Synthesis and Biological Evaluation of Calothrixins B and their Deoxygenated Analogues

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Supporting Information

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(*E*)-1-(2-(2-Nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13a

A solution of ylide **11** (6 g, 10.47 mmol) and 2-nitrobenzaldehyde **12a** (1.74 g, 11.52 mmol) in dry DCM (80 mL) was refluxed for 8 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with cold methanol (20 mL) afforded **13a** (4.28 g, 92%); as a yellow solid. mp: 154-156 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, J = 8.1 Hz, 1 H, ArH), 8.10 (d, J = 8.1 Hz, 1 H, ArH), 7.94 (t, J = 6.5 Hz, 2 H, ArH), 7.80-7.77 (m, 3 H, ArH), 7.71 (d, J = 16.2Hz, 1 H, vinylic -CH), 7.60-7.51 (m, 2 H, ArH), 7.43-7.31 (m, 4 H, ArH), 7.19 (d, J = 15.9 Hz, 1 H, vinylic -CH), 2.50 (s, 3 H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.3, 147.9, 139.9, 137.6, 135.9, 135.0, 134.5, 134.0, 131.6, 129.8, 129.5, 129.3, 127.9, 126.9, 126.3, 125.2, 125.1, 123.7, 123.1, 121.8, 114.6, 30.9 ppm; HRMS (EI): m/z cacld for $C_{24}H_{18}N_2O_5S$ [M^+]: 446.0936; found: 446.0930.

(*E*)-1-(2-(3-Methoxy-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13b

A solution of ylide **11** (3 g, 5.23 mmol) and 3-methoxy-2-nitrobenzaldehyde **12b**[1] (1.04 g, 5.75 mmol) in dry DCE (50 mL) was refluxed for 12 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) afforded **13b** (2.12 g, 85%) as a yellow solid. mp: 218-220 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 8.1 Hz, 1 H, ArH), 7.97 (d, J = 7.8 Hz, 1 H, ArH), 7.79 (d, J = 16.2 Hz, 1 H, vinylic –CH) , 7.72-7.70 (m, 2 H, ArH), 7.55-7.46 (m, 3 H, ArH), 7.42-7.31 (m, 4 H, ArH), 7.09 (d, J = 7.8 Hz, 1 H, ArH), 6.52 (d, J = 15.9 Hz, 1 H, vinylic -CH), 3.94 (s, 3 H, -OMe), 2.43 (s, 3 H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.0, 151.1, 140.7, 139.6, 137.6, 136.0, 134.6, 131.8, 131.5, 129.5, 129.3, 127.9, 126.8, 126.4, 125.2, 123.7, 123.6, 121.9, 118.4, 114.5, 113.1, 56.6, 30.6 ppm; HRMS (EI): m/z cacld for $C_{25}H_{20}N_2O_6S$ [M^+]: 476.1042; found: 476.1040.

(*E*)-1-(2-(5-Methoxy-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13c

A solution of ylide **11** (3 g, 5.23 mmol) and 5-methoxy-2-nitrobenzaldehyde **12c**[2] (1.17 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 10 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13c** (2.29 g, 92%) as a yellow solid. mp: 180-184 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.23-8.16 (m, 2 H, ArH), 7.95 (d, J = 7.2 Hz, 1 H, ArH), 7.80-7.77 (m, 2 H, ArH), 7.65 (d, J = 15.6 Hz, 1 H, vinylic –CH), 7.51 (d, J = 7.5 Hz, 1 H, ArH), 7.50-7.40 (m, 3 H, ArH), 7.37-7.29 (m, 3 H, ArH), 7.00 (d, J = 8.7 Hz, 1 H, ArH), 3.99 (s, 3 H, -OMe), 2.52 (s, 3 H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.3, 163.8, 140.8, 139.9, 137.6, 136.0, 135.9, 134.7, 134.5, 132.0, 129.5 128.0, 126.9, 126.2, 125.2, 123.6, 123.0, 121.8, 114.5 (2C), 114.4, 56.2, 30.9 ppm; Anal. Calcd for $C_{25}H_{20}N_2O_6S$, C: 63.02; H: 4.23; N: 5.88. Found, C: 63.15; H: 4.35; N: 5.96.

(*E*)-1-(2-(4, 5-Dimethoxy-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13d

A solution of ylide **11** (5 g, 8.72 mmol) and 4, 5-dimethoxy-2-nitrobenzaldehyde **12d** (2.03 g, 9.60 mmol) in dry DCM (70 mL) was refluxed for 12 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with cold methanol (15 mL) afforded **13d** (3.86 g, 88%) as a yellow solid.Yield: mp: 136-138 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, J = 8.1 Hz, 1 H, ArH), 7.97 (d, J = 7.8 Hz, 1 H,

ArH), 7.76 (d, *J* = 7.8 Hz, 2 H, ArH), 7.71 (s, 1 H, ArH), 7.62 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 7.53 (t, *J* = 7.5 Hz, 1 H, ArH), 7.42-7.39 (m, 2 H, ArH), 7.37-7.29 (m, 4 H, ArH), 4.11 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 2.53 (s, 3 H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.3, 153.7, 149.5, 140.4, 140.2, 137.6, 135.9, 134.5, 129.4, 128.0, 126.8, 126.7, 126.2, 125.2, 123.4, 122.0, 121.9, 114.5, 110.3, 108.0, 56.7, 56.6, 30.8 ppm; HRMS (EI): m/z cacld for $C_{26}H_{22}N_2O_7S$ [M^+]: 506.1148; found: 506.1140.

(*E*)-1-(2-(2-(6-Nitrobenzo[d][1,3]dioxol-5-yl)vinyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13e

A solution of ylide **11** (5 g, 8.72 mmol) and 6-nitrobenzo[*d*][1,3]dioxole-5-carbaldehyde **12e** (1.87 g, 9.60 mmol) in dry 1,2-DCE (70 mL) was refluxed for 6 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (20 mL) afforded **13e** (3.84 g, 90%) as a yellow solid. mp: 184-188 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 1 H, ArH), 7.95 (d, *J* = 7.8 Hz, 1 H, ArH), 7.77 (d, *J* = 7.8 Hz, 2 H, ArH), 7.61 (s, 1 H, ArH), 7.55-7.51 (m, 3 H, ArH), 7.43-7.28 (m, 5 H, ArH), 7.19 (d, *J* = 15.6 Hz, 1 H, vinylic -CH), 6.21 (s, 2 H, $-CH_2$) 2.49 (s, 3 H, $-CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.2, 152.5, 148.6, 142.4, 140.0, 137.6, 135.9, 135.5, 134.5, 129.4, 128.6, 128.0, 126.9, 126.2, 125.2, 123.6, 122.1, 121.8, 114.5, 107.6, 105.8, 103.4, 30.9 ppm; HRMS (EI): m/z cacld for $C_{25}H_{18}N_2O_7S$ [M^+]: 490.0835; found: 490.0841.

(*E*)-1-(2-(4-Bromo-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13f

A solution of ylide **11** (3 g, 5.23 mmol) and 4-bromo-2-nitrobenzaldehyde **12f**[3] (1.32 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 10 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13f** (2.47 g, 90%) as a yellow solid. mp: 176-178 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H, ArH), 8.02-7.91 (m, 3 H, ArH), 7.79-7.67 (m, 4 H), 7.55 (d, *J* = 7.5 Hz, 1 H, ArH), 7.52-7.32 (m, 4 H), 7.17 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 2.50 (s, 3 H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 196.7, 147.1, 140.5, 137.1, 135.3, 135.2, 133.9, 133.3, 133.0, 131.9, 130.0, 128.3, 127.8, 127.1, 127.0, 126.4, 125.3, 124.1, 123.0, 122.0, 114.5, 31.0 ppm; HRMS (EI): m/z cacld for $C_{24}H_{17}BrN_2O_5S$ [M^+]: 524.0042; found: 514.0040.

(*E*)-1-(2-(4-Chloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13g

A solution of ylide **11** (5 g, 8.72 mmol) and 4-chloro-2-nitrobenzaldehyde **12g**[4] (1.78, 9.60 mmol) in dry DCM (70 mL) was refluxed for 6 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (20 mL) afforded **13g (**3.93 g, 94%); as a yellow solid. mp: 160-162 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 1 H, ArH), 8.10 (d, *J* = 8.1 Hz, 1 H, ArH), 7.94-7.90 (m, 2 H, ArH), 7.76-7.67 (m, 4 H, ArH), 7.54 (t, *J* = 7.2 Hz, 1 H, ArH), 7.37-7.32 (m, 4 H, ArH), 7.12 (d, *J* = 15.9 Hz, 1 H, vinylic –CH), 2.49 (s, 3H, $-CH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.1, 148.0, 139.3, 137.6, 136.0, 135.6, 134.5, 134.1, 133.5, 130.3, 130.0, 129.5, 127.8, 126.8, 126.4, 125.3, 123.9, 123.7, 121.8, 114.6, 30.9 ppm; HRMS (EI): m/z cacld for $C_{24}H_{17}ClN_2O_5S$ [M^+]: 480.0547; found: 480.0540.

(*E*)-1-(2-(4-Fluoro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13h

A solution of ylide **11** (5 g, 8.72 mmol) and 4-fluoro-2-nitrobenzaldehyde **12h**[5] (1.61 g, 9.60 mmol) in dry DCM (70 mL) was refluxed for 6 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (20 mL) afforded **13h** as a yellow solid. (3.76 g, 93%); mp: 142-144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H, ArH), 7.94-7.92 (m, 2 H, ArH), 7.85-7.82 (m, 1 H, ArH), 7.76 (d, *J* = 7.5 Hz, 2 H, ArH), 7.65 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 7.56-7.51 (m, 2 H, ArH), 7.42-7.31 (m, 4 H, ArH), 7.14 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 2.50 (s, 3 H, -CH_3) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.1, 162.2 (d, *J* = 252.8 Hz), 148.2 (d, *J* = 8.3 Hz), 139.6, 137.6, 135.9, 134.5, 133.8, 131.2 (d, *J* = 8.3 Hz), 129.5, 128.1 (d, *J* = 4.5 Hz), 127.9, 126.8, 126.4 (d, *J* = 15.8 Hz), 125.2, 123.7, 123.3, 121.8, 121.5 (d, *J* = 21.8 Hz), 114.5, 112.7 (d, *J* = 27 Hz), 30.9 ppm; HRMS (EI): m/z cacld for $C_{24}H_{17}FN_2O_5S$ [M^+]: 464.0842; found: 464.0840.

(*E*)-1-(2-(5-Bromo-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13i

A solution of ylide **11** (3 g, 5.23 mmol) and 5-bromo-2-nitrobenzaldehyde **12i**[6] (1.74 g, 11.52 mmol) in dry DCM (50 mL) was refluxed for 12 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with cold methanol (15 mL) afforded **13i** (2.47 g, 90%) as a yellow solid. mp: 170-172 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H, ArH), 8.02-7.91 (m, 3 H, ArH), 7.79-7.67 (m, 4 H, ArH), 7.55 (t, *J* = 7.5 Hz, 1 H, ArH), 7.52-7.32 (m, 4 H, ArH), 7.17 (d, *J*=15.9Hz, 1 H, vinylic –CH), 2.50 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 196.7, 147.1, 140.5, 137.1, 135.3, 135.2, 133.9, 133.3, 133.0, 131.9, 130.0, 128.3, 127.8, 127.1, 127.0, 126.4, 125.3, 124.1, 123.0, 122.0, 114.5, 31.0 ppm; Anal. Calcd for $C_{24}H_{17}BrN_2O_5S$, C: 54.87; H: 3.26; N: 5.33. Found, C: 55.02; H: 3.19; N: 5.51.

(*E*)-1-(2-(5-Chloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13j

A solution of ylide **11** (3 g, 5.23 mmol) and 5-chloro-2-nitrobenzaldehyde **12j**[7] (1.06 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 10 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13j** (2.29 g, 91%) as a yellow solid. mp: 166-168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 1 H, ArH), 8.07 (d, *J* = 8.7 Hz, 1 H, ArH), 7.92 (d, *J* = 7.8 Hz, 1 H, ArH), 7.86 (s, 1 H, ArH), 7.79-7.76 (m, 2 H, ArH), 7.70 (d, *J* = 15.6 Hz, 1 H, vinylic -CH), 7.57-7.51 (m, 2 H, ArH), 7.44-7.39 (m, 3 H, ArH), 7.34 (t, *J* = 7.5 Hz, 1 H, ArH), 7.19 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 2.50 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.0, 146.0, 140.5, 139.1, 136.0, 134.6, 133.5, 133.4, 129.6, 129.5, 129.1, 127.8, 126.8, 126.7, 125.2, 124.3, 124.0, 121.8, 114.6, 31.0 ppm; Anal. Calcd for $C_{24}H_{17}ClN_2O_5S$, C: 59.94; H: 3.56; N: 5.82. Found, C: 59.83; H: 3.69; N: 5.98.

(*E*)-1-(2-(2-Chloro-6-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13k

A solution of ylide **11** (3 g, 5.23 mmol) and 2-chloro-6-nitrobenzaldehyde **12k**[8] (1.06, 5.75 mmol) in dry DCE (50 mL) was refluxed for 12 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) afforded **13k** (2.01 g, 80%) as a yellow solid. mp: 156-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H, ArH), 7.77-7.73 (m, 5 H, ArH), 7.70 (s, 1 H, ArH), 7.54 (t, *J* = 7.5 Hz, 1 H, ArH), 7.48-7.35 (m, 4 H, ArH), 7.31 (d, *J* = 7.5 Hz, 1 H, Ar-H), 6.88 (d, *J*=16.2

Hz, 1 H, vinylic –CH), 2.60 (s, 3H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 198.6, 150.4, 138.2, 137.6, 136.0, 135.2, 134.4, 134.2, 129.9, 129.4, 128.7, 127.9, 126.9 (2C), 126.4, 125.1, 124.5, 123.0, 121.3, 114.8, 30.8 ppm; Anal. Calcd for $C_{24}H_{17}ClN_2O_5S$, C: 59.94; H: 3.56; N: 5.82. Found, C: 59.83; H: 3.69; N: 5.98.

***(E)*-1-(2-(3-Chloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13l**

A solution of ylide **11** (3 g, 5.23 mmol) 3-chloro-2-nitrobenzaldehyde **12l**[9] (1.06 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 12 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13l (**2.24 g, 89%) as a yellow solid. mp: 166-168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 8.1 Hz, 1 H, ArH), 7.86 (d, J = 7.8 Hz, 1 H, ArH), 7.77-7.71 (m, 2 H, ArH), 7.63-7.60 (m, 2 H, ArH), 7.47 (m, 3 H, ArH), 7.35-7.29 (m, 3 H, ArH), 7.24-7.18 (m, 1 H, ArH), 6.44 (d, J = 15.9 Hz, 1 H, vinylic –CH), 2.36 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 196.8, 148.5, 138.9, 137.5, 136.0, 134.6, 131.4, 130.8, 130.6, 130.0, 129.5, 127.8, 126.7, 126.5, 125.8, 125.5, 125.2, 124.7, 123.9, 121.9, 114.5, 30.7 ppm; Anal. Calcd for $C_{24}H_{17}ClN_2O_5S$, C: 59.94; H: 3.56; N: 5.82. Found, C: 59.81; H: 3.72; N: 5.92.

(*E*)-1-(2-(5-Bromo-4-fluoro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13m

A solution of ylide **11** (3 g, 5.23 mmol) and 5-bromo-4-fluoro-2-nitrobenzaldehyde **12m**[10] (1.42 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 8 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13m** (2.52 g (89%) as a yellow solid. mp: 218-222 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, J = 8.1 Hz, 1 H, ArH), 8.03 (d, J = 6.6 Hz, 1 H, ArH), 7.83-7.81 (m, 2 H, ArH), 7.67 (d, J = 7.5 Hz, 2 H, ArH), 7.57 (d, J = 15.6 Hz, 1 H, vinylic –CH), 7.45 (t, J = 6.9 Hz, 1 H, ArH), 7.35-7.27 (m, 3 H, ArH), 7.25-7.22 (m, 1 H, ArH), 7.07 (d, J = 15.9 Hz, 1 H, vinylic -CH), 2.42 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.0, 158.7 (d, J = 254.8 Hz), 146.8, 139.0, 137.6, 136.0, 134.6, 132.6, 129.5, 129.3, 129.2, 127.8, 126.8, 126.4, 125.2, 124.2, 121.8, 116.6 (d, J = 21.9 Hz), 114.6, 113.5 (d, J = 27.8 Hz), 31.0 ppm; HRMS (EI): m/z cacld for $C_{24}H_{16}BrFN_2O_5S$ [M^+]: 541.9947; found: 541.9945.

(*E*)-1-(2-(5-Chloro-4-fluoro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13n

A solution of ylide **11** (3 g, 5.23 mmol) and 5-chloro-4-fluoro-2-nitrobenzaldehyde **12n**[11] (1.17 g, 5.75 mmol) in dry chloroform (50 mL) was refluxed for 8 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13n** (2.35 g, 90%) as a yellow solid. mp: 174-178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 7.5 Hz, 1 H, ArH), 7.98-7.90 (m, 3 H, ArH), 7.77-7.75 (m, 2 H, ArH), 7.65 (d, J = 15.9 Hz, 1 H, vinylic –CH) , 7.55 (t, J = 7.5 Hz, 1 H, ArH), 7.44-7.37 (m, 3 H, ArH), 7.34 (d, J = 7.5 Hz, 1 H, ArH), 7.16 (d, J = 15.9 Hz, 1 H, vinylic –CH), 2.50 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 197.0, 157.5 (d, J = 257.1 Hz), 145.9, 138.9, 137.6, 136.0, 134.6, 132.6, 131.2, 129.5, 129.2, 129.1, 128.2 (d, J = 17.3 Hz), 127.8, 126.8, 126.5, 125.2, 124.1 (d, J = 19.6

Hz), 121.8, 114.6, 113.9 (d, *J* = 26.4 Hz), 31.0 ppm; HRMS (EI): m/z cacld for $C_{24}H_{16}ClFN_2O_5S$ [M^+]: 498.0452; found: 498.0450.

(*E*)-1-(2-(4,5-Dichloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13o

A solution of ylide **11** (5 g, 8.72 mmol) and 4,5-dichloro-2-nitrobenzaldehyde **12o** (2.10 g, 9.60 mmol) in dry DCM (70 mL) was refluxed for 10 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (20 mL) gave **13o** (4.17 g, 93%) as a yellow solid. mp: 166-168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24-8.22 (m, 2 H, ArH), 7.98 (s, 1 H, ArH), 7.91 (d, *J* = 7.8 Hz, 1 H, ArH), 7.77-7.67 (m, 3 H, ArH), 7.55 (t, *J* = 7.5 Hz, 1 H, ArH), 7.44-7.32 (m, 4 H, ArH), 7.14 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 2.50 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 196.9, 145.8, 139.1, 138.8, 137.6, 136.0, 134.6, 133.8, 132.5, 131.4, 130.5, 129.5, 127.8, 127.1, 126.8, 126.5, 125.3, 124.6, 124.1, 121.8, 114.6, 31.0 ppm; HRMS (EI): m/z cacld for $C_{24}H_{16}Cl_2N_2O_5S$ [M^+]: 514.0157; found: 514.0160.

(*E*)-1-(2-(3, 5-Dichloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)ethanone 13p

A solution of ylide **11** (3 g, 5.23 mmol) and 3,5-dichloro-2-nitrobenzaldehyde **12p**[12] (1.17 g, 5.75 mmol) in dry DCE (50 mL) was refluxed for 8 h under N_2. Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (10 mL) gave **13p** (2.42 g, 90%) as a yellow solid. mp: 216-218 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H, ArH), 7.90 (d, *J* = 7.8 Hz, 1 H, ArH), 7.84-7.79 (m, 2 H, ArH), 7.69 (d, *J* = 7.5 Hz, 2 H, ArH), 7.57-7.53 (m, 2 H, ArH), 7.44 -7.39 (m, 3 H, ArH),), 7.33 (t, *J* = 7.5 Hz, 1 H, ArH), 6.51 (d, *J* = 15.9 Hz, 1 H, vinylic –CH), 2.44 (s, 3 H, -CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 196.6, 147.0, 138.2, 137.5, 137.3, 136.1, 134.7, 131.3, 130.4, 129.5, 129.3, 127.7, 126.9, 126.7, 126.6, 125.8, 125.6, 125.3, 124.3, 121.9, 114.6, 30.8 ppm; HRMS (EI): m/z cacld for $C_{24}H_{16}Cl_2N_2O_5S$ [M^+]: 514.0157; found: 514.0150.

(*E*)-Ethyl 3-(2-(2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylate 17a

To a solution of phosphonate ester **16** (5 g, 10 mmol) in dry DMF, K_2CO_3 (2.76 g, 20 mmol) and 2-nitrobenzaldehyde (1.6 g, 11 mmol) **12a** were added and allowed to stirr at room temperature for 12 h. It was then poured over crushed ice (50 g). The precipitated solid was filtered, washed with water and air dried. The crude product was purified by trituration with methanol (10 mL) to afford compound **17a** (4.32 g, 87%) as a yellow solid. mp: 162-164 °C.

(*E*)-Ethyl-3-(2-(4-fluoro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylate 17b

The Wittig-Horner reaction of phosphonate ester **16** (5 g, 10 mmol) with 4-fluoro-2-nitrobenzaldehyde **12h** (1.82 g, 11 mmol) in the presence of K_2CO_3 (2.76 g, 20 mmol) following the same procedure as that of **17a** afforded compound **17b (**4.53 g, 88%) as a yellow solid. mp: 162-164 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1 H, ArH), 7.84 (dd, *J* = 8.7 Hz, *J* = 5.4 Hz, 1 H, ArH), 7.77-7.76 (m, 2 H, ArH), 7.72-7.68 (m, 3 H, ArH), 7.52 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 7.42 (d, *J* = 8.4 Hz, 1 H, ArH), 7.36-7.26 (m, 5 H, ArH), 7.02 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 6.50 (d, *J* = 16.2 Hz, 1 H, vinylic -CH), 4.19 (q, *J* = 7.2 Hz, 2 H, -OCH_2), 1.24 (t, *J* = 7.2 Hz, 3H, -CH_3) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ

167.0, 162 (d, *J* = 253 Hz), 148.1 (d, *J* = 11 Hz), 139.0, 137.5, 136.9, 134.3, 132.9, 131.2 (d, *J* = 11 Hz), 129.4, 128.7, 128.0, 126.8, 126.3, 125.0, 122.9, 121.4 (d, *J* = 21 Hz), 120.9, 119.2, 115.3, 112.6 (d, *J* = 26 Hz), 60.6, 14.3; DEPT 135: *δ* 135.7, 134.3, 133.0, 131.2 (d, *J* = 11 Hz), 129.4, 128.9, 126.8, 126.3, 125.0, 122.9, 121.4 (d, *J* = 21 Hz), 120.9, 115.3 (d, *J* = 26 Hz), 60.6, 14.3 ppm; Anal. Calcd for $C_{27}H_{21}FN_2O_6S$, C: 62.30; H: 4.07; N: 5.38 Found, C: 62.12; H: 4.19; N: 5.14.

(*E*)-Ethyl 3-(2-(4-chloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylate 17c

The Wittig-Horner reaction of phosphonate ester **16** (5 g, 10 mmol) with 4-chloro-2-nitrobenzaldehyde **12g** (2.05 g, 11 mmol) in the presence of K_2CO_3 (2.76 g, 20 mmol) following the same procedure as that of **17a** afforded compound **17c (**4.51 g, 85%) as a yellow solid. mp: 142-144 ^oC; ^1H NMR (300 MHz, $CDCl_3$): *δ* 8.22 (d, *J* = 8.1 Hz, 1 H, ArH), 8.03 (s, 1 H, ArH), 7.81-7.59 (m, 3 H, ArH), 7.73-7.62 (m, 3 H, ArH), 7.57 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 7.45 (d, *J* = 7.2 Hz, 1 H, ArH), 7.35-7.26 (m, 4 H, ArH), 7.00 (d, *J* = 15.9 Hz, 1 H, vinylic -CH), 6.56 (d, *J* = 15.0 Hz, 1 H, vinylic -CH), 4.19 (q, *J* = 6.9 Hz, 2 H, OCH_2), 1.24 (t, *J* = 7.2 Hz, 3H, $-CH_3$) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$): *δ* 167.0, 148.0, 138.9, 137.5, 136.9, 135.6, 135.1, 134.3, 133.9, 132.6, 130.7, 130.4, 129.4, 128.0, 126.8, 126.4, 125.1, 125.0, 123.4, 121.1, 121.0, 119.3 115.3, 60.7, 14.3 ppm. DEPT 135: *δ* 135.6, 134.3, 133.9, 132.7, 130.4, 129.4, 126.8, 126.4, 125.1, 125.0, 123.3, 121.0 (2C), 115.3 (d, *J* = 26 Hz), 60.7, 14.3 ppm; Anal. Calcd for $C_{27}H_{21}ClN_2O_6S$, C: 60.39; H: 3.94; N: 5.22 Found, C: 60.18; H: 4.02; N: 5.12.

(*E*)-3-(2-Methyl-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylonitrile 31

A solution of indole-3-carbaldehyde **30** (5 g, 16.7 mmol) and (cyanomethylene)triphenyl phosphorane[13] (6.05 g, 20.1 mmol) in dry xylenes under N_2 was refluxed for 8 h. Subsequent removal of solvent in *vacuo* followed by trituration of the crude product with methanol (5 mL) gave 3-vinylindole **31** (4.52 g, 84%) as a colourless solid. mp: 177-180 ˚C; ^1H NMR (300 MHz, $CDCl_3$): *δ* 8.22 (d, *J* = 7.8 Hz, 1 H), 7.75 (d, *J* = 7.8 Hz, 2 H), 7.58-7.50 (m, 2 H), 7.45-7.38 (m, 3 H), 7.34-7.25 (m, 2 H), 5.84 (d, *J* = 16.5 Hz, 1 H), 2.63 (s, 3 H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): *δ* 141.5, 139.9, 138.6, 136.6, 134.4, 129.6, 126.5, 125.3, 124.6, 119.3, 118.8, 115.6, 114.8, 96.3, 13.2 ppm.

(*E*)-3-(2-(Bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylonitrile 32

A mixture of 2-methyl-3-vinylindole **31** (4 g, 12.4 mmol) and NBS (2.65 g, 14.9 mmol) in dry CCl_4 (60 mL) containing a catalytic amount of AIBN (40 mg) was refluxed for 45 min. The reaction mixture was then cooled to room temperature. The floated succinimide was filtered off and the filtrate was concentrated in *vacuo* to obtain crude product which upon trituration with cold methanol (10 mL) afforded bromo compound **32** (4.53 g, 91%) as a white solid; mp: 198-201 ˚C; ^1H NMR (300 MHz, $CDCl_3$): *δ* 8.09 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.1 Hz, 2 H), 7.58-7.47 (m, 3 H), 7.42-7.36 (m, 3 H), 7.33-7.26 (m, 1 H), 6.0 (d, *J* = 16.8 Hz, 1 H), 5.05 (s, 2 H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): *δ* 140.0, 138.0, 136.9, 136.6, 134.6, 129.5, 127.1, 126.9, 126.2, 125.0, 120.0, 118.4, 118.1, 115.2, 99.7, 20.9 ppm.

Preparation of vinyl indoles 33a-c

A solution of bromo compound **32** and triphenylphosphine in dry THF (50 mL) was reflux for 3 h. After consumption of the starting material, the solvent was removed in *vacuo* to give the phosphonium salt. The mixture of the crude phosphonium salt, 2-nitroarylaldehydes and K_2CO_3 in DCM (50 mL) was stirred at room temperature 8 h. After the reaction was completed (monitored by TLC), the mixture was diluted using DCM (50 mL), washed with water (2 x 100 mL) and dried (Na_2SO_4). Removal of the solvent in *vacuo* followed by trituration of the crude product with MeOH (10 mL) afforded vinyl compounds **33a-c** as yellow solids.

(*E*)-3-(2-(2-Nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylonitrile 33a

Wittig reaction of 2-indolylmethylphosphonium salt [prepared using bromo compound **32** (1.5 g, 3.74 mmol) and triphenylphosphine (1.08 g, 4.1mmol)] with 2-nitrobenzaldehyde **12a** (0.62 g, 4.12 mmol) using K_2CO_3 (1.03 g, 7.48 mmol) in DCM (50 mL) at room temperature for 8 h followed by workup as per the above mentioned procedure afforded vinyl indole **33a** (1.37 g, 81%) as a yellow solid. mp 175-178 ˚C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.21-8.14 (m, 2 H), 8.03-7.96 (m, 2 H), 7.92-7.83 (m, 3 H), 7.71-7.66 (m, 3 H), 7.60-7.49 (m, 4 H), 7.39 (t, J = 7.5 Hz, 1 H), 7.17 (d, J = 15.9 Hz, 1 H), 6.49 (d, J = 17.1 Hz, 1 H); ^{13}C-NMR (75.4 MHz, DMSO-d_6): δ 147.7, 141.2, 139.3, 135.9, 135.7, 135.4, 134.3, 134.2, 130.3, 129.9, 128.7, 128.5, 126.9, 126.6, 125.3, 121.0, 120.9, 118.2, 117.0, 115.9, 114.9, 100.1 ppm.

(*E*)-3-(2-(4-Fluoro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylonitrile 33b

Wittig reaction of phosphonium salt [prepared using bromo compound **32** (1 g, 2.5 mmol) and triphenylphosphine (0.72 g, 2.74mmol)] with 4-fluoro-2-nitrobenzaldehyde **12h** (0.46 g, 2.7 mmol) using K_2CO_3 (0.69 g, 5 mmol) in DCM (50 mL) at room temperature for 8 h followed by workup as per the above mentioned procedure afforded vinyl indole **33b** (0.92 g, 78%) as a yellow solid. mp 186-188 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, J = 8.1 Hz, 1 H), 8.23 (dd, J_1 = 9 Hz, J_2 = 5.1 Hz, 1 H), 7.79 (d, J = 7.8 Hz, 2 H), 7.68 (d, J = 7.8 Hz, 1 H), 7.63-7.51 (m, 4 H), 7.47-7.38 (m, 4 H), 7.26 (s, 1 H), 7.13 (d, J = 15.9 Hz, 1 H), 6.02 (d, J = 16.8 Hz, 1 H); ^{13}C-NMR (75.4 MHz, DMSO-d_6): δ 164.3 (d, J = 253.3 Hz), 144.2 (d, J = 2.3 Hz), 141.1, 139.5, 136.3, 135.7, 135.1, 134.8 (d, J = 9.8 Hz), 133.8, 129.9, 128.2 (d, J = 10.5 Hz), 126.7, 126.5, 125.3, 122.4, 121.2, 118.9, 117.8, 116.7 (d, J = 24.1 Hz), 115.8 (d, J = 24.9 Hz), 114.7, 99.0 ppm.

(*E*)-3-(2-(4-Chloro-2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylonitrile 33c

Wittig reaction of phosphonium salt [prepared using bromo compound **32** (1 g, 2.5 mmol) and triphenylphosphine (0.72 g, 2.74 mmol)] with 4-fluoro-2-nitrobenzaldehyde **12g** (0.51 g, 2.7 mmol) using K_2CO_3 (0.69 g, 5 mmol) in DCM (50 mL) at room temperature for 8 h followed by workup as per the above mentioned procedure afforded vinyl indole **33c** (0.9 g, 74%) as a yellow solid. mp 231-233 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, J = 8.4 Hz, 1 H), 8.15 (d, J = 1.8 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.79-7.76 (m, 2 H), 7.73-7.64 (m, 2 H), 7.59-7.53 (m, 3 H), 7.51-7.36 (m, 4 H), 7.04 (d, J = 15.9 Hz, 1

H), 6.02 (d, *J* = 16.8 Hz, 1 H); ^{13}C-NMR (75.4 MHz, DMSO-d_6): δ 148.1, 141.1, 139.6, 136.3, 135.7, 135.1, 134.0, 133.7, 133.6, 132.8, 130.6, 129.9, 126.6, 126.5, 125.3, 124.7, 121.8, 121.1, 118.9, 117.7, 114.6, 98.6 ppm.

(*E/Z*)-3-(3-Methyl-1-(phenylsulfonyl)-1*H*-indol-2-yl)acrylonitrile 37

Wittig reaction of indole-2-carbaldehyde **36** (5 g, 16.7 mmol) with (cyanomethylene)triphenyl phosphorane[13] (6.05 g, 20.1 mmol) in dry xylene was refluxed for 8 h under $N_{2..}$ Removal of solvent in *vacuo* followed by trituration of the crude product with methanol (5 mL) gave mixture of E/Z isomers of 2-vinylindole **37** (4.6 g, 1:2, 86%) as a colourless solid. mp 150-153 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 0.5 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 16.8 Hz, 0.5 H), 7.65-7.56 (m, 4 H), 7.46-7.36 (m, 4 H), 7.34-7.29 (m, 3 H), 7.27-7.19 (m, 2 H), 5.69 (d, *J* = 11.4 Hz, 1 H), 5.51 (d, *J* = 16.8 Hz, 0.5 H), 2.24 (s, 1.5 H), 2.21 (s, 3 H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 141.1, 140.2, 137.5, 137.2, 137.1, 137.0, 134.1, 133.0, 132.4, 131.5, 130.6, 130.1, 129.2, 127.3, 127.0, 126.7, 126.6, 126.5, 125.5, 124.7, 124.5, 124.4, 121.6, 120.5, 120.1, 116.5, 115.8, 115.6, 115.2, 100.4, 100.1,11.5, 10.9 ppm;

(*E*)-3-(3-(Bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-2-yl)acrylonitrile 38

A mixture of 2-methyl-3-vinylindole **37** (2 g, 6.2 mmol) and NBS (1.22 g, 6.8 mmol) in dry CCl_4 (40 mL) containing a catalytic amount of AIBN (40 mg) was refluxed for 45 min. The reaction mixture was then cooled to room temperature. The floated succinimide was filtered off and the filtrate was concentrated in *vacuo* to obtain crude product which upon trituration with cold methanol (10 mL) afforded bromo compound **38** (2.22 g, 89%) as a white solid; mp 176-179 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 1 H), 8.04 (d, *J* = 16.5 Hz, 1 H), 7.74-7.72 (m, 3 H), 7.64-7.55 (m, 2 H), 7.52-7.37(m, 4 H), 5.98 (d, *J* = 16.5 Hz, 1 H), 4.59 (s, 2 H); ^{13}C-NMR ($CDCl_3$, 75.4 MHz): δ 139.0, 137.5, 136.8, 134.6, 132.1, 129.5, 128.4, 127.6, 126.6, 124.9, 122.8, 119.8, 117.1, 115.2, 102.6, 22.6 ppm;

(*E*)-3-(3-(2-nitrostyryl)-1-(phenylsulfonyl)-1*H*-indol-2-yl)acrylonitrile 39

Wittig reaction of phosphonium salt [prepared using bromo compound **32** (1.5 g, 3.74 mmol) and triphenylphosphine (1.08 g, 4.1 mmol)] with 2-nitrobenzaldehyde **12a** (0.62 g, 4.12 mmol) using K_2CO_3 (1.03 g, 7.48mmol) in DCM (50 mL) at room temperature for 6 h followed by workup adapting the same procedure as that of **33a** afforded **39** (1.41 g, 83%) as a yellow solid. mp 167-170 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1 H), 8.04 (d, *J* = 16.5 Hz, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 7.8 Hz, 1 H), 7.69-7.61 (m, 5 H), 7.49-7.47 (m, 1 H), 7.44-7.30 (m, 5 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 5.55 (d, *J* = 16.5 Hz, 1 H); ^{13}C-NMR (DMSO-d_6, 75.4 MHz): δ 147.5, 138.9, 136.5, 136.0, 135.0, 133.7, 132.8, 131.9, 129.9, 129.0, 128.6, 127.6, 127.4, 126.5, 125.3, 124.6, 123.5, 123.1, 121.4, 118.1, 115.1, 104.3 ppm.

Table 1. HPLC method for compound purity determinations

<table>
<tr><td>Chromatographic conditions</td><td>Compounds</td></tr>
<tr><td>Mobile phase</td><td>Preparation of Mobile phase-A:
Weigh and transfer about 0.63 g of Ammonium formate into a beaker containing 1000 mL of Water. Mix well and filter through 0.45 µm membrane, degas.
Preparation of Mobile phase-B:
Mix 500 mL of Acetonitrile and 500 mL Methanol. Degas.</td></tr>
<tr><td>Sample solution</td><td>Preparation of sample solution:
Weigh accurately and transfer about 5 mg of sample into a 25 mL volumetric flask. Add 10 mL of acetonitrile to dissolve and make upto the volume with diluent.</td></tr>
<tr><td>Diluent</td><td>Mix 300 mL of Mobile phase-A and 700 mL of Mobile phase-B and degas.</td></tr>
<tr><td>Column</td><td>Make & Name : Agilent Technologies & Zorbax Rx-C18
Dimensions : 250 mm x 4.6 mm, 5.0 µm</td></tr>
<tr><td>Column compartment temperature</td><td>25°C</td></tr>
<tr><td>Sample compartment temperature</td><td>25°C</td></tr>
<tr><td>Flow rate</td><td>1.0 mL/min</td></tr>
<tr><td>Gradient program</td><td>
<table>
<tr><th>Time (min)</th><th>Mobile phase-A (%)</th><th>Mobile phase-B (%)</th></tr>
<tr><td>0.00</td><td>80</td><td>20</td></tr>
<tr><td>5.00</td><td>80</td><td>20</td></tr>
<tr><td>30.00</td><td>30</td><td>70</td></tr>
<tr><td>50.00</td><td>30</td><td>70</td></tr>
<tr><td>50.10</td><td>80</td><td>20</td></tr>
<tr><td>55.00</td><td>80</td><td>20</td></tr>
</table>
</td></tr>
<tr><td>Wavelength of detection</td><td>280 nm</td></tr>
<tr><td>Injection volume</td><td>20 µL</td></tr>
<tr><td>Run time</td><td>50-60 minutes</td></tr>
</table>

Table 2. *In vitro* LC_{50} data for calothrixins **1**, **2** and **15b-p** against nine human tumor cell lines

	LC_{50} Average ± S.D. (μM)[a]								
Compound	**Jurkat**	**HeLa**	**SiHa**	**MCF7**	**HCT116**	**HCT116 p53-/-**	**MDA-MB 231**	**U251**	**NCI-H460**
1	>4	>4	>4	>4	>4	>4	>4	>4	>4
2	>4	>4	>4	4.00	>4	>4	>4	>4	>4
15b	>4	>4	>4	>4	>4	>4	>4	>4	>4
15c	>4	>4	>4	>4	>4	>4	>4	>4	>4
15d	>4	>4	>4	>4	>4	>4	>4	>4	>4
15e	>4	>4	>4	>4	>4	>4	>4	>4	>4
15f	>4	>4	>4	>4	>4	>4	>4	>4	>4
15g	>4	>4	>4	>4	>4	>4	>4	>4	>4
15h	>4	>4	>4	>4	>4	>4	>4	>4	>4
15i	>4	>4	>4	4.00	>4	>4	>4	>4	>4
15j	>4	>4	>4	>4	>4	>4	>4	>4	>4
15k	>4	>4	>4	>4	>4	>4	>4	>4	>4
15l	>4	>4	>4	>4	>4	>4	>4	>4	>4
15m	>4	>4	>4	>4	>4	>4	>4	>4	>4
15n	>4	>4	>4	>4	>4	>4	>4	>4	>4
15o	>4	>4	>4	>4	>4	>4	>4	>4	>4
15p	>4	>4	>4	>4	>4	>4	>4	>4	>4
CPT	>4	>4	>4	>4	>4	>4	>4	>4	>4

[a] Values represents mean from at least two independent experiment

Table 3. *In vitro* LC_{50} data for quinocarbazoles **21a-c**, **25a, b** and **29**, naphthocarbazole **31** against ten human tumor cell lines

	LC_{50} Average ± S.D. (μM)[a]											
Name	**Jurkat**	**HeLa**	**SiHa**	**MCF7**		**HCT116**	**MDA-MB 231**	**U251**	**NCI-H460**		**HEK293**	**A549**
21a	>4	>4	>4	>4		>50	>4	>4	40	± 1.2	>4	>4
21b	>4	>4	>4	4.0	± 0.0	>50	>4	>4	>4		>4	>4
21c	>4	>4	>4	>4		>50	>4	>4	>50		>4	>4
25a	>4	>4	>4	>4		>50	>4	>4	40	± 3.2	>4	>4
25b	>4	4.0	>4	>4		>50	>4	>4	>50		>4	>4
29	>4	>4	>4	>4		>50	>4	>4	>50		>4	>4
46	>4	>4	>4	>4		>50	>4	>4	>50		>4	>4

[a] Values represents mean from at least two independent experiments

Table 4. *In vitro* LC_{50} data for amino quinocarbazoles **35a-c, 41** and **44** against seven human tumor cell lines

	LC_{50} Average ± S.D. (μM)[a]									
Name	**HeLa**		**SiHa**	**MCF7**		**HCT116**	**MDA-MB 231**	**U251**	**NCI-H460**	
35a	>4		>4	>4		>4	>4	>4	>4	
35b	>4		>4	>4		>4	>4	>4	>4	
35c	4.00		>4	3.00	± 0.7	>4	>4	4.00	± 0.0	4.00	± 0.0
41	4.00		>4	4.00	± 0.0	>4	>4	4.00	± 0.0	4.00	± 0.0
44	>4		>4	3.00	± 0.9	>4	>4	>4		>4	

[a]Values represents mean from at least two independent experiments

HeLa cell cycle perturbation by calothrixins (**1**, **2** and **15h**)

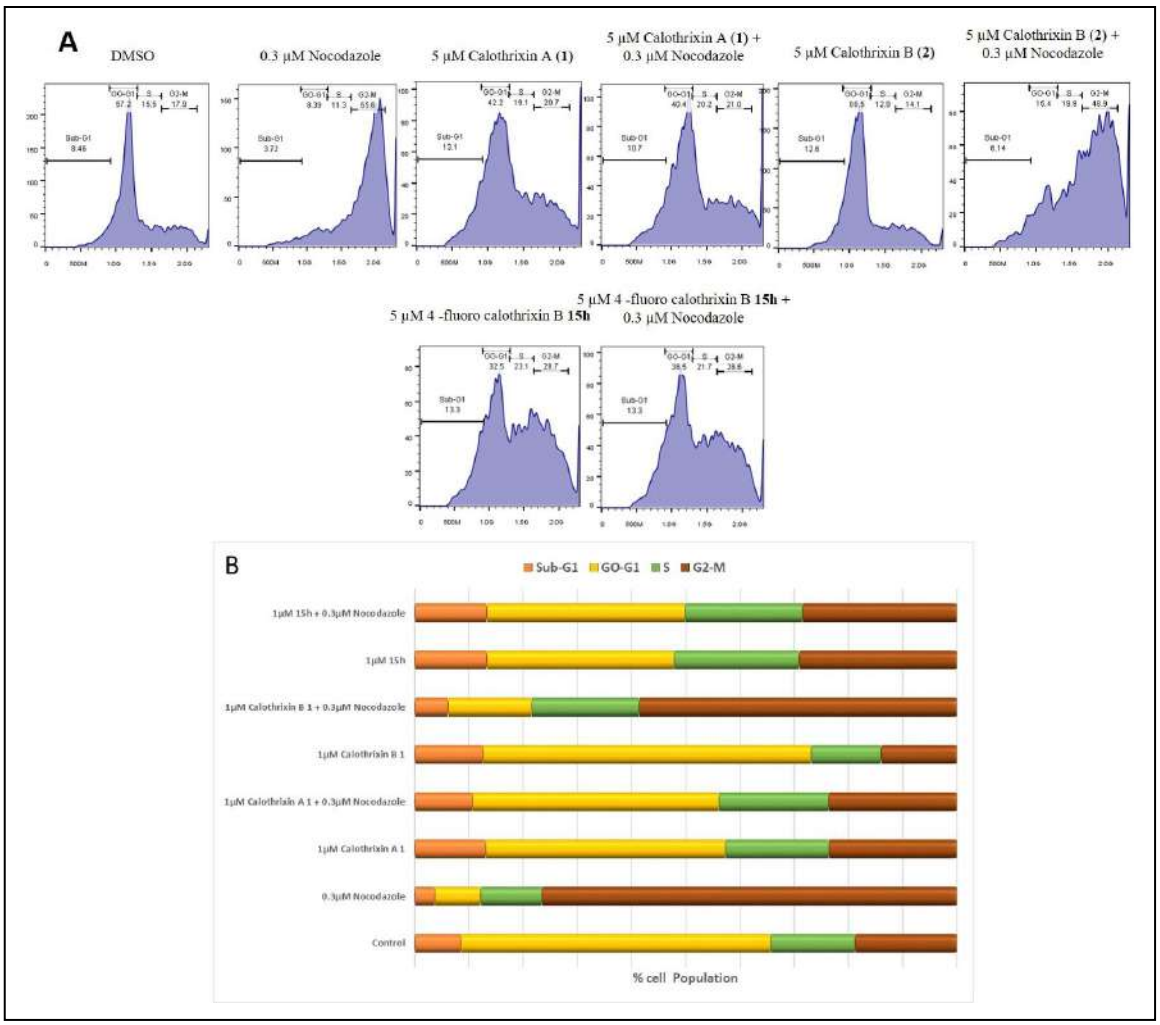


Fig. 1. (A) Cell cycle perturbation by calothrixins (**1**, **2** and, **15h**) in the presence or absence of nocodazole. HeLa cells were treated with 5 µM of calothrixin and its analogues for 20 h or 3 h pre-treatment with 17 h in the presence of nocodazole followed by propidium iodide staining. Population of cells in different phases of cell cycle were analysed by flow cytometry (B) Percentages of HeLa cells in the different phases of the cell cycle.

DNA binding studies with calothrixin/quinocarbazole analogues

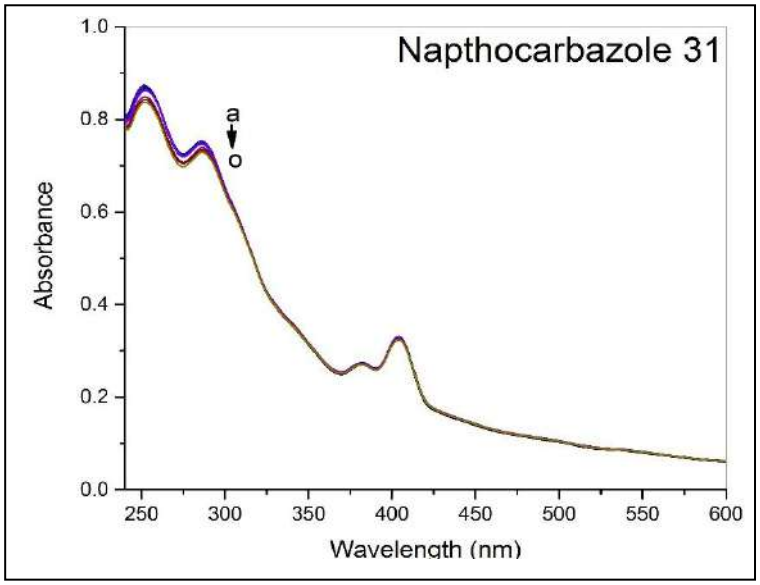


Fig. 2. Effects of increasing concentrations of CT-DNA on the UV-Vis absorption spectra of napthocarbazole (31) Conditions: Calothrixins or quinocarbazoles, 3×10−5 mol L−1; CctDNA (×10−6 mol L−1); a→o: 0; 2; 5; 10; 15; 20; 25; 30; 35; 40; 45; 50; 60; 80; 100. The arrow shows the intensity changes in increasing CT-DNA concentration

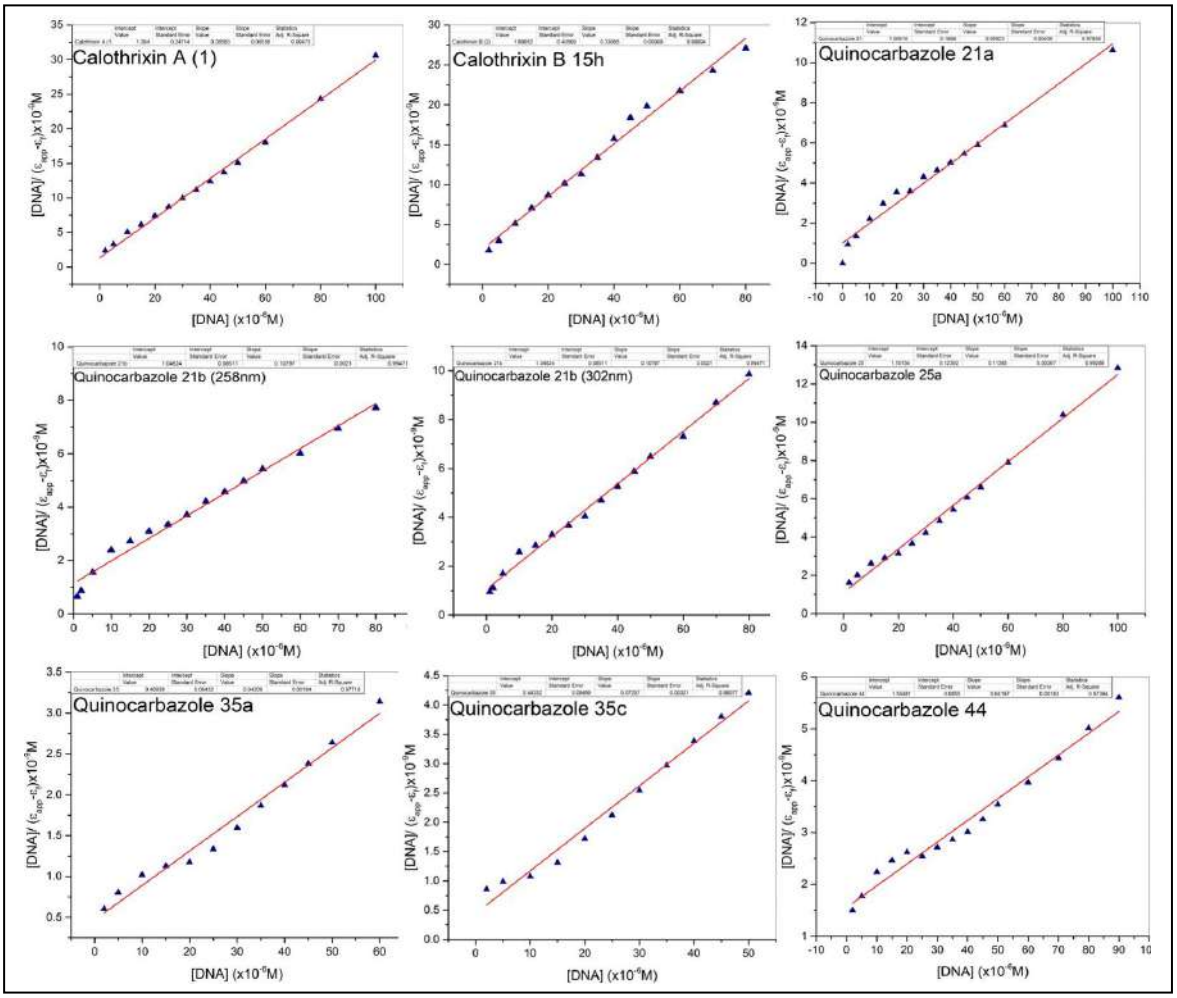


Fig. 3. Plots of [DNA]/(ε_{app}-ε_f) x10^{-9} M *vs* [DNA] (x10^{-6} M) used to calculate the binding constants of calothrixin/quinocarbazole-DNA complex

Plasmid DNA unwinding studies with quinocarbazole analogues

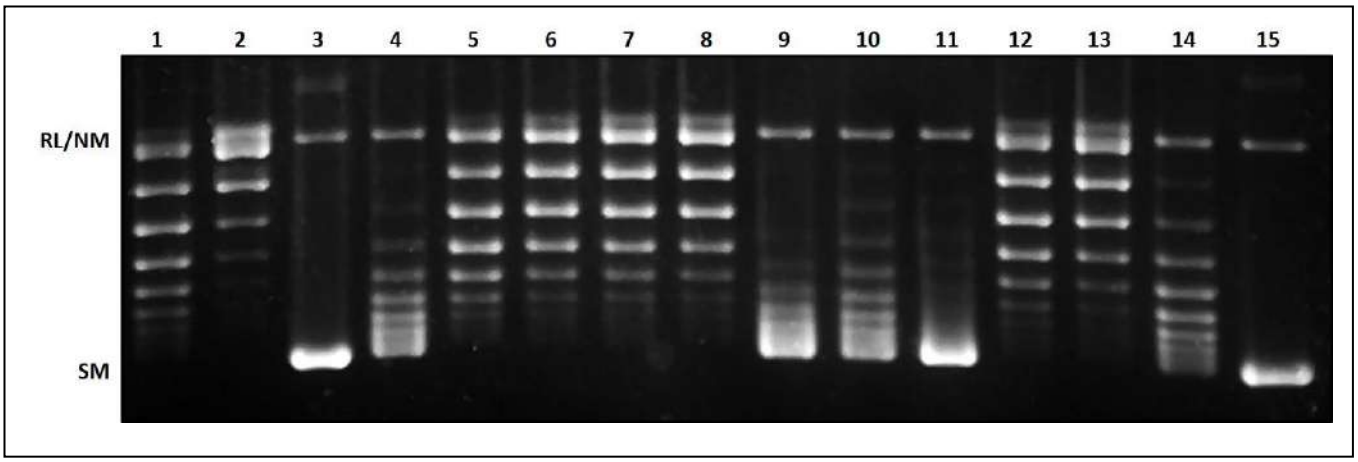
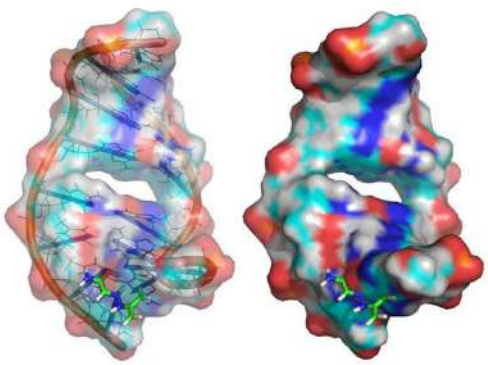
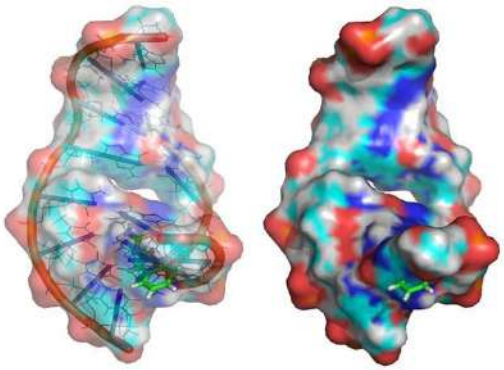


Fig. 4. Analysis of binding mode of quinocarbazoles with DNA by agarose-gel electrophoresis. Lane 1, relaxed pBluescript (SK+) plasmid DNA generated by treatment of plasmid DNA with excess hTopI, followed by phenol/chloroform extraction and ethanol precipitation; lane 2, relaxed plasmid DNA with hTopI; lane 3-5, same as lane 2 but in presence of decreasing concentrations of EtBr; lanes 6, 7, same as lane 2, but in presence of increasing concentration of etoposide; lane 8-11 and 12-15, same as lane 2 but in presence of increasing concentrations (40, 50, 60 and 70 μM) of quinocarbazoles 21a and 25a, respectively. NM, nicked monomer; RL, relaxed monomer; SM, supercoiled monomer.

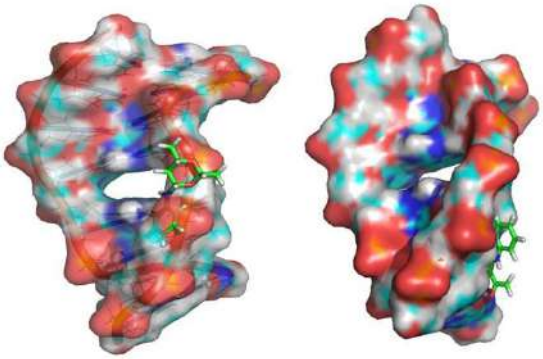
Molecular docking studies of calothrixins with DNA



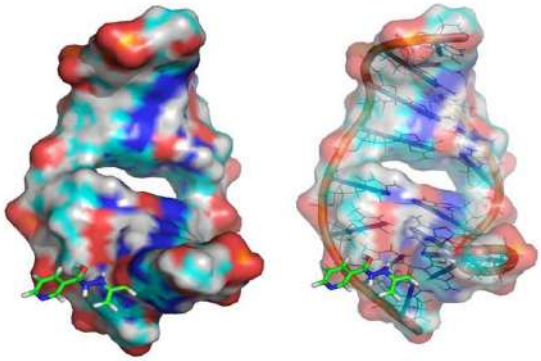
Calothrixin B 2 (Energy value -7.2 Kcal mol^{-1})



3-Chloro calothrixin B 15g (Energy value -6.5 Kcal mol^{-1})



3-Fluoro calothrixin B 15h (Energy value -5.6 Kcal mol^{-1})



1-Chloro calothrixin15k (Energy value -4.2 Kcal mol^{-1})

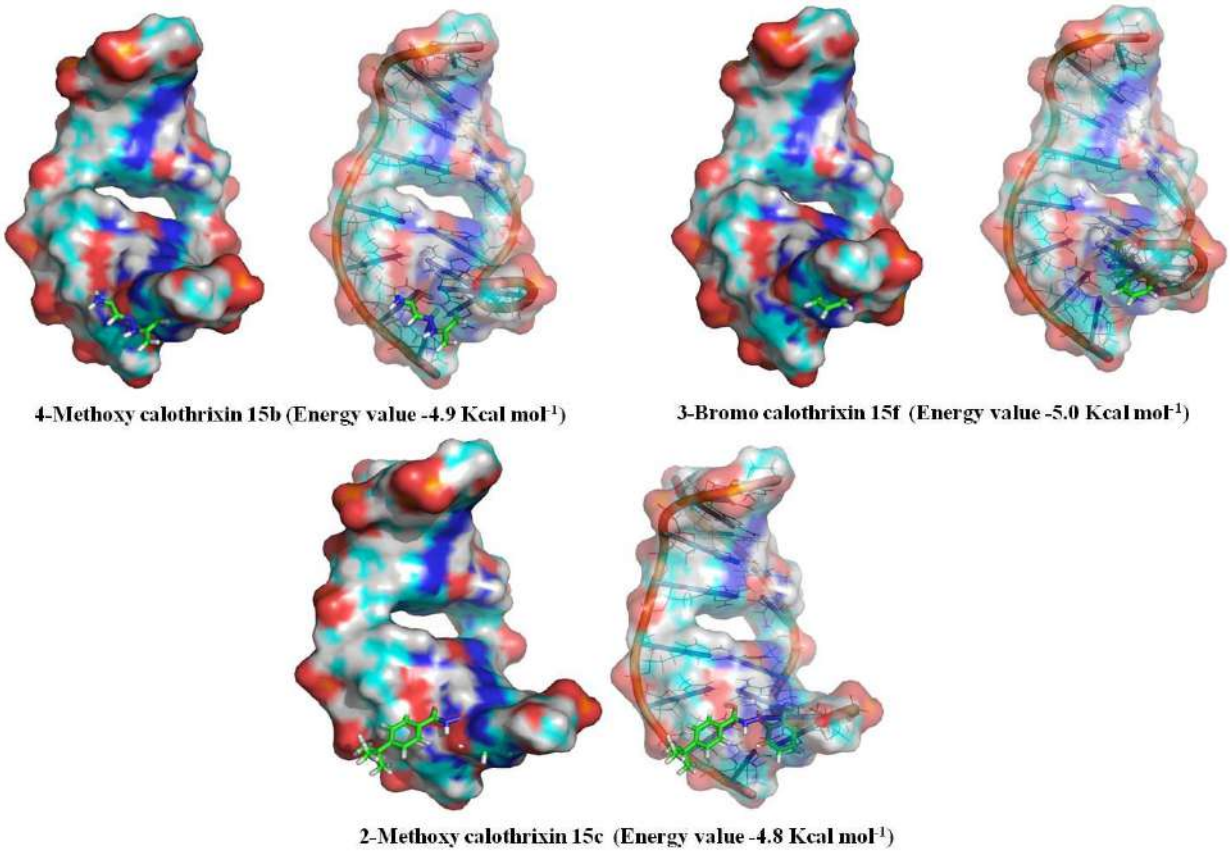


Fig. 5. The docked structure of calothrixin B analogues with 1DSC DNA

Table 5. *In silico* calculations of free binding energy scores for the calothrixin and quinocarbazole ligands docked with octamer DNA

S.NO	Name of the compound	BINDING ENERGY (Kcal mol^{-1})	INTERACTING BASE PAIRS WITH DYE
1	**2**	-7.2	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
2	**21b**	-6.8	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
3	**15l**	-6.7	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
4	**15g**	-6.5	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
5	**21a**	-6.5	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
6	**31**	-6.1	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
7	**29**	-5.8	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
8	**15h**	-5.6	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
9	**15f**	-5.0	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
10	**15p**	-5.1	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
11	**15b**	-4.9	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
12	**15c**	-4.8	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
13	**25a**	-4.5	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
14	**21c**	-4.3	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
15	**15k**	-4.2	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
16	**25b**	-4.1	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
17	**15e**	-3.6	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
18	**15j**	-3.5	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
19	**15o**	-3.3	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
20	**15m**	-3.0	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
21	**1**	-2.9	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
22	**15d**	-2.9	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
23	**15i**	-2.8	5' *GP*AP*AP*GP*CP*TP*TP*C 3'
24	**15n**	-2.7	5' *GP*AP*AP*GP*CP*TP*TP*C 3'

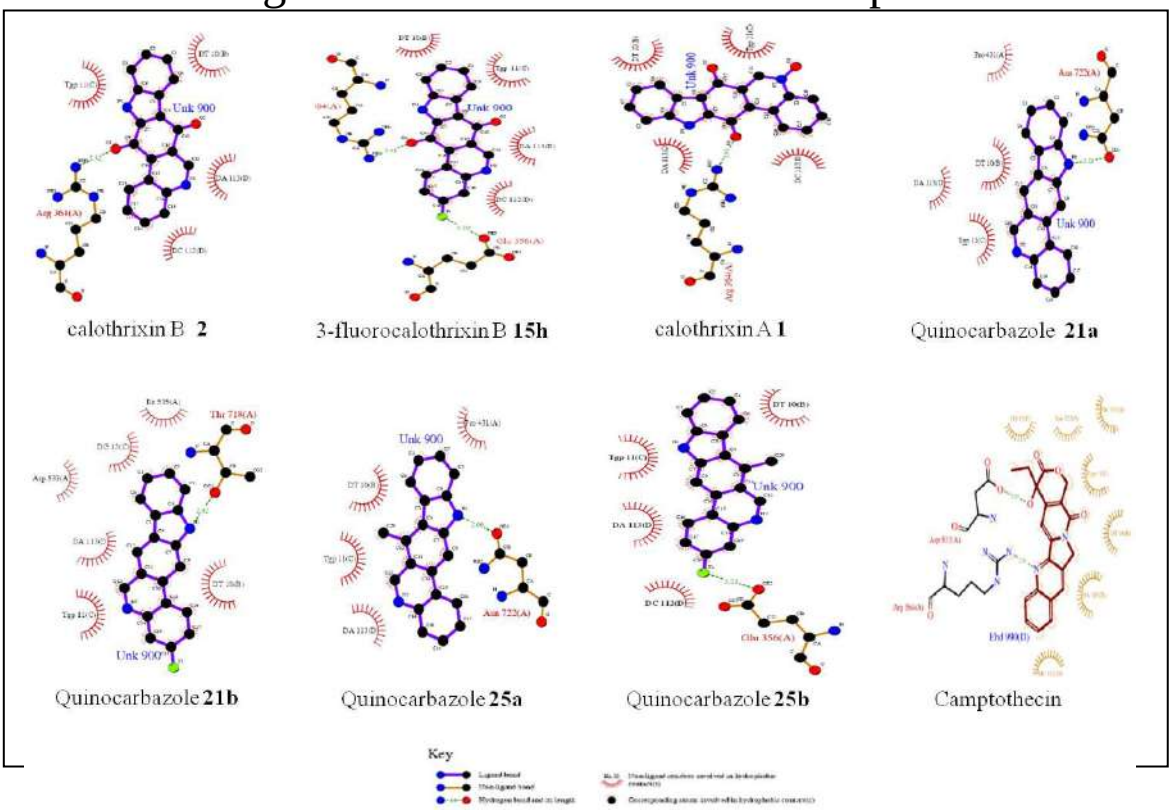


Fig. 6. LIGPLOT showing interactions of calothrixins/quinocarbazoles with amino acids at the active site of human topoisomerase I [PDB ID: 1T8I]

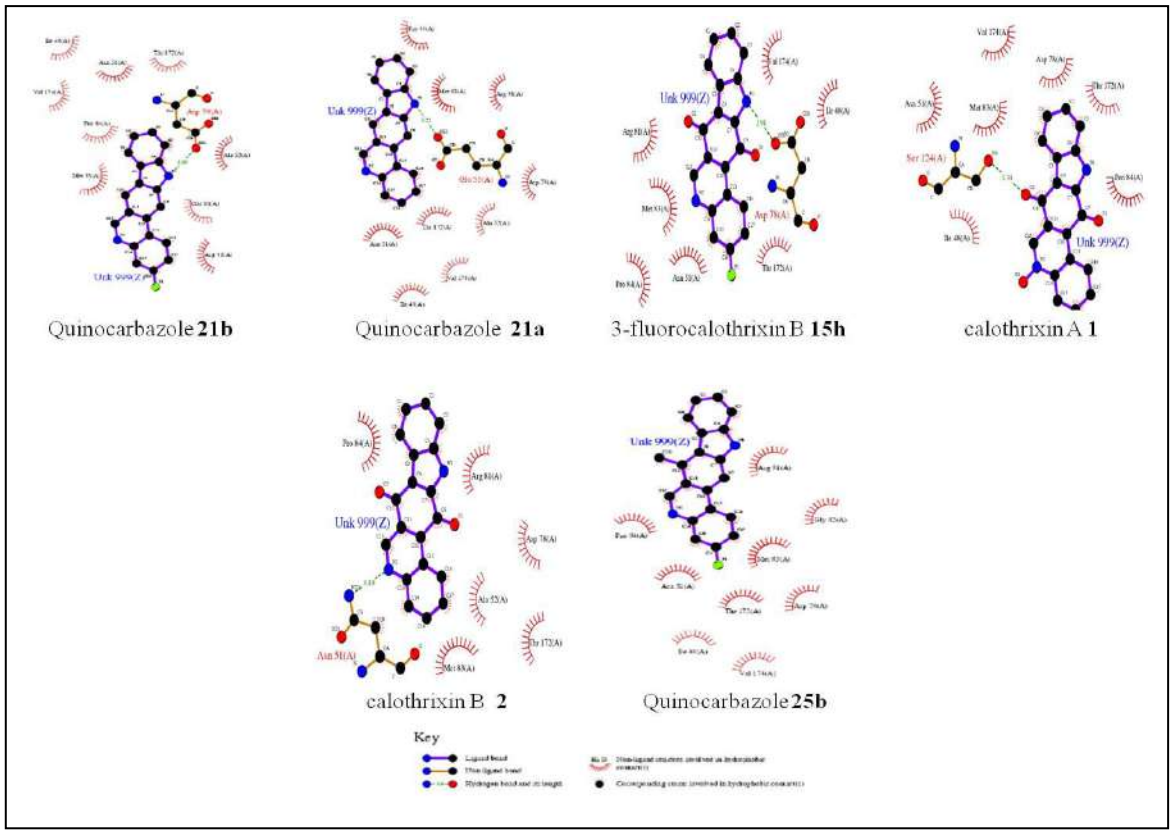


Fig. 7. LIGPLOT showing interactions of calothrixins/quinocarbazoles with amino acids at the ATPase binding domain of type II topoisomerase [PDB ID: 4LPB]

Table 6. Induced Fit docking results of calothrixins/ quinocarbazoles with human Topoisomerase I

Compound No.	ΔG (Kcal/mol)	Glide Energy (Kcal/mol)	Hydrogen bonded Interactions	Hydrogen Bonding Distance (Å)
15h	-7.59	-53.38	(Arg 364)N-H…O (Glu356)O-H…F	2.81 3.20
2	-7.20	-46.82	(Arg 364)N-H…O	2.82
1	-6.84	-42.19	(Arg 364)N-H…O	2.81
25a	-6.27	-44.62	N-H…O(Asn722)	2.66
21b	-6.16	-42.09	(Thr178)N-H…O	2.82
21a	-5.94	-41.52	N-H…O(Asn 722)	3.05
25b	-5.81	-39.28	(Glu356)O-H…F	3.21
Camptothecin	-6.98	-50.04	(Arg 364) N-H…N O-H…O (Asp 533)	2.91 3.25

Table 7. Induced Fit docking results of calothrixins/ quinocarbazoles with ATPase binding domain of type II bacterial topoisomerase

Compound No.	ΔG (Kcal/mol)	Glide Energy (Kcal/mol)	Hydrogen bonded Interactions	Hydrogen Bonding Distance (Å)	Hydrophophobic Interactions
21b	-8.96	-58.04	N-H…O(Asp 78)	3.03	Ile 48, Asn 51, Ala 52, Glu55, Arg 81, Met83, Pro84, Thr 172
21a	-7.37	-54.29	N-H…O(Glu 55)	3.22	Ile 48, Asn 51, Glu55, Arg 81, Met83, Pro84, Thr 172
15h	-6.91	-51.74	N-H…O(Asp 78)	2.91	Ala 52, Asp 78, Arg 81, Met 83, Pro 84
1	-6.43	-53.38	(Ser124)O-H…O	3.34	Ile 48, Asn 51, Arg 81, Met 83, Pro 84, Thr 172, Val 174
2	-6.72	-49.52	N-H…N(Asn 51)	3.10	Ile 48, Asn 51, Asp 78, Met 83, Pro 84, Thr 172, Val 174
25b	-5.41	-48.43	----	----	Pro 84, Arg 81, Asp 78, Ala52, Thr 172, Met 83
25a	-2.35	-38.65	----	---	Ile 48, Asn 51, Asp 78, Gly 82, Met 83, Pro 84,Thr 172, Val 174

Table 8. Hematology parameters following oral administration of **15h** to SCID mice for 7 days.

Measured hematological parameters	Dose groups			
	Control (n=6)	10 mg/kg bw/d (n=6)	30 mg/kg bw/d (n=6)	50 mg/kg bw/d (n=6)
Red blood cells ($x10^6$/µL)	9.78 ± 0.1	9.70 ± 0.4	9.94 ± 0.4	9.70 ± 0.6
White blood cells ($x10^3$/µL)	1.42 ± 0.4	1.13 ± 0.1	1.23 ± 0.7	1.65 ± 1.3
Hemoglobin (g/dL)	14.37 ± 0.6	14.7 ± 0.2	14.87 ± 0.4	14.35 ± 1.4
Hematocrit (%)	49.82 ± 1.5	50.70 ± 1.1	51.23 ± 1.9	49.42 ± 3.5
MCV (fL)	50.92 ± 1.2	43.27 ± 1.5	51.57 ± 0.3	51.25 ± 1.4
MCH (pg)	14.7 ± 0.5	15.17 ± 0.5	14.97 ± 0.3	14.88 ± 0.8
MCHC (%)	28.85 ± 0.6	29.00 ± 0.7	29.03 ± 0.5	28.96 ± 0.9
Platelets ($x10^3$/µL)	1408 ± 310	1288 ± 176	1185 ± 303	1280 ± 169

Abbreviations: bw, body weight; MCH, mean corpuscular hemoglobin; MCHC, mean corpuscular hemoglobin concentration; MCV, mean corpuscular volume
Values are expressed as mean ± standard deviation.

Table 9. Relative organ weights following oral administration of **15h** to SCID mice for 7 days.

Measure hematological parameters	Dose groups			
	Control (n = 6)	10 mg/kg bw/d (n = 6)	30 mg/kg bw/d (n = 6)	50 mg/kg bw/d (n = 6)
Adrenals (mg)	20.7 ± 5	20 ± 4	19.0 ± 3	21.5 ± 5
Ovaries (mg)	32.7 ± 3.4	30.0 ± 6	34.0 ± 2.2	31.0 ± 2.4
Spleen (g)	0.081 ± 0.08	0.080 ± 0.06	0.078 ± 0.01	0.079 ± 0.05
Heart (g)	0.15 ± 0.013	0.13 ± 0.027	0.17 ± 0.015	0.15 ± 0.015
Brain (g)	0.49 ± 0.01	0.50 ± 0.026	0.54 ± 0.02	0.48 ± 0.04
Kidneys (g)	0.40 ± 0.04	0.43 ± 0.055	0.37 ± 0.02	0.40 ± 0.06
Liver (g)	1.58 ± 0.164	1.86 ± 0.24	1.60 ± 0.36	1.8 ± 0.34

Abbreviations: bw, body weight,
All values are reported as mean ± SD.

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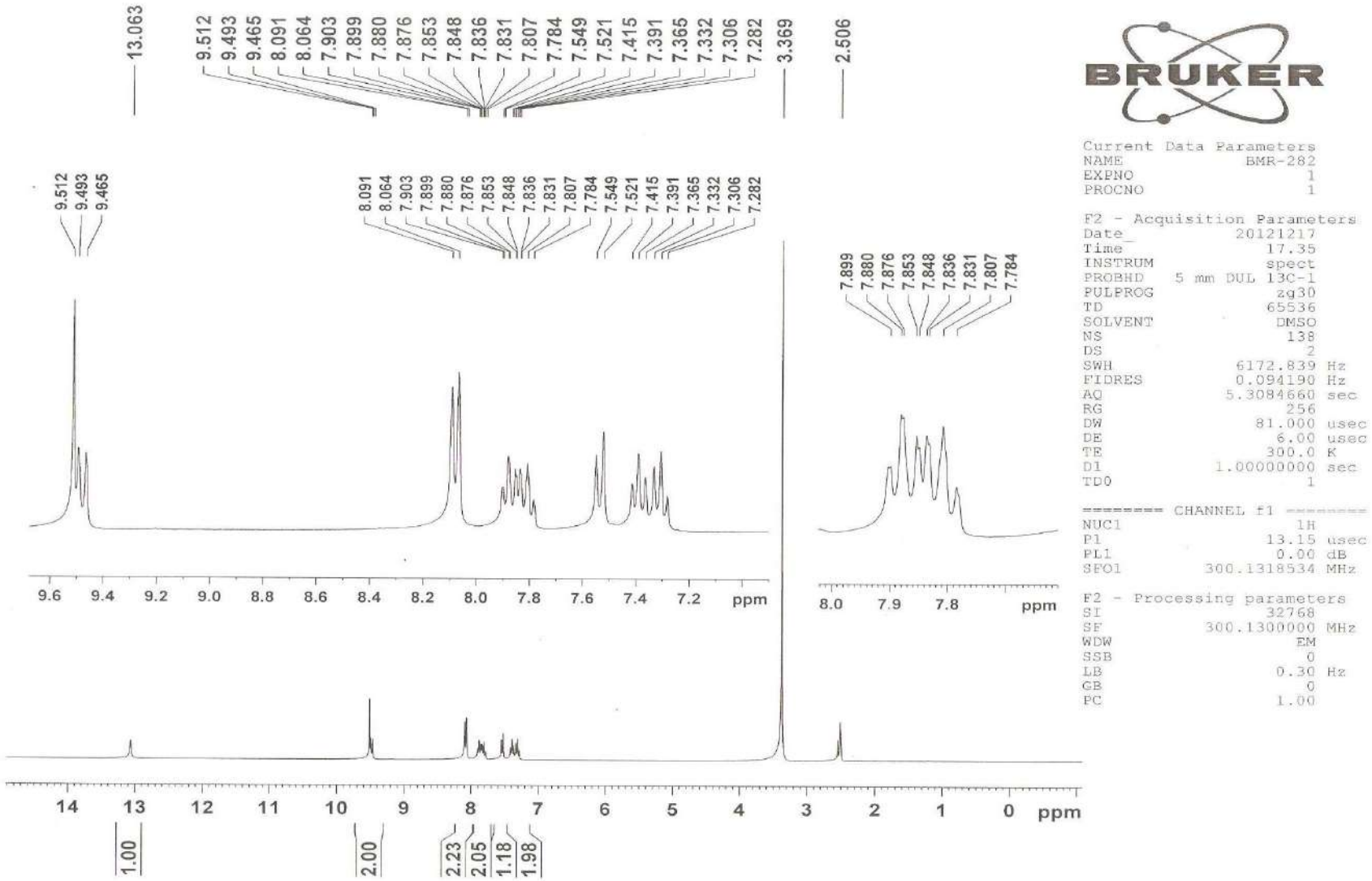


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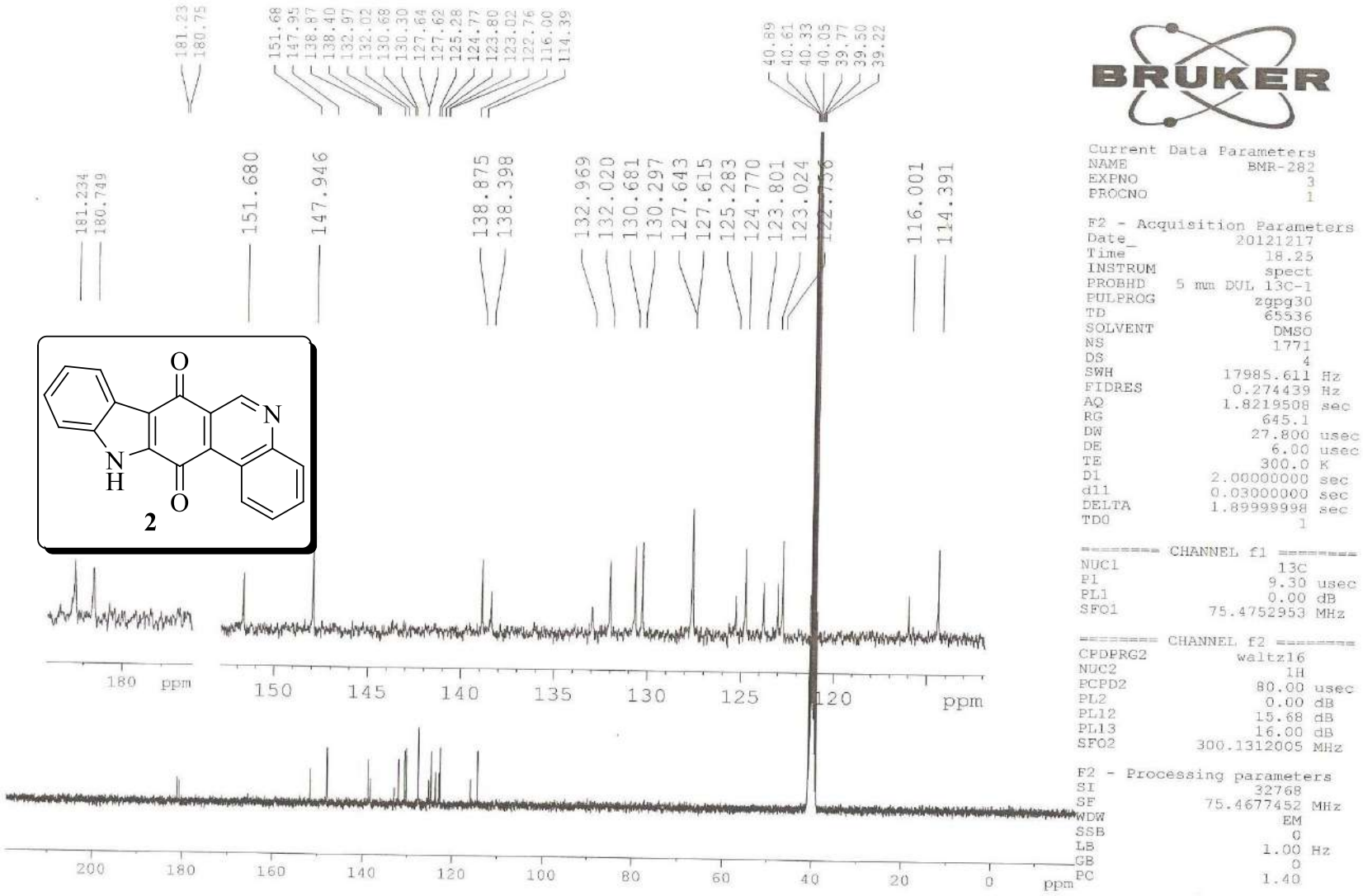

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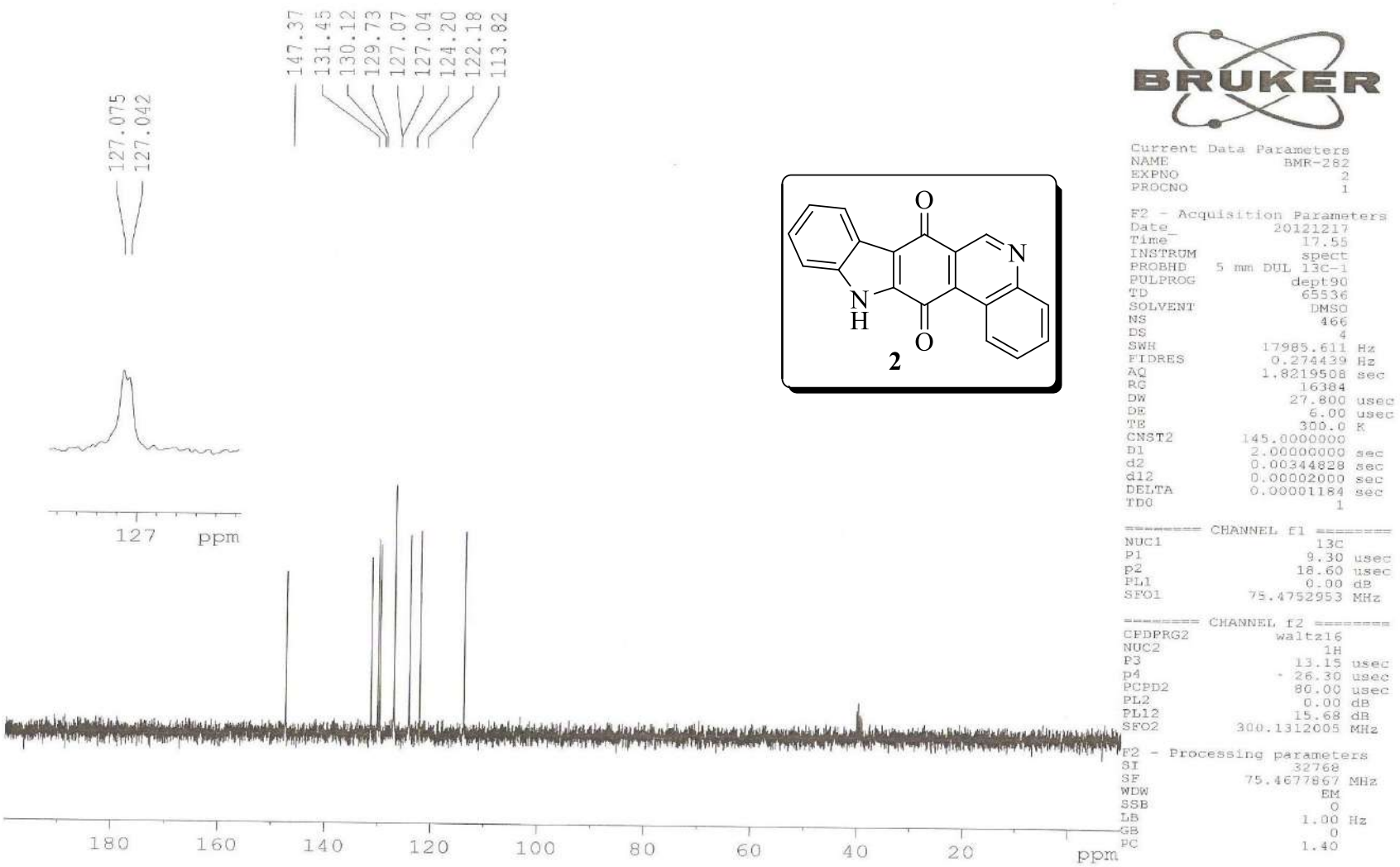

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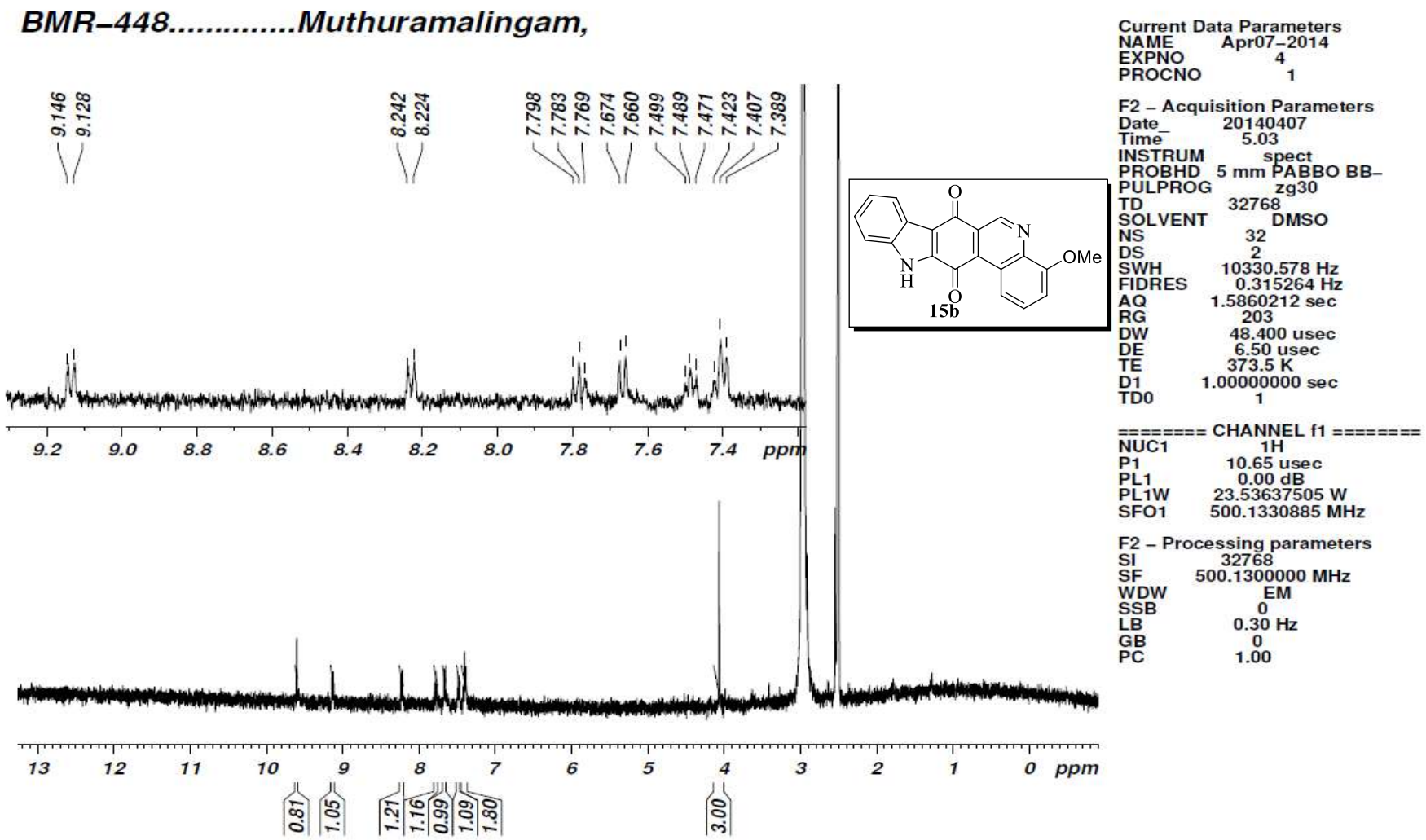

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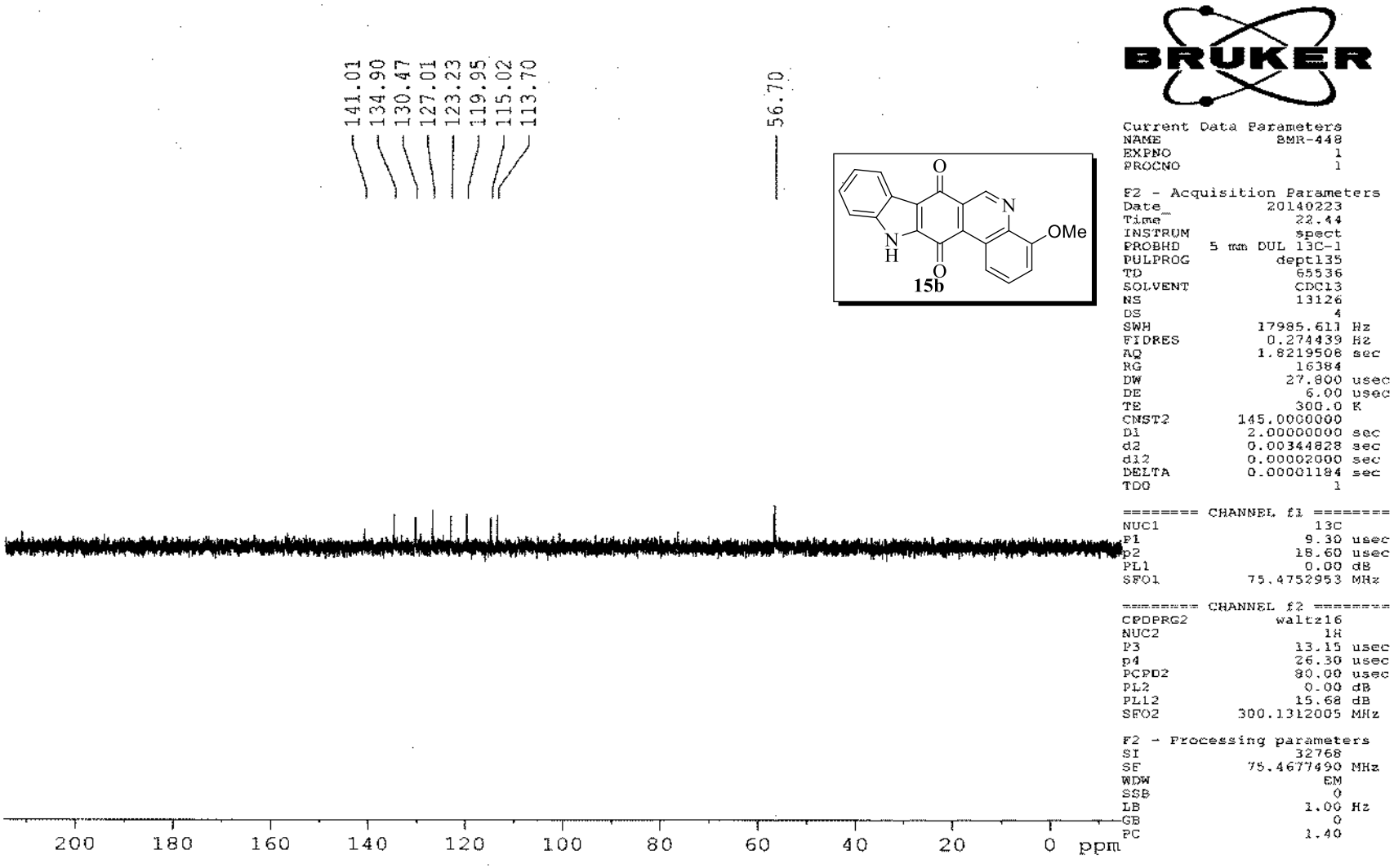

BRUKER

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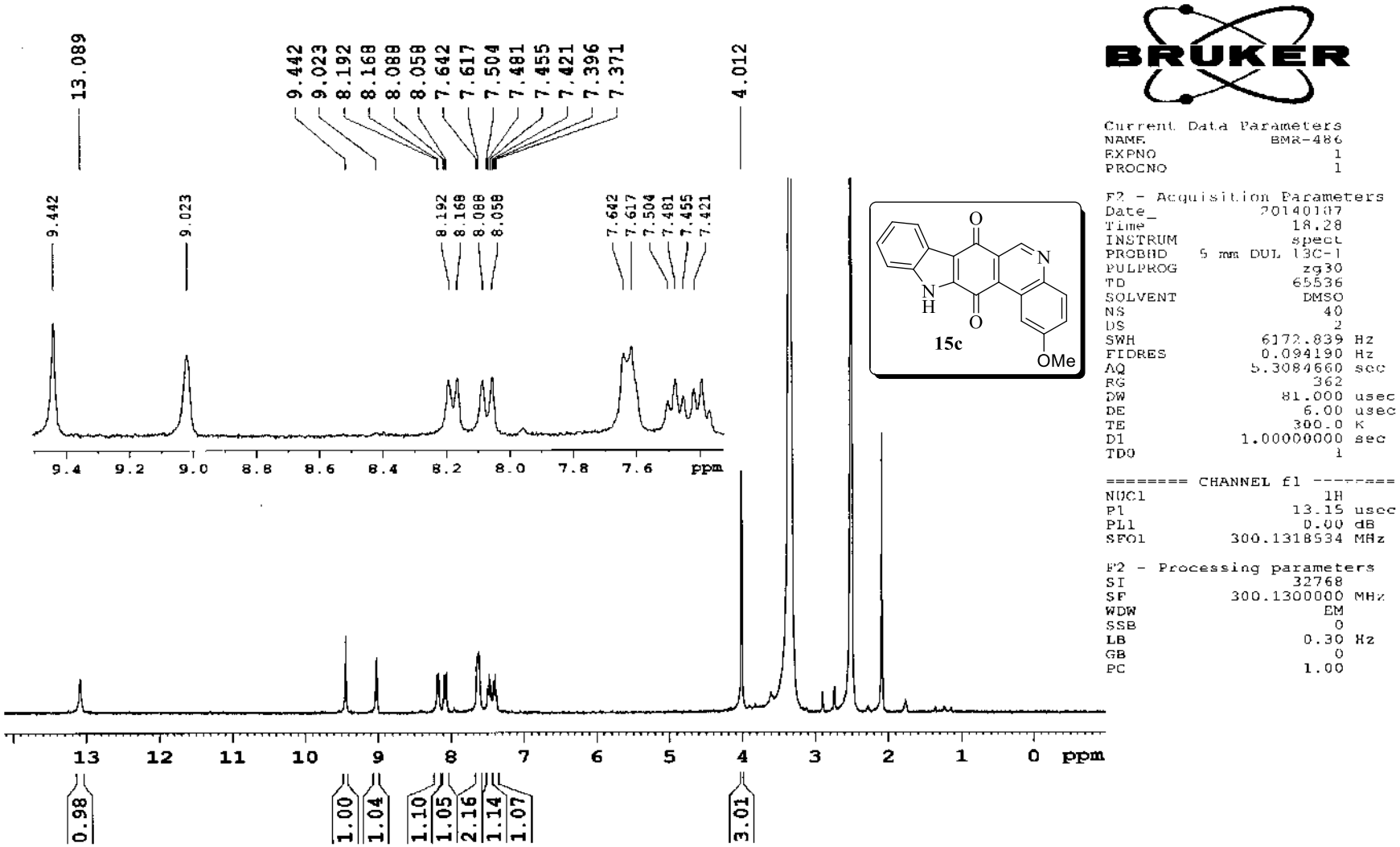

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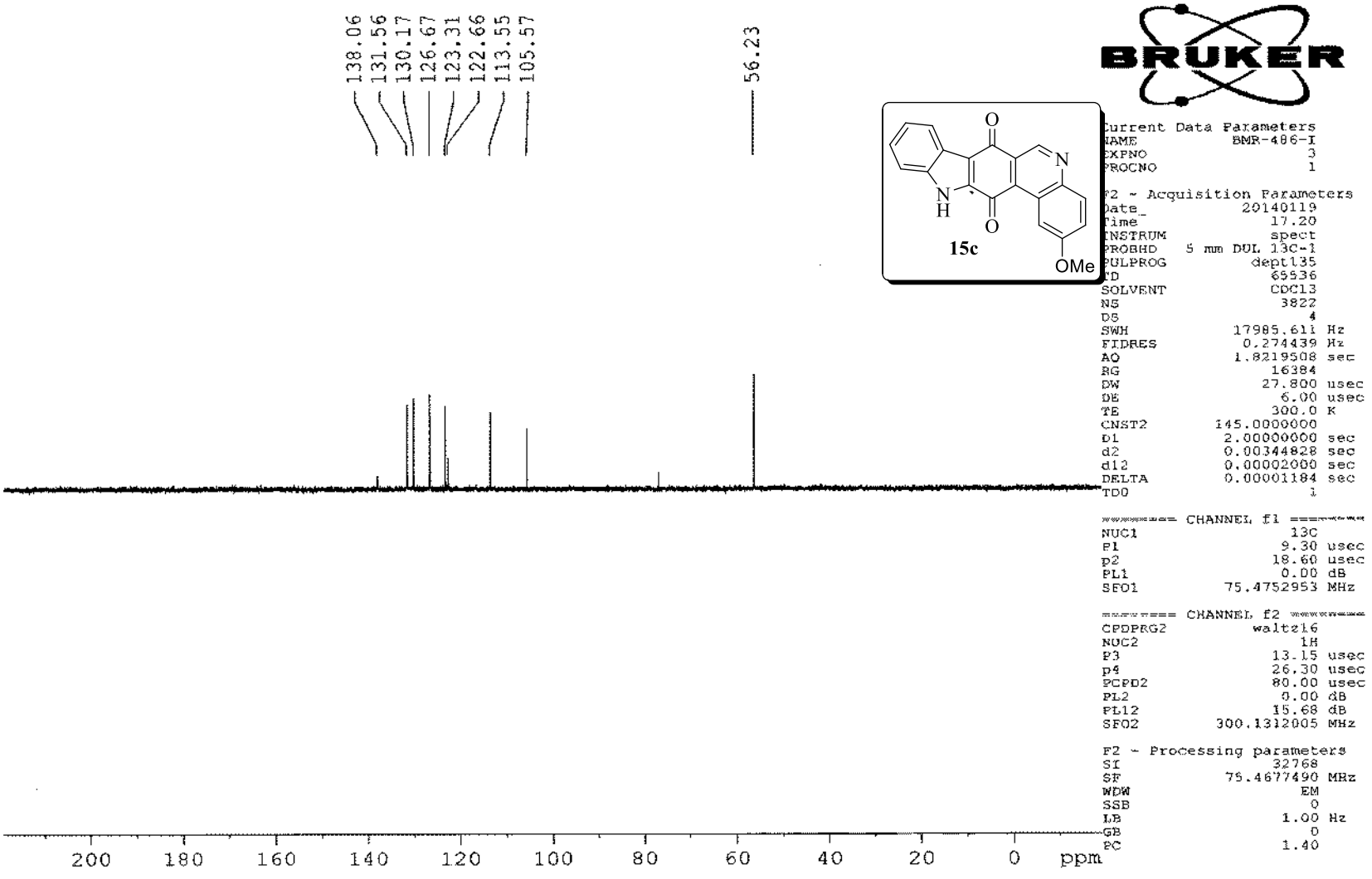
^{1}H-NMR spectrum of compound **15c**

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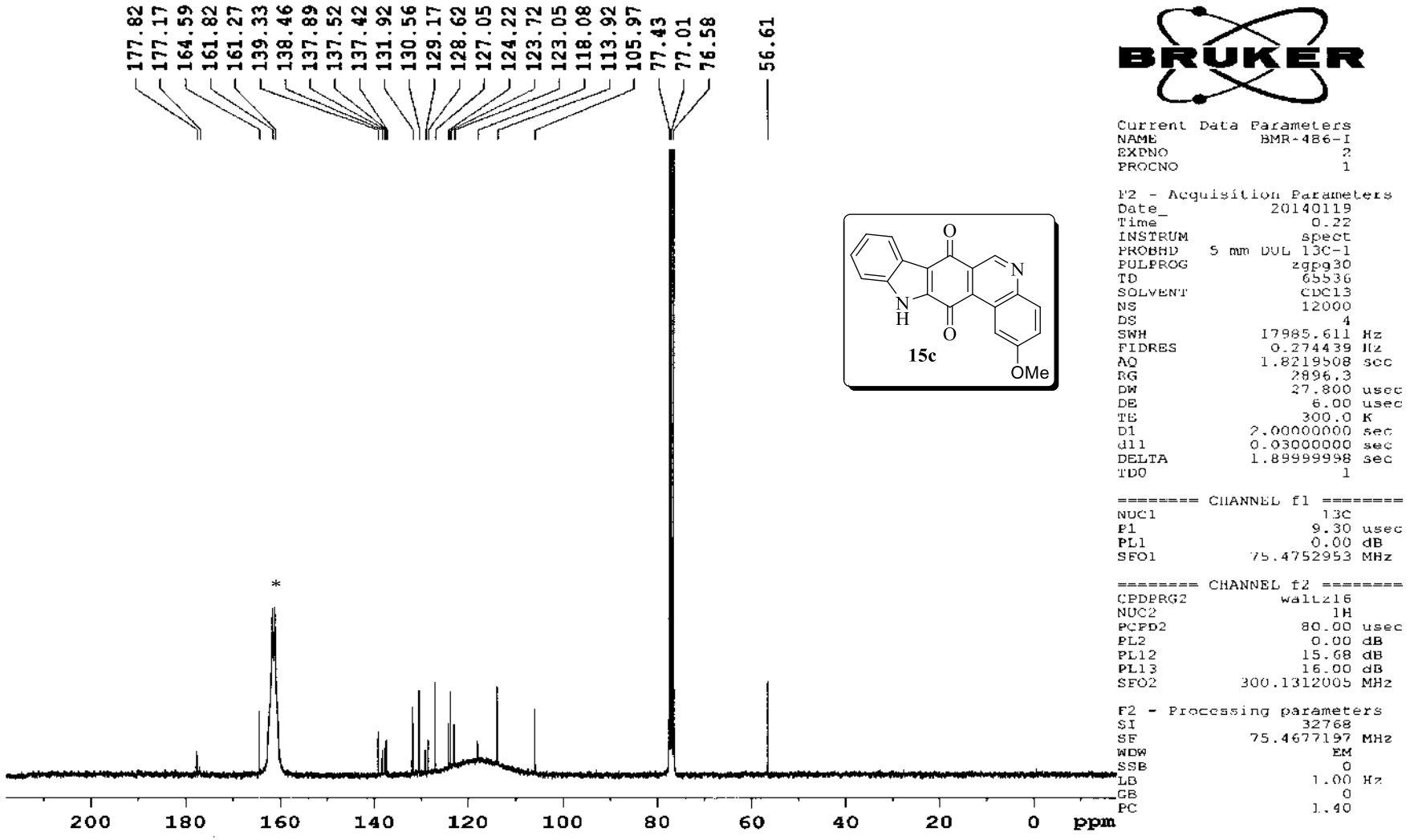
PL2                     9.00 dB
PL12                   15.68 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF                79.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15c**



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```
Current Data Parameters
NAME                  BMR-486-I
EXPNO                         2
PROCNO                        1

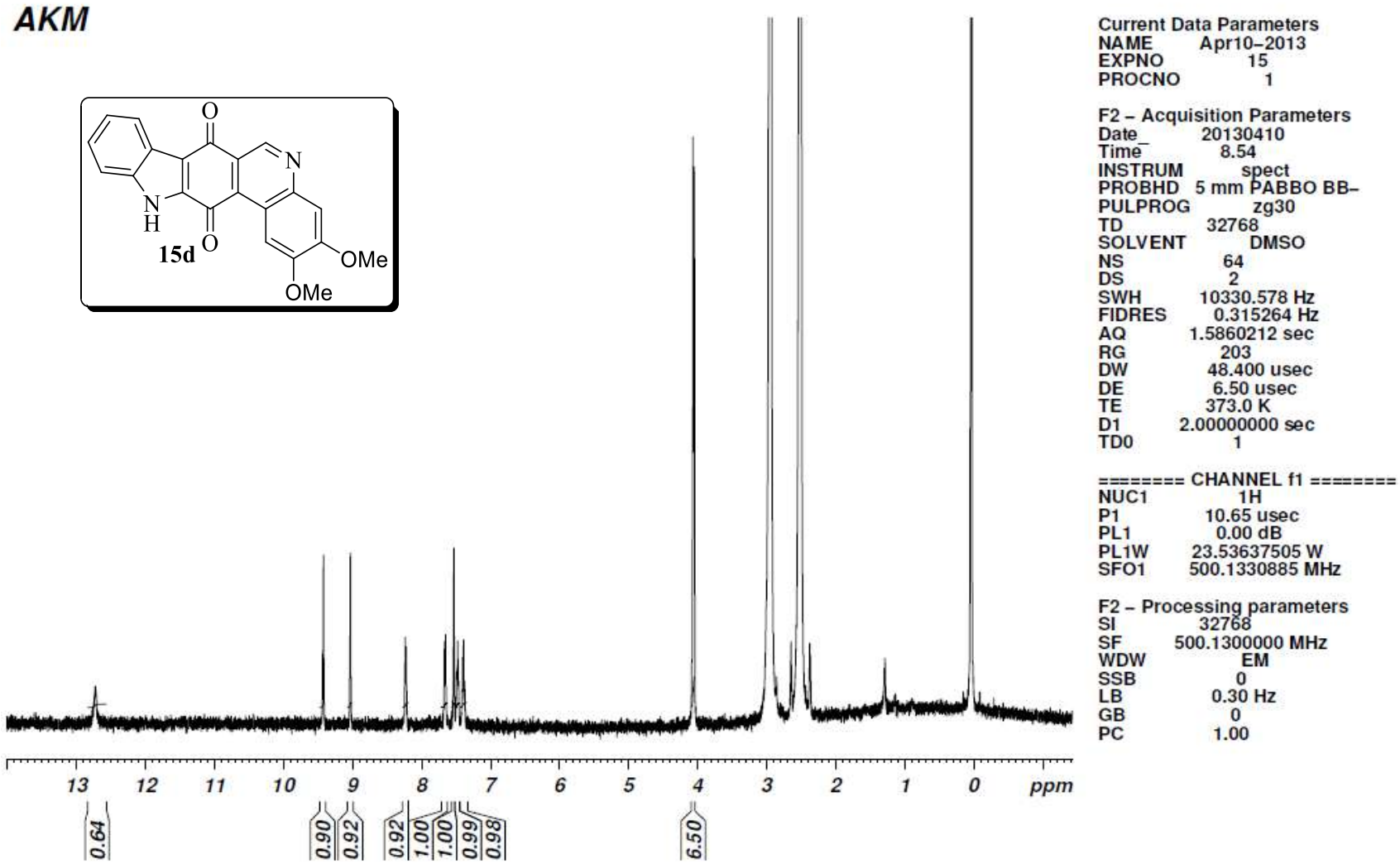
F2 - Acquisition Parameters
Date_                  20140119
Time                       0.22
INSTRUM                   spect
PROBHD     5 mm DUL 13C-1
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                       12000
DS                           4
SWH                  17985.611 Hz
FIDRES                0.274439 Hz
AQ                   1.8219508 sec
RG                      2896.3
DW                      27.800 usec
DE                       6.00 usec
TE                      300.0 K
D1                   2.00000000 sec
d11                  0.03000000 sec
DELTA                1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.30 usec
PL1                       0.00 dB
SFO1                75.4752953 MHz

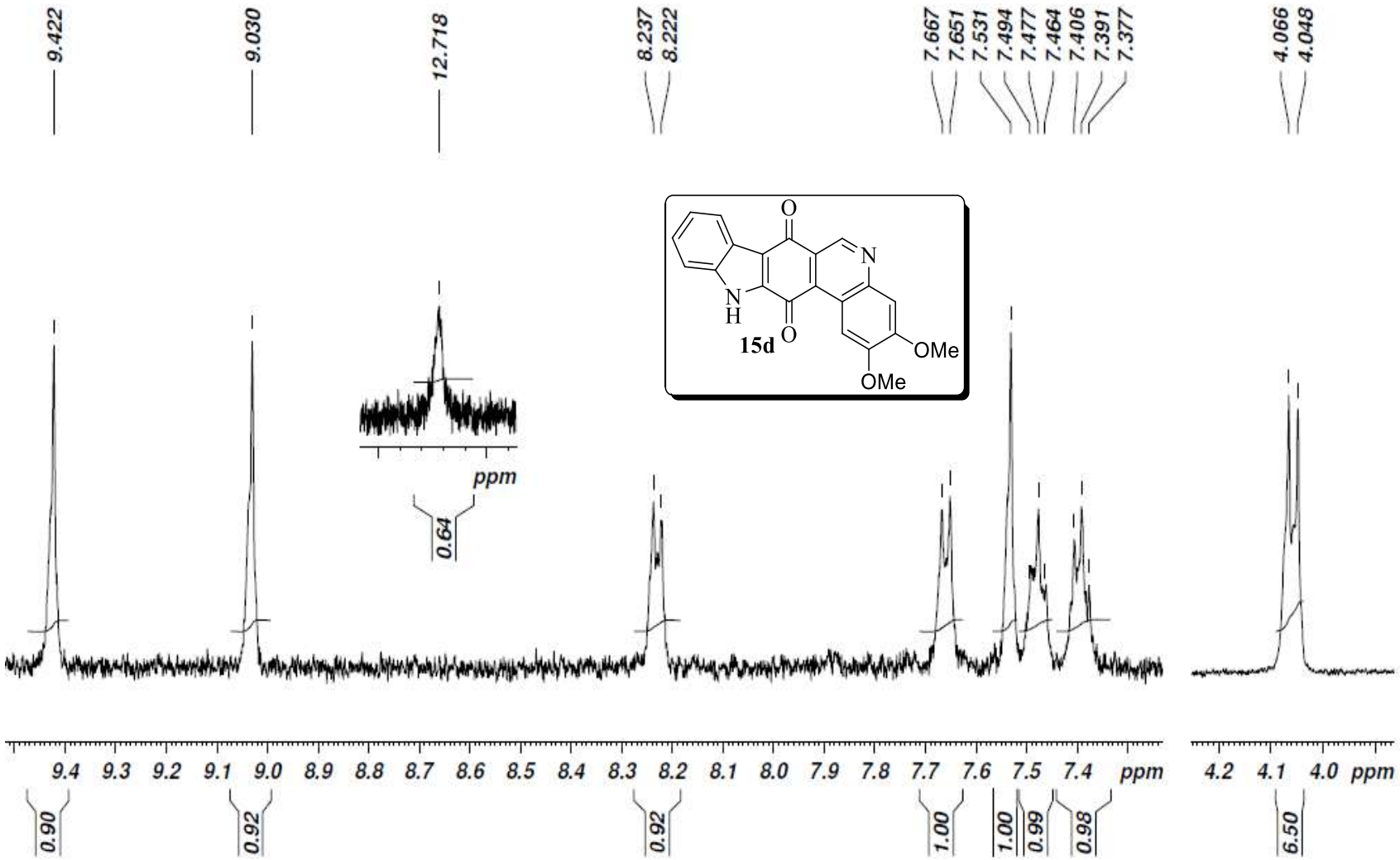
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       0.00 dB
PL12                     15.68 dB
PL13                     16.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                  75.4677197 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

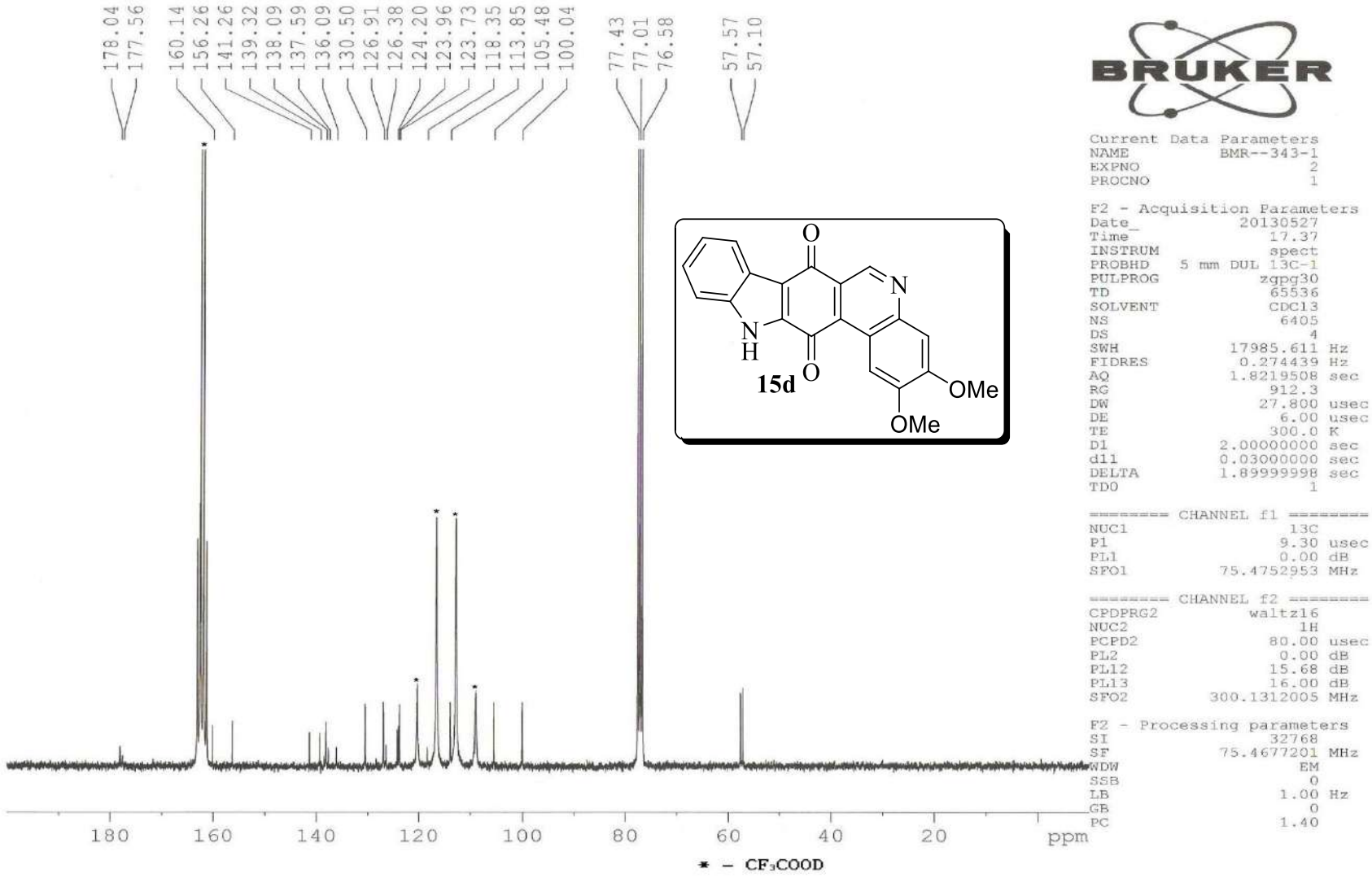
^{13}C-NMR spectrum of compound *-CF_3COOD



^{1}H-NMR spectrum of compound **15d**



^{1}H-NMR spectrum of compound **15d** (Expanded region)



BRUKER

Current Data Parameters
NAME BMR--343-1
EXPNO 2
PROCNO 1

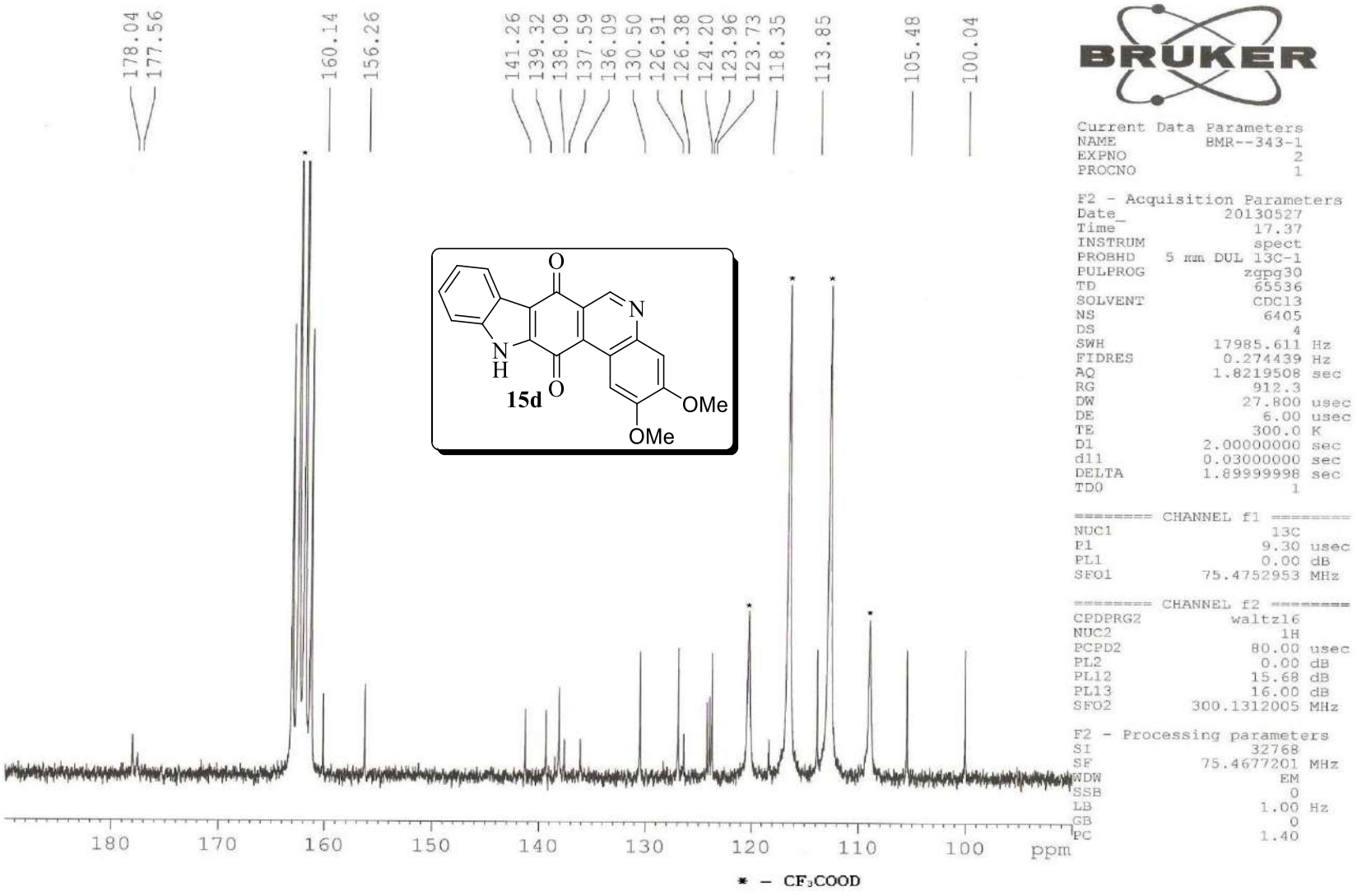
F2 - Acquisition Parameters
Date_ 20130527
Time 17.37
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6405
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 912.3
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677201 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C-NMR spectrum of compound **15d**



Current Data Parameters
NAME BMR--343-1
EXPNO 2
PROCNO 1

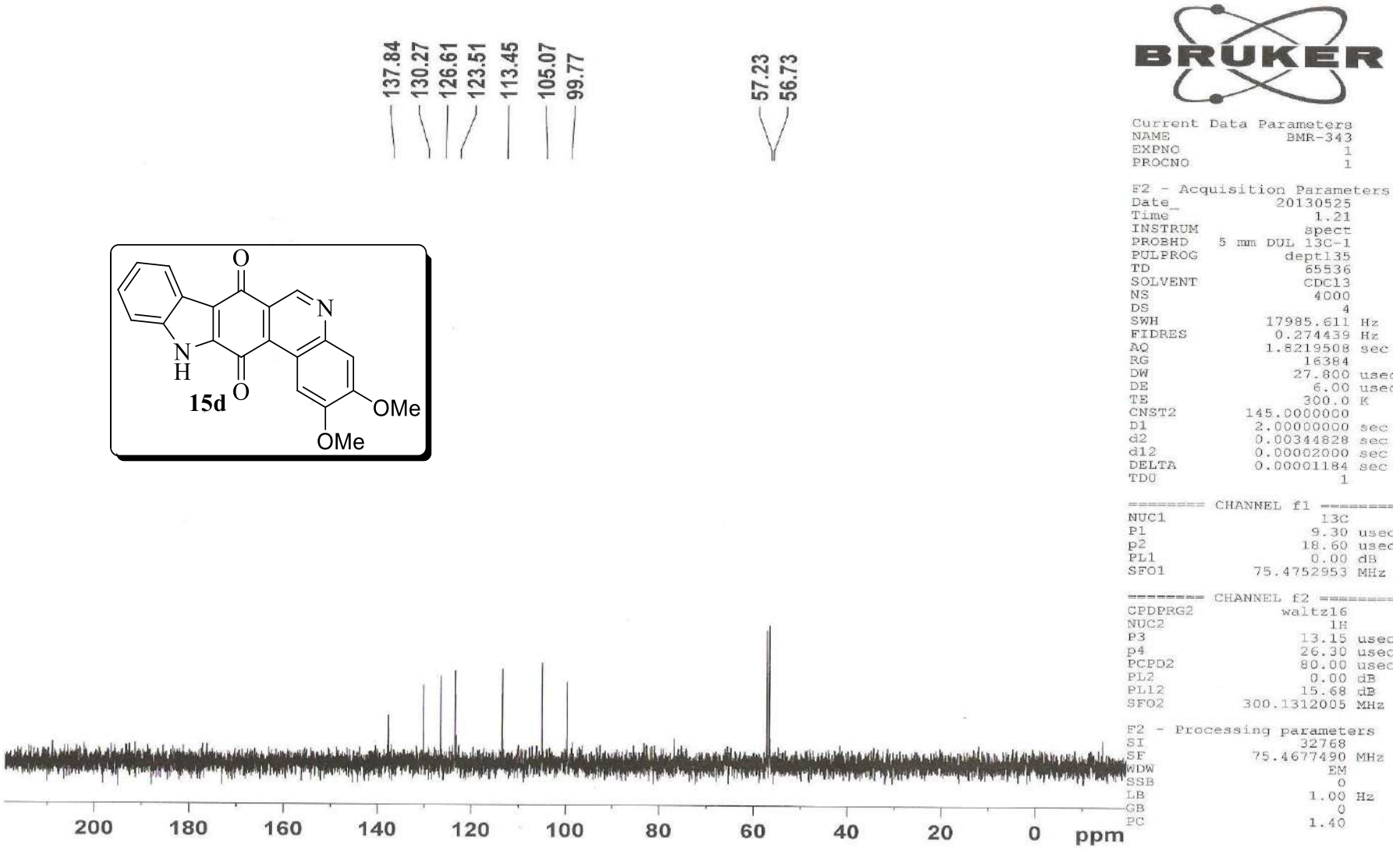
F2 - Acquisition Parameters
Date_ 20130527
Time 17.37
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6405
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 912.3
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677201 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C-NMR spectrum of compound **15d** (Expanded region 190-90 ppm)



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```
Current Data Parameters
NAME                  BMR-343
EXPNO                       1
PROCNO                      1

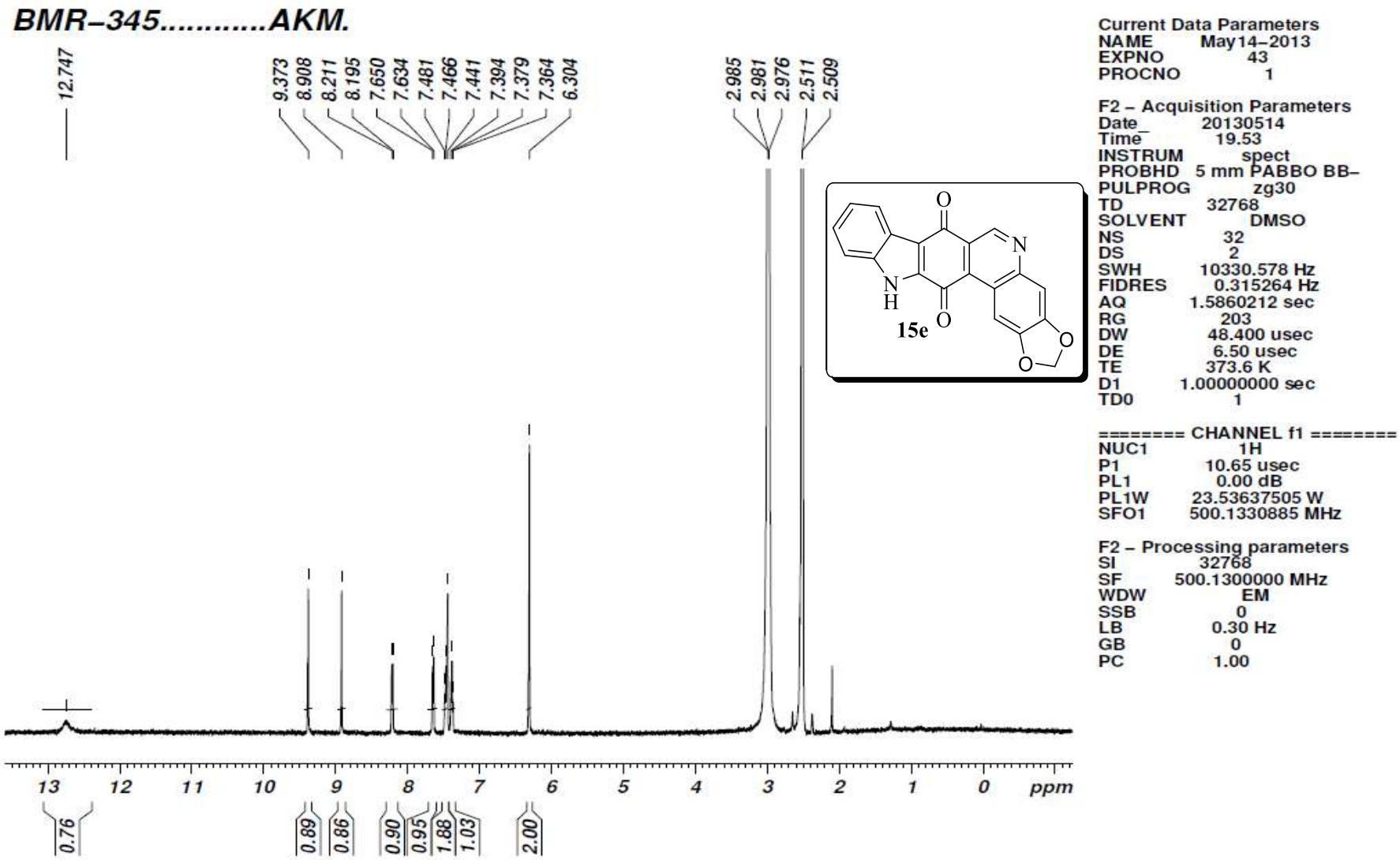
F2 - Acquisition Parameters
Date_              20130525
Time                   1.21
INSTRUM               spect
PROBHD    5 mm DUL 13C-1
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                    4000
DS                       4
SWH              17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   16384
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
CNST2          145.0000000
D1               2.00000000 sec
d2               0.00344828 sec
d12              0.00002000 sec
DELTA            0.00001184 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.30 usec
p2                   18.60 usec
PL1                   0.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
P3                   13.15 usec
p4                   26.30 usec
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.68 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF             75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15d**



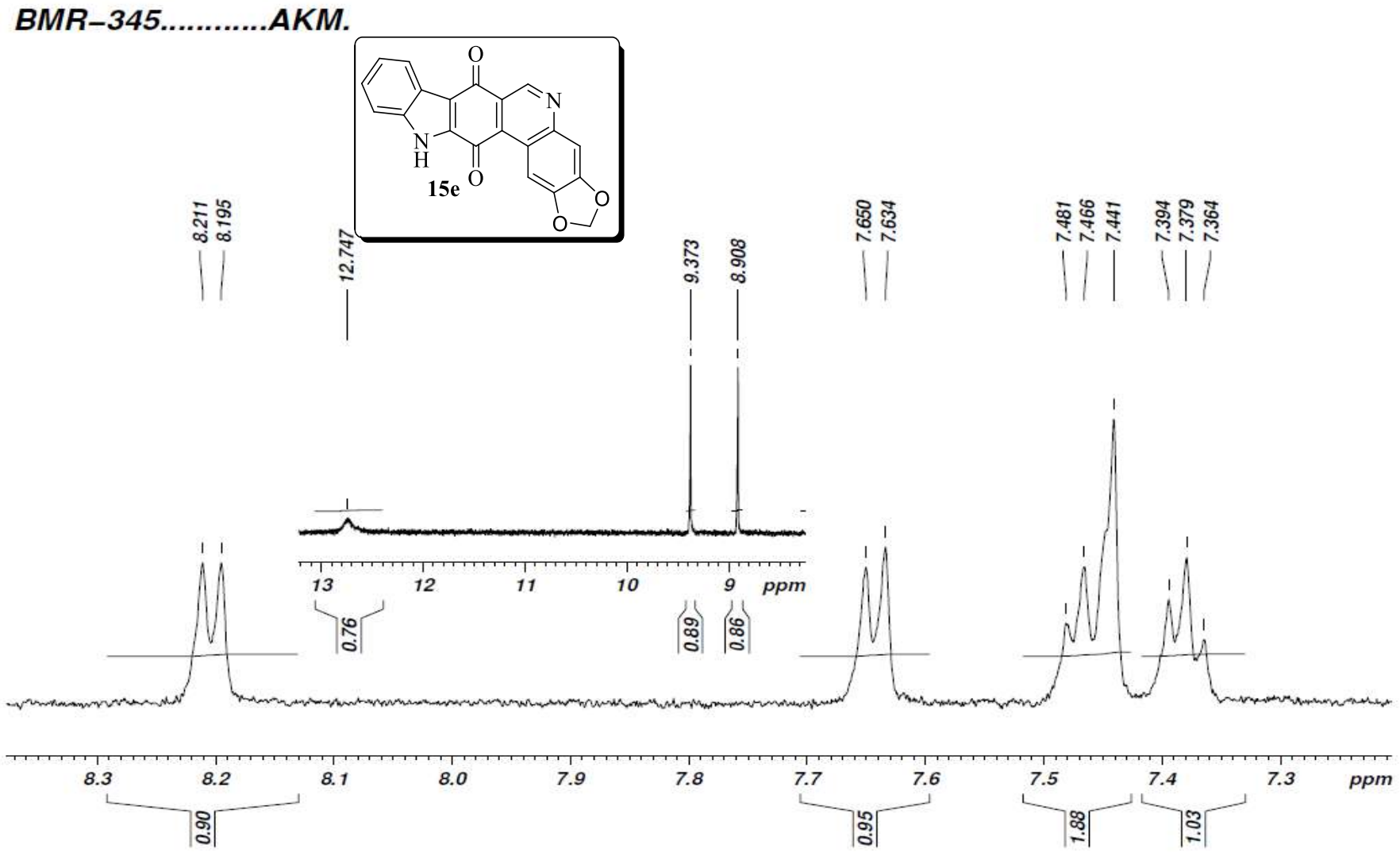
Current Data Parameters
NAME May14–2013
EXPNO 43
PROCNO 1

F2 – Acquisition Parameters
Date_ 20130514
Time 19.53
INSTRUM spect
PROBHD 5 mm PABBO BB–
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 203
DW 48.400 usec
DE 6.50 usec
TE 373.6 K
D1 1.00000000 sec
TD0 1

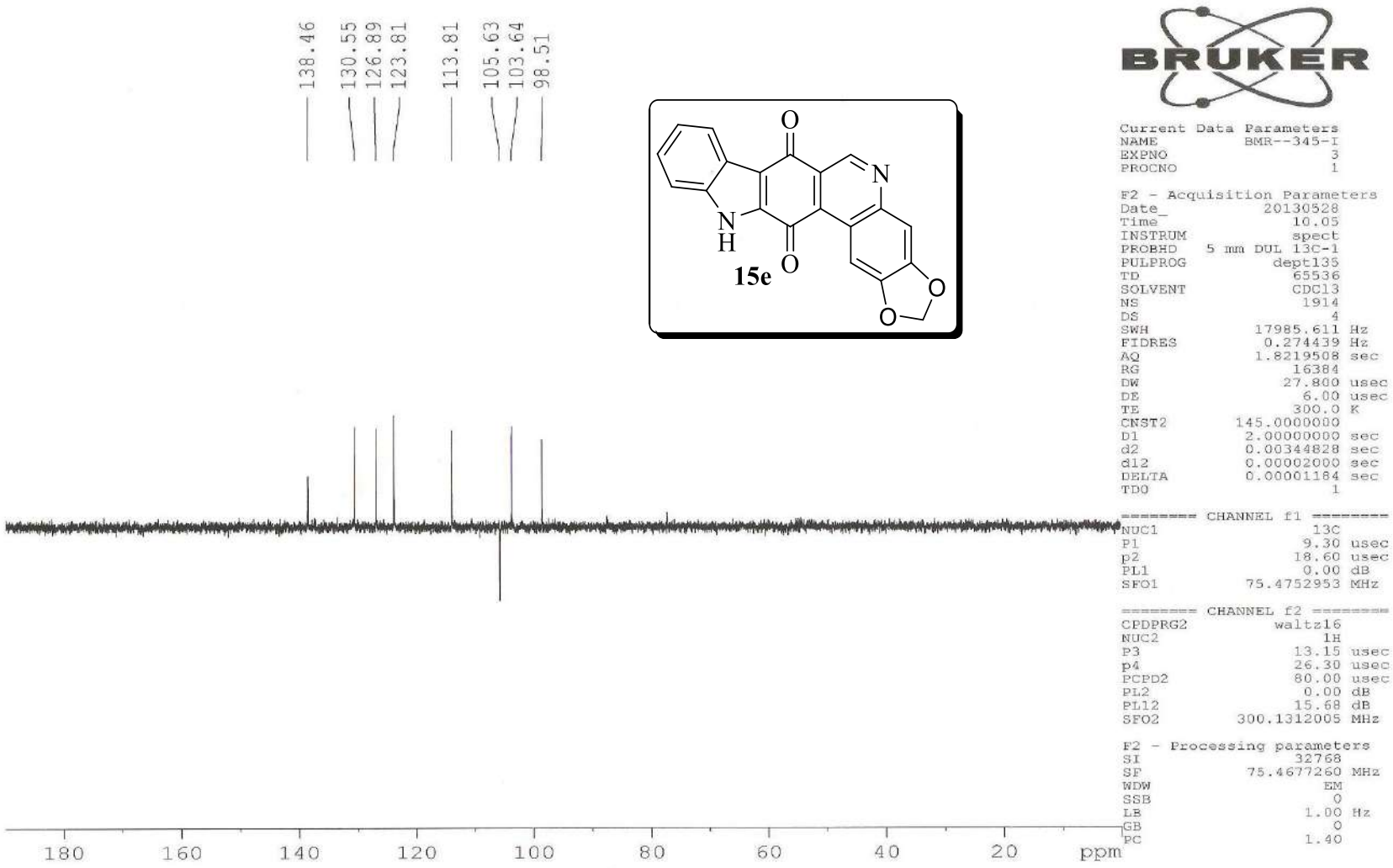
======== CHANNEL f1 ========
NUC1 1H
P1 10.65 usec
PL1 0.00 dB
PL1W 23.53637505 W
SFO1 500.1330885 MHz

F2 – Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H-NMR spectrum of compound **15e**



^{1}H-NMR spectrum of compound **15e** (Expanded region)



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```
Current Data Parameters
NAME                 BMR--345-I
EXPNO                         3
PROCNO                        1

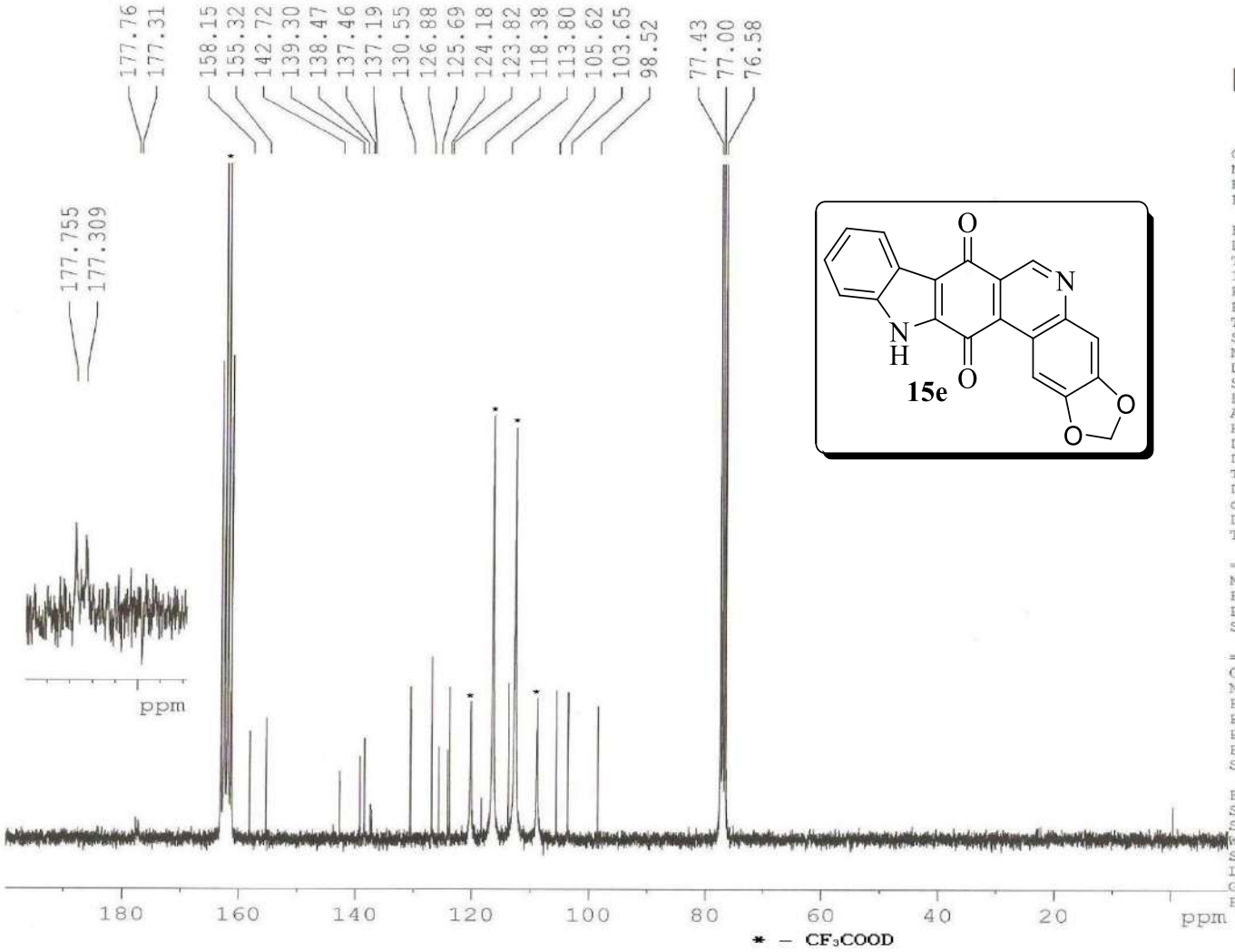
F2 - Acquisition Parameters
Date_                  20130528
Time                      10.05
INSTRUM                   spect
PROBHD     5 mm DUL 13C-1
PULPROG                dept135
TD                        65536
SOLVENT                   CDCl3
NS                         1914
DS                            4
SWH                   17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                        16384
DW                       27.800 usec
DE                        6.00 usec
TE                       300.0 K
CNST2                145.0000000
D1                   2.00000000 sec
d2                   0.00344828 sec
d12                  0.00002000 sec
DELTA                0.00001184 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.30 usec
p2                        18.60 usec
PL1                        0.00 dB
SFO1                 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
P3                        13.15 usec
p4                        26.30 usec
PCPD2                     80.00 usec
PL2                        0.00 dB
PL12                      15.68 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                   75.4677260 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15e**




```
Current Data Parameters
NAME                  BMR--345-I
EXPNO                          2
PROCNO                         1

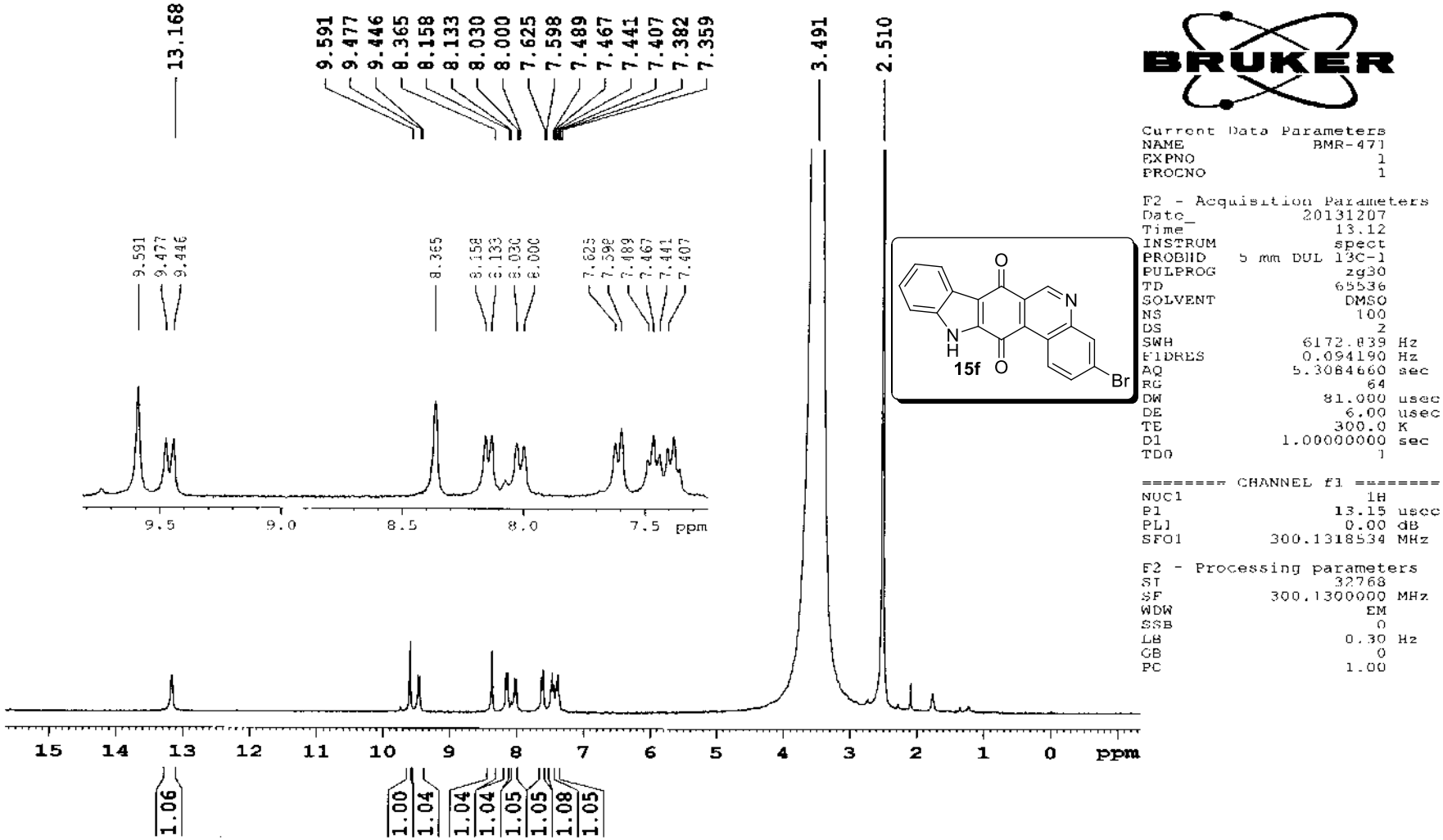
F2 - Acquisition Parameters
Date_                   20130528
Time                        1.20
INSTRUM                    spect
PROBHD    5 mm DUL 13C-1
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         8108
DS                            4
SWH                   17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                       1448.2
DW                       27.800 usec
DE                        6.00 usec
TE                       300.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                          9.30 usec
PL1                         0.00 dB
SFO1                 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                      80.00 usec
PL2                         0.00 dB
PL12                       15.68 dB
PL13                       16.00 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                           32768
SF                   75.4677259 MHz
WDW                             EM
SSB                              0
LB                          1.00 Hz
GB                               0
PC                          1.40
```

^{13}C-NMR spectrum of compound **15e**



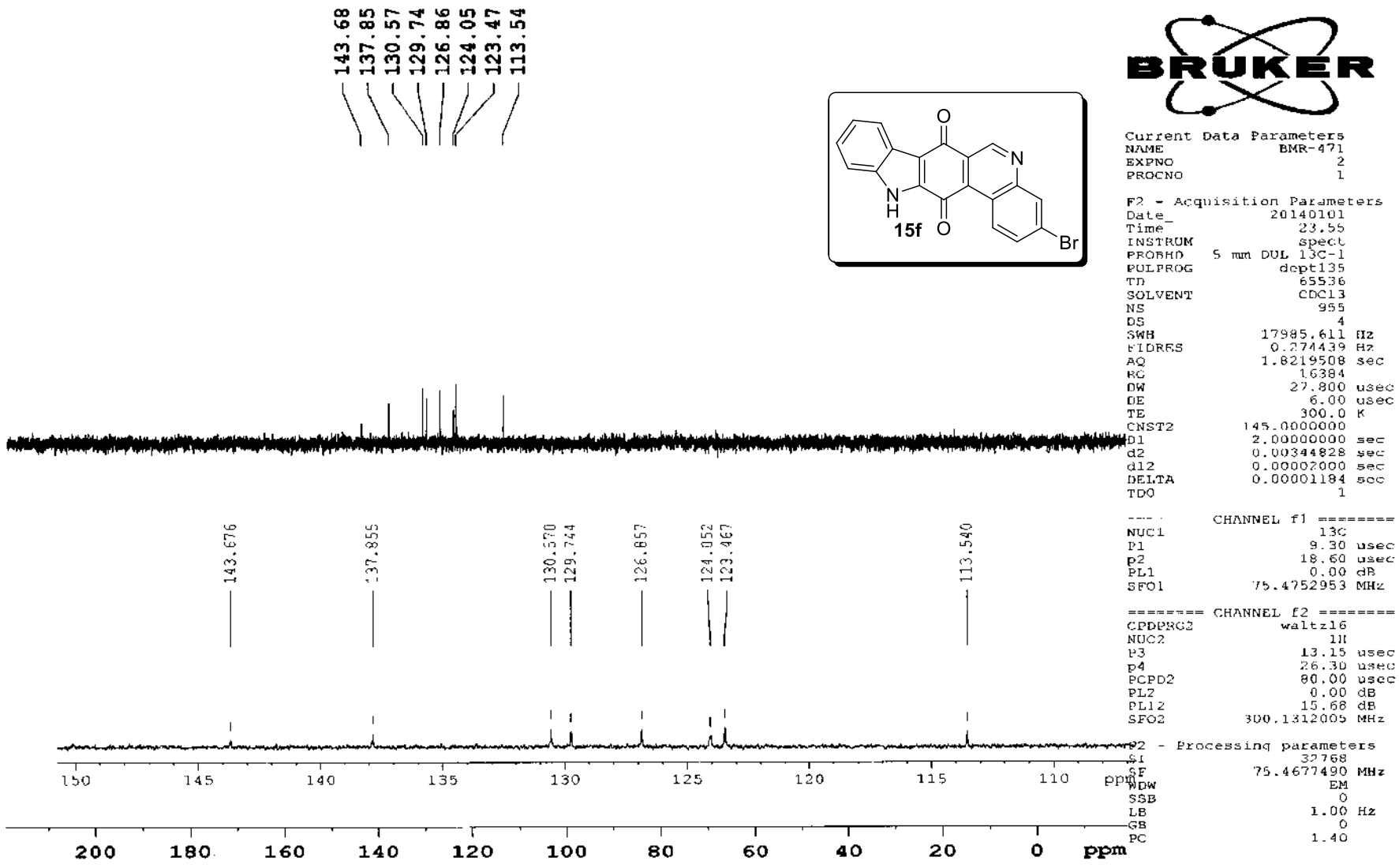
Current Data Parameters
NAME BMR-471
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131207
Time 13.12
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 100
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 64
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

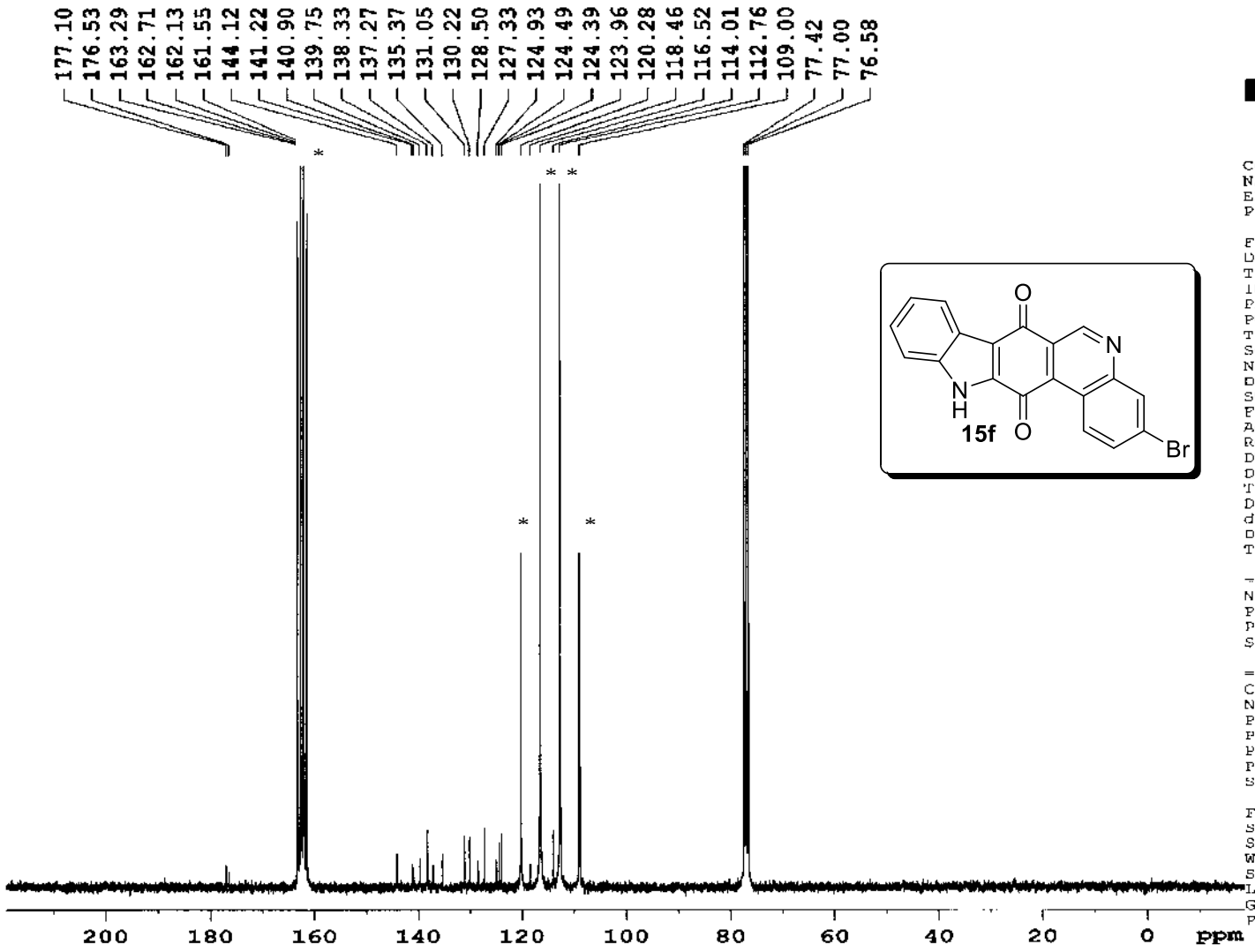
======== CHANNEL f1 ========
NUC1 1H
P1 13.15 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H-NMR spectrum of compound **15f**



DEPT 135-^{13}C NMR spectrum of compound **15f**



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```
Current Data Parameters
NAME                  BMR-471
EXPNO                       3
PROCNO                      1

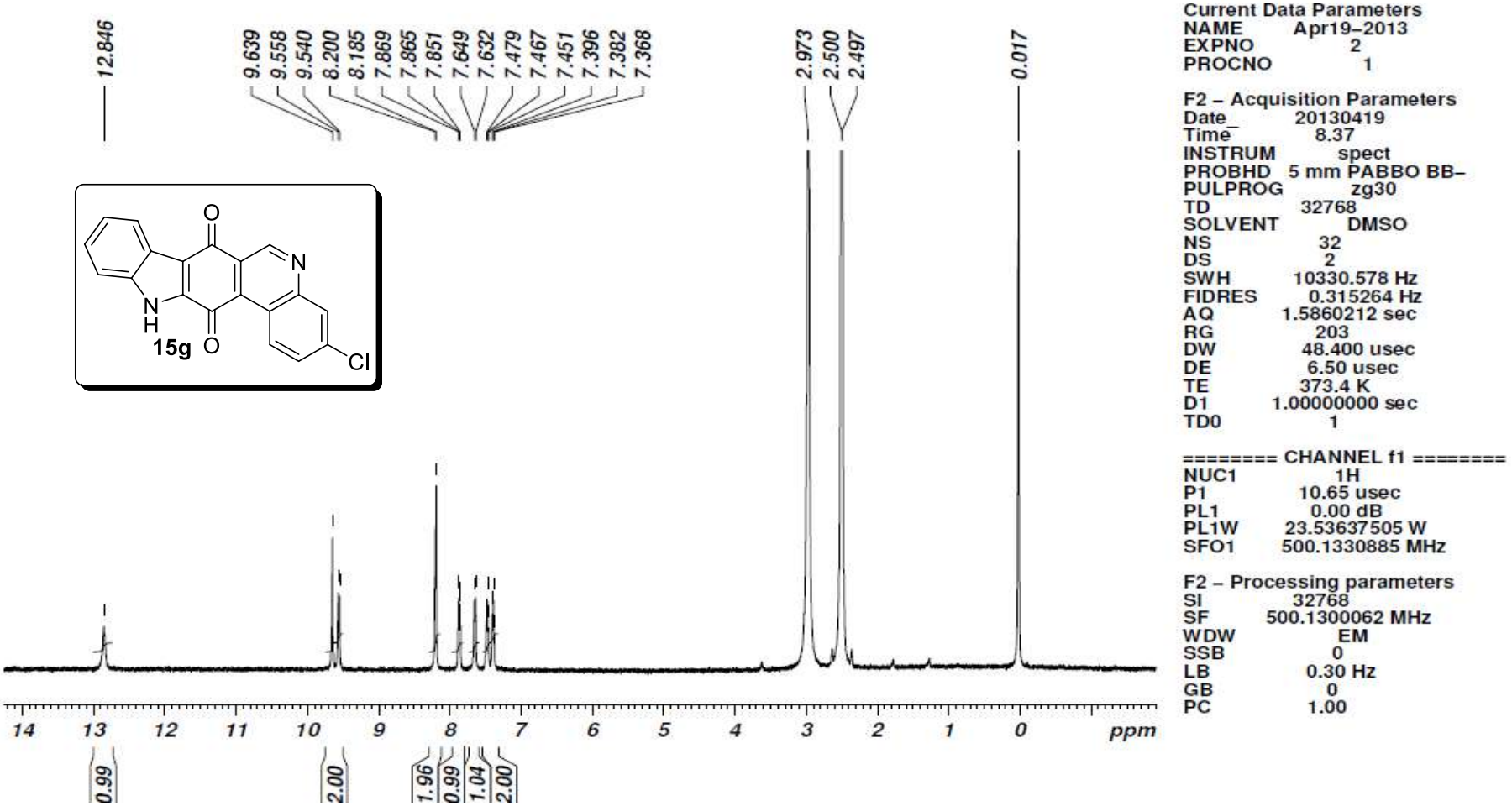
F2 - Acquisition Parameters
Date                 20140102
Time                     8.14
INSTRUM                  spect
PROBHD     5 mm DUL 13C-1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       8701
DS                          4
SWH                 17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                     2298.8
DW                     27.800 usec
DE                      6.00 usec
TE                     300.0 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.30 usec
PL1                      0.00 dB
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.68 dB
PL13                    16.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                  75.4677118 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                          1.40
```

^{13}C-NMR spectrum of com[illegible] *-CF_3COOD [illegible]



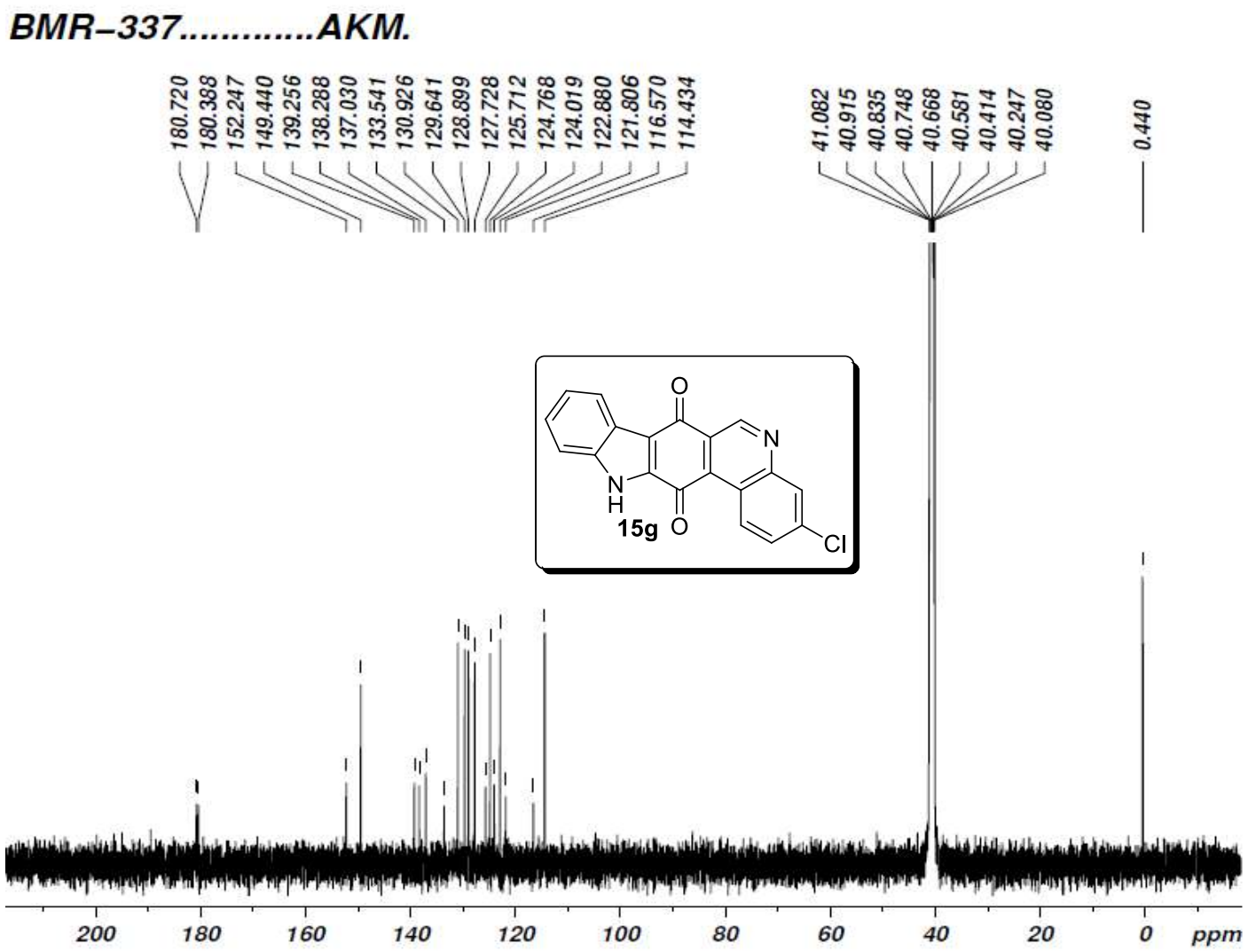
Current Data Parameters
NAME Apr19–2013
EXPNO 2
PROCNO 1

F2 – Acquisition Parameters
Date_ 20130419
Time 8.37
INSTRUM spect
PROBHD 5 mm PABBO BB–
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 203
DW 48.400 usec
DE 6.50 usec
TE 373.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.65 usec
PL1 0.00 dB
PL1W 23.53637505 W
SFO1 500.1330885 MHz

F2 – Processing parameters
SI 32768
SF 500.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H-NMR spectrum of compound **15g**



Current Data Parameters
NAME Apr19–2013
EXPNO 1
PROCNO 1

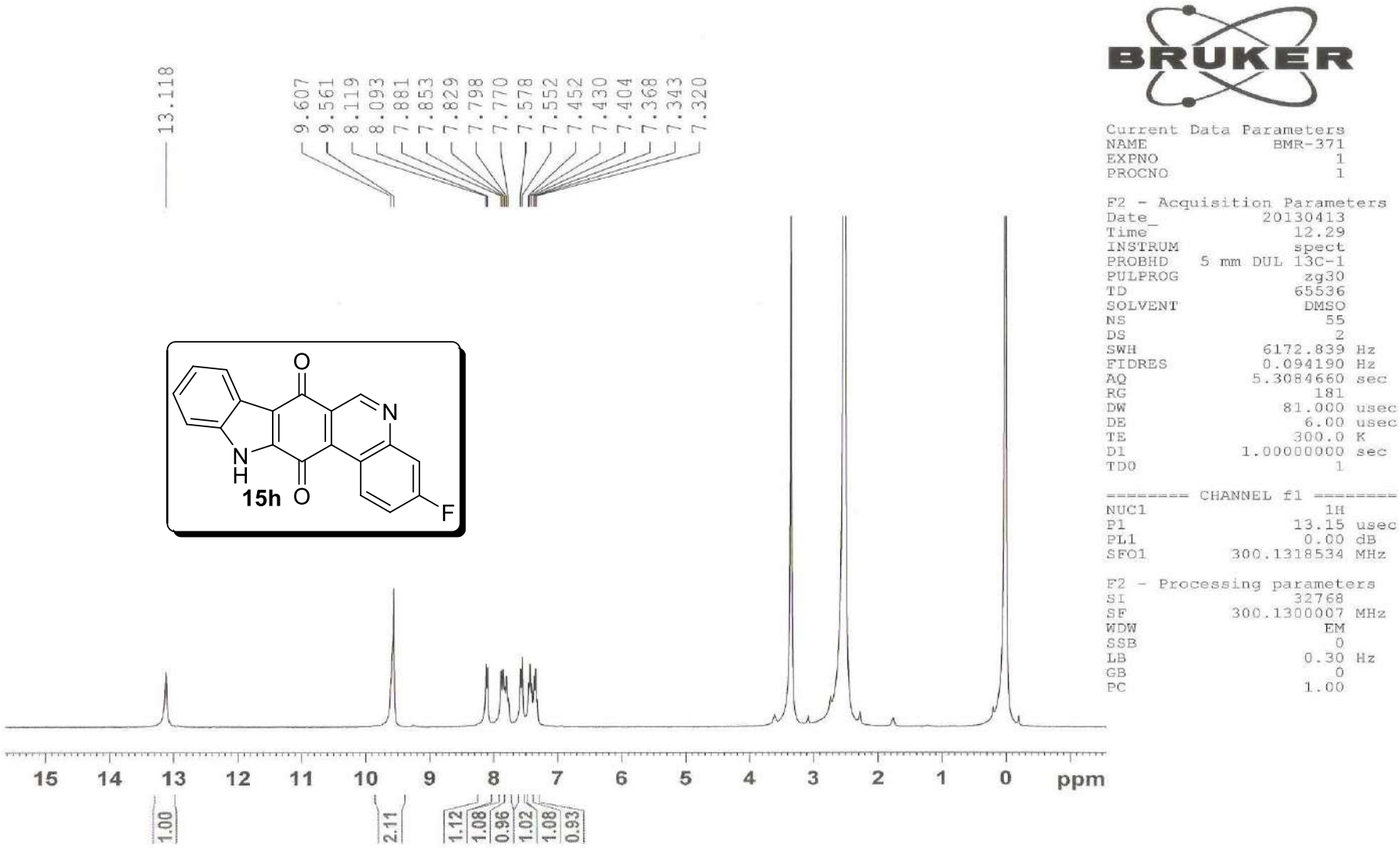
F2 – Acquisition Parameters
Date_ 20130419
Time 3.42
INSTRUM spect
PROBHD 5 mm PABBO BB–
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 5684
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 372.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.80 usec
PL1 0.00 dB
PL1W 70.83519745 W
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.51 dB
PL13 18.00 dB
PL2W 23.53637505 W
PL12W 0.41757989 W
PL13W 0.37302643 W
SFO2 500.1320005 MHz

F2 – Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C-NMR spectrum of compound **15g**



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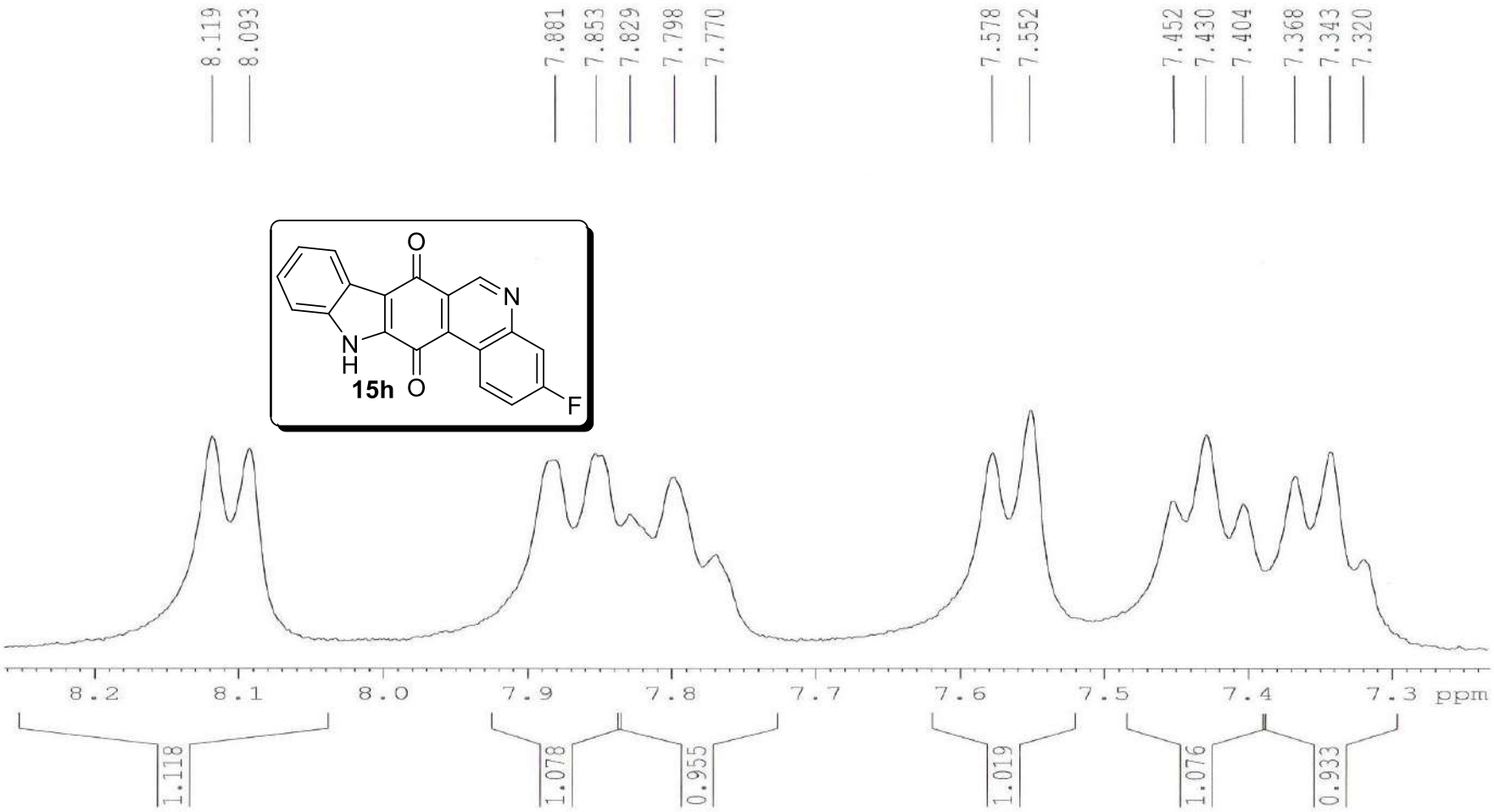
```
Current Data Parameters
NAME                  BMR-371
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130413
Time                   12.29
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       55
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                      181
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                         1

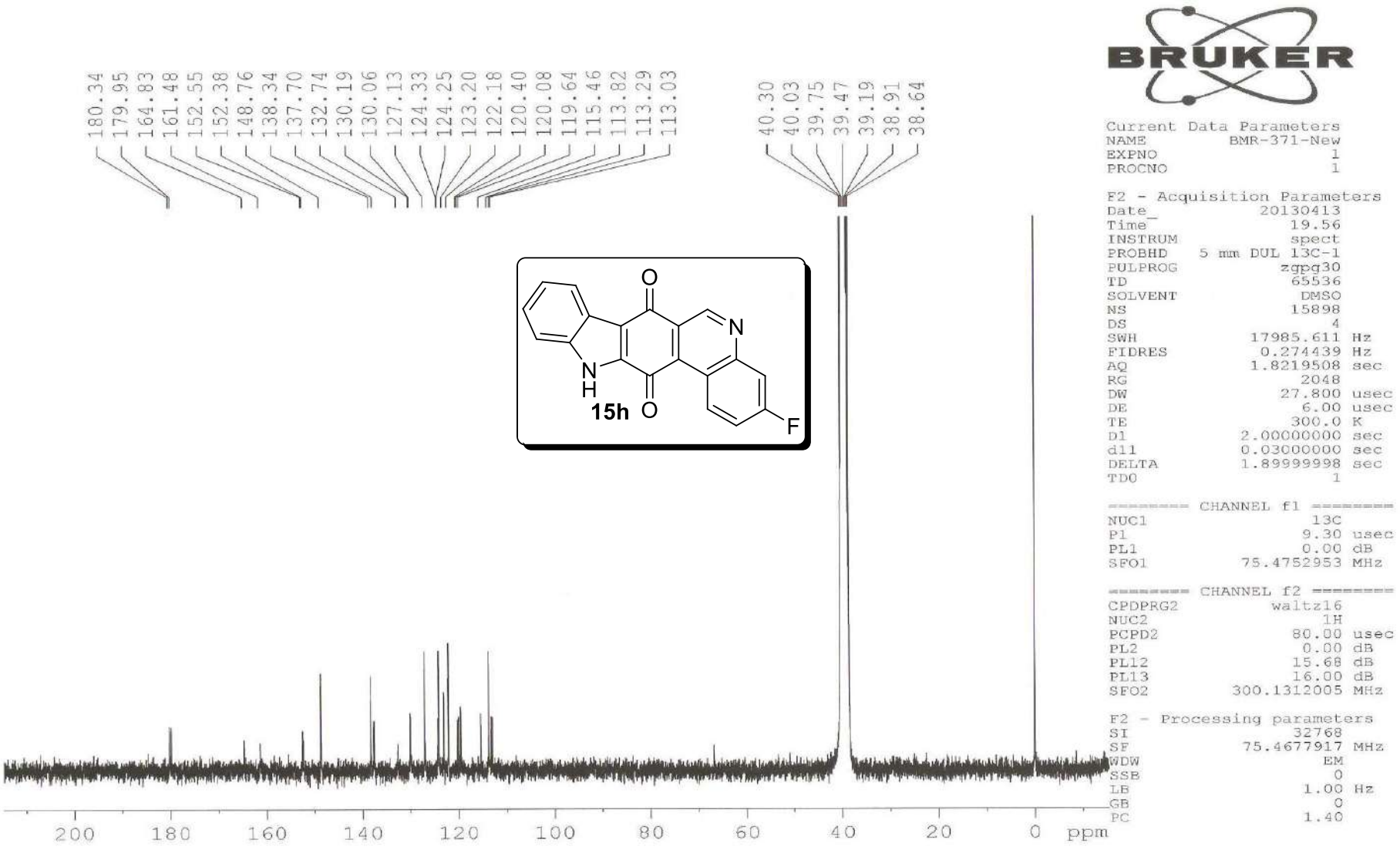
======== CHANNEL f1 ========
NUC1                       1H
P1                    13.15 usec
PL1                    0.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                      32768
SF             300.1300007 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                     1.00
```

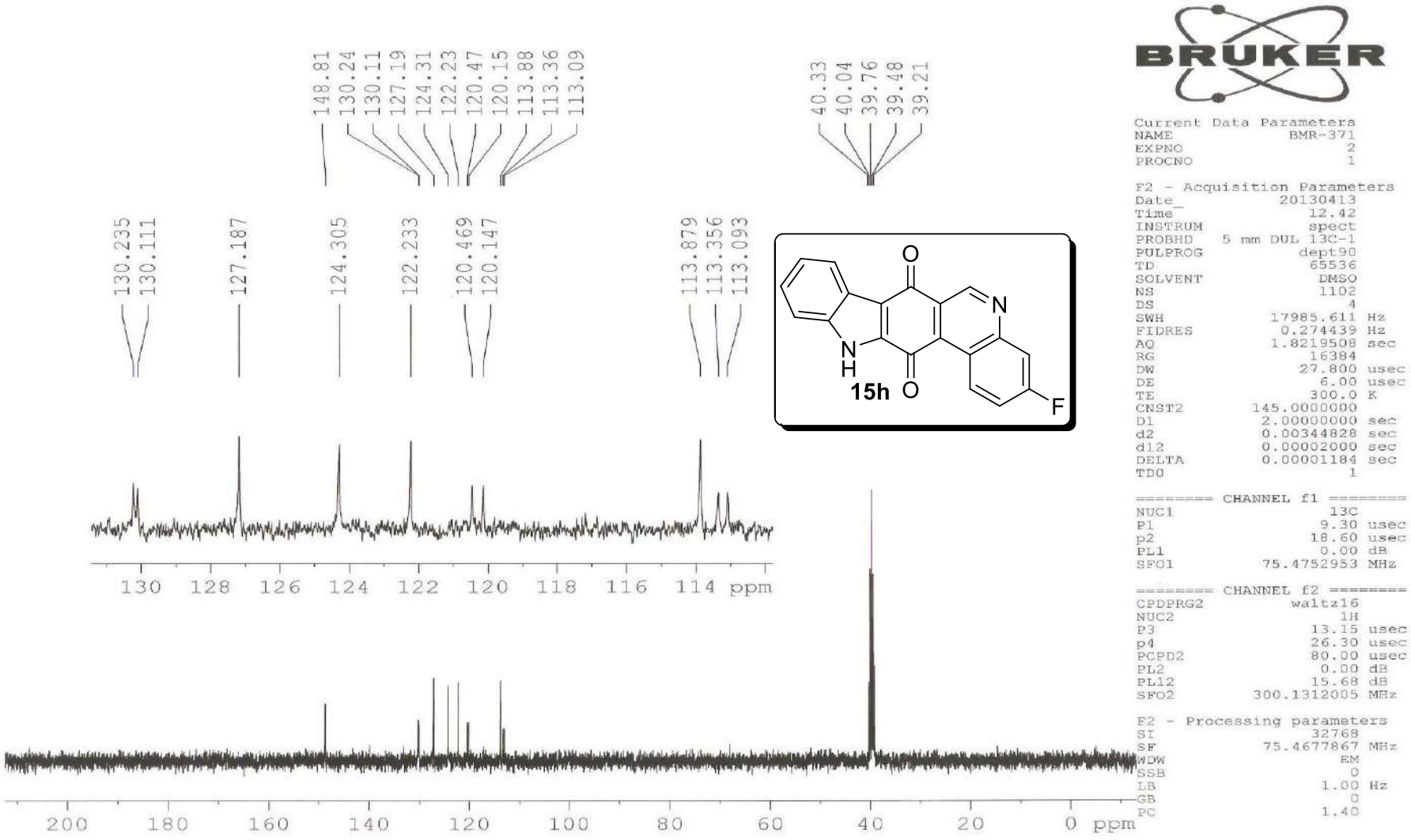
^{1}H-NMR spectrum of compound **15h**



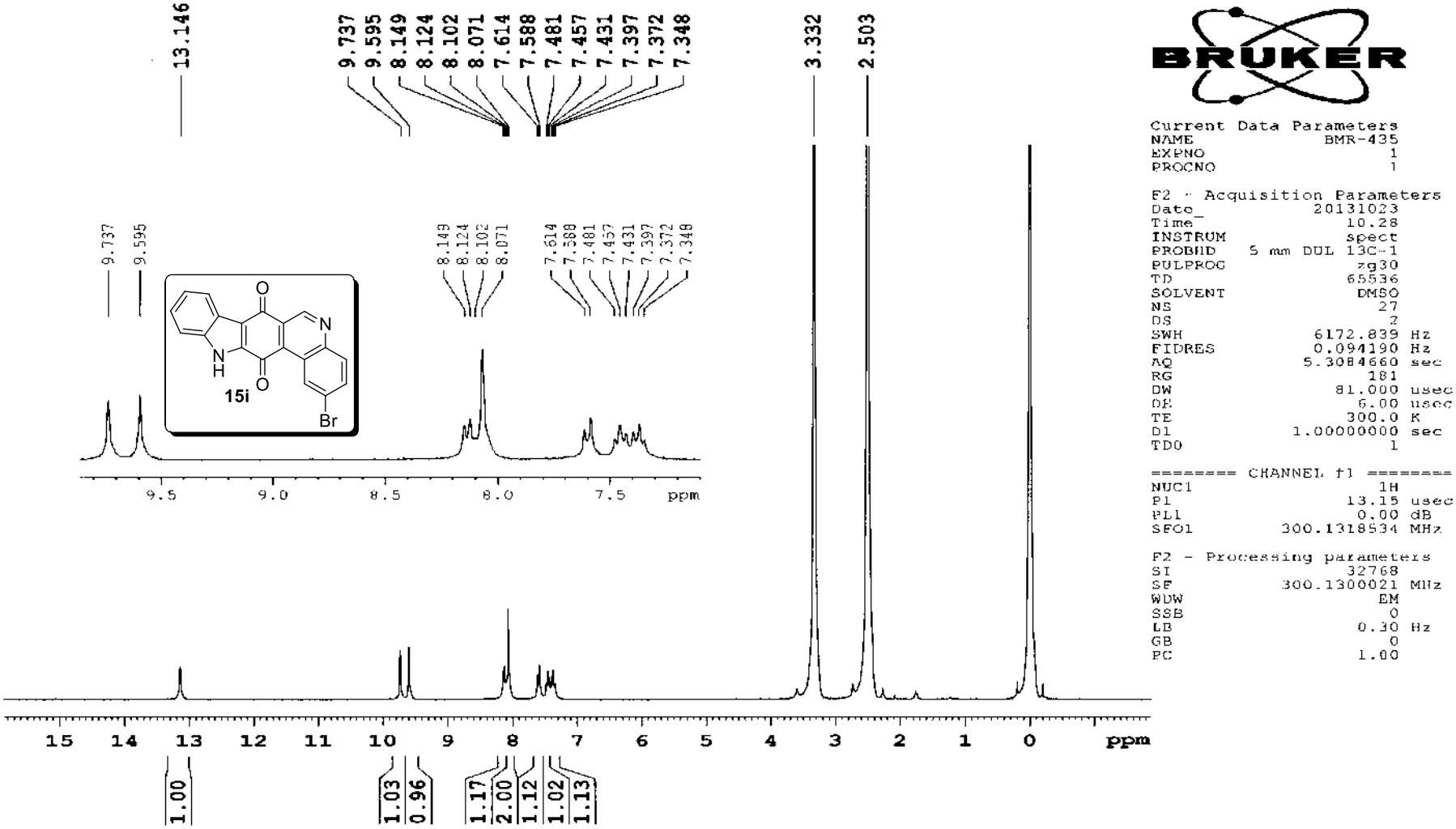
^{1}H-NMR spectrum of compound **15h** (Expanded region 8.3-7.3 ppm)



^{13}C-NMR spectrum of compound **15h**



DEPT 90-^{13}C NMR spectrum of compound **15h**



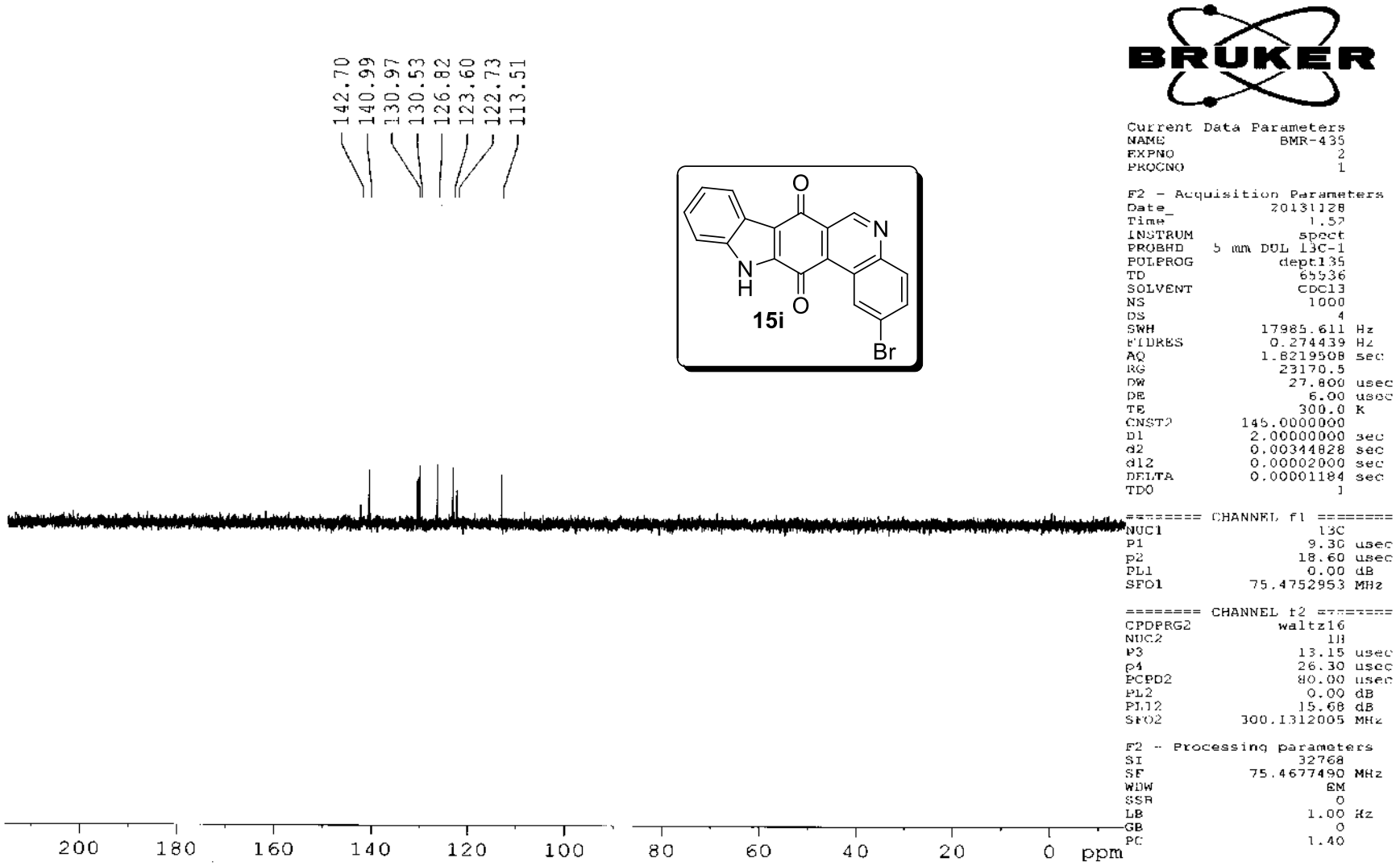
Current Data Parameters
NAME BMR-435
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131023
Time 10.28
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 27
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.15 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300021 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H-NMR spectrum of compound **15i**




```
Current Data Parameters
NAME                  BMR-435
EXPNO                       2
PROCNO                      1

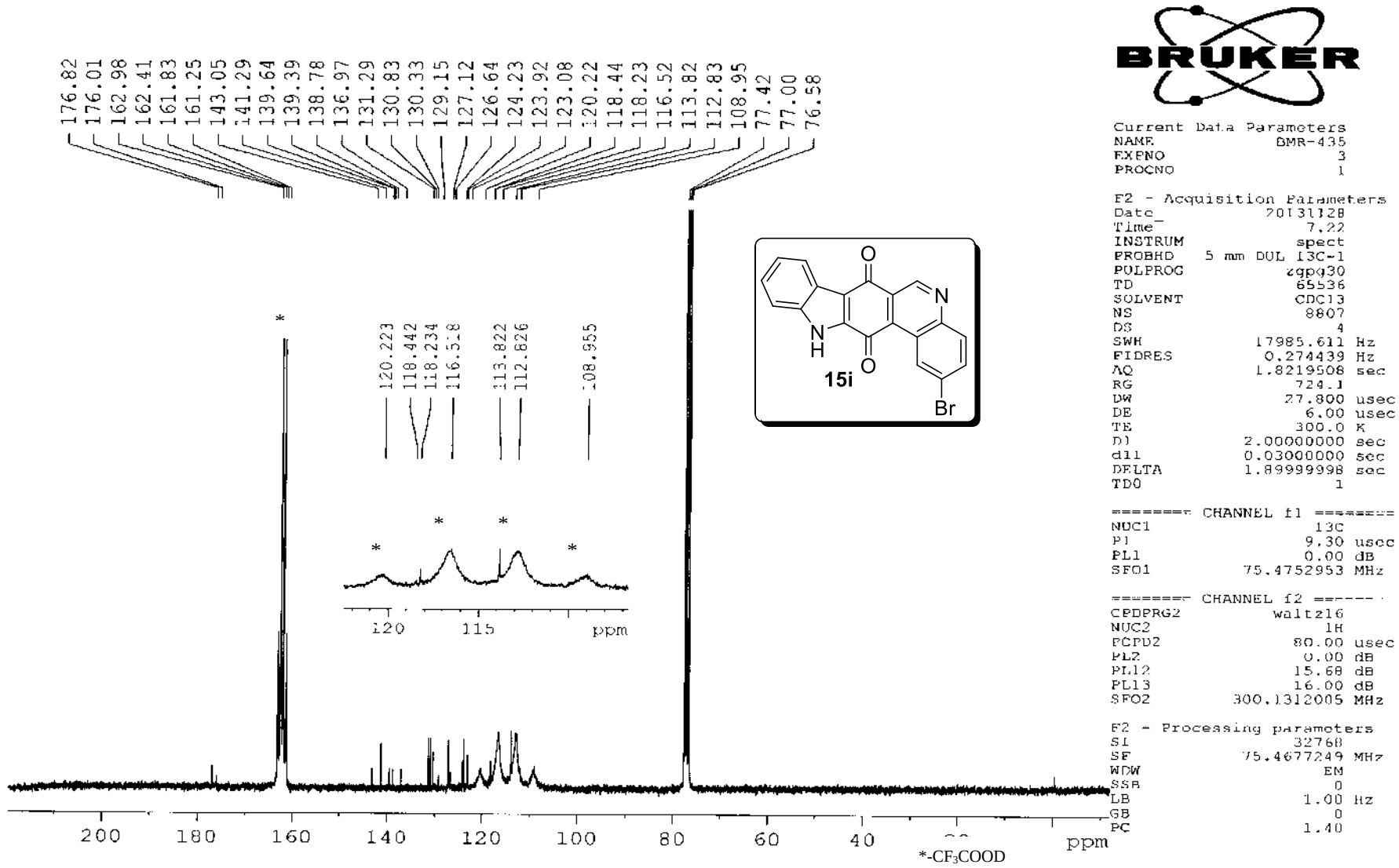
F2 - Acquisition Parameters
Date_              20131128
Time                   1.52
INSTRUM               spect
PROBHD    5 mm DUL 13C-1
PULPROG            dept135
TD                    65536
SOLVENT               CDCl3
NS                     1000
DS                        4
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                  23170.5
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
CNST2            145.0000000
D1                2.00000000 sec
d2                0.00344828 sec
d12               0.00002000 sec
DELTA             0.00001184 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.30 usec
p2                      18.60 usec
PL1                      0.00 dB
SFO1               75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                      13.15 usec
p4                      26.30 usec
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.68 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                 75.4677490 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                       1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15i**



Current Data Parameters
NAME BMR-435
EXPNO 3
PROCNO 1

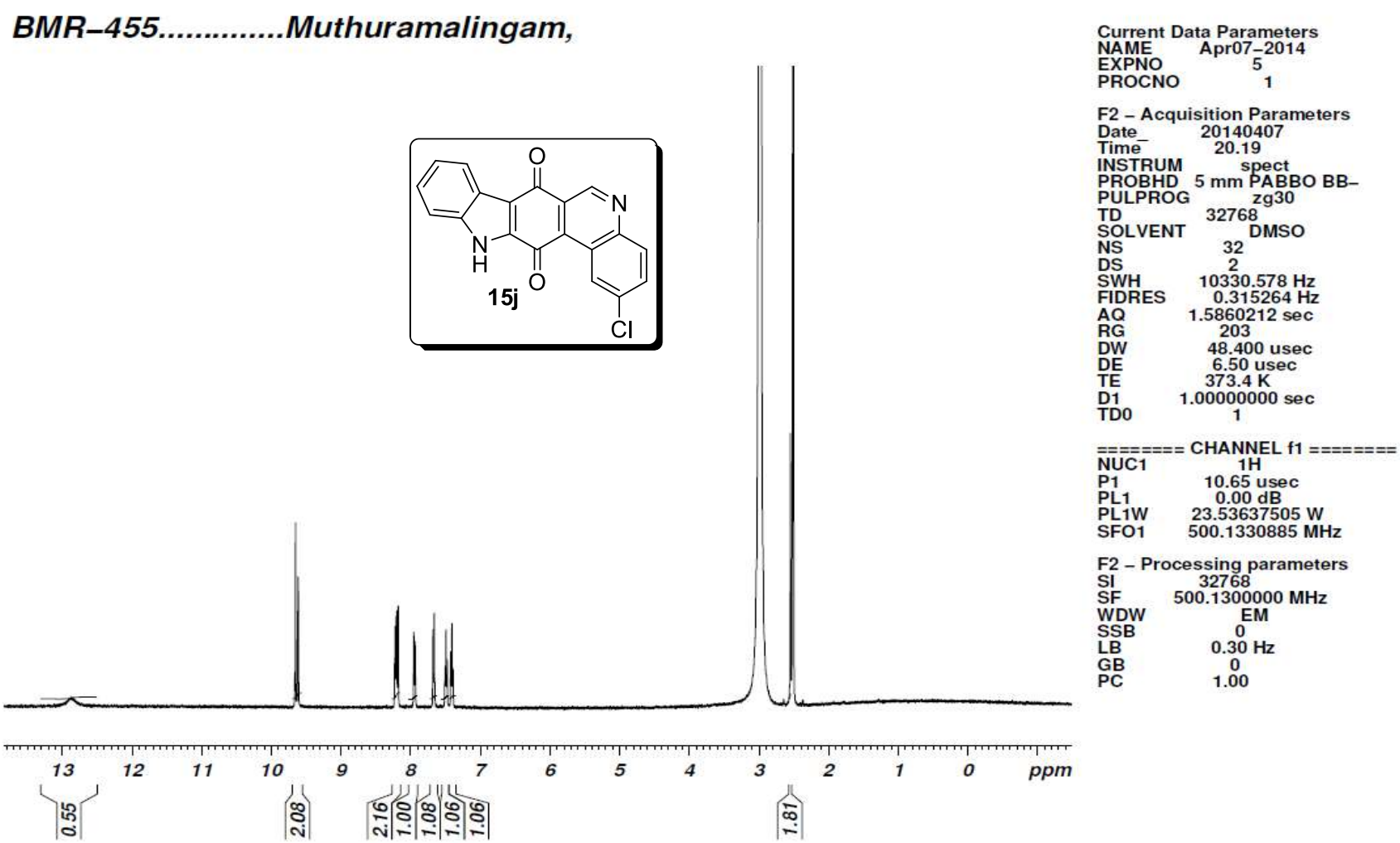
F2 - Acquisition Parameters
Date_ 20131128
Time 7.22
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8807
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 724.1
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677249 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C-NMR spectrum of compound **15i**



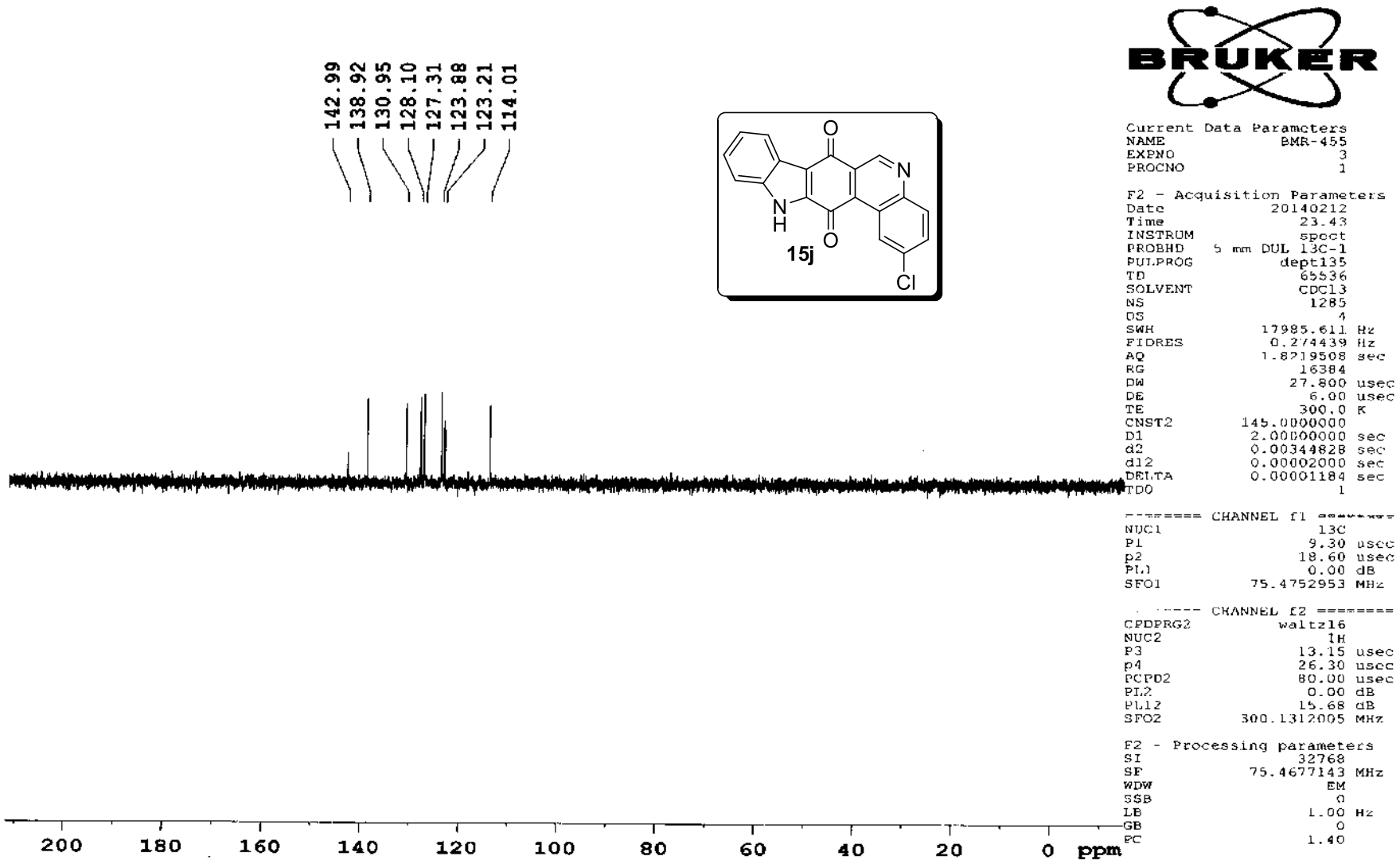
Current Data Parameters
NAME Apr07–2014
EXPNO 5
PROCNO 1

F2 – Acquisition Parameters
Date_ 20140407
Time 20.19
INSTRUM spect
PROBHD 5 mm PABBO BB–
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 203
DW 48.400 usec
DE 6.50 usec
TE 373.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.65 usec
PL1 0.00 dB
PL1W 23.53637505 W
SFO1 500.1330885 MHz

F2 – Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H-NMR spectrum of compound **15j**



BRUKER

```
Current Data Parameters
NAME                  BMR-455
EXPNO                       3
PROCNO                      1

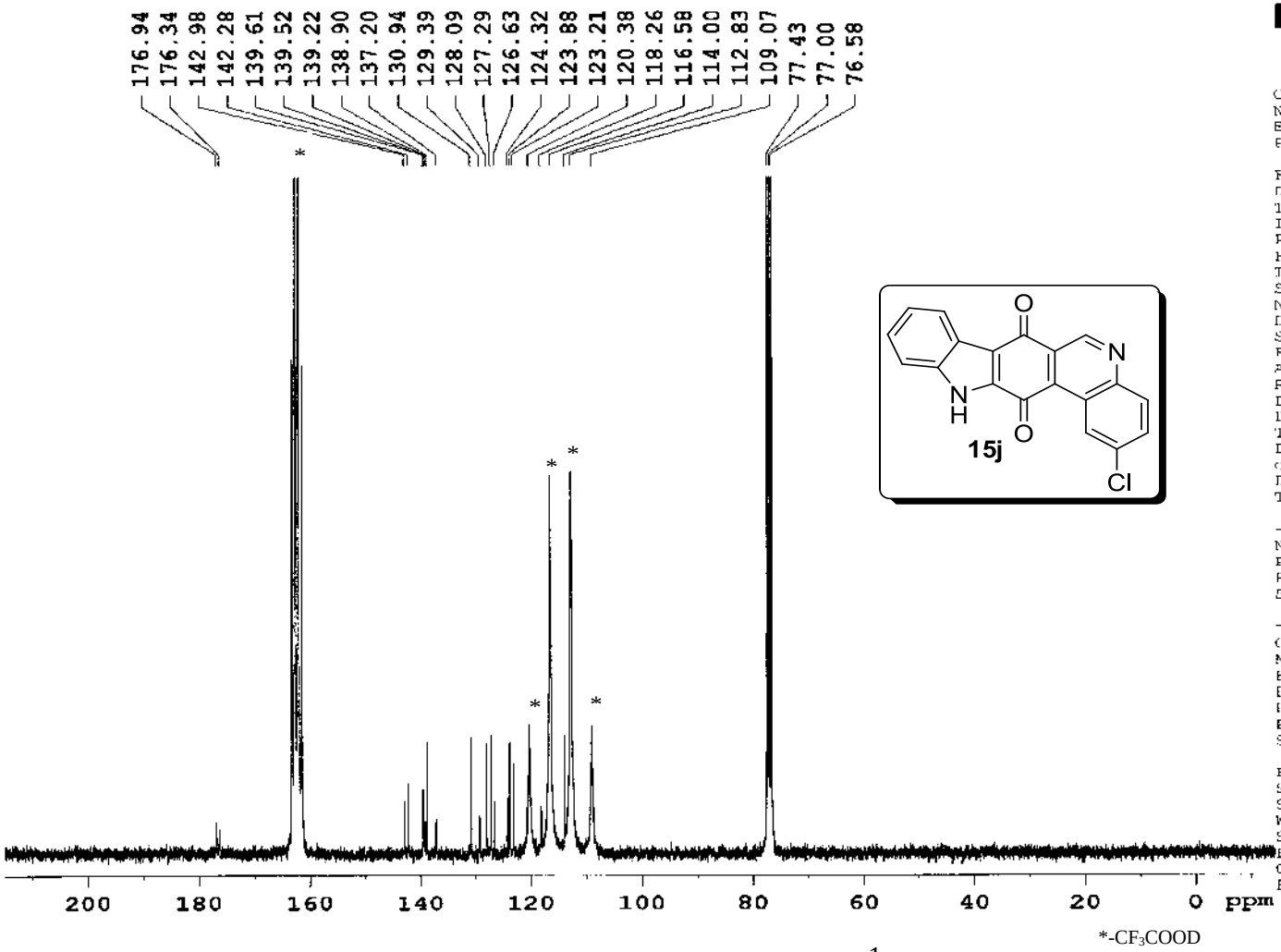
F2 - Acquisition Parameters
Date                 20140212
Time                    23.43
INSTRUM                 spect
PROBHD    5 mm DUL 13C-1
PULPROG               dept135
TD                      65536
SOLVENT                 CDCl3
NS                       1285
DS                          4
SWH                17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                      16384
DW                     27.800 usec
DE                      6.00 usec
TE                     300.0 K
CNST2              145.0000000
D1                   2.00000000 sec
d2                   0.00344828 sec
d12                  0.00002000 sec
DELTA                0.00001184 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.30 usec
p2                      18.60 usec
PL1                      0.00 dB
SFO1               75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                      13.15 usec
p4                      26.30 usec
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.68 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                 75.4677143 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

DEPT 135-^{13}CNMR spectrum of compound **15j**




```
Current Data Parameters
NAME                  BMR-455
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140713
Time                   7.28
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     9315
DS                        4
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219608 sec
RG                   2896.3
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.30 usec
PL1                   0.00 dB
SFO1           75.4752953 MHz

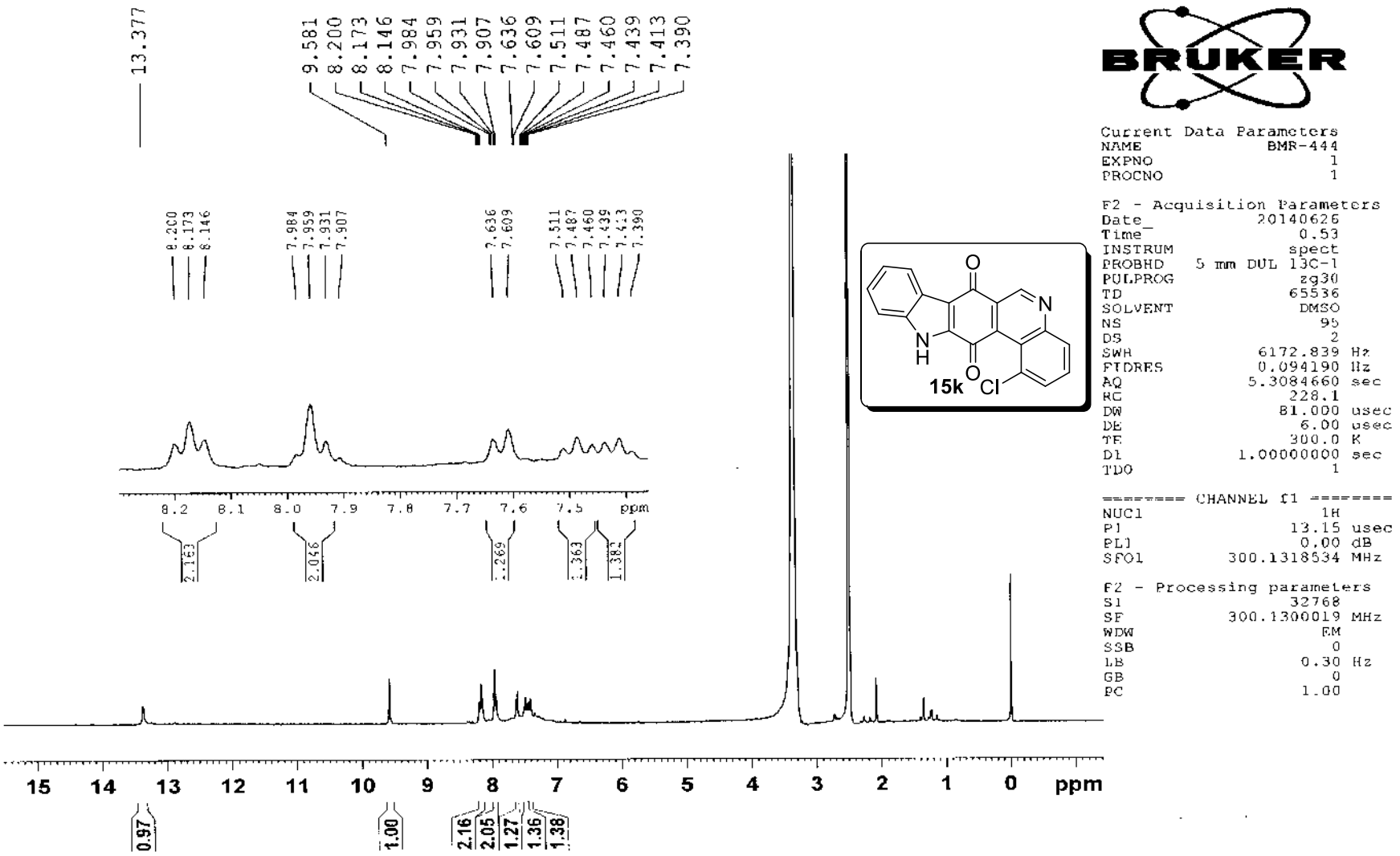
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.68 dB
PL13                 16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF             75.4677148 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```

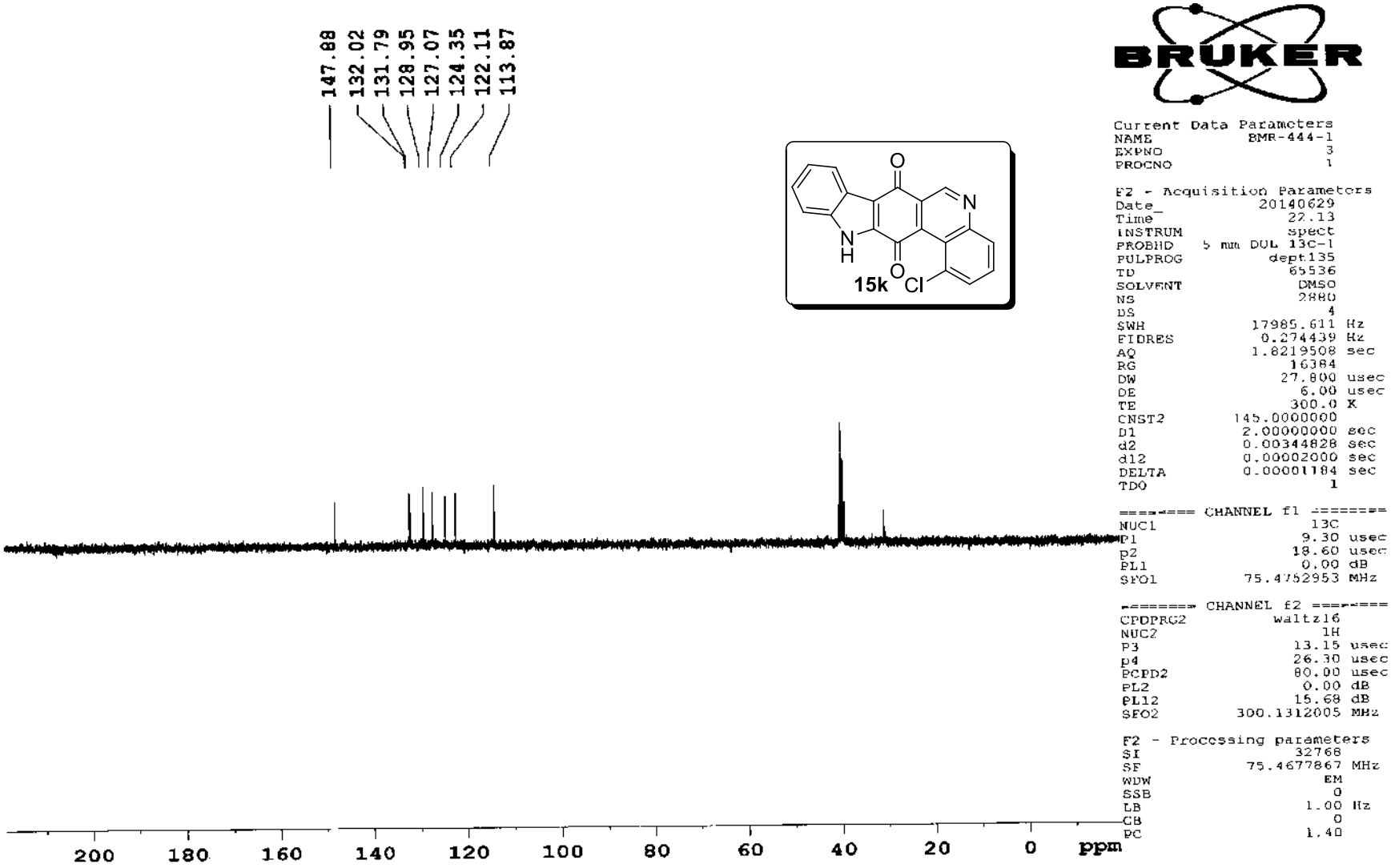
*-CF_3COOD

1

^{3}C-NMR spectrum of compound **15j**



^{1}H-NMR spectrum of compound **15k**




```
Current Data Parameters
NAME                  BMR-444-1
EXPNO                         3
PROCNO                        1

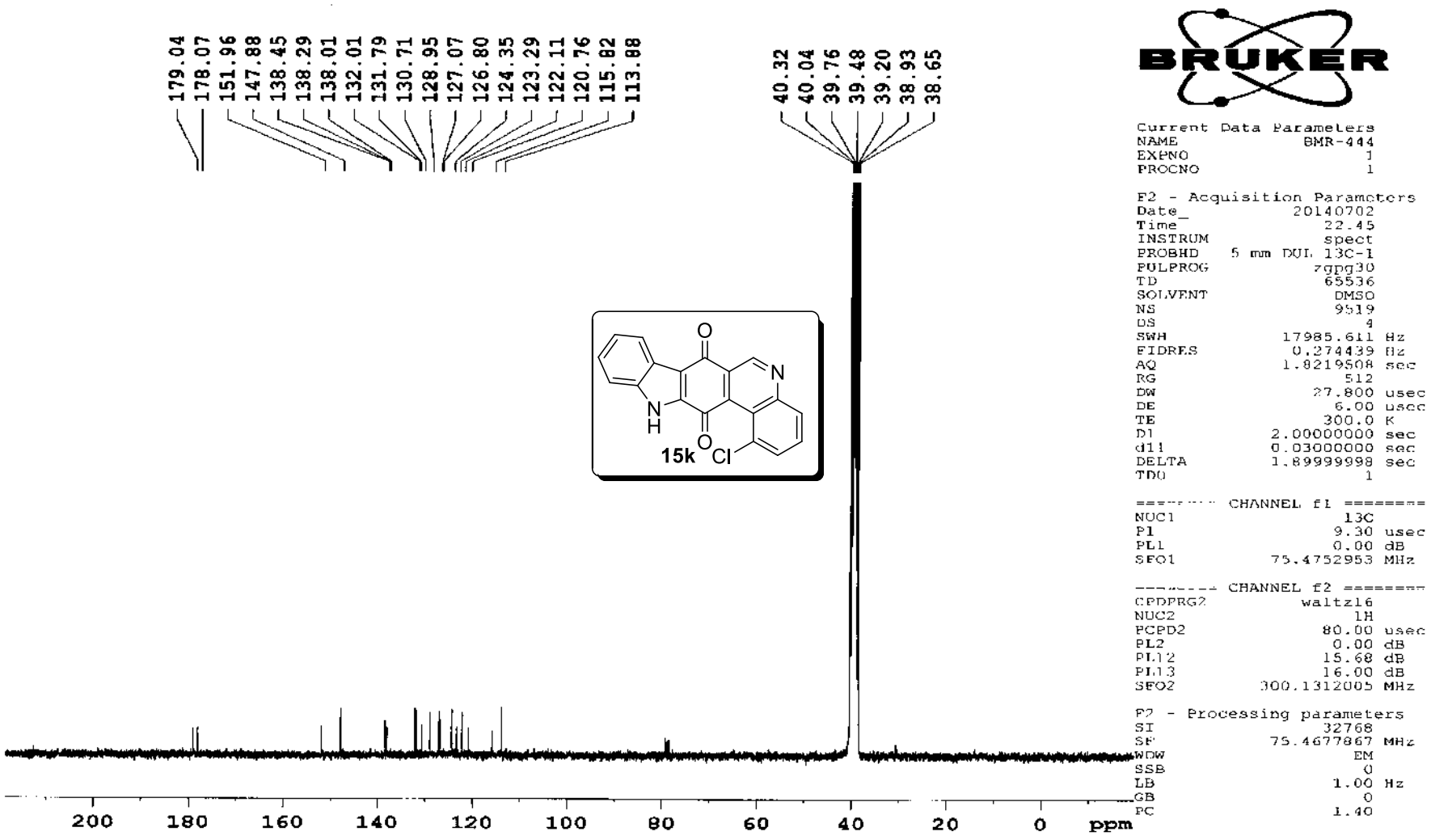
F2 - Acquisition Parameters
Date_                  20140629
Time                      22.13
INSTRUM                   spect
PROBHD    5 mm DUL 13C-1
PULPROG                dept135
TD                        65536
SOLVENT                    DMSO
NS                         2880
DS                            4
SWH                   17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                        16384
DW                       27.800 usec
DE                        6.00 usec
TE                       300.0 K
CNST2                145.0000000
D1                   2.00000000 sec
d2                   0.00344828 sec
d12                  0.00002000 sec
DELTA                0.00001184 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.30 usec
p2                        18.60 usec
PL1                        0.00 dB
SFO1                 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
P3                        13.15 usec
p4                        26.30 usec
PCPD2                     80.00 usec
PL2                        0.00 dB
PL12                      15.68 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                   75.4677867 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15k**



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```
Current Data Parameters
NAME                  BMR-444
EXPNO                       1
PROCNO                      1

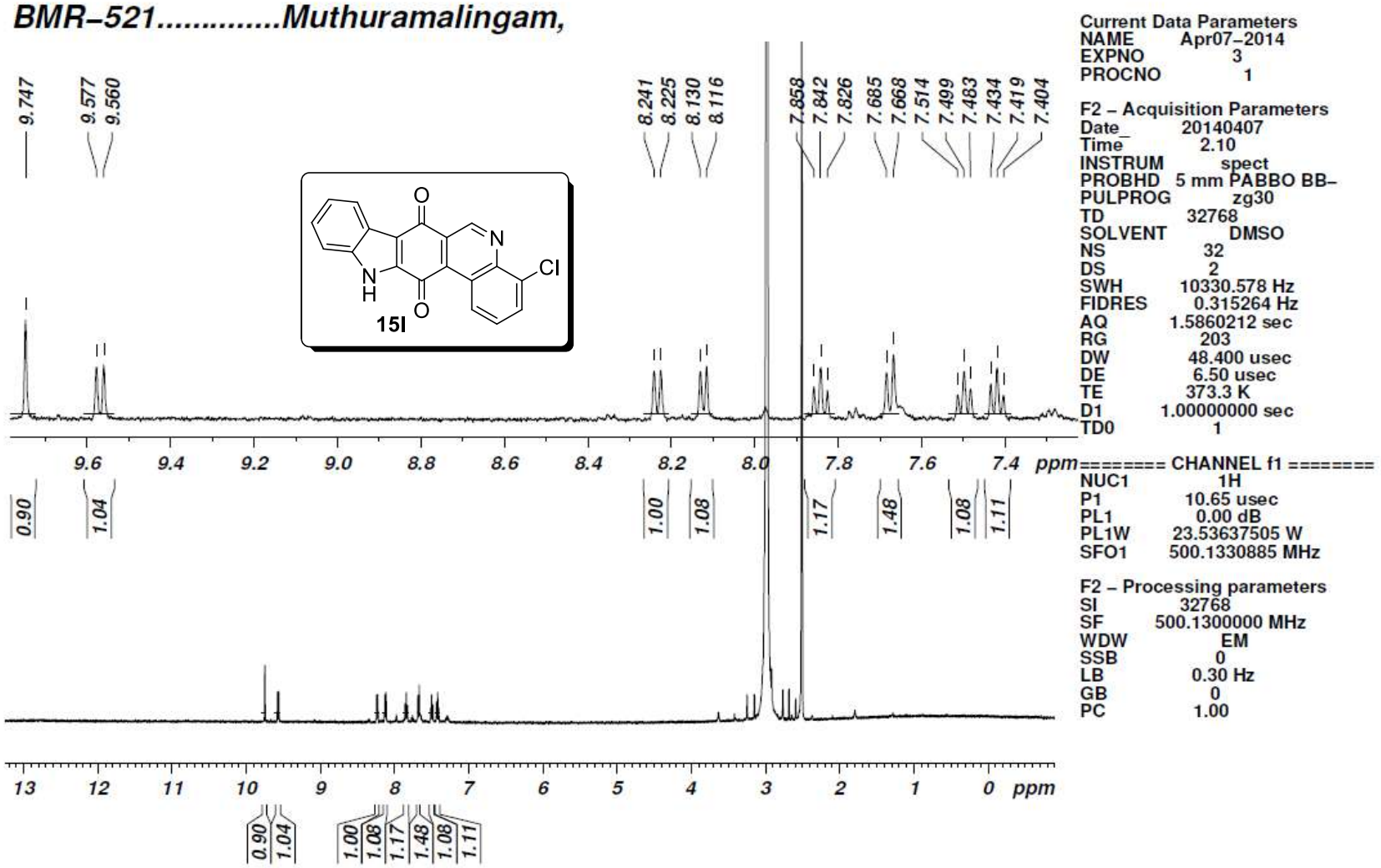
F2 - Acquisition Parameters
Date_              20140702
Time                   22.45
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                     65536
SOLVENT                DMSO
NS                      9519
DS                         4
SWH              17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                       512
DW                  27.800 usec
DE                   6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                   9.30 usec
PL1                  0.00 dB
SFO1          75.4752953 MHz

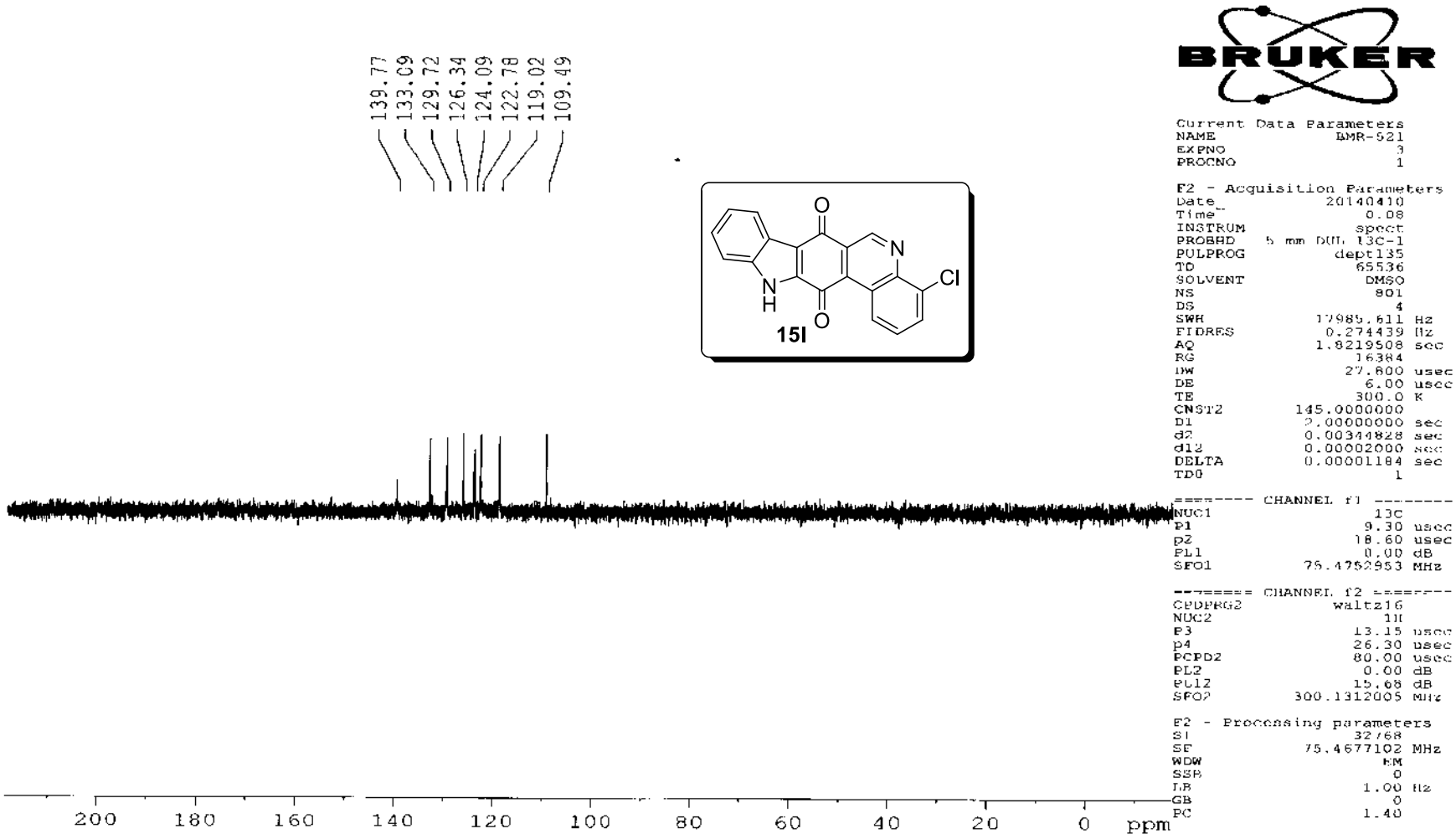
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.68 dB
PL13                16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                      32768
SF            75.4677867 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                       1.40
```

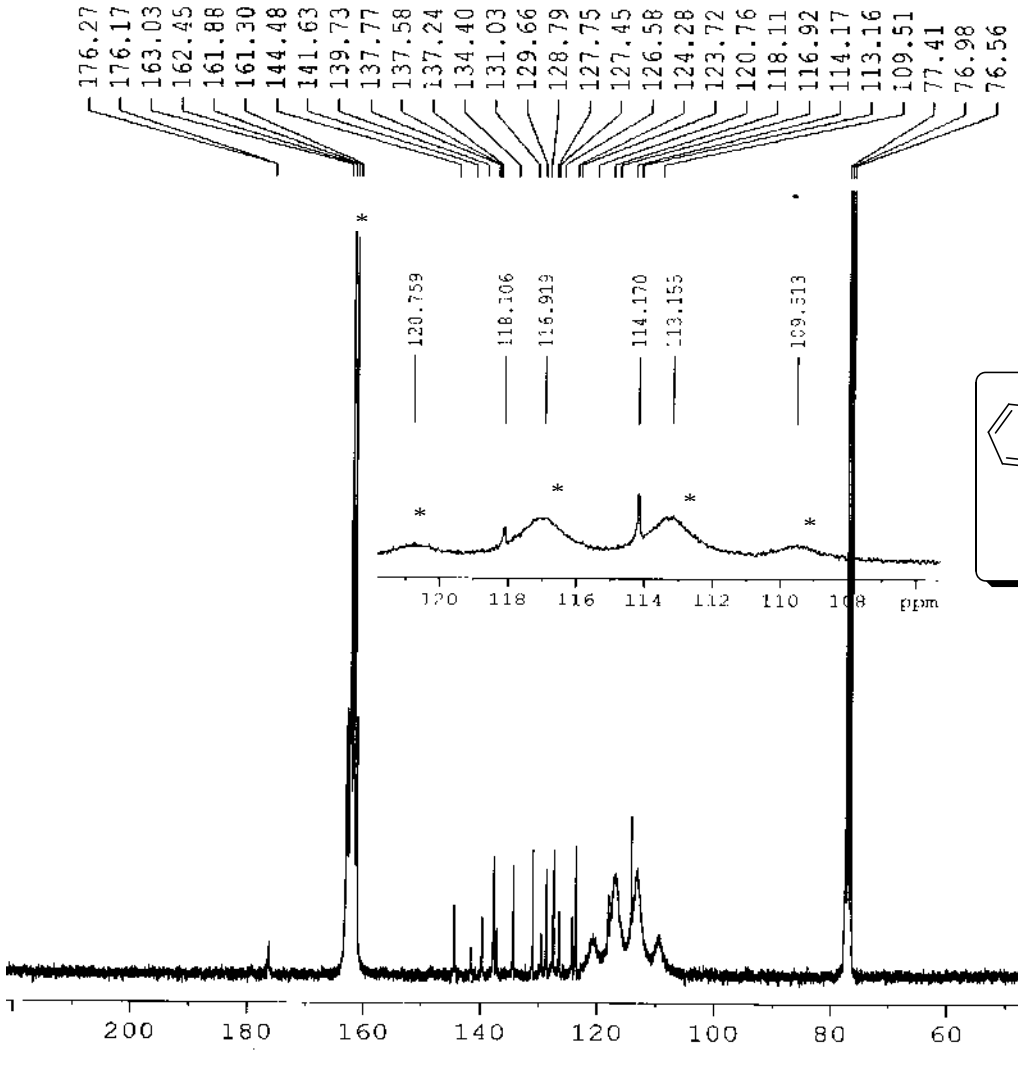
^{13}C-NMR spectrum of compound **15k**

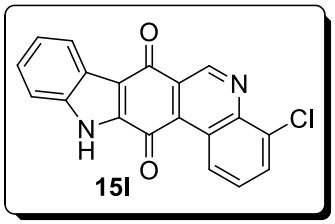


^{1}H-NMR spectrum of compound **15l**



DEPT 135-^{13}C NMR spectrum of compound **15l**






```
Current Data Parameters
NAME          BMR-521-C13
EXPNO                   1
PROCNO                  1

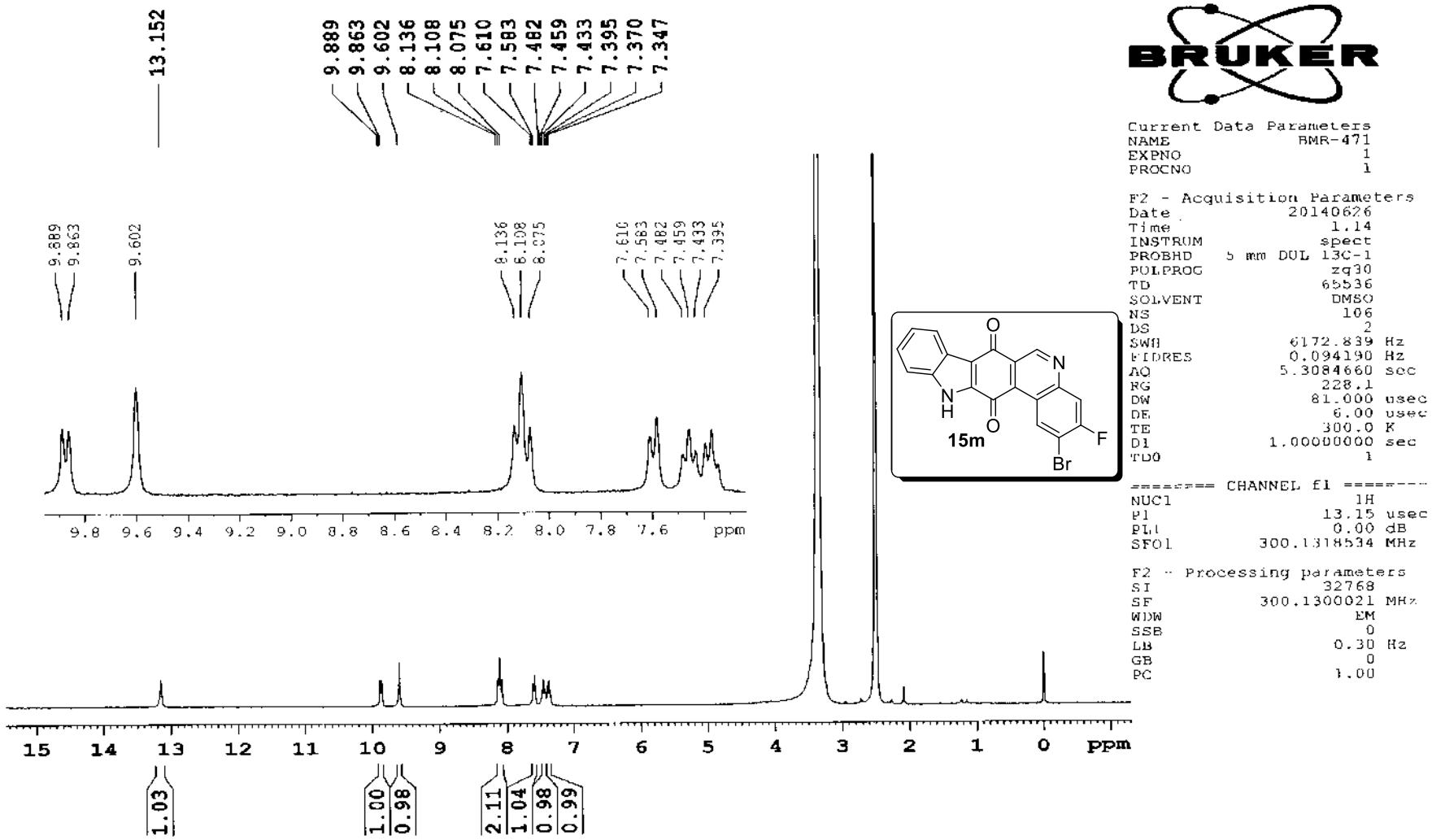
F2 - Acquisition Parameters
Date_            20140410
Time                0.51
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 8890
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG               9195.2
DW               27.800 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.30 usec
PL1                0.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.68 dB
PL13              16.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4674176 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

^{13}C-NMR spectrum of compound **15l**



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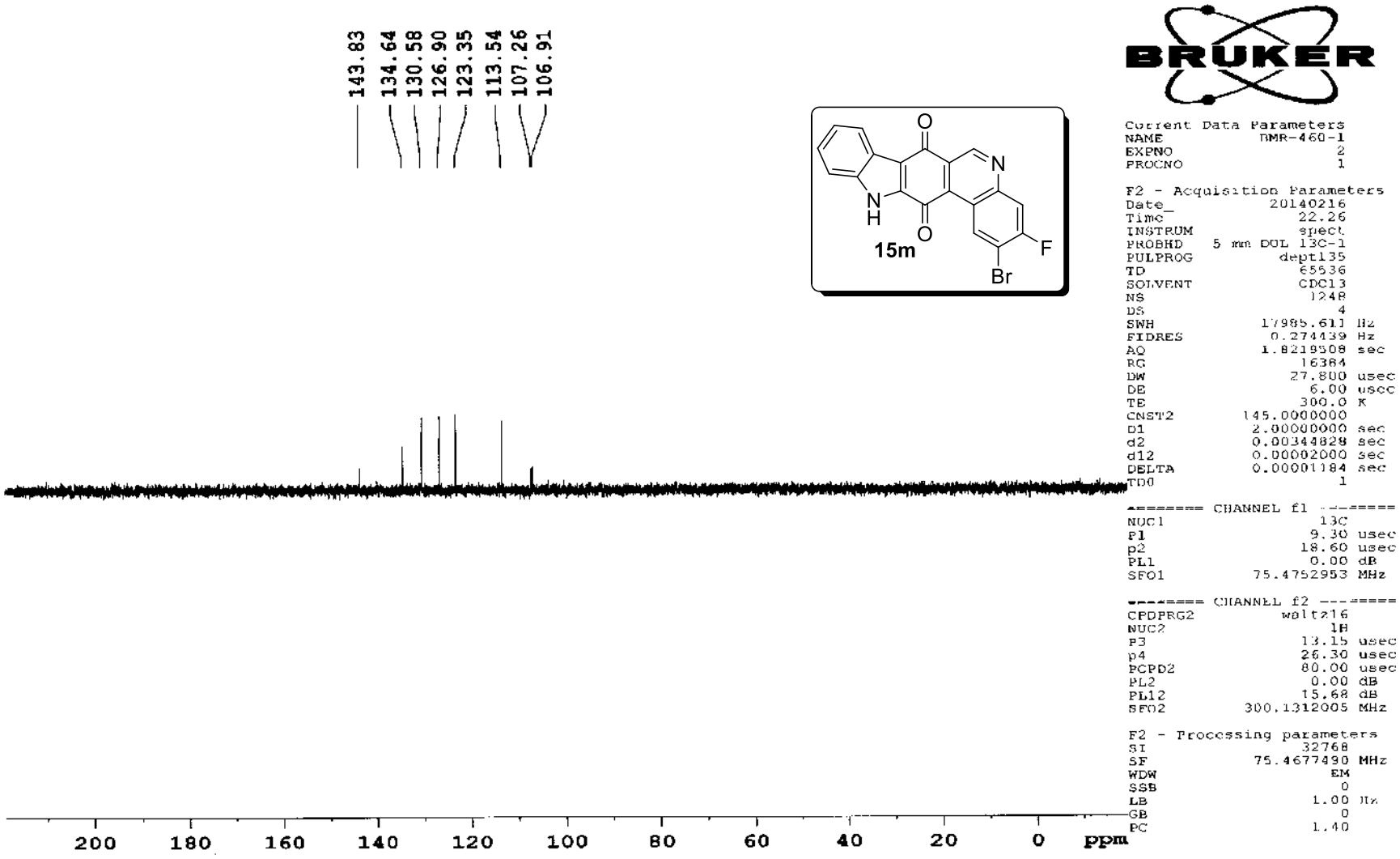
```
Current Data Parameters
NAME                  BMR-471
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date                 20140626
Time                     1.14
INSTRUM                 spect
PROBHD     5 mm DUL 13C-1
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                       106
DS                         2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                      228.1
DW                     81.000 usec
DE                      6.00 usec
TE                     300.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.15 usec
PL1                     0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                     32768
SF            300.1300021 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

^{1}H-NMR spectrum of compound **15m**




```
Current Data Parameters
NAME                  BMR-460-1
EXPNO                         2
PROCNO                        1

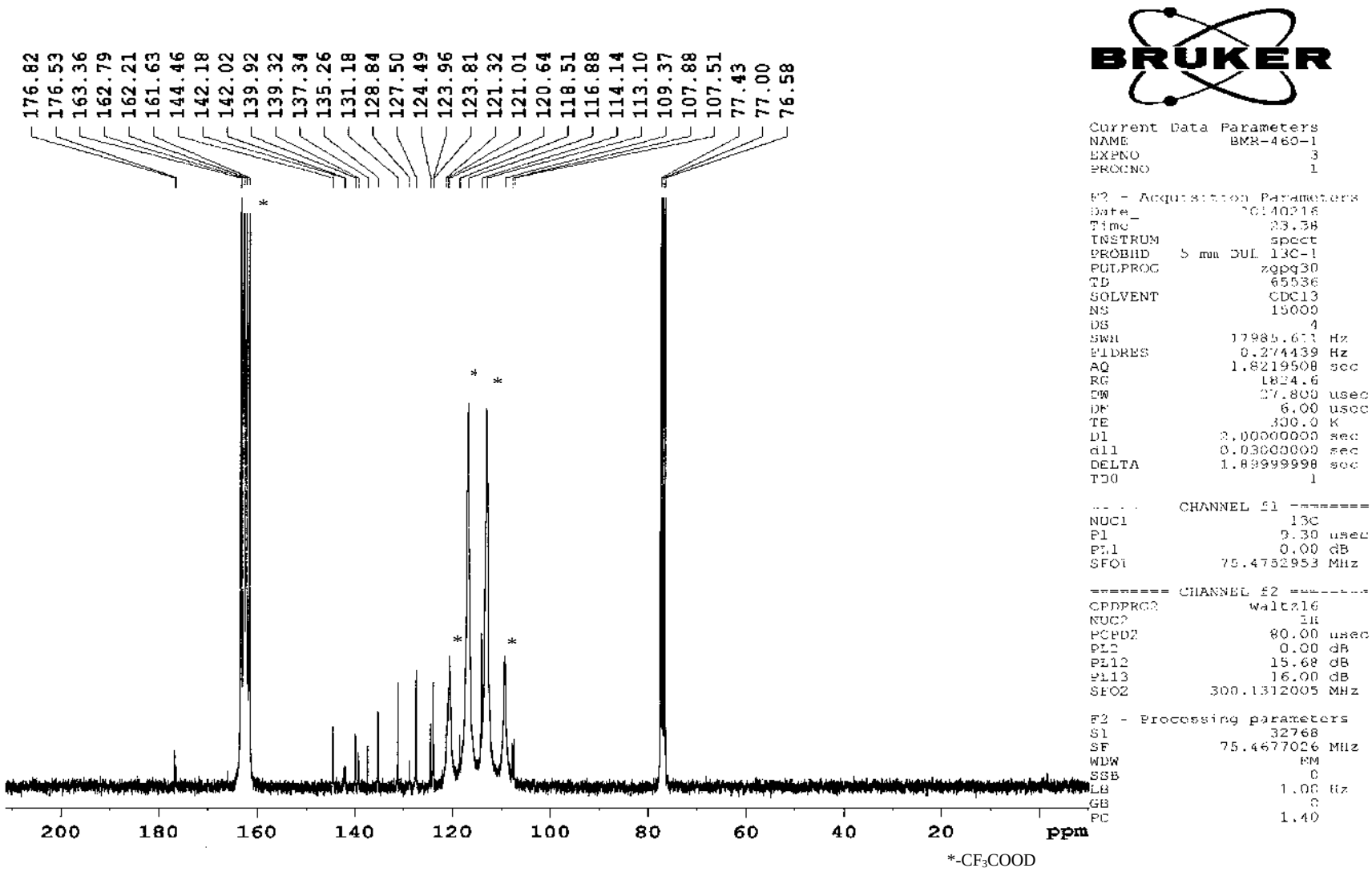
F2 - Acquisition Parameters
Date_               20140216
Time                   22.26
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG              dept135
TD                     65536
SOLVENT                CDCl3
NS                      1248
DS                         4
SWH                17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                        16384
DW                       27.800 usec
DE                        6.00 usec
TE                       300.0 K
CNST2               145.0000000
D1                    2.00000000 sec
d2                    0.00344828 sec
d12                   0.00002000 sec
DELTA                 0.00001184 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.30 usec
p2                        18.60 usec
PL1                        0.00 dB
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
P3                        13.15 usec
p4                        26.30 usec
PCPD2                     80.00 usec
PL2                        0.00 dB
PL12                      15.68 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                 75.4677490 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

DEPT 135-^{13}C NMR spectrum of compound **15m**




```
Current Data Parameters
NAME                  BMR-460-1
EXPNO                         3
PROCNO                        1

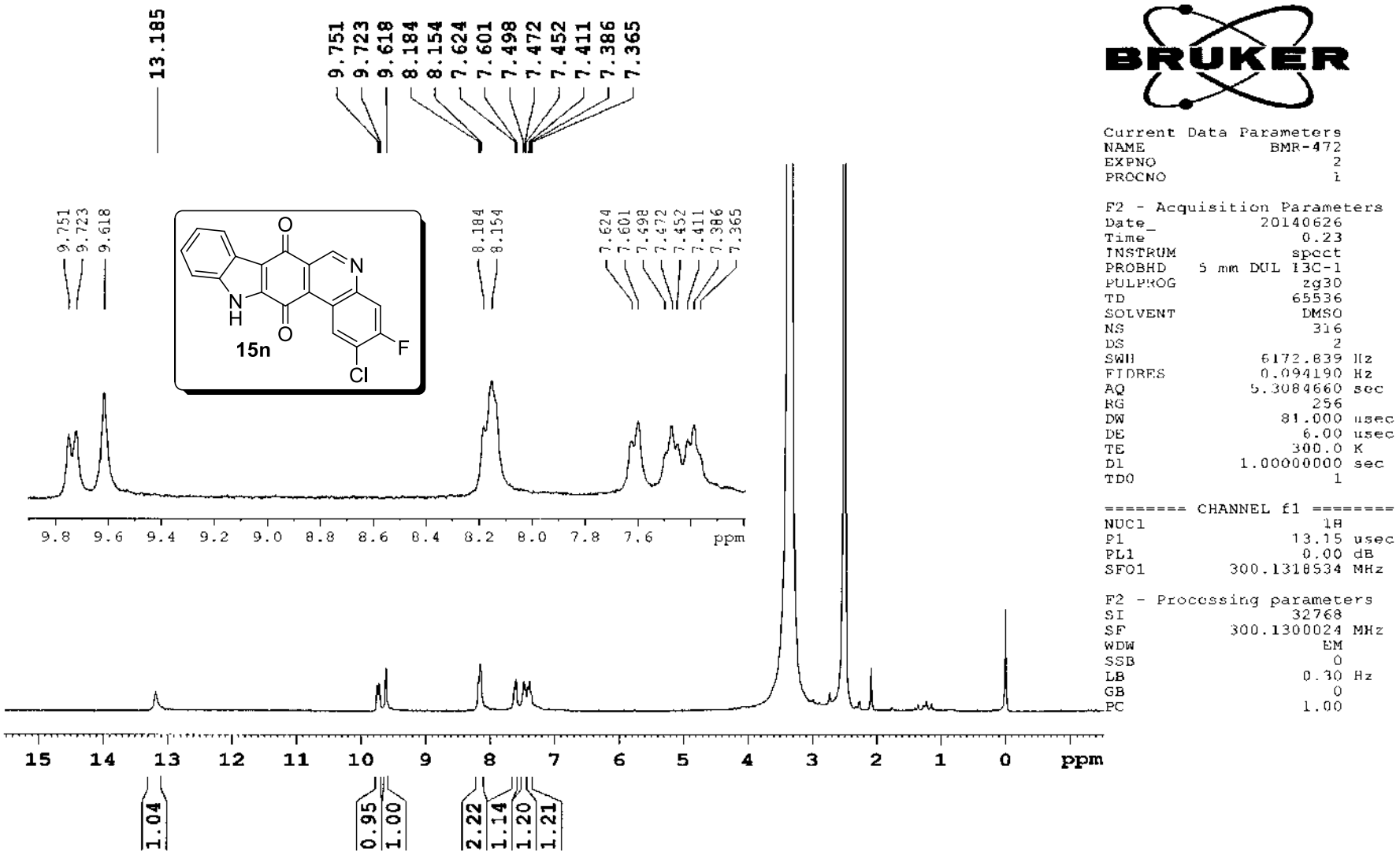
F2 - Acquisition Parameters
Date_               20140216
Time                      23.38
INSTRUM                   spect
PROBHD     5 mm DUL 13C-1
PULPROG                zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                        15000
DS                            4
SWH                 17985.611 Hz
FIDRES               0.274439 Hz
AQ                   1.8219508 sec
RG                       1824.6
DW                       27.800 usec
DE                        6.00 usec
TE                       300.0 K
D1                   2.00000000 sec
d11                  0.03000000 sec
DELTA                1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.30 usec
PL1                        0.00 dB
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL2                        0.00 dB
PL12                      15.68 dB
PL13                      16.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                 75.4677026 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

^{13}C-NMR spectrum of compound **15m**



BRUKER

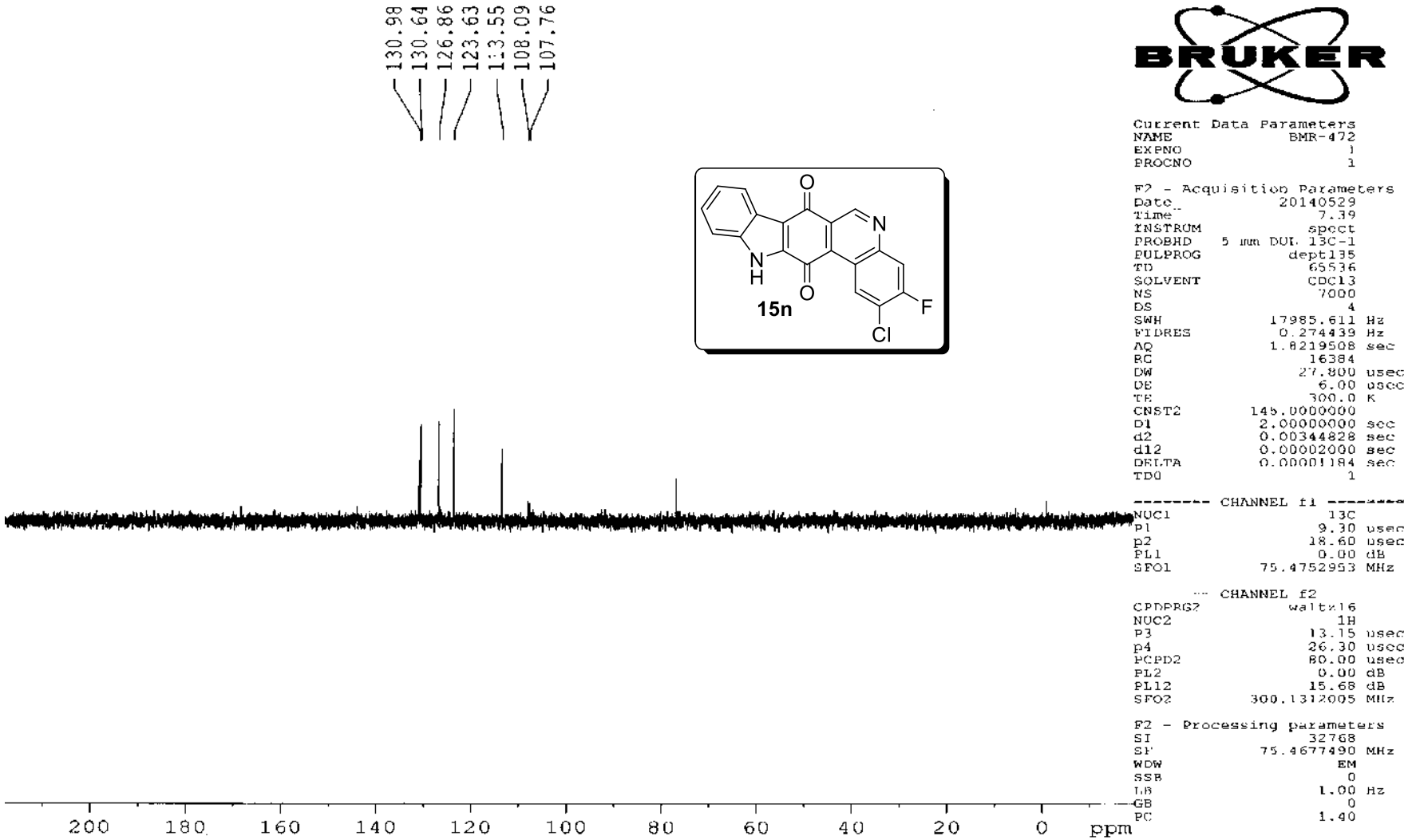
```
Current Data Parameters
NAME                  BMR-472
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140626
Time                   0.23
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                      316
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                      256
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.15 usec
PL1                      0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                      32768
SF            300.1300024 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

^{1}H-NMR spectrum of compound **15n**




```
Current Data Parameters
NAME                  BMR-472
EXPNO                       1
PROCNO                      1

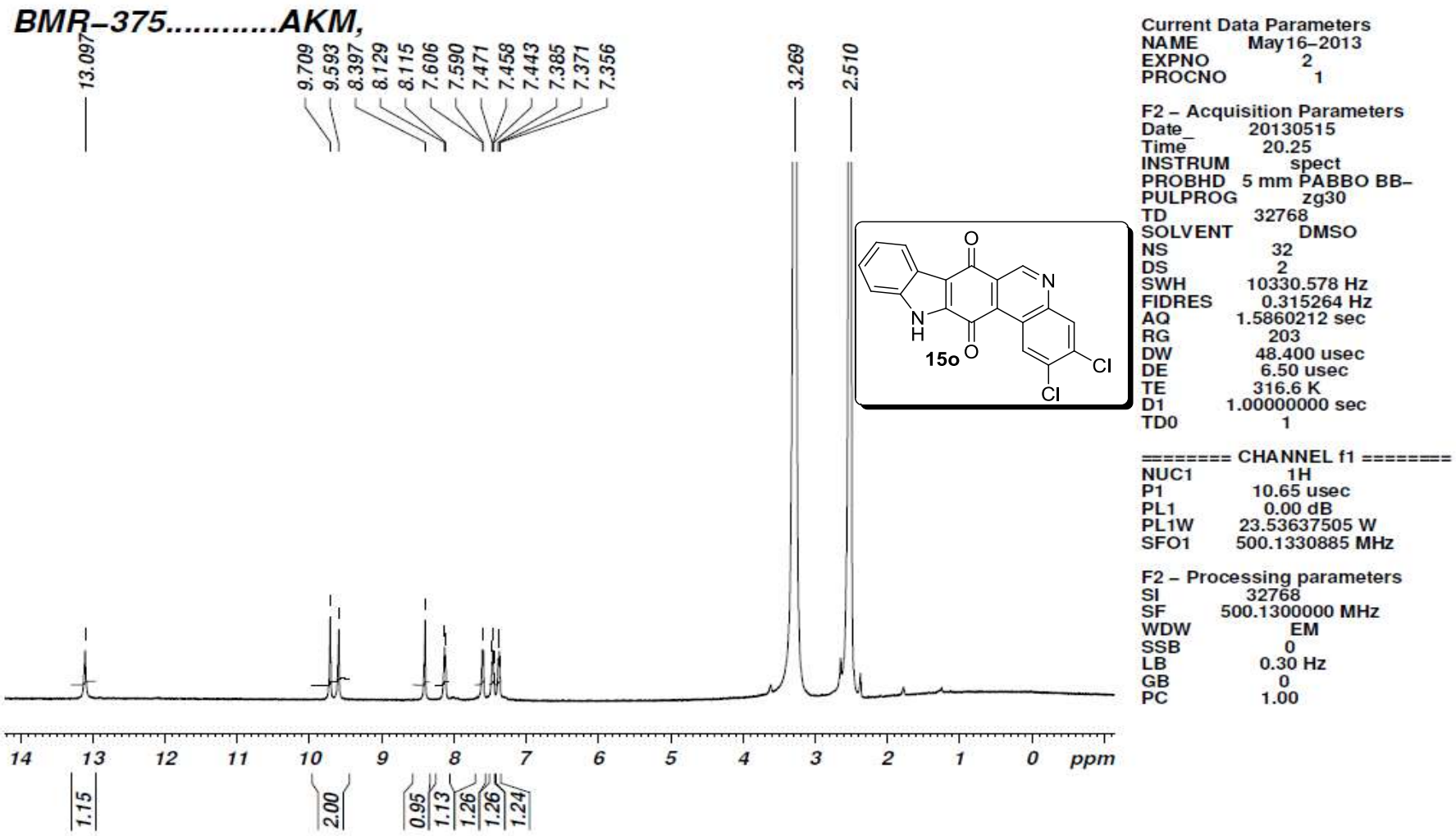
F2 - Acquisition Parameters
Date_              20140529
Time                   7.39
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG             dept135
TD                    65536
SOLVENT               CDCl3
NS                     7000
DS                        4
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                    16384
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
CNST2           145.0000000
D1                2.00000000 sec
d2                0.00344828 sec
d12               0.00002000 sec
DELTA             0.00001184 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.30 usec
p2                      18.60 usec
PL1                      0.00 dB
SFO1              75.4752953 MHz

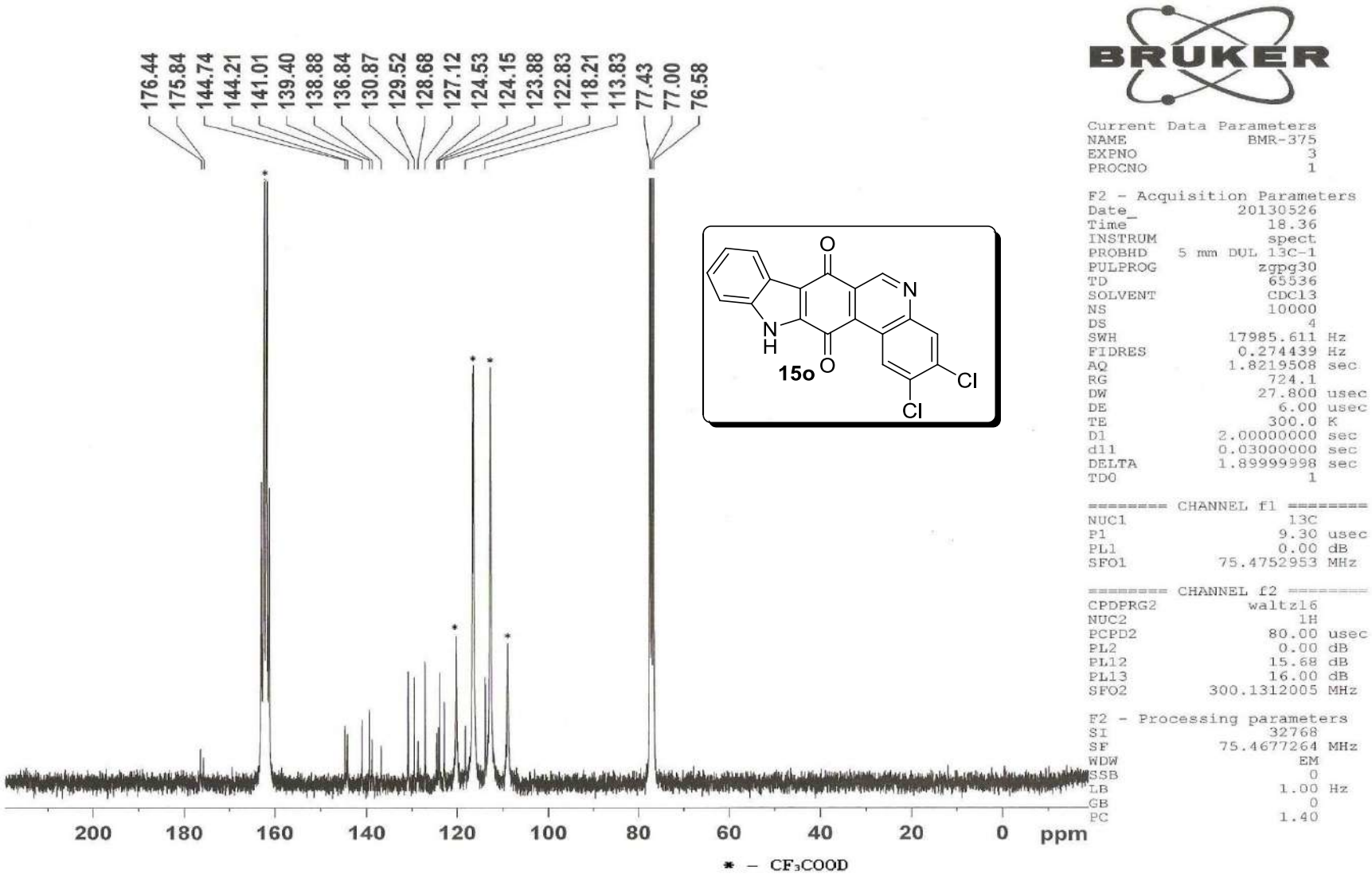
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                      13.15 usec
p4                      26.30 usec
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.68 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                75.4677490 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

DEPT 135-^{13}CNMR spectrum of compound **15n**



^{1}H-NMR spectrum of compound **15o**



BRUKER

```
Current Data Parameters
NAME                  BMR-375
EXPNO                       3
PROCNO                      1

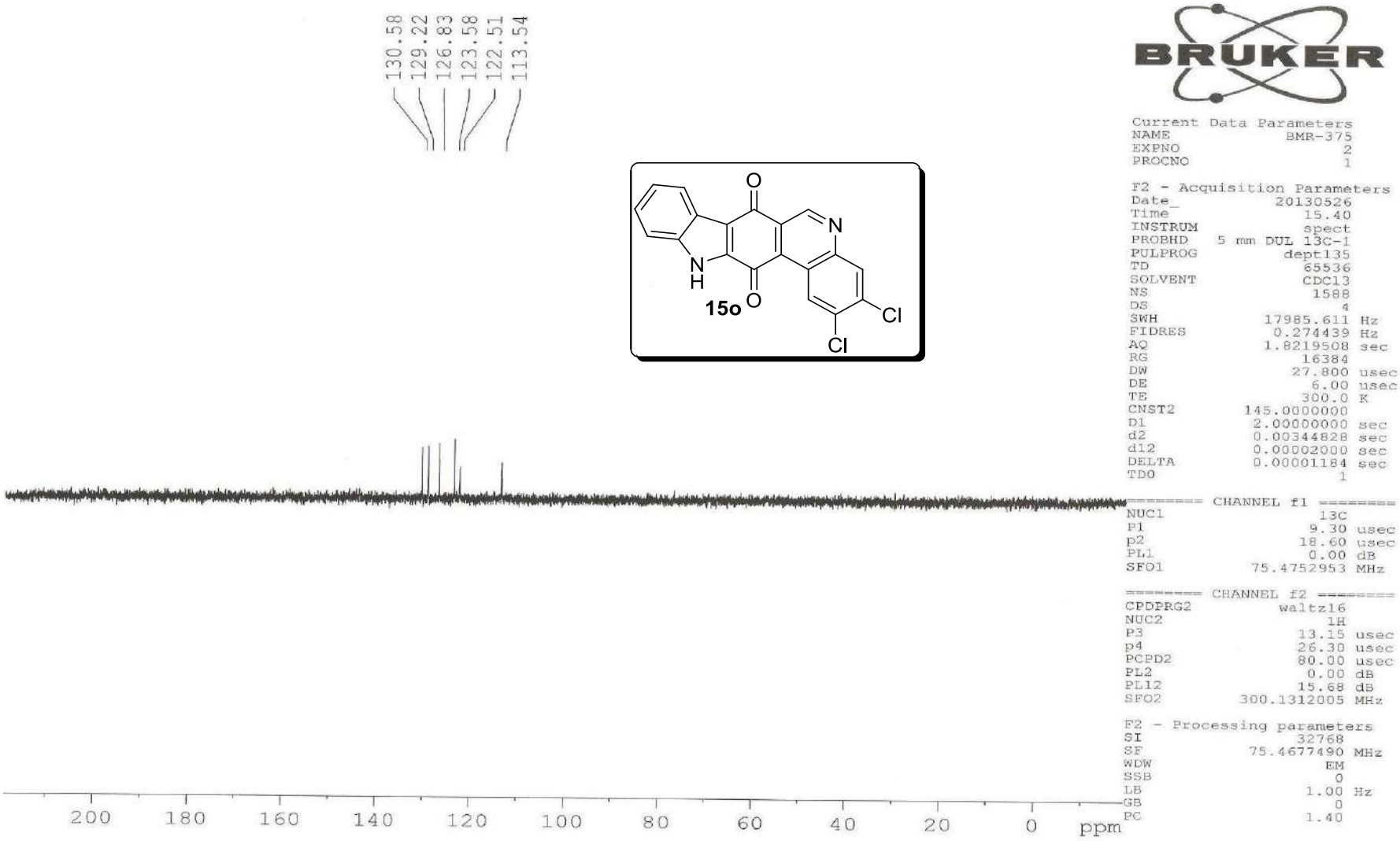
F2 - Acquisition Parameters
Date_              20130526
Time                  18.36
INSTRUM               spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                   10000
DS                       4
SWH              17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   724.1
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.30 usec
PL1                   0.00 dB
SFO1           75.4752953 MHz

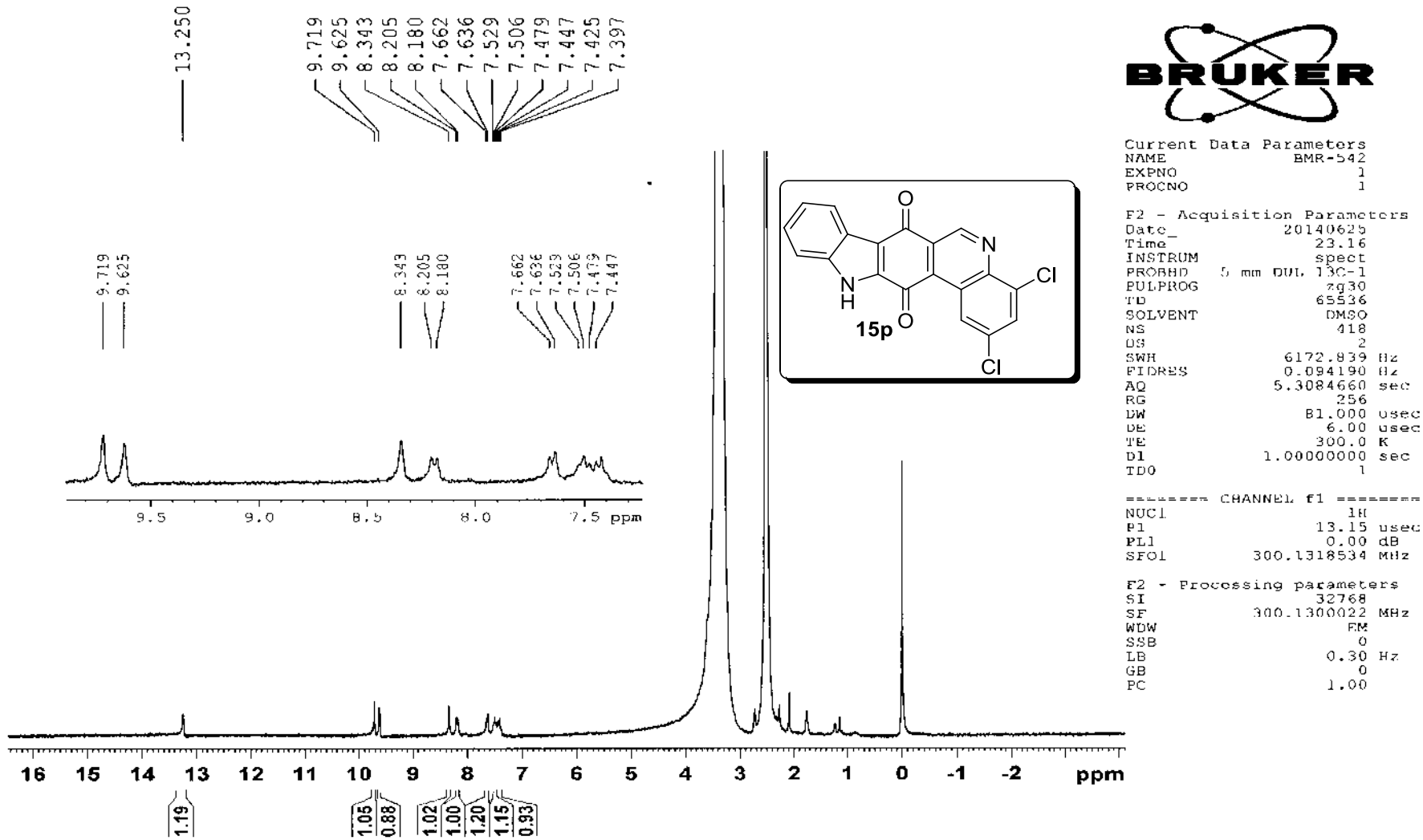
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.68 dB
PL13                 16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                      32768
SF             75.4677264 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                     1.40
```

^{13}C-NMR spectrum of compound **15o**



DEPT 135-^{13}C NMR spectrum of compound **15o**



BRUKER

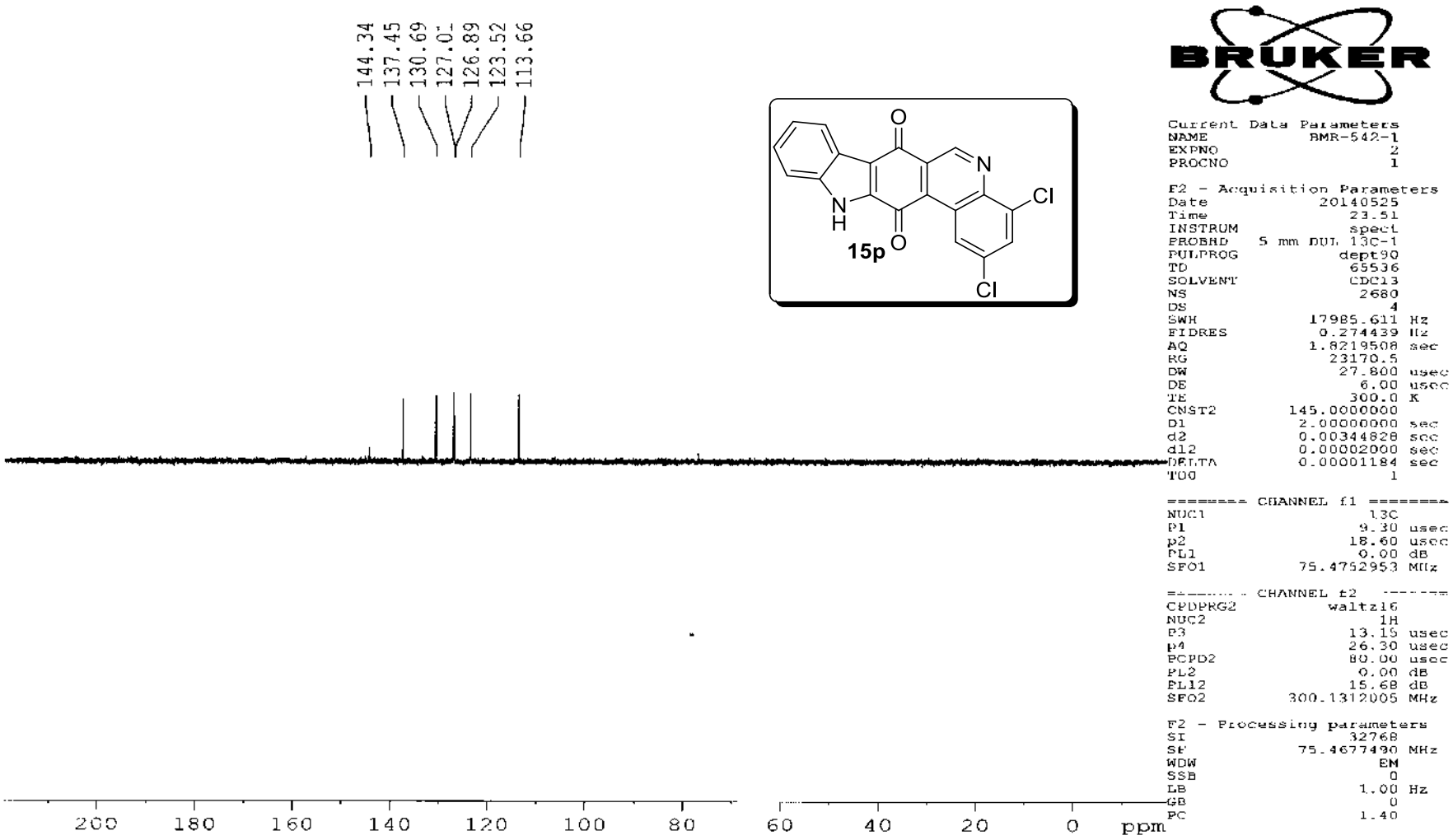
```
Current Data Parameters
NAME                  BMR-542
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140625
Time                  23.16
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                      418
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                      256
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                         1

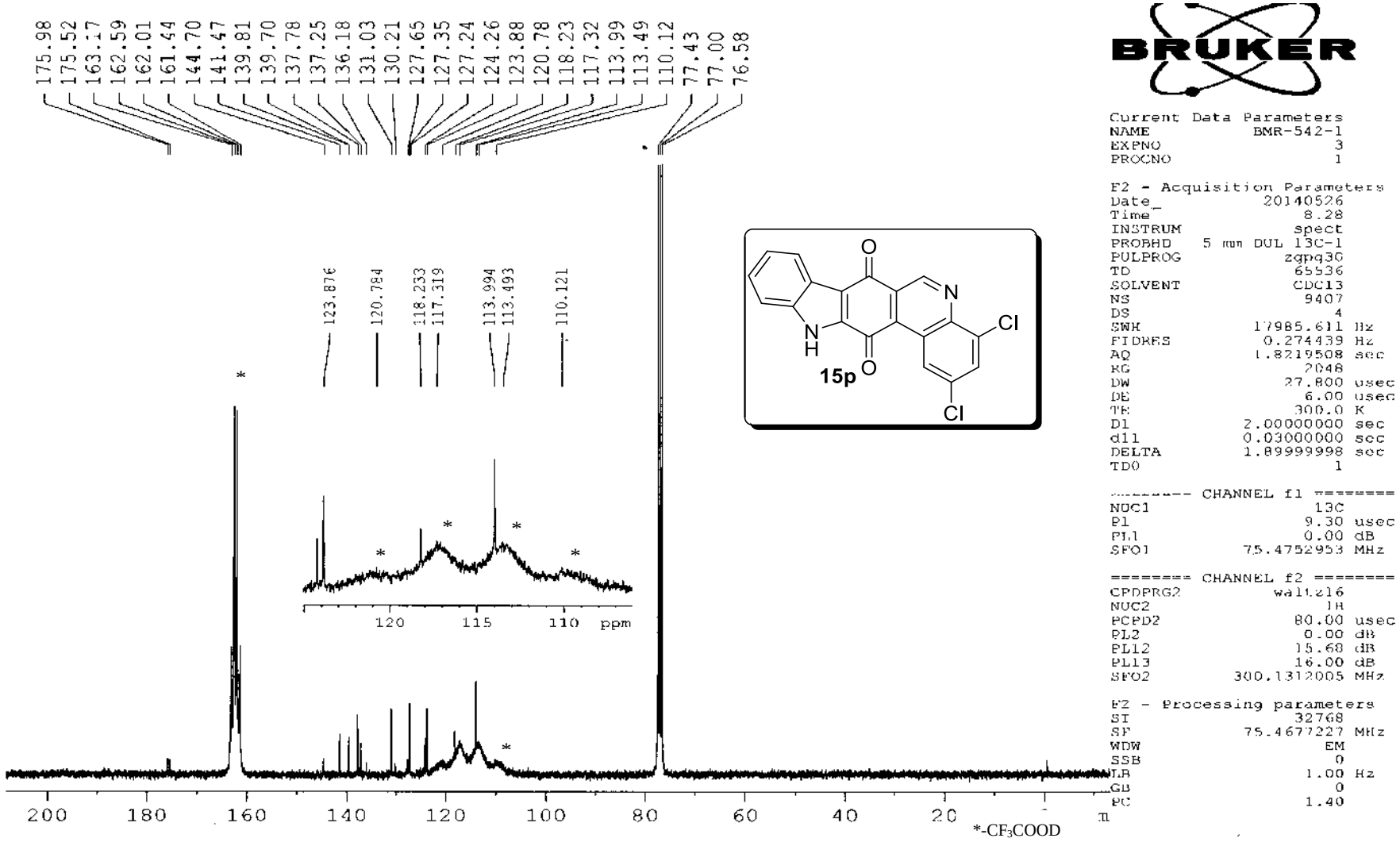
======== CHANNEL f1 ========
NUC1                       1H
P1                      13.15 usec
PL1                      0.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                      32768
SF             300.1300022 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

^{1}H-NMR spectrum of compound **15p**



DEPT 135-^{13}C NMR spectrum of compound **15p**

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Current Data Parameters
NAME                  BMR-542-1
EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
Date_              20140526
Time                   8.28
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                  65536
SOLVENT               CDCl3
NS                     9407
DS                        4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                     2048
DW                  27.800 usec
DE                   6.00 usec
TE                   300.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   9.30 usec
PL1                  0.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.68 dB
PL13                16.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF              75.4677227 MHz
WDW                       EM
SSB                        0
LB                   1.00 Hz
GB                         0
PC                      1.40
```
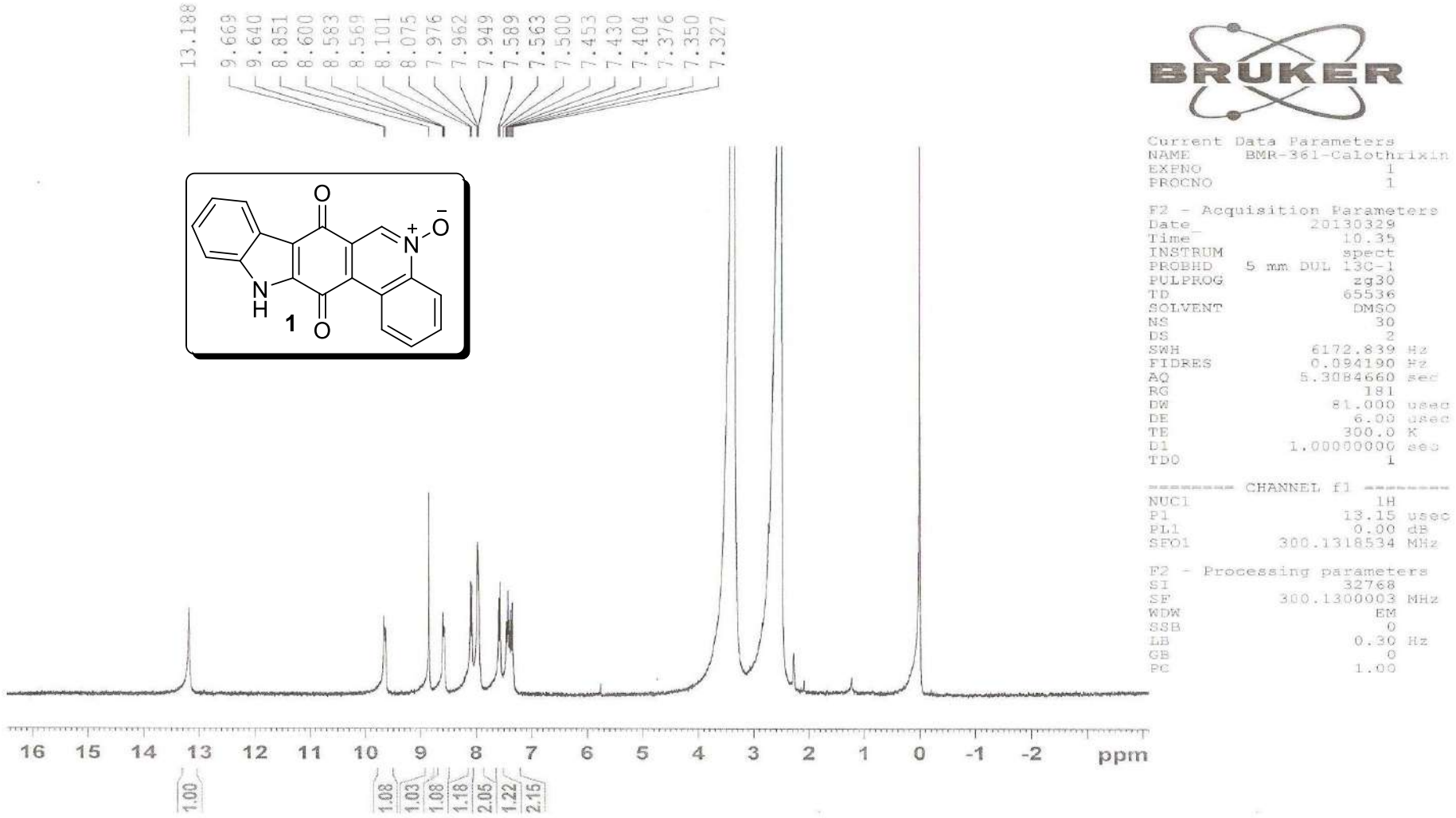
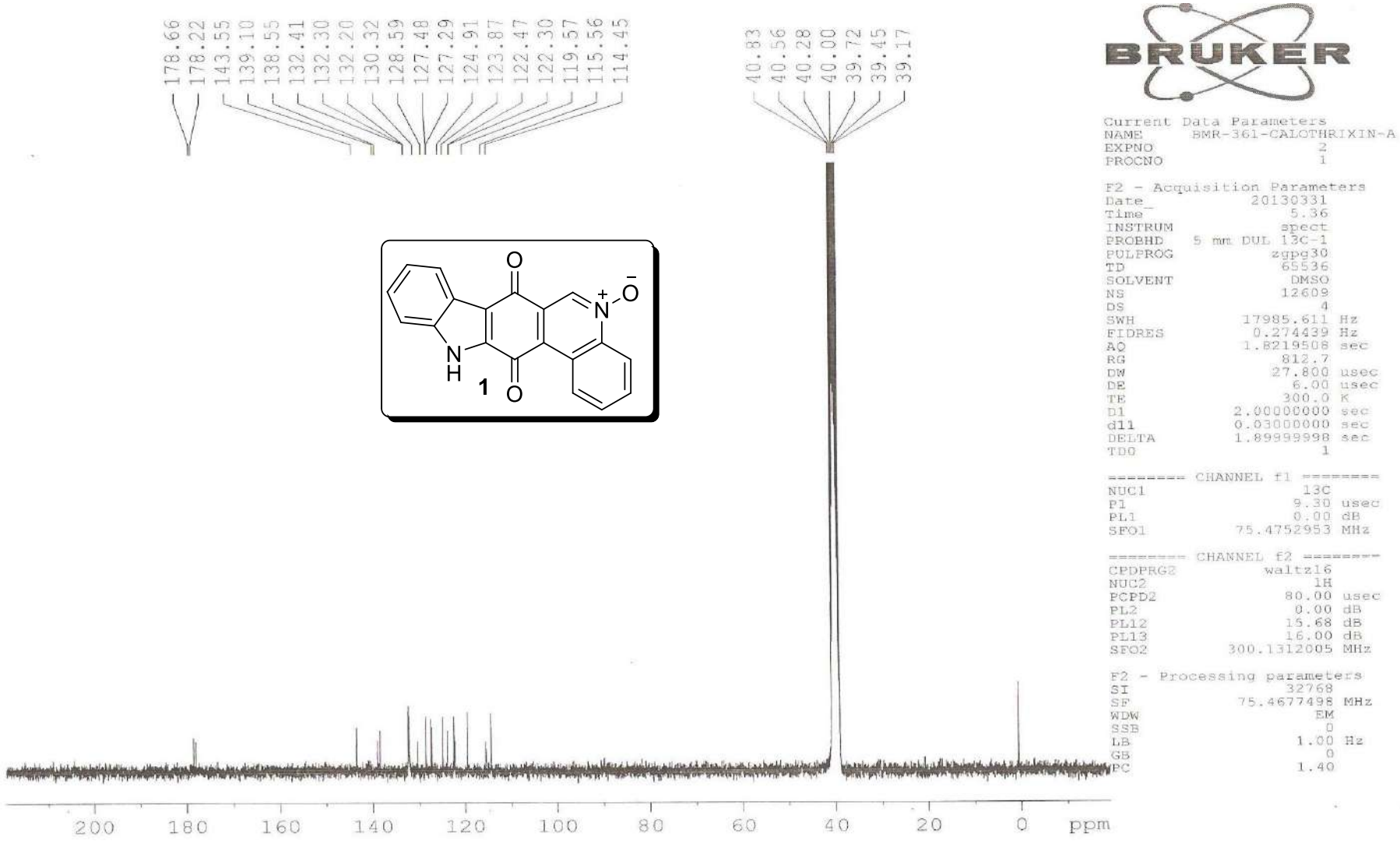

^{13}C-NMR spectrum of compound **15p**



^{1}H-NMR spectrum of compound **1**



BRUKER

Current Data Parameters
NAME BMR-361-CALOTHRIXIN-A
EXPNO 2
PROCNO 1

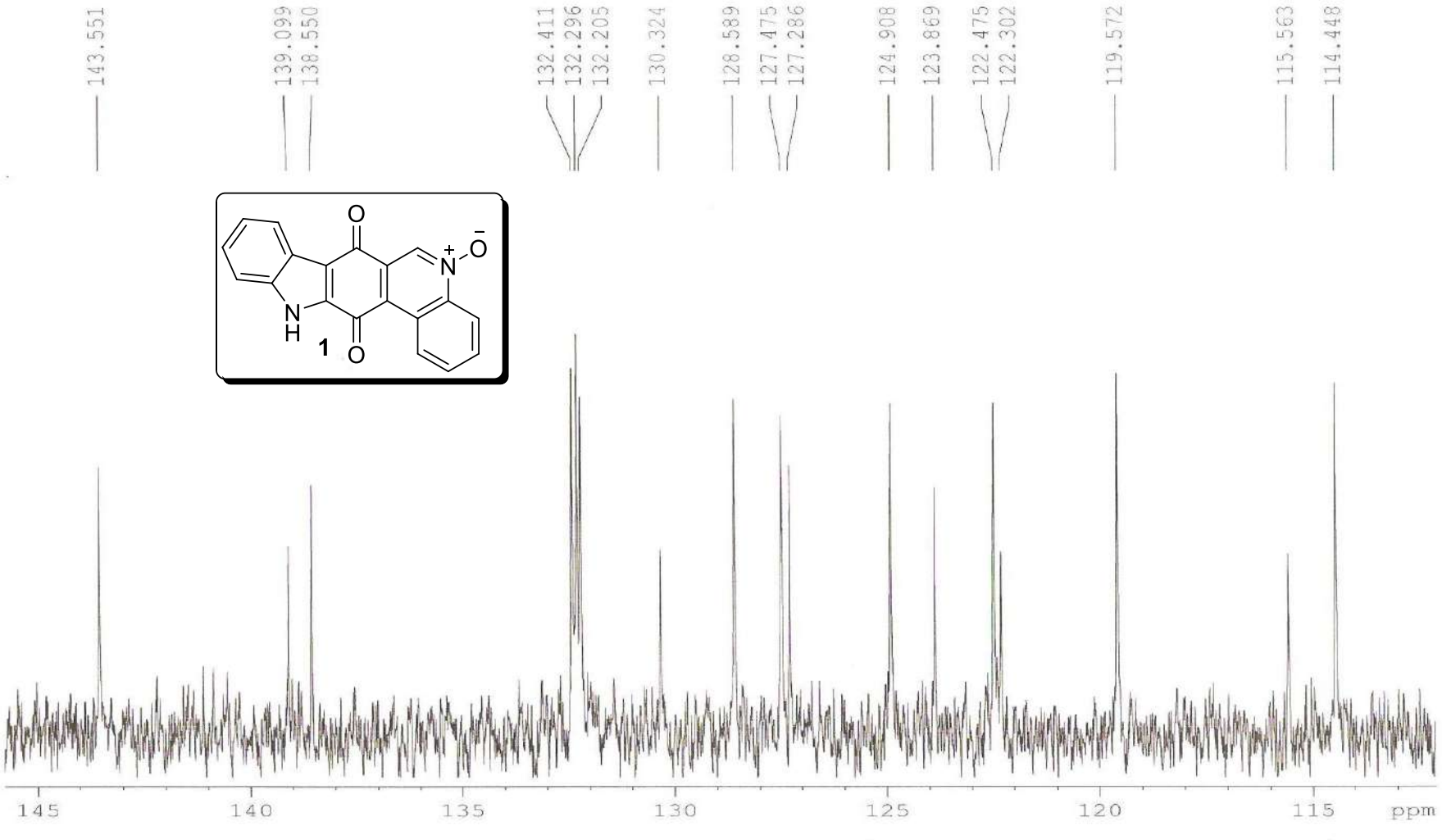
F2 - Acquisition Parameters
Date_ 20130331
Time 5.36
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 12609
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 812.7
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

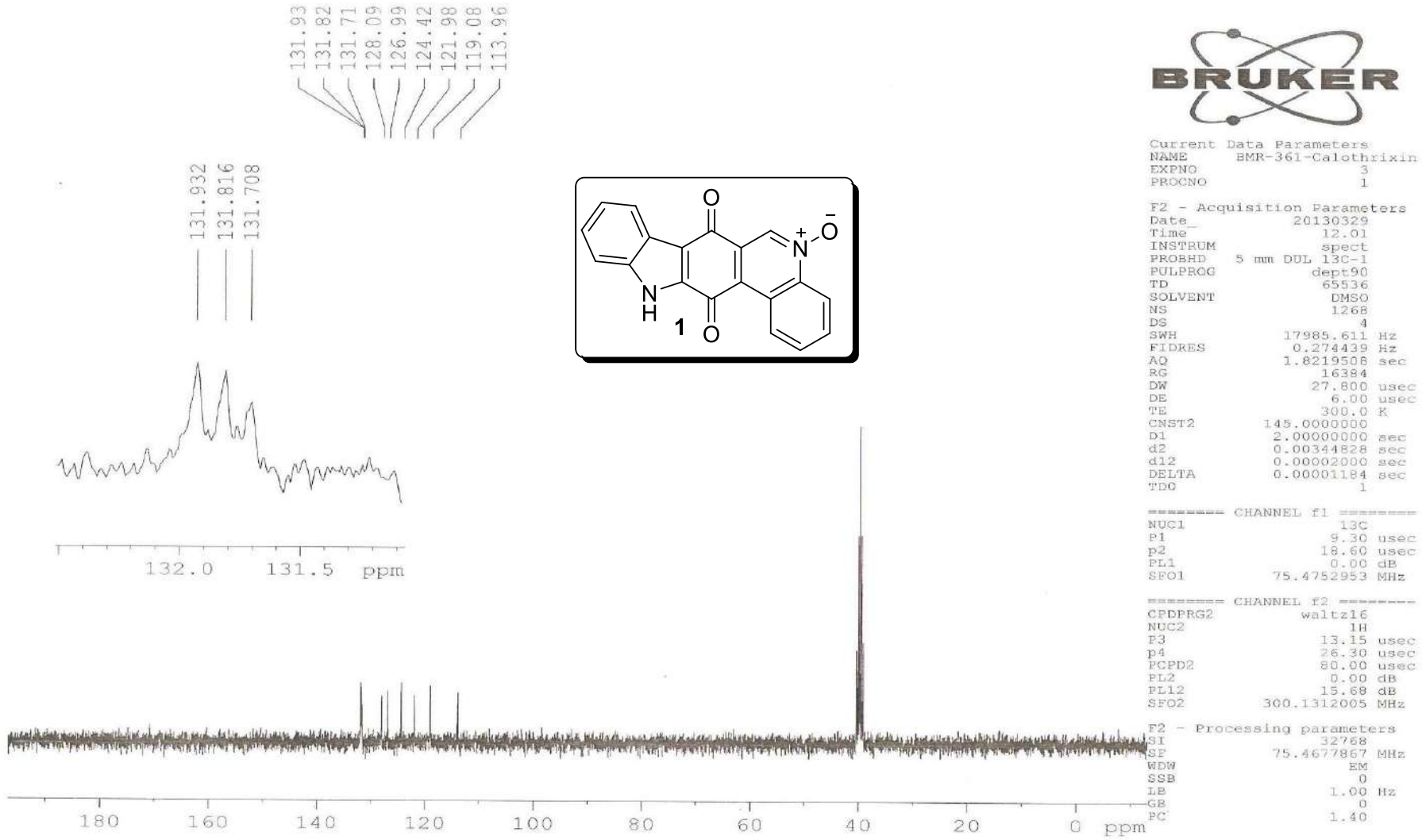
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677498 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

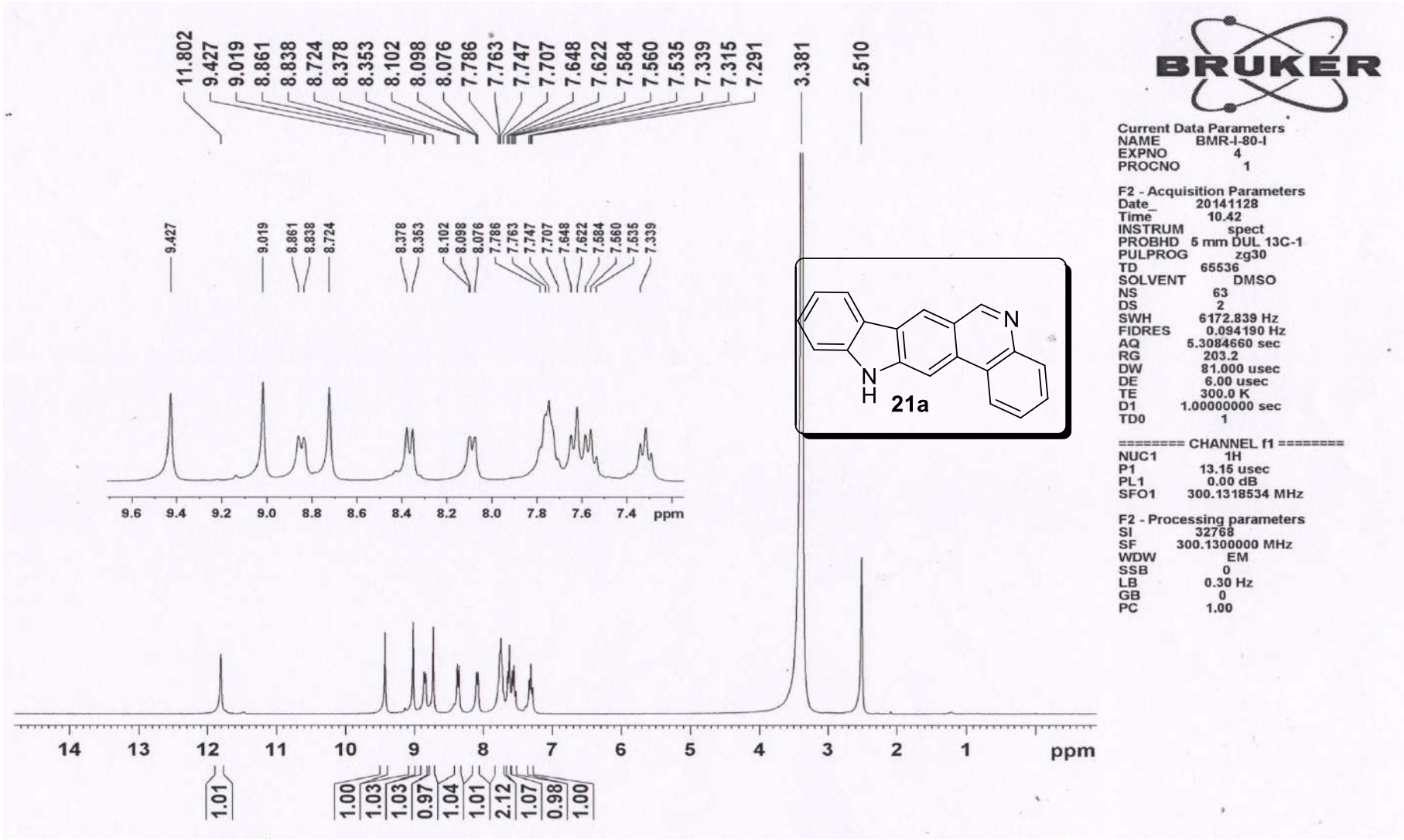
^{13}C-NMR spectrum of compound **1**



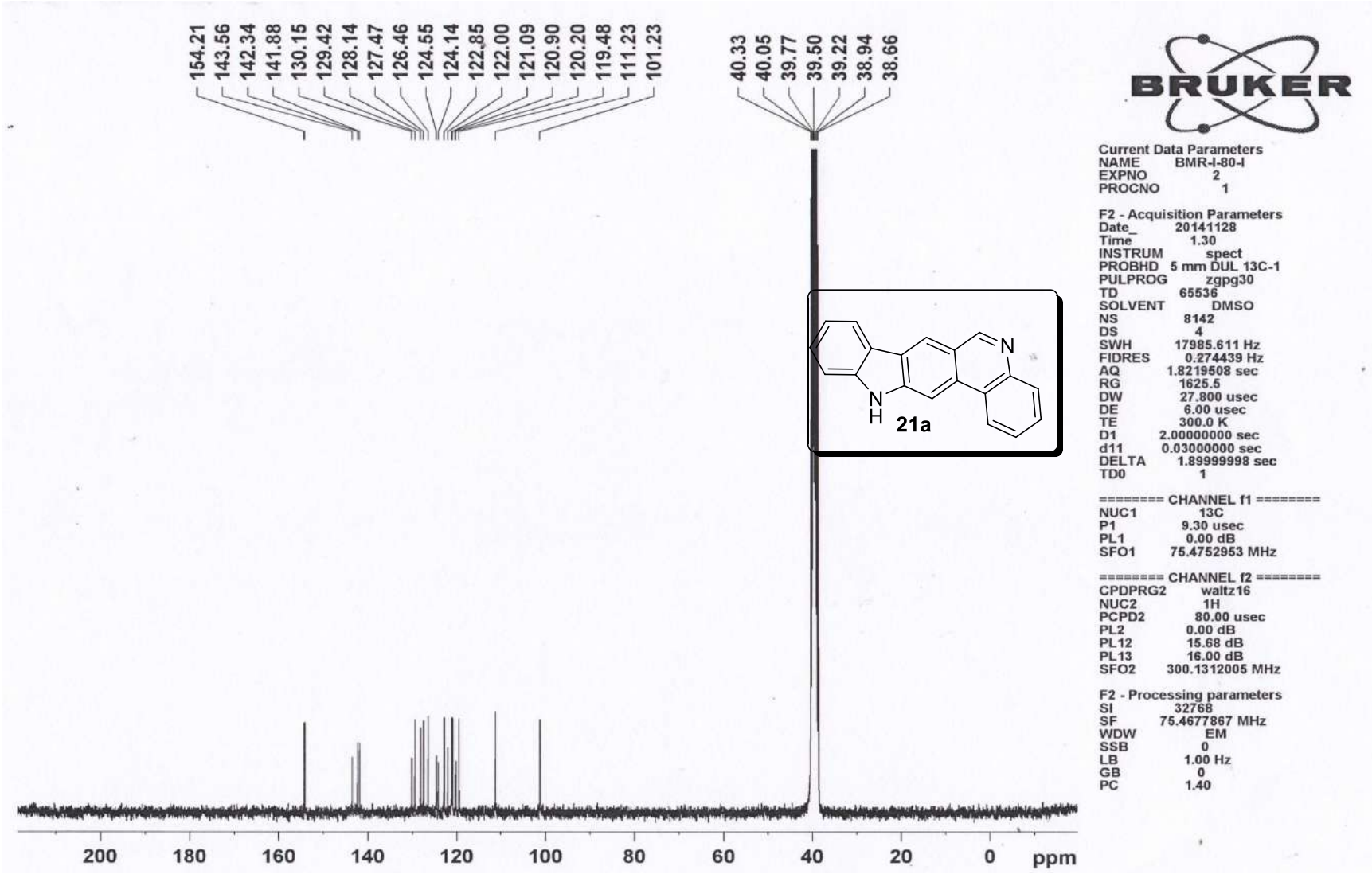
^{13}C-NMR spectrum of compound **1** (Expanded region 145-110 ppm)



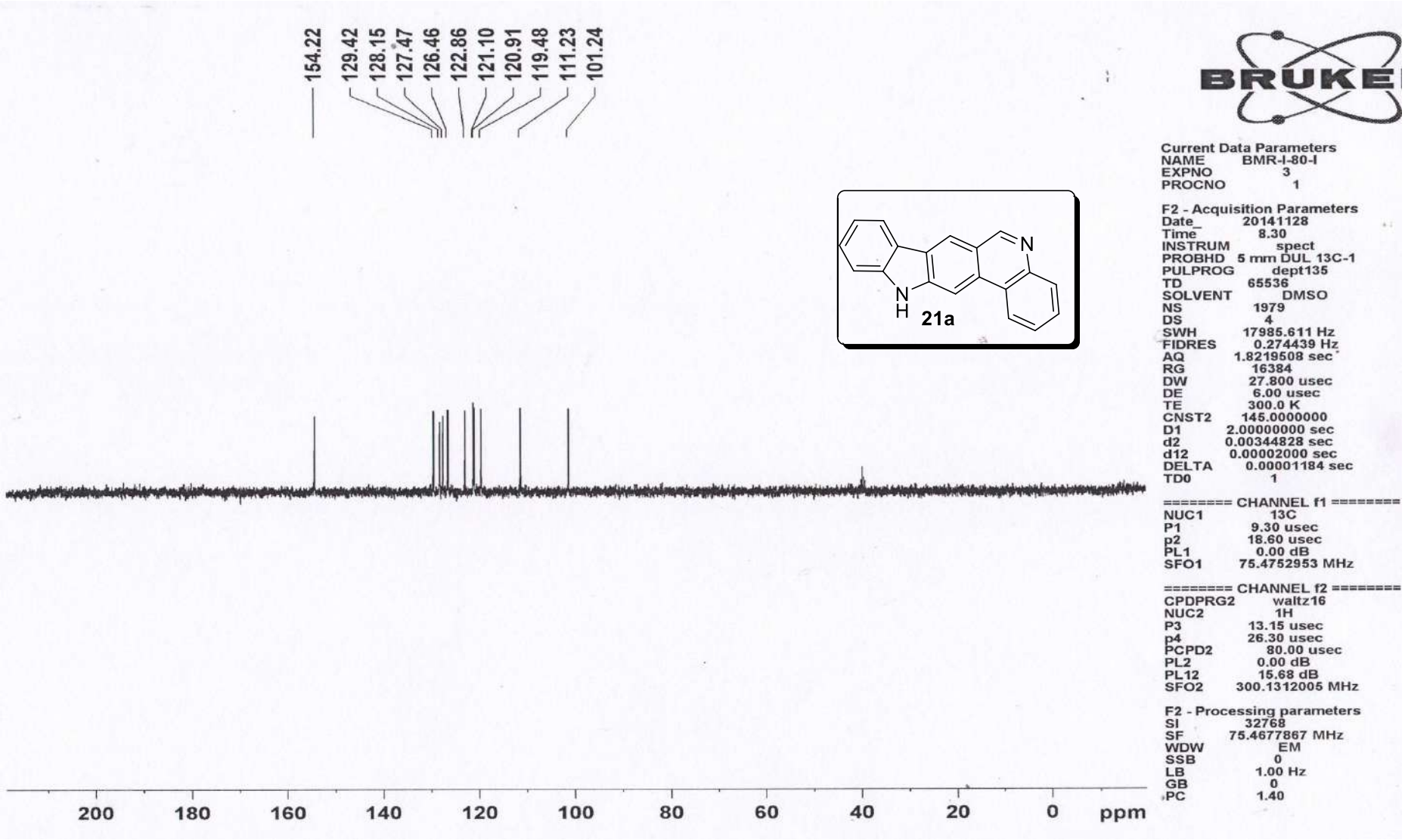
DEPT 90-^{13}C NMR spectrum of compound **1**



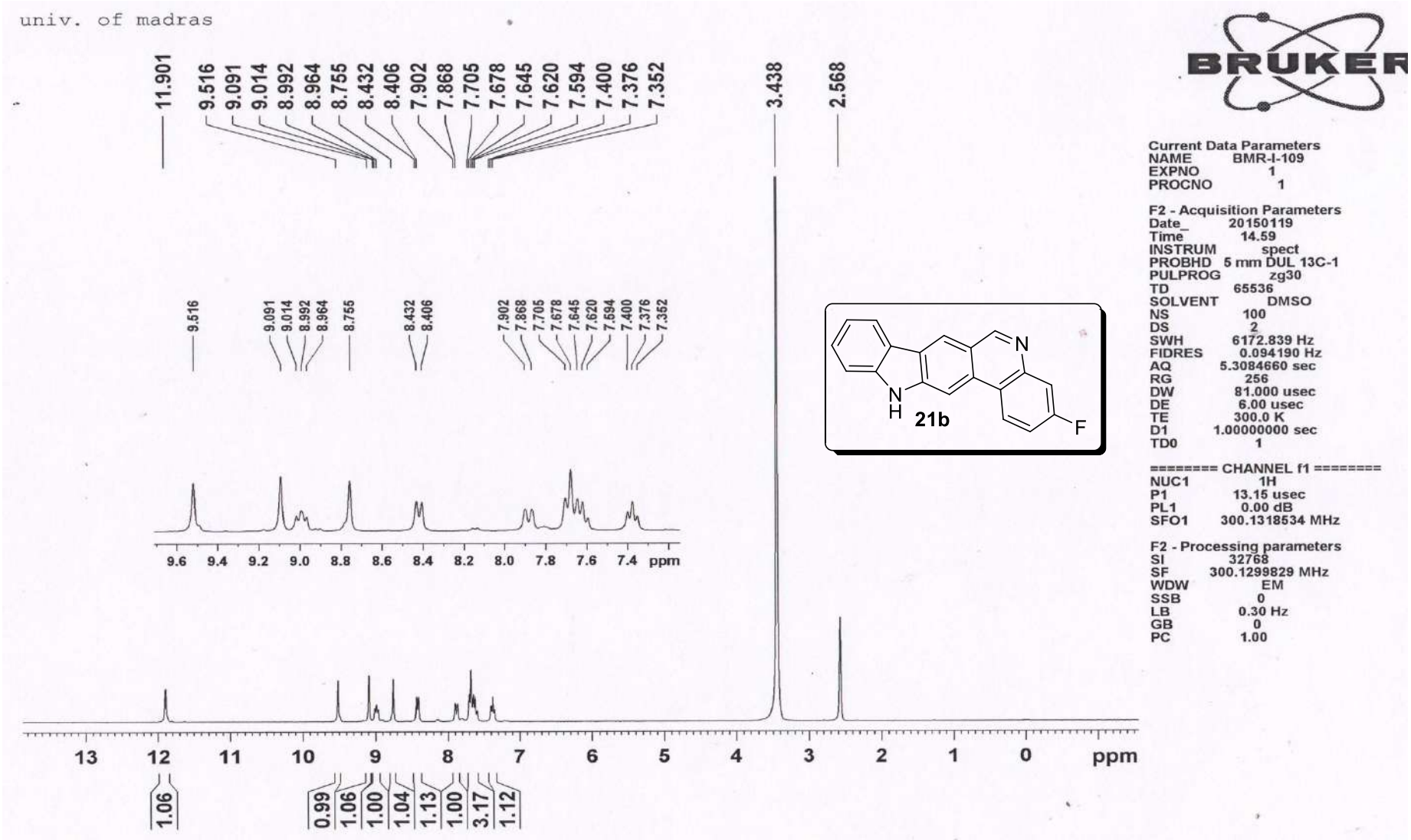
^{1}H-NMR spectrum of compound **21a**



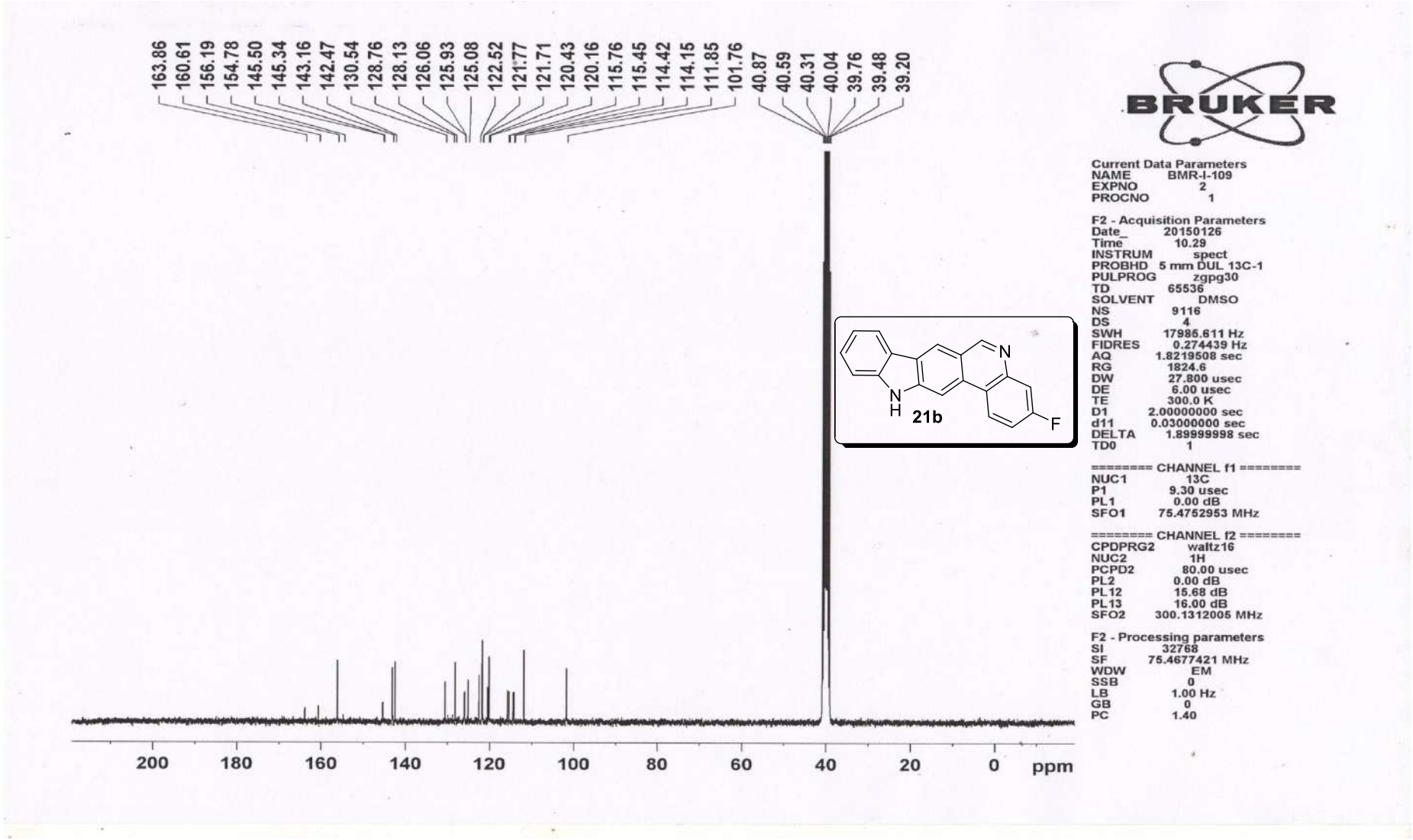
^{13}C-NMR spectrum of compound **21a**



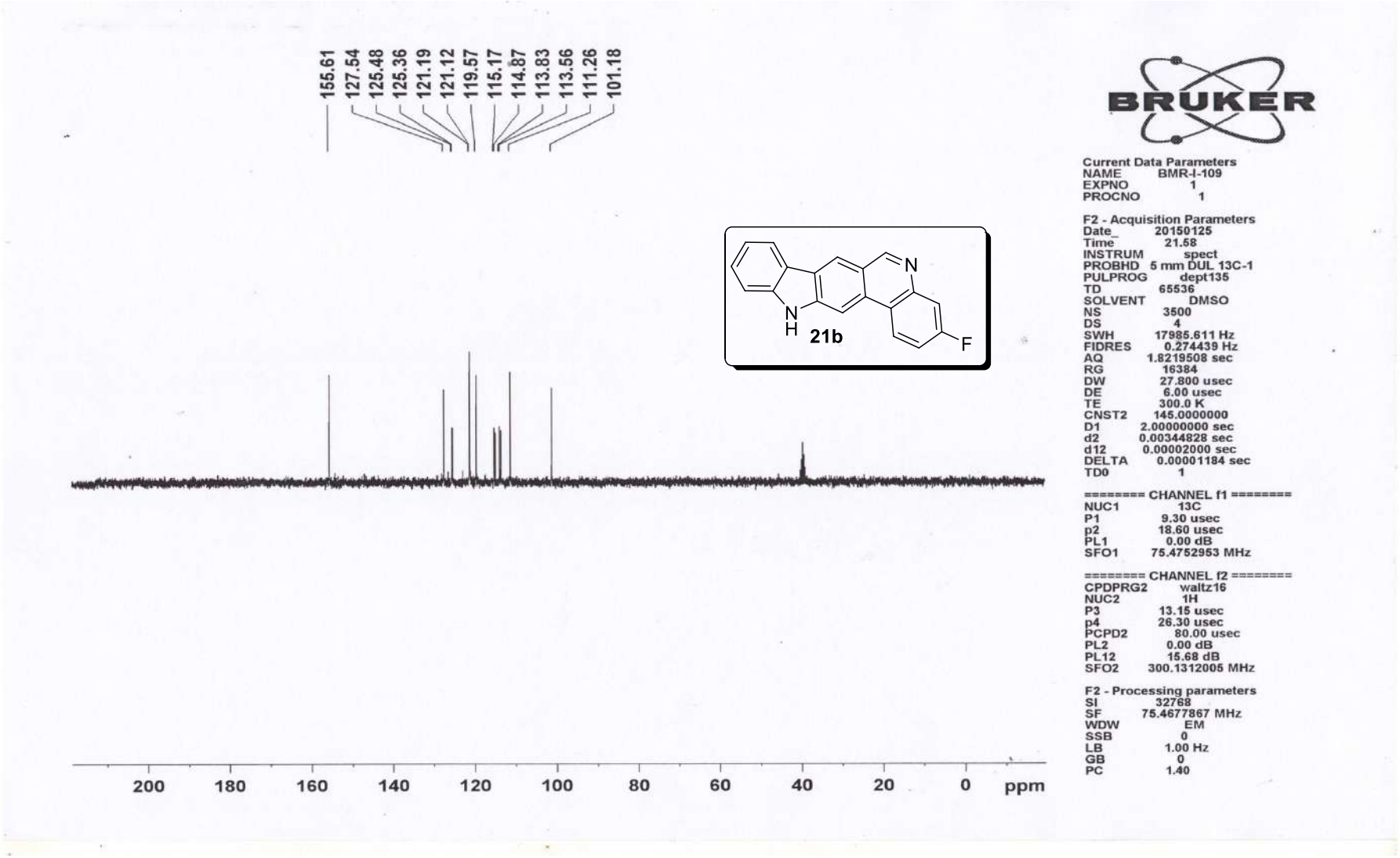
DEPT 135-^{13}C NMR spectrum of compound **21a**



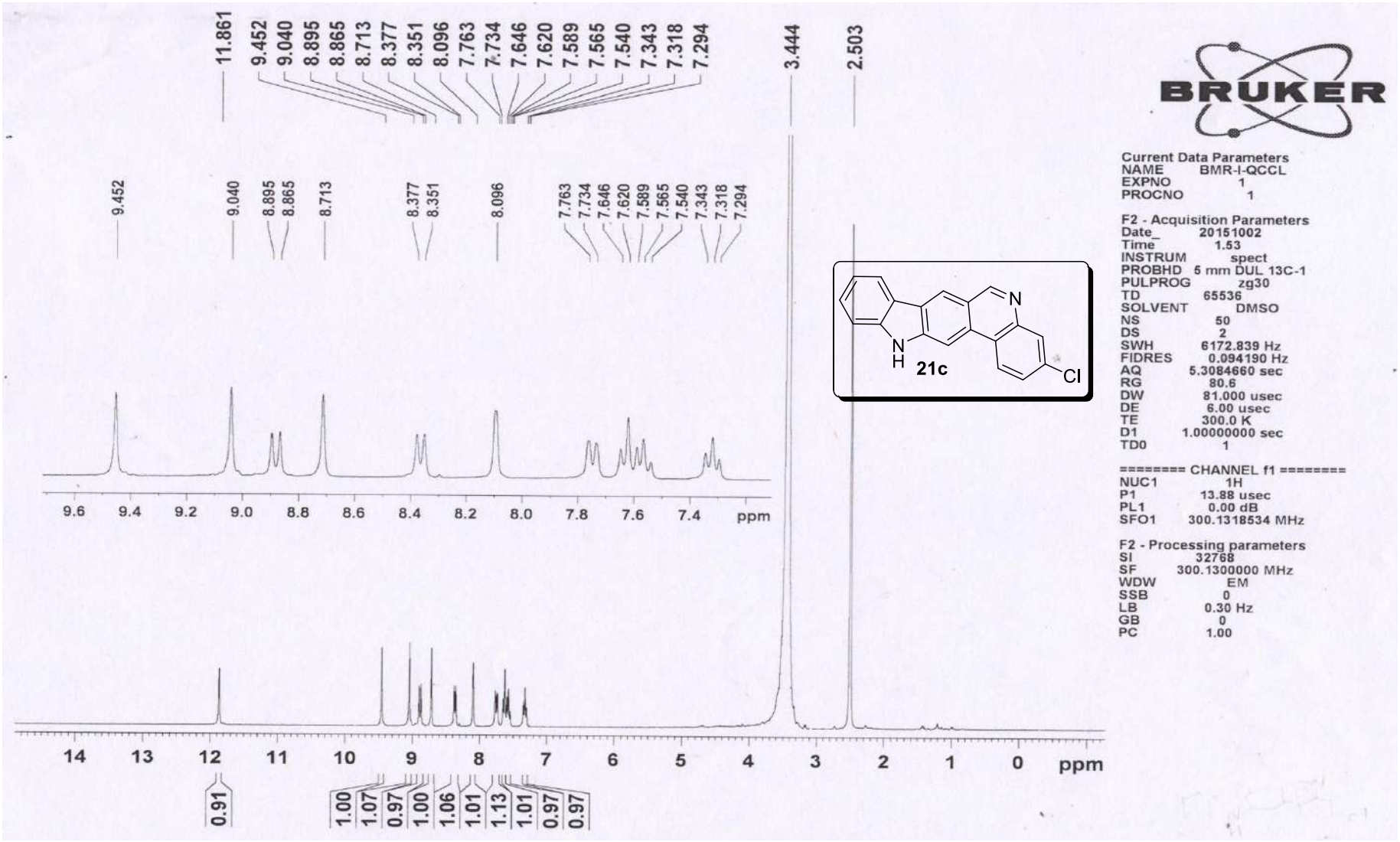
^{1}H-NMR spectrum of compound **21b**



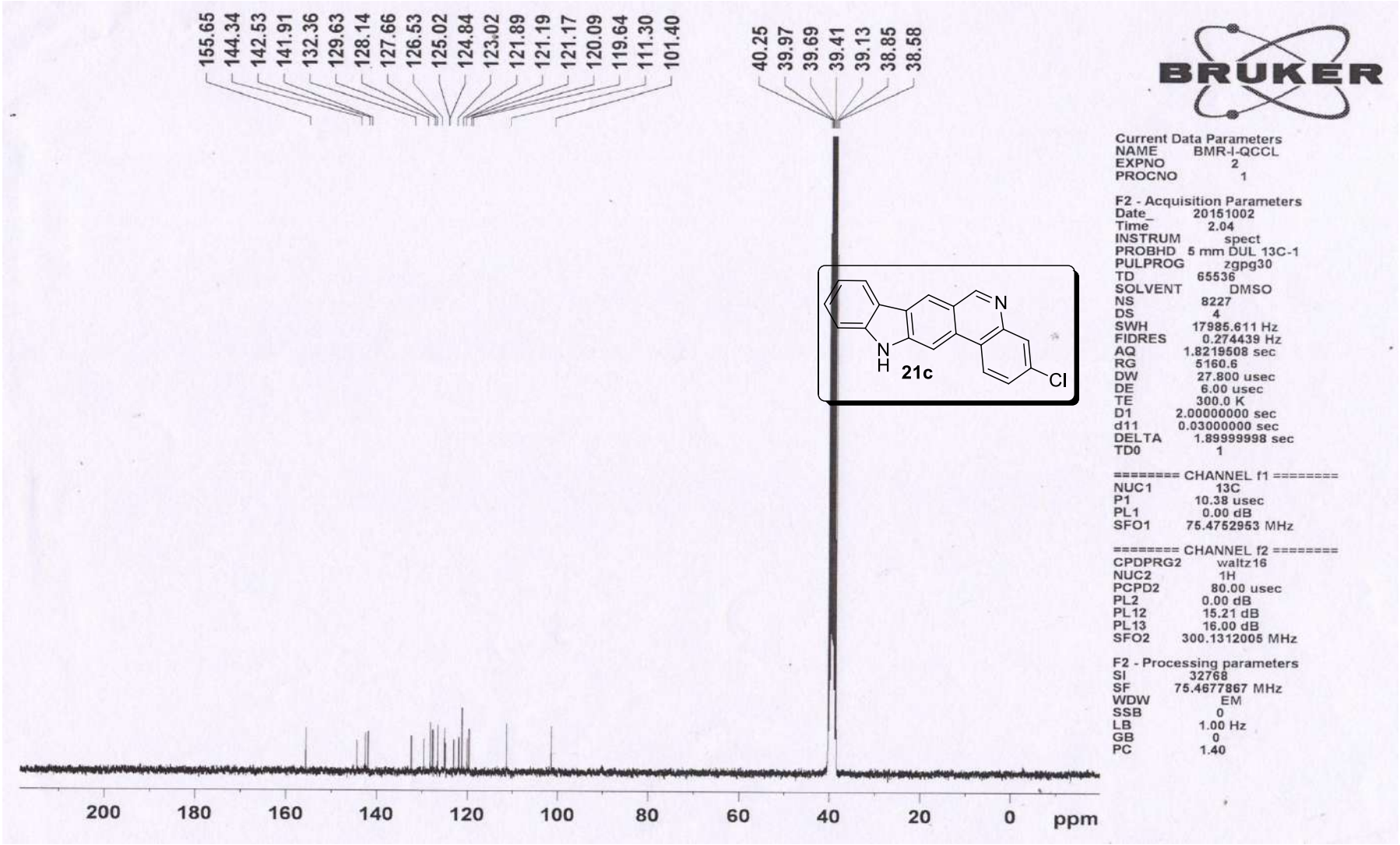
^{13}C -NMR spectrum of compound **21b**



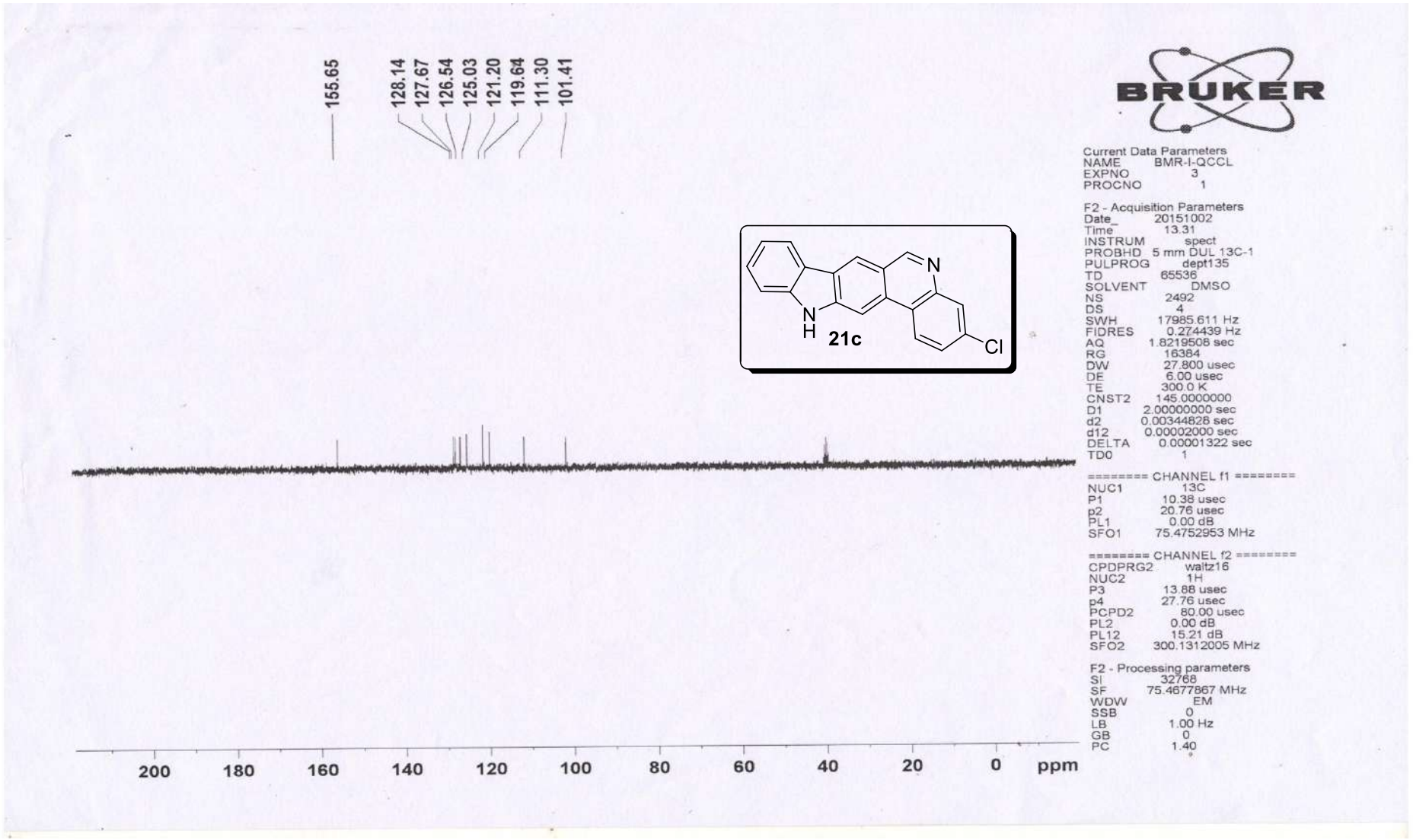
DEPT 135-^{13}C NMR spectrum of compound **21b**



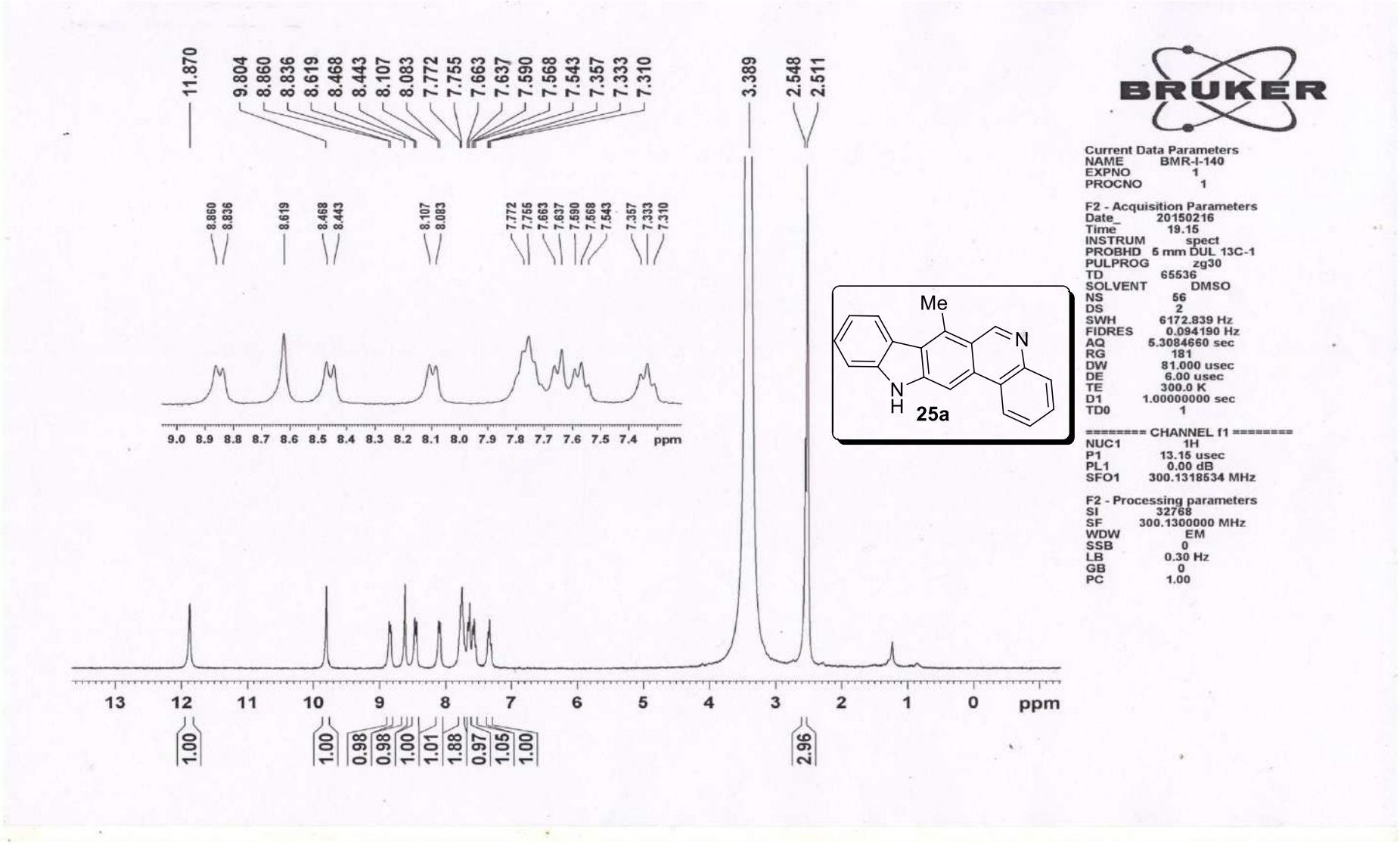
^{1}H-NMR spectrum of compound **21c**



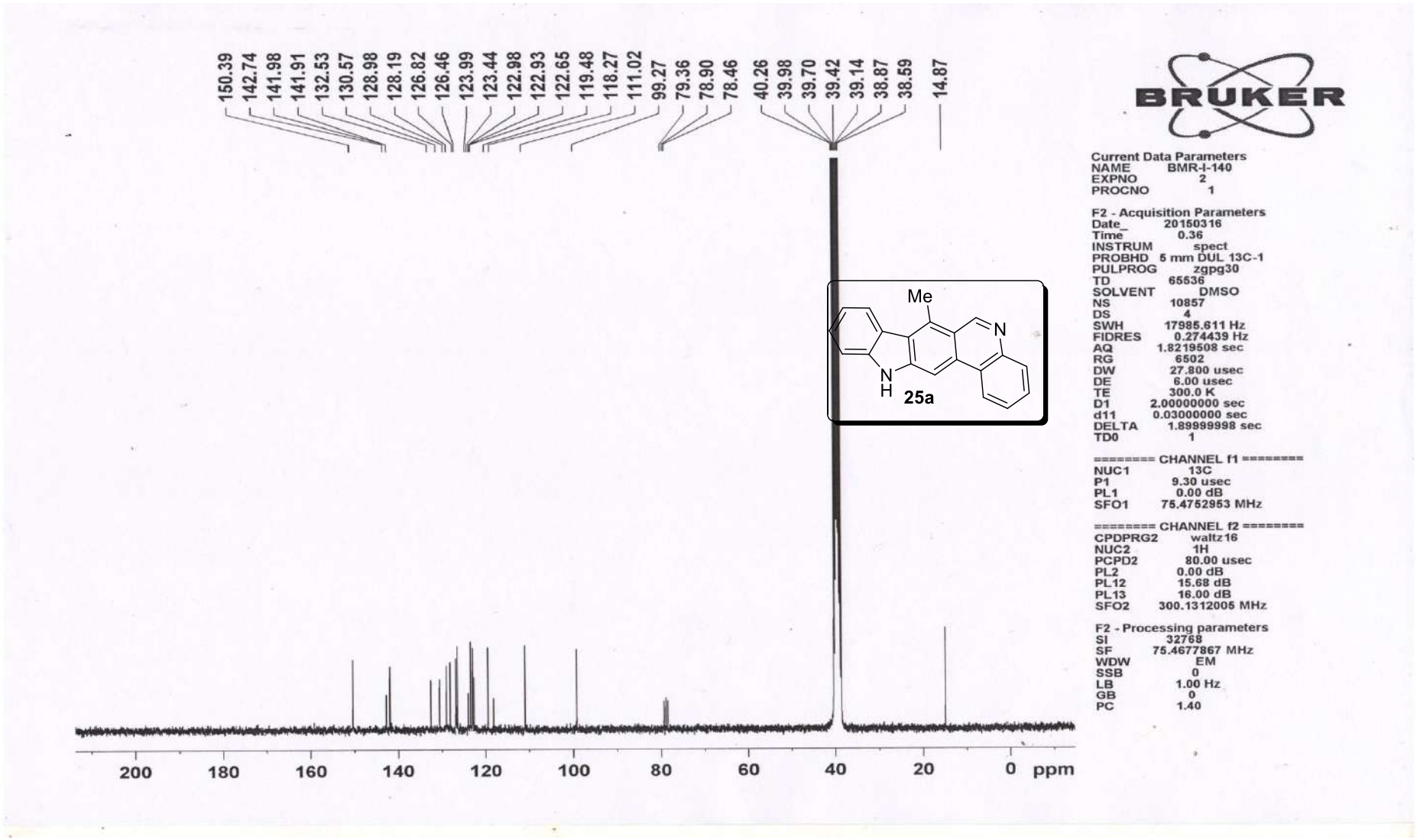
^{13}C-NMR spectrum of compound **21c**



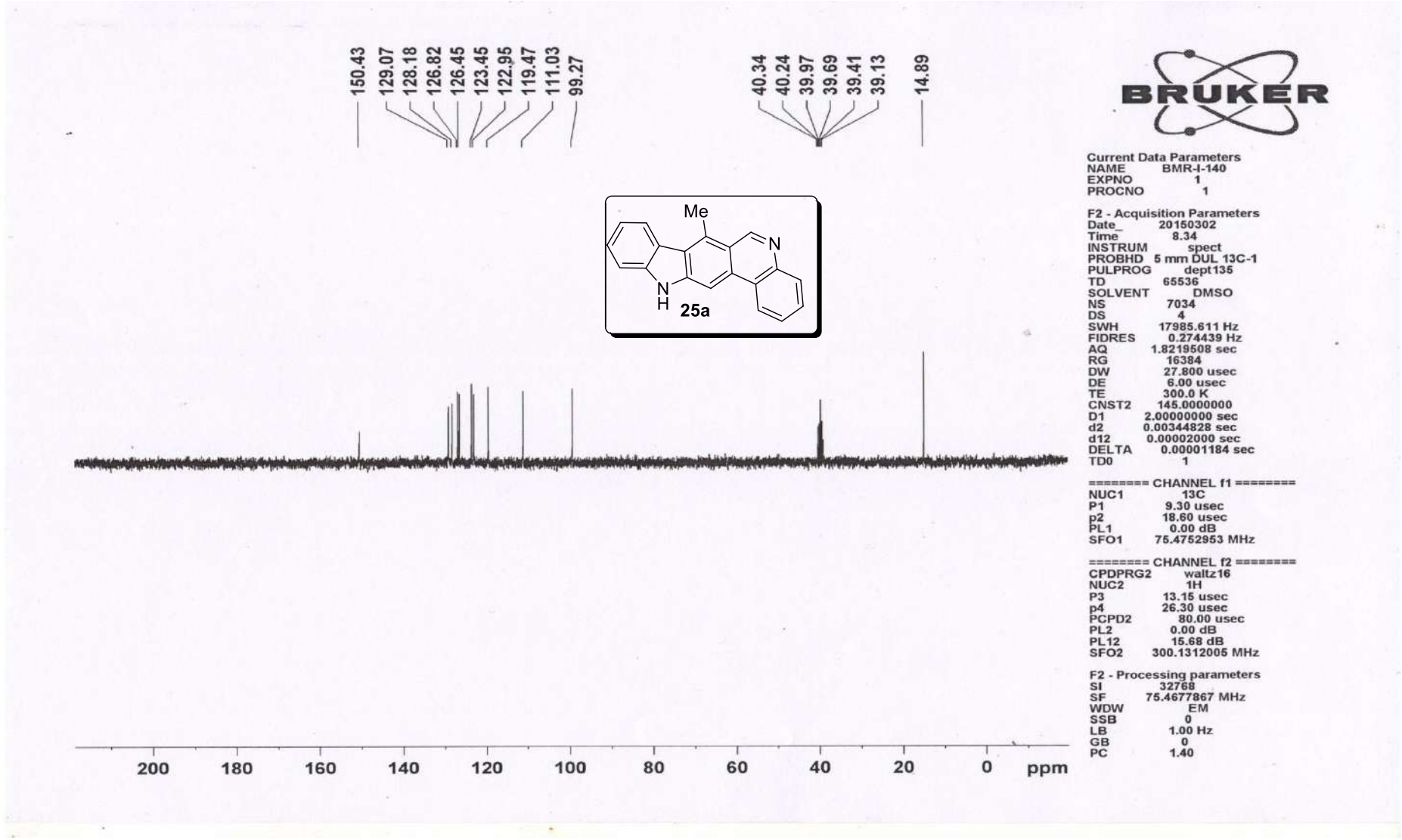
DEPT 135-^{13}C NMR spectrum of compound **21c**



^{1}H-NMR spectrum of compound **25a**



^{13}C-NMR spectrum of compound **25a**



BRUKER

Current Data Parameters
NAME BMR-I-140
EXPNO 1
PROCNO 1

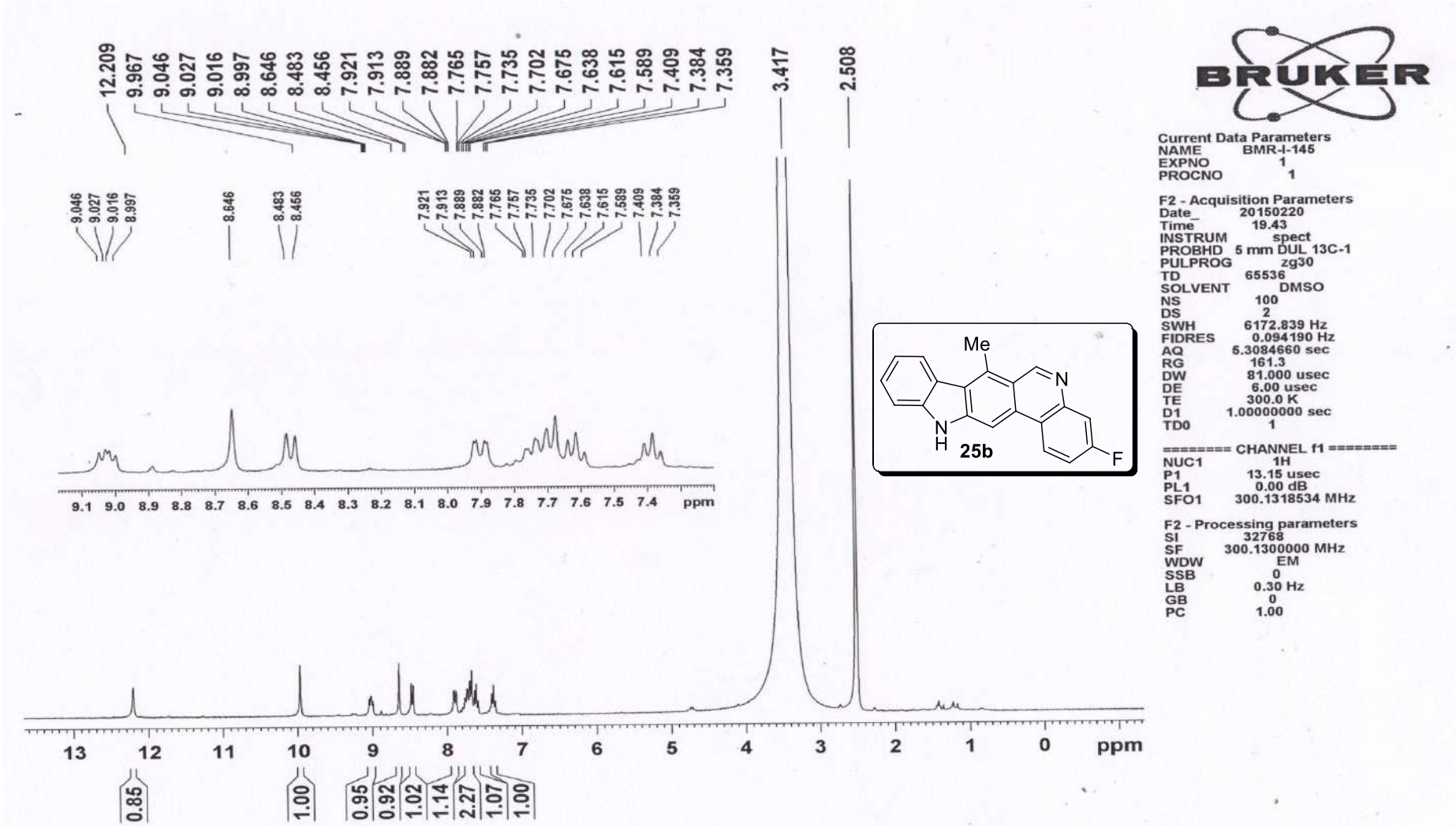
F2 - Acquisition Parameters
Date_ 20150302
Time 8.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG dept135
TD 65536
SOLVENT DMSO
NS 7034
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
D1 2.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 0.00001184 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
p2 18.60 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

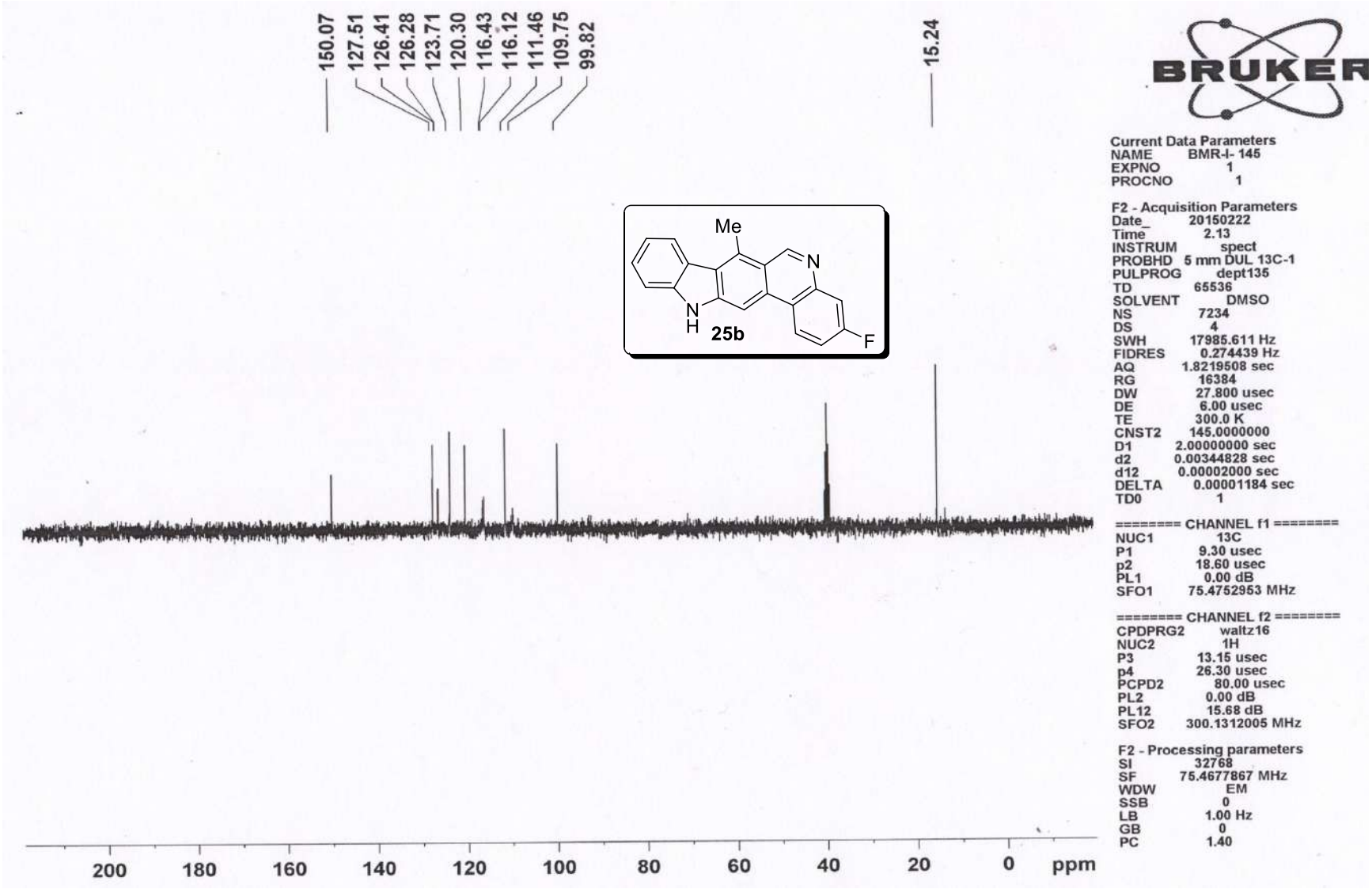
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P3 13.15 usec
p4 26.30 usec
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.68 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677867 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

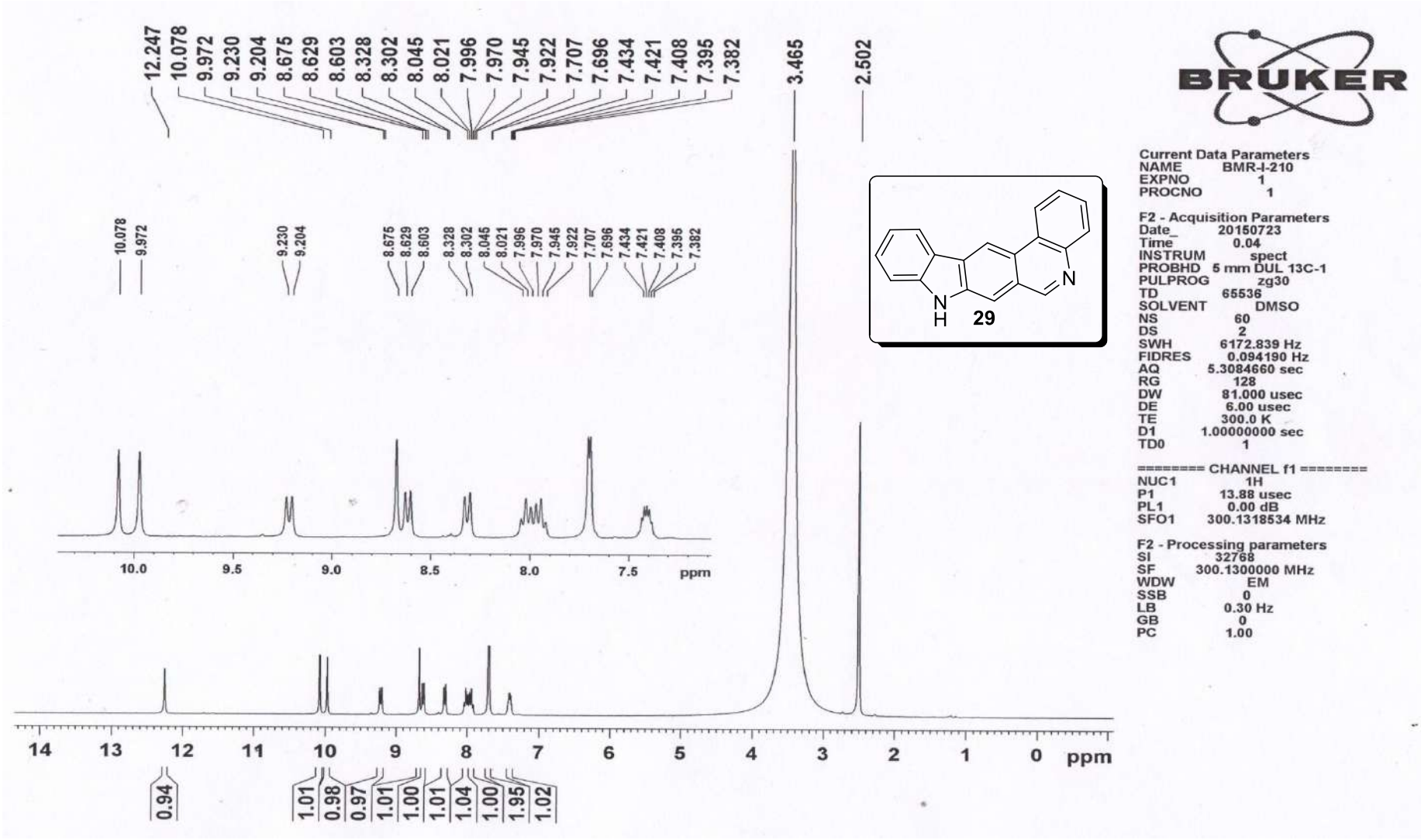
DEPT 135-^{13}C NMR spectrum of compound **25a**



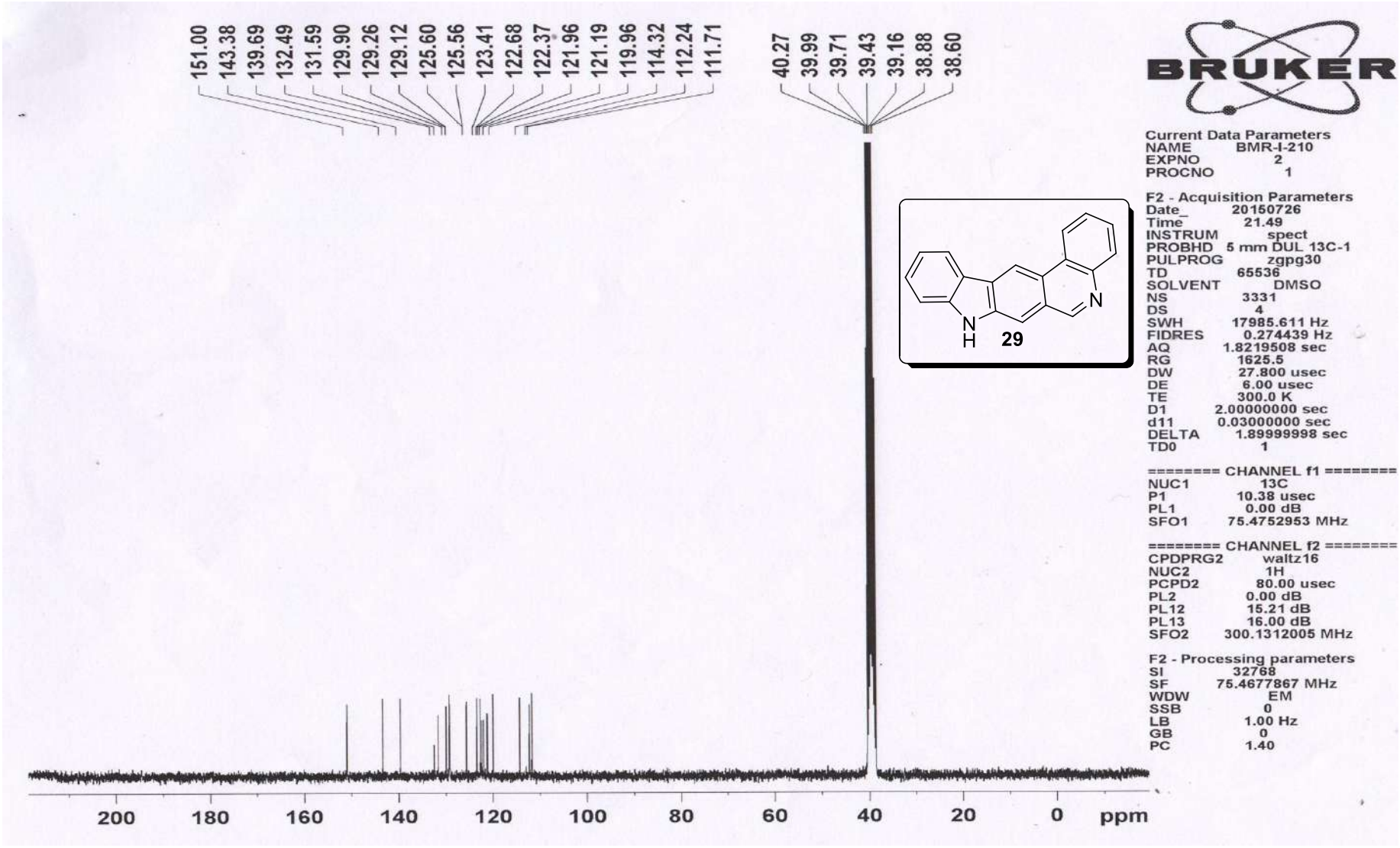
^{1}H-NMR spectrum of compound **25b**



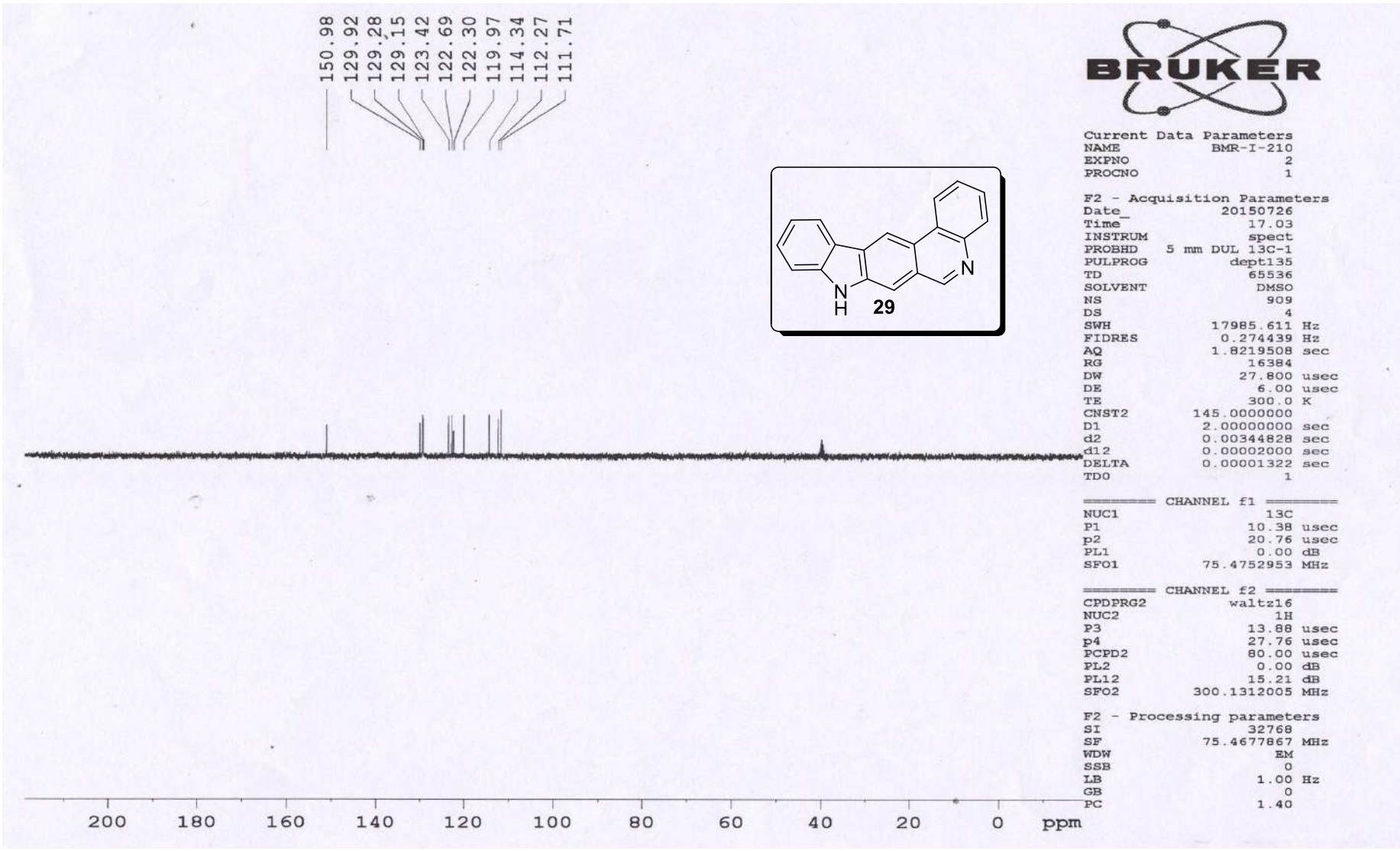
DEPT 135-^{13}C NMR spectrum of compound **25b**



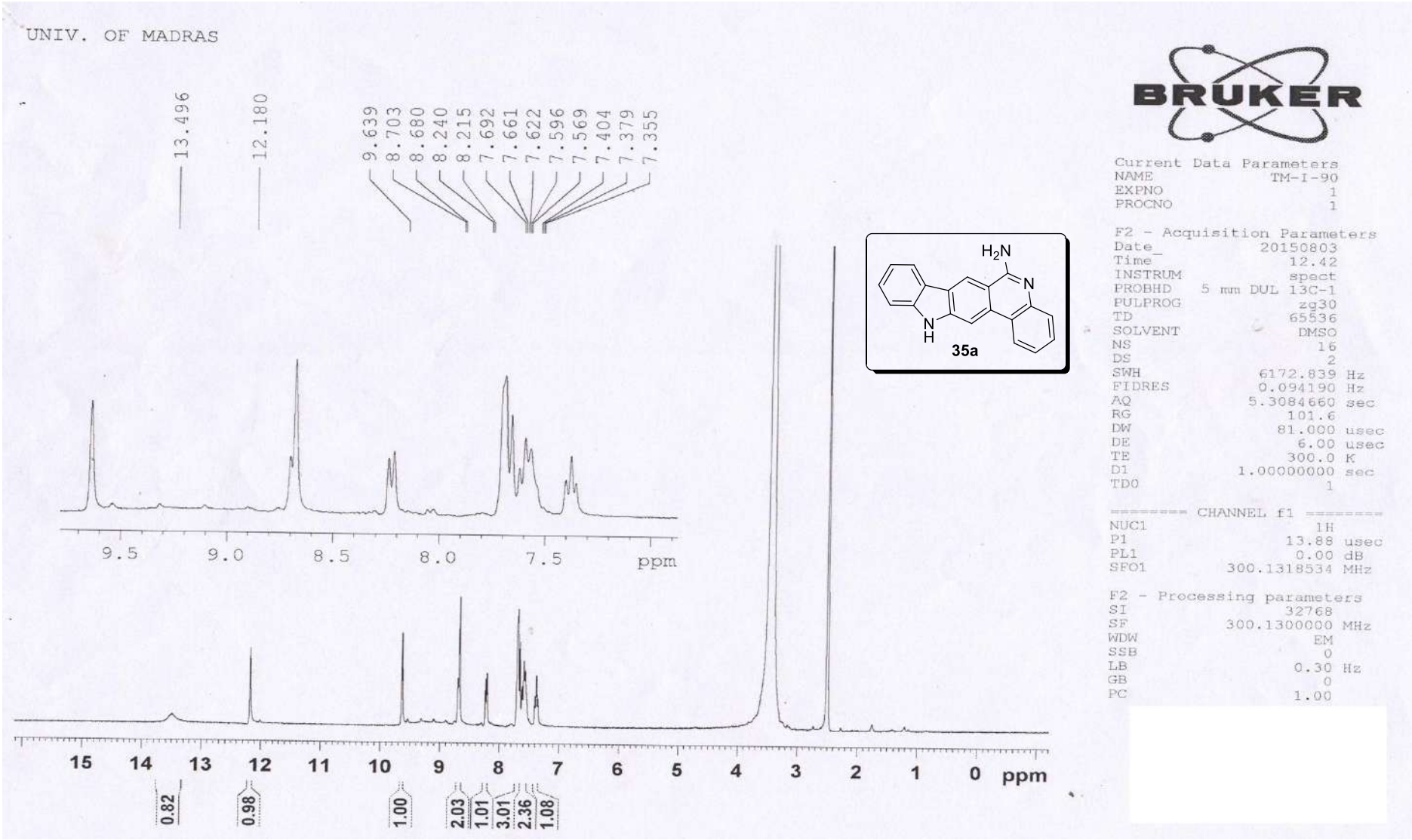
^{1}H-NMR spectrum of compound **29**



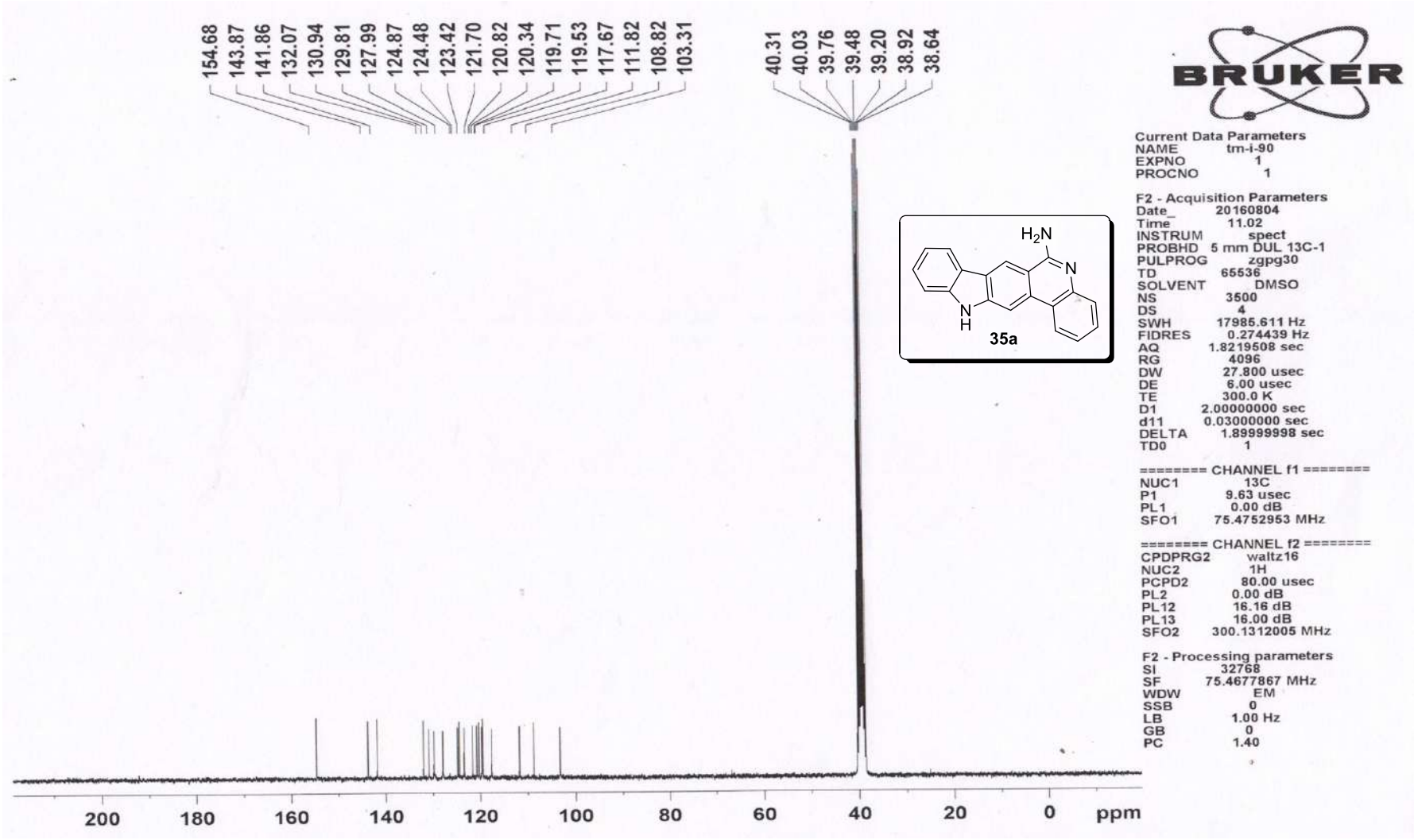
^{13}C-NMR spectrum of compound **29**



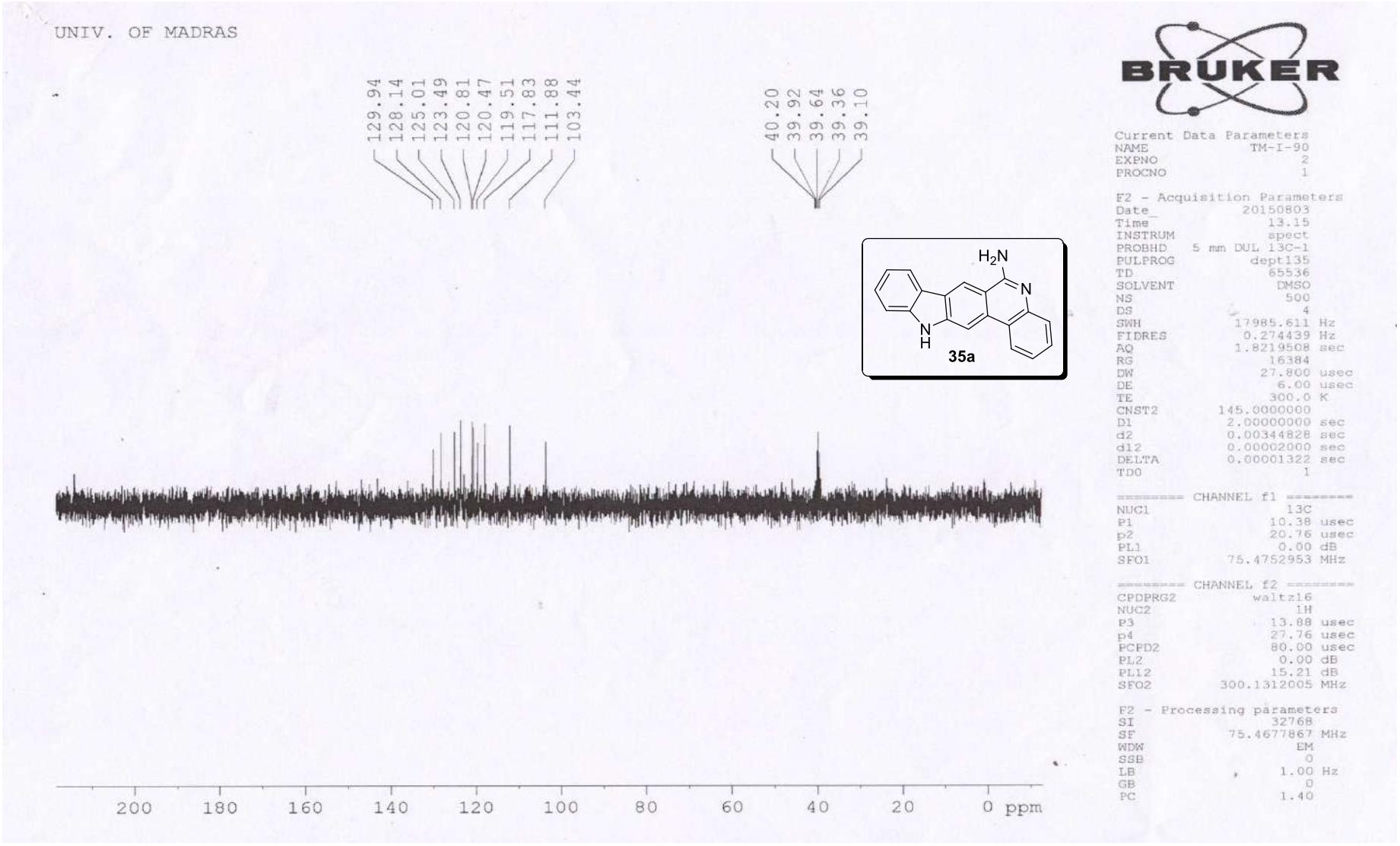
DEPT 135-^{13}C NMR spectrum of compound **29**



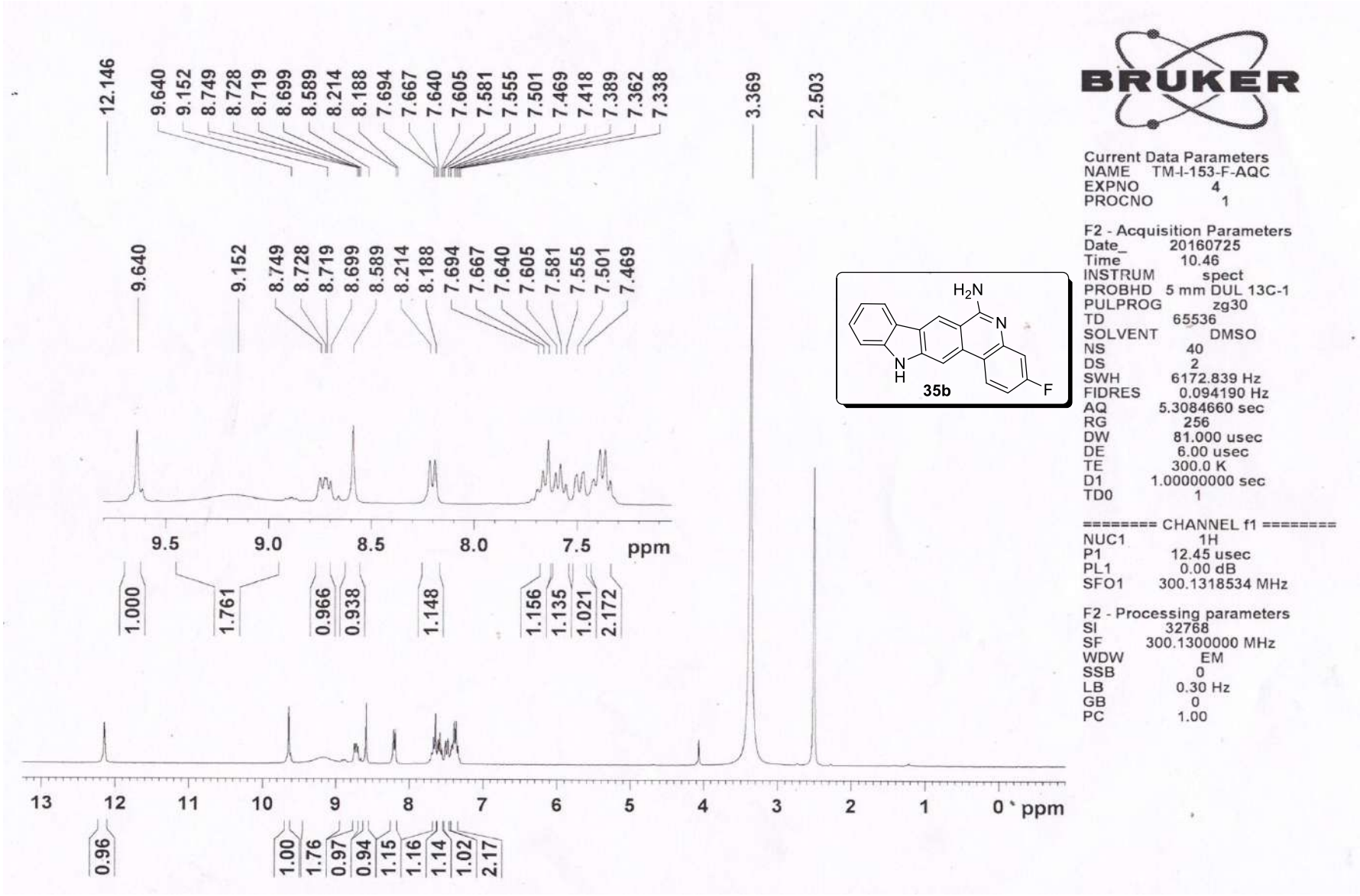
^{1}H-NMR spectrum of compound **35a**



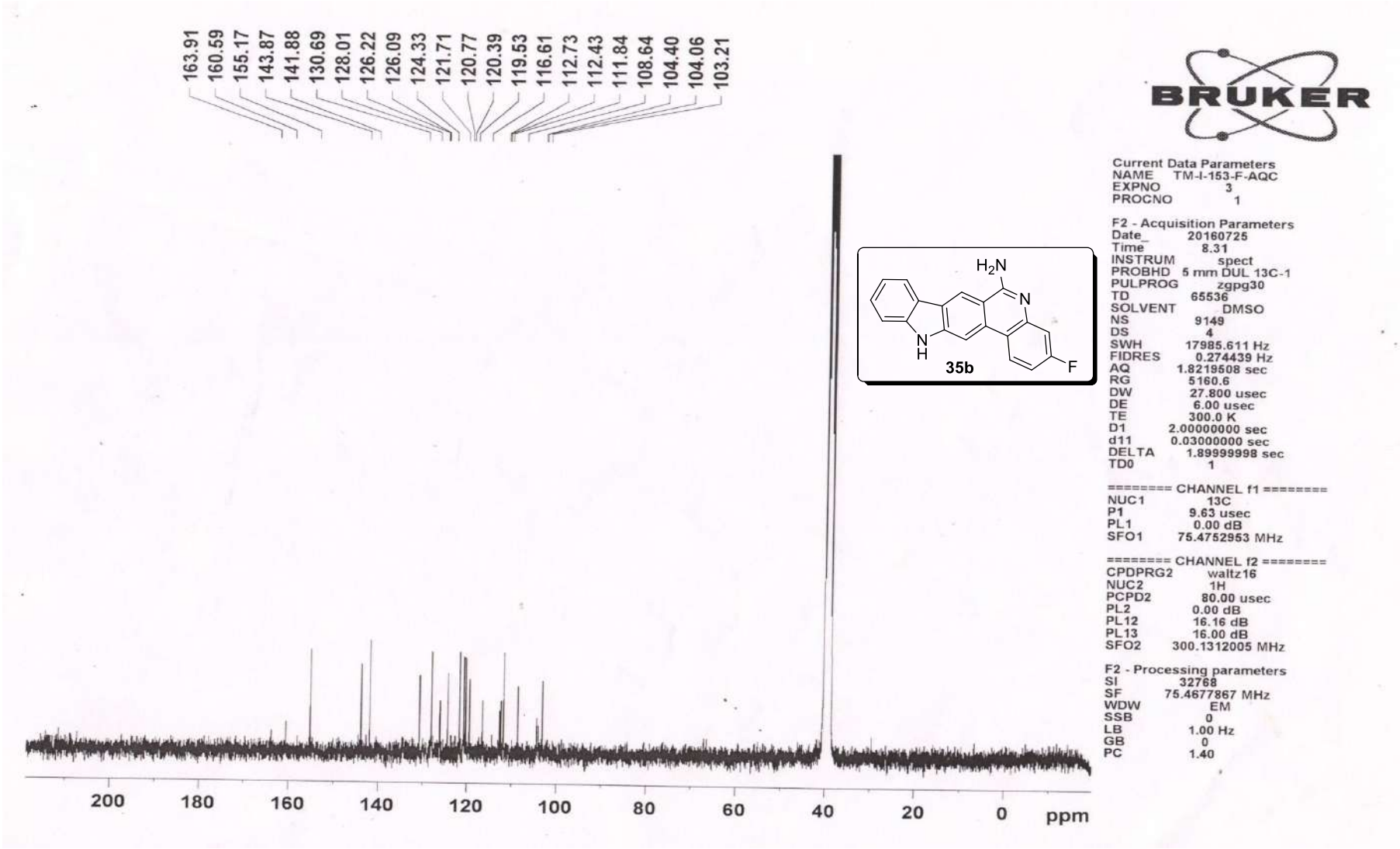
^{13}C-NMR spectrum of compound **35a**



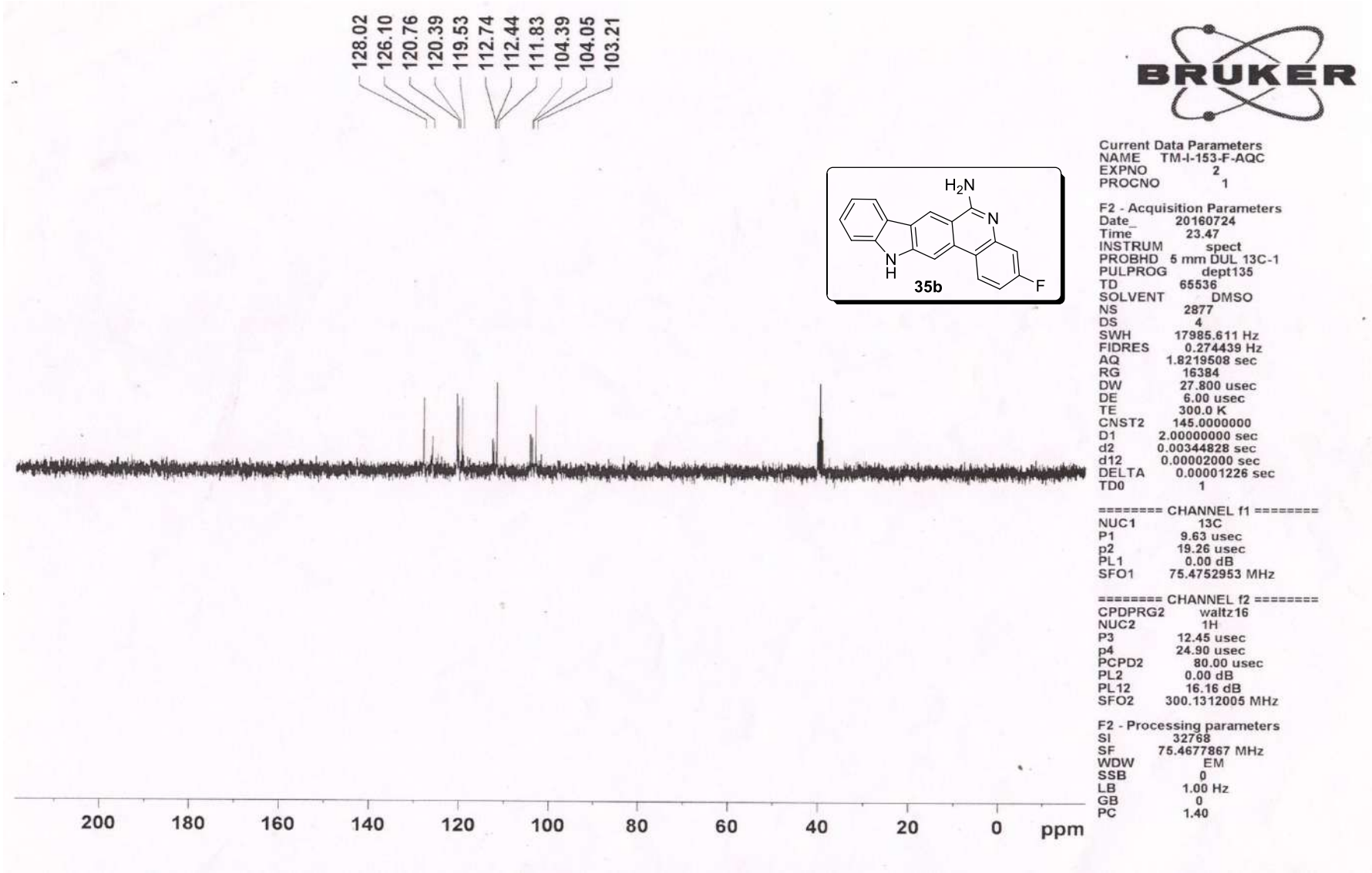
DEPT 135-^{13}C NMR spectrum of compound **35a**



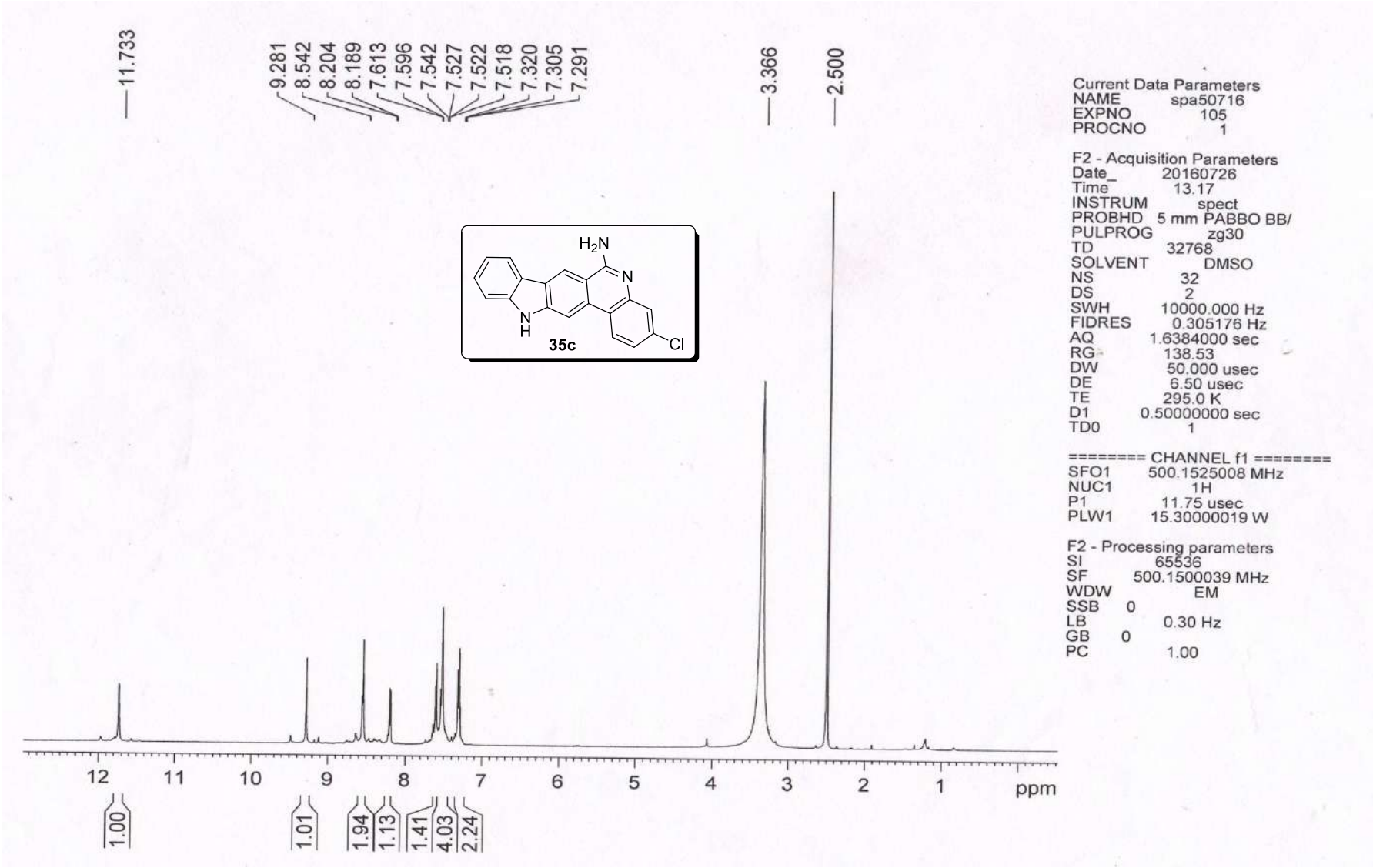
^{1}H-NMR spectrum of compound **35b**



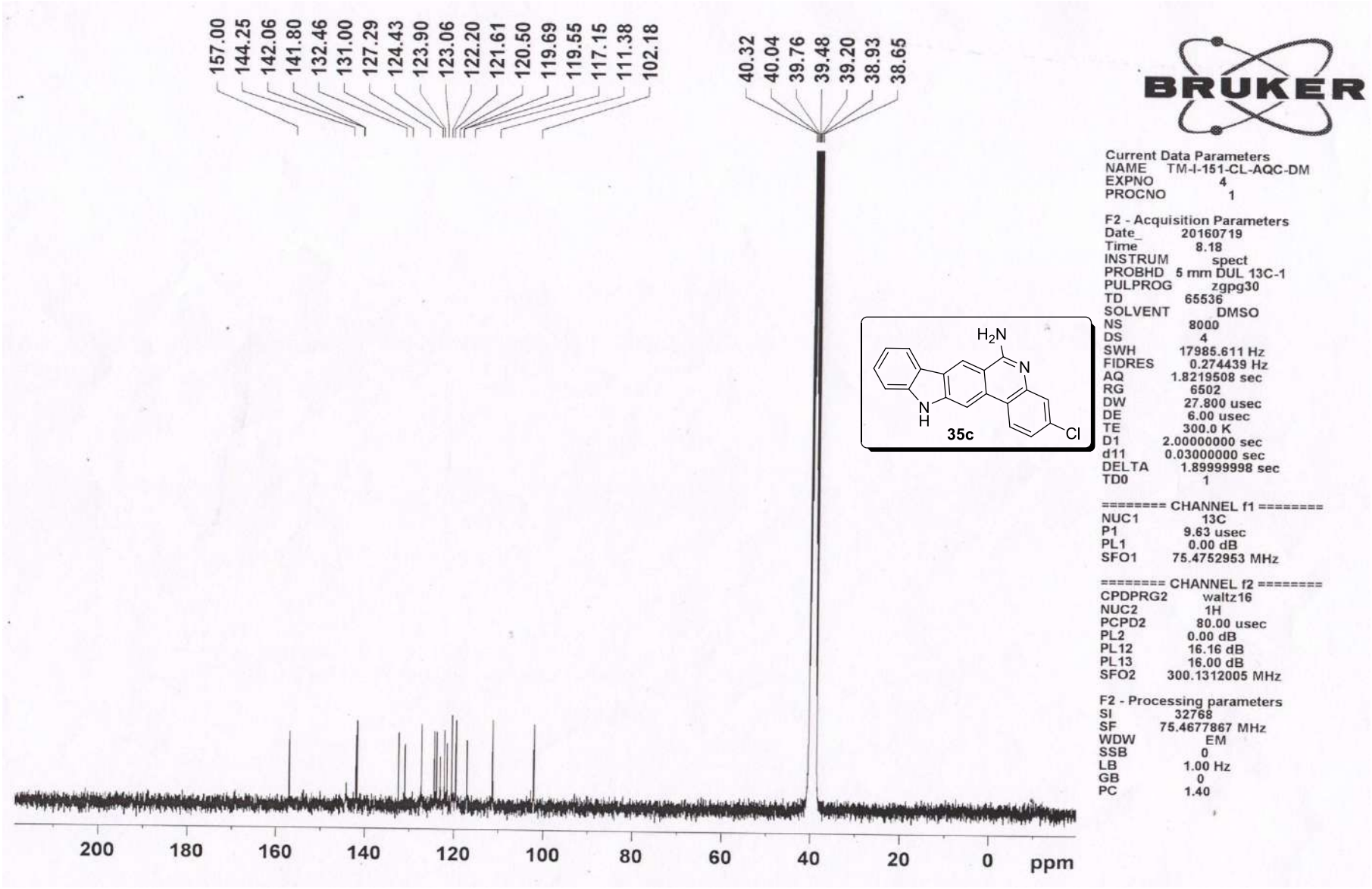
^{13}C-NMR spectrum of compound **35b**



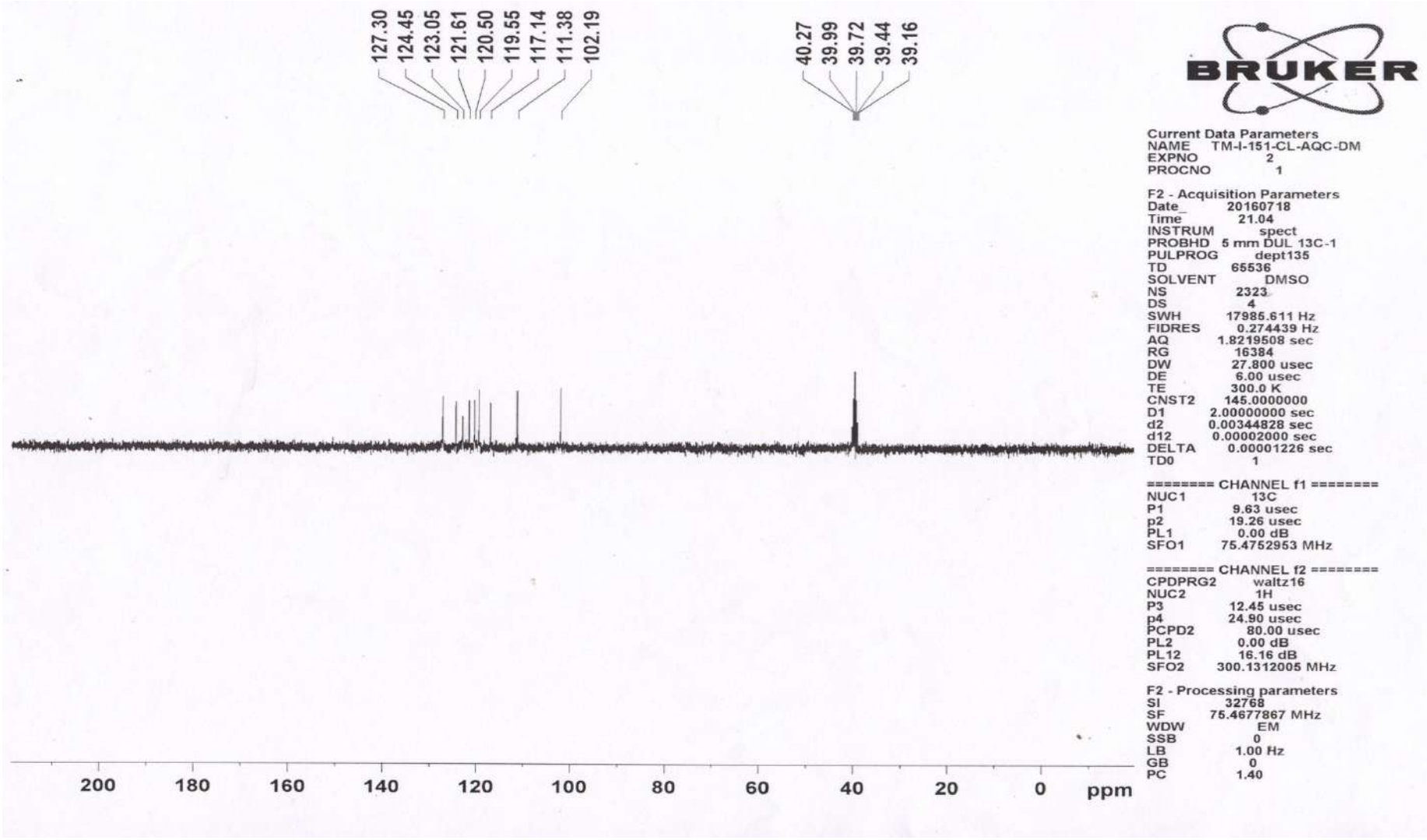
DEPT 135-^{13}C NMR spectrum of compound **35b**



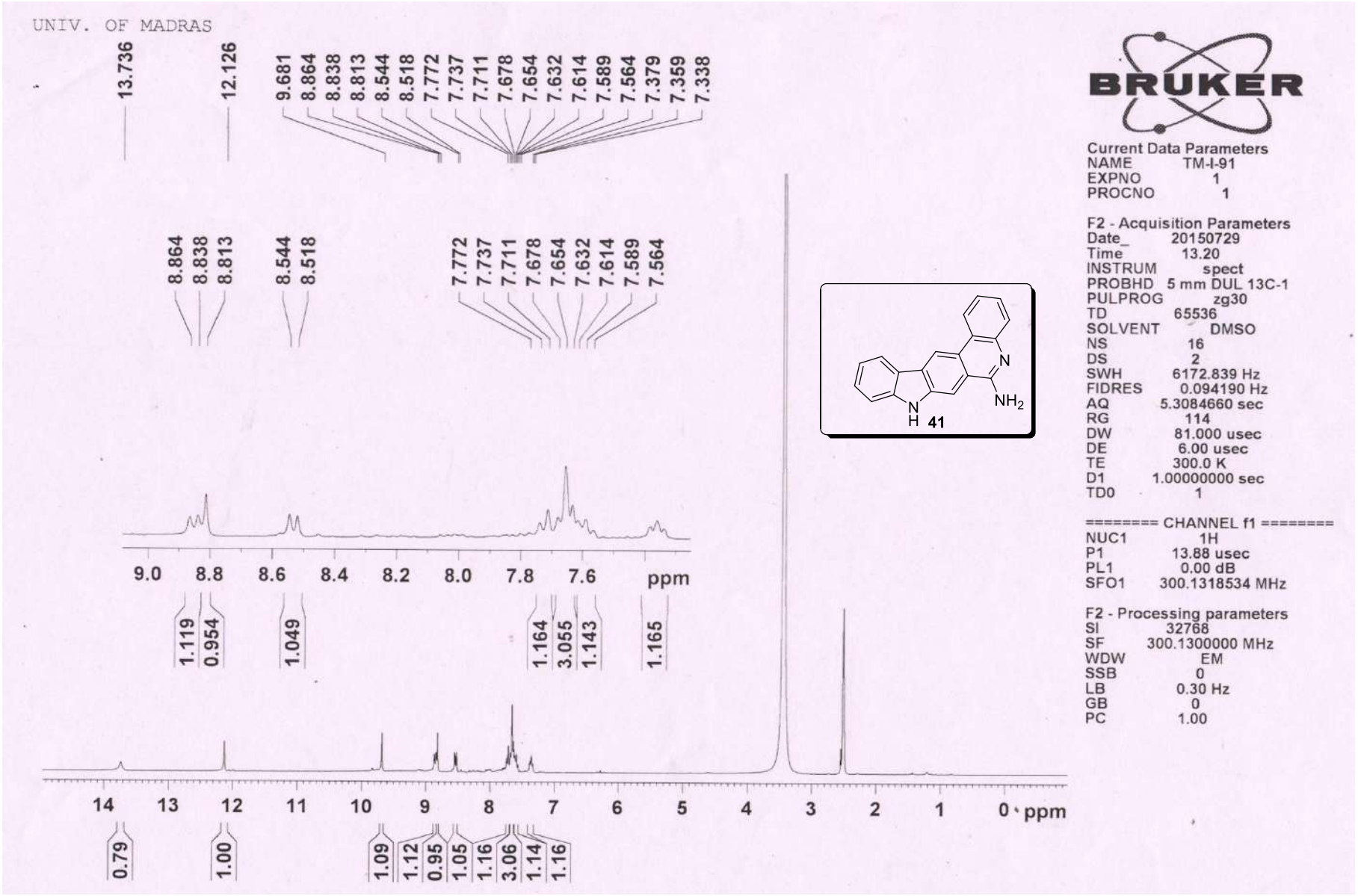
^{1}H-NMR spectrum of compound **35c**



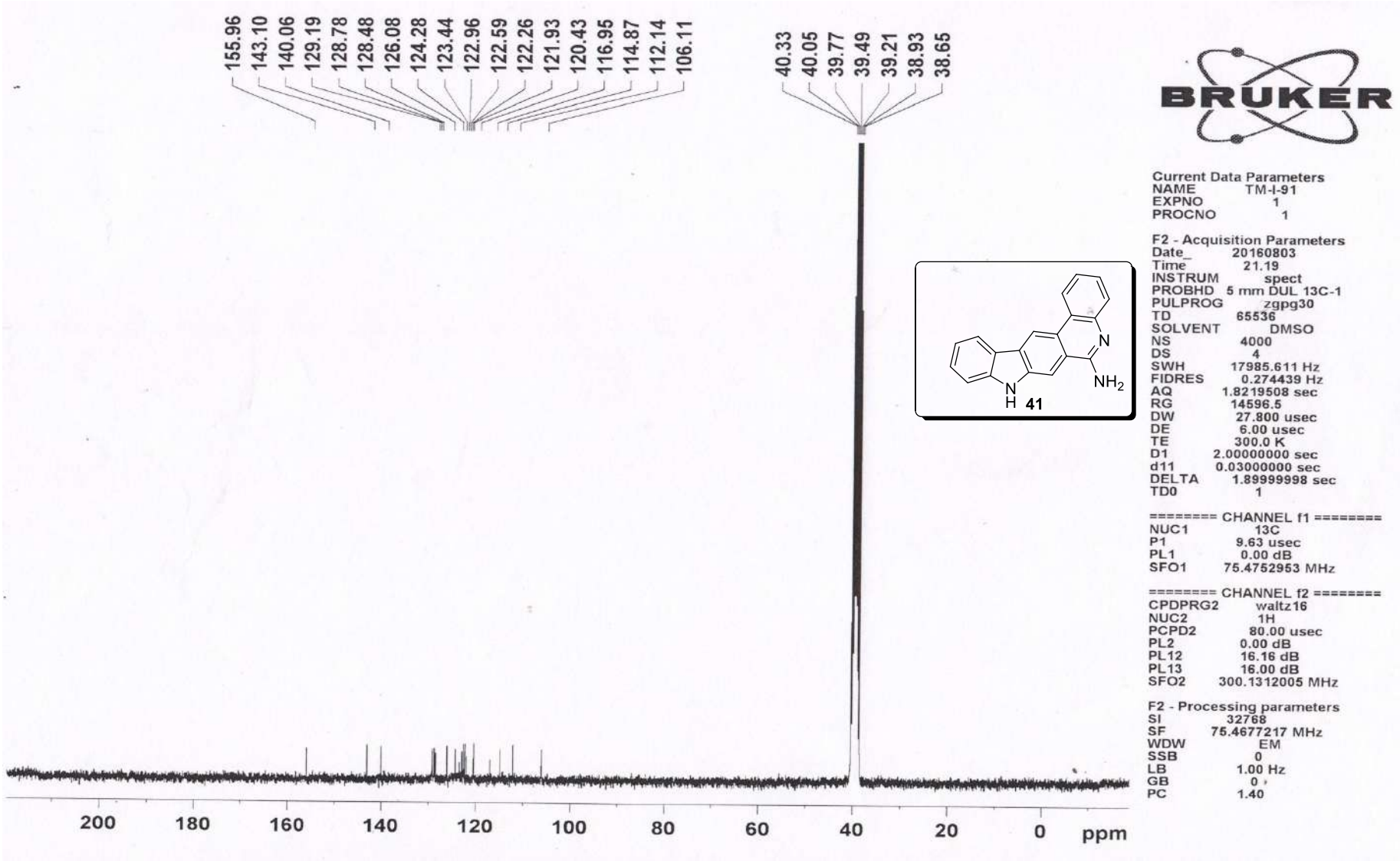
^{13}C-NMR spectrum of compound **35c**



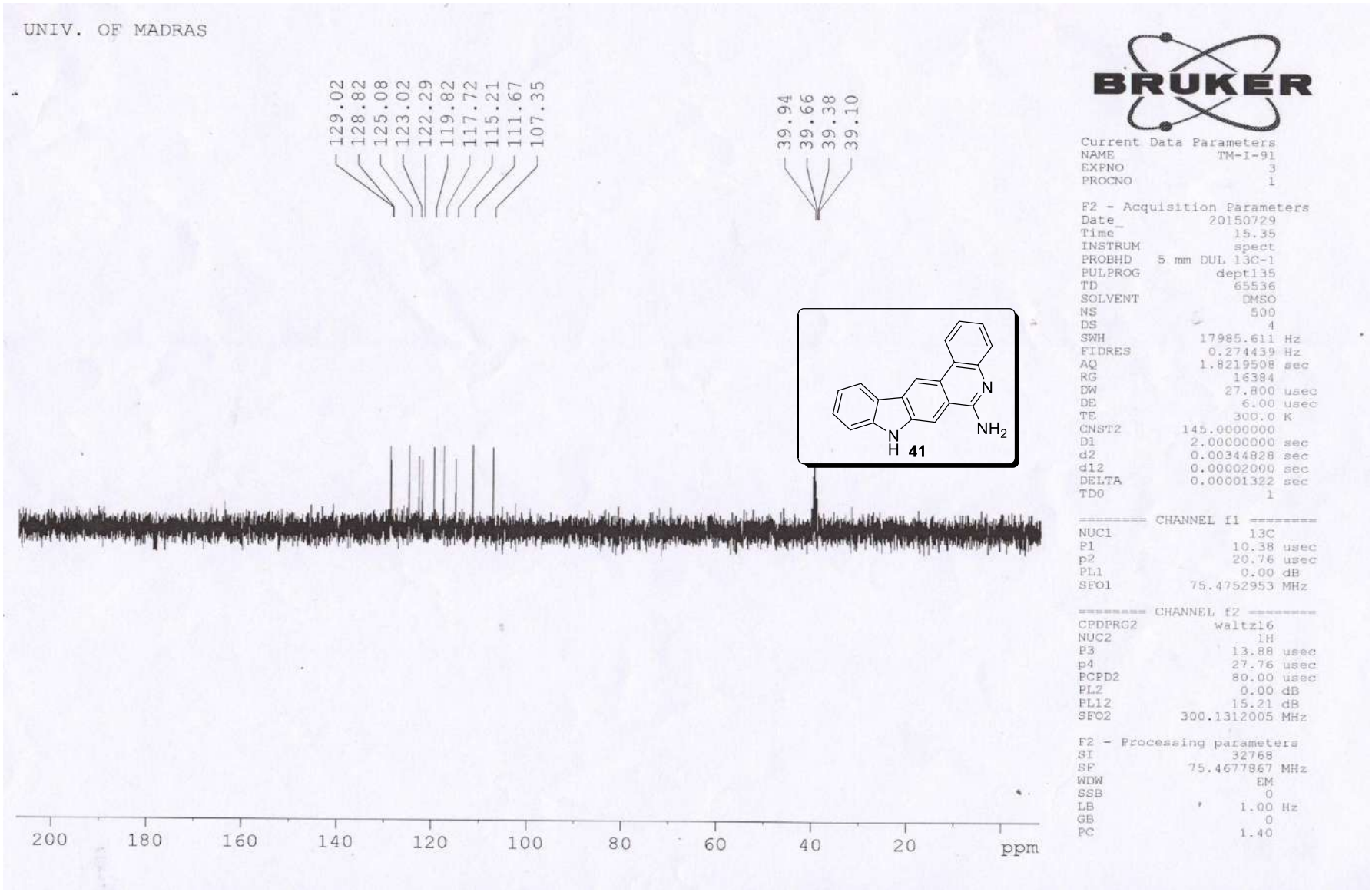
DEPT 135-^{13}C NMR spectrum of compound **35c**



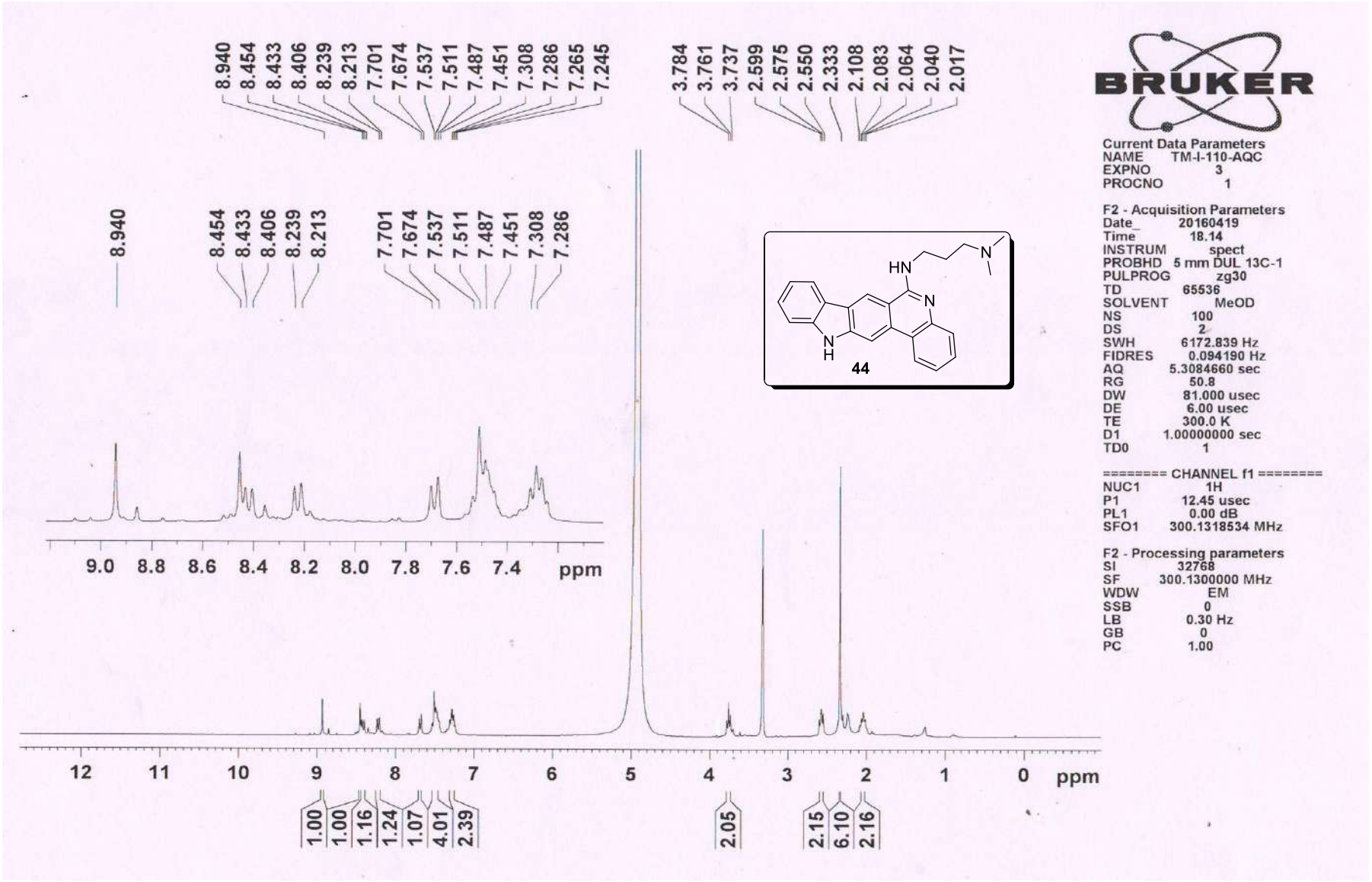
^{1}H-NMR spectrum of compound **41**



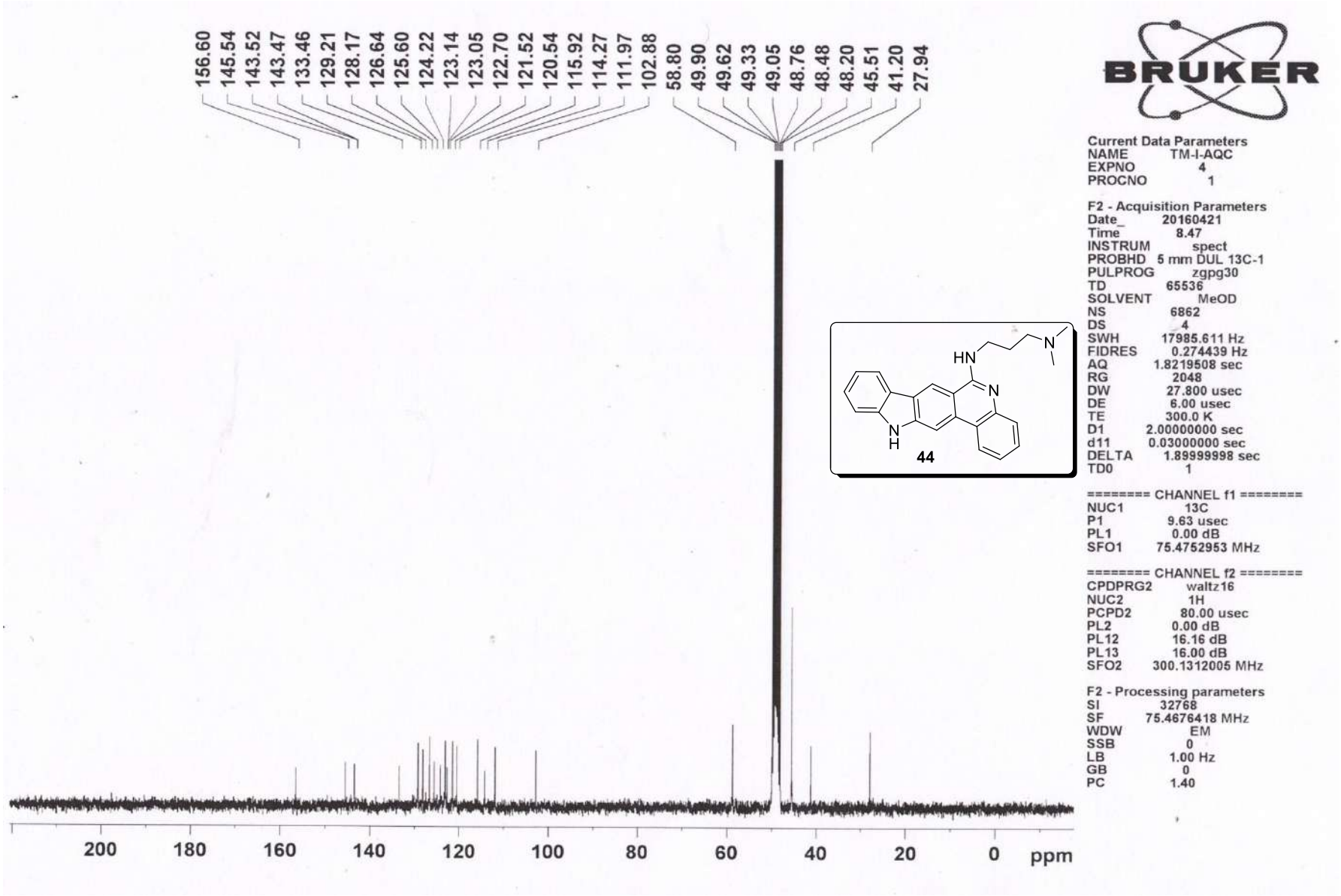
^{13}C-NMR spectrum of compound **41**



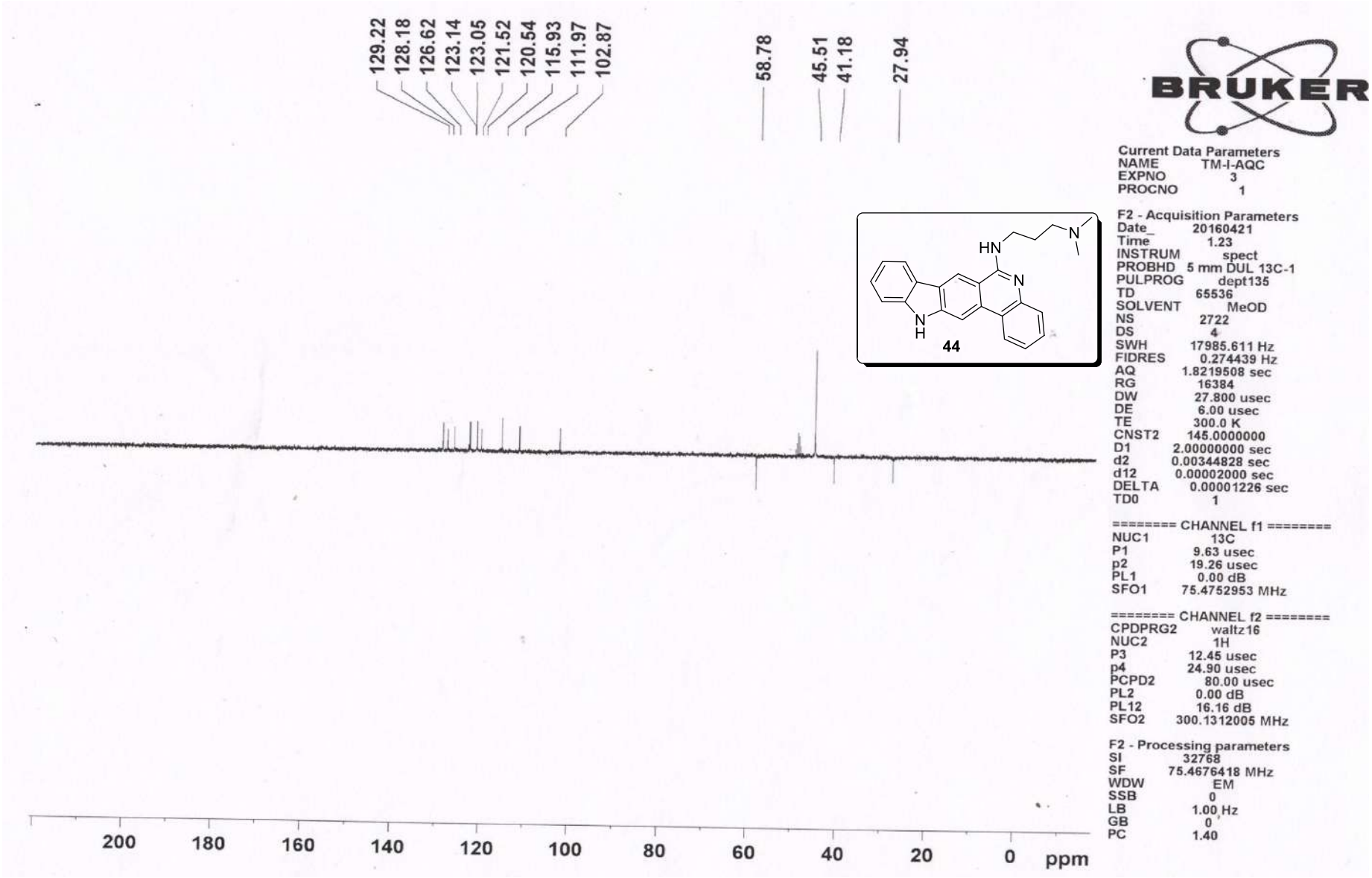
DEPT 135-^{13}C NMR spectrum of compound **41**



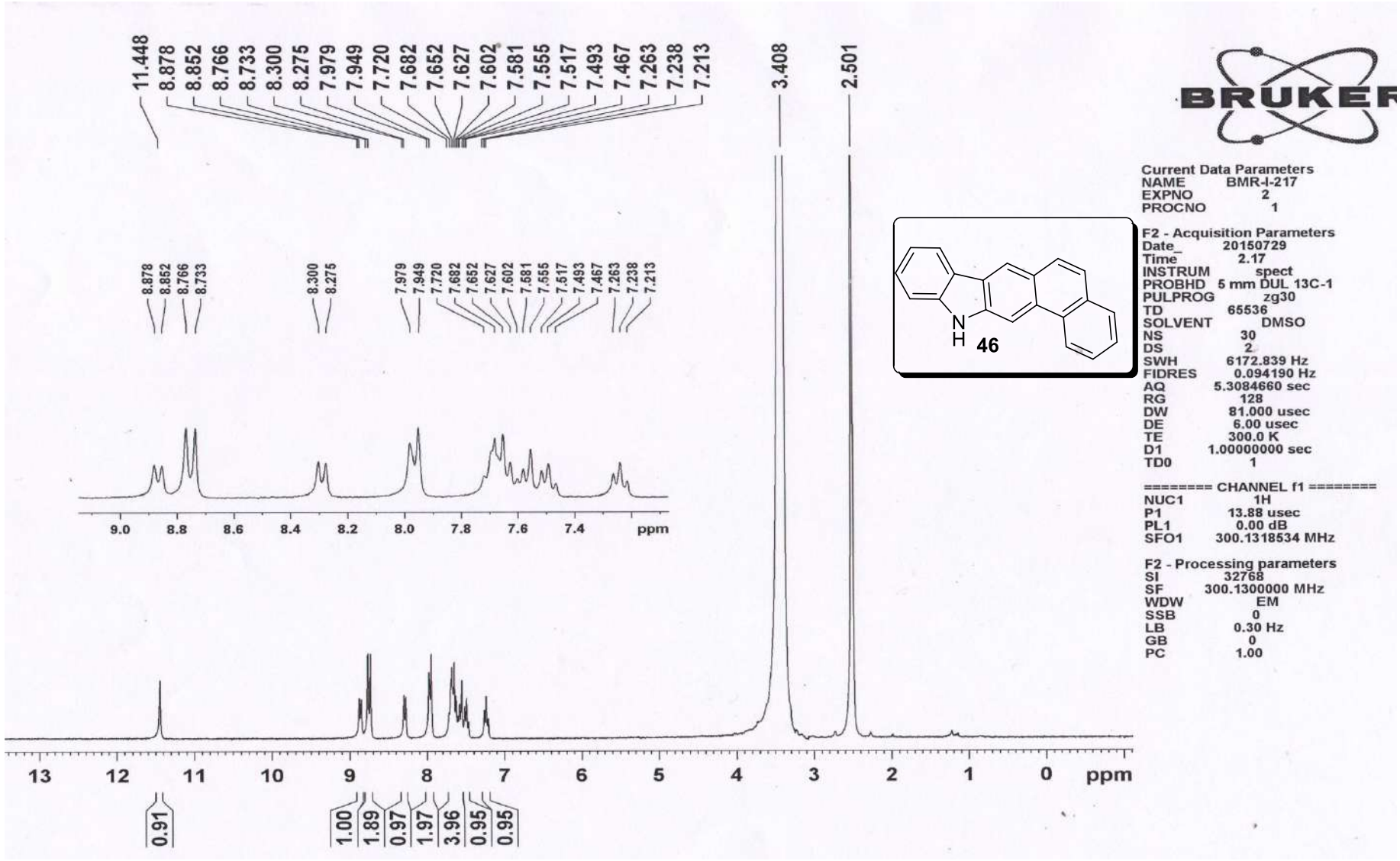
^{1}H-NMR spectrum of compound **44**



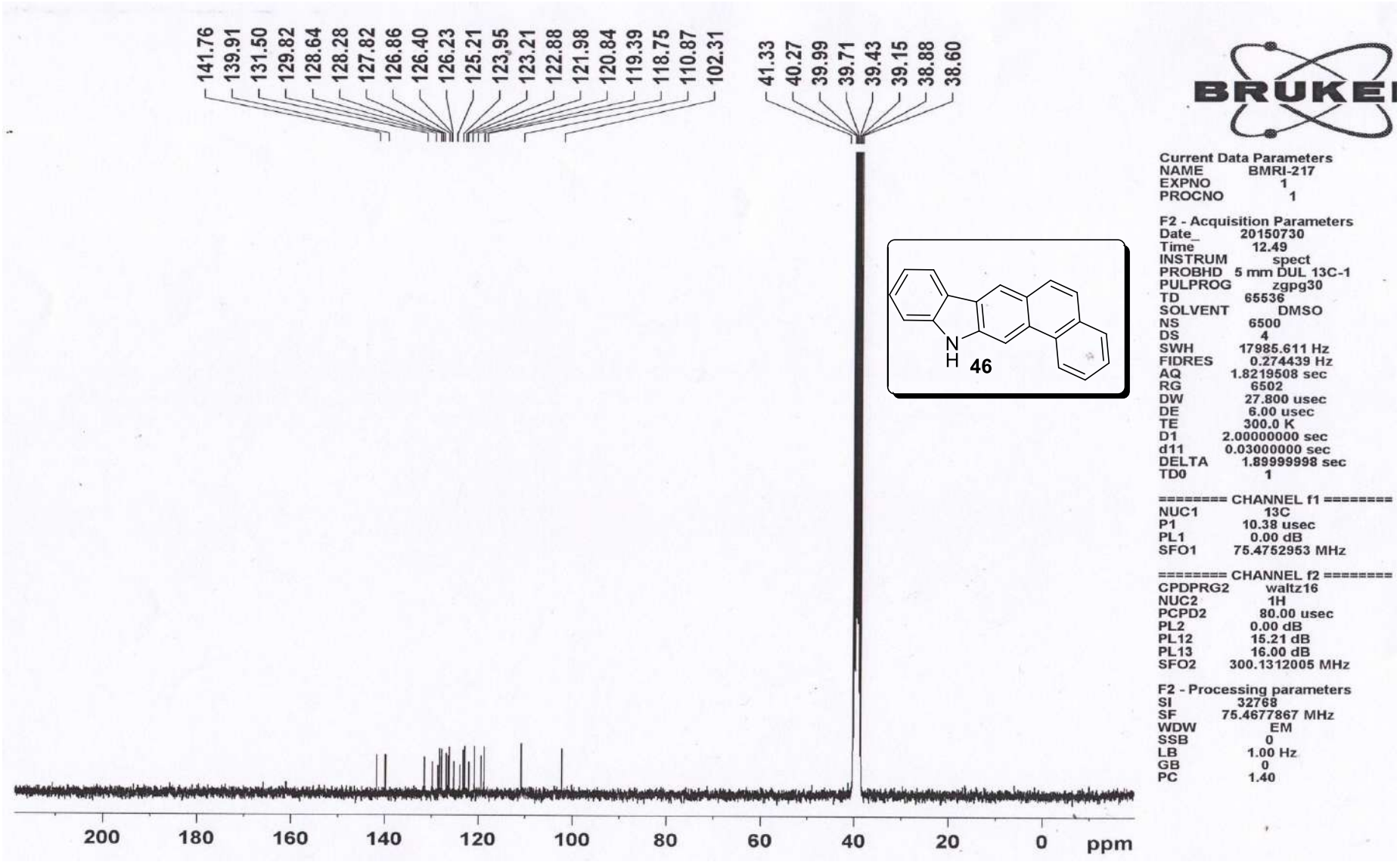
^{13}C-NMR spectrum of compound **44**



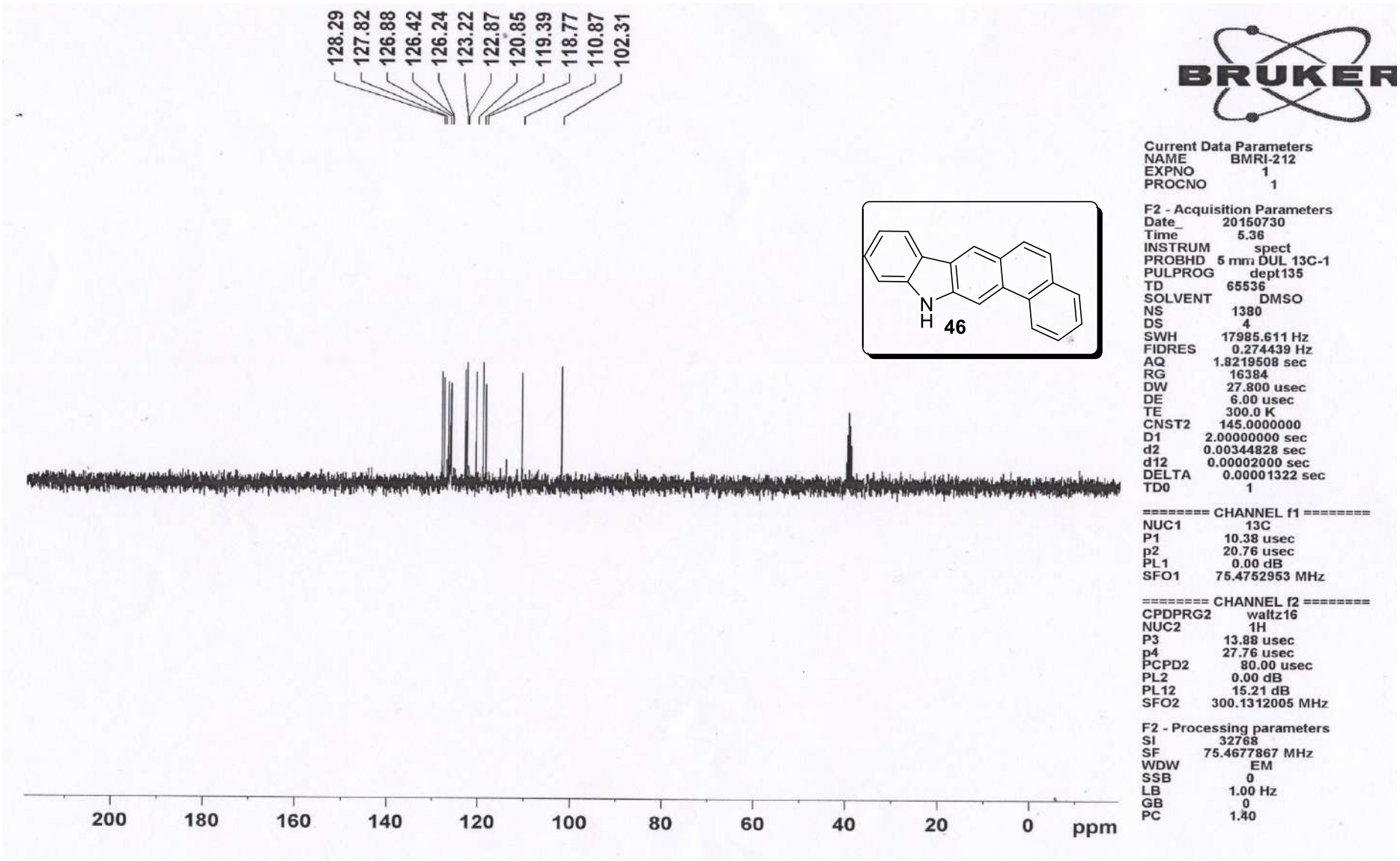
DEPT 135-^{13}C NMR spectrum of compound **44**



^{1}H-NMR spectrum of compound **46**



^{13}C-NMR spectrum of compound **46**



DEPT 135-^{13}C NMR spectrum of compound **46**