Electronic Supplementary Material (ESI) for Chemical Science

Metal-Free Oxidative Tandem Coupling of Activated Alkenes with Carbonyl C(sp^2)-H Bonds and Aryl C(sp^2)-H Bonds Using TBHP

Ming-Bo Zhou, Ren-Jie Song,* Xuan-Hui Ouyang, Yu Liu, Wen-Ting Wei, Guo-Bo Deng, and Jin-Heng Li*

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

jhli@hnu.edu.cn and srj0731@gmail.com

Supporting Information

List of Contents

(A) Typical experimental procedure

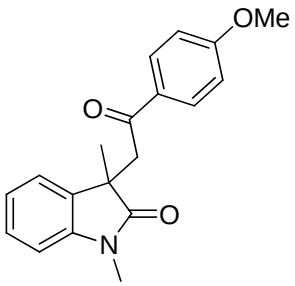
(a) Synthesis of Substrates 1:

All of compounds **1** were synthesized according to the known literatures, and the NMR spectra were consisted with the reported data.[1]

(b) Typical Experimental Procedure for the TBHP-Mediated Oxidative Tandem Coupling of *N*-Arylacrylamides (1) with Carbonyl C(sp^2)-H Bonds (2):

To a Schlenk tube were added *N*-arylacrylamide **1** (0.3 mmol), carbonyl compound **2** (2 equiv), TBHP (anhydrous, 2 equiv) and EtOAc (2 mL). Then the tube was charged with argon, and was stirred at 105 ^{o}C for 36 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product.

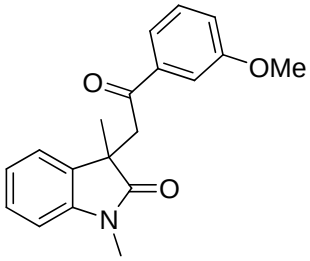
(B) Analytical data



3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3):

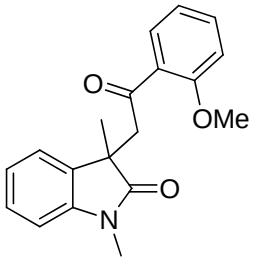
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.0 Hz, 2H), 7.27-7.22 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.98-6.95 (m, 1H), 6.88 (t, *J* = 6.0 Hz, 1H), 6.86 (d, *J* =

7.0 Hz, 2H), 3.83 (s, 3H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.59 (d, *J* = 18.0 Hz, 1H), 3.31 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ: 194.5, 180.7, 163.5, 143.8, 133.9, 130.2, 129.5, 127.7, 122.1, 121.7, 113.6, 108.1, 55.4, 45.6, 45.3, 26.4, 24.9; IR (KBr, cm^{-1}): 1702, 1686; LRMS (EI, 70 eV) *m/z* (%): 309 (M^+, 28), 264 (10), 174 (13), 160 (28), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_3$ ($[M+H]^+$) 310.1438, found 310.1460.



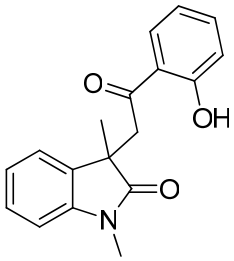
3-(2-(3-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (4):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.06-7.03 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.71 (d, *J* = 18.0 Hz, 1H), 3.64 (d, *J* = 18.0 Hz, 1H), 3.30 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.9, 180.5, 159.6, 143.7, 137.6, 133.6, 129.3, 127.7, 122.1, 121.6, 120.5, 119.9, 111.8, 108.0, 55.3, 46.0, 45.2, 26.3, 24.9; IR (KBr, cm^{-1}): 1699, 1688; LRMS (EI, 70 eV) *m/z* (%): 309 (M^+, 96), 264 (28), 250 (11), 160 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_3$ ($[M+H]^+$) 310.1438, found 310.1445.



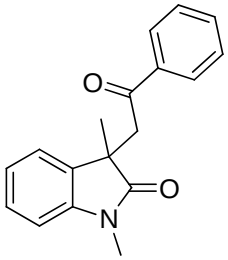
3-(2-(2-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (5):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.37 (m, 2H), 7.25-7.22 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.98-6.95 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.88-6.85 (m, 2H), 3.91 (s, 3H), 3.75 (d, *J* = 18.0 Hz, 1H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.28 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.0, 180.8, 158.6, 143.8, 134.0, 133.6, 130.3, 127.6, 122.6, 122.0, 121.8, 120.5, 111.3, 108.0, 55.5, 51.2, 45.7, 26.4, 25.0; IR (KBr, cm^{-1}): 1694, 1681; LRMS (EI, 70 eV) *m/z* (%): 309 (M^+, 49), 264 (12), 160 (33), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_3$ ($[M+H]^+$) 310.1438, found 310.1454.



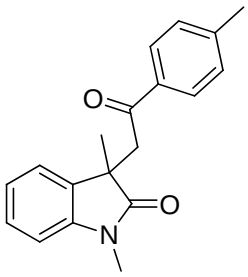
3-(2-(2-Hydroxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (6):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.7 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90-6.86 (m, 3H), 3.73 (d, *J* = 18.0 Hz, 1H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 202.0, 180.3, 162.2, 143.8, 136.4, 133.6, 133.4, 129.6, 128.0, 122.3, 121.7, 118.8, 118.5, 108.2, 45.4, 45.1, 26.5, 25.0; IR (KBr, cm^{-1}): 1673, 1685; LRMS (EI, 70 eV) *m/z* (%): 295 (M^+, 42), 160 (28), 135 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{18}NO_3$ ($[M+H]^+$) 296.1281, found 296.1280.



1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (7):

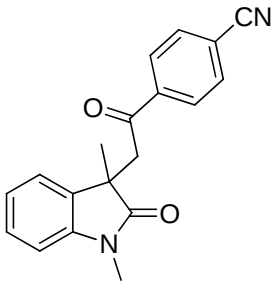
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 3.75 (d, *J* = 18.0 Hz, 1H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.33 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.9, 180.4, 143.7, 136.3, 133.6, 133.0, 128.3, 127.8, 127.7, 122.0, 121.6, 108.0, 45.9, 45.1, 26.3, 24.8; IR (KBr, cm^{-1}): 1676, 1694; LRMS (EI, 70 eV) *m/z* (%): 279 (M^+, 87), 234 (22), 220 (8), 160 (100); HRMS *m/z* (ESI) calcd for $C_{18}H_{18}NO_2$ ($[M+H]^+$) 280.1332, found 280.1342.



1,3-Dimethyl-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (8):

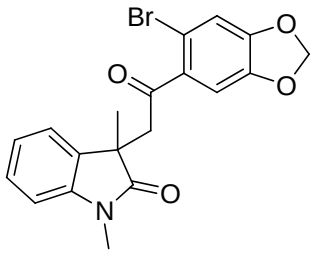
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.0 Hz, 2H), 7.26-7.22 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.98-6.96 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.62 (d, *J* = 18.0 Hz, 1H), 3.30 (s, 3H), 2.36 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.6, 180.6, 143.9, 143.8, 133.9, 133.8, 129.1, 128.0, 127.7, 122.0, 121.7, 108.0, 45.8, 45.2, 26.4, 24.8, 21.5; IR

(KBr, cm^{-1}): 1670, 1682; LRMS (EI, 70 eV) *m/z* (%): 293 (M^+, 78), 248 (23), 174 (30), 160 (79), 119 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_2$ ($[M+H]^+$) 294.1489, found 294.1493.



4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzonitrile (9):

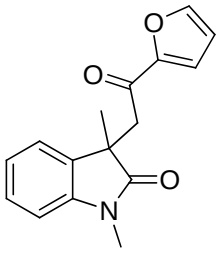
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 3.66 (s, 2H), 3.30 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.9, 180.1, 143.8, 139.2, 133.2, 132.4 128.4, 128.1, 122.3, 121.8, 117.8, 116.5, 108.3, 46.2, 45.3, 26.4, 24.8; IR (KBr, cm^{-1}): 1694, 1680; LRMS (EI, 70 eV) *m/z* (%): 304 (M^+, 37), 259 (13), 245 (7), 160 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{17}N_2O_2$ ($[M+H]^+$) 305.1285, found 305.1288.



3-(2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (10):

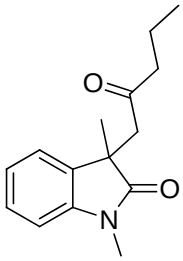
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.29-7.25 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H),

5.99 (s, 2H), 3.64 (d, *J* = 17.5 Hz, 1H), 3.56 (d, *J* = 17.0 Hz, 1H), 3.27 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7, 180.1, 150.1, 147.3, 143.8, 134.2, 133.1, 128.0, 122.3, 122.2, 113.5, 111.1, 108.9, 108.2, 102.3, 49.7, 45.9, 26.4, 24.6; IR (KBr, cm^{-1}): 1710, 1681; LRMS (EI, 70 eV) *m/z* (%): 403 (M^++2, 15), 401 (M^+, 15), 322 (90), 229 (54), 227 (56), 160 (70), 158 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{17}BrNO_4$ ($[M+H]^+$) 402.0335, found 402.0334.



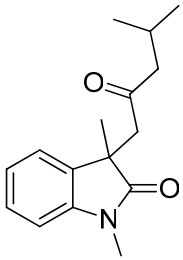
3-(2-(Furan-2-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (11):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 1.5 Hz, 1H), 7.26-7.23 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 6.99-6.96 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 3.5 Hz, 1H), 3.58 (d, *J* = 17.5 Hz, 1H), 3.43 (d, *J* = 17.5 Hz, 1H), 3.29 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 185.4, 180.3, 152.4, 146.2, 143.8, 133.4, 127.9, 122.2, 122.1, 116.9, 112.2, 108.1, 45.4, 45.3, 26.4, 24.5; IR (KBr, cm^{-1}): 1673, 1682; LRMS (EI, 70 eV) *m/z* (%): 269 (M^+, 36), 224 (15), 210 (12), 160 (100); HRMS *m/z* (ESI) calcd for $C_{16}H_{16}NO_3$ ($[M+H]^+$) 270.1130, found 270.1138.



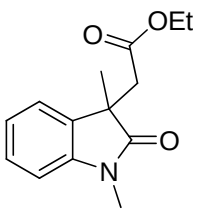
1,3-Dimethyl-3-(2-oxopentyl)indolin-2-one (12):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.28 (s, 3H), 3.08 (s, 2H), 2.31-2.18 (m, 2H), 1.47-1.43 (m, 2H), 1.34 (s, 3H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 206.9, 180.4, 143.7, 133.5, 127.8, 122.1, 121.7, 108.1, 49.7, 45.2, 44.7, 29.7, 24.4, 16.9, 13.5; IR (KBr, cm^{-1}): 1699, 1673; LRMS (EI, 70 eV) *m/z* (%): 246 (M^++1, 13), 245 (M^+, 70), 200 (5), 174 (100); HRMS *m/z* (ESI) calcd for $C_{15}H_{20}NO_2$ ($[M+H]^+$) 246.1489, found 246.1494.



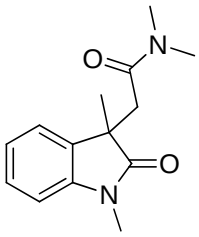
1,3-Dimethyl-3-(4-methyl-2-oxopentyl)indolin-2-one (13):

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.22 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.27 (s, 3H), 3.06 (s, 2H), 2.17-2.07 (m, 2H), 2.04-1.92 (m, 1H), 1.32 (s, 3H), 0.78 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.8, 180.3, 143.6, 133.4, 127.8, 122.1, 121.6, 108.1, 51.7, 50.1, 45.1, 26.3, 24.4 (2C), 22.4, 22.3; IR (KBr, cm^{-1}): 1697, 1678; LRMS (EI, 70 eV) *m/z* (%): 259 (M^+, 68), 244 (11), 174 (100), 160 (72); HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_2$ ($[M+H]^+$) 260.1651, found 260.1643.



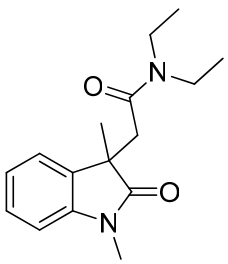
Ethyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (14):

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.94-3.81 (m, 2H), 3.25 (s, 3H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H), 0.99 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.9, 169.7, 143.6, 132.9, 128.1, 122.3 (2C), 108.0, 60.3, 45.6, 41.7, 26.3, 24.4, 13.8; IR (KBr, cm^{-1}): 1722, 1683; LRMS (EI, 70 eV) *m/z* (%): 247 (M^+, 44), 202 (5), 160 (100); HRMS *m/z* (ESI) calcd for $C_{14}H_{18}NO_3$ ($[M+H]^+$) 248.1281, found 248.1285.



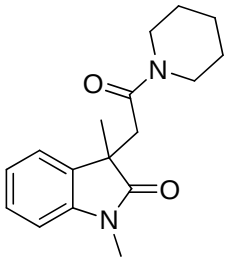
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylacetamide (15):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.27 (s, 3H), 3.01 (d, *J* = 16.5 Hz, 1H), 2.96 (s, 3H), 2.95 (d, *J* = 16.5 Hz, 1H), 2.76 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 180.9, 168.9, 143.8, 134.3, 127.6, 121.9, 121.5, 108.1, 45.7, 40.7, 37.2, 35.3, 26.3, 24.8; IR (KBr, cm^{-1}): 1698, 1678; LRMS (EI, 70 eV) *m/z* (%): 246 (M^+, 56), 174 (87), 160 (100); HRMS *m/z* (ESI) calcd for $C_{14}H_{19}N_2O_2$ ($[M+H]^+$) 247.1441, found 247.1453.



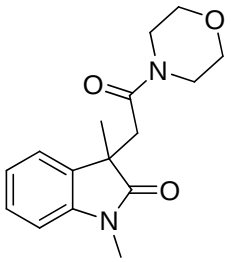
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-diethylacetamide (16):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.41 (s, 3H), 3.32-3.23 (m, 2H), 3.22-3.13 (m, 2H), 2.98 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 180.9, 167.9, 143.8, 134.3, 127.6, 121.9, 121.6, 108.8, 45.9, 41.9, 40.3, 39.8, 26.4, 24.8, 14.3, 12.9; IR (KBr, cm^{-1}): 1693, 1678; LRMS (EI, 70 eV) *m/z* (%): 274 (M^+, 29), 174 (50), 72 (100); HRMS *m/z* (ESI) calcd for $C_{16}H_{23}N_2O_2$ ($[M+H]^+$) 275.1754, found 275.1752.



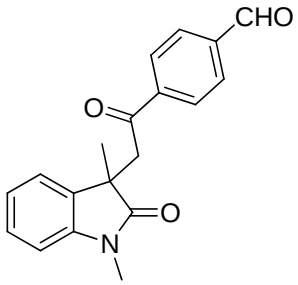
1,3-Dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (17):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.37-3.32 (m, 4H), 3.27 (s, 3H), 3.02 (d, *J* = 16.5 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 1.58-1.50 (m, 6H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 181.0, 167.1, 143.8, 134.4, 127.6, 122.0, 121.6, 108.1, 46.6, 45.8, 42.6, 40.5, 26.4, 25.0, 24.4; IR (KBr, cm^{-1}): 1696, 1676; LRMS (EI, 70 eV) *m/z* (%): 286 (M^+, 21), 174 (18), 160 (20), 126 (100). HRMS *m/z* (ESI) calcd for $C_{17}H_{23}N_2O_2$ ($[M+H]^+$) 287.1754, found 275.1747.



1,3-Dimethyl-3-(2-morpholino-2-oxoethyl)indolin-2-one (18):

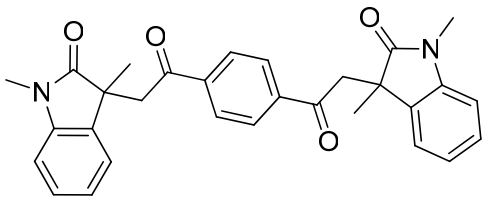
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.63-3.60 (m, 2H), 3.54-3.53 (m, 2H), 3.49-3.32 (m, 4H), 3.27 (s, 3H), 3.01 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 180.7, 167.6, 143.7, 134.0, 127.8, 122.1, 121.6, 108.1, 66.7, 66.4, 45.9, 45.7, 41.7, 40.2, 26.4, 24.9; IR (KBr, cm^{-1}): 1704, 1682; LRMS (EI, 70 eV) *m/z* (%): 289 (M^++1, 9), 288 (M^+, 46), 202 (25), 174 (100); HRMS *m/z* (ESI) calcd for $C_{16}H_{21}N_2O_3$ ($[M+H]^+$) 289.1547, found 289.1555.



4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzaldehyde (19):

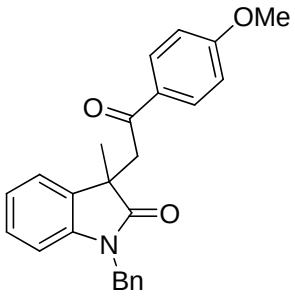
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.1 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 4.0 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 3.74 (d, *J* = 18.0 Hz, 1H), 3.69 (d, *J* = 18.0 Hz, 1H), 3.31 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 191.4, 180.2, 143.7, 140.4, 139.0, 133.3, 129.6, 128.4, 127.9, 122.2, 121.7, 108.2, 46.4, 45.2,

26.4, 24.8; IR (KBr, cm^{-1}): 1723, 1683, 1600; LRMS (EI, 70 eV) *m/z* (%): 308 (M^++1, 11), 307 (M^+, 44), 262 (17), 248 (7), 174 (23), 160 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{18}NO_3$ ($[M+H]^+$) 308.1281, found 308.1288.



3,3'-(1,4-Phenylenebis(2-oxoethane-2,1-diyl))bis(1,3-dimethylindolin-2-one) (20):

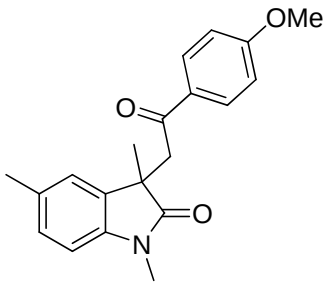
White solid, mp 183.5-184.3 ^oC (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.83 (s, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.71-3.61 (m, 2H), 3.30 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 180.3, 143.8, 139.4, 133.4, 128.1, 128.0, 122.2, 121.7, 108.2, 46.3, 45.2, 26.4, 24.9; IR (KBr, cm^{-1}): 1715, 1686, 1598; LRMS (EI, 70 eV) *m/z* (%): 480 (M^+, 56), 435 (12), 306 (16), 174 (38), 160 (100); HRMS *m/z* (ESI) calcd for $C_{30}H_{29}N_2O_4$ ($[M+H]^+$) 481.2127, found 481.2134.



1-Benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one (21):

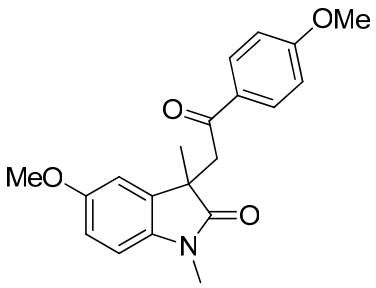
Yellow Soild, mp 101.2-102.3 ^oC (uncorrected);; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.07 (d, *J* = 15.5 Hz, 1H), 4.95

(d, *J* = 15.5 Hz, 1H), 3.79 (s, 3H), 3.74-3.65 (m, 2H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.3, 180.6, 163.4, 142.7, 136.2, 133.8, 130.2, 129.4, 128.6, 127.5, 127.2, 127.1, 122.0, 121.6, 113.5, 109.1, 55.3, 45.4, 45.3, 43.8, 25.4; IR (KBr, cm^{-1}): 1713, 1686; LRMS (EI, 70 eV) *m/z* (%): 385 (M^+, 42), 250 (9), 235 (50), 135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{24}NO_3$ ($[M+H]^+$) 386.1751, found 386.1757.



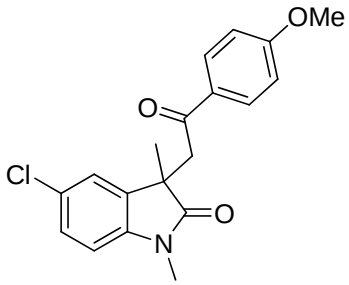
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,5-trimethylindolin-2-one (22):

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 6.86 (d, *J* = 6.5 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.65 (d, *J* = 18.0 Hz, 1H), 3.59 (d, *J* = 18.0 Hz, 1H), 3.28 (s, 3H), 2.27 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.6, 180.7, 163.4, 133.9, 131.5, 130.2, 129.5, 128.0, 122.7, 113.5, 107.8, 55.4, 45.6, 45.3, 26.4, 25.0, 21.1; IR (KBr, cm^{-1}): 1701, 1683; LRMS (EI, 70 eV) *m/z* (%): 323 (M^+, 87), 278 (30), 174 (88), 135 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_3$ ($[M+H]^+$) 324.1594, found 324.1621.



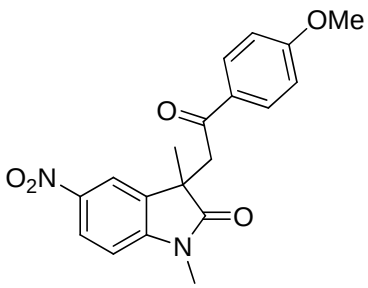
5-Methoxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (23):

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H), 6.86 (dd, *J* = 7.0 Hz, 2.0 Hz, 2H), 6.80-6.75 (m, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 3.63 (d, *J* = 17.5 Hz, 1H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.28 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.5, 180.4, 163.5, 155.7, 137.4, 135.4, 130.2, 129.5, 113.6, 111.4, 109.9, 108.2, 55.7, 55.4, 45.7, 45.6, 26.5, 25.0; IR (KBr, cm^{-1}): 1700, 1684; LRMS (EI, 70 eV) *m/z* (%): 339 (M^+, 94), 294 (40), 280 (12), 254 (11), 190 (100), 135 (91); HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_4$ ($[M+H]^+$) 340.1543, found 340.1555.



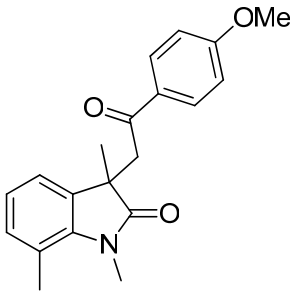
5-Chloro-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (24):

Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 6.88-6.86 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.66 (d, *J* = 18.0 Hz, 1H), 3.62 (d, *J* = 18.0 Hz, 1H), 3.29 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.2, 180.2, 163.6, 142.5, 135.7, 130.2, 129.2, 127.6, 127.3, 122.2, 113.6, 109.0, 55.4, 45.7, 45.4, 26.5, 24.8; IR (KBr, cm^{-1}): 1694, 1680; LRMS (EI, 70 eV) *m/z* (%): 345 (M^++2, 18), 343 (M^+, 54), 298 (10), 194 (25), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{19}ClNO_3$ ($[M+H]^+$) 344.1048, found 344.1054.



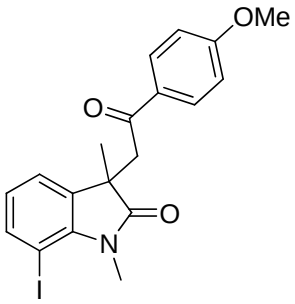
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-5-nitroindolin-2-one (25):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 7.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.78 (d, *J* = 18.0 Hz, 1H), 3.73 (d, *J* = 18.0 Hz, 1H), 3.39 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.2, 180.8, 163.9, 149.8, 143.1, 135.0, 130.3, 128.8, 125.3, 117.3, 113.8, 107.6, 55.5, 46.0, 45.1, 26.9, 24.7; IR (KBr, cm^{-1}): 1692, 1676; LRMS (EI, 70 eV) *m/z* (%): 354 (M^+, 13), 306 (10), 219 (30), 205 (39), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{19}N_2O_5$ ($[M+H]^+$) 355.1294, found 355.1287.



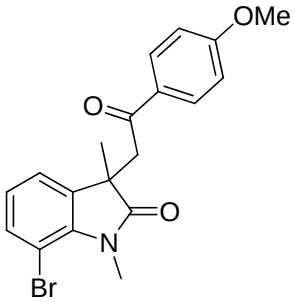
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,7-trimethylindolin-2-one (26):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 7.0 Hz, 2H), 6.87-6.84 (m, 3H), 3.83 (s, 3H), 3.64 (d, *J* = 18.0 Hz, 1H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.58 (s, 3H), 2.61 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.6, 181.5, 163.4, 141.6, 134.5, 131.5, 130.2, 129.5, 122.0, 119.6, 119.4, 113.6, 55.4, 45.9, 44.7, 29.8, 25.5, 19.1; IR (KBr, cm^{-1}): 1699, 1686; LRMS (EI, 70 eV) *m/z* (%): 323 (M^+, 60), 264 (4), 174 (68), 135 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_3$ ($[M+H]^+$) 324.1594, found 324.1616.



7-Iodo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (27):

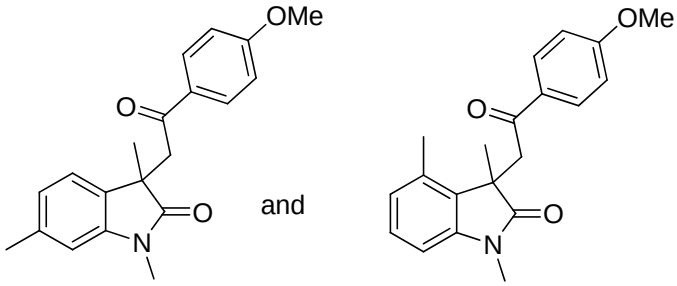
Red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (t, *J* =7.0 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.64 (s, 2H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.3, 181.5, 163.6, 144.2, 140.2, 137.1, 130.2, 129.2, 123.8, 121.2, 113.6, 71.9, 55.4, 45.9, 44.8, 30.3, 25.3; IR (KBr, cm^{-1}): 1695, 1680; LRMS (EI, 70 eV) *m/z* (%): 435 (M^+, 43), 300 (6), 286 (13), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{19}INO_3$ ($[M+H]^+$) 436.0404, found 436.0401.



7-Bromo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (28):

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.79 (t, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.65 (s, 2H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.3, 181.2, 163.6, 141.2, 137.1, 133.3, 130.2, 129.2, 123.2, 120.5, 113.6, 102.6, 55.4, 46.0, 45.0, 30.0, 25.3; IR (KBr, cm^{-1}): 1697, 1682; LRMS (EI, 70 eV) *m/z* (%):

389 (M^++2, 12), 387 (M^+, 12), 240 (6), 238 (6), 135 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{19}BrNO_3$ ($[M+H]^+$) 388.0543, found 388.0539.

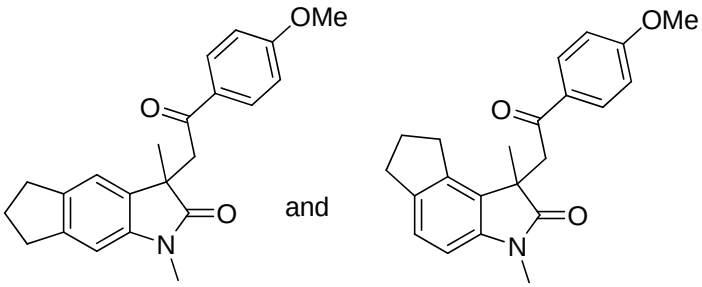


3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,6-trimethylindolin-2-one (29)

and 3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,4-trimethylindolin-2-one (29´):

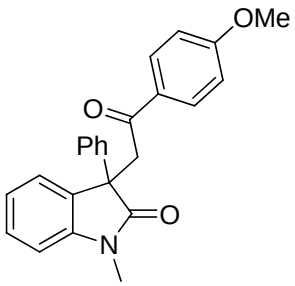
29:29´ = 2:1

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.85-7.79 (m, 2H), 7.16 (m, 0.6H), 7.01 (d, *J* = 7.5 Hz, 0.4H), 6.89-6.84 (m, 2H), 6.77 (d, *J* = 7.5 Hz, 0.5H), 6.72 (d, *J* = 8.0 Hz, 1.5H), 3.92 (d, *J* = 18.0 Hz, 0.6H), 3.81 (s, 3H), 3.67-3.62 (m, 1H), 3.56 (d, *J* = 18.0 Hz, 0.4H), 3.28 (s, 1H), 3.26 (s, 2H), 2.35 (s, 1H), 2.86 (s, 2H), 1.47 (s, 2H), 1.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 181.0, 180.6, 163.4, 144.0, 143.8, 137.7, 132.6, 130.9, 130.5, 130.2, 130.1, 129.5, 129.2, 128.6, 127.5, 124.7 (2C), 122.5, 121.4, 113.6, 113.5, 109.1, 105.9, 55.3, 46.1, 45.6, 45.1, 44.5, 29.6, 26.4, 24.9, 22.8, 21.7, 18.1; IR (KBr, cm^{-1}): 1701, 1678; LRMS (EI, 70 eV) *m/z* (%): 323 (M^+, 79), 308 (6), 174 (77), 173 (83), 135 (100); LRMS (EI, 70 eV) *m/z* (%): 323 (M^+, 60), 264 (4), 174 (68), 135 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{22}NO_3$ ($[M+H]^+$) 324.1594, found 324.1619.



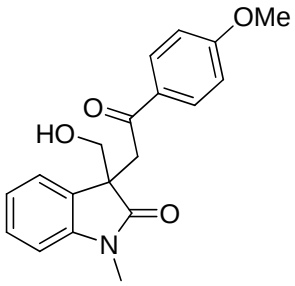
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[*f*]indol-2(1*H*)-one (30) and 1-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[*e*] indol-2(1*H*)-one (30´): 30:30´ = 2:1

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 9.0 Hz, 0.7H), 7.81 (d, *J* = 8.5 Hz, 1.3H), 7.08 (d, *J* = 7.5 Hz, 0.6H), 6.99 (s, 0.4H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.78 (s, 0.4H), 6.68 (d, *J* = 8.0 Hz, 0.6H), 3.82 (s, 3H), 3.78 (d, *J* = 17.5 Hz, 0.6H), 3.65 (d, *J* = 16.0 Hz, 0.7H), 3.57 (d, *J* = 18.0 Hz, 0.6H), 3.29 (s, 1H), 3.27 (s, 2H), 2.93-2.69 (m, 4H), 2.07-1.99 (m, 2H), 1.43 (s, 2H), 1.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.7, 194.6, 180.4, 163.4, 143.4, 142.3, 142.2, 138.9, 138.2, 137.5, 132.1, 130.2 (2C), 129.6, 129.3, 128.5, 122.9, 118.0, 113.5 (2C), 106.1, 104.7, 55.4, 45.7, 45.5, 45.2, 44.5, 32.2, 32.4, 31.5, 30.0, 26.6, 26.4, 25.7, 25.4, 25.2, 23.0; IR (KBr, cm^{-1}): 1703, 1680; LRMS (EI, 70 eV) *m/z* (%): 349 (M^+, 48), 304 (20), 200 (100), 135 (34); LRMS (EI, 70 eV) *m/z* (%): 349 (M^+, 29), 200 (26), 199 (100), 135 (16); HRMS *m/z* (ESI) calcd for $C_{22}H_{24}NO_3$ ($[M+H]^+$) 350.1756, found 350.1760.



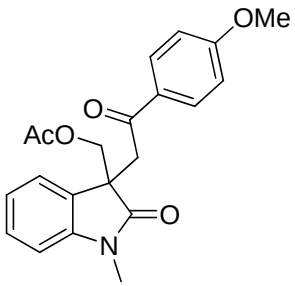
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-3-phenylindolin-2-one (32):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 6.5 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.31-7.22 (m, 5H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 7.0 Hz, 2H), 4.07 (d, *J* = 18.0 Hz, 1H), 4.03 (d, *J* = 18.0 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.1, 178.7, 163.5, 144.7, 139.6, 131.6, 130.2, 129.4, 128.5, 128.2, 127.4, 126.7, 124.0, 122.0, 113.6, 108.3, 55.3, 53.1, 46.5, 26.6; IR (KBr, cm^{-1}): 1700, 1671; LRMS (EI, 70 eV) *m/z* (%): 371 (M^+, 56), 326 (10), 278 (15), 236 (24), 222 (75), 135 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{22}NO_3$ ($[M+H]^+$) 372.1594, found 372.1596.



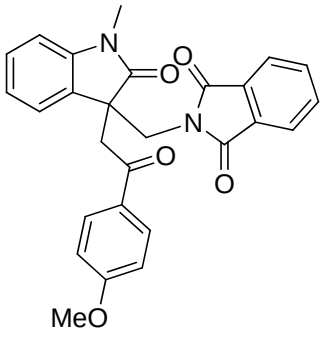
3-(Hydroxymethyl)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (33):

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 9.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.91 (d, *J* = 18.0 Hz, 1H), 3.84 (s, 3H), 3.83-3.76 (m, 2H), 3.70 (d, *J* = 11.0 Hz, 1H), 3.33 (s, 3H), 2.04 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.9, 179.4, 163.6. 144.5, 130.3, 129.7, 129.5, 128.5, 122.4 (2C), 113.7, 108.4, 67.2, 55.4, 50.9, 41.5, 26.4; IR (KBr, cm^{-1}): 1797, 1668; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 2), 323 (52), 278 (19), 174 (100), 135 (81); HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_4$ ($[M+H]^+$) 326.1392, found 326.1385.



(3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (34):

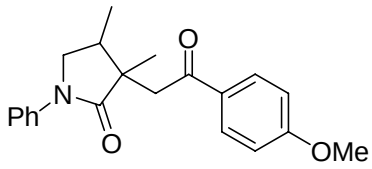
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (dt, *J* = 7.5 Hz, 3.5 Hz, 2H), 7.29 (d, *J* = 10.0 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 6.97 (dt, *J* = 9.5 Hz, 1.5 Hz, 1H), 6.91-6.85 (m, 3H), 4.52 (d, *J* = 13.5 Hz, 1H), 4.16 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H), 3.79 (d, *J* = 22.0 Hz, 1H), 3.63 (d, *J* = 22.0 Hz, 1H), 3.31 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.7, 177.4, 170.3, 163.7, 144.6, 130.3, 129.5, 129.4, 128.5, 122.9, 122.2, 113.7, 108.2, 67.6, 55.4, 49.3, 41.6, 26.5, 20.6; IR (KBr, cm^{-1}): 1716, 1684, 1600; LRMS (EI, 70 eV) *m/z* (%): 367 (M^+, 31), 295 (14), 263 (7), 174 (35), 160 (100), 135 (83); HRMS *m/z* (ESI) calcd for $C_{21}H_{22}NO_5$ ($[M+H]^+$) 368.1492, found 368.1491.



2-((3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl)isoindoline-1,3-dione (35):

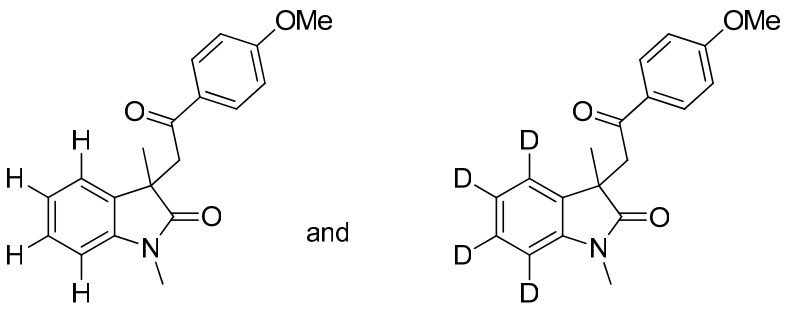
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.5 Hz, 2H), 7.77 (t, *J* = 6.0 Hz, 4H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 3H), 6.77 (t, *J* = 7.5 Hz, 1H),

4.00 (d, *J* = 9.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.73 (s, 3H), 3.72 (d, *J* = 9.5 Hz, 1H), 3.50 (d, *J* = 17.5 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.2, 177.7, 167.8, 163.5, 144.5, 134.4, 131.8, 130.5, 130.3, 129.4, 128.0, 123.7, 122.8, 121.9, 113.6, 108.0, 74.5, 55.4, 50.5, 41.5, 26.5, 21.0; IR (KBr, cm^{-1}): 1706, 1688; LRMS (EI, 70 eV) *m/z* (%): 454 (M^+, 8), 319 (25), 160 (10), 135 (73); HRMS *m/z* (ESI) calcd for $C_{27}H_{23}N_2O_5$ ($[M+H]^+$) 455.1607, found 455.1613.



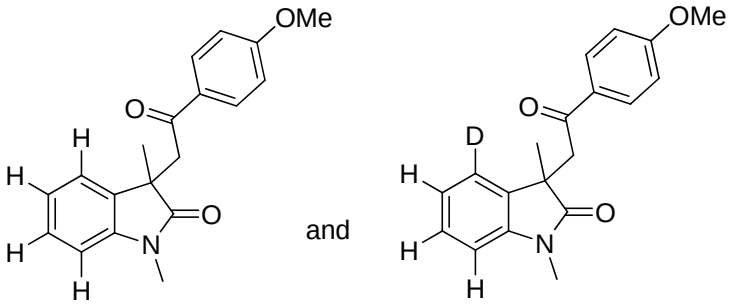
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-3,4-dimethyl-1-phenylpyrrolidin-2-one (36):

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.95 (m, 2H), 7.67-7.64 (m, 2H), 7.38-7.32 (m, 2H), 7.14-7.10 (m, 1H), 6.97-6.90 (m, 2H), 3.90-3.84 (m, 1H), 3.86 (s, 3H), 3.46-3.41 (m, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 3.19 (d, *J* = 17.2 Hz, 1H), 2.87-2.76 (m, 1H), 1.15 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.3, 178.1, 163.5, 139.8, 130.4, 130.3, 128.8, 124.1, 119.8, 113.7, 55.5, 52.6, 46.5, 43.4, 32.8, 18.2, 12.6; IR (KBr, cm^{-1}): 1698, 1671; LRMS (EI, 70 eV) *m/z* (%): 337 (M^+, 22), 160 (31), 135 (100); HRMS *m/z* (ESI) calcd for $C_{21}H_{24}NO_3$ ($[M+H]^+$) 338.1756, found 338.1762.



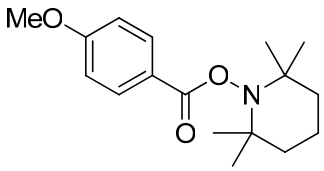
3 and 3-*D*$_4$:

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 0.5H), 7.13 (d, *J* = 7.5 Hz, 0.5H), 6.96 (t, *J* = 7.5 Hz, 0.5H), 6.89 (d, *J* = 7.5 Hz, 0.5H), 6.85 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.30 (s, 3H), 1.43 (s, 3H).



3 and 3-*D*$_1$:

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 9.0 Hz, 2H), 7.25 (t, 7.5 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 0.5H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.67 (d, *J* = 18.0 Hz, 1H), 3.59 (d, *J* = 17.5 Hz, 1H), 3.30 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.6, 134.7, 132.9, 120.9, 116.6, 115.3, 99.5; LRMS (EI, 70 eV) *m/z* (%): 119 (M^+, 100), 88 (50).



2,2,6,6-Tetramethylpiperidin-1-yl 4-methoxybenzoate (36):[2]

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 6.8 Hz, 2H), 76.94 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H), 1.80-1.66 (m, 3H), 1.59-1.55 (m, 2H), 1.47-1.41 (m, 1H), 1.26 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 163.2, 131.5, 121.9,

113.6, 60.2, 55.3, 38.9, 31.9, 20.8, 16.9; LRMS (EI, 70 eV) *m/z* (%): 291 (M^+, 18), 140 (100).

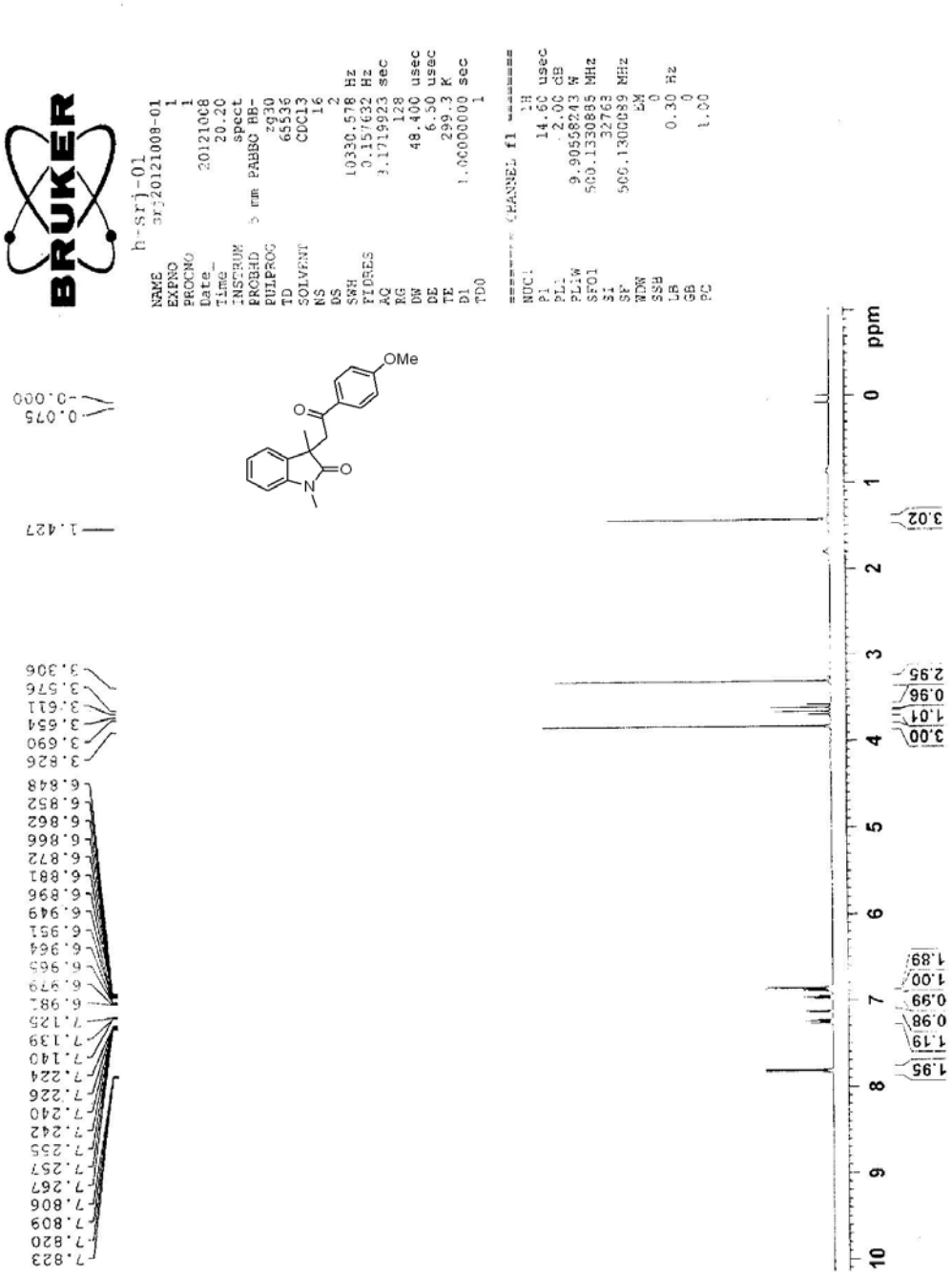
(D) Reference

(1) (a) Mu, X.; Wu, T.; Wang, H.-Y.; Guo, Y.-L.; Liu, G.-S. *J. Am. Chem. Soc.* **2012**, *134*, 878. (b) Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J. *Chem. Eur. J.* **2007**, *13*, 961. (c) Jones, K.; Thompson, M.; Wright, C. *J. Chem. Soc., Chem. Commun.* **1986**, 715.

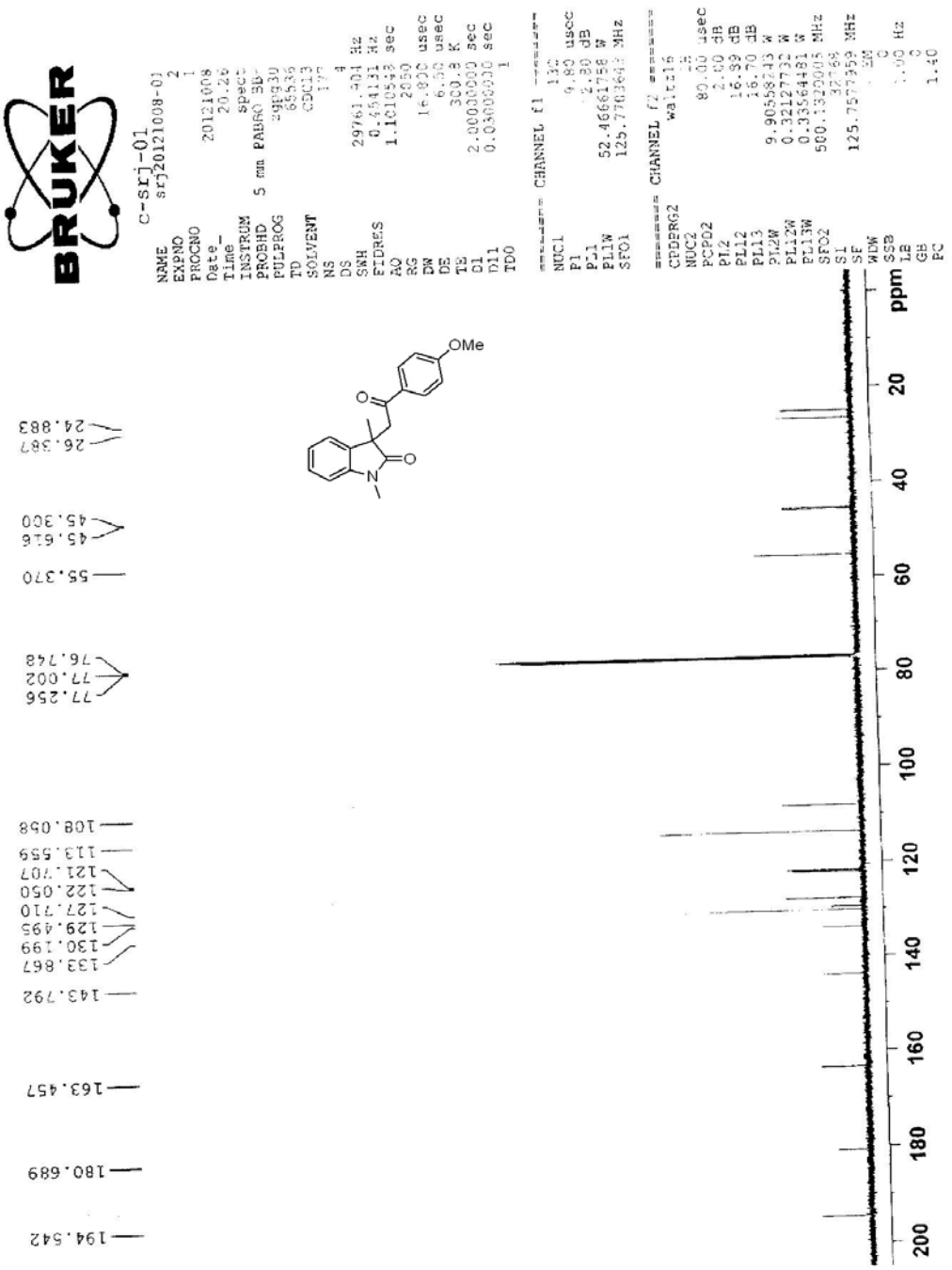
(2) Guin, J.; Sarkar, S. D.; Grimme, S.; Studer, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 8727.

(D) Spectra

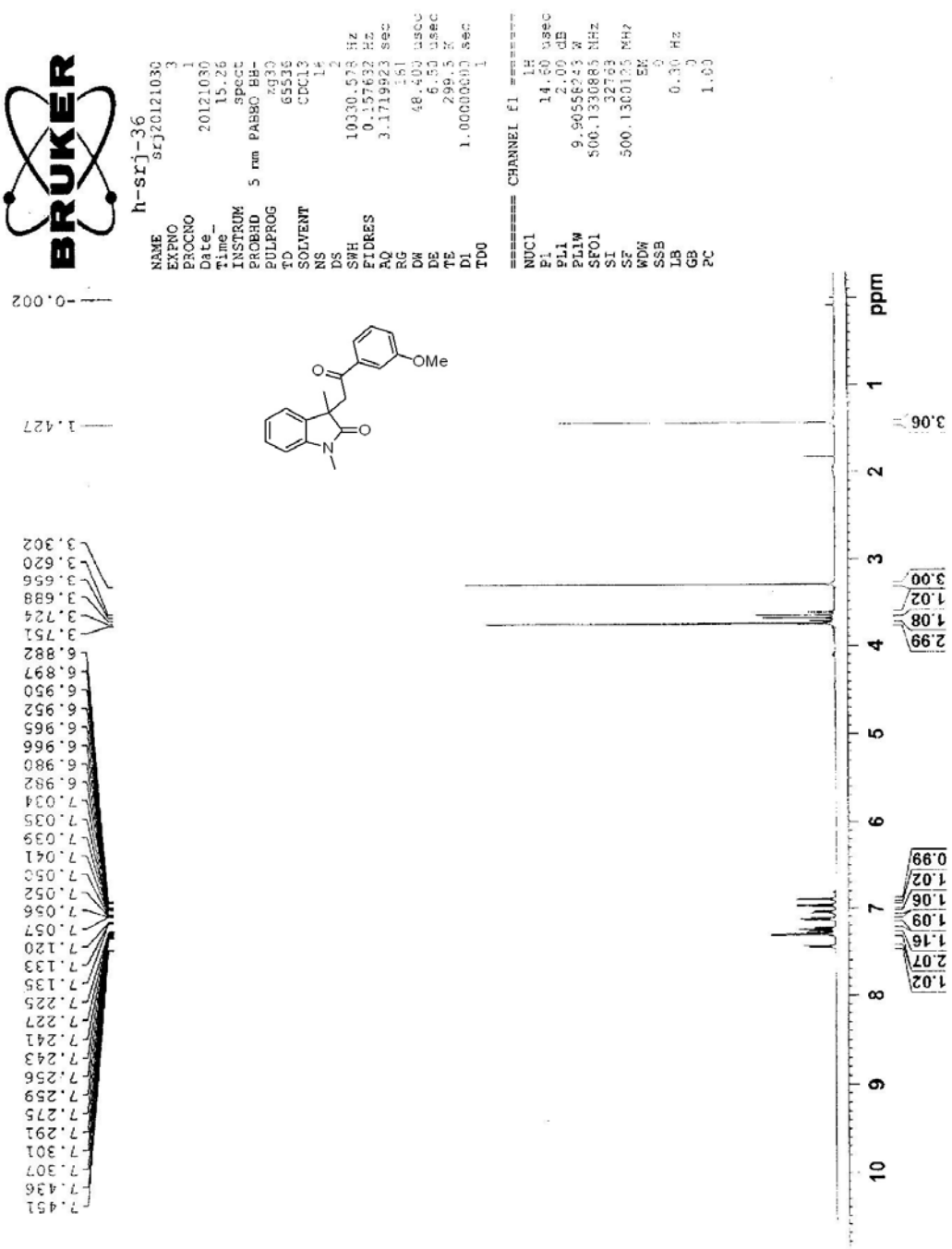
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3)



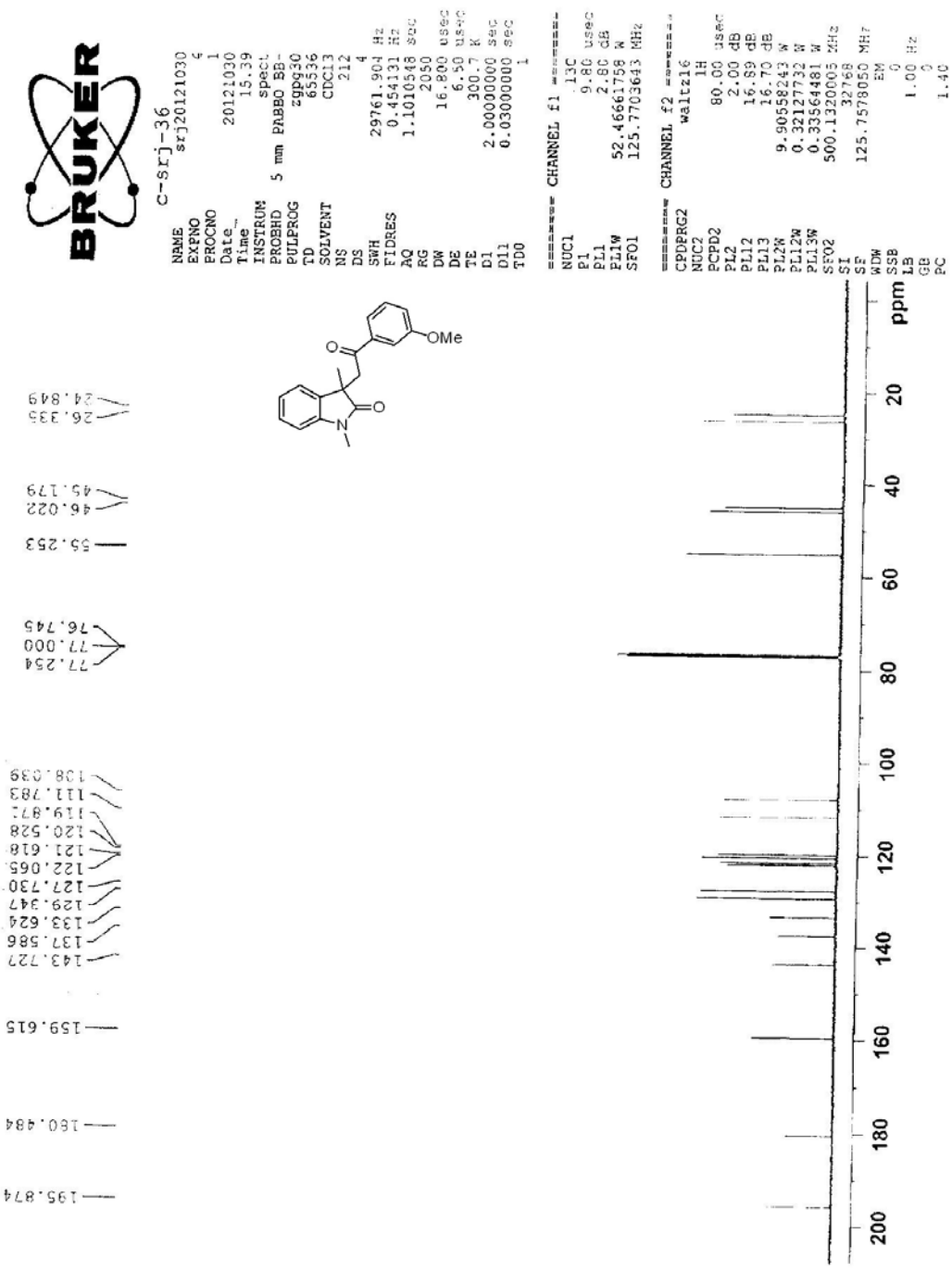
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3)



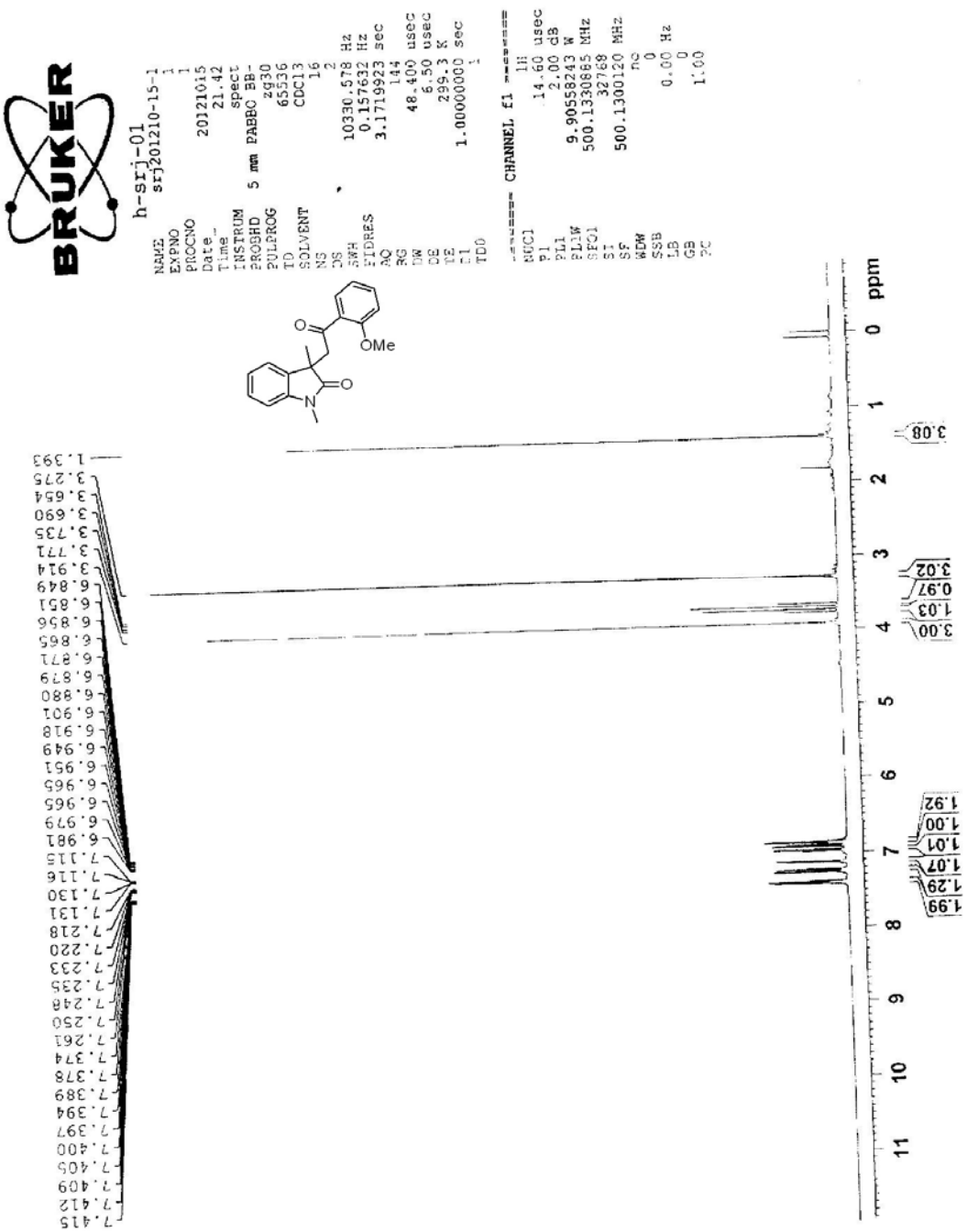
3-(2-(3-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (4)



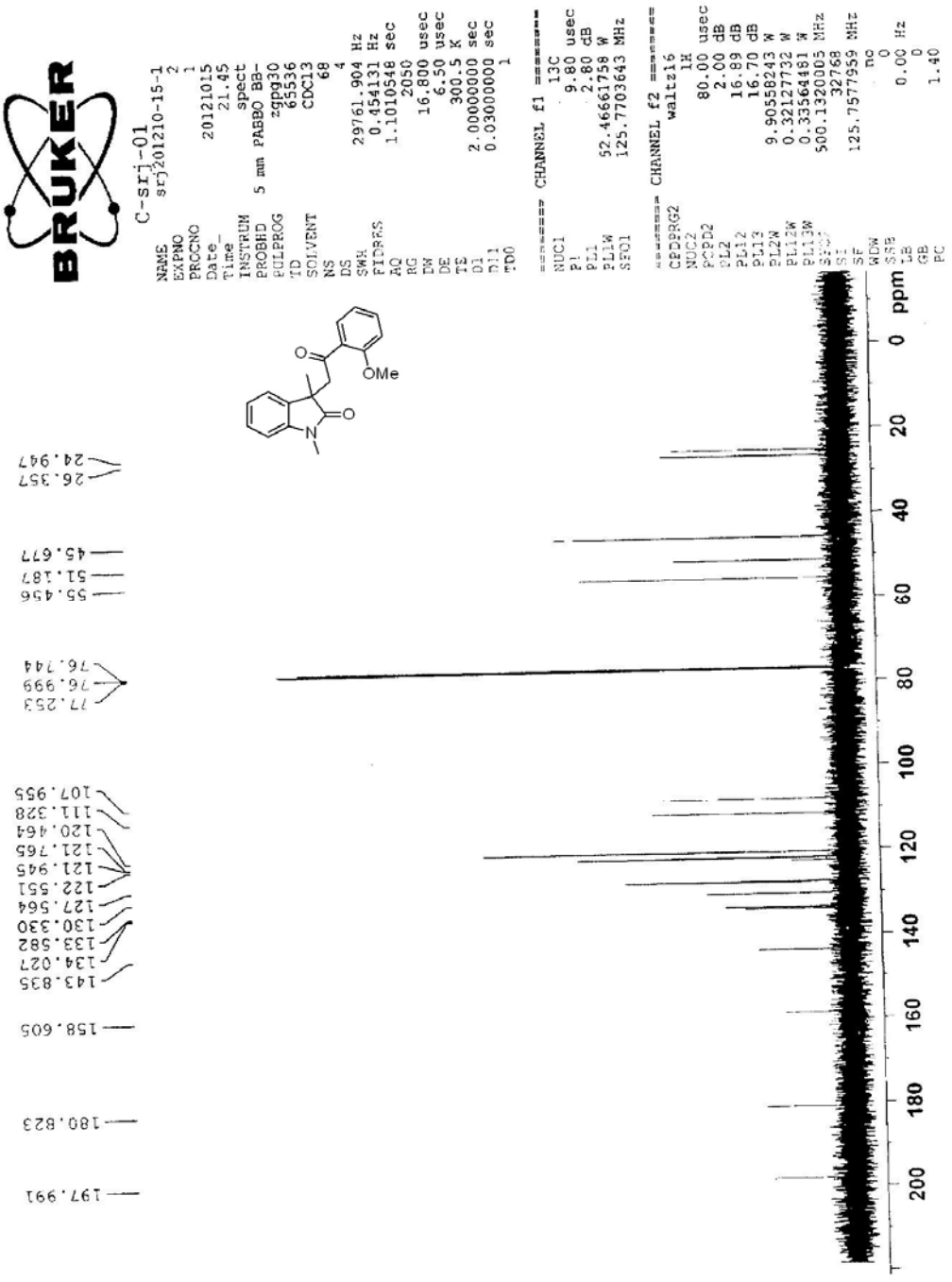
3-(2-(3-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (4)



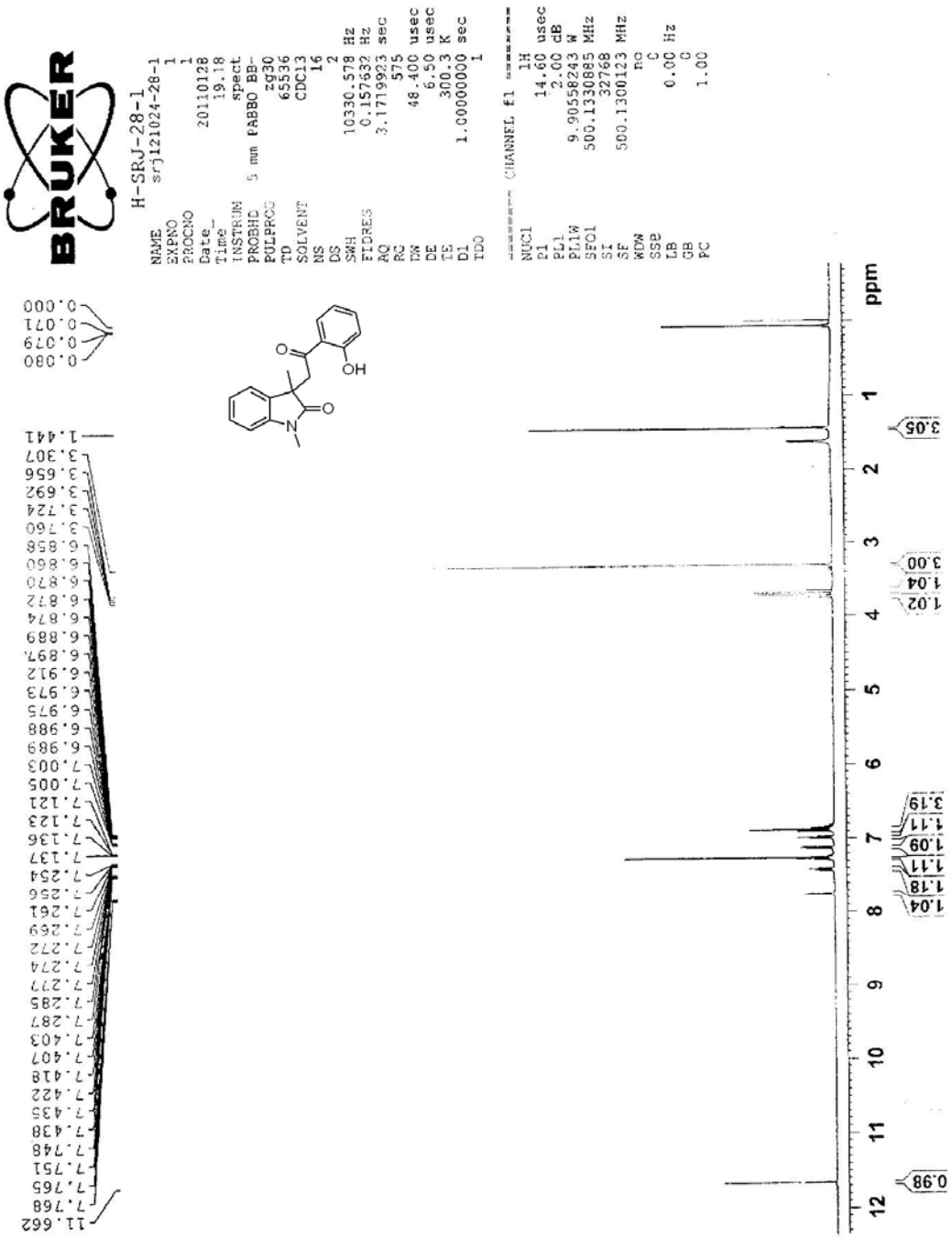
3-(2-(2-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (5)



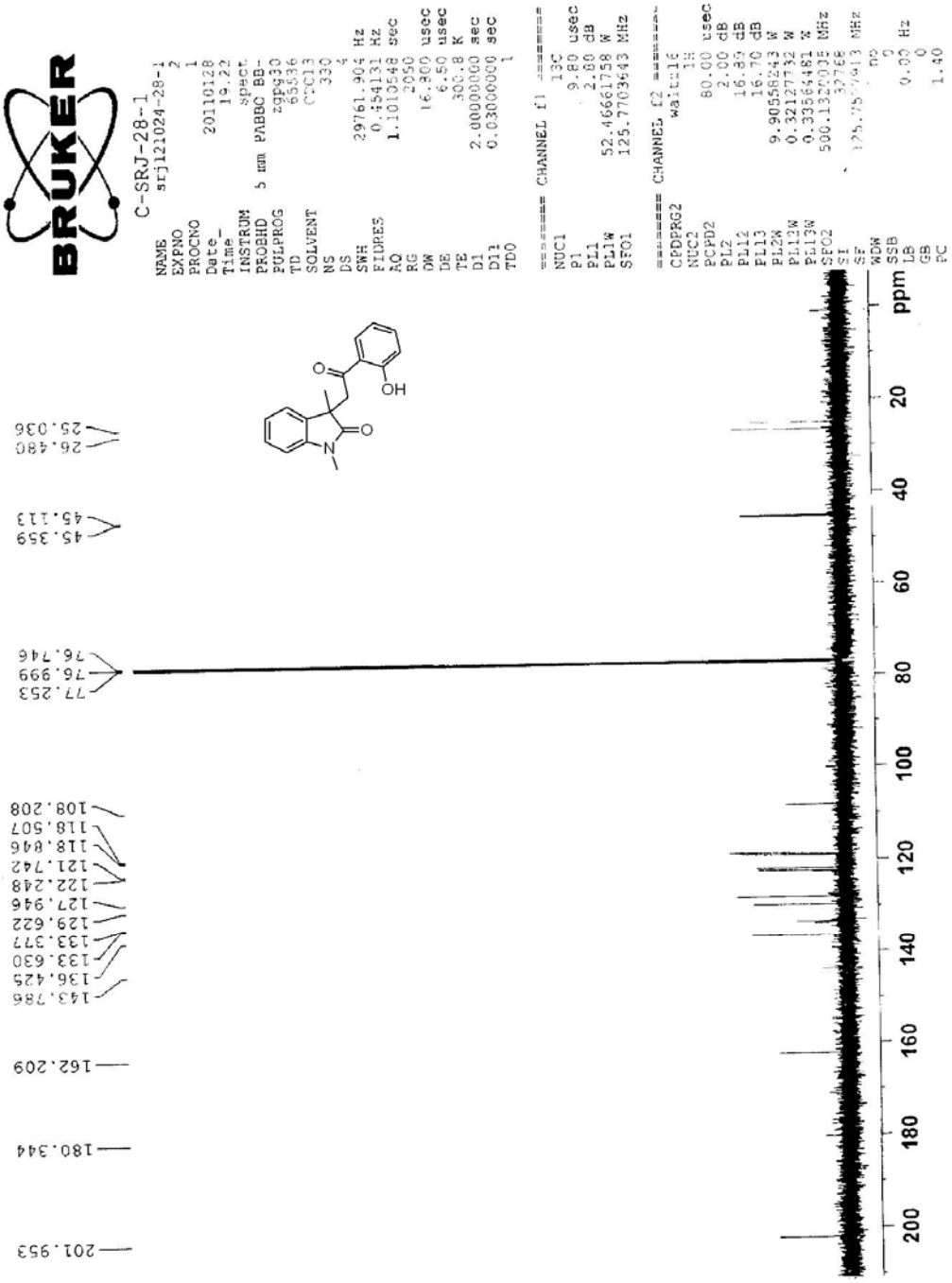
3-(2-(2-Methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (5)



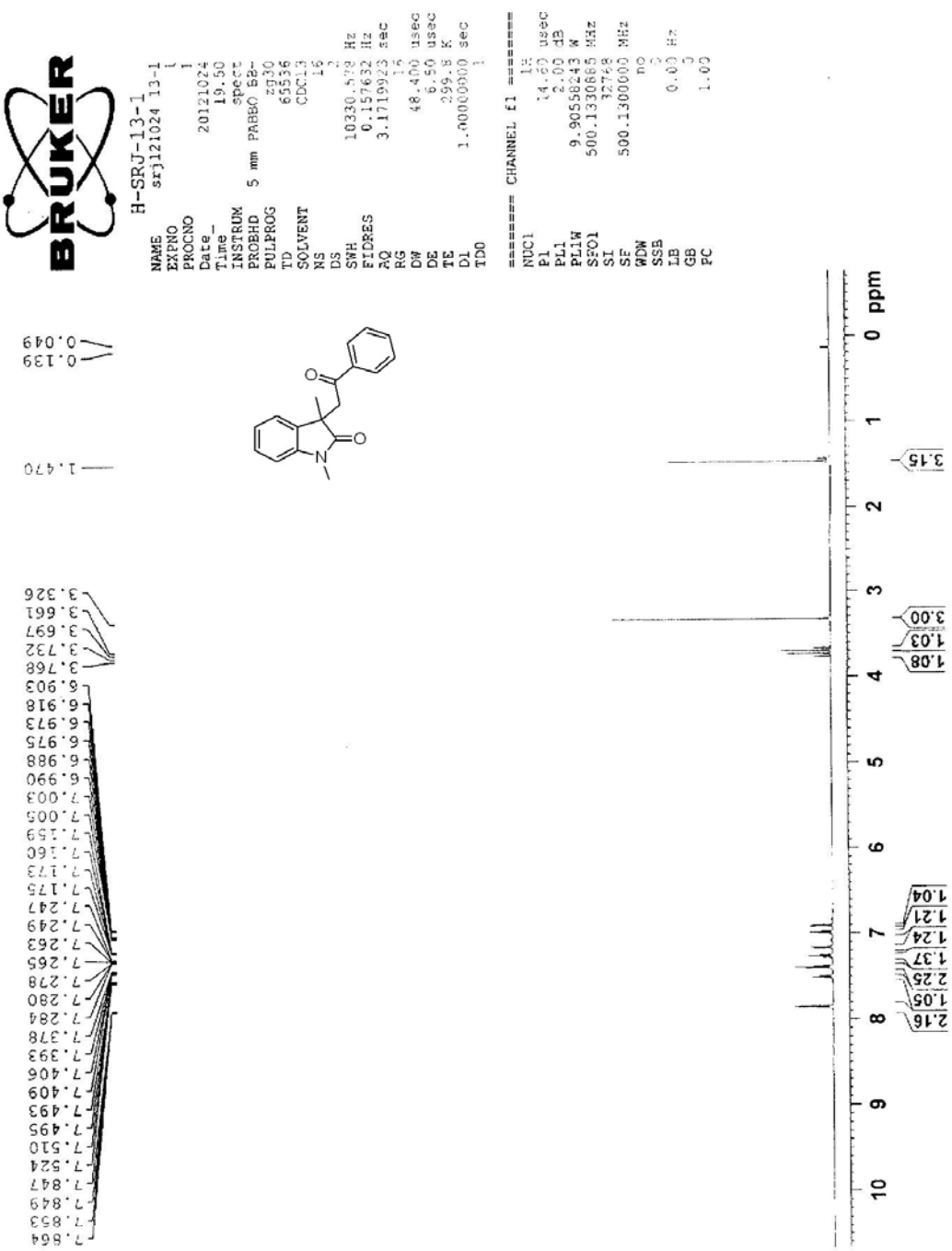
3-(2-(2-Hydroxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (6)



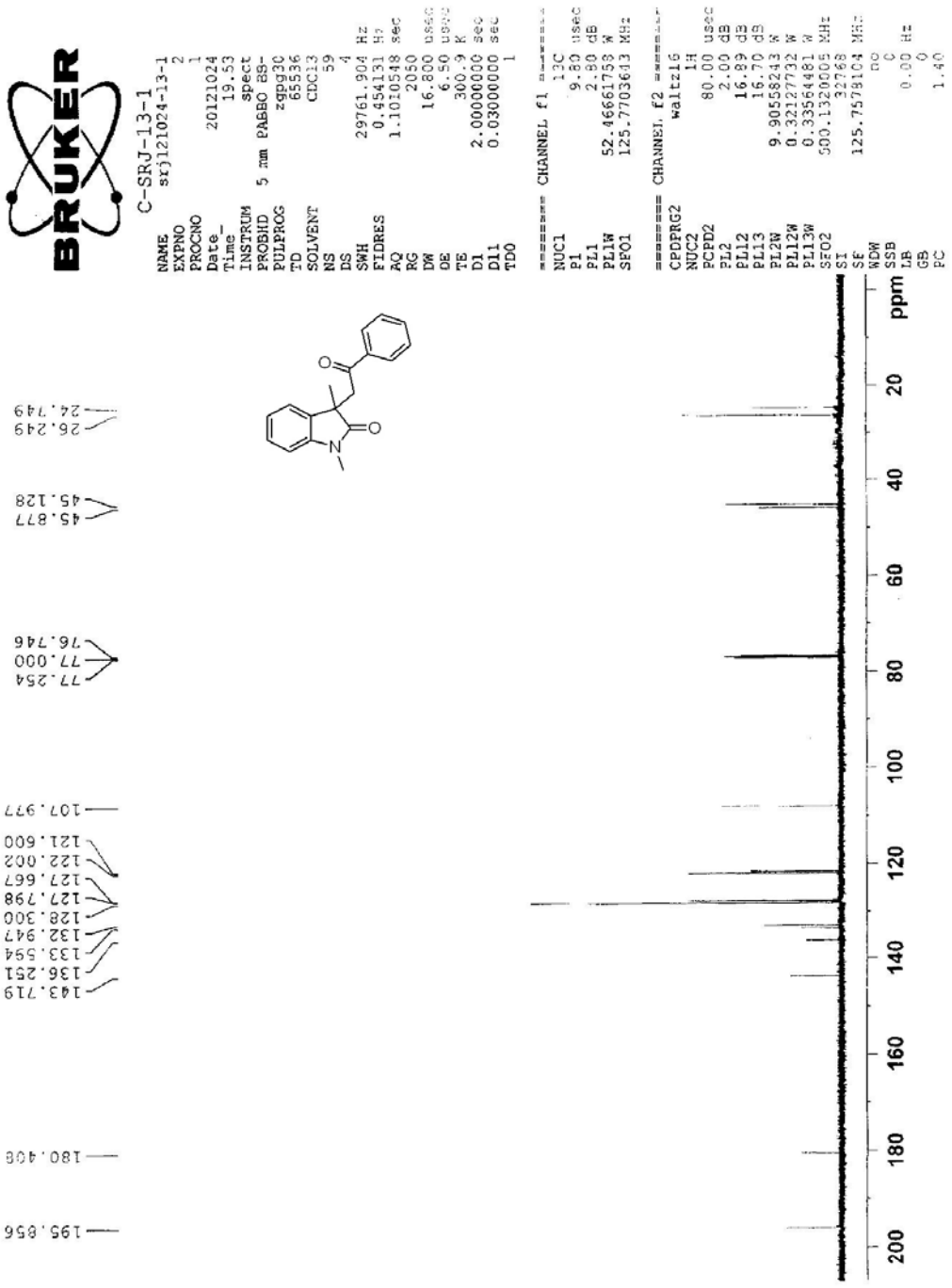
3-(2-(2-Hydroxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (6)



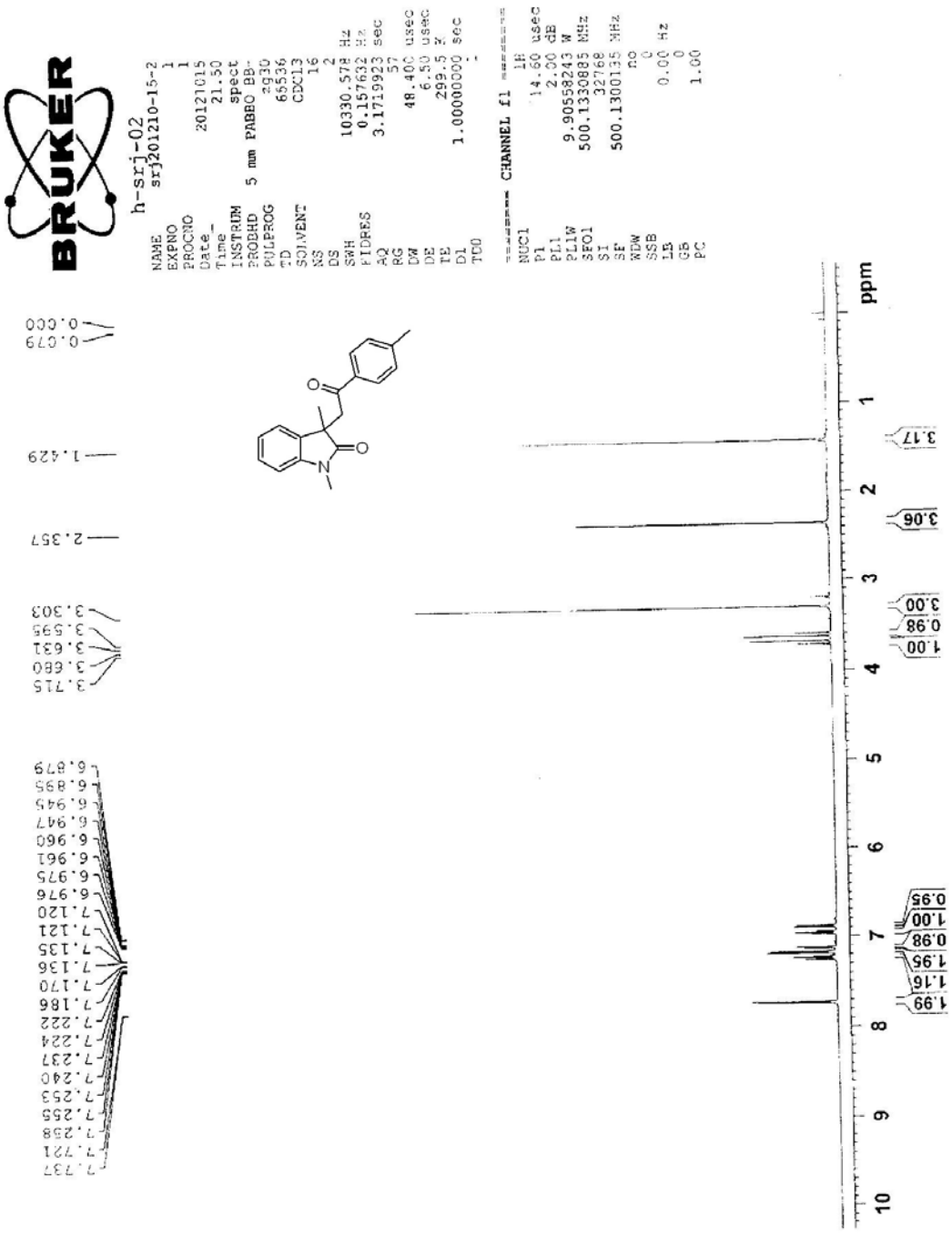
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (7)



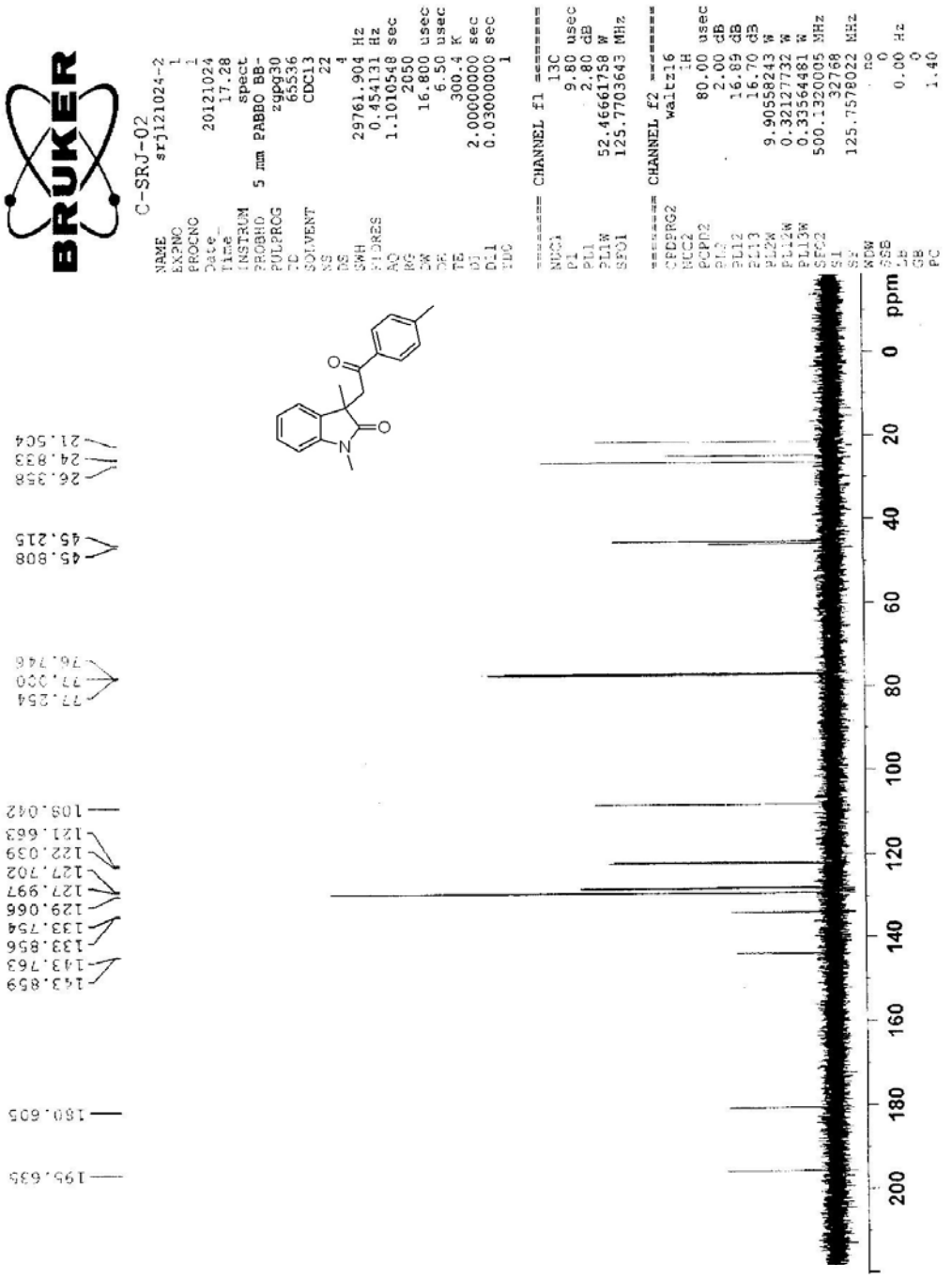
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (7)



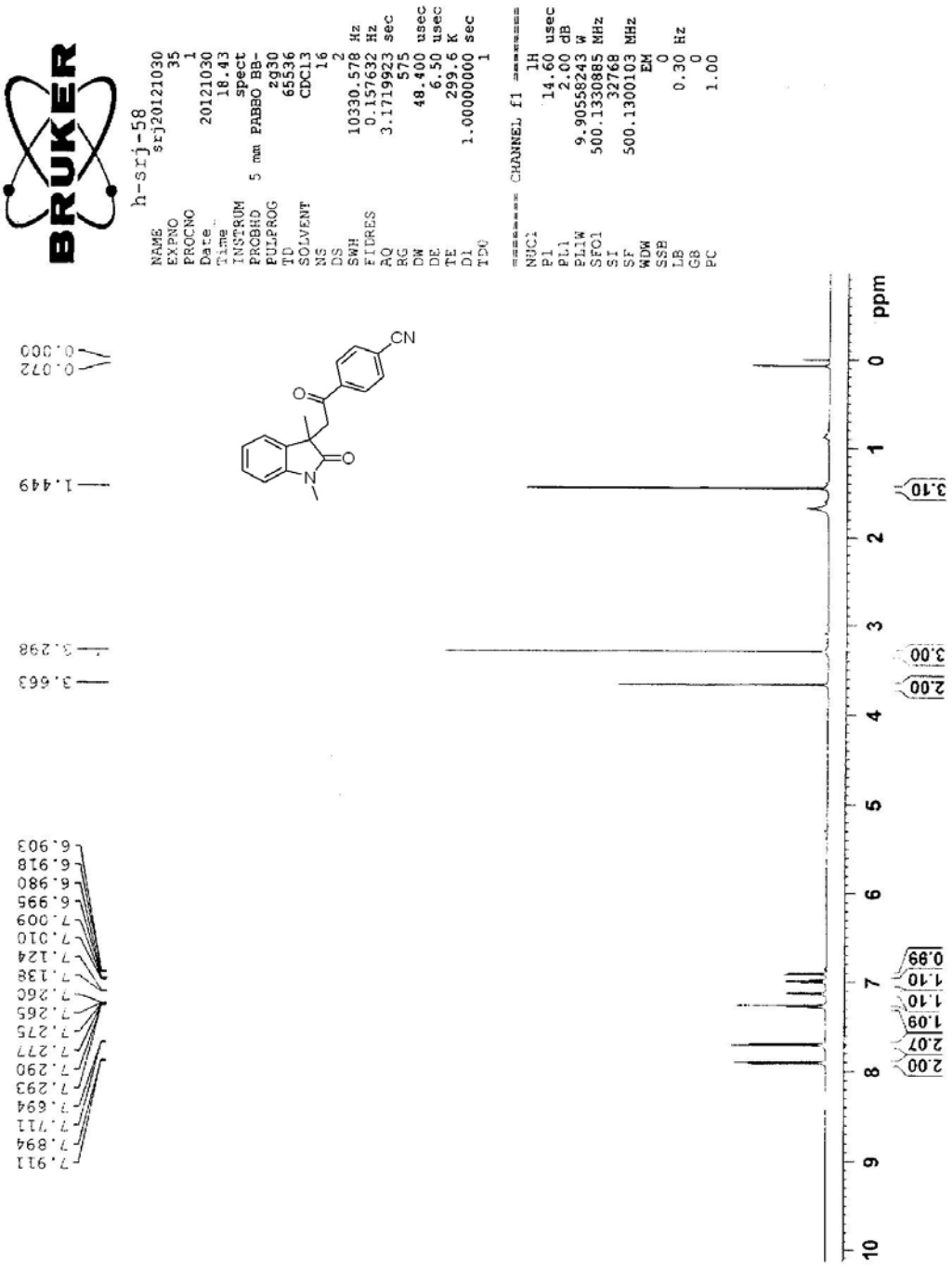
1,3-Dimethyl-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (8)



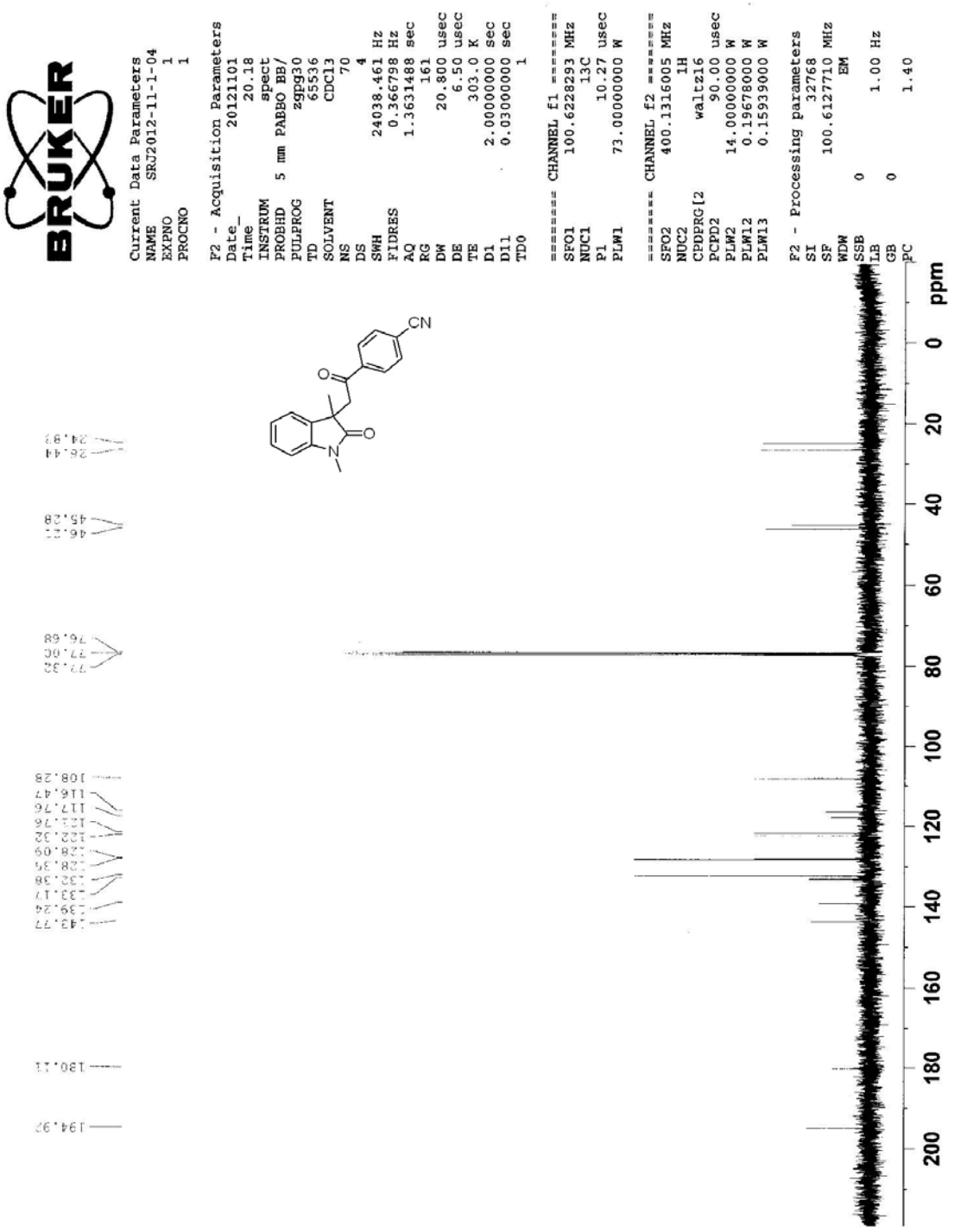
1,3-Dimethyl-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (8)



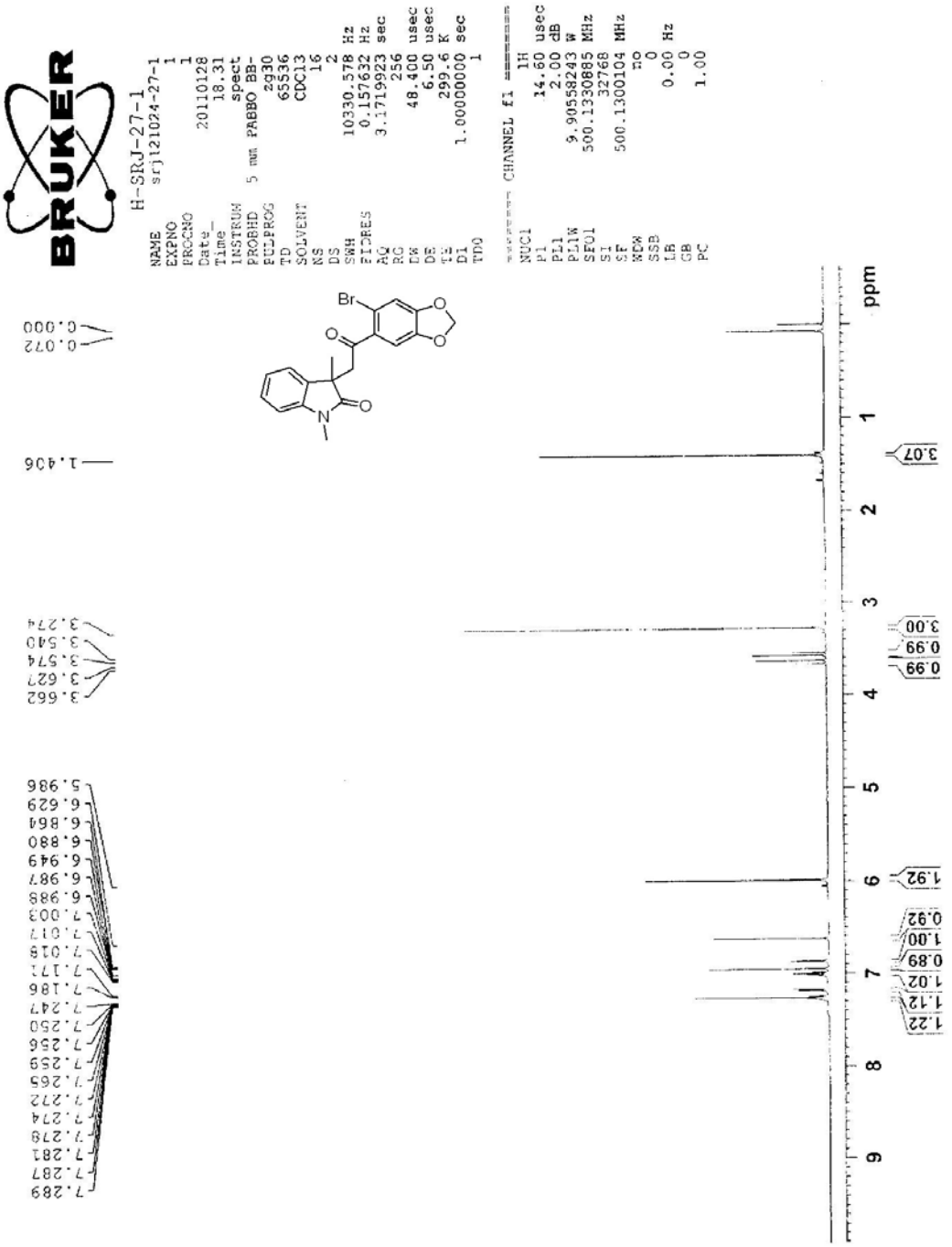
4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzonitrile (9)



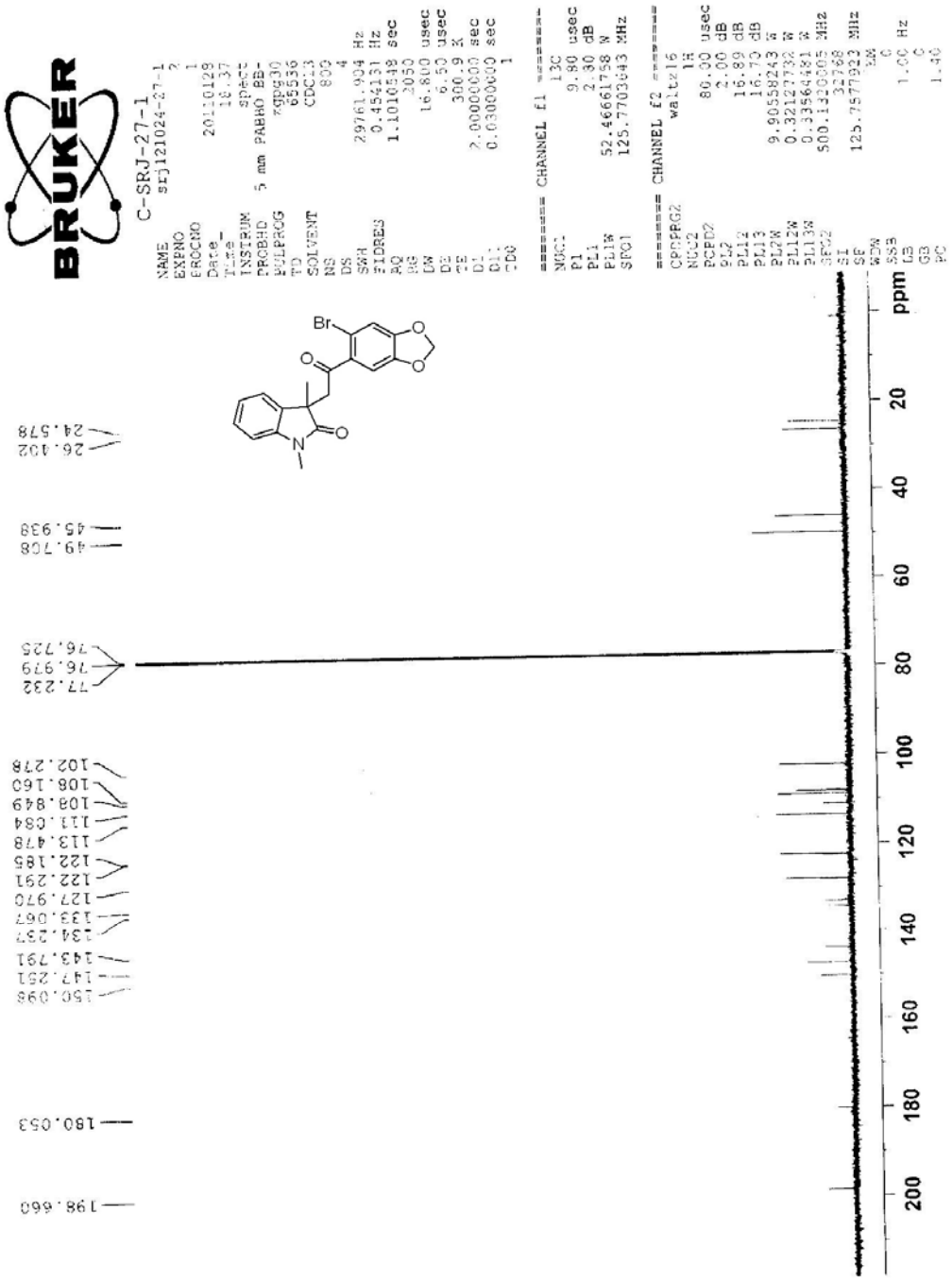
4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzonitrile (9)



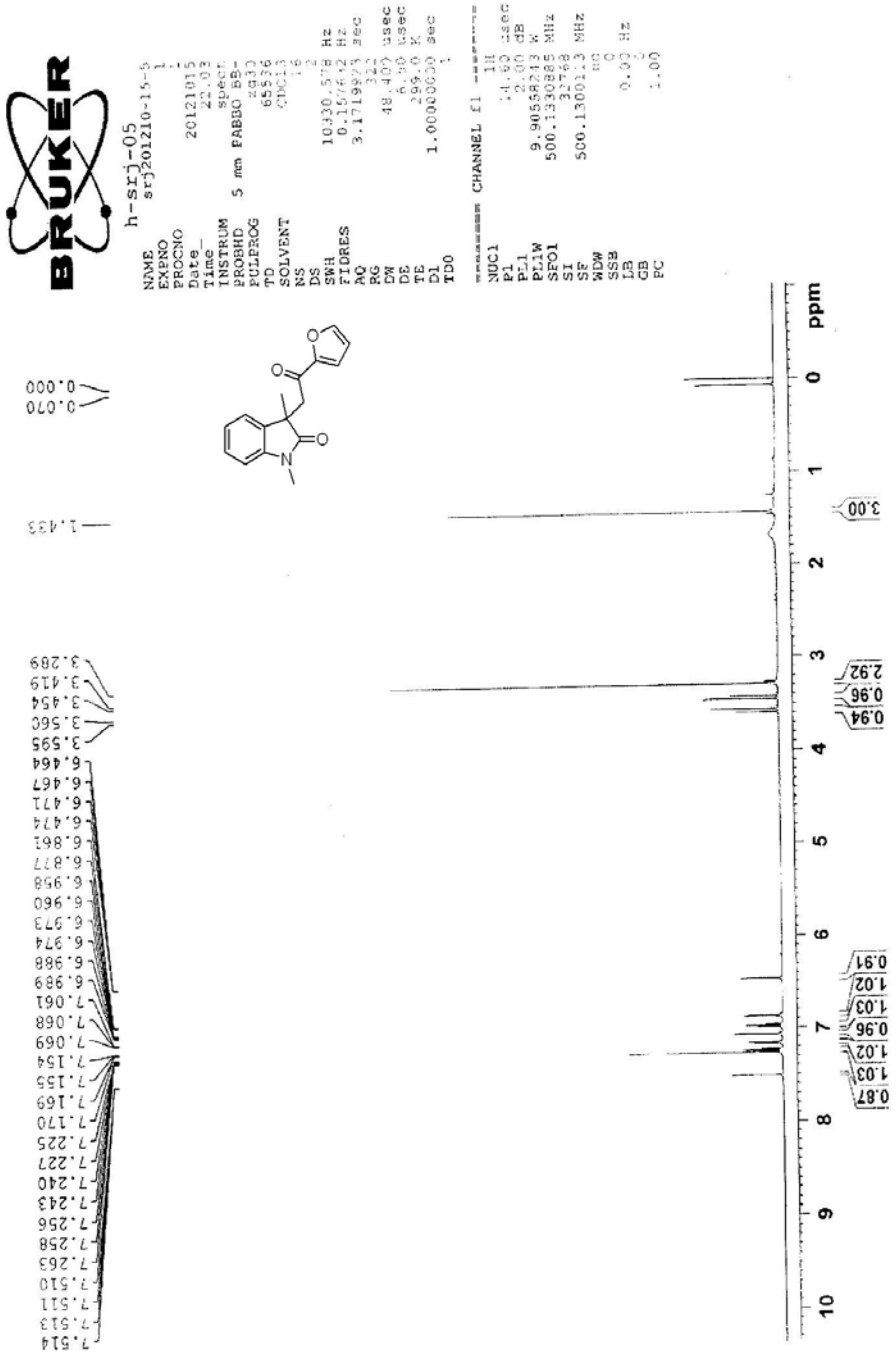
3-(2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (10)



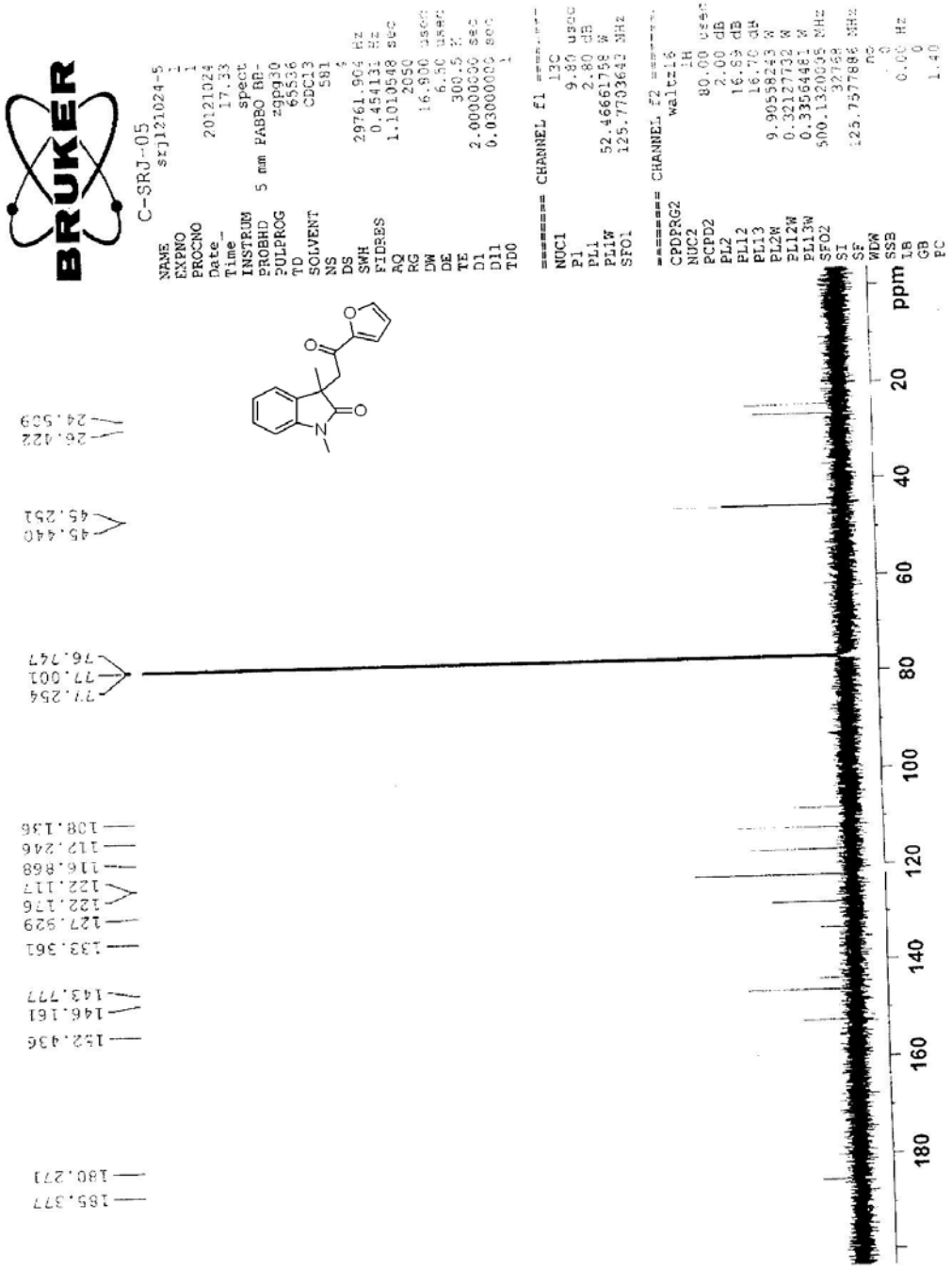
3-(2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (10)



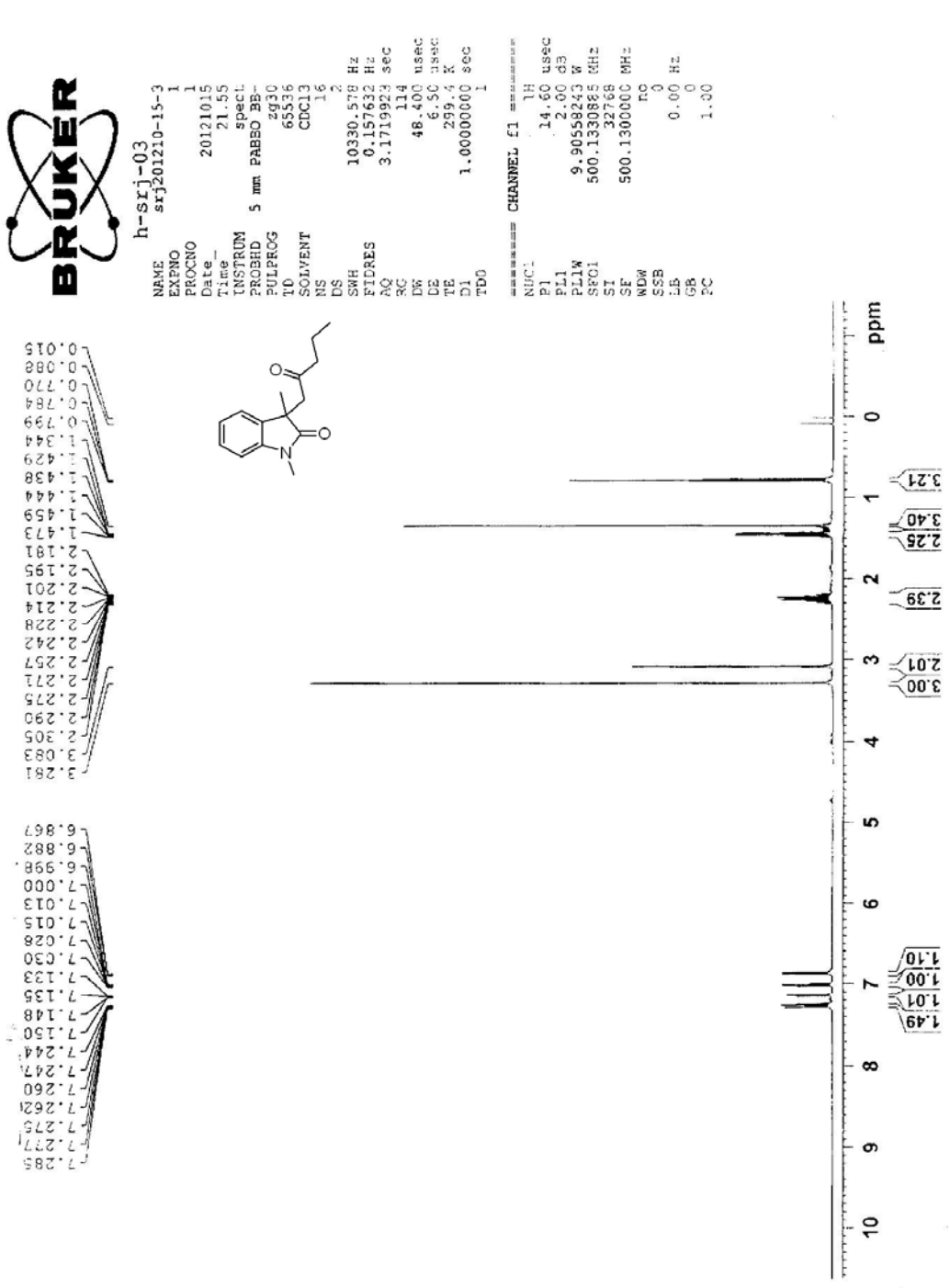
3-(2-(Furan-2-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (11)



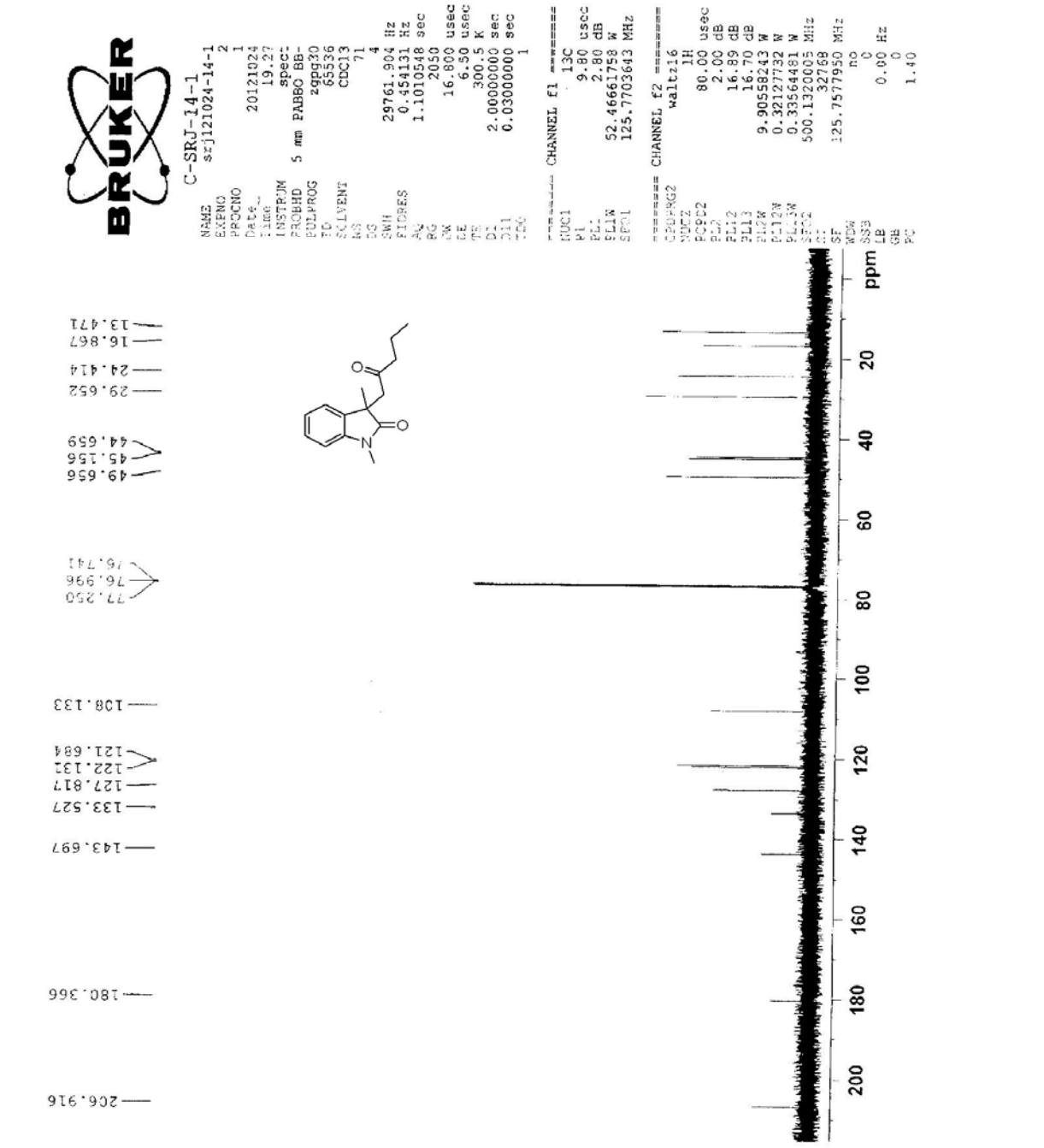
3-(2-(Furan-2-yl)-2-oxoethyl)-1,3-dimethylindolin-2-one (11)



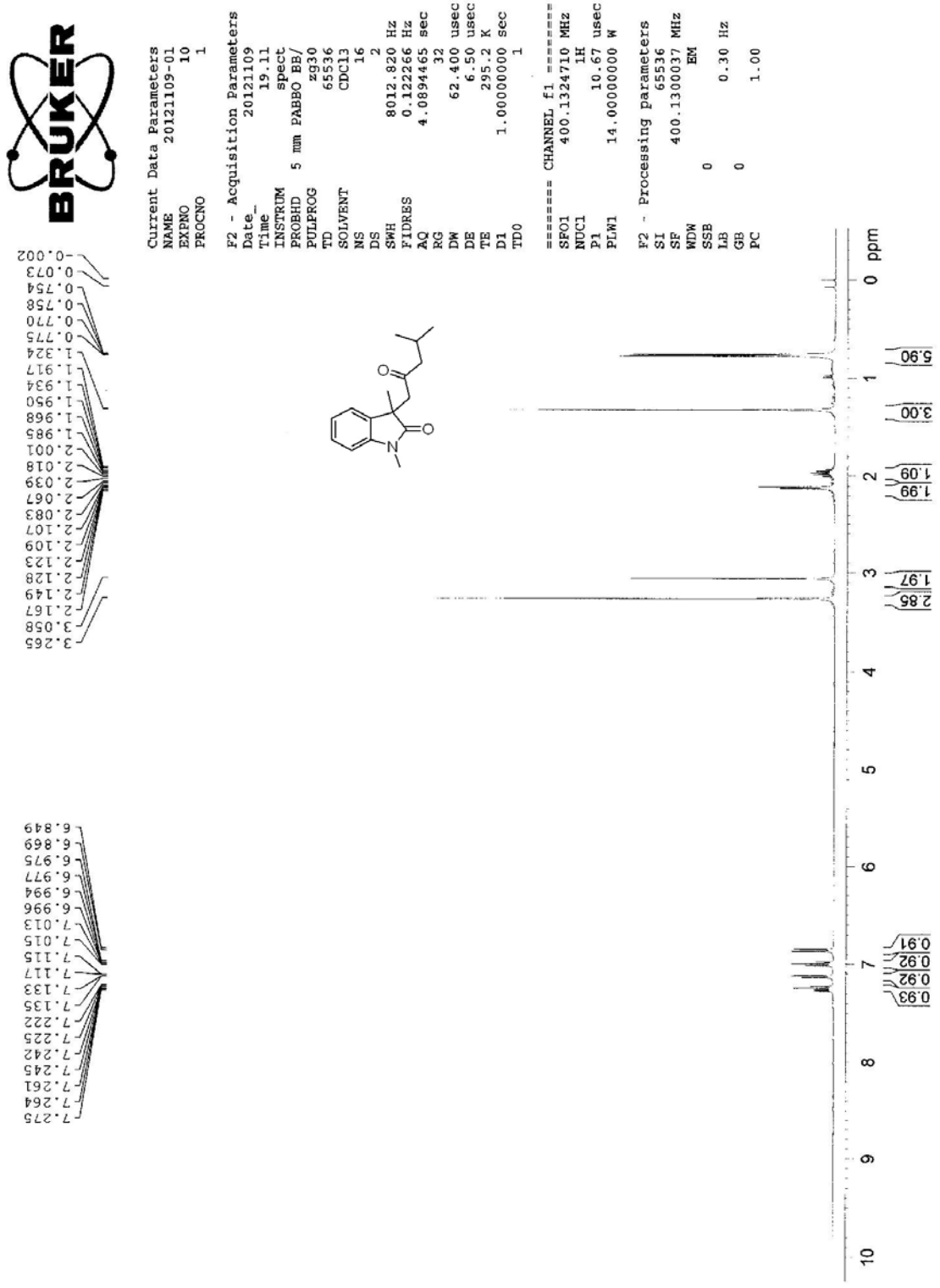
1,3-Dimethyl-3-(2-oxopentyl)indolin-2-one (12)



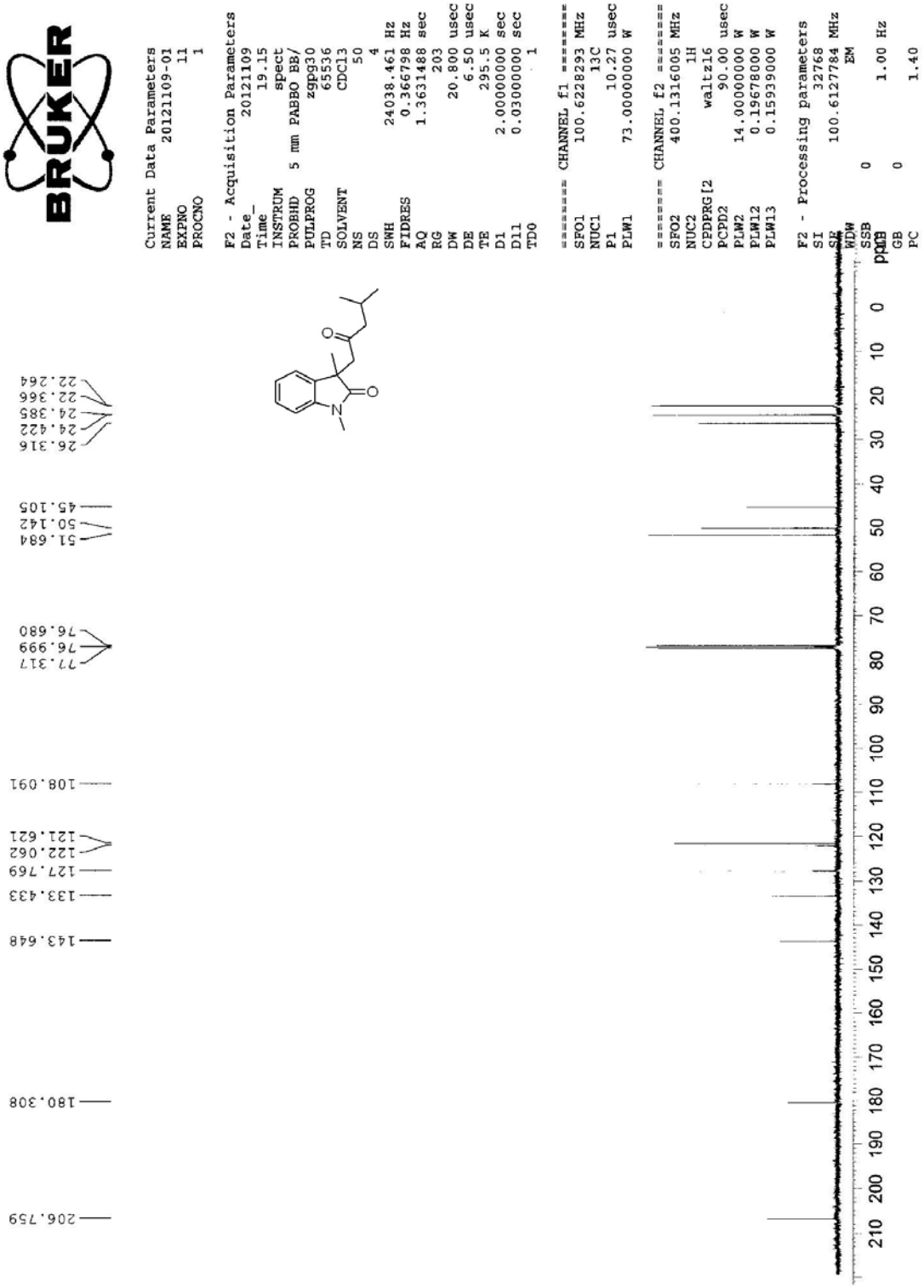
1,3-Dimethyl-3-(2-oxopentyl)indolin-2-one (12)



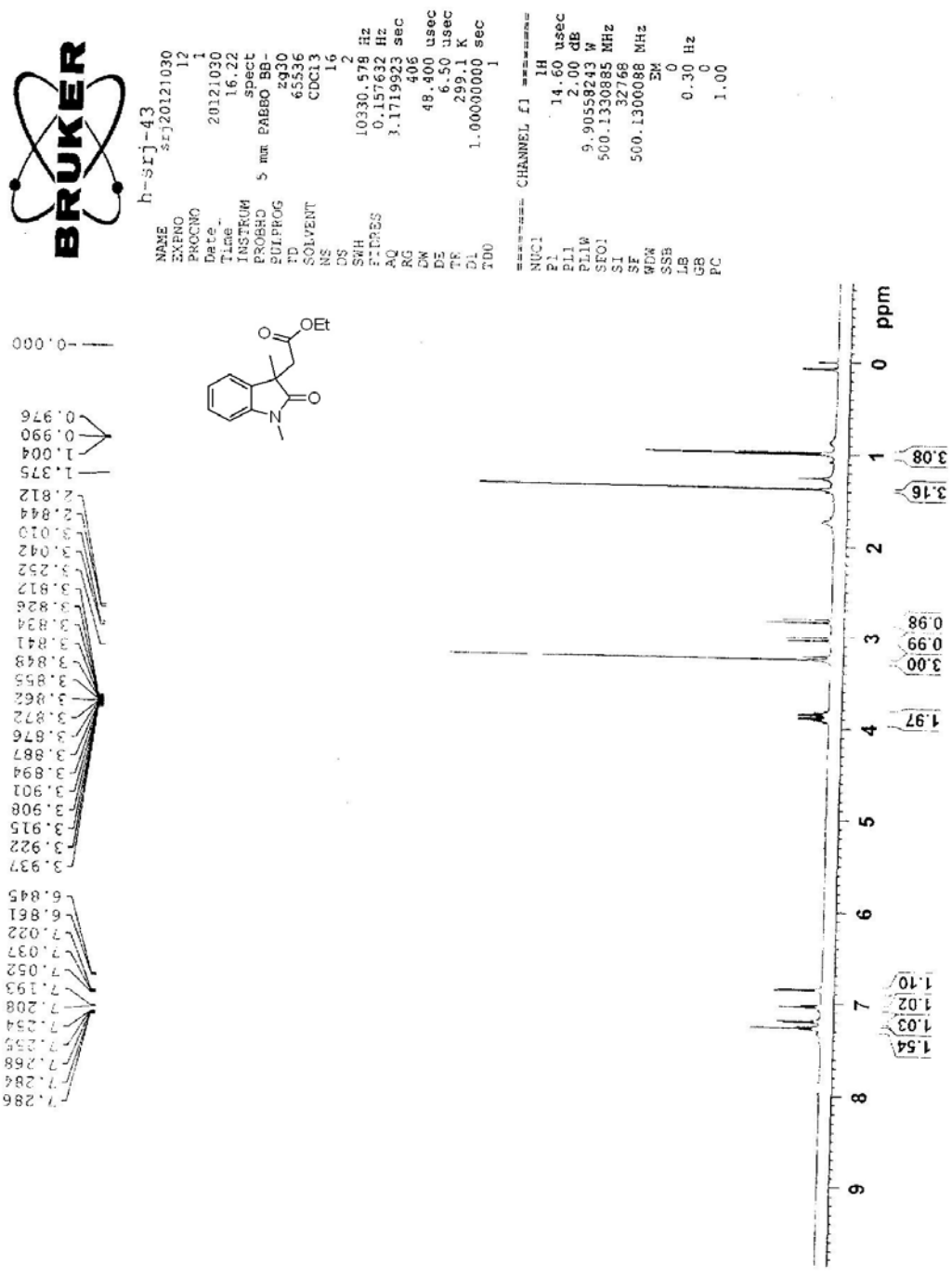
1,3-Dimethyl-3-(4-methyl-2-oxopentyl)indolin-2-one (13)



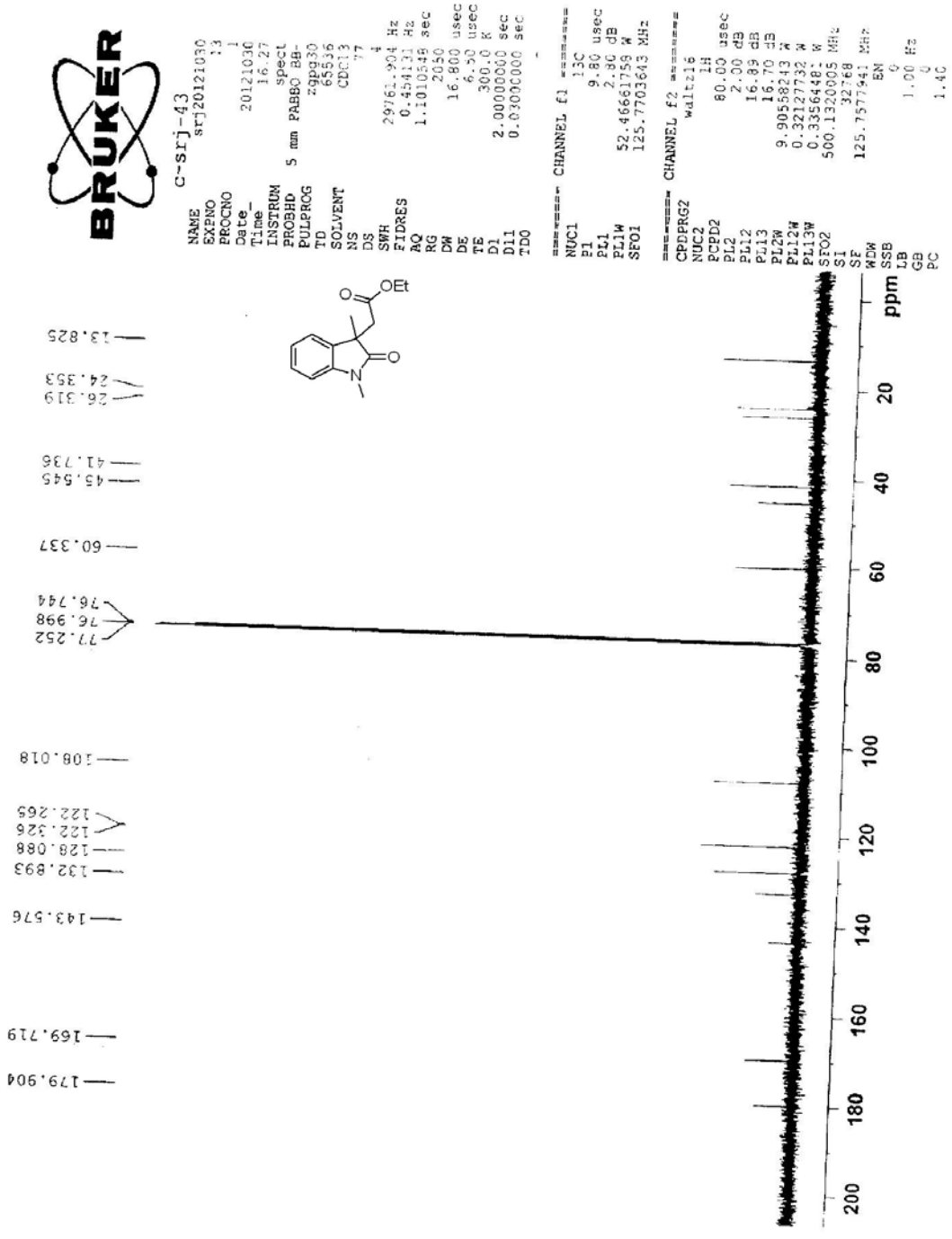
1,3-Dimethyl-3-(4-methyl-2-oxopentyl)indolin-2-one (13)



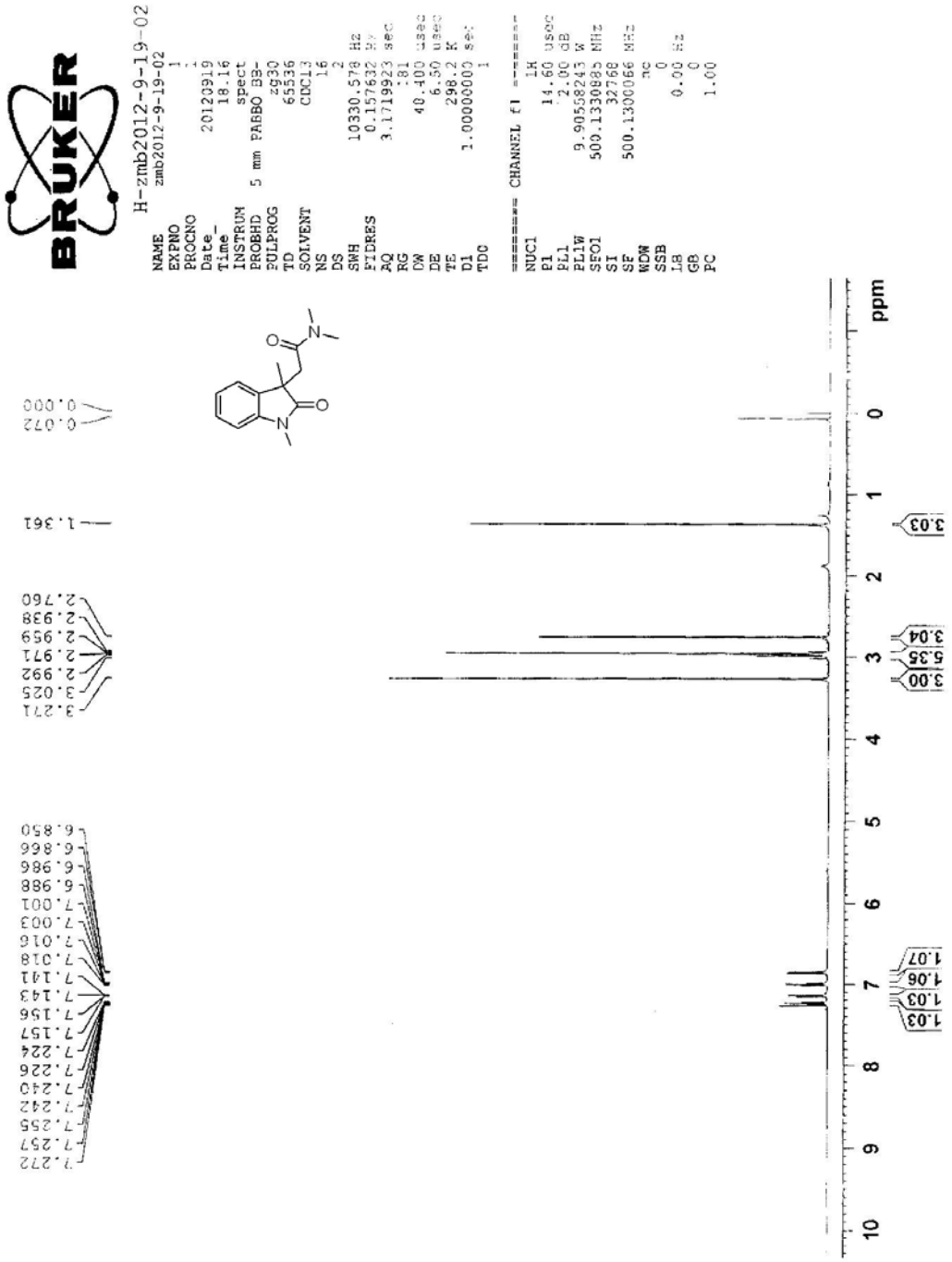
Ethyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (14)



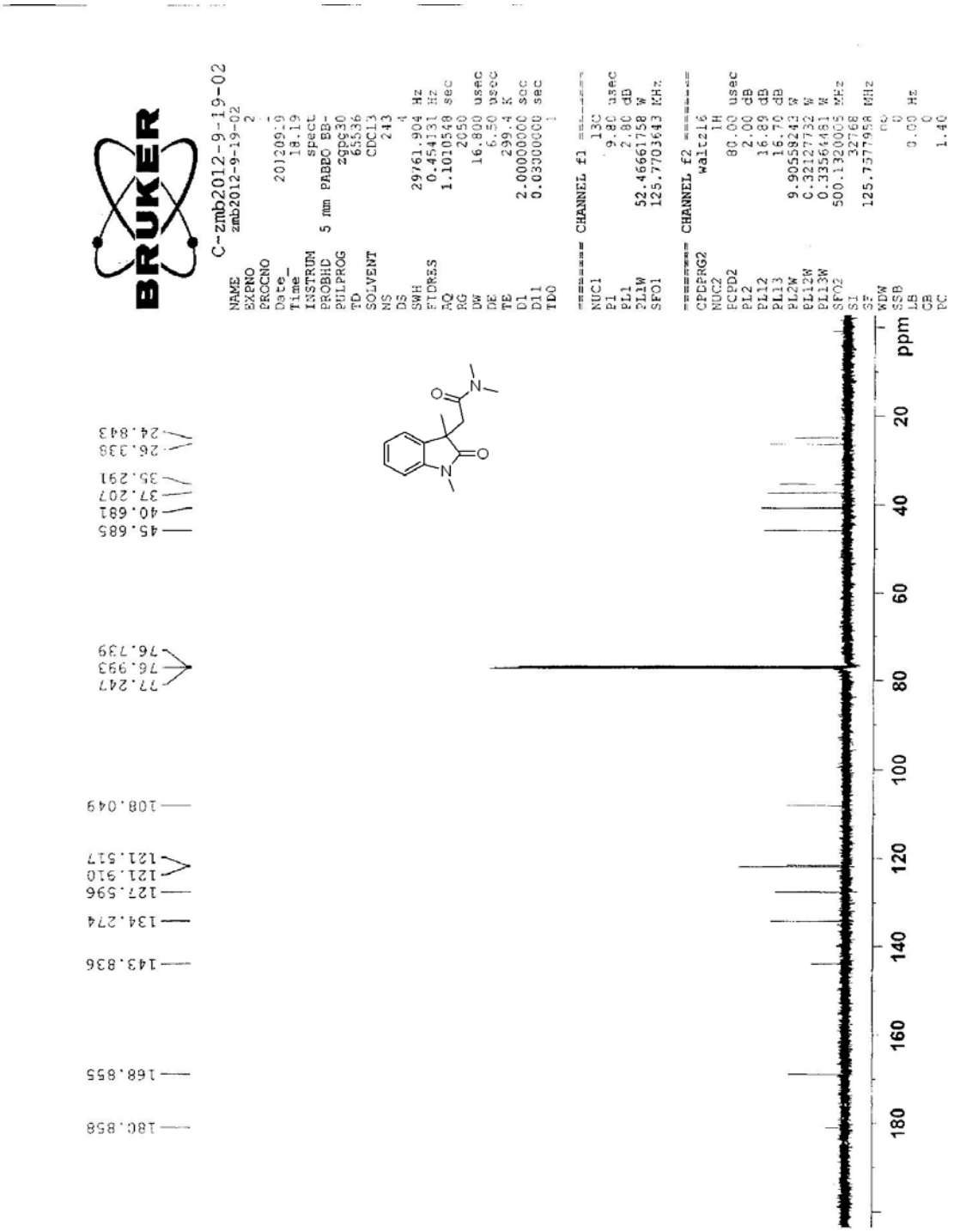
Ethyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (14)



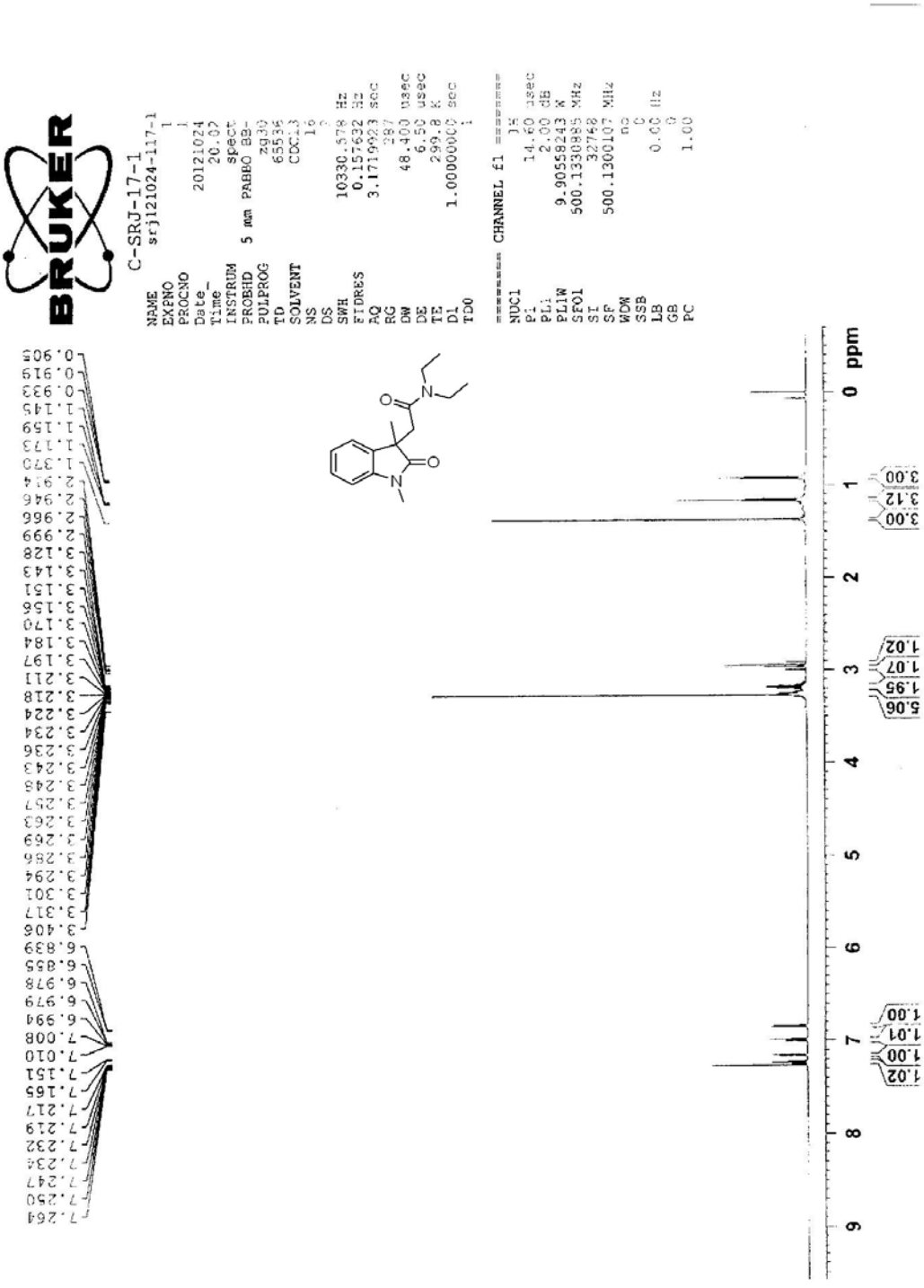
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylacetamide (15)



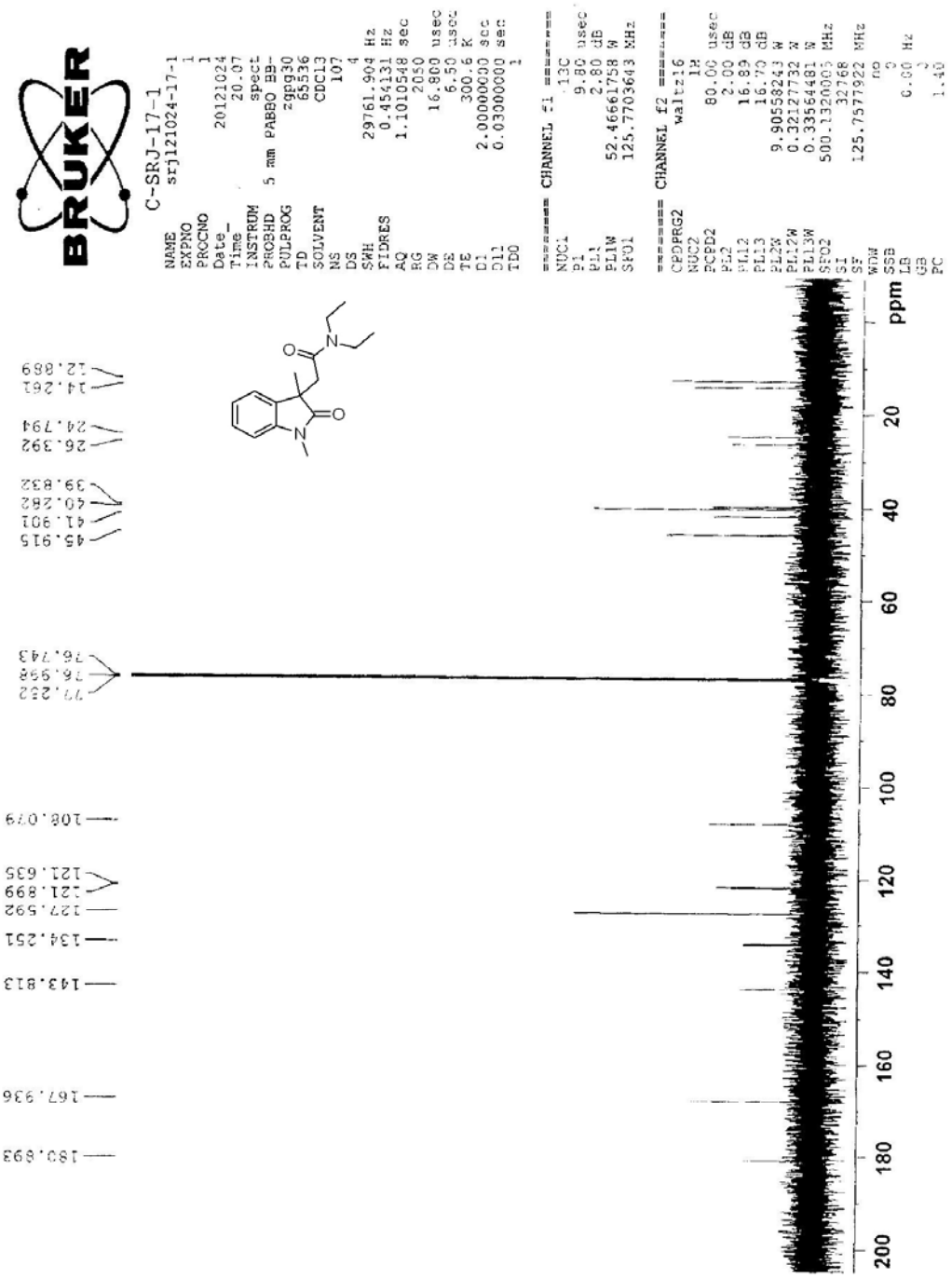
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylacetamide (15)



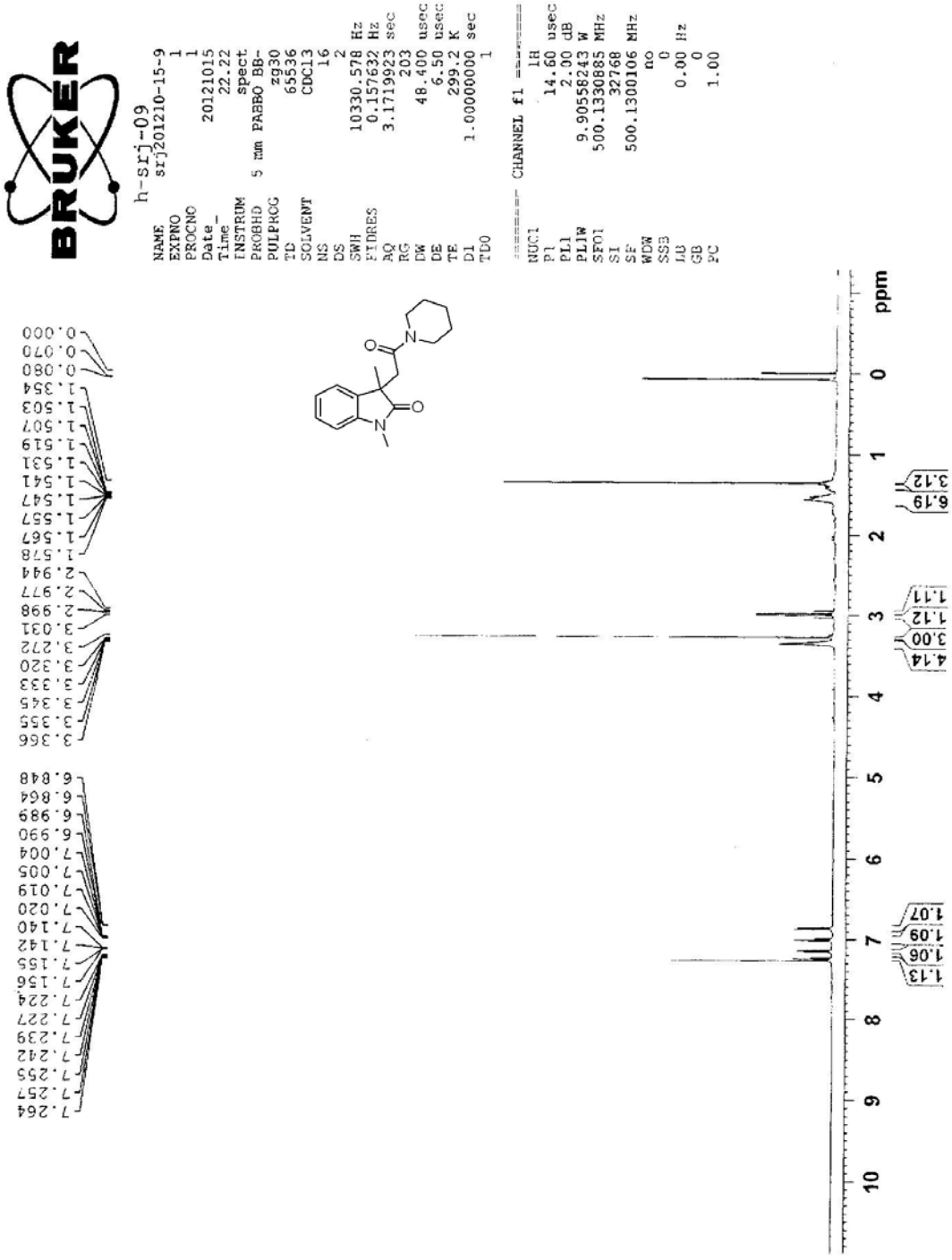
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-diethylacetamide (16)



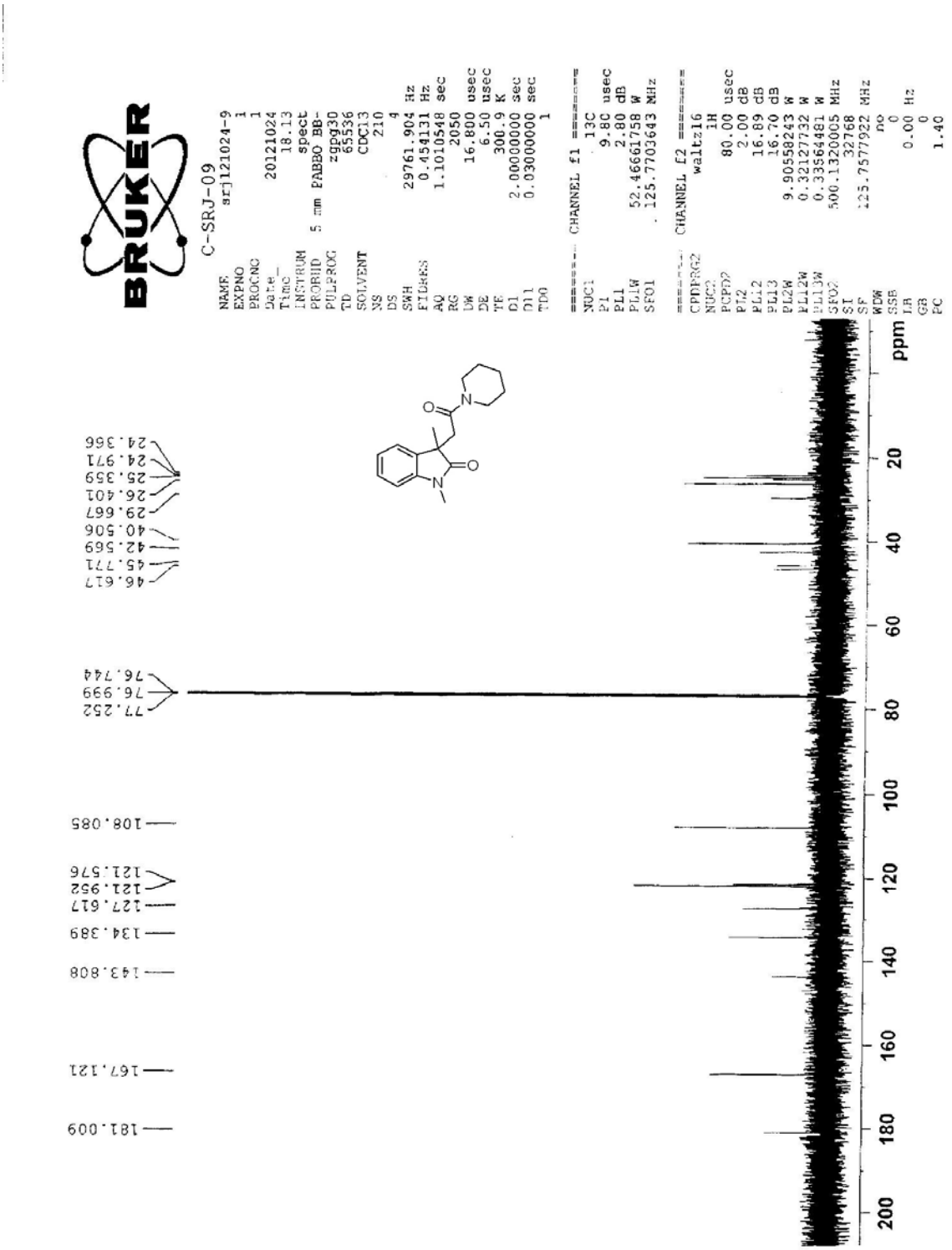
2-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-diethylacetamide (16)



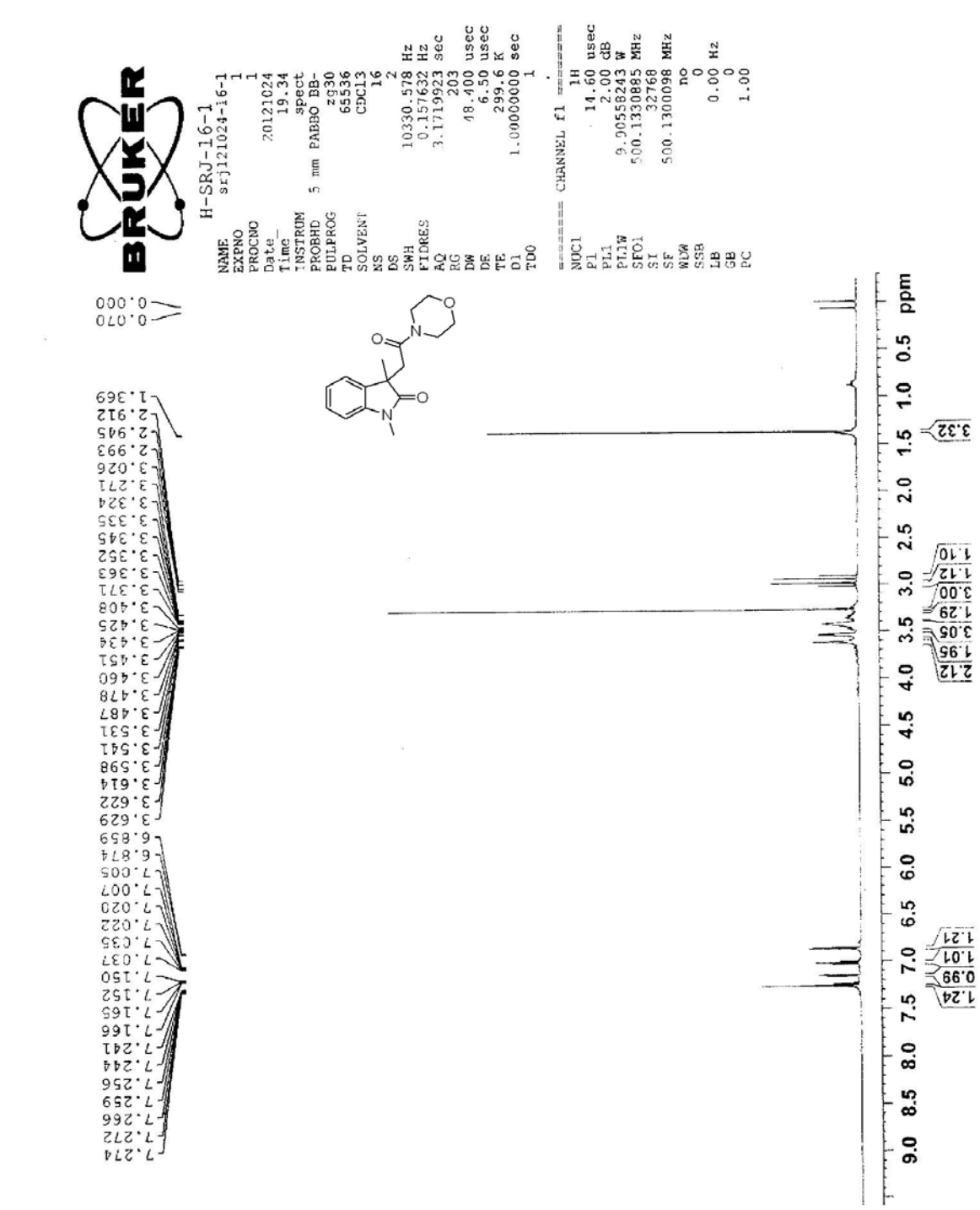
1,3-Dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (17)



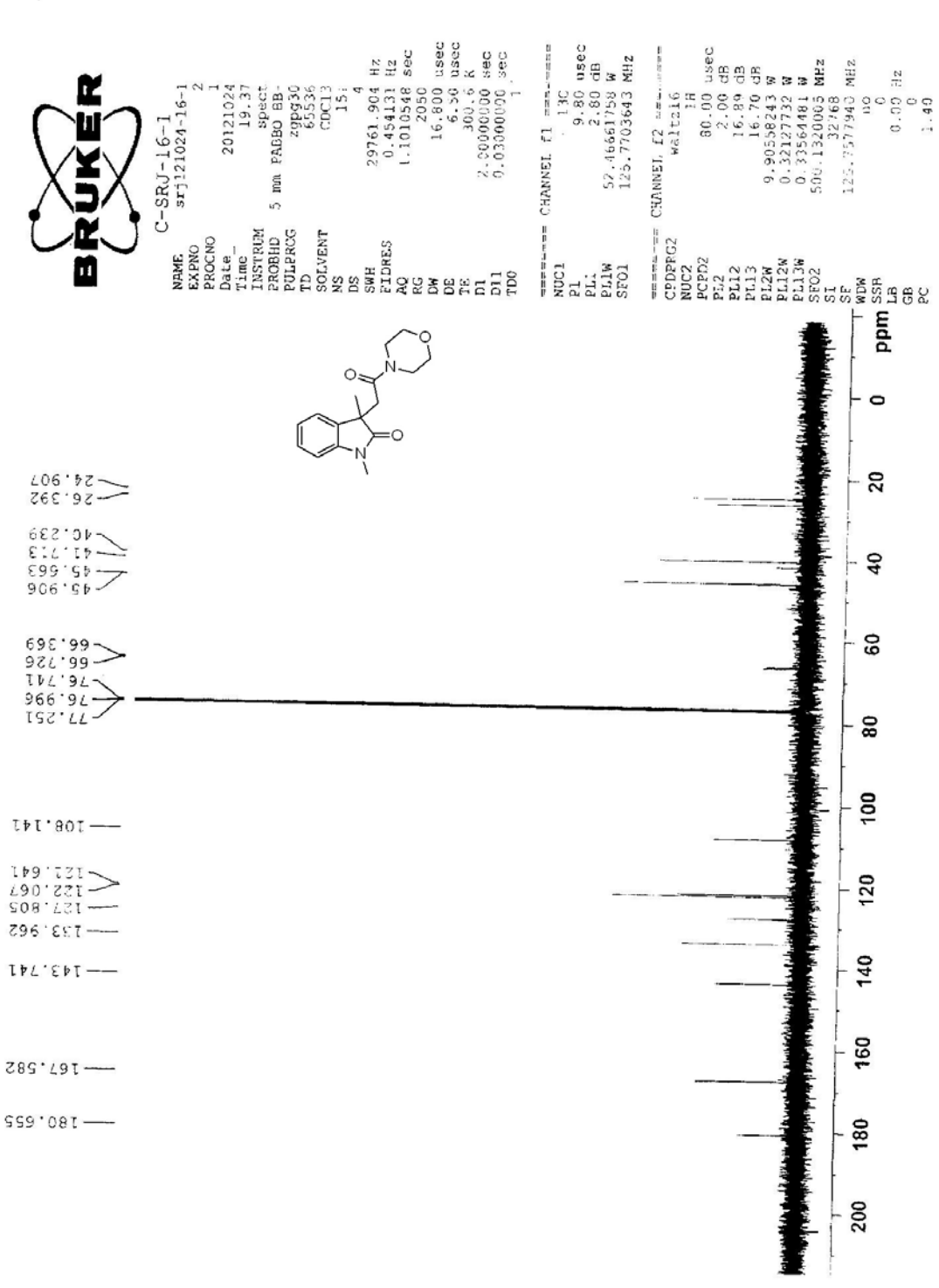
1,3-Dimethyl-3-(2-oxo-2-(piperidin-1-yl)ethyl)indolin-2-one (17)



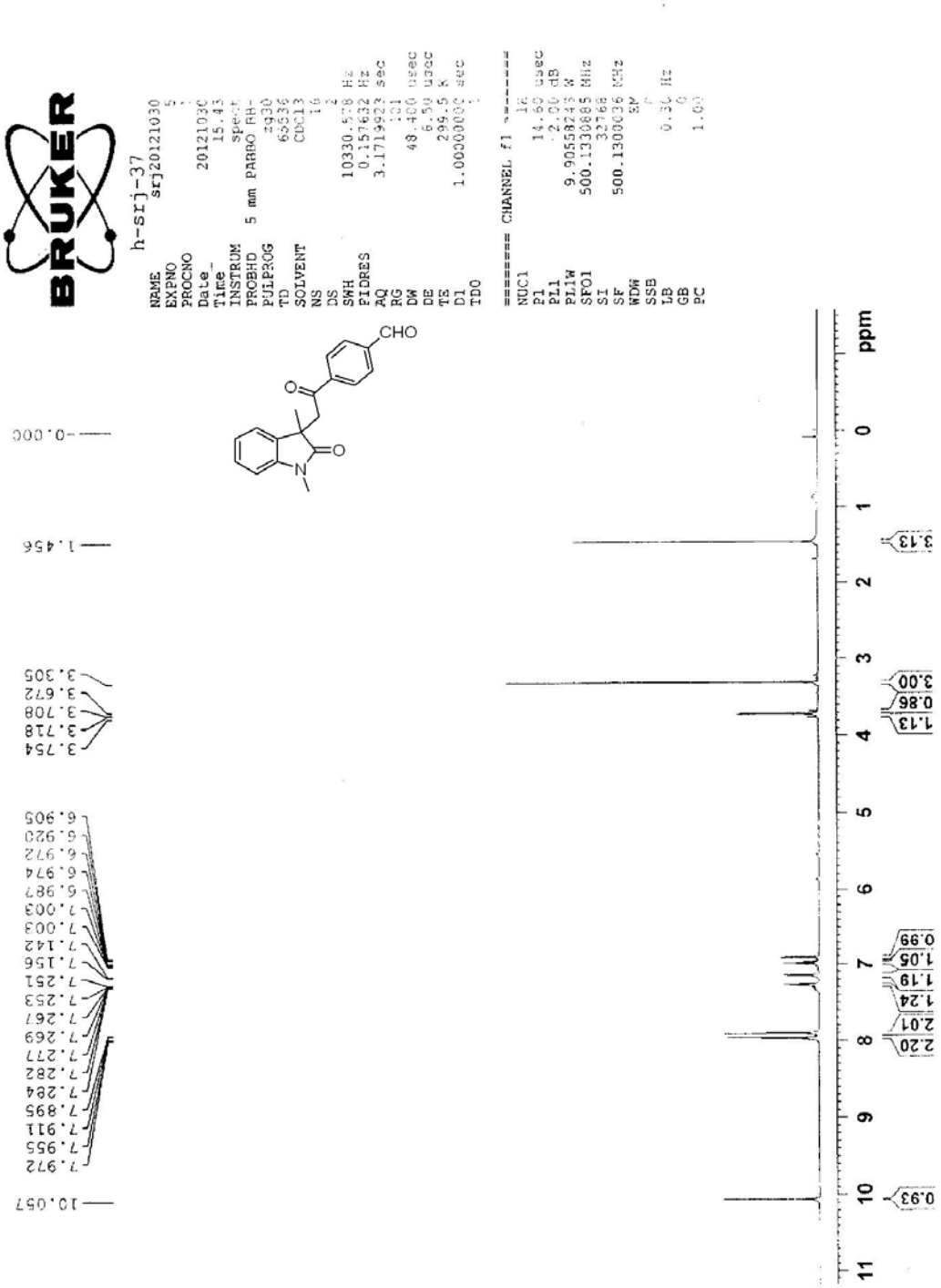
1,3-Dimethyl-3-(2-morpholino-2-oxoethyl)indolin-2-one (18)



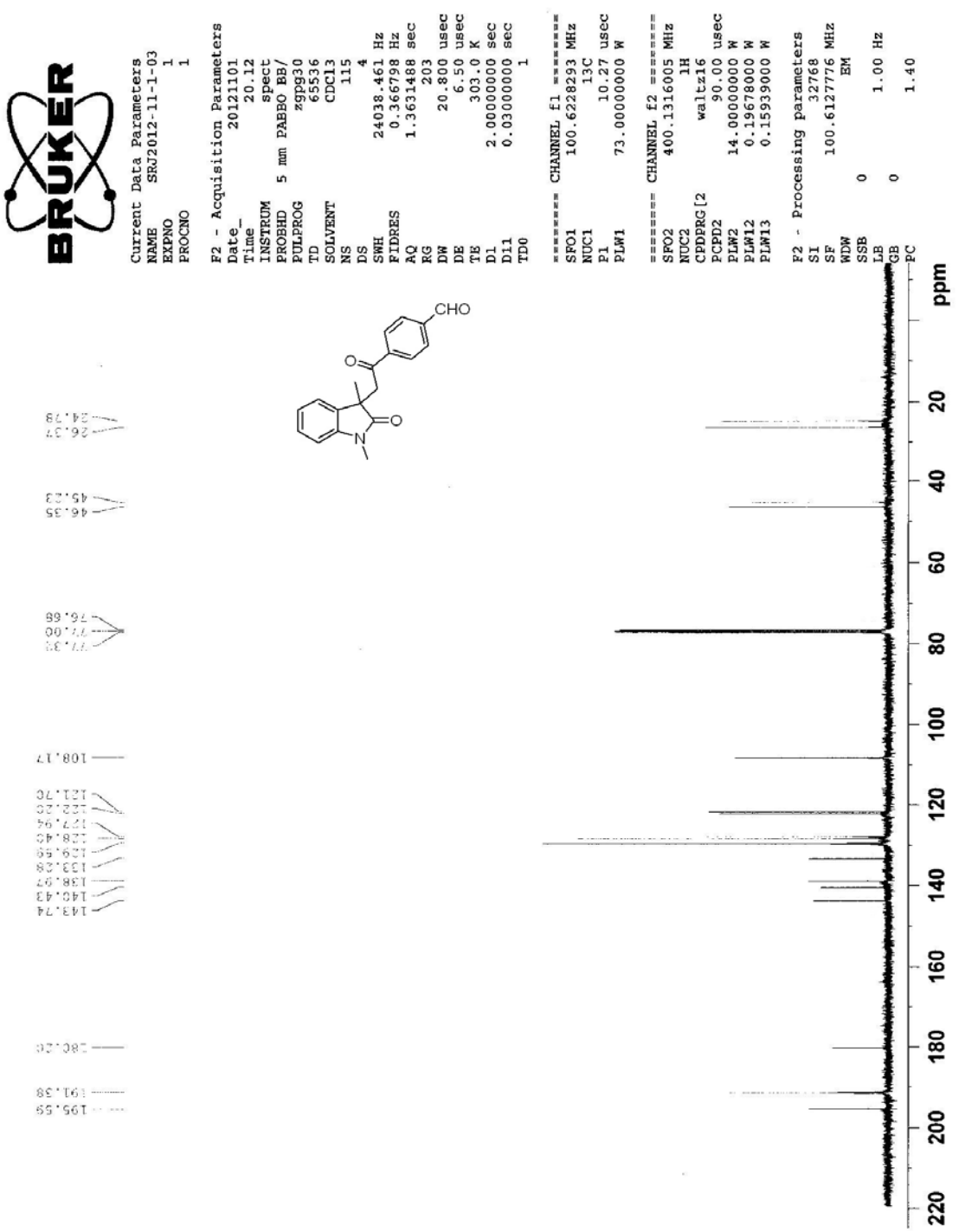
1,3-Dimethyl-3-(2-morpholino-2-oxoethyl)indolin-2-one (18)



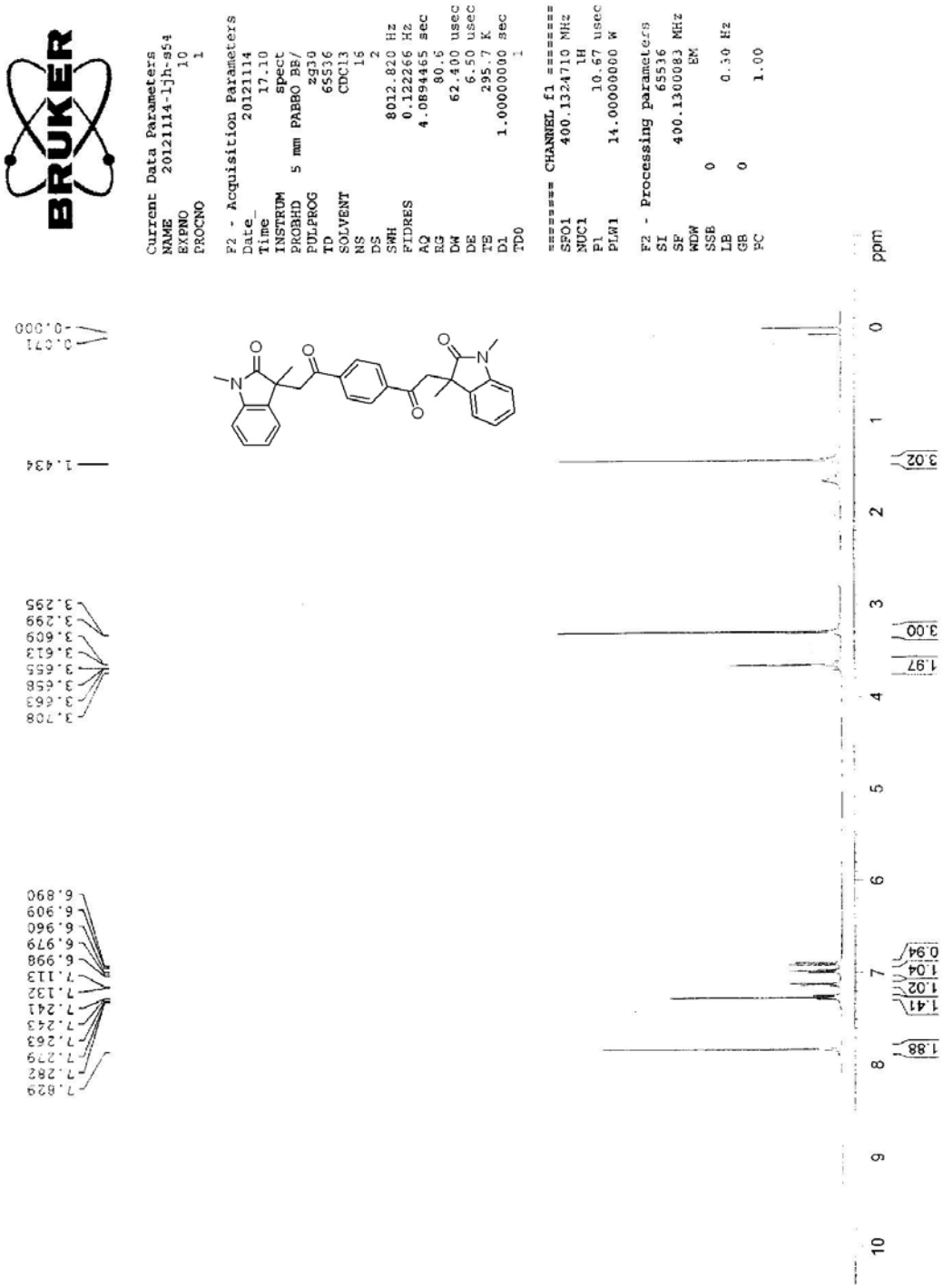
4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzaldehyde (19)



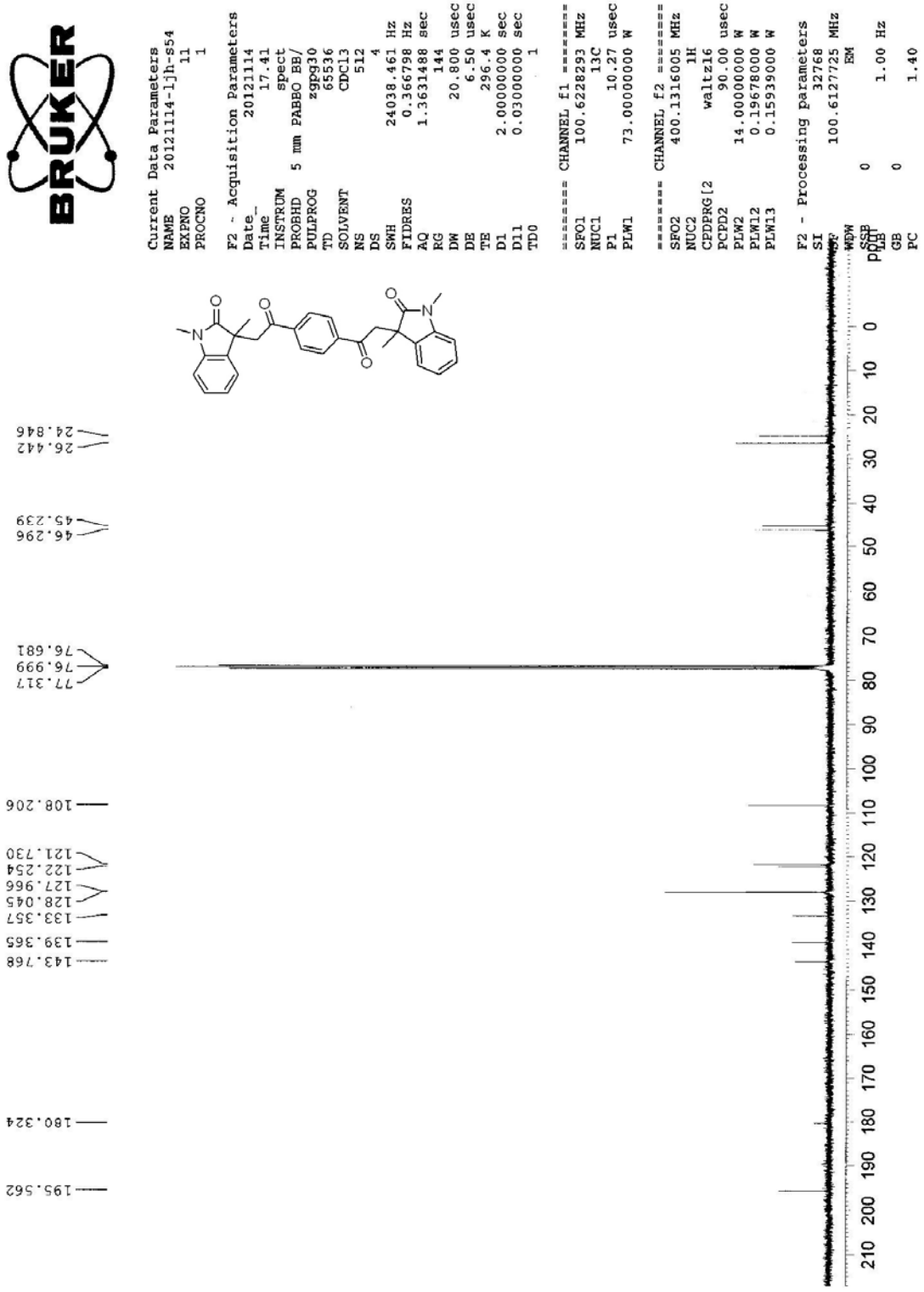
4-(2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetyl)benzaldehyde (19)



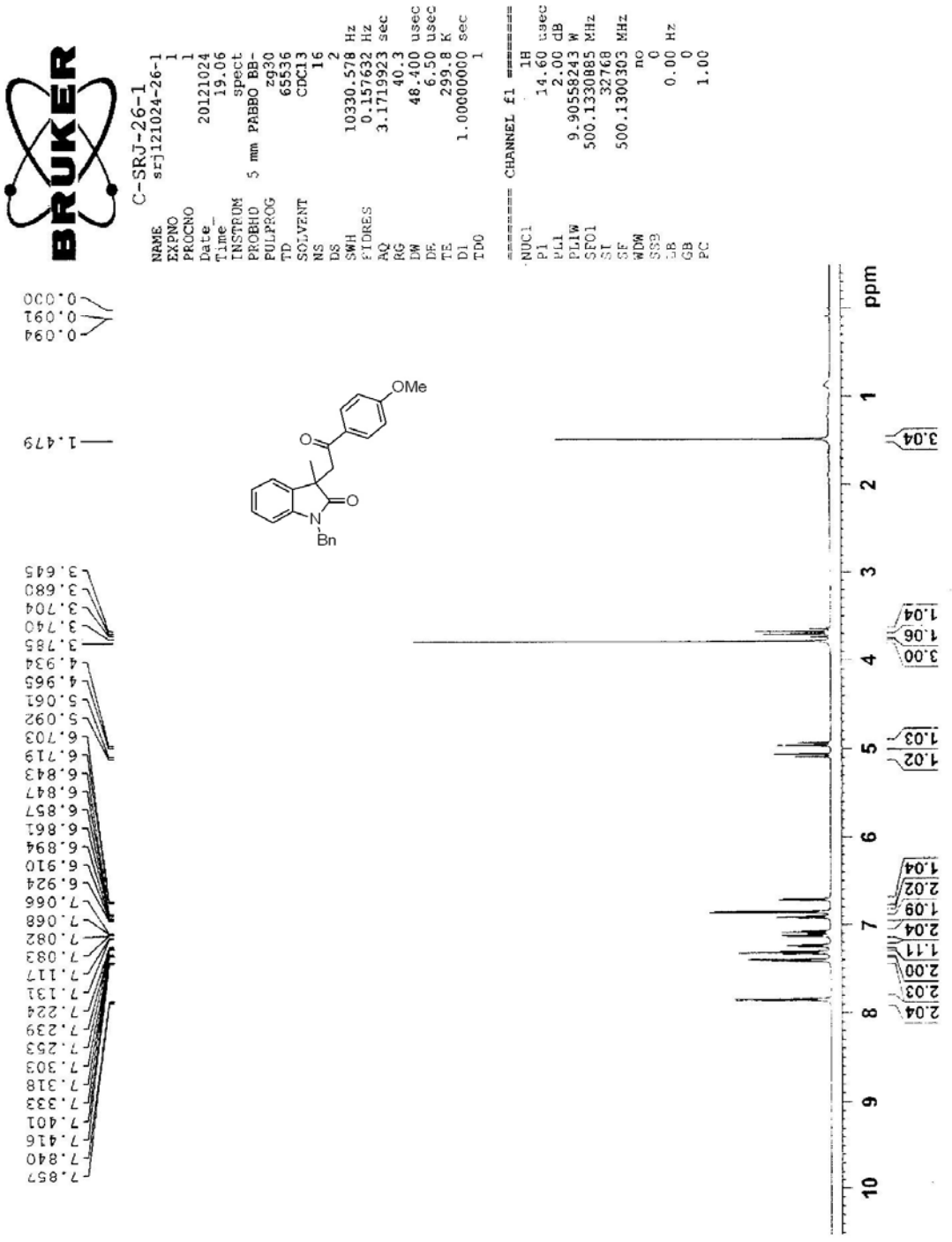
3,3'-(1,4-Phenylenebis(2-oxoethane-2,1-diyl))bis(1,3-dimethylindolin-2-one) (20)



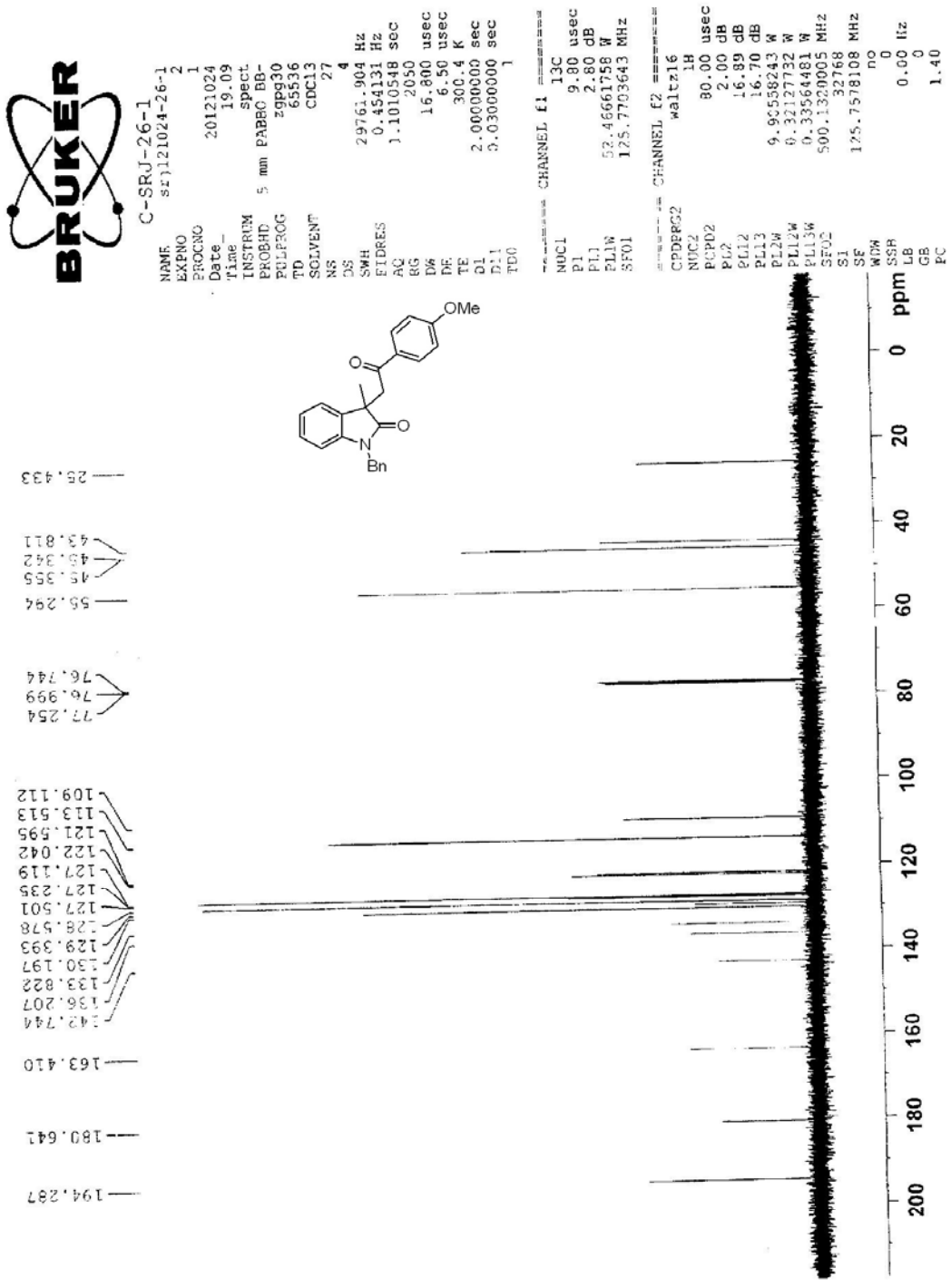
3,3'-(1,4-Phenylenebis(2-oxoethane-2,1-diyl))bis(1,3-dimethylindolin-2-one) (20)



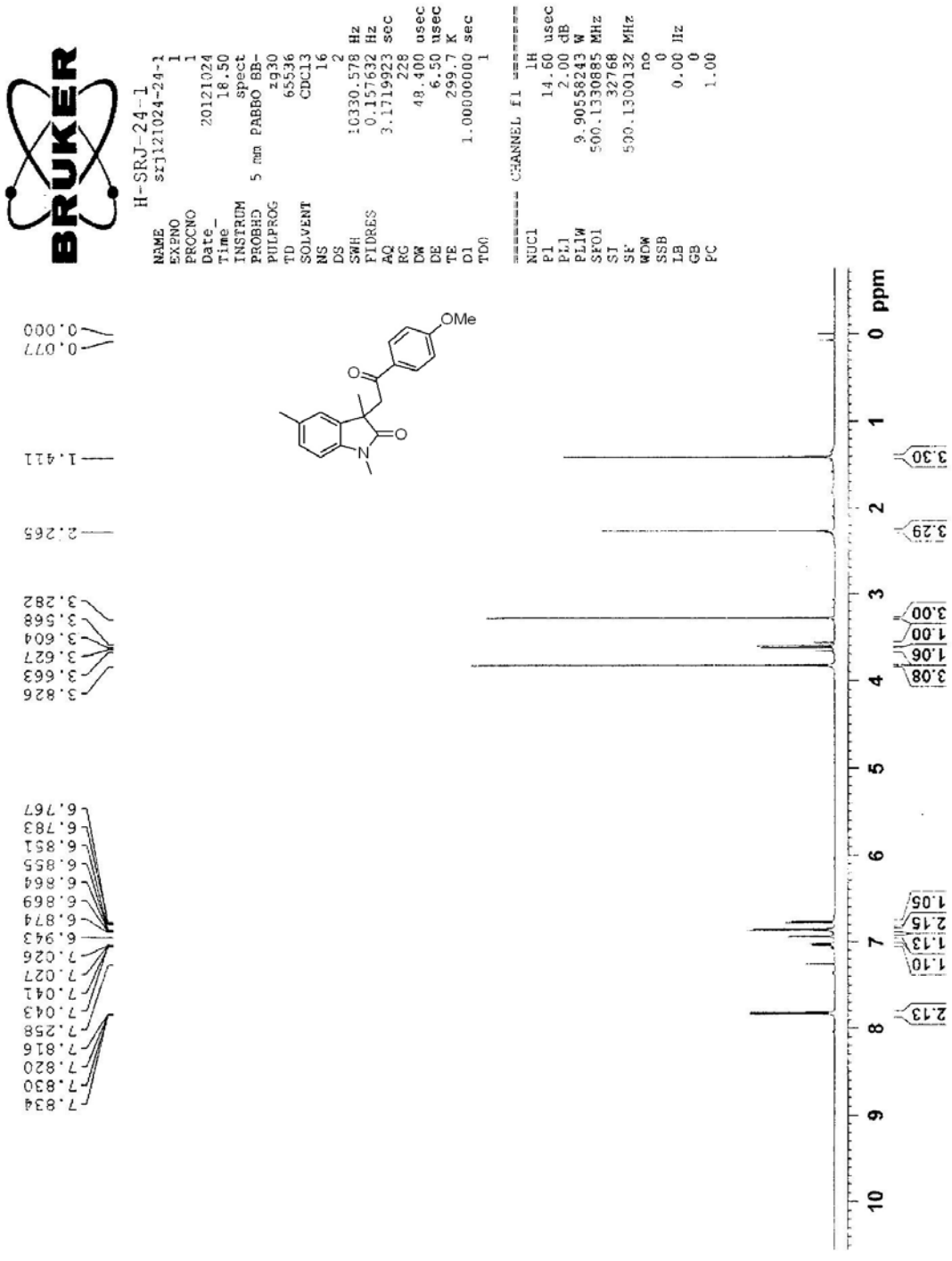
1-Benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one (21)



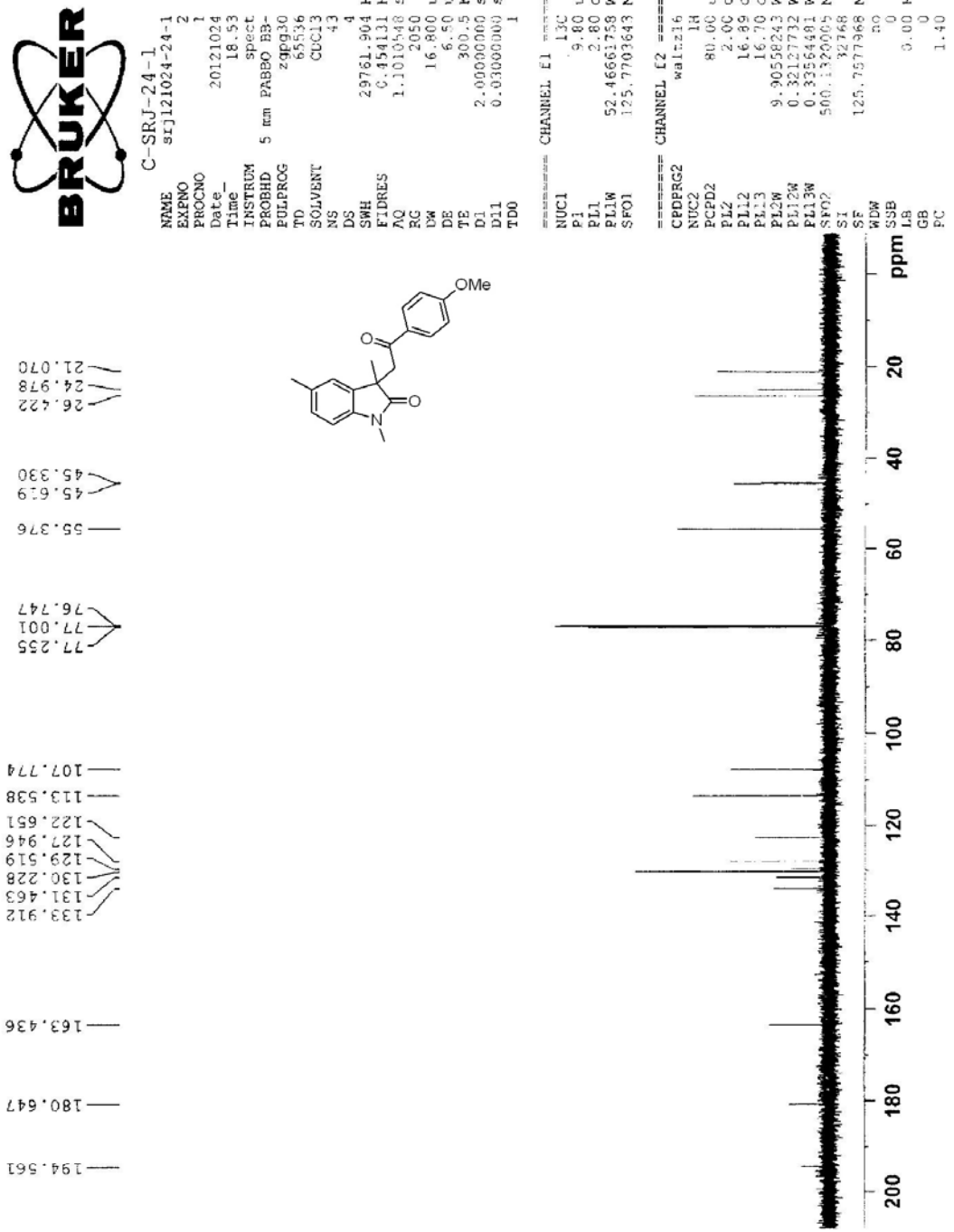
1-Benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one (21)



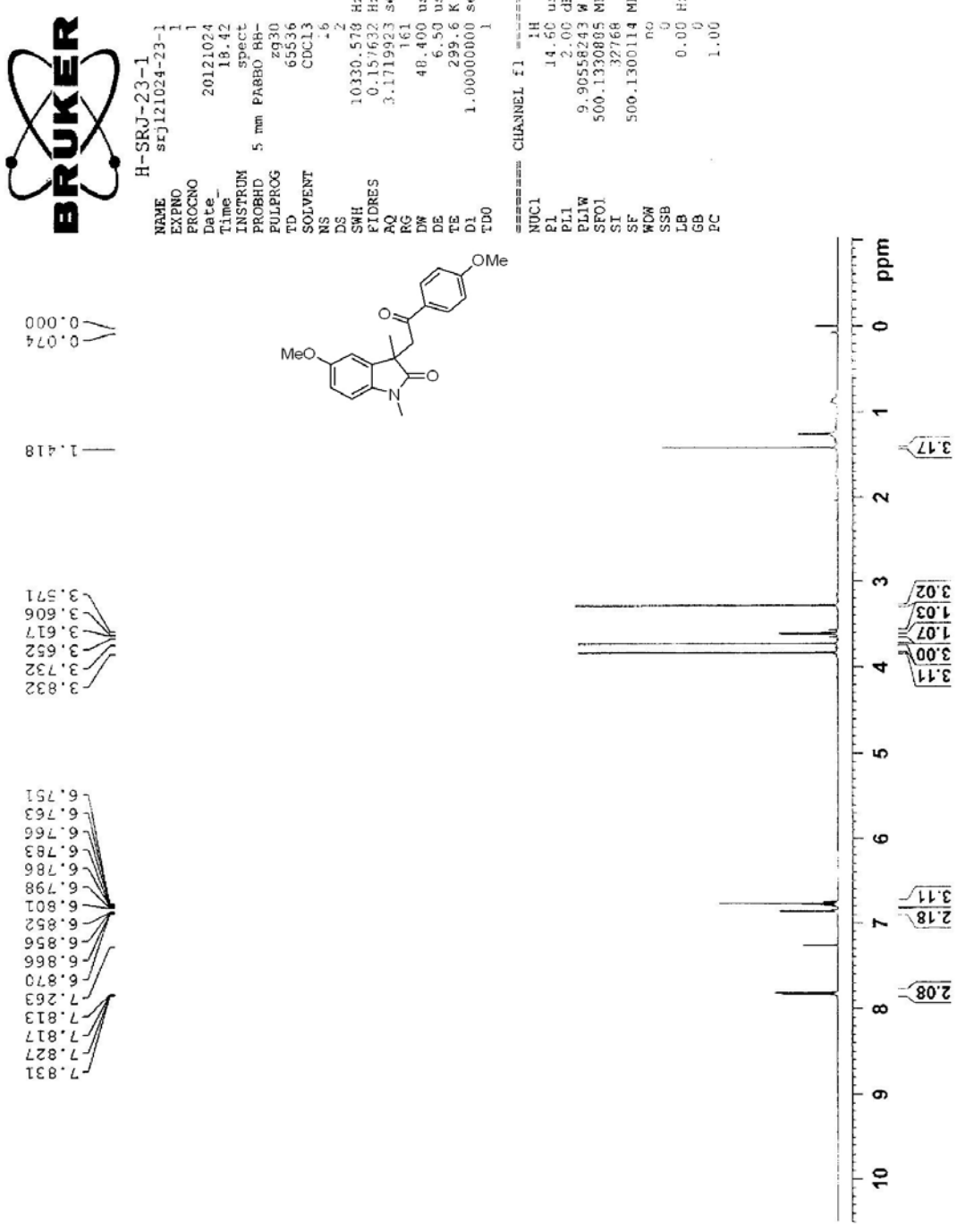
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,5-trimethylindolin-2-one (22)



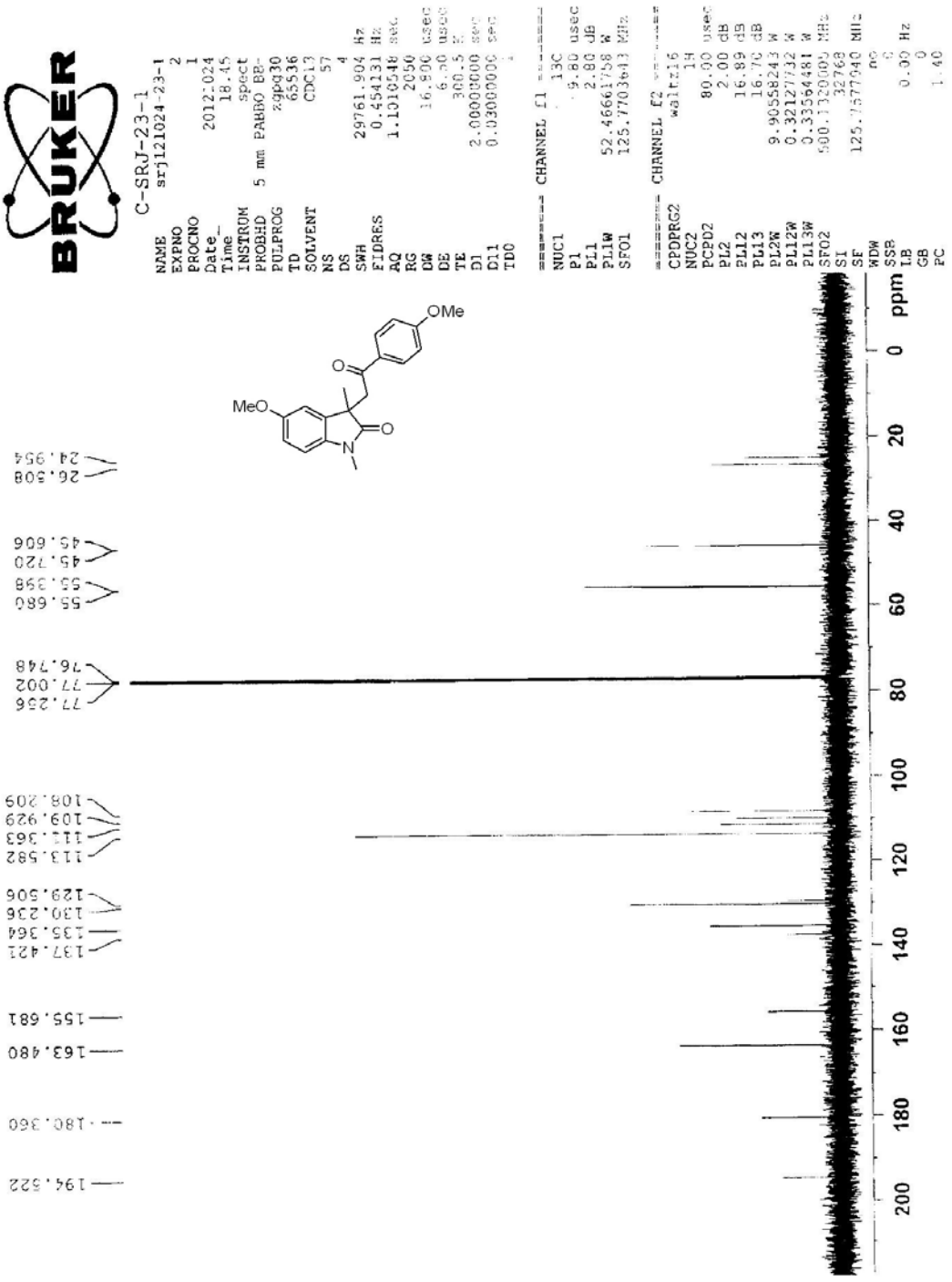
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,5-trimethylindolin-2-one (22)



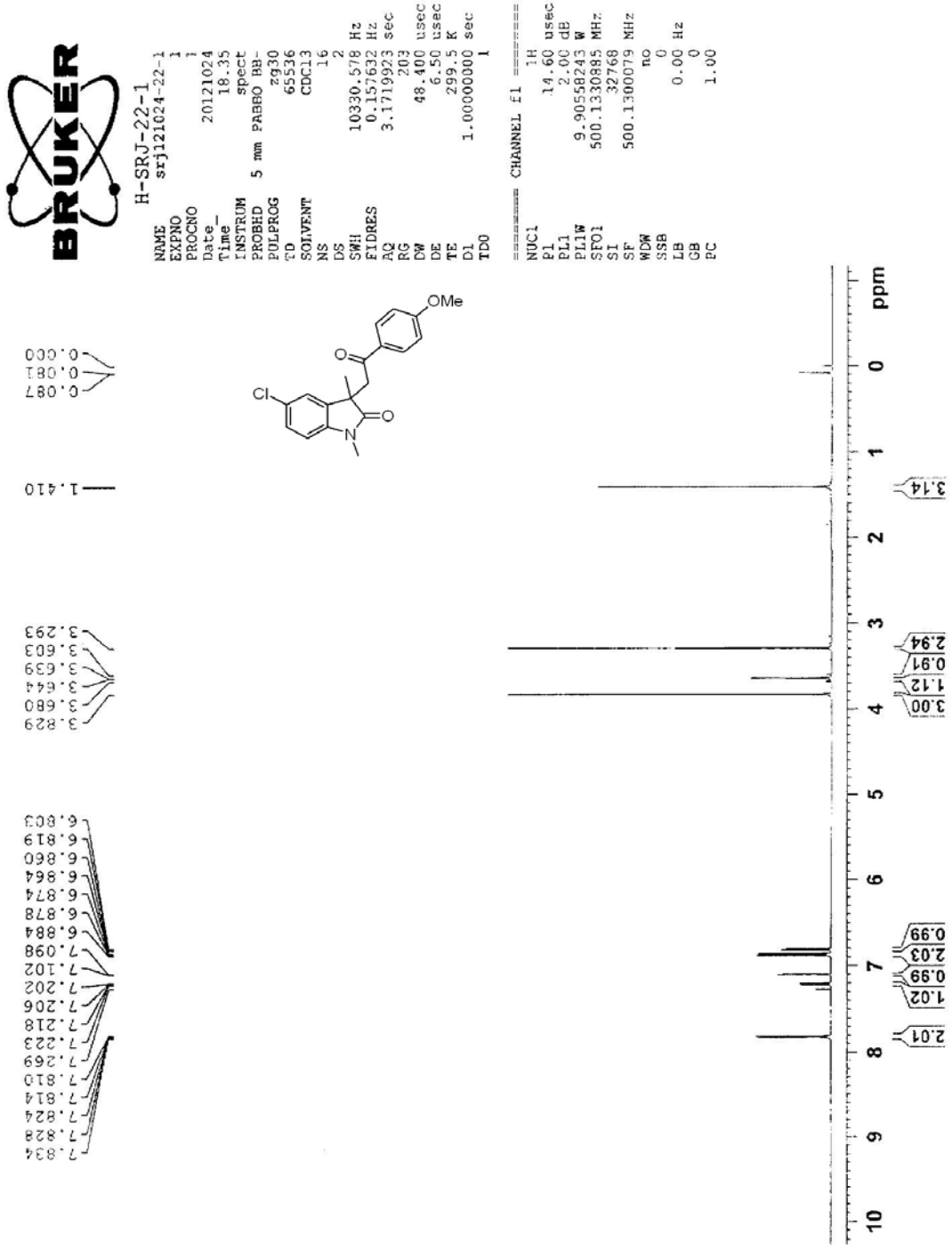
5-Methoxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (23)



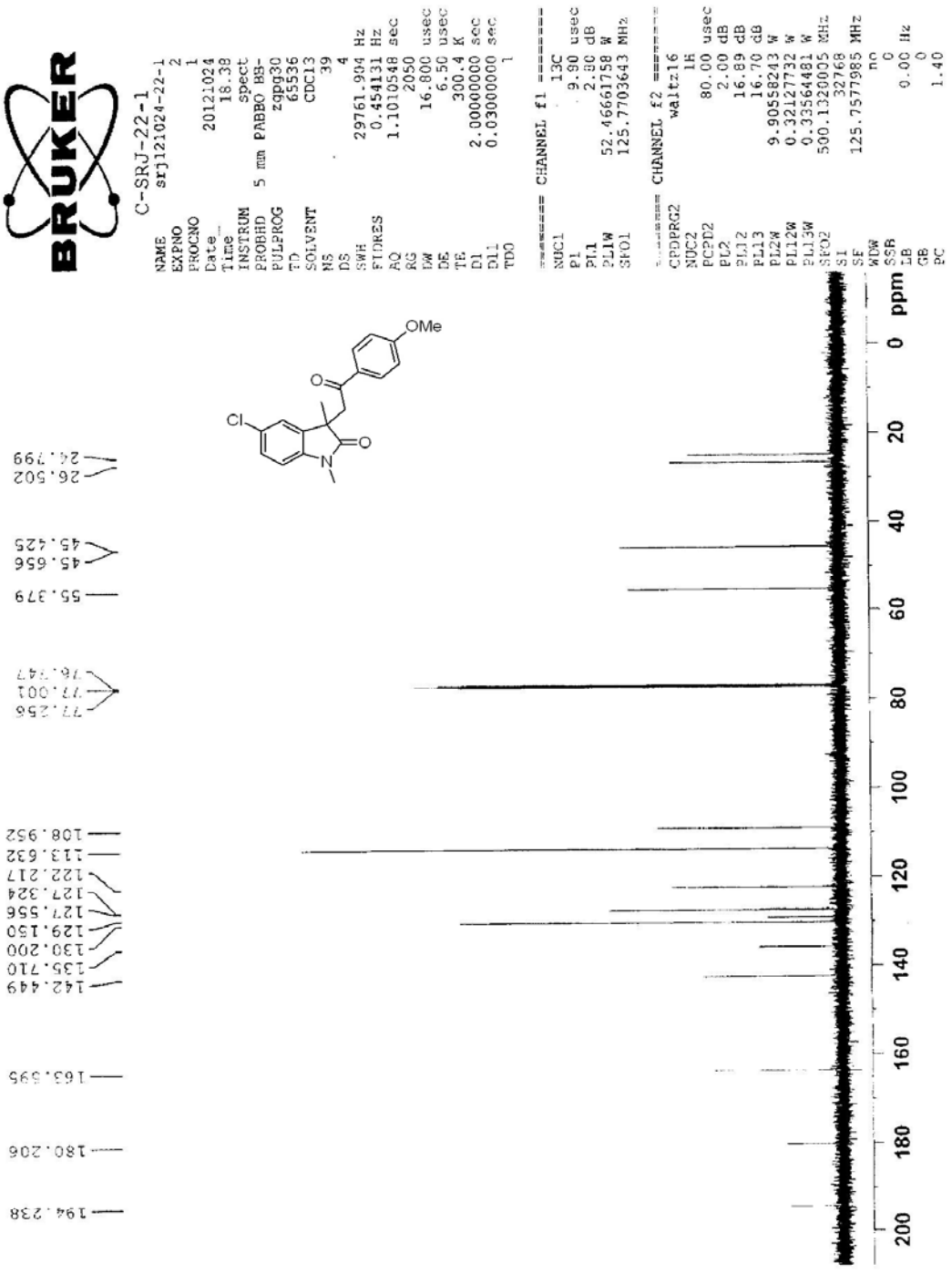
5-Methoxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (23)



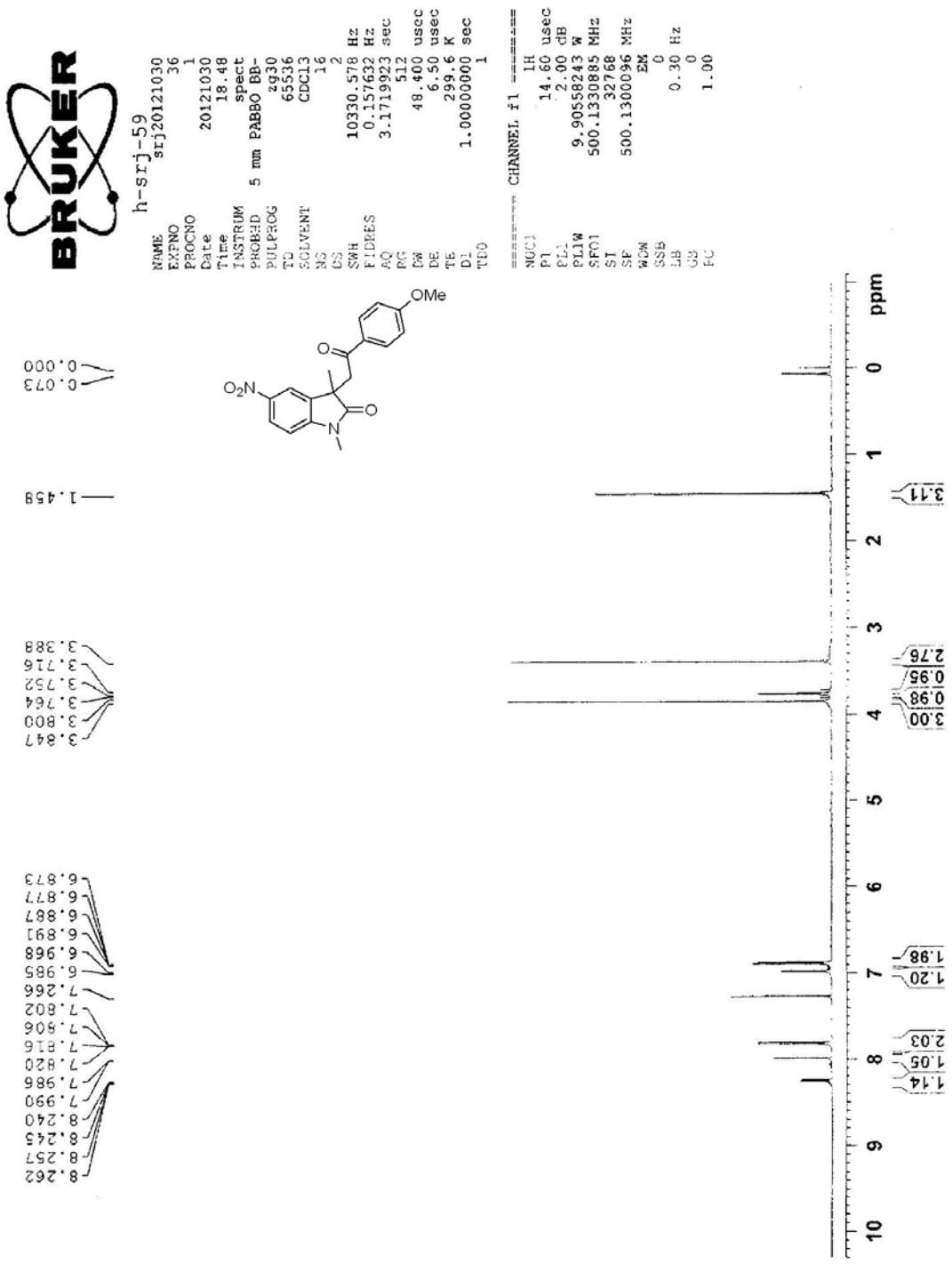
5-Chloro-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (24)



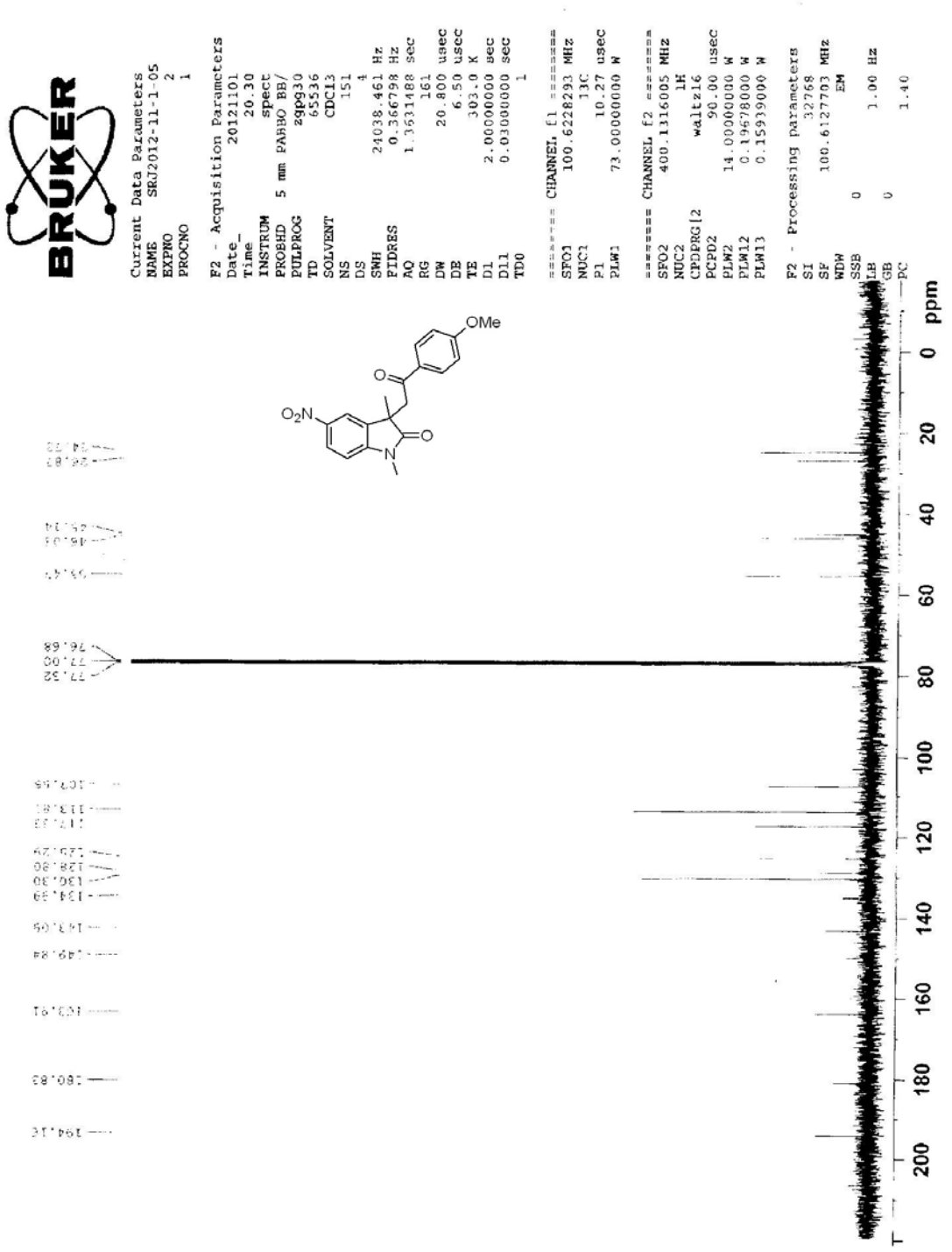
5-Chloro-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (24)



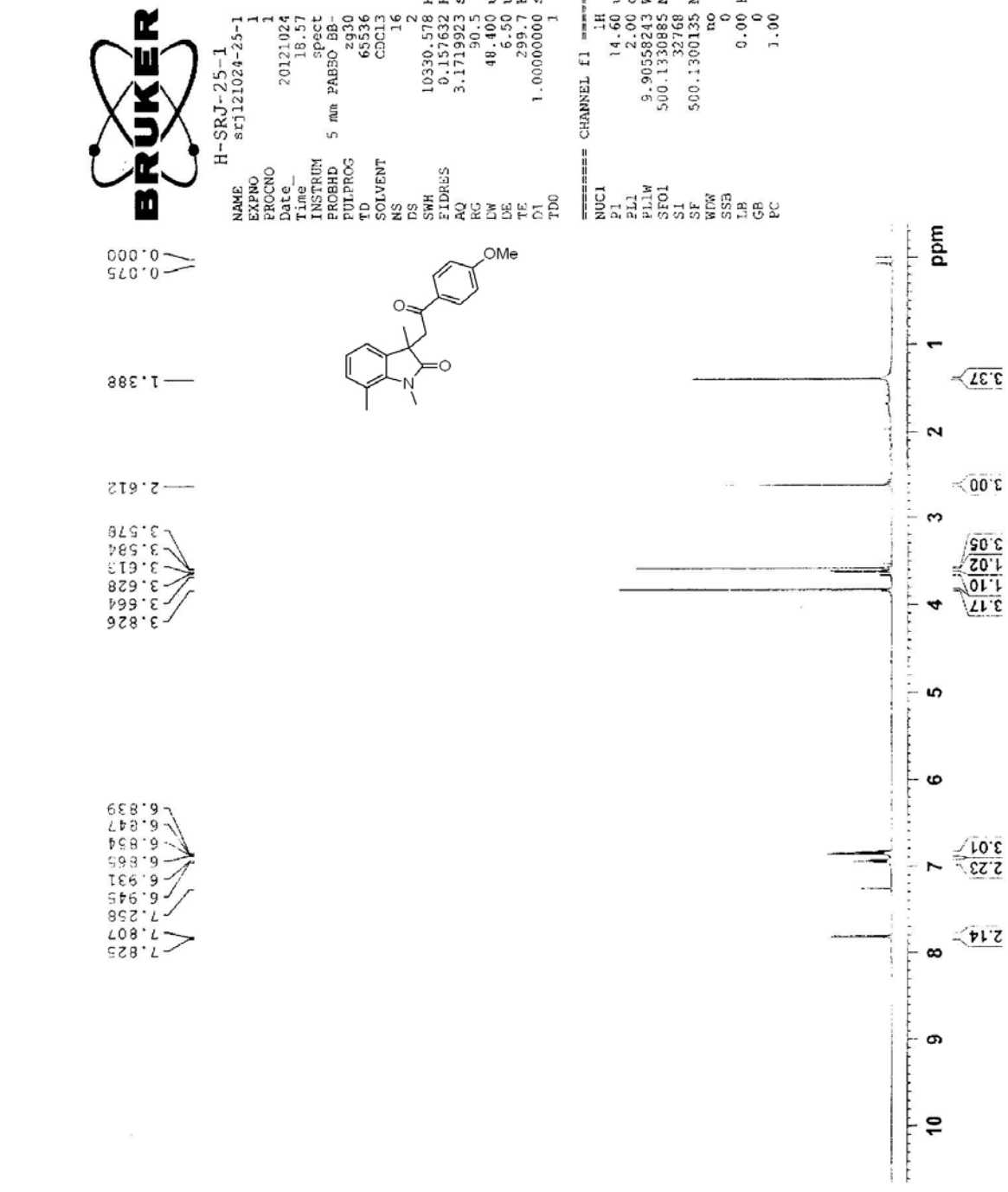
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-5-nitroindolin-2-one (25)



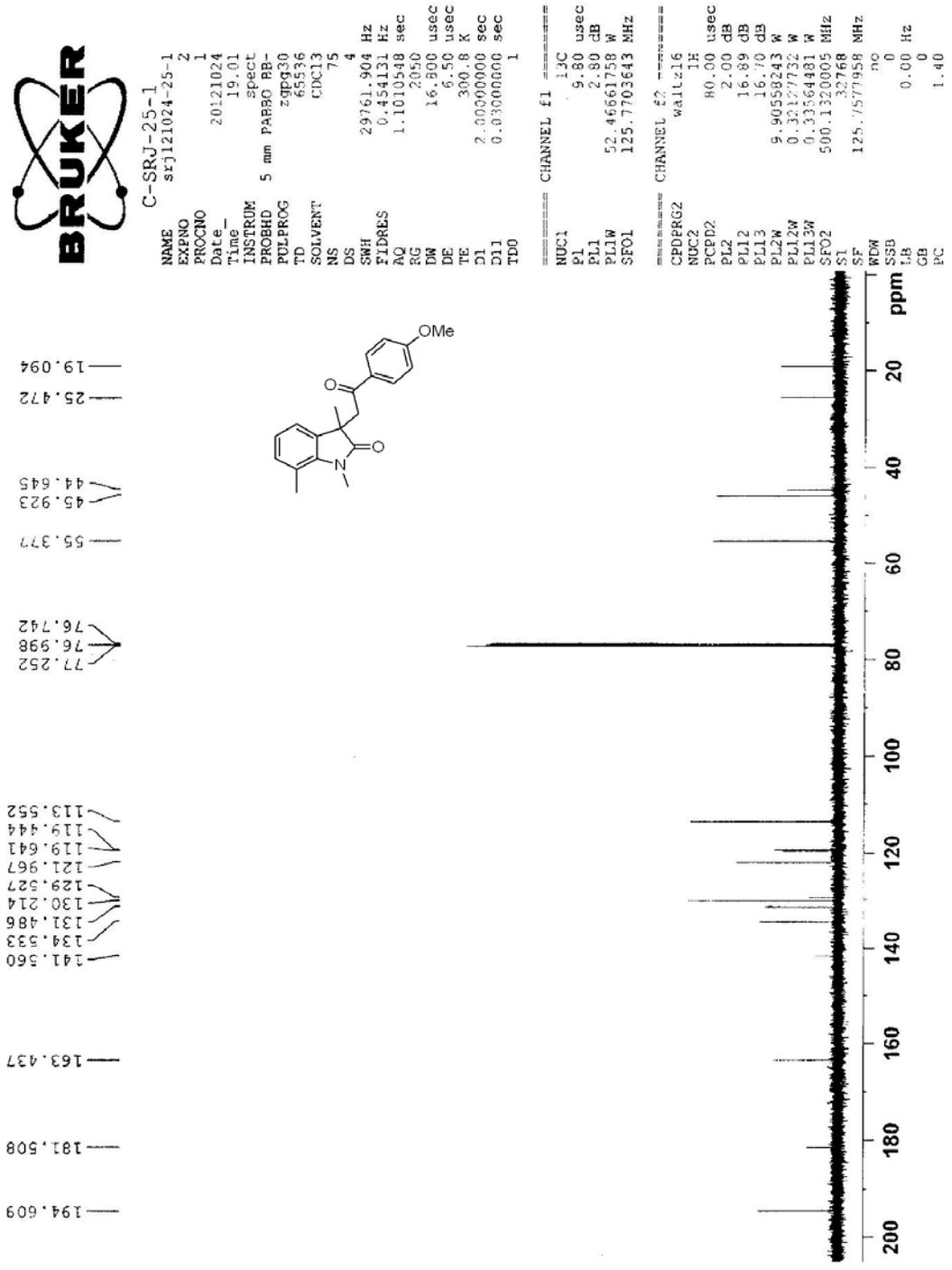
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-5-nitroindolin-2-one (25)



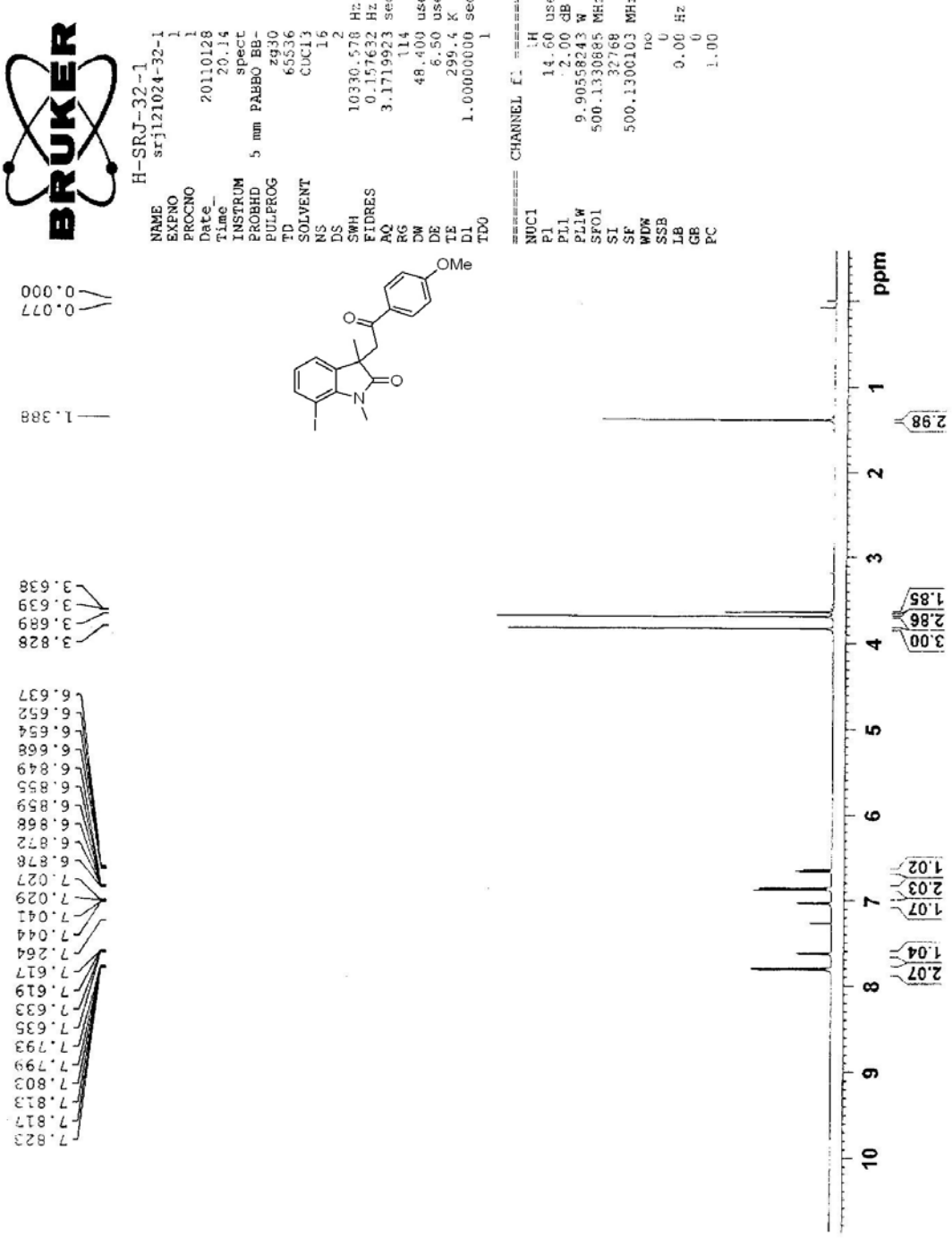
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,7-trimethylindolin-2-one (26)



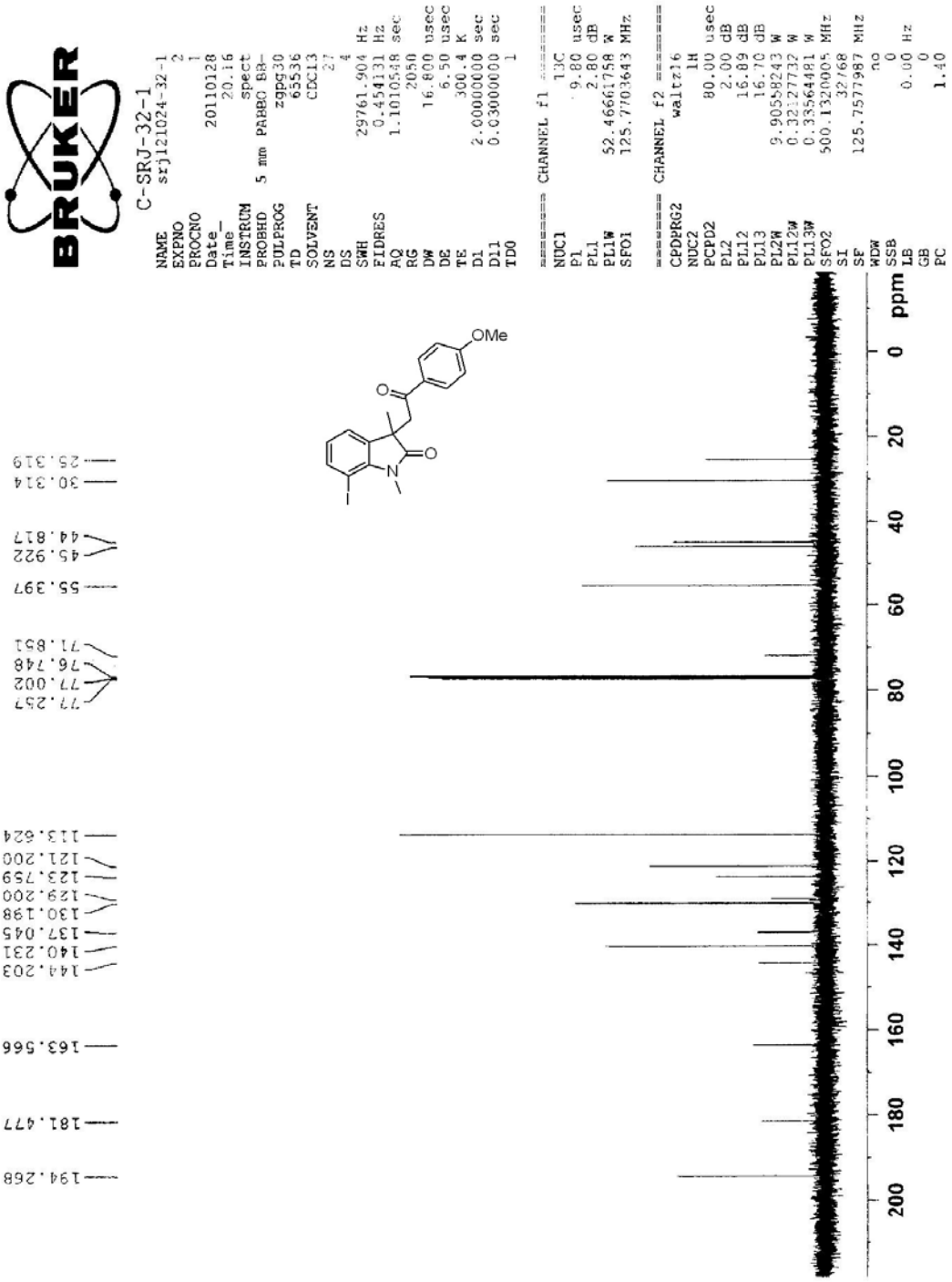
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,7-trimethylindolin-2-one (26)



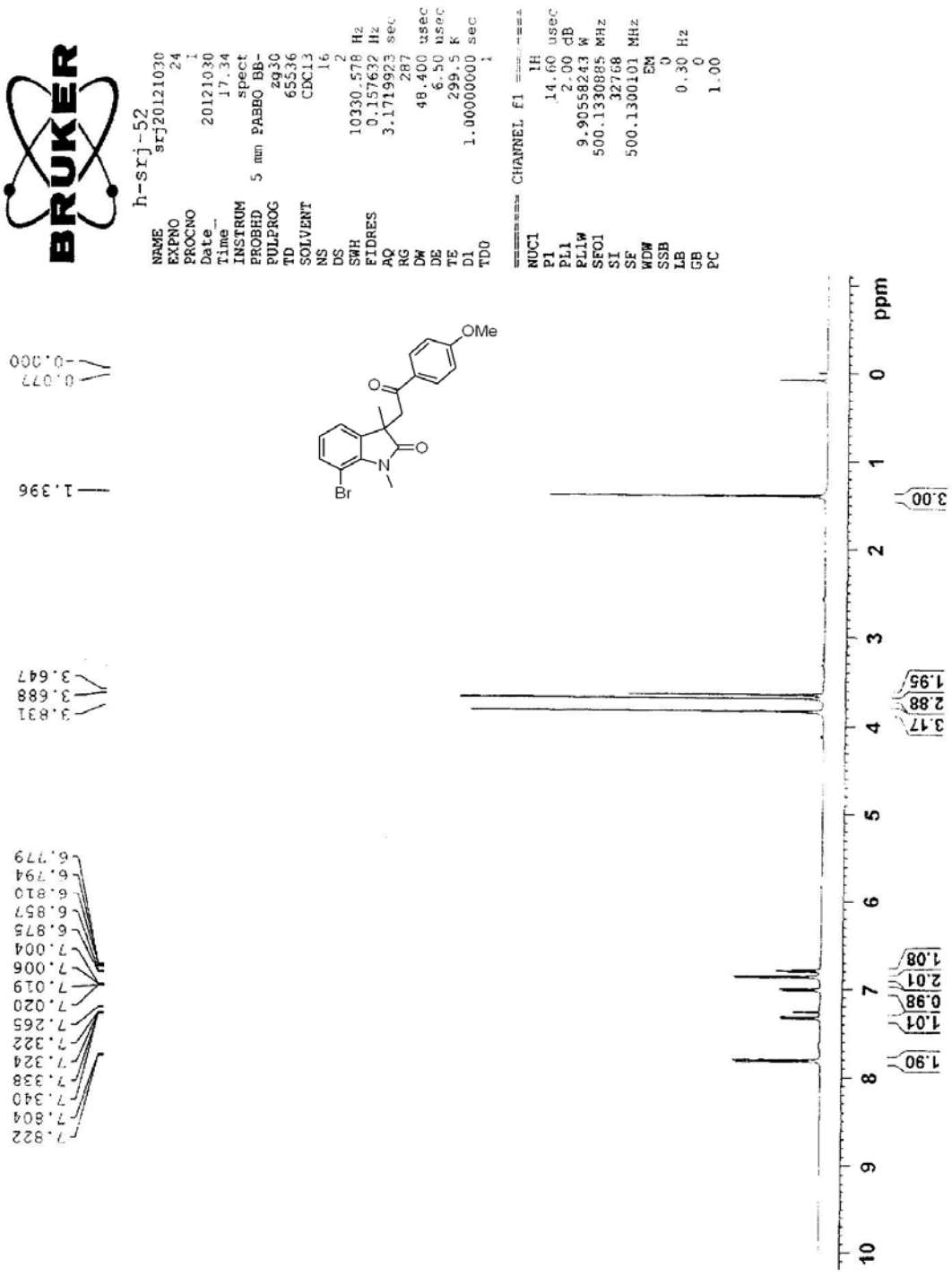
7-Iodo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (27)



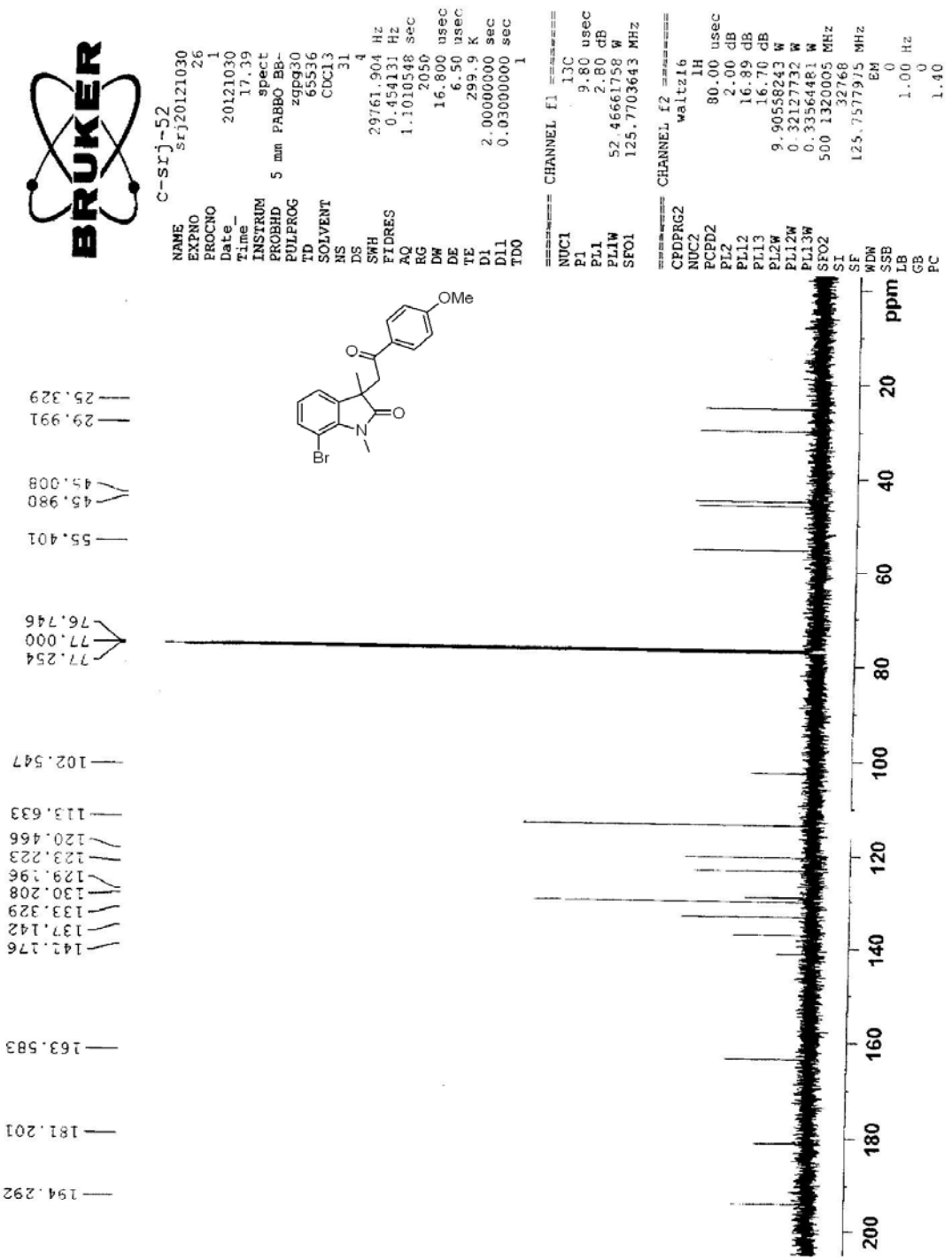
7-Iodo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (27)



7-Bromo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (28)

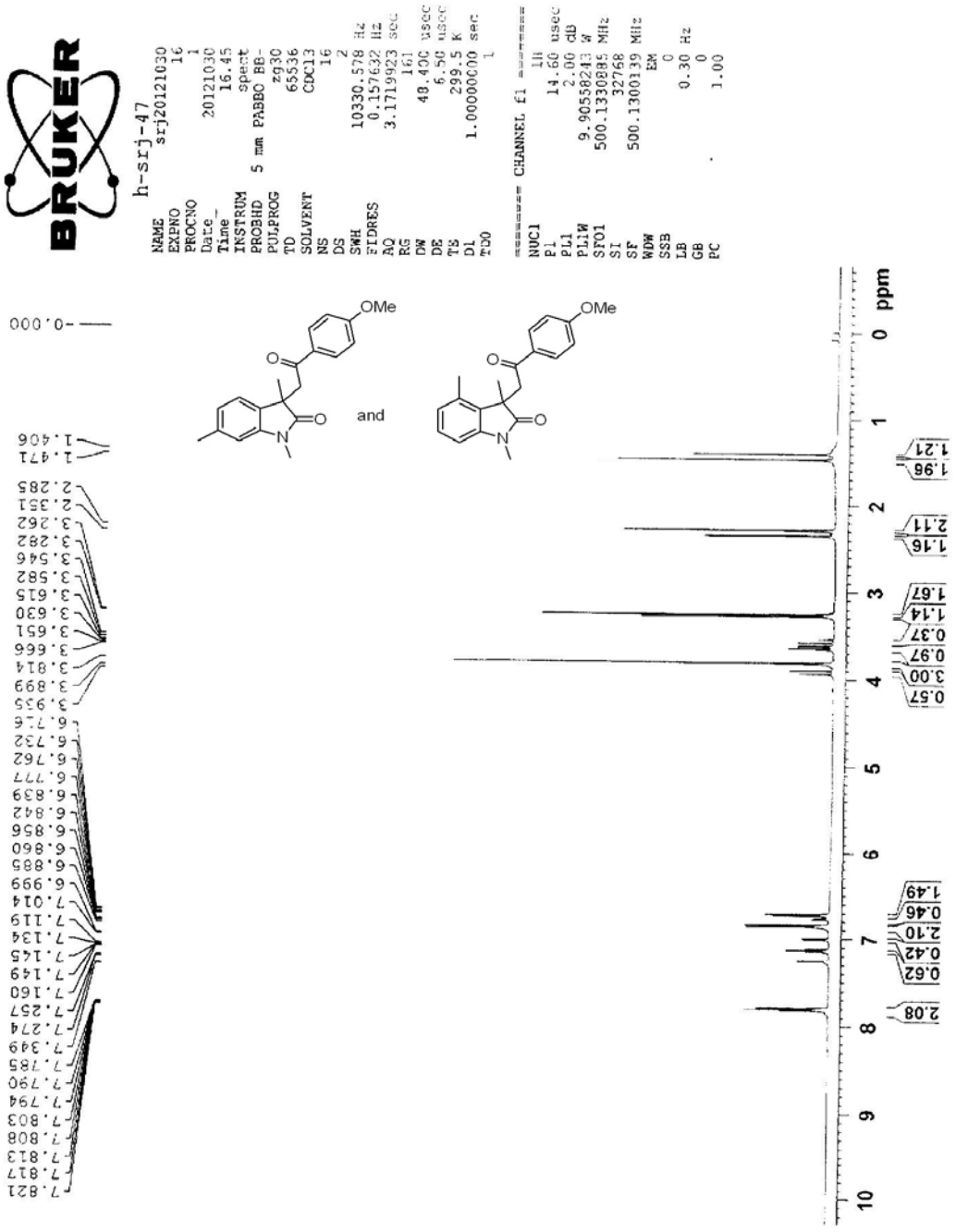


7-Bromo-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (28)



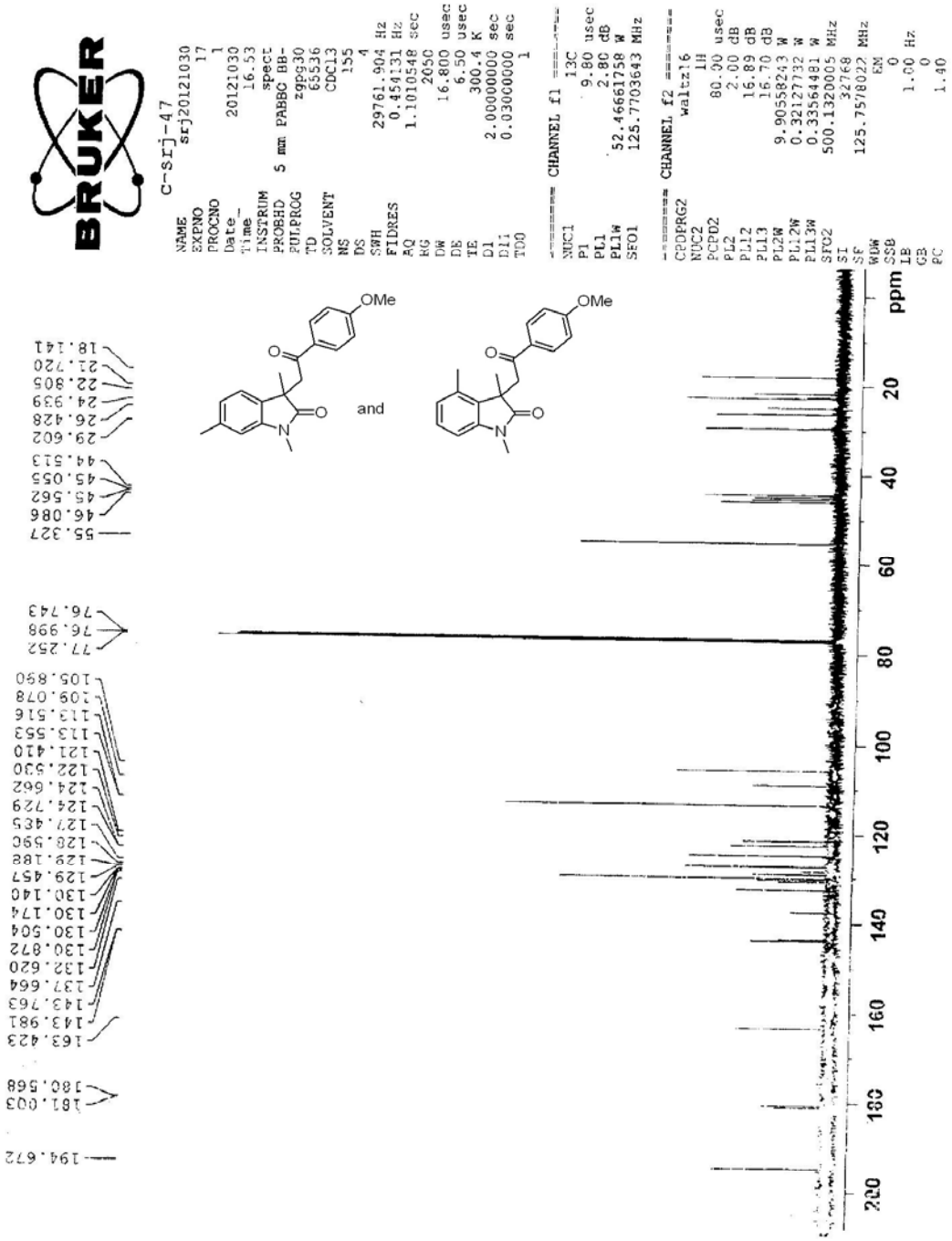
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,6-trimethylindolin-2-one (29)

and 3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,4-trimethylindolin-2-one (29′)

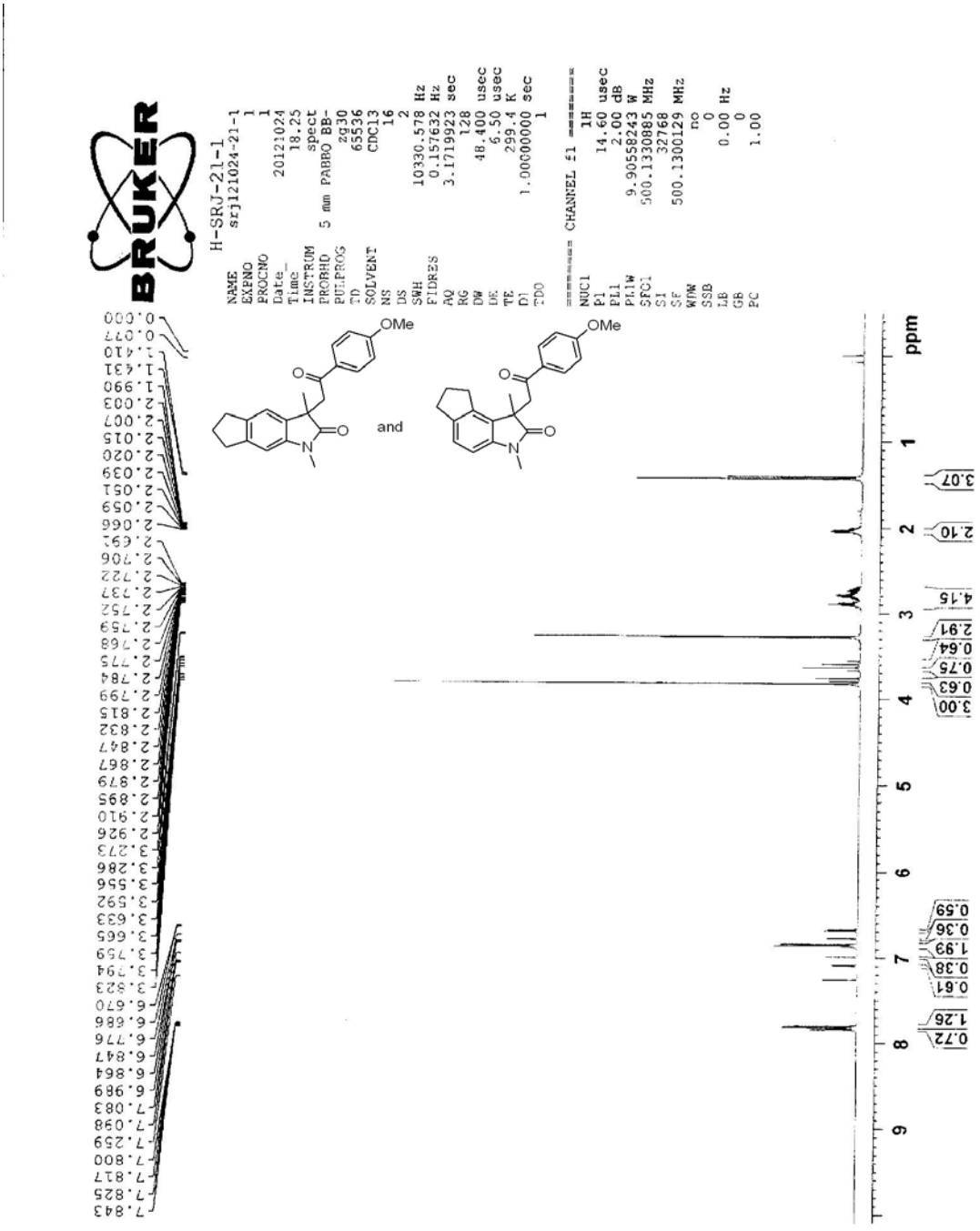


3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,6-trimethylindolin-2-one (29)

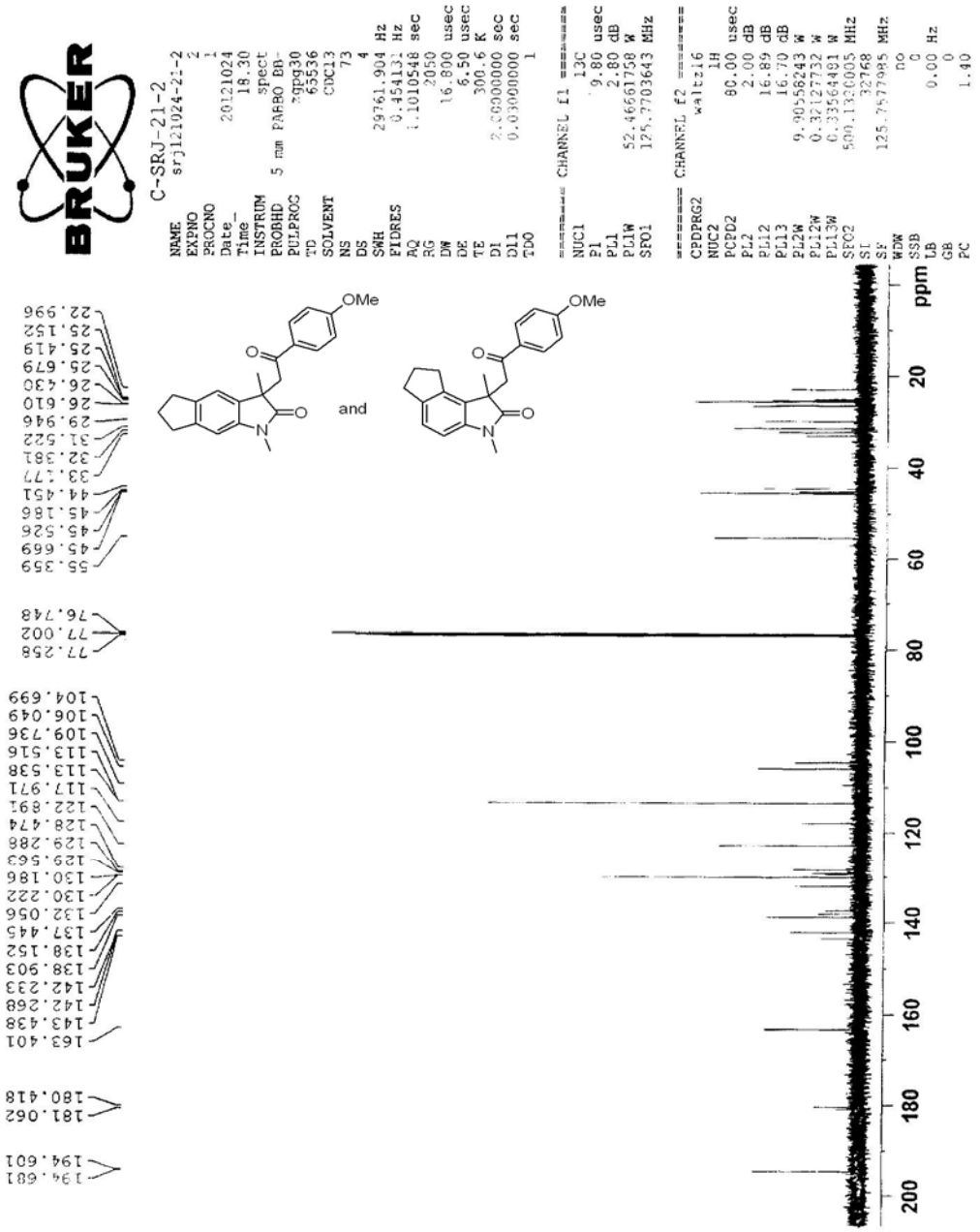
and 3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3,4-trimethylindolin-2-one (29´)



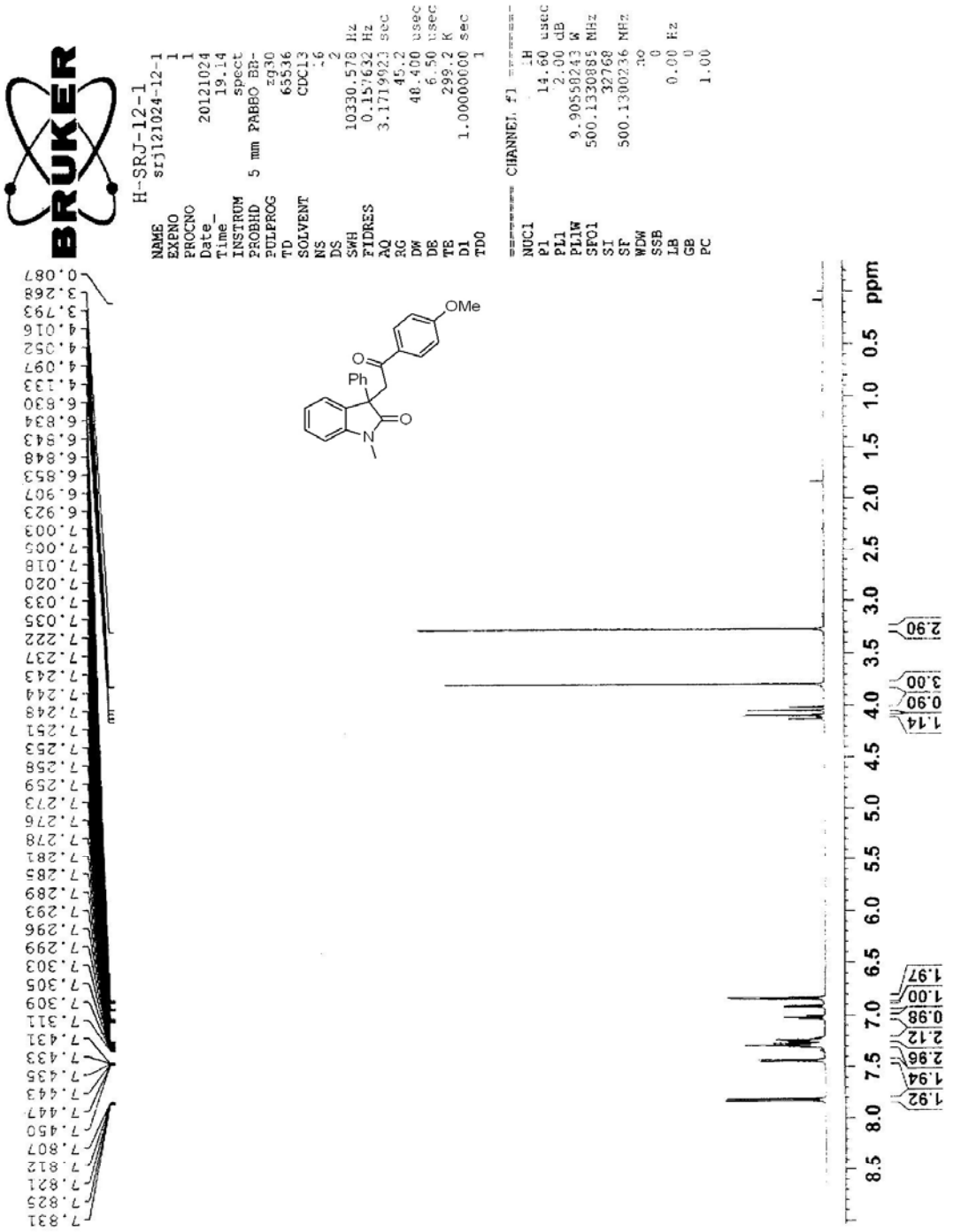
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[*f*]indol-2(1*H*)-one (30) and 1-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[*e*] indol-2(1*H*)-one (30′)



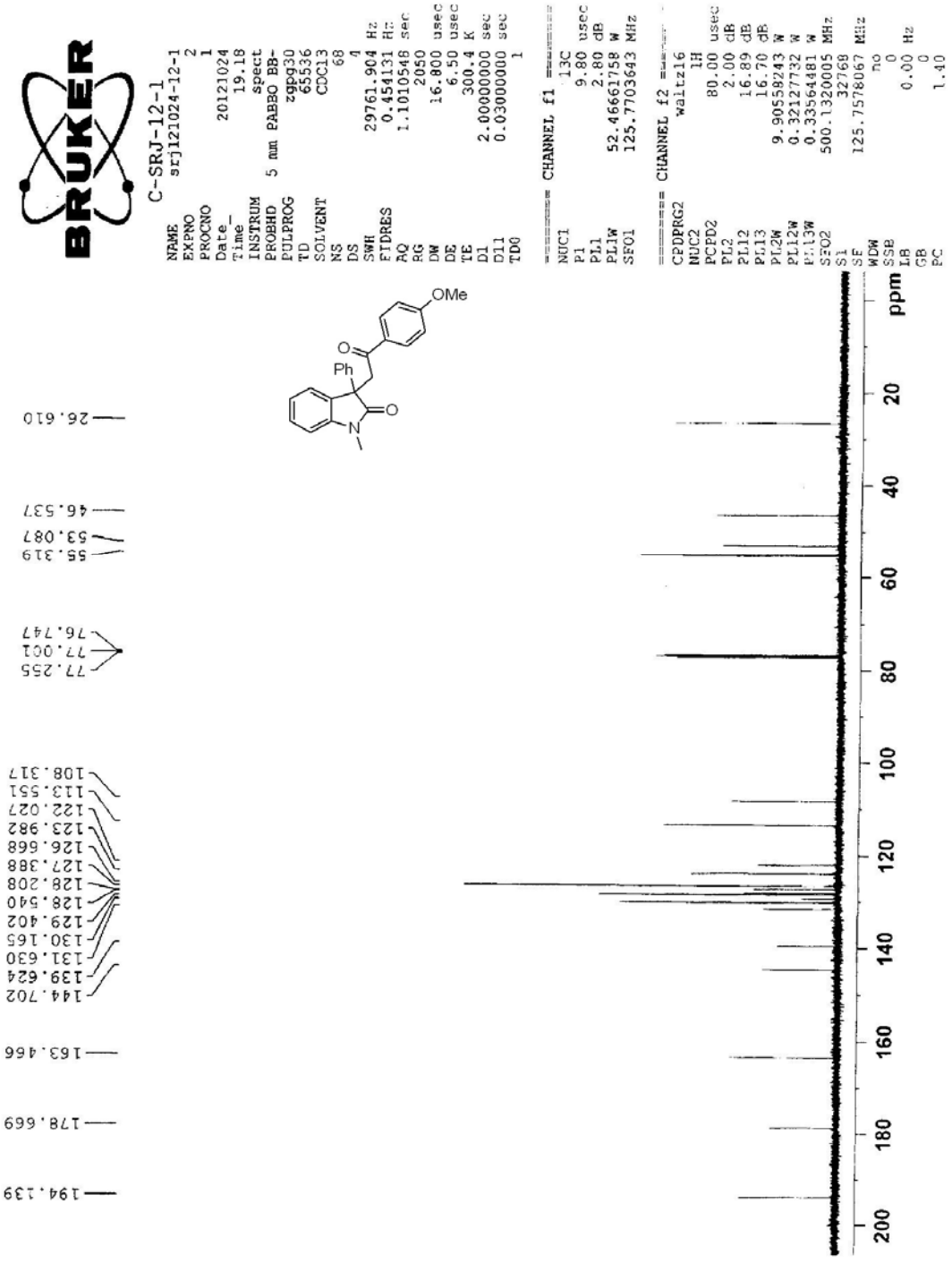
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,5,6,7-tetrahydrocyclopenta[*f*]indol-2(1*H*)-one (30) and 1-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-dimethyl-3,6,7,8-tetrahydrocyclopenta[*e*] indol-2(1*H*)-one (30′)



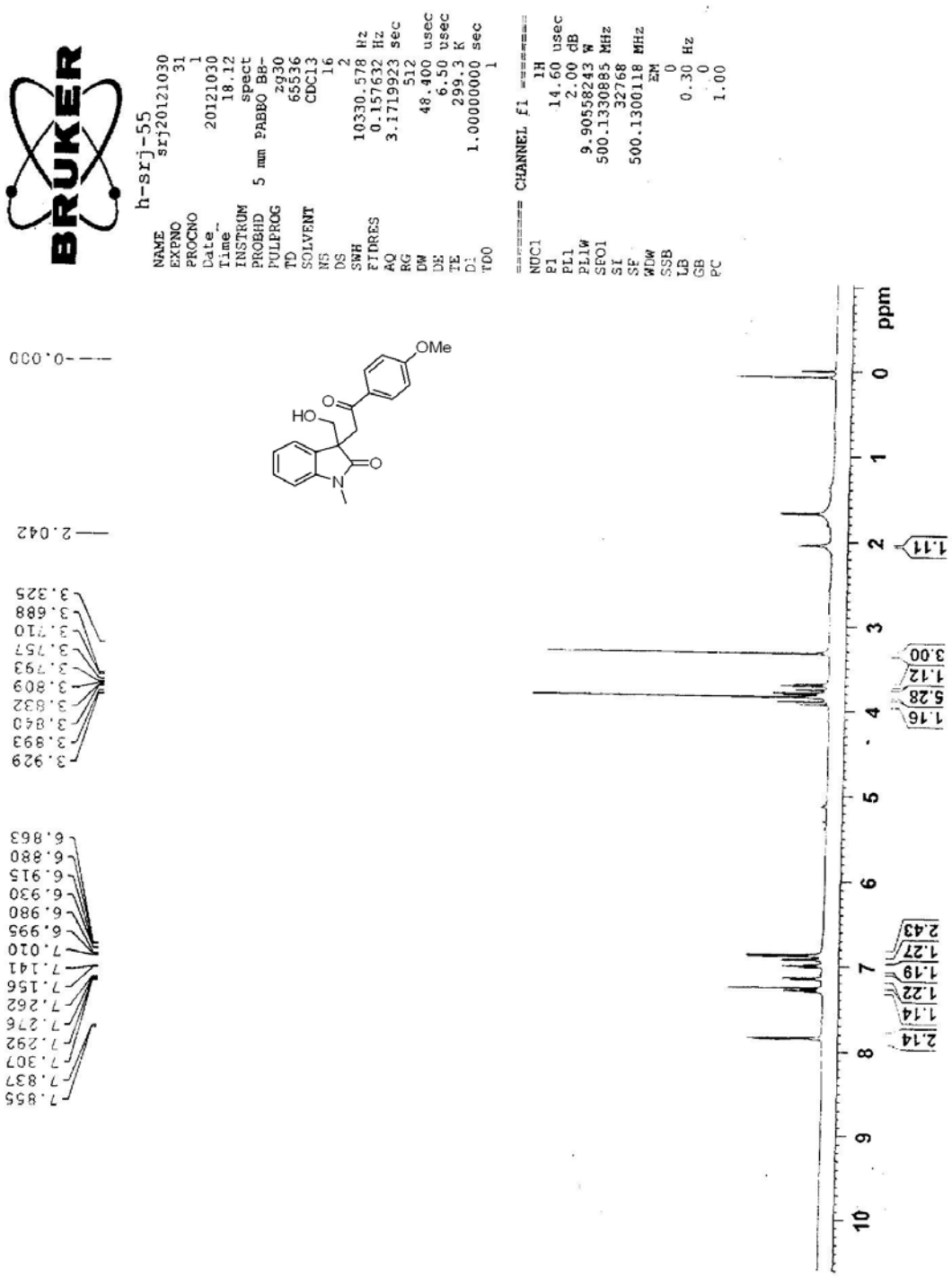
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-3-phenylindolin-2-one (32)



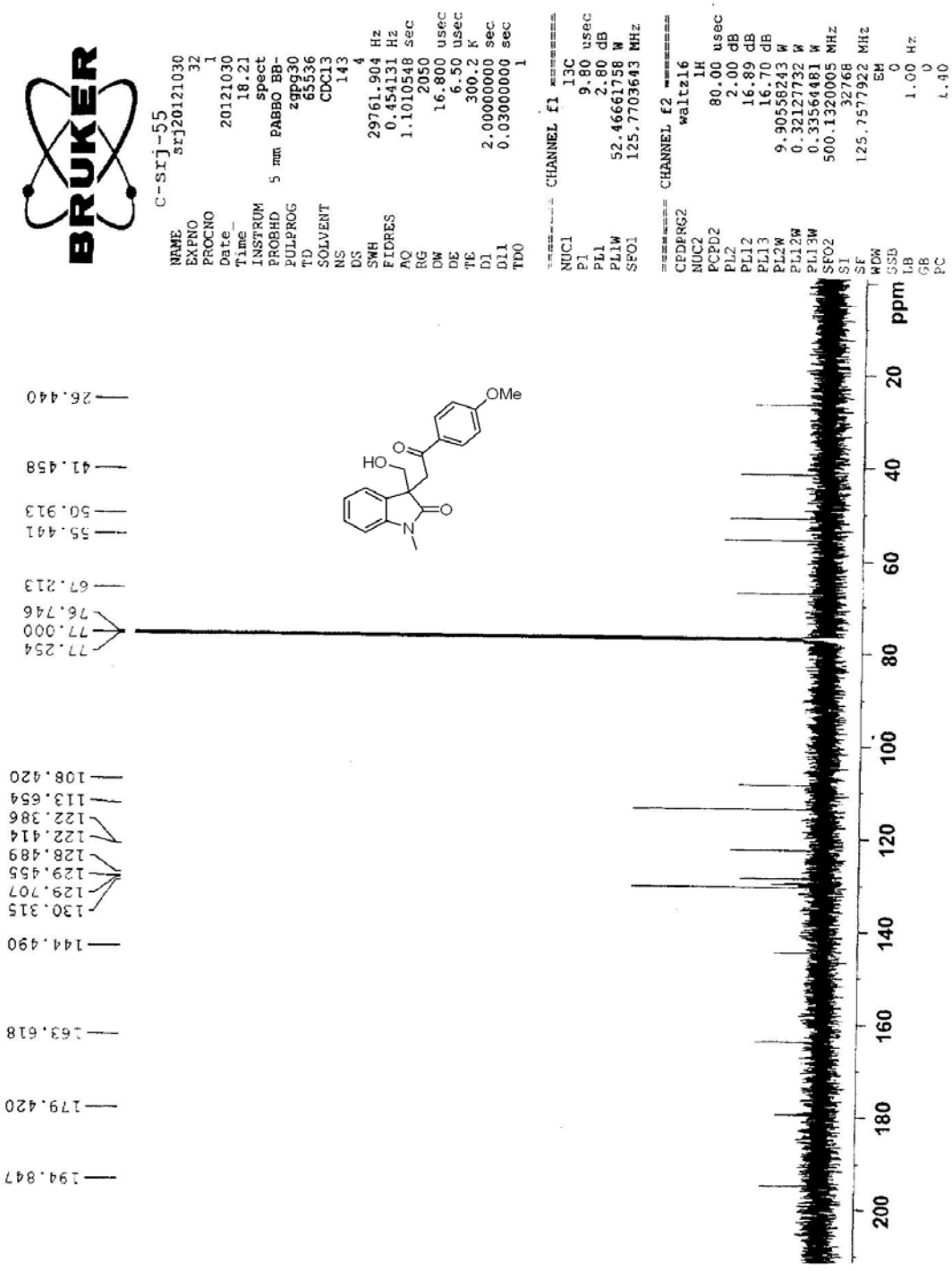
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-3-phenylindolin-2-one (32)



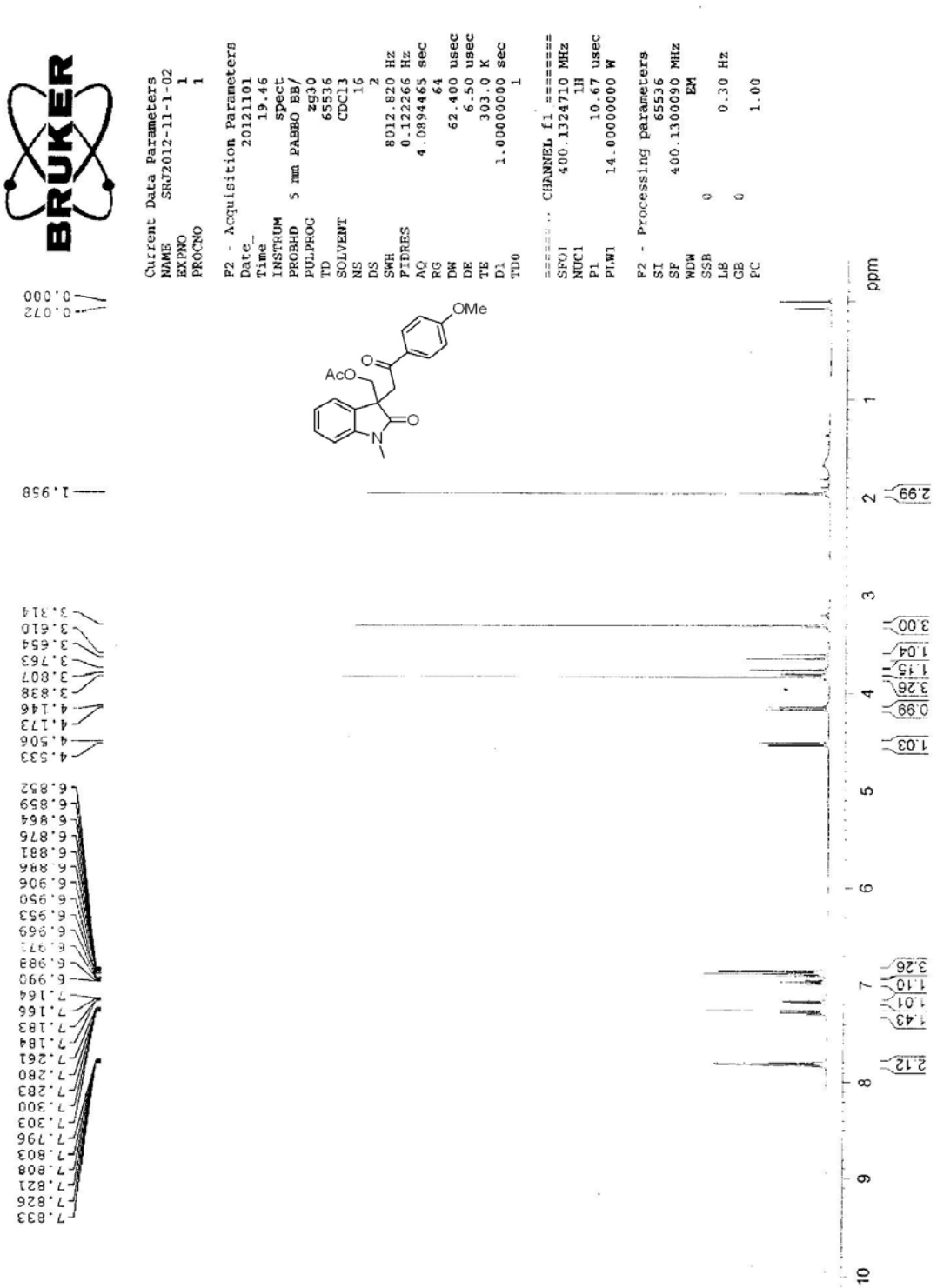
3-(Hydroxymethyl)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (33)



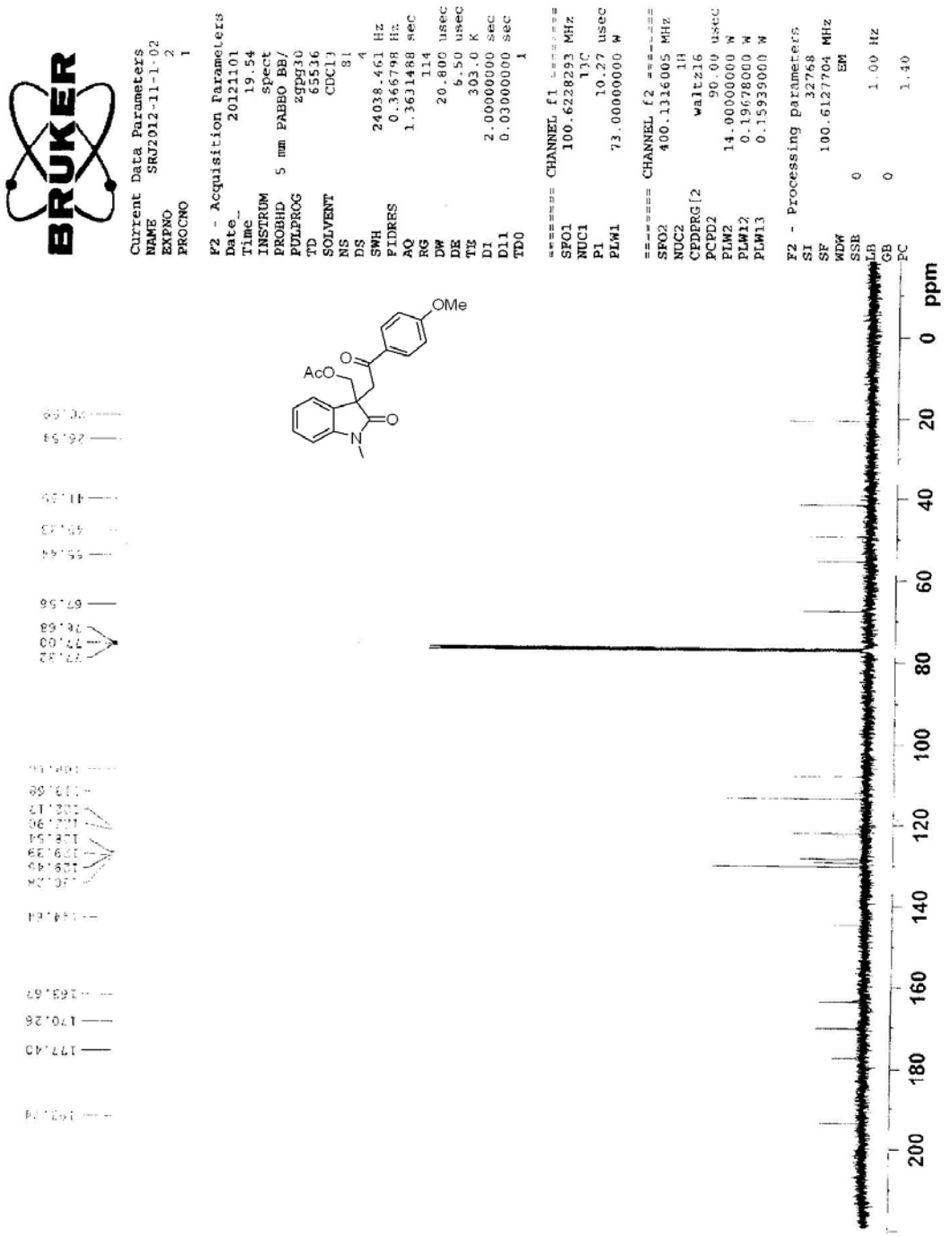
3-(Hydroxymethyl)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (33)



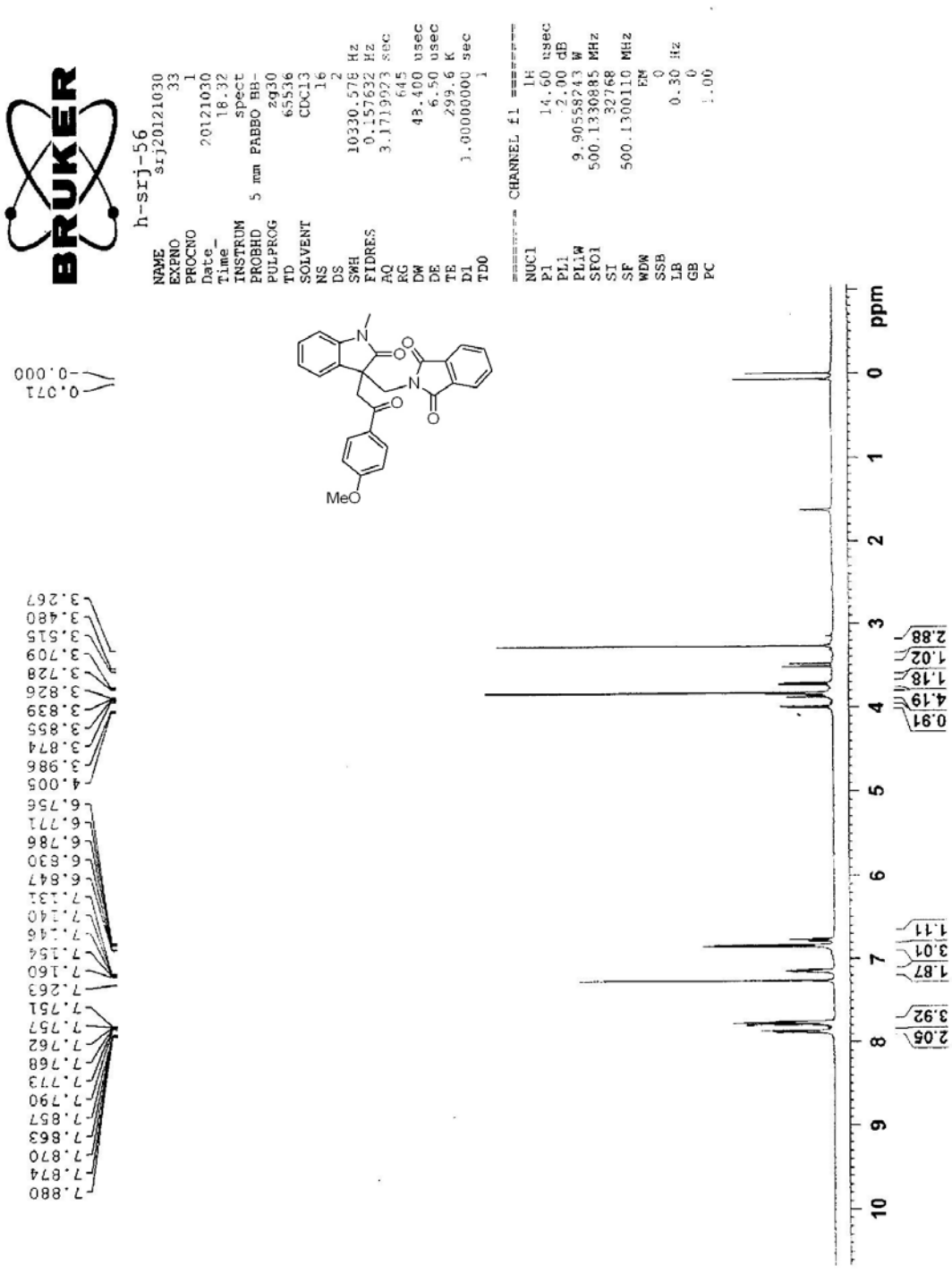
(3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (34)



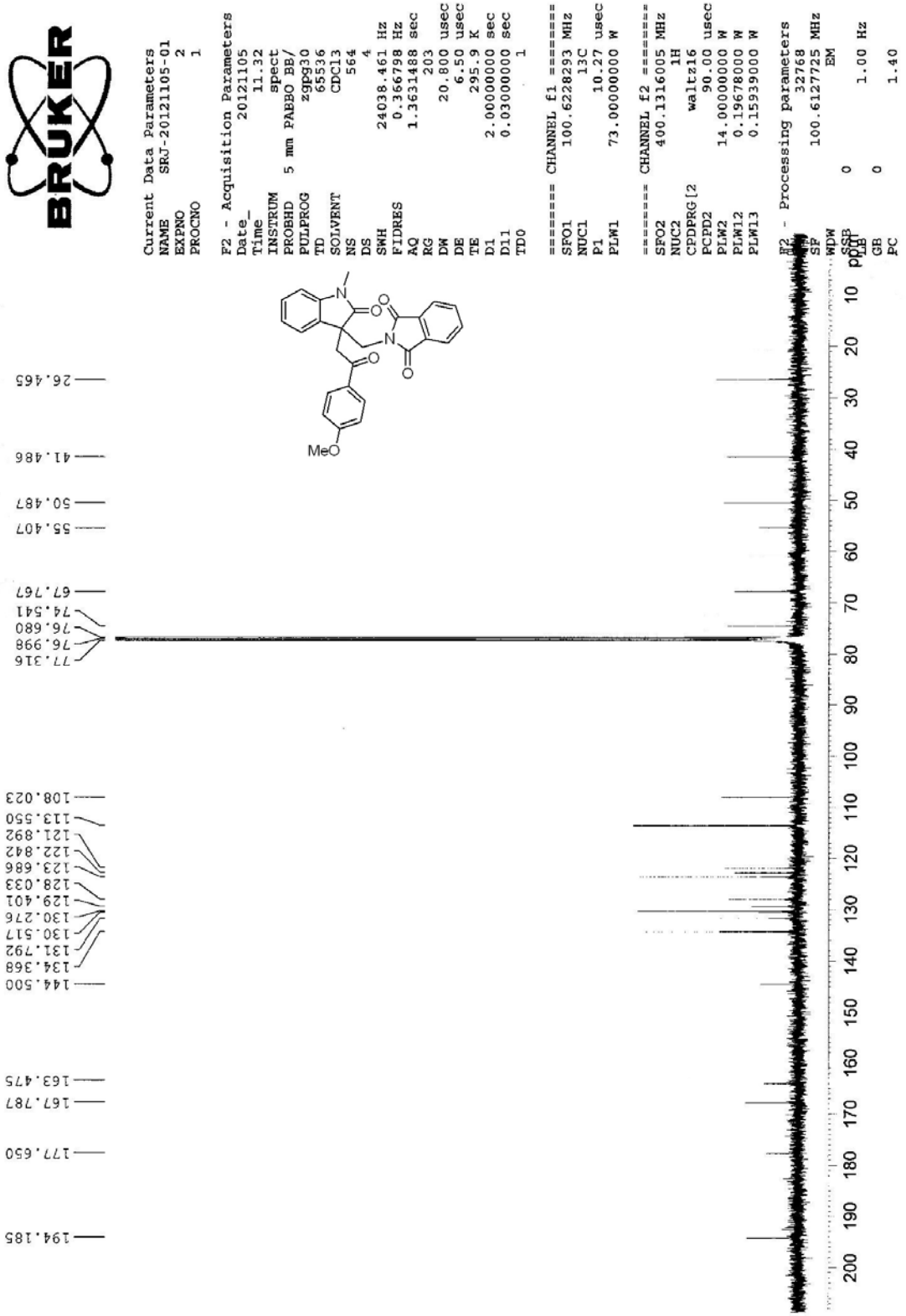
(3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (34)



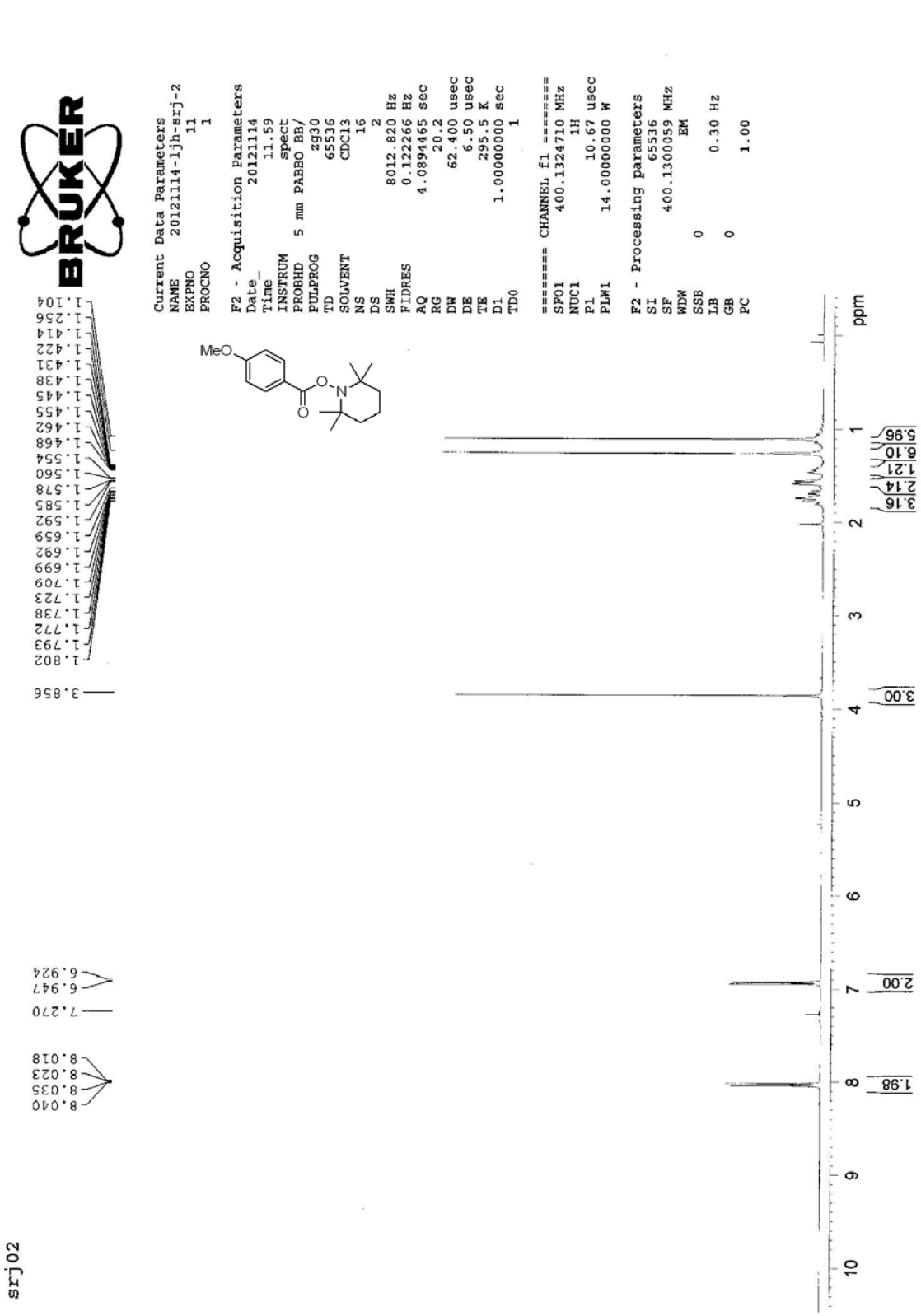
2-((3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl)isoindoline-1,3-dione (35)



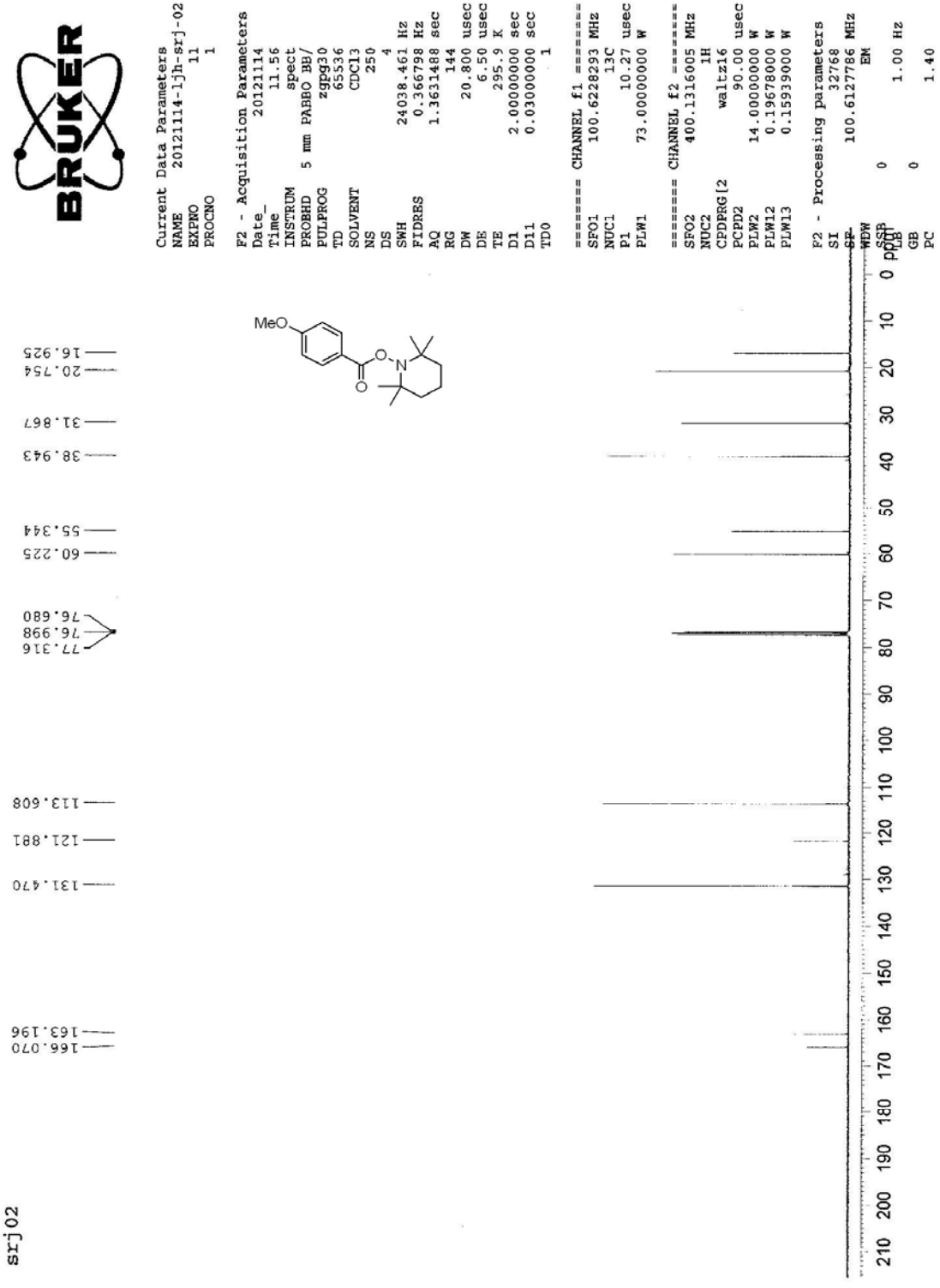
2-((3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl)isoindoline-1,3-dione (35)



2,2,6,6-Tetramethylpiperidin-1-yl 4-methoxybenzoate (36)

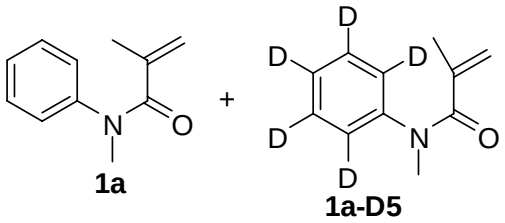


2,2,6,6-Tetramethylpiperidin-1-yl 4-methoxybenzoate (36)



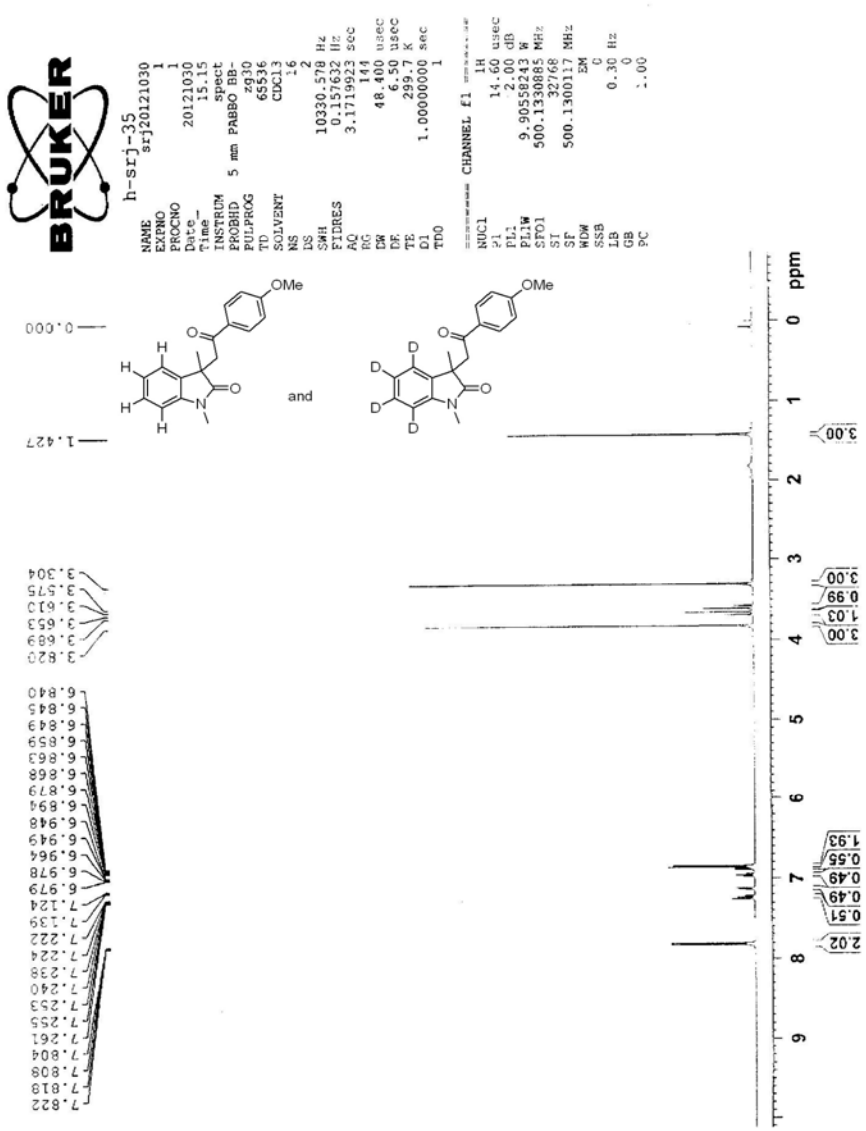
3 and 3-*D4*

Intermolecular KIE Experiment



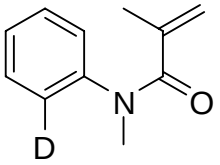
1a **1a-D5**

43% yield (11 h), $k_{H/D}$ = 1.0



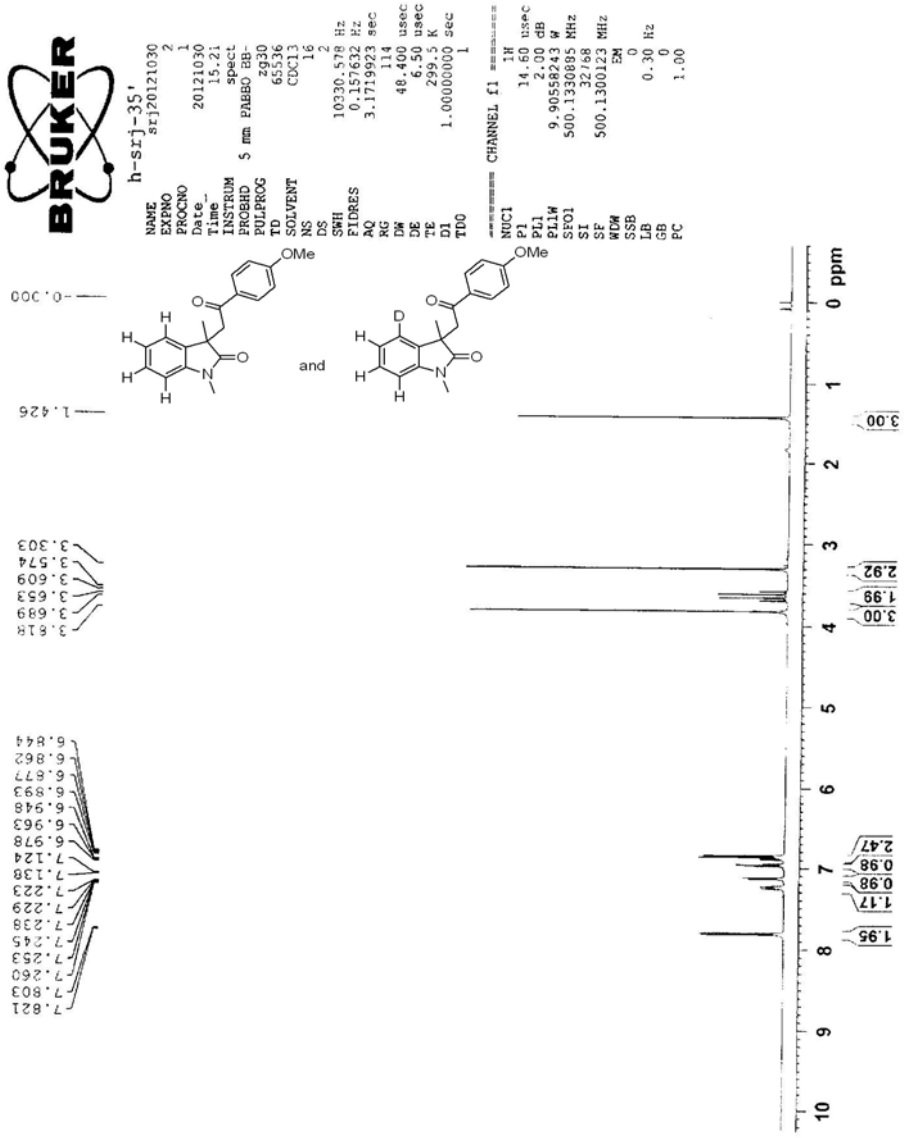
3 and 3-*D1*

Intramolecular KIE Experiment

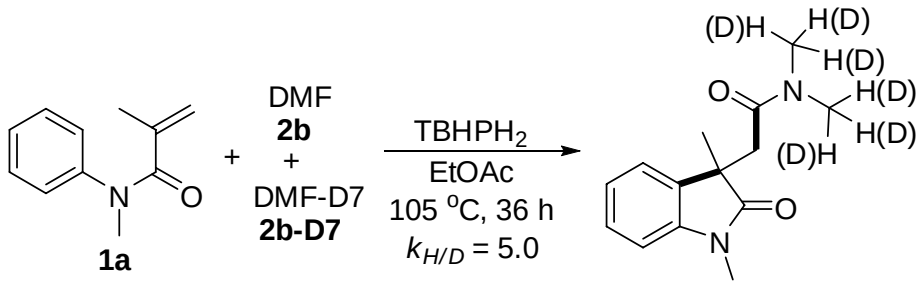


1a-D1

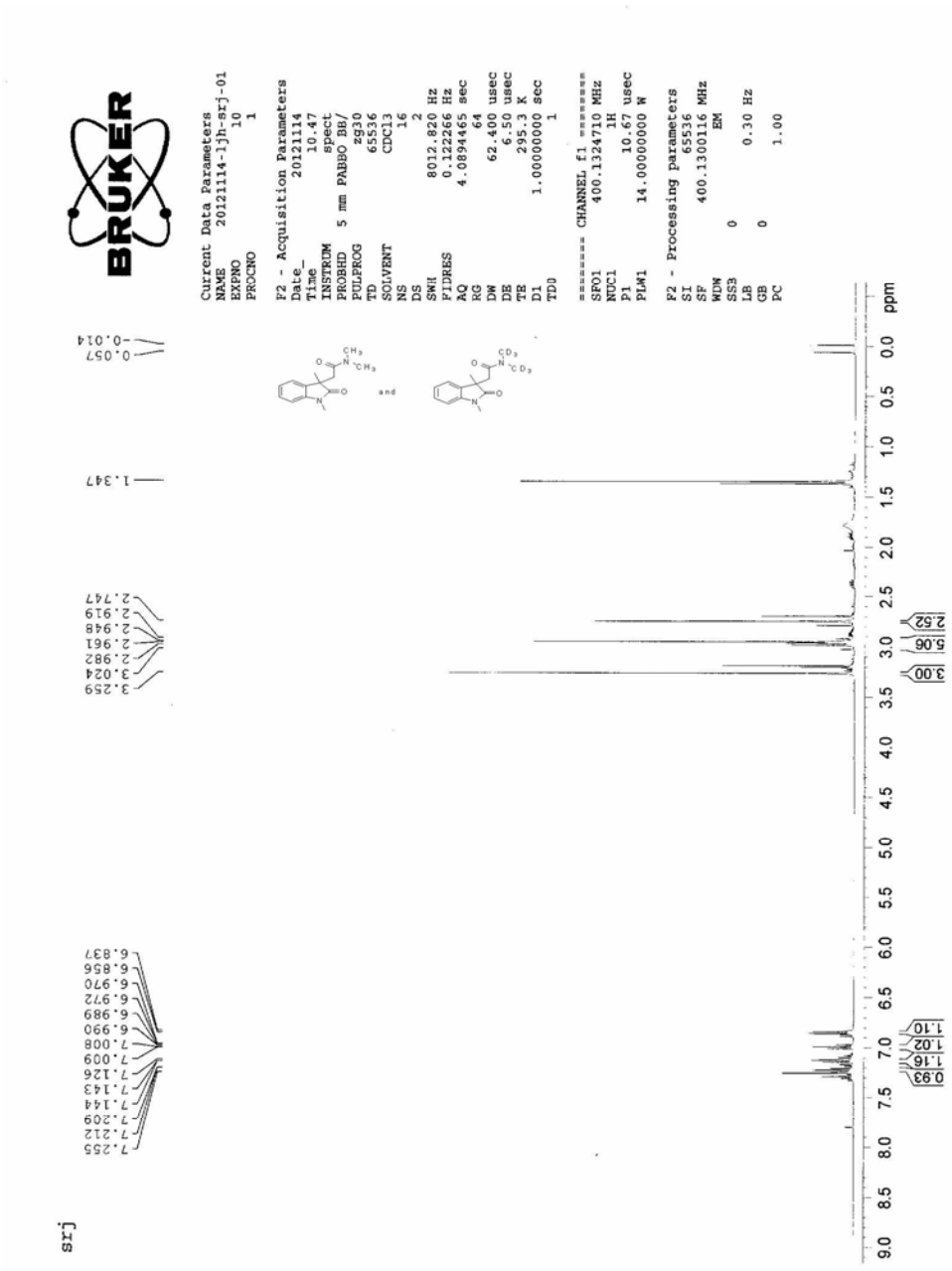
76% yield (36 h), $k_{H/D}$ = 1.0



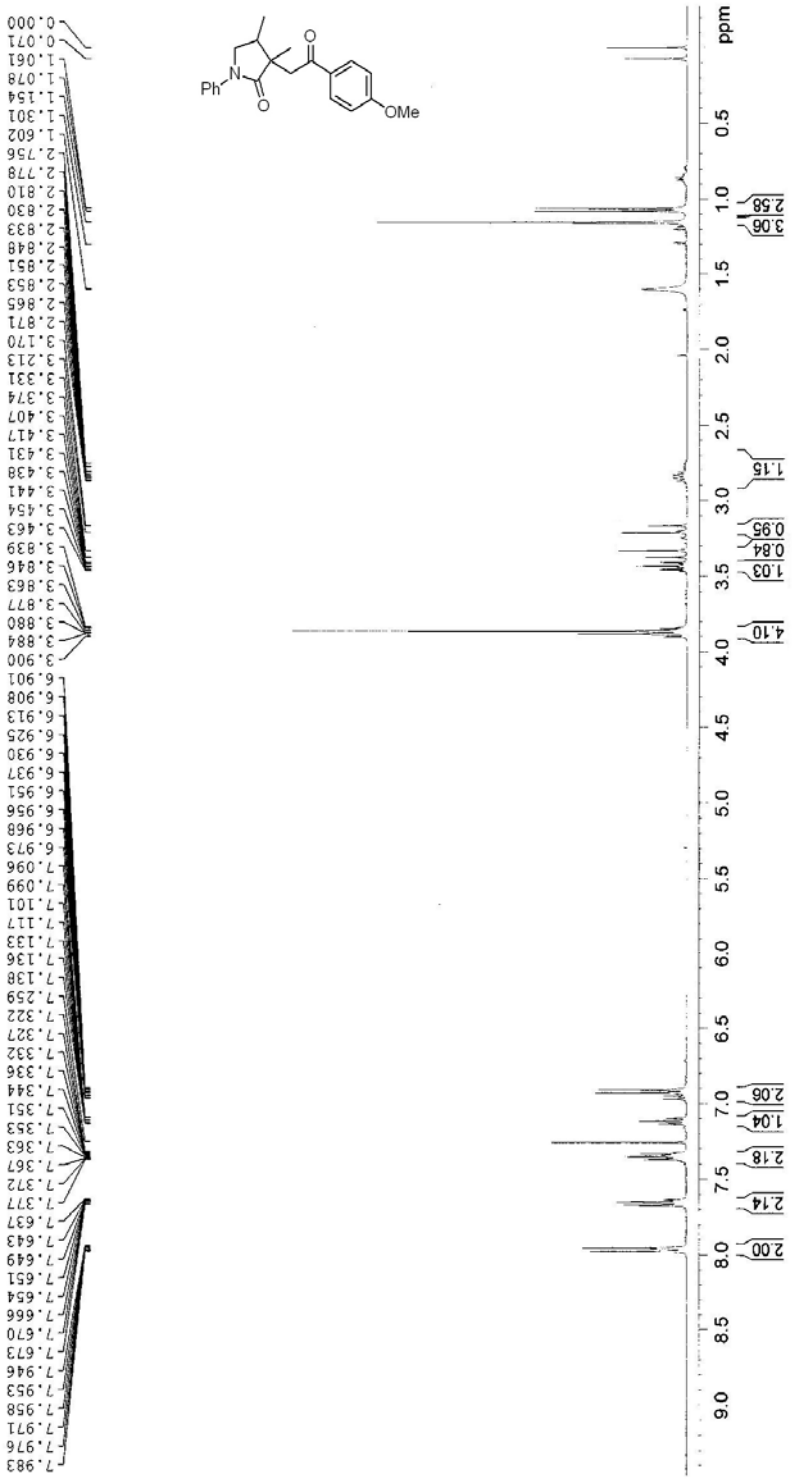
15-D6



15 + 15-D6 = 75%



3-(2-(4-Methoxyphenyl)-2-oxoethyl)-3,4-dimethyl-1-phenylpyrrolidin-2-one (36)



3-(2-(4-Methoxyphenyl)-2-oxoethyl)-3,4-dimethyl-1-phenylpyrrolidin-2-one (36)