Synthesis of (2-Oxoindolin-3-ylidene)methyl Acetates involving a C-H Functionalization Process

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(A) Typical experimental procedure

(a) Materials:

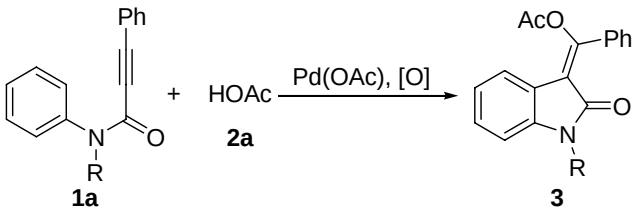
Substrates were prepared according to the known procedures.[1]

(b) Typical experimental procedure for the palladium-catalyzed C-H functionalization reactions of *N*-aryl-*N*-substituted-propiolamides.

A mixture of aniline (0.2 mmol), $Pd(OAc)_2$ (10 mol %) and $PhI(OAc)_2$ (1.2 equiv or 2 equiv) in HOAc (**2a**; 3 mL) or acid (**2b-i**; 5 equiv)/MeCN (3 mL) was stirred at 80 ^oC for the indicated time until complete consumption of starting material as monitored by TLC. After the reaction was finished, the mixture was poured into ethyl acetate, which was washed with brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product.

(B) Table S1.

Table S1. Screening Conditions[a]



Entry	[O] (equiv)	Solvent	Time (h)	Yield (%)[b]
1[c]	$PhI(OAc)_2$ (2.0)	MeCN	10	trace
2[d]	$PhI(OAc)_2$ (2.0)	MeCN	10	56
3[e]	$PhI(OAc)_2$ (2.0)	MeCN	10	80
4	$PhI(OAc)_2$ (2.0)	MeCN	10	89
5	$PhI(OAc)_2$ (2.0)	HOAc	2	91
6	oxone (2.0)	HOAc	10	messy
7	$K_2S_2O_8$ (2.0)	HOAc	10	messy
8	$Cu(OAc)_2$ (2.0)	HOAc	10	9
9	$Cu(OAc)_2$ (2.0)/O_2 (1 atm)	HOAc	48	34
10	O_2 (1 atm)	HOAc	10	trace
11	$PhI(OAc)_2$ (1.2)	HOAc	2	90
12[f]	$PhI(OAc)_2$ (1.2)	HOAc	5	89
13[g]	$PhI(OAc)_2$ (1.2)	HOAc	5	0
14[h]	$PhI(OAc)_2$ (1.2)	HOAc	2	38
15[i]	$PhI(OAc)_2$ (1.2)	HOAc	2	88

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), [O], and HOAc (10 equiv) in solvent (3 mL) at 80 ^oC. [b] Isolated yield. [c] Without HOAc, A 17% yield of 1-methyl-3-(diphenylmethylene)indolin-2-one (**4**) was isolated. [d] HOAc (2 equiv). A 6% yield of the by-product **4** was isolated. [e] HOAc (5 equiv). [f] $Pd(OAc)_2$ (5 mol %). [g] Without $Pd(OAc)_2$. [h] At room temperature. [i] At 100 ^oC.

(C) Analytical data for 3, 5, 8-17, 19, 21, 23, 25 and 27-32

(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (3): Yellow solid, mp 171.1-172.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.68 (d, *J* = 9.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.45-7.43 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.6, 166.1, 156.9, 142.7, 133.2, 130.7, 129.4, 129.3, 127.9, 123.6, 122.2, 121.5, 116.9, 108.0, 25.9, 21.3; IR (KBr, cm^{-1}): 1774, 1688, 1603; LRMS (EI, 70 eV) *m/z* (%): 293 (M^{+}, 3), 251 (78), 173 (100); HRMS (EI) for $C_{18}H_{15}NO_3$ (M^{+}): calcd. 293.1052, found 293.1051.

(*E*)-(1-*p*-Methylbenzyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (5): Yellow solid, mp 130.6-104.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.74-7.72 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 3H), 7.17 (td *J* = 8.0 Hz, 3H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.86 (s, 2H), 2.37 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.6, 166.1, 157.1, 142.0, 137.2, 133.2, 133.0, 130.8, 129.4 (2C), 129.3, 127.9, 127.4, 123.7, 122.2, 121.6, 116.7, 109.0, 43.4, 29.7, 21.3, 21.1; IR (KBr, cm^{-1}): 1762, 1701, 1599; LRMS (EI, 70 eV) *m/z* (%):383 (M^{+}, 1), 341 (60), 263 (8), 105 (100); HRMS (EI) for $C_{25}H_{21}NO_3$ (M^{+}): calcd. 383.1521, found 383.1521.

(*E*)-Methyl 3-(acetoxy(phenyl)methylene)-1-methyl-2-oxoindoline-5-carboxylate (8): Yellow solid, mp 159.8-160.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.27 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.26-7.24 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.23 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.6, 166.9, 166.3, 158.3, 146.2, 132.8, 131.5, 131.1, 129.3, 128.0, 125.1, 124.0, 121.4, 115.9, 107.4, 52.1, 26.2, 21.3; IR (KBr, cm^{-1}): 1766, 1713, 1692, 1607; LRMS (EI, 70 eV) *m/z* (%): 351 (M^{+}, 4), 309 (87), 231 (100); HRMS (EI) for $C_{20}H_{17}NO_5$ (M^{+}): calcd. 351.1107, found 351.1106.

(*E*)-(1-Methyl-5-nitro-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (9): Yellow solid, mp 184.2-186.0 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.48 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.72 (d,

J = 7.6 Hz, 2H), 7.51-7.44 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 1H), 3.27 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.3, 166.1, 160.2, 147.3, 143.1, 132.4, 131.6, 129.3, 128.1, 125.7, 121.9, 119.2, 114.8, 107.8, 26.4, 21.3; IR (KBr, cm^{-1}): 1752, 1708, 1608; LRMS (EI, 70 eV) *m/z* (%): 338 (M^+, 2), 296 (100); HRMS (EI) for $C_{18}H_{14}N_2O_5$ (M^+): calcd. 338.0903., found 338.0903.

(*E*)-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (10): Yellow solid, mp 122.9-124.1 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.68 (d, *J* = 7.2 Hz, 2H), 7.50 (s, 1H), 7.30-7.27 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 3.18 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.4, 165.7, 158.2, 141.1, 132.8, 131.0, 129.3, 128.9, 127.9, 127.4, 124.0, 122.9, 116.0, 108.7, 26.1, 21.4; IR (KBr, cm^{-1}): 1770, 1721, 1627; LRMS (EI, 70 eV) *m/z* (%): 329 (M^+ + 2, 2), 327 (M^+, 5), 287 (26), 285 (78), 209 (33), 207 (100); HRMS (EI) for $C_{18}H_{14}ClNO_3$ (M^+): calcd. 327.0662, found 327.0662.

(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (11): Yellow solid, mp 142.8-143.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.66 (d, *J* = 7.2 Hz, 2H), 7.50-7.43 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.3, 166.3, 158.1, 138.6, 133.1, 131.4, 130.9, 129.4, 127.9, 124.2, 122.8, 122.1, 115.8, 115.6, 29.3, 21.3 ; IR (KBr, cm^{-1}): 1773, 1715, 1618; LRMS (EI, 70 eV) *m/z* (%): 329 (M^+ + 2, 2), 327 (M^+, 5), 287 (19), 285 (57), 209 (30), 207 (100); HRMS (EI) for $C_{18}H_{14}ClNO_3$ (M^+): calcd. 327.0662, found 327.0662.

(*E*)-(7-Bromo-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (12): Yellow solid, mp 175.6-176.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.65 (d, *J* = 7. Hz, 2H), 7.53 (d, 2*J* = 7.6 Hz, 1H), 7.46-7.39 (m, 4H), 6.89 (t, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.3, 166.5, 158.0, 139.9, 134.7, 133.1, 130.9, 129.4, 127.9, 124.5, 123.2, 122.6, 115.7, 102.5, 29.5, 21.4; IR (KBr, cm^{-1}): 1774, 1717, 1659; LRMS (EI, 70 eV) *m/z* (%): 373 (M^+ + 2, 2), 371 (M^+, 2),

331 (87), 329 (87), 252 (94), 250 (100); HRMS (EI) for $C_{18}H_{14}BrNO_3$ (M^+): calcd. 371.0157, found 371.0157.

(*E*)-(7-Methoxy-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (13): Yellow solid, mp 157.2-158.3 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 7.67 (d, *J* = 7.2Hz, 2H), 7.45-7.41 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.46 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.5, 166.3, 157.0, 145.2, 133.4, 131.0, 130.6, 129.4, 127.8, 122.8, 122.5, 117.1, 116.7, 113.5, 56.2, 29.3, 21.3; IR (KBr, cm^{-1}): 1773, 1688, 1603; LRMS (EI, 70 eV) *m/z* (%): *3*23 (M^+, 5), 281 (100); HRMS (EI) for $C_{19}H_{17}NO_4$ (M^+): calcd. 323.1158, found 323.1158.

(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(p-tolyl)methyl acetate (14): Yellow solid, mp 179.2-180.3 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 7.60 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.30-7.23 (m, 4H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.6, 166.2, 157.2, 142.6, 141.2, 130.3, 129.3, 129.1, 128.6, 122.1, 121.7, 121.5, 116.4, 107.9, 25.9, 21.7, 21.3; IR (KBr, cm^{-1}): 1754, 1704, 1599; LRMS (EI, 70 eV) *m/z* (%): 307 (M^+, 4), 265 (100); HRMS (EI) for $C_{19}H_{17}NO_3$ (M^+): calcd. 307.1208, found 307.1208.

(*E*)-(2-Chlorophenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (15): Yellow solid, mp 124.8-125.7 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 7.62 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.40-7.30 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.2, 165.8, 153.2, 143.1, 133.3, 132.5, 132.4, 131.0, 129.7, 129.6, 126.3, 124.2, 122.3, 120.8, 118.4, 108.0, 25.9, 21.1; IR (KBr, cm^{-1}): 1762, 1617, 1603; LRMS (EI, 70 eV) *m/z* (%): 327 (M^+, 2), 287 (5), 285 (16), 250 (-Cl, 66), 207 (16), 44(25), 32 (100); HRMS (EI) for $C_{18}H_{14}ClNO_3$ (M^+): calcd. 327.0662, found 327.0660.

(*E*)-(4-Aacetylphenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (16): Yellow solid, mp 165.4 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.02 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.62 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz) δ: 197.3, 167.5, 165.9, 155.1, 143.0, 138.2, 137.7, 129.8, 129.7, 127.8, 123.9, 122.4, 121.1, 117.9, 108.1, 26.7, 25.9, 21.2; IR (KBr, cm^{-1}): 1762, 1701, 1603; LRMS (EI, 70 eV) *m/z* (%): 335 (M^{+}, 3), 293 (94), 173 (100); HRMS (EI) for $C_{20}H_{17}NO_4$ (M^{+}): calcd. 335.1158, found 335.1158.

(*E*)-1-(1-Methyl-2-oxoindolin-3-ylidene)ethyl acetate (17): Yellow solid, mp 98.8-100.2 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.46 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 2.68 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.2, 159.8, 141.7, 128.7, 123.3, 122.1, 121.0, 120.9, 116.3, 107.8, 25.8, 21.2, 18.1; IR (KBr, cm^{-1}): 1762, 1701, 1607; LRMS (EI, 70 eV) *m/z* (%): 231 (M^{+}, 16), 189 (100); HRMS (EI) for $C_{13}H_{13}NO_3$ (M^{+}): calcd. 231.0895, found 231.0894.

(*E*)-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)(thiophen-2-yl)methyl acetate (19): Yellow solid, mp 179.0-181.0 ^{o}C (uncorrected); ^{1}H NMR (500 MHz) δ: 8.34 (d, *J* = 5.0 Hz, 1H), 7.63 (d, *J* = 6.0 Hz, 1H), 7.22-7.17 (m, 2H), 7.00 (t, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 3.27 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (125 MHz) δ: 167.6, 165.9, 159.7, 150.9, 138.2, 135.3, 133.7, 132.1, 127.8, 115.2, 115.0, 111.1, 110.8, 108.1, 26.1, 21.6; IR (KBr, cm^{-1}): 1723, 1712, 1697; LRMS (EI, 70 eV) *m/z* (%): 335 (M^{+} + 2, 3), 333 (M^{+}, 8), 291 (-Cl, 100); HRMS (EI) for $C_{16}H_{12}{}^{35}ClNO_3S$ (M^{+}): calcd. 333.0226 found 333.0224.

(*E*)-(1,6-dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (21): Yellow solid, mp 198.5-199.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.70-7.66 (m, 2H), 7.44-7.39 (m, 4H), 6.85 (d, *J* = 10.4 Hz, 1H), 6.64 (s, 1H), 3.16 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz) δ: 167.6, 166.4, 155.7, 142.8, 139.9, 133.2, 130.5, 129.3, 127.8, 123.4, 122.8, 118.8, 116.9, 108.9, 25.8, 22.0,

21.3; IR (KBr, cm^{-1}): 1771, 1700, 1640, 1613; LRMS (EI, 70 eV) *m/z* (%): 307 (M^+, 5), 265 (100); HRMS (EI) for $C_{19}H_{17}NO_3$ (M^+): calcd. 307.1208, found 307.1208.

(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-nitrobenzoate (23): Yellow solid, mp 172.7-173.1 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 8.42 (s, 4H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.48-7.39 (m, 4H), 7.29-7.26 (m, 3H), 6.92 (t, *J* = 7.2 Hz,1), 6.84 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (100 MHz) δ: 165.8, 161.8, 156.2, 151.4, 142.9, 133.9, 132.6, 131.5, 131.0, 129.7, 129.4, 128.0, 124.2, 123.6, 122.3, 121.2, 117.6, 108.2, 26.0; IR (KBr, cm^{-1}): 1744, 1700, 1629, 1602; LRMS (EI, 70 eV) *m/z* (%): 251 (M^+-150, 4), 120 (100); HRMS (EI) for $C_{23}H_{16}N_2O_5$ (M^+): calcd. 400.1059, found 400.1059.

(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-bromo-4-fluorobenzoate (25): Kelly solid, mp 172.5-173.2 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 8.23, 8.21 (dd, *J* = 6.8 Hz, 6.0 Hz, 1H), 7.75 (d, *J* = 9.6 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48-7.40 (m, 4H), 7.24-7.19 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz) δ: 166.1, 161.1, 157.7, 138.6, 134.8, 134.7, 132.7, 131.5, 131.0, 129.5, 128.0, 124.0, 123.2, 122.9, 122.3, 116.4, 115.6, 115.3, 115.1, 29.4; IR (KBr, cm^{-1}): 1749, 1717, 1651, 1591; LRMS (EI, 70 eV) *m/z* (%): 487 (M^+ + 2, 5), 485 (M^+, 5), 202 (96), 200 (100); HRMS (EI) for $C_{23}H_{14}BrClFNO_3$ (M^+): calcd. 484.9830, found 484.9829.

(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-bromobenzoate (27): Yellow solid, mp 151.6-153.4 ^oC (uncorrected); ^1H NMR (400 MHz) δ: 8.24 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.44-7.39 (m, 3H), (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz) δ: 166.1, 163.6, 156.8, 140.5, 134.3, 133.1, 131.5, 130.7, 130.4, 129.7, 129.4, 129.0, 128.7, 127.9, 124.8, 121.6, 117.4, 107.7, 26.0, 21.2; IR (KBr, cm^{-1}): 1728, 1705, 1635, 1590; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+ - Br, 12), 236 (2), 105 (100); HRMS (EI) for $C_{24}H_{18}BrNO_3$ (M^+): calcd. 447.0470, found 447.0470.

(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-iodobenzoate (28): Yellow solid, mp 151.9-152.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.16, 8.13 (dd, *J* = 8.0 Hz, 8.0 Hz, 2H), 7.82-7.80 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.47-7.46 (m, 3H), 7.31 (s, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz) δ: 166.1, 163.1, 156.2, 142.3, 140.6, 133.9, 132.9, 132.7, 132.0, 131.6, 130.7, 129.8, 129.6, 128.3, 128.0, 124.9, 121.3, 117.8, 107.7, 95.1, 26.0, 21.3; IR (KBr, cm^{-1}): 1738, 1700, 1629, 1607; LRMS (EI, 70 eV) *m/z* (%): 495 (M^{+}, 11), 368 (14), 231 (100); HRMS (EI) for $C_{24}H_{18}INO_3$ (M^{+}): calcd. 495.0331, found 495.0331.

(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-vinylbenzoate (29) : Yellow solid, mp 178.3-179.6 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.19 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 4H), 7.35 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.84, 6.79 (dd, *J* = 10.8 Hz, 10.8 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.95 (d, *J* = 17.6 Hz, 1H), 5.47 (d, *J* = 10.8 Hz, 1H), 3.19 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz) δ: 166.1, 163.4, 143.3, 140.5, 135.8, 133.2, 131.5, 130.8, 130.6, 129.7, 129.6, 129.4, 127.9, 127.7, 126.7, 124.8, 124.5, 117.6, 107.7, 107.6, 26.0, 21.3; IR (KBr, cm^{-1}): 1738, 1695, 1618, 1635; LRMS (EI, 70 eV) *m/z* (%): 256 (M^{+} - 139, 42), 187 (31), 131 (25), 40 (100); HRMS (EI) for $C_{26}H_{21}INO_3$ (M^{+}): calcd. 395.1521, found 395.1520.

(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-acetylbenzoate (30): Yellow solid, mp 161.1-162.0 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 8.20 (d, *J* = 7.2 Hz, 1H), 7.76-7.70 (m, 3H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.46-7.44 (m, 4H), 7.37 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz) δ: 166.1, 163.7, 156.8, 140.5, 134.3, 133.2, 131.5, 130.7, 130.6, 130.5, 130.4, 130.0, 129.7, 129.6, 129.4, 129.0, 128.8, 124.9, 121.6, 117.4, 107.6, 30.2, 26.0, 21.2; IR (KBr, cm^{-1}): 1733, 1711, 1700, 1607, 1646; LRMS (EI, 70 eV) *m/z* (%): 265 (M^{+} - 147, 91), 187 (26), 147 (100); HRMS (EI) for $C_{26}H_{21}INO_4$ (M^{+}): calcd. 411.1471, found 411.1470.

(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl pivalate (31) : Yellow solid, mp 155.2-156.3 ^{o}C (uncorrected); ^{1}H NMR (400 MHz) δ: 7.64-7.62 (m, 2H), 7.48 (s, 1H), 7.44-7.41 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 2.34 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz) δ: 175.1, 166.2, 157.3, 140.5, 133.3, 131.3, 130.4, 129.5, 129.4, 127.7, 124.7, 121.6, 117.1, 107.6, 39.5, 27.2, 25.9, 21.2; IR (KBr, cm^{-1}): 1744, 1695, 1635, 1618; LRMS (EI, 70 eV) *m/z* (%): 349 (M^{+}, 23), 325 (11), 265 (100); HRMS (EI) for $C_{22}H_{23}NO_3$ (M^{+}): calcd. 349.1678, found 349.1678.

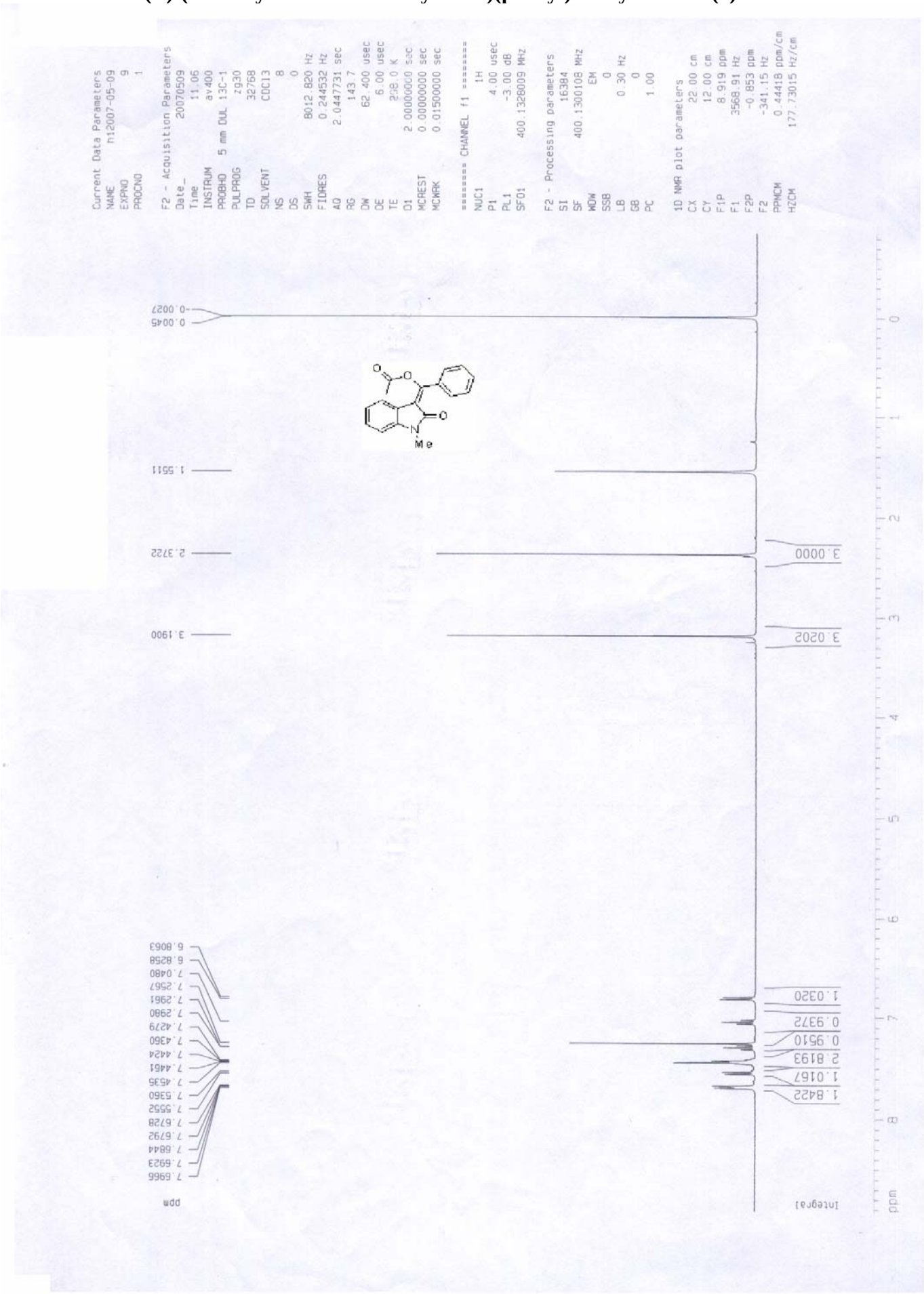
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 3-phenylpropanoate (32): Yellow oil; ^{1}H NMR (400 MHz) δ: 7.60 (d, *J* = 6.8 Hz, 2H), 7.59-7.41 (m, 4H), 7.31-7.20 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.15 (s, 3H), 3.06-2.96 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz) δ: 169.8, 166.1, 156.6, 140.5, 139.8, 133.3, 133.2, 130.6, 129.7, 129.4, 128.7, 128.3, 127.8, 126.6, 124.6, 121.5, 117.0, 107.7, 36.2, 30.5, 26.0, 21.4; IR (KBr, cm^{-1}): 1738, 1696, 1618, 1601; LRMS (EI, 70 eV) *m/z* (%): 397 (M^{+}, 5), 205 (100); HRMS (EI) for $C_{26}H_{23}INO_3$ (M^{+}): calcd. 397.1678, found 397.1677.

(D) References

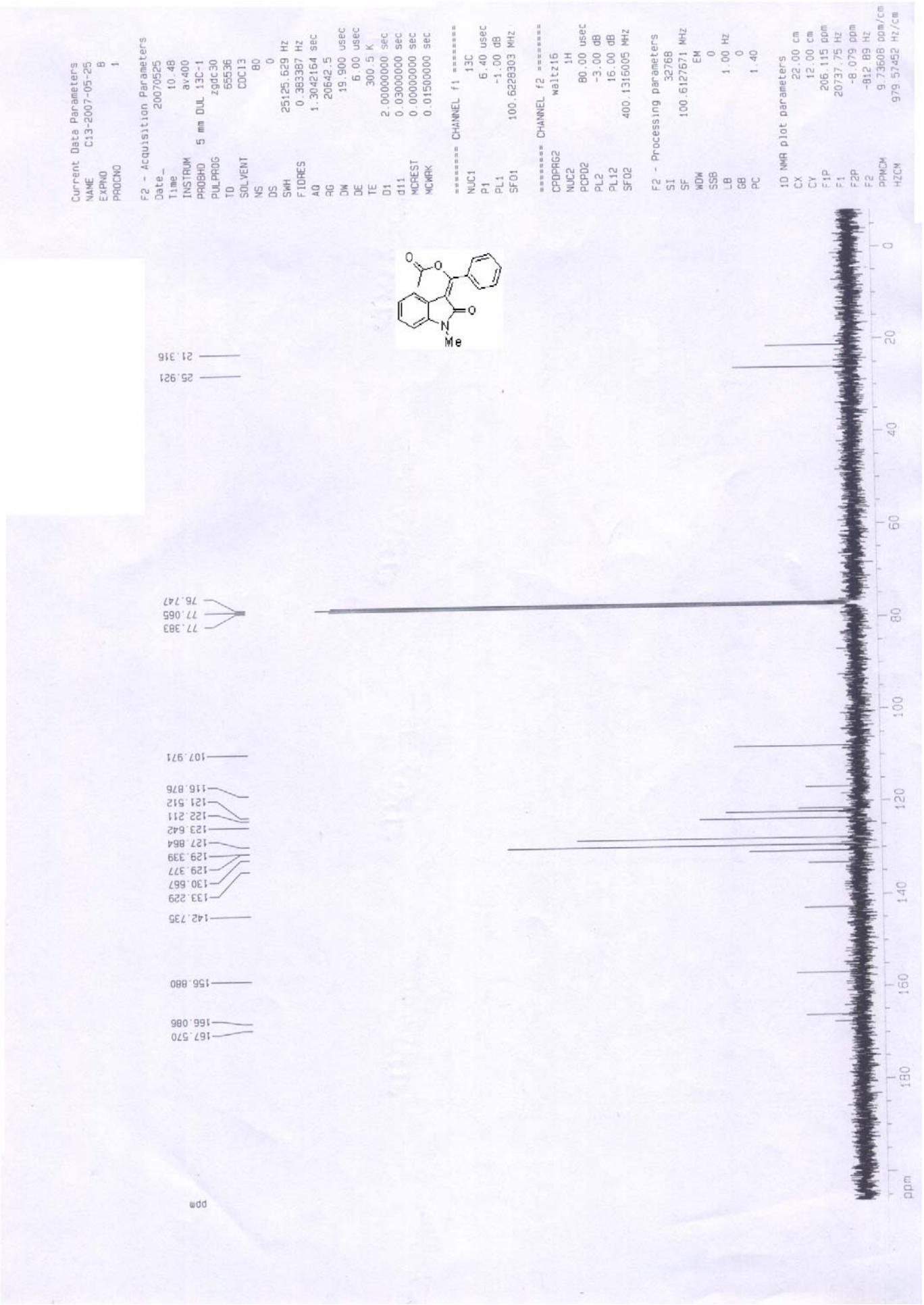
(1) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927 and references cited therein.

(E) Spectra

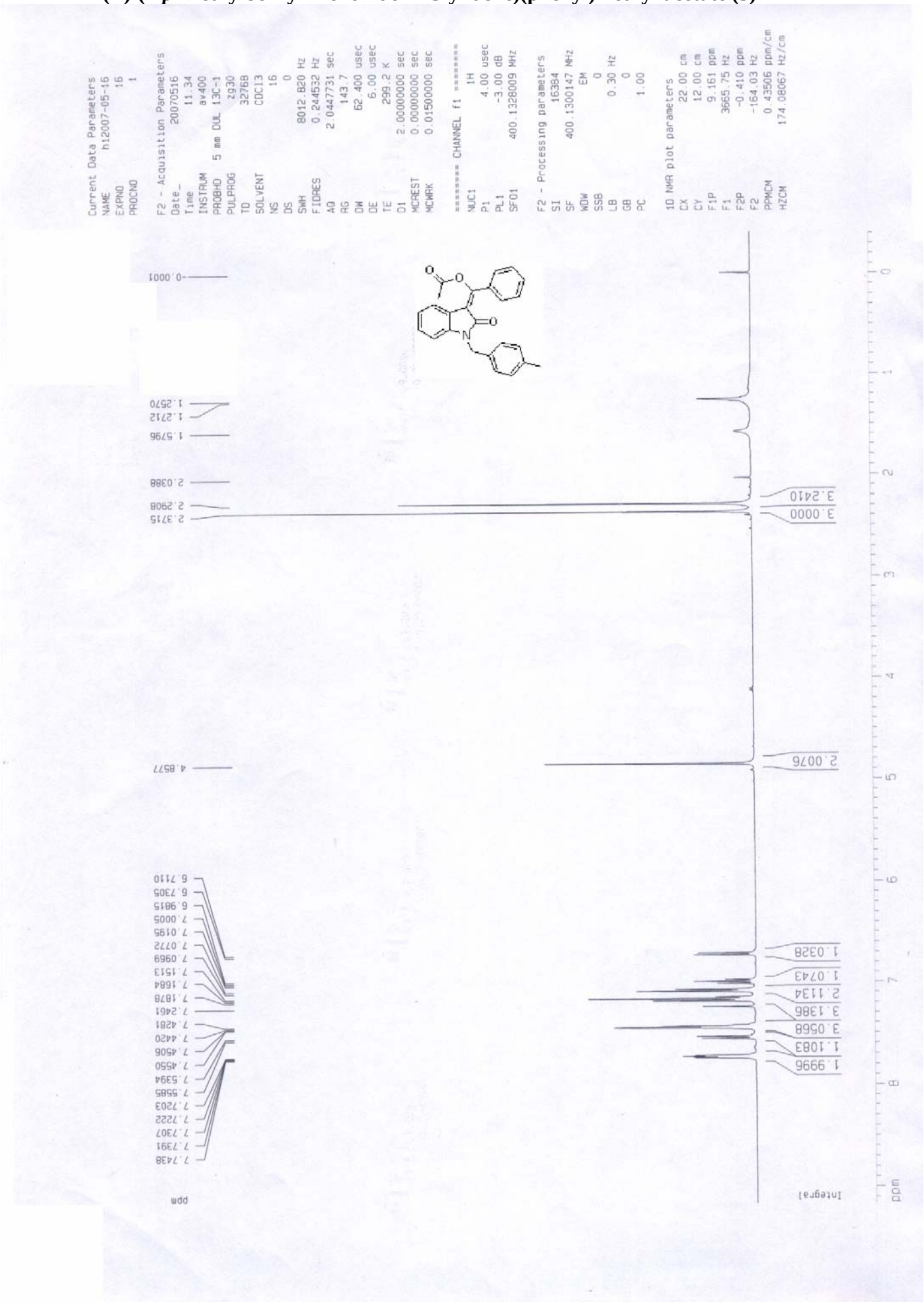
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (3)



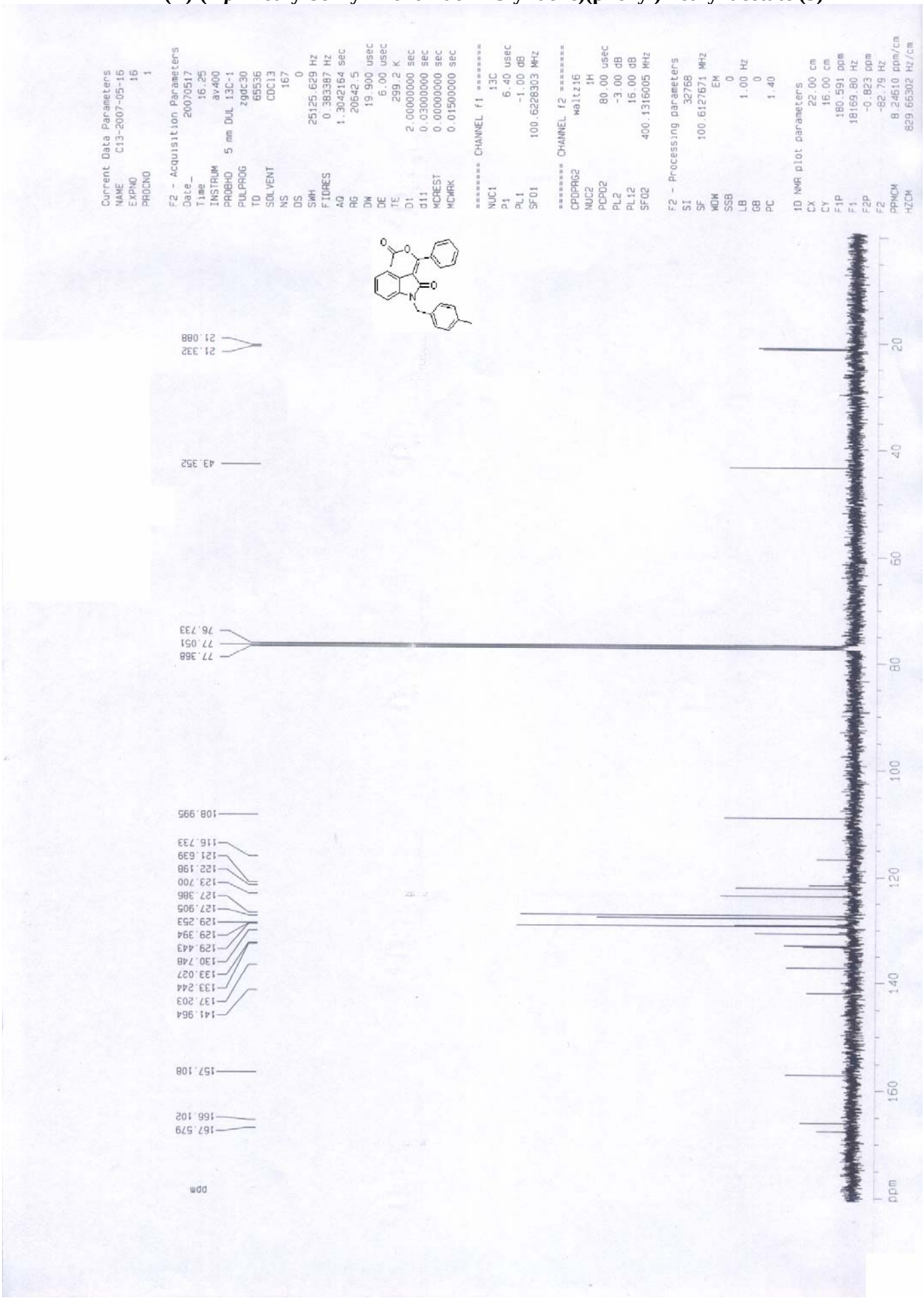
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (3)



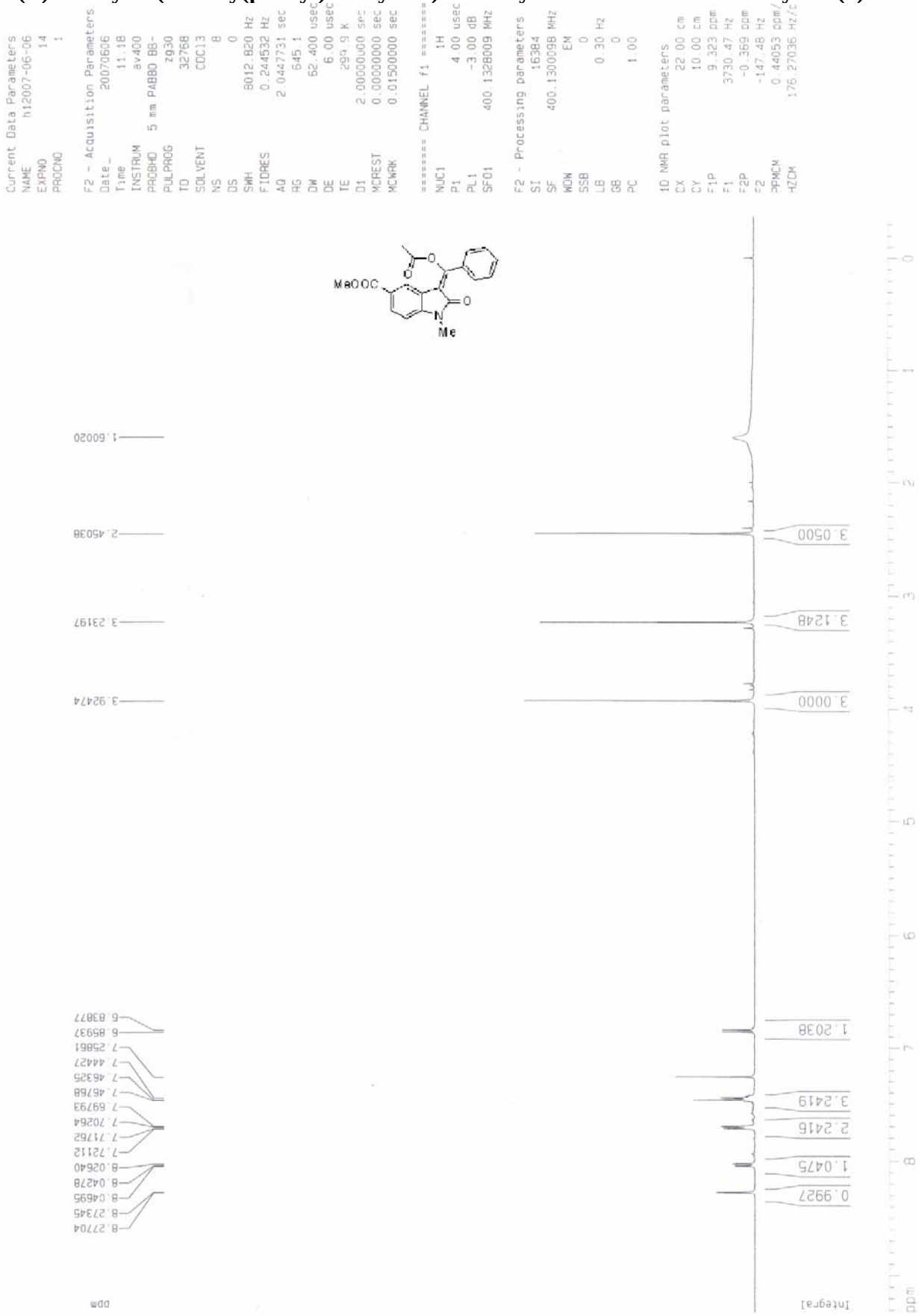
(*E*)-(1-*p*-Methylbenzyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (5)



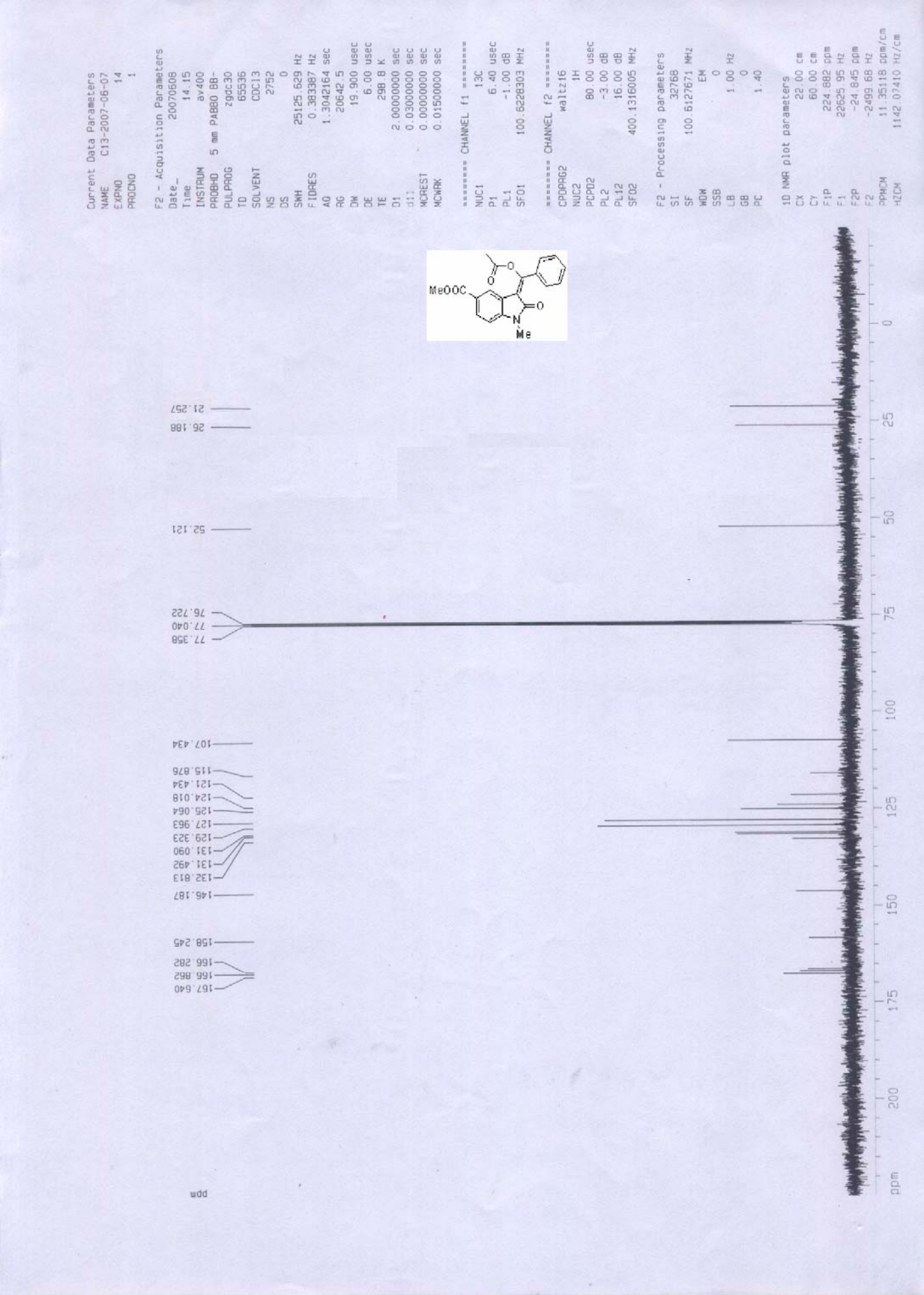
(*E*)-(1-*p*-Methylbenzyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (5)



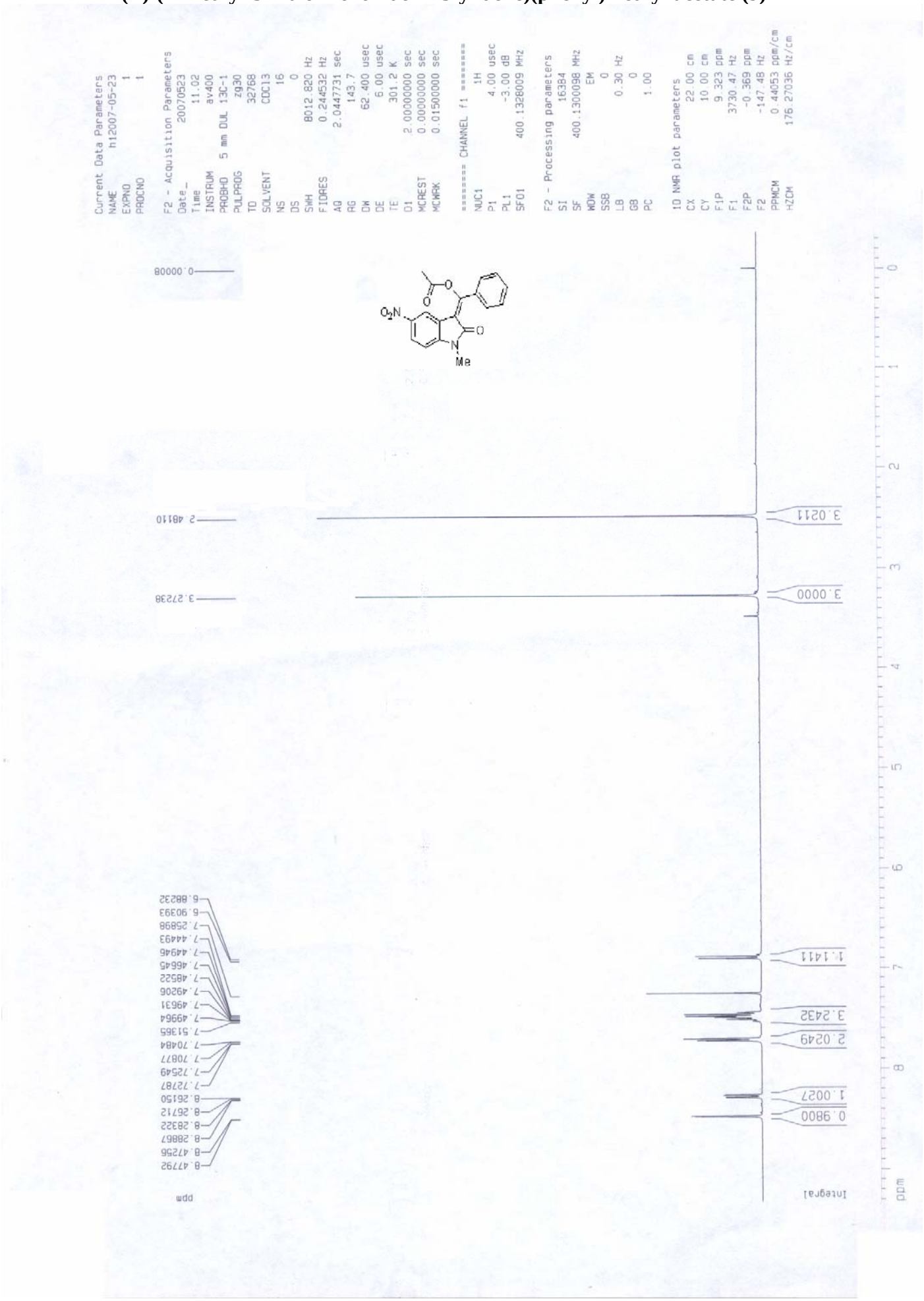
(*E*)-Methyl 3-(acetoxy(phenyl)methylene)-1-methyl-2-oxoindoline-5-carboxylate (8)



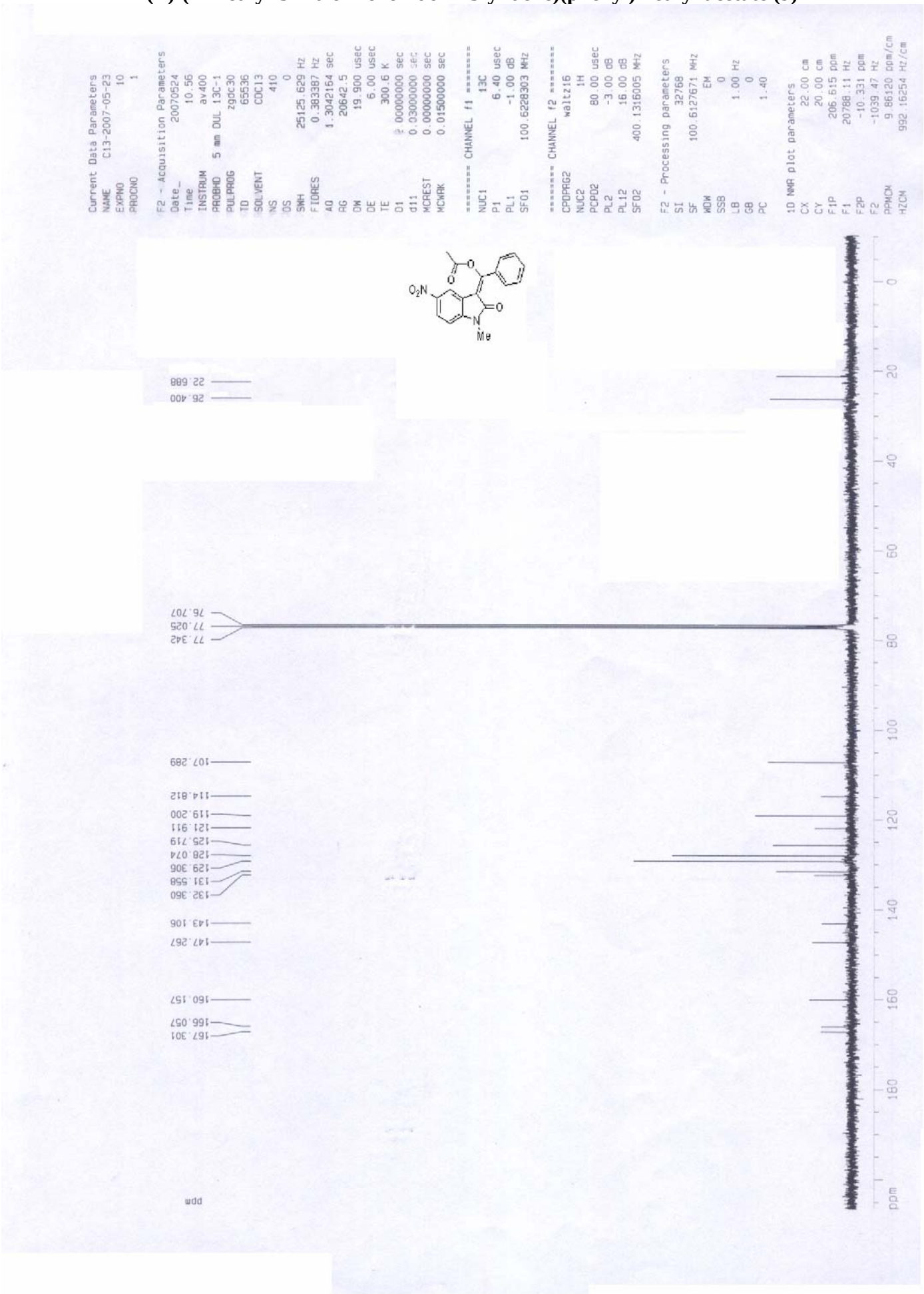
(*E*)-Methyl 3-(acetoxy(phenyl)methylene)-1-methyl-2-oxoindoline-5-carboxylate (8)



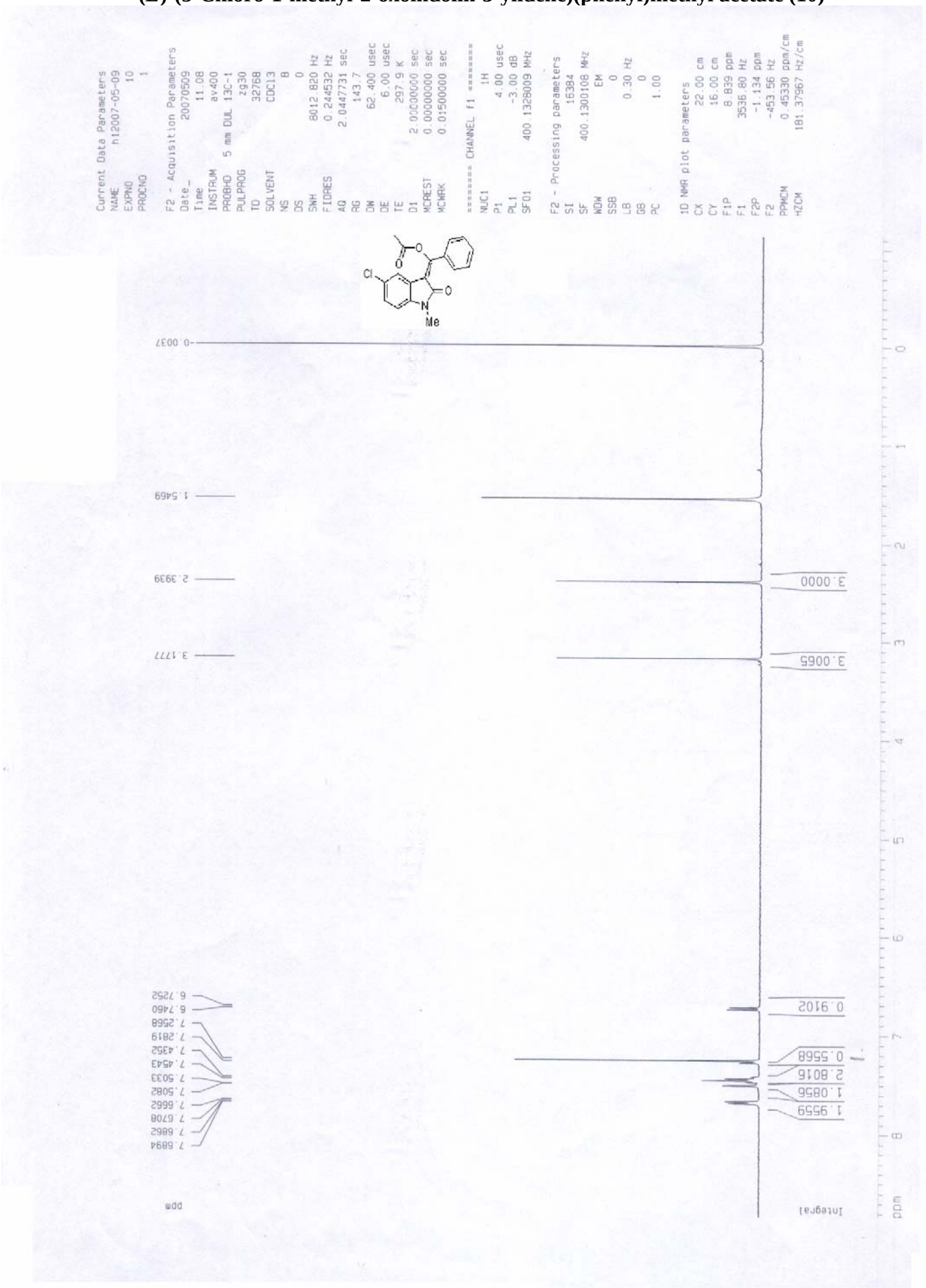
(*E*)-(1-Methyl-5-nitro-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (9)



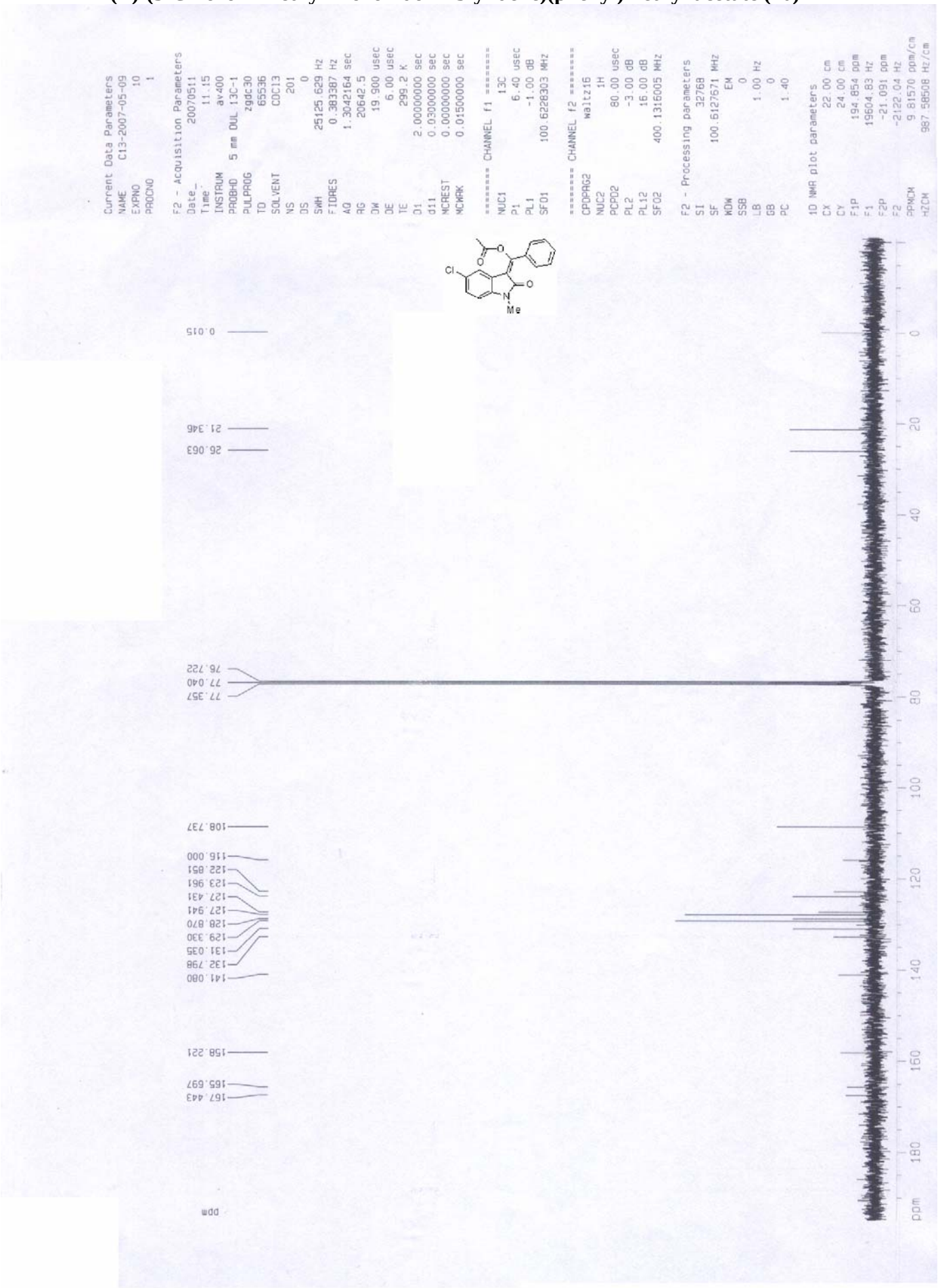
(*E*)-(1-Methyl-5-nitro-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (9)



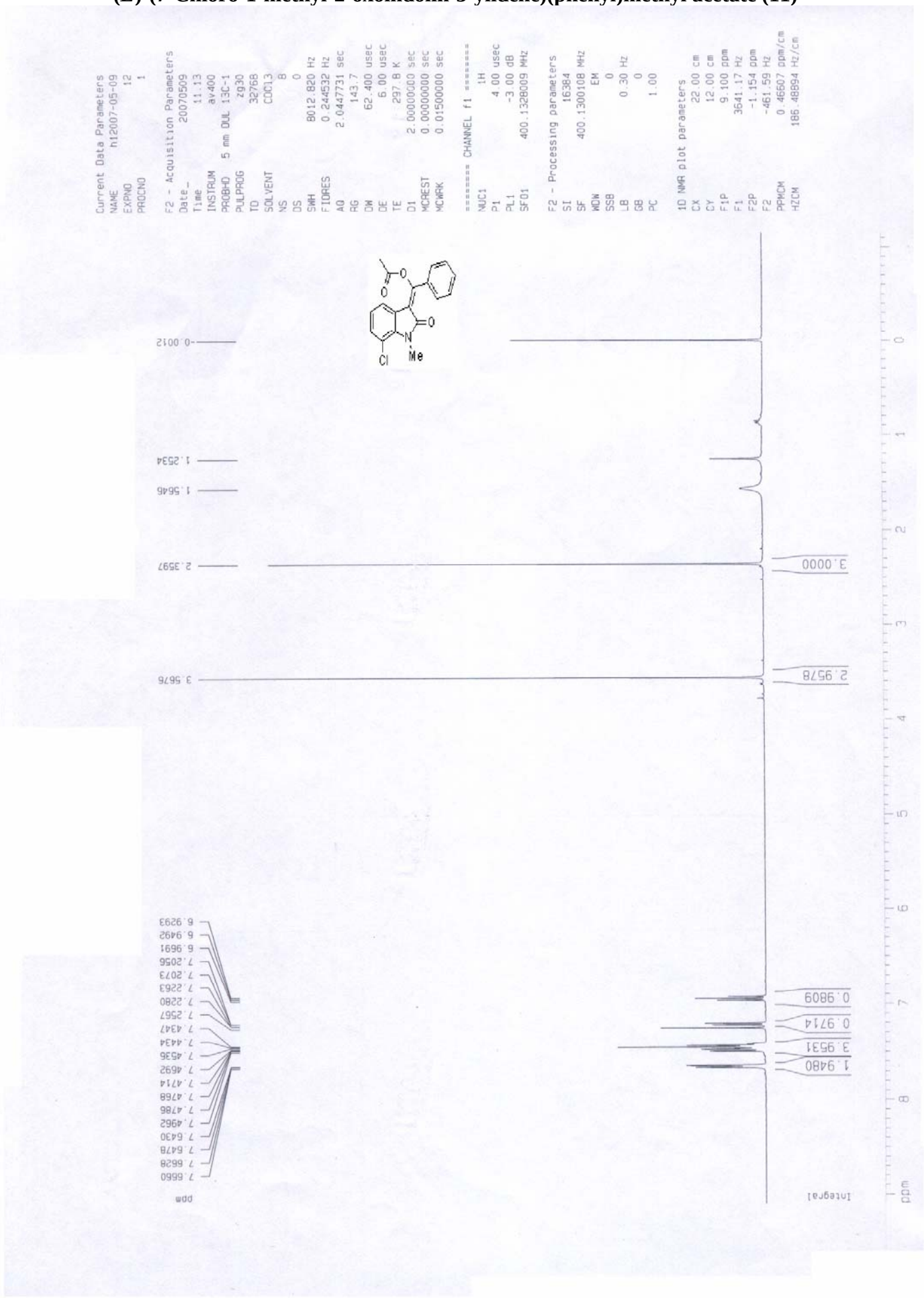
(*E*)-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (10)



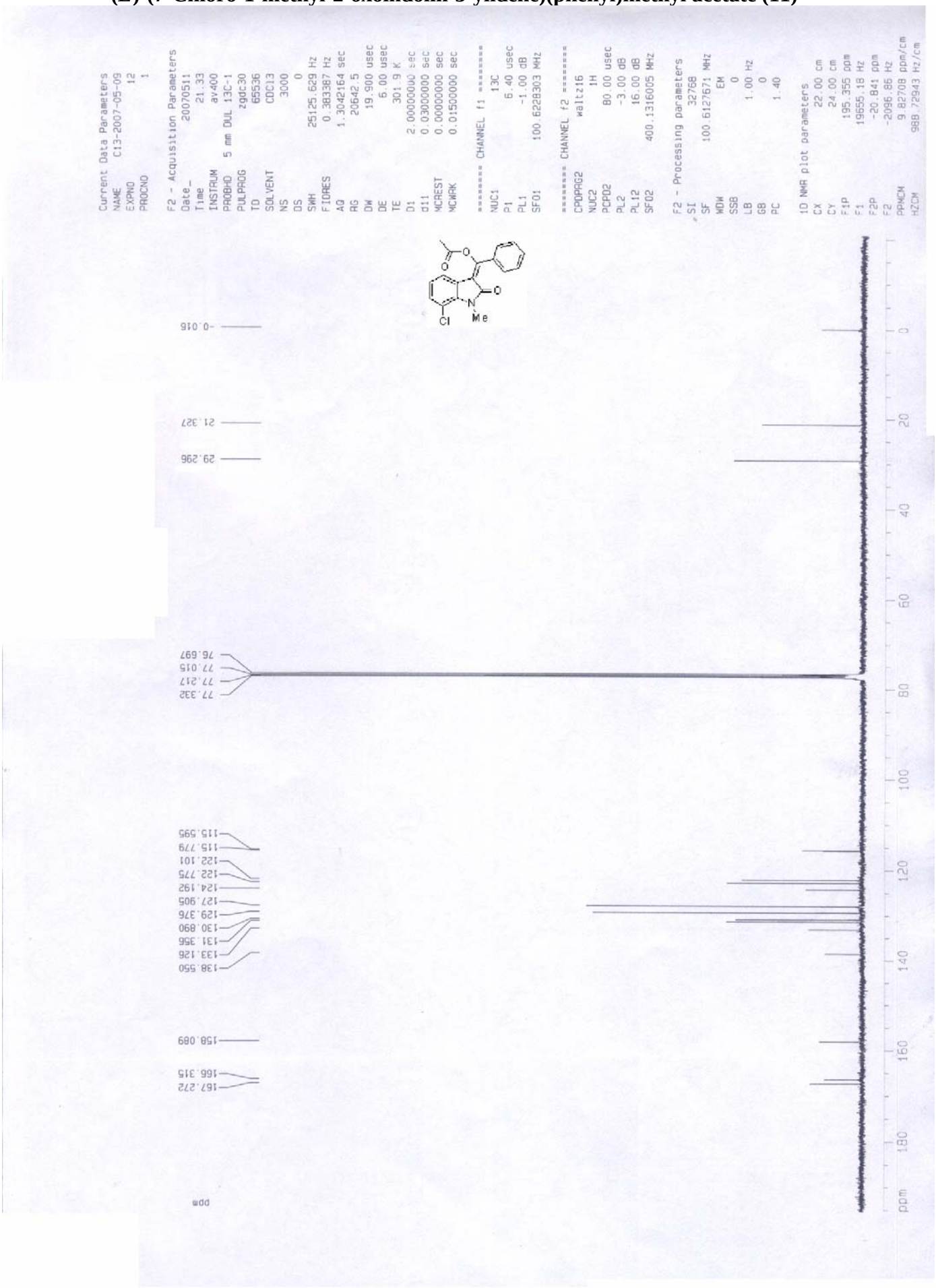
(*E*)-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (10)



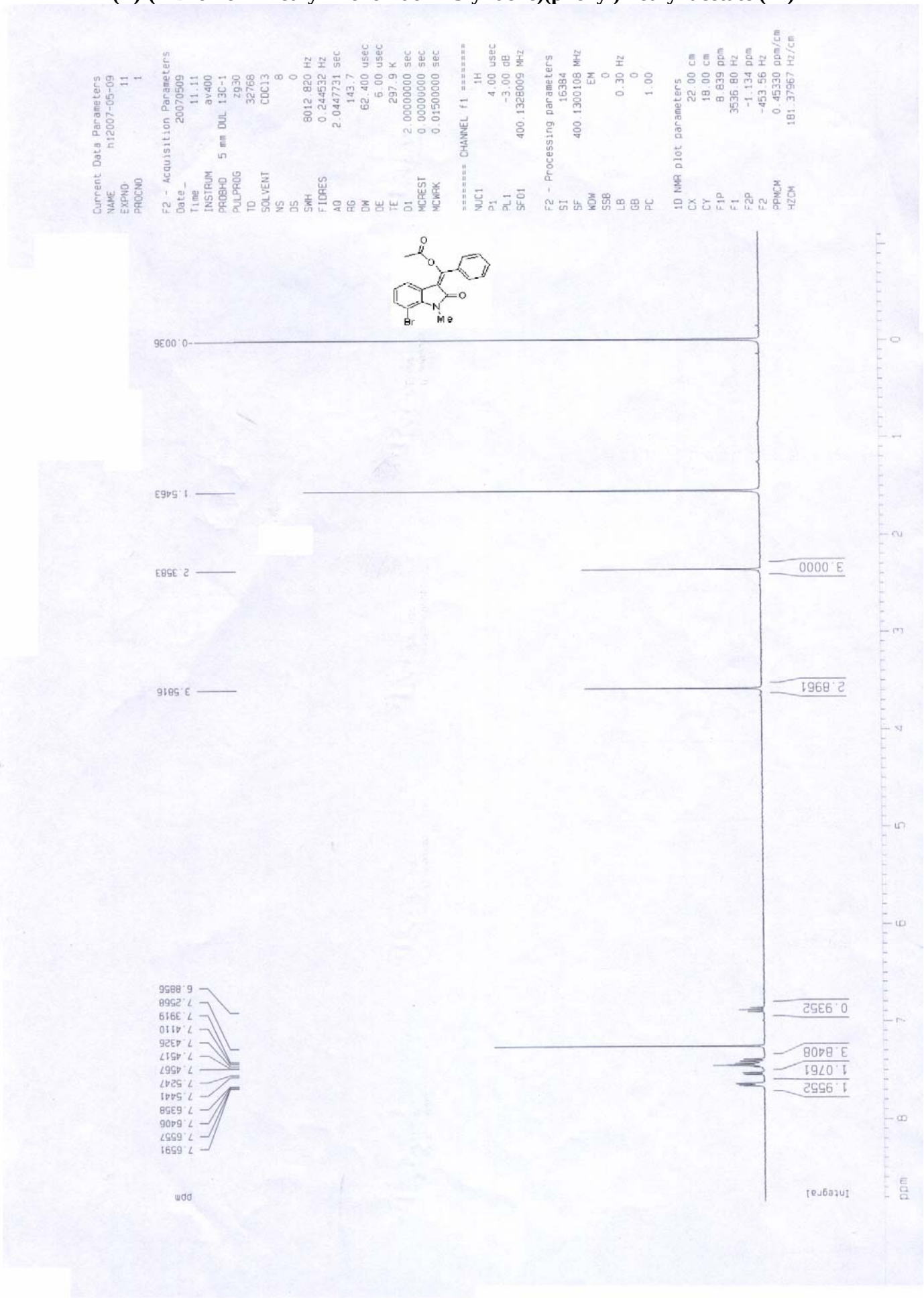
(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (11)



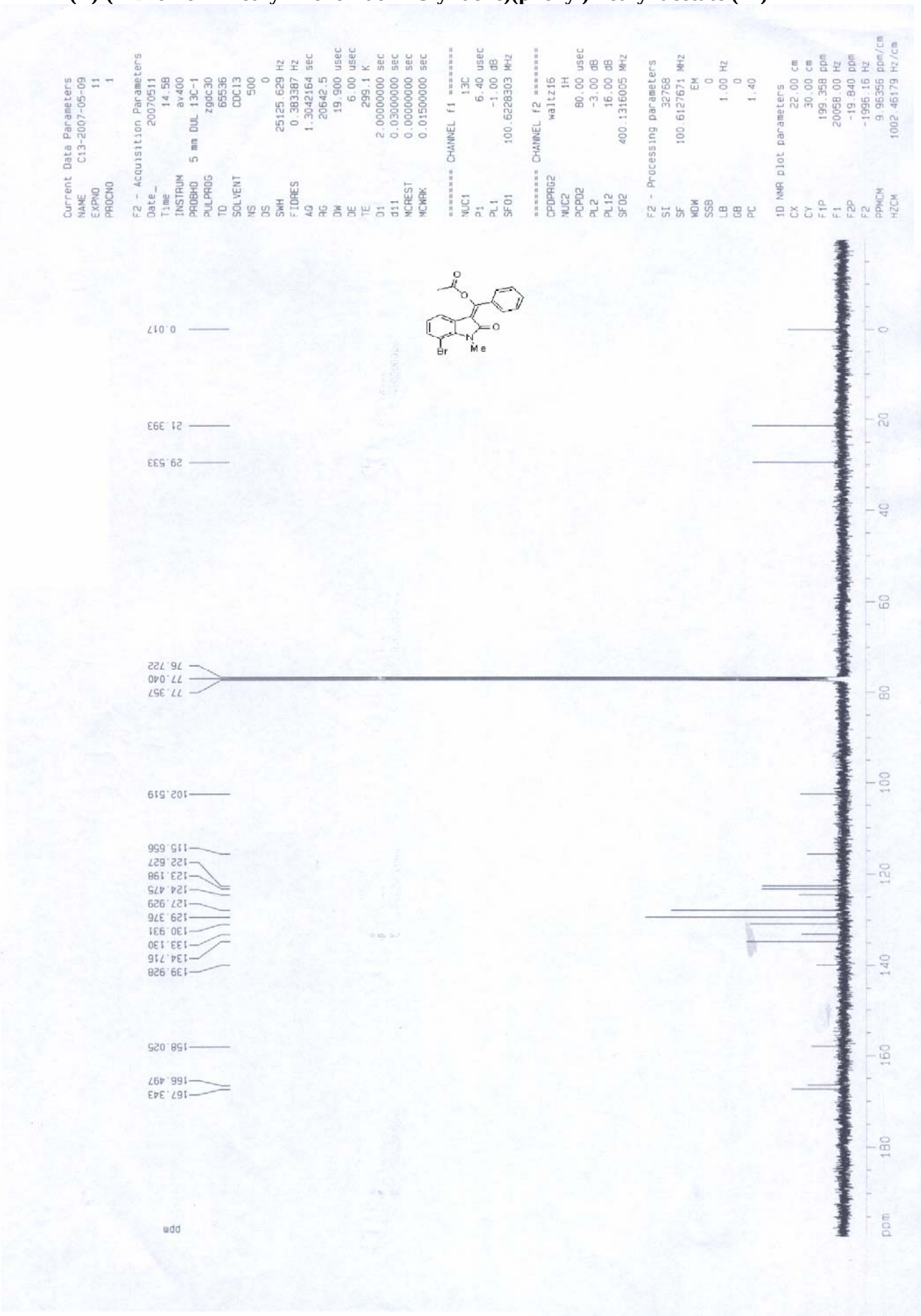
(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (11)



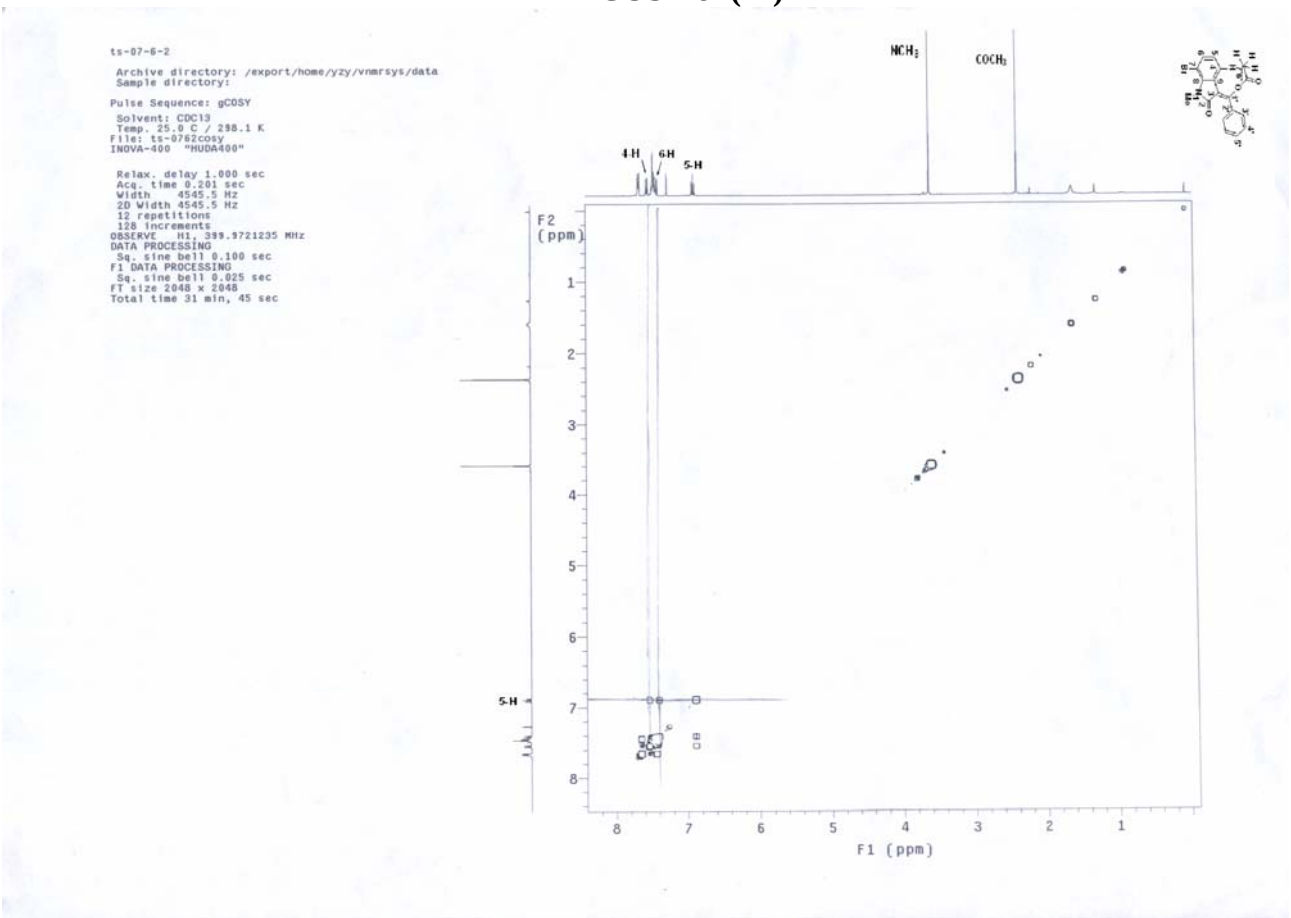
(*E*)-(7-Bromo-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (12)



(*E*)-(7-Bromo-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (12)



H-H COSY of (12)


ts-07-6-2
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Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: ts-0762cosy
INOVA-400 "HUDA400"
Relax. delay 1.000 sec
Acq. time 0.201 sec
Width 4545.5 Hz
2D Width 4545.5 Hz
12 repetitions
128 increments
OBSERVE H1, 399.9721235 MHz
DATA PROCESSING
Sq. sine bell 0.100 sec
F1 DATA PROCESSING
Sq. sine bell 0.025 sec
FT size 2048 x 2048
Total time 31 min, 45 sec
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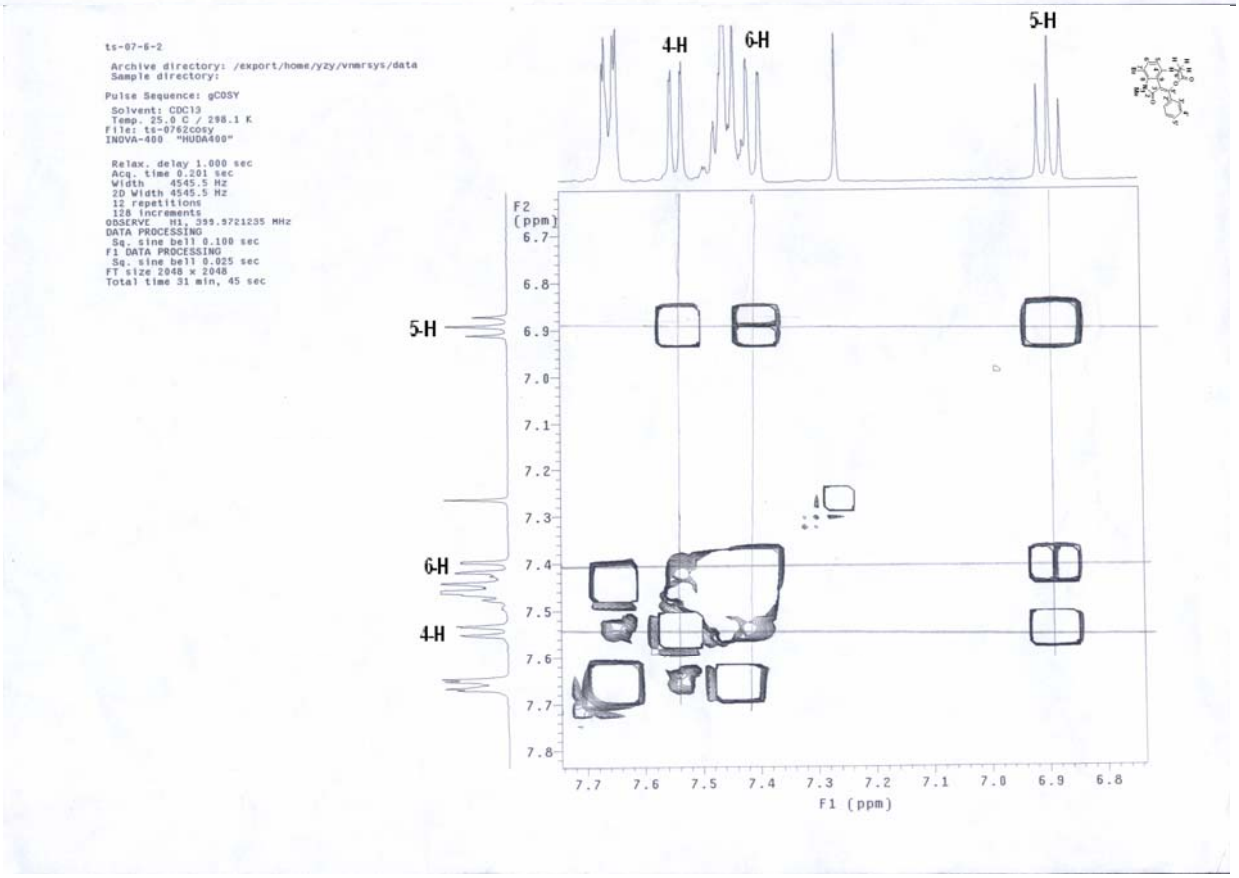
COCH3
4-H
6-H
5-H
F2 (ppm)
F1 (ppm)


ts-07-6-2
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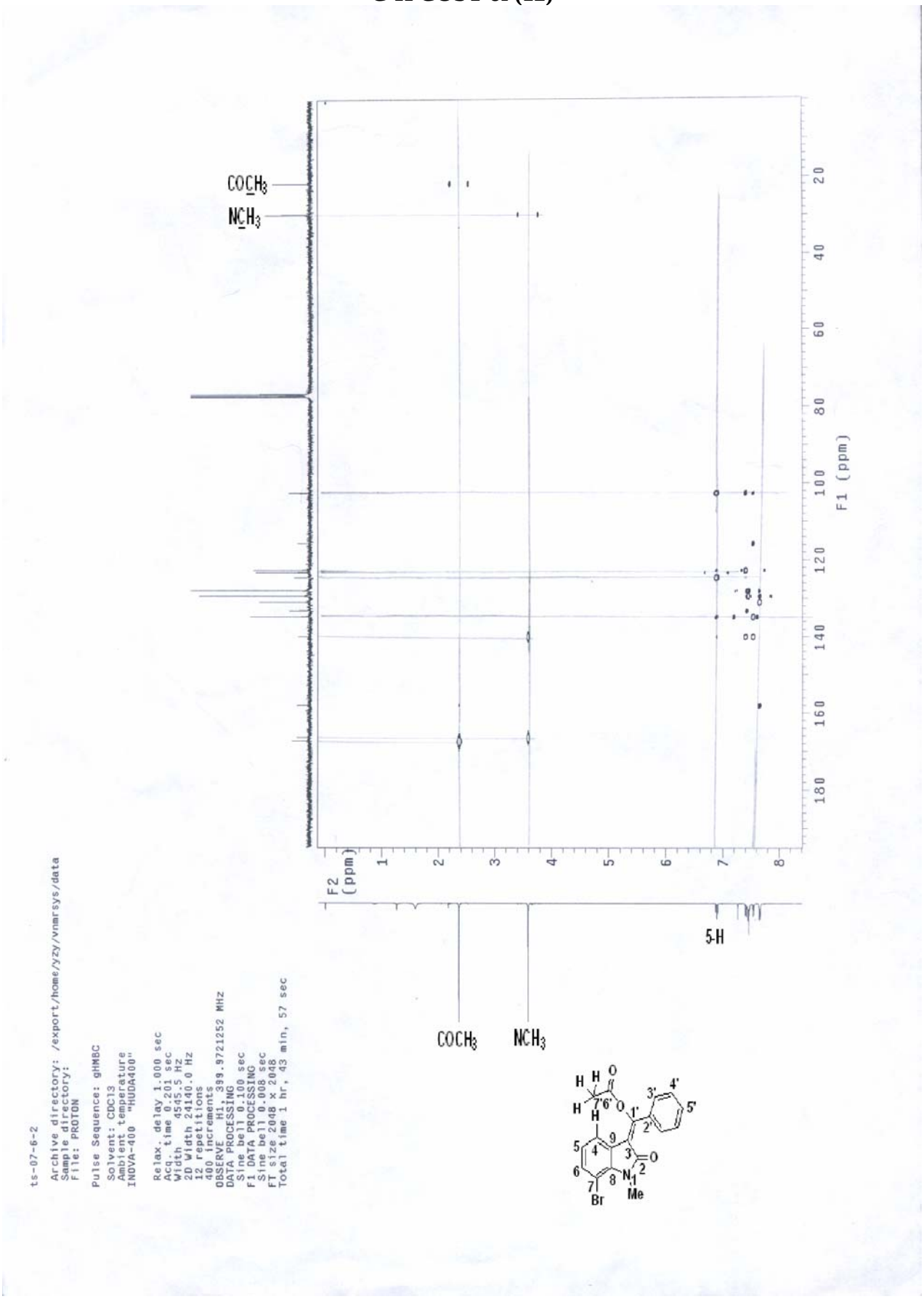
Sample directory:
Pulse Sequence: gCOSY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: ts-0762cosy
INOVA-400 "HUDA400"
Relax. delay 1.000 sec
Acq. time 0.201 sec
Width 4545.5 Hz
2D Width 4545.5 Hz
12 repetitions
128 increments
OBSERVE H1, 399.9721235 MHz
DATA PROCESSING
Sq. sine bell 0.100 sec
F1 DATA PROCESSING
Sq. sine bell 0.025 sec
FT size 2048 x 2048
Total time 31 min, 45 sec
4-H
6-H
5-H
F2 (ppm)
F1 (ppm)

C-H COSY of (12)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Pulse Sequence: gHMBC
Solvent: CDCl3
Ambient temperature
INOVA-400 "HUDA400"
Relax. delay 1.000 sec
Acq. time 0.201 sec
Width 4545.5 Hz
2D Width 24140.0 Hz
12 repetitions
400 increments
OBSERVE H1, 399.9721252 MHz
DATA PROCESSING
Sine bell 0.100 sec
F1 DATA PROCESSING
Sine bell 0.008 sec
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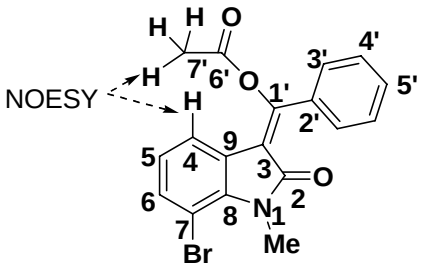
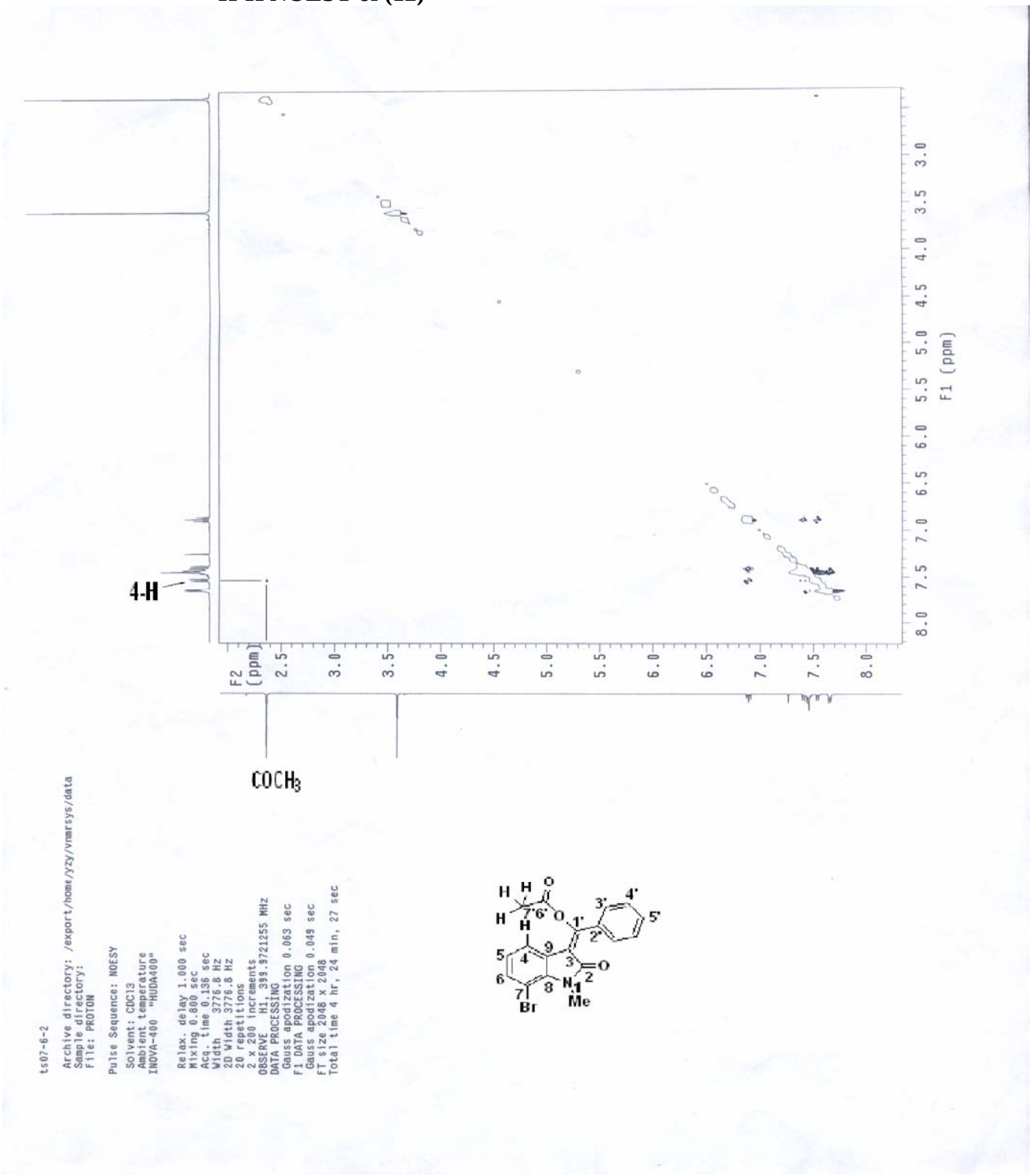
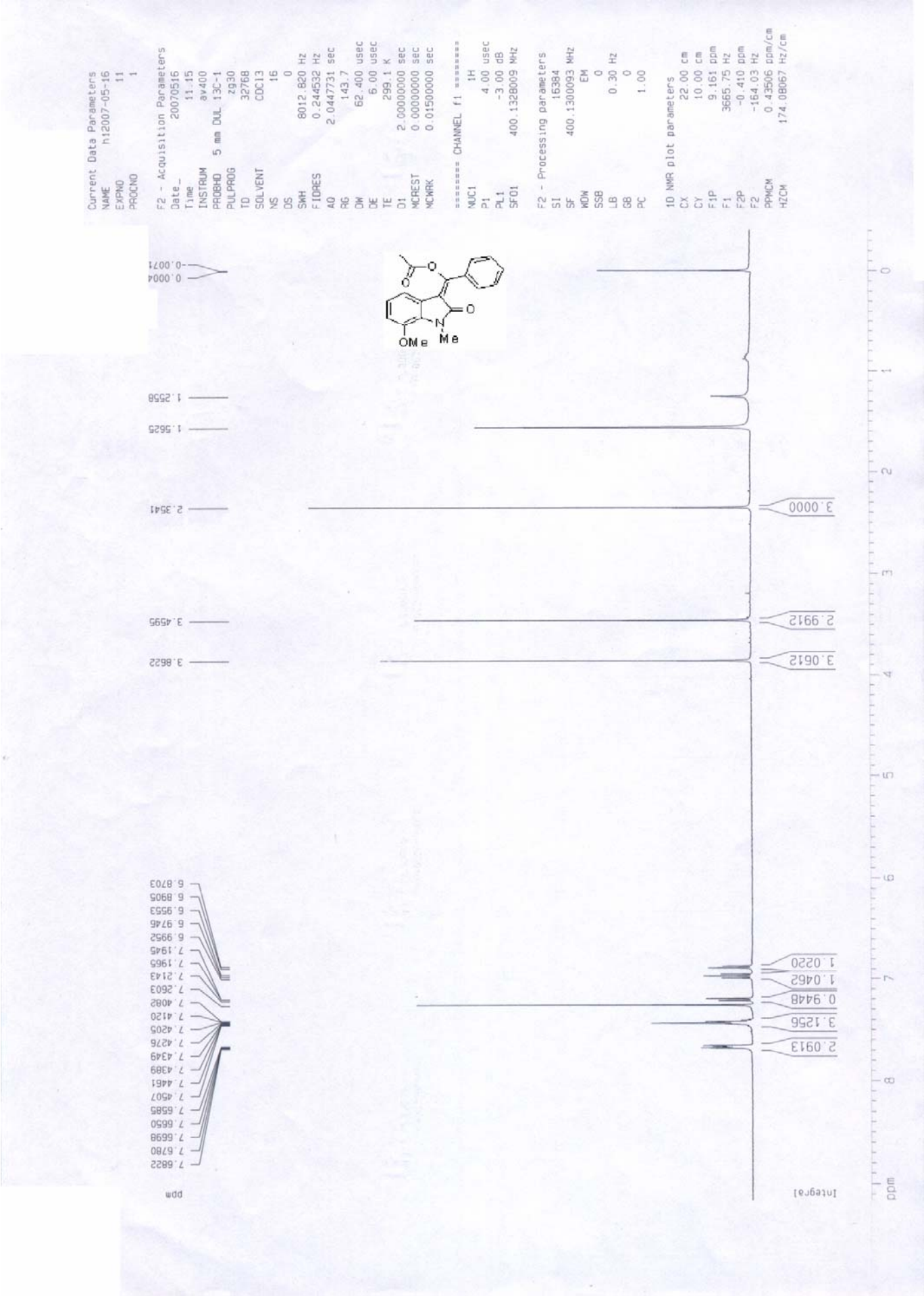
Total time 1 hr, 43 min, 57 sec
COCH3
NCH3
F2 (ppm)
F1 (ppm)
5-H
Br
Me



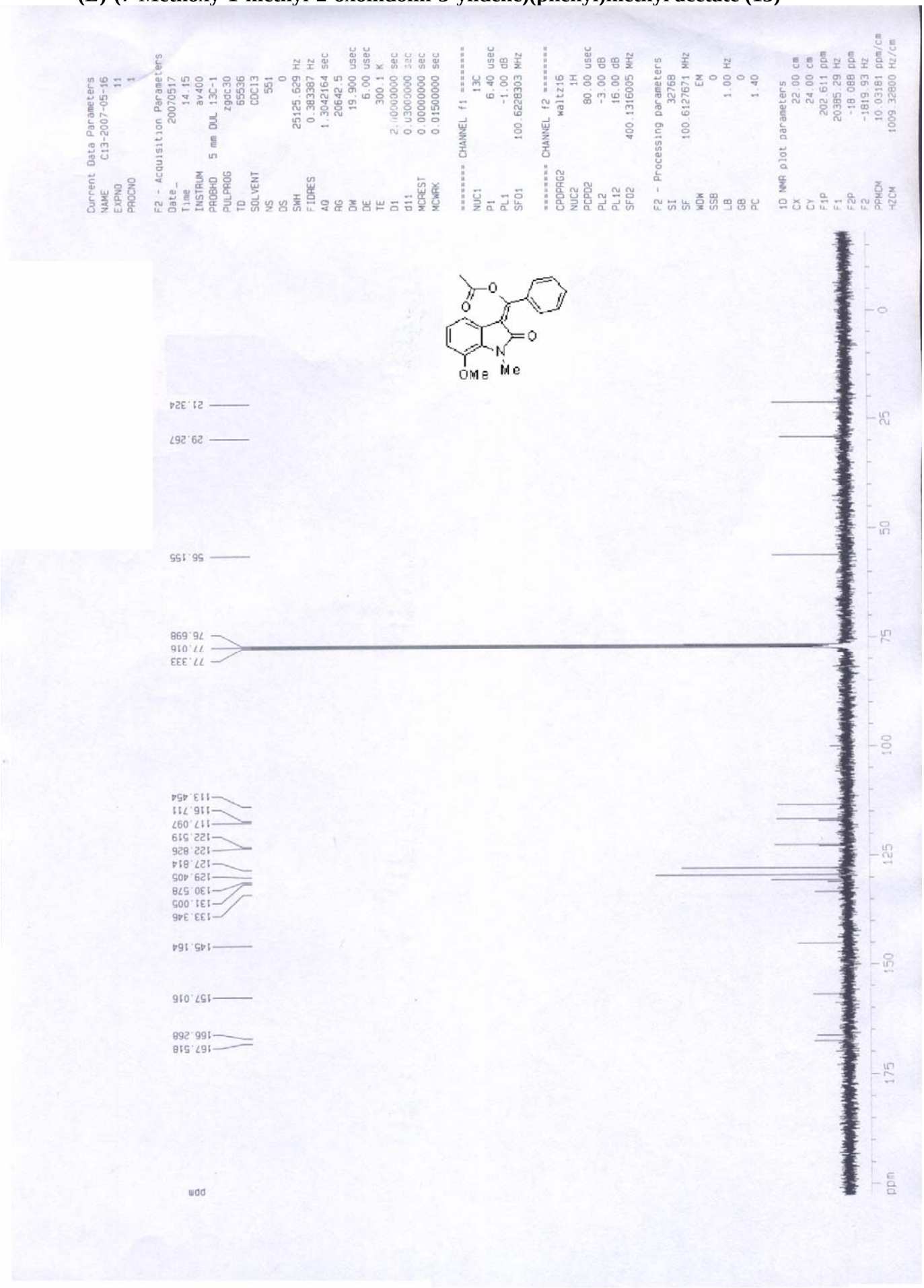
H-H NOESY of (12)



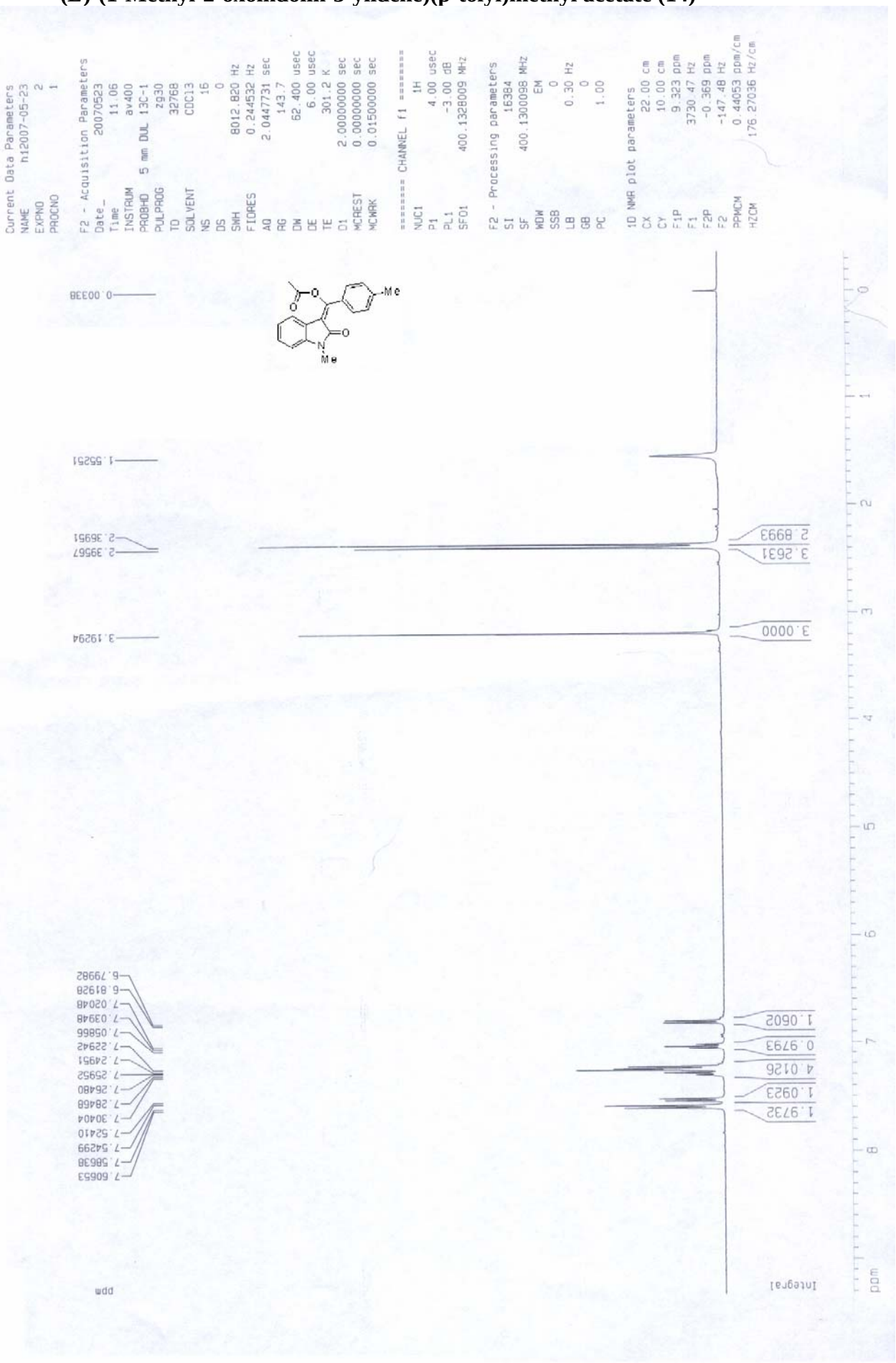
(*E*)-(7-Methoxy-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (13)



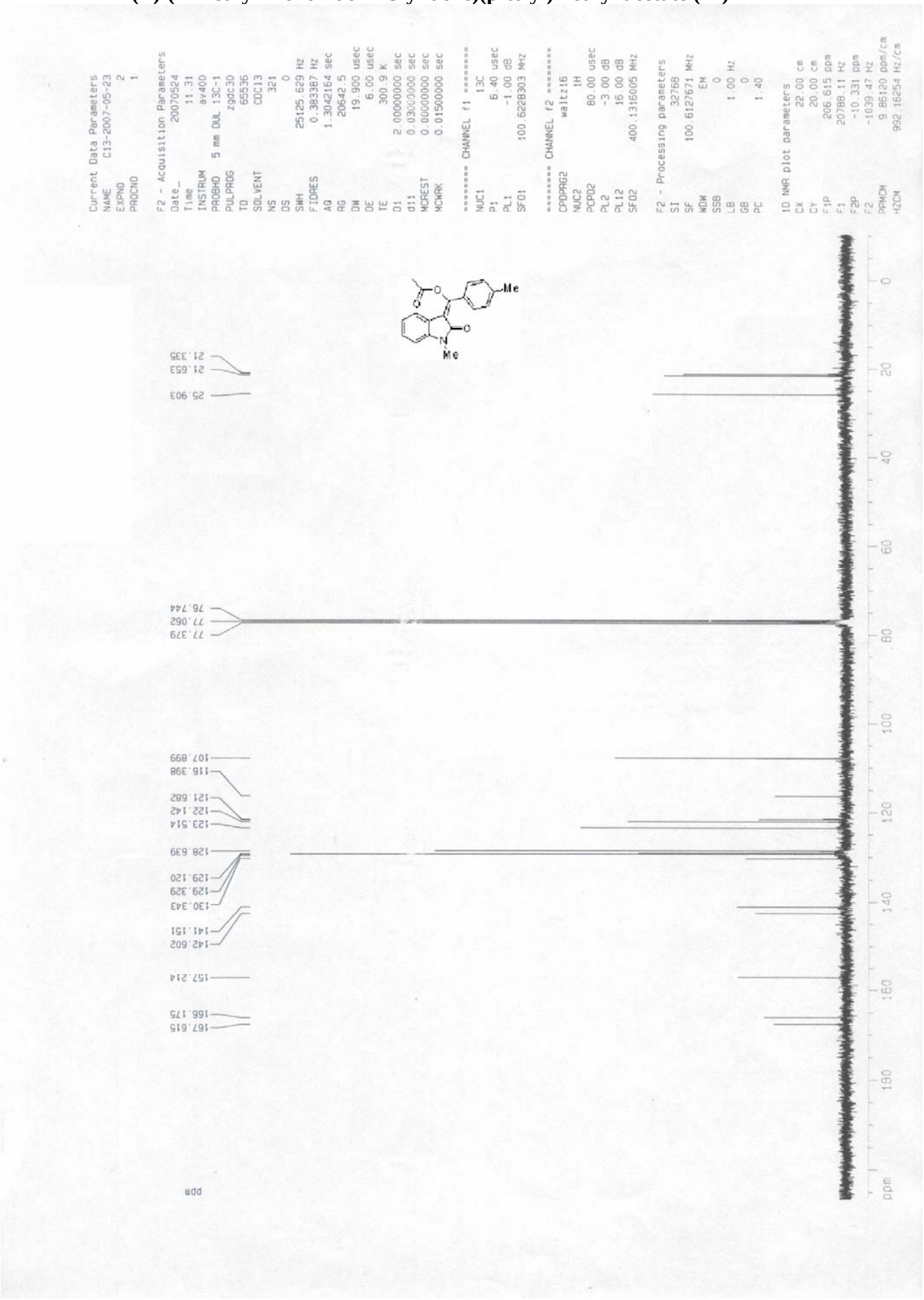
(*E*)-(7-Methoxy-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (13)



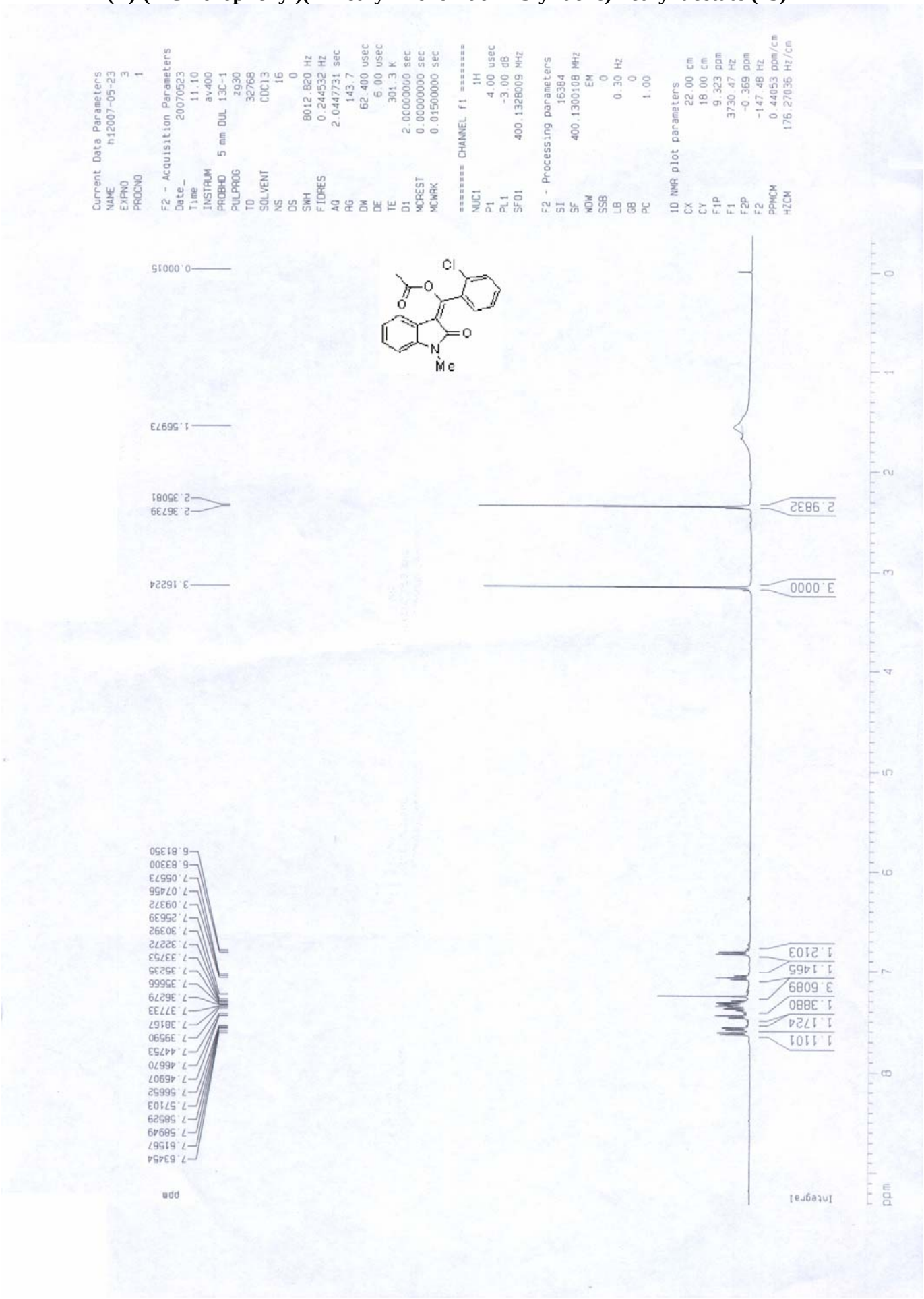
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(p-tolyl)methyl acetate (14)



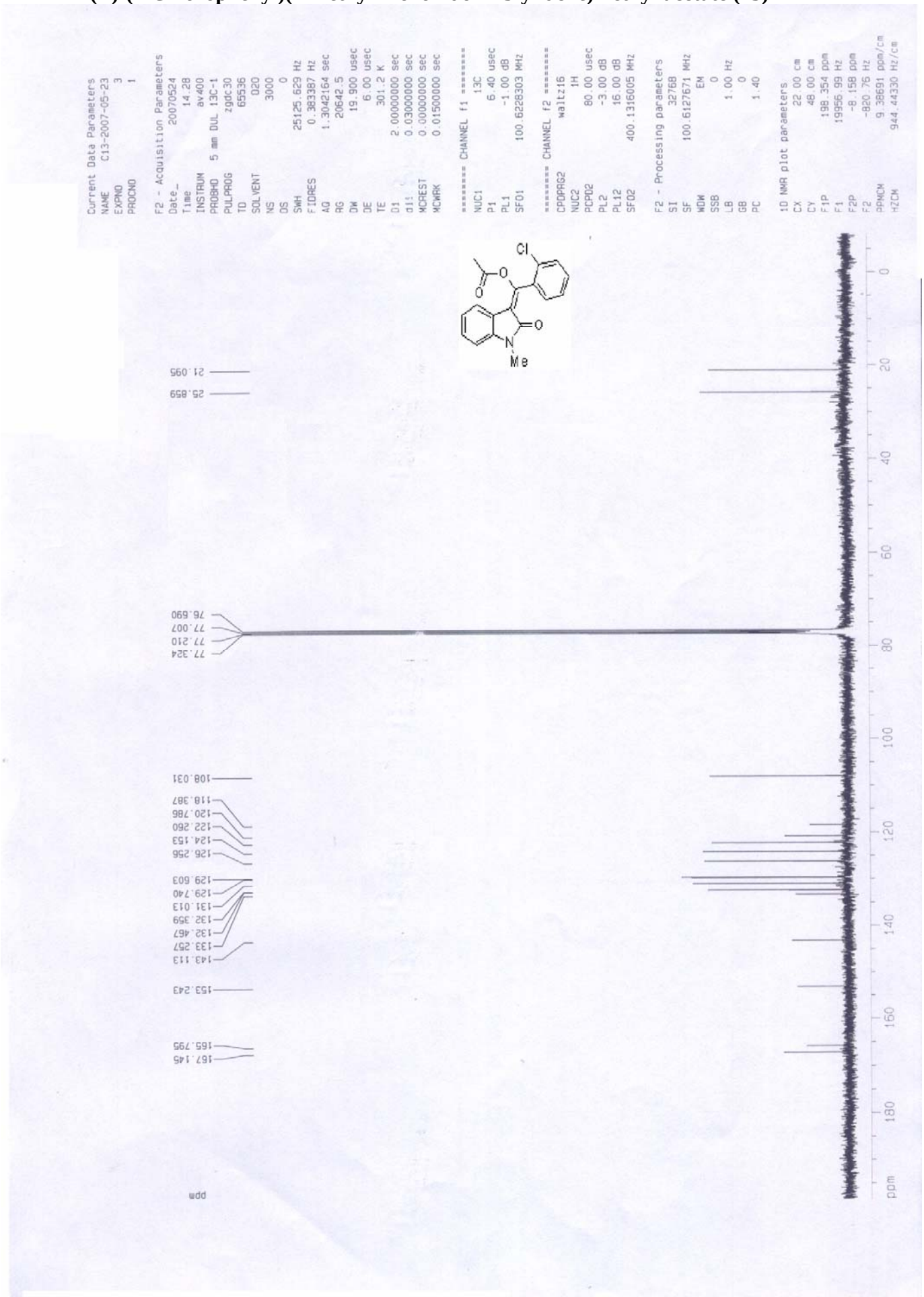
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(p-tolyl)methyl acetate (14)



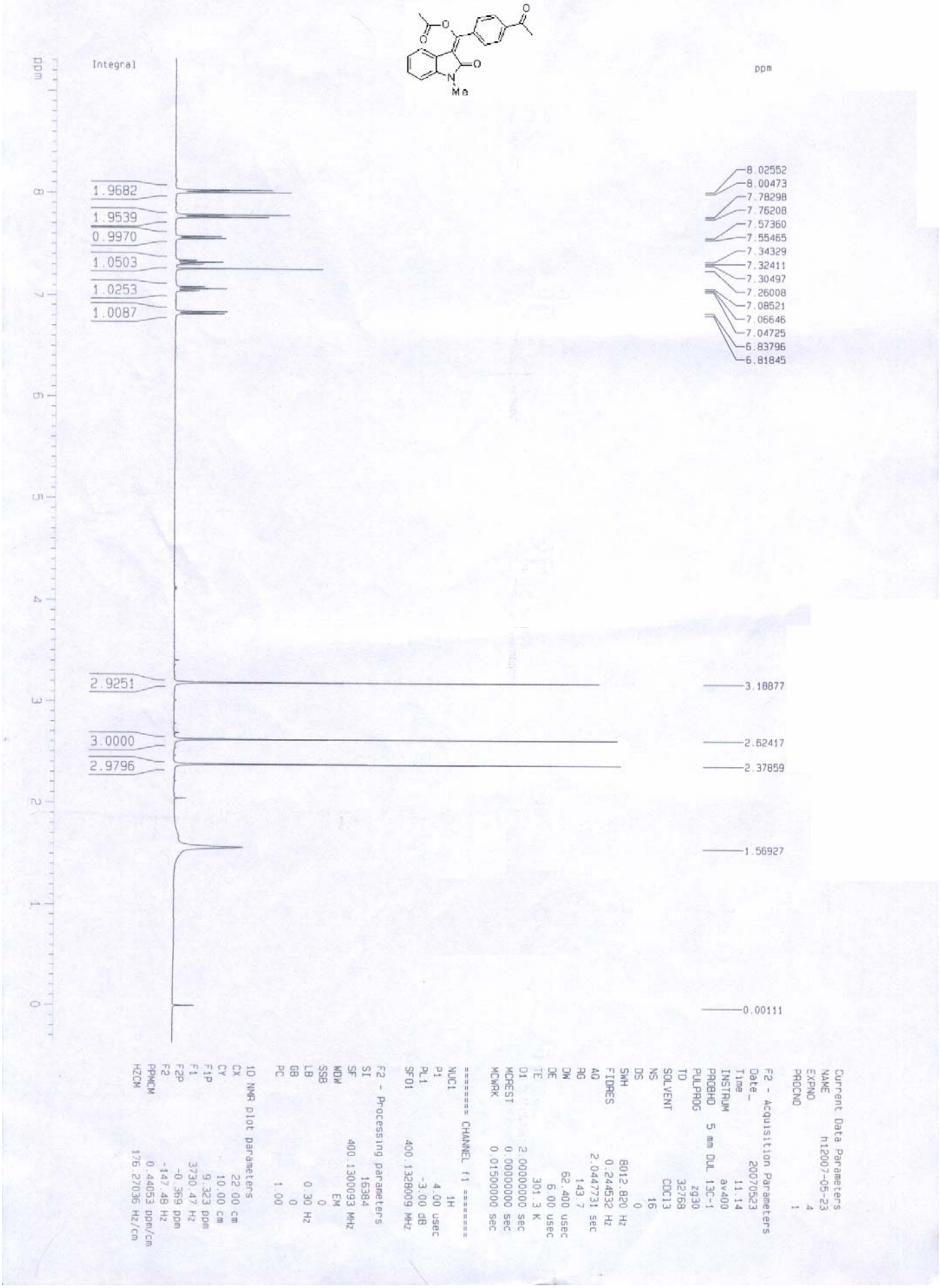
(*E*)-(2-Chlorophenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (15)



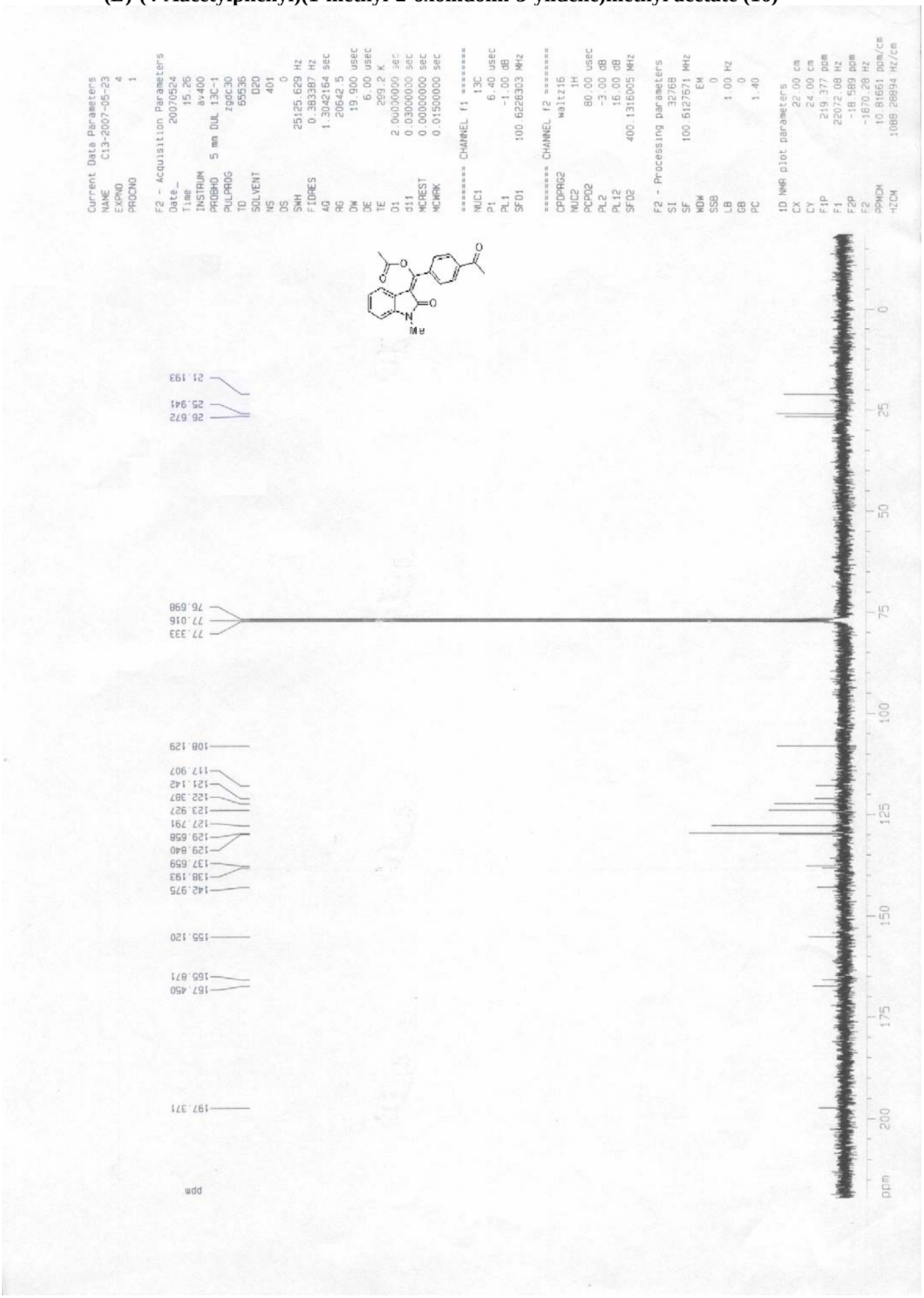
(*E*)-(2-Chlorophenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (15)



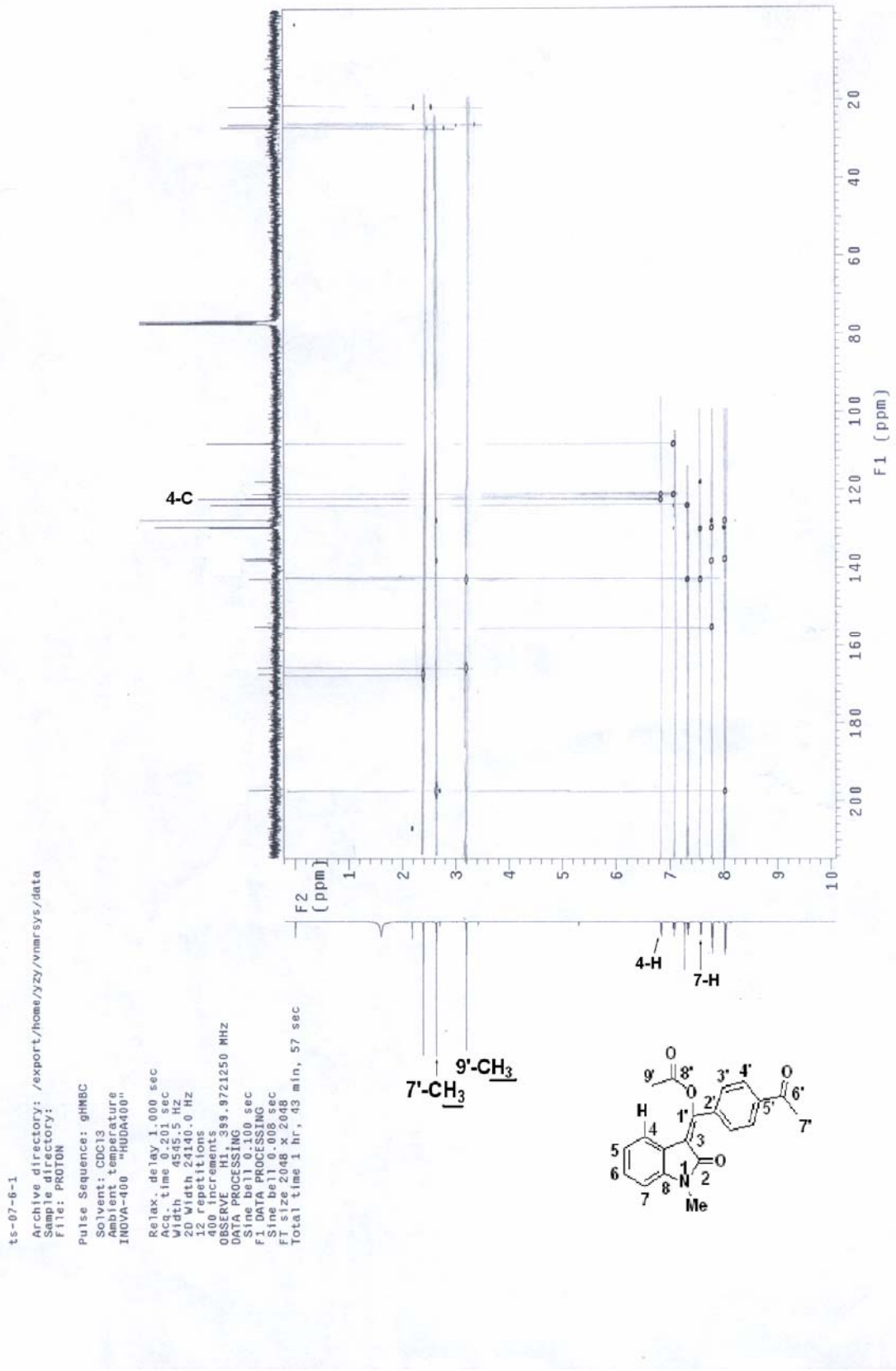
(*E*)-(4-Aacetylphenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (16)



(*E*)-(4-Aacetylphenyl)(1-methyl-2-oxoindolin-3-ylidene)methyl acetate (16)



C-H-COSY of (16)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Solvent: CDCl3
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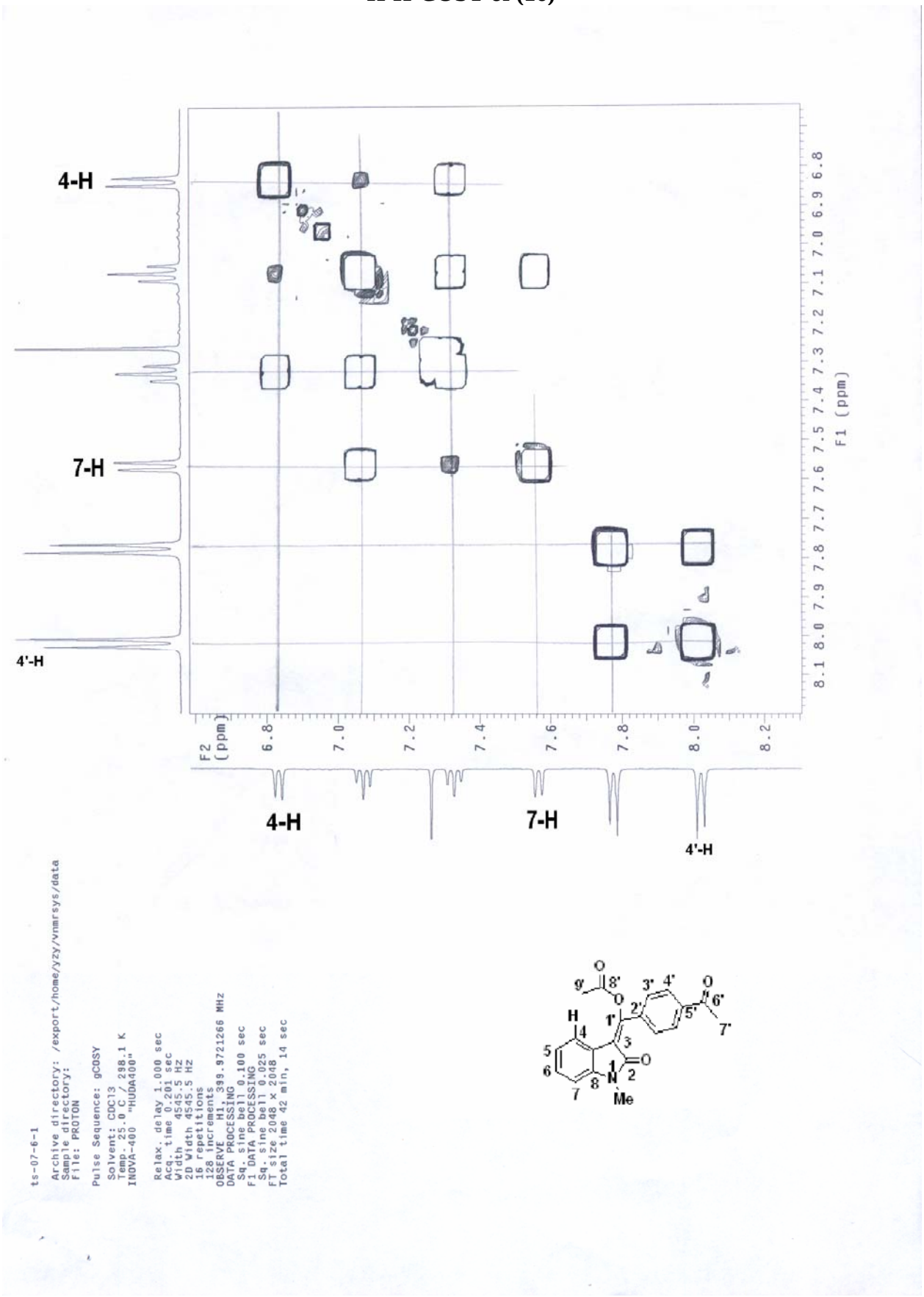
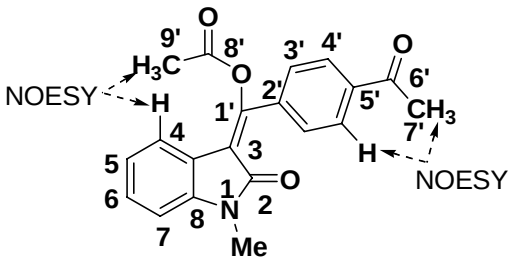
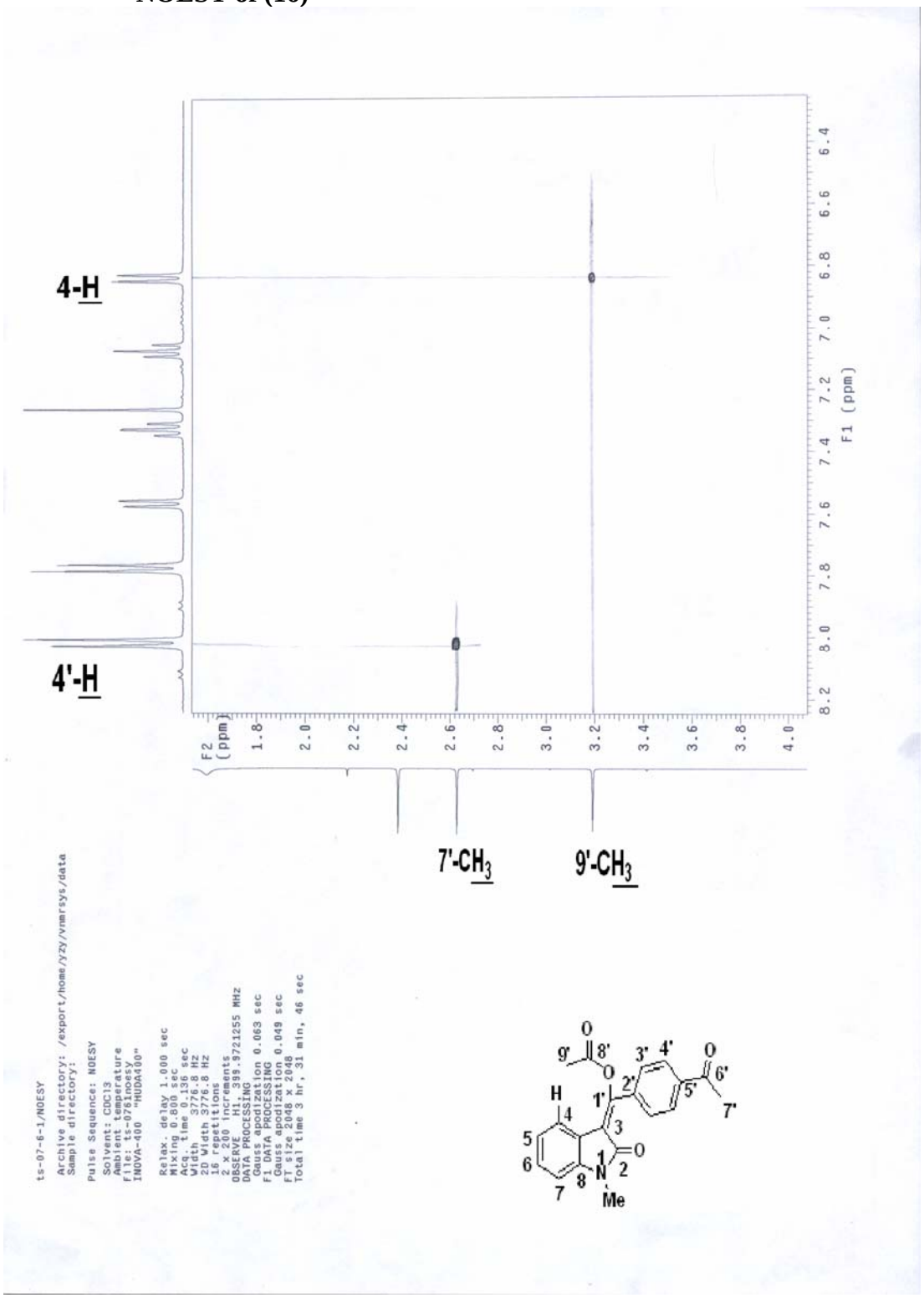
Acq. time 0.201 sec
Width 4545.5 Hz
2D Width 24140.0 Hz
12 repetitions
400 increments
OBSERVE H1, 399.9721250 MHz
DATA PROCESSING
Sine bell 0.100 sec
F1 DATA PROCESSING
Sine bell 0.008 sec
FT size 2048 x 2048
Total time 1 hr, 43 min, 57 sec
4-C
F1 (ppm)
F2 (ppm)
4-H
7-H
7'-CH3
9'-CH3
Me

H-H-COSY of (16)


4-H
7-H
4'-H
F2 (ppm)
F1 (ppm)
ts-07-6-1
Archive directory: /export/home/yzy/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: gCOSY
Solvent: CDCl3
Temp: 25.0 °C / 298.1 K
INOVA-400 "HUDA400"
Relax. delay 1.000 sec
Acq. time 0.201 sec
Width 4545.5 Hz
2D Width 4545.5 Hz
16 repetitions
128 increments
OBSERVE H1, 399.9721266 MHz
DATA PROCESSING
Sq. sine bell 0.100 sec
F1 DATA PROCESSING
Sq. sine bell 0.025 sec
FT size 2048 x 2048
Total time 42 min, 14 sec


NOESY
NOESY
9'
8'
3'
4'
6'
7'
1'
2'
5'
1
2
3
4
5
6
7
8
Me

NOESY of (16)


4-H
4'-H
7'-CH3
9'-CH3
F2 (ppm)
F1 (ppm)
ts-07-6-1/NOESY
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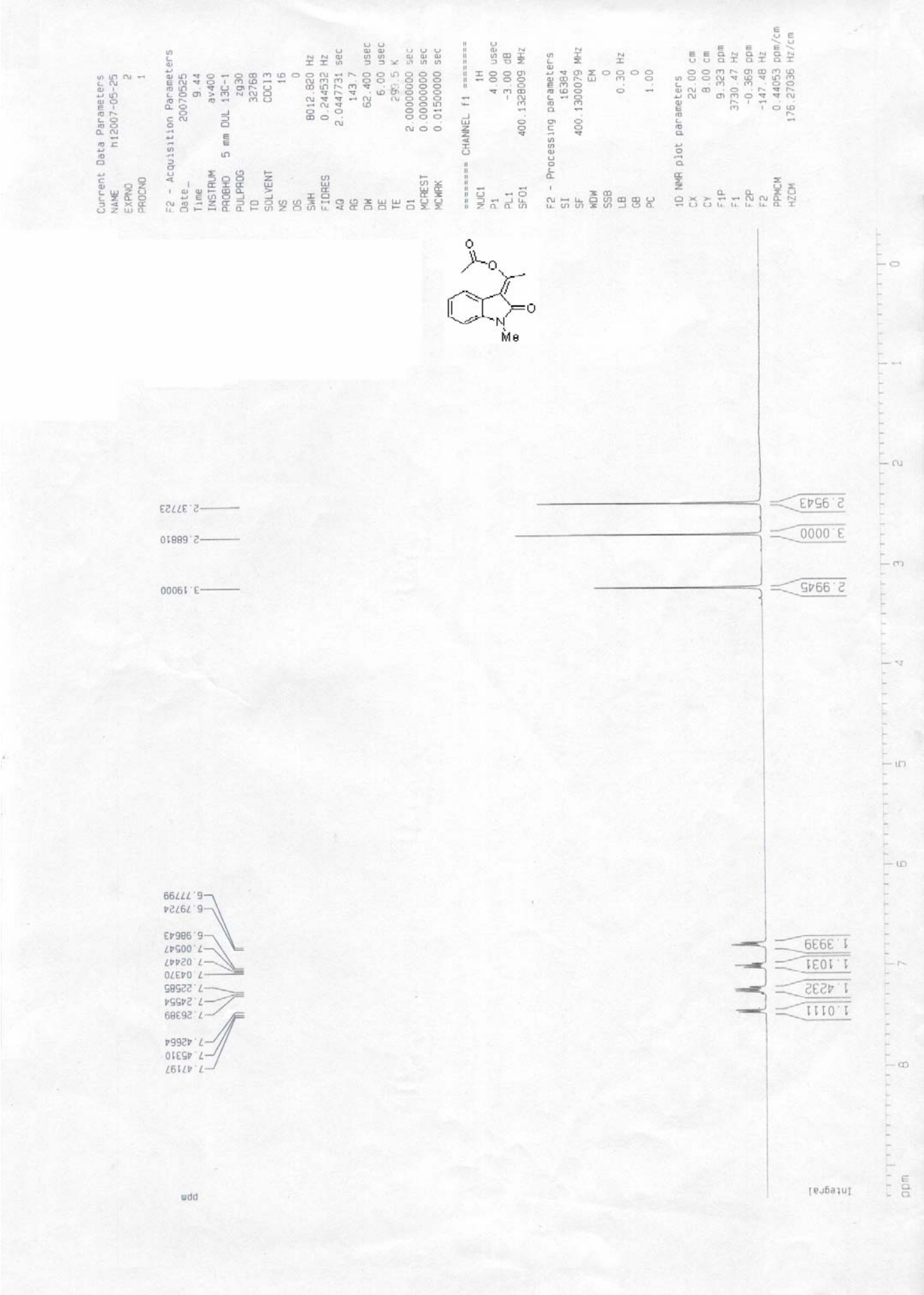
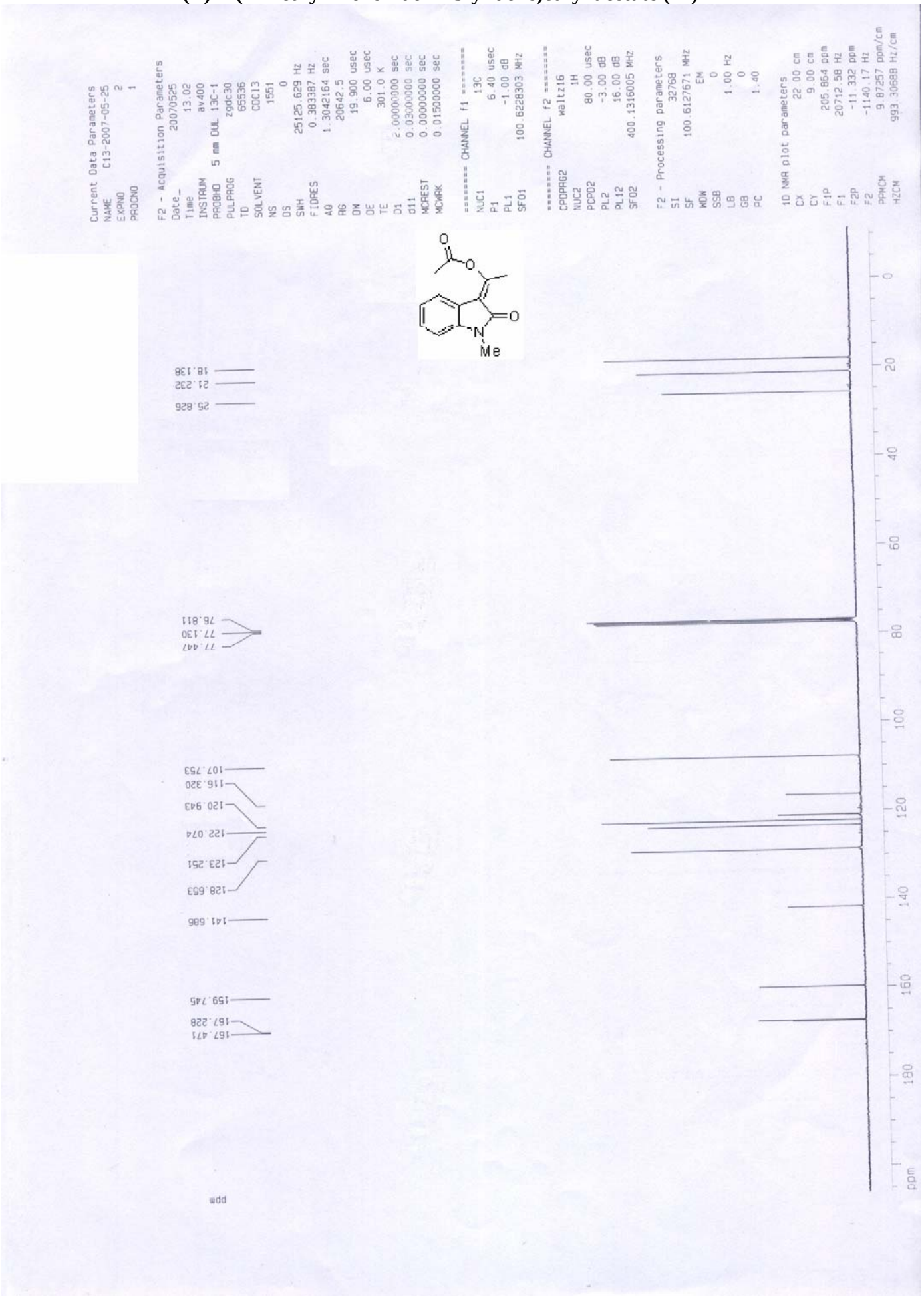
Sample directory:
Pulse Sequence: NOESY
Solvent: CDCl3
Ambient temperature
file: ts-076inoesy
INOVA-400 "HUDA400"
Relax. delay 1.000 sec
Mixing 0.000 sec
Acq. time 0.136 sec
Width 3776.8 Hz
2D Width 3776.8 Hz
16 repetitions
2 x 200 increments
OBSERVE H1, 399.9721255 MHz
DATA PROCESSING
Gauss apodization 0.063 sec
F1 DATA PROCESSING
Gauss apodization 0.049 sec
FT size 2048 x 2048
Total time 3 hr, 31 min, 46 sec

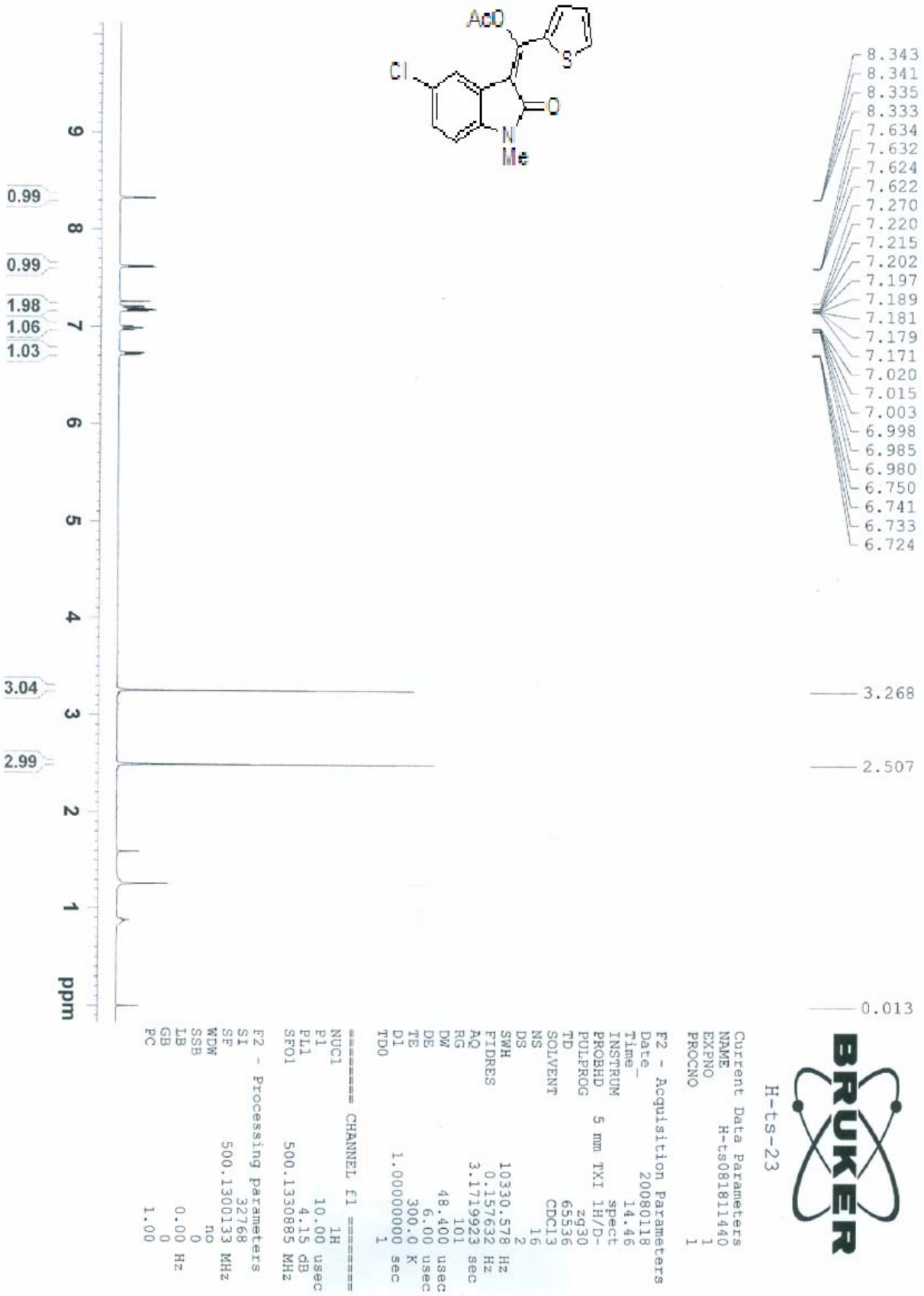
(*E*)-1-(1-Methyl-2-oxoindolin-3-ylidene)ethyl acetate (17)



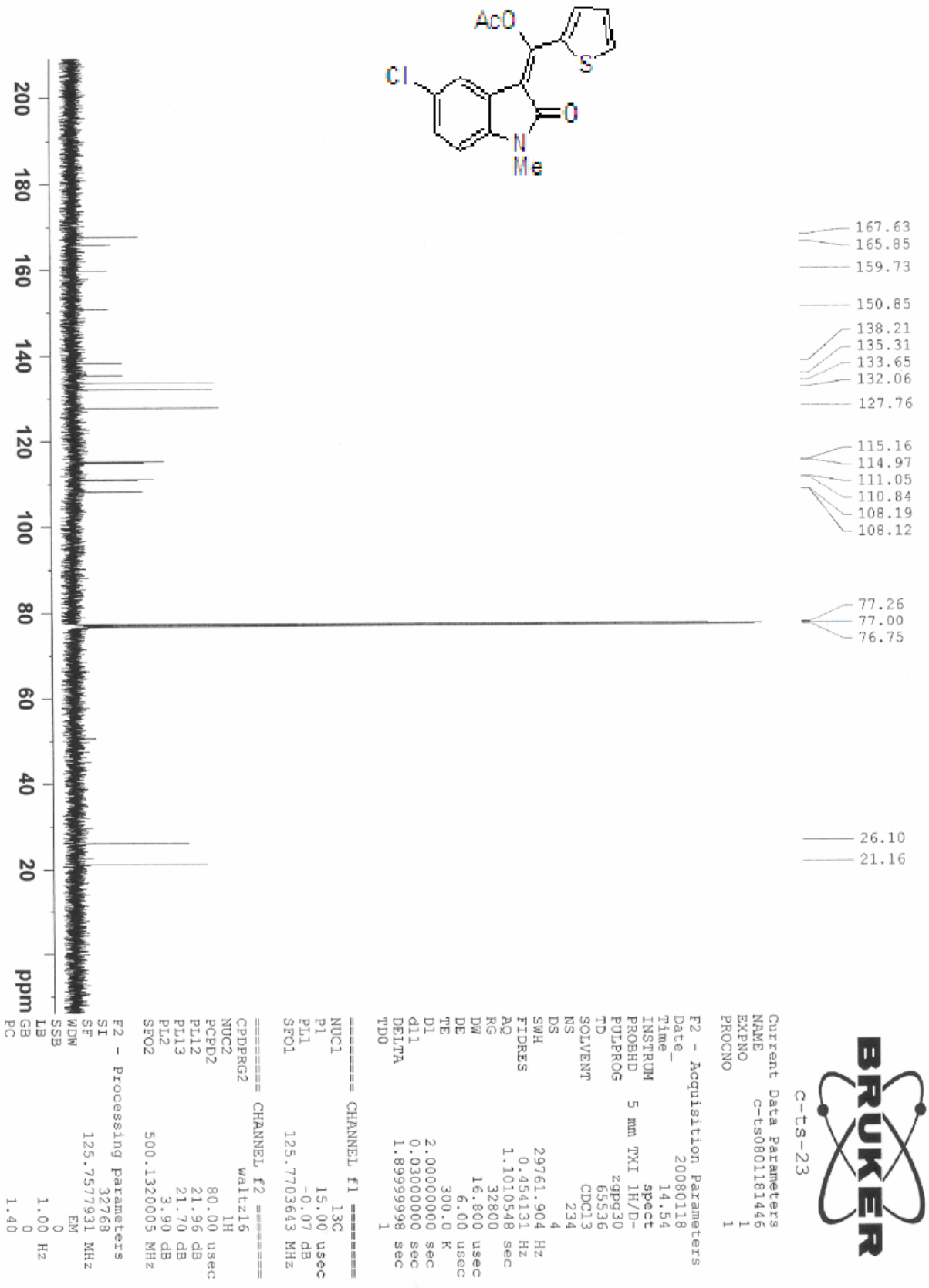
(*E*)-1-(1-Methyl-2-oxoindolin-3-ylidene)ethyl acetate (17)



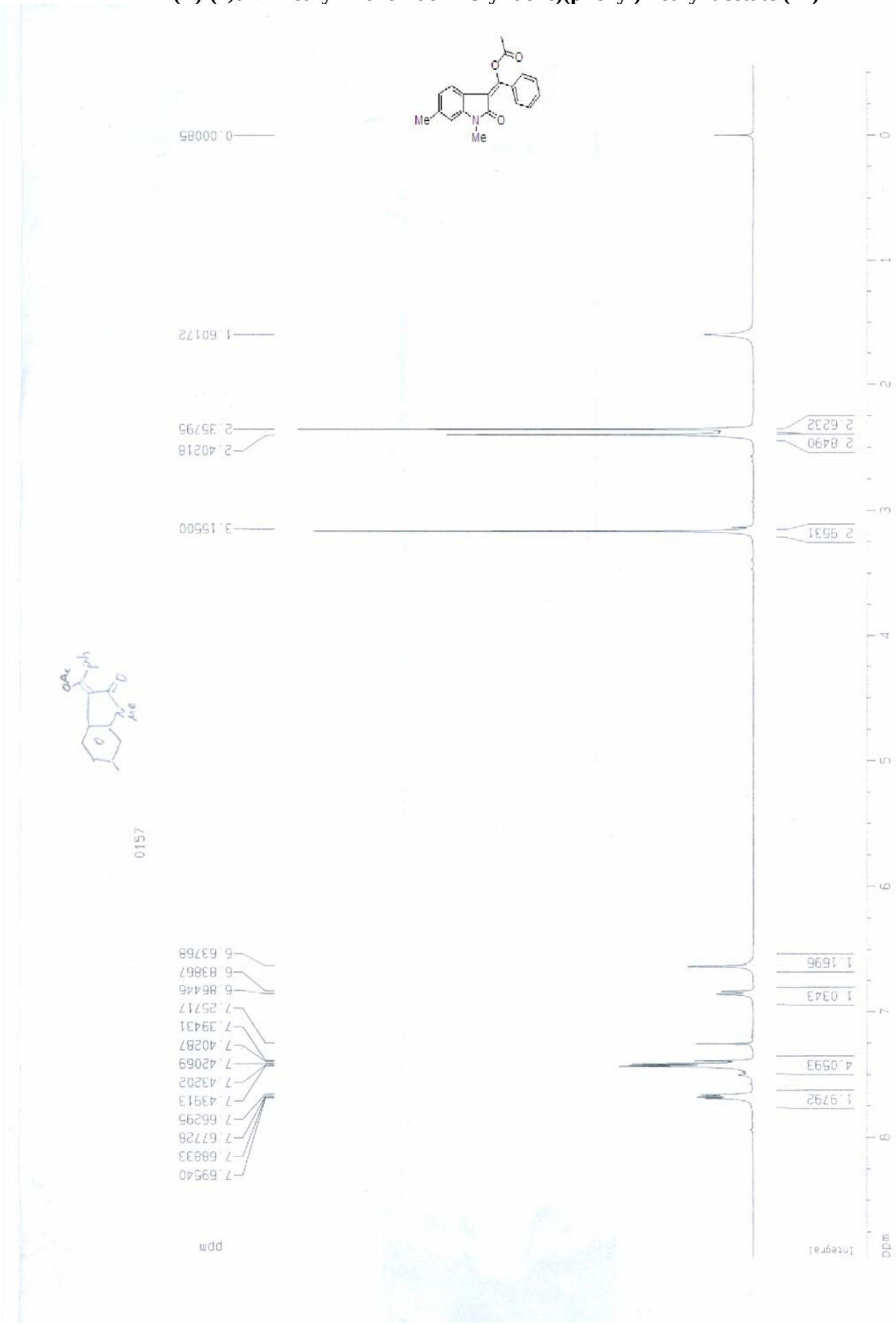
(*E*)-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)(thiophen-2-yl)methyl acetate (19)



(*E*)-(5-Chloro-1-methyl-2-oxoindolin-3-ylidene)(thiophen-2-yl)methyl acetate (19)

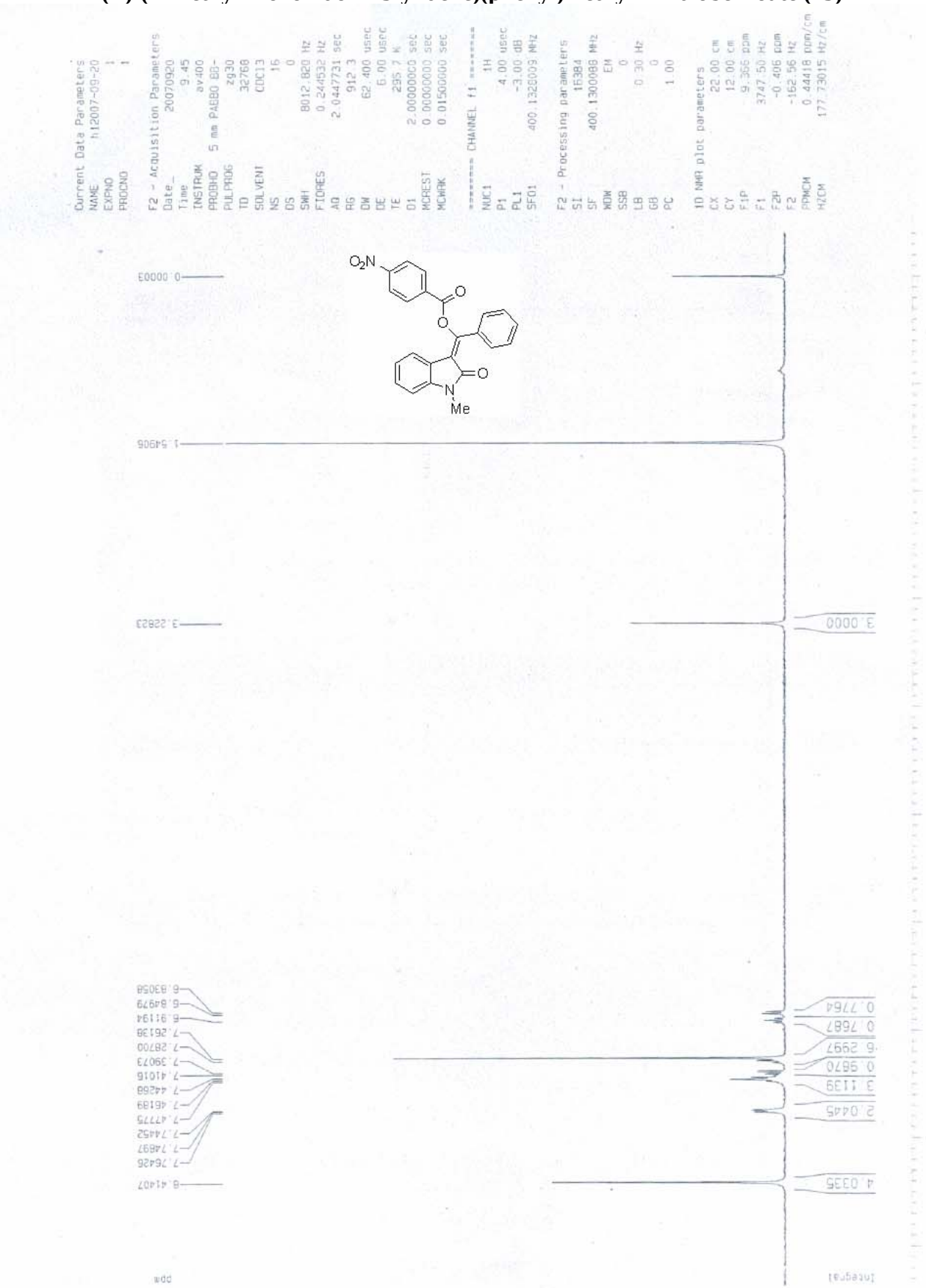


(*E*)-(1,6-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (21)

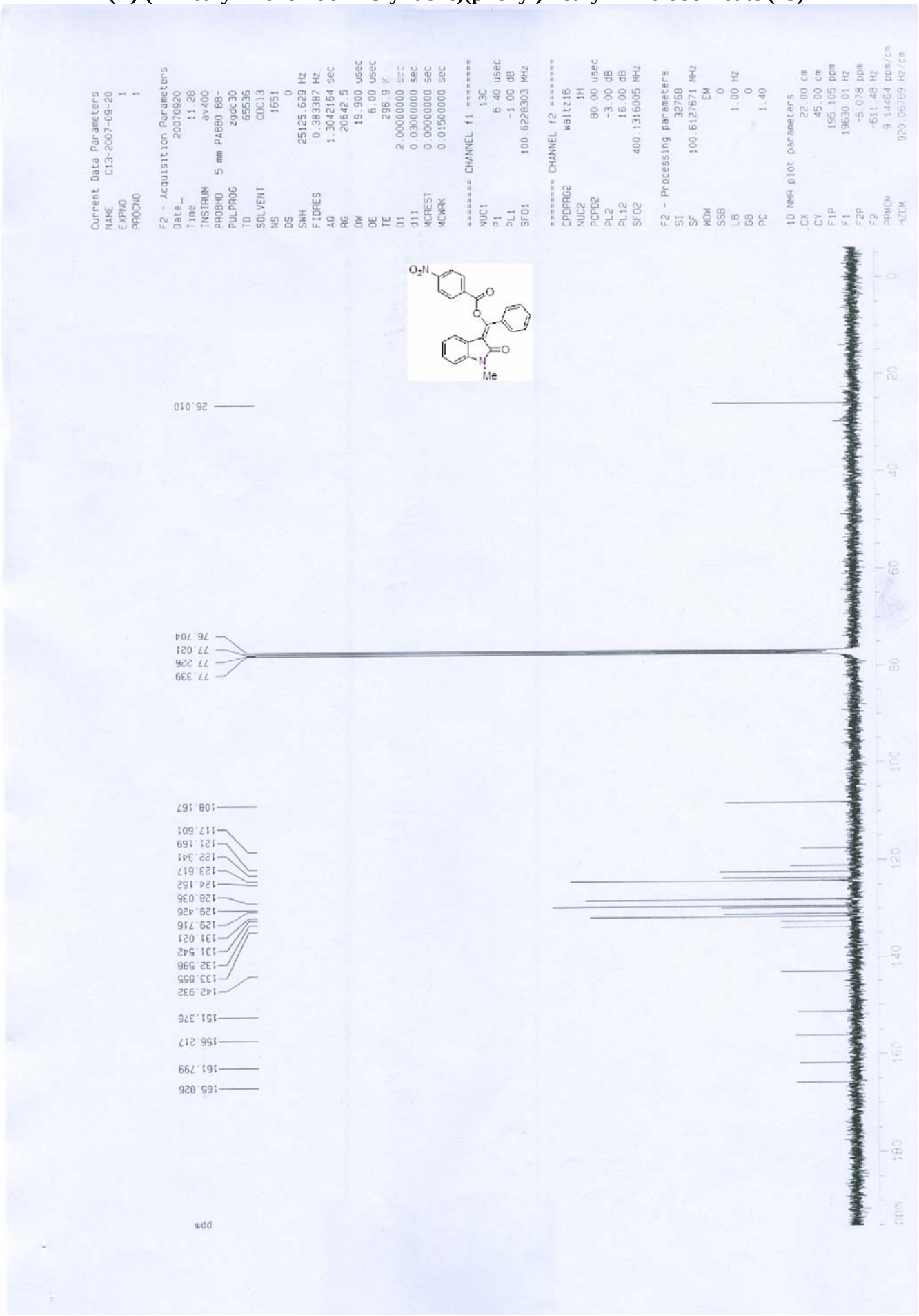


(*E*)-(1,6-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl acetate (21)

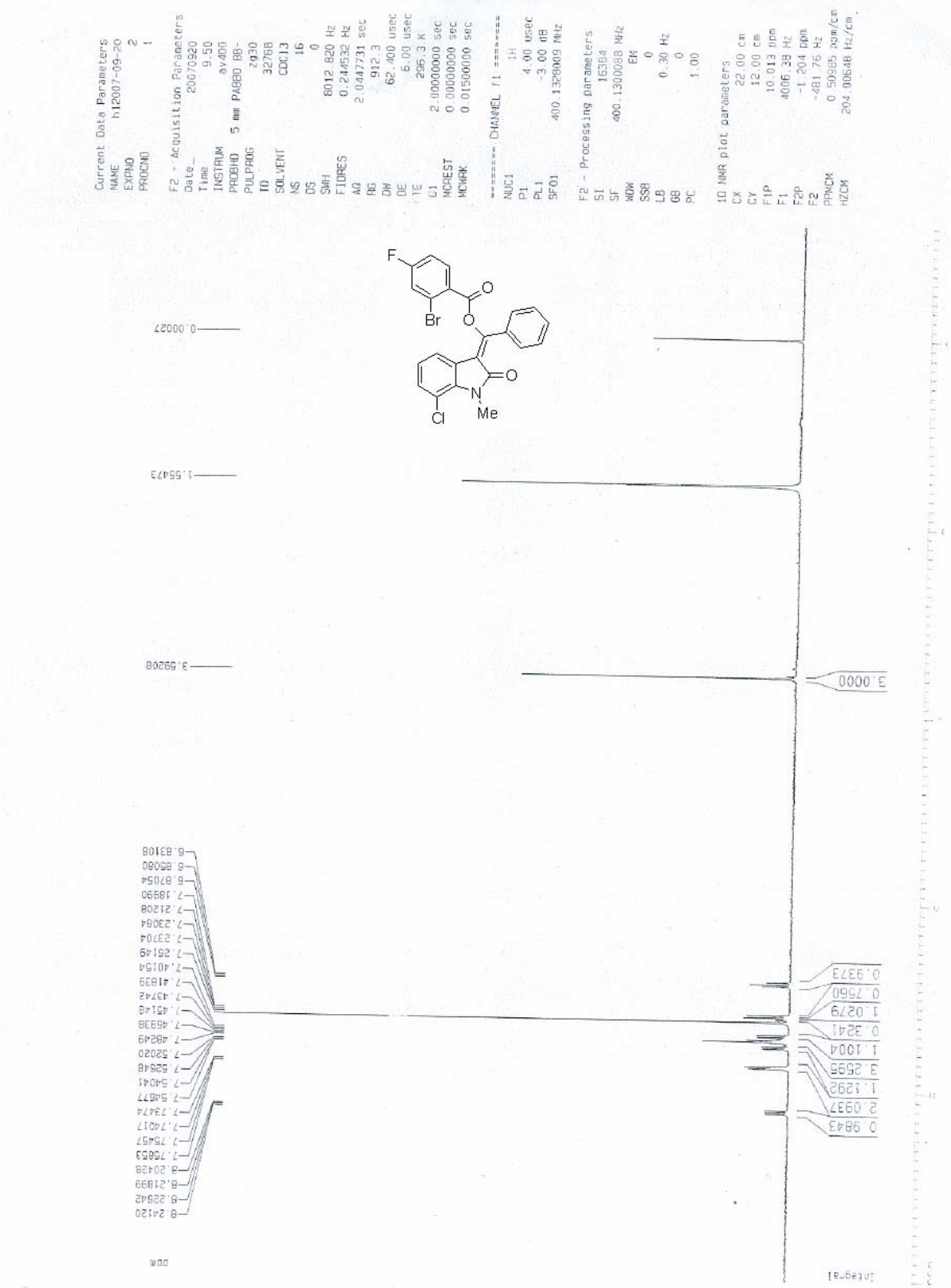
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-nitrobenzoate (23)



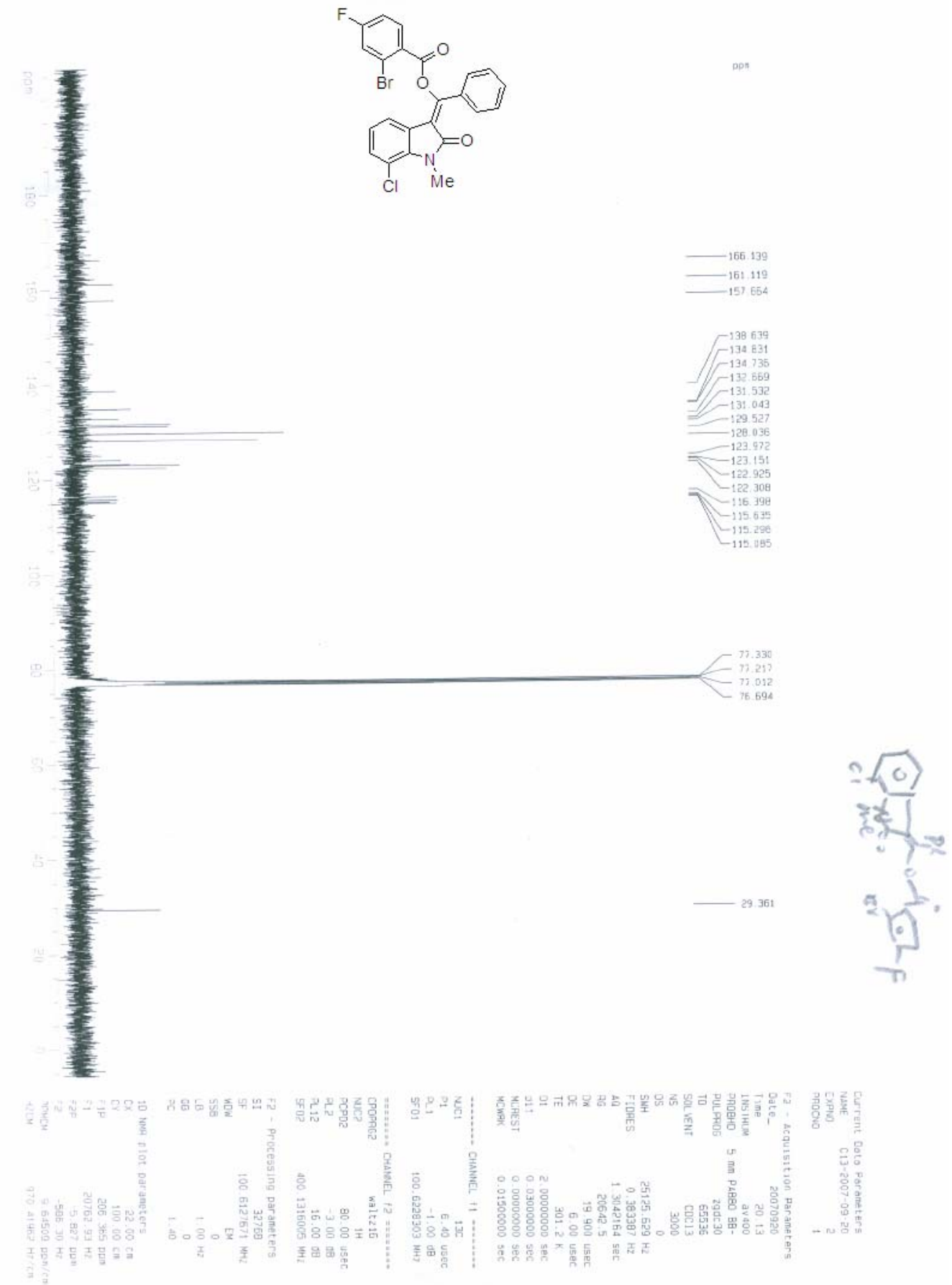
(*E*)-(1-Methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-nitrobenzoate (23)



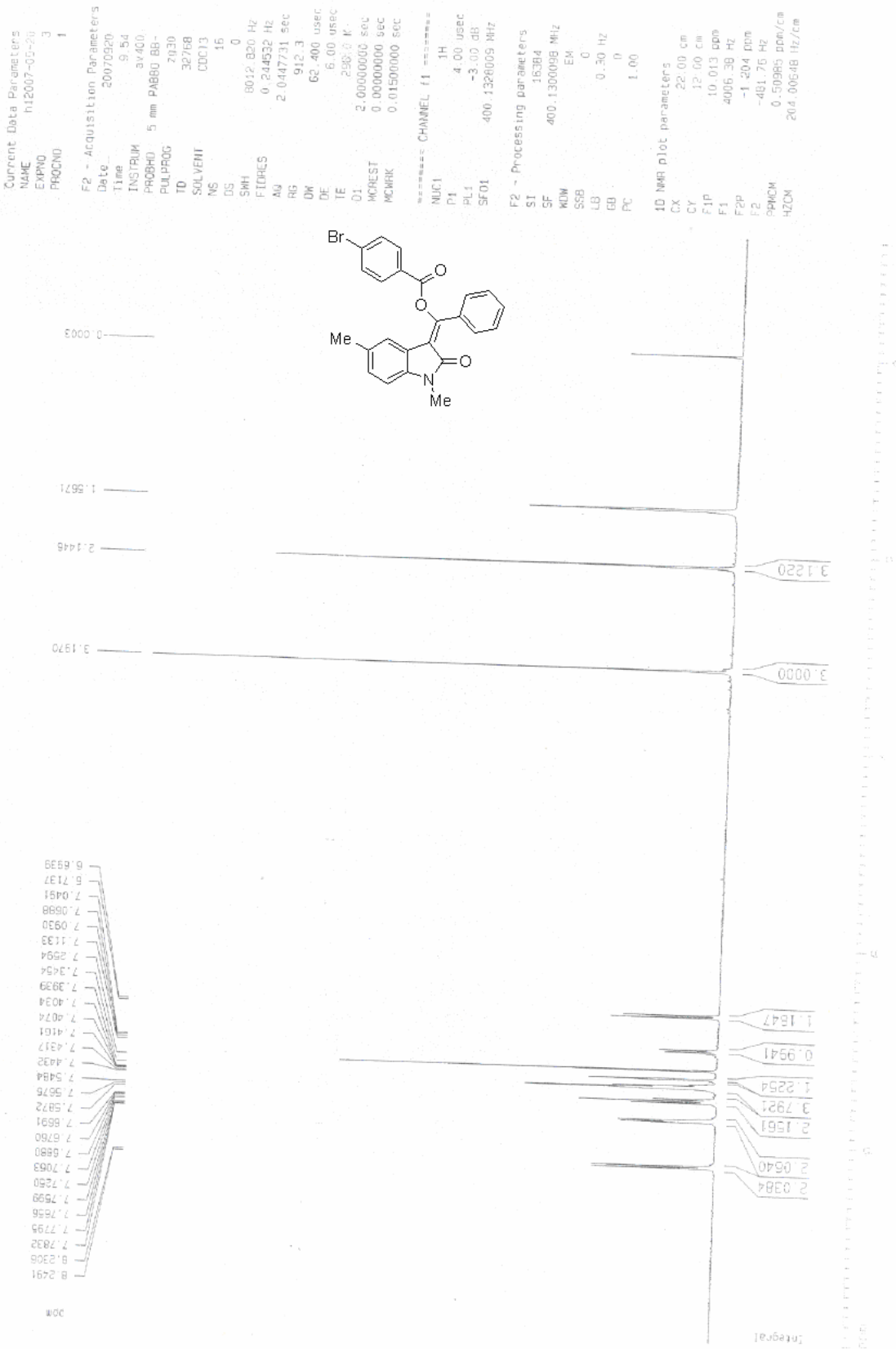
(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-bromo-4-fluorobenzoate (25)



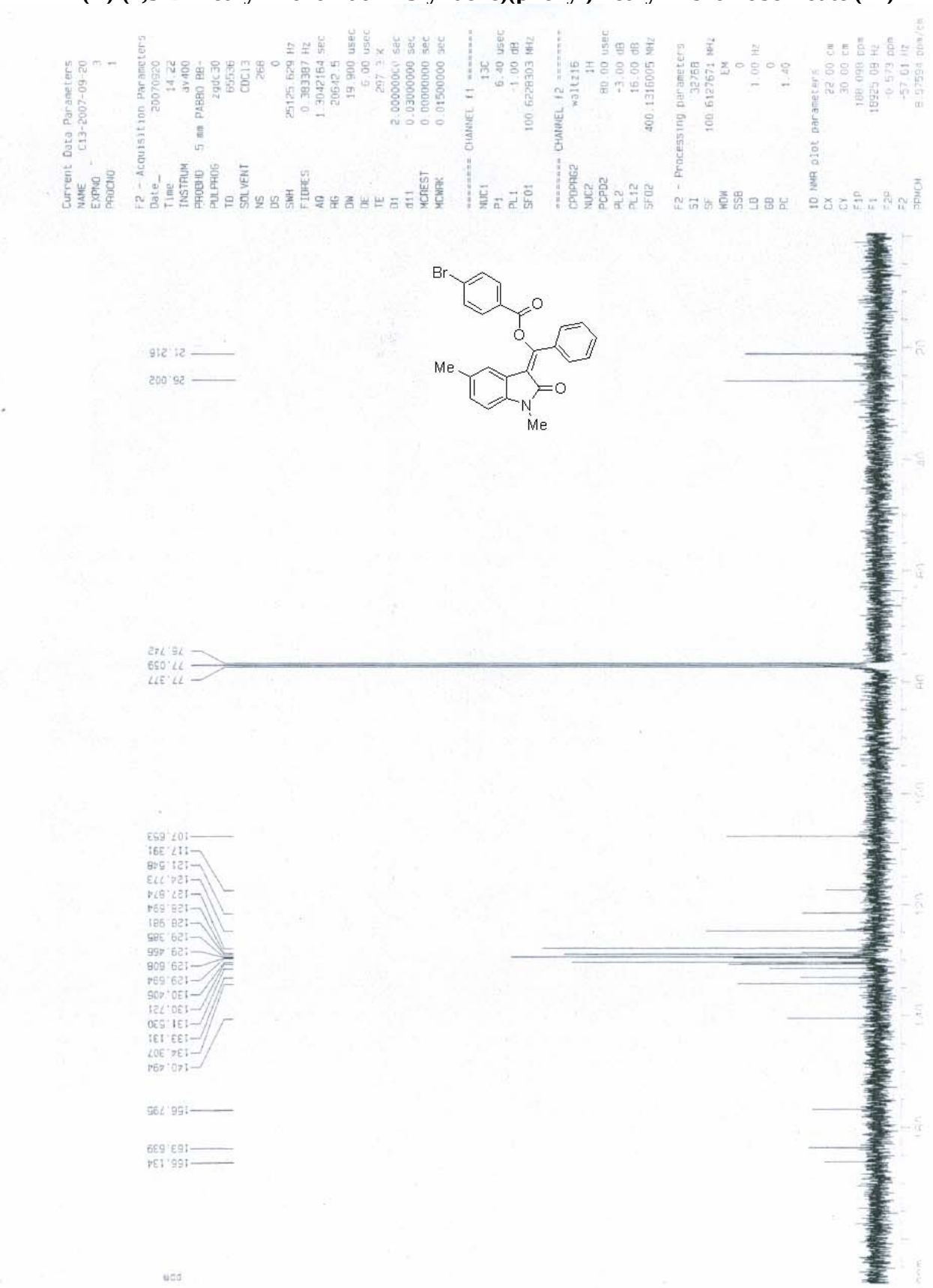
(*E*)-(7-Chloro-1-methyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-bromo-4-fluorobenzoate (25)



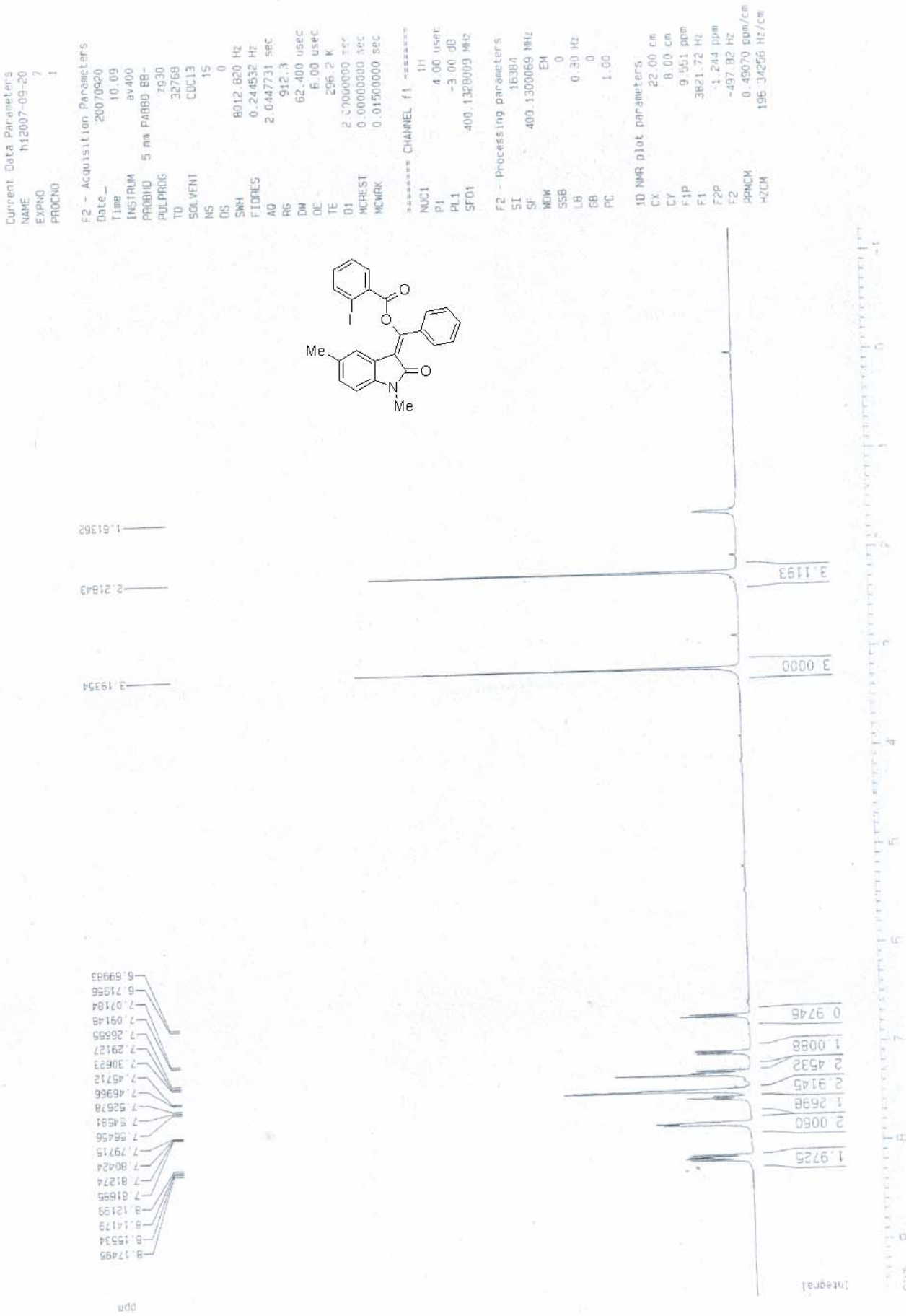
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-bromobenzoate (27)



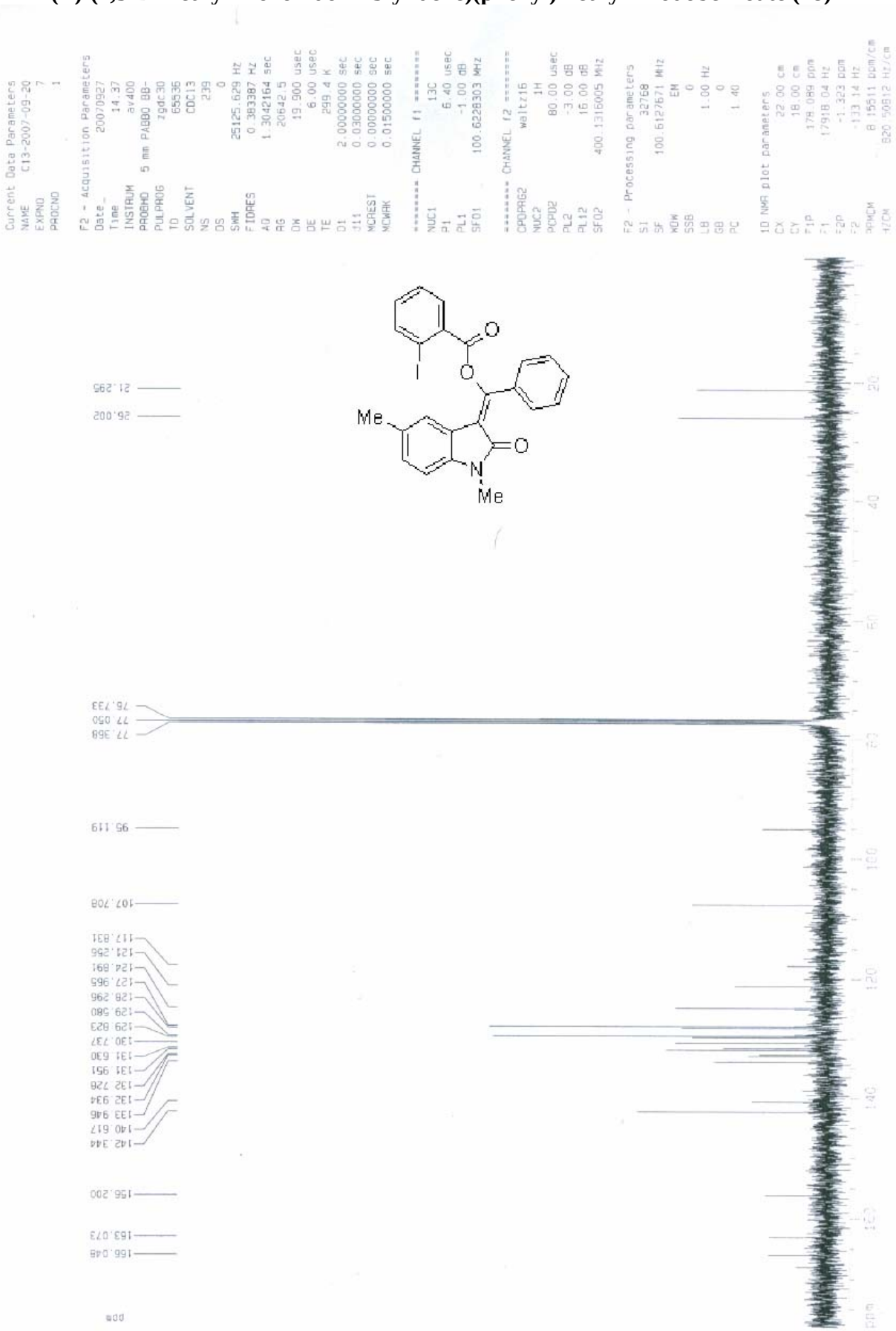
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-bromobenzoate (27)



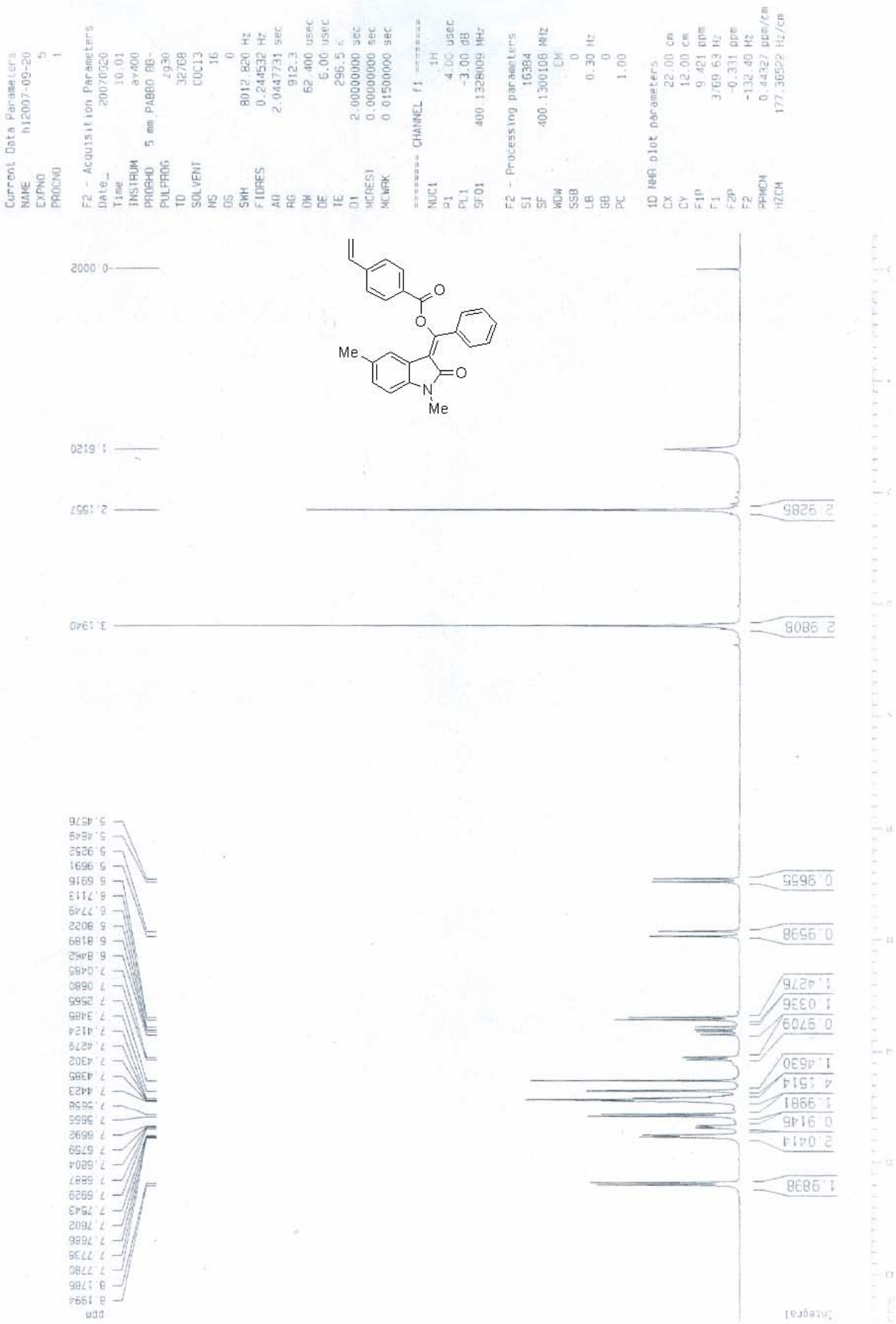
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-iodobenzoate (28)



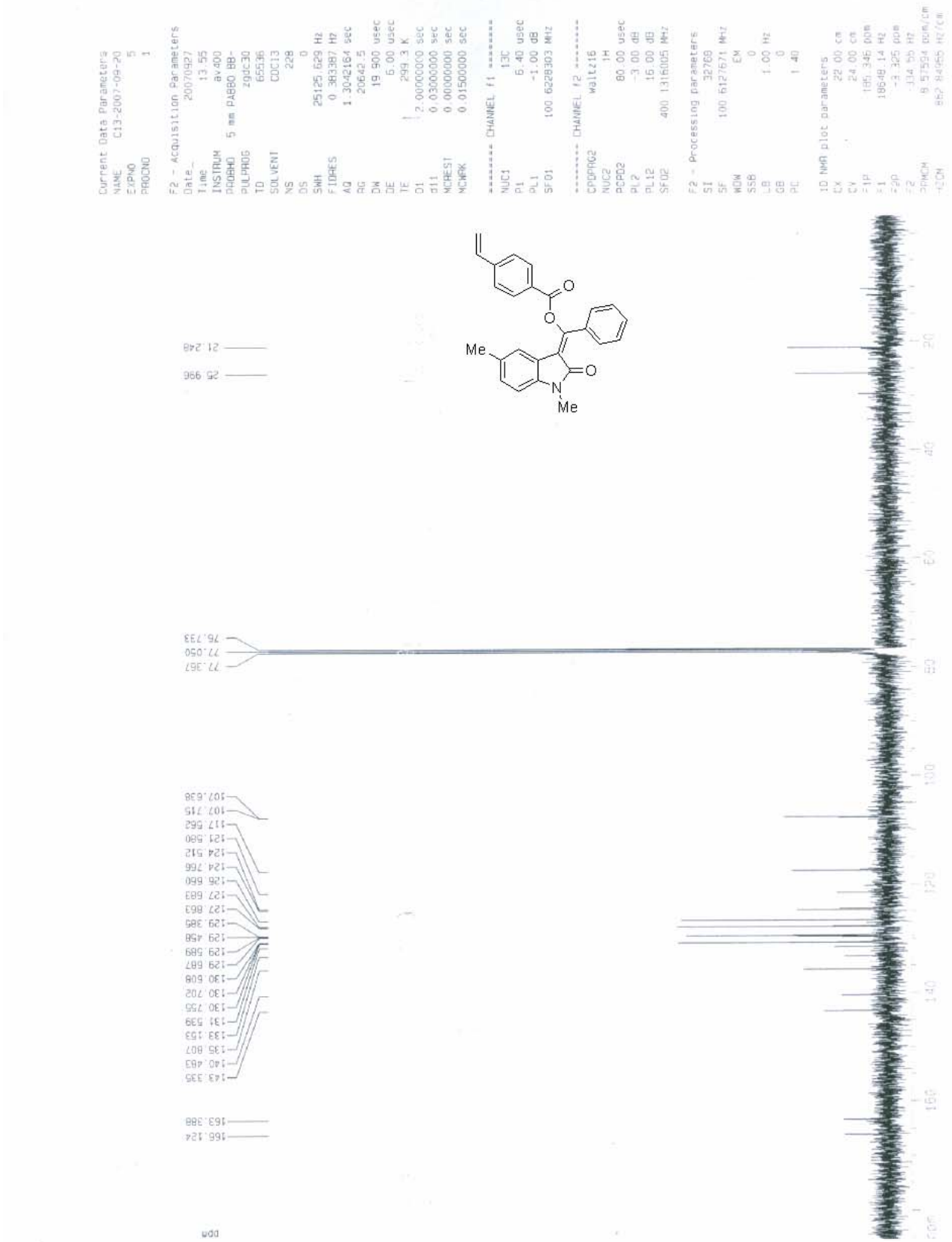
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-iodobenzoate (28)



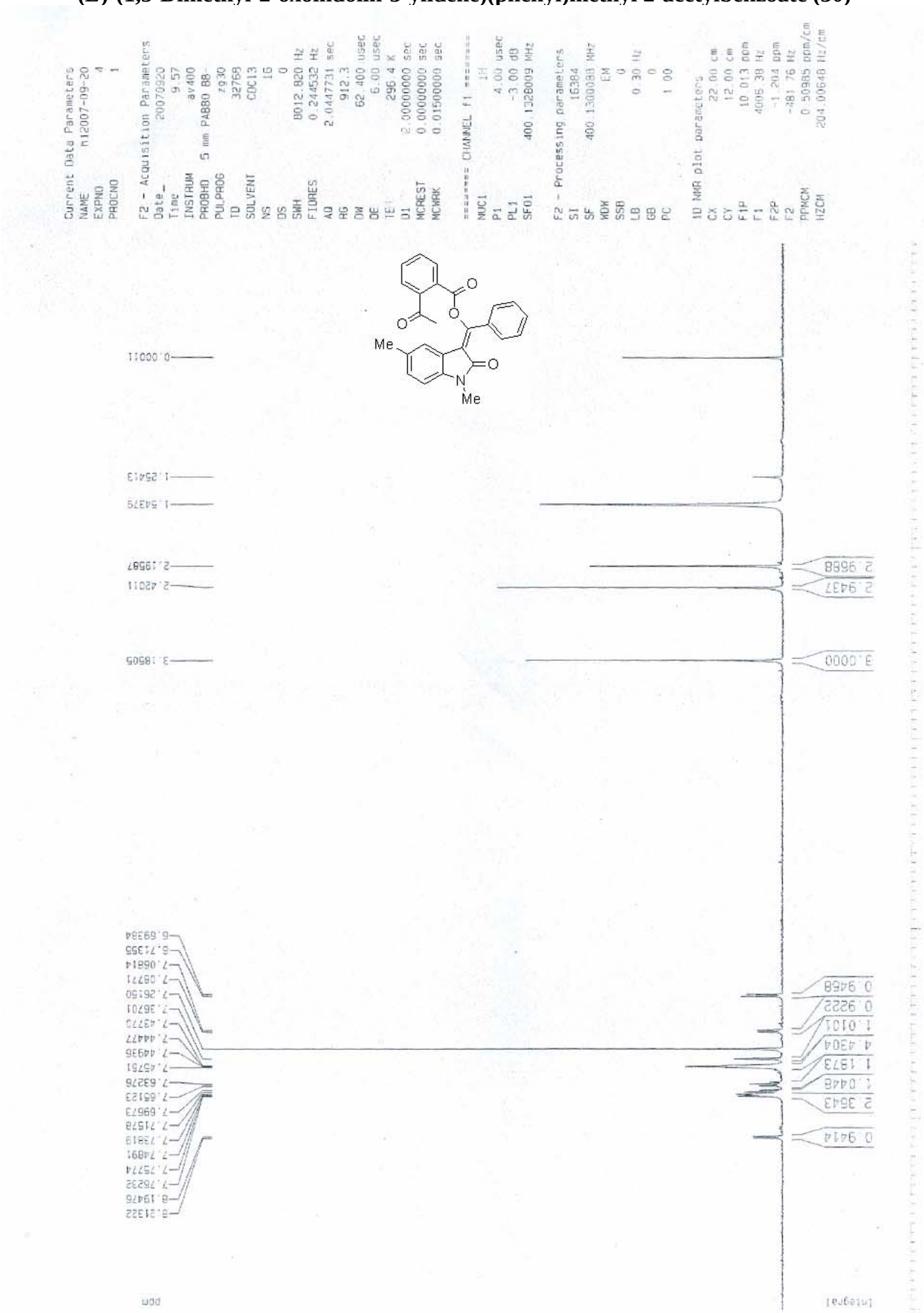
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-vinylbenzoate (29)



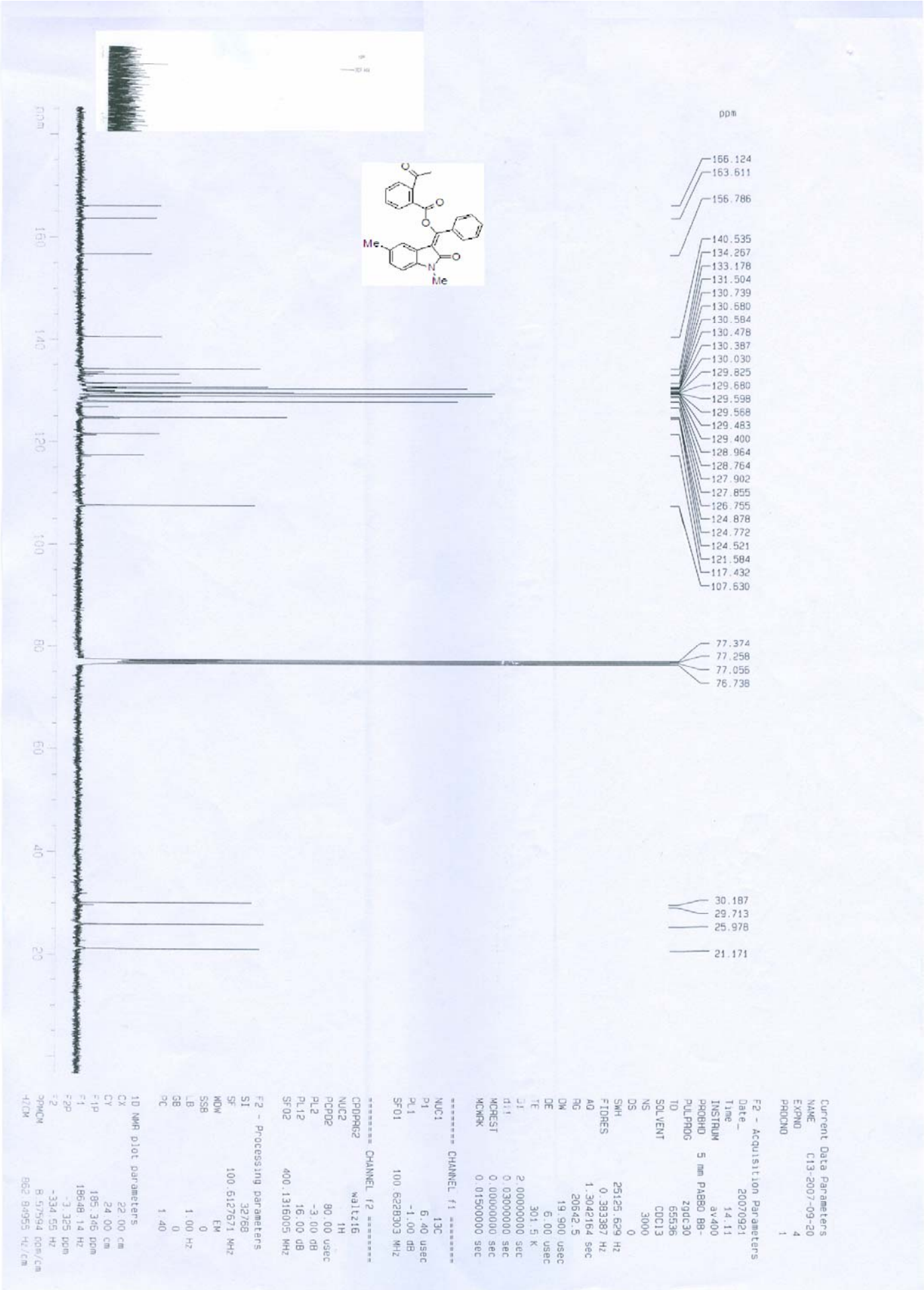
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 4-vinylbenzoate (29)



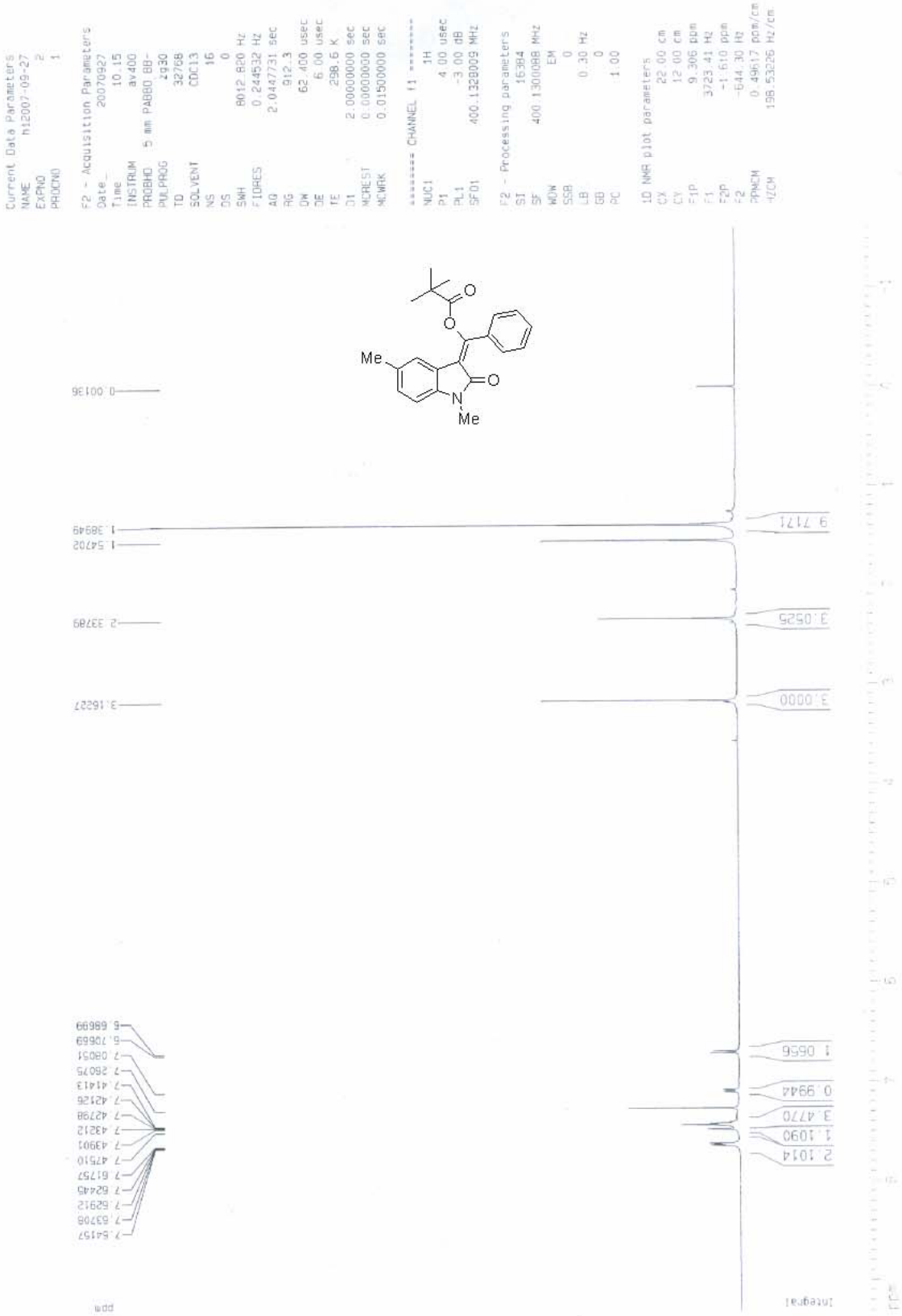
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-acetylbenzoate (30)



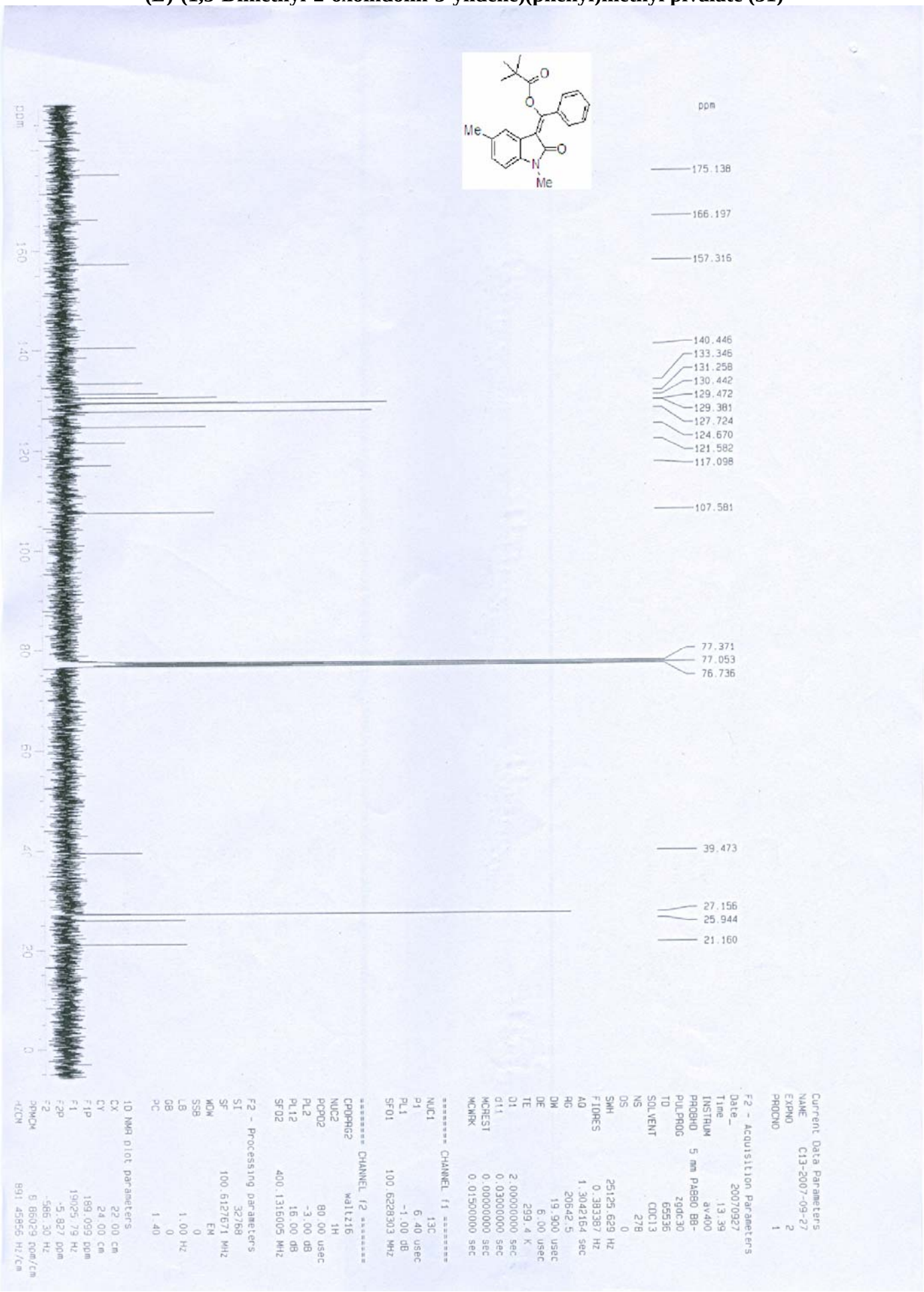
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 2-acetylbenzoate (30)



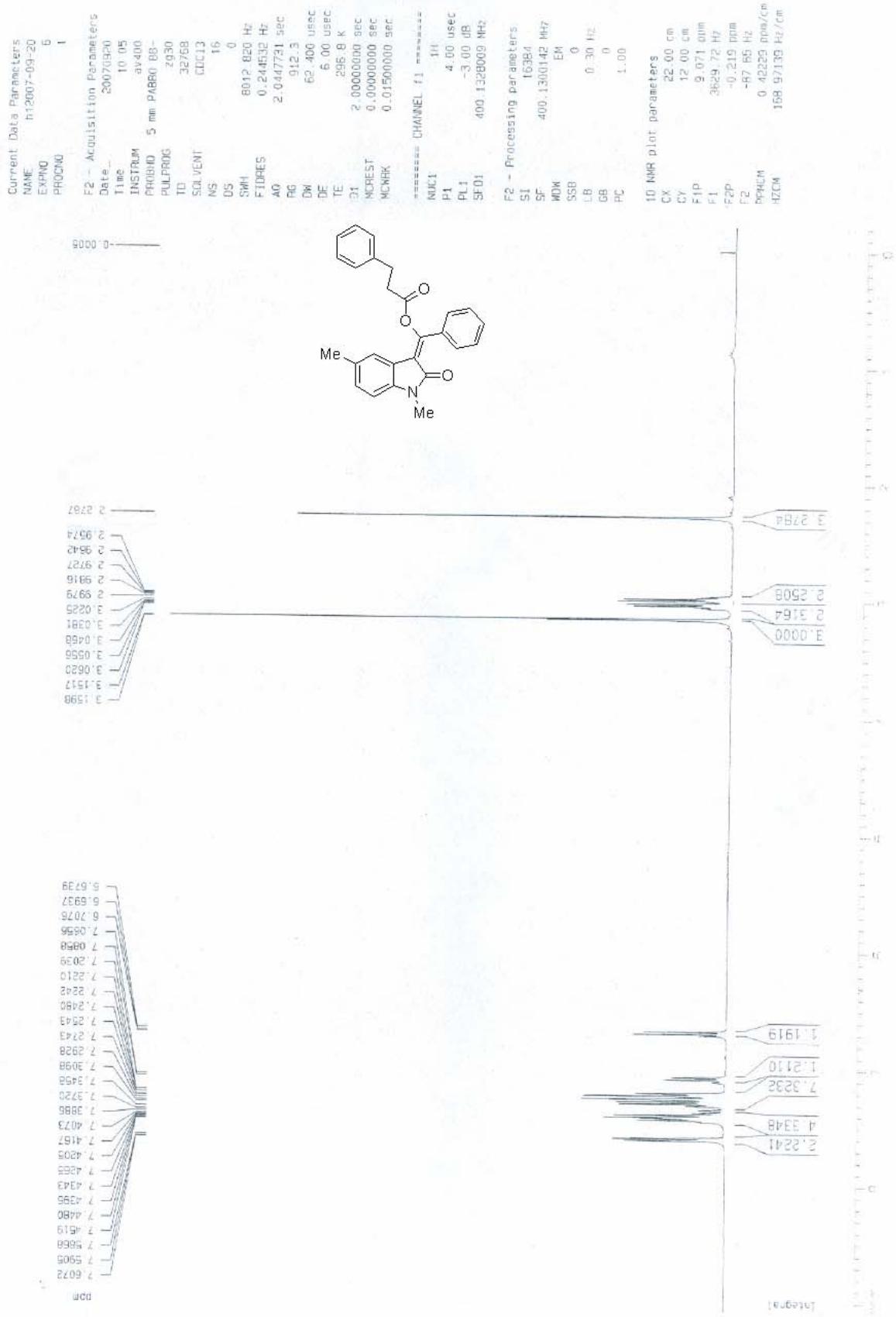
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl pivalate (31)



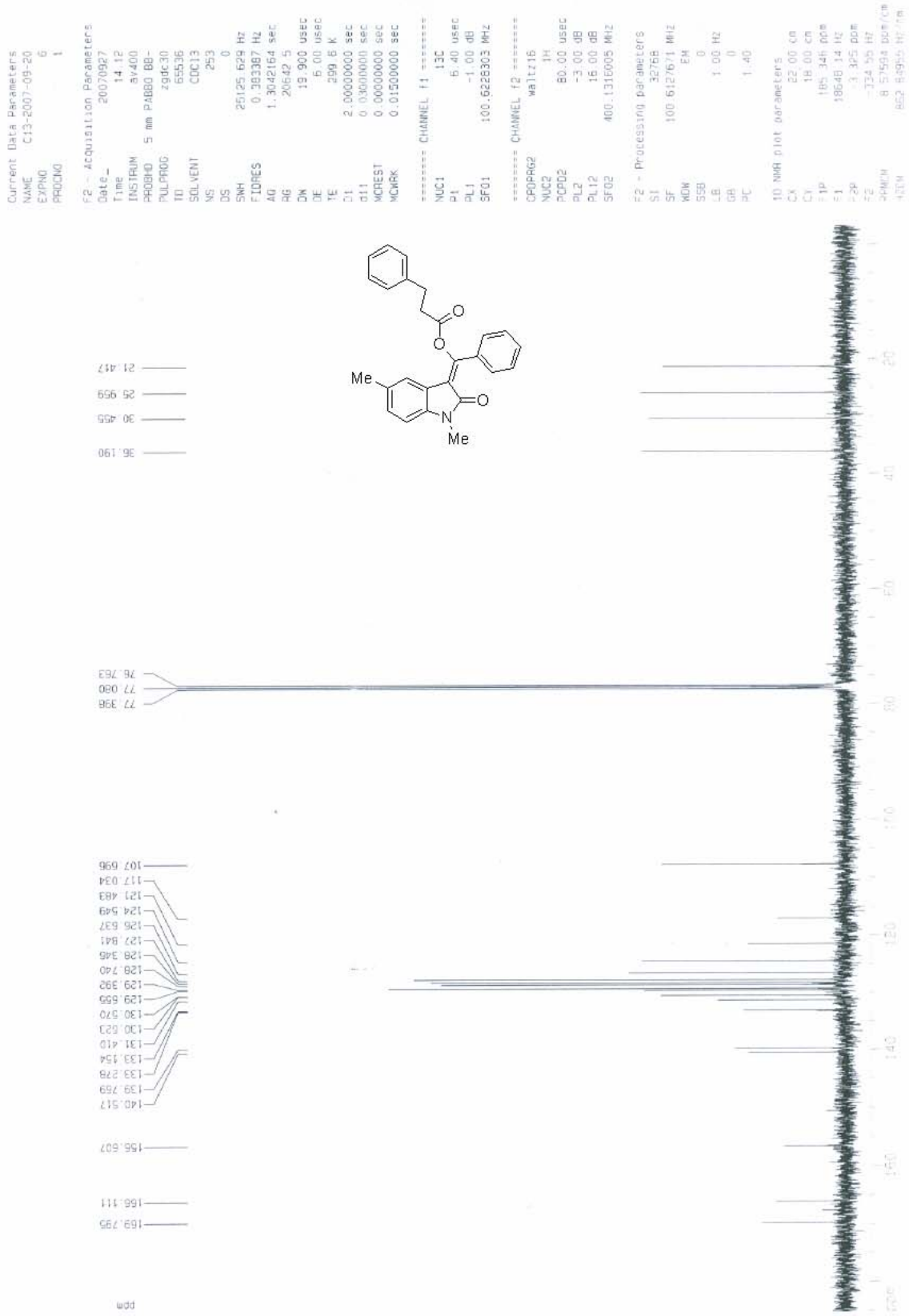
(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl pivalate (31)



(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 3-phenylpropanoate (32)



(*E*)-(1,5-Dimethyl-2-oxoindolin-3-ylidene)(phenyl)methyl 3-phenylpropanoate (32)



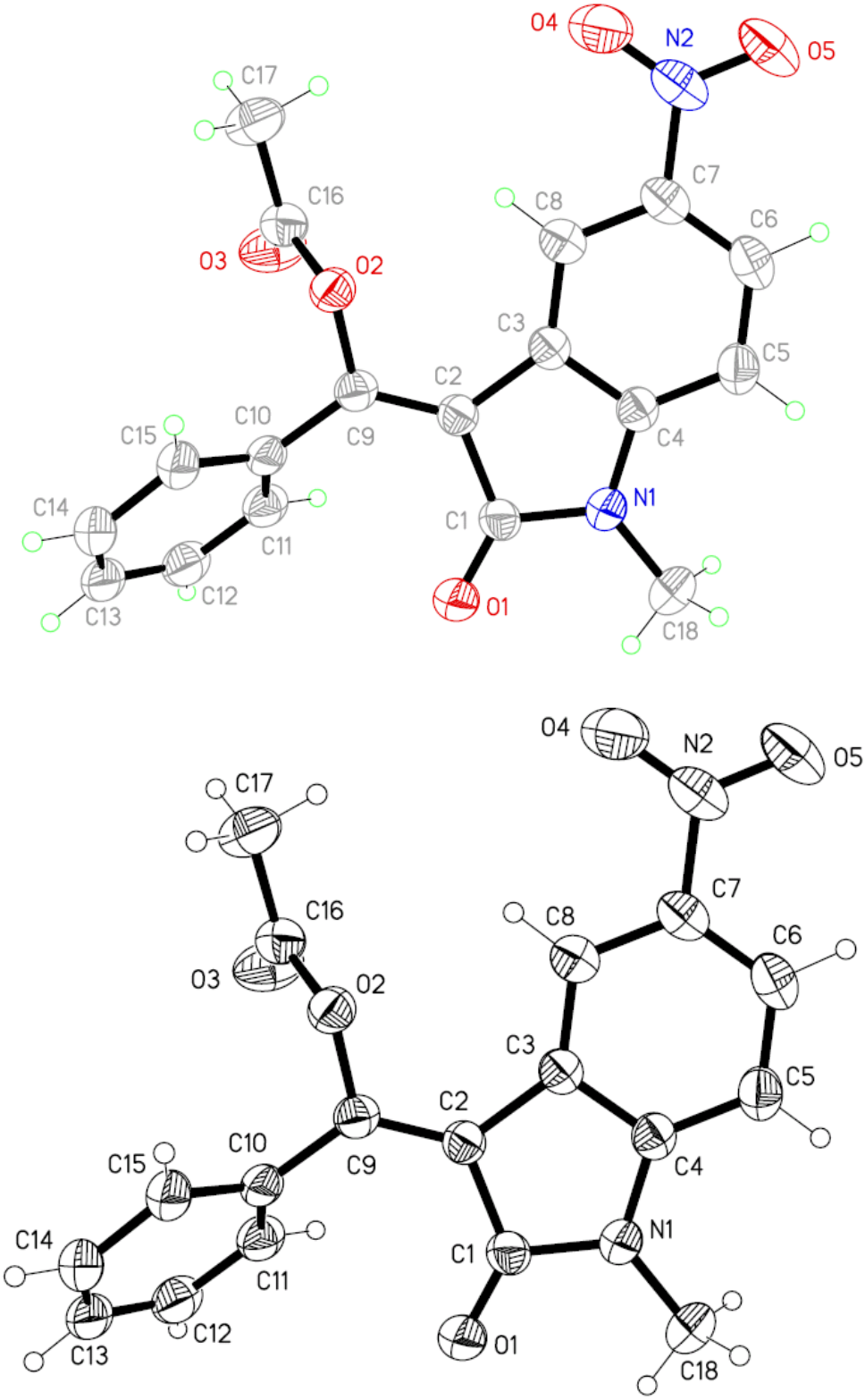


Figure S1: X-ray analysis of the products **9.**

Table 1. Crystal data and structure refinement for LJH72m.

Identification code	ljh72m
Empirical formula	C18 H14 N2 O5
Formula weight	338.31
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 13.7516(12) A alpha = 90 deg. b = 7.3164(7) A beta = 92.782(2) deg. c = 16.1177(15) A gamma = 90 deg.
Volume	1619.7(3) A^3
Z, Calculated density	4, 1.387 Mg/m^3
Absorption coefficient	0.103 mm^-1
F(000)	704
Crystal size	0.37 x 0.20 x 0.18 mm
Theta range for data collection	1.90 to 25.02 deg.
Limiting indices	-16<=h<=14, -8<=k<=8, -19<=l<=14
Reflections collected / unique	8179 / 2861 [R(int) = 0.0219]
Completeness to theta = 25.02	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9787 and 0.9629
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2861 / 0 / 228
Goodness-of-fit on F^2	1.157
Final R indices [I>2sigma(I)]	R1 = 0.0608, wR2 = 0.1359
R indices (all data)	R1 = 0.0775, wR2 = 0.1441
Largest diff. peak and hole	0.193 and -0.153 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for LJH72m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	6607(1)	3117(3)	-1115(1)	72(1)
O(2)	8261(1)	1005(2)	1107(1)	58(1)
O(3)	7968(2)	3167(3)	2042(1)	96(1)
O(4)	11613(2)	1727(4)	973(2)	97(1)
O(5)	12435(1)	2930(3)	11(2)	101(1)
N(1)	8170(1)	3643(3)	-1474(1)	57(1)
N(2)	11667(2)	2438(3)	290(2)	73(1)
C(1)	7472(2)	3086(3)	-938(2)	54(1)
C(2)	8017(2)	2458(3)	-163(1)	50(1)
C(3)	9048(2)	2651(3)	-330(1)	49(1)
C(4)	9101(2)	3386(3)	-1127(2)	52(1)
C(5)	9981(2)	3782(4)	-1473(2)	65(1)
C(6)	10823(2)	3446(4)	-998(2)	66(1)
C(7)	10772(2)	2744(3)	-213(2)	57(1)
C(8)	9898(2)	2307(3)	133(2)	53(1)
C(9)	7615(2)	1822(3)	521(1)	52(1)
C(10)	6583(2)	1728(4)	708(1)	55(1)
C(11)	5988(2)	3246(4)	617(2)	66(1)
C(12)	5017(2)	3119(5)	779(2)	81(1)
C(13)	4634(2)	1468(6)	1010(2)	89(1)
C(14)	5218(2)	-35(5)	1117(2)	82(1)
C(15)	6195(2)	93(4)	983(2)	66(1)
C(16)	8349(2)	1764(4)	1881(2)	64(1)
C(17)	8994(2)	648(5)	2444(2)	86(1)
C(18)	7925(2)	4455(5)	-2277(2)	80(1)

Table 3. Bond lengths [A] and angles [deg] for LJH72m.

O(1)-C(1)	1.209(3)
O(2)-C(16)	1.366(3)
O(2)-C(9)	1.398(3)
O(3)-C(16)	1.186(3)
O(4)-N(2)	1.224(3)
O(5)-N(2)	1.223(3)
N(1)-C(1)	1.384(3)
N(1)-C(4)	1.384(3)
N(1)-C(18)	1.448(3)
N(2)-C(7)	1.457(3)
C(1)-C(2)	1.498(3)
C(2)-C(9)	1.341(3)
C(2)-C(3)	1.462(3)
C(3)-C(8)	1.379(3)
C(3)-C(4)	1.398(3)
C(4)-C(5)	1.387(3)
C(5)-C(6)	1.379(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.370(4)
C(6)-H(6)	0.9300
C(7)-C(8)	1.386(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.466(3)
C(10)-C(11)	1.383(3)
C(10)-C(15)	1.391(4)
C(11)-C(12)	1.376(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.377(5)
C(12)-H(12)	0.9300
C(13)-C(14)	1.368(5)
C(13)-H(13)	0.9300
C(14)-C(15)	1.374(4)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.482(4)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(16)-O(2)-C(9)	117.96(19)
C(1)-N(1)-C(4)	111.3(2)
C(1)-N(1)-C(18)	122.7(2)
C(4)-N(1)-C(18)	125.9(2)
O(5)-N(2)-O(4)	123.1(3)
O(5)-N(2)-C(7)	118.2(3)
O(4)-N(2)-C(7)	118.7(2)
O(1)-C(1)-N(1)	123.4(2)
O(1)-C(1)-C(2)	130.5(2)
N(1)-C(1)-C(2)	106.0(2)
C(9)-C(2)-C(3)	128.8(2)
C(9)-C(2)-C(1)	125.6(2)
C(3)-C(2)-C(1)	105.55(19)
C(8)-C(3)-C(4)	119.1(2)
C(8)-C(3)-C(2)	133.4(2)
C(4)-C(3)-C(2)	107.5(2)
N(1)-C(4)-C(5)	128.1(2)
N(1)-C(4)-C(3)	109.6(2)
C(5)-C(4)-C(3)	122.3(2)

C(6)-C(5)-C(4)	117.8(3)
C(6)-C(5)-H(5)	121.1
C(4)-C(5)-H(5)	121.1
C(7)-C(6)-C(5)	119.9(2)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(6)-C(7)-C(8)	122.9(2)
C(6)-C(7)-N(2)	119.4(2)
C(8)-C(7)-N(2)	117.7(3)
C(3)-C(8)-C(7)	118.0(2)
C(3)-C(8)-H(8)	121.0
C(7)-C(8)-H(8)	121.0
C(2)-C(9)-O(2)	115.5(2)
C(2)-C(9)-C(10)	128.8(2)
O(2)-C(9)-C(10)	115.5(2)
C(11)-C(10)-C(15)	119.4(2)
C(11)-C(10)-C(9)	121.0(2)
C(15)-C(10)-C(9)	119.7(2)
C(12)-C(11)-C(10)	120.0(3)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	119.9(3)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.6(3)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	119.9(3)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-C(10)	120.1(3)
C(14)-C(15)-H(15)	119.9
C(10)-C(15)-H(15)	119.9
O(3)-C(16)-O(2)	122.1(3)
O(3)-C(16)-C(17)	126.9(3)
O(2)-C(16)-C(17)	111.0(3)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(1)-C(18)-H(18A)	109.5
N(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for LJH72m.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	54(1)	104(2)	58(1)	1(1)	0(1)	3(1)
O(2)	55(1)	67(1)	53(1)	3(1)	4(1)	9(1)
O(3)	110(2)	96(2)	79(2)	-24(1)	-22(1)	27(1)
O(4)	73(2)	119(2)	96(2)	-1(2)	-16(1)	8(1)
O(5)	47(1)	118(2)	138(2)	-17(2)	5(1)	-7(1)
N(1)	56(1)	70(1)	46(1)	-1(1)	5(1)	1(1)
N(2)	49(1)	70(2)	98(2)	-23(2)	-1(1)	2(1)
C(1)	46(2)	64(2)	51(1)	-7(1)	4(1)	3(1)
C(2)	48(1)	55(1)	47(1)	-5(1)	4(1)	-1(1)
C(3)	49(1)	46(1)	50(1)	-9(1)	6(1)	0(1)
C(4)	55(2)	51(1)	52(1)	-10(1)	7(1)	-1(1)
C(5)	66(2)	69(2)	60(2)	-6(1)	16(1)	-7(1)
C(6)	53(2)	67(2)	81(2)	-18(2)	18(1)	-9(1)
C(7)	48(1)	50(1)	74(2)	-18(1)	2(1)	-1(1)
C(8)	52(1)	46(1)	61(2)	-8(1)	3(1)	4(1)
C(9)	52(1)	56(1)	47(1)	-3(1)	2(1)	7(1)
C(10)	51(1)	75(2)	38(1)	-2(1)	5(1)	4(1)
C(11)	61(2)	86(2)	51(2)	-1(1)	5(1)	16(1)
C(12)	60(2)	131(3)	54(2)	4(2)	9(1)	29(2)
C(13)	48(2)	172(4)	47(2)	12(2)	10(1)	3(2)
C(14)	62(2)	126(3)	59(2)	15(2)	10(1)	-15(2)
C(15)	59(2)	86(2)	54(2)	8(1)	10(1)	0(1)
C(16)	60(2)	71(2)	60(2)	-1(1)	-2(1)	-2(1)
C(17)	95(2)	92(2)	70(2)	12(2)	-17(2)	4(2)
C(18)	85(2)	104(2)	51(2)	10(2)	2(1)	-1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for LJH72m.

	x	y	z	U(eq)
H(5)	10002	4258	-2006	77
H(6)	11426	3697	-1210	80
H(8)	9886	1798	661	64
H(11)	6244	4353	446	79
H(12)	4621	4147	732	98
H(13)	3971	1375	1095	107
H(14)	4955	-1142	1280	98
H(15)	6598	-915	1076	79
H(17A)	9047	1210	2982	130
H(17B)	9628	566	2222	130
H(17C)	8725	-557	2491	130
H(18A)	8269	5589	-2325	120
H(18B)	7237	4677	-2329	120
H(18C)	8108	3636	-2708	120

Table 6. Torsion angles [deg] for LJH72m.

C(4)-N(1)-C(1)-O(1)	-177.3(2)
C(18)-N(1)-C(1)-O(1)	5.1(4)
C(4)-N(1)-C(1)-C(2)	1.6(3)
C(18)-N(1)-C(1)-C(2)	-176.0(2)
O(1)-C(1)-C(2)-C(9)	-1.9(4)
N(1)-C(1)-C(2)-C(9)	179.3(2)
O(1)-C(1)-C(2)-C(3)	176.8(3)
N(1)-C(1)-C(2)-C(3)	-2.0(2)
C(9)-C(2)-C(3)-C(8)	-1.5(4)
C(1)-C(2)-C(3)-C(8)	179.8(2)
C(9)-C(2)-C(3)-C(4)	-179.7(2)
C(1)-C(2)-C(3)-C(4)	1.7(2)
C(1)-N(1)-C(4)-C(5)	-179.8(2)
C(18)-N(1)-C(4)-C(5)	-2.3(4)
C(1)-N(1)-C(4)-C(3)	-0.6(3)
C(18)-N(1)-C(4)-C(3)	176.9(2)
C(8)-C(3)-C(4)-N(1)	-179.2(2)
C(2)-C(3)-C(4)-N(1)	-0.7(3)
C(8)-C(3)-C(4)-C(5)	0.0(3)
C(2)-C(3)-C(4)-C(5)	178.5(2)
N(1)-C(4)-C(5)-C(6)	178.4(2)
C(3)-C(4)-C(5)-C(6)	-0.7(4)
C(4)-C(5)-C(6)-C(7)	0.0(4)
C(5)-C(6)-C(7)-C(8)	1.3(4)
C(5)-C(6)-C(7)-N(2)	-178.5(2)
O(5)-N(2)-C(7)-C(6)	4.5(4)
O(4)-N(2)-C(7)-C(6)	-176.4(2)
O(5)-N(2)-C(7)-C(8)	-175.3(2)
O(4)-N(2)-C(7)-C(8)	3.7(4)
C(4)-C(3)-C(8)-C(7)	1.2(3)
C(2)-C(3)-C(8)-C(7)	-176.8(2)
C(6)-C(7)-C(8)-C(3)	-2.0(4)
N(2)-C(7)-C(8)-C(3)	177.9(2)
C(3)-C(2)-C(9)-O(2)	-9.7(4)
C(1)-C(2)-C(9)-O(2)	168.7(2)
C(3)-C(2)-C(9)-C(10)	176.0(2)
C(1)-C(2)-C(9)-C(10)	-5.6(4)
C(16)-O(2)-C(9)-C(2)	119.0(2)
C(16)-O(2)-C(9)-C(10)	-65.9(3)
C(2)-C(9)-C(10)-C(11)	-50.8(4)
O(2)-C(9)-C(10)-C(11)	134.9(2)
C(2)-C(9)-C(10)-C(15)	129.5(3)
O(2)-C(9)-C(10)-C(15)	-44.9(3)
C(15)-C(10)-C(11)-C(12)	-1.6(4)
C(9)-C(10)-C(11)-C(12)	178.7(2)
C(10)-C(11)-C(12)-C(13)	-1.7(4)
C(11)-C(12)-C(13)-C(14)	2.9(4)
C(12)-C(13)-C(14)-C(15)	-0.8(4)
C(13)-C(14)-C(15)-C(10)	-2.5(4)
C(11)-C(10)-C(15)-C(14)	3.7(4)
C(9)-C(10)-C(15)-C(14)	-176.6(2)
C(9)-O(2)-C(16)-O(3)	-7.0(4)
C(9)-O(2)-C(16)-C(17)	175.1(2)

Symmetry transformations used to generate equivalent atoms:

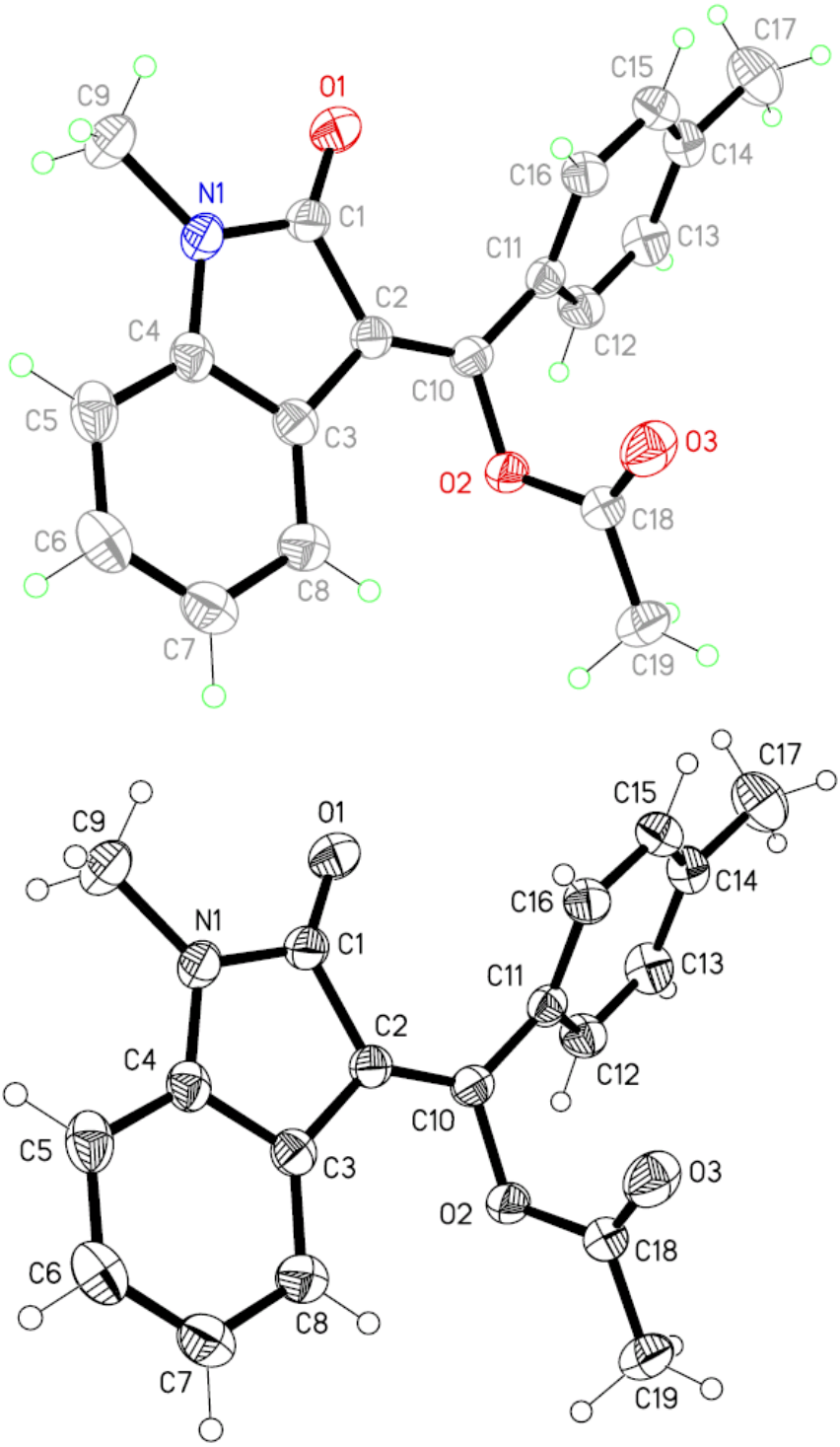


Figure S1: X-ray analysis of the products **14**

Table 1. Crystal data and structure refinement for LJH.

Identification code	ljh
Empirical formula	C19 H17 N O3
Formula weight	307.34
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 14.2881(11) A alpha = 90 deg. b = 8.7176(7) A beta = 90 deg. c = 25.912(2) A gamma = 90 deg.
Volume	3227.6(4) A^3
Z, Calculated density	8, 1.265 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	1296
Crystal size	0.33 x 0.24 x 0.17 mm
Theta range for data collection	2.12 to 25.02 deg.
Limiting indices	-17<=h<=15, -10<=k<=9, -29<=l<=30
Reflections collected / unique	15786 / 2847 [R(int) = 0.0392]
Completeness to theta = 25.02	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9856 and 0.9722
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2847 / 0 / 211
Goodness-of-fit on F^2	1.268
Final R indices [I>2sigma(I)]	R1 = 0.0770, wR2 = 0.1608
R indices (all data)	R1 = 0.0922, wR2 = 0.1674
Largest diff. peak and hole	0.282 and -0.156 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for LJH. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-348(2)	7168(2)	3656(1)	65(1)
O(2)	374(1)	2253(2)	3510(1)	46(1)
O(3)	1823(2)	2444(3)	3823(1)	68(1)
N(1)	-1008(2)	6223(3)	4393(1)	51(1)
C(1)	-498(2)	6111(3)	3949(1)	47(1)
C(2)	-208(2)	4457(3)	3908(1)	41(1)
C(3)	-600(2)	3697(3)	4362(1)	43(1)
C(4)	-1065(2)	4822(3)	4650(1)	45(1)
C(5)	-1485(2)	4502(4)	5117(1)	56(1)
C(6)	-1445(2)	3016(4)	5296(1)	61(1)
C(7)	-1010(2)	1881(4)	5017(1)	60(1)
C(8)	-585(2)	2205(3)	4549(1)	53(1)
C(9)	-1446(3)	7641(4)	4555(2)	73(1)
C(10)	293(2)	3863(3)	3521(1)	41(1)
C(11)	740(2)	4610(3)	3076(1)	41(1)
C(12)	649(2)	3980(4)	2587(1)	52(1)
C(13)	1083(2)	4641(4)	2168(1)	57(1)
C(14)	1644(2)	5920(4)	2224(1)	53(1)
C(15)	1755(2)	6530(4)	2711(1)	53(1)
C(16)	1303(2)	5891(3)	3131(1)	47(1)
C(17)	2132(3)	6613(5)	1759(1)	84(1)
C(18)	1222(2)	1671(3)	3641(1)	47(1)
C(19)	1270(3)	3(4)	3526(2)	74(1)

Table 3. Bond lengths [A] and angles [deg] for LJH.

O(1)-C(1)	1.213(3)
O(2)-C(18)	1.357(3)
O(2)-C(10)	1.409(3)
O(3)-C(18)	1.189(4)
N(1)-C(1)	1.366(4)
N(1)-C(4)	1.393(4)
N(1)-C(9)	1.448(4)
C(1)-C(2)	1.504(4)
C(2)-C(10)	1.336(4)
C(2)-C(3)	1.463(4)
C(3)-C(8)	1.388(4)
C(3)-C(4)	1.400(4)
C(4)-C(5)	1.379(4)
C(5)-C(6)	1.377(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.373(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.386(4)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.470(4)
C(11)-C(16)	1.384(4)
C(11)-C(12)	1.387(4)
C(12)-C(13)	1.376(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.381(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.380(4)
C(14)-C(17)	1.518(5)
C(15)-C(16)	1.383(4)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.486(4)
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(18)-O(2)-C(10)	116.2(2)
C(1)-N(1)-C(4)	111.8(2)
C(1)-N(1)-C(9)	122.4(3)
C(4)-N(1)-C(9)	125.8(3)
O(1)-C(1)-N(1)	124.5(3)
O(1)-C(1)-C(2)	129.5(3)
N(1)-C(1)-C(2)	106.0(2)

C(10)-C(2)-C(3)	129.3(3)
C(10)-C(2)-C(1)	124.9(3)
C(3)-C(2)-C(1)	105.8(2)
C(8)-C(3)-C(4)	118.6(3)
C(8)-C(3)-C(2)	134.4(3)
C(4)-C(3)-C(2)	107.0(2)
C(5)-C(4)-N(1)	128.5(3)
C(5)-C(4)-C(3)	122.2(3)
N(1)-C(4)-C(3)	109.4(2)
C(6)-C(5)-C(4)	117.8(3)
C(6)-C(5)-H(5)	121.1
C(4)-C(5)-H(5)	121.1
C(7)-C(6)-C(5)	121.3(3)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(6)-C(7)-C(8)	120.8(3)
C(6)-C(7)-H(7)	119.6
C(8)-C(7)-H(7)	119.6
C(7)-C(8)-C(3)	119.3(3)
C(7)-C(8)-H(8)	120.3
C(3)-C(8)-H(8)	120.3
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(2)-C(10)-O(2)	116.5(2)
C(2)-C(10)-C(11)	130.5(3)
O(2)-C(10)-C(11)	112.9(2)
C(16)-C(11)-C(12)	118.0(3)
C(16)-C(11)-C(10)	121.9(3)
C(12)-C(11)-C(10)	120.0(3)
C(13)-C(12)-C(11)	120.8(3)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(12)-C(13)-C(14)	121.2(3)
C(12)-C(13)-H(13)	119.4
C(14)-C(13)-H(13)	119.4
C(15)-C(14)-C(13)	118.3(3)
C(15)-C(14)-C(17)	121.4(3)
C(13)-C(14)-C(17)	120.4(3)
C(14)-C(15)-C(16)	120.8(3)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	121.0(3)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

O(3)-C(18)-O(2)	122.2(3)
O(3)-C(18)-C(19)	126.9(3)
O(2)-C(18)-C(19)	110.9(3)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for LJH.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	66(2)	47(1)	84(2)	14(1)	10(1)	12(1)
O(2)	41(1)	37(1)	60(1)	-3(1)	-1(1)	-2(1)
O(3)	53(1)	58(1)	94(2)	-7(1)	-23(1)	6(1)
N(1)	42(1)	44(1)	67(2)	-10(1)	7(1)	3(1)
C(1)	38(2)	41(2)	62(2)	2(2)	-2(1)	1(1)
C(2)	36(2)	39(2)	46(2)	1(1)	-3(1)	0(1)
C(3)	36(2)	46(2)	49(2)	-3(1)	-5(1)	-4(1)
C(4)	33(2)	51(2)	50(2)	-8(1)	-2(1)	-5(1)
C(5)	41(2)	70(2)	56(2)	-16(2)	3(2)	-6(2)
C(6)	54(2)	81(3)	47(2)	4(2)	2(2)	-14(2)
C(7)	60(2)	61(2)	59(2)	12(2)	1(2)	-8(2)
C(8)	57(2)	49(2)	54(2)	4(2)	2(2)	0(2)
C(9)	65(2)	53(2)	100(3)	-15(2)	14(2)	11(2)
C(10)	36(2)	37(2)	50(2)	-3(1)	-7(1)	0(1)
C(11)	37(2)	40(2)	45(2)	-1(1)	-3(1)	5(1)
C(12)	52(2)	50(2)	53(2)	-7(2)	-4(2)	-7(2)
C(13)	61(2)	70(2)	41(2)	-9(2)	-3(2)	-3(2)
C(14)	46(2)	61(2)	52(2)	4(2)	1(1)	0(2)
C(15)	51(2)	50(2)	60(2)	0(2)	1(2)	-8(2)
C(16)	48(2)	47(2)	46(2)	-7(1)	-3(1)	-4(1)
C(17)	84(3)	105(3)	62(2)	13(2)	10(2)	-15(2)
C(18)	44(2)	43(2)	53(2)	4(1)	3(1)	2(1)
C(19)	68(2)	41(2)	114(3)	2(2)	6(2)	8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for LJH.

	x	y	z	U(eq)
H(5)	-1785	5266	5306	67
H(6)	-1718	2775	5611	73
H(7)	-1001	883	5144	72
H(8)	-293	1431	4362	64
H(9A)	-1222	8469	4345	109
H(9B)	-1294	7840	4910	109
H(9C)	-2113	7554	4519	109
H(12)	291	3100	2541	62
H(13)	996	4219	1842	69
H(15)	2139	7380	2758	64
H(16)	1378	6330	3456	57
H(17A)	2054	5950	1466	126
H(17B)	2787	6730	1832	126
H(17C)	1865	7599	1684	126
H(19A)	1841	-412	3663	112
H(19B)	1255	-150	3159	112
H(19C)	746	-508	3681	112

Table 6. Torsion angles [deg] for LJH.

C(4)-N(1)-C(1)-O(1)	179.8(3)
C(9)-N(1)-C(1)-O(1)	1.5(5)
C(4)-N(1)-C(1)-C(2)	1.0(3)
C(9)-N(1)-C(1)-C(2)	-177.2(3)
O(1)-C(1)-C(2)-C(10)	0.3(5)
N(1)-C(1)-C(2)-C(10)	178.9(3)
O(1)-C(1)-C(2)-C(3)	-178.7(3)
N(1)-C(1)-C(2)-C(3)	0.0(3)
C(10)-C(2)-C(3)-C(8)	1.2(5)
C(1)-C(2)-C(3)-C(8)	-179.9(3)
C(10)-C(2)-C(3)-C(4)	-179.9(3)
C(1)-C(2)-C(3)-C(4)	-1.0(3)
C(1)-N(1)-C(4)-C(5)	177.1(3)
C(9)-N(1)-C(4)-C(5)	-4.6(5)
C(1)-N(1)-C(4)-C(3)	-1.8(3)
C(9)-N(1)-C(4)-C(3)	176.5(3)
C(8)-C(3)-C(4)-C(5)	1.8(4)
C(2)-C(3)-C(4)-C(5)	-177.3(3)
C(8)-C(3)-C(4)-N(1)	-179.2(3)
C(2)-C(3)-C(4)-N(1)	1.7(3)
N(1)-C(4)-C(5)-C(6)	-179.5(3)
C(3)-C(4)-C(5)-C(6)	-0.8(4)
C(4)-C(5)-C(6)-C(7)	-0.6(5)
C(5)-C(6)-C(7)-C(8)	0.9(5)
C(6)-C(7)-C(8)-C(3)	0.1(5)
C(4)-C(3)-C(8)-C(7)	-1.4(4)
C(2)-C(3)-C(8)-C(7)	177.4(3)
C(3)-C(2)-C(10)-O(2)	8.0(4)
C(1)-C(2)-C(10)-O(2)	-170.6(2)
C(3)-C(2)-C(10)-C(11)	-176.0(3)
C(1)-C(2)-C(10)-C(11)	5.3(5)
C(18)-O(2)-C(10)-C(2)	-107.2(3)
C(18)-O(2)-C(10)-C(11)	76.1(3)
C(2)-C(10)-C(11)-C(16)	49.0(4)
O(2)-C(10)-C(11)-C(16)	-135.0(3)
C(2)-C(10)-C(11)-C(12)	-134.8(3)
O(2)-C(10)-C(11)-C(12)	41.2(4)
C(16)-C(11)-C(12)-C(13)	-2.0(4)
C(10)-C(11)-C(12)-C(13)	-178.4(3)
C(11)-C(12)-C(13)-C(14)	2.0(5)
C(12)-C(13)-C(14)-C(15)	-0.4(5)
C(12)-C(13)-C(14)-C(17)	178.7(3)
C(13)-C(14)-C(15)-C(16)	-1.1(5)
C(17)-C(14)-C(15)-C(16)	179.7(3)
C(14)-C(15)-C(16)-C(11)	1.2(5)
C(12)-C(11)-C(16)-C(15)	0.4(4)
C(10)-C(11)-C(16)-C(15)	176.7(3)
C(10)-O(2)-C(18)-O(3)	10.0(4)
C(10)-O(2)-C(18)-C(19)	-169.9(3)

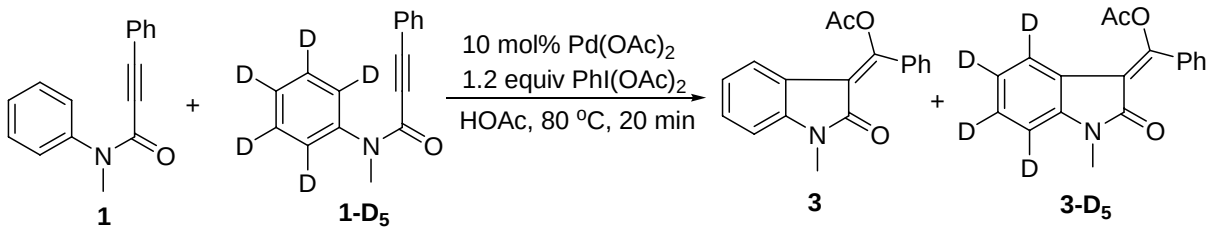
Symmetry transformations used to generate equivalent atoms:

(F) The kinetic isotope effect

To elucidate the mechanism, the kinetic isotope effect of the reaction was examined. It was found that an intermolecular K_H/K_D value of competitive experiment of **2e** and **2e-D$_5$** was 1 (Figure S3). The results showed that the C-H functionalization is not the rate-determining step (from **C** to product in Scheme 2 of the text).[2] Subsequently, the reaction of **2e-D$_1$** was also conducted, and it provided an intramolecular isotope effect of 3.2 (Figure S4). The results indicated that the mechanism of C-H activation was not compatible with the S_EAr mechanism.[3]

(2) (a) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927. (b) Pinto, A.; Neuville, L.; Zhu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 3291.

(3) (a) Hennessy, E. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 12084. (b) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581.



(S1)

A mixture of aniline **1** (0.1 mmol), **1-D5** (0.1 mmol), $Pd(OAc)_2$ (10 mol%) and $PhI(OAc)_2$ (1.2 equiv) in HOAc (**2a**; 3 mL) was stirred at 80 ^oC for about 20 min. After the reaction was cooled,, the mixture was poured into ethyl acetate, which was washed with brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude material was determined by GC-MS analysis and ^1H NMR (500 MHZ) (Figure S3).

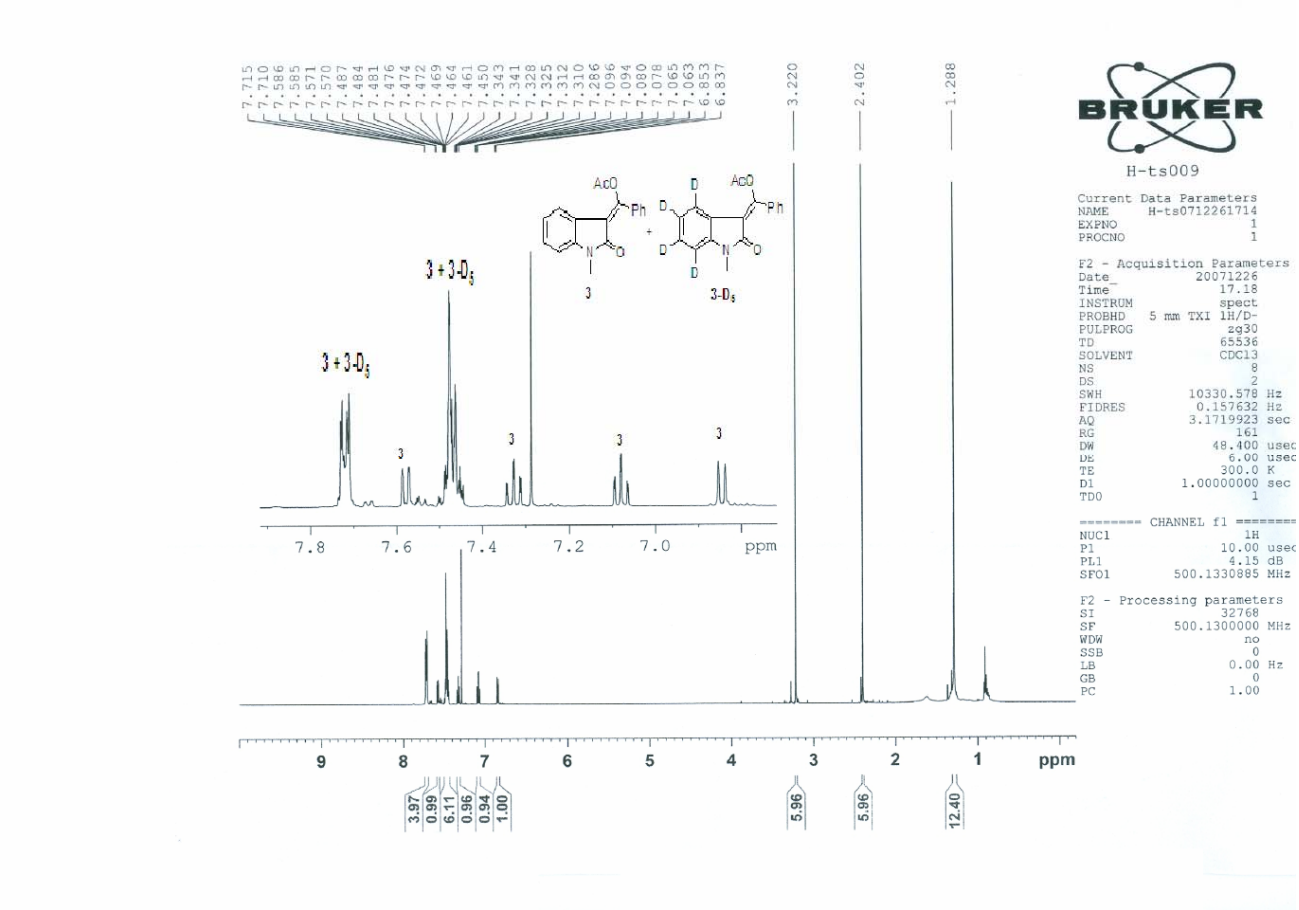
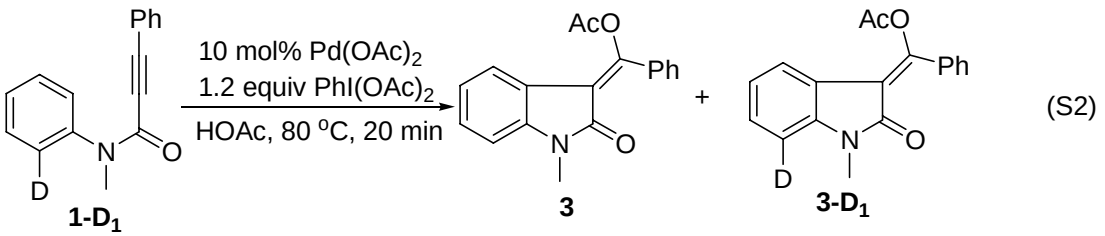
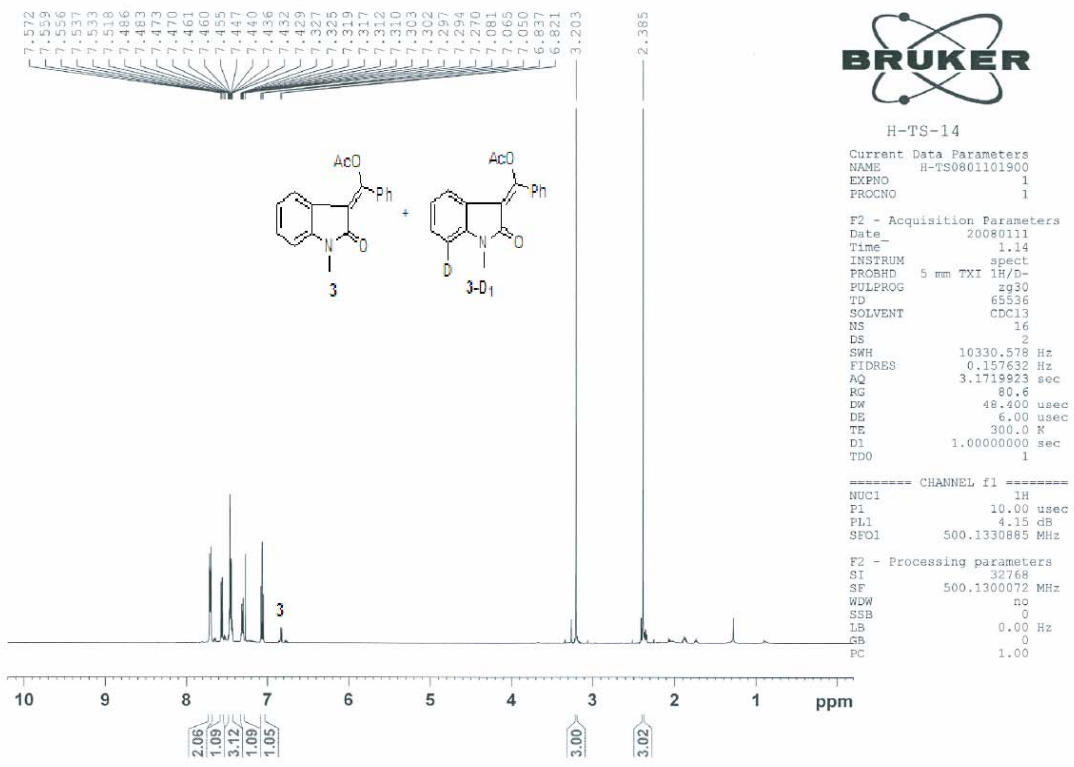


Figure S3. The intermolecular competition experiment between amides **1** and **1-D$_5$**.



(S2)

A mixture of aniline **1-D$_1$** (0.2 mmol), $Pd(OAc)_2$ (10 mol%) and $PhI(OAc)_2$ (1.2 equiv or 2 equiv) in HOAc (**2a**; 3 mL) was stirred at 80 ^{o}C for 2 h as monitored by TLC. After the reaction was finished, the mixture was poured into ethyl acetate, which was washed with brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product.



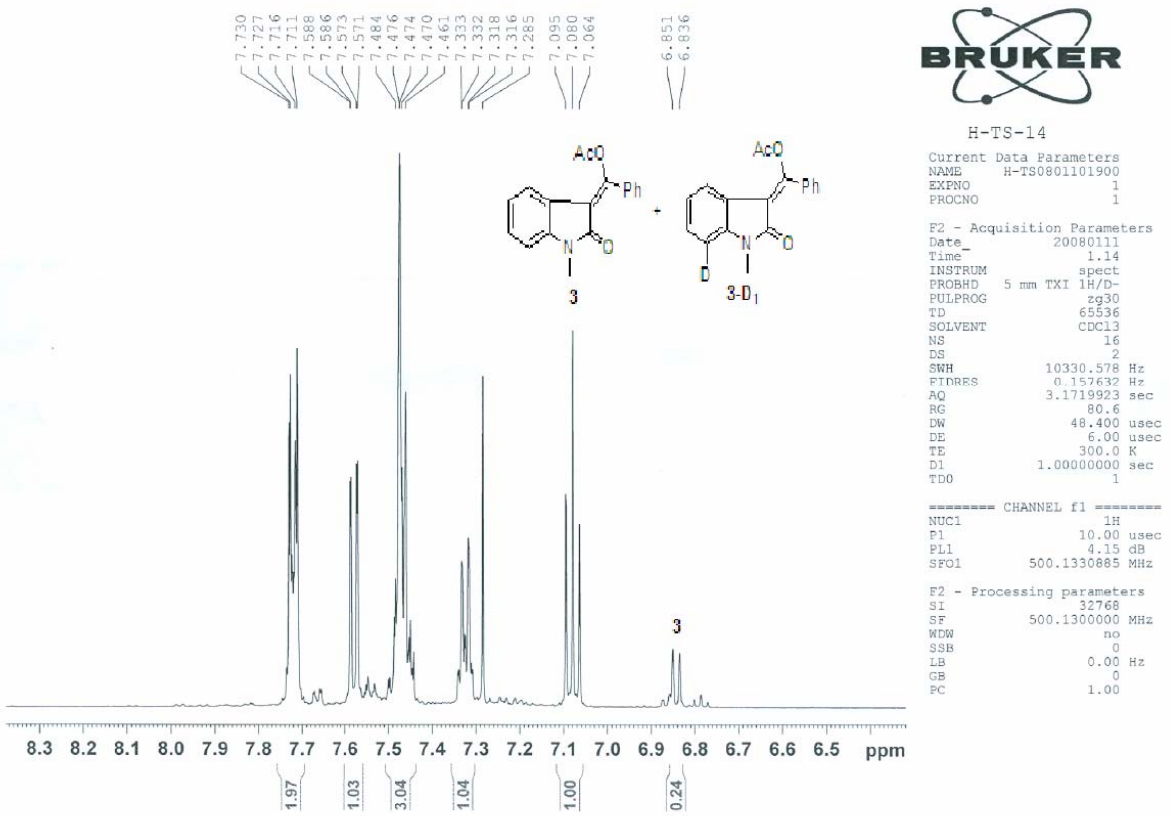


Figure S4. Aromatic region of the precuts **3** and **3-D$_1$**