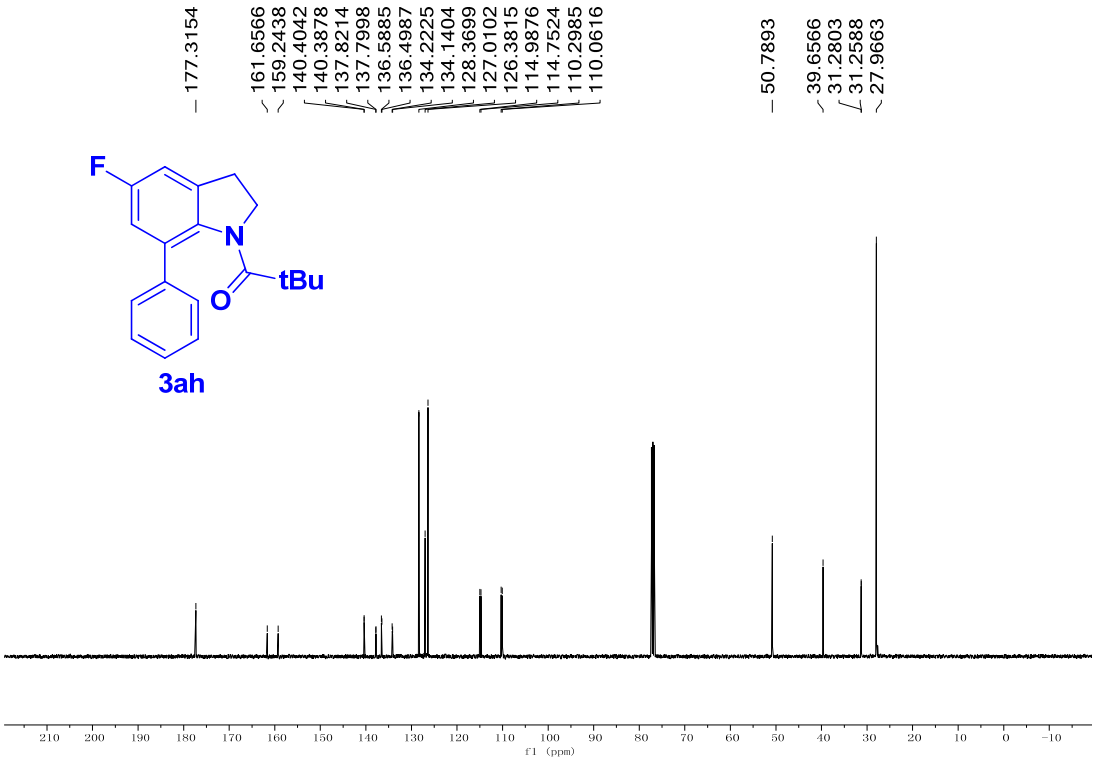
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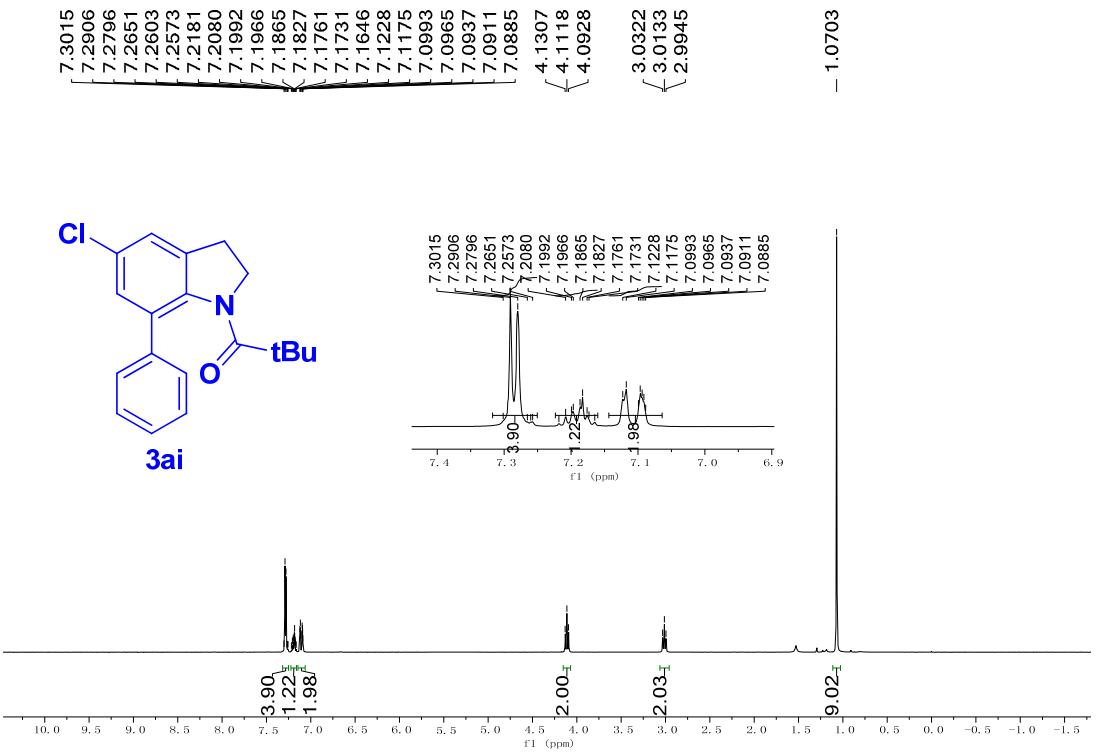
f1 (ppm)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7.1228
7.1175
7.0993
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7.0911
7.0885
4.1307
4.1118
4.0928
3.0322
3.0133
2.9945
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O
tBu
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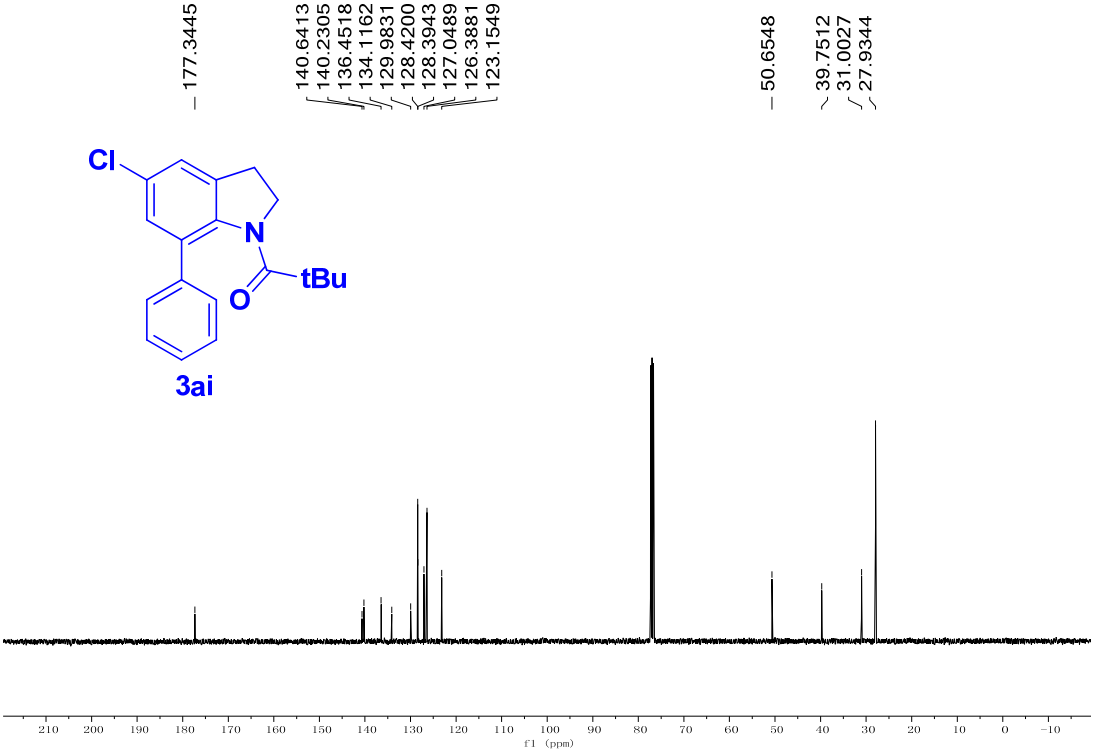
9.02
f1 (ppm)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tBu
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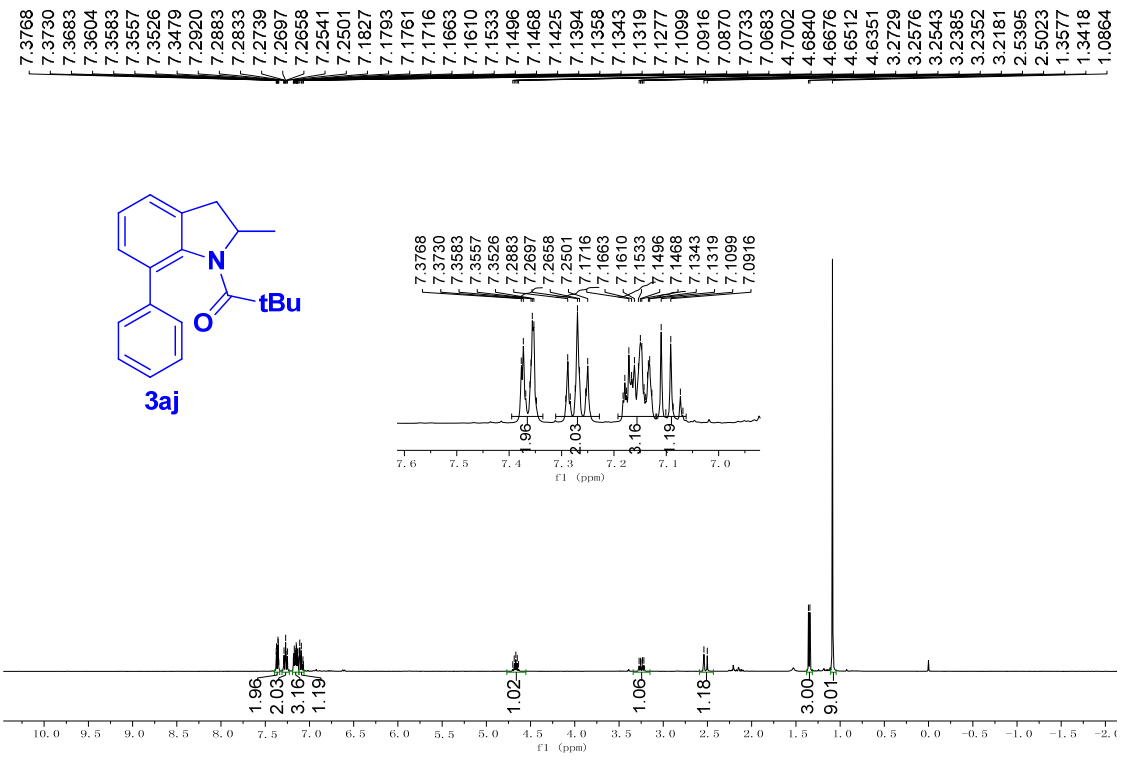
f1 (ppm)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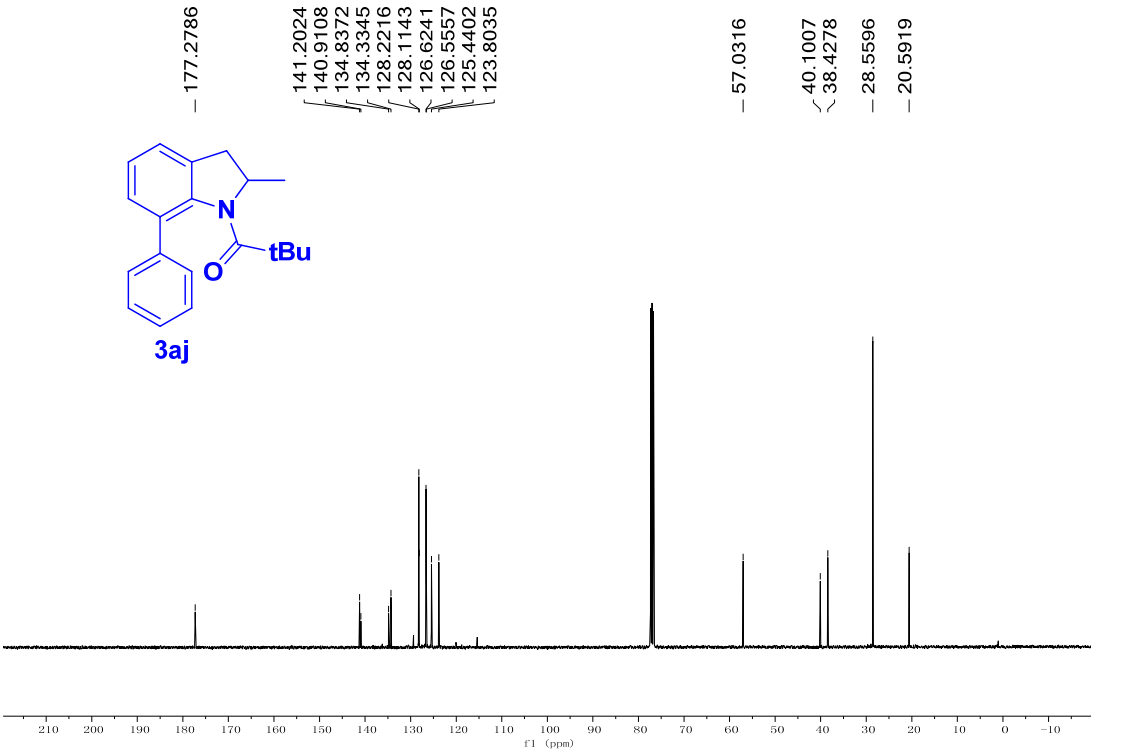
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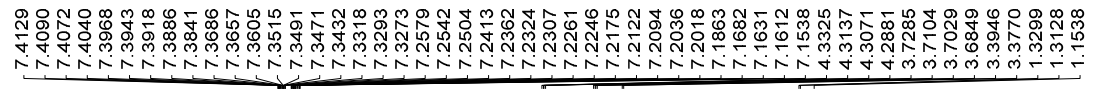
3aj
f1 (ppm)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7.3432
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7.2413
7.2362
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7.2018
7.1863
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7.1631
7.1612
7.1538
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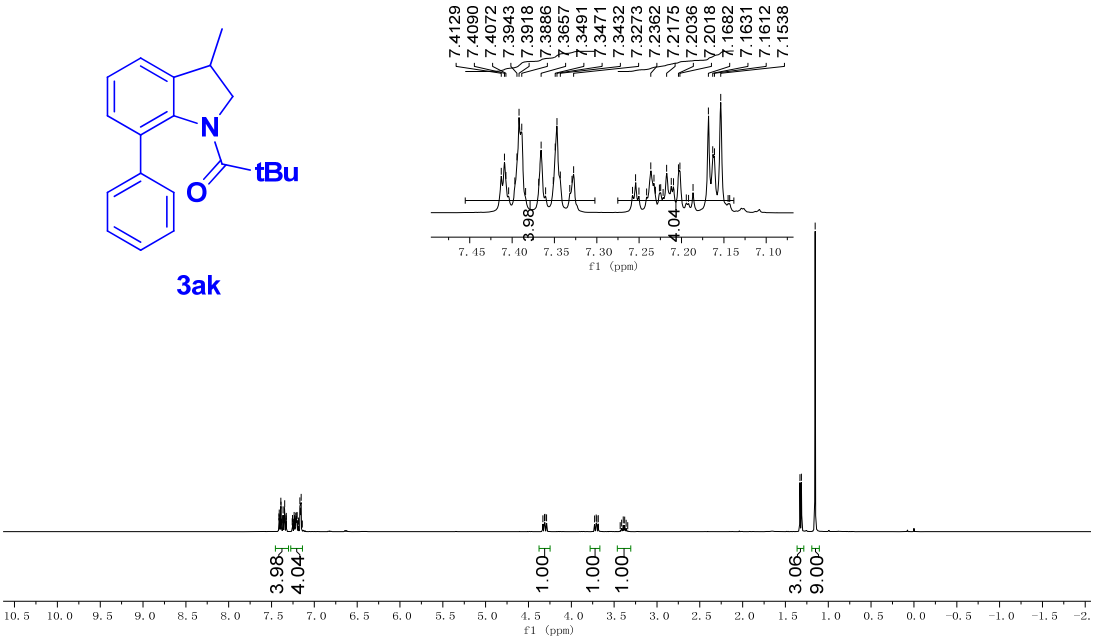
1.3128
1.1538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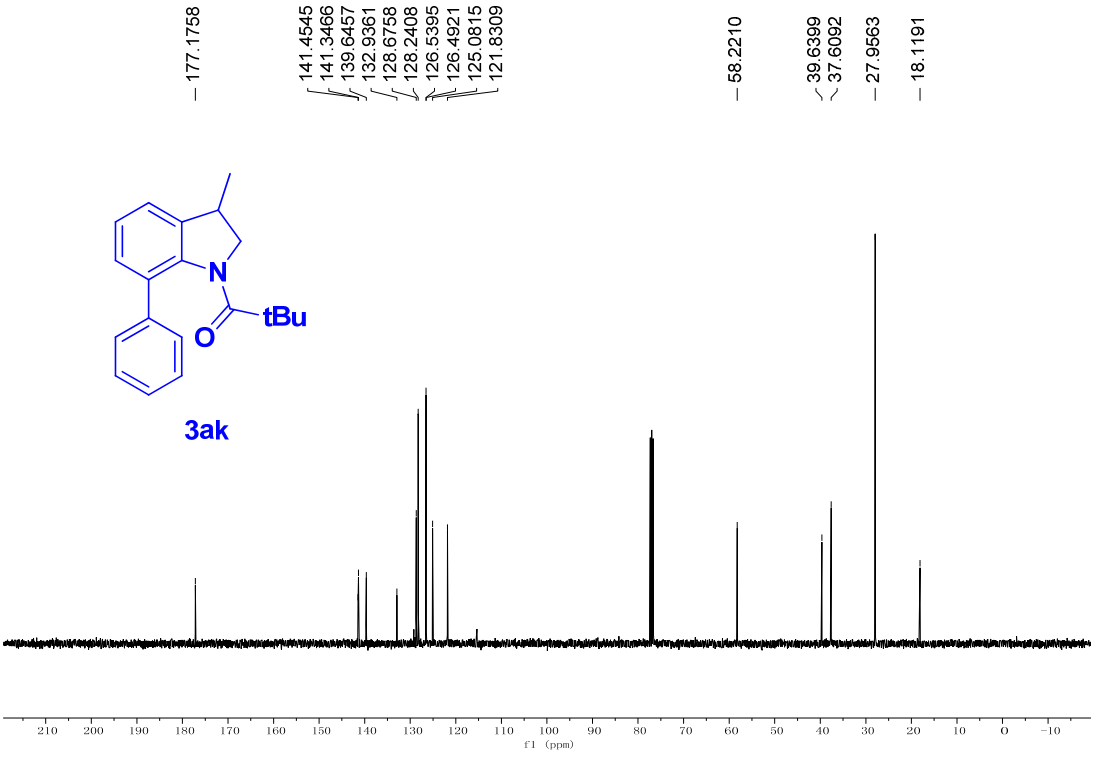
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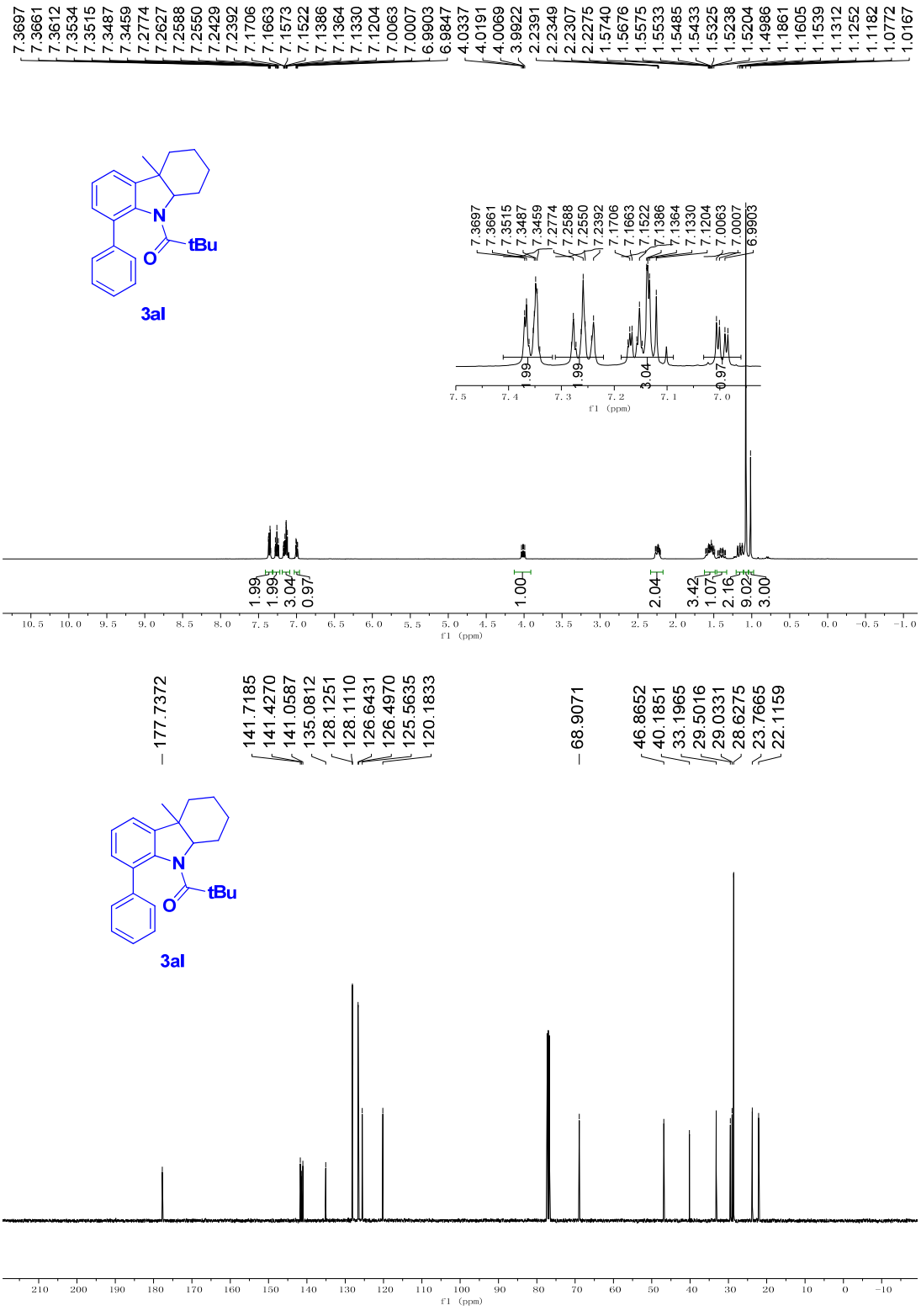
3ak
f1 (ppm)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7.1330
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6.9847
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2.2307
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O
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3al
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1.99
3.04
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1.07
2.16
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3.00
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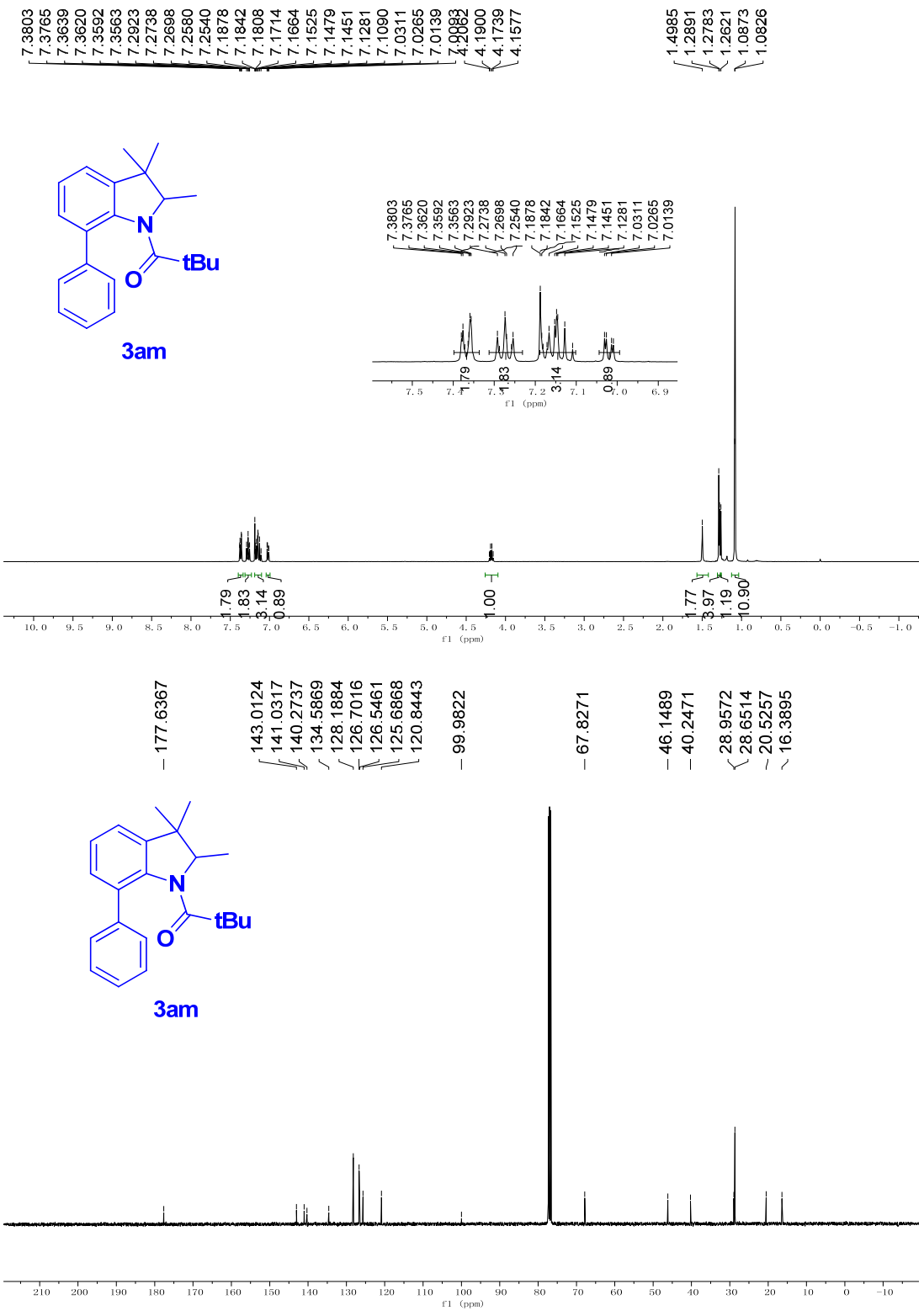
f1 (ppm)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4.1739
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1.2891
1.2783
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1.0826
N
O
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10.90
f1 (ppm)
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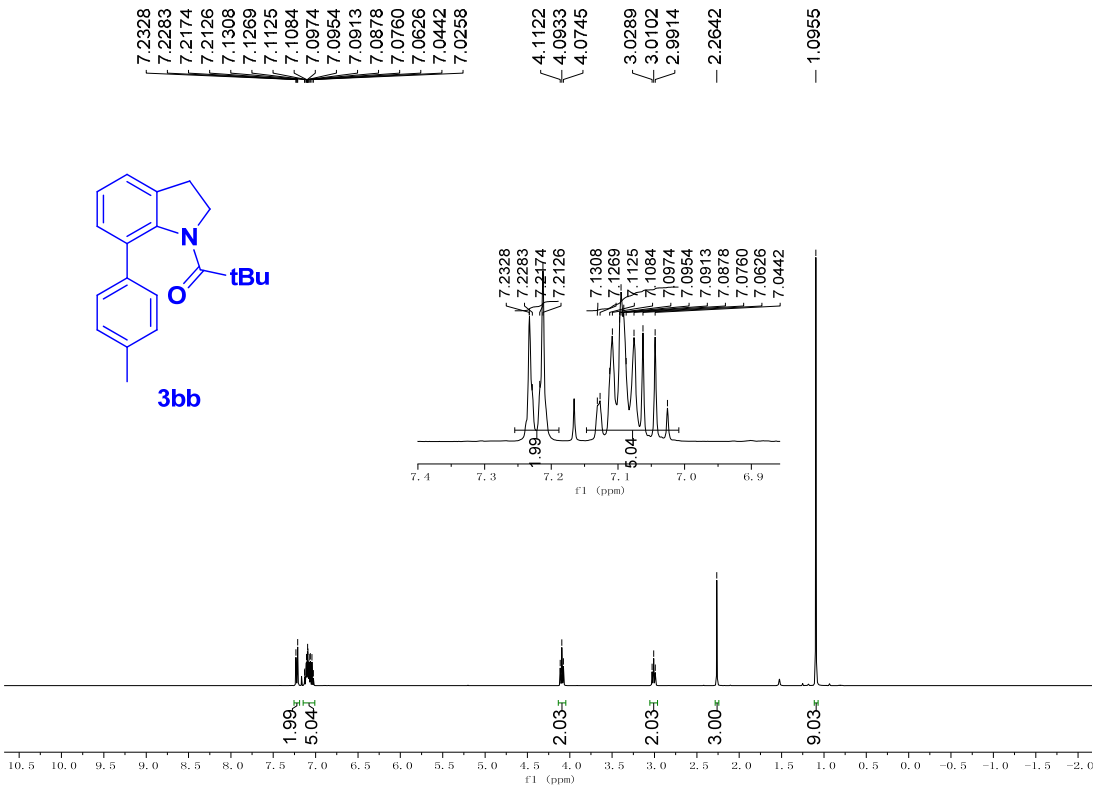
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7.0626
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7.0258
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4.0745
3.0289
3.0102
2.9914
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O
N
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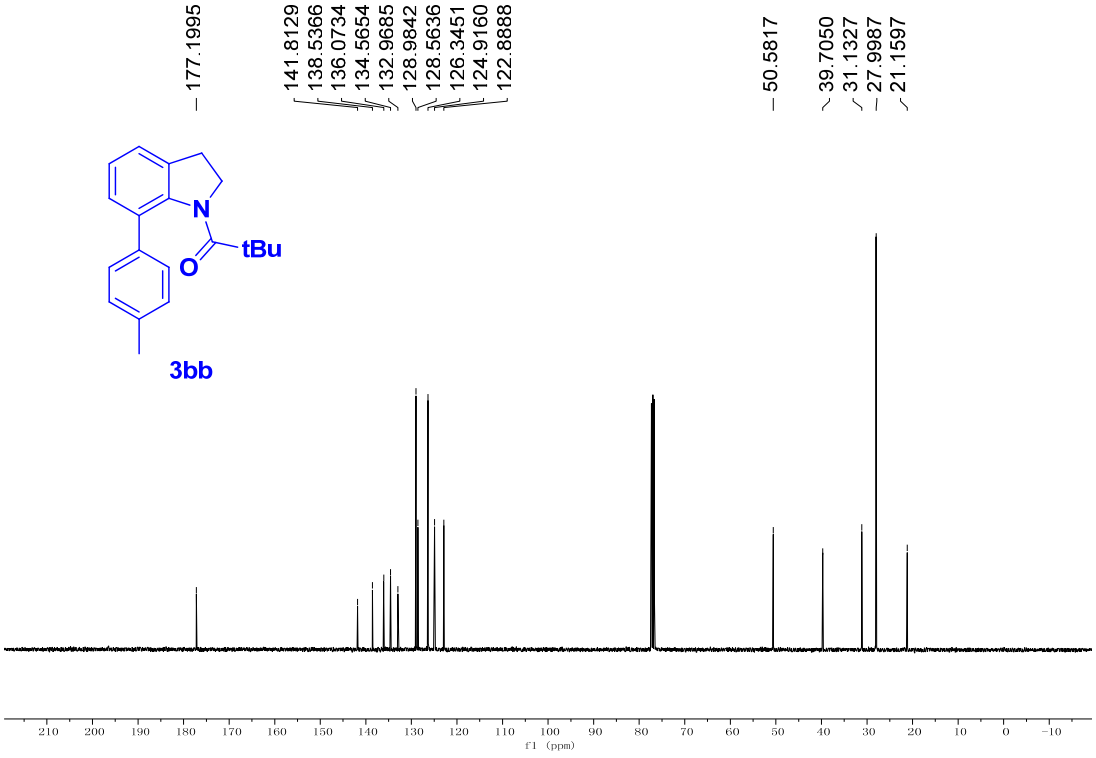
2.03
3.00
9.03
f1 (ppm)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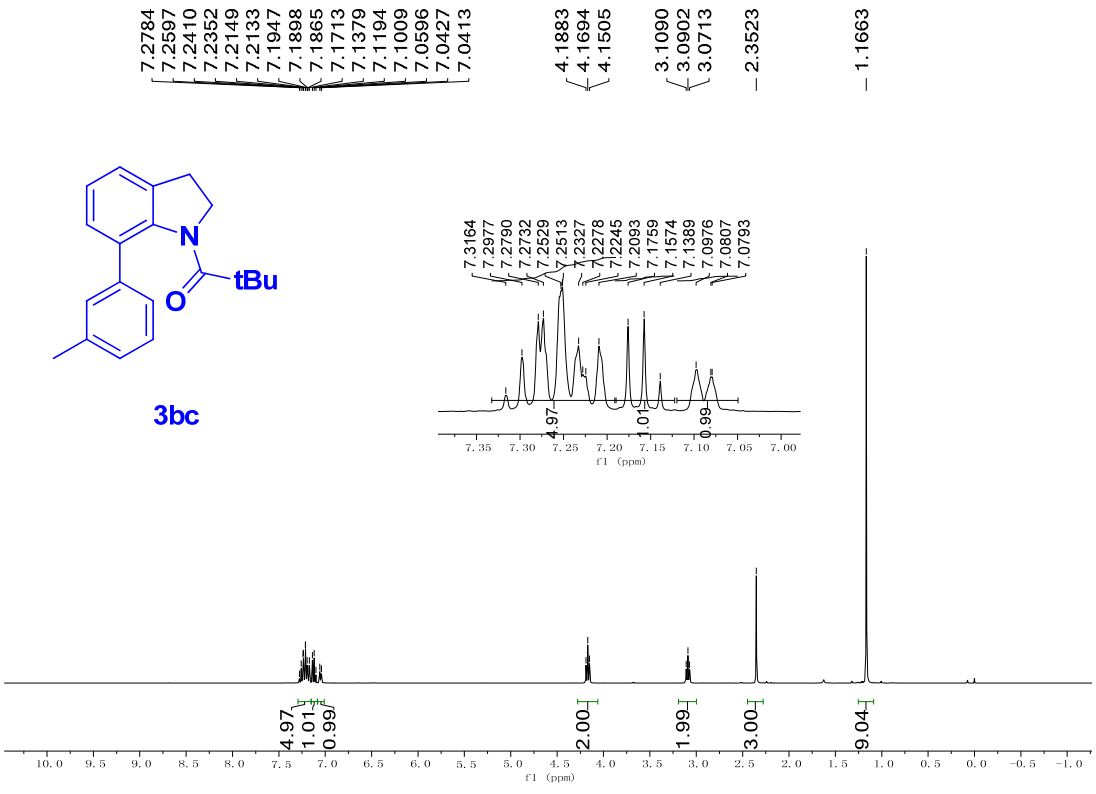
O
N
3bb
f1 (ppm)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7.0427
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4.1883
4.1694
4.1505
3.1090
3.0902
3.0713
2.3523
1.1663
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O
tBu
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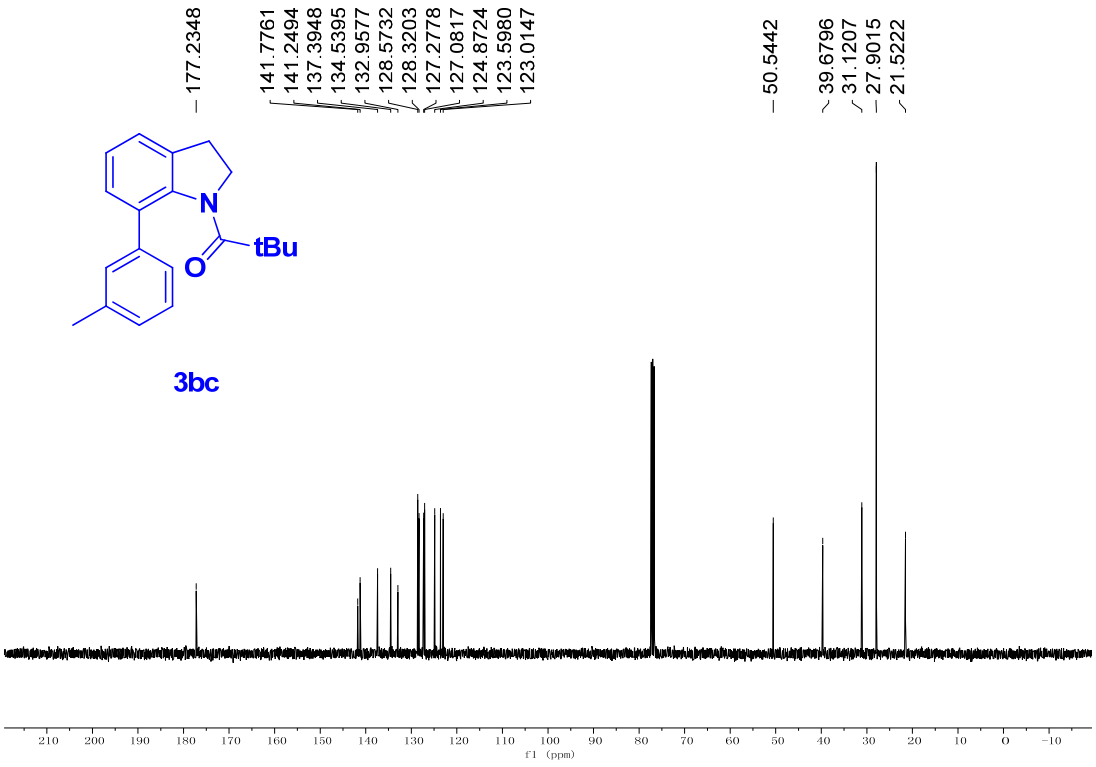
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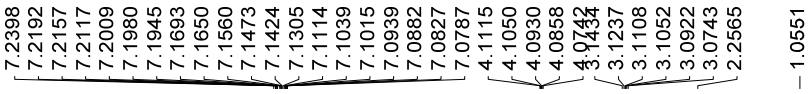
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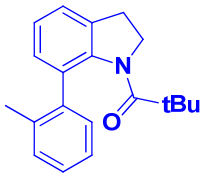
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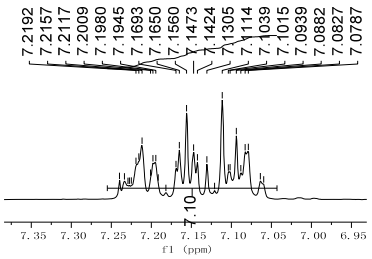
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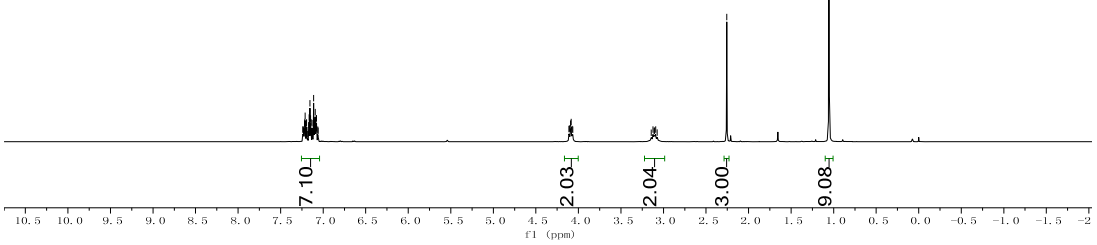
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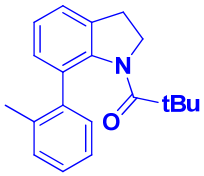
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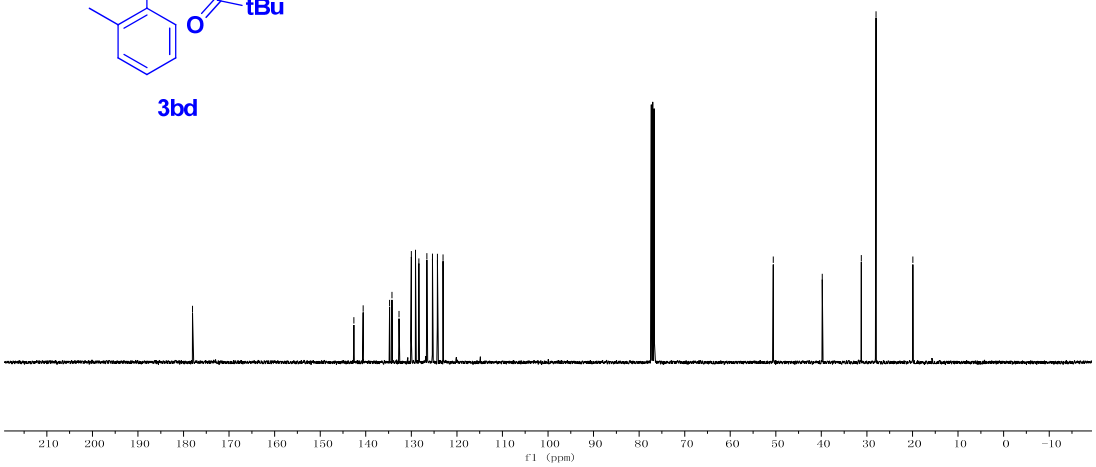
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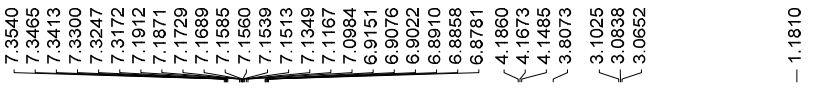
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6.9022
6.8910
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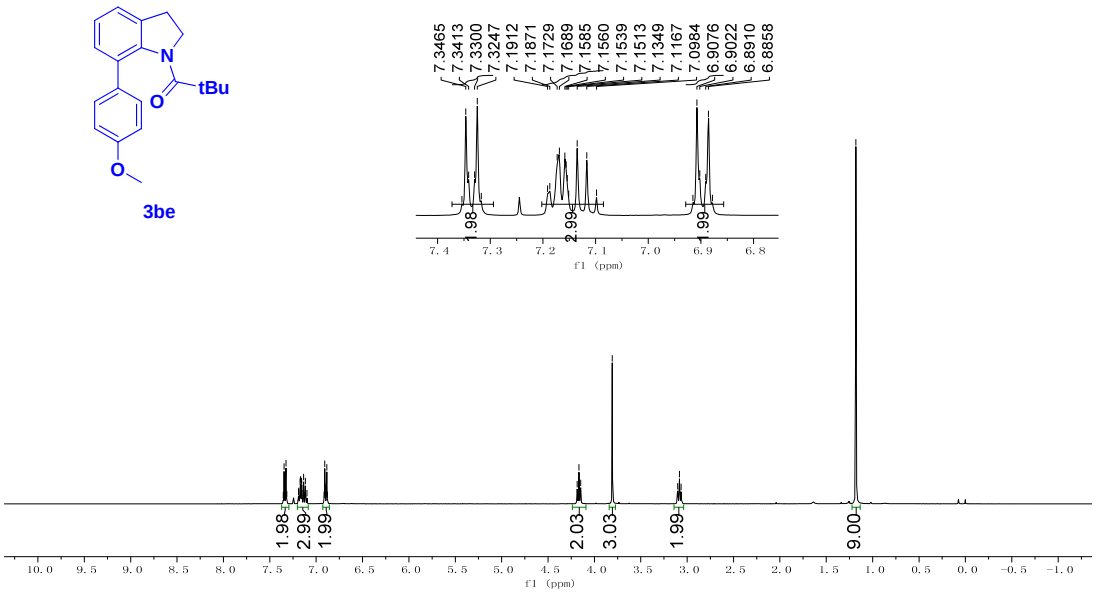
1.1810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1.99
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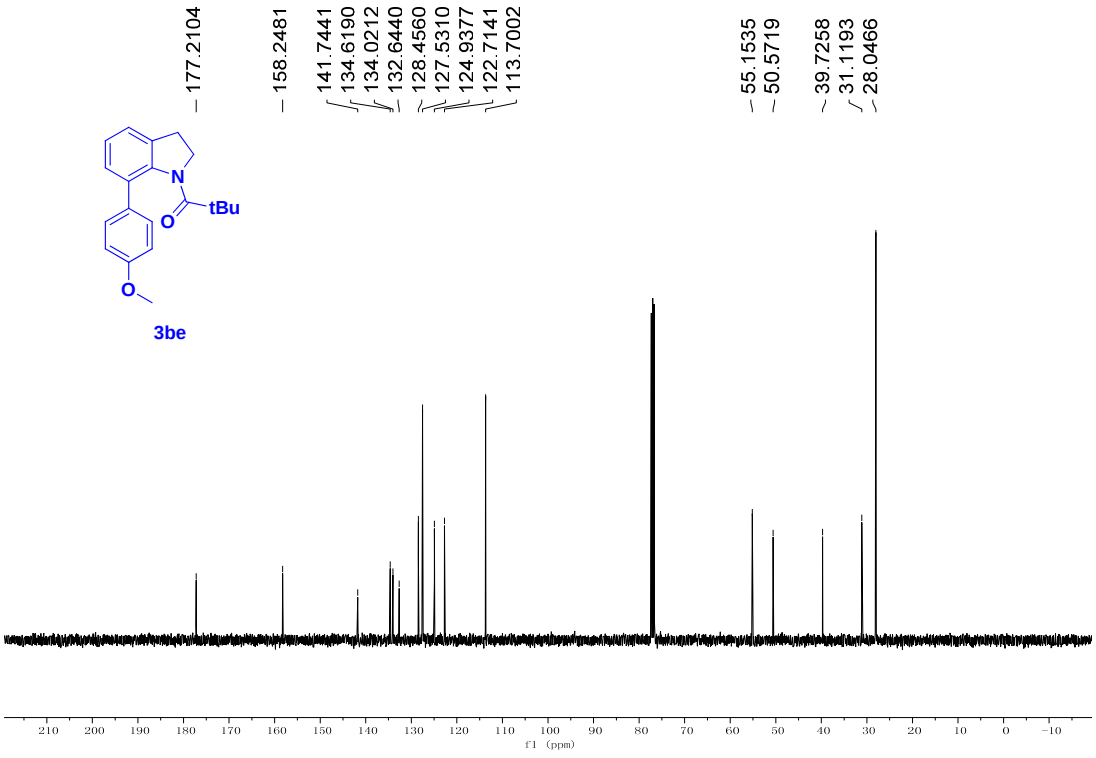
9.00
f1 (ppm)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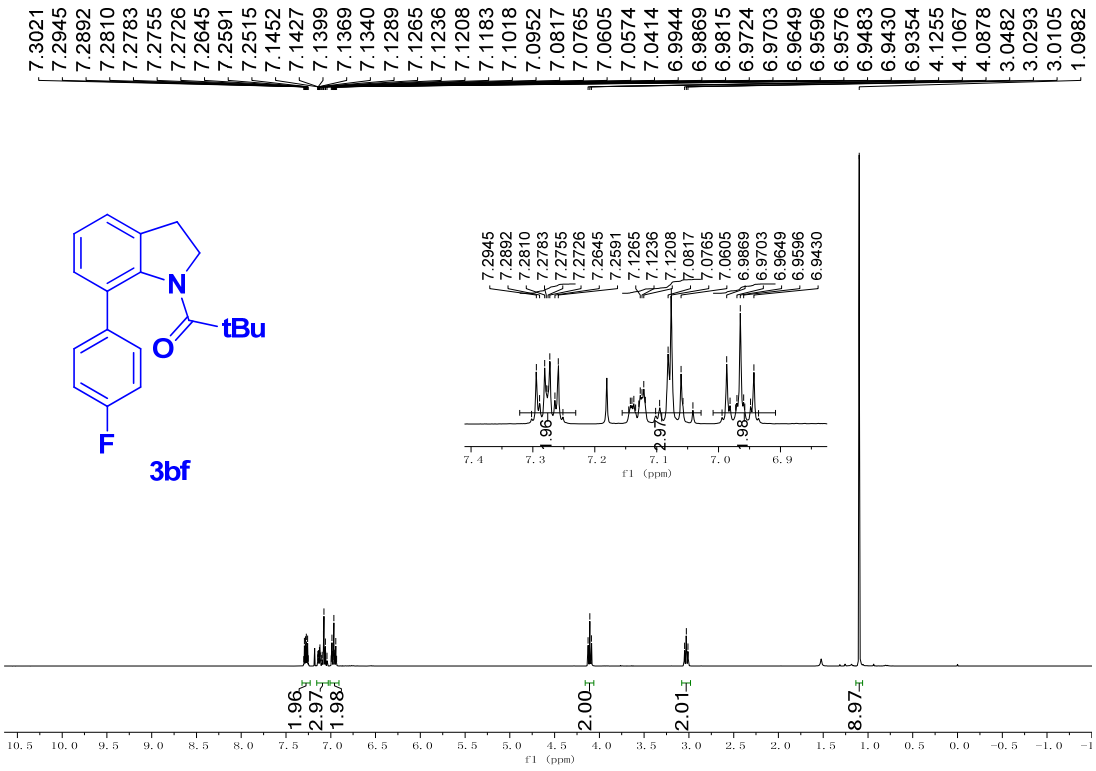
O
3be
f1 (ppm)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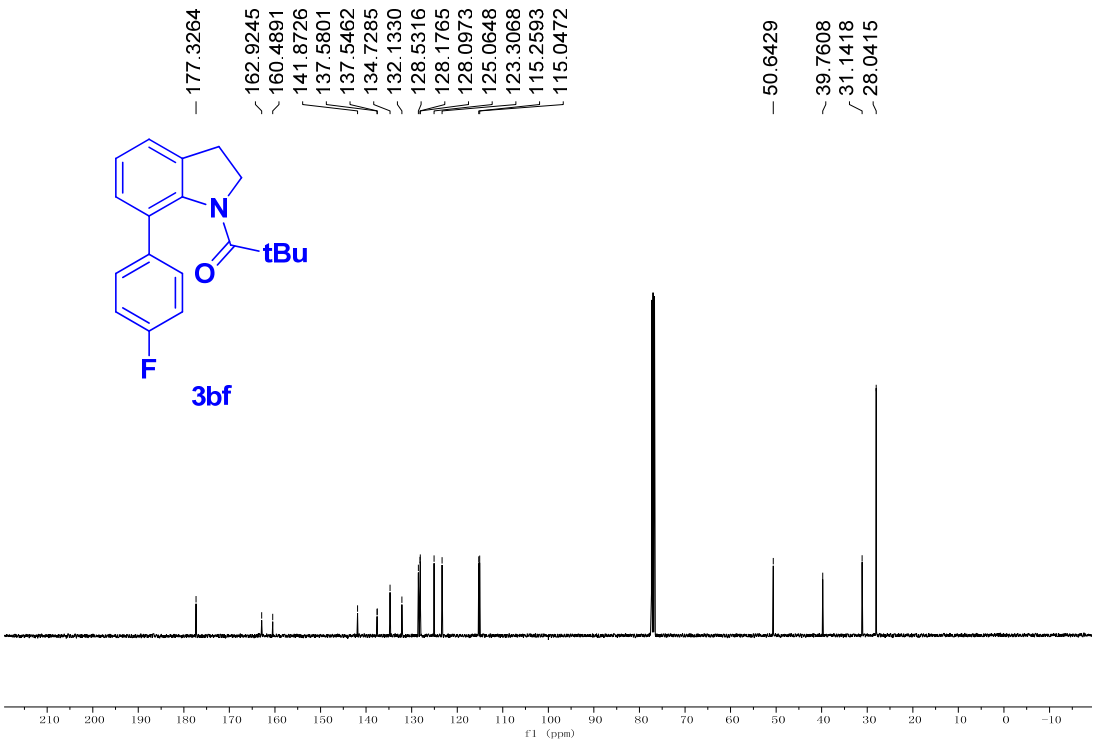
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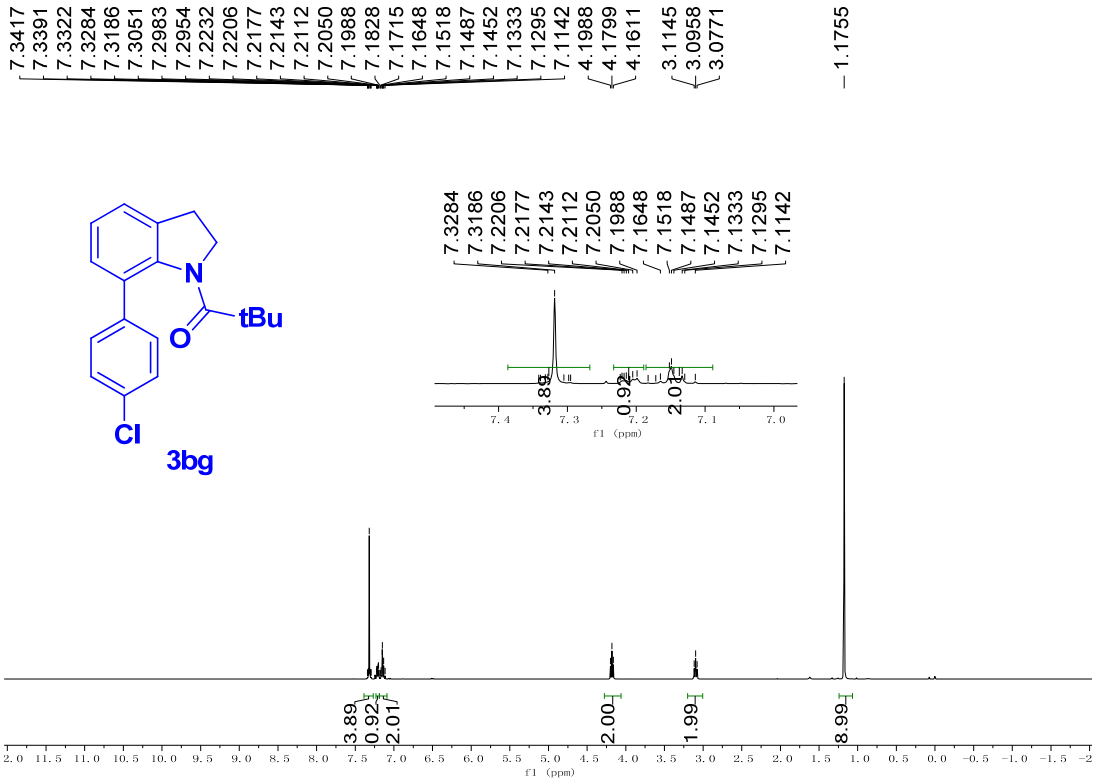
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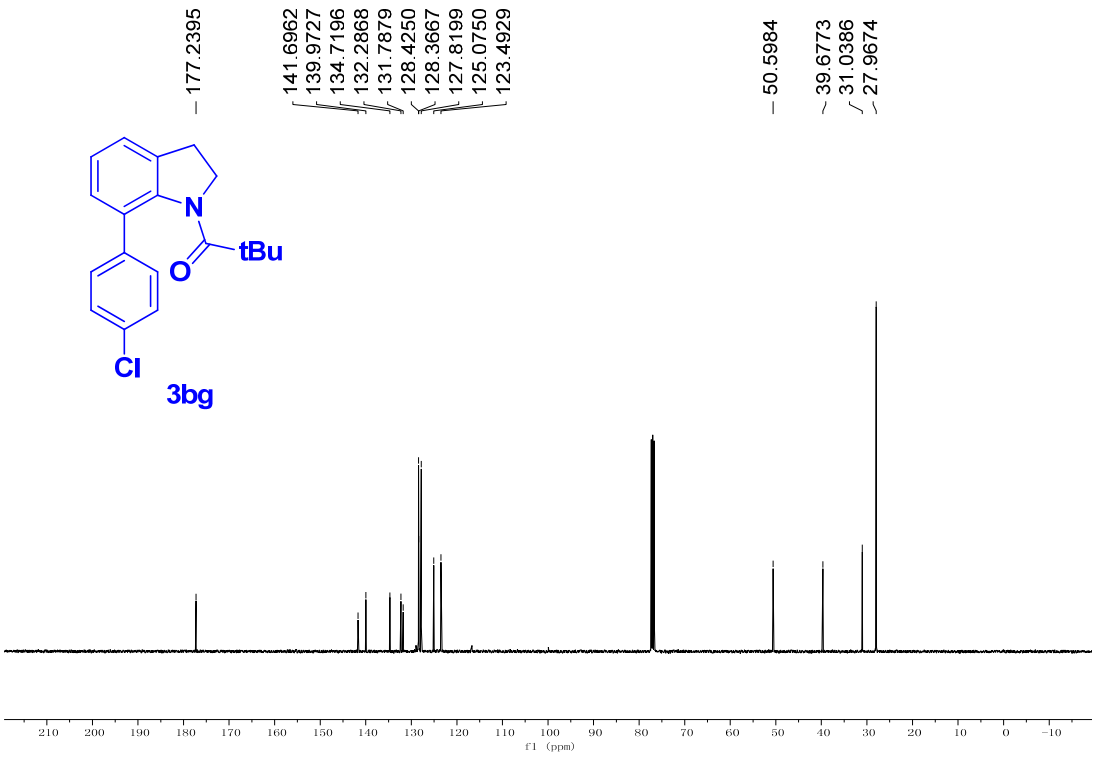
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Cl
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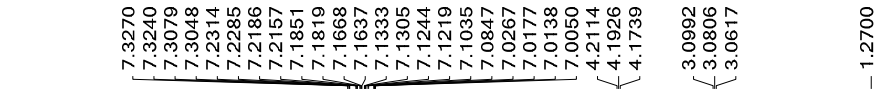
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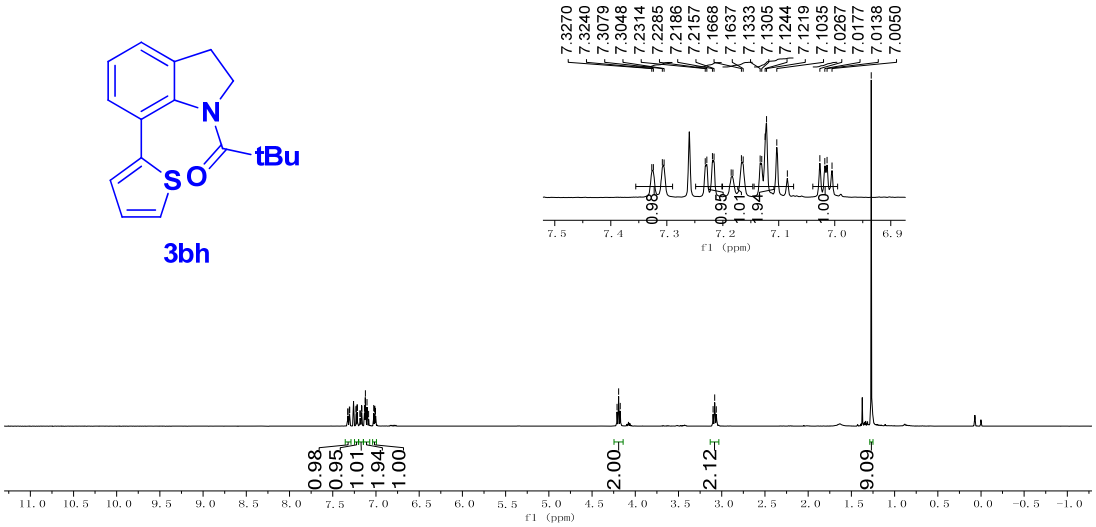
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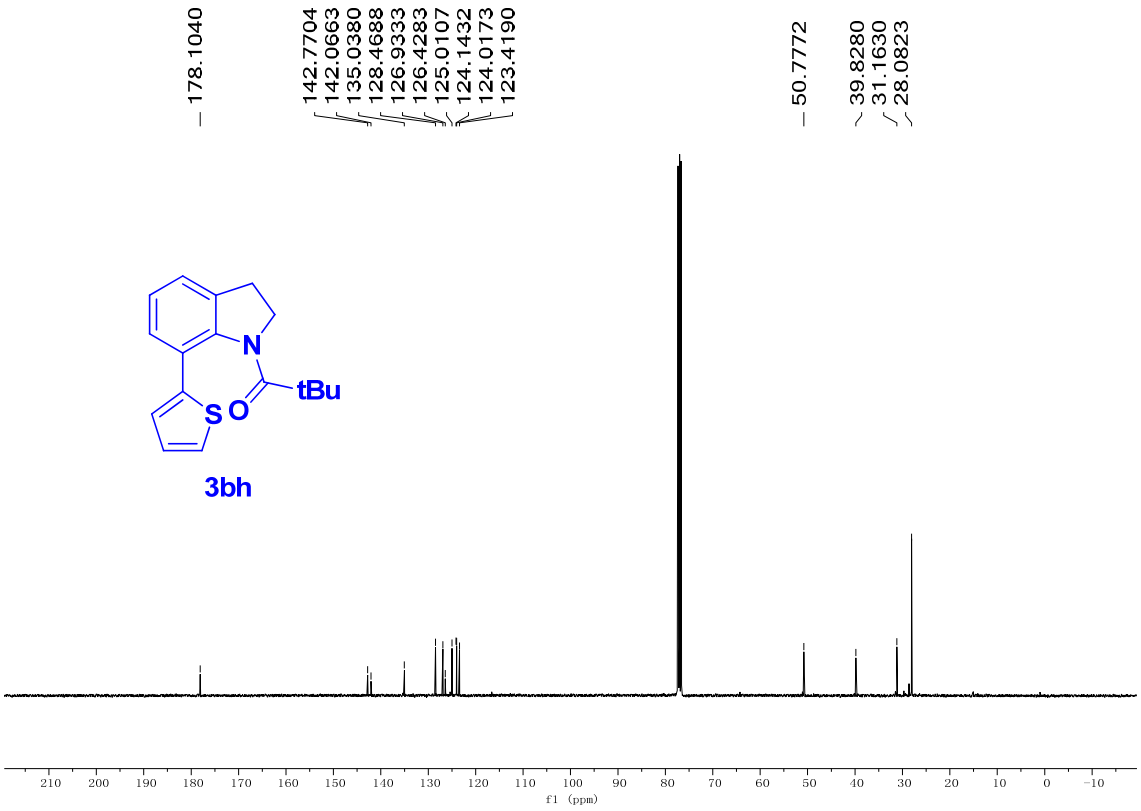
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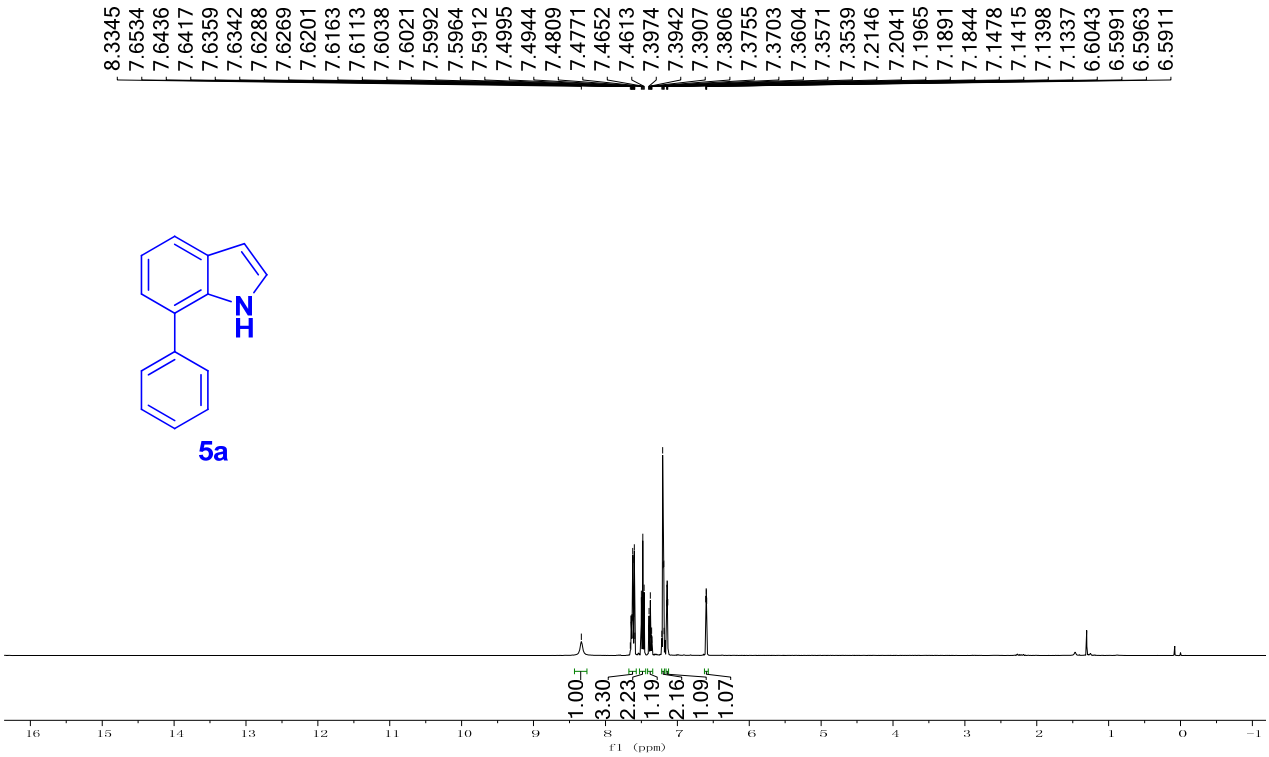
N
tBu
S O
3bh
f1 (ppm)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7.4771
7.4652
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7.3974
7.3942
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7.3806
7.3755
7.3703
7.3604
7.3571
7.3539
7.2146
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7.1965
7.1891
7.1844
7.1478
7.1415
7.1398
7.1337
6.6043
6.5991
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H
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3.30
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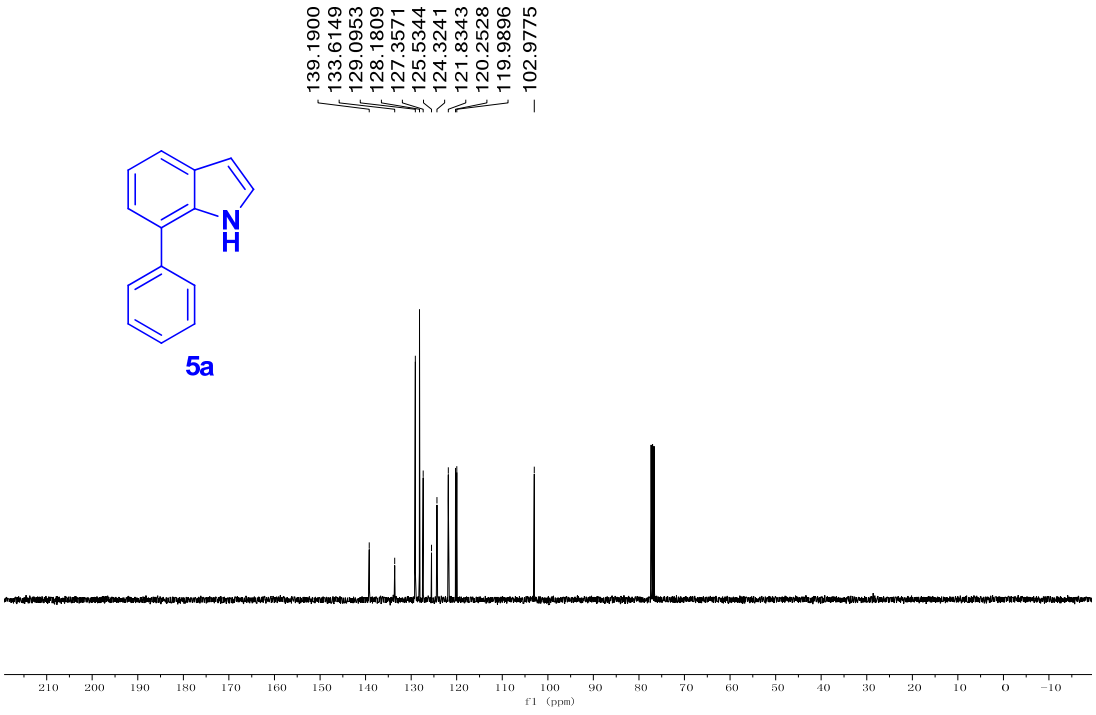
f1 (ppm)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H
5a
f1 (ppm)