Palladium-Catalyzed Intramolecular *5-exo-dig* Hydroarylations of *N*-Arylpropiolamides: Thermodynamics-Controlled Stereoselective Synthesis of 3-Methyleneoxindoles

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Supporting Information

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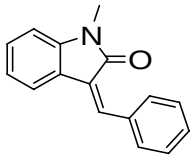
(A) Typical experimental procedure

Typical Experimental Procedure for Palladium-Catalyzed Intramolecular Hydroarylation of N-Arylpropiolamides (1):

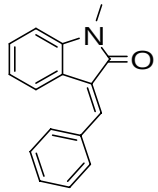
To a flame-dried Schlenk tube was charged with *N*-arylpropiolamides **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), dppf (10 mol %) and toluene (1 mL). The mixture was stirred at the indicated temperature (80 °C or 140°C) for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered by a crude column with ethyl acetate as eluent, and evaporated in vacuum. The residue was purified by flash column chromatography on a silica gel using EtOAc/petroleum ether (1:15) as eluant to give the product **2**.

(B) Analytical data for (*Z*)-2 and (*E*)-2



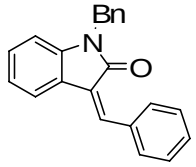
(*Z*)-3-Benzylidene-1-methylindolin-2-one (2a)[1,2]

Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 7.8 Hz, 2H), 7.52 (s, 1H), 7.50-7.40 (m, 4H), 7.30-7.25 (m, 1H), 7.07-7.02 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1, 142.3, 137.0, 133.8, 131.9, 130.4, 128.8, 128.2, 126.3, 124.3, 121.8, 118.9, 107.8, 25.9; LRMS (EI, 70 eV) *m/z* (%): 235 (M^+, 100), 234 (82), 206 (18), 158 (51).



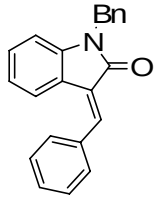
(*E*)-3-Benzylidene-1-methylindolin-2-one (2a)[1,2]

Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.86 (s, 1H), 7.65-7.61 (m, 3H), 7.49-7.41 (m, 3H), 7.29-7.24 (m, 1H), 6.90-6.81 (m, 2H), 3.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.5, 144.2, 137.1, 134.9, 129.7, 129.5, 129.2, 128.6, 127.2, 122.7, 121.7, 121.1, 108.1, 26.1; LRMS (EI, 70 eV) *m/z* (%): 235 (M^+, 100), 234 (81), 206 (18), 158 (50).



(*Z*)-1-Benzyl-3-benzylideneindolin-2-one (2b)[1,2]

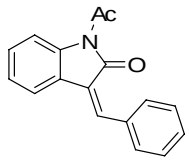
Yellow solid; ^{1}HNMR (300MHz, $CDCl_3$) δ: 8.34 (d, *J* = 7.2 Hz, 2H), 7.61 (s, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.49-7.46 (m, 3H), 7.35-7.27 (m, 6H), 7.08-7.05 (m, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.01 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1, 141.5, 137.5, 136.2, 133.8, 132.0, 130.6, 128.8, 128.7, 128.3, 127.5, 127.4, 125.9, 124.4, 121.9, 119.0, 108.8, 43.6; LRMS (EI, 70 eV) *m/z* (%): 311 (M^+, 38), 165 (20), 91 (100).



(*E*)-1-Benzyl-3-benzylideneindolin-2-one (2b)[1,2]

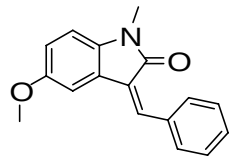
Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.70-7.65 (m, 3H),

7.52-7.47 (m, 3H), 7.38-7.34 (m, 5H), 7.19-7.14 (m, 1H), 6.89-6.86 (m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 5.02 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 143.3, 137.6, 136.0, 134.9, 132.0, 129.7, 129.6, 129.3, 128.8, 128.7, 127.6, 127.4, 127.1, 122.8, 121.9, 121.3, 109.2, 43.8; LRMS (EI, 70 eV) *m/z* (%): 311 (M^+, 38), 165 (18), 91 (100).



(*Z*)-1-Acetyl-3-benzylideneindolin-2-one (2c)

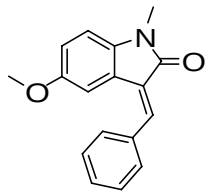
Yellow solid (mp 104.1-106.3 ^{o}C); IR (KBr, cm^{-1}): 2915, 1684, 1595, 1449, 1114; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.32 (d, J = 8.2 Hz, 1H), 7.90 (s, 1H), 7.73-7.65 (m, 3H), 7.51-7.47 (m, 3H), 7.36-7.27 (m, 1H), 7.05-7.03 (m, 1H), 2.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.9, 168.6, 140.2, 138.7, 134.4, 131.8, 130.3, 130.1, 129.2, 128.8, 128.4, 124.5, 122.1, 116.7, 26.9; LRMS (EI, 70 eV) *m/z* (%): 263 (M^+, 32), 221 (100), 220 (67), 144 (39); HRMS (ESI) $C_{17}H_{13}NO_2Na[M+Na]^+$: Caled. 286.0843, Found 286.0840.



(*Z*)-3-Benzylidene-5-methoxy-1-methylindolin-2-one (2e)[1]

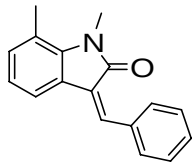
Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.30 (d, J = 6.1 Hz, 2H), 7.49 (s, 1H), 7.46-7.43 (m, 3H), 7.12 (s, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 8.4 Hz,1H), 3.85 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.0, 155.6, 137.1, 136.4, 133.7, 131.9, 130.5, 128.2, 126.4, 125.3, 113.9, 108.2, 105.8, 55.9, 25.9; LRMS (EI,

70 eV) *m/z* (%): 265 (M^+, 100), 222 (19), 142 (26), 131 (30).



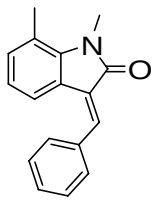
(*E*)-3-Benzylidene-5-methoxy-1-methylindolin-2-one (2e)[1]

Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.48-7.43 (m, 3H), 7.22 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3, 155.1, 138.2, 137.4, 134.8, 129.6, 129.2, 128.6, 127.6, 121.9, 114.4, 109.9, 108.3, 55.7, 26.2; LRMS (EI, 70 eV) *m/z* (%): 265 (M^+, 100), 222 (21), 142 (25), 131 (32).



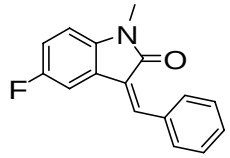
(*Z*)-3-Benzylidene-1,7-dimethylindolin-2-one (2f)

Yellow solid (mp 92.1-94.5 ^{o}C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.30-8.27 (m, 2H), 7.52 (s, 1H), 7.46-7.39 (m, 4H), 7.01-6.94 (m, 2H), 3.56 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.7, 140.2, 136.6, 133.9, 132.6, 131.9, 130.3, 128.2, 125.9, 124.8, 121.7, 119.5, 116.9, 29.1, 18.9; IR (KBr, cm^{-1}): 2925, 1690, 1595, 1451, 1116; LRMS (EI, 70 eV) *m/z* (%): 249 (M^+, 100), 248 (73), 172 (33), 124 (48). HRMS (ESI) $C_{17}H_{15}NONa[M+Na]^+$: Caled. 272.1051, Found 272.1046.



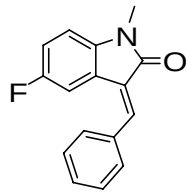
(*E*)-3-Benzylidene-1, 7-dimethylindolin-2-one (2f)

Light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.63-7.60 (m, 2H), 7.49-7.42 (m, 4H), 6.99 (d, *J* =7.7 Hz, 1H), 6.74 (m, 1H), 3.56 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 142.1, 136.9, 135.1, 133.6, 129.3, 129.2, 128.6, 127.1, 121.7, 121.6, 120.8, 119.8, 29.7, 19.3; IR (KBr, cm^{-1}): 2925, 1700, 1448, 1360, 1127; LRMS (EI, 70 eV) *m/z* (%): 249 (M^+, 100), 248 (73), 172 (32), 124 (26); HRMS(ESI) $C_{17}H_{15}NONa[M+Na]^+$: Caled. 272.1051, Found 272.1046.



(*Z*)-3-Benzylidene-5-fluoro-1-methylindolin-2-one (2g)

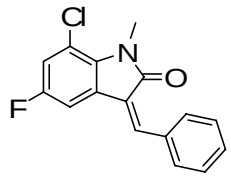
Light-yellow solid (mp 98.8-100.2 ^{o}C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.32-8.29 (m, 2H), 7.48-7.44 (m, 4H), 7.21 (m, 1H), 7.6.98-6.97 (m, 1H), 6.72-6.68 (m, 1H), 3.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.9, 159.0 (d, *J* = 237.5 Hz, 1C), 138.3, 133.4, 132.2, 130.9, 128.3, 125.7, 114.9 (d, *J* = 23.8 Hz, 1C), 108.3, 108.2, 106.8, 106.5, 26.0; IR (KBr, cm^{-1}): 2922, 1699, 1486, 1271; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 100), 252 (70), 224 (15), 176 (52); HRMS (ESI) $C_{16}H_{12}FNONa[M+Na]^+$: Caled. 276.0801, Found 276.0795.



(*E*)-3-Benzylidene-5-fluoro-1-methylindolin-2-one (2g)

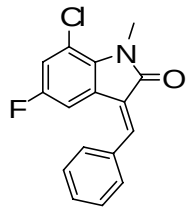
Yellow solid (mp 102.4.-106.2 ^{o}C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 (s, 1H), 7.63-7.60 (m, 2H), 7.52-7.46 (m, 3H), 7.36-7.32 (m, 1H), 6.98-6.94 (m, 1H), 6.75-6.71 (m, 1H), 3.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.2, 158.4 (d, *J* =

237.0 Hz, 1C), 140.3, 138.6, 134.4, 129.9, 129.2, 126.9, 122.0, 115.9 (d, J = 23.8 Hz, 1C), 110.6, 110.2, 108.4, 26.3; IR (KBr, cm^{-1}): 2924, 1706, 1479, 1285; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 100), 252 (68), 224 (16), 176 (53); HRMS (ESI) $C_{16}H_{12}FNONa[M+Na]^+$: Caled. 276.0801, Found 276.0795.



(Z)-3-Benzylidene-7-chloro-5-fluoro-1-methylindolin-2-one (2h)

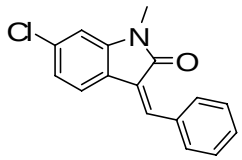
Light-yellow solid (mp 129.6-131.2 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ: 8.32-8.29 (m, 2H), 7.51(s, 1H), 7.48-7.46 (m, 3H), 7.19-7.16 (m, 1H), 6.99-6.96 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1, 157.9 (d, J = 241.3 Hz, 1C), 139.5, 133.1, 132.3, 131.3, 128.4, 127.7, 117.4, 117.0, 115.2, 105.5, 105.1, 29.7; IR (KBr, cm^{-1}): 2923, 1692, 1473, 1089; LRMS (EI, 70 eV) *m/z* (%): 287 (M^+, 100), 286 (93), 210 (45); HRMS (ESI) $C_{16}H_{11}ClFNONa[M+Na]^+$: Caled. 310.0411, Found 310.0405.



(*E*)-3-benzylidene-7-chloro-5-fluoro-1-methylindolin-2-one (2h)

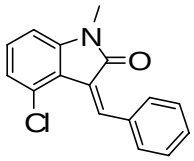
Light-yellow solid (mp 147.9-152.3 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 7.59-7.56 (m, 2H), 7.50-7.47 (m, 3H), 7.28-7.24 (m, 1H), 6.97-6.95 (m, 1H) 3.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 157.4 (d, J = 240.7 Hz), 140.1, 134.1, 130.2, 129.1, 128.9, 125.9, 124.3, 118.4, 118.1, 109.2, 108.2, 29.7; IR (KBr, cm^{-1}): 2922, 1708, 1468, 1119; LRMS (EI, 70 eV) *m/z* (%): 287 (M^+, 100), 286 (93), 210

(45); HRMS (ESI) $C_{16}H_{11}ClFNONa[M+Na]^+$: Caled. 310.0411, Found 310.0405.



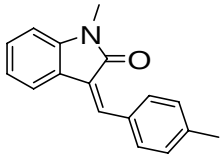
(*Z*)-3-Benzylidene-6-chloro-1-methylindolin-2-one (2i)

Light-yellow solid (mp 123.0-126.3 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ: 8.29-8.27 (m, 2H), 7.51(s, 1H), 7.46-7.42 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.81 (m, 1H), 3.26 (s, 3H); $^{13}CNMR$ (75 MHz, $CDCl_3$) δ: 166.0, 143.2, 137.7, 134.5, 133.6, 132.0, 130.7, 129.3, 128.7, 128.3, 125.0, 122.8, 121.6, 119.8, 108.5, 26.0; IR (KBr, cm^{-1}): 2921, 1699, 1606, 1071; LRMS (EI, 70 eV) *m/z* (%): 269 (M^+, 100), 268 (74), 192 (34). HRMS (ESI) $C_{16}H_{12}ClNONa[M+Na]^+$: Caled. 292.0505, Found 292.0500.



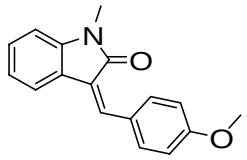
(*Z*)-3-Benzylidene-4-chloro-1-methylindolin-2-one (2i')

Yellow solid (mp 123.4-125.8 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ: 8.59 (s, 1H), 8.11-8.08 (m, 2H), 7.45-7.43 (m, 3H), 7.21-7.18 (m, 1H), 7.15 (m, 1H), 6.75 (m, 1H), 3.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.2, 148.7, 144.1, 135.1, 132.7, 130.1, 125.8, 124.5, 94.1, 38.8, 31.4; IR (KBr, cm^{-1}): 2920, 1679, 1606, 1456, 1114; LRMS (EI, 70 eV) *m/z* (%): 269 (M^+, 92), 268 (100), 192 (54); HRMS (ESI) $C_{16}H_{12}ClNONa[M+Na]^+$: Caled. 292.0505, Found 292.0500.



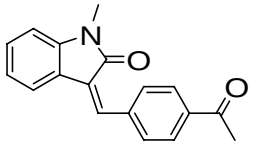
(*Z*)-1-Methyl-3-(4-methylbenzylidene)indolin-2-one (2j)[1]

Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 8.1 Hz, 2H), 7.53-7.52 (m, 2H), 7.31 (m, 3H), 7.09-7.04 (m, 1H), 6.81(d, *J* = 7.7 Hz, 1H), 3.28 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.2, 142.1, 141.1, 137.2, 132.1, 131.2, 129.0, 128.5, 125.0, 124.6, 121.7, 118.7, 107.8, 25.9, 21.7; LRMS (EI, 70 eV) *m/z* (%): 249 (M^+, 100), 248 (77), 158 (37).



(*Z*)-3-(4-Methoxybenzylidene)-1-methylindolin-2-one (2k)[1]

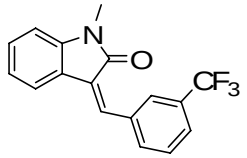
Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 8.9 Hz,1H), 7.82-7.52 (m, 2H), 7.49 (s, 1H), 7.05 (m, 1H), 7.00-6.96 (m, 3H), 6.81 (m, 1H), 3.88 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.8, 137.4, 137.1, 134.4, 131.4, 128.1, 121.4, 121.7, 118.4, 114.0, 113.7, 108.1, 107.7, 55.4, 26.2; LRMS (EI, 70 eV) *m/z* (%): 265 (M^+, 100), 264 (31), 222 (36).



(*Z*)-3-(4-Acetylbenzylidene)-1-methylindolin-2-one (2l)

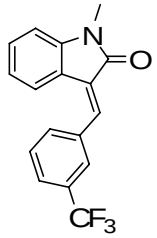
Light-red solid (mp 165.3-166.3 ^{o}C.); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.53-7.50 (m, 2H), 7.30 (m, 1H), 7.06 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.5, 165.8, 142.7, 138.1, 137.5, 134.8, 131.7, 129.6, 128.2, 128.0, 123.8, 122.0, 119.3, 108.0, 26.7, 25.9; IR (KBr, cm^{-1}): 2918, 1729, 1674, 1258, 1081; LRMS (EI, 70 eV) *m/z* (%): 277 (M^+, 100), 262 (53), 234 (39), 280 (100), 129 (49); HRMS (ESI)

$C_{18}H_{15}NO_2Na[M+Na]^+$: Caled. 300.1000, Found 300.0995.



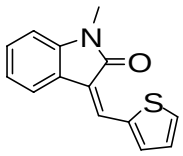
(*Z*)-1-Methyl-3-(3-(trifluoromethyl)benzylidene)indolin-2-one (2m)

Yellow solid (mp 116.2-119.1 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ: 8.54 (s, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 7.65-7.52 (m, 3H), 7.50 (s, 1H),7.32-7.27 (m, 1H), 7.11-7.08 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.9, 142.6, 134.7, 134.6, 134.3, 130.8, 129.5, 128.7, 128.5, 128.0 (q, *J* = 270.9 Hz, 1C), 127.8, 126.5, 123.7, 122.0, 119.2, 108.1, 26.0; IR (KBr, cm^{-1}): 2926, 1691, 1495, 1331; LRMS (EI, 70 eV) *m/z* (%): 303 (M^+, 100), 302 (46), 274 (18), 158 (70). HRMS (ESI) $C_{17}H_{12}F_3NONa[M+Na]^+$: Caled. 326.0763, Found 326.0767.



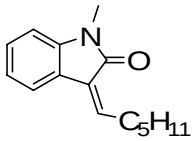
(*E*)-1-Methyl-3-(3-(trifluoromethyl)benzylidene)indolin-2-one (2m)

Yellow solid (mp 145.2-146.7 ^oC); ^1H NMR (300 MHz, $CDCl_3$) δ:7.90 (s, 1H), 7.82-7.79 (m, 2H),7.68-7.60 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.30-7.27 (m, 1H), 6.88 (m, 2H), 3.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.0, 144.6, 135.8, 134.6, 132.4, 130.9, 130.4, 129.2, 128.7, 127.8 (q, *J* = 270.3 Hz, 1C), 127.4, 125.9, 122.6, 121.9, 120.6, 108.4, 26.2; IR (KBr, cm^{-1}): 2923, 1688, 1496, 1335; LRMS (EI, 70 eV) *m/z* (%): 303 (M^+, 100), 302 (44), 274 (18), 158 (70); HRMS (ESI) $C_{17}H_{12}F_3NONa[M+Na]^+$: Caled. 326.0763, Found 326.0767.



(*Z*)-1-Methyl-3-(thiophen-2-ylmethylene)indolin-2-one (2n)

Light-yellow solid (mp 126.5-129.0 ^{o}C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.67-7.62 (m, 2H), 7.48-7.43 (m, 2H), 7.27-7.25 (m, 1H), 6.92-6.82 (m, 2H), 3.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.5, 144.2, 137.2, 134.9, 129.8, 129.3, 128.6, 128.2, 127.2, 122.7, 121.8, 121.1, 108.2, 26.2; IR (KBr, cm^{-1}): 2926, 1692, 1615, 1334; LRMS (EI, 70 eV) *m/z* (%): 241 (M^+, 100), 240 (40), 212 (17), 158 (16). HRMS (ESI) $C_{14}H_{11}NOSNa[M+Na]^+$: Caled. 264.0454, Found 264.0449.



(*Z*)-3-Hexylidene-1-methylindolin-2-one (2o)

Light-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.4 Hz, 1H), 7.27 (s, 1H), 7.05-7.02 (m, 1H), 6.91-6.86 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 3.02 (m, 2H), 1.59-1.55 (m, 2H), 1.42-1.36 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.4, 142.9, 141.9, 128.4, 126.8, 123.0, 121.7, 118.8, 107.4, 31.6, 28.8, 27.7, 25.6, 22.5, 14.0; IR (KBr, cm^{-1}): 2926, 2856, 1703, 1489; LRMS (EI, 70 eV) *m/z* (%): 229 (M^+, 71), 186 (100), 160 (53); HRMS (ESI) $C_{15}H_{19}NONa[M+Na]^+$: Caled. 252.1364, Found 252.1359.

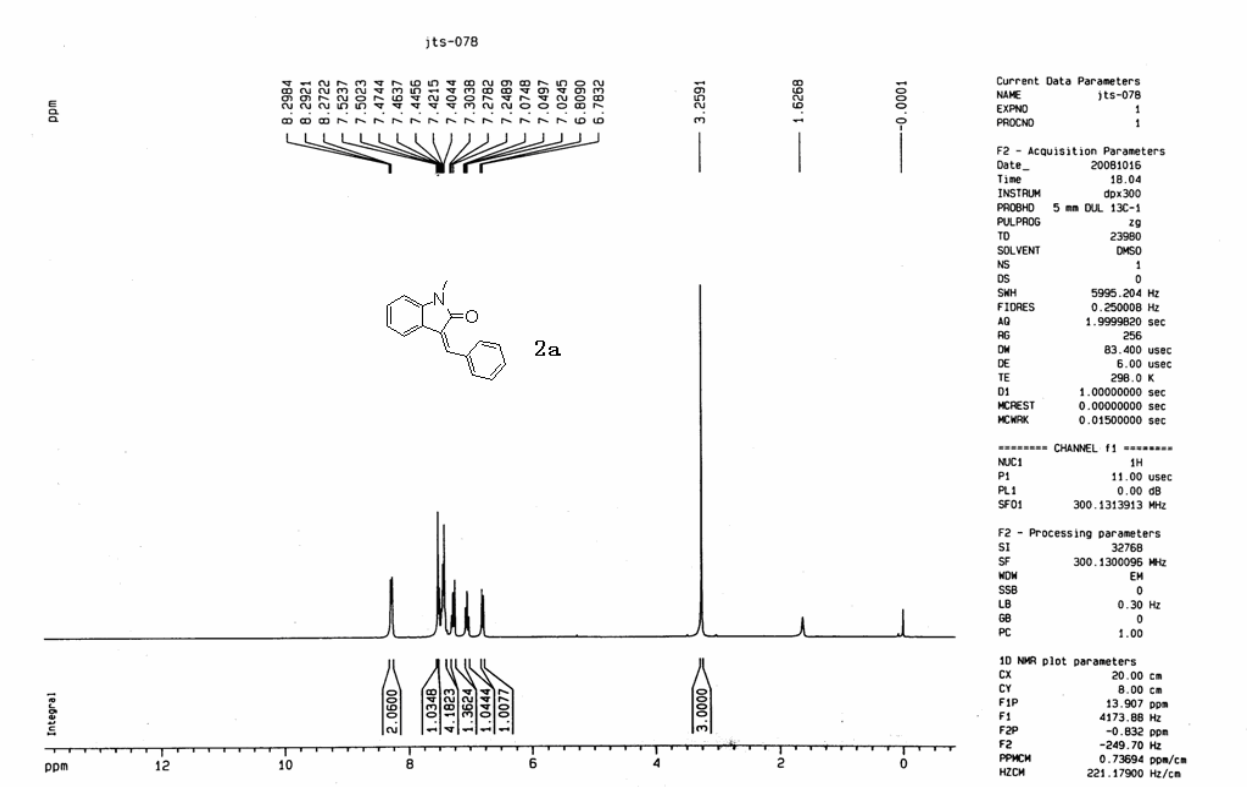
(C) **References**

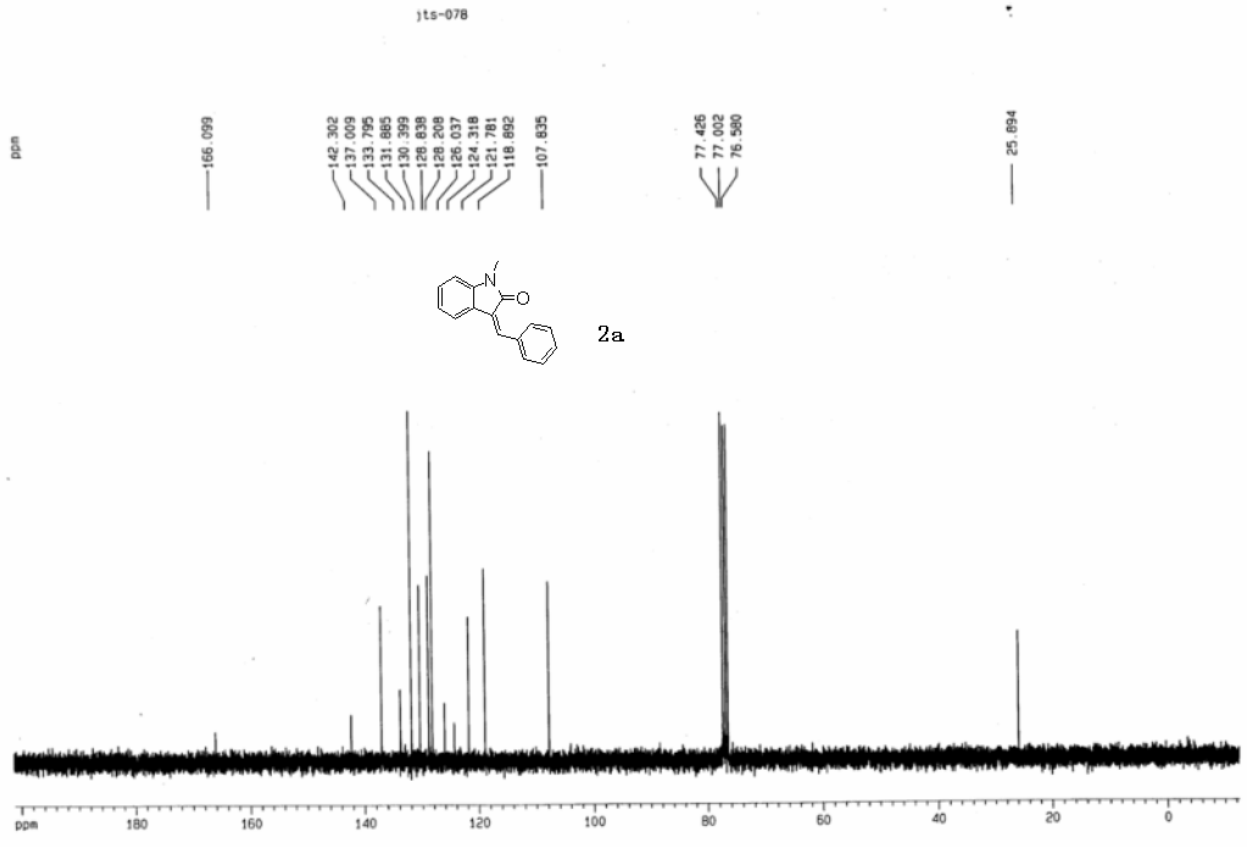
(1) Teichert, A.; Jantos, K.; Harms, K.; Studer, A. *Org. Lett*. **2004**, *6*, 3477-3480.

(2) Park, J. H.; Kim, E.; Chung, Y. K. *Org. Lett*. **2008**, *10*, 4719-4721.

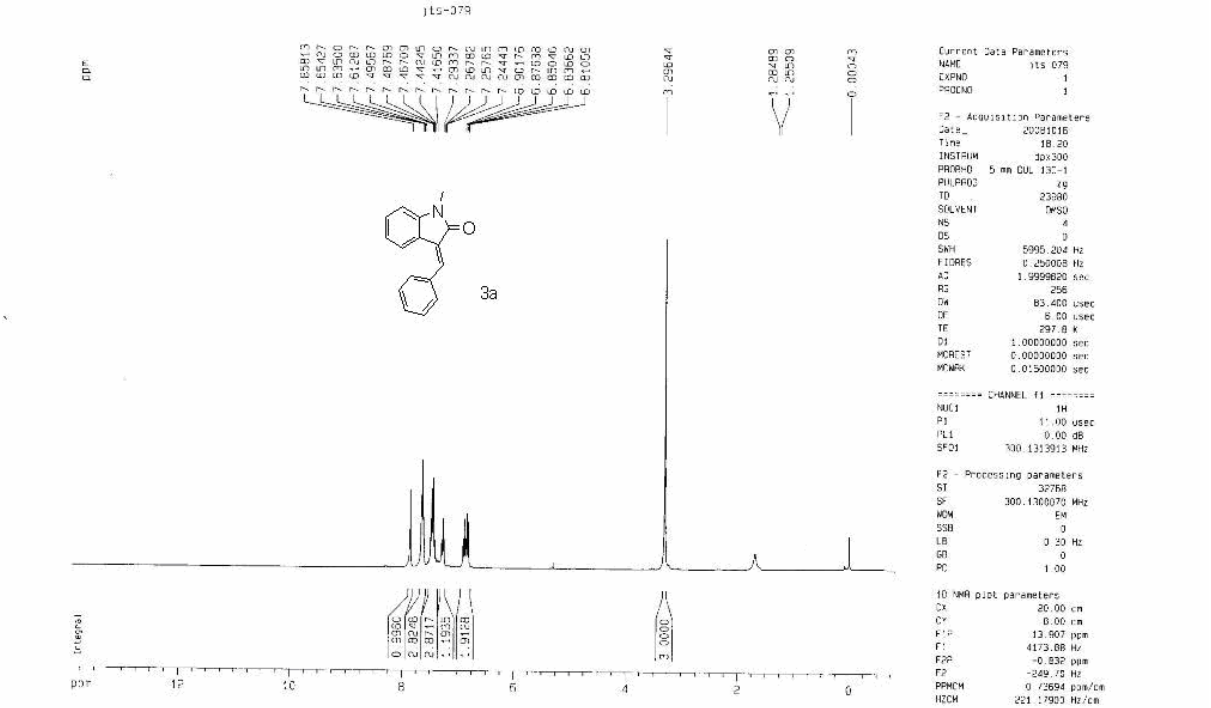
(D) Spectra

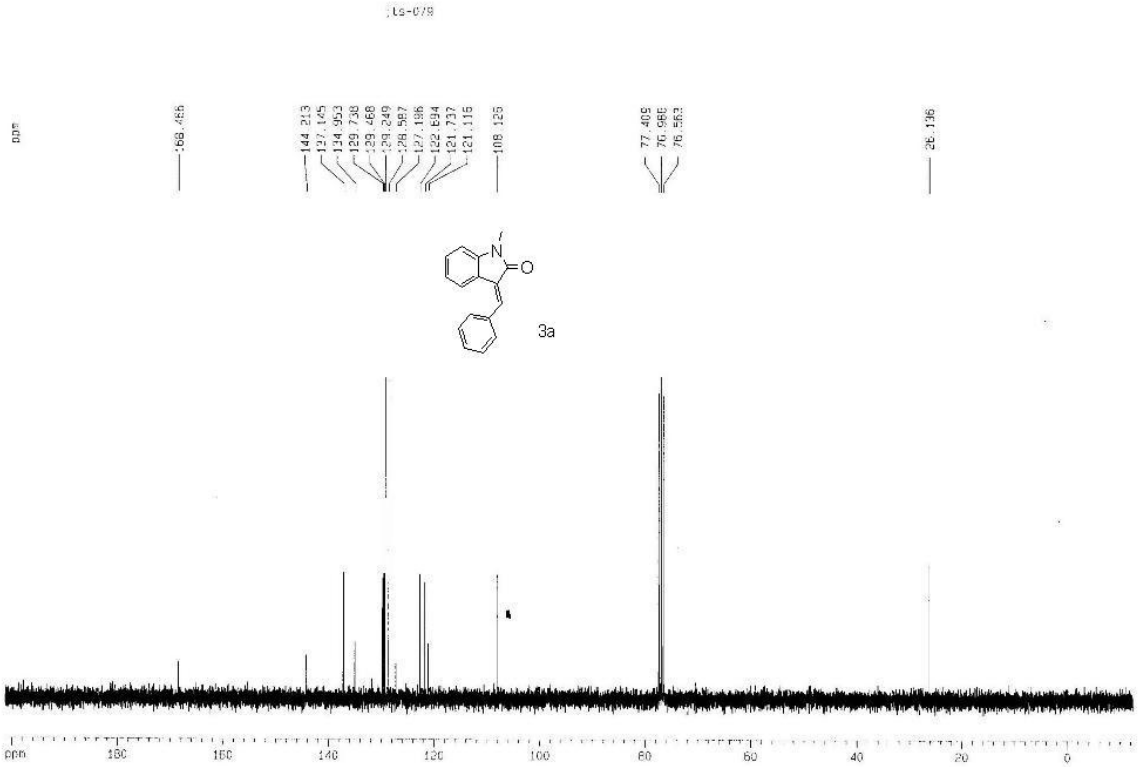
(*Z*)-3-Benzylidene-1-methylindolin-2-one (2a)



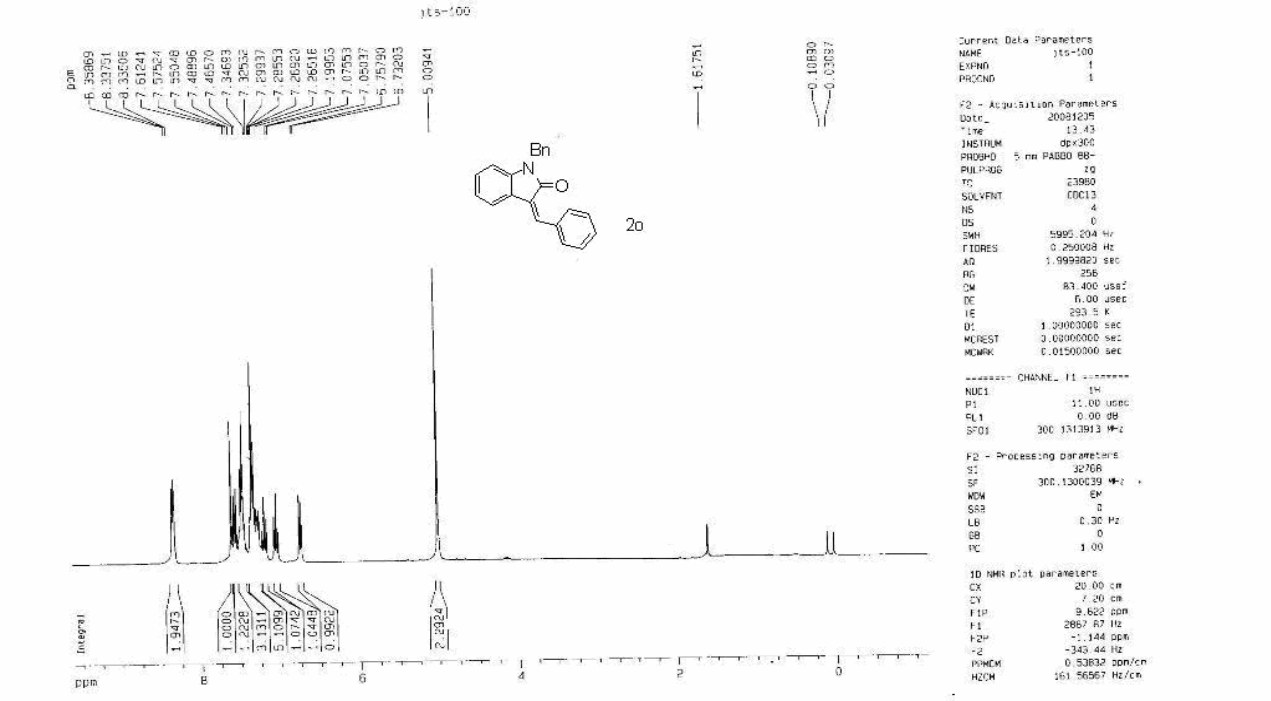


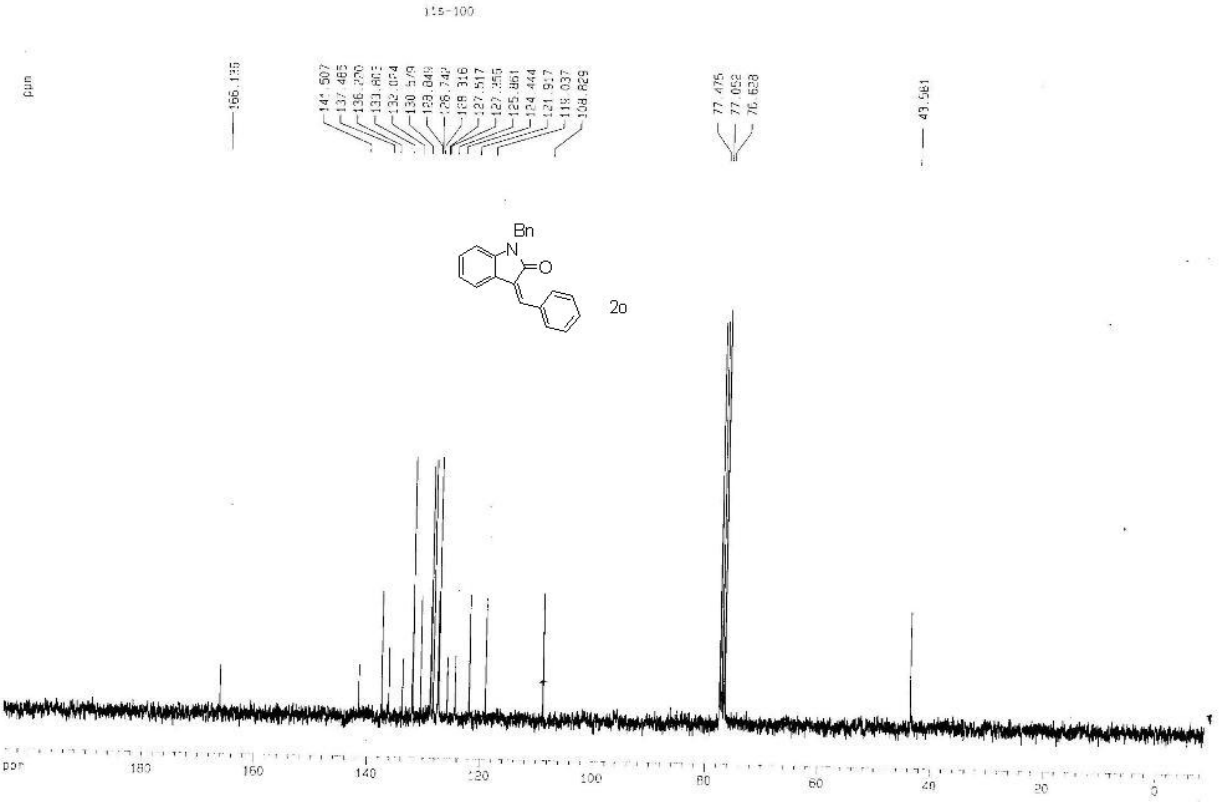
(*E*)-3-Benzylidene-1-methylindolin-2-one (2a)



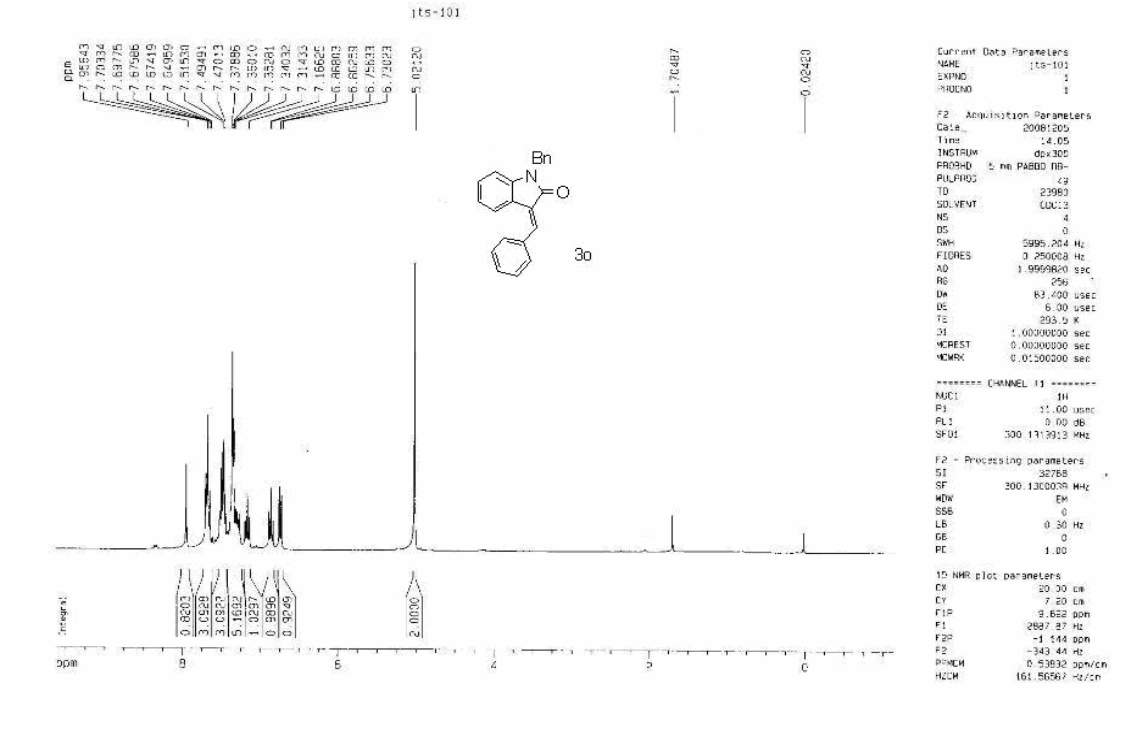


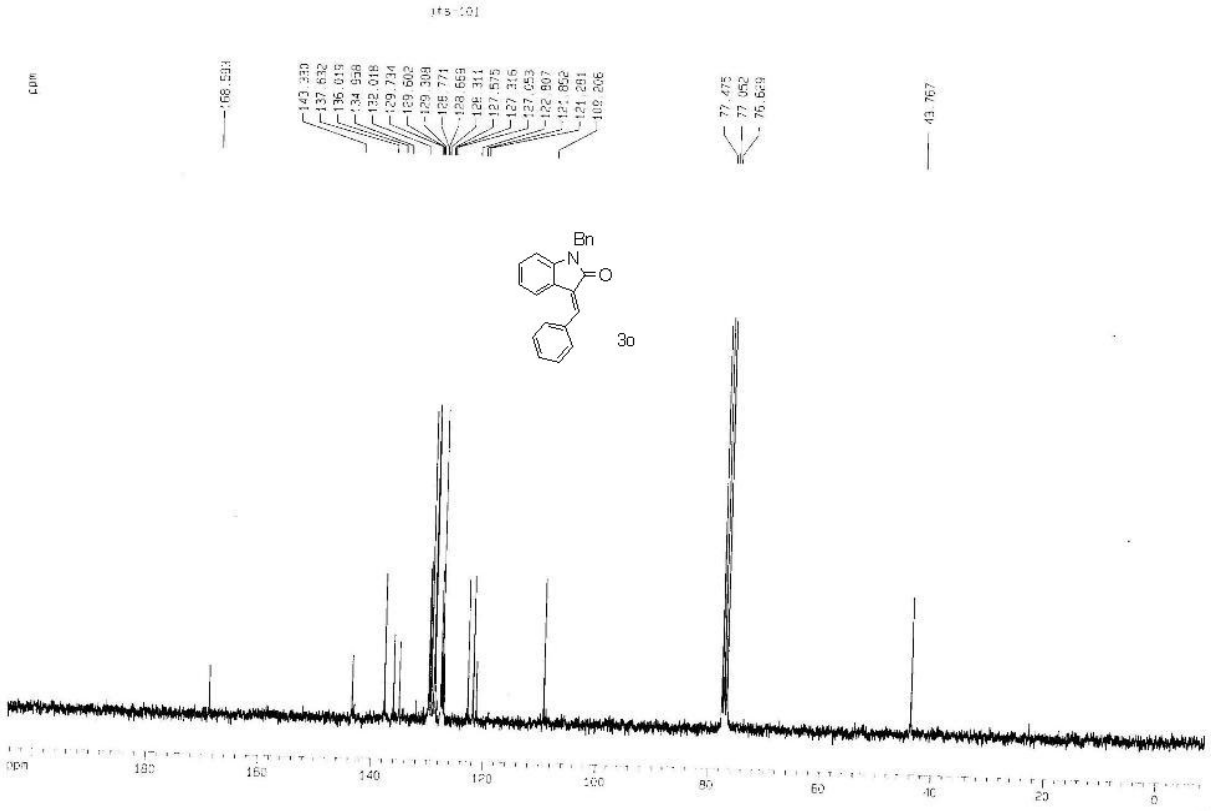
(*Z*)-1-Benzyl-3-benzylideneindolin-2-one (2b)



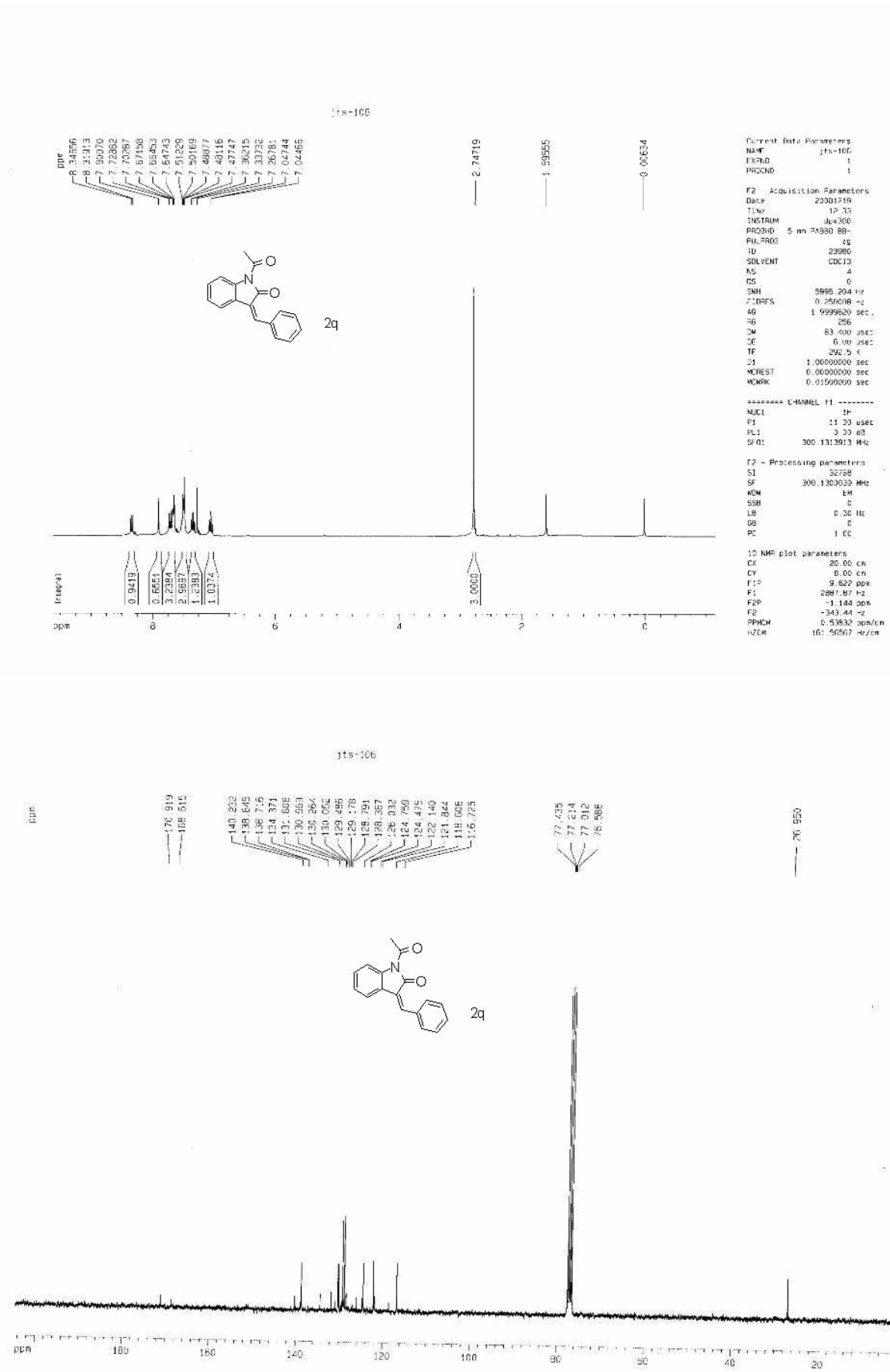


(*E*)-1-Benzyl-3-benzylideneindolin-2-one (2b)

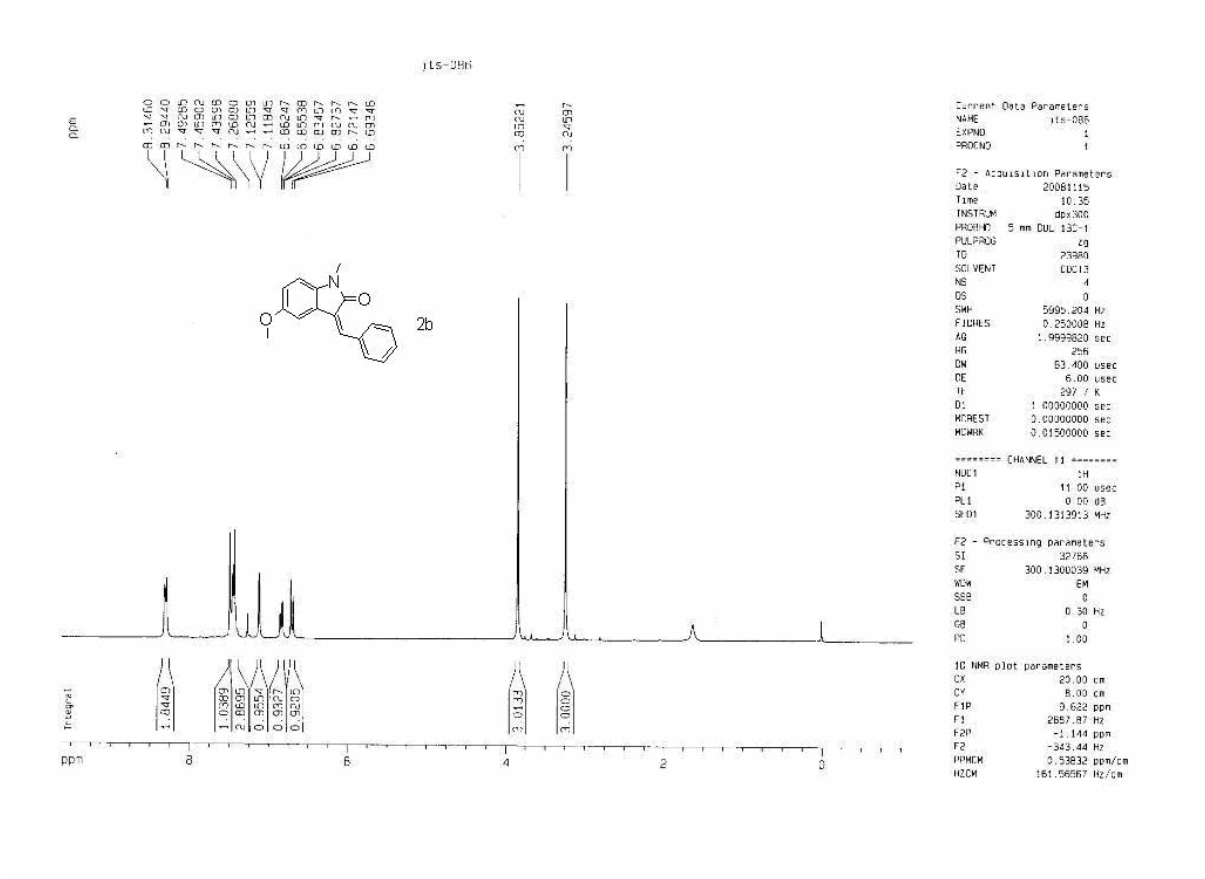


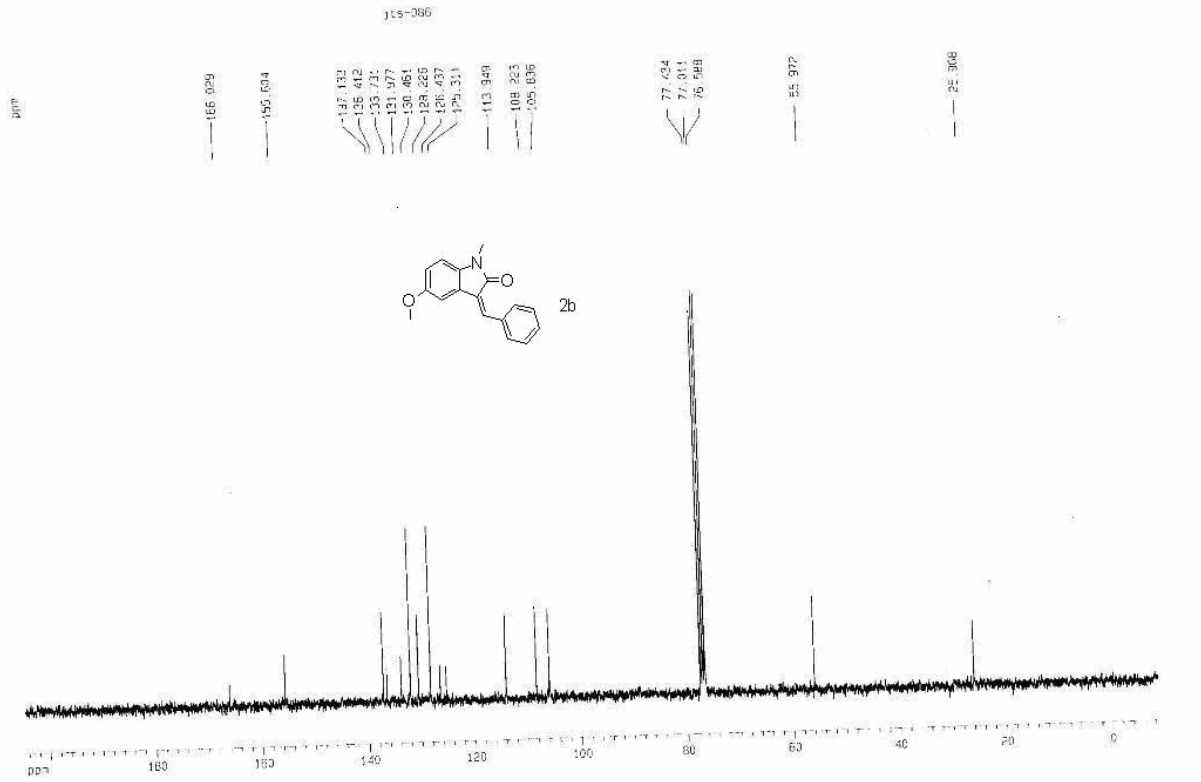


(*Z*)-1-Acetyl-3-benzylideneindolin-2-one (2c)

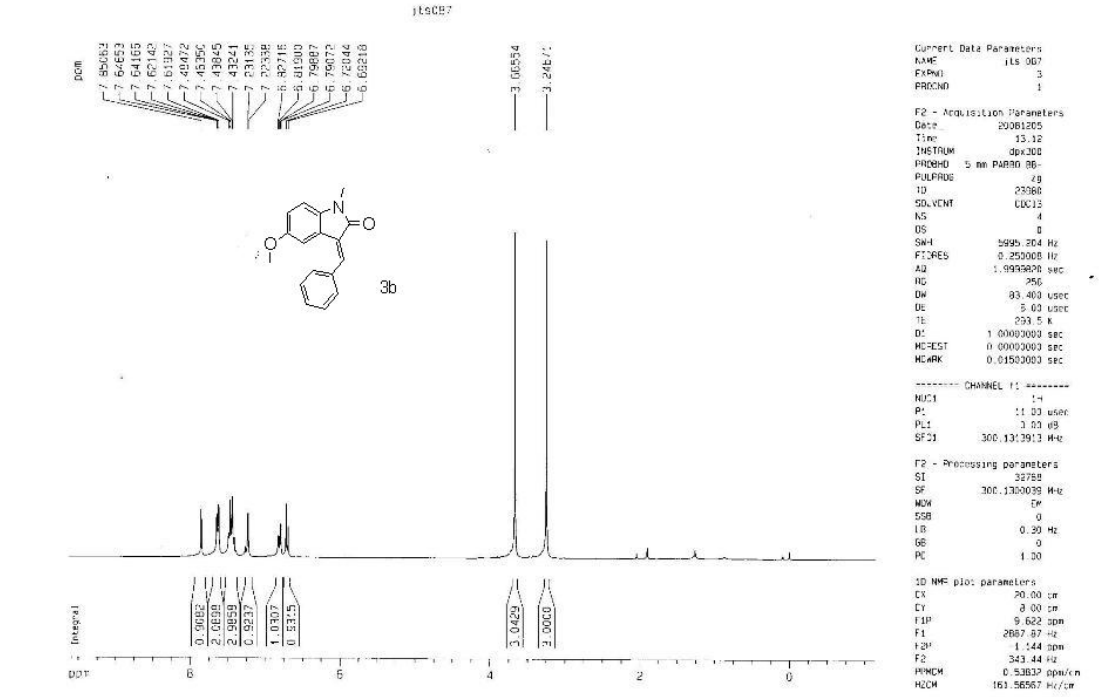


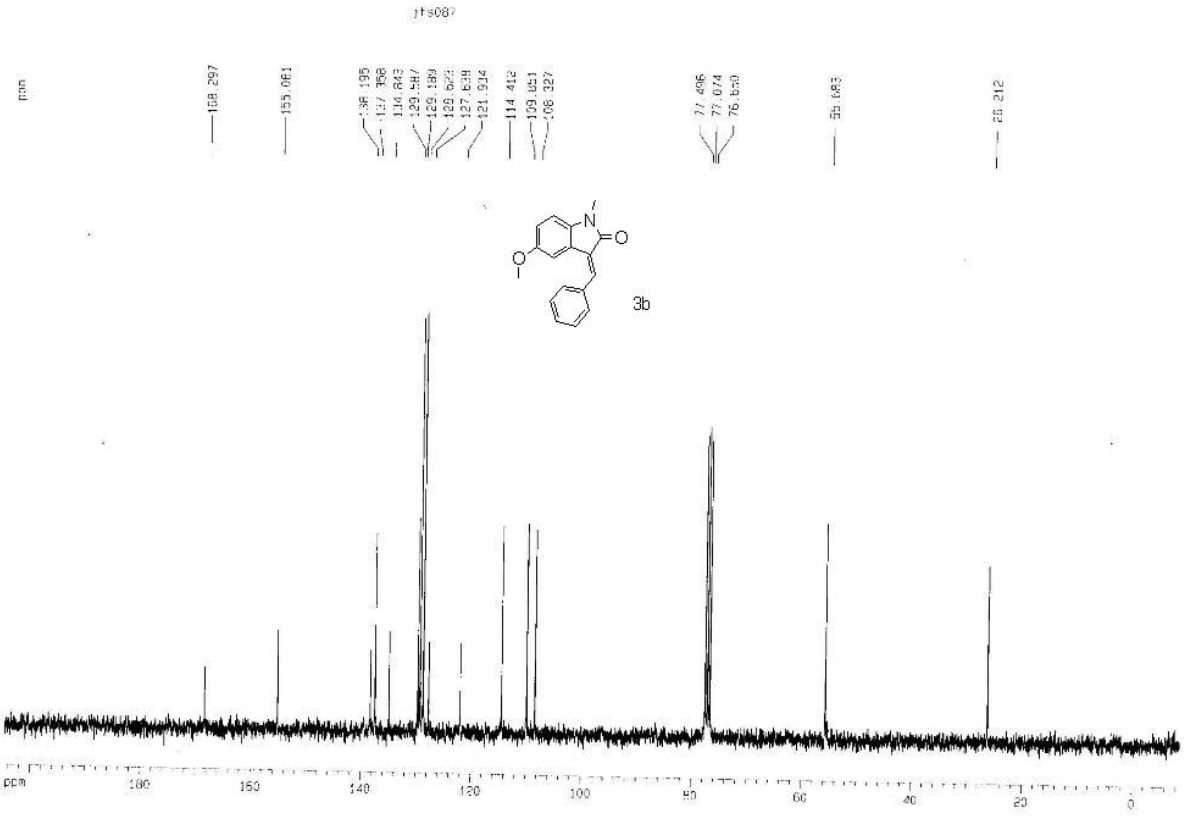
(*Z*)-3-Benzylidene-5-methoxy-1-methylindolin-2-one (2e)



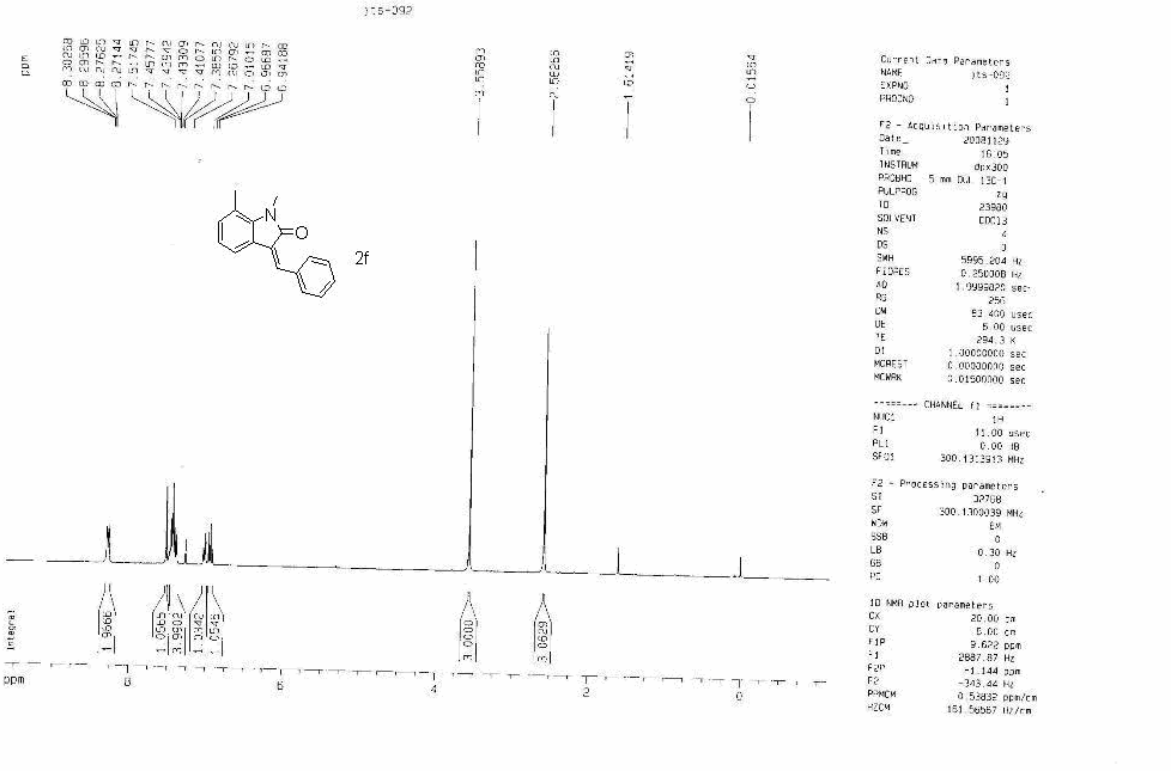


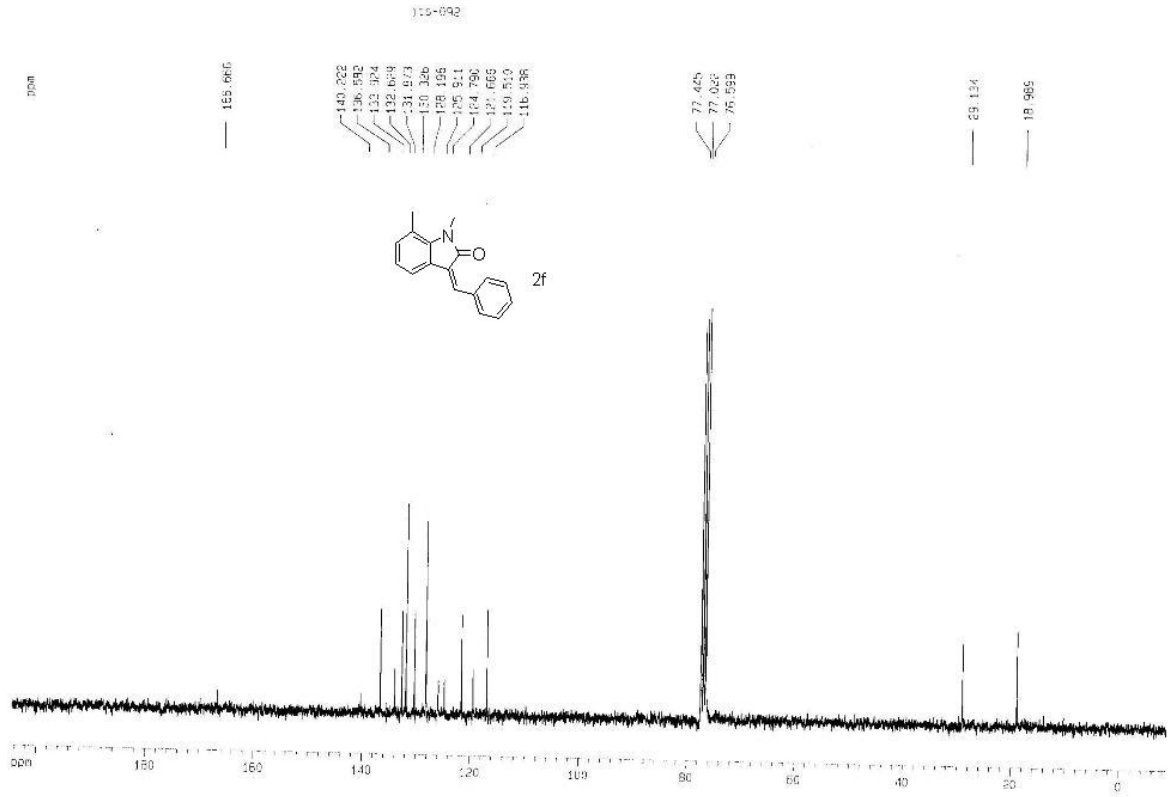
(*E*)-3-Benzylidene-5-methoxy-1-methylindolin-2-one (2e)



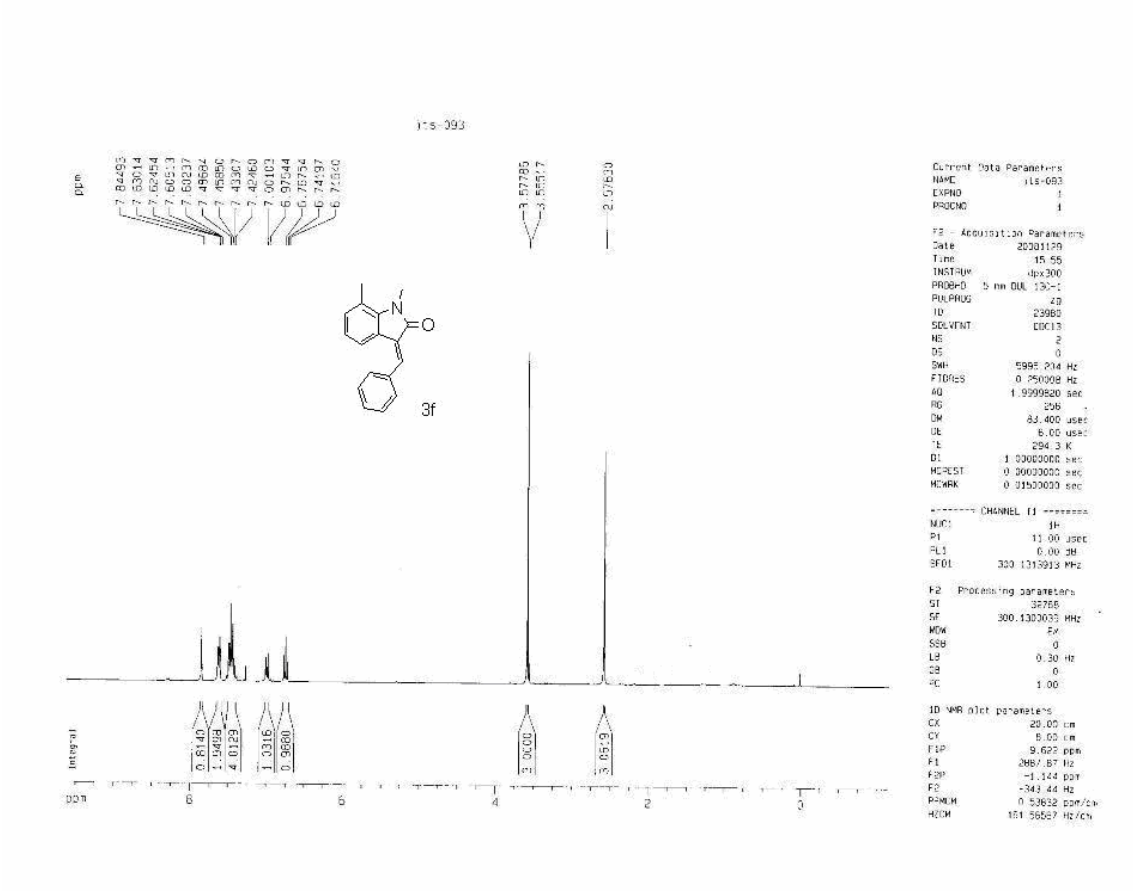


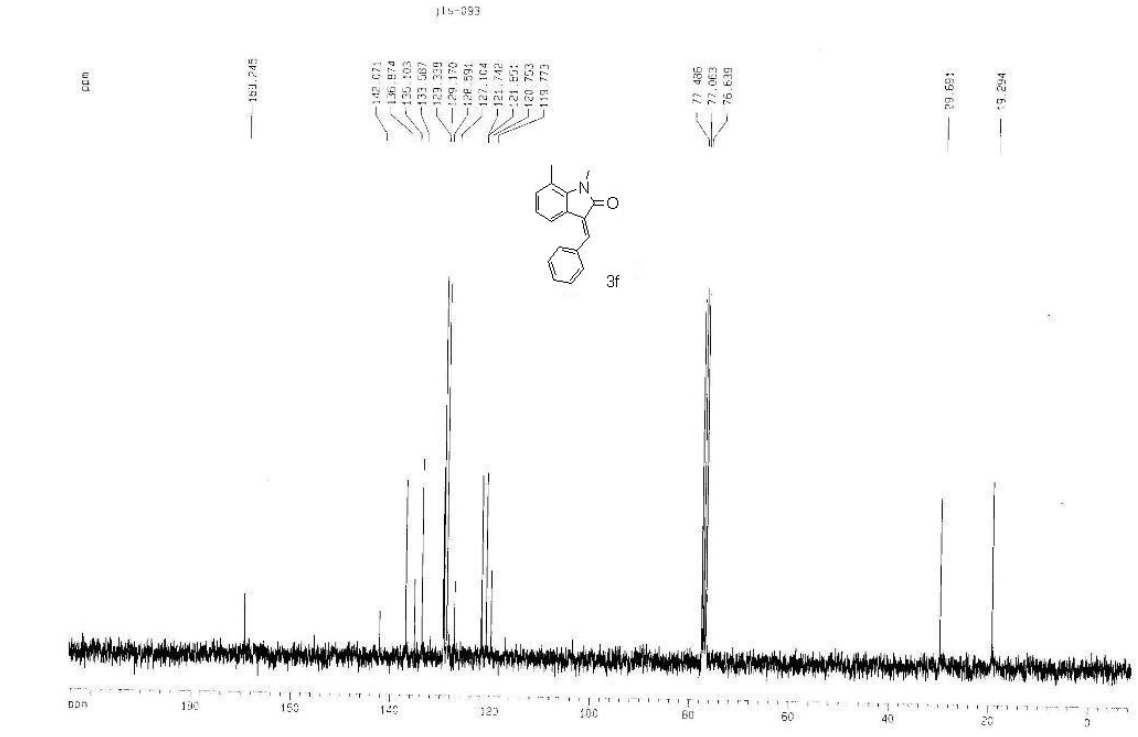
(*Z*)-3-Benzylidene-1,7-dimethylindolin-2-one (2f)



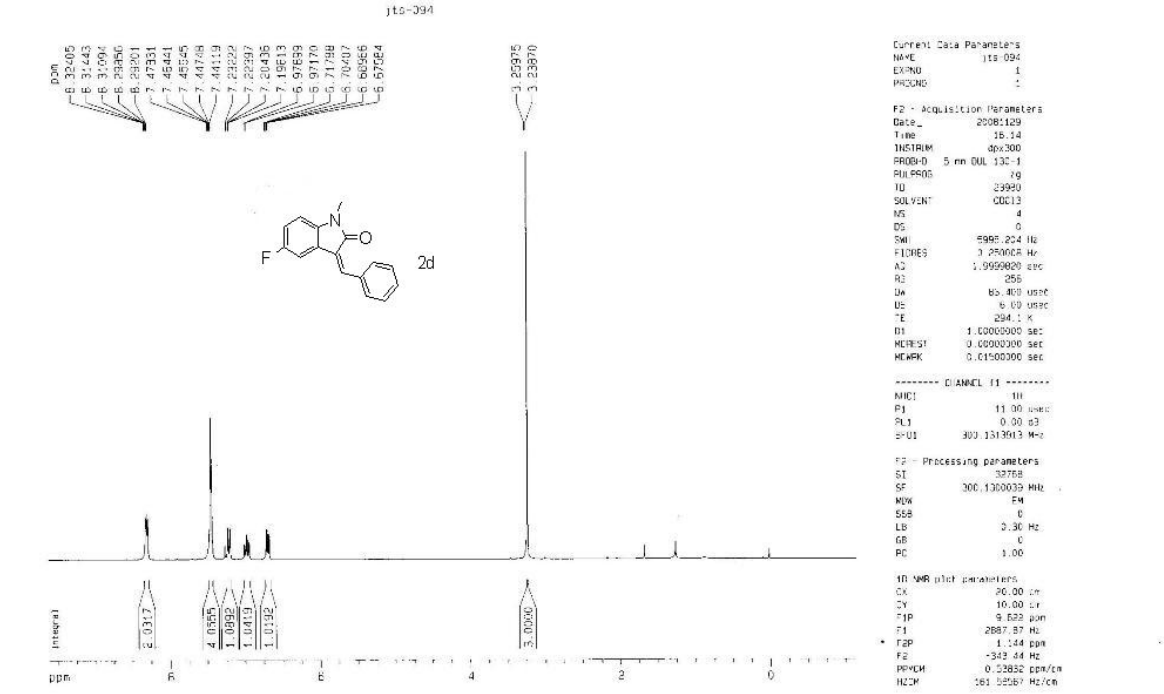


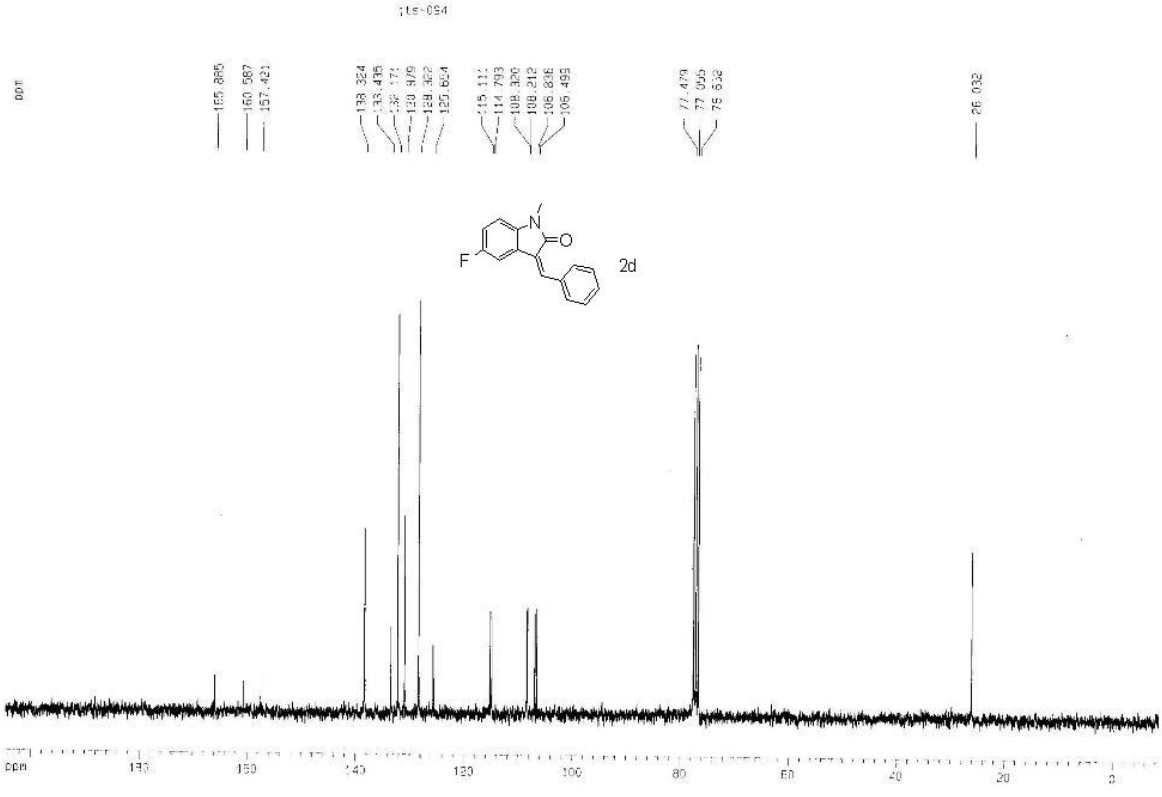
(*E*)-3-Benzylidene-1,7-dimethylindolin-2-one (2f)



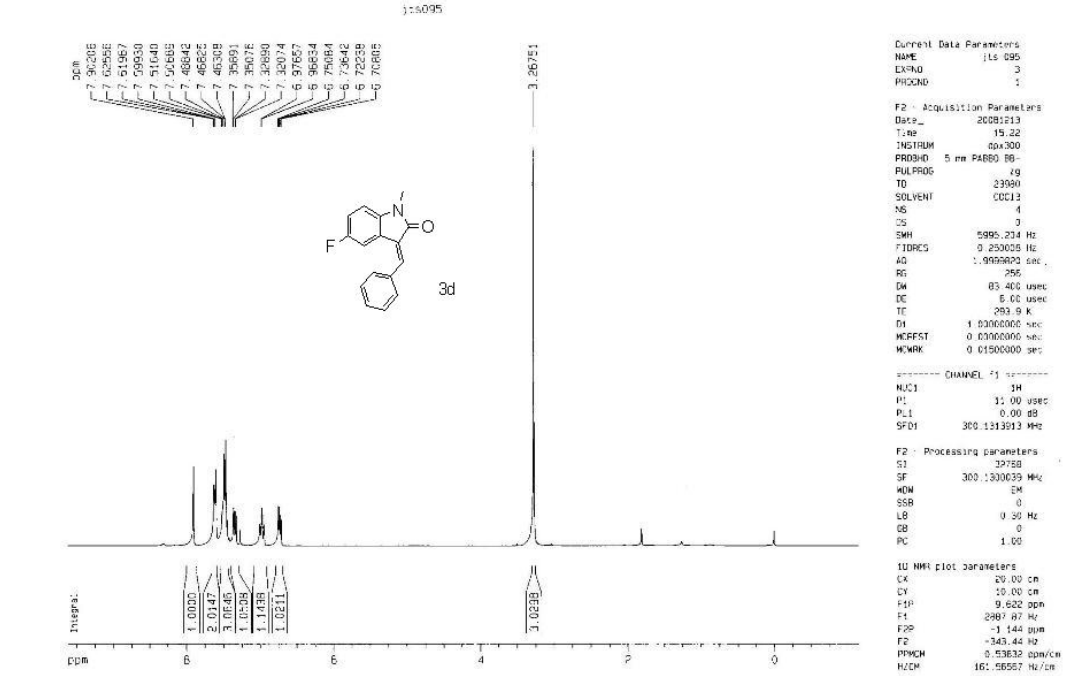


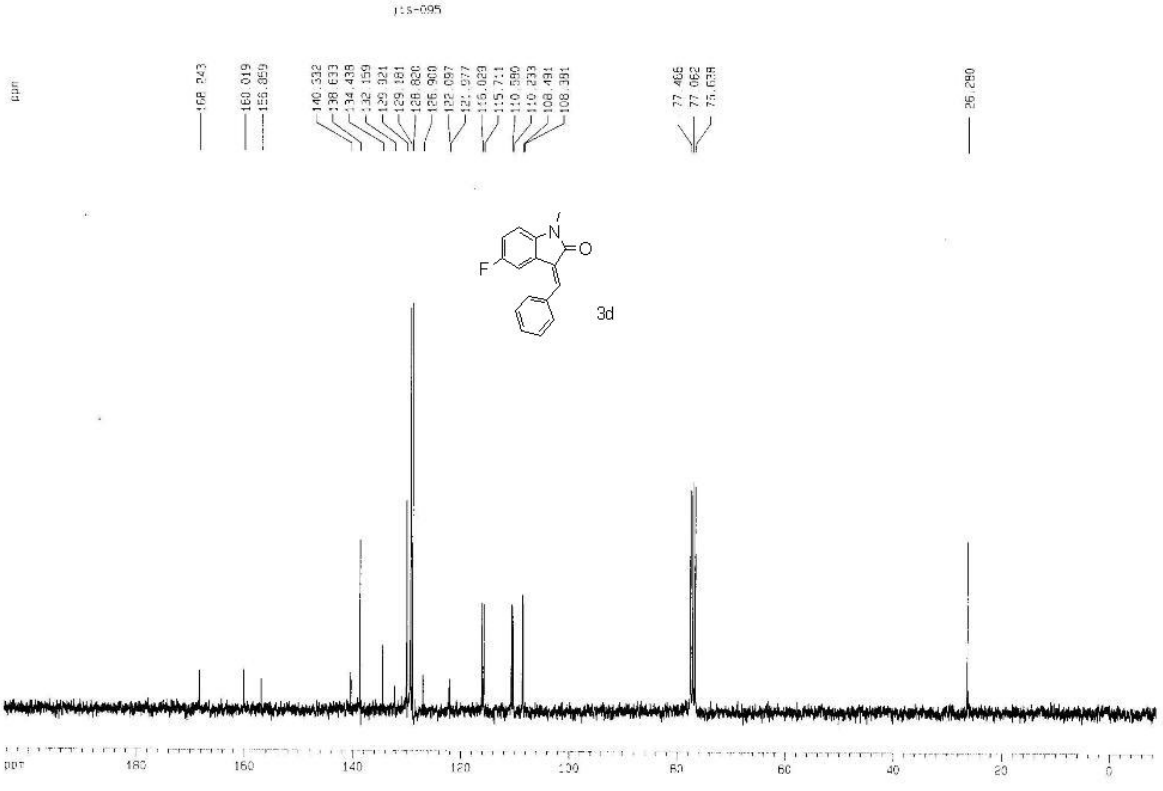
(*Z*)-3-Benzylidene-5-fluoro-1-methylindolin-2-one (2g)



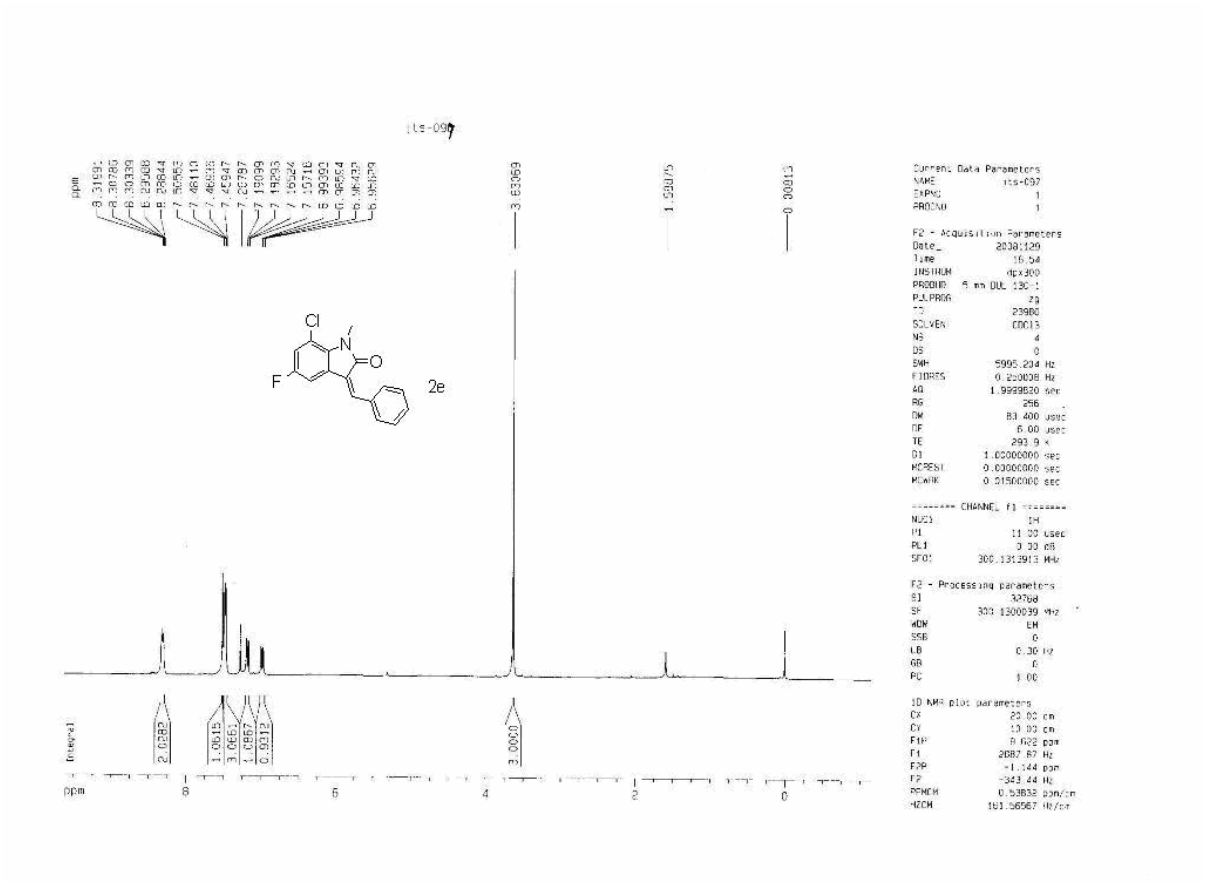


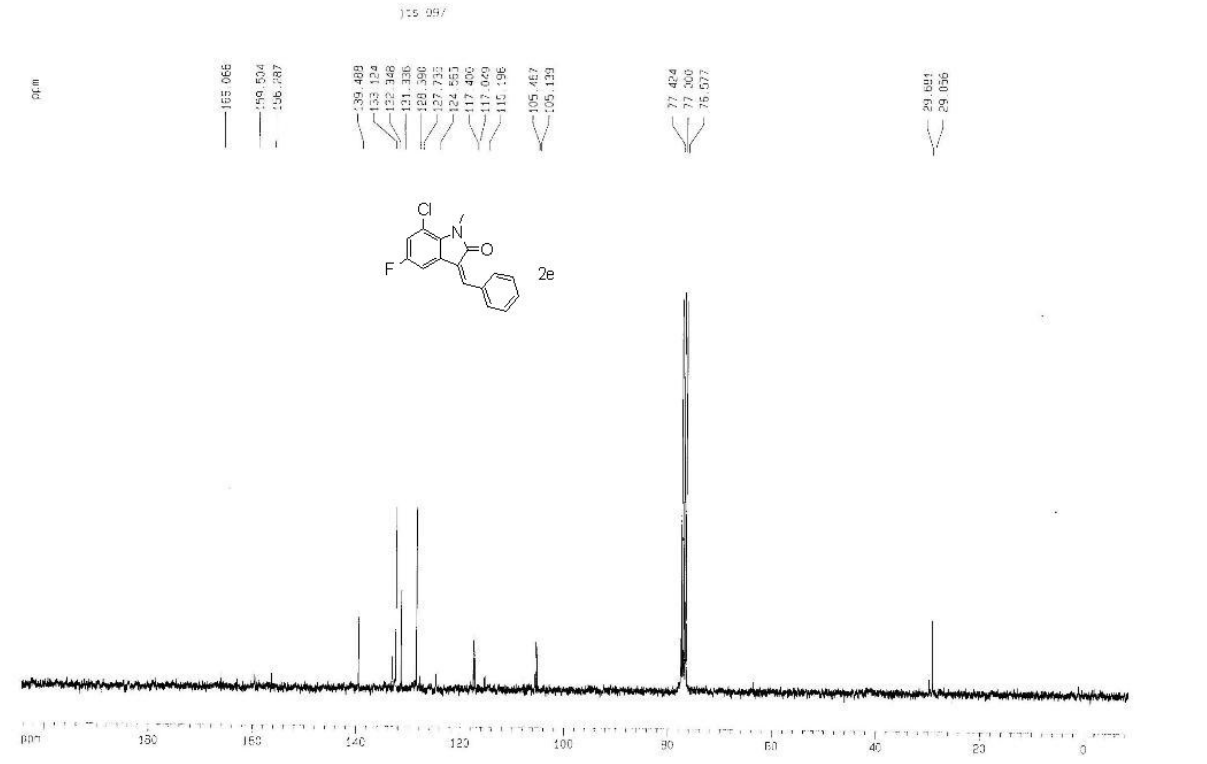
(*E*)-3-Benzylidene-5-fluoro-1-methylindolin-2-one (2g)



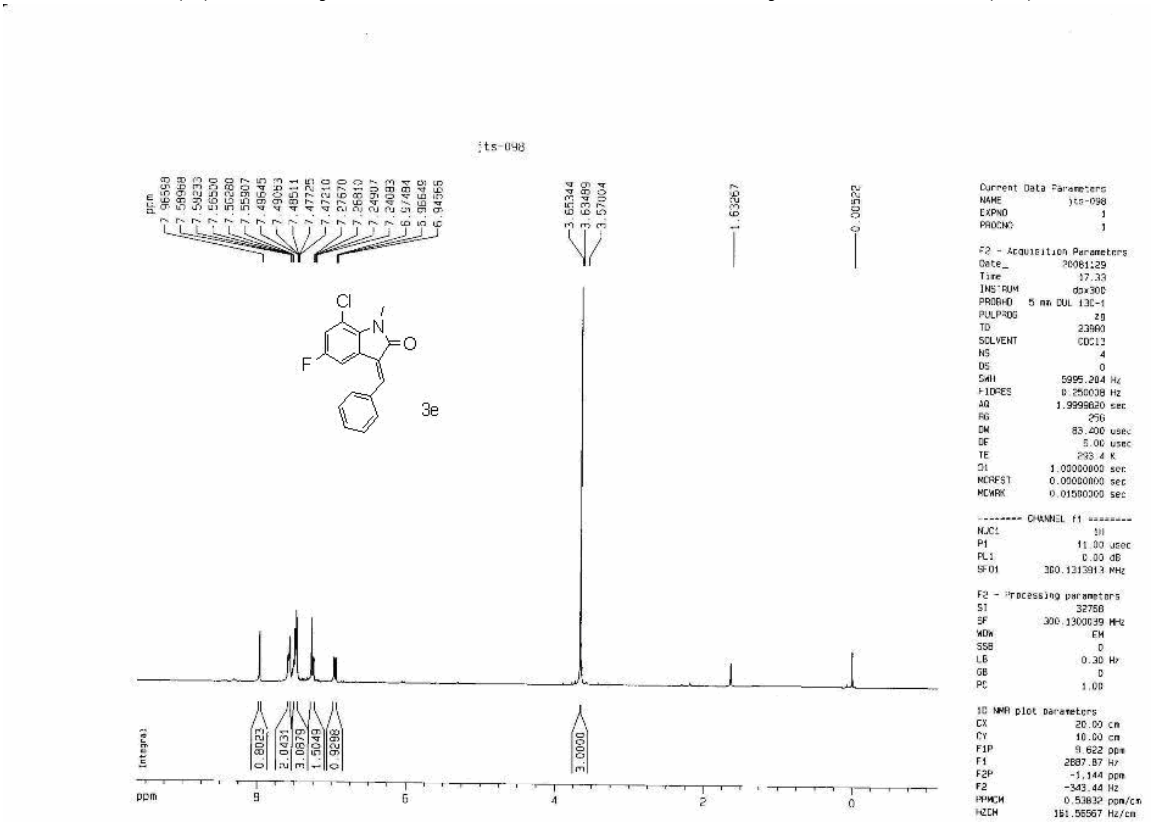


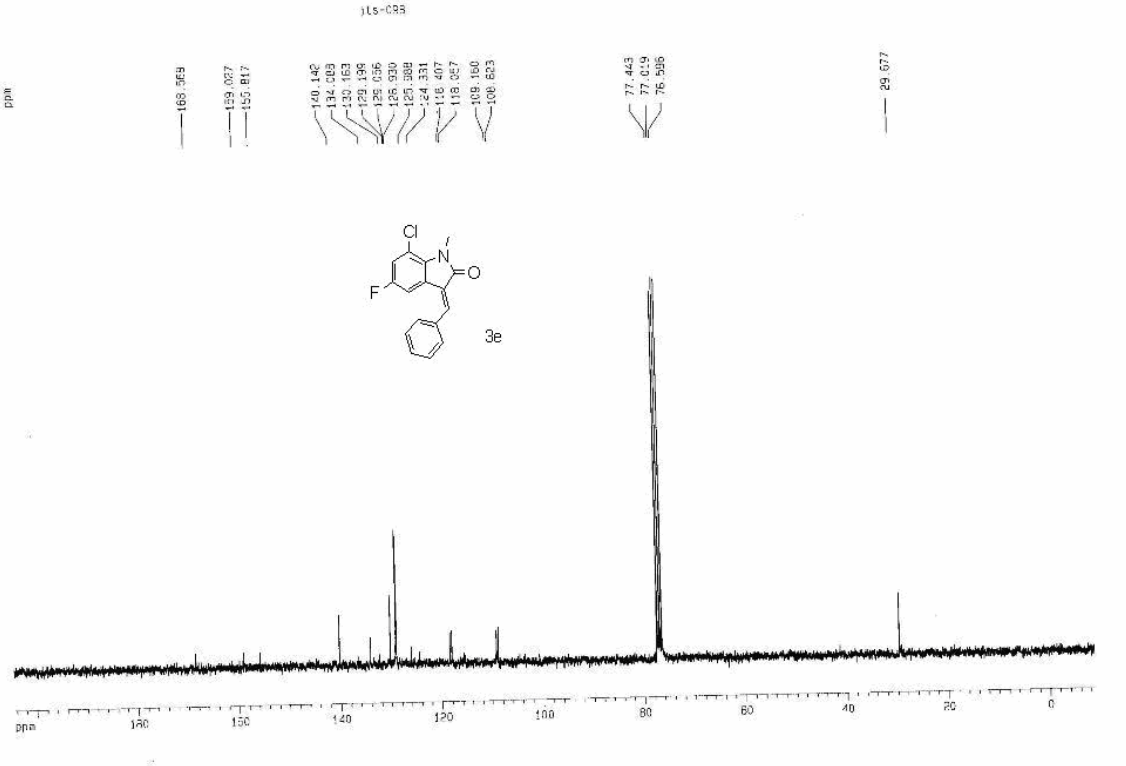
(Z)-3-Benzylidene-7-chloro-5-fluoro-1-methylindolin-2-one (2h)



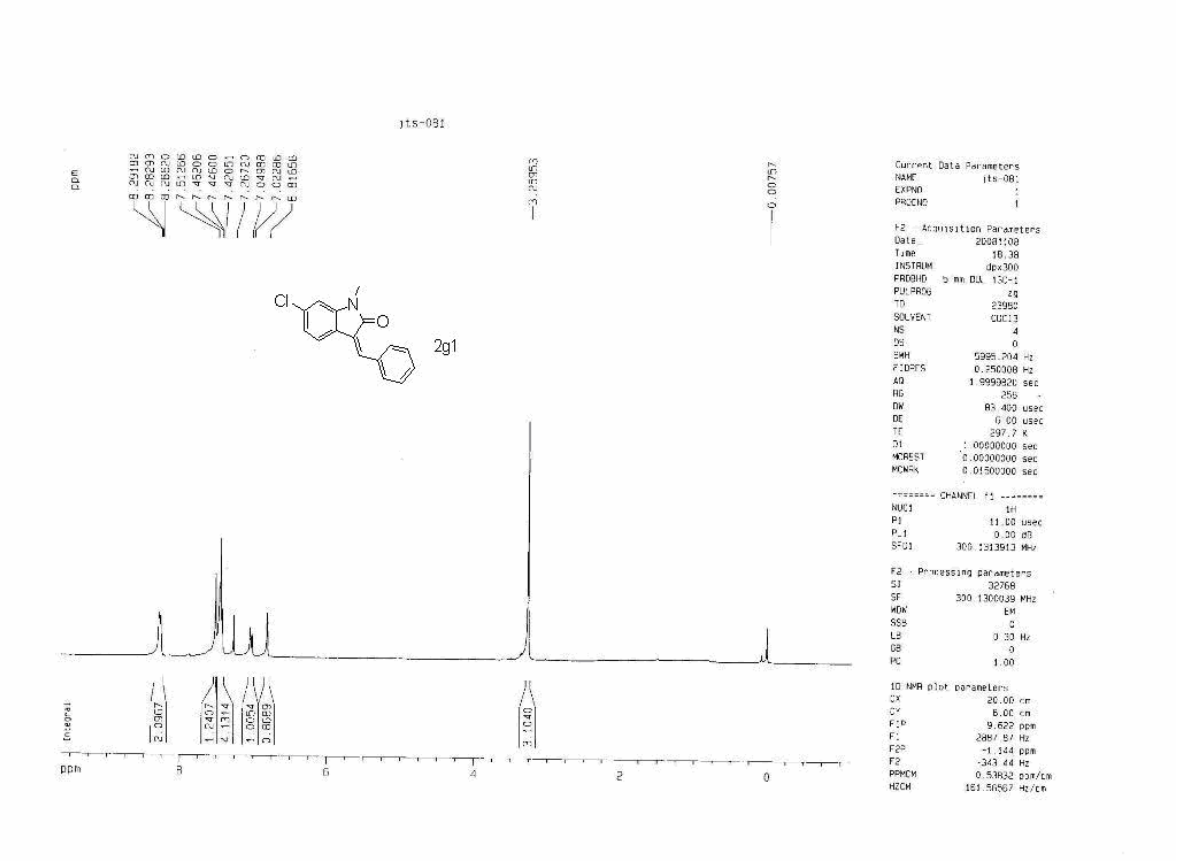


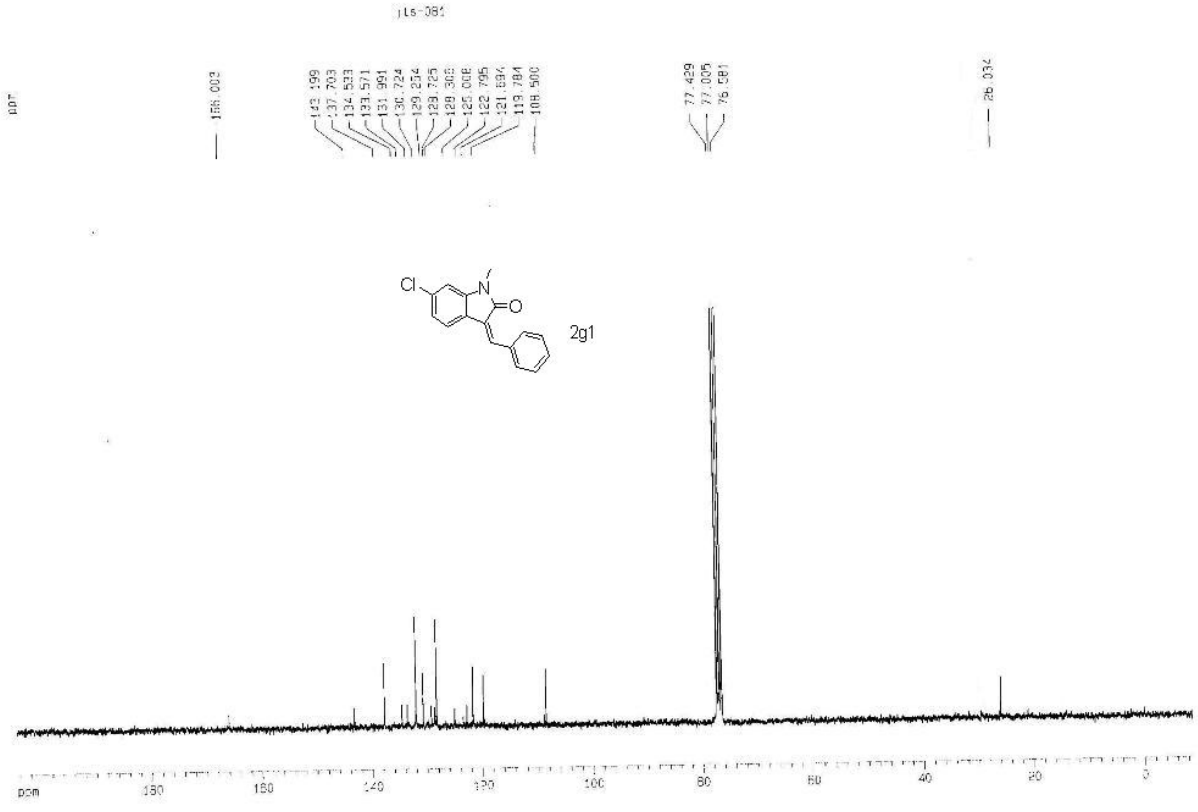
(*E*)-3-Benzylidene-7-chloro-5-fluoro-1-methylindolin-2-one (2h)



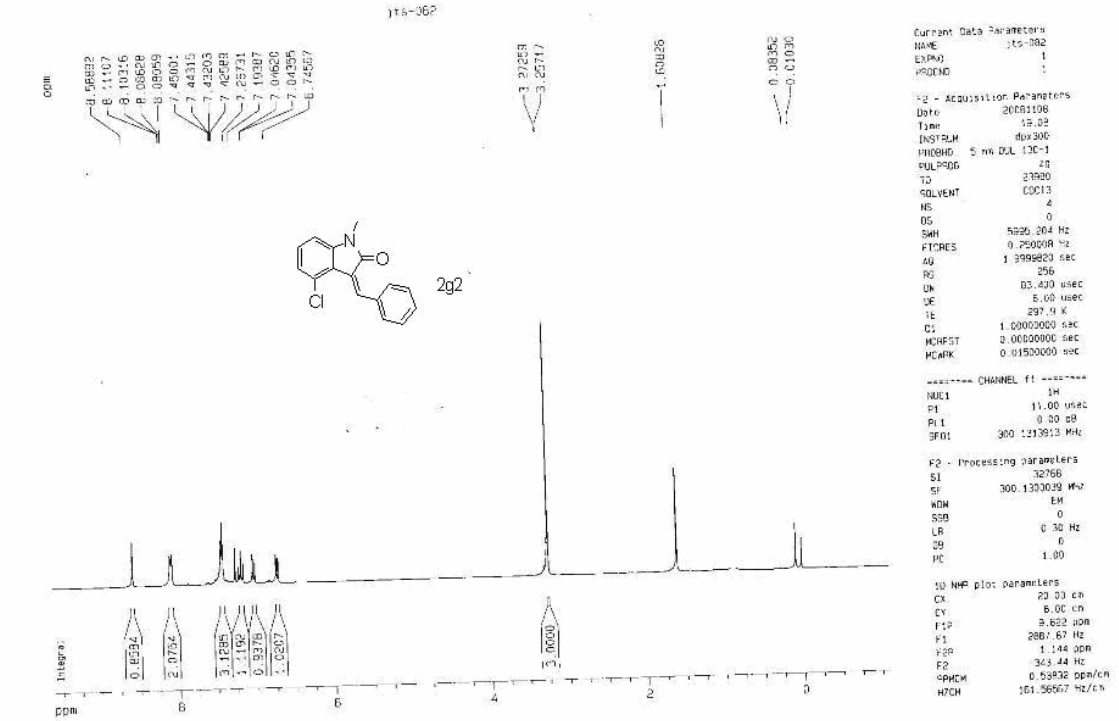


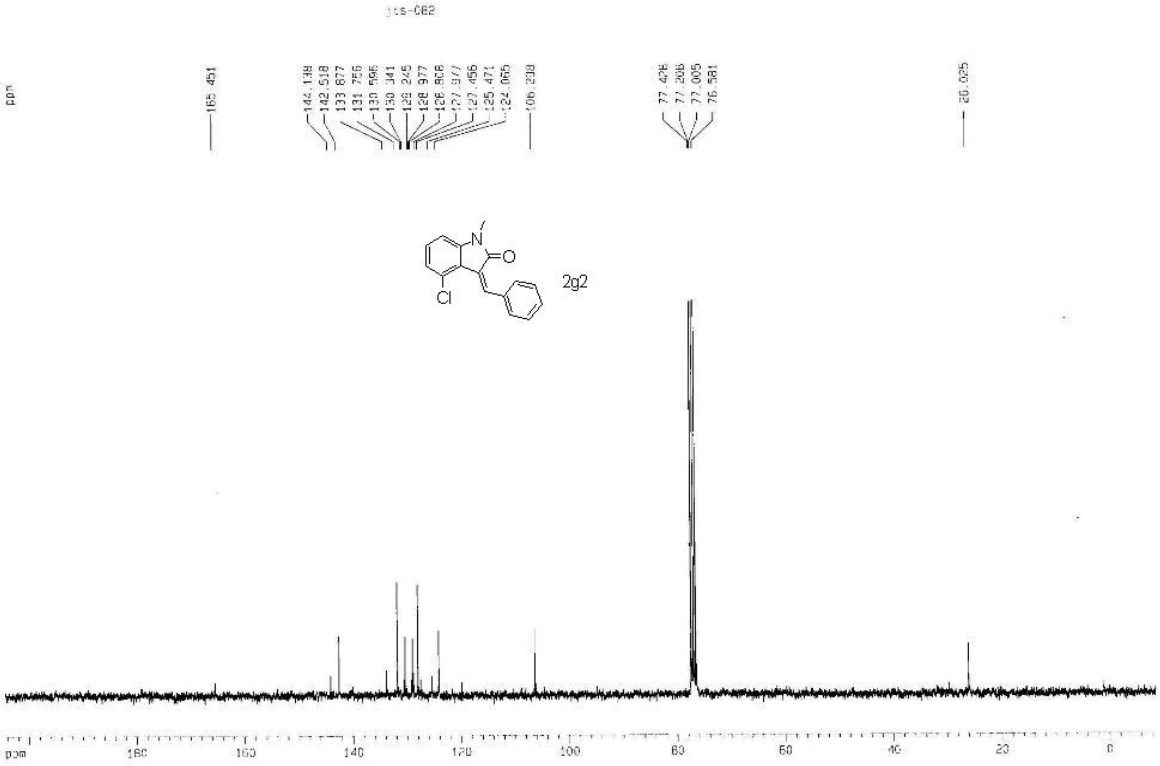
(*Z*)-3-Benzylidene-6-chloro-1-methylindolin-2-one (2i)



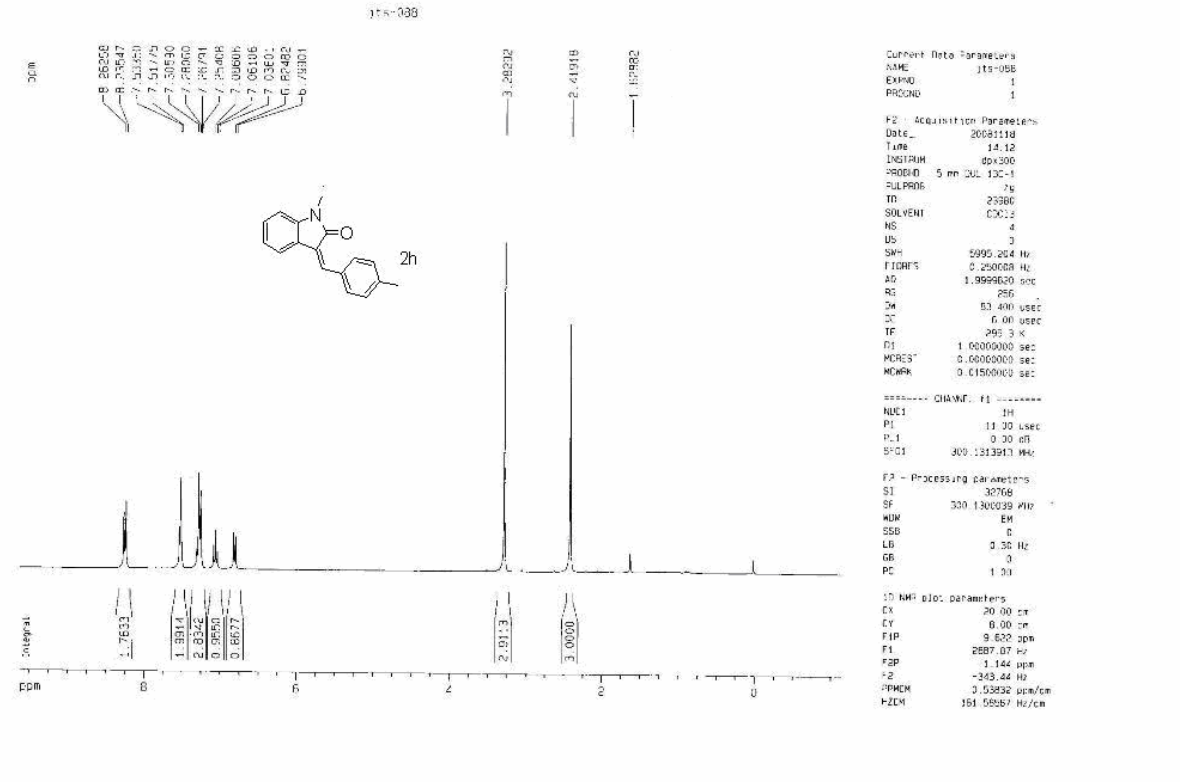


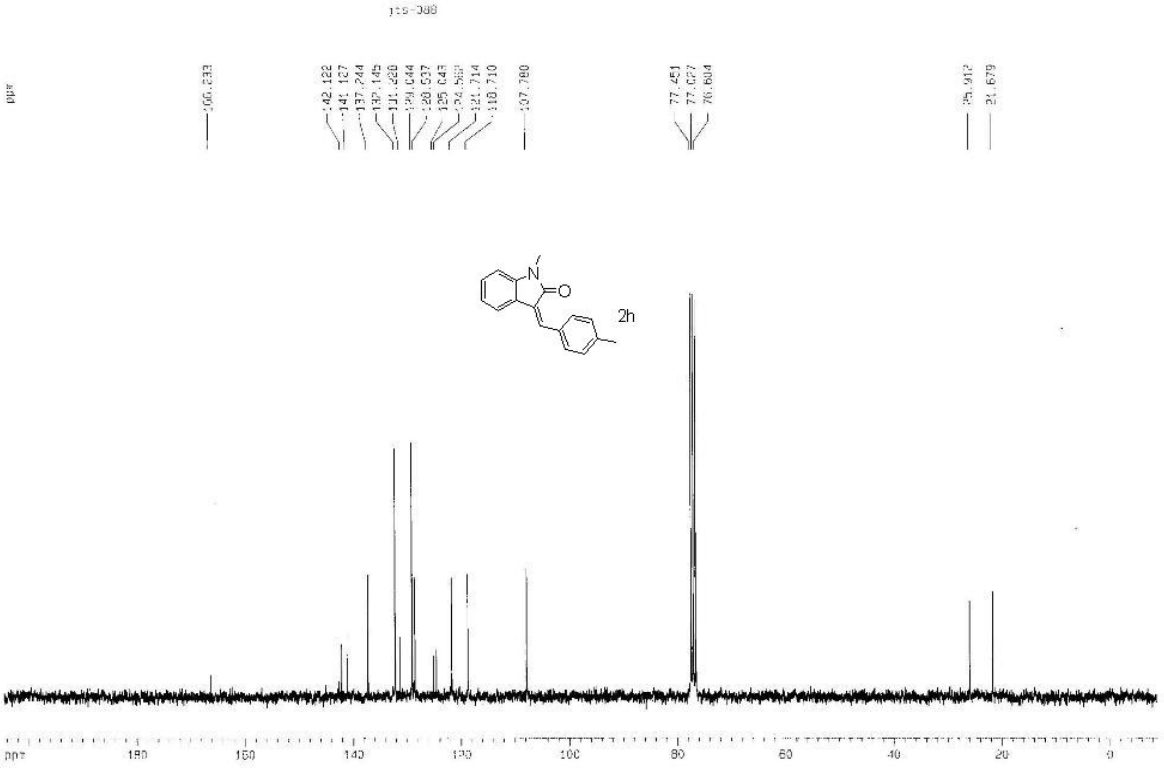
(*Z*)-3-Benzylidene-6-chloro-1-methylindolin-2-one (2i')



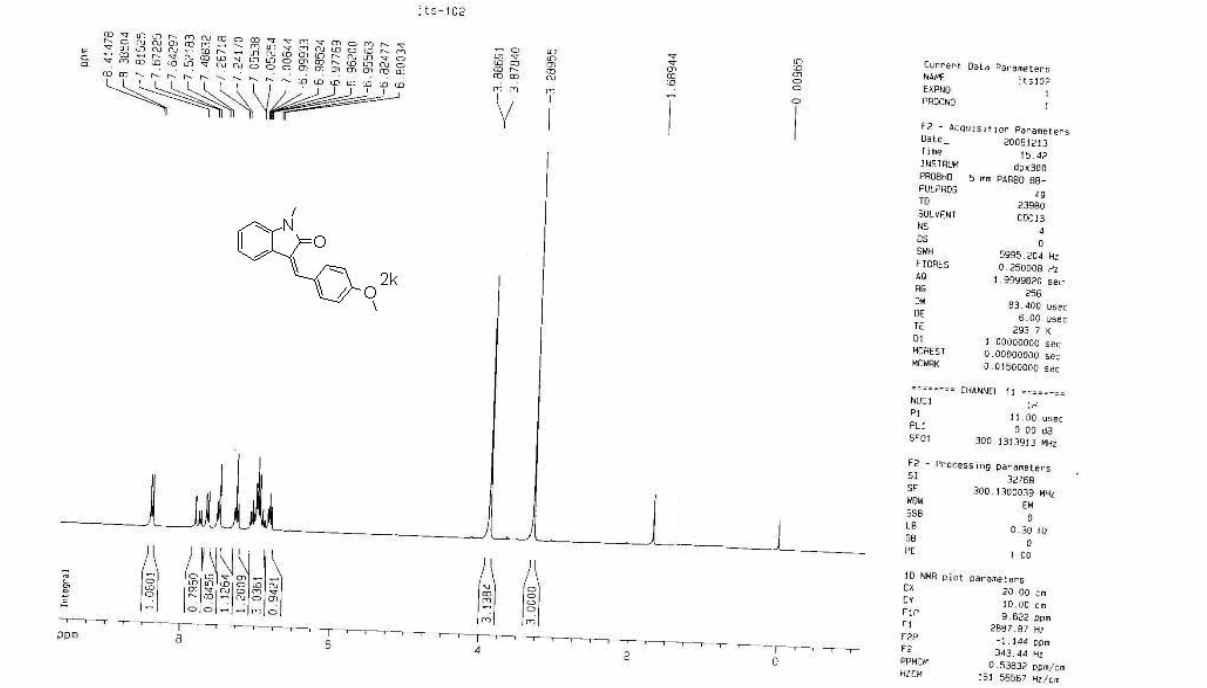


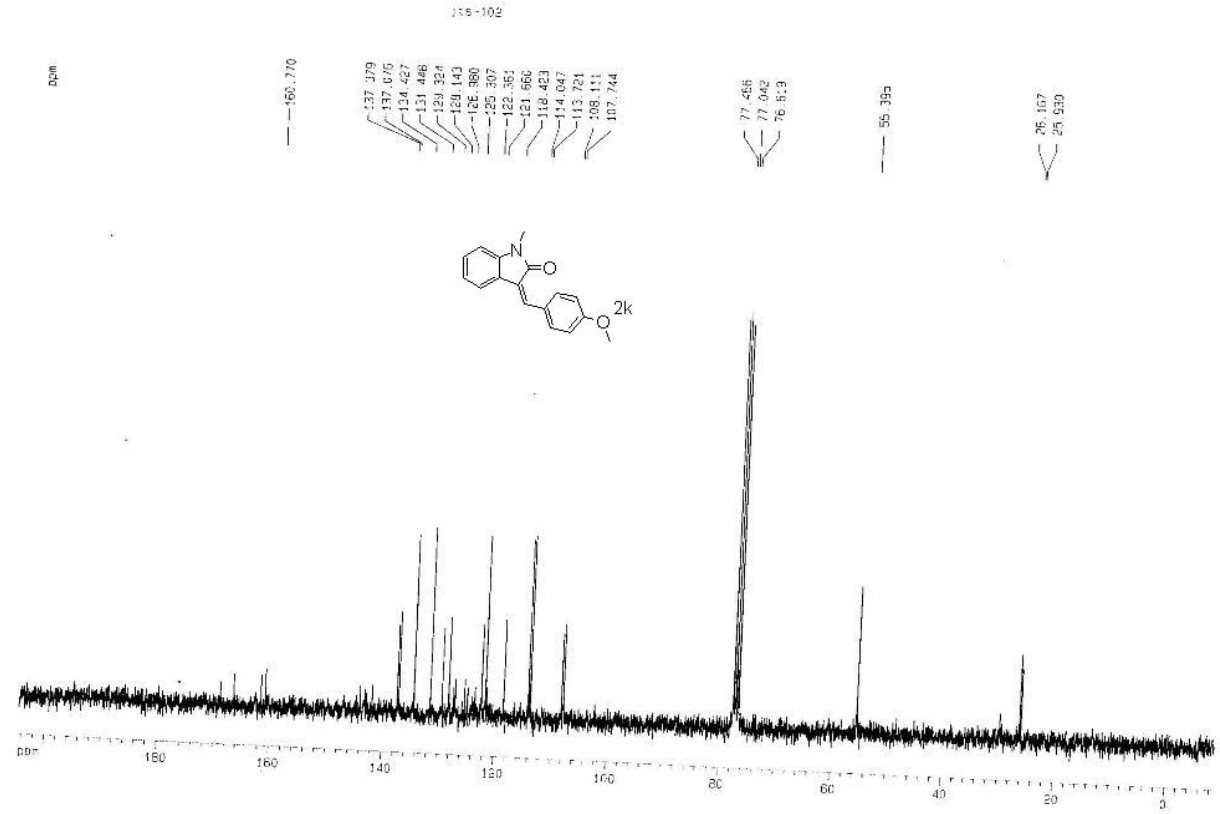
(*Z*)-1-Methyl-3-(4-methylbenzylidene)indolin-2-one (2j)



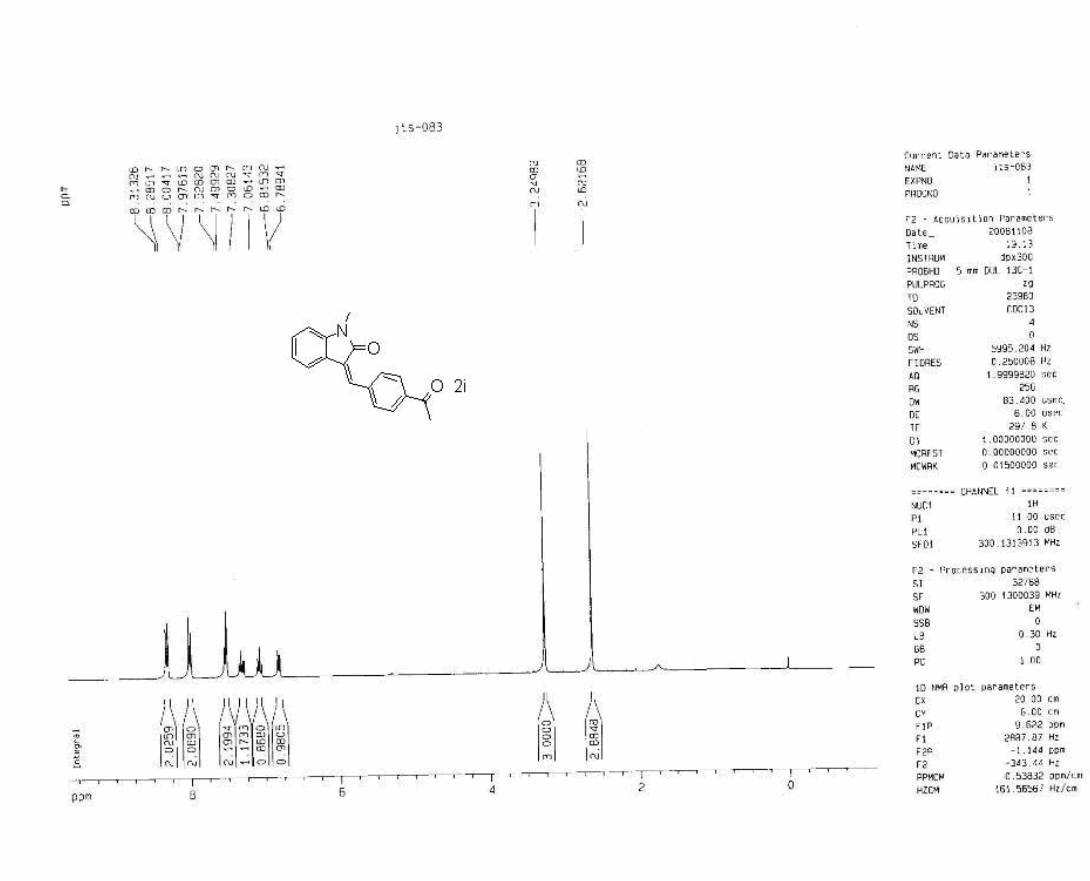


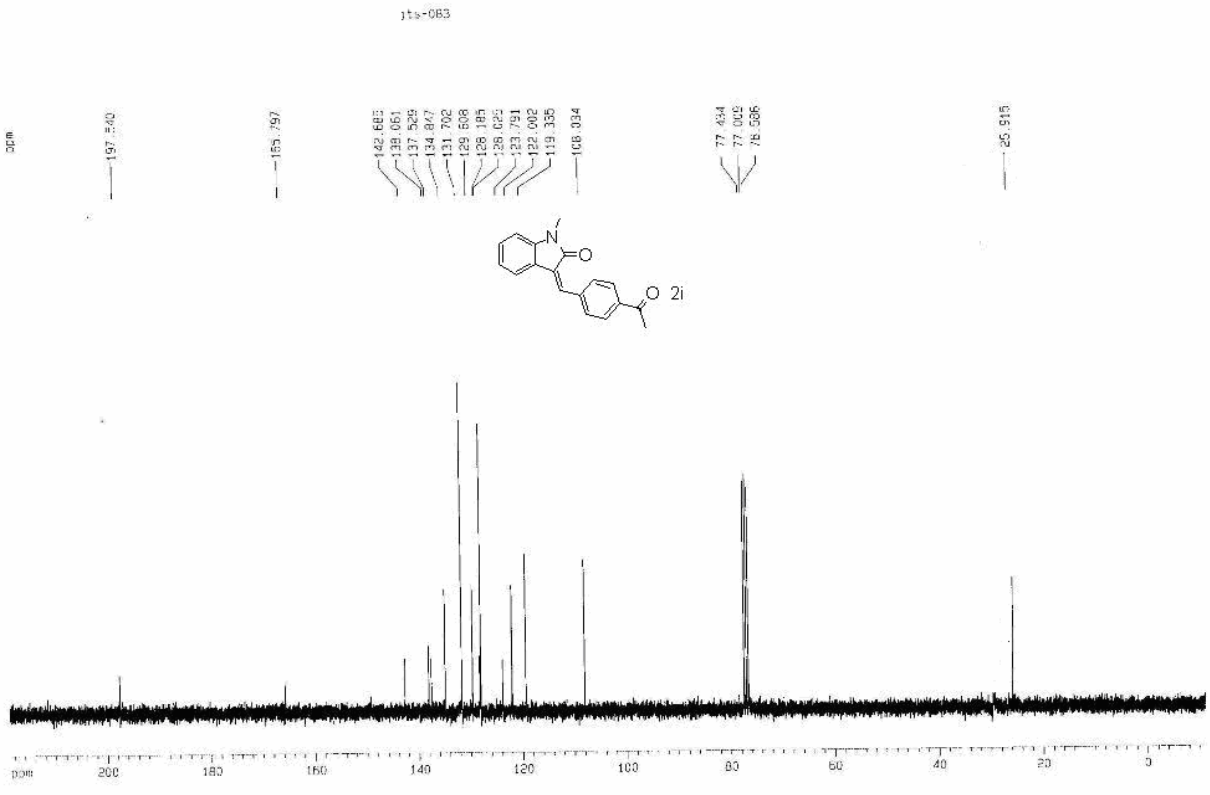
(*Z*)-3-(4-Methoxybenzylidene)-1-methylindolin-2-one (2k)



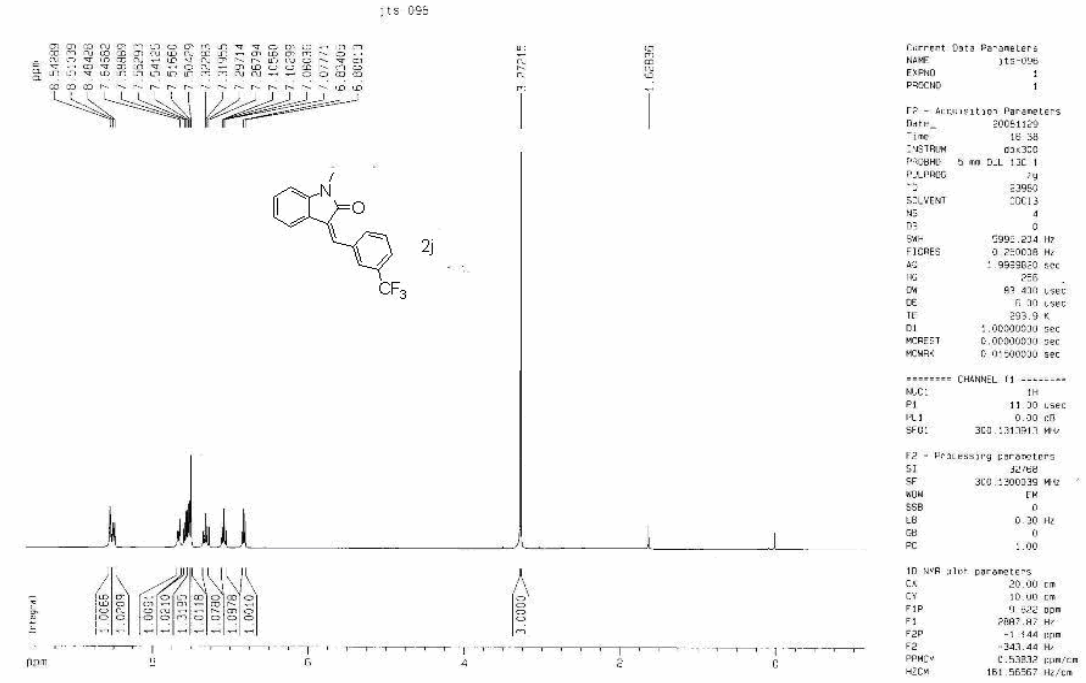


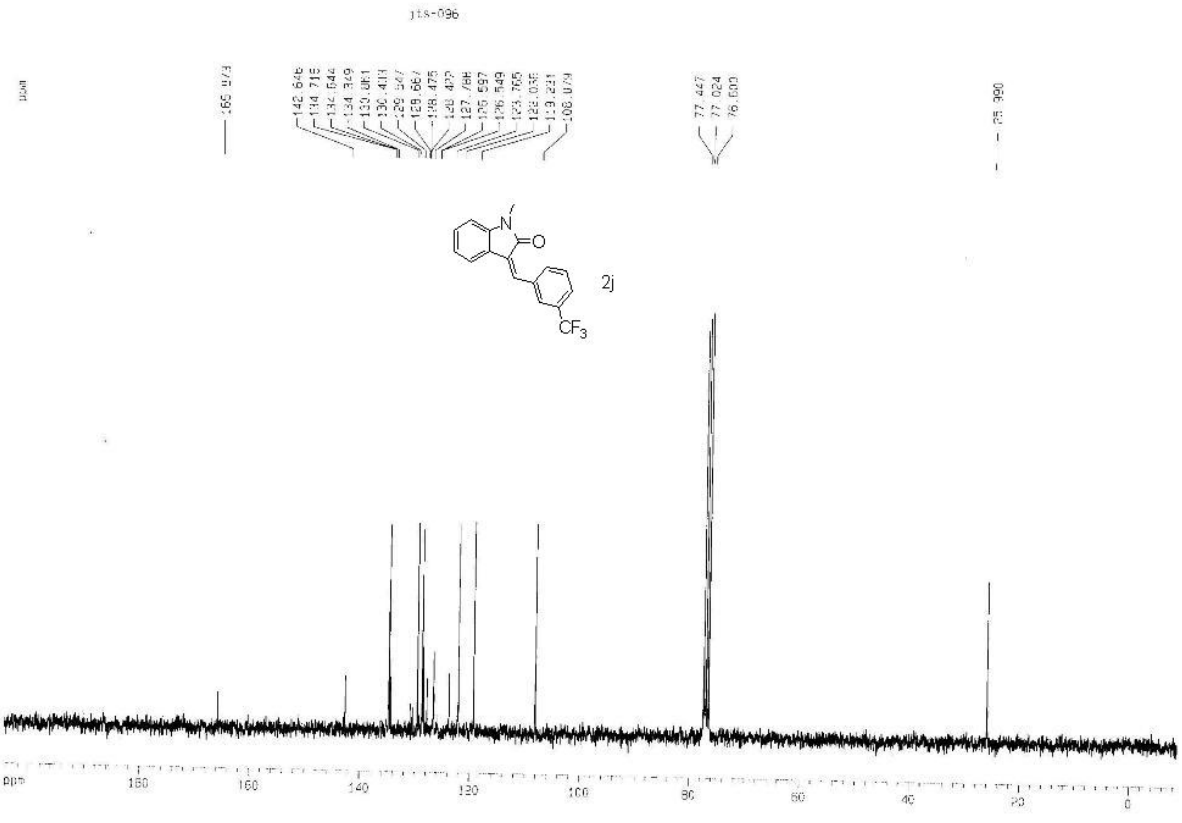
(*Z*)-3-(4-Acetylbenzylidene)-1-methylindolin-2-one (2l)



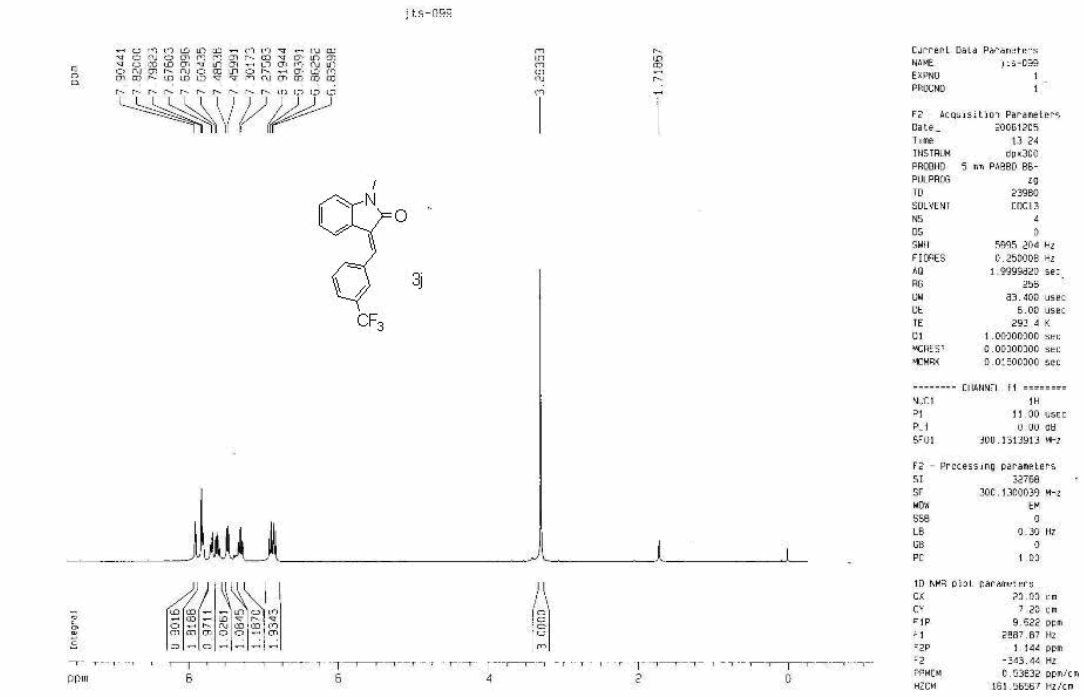


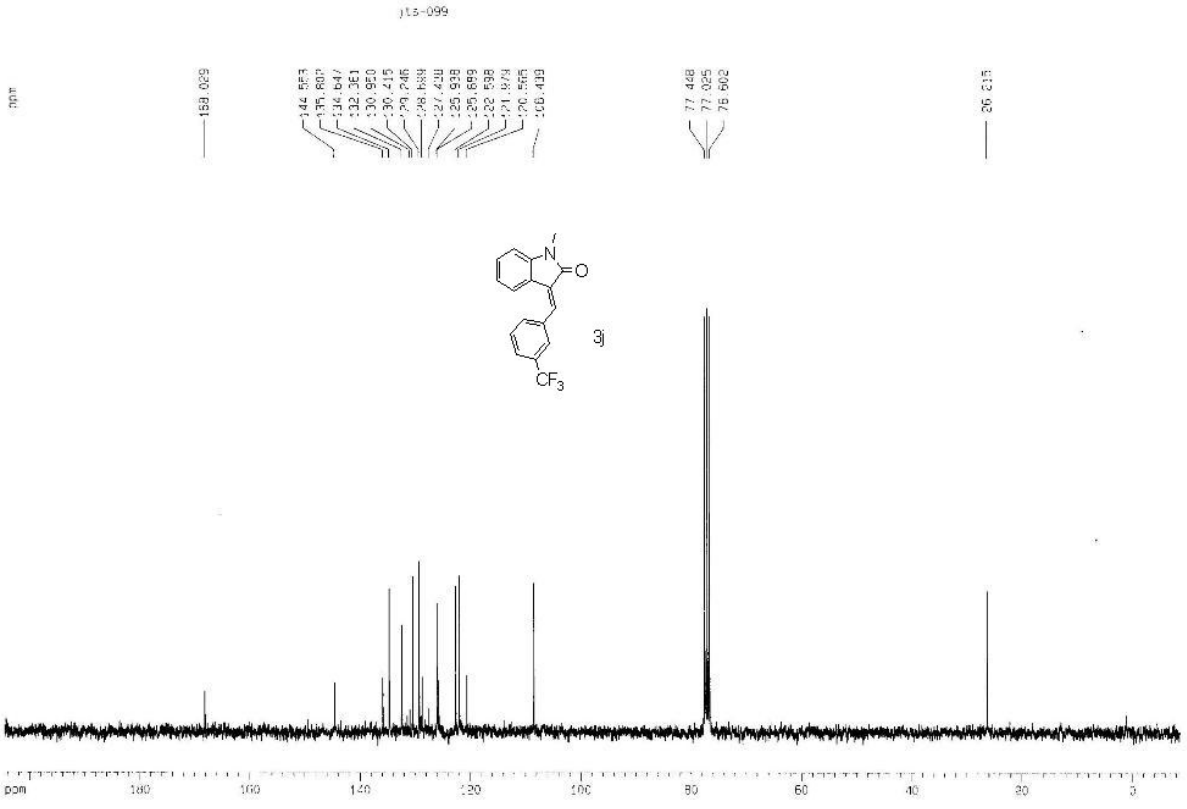
(*Z*)-1-Methyl-3-(3-(trifluoromethyl)benzylidene)indolin-2-one (2m)



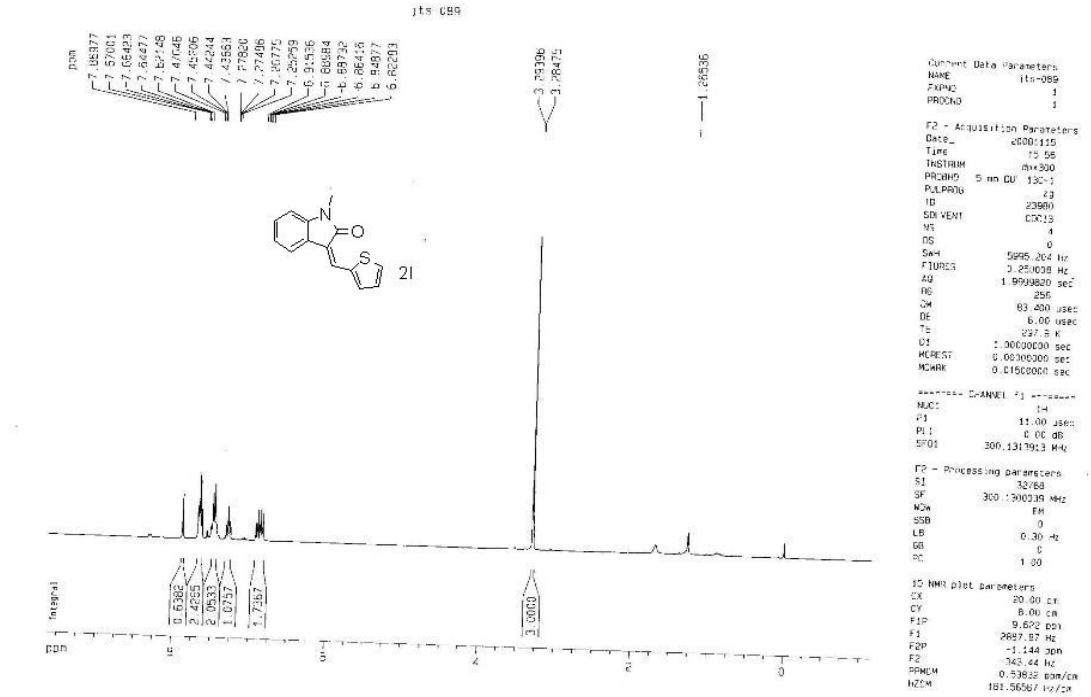


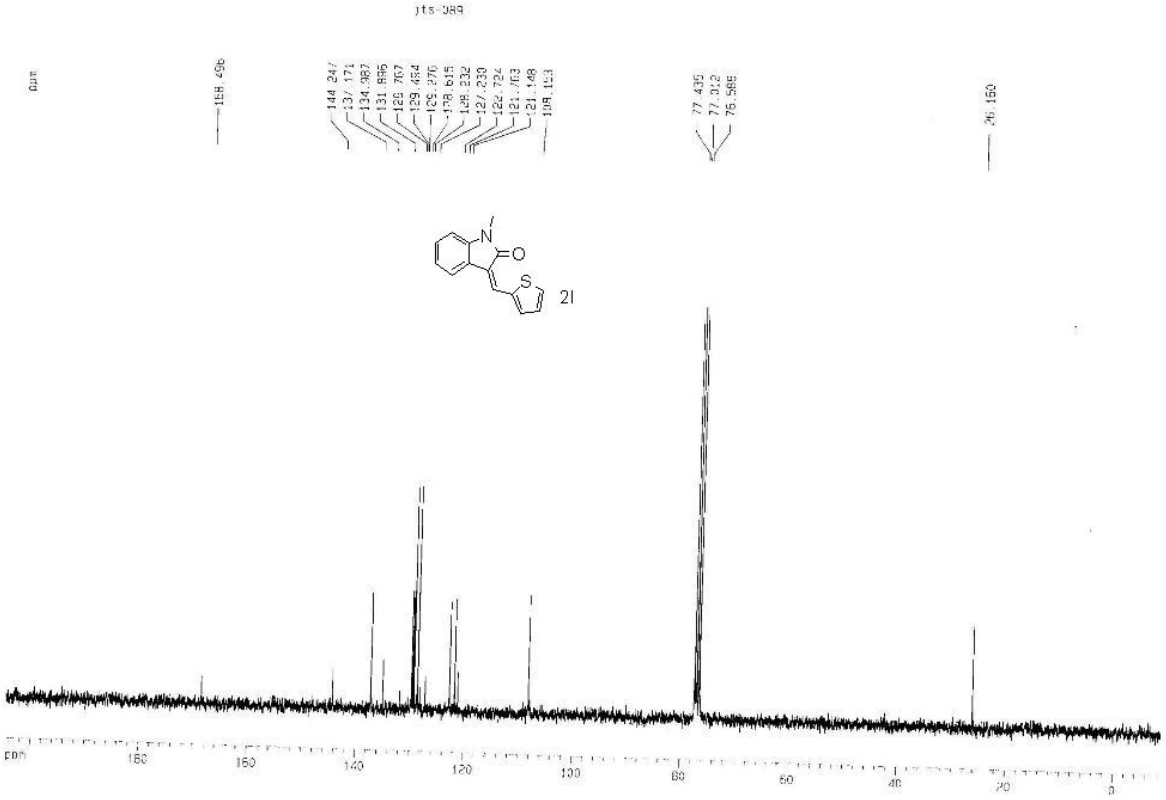
(*E*)-1-Methyl-3-(3-(trifluoromethyl)benzylidene)indolin-2-one (2m)



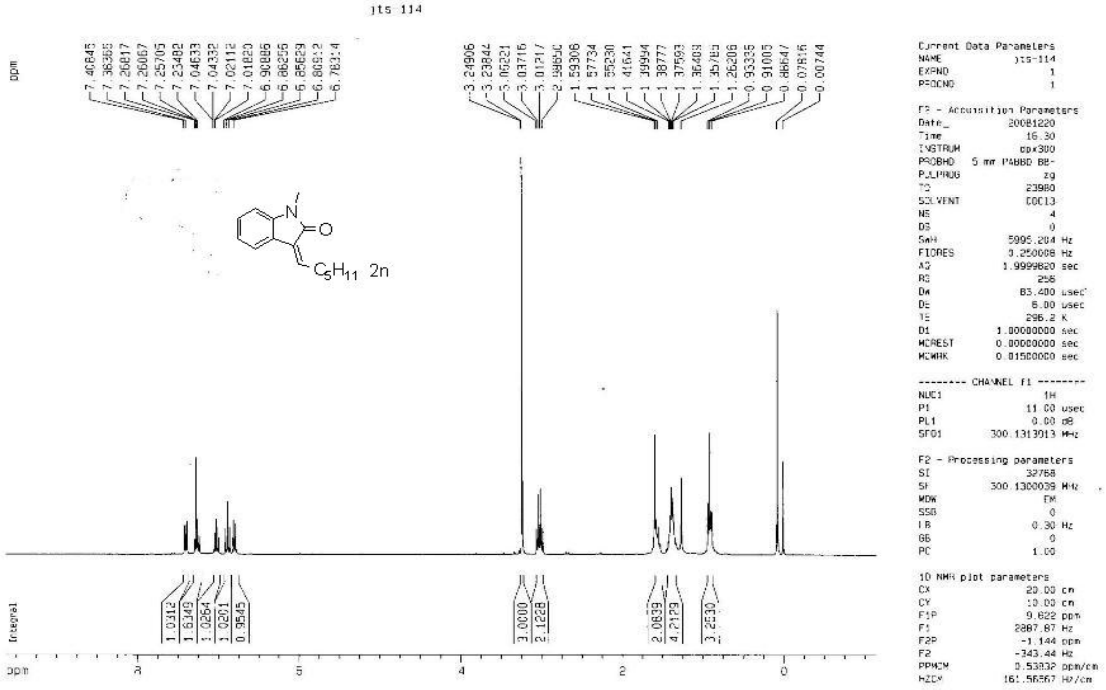


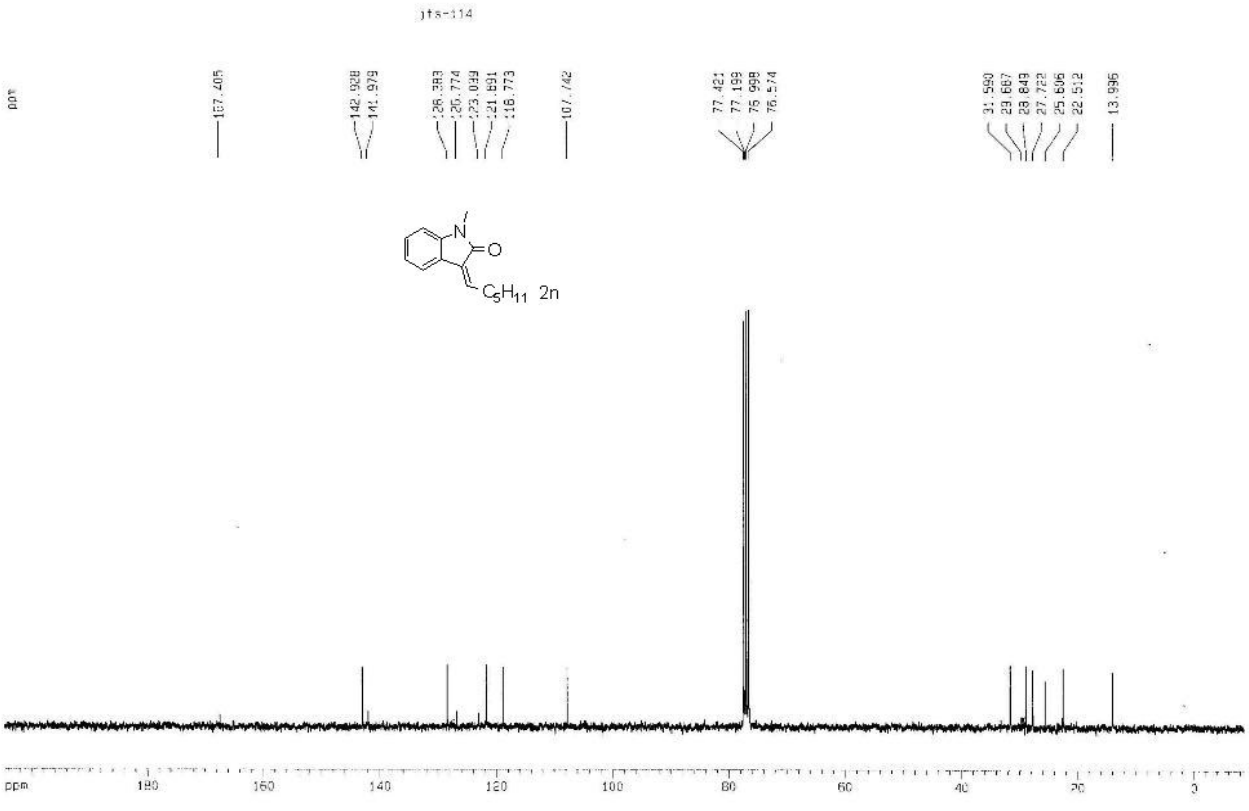
(*Z*)-1-Methyl-3-(thiophen-2-ylmethylene)indolin-2-one (2n)



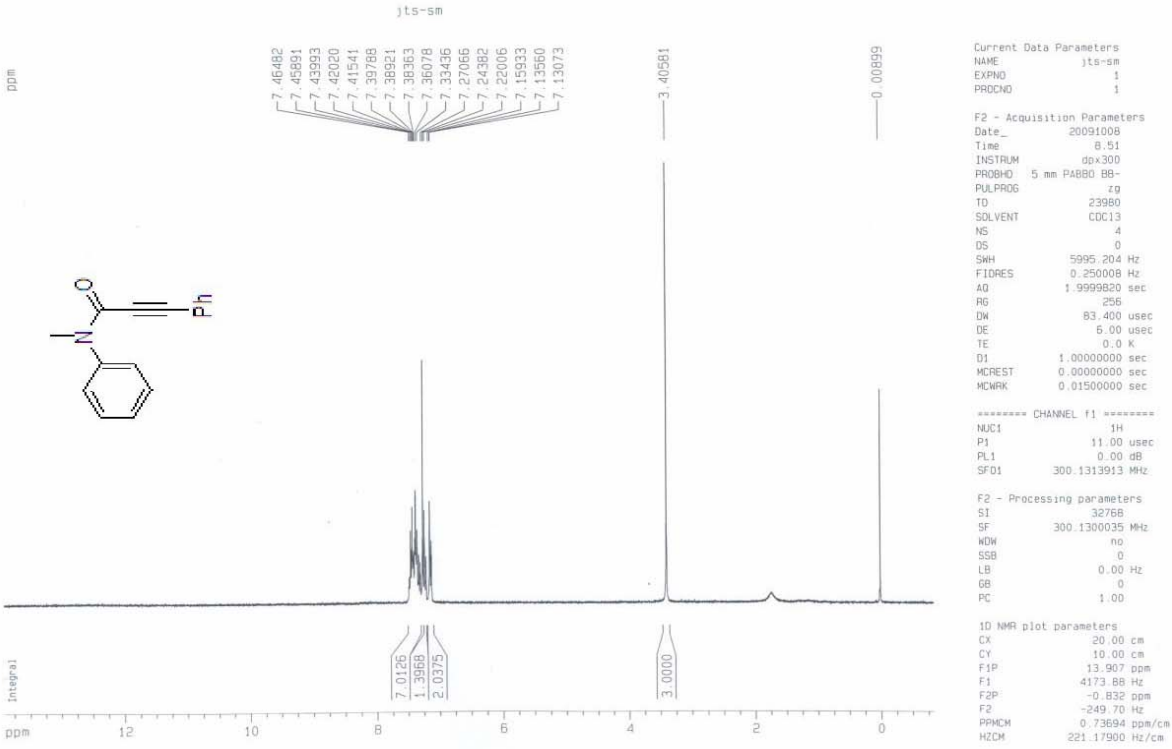


(*Z*)-3-Hexylidene-1-methylindolin-2-one (2o)

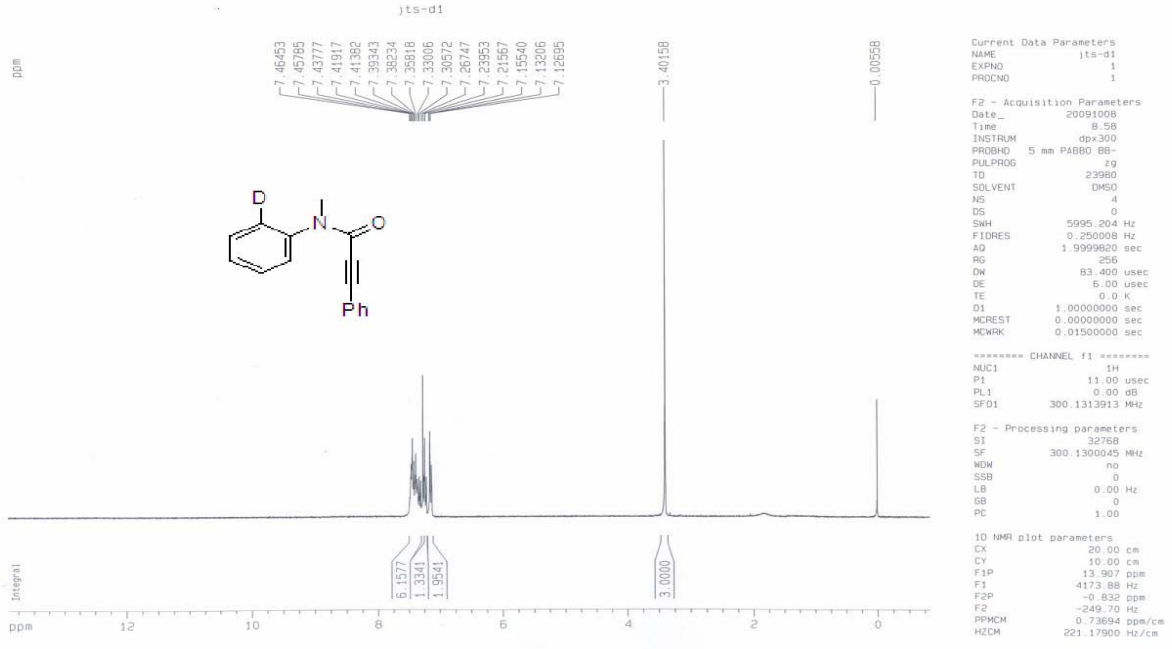




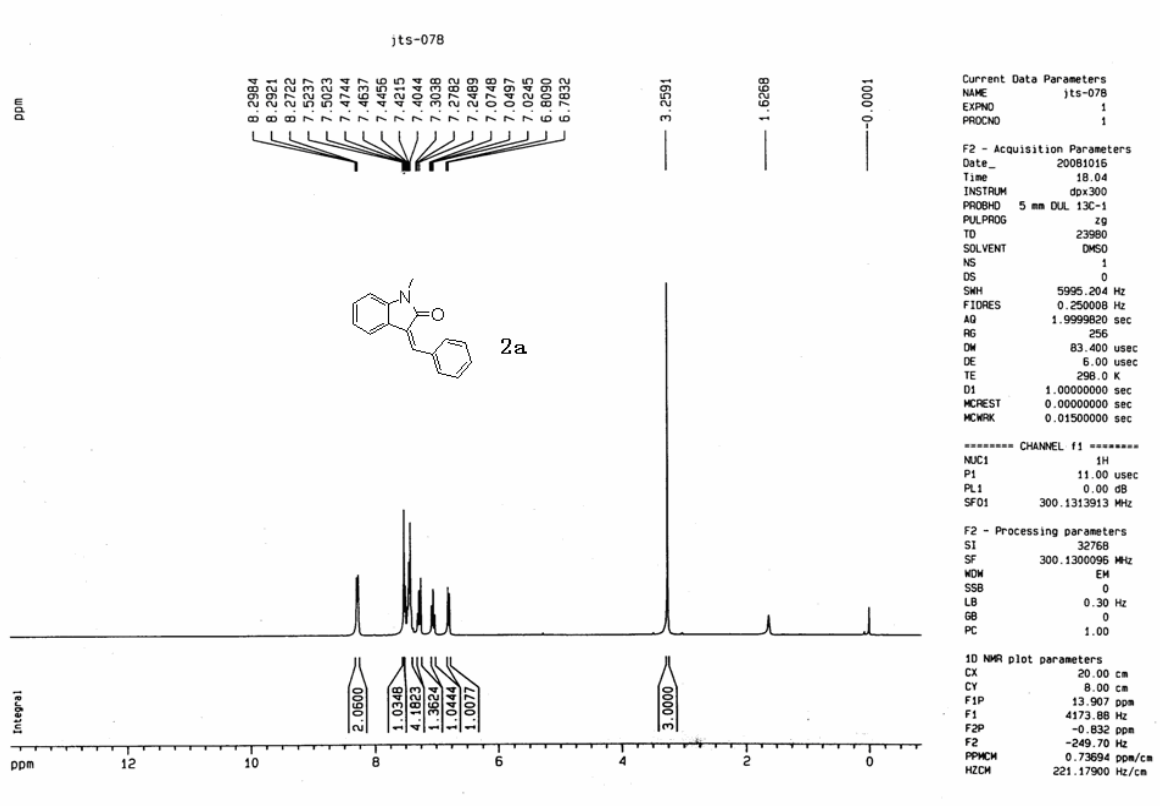
Substrate 1a



Substrate 1a-D1



(*Z*)-3a-D1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7.2782
7.2489
7.0748
7.0497
7.0245
6.8090
6.7832
3.2591
1.6268
-0.0001
2a
Integral
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1.0348
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1.3624
1.0444
1.0077
3.0000
ppm
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10
8
6
4
2
0
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PROCNO 1
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Time 18.04
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TD 23980
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DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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PL1 0.00 dB
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F2 - Processing parameters
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SF 300.1300096 MHz
WDW EM
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LB 0.30 Hz
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PC 1.00
1D NMR plot parameters
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CY 8.00 cm
F1P 13.907 ppm
F1 4173.88 Hz
F2P -0.832 ppm
F2 -249.70 Hz
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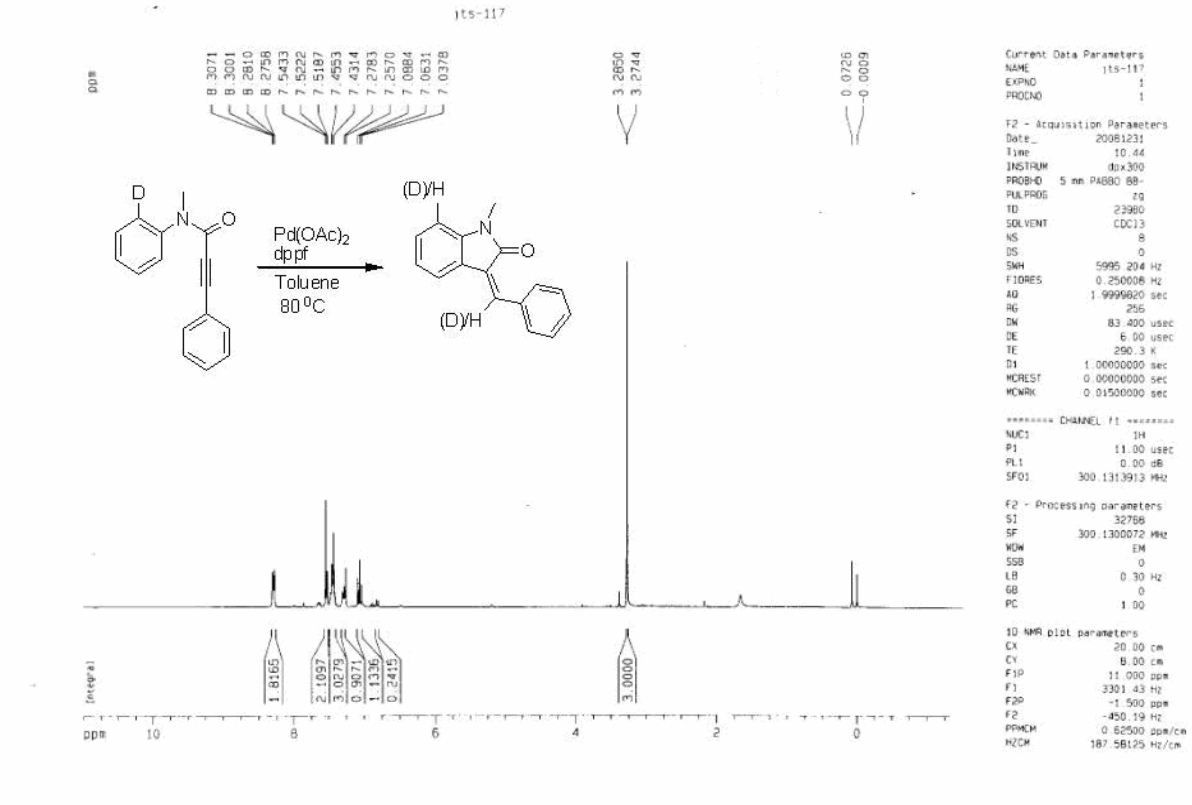
HZCM 221.17900 Hz/cm

(*Z*)-3a-D1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7.2570
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7.0631
7.0378
3.2850
3.2744
0.0726
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D
N
O
Pd(OAc)2
dppf
Toluene
80 °C
(D)/H
(D)/H
Integral
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3.0000
ppm
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8
6
4
2
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PROCNO 1
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TD 23980
SOLVENT CDCl3
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FIDRES 0.250008 Hz
AQ 1.9999820 sec
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DE 6.00 usec
TE 290.3 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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1D NMR plot parameters
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CY 8.00 cm
F1P 11.000 ppm
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F2P -1.500 ppm
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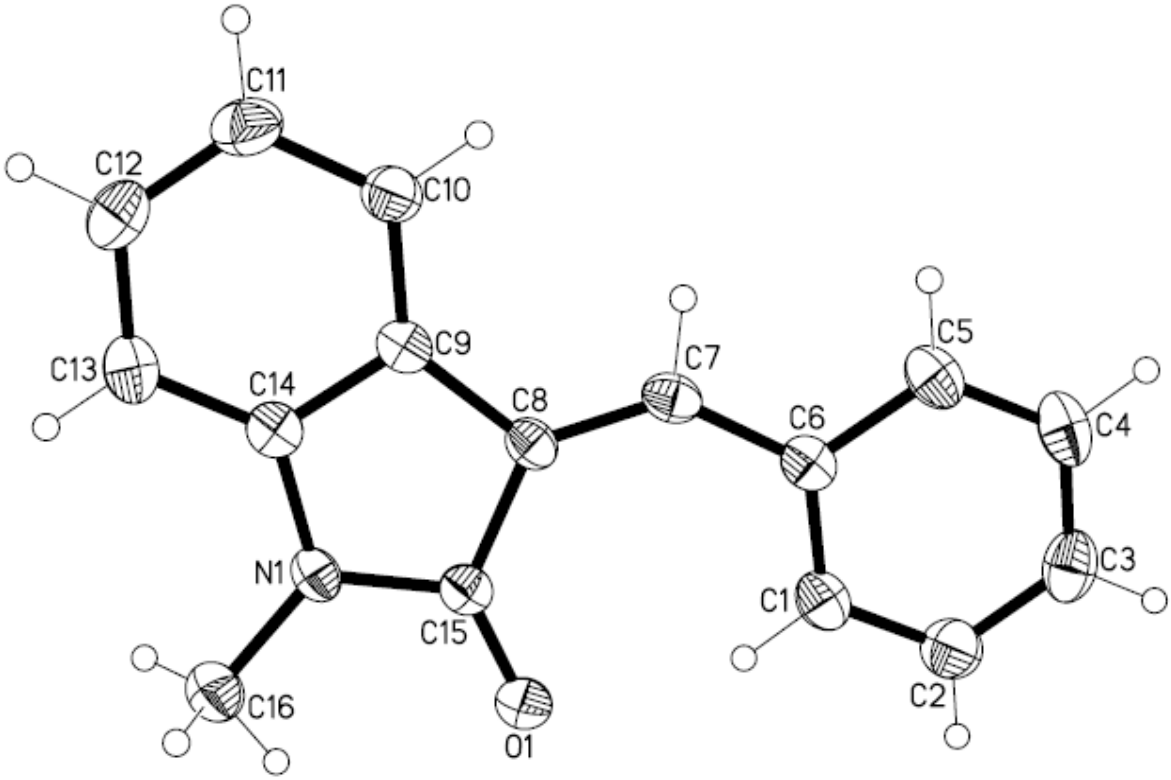
HZCM 187.58125 Hz/cm

ORTEP Diagram of the Single-Crystal X-Ray Structure of (*Z*)-**2a**.



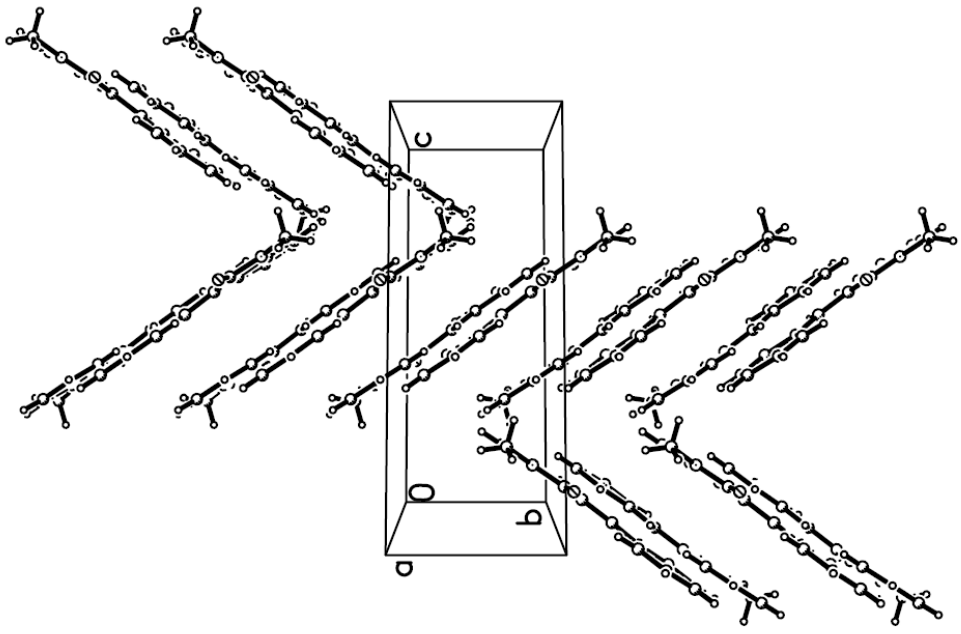


Table 1. Crystal data and structure refinement for 2241m.

Identification code	2241m
Empirical formula	C16 H13 N O
Formula weight	235.27
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 29.549(10) A alpha = 90 deg. b = 5.6866(18) A beta = 109.502(7) deg. c = 15.507(5) A gamma = 90 deg.
Volume	2456.2(14) A^3
Z, Calculated density	8, 1.272 Mg/m^3
Absorption coefficient	0.080 mm^-1
F(000)	992
Crystal size	0.29 x 0.19 x 0.17 mm
Theta range for data collection	2.68 to 25.02 deg.
Limiting indices	-33<=h<=34, -6<=k<=5, -18<=l<=17
Reflections collected / unique	6125 / 2164 [R(int) = 0.0420]
Completeness to theta = 25.02	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9866 and 0.9773
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2164 / 0 / 163

Goodness-of-fit on F^2	1.256
Final R indices [I>2sigma(I)]	R1 = 0.1013, wR2 = 0.1966
R indices (all data)	R1 = 0.1304, wR2 = 0.2101
Largest diff. peak and hole	0.211 and -0.216 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2241m.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2061(1)	5906(5)	1027(2)	52(1)
N(1)	1625(1)	3453(5)	1606(2)	39(1)
C(1)	1732(1)	9796(7)	-332(3)	50(1)
C(2)	1904(2)	11409(8)	-806(3)	59(1)
C(3)	1619(2)	13220(8)	-1266(3)	59(1)
C(4)	1154(2)	13421(7)	-1274(3)	61(1)
C(5)	982(2)	11814(7)	-796(3)	50(1)
C(6)	1266(1)	9965(6)	-304(2)	41(1)
C(7)	1051(1)	8384(6)	191(2)	41(1)
C(8)	1199(1)	6525(6)	750(2)	37(1)
C(9)	888(1)	5158(6)	1128(2)	37(1)
C(10)	413(1)	5365(7)	1059(3)	49(1)
C(11)	211(2)	3707(8)	1471(3)	59(1)
C(12)	481(2)	1845(8)	1942(3)	58(1)
C(13)	961(1)	1597(7)	2032(3)	48(1)
C(14)	1154(1)	3270(6)	1616(2)	38(1)
C(15)	1678(1)	5368(6)	1107(2)	37(1)
C(16)	2013(1)	1849(7)	2064(3)	55(1)

Table 3. Bond lengths [A] and angles [deg] for 2241m.

O(1)-C(15)	1.218(4)
N(1)-C(15)	1.375(4)
N(1)-C(14)	1.403(4)
N(1)-C(16)	1.452(4)
C(1)-C(2)	1.375(5)
C(1)-C(6)	1.396(5)
C(1)-H(1)	0.9300
C(2)-C(3)	1.370(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.375(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.375(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.401(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.458(5)
C(7)-C(8)	1.345(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.468(5)
C(8)-C(15)	1.490(5)
C(9)-C(10)	1.375(5)
C(9)-C(14)	1.394(5)
C(10)-C(11)	1.382(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.380(6)
C(11)-H(11)	0.9300
C(12)-C(13)	1.384(5)
C(12)-H(12)	0.9300
C(13)-C(14)	1.376(5)
C(13)-H(13)	0.9300
C(16)-H(16A)	0.9945
C(16)-H(16B)	0.9530
C(16)-H(16C)	0.9170
C(15)-N(1)-C(14)	111.4(3)
C(15)-N(1)-C(16)	123.6(3)
C(14)-N(1)-C(16)	125.0(3)
C(2)-C(1)-C(6)	121.0(4)
C(2)-C(1)-H(1)	119.5
C(6)-C(1)-H(1)	119.5

C(3)-C(2)-C(1)	120.4(4)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	120.4(4)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	119.1(4)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	122.1(4)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(1)-C(6)-C(5)	116.8(4)
C(1)-C(6)-C(7)	125.6(3)
C(5)-C(6)-C(7)	117.6(3)
C(8)-C(7)-C(6)	135.9(3)
C(8)-C(7)-H(7)	112.0
C(6)-C(7)-H(7)	112.0
C(7)-C(8)-C(9)	124.1(3)
C(7)-C(8)-C(15)	130.7(3)
C(9)-C(8)-C(15)	105.2(3)
C(10)-C(9)-C(14)	118.9(3)
C(10)-C(9)-C(8)	133.0(3)
C(14)-C(9)-C(8)	108.1(3)
C(9)-C(10)-C(11)	119.5(4)
C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.2
C(12)-C(11)-C(10)	120.3(4)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(13)	121.5(4)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(14)-C(13)-C(12)	117.0(4)
C(14)-C(13)-H(13)	121.5
C(12)-C(13)-H(13)	121.5
C(13)-C(14)-C(9)	122.7(3)
C(13)-C(14)-N(1)	128.7(3)
C(9)-C(14)-N(1)	108.6(3)
O(1)-C(15)-N(1)	122.7(3)
O(1)-C(15)-C(8)	130.6(3)
N(1)-C(15)-C(8)	106.7(3)
N(1)-C(16)-H(16A)	104.9
N(1)-C(16)-H(16B)	108.1

H(16A)-C(16)-H(16B)	107.2
N(1)-C(16)-H(16C)	112.1
H(16A)-C(16)-H(16C)	110.1
H(16B)-C(16)-H(16C)	113.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 2241m.
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)	38(2)	51(2)	65(2)	9(1)	15(1)	4(1)
N(1)	41(2)	35(2)	41(2)	4(1)	12(1)	9(1)
C(1)	54(3)	51(3)	42(2)	5(2)	12(2)	7(2)
C(2)	56(3)	68(3)	56(3)	6(2)	21(2)	2(2)
C(3)	83(3)	51(3)	47(3)	1(2)	27(2)	-9(2)
C(4)	84(3)	50(3)	50(3)	12(2)	24(2)	15(2)
C(5)	59(3)	50(2)	42(2)	0(2)	18(2)	15(2)
C(6)	45(2)	40(2)	36(2)	-7(2)	12(2)	6(2)
C(7)	36(2)	44(2)	43(2)	-6(2)	12(2)	7(2)
C(8)	38(2)	37(2)	32(2)	-2(2)	9(2)	5(2)
C(9)	38(2)	39(2)	33(2)	-4(2)	10(2)	4(2)
C(10)	43(2)	57(3)	46(2)	4(2)	14(2)	5(2)
C(11)	46(2)	74(3)	62(3)	-2(3)	26(2)	1(2)
C(12)	65(3)	62(3)	56(3)	0(2)	32(2)	-9(2)
C(13)	64(3)	39(2)	43(2)	-1(2)	20(2)	5(2)
C(14)	43(2)	37(2)	32(2)	-9(2)	11(2)	1(2)
C(15)	38(2)	36(2)	34(2)	-5(2)	8(2)	1(2)
C(16)	52(2)	49(3)	60(3)	6(2)	14(2)	6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 2241m.

	x	y	z	U(eq)
H(1)	1929	8573	-25	60
H(2)	2216	11271	-815	71
H(3)	1741	14319	-1574	71
H(4)	958	14629	-1597	73
H(5)	668	11960	-800	60
H(7)	731	8755	96	50
H(10)	230	6612	737	59
H(11)	-109	3848	1430	70
H(12)	337	730	2206	70
H(13)	1144	355	2358	58
H(16A)	2266	2165	1786	66
H(16B)	2141	2299	2691	66
H(16C)	1919	307	1977	66

Table 6. Torsion angles [deg] for 2241m.