Supplementary Material (ESI) for Green Chemistry

"On water"-promoted direct alkynylation of isatins catalyzed by NHC-silver complex for efficient synthesis of 3-hydroxy-3-ethynylindolin-2-ones

Xiao-Pu Fu[a], Li Liu[a]*, Dong Wang[a], Yong-Jun Chen[a] and Chao-Jun Li[b]*

[a] Beijing National Laboratory for Molecular Science (BNLMS), Laboratory for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences Beijing 100190, China, lliu@iccas.ac.cn

[b] Department of Chemistry, McGill University, Montreal, Quebec, H3A 2K6 Canada. *Fax:+1(514)3983797; Tel: +1(514)3988457;* cj.li@mcgill.ca

Supporting Information

1. General Method

All the ^{1}H and ^{13}C NMR were recorded on Bruker-AV 300 spectrometer and chemical shifts reported in $CDCl_3$ or DMSO-d_6 with tetramethylsilane as an internal standard. IR spectra were recorded on a Bruker tensor 27 infrared spectrometer. Melting points were measured on Beijing-Tiker X-4 apparatus without correction. HRMS spectra were recorded on GCT-Mass Micromass spectrometer. Common reagents were purchased from commercial sources and were used without further purification. Column chromatography was performed using silica gel (200-300mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates.

2. General procedure for the synthesis of *N*-heterocyclic carbene (NHC) silver complexes 1a-g

The N-Heterocyclic carbene-silver complexes **1a-g** were synthesized according to the procedure reported in literatures [1, 2,3].

3. General procedure for the synthesis of N-benzylisatins and N-Methylisatin

N-benzylisatins and N-Methylisatin were prepared by alkylating isatin with propargyl bromide and methyl iodide according to the reported procedures[4, 5], respectively.

4. Typical procedure for the alkynylation of isatins catalyzed by NHC-Ag complexes on water

To a mixture of N-benzylisatine **2a** (118.7mg, 0.5mmol) and ImesAgCl **1a** (11.2 mg, 5 mo%) in water (2 mL) were added phenylacetylene **3a** (110 µL, 1.0 mmol) and DIPEA (8.5µL, 10 mol %). The reaction mixture was stirred for 4 hours at 40 ^{o}C and extracted with DCM (2 x 15 mL). The combined organic phase was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to give 1-benzyl-3-hydroxy-3-(phenylethynyl)indolin-2-one **4a** (168 mg, 98%).

References

1. T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay and J. A. C. Clyburne**,** *Inorg. Chem.***,** 2003**,** **42**, 1391–1393.

2. P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy and S. P. Nolan, *Organometallics*, 2005**, 24,** 6301–6309.

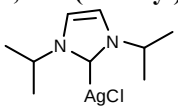
3. C. L. Winn, F. Guillen, J. Pytkowic, S. Roland, P. Mangeney, A. Alexakis, *J. Organomet. Chem.*, 2005, **690,** 5672.

4. T. Itoh, H. Ishikawa and Y. Hayashi, *Org. Lett.*, 2009, **11**, 3854–3857.

5. L. J. Macpherson, A. E. Dubin, M. J. Evans, F. Marr, P. G. Schultz, B. F. Cravatt and A. Patapoutian, *Nature*, 2007, **445**, 541-545.

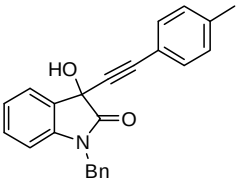
5. Characterization data

1,3-bis(isobutyl)imidazol-2-ylidene-silver(I) chloride (IiPrAgCl, 1f)



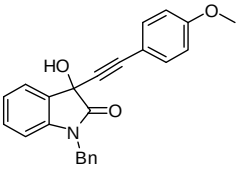
Pale brown solid, IR (KBr, cm^{-1}) 3101, 2969, 1215, 764; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47 (d, 12H, *J* = 6.6 Hz), 4.69 (m, 2H), 7.04(s, 2H); ^{13}C NMR ($CDCl_3$, 75MHz) δ 23.5, 53.9, 117.3, 176.0; ESI-HRMS(m/z): $[M-Cl]^+$ calcd. for $C_9H_{16}AgN_2$, 259.0354, found 259.0359.

1-benzyl-3-hydroxy-3-(p-tolylethynyl)indolin-2-one (4b)



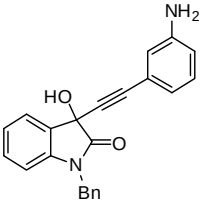
white solid, m.p.= 200-202 °C; IR (KBr, cm^{-1}) 3303, 2223, 1705, 1612; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 3.52 (brs, 1H), 4.93 (s, 2H), 6.72 (d, 1H, *J* = 7.8 Hz), 7.09(d, 2H, *J* = 8.1 Hz), 7.11 (t, 1H, *J* = 7.8 Hz), 7.21-7.32 (m, 6H), 7.39(d, 2H, *J* = 8.1 Hz) 7.61 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 21.5, 44.1,69.6, 84.8, 86.8, 109.9, 118.5, 123.7, 124.8, 127.1, 127.8, 128.9, 129.0,130.3, 132.0, 135.0, 139.3, 142.2, 174.2; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{19}NO_2Na$, 376.1307, found 376.1308.

1-benzyl-3-hydroxy-3-((4-methoxyphenyl)ethynyl)indolin-2-one (4c)



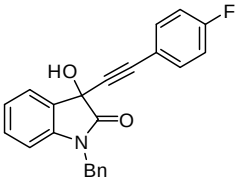
white solid, m.p.= 173-175 °C; IR (KBr, cm^{-1}) 3292, 2222, 1708, 1605, 1509; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.58 (brs, 1H), 3.80(s, 3H), 4.93(s, 2H), 6.71 (d, 1H, *J* = 7.8 Hz), 6.81 (d, 2H, *J* = 8.8 Hz), 7.11(t, 1H, *J* = 7.5 Hz), 7.21-7.32(m, 6H), 7.39 (d, 2H, *J* = 8.8 Hz), 7.61 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 44.1, 55.3, 69.7, 84.2, 86.7, 109.9, 113.6, 113.9, 123.7, 124.7, 127.1, 127.7, 128.9, 129.1, 130.3, 133.6, 135.0, 142.1, 160.1, 174.2; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{19}NO_3Na$, 392.1257, found 392.1257.

1-benzyl-3-hydroxy-3-((3-aminophenyl)ethynyl)indolin-2-one (4d)



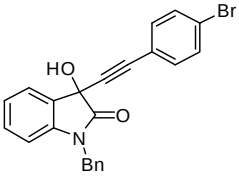
Pale yellow solid, m.p.= 192-194 °C; IR (KBr, cm^{-1}) 3303, 2229, 1692, 1607; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.28 (brs, 1H), 4.92 (s, 2H), 5.22 (brs, 2H), 6.51-6.60(m, 3H), 6.95(d, 1H, *J*=7.8 Hz), 7.00 (t, 1H, *J* = 7.8 Hz), 7.10 (t, 1H, *J* = 7.3 Hz), 7.27-7.36(m, 6H), 7.50(d, 1H, *J* =6.8 Hz); ^{13}C NMR (DMSO-D6, 75MHz) δ 42.7, 68.8, 85.4, 86.1, 109.7, 114.9, 116.4, 118.7, 121.4, 123.2, 124.2, 127.1, 127.5, 128.7, 129.2, 129.8, 130.4, 136.0, 141.4, 148.7, 173.4; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{18}N_2O_2Na$, 377.1259, found 377.1261.

1-benzyl-3-hydroxy-3-((4-fluorophenyl)ethynyl)indolin-2-one (4e)



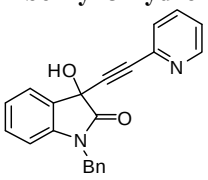
white solid, m.p.= 160-162 °C; IR (KBr, cm^{-1}) 3316, 2224, 1705, 1615, 1507; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.07 (brs, 1H), 4.92(s, 2H), 6.72(d, 1H, *J* = 7.8 Hz), 6.96 (t, 2H, *J* =8.8 Hz), 7.12 (t, 1H, *J* = 7.5 Hz), 7.25-7.30(m, 6H), 7.40-7.45(m, 2H), 7.61 (d, 1H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 44.1, 69.6, 85.3, 85.5, 109.9, 115.5(d, *J* =22.0 Hz), 117.7(d, *J* =3.0 Hz) , 123.8, 124.8, 127.1, 127.8, 128.9 129.0, 130.4, 134.0 (d, *J* =8.5 Hz), 134.9, 142.1, 162.9 (d, *J* =249.1 Hz), 174.3; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{16}FNO_2Na$, 380.1054, found 380.1057.

1-benzyl-3-hydroxy-3-((4-bromophenyl)ethynyl)indolin-2-one (4f)



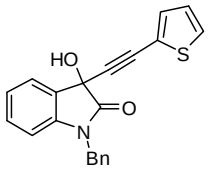
white solid, m.p.= 178-180 °C; IR (KBr, cm^{-1}) 3285, 2229, 1704, 1615, 1488; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.44 (brs, 1H), 4.91(s, 2H), 6.71(d, 1H, *J* = 7.8 Hz), 7.11 (t, 1H, *J* =7.4 Hz), 7.21-7.30 (m, 8H), 7.38 (d, 2H, *J* = 8.5 Hz),7.61 (d, 1H, *J* =7.4 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 44.1, 69.6, 85.4, 86.7, 110.0, 120.6, 123.4, 123.8, 124.8, 127.1, 127.8, 128.8, 128.9, 130.4, 131.5, 133.5, 134.9, 142.1, 174.2; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{16}BrNO_2Na$, 440.0256, found 440.0257.

1-benzyl-3-hydroxy-3-(pyridin-2-ylethynyl)indolin-2-one (4g)



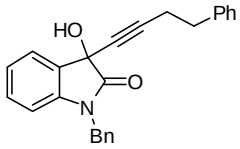
white solid, m.p.= 173-175 ^{o}C; IR (KBr, cm^{-1}) 3062, 1729, 1612; ^{1}H NMR (DMSO--d_6, 300 MHz) δ 4.88-5.00 (m, 2H), 6.98(d, 1H, *J* = 7.8 Hz), 7.29-7.43(m, 7H), 7.44 (s, 1H), 7.54 (t, 2H, *J* = 7.6 Hz), 7.82 (td, 1H, *J* =1.5, 7.7 Hz,), 8.56 (d, 1H, *J* =4.7 Hz); ^{13}C NMR (DMSO-D6, 75MHz) δ 42.8, 68.7, 83.9, 86.5, 109.9, 123.3, 124.0, 124.4, 127.2, 127.4, 127.5, 128.7, 129.8, 130.1, 135.9, 136.9, 141.3, 141.6, 150.1, 172.9; ESI-HRMS(m/z): $[M+H]^+$ calcd. for $C_{22}H_{17}N_2O_2$, 341.1280, found 341.1285.

1-benzyl-3-hydroxy-3-(thiophen-2-ylethynyl)indolin-2-one (4h)



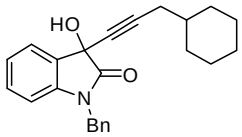
white solid, m.p.= 165-167 ^{o}C; IR (KBr, cm^{-1}) 3292, 2217, 1709, 1614, 1489; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.08 (brs, 1H), 4.91 (s, 2H), 6.71 (d, 1H, *J* = 7.8 Hz), 6.93 (t, 1H, *J* = 4.5 Hz),7.11 (t, 1H, *J* = 7.5 Hz),7.24-7.29 (m, 8H), 7.61 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 44.1, 69.7, 80.0, 89.2, 110.0, 121.5, 123.8, 124.8, 126.9, 127.1, 127.8, 128.2, 128.7, 128.9, 130.4, 133.5, 134.9, 142.1, 174.0; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{15}NO_2SNa$, 368.0715, found 368.0716.

1-benzyl-3-hydroxy-3-(4-phenylbut-1-ynyl)indolin-2-one (4i)



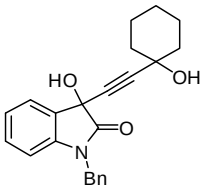
white solid, m.p.= 152-154 ^{o}C; IR (KBr, cm^{-1}) 3284, 2234, 1710, 1614, 1490; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.50 (t, 2H, *J* = 7.5 Hz), 2.80 (t, 2H, *J* = 7.5 Hz), 3.69(brs, 1H), 4.81-4.95 (m, 2H), 6.67 (d, 1H, *J* = 7.5 Hz), 7.07(t, 1H, *J* = 7.5 Hz), 7.13-7.28 (m, 11H), 7.48 (d, 1H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 21.2, 34.5, 44.0, 69.2, 77.8, 87.2, 109.7, 123.6, 124.6, 126.3, 127.1,127.7, 128.3, 128.5, 128.8, 129.2, 130.1, 135.0, 140.2, 142.0, 174.3; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{21}NO_2Na$, 390.1463, found 390.1465.

1-benzyl-3-hydroxy-3-(3-cyclohexylprop-1-ynyl)indolin-2-one (4j)



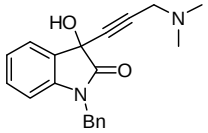
white solid, m.p.= 152-154 ^{o}C; IR (KBr, cm^{-1}) 3307, 2918, 2849, 2230, 1613, 1489; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90-1.01 (m, 2H), 1.12-1.23(m, 3H), 1.46-1.48(m, 1H), 1.61-1.84 (m, 5H), 2.12 (d, 2H, *J* = 6.6 Hz), 3.61 (brs, 1H), 4.81-4.98 (m, 2H), 6.68 (d, 1H, *J* = 7.5 Hz), 7.08 (t, 1H, *J* = 7.8 Hz), 7.20 (t, 1H, *J* = 7.5 Hz),7.26-7.29 (m, 5H), 7.52 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 26.0, 26.2, 26.6, 32.6, 37.0, 43.9, 69.3, 77.8, 87.1, 109.7, 123.6, 124.5, 127.1, 127.7, 128.8, 129.4, 130.1, 135.1, 142.0, 174.4; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{25}NO_2Na$, 382.1777, found 382.1778. .

1-benzyl-3-hydroxy-3-((1-hydroxycyclohexyl)ethynyl)indolin-2-one (4k)



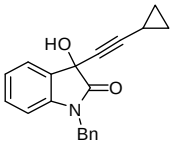
white solid, m.p.= 113-115 ^{o}C; IR (KBr, cm^{-1}) 3354, 2930, 2855, 2231, 1714, 1615; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18-1.26 (m, 1H), 1.43-1.61(m, 7H), 1.90(m, 2H), 3.11 (brs, 1H), 4.77 (brs, 1H), 4.83-4.96 (m, 2H), 6.68 (d, 1H, *J* = 7.8 Hz), 7.08 (t, 1H, *J* = 7.2 Hz), 7.18-7.28(m, 6H), 7.54 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz) δ 23.1, 25.0, 39.3, 39.4, 43.9, 68.5, 69.2, 80.9, 90.9, 109.8,123.8, 124.6, 127.0, 127.7, 128.8,129.3, 130.1, 134.9, 141.8, 174.7; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{23}NO_3Na$, 384.1570, found 384.1570.

1-benzyl-3-hydroxy-3-(3-(dimethylamino)prop-1-ynyl)indolin-2-one (4l)



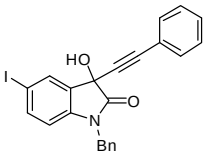
white solid, m.p.= 165-167 ^{o}C; IR (KBr, cm^{-1}) 2360, 1726, 1611, 1485, 1469; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 6H), 3.29-3.43(m, 2H), 4.78-4.98(m, 2H), 6.68 (d, 1H, *J* = 7.8 Hz), 7.06(t, 2H, *J* = 7.5 Hz), 7.16-7.29(m, 6H), 7.55 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz); δ 43.6, 43.8, 47.6, 68.9, 80.8, 83.4, 109.6, 123.5, 124.4, 127.1, 128.8, 129.9, 130.0, 135.2, 141.9, 174.5; ESI-HRMS (m/z): $[M+H]^+$ calcd. for $C_{20}H_{21}N_2O_2$, 321.1596, found 321.1598.

1-benzyl-3-hydroxy-3-(cyclopropylethynyl)indolin-2-one (4m)



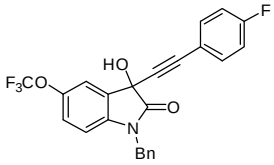
white solid, m.p.= 179-181 ^{o}C; IR (KBr, cm^{-1}) 3316, 2236, 1713, 1615; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.74-0.80 (m, 4H), 1.24-1.33(m, 1H), 3.31(brs, 1H), 4.89 (s, 2H), 6.68(d, 1H, *J* = 7.8 Hz), 7.08(t, 1H, *J* = 7.5 Hz), 7.21(t, 1H, *J* = 7.8 Hz), 7.26-7.34 (m, 5H); 7.51(d, 1H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75MHz); δ -0.4, 8.4, 8.5, 44.0, 69.2, 72.0, 91.2, 109.7, 123.6, 124.5, 127.1, 127.7, 128.8, 129.3, 130.1, 135.1, 142.0, 174.3 ; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{17}NO_2Na$, 326.1149, found 326.1152.

1-benzyl-3-hydroxy-5-iodo-3-(phenylethynyl)indolin-2-one (4n)



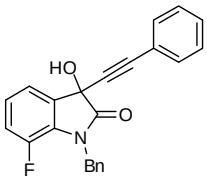
white solid, m.p.= 203-205 ^{o}C; IR (KBr, cm^{-1}) 3269, 2228, 1712, 1606, 1482; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.05(brs, 1H), 4.90 (s, 2H), 6.47(d, 1H, *J* = 8.1 Hz), 7.28(m, 8H), 7.45-7.47(m, 2H), 7.55(d, 1H, *J* =8.1 Hz), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz); δ44.1, 69.2, 84.8, 86.2, 87.2, 112.0, 121.3, 127.1, 128.0, 128.3, 129.0, 129.2, 131.0, 132.1, 133.6, 134.5, 139.1, 141.8, 173.5 ; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{16}INO_2Na$, 488.0116, found 488.0118.

1-benzyl-3-hydroxy-5-(trifluoromethoxy)-3-((4-fluorophenyl)ethynyl)indolin-2-one (4o)



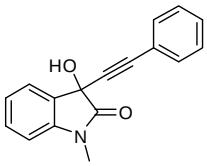
white solid, m.p.= 168-170 ^{o}C; IR (KBr, cm^{-1}) 3292, 2229, 1718, 1507; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.53(brs, 1H), 4.92(s, 2H), 6.69(d, 1H, *J* = 8.4 Hz), 6.96(t, 2H, *J* = 8.4 Hz), 7.10(d, 1H, *J* = 8.4 Hz), 7.29(m, 5H), 7.40-7.44(m, 2H), 7.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 75MHz); δ44.3, 69.5, 84.4, 86.2, 110.6, 115.6(d, *J*=22Hz), 117.4(d, *J*=3.4Hz), 118.7, 120.4(d, *J*=256Hz), 123.4, 127.1, 128.0, 129.0, 130.3, 134.1(d, *J*=8.5Hz), 134.4, 140.6, 145.5, 163.0(d, J=250Hz), 174.2; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{24}H_{15}F_4NO_3Na$, 464.0880, found 464.0880.

1-benzyl-3-hydroxy-7-fluoro-3-(phenylethynyl)indolin-2-one (4p)



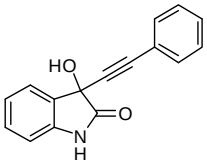
white solid, m.p.= 158-160 ^{o}C; IR (KBr, cm^{-1}) 3335, 2239, 1719, 1629, 1497; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.07(brs, 1H), 5.00-5.12 (m, 2H), 7.01-7.05(m, 2H), 7.26-7.33(m, 8H), 7.41-7.44(m, 3H); ^{13}C NMR ($CDCl_3$, 75MHz); δ45.7(d, *J*=4.6Hz), 69.6(d, *J*=2.6Hz), 85.0, 86.9, 118.4(d, *J*=19.4Hz), 120.7(d, *J*=3.0Hz), 121.4, 124.6(d, *J*=6.3Hz), 127.3, 127.6; 128.2, 128.6, 128.7, 129.0, 131.8, 132.0, 136.1, 147.5(d, *J*=243.8Hz), 174.2; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{16}FNO_2Na$, 380.1055, found 380.1057.

1-methyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (4q)



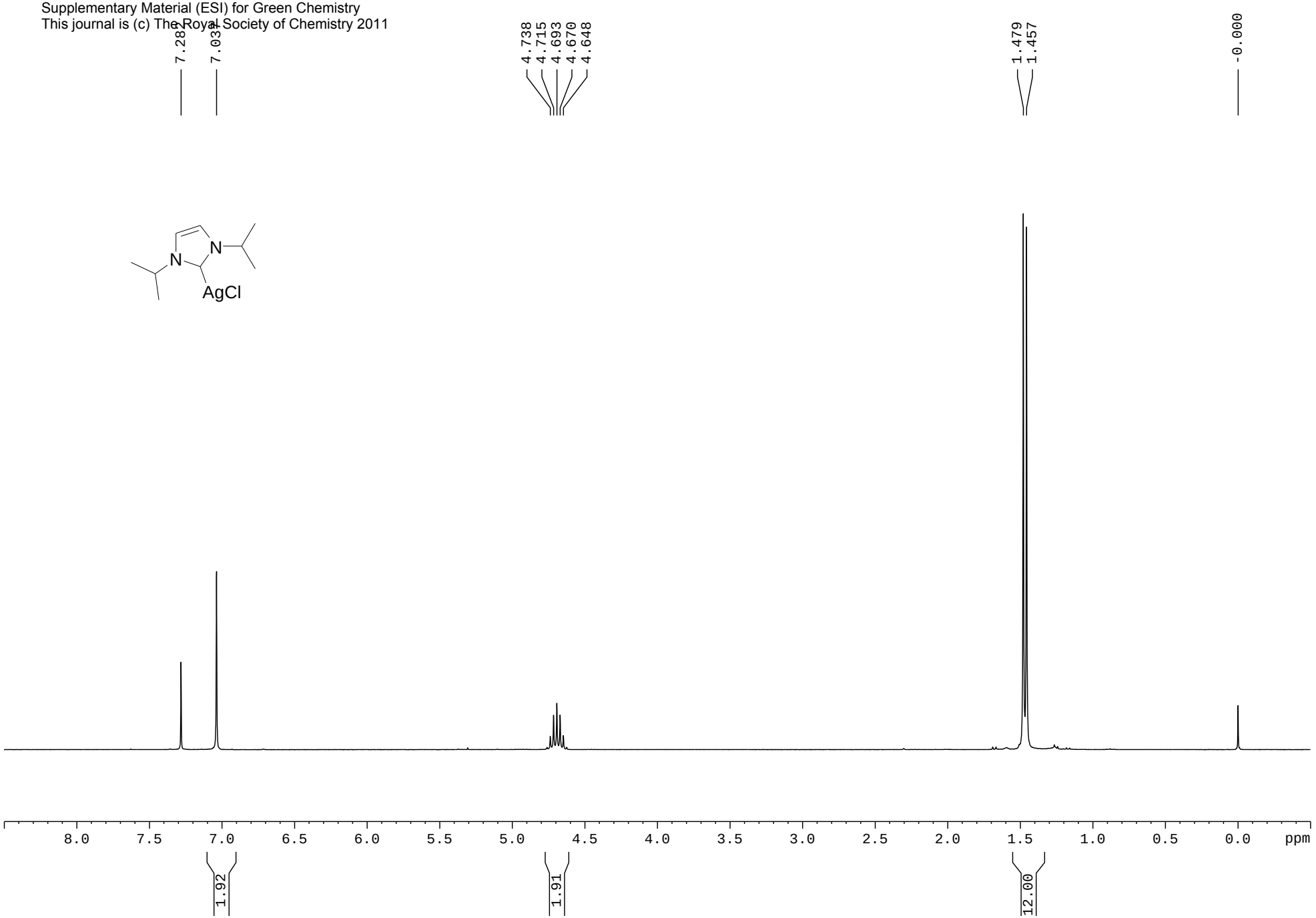
white solid, m.p.= 154-156 ^{o}C; IR (KBr, cm^{-1}) 3296, 2221, 1711, 1614; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23(s, 3H), 3.83(brs, 1H), 6.85(d, 1H, *J* = 8.4 Hz), 7.15(t, 1H, *J* = 7.5 Hz), 7.24-7.44(m, 6H), 7.61 (d, 1H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75MHz); δ 26.6, 69.5, 85.6, 86.2, 108.8, 121.3, 123.7, 124.7, 128.1, 128.8, 129.0, 130.4, 132.0, 142.9, 174.1; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{13}NO_2Na$, 286.0834, found 286.0839.

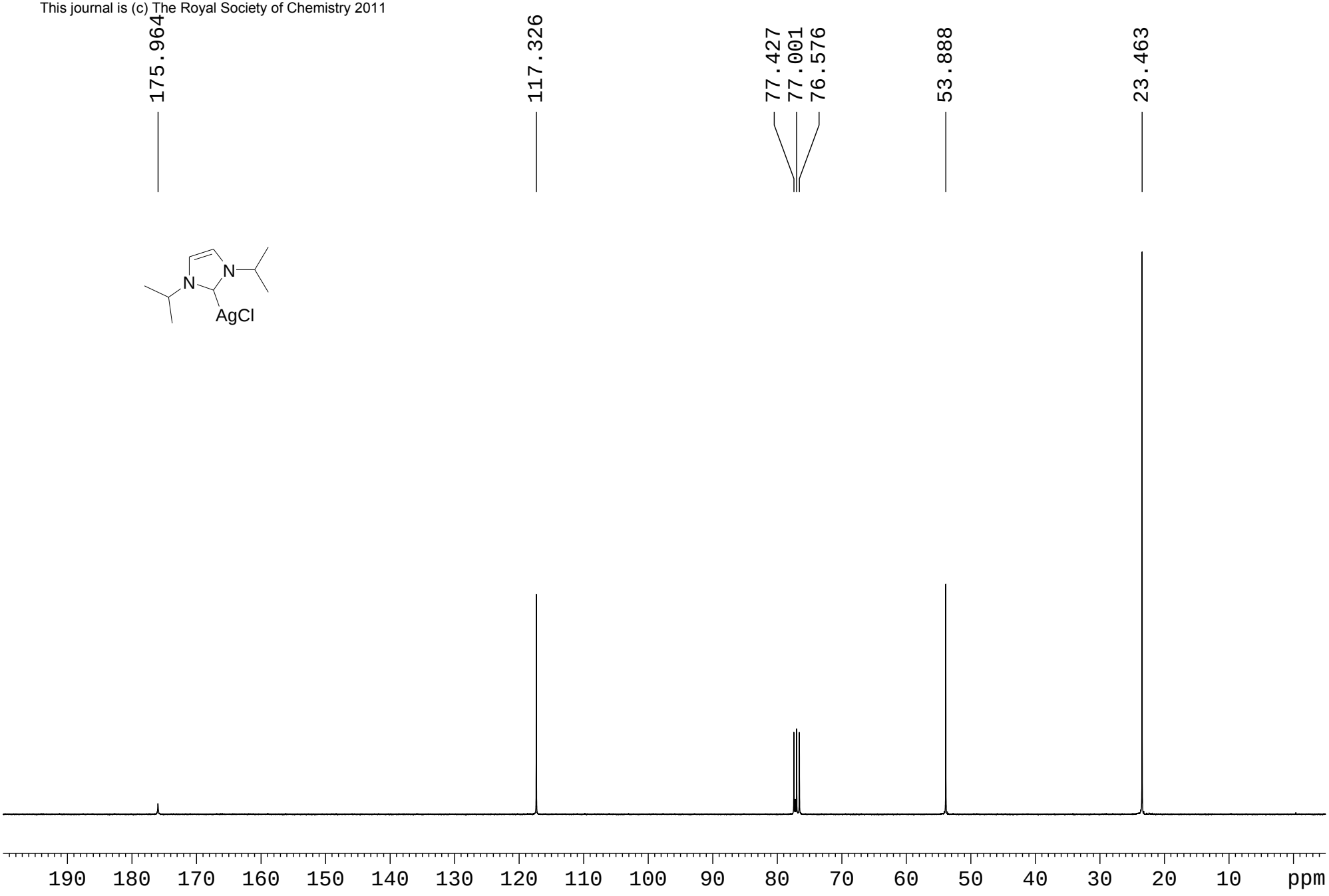
3-hydroxy-3-(phenylethynyl)indolin-2-one (4r)

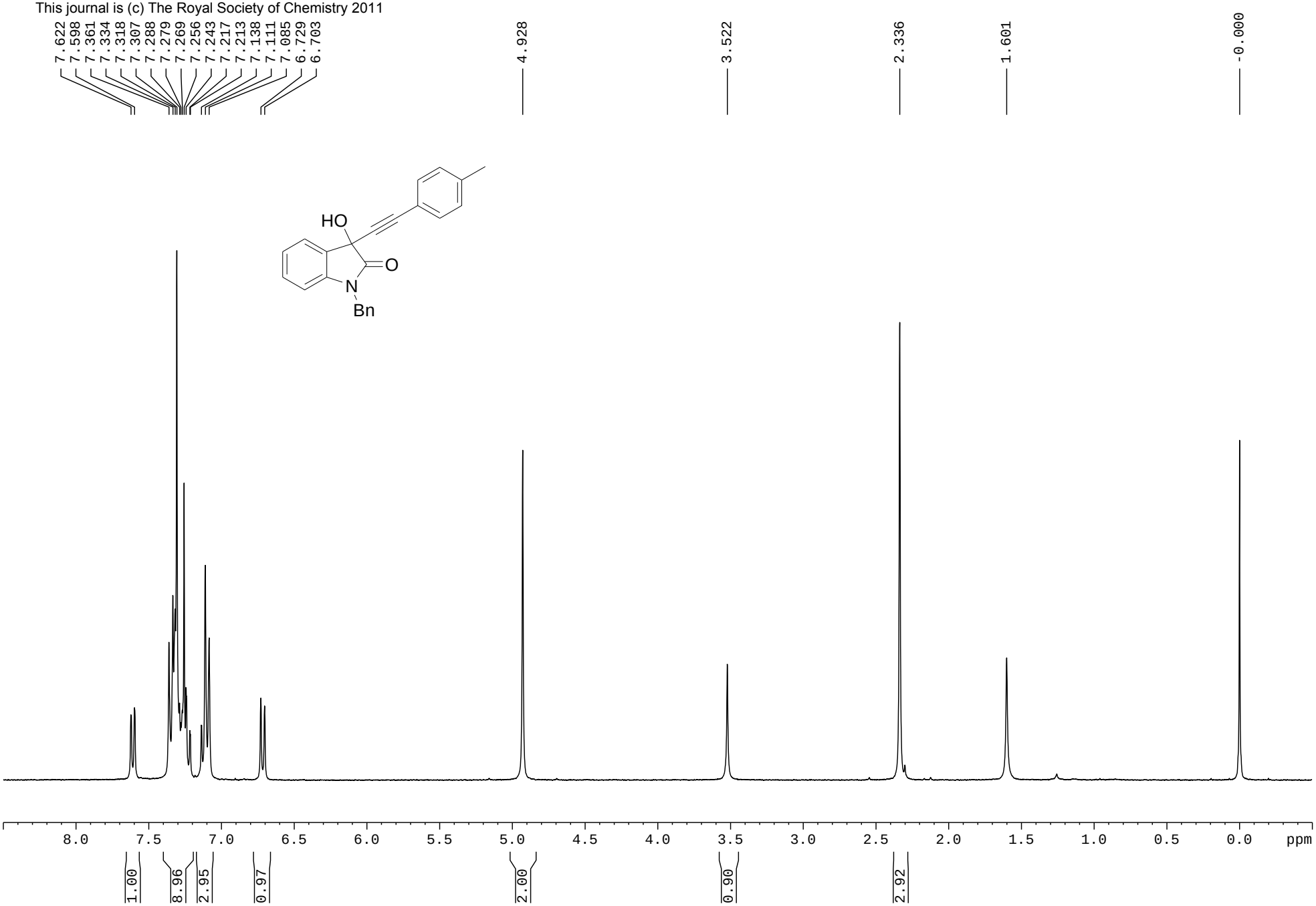


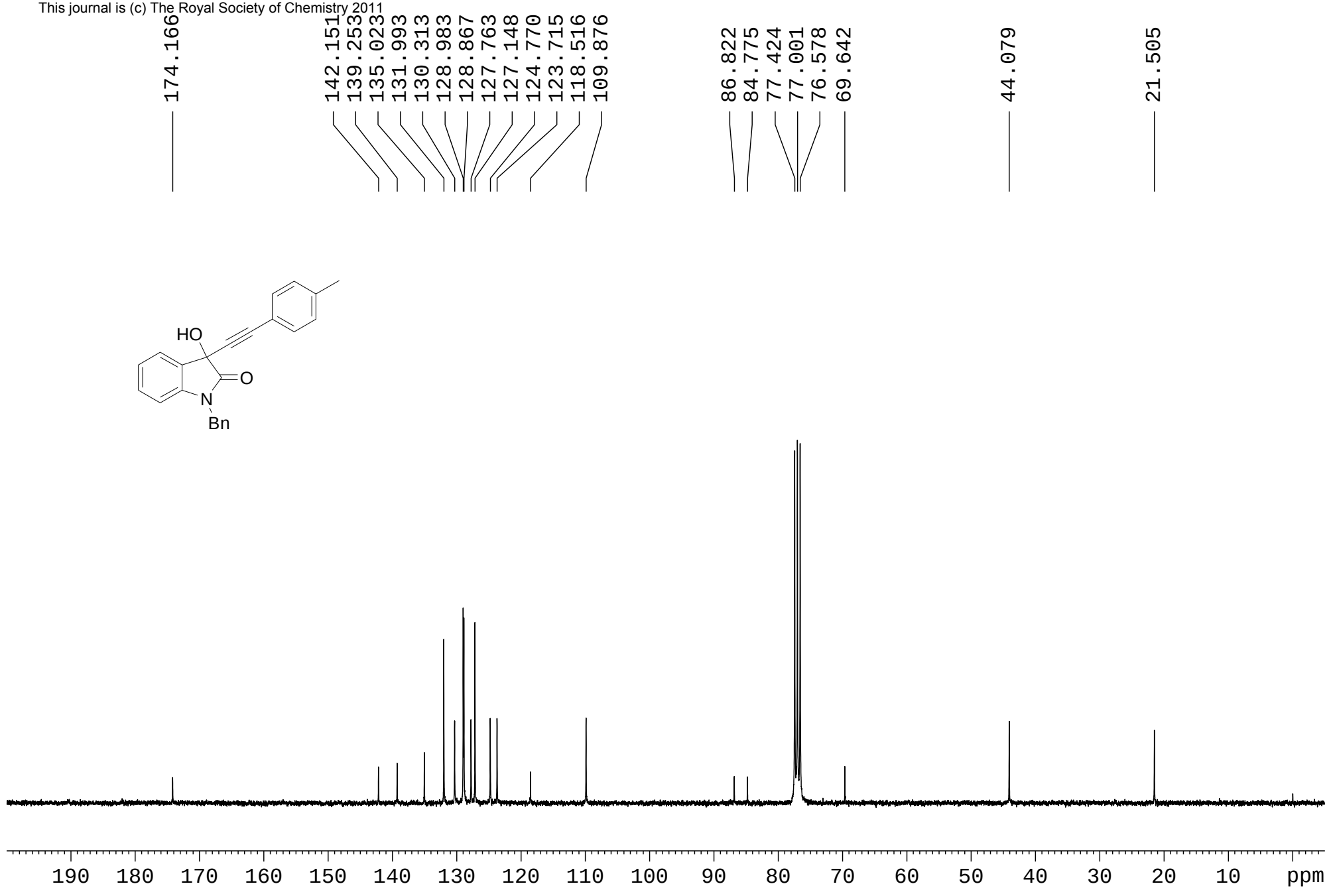
white solid, m.p.= 212-214 ^{o}C; IR (KBr, cm^{-1}) 3300, 2224, 1711, 1622; ^{1}H NMR (DMSO--d_6, 300 MHz) δ 6.86(d, 1H, *J* = 8.4 Hz), 7.04(t,1H, *J* = 7.5 Hz), 7.06(brs, 1H), 7.26(t,1H, *J* = 7.5 Hz), 7.39-7.49(m, 6H), 10.54(brs, 1H); ^{13}C NMR ($CDCl_3$, 75MHz); δ 69.0, 84.1, 87.9, 121.3, 122.3, 124.4，128.7, 129.0, 130.0, 131.0, 131.4, 141.2, 174.6; ESI-HRMS(m/z): $[M+Na]^+$ calcd. for $C_{16}H_{11}NO_2Na$, 272.0676, found 272.0682.

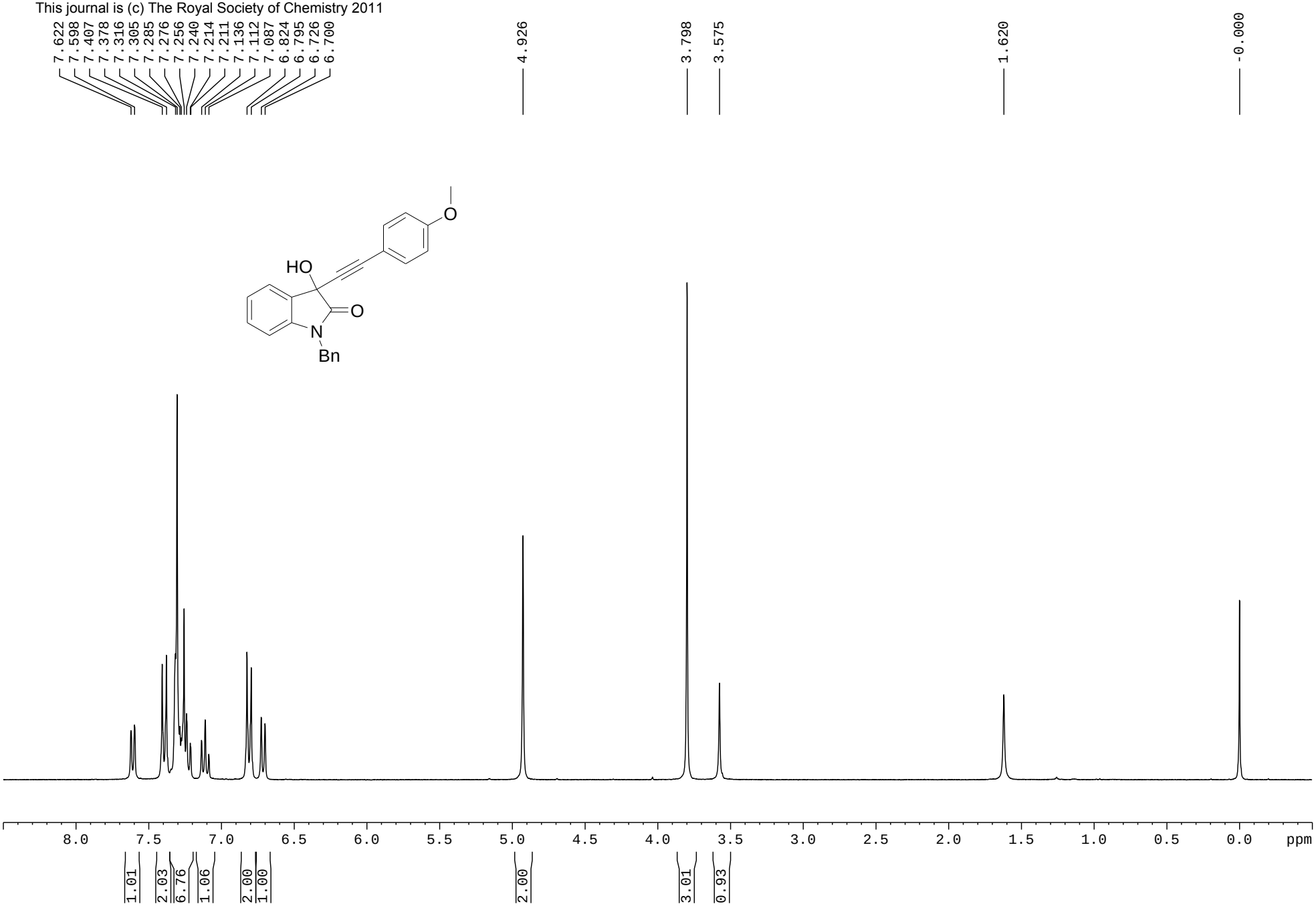
6. ^{1}H and ^{13}C NMR Spectra

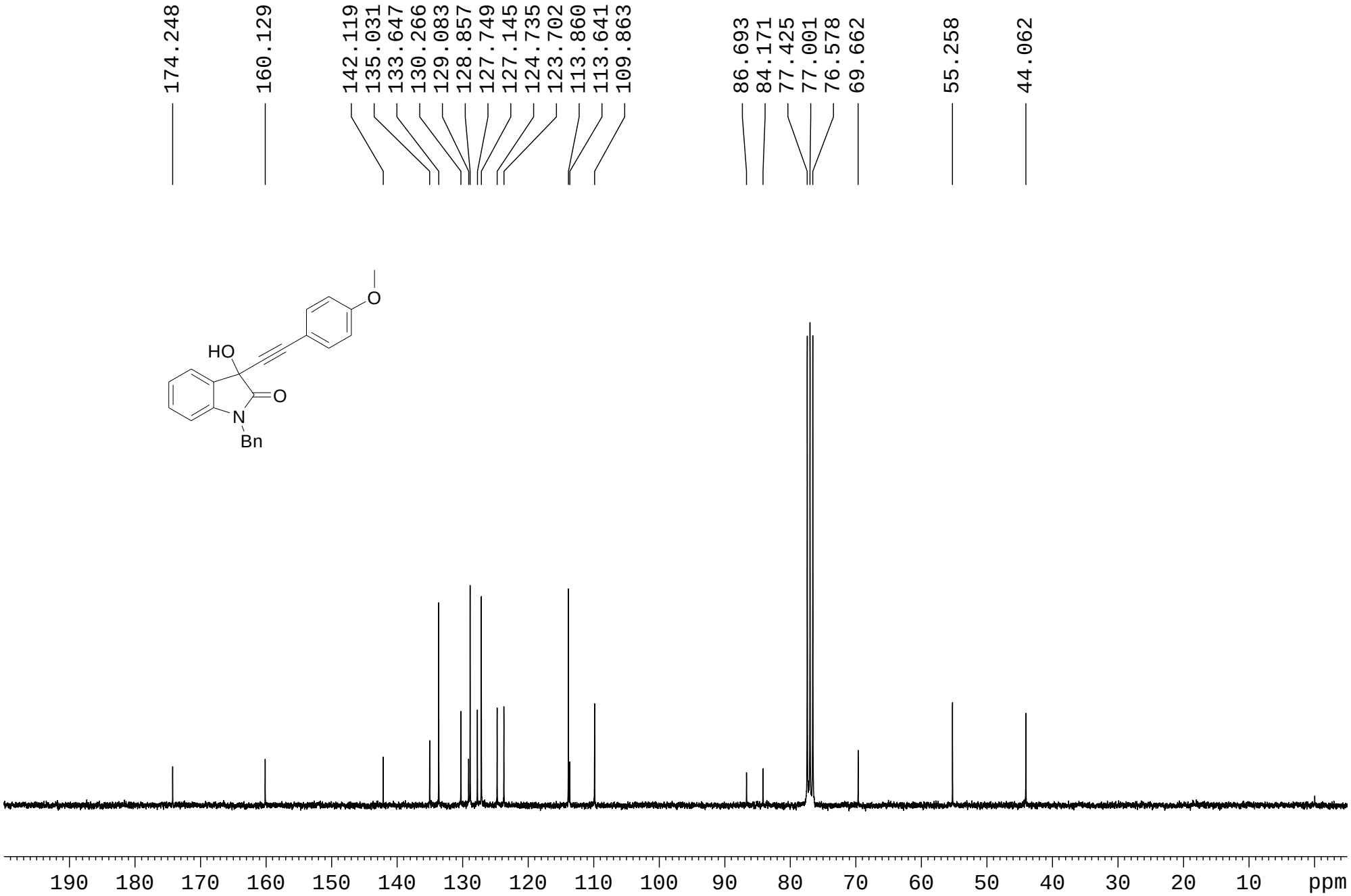


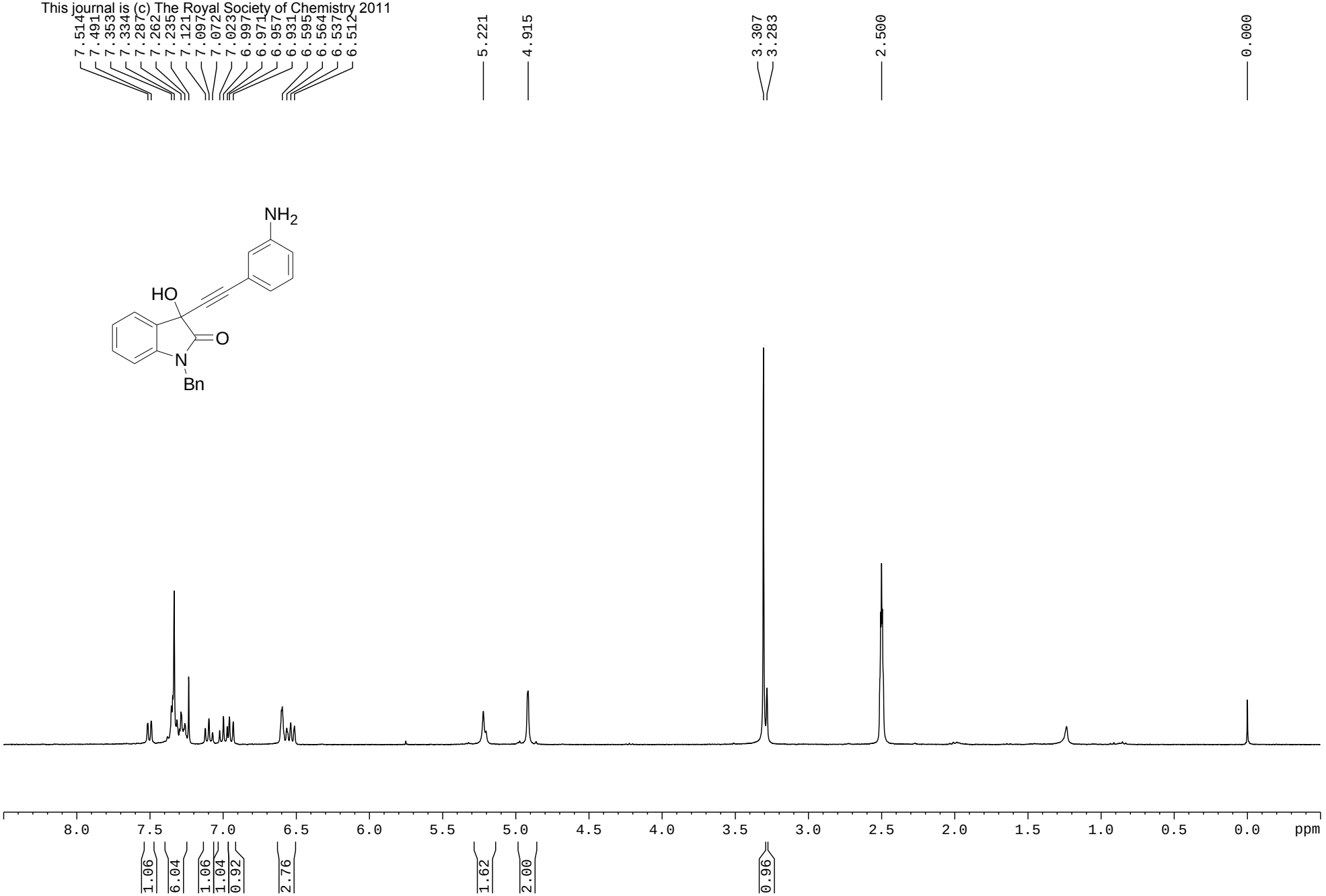


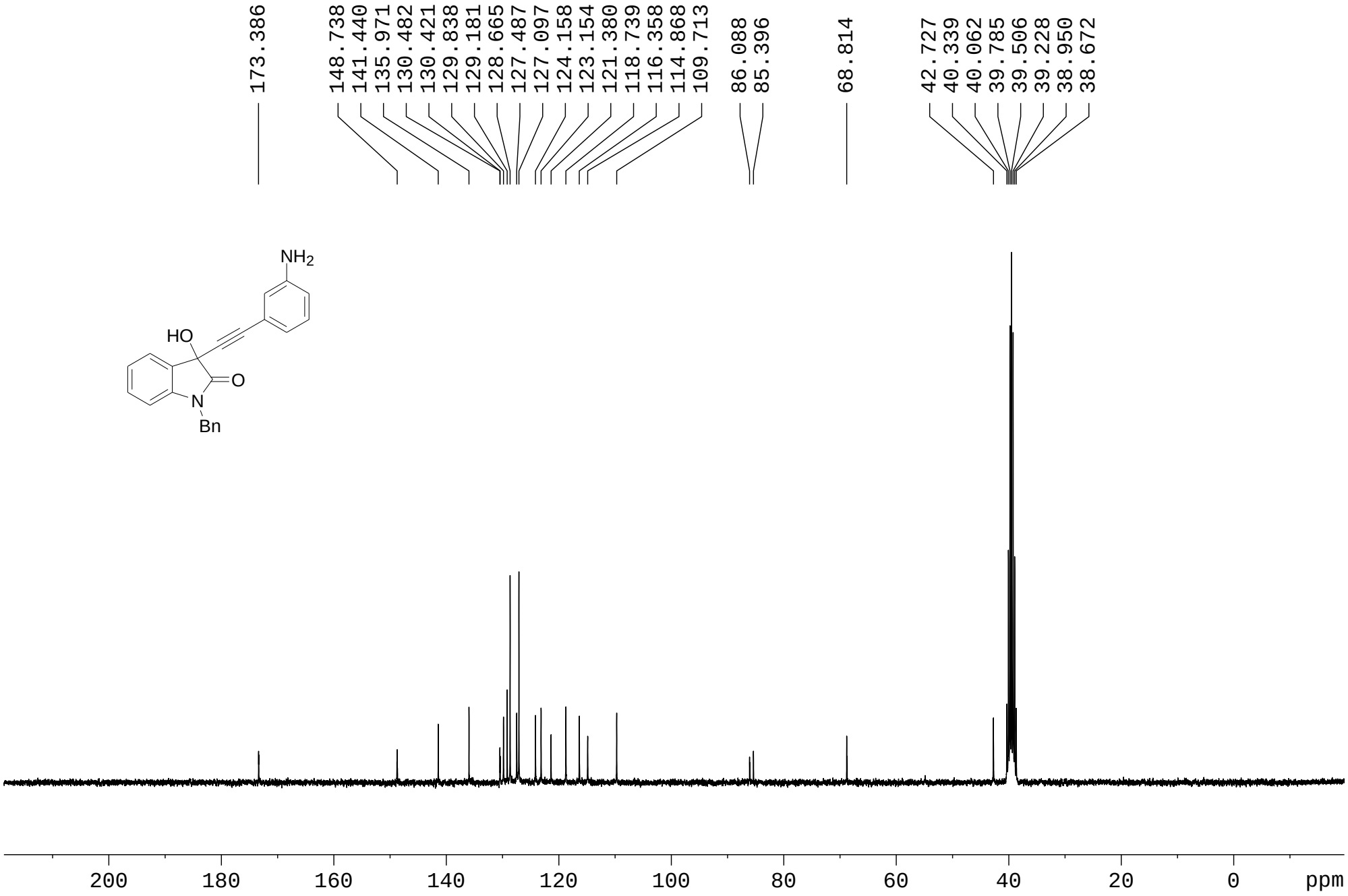








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124.158
123.154
121.380
118.739
116.358
114.868
109.713
86.088
85.396
68.814
42.727
40.339
40.062
39.785
39.506
39.228
38.950
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O
N
Bn
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40
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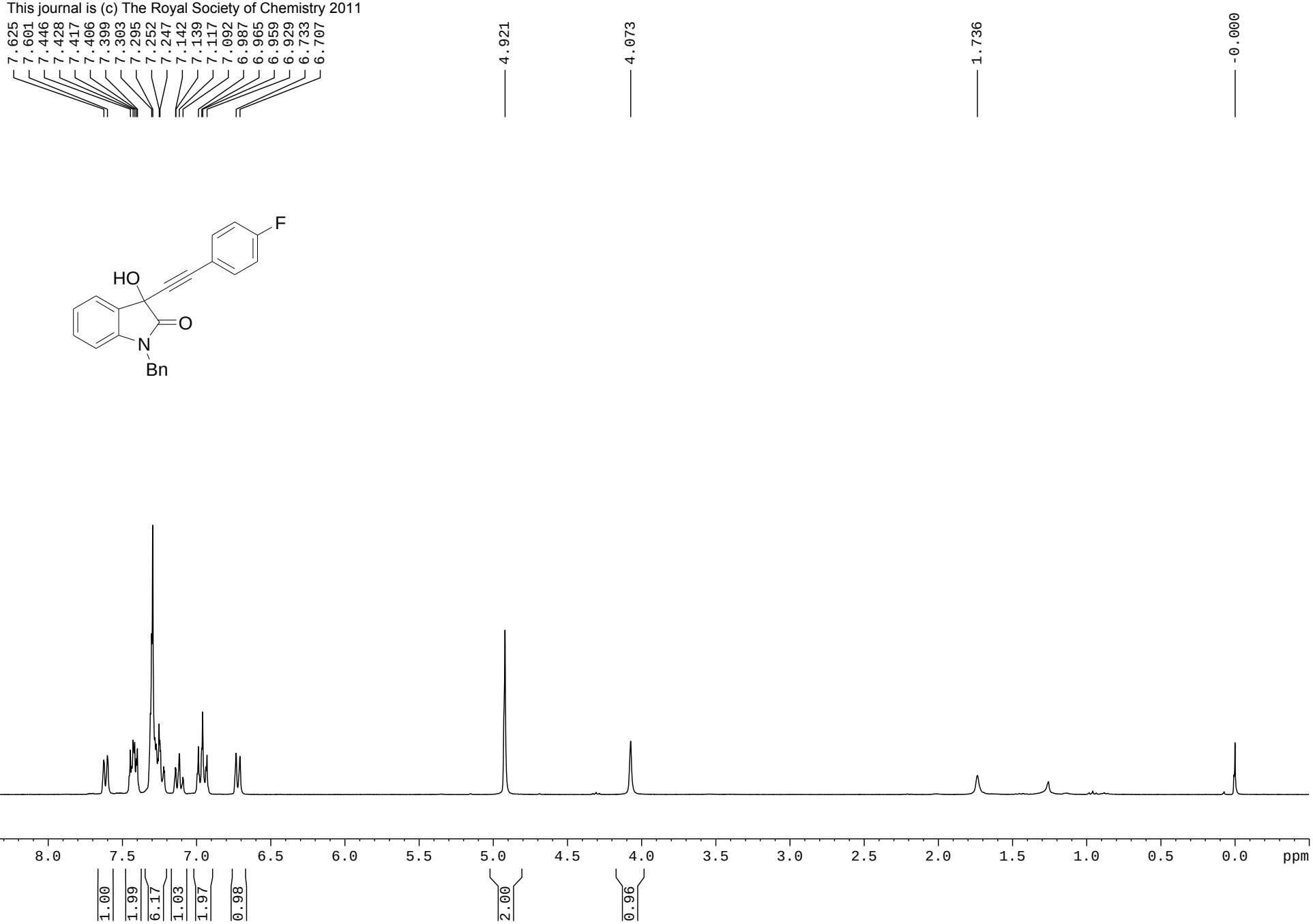
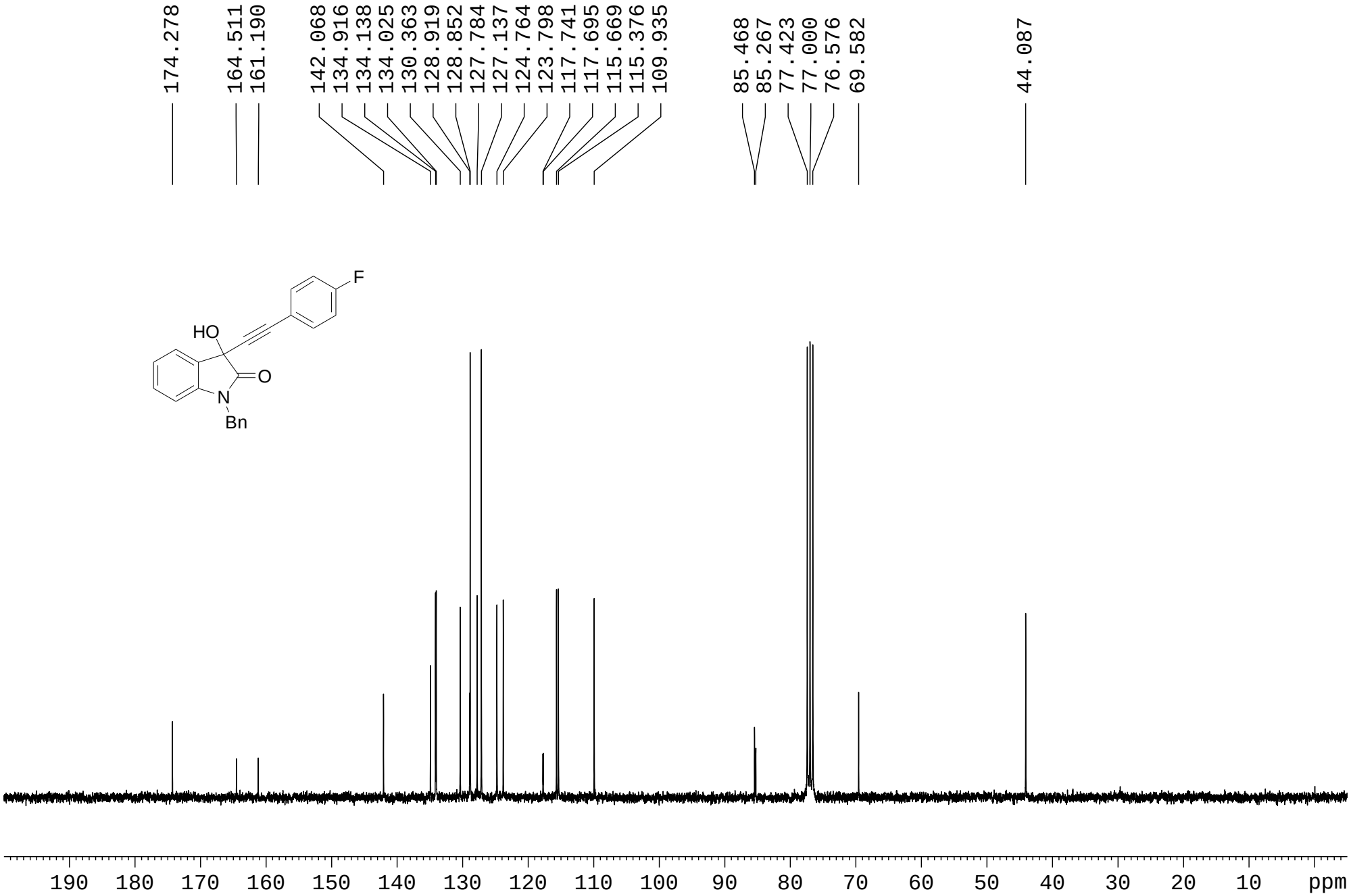
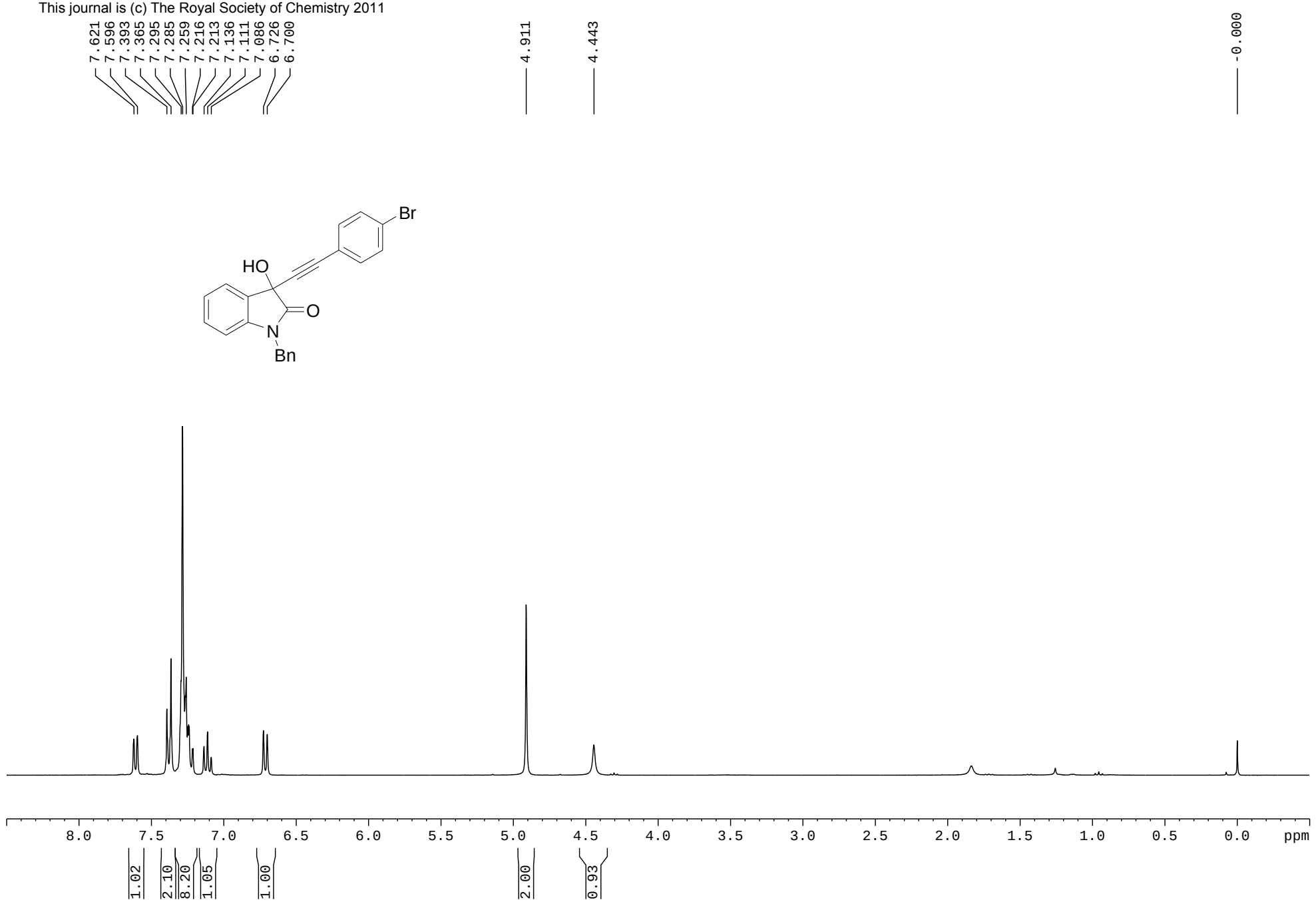
0
ppm



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7.216
7.213
7.136
7.111
7.086
6.726
6.700
4.911
4.443
-0.000
Br
HO
O
N
Bn
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.5
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ppm
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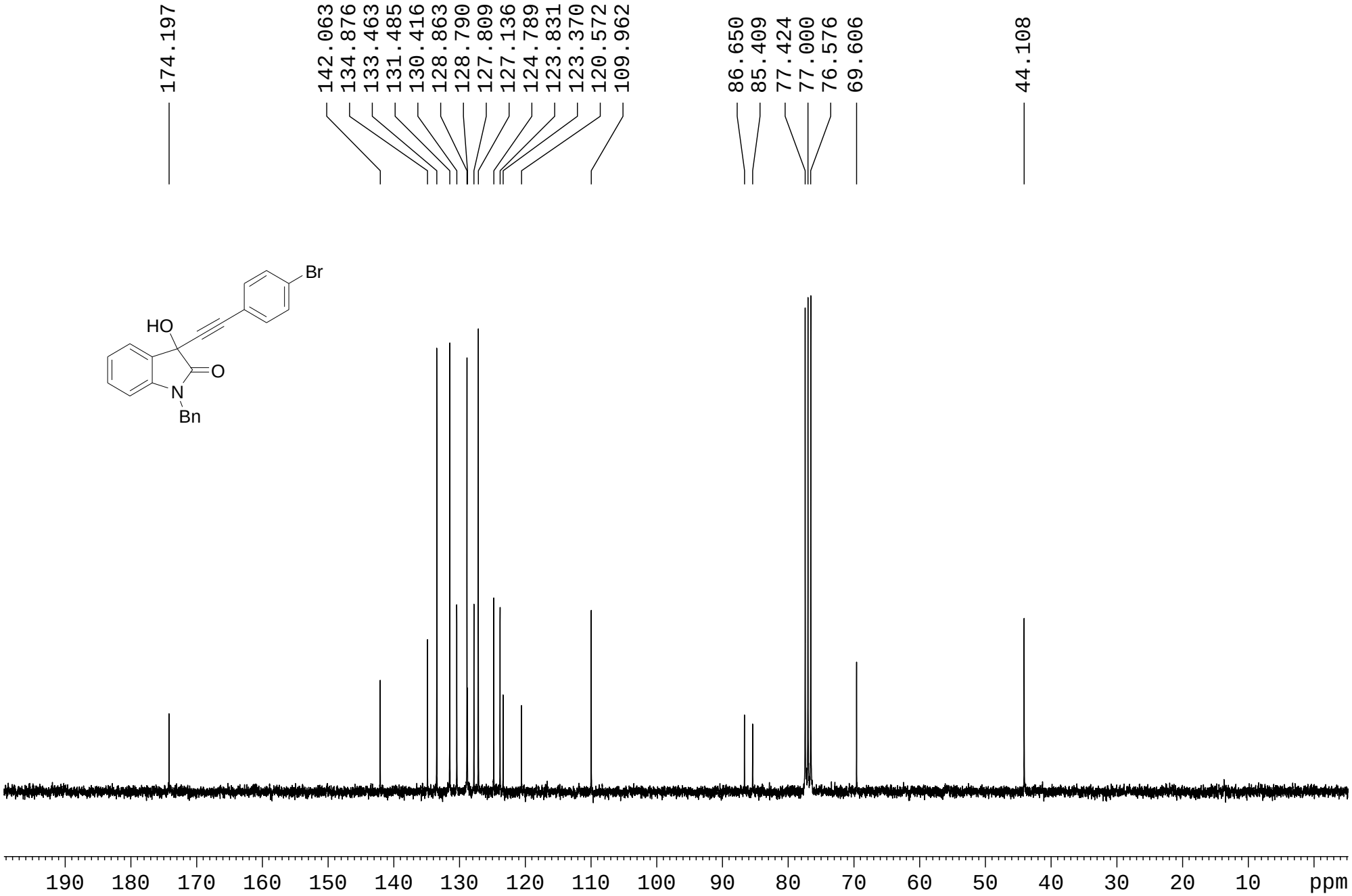
1.00
2.00
0.93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109.962
86.650
85.409
77.424
77.000
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Bn
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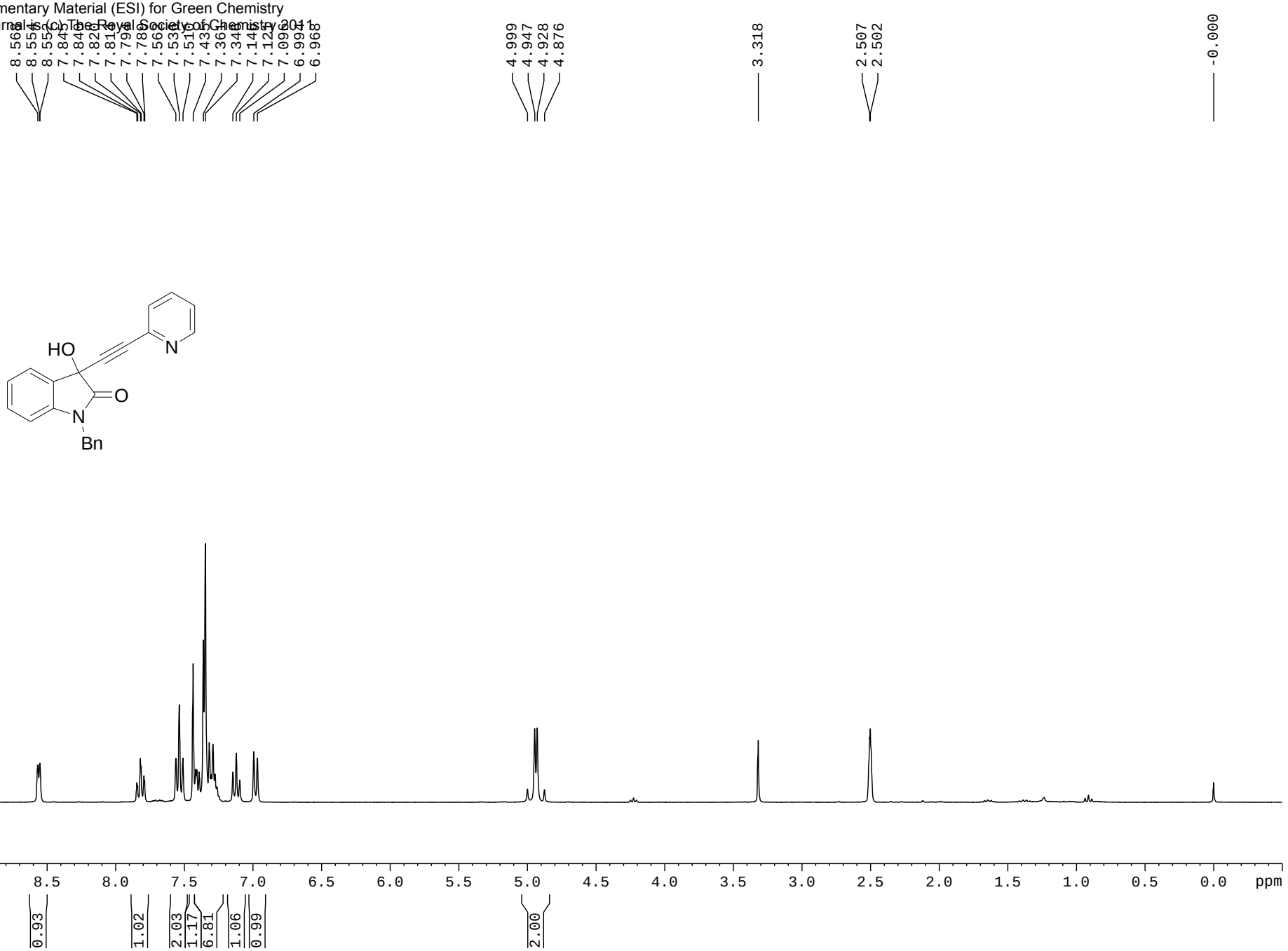

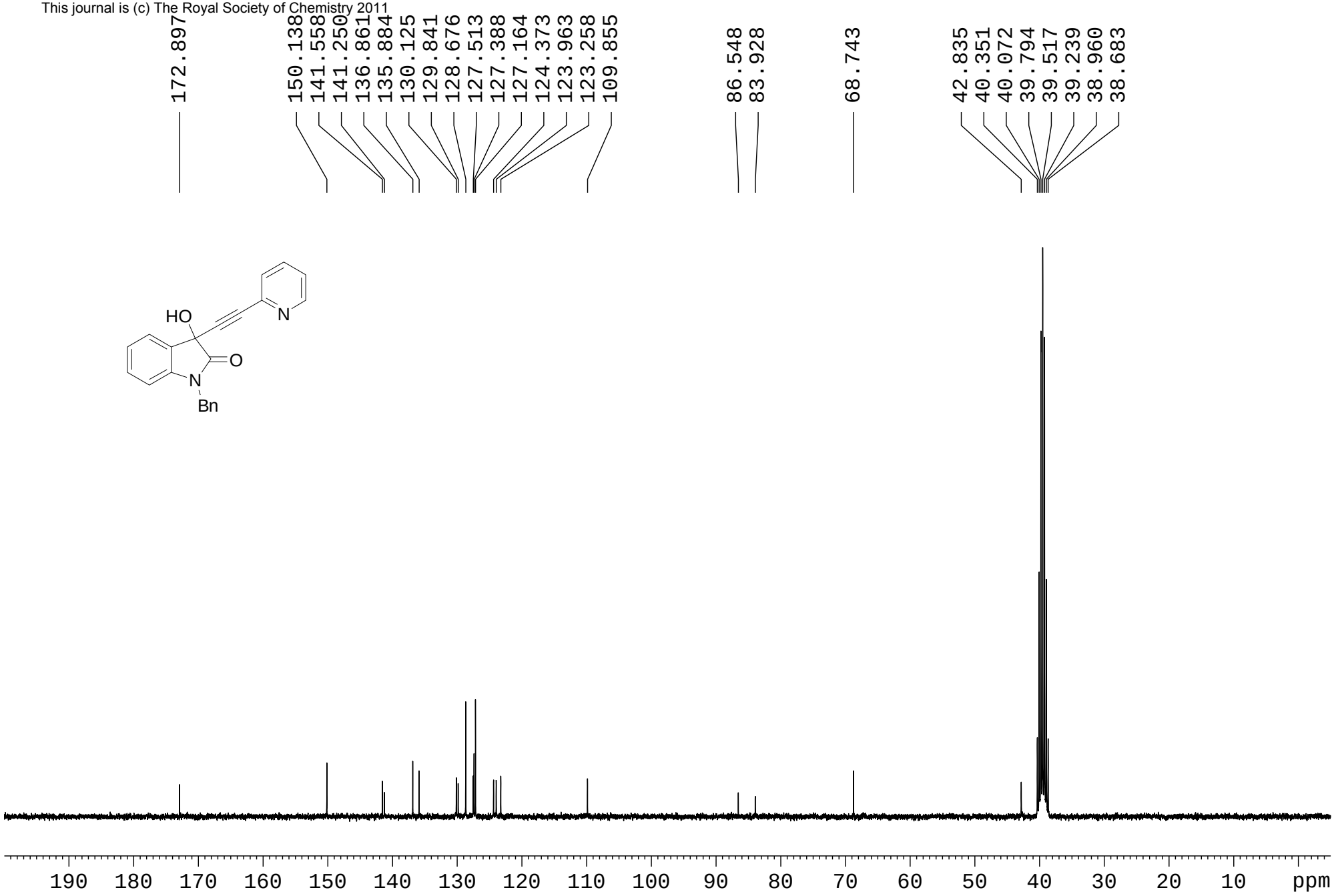

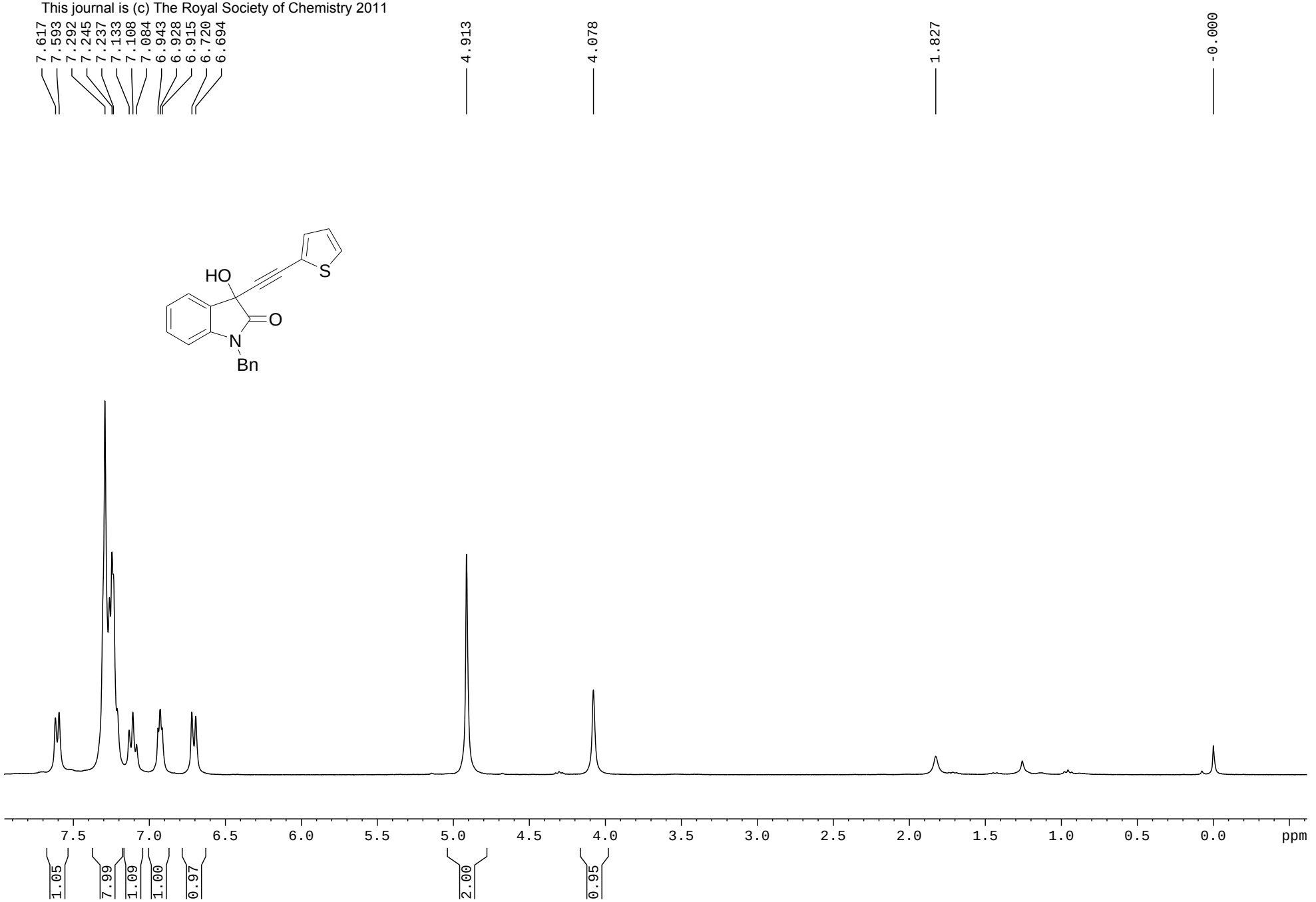
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6.694
4.913
4.078
1.827
-0.000
HO
S
O
N
Bn
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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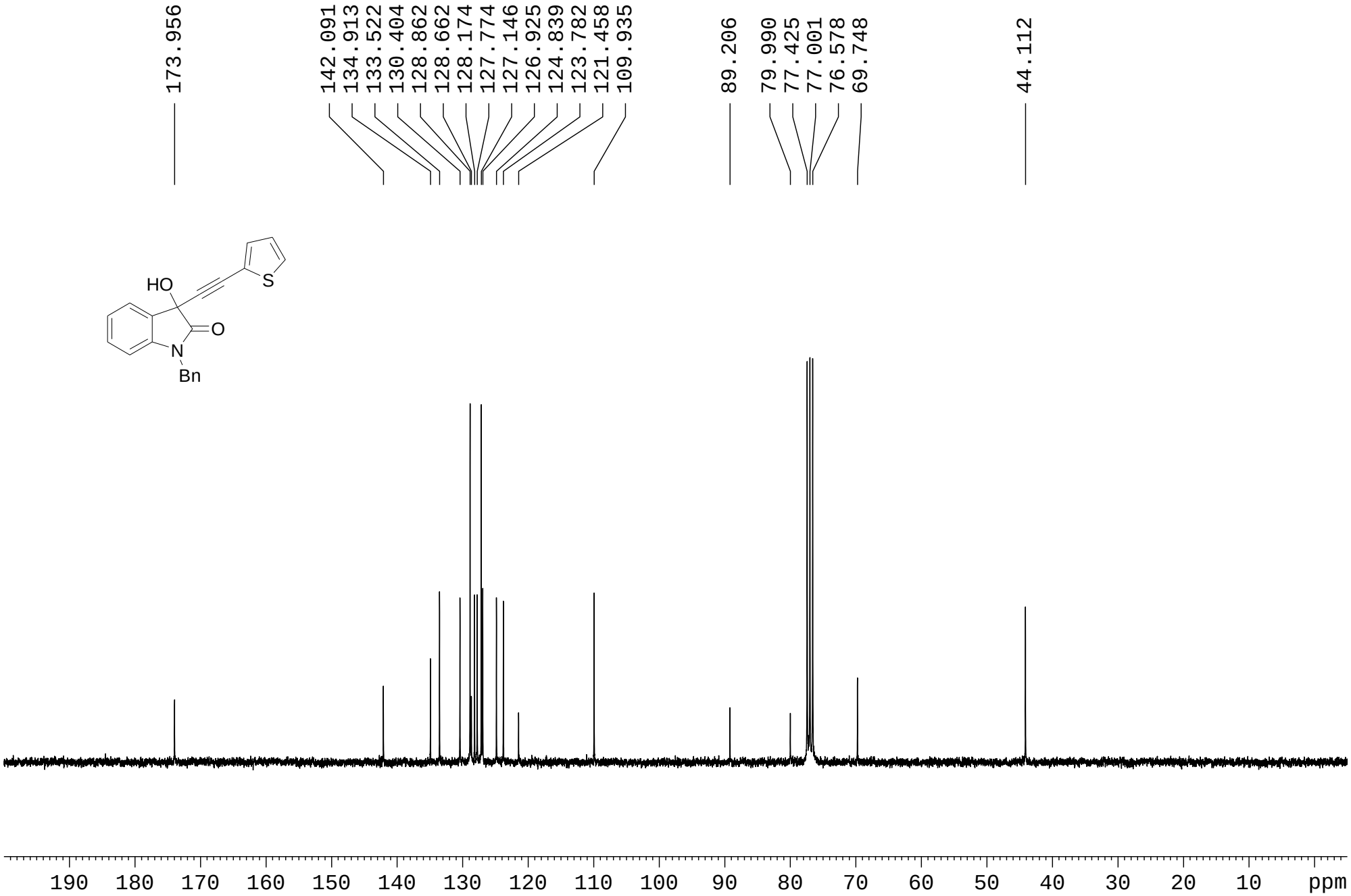
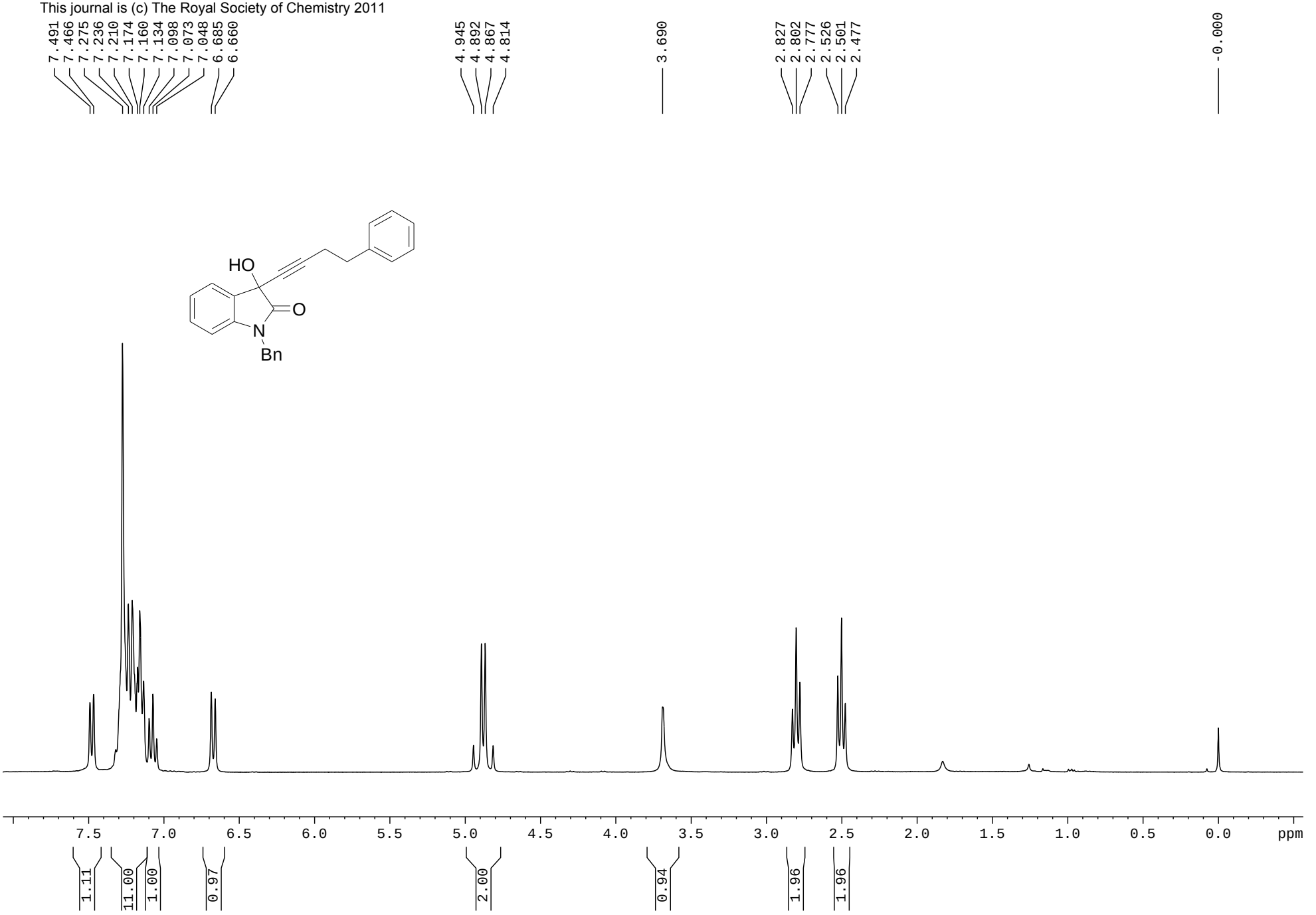
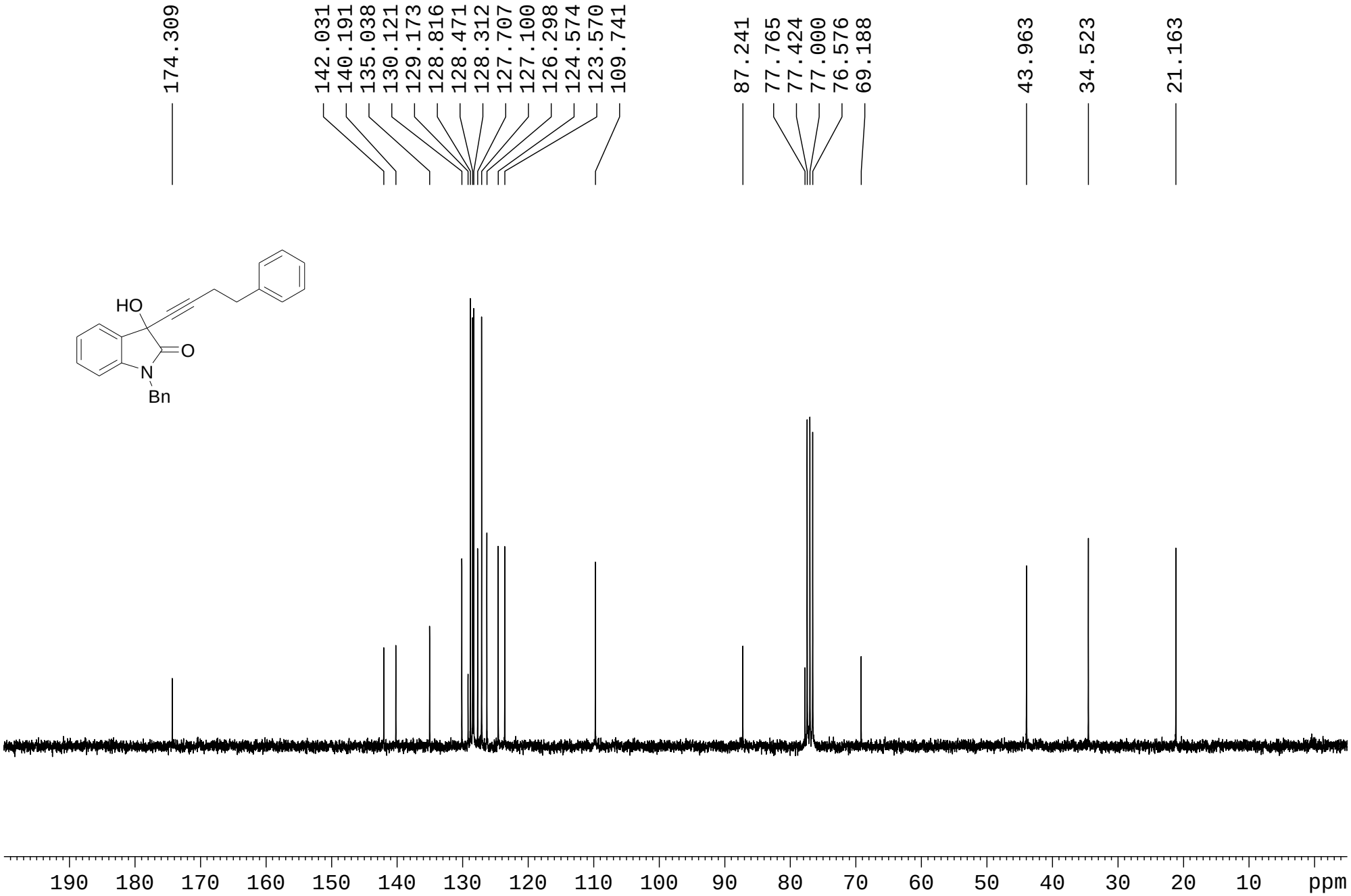
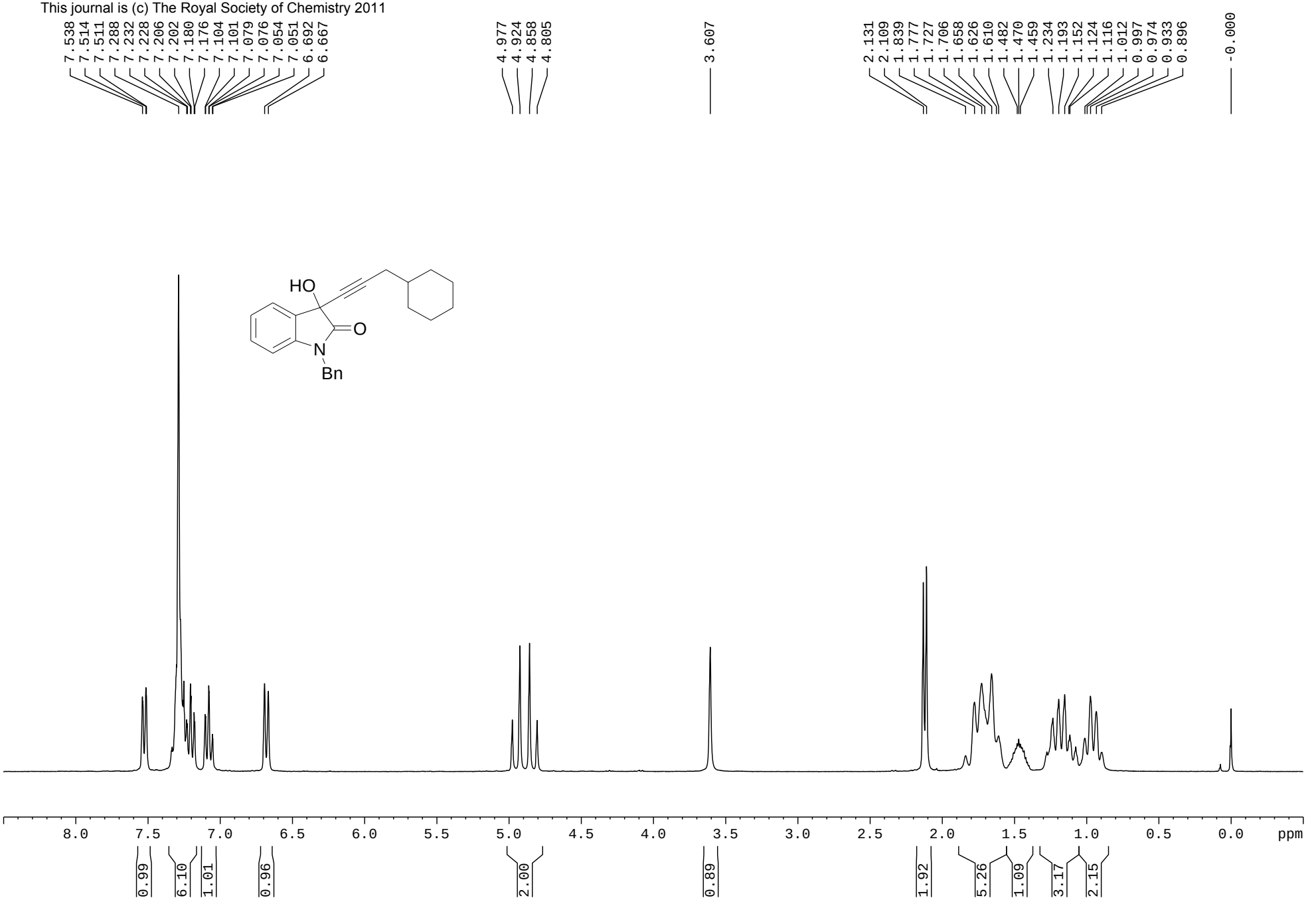
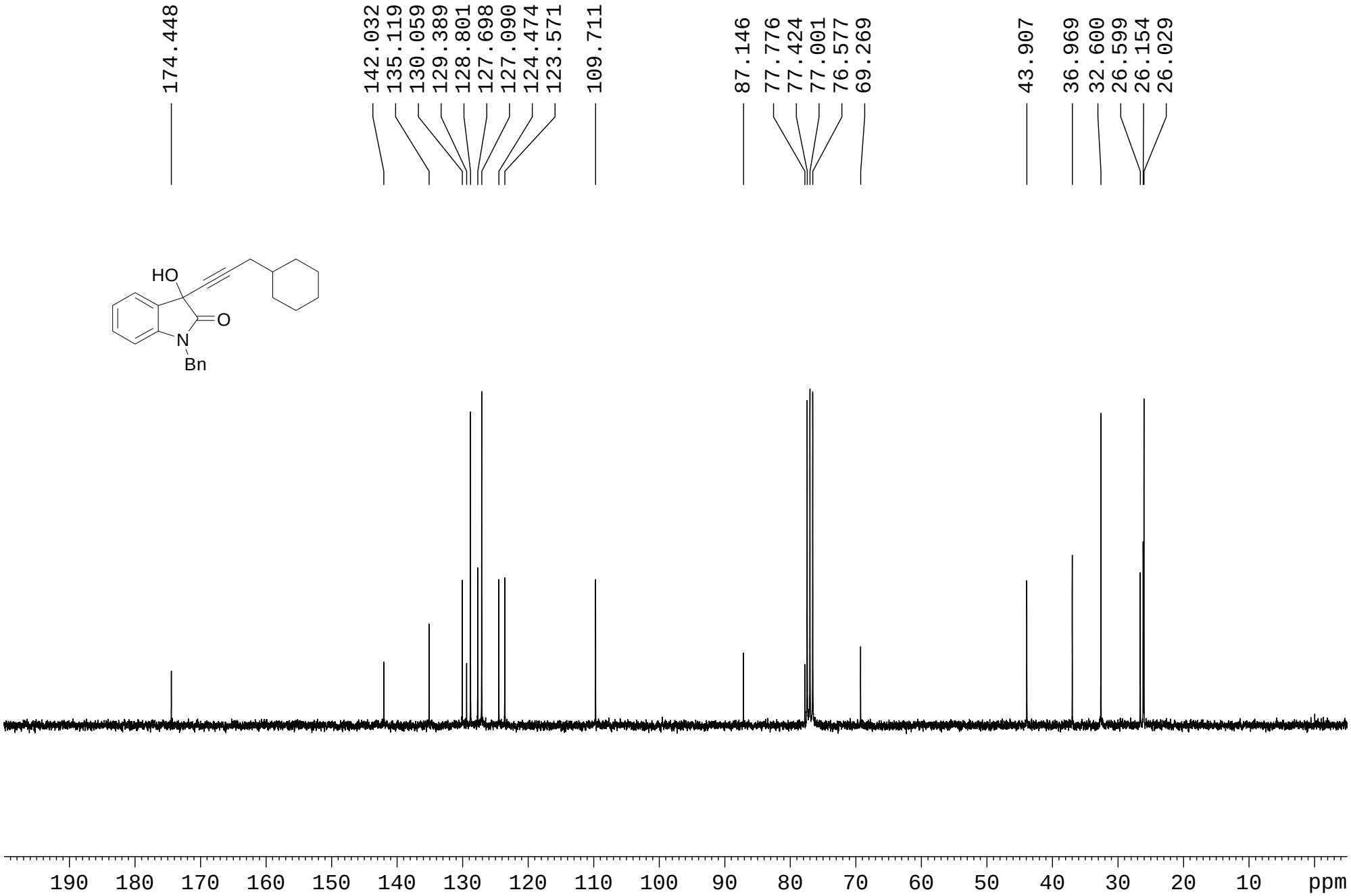
0.97
2.00
0.95







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26.029
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O
N
Bn
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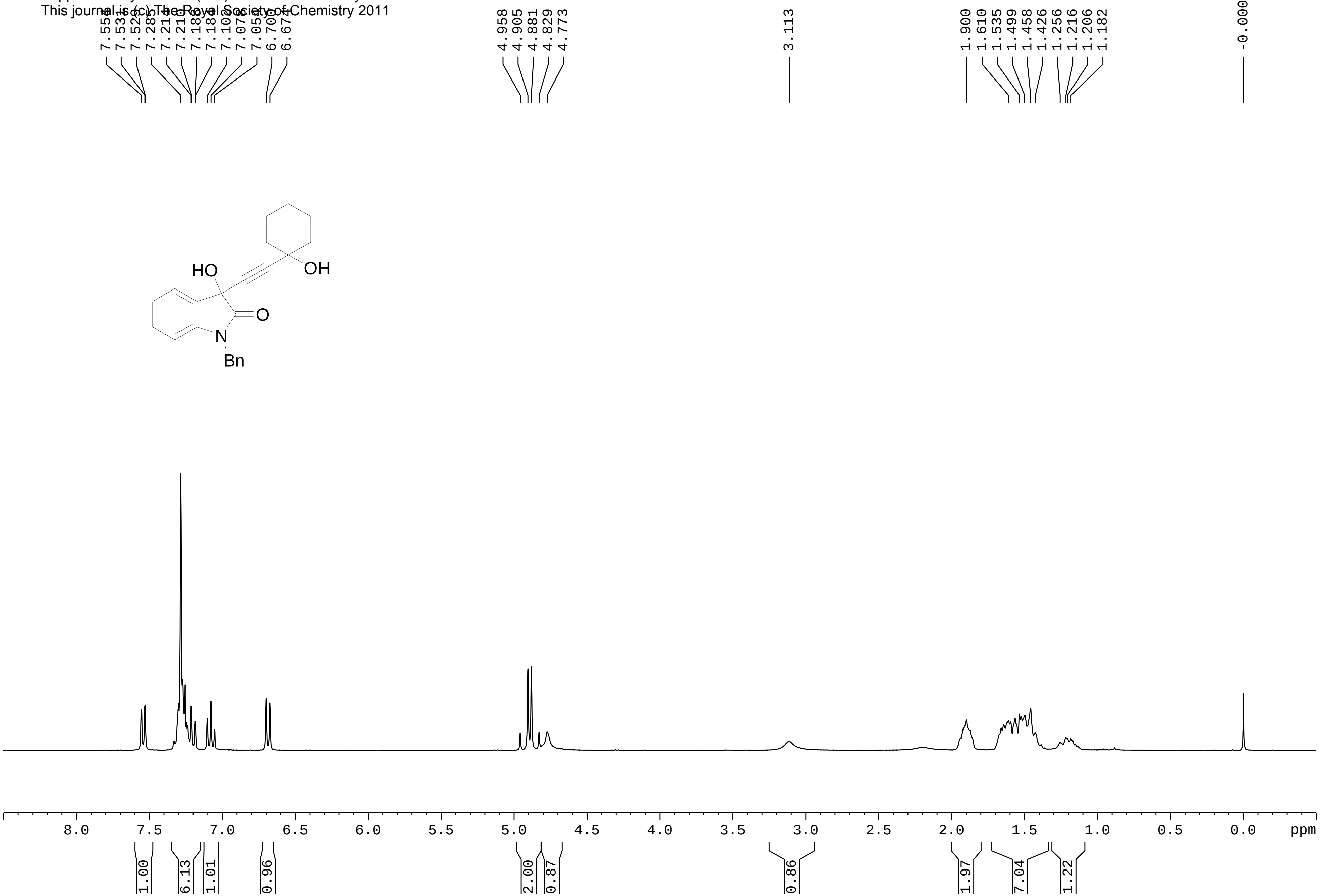
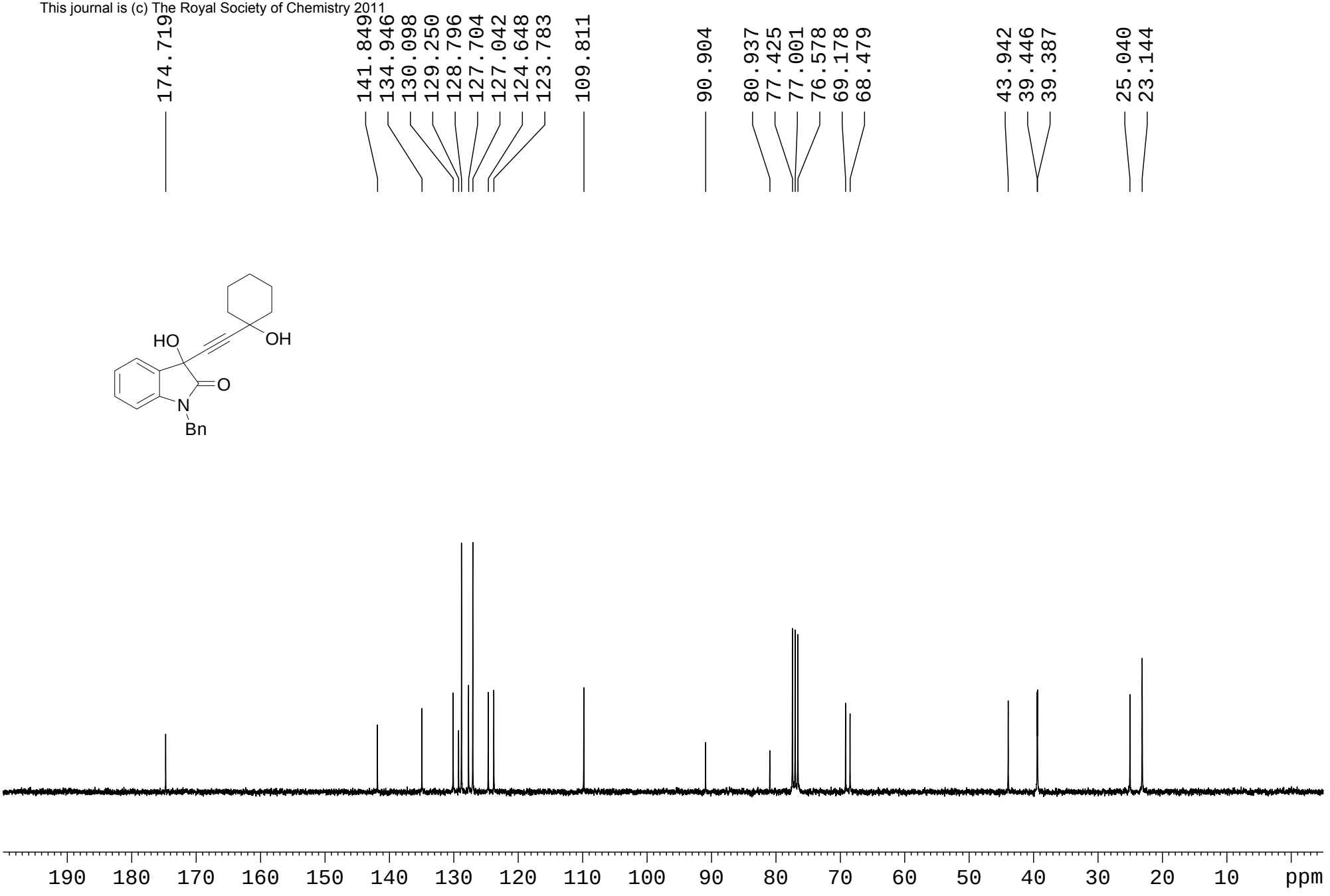
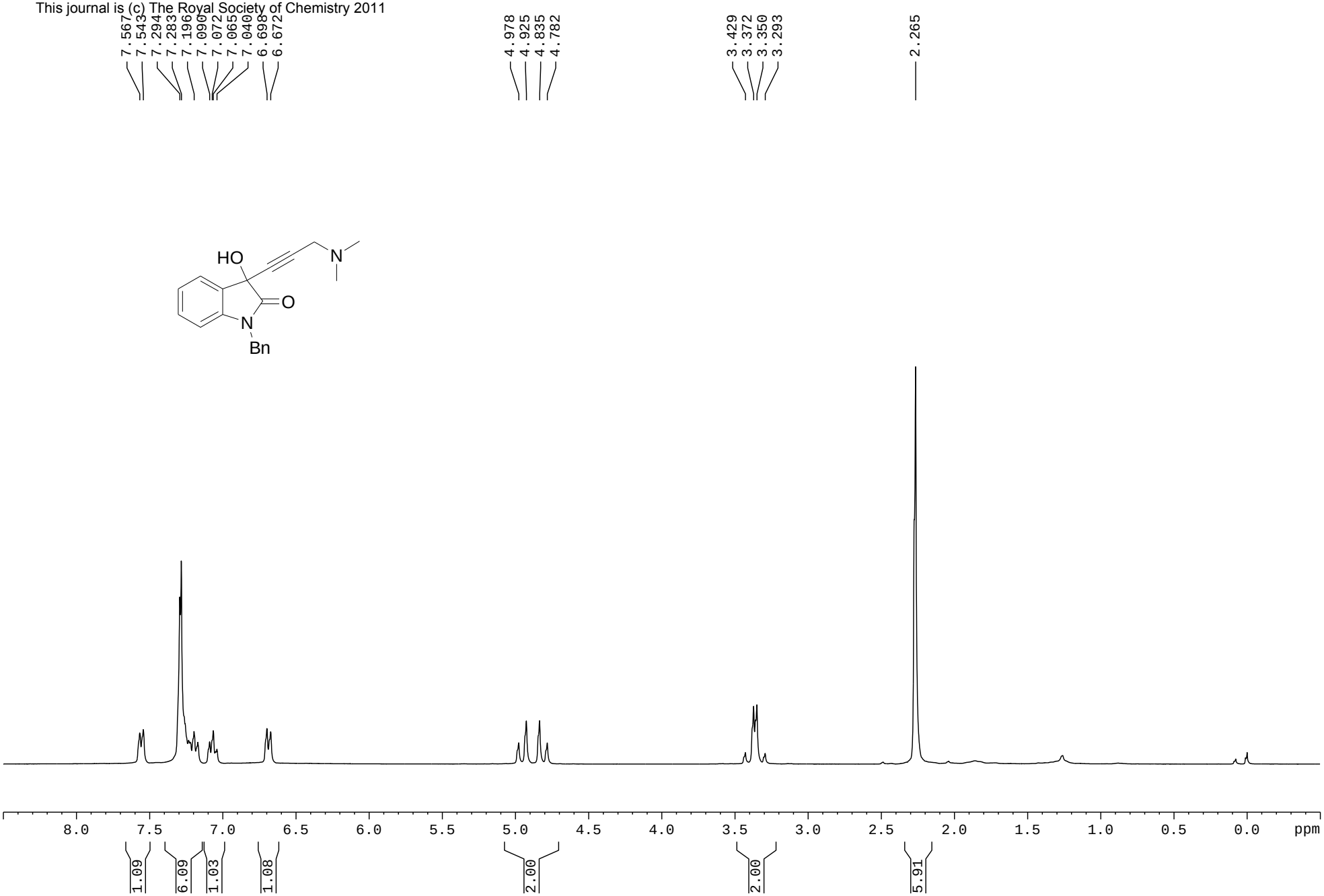
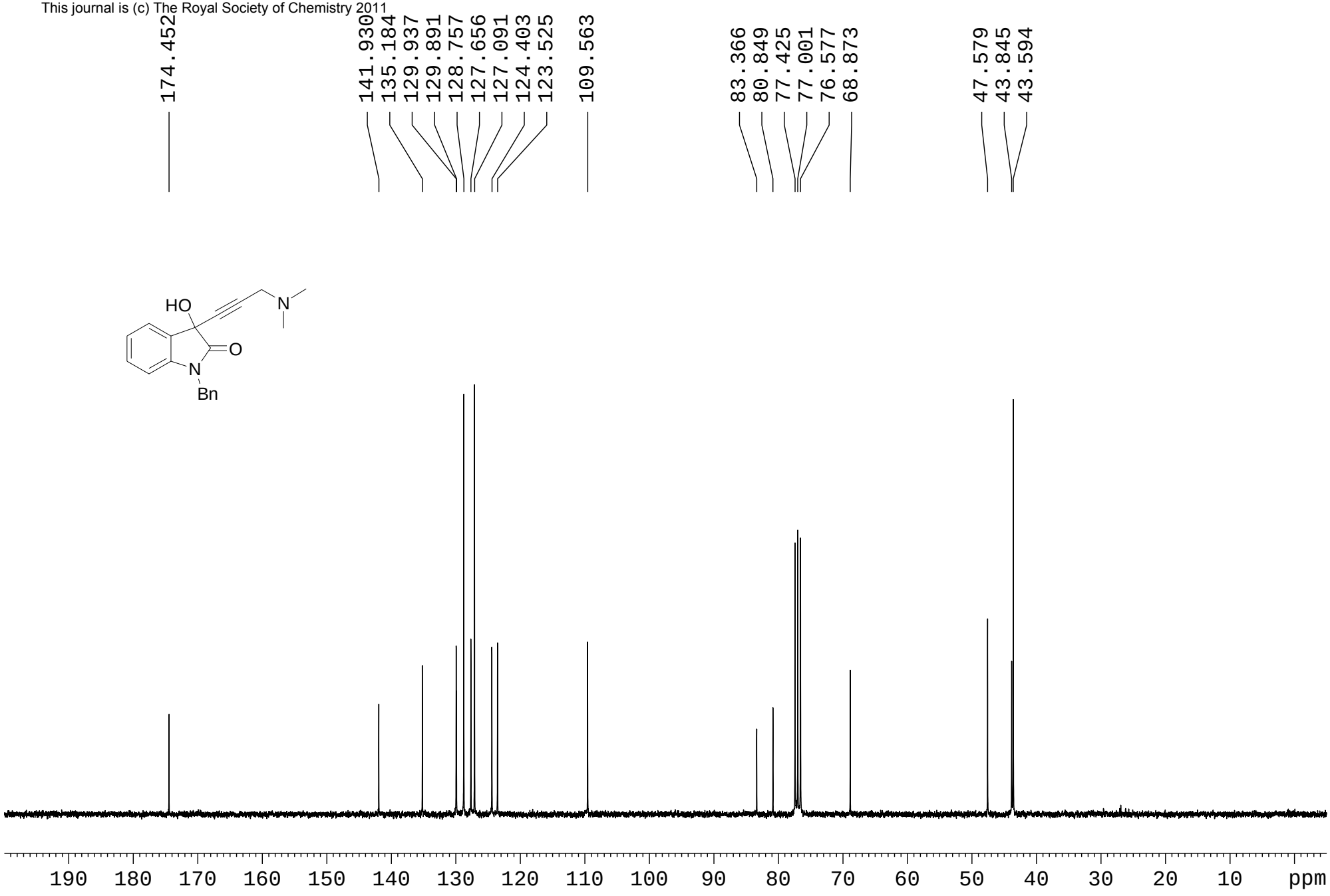
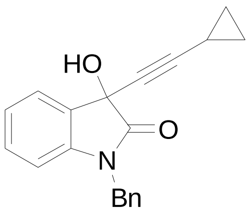
ppm

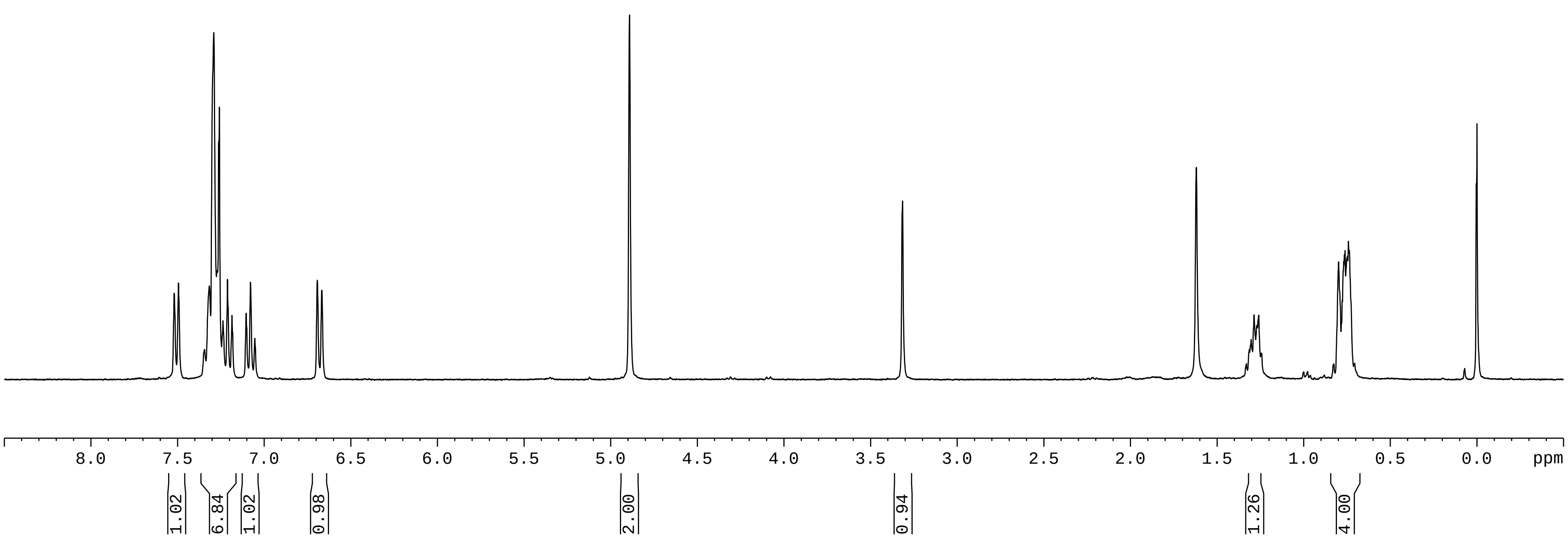


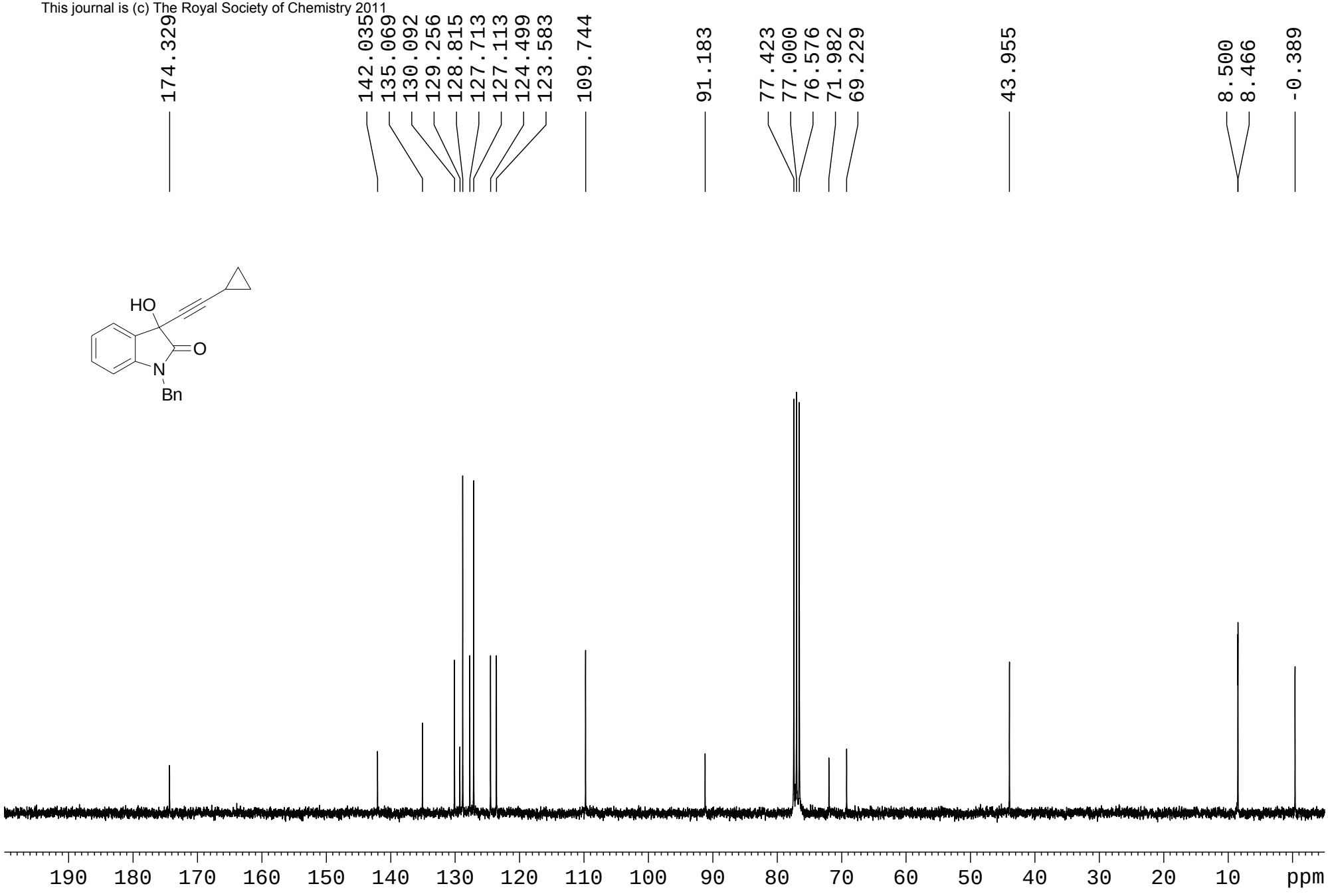


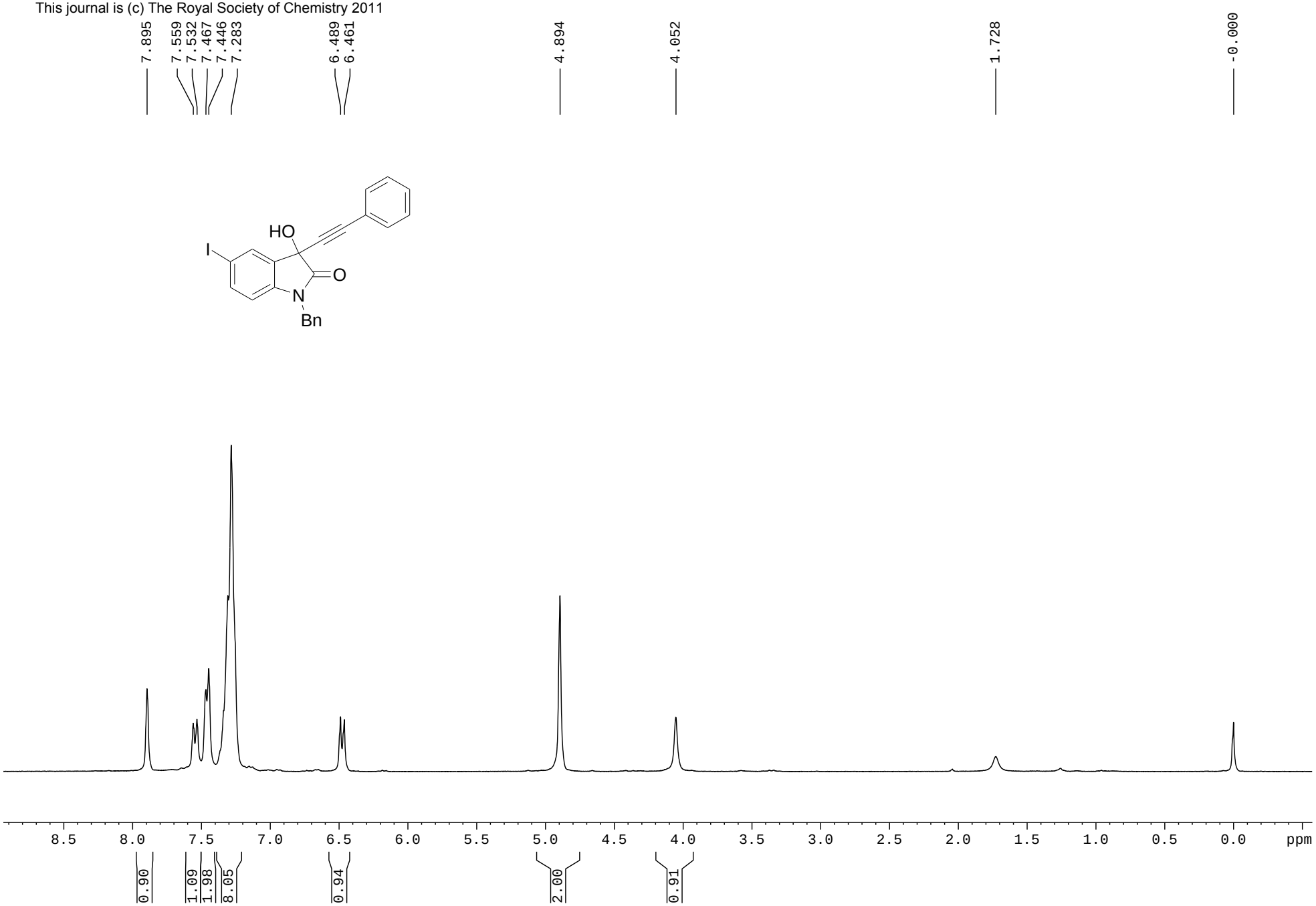


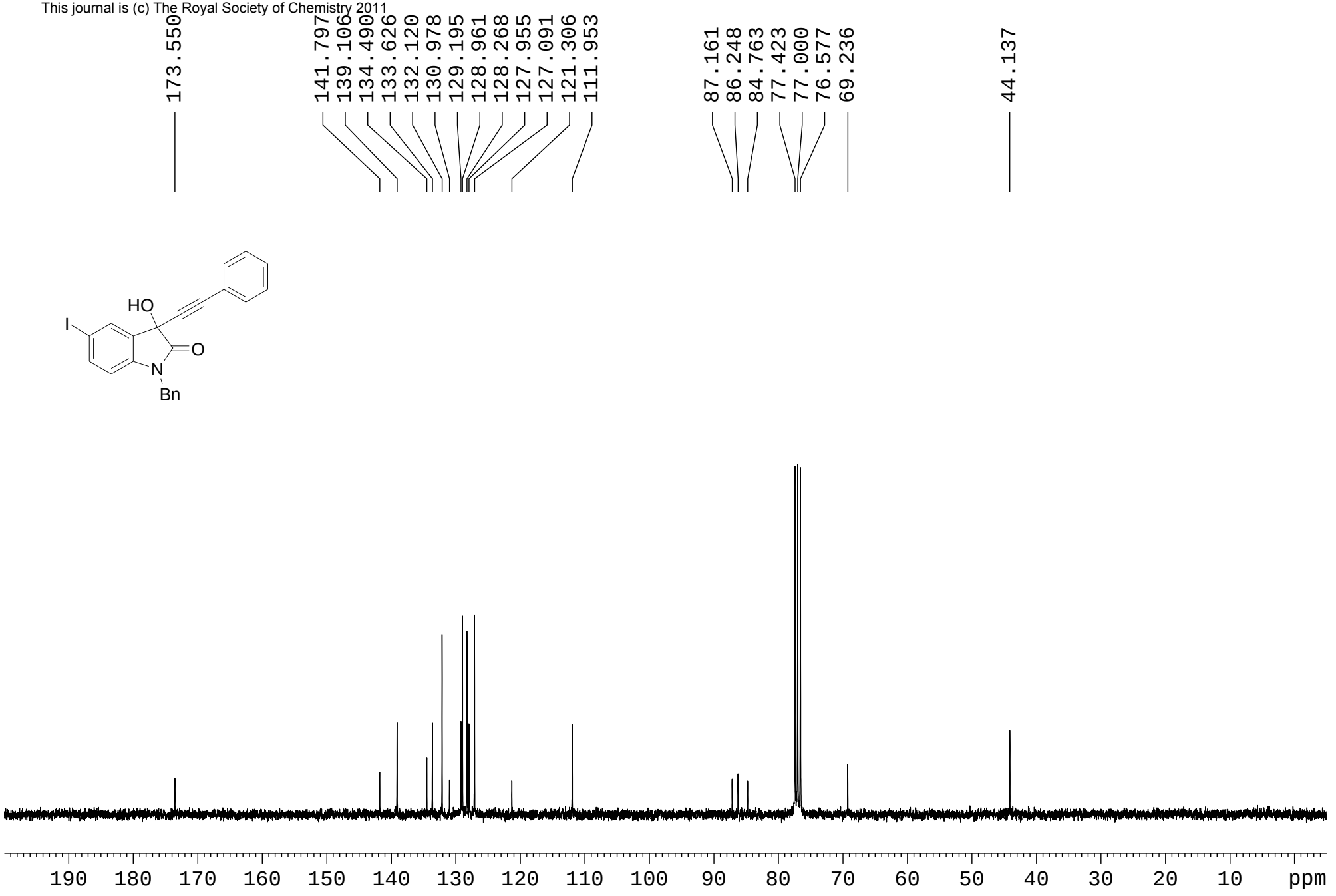


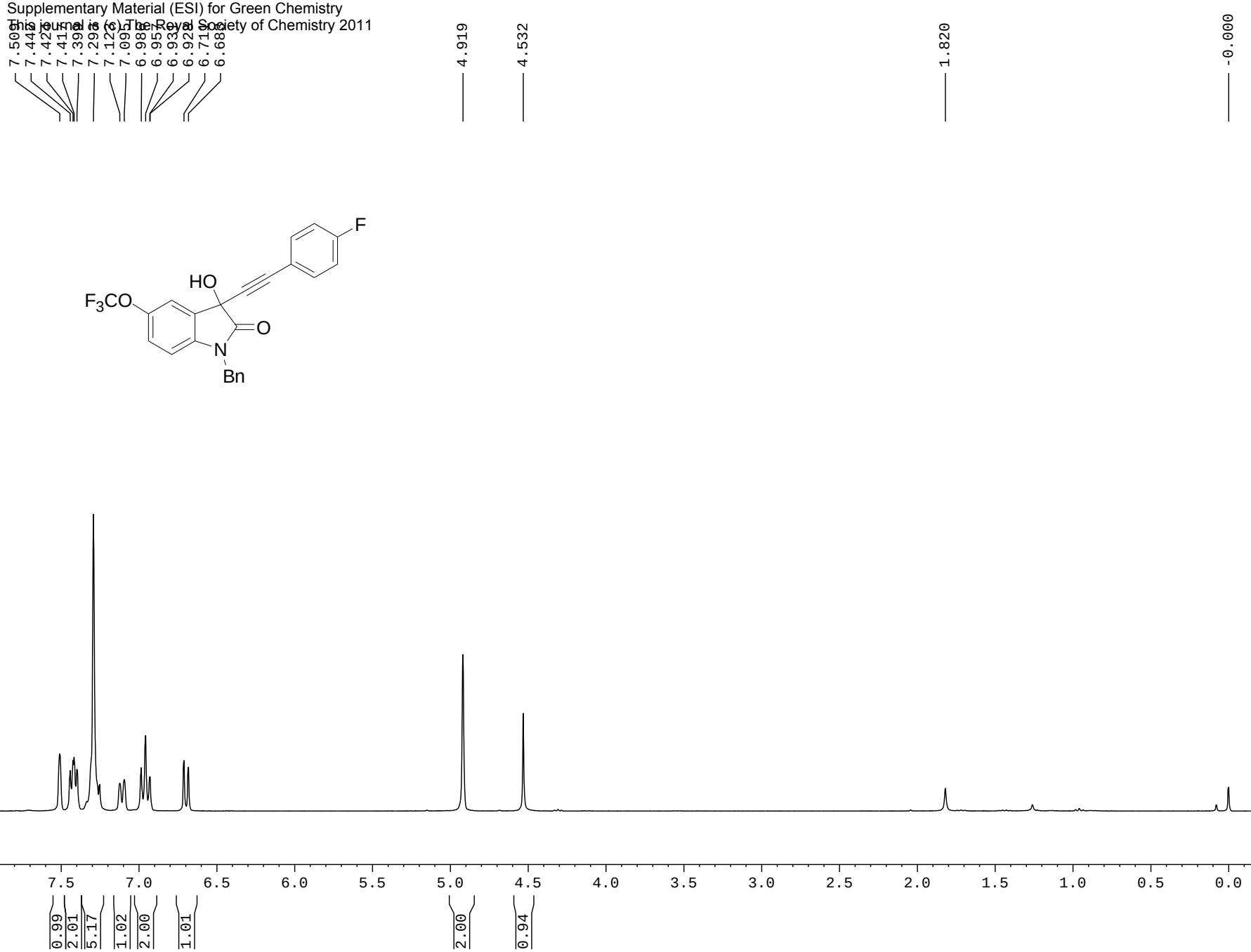


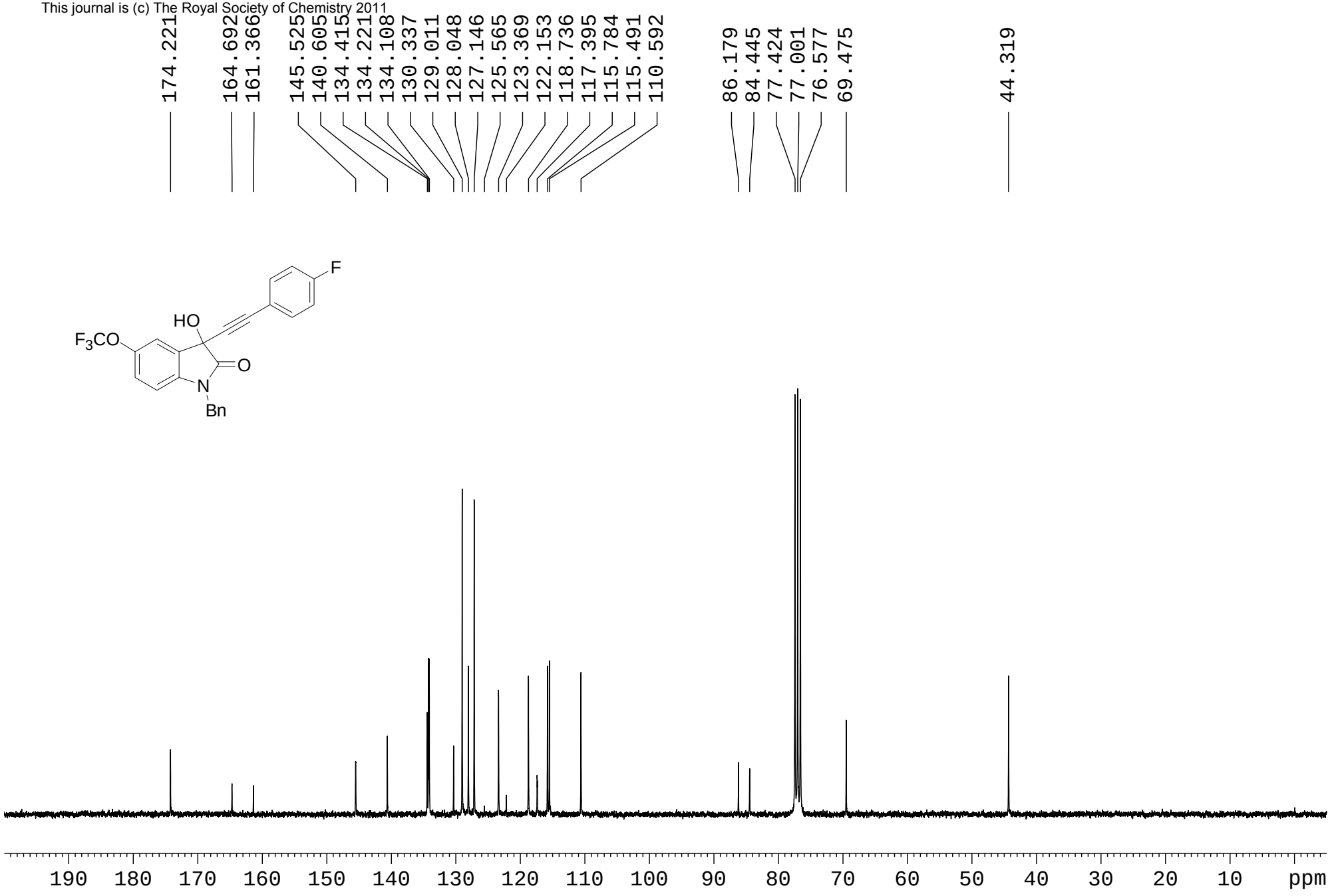


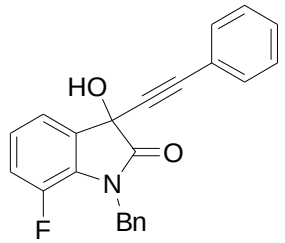


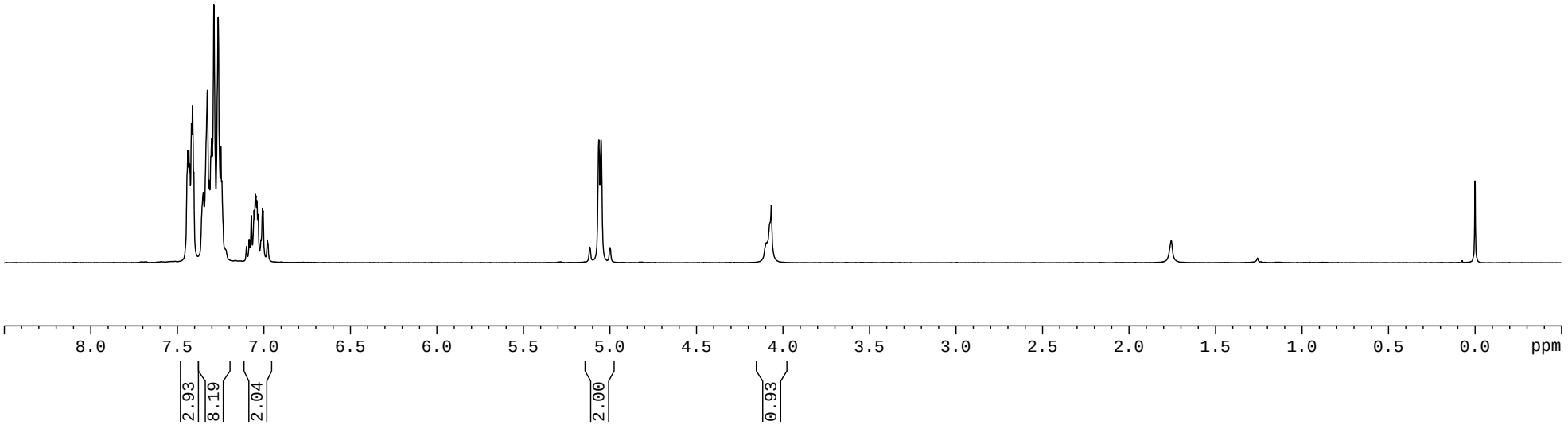


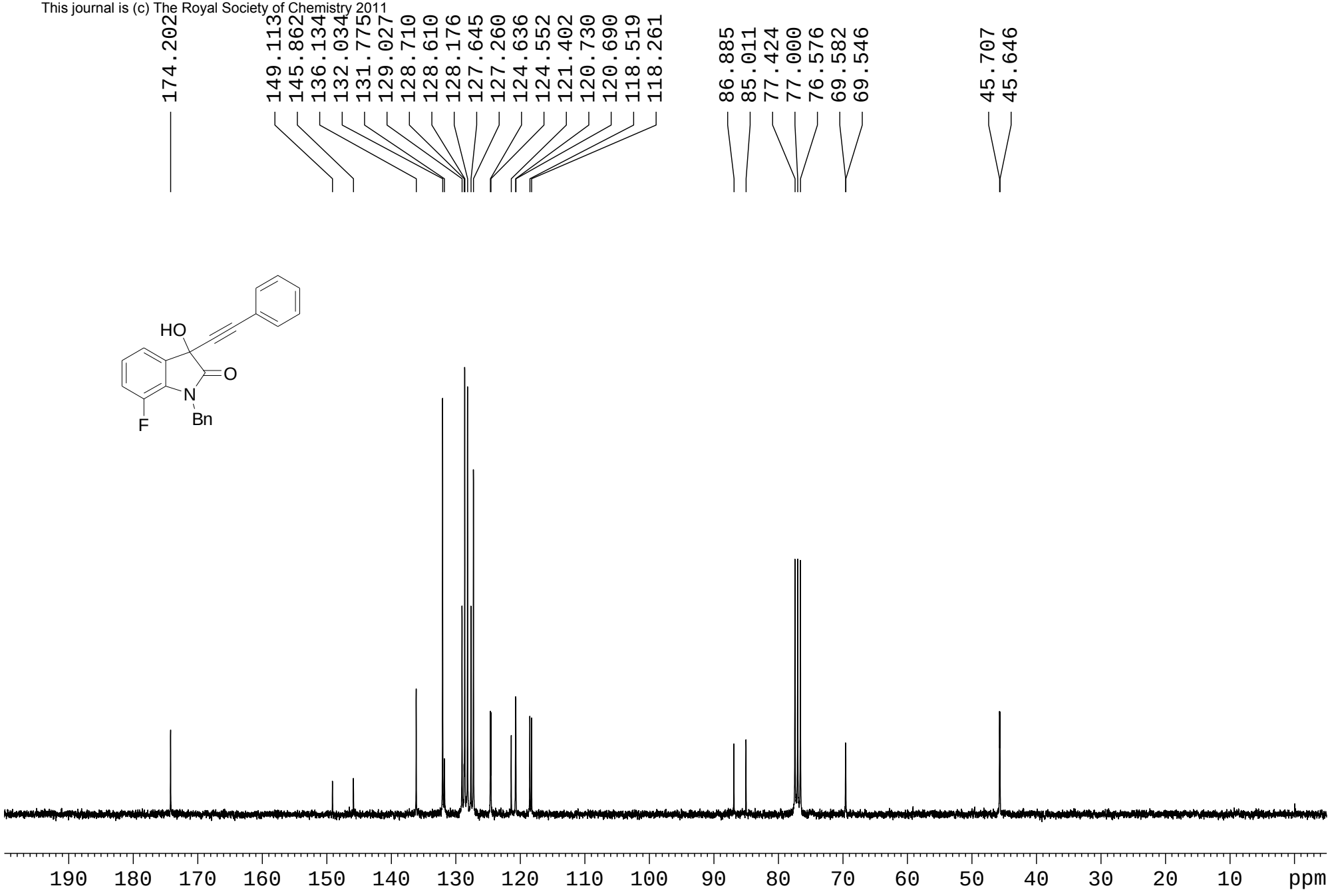


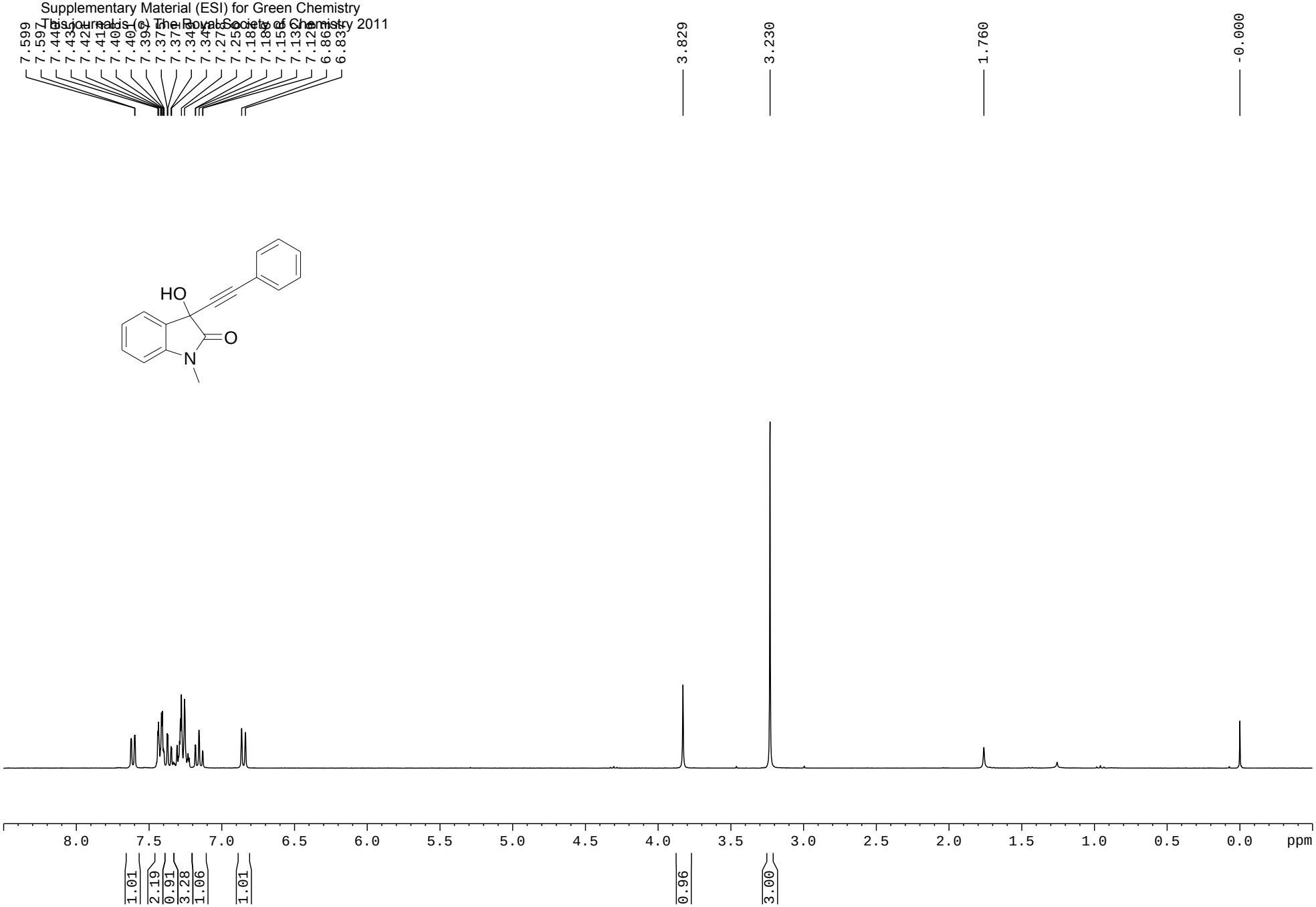


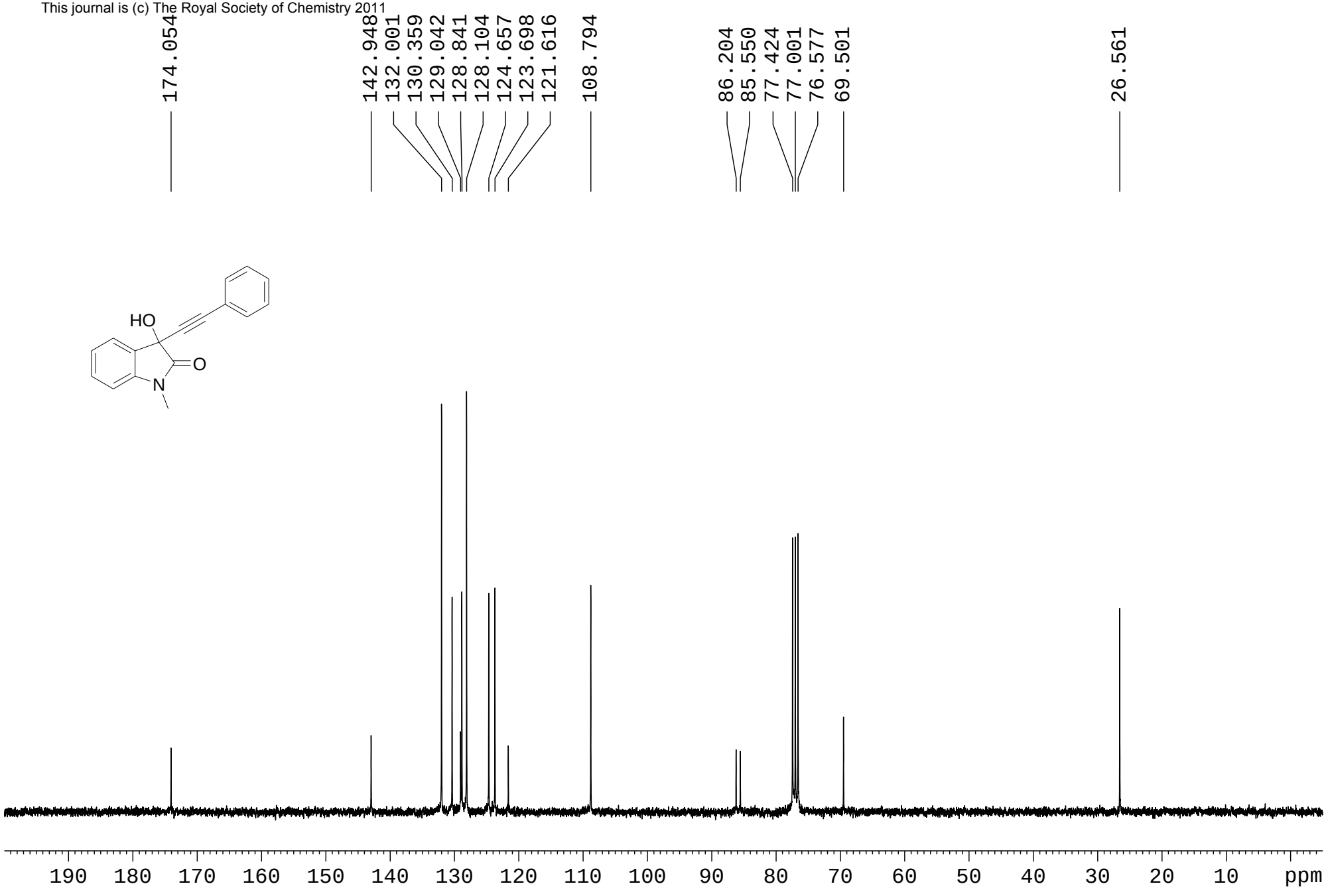


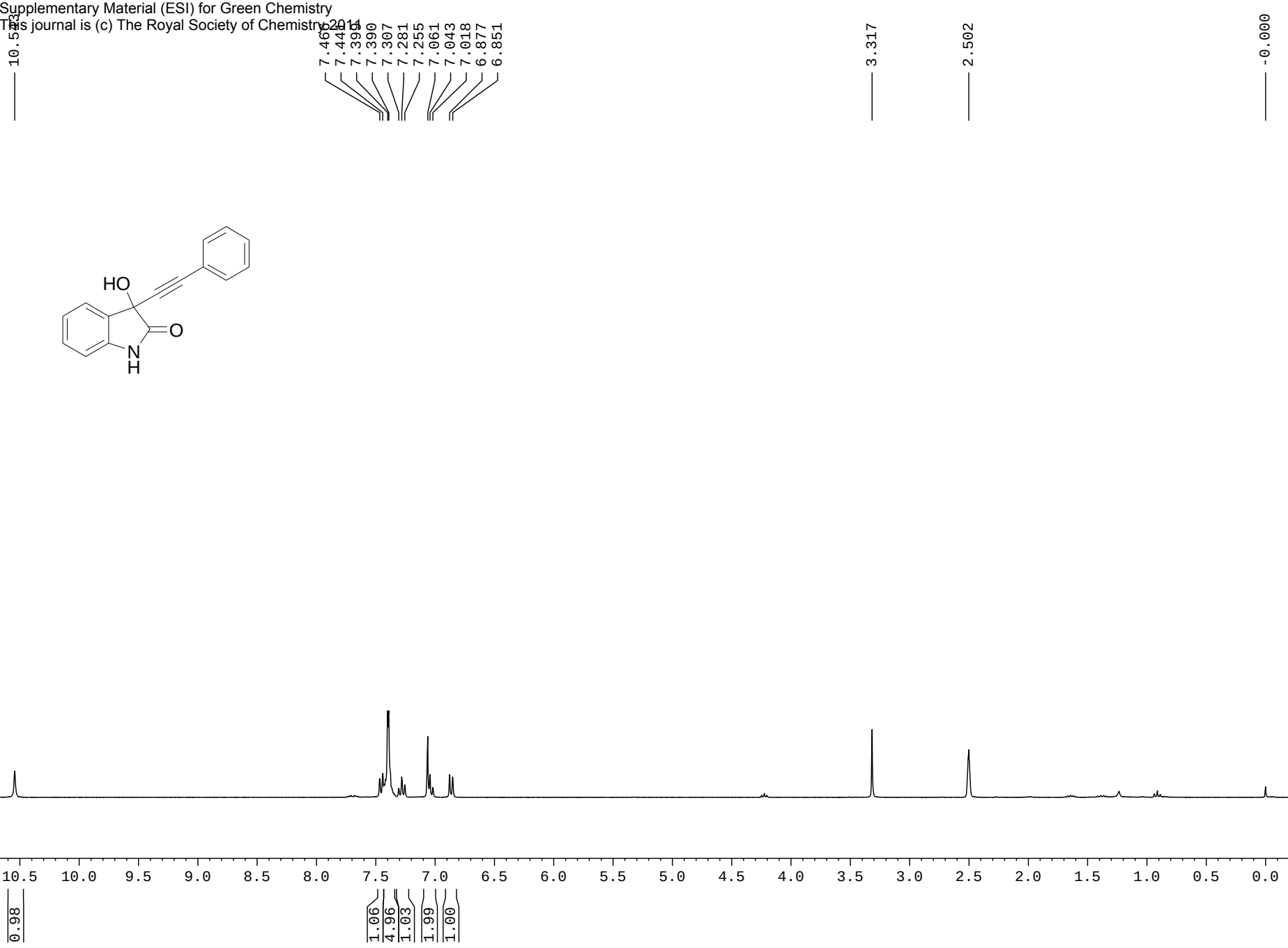


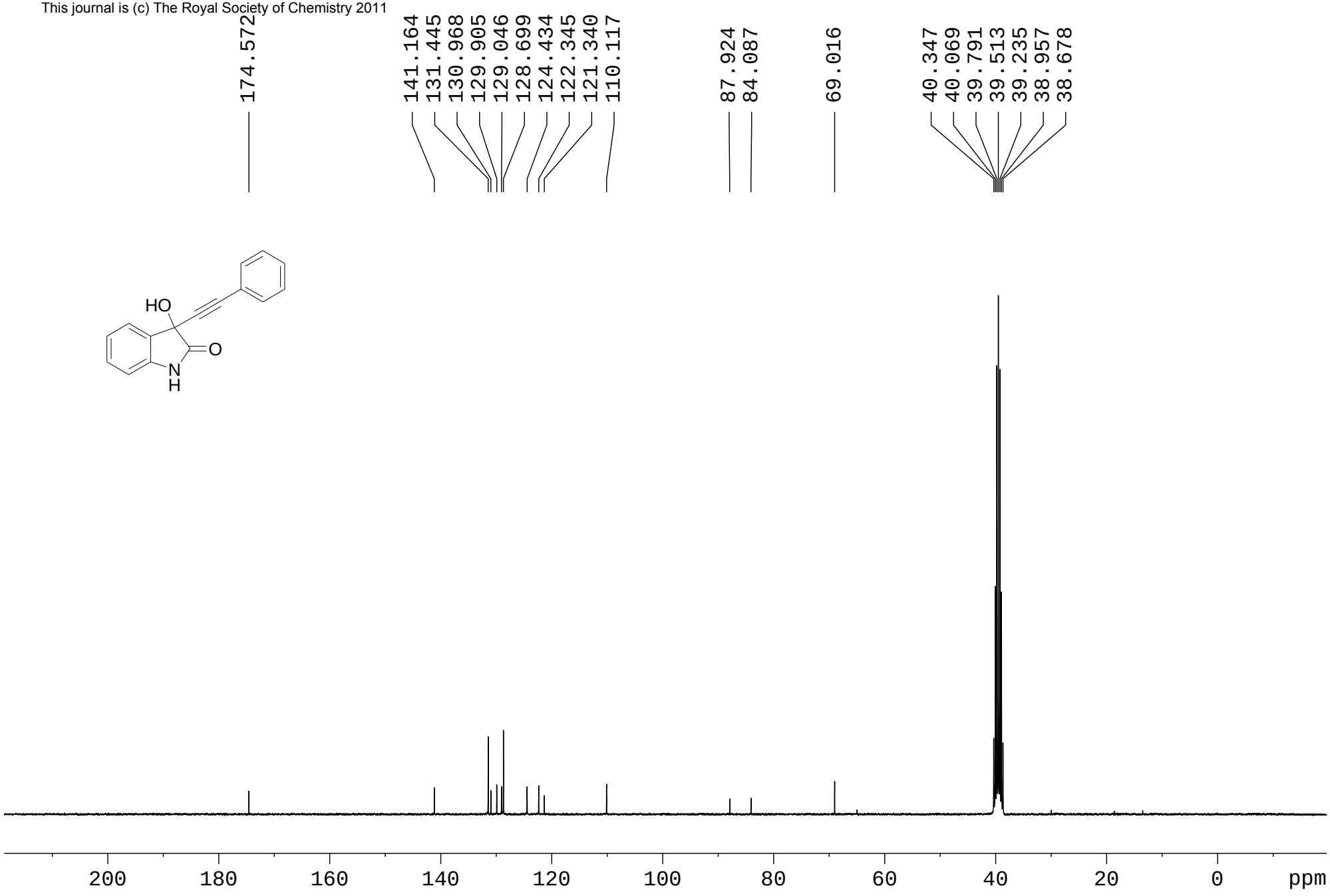








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39.235
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HO
O
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm