Supporting Information

Palladium-Catalyzed Sequential Heck Coupling/C-C Bond Activation Approach to Oxindoles with All-Carbon-Quaternary Centers

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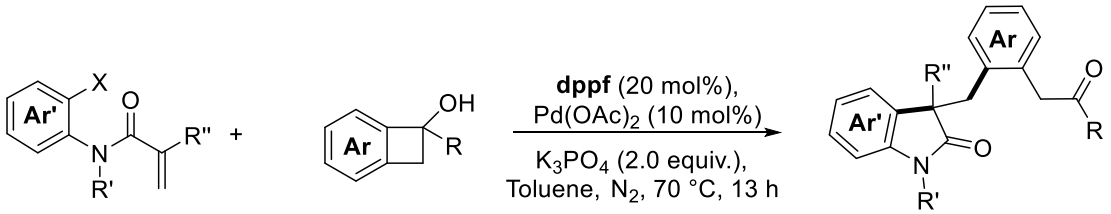
Table of Contents

1. General information

^{1}H, ^{13}C, and ^{19}F NMR spectrometers were recorded on Bruker-400 MHz instruments internally referenced to tetramethylsilane (0.0 ppm) or residue of $CDCl_3$ (7.26 ppm) signal. Melting points were measured using a XT4A microscopic apparatus. IR spectra were obtained on a Bruker VECTOR22 spectrophotometer in KBr pellets. All reactions were performed under an inert atmosphere of dry nitrogen in glassware, unless otherwise stated. Solvents and chemicals were bought from commercial sources and used directly unless otherwise stated. Column chromatography was performed on 300-400 mesh silica gel. The substrates 1a[1-6] and 2[7] were synthesized according to published procedures. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates.

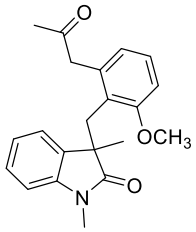
2. General Procedure for the Synthesis of Products 3 and Characterization Data



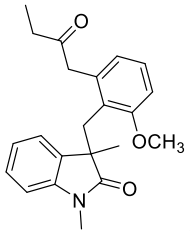
1 **2** **3**

To a 10 mL Schlenk tube, **1** (0.1 mmol), **2** (0.12 mmol), K_3PO_4 (0.2 mmol, 2.0 equiv.), $Pd(OAc)_2$ (0.01 mmol, 10 mol%), **dppf** (0.02 mmol, 20.0mol%), and toluene (1.0 mL) were added sequentially under a N_2 atmosphere. The reaction mixture was stirred at 70 °C for 13 h. After the reaction was complete (monitored by TLC), the resulting mixture was filtered with ethyl acetate and concentrated, then the residue was purified by preparative TLC (petroleum ether : ethyl acetate = 3 : 1) directly and delivered the desired product.

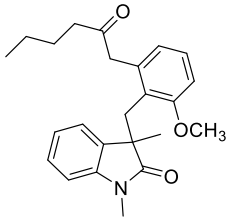
Characterization data of the products.



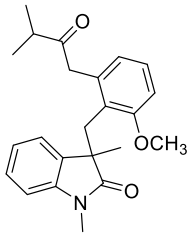
3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one （3aa）: White Solid; (99% yield, petroleum ether: ethyl acetate = 3 : 1, R_f = 0.28) m.p. = 107 – 108 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.87 (td, *J* = 7.5, 0.9 Hz, 1H), 6.76 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 3.57 (s, 3H), 3.49 (dd, *J* = 19.9, 16.6 Hz, 2H), 3.37 (d, *J* = 14.0 Hz, 1H), 3.15 (s, 3H), 2.90 (d, *J* = 13.9 Hz, 1H), 2.03 (s, 3H), 1.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 181.0, 158.4, 142.8, 135.5, 133.6, 127.6, 127.5, 124.4, 124.1, 122.7, 121.6, 108.7, 107.6, 54.6, 49.1, 48.4, 33.1, 29.5, 26.2, 22.97.. IR (KBr, cm^{-1}): 2965, 2923, 1711, 1613, 1584, 1493, 1471, 1377, 1351, 1261, 1158, 1104, 749. HRMS (ESI): calcd for $C_{21}H_{23}NNaO_3$ $[M+Na]^+$ 360.1570 , found 360.1568.



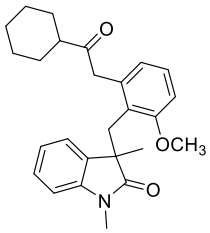
3-(2-methoxy-6-(2-oxobutyl)benzyl)-1,3-dimethylindolin-2-one (3ab): Yellow oil; (99% yield, petroleum ether: ethyl acetate = 3 : 1, R_f = 0.34). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.87 (td, *J* = 7.5, 1.1 Hz, 1H), 6.74 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 2H), 3.57(s, 3H), 3.45 (s, 2H), 3.36 (d, *J* = 13.9 Hz, 1H), 3.15 (s, 3H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.35-2.29 (m, 2H), 1.38 (s, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 181.0, 158.4, 142.8, 135.8, 133.7, 127.6, 127.5, 124.4, 124.1, 122.7, 121.7, 108.6, 107.6, 54.6, 49.1, 47.2, 35.3, 33.1, 26.2, 22.9, 7.8. IR (KBr, cm^{-1}): 2970, 2937, 1715, 1613, 1584, 1494, 1471, 1377, 1350, 1302, 1264, 1106, 755. HRMS (ESI): calcd for $C_{22}H_{26}NO_3$ $[M+H]^+$ 352.1907 , found 352.1901.



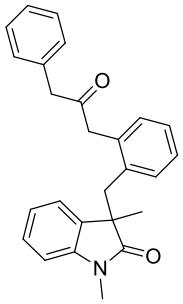
3-(2-methoxy-6-(2-oxohexyl)benzyl)-1,3-dimethylindolin-2-one (3ac): Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.52). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.63 (d, *J* = 6.9 Hz, 2H), 3.57 (s, 3H), 3.45 (s, 2H), 3.36 (d, *J* = 14.0 Hz, 1H), 3.15 (s, 3H), 2.87 (d, *J* = 13.9 Hz, 1H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.49-1.42 (m, 2H), 1.37 (s, 3H), 1.27 – 1.17 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 181.0, 158.4, 142.8, 135.7, 133.7, 127.5, 127.5, 124.4, 124.1, 122.7, 121.7, 108.6, 107.5, 54.6, 49.1, 47.6, 41.9, 33.2, 26.2, 25.9, 22.9, 22.3, 13.9. IR (KBr, cm^{-1}): 2960, 2933, 1714, 1614, 1584, 1493, 1471, 1377, 1349, 1262, 1106, 754. HRMS (ESI): calcd for $C_{24}H_{30}NO_3$ $[M+H]^+$ 388.2220, found 380.2224.



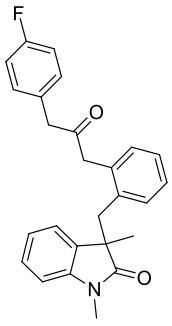
3-(2-methoxy-6-(3-methyl-2-oxobutyl)benzyl)-1,3-dimethylindolin-2-one (3ad): Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.46). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, J = 7.7, 1.2 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 6.89 (td, J = 7.5, 1.0 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.64 (dd, J = 8.3, 1.1 Hz, 1H), 6.60 (dd, J = 7.7, 1.1 Hz, 1H), 3.57 (s, 3H), 3.56 – 3.45 (m, 2H), 3.35 (d, J = 14.0 Hz, 1H), 3.16 (s, 3H), 2.80 (d, J = 14.0 Hz, 1H), 2.61-2.54 (m, 1H), 1.38 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1, 181.1, 158.3, 142.8, 135.8, 133.8, 127.5, 127.4, 124.5, 124.1, 122.8, 121.7, 108.6, 107.5, 54.6, 49.1, 45.2, 40.2, 33.3, 26.2, 22.7, 18.5, 18.3. IR (KBr, cm^{-1}): 2968, 2933, 1714, 1614 ,1584, 1494, 1471, 1377, 1349, 1301, 1261, 1106, 755. HRMS (ESI): calcd for $C_{23}H_{28}NO_3$ $[M+H]^+$ 366.2064, found 366.2058.



3-(2-(2-cyclohexyl-2-oxoethyl)-6-methoxybenzyl)-1,3-dimethylindolin-2-one (3ae): Yellow oil; (92% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.48). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.88 (td, *J* = 7.5, 0.6 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 3.56 (s, 3H), 3.54 – 3.43 (m, 2H), 3.33 (d, *J* = 13.9 Hz, 1H), 3.16 (s, 3H), 2.78 (d, *J* = 14.0 Hz, 1H), 2.33 – 2.27 (m, 1H), 1.74 (d, *J* = 8.7 Hz, 4H), 1.64 (d, *J* = 9.4 Hz, 1H), 1.38 (s, 3H), 1.30 – 1.17 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 181.1, 158.3, 142.8, 135.8, 133.8, 127.5, 127.4, 124.5, 124.2, 122.9, 121.7, 108.6, 107.5, 54.6, 50.3, 49.1, 45.4, 33.3, 28.8, 28.4, 26.2, 25.8, 25.7, 25.6, 22.8. IR (KBr, cm^{-1}): 2931, 1715, 1613, 1584, 1493, 1471, 1452, 1376, 1349, 1262, 1106, 749. HRMS (ESI): calcd for $C_{26}H_{32}NO_3$ $[M+H]^+$ 406.2377, found 406.2372.

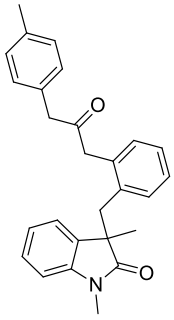


1,3-dimethyl-3-(2-(2-oxo-3-phenylpropyl)benzyl)indolin-2-one (3af): Yellow solid; (89% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.53), m.p.= 106 - 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 3H), 7.05 (td, *J* = 7.5, 1.5 Hz, 1H), 7.00 – 6.91 (m, 3H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 3.68 (s, 2H), 3.68 (d, *J* = 17.0 Hz, 3H), 3.60 (d, *J* = 17.1 Hz, 1H), 2.97 (s, 3H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.87 (d, *J* = 13.9 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 180.1, 143.2, 135.2, 134.2, 133.2, 132.9, 130.8, 130.7, 129.5, 128.8, 128.0, 127.1, 126.9, 126.4, 123.3, 122.1, 107.9, 49.6, 49.5, 46.7, 40.0, 26.0, 23.0. IR (KBr, cm^{-1}): 2967, 1715, 1614, 1495, 1471, 1424, 1380, 1351, 1261, 1247, 1161, 1121, 744. HRMS (ESI): calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958, found384.1954.

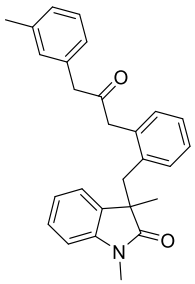


3-(2-(3-(4-fluorophenyl)-2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3ag): Yellow oil; (86% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.42). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.14 – 7.10 (m, 2H), 7.07 – 7.02 (m, 2H), 6.99 (dd, *J* = 7.1, 4.4 Hz, 3H), 6.94 (td, *J* = 7.5, 1.5 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 17.0 Hz, 1H), 3.65 (s, 2H), 3.61 (d, *J* = 17.0 Hz, 1H), 2.97 (m,

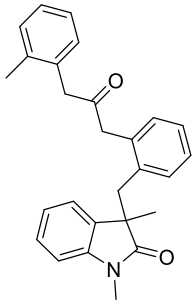
4H), 2.90 (d, J = 13.8 Hz, 1H), 1.40 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.75. ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 162.0 (d, C-F, $^1J_{C\text{-}F}$ = 245.4 Hz), 180.07, 143.2, 135.1, 133.1, 132.8, 131.06 (d, C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 130.95, 130.7, 129.9 (d, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 128.0, 126.91, 126.4, 123.3, 122.2, 115.51 (d, C-F, $^2J_{C\text{-}F}$ = 21.4 Hz), 107.9, 49.5, 48.3, 46.8, 40.0, 26.0, 23.0. IR (KBr, cm^{-1}): 2968, 2929, 1717, 1615, 1493, 1471, 1421, 1349, 1227, 1222, 1159, 1100, 744. HRMS (ESI): calcd for $C_{26}H_{25}FNO_2$ $[M+H]^+$ 402.1864, found.402.1860.



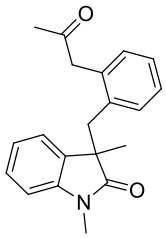
1,3-dimethyl-3-(2-(2-oxo-3-(p-tolyl)propyl)benzyl)indolin-2-one (3ah): Yellow oil; (72% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.47). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (td, J = 7.7, 1.4 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 7.03 (dd, J = 7.5, 1.4 Hz, 1H), 6.99 – 6.90 (m, 3H), 6.87 (dd, J = 7.6, 1.5 Hz, 1H), 6.78 (dd, J = 7.5, 1.3 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 3.61 (dd, J = 26, 16.8 Hz, 4H), 2.97 (s, 3H), 2.94 (d, J = 14.0 Hz, 1H), 2.86 (d, J = 13.9 Hz, 1H), 2.34 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 180.1, 143.1, 136.7, 135.1, 133.3, 132.9, 131.1, 130.8, 130.7, 129.5, 129.4, 128.0, 126.8, 126.3, 123.3, 122.1, 107.9, 49.6, 49.1, 46.5, 40.0, 26.0, 22.9, 21.1. IR (KBr, cm^{-1}): 2970, 2926, 1714, 1614, 1494, 1471, 1423, 1379, 1352, 1245, 1159, 1121, 737. HRMS (ESI): calcd for $C_{27}H_{28}NO_2$ $[M+H]^+$ 398.2115, found 398.2111.



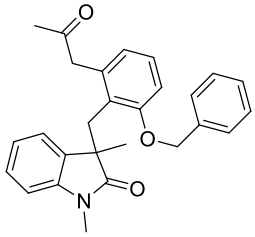
1,3-dimethyl-3-(2-(2-oxo-3-(m-tolyl)propyl)benzyl)indolin-2-one (3ai): Yellow oil; (93% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.47). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 1H), 7.18 (dd, J = 7.7, 1.3 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.04 (td, J = 7.5, 1.3 Hz, 1H), 7.01 – 6.97 (m, 3H), 6.97 – 6.94 (m, 1H), 6.93 – 6.91 (m, 1H), 6.90 – 6.86 (m, 1H), 6.79 (dd, J = 7.7, 1.1 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 3.67 – 3.57 (m, 4H), 2.97 – 2.84 (m, 4H), 2.86 (d, J = 13.9 Hz, 1H), 2.34 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 180.0, 143.2, 138.4, 135.2, 134.1, 133.3, 132.9, 130.8, 130.7, 130.3, 128.7, 128.0, 127.8, 126.8, 126.5, 126.3, 123.3, 122.1, 107.9, 49.6, 49.5, 46.6, 40.0, 26.0, 22.9, 21.4. IR (KBr, cm^{-1}): 2967, 2928, 1714, 1614, 1494, 1471, 1379, 1352, 1327, 1120, 739. HRMS (ESI): calcd for $C_{27}H_{28}NO_2$ $[M+H]^+$ 398.2115, found 398.2110.



1,3-dimethyl-3-(2-(2-oxo-3-(o-tolyl)propyl)benzyl)indolin-2-one (3aj): Yellow oil; (82% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.48). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.17 (m, 4H), 7.11 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.05 (td, *J* = 7.4, 1.4 Hz, 1H), 6.98 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.95 (s, 1H), 6.92 (dd, *J* = 6.5, 1.2 Hz, 1H), 6.89 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.80 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.69 (d, *J* = 2.2 Hz, 2H), 3.65 – 3.55 (m, 2H), 2.98 – 2.95 (m, 4H), 2.89 (d, *J* = 13.9 Hz, 1H), 2.19 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 180.0, 143.1, 137.0, 135.1, 133.3, 133.1, 132.8, 130.9, 130.6, 130.5, 130.5, 128.0, 127.4, 126.8, 126.4, 126.3, 123.3, 122.1, 107.9, 49.6, 47.6, 46.6, 40.0, 26.0, 22.9, 19.7. IR (KBr, cm^{-1}): 2963, 2927, 1713, 1614, 1494, 1471, 1454, 1380, 1351, 1123, 1058, 1027, 742. HRMS (ESI): calcd for $C_{27}H_{28}NO_2$ $[M+H]^+$ 398.2115, found 398.2119.

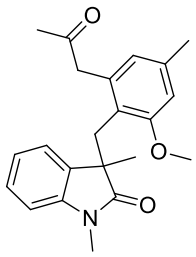


1,3-dimethyl-3-(2-(2-oxopropyl)benzyl)indolin-2-one (3ak): Yellow solid; (82% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.29), m.p.= 65 - 66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 7.09 – 6.99 (m, 3H), 6.96 – 6.93 (m, 2H), 6.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.65 (d, *J* = 16.7 Hz, 1H), 3.57 (d, *J* = 16.7 Hz, 1H), 3.10 (d, *J* = 13.8 Hz, 1H), 3.03 (d, *J* = 13.9 Hz, 1H), 3.00 (s, 3H), 2.08 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 180.1, 143.2, 135.0, 133.5, 132.9, 131.0, 130.6, 128.0, 127.0, 126.3, 123.4, 122.2, 108.0, 49.6, 48.4, 40.0, 29.5, 26.0, 23.1. IR (KBr, cm^{-1}): 2968, 2928, 1709, 1613, 1494, 1471, 1454, 1379, 1353, 1159, 1121, 1029, 750. HRMS (ESI): calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$ 308.1645, found 308.1638.

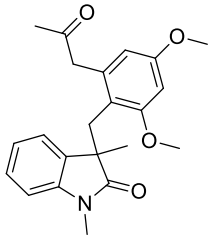


3-(2-(benzyloxy)-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3al): Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.31). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.79 (td, *J* = 7.6, 1.0 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.61 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 3.62 (d, *J* = 16.6 Hz, 1H), 3.54 (d, *J* = 16.6 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 3.06 (s, 3H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.07 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 206.5, 181.0, 157.7, 142.7, 137.1, 135.6, 133.7, 128.5, 127.7, 127.7, 127.5, 127.2, 124.8, 124.1, 123.1, 121.7, 110.1, 107.6, 69.7, 48.9, 48.4, 33.0,

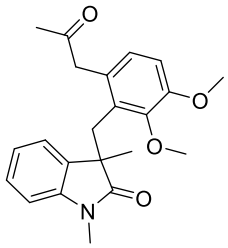
29.5, 26.1, 23.1. IR (KBr, cm^{-1}): 2963, 2930, 1717, 1615, 1493, 1471, 1451, 1377, 1352, 1264, 1158, 1101, 737. HRMS (ESI): calcd for $C_{27}H_{28}NO_3$ $[M+H]^+$ 414.2064, found 414.2060.



3-(2-methoxy-4-methyl-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3am): Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.31)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.7, 1.1 Hz, 1H), 6.89 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 3.2 Hz, 2H), 3.57 (s, 3H), 3.42 (dd, *J* = 18.84, 16.44 Hz, 2H), 3.32 (d, *J* = 14.1 Hz, 1H), 3.16 (s, 3H), 2.84 (d, *J* = 14.0 Hz, 1H), 2.26 (s, 3H), 2.02 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 181.1, 158.3, 142.8, 137.4, 135.2, 133.9, 127.5, 124.1, 123.3, 121.7, 121.3, 109.8, 107.6, 54.6, 49.1, 48.4, 32.9, 29.4, 26.2, 22.8, 21.5. IR (KBr, cm^{-1}): 2963, 2933, 1714, 1613, 1493, 1471, 1377, 1352, 1302, 1159, 1106, 743. HRMS (ESI): calcd for $C_{22}H_{26}NO_3$ $[M+H]^+$ 352.1907, found 352.1904.

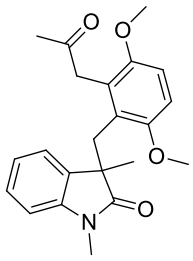


3-(2,4-dimethoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3an): Yellow solid; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.21), m.p.= 101 - 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.7, 1.3 Hz, 1H), 6.89 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 6.17 (d, *J* = 2.5 Hz, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 3.45 (s, 2H), 3.29 (d, *J* = 14.2 Hz, 1H), 3.15 (s, 3H), 2.83 (d, *J* = 14.2 Hz, 1H), 2.03 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 181.1, 159.4, 159.0, 142.8, 136.1, 133.8, 127.5, 124.1, 121.7, 116.9, 107.6, 106.2, 96.9, 55.2, 54.7, 49.3, 48.7, 32.8, 29.4, 26.2, 22.7. IR (KBr, cm^{-1}): 2964, 2937, 1714, 1612, 1494, 1471, 1377, 1351, 1306, 1205, 1150, 741. HRMS (ESI): calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856, found 368.1854.

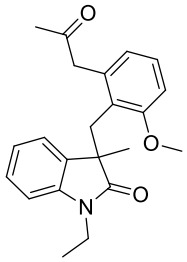


3-(2,3-dimethoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3ao): Yellow oil; (92% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.21). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 6.85 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 – 6.75 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.66 (m, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.31 – 3.20 (m, 5H), 3.08 (d, *J* = 16.8 Hz, 1H), 2.76 (d, *J* = 13.9 Hz, 1H), 1.96 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 181.2, 151.5, 148.6, 142.7, 133.4, 129.9, 127.7, 127.5, 125.8, 124.2, 122.1, 111.2, 107.7, 60.2, 55.7, 49.0, 47.8, 33.6, 29.4, 26.3, 23.0. IR (KBr, cm^{-1}): 2968, 2937, 1715, 1612, 1487, 1377, 1349,

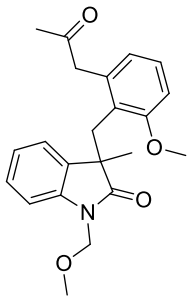
1283, 1228, 1158, 1103, 741. HRMS (ESI): calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856, found 368.1853.



3-(3,6-dimethoxy-2-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3ap): Yellow solid; (98% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.21), m.p. = 83 - 84 °C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 6.87 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.75 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 1H), 6.59 (d, *J* = 8.9 Hz, 1H), 3.69 (s, 3H), 3.62 (d, *J* = 17.1 Hz, 1H), 3.53 (s, 3H), 3.38 (d, *J* = 17.1 Hz, 1H), 3.31 (d, *J* = 14.0 Hz, 1H), 3.16 (s, 3H), 2.92 (d, *J* = 14.0 Hz, 1H), 2.05 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 181.0, 152.3, 151.5, 142.8, 133.7, 127.5, 125.9, 125.7, 124.1, 121.6, 109.1, 108.5, 107.6, 55.8, 54.8, 48.9, 42.3, 33.4, 29.5, 26.2, 23.1. IR (KBr, cm^{-1}): 2965, 2938, 1711, 1614, 1471, 1377, 1353, 1259, 1150, 1106, 741. HRMS (ESI): calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856, found 368.1853.

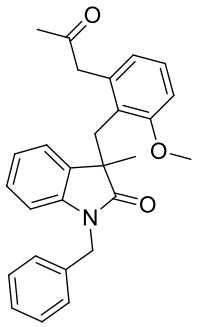


1-ethyl-3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methylindolin-2-one (3ba): Yellow oil; (95% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.46). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.6, 1.4 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.1 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.66 – 6.59 (m, 2H), 3.78 – 3.70 (m, 1H), 3.66 – 3.61 (m, 1H), 3.59 (d, *J* = 6.4 Hz, 1H), 3.51 (s, 3H), 3.47 (d, *J* = 16.6 Hz, 1H), 3.36 (d, *J* = 13.9 Hz, 1H), 2.88 (d, *J* = 13.8 Hz, 1H), 2.04 (s, 3H), 1.39 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 180.5, 158.4, 141.8, 135.7, 134.1, 127.6, 127.4, 124.4, 124.3, 122.7, 121.5, 108.7, 107.6, 54.6, 49.1, 48.6, 34.4, 33.4, 29.5, 22.9, 12.6. IR (KBr, cm^{-1}): 2973, 2934, 1705, 1583, 1511, 1489, 1469, 1376, 1358, 1260, 1221, 1106, 743. HRMS (ESI): calcd for $C_{22}H_{26}NO_3$ $[M+H]^+$ 352.1907, found 352.1903.

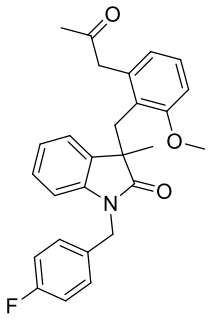


3-(2-methoxy-6-(2-oxopropyl)benzyl)-1-(methoxymethyl)-3-methylindolin-2-one (3ca): Yellow oil; (97% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.45). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.96-6.93 (m, 2H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.63 (dd, *J* = 7.9, 5.1 Hz, 2H), 5.09 (d, *J* = 10.8 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 3.63

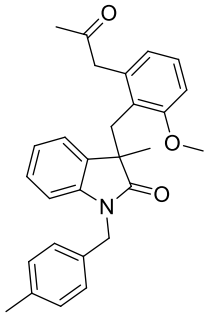
(d, *J* = 16.6 Hz, 1H), 3.53 – 3.49 (m, 4H), 3.40 (d, *J* = 13.9 Hz, 1H), 3.12 (s, 3H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.06 (s, 3H), 1.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 181.4, 158.4, 140.9, 135.7, 133.4, 127.7, 127.6, 124.3, 124.2, 122.8, 122.2, 109.0, 108.8, 71.2, 55.8, 54.5, 49.6, 48.7, 33.5, 29.5, 23.7. IR (KBr, cm^{-1}): 2935, 1715, 1614, 1488, 1470, 1351, 1261, 1185, 1158, 1112, 1085, 1028, 738. HRMS (ESI): calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856, found 368.1853.



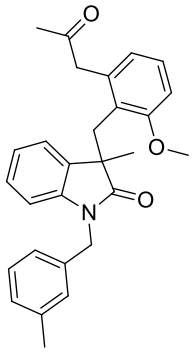
1-benzyl-3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methylindolin-2-one (3da): Yellow oil; (90% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.42). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 3H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.07-7.02 (m, 1H), 7.01 – 6.99 (m, 2H), 6.91 – 6.88 (m, 2H), 6.64 (dd, *J* = 13.6, 7.9 Hz, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 5.06 (d, *J* = 15.8 Hz, 1H), 4.63 (d, *J* = 15.8 Hz, 1H), 3.74 (d, *J* = 16.8 Hz, 1H), 3.51 – 3.45 (m, 2H), 3.43 (s, 3H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.05 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 180.9, 158.4, 141.9, 135.9, 135.8, 133.9, 128.7, 127.7, 127.4, 127.3, 126.9, 124.5, 124.3, 122.9, 121.7, 108.8, 108.6, 54.5, 49.4, 48.6, 43.4, 33.6, 29.6, 23.7. IR (KBr, cm^{-1}): 2966, 1709, 1611, 1583, 1489, 1469, 1376, 1357, 1260, 1222, 1176, 1108, 754. HRMS (ESI): calcd for $C_{27}H_{28}NO_3$ $[M+H]^+$ 414.2064, found 414.2060.



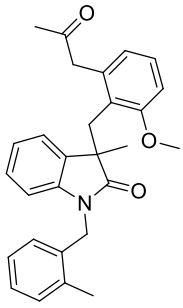
1-(4-fluorobenzyl)-3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methylindolin-2-one (3ea): Yellow oil; (97% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.35). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 7.05 (td, *J* = 7.4, 1.8 Hz, 1H), 6.97 – 6.90 (m, 6H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 15.8 Hz, 1H), 4.55 (d, *J* = 15.8 Hz, 1H), 3.80 (d, *J* = 16.8 Hz, 1H), 3.53 – 3.44 (m, 2H), 3.39 (s, 3H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.06 (s, 3H), 1.49 (s, 3H).^{19}F NMR (376 MHz, CDCl3) δ -115.16 (s).^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 180.8, 162.0 (d, C-F, $^1J_{C\text{-}F}$ = 245.4 Hz), 158.4, 141.6, 135.8, 133.9, 131.6 (d, C-F, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.5 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 127.7, 127.4, 124.44, 124.36, 123.0, 121.8, 115.6 (d, C-F, $^2J_{C\text{-}F}$ = 21.5 Hz), 108.8, 108.4, 54.4, 49.5, 48.7, 42.8, 33.6, 29.6, 23.9. IR (KBr, cm^{-1}): 2930, 1710, 1612, 1583, 1511, 1489, 1470, 1377, 1358, 1261, 1178, 1109, 749. HRMS (ESI): calcd for $C_{27}H_{27}FNO_3$ $[M+H]^+$ 432.1969, found 432.1963.



3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methyl-1-(4-methylbenzyl)indoli-2-one (3fa): Yellow oil; (88% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.44). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 1H), 7.06 – 7.02 (m, 3H), 6.93 – 6.86 (m, 4H), 6.65 (dd, *J* = 10.5, 8.1 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.60 (d, *J* = 15.7 Hz, 1H), 3.71 (d, *J* = 16.8 Hz, 1H), 3.49 (d, *J* = 8.0 Hz, 1H), 3.45 (s, 4H), 2.98 (d, *J* = 13.9 Hz, 1H), 2.30 (s, 3H), 2.04 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 180.9, 158.4, 141.9, 137.0, 135.8, 133.9, 132.9, 129.4, 127.7, 127.4, 126.9, 124.5, 124.2, 122.9, 121.6, 108.8, 108.7, 54.5, 49.4, 48.6, 43.2, 33.5, 29.6, 23.7, 21.1. IR (KBr, cm^{-1}): 2971, 1716, 1614, 1583, 1516, 1488, 1471, 1359, 1261, 1177, 1109, 744. HRMS (ESI): calcd for $C_{28}H_{30}NO_3$ $[M+H]^+$ 428.2220, found 428.2216.

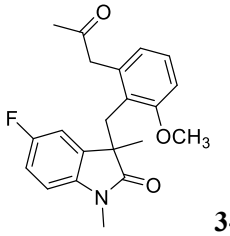


3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methyl-1-(3-methylbenzyl)indolin -2-one (3ga): Yellow oil; (70% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.44). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (q, *J* = 7.7 Hz, 2H), 7.06 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.90 – 6.84 (m, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.99 (d, *J* = 15.7 Hz, 1H), 4.64 (d, *J* = 15.8 Hz, 1H), 3.67 (d, *J* = 16.7 Hz, 1H), 3.48 (d, *J* = 11.9 Hz, 1H), 3.47 (s, 3H), 3.44 (d, *J* = 8.1 Hz, 1H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.30 (s, 3H), 2.04 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 181.0, 158.4, 142.0, 138.3, 136.0, 135.7, 133.8, 128.6, 128.2, 127.7, 127.7, 127.4, 124.5, 124.2, 123.9, 122.8, 121.7, 108.8, 108.7, 54.5, 49.3, 48.6, 43.5, 33.4, 29.5, 23.6, 21.5. IR (KBr, cm^{-1}): 2965, 2928, 1710, 1611, 1583, 1489, 1468, 1379, 1358, 1260, 1177, 1108, 756. HRMS (ESI): calcd for $C_{28}H_{30}NO_3$ $[M+H]^+$ 428.2220, found 428.2221.

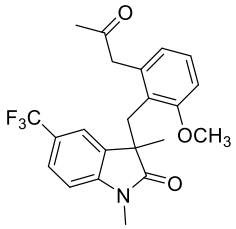


3-(2-methoxy-6-(2-oxopropyl)benzyl)-3-methyl-1-(2-methylbenzyl)indolin-2-one (3ha): Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.36). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.11 (m, 3H), 7.04 (td, *J* = 7.5, 1.8 Hz, 1H), 7.98 – 6.90 (m, 3H), 6.65 (dd, *J*

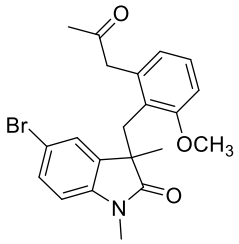
= 7.8, 5.1 Hz, 2H), 6.48 (dd, *J* = 11.6, 7.7 Hz, 2H), 5.03 (d, *J* = 16.5 Hz, 1H), 4.62 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 16.8 Hz, 1H), 3.51 (d, *J* = 4.0 Hz, 1H), 3.47 (s, 4H), 3.04 (d, *J* = 13.9 Hz, 1H), 2.37 (s, 3H), 2.07 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 181.0, 158.4, 142.1, 135.8, 135.4, 133.8, 133.3, 130.4, 127.7, 127.4, 127.1, 126.3, 125.6, 124.44, 124.38 122.9, 121.7, 108.8, 108.7, 54.5, 49.5, 48.7, 41.5, 33.5, 29.6, 23.8, 19.2. IR (KBr, cm^{-1}): 2967, 2930, 1715, 1614, 1489, 1470, 1379, 1324, 1261, 1224, 1177, 1108, 743. HRMS (ESI): calcd for $C_{28}H_{30}NO_3$ $[M+H]^+$ 428.2220, found 428.2219.



3-fluoro-3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3ia): Yellow solid; (86% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.26) m.p.= 142 - 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.9 Hz, 1H), 6.86 (td, *J* = 8.6, 2.6 Hz, 1H), 6.65 – 6.50 (m, 4H), 3.62 (d, *J* = 1.6 Hz, 2H), 3.59 (s, 3H), 3.36 (d, *J* = 14.0 Hz, 1H), 3.11 (s, 3H), 2.97 (d, *J* = 14.0 Hz, 1H), 2.10 (s, 3H), 1.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.09. ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 180.6, 158.8 (d, C-F, $^1J_{C\text{-}F}$ = 238.9 Hz), 158.1, 138.8 (d, C-F, $^4J_{C\text{-}F}$ 1.9 Hz), 135.4 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 135.4, 127.8, 124.1, 122.9, 113.5 (d, C-F, $^2J_{C\text{-}F}$ = 23.5 Hz), 112.4 (d, C-F, $^2J_{C\text{-}F}$ = 25.0 Hz), 108.7, 107.8 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 54.6, 49.7 (d, C-F, $^4J_{C\text{-}F}$ = 1.8 Hz), 48.3, 33.0, 29.5, 26.3, 23.3. IR (KBr, cm^{-1}): 2967, 1710, 1621, 1355, 1277, 1158, 1112, 1073, 1026, 879, 810, 764, 744. HRMS (ESI): calcd for $C_{21}H_{23}FNO_3$ $[M+H]^+$ 356.1656, found 356.1655.

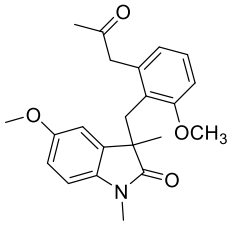


3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3-dimethyl-5-(trifluoromethyl) indolin-2-one (3ja): Yellow oil; (79% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.33). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.18 (d, *J* = 0.9 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 3.71 – 3.61 (m, 2H), 3.53 (s, 3H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.13 (s, 3H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.12 (s, 3H), 1.43 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.23. ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 180.9, 157.9, 145.8, 135.2, 134.0, 127.9, 125.2 (q, C-F, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.6 (q, C-F, $^1J_{C\text{-}F}$ = 271.5 Hz), 123.8 (q, C-F, $^2J_{C\text{-}F}$ = 32.4 Hz), 123.8, 123.0, 121.4 (q, C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 108.6, 107.2, 54.5, 49.3, 48.3, 33.1, 29.5, 26.4, 23.4. IR (KBr, cm^{-1}): 2970, 1716, 1623, 1462, 1422, 1377, 1353, 1289, 1259, 1162, 1116, 1063, 738. HRMS (ESI): calcd for $C_{22}H_{23}F_3NO_3$ $[M+H]^+$ 406.1625, found 406.1629.

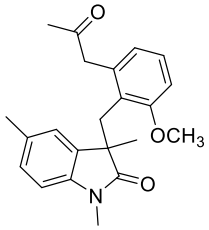


5-bromo-3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-

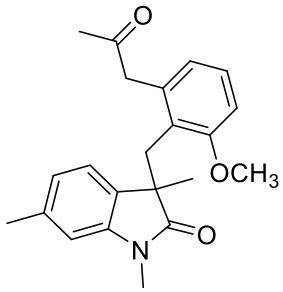
one (3ka): Yellow solid; (75% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.30) m.p.= 143 - 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 3.67 (s, 2H), 3.59 (s, 3H), 3.36 (d, *J* = 14.0 Hz, 1H), 3.08 (s, 3H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.12 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 180.3, 158.0, 141.9, 135.6, 135.3, 130.2, 127.8, 127,7, 123.9, 122.9, 114.3, 108.9, 108.6, 54.7, 49.6, 48.3, 33.1, 29.6, 26.3, 23.3. IR (KBr, cm^{-1}): 2974, 2902, 1708, 1607, 1489, 1467, 1377, 1256, 1077, 1050, 913, 742, 534. HRMS (ESI): calcd for $C_{21}H_{23}BrNO_3$ $[M+H]^+$ 416.0856, found 416.0857.



5-methoxy-3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3-dimethylindolin-2-one (3la): Yellow oil; (81.1% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.17).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.9 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.66 (td, *J* = 8.3, 5.6 Hz, 3H), 6.37 (d, *J* = 2.5 Hz, 1H), 3.66 (s, 3H), 3.61 (s, 3H), 3.49 (dd, *J* = 24.2, 16.6 Hz, 2H), 3.36 (d, *J* = 14.0 Hz, 1H), 3.14 (s, 3H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.04 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 180.7, 158.4, 155.4, 136.4, 135.6, 135.0, 127.7, 124.4, 122.7, 112.1, 111.5, 108.8, 107.7, 55.7, 54.7, 49.5, 48.4, 33.0, 29.5, 26.3, 23.1. IR (KBr, cm^{-1}): 2931, 1705, 1600, 1497, 1471, 1357, 1289, 1159, 1113, 1075, 1038, 912, 741. HRMS (ESI): calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856, found 368.1859.

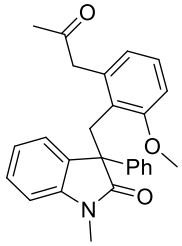


3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3,5-trimethylindolin-2-one (3ma): white solid; (91% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.28) m.p.= 125 - 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.9 Hz, 1H), 6.97 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.66 (s, 1H), 6.65 – 6.61 (m, 2H), 6.58 (d, *J* = 1.1 Hz, 1H), 3.59 (s, 3H), 3.49 (s, 2H), 3.36 (d, *J* = 13.9 Hz, 1H), 3.13 (s, 3H), 2.89 (d, *J* = 13.9 Hz, 1H), 2.23 (s, 3H), 2.04 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 180.9, 158.4, 140.4, 135.6, 133.7, 131.0, 127.7, 127.6, 125.1, 124.5, 122.6, 108.6, 107.2, 54.6, 49.2, 48.3, 33.1, 29.5, 26.2, 22.9, 21.1. IR (KBr, cm^{-1}): 2965, 2935, 1705, 1603, 1499, 1469, 1354, 1264, 1112, 1056, 913, 747. HRMS (ESI): calcd for $C_{22}H_{26}NO_3$ $[M+H]^+$ 352.1907, found.352.1910.



3-(2-methoxy-6-(2-oxopropyl)benzyl)-1,3,6-trimethylindolin-2-

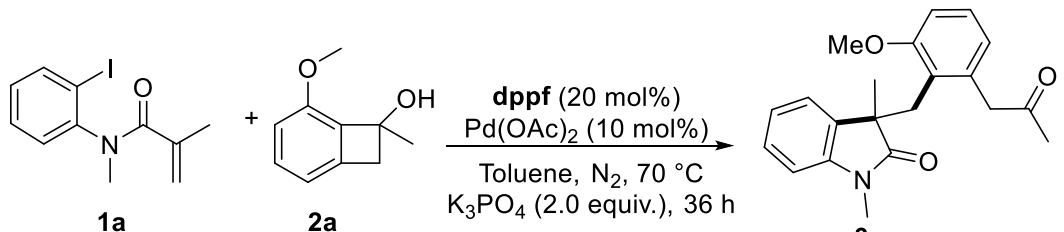
one(3na): Yellow oil; (75.2% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.22).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.9 Hz, 1H), 6.71 – 6.60 (m, 4H), 6.58 (s, 1H), 3.62 (s, 3H), 3.51 – 3.40 (m, 2H), 3.36 (d, *J* = 13.9 Hz, 1H), 3.14 (s, 3H), 2.86 (d, *J* = 13.9 Hz, 1H), 2.32 (s, 3H), 2.02 (s, 3H), 1.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 206.72, 181.34, 158.42, 142.81, 137.56, 135.55, 130.67, 127.6, 124.5, 123.8, 122.7, 122.2, 108.8, 108.6, 54.7, 48.9, 48.4, 33.0, 29.5, 26.2, 23.1, 21.8.IR (KBr, cm-1): 2929, 1710, 1621, 1470, 1584, 1380, 1262, 1106, 812, 530. HRMS (ESI): calcd for $C_{22}H_{25}NNaO_3$ $[M+Na]^+$ 374.1727, found 374.1730.



3-(2-methoxy-6-(2-oxopropyl)benzyl)-1-methyl-3-phenylindolin-2-one (3oa):

Yellow oil; (99% yield, petroleum ether : ethyl acetate = 3 : 1, R_f = 0.34). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.32 – 7.21 (m, 3H), 7.20 – 7.14 (m, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.90 (q, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 3.81 (d, *J* = 13.9 Hz, 1H), 3.59 (dd, *J* = 15.4, 11.6 Hz, 2H), 3.48 (d, *J* = 16.9 Hz, 1H), 3.32 (s, 3H), 3.09 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 178.8, 158.1, 143.6, 140.8, 135.2, 130.7, 128.3, 127.8, 127.6, 127.4, 127.2, 126.9, 124.6, 122.7, 121.3, 108.3, 107.6, 56.8, 54.3, 48.2, 34.9, 29.5, 26.4. IR (KBr, cm^{-1}): 2969, 1706, 1611, 1494, 1471, 1374, 1354, 1260, 1157, 1131, 1095, 753. HRMS (ESI): calcd for $C_{26}H_{26}NO_3$ $[M+H]^+$ 400.1907, found 400.1910.

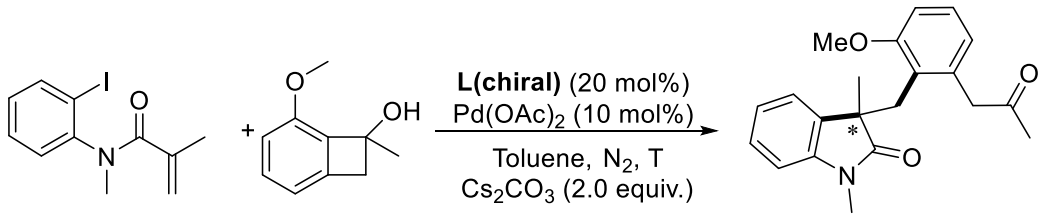
3. Gram-Scale Reaction

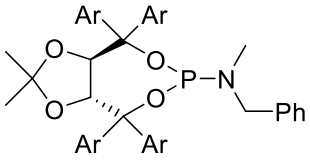


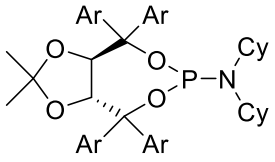
To a 100 mL Schlenk tube, **1** (1.00g, 3.32 mmol), **2** (654 mg, 3.99 mmol), K_3PO_4 (1.41 g, 2.0 equiv), $Pd(OAc)_2$ (74.54 mg, 10 mol %), **dppf** (368.10 mg, 20.0 mol%), and toluene (33 mL) were added sequentially under a N_2 atmosphere. The reaction mixture was stirred at 70 °C for 36 h. After the reaction was complete (monitored by TLC), The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to furnish 1.07 g (95% yield) of the **3aa**.

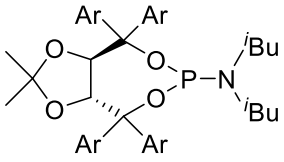
4. Primitive Results of Enantioselective Reaction

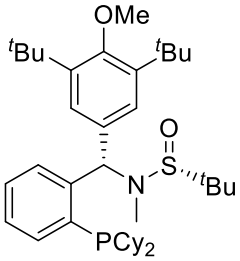
Table S1. Optimization of enantioselective reaction[a]

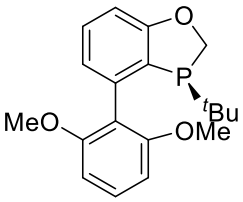


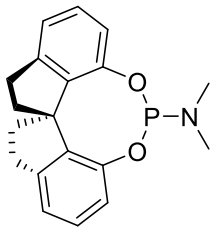

L(chiral) 1: Ar = 4-^{t}BuC$_6$H$_4$

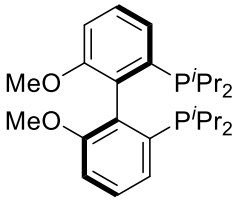

L(chiral) 2: Ar = 4-^{t}BuC$_6$H$_4$

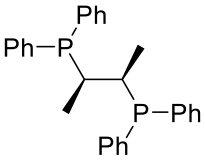

L(chiral) 3: Ar = 4-^{t}BuC$_6$H$_4$

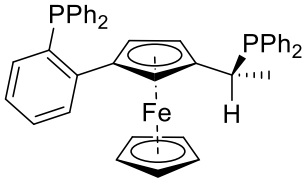

L(chiral) 4


L(chiral) 5


L(chiral) 6


L(chiral) 7


L(chiral) 8

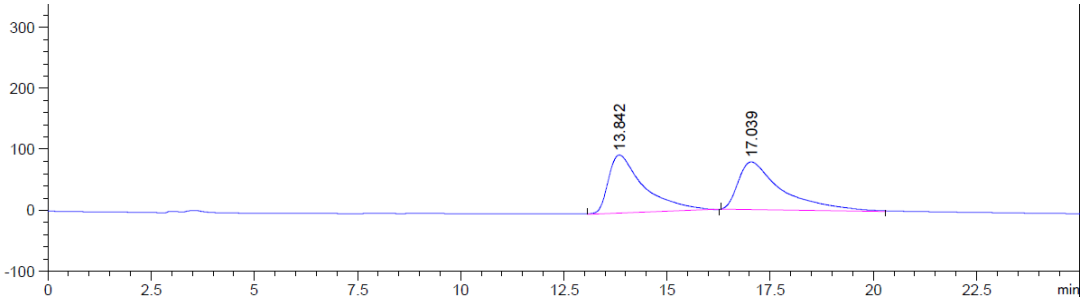

L(chiral) 9

Entry	L(chiral)	T (℃)	Yield (%)[b]	ee (%)[c]
1	**1**	80	29	33
2	**2**	80	15	4
3	**3**	80	18	14
4	**4**	80	52	29
5	**5**	80	83	10
6	**6**	80	80	12
7	**7**	80	19	36
8	**8**	80	89	1
9	**9**	80	49	6
10	**1**	60	49	41
11	**1**	40	29	38

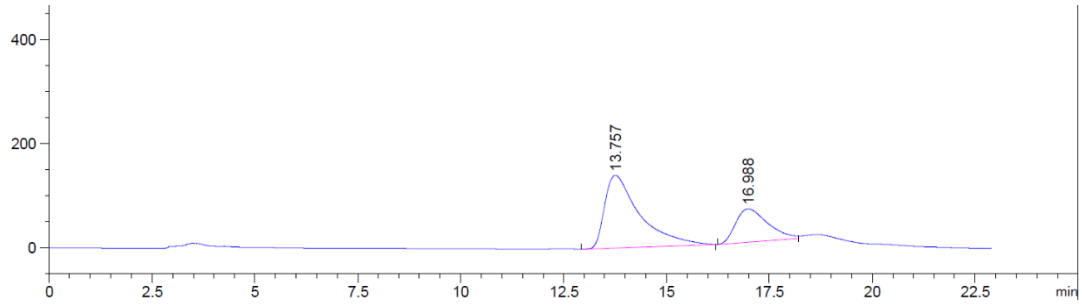
[a]Reaction conditions, unless otherwise noted: **1a** (0.1 mmol), **2a** (0.12 mmol), L(Chiral) (20 mol%), Pd(OAc)$_2$ (10 mol%), Cs_2CO_3 (2.0 equiv.) and 1 mL toluene under N_2 for 13 h. [b]Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

To a 10 mL Schlenk tube, **1a** (0.1 mmol), **2a** (0.12 mmol), Cs_2CO_3 (0.2 mmol, 2.0 equiv.),

$Pd(OAc)_2$ (0.01 mmol, 10 mol%), **L(chiral)** (0.02 mmol, 20.0 mol%), and toluene (1.0 mL) were added sequentially under a N_2 atmosphere. The reaction mixture was stirred at 80 °C (entry 10 at 60 °C and entry 10 at 40 °C) for 13 h. The resulting mixture was filtered with ethyl acetate and concentrated, then the residue was purified by preparative TLC (petroleum ether : ethyl acetate = 3 : 1) directly and delivered the desired product. (49% yield, 41% ee (determined by HPLC analysis [Daicel CHIRALPAK OD-H column, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 13.8 min, t (minor) = 17.0 min].



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.842	MM	0.9956	5706.30371	95.52834	49.8650
2	17.039	MM	1.2234	5737.19141	78.16105	50.1350



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.757	MM	0.9847	8255.93945	139.74226	70.4617
2	16.988	MM	0.9031	3460.97192	63.87343	29.5383

5. X-Ray Crystal Structure of Enantiopure 3aa

The crystal of **3aa** (CCDC 2120493) suitable for X-ray analysis was prepared by slow evaporation of the solvent of the solution of **3aa** in *n*-hexane/acetone at room temperature (Figure S1).

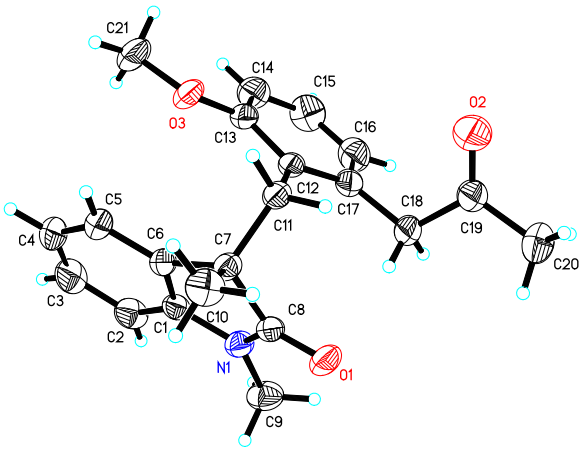


Figure S1. X-ray crystal structure of **3aa**

Table S2. Crystal data and structure refinement for **3aa**

Identification code	**3aa**	
Empirical formula	$C_{21}H_{23}NO_3$	
Formula weight	337.40	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.2614(3) Å	α = 90°
	b = 13.2824(5) Å	β = 110.0190(10)°
	c = 8.9573(3) Å	γ = 90°
Volume	923.51(6) $Å^3$	
Z	2	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	360	
Crystal size	0.170 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.624 to 25.996°.	
Index ranges	-10<=h<=10, -16<=k<=16, -11<=l<=11	
Reflections collected	8924	
Independent reflections	3570 [R(int) = 0.0249]	
Completeness to theta = 25.242°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6986	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3570 / 1 / 231	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0959	

R indices (all data)	R1 = 0.0460, wR2 = 0.1035
Absolute structure parameter	-0.1(5)
Extinction coefficient	0.12(3)
Largest diff. peak and hole	0.148 and -0.115 e.Å^{-3}

Table S3. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) **3aa**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	5587(2)	4326(2)	7803(2)	70(1)
O(2)	768(3)	6536(4)	7867(3)	120(1)
O(3)	-277(2)	4657(2)	2401(2)	64(1)
N(1)	5844(2)	4622(2)	5383(2)	50(1)
C(1)	4974(3)	4316(2)	3806(3)	49(1)
C(2)	5482(4)	4451(3)	2505(3)	66(1)
C(3)	4465(5)	4010(3)	1090(3)	79(1)
C(4)	3049(5)	3455(3)	1007(3)	75(1)
C(5)	2540(4)	3327(2)	2328(3)	63(1)
C(6)	3511(3)	3779(2)	3730(3)	47(1)
C(7)	3342(3)	3770(2)	5355(3)	48(1)
C(8)	5032(3)	4259(2)	6359(3)	49(1)
C(9)	7494(4)	5136(3)	5955(4)	73(1)
C(10)	3219(4)	2713(3)	5979(4)	71(1)
C(11)	1809(3)	4422(2)	5470(3)	50(1)
C(12)	1551(3)	5444(2)	4698(3)	48(1)
C(13)	507(3)	5527(2)	3093(3)	53(1)
C(14)	260(4)	6436(3)	2290(4)	72(1)
C(15)	1011(6)	7288(3)	3086(5)	86(1)
C(16)	1966(5)	7244(3)	4658(5)	78(1)
C(17)	2267(3)	6331(2)	5488(3)	59(1)
C(18)	3301(4)	6368(3)	7231(4)	70(1)
C(19)	2306(4)	6549(2)	8327(4)	65(1)
C(20)	3353(5)	6722(3)	10039(4)	83(1)
C(21)	-1131(4)	4648(4)	724(3)	87(1)

Table S4. Bond lengths [Å] and angles [°] fo**r 3aa**.

O(1)-C(8)	1.218(3)
O(2)-C(19)	1.194(4)
O(3)-C(13)	1.366(4)
O(3)-C(21)	1.424(3)
N(1)-C(8)	1.360(3)
N(1)-C(1)	1.408(3)
N(1)-C(9)	1.452(4)
C(1)-C(2)	1.378(4)
C(1)-C(6)	1.386(4)
C(2)-C(3)	1.388(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.363(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.395(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.375(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.510(3)
C(7)-C(8)	1.523(3)
C(7)-C(10)	1.528(4)
C(7)-C(11)	1.567(4)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600

C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.505(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(17)	1.397(4)
C(12)-C(13)	1.405(3)
C(13)-C(14)	1.384(4)
C(14)-C(15)	1.369(6)
C(14)-H(14)	0.9300
C(15)-C(16)	1.359(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.400(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.501(4)
C(18)-C(19)	1.500(4)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.498(4)
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(13)-O(3)-C(21)	118.2(3)
C(8)-N(1)-C(1)	110.4(2)
C(8)-N(1)-C(9)	123.3(2)
C(1)-N(1)-C(9)	125.8(2)
C(2)-C(1)-C(6)	122.5(2)
C(2)-C(1)-N(1)	127.8(3)
C(6)-C(1)-N(1)	109.58(19)
C(1)-C(2)-C(3)	116.9(3)
C(1)-C(2)-H(2)	121.5
C(3)-C(2)-H(2)	121.5
C(4)-C(3)-C(2)	121.2(3)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	121.5(3)
C(3)-C(4)-H(4)	119.3
C(5)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	118.0(3)
C(6)-C(5)-H(5)	121.0
C(4)-C(5)-H(5)	121.0
C(5)-C(6)-C(1)	119.8(2)
C(5)-C(6)-C(7)	131.3(2)
C(1)-C(6)-C(7)	108.9(2)
C(6)-C(7)-C(8)	101.4(2)
C(6)-C(7)-C(10)	113.5(2)
C(8)-C(7)-C(10)	109.8(2)
C(6)-C(7)-C(11)	113.7(2)
C(8)-C(7)-C(11)	108.9(2)
C(10)-C(7)-C(11)	109.2(2)
O(1)-C(8)-N(1)	124.6(2)
O(1)-C(8)-C(7)	126.4(2)
N(1)-C(8)-C(7)	109.02(19)
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5

H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(7)	117.31(19)
C(12)-C(11)-H(11A)	108.0
C(7)-C(11)-H(11A)	108.0
C(12)-C(11)-H(11B)	108.0
C(7)-C(11)-H(11B)	108.0
H(11A)-C(11)-H(11B)	107.2
C(17)-C(12)-C(13)	117.3(3)
C(17)-C(12)-C(11)	124.0(2)
C(13)-C(12)-C(11)	118.8(2)
O(3)-C(13)-C(14)	122.6(2)
O(3)-C(13)-C(12)	115.4(2)
C(14)-C(13)-C(12)	122.0(3)
C(15)-C(14)-C(13)	119.4(3)
C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3
C(16)-C(15)-C(14)	120.2(4)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	121.5(3)
C(15)-C(16)-H(16)	119.3
C(17)-C(16)-H(16)	119.3
C(12)-C(17)-C(16)	119.6(3)
C(12)-C(17)-C(18)	123.1(3)
C(16)-C(17)-C(18)	117.3(3)
C(19)-C(18)-C(17)	116.2(2)
C(19)-C(18)-H(18A)	108.2
C(17)-C(18)-H(18A)	108.2
C(19)-C(18)-H(18B)	108.2
C(17)-C(18)-H(18B)	108.2
H(18A)-C(18)-H(18B)	107.4
O(2)-C(19)-C(20)	121.9(3)
O(2)-C(19)-C(18)	121.9(3)
C(20)-C(19)-C(18)	116.2(3)
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(3)-C(21)-H(21A)	109.5
O(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2x10^3$) for **3aa**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	56(1)	111(2)	38(1)	-5(1)	6(1)	5(1)

O(2)	64(2)	205(4)	96(2)	-34(2)	34(1)	-7(2)
O(3)	50(1)	83(1)	46(1)	-11(1)	1(1)	-8(1)
N(1)	41(1)	58(1)	49(1)	-1(1)	13(1)	-2(1)
C(1)	48(1)	56(1)	44(1)	6(1)	17(1)	12(1)
C(2)	67(2)	82(2)	60(2)	14(2)	34(1)	12(2)
C(3)	95(3)	105(3)	45(2)	9(2)	35(2)	26(2)
C(4)	79(2)	97(3)	44(2)	-16(2)	13(1)	16(2)
C(5)	56(2)	76(2)	51(2)	-15(1)	12(1)	0(1)
C(6)	45(1)	58(2)	40(1)	-3(1)	15(1)	4(1)
C(7)	42(1)	62(2)	38(1)	0(1)	12(1)	-2(1)
C(8)	39(1)	65(2)	41(1)	-1(1)	10(1)	8(1)
C(9)	49(2)	74(2)	89(2)	1(2)	15(2)	-9(1)
C(10)	72(2)	73(2)	71(2)	11(2)	28(2)	1(2)
C(11)	38(1)	74(2)	40(1)	-5(1)	16(1)	-6(1)
C(12)	34(1)	70(2)	44(1)	-7(1)	17(1)	-1(1)
C(13)	39(1)	69(2)	49(1)	-5(1)	14(1)	1(1)
C(14)	73(2)	84(2)	59(2)	9(2)	21(2)	10(2)
C(15)	98(3)	72(2)	90(2)	9(2)	35(2)	3(2)
C(16)	75(2)	66(2)	98(3)	-19(2)	34(2)	-12(2)
C(17)	43(1)	73(2)	63(2)	-19(2)	21(1)	-6(1)
C(18)	50(2)	88(2)	67(2)	-32(2)	16(1)	-7(2)
C(19)	58(2)	68(2)	68(2)	-16(2)	20(1)	-5(1)
C(20)	97(3)	93(2)	61(2)	-9(2)	29(2)	-7(2)
C(21)	68(2)	127(3)	49(2)	-18(2)	-1(1)	-4(2)

Table S6. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) For **3aa.**

Atom	**x**	**y**	**z**	**U(eq)**
H(2)	6461	4820	2572	80
H(3)	4755	4094	182	95
H(4)	2407	3155	49	90
H(5)	1572	2947	2262	75
H(9A)	7590	5501	6907	109
H(9B)	7575	5597	5158	109
H(9C)	8407	4651	6179	109
H(10A)	3209	2756	7045	106
H(10B)	4194	2322	5970	106
H(10C)	2178	2396	5312	106
H(11A)	755	4040	5002	60
H(11B)	1968	4514	6586	60
H(14)	-411	6466	1219	87
H(15)	868	7900	2550	103
H(16)	2429	7834	5193	94
H(18A)	3914	5735	7525	83
H(18B)	4157	6895	7403	83
H(20A)	3405	7430	10263	125
H(20B)	4498	6467	10251	125
H(20C)	2828	6379	10699	125
H(21A)	-325	4817	205	130
H(21B)	-2050	5131	442	130
H(21C)	-1593	3989	394	130

Table S7. Torsion angles [°] for **3aa**.

C(8)-N(1)-C(1)-C(2)	-173.4(3)

C(9)-N(1)-C(1)-C(2)	-1.0(4)
C(8)-N(1)-C(1)-C(6)	2.8(3)
C(9)-N(1)-C(1)-C(6)	175.2(3)
C(6)-C(1)-C(2)-C(3)	-0.8(4)
N(1)-C(1)-C(2)-C(3)	175.0(3)
C(1)-C(2)-C(3)-C(4)	-1.1(5)
C(2)-C(3)-C(4)-C(5)	1.5(5)
C(3)-C(4)-C(5)-C(6)	0.1(5)
C(4)-C(5)-C(6)-C(1)	-1.9(4)
C(4)-C(5)-C(6)-C(7)	-178.4(3)
C(2)-C(1)-C(6)-C(5)	2.3(4)
N(1)-C(1)-C(6)-C(5)	-174.2(2)
C(2)-C(1)-C(6)-C(7)	179.5(2)
N(1)-C(1)-C(6)-C(7)	3.1(3)
C(5)-C(6)-C(7)-C(8)	169.9(3)
C(1)-C(6)-C(7)-C(8)	-6.9(3)
C(5)-C(6)-C(7)-C(10)	52.2(4)
C(1)-C(6)-C(7)-C(10)	-124.6(2)
C(5)-C(6)-C(7)-C(11)	-73.4(4)
C(1)-C(6)-C(7)-C(11)	109.8(2)
C(1)-N(1)-C(8)-O(1)	172.9(3)
C(9)-N(1)-C(8)-O(1)	0.2(4)
C(1)-N(1)-C(8)-C(7)	-7.5(3)
C(9)-N(1)-C(8)-C(7)	179.9(2)
C(6)-C(7)-C(8)-O(1)	-171.7(3)
C(10)-C(7)-C(8)-O(1)	-51.4(4)
C(11)-C(7)-C(8)-O(1)	68.1(3)
C(6)-C(7)-C(8)-N(1)	8.7(3)
C(10)-C(7)-C(8)-N(1)	129.0(2)
C(11)-C(7)-C(8)-N(1)	-111.5(2)
C(6)-C(7)-C(11)-C(12)	-43.6(3)
C(8)-C(7)-C(11)-C(12)	68.7(3)
C(10)-C(7)-C(11)-C(12)	-171.4(2)
C(7)-C(11)-C(12)-C(17)	-92.4(3)
C(7)-C(11)-C(12)-C(13)	88.7(3)
C(21)-O(3)-C(13)-C(14)	11.3(4)
C(21)-O(3)-C(13)-C(12)	-170.3(2)
C(17)-C(12)-C(13)-O(3)	-175.0(2)
C(11)-C(12)-C(13)-O(3)	3.9(3)
C(17)-C(12)-C(13)-C(14)	3.4(4)
C(11)-C(12)-C(13)-C(14)	-177.7(2)
O(3)-C(13)-C(14)-C(15)	176.3(3)
C(12)-C(13)-C(14)-C(15)	-1.9(5)
C(13)-C(14)-C(15)-C(16)	-1.1(6)
C(14)-C(15)-C(16)-C(17)	2.6(6)
C(13)-C(12)-C(17)-C(16)	-1.8(4)
C(11)-C(12)-C(17)-C(16)	179.3(3)
C(13)-C(12)-C(17)-C(18)	175.4(2)
C(11)-C(12)-C(17)-C(18)	-3.5(4)
C(15)-C(16)-C(17)-C(12)	-1.1(5)
C(15)-C(16)-C(17)-C(18)	-178.5(3)
C(12)-C(17)-C(18)-C(19)	-89.6(4)
C(16)-C(17)-C(18)-C(19)	87.7(4)
C(17)-C(18)-C(19)-O(2)	9.4(6)
C(17)-C(18)-C(19)-C(20)	-172.2(3)

Table S8. Hydrogen bonds for **3aa** [Å and °].

D-H···A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

C(18)-H(18A)···O(1)	0.97	2.29	3.243(4)	167.8

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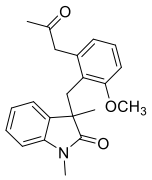
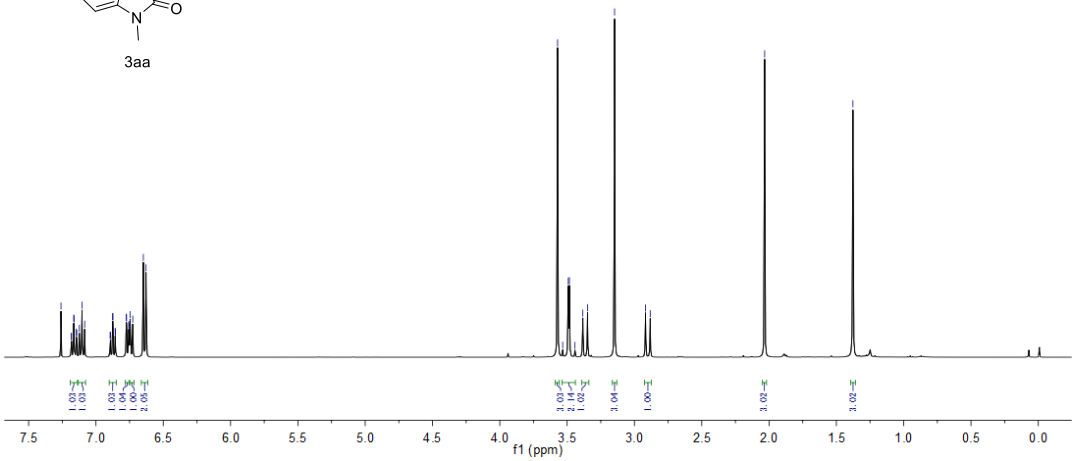
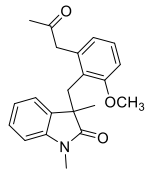
7. ^{1}H, ^{19}F, ^{13}C NMR Spectras

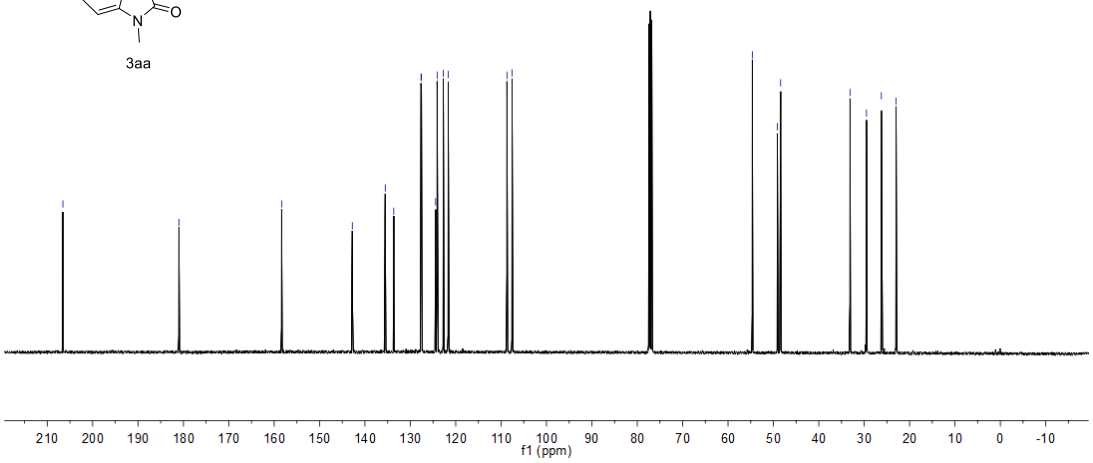


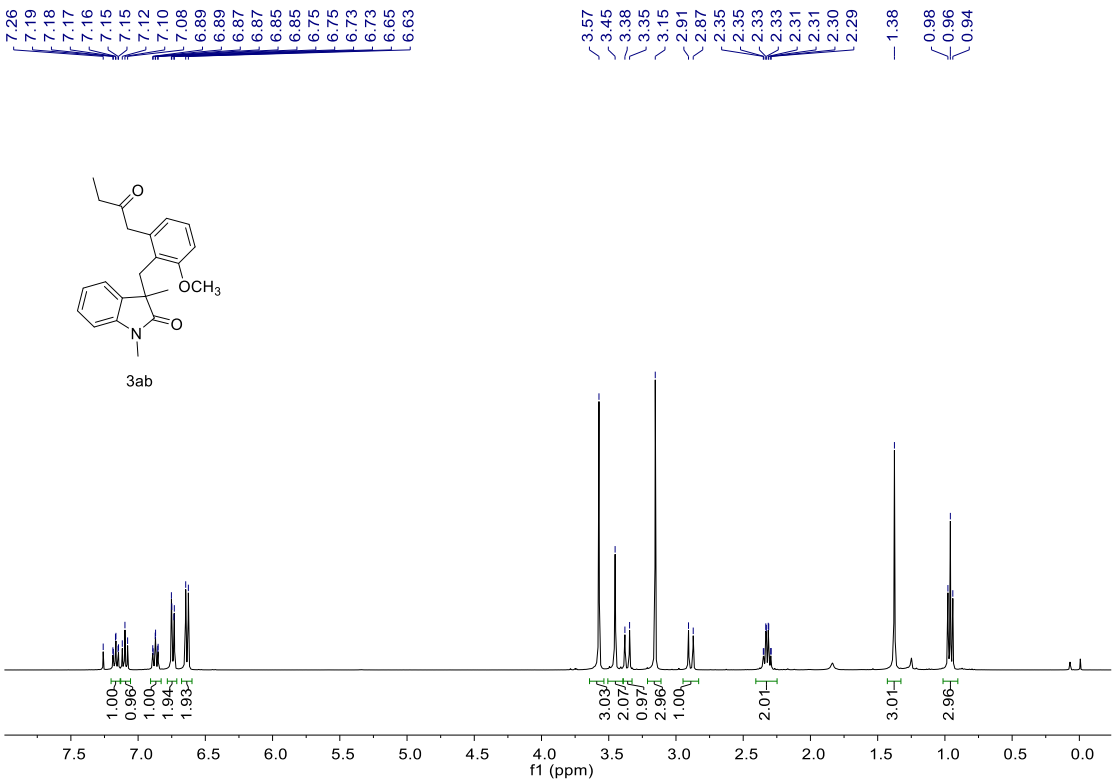
3aa





3aa

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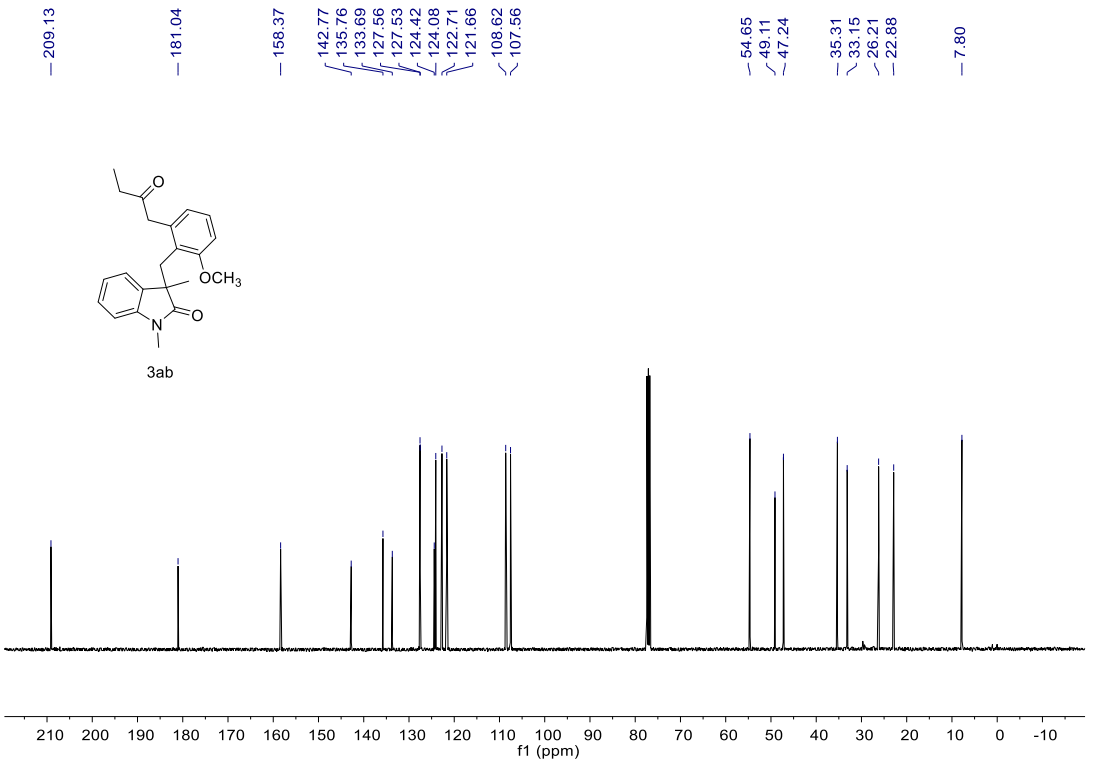
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54.65
49.11
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33.15
26.21
22.88
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O
OCH3
N
O
3ab
210
200
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180
170
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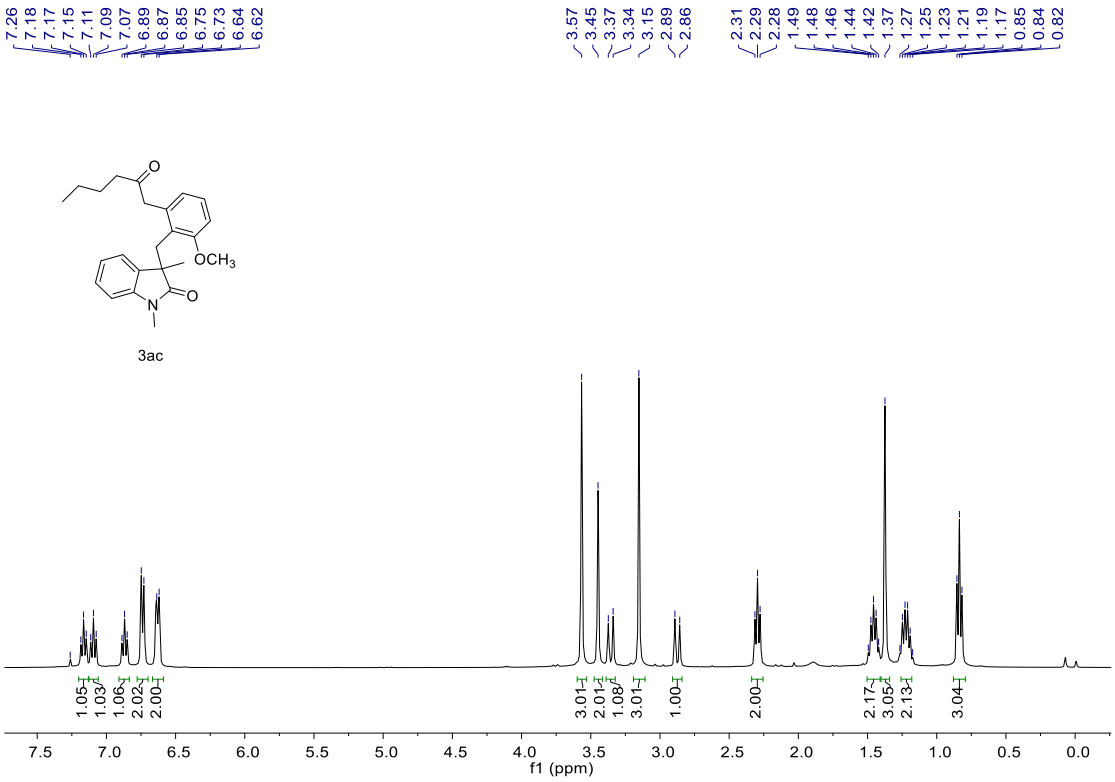
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O
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N
O
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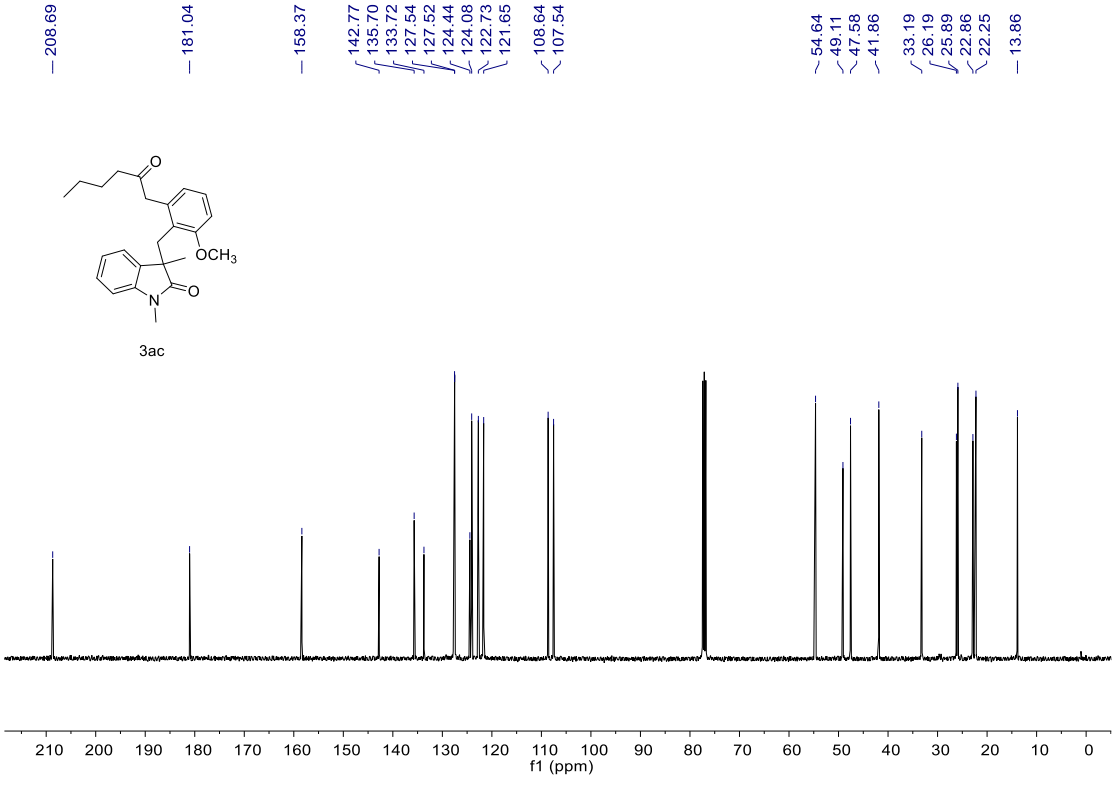
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O
OCH3
N
O
3ac
210
200
190
180
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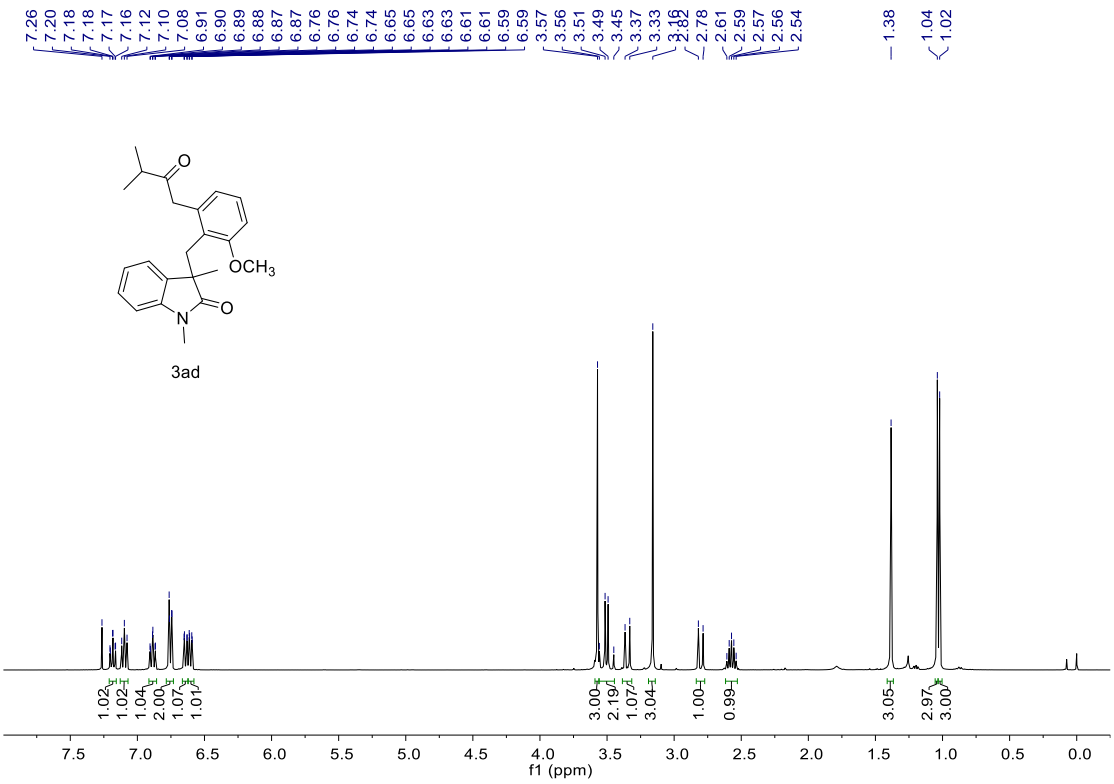
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1.02
OCH3
O
N
O
3ad
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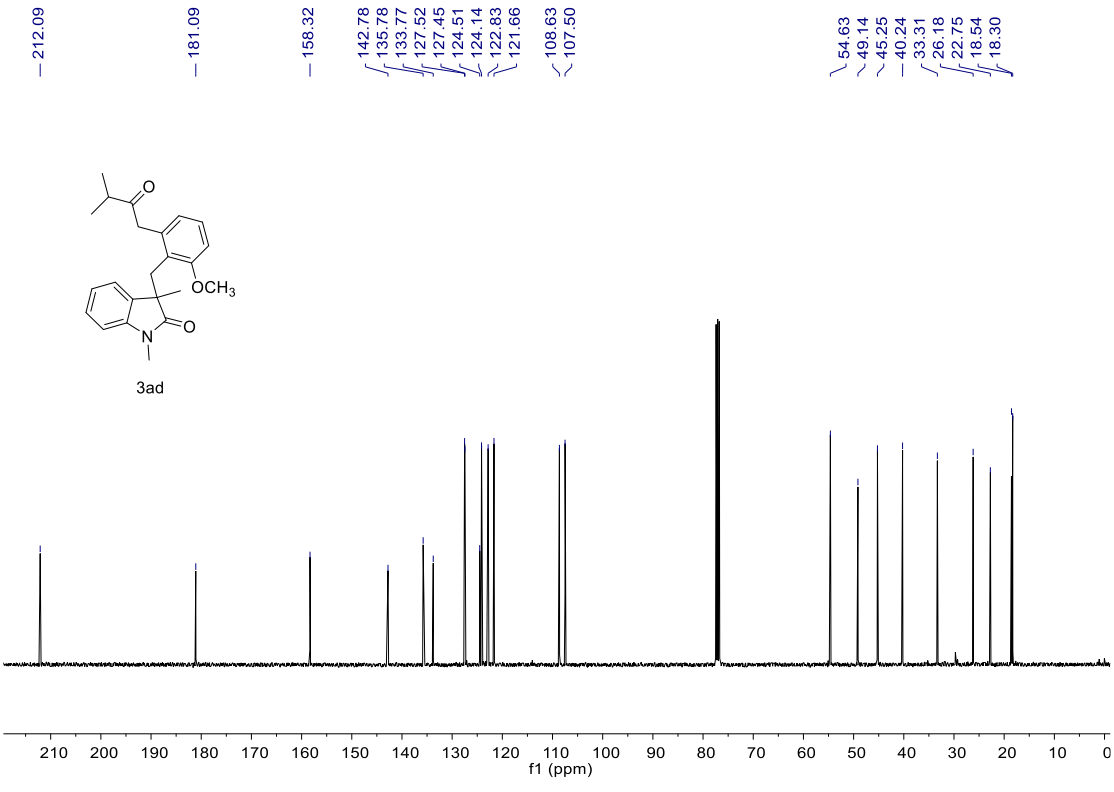
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49.14
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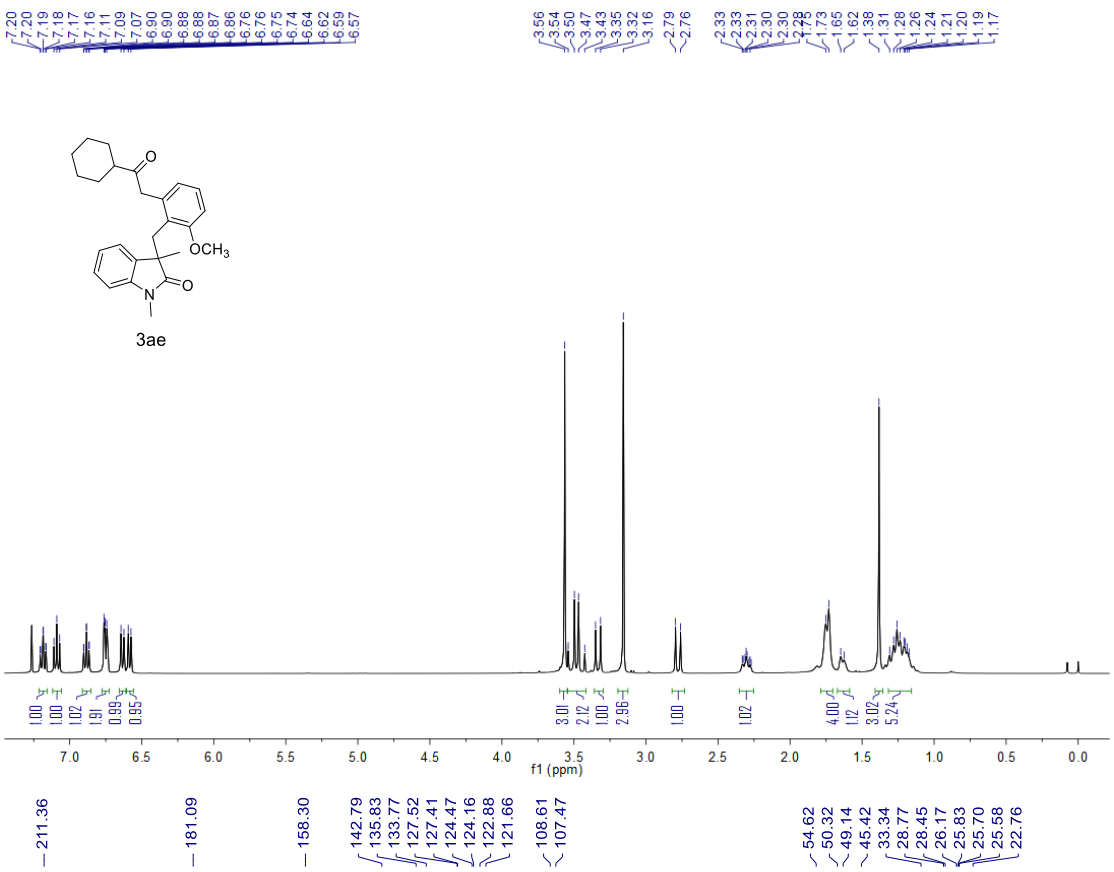
O
3ad
f1 (ppm)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3.56 3.54 3.50 3.47 3.43 3.35 3.32 3.16 2.79 2.76 2.33 2.33 2.31 2.30 2.30 2.28 1.73 1.65 1.62 1.38 1.31 1.28 1.26 1.24 1.21 1.20 1.19 1.17
OCH3
O
N
3ae
1.00 1.00 1.02 1.91 0.99 0.95 3.01 2.12 1.00 2.96 1.00 1.02 4.00 1.12 3.02 5.24
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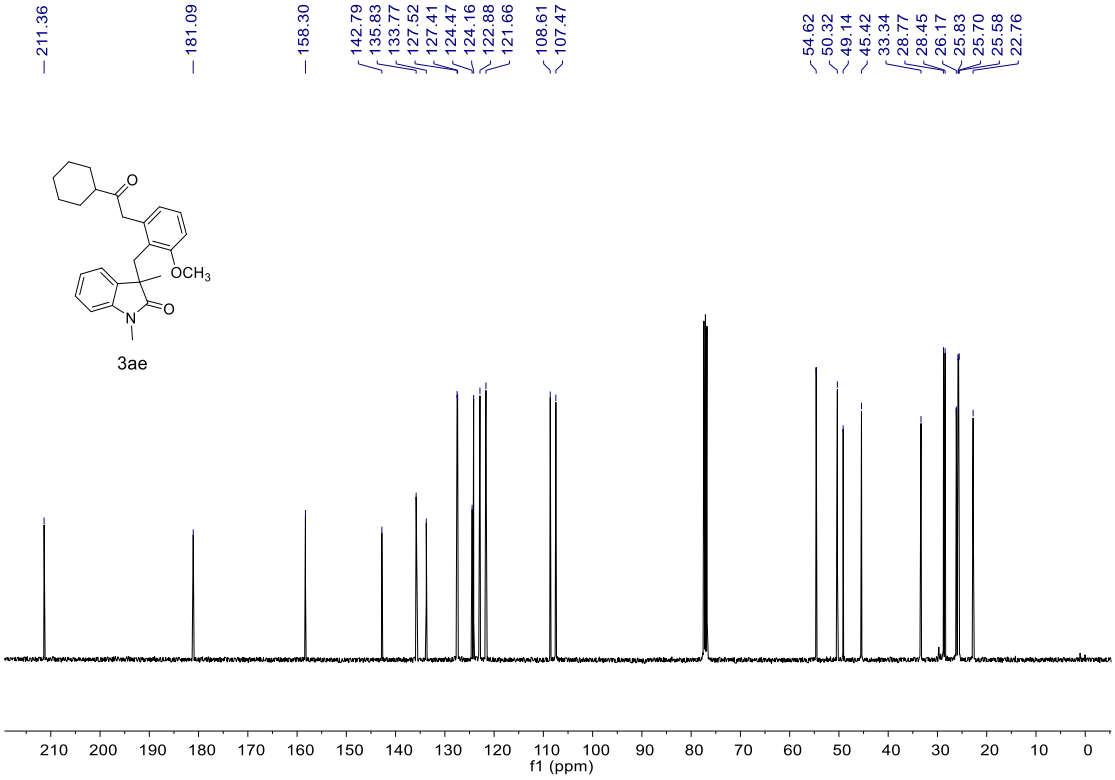
f1 (ppm)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OCH3
O
N
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.36
7.35
7.34
7.34
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7.27
7.26
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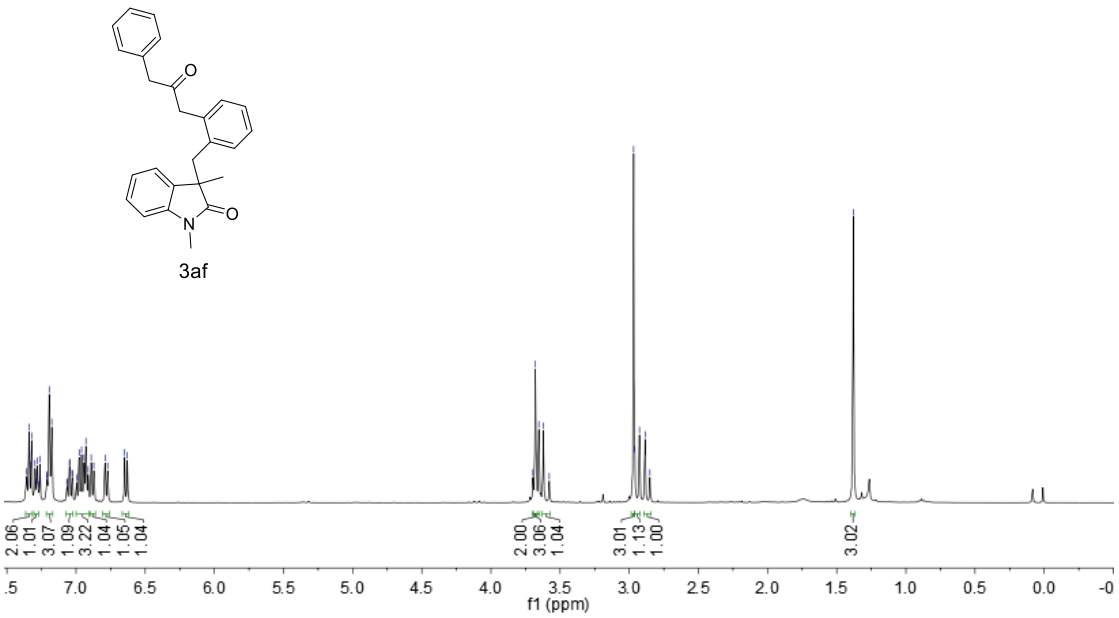
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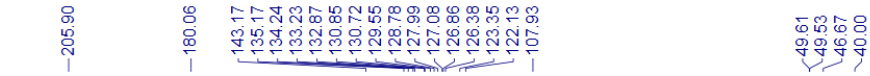
1.00
3.02
f1 (ppm)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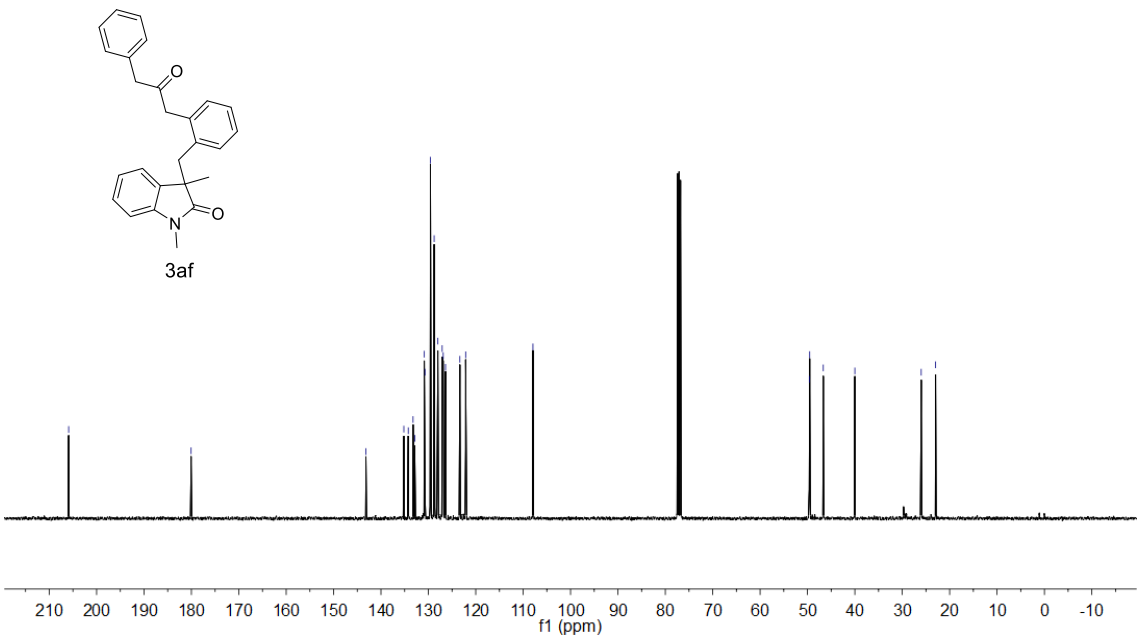
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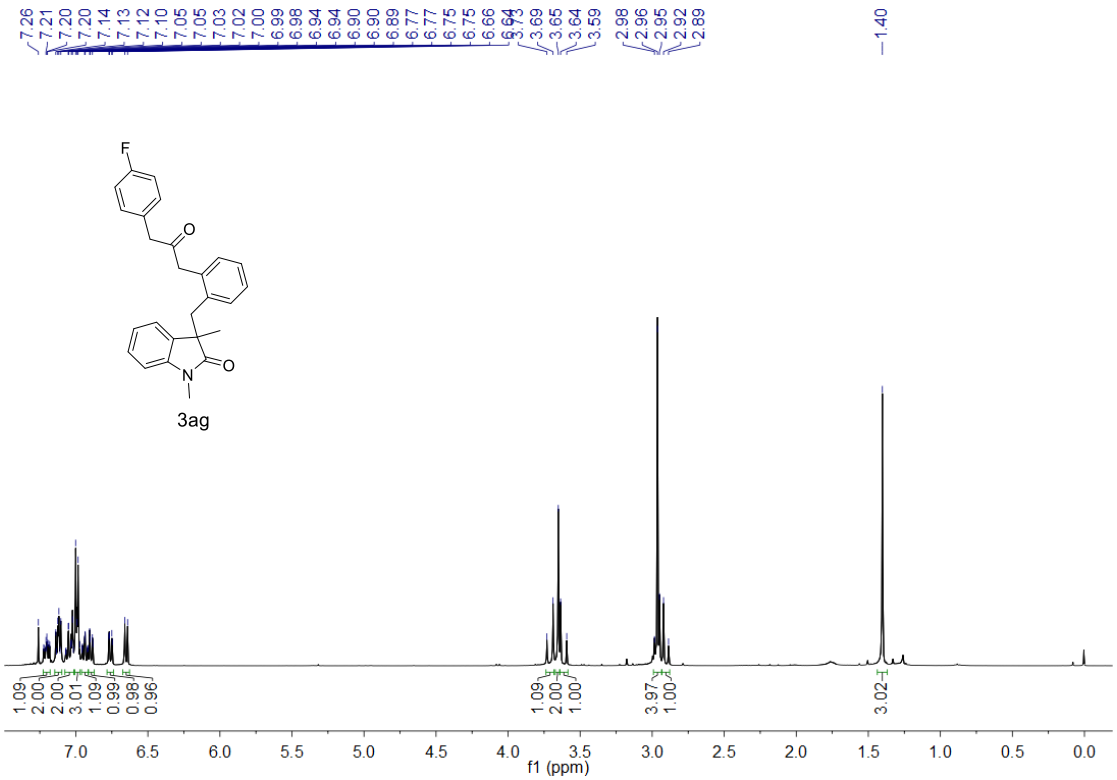
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2.92
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F
O
O
N
3ag
1.09
2.00
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1.09
2.00
1.00
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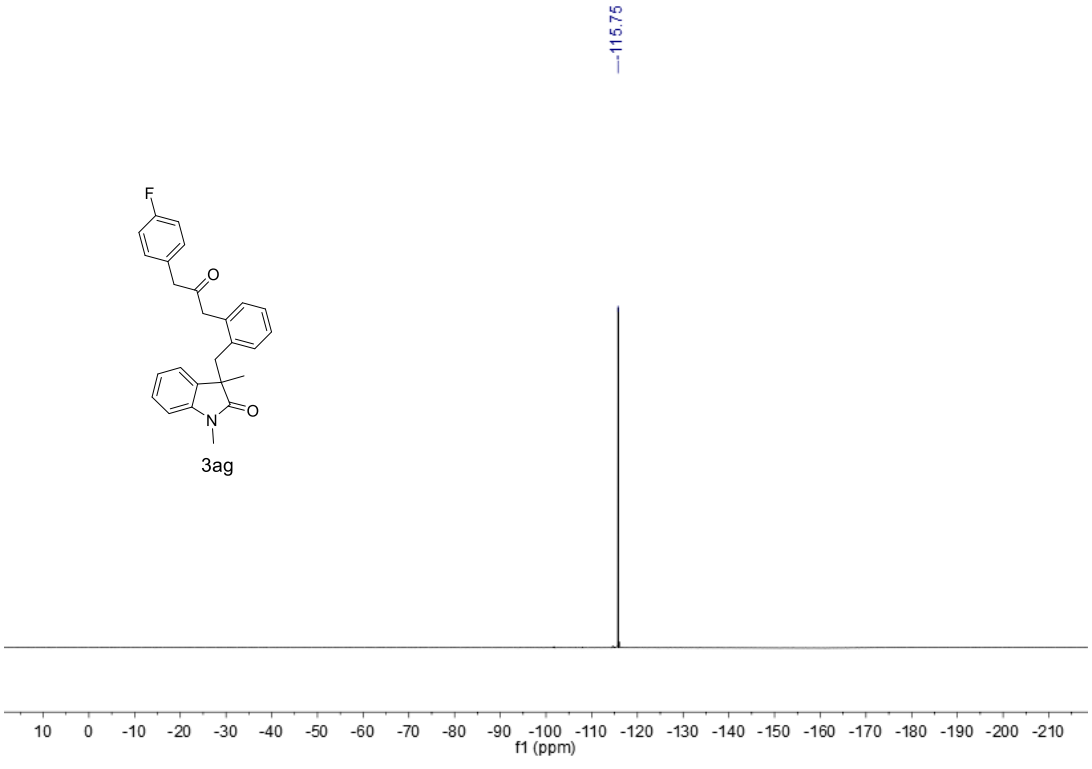
f1 (ppm)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-180
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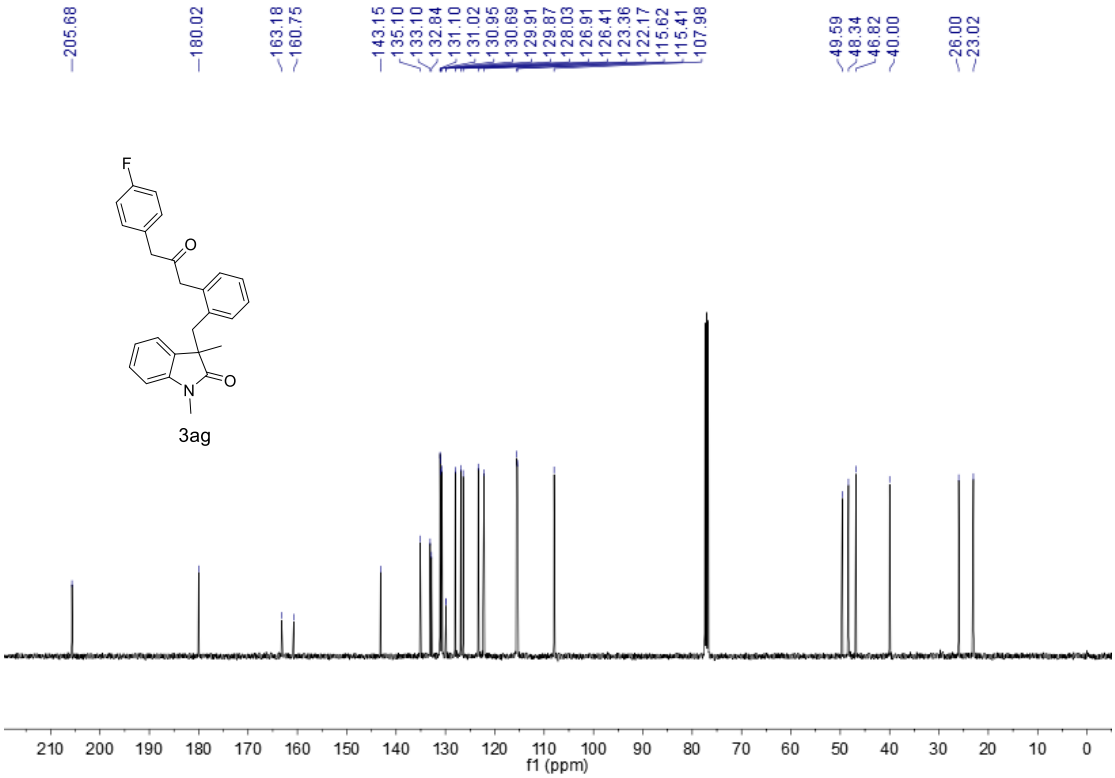
f1 (ppm)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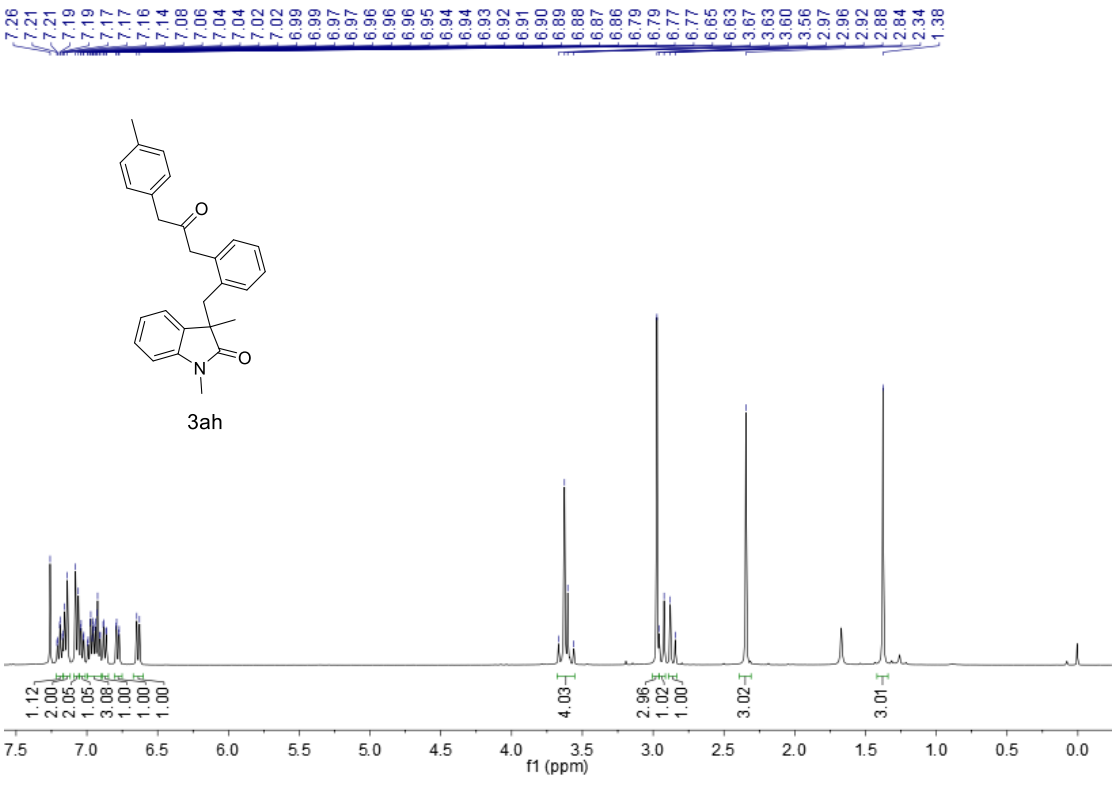
3ag
f1 (ppm)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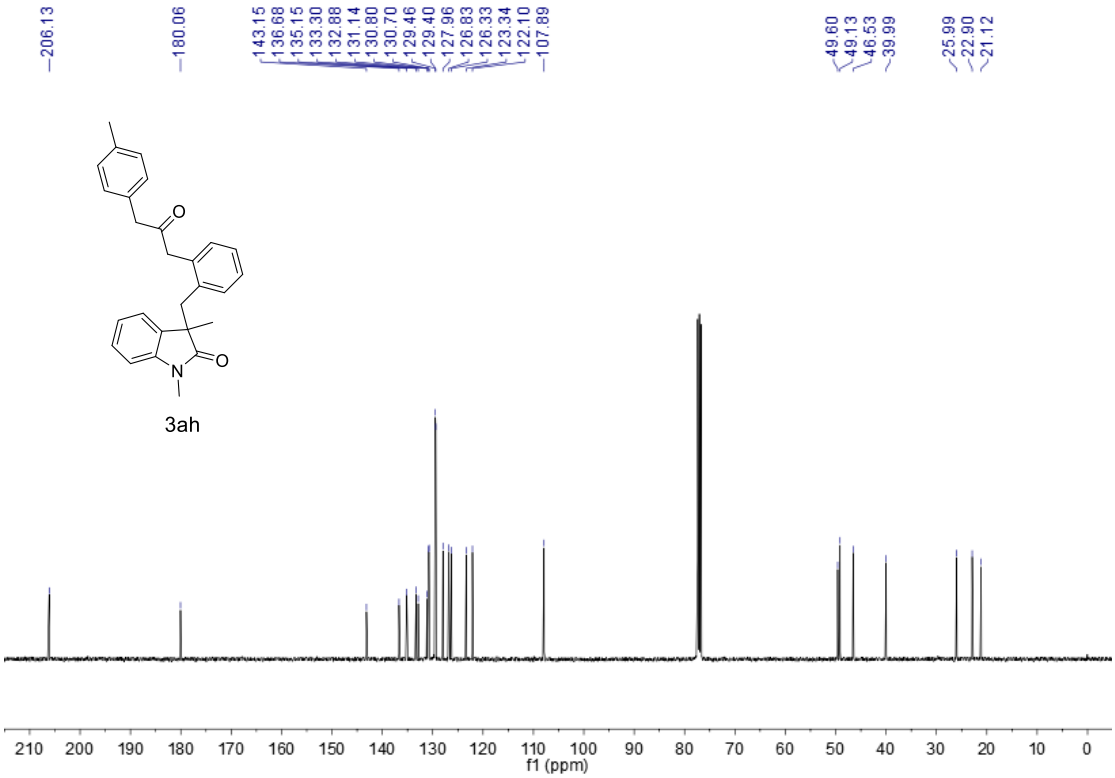
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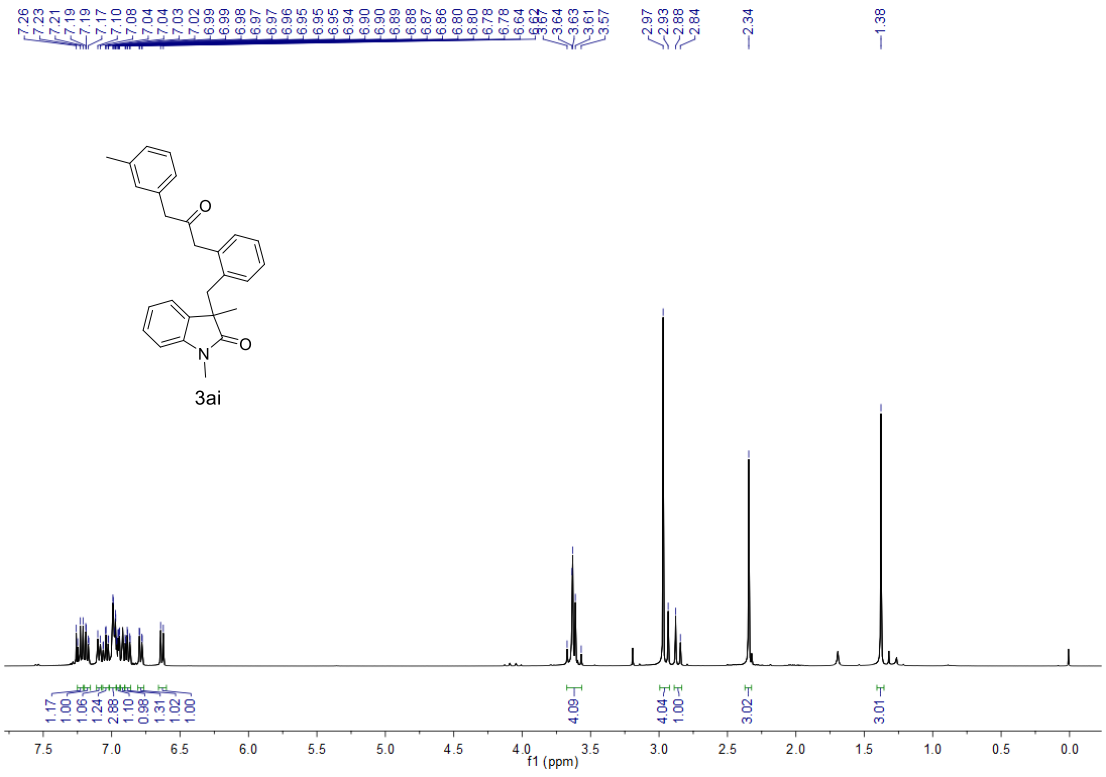
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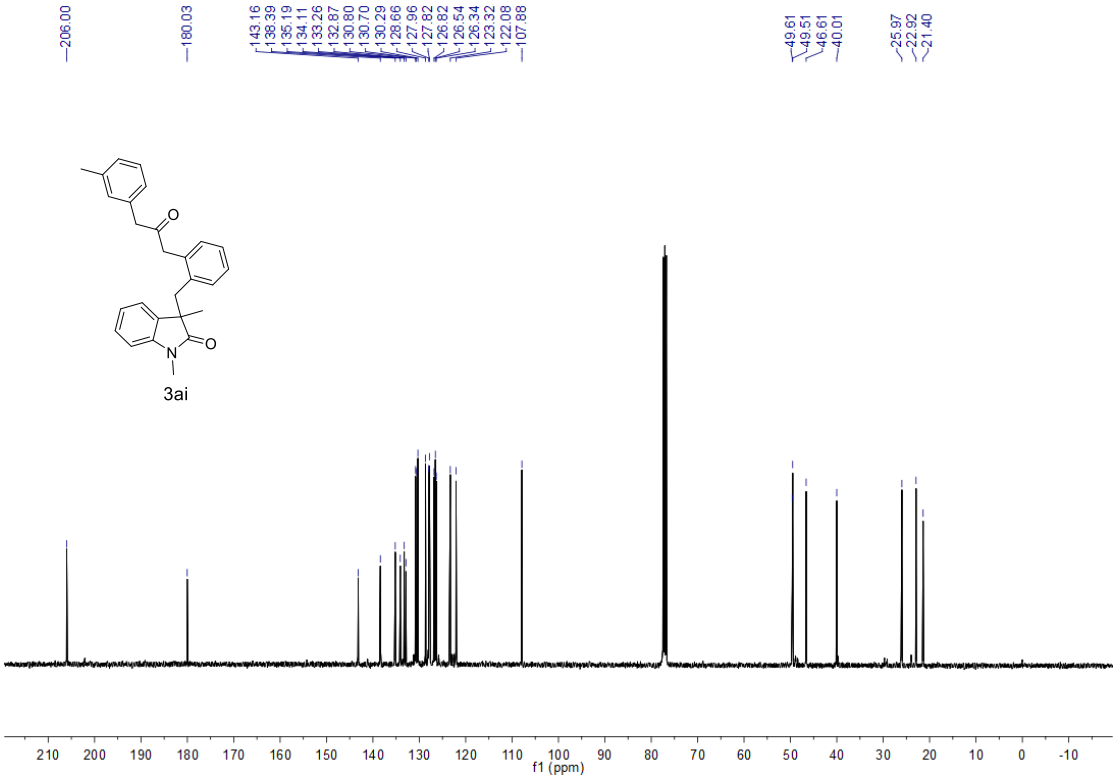
f1 (ppm)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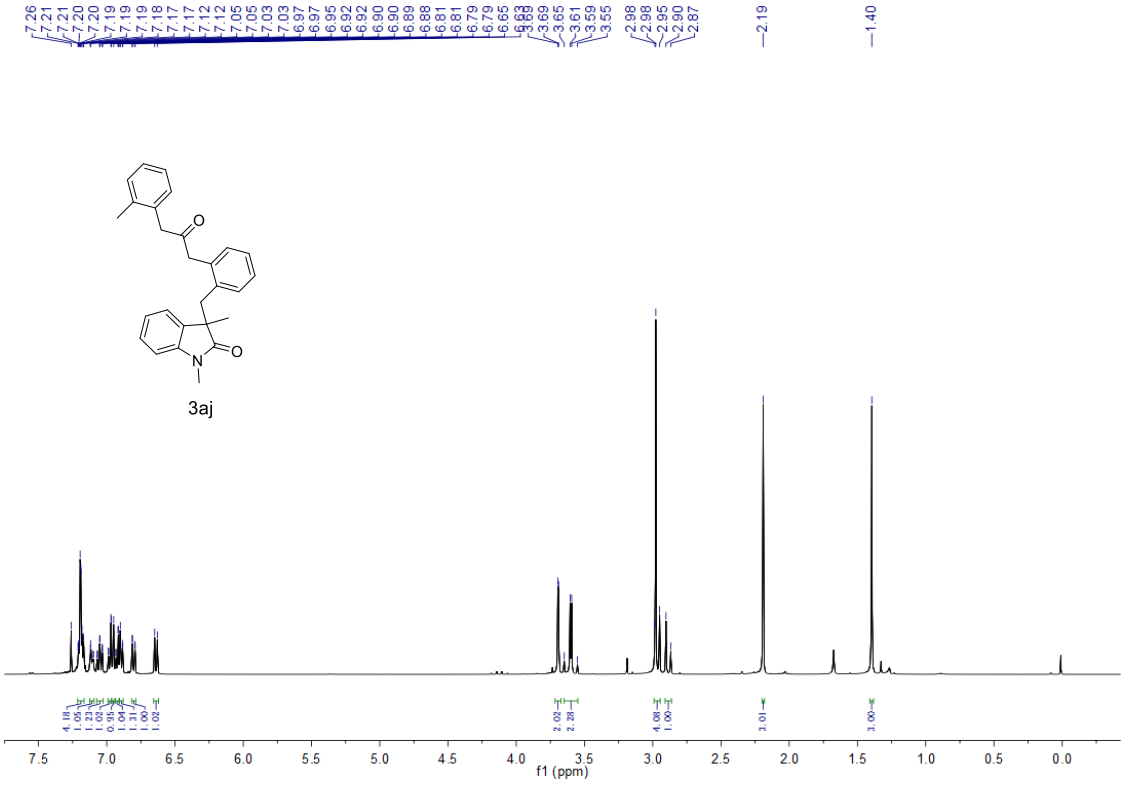
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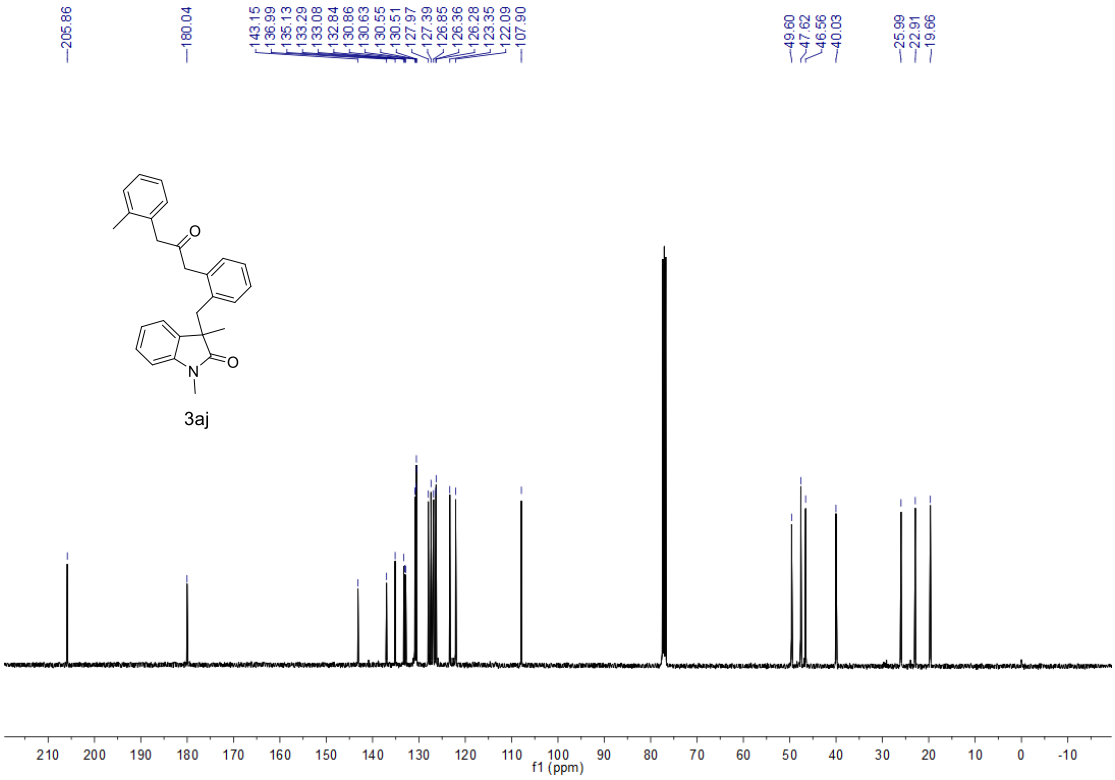
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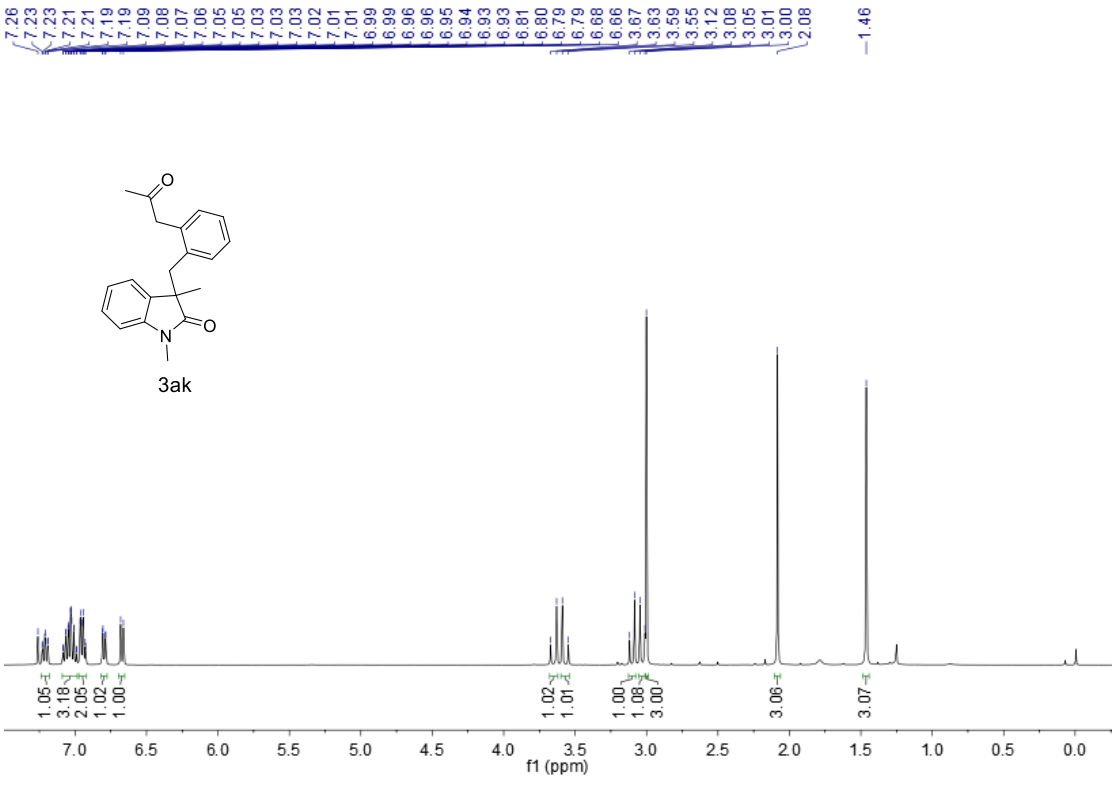
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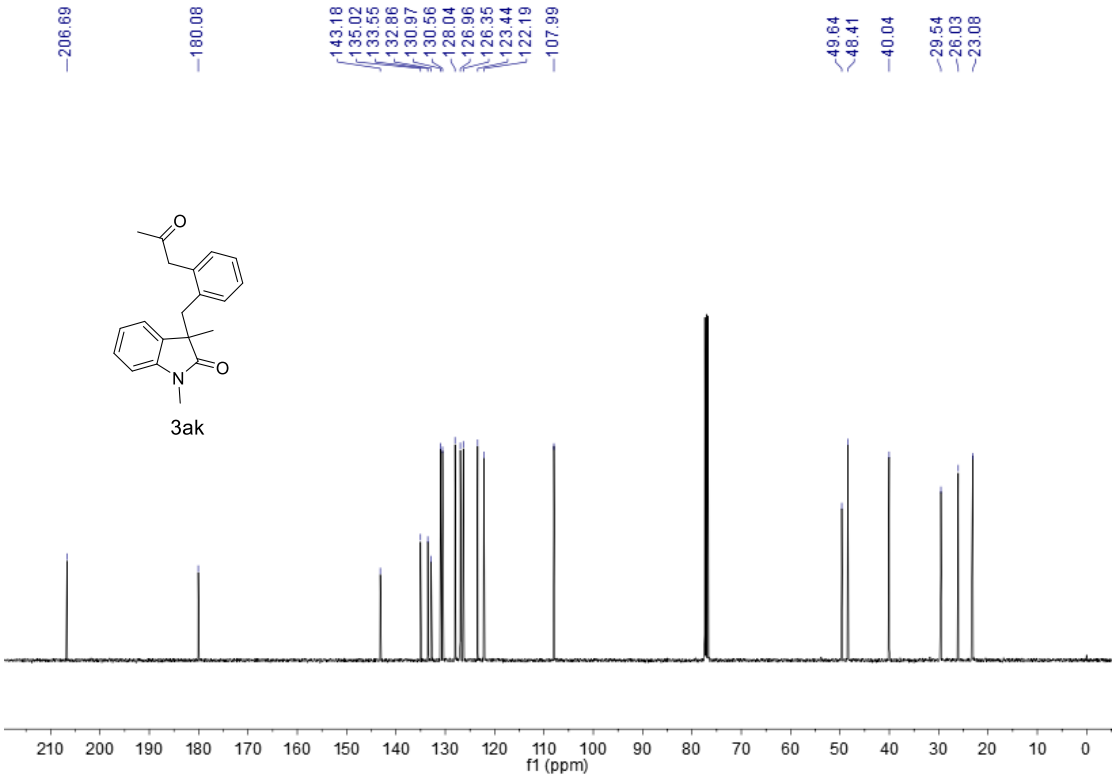
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26.03
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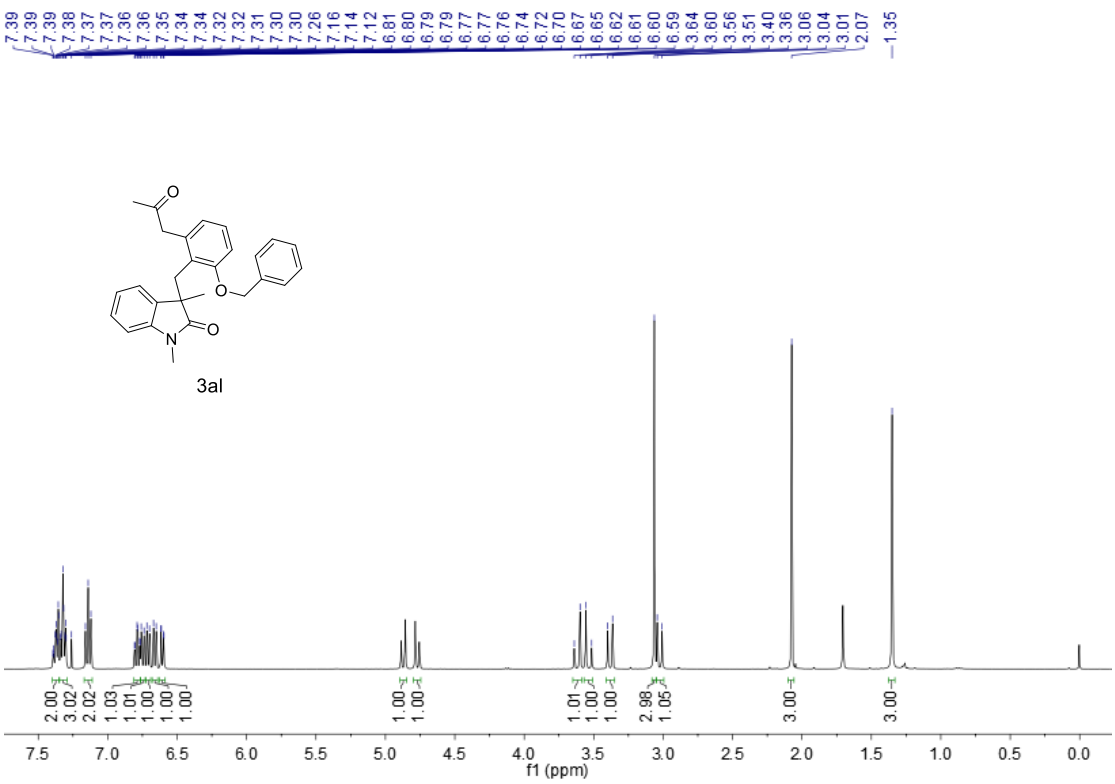
f1 (ppm)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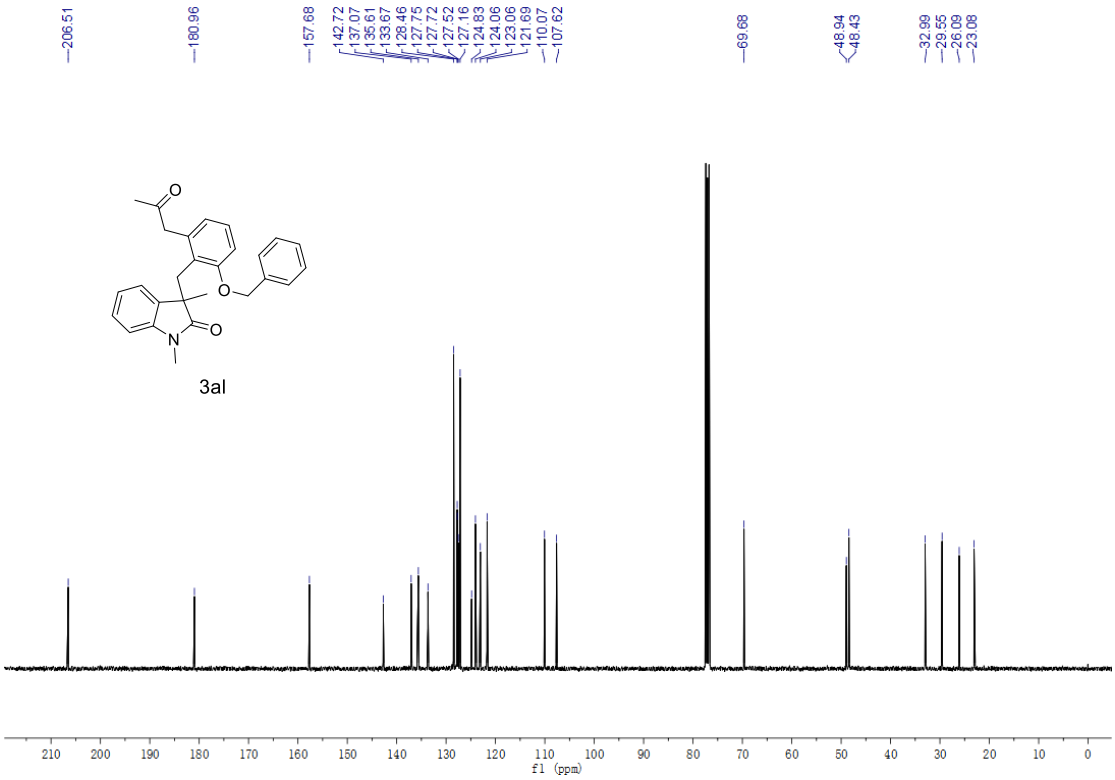
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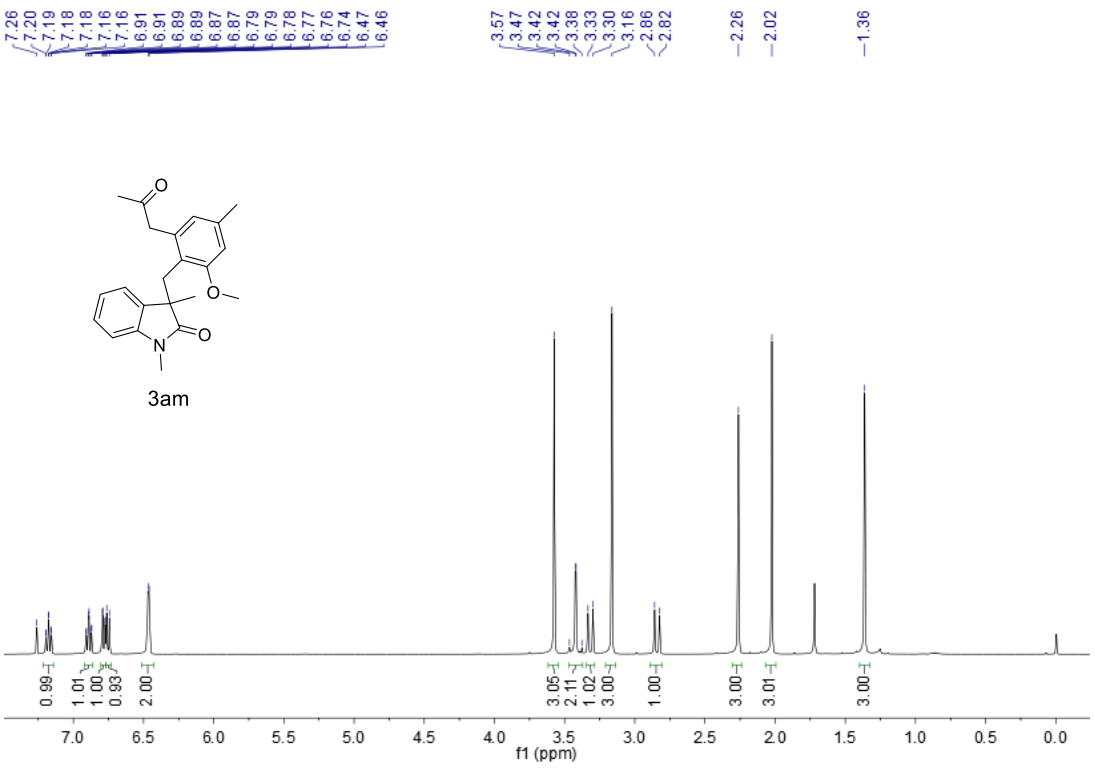
3al
f1 (ppm)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6.89
6.87
6.87
6.79
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6.74
6.47
6.46
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3.47
3.42
3.42
3.38
3.33
3.30
3.16
2.86
2.82
2.26
2.02
1.36
3am
0.99
1.01
1.00
0.93
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2.11
1.02
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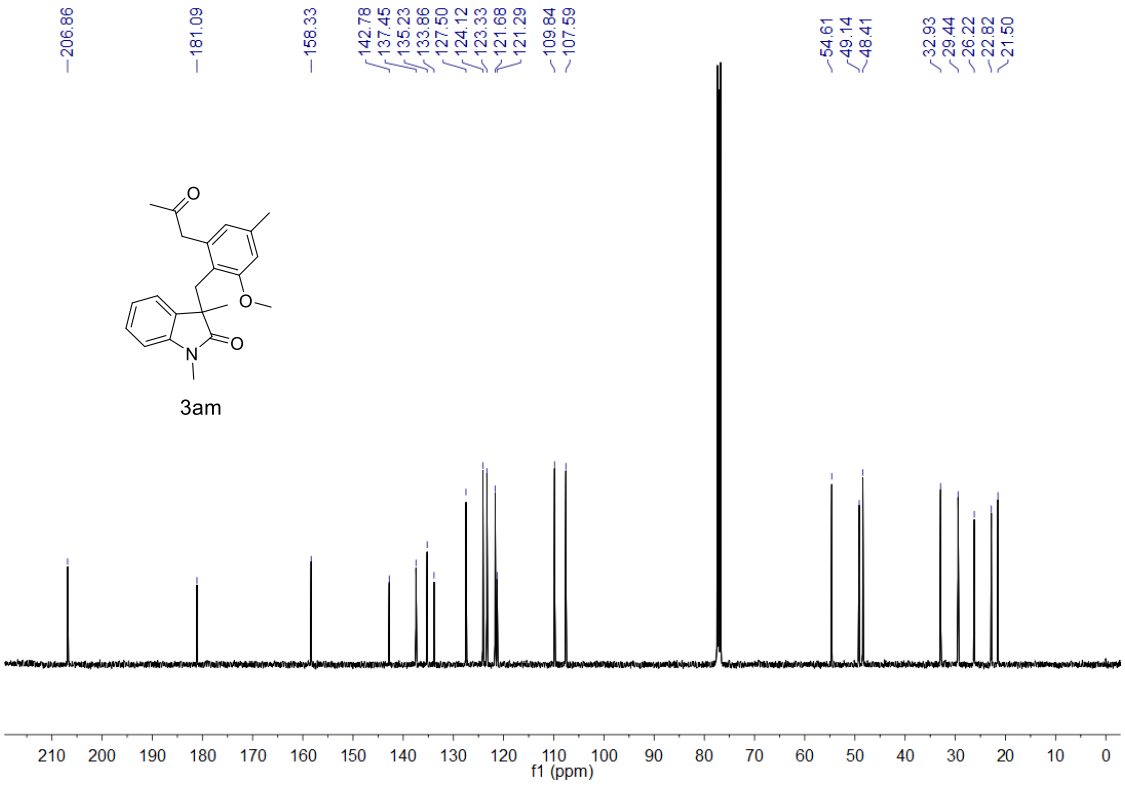
3.00
f1 (ppm)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54.61
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48.41
32.93
29.44
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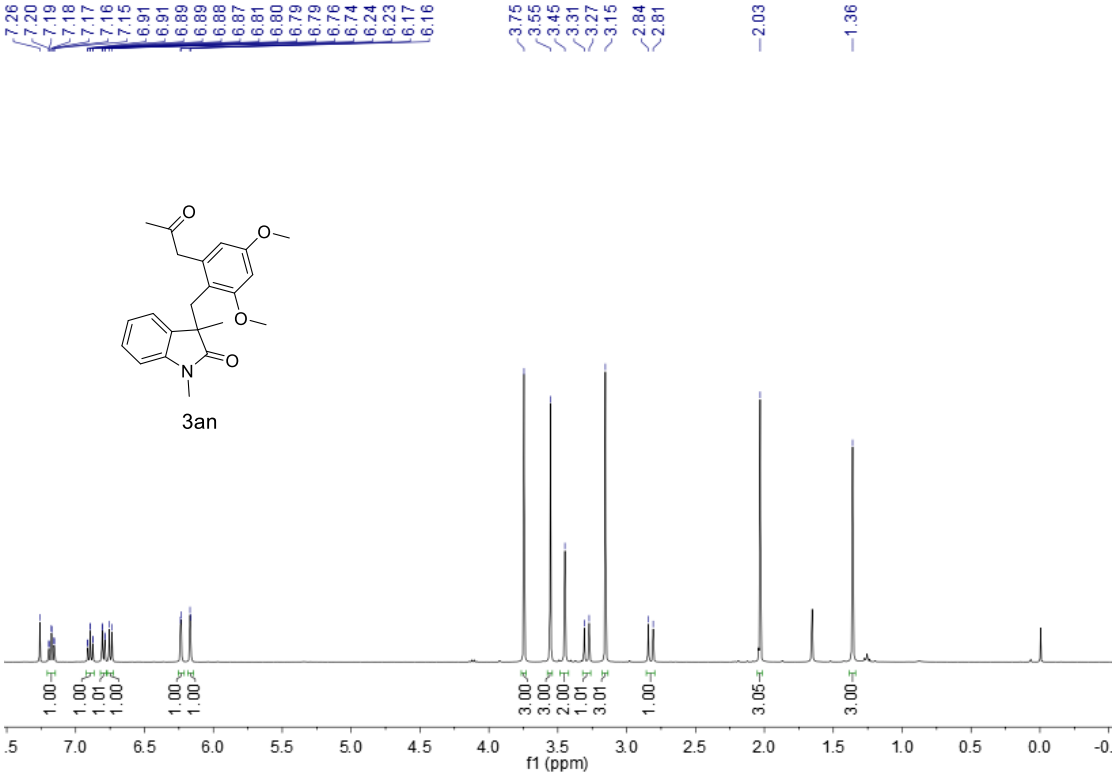
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6.79
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6.74
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6.16
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3.45
3.31
3.27
3.15
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2.81
2.03
1.36
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O
O
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3an
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1.00
1.01
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3.00
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1.01
3.01
1.00
3.05
3.00
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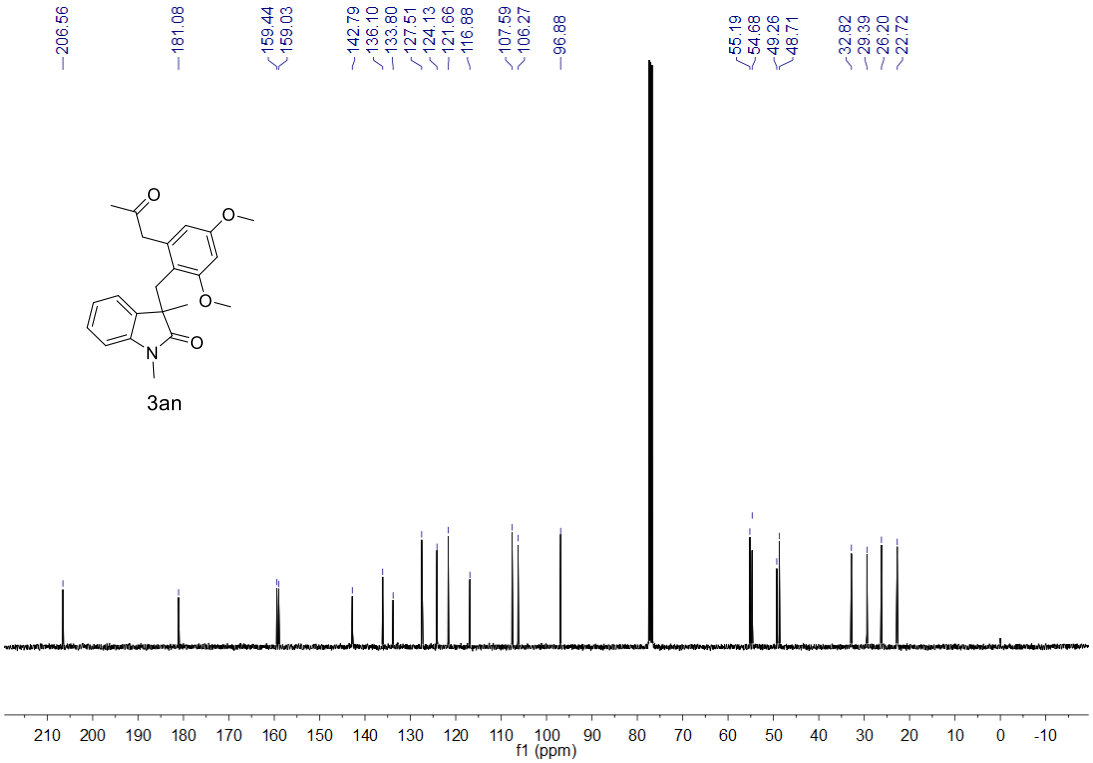
f1 (ppm)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32.82
29.39
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O
N
3an
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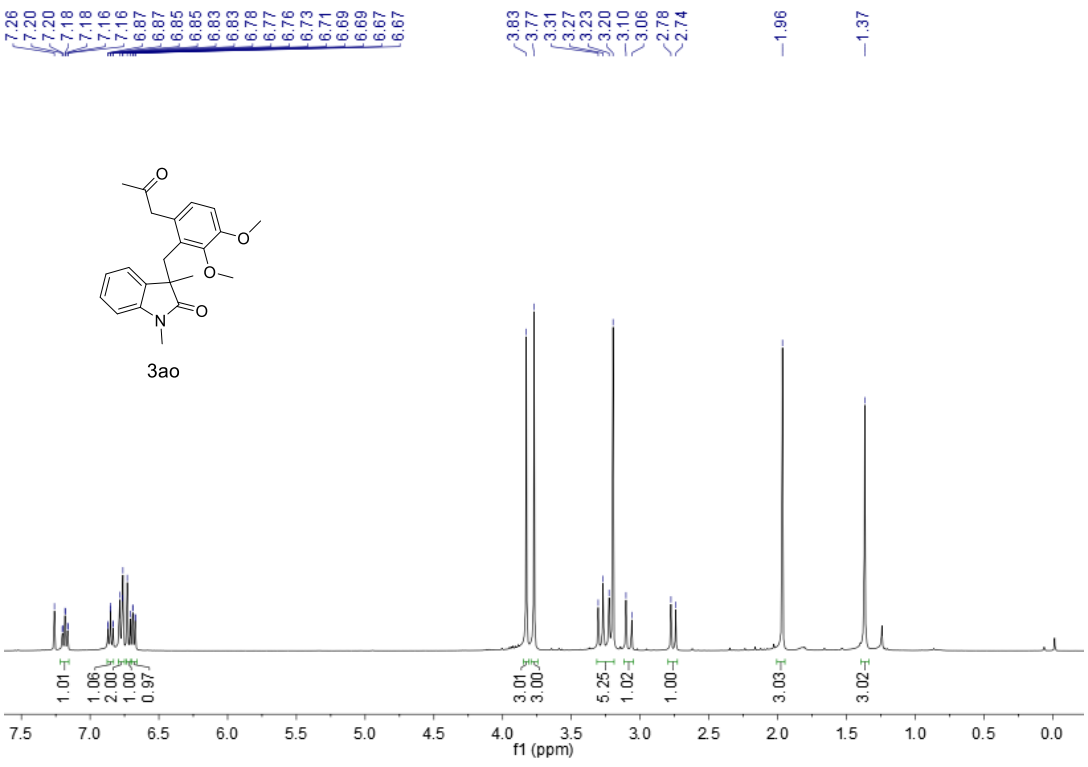
f1 (ppm)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6.76
6.73
6.71
6.69
6.69
6.67
6.67
3.83
3.77
3.31
3.27
3.23
3.20
3.10
3.06
2.78
2.74
1.96
1.37
O
O
O
O
N
3ao
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1.06
2.00
1.00
0.97
3.01
3.00
5.25
1.02
1.00
3.03
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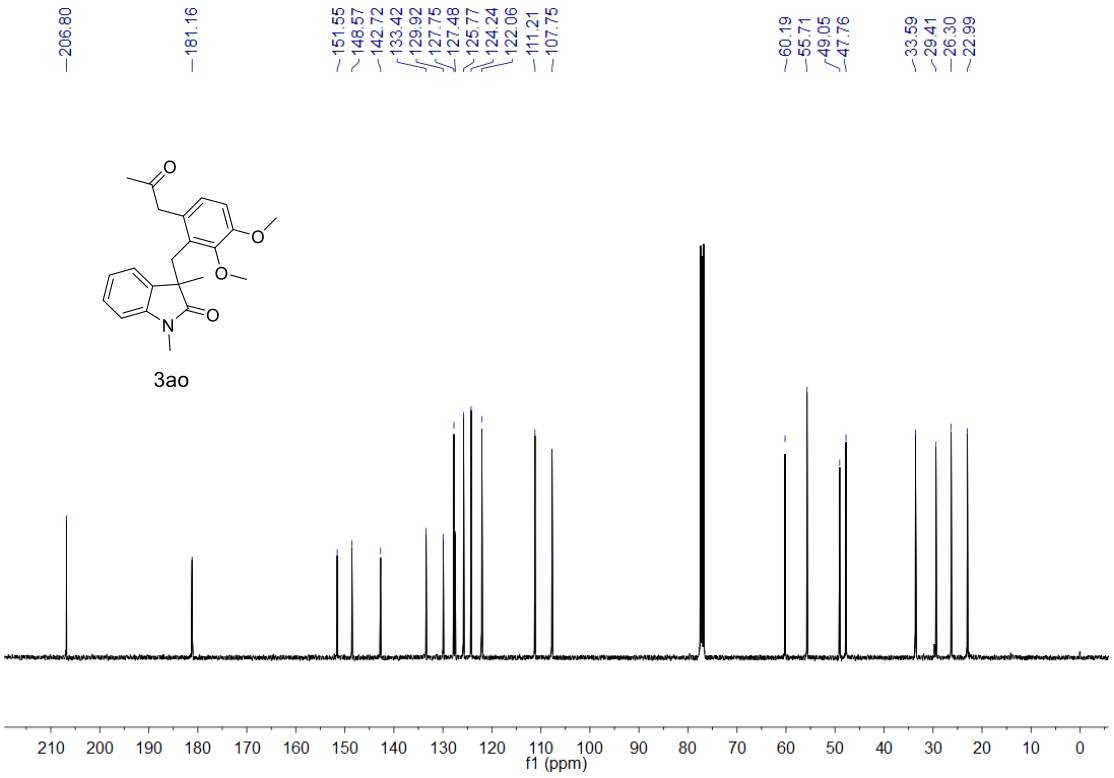
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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29.41
26.30
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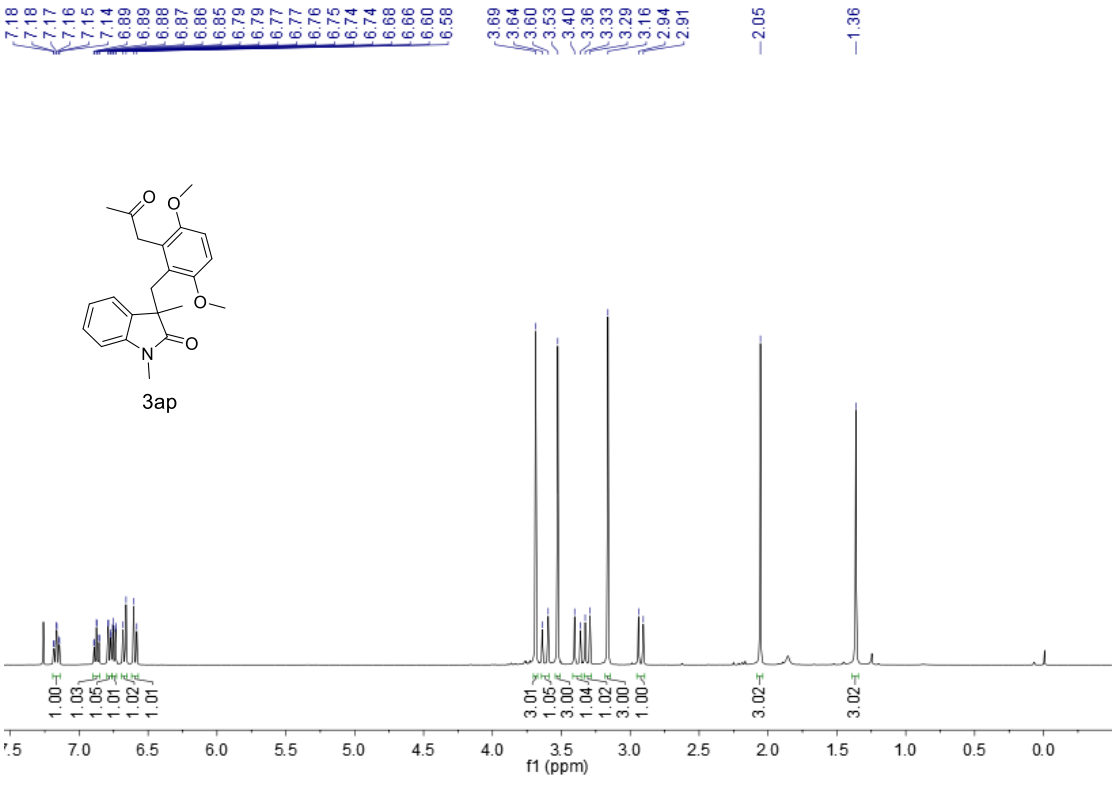
3ao
f1 (ppm)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6.74
6.74
6.68
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3.60
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2.05
1.36
3ap
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1.03
1.05
1.01
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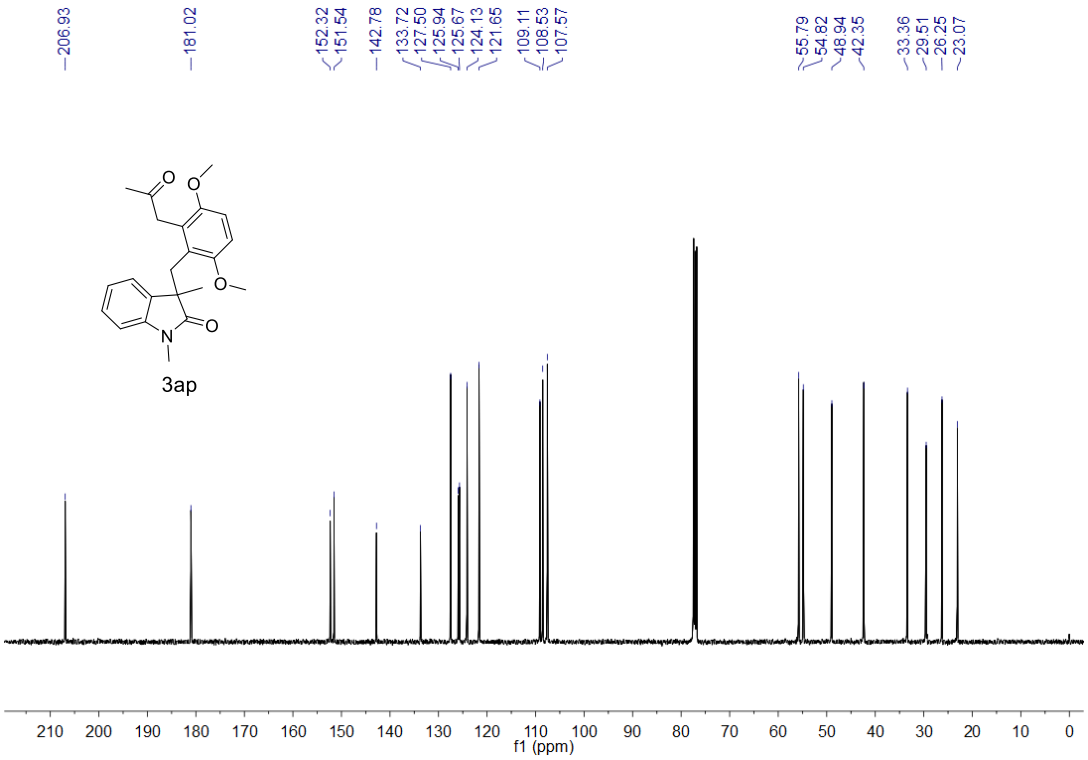
3.02
f1 (ppm)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121.65
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54.82
48.94
42.35
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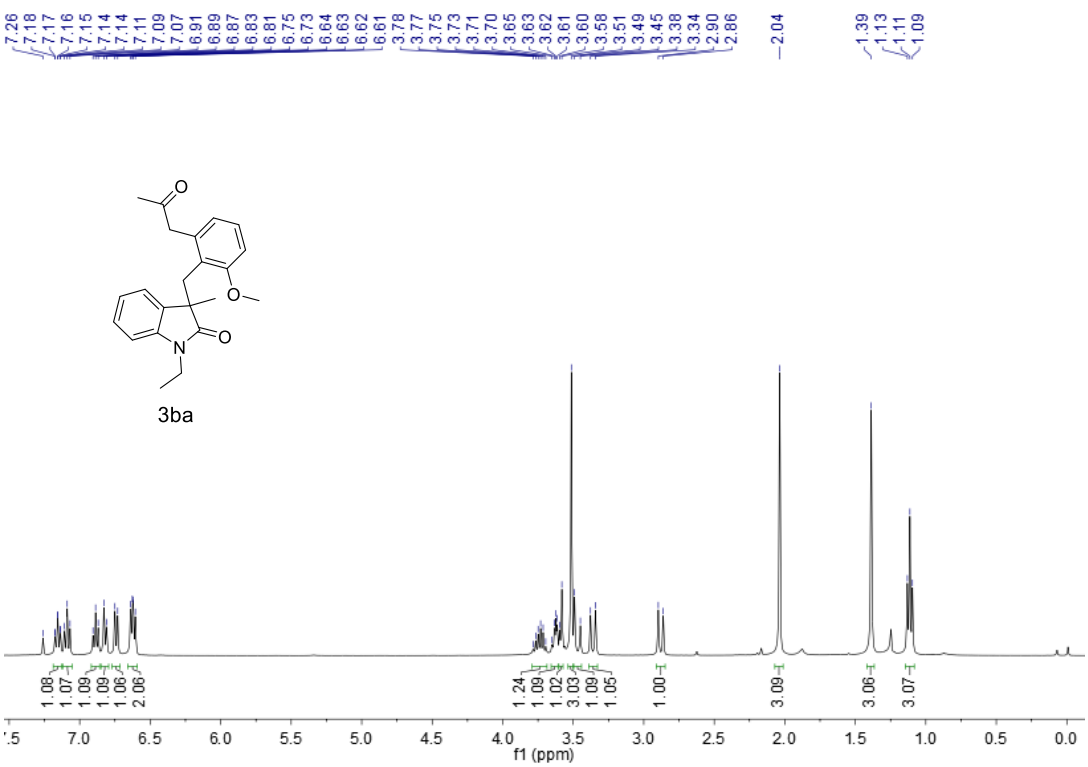
29.51
26.25
23.07
3ap
f1 (ppm)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7.07
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6.87
6.83
6.81
6.75
6.73
6.64
6.63
6.62
6.61
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3.77
3.75
3.73
3.71
3.70
3.65
3.63
3.62
3.61
3.60
3.58
3.51
3.49
3.45
3.38
3.34
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2.86
2.04
1.39
1.13
1.11
1.09
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1.07
1.09
1.09
1.06
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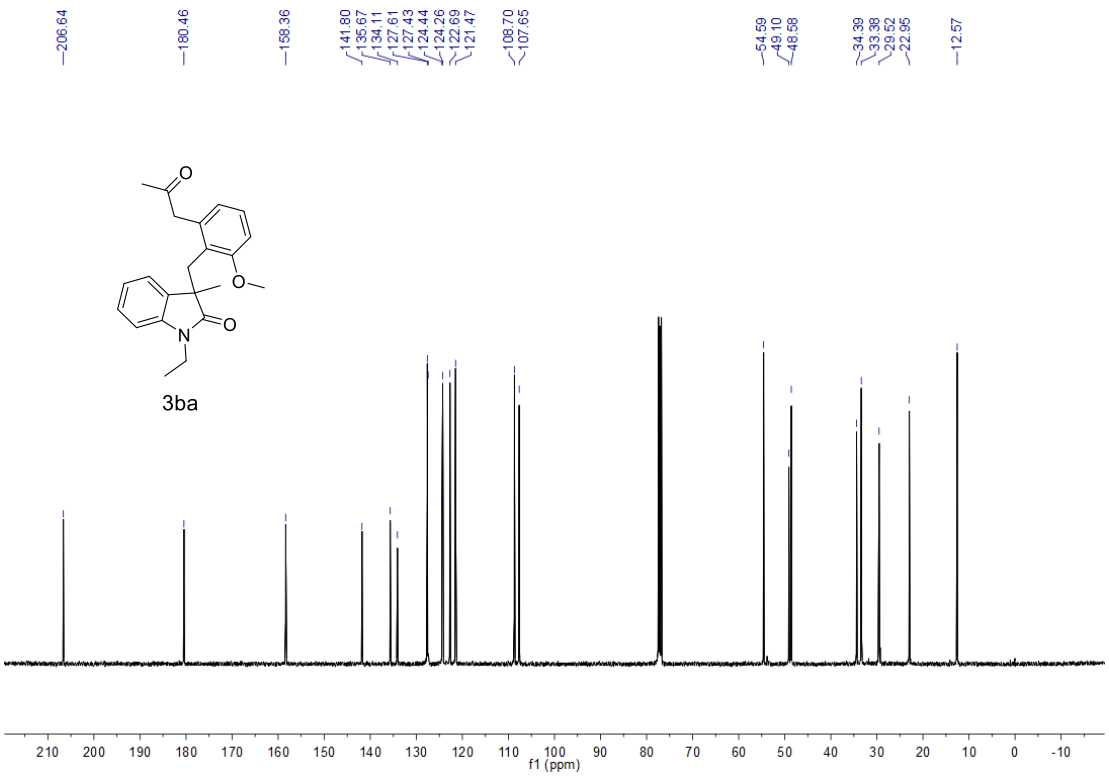
3.06
3.07
f1 (ppm)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121.47
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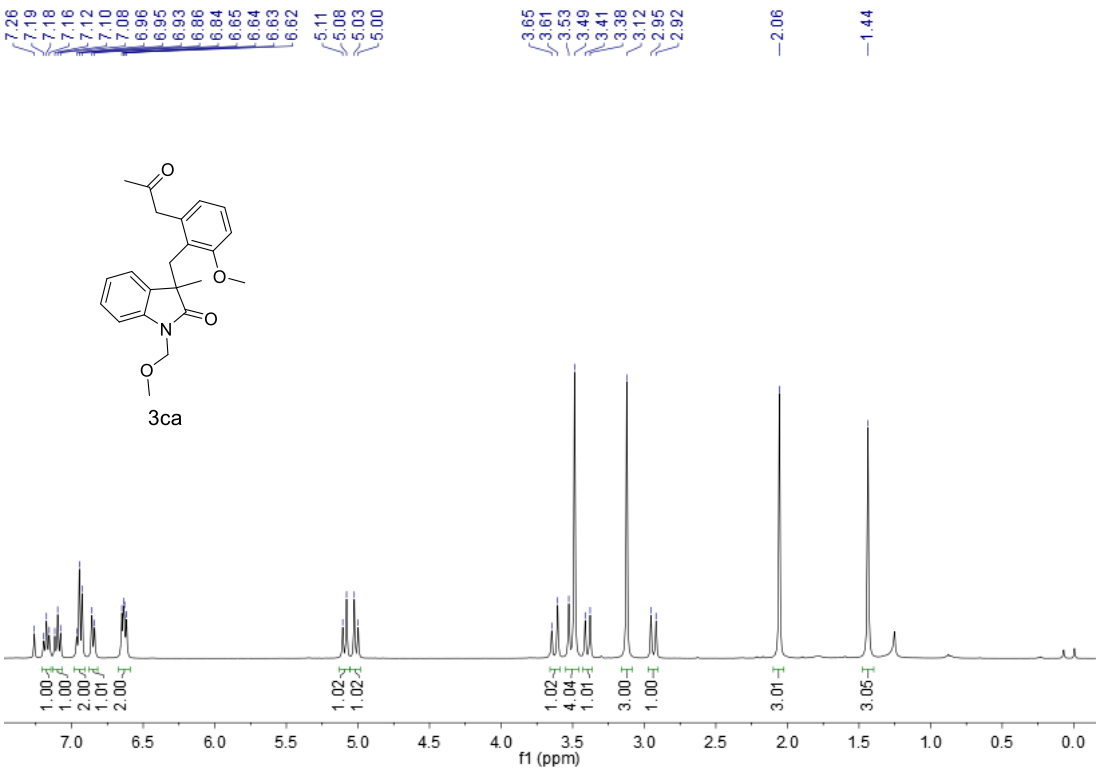
29.52
22.95
12.57
3ba
f1 (ppm)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6.93
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6.84
6.65
6.64
6.63
6.62
5.11
5.08
5.03
5.00
3.65
3.61
3.53
3.49
3.41
3.38
3.12
2.95
2.92
2.06
1.44
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1.00
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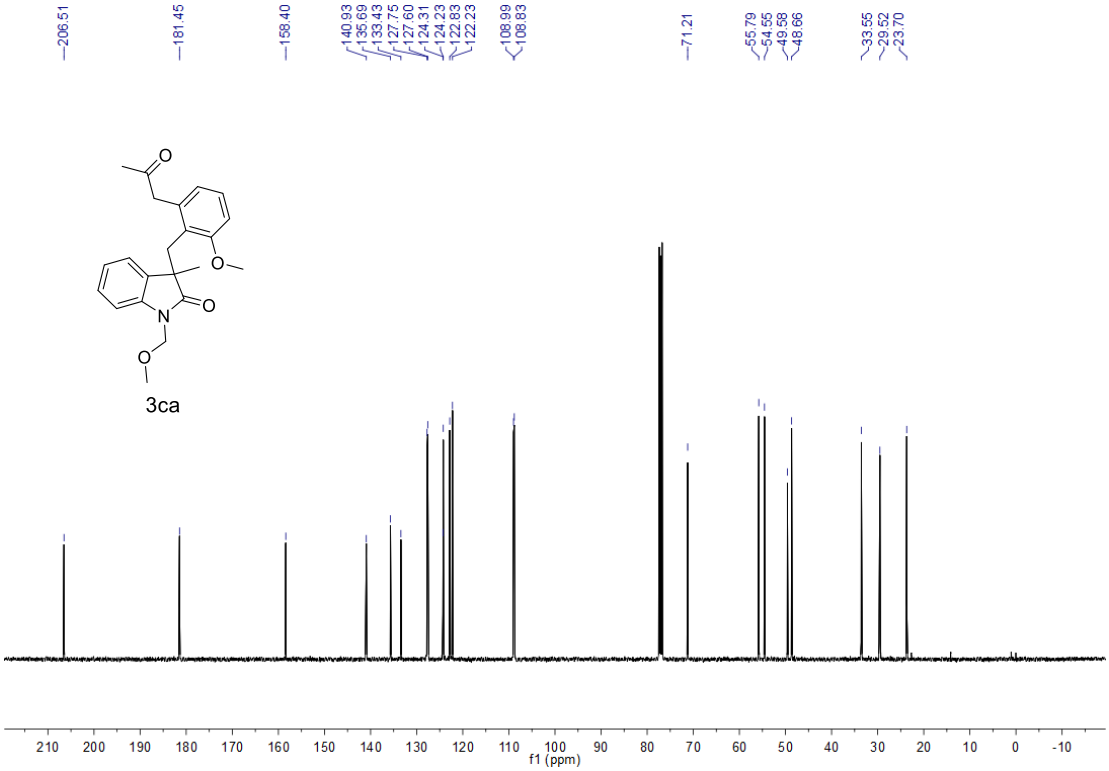
3.00
1.00
3.01
3.05
f1 (ppm)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54.55
49.58
48.66
33.55
29.52
23.70
3ca
f1 (ppm)


7.26
7.25
7.24
7.23
7.23
7.22
7.21
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7.12
7.07
7.06
7.05
7.04
7.04
7.03
7.02
7.01
7.00
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6.65
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6.57
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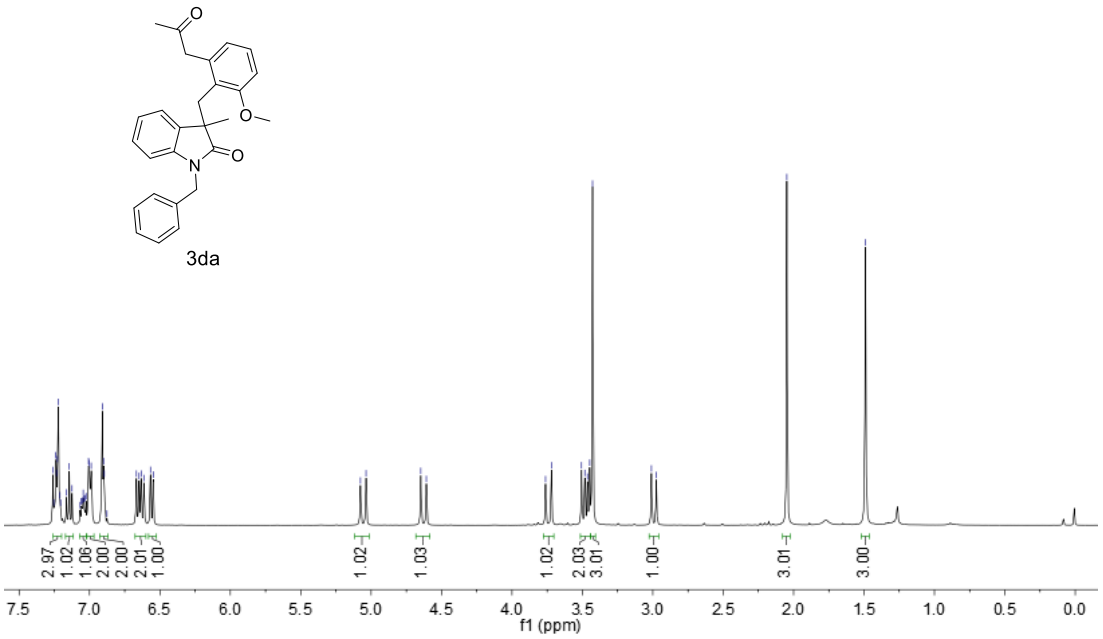
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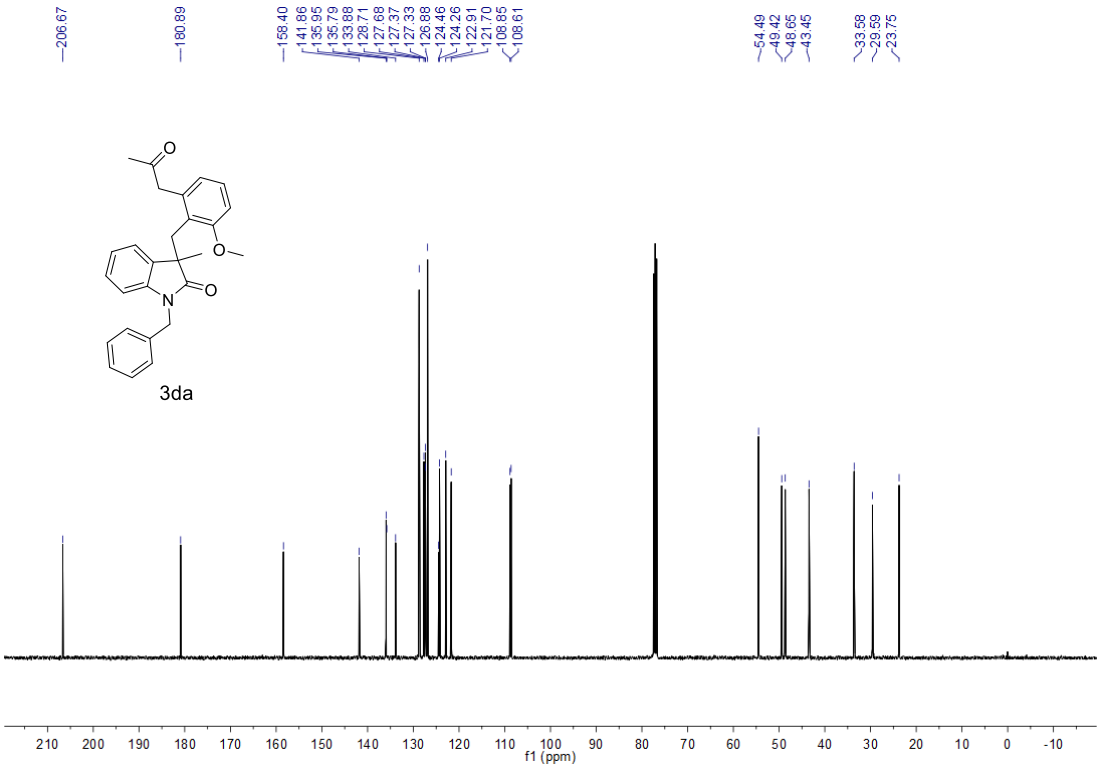
f1 (ppm)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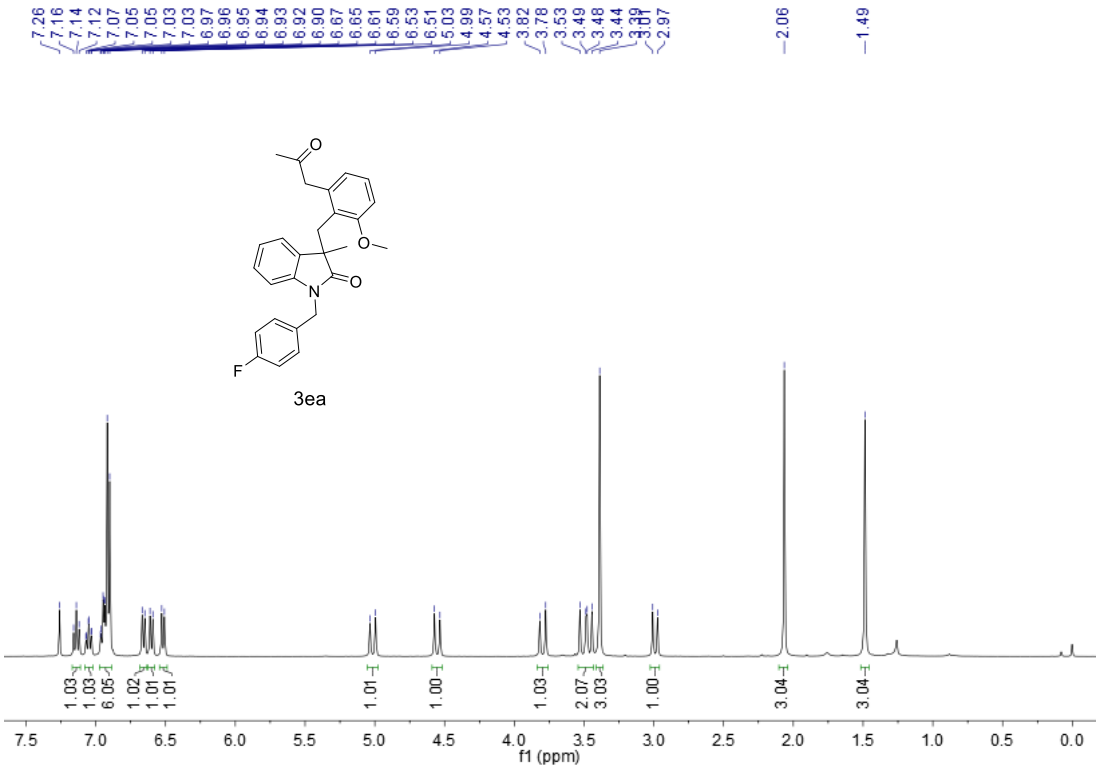
f1 (ppm)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7.05
7.03
7.03
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6.96
6.95
6.94
6.93
6.92
6.90
6.67
6.65
6.61
6.59
6.53
6.51
5.03
4.99
4.57
4.53
3.82
3.78
3.53
3.49
3.48
3.44
3.01
2.97
2.06
1.49
O
O
O
N
F
3ea
1.03
1.03
6.05
1.02
1.01
1.01
1.01
1.00
1.03
2.07
3.03
1.00
3.04
3.04
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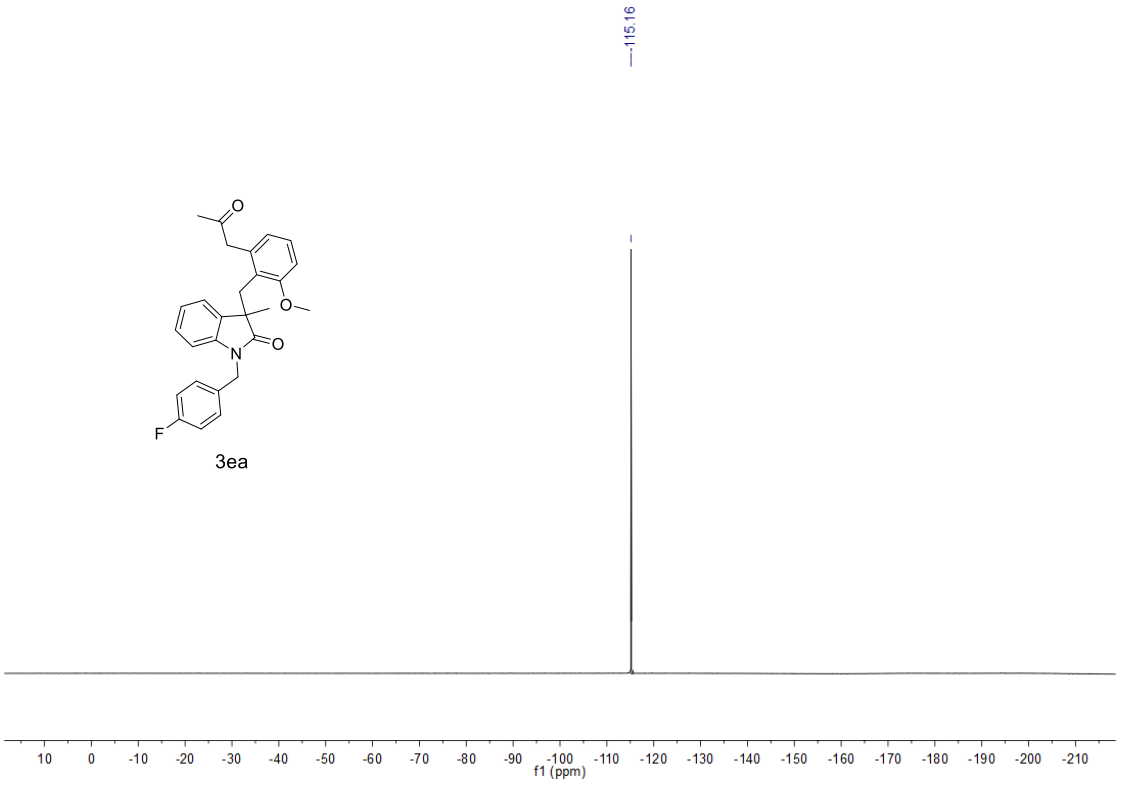
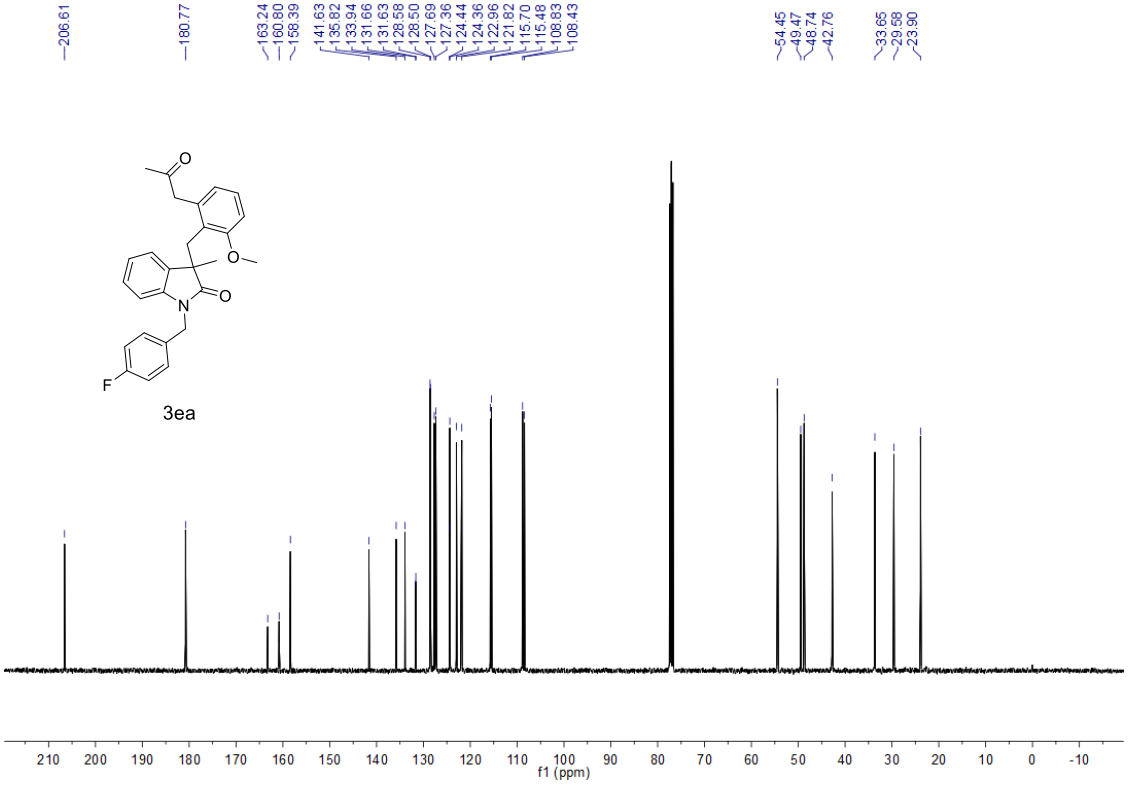
f1 (ppm)


-115.16
O
O
O
N
F
3ea
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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127.69
127.36
124.44
124.36
122.96
121.82
115.70
115.48
108.83
108.43
54.45
49.47
48.74
42.76
33.65
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23.90
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O
O
N
F
3ea
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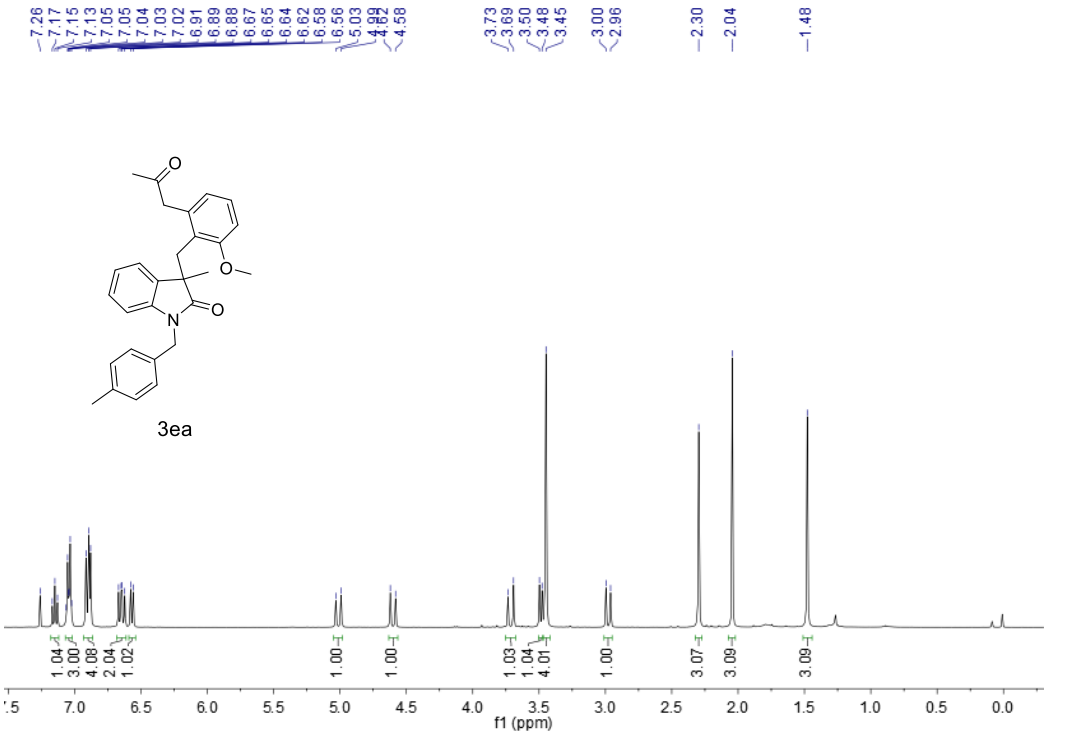
f1 (ppm)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6.58
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4.58
3.73
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3.48
3.45
3.00
2.96
2.30
2.04
1.48
O
O
N
O
3ea
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3.00
4.08
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1.03
1.04
4.01
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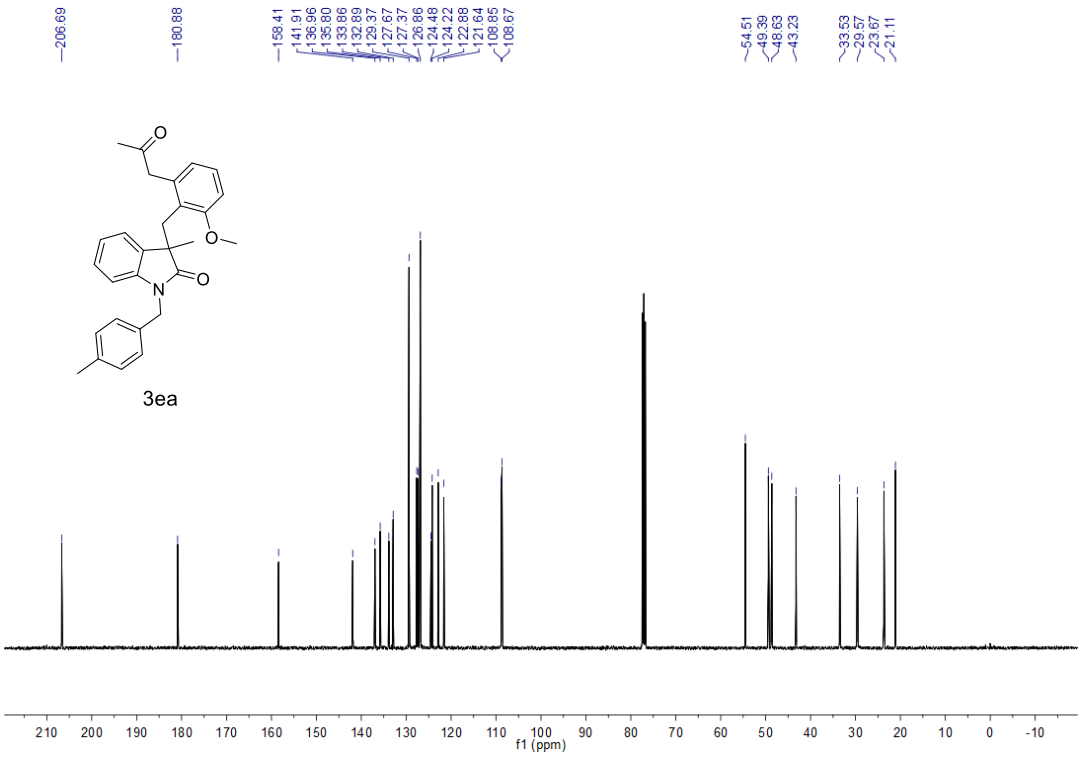
3.09
3.09
f1 (ppm)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124.22
122.88
121.64
108.85
108.67
54.51
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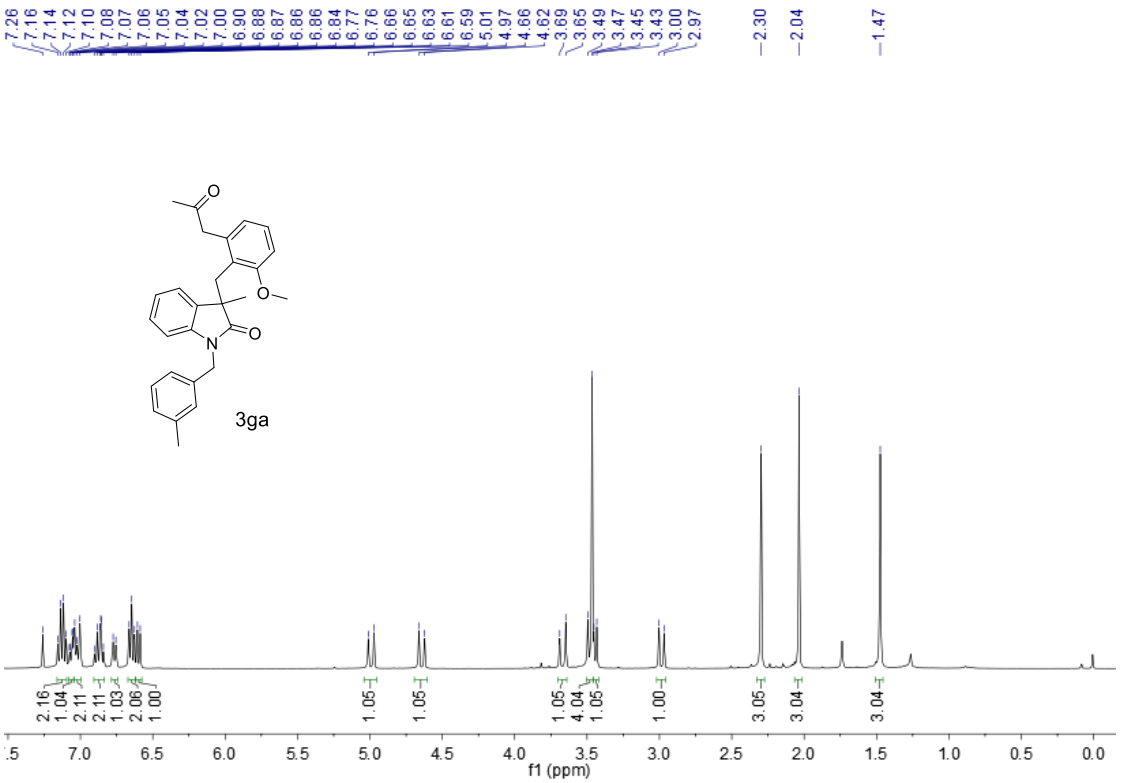
43.23
33.53
29.57
23.67
21.11
O
O
N
O
3ea
f1 (ppm)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7.04
7.02
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6.86
6.84
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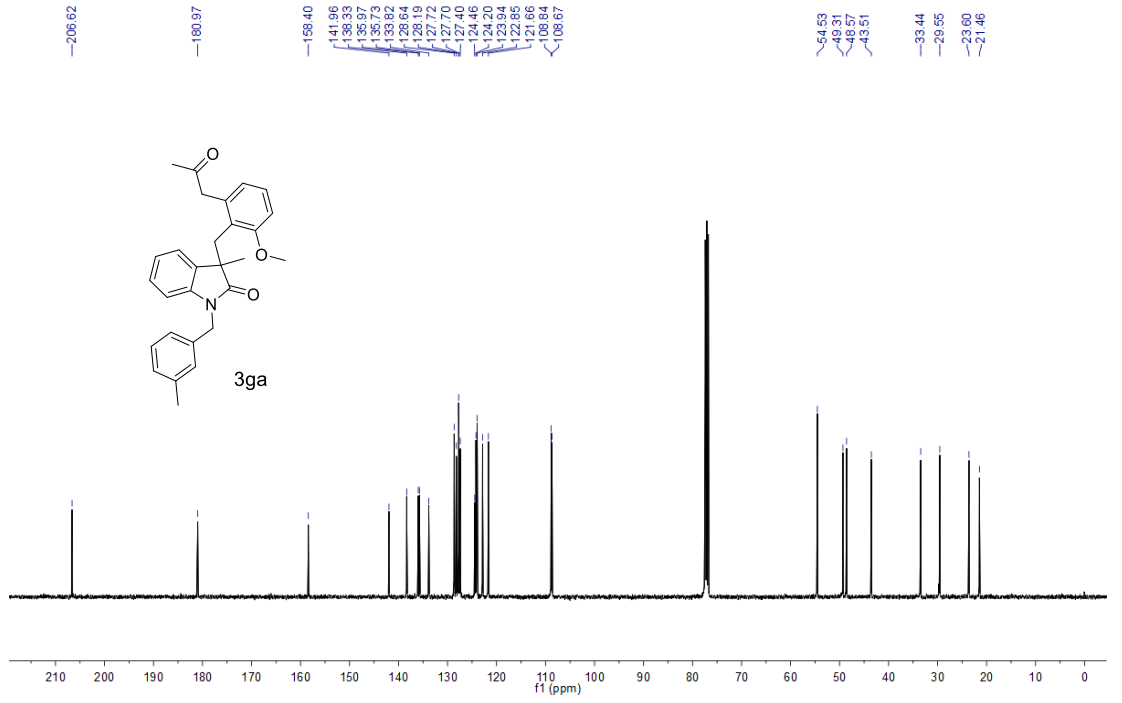
3.04
f1 (ppm)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127.40
124.46
124.20
123.94
122.85
121.66
108.84
108.67
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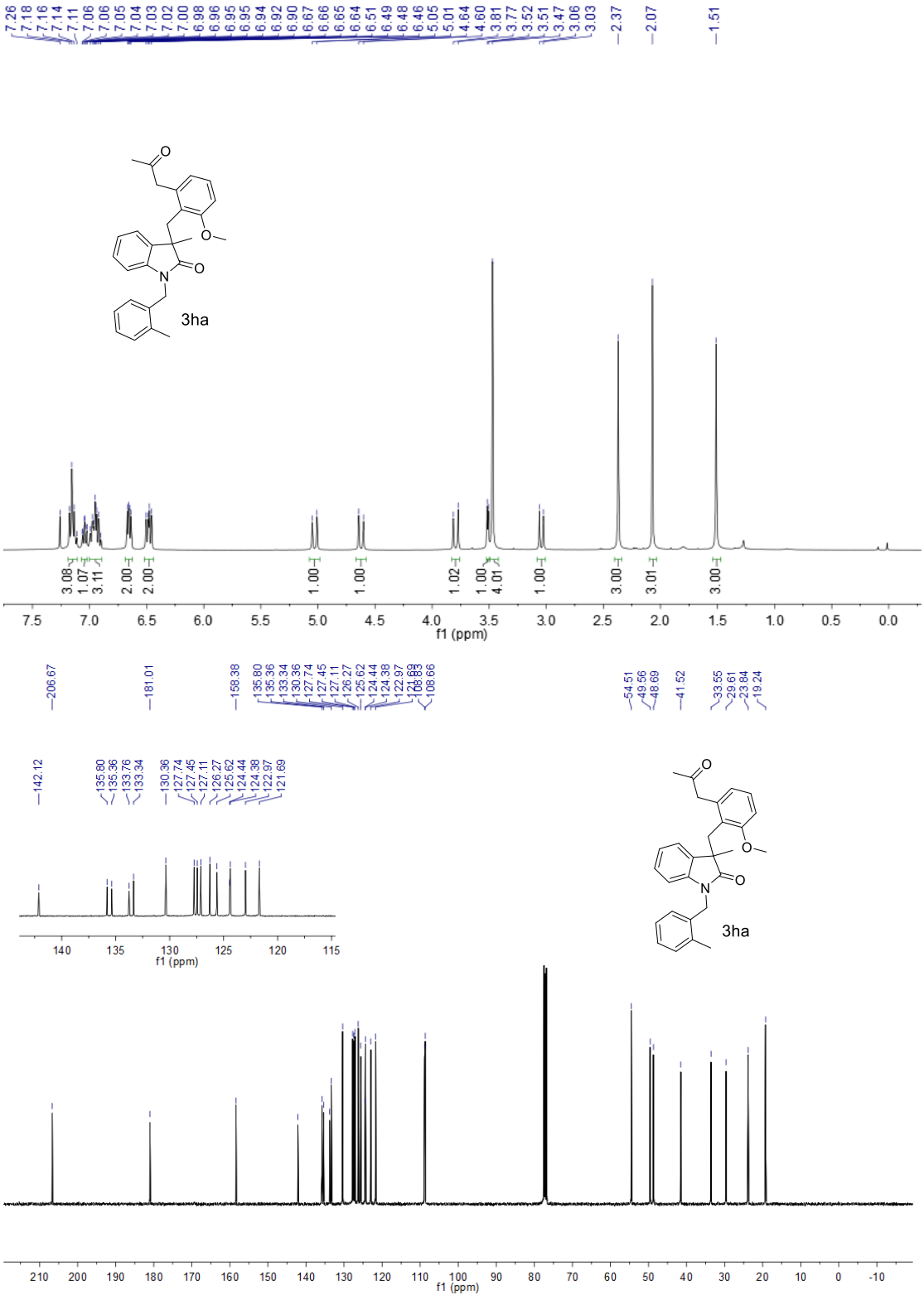
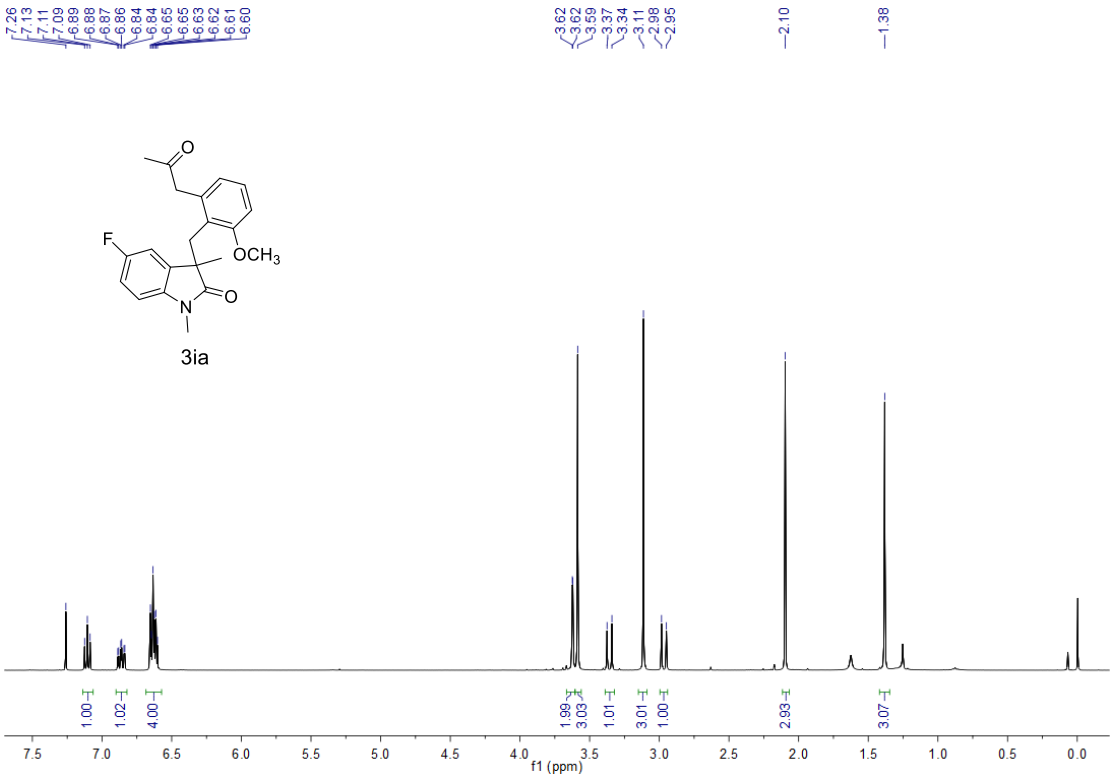
29.55
23.60
21.46
3ga
f1 (ppm)


3ha
f1 (ppm)
3ha
f1 (ppm)
f1 (ppm)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6.84
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6.62
6.61
6.60
3.62
3.62
3.59
3.37
3.34
3.11
2.98
2.95
2.10
1.38
O
F
OCH3
O
N
1.00
1.02
4.00
1.99
3.03
1.01
3.01
1.00
2.93
3.07
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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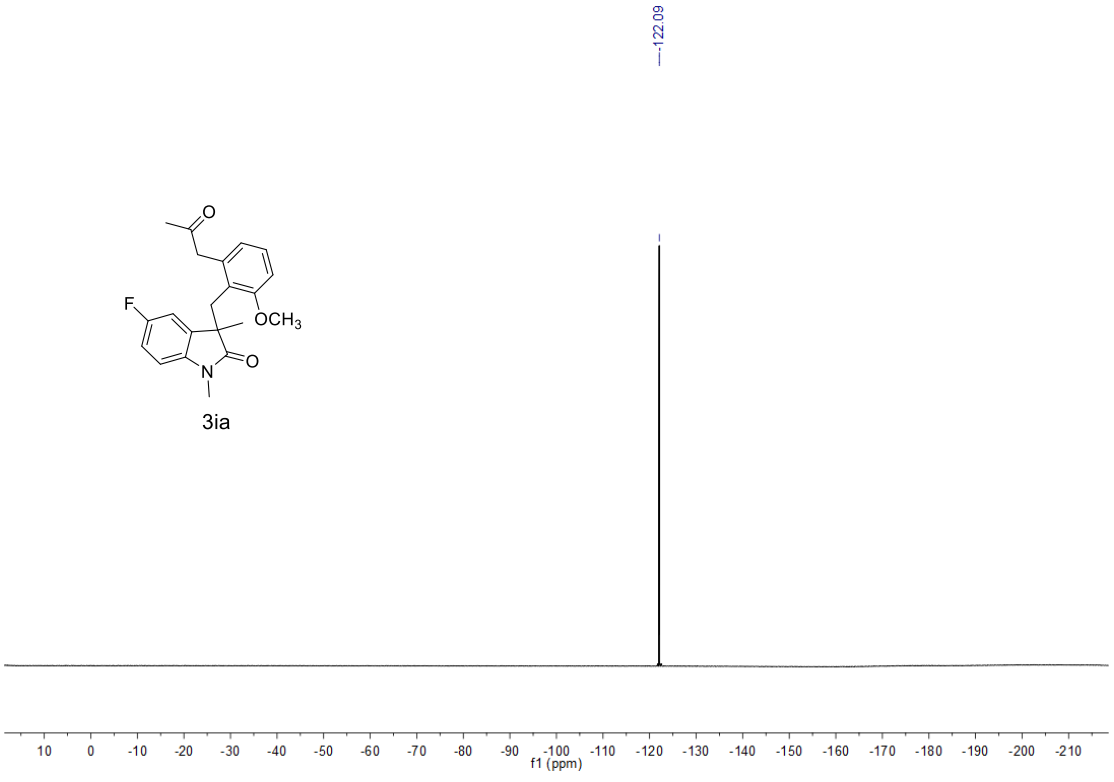
1.0
0.5
0.0
f1 (ppm)

3ia


-122.09
O
F
OCH3
O
N
10
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-10
-20
-30
-40
-50
-60
-70
-80
-90
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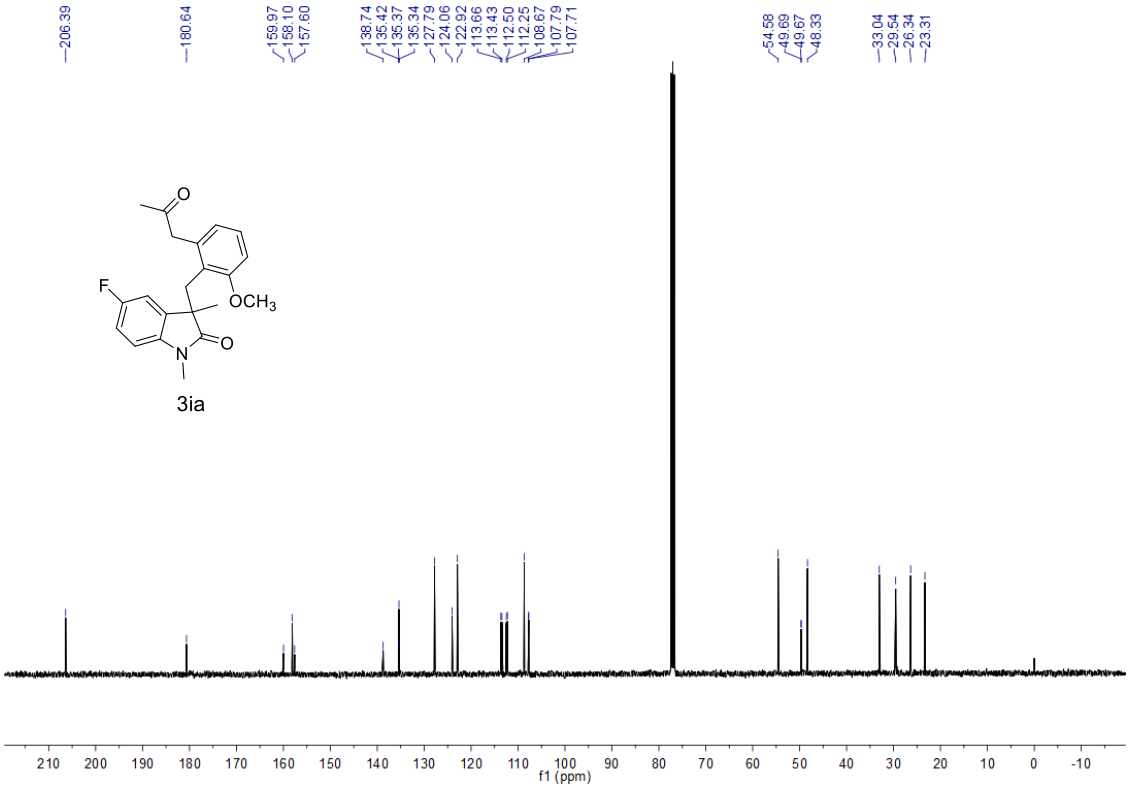
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3ia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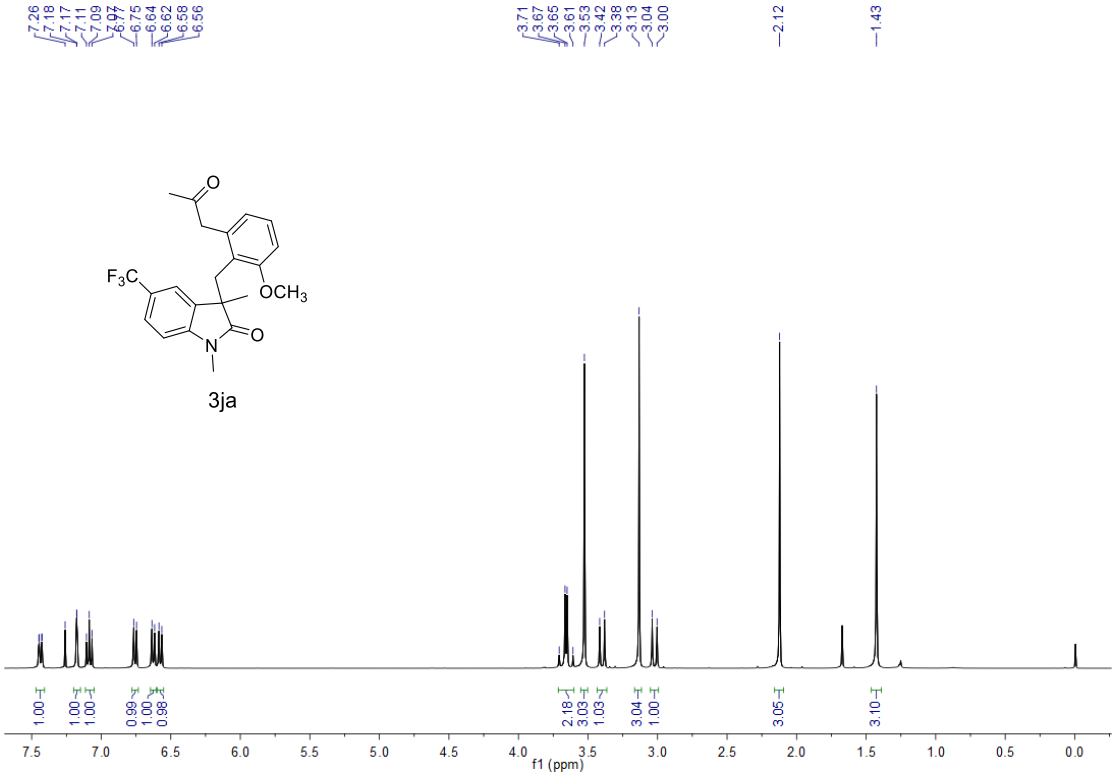
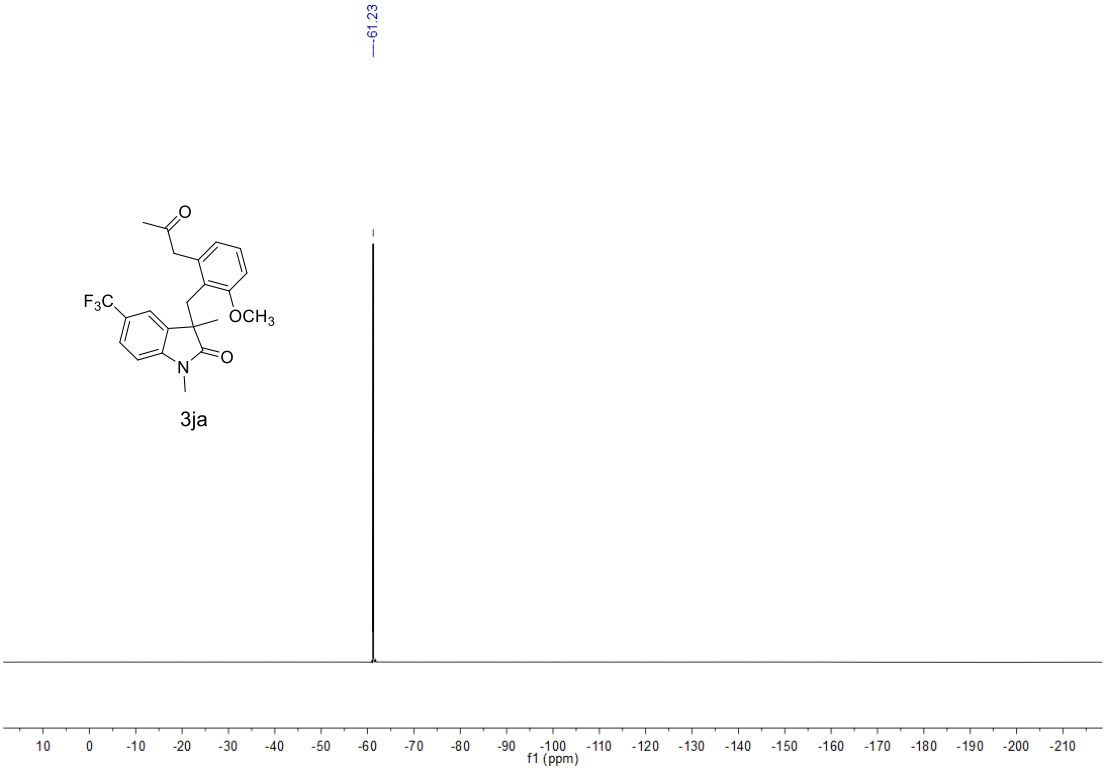
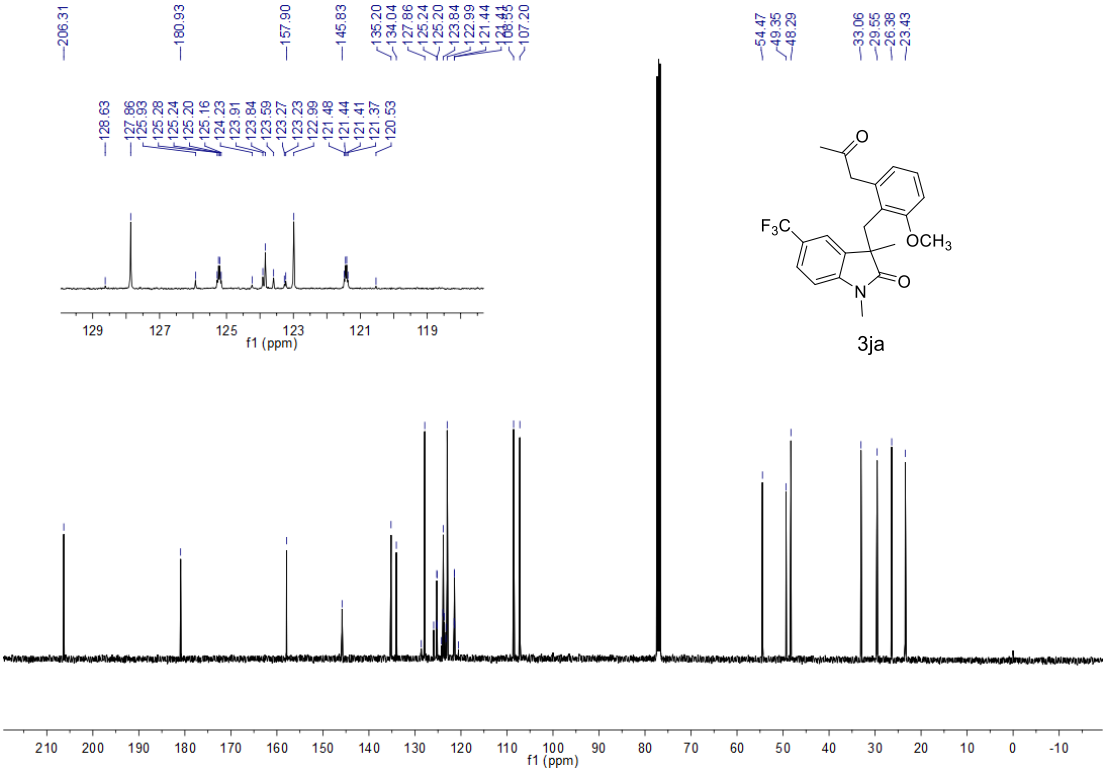
113.43
112.50
112.25
108.67
107.79
107.71
54.58
49.69
49.67
48.33
33.04
29.54
26.34
23.31
O
F
OCH3
N
O
f1 (ppm)

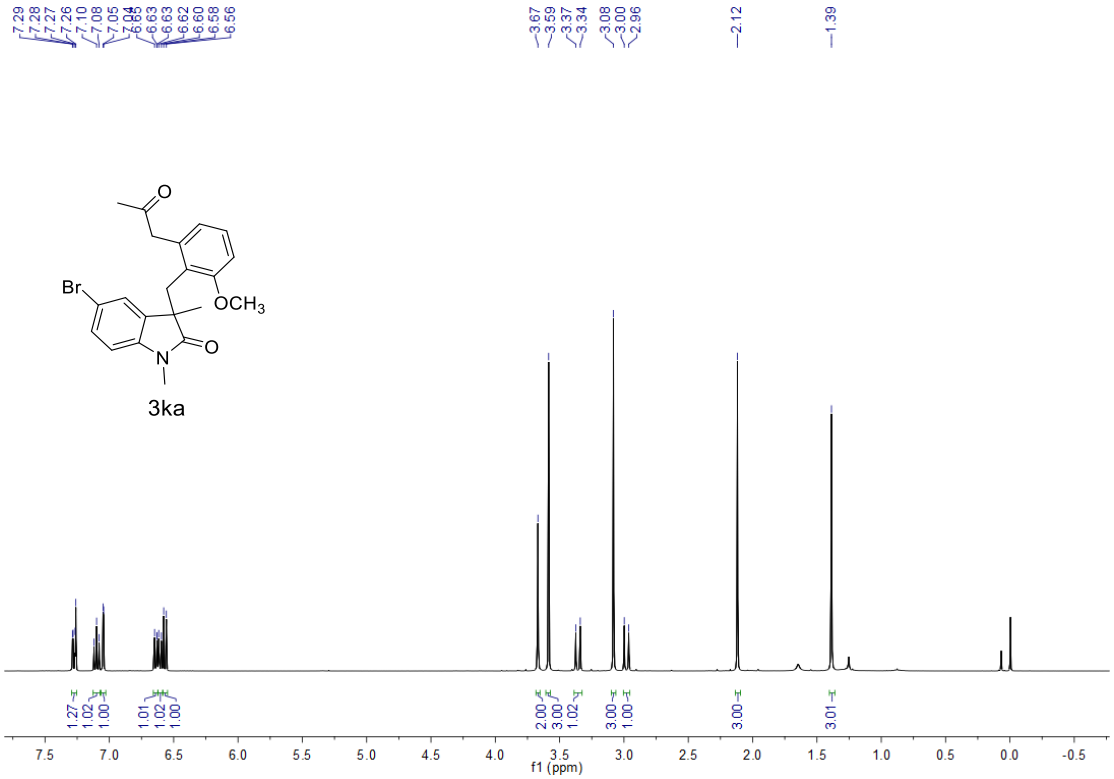
3ia

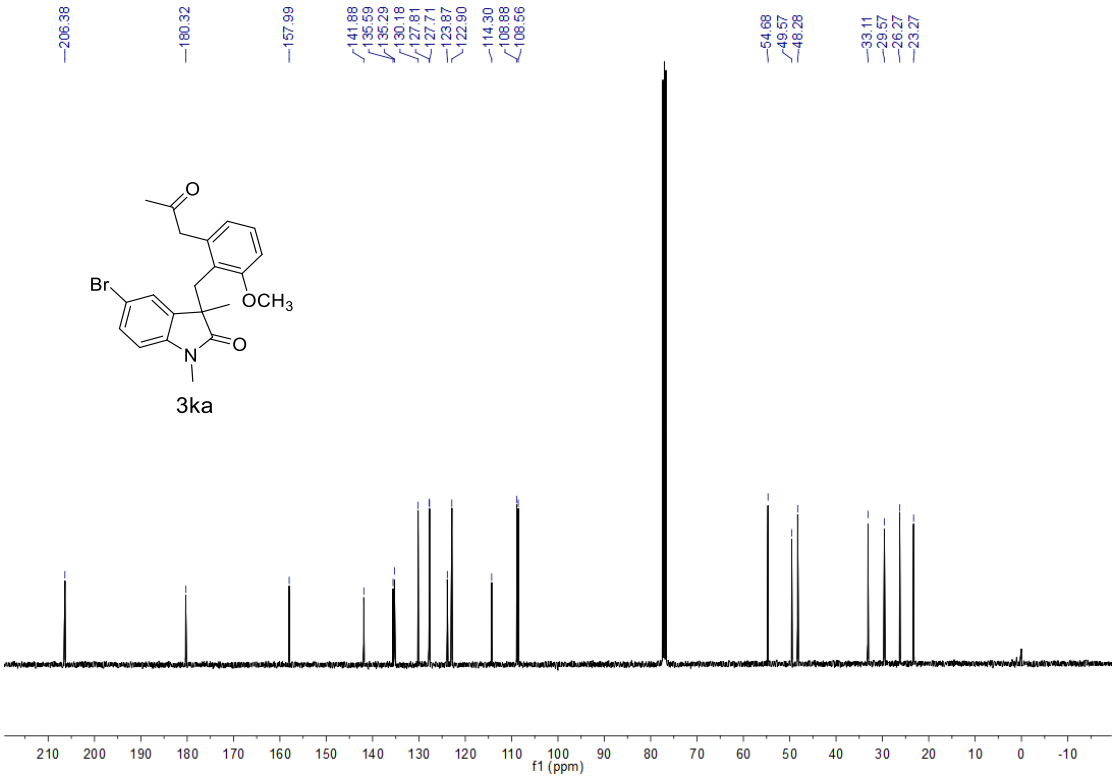

7.26
7.18
7.17
7.11
7.09
7.07
6.77
6.75
6.64
6.62
6.58
6.56
3.71
3.67
3.65
3.61
3.53
3.42
3.38
3.13
3.04
3.00
2.12
1.43
1.00
1.00
1.00
0.99
1.00
0.98
2.18
3.03
1.03
3.04
1.00
3.05
3.10
f1 (ppm)

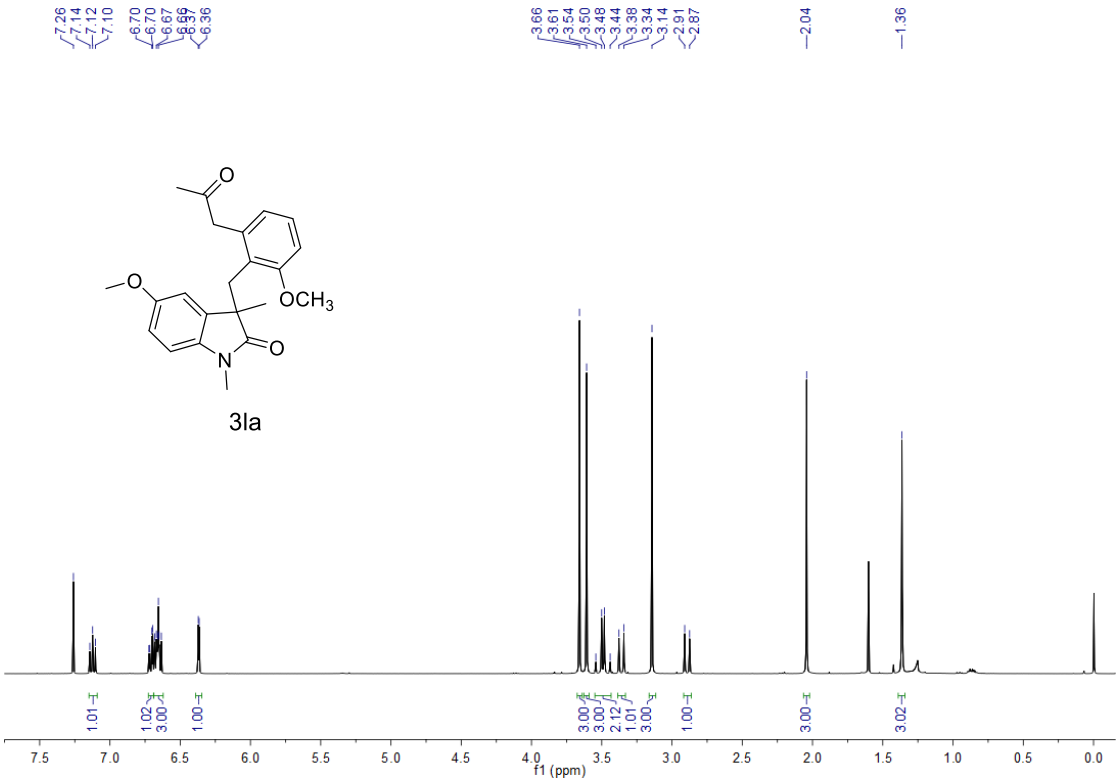
3ja


-61.23
O
F3C
OCH3
O
N
3ja
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

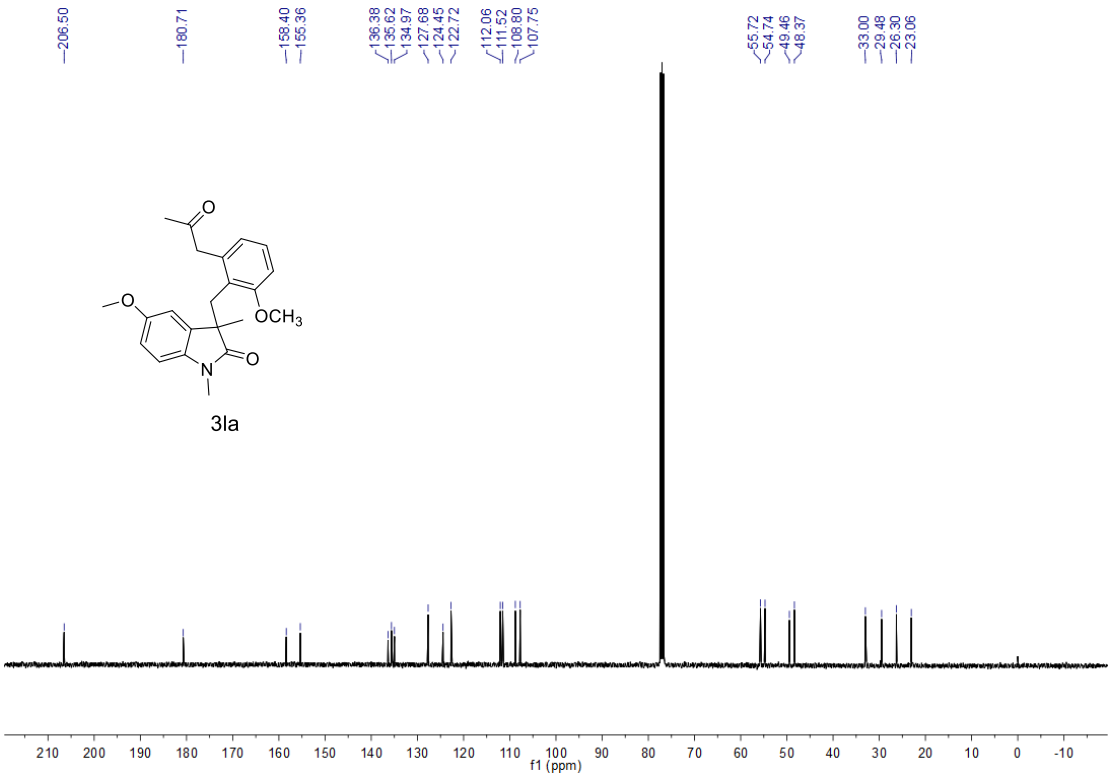

206.31
180.93
157.90
145.83
135.20
134.04
127.86
125.24
125.20
123.84
122.99
121.44
107.20
54.47
49.35
48.29
33.06
29.55
26.38
23.43
128.63
127.86
125.93
125.28
125.24
125.20
125.16
124.23
123.91
123.84
123.59
123.27
123.23
122.99
121.48
121.44
121.41
121.37
120.53
129 127 125 123 121 119
f1 (ppm)
O
F3C
OCH3
O
N
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.29
7.28
7.27
7.26
7.10
7.08
7.05
6.63
6.62
6.60
6.58
6.56
3.67
3.59
3.37
3.34
3.08
3.00
2.96
2.12
1.39
Br
OCH3
O
N
O
3ka
1.27
1.02
1.00
1.01
1.02
1.00
2.00
3.00
1.02
3.00
1.00
3.00
3.01
f1 (ppm)

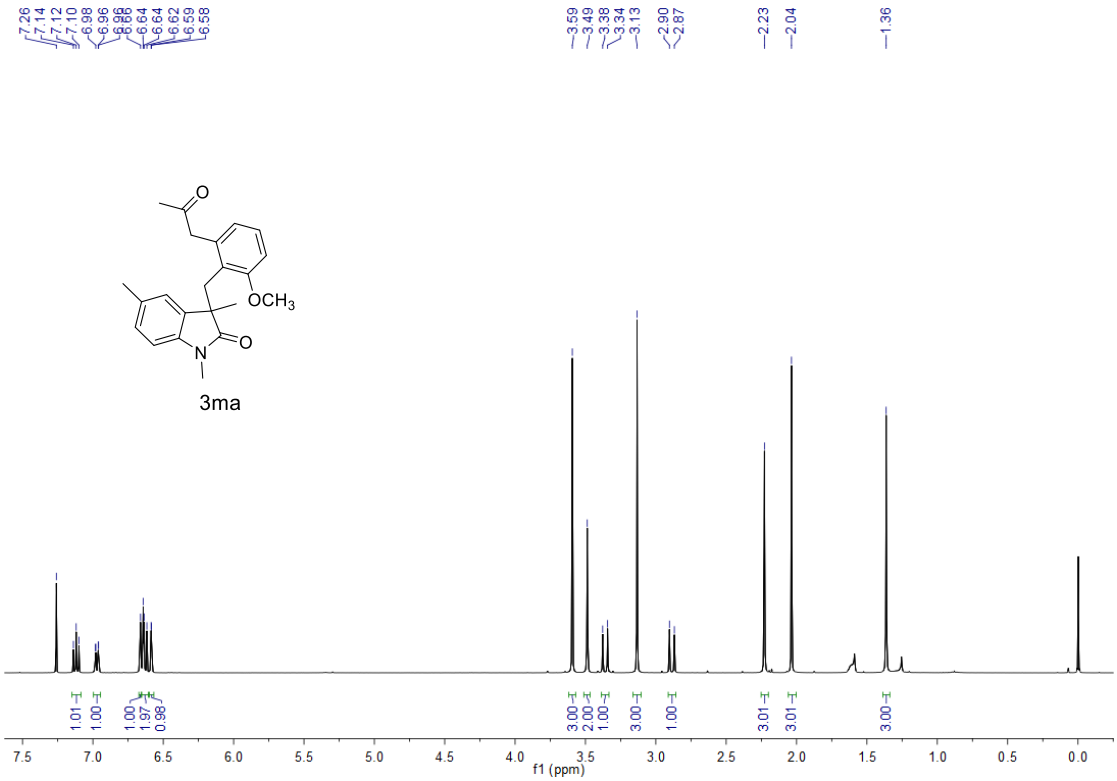

206.38
180.32
157.99
141.88
135.59
135.29
130.18
127.81
127.71
123.87
122.90
114.30
108.88
108.56
54.68
49.57
48.28
33.11
29.57
26.27
23.27
Br
OCH3
O
N
O
3ka
f1 (ppm)

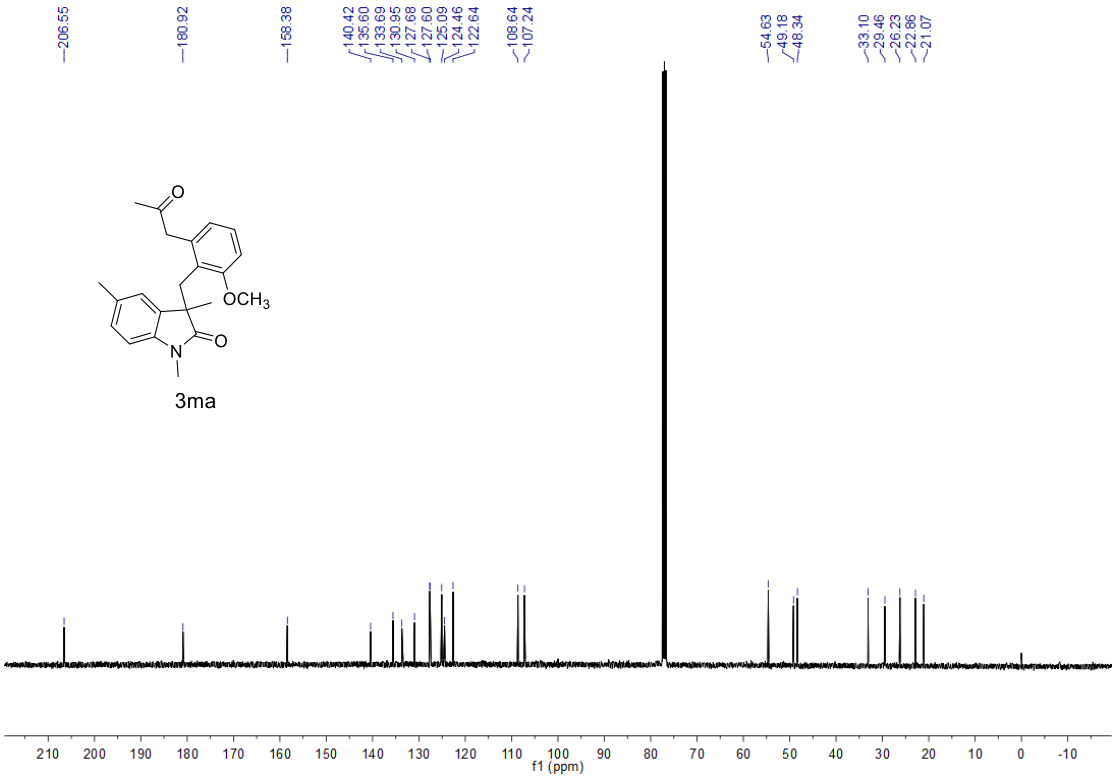

7.26
7.14
7.12
7.10
6.70
6.70
6.67
6.66
6.36
3.66
3.61
3.54
3.50
3.48
3.44
3.38
3.34
3.14
2.91
2.87
2.04
1.36
O
O
OCH3
O
N
O
1.01
1.02
3.00
1.00
3.00
3.00
2.12
1.01
3.00
1.00
3.00
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

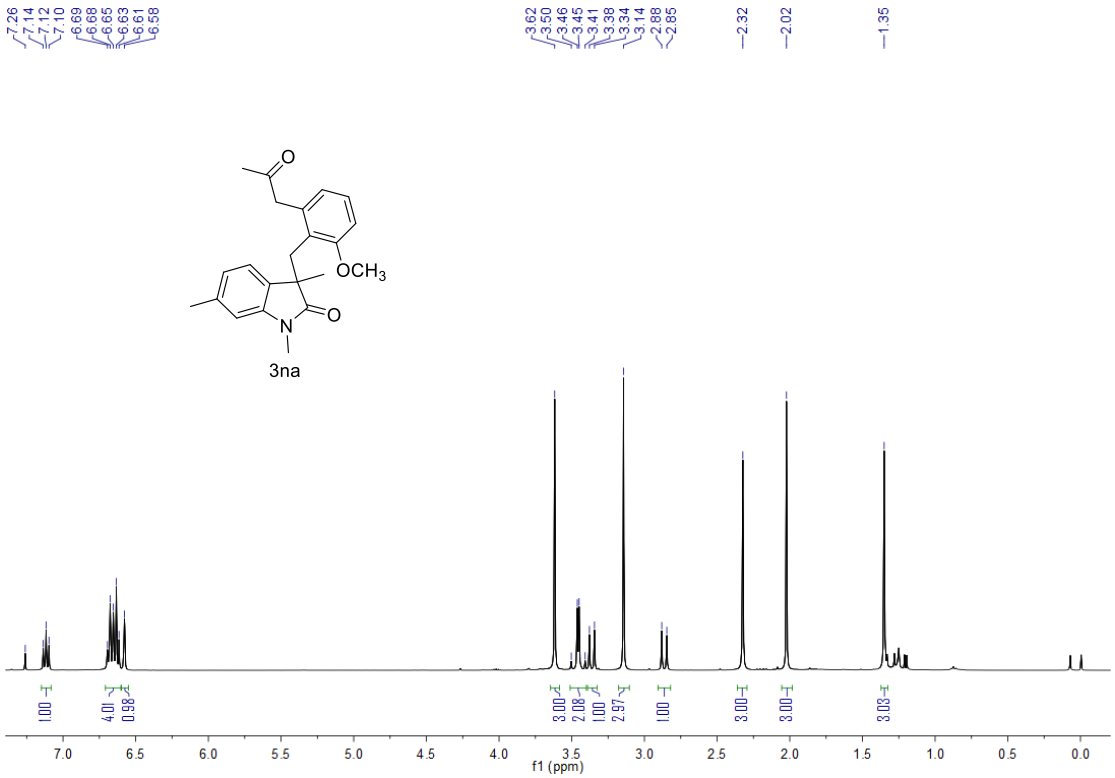
3la

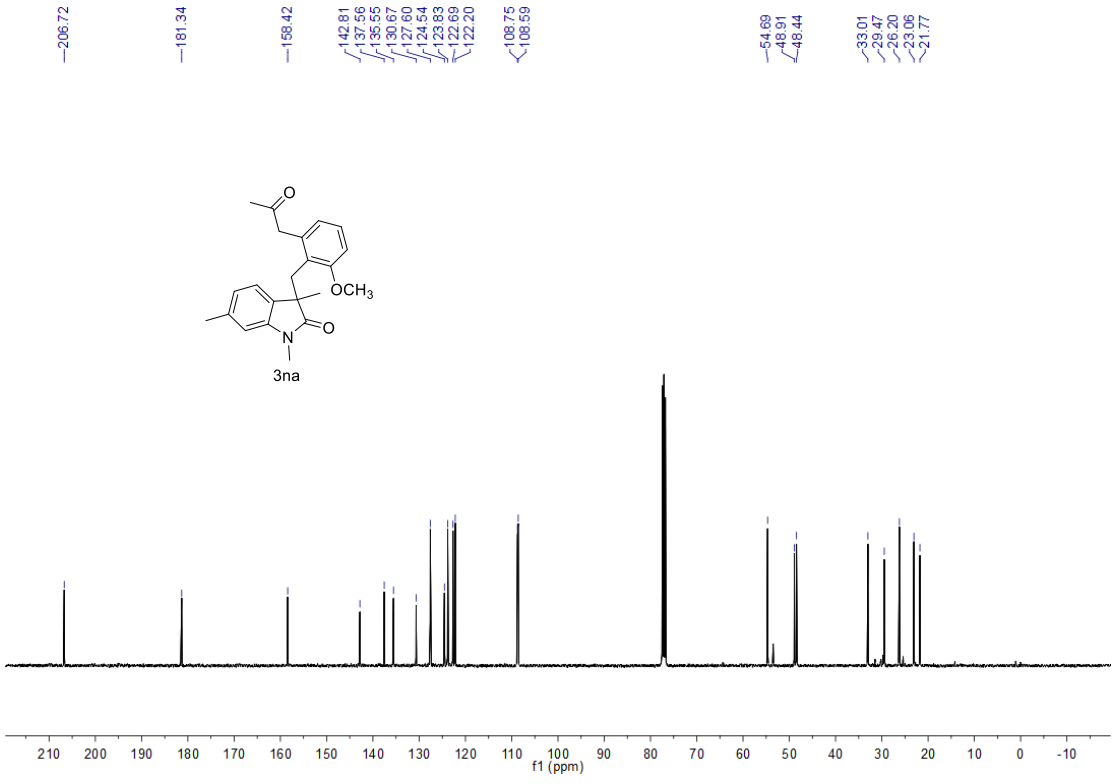

206.50
180.71
158.40
155.36
136.38
135.62
134.97
127.68
124.45
122.72
112.06
111.52
108.80
107.75
55.72
54.74
49.46
48.37
33.00
29.48
26.30
23.06
O
O
OCH3
O
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

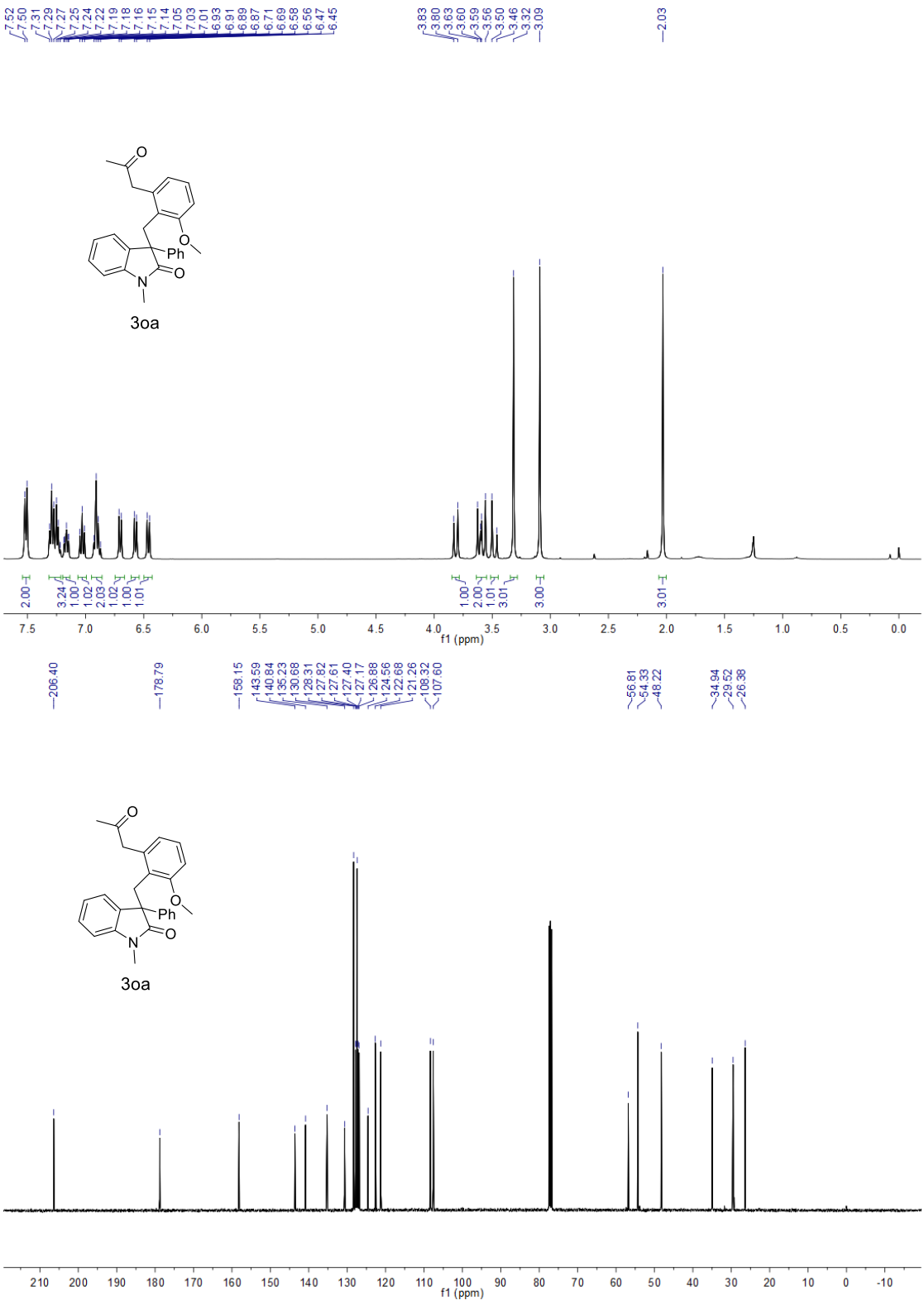
3la


7.26
7.14
7.12
7.10
6.98
6.96
6.66
6.64
6.62
6.59
6.58
3.59
3.49
3.38
3.34
3.13
2.90
2.87
2.23
2.04
1.36
OCH3
O
N
3ma
1.01
1.00
1.00
1.97
0.98
3.00
2.00
1.00
3.00
1.00
3.01
3.01
3.00
f1 (ppm)


206.55
180.92
158.38
140.42
135.60
133.69
130.95
127.68
127.60
125.09
124.46
122.64
108.64
107.24
54.63
49.18
48.34
33.10
29.46
26.23
22.86
21.07
OCH3
O
N
3ma
f1 (ppm)


7.26
7.14
7.12
7.10
6.69
6.68
6.65
6.63
6.61
6.58
3.62
3.50
3.46
3.45
3.41
3.38
3.34
3.14
2.88
2.85
2.32
2.02
1.35
OCH3
O
N
O
3na
1.00
4.01
0.98
3.00
2.08
1.00
2.97
1.00
3.00
3.00
3.03
f1 (ppm)


206.72
181.34
158.42
142.81
137.56
135.55
130.67
127.60
124.54
123.83
122.69
122.20
108.75
108.59
54.69
48.91
48.44
33.01
29.47
26.20
23.06
21.77
OCH3
O
N
O
3na
f1 (ppm)


7.52
7.50
7.31
7.29
7.27
7.25
7.24
7.22
7.19
7.18
7.16
7.15
7.14
7.05
7.03
7.01
6.93
6.91
6.89
6.87
6.71
6.69
6.58
6.56
6.47
6.45
3.83
3.80
3.63
3.60
3.59
3.56
3.50
3.46
3.32
3.09
2.03
O
O
Ph
N
O
3oa
2.00
3.24
1.00
1.02
2.03
1.02
1.00
1.01
1.00
2.00
1.01
3.01
3.00
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
206.40
178.79
158.15
143.59
140.84
135.23
130.68
128.31
127.82
127.61
127.40
127.17
126.88
124.56
122.68
121.26
108.32
107.60
56.81
54.33
48.22
34.94
29.52
26.38
O
O
Ph
N
O
3oa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)