Supporting Information for

Alkene carboamination/oxidative denitrogenation of 3-allyl-3-hydrazinylindolin-2-ones: one-pot entry to spiro cyclopropyloxindoles

Marco Manenti,[*a] *Tommaso Villa,*[a] *Giovanni Macetti*[a] *and Alessandra Silvani*[a]

[a] *Department of Chemistry, University of Milan, via C. Golgi 19, Milano, 20133, Italy. Email: marco.manenti@unimi.it*

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tert-butyl 2-(3-allyl-1-benzyl-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**3a**)

Synthetized according to the general procedure using conditions A starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 6:4) to afford pure compound **3a** as a light-yellow sticky foam (549 mg, 93%); spectroscopic data matches the literature-reported ones: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (br d, *J*= 7.4 Hz, 1H), 7.34–7.22 (m, 5H), 7.17 (t, *J*= 7.5 Hz, 1H), 7.04 (t, *J*= 7.5 Hz, 1H), 6.85 (d, *J*= 7.6 Hz, 1H), 6.08 (br s, 1H), 5.55-5.50 (m, 1H), 5.09 (d, *J*= 17.0 Hz, 1H), 5.00 (d, *J*= 10.2 Hz, 1H), 4.94 (br d, *J*= 16.0 Hz, 1H), 4.87 (br d, *J*= 16.0 Hz, 1H), 4.64 (br s, 1H), 2.73 (dd, J_2= 13.3, J_3= 6.8 Hz, 1H), 2.64 (dd, J_2= 13.3, J_3= 8.5 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 156.0, 143.2, 135.6, 130.7, 129.2, 128.7 (2C), 127.8, 127.6, 127.2 (2C), 125.2, 122.6, 120.1, 109.1, 80.5, 68.6, 43.8, 39.6, 28.1 (3C); HRMS (ESI) calcd for $C_{23}H_{27}N_3O_3Na$ $[M+Na]^+$ 416.1945 found 416.1951

tert-butyl 2-(3-allyl-1-methyl-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**3b**)

Synthetized according to the general procedure using conditions A starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 7:3) to afford pure compound **3b** as a light-yellow sticky foam (380 mg, 80%); spectroscopic data matches the literature-reported ones: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J*= 7.8 Hz, 1H), 7.29 (t, *J*= 7.8Hz, 1H), 7.07 (t, *J*= 7.8Hz, 1H), 6.80 (d, *J*= 7.8Hz, 1H), 5.98 (br s, 1H), 5.48 (m, 1H), 5.08–4.94 (m, 2H), 3.18 (s, 3H), 2.97 (br s, 1H), 2.67 (dd, J_2= 15.6 J_3= 6.8 Hz, 1H), 2.55 (dd, J_2= 15.6, J_3= 8.5 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 156.1, 143.9, 130.6, 129.2, 127.7, 125.2, 122.5, 119.8, 107.9, 80.3, 68.6, 39.5, 28.1 (3C), 26.1; HRMS (ESI) calcd for $C_{17}H_{23}N_3O_3Na$ $[M+Na]^+$ 340.1632 found 340.1626

tert-butyl 2-(3-allyl-1-benzyl-5-methoxy-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**3c**)

Synthetized according to the general procedure using conditions B starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 6:4) to afford pure compound **3c** as a yellow sticky foam (521 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 5H), 7.11 (br d, *J*= 2.7 Hz, 1H), 6.68 (dd, J_3= 8.7 Hz, J_4= 2.7 Hz, 1H), 6.52 (d, *J*= 8.7 Hz, 1H), 6.37 (br s, 1H), 5.57-5.47 (m, 1H), 5.09 (d, *J*= 17.2 Hz, 1H), 5.00 (d, *J*= 10.0 Hz, 1H), 4.91 (br d, *J*= 16.0 Hz, 1H), 4.80 (br d, *J*= 16.0 Hz, 1H), 4.71 (br s, 1H), 3.74 (s, 3H), 2.71 (dd, J_2= 13.6 Hz, J_3= 6.5 Hz, 1H), 2.63 (dd, J_2= 13.6 Hz, J_3= 8.3 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 156.1, 155.9, 136.5, 135.7, 130.7, 129.1, 128.7 (2C), 127.5, 127.2 (2C), 120.1, 114.1, 112.1, 109.5, 80.3, 69.0, 55.8, 43.8, 39.7, 28.1 (3C); HRMS (ESI) calcd for $C_{24}H_{29}N_3O_4Na$ $[M+Na]^+$ 446.2050 found 446.2046

tert-butyl 2-(3-allyl-5-bromo-1-methyl-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**3d**)

Synthetized according to the general procedure using conditions A starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 6:4) to afford pure compound **3d** as a yellow sticky foam (463 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J*= 2.1 Hz, 1H), 7.40 (dd, J_3= 8.2 Hz, J_4= 2.1 Hz, 1H), 6.66 (d, *J*= 8.2 Hz, 1H), 6.04 (br s, 1H), 5.52-5.41 (m, 1H), 5.06-4.98 (m, 2H), 4.56 (br s, 1H), 3.14 (s, 3H), 2.61 (dd, J_2= 13.5 Hz, J_3= 6.9 Hz, 1H), 2.50 (dd, J_2= 13.5 Hz, J_3= 8.5 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 156.1, 143.1, 132.0, 130.1, 129.9, 128.4, 120.5, 115.3, 109.5, 80.8, 68.9, 39.9, 28.1 (3C), 26.3; HRMS (ESI) calcd for $C_{17}H_{22}N_3O_3NaBr$ $[M+Na]^+$ 418.0737 (79-Br) found 418.0742

tert-butyl 2-(3-allyl-6-chloro-1-methyl-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**3e**)

Synthetized according to the general procedure using conditions B starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 6:4) to afford pure compound **3e** as a pale-yellow sticky foam (285 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J*= 8.4 Hz, 1H), 6.98 (dd, J_3= 8.4 Hz, J_4= 2.0 Hz, 1H), 6.74 (d, *J*= 2.0 Hz, 1H), 6.22 (br s, 1H), 5.47-5.37 (m, 1H), 4.99-4.92 (m, 2H), 4.58 (br s, 1H), 3.10 (s, 3H), 2.58 (dd, J_2= 13.3 Hz, J_3= 6.7 Hz, 1H), 2.47 (dd, J_2= 13.3 Hz, J_3= 8.1 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 156.2, 145.2, 134.9, 130.2 (2C), 126.2, 122.3, 120.2, 108.7, 80.5, 68.4, 39.5, 28.1 (3C), 26.2; HRMS (ESI) calcd for $C_{17}H_{22}N_3O_3NaCl$ $[M+Na]^+$ 374.1242 (35-Cl) found 374.1237

tert-butyl 2-(3-allyl-1-benzyl-2-oxo-7-(trifluoromethyl)indolin-3-yl)hydrazine-1-carboxylate (**3f**)

Synthetized according to the general procedure using conditions A starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 7:3) to afford pure compound **3f** as a yellow sticky foam (525 mg, 76%); spectroscopic data matches the literature-reported ones: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J*= 7.9 Hz, 1H), 7.56 (d, *J*= 7.9 Hz, 1H), 7.33–7.07 (m, 6H), 5.91 (br s, 1H), 5.48 (m, 1H), 5.20 (d, *J*= 16.6 Hz, 1H), 5.13 (d, *J*= 16.6 Hz, 1H), 5.06 (d, *J*= 17.6 Hz, 1H), 5.05 (d, *J*= 10.8 Hz, 1H), 3.34 (br s, 1H), 2.74–2.56 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 156.0, 141.5, 136.3, 130.9, 129.8, 129.1, 128.3 (2C), 127.5 (q, J_3= 6.0 Hz), 126.9, 125.8 (2C), 123.3 (q, J_1= 271.3 Hz), 122.2, 120.8, 112.8 (q, J_2= 33.9 Hz), 80.7, 67.0, 45.7, 40.0, 28.1 (3C); HRMS (ESI) calcd for $C_{24}H_{26}N_3O_3F_3Na$ $[M+Na]^+$ 484.1818 found 484.1826

*tert-butyl 2-(3-allyl-4-chloro-1-methyl-2-oxoindolin-3-yl)hydrazine-1-*carboxylate (**3g**)

Synthetized according to the general procedure using conditions B starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 7:3) to afford pure compound **3g** as a pale-yellow sticky foam (200 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J*= 8.1 Hz, 1H), 6.93 (d, *J*= 8.1 Hz, 1H), 6.62 (d, *J*= 8.1 Hz, 1H), 6.14 (br s, 1H), 5.24-5.13 (m, 1H), 4.96 (d, *J*= 17.2 Hz, 1H), 4.81 (br s, 1H), 4.78 (d, *J*= 10.4 Hz, 1H), 3.09 (s, 3H), 3.03 (dd, J_2= 13.5 Hz, J_3= 6.9 Hz, 1H), 2.67 (dd, J_2= 13.5 Hz, J_3= 7.7 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 156.1, 146.2, 131.9, 130.5, 130.3, 123.9, 123.7, 119.6, 106.5, 80.4, 70.2, 36.4, 28.0 (3C), 26.3; HRMS (ESI) calcd for $C_{17}H_{22}N_3O_3ClNa$ $[M+Na]^+$ 374.1242 (35-Cl) found 374.1246

benzyl 2-(3-allyl-1-benzyl-2-oxoindolin-3-yl)hydrazine-1-carboxylate (**4a**)

Synthetized according to the general procedure using conditions B starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 7:3) to afford pure compound **4a** as a pale-yellow sticky foam (589 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 1H), 7.26-7.10 (m, 12H), 6.98 (br s, 1H), 6.61 (d, *J*= 8.2 Hz, 1H), 5.50-5.40 (m, 1H), 5.04-4.83 (m, 6H), 4.72 (d, *J*= 16.6 Hz, 1H), 2.71 (dd, J_2= 13.5 Hz, J_3= 6.5 Hz, 1H), 2.61 (dd, J_2= 13.5 Hz, J_3= 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 157.0, 143.1, 136.2, 135.5, 130.5, 129.3, 128.8 (2C), 128.6, 128.5 (2C), 128.2, 128.1, 128.0, 127.6, 127.2 (2C), 125.2, 122.9, 120.3, 109.2, 68.8, 66.9, 43.8, 39.8; HRMS (ESI) calcd for $C_{26}H_{25}N_3O_3Na$ $[M+Na]^+$ 450.1788 found 450.1782

benzyl 2-(3-allyl-2-oxo-1-tritylindolin-3-yl)hydrazine-1-carboxylate (**4b**)

Synthetized according to the general procedure using conditions B starting from the corresponding isatin-derived hydrazone; Purified by FC (hexane / ethyl acetate 7:3) to afford pure compound **4b** as a pale-yellow sticky foam (712 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 7H), 7.27-7.14 (m, 12H), 7.09-6.89 (m, 4H), 6.27 (d, *J*= 8.2 Hz, 1H), 5.88 (br s, 1H), 5.68-5.58 (m, 1H), 5.21-5.14 (m, 2H), 5, 01 (d, *J*= 12.6 Hz, 1H), 4.88 (br d, *J*= 12.6 Hz, 1H), 4.42 (br s, 1H), 2.75 (dd, J_2= 13.2 Hz, J_3= 6.2 Hz, 1H), 2.63 (dd, J_2= 13.2 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 156.2, 143.9, 141.9, 136.3, 130.8, 129.3 (7C), 128.4 (2C), 128.0, 127.9, 127.8, 127.7 (8C), 127.0 (4C), 124.6, 122.6, 120.3, 115.9, 75.2, 68.7, 66.6, 40.4; HRMS (ESI) calcd for $C_{38}H_{33}N_3O_3Na$ $[M+Na]^+$ 602.2414 found 602.2409

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzylspiro[cyclopropane-1,3'-indolin]-2'-one (**5aa**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5aa** as a yellow foam (46 mg, 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (d, *J*= 8.0 Hz, 2H), 7.47-7.41 (m, 4H), 7.35-7.10 (m, 10H), 7.04 (t, *J*= 7.5 Hz, 1H), 6.83 (d, *J*= 8.0 Hz, 1H), 5.09 (d, *J*= 15.9 Hz, 1H), 4.93 (d, *J*= 15.9 Hz, 1H), 3.11-2.99 (m, 2H), 2.37-2.29 (m, 1H), 2.14 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.61 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 143.9, 141.6, 139.9, 139.8, 136.8, 129.4 (4C), 129.3 (2C), 128.9, 128.2,

127.9 (4C), 127.8, 127.7 (2C), 127.5, 122.4, 121.5, 109.9, 44.7, 34.7, 34.0, 32.8, 24.8; HRMS (ESI) calcd for $C_{30}H_{25}NONa$ $[M+Na]^+$ 438.1828 found 438.1833

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzylspiro[cyclopropane-1,3'-indolin]-2'-one (**5ab**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ab** as a pale-yellow foam (32 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J*= 8.0 Hz, 2H), 7.48-7.41 (m, 4H), 7.35-7.21 (m, 8H), 7.13 (dt, J_3= 7.7 Hz, J_4= 1.3 Hz, 1H), 6.99 (dt, J_3= 7.7 Hz, J_4= 1.0 Hz, 1H), 6.84 (dd, J_3= 7.7 Hz, J_4= 1.0 Hz, 1H), 6.77 (d, *J*= 7.7 Hz, 1H), 5.18 (d, *J*= 15.8 Hz, 1H), 4.84 (d, *J*= 15.8 Hz, 1H), 3.35 (d, *J*= 7.3 Hz, 2H), 2.29-2.21 (m, 1H), 1.97 (dd, J_2= 4.3 Hz, J_3= 8.0 Hz, 1H), 1.90 (dd, J_2= 4.3 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 142.9, 141.7, 140.7, 139.6, 136.9, 132.0, 129.5 (2C), 129.4 (4C), 128.1, 127.92 (2C), 127.87 (2C), 127.7, 127.6 (2C), 127.2, 122.7, 118.6, 109.4, 44.6, 35.7, 32.4, 31.7, 26.3; HRMS (ESI) calcd for $C_{30}H_{25}NONa$ $[M+Na]^+$ 438.1828 found 438.1831

(1R,2R)-1'-benzyl-2-(4-methoxybenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ba**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-anisole using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ba** as a yellow foam (29 mg, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J*= 7.7 Hz, 2H), 7.24 (t, *J*= 7.7 Hz, 2H), 7.17 (t, *J*= 7.7 Hz, 2H), 7.08 (d, *J*= 7.7 Hz, 1H), 7.02 (t, *J*= 7.7 Hz, 1H), 6.97 (d, *J*= 8.7 Hz, 2H), 6.80 (d, *J*= 7.7 Hz, 1H), 6.75 (d, *J*= 8.7 Hz, 2H), 5.08 (d, *J*= 16.1 Hz, 1H), 4.90 (d, *J*= 16.1 Hz, 1H), 3.76 (s, 3H), 3.00-2.88 (m, 2H), 2.29-2.21 (m, 1H), 2.09 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.57 (dd, partially under water signal); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 158.7, 143.9, 141.9, 136.9, 132.8, 129.7 (2C), 129.4 (2C), 128.1, 127.8 (2C), 127.4, 122.3, 121.5, 114.5 (2C), 109.8, 55.9, 44.6, 35.1, 33.5, 30.4, 24.8; HRMS (ESI) calcd for $C_{25}H_{23}NO_2Na$ $[M+Na]^+$ 392.1621 found 392.1627

(1R,2S)-1'-benzyl-2-(4-methoxybenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5bb**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-anisole using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5bb** as a light-yellow foam (26 mg, 28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 6H), 7.10 (d, *J*= 8.3 Hz, 2H), 6.97 (t, *J*= 8.3 Hz, 1H), 6.81-6.72 (m, 4H), 5.18 (d, *J*= 16.2 Hz, 1H), 4.81 (d, *J*= 16.2 Hz, 1H), 3.77 (s, 3H), 3.23 (d, *J*= 7.6 Hz, 2H), 2.22-2.14 (m, 1H), 1.92 (dd, J_2= 4.3 Hz, J_3= 8.0 Hz, 1H), 1.86 (dd, J_2= 4.3 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 158.6, 142.8, 136.9, 133.7, 132.1, 130.0 (2C), 129.3 (2C), 128.1, 127.9 (2C), 127.1, 122.6, 118.6, 114.6 (2C), 109.4, 55.9, 44.6, 36.2, 31.9, 31.7, 26.3; HRMS (ESI) calcd for $C_{25}H_{23}NO_2Na$ $[M+Na]^+$ 392.1621 found 392.1624

(1R,2R)-1'-benzyl-2-(4-nitrobenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ca**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-nitrobenzene using conditions-A; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5ca** as a dark-yellow foam (18 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J*= 8.7 Hz, 1H), 7.34-7.27 (m, 3H), 7.24-7.14 (m, 6H), 7.06-7.02 (m, 2H), 6.83 (d, *J*= 8.0 Hz, 1H), 5.08 (d, *J*= 15.7 Hz, 1H), 4.88 (d, *J*= 8.0 Hz, 1H), 3.20 (dd, J_2= 15.5 Hz, J_3= 6.7 Hz, 1H), 3.03 (dd, J_2= 15.5 Hz, J_3= 8.1 Hz, 1H), 2.29-2.21 (m, 1H), 2.14 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.59 (dd, J_2= 4.4 Hz, J_3= 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 148.3, 144.2, 143,9, 136.7, 129.9, 129.5 (2C), 129.4 (2C), 128.3, 127.8 (3C), 124.4 (2C), 122.5, 121.3, 110.1, 44.7, 34.1, 33.6, 32.5, 24.2; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3Na$ $[M+Na]^+$ 407.1366 found 407.1372

(1R,2S)-1'-benzyl-2-(4-nitrobenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5cb**)

Synthetized according to the general procedure starting from compound **3a** and 4-Br-nitrobenzene using conditions-A; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5cb** as a yellow foam (22 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J*= 8.7 Hz, 1H), 7.38-7.27 (m, 5H), 7.19-7.07 (m, 4H), 7.00 (dt, J_3= 7.7 Hz, J_4= 1.0 Hz, 1H), 6.84-6.76 (m, 2H), 5.15 (d, *J*= 15.5 Hz, 1H), 4.79 (d, *J*= 15.5 Hz, 1H), 3.48-3.37 (m, 2H), 2.33-2.15 (m, 1H), 1.95-1.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 149.4, 142.8, 139.0,

136.7, 131.3, 129.8 (2C), 129.4 (2C), 128.3, 127.9 (2C), 127.5, 124.4 (2C), 122.9, 118.7, 109.6, 44.6, 34.4, 32.6, 31.4, 25.9; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3Na$ $[M+Na]^+$ 407.1366 found 407.1363

(1R,2R)-1'-benzyl-2-(naphthalen-1-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5da**)

Synthetized according to the general procedure starting from compound **3a** and 1-Br-naphtalene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5da** as a pale-yellow foam (24 mg, 24%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 1H), 7.90-7.81 (m, 1H), 7.32 (d, *J*= 8.4 Hz, 1H), 7.51-7.43 (m, 2H), 7.34-7.28 (m, 4H), 7.24-7.14 (m, 4H), 7.07-7.01 (m, 2H), 6.83 (d, *J*= 7.9 Hz, 1H), 5.07 (d, *J*= 15.7 Hz, 1H), 4.95 (d, *J*= 15.7 Hz, 1H), 3.44 (d, *J*= 6.9 Hz, 2H), 2.49-2.41 (m, 1H), 2.15 (dd, J_2= 4.4 Hz, J_3= 8.9 Hz, 1H), 1.64 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H), 1.56 (s, residual water signal); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 144.0, 141.6, 136.8, 136.7, 134.4, 132.5, 129.5, 129.4 (2C), 128.2, 127.9 (2C), 127.7, 127.5, 126.7, 126.3, 126.2, 125.9, 124.1, 122.4, 121.5, 109.9, 44.7, 33.6, 32.6, 31.3, 25.1; HRMS (ESI) calcd for $C_{28}H_{23}NONa$ $[M+Na]^+$ 412.1672 found 412.1667

(1R,2S)-1'-benzyl-2-(naphthalen-1-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5db**)

Synthetized according to the general procedure starting from compound **3a** and 1-Br-naphtalene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5db** as a pale-yellow foam (21 mg, 21%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J*= 8.2 Hz, 1H), 7.85 (dd, J_3= 7.8 Hz, J_4= 1.6 Hz, 1H), 7.72 (d, *J*= 7.8 Hz, 1H), 7.54-7.46 (m, 2H), 7.34-7.27 (m, 5H), 7.25-7.22 (m, 3H), 7.11 (dt, J_3= 7.6 Hz, J_4= 1.2 Hz, 1H), 6.96 (dt, J_3= 7.6 Hz, J_4= 1.0 Hz, 1H), 6.81 (d, *J*= 7.6 Hz, 1H), 6.76 (d, *J*= 7.8 Hz, 1H), 5.17 (d, *J*= 16.0 Hz, 1H), 4.85 (d, *J*= 16.0 Hz, 1H), 3.81 (dd, J_2= 15.6 Hz, J_3= 6.6 Hz, 1H), 3.70 (dd, J_2= 15.6 Hz, J_3= 7.4 Hz, 1H), 2.42-2.35 (m, 1H), 2.01 (dd, J_2= 4.5 Hz, J_3= 8.0 Hz, 1H), 1.89 (dd, J_2= 4.5 Hz, J_3= 8.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 142.2, 137.1, 136.2, 133.8, 132.1, 131.3, 128.7 (3C), 127.5, 127.3 (2C), 126.8, 126.5, 126.0, 125.7, 125.65, 125.57, 123.8, 122.0, 118.1, 108.8, 44.0, 34.3, 31.4, 28.8, 25.7; HRMS (ESI) calcd for $C_{28}H_{23}NONa$ $[M+Na]^+$ 412.1672 found 412.1678

(1R,2R)-1'-benzyl-2-(2,4,6-trimethylbenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ea**)
Synthetized according to the general procedure starting from compound **3a** and Br-mesitylene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ea** as a yellow foam (22 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 5H), 7.22-7.12 (m, 3H), 7.06 (dt, J_3= 7.5 Hz, J_4= 1.1 Hz, 1H), 6.89-6.84 (m, 2H), 5.04-4.96 (m, 2H), 3.00-2.94 (m, 1H), 2.89-2.83 (m, 1H), 2.35 (s, 3H), 2.27 (s, 6H), 2.08-1.98 (m, 2H), 1.59 (br dd, J_2= 3.6 Hz, J_3=, 6.6 Hz, 1H), 1.56 (s, residual water signal); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 144.1, 142.0, 136.8, 136.4, 134.9, 129.8 (2C), 129.4 (2C), 128.2, 127.9 (2C), 127.3, 124.1, 122.7, 122.3, 121.6, 109.9, 44.8, 33.0, 32.8, 28.5, 26.3, 21.0, 20.5; HRMS (ESI) calcd for $C_{27}H_{27}NONa$ $[M+Na]^+$ 404.1985 found 404.1992

(1R,2S)-1'-benzyl-2-(2,4,6-trimethylbenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5eb**)

Synthetized according to the general procedure starting from compound **3a** and Br-mesitylene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5eb** as a pale-yellow foam (23 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 7.13 (dt, J_3= 7.8 Hz, J_4= 1.3 Hz, 1H), 6.97 (dt, J_3= 7.4 Hz, J_4= 1.1 Hz, 1H), 6.88 (s, 2H), 6.81 (d, *J*= 7.8 Hz, 1H), 6.74 (d, *J*= 7.4 Hz, 1H), 5.04 (s, 2H), 3.40 (dd, J_2= 14.7 Hz, J_3= 8.3 Hz, 1H), 3.08 (dd, J_2= 14.7 Hz, J_3= 3.0 Hz, 1H), 2.35 (s, 6H), 2.27 (s, 3H), 2.00-1.93 (m, 2H), 1.83-1.77 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 142.9, 137.3 (2C), 137.0, 136.3, 135.6, 132.0, 129.7 (2C), 129.4 (2C), 128.2, 128.1 (2C), 127.1, 122.7, 118.6, 109.4, 44.8, 34.1, 32.2, 27.3, 26.5, 21.5, 21.1 (2C); HRMS (ESI) calcd for $C_{27}H_{27}NONa$ $[M+Na]^+$ 404.1985 found 404.1980

(1R,2S)-1'-benzyl-2-((6-phenylpyridin-2-yl)methyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5fa**)

Synthetized according to the general procedure starting from compound **4a** and 6-Br-2-phenylpyridine using conditions-B; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5fa** as a yellow foam (39 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J_3= 8.3 Hz, J_4= 1.4 Hz, 2H), 7.59-7.52 (m, 2H), 7.46-7.36 (m, 5H), 7.26-7.24 (m, 3H), 7.18-7.15 (m, 2H), 7.03 (dd, J_3= 7.7 Hz, J_4= 1.2 Hz, 1H), 6.95 (dd, J_3= 7.3 Hz, J_4= 1.4 Hz, 1H), 6.80 (d, *J*= 8.3 Hz, 1H), 5.04 (d, *J*= 15.8 Hz, 1H), 4.93 (d, *J*= 15.8 Hz, 1H), 3.32 (dd, J_2= 15.2

Hz, J_3= 7.3 Hz, 1H), 3.20 (dd, J_2= 15.2 Hz, J_3= 7.4 Hz, 1H), 2.54-2.46 (m, 1H), 2.14 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.67 (dd, J_2= 4.4 Hz, J_3= 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.5, 140.1, 137.8, 136.9, 129.5, 129.3 (4C), 128.1, 127.8 (2C), 127.6 (2C), 127.3, 124.7, 124.5, 122.4, 121.7, 121.2, 118.7, 109.8, 44.7, 37.1, 33.3, 32.6, 24.8; HRMS (ESI) calcd for $C_{29}H_{24}N_2ONa$ $[M+Na]^+$ 439.1781 found 439.1777

(1R,2R)-1'-benzyl-2-((6-phenylpyridin-2-yl)methyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5fb**)

Synthetized according to the general procedure starting from compound **4a** and 6-Br-2-phenylpyridine using conditions-B; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5fb** as a light-yellow foam (31 mg, 29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.58-7.51 (m, 2H), 7.32-7.29 (m, 3H), 7.16-7.10 (m, 6H), 7.06-7.01 (m, 2H), 6.92 (dd, J_3= 7.5 Hz, J_4= 0.9 Hz, 1H), 6.73 (d, J= 7.8 Hz, 1H), 5.09 (d, J= 15.9 Hz, 1H), 4.79 (d, J= 15.9 Hz, 1H), 3.61 (dd, J_2= 15.7 Hz, J_3= 8.6 Hz, 1H), 3.52 (dd, J_2= 15.7 Hz, J_3= 5.7 Hz, 1H), 2.60-2.52 (m, 1H), 1.98-1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 160.9, 157.3, 143.0, 140.1, 137.5, 136.8, 132.3, 129.2 (5C), 127.9, 127.7 (2C), 127.4 (2C), 127.0, 122.6, 122.0, 118.8, 118.4, 109.4, 44.5, 35.1, 34.0, 31.7, 25.9; HRMS (ESI) calcd for $C_{29}H_{24}N_2ONa$ $[M+Na]^+$ 439.1781 found 439.1787

(1R,2R)-1'-benzyl-2-propylspiro[cyclopropane-1,3'-indolin]-2'-one (**5ga**)

Synthetized according to the general procedure starting from compound **4a** and vinyl bromide (1M THF) using conditions-B; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ga** as a light-yellow foam (29 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4H), 7.25-7.22 (m, 1H), 7.17-7.11 (m, 1H), 6.98-6,97 (m, 2H), 6.80 (d, J= 7.8 Hz, 1H), 5.02 (d, J= 15.9 Hz, 1H), 4.97 (d, J= 7.8 Hz, 1H), 2.05-1.94 (m, 3H), 1.74-1.67 (m, 1H), 1.65-1.59 (m, 1H), 1.43-1.37 (m, 1H), 1.34-1.28 (m, 1H), 0.88 (t, J= 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 143.2, 136.3, 136.1, 128.7 (2C), 127.5, 127.2 (2C), 126.4, 121.6, 120.6, 109.0, 44.1, 33.4, 31.7, 30.2, 25.0, 22.4, 13.7; HRMS (ESI) calcd for $C_{20}H_{21}NONa$ $[M+Na]^+$ 314.1515 found 314.1508

(1R,2S)-1'-benzyl-2-propylspiro[cyclopropane-1,3'-indolin]-2'-one (**5gb**)

Synthetized according to the general procedure starting from compound **4a** and vinyl bromide (1M THF) using conditions-B; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5gb** as a colourless foam (20 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (5H), 7.11 (dt, J_3= 7.6 Hz, J_4= 1.2 Hz, 1H), 6.98 (dt, J_3= 7.6 Hz, J_4= 1.1 Hz, 1H), 6.81 (d, J= 7.6 Hz, 1H), 6.77 (d, J= 7.6 Hz, 1H), 5.07 (d, J= 15.6 Hz, 1H), 4.92 (d, J= 15.6 Hz, 1H), 1.97-1.86 (m, 3H), 1.80-1.74 (m, 2H), 1.56 (s, residual water signal), 1.43-1.36 (m, 2H), 0.91 (t, J= 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 142.8, 137.1, 132.5, 129.3 (2C), 128.1, 128.0 (2C), 126.9, 122.5, 118.4, 109.3, 44.6, 35.6, 31.5, 28.8, 26.5, 23.4, 14.4; HRMS (ESI) calcd for $C_{20}H_{21}NONa$ $[M+Na]^+$ 314.1515 found 314.1521

(1R,2R)-2-(4-acetylbenzyl)-1'-benzylspiro[cyclopropane-1,3'-indolin]-2'-one (**5ha**)

Synthetized according to the general procedure starting from compound **4a** and 4-Br-acetphenone using conditions-B; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5ha** as a yellow foam (32 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J= 8.3 Hz, 2H), 7.30-7.23 (m, 5H), 7.17 (dt, J_3= 7.6 Hz, J_4= 1.5 Hz, 1H), 7.13 (d, J= 8.3 Hz, 2H), 7.08-6.99 (m, 2H), 6.82 (d, J= 7.6 Hz, 1H), 5.07 (d, J= 15.9 Hz, 1H), 4.90 (d, J= 15.9 Hz, 1H), 3.11 (dd, J_2= 15.4 Hz, J_3= 7.0 Hz, 1H), 3.00 (dd, J_2= 15.4 Hz, J_3= 7.6 Hz, 1H), 2.55 (s, 3H), 2.31-2.23 (m, 1H), 2.12 (dd, J_2= 4.5 Hz, J_3= 9.0 Hz, 1H), 1.58 (dd, J_2= 4.5 Hz, J_3= 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 176.8, 145.7, 143.2, 136.1, 135.4, 130.9, 128.8 (2C), 128.6 (2C), 128.3 (2C), 127.6, 127.2 (2C), 127.0, 121.8, 120.8, 109.4, 44.1, 33.7, 33.4, 32.0, 26.6, 23.9; HRMS (ESI) calcd for $C_{26}H_{23}NO_2Na$ $[M+Na]^+$ 404.1621 found 404.1616

(1R,2S)-2-(4-acetylbenzyl)-1'-benzylspiro[cyclopropane-1,3'-indolin]-2'-one (**5hb**)

Synthetized according to the general procedure starting from compound **4a** and 4-Br-acetphenone using conditions-B; purified by FC (hexane / ethyl acetate 8:2) to afford pure compound **5hb** as a pale-yellow foam (29 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J= 8.3 Hz, 2H), 7.30-7.25 (m, 5H), 7.21-7.19 (m, 2H), 7.13 (dt, J_3= 7.7 Hz, J_4= 1.3 Hz, 1H), 6.99 (dt, J_3= 7.5 Hz, J_4= 1.0 Hz, 1H), 6.83 (dd, J_3= 7.5 Hz, J_4= 1.5 Hz,

1H), 6.77 (d, *J*= 7.7 Hz, 1H), 5.17 (d, *J*= 15.7 Hz, 1H), 4.81 (d, *J*= 15.7 Hz, 1H), 3.38 (d, *J*= 7.1 Hz, 1H), 2.56 (s, 3H), 2.24-2.17 (m, 1H), 1.95-1.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 175.6, 146.7, 142.2, 136.2, 135.3, 131.0, 128.73 (2C), 128.69 (2C), 128.6 (2C), 127.5, 127.3 (2C), 126.7, 122.1, 118.0, 108.9, 44.0, 34.3, 32.1, 30.9, 26.6, 25.4; HRMS (ESI) calcd for $C_{26}H_{23}NO_2Na$ $[M+Na]^+$ 404.1621 found 404.1625

(1R,2R)-1'-benzyl-2-(3-chlorobenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ia**)

Synthetized according to the general procedure starting from compound **3a** and 3-Br-chlorobenzene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ia** as a yellow foam (35 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 3H), 7.24 (br s, 1H), 7.21-7.11 (m, 4H), 6.94 (br d, *J*= 7.0 Hz, 1H), 6.82 (d, *J*= 8.0 Hz, 1H), 5.09 (d, *J*= 15.8 Hz, 1H), 4.91 (d, *J*= 15.8 Hz, 1H), 3.02 (dd, J_2= 15.4 Hz, J_3= 7.4 Hz, 1H), 2.95 (dd, J_2= 15.4 Hz, J_3= 7.3 Hz, 1H), 2.31-2.22 (m, 1H), 2.11 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.56 (dd, J_2= 4.4 Hz, J_3= 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 145.0, 143.3, 142.0, 136.1, 131.9, 129.7, 128.8 (2C), 128.4, 127.5, 127.1 (2C), 126.9, 126.5, 126.3, 121.8, 120.8, 109.3, 44.1, 33.5, 33.4, 32.0, 24.0; HRMS (ESI) calcd for $C_{24}H_{20}NOClNa$ $[M+Na]^+$ 396.1126 (35-Cl) found 396.1118

(1R,2S)-1'-benzyl-2-(3-chlorobenzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ib**)

Synthetized according to the general procedure starting from compound **3a** and 3-Br-chlorobenzene using conditions-A; purified by FC (hexane / ethyl acetate 9:1) to afford pure compound **5ib** as a light-yellow foam (27 mg, 28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 6H), 7.18-7.03 (m, 4H), 6.99 (dt, J_3= 7.5 Hz, J_4= 1.1 Hz, 1H), 6.82 (d, *J*= 7.5 Hz, 1H), 6.76 (d, *J*= 7.5 Hz, 1H), 5.17 (d, *J*= 15.8 Hz, 1H), 4.83 (d, *J*= 15.8 Hz, 1H), 3.29 (d, *J*= 7.2 Hz, 2H), 2.22-2.14 (m, 1H), 1.93-1.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 143.0, 142.2, 136.2, 131.1, 129.8, 128.8 (2C), 128.5, 127.5, 127.2 (2C), 126.6 (2C), 126.3, 122.1, 118.0, 109.3, 108.9, 44.0, 34.4, 31.7, 30.9, 25.5; HRMS (ESI) calcd for $C_{24}H_{20}NOClNa$ $[M+Na]^+$ 396.1126 (35-Cl) found 396.1131

(1R,2R)-1'-benzyl-2-(4-(dimethylamino)benzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ja**)

Synthetized according to the general procedure starting from compound **4a** and N,N-dimethyl-4-Br-aniline using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5ja** as a dark-yellow foam (24 mg, 25%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.27 (m, 2H), 7.19-7.13 (m, 3H), 7.09 (dd, J_3= 7.5 Hz, J_4= 1.0 Hz, 1H), 7.01 (dt, J_3= 7.5 Hz, J_4= 1.0 Hz, 1H), 6.95 (d, *J*= 8.7 Hz, 2H), 6.81 (d, *J*= 7.5 Hz, 1H), 6.72 (t, *J*= 7.5 Hz, 1H), 6.62 (d, *J*= 8.7 Hz, 2H), 5.07 (d, *J*= 15.9 Hz, 1H), 4.92 (d, *J*= 15.9, 1H), 2.92-2.91 (m, 2H), 2.90 (s, 6H), 2.31-2.23 (m, 1H), 2.08 (dd, J_2= 4.3 Hz, J_3= 9.0 Hz, 1H), 1.55 (dd, J_2= 4.3 Hz, J_3= 7.9 Hz, 1H, partially overlapped with residual water signal); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 149.3, 143.2, 141.7 (2C), 136.3, 129.0, 128.8 (2C), 128.7 (2C), 127.4, 127.2 (2C), 126.6, 121.6, 120.9, 113.0, 109.1, 44.0, 40.9, 40.8, 34.7, 32.8, 32.1, 24.3; HRMS (ESI) calcd for $C_{26}H_{26}N_2ONa$ $[M+Na]^+$ 405.1937 found 405.1944

(1R,2S)-1'-benzyl-2-(4-(dimethylamino)benzyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5jb**)

Synthetized according to the general procedure starting from compound **4a** and N,N-dimethyl-4-Br-aniline using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5jb** as a yellow foam (18 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32-5.25 (m, 5H), 7.12-7.06 (m, 3H), 6.96 (t, *J*= 7.6 Hz, 1H), 6.80 (d, *J*= 7.6 Hz, 1H), 6.74 (d, *J*= 7.6 Hz, 1H), 6.65 (d, *J*= 8.6 Hz, 2H), 5.18 (d, *J*= 15.9 Hz, 1H), 4.84 (d, *J*= 15.9 Hz, 1H), 3.22-3.17 (m, 1H), 2.91 (s, 6H), 2.22-2.14 (m, 1H), 1.93 (dd, J_2= 4.3 Hz, J_3= 8.0 Hz, 1H), 1.85 (dd, J_2= 4.3 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 149.2, 142.2, 136.4, 136.0, 131.6, 129.0 (2C), 128.7 (3C), 127.4, 127.3 (2C), 126.3, 121.9, 117.9, 113.1, 108.7, 44.0, 40.9 (2C), 36.0, 31.2 (2C), 25.8; HRMS (ESI) calcd for $C_{26}H_{26}N_2ONa$ $[M+Na]^+$ 405.1937 found 405.1933

(1R,2R)-1'-benzyl-2-((1-methyl-1H-indol-5-yl)methyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ka**)

Synthetized according to the general procedure starting from compound **4a** and N-methyl-5-Br-indole using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5ka** as a yellow foam (16 mg, 16%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.37 (m, 2H), 7.32-7.26 (m, 3H), 7.20-7.14 (m, 4H), 7.05-7.01

(m, 2H), 6.99-6.95 (m 1H), 6.80 (d, *J*= 7.8 Hz, 1H), 6.37 (d, *J*= 3.1 Hz, 1H), 5.06 (d, *J*= 15.9 Hz, 1H), 4.93 (d, *J*= 15.9 Hz, 1H), 3.76 (s, 3H), 3.10-3.07 (m, 2H), 2.40-2.33 (m, 1H), 2.10 (dd, J_2= 4.3 Hz, J_3= 9.0 Hz, 1H), 1.60 (dd, J_2= 4.3 Hz, J_3= 7.3 Hz, 1H, partially overlapped with residual water signal); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 143.9, 142.6, 136.9, 136.2, 131.5, 129.7, 129.4 (2C), 128.1, 127.8 (2C), 127.3, 124.2, 122.8, 122.3, 121.6, 120.6, 109.84, 109.79, 101.3, 44.7, 35.6, 34.5, 33.5, 32.9, 25.2; HRMS (ESI) calcd for $C_{27}H_{24}N_2ONa$ $[M+Na]^+$ 415.1781 found 415.1788

(1R,2S)-1'-benzyl-2-((1-methyl-1H-indol-5-yl)methyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5kb**)

Synthetized according to the general procedure starting from compound **4a** and N-methyl-5-Br-indole using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5kb** as a yellow foam (25 mg, 25%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (br s, 1H), 7.26-7.19 (m, 6H), 7.10-7.06 (m, 2H), 7.01 (d, *J*= 3.1 Hz, 1H), 6.94 (dt, J_3= 7.6 Hz, J_4= 1.1 Hz, 1H), 6.79 (dd, J_3= 7.6 Hz, J_4= 1.4 Hz, 1H), 6.71 (d, *J*= 7.6 Hz, 1H), 6.38 (d, *J*= 3.1 Hz, 1H), 5.20 (d, *J*= 15.4 Hz, 1H), 4.84 (d, *J*= 15.4 Hz, 1H), 3.76 (s, 3H), 3.40 (dd, J_2= 14.8 Hz, J_3= 6.9 Hz, 1H), 3.35 (dd, J_2= 14.8 Hz, J_3= 7.2 Hz, 1H), 2.31-2.23 (m, 1H), 1.98 (dd, J_2= 4.4 Hz, J_3= 8.0 Hz, 1H), 1.86 (dd, J_2= 4.4 Hz, J_3= 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 142.8 (2C), 137.0, 136.1, 132.5, 132.2, 129.6, 129.4 (2C), 128.0, 127.9 (2C), 126.9, 123.2, 122.6, 120.8, 118.6, 109.8, 109.4, 101.3, 44.6, 37.1, 33.5, 32.9, 31.9, 26.6; HRMS (ESI) calcd for $C_{27}H_{24}N_2ONa$ $[M+Na]^+$ 415.1781 found 415.1776

(1R,2S)-1'-benzyl-2-(thiophen-3-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5la**)

Synthetized according to the general procedure starting from compound **4a** and 3-Br-thiophene using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5la** as a yellow foam (17 mg, 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 7.20-7.16 (m 2H), 7.08-7.00 (m, 2H), 6.83-6.80 (m, 2H), 6.76 (dd, J_3= 5.0 Hz, J_4= 1.4 Hz, 1H), 5.09 (d, *J*= 15.9 Hz, 1H), 4.91 (d, *J*= 15.9 Hz, 1H), 3.10 (dd, J_2= 15.4 Hz, J_3= 6.9 Hz, 1H), 2.95 (dd, J_2= 15.4 Hz, J_3= 7.6 Hz, 1H), 2.33-2.26 (m, 1H), 2.12 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.57 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 143.2, 140.2, 136.2, 128.8 (2C), 128.2, 127.8, 127.5, 127.2 (2C), 126.8, 125.6, 121.7, 120.7 (2C), 109.2, 44.0, 33.8, 32.0, 28.6, 24.0; HRMS (ESI) calcd for $C_{22}H_{19}NOSNa$ $[M+Na]^+$ 368.1080 found 368.1087

(1R,2R)-1'-benzyl-2-(thiophen-3-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5lb**)

Synthetized according to the general procedure starting from compound **4a** and 3-Br-thiophene using conditions-B; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5l,b** as a light-yellow foam (28 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 3H), 7.23-7.19 (m, 2H), 7.16 (s, 1H), 7.13 (dt, J_3= 7.6 Hz, J_4= 1.3 Hz, 1H), 6.99 (dt, J_3= 7.6 Hz, J_4= 1.0 Hz, 1H), 6.92 (dd, , J_3= 5.0 Hz, J_4= 1.3 Hz, 1H), 6.86-6.83 (m, 2H), 6.77 (d, *J*= 7.6 Hz, 1H), 5.17 (d, *J*= 15.9 Hz, 1H), 4.81 (d, *J*= 7.6 Hz, 1H), 3.32 (d, *J*= 7.3 Hz, 2H), 2.27-2.19 (m, 1H), 1.94-1.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 142.2, 141.3, 136.3, 128.8 (2C), 128.1, 127.7, 127.5, 127.3 (2C), 126.5, 122.8, 122.0, 118.0 (2C), 108.8, 44.0, 34.5, 33.0, 27.0, 23.2; HRMS (ESI) calcd for $C_{22}H_{19}NOSNa$ $[M+Na]^+$ 368.1080 found 368.1076

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-tritylspiro[cyclopropane-1,3'-indolin]-2'-one (**5ma**)

Synthetized according to the general procedure starting from compound **4b** and 4-Br-biphenyl using conditions-B; purified by FC (hexane / ethyl acetate 95:5) to afford pure compound **5ma** as a dark-yellow foam (50 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J*= 7.6 Hz, 2H), 7.51-7.48 (m, 3H), 7.46-7.42 (m, 8H), 7.37 (d, *J*= 7.6Hz, 1H), 7.24-7.22 (m, 3H), 7.21-7.18 (m, 5H), 7.13 (d, *J*= 8.0 Hz, 2H), 7.04 (dd, J_3= 7.5 Hz, J_4= 1.5 Hz, 1H), 6.95 (dt, J_3= 7.5 Hz, J_4= 1.1 Hz, 1H), 6.89 (dt, J_3= 7.5 Hz, J_4= 1.5 Hz, 1H), 6.36 (d, *J*= 8.0 Hz, 1H), 3.19 (dd, J_2= 15.4 Hz, J_3= 6.0 Hz, 1H), 2.99 (dd, J_2= 15.4 Hz, J_3= 8.8 Hz, 1H), 2.29-2.21 (m, 1H), 2.05 (dd, J_2= 4.4 Hz, J_3= 9.1 Hz, 1H), 1.51, (dd, J_2= 4.4 Hz, J_3= 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 145.0, 143.8, 142.4 (3C), 141.0, 139.4, 131.9, 129.5 (5C), 128.8 (2C), 128.6 (2C), 127.6 (5C), 127.2, 127.1 (2C), 127.0 (2C), 126.8 (4C), 125.3, 122.8, 121.2, 120.2, 115.9, 74.4, 34.9, 32.9, 32.7, 24.3; HRMS (ESI) calcd for $C_{42}H_{33}NONa$ $[M+Na]^+$ 590.2454 found 590.2461

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-tritylspiro[cyclopropane-1,3'-indolin]-2'-one (**5mb**)

Synthetized according to the general procedure starting from compound **4b** and 4-Br-biphenyl using conditions-B; purified by FC (hexane / ethyl acetate 95:5) to afford pure compound **5mb** as a yellow foam (49 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 4H), 7.50-7.39 (m, 8H), 7.34 (tt, J_3= 7.2 Hz, J_4= 1.5 Hz, 1H), 7.28-7.16 (m, 11H), 6.92 (t, *J*= 7.6 Hz, 1H), 6.85 (dt, J_3= 7.6 Hz, J_4= 1.6 Hz, 1H), 6.79 (dd, J_3= 7.6 Hz, J_4= 1.5 Hz, 1H), 6.28 (d, *J*= 7.9 Hz, 1H), 3.34-3.24 (m, 2H), 2.25, 2.17 (m, 1H), 1.85 (dd, J_2= 4.4 Hz, J_3= 8.0 Hz, 1H), 1.79 (dd, J_2= 4.4 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 142.8, 142.5 (3C), 141.2, 140.3, 139.1, 131.8, 129.4 (6C), 128.8 (2C), 128.6 (2C), 127.5 (6C), 127.2 (2C), 127.1 (2C), 126.7 (4C), 125.1, 121.5, 117.4, 115.4, 74.6, 35.1, 31.6, 31.4, 25.1; HRMS (ESI) calcd for $C_{42}H_{33}NONa$ $[M+Na]^+$ 590.2454 found 590.2449

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5na**)

Synthetized according to the general procedure starting from compound **3b** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5na** as a light-yellow foam (22 mg, 26%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 2H), 7.48 (d, *J*= 8.1 Hz, 2H), 7.42 (t, *J*= 7.4 Hz, 2H), 7.35-7.32 (m, 2H), 7.20 (d, *J*= 8.1 Hz, 2H), 7.12-7.08 (m, 2H), 6.95 (d, *J*= 7.8 Hz, 1H), 3.30 (s, 3H), 3.01 (d, *J*= 7.1 Hz, 2H), 2.30-2.22 (m, 1H), 2.05 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.53 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 144.3, 140.9, 139.8, 139.3, 139.2, 128.8 (2C), 128.7 (2C), 127.2 (2C), 127.1, 127.0 (2C), 126.9, 121.7, 120.8, 108.2, 33.6, 33.4, 32.1, 31.1, 24.3; HRMS (ESI) calcd for $C_{24}H_{21}NONa$ $[M+Na]^+$ 362.1515 found 362.1509

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5nb**)

Synthetized according to the general procedure starting from compound **3b** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5nb** as a light-yellow foam (31 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J*= 7.6 Hz, 2H), 7.52 (d, *J*= 8.1 Hz, 2H), 7.43 (t, *J*= 7.6 Hz, 2H), 7.35-7.24 (m, 4H), 7.04 (dt, J_3= 7.5 Hz, J_4= 1.1 Hz, 1H), 6.91 (d, *J*= 7.6 Hz, 1H), 6.83 (dd, J_3= 7.5 Hz, J_4= 1.4 Hz, 1H), 3.35 (dd, J_2= 15.0 Hz, J_3= 7.7 Hz, 1H, partially overlapped with methyl signal at 3.33 ppm), 3.33 (s, 3H), 3.25 (dd, J_2= 15.0 Hz, J_3= 6.5 Hz, 1H), 2.24-2.16 (m, 1H), 1.90 (dd, J_2= 4.4 Hz, J_3= 7.9 Hz, 1H), 1.85 (dd, J_2= 4.4 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 143.1, 141.1, 140.2, 139.1, 131.3, 128.8 (2C), 128.7 (2C), 127.3 (2C), 127.1, 127.0 (2C), 126.6, 122.0, 118.0, 107.8, 34.6, 31.7, 31.2, 26.6, 25.5; HRMS (ESI) calcd for $C_{24}H_{21}NONa$ $[M+Na]^+$ 362.1515 found 362.1519

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-5'-bromo-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5oa**)

Synthetized according to the general procedure starting from compound **3d** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5oa** as a dark-yellow foam (35 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.49 (d, *J*= 8.4 Hz, 2H), 7.44-7.40 (m, 3H), 7.35-7.32 (m, 1H), 7.21-7.19 (m, 3H), 6.80 (d, *J*= 8.2 Hz, 1H), 3.27 (s, 3H), 2.99 (d, *J*= 7.3 Hz, 2H), 2.33-2.25 (m, 1H), 2.07 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.55 (dd, J_2= 4.4 Hz, J_3= 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 143.3, 142.2, 140.8, 139.4, 138.7, 129.6, 128.8 (2C), 128.6 (2C), 127.3 (2C), 127.2, 127.0 (2C), 123.9, 114.4, 109.5, 34.0, 33.6, 32.1, 26.7, 24.9; HRMS (ESI) calcd for $C_{24}H_{20}NBrONa$ $[M+Na]^+$ 440.0620 (79-Br) found 440.0626

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-5'-bromo-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5ob**)

Synthetized according to the general procedure starting from compound **3d** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **5ob** as a yellow foam (32 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J_3= 7.6 Hz, J_4= 1.3 Hz, 2H), 7.50 (d, *J*= 8.2 Hz, 2H), 7.42 (t, *J*= 7.6 Hz, 2H), 7.37-7.30 (m, 2H), 7.26 (d, *J*= 8.2 Hz, 2H), 6.92 (d, J_4= 1.8 Hz, 1H), 6.75 (d, *J*= 8.4 Hz, 1H), 3.31 (dd, J_2= 14.9 Hz, J_3= 7.9 Hz, 1H, partially overlapped with methyl signal), 3.28 (s, 3H), 3.23 (dd, J_2= 14.9 Hz, J_3= 7.5 Hz, 1H), 2.23-2.15 (m, 1H), 1.91 (dd, J_2= 4.5 Hz, J_3= 8.1 Hz, 1H), 1.85 (dd, J_2= 4.5 Hz, J_3= 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 142.1, 141.0, 139.8, 139.1, 133.5, 129.3, 128.8 (4C), 127.3 (2C), 127.1, 127.0 (2C), 121.3, 114.7, 109.2, 35.2, 31.6, 31.2, 26.6, 25.8; HRMS (ESI) calcd for $C_{24}H_{20}NBrONa$ $[M+Na]^+$ 440.0620 (79-Br) found 440.0617

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzyl-5'-methoxyspiro[cyclopropane-1,3'-indolin]-2'-one (**5pa**)

Synthetized according to the general procedure starting from compound **3c** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 80:20) to afford pure compound **5pa** as a yellow foam (23 mg, 21%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.47-7.41 (m, 4H), 7.35-7.23 (m, 6H), 7.16 (d, *J*= 8.1 Hz, 2H), 6.71-6.70 (m, 3H), 5.05 (d, *J*= 16.0 Hz, 1H), 4.90 (d, *J*= 16.0 Hz, 1H), 3.78 (s, 3H), 3.09-2.99 (m, 2H), 2.36-2.28 (m, 1H), 2.13 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.55 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 155.3, 140.9, 139.3, 139.1, 136.9, 136.3, 129.8, 128.7 (3C), 128.6 (2C), 127.5, 127.2 (4C), 127.1 (2C), 127.0 (2C), 110.5, 109.4, 109.1, 55.9, 44.1, 33.9, 33.3, 32.4, 24.3; HRMS (ESI) calcd for $C_{31}H_{27}NO_2Na$ $[M+Na]^+$ 468.1934 found 468.1939

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzyl-5'-methoxyspiro[cyclopropane-1,3'-indolin]-2'-one (**5pb**)

Synthetized according to the general procedure starting from compound **3c** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 80:20) to afford pure compound **5pb** as a light-yellow foam (34 mg, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.48 (br d, *J*= 8.1 Hz, 2H), 7.43 (br t, *J*= 7.7 Hz, 2H), 7.31-7.22 (m, 8H), 6.64 (d, *J*= 1.5 Hz, 2H), 6.45 (br t, *J*= 1.5 Hz, 1H), 5.17 (d, *J*= 15.8 Hz, 1H), 4.81 (d, *J*= 15.8 Hz, 1H), 3.74 (s, 3H), 3.36 (d, *J*= 7.2 Hz, 2H), 2.25-2.18 (m, 1H), 1.97 (dd, J_2= 4.4 Hz, J_3= 8.0 Hz, 1H), 1.87 (dd, J_2= 4.4 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 155.8, 141.3, 141.0, 139.0, 136.3, 135.8, 132.8, 128.8 (2C), 128.75 (3C), 128.72 (2C), 127.4, 127.3 (2C), 127.2 (2C), 127.1, 127.0, 110.8, 109.1, 105.7, 55.8, 44.1, 35.2, 31.8, 31.4, 25.7; HRMS (ESI) calcd for $C_{31}H_{27}NO_2Na$ $[M+Na]^+$ 468.1934 found 468.1928

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-6'-chloro-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5qa**)

Synthetized according to the general procedure starting from compound **3e** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5qa** as a yellow foam (27 mg, 29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 2H), 7.48 (br d, *J*= 8.4 Hz, 2H), 7.42 (br t, *J*= 7.5 Hz, 2H), 7.35-7.31 (m, 1H), 7.17 (br d, *J*= 8.4 Hz, 2H), 7.04 (d, *J*= 1.8 Hz, 1H), 7.01 (s, 1H), 6.94 (d, *J*= 1.8 Hz, 1H), 3.27 (s, 3H), 2.98 (br d, *J*= 7.5 Hz, 2H), 2.30-2.23 (m, 1H), 2.06 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.56 (s, residual water signal), 1.53 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 145.3, 141.1, 140.8, 139.4, 138.8, 132.7, 128.8 (2C), 128.6 (2C), 127.3 (2C), 127.2, 127.0 (2C), 121.52, 121.47, 108.9, 33.7, 33.6, 31.9, 26.7, 24.5; HRMS (ESI) calcd for $C_{24}H_{20}NClONa$ $[M+Na]^+$ 396.1126 (35-Cl) found 396.1131

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-6'-chloro-1'-methylspiro[cyclopropane-1,3'-indolin]-2'-one (**5qb**)

Synthetized according to the general procedure starting from compound **3e** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5qb** as a light-yellow foam (22 mg, 24%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (br d, *J*= 7.6 Hz, 2H), 7.49 (d, *J*= 8.3 Hz, 2H), 7.41 (br t, *J*= 7.6 Hz, 2H), 7.32 (br tt, J_3= 7.6 Hz, J_4= 1.4 Hz, 1H), 7.25 (d, *J*= 8.3 Hz, 2H), 6.98 (dd, J_3= 8.0 Hz, J_4= 1.7 Hz, 1H), 6.88 (d, *J*= 1.7 Hz, 1H), 6.71 (d, *J*= 8.0 Hz, 1H), 3.33-3.19 (m, 5H), 2.20-2.12 (m, 1H), 1.89 (dd, J_2= 4.5 Hz, J_3= 8.0 Hz, 1H), 1.83 (dd, J_2= 4.5 Hz, J_3= 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 144.2, 141.0, 139.9, 139.6, 139.1, 132.3, 128.7 (4C), 127.3 (2C), 127.1, 127.0 (2C), 121.7, 118.8, 108.5, 34.9, 31.6, 30.9, 26.6, 25.6; HRMS (ESI) calcd for $C_{24}H_{20}NClONa$ $[M+Na]^+$ 396.1126 (35-Cl) found 396.1123

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzyl-7'-(trifluoromethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5ra**)

Synthetized according to the general procedure starting from compound **3f** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5ra** as a dark-yellow foam (30 mg, 25%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 3H), 7.49 (d, *J*= 8.2 Hz, 2H), 7.45 (t, *J*= 7.3 Hz, 2H), 7.38-7.33 (m, 1H), 7.32 (br d, *J*= 7.6 Hz, 1H), 7.22-7.12 (m, 6H), 7.01 (br d, *J*= 7.3 Hz, 2H), 5.40 (d, *J*= 17.0 Hz, 1H), 5.24 (d, *J*= 17.0 Hz, 1H), 3.16 (dd, J_2= 15.1 Hz, J_3= 6.9 Hz, 1H), 3.01 (dd, J_2= 15.1 Hz, J_3= 7.7 Hz, 1H), 2.46-2.38 (m, 1H), 2.25 (dd, J_2= 4.5 Hz, J_3= 9.1 Hz, 1H), 1.73 (dd, J_2= 4.5 Hz, J_3= 8.0 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 141.3, 140.8, 139.5, 138.6, 136.7, 130.9, 128.8 (2C), 128.6 (2C), 128.4 (2C), 127.4 (2C), 127.3, 127.0 (2C), 126.7, 125.5 (2C), 125.1 (q, J_3= 6.0 Hz), 124.2, 123.5 (q, J_1= 271.7 Hz), 121.1, 113.0 (q, J_2=32.5 Hz), 45.6 (q, *J*= 4.8 Hz), 36.3, 33.0, 31.2, 24.9; HRMS (ESI) calcd for $C_{31}H_{24}NF_3ONa$ $[M+Na]^+$ 506.1702 found 506.1706

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)-1'-benzyl-7'-(trifluoromethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**5rb**)

Synthetized according to the general procedure starting from compound **3f** and 4-Br-biphenyl using conditions-A; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **5rb** as a yellow foam (49 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58 (m, 3H), 7.52 (d, *J*= 8.2 Hz, 2H), 7.46 (br t, *J*= 7.5 Hz, 2H), 7.38-7.34 (m, 2H), 7.27-7.19 (m, 5H), 7.12 (br d, *J*= 8.0 Hz, 1H), 7.09-7.01 (m, 2H), 5.41 (d, *J*= 17.0 Hz, 1H), 5.24 (d, *J*= 17.0 Hz, 1H), 3.38 (dd, J_2= 15.1, J_3= 6.9, 1H), 3.34 (dd, J_2= 15.1, J_3= 7.4 Hz, 1H), 2.41-2.33 (m, 1H), 2.06 (dd, J_2= 4.5 Hz, J_3= 8.1 Hz, 1H), 1.98 (dd, J_2= 4.5 Hz, J_3= 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 143.4, 140.9, 139.5, 139.2, 136.8, 134.0, 128.9 (2C), 128.8 (2C), 128.4 (2C), 127.3 (2C), 127.2, 127.0 (2C), 126.7, 125.7 (2C), 124.8 (q, J_3= 6.0 Hz), 123.5 (q, J_1= 272.2 Hz), 121.54, 121.49, 112.6 (q, J_2= 32.1 Hz), 45.7 (q, *J*= 4.5 Hz), 36.3, 31.5, 31.4, 27.0; HRMS (ESI) calcd for $C_{31}H_{24}NF_3ONa$ $[M+Na]^+$ 506.1702 found 506.1698

(1R,2R)-2-([1,1'-biphenyl]-4-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**7a**)

(35mg, 72%); m.p. 166-168°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (br s, 1H), 7.57 (d, *J*= 7.6 Hz, 2H), 7.49 (d, *J*= 8.2 Hz, 2H), 7.43 (t, *J*= 7.6 Hz, 2H), 7.33 (tt, J_3= 7.6 Hz, J_4= 1.4 Hz, 1H), 7.24 (t, *J*= 7.7 Hz, 1H), 7.20 (d, *J*= 8.2 Hz, 2H), 7.11-7.02 (m, 3H), 3.04 (d, *J*= 7.3 Hz, 2H), 2.33-2.25 (m, 1H), 2.09 (dd, J_2= 4.4 Hz, J_3= 9.0 Hz, 1H), 1.57 (dd, J_2= 4.4 Hz, J_3= 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 141.6 (2C), 140.9, 139.3, 139.1, 128.8 (2C), 128.6 (2C), 127.3 (2C), 127.1, 127.0 (2C), 126.9, 121.7, 121.1, 110.2, 33.7, 33.5, 32.6, 24.4; HRMS (ESI) calcd for $C_{23}H_{19}NONa$ $[M+Na]^+$ 348.1359 found 348.1356

(1R,2S)-2-([1,1'-biphenyl]-4-ylmethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (**7b**)

(38mg, 77%); m.p. 167-169°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (br s, 1H), 7.56 (d, *J*= 7.4 Hz, 2H), 7.50 (d, *J*= 8.2 Hz, 2H), 7.42 (t, *J*= 7.4 Hz, 2H), 7.34-7.29 (m, 3H), 7.19 (dt, J_3= 7.6 Hz, J_4= 1.3 Hz, 1H), 7.01 (dt, J_3= 7.6 Hz, J_4= 1.0 Hz, 1H), 6.97 (d, *J*= 7.6 Hz, 1H), 6.82 (d, *J*= 7.6 Hz, 1H), 3.34 (dd, J_2= 15.0 Hz, J_3= 7.2 Hz, 1H), 3.28 (dd, J_2= 15.0 Hz, J_3= 7.0 Hz, 1H), 2.25-2.17 (m, 1H), 1.93 (dd, J_2= 4.4 Hz, J_3= 8.0 Hz, 1H), 1.87 (dd, J_2= 4.4 Hz, J_3= 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 141.0, 140.3, 140.1, 139.1, 131.9, 128.8 (2C), 128.7 (2C), 127.3 (2C), 127.1, 127.0 (2C), 126.6, 122.0, 118.3, 109.7, 35.2, 31.7, 31.6, 25.7; HRMS (ESI) calcd for $C_{23}H_{19}NONa$ $[M+Na]^+$ 348.1359 found 348.1354

(E)-3-(3-([1,1'-biphenyl]-4-yl)allyl)-1-benzyl-7-(trifluoromethyl)indolin-2-one (**8a**)

Synthetized according to the general procedure starting from compound **5r**; purified by FC (hexane / ethyl acetate 80:20) to afford pure compound **8a** as a yellow foam (62 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J_3= 7.6 Hz, J_4= 1.3 Hz, 2H), 7.58-7.54 (m, 4H), 7.45 (t, *J*= 7.6 Hz, 2H), 7.38-7.35 (m, 3H), 7.16 (t, *J*= 7.7 Hz, 1H), 7.13-7.06 (m, 5H), 6.54 (d, *J*= 16.0 Hz, 1H), 6.18-6.10 (m, 1H), 5.35 (d, *J*= 17.1 Hz, 1H), 5.12 (d, *J*= 17.1 Hz, 1H), 3.74-3.71 (m, 1H), 3.14-3.07 (m, 1H), 3.00-2.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 140.7, 140.4, 136.3, 135.8, 133.7, 131.3, 131.0, 128.8 (2C), 128.4 (2C), 127.8, 127.4, 127.3 (2C), 126.9 (2C), 126.8 (3C), 126.3 (q, J_3= 6.3 Hz), 125.6 (2C), 124.5, 123.4 (q, J_1= 272.1 Hz), 121.9, 112.8 (q, J_2= 34.0 Hz), 45.4 (q, *J*= 5.0 Hz), 44.3, 34.3; HRMS (ESI) calcd for $C_{31}H_{24}NF_3ONa$ $[M+Na]^+$ 506.1702 found 506.1708

(E)-3-(3-([1,1'-biphenyl]-4-yl)allyl)-1-tritylindolin-2-one (**8b**)

Synthetized according to the general procedure starting from compound **5m**; purified by FC (hexane / ethyl acetate 90:10) to afford pure compound **8b** as a yellow foam (65 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J*= 7.6 Hz, 2H), 7.52 (d, *J*= 8.5 Hz, 2H), 7.47-7.39 (m, 9H), 7.35 (br t, *J*= 7.6 Hz, 1H), 7.30 (d, *J*= 8.5

Hz, 2H), 7.20-7.15 (m, 9H), 6.94 (dt, J_3= 7.8 Hz, J_4= 1.2 Hz, 1H), 6.88 (dt, J_3= 7.8 Hz, J_4= 1.7 Hz, 1H), 6.49 (d, *J*= 16.0 Hz, 1H), 6.26 (d, *J*= 7.8 Hz, 1H), 6.04-5.96 (m, 1H), 3.70-3.67 (m, 1H), 3.02-2.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 144.1 (3C), 144.4, 142.2, 140.8, 140.1, 136.2, 133.0, 129.6 (6C), 128.8 (2C), 128.6, 127.5 (6C), 127.3, 127.2 (2C), 126.9, 126.8 (3C), 126.7 (2C), 126.5, 125.3, 123.5, 121.8, 115.8, 74.4, 46.3, 34.2; HRMS (ESI) calcd for $C_{42}H_{33}NONa$ $[M+Na]^+$ 590.2454 found 590.2449

(E)-3-(3-([1,1'-biphenyl]-4-yl)allyl)indolin-2-one (**8c**)

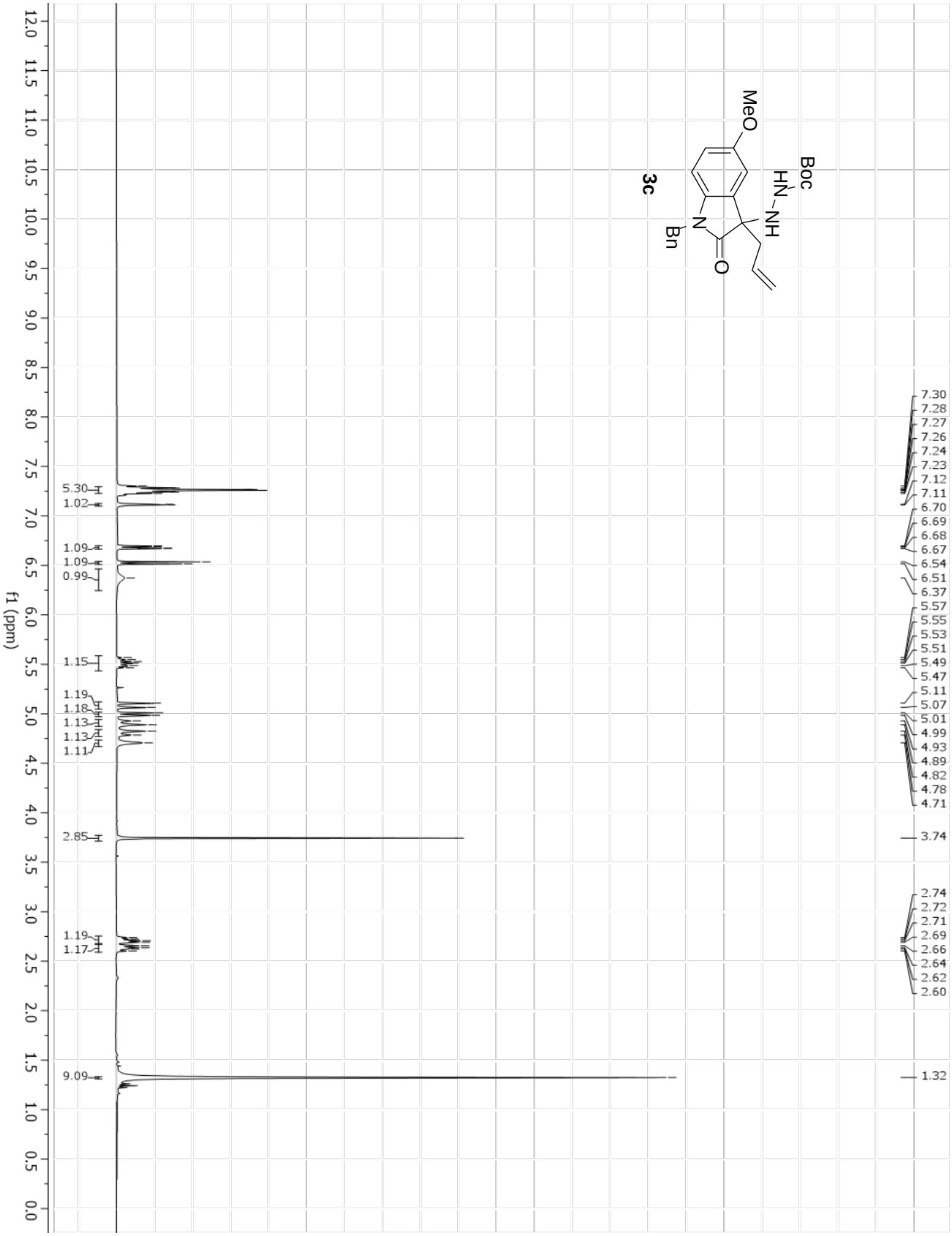
Synthetized according to the general procedure starting from compound **7**; purified by FC (hexane / ethyl acetate 70:30) to afford pure compound **8c** as a pale-yellow foam (35 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H) 7.57 (br d, *J*= 7.4 Hz, 2H), 7.51 (d, *J*= 8.4 Hz, 2H), 7.43 (t, *J*= 7.4 Hz, 2H), 7.36-7.33 (m, 3H), 7.29 (d, *J*= 7.6 Hz, 1H), 7.22 (t, *J*= 7.6 Hz, 1H), 7.03 (dt, J_3= 7.6 Hz, J_4= 1.1 Hz, 1H), 6.89 (d, *J*= 7.6 Hz, 1H), 6.51 (d, *J*= 16.0 Hz, 1H), 6.25-6.17 (m, 1H), 3.62 (dd, J_3= 7.8 Hz, J_3= 5.1 Hz, 1H), 3.06-3.00 (m, 1H), 2.79-2.71 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 141.3, 140.7, 137.1, 136.1, 132.8, 130.2, 128.8 (2C), 128.1, 127.2 (3C), 126.9 (2C), 126.6 (2C), 125.6, 124.6, 122.4, 109.7, 46.0, 34.3; HRMS (ESI) calcd for $C_{23}H_{19}NONa$ $[M+Na]^+$ 348.1359 found 348.1365

(E)-1-benzyl-3-(3-(thiophen-3-yl)allyl)indolin-2-one (**8d**)

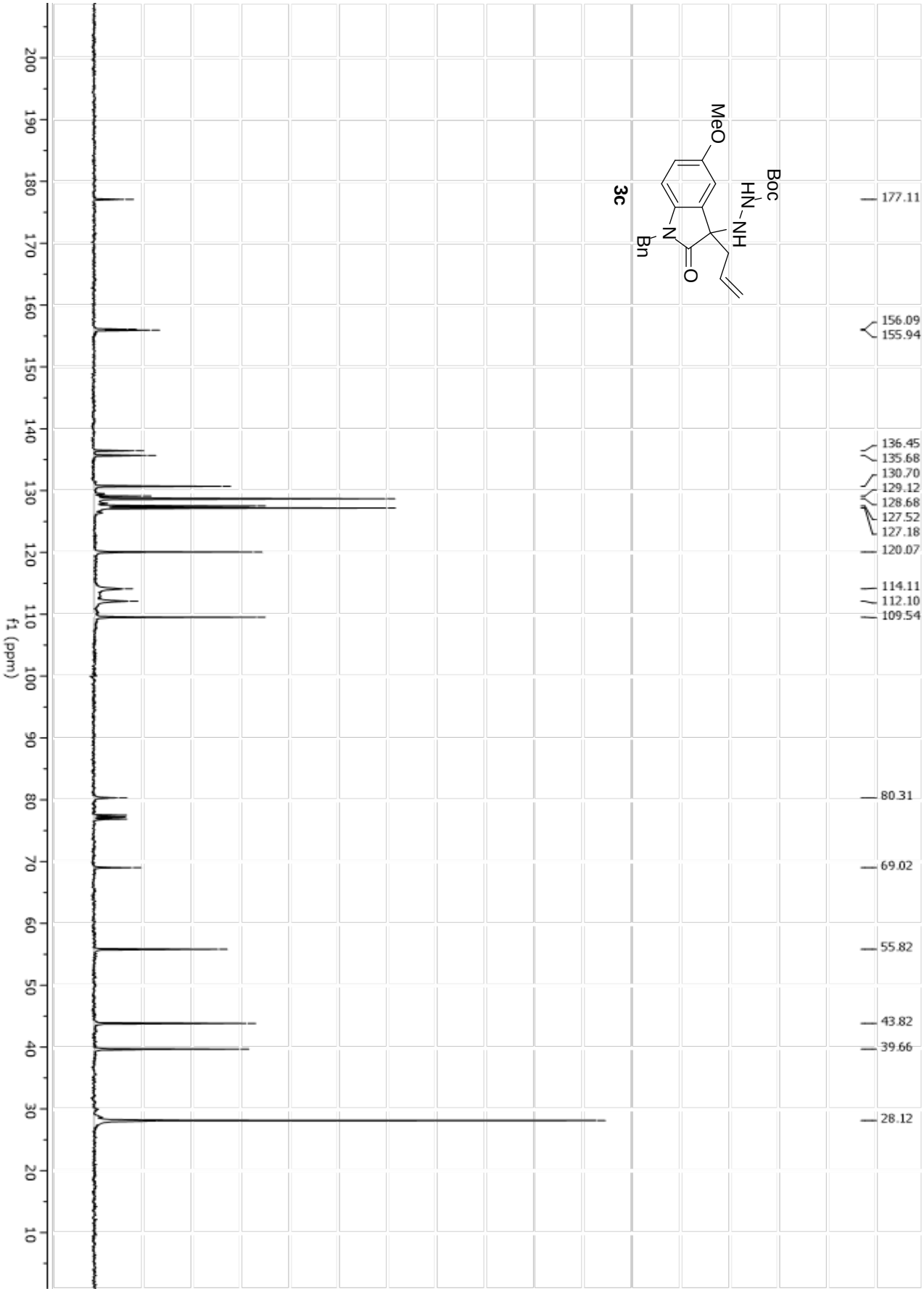
Synthetized according to the general procedure starting from compound **5l**; purified by FC (hexane / ethyl acetate 85:15) to afford pure compound **8d** as an off-white waxy residue (30 mg, 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J*= 7.5 Hz, 1H), 7.23-6.99 (m, 10H), 6.66 (d, *J*= 7.7 Hz, 1H), 6.50 (d, *J*= 15.9 Hz, 1H), 5.94-5.87 (m, 1H), 5.14 (d, *J*= 15.9 Hz, 1H), 4.68 (d, *J*= 15,9 Hz, 1H), 3.70-3.67 (m, 1H), 3.05-2.98 (m, 1H), 2.88-2.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 143.5, 139.7, 135.7, 128.7 (2C), 128.4, 128.0, 127.8, 127.5, 127.1 (2C), 125.8, 125.1, 124.9, 124.1, 122.4, 121.6, 109.1, 45.7, 43.7, 34.1; HRMS (ESI) calcd for $C_{22}H_{19}NOSNa$ $[M+Na]^+$ 368.1080 found 368.1088

Copies of ^{1}H NMR and ^{13}C NMR spectra of the new compounds

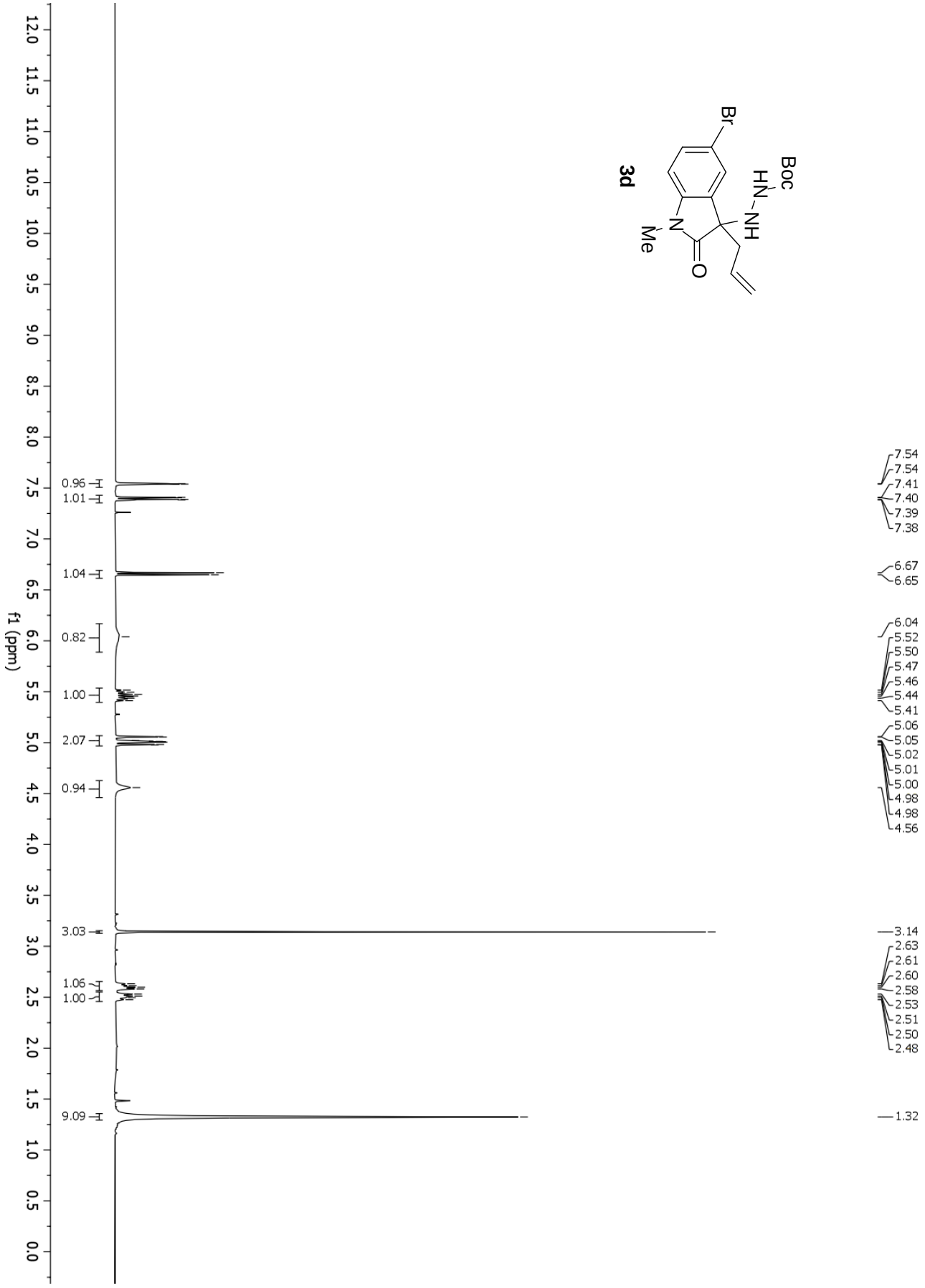
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3c**



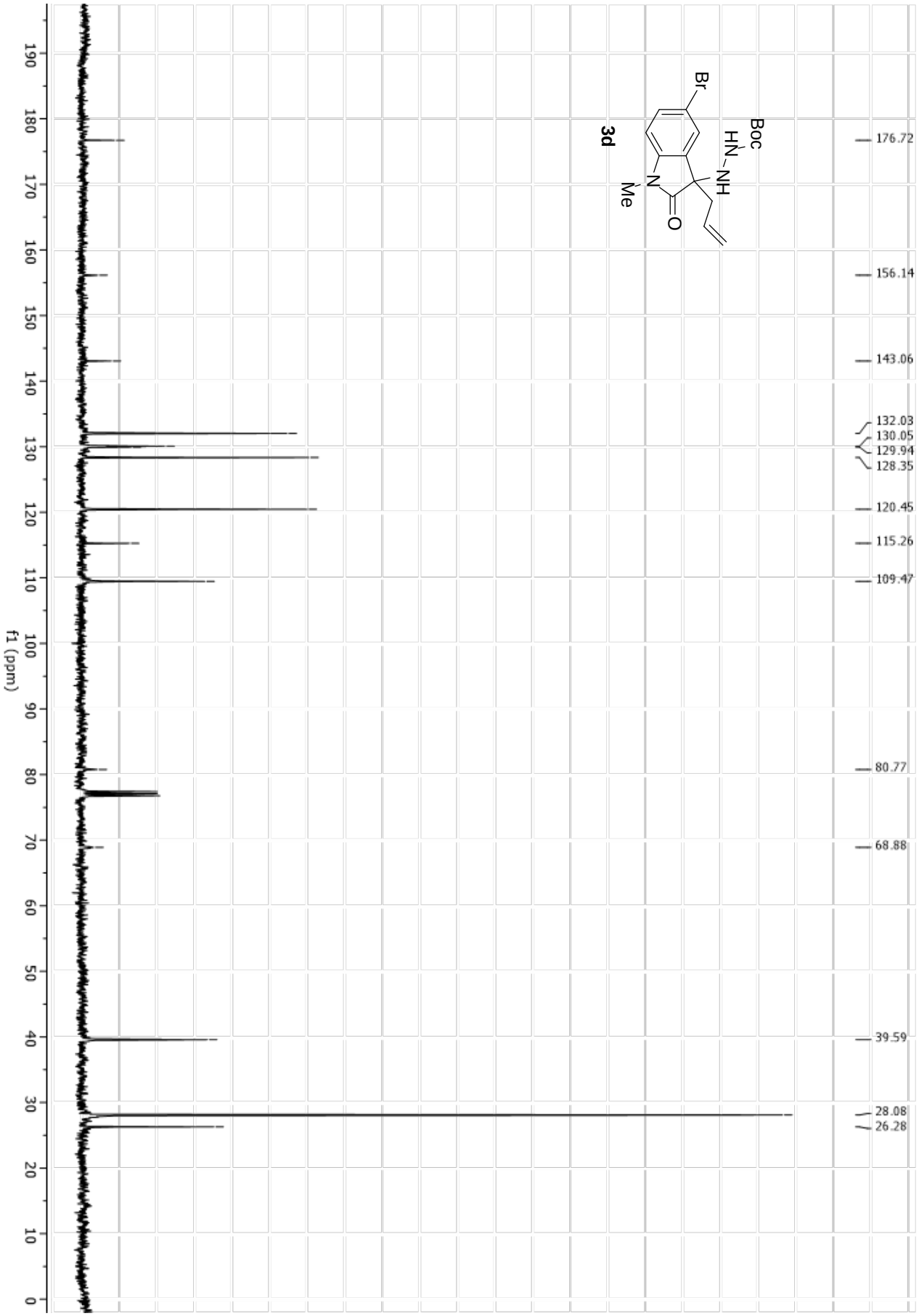
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3c**



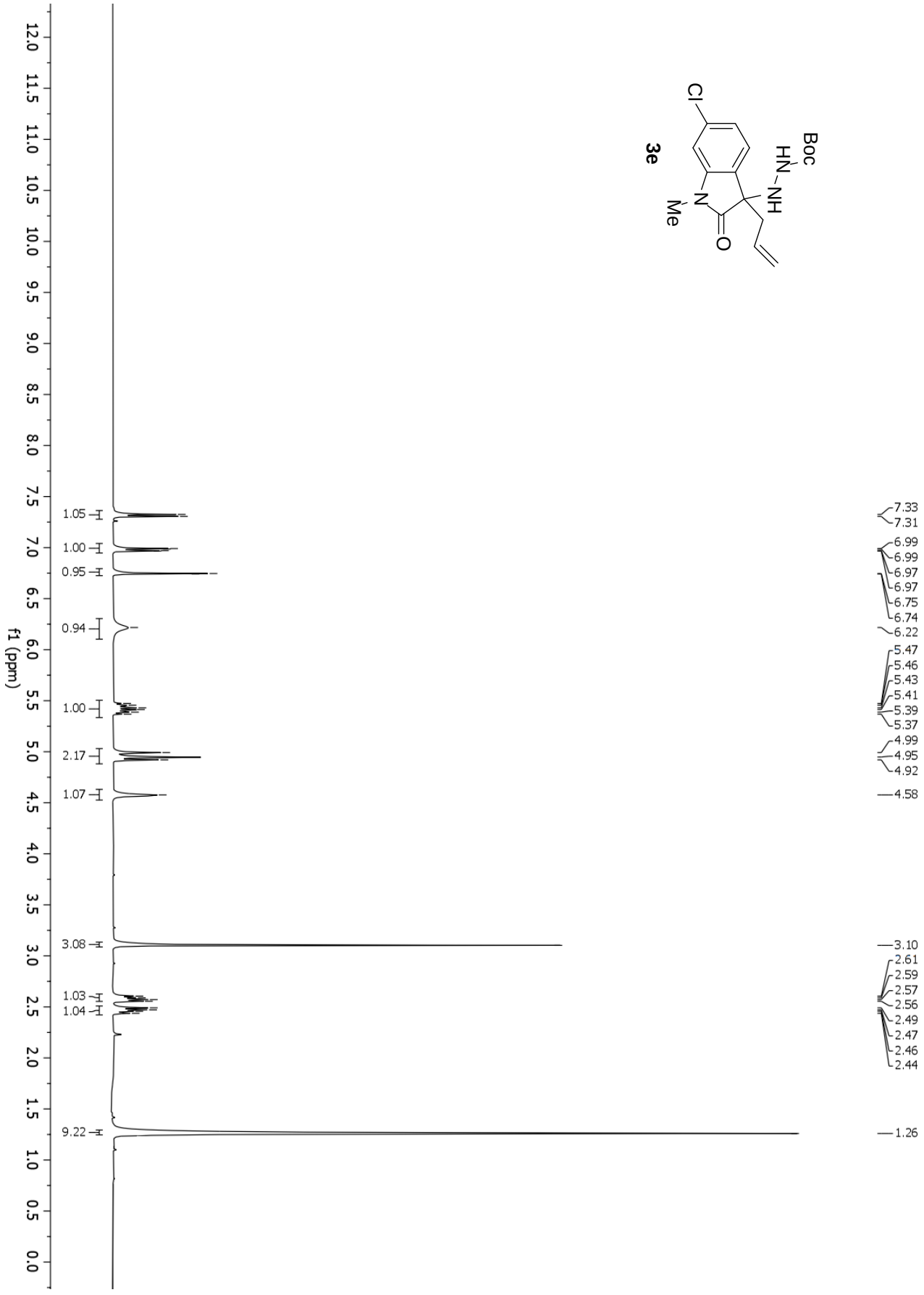
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3d**



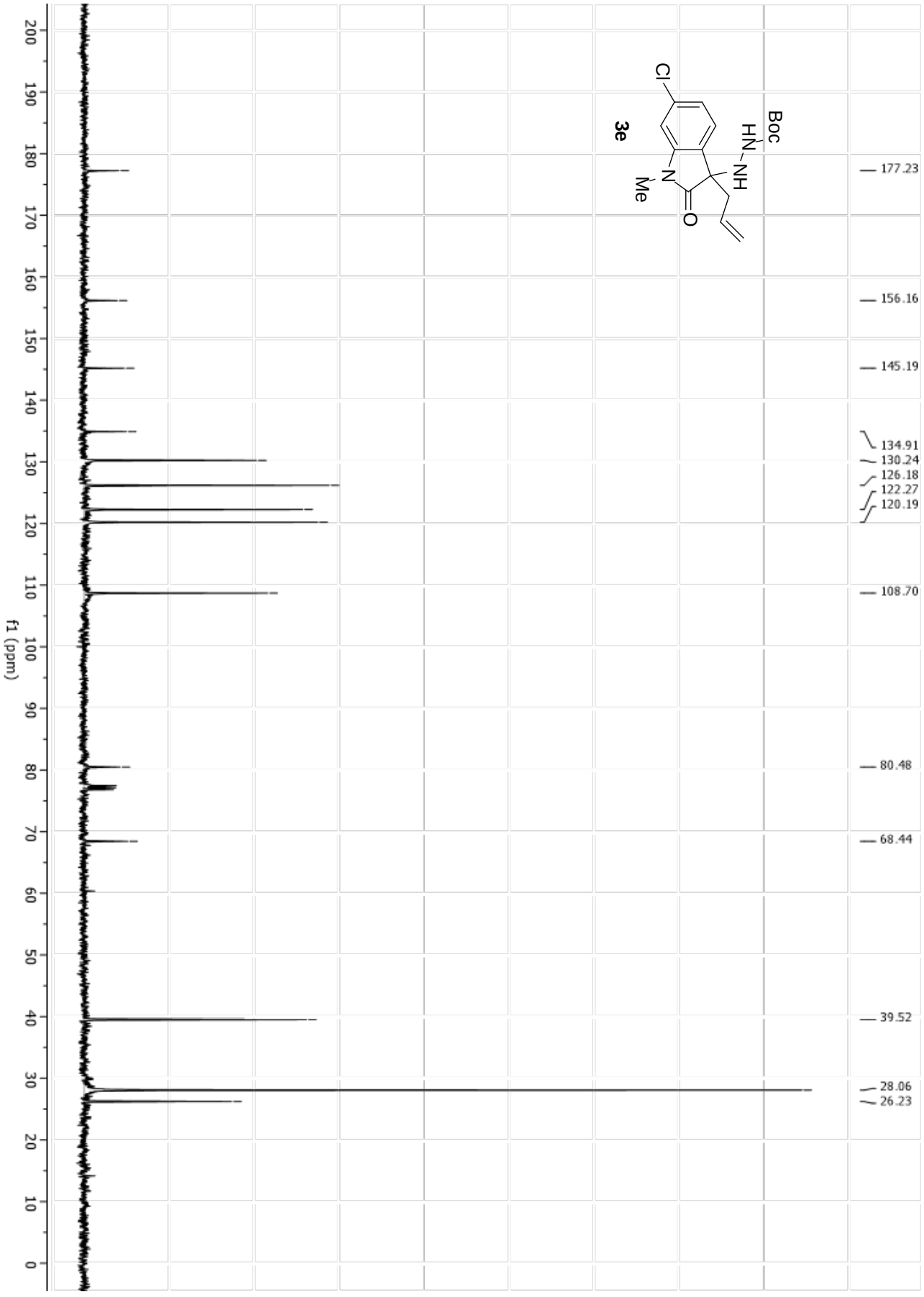
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3d**



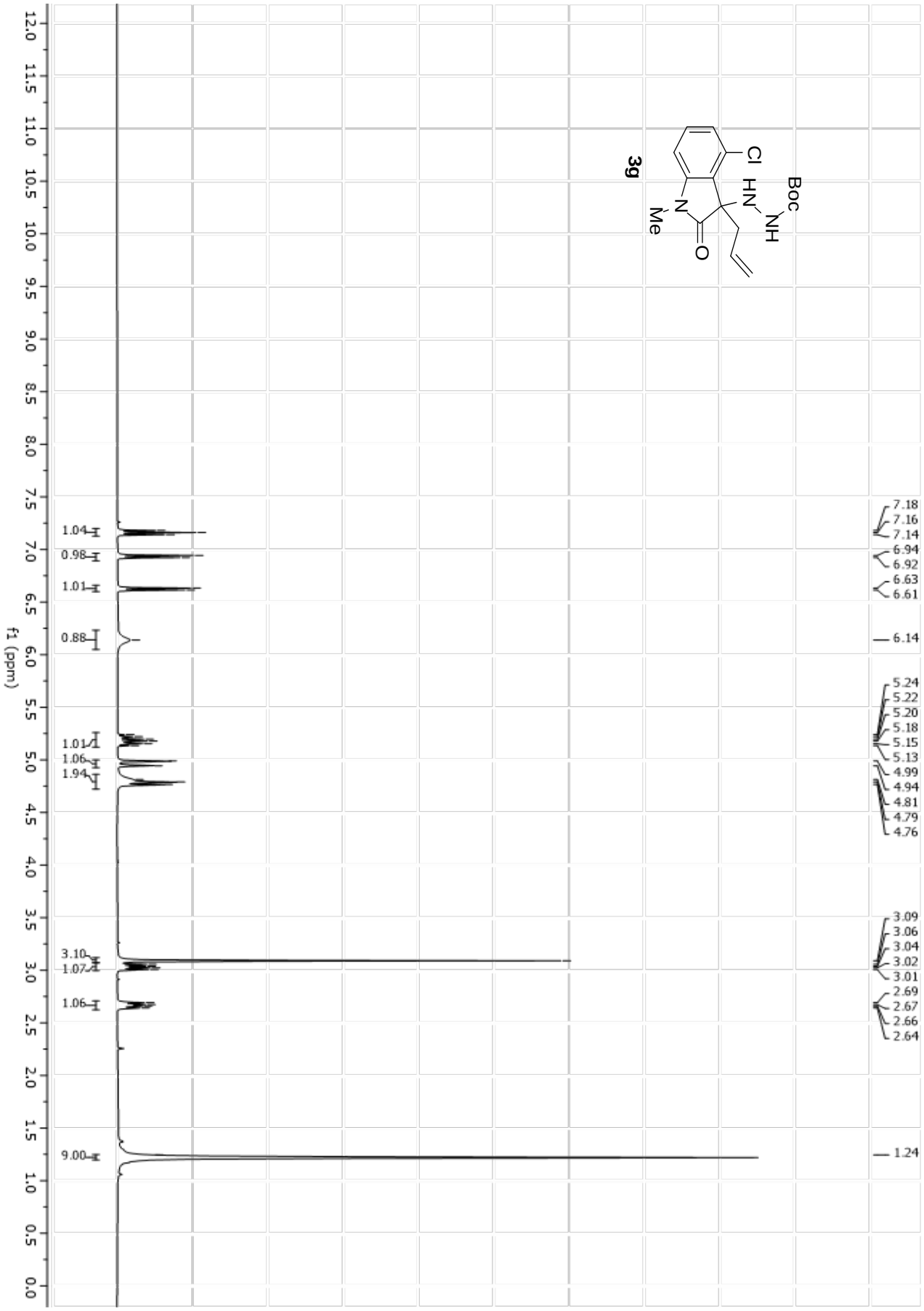
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3e**



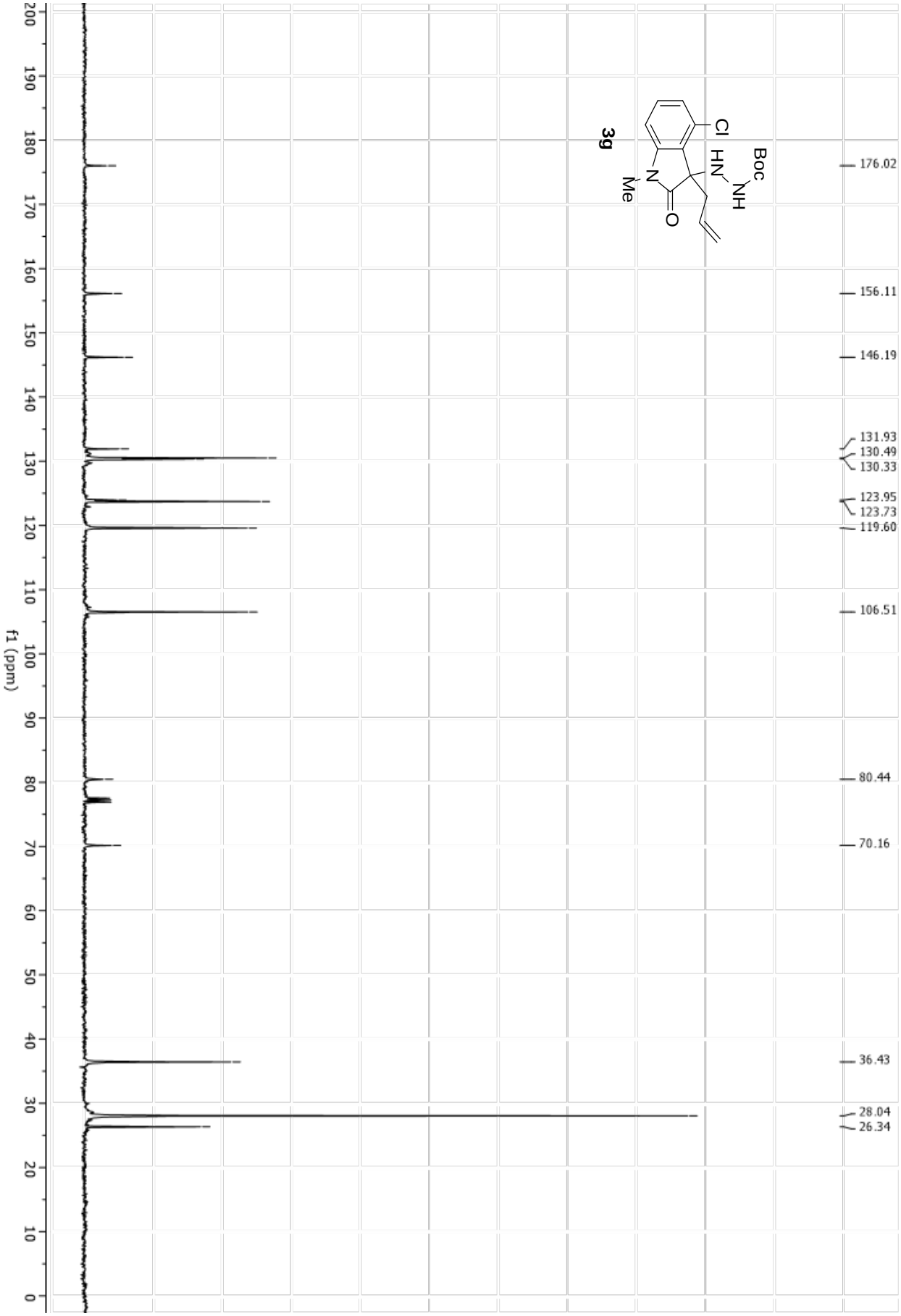
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3e**



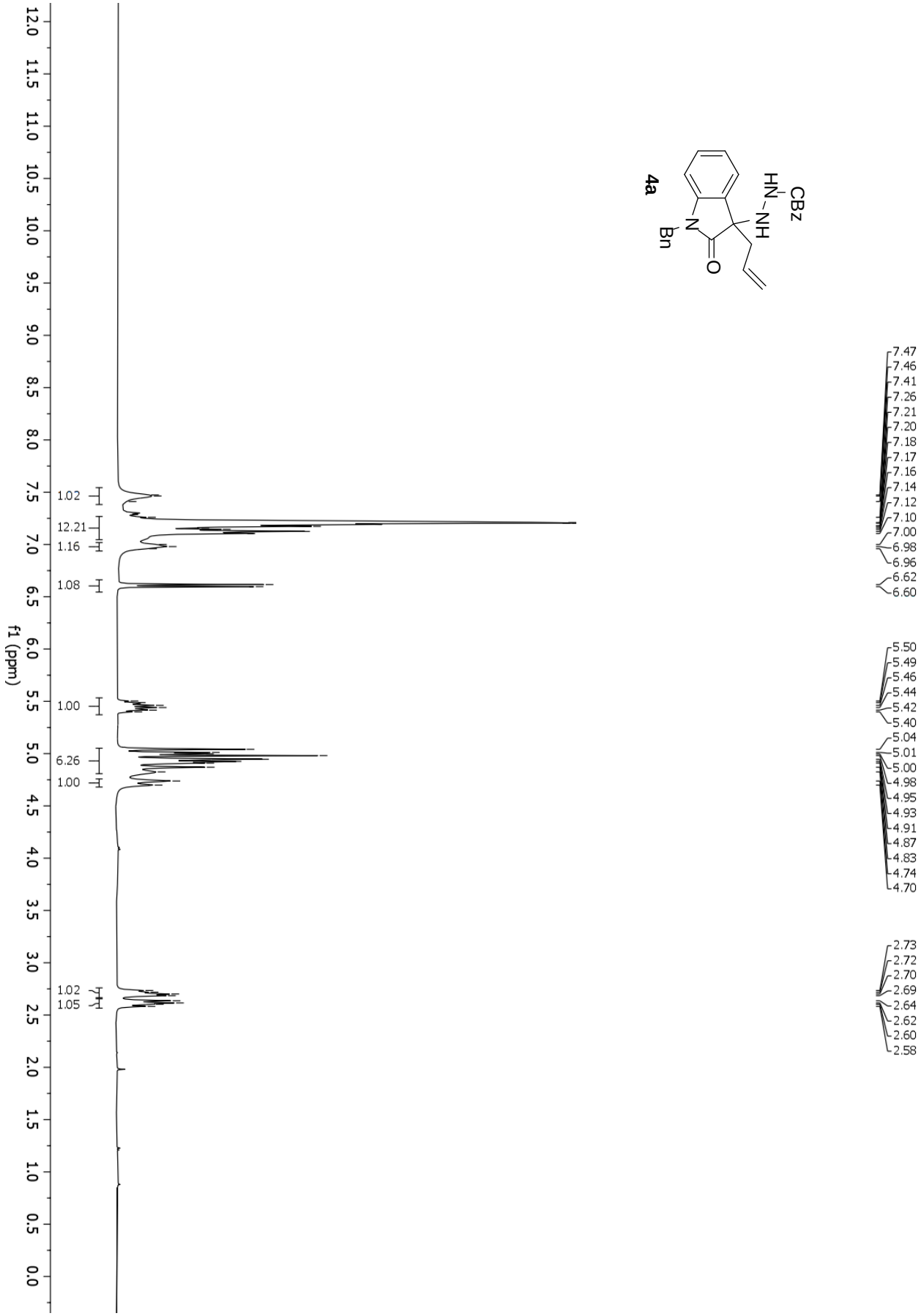
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3g**



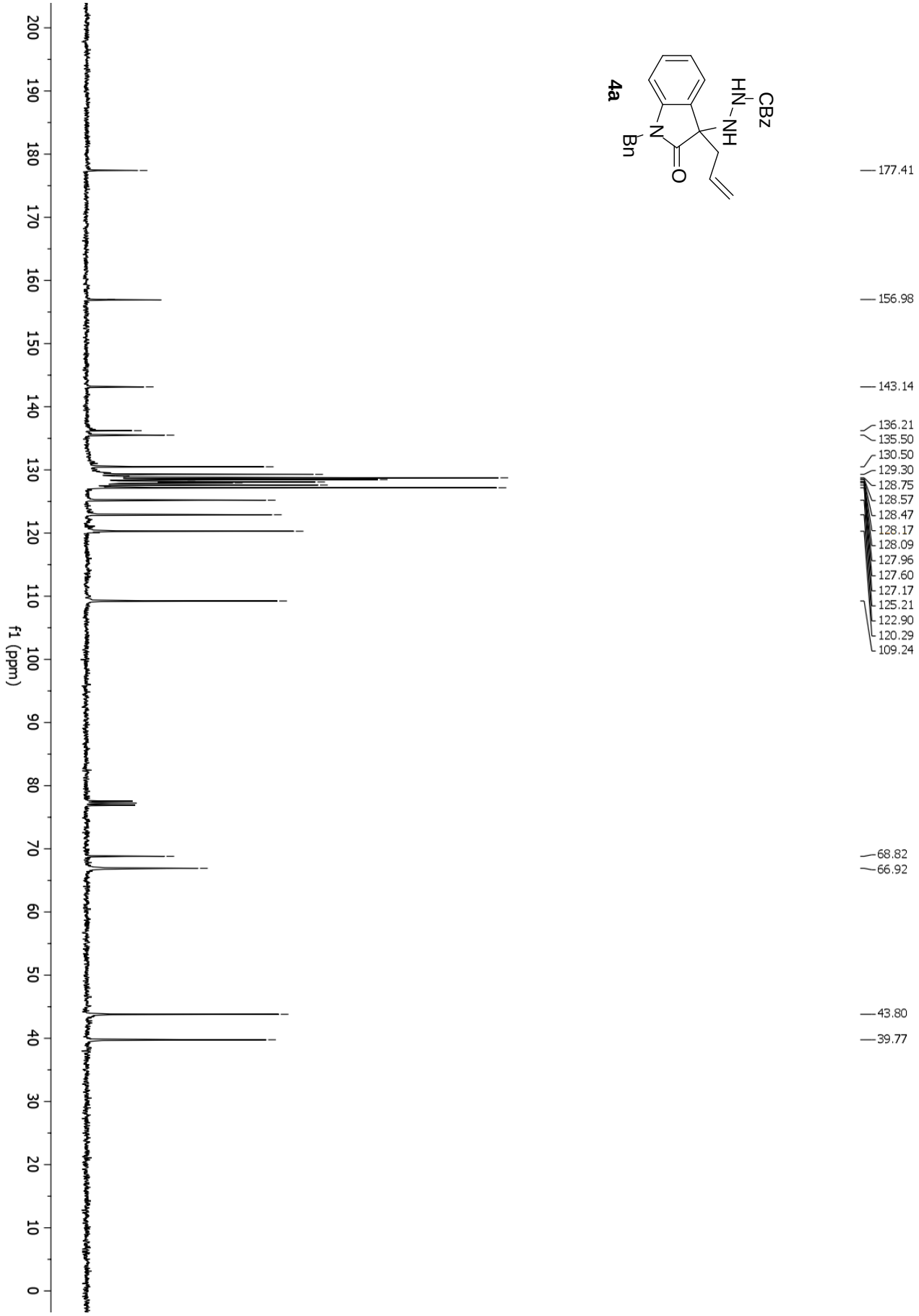
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3g**



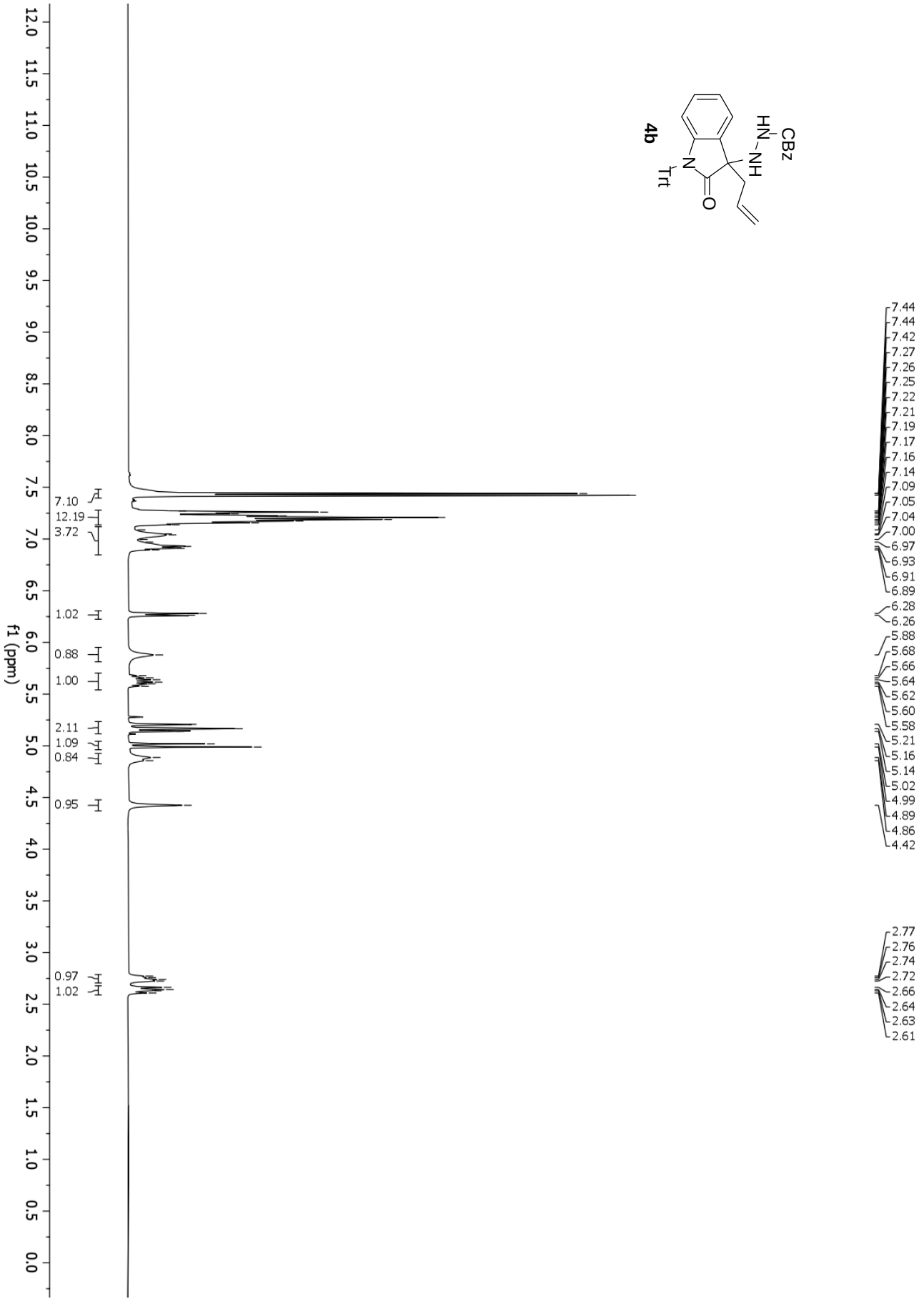
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4a**



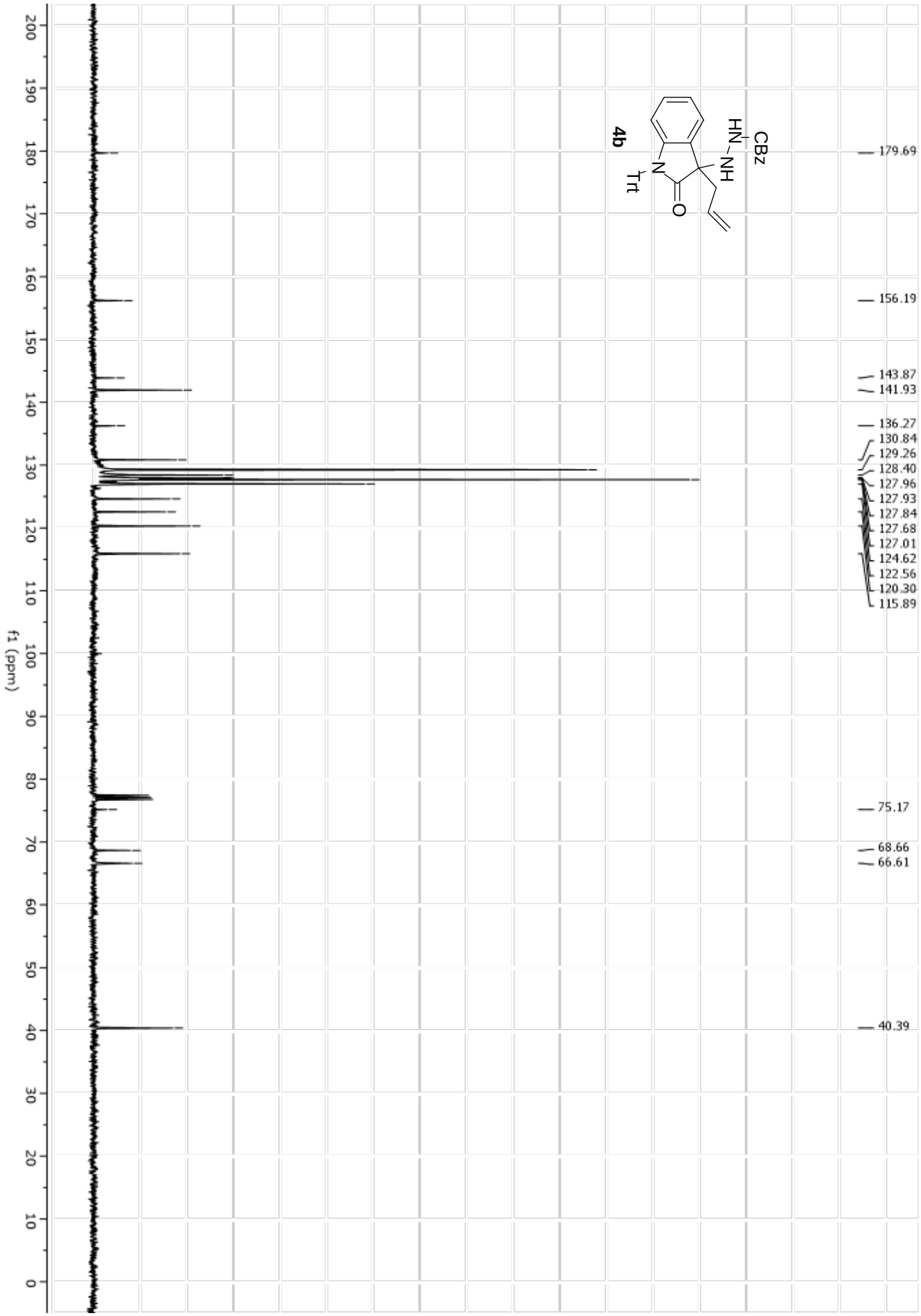
^{13}C NMR Spectra (101 MHz, $CDCl_3$) of compound **4a**



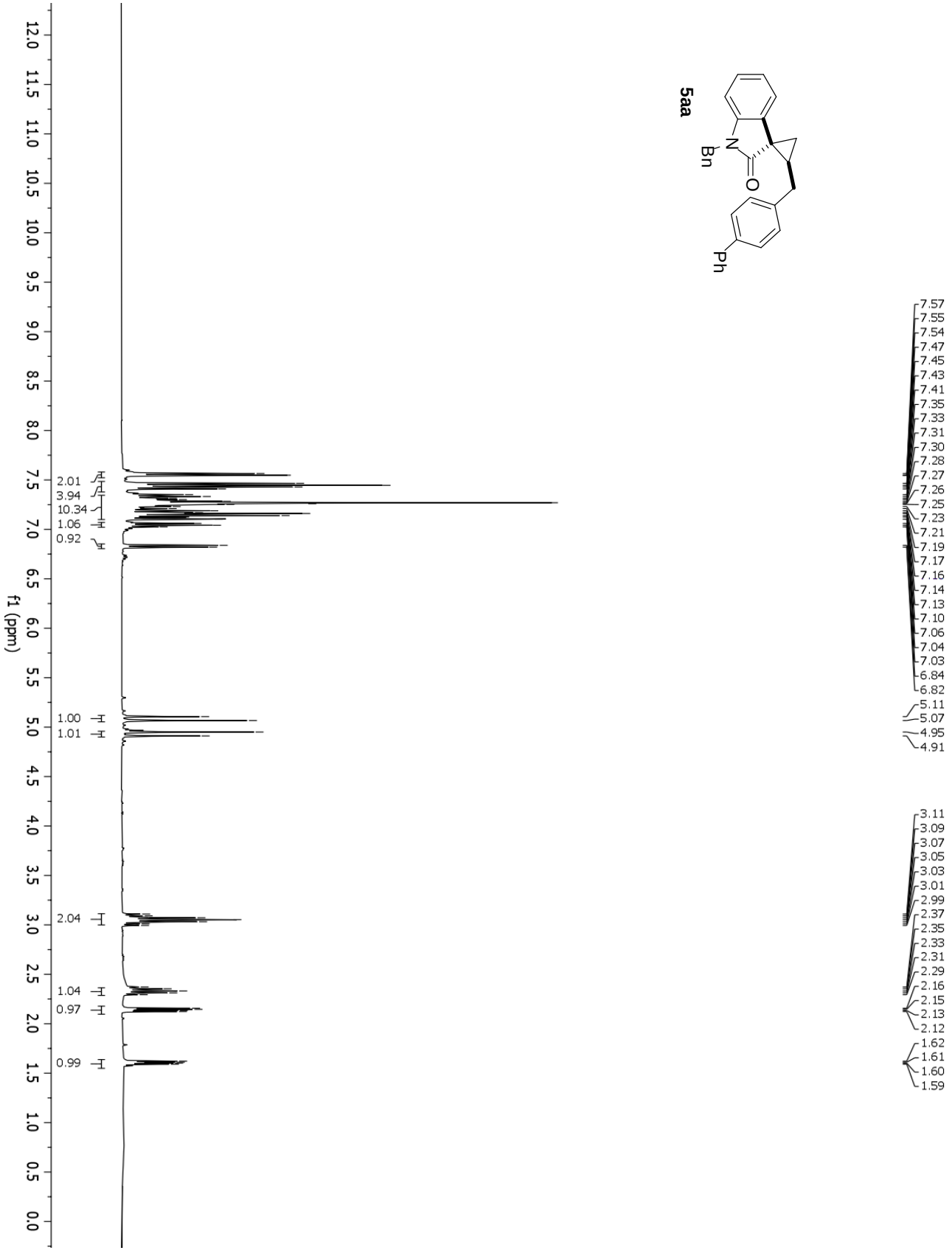
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4b**



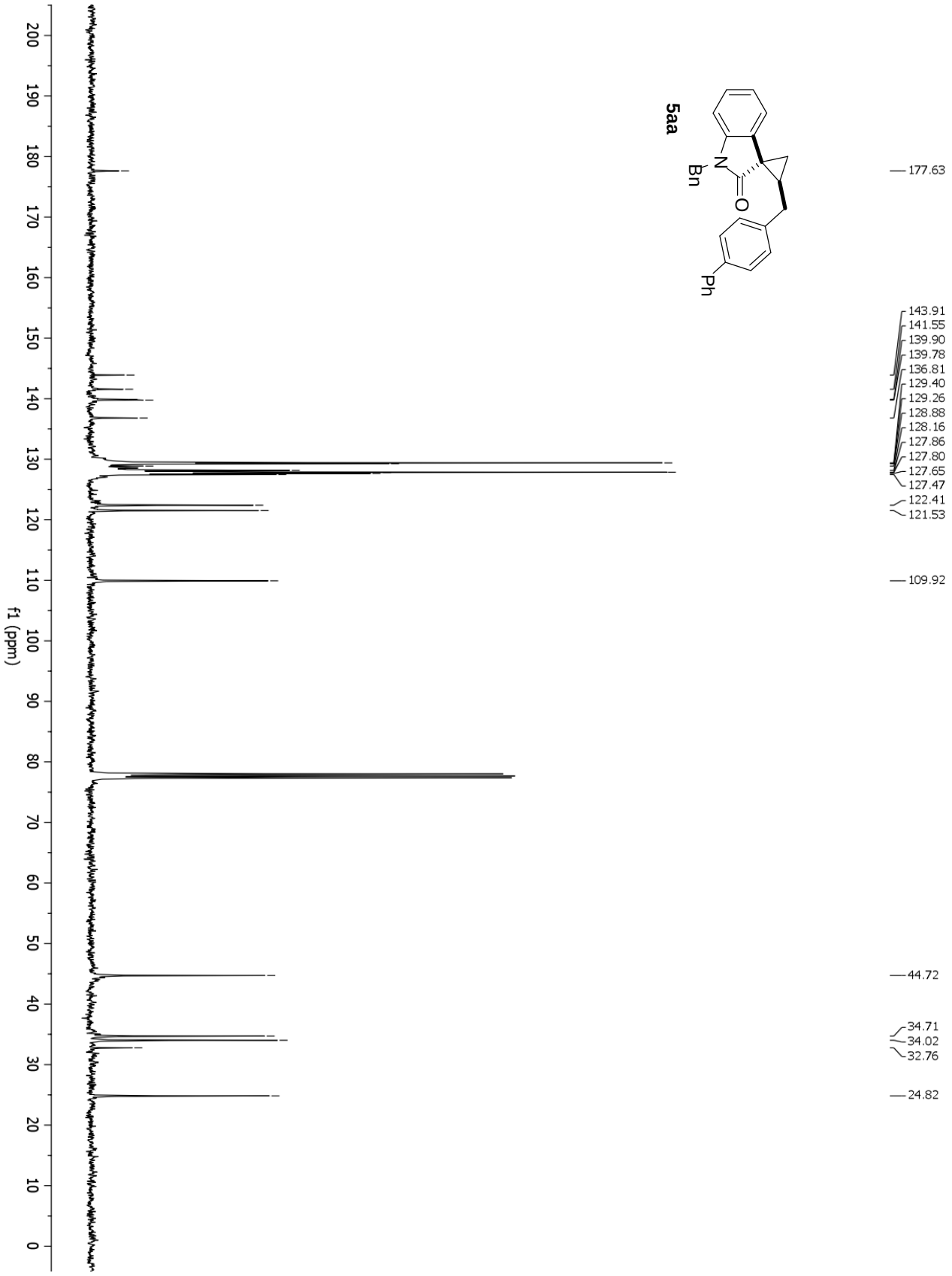
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4b**



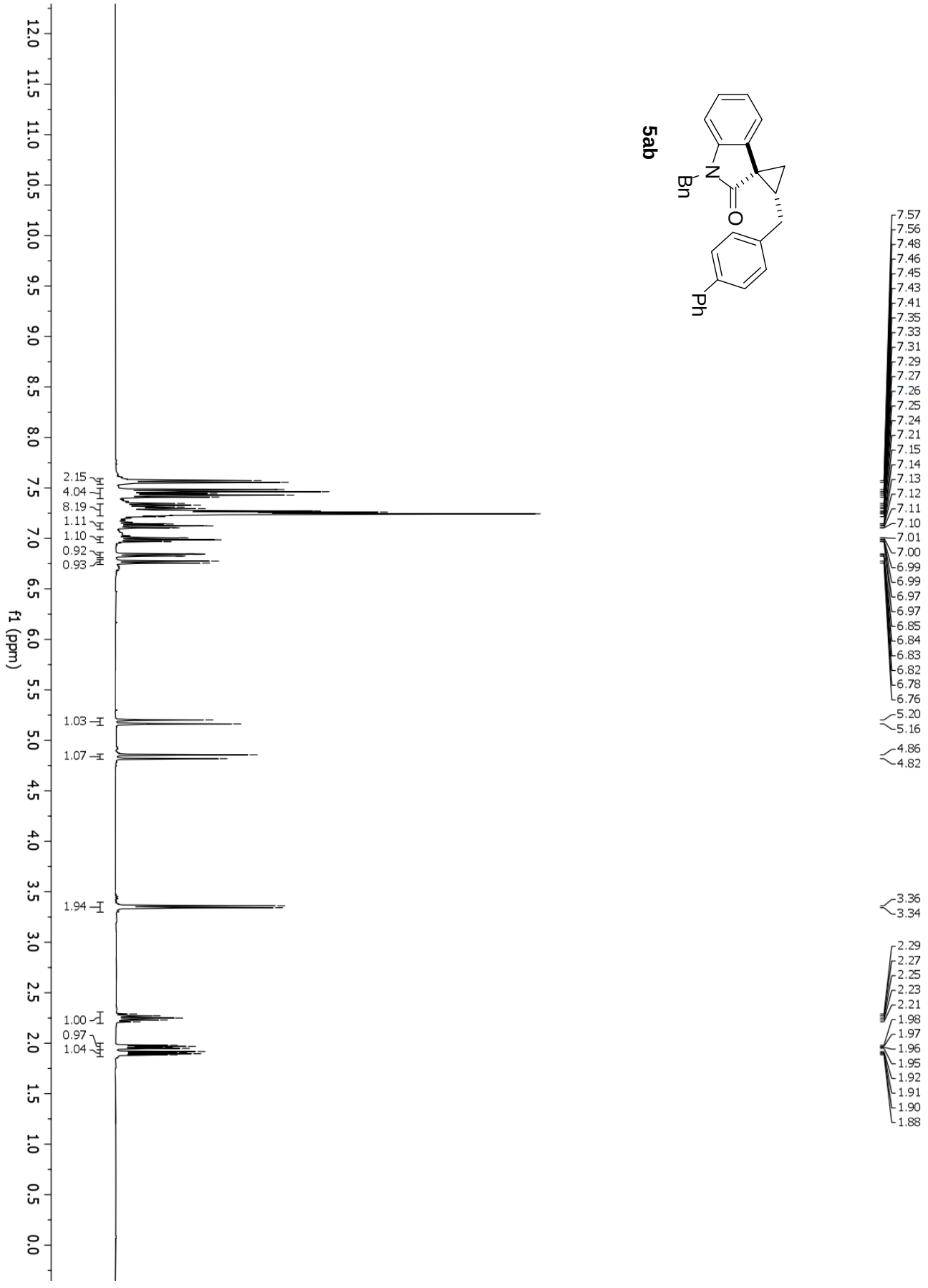
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5aa**



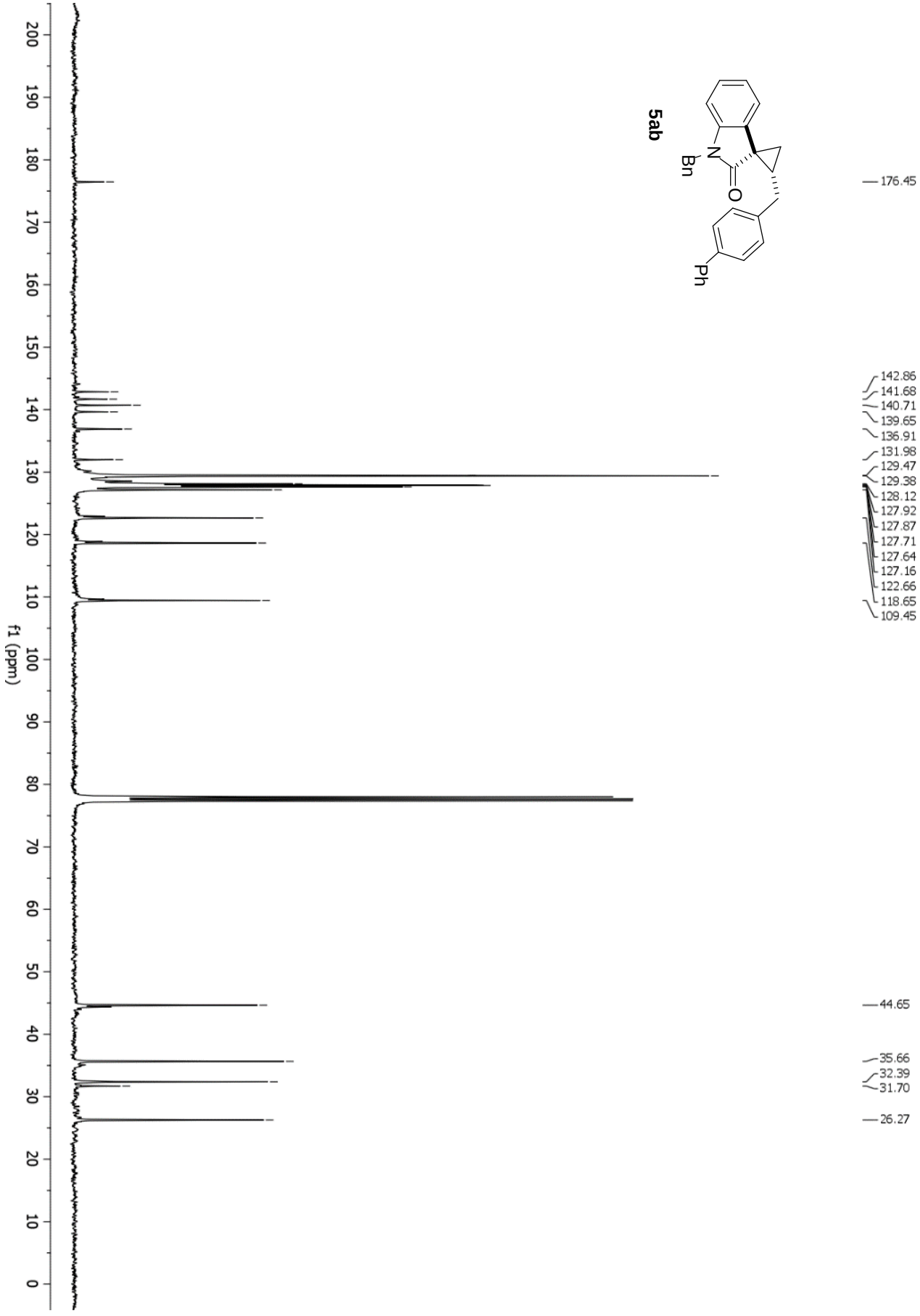
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5aa**



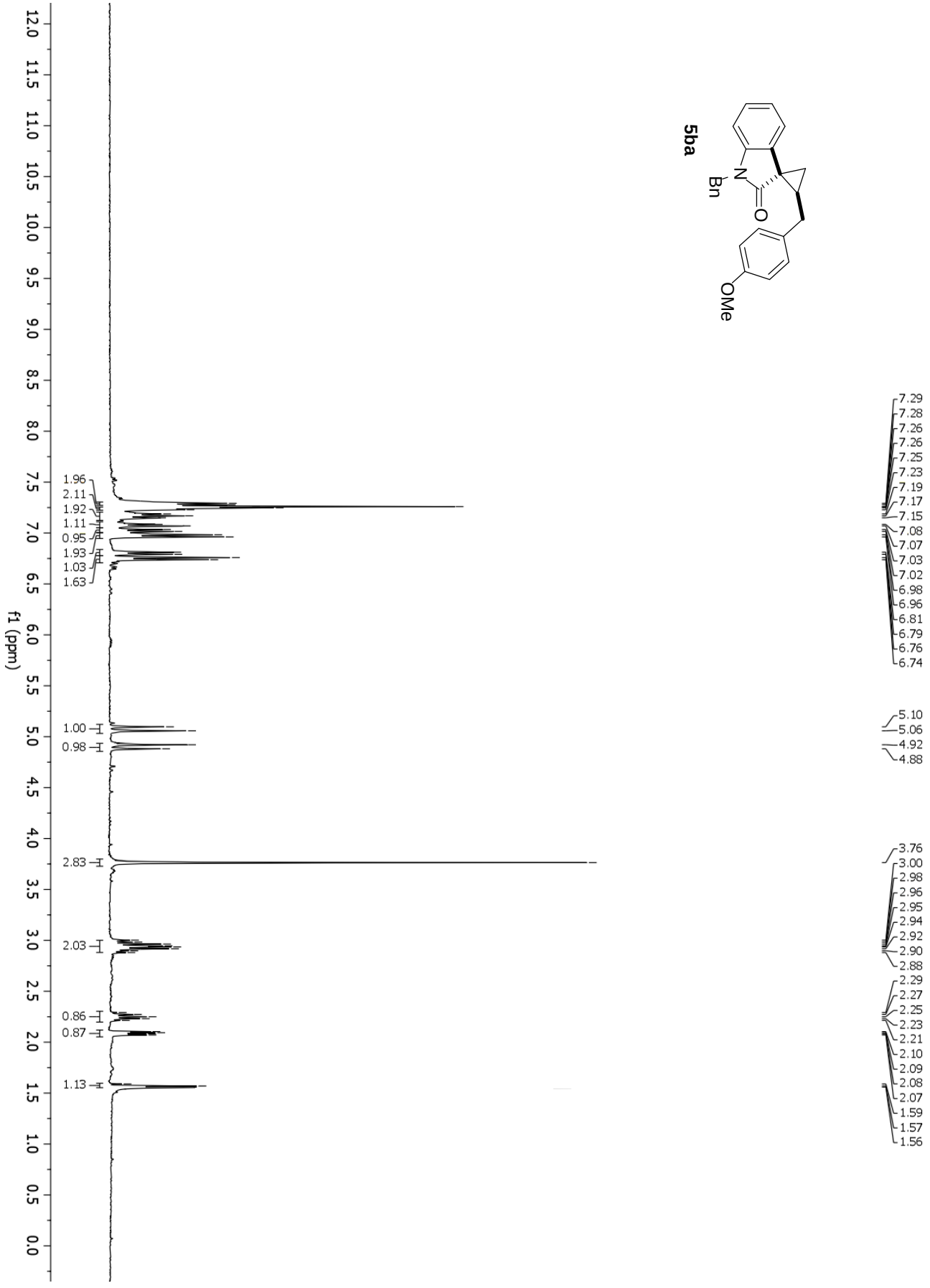
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ab**



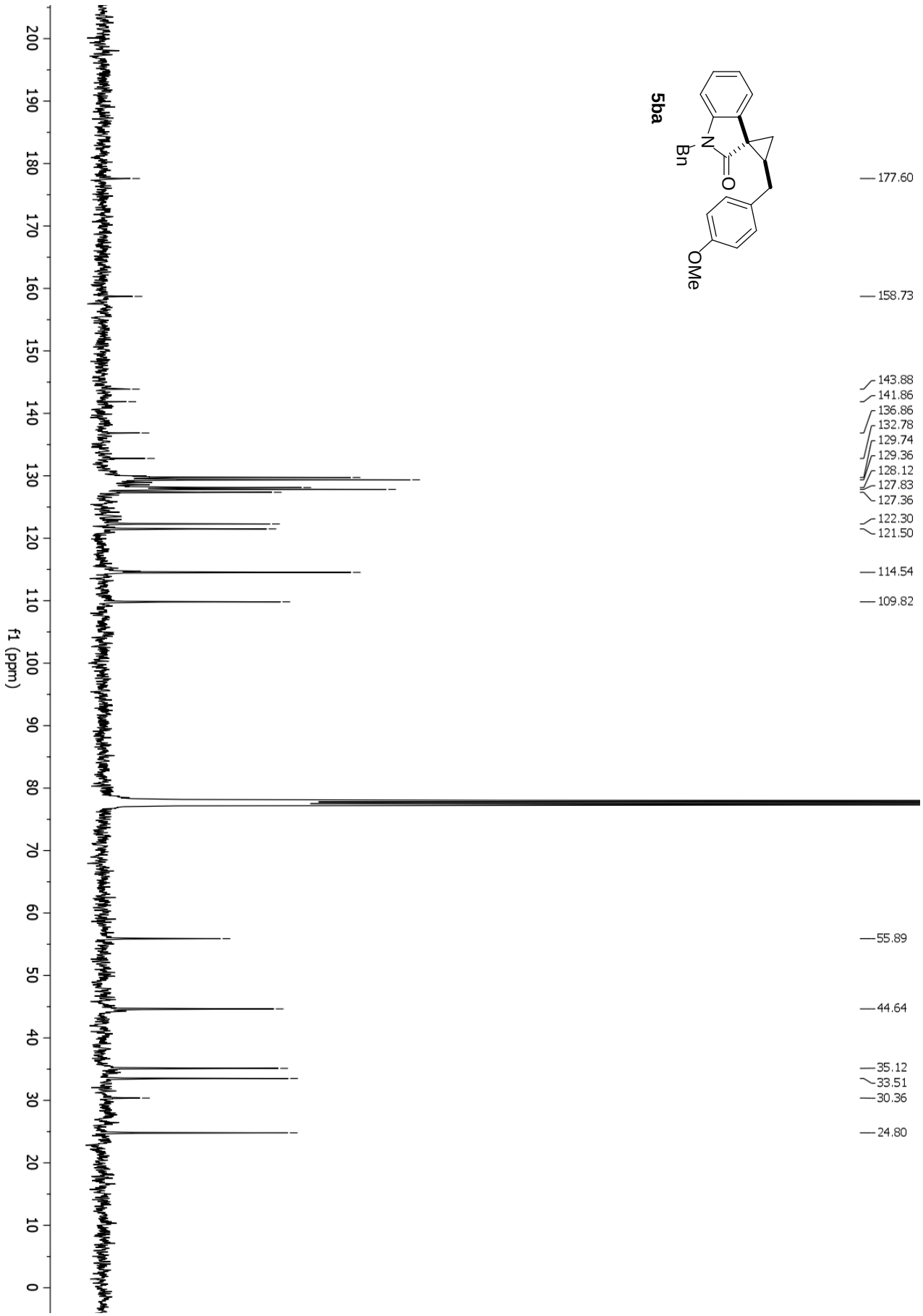
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ab**



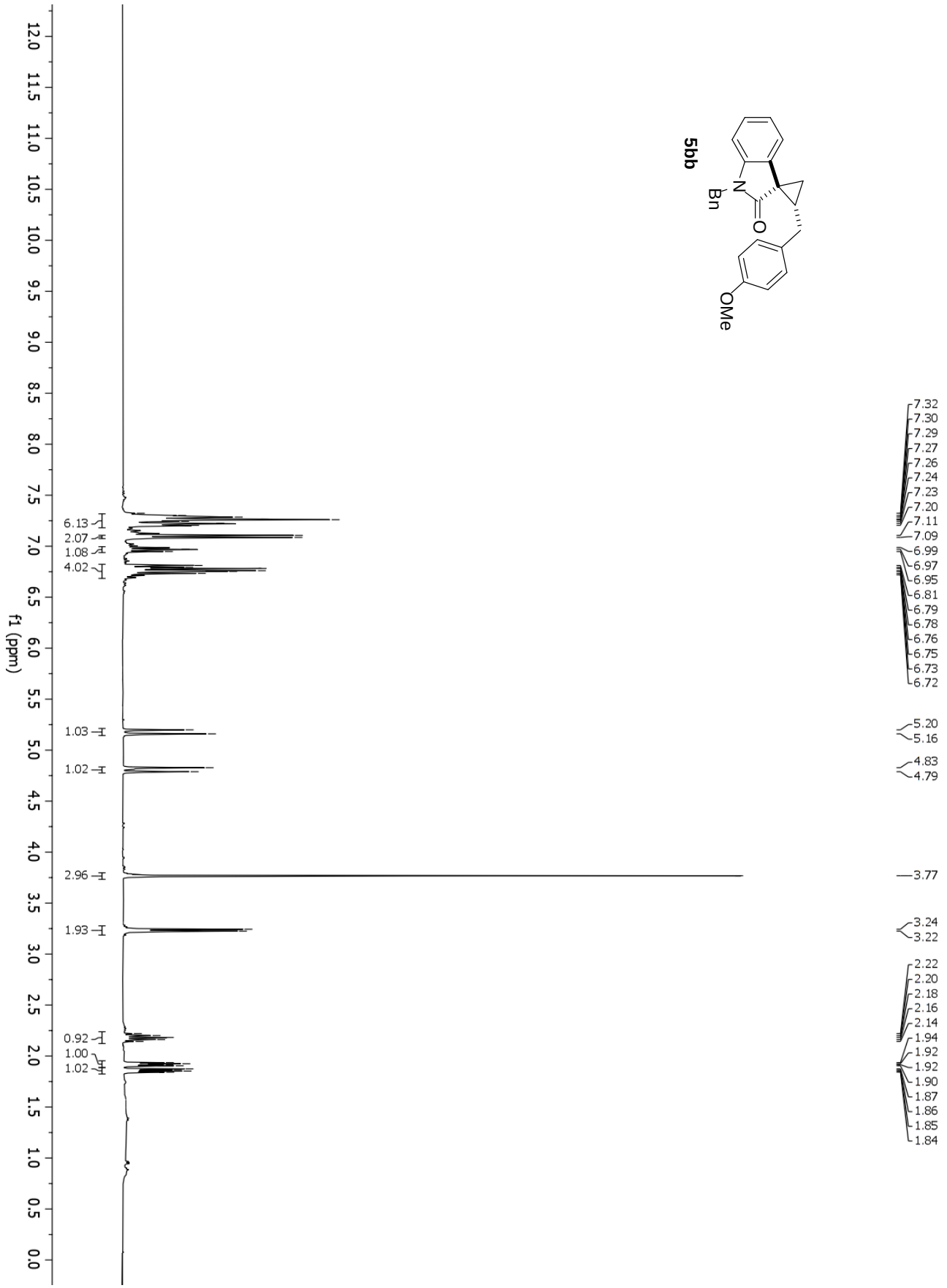
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5ba**



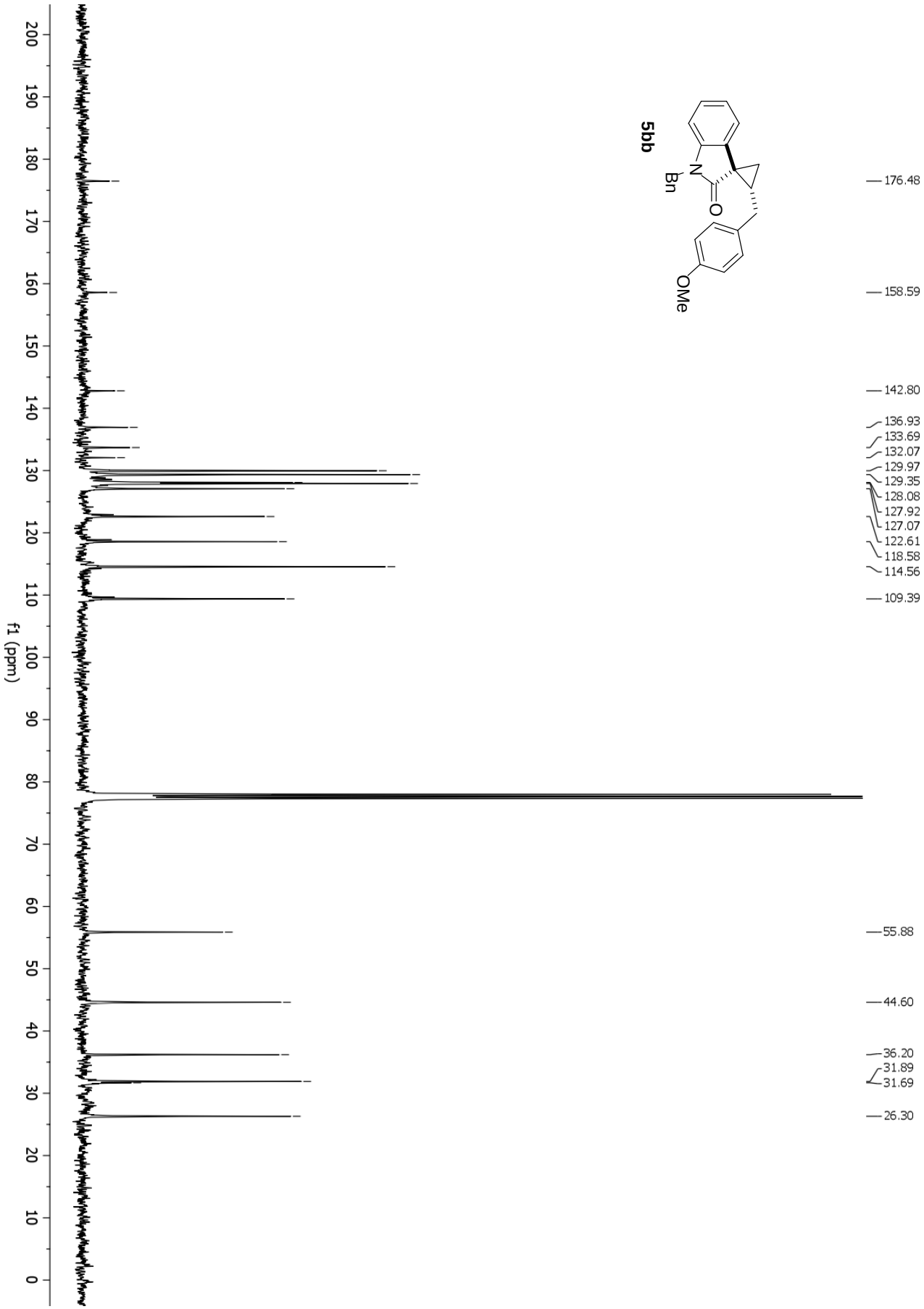
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5ba**



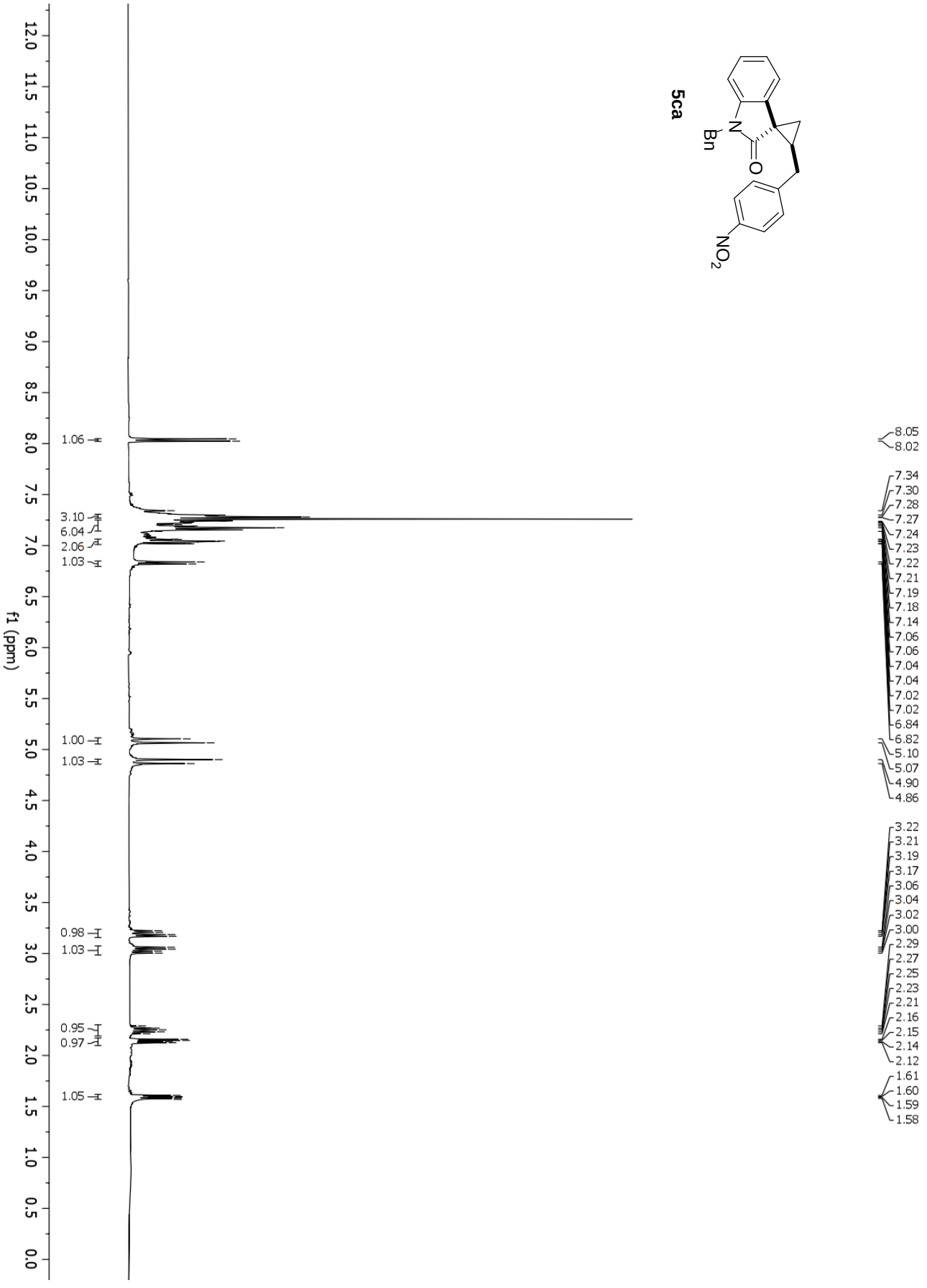
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5bb**



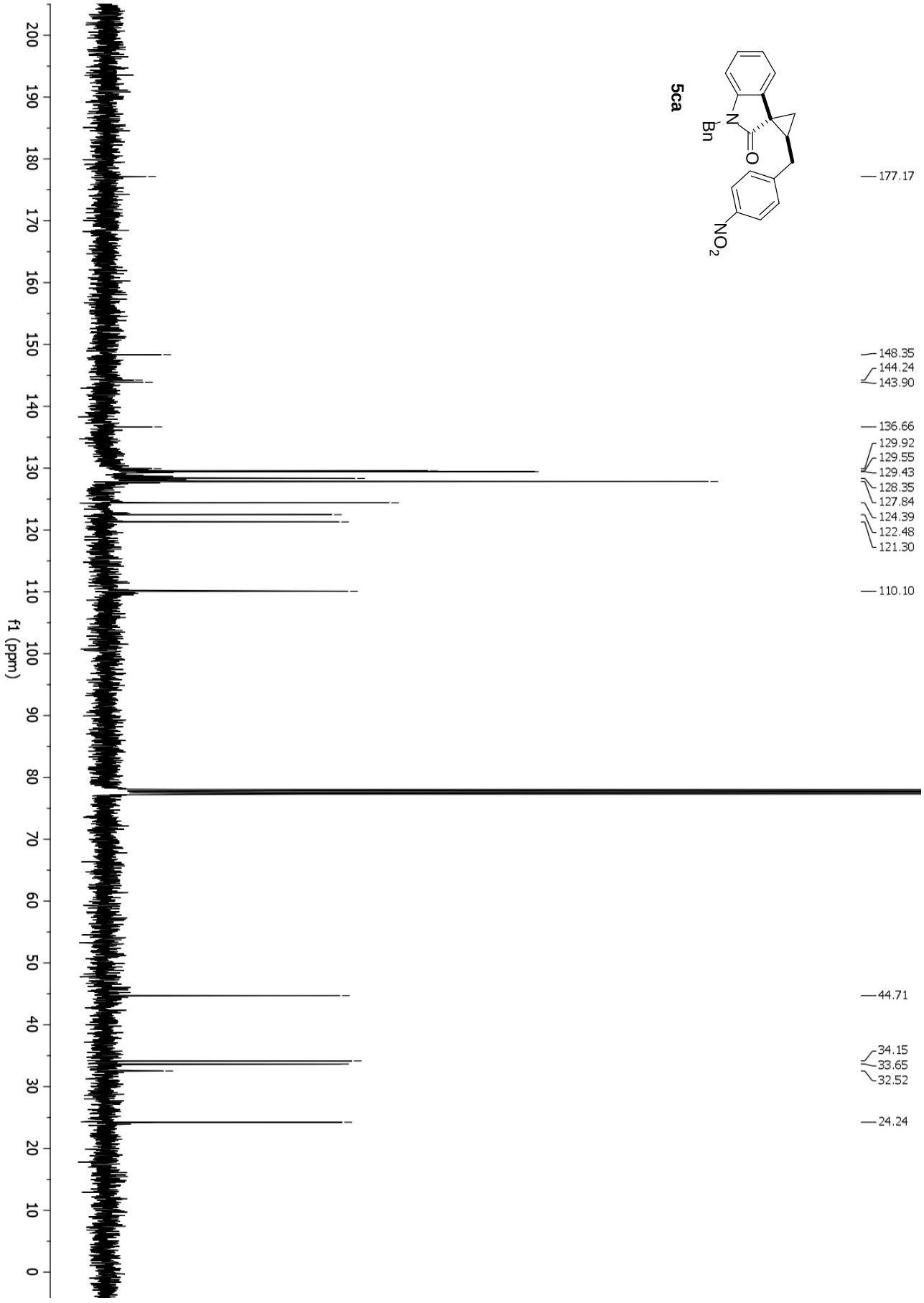
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5bb**



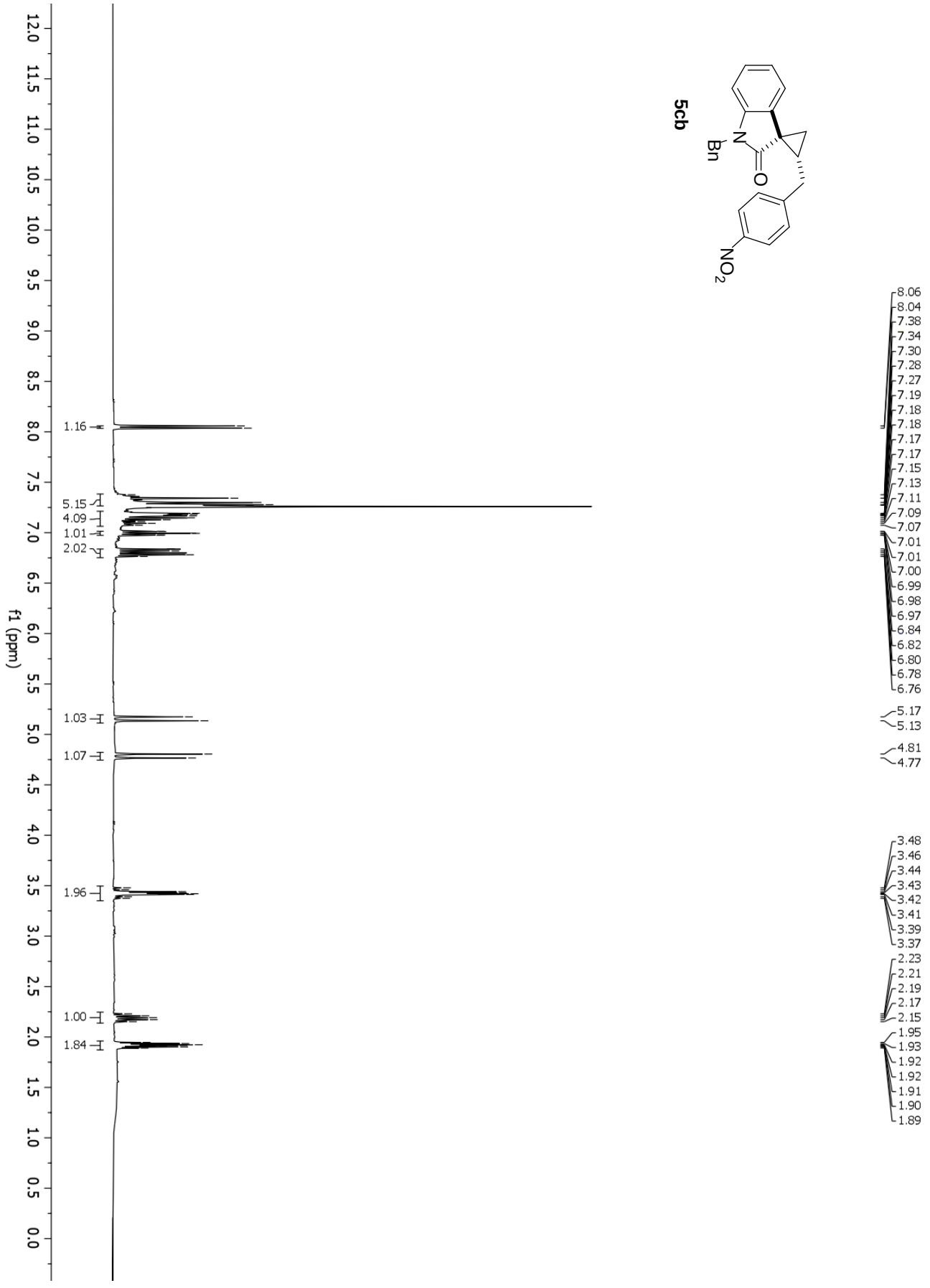
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ca**



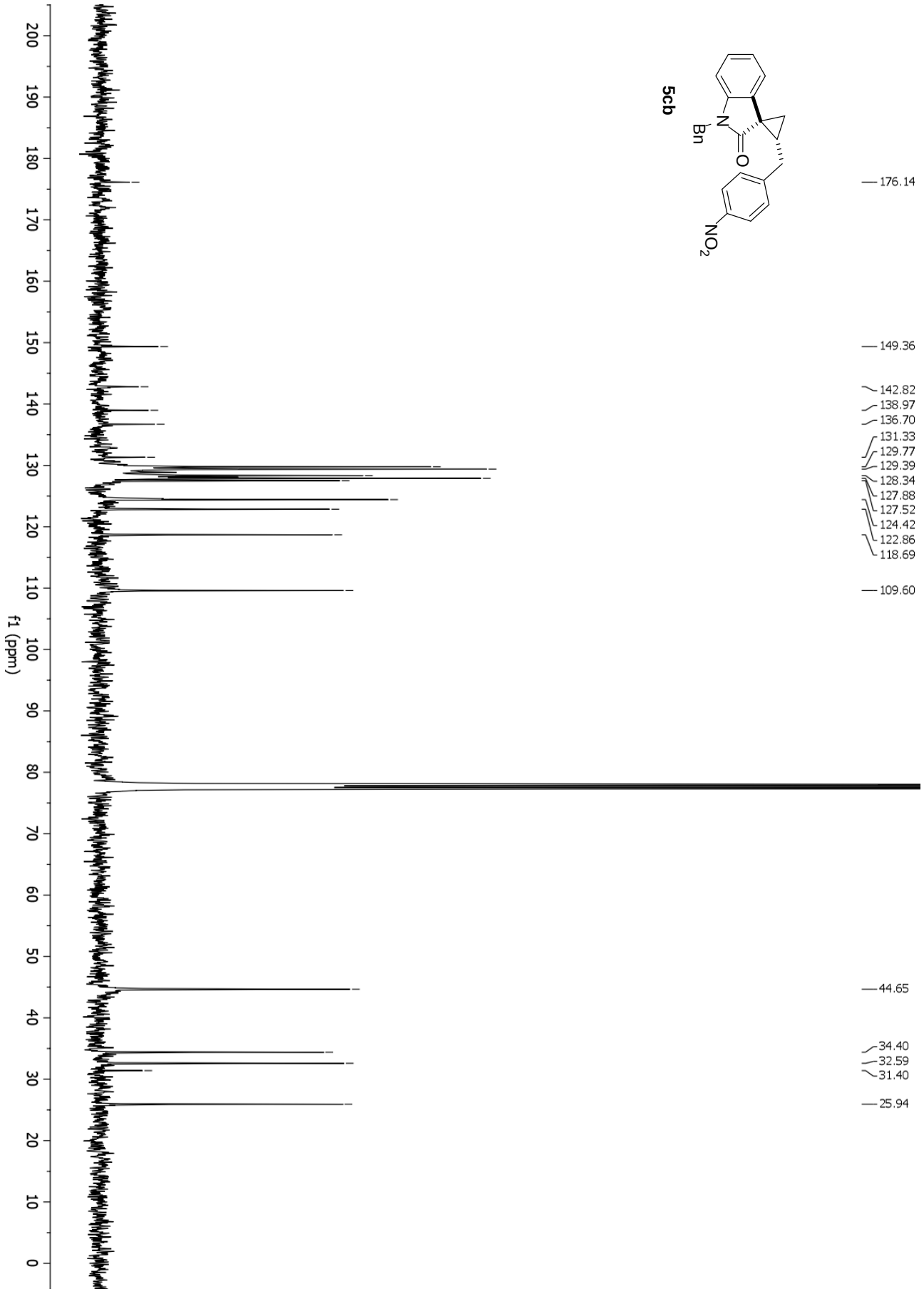
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ca**



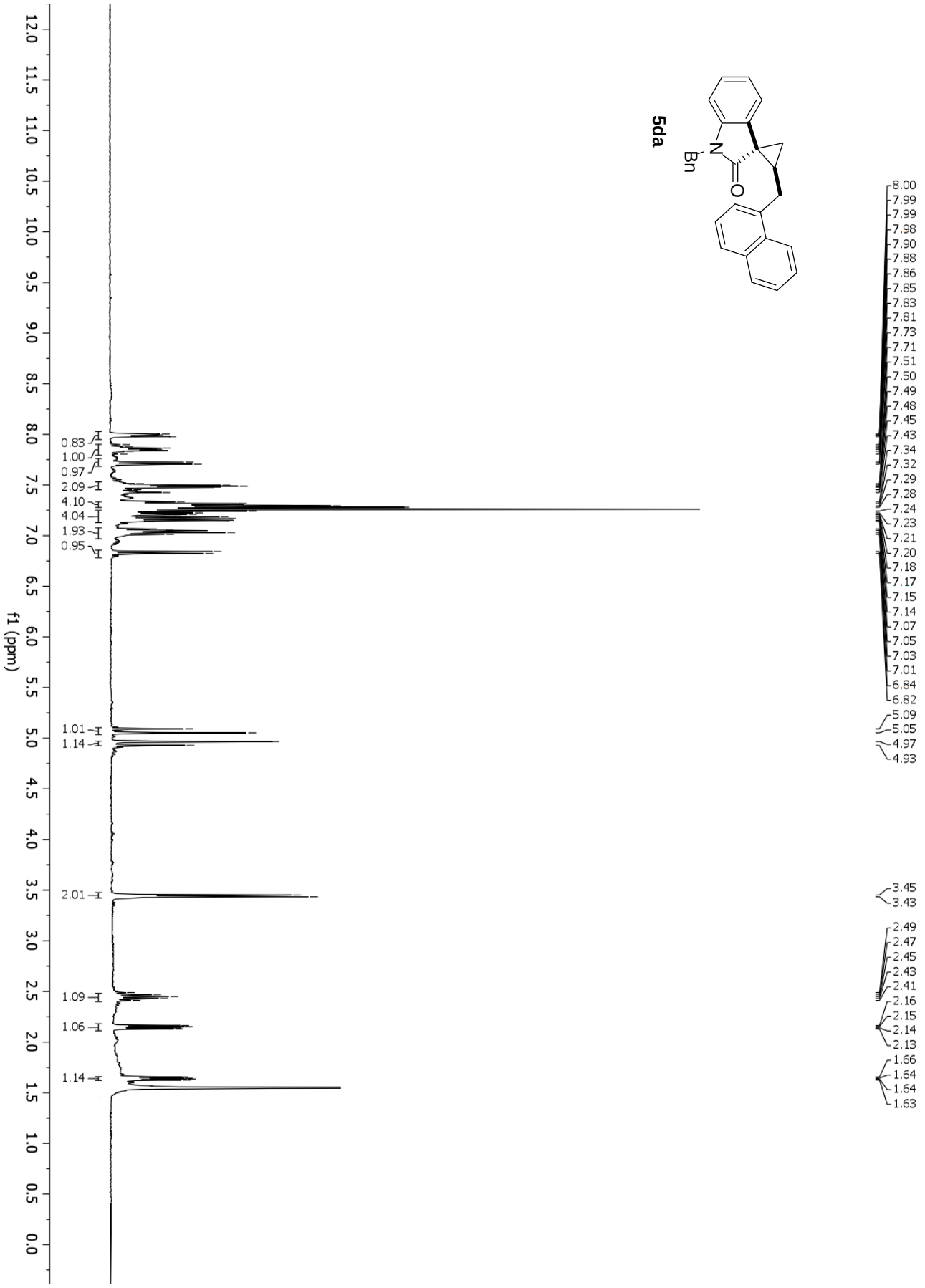
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5cb**



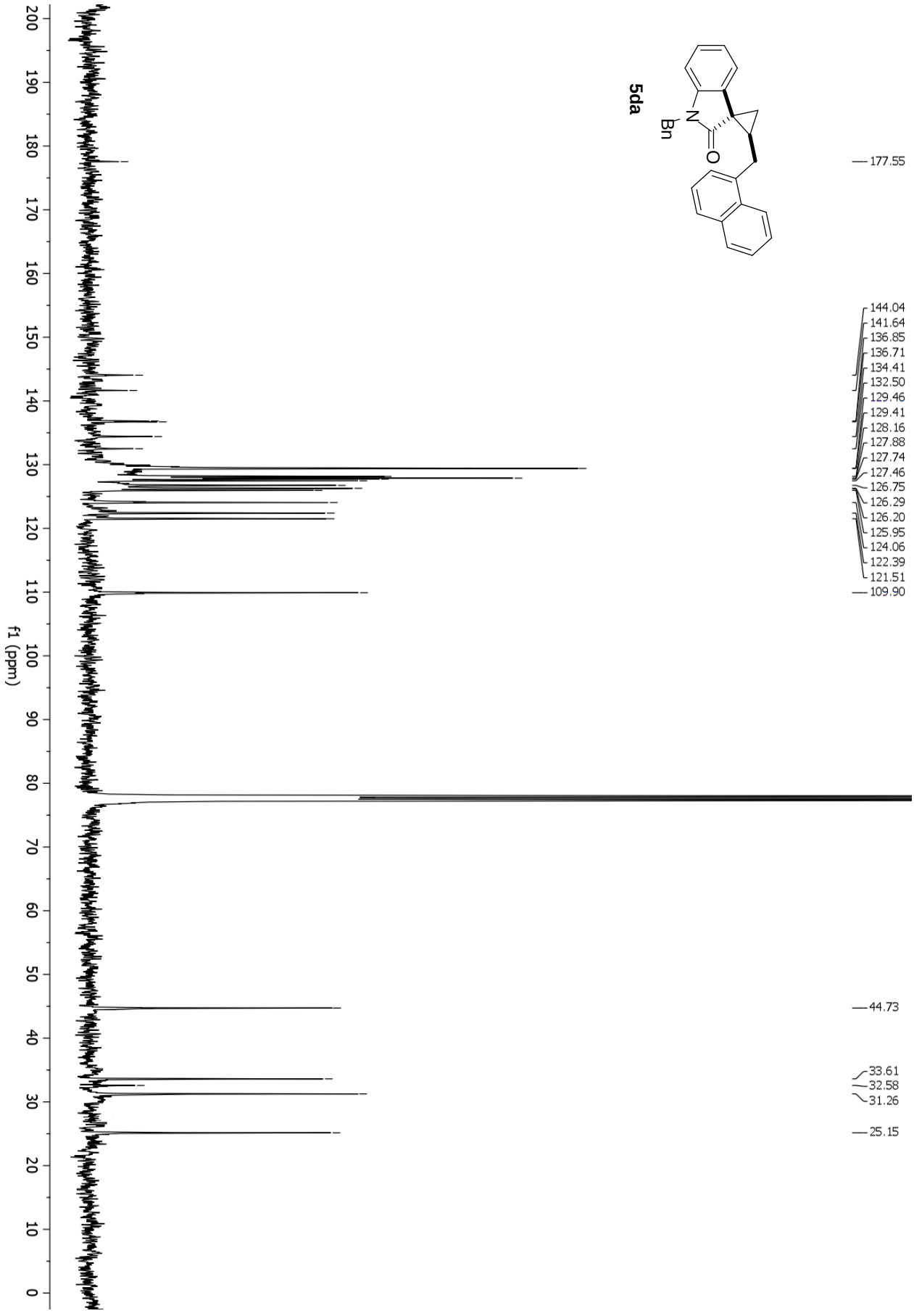
^{13}C NMR spectra (400 MHz, $CDCl_3$) of compound **5cb**



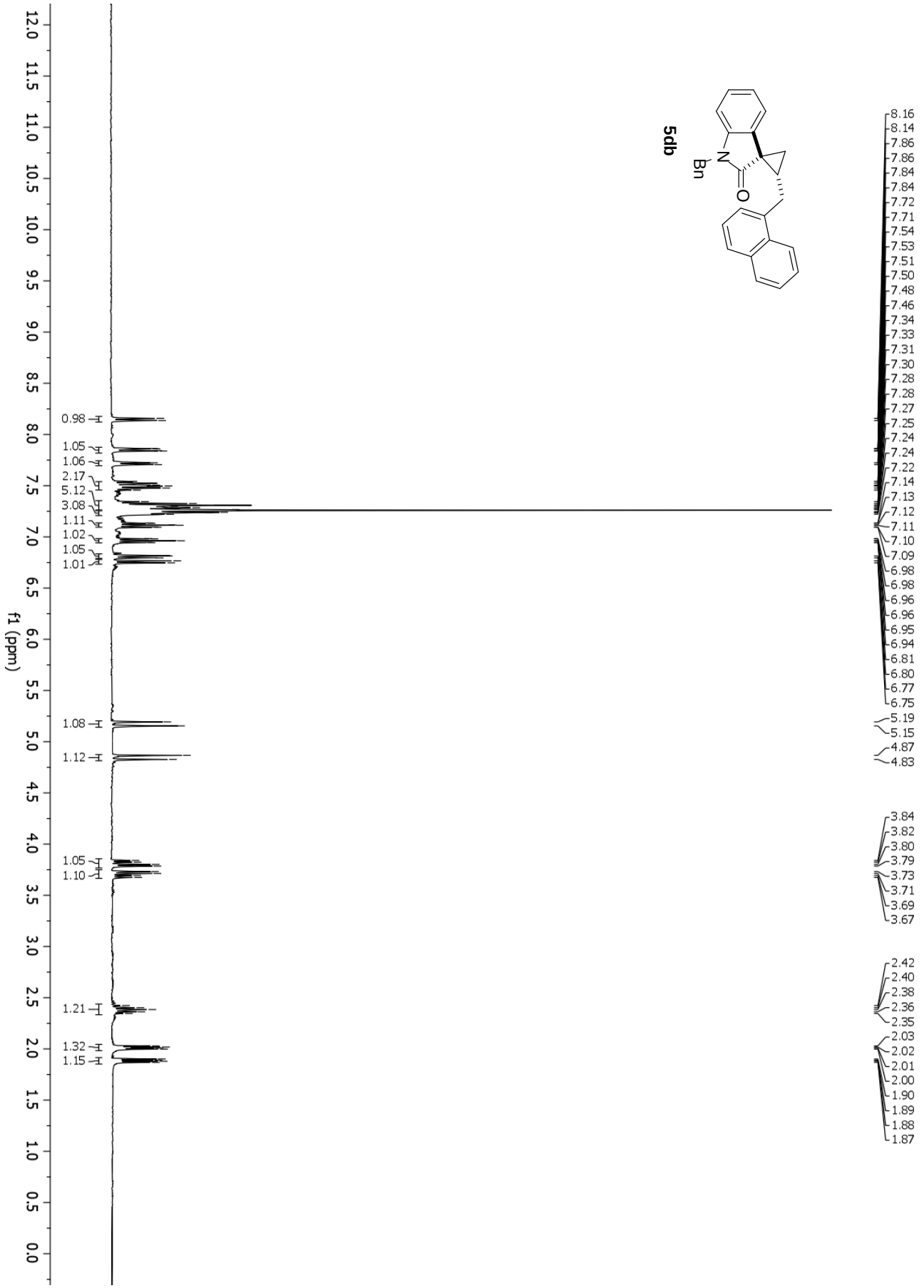
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5da**



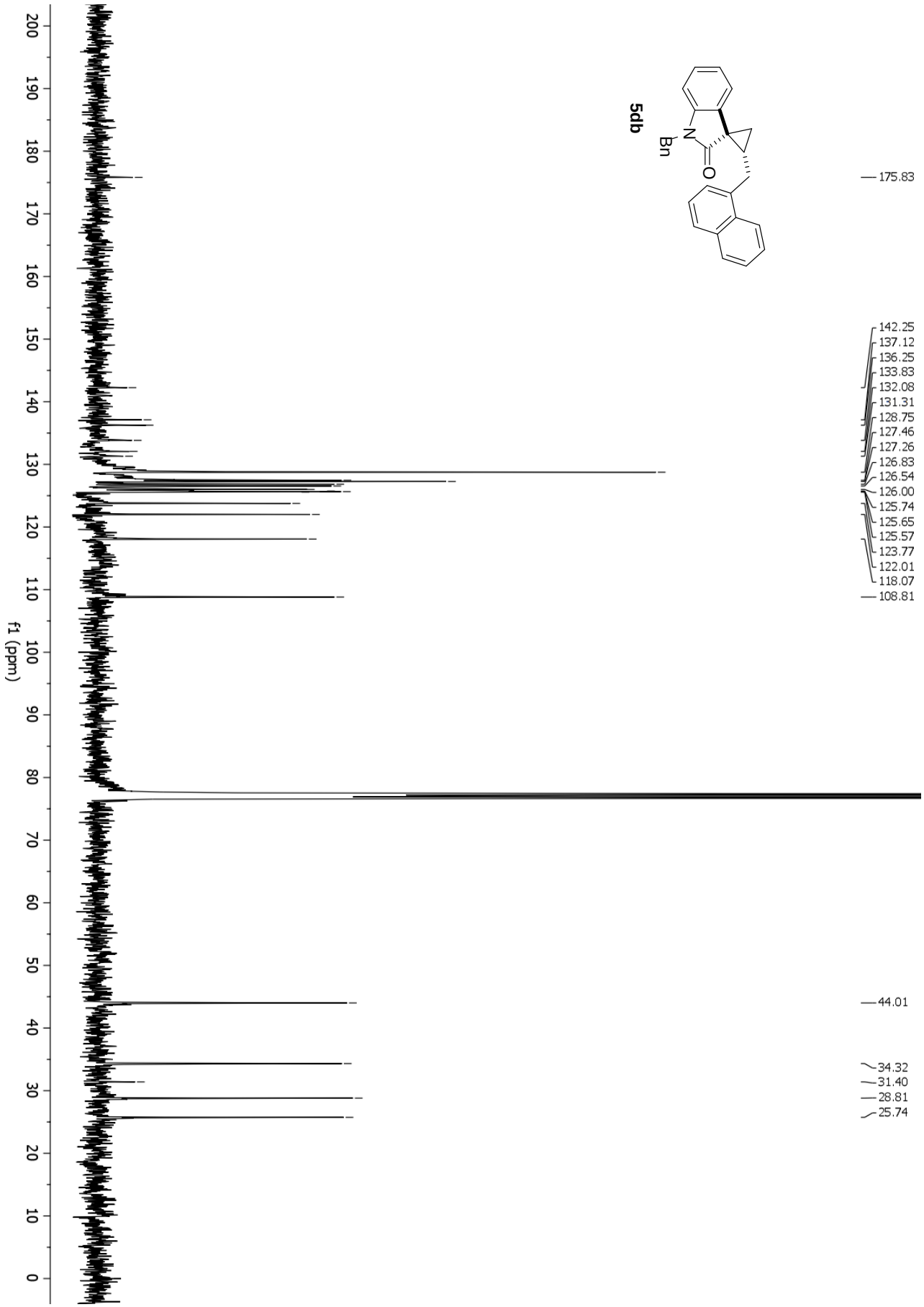
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5da**



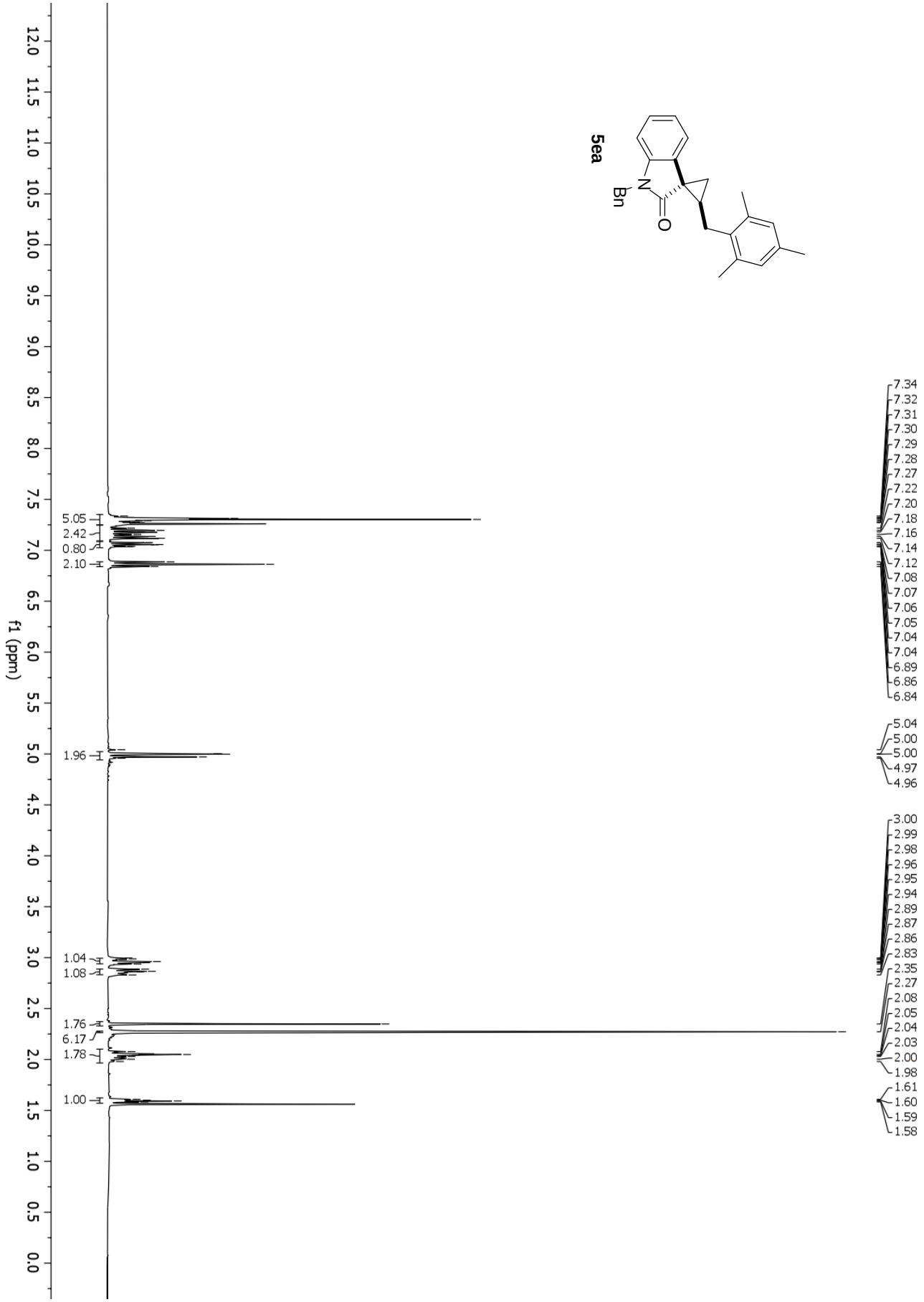
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5db**



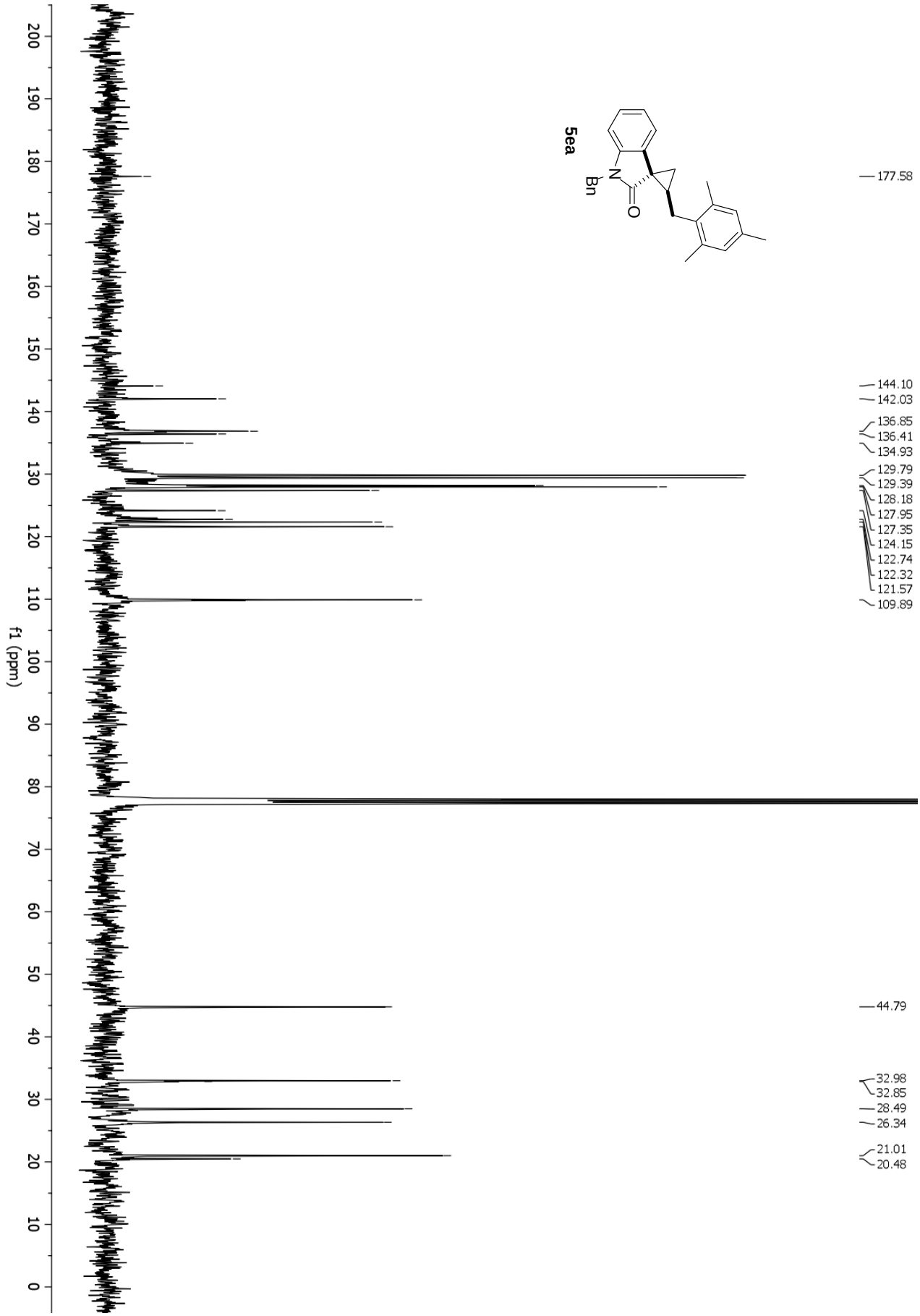
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5db**



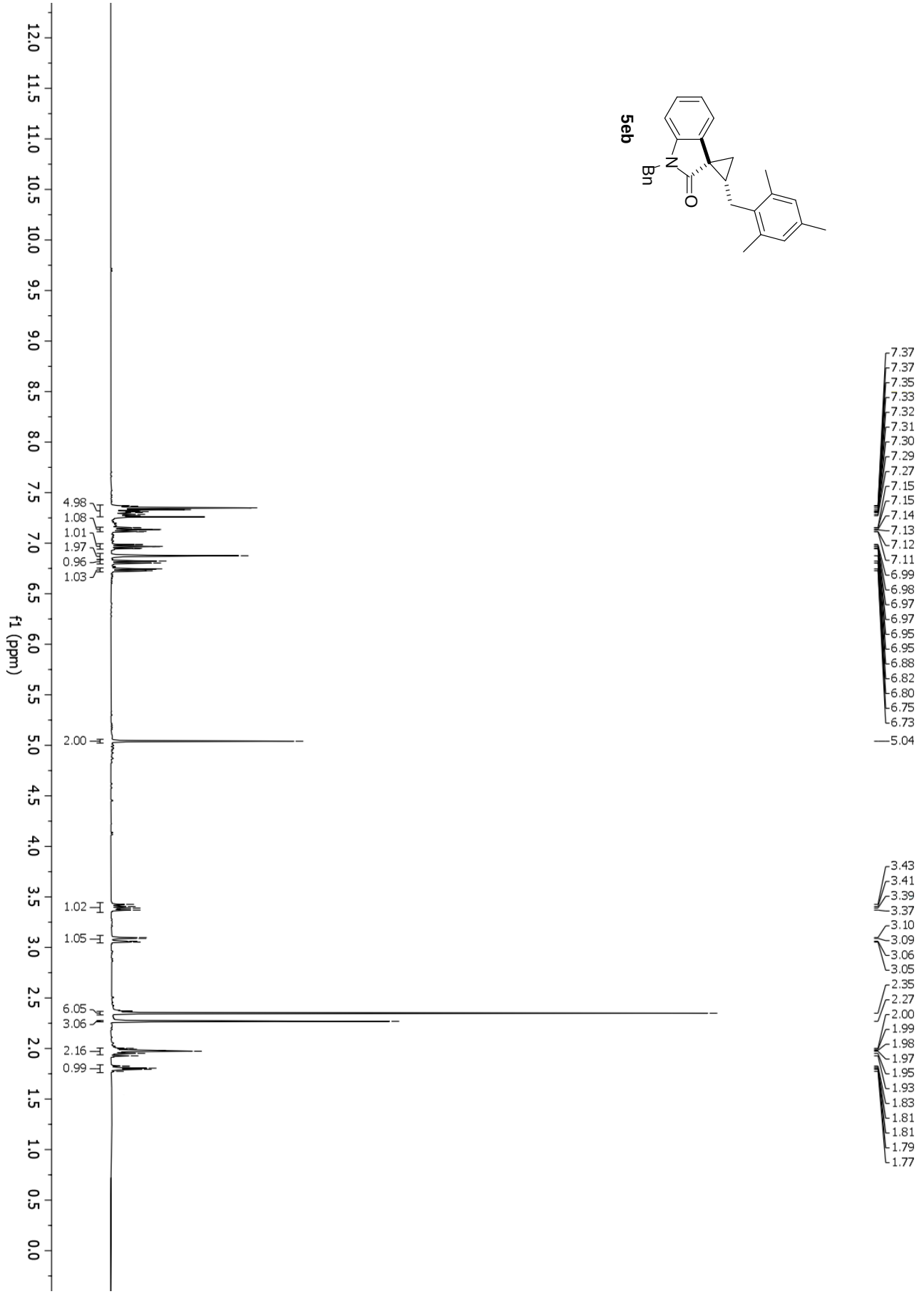
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ea**



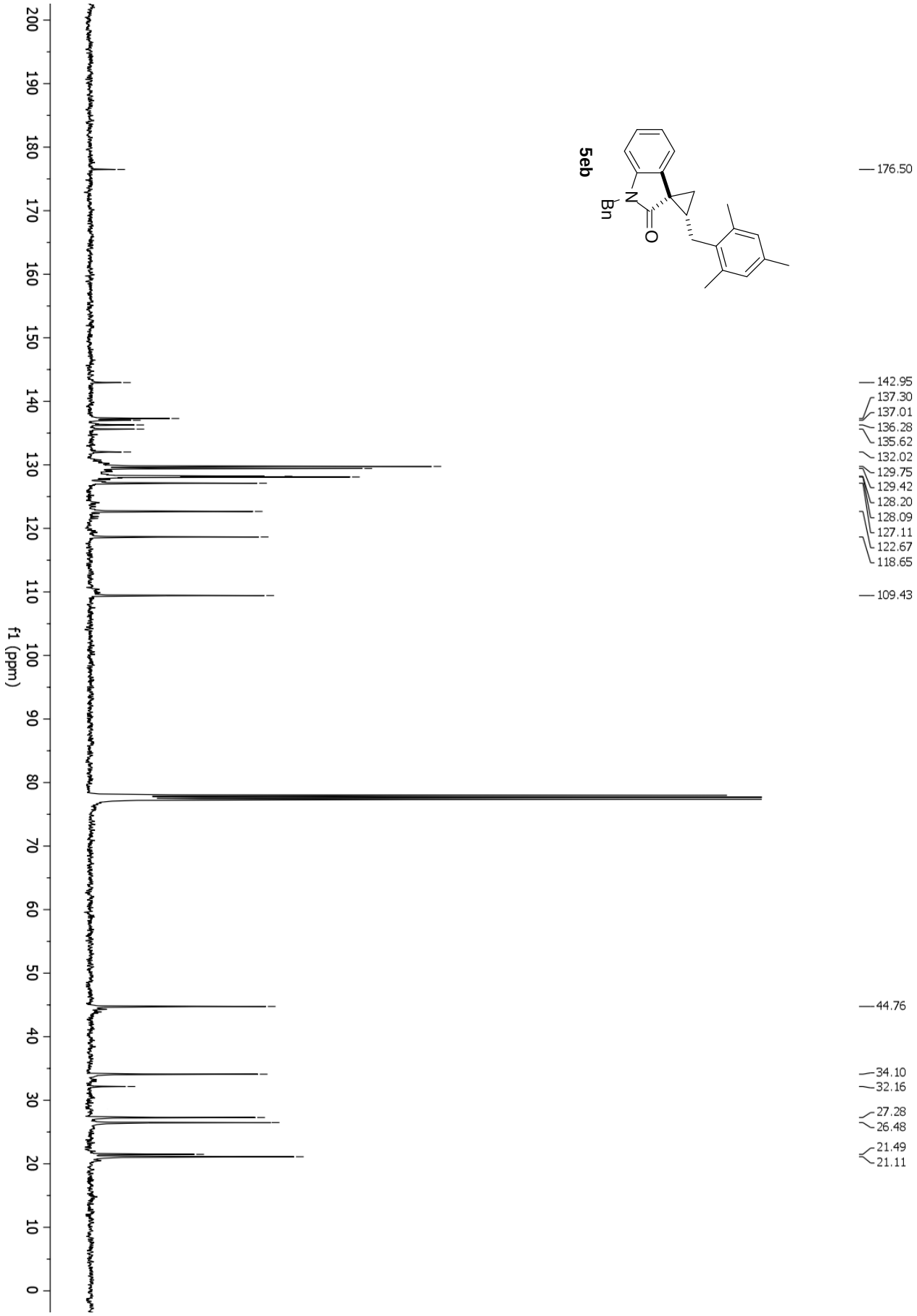
^{13}C NMR spectra (400 MHz, $CDCl_3$) of compound **5ea**



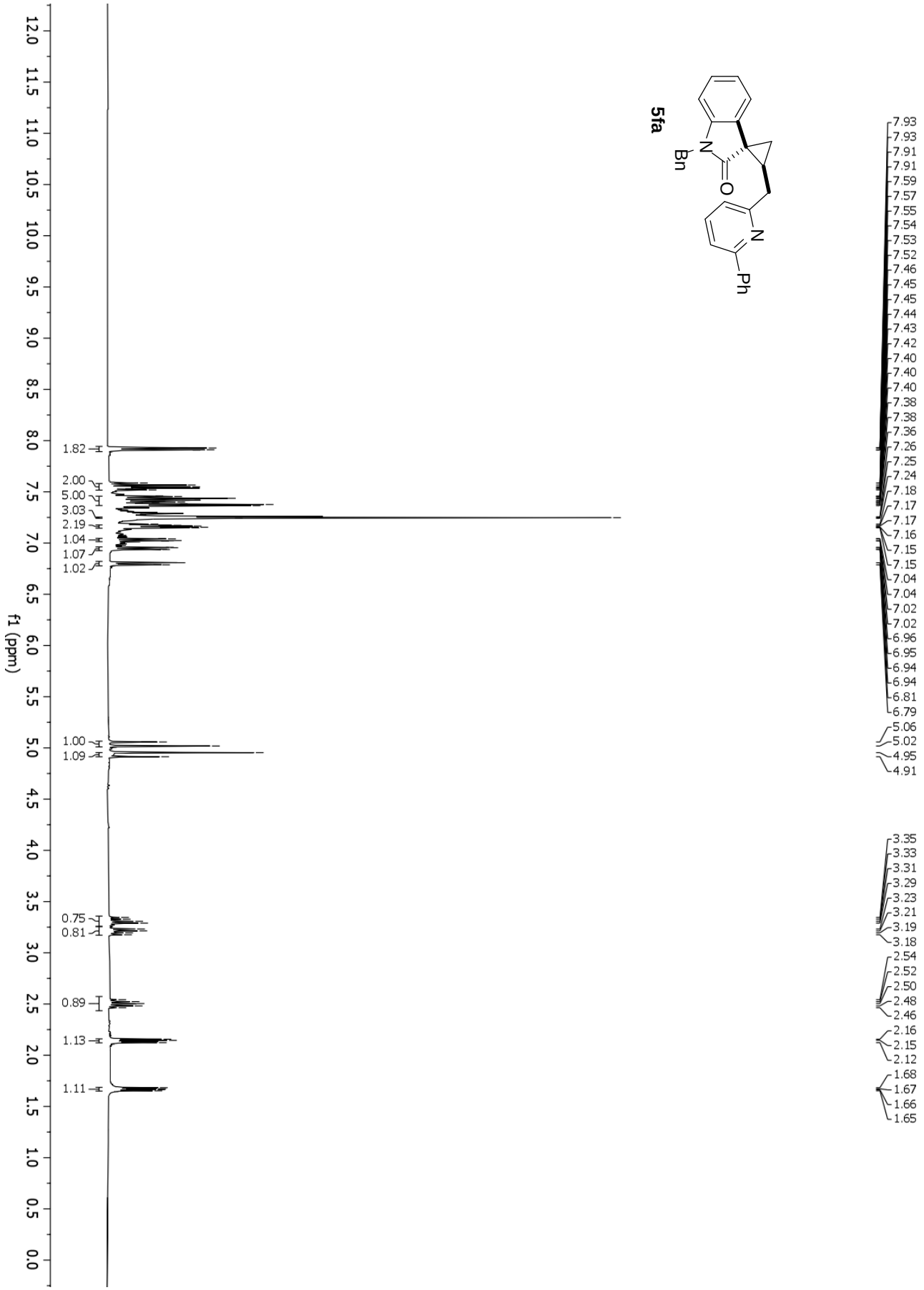
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5eb**



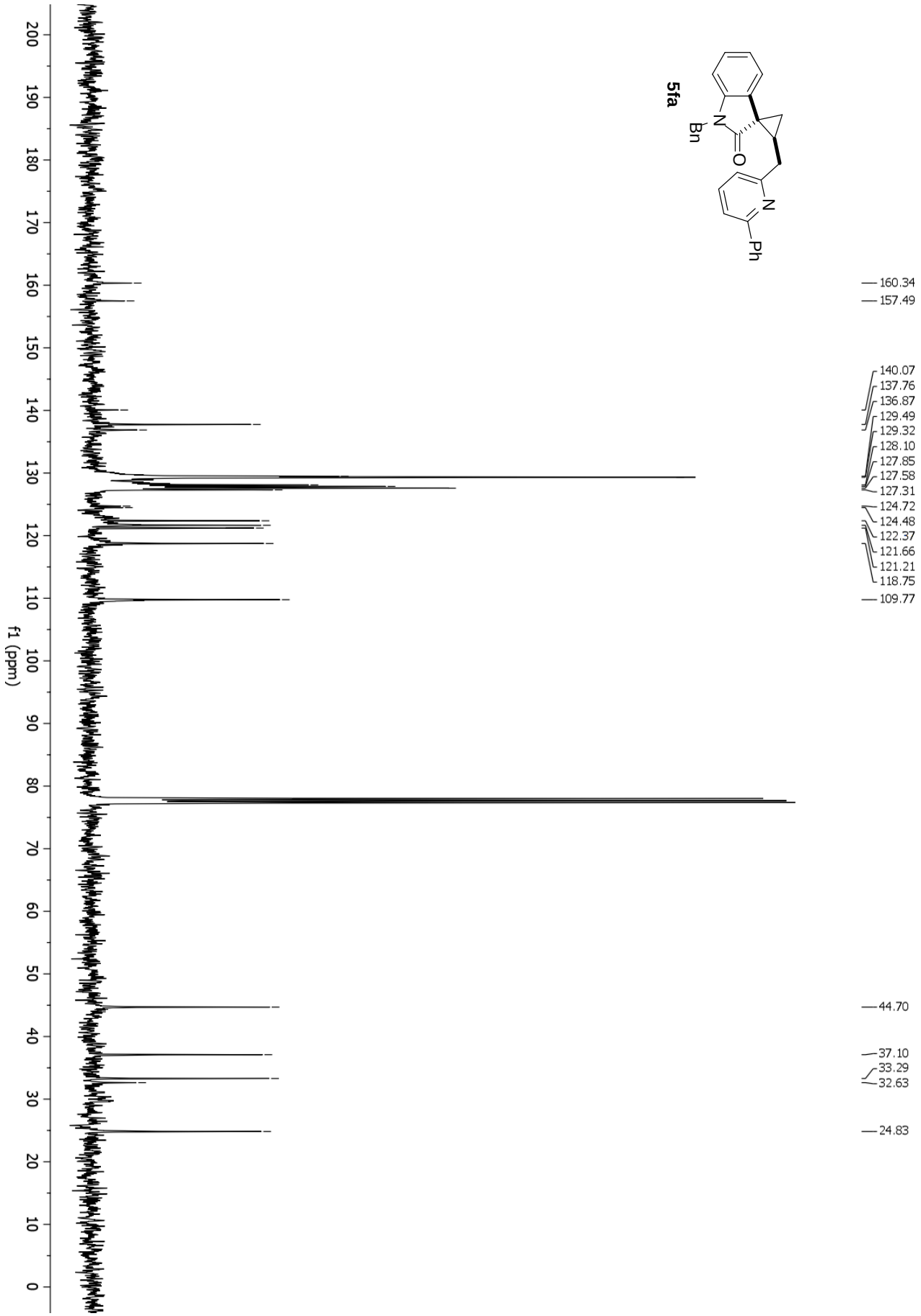
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5eb**



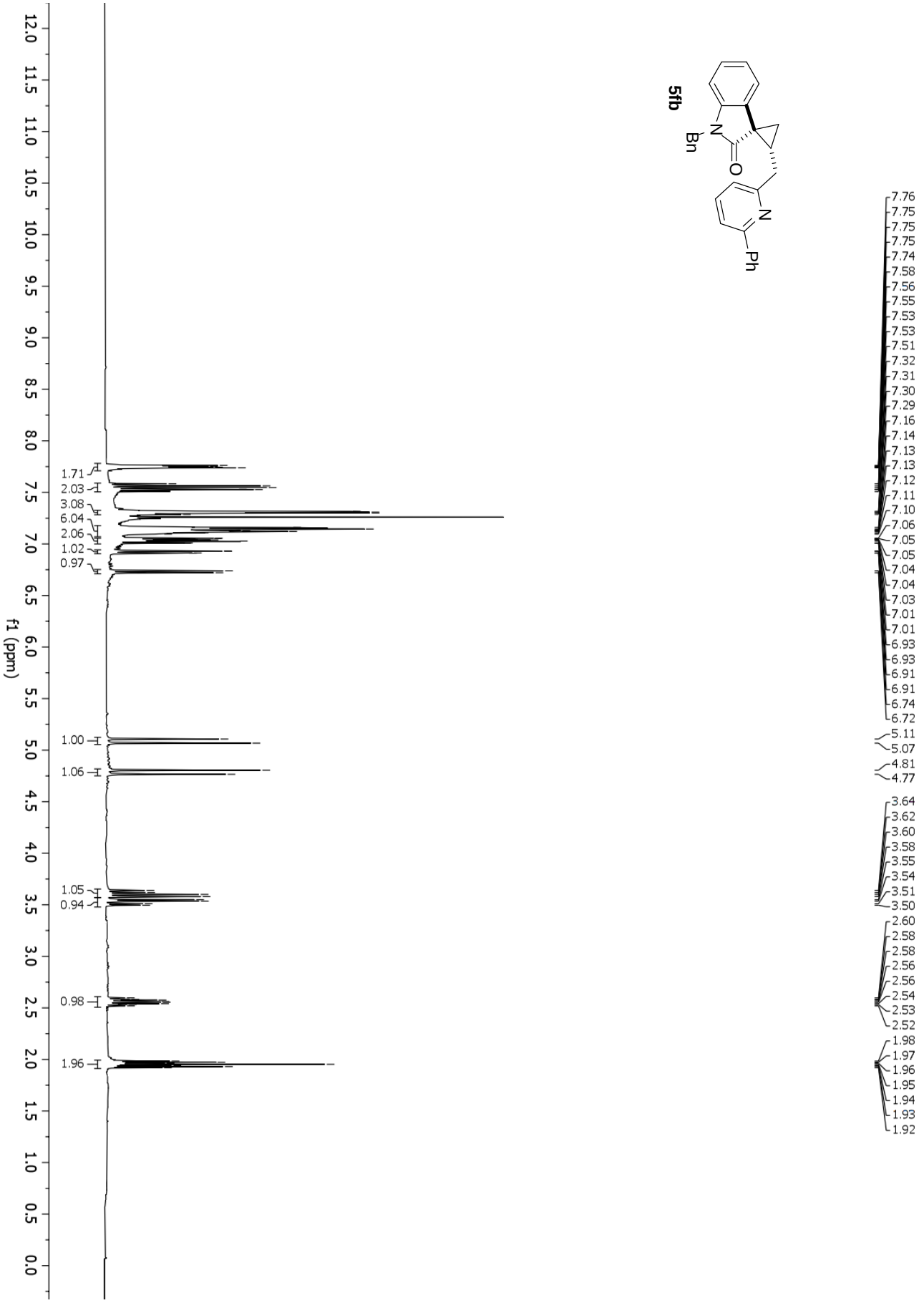
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5fa**



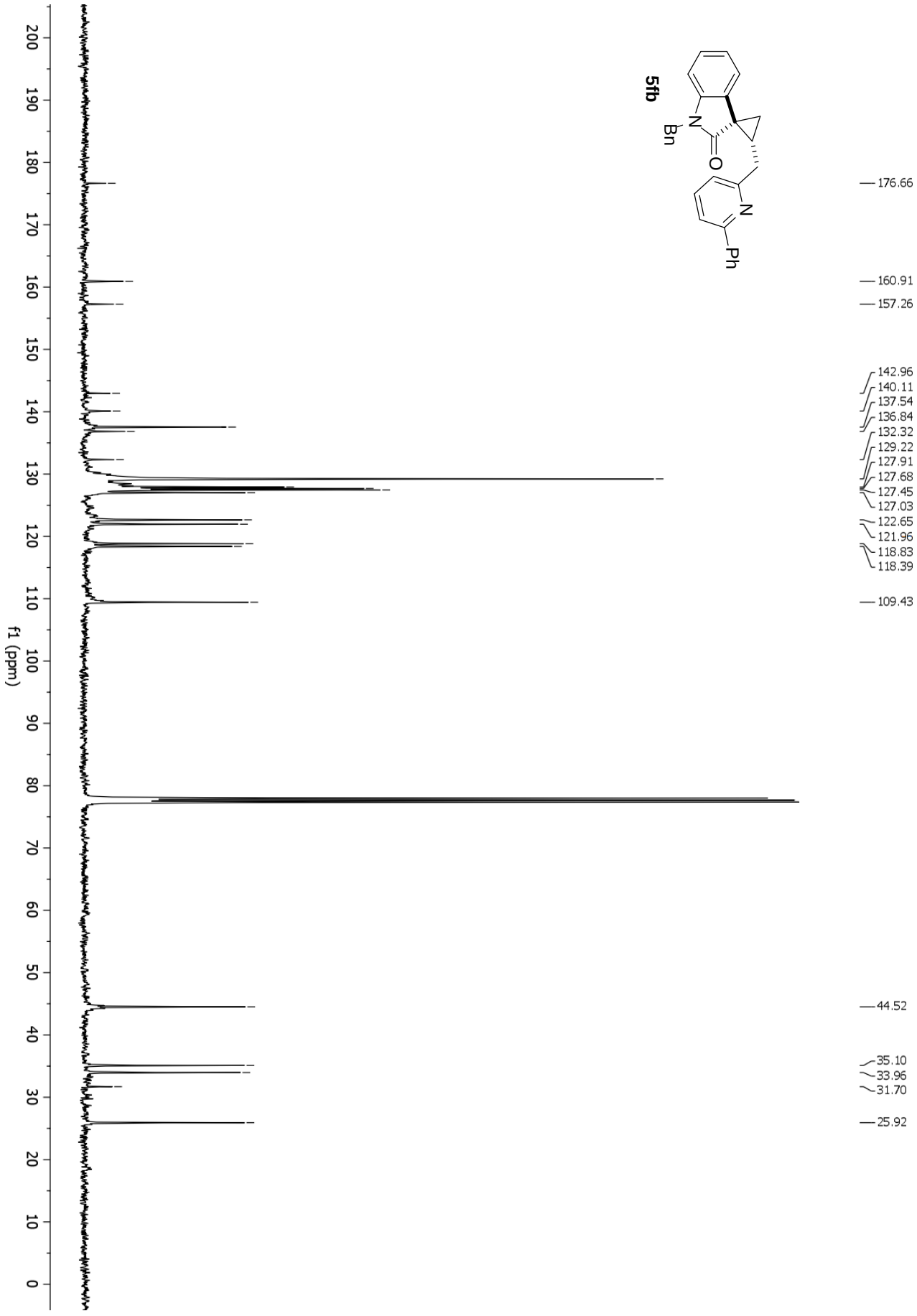
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5fa**



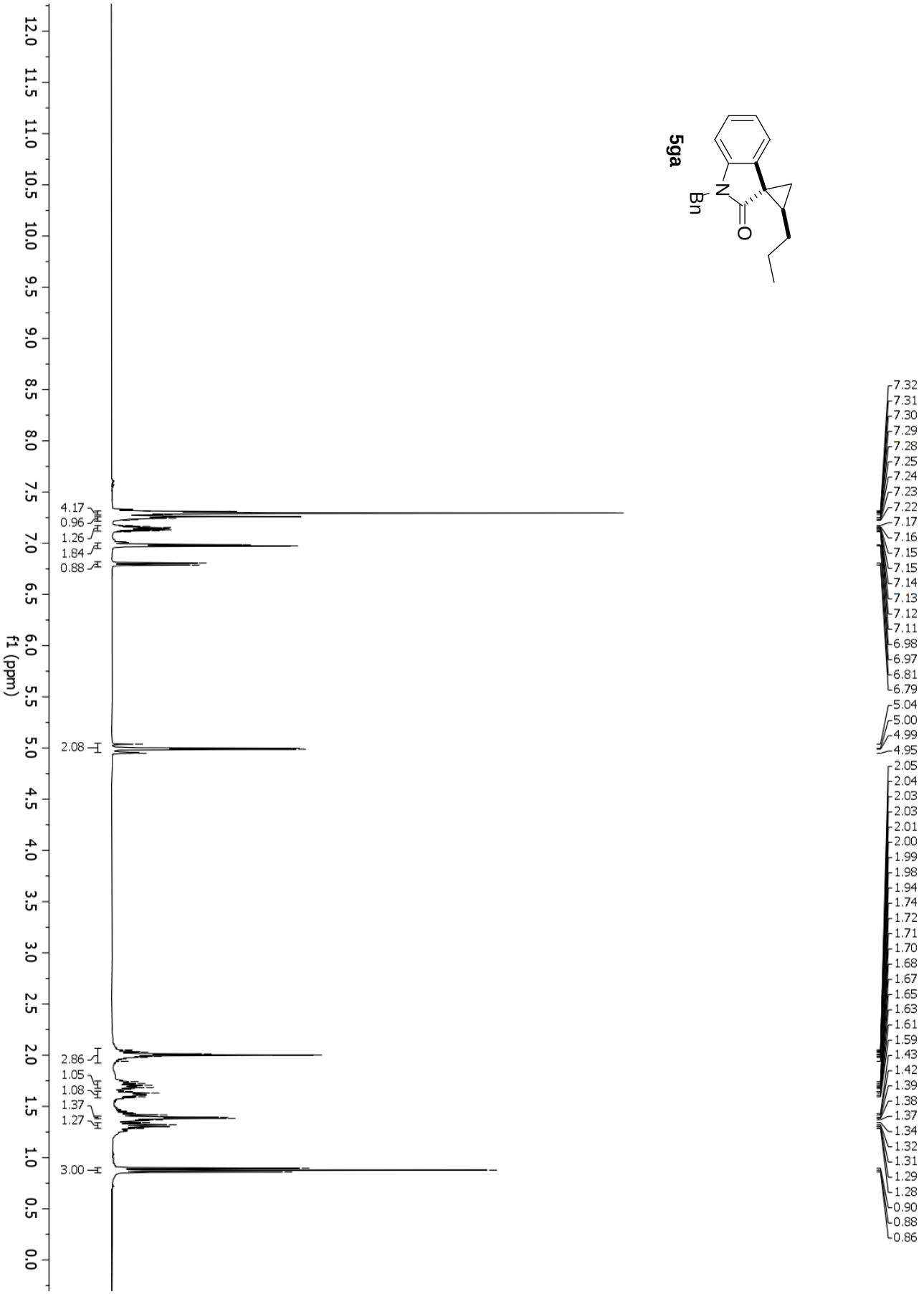
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5fb**



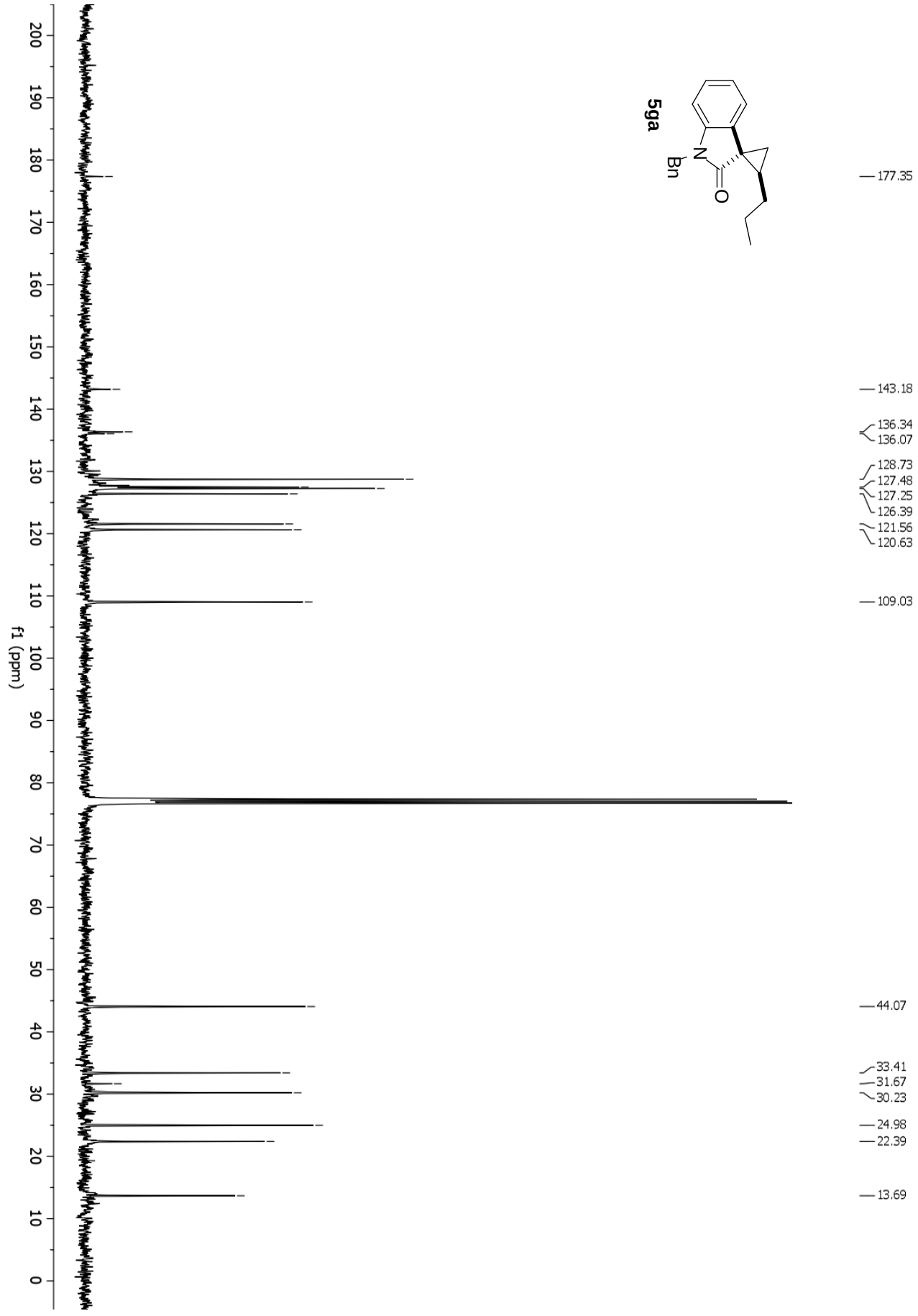
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5fb**



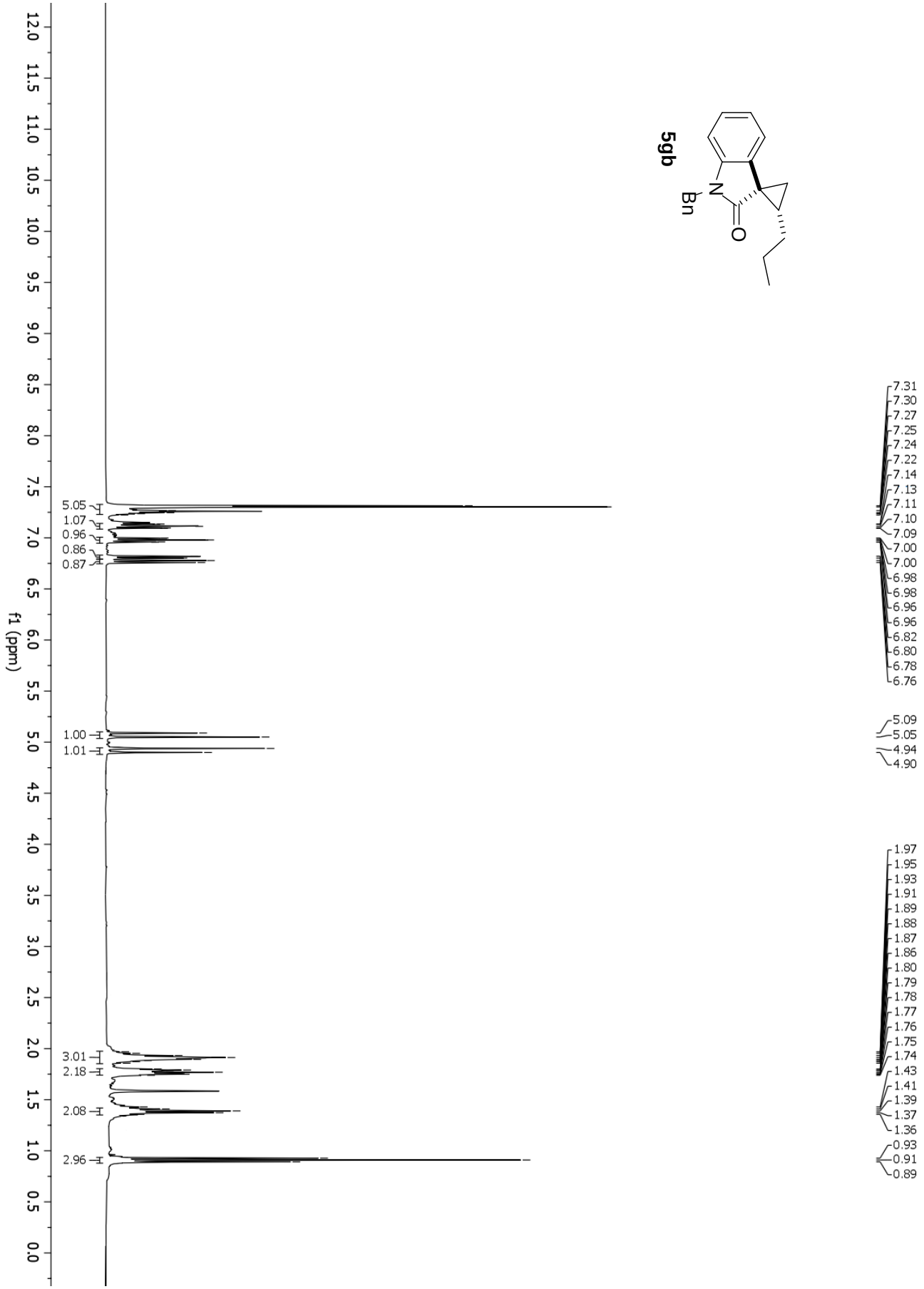
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ga**



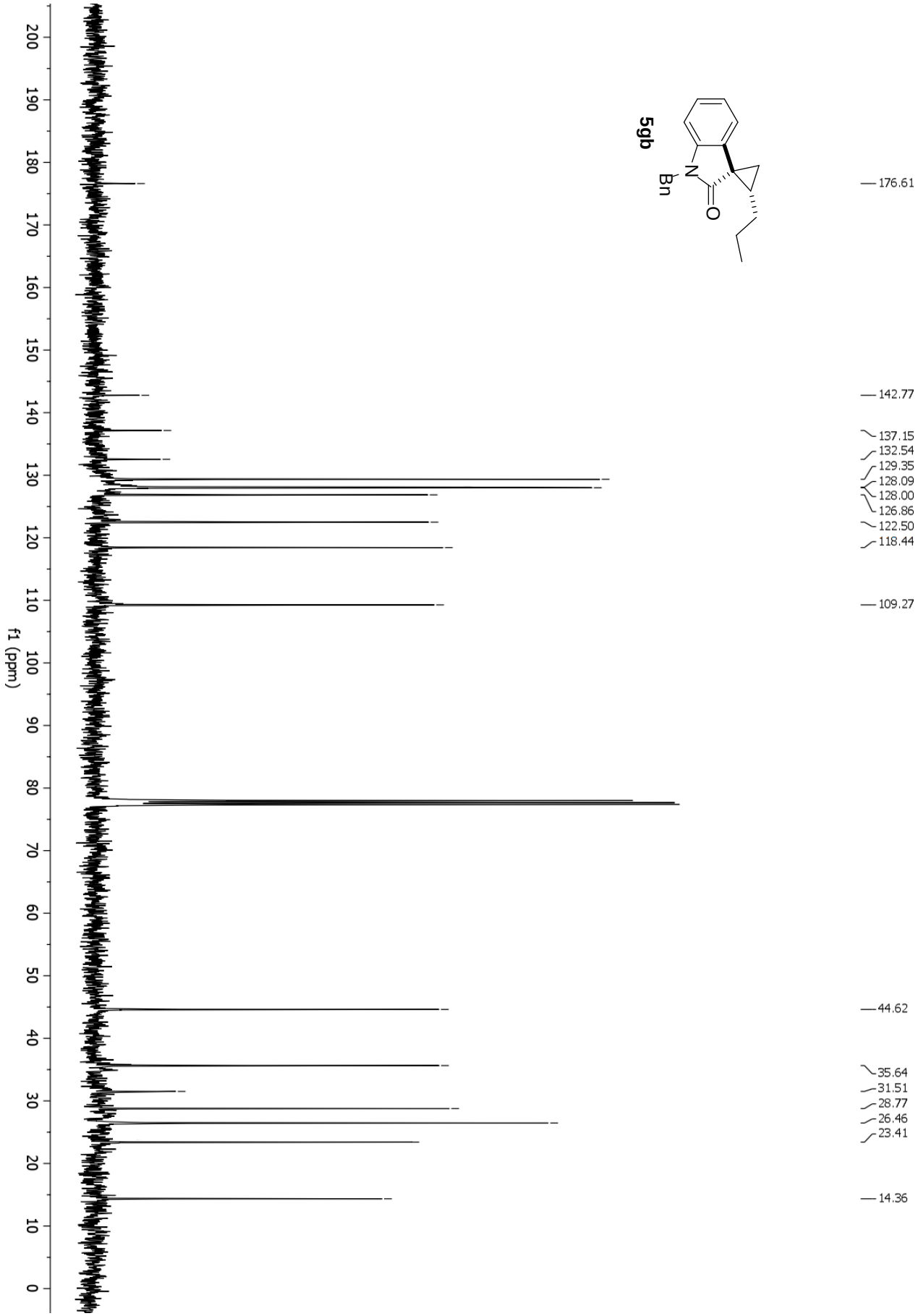
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ga**



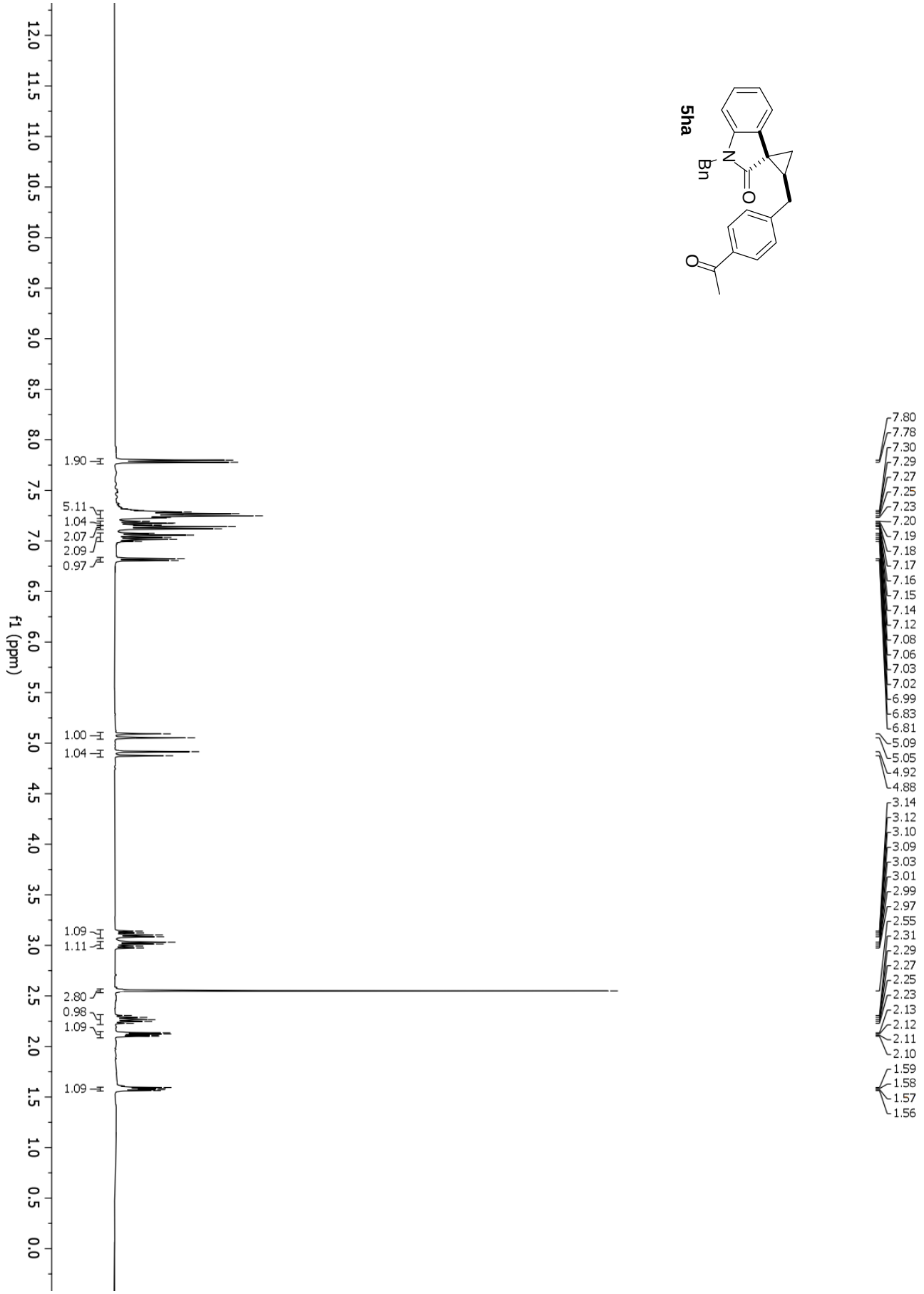
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5gb**



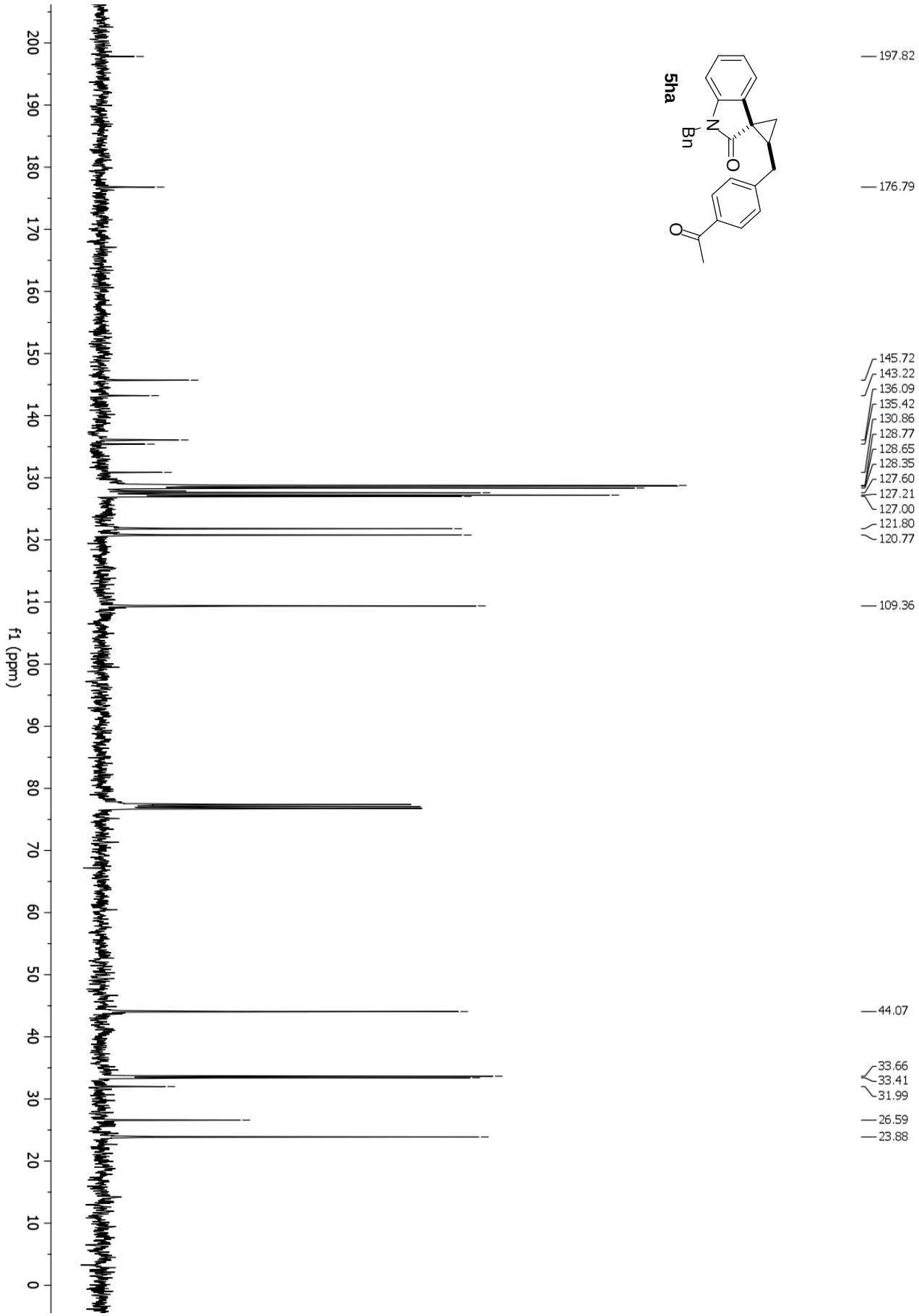
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5gb**



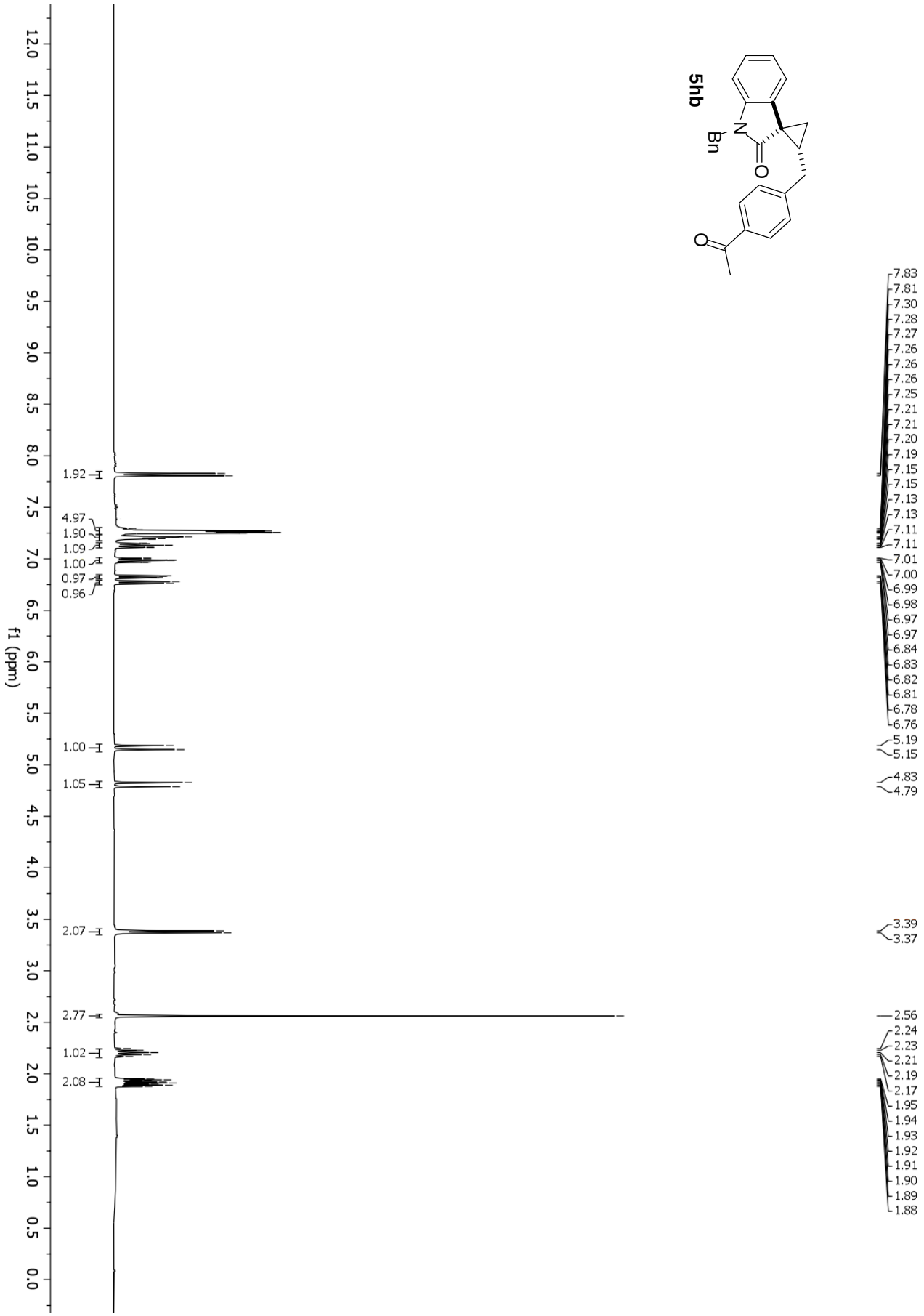
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ha**



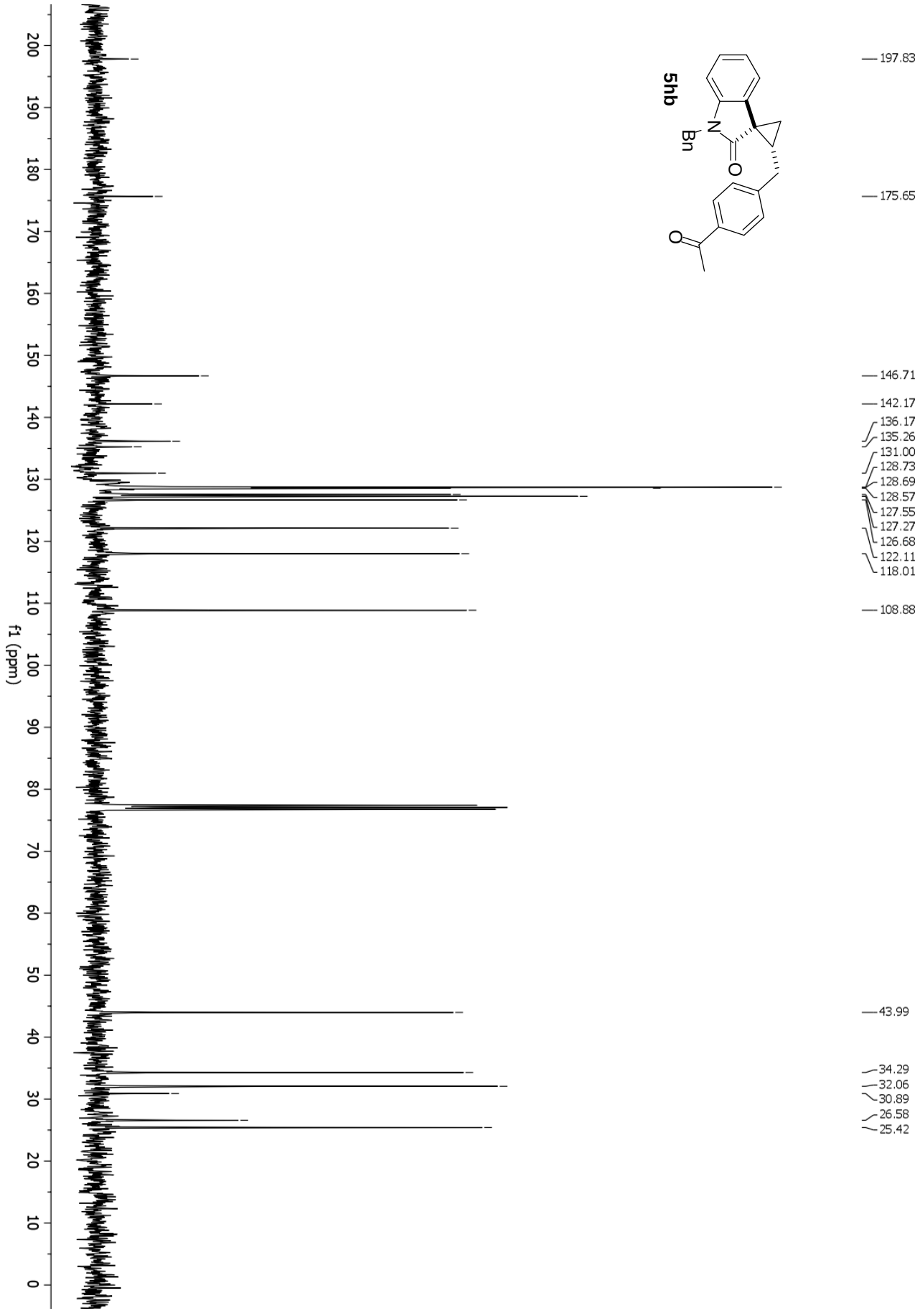
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ha**



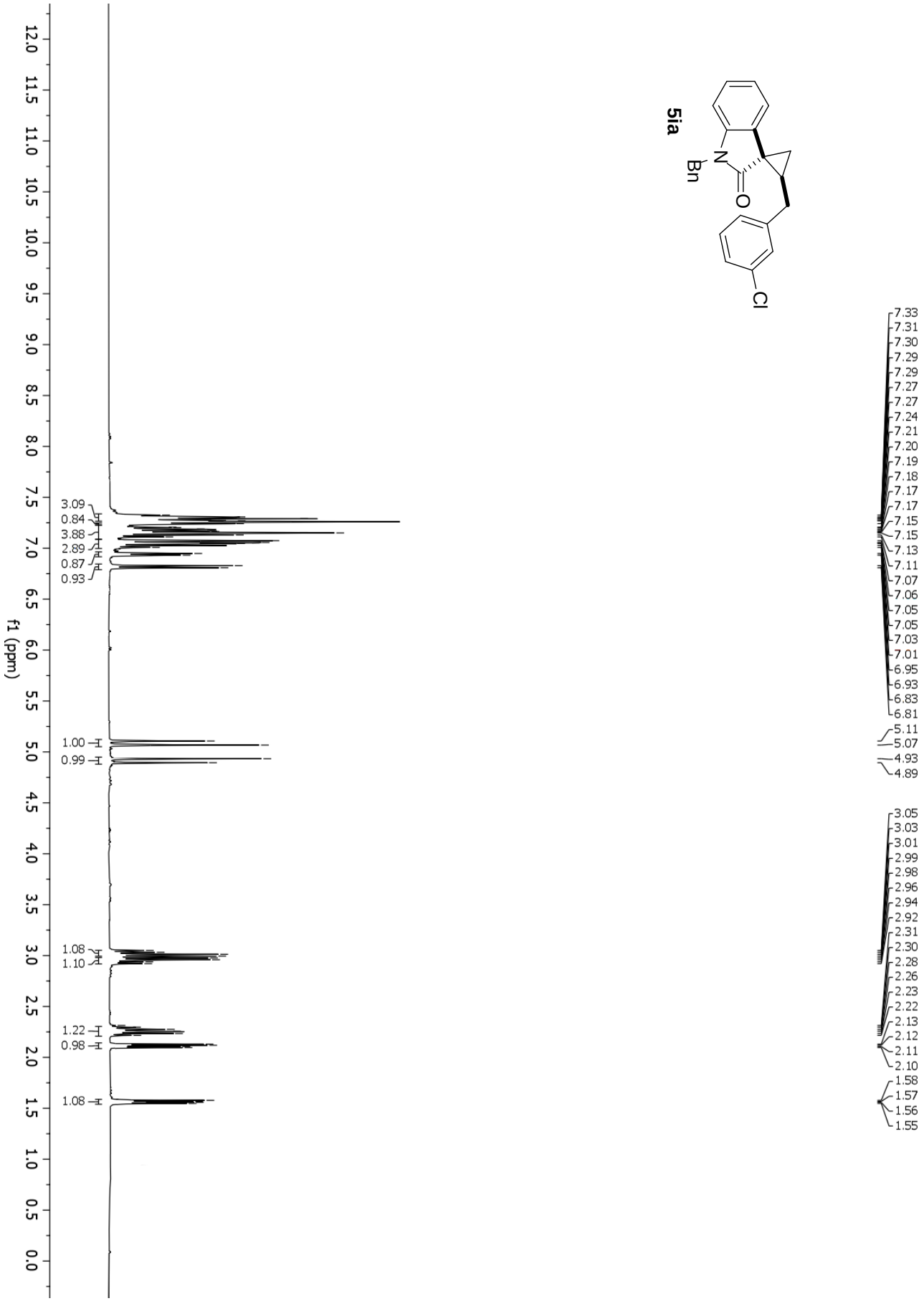
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5hb**



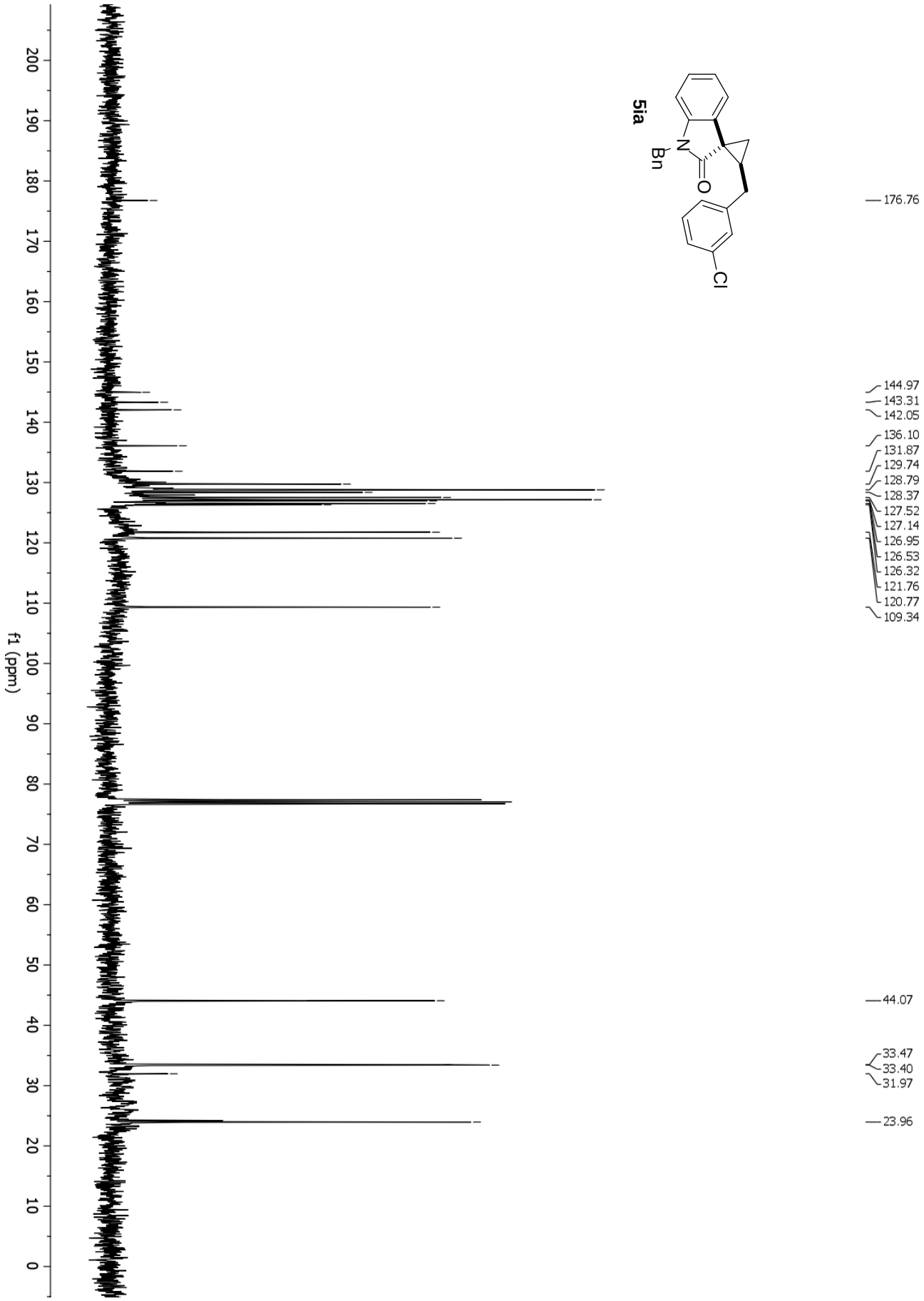
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5hb**



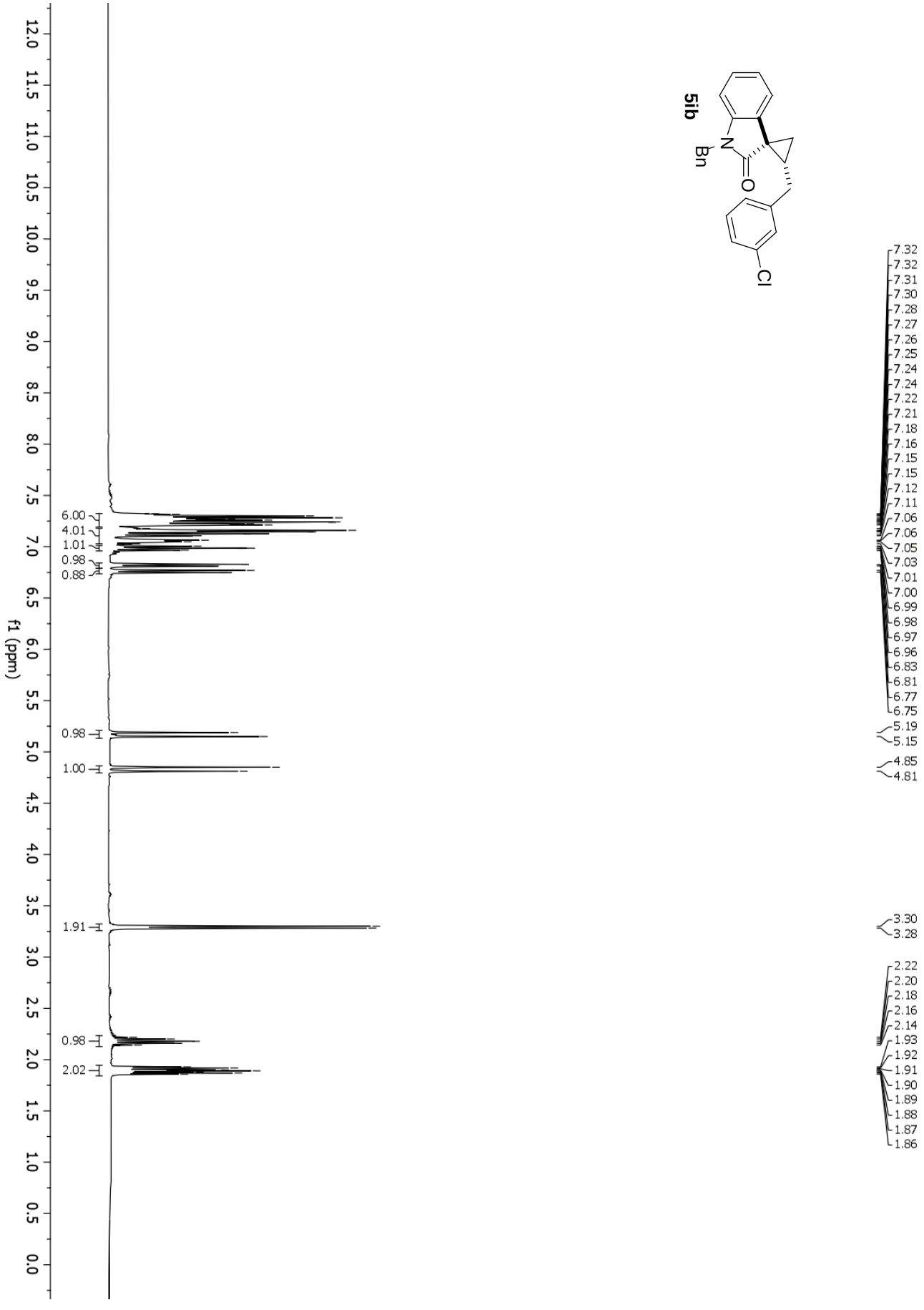
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ia**



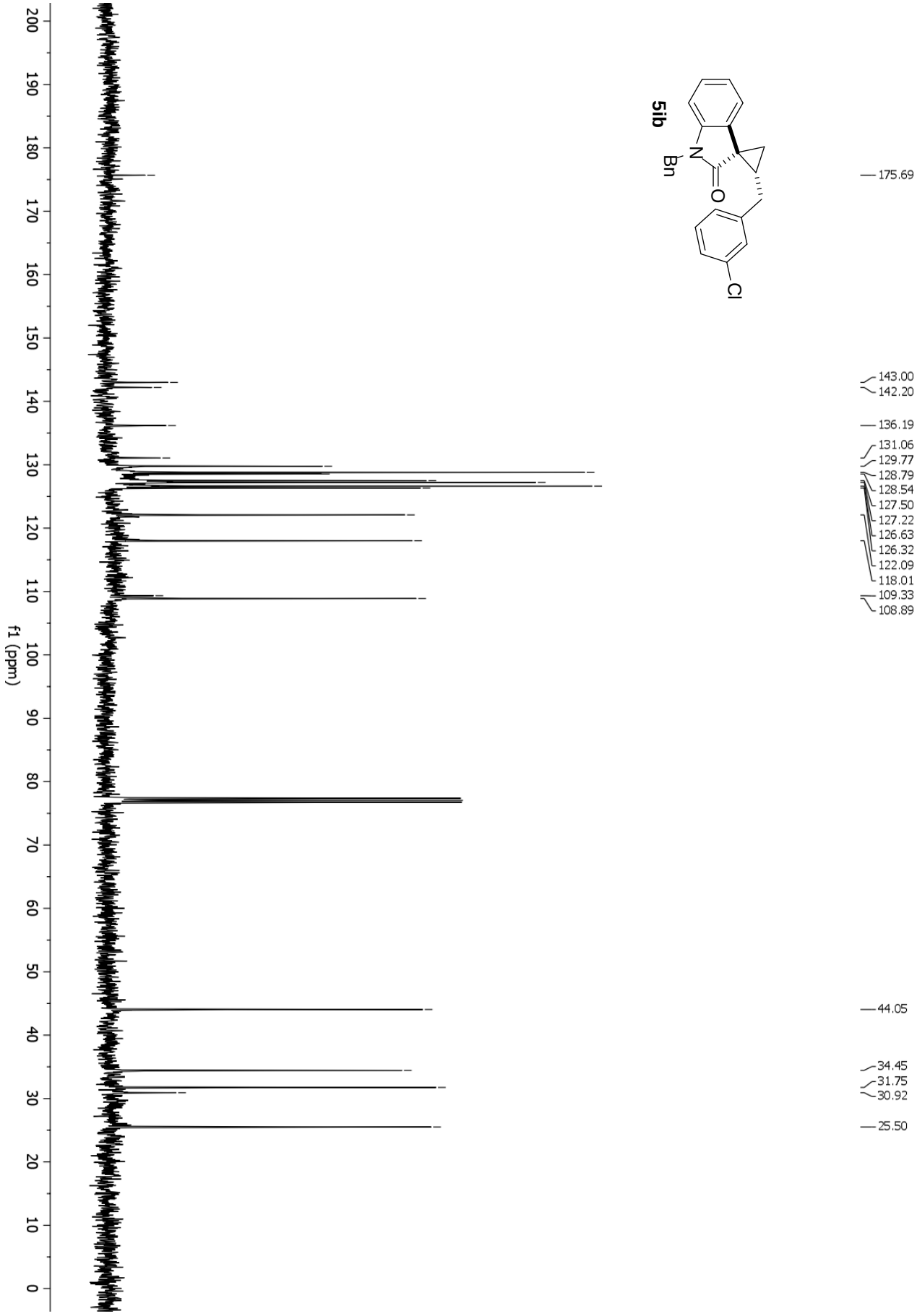
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ia**



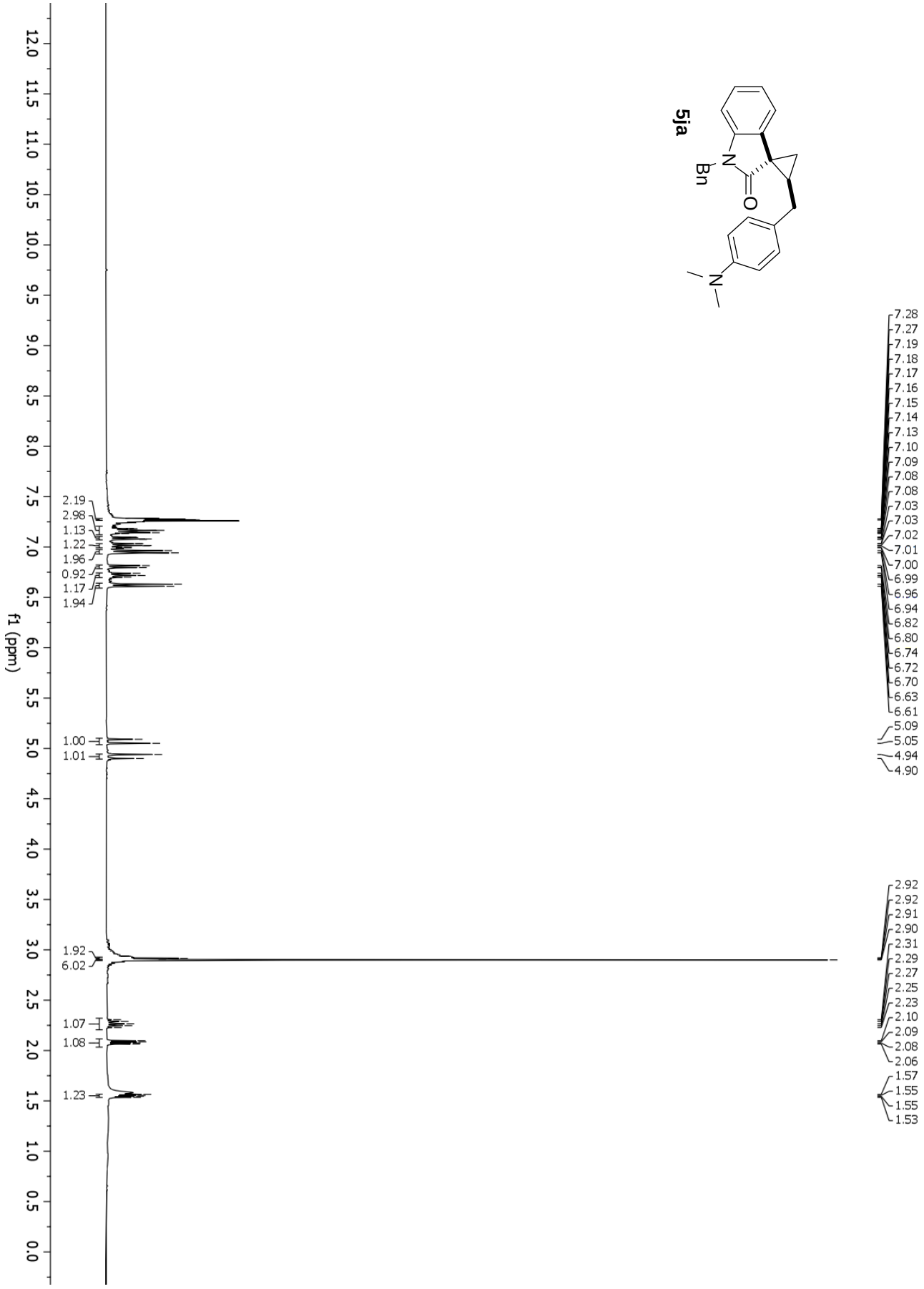
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ib**



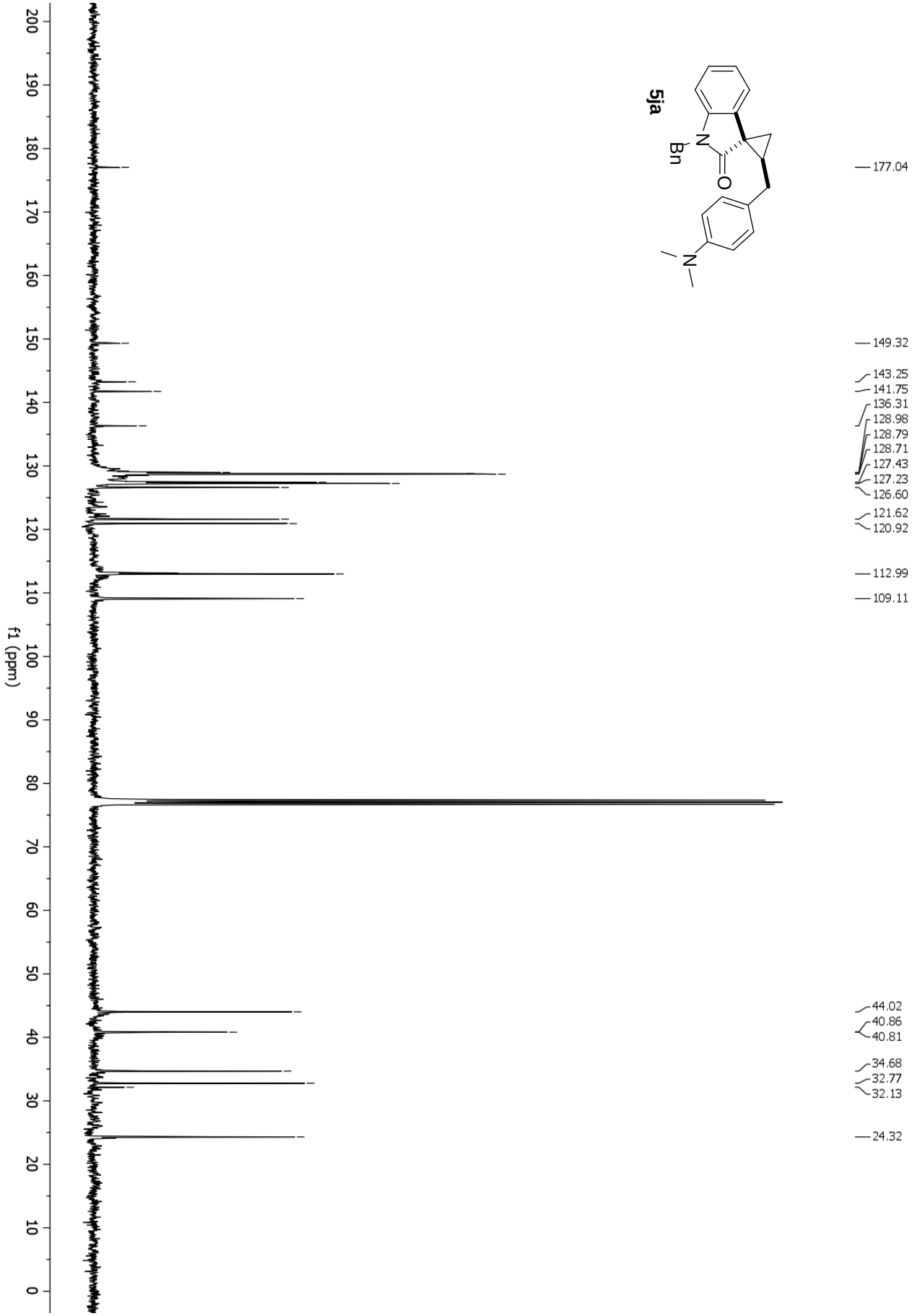
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ib**



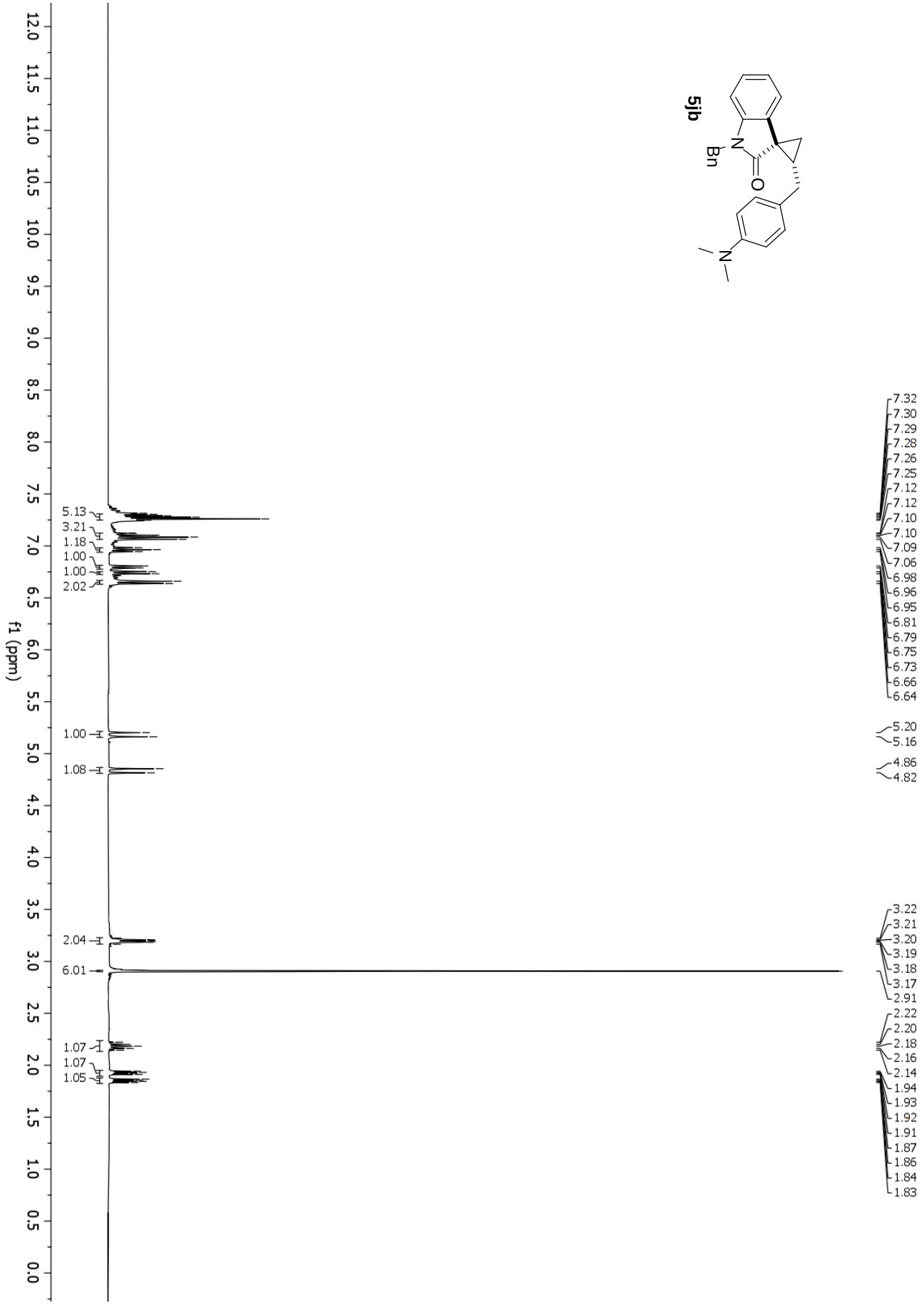
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ja**



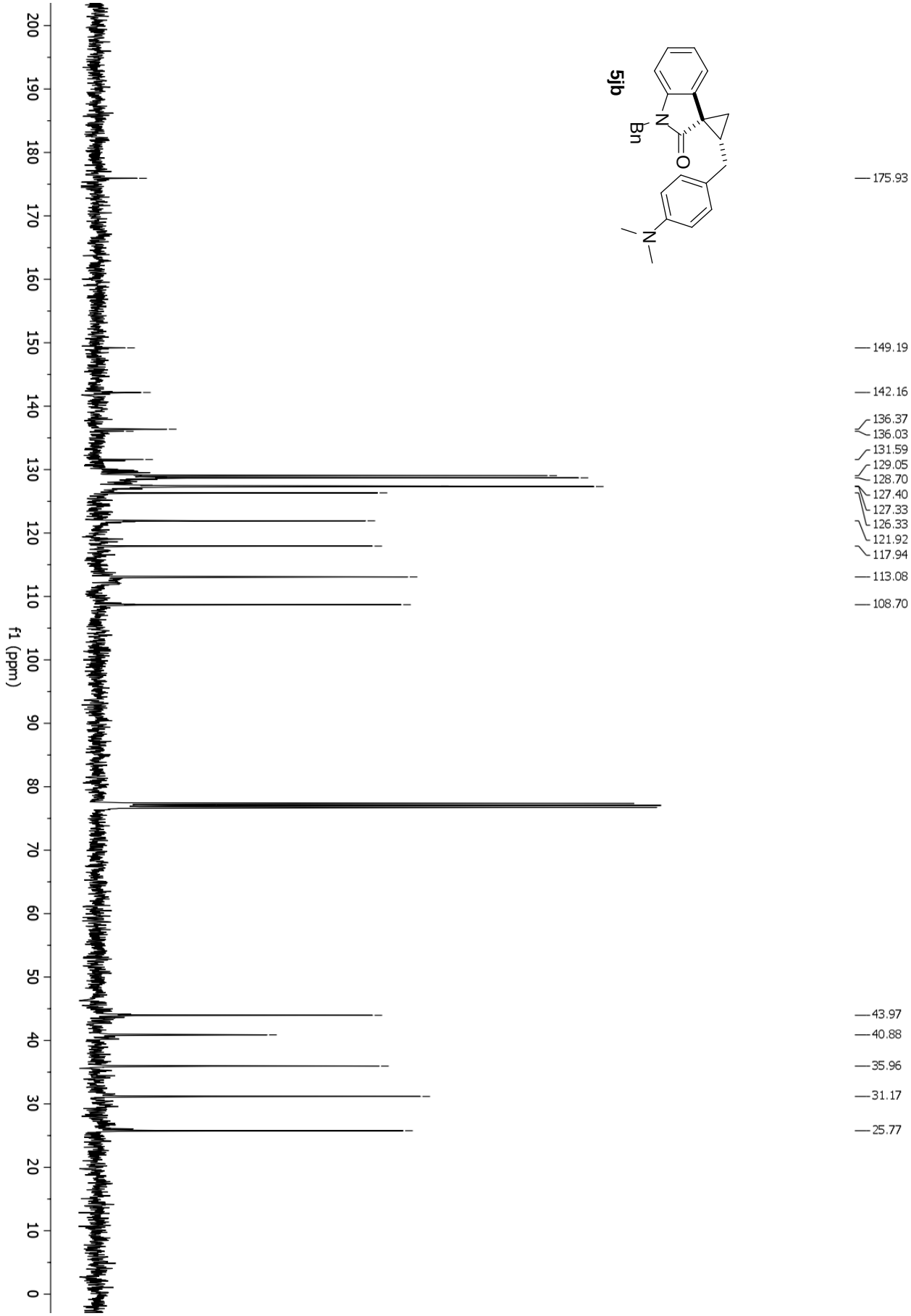
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ja**



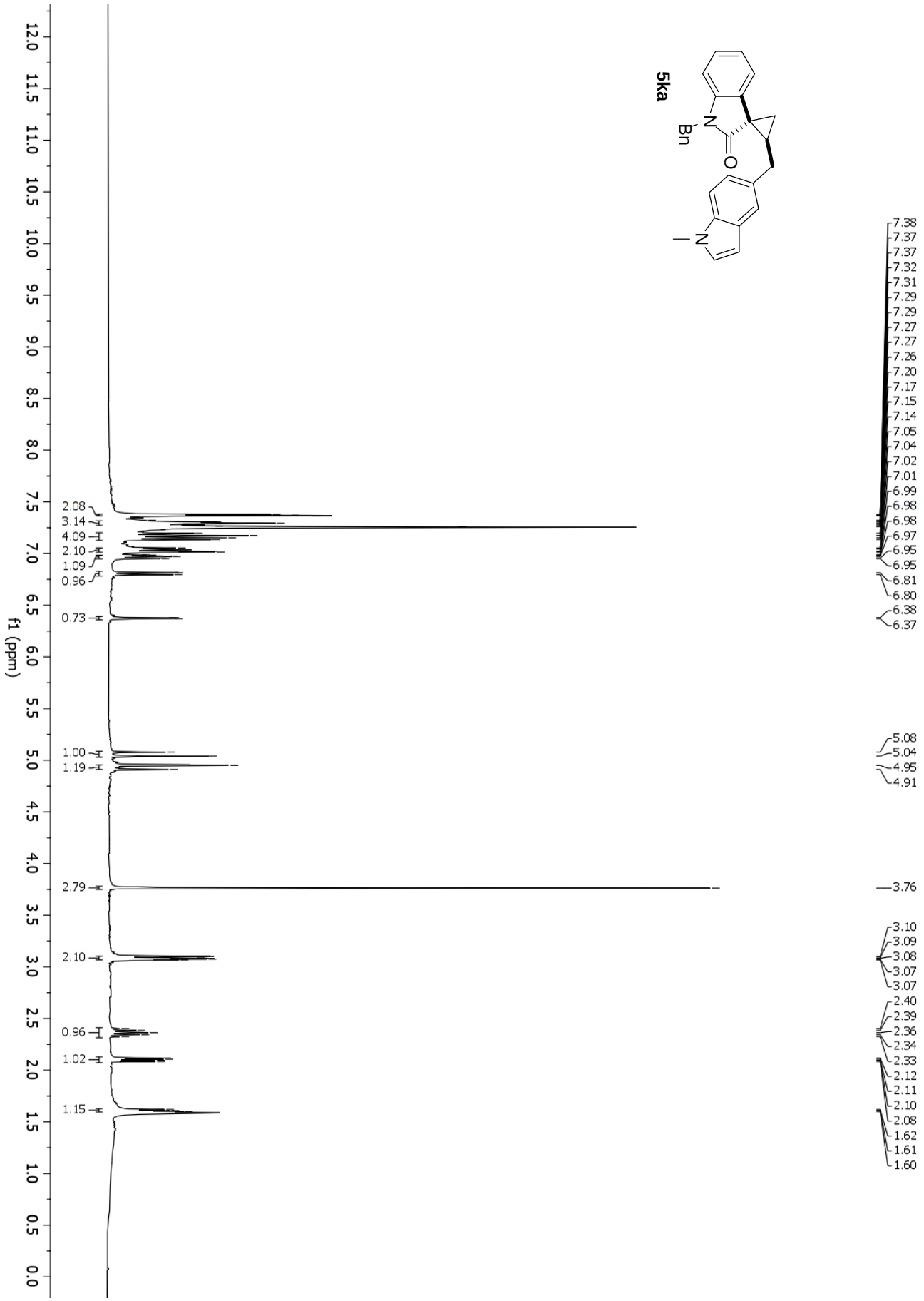
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5jb**



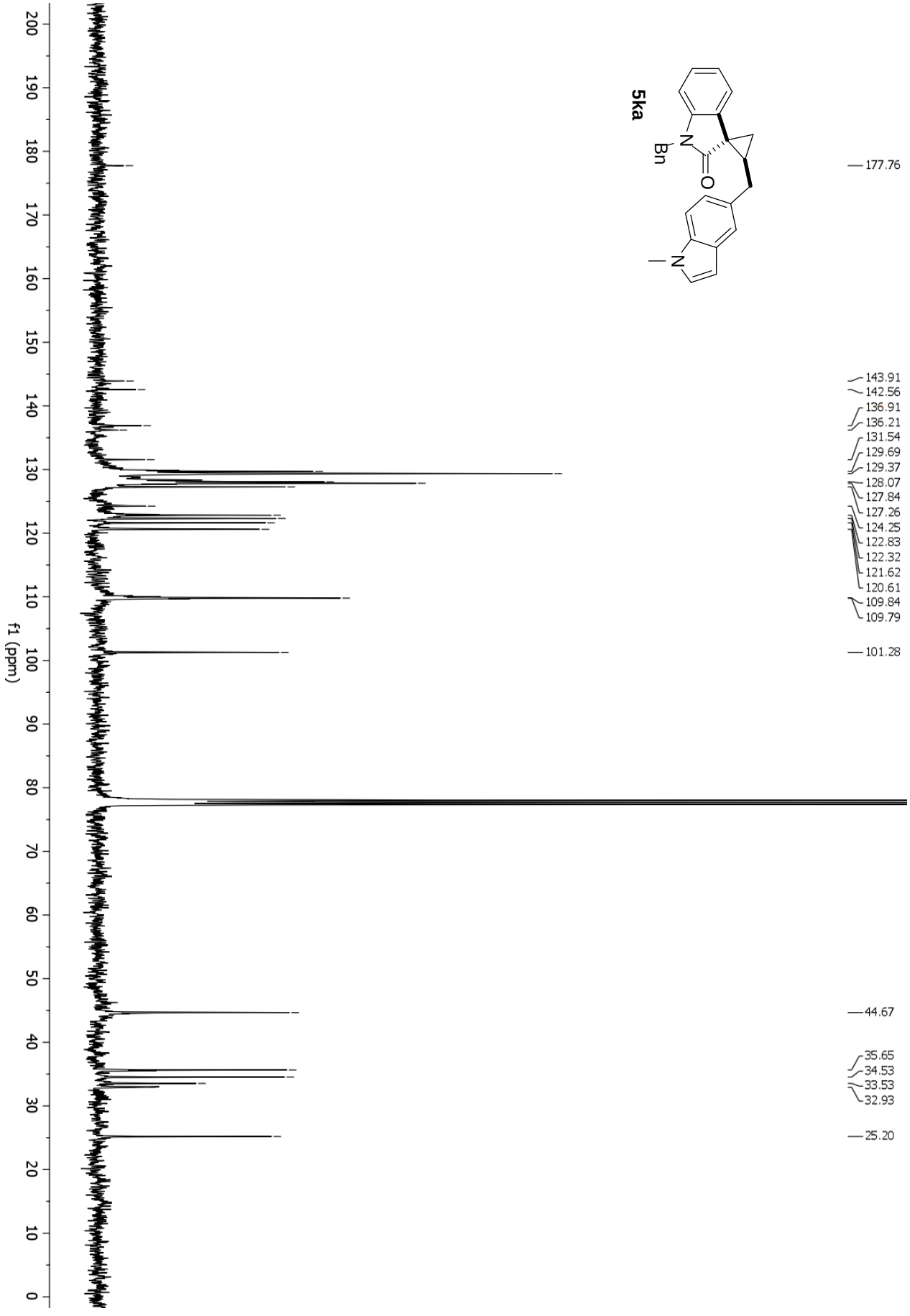
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5jb**



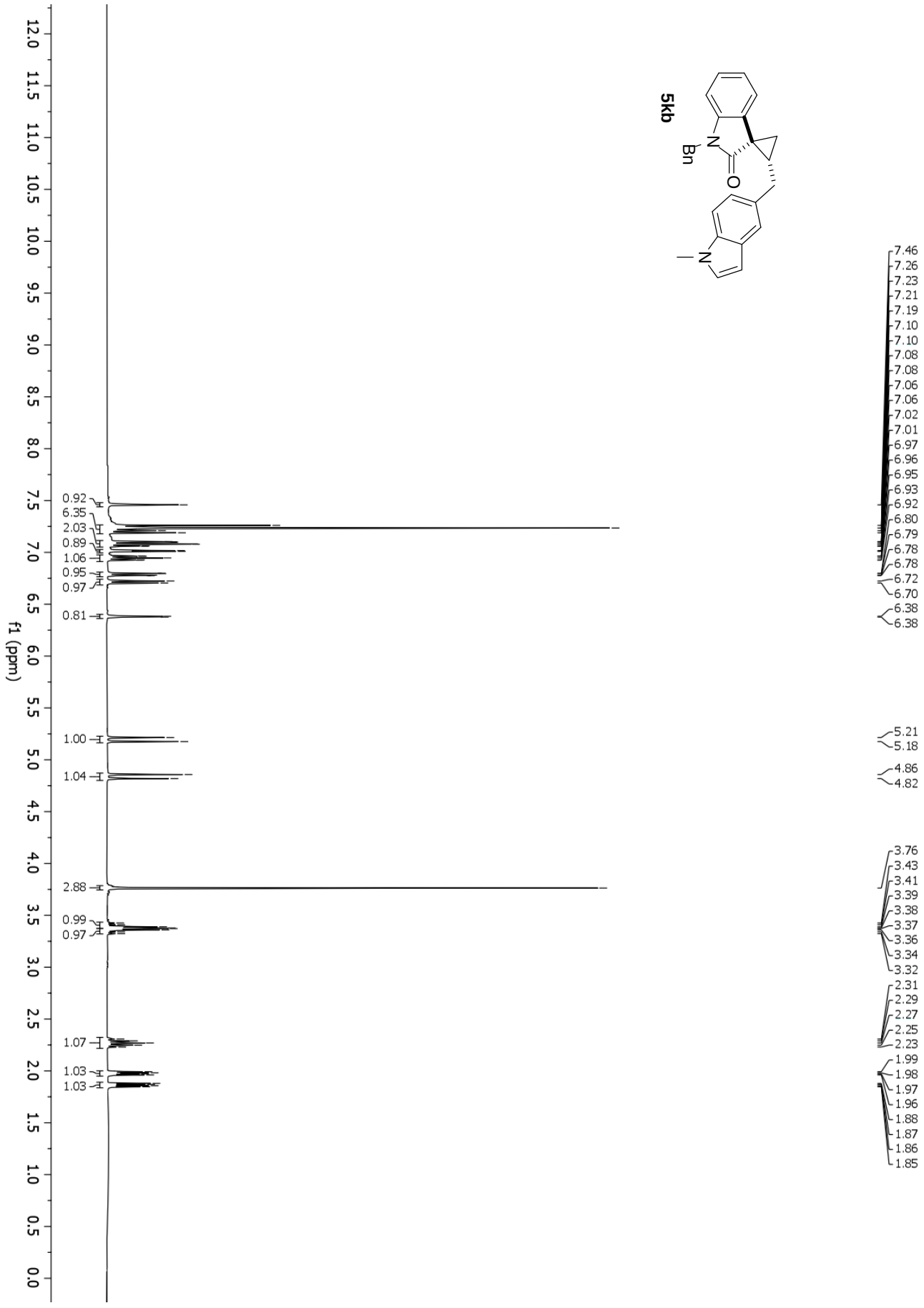
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ka**



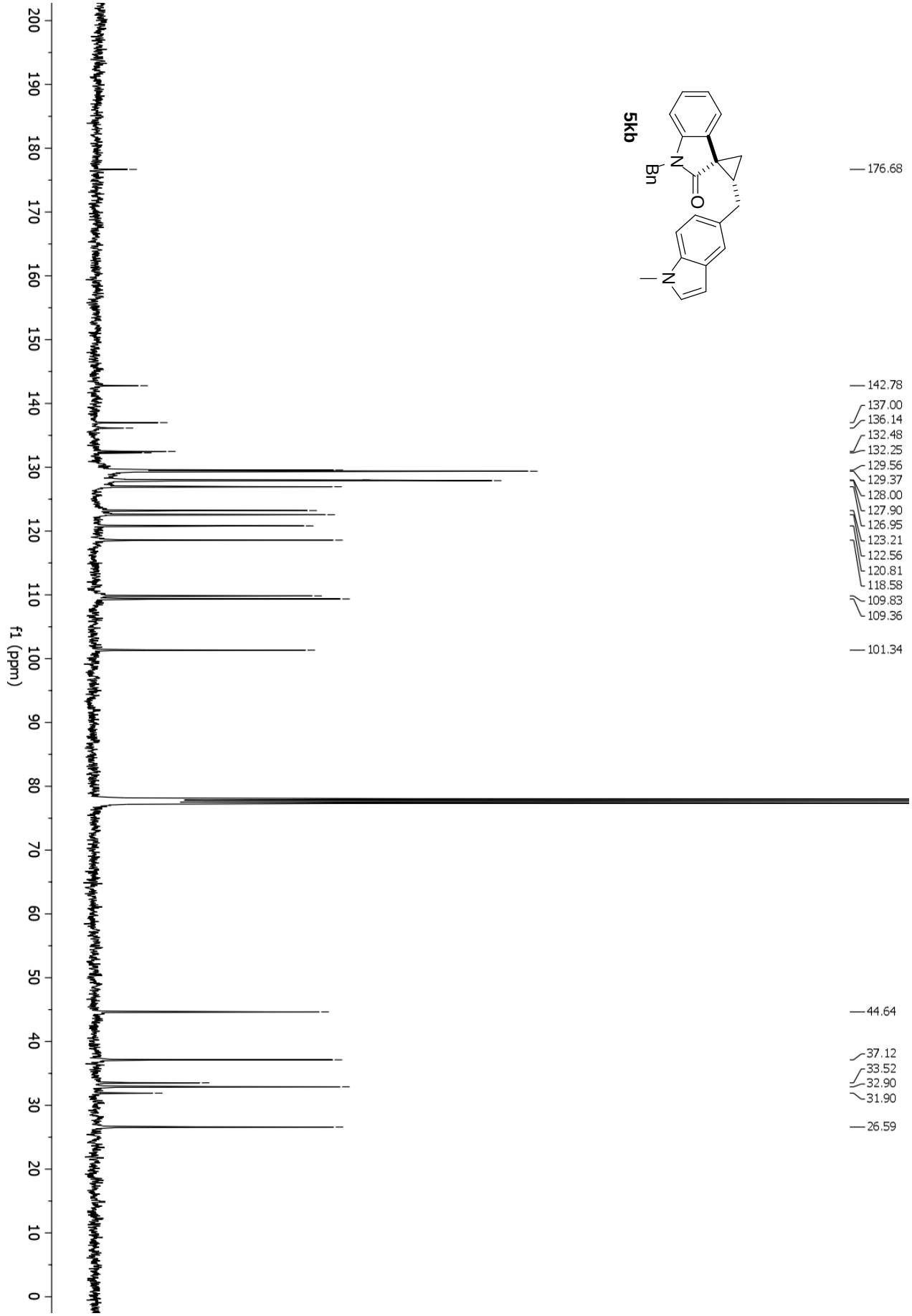
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ka**



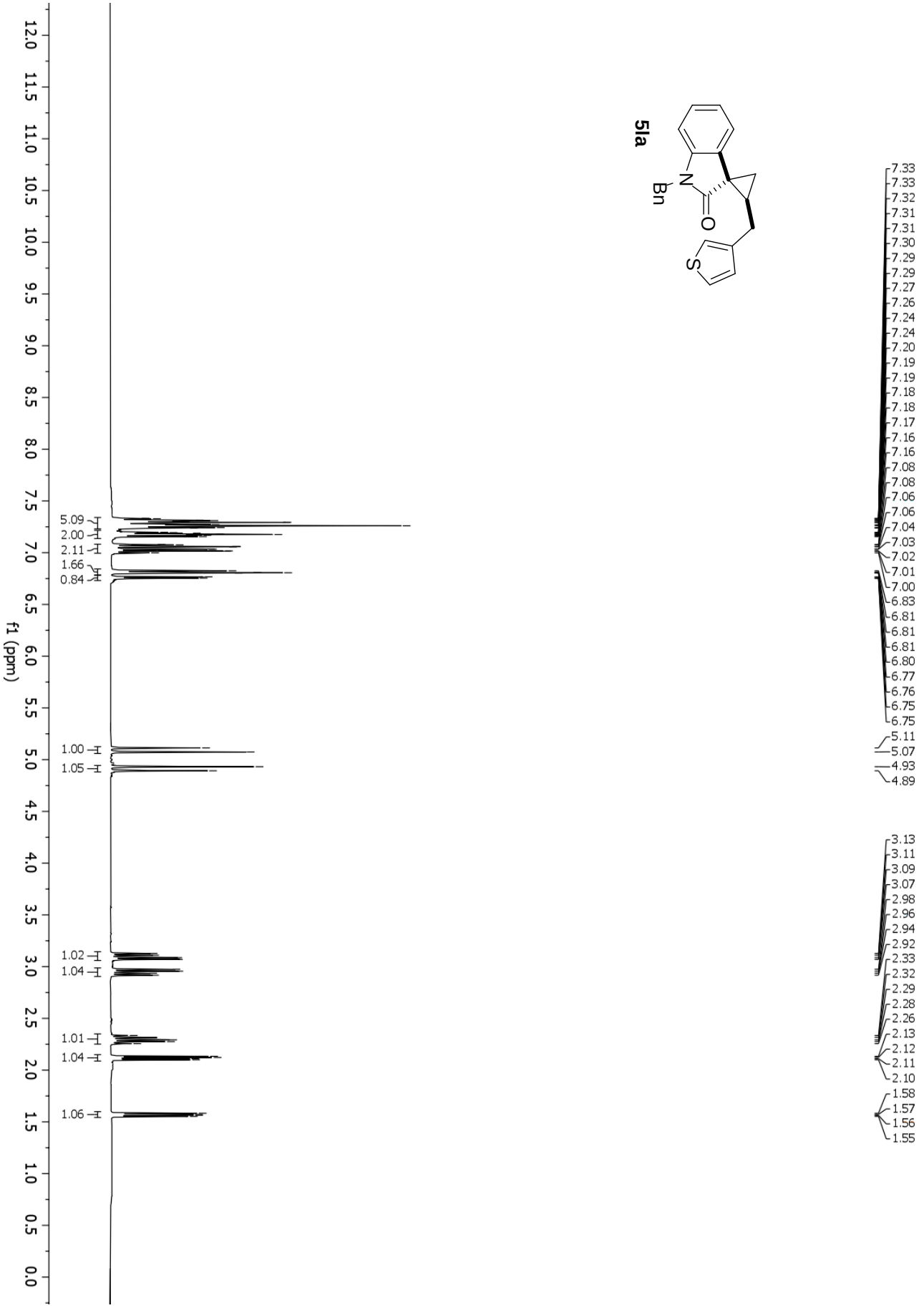
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5kb**



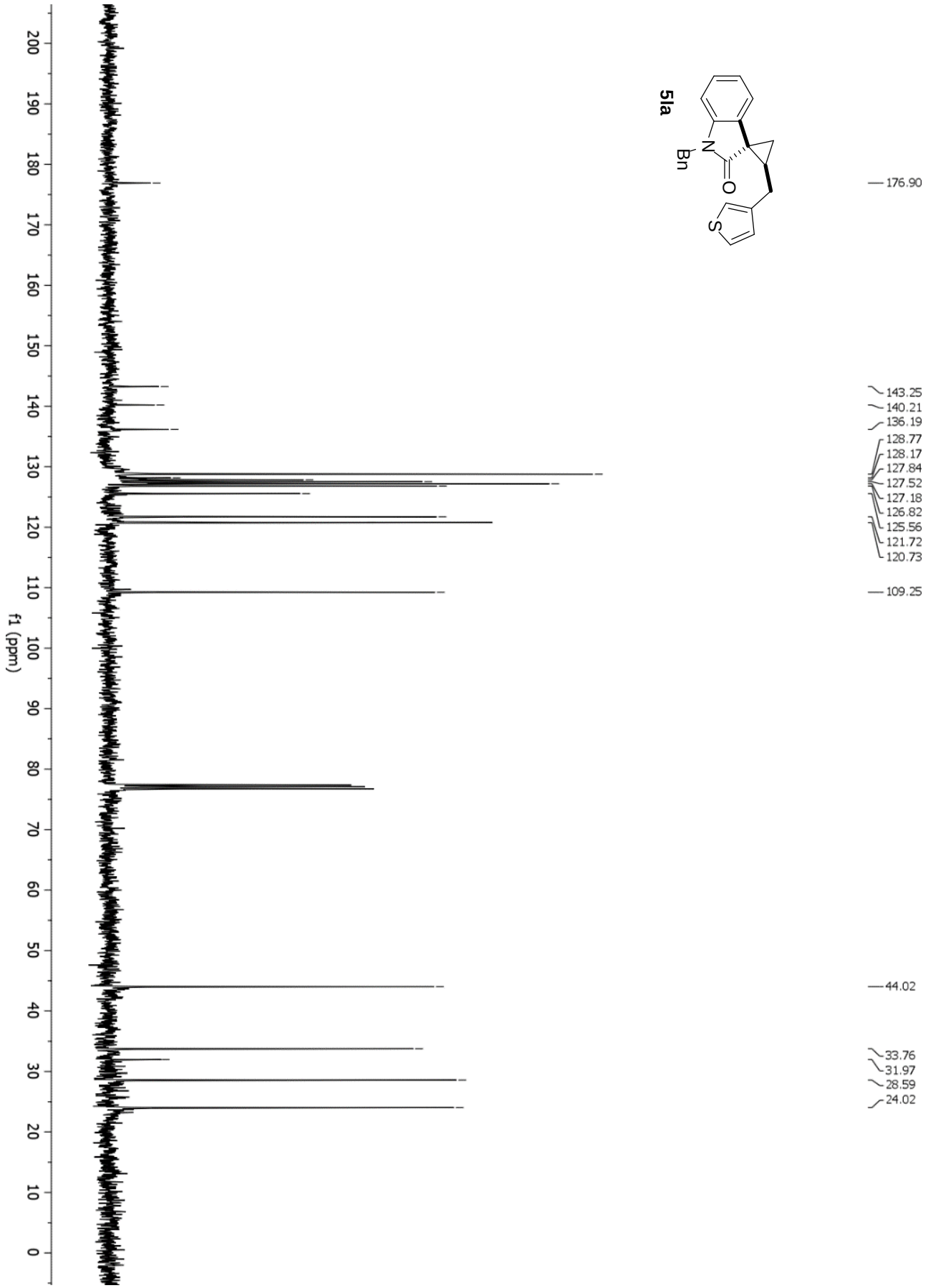
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5kb**



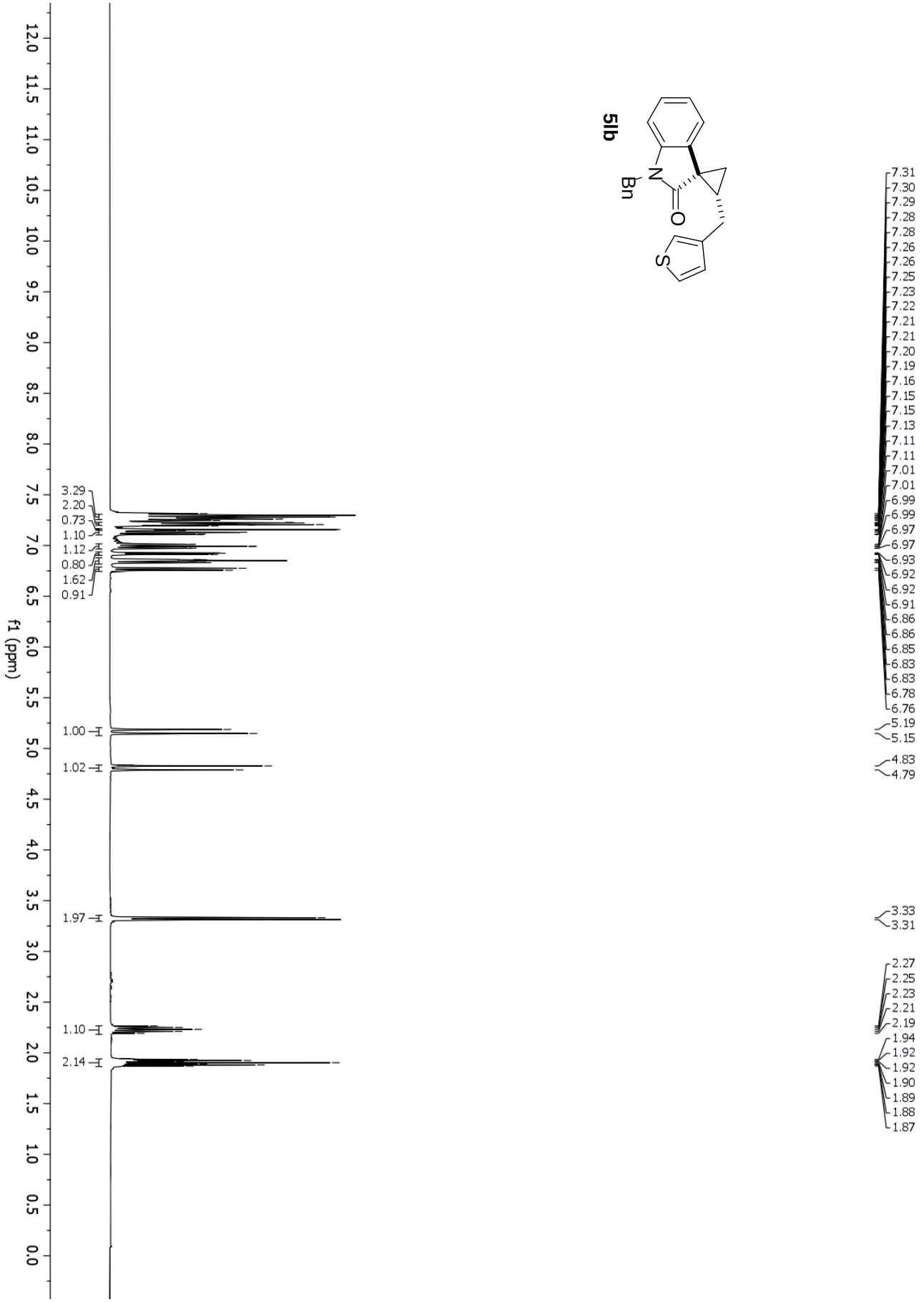
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5la**



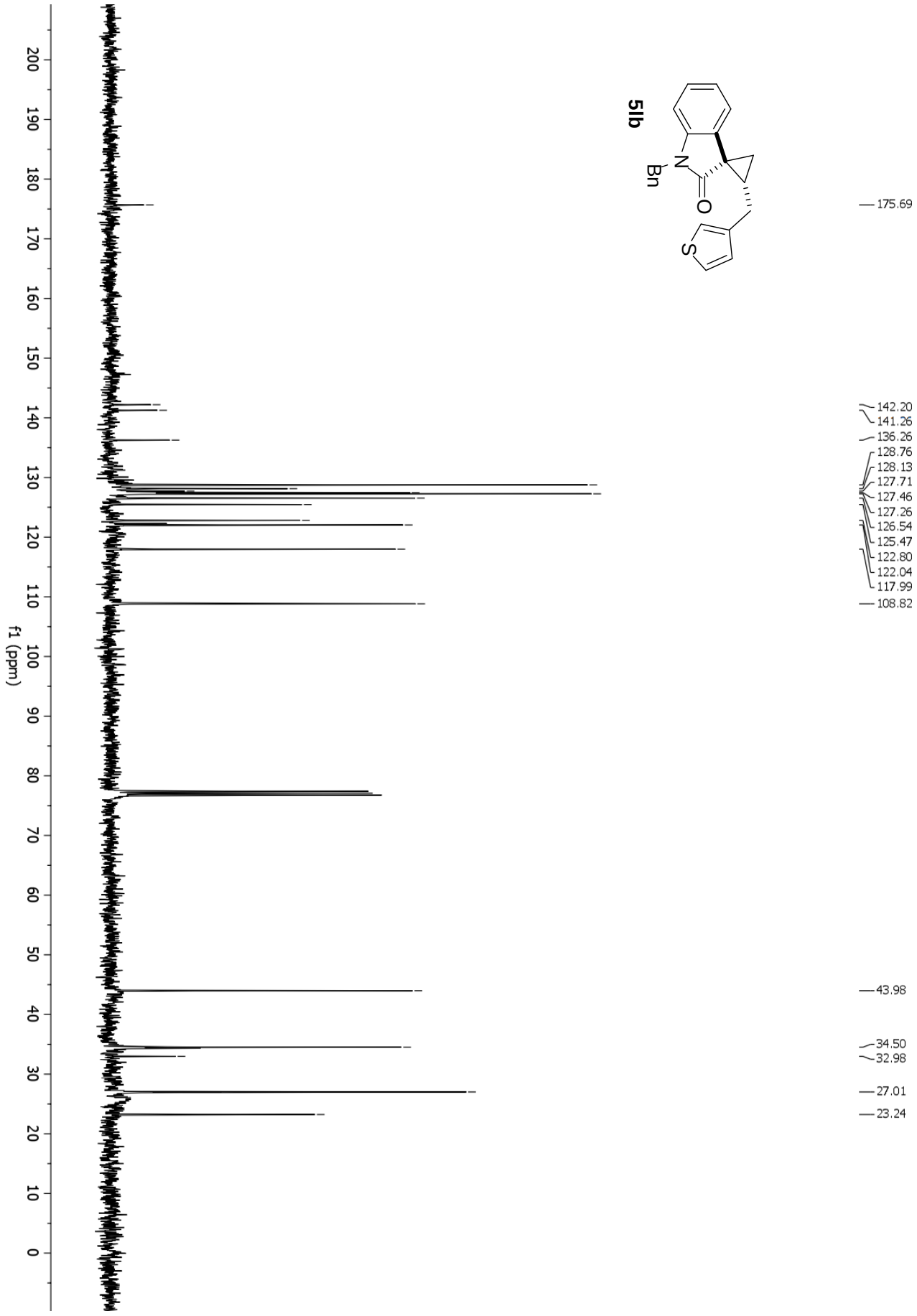
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5la**



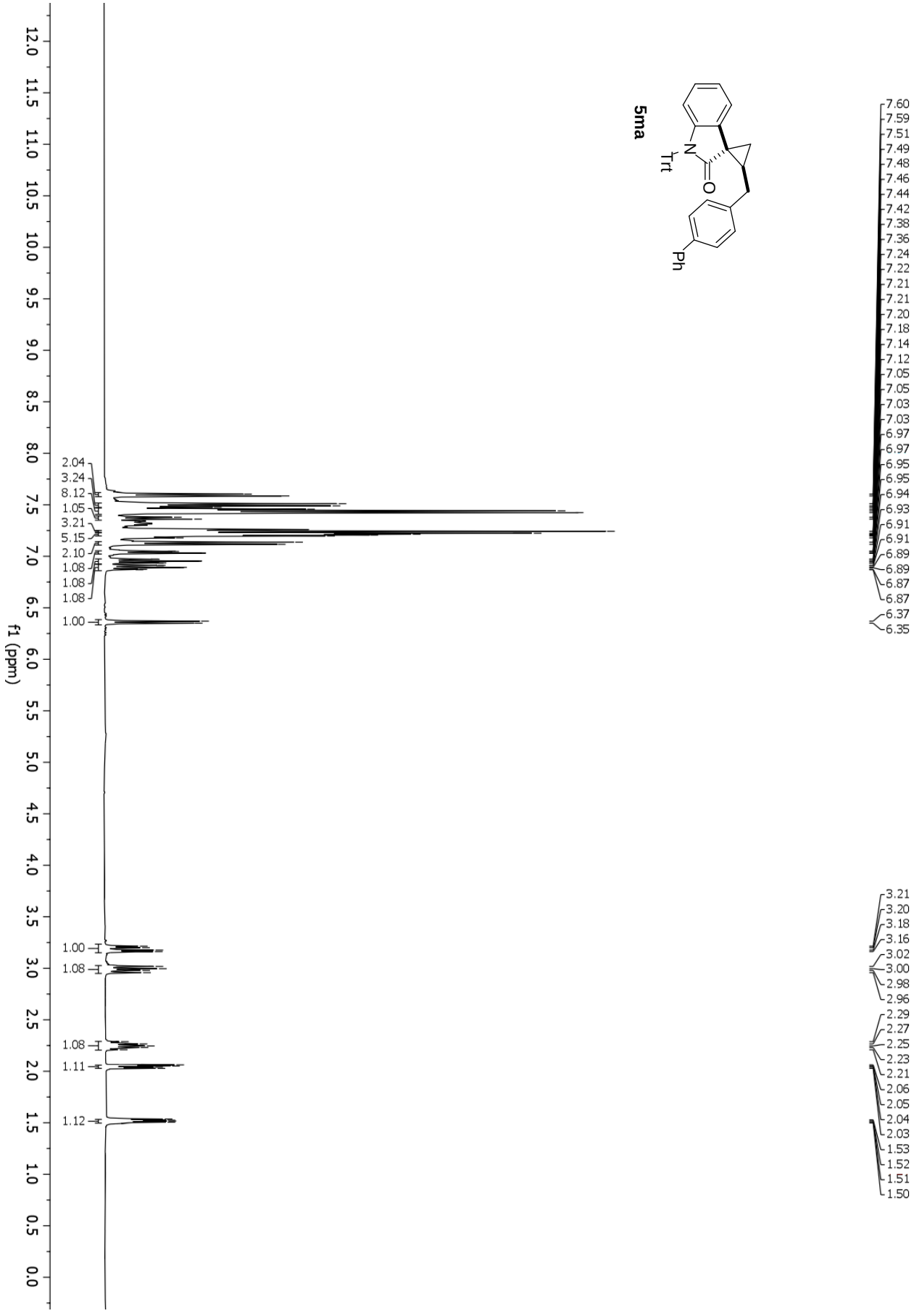
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5lb**



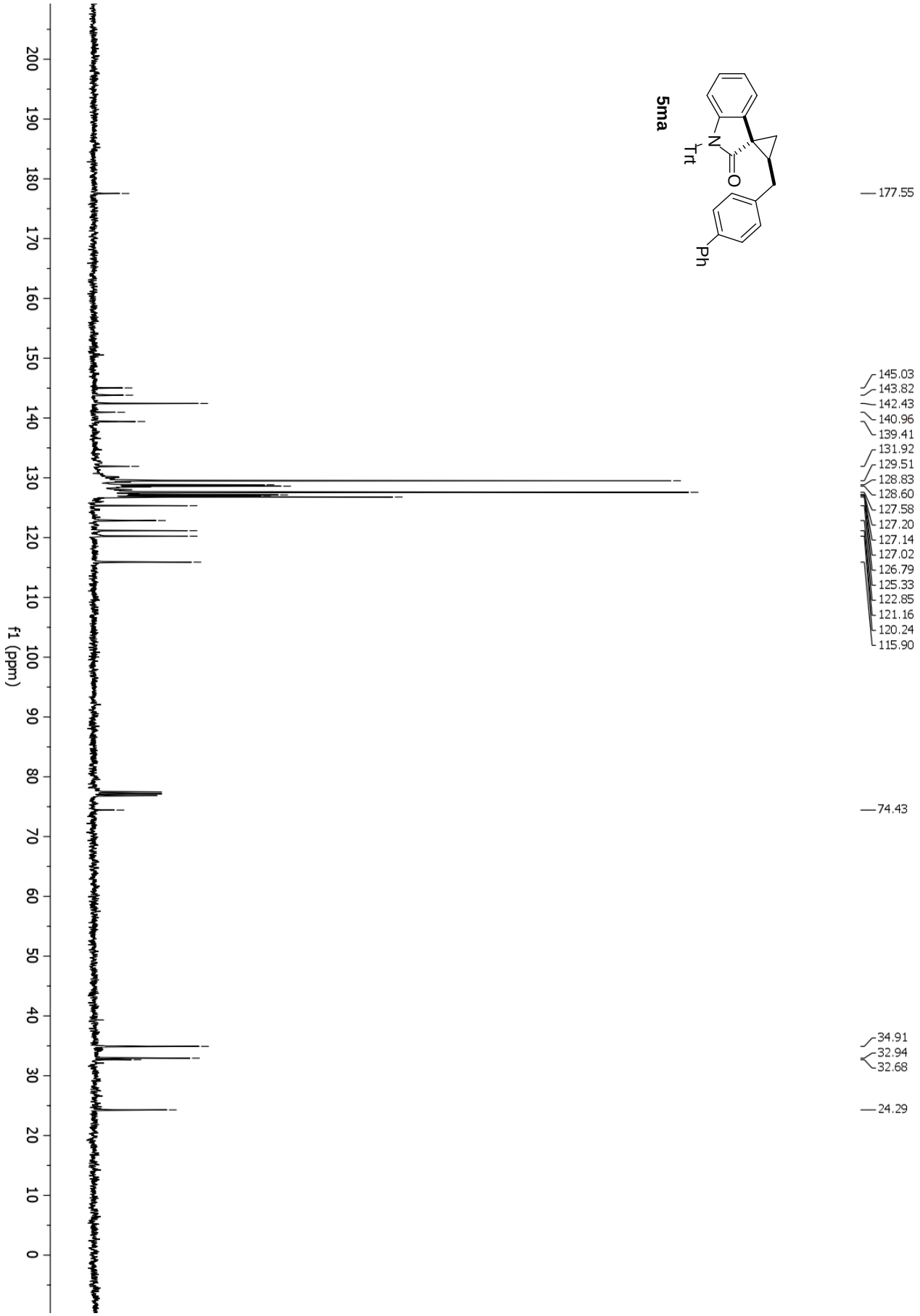
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5lb**



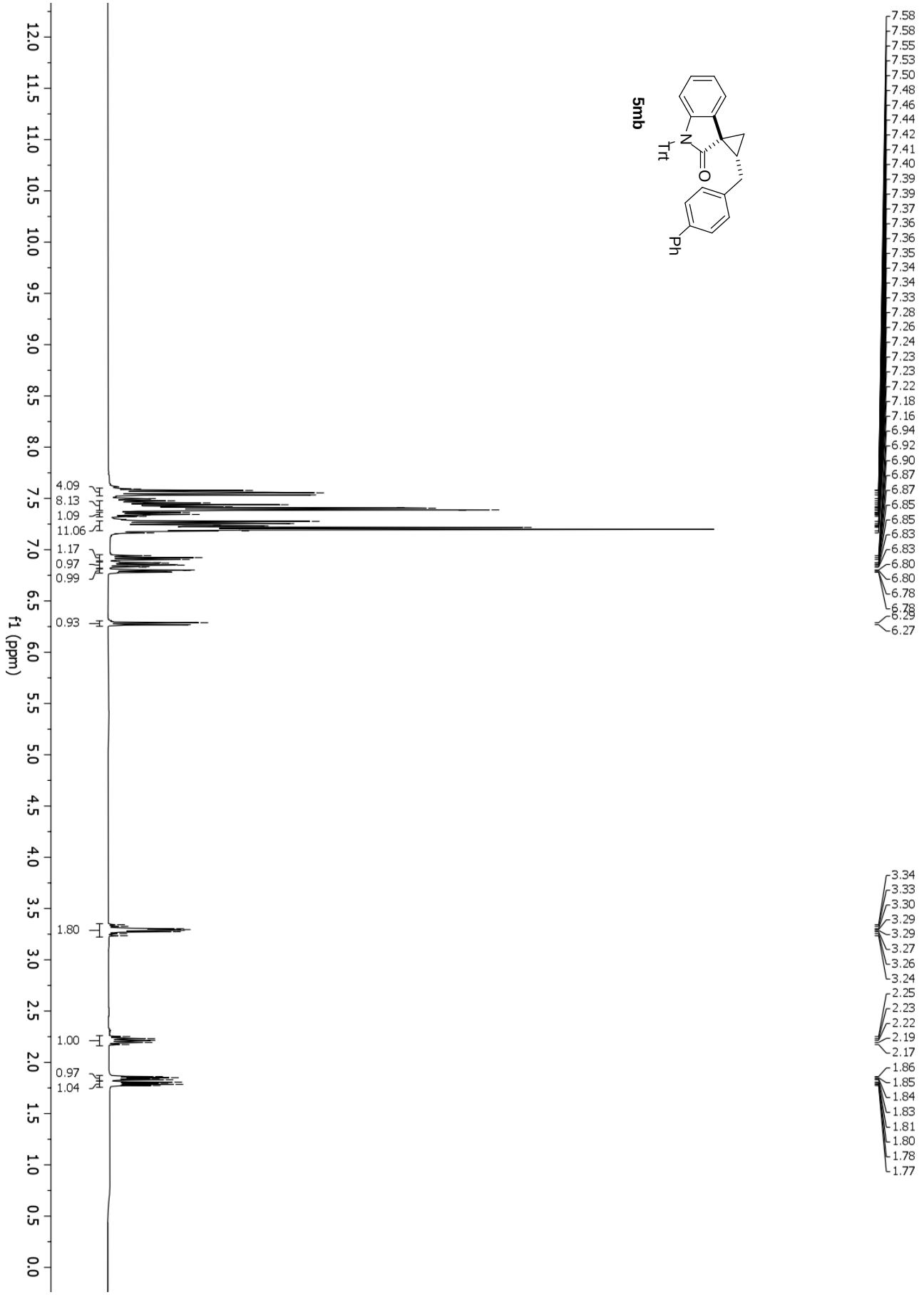
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ma**



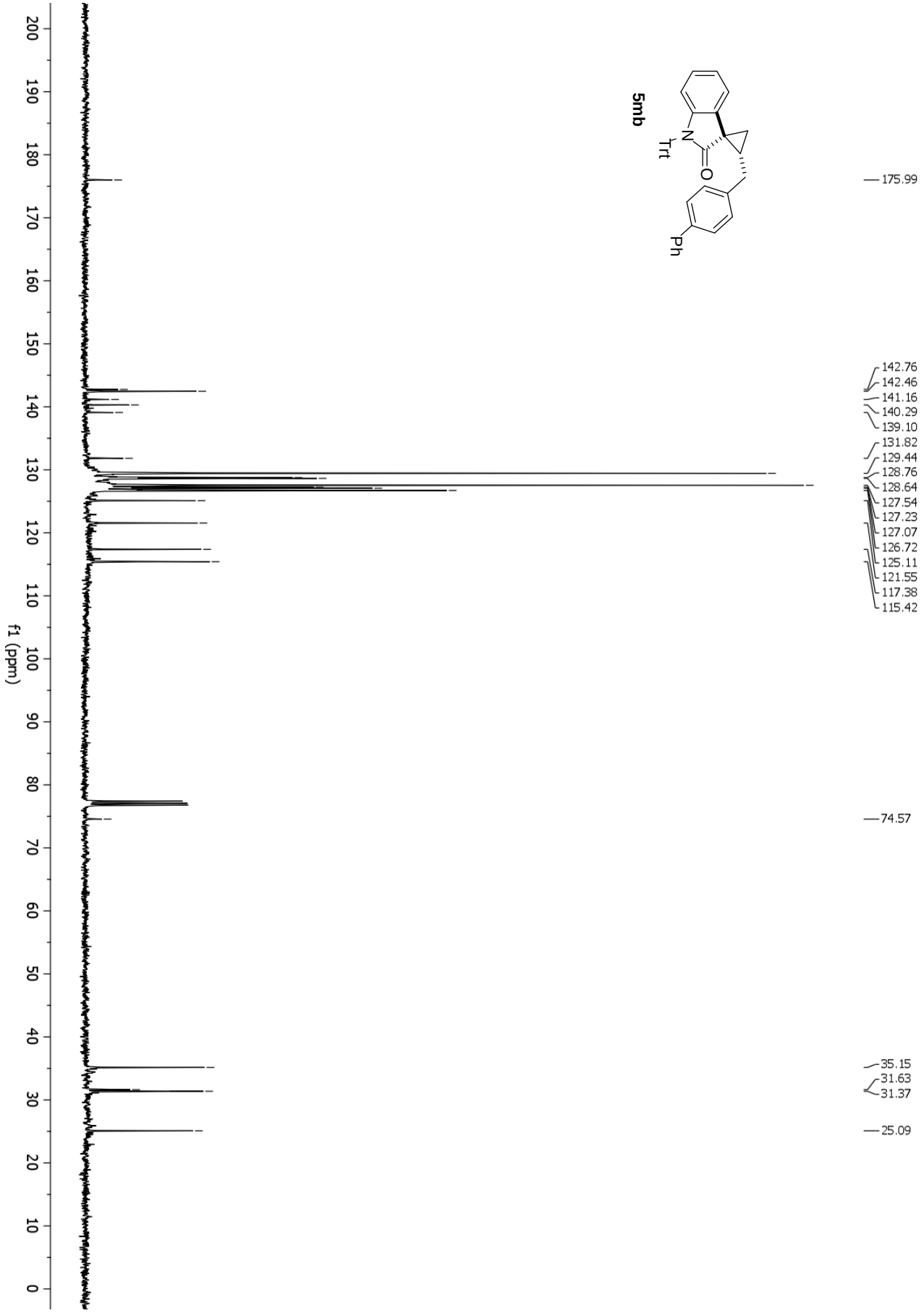
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ma**



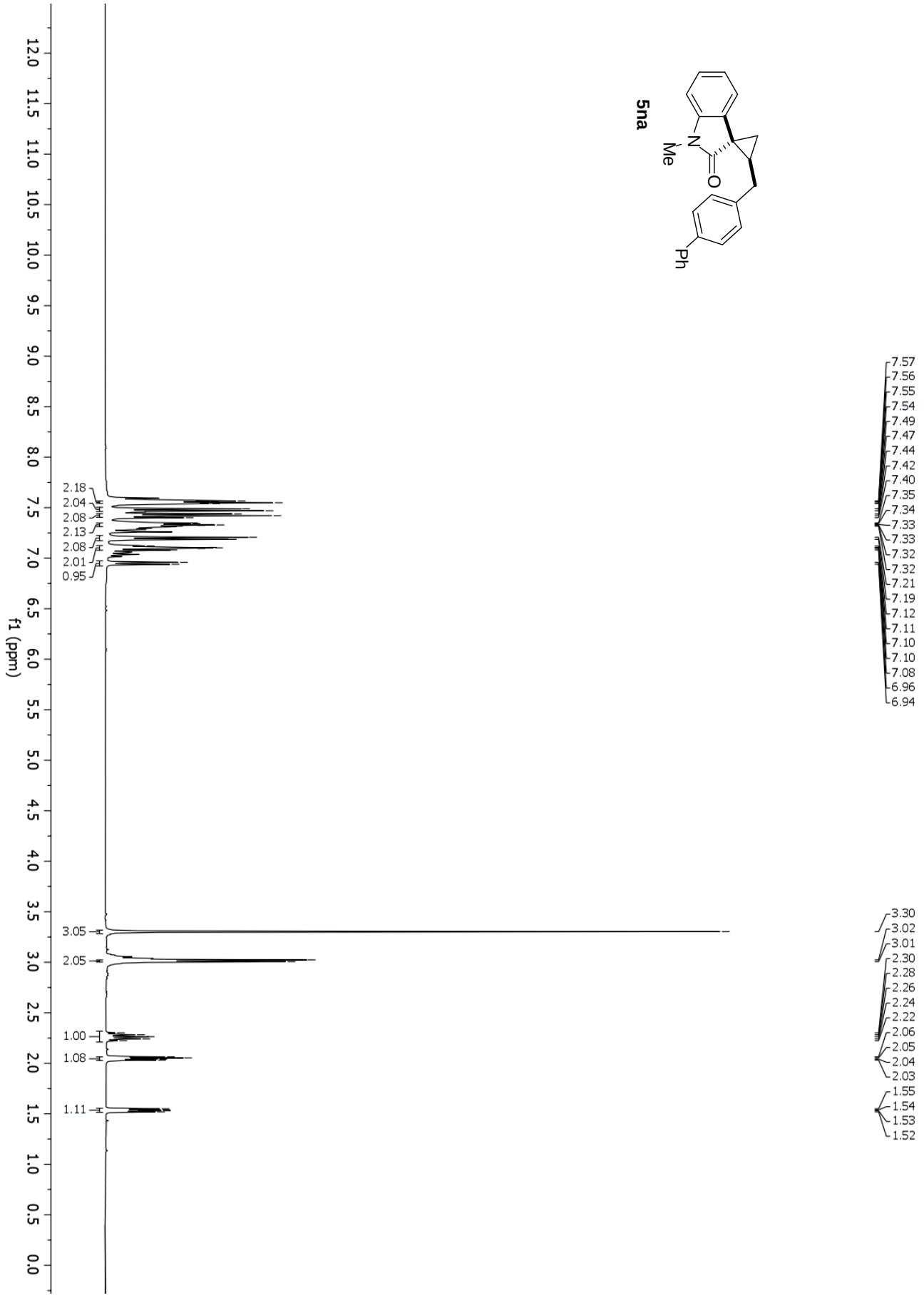
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5mb**



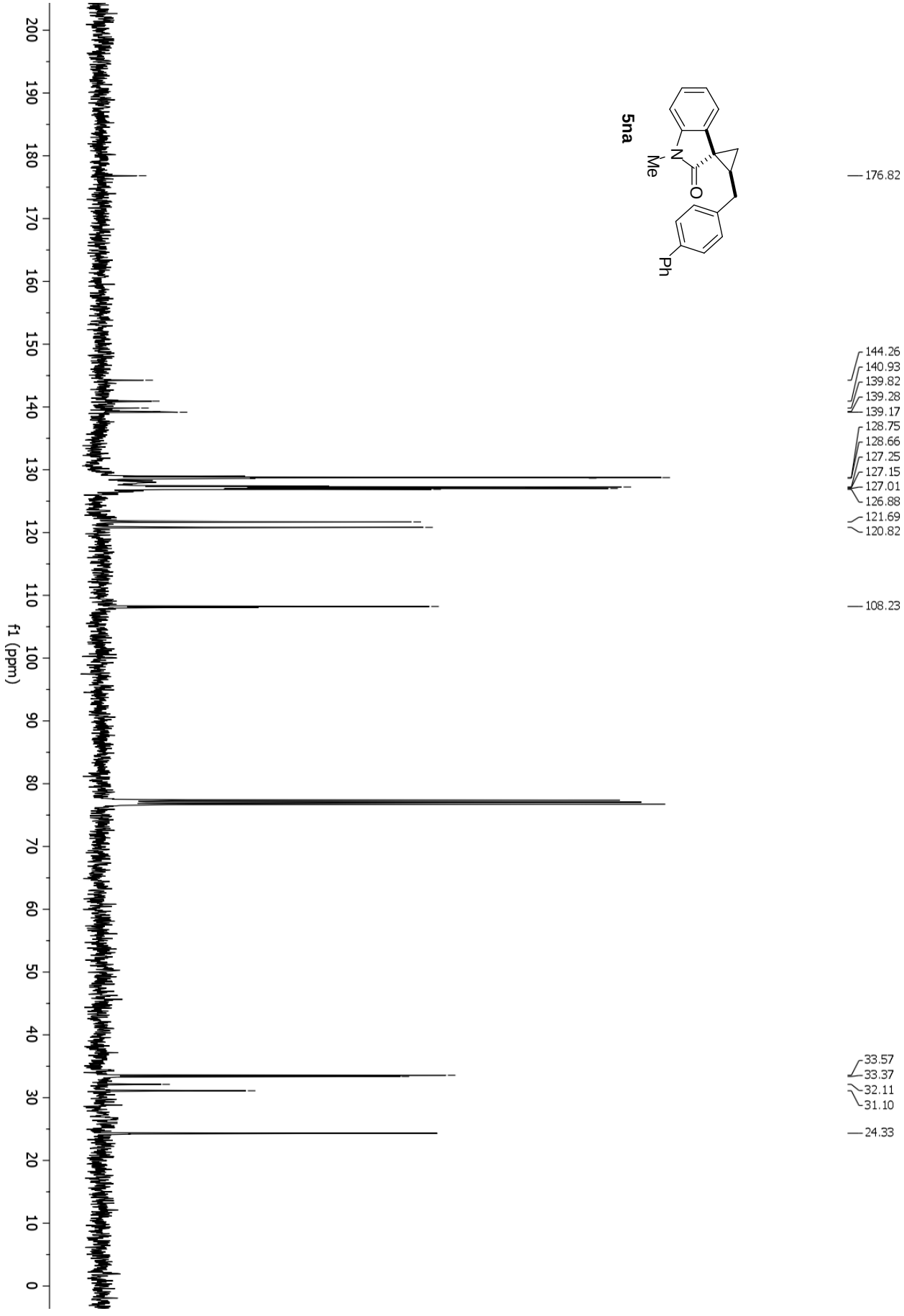
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5mb**



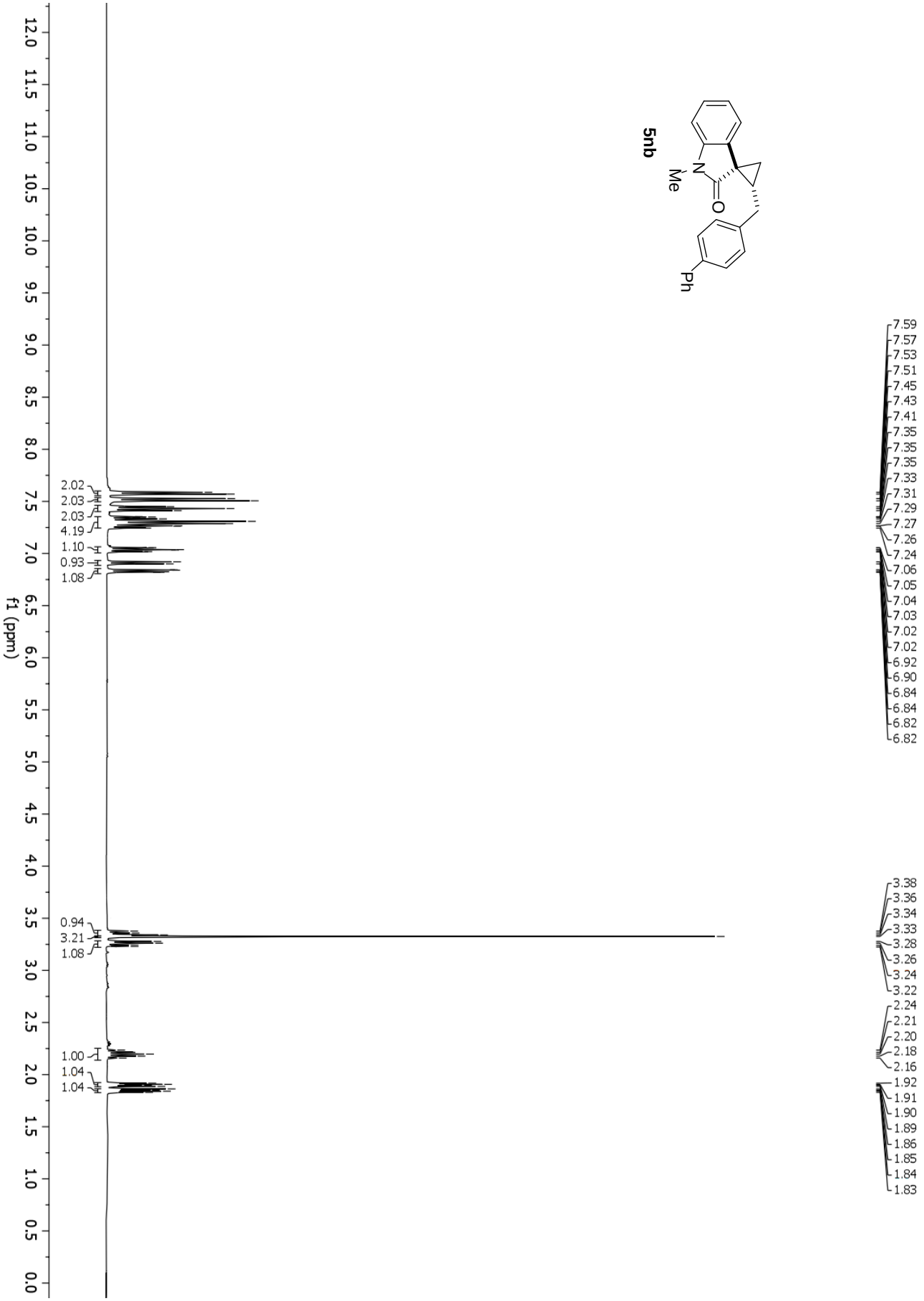
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5na**



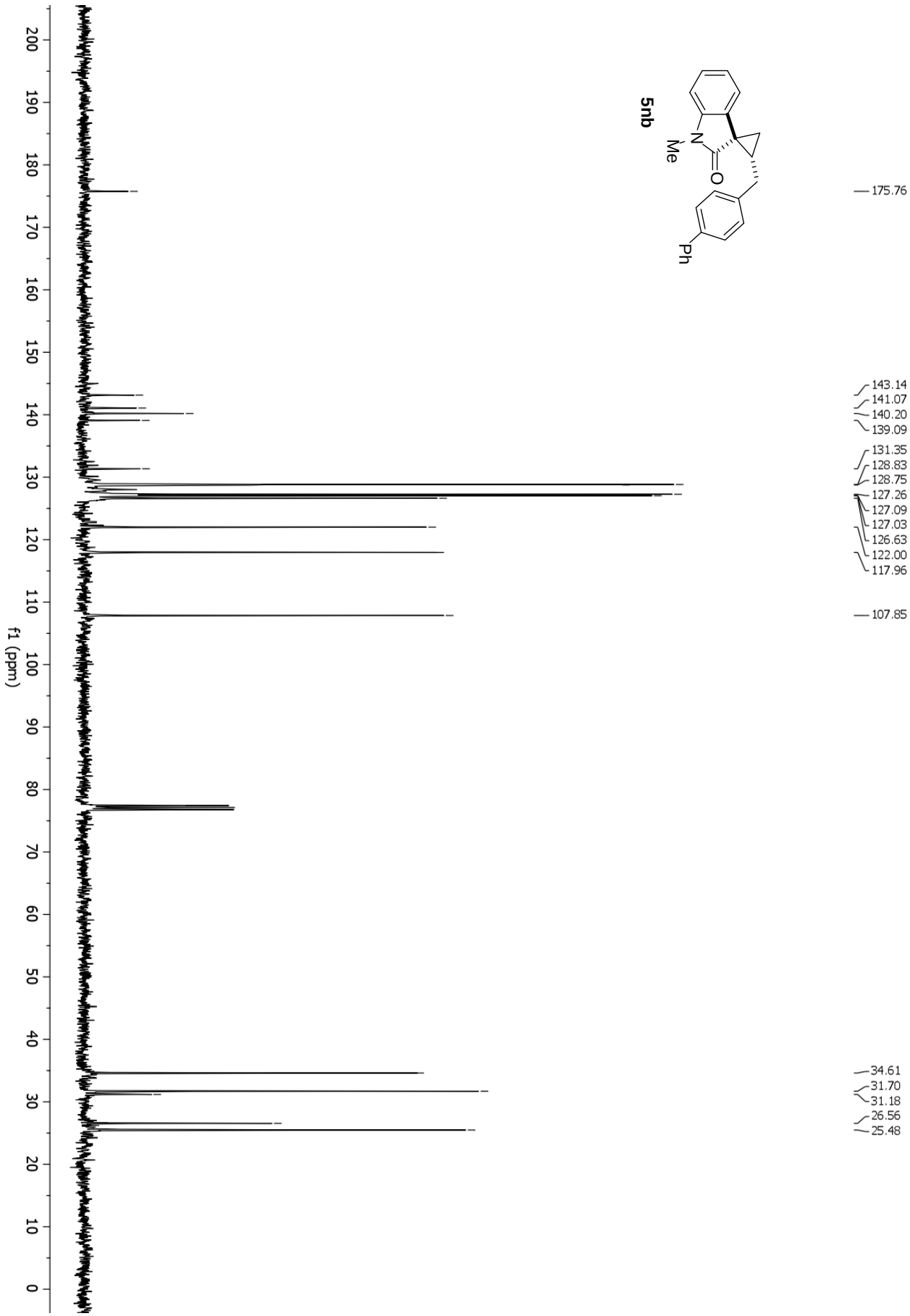
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5na**



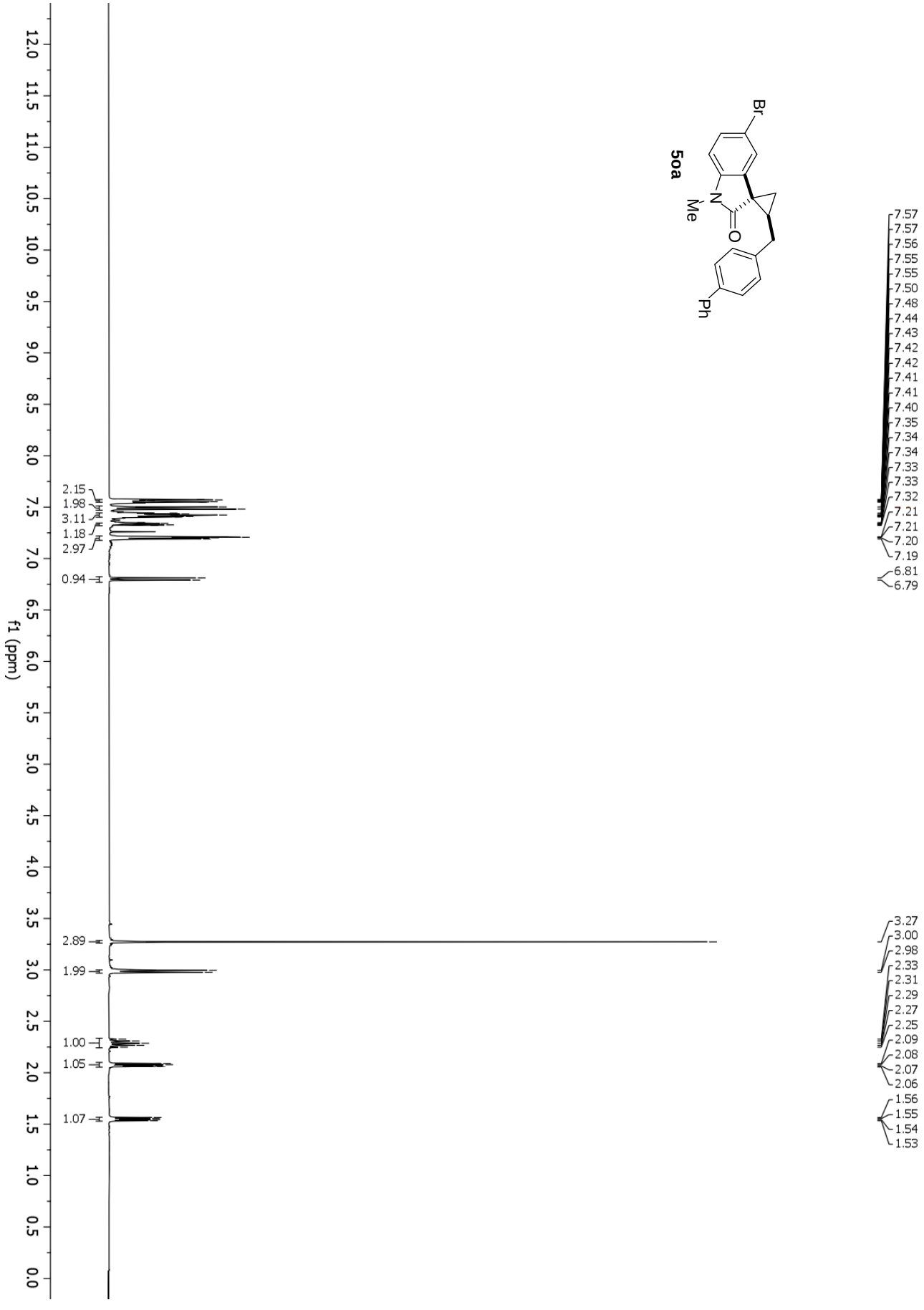
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5nb**



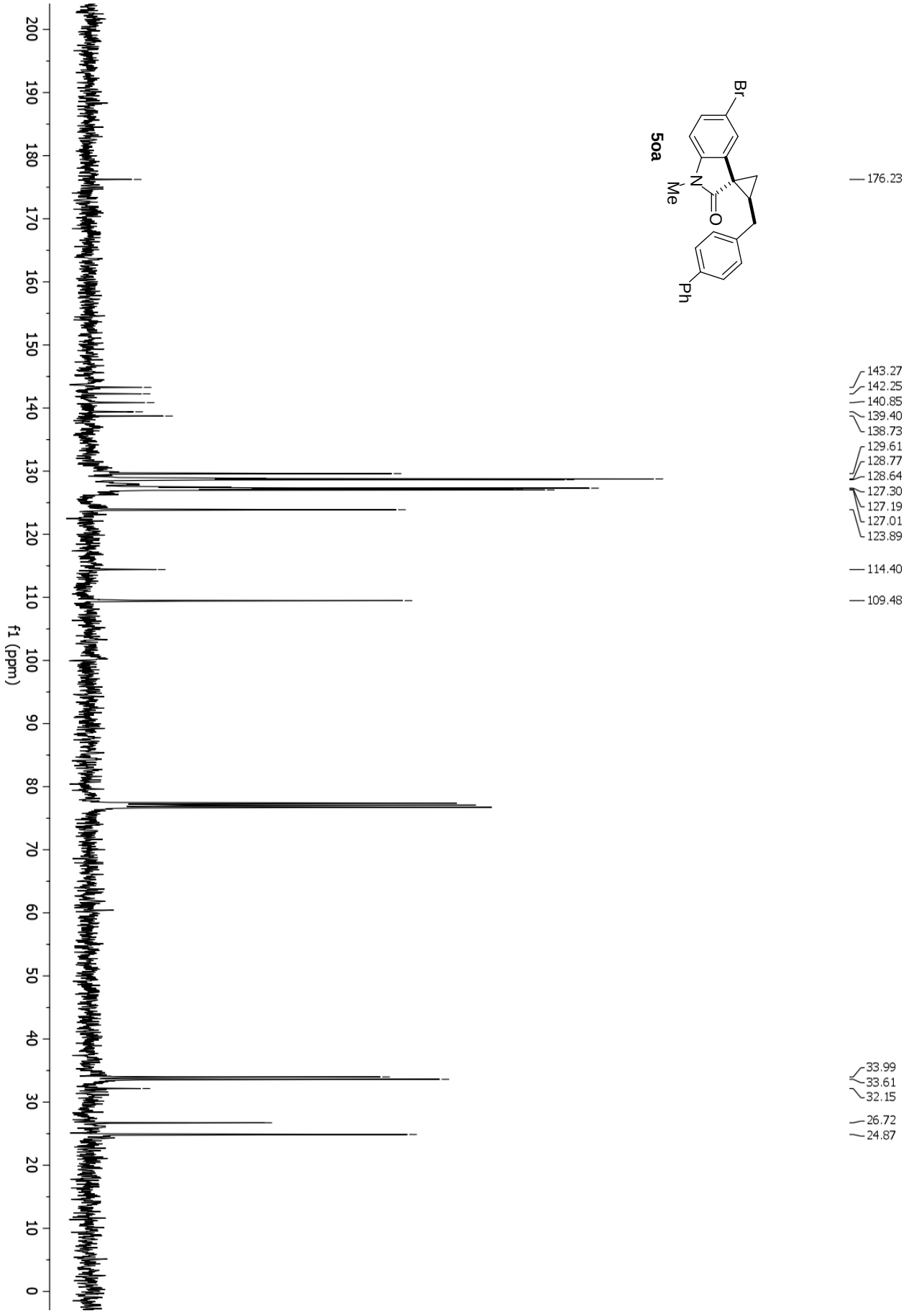
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5nb**



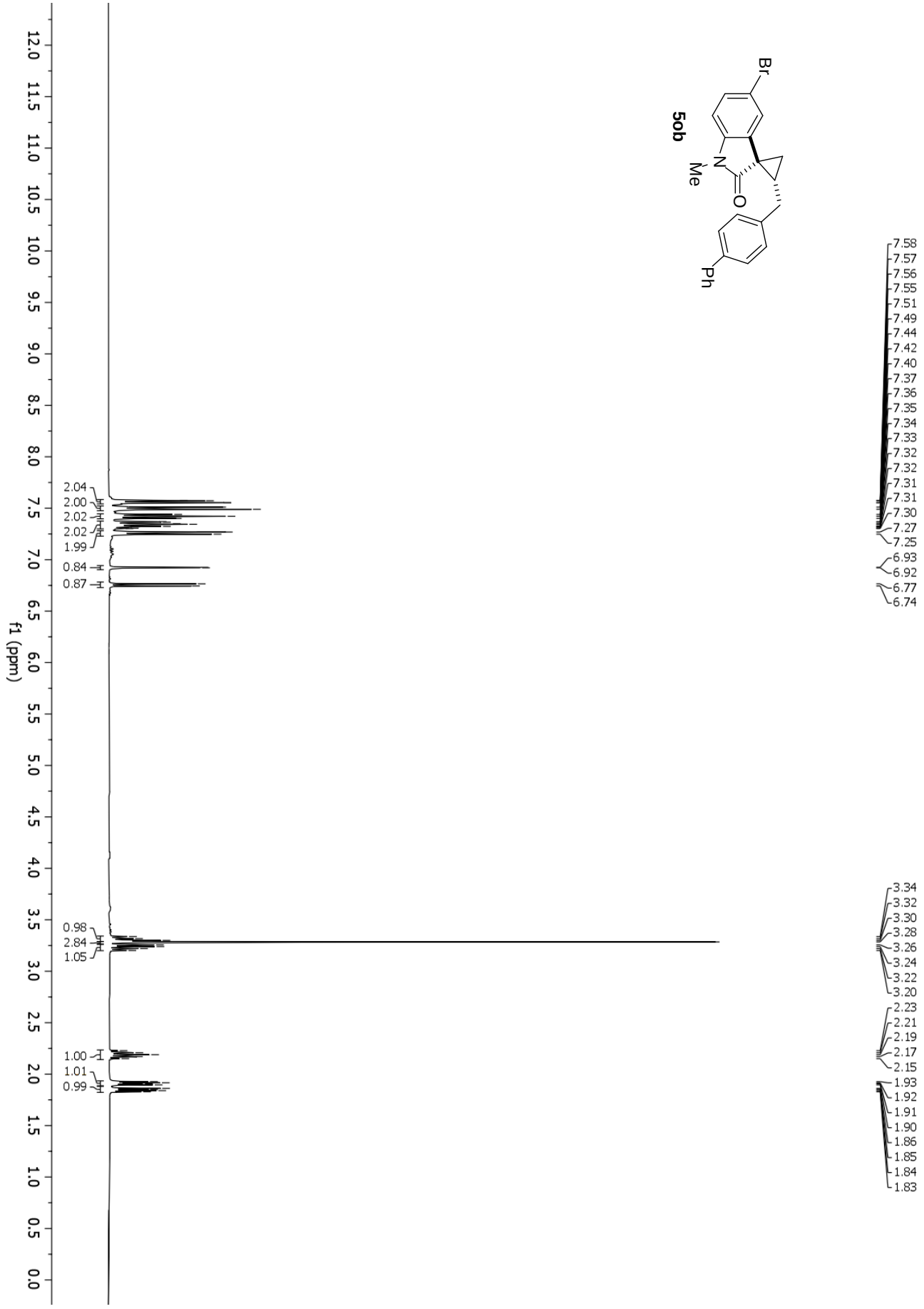
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5oa**



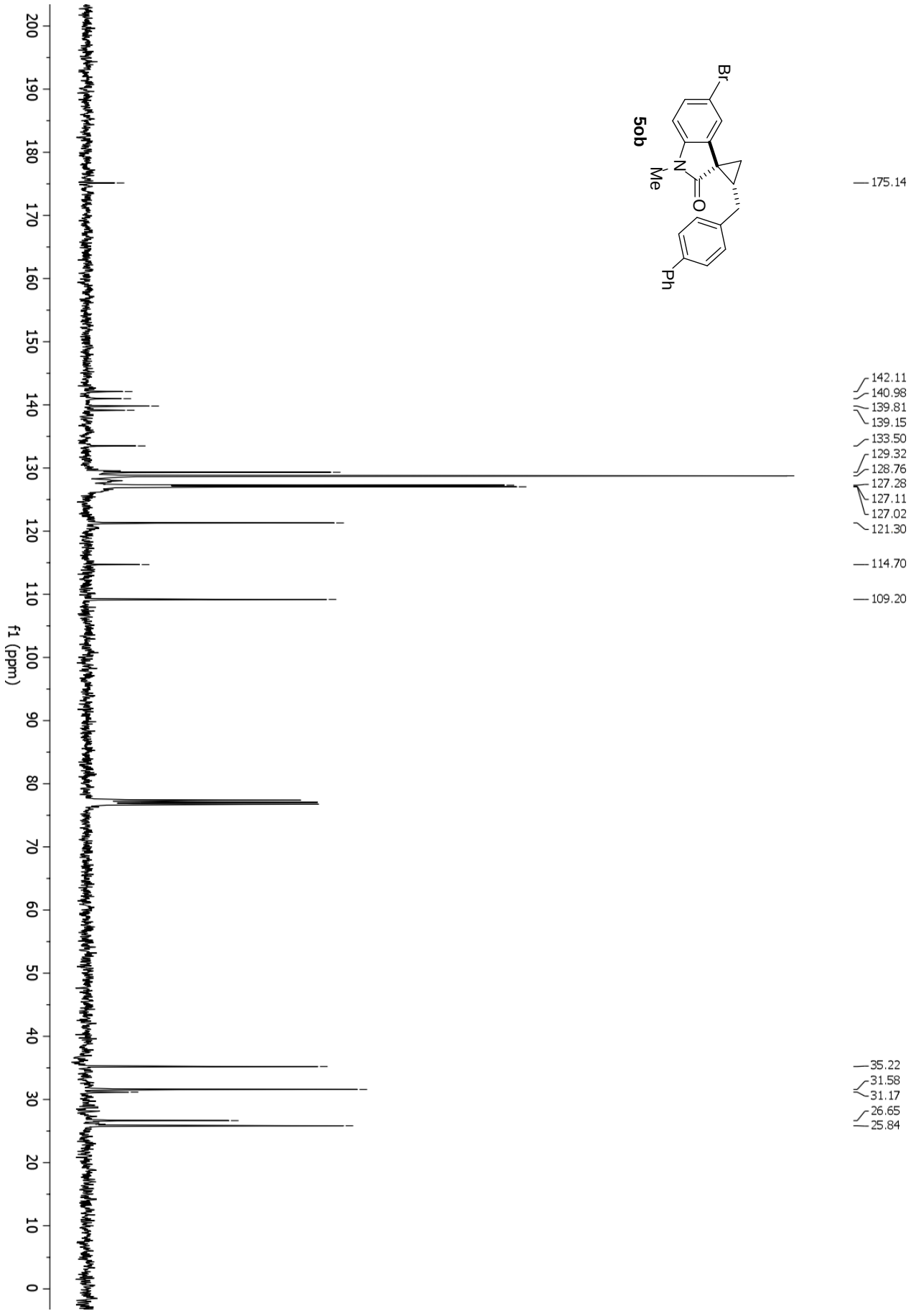
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5oa**



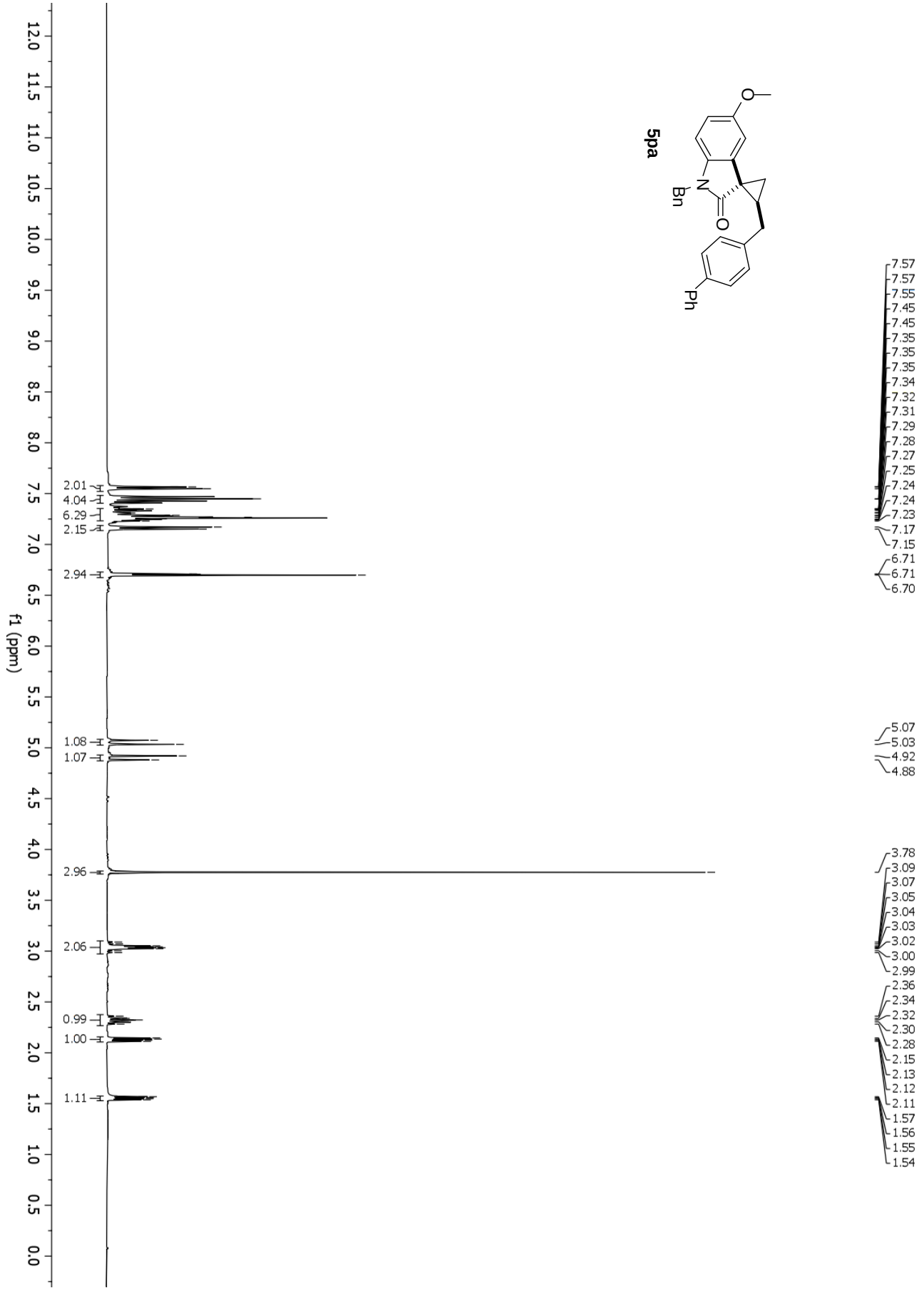
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5ob**



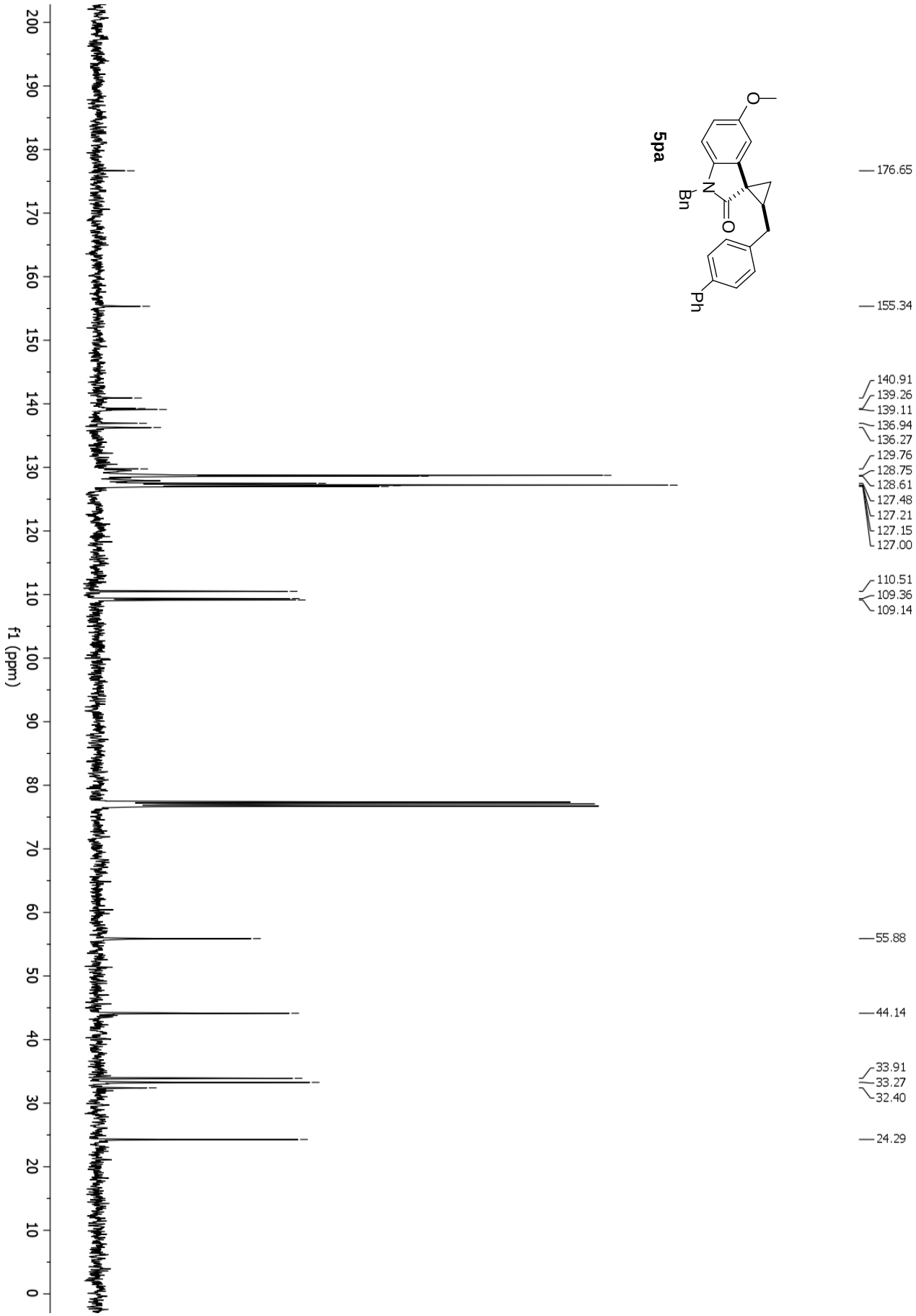
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ob**



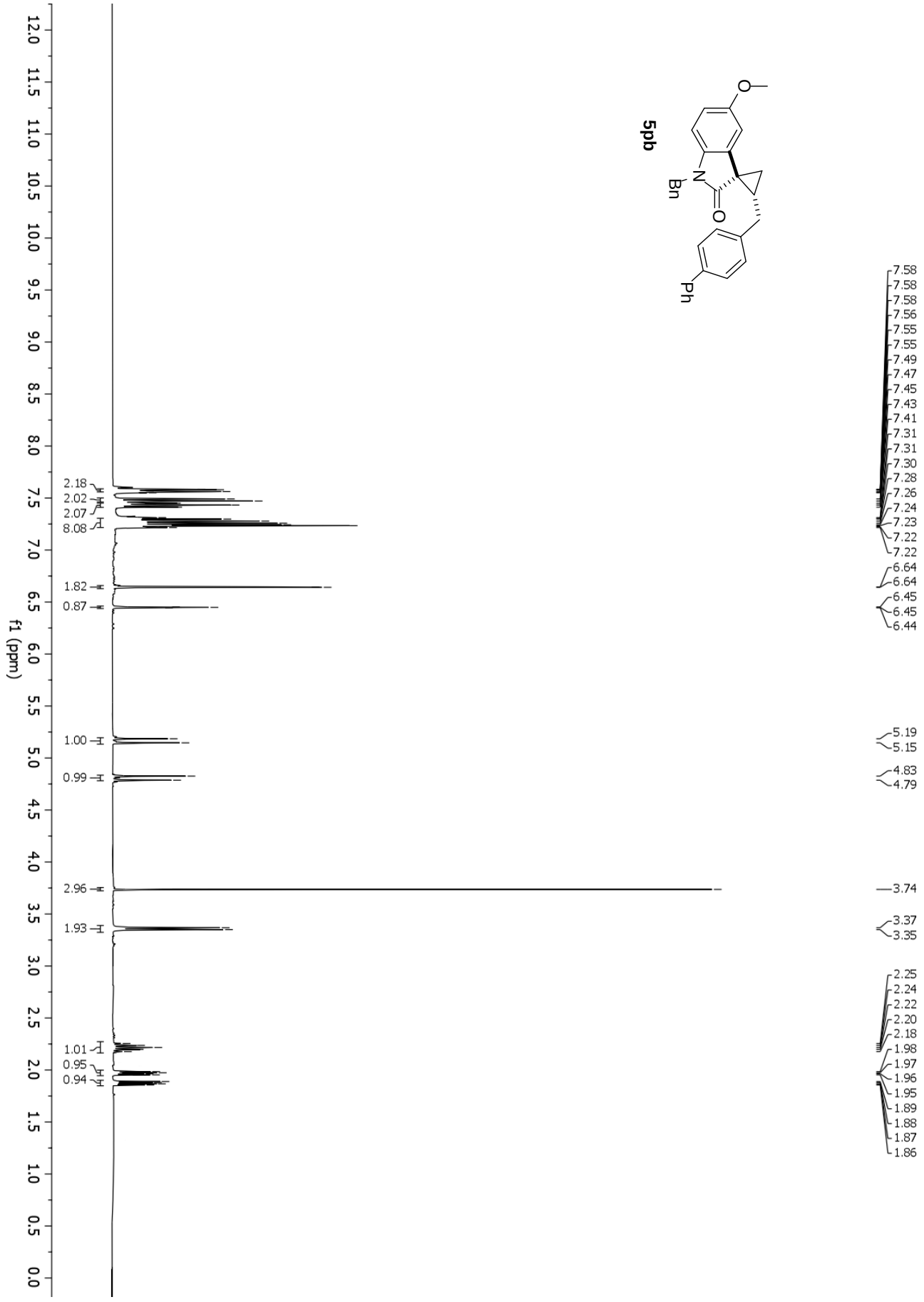
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5pa**



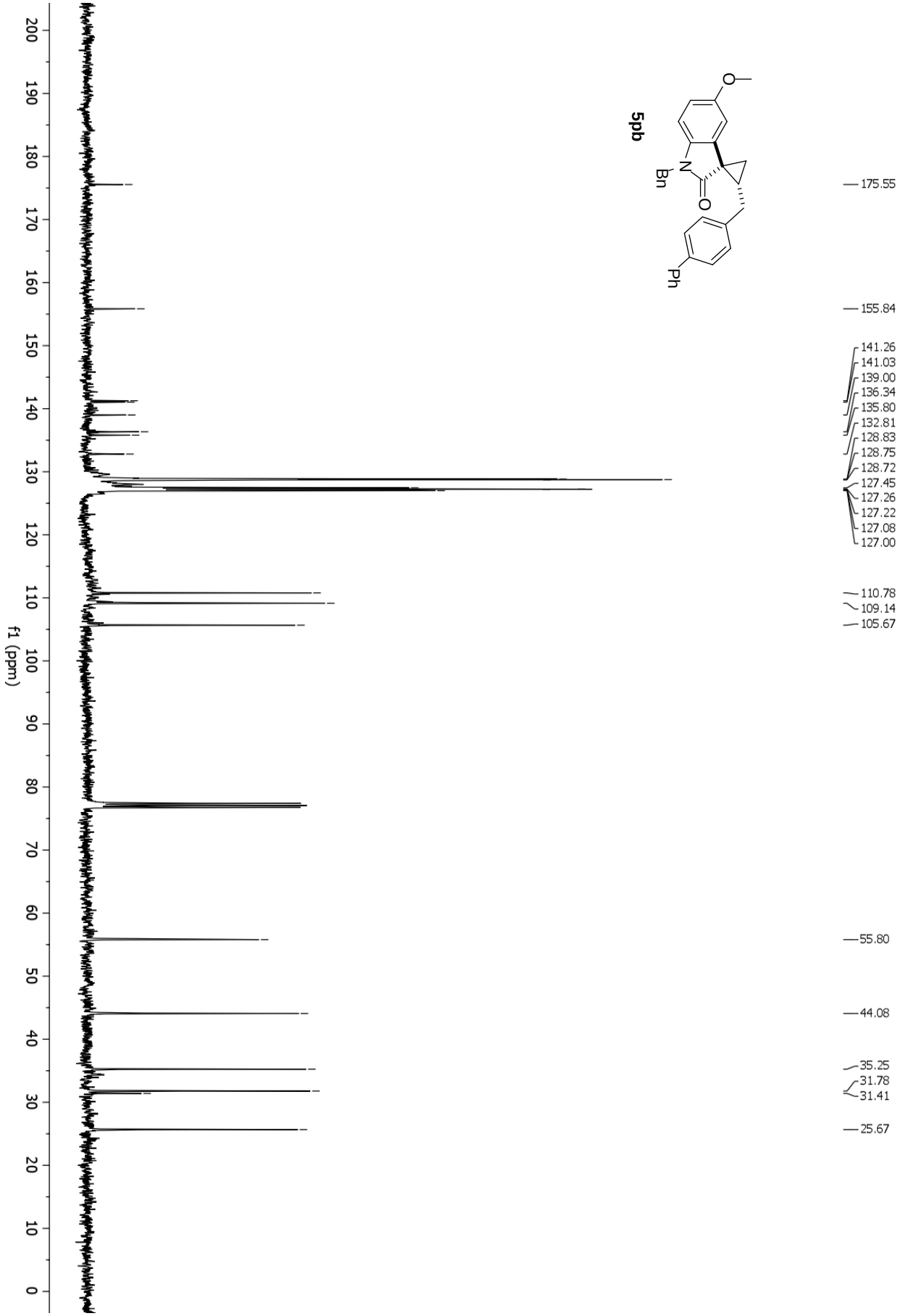
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5pa**



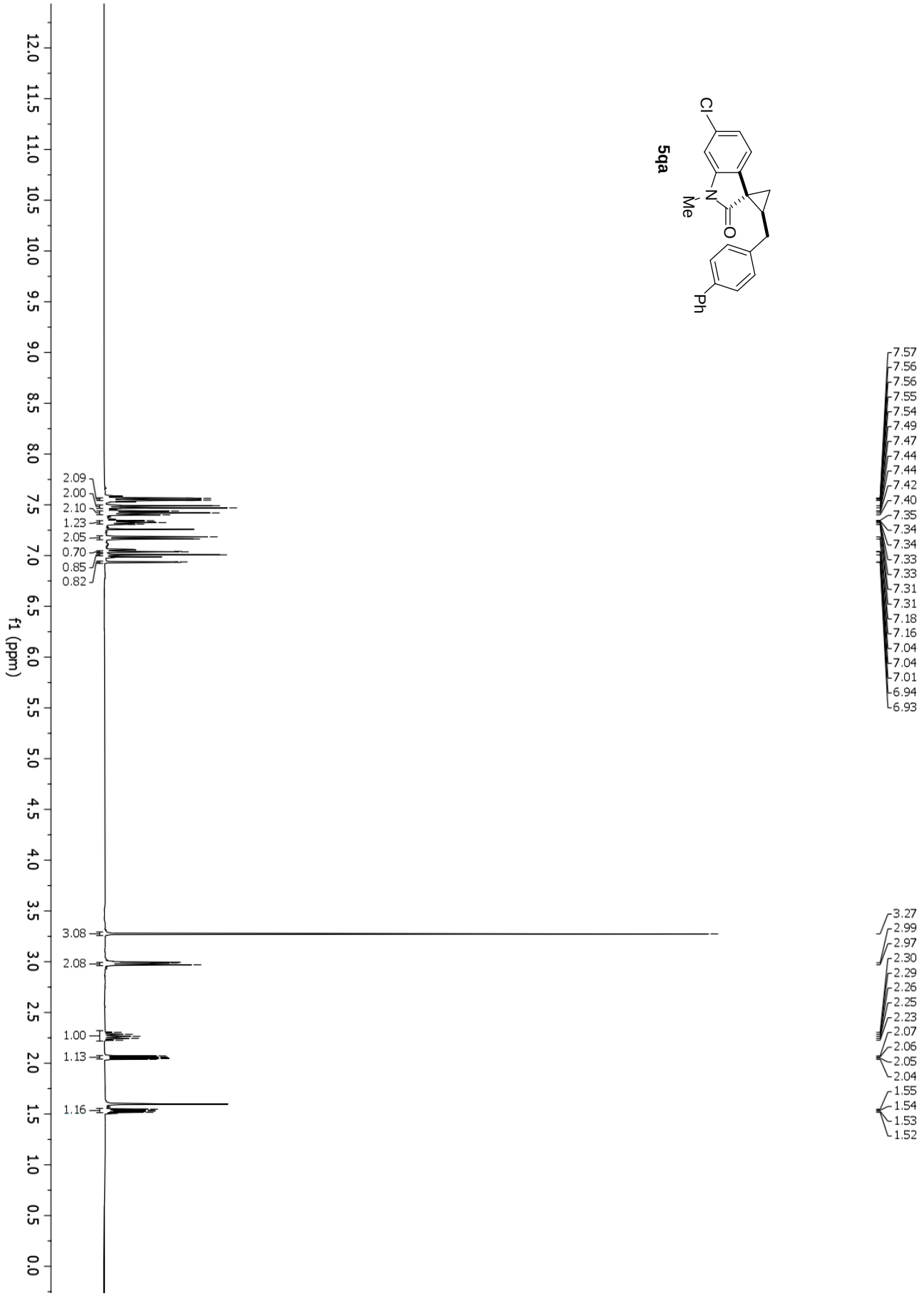
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5pb**



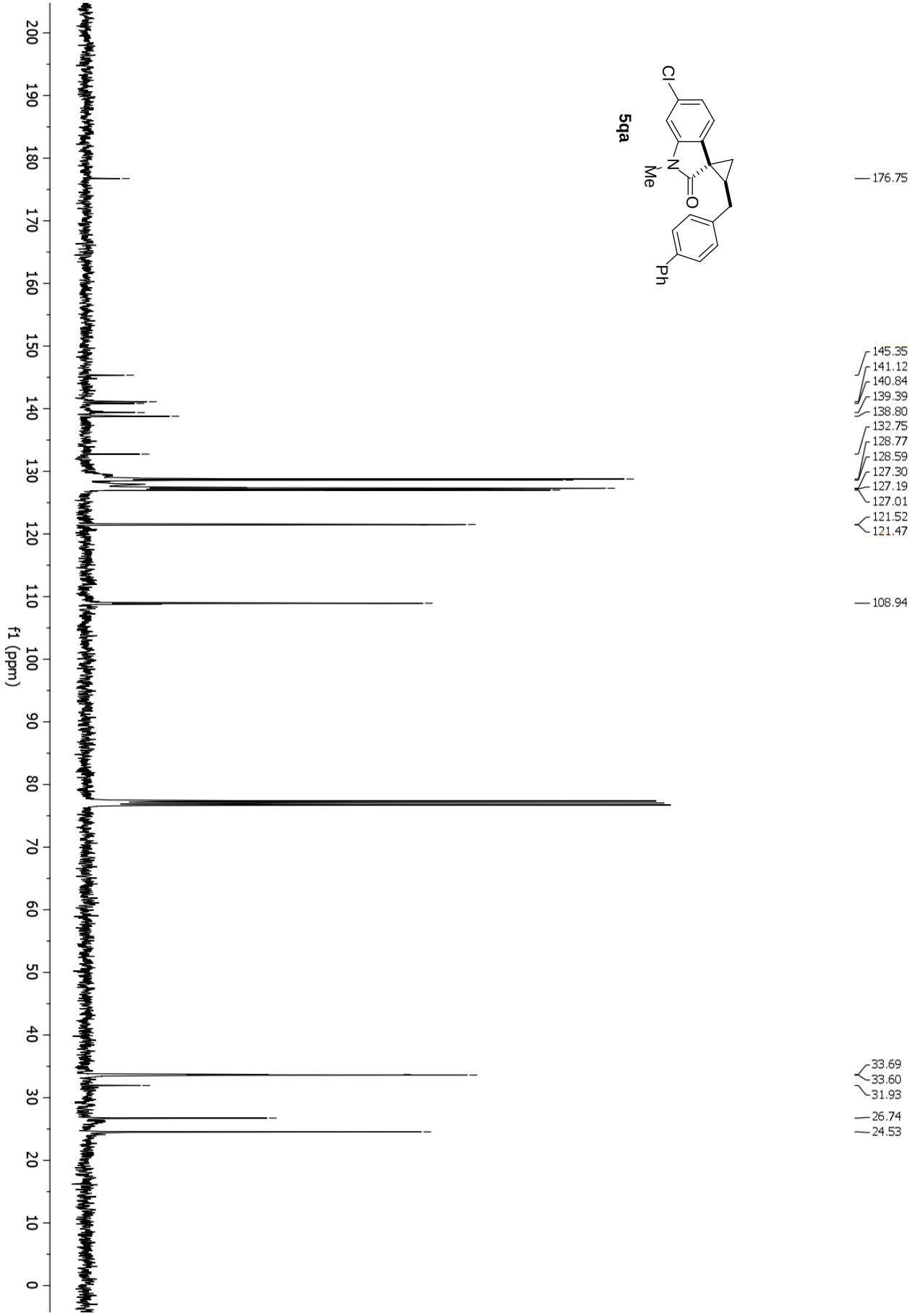
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5pb**



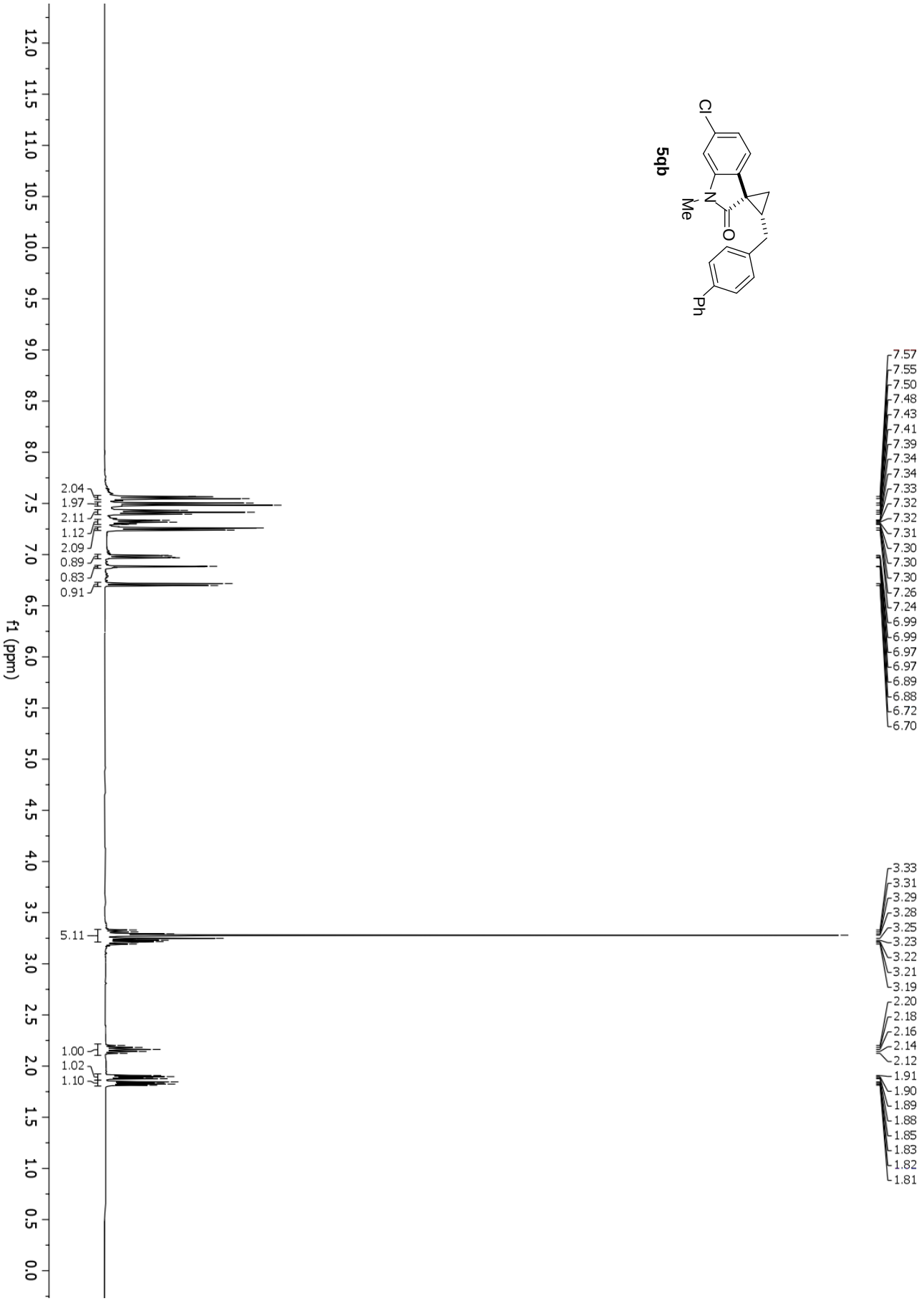
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5qa**



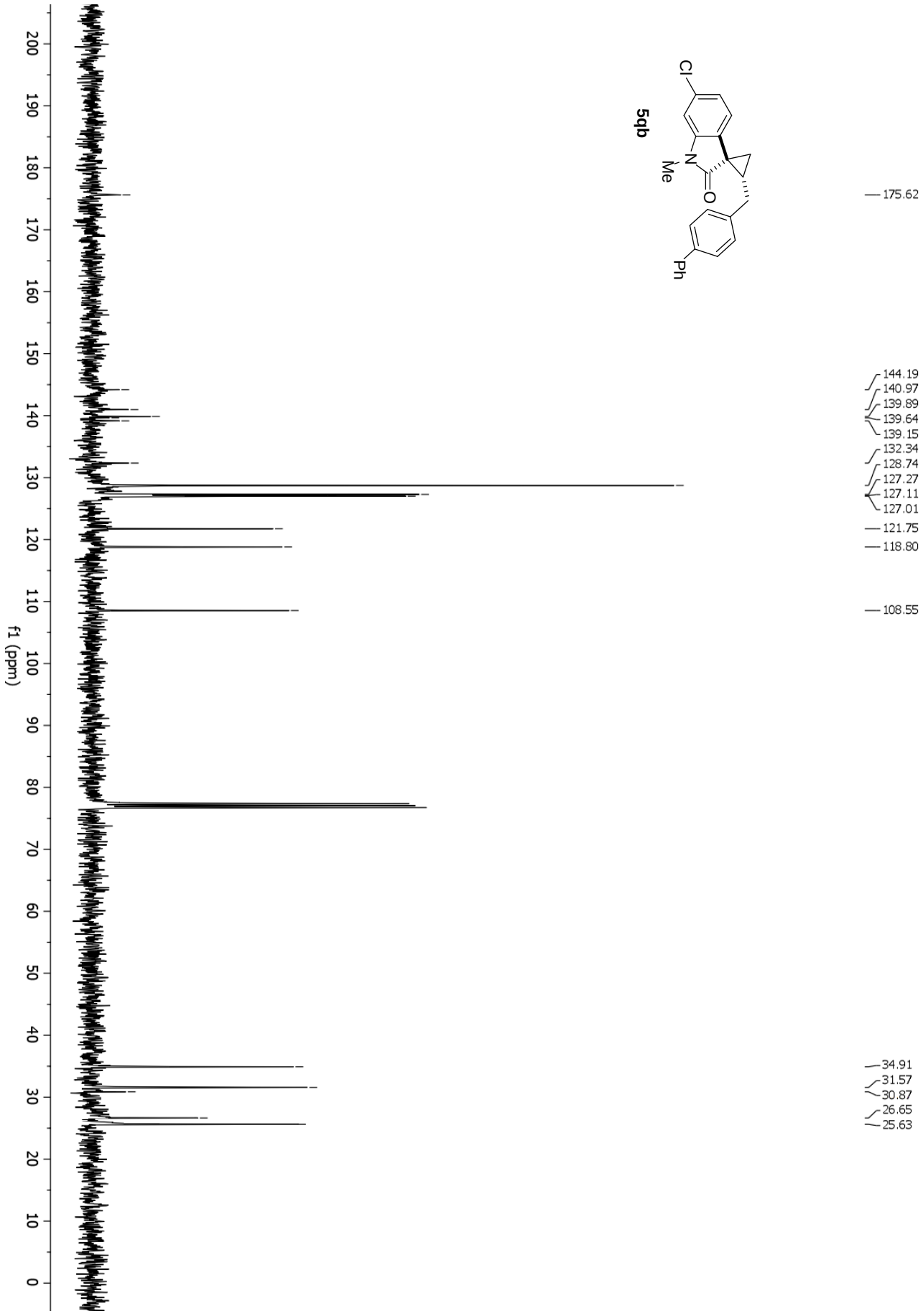
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5qa**



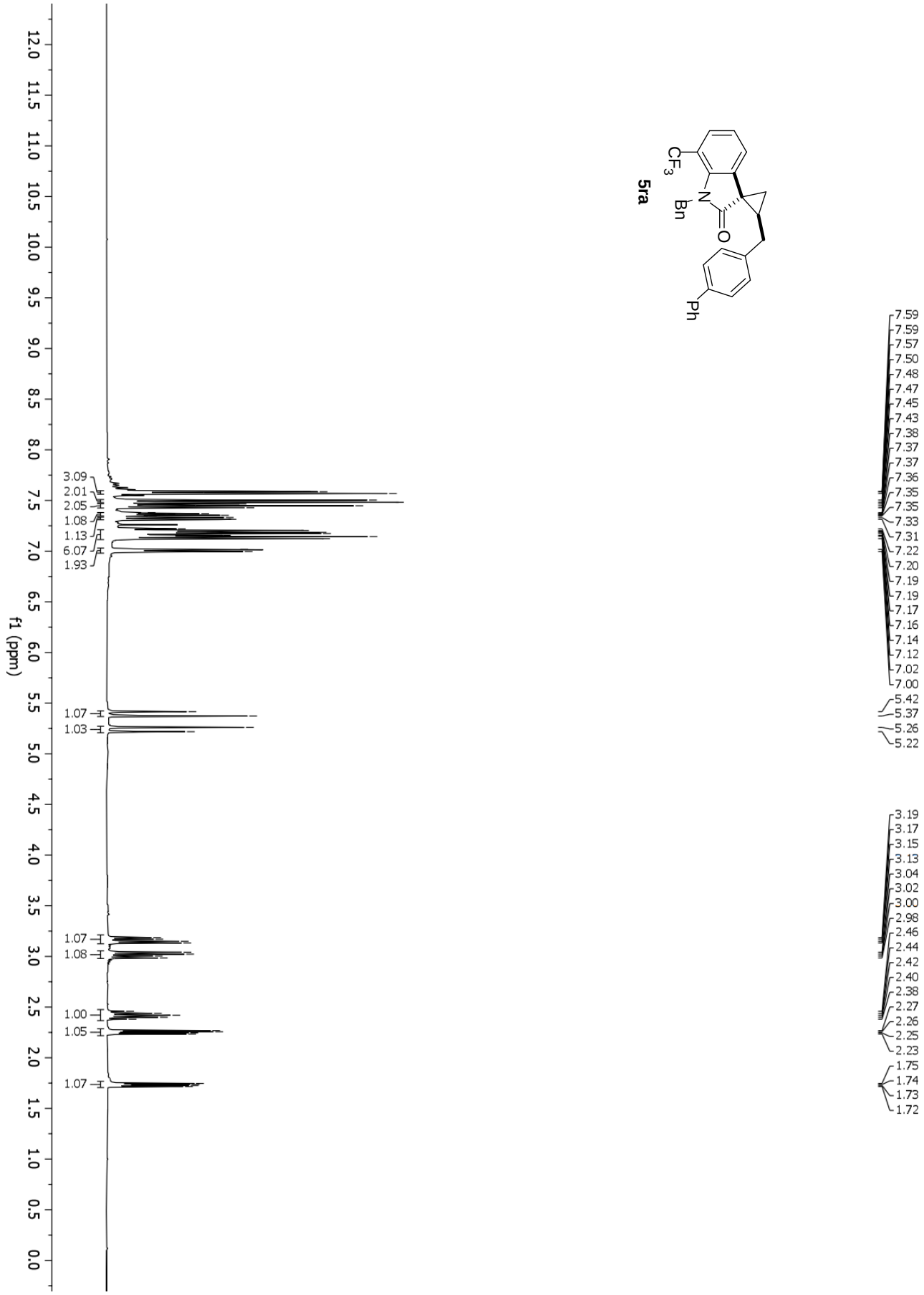
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5qb**



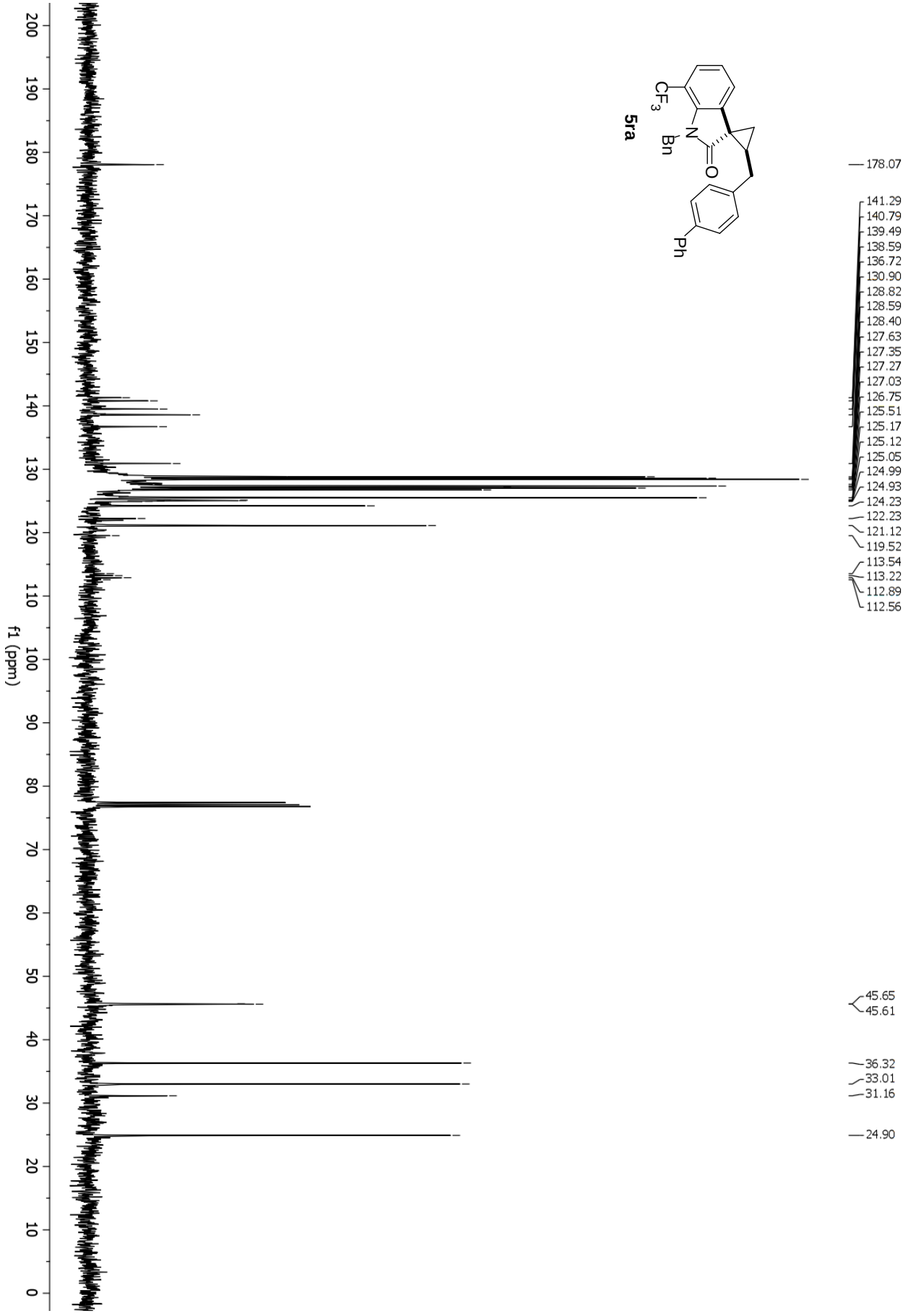
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5qb**



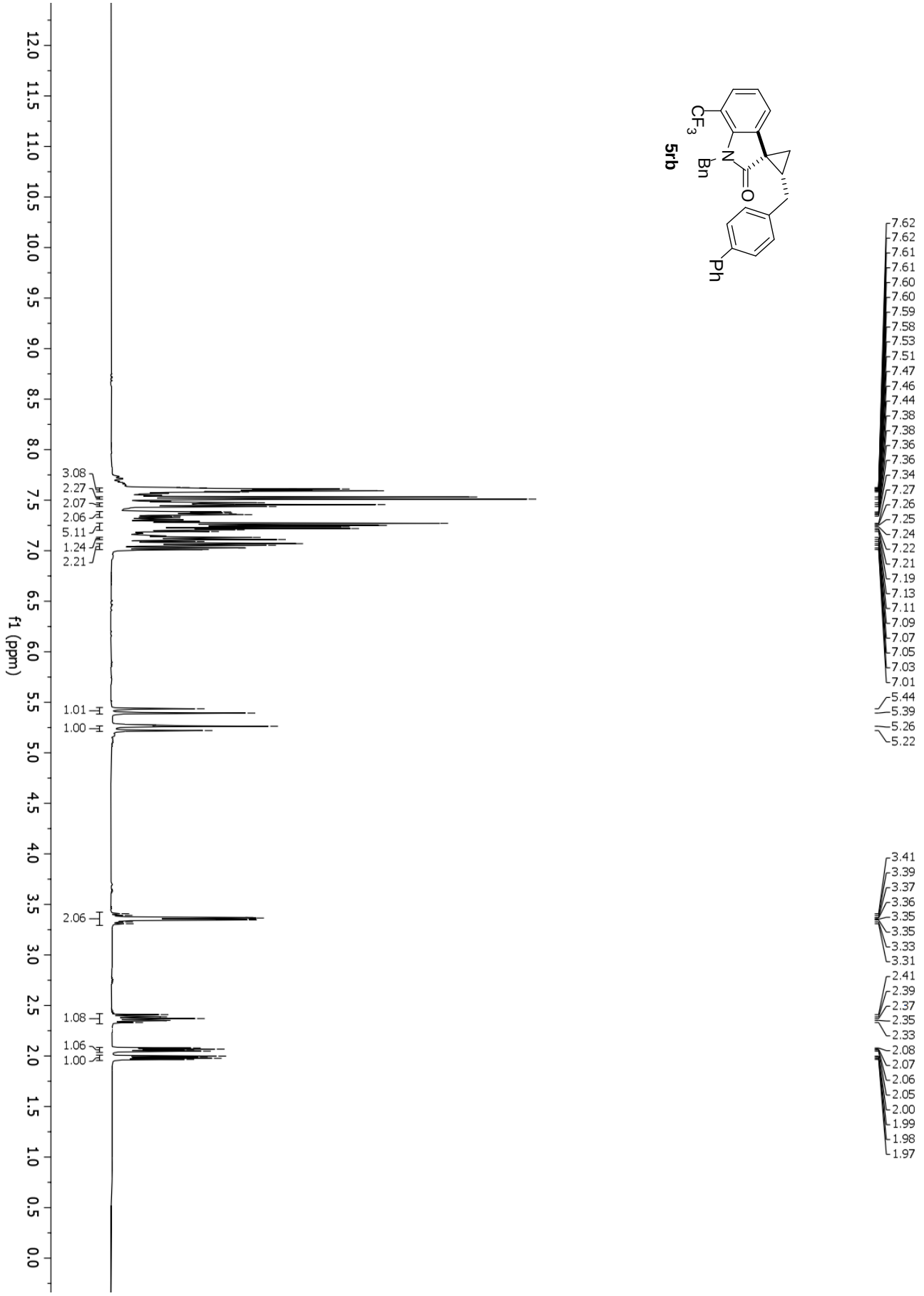
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5ra**



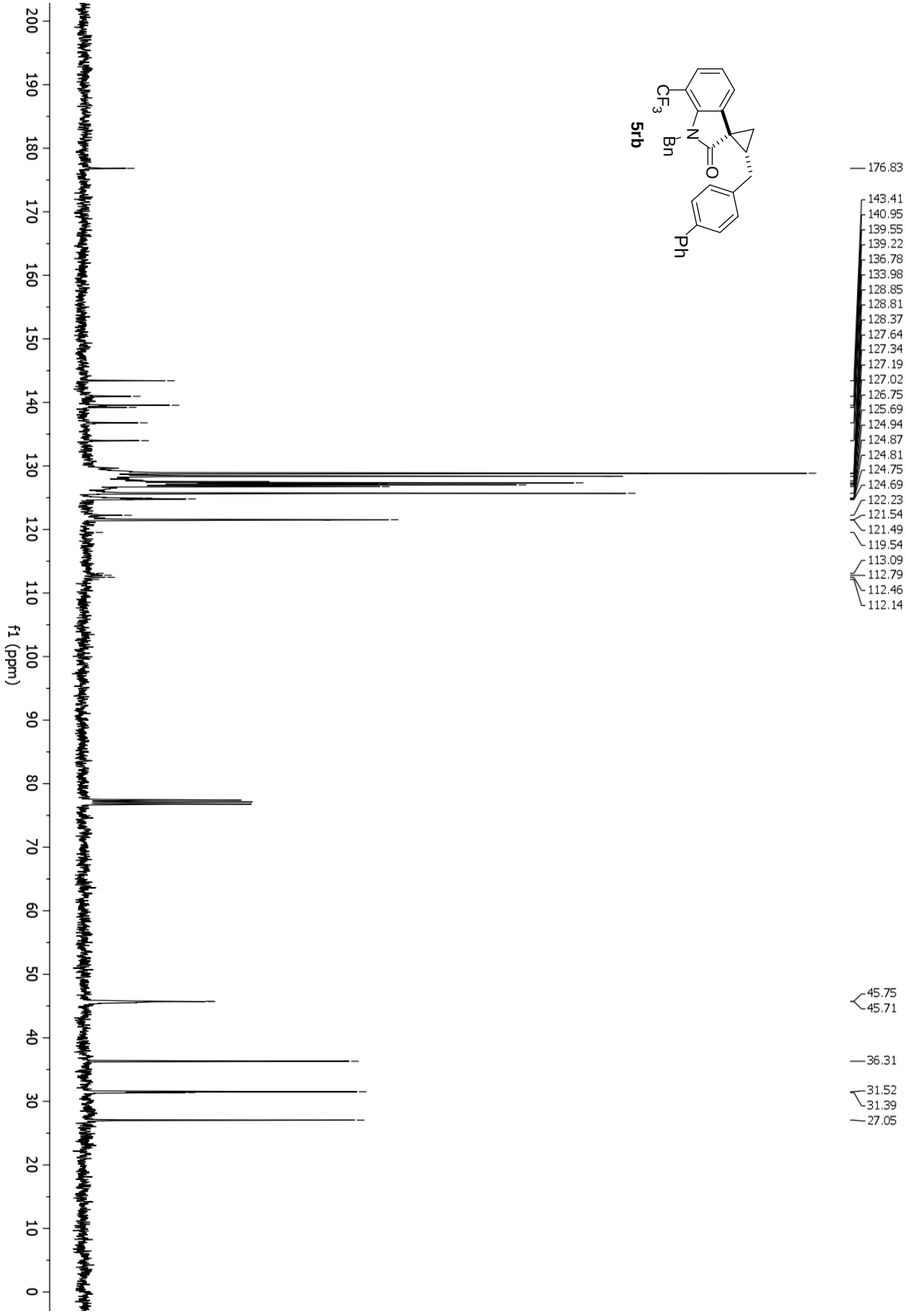
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5ra**



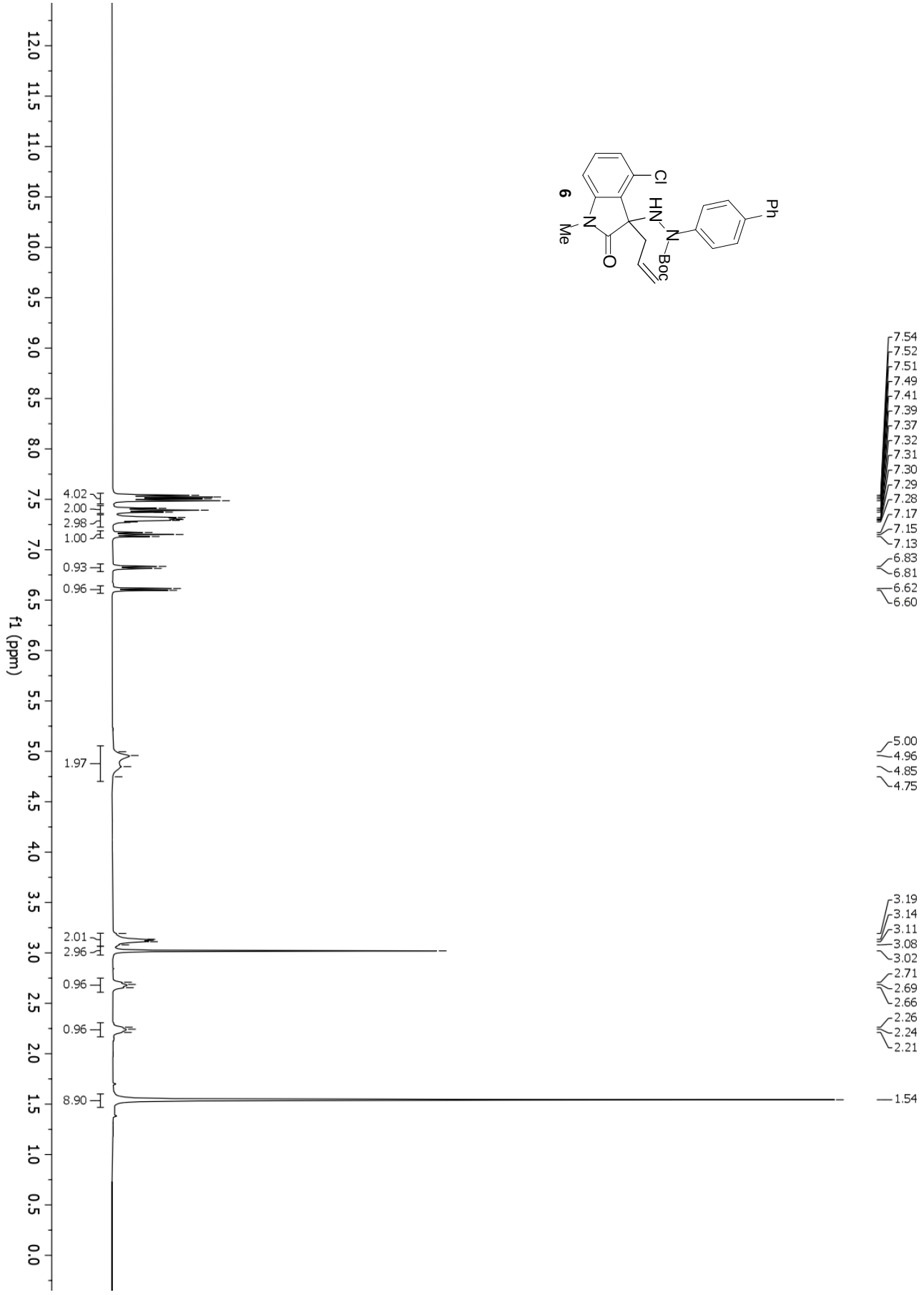
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5rb**



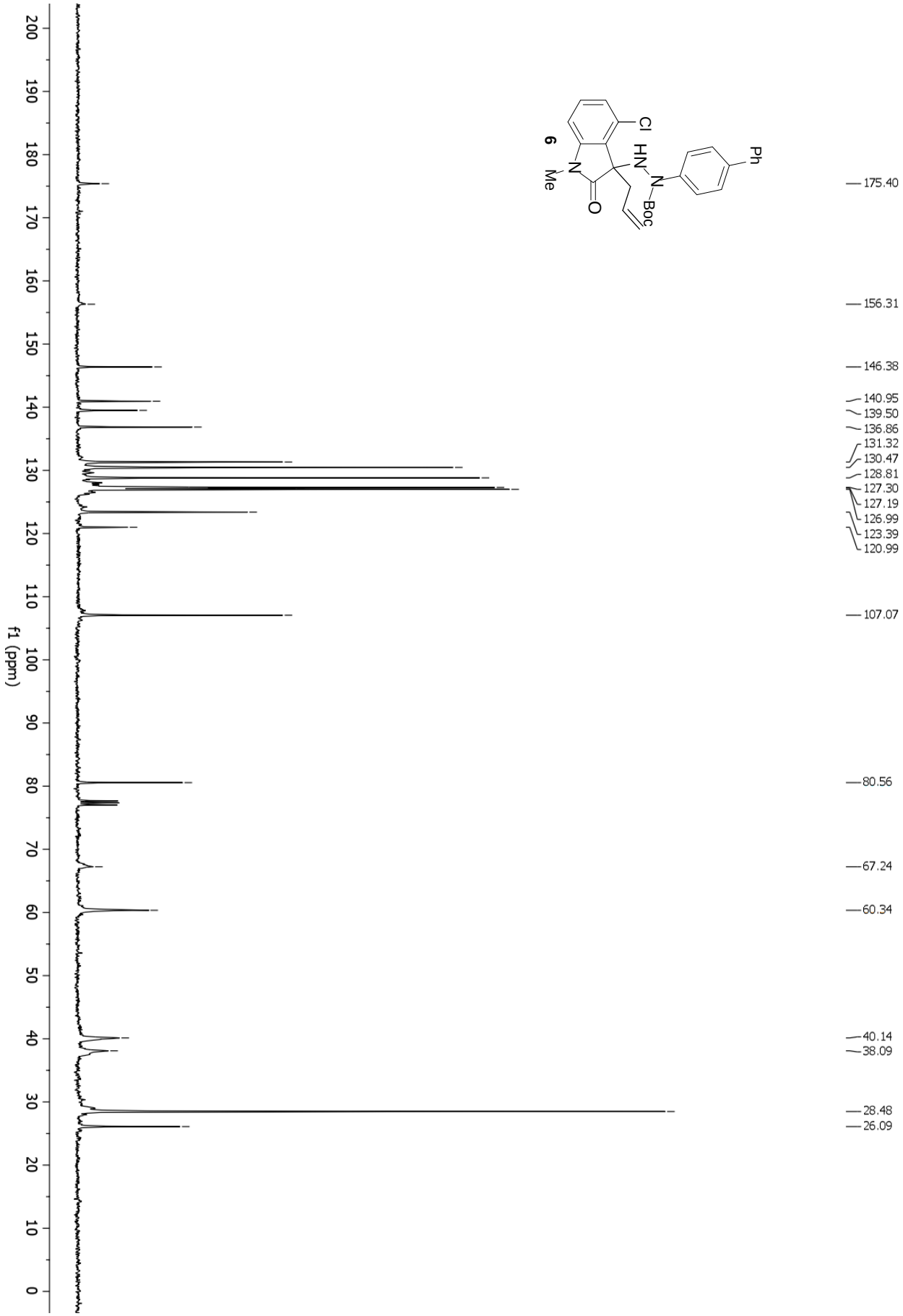
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5rb**



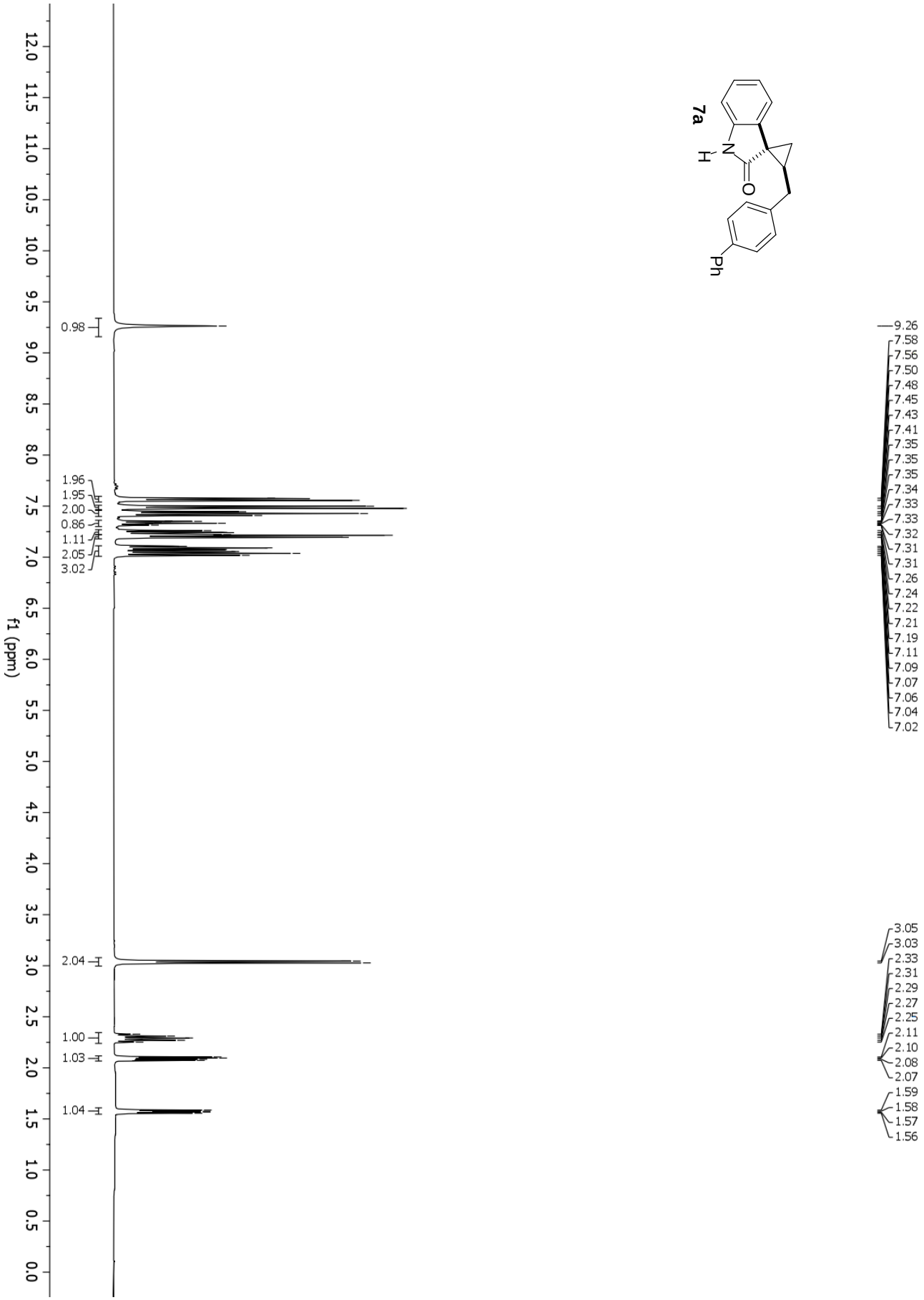
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **6**



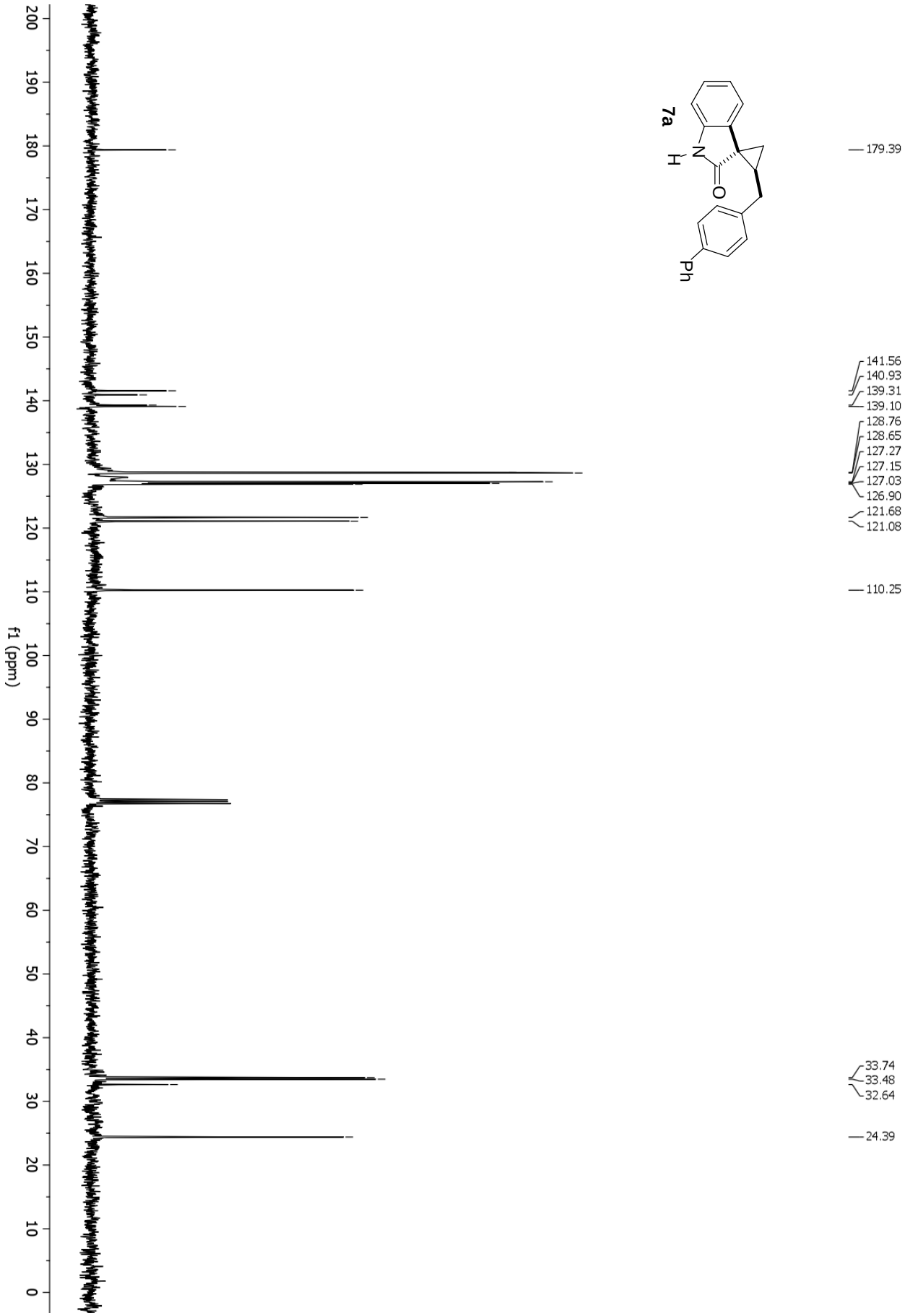
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **6**



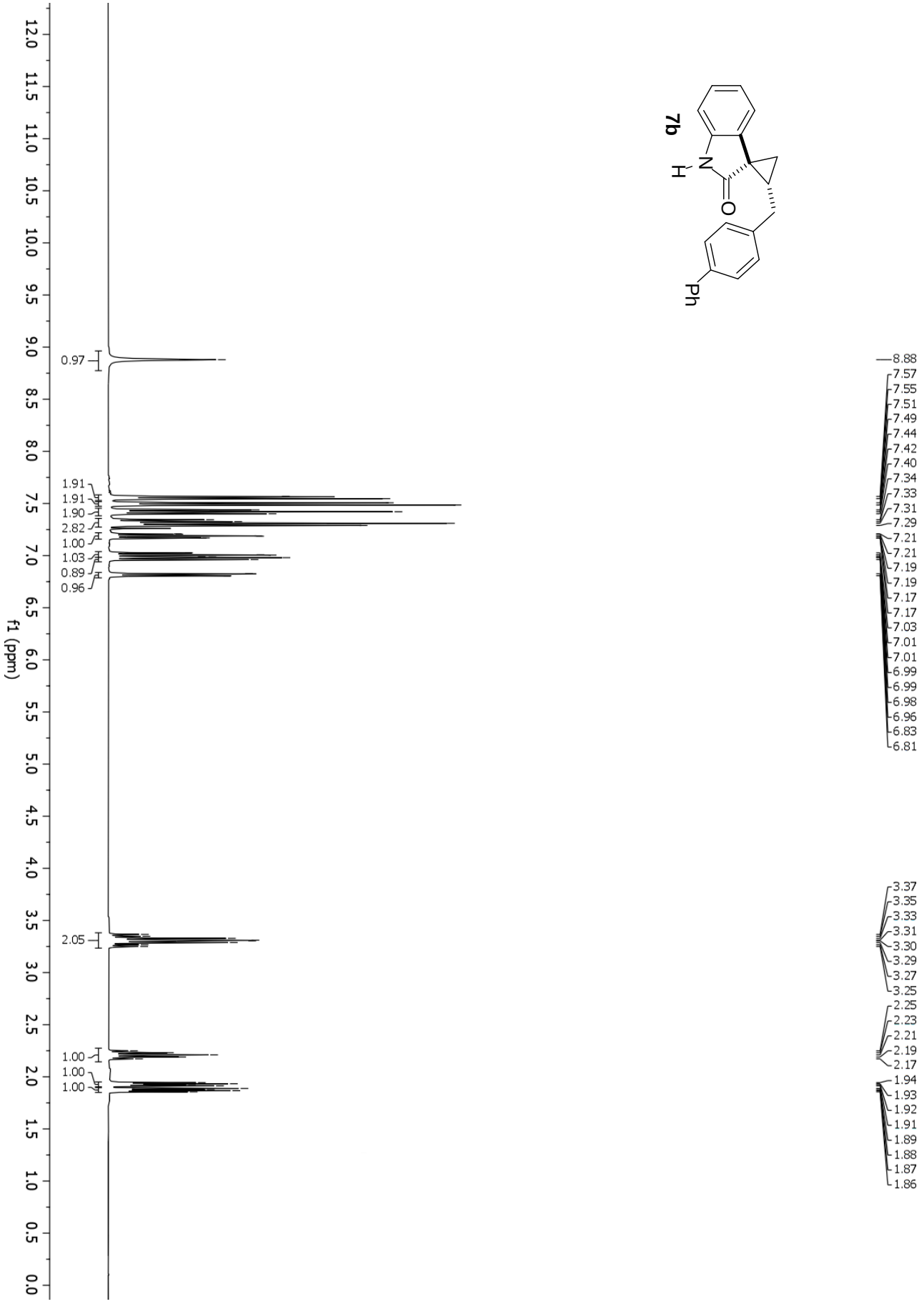
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **7a**



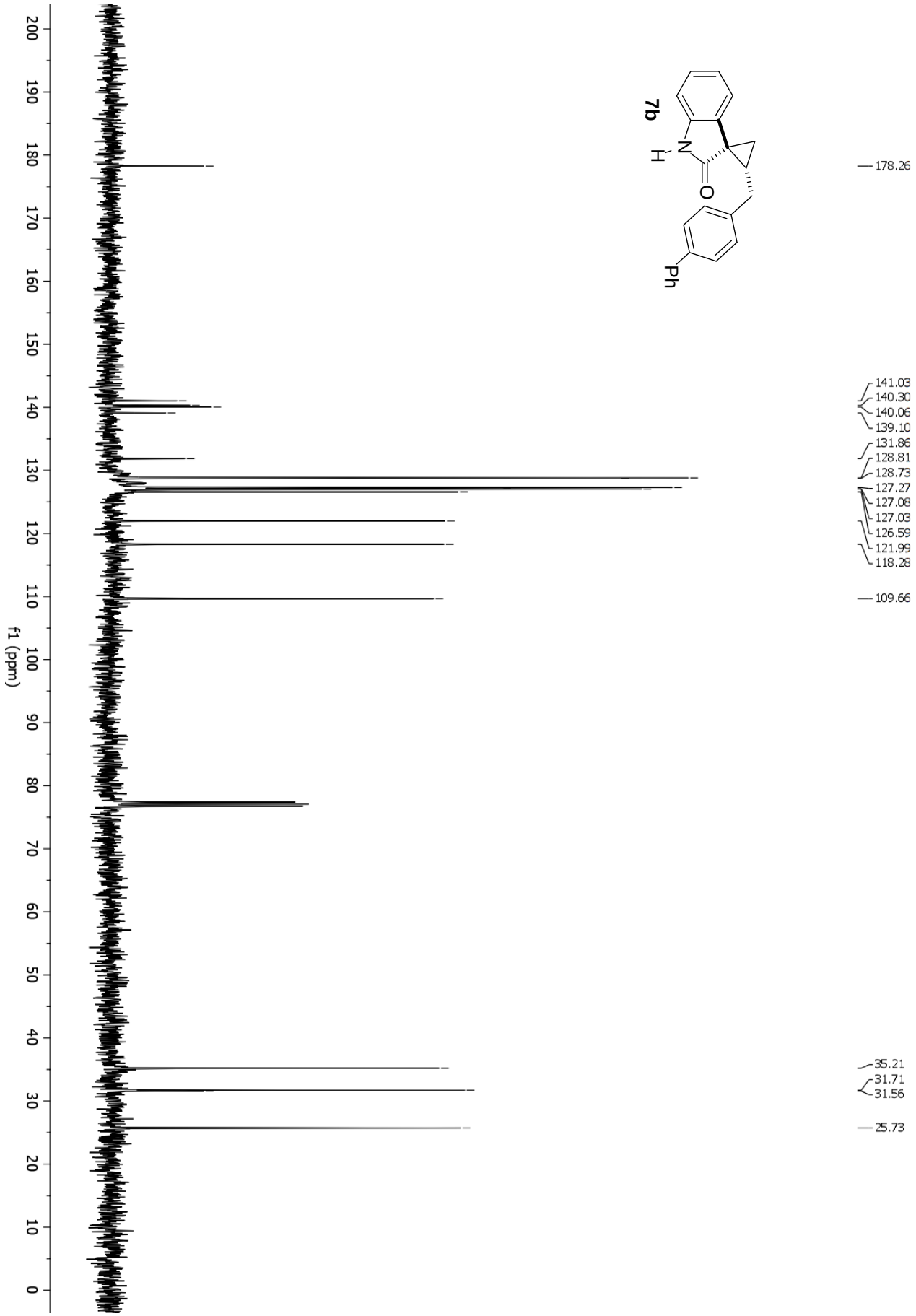
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **7a**



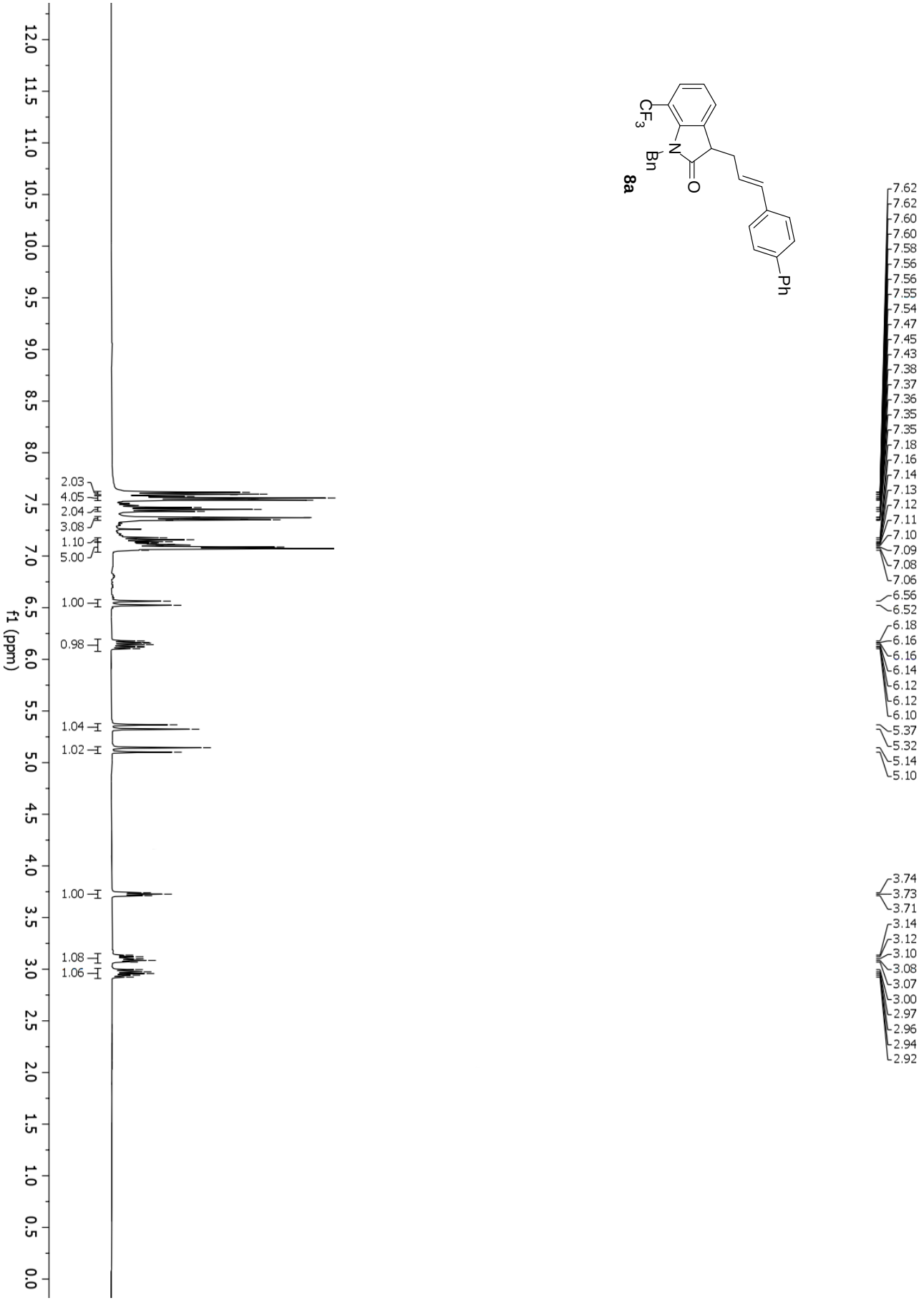
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **7b**



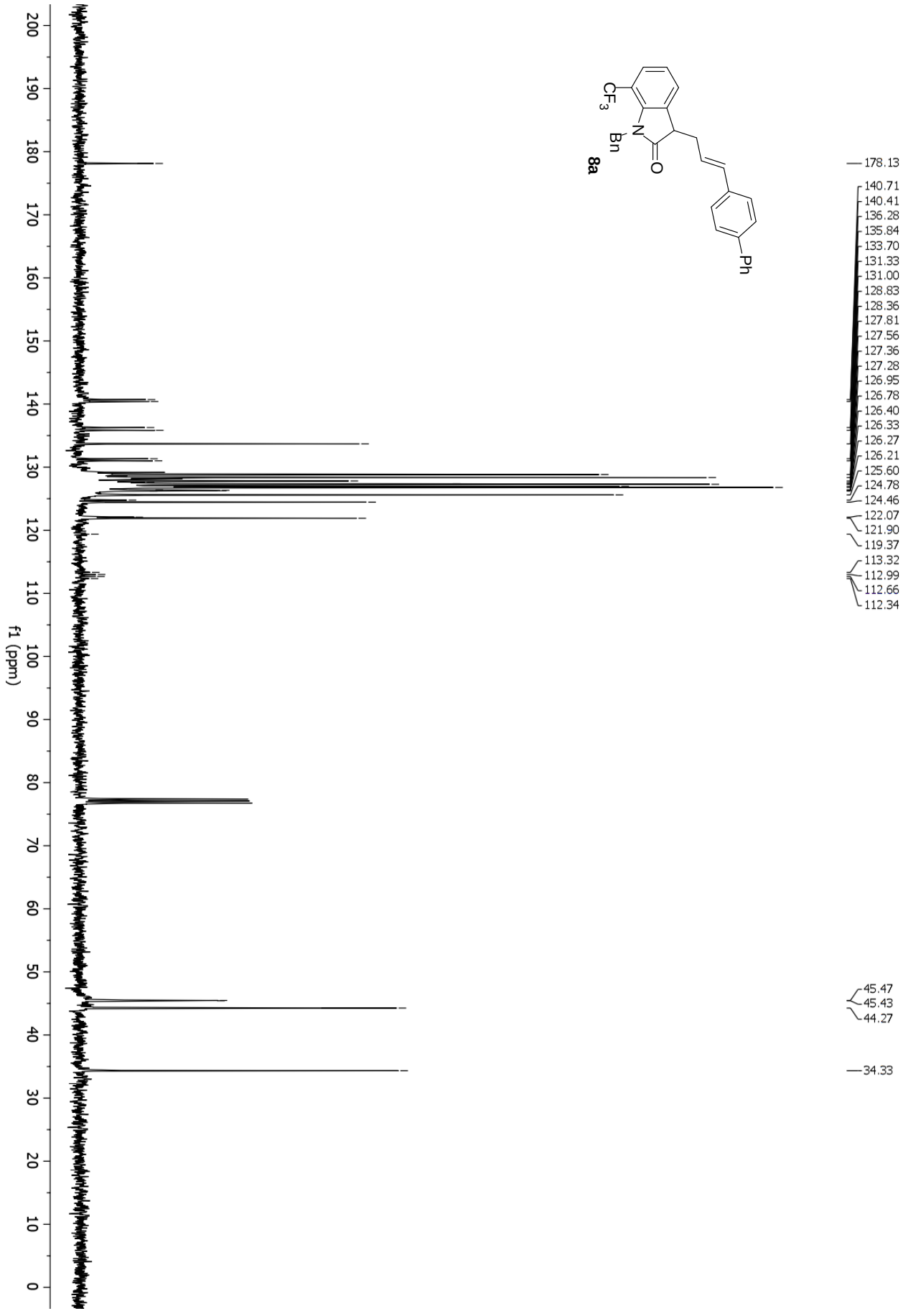
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **7b**



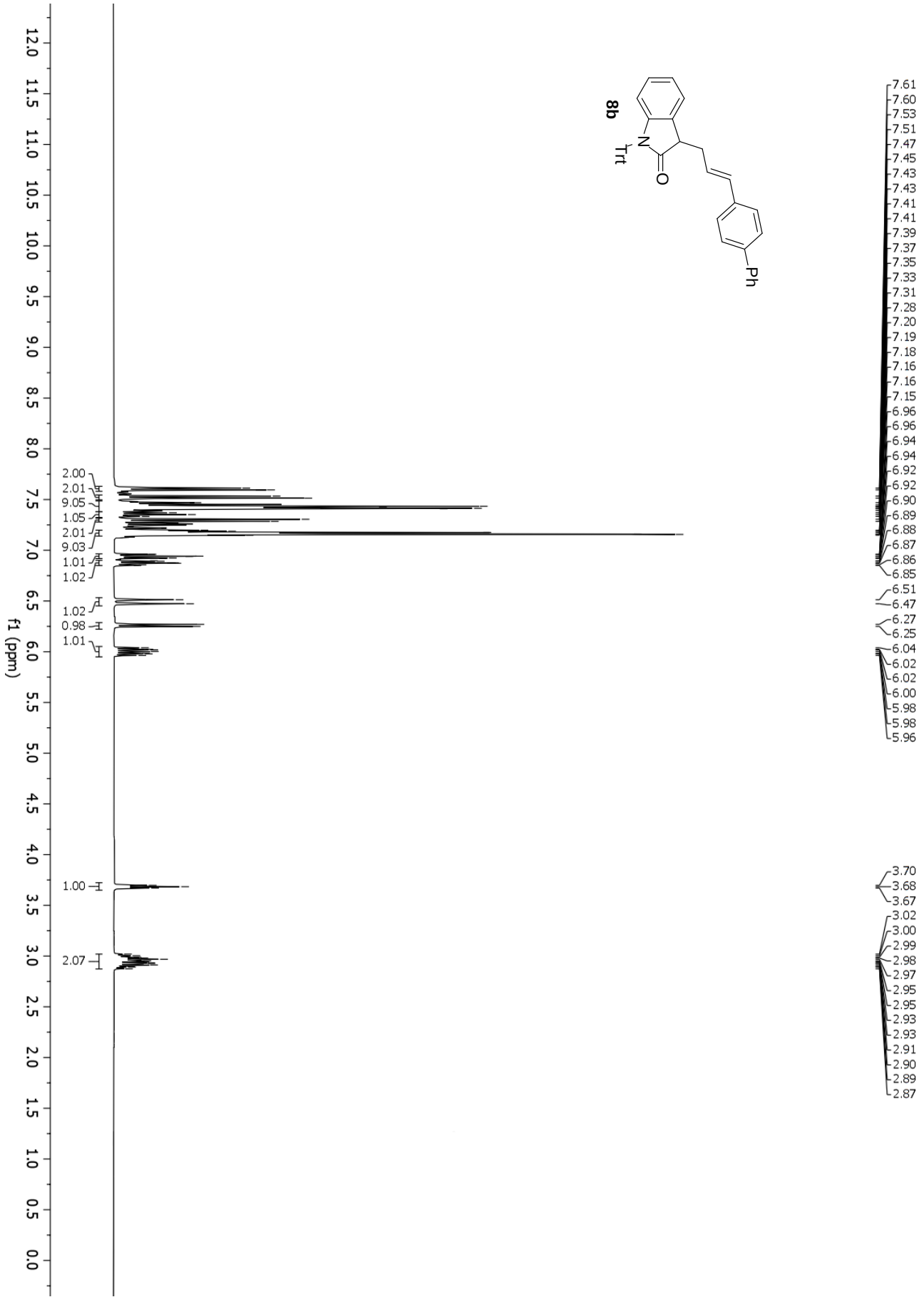
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **8a**



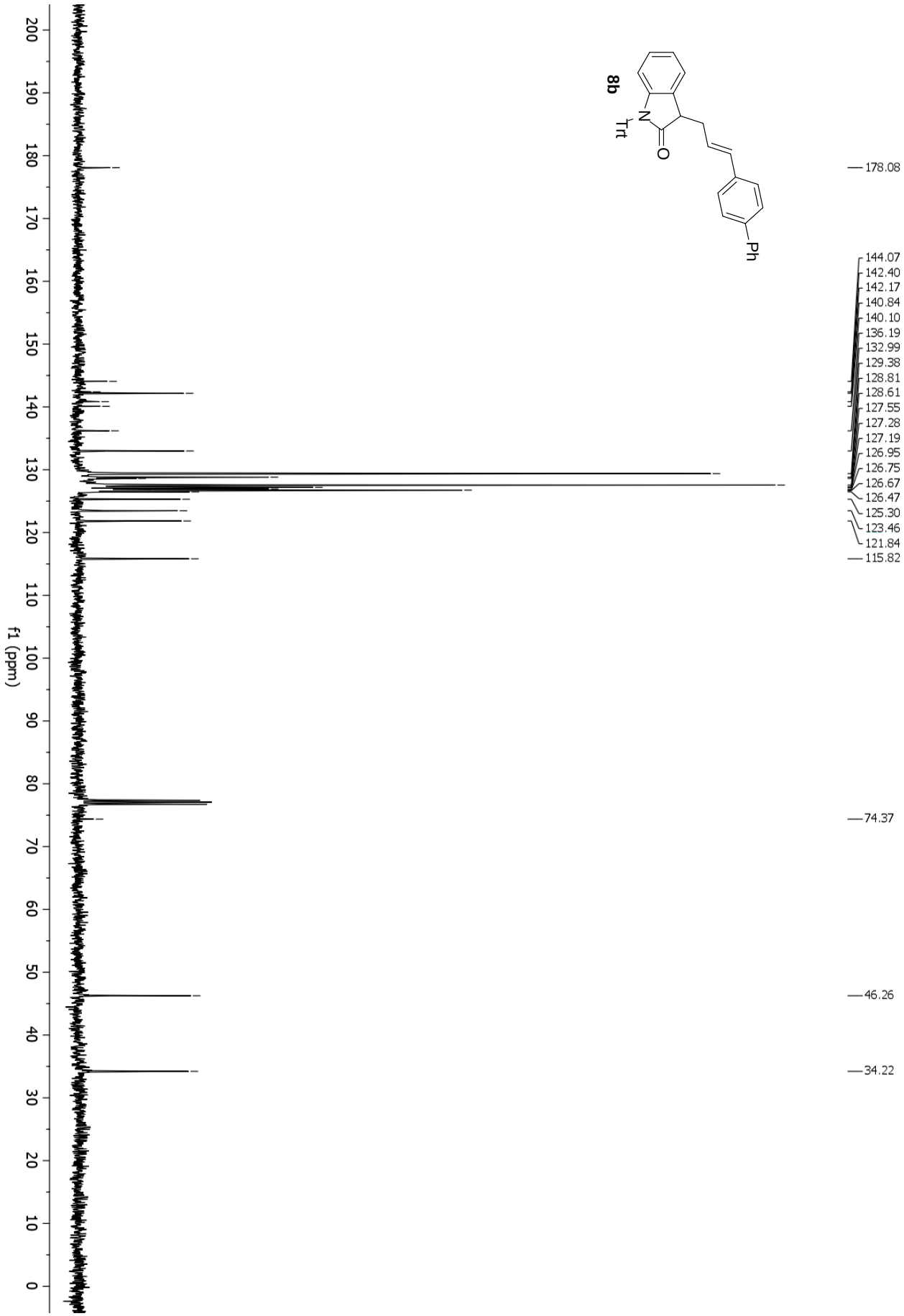
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **8a**



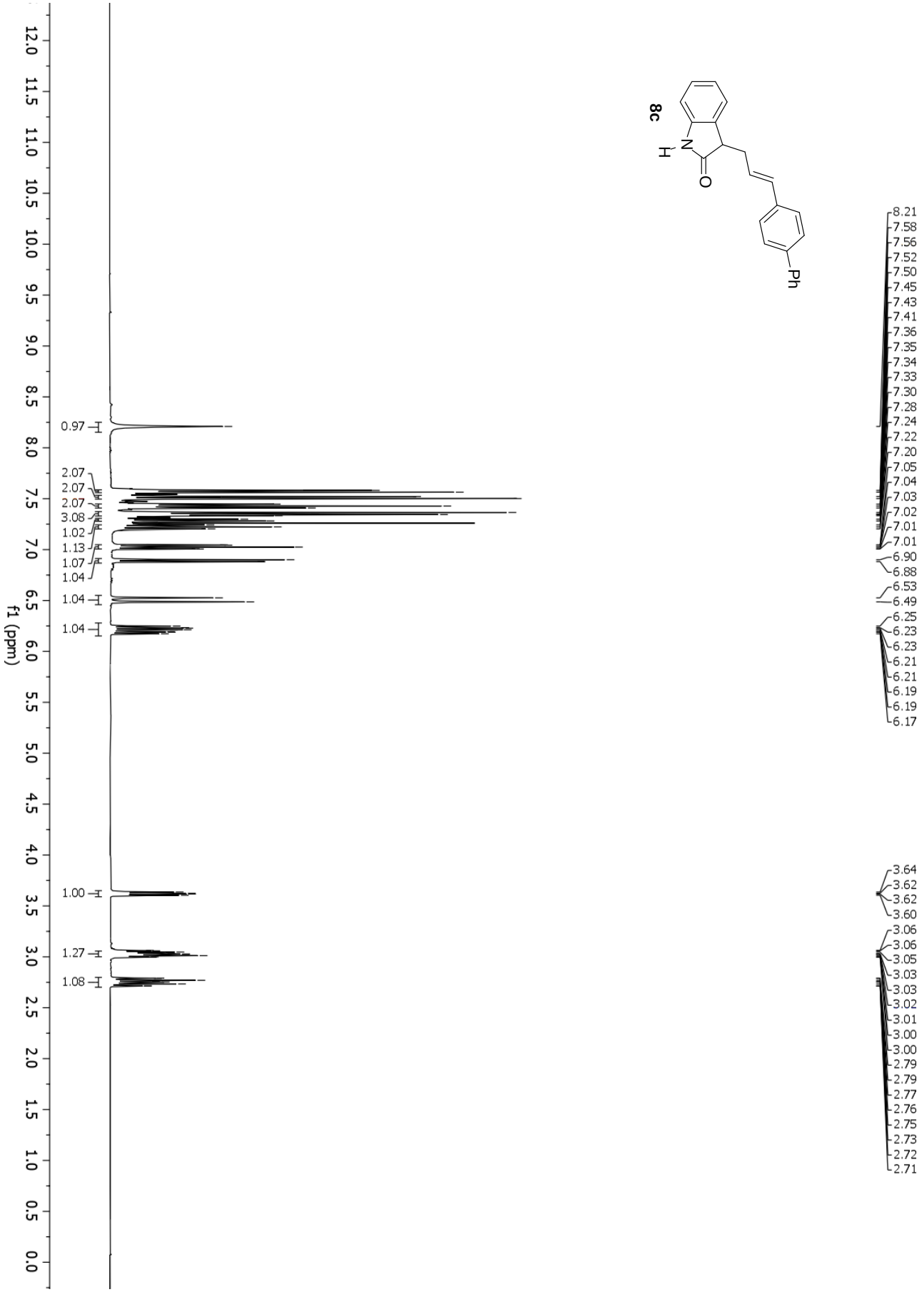
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **8b**



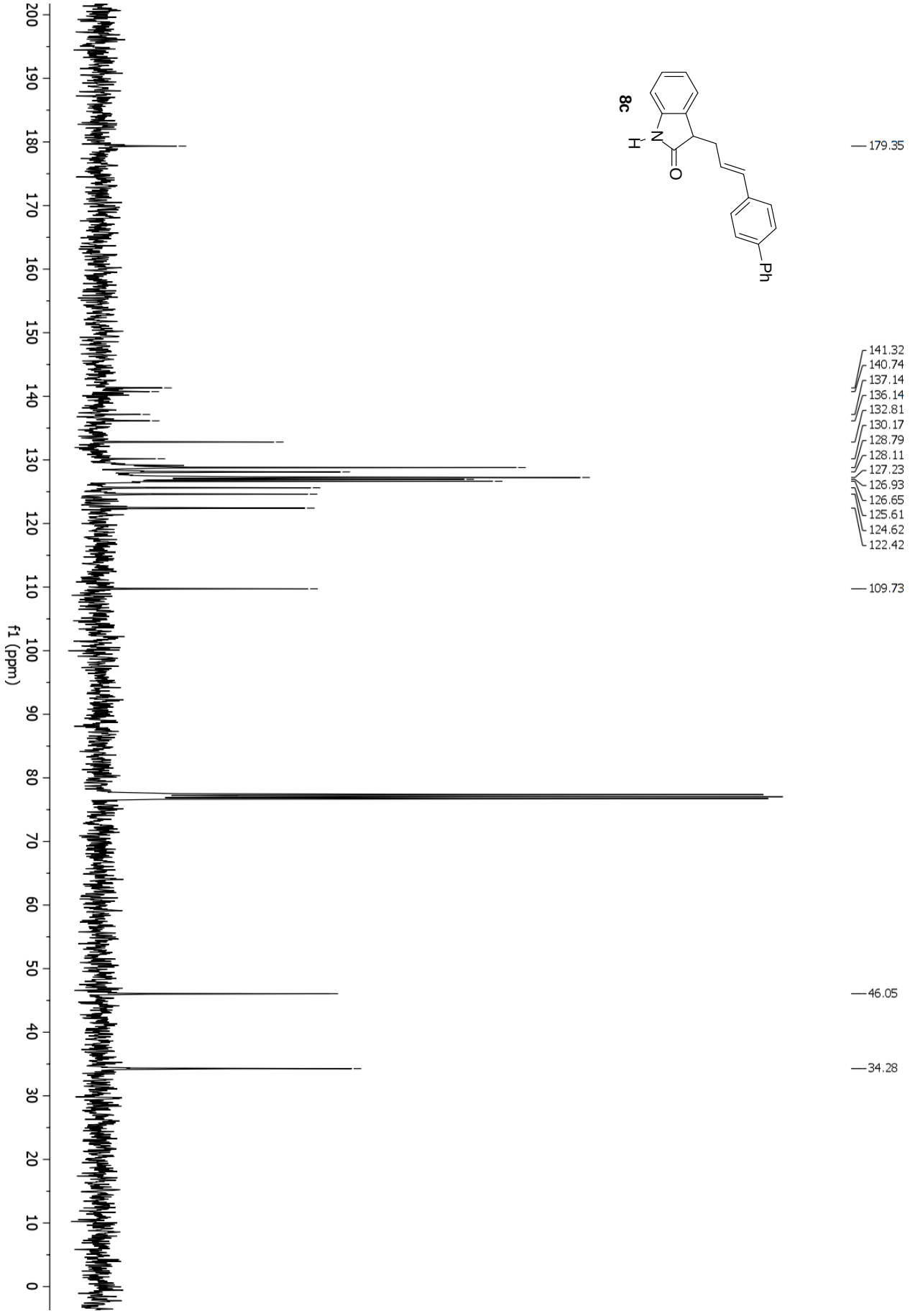
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **8b**



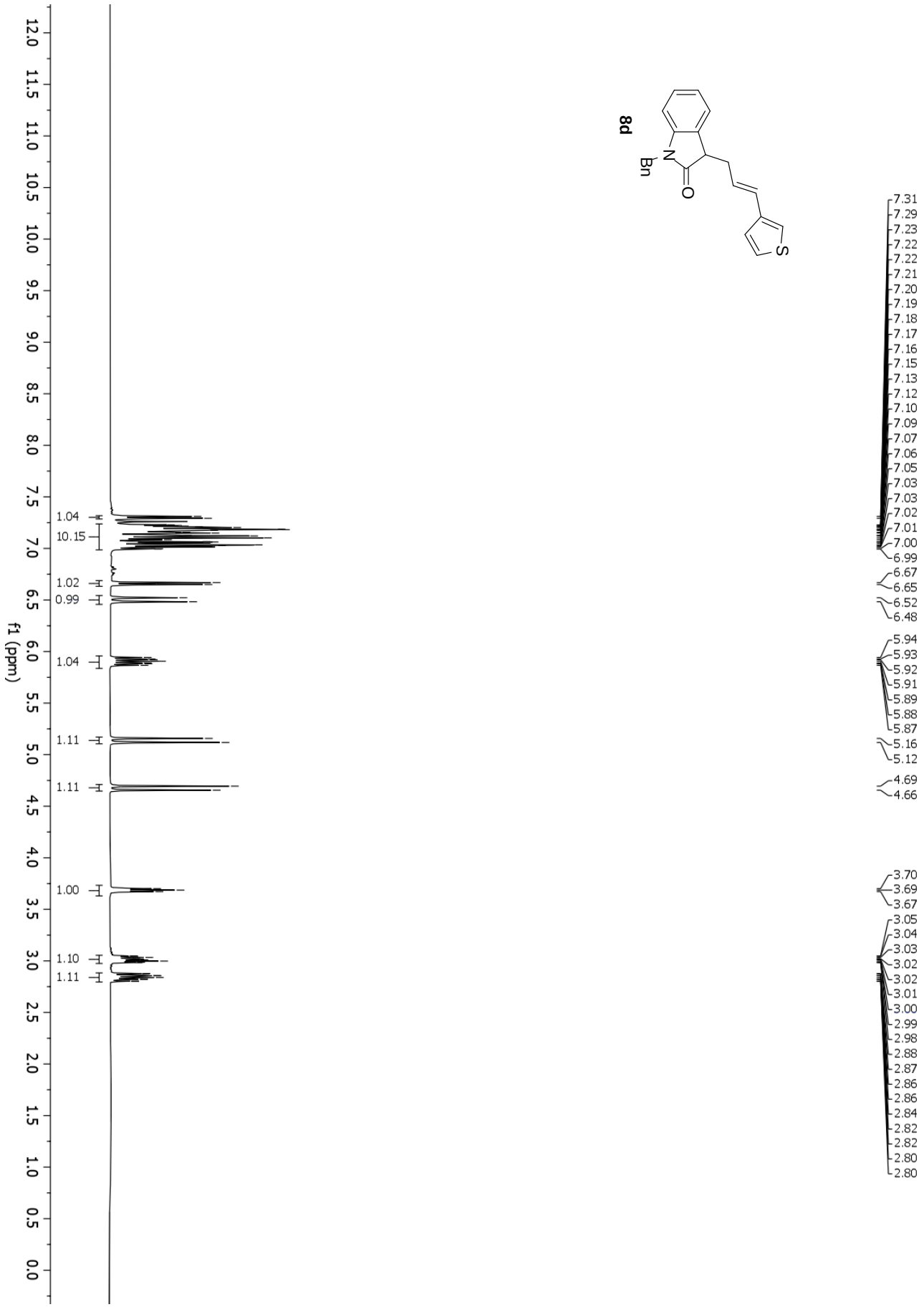
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **8c**



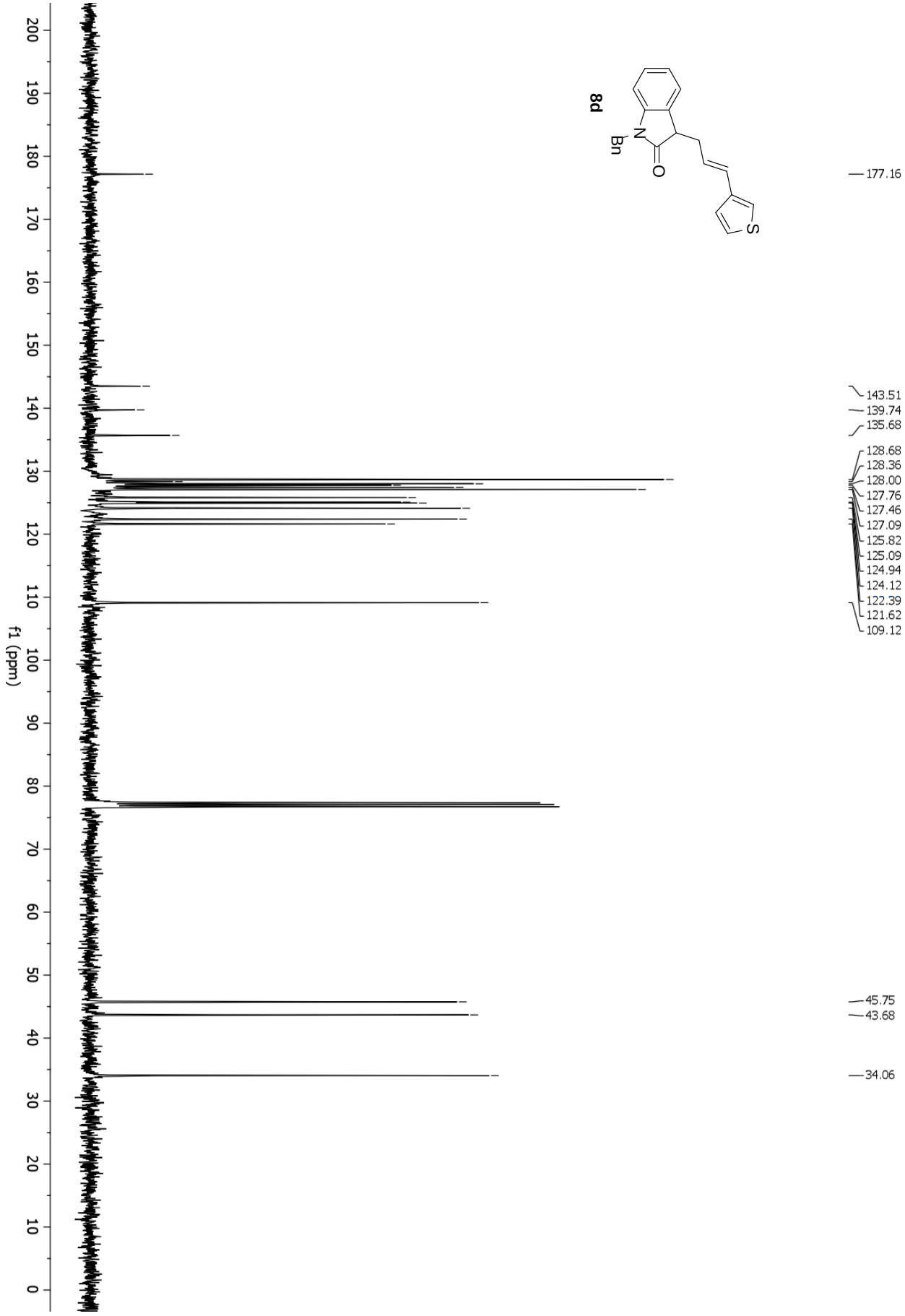
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **8c**



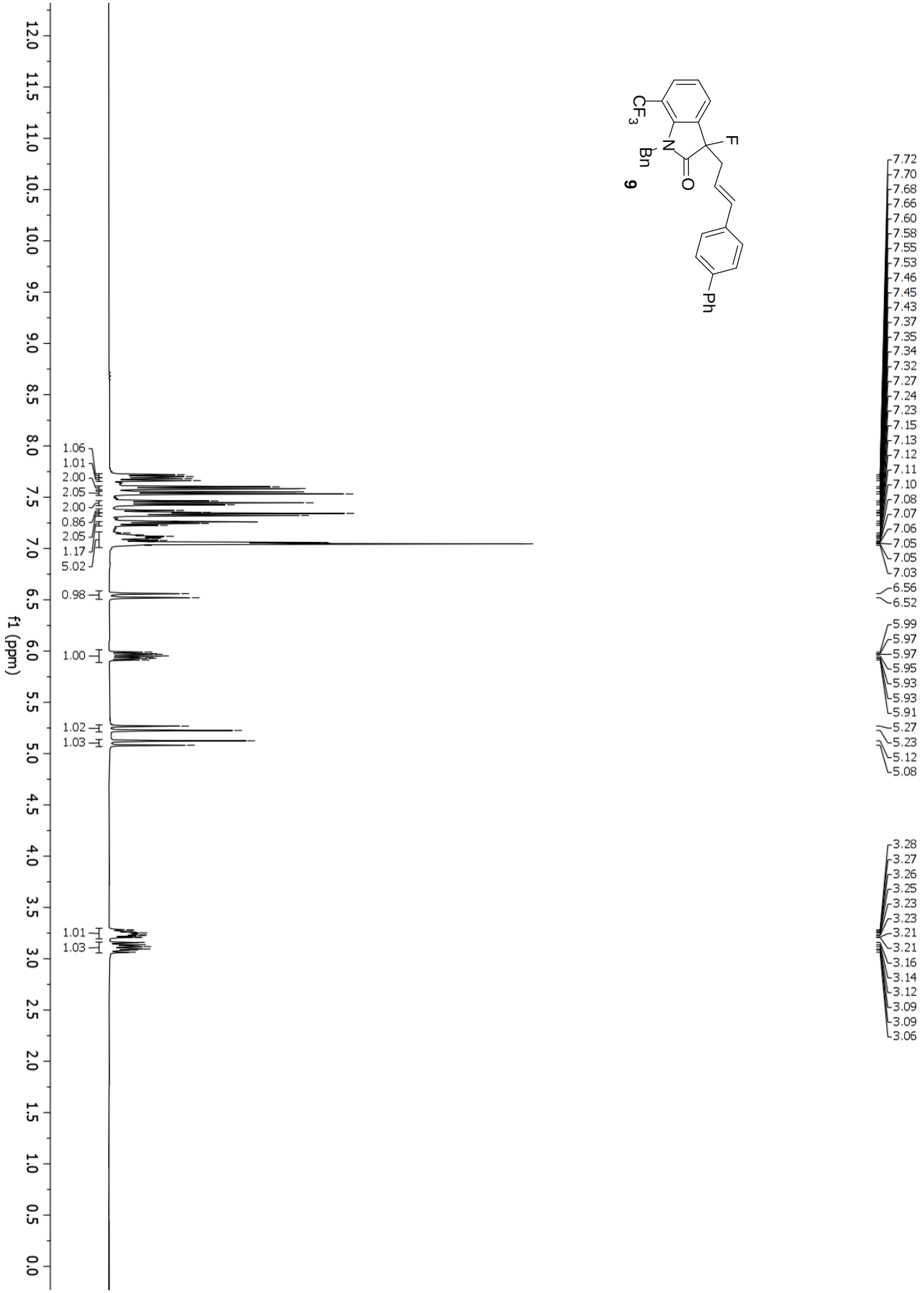
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **8d**



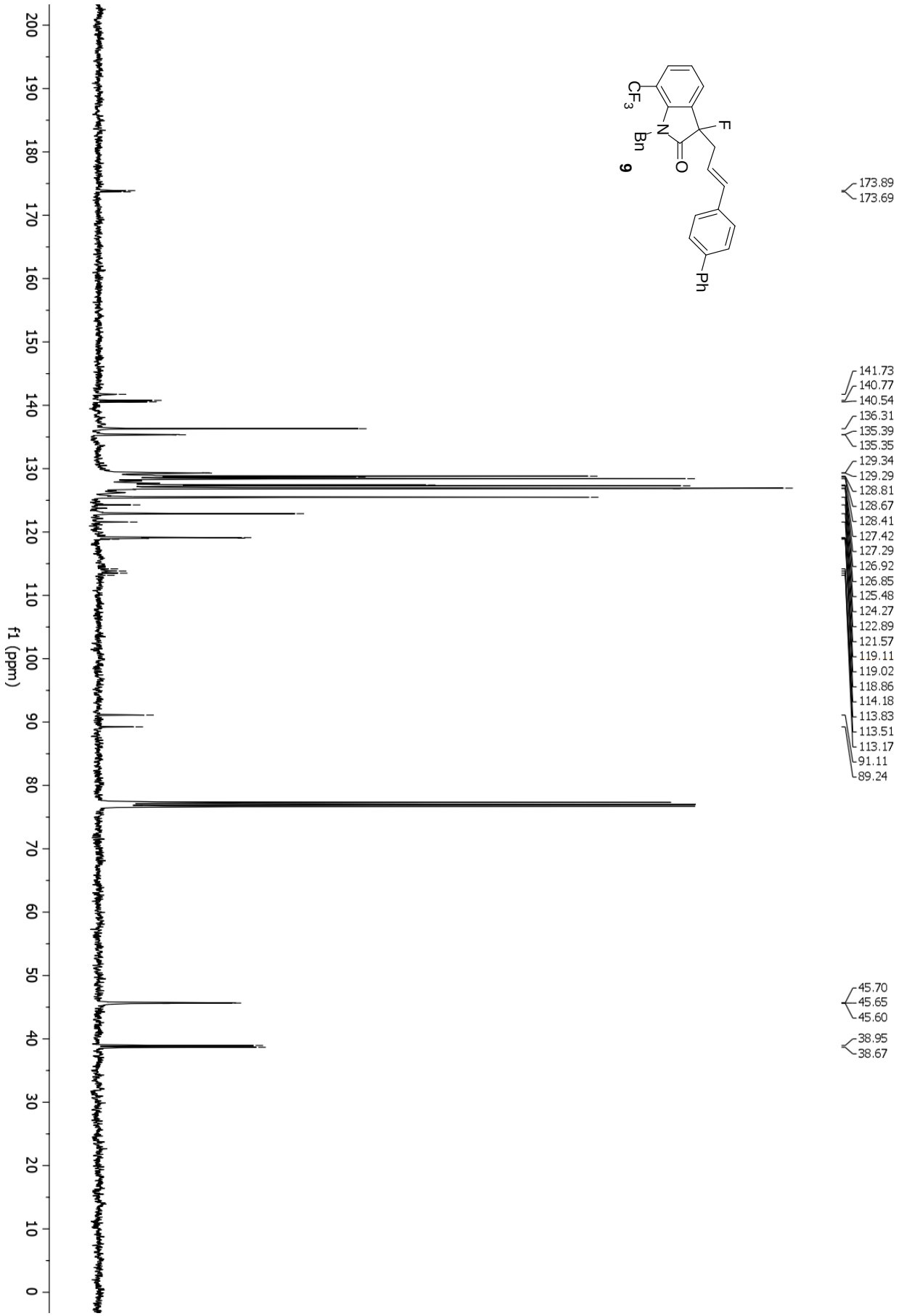
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **8d**



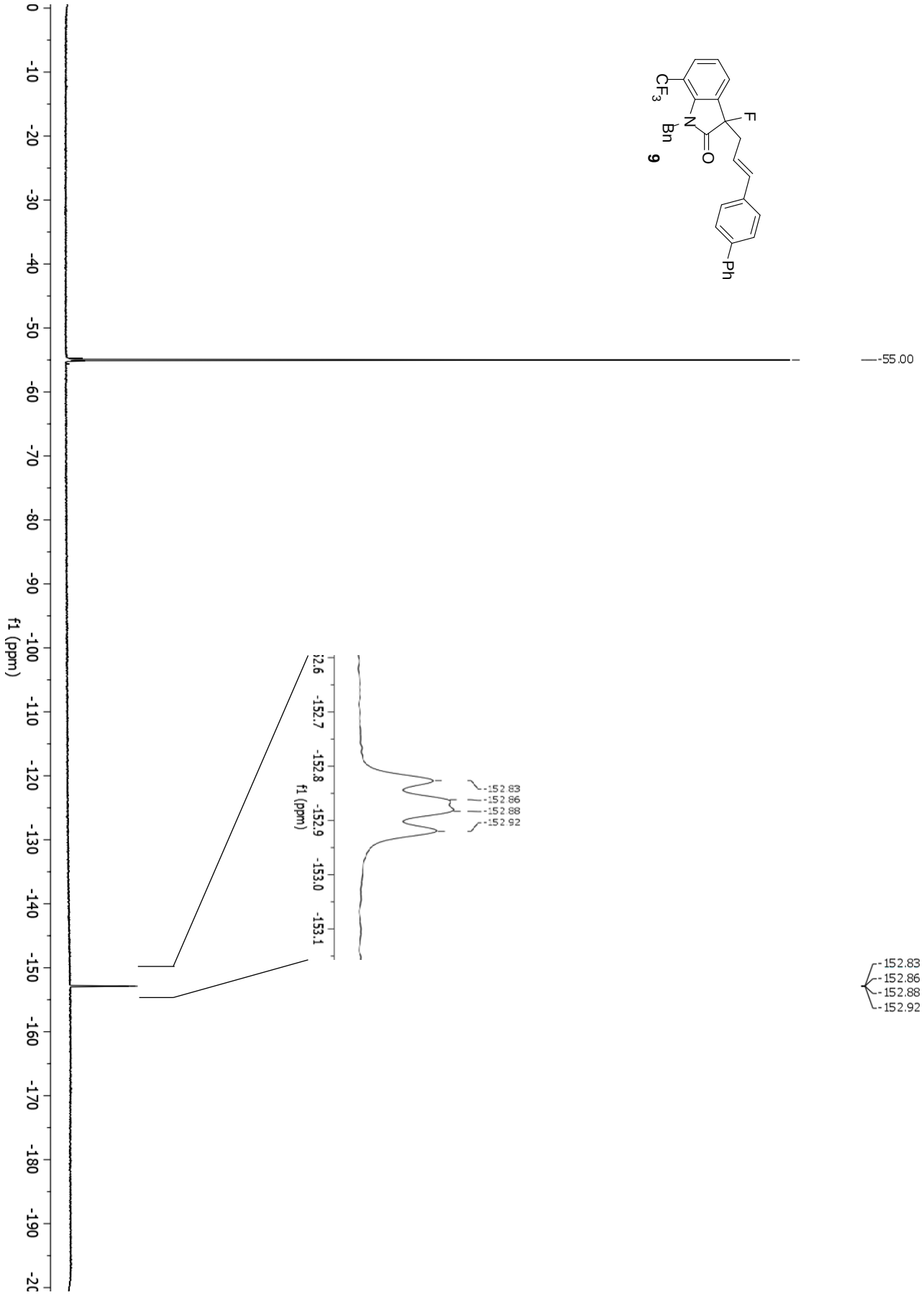
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **9**



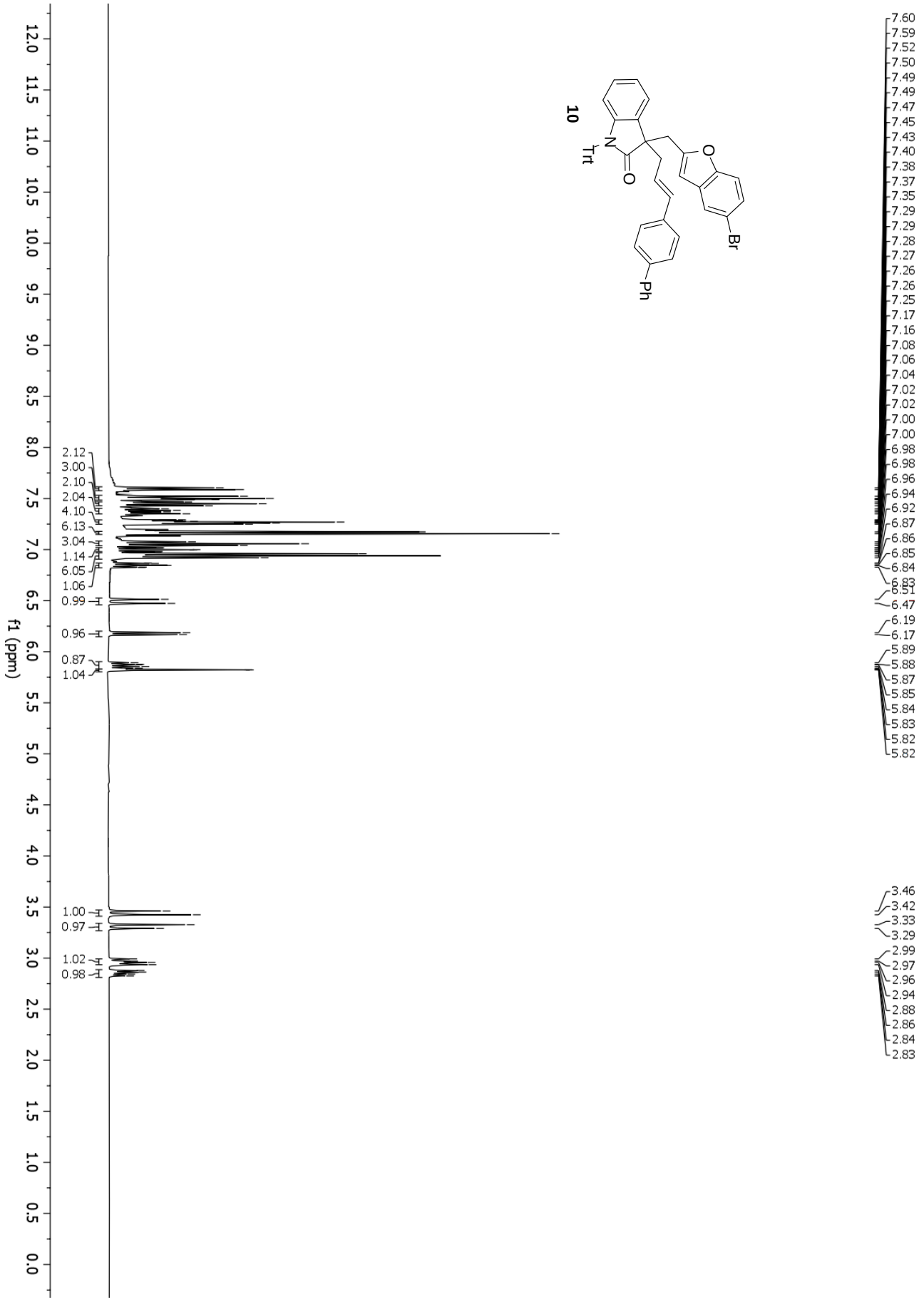
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **9**



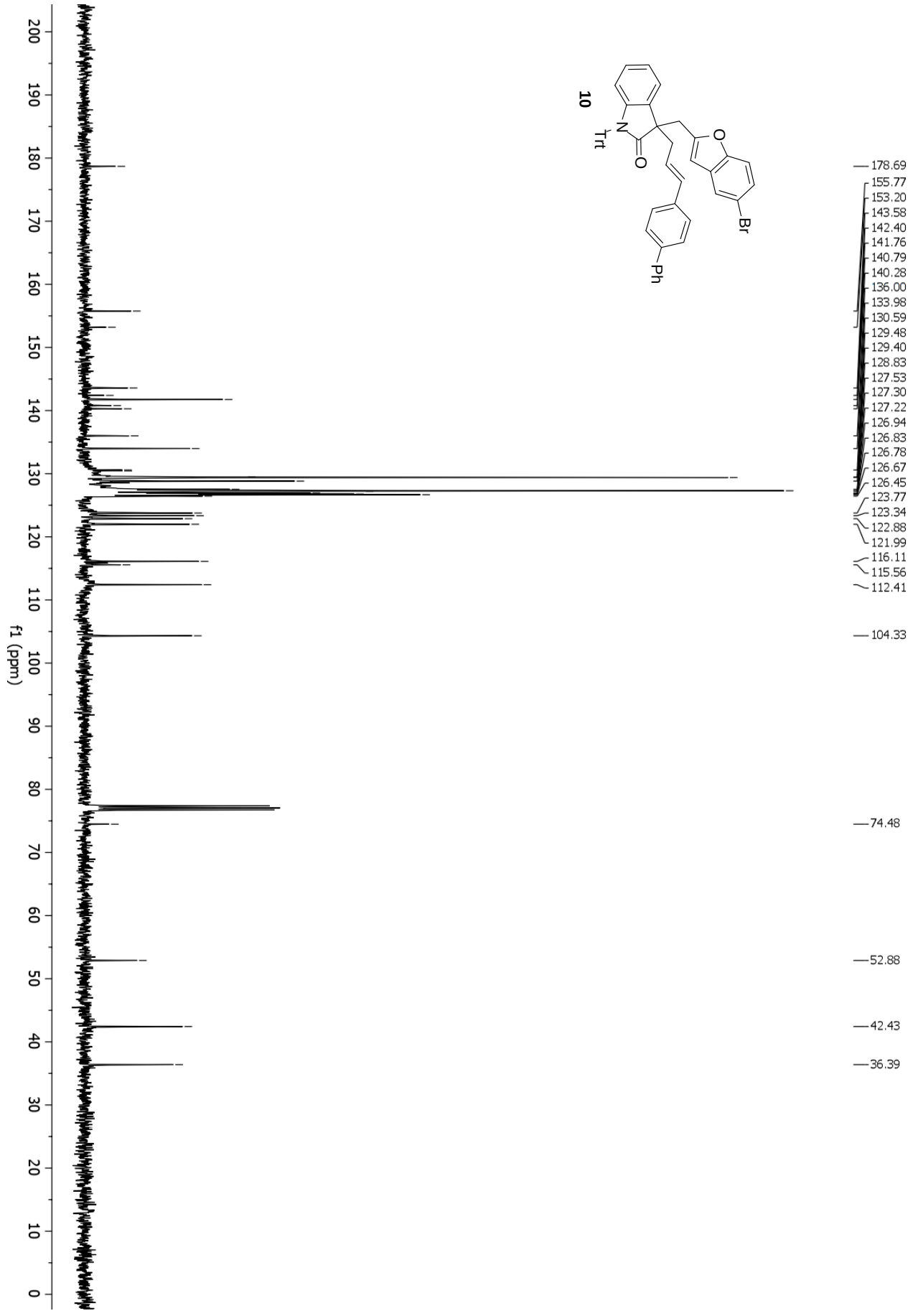
^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **9**



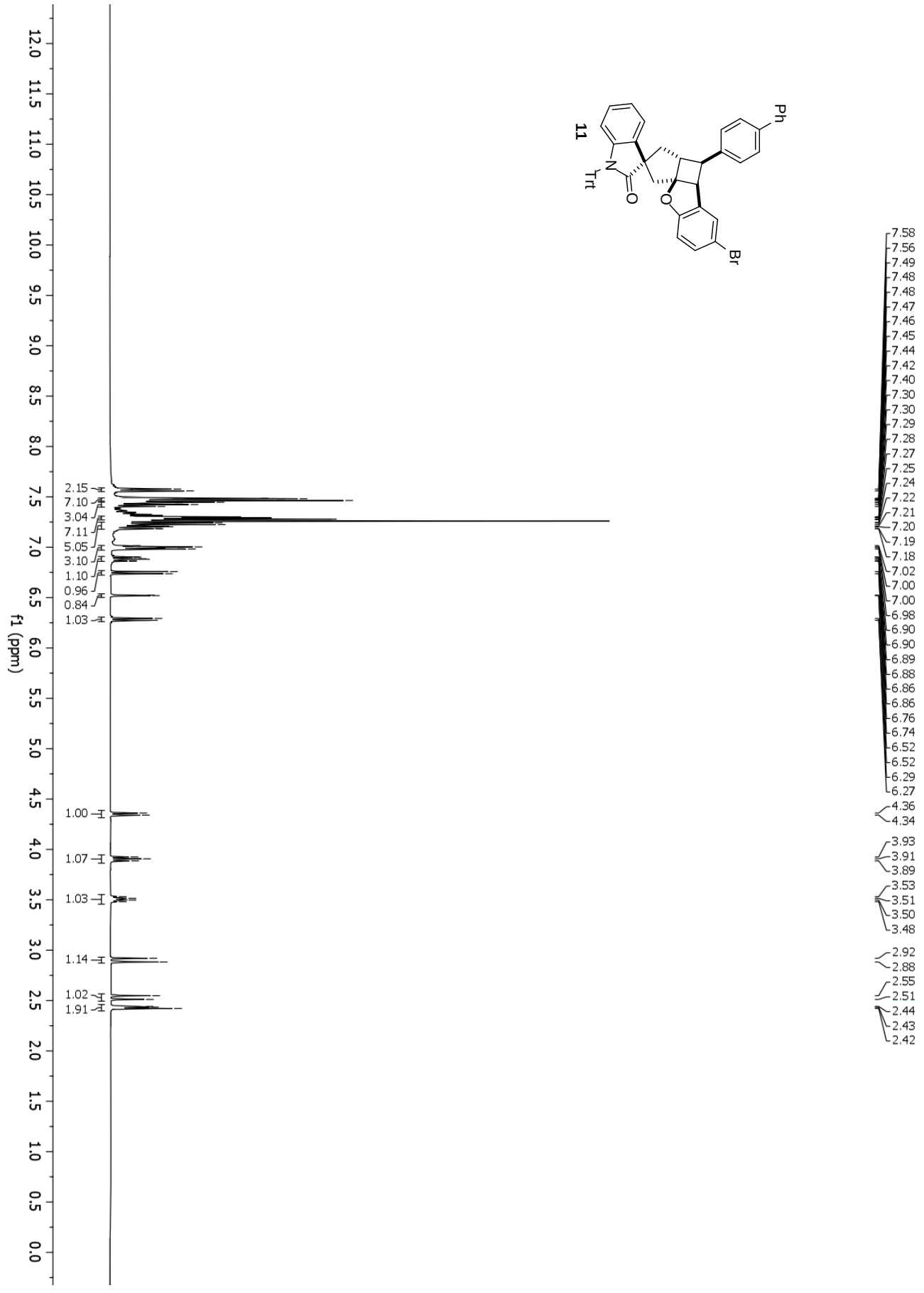
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10**



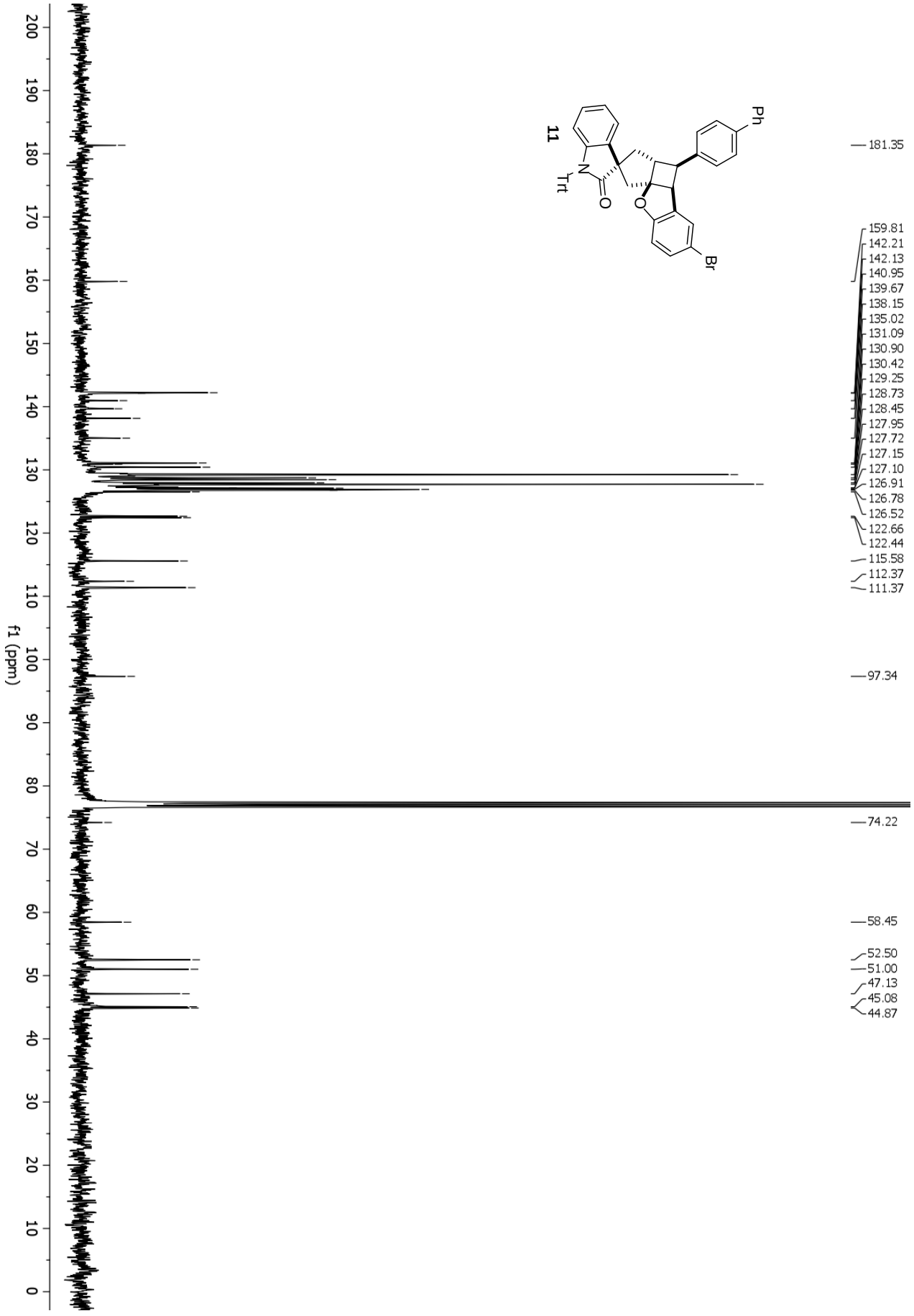
^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **10**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **11**



^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **11**



Diagnostic NMR signals for the relative configuration attribution of compounds 5 and 7

To assign the relative configuration of our pairs of diastereoisomers, we relay on an NMR pattern common to all diastereoisomers **5** and **7**. In fact, cyclopropyl methylene's signals were heavily influenced by the relative configuration of the nearby stereocenters, arising an "open" system in one of the two diastereoisomer and a "closed" system in the other one (figure 1). Since we unambiguously assign the relative (R),(S) configuration of compound **7b** via single-crystal X-ray diffraction analysis (see below) and, since that compound shows a "closed" methylene's system, we deduced that the "closed" system is related to (R),(S) relative stereochemistry, while the "open" system is related to a relative (R),(R) configuration. Moreover, as last observation, the polarity of the relative (R),(R) configuration diastereoisomers seems to be higher than the corresponding (R),(S) counterpart, another common pattern observed for every products **5** and for **7**.

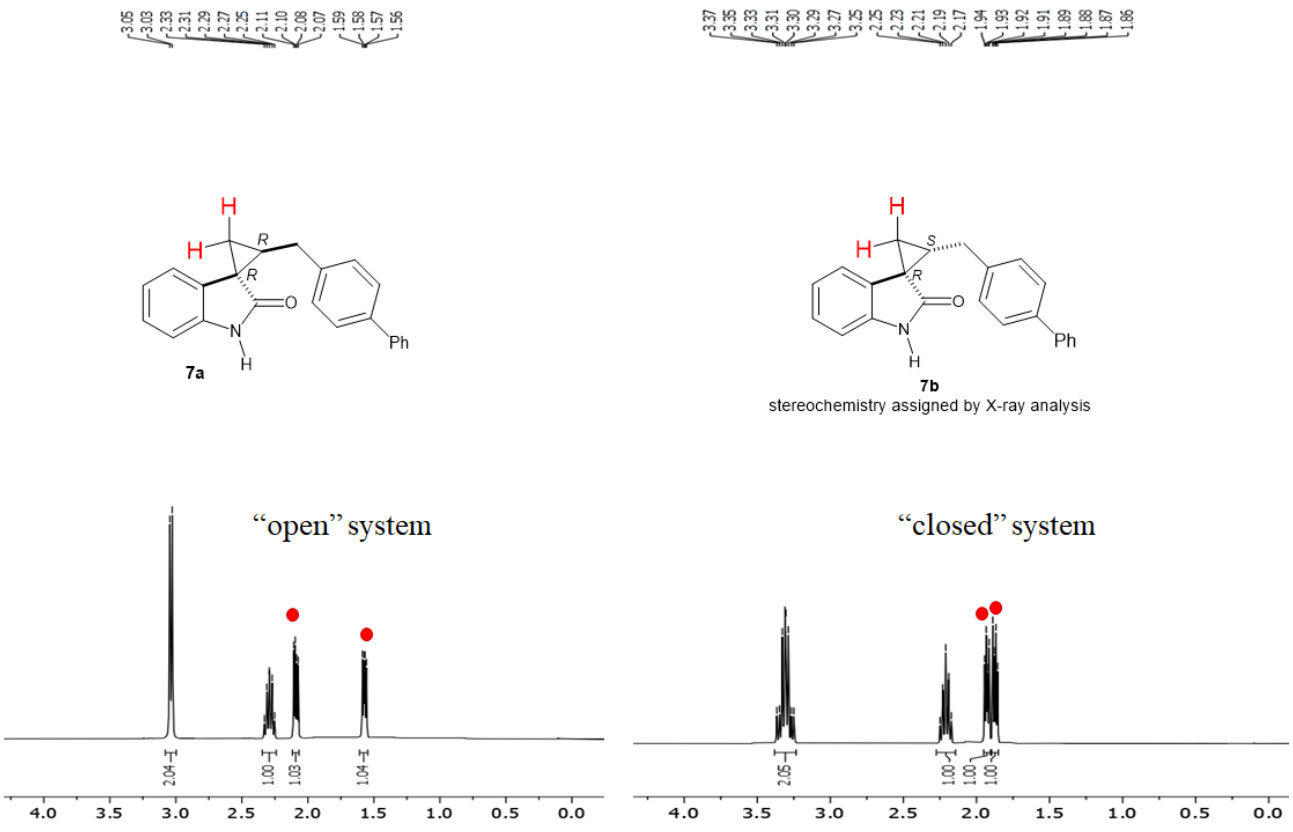


Figure 1: Comparison between the two cyclopropyl methylene's signals of compounds **7a** and **7b**, in which is possible to clearly observed the different "open" and "closed" system associated to the two different diastereoisomers. The relative configuration of compound **7b** was assigned by single-crystal X-ray analysis.

Diagnostic 2D-NOESY NMR signals for the relative configuration attribution of compound 11

To assign the relative configuration of compound **11** stereocenters, firstly we employed 2D-COSY and 2D-NOESY spectroscopy to unambiguously assign every aliphatic ^{1}H NMR signal to its corresponding hydrogen (figure 2).

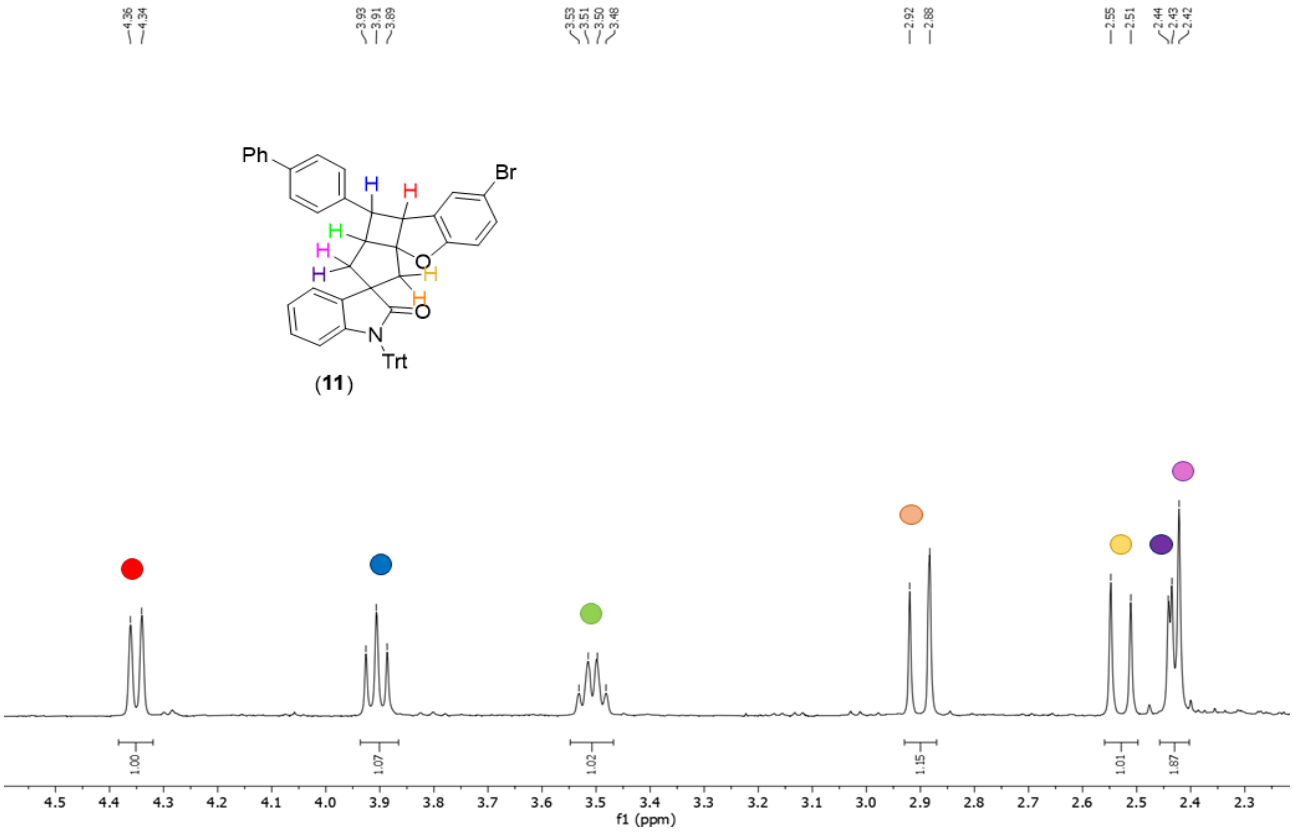


Figure 2: Identification of aliphatic ^{1}H NMR signals and attribution to their corresponding hydrogens.

Next, from 2D-NOESY spectra, the syn- conformation between H and H and the anti- conformation between H and H were assigned unambiguously. Moreover, again from 2D-NOESY signals, the relative syn-stereochemistry between H and H and between H and H were assigned (figure 3). It is noteworthy to remember that, in fused bicyclic systems, the five-membered ring junction should assume a syn-conformation in order to minimize the ring strain, so an anti- conformation is less favoured due to higher ring strain and it is generally observed only for cycles with more than 7 atoms. For this reason, both the 5-membered rings were assumed to have a syn- conformation around to the cyclobutane ring.

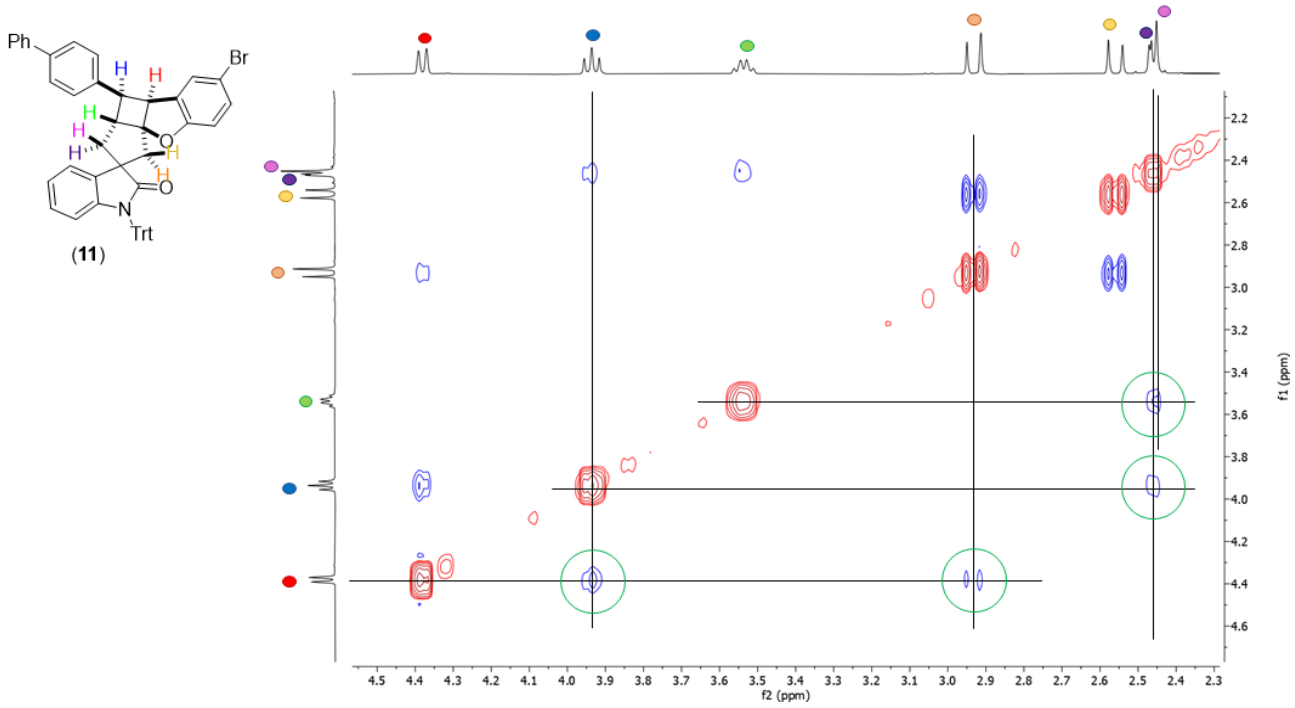


Figure 3: Identification of relevant NOE signals used for the relative stereochemistry attribution.

Finally, also some of the aromatic signals were assigned, and from the corresponding NOE signals the relative configuration of the last stereocenter was assigned (figure 4).

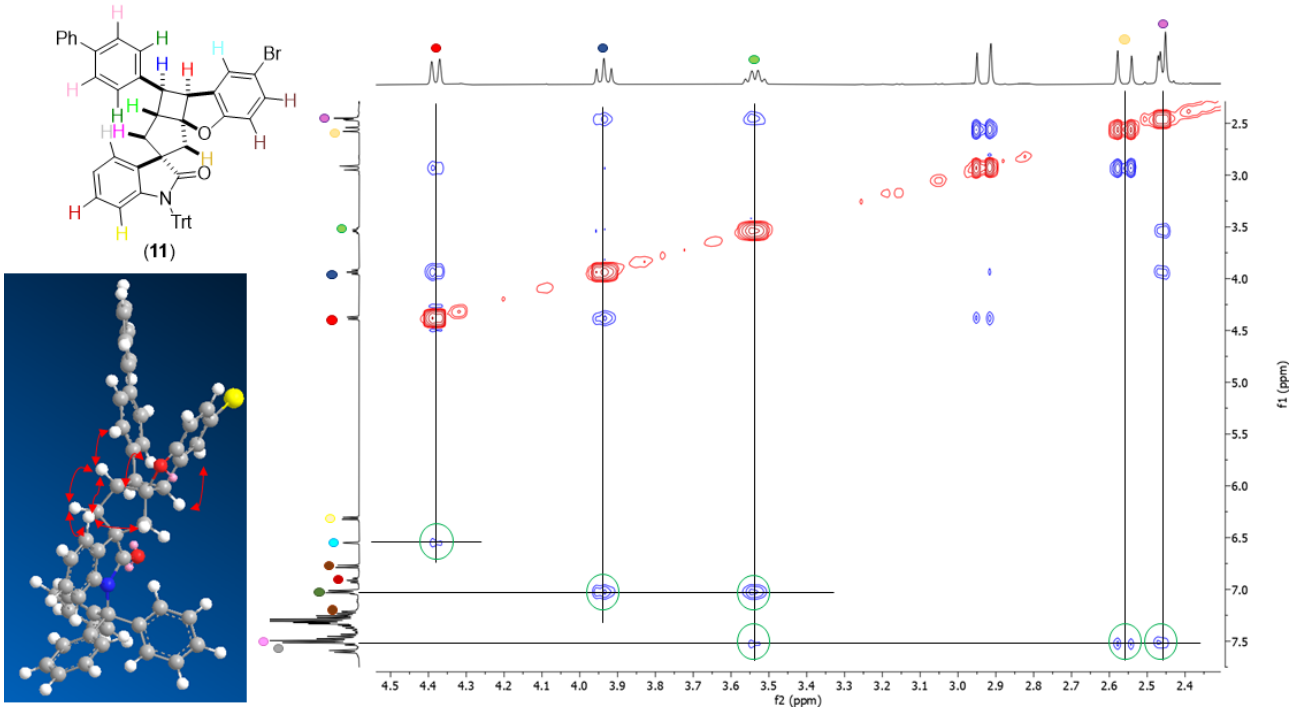


Figure 4: Identification of relevant NOE signals used for the relative configuration attribution. The red arrows in the molecular model represent observed relevant NOE signals. Model generated using Chem3D software and represented as product's most stable conformation.

To further confirmed the last attribution, since H and H signals in the aromatic region are overlapped, from the molecular model it is possible to observe that, if the relative stereochemistry of the oxindole's spiro C-3 was the opposite, a strong NOE signal between aromatic H and the two cyclobutane's H and H should be observed (figure 5). However, as seen in the reported 2D-NOESY spectra, no such signals were observed, as counterproof of the right assignment of the relative stereochemistry.

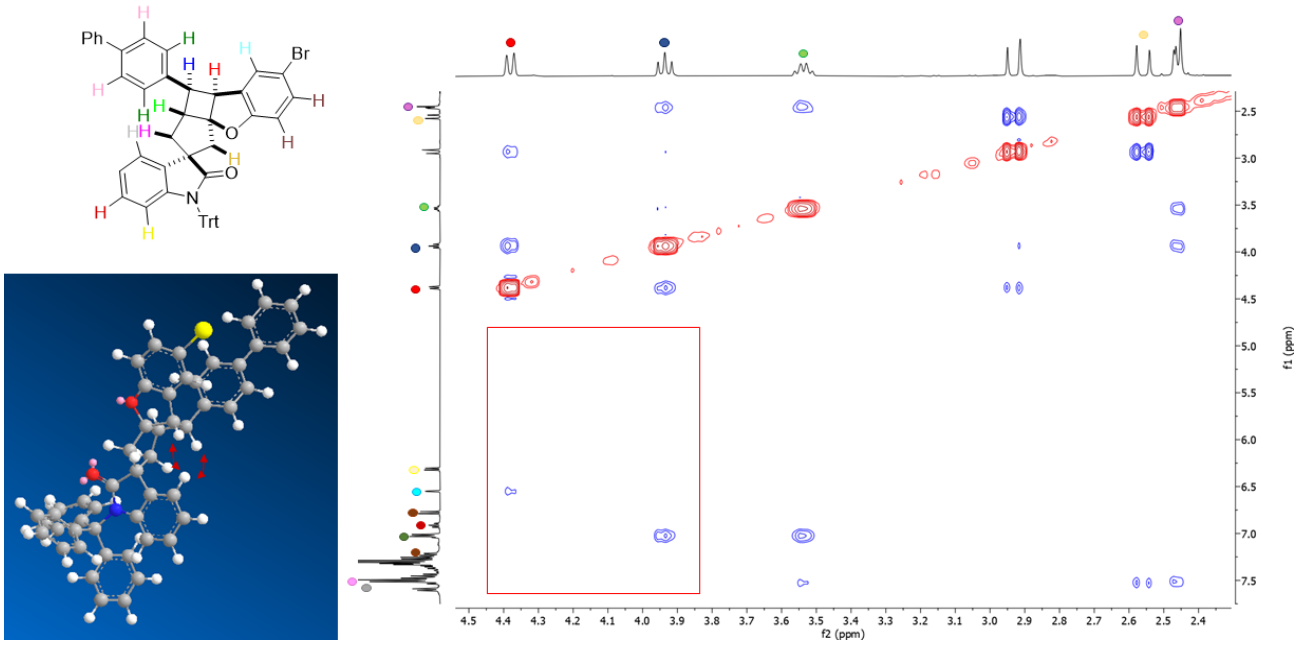


Figure 5: Molecular model representation of the opposite configuration at the oxindole's C-3 stereocenter. The red arrows in the molecular model represent expected, but not observed, relevant NOE signals. Model generated using Chem3D software and represented as product's most stable conformation.

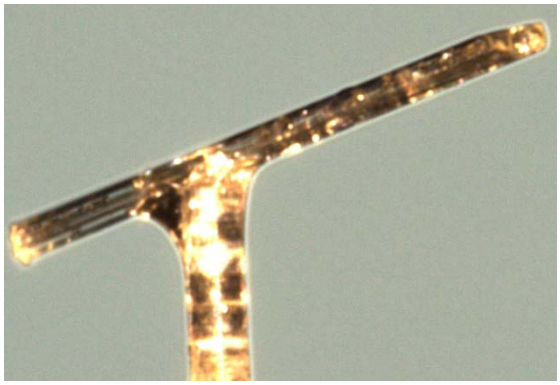
Single crystal X-ray diffraction analyses

CCDC 2307637 - 2307638 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structureswww.ccdc.cam.ac.uk/structures.

Data of compound 7b

Material appearance: colorless needles

Time of the last crystallization: 1 week
Crystallization method: slow evaporation



Sample specs:
Sample description: needle, transparent, colourless with dimensions 1.0 x 0.1 x 0.05 mm.
Mounting: on a glass fiber, with perfluorinated oil.
Comments: The sample shows weak pleochroism (from colorless to brown/grey) under polarized light. It was cut from a larger agglomerate using a blade and polished by mechanical ablation in a drop of perfluorinated oil.

Instrumental specs:
Device: Rigaku XtaLAB Synergy-S 4-circle diffractometer
Source: microfocus sealed tube
Detector: Hybrid Photon Counting (HPC)
Experiment temperature: 100(2) K
Cryostat: Oxford Cryosystem1000, N_2 flow
Wavelength: Mo K_α (0.71073 Å).
Data collection extent: full sphere within $\sin\vartheta/\lambda = 0.6$ Å^{-1}
Data collections specs: Detector-to-sample distance: variable, several ω-scan run.
Measured reflections: 39576, 8604 independent
Maximum resolution (ϑ): 31.303°
Completeness: 100.0% (ϑ full), 79.8% (ϑ max)

Data reduction programs:
Integration: CrysalisPro
Reduction: CrysalysPro
Structure solution and refinement: Shelxs 2018, Shelxl 2018

Unit cell, lattice and crystal system:
Bravais lattice: Triclinic, Primitive
Space group: P -1, N. 2
Point group: -1

Laue group: -1
Unit cell (Å, °, Å^3): a = 11.5430(6), b = 11.9861(9), c = 13.8670(9), α = 84.966(6), β = 76.217(5), γ = 62.126(6), V = 1646.5(2) as estimated from 8484 intense reflections among 2.775 e 31.006° of ϑ (final integration result).
Formula units in cell (Z): 4
Formula units in the asymmetric unit (Z'): 2
Number of electrons in cell (F_{000}): 688
Computed density: 1.313 g/cm^3
Linear absorption coefficient (μ): 0.080 mm^{-1}

Main statistical results:
Final stats for the spherical atom model (Shelxl):
Scale factor: 0.2714(16)
Secondary extinction coefficient: none
$<\Delta/\sigma>$ = 0.000
R1(F) = 0.1597 for 5996 $F_o > 4\sigma(F_o)$, 0.1936 for all the 8604 independent data
wR(F^2) = 0.4461 for all the measured data
Goodness-of-fit = 1.125
$\Delta\rho_{MAX/MIN}$ = +0.90 e/Å^3 at ~ 1.01 Å from the O1B oxygen / –0.65 e/Å^3 at ~ 1.022 Å from the C2A carbon

Molecular schemes

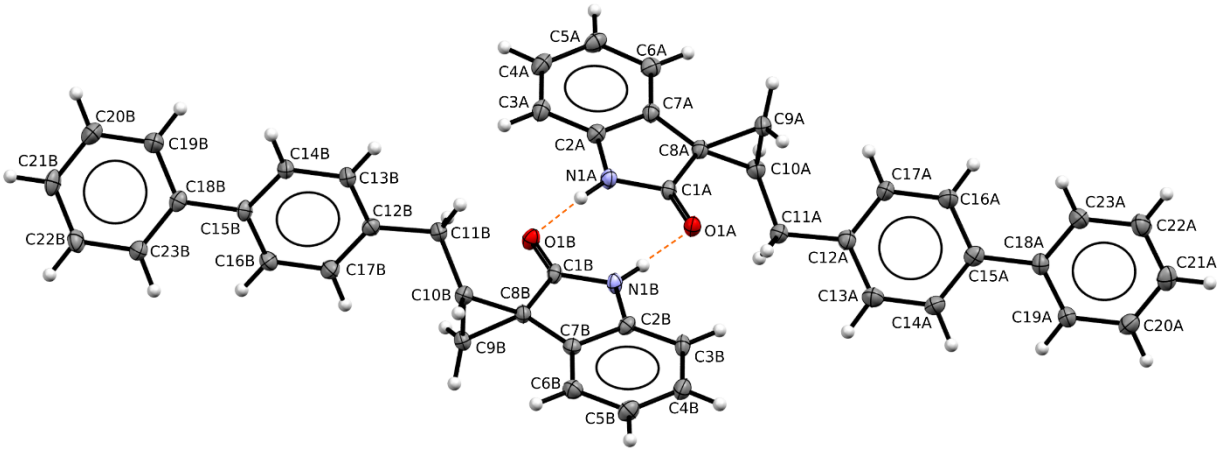


Figure 6. Asymmetric unit of **7b** at 100K, with the non-H atom-numbering scheme. Thermal ellipsoids of non-H atoms were drawn at the 50% probability level. The usual color code was employed for atoms (grey: C; white: H; blue: N; red: O).

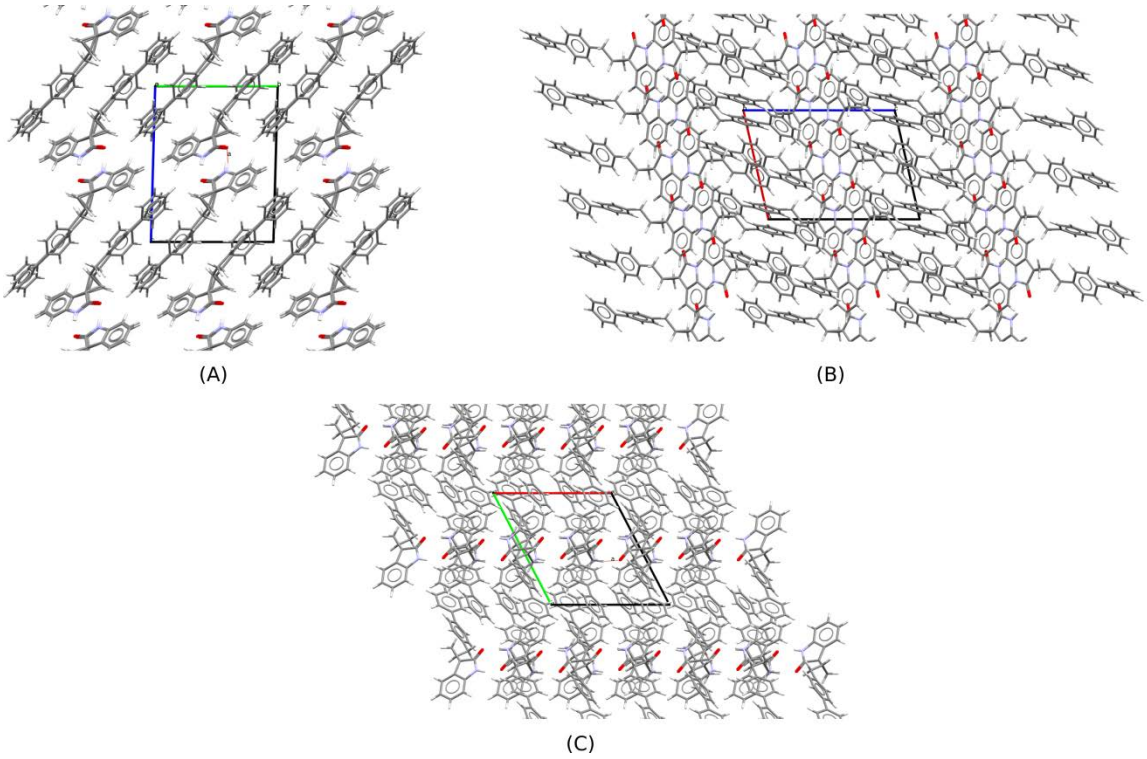


Figure 7. Crystal packing of **7b** at 100 K, as seen (A) along the *a* cell axis; (B) the *b* cell axis; (C) the *c* cell axis. Color code as in Figure 6.

Discussion and conclusions:

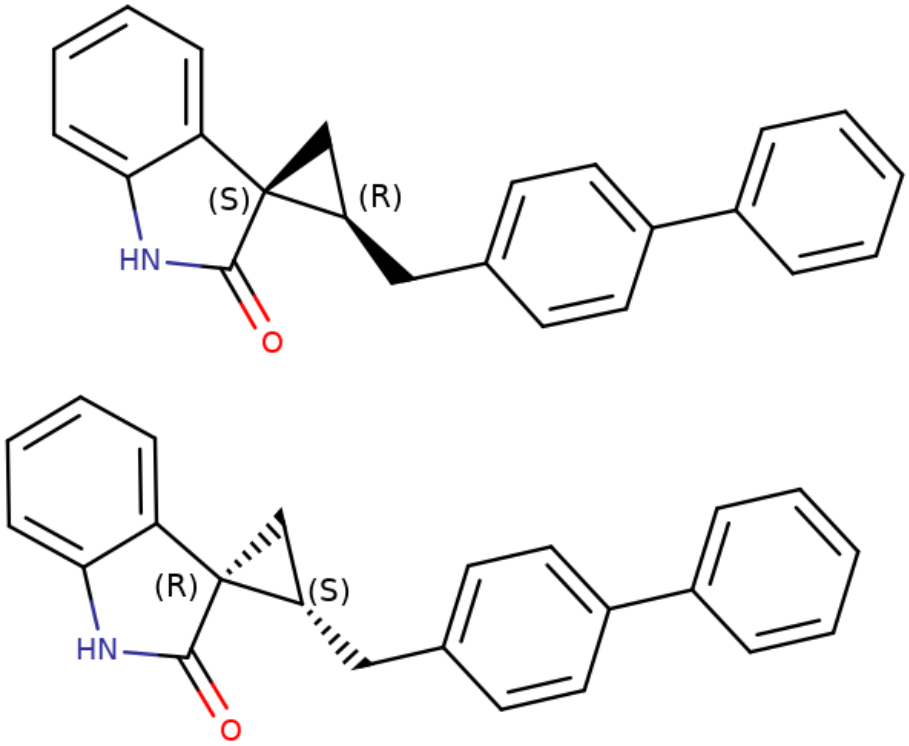


Figure 8. Molecular structure of **7b**, with the CIP descriptors highlighted in parentheses.

(1) The least squares statistical results reveal that the overall quality of the data collected is poor. The reasons are twofold. First, the crystal is twinned. The software was able to detect at least two different crystal orientations, although many more reflections were not indexed and therefore other, less important, components were also present. Since the data quality was not good enough to treat the second component in a confident way, we chose to consider only the primary component. Second, the collected spots are weak, as the crystal is weakly diffractive with the Mo X-ray source. However, the refined geometry is reliable enough to secure the chemical connectivity. No unexpected distortions or obviously wrong atom-atom bond lengths are present.

(2) The compound crystallizes in the triclinic achiral centric space group P-1 (N. 2) as a meso-form. Both stereoisomers are present in the crystal, and the asymmetric unit contains 2 molecules (Z'=2), for a total of 4 molecules in the crystal unit cell (Z=4). Figures 6 and 8 show the absolute configuration of the chiral centers C8A(S), C10A(R) and C8B(R), C10B(S).

(3) The two molecules in the ASU are almost symmetrical, as testified also by the symmetric geometrical parameters of the cyclic NH···O hydrogen bonds. The geometric analysis carried out with PLATON [A. L. Spek, Acta Cryst. 2009, D65, 148-155] finds indeed a 92% superposition due to a pseudo-inversion centre among the coordinates of the C, N, O atoms. However, this is not enough to fully symmetrize the system adding a true further inversion centre to the unit cell. The reason resides in the differences in the torsion angles within the biphenyl substituents. For instance, the torsion C8-C10-C11-C12 differs by ~9°: 147.66° and 156.85°, in absolute values. Accordingly, no obvious cell transformations were found to define possible higher-symmetry monoclinic structures.

(4) Fig. 7 shows the main packing motif of **7b**. The two enantiomers in the asymmetric unit interact through cyclic hydrogen bonds set up between the two amido groups of the γ–lactam ring (Figure 6). Table 1 reports the main geometrical data of the two hydrogen bonds involved between the two enantiomers. The hydrogen atoms of the N atoms have been added using geometric restraints, as the data quality was not sufficient to detect them as Fourier differences.

Table 1 N-H···O hydrogen bond contacts (HBs)

D–H···A	$d_{D–H}$, Å	$d_{H···A}$, Å	$d_{D···A}$, Å	α_{DHA}, °	Symmetry operation
N1A–H1NA···O1B	0.88	1.95	2.819(4)	168	x, y, z
N1B–H1NB··O1A	0.88	1.97	2.835(3)	168	x, y, z

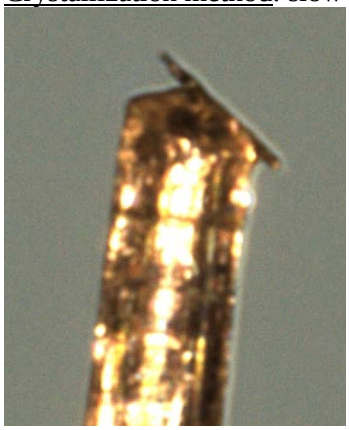
Few other intermolecular and intramolecular contacts are present, although these are only week C-H···O interactions (Table 2). No significant π-π stacking interactions are recognizable, and the aromatic rings are oriented in the space to maximize the packing efficiency, as expected.

Table 2: C-H···O HB contacts.

D–H···A	$d_{D–H}$, Å	$d_{H···A}$, Å	$d_{D···A}$, Å	α_{DHA}, °	Symmetry operation
C11A–H11B ··O1A	0.99	2.36	3.137(7)	135	intramolecular
C11B–H11C···O1B	0.99	2.38	3.115(7)	130	intramolecular
C9A–H9AA···O1B	0.99	2.59	3.416(7)	141	1-x, 1-y, 1-z
C9B–H9BB···O1A	0.99	2.51	3.374(8)	145	2-x, 1-y, 1-z
C21A–H21A···O1B	0.99	2.56	3.430(8)	152	x, 1+y, -1+z
C21B–H21B···O1A	0.95	2.57	3.413(6)	148	x, 1+y, -1+z

Data of compound 11

Material appearance: colorless needles
Crystallization method: slow evaporation, CH_2Cl_2 as solvent



Sample specs:

Sample description: needle, transparent, colourless with dimensions 1.0 x 0.1 x 0.1 mm.
Mounting: on a glass fiber, with perfluorinated oil.
Comments: The sample shows weak pleochroism (from colorless to blue) under polarized light. It was cut from a larger agglomerate using a blade, separated and polished by mechanical ablation in a drop of perfluorinated oil.

Instrumental specs:

Device: Rigaku XtaLAB Synergy-S 4-circle diffractometer
Source: microfocus sealed tube
Detector: Hybrid Photon Counting (HPC)
Experiment temperature: 293(2) K
Cryostat: Oxford Cryosystem1000, N_2 flow
Wavelength: Cu K_a (1.54184 Å).
Data collection extent: full sphere within $\sin\vartheta/\lambda = 0.5$ Å^{-1}
Data collections specs: Detector-to-sample distance: variable, several w-scan run.
Measured reflections: 26125, 5126 independent
Maximum resolution (ϑ): 51.83°
Completeness: 97.4% (ϑ full), 97.4% (ϑ max)

Data reduction programs:
Integration: CrysalisPro
Reduction: CrysalysPro
Structure solution and refinement: Shelx

Unit cell, lattice and crystal system:
Bravais lattice: Monoclinic, Primitive
Space group: P $2_1/n$ (number 14)
Point group: 2/m
Laue group: 2/m
Unit cell (Å, °, Å^3): a = 21.2019(13), b = 9.5258(5), c = 24.3433(9), b = 105.859(6), V = 4729.3(5) as estimated from 4458 intense reflections among 3.2170 e 50.0650° of ϑ (final integration result).
Formula units in cell (Z): 4
Formula units in the asymmetric unit (Z'): 1
Number of electrons in cell (F_{000}): 1608
Computed density: 1.091 g/cm^3

Linear absorption coefficient (μ): 1.454 mm^{-1}

Main statistical results:
Final stats for the spherical atom model (Shelxl):
Scale factor: 0.2766(10)
Secondary extinction coefficient:
$<\Delta/\sigma>$ = 0.000
R1(F) = 0.0732 for 2469 $F_o > 4s(F_o)$, 0.1506 for all the 5126 independent data
$wR(F^2)$ = 0.2096 for all the measured data
Goodness-of-fit = 0.950
$\Delta\rho_{MAX/MIN}$ = +0.32 e/$Å^3$ at ~ 1.47 Å from the Br1 bromine atom / –0.41 e/$Å^3$ at ~ 1.019 Å from the Br1 bromine.

Molecular schemes

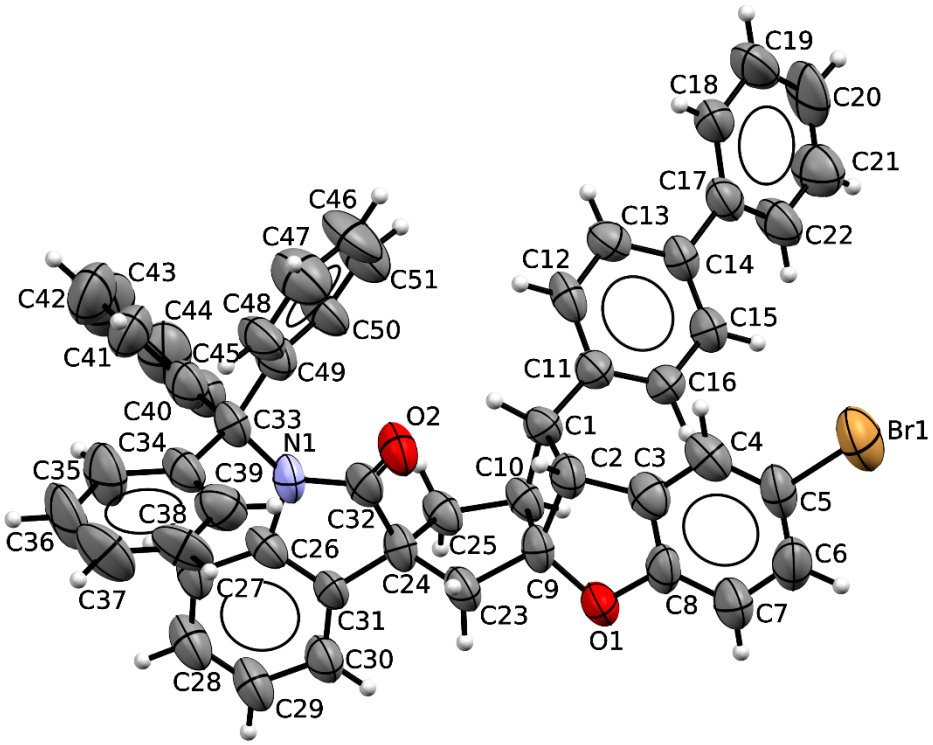


Figure 9. Asymmetric unit of **11** at RT, with the non-H atom-numbering scheme. Thermal ellipsoids of non-H atoms were drawn at the 50% probability level. Atom color code is grey: C; white: H; blue: N; red: O; gold: Br.

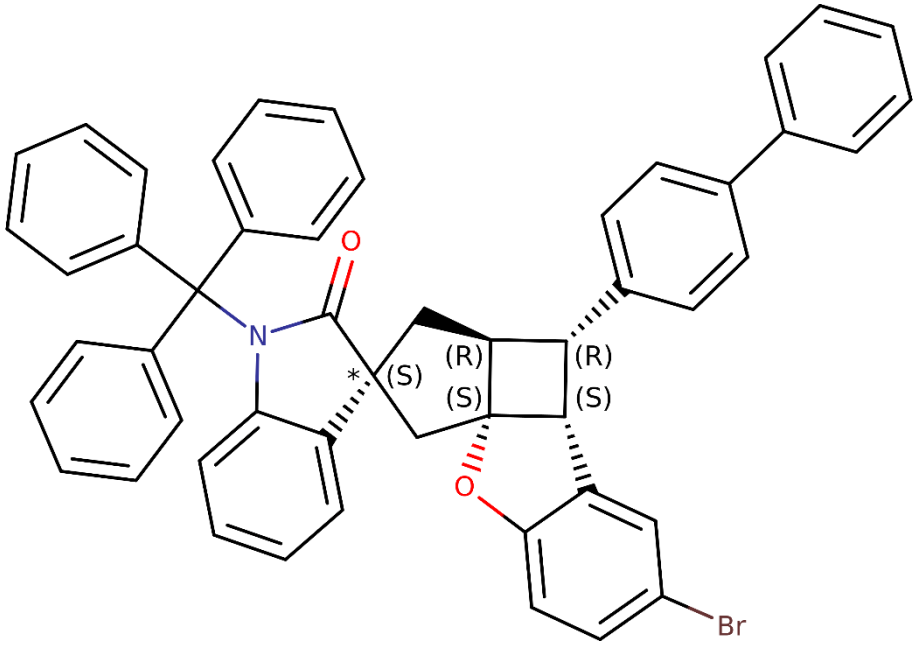


Figure 10. Molecular structure of one of the enantiomers (C24(S)-C10(S)-C9(R)-C1(S)-C2(R)) of compound **11**. Since the crystal space group is centrosymmetric, the other enantiomer is also present, but it is not depicted here.

Discussion and conclusions:

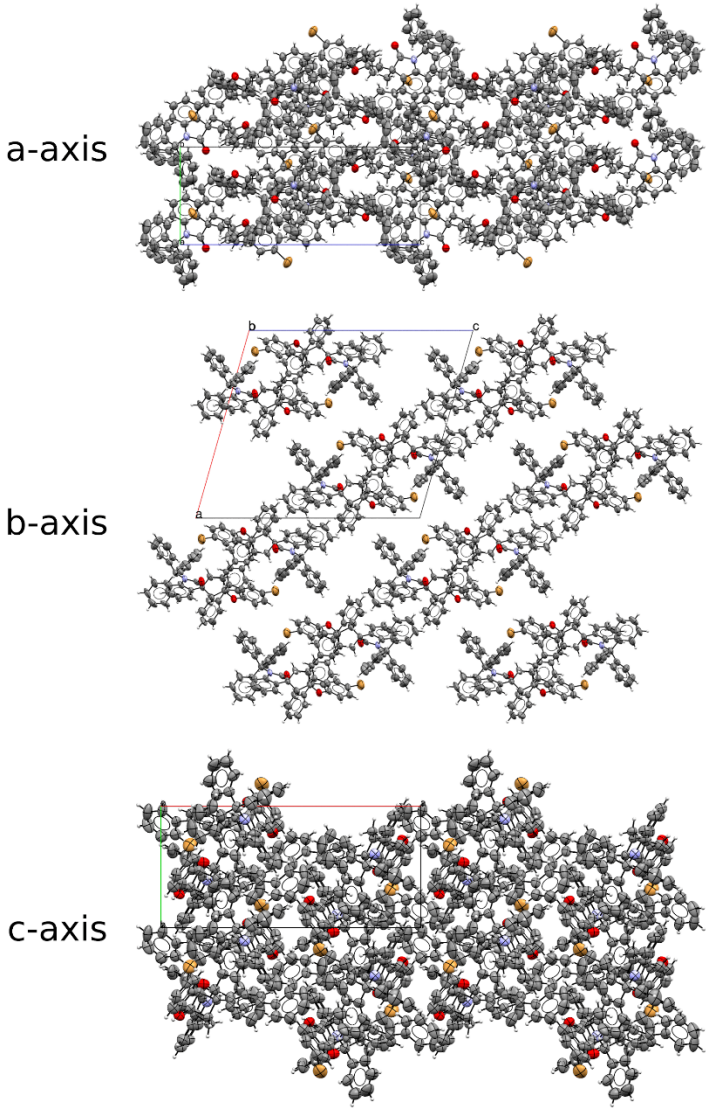


Figure 11. Crystal packing of **11** at RT, as seen along the *a* (top), *b* (center) and *c* (bottom) *cell axis*

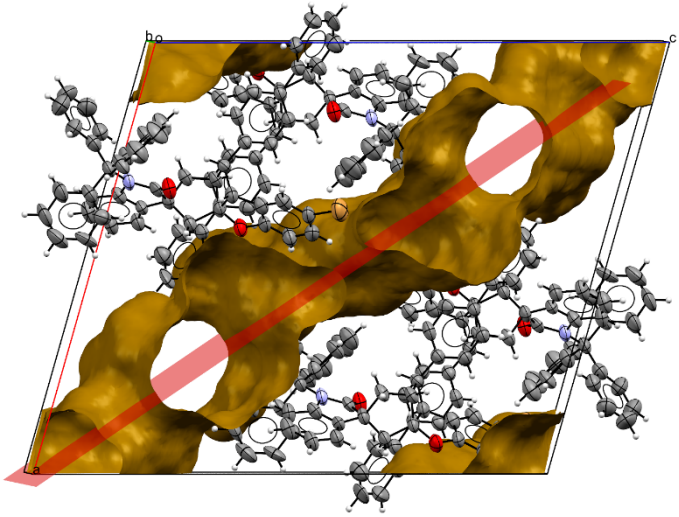


Figure 12. Void volume view along the b cell axis. The (101) crystallographic plane is depicted in red. The size of the void is ~28 % of the total unit cell volume.

Data refinement

Data integration reveals that the collected crystal exhibits twinning, with the primary component constituting roughly 78% of the total composition. Due to low data quality, we made the decision to focus solely on the primary component. Furthermore, the crystal sample exhibits weak or even non-existent diffraction at high 2ϑ angles, primarily due to the presence of a significant intrinsic disorder (as discussed in the crystal structure section). Consequently, the collected data has a maximum ϑ resolution of about 50°. Nevertheless, the refined geometry is sufficiently reliable to secure the correct chemical connectivity. No unexpected distortions or significant deviation in atom-atom bond lengths are observed.

Molecular structure

The title compound crystallizes in the monoclinic, achiral, centrosymmetric space group $P2_1/n$ (No. 14) as a meso-form. The crystal contains both stereoisomers, with the asymmetric unit consisting of a single molecule (Z'=1), resulting in a total of four molecules in the crystal unit cell (Z=4).

One enantiomer (C24(S)-C10(S)-C9(R)-C1(S)-C2(R), calculated in accordance with the Cahn-Ingold-Prelog rules) is reported in Figures 9 and 11, while the other stereoisomer is not reported but is present in the crystal because of the presence of the inversion center symmetry elements.

Crystal structure

Figure 10 illustrates the crystal packing of the title compound along the three principal lattice axes. Notably, there are no strong intermolecular interactions between the molecules in the crystal, primarily due to the absence of strong donor-acceptor pairs of atoms. This lack of strong interactions likely accounts for the formation of extensive void channels lying on the (101) plane, which are prominently visible in Figure 12. This is further supported by the calculated density value of 1.091 g/cm^3, a notably low value for an organic molecule. The total calculated void volume within the unit cell is approximately 1310 Å, accounting for roughly 28 % of the total cell volume. This area is expected to contain disordered solvent molecules. The analysis of the residual electron density in the void area by using the SQUEEZE procedure (A. L. Spek, Acta

Cryst. Sect. C, 2015, 71, 9-18) estimate the presence of 328 electrons. This amount corresponds to an average of about 7.8 CH_2Cl_2 molecules per unit cell, or roughly 2 solvent molecules for every MM103 molecule. For these reasons, the SQUEEZE procedure was applied to remove the contribution of the disordered solvent from the structure factors. This procedure leads to a significant improvement of the R agreement factor, from about 13% to almost 7%.

For completeness, Table 3 provides the geometrical data concerning the limited number of intra- and inter-molecular weak C-H···O interactions. Most of these interactions are intramolecular, which is something expected due to the conformational rigidity of the molecule. No significant π-π stacking interactions are recognizable, and the aromatic rings are oriented in the space to maximize the packing efficiency, as expected.

Table 3: weak C-H···O HB contacts.

D–H···A	$d_{D–H}$, Å	$d_{H···A}$, Å	$d_{D···A}$, Å	α_{DHA}, °	Symmetry operation
C1–H1 ··O2	0.99	2.43	3.120(9)	126	intramolecular
C2–H2···O2	0.99	2.51	3.070(9)	115	intramolecular
C45–H45···N1	0.94	2.46	2.831(11)	103	intramolecular
C22–H22···O2	0.94	2.29	3.212(11)	166	½-x, ½+y, ½-z