Copper Promoted radical addition/cyclization of Azobisisobutyronitrile with Arylacrylamides: a Convenient Process to Synthesize 3- (2´-cyano Alkyl) Oxindoles

Ruihong Wang and Weiliang Bao*
Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028, People's Republic of China
Phone/fax: (+86)-571-8827-3814
E-mail: wlbao@zju.edu.cn

Supporting Information

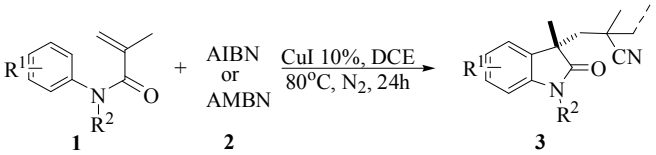
Table of Contents

General Remarks.

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All reactions were carried out in a Schlenk tube equipped with a magnetic stir bar. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F254 were used for thin-layer chromatography (TLC) analysis. All products were confirmed by ^{1}H NMR, ^{13}C NMR and HRMS. ^{1}H NMR and ^{13}C NMR

spectra were recorded on Bruker Avance 400, and tetramethylsilane (TMS) or $CDCl_3$(7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR) was used as a references. Data for ^1H were reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for ^{13}C NMR were reported as ppm. High resolution mass spectra (HRMS) were performed on a Waters Micromass GCT instrument.

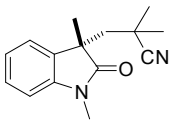
Experimental Procedure



1 **2** **3**

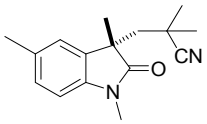
In an oven-dried Schlenk tube equipped with a magnetic stir bar, CuI (0.05 mmol) and **1** (0.5 mmol) was added. Then under nitrogen, 1 mL DCE was added. The resulting mixture was stirred at 80 °C for 24 h while **2** (1.5 mmol) dissolved in 1 mL DCE was added through micro injection pump into the mixture. Then the mixture was cooled down to room temperature and filtered through a pad of filter paper with the help of 50 mL of ethyl acetate. After evaporating the solvent under reduced pressure, the residue was purified by column chromatography (200-300 mesh silica gel) using ethyl acetate-petroleum ether as the eluent to give the pure product **3**(AcOEt / petroleum ether v/v = 1/4). All solid products were further purified by recrystallization.

Date



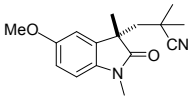
3a

3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: White solid, m.p. 118-120 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.32 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H), 2.33 (d, J = 14.4 Hz, 1H), 2.17 (d, J = 14.4 Hz, 1H), 1.37 (s, 3H), 1.17 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.6, 143.2, 130.9, 128.6, 124.7, 124.0, 122.5, 108.5, 47.0, 46.6, 30.7, 26.7, 27.4, 26.7, 26.4; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{15}H_{18}N_2O$ 242.1419, found 242.1422.



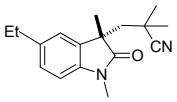
3b

2,2-Dimethyl-3-(1,3,5-trimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-propionitrile: White solid, m.p. 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14-7.12 (m, 2H), 6.79 (d, J = 3.6 Hz, 1H), 3.22 (s, 3H), 2.36-2.30 (m, 4H), 2.15 (d, J = 14.8 Hz, 1H), 1.34 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.6, 140.7, 132.0, 130.9, 128.8, 125.6, 124.1, 108.2, 47.0, 46.5, 30.8, 29.7, 27.5, 26.5, 26.4, 21.2; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O$ 256.1576, found 256.1585.



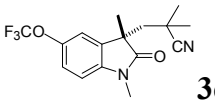
3c

3-(5-Methoxy-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.95 (d, J = 1.6 Hz, 1H), 6.86 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.22 (s, 3H), 2.33 (d, J = 14.4 Hz, 1H), 2.15 (d, J = 14.4 Hz, 1H), 1.34 (s, 3H), 1.19 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.3, 156.0, 136.7, 132.2, 124.1, 113.2, 112.2, 108.8, 56.0, 47.4, 46.4, 30.8, 29.7, 27.5, 26.4; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O_2$ 272.1525, found 272.1526.



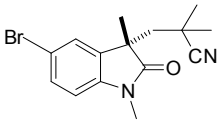
3d

3-(5-Ethyl-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: White solid, m.p. 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.16-7.14 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 2.32 (d, J = 14.8 Hz, 1H), 2.16 (d, J = 15.2 Hz, 1H), 1.35 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H), 1.17 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.7, 140.9, 138.7, 130.9, 127.7, 124.5, 124.1, 108.2, 47.1, 46.5, 30.8, 29.7, 28.7, 27.5, 26.5, 26.4, 15.9; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{17}H_{22}N_2O_2$ 286.1681, found 286.1685.



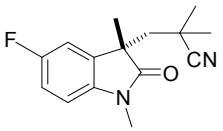
3e

3-(1,3-Dimethyl-2-oxo-5-trifluoromethoxy-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: White solid, m.p. 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23-7.19 (m, 2H), 6.90 (d, J = 8.24 Hz, 1H), 3.25 (s, 3H), 2.36 (d, J = 14.8 Hz, 1H), 2.12 (d, J = 14.4 Hz, 1H), 1.37 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 144.7, 141.9, 132.7, 123.5, 121.9, 121.8, 118.5, 109.0, 47.3, 46.7, 30.6, 29.4, 27.4, 27.2, 26.5; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{17}F_3N_2O_2$ 326.1242, found 326.1244.



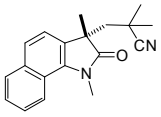
3f

3-(5-Bromo-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: Yellow solid, m.p. 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.42 (m, 2H), 6.79 (d, J = 7.6 Hz, 1H), 3.23 (s, 3H), 2.33 (d, J = 14.4 Hz, 1H), 2.11 (d, J = 14.4 Hz, 1H), 1.36 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 131.5, 127.8, 110.0, 47.2, 46.6, 30.6, 29.6, 27.3, 27.2, 26.5; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{15}H_{17}BrN_2O$ 320.0524, found 320.0524.



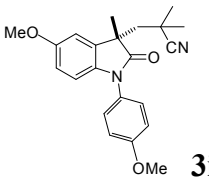
3g

3-(5-Fluoro-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: White solid, m.p. 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.07-7.02 (m, 2H), 6.85-6.82 (m, 1H), 3.24 (d, J = 0.8 Hz, 3H), 2.33 (d, J = 14.4 Hz, 1H), 2.13 (d, J = 14.4 Hz, 1H), 1.35 (s, 3H), 1.18 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 160.4, 158.0, 139.1, 139.1, 132.7, 132.7, 123.7, 115.0, 114.8, 112.9, 112.6, 109.0, 109.0, 47.5, 47.5, 46.5, 30.6, 29.7, 27.3, 26.9, 26.5; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{15}H_{17}FN_2O$ 260.1325, found 260.1327.



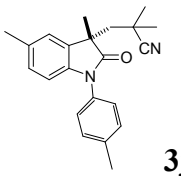
3h

3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)-2,2-dimethyl-propionitrile: Pale yellow solid, m.p. 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (d, J = 8.0 Hz, 1H), 7.50-7.35 (m, 4H), 6.91 (d, J = 8.0 Hz, 1H), 3.46 (s, 3H), 2.79 (d, J = 14.4 Hz, 1H), 2.17 (d, J = 14.4 Hz, 1H), 1.67(s, 3H), 1.06 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.5, 136.4, 135.4, 133.5, 126.9, 126.7, 126.6, 124.4, 123.9, 122.9, 119.6, 108.8, 52.5, 45.8, 34.8, 30.9, 29.7, 29.5, 27.4; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{19}H_{20}N_2O$ 292.1576, found 292.1581.



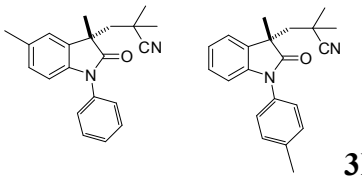
3i

3-[5-Methoxy-1-(4-methoxy-phenyl)-3-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl]-2,2-dimethyl-propionitrile: Yellow solid, m.p. 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 (d, J = 8.8 Hz, 2H), 6.97-6.93 (m, 3H), 6.73-6.67 (m, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 2.34 (d, J = 14.4 Hz, 1H), 2.18 (d, J = 14.4 Hz, 1H), 1.39 (s, 3H), 1.22 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.9, 159.1, 156.1, 136.9, 131.9, 127.5, 127.3, 124.3, 114.9, 113.4, 112.1, 110.2, 56.0, 55.6, 47.5, 46.4, 30.9, 30.0, 28.4, 26.3; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{22}H_{24}N_2O_3$ 364.1787, found 364.1789.



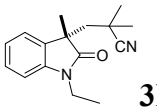
3j

3-(3,5-Dimethyl-2-oxo-1-p-tolyl-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: Yellow solid, m.p. 153-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (s, 4H), 7.21 (s, 1H), 7.04 (d, J = 8 Hz, 1H), 6.76 (d, J = 8 Hz, 1H), 2.40-2.36 (m, 7H), 2.26 (d, J = 14.4 Hz, 1H), 1.45 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):179.1, 140.8, 137.9, 132.4, 130.0, 130.6, 130.2, 128.7, 126.0, 125.9, 124.3, 109.6, 47.2, 46.5, 30.9, 30.0, 28.3, 26.3, 21.2, 21.2; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{22}H_{24}N_2O$ 332.1889, found 332.1885.



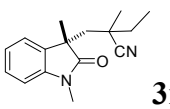
3k + **3k'**

3-(3,5-Dimethyl-2-oxo-1-phenyl-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile and 2,2-Dimethyl-3-(3-methyl-2-oxo-1-p-tolyl-2,3-dihydro-1H-indol-3-yl)-propionitrile:
Yellow solid, m.p. 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54-7.39 (m, 2H), 7.34-7.12 (m, 4H), 7.16-7.05 (m, 1H), 6.87 (d, J = 7.6 Hz, 0.73H), 6.79 (d, J = 8.0 Hz, 0.26H), 2.42-2.37 (m, 4H), 2.31-2.25 (m, 1H), 1.47 (s, 3H), 1.28 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.1, 143.3, 138.1, 131.8, 130.7, 130.3, 129.6, 128.5, 126.2, 126.2, 125.0, 124.2, 122.8, 109.9, 47.2, 46.5, 30.9, 30.0, 28.3, 28.3, 26.4, 21.2; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{21}H_{22}N_2O$ 318.1732, found 318.1732.



3l

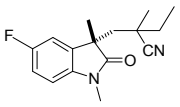
3-(1-Ethyl-3-methyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionitrile: Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.30 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.89-3.71 (m, 2H), 2.33 (d, J = 14.4 Hz, 1H), 2.21 (d, J = 14.4 Hz, 1H), 1.34 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.21 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.2, 142.1, 131.1, 128.5, 125.0, 124.1, 122.2, 108.6, 46.9, 46.2, 34.8, 30.8, 29.7, 27.9, 26.3, 12.3; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O$ 256.1576, found 256.1572.



3m

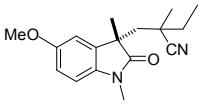
2-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-indol-3-ylmethyl)-2-methyl-butyronitrile: Yellow thick liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.19 (m, 2H), 7.06-

6.99 (m, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.16 (s, 3H), 2.35 (d, J = 14.4 Hz, 0.5H), 2.21-1.13 (m, 1H), 1.96 (d, J = 14.4 Hz, 0.5H), 1.35-1.18 (m, 5H), 0.93-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 180.0, 179.5, 143.4, 143.0, 131.5, 130.9, 128.6, 128.5, 124.9, 124.2, 123.2, 122.7, 122.5, 122.2, 108.6, 108.4, 46.9, 46.9, 45.4, 44.5, 35.6, 35.5, 35.2, 33.2, 27.8, 27.6, 26.4, 26.4, 25.8, 22.8, 9.1, 9.0; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O$ 256.1576, found 256.1579.



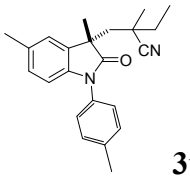
3n

2-(5-Fluoro-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-ylmethyl)-2-methyl-butyronitrile: Thick pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.12-7.01 (m, 2H), 6.84 (m, 1H), 3.24 (s, 3H), 2.44 (d, J = 14.4 Hz, 0.5H), 2.23 (s, 1H), 2.01 (d, J = 14.4 Hz, 0.5H) 1.36-1.48 (m, 5H), 1.04-0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.5 179.0, 160.4, 160.3, 158.0, 157.9, 139.3, 139.3, 139.0, 139.0, 133.3, 133.2, 132.7, 132.6, 123.0, 122.5, 115.0, 114.9, 114.7, 114.7, 113.0, 112.8, 112.4, 112.1, 109.2, 109.1, 109.0, 108.9, 47.4, 47.4, 47.3, 47.3, 45.3, 44.5, 35.5, 35.4, 35.2, 33.4, 27.7, 27.5, 26.5, 26.5, 25.9, 23.0, 9.0, 8.9; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{19}FN_2O$ 274.1481, found 274.1486.



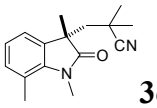
3o

2-(5-Methoxy-1,3-dimethyl-2-oxo-2,3-dihydro-1H-indol-3-ylmethyl)-2-methyl-butyronitrile: Thick pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.99 (d, J = 2.4 Hz, 1H), 6.88-6.85 (m, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.79 (s, 0.33H), 3.82 (s, 3H), 3.22 (s, 3H), 2.24 (s, 2H), 1.60-1.50 (m, 1H), 1.47-1.38(m, 1H), 1.34 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H),0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.7, 156.0, 136.5, 132.1, 123.5, 113.4, 112.3, 108.8, 56.0, 47.3, 44.3, 35.5, 35.4, 28.0, 26.5, 22.5; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{17}H_{22}N_2O_2$ 286.1681, found 281.1685.



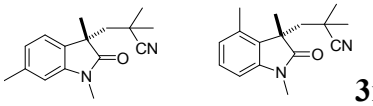
3p

2-(3,5-Dimethyl-2-oxo-1-p-tolyl-2,3-dihydro-1H-indol-3-ylmethyl)-2-methyl-butyronitrile: Yellow solid, m.p. 153-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32-7.24 (m, 4H), 7.24 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 2.41 (s, 3H), 2.37-2.27 (m, 5H), 1.66-1.57 (m, 1H), 1.54-1.49 (m,1H), 1.45 (s, 3H), 1.09 (s, 3H), 1.03 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.5, 140.7, 137.9, 132.5, 130.6, 130.2, 128.7, 126.1, 126.0, 123.6, 109.5, 47.1, 44.5, 35.7, 35.6, 28.5, 22.7, 21.2, 21.2, 9.0; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{23}H_{26}N_2O$ 346.2045, found 346.2041.



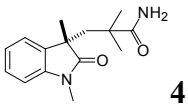
3q

2,2-Dimethyl-3-(1,3,7-trimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-propionitrile: White solid; m.p. 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13 (d, J = 6.8 Hz, 1H), 7.06 (d, J = 6.8 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 3.52 (s, 3H), 2.61(s, 3H), 2.32 (d, J = 14.4 Hz, 1H), 2.12 (d, J = 14.4 Hz, 1H), 1.33 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 180.4, 141.0, 137.9, 132.3, 131.6, 124.0, 122.5, 122.4, 120.2, 46.8, 46.3, 30.7, 29.8, 29.6, 27.8, 26.9, 19.1; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O$ 256.1576, found 256.1576.



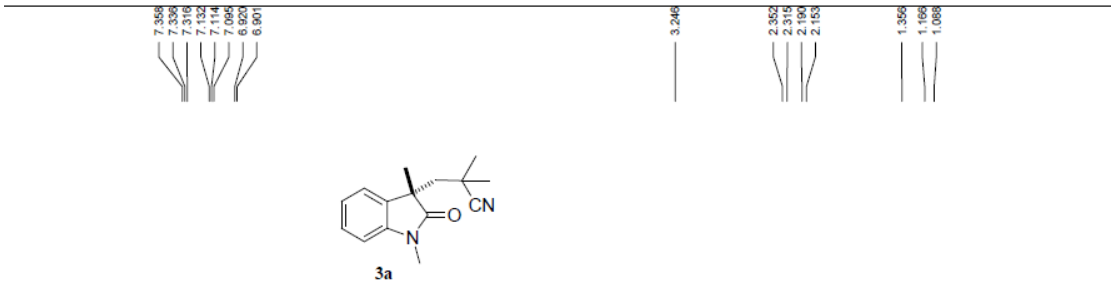
3r + 3r'

2,2-Dimethyl-3-(1,3,6-trimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-propionitrile and 2,2-Dimethyl-3-(1,3,4-trimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-propionitrile: Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26-7.18 (m, 1H), 6.92 (d, J = 3.6 Hz, 0.38H), 6.87 (d, J = 3.6 Hz, 0.62H), 6.76-6.73 (m, 1H), 3.22 (s, 3H), 2.45 (s, 1.83H), 2.40 (s, 1.15H), 2.38-2.12 (m, 2H), 1.42 (s, 1.85H), 1.32 (s, 1.15H), 1.19 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 180.0, 179.6, 143.4, 143.2, 138.8, 135.8, 128.5, 128.2, 127.9, 125.3, 124.5, 124.1, 123.4, 123.0, 109.4, 106.2, 47.7, 46.8, 46.5, 45.2, 30.9, 30.7, 29.7, 29.2, 27.6, 26.6, 26.4, 26.4, 26.3, 26.2, 24.6, 21.9, 18.9; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{16}H_{20}N_2O$ 256.1576, found 256.1573.



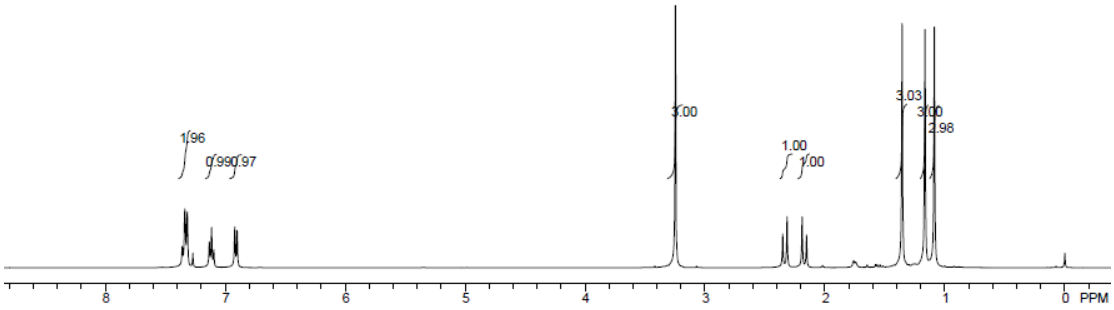
4

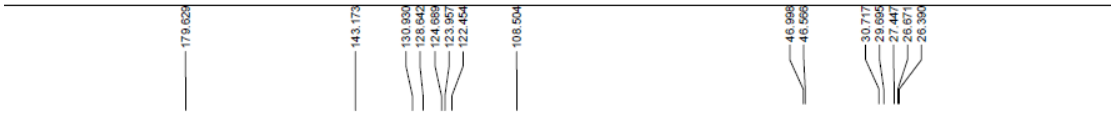
3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-indol-3-yl)-2,2-dimethyl-propionamide: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28-7.23 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 5,17 (br, 2H), 3.22 (s, 3H), 2.64 (d, J = 14.4 Hz, 1H), 2.17 (d, J = 14.4 Hz, 1H), 1.31 (s, 3H), 1.05 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 181.0, 180.2, 142.9, 132.0, 127.8, 125.5, 122.3, 107.8, 47.4, 46.4, 41.6, 27.8, 26.3, 22.4; HRMS (TOF MS EI$^+$) $[M]^+$ calculated for $C_{15}H_{20}N_2O_2$ 260.1525, found 260.1526.

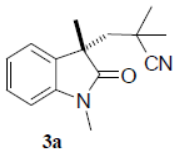

7.368
7.336
7.316
7.132
7.114
7.095
6.920
6.901
3.248
2.352
2.315
2.190
2.153
1.356
1.166
1.088

O
CN
N

3a

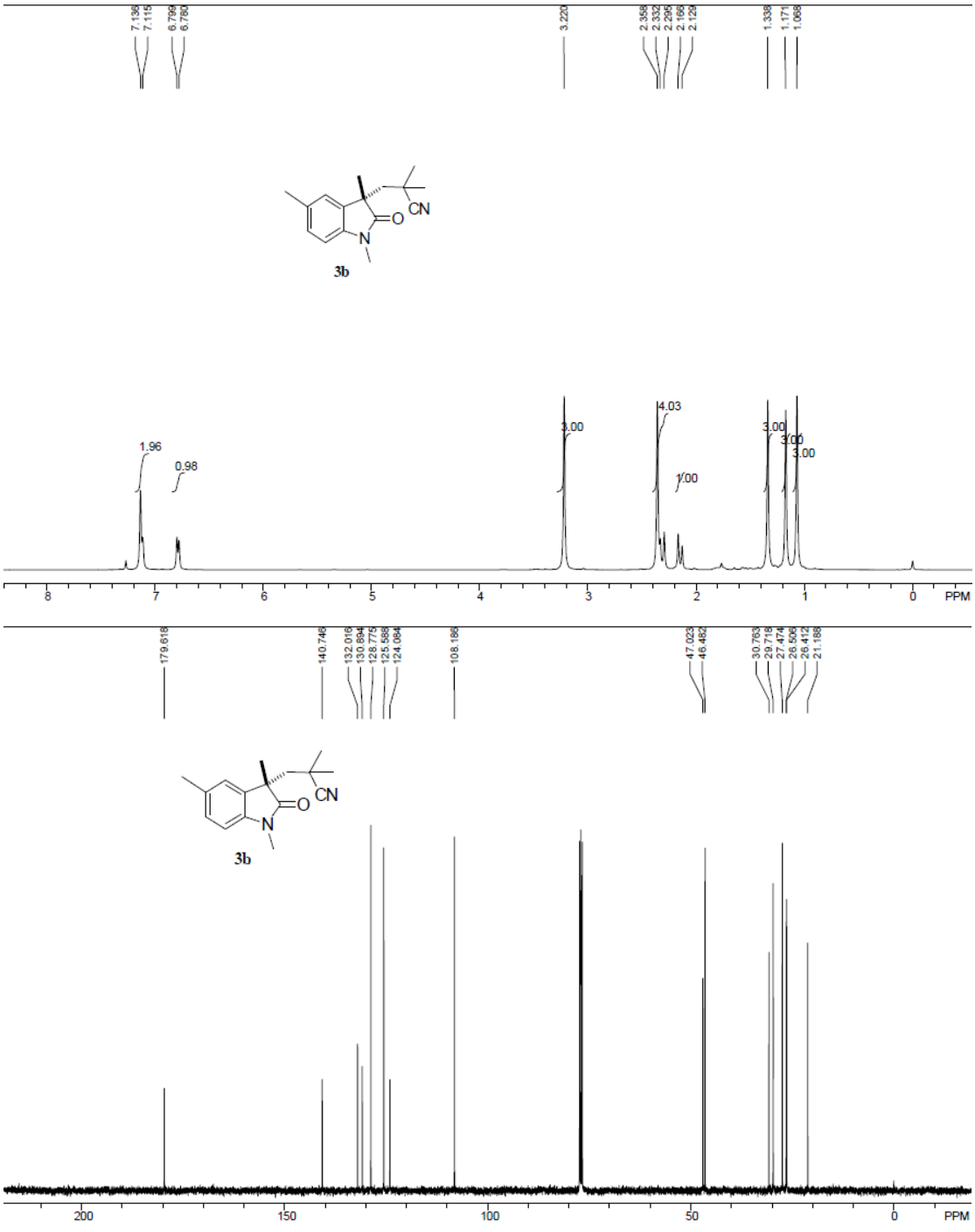

1.96
0.99
0.97
3.00
1.00
1.00
3.03
3.00
2.98
8
7
6
5
4
3
2
1
0
PPM

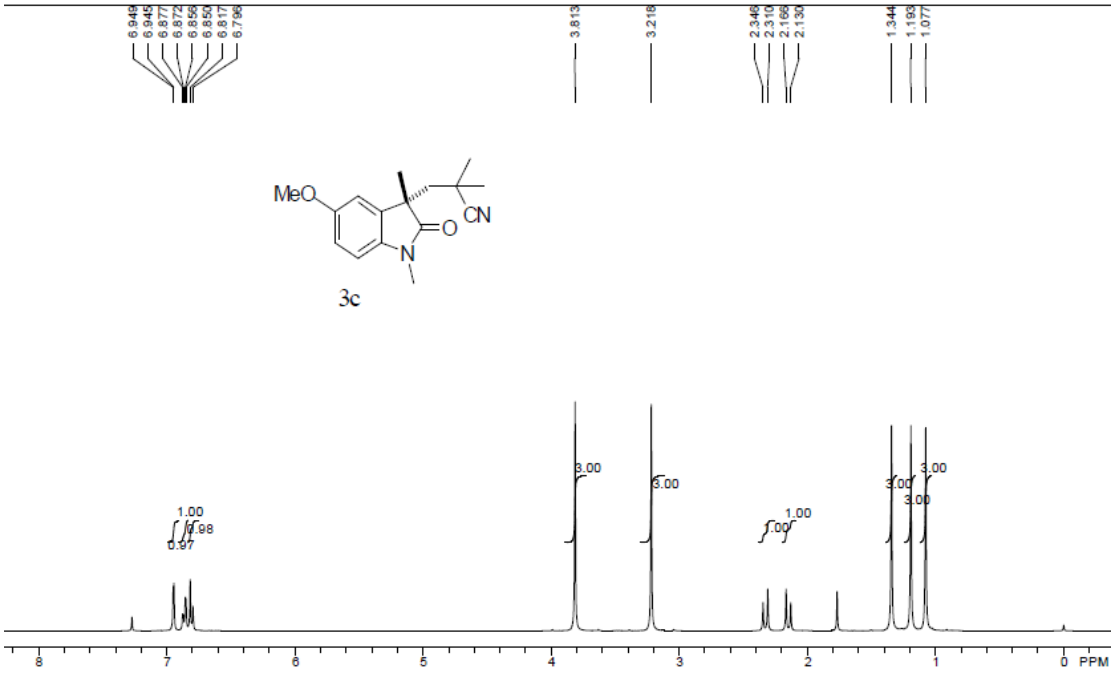

179.628
143.173
130.930
128.642
124.688
123.957
122.454
108.504
46.998
46.566
30.717
29.695
27.447
26.671
26.390

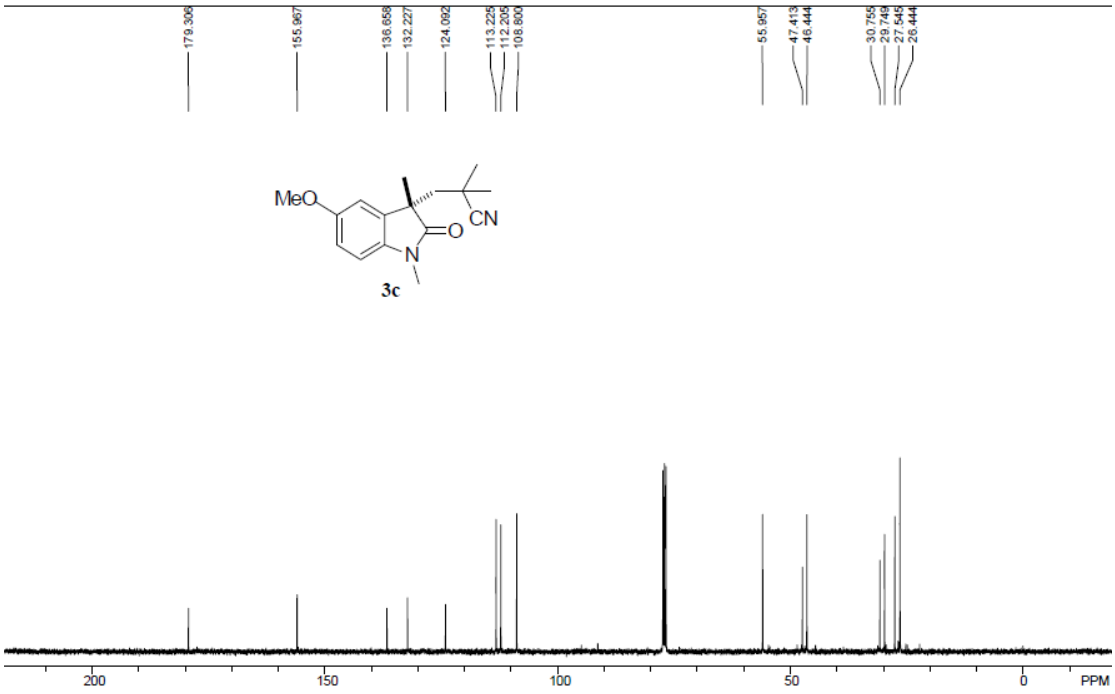

O
CN
N

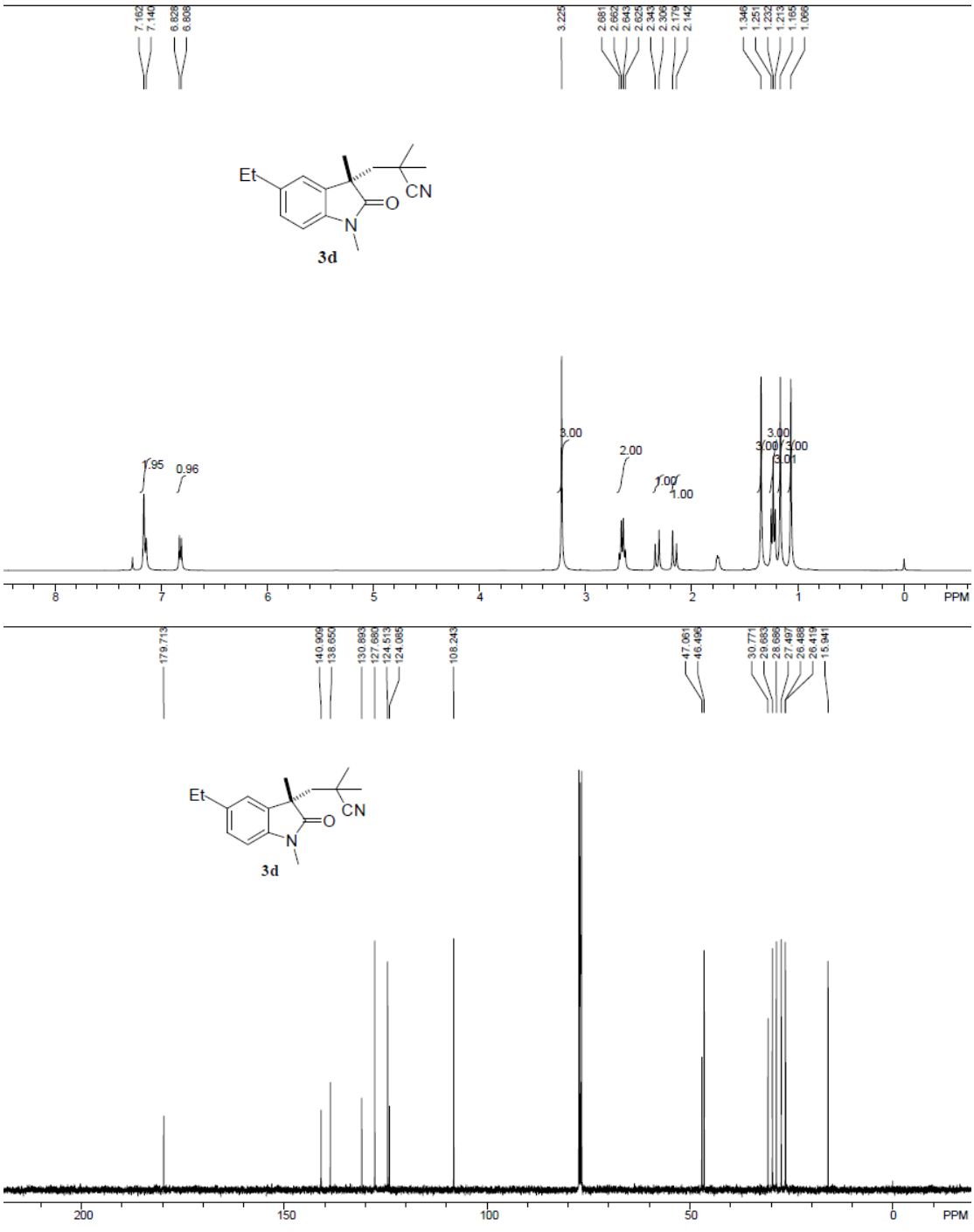
3a

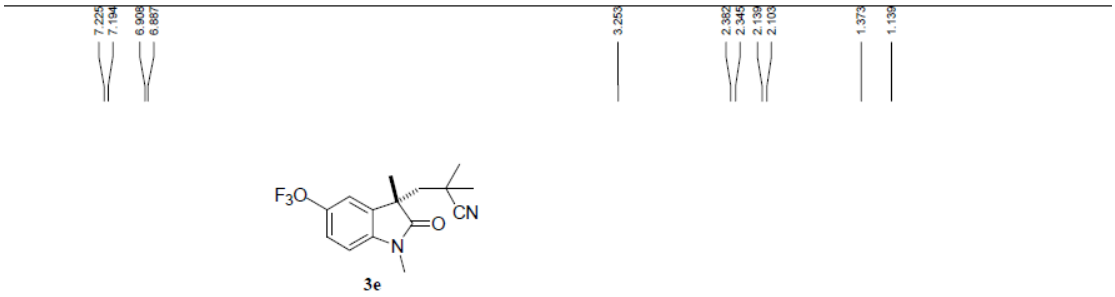
200
150
100
50
0
PPM


7.136
7.115
6.799
6.780
3.220
2.358
2.332
2.295
2.166
2.129
1.338
1.171
1.068
CN
O
N
3b
1.96
0.98
3.00
4.03
1.00
3.00
3.00
3.00
8
7
6
5
4
3
2
1
0
PPM
179.618
140.748
132.016
130.894
128.775
125.588
124.084
108.186
47.023
46.482
30.763
29.718
27.474
26.506
26.412
21.188
CN
O
N
3b
200
150
100
50
0
PPM


6.949
6.945
6.877
6.872
6.856
6.850
6.817
6.796
3.813
3.218
2.346
2.310
2.166
2.130
1.344
1.193
1.077
MeO
O
CN
N
3c
1.00
0.98
0.97
3.00
3.00
1.00
1.00
3.00
3.00
3.00
8
7
6
5
4
3
2
1
0
PPM

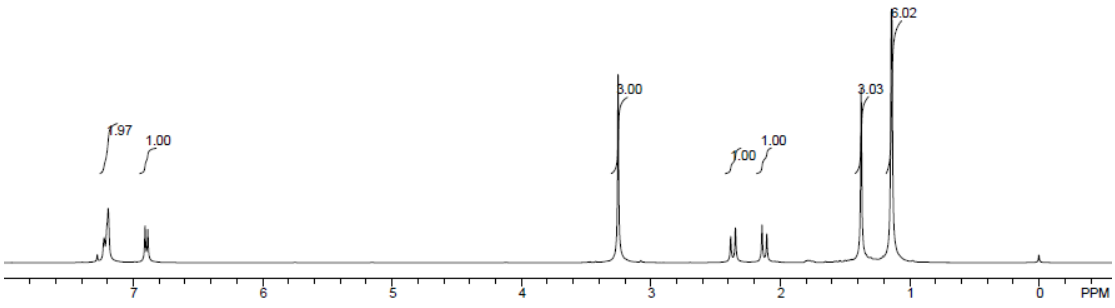

179.306
155.967
136.658
132.227
124.092
113.225
112.205
108.800
55.957
47.413
46.444
30.755
29.749
27.545
26.444
MeO
O
CN
N
3c
200
150
100
50
0
PPM

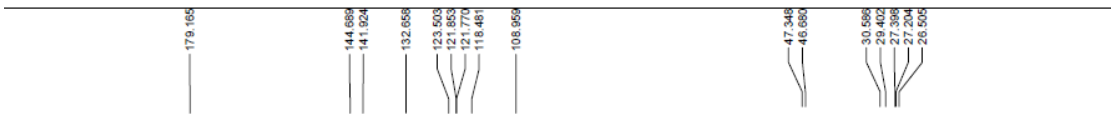

7.162
7.140
6.828
6.808
3.225
2.681
2.662
2.643
2.625
2.343
2.306
2.179
2.142
1.346
1.251
1.232
1.213
1.165
1.066
Et
CN
O
N
3d
3.00
2.00
1.00
1.00
3.00
3.00
3.00
3.01
1.95
0.96
8
7
6
5
4
3
2
1
0
PPM
179.713
140.909
138.659
130.893
127.680
124.513
124.085
106.243
47.061
46.496
30.771
29.683
28.686
27.497
26.488
26.419
15.941
Et
CN
O
N
3d
200
150
100
50
0
PPM

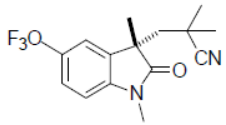

7.225
7.194
6.908
6.887
3.253
2.382
2.345
2.139
2.103
1.373
1.139

F3O
CN
O
N

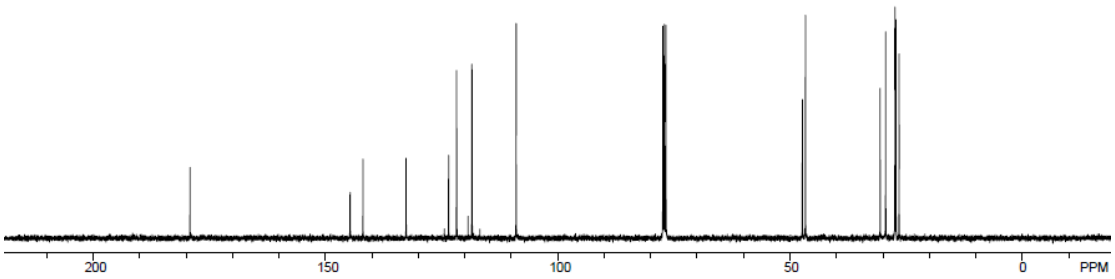
3e

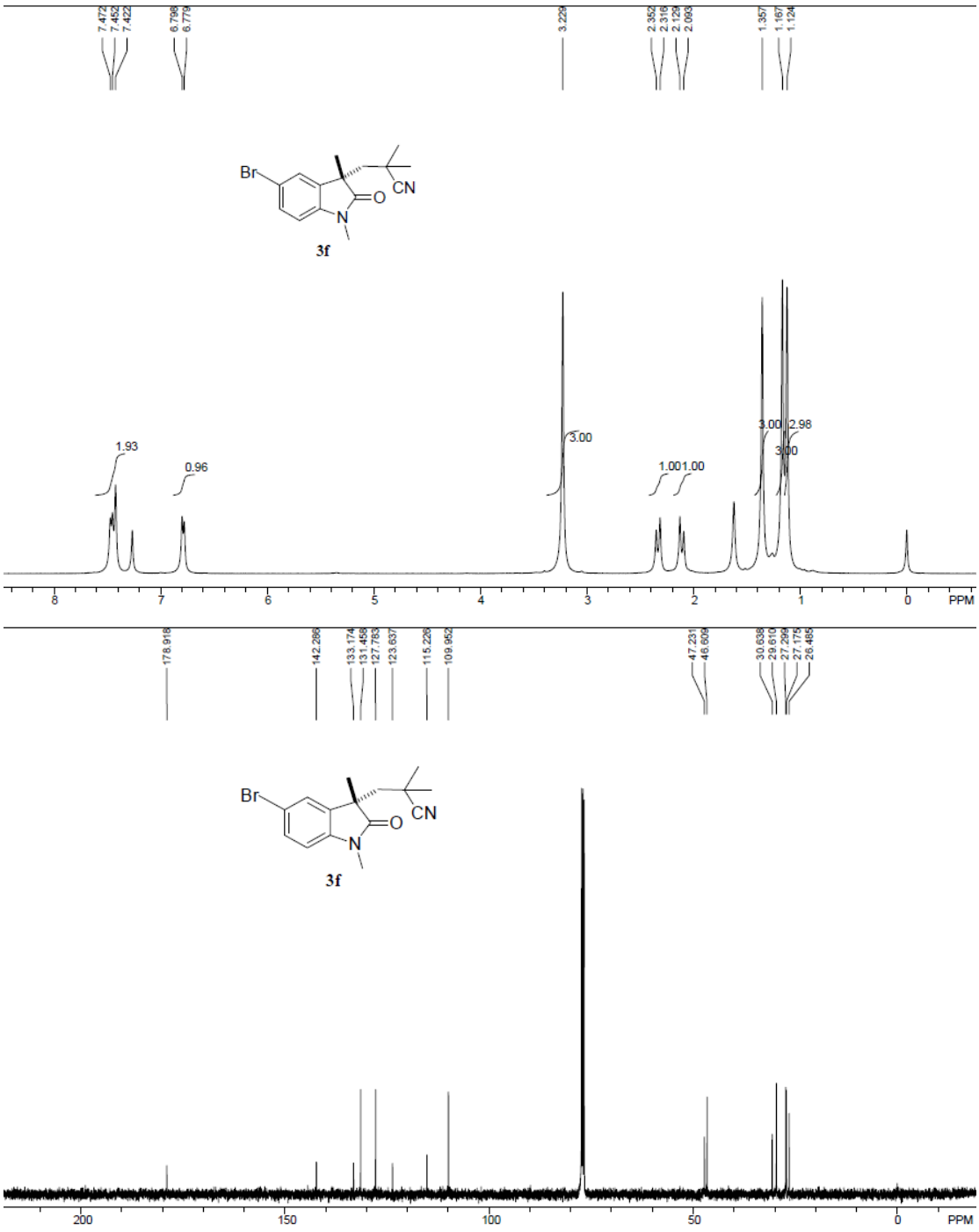

1.97
1.00
3.00
1.00
1.00
3.03
6.02
7
6
5
4
3
2
1
0
PPM


179.165
144.689
141.924
132.658
123.503
121.853
121.770
118.461
108.959
47.348
46.680
30.586
29.402
27.398
27.204
26.505

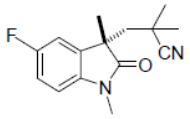

F3O
CN
O
N

3e

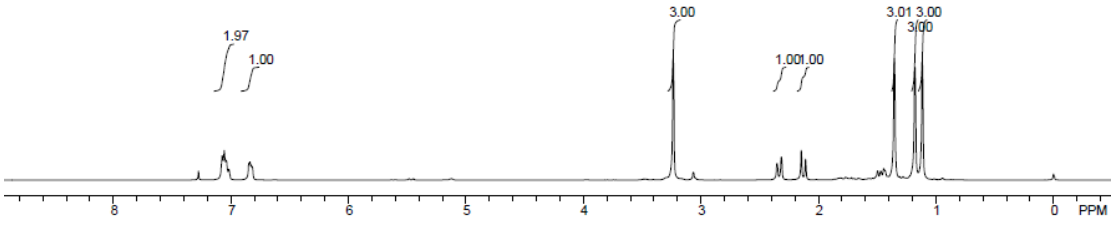

200
150
100
50
0
PPM


7.472
7.452
7.422
6.798
6.779
3.229
2.352
2.316
2.129
2.093
1.357
1.167
1.124
Br
O
CN
N
3f
1.93
0.96
3.00
1.00
1.00
3.00
2.98
3.00
8
7
6
5
4
3
2
1
0
PPM
178.918
142.286
133.174
131.458
127.783
123.637
115.226
109.952
47.231
46.609
30.638
29.610
27.299
27.175
26.485
Br
O
CN
N
3f
200
150
100
50
0
PPM

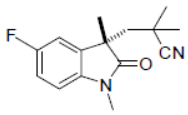

7.074
7.056
7.039
7.017
6.847
6.838
6.827
6.817
3.235
2.351
2.315
2.145
2.109
1.353
1.177
1.115


F
O
N
CN

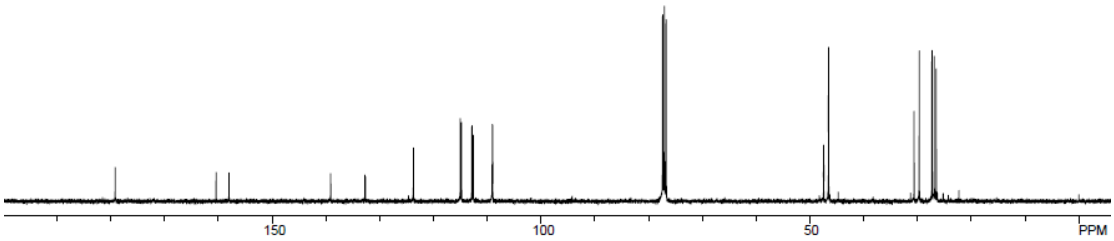
3g

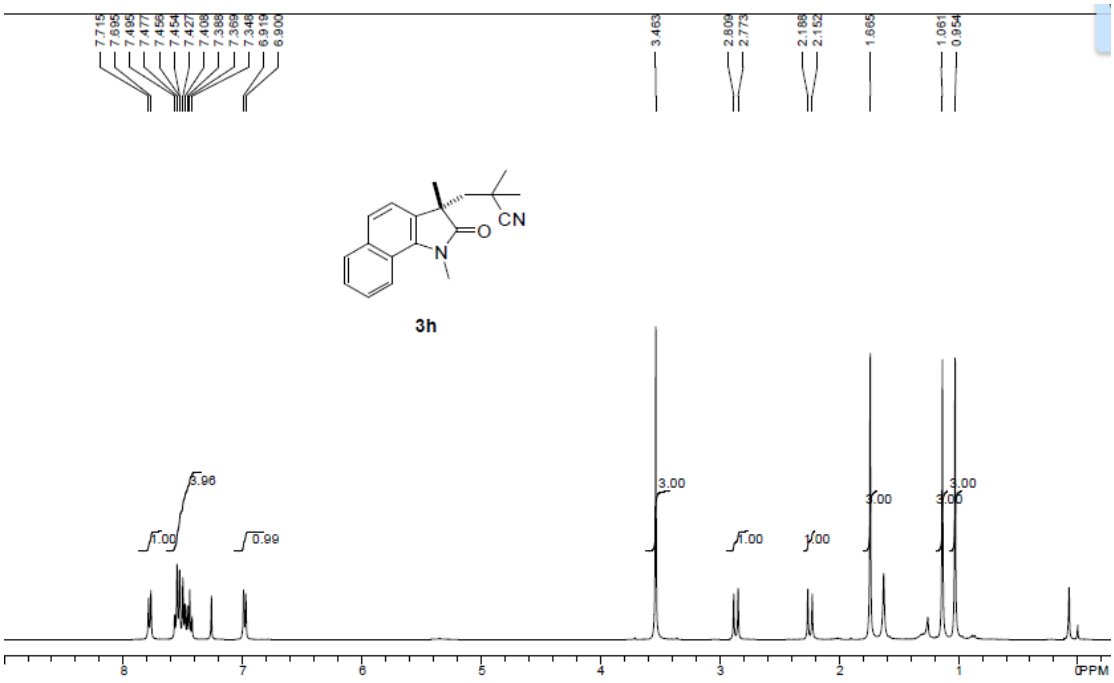

1.97
1.00
3.00
1.00
1.00
3.01
3.00
3.00
8
7
6
5
4
3
2
1
0
PPM

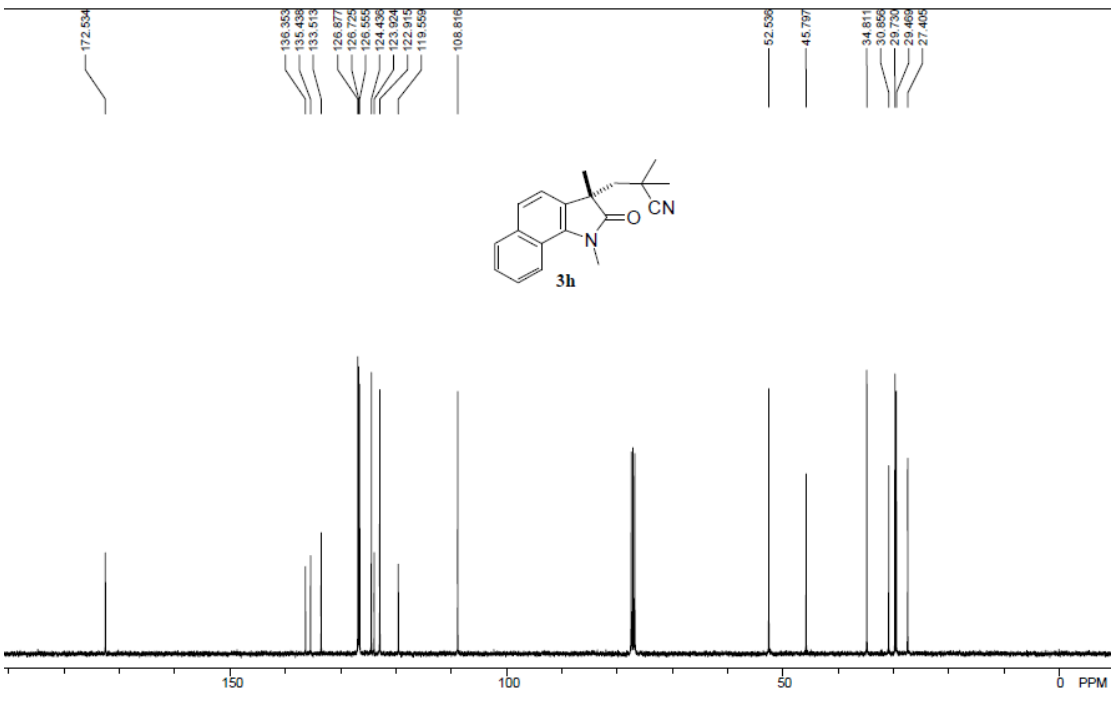

179.189
160.424
158.026
139.130
139.116
132.733
132.651
123.736
115.022
114.790
112.856
112.605
109.072
108.993
47.466
47.452
46.541
30.644
29.688
27.331
26.888
26.529

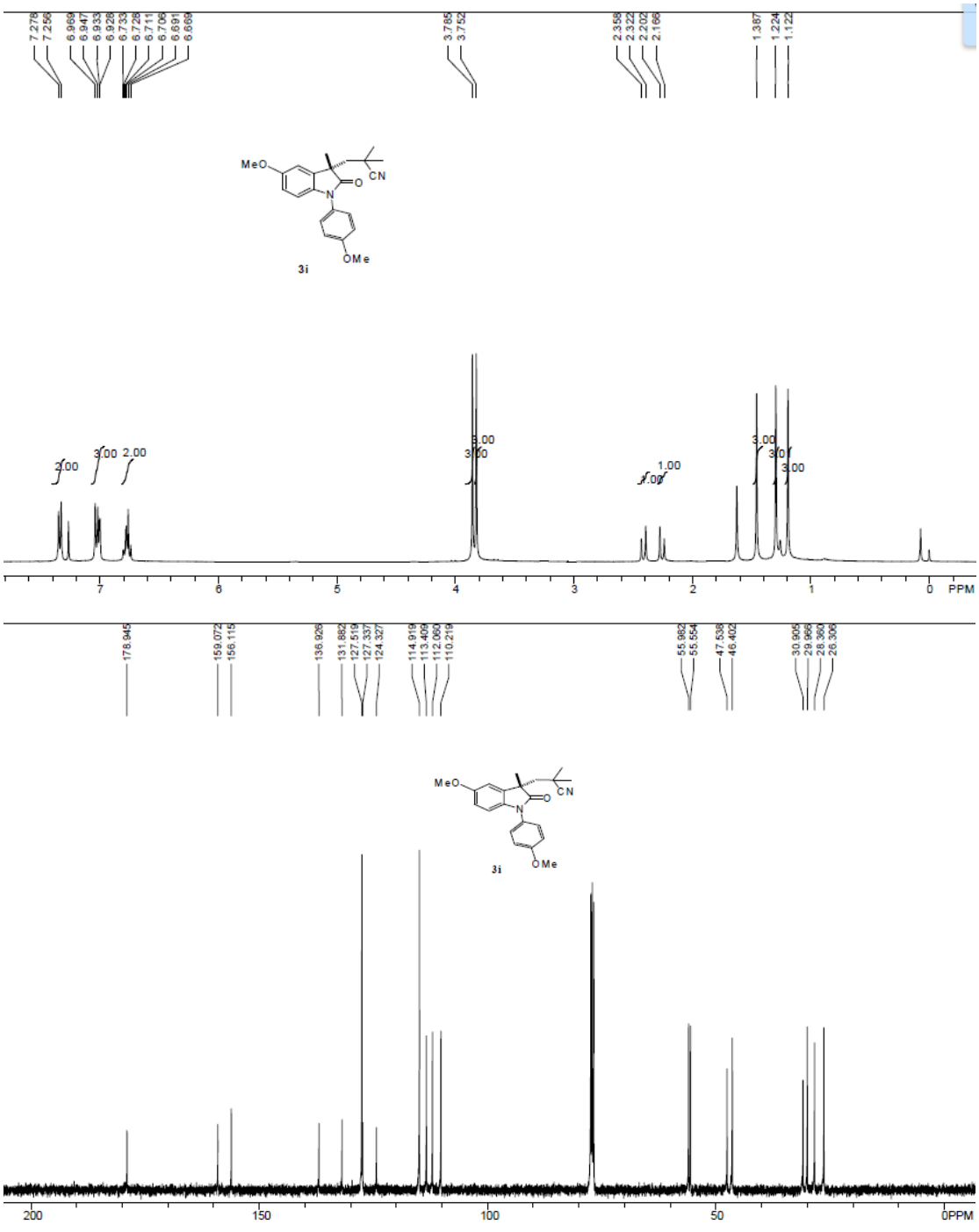

F
O
N
CN

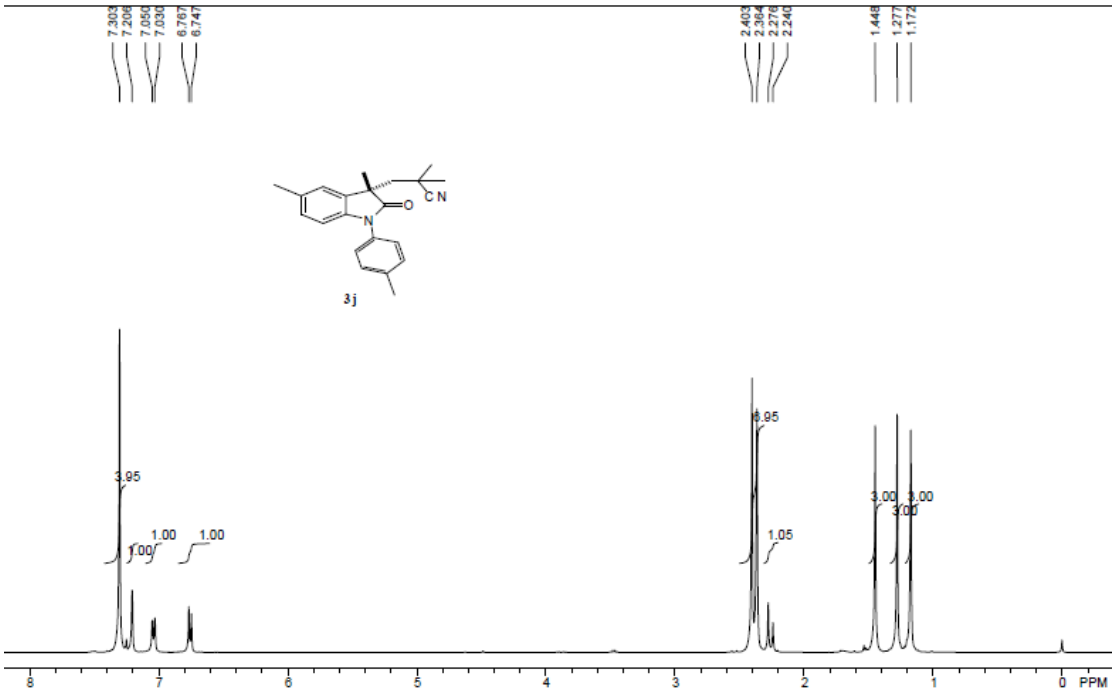
3g

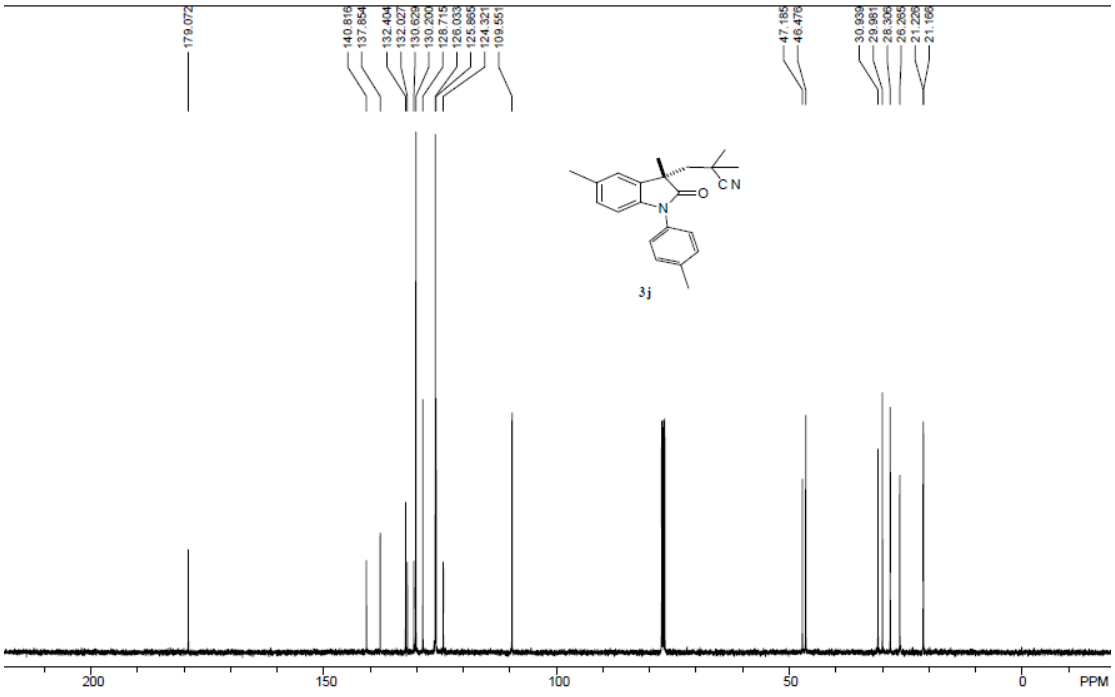

150
100
50
PPM

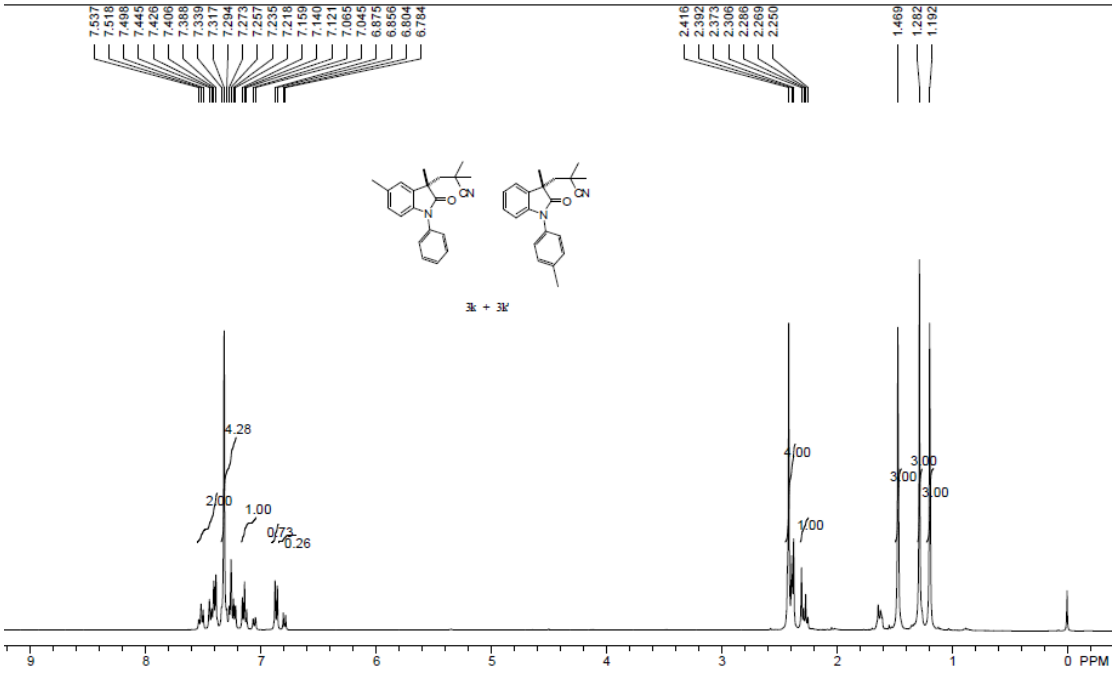

7.715
7.695
7.495
7.477
7.456
7.454
7.427
7.408
7.388
7.369
7.348
6.919
6.900
3.463
2.809
2.773
2.188
2.152
1.665
1.061
0.954
CN
O
N
3h
3.96
1.00
0.99
3.00
1.00
1.00
3.00
3.00
3.00
8
7
6
5
4
3
2
1
0 PPM

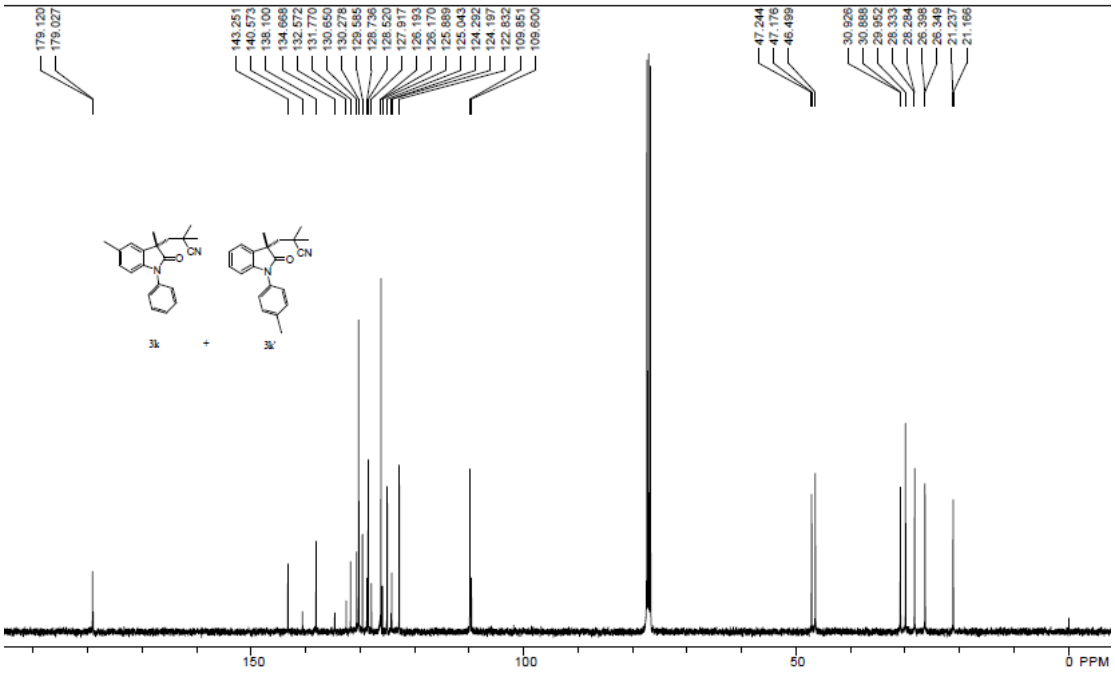

172.534
136.353
135.438
133.513
126.877
126.726
126.555
124.439
123.924
122.915
119.559
108.816
52.536
45.797
34.811
30.856
29.730
29.469
27.405
CN
O
N
3h
150
100
50
0 PPM

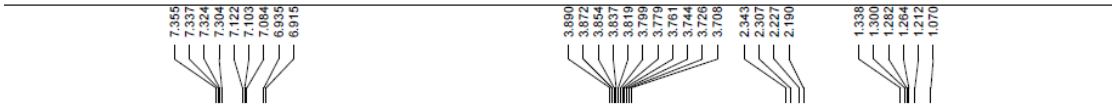

7.278
7.256
6.969
6.947
6.933
6.928
6.733
6.728
6.711
6.706
6.691
6.669
3.765
3.752
2.358
2.322
2.202
2.166
1.387
1.234
1.122
MeO
CN
O
N
OMe
3i
3.00
3.00
2.00
3.00
3.00
1.00
1.00
3.00
3.00
3.00
7
6
5
4
3
2
1
0
PPM
178.945
159.072
156.115
136.928
131.882
127.519
127.337
124.327
114.919
113.409
112.060
110.219
55.982
55.554
47.538
46.402
30.905
29.966
28.360
26.306
MeO
CN
O
N
OMe
3i
200
150
100
50
0PPM

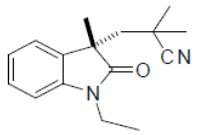

7.303
7.206
7.050
7.030
6.767
6.747
2.403
2.364
2.276
2.240
1.448
1.277
1.172
CN
O
N
3j
3.95
1.00
1.00
1.00
6.95
1.05
3.00
3.00
3.00
8
7
6
5
4
3
2
1
0
PPM


179.072
140.816
137.854
132.404
132.027
130.629
130.200
128.715
126.033
125.865
124.321
109.551
47.185
46.476
30.939
29.981
28.306
26.285
21.226
21.166
CN
O
N
3j
200
150
100
50
0
PPM

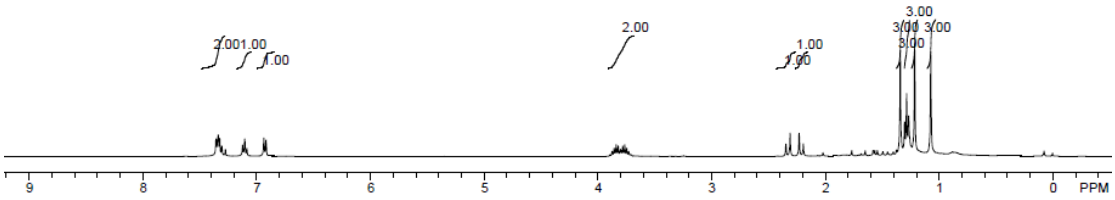

7.537
7.518
7.498
7.445
7.426
7.406
7.388
7.339
7.317
7.294
7.273
7.257
7.235
7.218
7.159
7.140
7.121
7.065
7.045
6.875
6.856
6.804
6.784
2.416
2.392
2.373
2.306
2.286
2.269
2.250
1.469
1.282
1.192
3k + 3k'
4.28
2.00
1.00
0.73
0.26
4.00
1.00
3.00
3.00
3.00
9
8
7
6
5
4
3
2
1
0 PPM


179.120
179.027
143.251
140.573
138.100
134.688
132.572
131.770
130.650
130.278
129.585
128.736
128.520
127.917
126.193
126.170
125.889
125.043
124.292
124.197
122.832
109.851
109.600
47.244
47.176
46.499
30.926
30.888
29.952
28.333
28.284
26.398
26.349
21.237
21.166
3k + 3k'
150
100
50
0 PPM

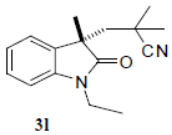

7.355
7.337
7.324
7.304
7.122
7.103
7.084
6.935
6.915
3.890
3.872
3.854
3.837
3.819
3.799
3.779
3.761
3.744
3.726
3.708
2.343
2.307
2.227
2.190
1.338
1.300
1.282
1.264
1.212
1.070


CN
O
N

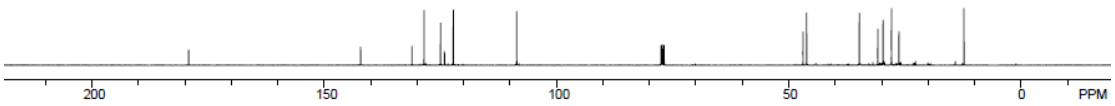
31

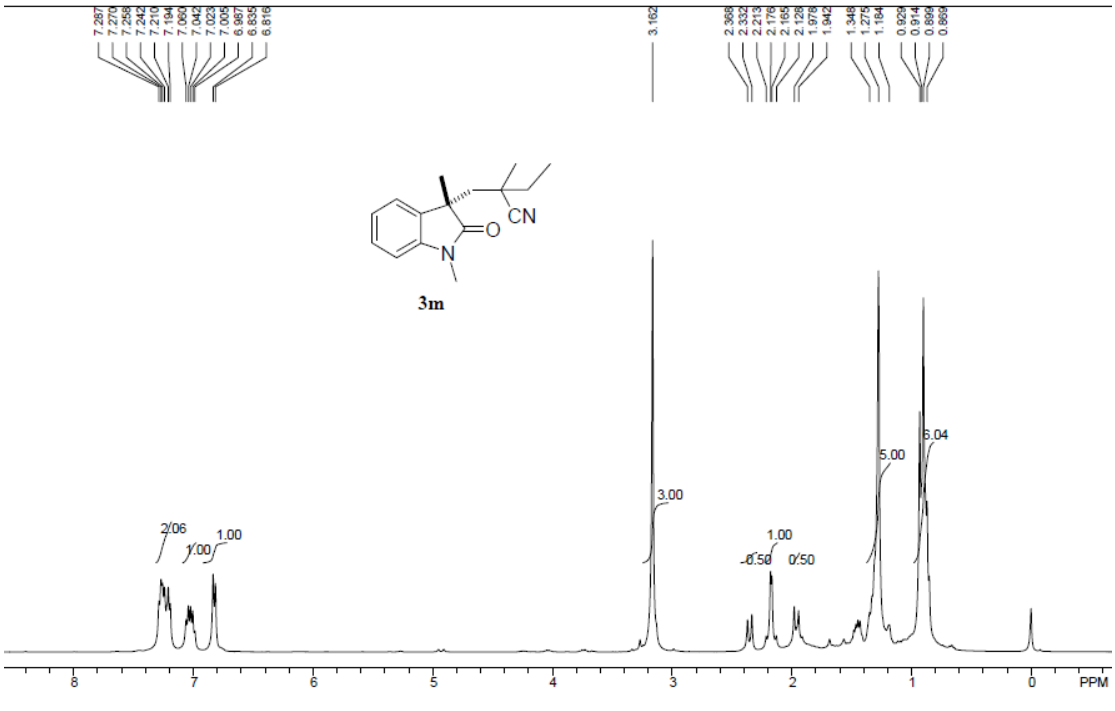

2.00
1.00
2.00
1.00
3.00
3.00
3.00
3.00
9
8
7
6
5
4
3
2
1
0
PPM

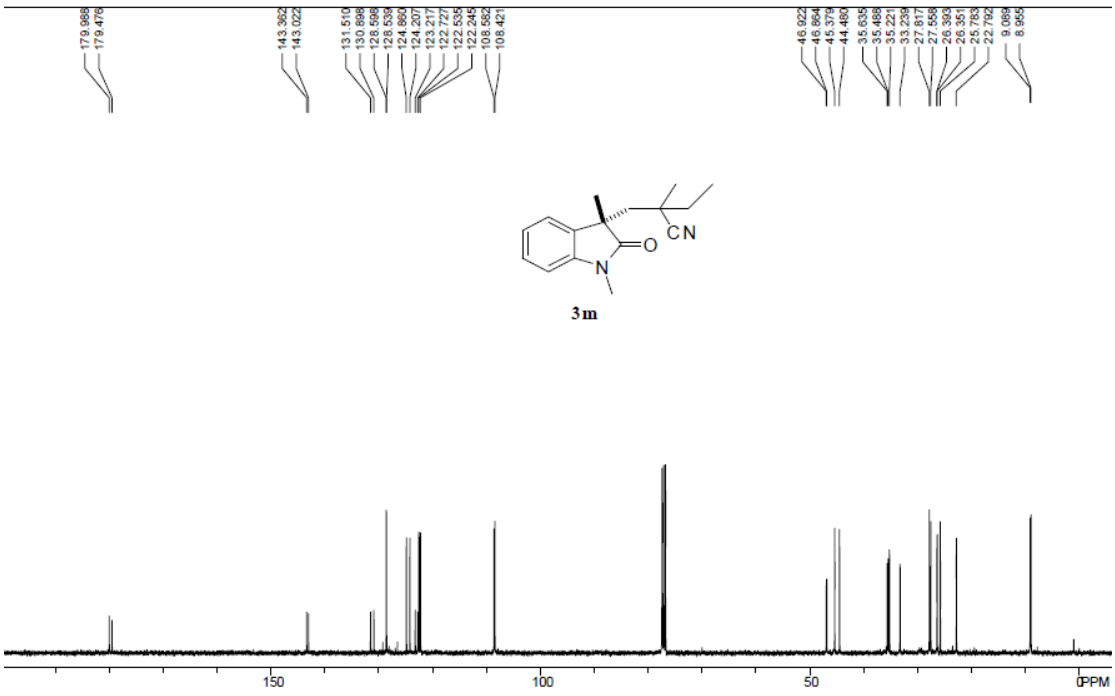

179.180
142.149
131.121
128.511
124.964
124.115
122.228
108.575
46.928
46.153
34.795
30.827
29.700
27.871
26.261
12.260


CN
O
N

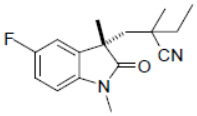
31


200
150
100
50
0
PPM

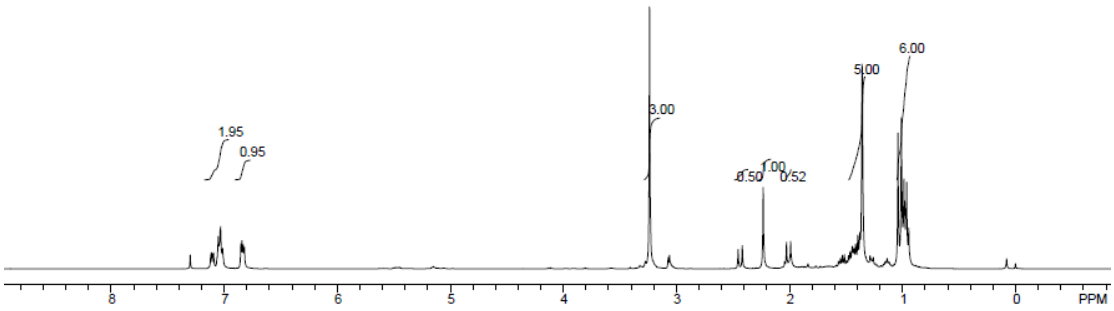

7.287
7.270
7.258
7.243
7.210
7.194
7.060
7.042
7.023
7.005
6.987
6.835
6.816
3.162
2.368
2.332
2.213
2.176
2.165
2.128
2.078
1.942
1.348
1.275
1.184
0.929
0.914
0.899
0.869
CN
O
N
3m
2.06
1.00
1.00
3.00
1.00
0.50
0.50
5.00
6.04
8
7
6
5
4
3
2
1
0
PPM

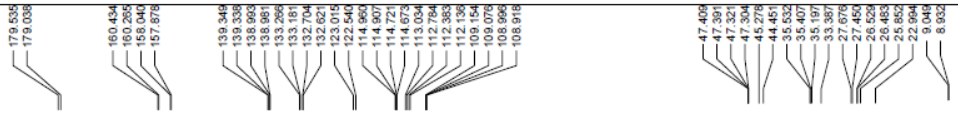

179.988
179.476
143.362
143.022
131.510
130.898
128.598
128.539
124.860
124.207
123.217
122.727
122.535
122.245
108.562
108.421
46.922
46.854
45.379
44.460
35.635
35.488
35.221
33.239
27.817
27.558
26.393
26.351
25.783
22.792
9.069
8.955
CN
O
N
3m
150
100
50
0
PPM

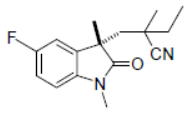

7.119
7.113
7.099
7.094
7.063
7.042
7.032
7.013
7.007
6.853
6.842
6.821
3.237
2.453
2.417
2.232
2.025
1.989
1.477
1.463
1.444
1.441
1.427
1.414
1.395
1.376
1.357
1.039
1.010
0.987
0.953
0.944


F
O
N
CN

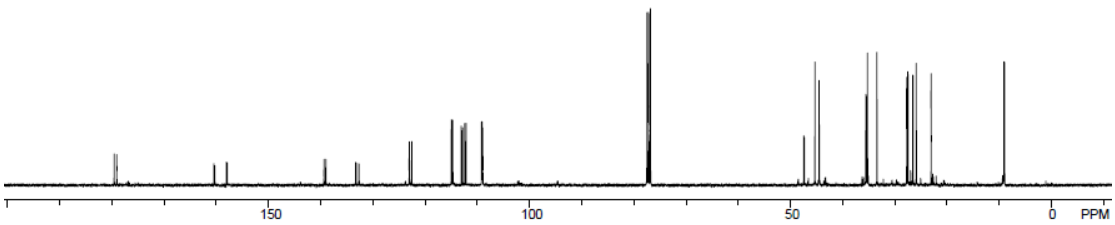
3n

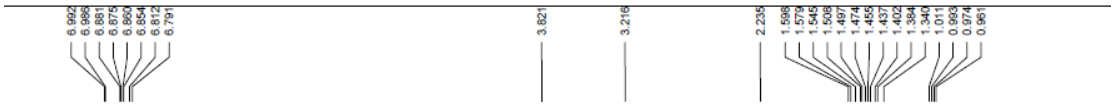

1.95
0.95
3.00
0.50
1.00
0.52
5.00
6.00
8
7
6
5
4
3
2
1
0
PPM

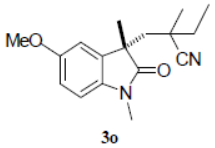

179.535
179.038
160.434
160.265
158.040
157.878
139.349
139.338
138.993
138.981
133.266
133.181
132.704
132.621
123.015
122.540
114.960
114.907
114.721
114.673
113.034
112.794
112.383
112.136
109.154
109.076
108.996
108.918
47.409
47.391
47.321
47.304
45.278
44.451
35.532
35.407
35.197
33.397
27.676
27.450
26.524
26.483
25.852
22.994
9.049
8.932


F
O
N
CN

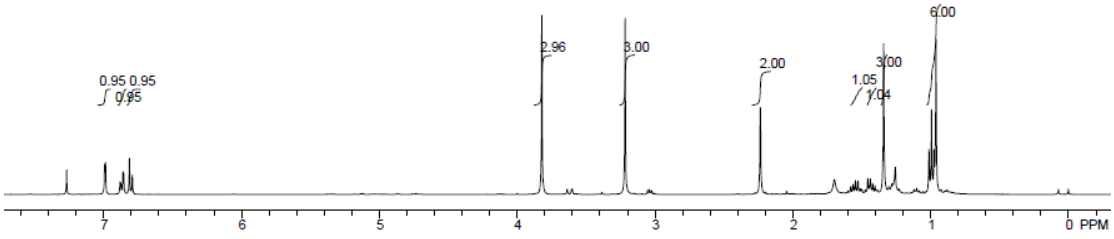
3n


150
100
50
0
PPM

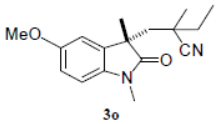

6.992
6.986
6.881
6.875
6.860
6.854
6.812
6.791
3.821
3.216
2.235
1.598
1.578
1.545
1.508
1.497
1.474
1.455
1.437
1.402
1.384
1.340
1.011
0.993
0.974
0.961


MeO
O
CN
N

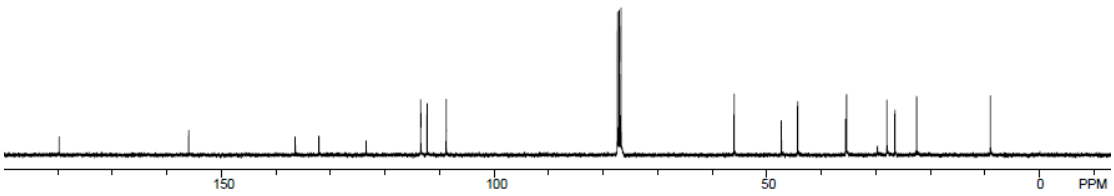
3o

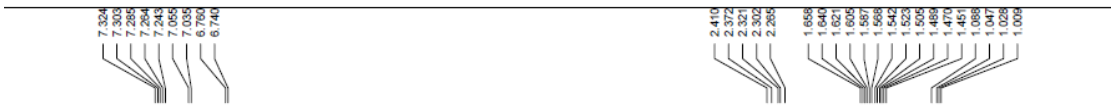

0.95
0.95
2.96
3.00
2.00
1.05
1.04
3.00
6.00
7
6
5
4
3
2
1
0 PPM

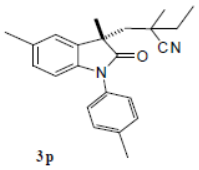

179.725
155.969
136.476
132.116
123.458
113.447
112.277
108.780
55.990
47.309
44.331
35.528
35.363
27.960
26.495
22.503
8.966


MeO
O
CN
N

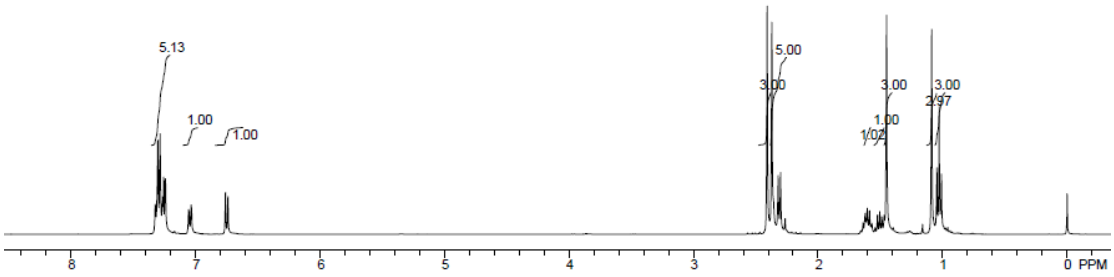
3o


150
100
50
0 PPM

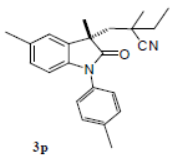

7.324
7.303
7.285
7.264
7.243
7.055
7.035
6.760
6.740
2.410
2.372
2.321
2.302
2.265
1.658
1.640
1.621
1.605
1.587
1.568
1.542
1.523
1.505
1.489
1.470
1.451
1.088
1.047
1.026
1.009


CN
O
N

3p

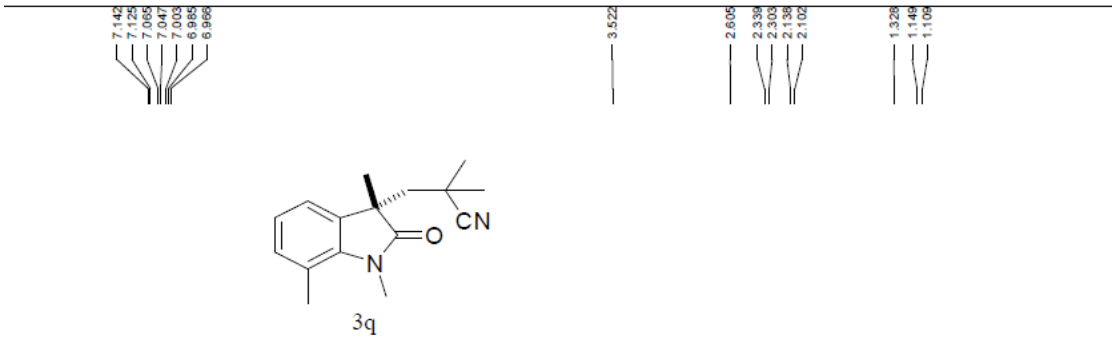

5.13
1.00
1.00
5.00
3.00
3.00
1.00
1.02
3.00
2.97
8
7
6
5
4
3
2
1
0 PPM


179.472
140.694
137.907
132.488
132.014
130.555
130.221
128.668
126.091
125.966
123.559
109.479
47.059
44.483
35.708
35.573
28.528
22.662
21.217
21.171
9.019

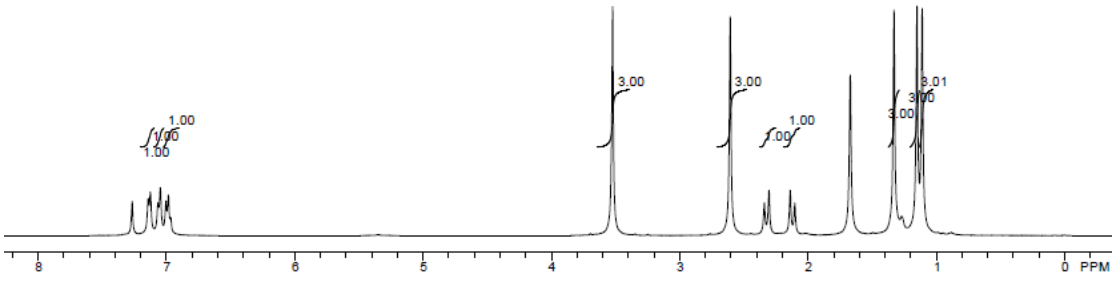

CN
O
N

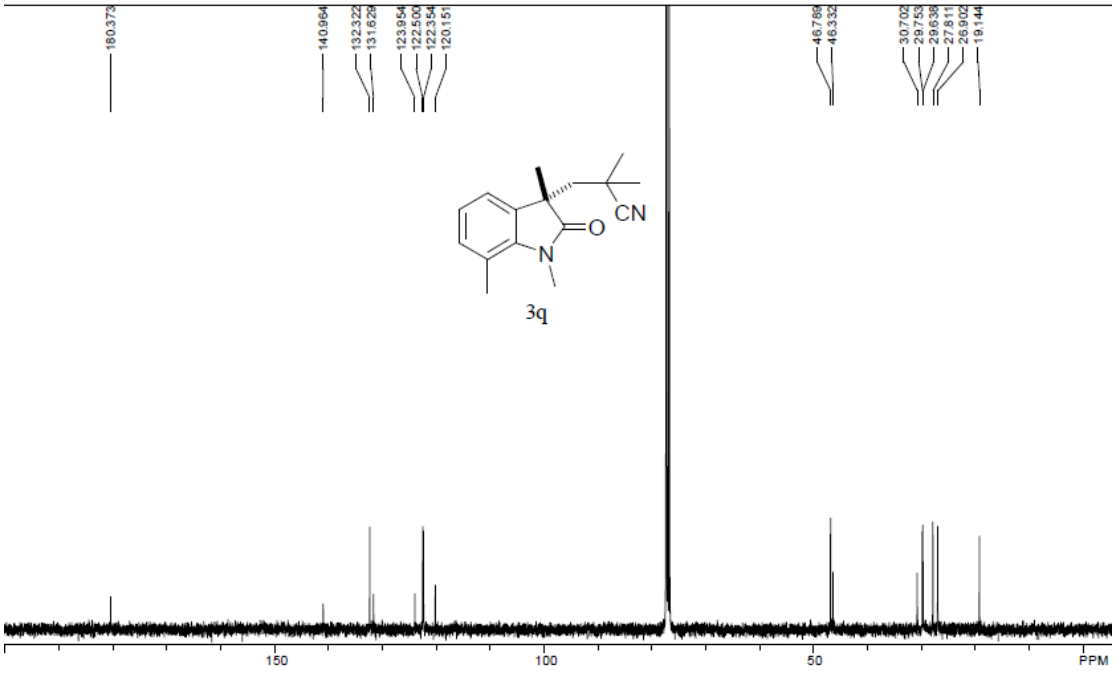
3p

150
100
50
0
PPM


7.142
7.125
7.065
7.047
7.003
6.985
6.966
3.522
2.605
2.339
2.303
2.138
2.102
1.328
1.149
1.109
CN
O
N

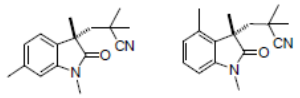
3q


1.00
1.00
3.00
3.00
1.00
3.00
3.00
3.01
8
7
6
5
4
3
2
1
0
PPM

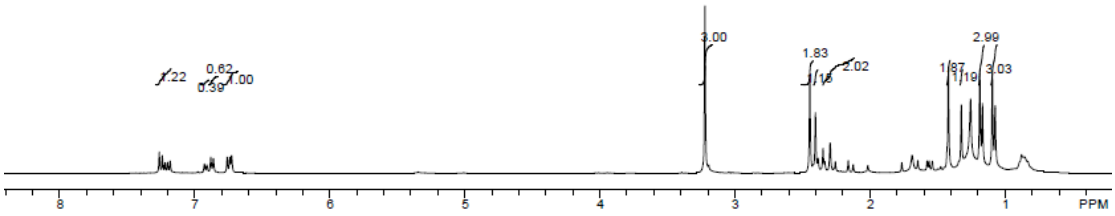

180.373
140.964
132.322
131.629
123.954
122.500
122.354
120.151
46.789
46.332
30.702
29.753
29.638
27.811
26.902
19.144
CN
O
N
150
100
50
PPM

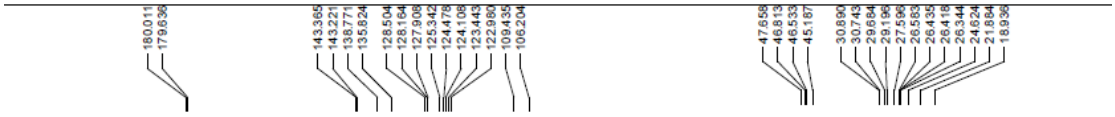
3q

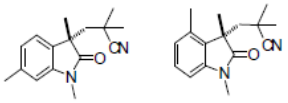

7.262
7.239
7.219
7.200
7.182
6.928
6.909
6.880
6.861
6.759
6.740
6.726
3.220
2.445
2.403
2.383
2.346
2.333
2.294
2.255
2.159
2.123
1.416
1.323
1.186
1.167
1.093
1.072


CN
O
N
CN
O
N

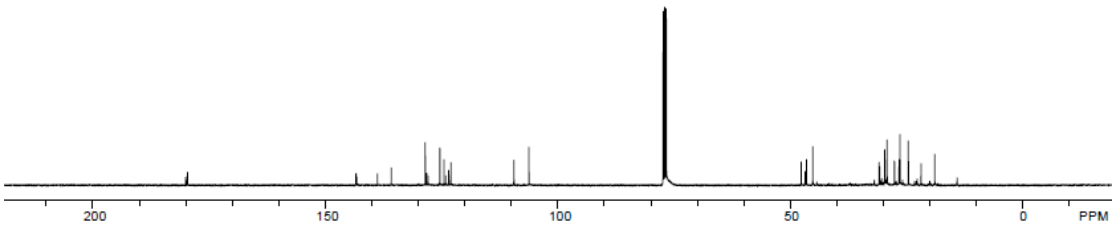
3r + 3r'


3.00
1.83
2.02
2.99
3.03
1.87
1.19
0.62
0.39
1.00
8
7
6
5
4
3
2
1
PPM

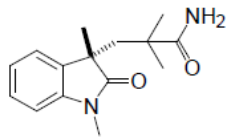

180.011
179.636
143.365
143.221
138.771
135.824
128.504
128.164
127.908
125.342
124.478
124.108
123.443
122.980
109.435
106.204
47.659
46.813
46.533
45.187
30.890
30.743
29.684
29.186
27.596
26.583
26.435
26.418
26.344
24.624
21.884
18.936


CN
O
N
CN
O
N

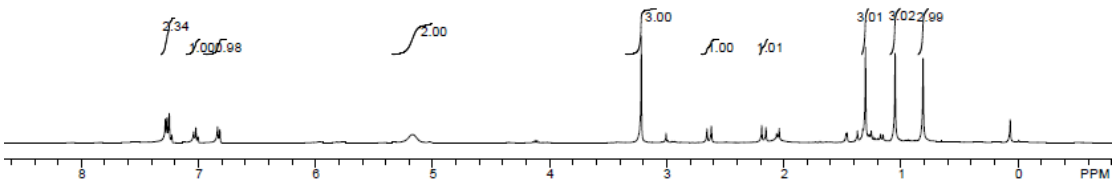
3r + 3r'

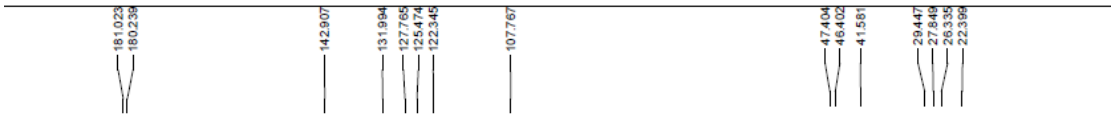

200
150
100
50
0
PPM

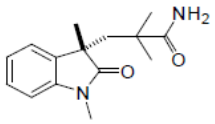

7.283
7.268
7.249
7.229
7.041
7.022
7.003
6.837
6.817
5.173
3.220
2.657
2.621
2.192
2.155
1.306
1.052
0.814


NH2
O
O
N

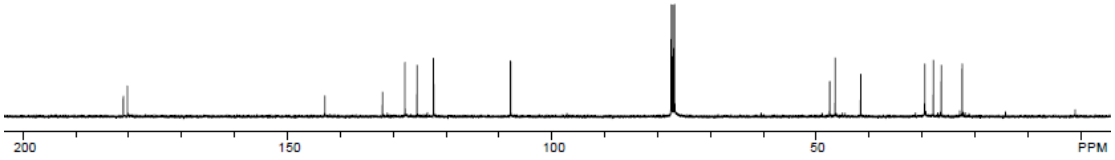
4

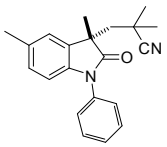

2.34
1.00
0.98
2.00
3.00
1.00
1.01
3.01
3.02
2.99
8
7
6
5
4
3
2
1
0
PPM

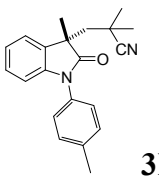

181.023
180.239
142.907
131.994
127.765
125.474
122.345
107.767
47.404
46.402
41.581
29.447
27.849
26.335
22.399


NH2
O
O
N

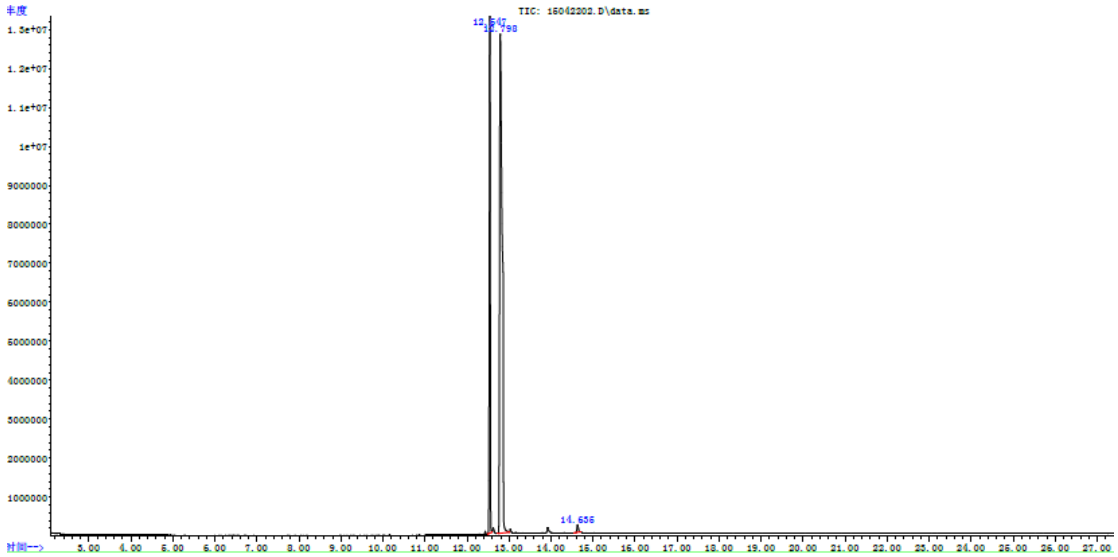
4


200
150
100
50
PPM


CN
O
N


CN
O
N

3k + 3k'



1	12.547	1195	1202	1208	BV	13069336	198649318	36.29%	26.481%
2	12.798	1223	1231	1255	BV	12843057	547413181	100.00%	72.973%
3	14.635	1430	1442	1448	BV	195493	4099055	0.75%	0.546%