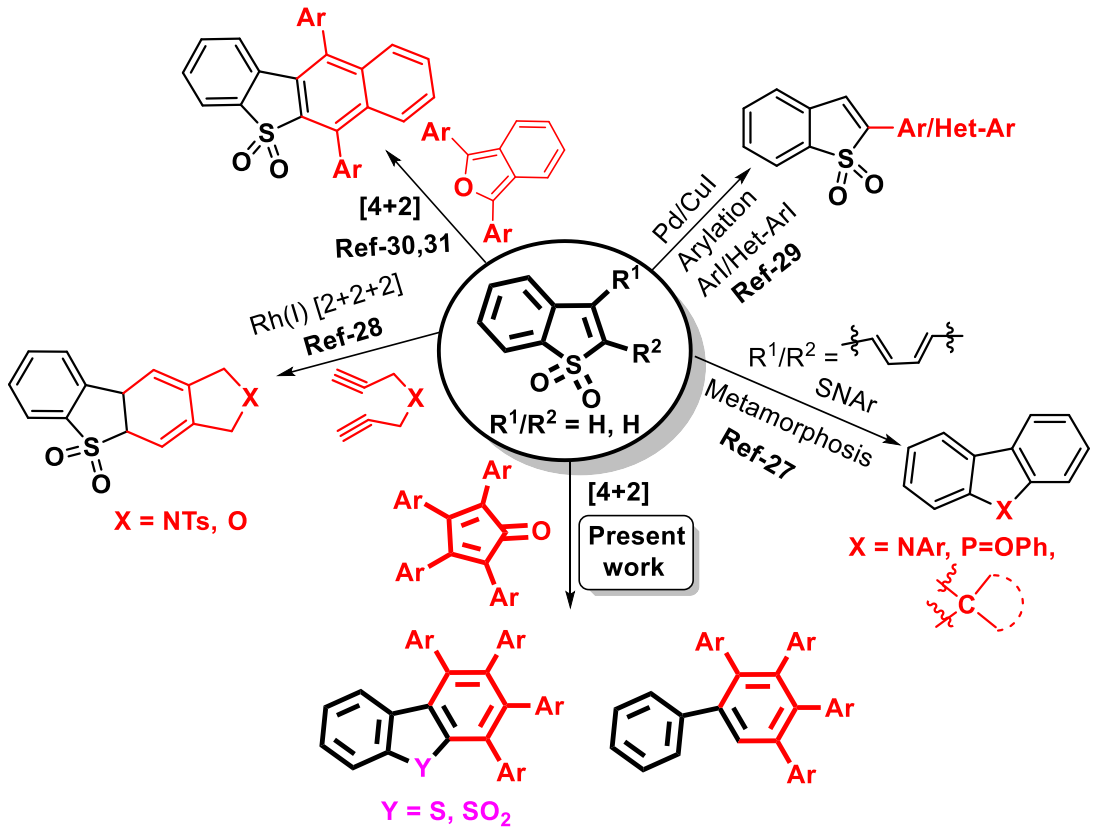
Electronic Supplementary Material (ESI) for Chemical Communications.

Diels-Alder Reaction of Tetraarylcyclopentadienones with Benzo[*b*]thiophene *S,S*-dioxides: An Unprecedented De-Oxygenation Vs Sulfur Dioxide Extrusion

Palani Manikandan,[a] Jayachandran Karunakaran,[a] Elumalai Varathan,[b] Georg Schreckenbach,[b] and Arasambattu K Mohanakrishnan*

Table of contents:



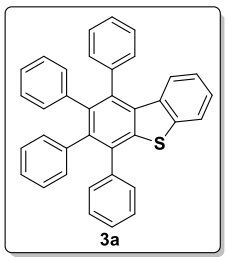
Scheme 1 Synthetic Transformations of Benzothiophene dioxides

2. Experimental Section

General

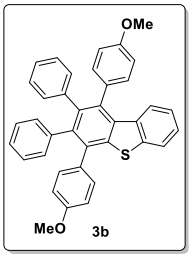
All melting points were uncorrected. Solvents were dried by standard procedures. All the experiments carried out under the nitrogen atmosphere unless otherwise stated. The progression of all the reaction was monitored by TLC using hexanes/ethyl acetate mixture. Column chromatography was carried out on Silica gel (230-400 mesh, Merck) by increasing polarity. ^{1}H, ^{13}C and DEPT 135 spectra were recorded in $CDCl_3$using TMS as an internal standard on Bruker 300 MHz spectrometer at room temperature. Chemical shift values were quoted in parts per million (ppm) and coupling constants were quoted in hertz (Hz). HRMS were recorded on Xevo G2S QTof (ESI) instruments. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrometer. Hitachi F-700 fluorescence spectrophotometer was used for fluorescence spectra measurements. The required cyclopentadienones **1a-i**[1,2] were prepared adopting the established procedure *via* condensation of benzil, 4,4'-dimethoxybenzil and acenaphthoquinone with substituted acetone. The dienophiles, benzo[*b*]thiophene dioxides **2a-e**, **5** and **10** were prepared as per the published procedures.[3]

1,2,3,4-Tetraphenyldibenzo[*b*,*d*]thiophene 3a



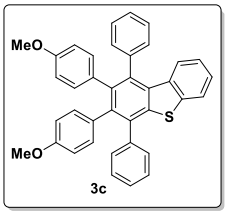
To a solution of cyclopentadienone **1a** (0.23 g, 0.59 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3a** (0.21 g, 71%) as a colorless solid. R_f = 0.30 (eluent: 100% hexane); mp 235-237 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.8 Hz, 1H, ArH), 7.35-7.20 (m, 11H, ArH), 7.02-6.96 (m, 1H, ArH), 6.87-6.81 (m, 10H, ArH), 6.63 (d, *J* = 9.0 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 140.6, 140.2, 140.0, 139.9, 139.8, 139.1, 138.9, 137.4, 136.4, 135.3, 132.5, 131.6, 131.4, 130.4, 130.1, 128.2, 128.0, 127.2, 127.0, 126.7, 126.5, 125.6, 125.4, 125.2, 123.8, 122.3 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.6, 131.4, 130.3, 130.1, 128.2, 128.0, 127.2, 127.0, 126.7, 126.5, 125.9, 125.6, 125.4, 125.2, 123.7, 122.3 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}S$ $[M+H]^+$: 489.1677, Found 489.1678.

1,4-Bis(4-methoxyphenyl)-2,3-diphenyldibenzo[*b*,*d*]thiophene 3b



To a solution of cyclopentadienone **1b** (0.26 g, 0.59 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded pentaarylbenzene **3b** (0.19 g, 69%) as a green solid. R_f = 0.20 (eluent: 10% ethyl acetate in hexane); mp 260-262 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.8 Hz, 1H, ArH), 7.35-7.27 (m, 3H, ArH), 7.17 (d, *J* = 8.4 Hz, 2H, ArH), 7.07 (t, *J* = 7.6 Hz, 1H, ArH), 6.92-6.78 (m, 15H, ArH), 3.84 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.74, 158.66, 141.0, 140.6, 140.1, 139.6, 139.1, 137.0, 136.7, 134.9, 132.9, 132.7, 132.4, 131.61, 131.56, 131.5, 131.4, 131.3, 126.8, 126.6, 125.9, 125.5, 125.31, 125.29, 123.8, 122.3, 113.8, 113.6, 55.2, 55.1 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.6, 131.4, 131.3, 131.2, 126.7, 126.5, 125.5, 125.3, 125.2, 123.7, 122.2, 113.8, 113.5, 55.2, 55.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{28}O_2S$ $[M+H]^+$: 549.1888, Found 549.1887

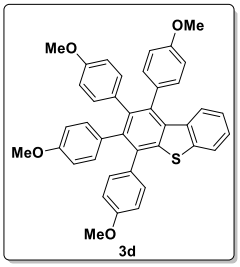
2,3-Bis(4-methoxyphenyl)-1,4-diphenyldibenzo[*b*,*d*]thiophene 3c



To a solution of cyclopentadienone **1c** (0.26 g, 0.58 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3c** (0.21 g, 72%) as a colorless solid. R_f = 0.15 (eluent: 10% ethyl acetate in hexane); mp 260-262 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.8 Hz, 1H, ArH), 7.33-7.20 (m, 11H, ArH), 7.01-6.95 (m, 1H, ArH), 6.78-6.61 (m, 4H, ArH), 6.60 (d, *J* = 9.0 Hz, 1H, ArH), 6.45-6.42 (m, 4H, ArH), 3.61 (s, 6H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.4, 157.2, 140.5, 140.4, 140.3, 138.9, 137.7, 136.4, 135.5, 132.5, 132.4, 130.3, 130.1, 128.2, 128.0, 127.5, 127.1, 126.9, 125.8, 125.1, 123.6, 122.2, 112.4, 112.2, 54.8 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.5, 132.4, 130.3, 130.1, 128.2, 128.0, 127.1,

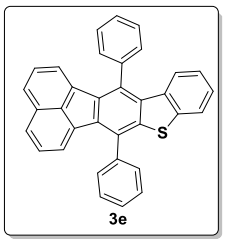
126.9, 125.8, 125.1, 123.6, 122.2, 112.4, 112.2 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{28}O_2S$ $[M+H]^+$: 549.1888, Found 549.1883.

1,2,3,4-Tetrakis(4-methoxyphenyl)dibenzo[*b*,*d*]thiophene 3d



To a solution of cyclopentadienone **1d** (0.28 g, 0.56 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3d** (0.17 g, 64%) as a colorless solid. R_f = 0.28 (eluent: 15% ethyl acetate in hexane); mp 278-280 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H, ArH), 7.21-7.13 (m, 3H, ArH), 7.03 (d, *J* = 8.7 Hz, 2H, ArH), 6.94 (t, *J* = 7.8 Hz, 1H, ArH), 6.77-6.62 (m, 10H, ArH), 6.39-6.35 (m, 3H, ArH), 3.73 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.54 (s, 6H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.6, 158.5, 157.3, 157.1, 140.7, 140.4, 139.4, 139.0, 137.3, 136.6, 135.0, 132.9, 132.73, 132.68, 132.63, 132.60, 132.5, 132.4, 131.3, 131.2, 125.7, 125.2, 123.6, 122.2, 113.8, 113.6, 112.4, 112.2, 55.16 (OCH_3), 55.09 (OCH_3), 54.9 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.5, 132.4, 131.3, 131.2, 125.7, 125.2, 123.6, 122.2, 113.8, 113.6, 112.4, 112.2, 55.2, 55.1, 55.0 ppm; HRMS (ESI): *m/z* Calcd for $C_{40}H_{34}O_4S[M+H]^+$: 609.2100, Found 609.2081.

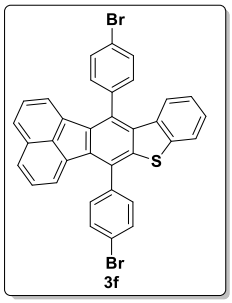
7,13-Diphenylbenzo[*d*]fluorantheno[8,9-*b*]thiophene 3e



To a solution of cyclopentadienone **1g** in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3e** (0.22 g, 67%) as a green solid. R_f = 0.30 (eluent: 5% ethyl acetate in hexane); mp 249-251 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71-7.69 (m, 8H, ArH), 7.66-7.59 (m, 5H, ArH), 7.36-7.28 (m, 2H, ArH), 7.27-7.21 (m, 1H, ArH), 7.08-7.02 (m, 1H, ArH), 6.96-6.87 (m, 2H, ArH), 6.51 (d, *J* = 7.2 Hz, 1H, ArH) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.1, 140.6, 139.5, 138.9, 136.7, 136.6, 135.8,

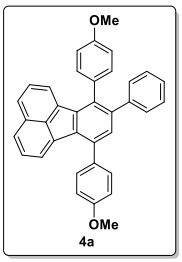
135.8, 135.2, 134.1, 133.9, 132.5, 132.1, 129.9, 129.5, 129.3, 129.2, 128.7, 128.5,127.9, 127.7, 126.6, 126.1, 125.8, 124.9, 124.1, 122.7, 122.6 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 129.9, 129.4, 129.3, 129.2, 128.7, 128.5, 127.9, 127.7, 126.6, 126.1, 125.8, 124.9, 124.1, 122.7, 122.6 ppm; HRMS (ESI): *m/z* Calcd for $C_{34}H_{20}S[M+H]^+$: 461.1364, Found 461.1358.

7,13-Bis(4-bromophenyl)benzo[*d*]fluoranthene[8,9-*b*]thiophene 3f



To a solution of cyclopentadienone **1g** (0.30 g, 0.58 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3f** (0.26 g, 70%) as a green solid. R_f = 0.30 (eluent: 10% ethyl acetate in hexane); mp 285-287 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H, ArH), 7.81 (d, *J* = 8.4 Hz, 2H, ArH), 7.77-7.72 (m, 3H, ArH), 7.63-7.56 (m, 2H, ArH), 7.50 (d, *J* = 8.1 Hz, 2H, ArH), 7.42-7.30 (m, 3H, ArH), 7.16-7.11 (m, 1H, ArH), δ 7.00 (d, *J* = 7.2 Hz, 1H, ArH), 6.92 (d, *J* = 8.1 Hz, 1H, ArH), 6.57 (d, *J* = 7.2 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.0, 140.6, 138.4, 137.7, 136.3, 136.2, 135.8, 135.5, 135.3, 133.9, 133.3, 132.9, 132.8, 132.4, 131.2, 131.1, 131.0, 130.0, 128.0, 127.8, 126.9, 126.4, 126.0, 124.7, 124.3, 123.1, 122.7 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.3, 132.8, 131.1, 127.9, 127.8, 126.9, 126.5, 126.1, 124.6, 124.3, 122.8, 122.7 ppm; HRMS (ESI):*m/z* Calcd for $C_{34}H_{18}Br_2S[M+H]^+$: 618.9554, Found 618.9572.

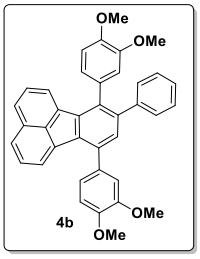
7,10-Bis(4-methoxyphenyl)-8-phenylfluoranthene 4a



The fluoranthene **4a** (0.24 g, 77%) was prepared according to the general procedure using cyclopentadienone **1g** (0.25 g, 0.60 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) as a green solid. R_f = 0.20 (eluent: 10% ethyl acetate in hexane); mp 223-226 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.66-7.59 (m, 1H, ArH), 7.53 (d, *J* = 8.7 Hz, 2H, ArH), 7.42 (d,*J* =

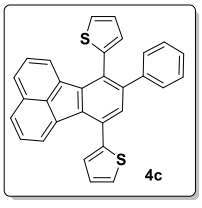
8.4 Hz, 2H, ArH), 7.30-7.20 (m, 5H, ArH), 7.04-6.89 (m, 3H, ArH), 6.53 (d, *J* = 7.2 Hz, 1H, ArH), 3.94 (s,3H, OCH_3), 3.89 (s, 3H, OCH_3) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.8, 159.7, 141.6, 140.6, 136.84, 136.76, 136.2, 136.0, 135.4, 133.9, 133.8, 132.9, 131.8, 131.7, 131.1, 130.5, 130.3, 127.9, 127.7, 126.5, 126.0, 125.7, 124.9, 124.0, 122.70, 122.67, 122.5, 115.3,114.8, 55.5 (OCH_3), 55.4 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.5, 130.3, 127.9, 127.7, 126.5, 126.0, 125.7, 124.9, 124.0, 122.70, 122.67, 122.5, 115.3, 114.8, 55.5, 55.4 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{26}O_2$ $[M+H]^+$: 491.2011, Found 491.2026.

7,10-Bis(3,4-dimethoxyphenyl)-8-phenylfluoranthene 4b



The fluoranthene **4b** (0.26 g, 76 %) was prepared according to the general procedure using cyclopentadienone **1h** (0.30 g, 0.60 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) as a green solid. R_f = 0.30 (eluent: 15% ethyl acetate in hexane); mp 178-200 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.8 Hz, 1H, ArH), 7.80 (d, *J* = 7.5Hz, 2H, ArH), 7.64 (d, *J* = 7.5 Hz, 1H, ArH), 7.56-7.47 (m, 4H, ArH), 7.45-7.37 (m, 5H, ArH), 7.31 (s, 1H, ArH), 7.25-7.22 (m, 2H, ArH), 7.10-7.07 (m, 2H, ArH), 4.06 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.9, 149.7, 149.5, 148.3, 139.8, 137.8, 136.2, 136.0, 135.7, 134.5, 133.5, 133.1, 131.0, 130.2, 129.9, 128.4, 127.9, 127.7, 127.65, 127.60, 124.1, 123.9, 122.8, 121.4, 119.7, 115.6, 112.9, 112.0, 103.2, 56.4 (OCH_3), 56.3 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.8, 130.0, 129.8, 128.2, 127.7, 127.5, 127.5, 127.4, 123.9, 123.8, 121.3, 119.6, 115.4, 112.7, 111.8, 102.9, 56.2, 56.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{30}O_4$ $[M+H]^+$: 551.2222, Found 551.2236.

2,2'-(8-Phenylfluorathene-7,10-diyl)dithiophene 4c

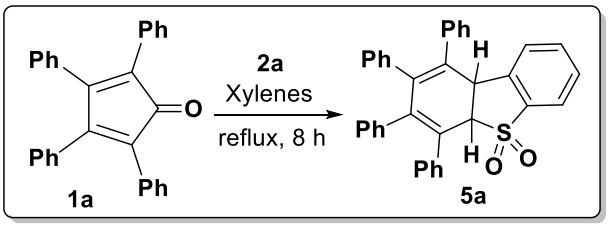


The fluoranthene **4c** (0.21 g, 67%) was prepared according to the general procedure using cyclopentadienone **1i** (0.22 g, 0.60 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) as a green solid. R_f = 0.25 (eluent: 15% ethyl acetate in hexane); mp 243-245 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.73-7.69 (m, 2H, ArH), 7.47-7.42 (m, 2H, ArH), 7.39-7.37 (m, 1H,

ArH), 7.35-7.31 (m, 4H, ArH), 7.28-7.25 (m, 2H, ArH), 7.18-7.16 (m, 4H, ArH), 7.05-7.02 (m, 2H, ArH), 6.79 (d, *J* = 7.2 Hz, 1H, ArH) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.23, 141.25, 140.5, 140.2, 139.6, 136.9, 135.9, 135.4, 133.0, 131.9, 129.7, 129.1, 128.2, 127.8, 127.6, 127.3, 127.12, 127.08, 127.05, 126.9, 126.8, 126.4, 125.9, 123.5, 123.1 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.9, 128.5, 127.2, 126.8, 126.60, 126.58, 126.3, 126.1, 126.1, 126.0, 125.9, 125.8, 125.4, 124.9, 122.5, 122.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{30}H_{18}S_2$ $[M+H]^+$: 443.0928, Found 443.0928.

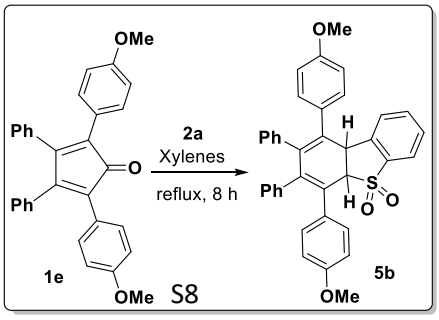
Control Experiments:

1,2,3,4-Tetraphenyl-4a,9b-dihydrodibenzo[*b*,*d*]thiophene *S*,*S*-dioxide 5a



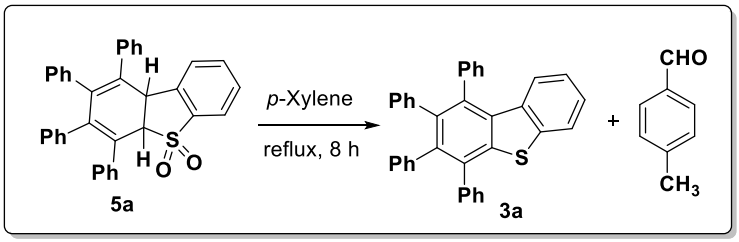
To a stirred solution of cyclopentadienone **1a** (0.23 g, 0.59 mmol) in dry xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and then the reaction mixture was refluxed for 8 h. The subsequent removal of solvent followed by column chromatographic purification on silica gel gave dihydrodibenzothiophene *S*,*S*-dioxide **5a** (0.24 g, 75%) as a colorless solid. R_f = 0.20 (eluent: 10 % ethyl acetate in hexane); mp 165-167 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$):*δ* 7.82 (d, *J* = 7.5 Hz, 1H, ArH), 7.40 (d, *J* = 7.5 Hz, 2H, ArH), 7.32 (t, *J* = 7.8 Hz, 1H, ArH), 7.18-7.08 (m, 4H, ArH), 6.97-6.96 (m, 3H, ArH), 6.90-6.86 (m, 5H, ArH), 6.73-6.61 (m, 8H, ArH), 5.01 (d, *J* = 8.7 Hz, 1H, CH), 4.67 (d, *J* = 8.7 Hz, 1H, CH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): *δ* 143.4, 140.1, 139.2, 139.0, 138.7, 138.5, 138.1, 132.9, 132.0, 131.0, 130.5, 129.8, 129.6, 129.3, 128.4, 128.0, 127.6, 127.1, 126.9, 126.7, 126.5, 126.2, 125.6, 125.3, 121.5, 121.5, 69.2, 45.0 ppm; DEPT 135-NMR (75 MHz, $CDCl_3$): *δ* 132.0, 131.0, 130.4, 129.8, 129.5, 129.2, 128.4, 127.9, 127.5, 127.1, 126.8, 126.7, 126.5, 126.2, 125.5, 121.4, 69.1, 44.9 ppm; HRMS (ESI): *m/z* calcd for $C_{36}H_{26}O_2S$ [M+H]+: 523.1732, Found: 523.1726

1,4-Bis(4-methoxyphenyl)-2,3-diphenyl-4a,9b-dihydrodibenzo[*b*,*d*]thiophene *S*,*S*-dioxide 5b

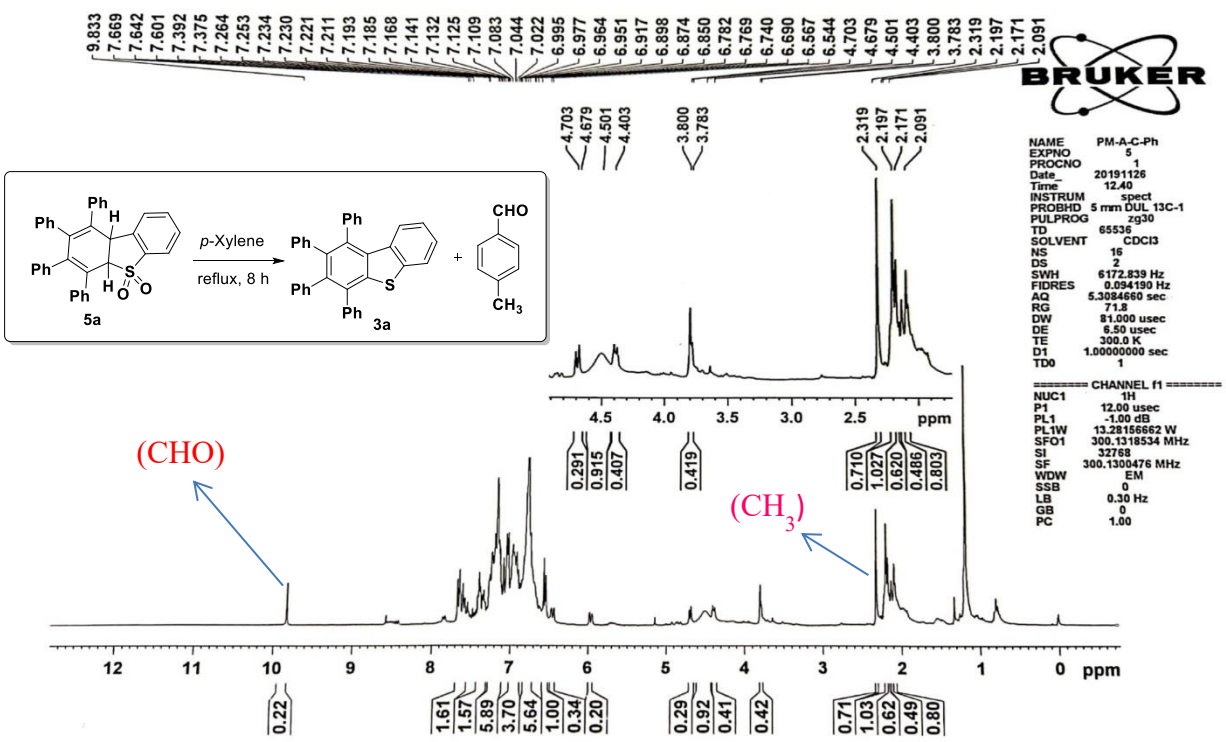


To a stirred solution of cyclopentadienone **1b** (0.26 g, 0.58 mmol) in dry xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and then the reaction mixture was refluxed for 8 h. The subsequent removal of solvent followed by column chromatographic purification on silica gel gave dihydrodibenzothiophene *S*,*S*-dioxide **5b** (0.21 g, 69 %)as a colorless solid. R_f = 0.20 (eluent: 10 % ethyl acetate in hexane); mp 146-148 ^oC; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.5 Hz, 1H, ArH), 7.30 (m, 3H, ArH), 7.33 (t, *J* = 7.8 Hz, 1H, ArH), 6.91-6.86 (m, 5H, ArH), 6.74-6.65 (m, 8H, ArH), 6.57 (d, *J* = 8.7 Hz, 2H, CH), 6.50 (d, *J* = 9.0 Hz, 2H, CH),4.97 (d, *J* = 8.7 Hz, 1H, CH), 4.66 (d, *J* = 8.7 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.4, 158.2, 142.7, 139.6, 139.1, 138.8, 138.6, 138.5, 132.4, 132.2, 132.0, 131.3, 131.14, 131.06, 130.5, 130.4, 129.7, 128.3, 127.2, 126.7, 126.1, 125.4, 124.6, 121.4, 113.5, 113.2, 69.4, 55.10 (OCH_3), 55.05 (OCH_3), 45.0 ppm; DEPT 135-NMR (75 MHz, $CDCl_3$): δ 132.0, 131.1, 131.0, 130.4, 130.3, 129.7, 128.3, 127.1, 126.6, 126.0, 125.3, 121.4, 113.4, 113.1, 69.3, 55.10, 55.05, 44.9 ppm; HRMS (ESI): *m/z* calcd for $C_{38}H_{30}O_4S$ [M+H]+: 583.1865, Found: 583.1861.

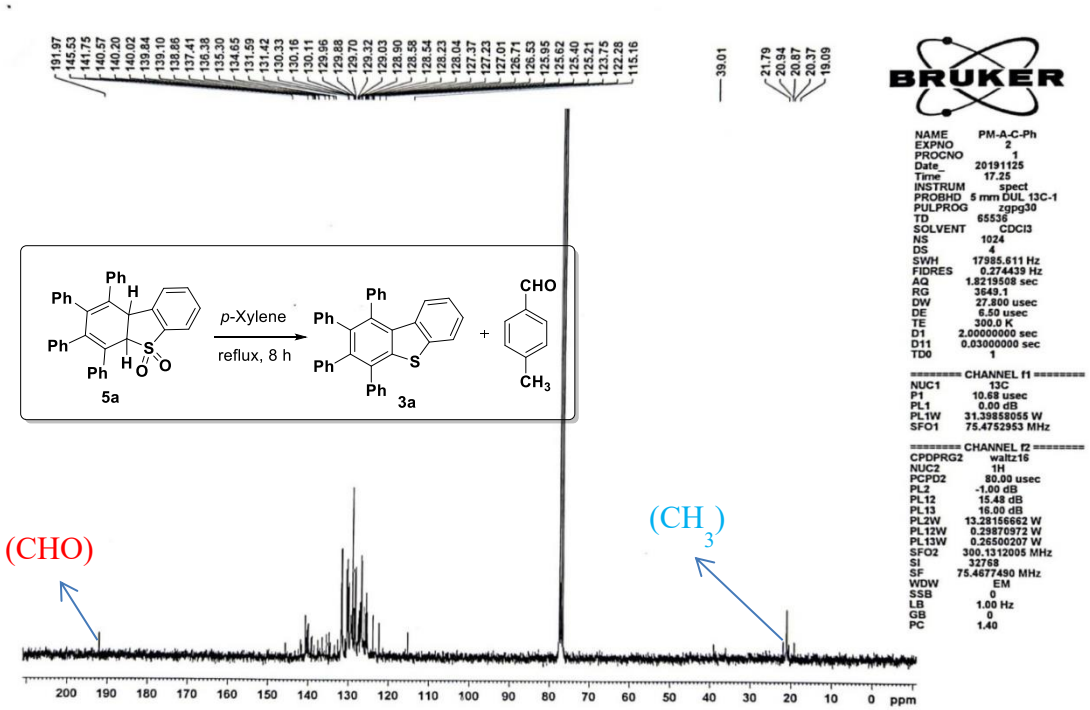
Thermolysis of dihydrodibenzothiophene 5a in *p*-xylene



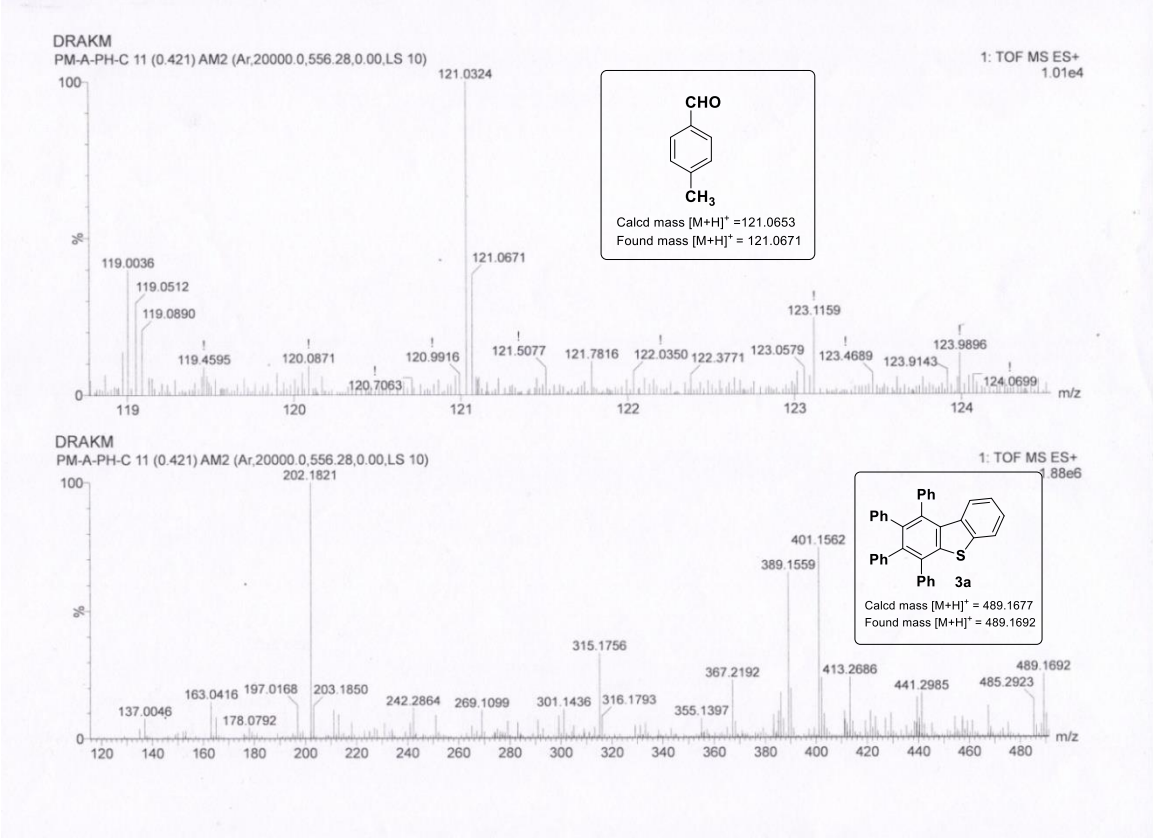
A solution of dihydrodibenzothiophene **5a** (0.1 g, 0.19 mmol) in *p*-xylene (10 mL) was refluxed for 8 h. The subsequent removal of solvent gave crude product. The crude product was analyzed by ^{1}H, ^{13}C NMR and mass spectra.



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

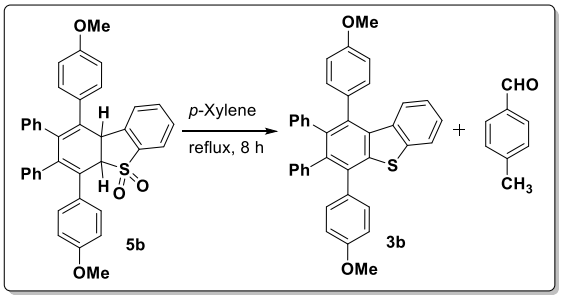


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

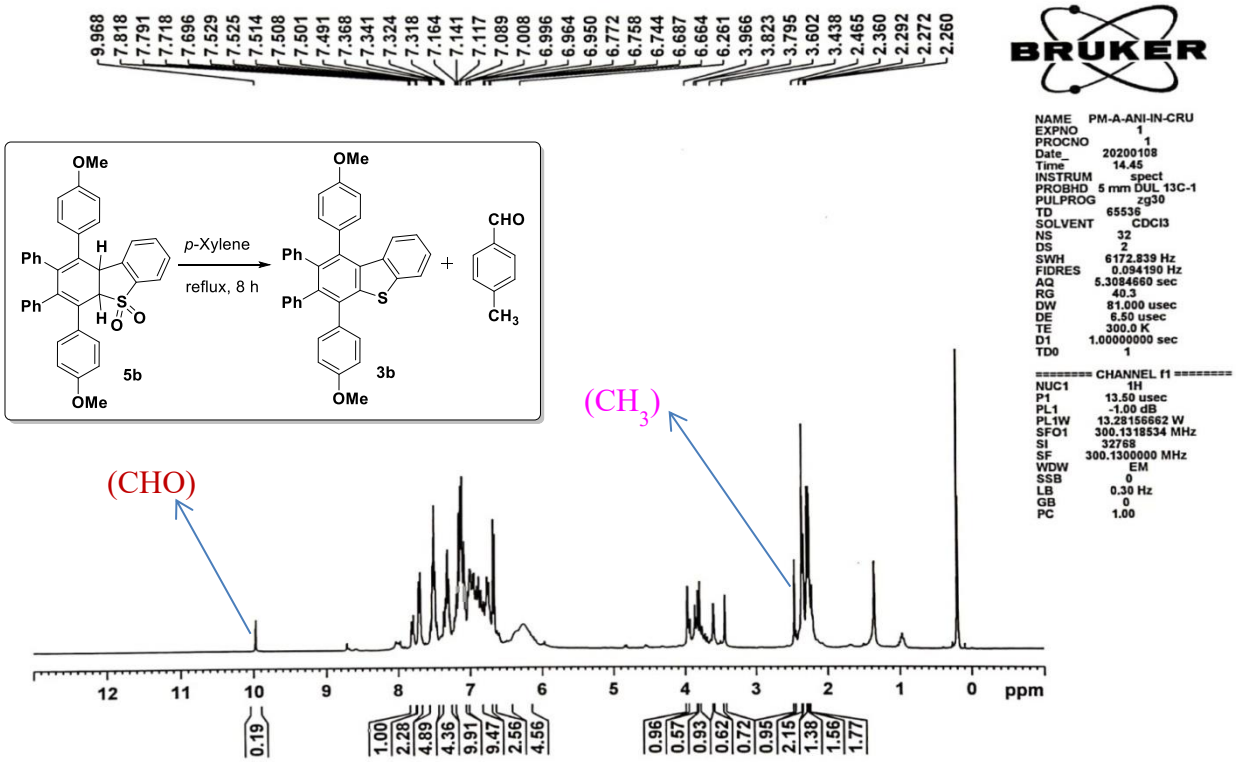


HRMS spectrum of crude product

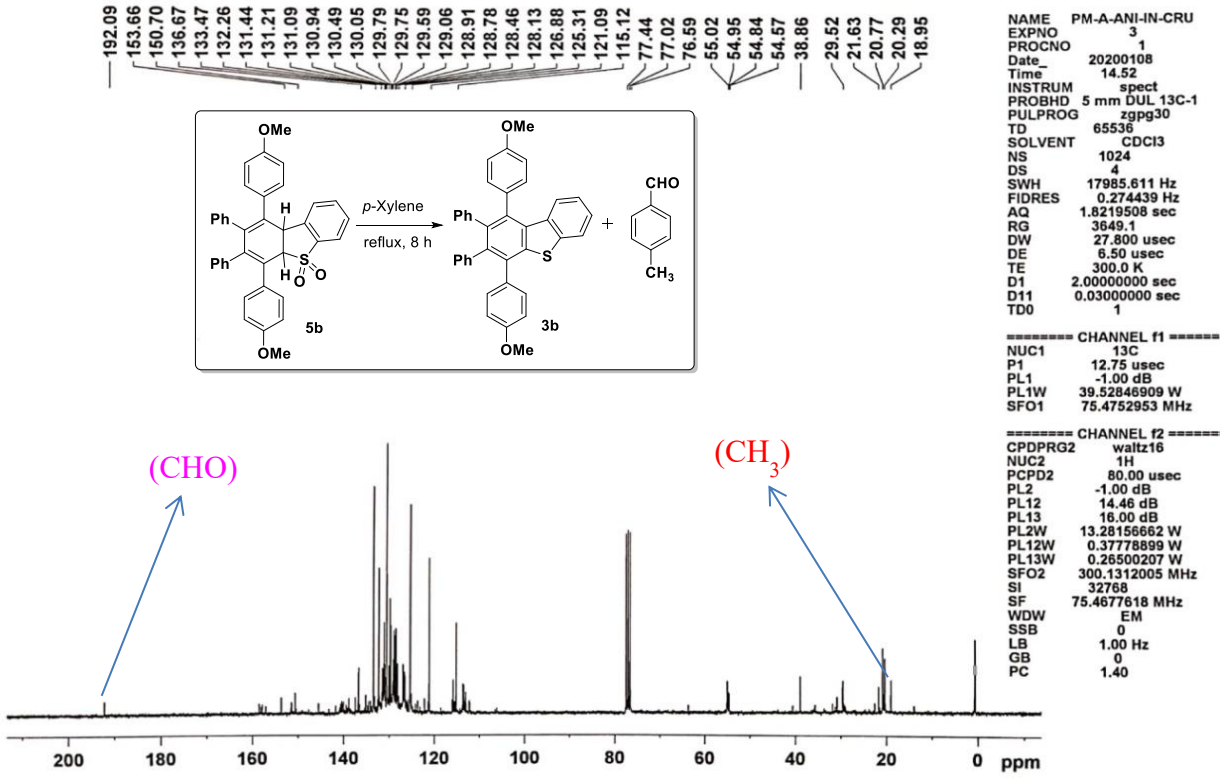
Thermolysis of dihydrodibenzothiophene 5b in *p*-xylene



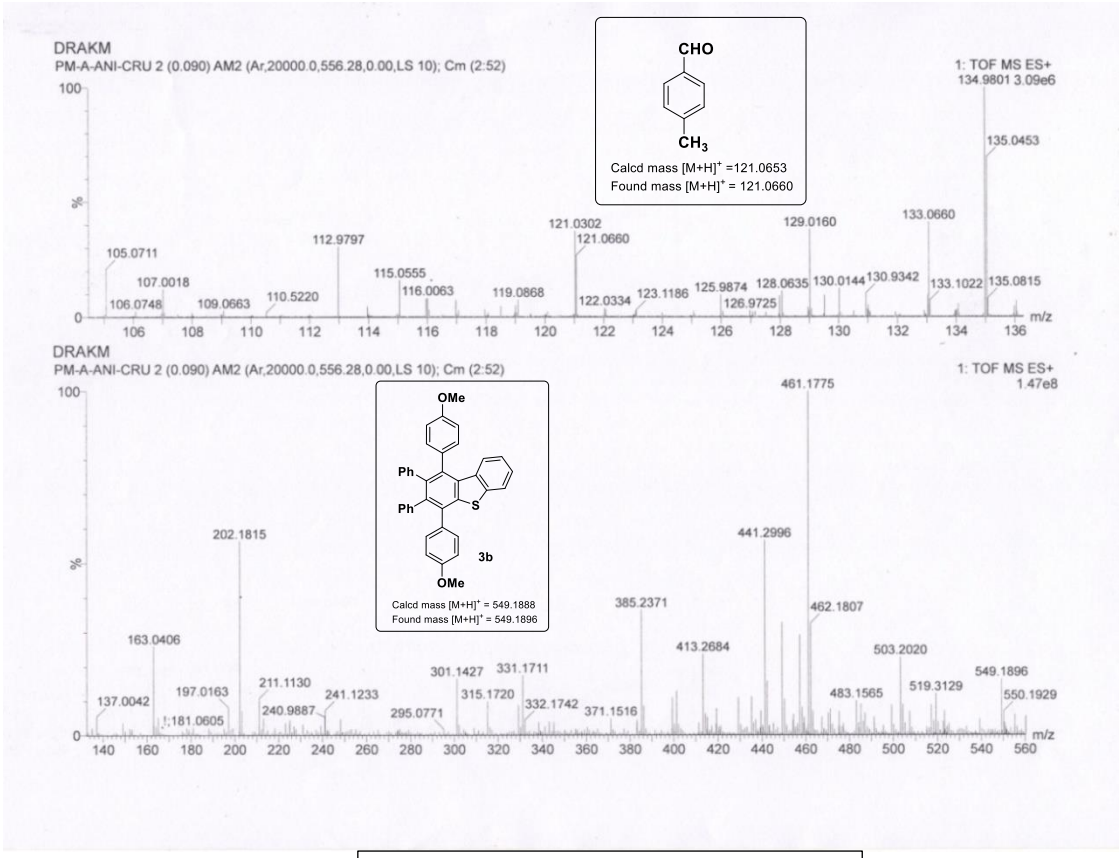
A solution of dihydrodibenzothiophene **5b** (0.1 g, 0.17 mmol) in *p*-xylene (10 mL) was refluxed for 8 h. The subsequent removal of solvent gave crude product. Then, the crude product was analyzed by ^{1}H, ^{13}C NMR and mass spectra.



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

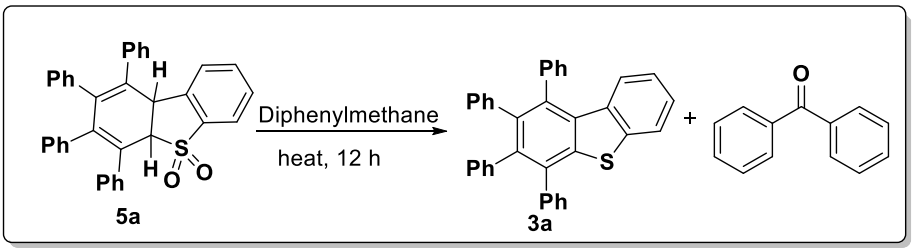


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

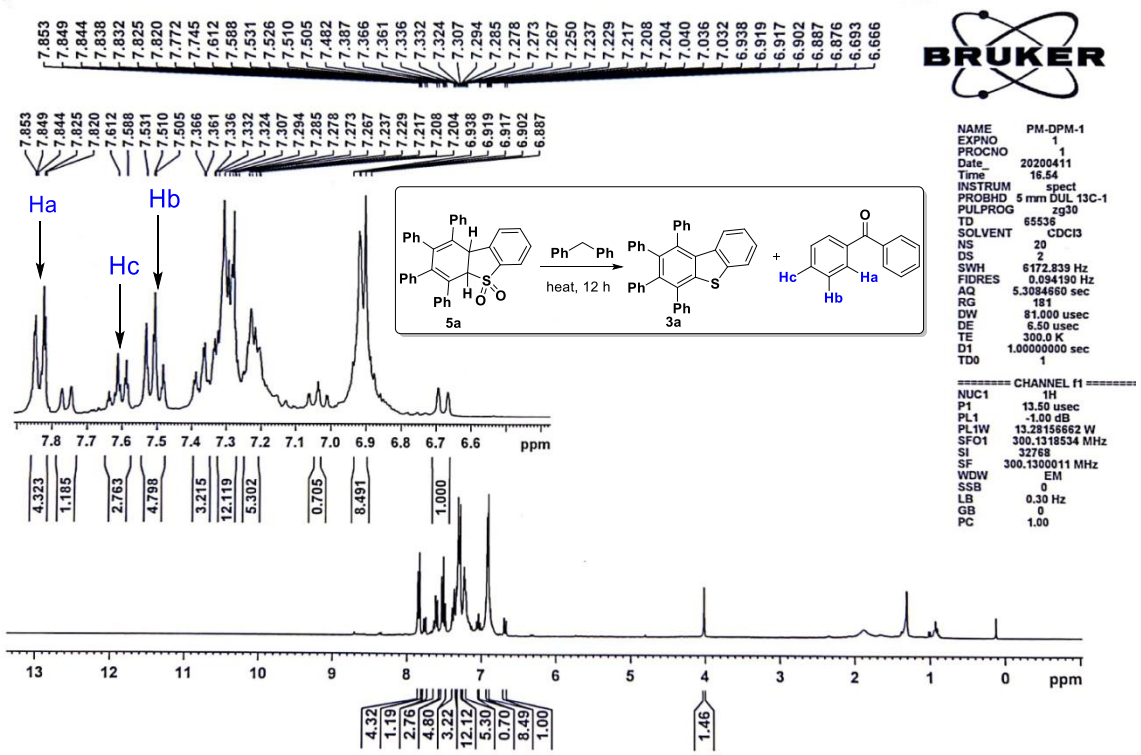


Mass spectrum of crude product

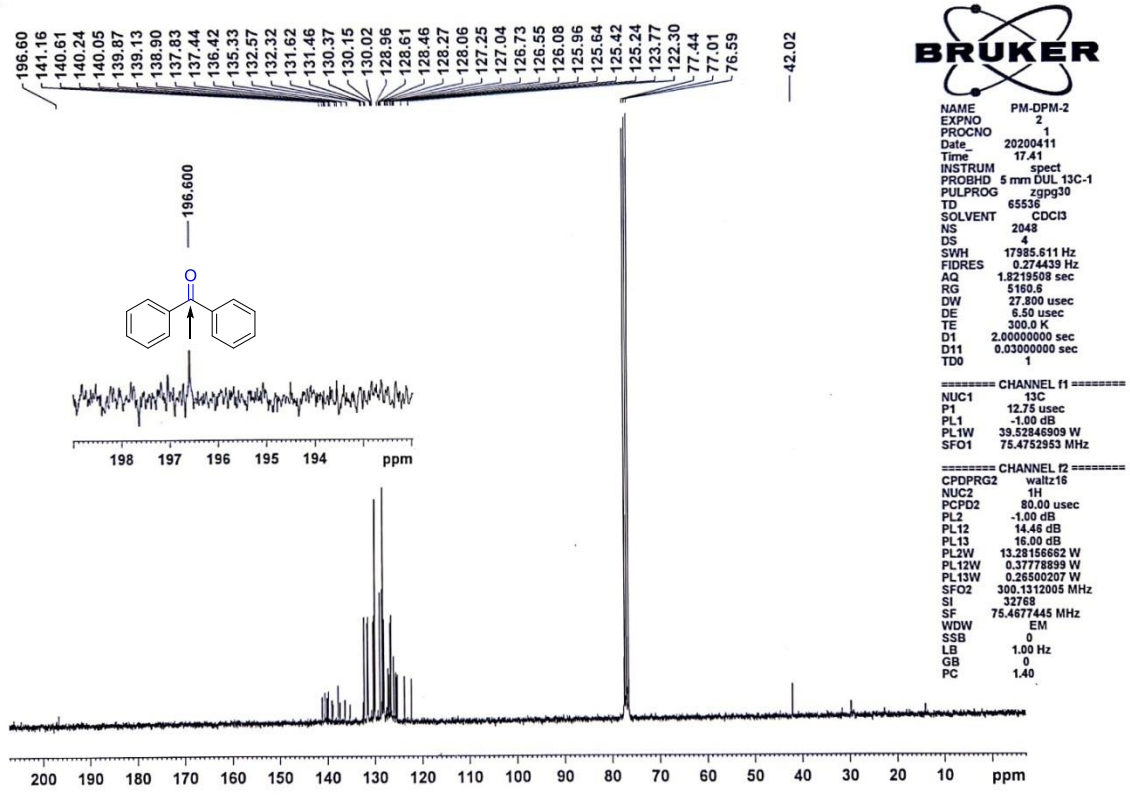
Thermolysis of dihydrodibenzothiophene 5a in the presence of diphenylmethane



A stirred suspension of dihydrodibenzothiophene **5a** (0.1 g, 0.19 mmol) in diphenylmethane (2 mL) was heated at 130 ^{o}C for 12 h. The subsequent removal of unreacted diphenylmethane followed column chromatography (silica gel; EA/hexane, 9:1) gave a mixture dibenzothiophene and benzophenone as a colorless solid. The product mixture was analyzed by ^{1}H and ^{13}C NMR.

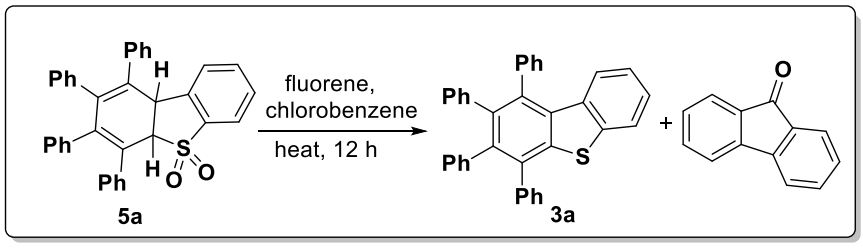


^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

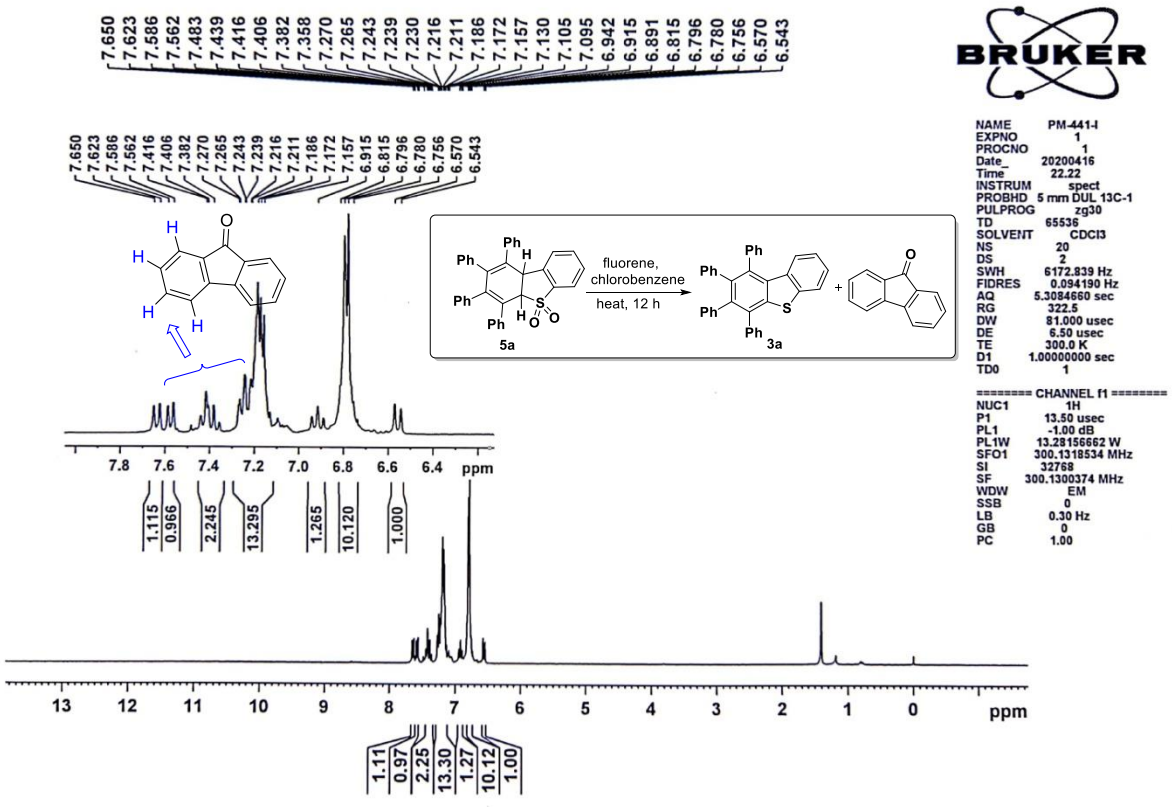


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

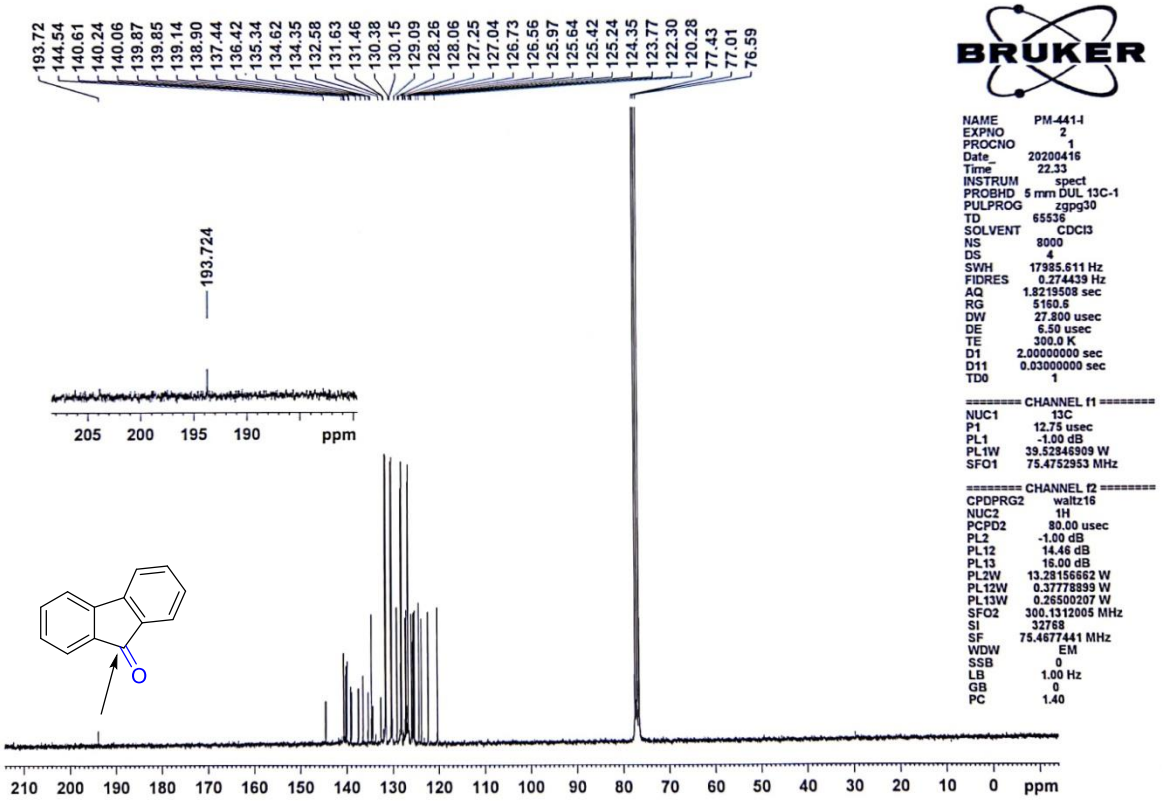
Thermolysis of dihydrodibenzothiophene 5a in the presence of fluorene



A stirred solution of dihydrodibenzothiophene **5a** (0.1 g, 0.19 mmol) and fluorene (0.1 g, 0.23 mmol) in chlorobenzene (2 mL) was refluxed for 12 h. The subsequent removal of solvent followed by column chromatography (silica gel; EA/hexane, 9:1) gave a mixture of dibenzothiophene and fluorenone as a colorless solid. The product was analyzed by ^{1}H and ^{13}C NMR.

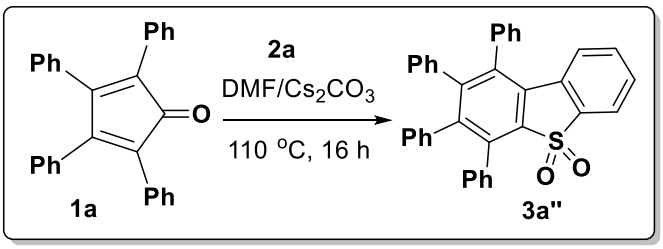


^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product



^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

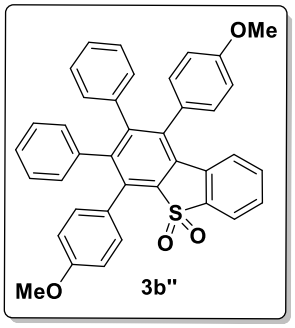
1,2,3,4-Tetraphenyldibenzo[*b*,*d*]thiophene *S*,*S*-dioxide 3a"



To a stirred solution of cyclopentadienone **1a** (0.23 g, 0.59 mmol), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) in DMF (15 mL), Cs_2CO_3 (0.39 g, 1.19 mmol) was added. It was then heated at 110 °C for ~16 h. After completion of reaction (monitored by TLC), it was poured into crushed ice (10 g) and stirred for 10 min. The reaction mixture was then extracted with ethyl acetate (2 x 15 mL) and dried (Na_2SO_4). Subsequent removal of solvent followed by chromatographic purification on silica gel gave tetraphenyldibenzothiophene *S*,*S*-dioxide **3a"**(0.20 g, 66%) as a colorless solid. R_f = 0.35 (eluent: 5% ethyl acetate in hexane); mp >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.5 Hz, 1H, ArH), 7.36-7.31 (m, 3H, ArH), 7.28-

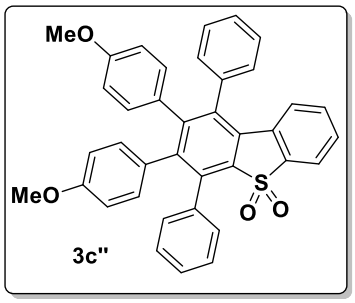
7.21 (m, 7H, ArH), 7.18-7.12 (m, 3H, ArH), 6.87-6.85 (m, 6H, ArH), 6.81-6.77 (m, 3H, ArH) 6.29-6.26 (m, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.6, 144.2, 139.2, 138.6, 138.4,138.4,138.1, 137.8, 135.9, 134.3, 133.0, 131.4, 130.93, 130.88, 130.6, 129.9, 129.5, 128.8, 128.7, 127.9, 127.8, 127.3, 126.94, 126.88, 126.23, 126.17, 125.2, 121.7 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.9, 130.9, 130.8, 130.5, 129.9, 128.6, 127.9, 127.7, 127.2, 126.9, 126.8, 126.2, 126.1, 125.1, 121.6 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}O_2S$ $[M+H]^+$: 521.1575, Found 521.1582.

1,4-Bis(4-methoxyphenyl)-2,3-diphenyldibenzo[*b,d*]thiophene *S,S*-dioxide 3b''



To a stirred solution of cyclopentadienone **1b** (0.25 g, 0.60 mmol), benzo[*b*]thiophene *S,S*-dioxide **2a** (0.10 g, 0.60 mmol) in DMF (15 mL), Cs_2CO_3 (0.39 g, 1.19 mmol) was added. It was then heated at 110 °C for ~16 h. After completion of reaction (monitored by TLC), it was poured into crushed ice (10 g) and stirred for 10 min. The reaction mixture was then extracted with ethyl acetate (2 x 15 mL) and dried (Na_2SO_4). Removal of solvent followed by chromatographic purification on silica gel gave dibenzothiophene *S,S*-dioxide **3b''** (0.23 g, 65%) as a colorless solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp 232-235 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.5 Hz, 1H, ArH), 7.32-7.24 (m, 1H, ArH), 7.20-7.18 (m, 3H, ArH), 7.14-7.05 (m, 1H, ArH), 6.97 (d, *J* = 8.4 Hz, 2H, ArH), 6.81-6.77 (m, 5H, ArH), 6.75 (s, 1H, ArH), 6.72-6.67 (m, 7H, ArH), 6.31 (d, *J* = 8.1 Hz, 1H, ArH), 3.71 (s, 3H, OCH_3), 3.3.67 (s, 3H, OCH_3) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.23, 159.21, 148.0, 144.5, 139.2, 138.6, 138.3, 138.1, 137.7, 136.1, 133.0, 132.1, 131.6, 131.0, 130.9, 130.6, 130.5, 129.4, 129.1, 127.0, 126.9, 126.6, 126.12, 126.07, 125.2, 121.6, 114.2, 112.9, 55.2 (OCH_3), 55.0 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.0, 132.0, 130.9, 130.9, 130.5, 129.3, 126.9, 126.8, 126.12, 126.07, 125.1, 121.5, 114.1, 112.9, 55.2, 55.0 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{28}O_4S$ $[M+H]^+$: 581.1787, Found 581.1779.

2,3-Bis(4-methoxyphenyl)-1,4-diphenyldibenzo[*b,d*]thiophene *S,S*-dioxide 3c''



To a stirred solution of cyclopentadienone **1c** (0.25 g, 0.60 mmol), benzo[*b*]thiophene *S,S*-dioxide **2a** (0.10 g, 0.60 mmol) in DMF (15 mL), Cs_2CO_3(0.39 g, 1.19 mmol) was added. It was then heated at 110 ˚C for ~16 h. After completion of reaction (monitored by TLC), it was poured into crushed ice (10 g) and stirred for 10 min. The reaction mixture was then extracted with ethyl acetate (2 x 15 mL) and dried (Na_2SO_4). Subsequent removal of solvent followed by chromatographic purification on silica gel gave dibenzothiophene *S,S*-dioxide **3c''** (0.20 g, 71%) as a colorless solid. R_f = 0.30 (eluent: 10% ethyl acetate in hexane); mp 258-260 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 1H, ArH), 7.25-7.23 (m, 2H, ArH), 7.21-7.19 (m, 4H, ArH), 7.18-7.15 (m, 3H, ArH), 7.09-7.06 (m, 3H, ArH), 6.63-6.58 (m, 4H, ArH), 6.37-6.34 (m, 4H, ArH), 6.16 (d, *J* = 8.1 Hz, 1H, ArH),3.51 (s, 6H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.84, 157.78, 147.6, 144.3, 139.2, 138.8, 138.7, 138.5, 135.8, 134.6, 133.0, 132.1, 131.8, 131.6, 130.9, 130.5, 129.9, 129.4, 128.7, 128.6, 127.9, 127.8, 127.4, 125.2, 121.6, 112.7, 112.6, 55.0 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.9, 132.0, 131.6, 130.8, 129.9, 129.3, 128.6, 127.8, 127.6, 127.3, 125.1, 121.5, 112.6, 112.5, 55.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{28}O_4S$ $[M+H]^+$: 581.1787, Found 581.1788.

3-Bromobenzothiophene

To a solution of benzothiophene (1 g, 7.46 mmol) in 1:2 AcOH/$CHCl_3$ (10:20 mL), NBS (1.59 g, 8.96 mmol) was added and stirred for 24 h at rt. The reaction mixture was then poured into cold water (100 mL), and then extracted using DCM (2 x 20 mL). The combined organic layer was washed with brine (30 mL) and dried (Na_2SO_4). Removal of solvent in *vacuo* followed by column chromatographic purification using hexane as the eluent gave 3-bromobenzothiophene (1.28 g, 81%) as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.1 Hz, 2H, ArH), 7.73-7.62 (m, 3H, ArH) ppm.

3-Bromobenzothiophene *S, S*-dioxide 2a′[5]

To a solution of 3-bromobenzothiophene (1 g, 4.69 mmol) in acetic acid (15 mL) was added 30% aqueous hydrogen peroxide (5 mL) and the mixture was heated for 1 h at 100 °C. The reaction

mixture was then poured into ice cold water and let stand overnight. The resulting solid was filtered and dried to afford 3-bromobenzothiophene S, S-dioxide (0.98 g, 85%) as a colorless solid; mp 181-182 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.8 Hz, 1H, ArH), 7.66-7.60 (m, 2H, ArH), 7.55 (d, *J* = 7.8 Hz, 1H, ArH), 6.95 (s, 1H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.4, 133.7, 131.6, 131.3, 129.9, 129.6, 124.7, 120.8 ppm.

Diels-Alder reaction of cyclopentadienone 1a with 3-bromobenzothiophene *S, S*-dioxide 2a′

To a solution of cyclopentadienone **1a** (0.23 g, 0.61 mmol) in xylenes (15 mL), 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide **2a′** (0.15 g, 0.61 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded tetraphenyldibenzothiophene *S*,*S*-dioxide **3a"**(0.16 g, 53%) as a colorless solid.

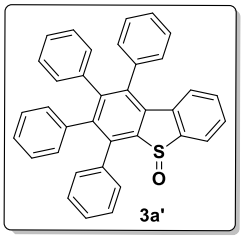
Diels-Alder reaction of cyclopentadienone 1b with 3-bromobenzothiophene *S, S*-dioxide 2a′

To a solution of cyclopentadienone **1b** (0.27 g, 0.61 mmol) in xylenes (15 mL), 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide **2a′** (0.15 g, 0.61 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded tetraphenyldibenzothiophene *S*,*S*-dioxide **3b"** (0.19 g, 55%) as a colorless solid.

Diels-Alder reaction of cyclopentadienone 1c with 3-bromobenzothiophene *S, S*-dioxide 2a′

To a solution of cyclopentadienone **1c** (0.27 g, 0.61 mmol) in xylenes (15 mL), 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide **2a′** (0.15 g, 0.61 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded tetraphenyldibenzothiophene *S*,*S*-dioxide **3c"** (0.17 g, 51%) as a colorless solid.

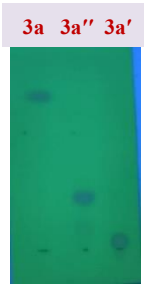
1,2,3,4-Tetraphenyldibenzo[*b, d*]thiophene *S*-oxide 3a'



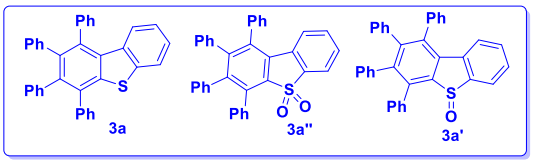
To a solution of dibenzothiophene **3a** (0.10 g, 0.20 mmol) in dry DCM (10 mL) and kept under N_2 at -10-0 °C, $BF_3.OEt_2$ (0.23 mL, 1.63 mmol) was added.[4] The reaction mixture was then stirred and 77% *m*-CPBA (0.040, 0.24 mmol) was added in 3 portions over 1.5 h at the same temparature. The reaction was monitered by TLC, and after the disapperance of the starting material, saturated aq. Na_2CO_3 (0.60 mL) was added to the mixture followed by solid K_2CO_3

(300 mg). The mixture was then filtered through a plug loaded with Na_2SO_4, K_2CO_3 and Na_2CO_3. It was then wahsed with DCM (10 mL). Subsequent removal of DCM followed by column chromatographic purification on silica gel afforded dibenzothiophene *S*-oxide **3a'** (60 mg, 58%) as a colorless solid. R_f = 0.20 (eluent: 25% ethyl acetate in hexane); mp 218-220 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 1H, ArH), 7.34-7.10 (m, 12H, ArH), 6.85-6.80 (m, 10H, ArH), 6.28 (d, *J* = 8.1 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 146.7, 145.9, 144.1, 142.4, 138.7, 138.5, 138.2, 137.8, 136.6, 134.5, 131.8, 130.74, 130.71, 130.0, 129.9, 128.8, 128.6, 128.4, 127.7, 127.5, 127.3, 126.9, 126.7, 126.04, 125.99, 125.6 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.8, 130.7, 130.7, 129.96, 129.89, 128.8, 128.6, 128.4, 127.6, 127.5, 127.3, 126.8, 126.7, 126.04, 125.99, 125.5 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}OS$ $[M+H]^+$: 505.1626, Found 505.1649.

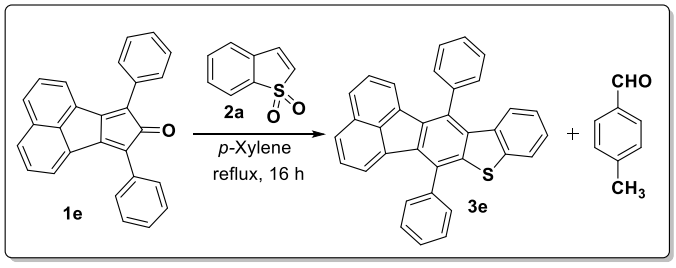
TLC picture of dibenzothiophene 3a, sulfone 3a" and sulfoxide 3a'



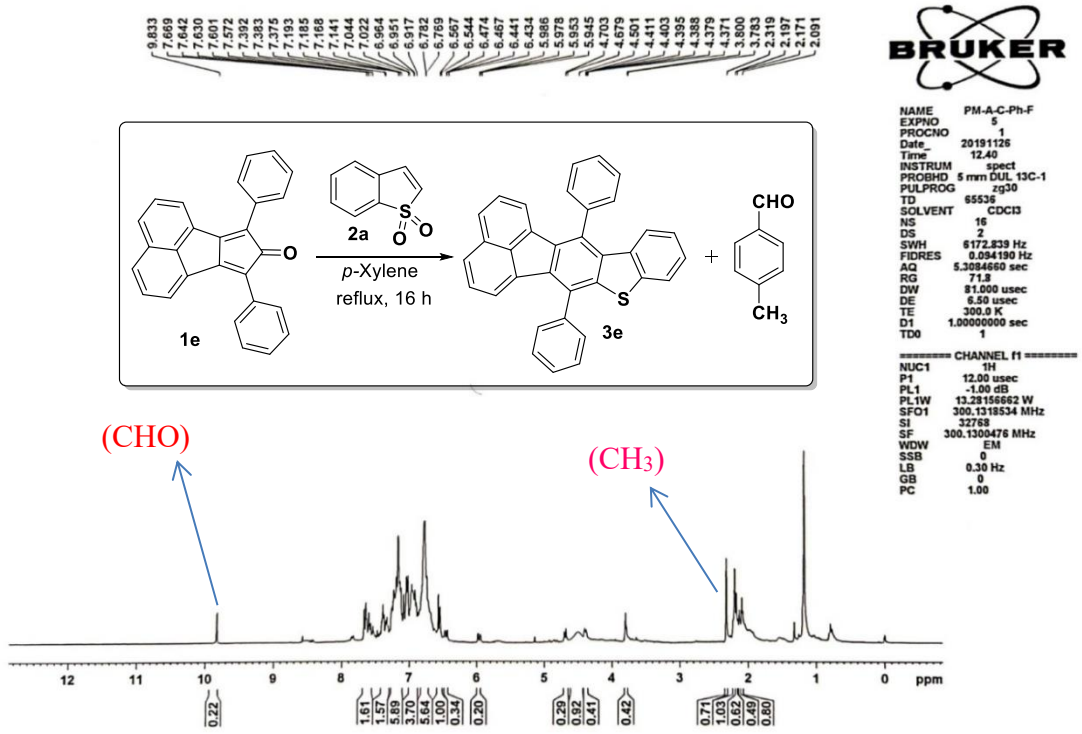
15% EA in Hexane



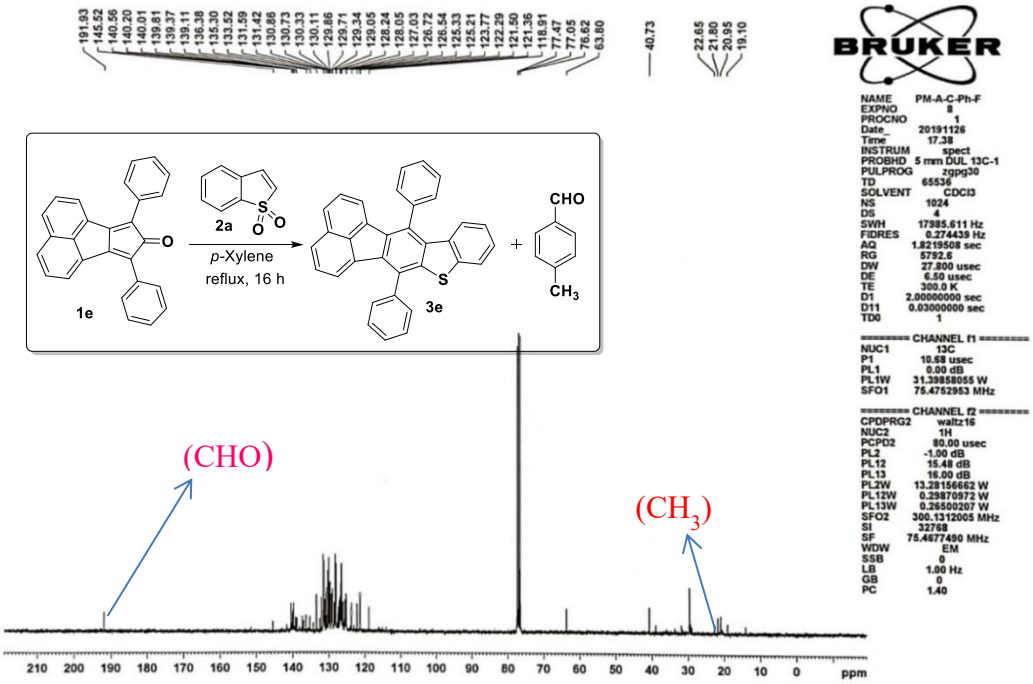
Diels-Alder reaction of 7,9-diphenyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one 1e with benzo[*b*]thiophene *S*, *S*-dioxide 2a in *p*-xylene



To a solution of cyclopentadienone **1e** (0.20 g, 0.56 mmol) in *p*-xylene (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) was added and refluxed for 16 h. The subsequent removal of solvent gave crude product. The crude product was analyzed by ^{1}H, ^{13}C NMR and mass spectra.

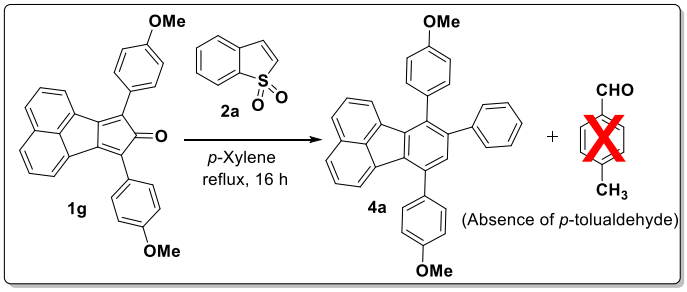


^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

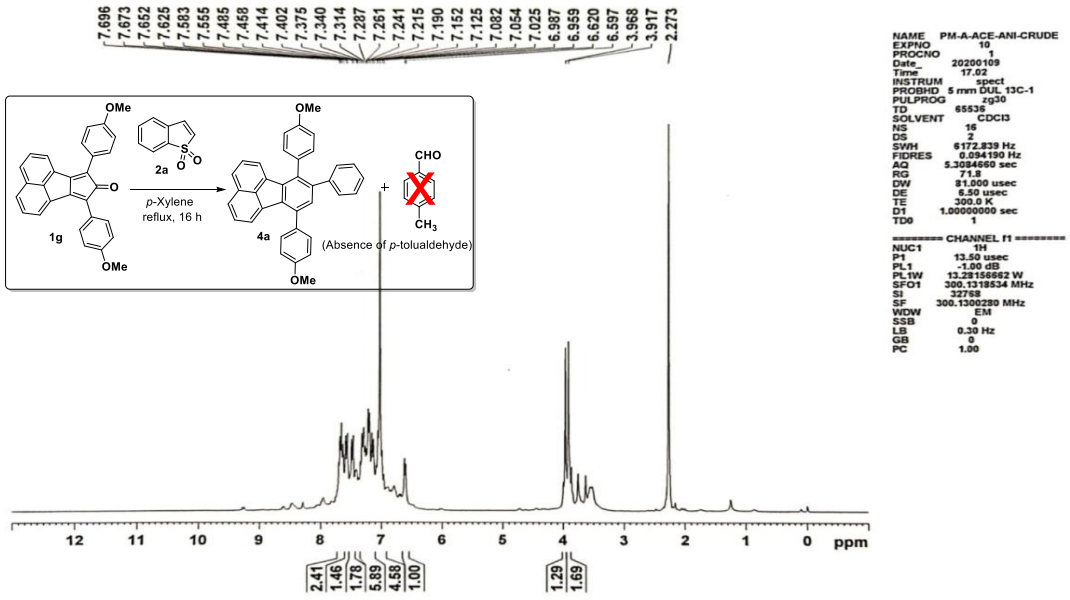


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

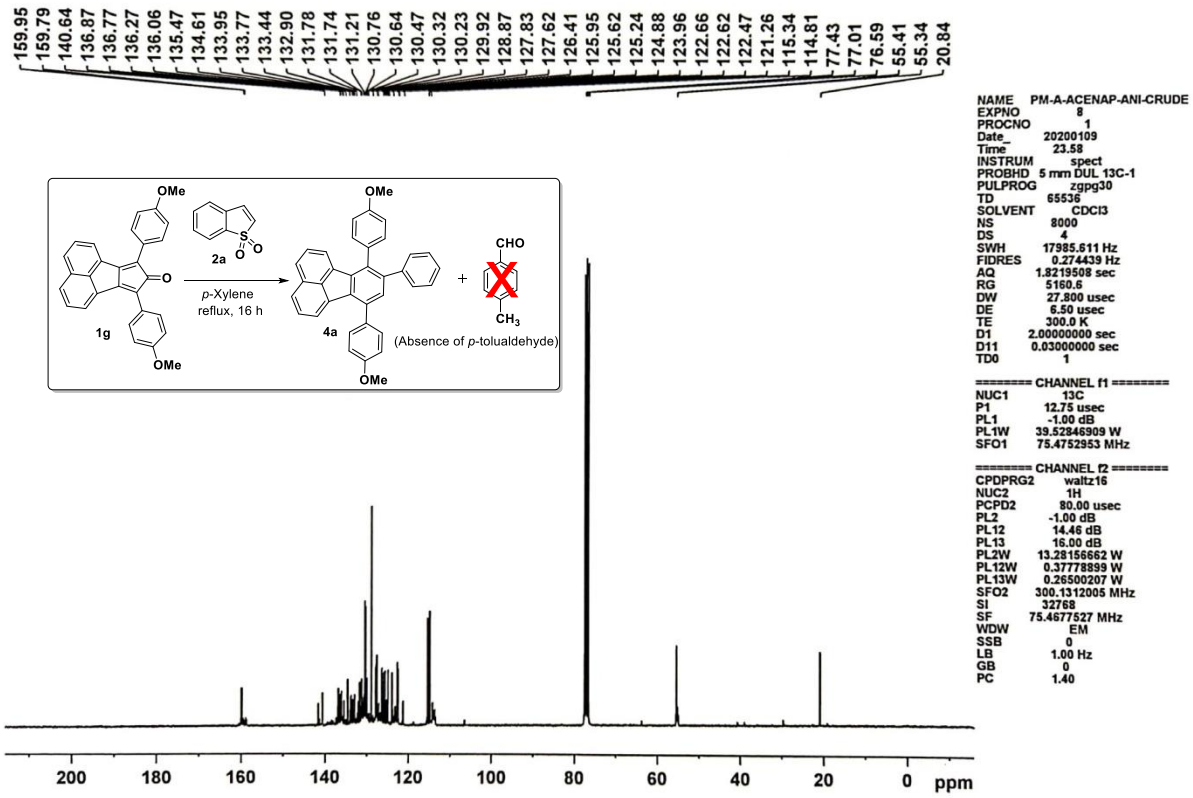
Diels-Alder reaction of 7,9-bis(4-methoxyphenyl)-8*H*-cyclopenta[a]acenaphthylen-8-one 1g with benzo[*b*]thiophene *S*, *S*-dioxide 2a in *p*-xylene



To a solution of cyclopentadienone**1a** (0.25 g, 0.60 mmol)in *p*-xylene (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide**2a** (0.10 g, 0.60 mmol)was added and refluxed for 16 h. Subsequent removal of solvent followed by ^{1}H, ^{13}C NMR and mass spectra.

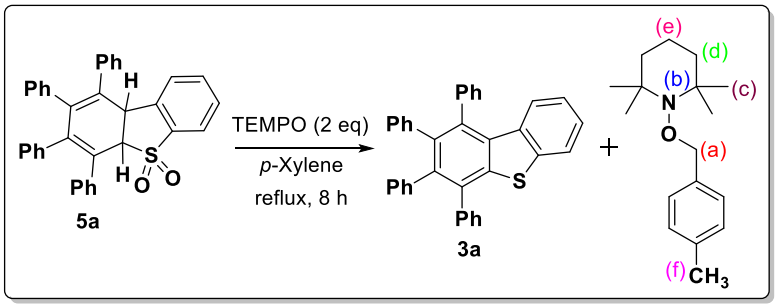


^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

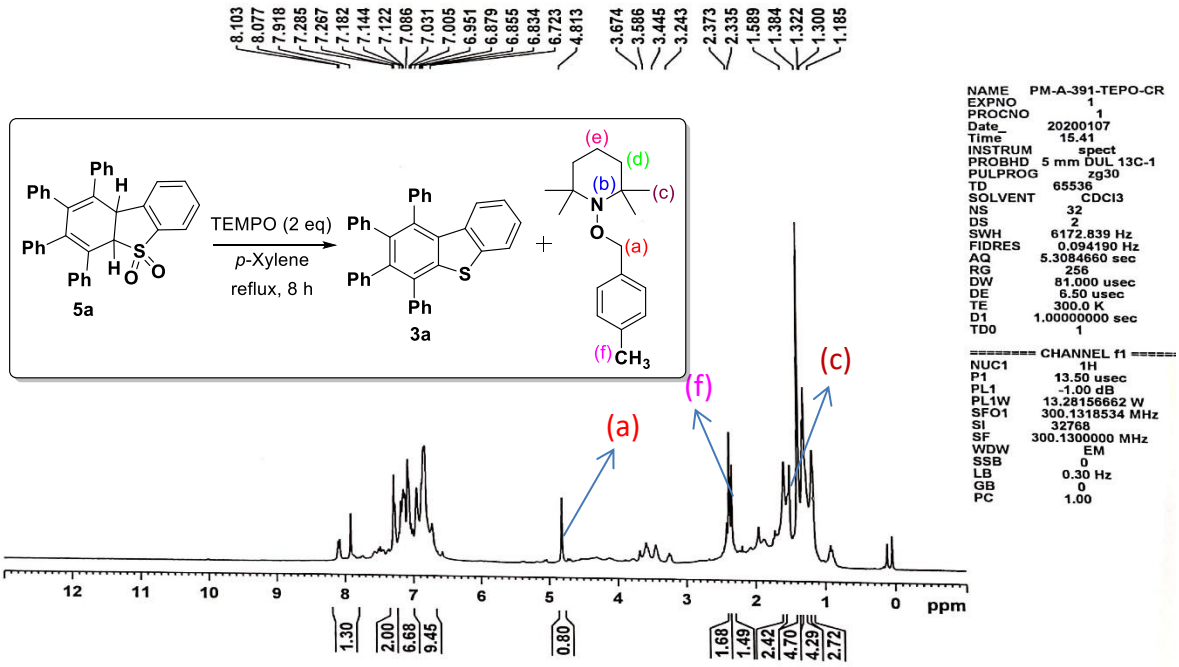


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

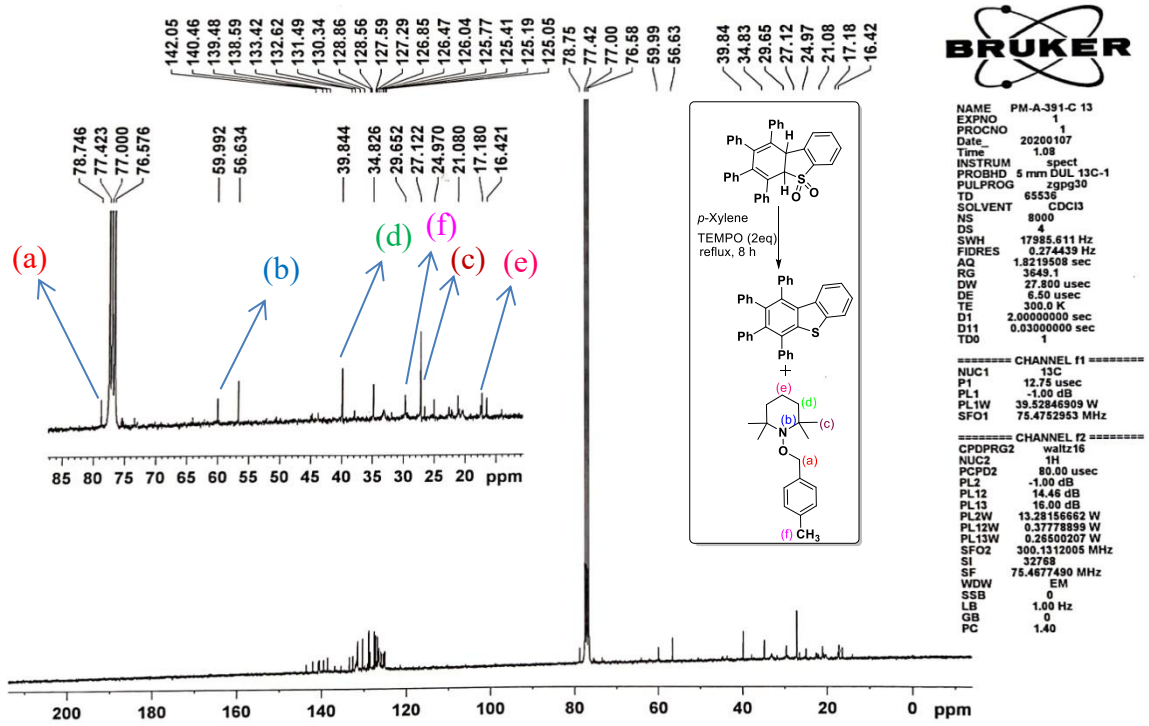
Thermolysis of dihydrodibenzothiophene 5a in the presence of TEMPO



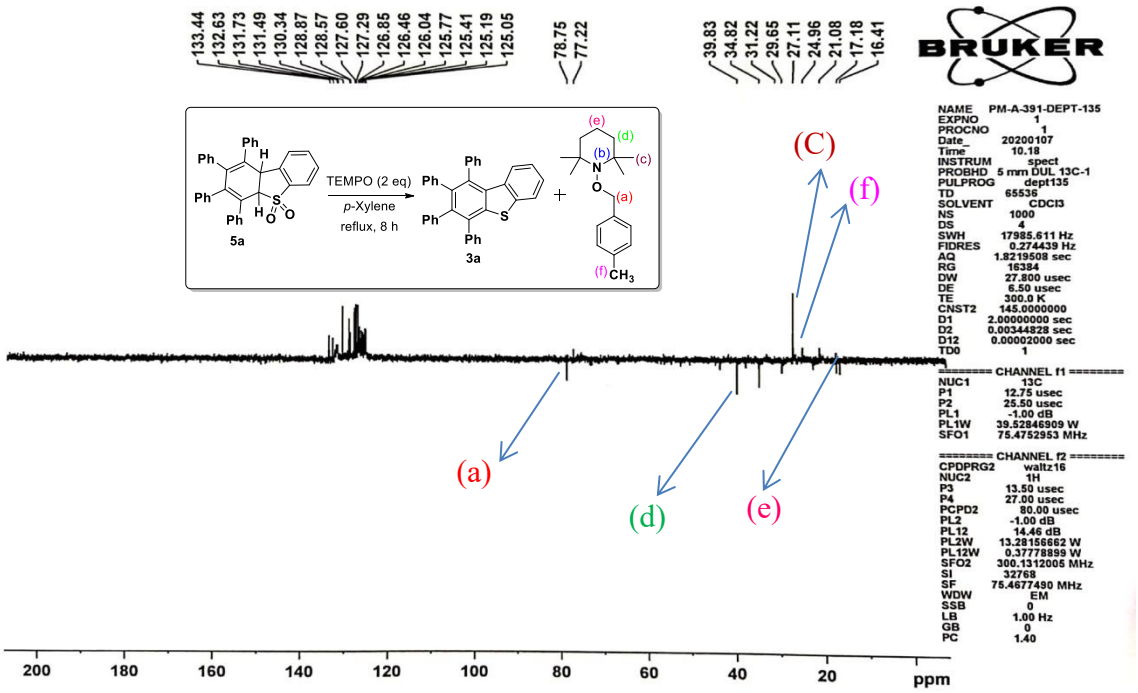
To a stirred solution of dihydrodibenzothiophene **5a** (0.1 g, 0.19 mmol) in dry *p*-xylene (10 mL), TEMPO (60 mg, 0.38 mmol) was added at refluxed for 8 h. The subsequent removal of solvent gave crude product. Then, the crude product was analyzed by ^{1}H, ^{13}C NMR and mass spectra.



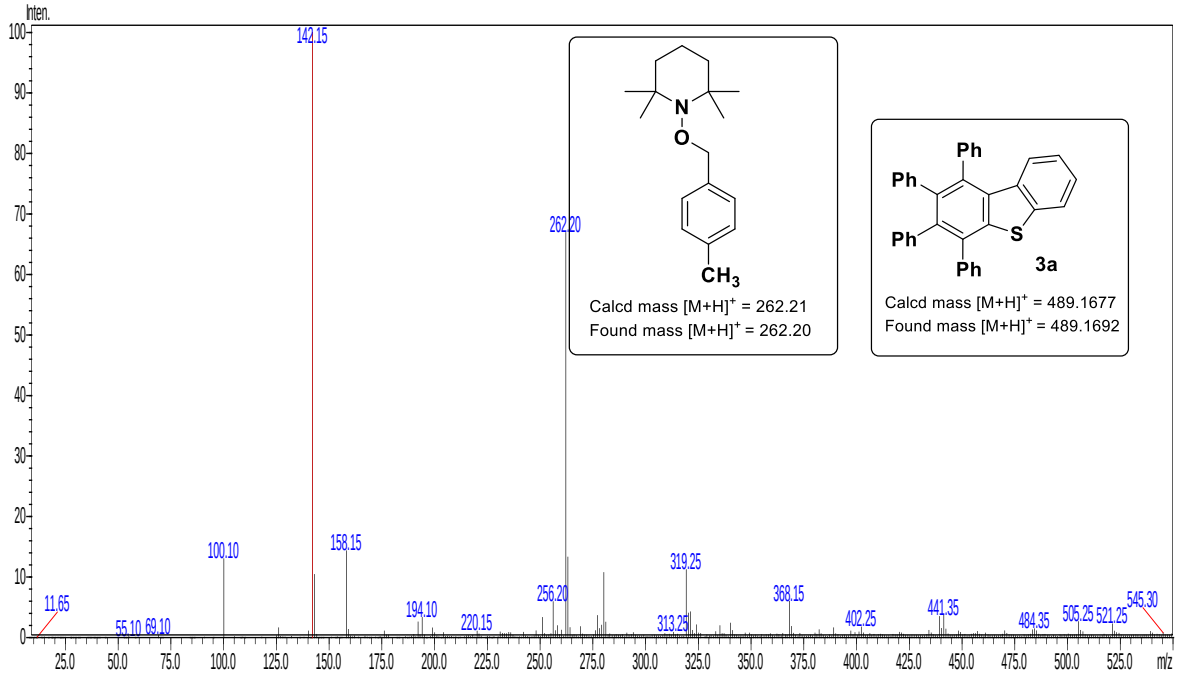
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product



^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

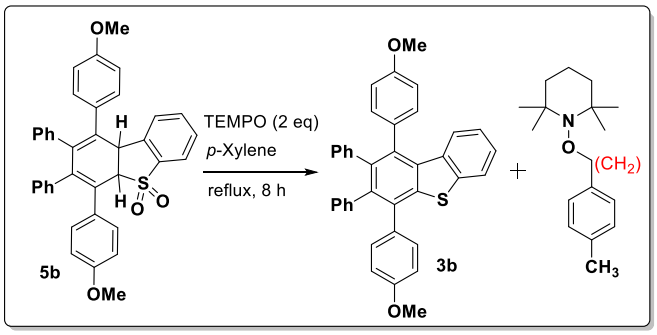


DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of crude product

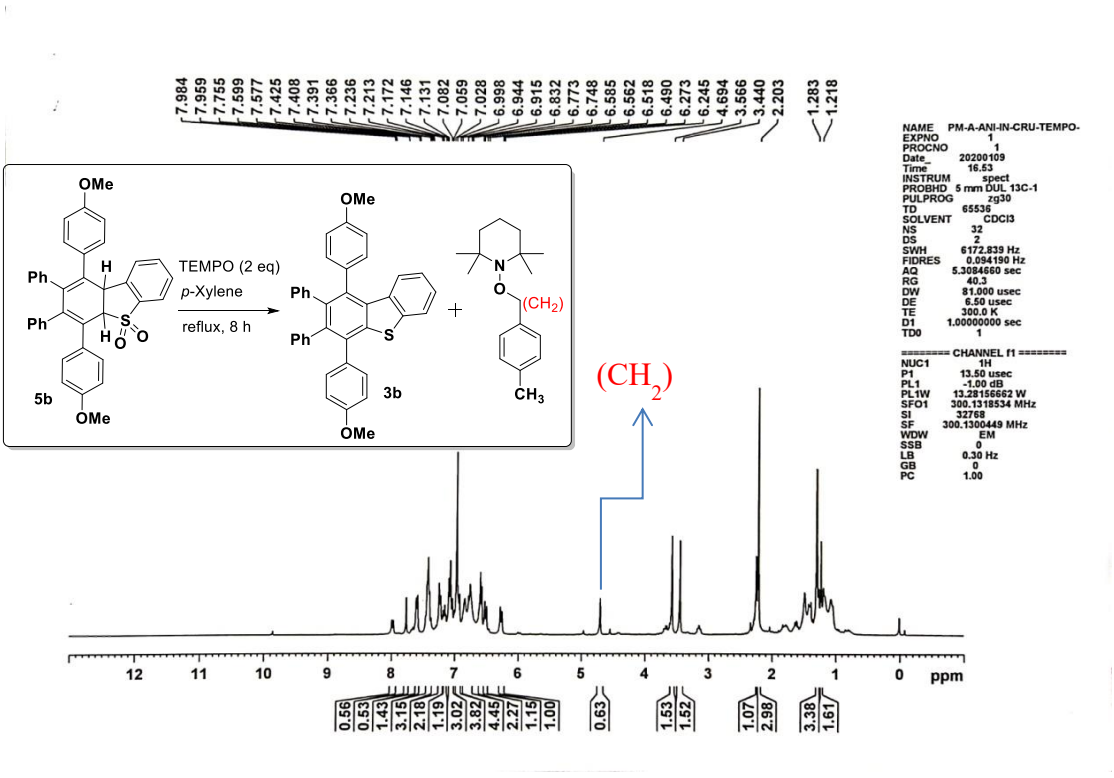


Mass spectrum of reaction mixture

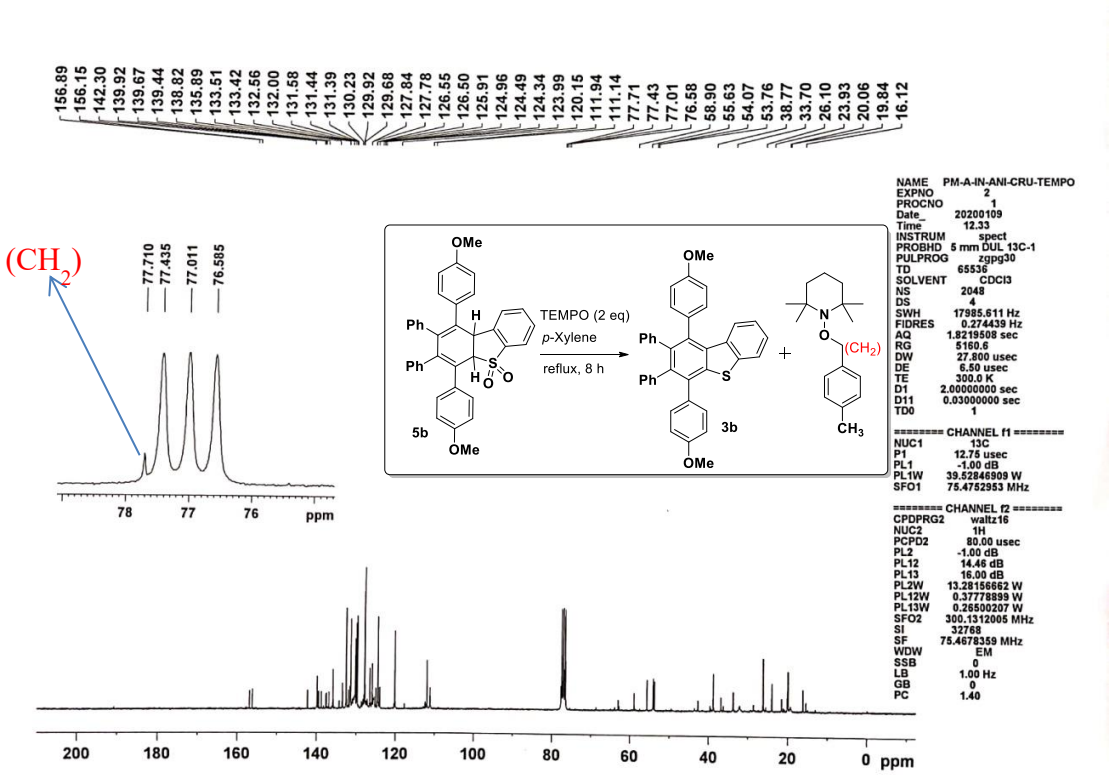
Thermolysis of dihydrodibenzothiophene 5b in the presence of TEMPO



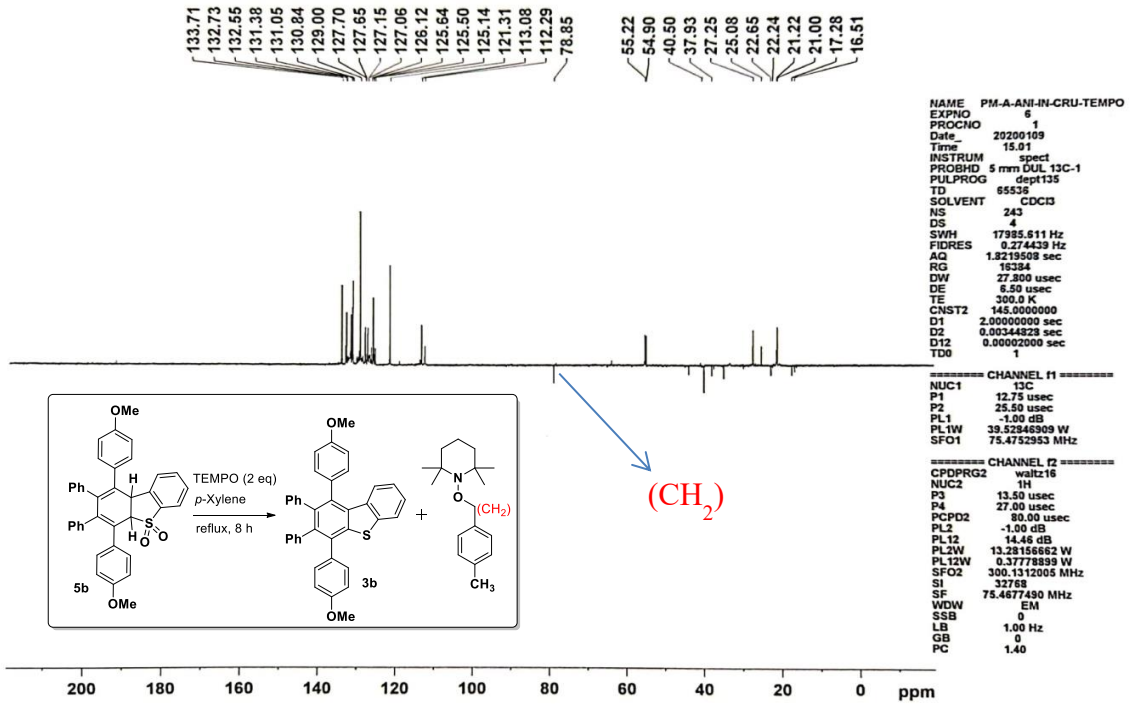
To a stirred solution of dihydrodibenzothiophene **5a** (0.1 g, 0.17 mmol) in dry *p*-xylene (10 mL), TEMPO (54 mg, 0.34 mmol) was added at refluxed for 8 h. The subsequent removal of solvent gave crude product. Then, the crude product was analysis by ^{1}H, ^{13}C NMR and mass spectra.



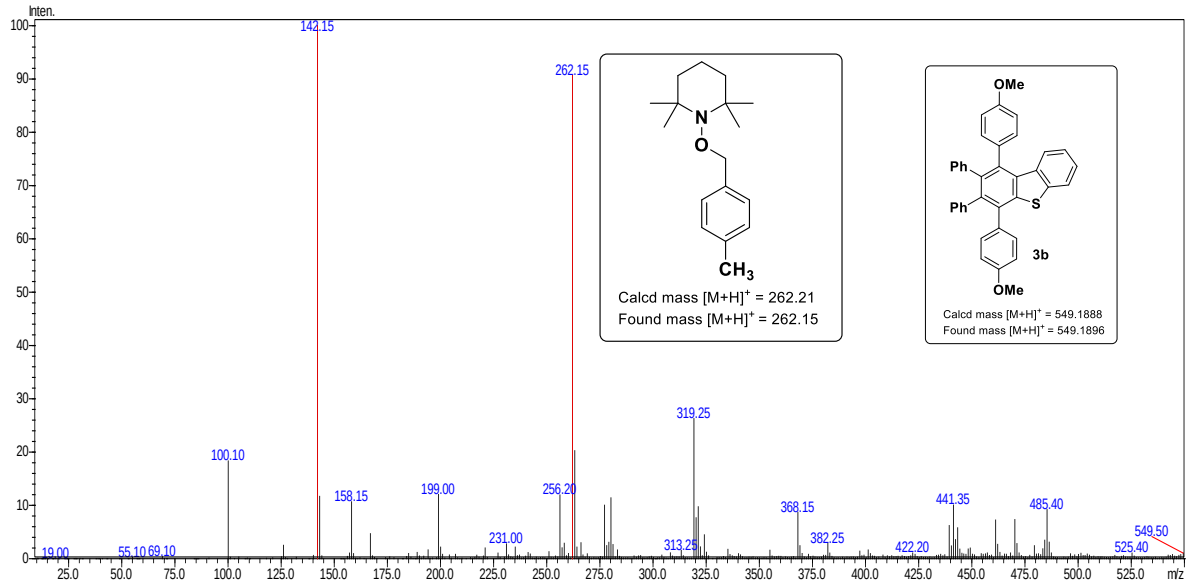
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product



^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of reaction mixture

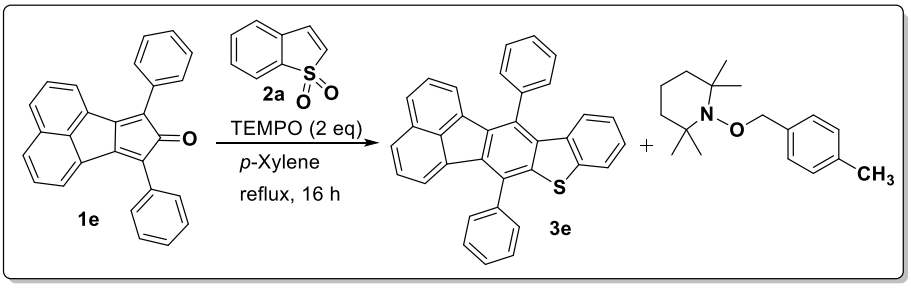


DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of crude product

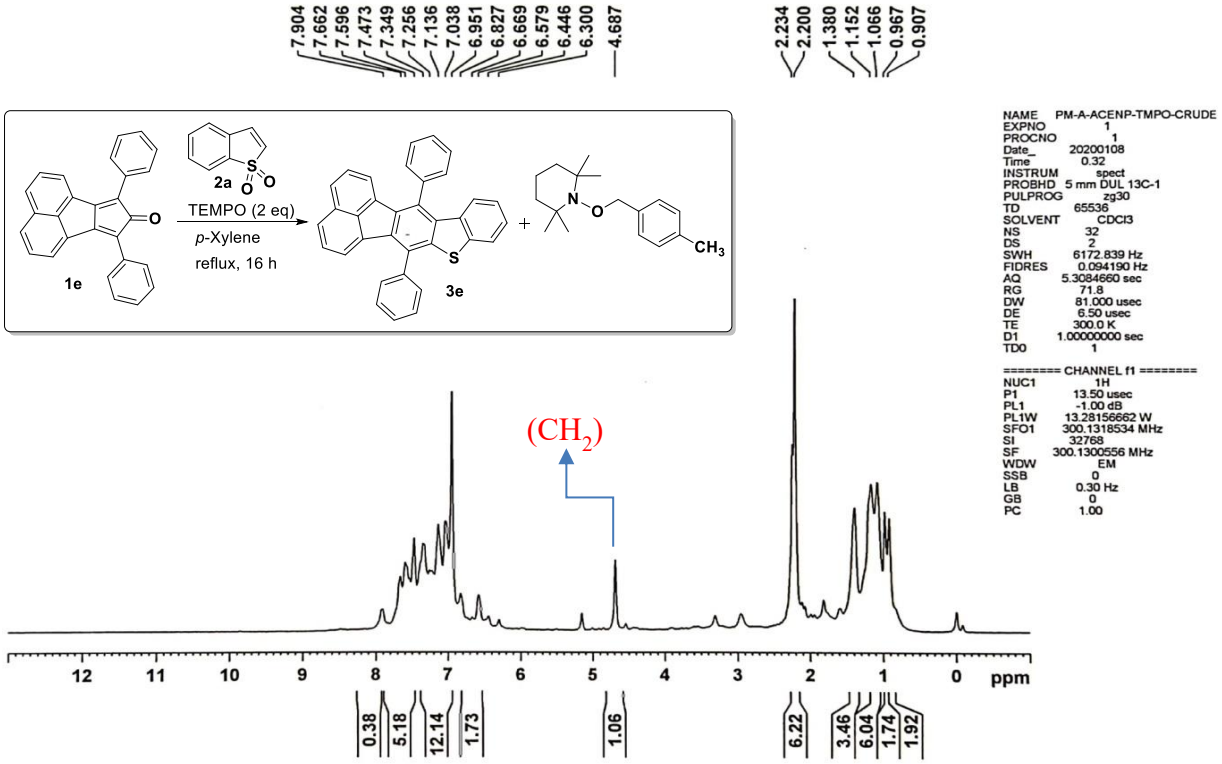


Mass spectrum of crude product

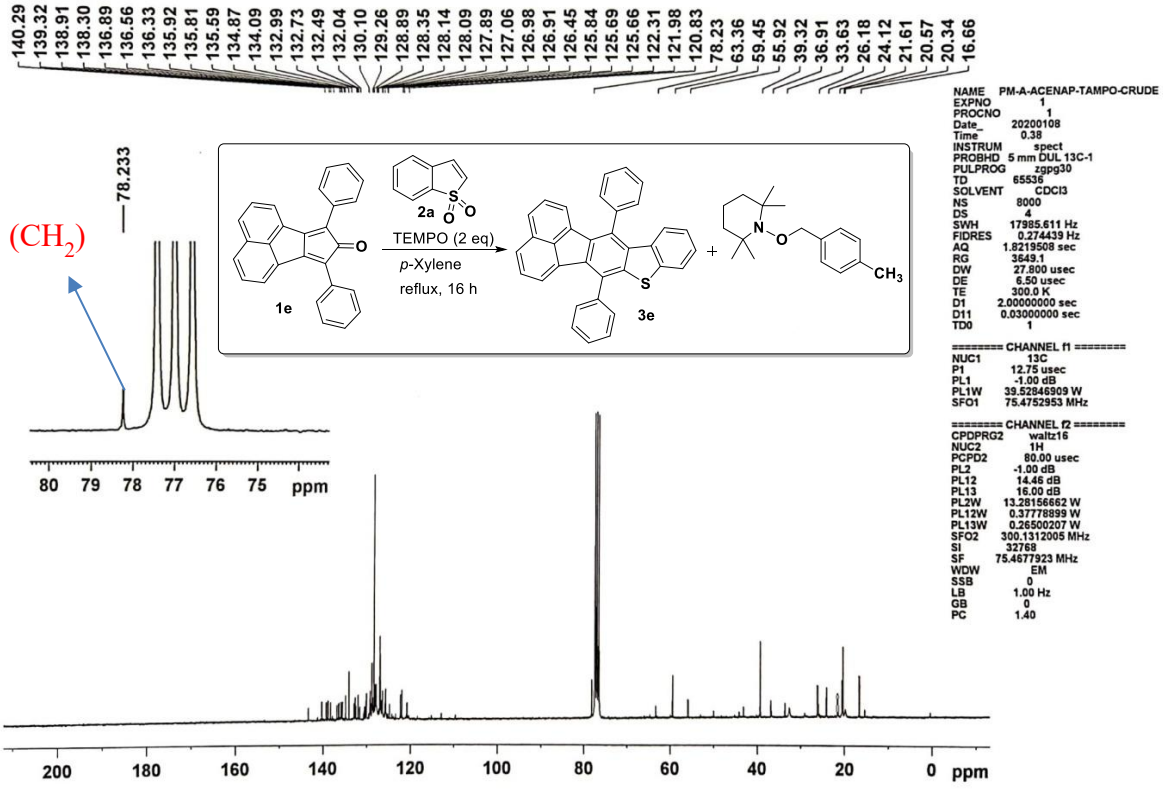
Diels-Alder reaction of 7,9-diphenyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one 1e with benzo[*b*]thiophene *S*, *S*-dioxide 2a in the presence of TEMPO



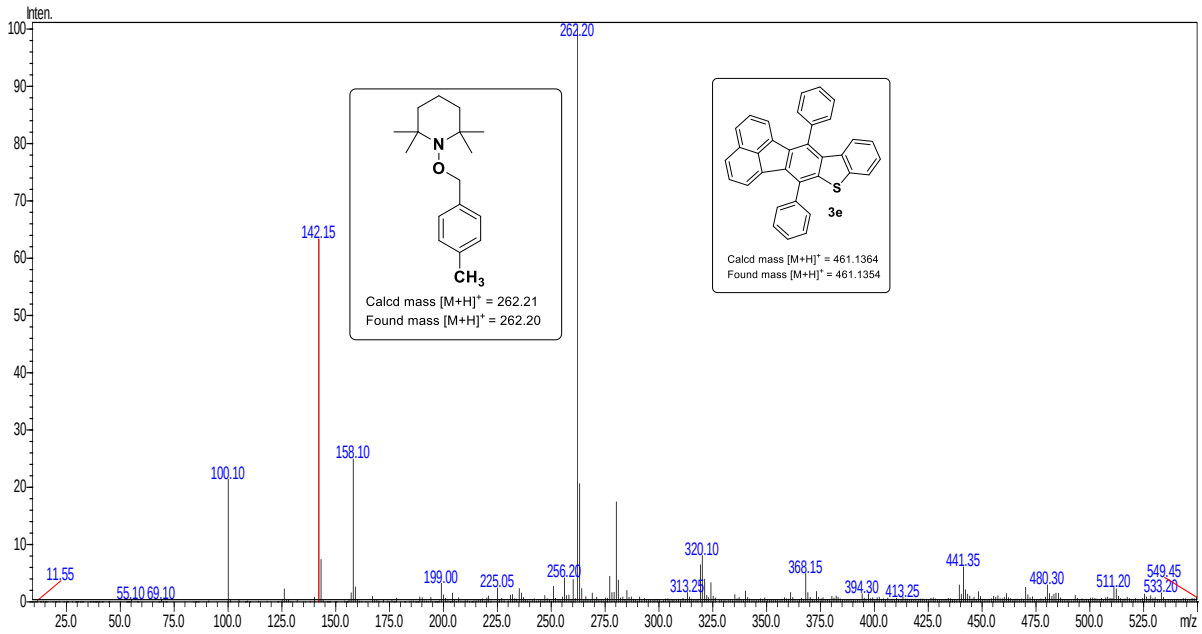
To a solution of cyclopentadienone **1e** (0.20 g, 0.56 mmol) in *p*-xylene (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol), TEMPO (75 mg, 0.15 mmol) was added at refluxed for 16 h. The subsequent removal of solvent gave crude product. Then, the crude product was analysis by ^{1}H, ^{13}C NMR and mass spectra.



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product

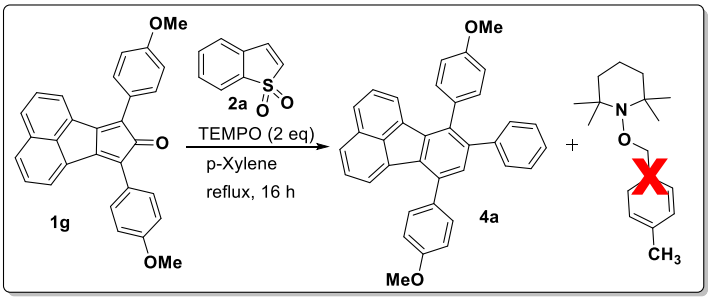


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

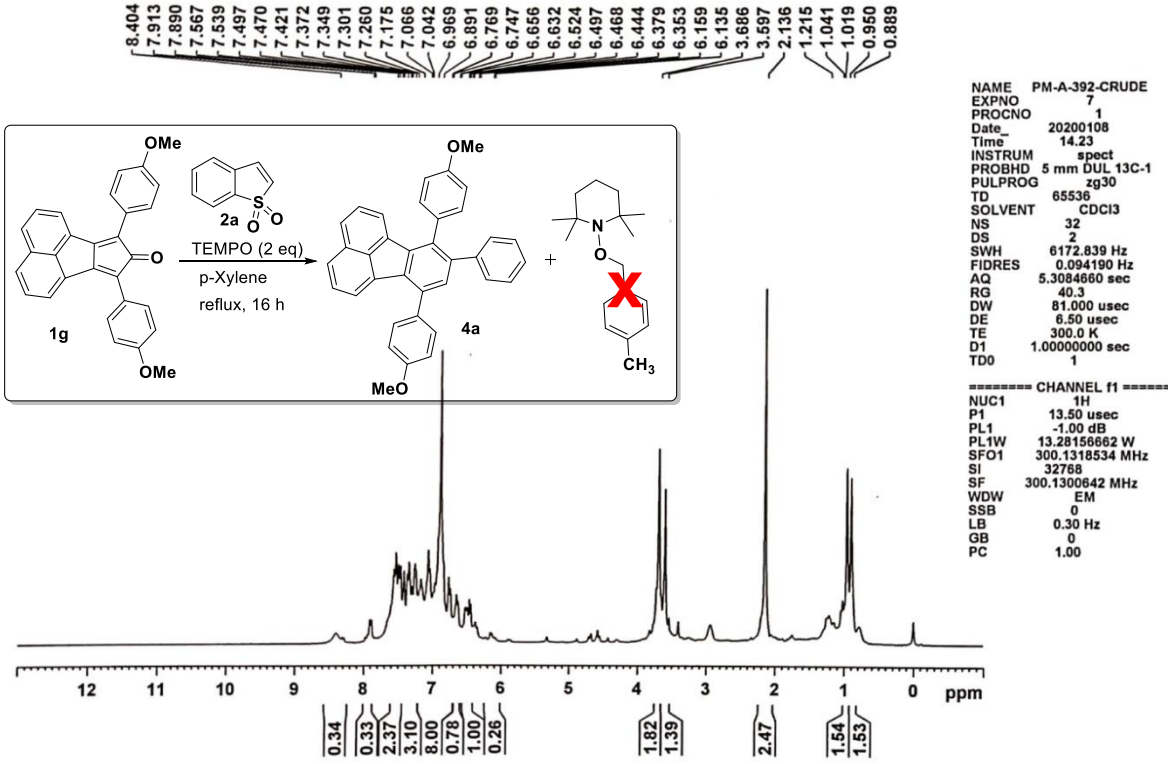


Mass spectrum of crude product

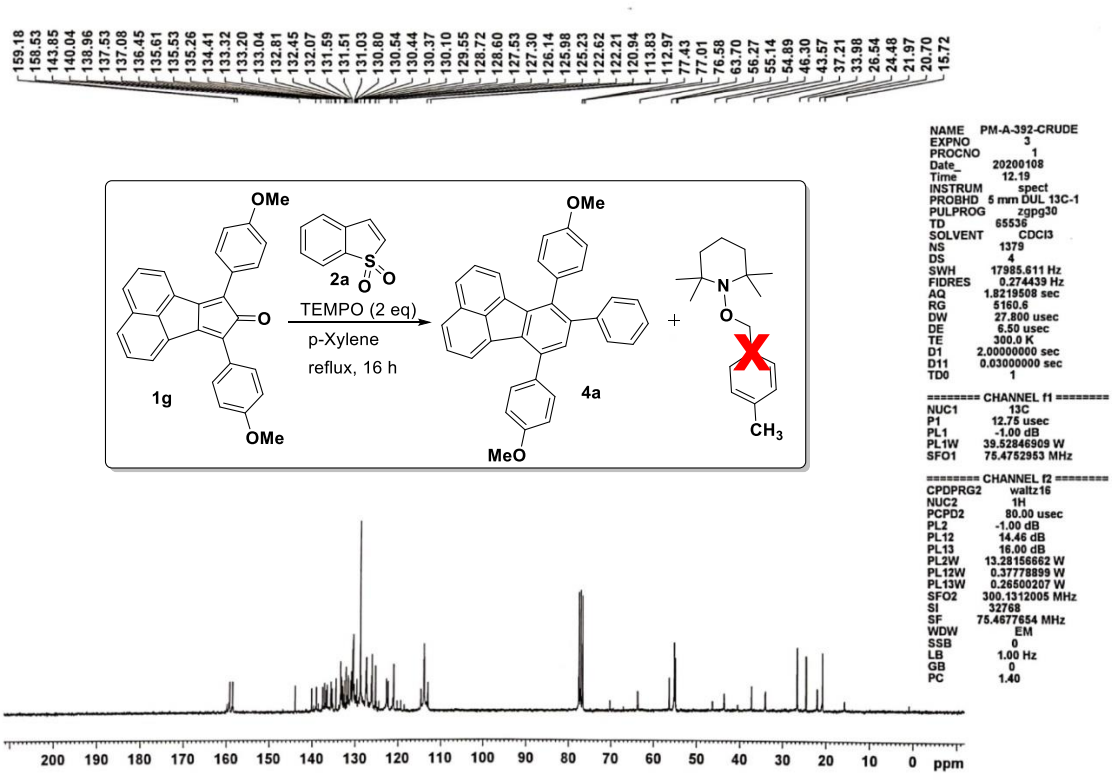
Diels-Alder reaction of 7,9-bis(4-methoxyphenyl)-8*H*-cyclopenta[a]acenaphthylen-8-one 1g with benzo[*b*]thiophene *S*, *S*-dioxide 2a in the presence of TEMPO



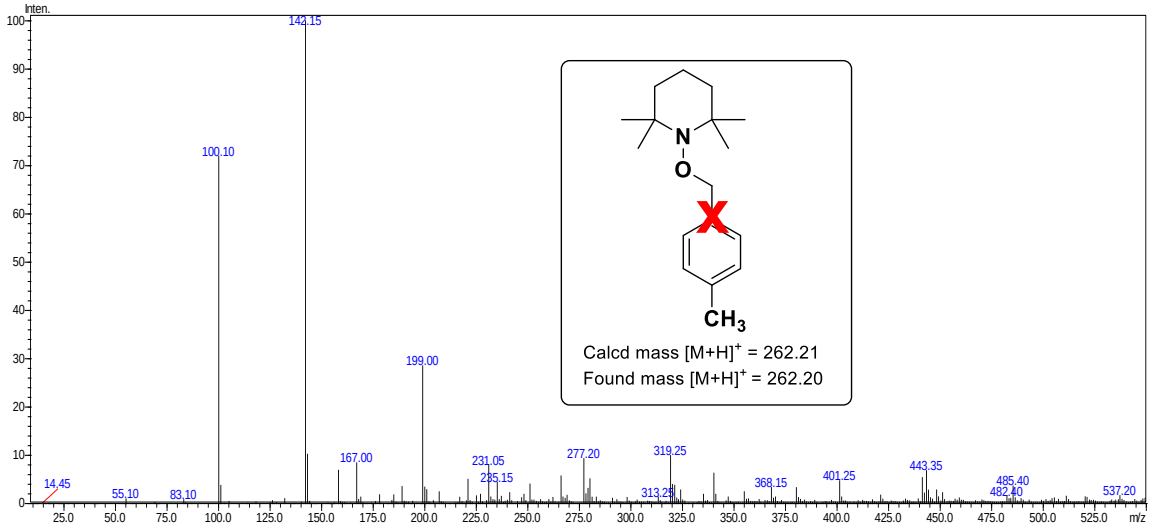
To a solution of cyclopentadienone **1g** (0.25 g, 0.60 mmol) in *p*-xylene (10 mL), benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.60 mmol) TEMPO (67 mg, 0.12 mmol) was added at refluxed for 16 h. The subsequent removal of solvent gave crude product. Then, the crude product was analysis by ^{1}H, ^{13}C NMR and mass spectra.



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of crude product



^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of crude product

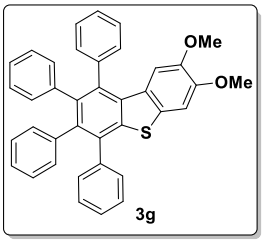


Mass spectrum of crude product

General procedure for preparation of dibenzothiophenes 3g-r/fluoranthene derivatives 4d-4q:

To a solution of cyclopentadienones (~0.5 mmol) in xylenes (10 mL), benzo[*b*]thiophene *S*,*S*-dioxides (~0.5 mmol) was added and refluxed for 16 h. Removal of solvent followed by column chromatographic purification (silica gel; EA/hexane) afforded the respective dibenzothiophenes **3g-r** as well as triarylfluoranthene and pentaarylbenzene analogues **4d-q**.

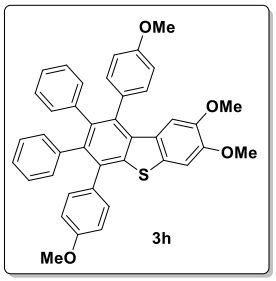
7,8-Dimethoxy-1,2,3,4-tetraphenyldibenzo[*b*,*d*]thiophene 3g



The dibenzothiophene **3g** (0.18 g, 75%) was prepared according to the general procedure using cyclopentadienone **1a** (0.17 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2a** (0.10 g, 0.44 mmol) as a colorless solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp 216-218 °C;^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28-7.23 (m, 5H, ArH), 7.20-7.18 (m, 5H, ArH), 7.07 (s, 1H, ArH), 6.81-6.78 (m, 10H, ArH), 6.07 (s, 1H, ArH), 3.82 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.7, 146.6, 140.3, 140.2, 139.9, 139.8, 138.7, 137.5,136.2, 135.2,

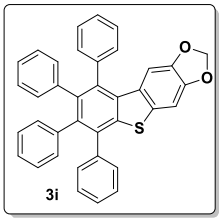
133.0, 131.54, 131.49, 130.7, 130.0, 129.2, 128.3, 128.0, 127.2, 126.9, 126.7, 126.5, 125.5, 125.4, 107.1,103.8, 55.9 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.5, 131.5, 130.7, 130.0, 128.3, 128.0, 127.2, 126.9, 126.7, 126.6, 125.6, 125.4, 107.1, 103.7, 55.9, 55.2 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{28}O_2S$ $[M+H]^+$: 549.1888, Found 549.1897.

7,8-dimethoxy-1,4-bis(4-methoxyphenyl)-2,3-diphenyldibenzo[b,d]thiophene 3h



The pentaarylbenzene **3h** (0.18 g, 72%) was prepared according to the general procedure using cyclopentadienone **1b** (0.19 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide (0.10 g, 0.44 mmol) as a colorless solid. R_f = 0.20 (eluent: 15% ethyl acetate in hexane); mp 240-242 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.25-7.23 (m, 2H, ArH), 7.19-7.14 (m, 3H, ArH), 6.88-6.84 (m, 14H, ArH), 6.16 (s, 1H, ArH), 3.89 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.50, 158.48, 148.7, 146.6, 140.6, 140.0, 139.1, 137.7, 135.7, 134.7, 133.0, 132.6, 132.3, 131.8, 131.5, 131.2, 129.4, 126.6, 125.4, 125.3, 113.7, 113.4, 107.2, 103.8, 56.0 (OCH_3), 55.3 (OCH_3), 55.2 (OCH_3), 55.1 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.8, 131.5, 131.5, 131.2, 126.7, 126.6, 125.4, 125.4, 125.3, 113.7, 113.4, 107.2, 103.8, 56.0, 55.3, 55.2, 55.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{40}H_{32}O_4S$ $[M+H]^+$: 609.2100, Found 609.2115.

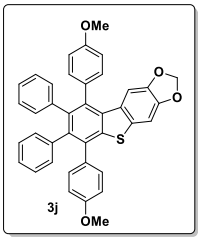
6,7,8,9-Tetraphenylbenzo[4',5']thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxole 3i



The dibenzothiophene **3i** (0.19 g, 75%) was prepared according to the general procedure using cyclopentadienone **1a** (0.18 g, 0.47 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.47 mmol) as a colorless solid. R_f = 0.20 (eluent: 5% ethyl acetate in hexane); mp 220-222 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 5H, ArH), 7.25-7.22 (m, 4H, ArH), 7.11 (s, 1H, ArH), 6.87 (m, 11H, ArH), 5.95 (s, 1H, ArH), 5.90 (s, 2H, OCH_2) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.1, 145.7, 140.1, 139.8, 139.7, 138.9, 137.6, 136.6, 135.1, 134.3, 132.4, 131.5, 131.4, 130.3, 130.0, 128.3, 128.1, 127.2, 127.1, 126.7, 126.5, 125.6, 125.4, 104.6, 101.7, 101.3 (OCH_2) ppm;

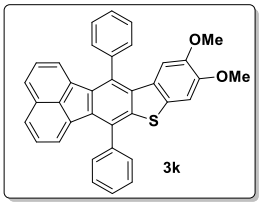
DEPT-135 NMR (100 MHz, $CDCl_3$): δ 131.5, 131.4, 130.3, 130.1, 130.0, 129.3, 128.4, 128.3, 128.0, 127.4, 127.2, 127.1, 126.6, 126.5, 125.5, 125.3, 104.6, 101.7, 101.2 ppm; HRMS (ESI): *m/z* Calcd for $C_{37}H_{24}O_2S$ $[M+H]^+$: 533.1575, Found 533.1582.

6,9-Bis(4-methoxyphenyl)-7,8-diphenylbenzo[4',5']thieno[2',3':4,5]benzo[1,2-d][1,3]dioxole 3j



The dibenzothiophene **3j** (0.19 g, 70%) was prepared according to the general procedure using cyclopentadienone **1b** (0.21 g, 0.47 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.47 mmol) as a colorless solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp 176-178 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H, ArH), 7.12-7.09 (m, 3H, ArH), 6.86-6.77 (m, 14H, ArH), 6.12 (s, 1H, ArH), 5.90 (s, 2H, OCH_2), 3.79 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.7, 147.2, 145.7, 140.8, 140.2, 140.1, 139.5, 137.9, 135.9, 134.8, 134.4, 132.9, 132.6, 132.1, 131.6, 131.5, 131.4, 131.2, 131.6, 126.7, 126.5, 125.5, 125.3, 113.9, 113.6, 104.8, 101.7, 101.3 (OCH_2), 55.2 (OCH_3), 55.1 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.5, 131.4, 131.3, 131.2, 126.7, 126.5, 125.4, 125.2, 113.8, 113.5, 104.7, 101.7, 101.2, 55.1, 55.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{39}H_{30}O_4S$ $[M]^+$: 593.1787, Found 593.1798.

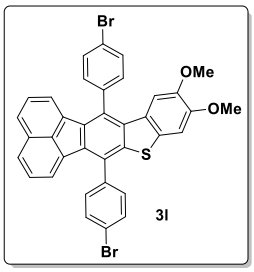
10,11-Dimethoxy-7,13-diphenylbenzo[*d*]fluorantheno[8,9-*b*]thiophene 3k



The dibenzothiophene **3k** (0.17 g, 74%) was prepared according to the general procedure using cyclopentadienone **1e** (0.15 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2b** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp 190-192 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78-7.66 (m, 12H, ArH), 7.37-7.26 (m, 2H, ArH), 7.15 (s, 1H, ArH), 6.93 (d, *J* = 6.9 Hz, 1H, ArH), 6.62 (d, *J* = 6.9 Hz, 1H, ArH), 6.39 (s, 1H, ArH), 3.90 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.7, 146.9, 140.8, 139.5, 138.9, 136.7, 136.0, 135.4, 134.0, 133.8, 133.2, 132.9, 132.6, 132.2, 129.9, 129.7, 129.5,129.3, 129.2, 128.6, 128.3, 127.8, 127.7, 126.3, 126.0, 122.5, 122.4, 106.7, 104.0, 56.0 (OCH_3), 55.2

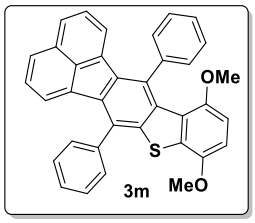
(OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 129.9, 129.7, 129.3, 129.2, 128.6, 128.3, 127.8, 127.7, 126.3, 126.0, 122.5, 122.4, 106.7, 104.0, 56.0, 55.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{24}O_2S$ $[M+H]^+$: 521.1575, Found 521.1575.

7,13-Bis(4-bromophenyl)-10,11-dimethoxybenzo[*d*]fluorantheno[8,9-*b*]thiophene 3l



The dibenzothiophene **3l** (0.21 g, 70%) was prepared according to the general procedure using cyclopentadienone **1f** (0.22 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2b** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.26 (eluent: 10% ethyl acetate in hexane); mp >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 7.80 (d, *J* = 8.1 Hz, 2H, ArH), 7.76-7.72 (m, 2H, ArH), 7.58-7.53 (m, 4H, ArH), 7.41-7.34 (m, 2H, ArH), 7.15 (s, 1H, ArH), 6.98 (d, *J* = 6.9 Hz, 1H, ArH), 6.73 (d, *J* = 6.9 Hz, 1H, ArH), 6.27 (s, 1H, ArH), 3.90 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.9, 147.1, 140.6, 138.4, 137.7, 136.3, 135.6, 135.3, 133.9, 133.8, 133.2, 133.1, 132.7, 132.6, 131.6, 131.6, 131.0, 129.9, 129.1, 127.9, 127.8, 126.6, 126.4, 122.9, 122.6, 122.53, 122.46, 106.4,104.2, 56.1 (OCH_3), 55.1 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.1, 132.7, 131.6, 131.0, 127.9, 127.8, 126.6, 126.4, 122.53, 122.46, 106.4, 104.1, 56.1, 55.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{22}Br_2O_2S$ $[M+H]^+$: 676.9786, Found 676.9763.

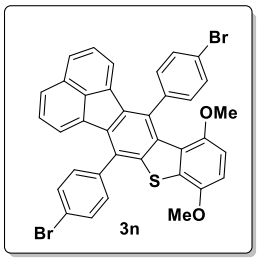
9,12-Dimethoxy-7,13-diphenylbenzo[*d*]fluorantheno[8,9-*b*]thiophene 3m



The dibenzothiophene **3m** (0.13 g, 57%) was prepared according to the general procedure using cyclopentadienone **1e** (0.15 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.25 (eluent: 10 % ethyl acetate in hexane); mp 290-292 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71-7.58 (m, 7H, ArH), 7.57-7.51 (m, 5H, ArH), 7.34-7.28 (m, 1H, ArH), 7.24-7.21 (m, 1H, ArH), 6.85-6.76 (m, 2H, ArH), 6.56 (d, *J* = 8.4 Hz, 1H, ArH), 6.04 (d, *J* = 7.2Hz, 1H, ArH), 3.92 (s, 3H, OCH_3), 3.09 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 150.4, 147.8, 144.3, 138.9, 137.5, 137.1, 135.7, 135.6, 134.0, 131.8, 131.2, 129.7, 129.4, 129.3,

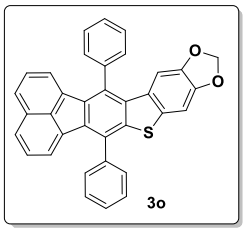
128.7, 128.0, 127.9, 127.4, 126.8, 126.6, 126.4, 125.8, 123.4, 122.5, 106.7,105.8, 56.2 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 129.4, 129.3, 128.7, 127.9, 127.8, 127.4, 126.6, 126.4, 125.8, 123.4, 122.5, 106.7, 105.8, 56.2, 55.2. HRMS(ESI): *m/z* Calcd for $C_{36}H_{25}O_2S$ $[M+H]^+$: 521.1575, Found 521.1575.

7,13-Bis(4-bromophenyl)-9,12-dimethoxybenzo[*d*]fluorantheno[8,9-*b*]thiophene 3n



The fluoranthene **3n** (0.10 g, 63%) was prepared according to the general procedure using cyclopentadienone **1f** (0.22 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.30 (eluent: 10% ethyl acetate in hexane); mp201-203 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.68-7.64 (m, 2H, ArH), 7.59 (d, *J* = 8.4 Hz, 2H, ArH), 7.50 (d, *J* = 8.4 Hz, 2H, ArH), 7.40-7.31 (m, 3H, ArH), 7.29-7.24 (m, 2H, ArH), 7.16-7.12 (m, 1H, ArH), 6.72 (d, *J* = 7.2 Hz, 1H, ArH), 6.66-6.62 (m, 2H, ArH), 6.54 (d, *J* = 9.3 Hz, 1H, ArH) 3.62 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.9, 149.5, 138.6, 137.2, 136.7, 136.7, 135.5, 135.2, 135.1, 134.9, 134.6, 131.9, 130.7, 130.6, 130.0, 129.9, 129.3, 128.8, 126.64, 126.56, 125.9, 122.2, 121.8, 120.9, 120.3, 116.5, 112.3,110.2, 54.7 (OCH_3), 54.5 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.7, 130.6, 130.0, 129.9, 126.6, 126.6, 125.9, 122.2, 121.8, 116.5, 112.2, 110.2, 54.7, 54.4 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{22}Br_2O_2S$ $[M+H]^+$: 676.9786, Found 676.9798.

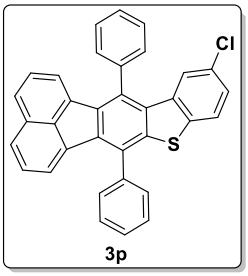
7,14-Diphenylfluorantheno[8'',9'':4',5']thieno[2',3':4,5]benzo[1,2-*d*][1,3]dioxole 3o



The dibenzothiophene **3o** (0.19 g, 79%) was prepared according to the general procedure using cyclopentadienone **1e** (0.17 g, 0.47 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.47 mmol) as a green solid. R_f = 0.25 (eluent: 5% ethyl acetate in hexane); mp 258-260 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71-7.58 (m, 12H, ArH), 7.35-7.24 (m, 2H, ArH), 7.09 (s, 1H, ArH), 6.92 (d, *J* = 7.2 Hz, 1H, ArH), 6.49 (d, *J* = 7.2 Hz, 1H, ArH), 6.22 (s, 1H, ArH), 5.90 (s, 2H, OCH_2) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.0, 145.9, 140.8, 139.3, 138.8, 136.7, 135.9, 135.6,

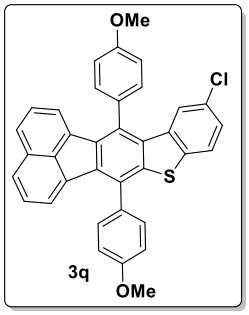
134.4, 134.0, 133.9, 133.1, 132.4, 132.0, 130.4, 130.0, 129.8, 129.3, 129.2, 129.2, 129.1, 128.7, 128.5, 127.8, 127.6, 126.3, 126.0, 122.5, 122.4, 104.2, 101.9, 101.3 (OCH_2) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.0, 129.3, 129.2, 129.1, 128.7, 128.5, 127.8, 127.6, 126.3, 126.0, 122.6, 122.4, 104.2, 101.3 ppm; HRMS (ESI): *m/z* Calcd for $C_{35}H_{20}O_2S$ $[M+H]^+$: 505.1262, Found 505.1263.

11-Chloro-7,13-diphenylbenzo[*b*]fluorantheno[8,9-*d*]thiophene 3p



To a solution of cyclopentadienone **1e** (0.18 g, 0.50 mmol) in xylenes (10 mL), 5-chlorobenzo[*b*]thiophene *S*,*S*-dioxide **2e** (0.10 g, 0.50 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3p** (0.16 g, 63%) as a green solid. R_f = 0.20 (eluent: 2% ethyl acetate in hexane); mp 276-278 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78-7.63 (m, 13H, ArH), 7.41-7.28 (m, 3H, ArH), 7.70 (d, *J* = 6.9 Hz, 1H, ArH), 6.81 (s, 1H, ArH), 6.64 (d, *J* = 7.2 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.0, 139.0, 138.79, 138.76, 137.9, 136.5, 136.0, 135.9, 135.7, 134.3, 134.1, 132.2, 131.7, 130.2, 130.1, 130.0, 129.5, 129.3, 129.1, 128.8, 128.7, 127.9, 127.7, 126.8, 126.3, 125.9, 124.8, 123.3, 122.94, 122.89 ppm; HRMS (ESI): *m/z* Calcd for $C_{34}H_{17}$ $[M-H_2ClS]^+$: 425.1325, Found 425.2155.

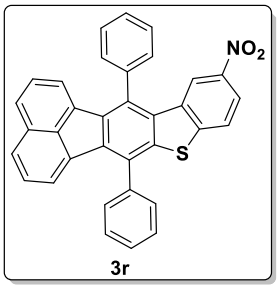
11-Chloro-7,13-bis(4-methoxyphenyl)benzo[*b*]fluorantheno[8,9-*d*]thiophene 3q



To a solution of cyclopentadienone **1g** (0.21 g, 0.50 mmol) in xylenes (10 mL), 5-chlorobenzo[*b*]thiophene *S*,*S*-dioxide **2e** (0.10 g, 0.50 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3q** (0.15 g, 59%) as a green solid. R_f = 0.15 (eluent: 5% ethyl acetate

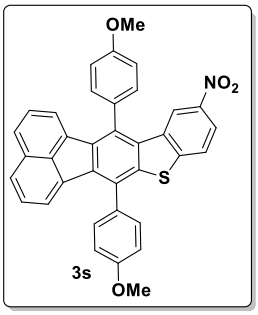
in hexane); mp 286-288 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78-7.72 (m, 2H, ArH), 7.66-7.61 (m, 3H, ArH), 7.52 (d, *J* = 8.1 Hz, 2H, ArH), 7.42-7.37 (m, 2H, ArH), 7.34-7.26 (m, 3H, ArH), 7.23-7.20 (m, 2H, ArH), 7.07 (d, *J* = 7.2 Hz, 1H, ArH), 6.91 (s, 1H, ArH), 6.71 (d, *J* = 6.9 Hz, 1H, ArH), 4.07 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.2, 160.1, 142.6, 138.8, 138.2, 136.8, 136.5, 136.2, 136.0, 134.1, 134.0, 132.1, 131.9, 131.2, 131.0, 130.5, 130.2, 130.1, 130.0, 127.9, 127.7, 126.7, 126.2, 125.9, 124.8, 123.3, 123.9, 115.9, 115.7, 114.9, 55.7, 55.4 ppm; HRMS (ESI): *m/z* Calcd for $C_{34}H_{17}$ $[M\text{-}C_2H_6O_2ClS]^+$: 425.1401, Found 425.2154.

11-Nitro-7,13-diphenylbenzo[*b*]fluorantheno[8,9-*d*]thiophene 3r



To a solution of cyclopentadienone **1e** (0.17 g, 0.47 mmol) in xylenes (10 mL), 5-nitrobenzo[*b*]thiophene *S*,*S*-dioxide **2f** (0.10 g, 0.47 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3r** (0.11 g, 46%) as a yellow solid. R_f = 0.20 (eluent: 5% ethyl acetate in hexane); mp 298-300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.15-8.12 (m, 1H, ArH), 7.82-7.64 (m, 14H, ArH), 7.14-7.33 (m, 2H, ArH), 7.01 (d, *J* = 6.9 Hz, 1H, ArH), 6.71 (d, *J* = 7.2 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.0, 145.3, 142.0, 138.4, 138.3, 136.8, 136.7, 136.5, 136.1, 135.4, 134.6, 134.1, 132.3, 131.7, 130.5, 130.1, 129.6, 129.2, 129.1, 128.8, 128.0, 127.8, 127.2, 126.6, 123.3, 122.7, 120.4, 120.1 ppm; HRMS (ESI): *m/z* Calcd for $C_{34}H_{19}NO_2S$ $[M+]^+$: 505.1136, Found 505.1138.

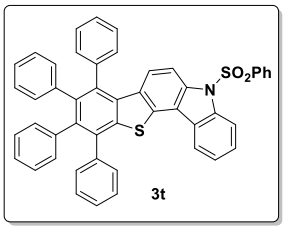
7,13-Bis(4-methoxyphenyl)-11-nitrobenzo[*b*]fluorantheno[8,9-*d*]thiophene 3s



To a solution of cyclopentadienone **1g** (0.19 g, 0.47 mmol) in xylenes (10 mL), 5-nitrobenzo[*b*]thiophene *S*,*S*-dioxide **2f** (0.10 g, 0.47 mmol) was added and refluxed for 24 h.

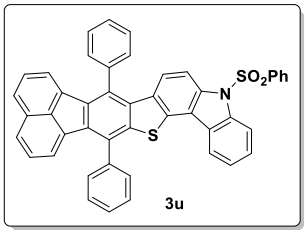
Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded dibenzothiophene **3s** (0.12 g, 44%) as a yellow solid. R_f = 0.20 (eluent: 10% ethyl acetate in hexane); mp 288-290 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.12-8.09 (m, 1H, ArH), 7.79-7.74 (m, 4H, ArH), 7.58 (d, *J* = 8.4 Hz, 2H, ArH), 7.49 (d, *J* = 8.4 Hz, 2H, ArH), 7.42-7.36 (m, 2H, ArH), 7.31 (d, *J* = 8.4 Hz, 2H, ArH), 7.18 (d, *J* = 8.4 Hz, 2H, ArH), 7.09 (d, *J* = 7.2 Hz, 1H, ArH), 6.83 (d, *J* = 6.9 Hz, 1H, ArH), 4.06 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.6, 160.3, 147.0, 145.2, 142.5, 137.0, 136.9, 136.8, 136.3, 135.6, 134.2, 134.1, 132.2, 132.0, 130.6, 130.4, 130.3, 130.0, 129.9, 128.0, 127.8, 127.0, 126.5, 123.2, 123.2, 122.6, 120.4, 120.0, 116.1, 115.0, 55.8, 55.4 ppm; HRMS (ESI): *m/z* Calcd for $C_{36}H_{23}NO_4S$ $[M+]^+$: 565.1348, Found 565.1353.

8,9,10,11-Tetraphenyl-5-(phenylsulfonyl)-5*H*-benzo[4,5]thieno[3,2-*c*]carbazole 3t



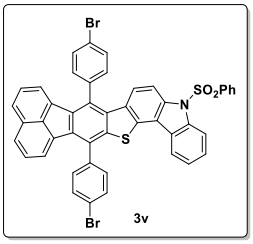
The dibenzothiophene **3t** (0.11 g, 61%) was prepared according to the general procedure using cyclopentadienone **1a** (0.09 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2g** (0.10 g, 0.25 mmol) as a colorless solid. R_f = 0.35 (eluent: 5% ethyl acetate in hexane); mp 210-212 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.1 Hz, 1H, ArH), 8.62 (s, 2H, ArH), 8.54-8.47 (m, 3H, ArH), 7.87-7.84 (m, 2H, ArH), 7.52-7.41 (m, 3H, ArH), 7.34-7.28 (m, 3H, ArH), 7.27-7.11 (m, 10H, ArH), 7.00-6.92 (m, 4H, ArH), 6.88 (s, 1H, ArH), 6.80-6.78 (m, 2H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.8, 142.6, 141.6, 140.5, 140.2, 139.5, 139.3, 139.2, 138.5, 134.2, 132.2, 132.0, 131.5, 131.1, 130.6, 130.4, 130.0, 129.4, 129.0, 128.4, 128.2, 127.9, 127.5, 127.2, 126.9, 126.8, 126.7, 126.5, 126.0, 125.2, 124.4, 123.6, 123.4, 122.7, 122.0, 115.6, 115.1 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.8, 131.8, 131.6, 130.0, 129.6, 129.1, 128.1, 127.7, 127.5, 126.8, 126.5, 126.4, 126.1, 125.6, 124.8, 124.0, 123.2, 123.0, 122.3, 115.2, 114.7 ppm; HRMS (ESI): *m/z* Calcd for $C_{48}H_{31}NO_2S_2$ $[M+H]^+$: 718.1874, Found 718.1887.

8,15-Diphenyl-5-(phenylsulfonyl)-5*H*-fluorantheno[8',9':4,5]thieno[3,2-*c*]carbazole 3u



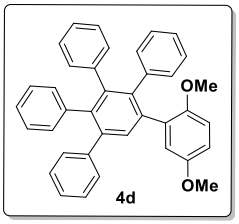
The dibenzothiophene **3u** (0.11 g, 65%) was prepared according to the general procedure using cyclopentadienone **1e** (0.09 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2g** (0.10 g, 0.25 mmol) as a green solid. R_f = 0.35 (eluent: 5% ethyl acetate in hexane); mp 174-176 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.27 (d, *J* = 4.5 Hz, 1H, ArH), 8.72-8.72 (m, 1H, ArH), 8.70-8.54 (m, 2H, ArH), 8.52 (d, *J* = 9.0 Hz, 1H, ArH), 8.41 (d, *J* = 4.8 Hz, 1H, ArH), 8.26 (s, 1H, ArH), 7.98-7.87 (m, 3H, ArH), 7.78-7.70 (m, 3H, ArH), 7.69-7.65 (m, 3H, ArH), 7.55-7.50 (m, 3H, ArH), 7.49-7.43 (m, 2H, ArH), 7.37-7.31 (m, 4H, ArH), 7.18 (s,1H, ArH), 7.12 (d, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.5, 136.7, 136.3, 135.6, 133.9, 132.7, 130.4, 130.1, 130.0, 129.9, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7, 128.1, 128.0, 127.9, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.7, 126.6, 126.5, 126.4, 124.3, 123.8, 123.7, 123.4, 123.3, 123.1, 122.9, 122.7, 122.5, 121.7, 115.2, 114.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{46}H_{27}NO_2S_2$ $[M+H]^+$: 690.1561, Found 690.1572.

8,15-Bis(4-bromophenyl)-5-(phenylsulfonyl)-5*H*-fluorantheno[8',9':4,5]thieno[3,2-*c*]carbazole 3v



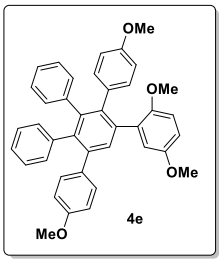
The dibenzothiophene **3v** (0.14 g, 67%) was prepared according to the general procedure using cyclopentadienone **1f** (0.13 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2g** (0.10 g, 0.25 mmol) as a green solid. R_f = 0.30 (eluent: 10% ethyl acetate in hexane); mp 240-242 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.9 Hz, 1H, ArH), 8.11 (d, *J* = 8.7 Hz, 1H, ArH), 7.80-7.68 (m, 7H, ArH), 7.60-7.57 (m, 2H, ArH), 7.50-7.45 (m, 4H, ArH), 7.42-7.31 (m, 6H, ArH), 7.25-7.20 (m, 3H, ArH), 6.82 (d, *J* = 7.2 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.2, 138.0, 137.7, 137.0, 136.9, 136.6, 136.0, 135.9, 135.4, 135.2, 133.8, 132.1, 131.9, 131.7, 130.8, 129.5, 129.0, 127.80, 127.74, 127.5, 127.1, 126.5, 126.3, 124.1, 123.4, 123.0, 122.1, 121.5, 121.1, 119.9, 113.3, 114.4 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.7, 132.1, 131.9, 131.7, 130.9, 130.8, 129.5, 129.0, 127.8, 127.7, 127.5, 127.1, 126.5, 124.1, 123.4, 123.1, 121.1, 119.9, 115.3, 114.4 ppm; HRMS (ESI): *m/z* Calcd for $C_{46}H_{25}Br_2NO_2S_2$ $[M+H]^+$: 845.9772, Found 845.9792.

2,5-Dimethoxy-3',4',5'-triphenyl-1,1':2',1''-terphenyl 4d



The pentaaryl **4d** (0.16 g, 67%) was prepared following the general procedure using cyclopentadienone **1a** (0.17 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a colorless solid. R_f = 0.15 (eluent: 10% ethyl acetate in hexane); mp 220-222 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.45 (s, 1H, ArH), 9.03 (d, *J* = 8.4 Hz, 1H, ArH) 7.39 (d, *J* = 8.4 Hz, 1H, ArH) 7.17-7.15 (m, 2H, ArH), 7.08-7.02 (m, 7H, ArH), 7.00-6.91 (m, 5H, ArH), 6.87-6.81 (m, 5H, ArH), 6.72-6.69 (m, 2H, ArH), 3.93 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.6, 152.0, 142.99, 142.96, 140.4, 140.1, 138.3, 132.2, 131.7, 130.7, 130.7, 130.5, 130.2, 129.8, 129.6, 128.4, 127.8, 127.4, 127.1, 126.8, 126.0, 125.6, 125.5, 124.8, 124.0, 123.2, 111.6, 111.4, 57.0 (OCH_3), 56.8 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.1, 131.7, 130.1, 129.7, 128.4, 127.7, 127.3, 127.0, 126.7, 125.9, 125.9, 125.5, 125.4, 124.8, 111.5, 111.3, 56.9, 56.7 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{30}O_2$ $[M+]^+$: 518.2246, Found 518.2217.

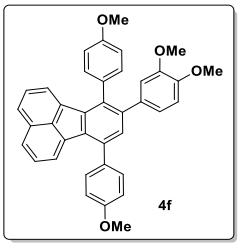
6,9-Dimethoxy-1,4-bis(4-methoxyphenyl)-2,3-diphenyldibenzo[*b*,*d*]thiophene 4e



The pentaarylbenzene **4e** (0.17 g, 68%) was prepared according to the general procedure using cyclopentadienone **1b** (0.19 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a colorless solid. R_f = 0.25 (eluent: 20% ethyl acetate in hexane); mp 246-248 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 1H, ArH), 7.13 (s, 1H, ArH), 6.98 (d, *J* = 8.7 Hz, 2H, ArH), 6.83-6.82 (m, 8H, ArH), 6.77-6.75 (m, 3H, ArH), 6.69-6.57 (m, 4H, ArH), 6.52-6.49 (m, 1H, ArH), 6.33 (d, *J* = 8.7 Hz, 2H, ArH), 3.61 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.0, 157.2, 153.0, 150.6, 141.4, 140.7, 140.4, 139.7, 139.6, 139.2, 137.8, 134.3, 132.8, 131.7, 131.6, 131.1, 126.9, 126.7, 126.5, 125.5, 125.2, 117.4, 113.5, 113.0, 111.4, 55.7 (OCH_3), 55.6 (OCH_3), 55.1 (OCH_3), 54.9 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.6, 131.1, 126.9, 126.7, 125.5, 125.2, 117.3, 113.5,

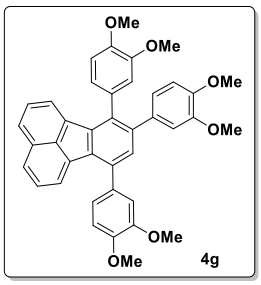
113.0, 111.4, 55.7, 55.6, 55.1, 54.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{40}H_{34}O_4$ $[M+H]^+$: 579.2535, Found 579.2551.

8-(3,4-Dimethoxyphenyl)-7,10-bis(4-methoxyphenyl)fluoranthene 4f



The dibenzothiophene **4f** (0.18 g, 72%) was prepared following the general procedure using cyclopentadienone **1g** (0.18 g, 0.43 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2b** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.35 (eluent: 20% ethyl acetate in hexane); mp 207-209 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H, ArH), 7.64 (d, *J* = 8.7 Hz, 2H, ArH), 7.59 (d, *J* = 8.4 Hz, 2H, ArH), 7.41-7.33 (m, 3H, ArH), 7.29 (d, *J* = 8.1 Hz, 3H, ArH), 7.23-7.17 (m, 3H, ArH), 7.04 (d, *J* = 6.9 Hz, 1H, ArH), 6.76 (d, *J* = 6.9 Hz, 1H, ArH), 6.48 (s, 1H, ArH), 4.02 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3) ppm;^{13}C-NMR (75 MHz,$CDCl_3$): δ 146.9, 141.3, 136.9, 135.8, 134.3, 133.8, 133.2, 133.0, 132.5, 131.9, 131.6, 131.2, 130.8, 130.4, 129.9, 129.7, 127.8, 127.7, 126.2, 125.9, 122.5, 122.4, 115.2, 114.7, 106.8, 104.1, 56.0 (OCH_3), 55.6 (OCH_3), 55.4 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.9, 130.5, 127.9, 127.7, 126.2, 125.9, 122.5, 122.4, 115.2, 114.7, 106.8, 104.0, 56.1, 55.6, 55.4, 55.2 ppm; HRMS (EI): *m/z* Calcd for $C_{38}H_{30}O_4$ $[M+H]^+$: 551.2222, Found 551.2241.

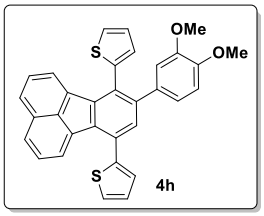
7,8,10-Tris(3,4-dimethoxyphenyl)fluoranthene 4g



The fluoranthene **4g** (0.20 g, 71%) was prepared according to the general procedure using cyclopentadienone **1h** (0.21 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2b** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.36 (eluent: 25% ethyl acetate in hexane); mp 212-214 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H, ArH), 7.40-7.33 (m, 3H, ArH), 7.29-7.22 (m, 4H, ArH), 7.20-7.14 (m, 3H, ArH), 7.07 (d, *J* = 7.2 Hz, 1H, ArH), 6.91 (d, *J* = 9.3 Hz 1H, ArH), 6.79 (d, *J* = 7.2 Hz, 1H, ArH), 6.48 (s, 1H, ArH), 4.07 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.91

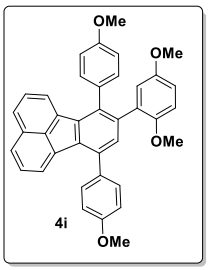
(s, 3H, OCH_3), 3.90 (s, 3H, OCH_3) 3.87 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.0, 148.7, 147.0, 141.1, 136.7, 136.1, 135.7, 134.2, 133.8, 133.2, 132.6, 132.0, 131.8, 131.4, 129.9, 129.6, 127.9, 127.8, 126.3, 126.1, 122.63, 122.55, 121.6, 121.5, 121.4, 112.4, 112.2, 111.8, 111.8, 106.8, 104.1, 56.3 (OCH_3), 56.1 (OCH_3), 56.0 (OCH_3), 55.3 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 127.9, 127.8, 126.3, 126.1, 122.6, 122.5, 121.6, 121.4, 121.4, 112.4, 112.3, 111.7, 106.8, 104.0, 56.2, 56.1, 55.9, 55.2 ppm; HRMS (EI): *m/z* Calcd for $C_{40}H_{34}O_6$ $[M+H]^+$: 611.2434, Found 611.2448.

7,10-Bis(4-methoxyphenyl)-8-phenylfluoranthene 4h



The fluoranthene **4h** (0.16 g, 72%) was prepared according to the general procedure using cyclopentadienone **1i** (0.16 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2b** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.18 (eluent: 10% ethyl acetate in hexane); mp 218-220 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78-7.76 (m, 2H, ArH), 7.52-7.48 (m, 2H, ArH), 7.45-7.37 (m, 5H, ArH), 7.25-7.22 (m, 1H, ArH), 7.14-7.07 (m, 2H, ArH), 6.95-6.77 (m, 4H, ArH), 3.85 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3) ppm;^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.9, 141.8, 141.3, 140.3, 140.1, 136.8, 136.0, 135.4, 133.2, 133.0, 131.9, 131.1, 129.7, 129.0, 128.1, 127.8, 127.7, 127.4, 127.2, 127.1, 126.9, 126.6, 126.0, 123.6, 123.1, 121.9, 113.0, 110.6, 55.8 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.9, 128.2, 127.8, 127.5, 127.2, 127.0, 126.6, 126.1, 123.7, 123.2, 122.0, 113.0, 110.6, 55.8 ppm; HRMS (ESI): *m/z* Calcd for $C_{32}H_{22}O_2S_2$ $[M+H]^+$: 503.1139, Found 503.1151.

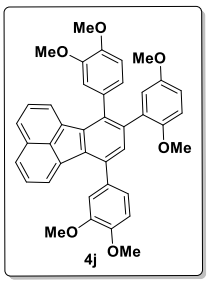
8-(2,5-Dimethoxyphenyl)-7,10-bis(4-methoxyphenyl)fluoranthene 4i



The fluoranthene **4i** (0.19 g, 76%) was prepared following the general procedure using cyclopentadienone **1g** (0.18 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.30 (eluent: 20% ethyl acetate in hexane); mp 194-196 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.2 Hz, 1H, ArH), 7.85-7.77 (m, 2H, ArH), 7.75-7.69

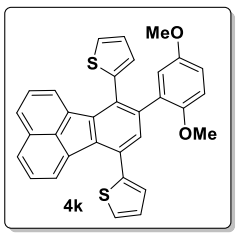
(m, 2H, ArH), 7.65-7.55 (m,2H,ArH), 7.39-7.36 (m, 1H, ArH), 7.33-7.28 (m, 2H,ArH), 7.24 (s, 1H, ArH), 7.08-7.04 (m, 2H, ArH), 6.87 (d, *J* = 8.4 Hz, 1H, ArH) 6.81 (d, *J* = 7.2 Hz, 1H, ArH), 6.76-6.69 (m, 2H, ArH), 6.45-6.61 (m, 1H, ArH), 3.93 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.6, 159.2, 158.6, 152.9, 150.9, 138.1, 138.0, 137.1, 136.8, 136.7, 136.3, 136.0, 133.2, 133.1, 131.8, 131.5, 131.1, 130.9, 130.4, 130.3, 129.7, 128.4, 127.6, 127.5, 126.4, 123.2, 122.7, 120.4, 117.4, 114.1, 113.9, 113.2, 113.2, 111.4, 55.7 (OCH_3), 55.7 (OCH_3), 55.4 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.5, 130.9, 130.4, 130.4, 127.6, 127.5, 126.4, 123.2, 122.8, 120.5, 117.4, 114.1, 113.9, 113.25, 113.19, 111.3, 55.7, 55.4, 55.2 ppm; HRMS (ESI): *m/z* Calcd for $C_{38}H_{30}O_4$ $[M+H]^+$: 551.2222, Found 551.2244.

8-(2,5-Dimethoxyphenyl)-7,10-bis(3,4-dimethoxyphenyl)fluoranthene 4j



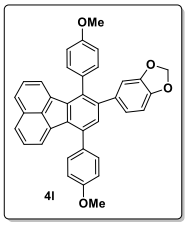
The fluoranthene **4j** (0.20 g, 71%) was prepared according to the general procedure using cyclopentadienone **1h** (0.21 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.20 (eluent: 25% ethyl acetate in hexane); mp 240-242 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74-7.69 (m, 2H, ArH), 7.39-7.31 (m, 3H, ArH), 7.29-7.24 (m, 3H, ArH), 7.06-7.03 (m, 1H, ArH), 6.97-6.84 (m, 4H, ArH), 6.75-6.69 (m, 3H, ArH), 3.99 (s, 3H OCH_3), 3.91 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.67 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.6, 148.9, 148.6, 148.2, 138.0, 137.3, 136.8, 136.8, 136.3, 136.1, 133.7, 133.1, 132.0, 131.3, 131.3, 129.8, 127.6, 127.4, 126.5, 123.3, 122.9, 122.3, 121.4, 117.7, 113.7, 113.3, 113.0, 111.7, 111.6, 111.0, 56.1 (OCH_3), 56.0 (OCH_3), 55.8 (OCH_3), 55.7 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.3, 127.6, 127.4, 126.5, 123.3, 122.8, 122.3, 121.4, 117.7, 113.7, 113.3, 113.0, 111.7, 111.5, 110.9, 56.0, 55.9, 55.8, 55.8 ppm; HRMS (EI): *m/z* Calcd for $C_{40}H_{34}O_6$ $[M+H]^+$: 611.2434, Found 611.2444.

2,2'-(8-(2,5-Dimethoxyphenyl)fluoranthene-7,10-diyl)dithiophene 4k



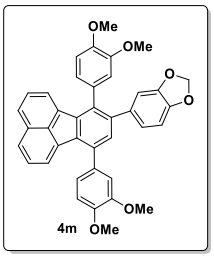
The fluoranthene **4k** (0.16 g, 73%) was prepared according to the general procedure using cyclopentadienone **1i** (0.16 g, 0.44 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2c** (0.10 g, 0.44 mmol) as a green solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp 132-134 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71-7.66 (m, 2H, ArH), 7.46 (d, *J* = 6.9 Hz, 1H, ArH), 7.40-7.37 (m, 3H, ArH), 7.34-7.22 (m, 3H, ArH), 7.16-7.14 (m, 1H, ArH), 6.96 (d, *J* = 3.3 Hz, 2H, ArH), 6.75 (d, *J*=7.2 Hz, 1H, ArH), 6.70-6.69 (m, 1H, ArH), 6.66-6.61 (m, 2H, ArH), 3.62 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.8, 151.0, 141.4, 139.9, 139.5, 139.1, 137.0, 136.0, 135.6, 132.9, 132.0, 130.6, 130.3, 130.2, 129.7, 127.7, 127.6, 127.4, 127.2, 126.9, 126.6, 125.9, 125.8, 123.3, 123.0, 117.1, 113.6, 111.4, 55.8 (OCH_3), 55.7 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 132.0, 127.7, 127.6, 127.4, 127.2, 126.9, 126.6, 125.9, 125.8, 123.3, 123.0, 117.1, 113.6, 111.4, 55.8, 55.7 ppm; HRMS (ESI): *m/z* Calcd for $C_{32}H_{22}O_2S_2$ $[M+H]^+$: 503.1139, Found 503.1136.

5-(7,10-Bis(4-methoxyphenyl)fluoranthen-8-yl)benzo[*d*][1,3]dioxole 4l



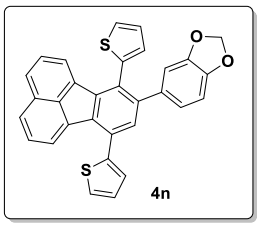
The fluoranthene **4l** (0.18 g, 71%) was prepared according to the general procedure using cyclopentadienone **1g** (0.19 g, 0.46 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.46 mmol) as a green solid. R_f = 0.30 (eluent: 10% ethyl acetate in hexane); mp 176-178 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.03-7.89 (m, 1H, ArH), 7.58-7.55 (m, 2H, ArH), 7.48 (d, *J* = 7.8 Hz, 2H, ArH), 7.24-7.11 (m, 6H, ArH), 6.94 (d, *J* = 7.8 Hz, 2H, ArH), 6.82 (d, *J* = 7.8 Hz, 2H, ArH), 6.64-6.52 (m, 3H,ArH), 5.74 (s, 2H, OCH_2), 3.78 (s, 3H, OCH_3),3.73 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 158.8, 146.9, 146.0, 140.7, 138.6, 137.5, 136.8, 136.1, 135.7, 135.2, 133.1, 132.5, 131.6, 131.34, 131.30, 130.2, 129.7, 128.3, 127.6, 127.5, 126.5, 123.5, 123.3, 122.8, 121.9, 114.02, 113.99, 110.5, 107.6, 100.8 (OCH_2), 55.4 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.4, 131.3, 127.7, 127.6, 126.6, 126.6, 123.6, 123.3, 122.8, 114.0, 110.5, 107.6, 100.8, 55.4, 55.2 ppm; HRMS (ESI): *m/z* Calcd for $C_{37}H_{26}O_4$ $[M+H]^+$: 535.1909, Found 535.1906.

5-(7,10-Bis(3,4-dimethoxyphenyl)fluoranthen-8-yl)benzo[*d*][1,3]dioxole 4m



The fluoranthene **4m** (0.17 g, 61%) was prepared according to the general procedure using cyclopentadienone **1h** (0.23 g, 0.47 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.47 mmol) as a green solid. R_f = 0.25 (eluent: 20% ethyl acetate in hexane); mp 215-217 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67-7.63 (m, 2H, ArH), 7.31-7.25 (m, 2H, ArH), 7.22-7.14 (m, 4H, ArH), 6.99-6.96 (m, 2H, ArH), 6.86 (s, 2H, ArH), 6.79-6.77 (m, 2H, ArH), 6.66-6.63 (m, 1H,ArH), 6.59-6.56 (m, 1H, ArH), 5.81 (s, 2H, OCH_2), 3.93 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.2, 148.9, 148.5, 146.9, 146.2, 140.7, 138.5, 137.6, 136.7, 136.0, 135.8, 135.3, 133.6, 133.2, 131.8, 131.1, 129.8, 127.6, 127.5, 126.6, 126.6, 123.4, 123.3, 122.9, 122.7, 121.3, 113.9, 112.8, 111.8, 111.5, 110.4, 107.6, 100.8 (OCH_2), 56.1 (OCH_3), 56.0 (OCH_3), 55.9 (OCH_3), 55.9 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.1, 127.6, 127.5, 126.6, 123.4, 123.3, 122.9, 122.6, 121.3, 113.9, 112.8, 111.7, 111.5, 110.4, 108.5, 107.6, 100.8, 56.1, 56.0, 55.9, 55.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{39}H_{30}O_6$ $[M+H]^+$: 595.2121, Found 595.2137.

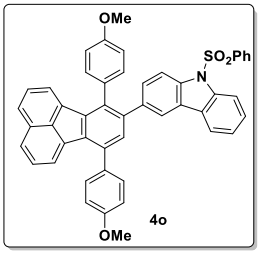
5-(7,10-Di(thiophen-2-yl)fluoranthen-8-yl)benzo[*d*][1,3]dioxole 4n



The fluoranthene **4n** (0.17 g, 71%) was prepared according to the general procedure using cyclopentadienone **1i** (0.17 g, 0.47 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2d** (0.10 g, 0.47 mmol) as a green solid. R_f = 0.35 (eluent: 5% ethyl acetate in hexane); mp 224-226 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.80-7.76 (m, 2H, ArH), 7.52-7.50 (m, 2H, ArH), 7.46-7.36 (m, 6H, ArH),7.24-7.23 (m, 1H, ArH), 7.16-7.13 (m, 1H, ArH), 7.10-7.09 (m, 1H, ArH), 6.85-6.79 (m, 2H, ArH), 6.72-6.69 (m, 1H, ArH), 5.93 (s, 2H, OCH_2) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.0, 146.4, 141.8, 141.2, 140.2, 139.6, 136.8, 135.9, 135.3, 134.5, 133.0, 131.9, 130.9, 129.7, 129.1, 128.1, 127.8, 127.6, 127.3, 127.1, 127.0, 126.9, 126.5, 126.0, 123.5, 123.2, 123.1, 110.1, 107.6, 100.9 (OCH_2) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.9, 128.1, 127.8, 127.6,

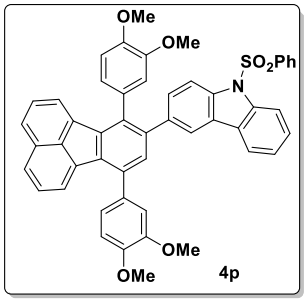
127.3, 127.1, 127.0, 126.9, 126.5, 126.0, 123.5, 123.2, 123.1, 110.1, 107.6, 110.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{31}H_{18}O_2S_2$ $[M+H]^+$: 487.0826, Found 487.0817.

4-(7,10-Bis(4-methoxyphenyl)fluoranthen-8-yl)-9-(phenylsulfonyl)-9*H*-carbazole 4o



The fluoranthene **4o** (0.13 g, 72%) was prepared according to the general procedure using cyclopentadienone **1g** (0.10 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2e** (0.10 g, 0.25 mmol) as a green solid. R_f = 0.25 (eluent: 15% ethyl acetate in hexane); mp 220-212 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.1 Hz, 1H, ArH), 8.09 (d, *J* = 8.4 Hz, 1H, ArH), 7.79-7.72 (m, 6H, ArH), 7.63 (d, *J* = 8.7 Hz, 2H, ArH), 7.48-7.43 (m, 2H, ArH), 7.40-7.38 (m, 2H, ArH), 7.35-7.29 (m, 6H, ArH), 7.25-7.23 (m, 2H, ArH), 7.09 (d, *J* = 8.7 Hz, 2H, ArH), 6.89-6.83 (m, 3H, ArH), 3.93 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.4, 158.8, 140.6, 138.4, 137.8, 137.6, 137.4, 136.9, 136.8, 136.1, 136.0, 135.9, 133.7, 133.2, 133.1, 131.4, 131.44, 131.36, 130.3, 129.8, 129.7, 129.0, 127.7, 127.6, 127.3, 126.6, 126.5, 126.1, 124.0, 123.4, 122.9, 121.2, 120.0, 115.2, 114.2, 114.1, 113.9, 55.4 (OCH_3), 55.2 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.7, 131.4, 131.4, 130.3, 129.7, 129.0, 127.7, 127.6, 127.3, 126.7, 126.5, 124.0, 123.4, 122.9, 121.2, 120.0, 115.2, 114.2, 114.1, 113.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{48}H_{33}NO_4S$ $[M+H]^+$: 720.2209, Found 720.2214.

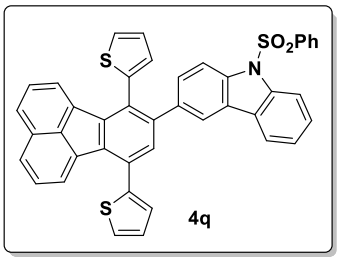
4-(7,10-Bis(3,4-dimethoxyphenyl)fluoranthen-8-yl)-9-(phenylsulfonyl)-9*H*-carbazole 4p



The fluoranthene **4p** (0.10 g, 63%) was prepared according to the general procedure using cyclopentadienone **1h** (0.12 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2e** (0.12 g, 0.25 mmol) as a green solid. R_f = 0.30 (eluent: 25% ethyl acetate in hexane); mp 152-154 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4 Hz, 1H, ArH), 8.13 (d, *J* = 8.7 Hz, 1H, ArH), 7.83-7.75 (m, 6H, ArH), 7.48-7.39 (m, 5H, ArH), 7.350-7.250 (m, 7H, ArH), 7.07 (d, *J* = 7.8 Hz, 1H, ArH), 6.97-6.83 (m, 4H, ArH), 4.01 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3),

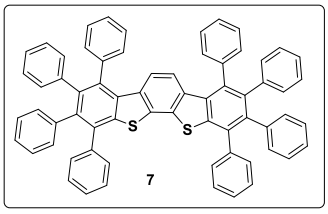
3.59 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.4, 149.2, 148.7, 140.6, 138.9, 138.2, 137.9, 137.5, 136.8, 136.2, 133.8, 133.7, 133.4, 131.9, 131.3, 130.0, 129.6, 129.1, 127.8, 127.7, 127.4, 126.9, 126.7, 126.5, 126.2, 124.1, 123.6, 123.2, 123.0, 121.4, 121.2, 119.9, 115.4, 114.4, 114.2, 113.0, 111.9, 111.7, 56.2 (OCH_3), 56.1 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.8, 131.2, 129.9, 129.0, 127.7, 127.6, 127.4, 126.7, 126.4, 124.0, 123.6, 123.0, 122.7, 121.2, 121.0, 119.8, 115.2, 114.2, 113.5, 112.4, 111.4, 111.1, 56.0, 55.8 ppm; HRMS (ESI): *m/z* Calcd for $C_{50}H_{37}NO_6S$ $[M+H]^+$: 780.2420, Found 780.2432.

4-(7,10-Di(thiophen-2-yl)fluoranthen-8-yl)-9-(phenylsulfonyl)-9*H*-carbazole 4q



The fluoranthene **4q** (0.11 g, 65%) was prepared according to the general procedure using cyclopentadienone **1i** (0.09 g, 0.25 mmol) and benzo[*b*]thiophene *S*,*S*-dioxide **2e** (0.10 g, 0.25 mmol) as a green solid. R_f = 0.35 (eluent: 5% ethyl acetate in hexane); mp 139-142 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1H, ArH), 8.10 (d, *J* = 8.4 Hz, 1H, ArH), 7.79-7.70 (m, 6H, ArH), 7.48-7.32 (m, 8H, ArH), 7.27-7.21 (m, 4H, ArH), 7.18-7.17 (m, 2H, ArH), 7.00-6.99 (m, 2H, ArH), 6.83 (d, *J* = 6.9 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.7, 141.1, 140.2, 139.5, 138.6, 137.8, 137.2, 137.1, 136.6, 135.8, 135.3, 133.7, 133.0, 132.0, 129.7, 129.3, 129.1, 129.0, 128.3, 127.8, 127.7, 127.4, 127.2, 127.2, 127.1, 127.0, 126.6, 126.5, 126.1, 126.0, 124.0, 123.6, 123.2, 120.9, 120.0, 115.2, 114.3 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 133.8, 132.0, 129.1, 129.0, 128.3, 127.8, 127.7, 127.4, 127.2, 127.2, 127.1, 127.0, 126.5, 126.0, 124.0, 123.6, 123.2, 120.9, 120.0, 115.2, 114.3 ppm; HRMS (ESI): *m/z* Calcd for $C_{42}H_{25}NO_2S_3$ $[M+H]^+$: 672.1126, Found 672.1140.

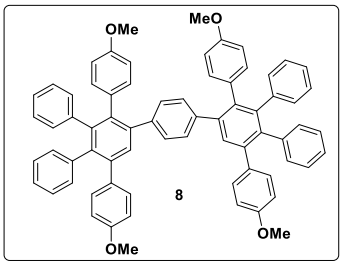
Preparation of bis-dibenzothiophene 7



To a solution of cyclopentadienone **1a** (0.28 g, 0.78 mmol) in xylenes (15 mL), benzodithiophene *S*,*S*-dioxide **5** (0.10 g, 0.39 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded bis-

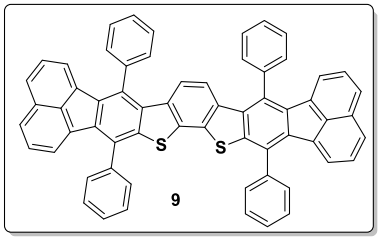
dibenzothiophene **7** (0.19 g, 61%) as a colorless solid. R_f = 0.20 (eluent: 5% ethyl acetate in hexane); mp > 300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.54 (s, 1H, ArH), 7.38-7.20 (m, 12H, ArH), 7.16-7.13 (m, 6H, ArH), 6.95-6.78 (m, 22H, ArH), 6.46 (d, *J* = 8.7 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.8, 141.6, 140.8, 140.6, 140.2, 140.1, 139.9, 139.80, 139.76, 139.73, 139.68, 139.6, 139.3, 139.0, 138.6, 137.2, 135.1, 134.4, 132.2, 131.6, 131.5, 131.4, 131.4, 130.2, 130.0, 129.9, 128.1, 128.0, 127.6, 127.2, 127.0, 127.0, 126.9, 126.7, 126.6, 126.5, 125.9, 125.7, 125.6, 125.4, 125.3, 124.3, 123.8 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.6, 131.5, 131.5, 131.4, 130.3, 130.0, 129.9, 128.2, 128.0, 127.6, 127.2, 127.0, 127.0, 126.9, 126.7, 126.6, 126.5, 126.3, 125.9, 125.7, 125.6, 125.4, 125.3, 124.3, 123.8 ppm; HRMS (ESI): *m/z* Calcd for $C_{66}H_{42}S_2$ $[M+H]^+$: 899.2806, Found 899.2802.

Preparation of pentacene 8



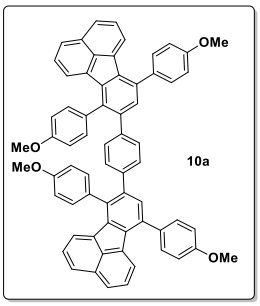
To a solution of cyclopentadienone **1b** (0.35 g, 0.79 mmol) in xylenes (15 mL), benzodithiophene *S,S*-dioxide **5** (0.10 g, 0.39 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded pentacene **8** (0.21g, 56%) as a colorless solid. R_f = 0.25 (eluent: 10% ethyl acetate in hexane); mp >300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 1H, ArH) 7.67 (d, *J* = 5.4Hz, 1H, ArH) 7.44 (d, *J* = 5.4 Hz, 1H, ArH), 7.35-7.28 (m, 4H, ArH), 7.07-7.03 (m, 11H, ArH), 6.96-6.92 (m, 6H, ArH), 6.88-6.85 (m, 4H, ArH) 6.76-6.72 (m, 14H, ArH) 3.75 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 162.8, 160.8, 159.1, 156.5, 155.3, 137.0, 135.9, 132.3, 131.8, 131.2, 130.7, 130.5, 129.8, 128.4, 127.7, 127.4, 127.3, 127.0, 125.6, 124.4, 123.8, 121.2, 119.0, 113.7, 113.6, 55.5 (OCH_3), 55.4 (OCH_3) ppm; HRMS (ESI): *m/z* Calcd for $C_{70}H_{54}O_4$ [M+H]: 958.4022, Found 958.4012.

Preparation of bis-acenaphthodibenzothiophene 9



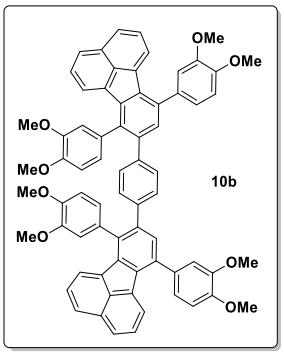
To a solution of cyclopentadienone **1e** (0.35 g, 0.79 mmol) in xylenes (15 mL), benzodithiophene *S,S*-dioxide **5** (0.10 g, 0.39 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded bis-dibenzothiophene **9** (0.18 g, 55%) as a green solid. R_f = 0.20 (eluent: 5% ethyl acetate in hexane); mp > 300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77-7.70 (m, 6H, ArH), 7.59-7.50 (m, 5H, ArH), 7.43-7.38 (m, 9H, ArH), 7.35-7.26 (m, 6H, ArH), 7.24-7.18 (m, 3H, ArH), 7.16-7.14 (m, 4H, ArH), 6.68 (d, *J* = 7.2 Hz, 1H, ArH) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.0, 140.8, 139.3, 138.2, 137.9, 136.6, 136.1, 135.9, 135.7, 133.1, 131.1, 130.3, 129.9, 129.7, 129.1, 128.6, 128.5, 127.8, 127.6, 127.5, 127.3, 126.6, 126.3, 123.3, 122.9 ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.1, 130.3, 129.9, 129.1, 128.6, 128.3, 127.7, 127.6, 127.5, 127.2, 126.5, 126.3, 123.3, 122.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{62}H_{34}S_2$ $[M+H]^+$: 843.2180, Found 843.2195.

1,4-Bis(7,10-bis(4-methoxyphenyl)fluoranthen-8-yl)benzene 10a



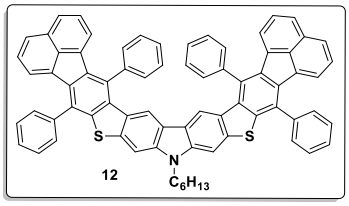
To a solution of cyclopentadienone **1g** (0.31 g, 0.79 mmol) in xylenes (15 mL), benzodithiophene *S,S*-dioxide **5** (0.10 g, 0.39 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded bis-fluoranthene **10a** (0.25 g, 71%) as a green solid. R_f = 0.25 (eluent: 20% ethyl acetate in hexane); mp 294-296 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75-7.70 (m, 4H, ArH), 7.67-7.64 (m, 4H, ArH), 7.56-7.50 (m, 6H, ArH), 7.42-7.34 (m, 7H, ArH), 7.32-7.29 (m, 3H, ArH), 7.24-7.21 (m, 4H, ArH), 7.04 (d, *J* = 6.9 Hz, 2H, ArH), 6.97 (d, *J* = 8.7 Hz, 2H, ArH), 6.63 (d, *J* = 7.2 Hz, 2H, ArH), 4.06 (s, 6H, OCH_3), 4.01 (s, 6H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.2, 160.0, 141.0, 138.0, 137.0, 136.9, 136.2, 135.3, 134.6, 134.1, 134.0, 133.9, 133.8, 133.6, 132.1, 131.9, 131.3, 130.7, 130.1, 128.0, 127.8, 126.5, 126.2, 125.6, 124.7, 122.9, 122.7, 121.5, 120.0, 115.5, 115.0, 55.6 (OCH_3), 55.5 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.5, 130.4, 127.8, 127.6, 126.0, 125.3, 124.5, 122.7, 122.5, 121.2, 119.8, 115.3, 114.8, 55.4, 55.3 ppm; HRMS (ESI): *m/z* Calcd for $C_{66}H_{46}O_4$ $[M+H]^+$: 903.3474, Found 903.3488.

1,4-Bis(7,10-bis(3,4-dimethoxyphenyl)fluoranthen-8-yl)benzene 10b



To a solution of cyclopentadienone **1h** (0.39 g, 0.79 mmol) in xylenes (15 mL), benzodithiophene *S*,*S*-dioxide **5** (0.10 g, 0.39 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded bis-fluoranthene **10b** (0.24 g, 61%) as a green solid. R_f = 0.20 (eluent: 30% ethyl acetate in hexane); mp 218-220 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.79 (s, 2H, ArH), 7.55-7.71 (m, 3H, ArH), 7.59 (d, *J* = 8.4 Hz, 2H, ArH), 7.40-7.301 (m, 9H, ArH), 7.25-7.19 (m, 6H, ArH), 7.05 (d, *J* = 7.8 Hz, 2H, ArH), 6.96-6.88 (m, 6H, ArH), 4.00 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.6, 148.6, 141.0, 139.7, 138.7, 138.1, 137.9, 137.8, 136.9, 136.23, 136.18, 133.7, 133.4, 132.0, 131.6, 130.0, 127.8, 127.7, 126.8, 126.7, 126.4, 123.7, 123.6, 123.2, 123.0, 122.6, 121.5, 114.3, 113.0, 112.0, 111.7, 56.3 (OCH_3), 56.2 (OCH_3), 56.13 (OCH_3), 56.07 (OCH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 131.4, 127.6, 127.5, 126.6, 126.5, 126.2, 123.5, 123.4, 123.4, 122.9, 122.7, 122.4, 121.3, 114.1, 112.8, 112.0, 111.7, 56.1, 56.0, 55.95, 55.90 ppm; HRMS (ESI): *m/z* Calcd for $C_{70}H_{54}O_8$ $[M+H]^+$: 1023.3897, Found 1023.3891.

10-Hexyl-7,13,20,23-tetraphenyl-10*H*-fluorantheno[8',9':4,5]thieno[2,3-*b*]fluorantheno[8',9':4,5]thieno[3,2-*h*]carbazole 12



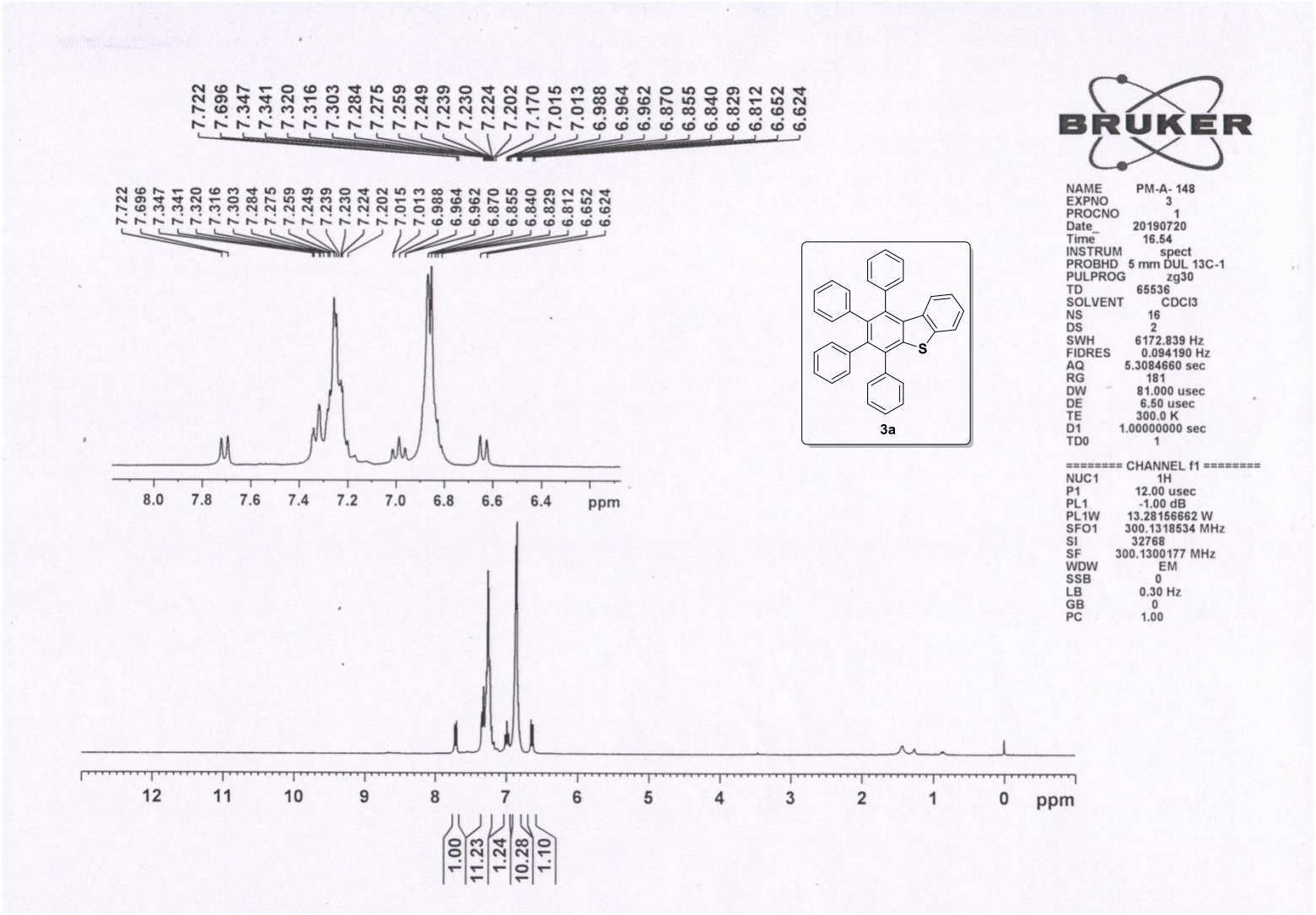
To a solution of cyclopentadienone **1e** (0.17 g, 0.47 mmol) in xylenes (15 mL), benzodithiophene *S*,*S*-dioxide **10** (0.10 g, 0.23 mmol) was added and refluxed for 24 h. Subsequent removal of solvent followed by column chromatographic purification on silica gel afforded bis-fluoranthene **12** (0.14 g, 58%) as a green solid. R_f = 0.30 (eluent: 15% ethyl acetate in hexane); mp > 300 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.99-7.94 (m, 2H, ArH), 7.89-7.84 (m, 4H, ArH), 7.73-7.62 (m, 18H, ArH), 7.61-7.59 (m, 4H, ArH), 7.35-7.28 (m, 4H, ArH), 6.91 (d, *J* = 6.9 Hz, 2H, ArH), 6.25

(d, *J* = 7.2 Hz, 2H, ArH), 4.22 (t, *J* = 6.6 Hz, 2H, N-CH_2), 1.83 (t, *J* = 6.9 Hz, 2H, CH_2), 1.36-1.26 (m, 6H, CH_2) 0.83 (t, *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.0, 140.0, 139.8, 139.2, 137.1, 136.5, 136.1, 134.4, 134.0, 133.6, 132.9, 132.0, 130.2, 130.0, 129.5, 129.38, 129.36, 128.9, 128.6, 127.9, 127.6, 126.3, 126.0, 122.7, 122.4, 121.9, 116.9, 101.2, 43.2 (N-CH_2), 31.6 (CH_2), 28.3 (CH_2), 26.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm; DEPT-135 NMR (75 MHz, $CDCl_3$): δ 130.1, 129.4, 129.31, 129.25, 128.9, 128.6, 128.2, 127.8, 127.5, 126.3, 125.9, 122.6, 122.3, 116.8, 101.1, 43.1, 31.5, 28.2, 26.9, 22.4, 13.9 ppm; HRMS (ESI): *m/z* Calcd for $C_{74}H_{49}NS_2$ $[M+H]^+$: 1016.3385, Found 1016.3398.

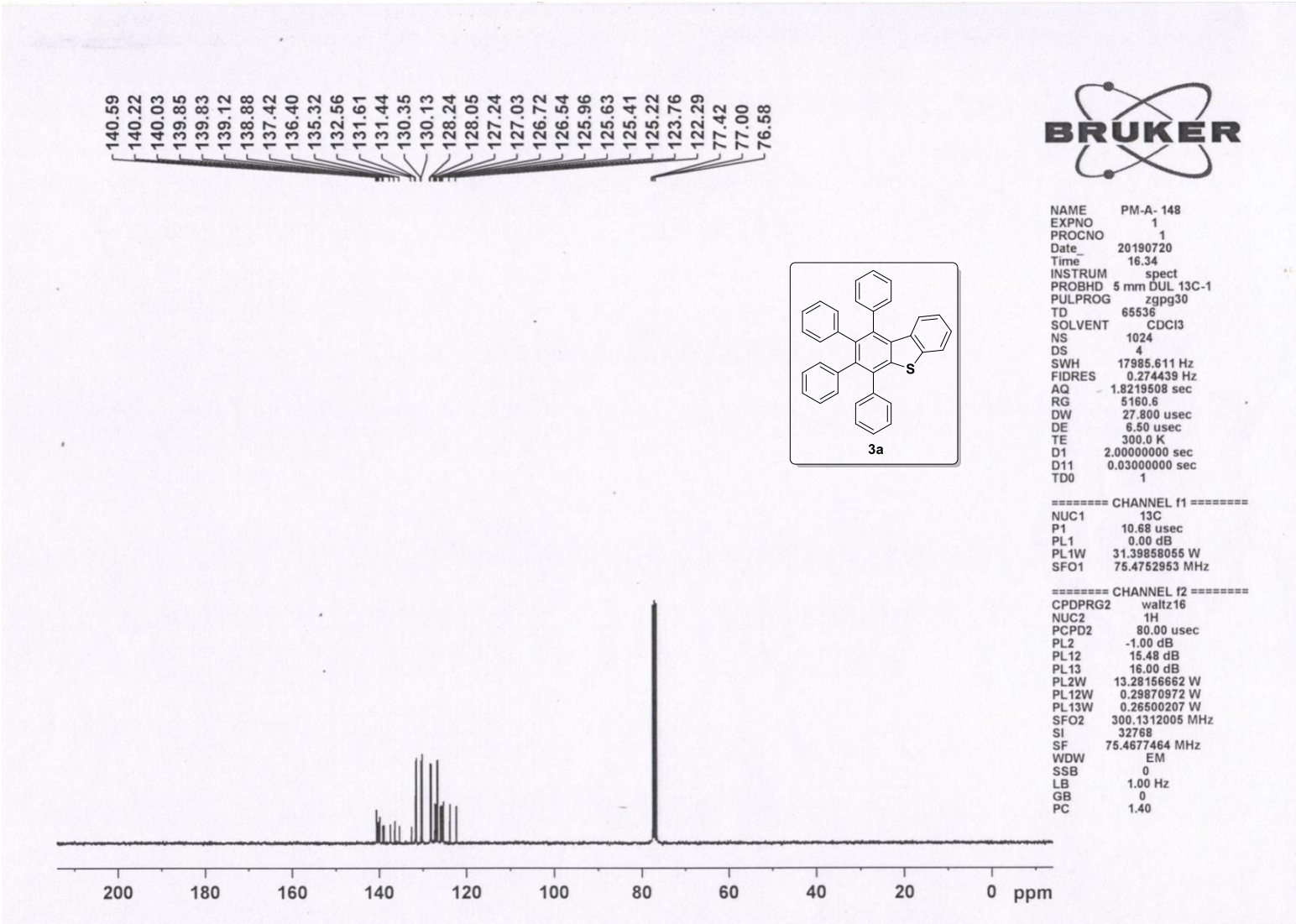
3. References

1. Karunakaran, J.; Mohanakrishnan, A. K. *Org. Lett*.**2018**, *20*, 966.
2. Iniesta, J.; Matsumoto, T.; Thiemann, T. *J. Chem. Res*.**2008**, *2*, 109.
3. Karunakaran, J.; Manikandan, P.; Sathish, M.; Mohanakrishnan, A. K. *ChemistrySelect* **2018**, *3*, 9409.
4. Yang, K.; Pulis, A. P.; Perry, G. J. P.; Procter, D. J. *Org. Lett*. **2018**, *20*, 7498.
5. Bordwell, F. G.; Albisetti, Jr. C. J. *J. Am. Chem. Soc.* **1948**, *17*, 1558

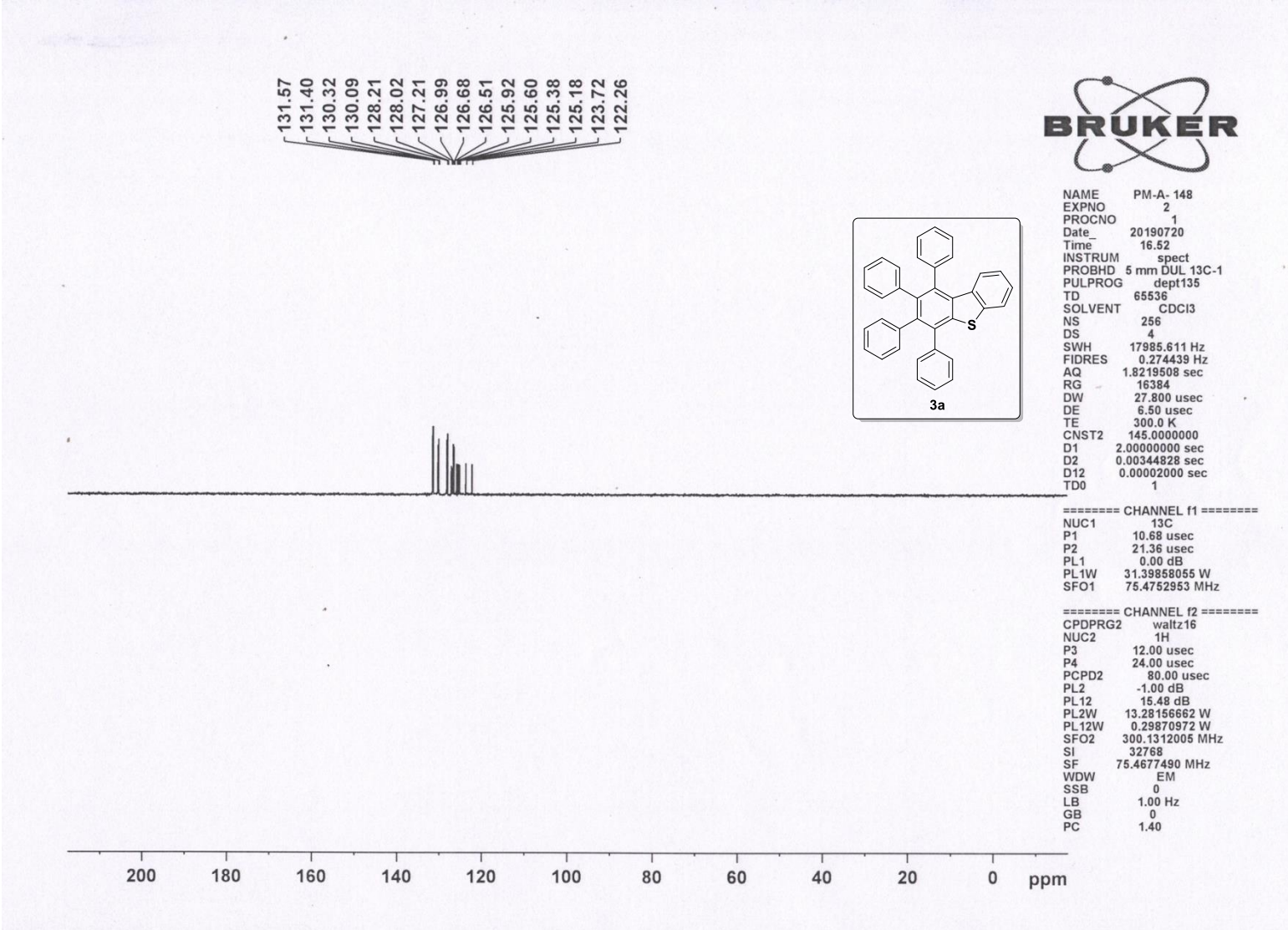
4. ^{1}H, ^{13}C and DEPT-135 NMR SPECTRA



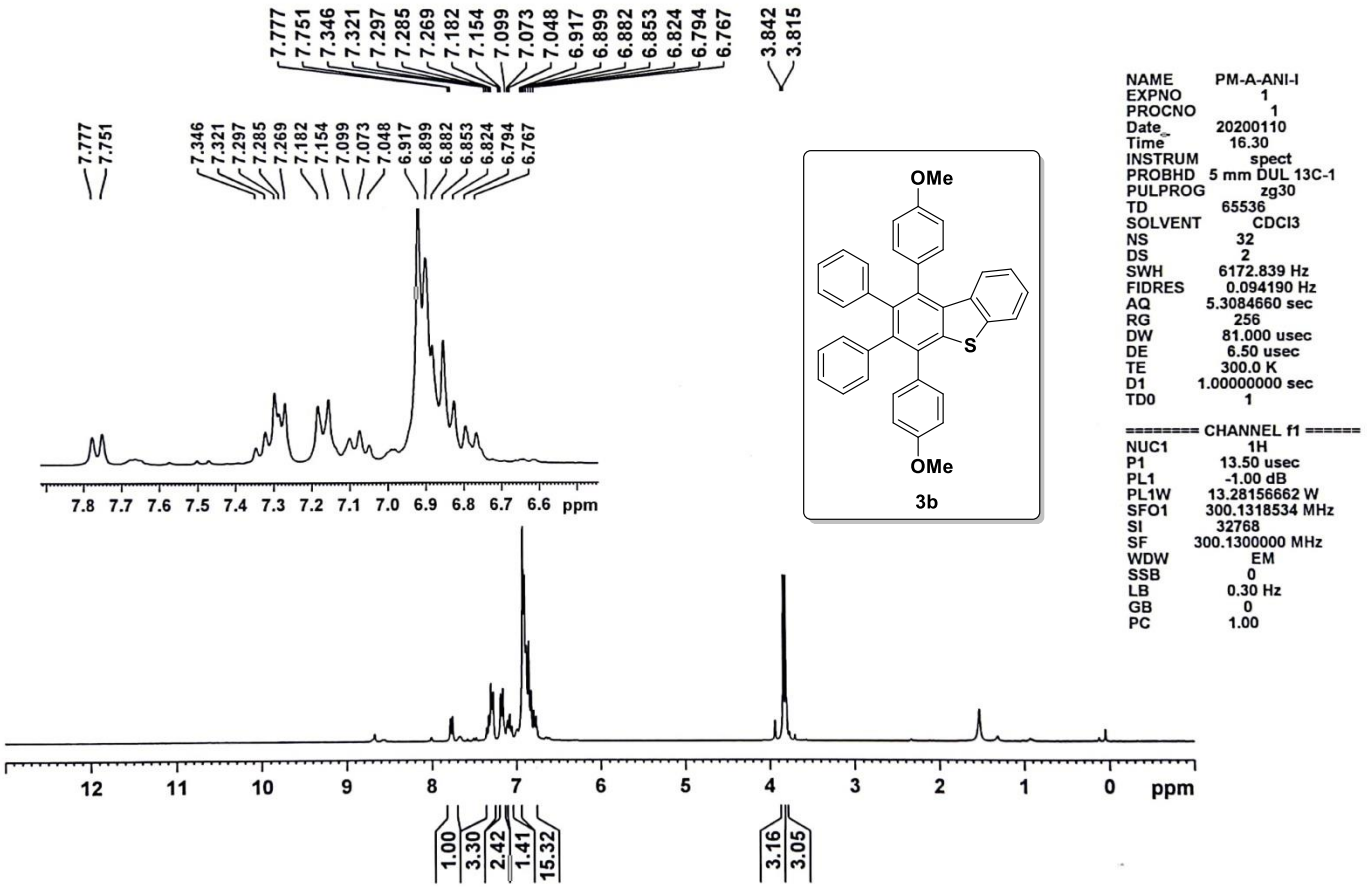
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3a**



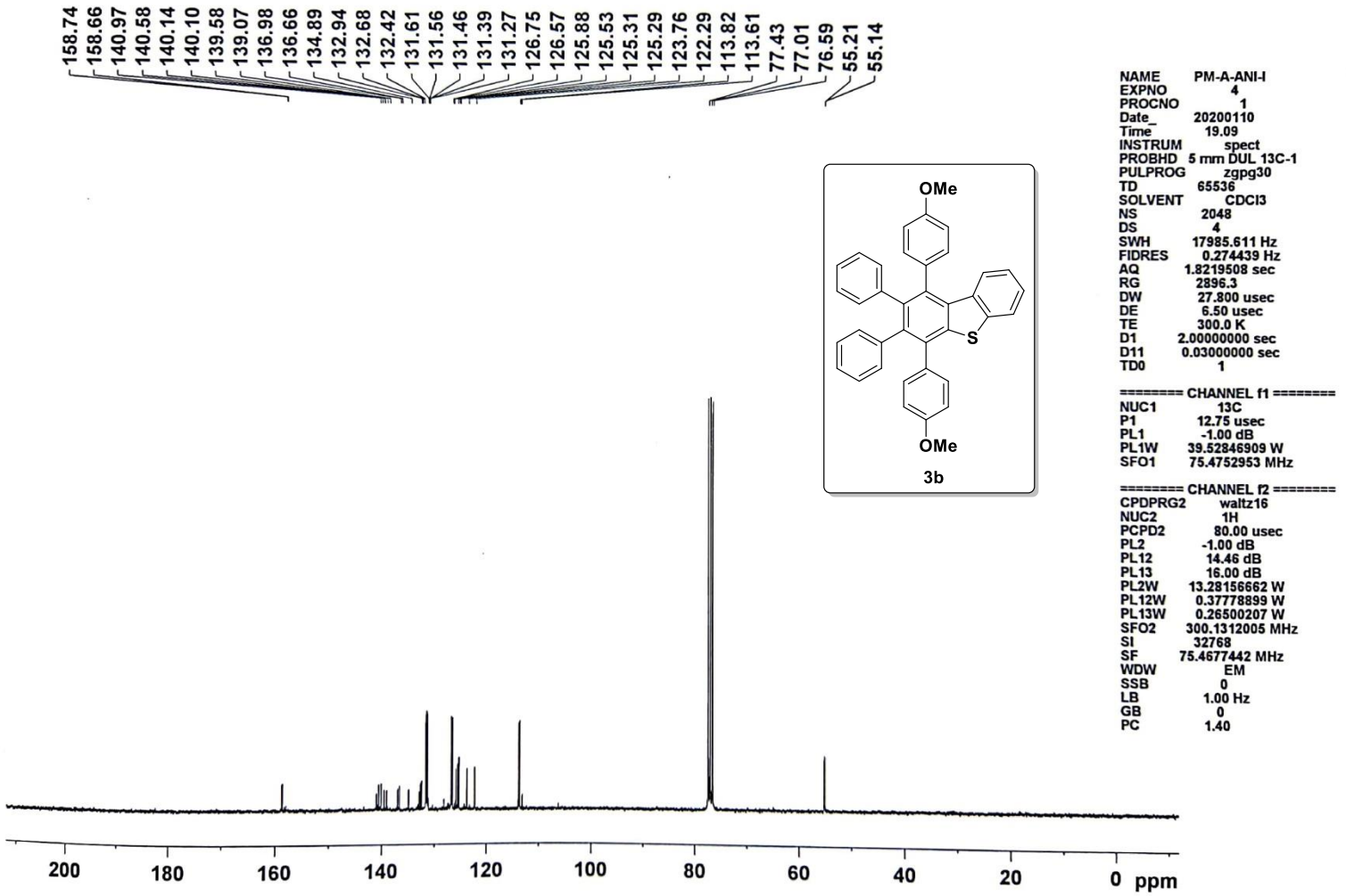
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3a**



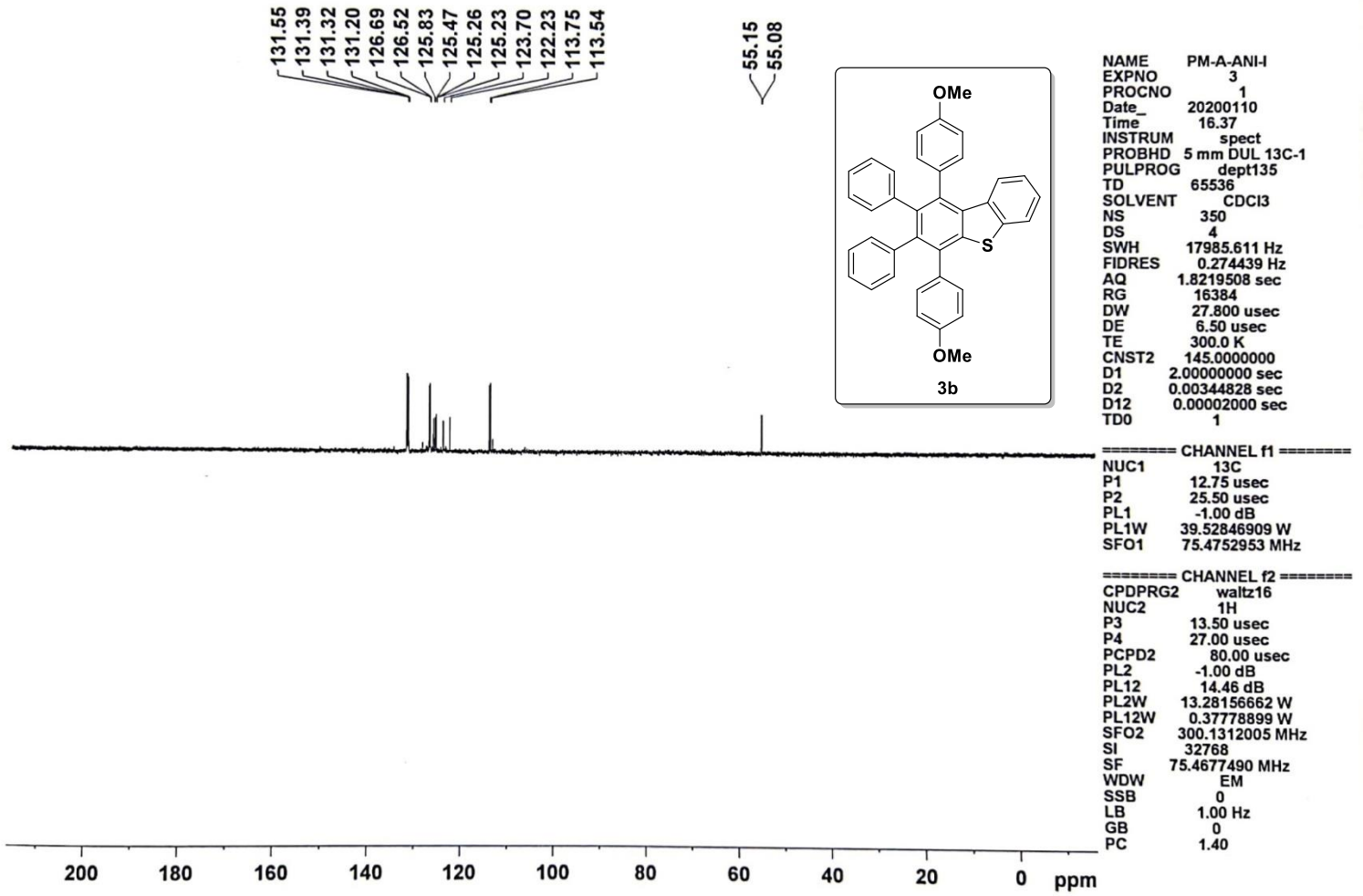
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3a**



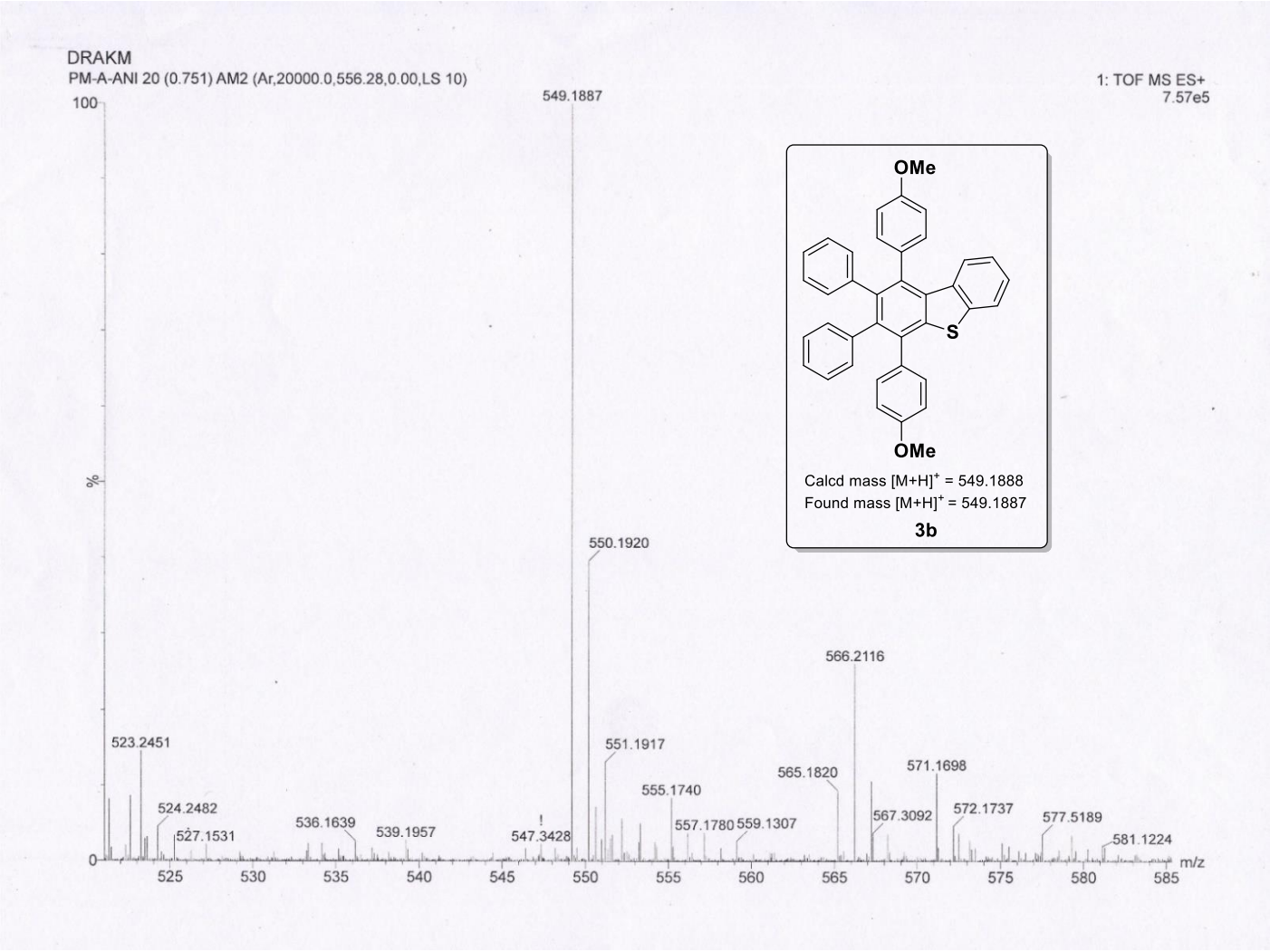
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3b**



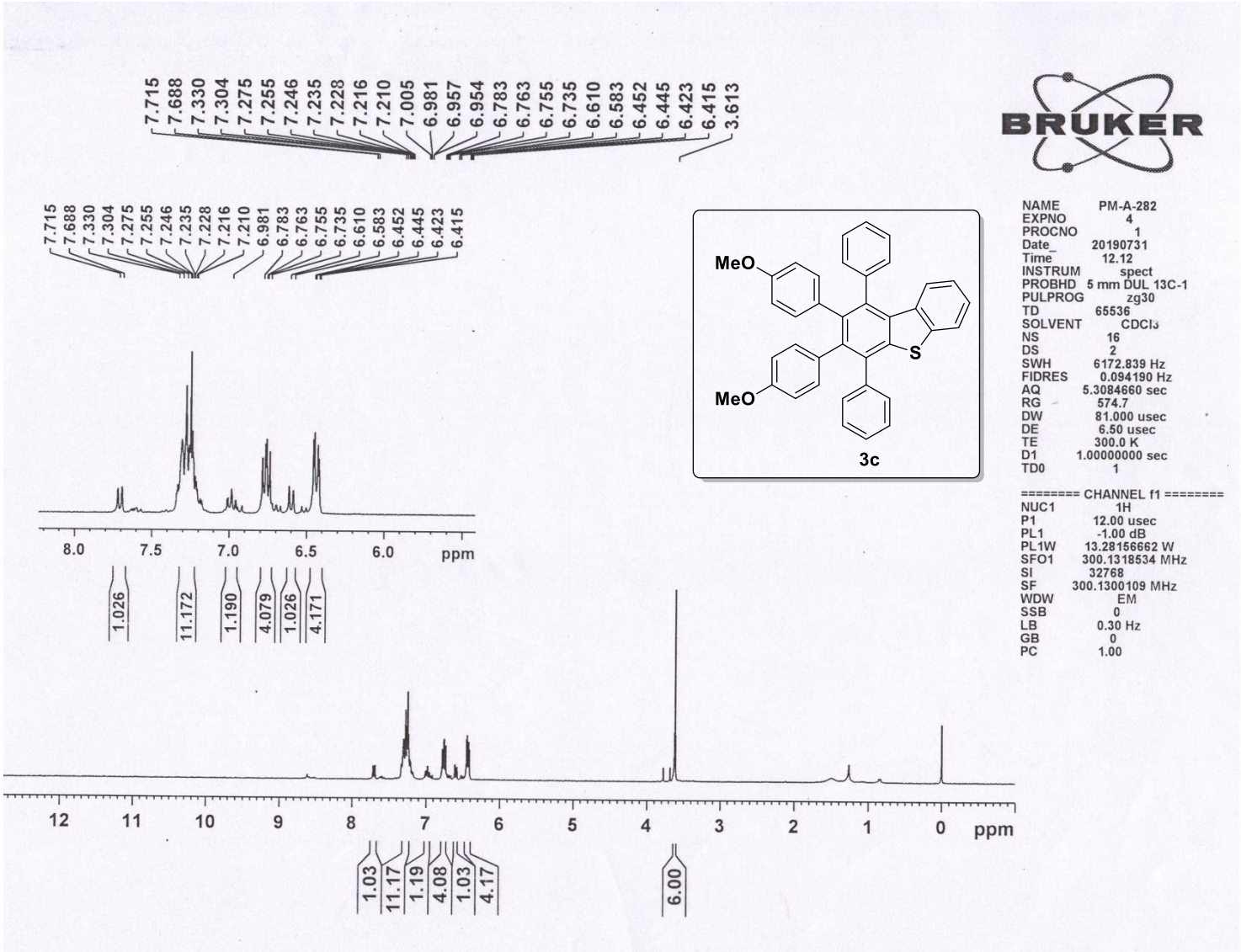
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3b**



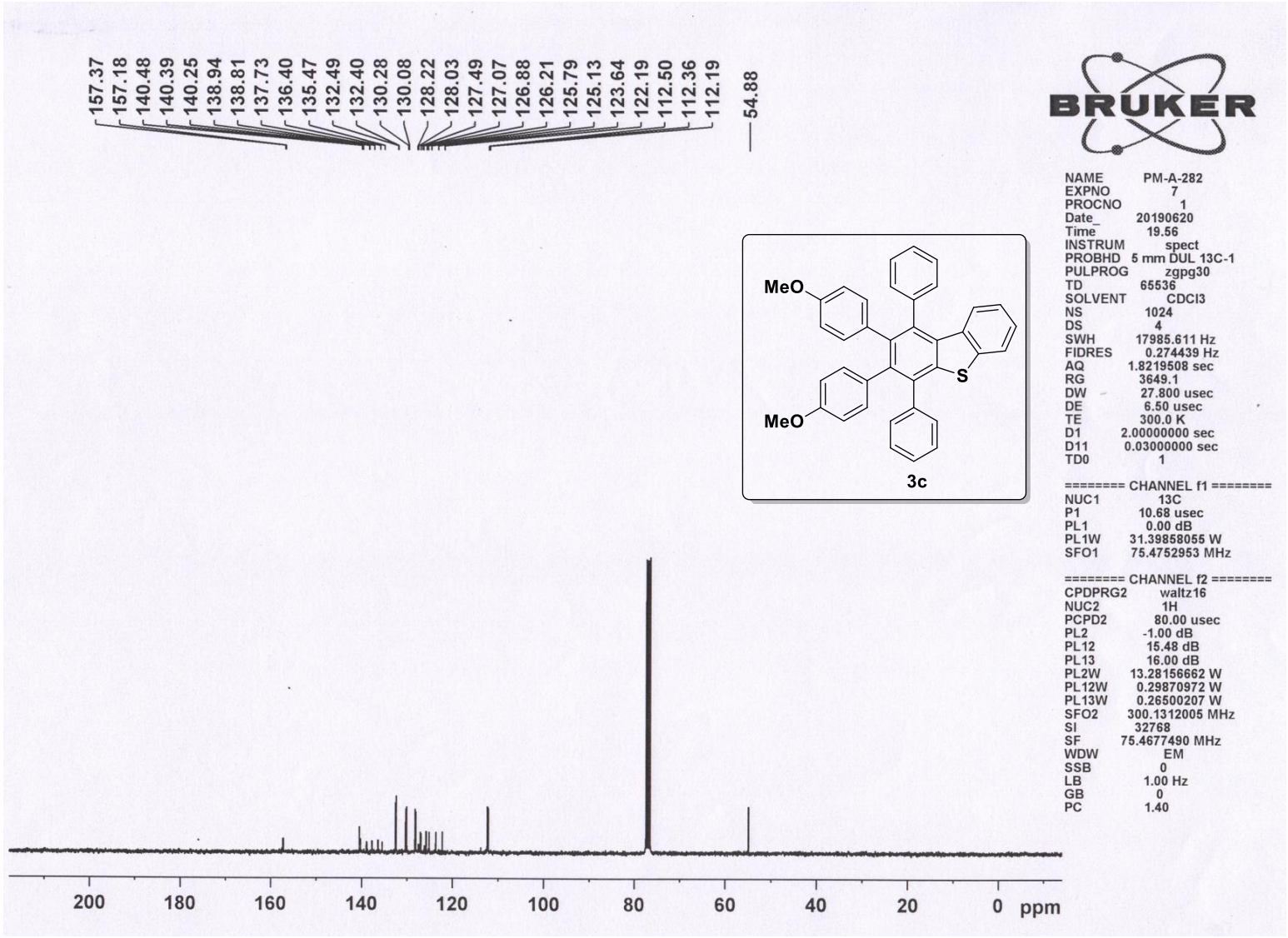
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3b**



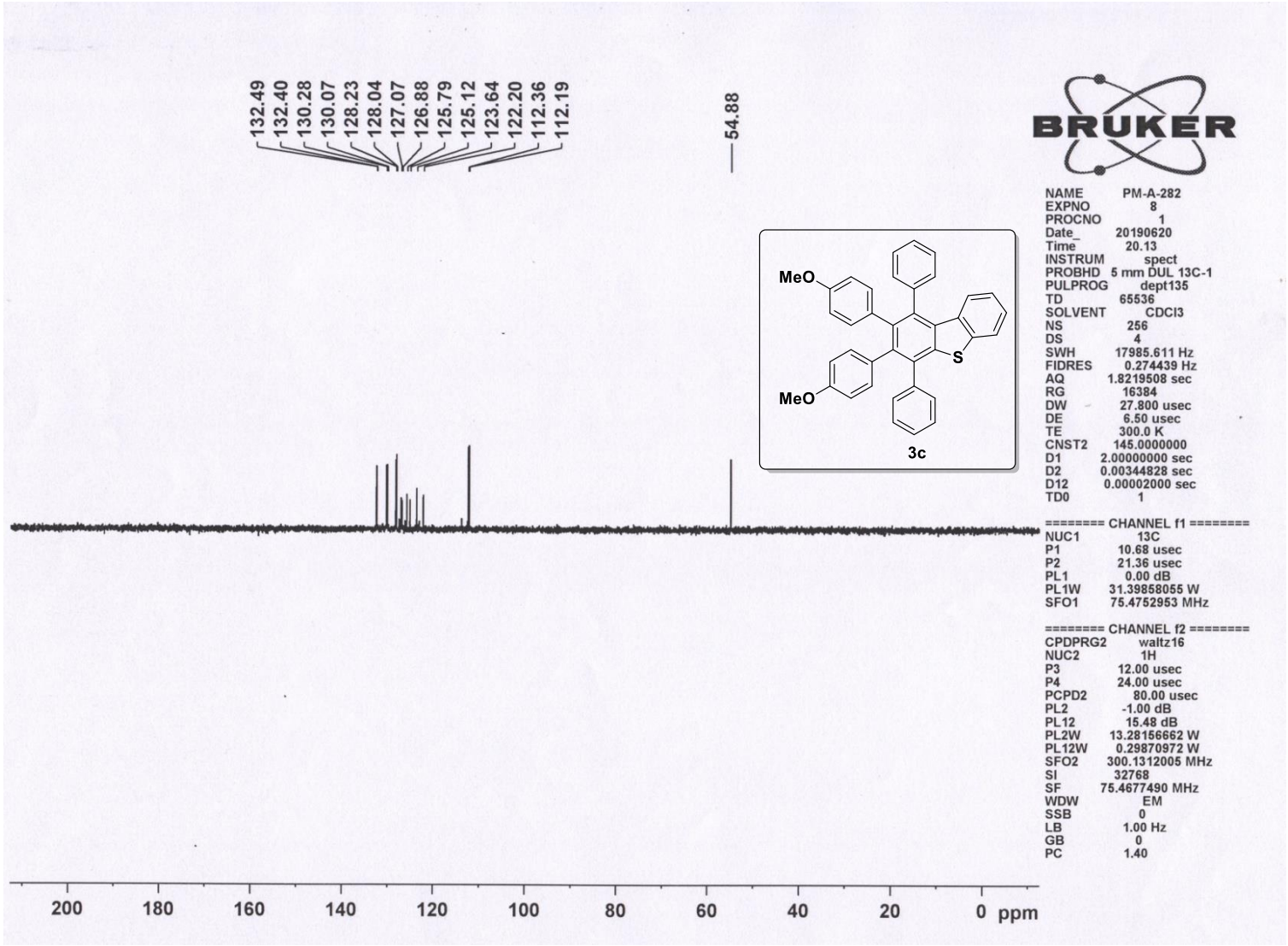
HRMS spectrum of compound **3b**



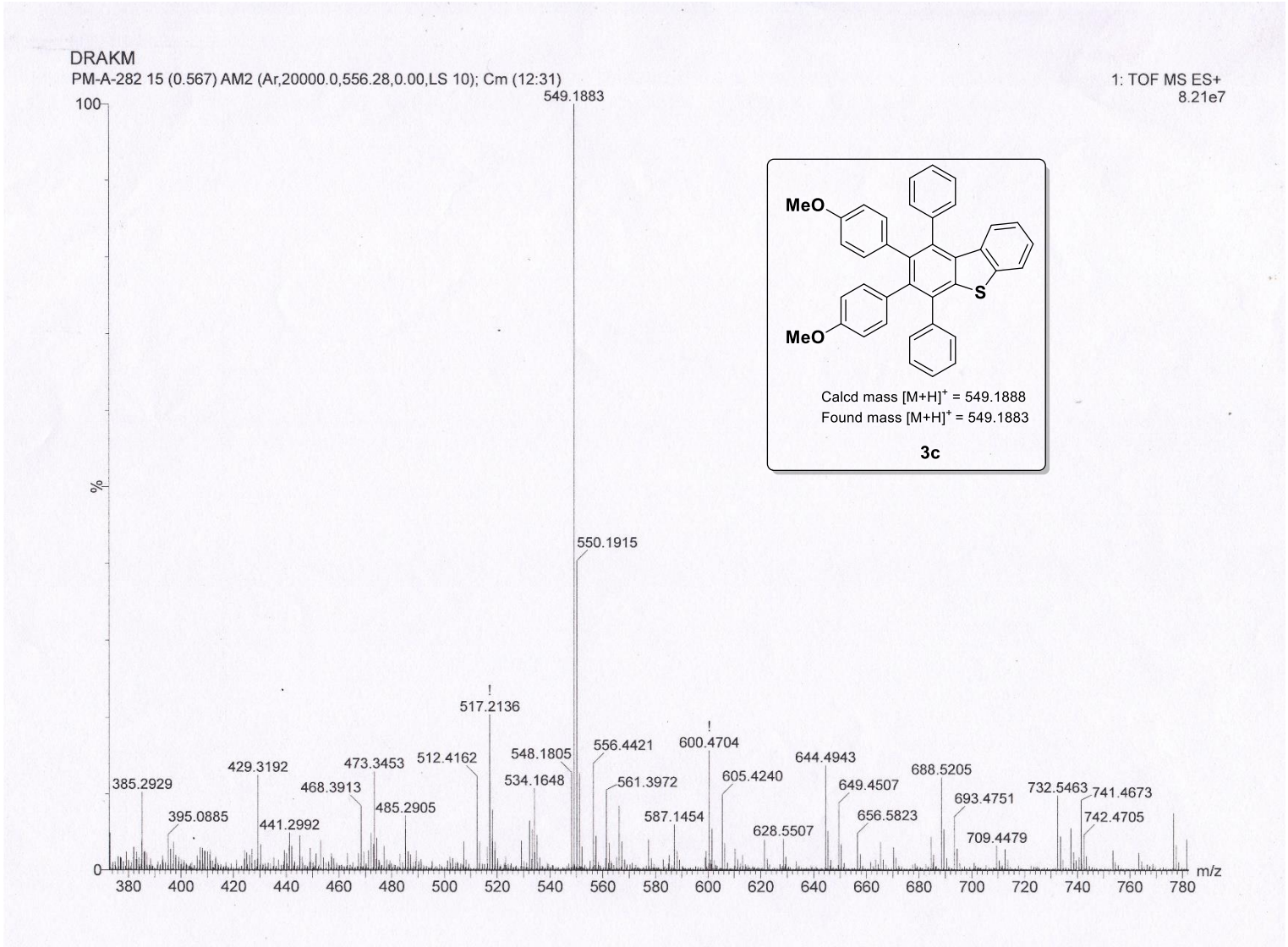
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3c**



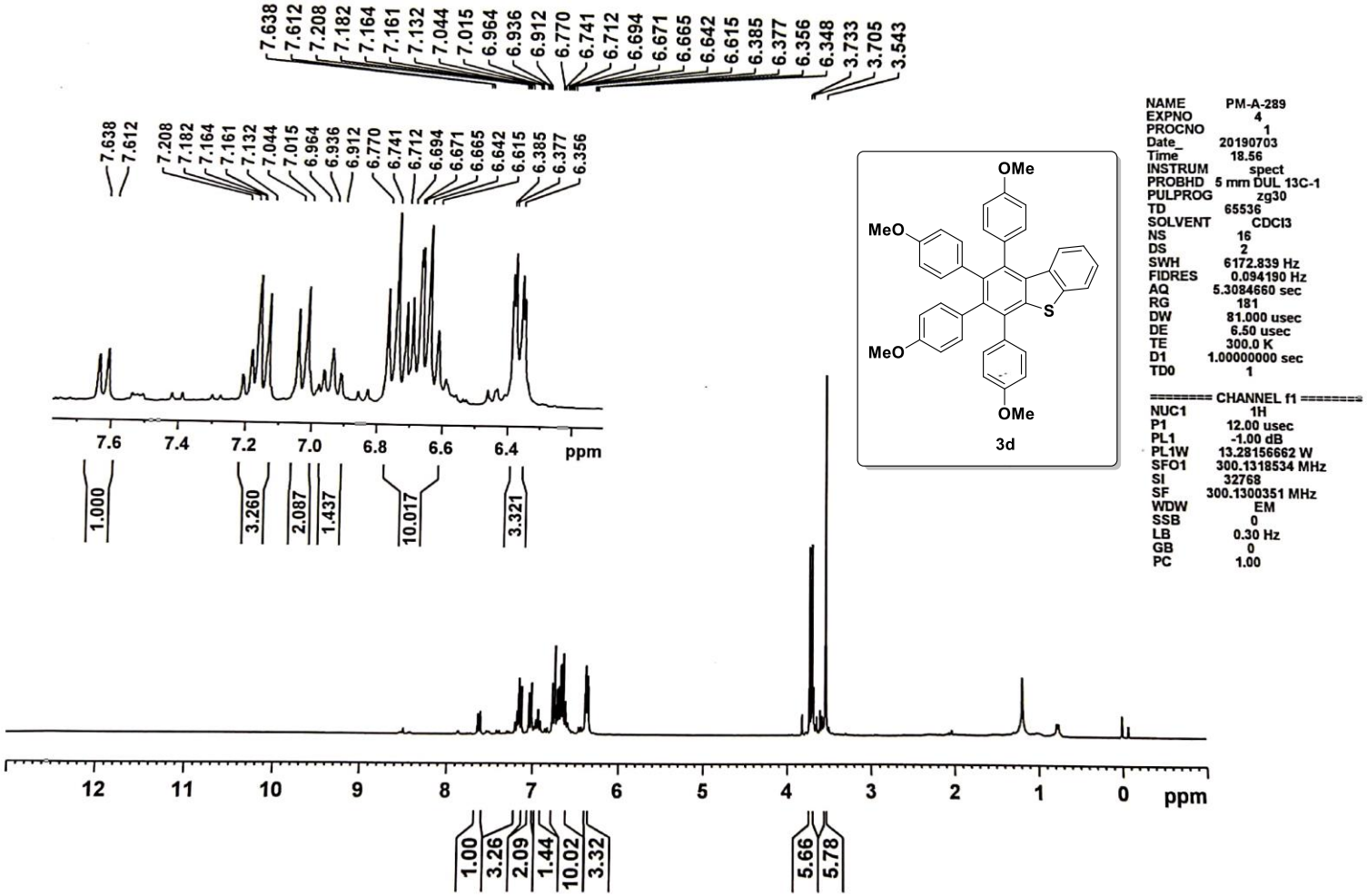
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3c**



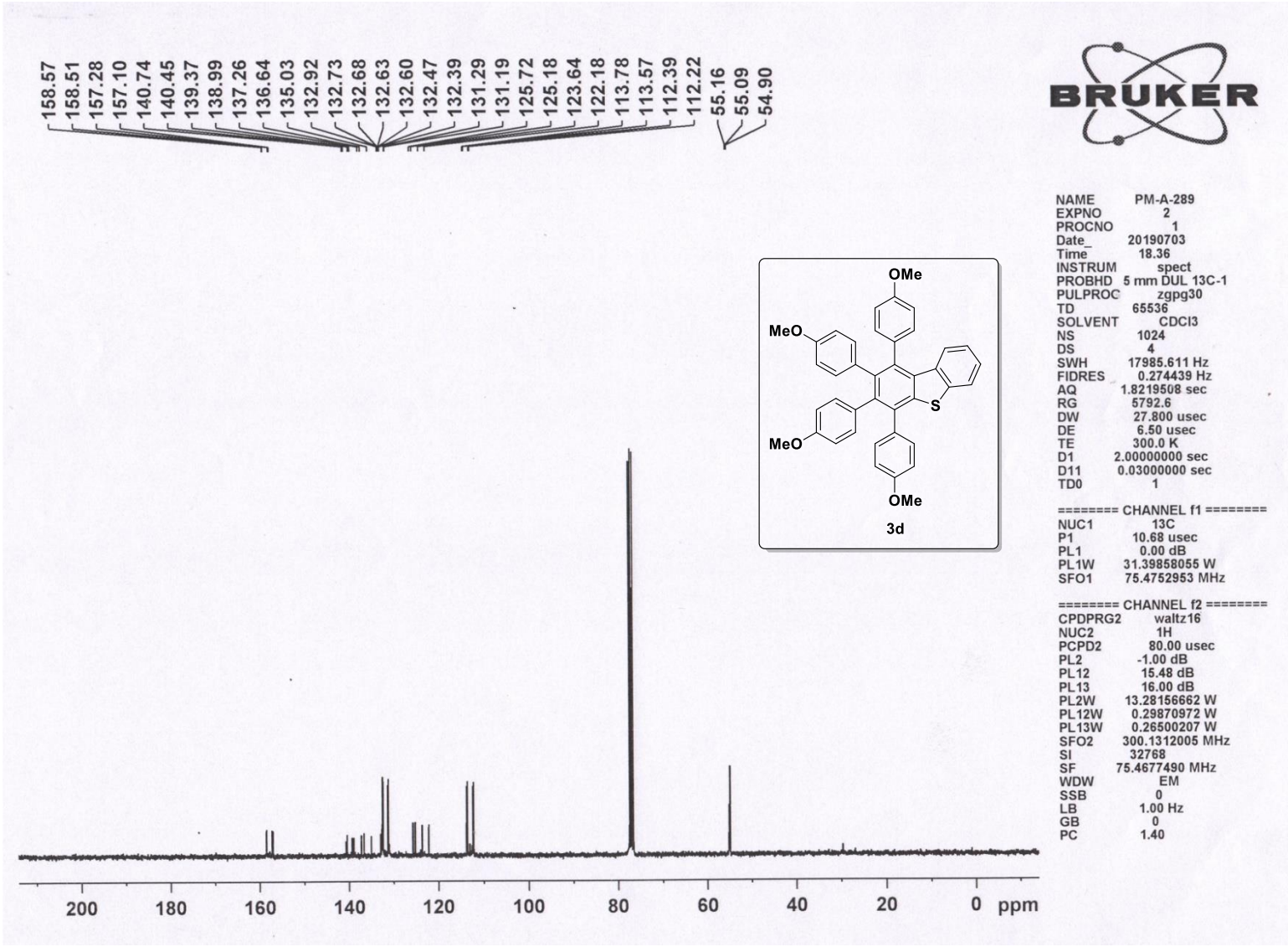
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3c**



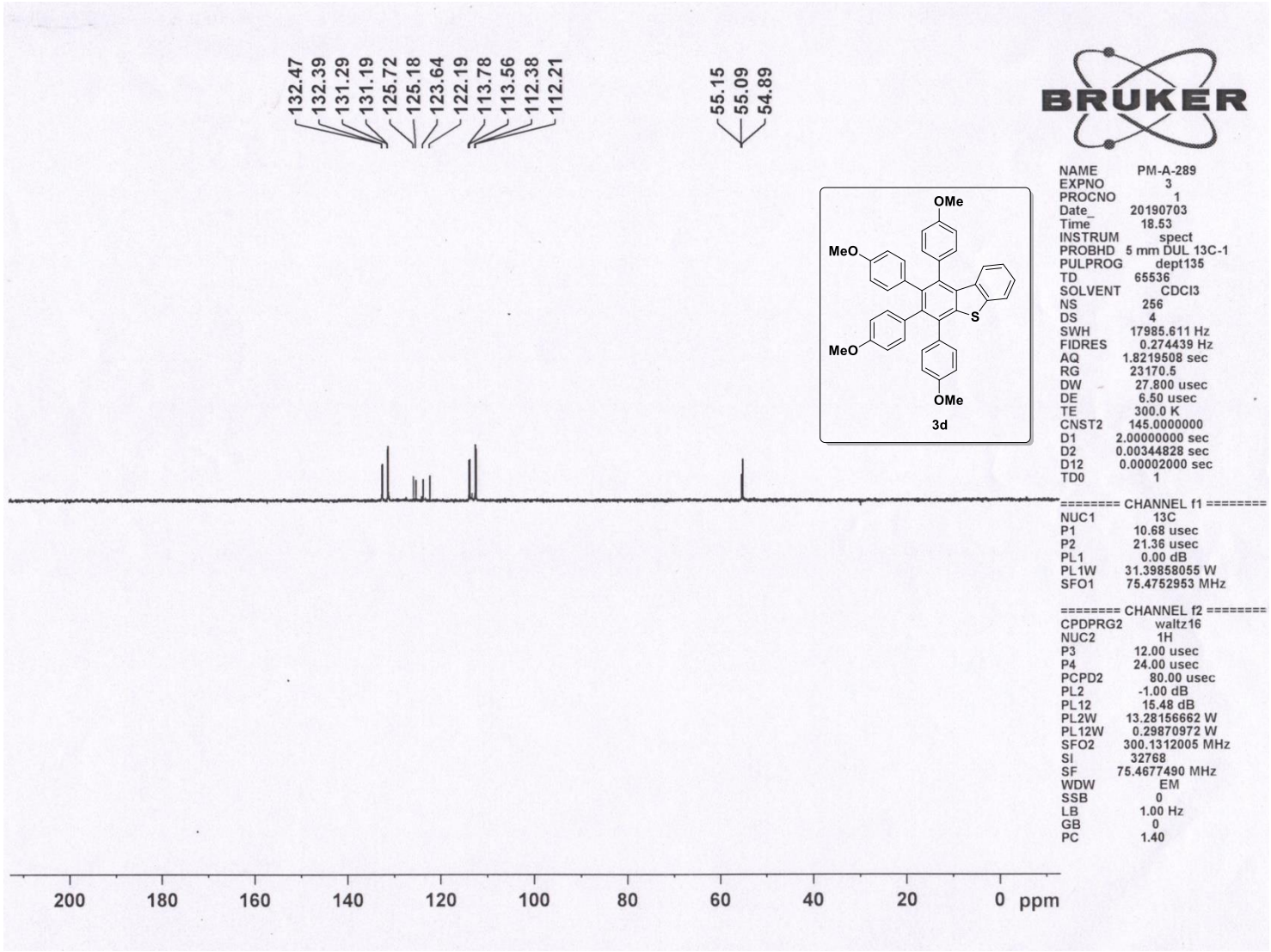
HRMS spectrum of compound **3c**



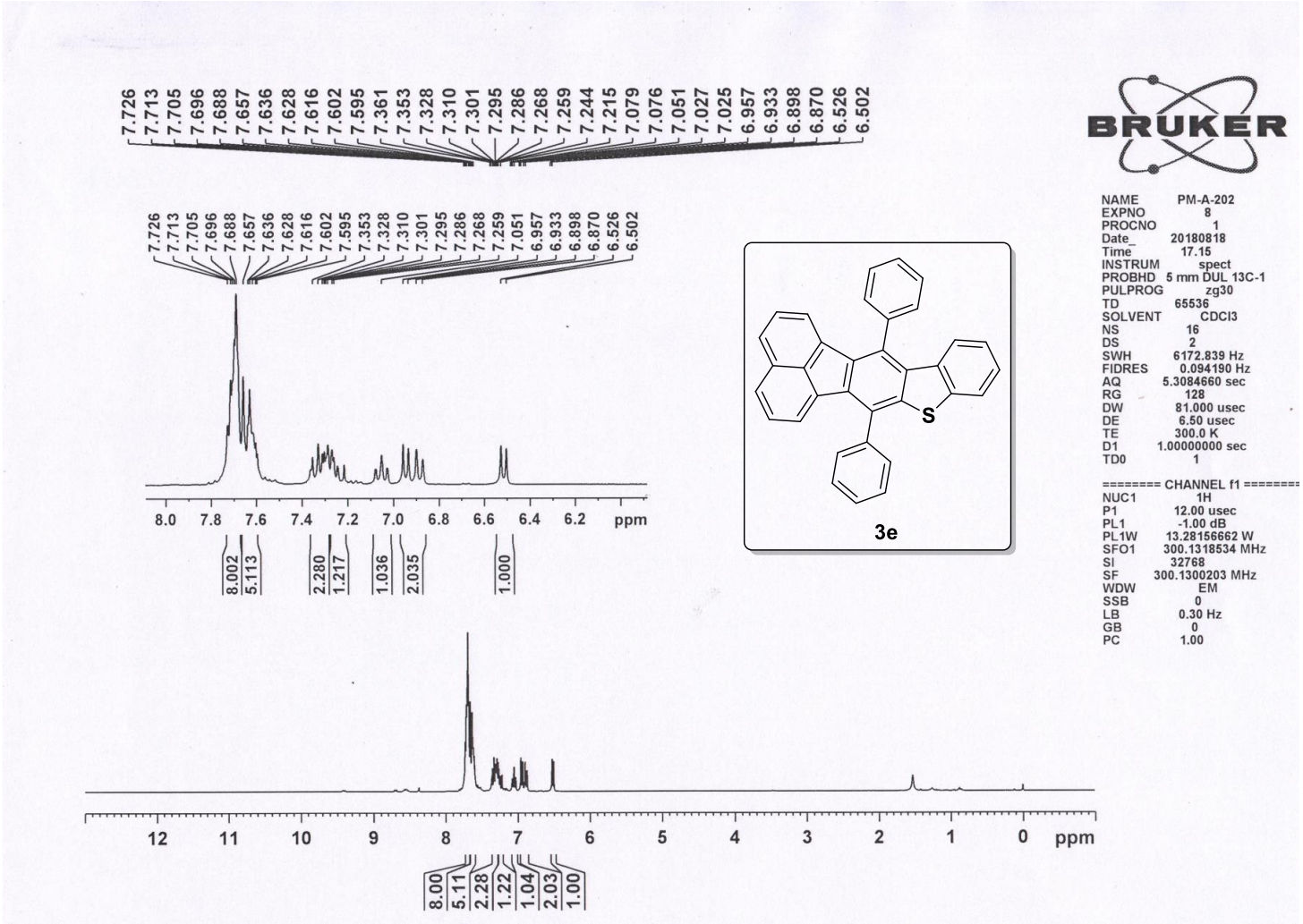
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound**3d**



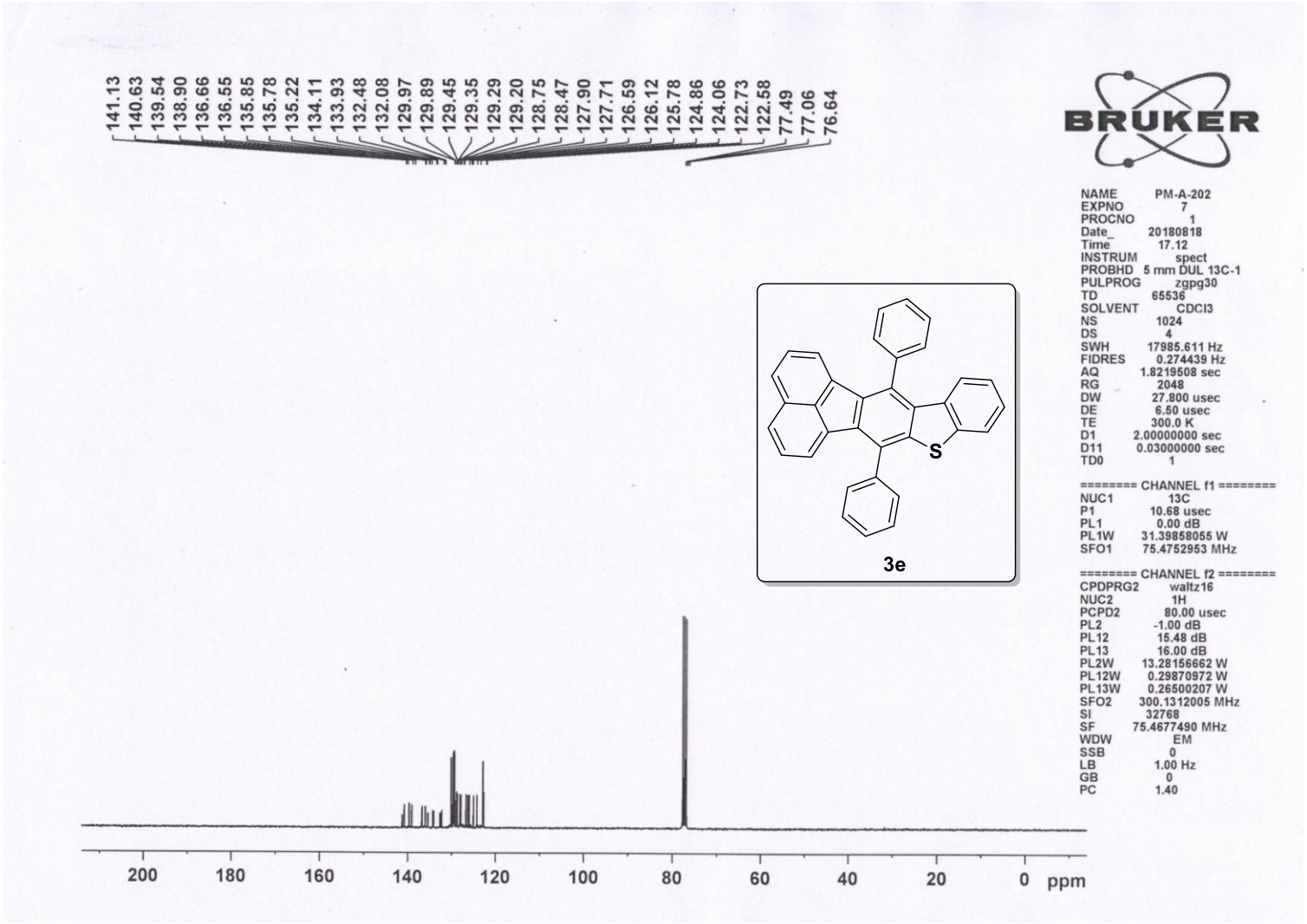
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3d**



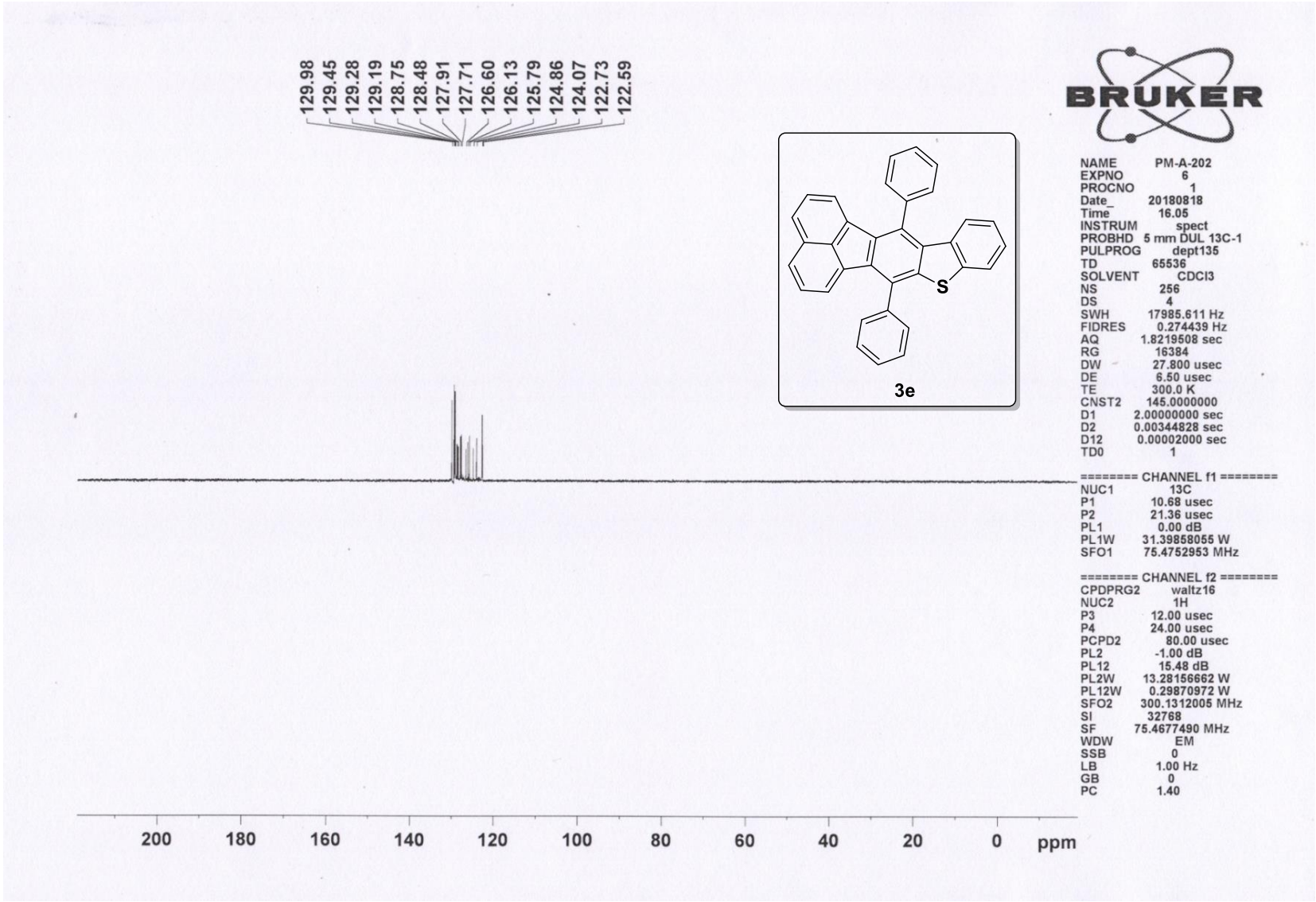
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3d**



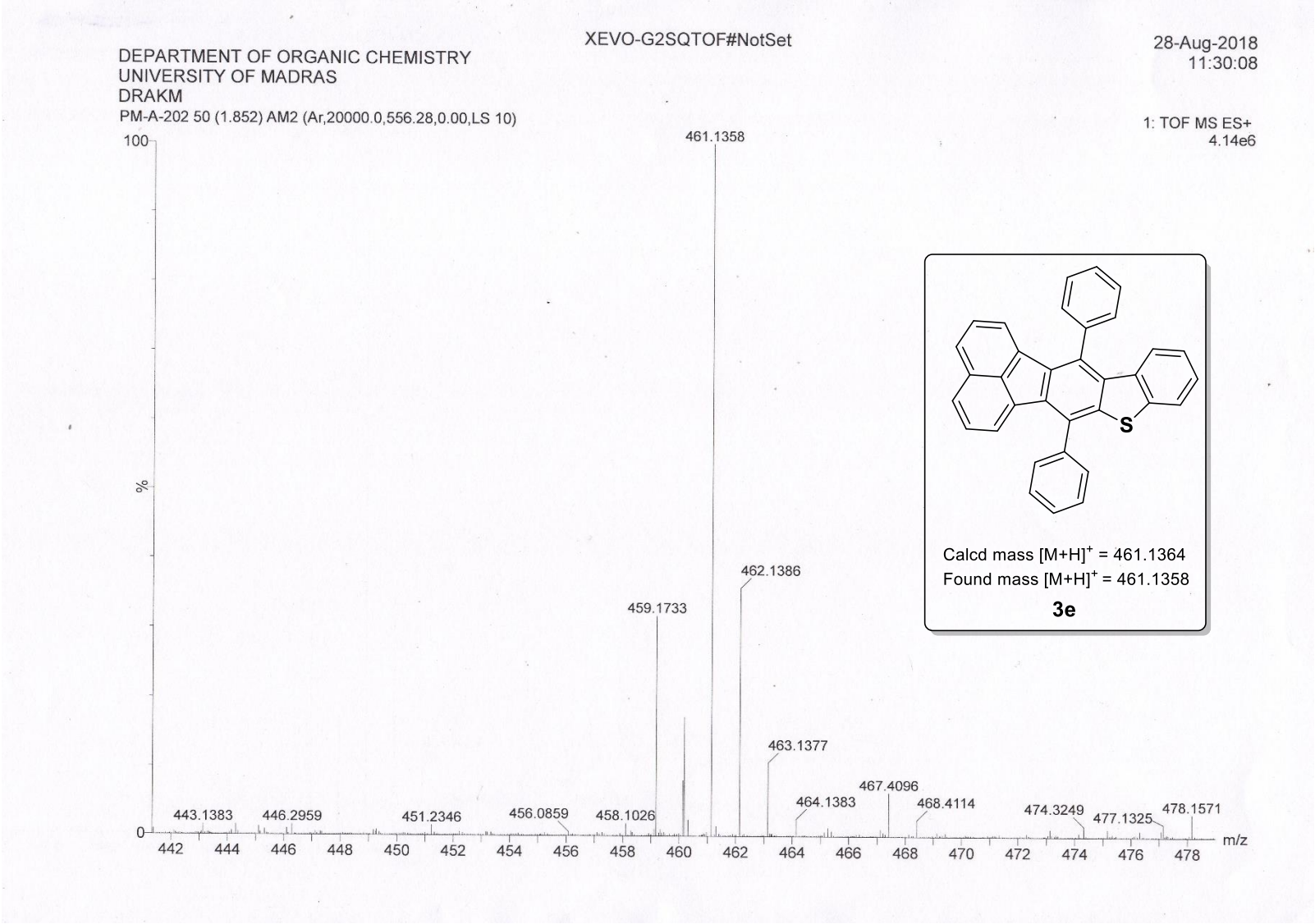
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3e**



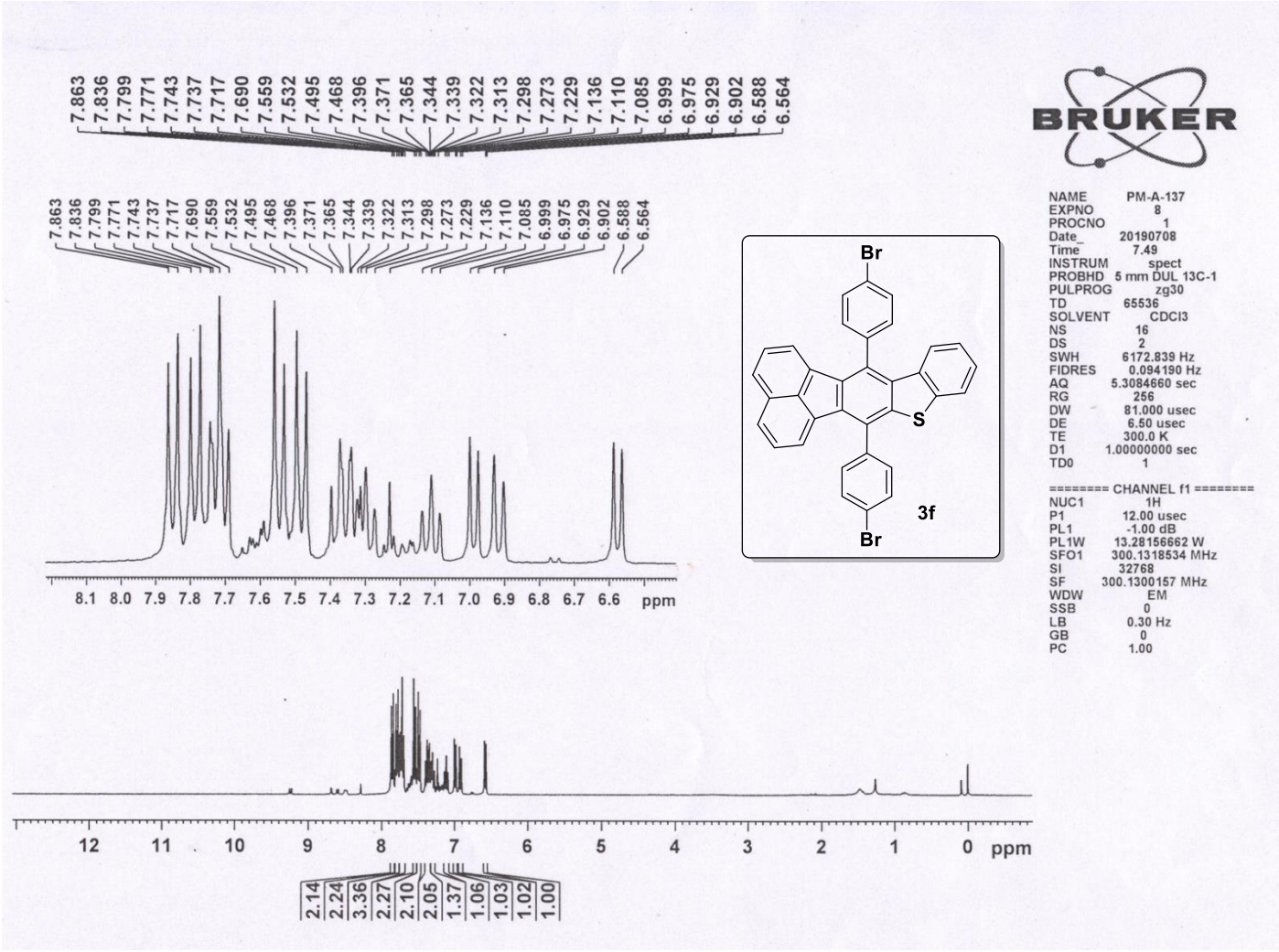
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3e**



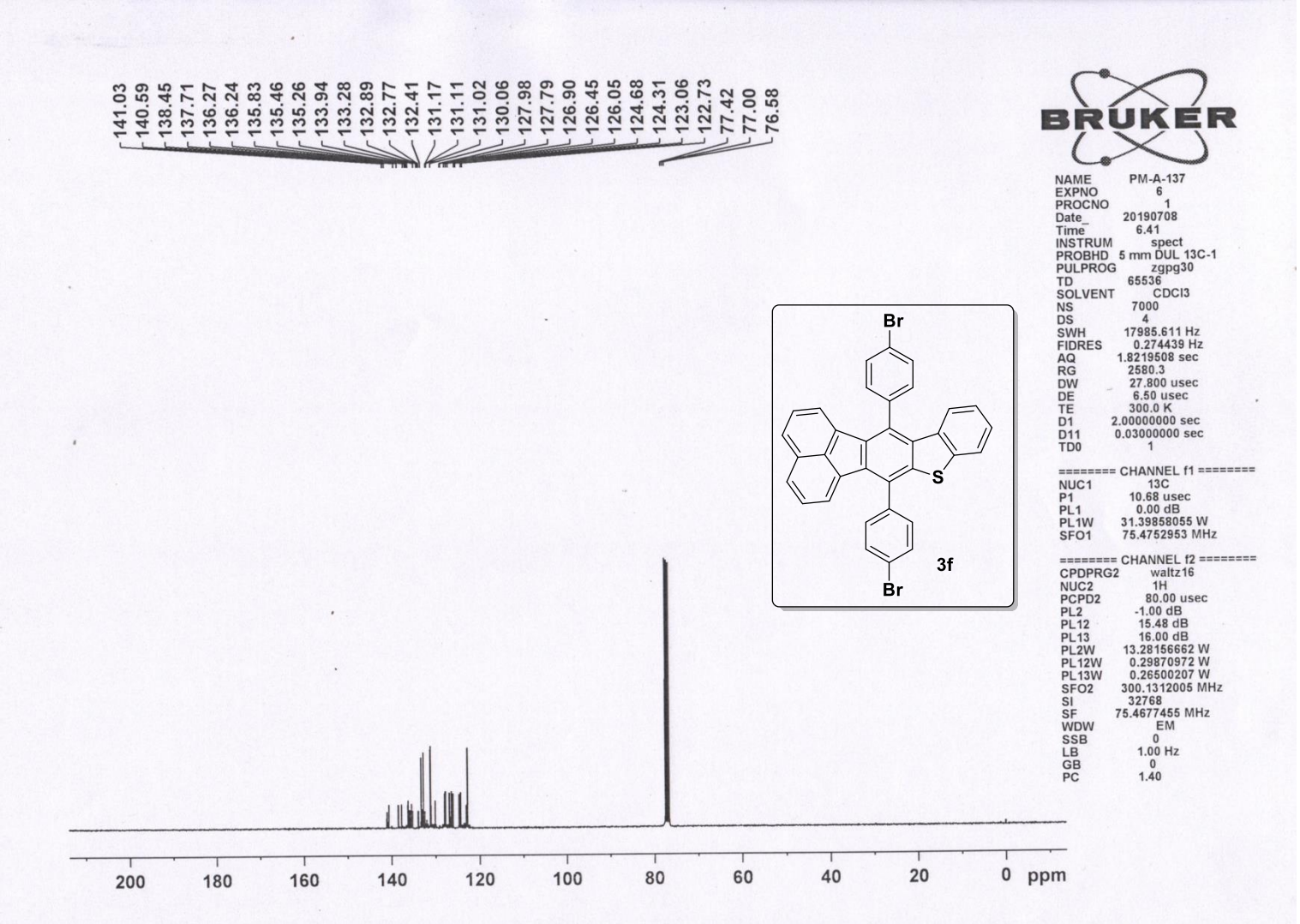
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3e**



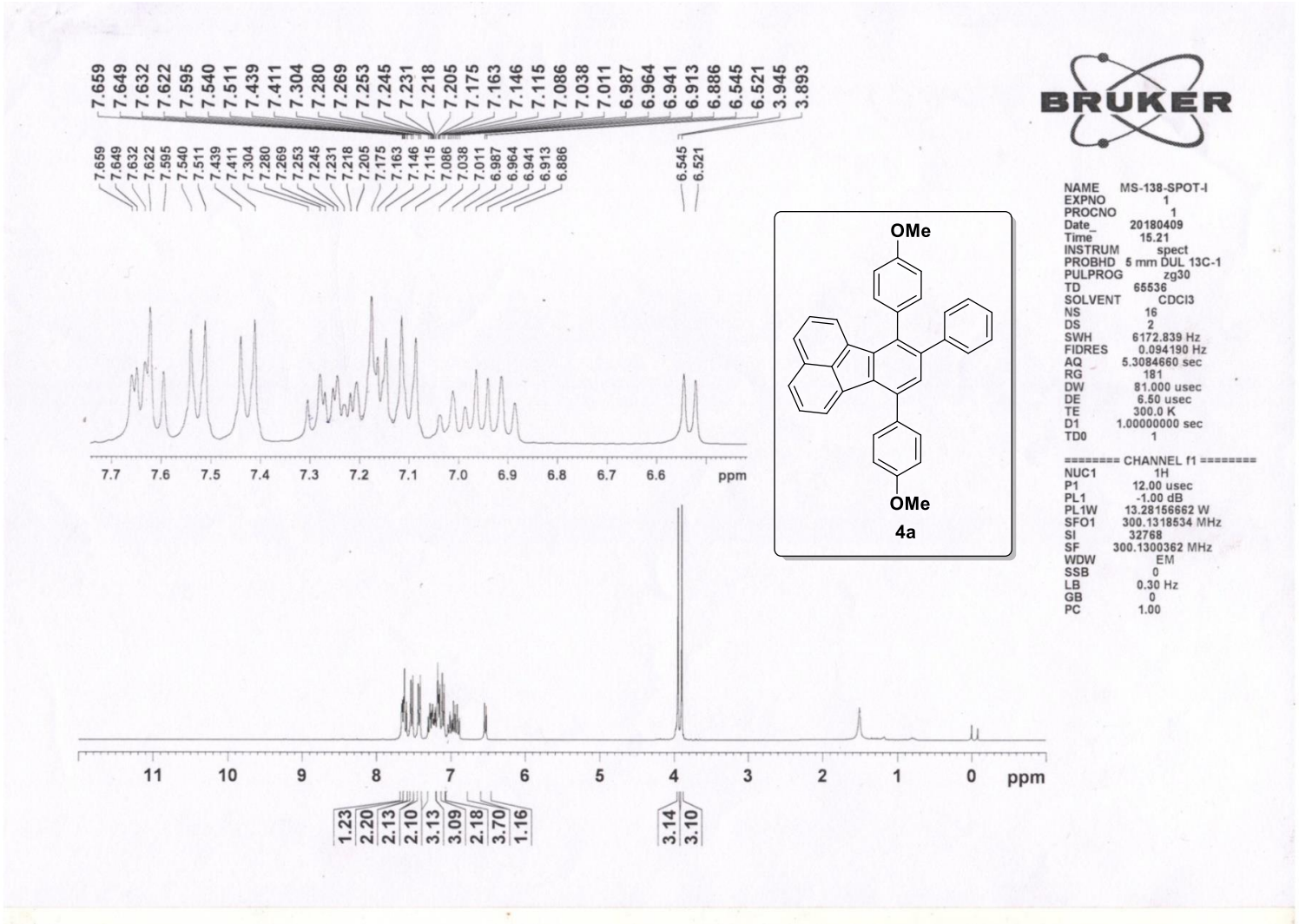
HRMS spectrum of compound **3e**



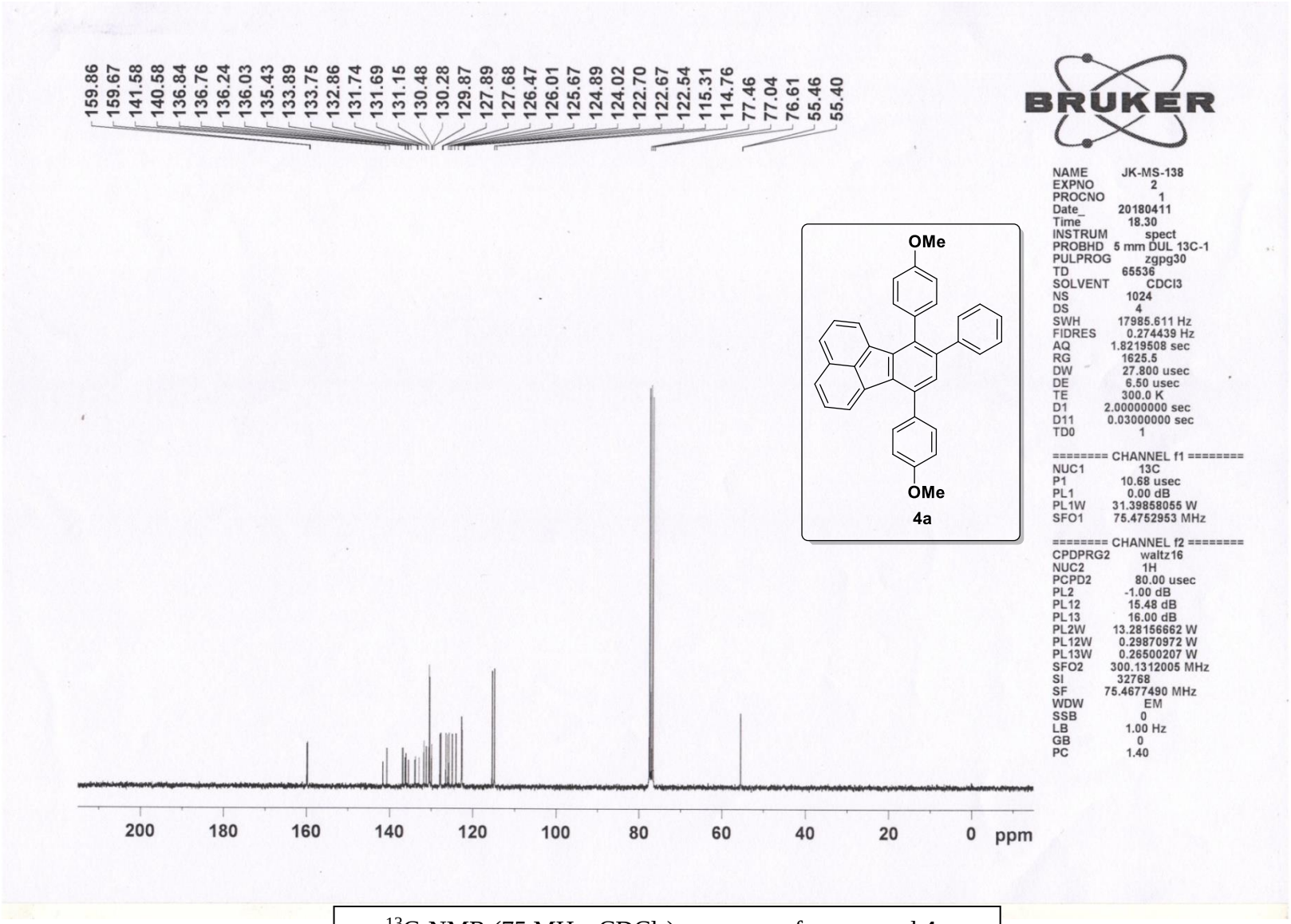
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3f**



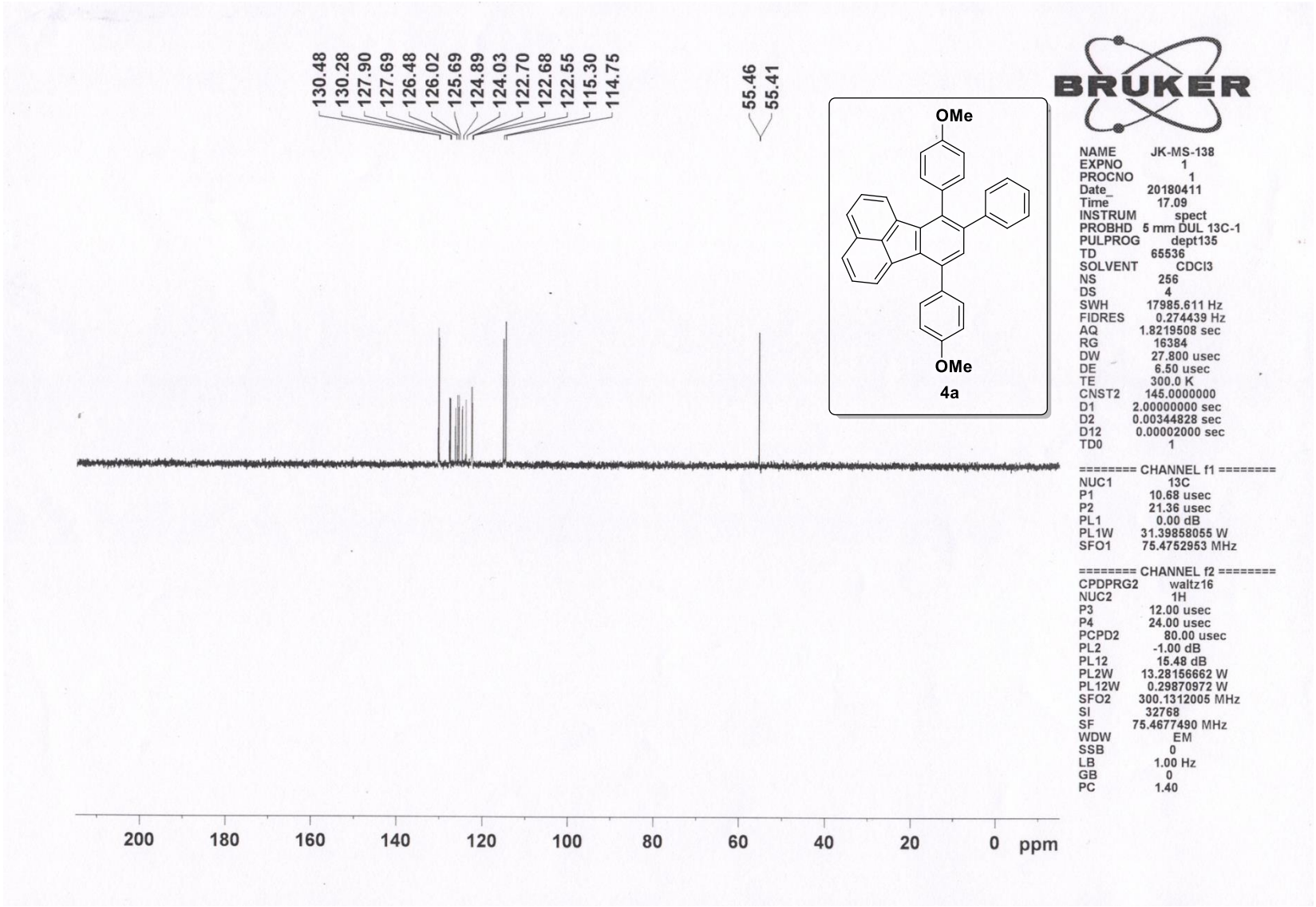
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3f**



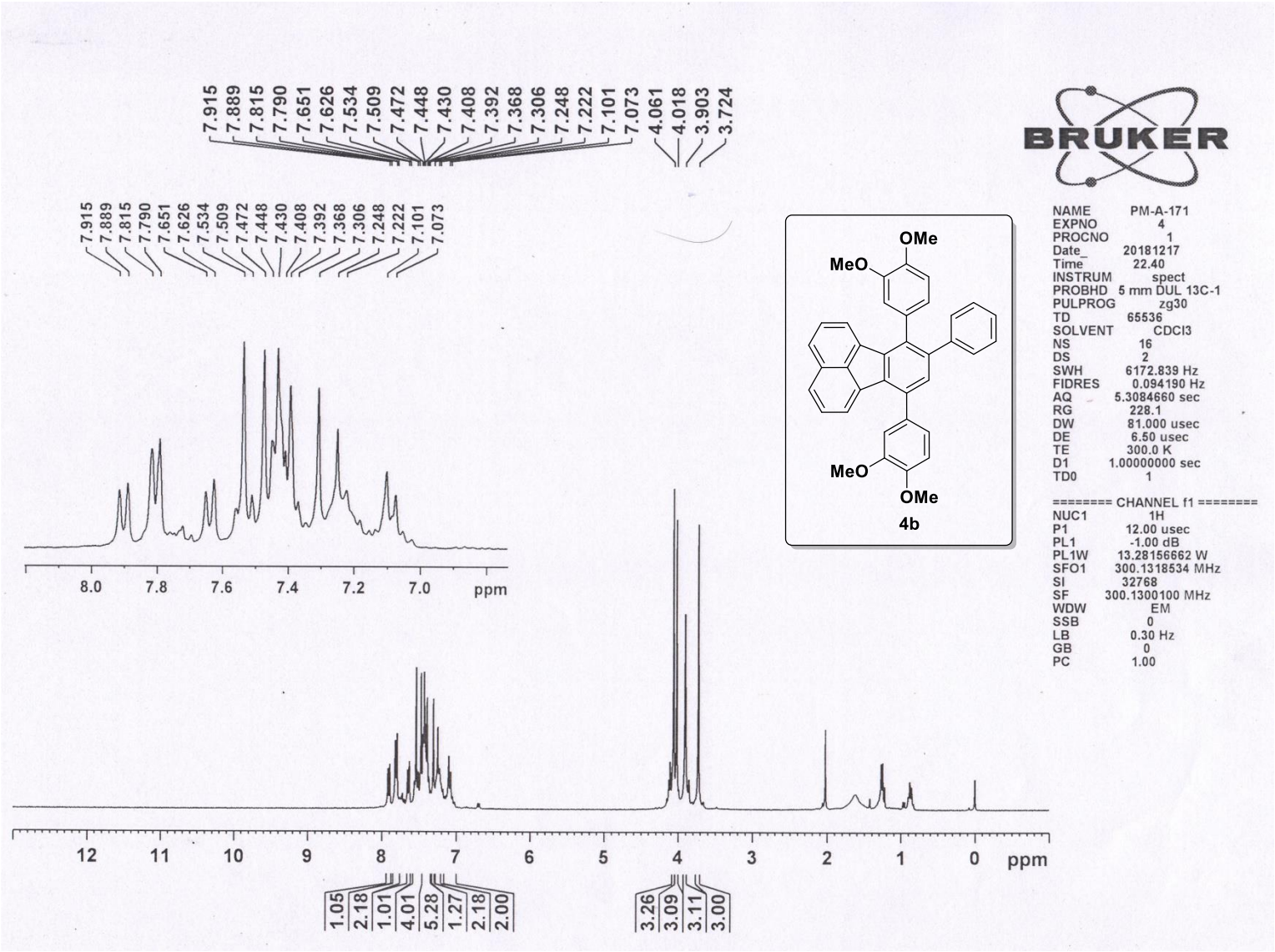
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4a**



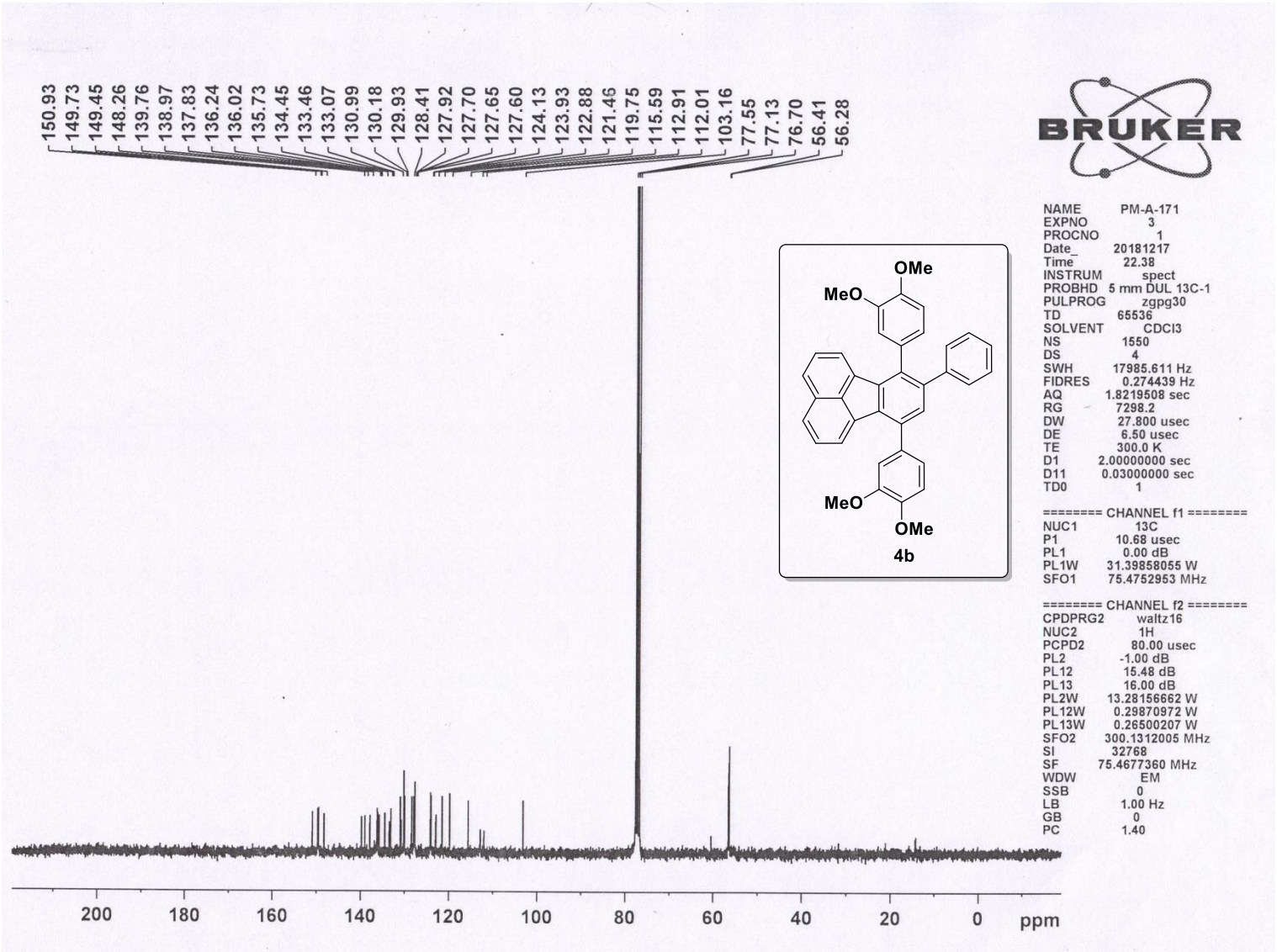
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4a**



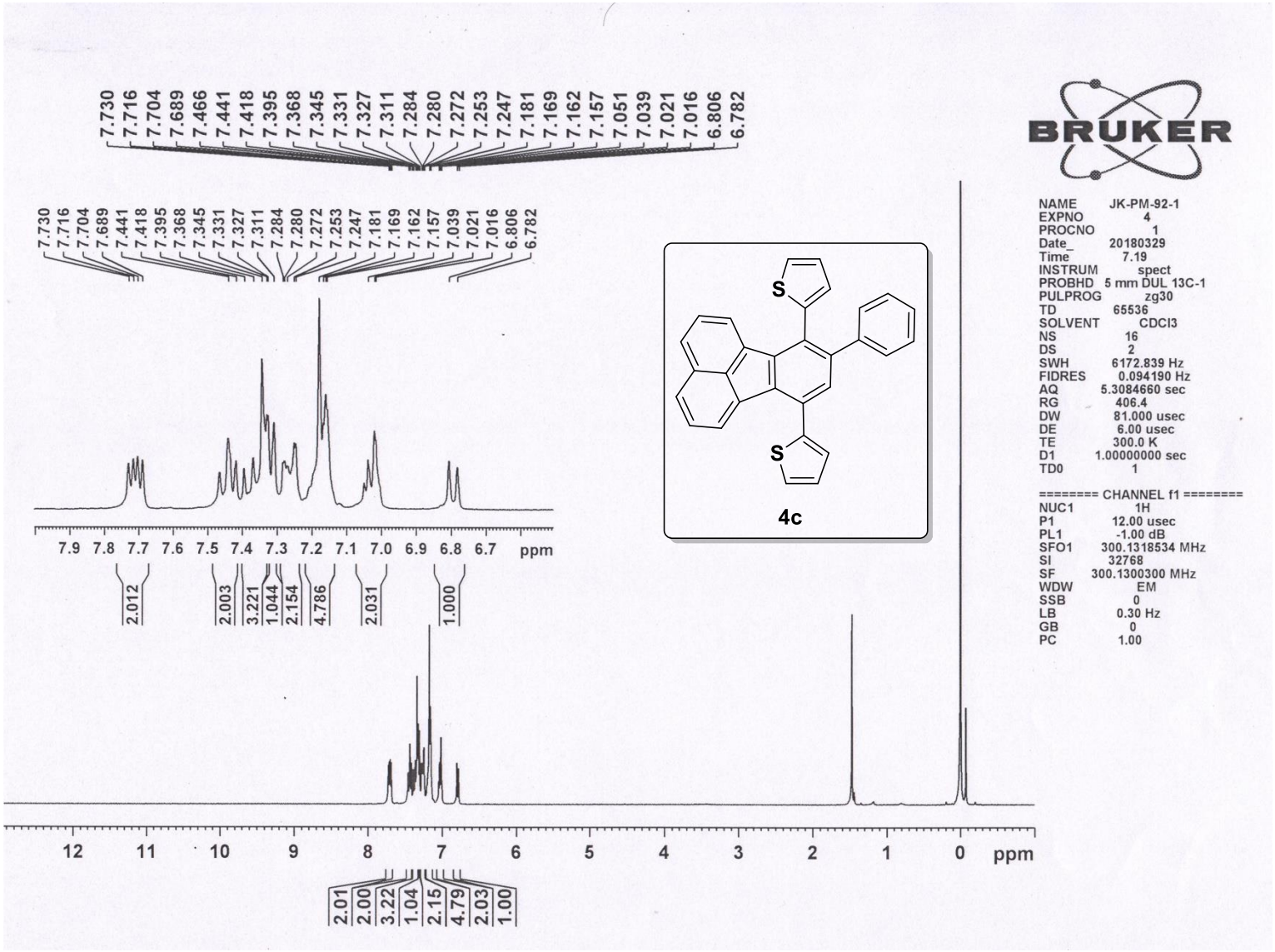
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **4a**



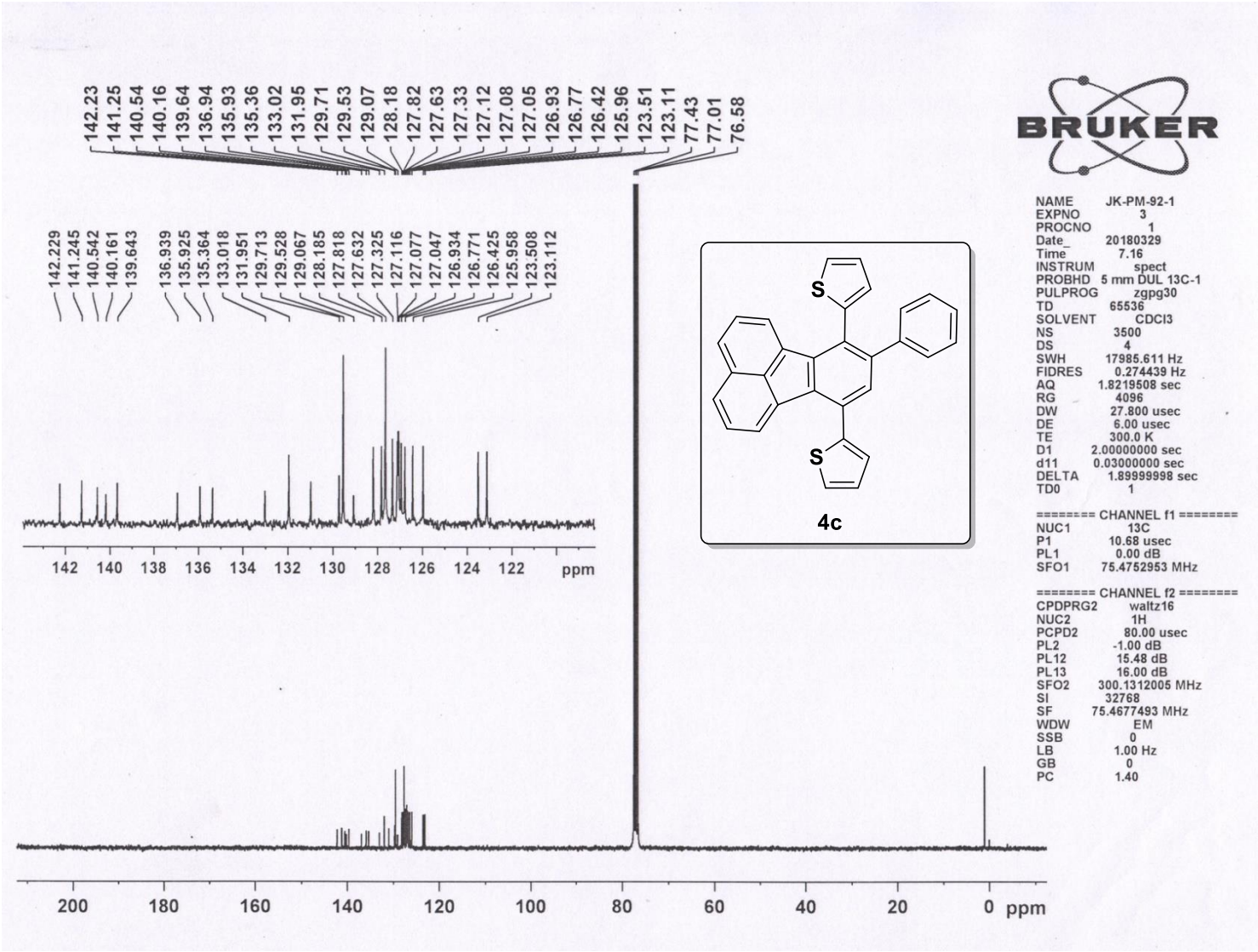
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4b**



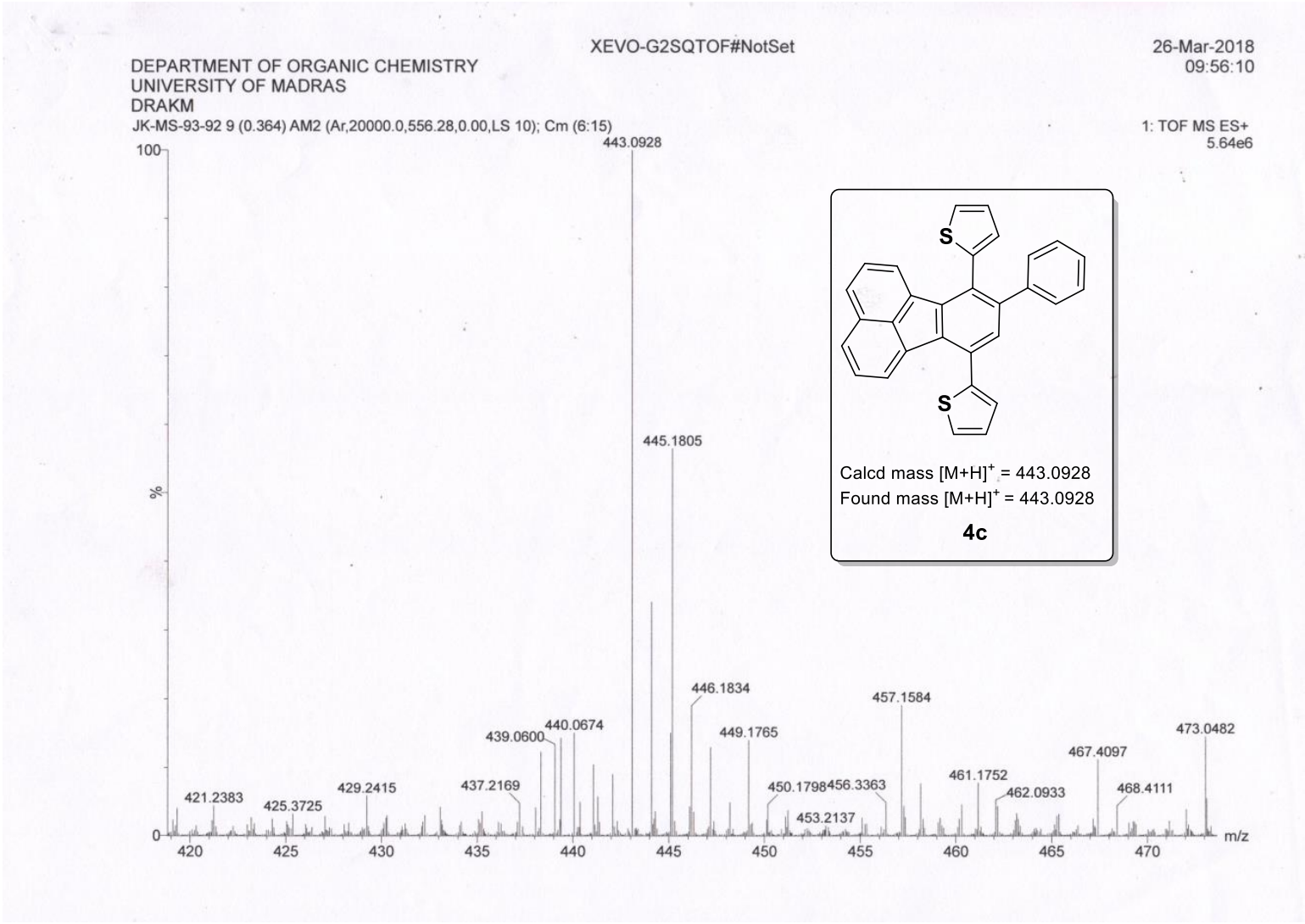
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4b**



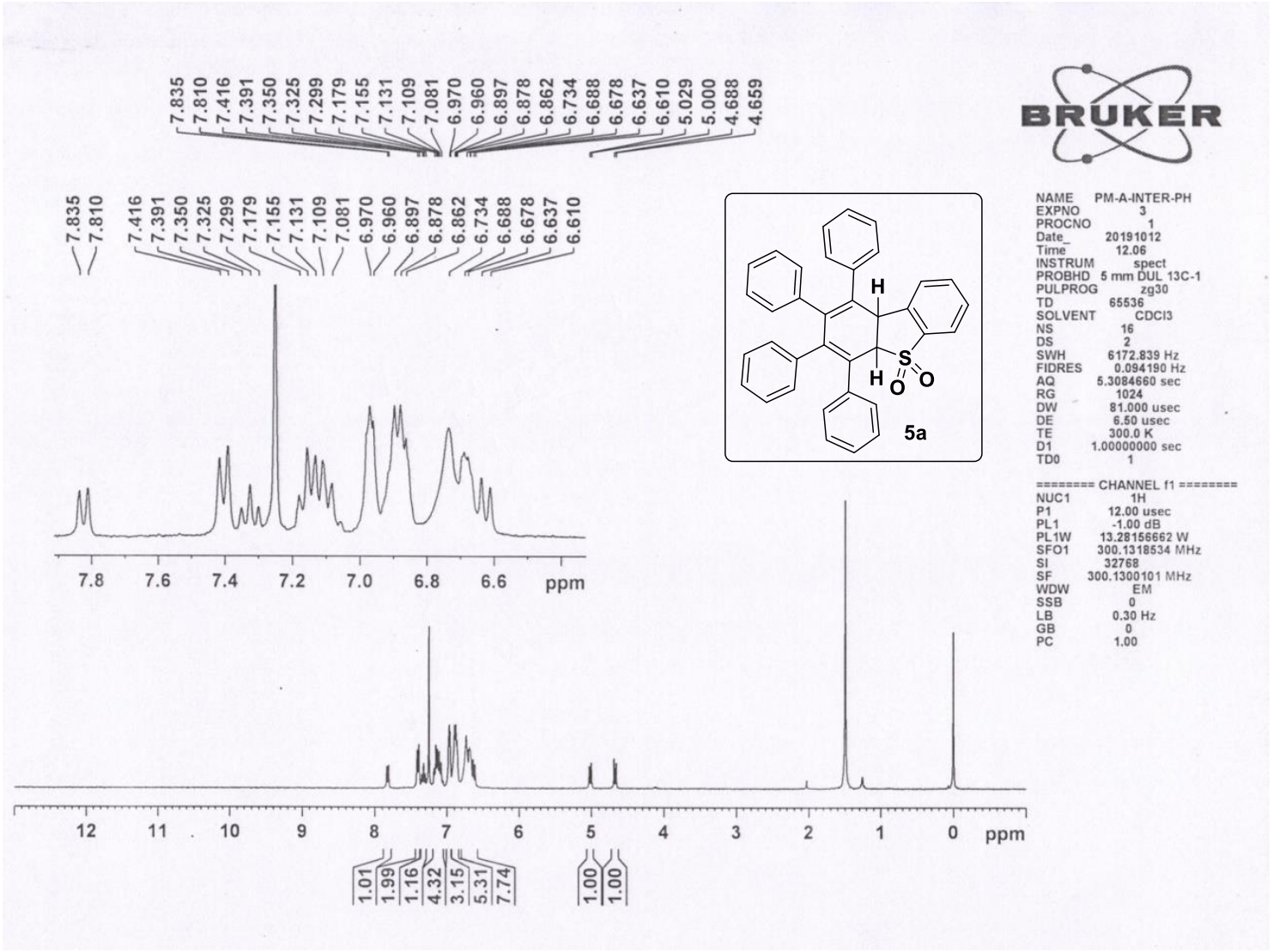
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4c**



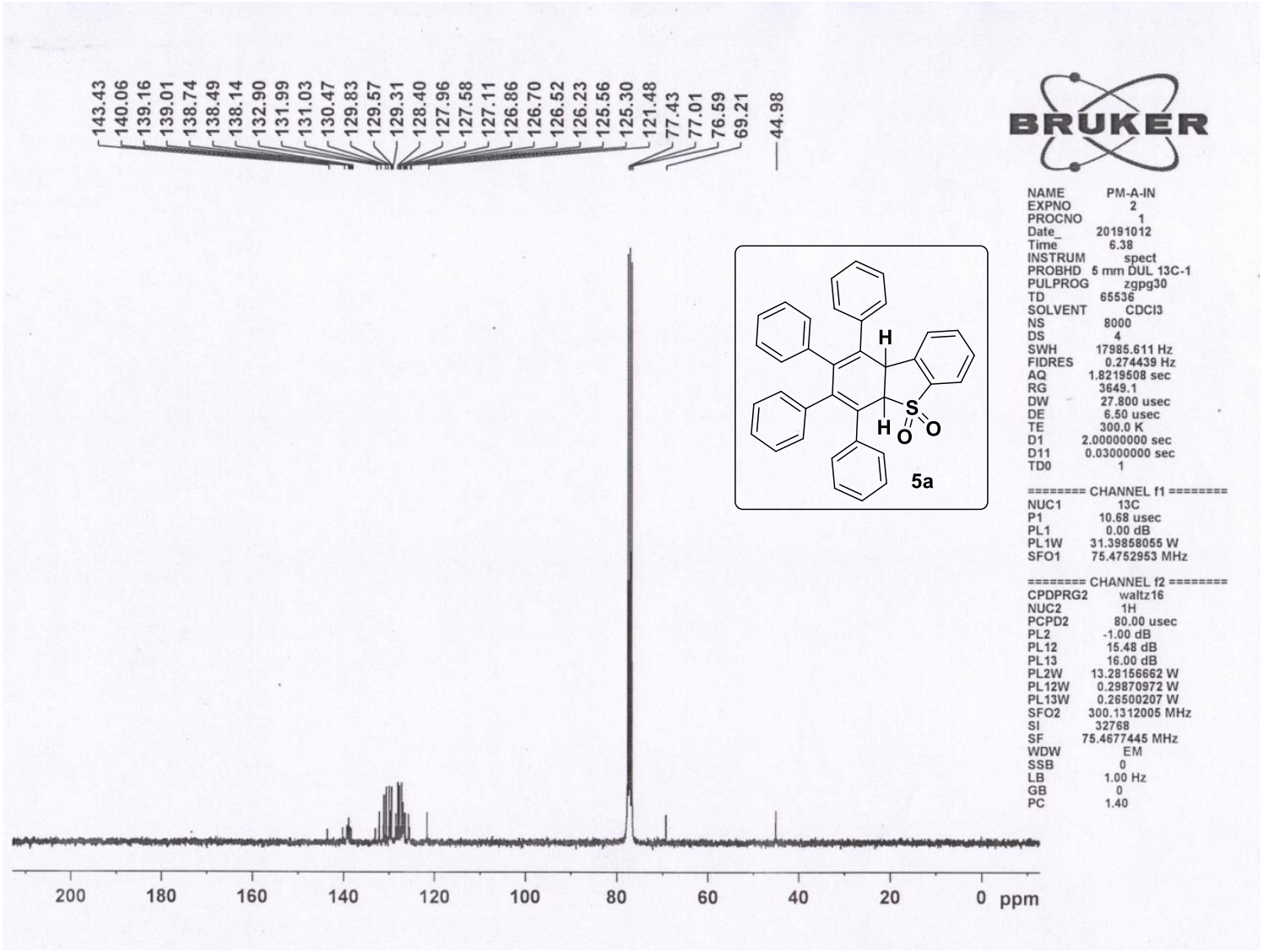
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4c**



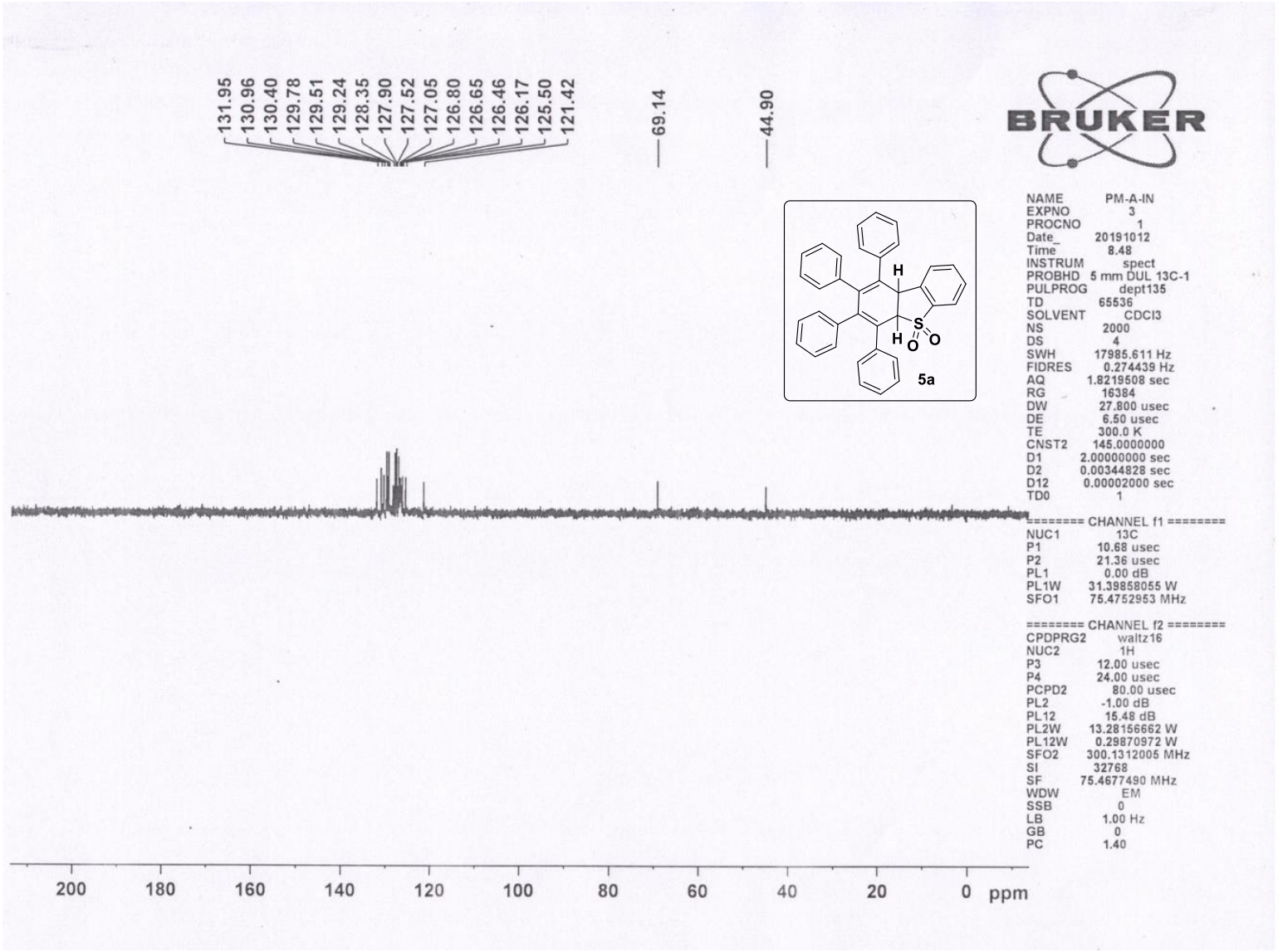
HRMS spectrum of compound **4c**



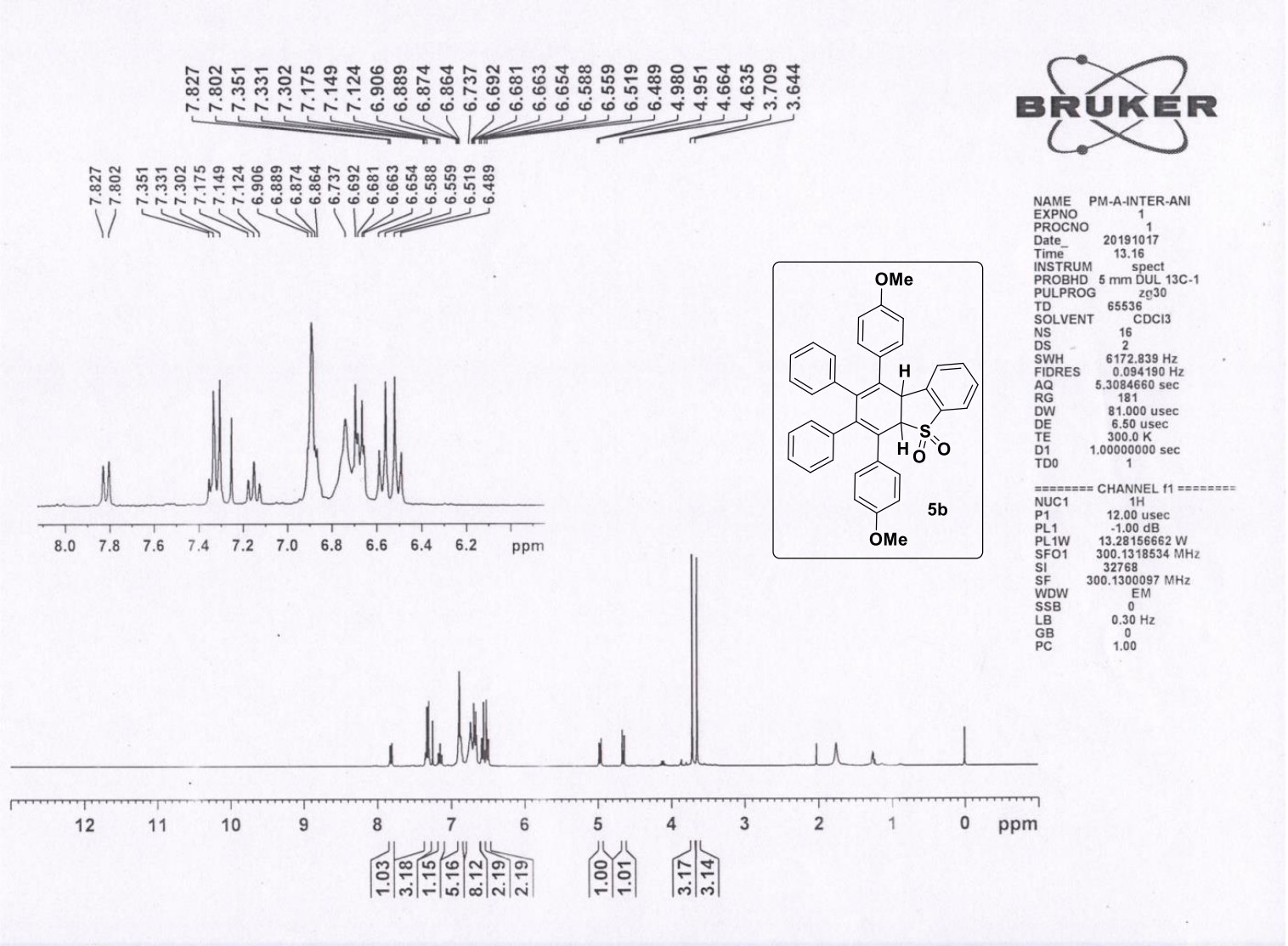
^{1}H NMR (300MHz, $CDCl_3$) spectrum of compound **5a**



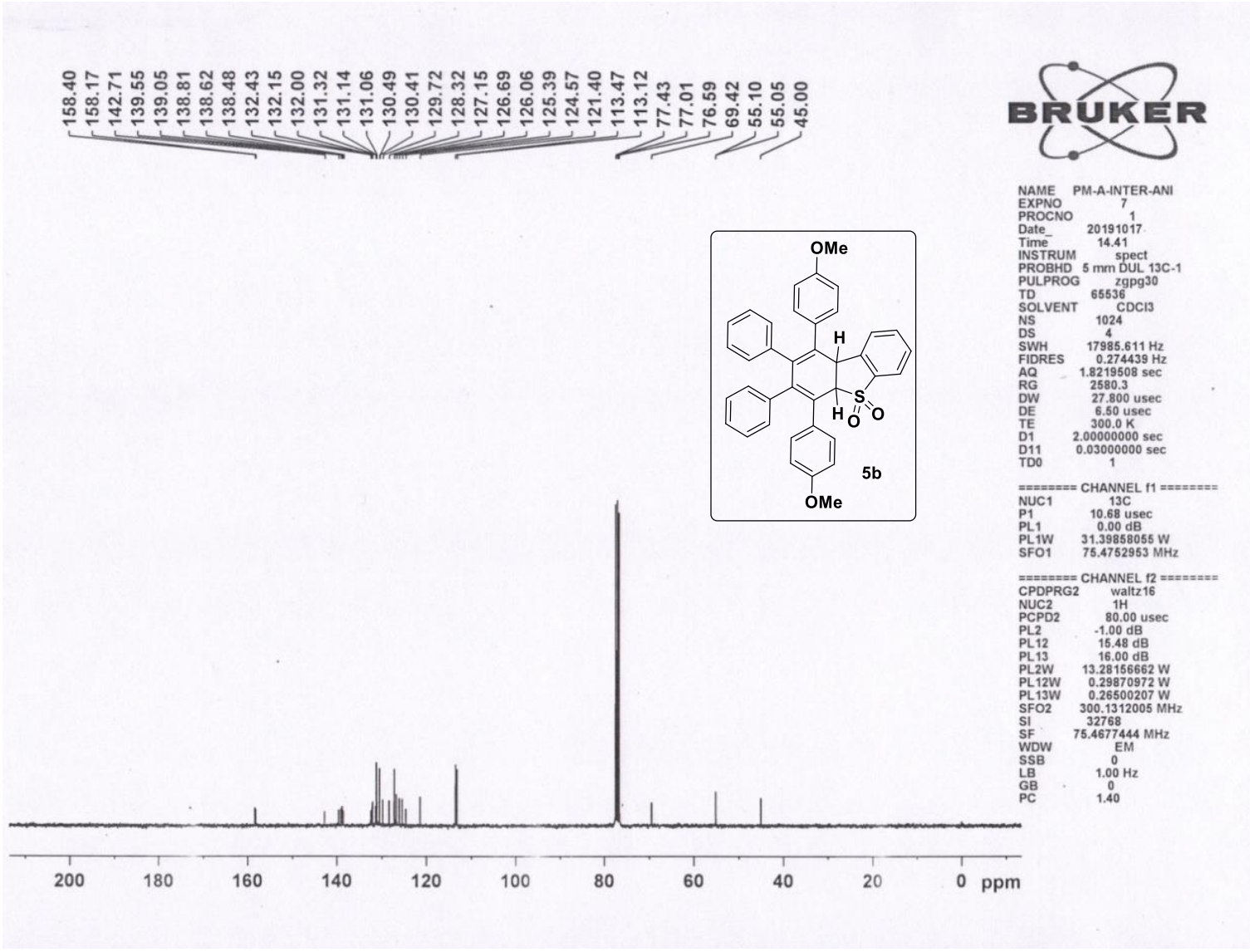
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **5a**



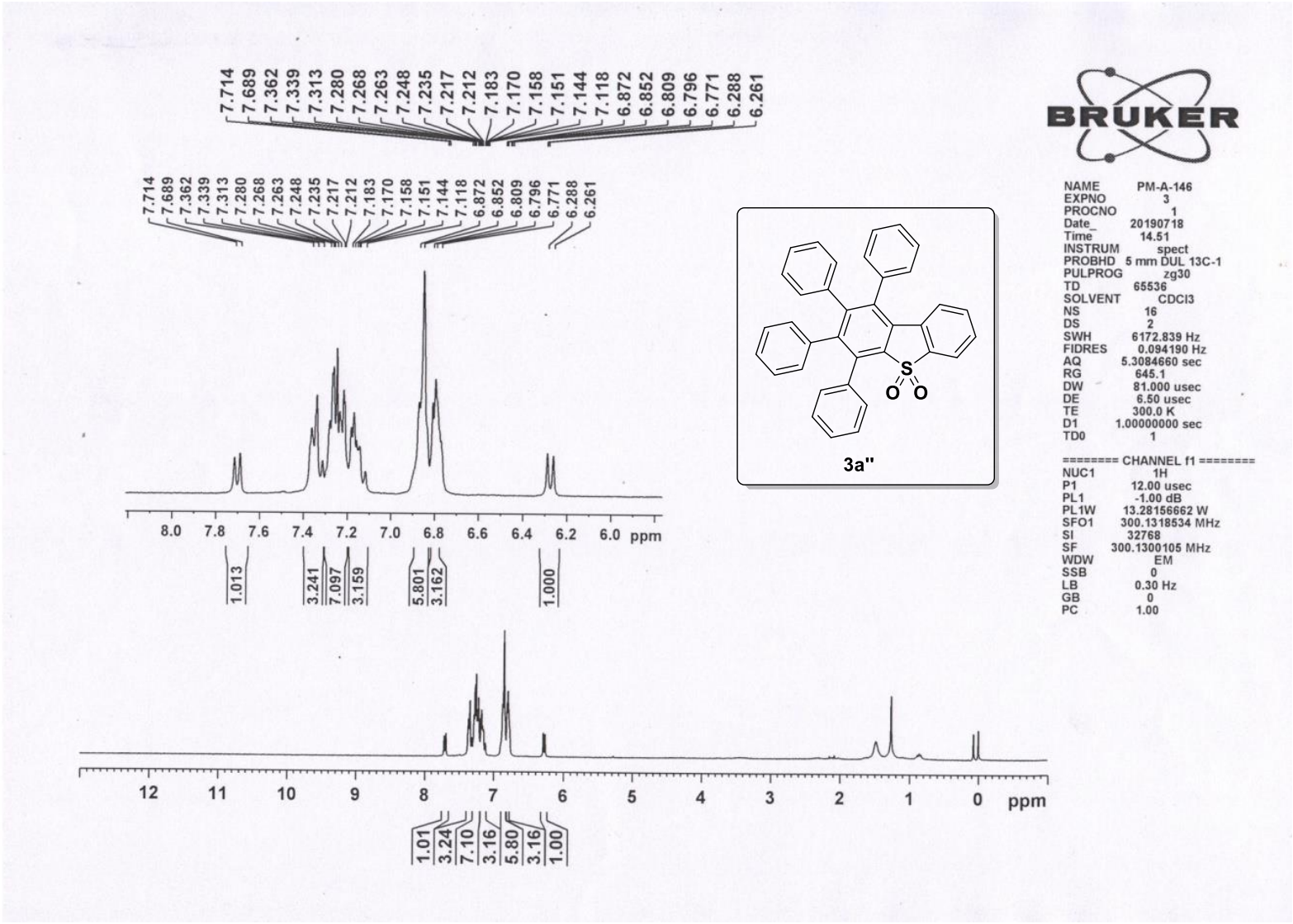
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **5a**



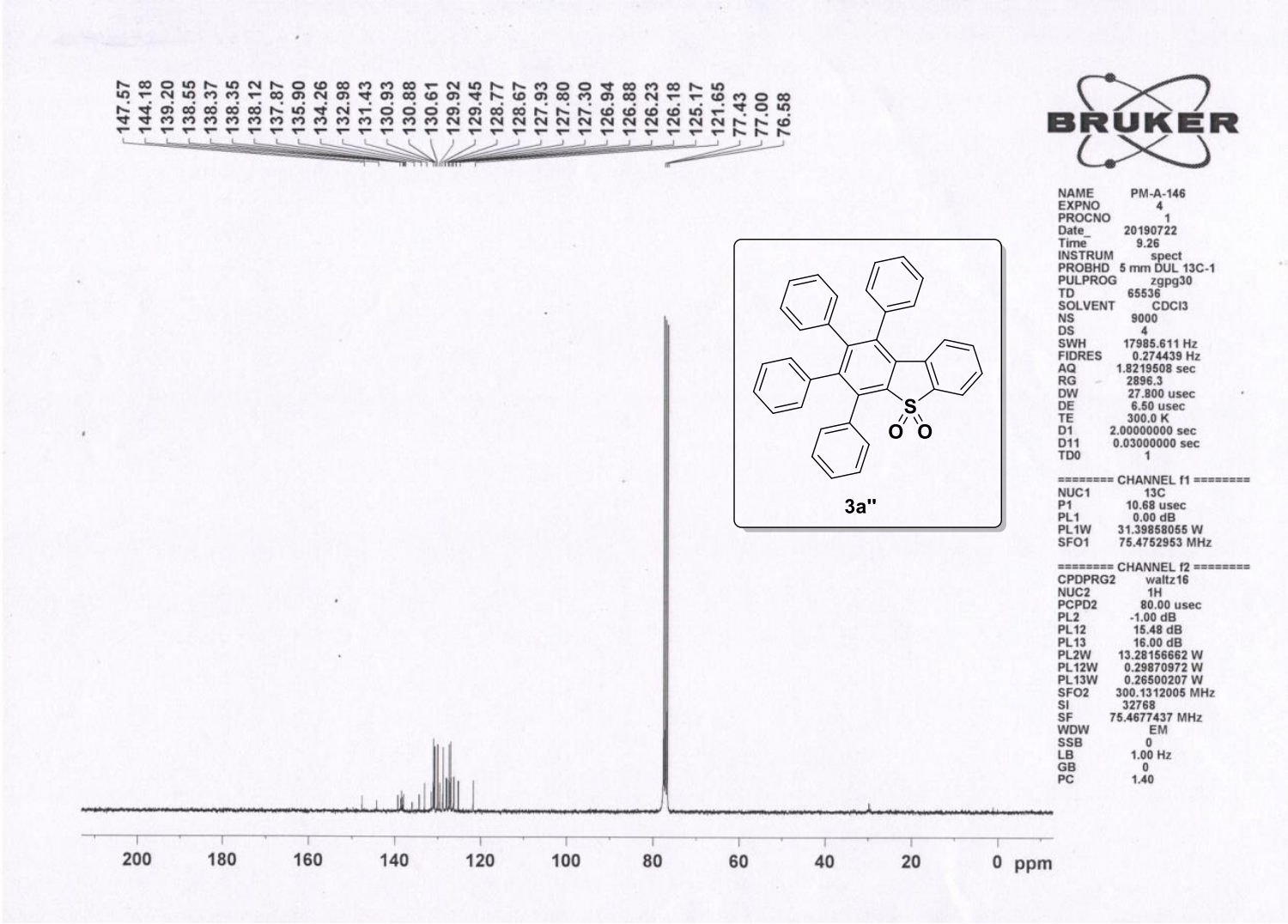
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **5b**



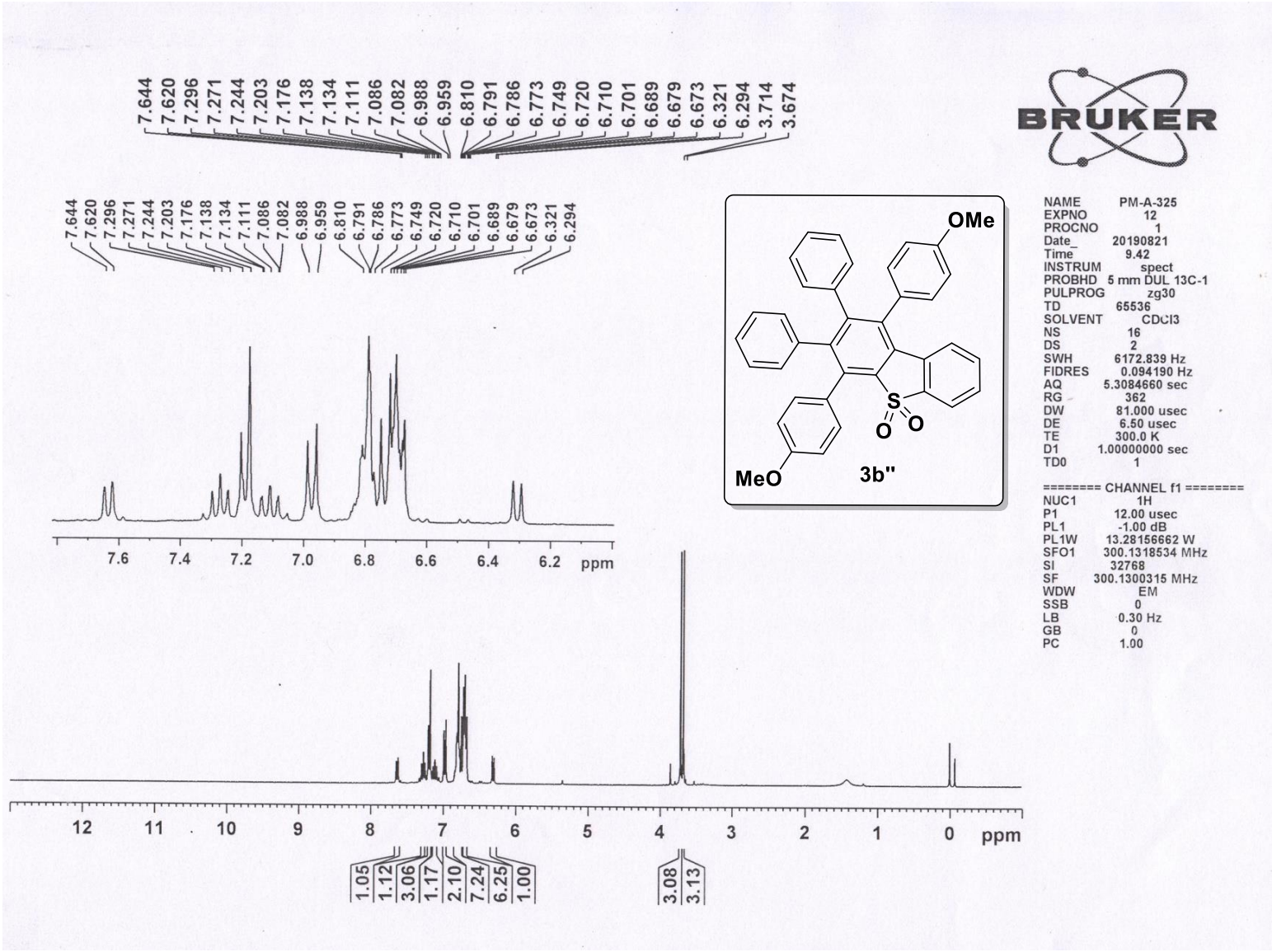
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **5b**



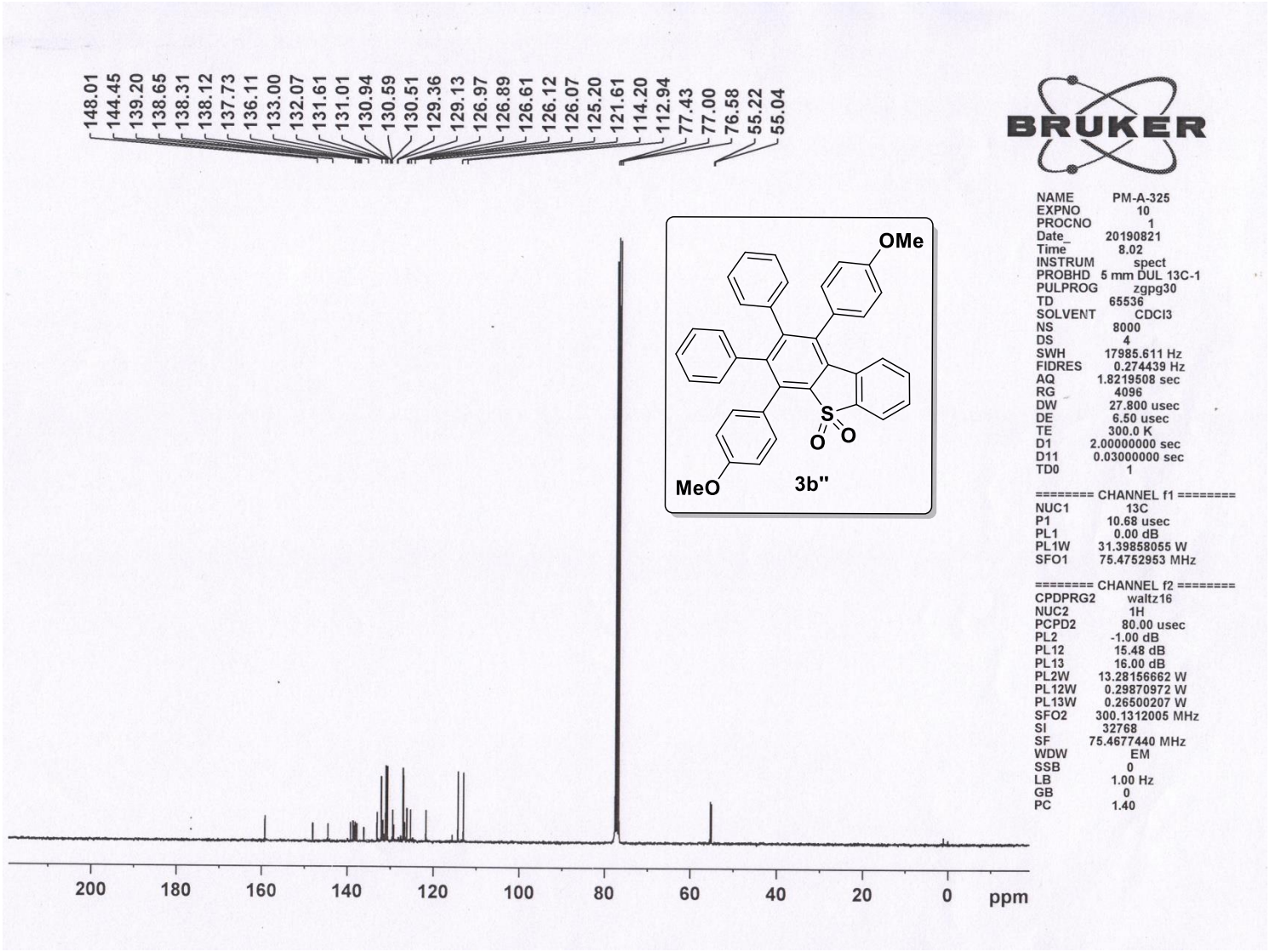
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3a''**



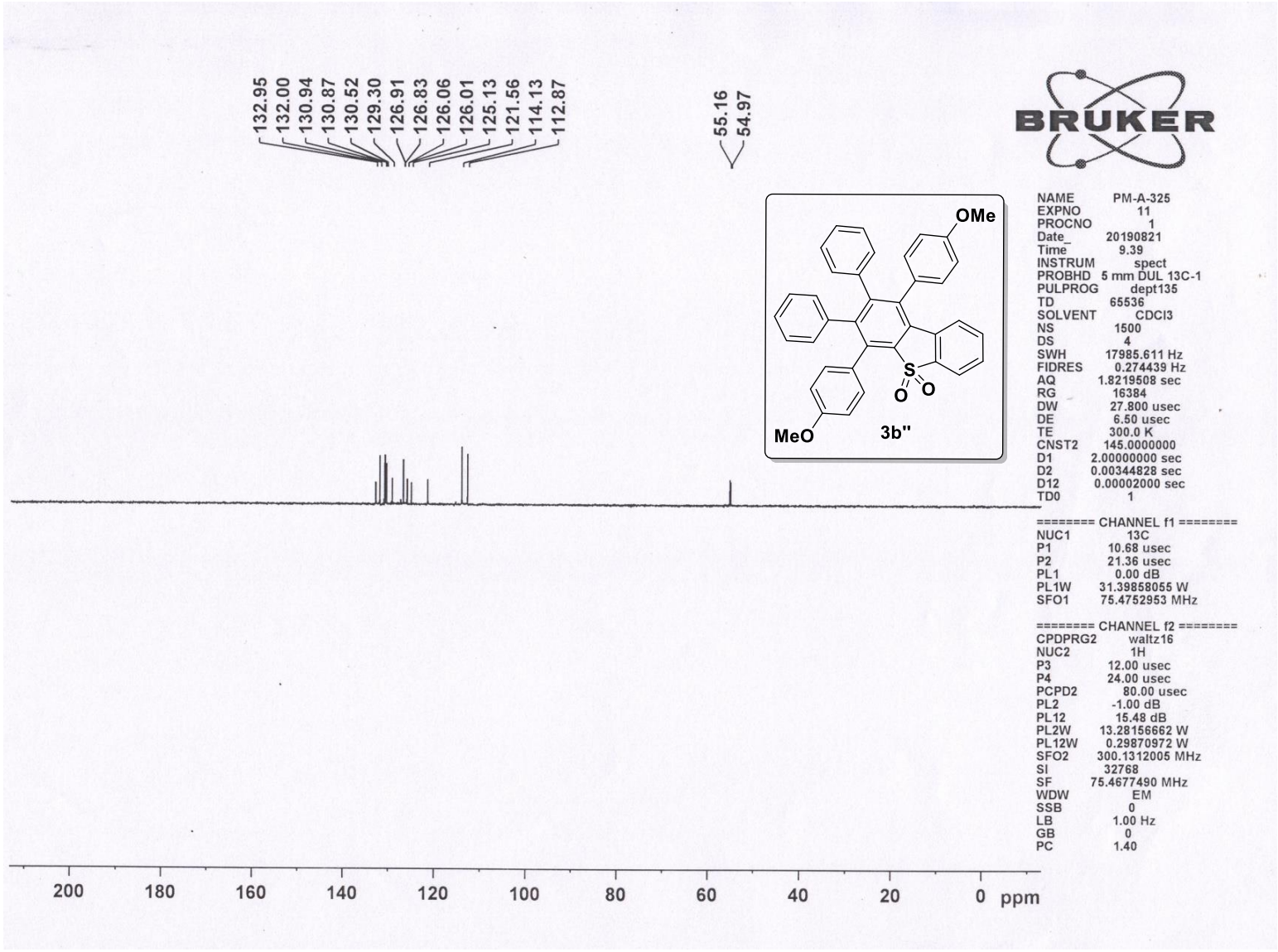
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **3a''**



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3b''**

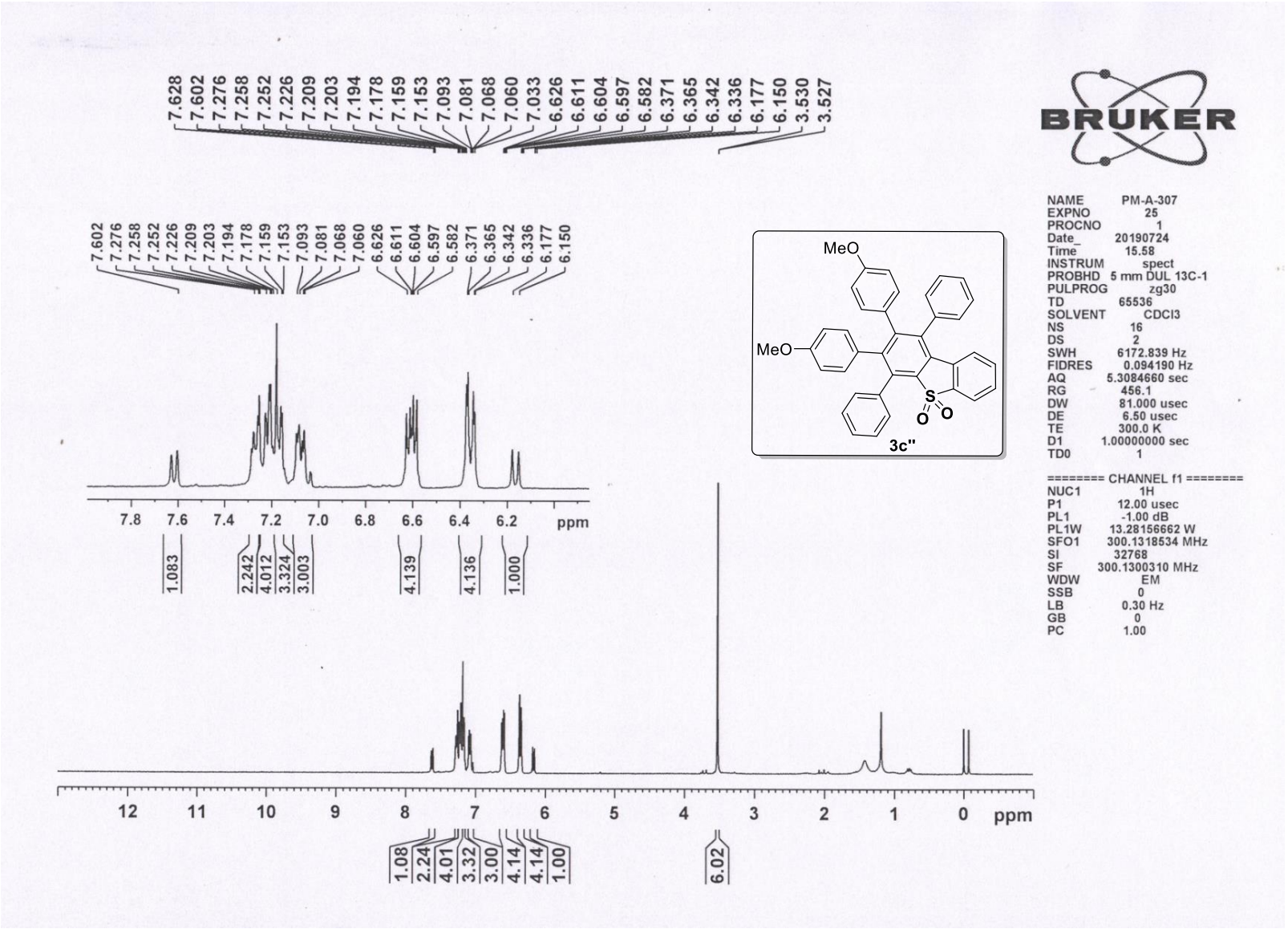


^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3b''**

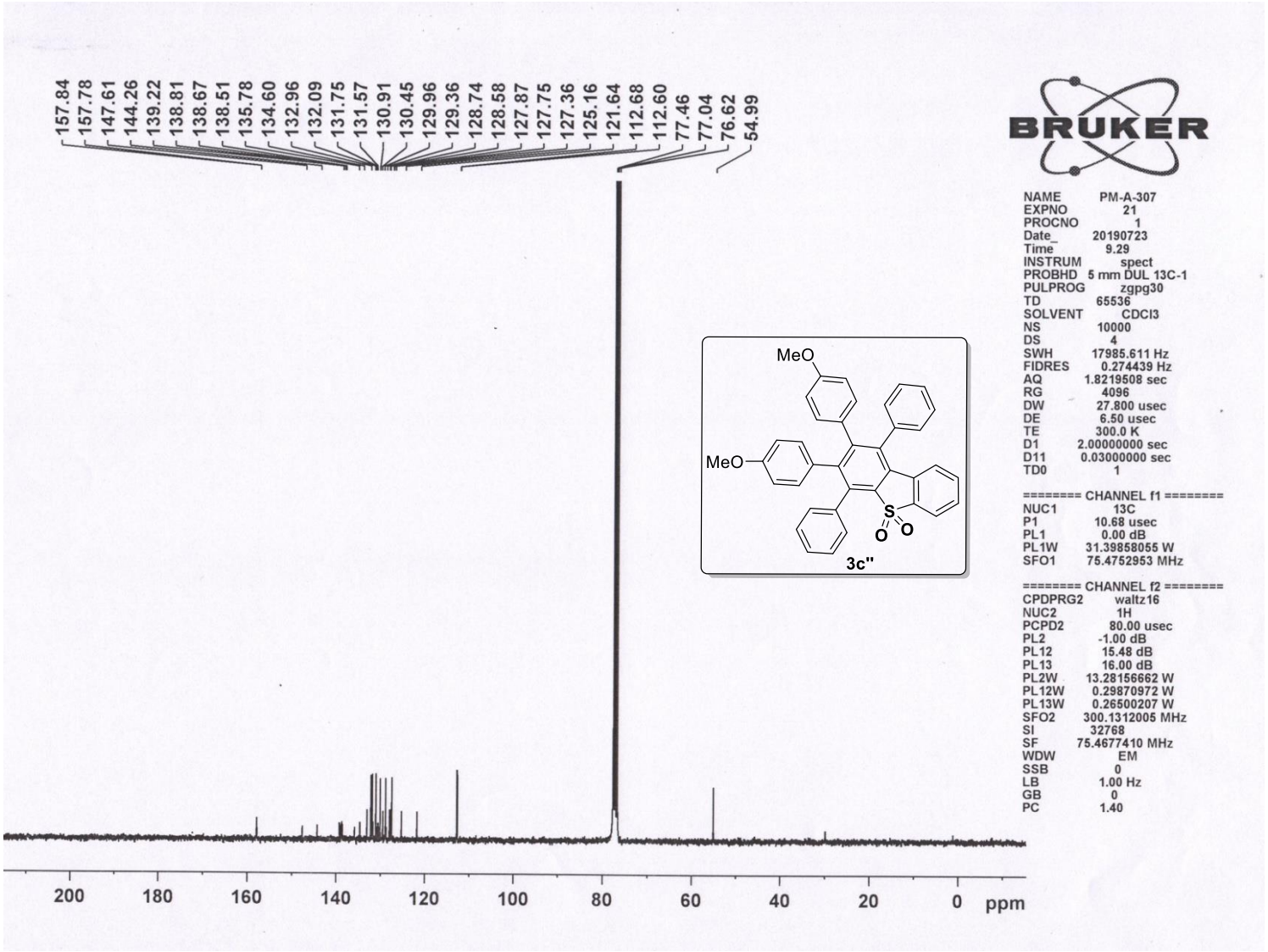



```
NAME         PM-A-325
EXPNO            11
PROCNO            1
Date_         20190821
Time              9.39
INSTRUM          spect
PROBHD   5 mm DUL 13C-1
PULPROG        dept135
TD             65536
SOLVENT         CDCl3
NS              1500
DS                 4
SWH        17985.611 Hz
FIDRES         0.274439 Hz
AQ          1.8219508 sec
RG                16384
DW             27.800 usec
DE              6.50 usec
TE              300.0 K
CNST2       145.0000000
D1         2.00000000 sec
D2         0.00344828 sec
D12        0.00002000 sec
TD0               1

======== CHANNEL f1 ========
NUC1              13C
P1             10.68 usec
P2             21.36 usec
PL1             0.00 dB
PL1W       31.39858055 W
SFO1       75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2              1H
P3             12.00 usec
P4             24.00 usec
PCPD2          80.00 usec
PL2            -1.00 dB
PL12           15.48 dB
PL2W       13.28156662 W
PL12W       0.29870972 W
SFO2       300.1312005 MHz
SI              32768
SF         75.4677490 MHz
WDW               EM
SSB               0
LB             1.00 Hz
GB                0
PC             1.40
```

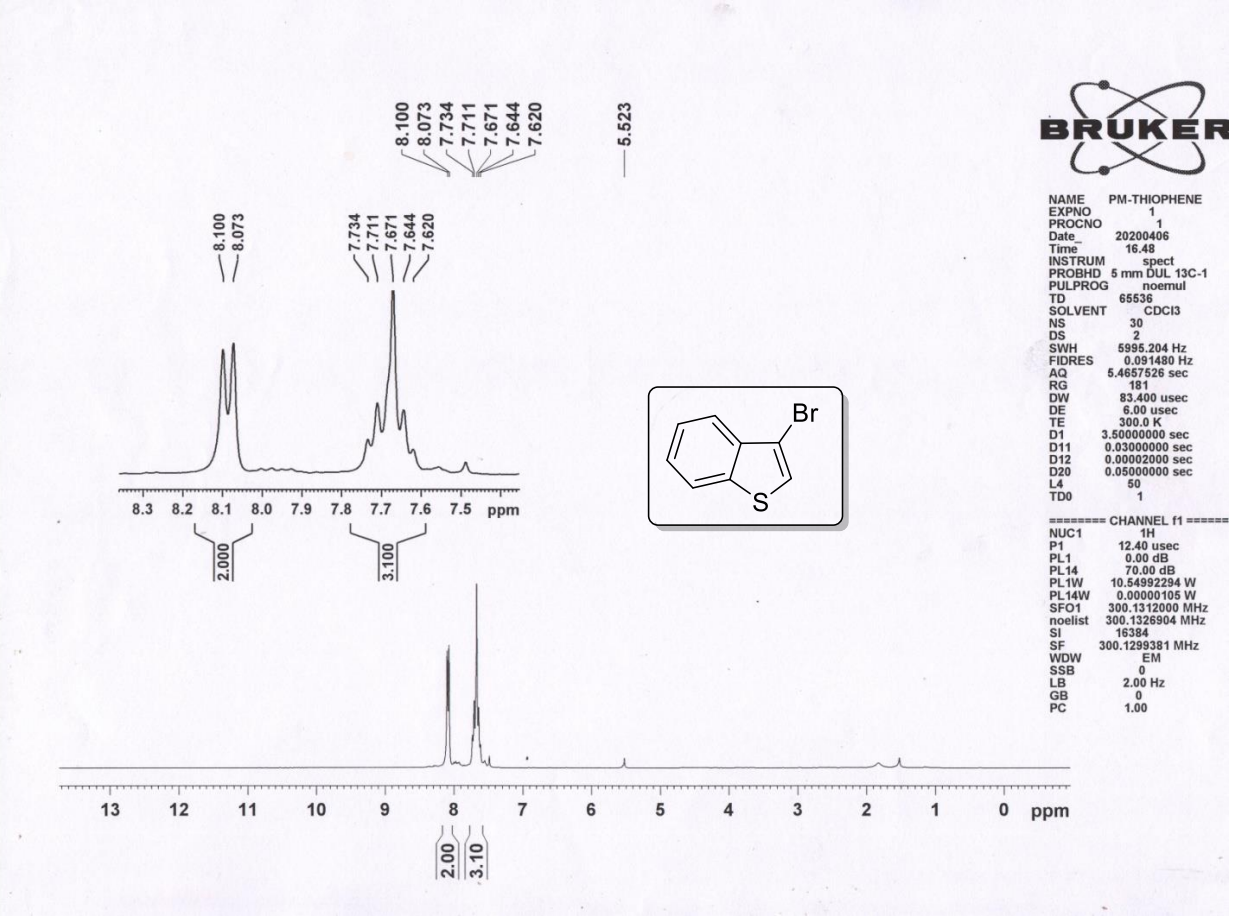
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **3b''**



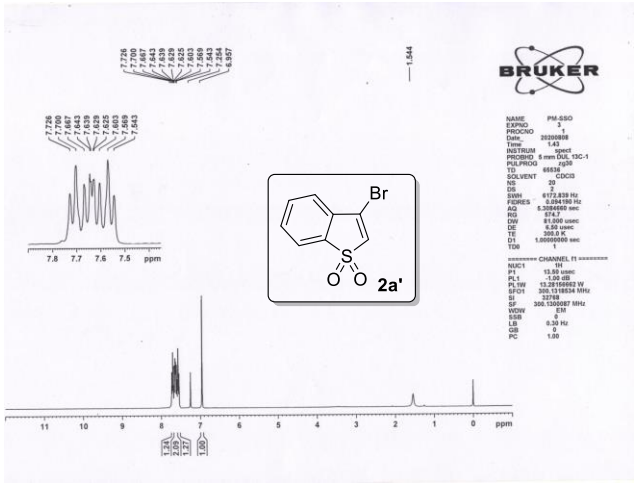
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3c''**



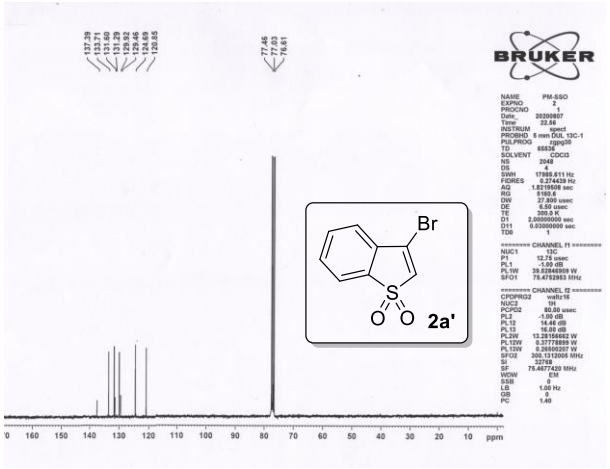
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3c''**



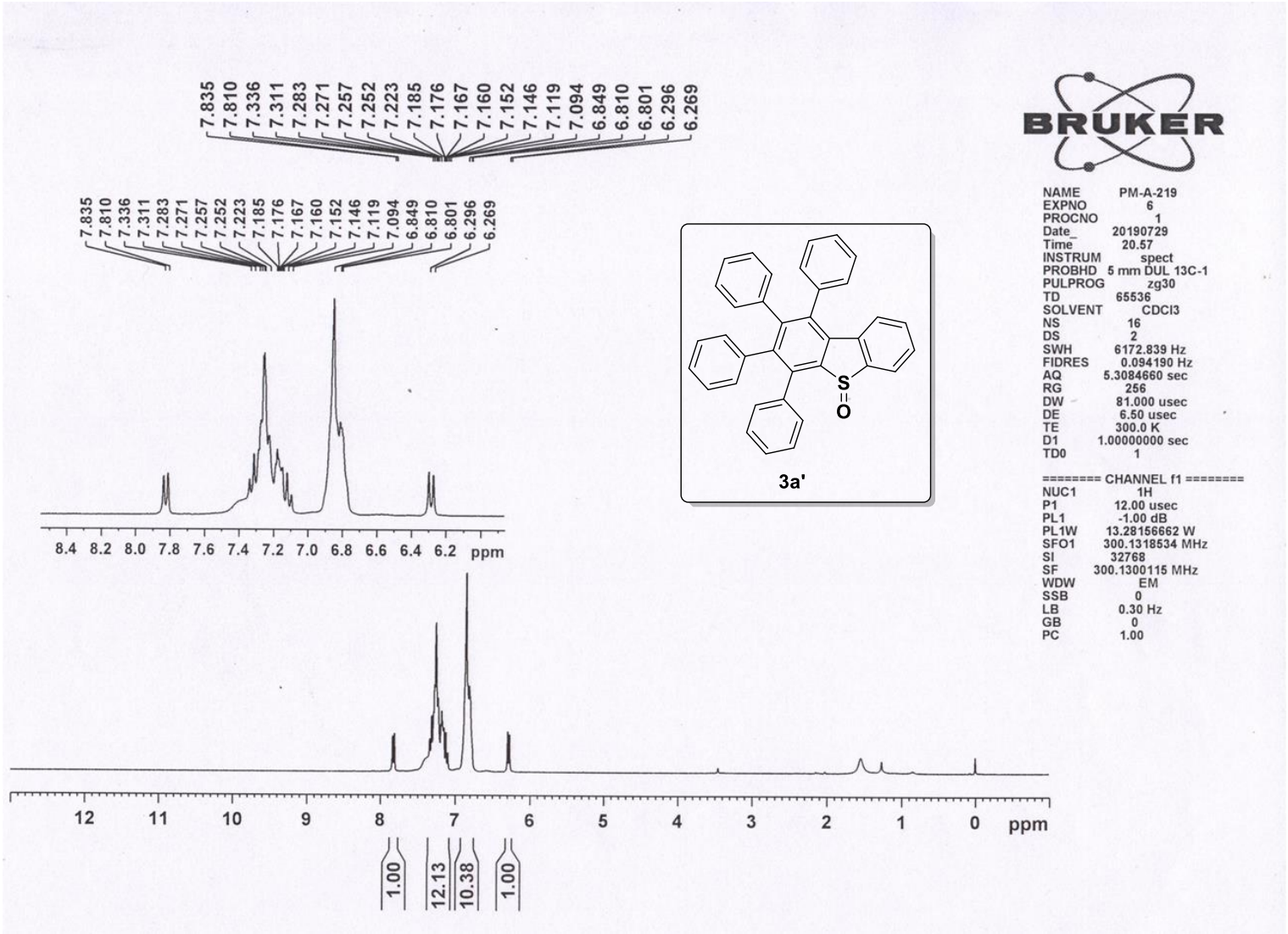
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 3-bromobenzothiophene



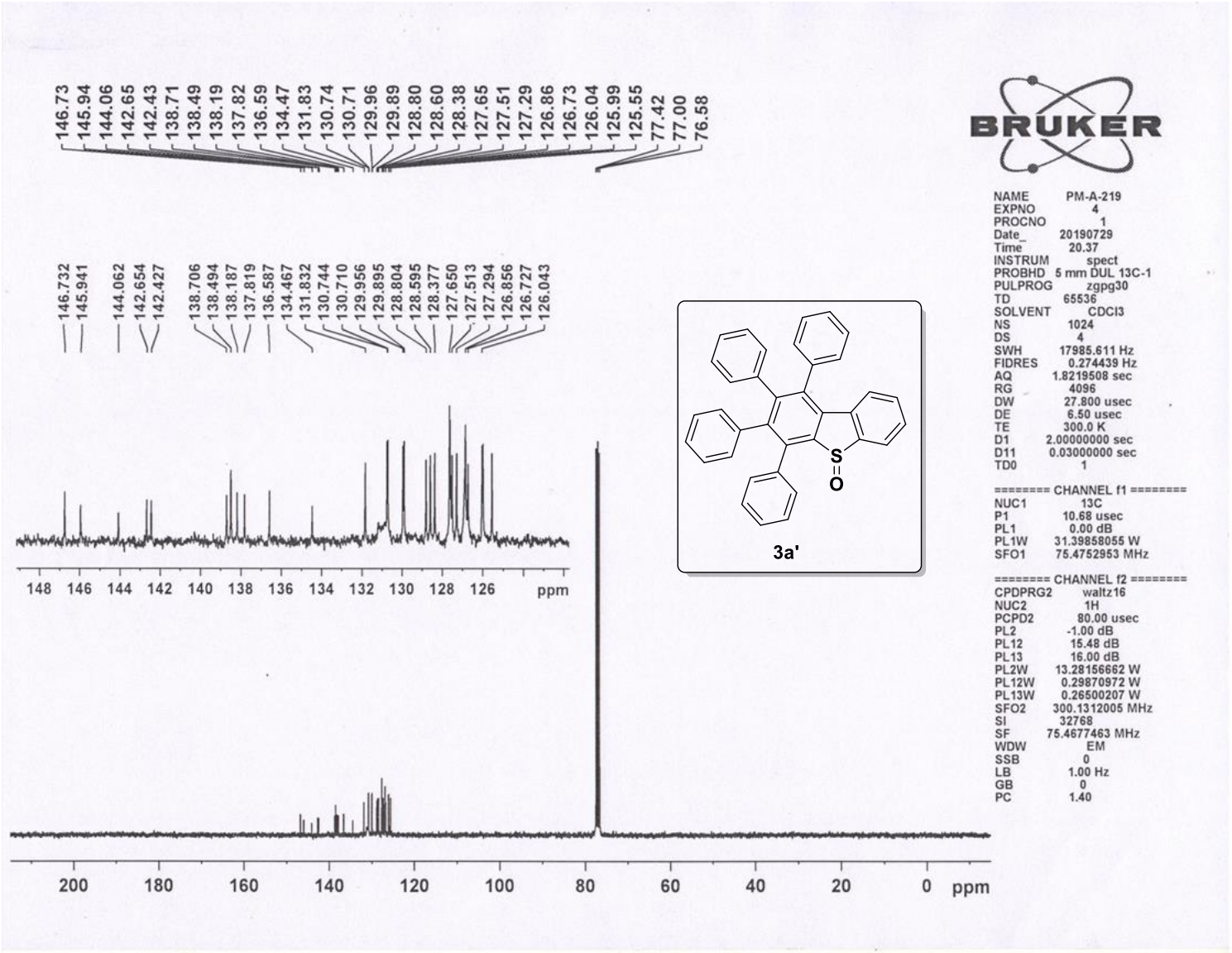
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **2a'**



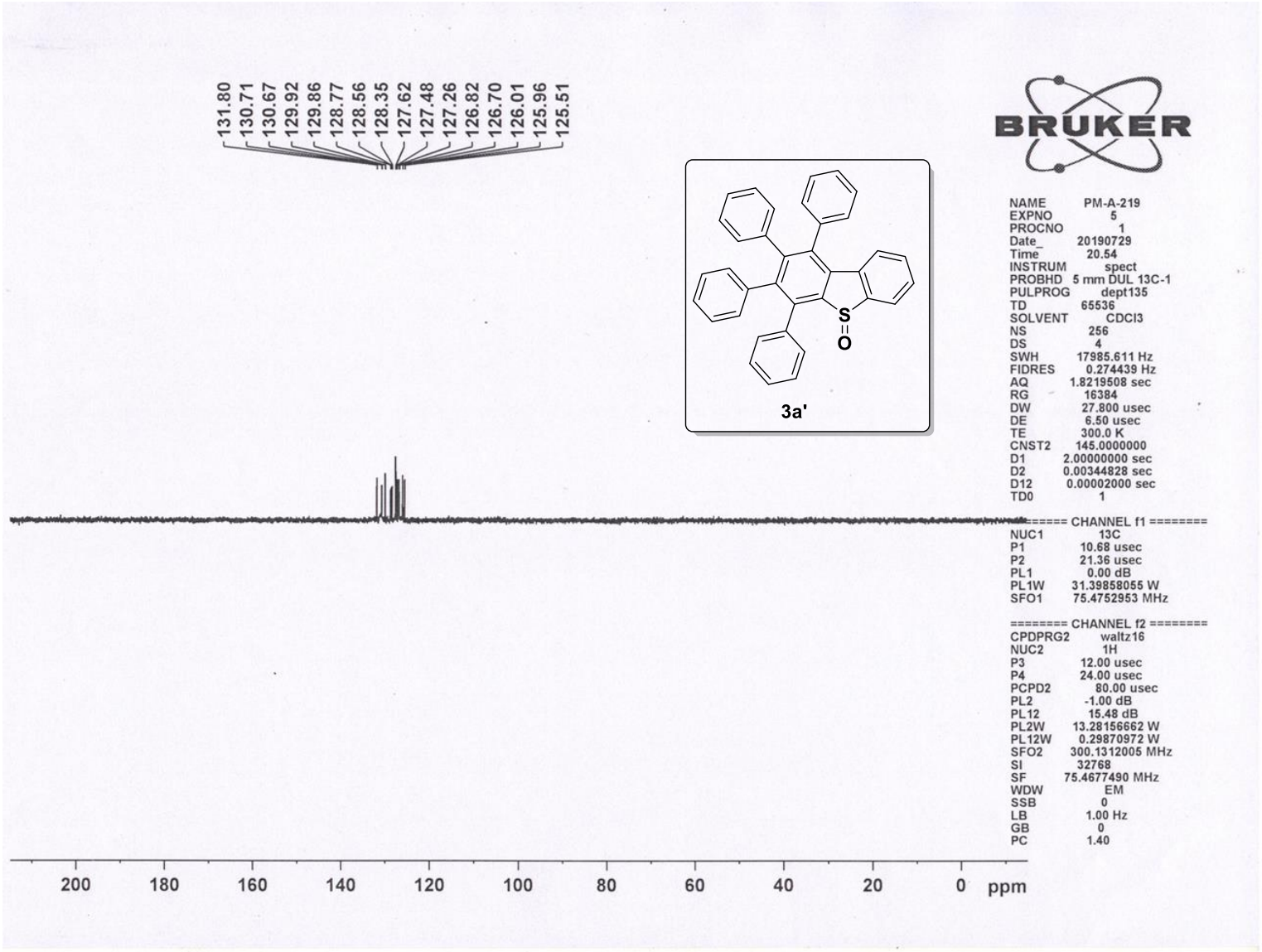
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **2a'**



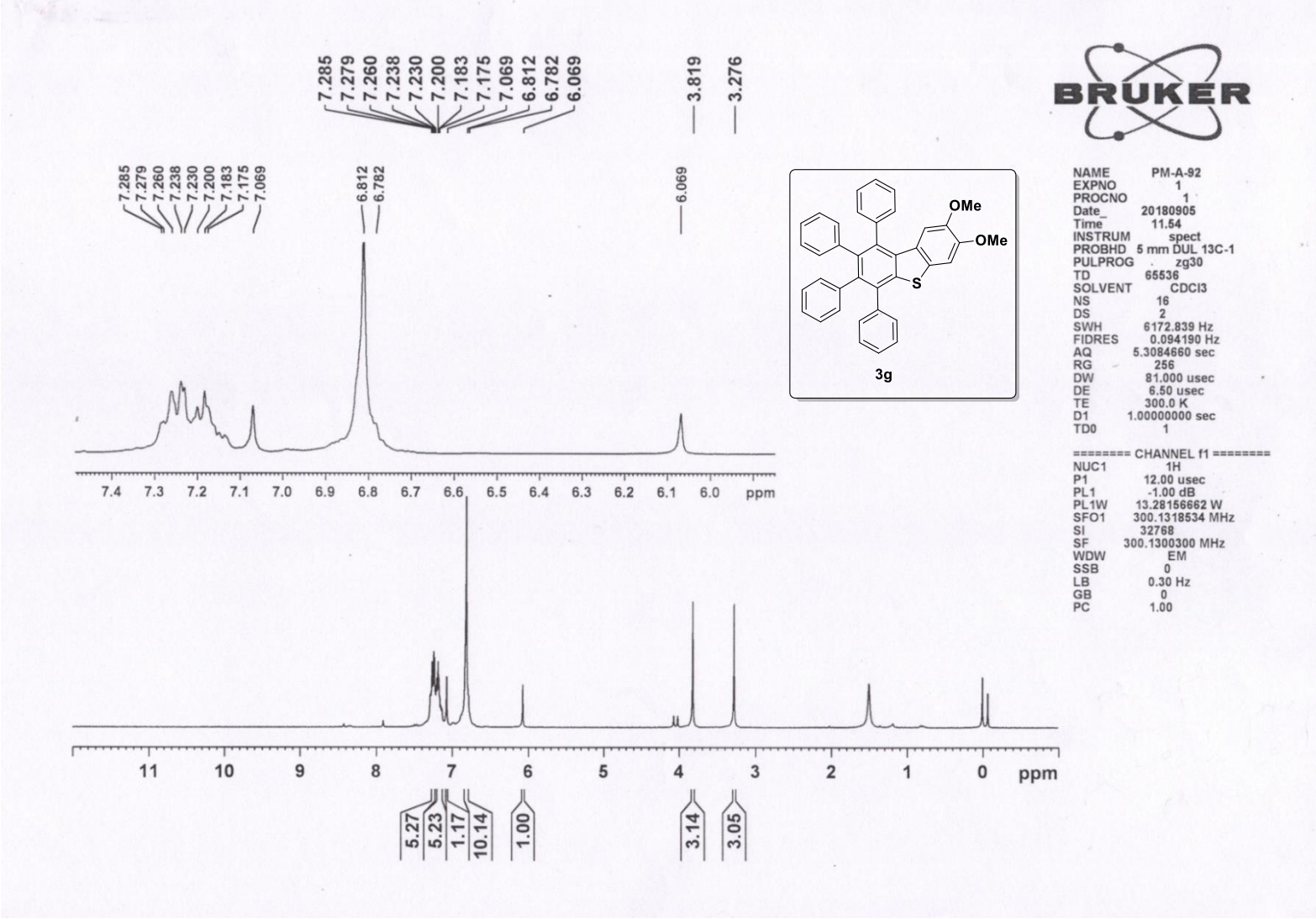
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **3a'**



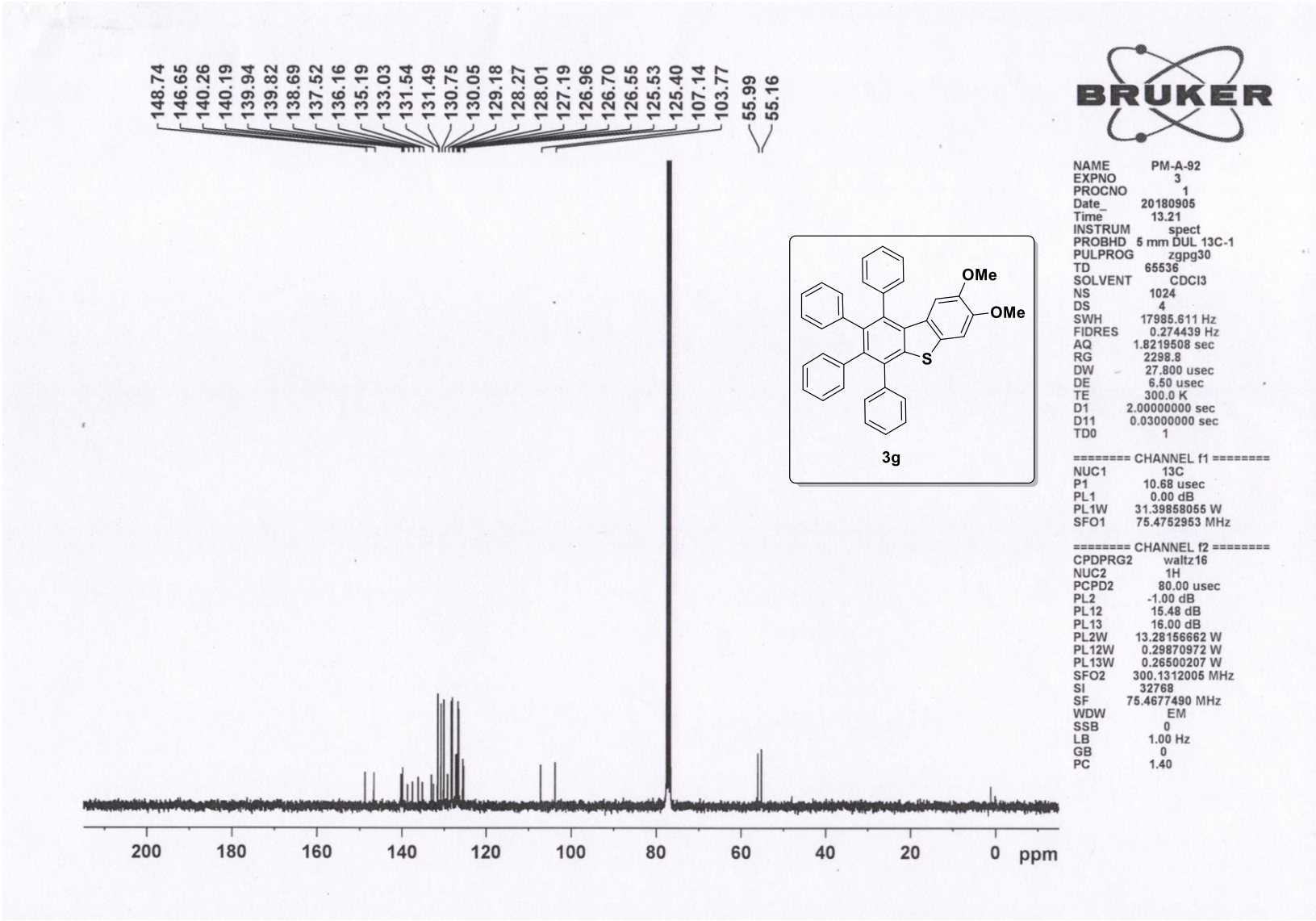
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **3a'**



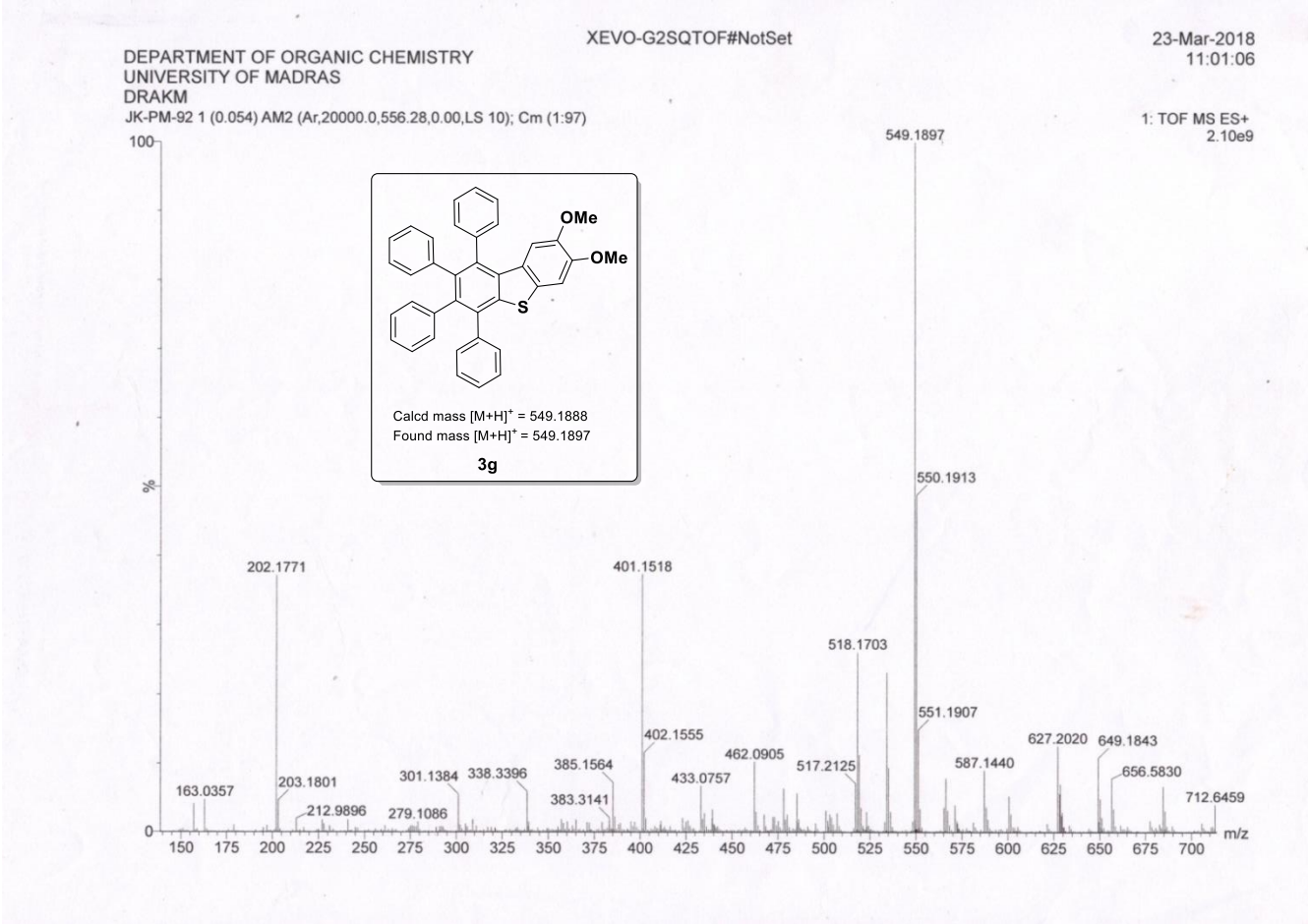
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3a'**



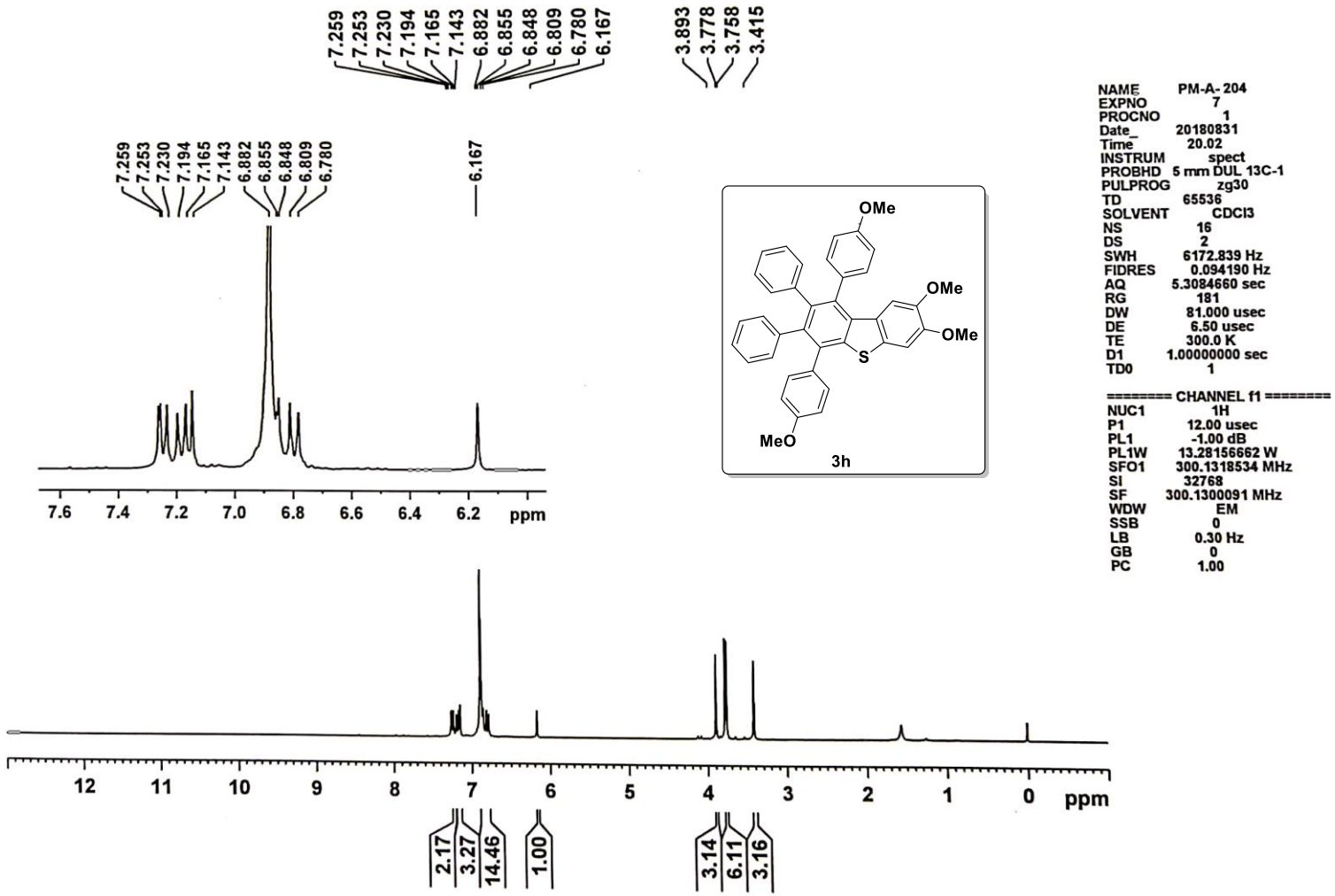
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3g**



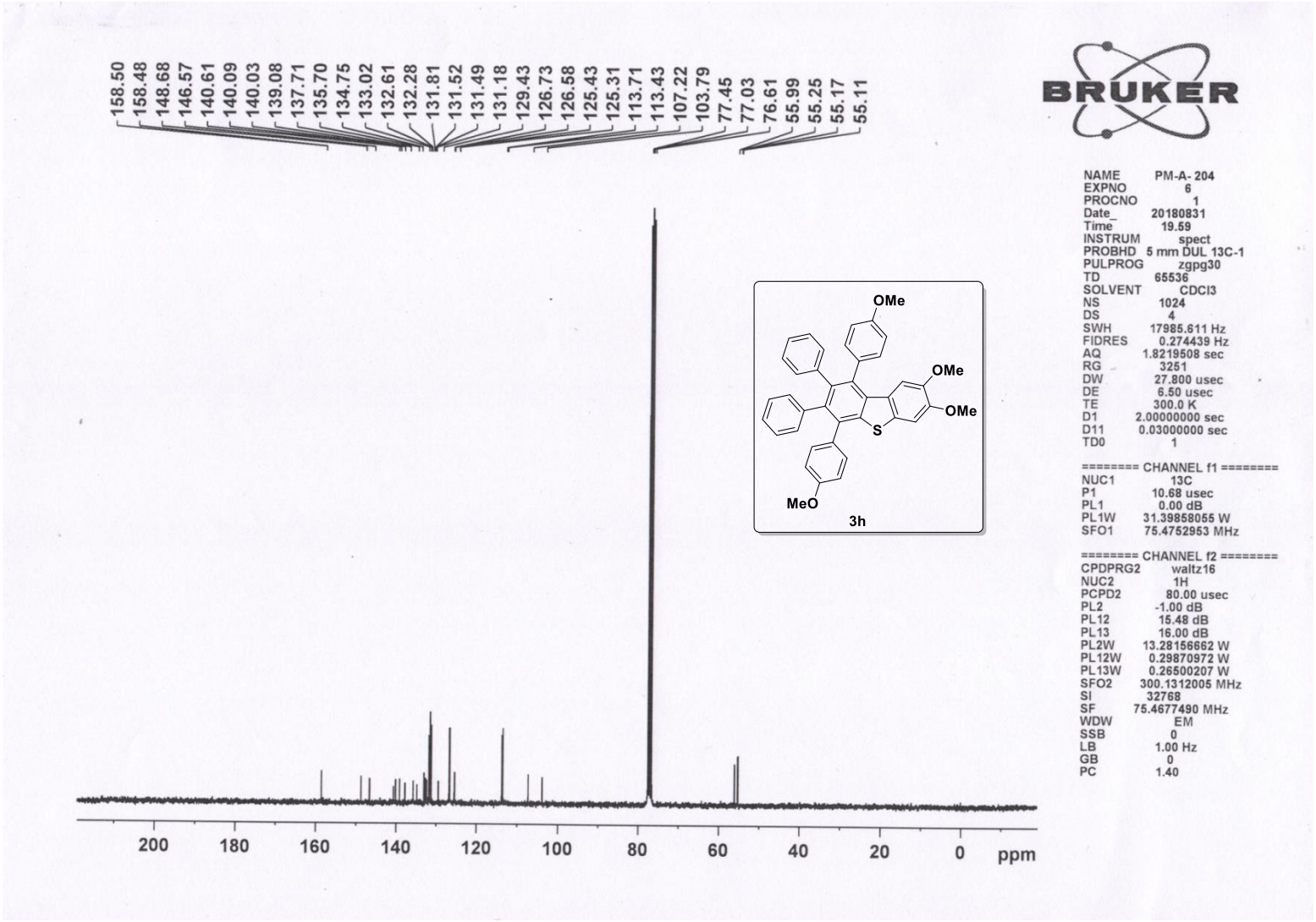
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3g**



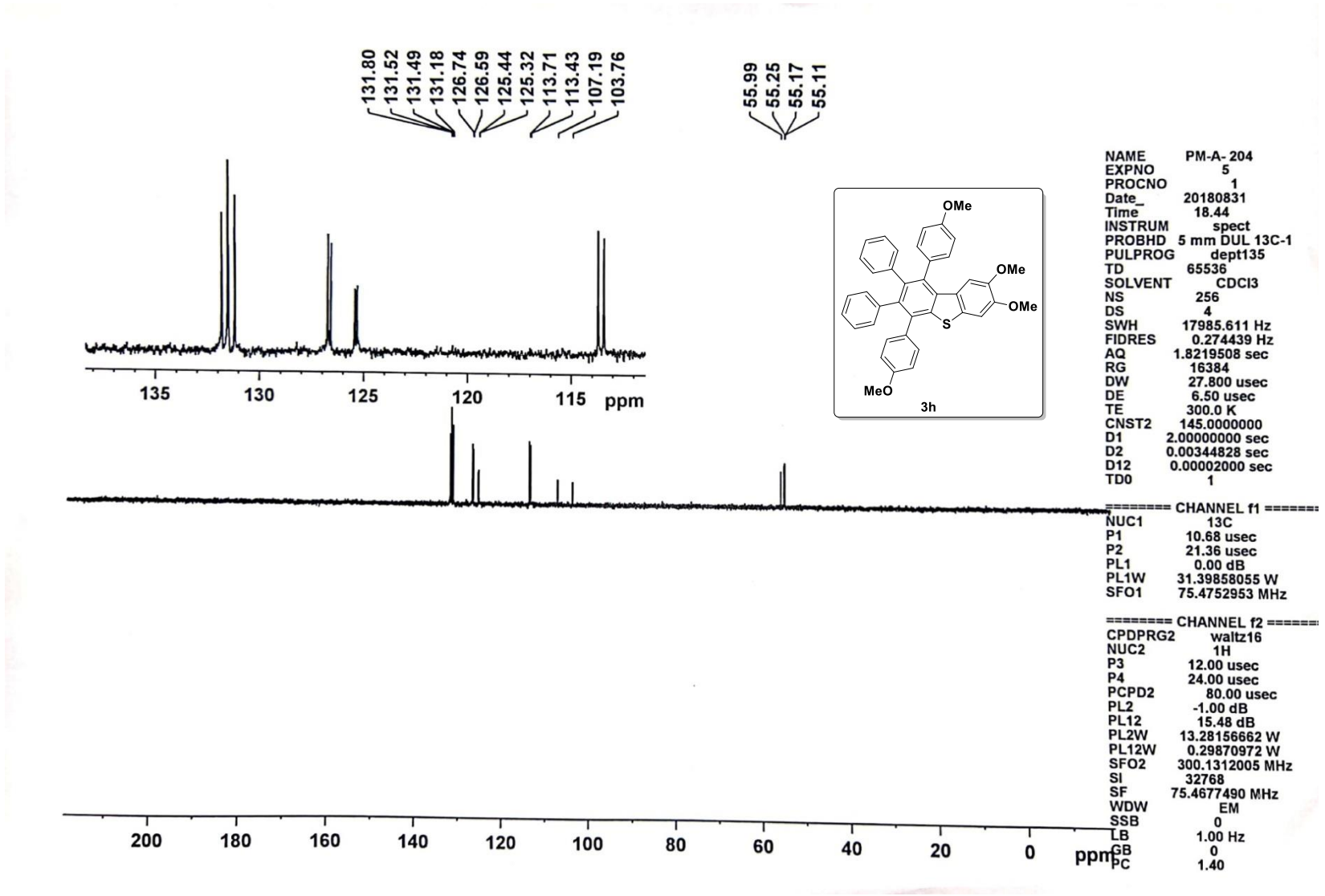
HRMS spectrum of compound **3g**



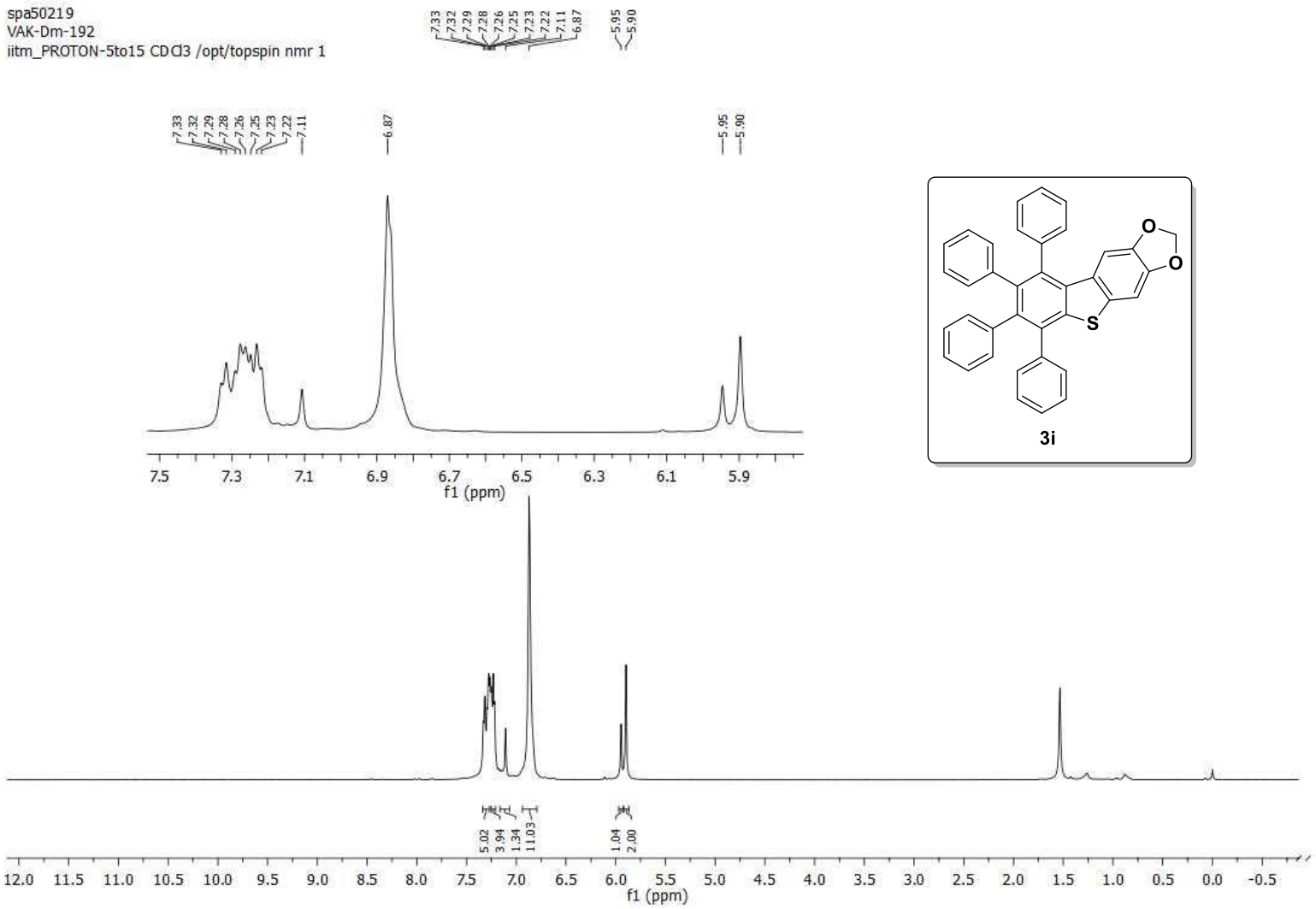
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3h**



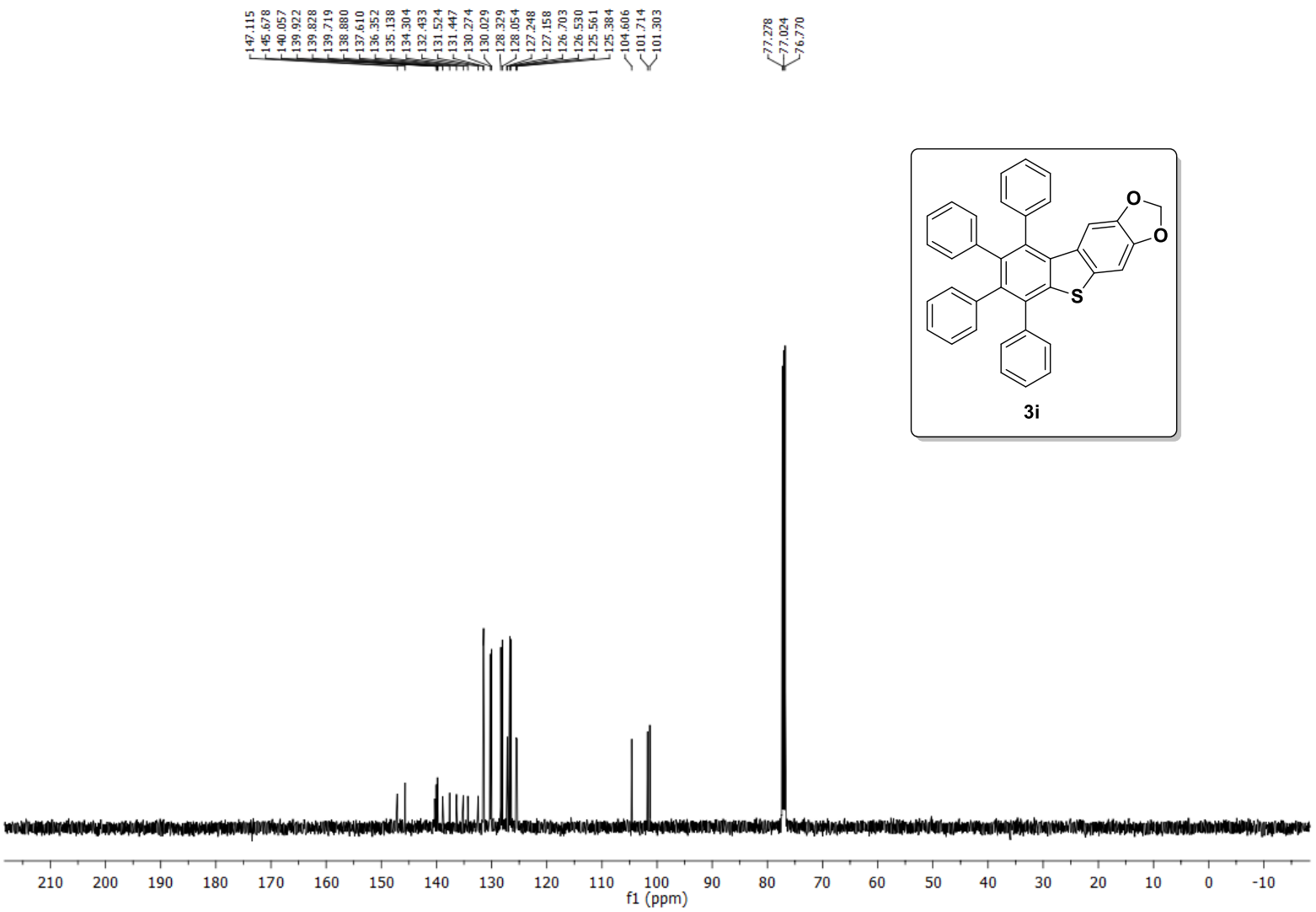
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3h**



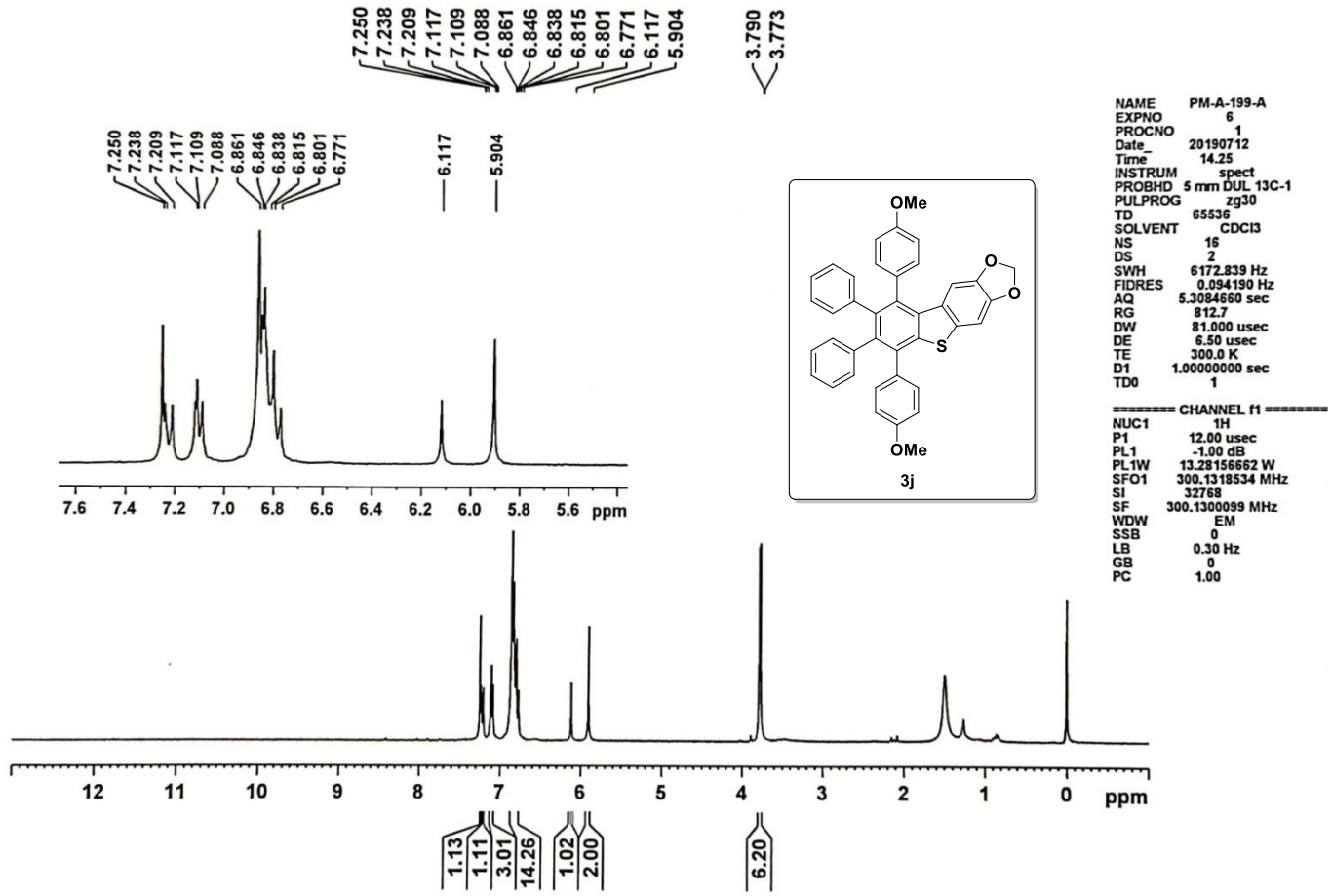
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **3h**



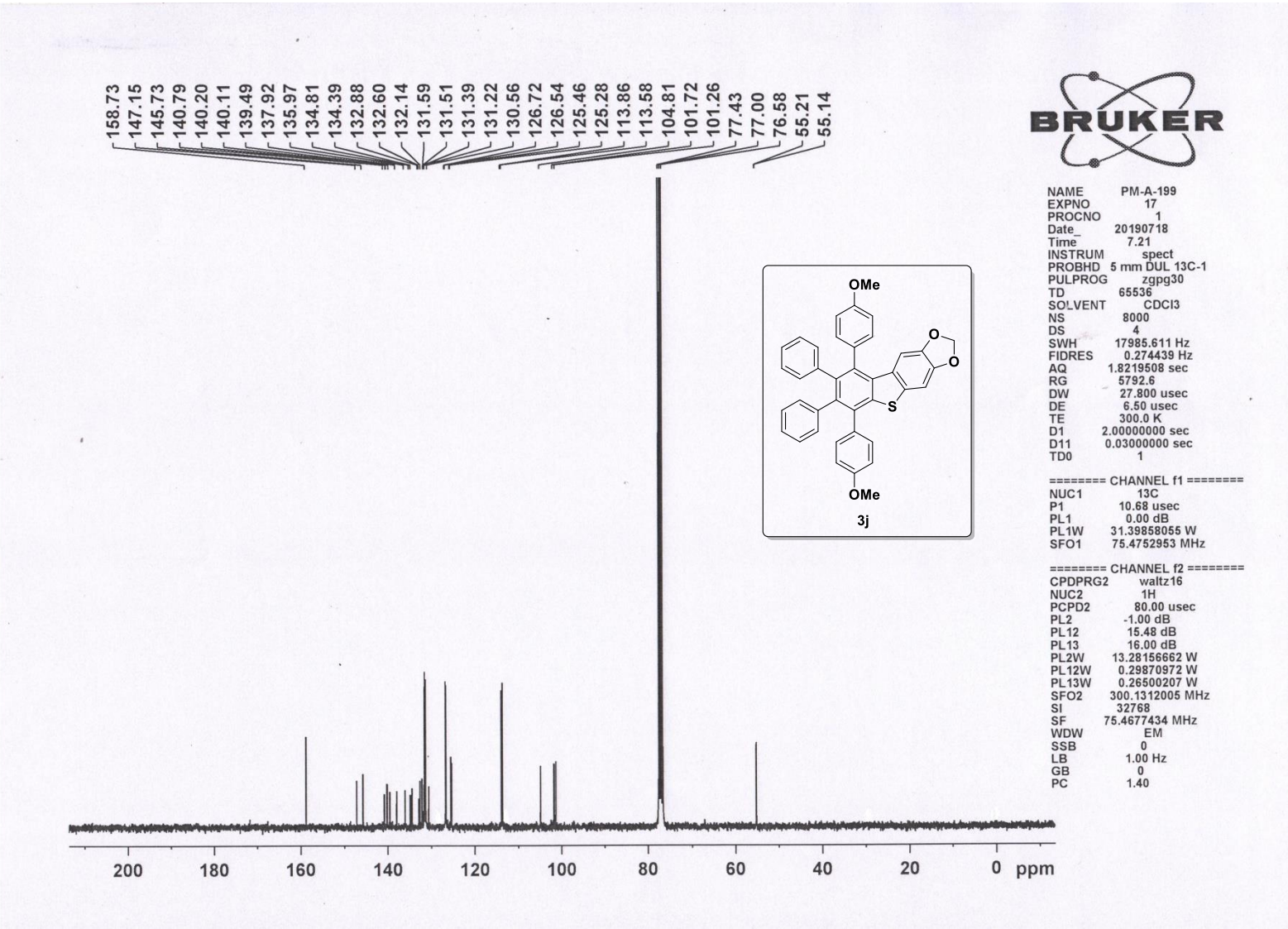
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



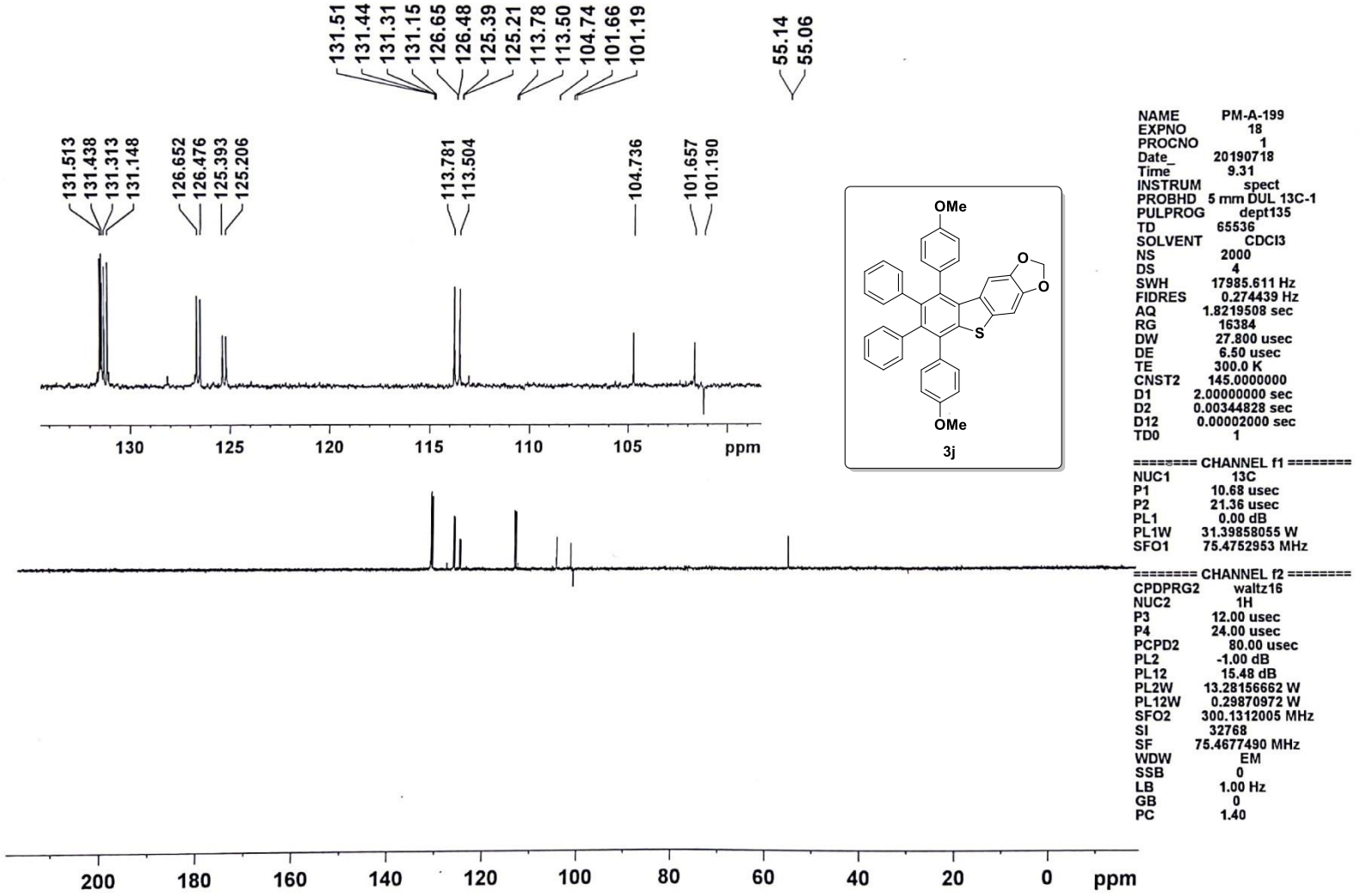
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**



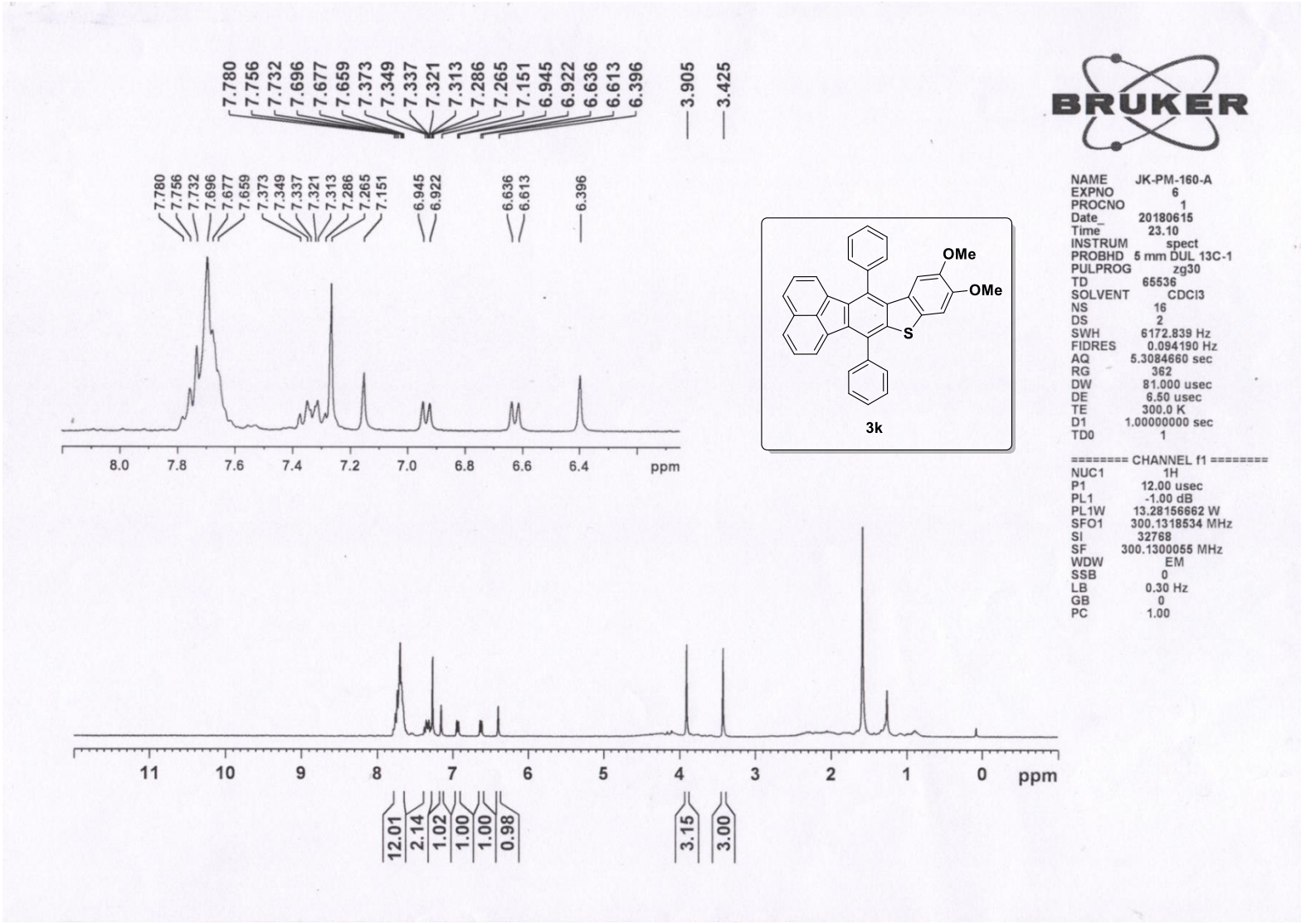
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3j**



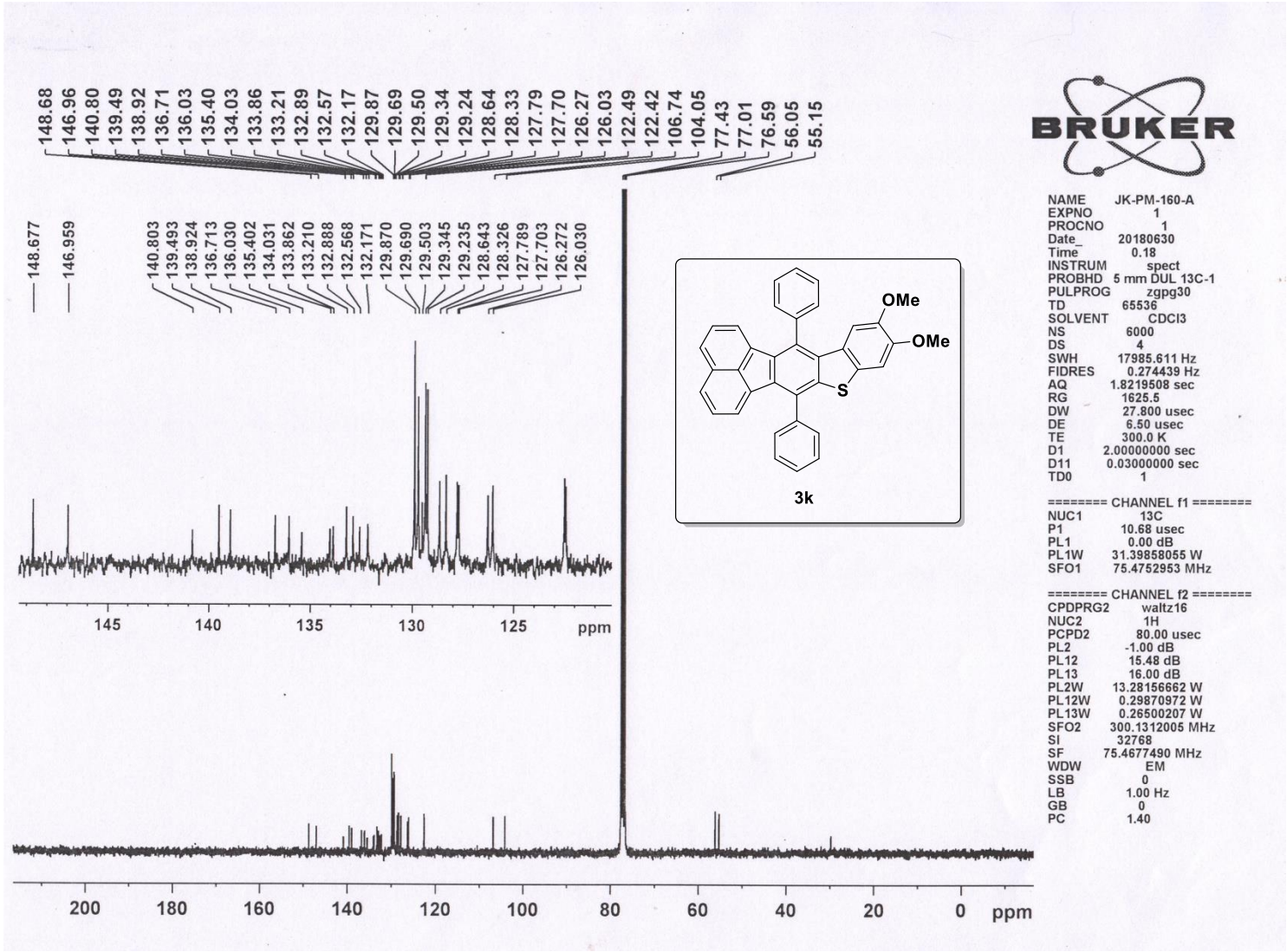
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3j**



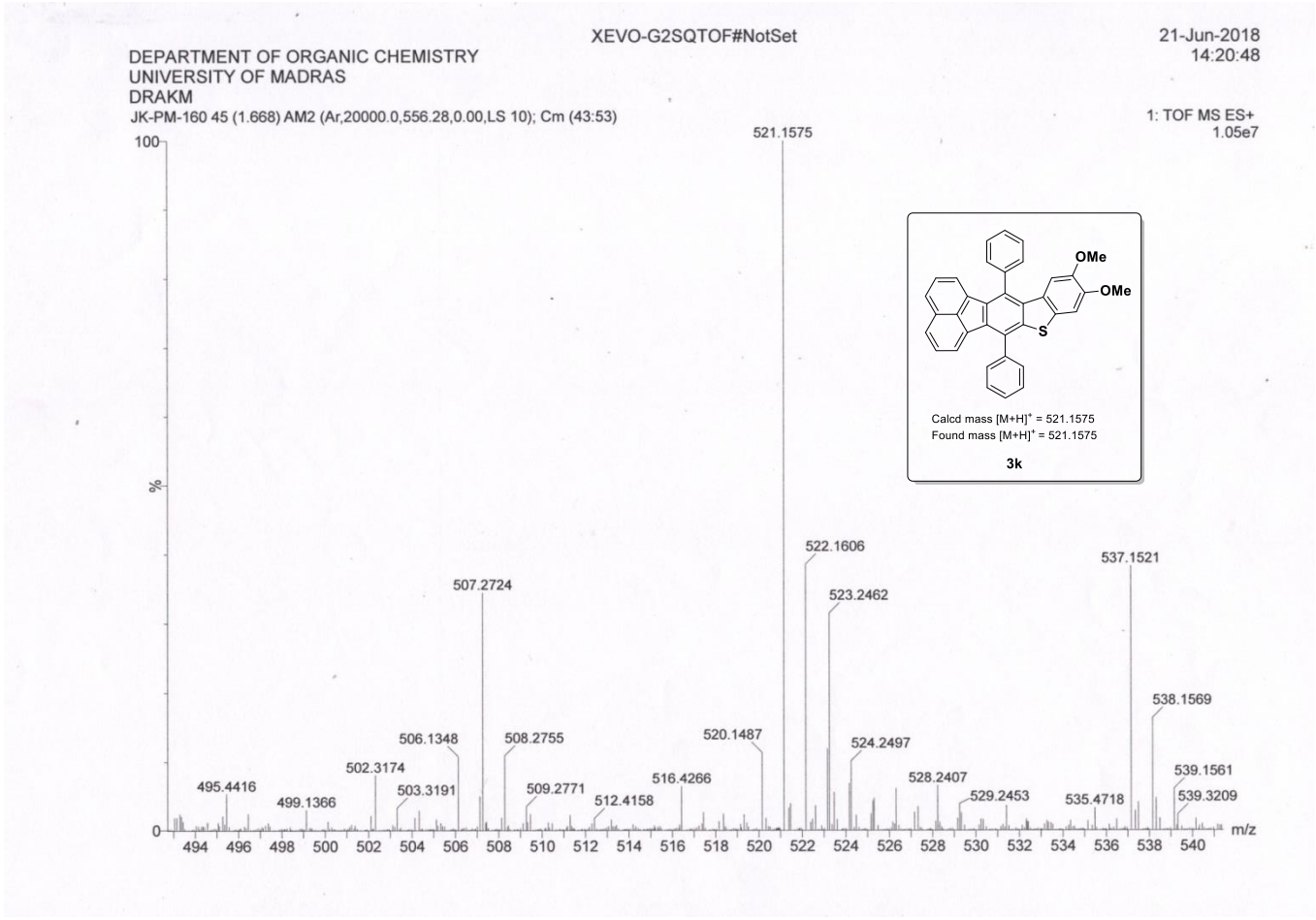
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **3j**



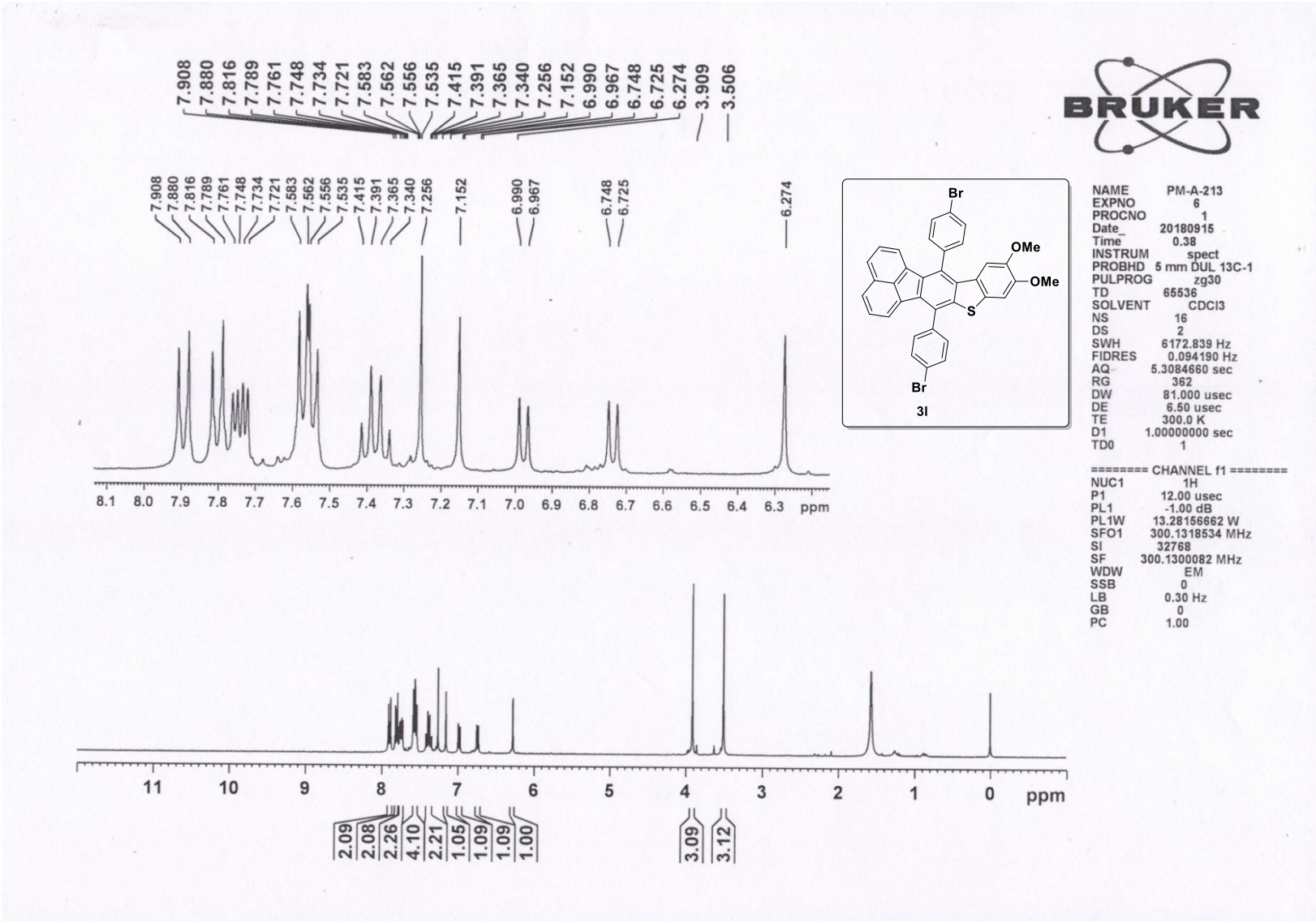
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3k**



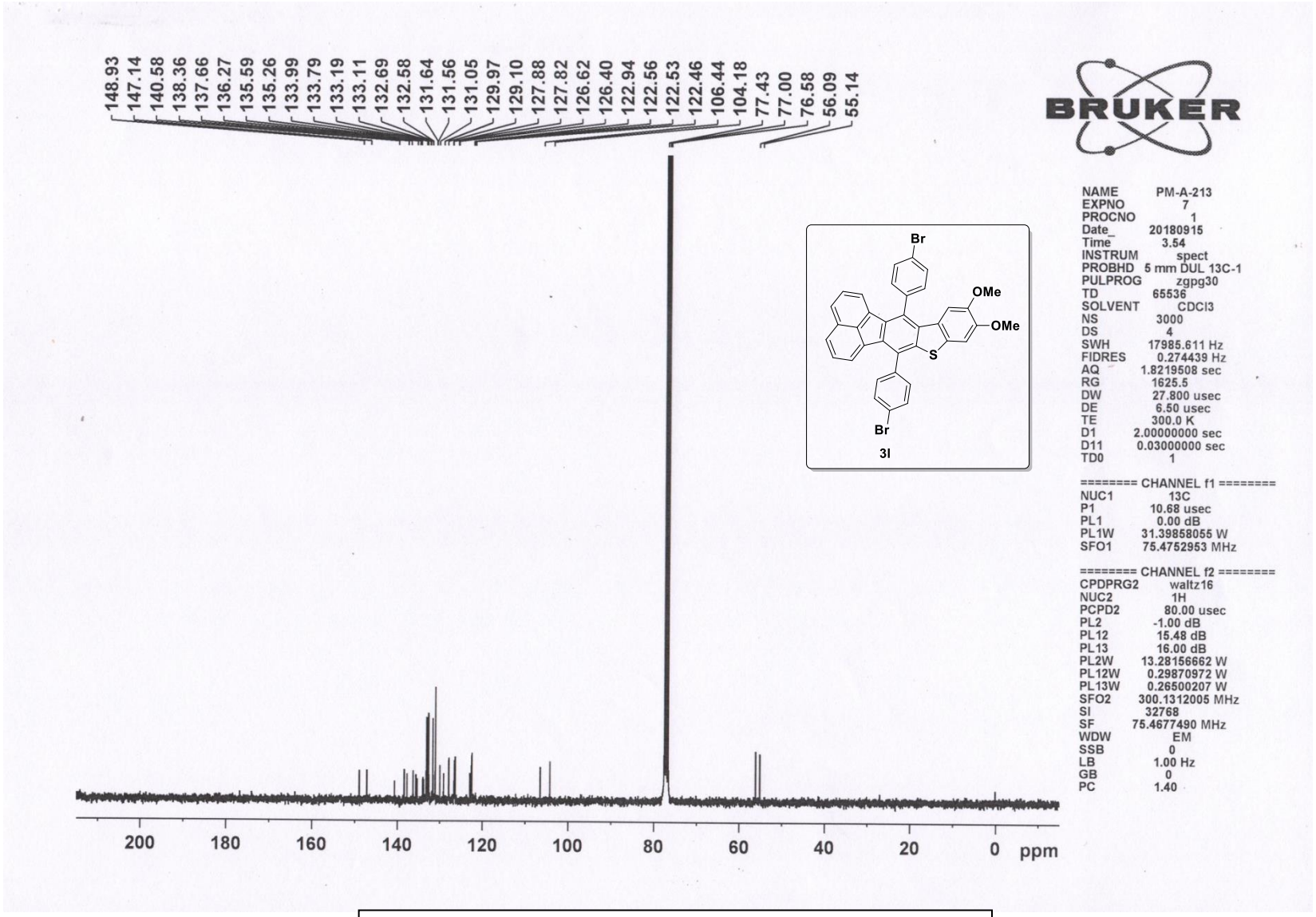
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3k**



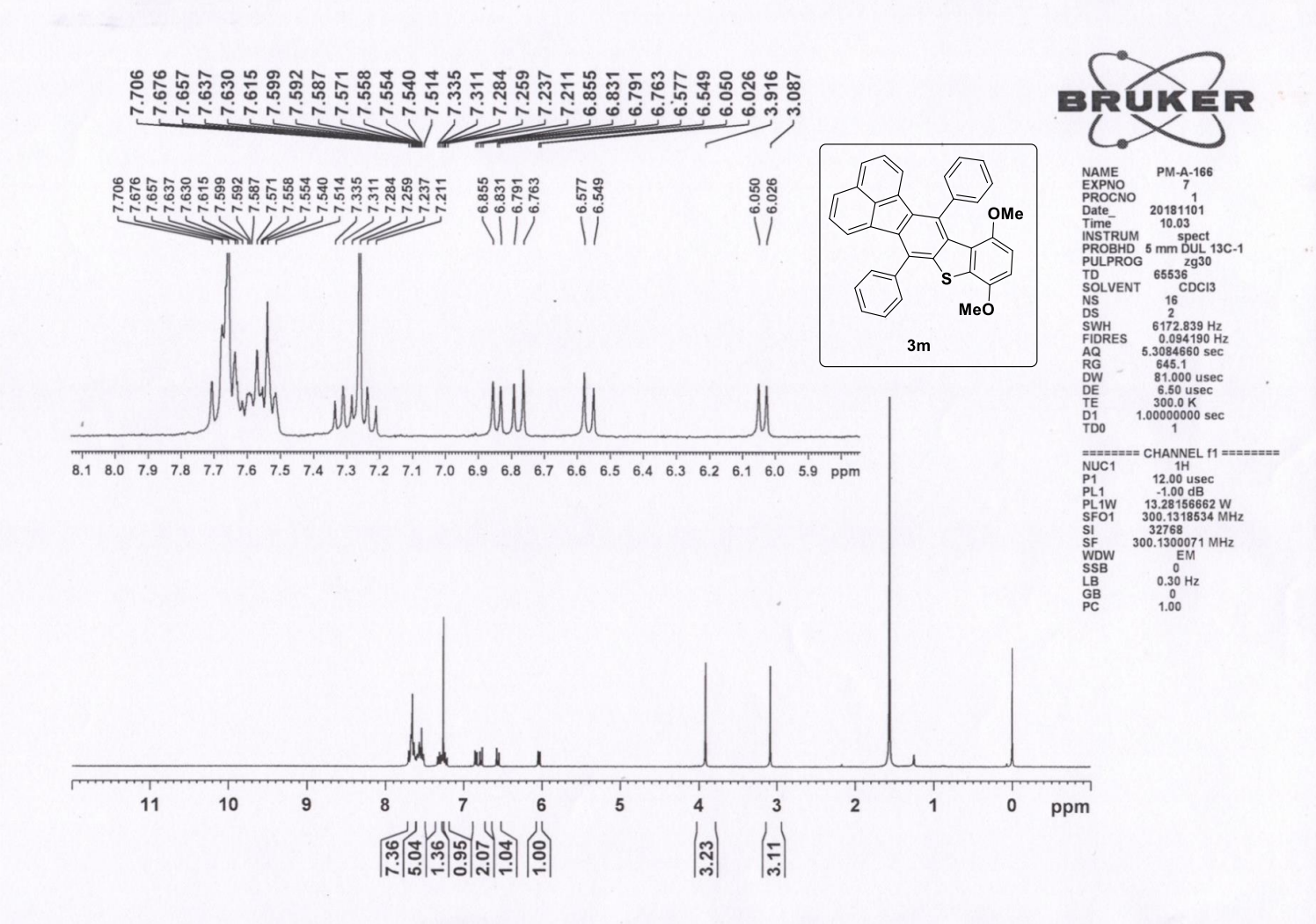
HRMS spectrum of compound **3k**



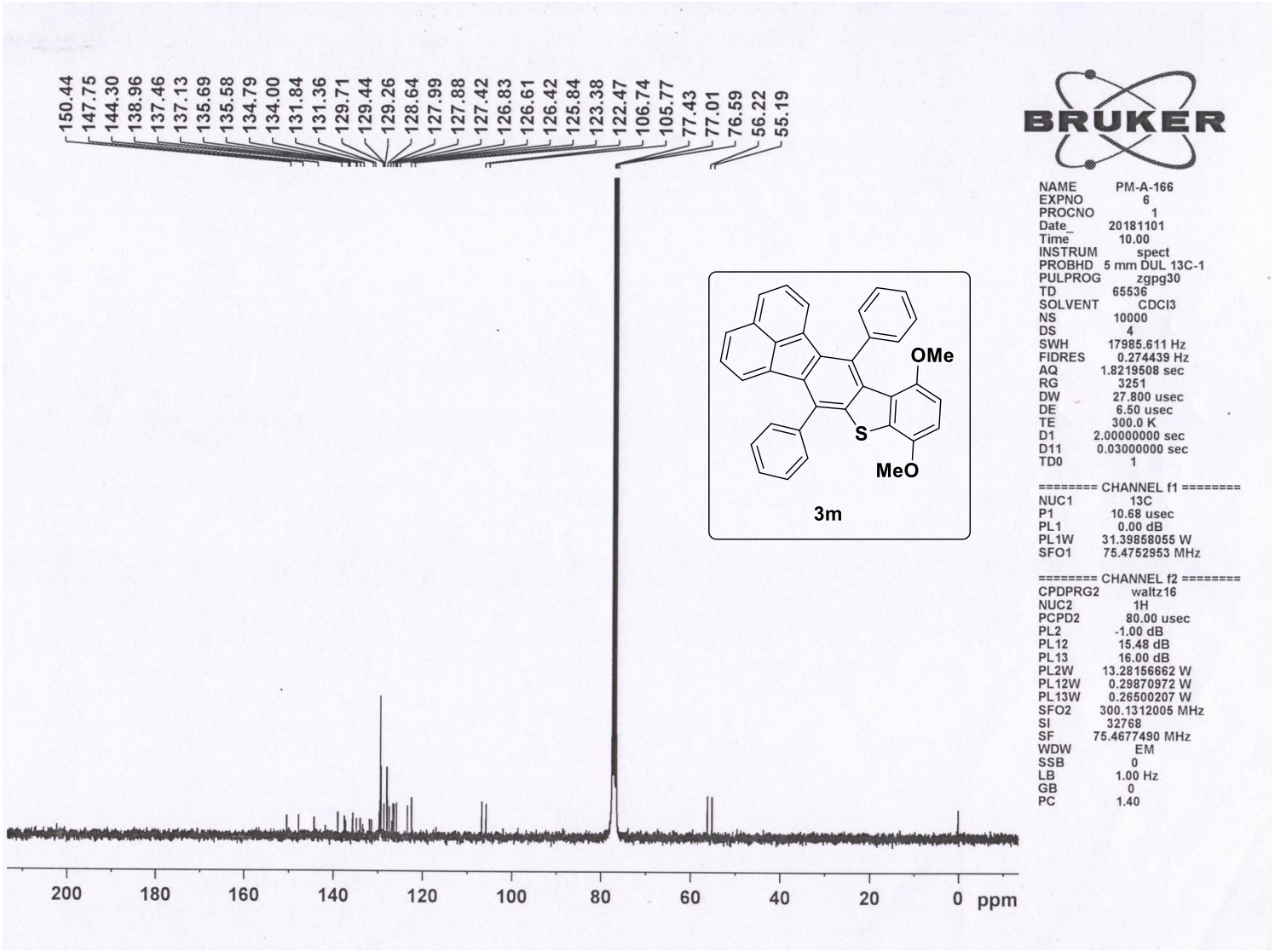
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3l**



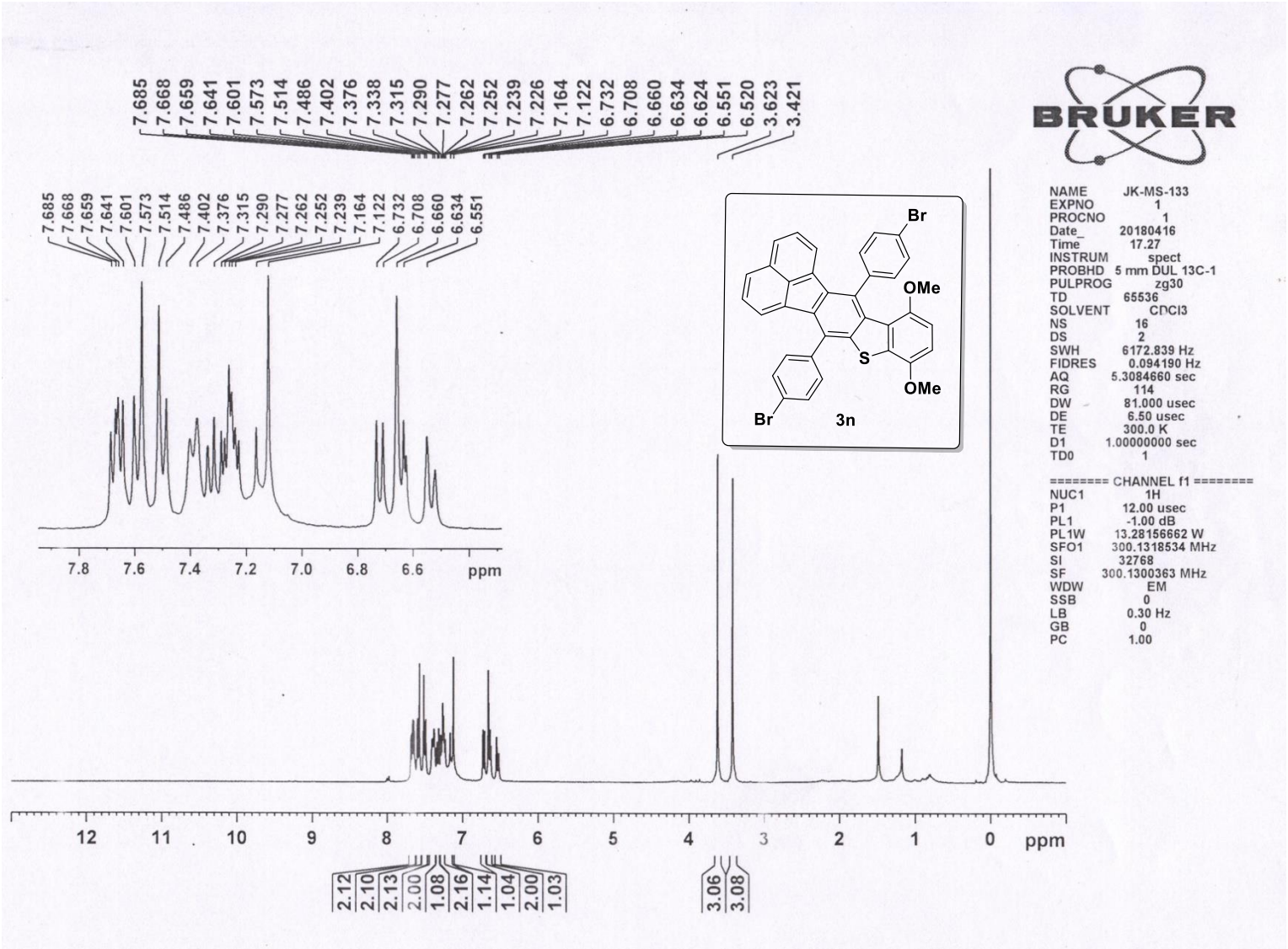
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3l**



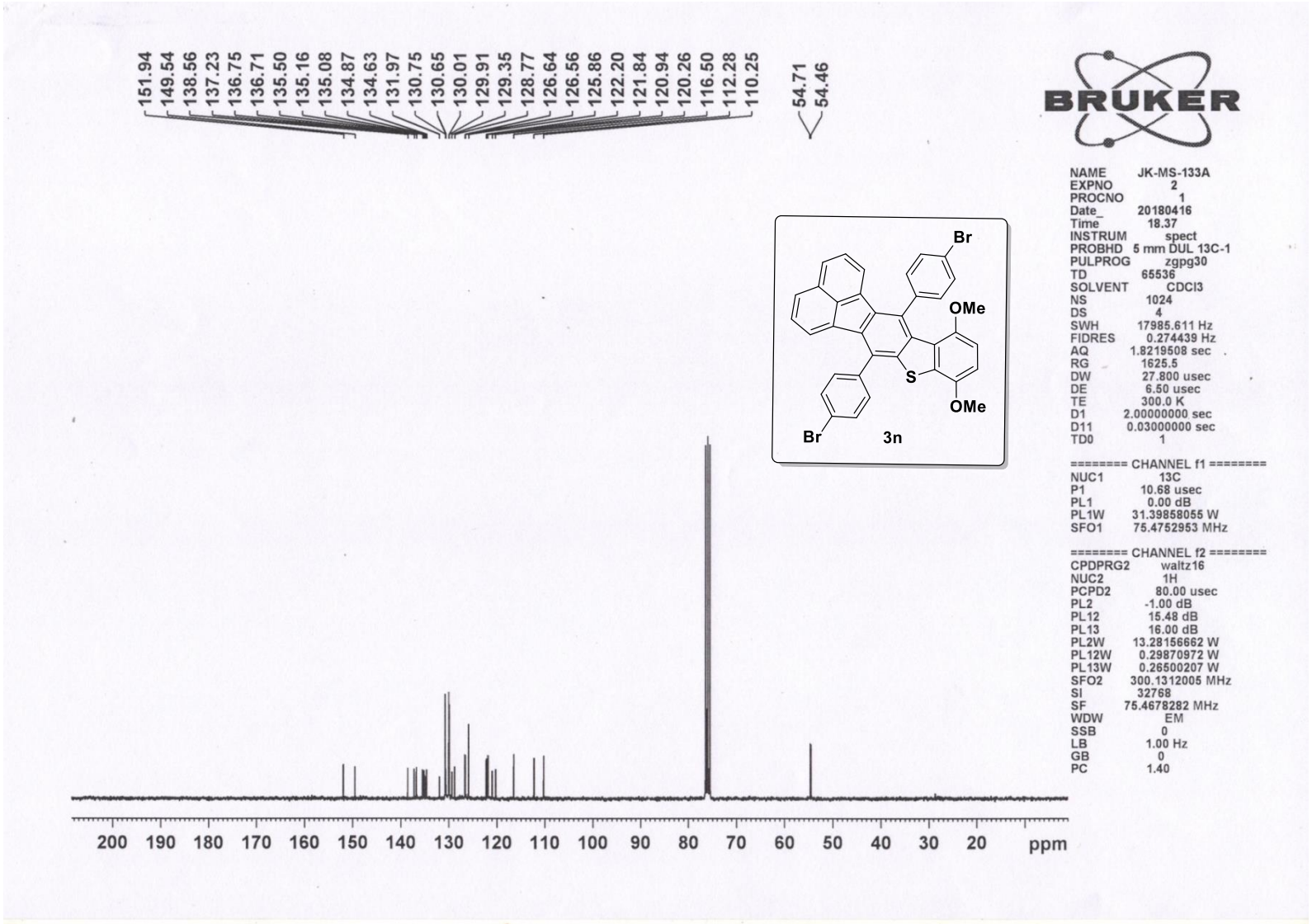
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3m**



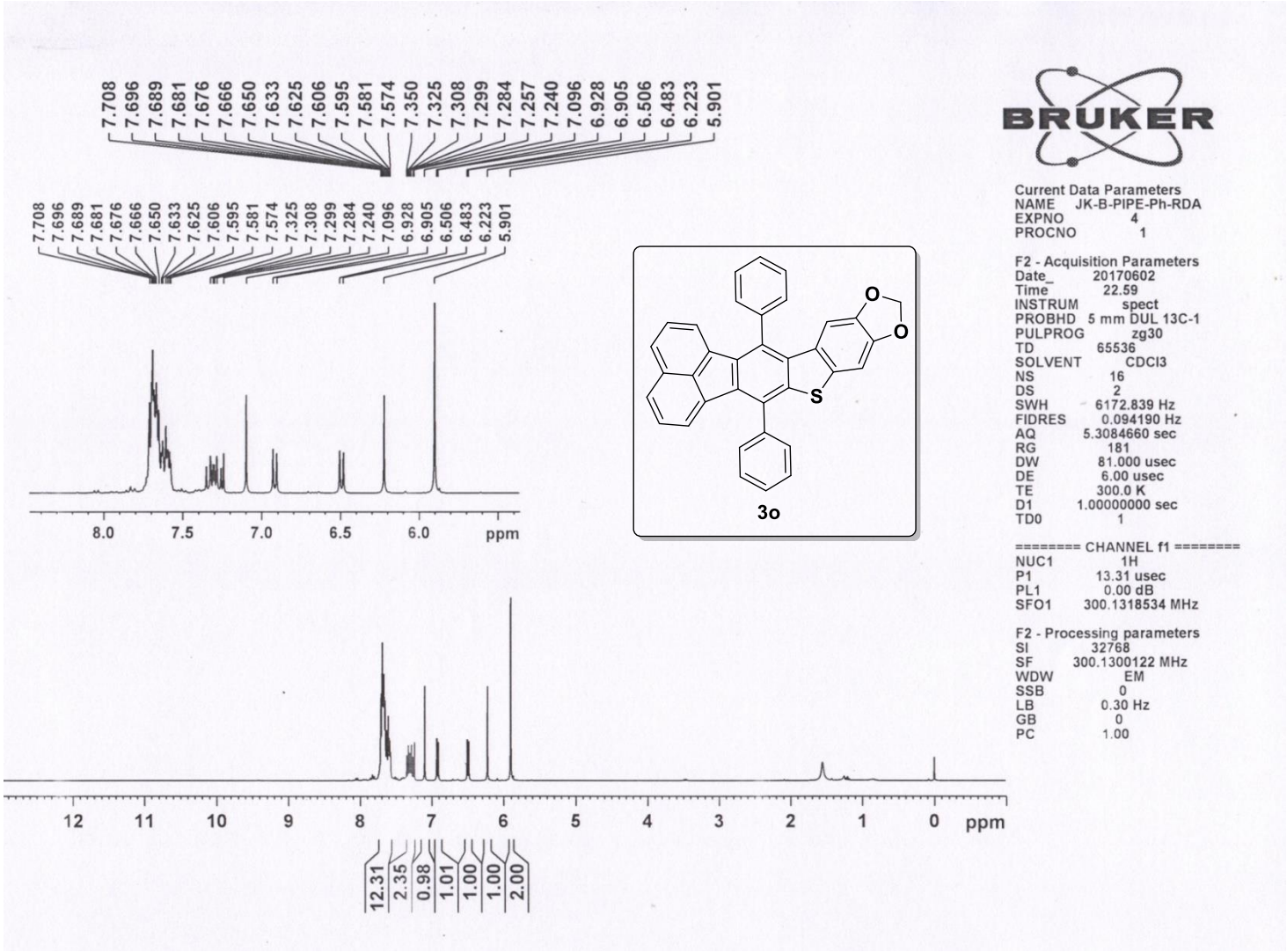
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3m**



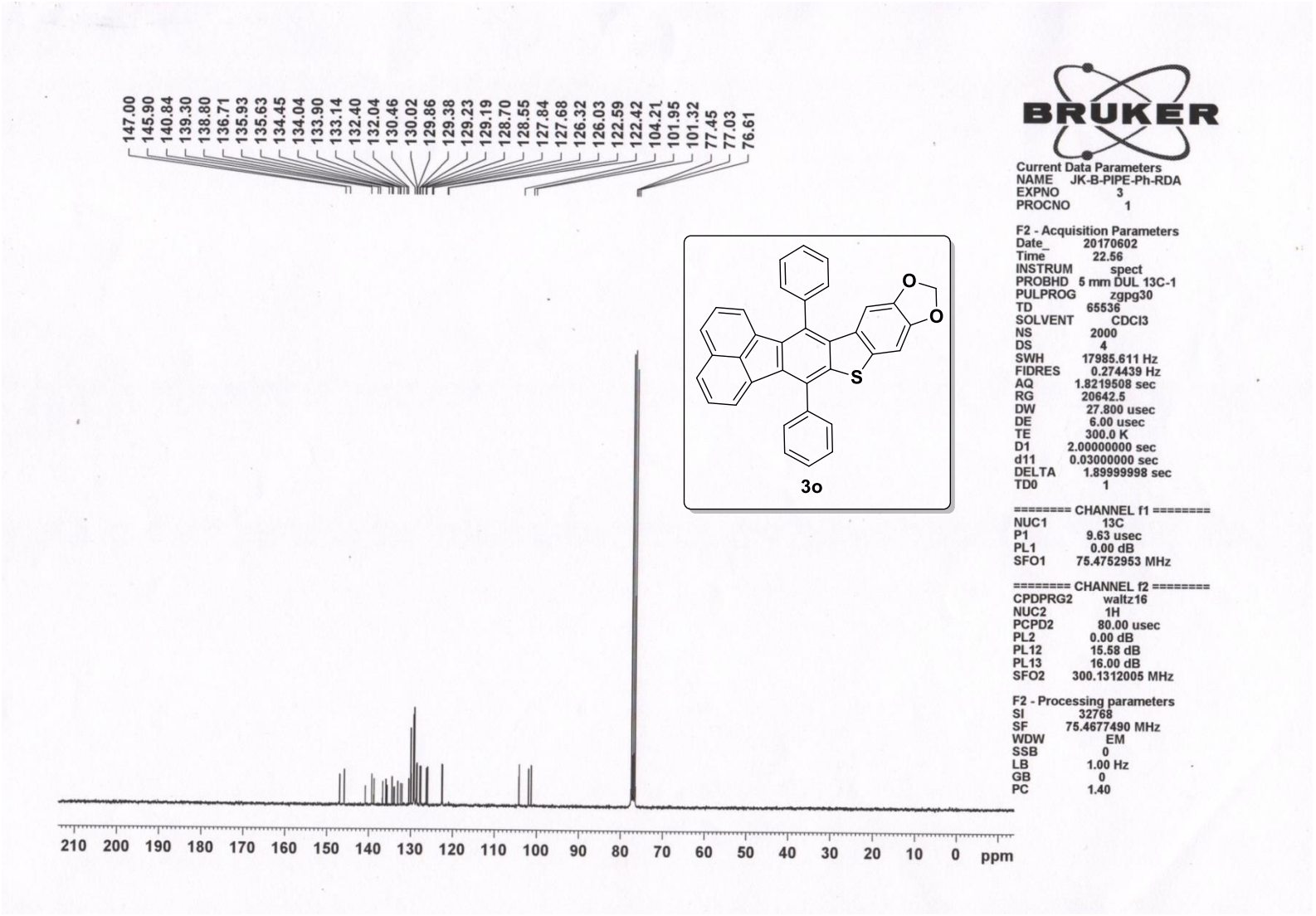
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3n**



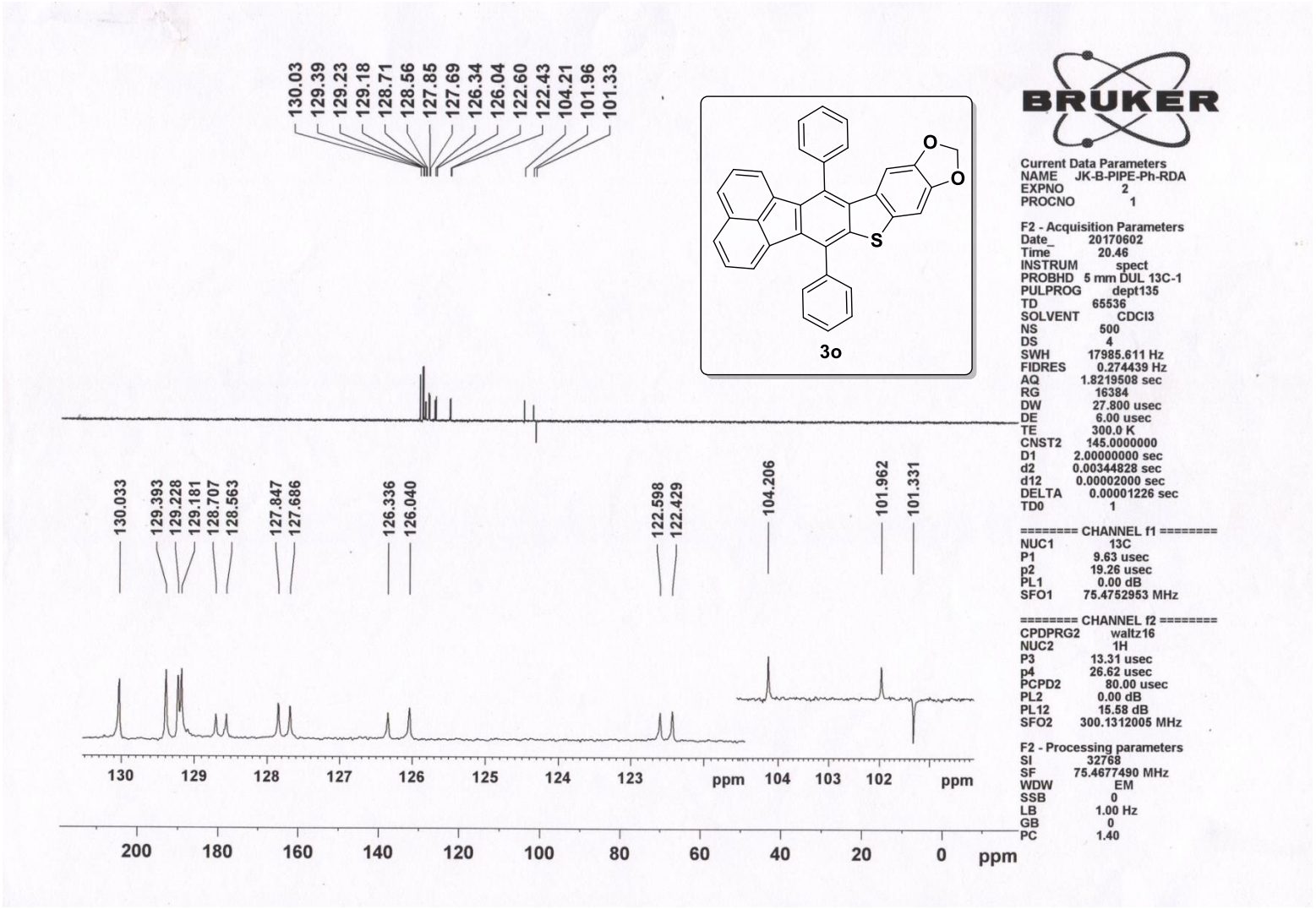
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3n**



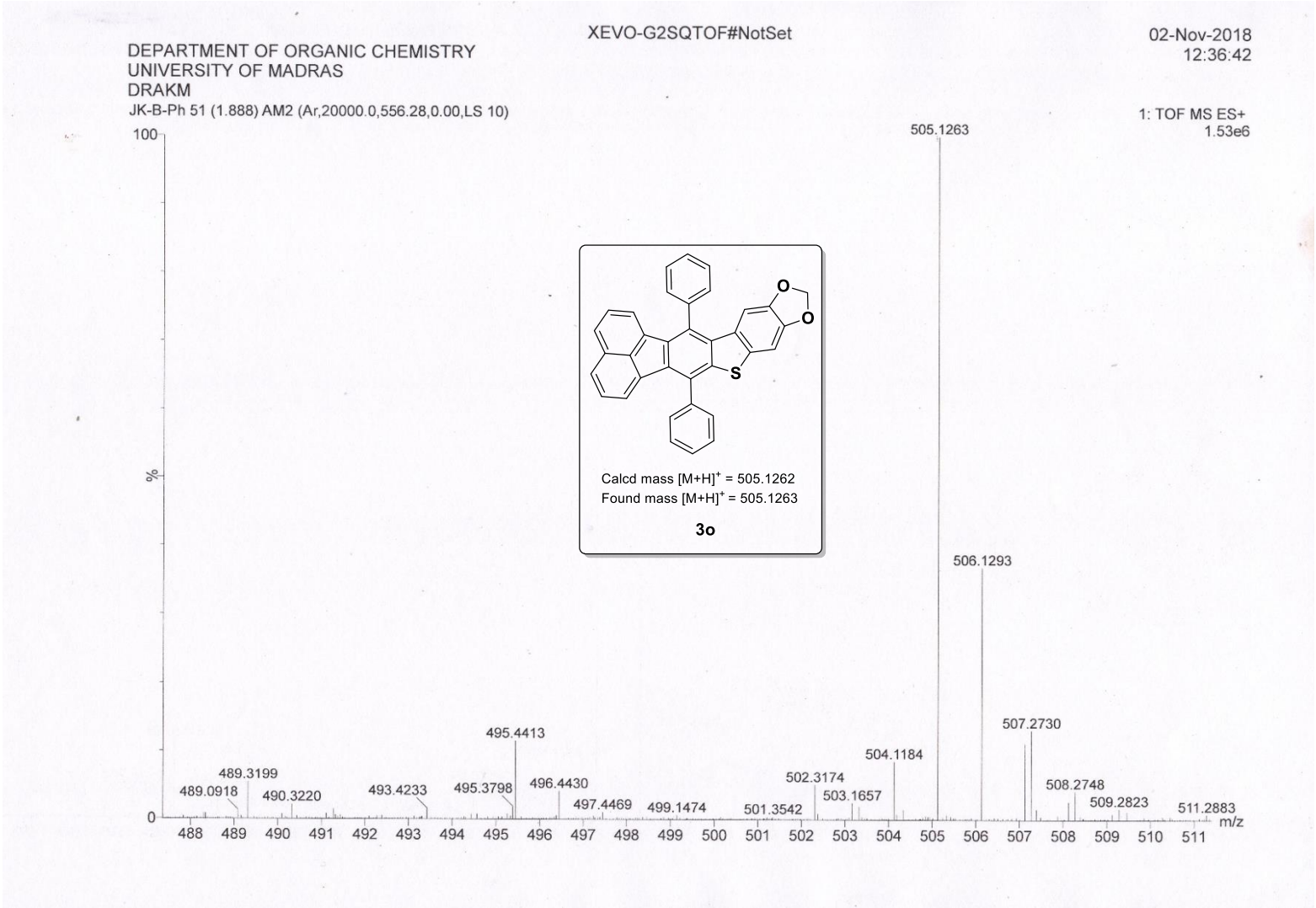
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3o**



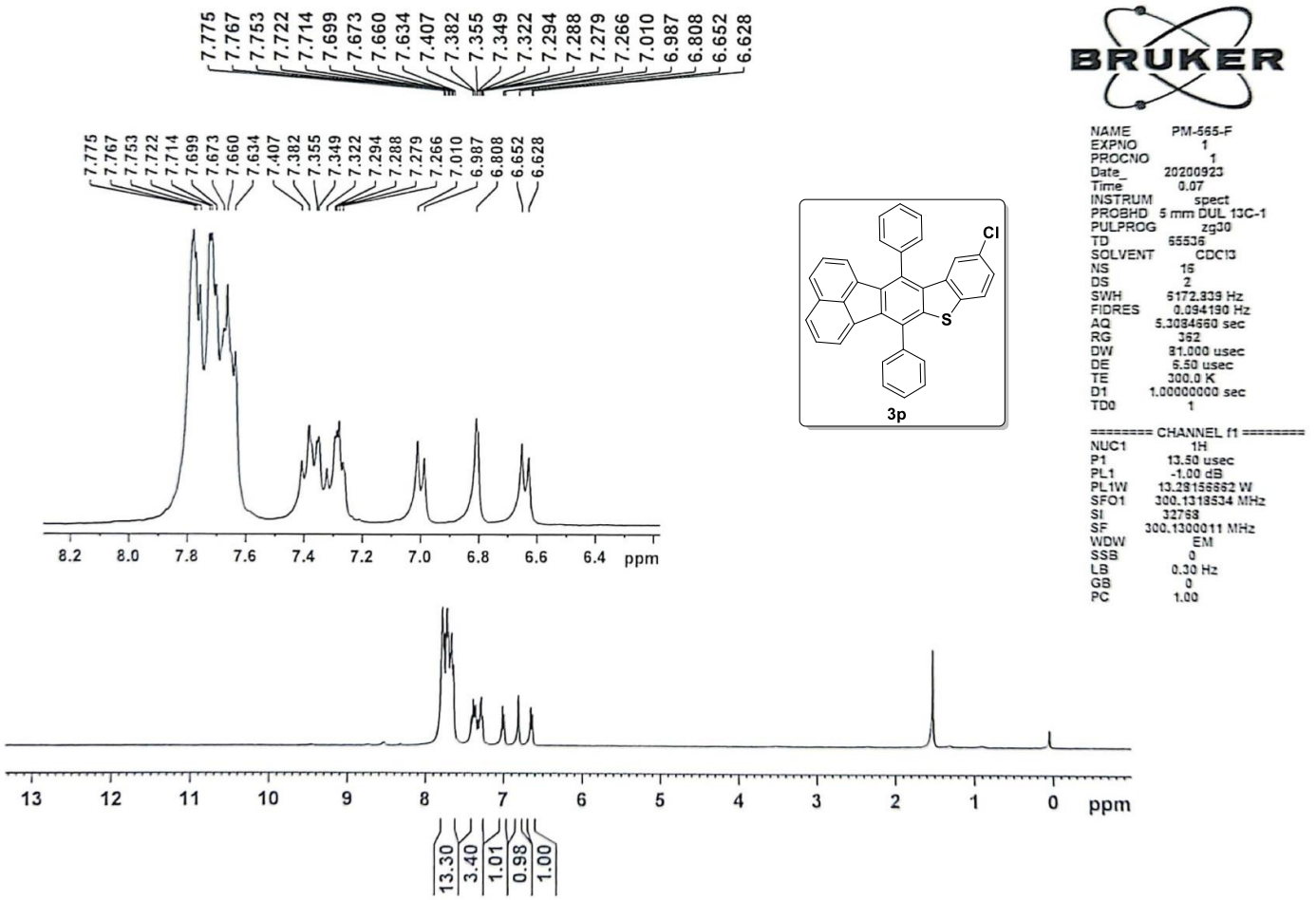
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3o**



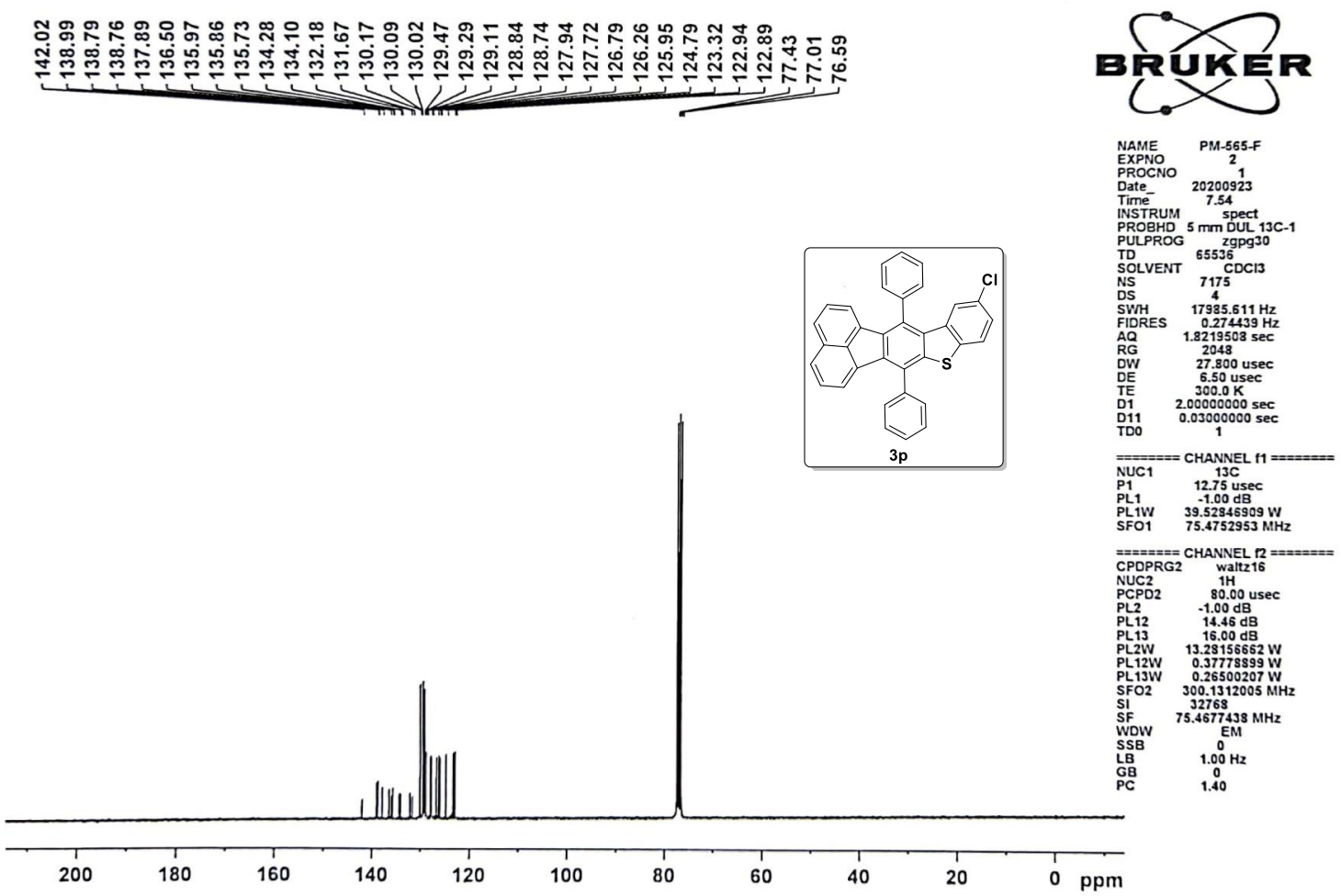
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **3o**



HRMS spectrum of compound **3o**



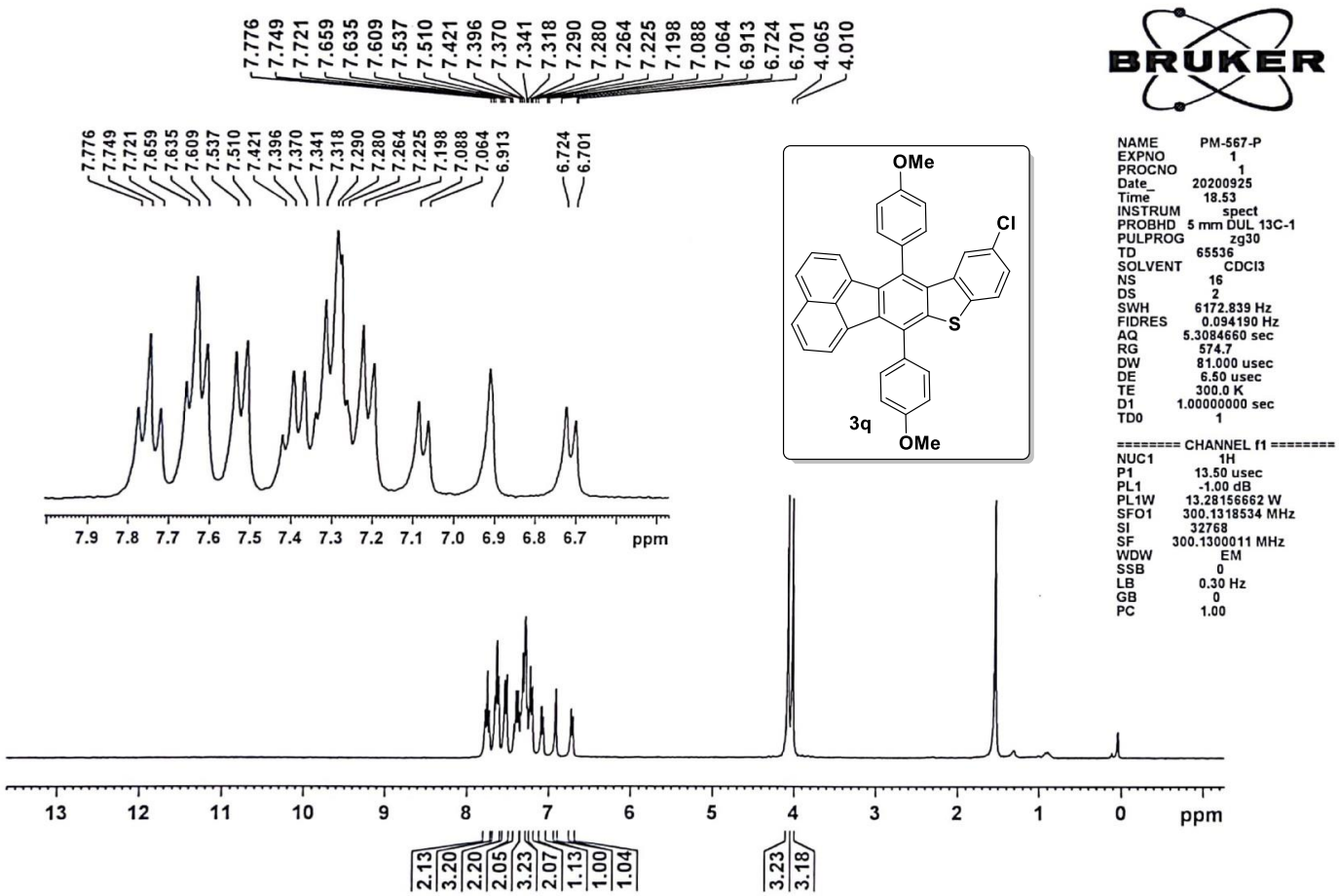
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3p**



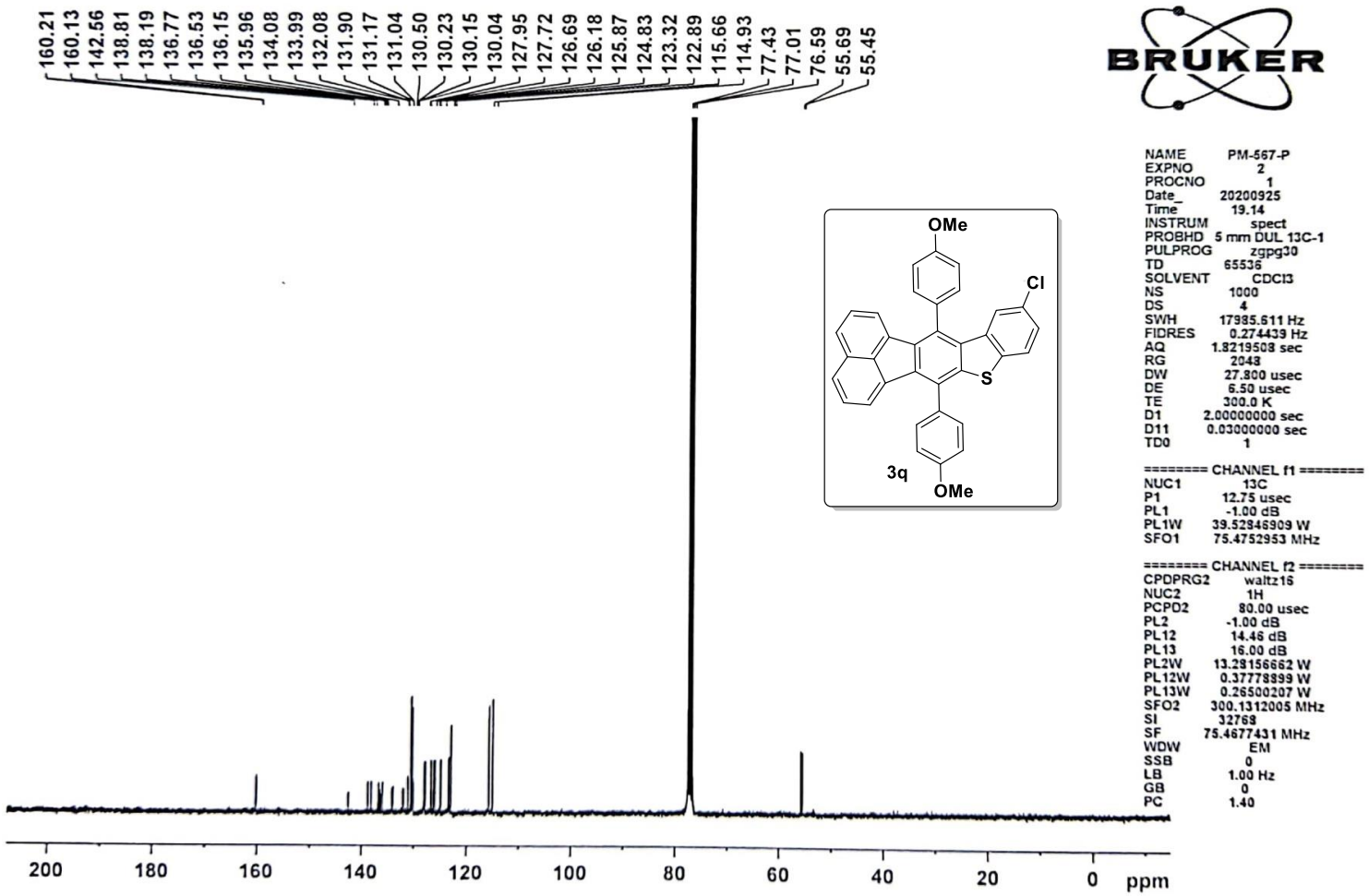
BRUKER

NAME	PM-565-F
EXPNO	2
PROCNO	1
Date_	20200923
Time	7.54
INSTRUM	spect
PROBHD	5 mm DUL 13C-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	7175
DS	4
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	2048
DW	27.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	12.75 usec
PL1	-1.00 dB
PL1W	39.52846909 W
SFO1	75.4752953 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.46 dB
PL13	16.00 dB
PL2W	13.28156662 W
PL12W	0.37778899 W
PL13W	0.26500207 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

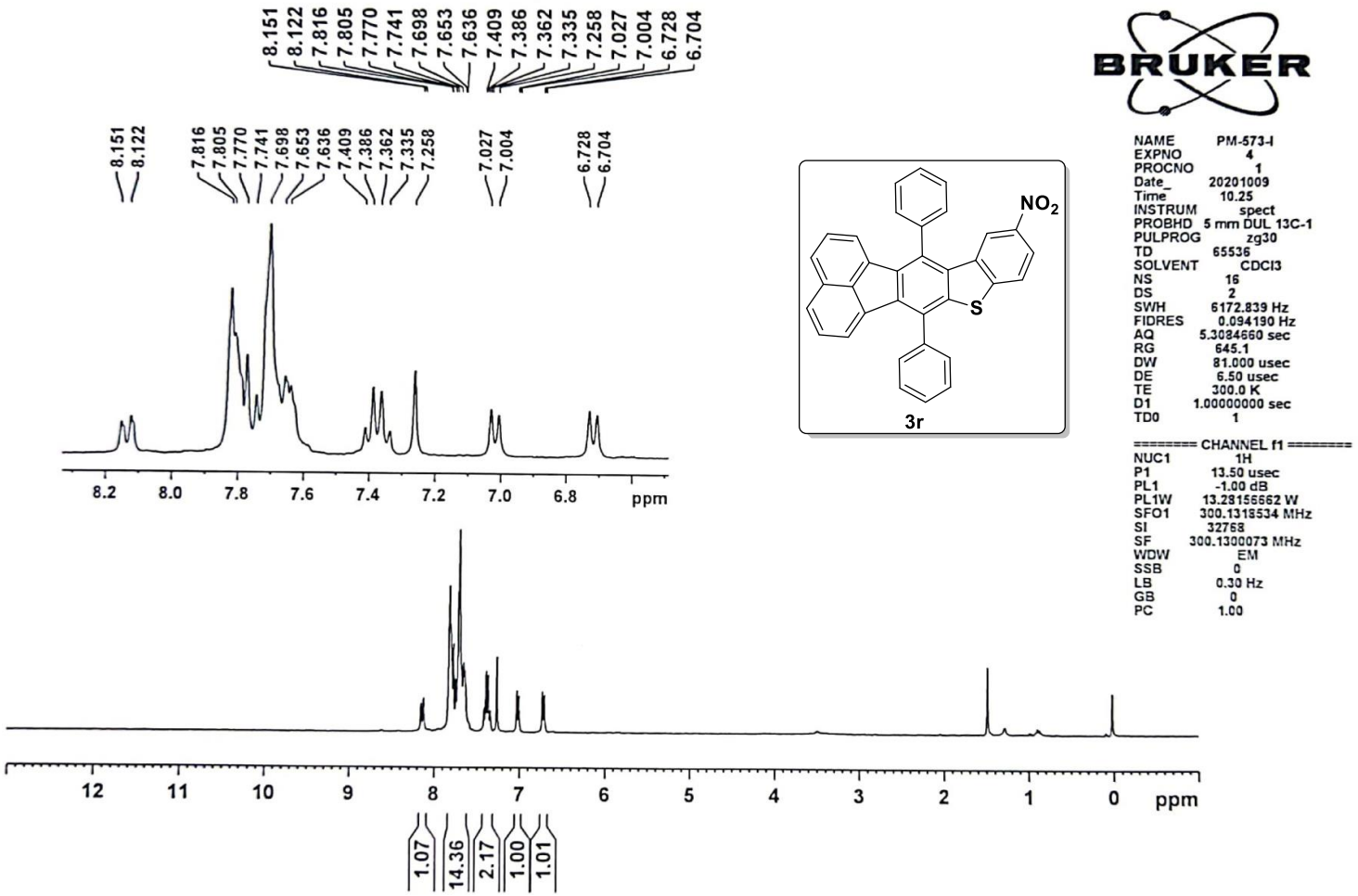
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3p**



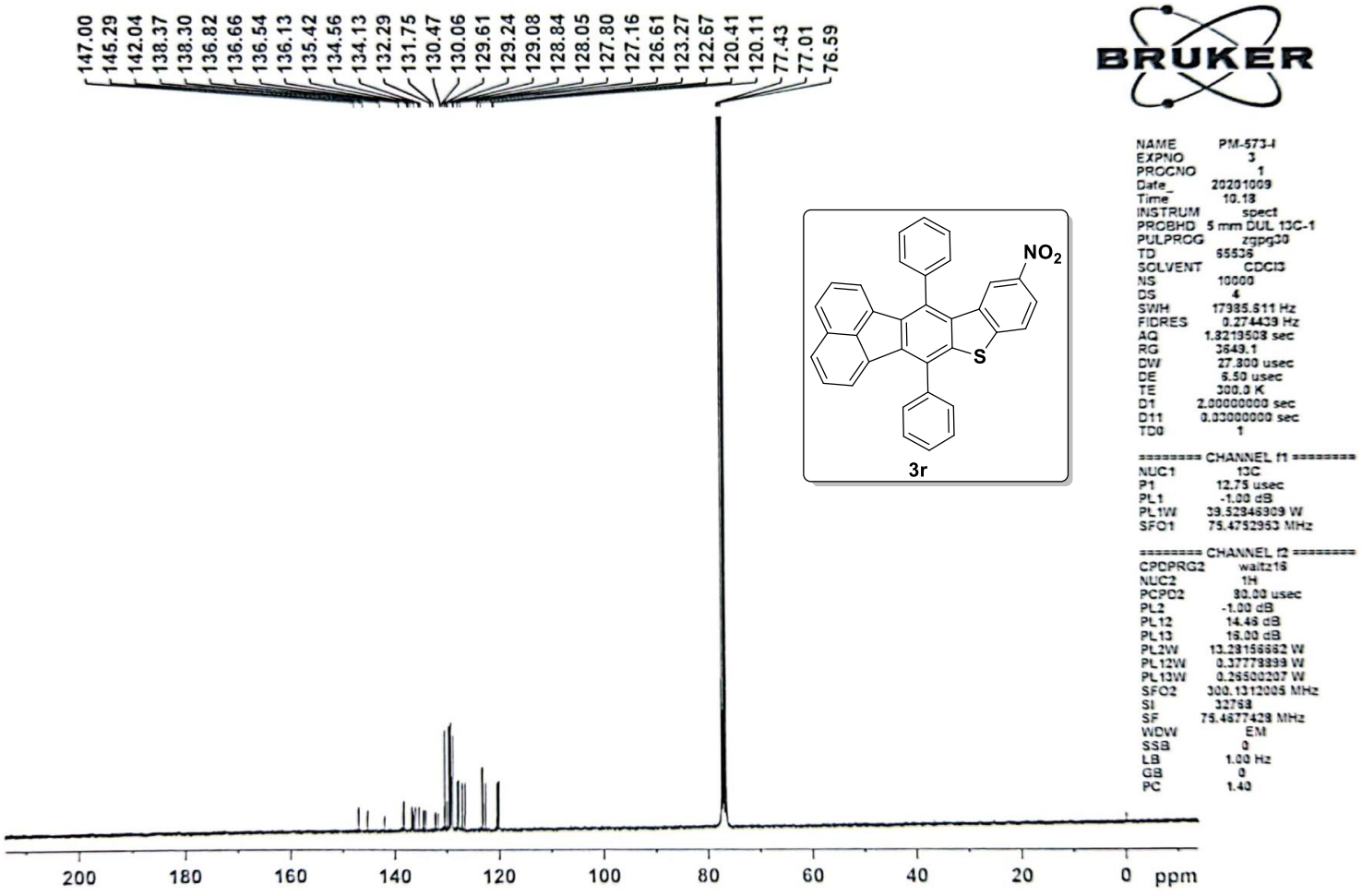
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3p**



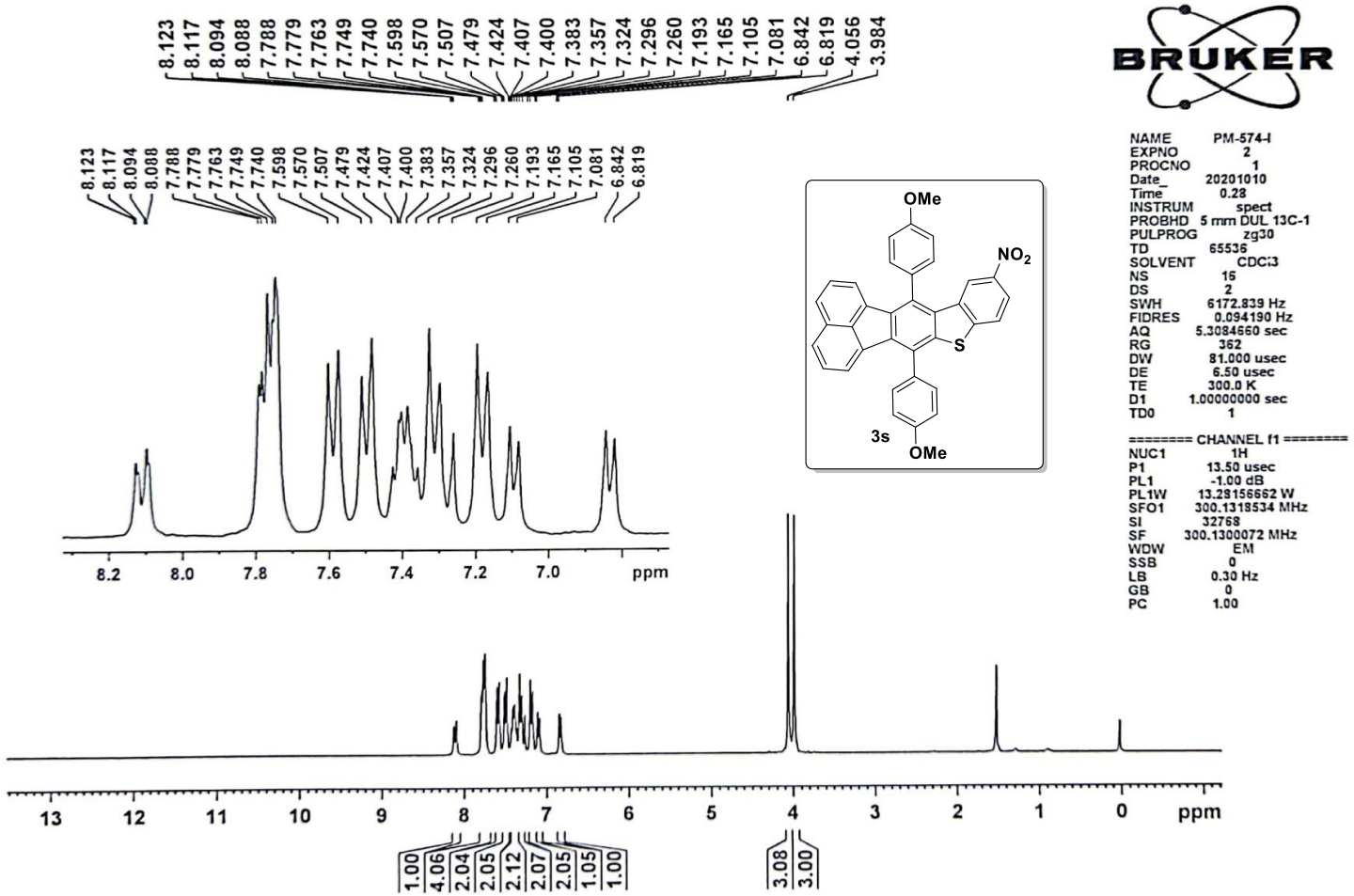
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3q**



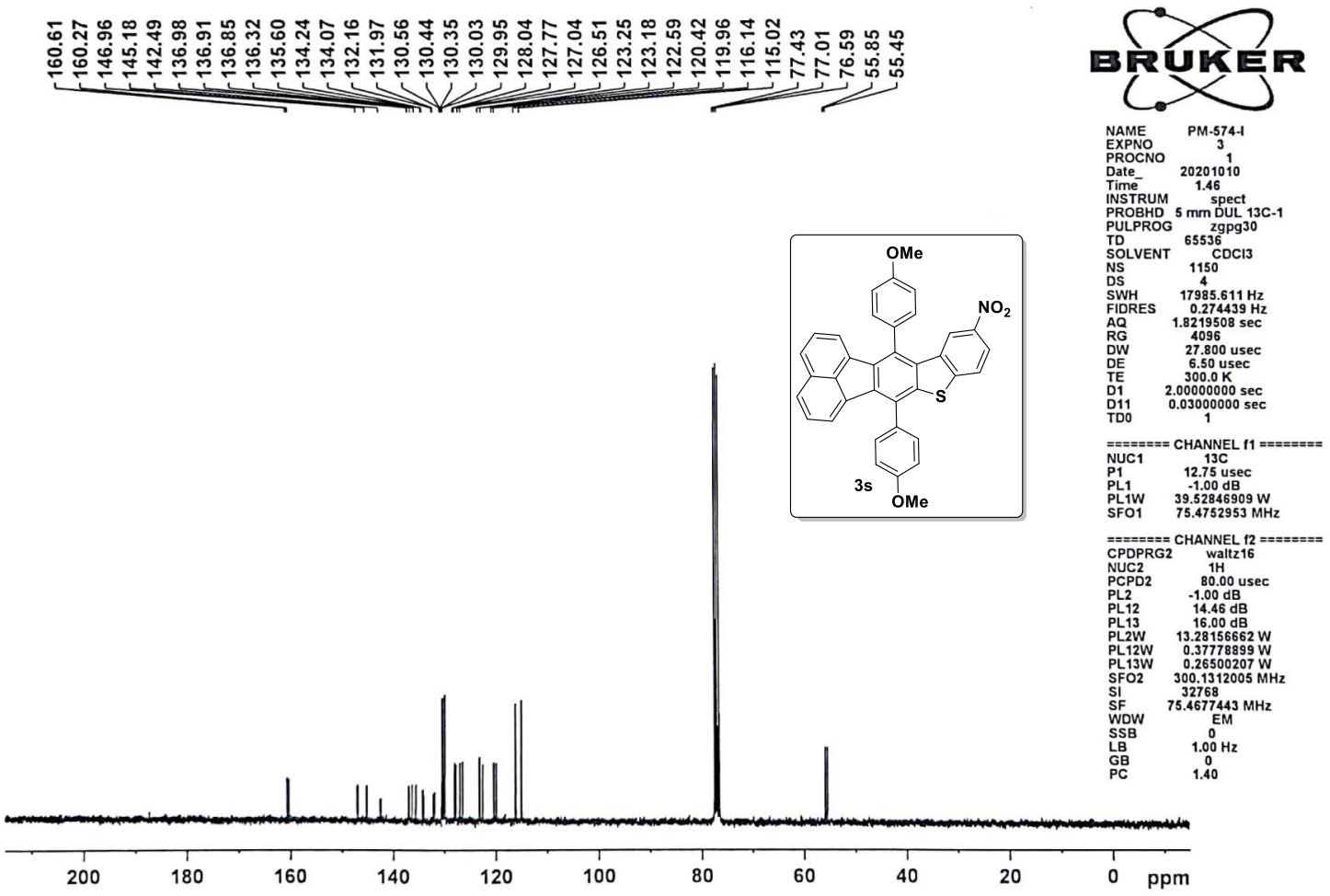
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3r**



^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3r**



^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3s**



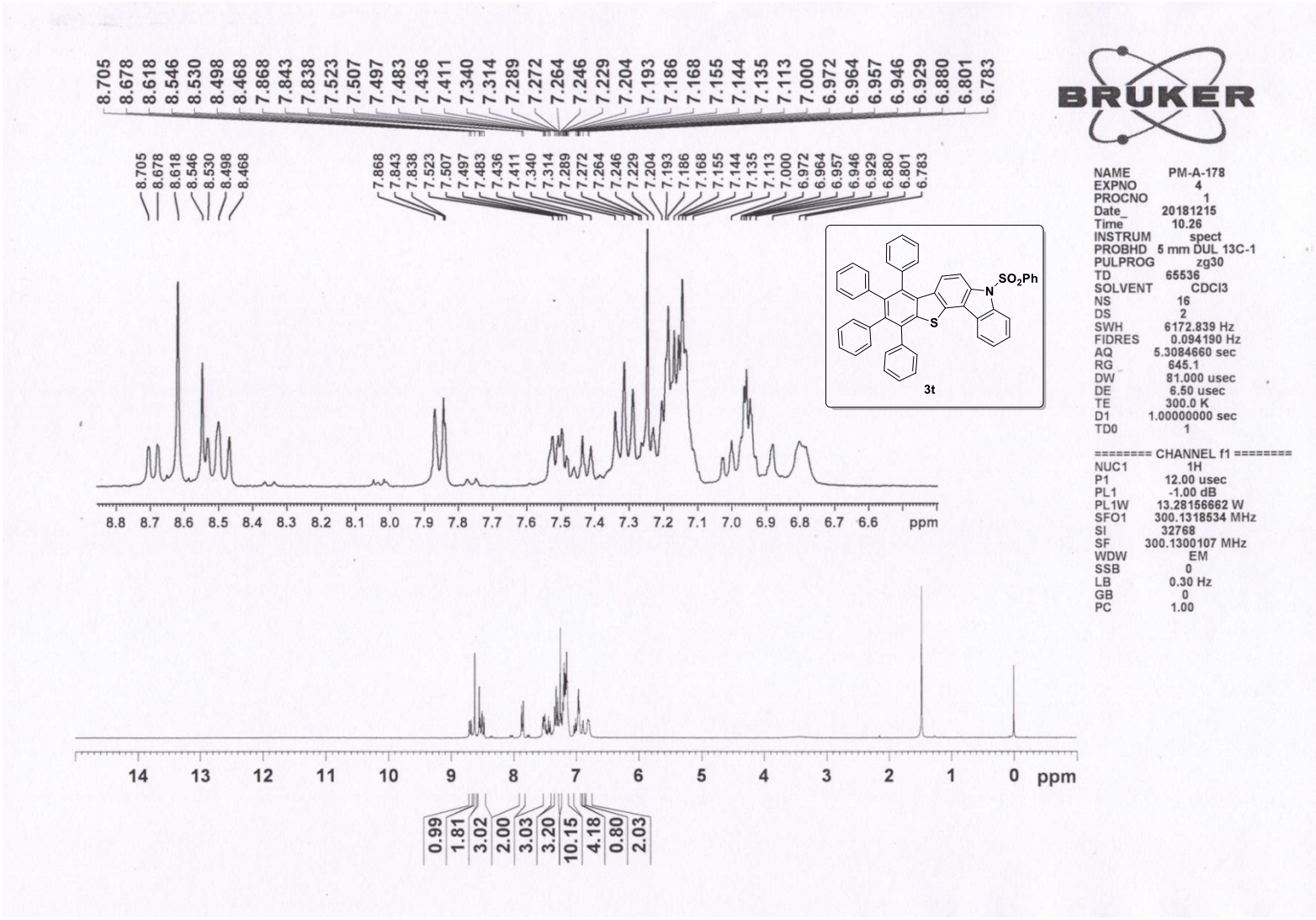
BRUKER

NAME PM-574-I
EXPNO 3
PROCNO 1
Date_ 20201010
Time 1.46
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1150
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

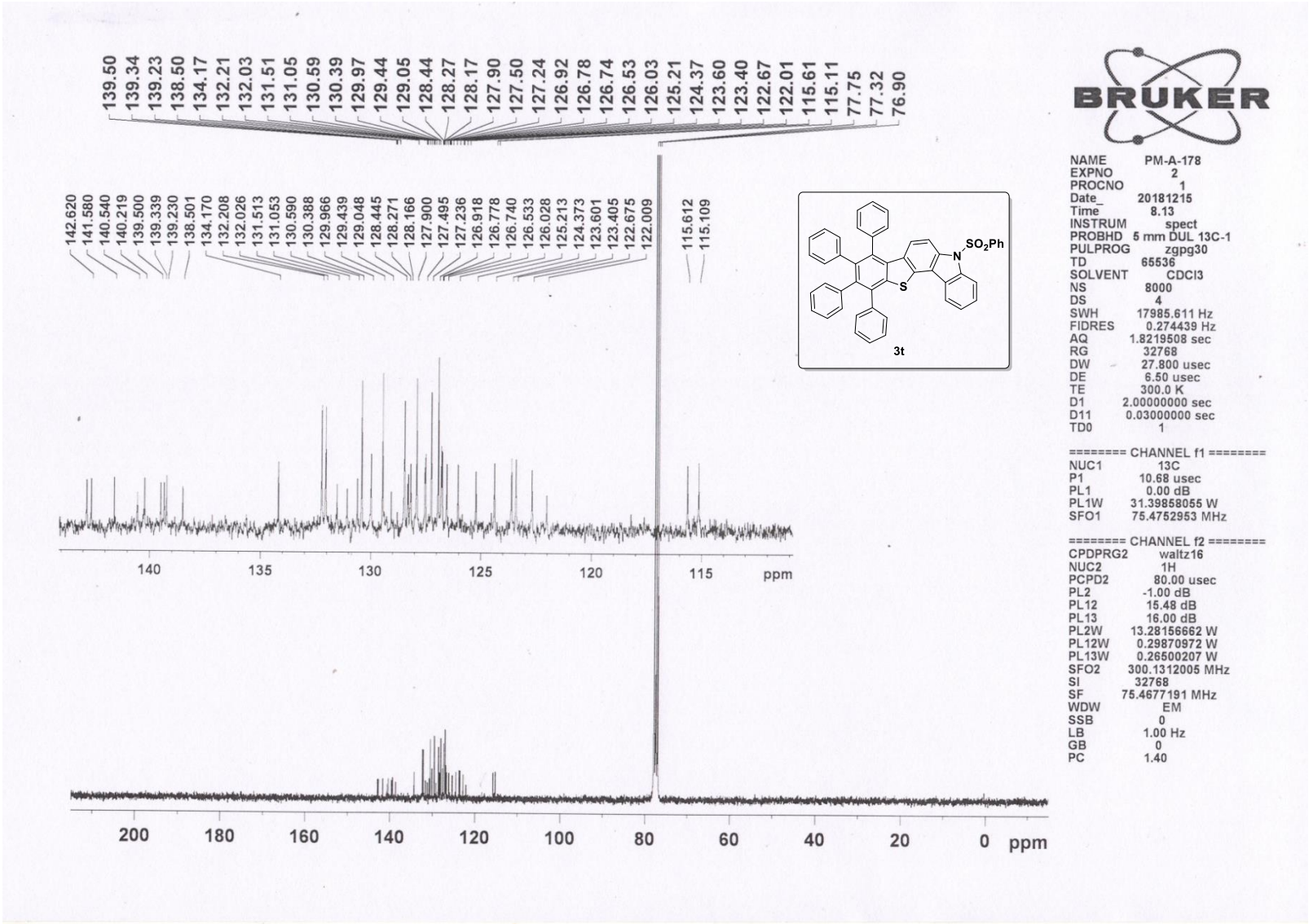
======== CHANNEL f1 ========
NUC1 13C
P1 12.75 usec
PL1 -1.00 dB
PL1W 39.52846909 W
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.46 dB
PL13 16.00 dB
PL2W 13.28156662 W
PL12W 0.37778899 W
PL13W 0.26500207 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677443 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

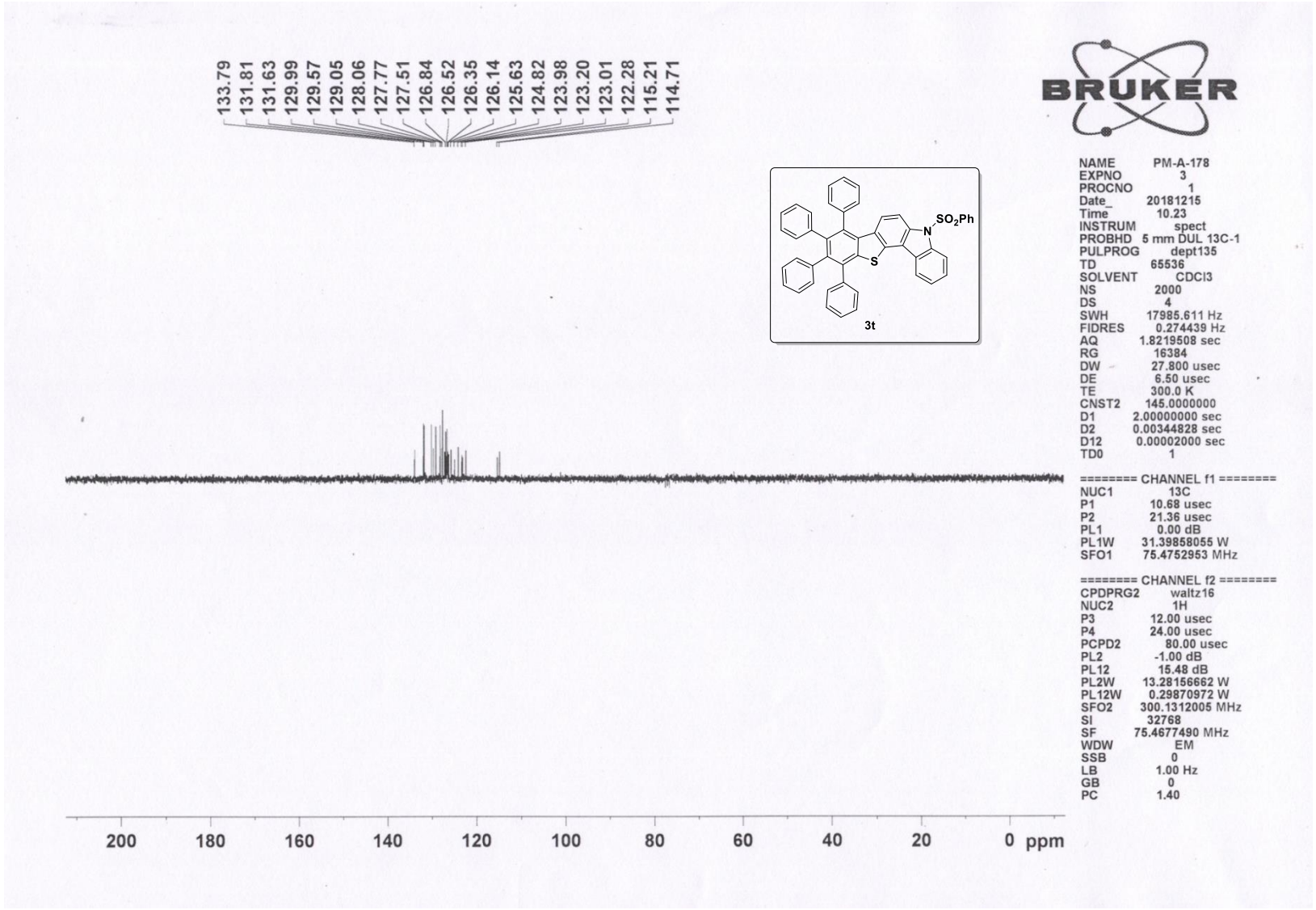
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3s**



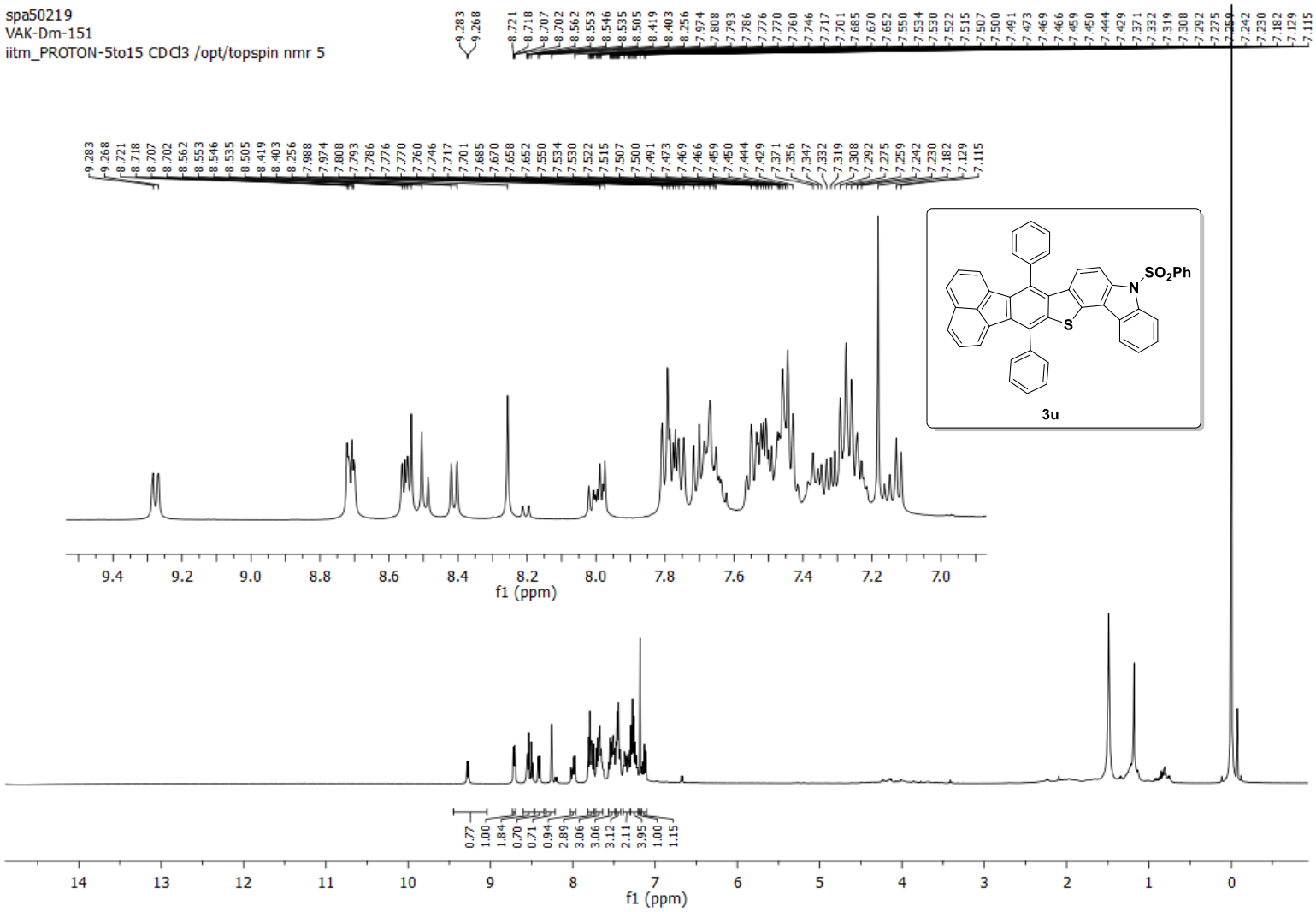
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3t**



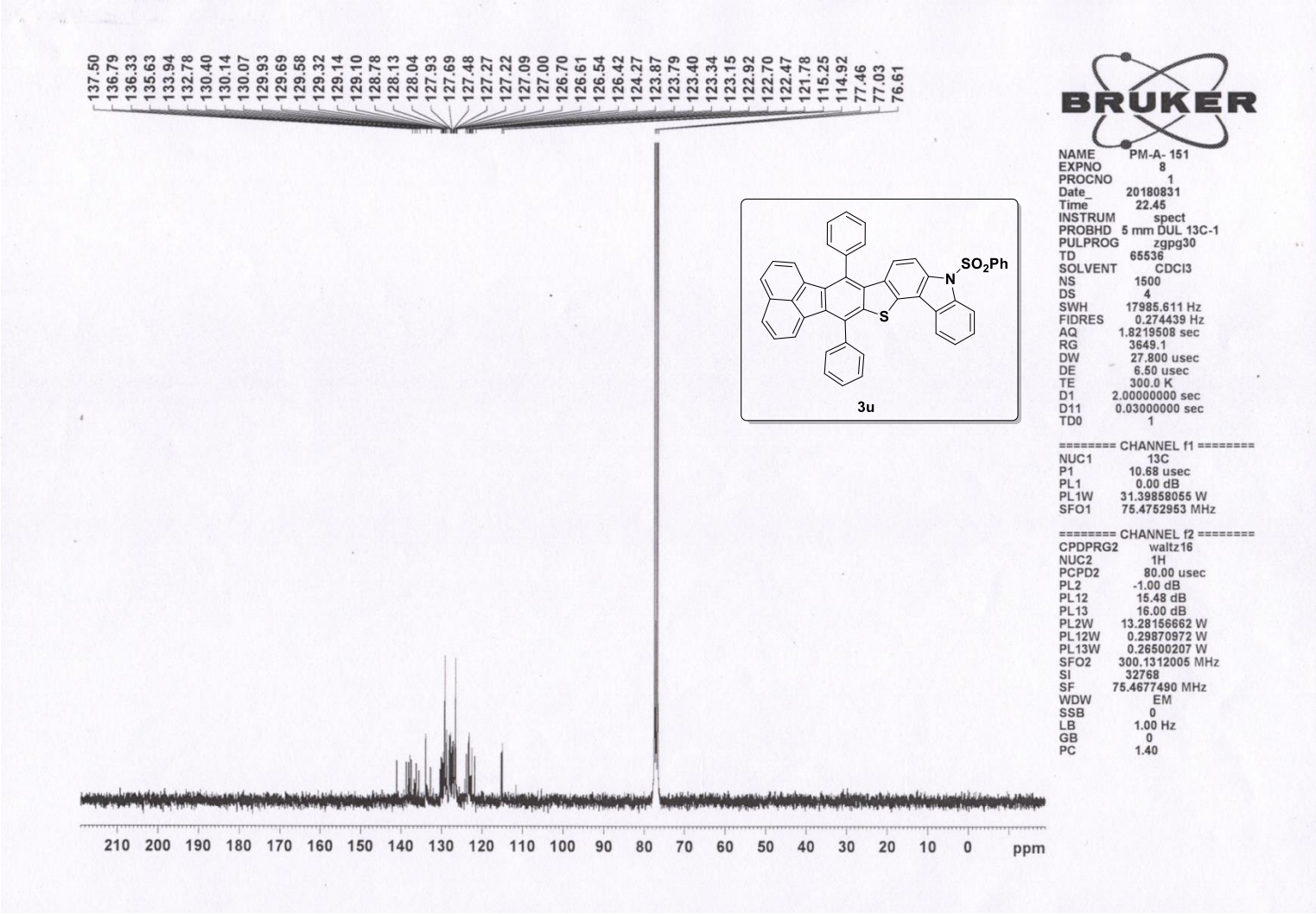
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3t**



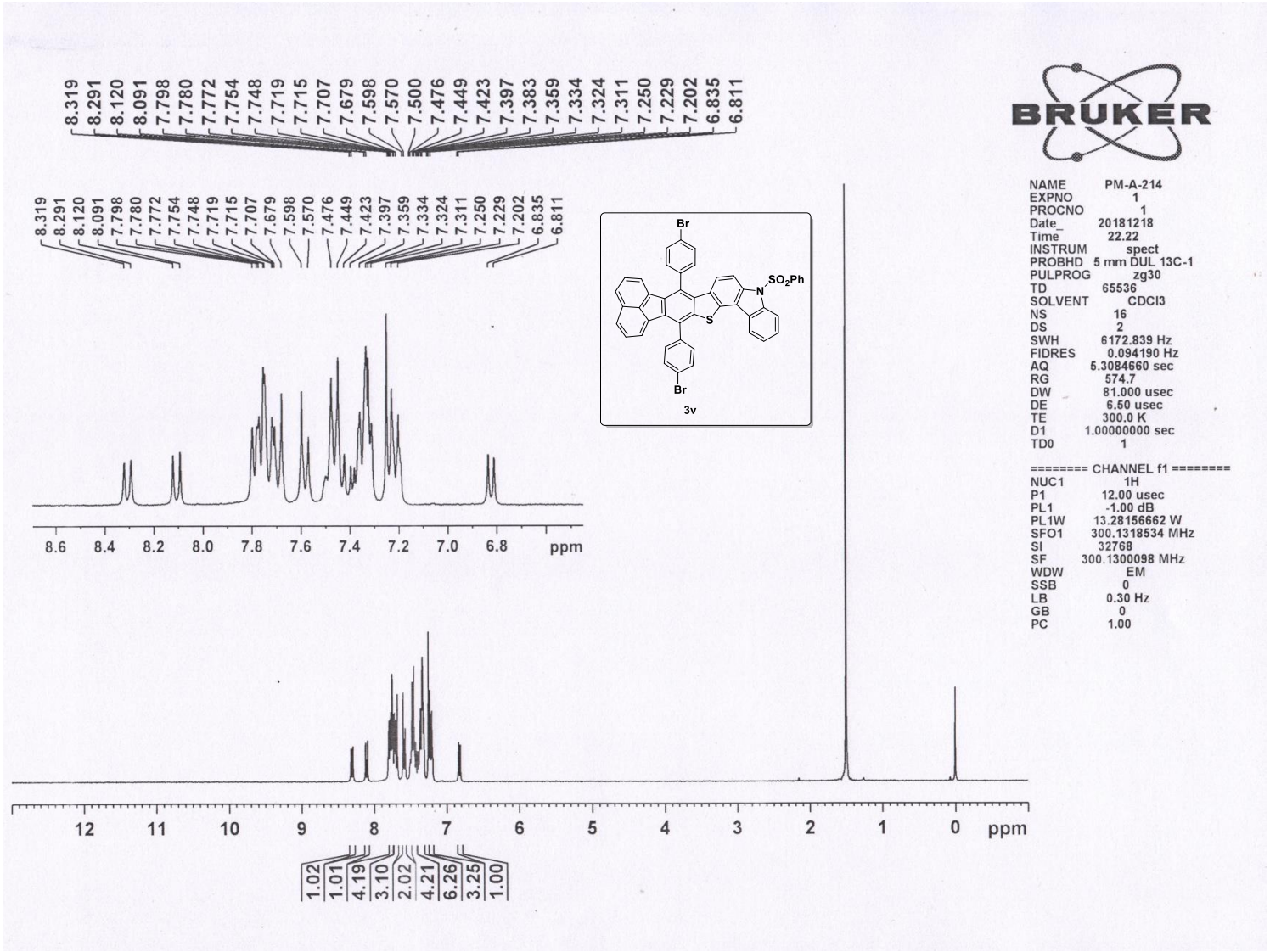
DEPT-135NMR (75 MHz, $CDCl_3$) spectrum of compound **3t**



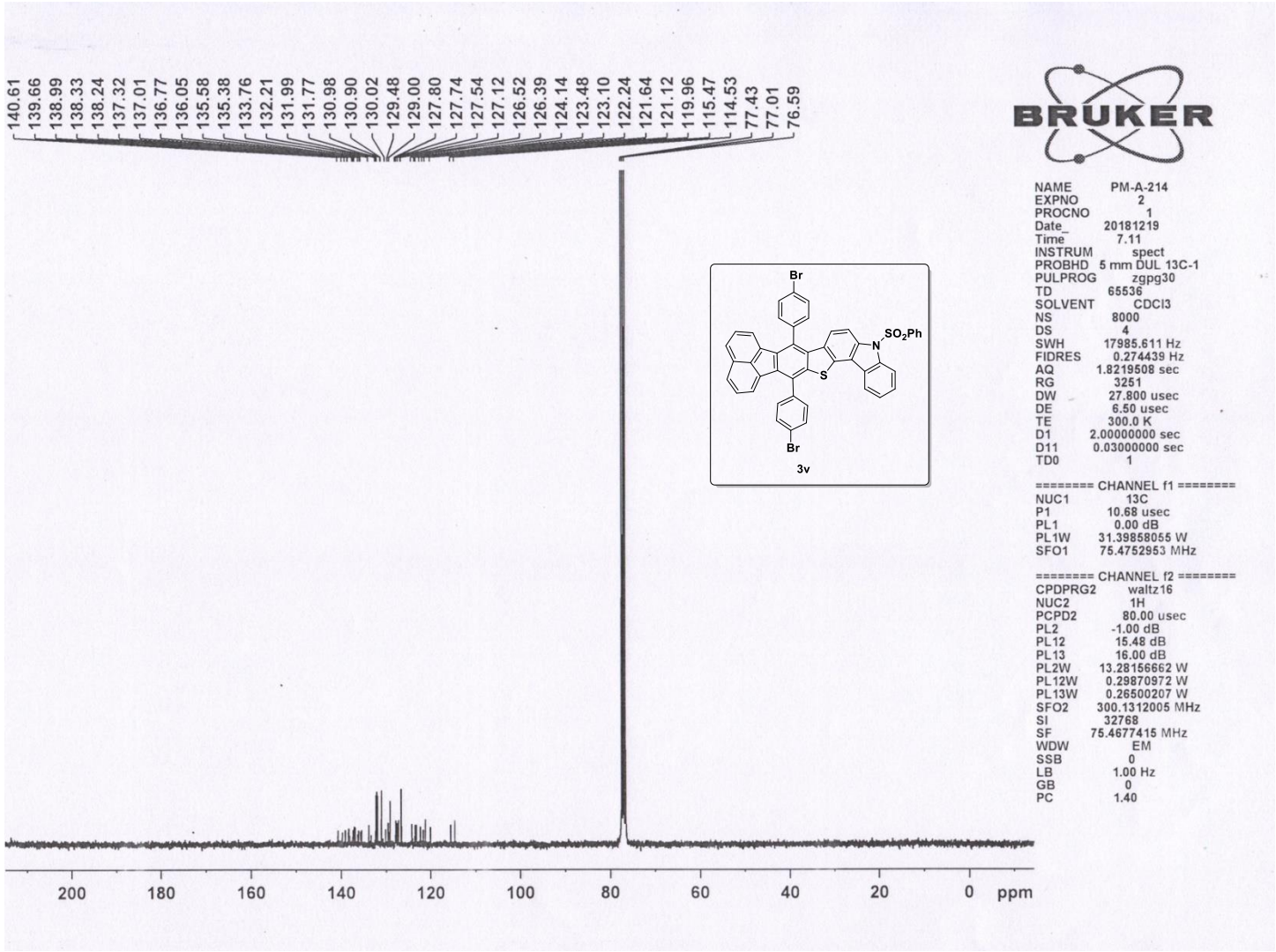
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3u**



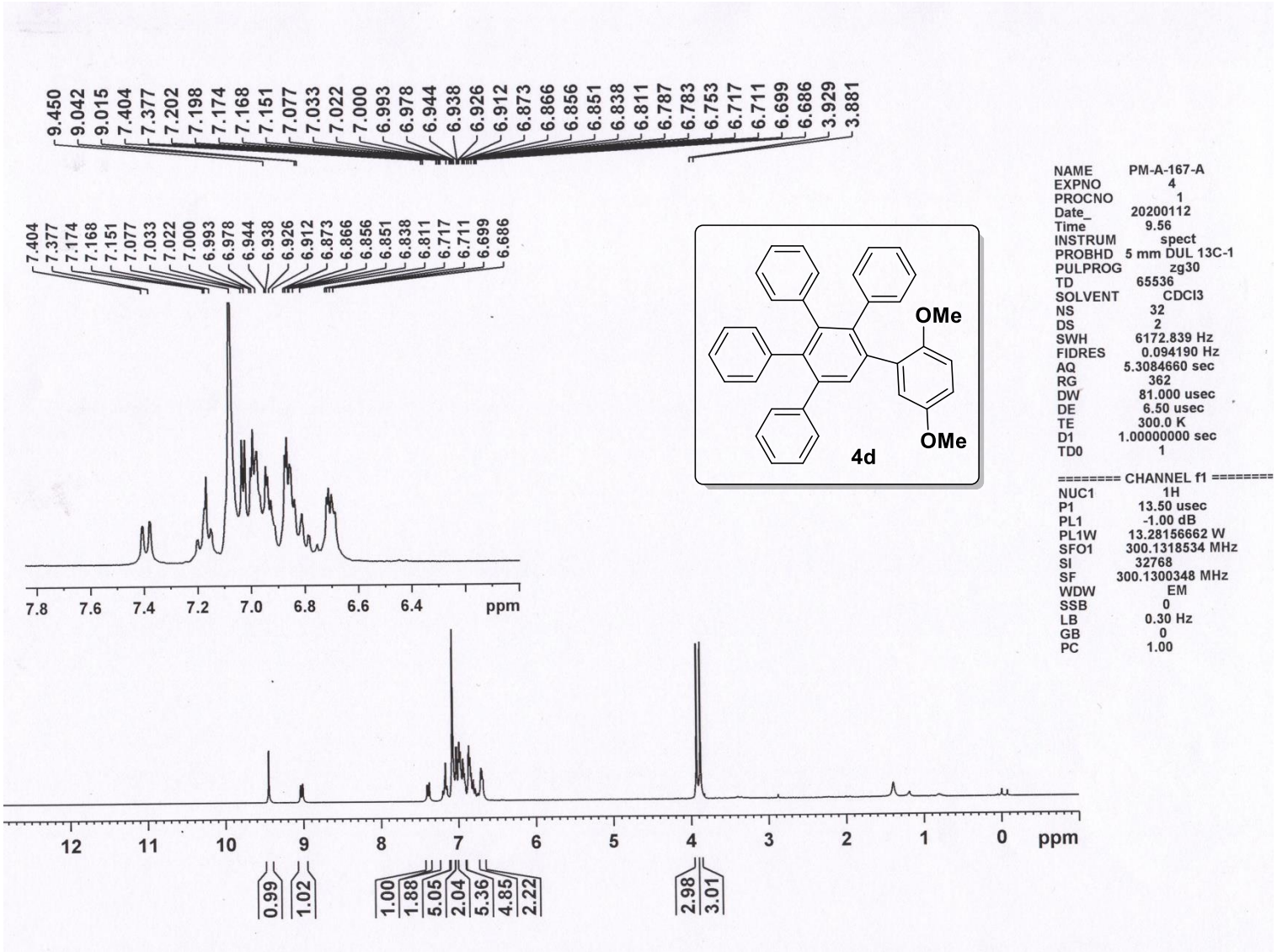
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3u**



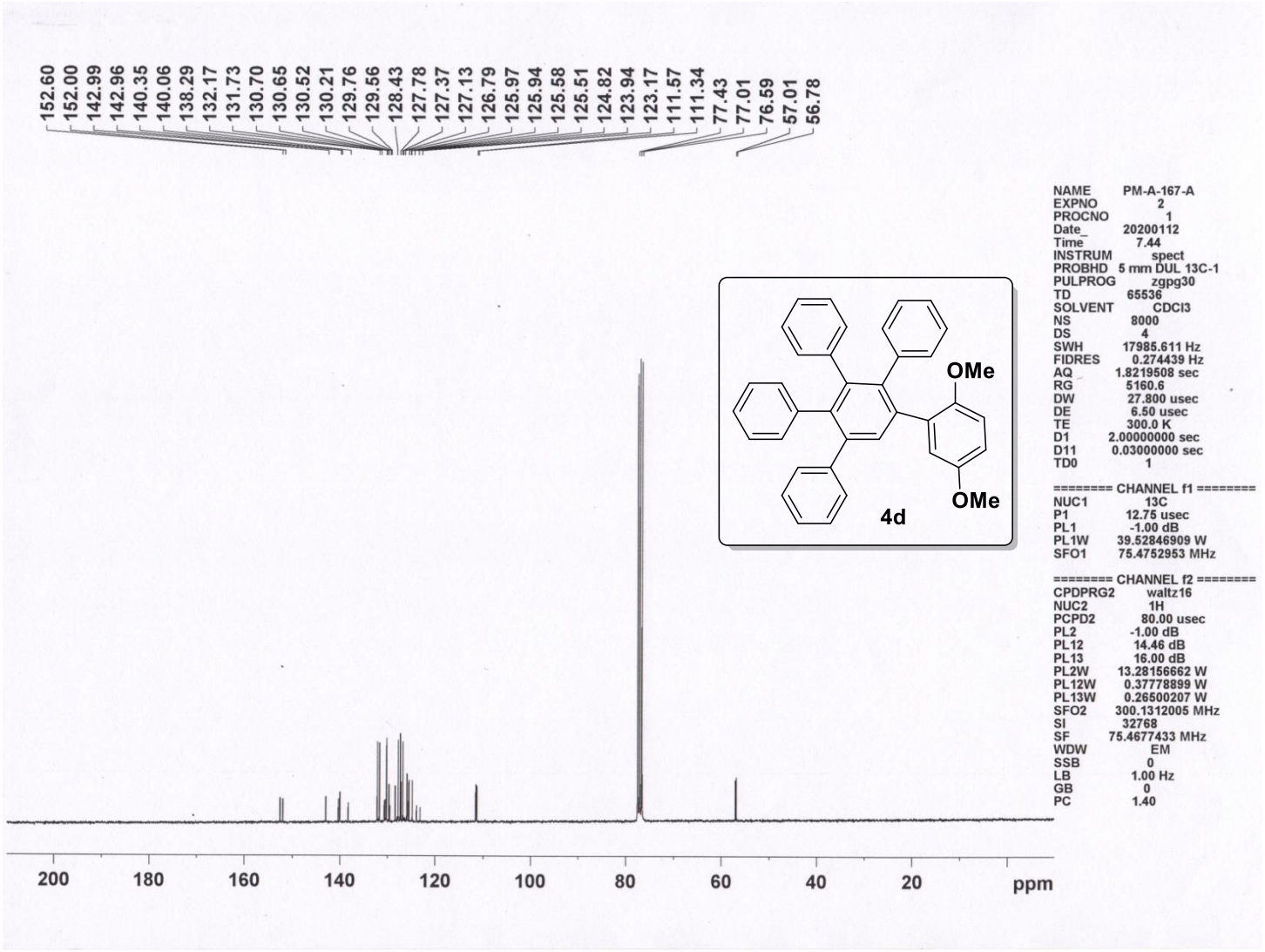
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **3v**



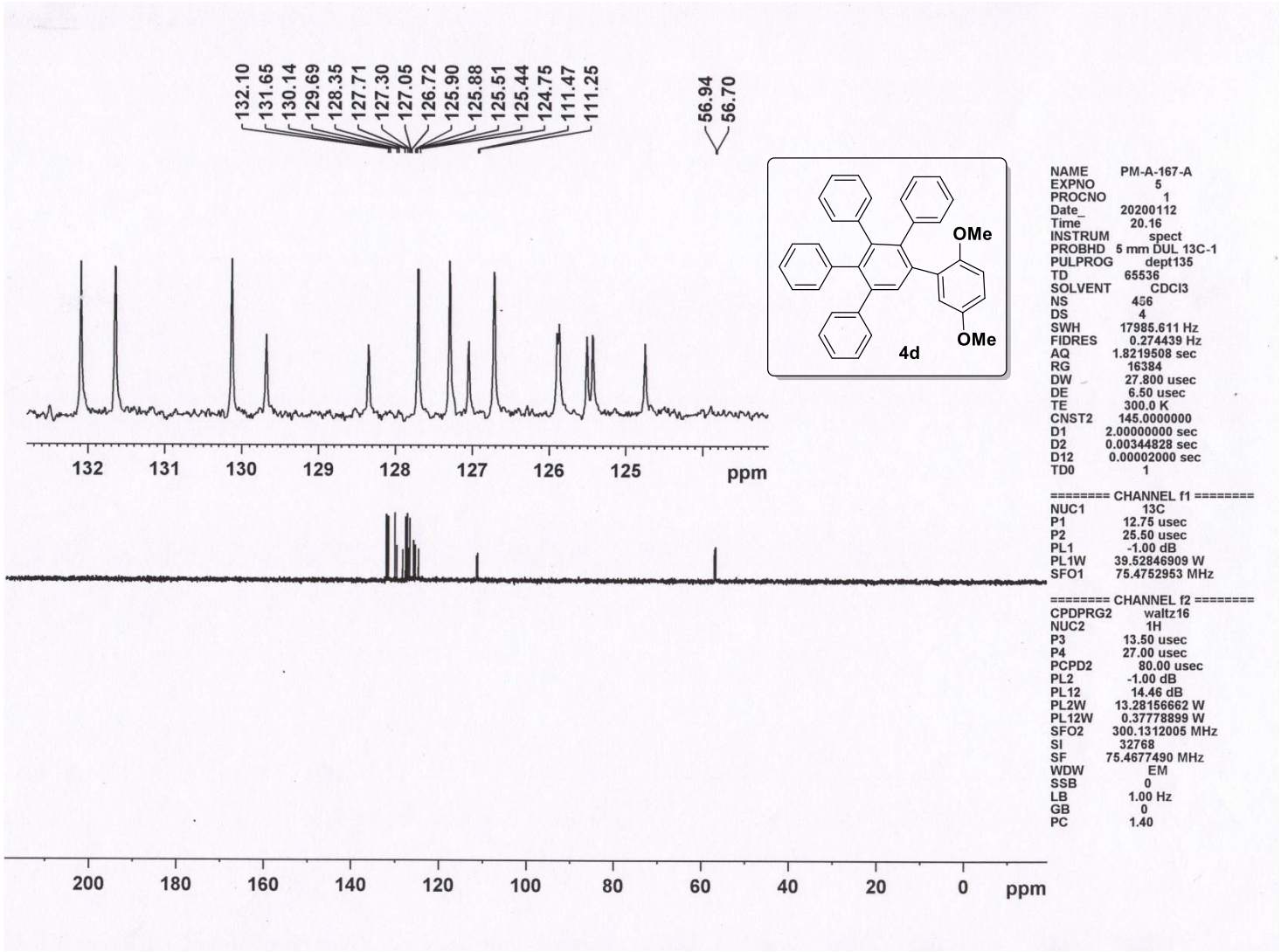
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **3v**



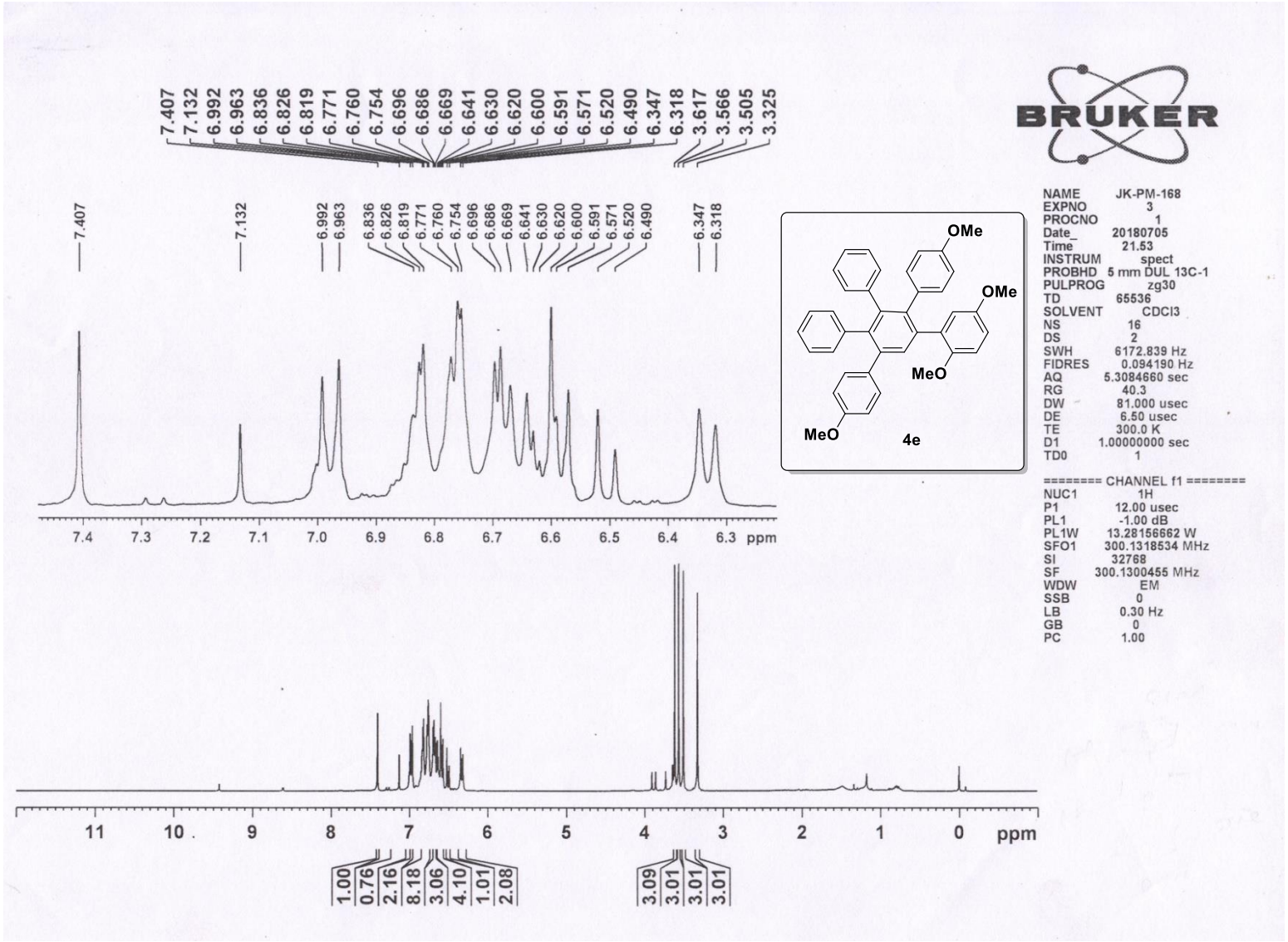
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4d**



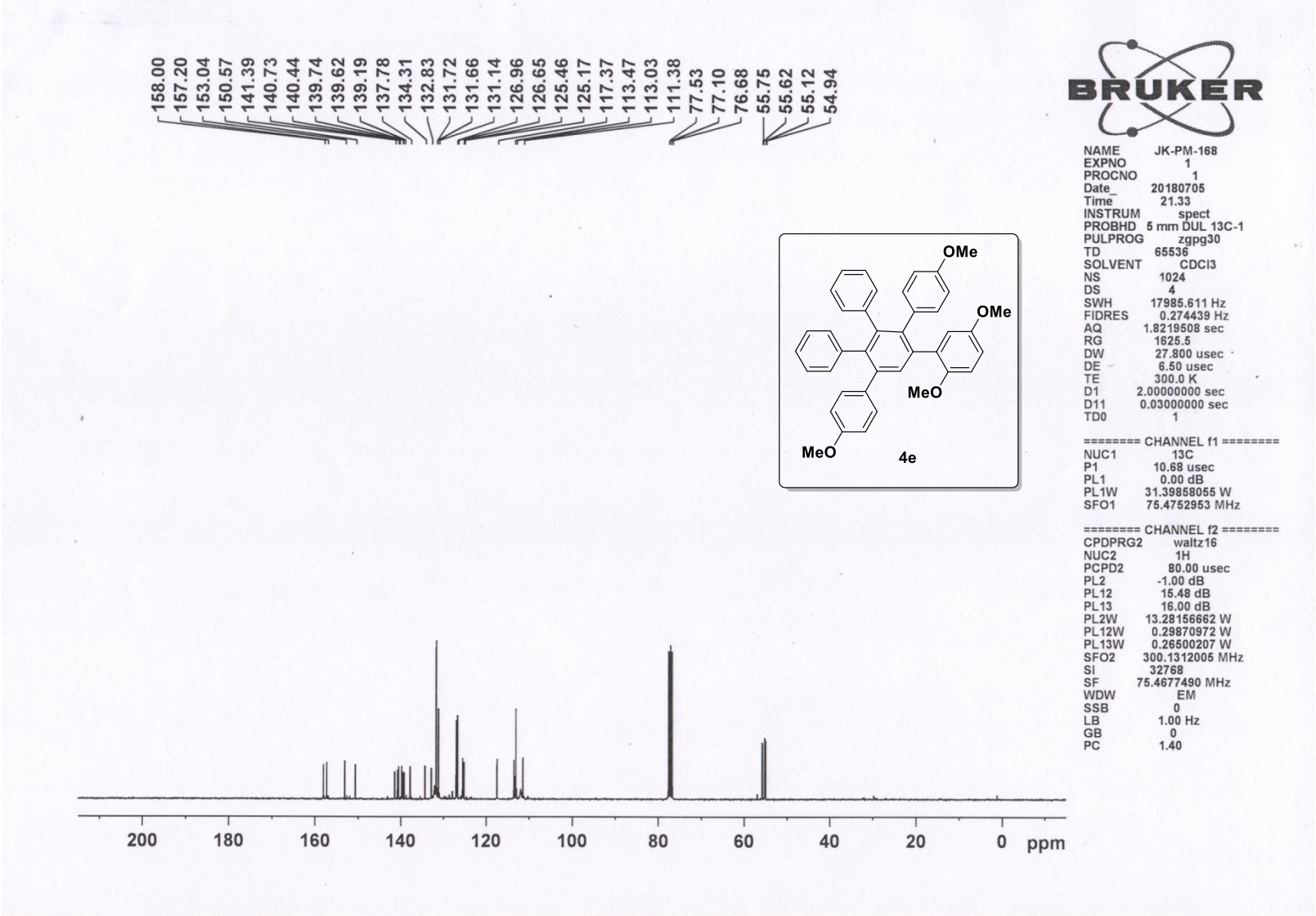
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4d**



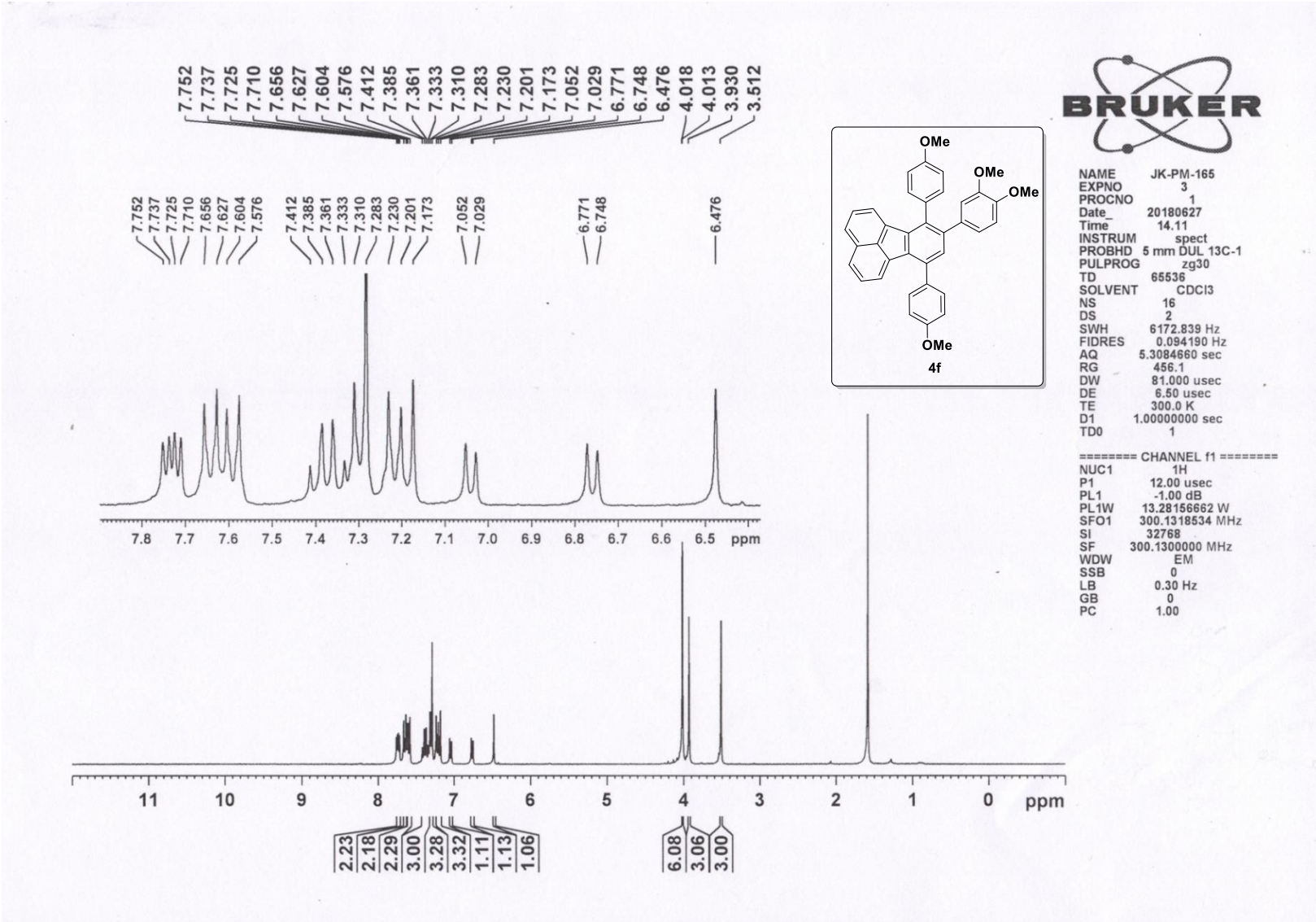
DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of **4d**



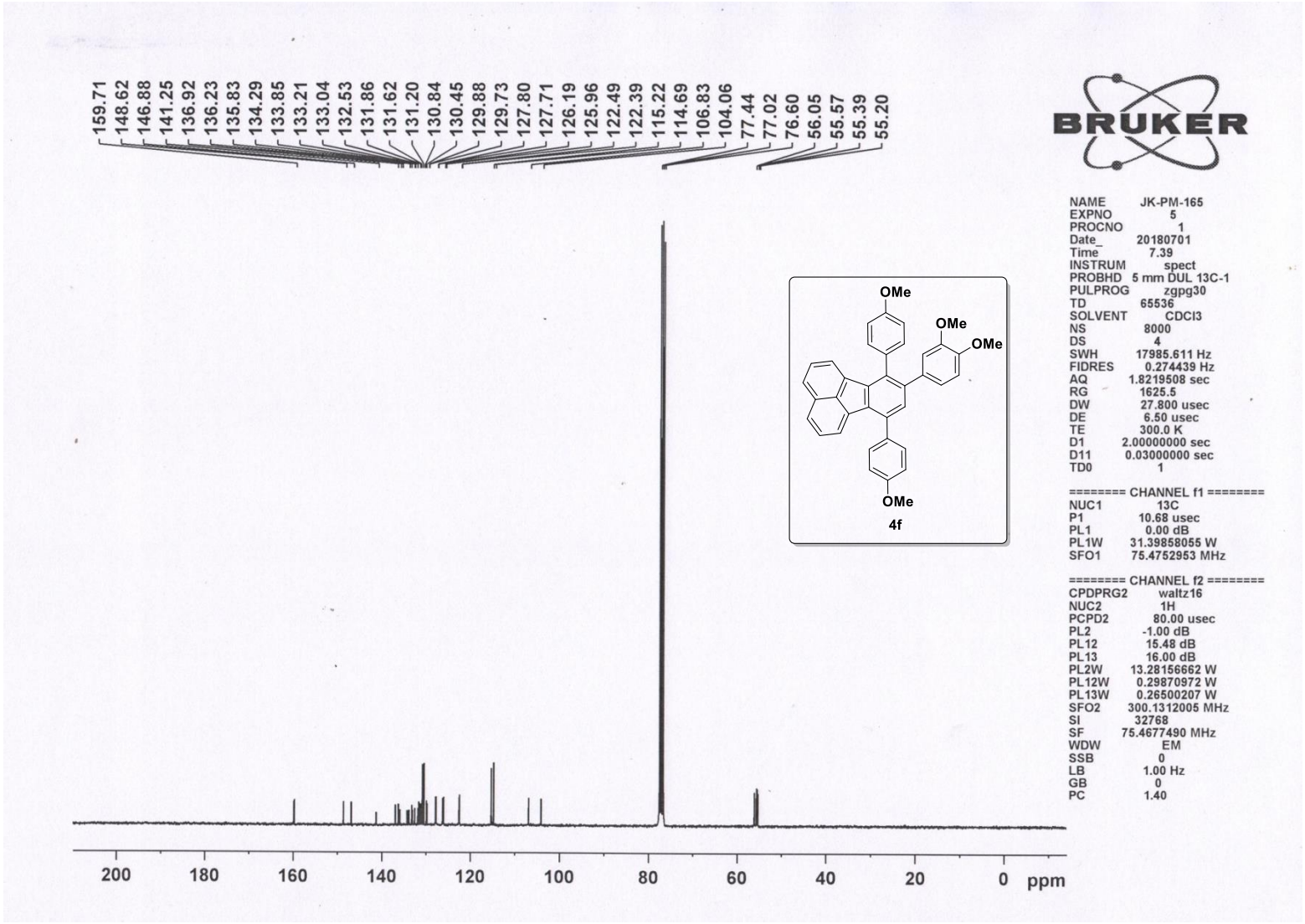
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4e**



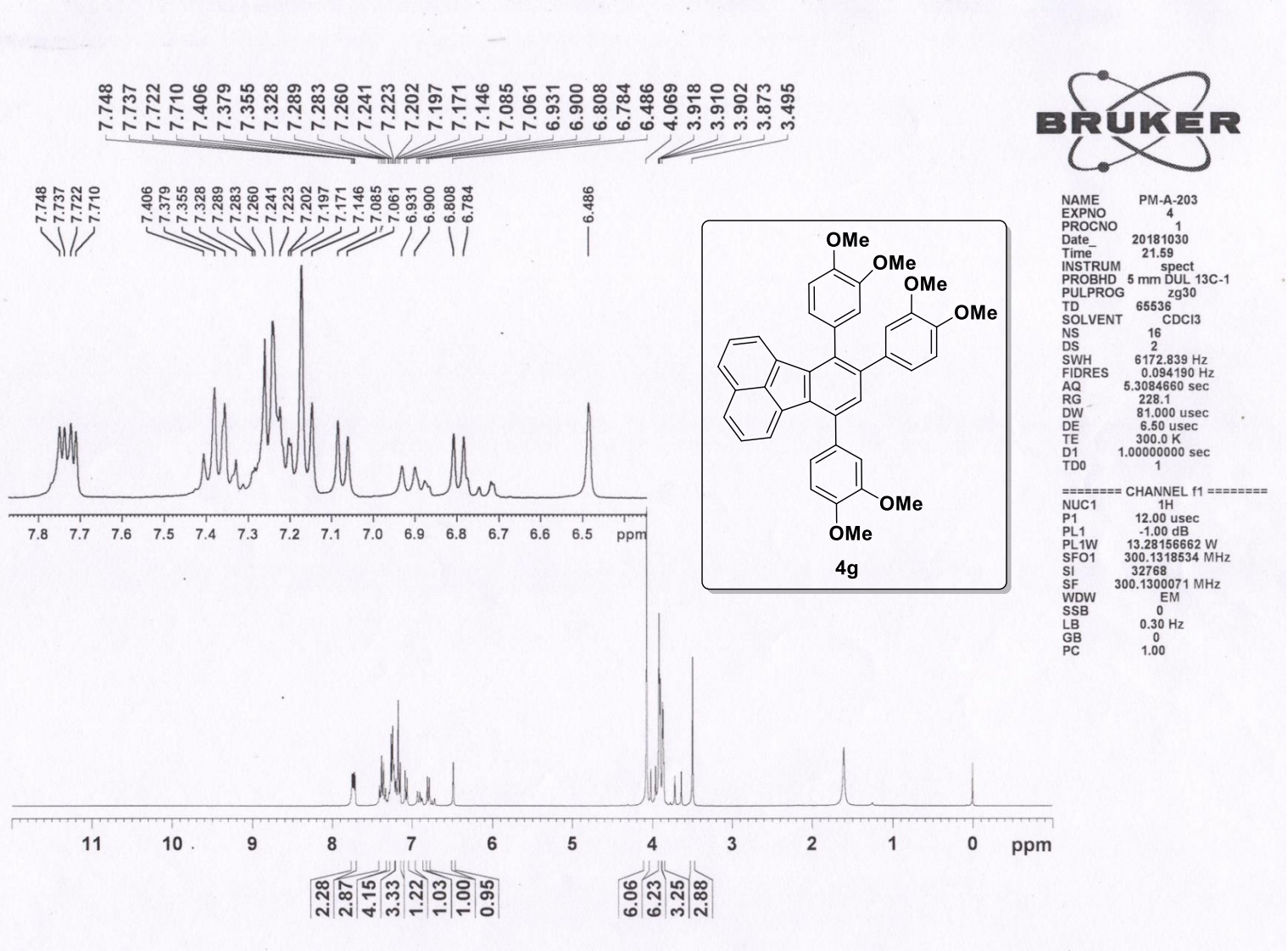
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4e**



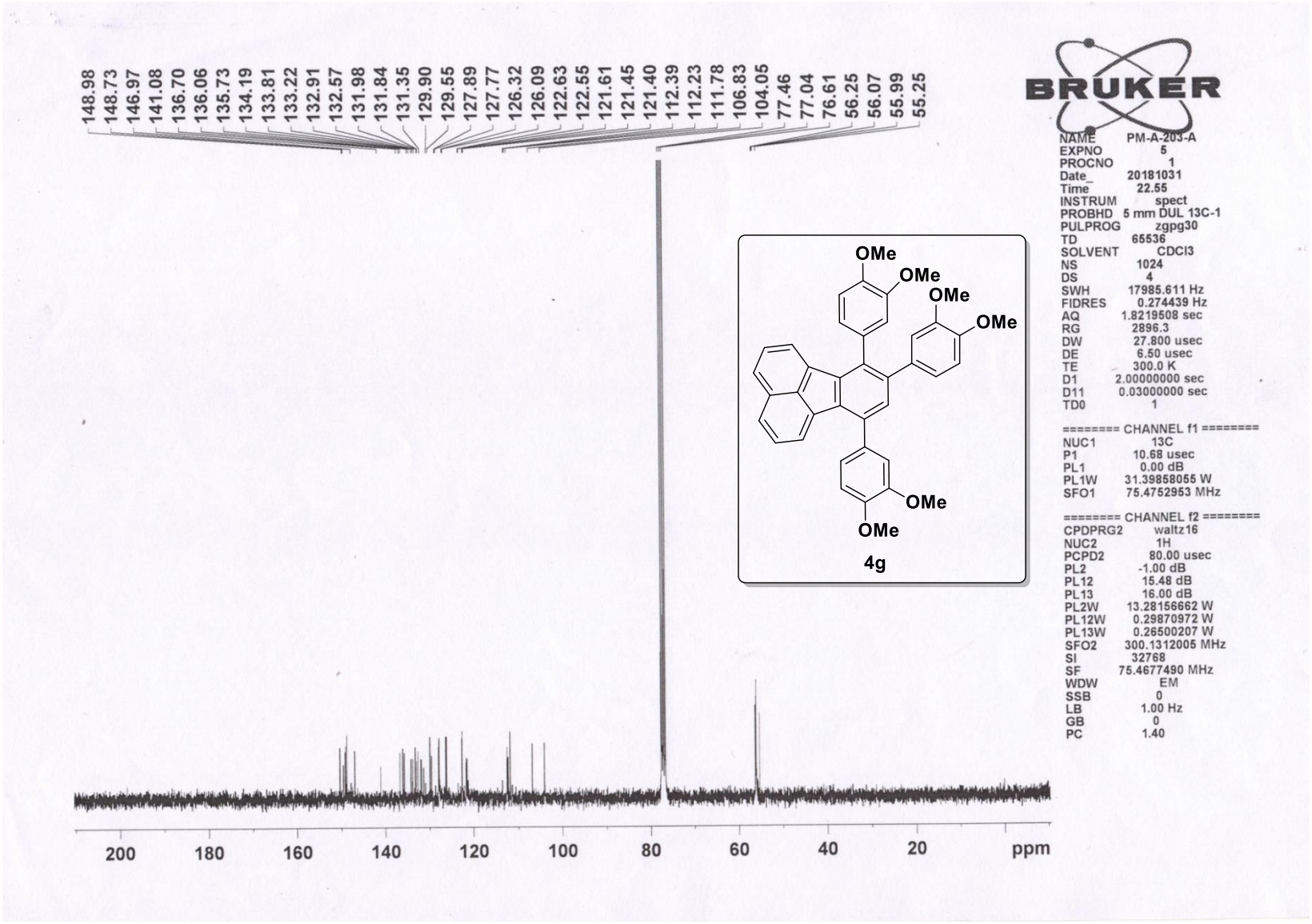
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4f**



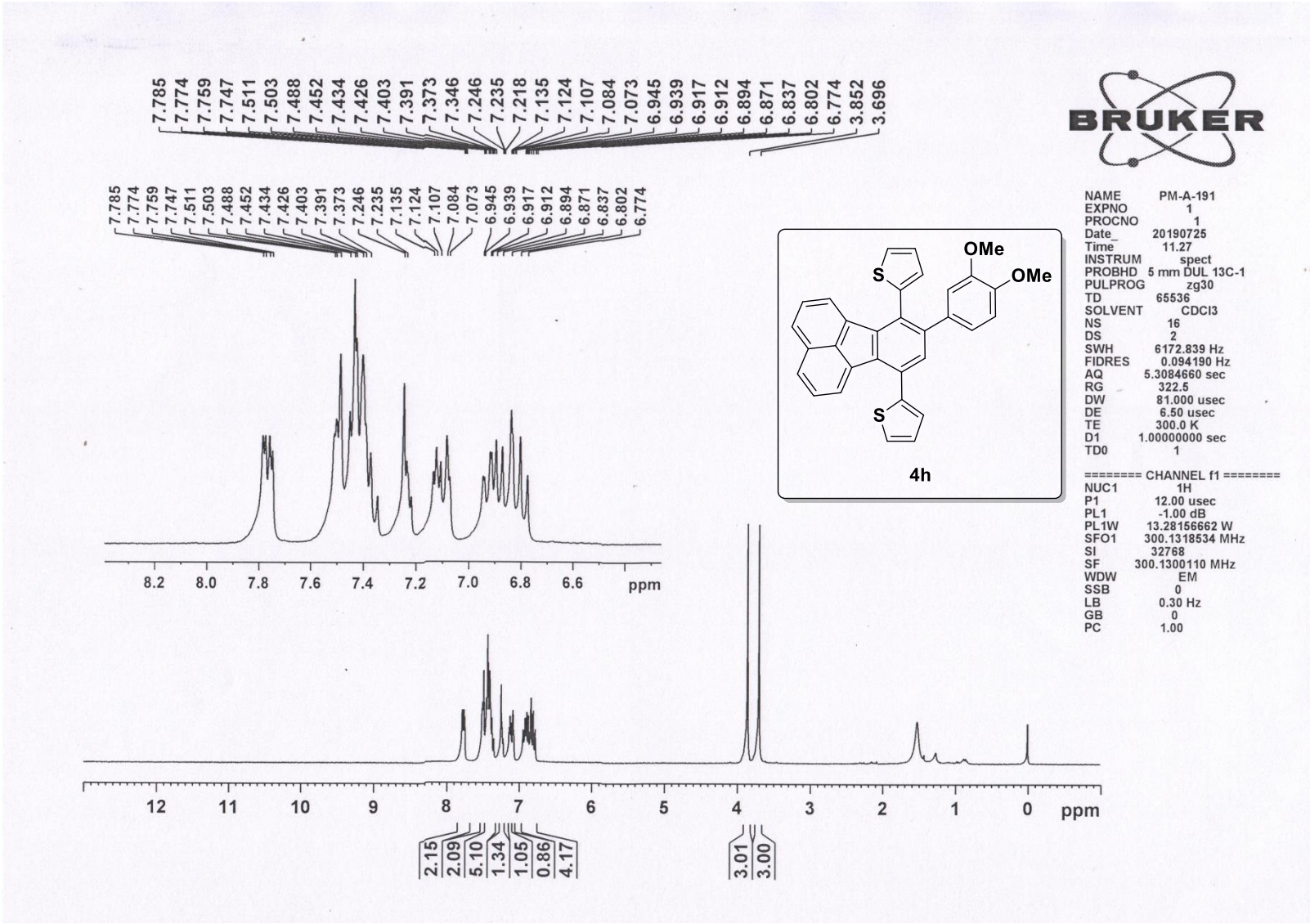
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4f**



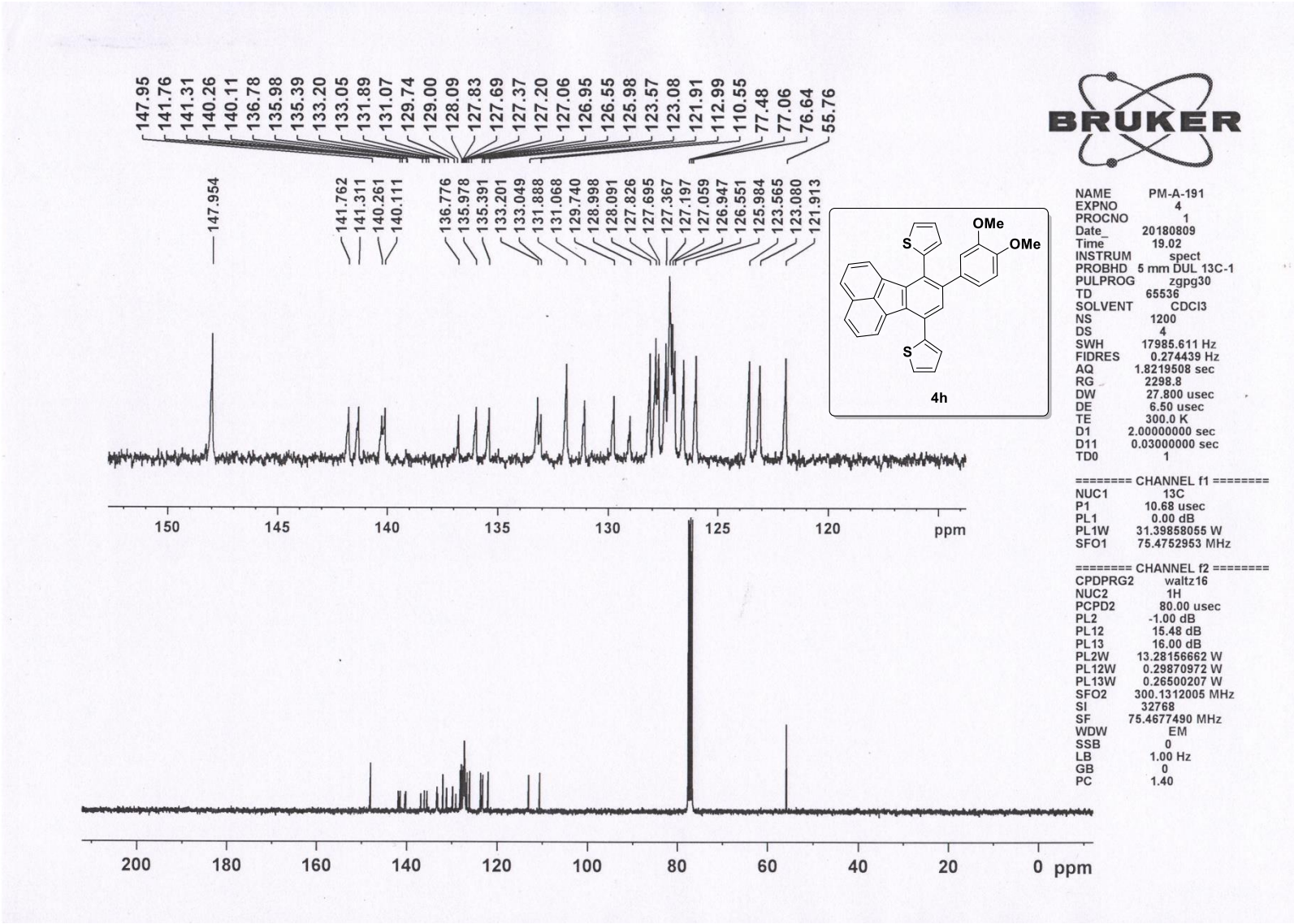
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4g**



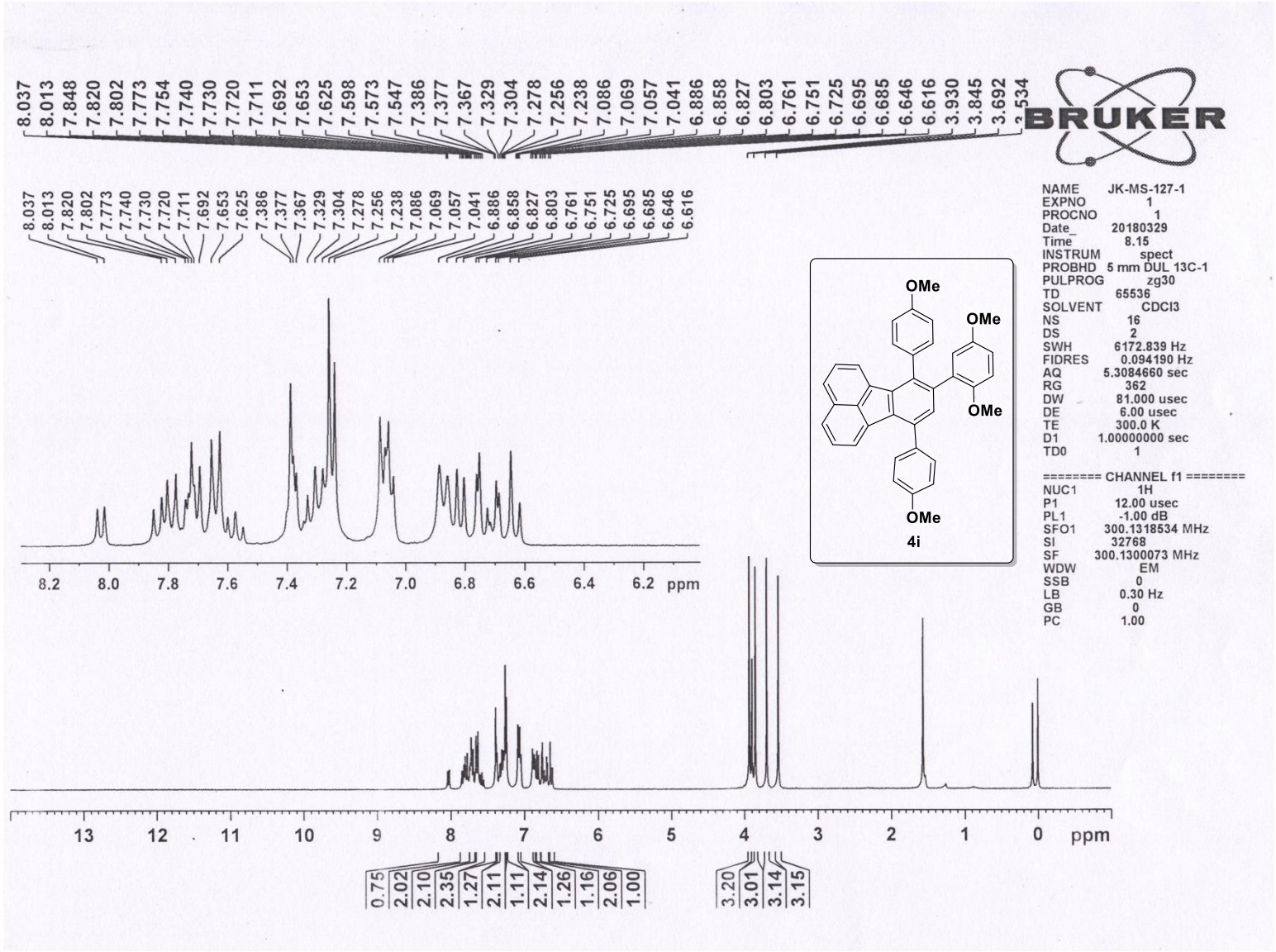
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4g**



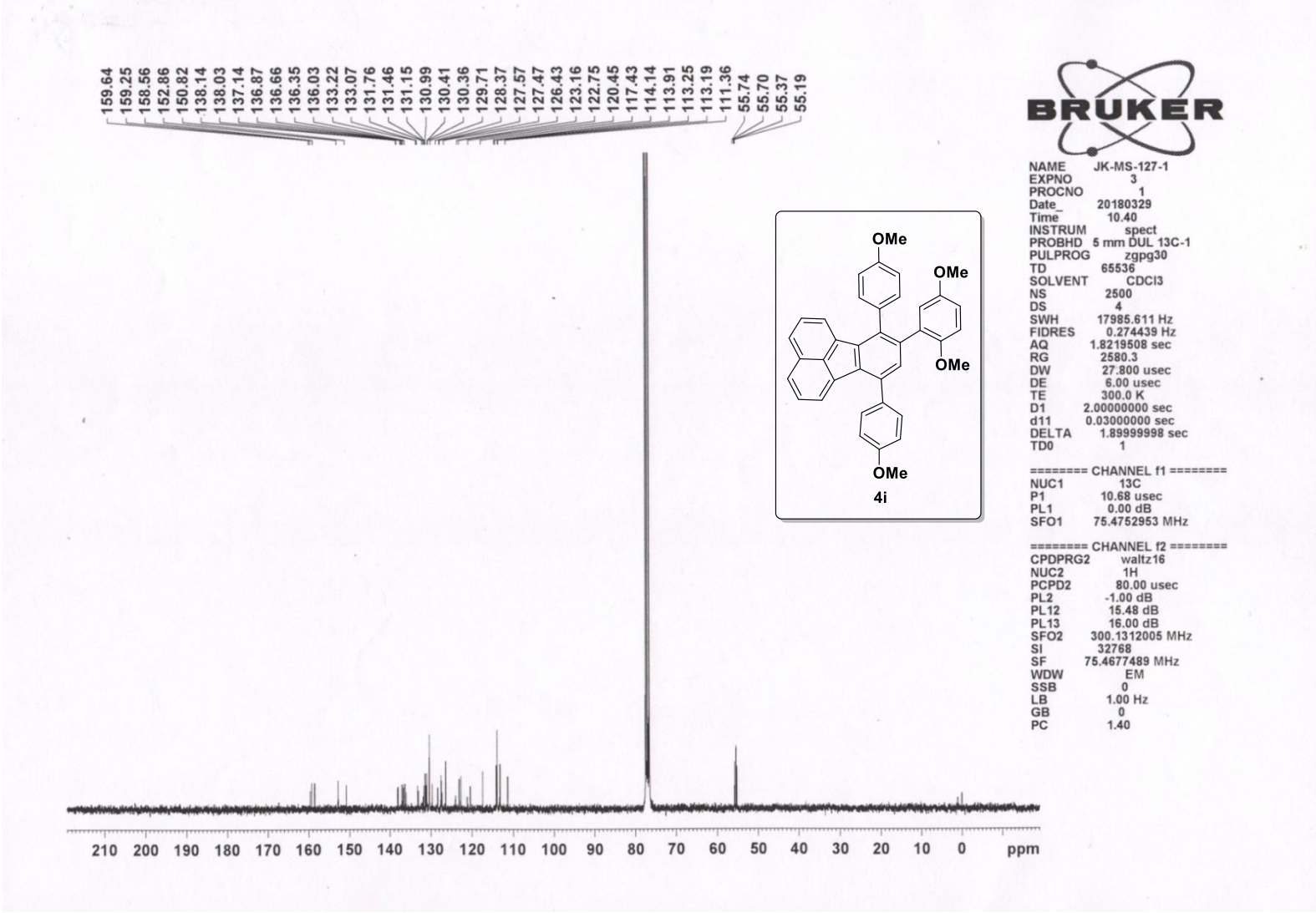
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4h**



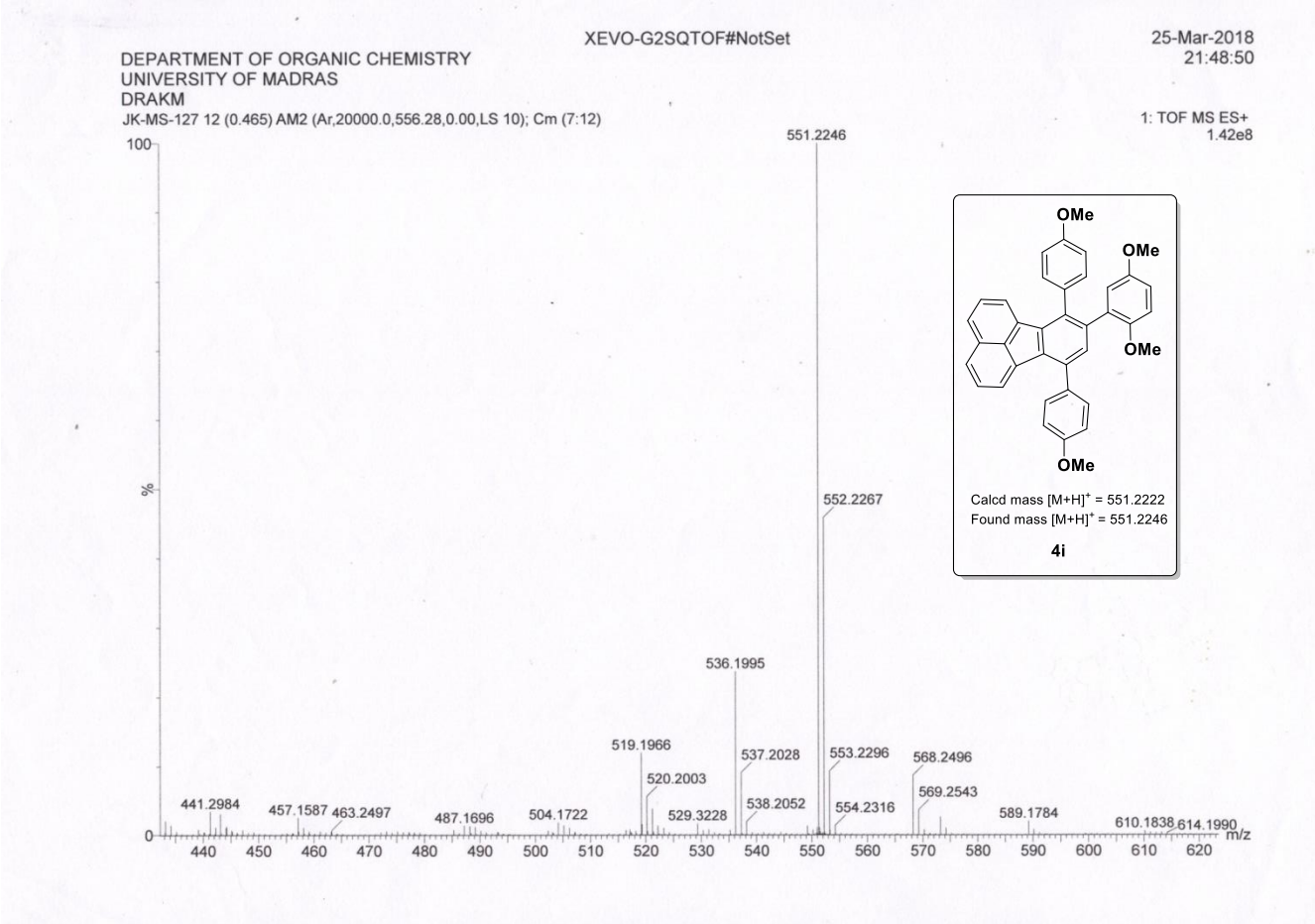
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4h**



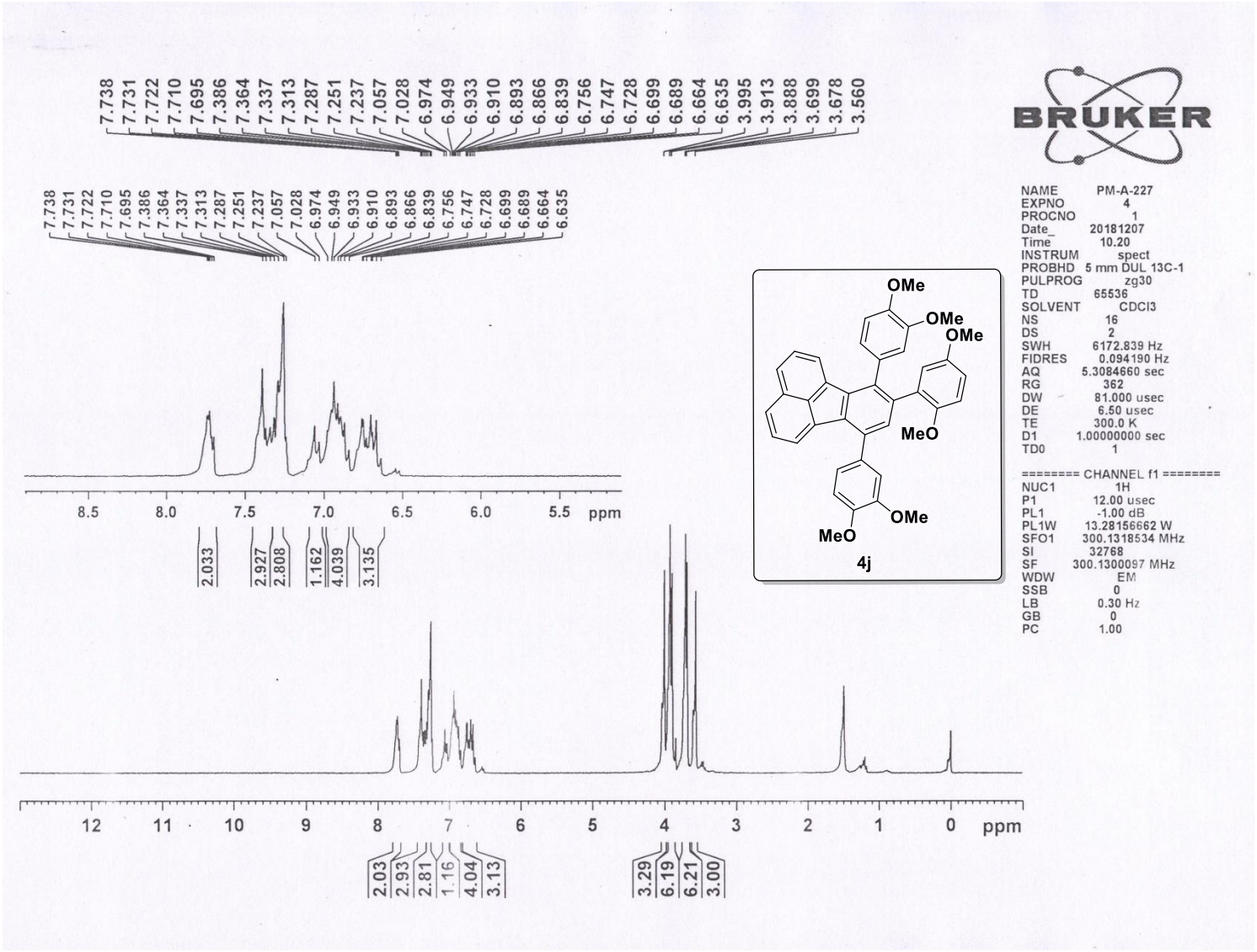
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4i**



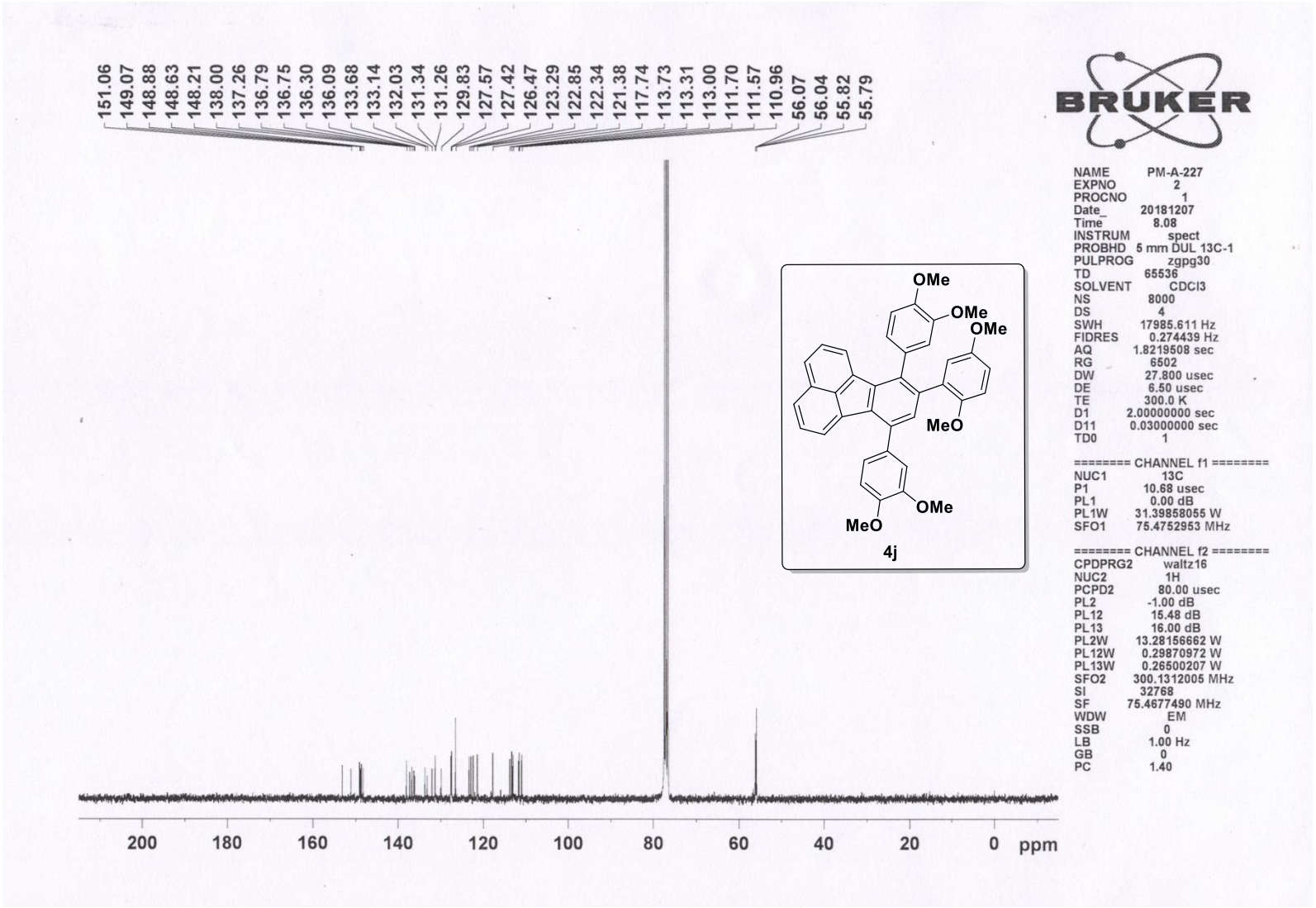
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4i**



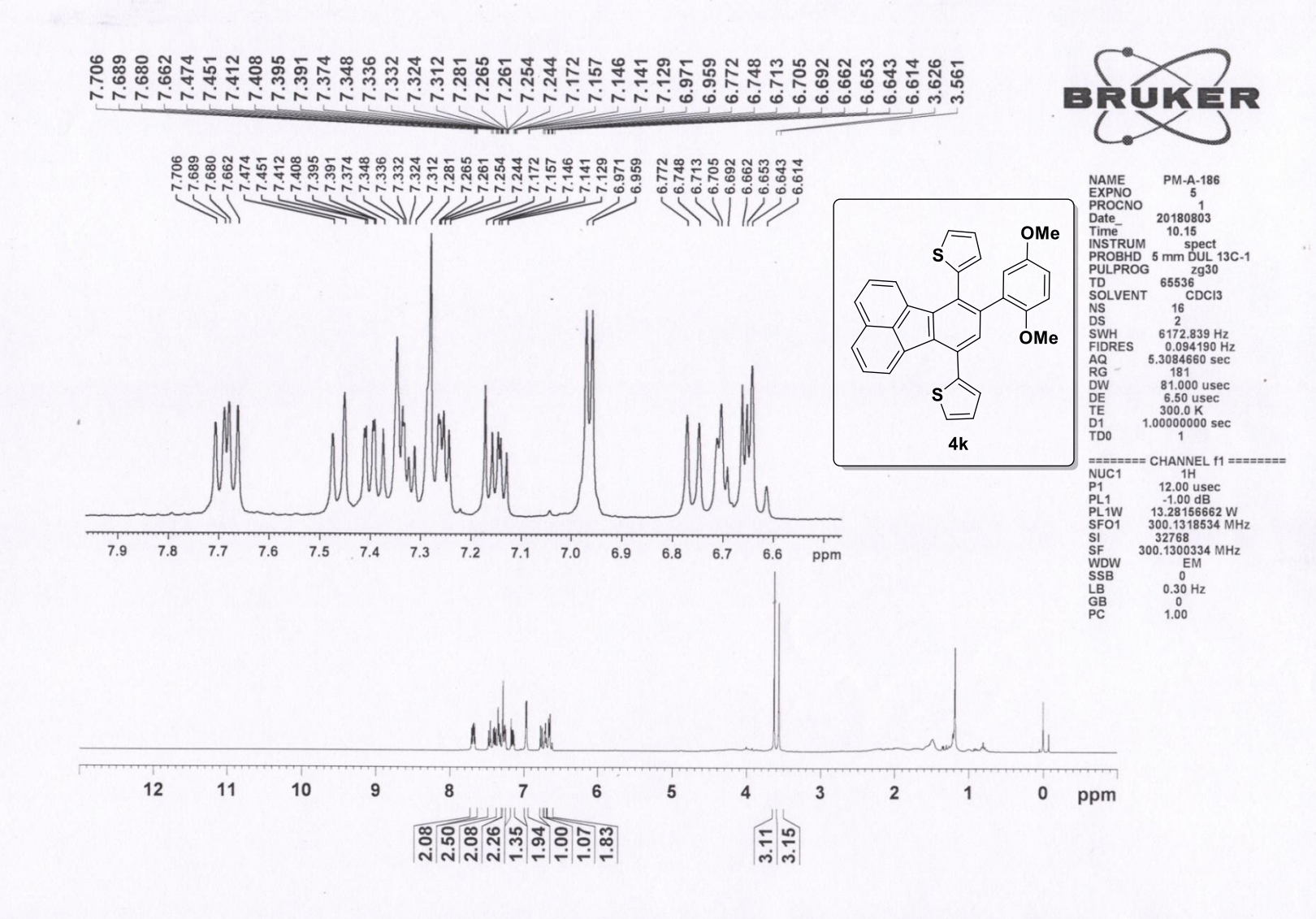
HRMS spectrum of compound **4i**



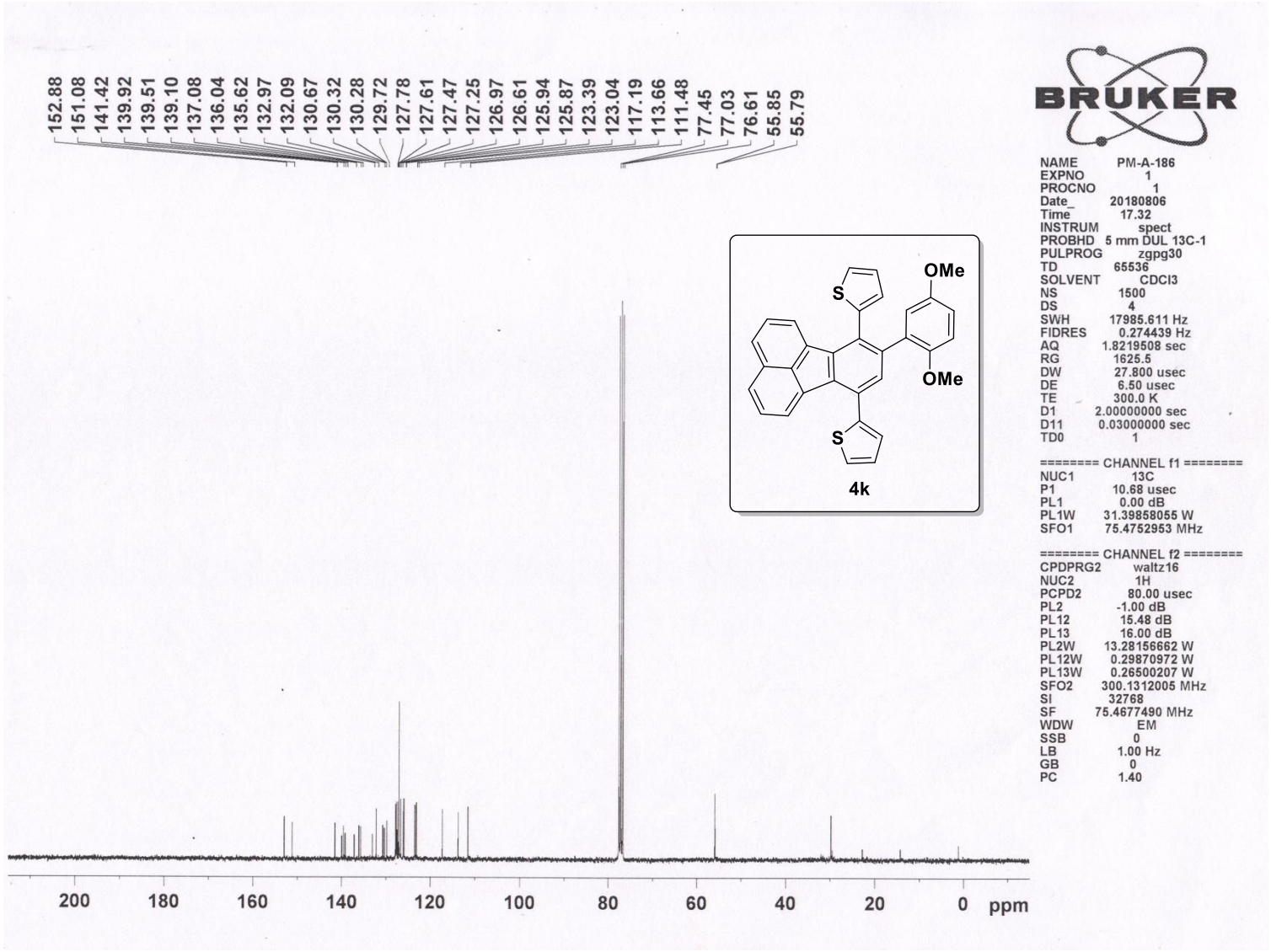
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4j**



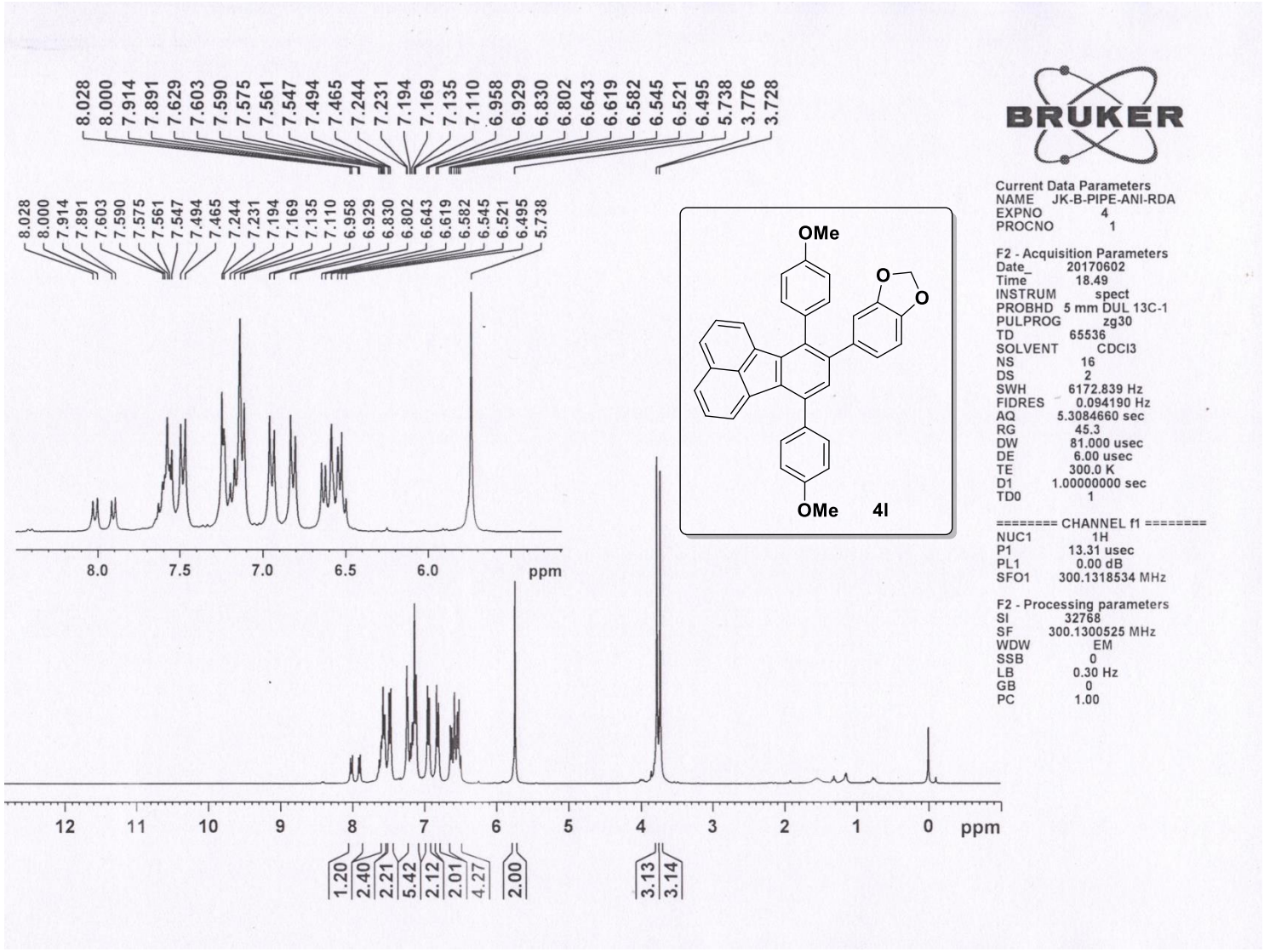
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4j**



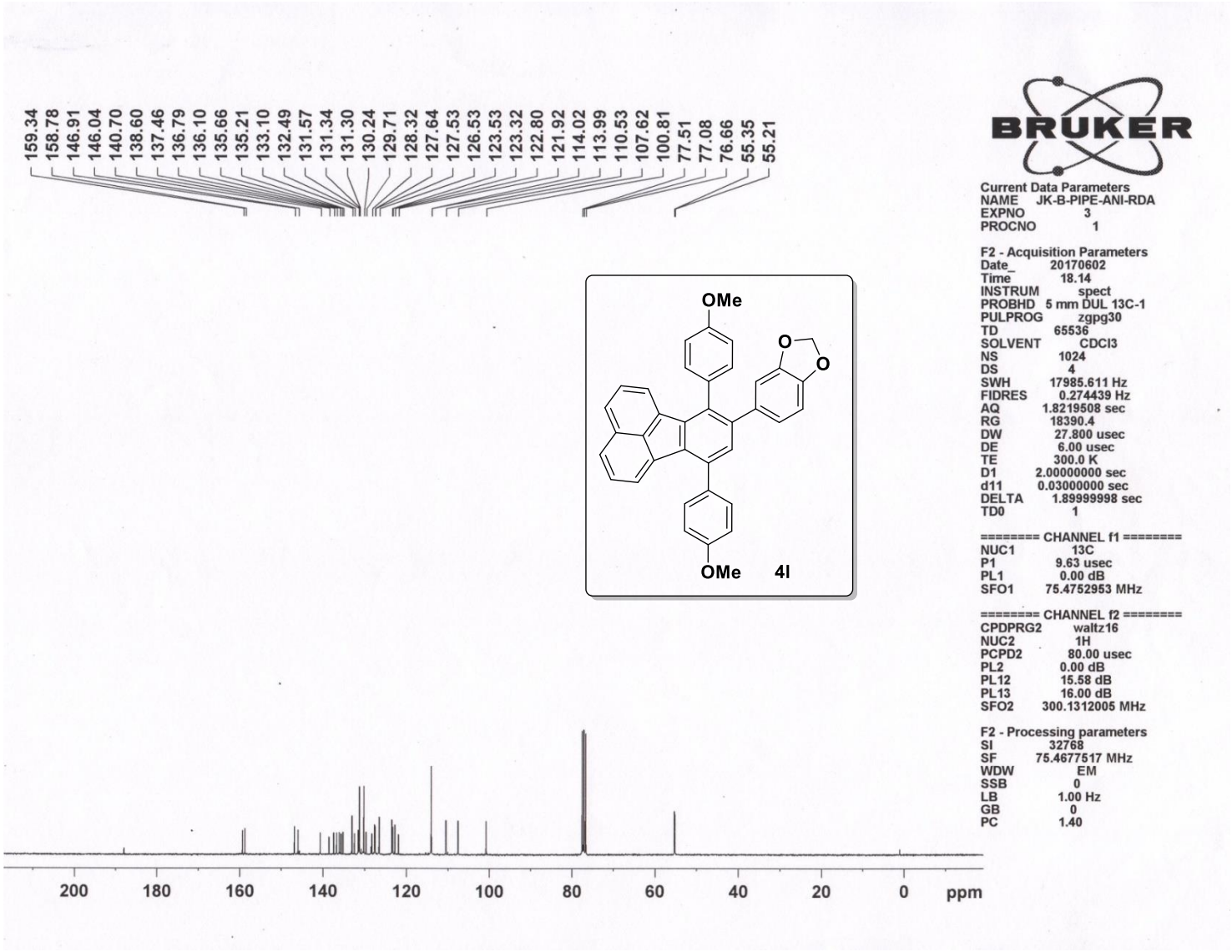
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4k**



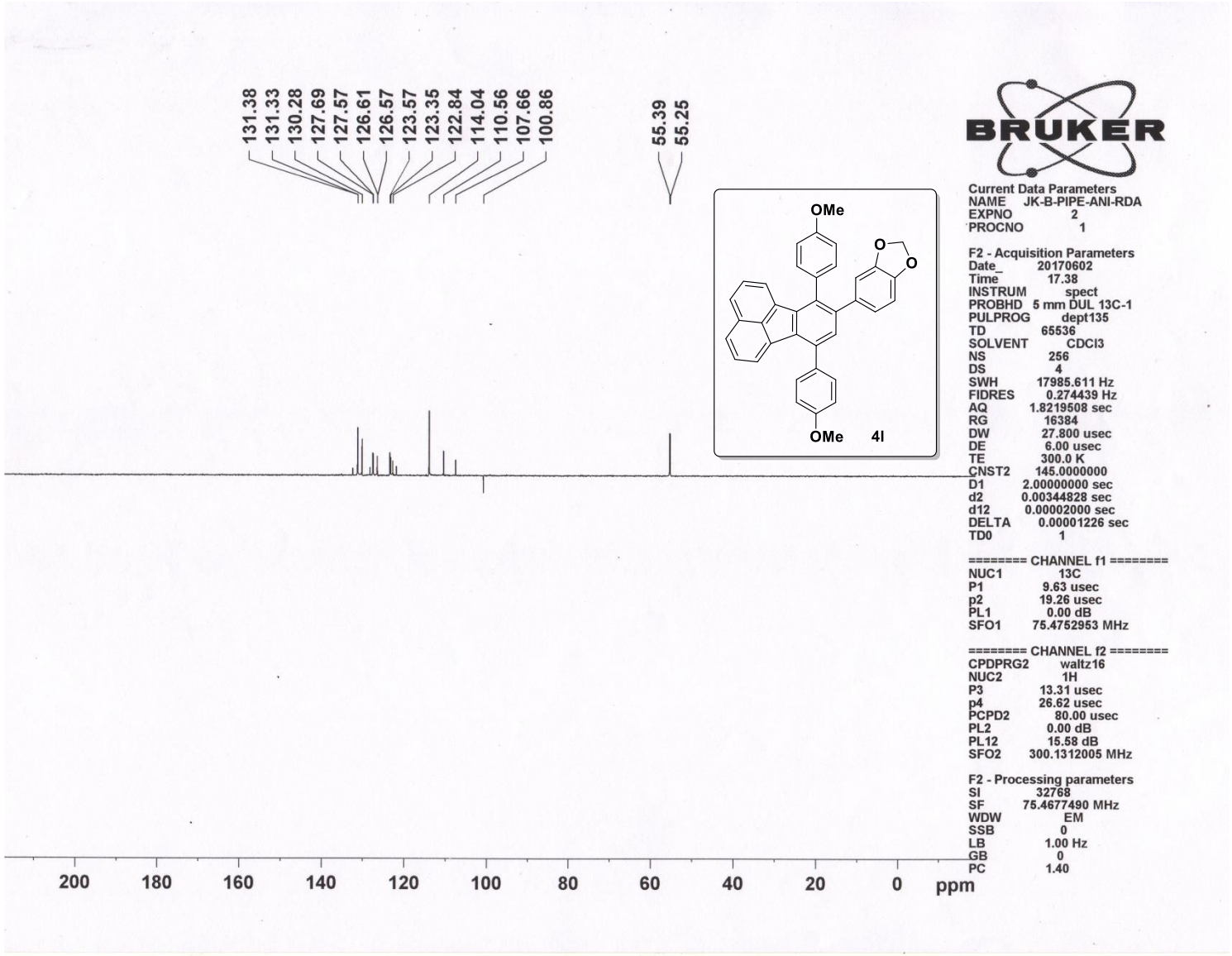
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4k**



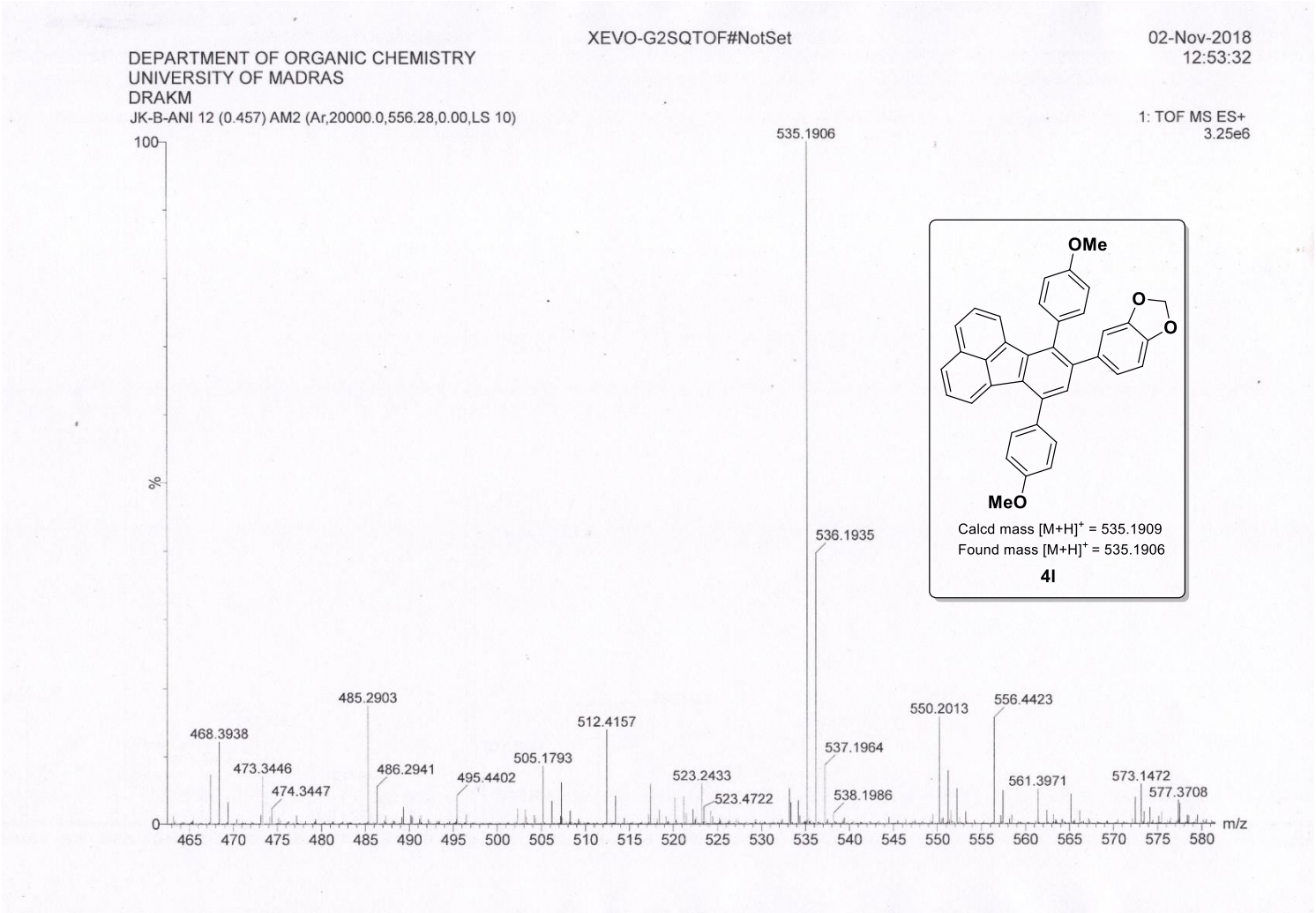
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4l**



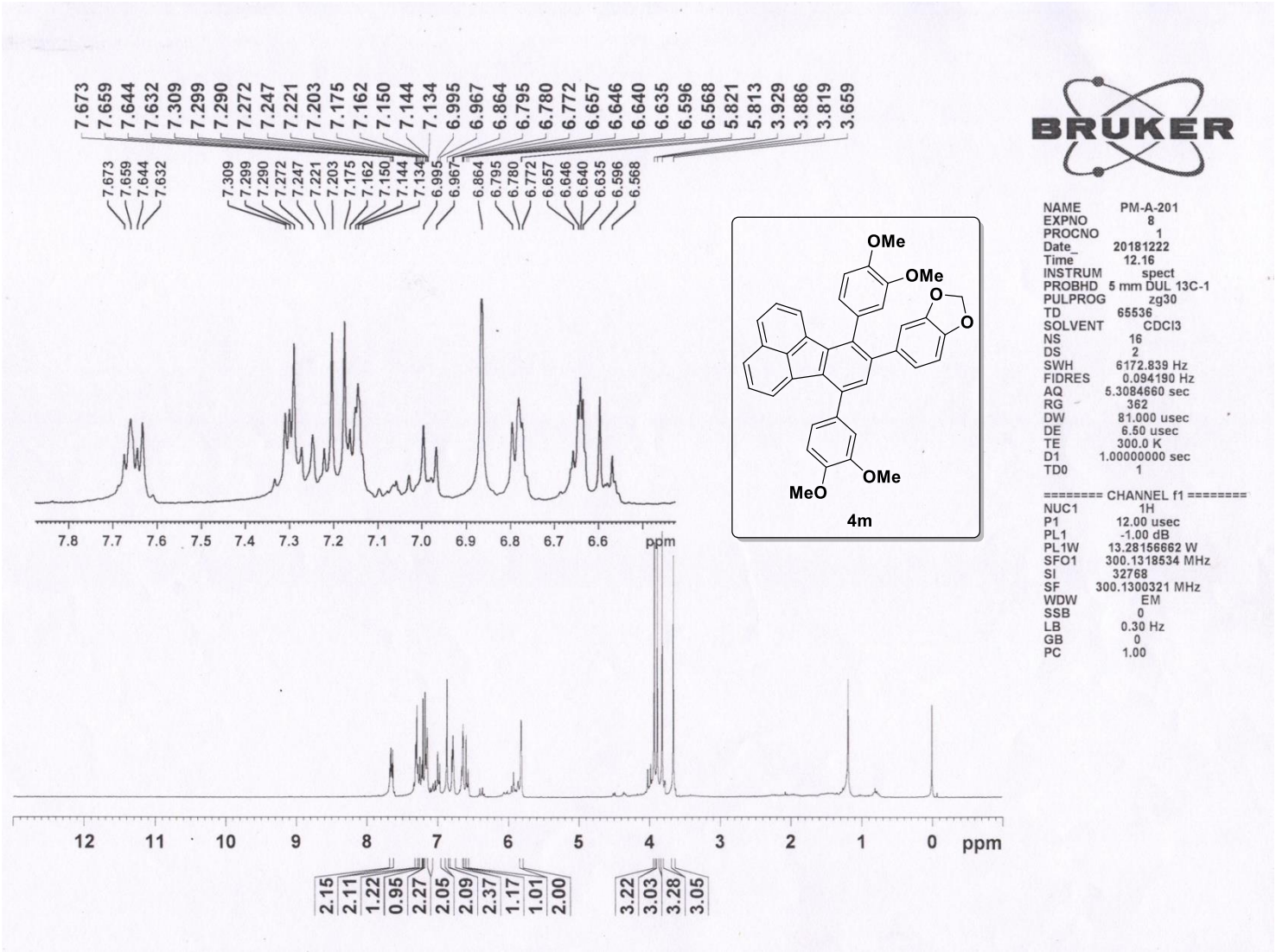
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4l**



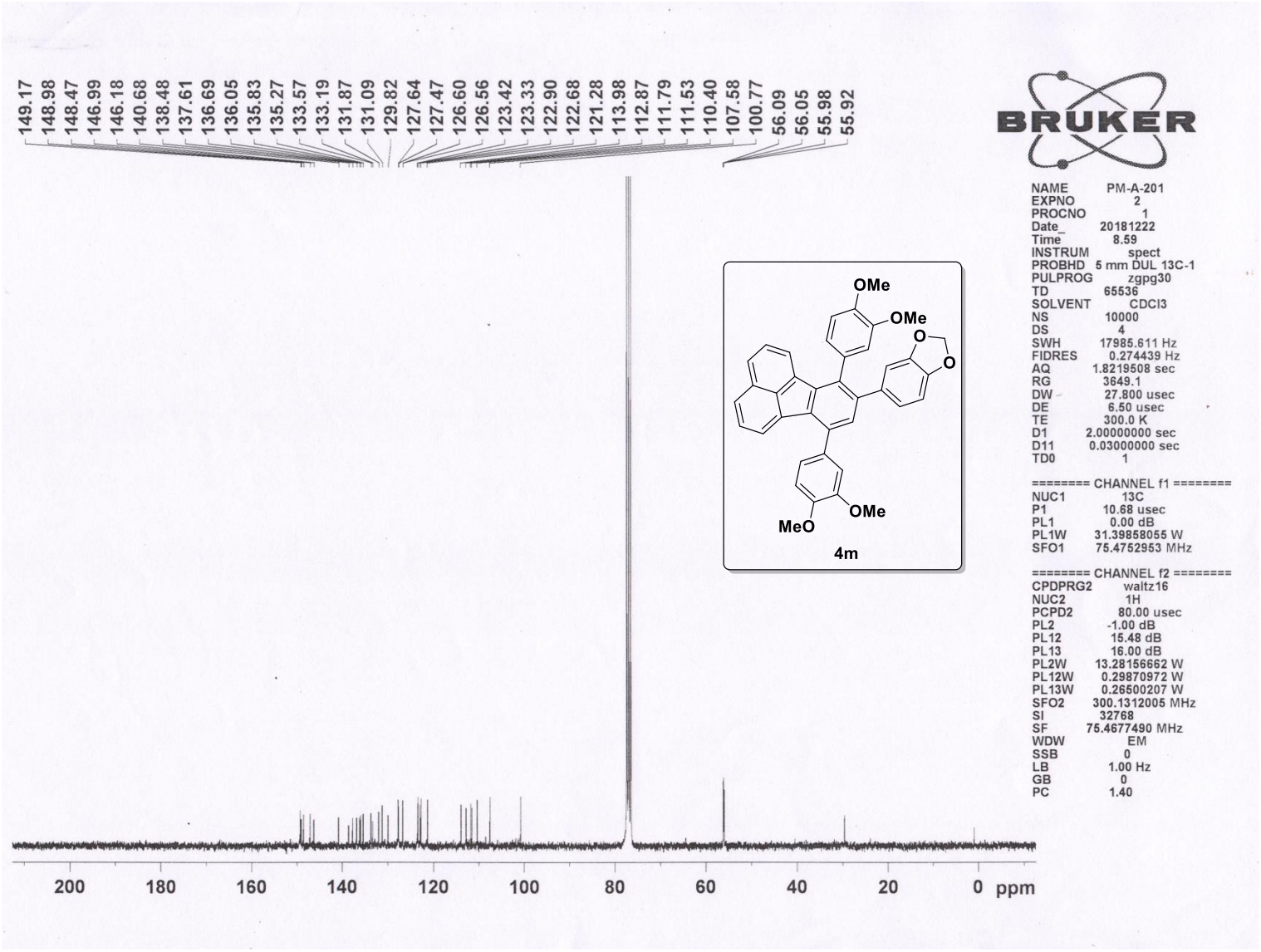
DEPT-135NMR (75 MHz, $CDCl_3$) spectrum of compound **4l**



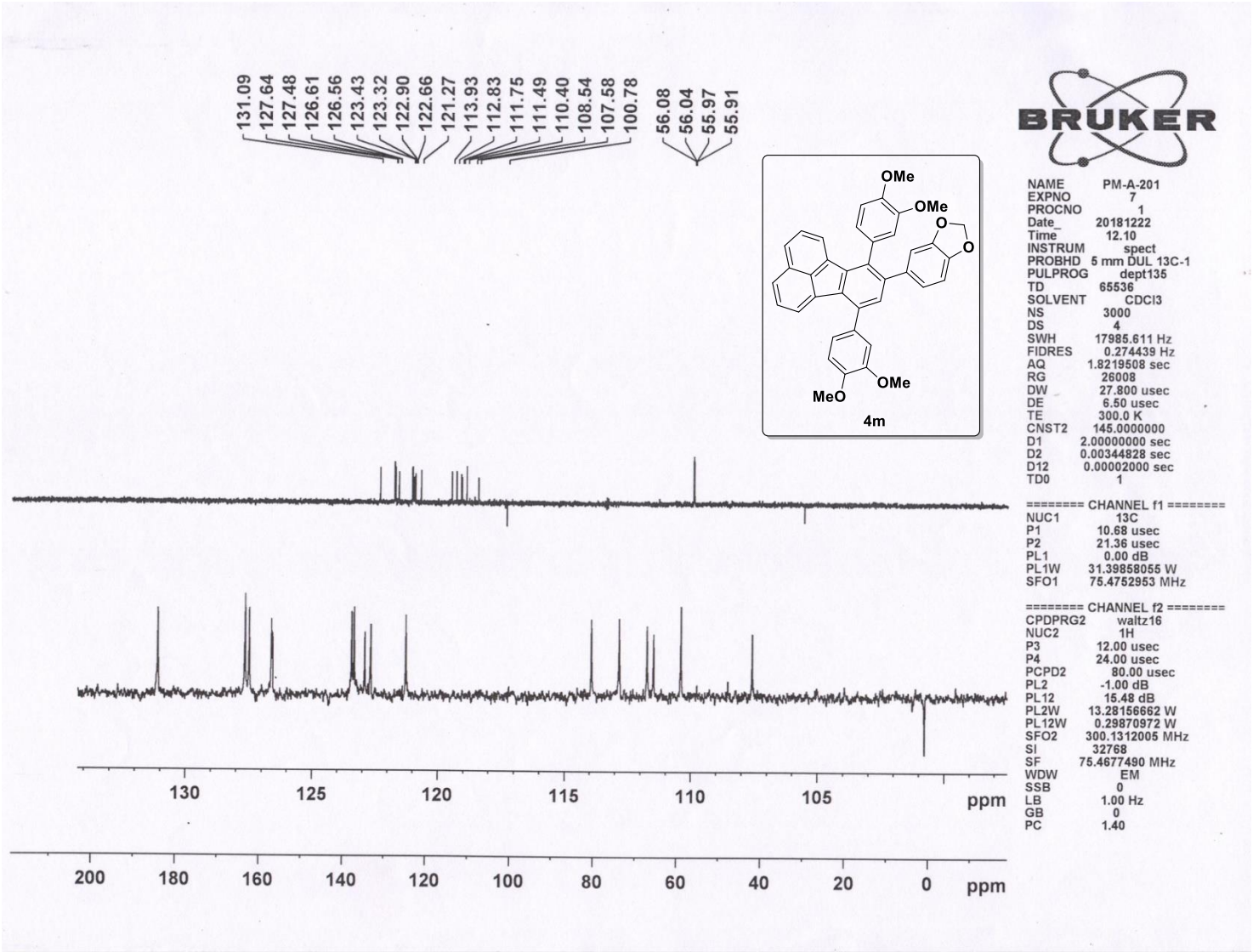
HRMS spectrum of compound **4l**



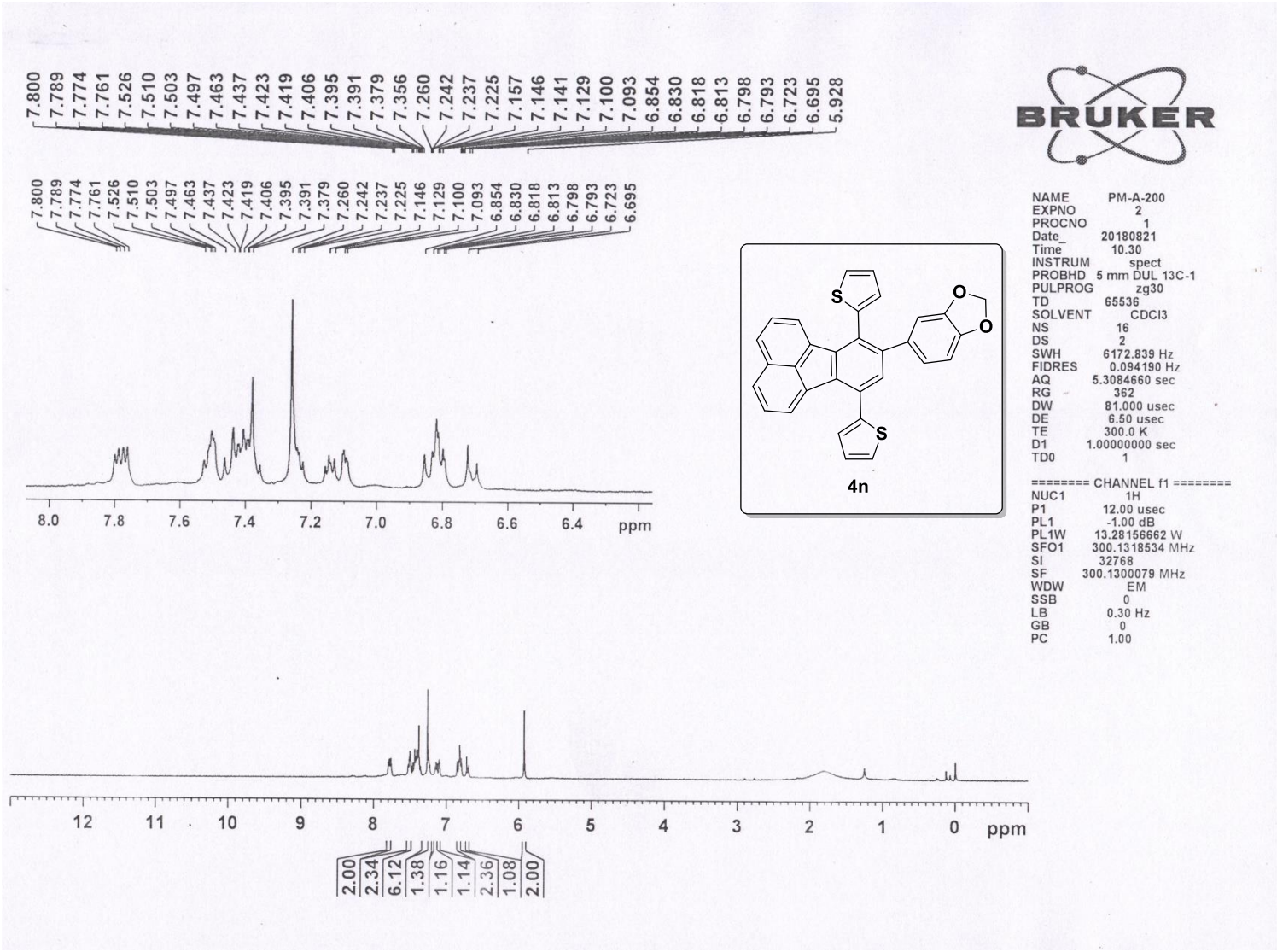
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4m**



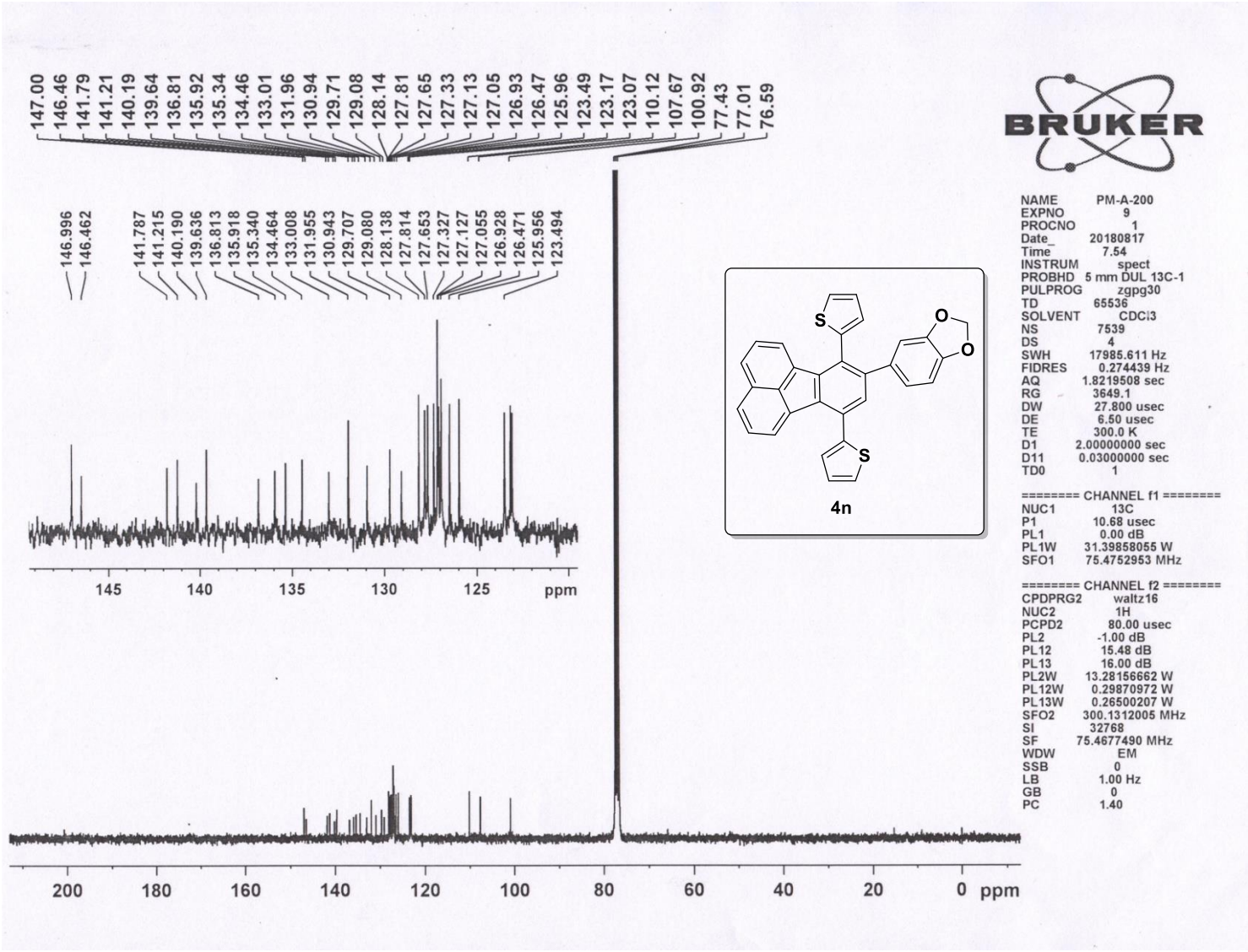
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4m**



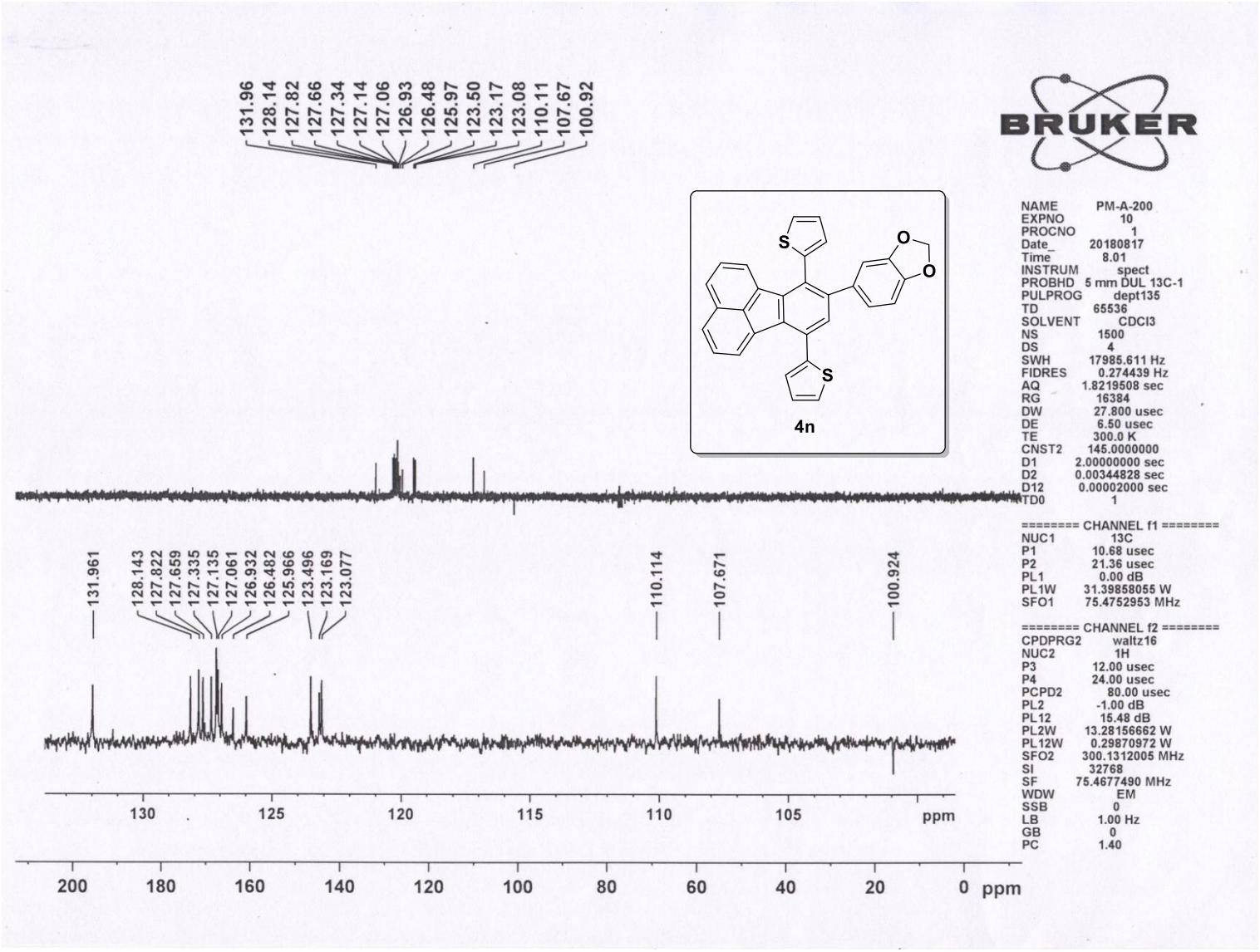
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **4m**



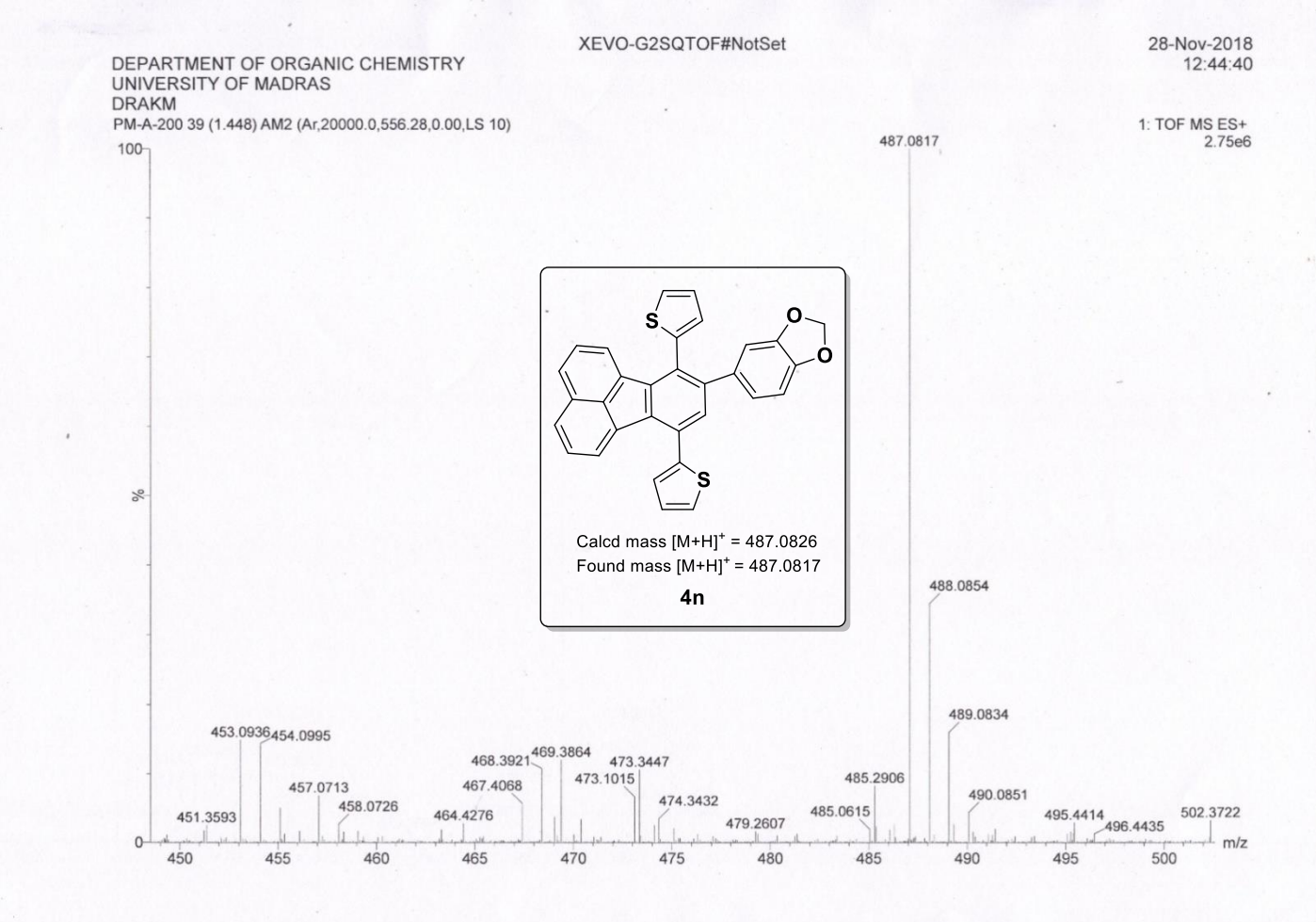
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4n**



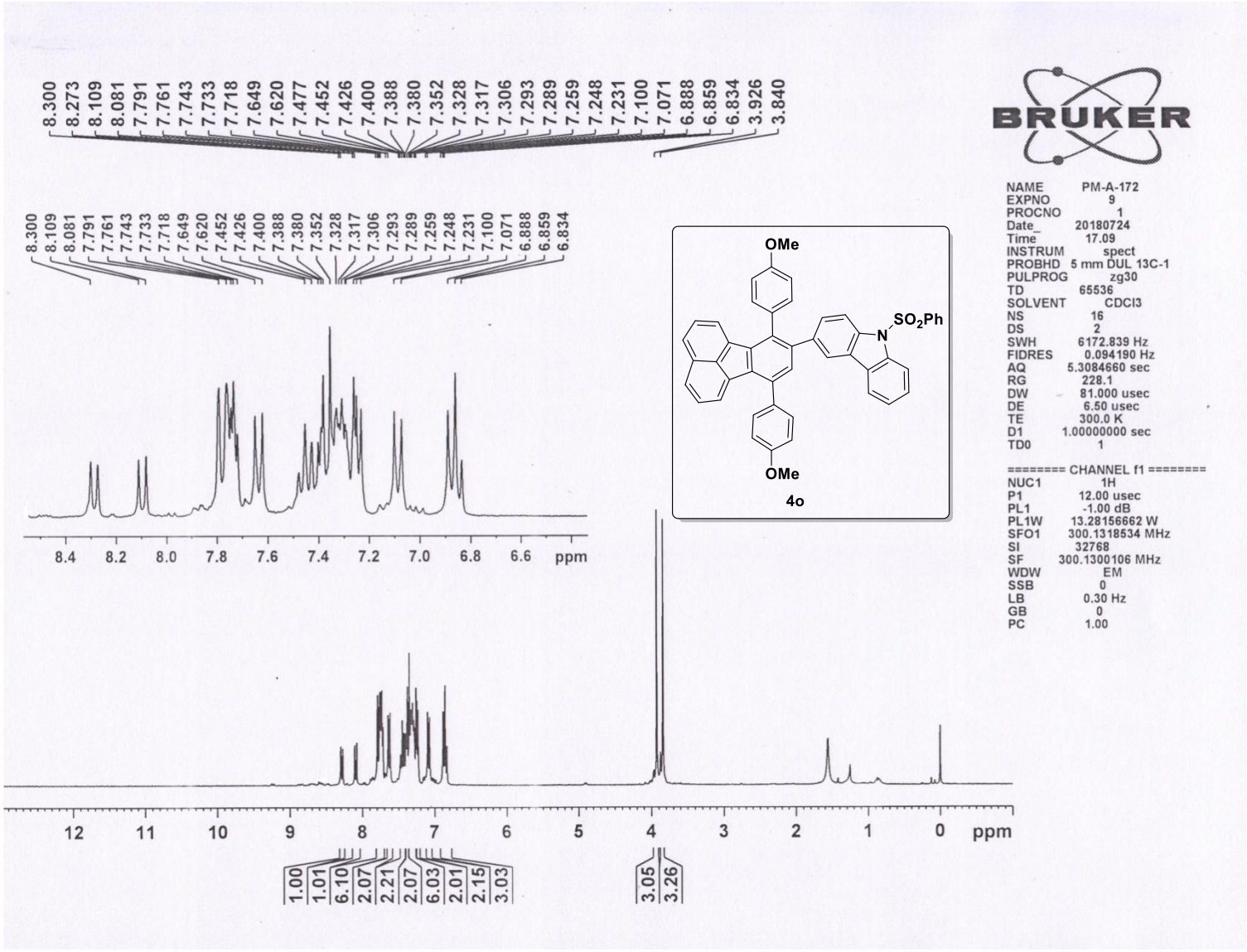
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4n**



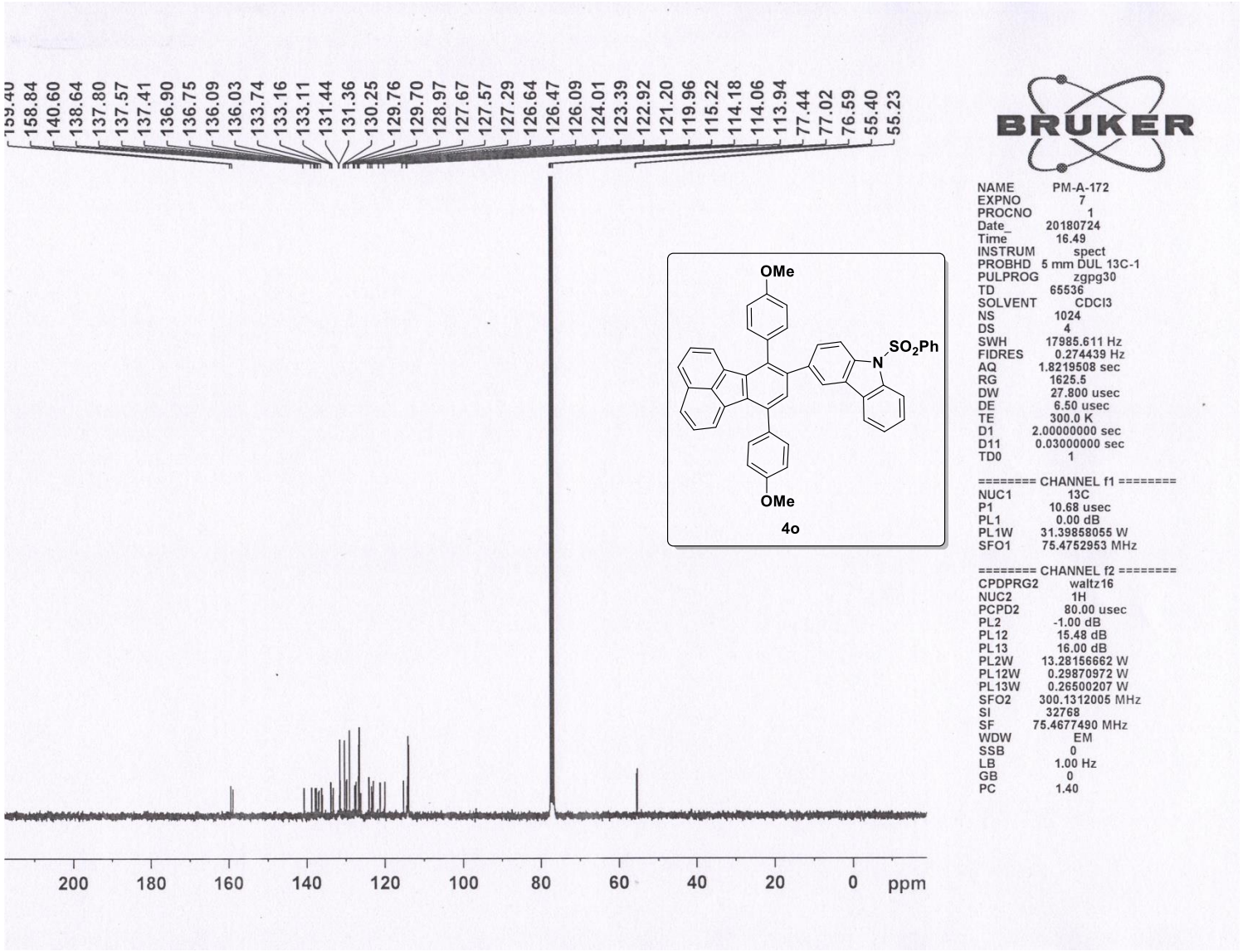
DEPT-135NMR (75 MHz, $CDCl_3$) spectrum of compound **4n**



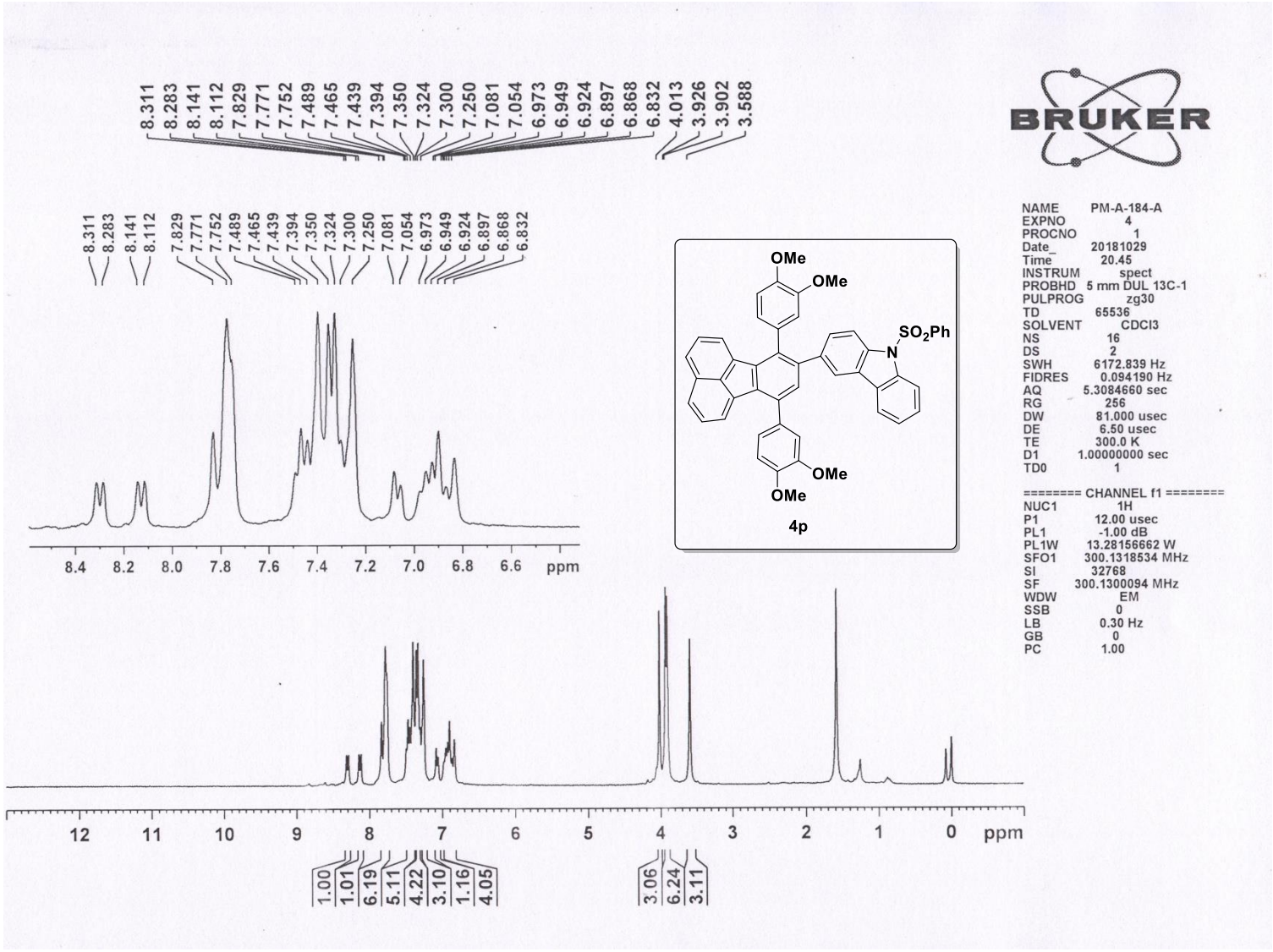
HRMS spectrum of compound **4n**



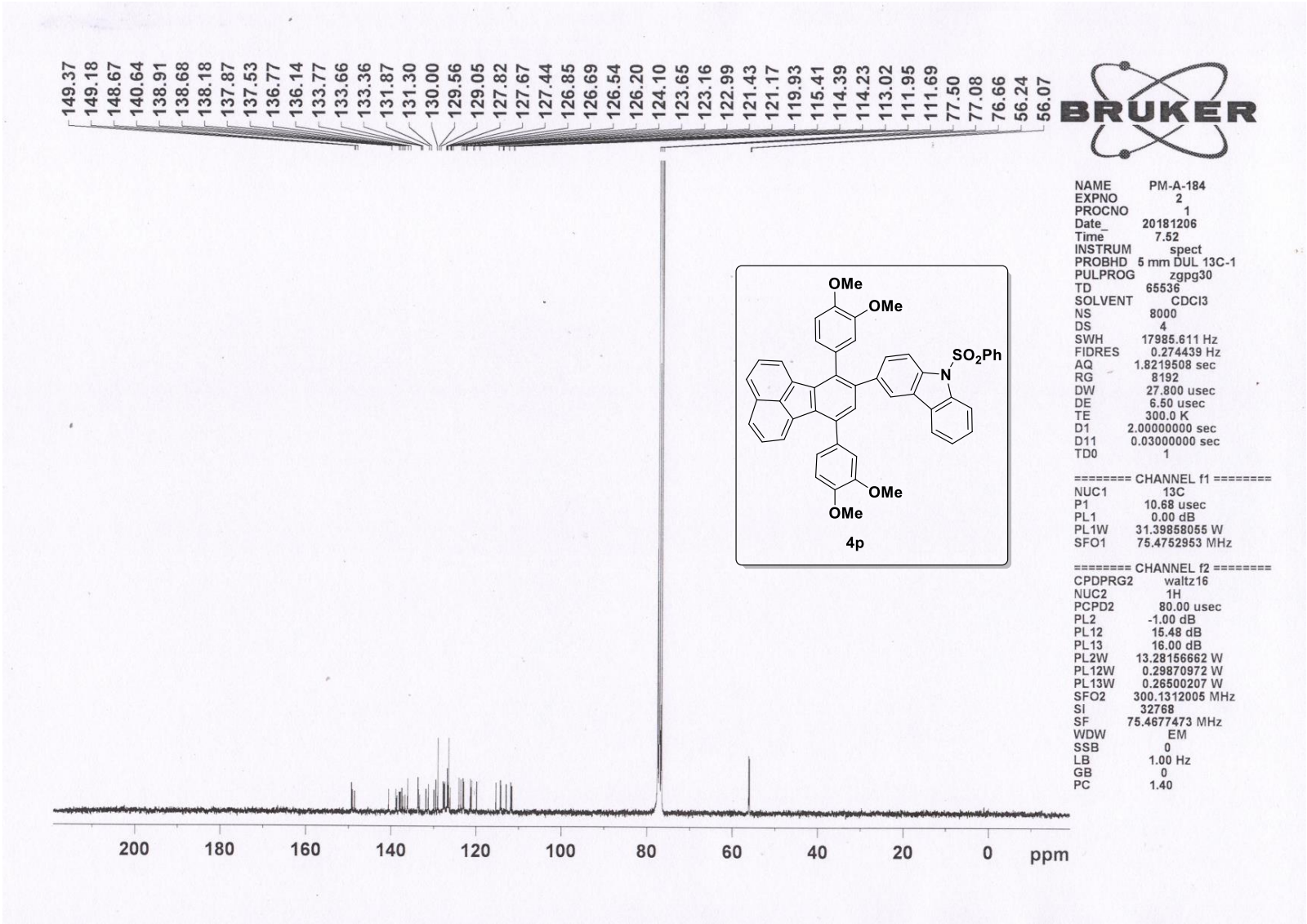
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4o**



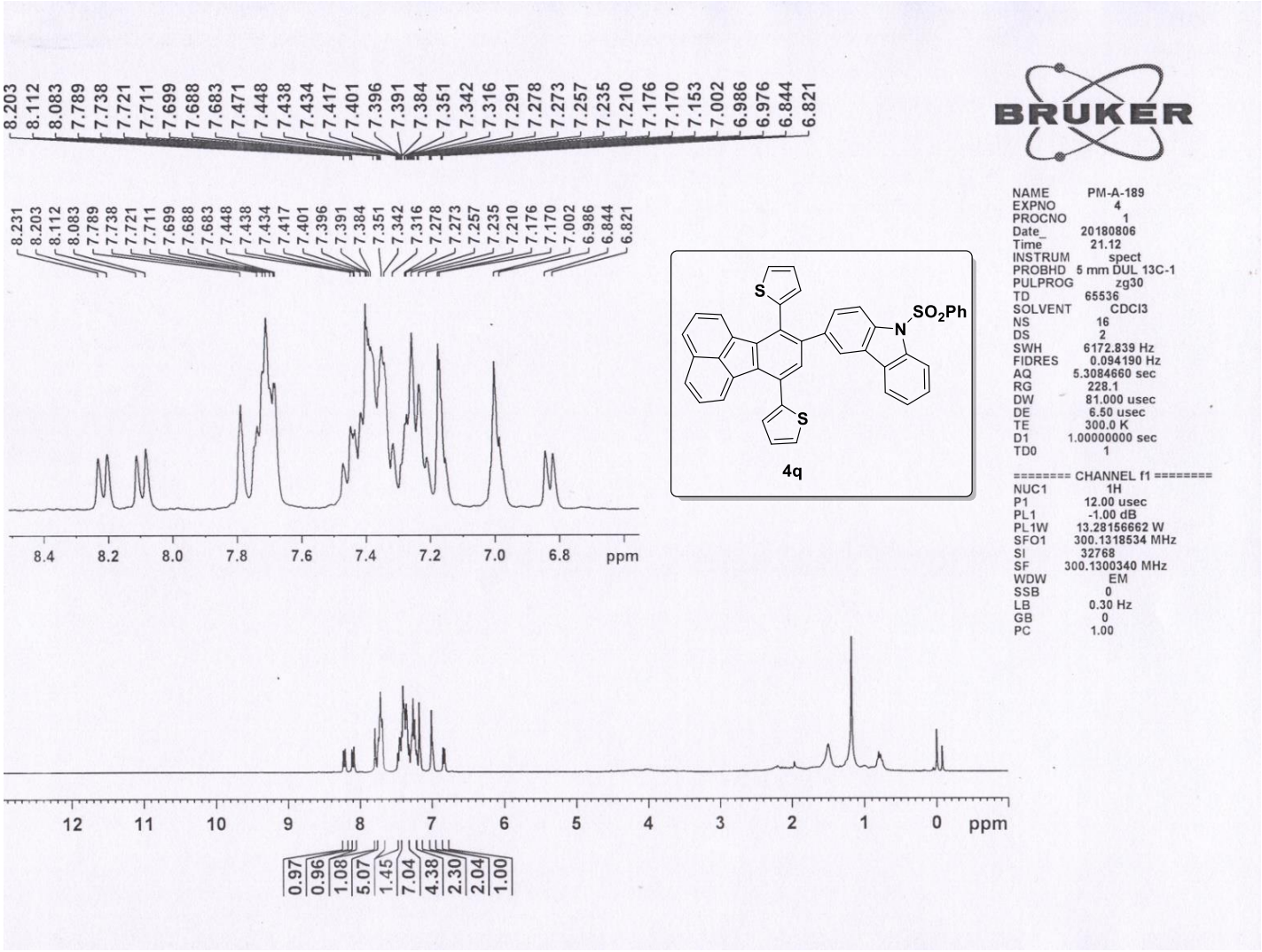
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4o**



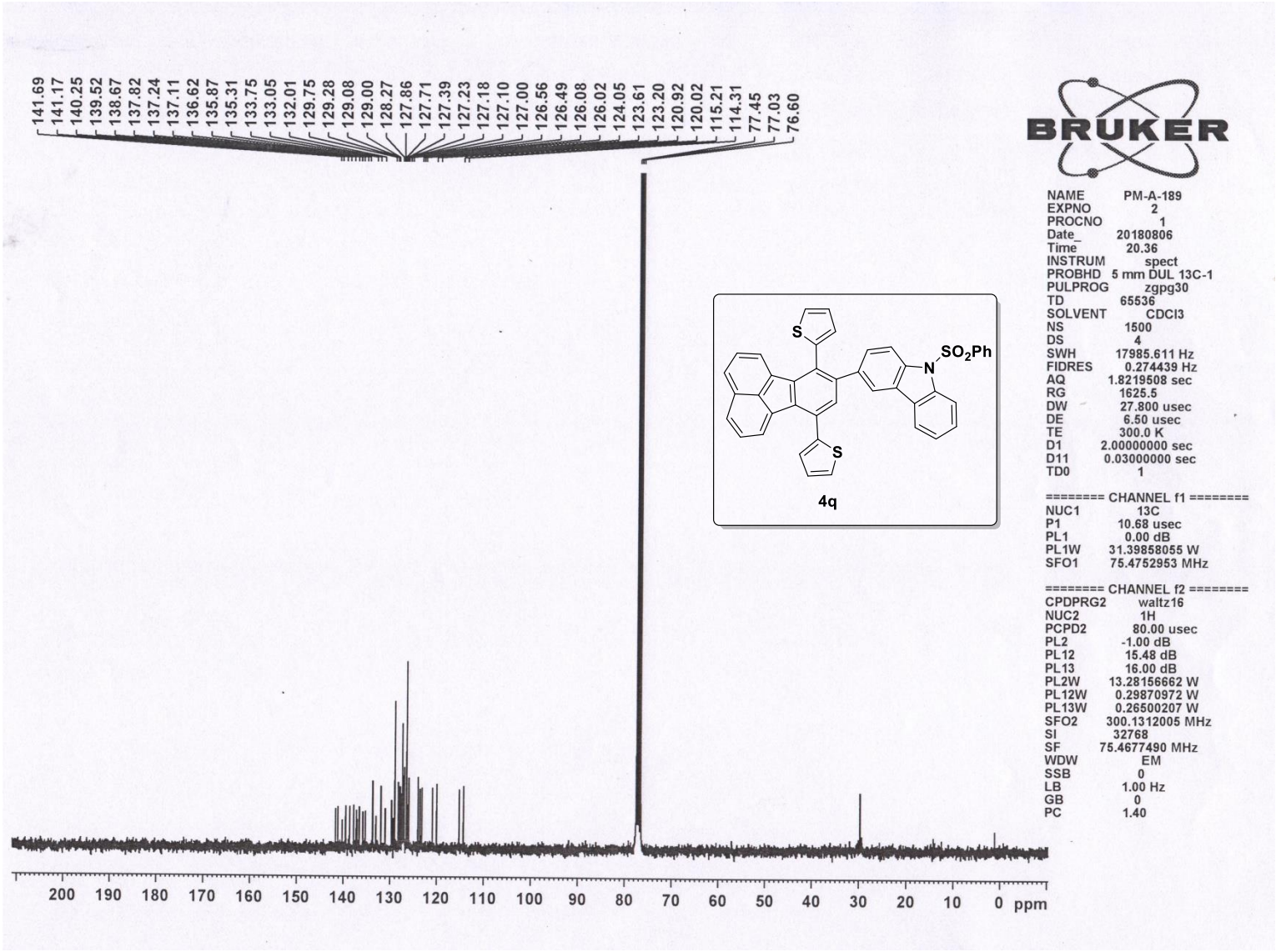
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4p**



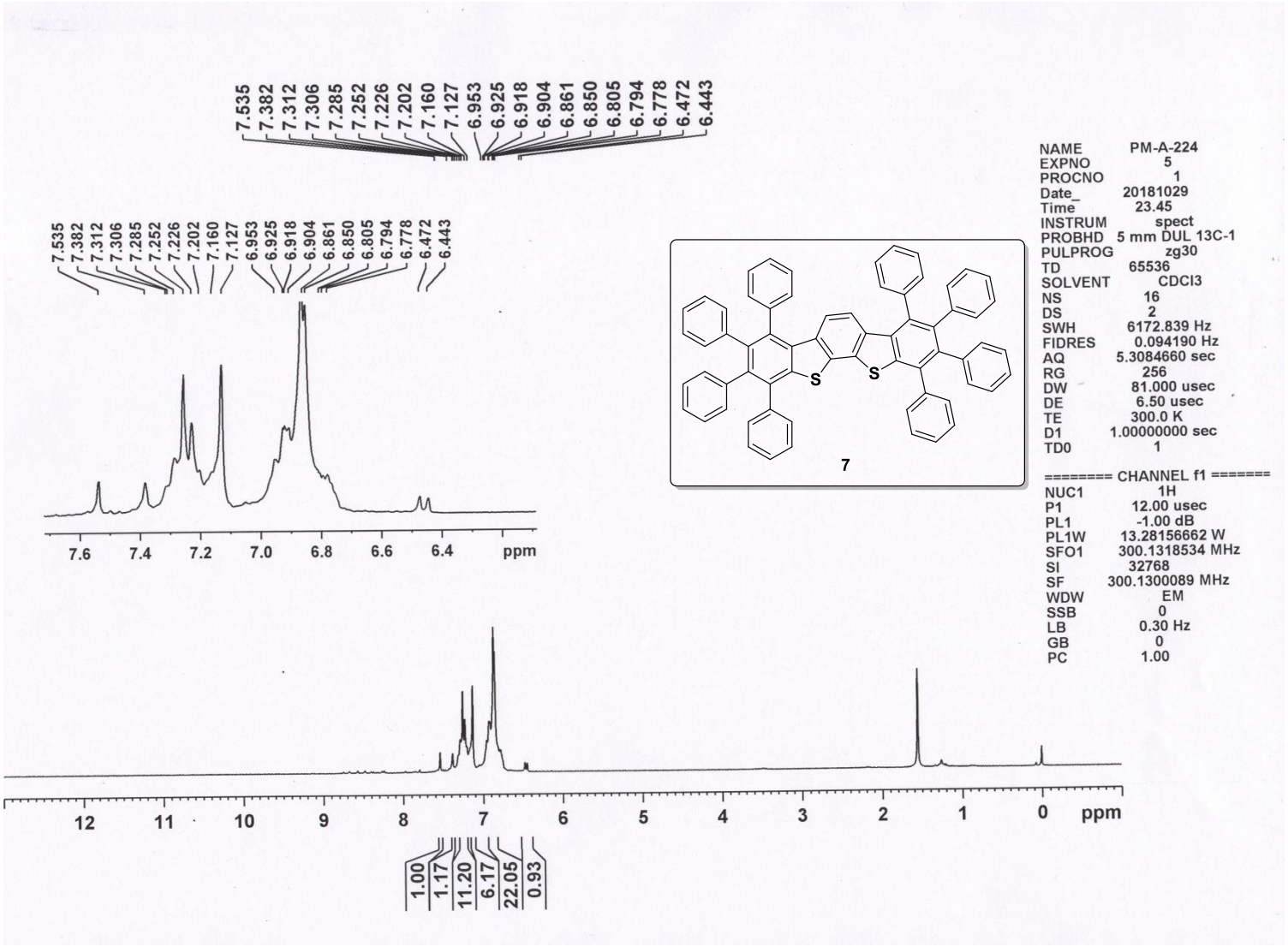
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4p**



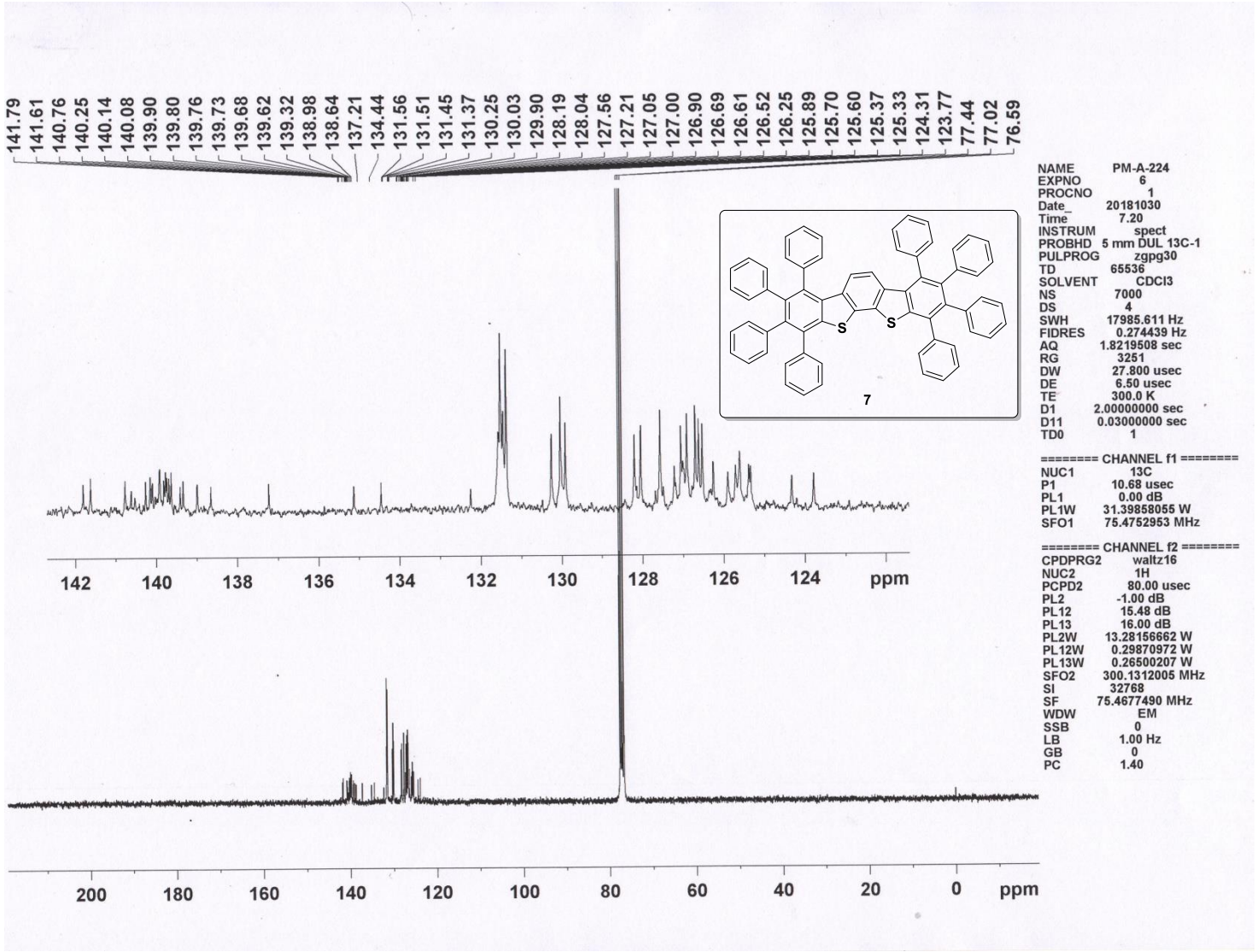
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **4q**



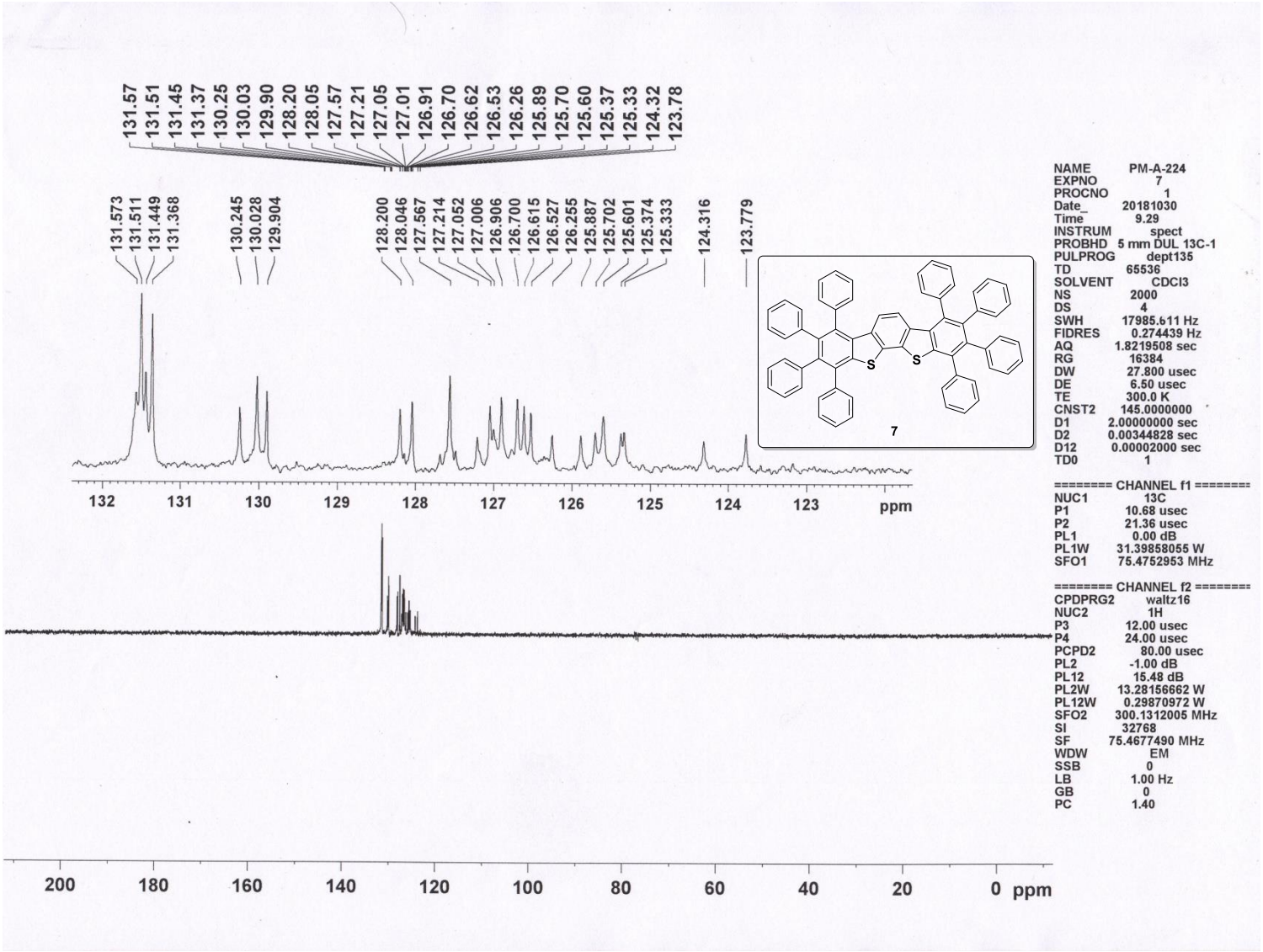
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **4q**



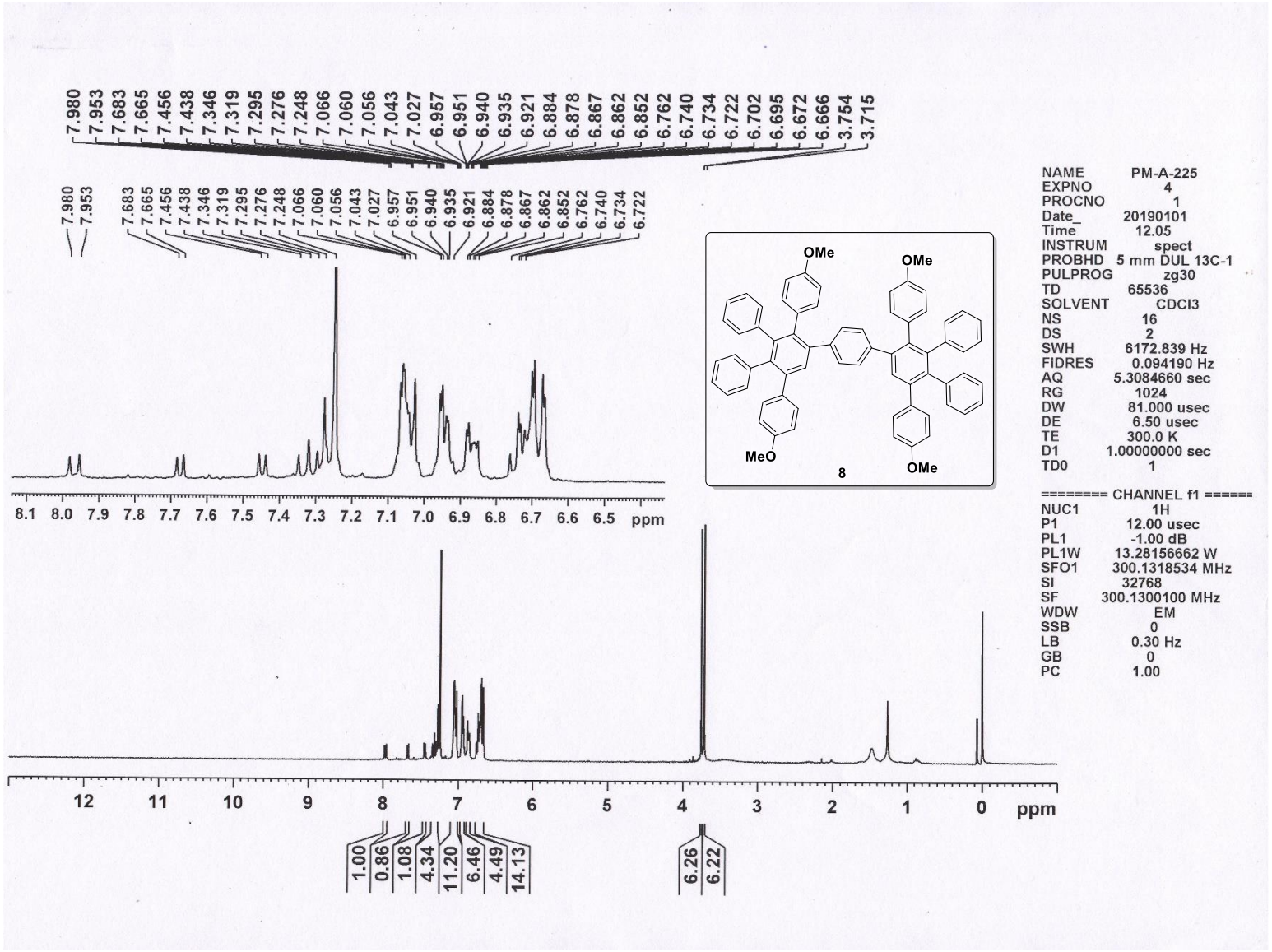
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **7**



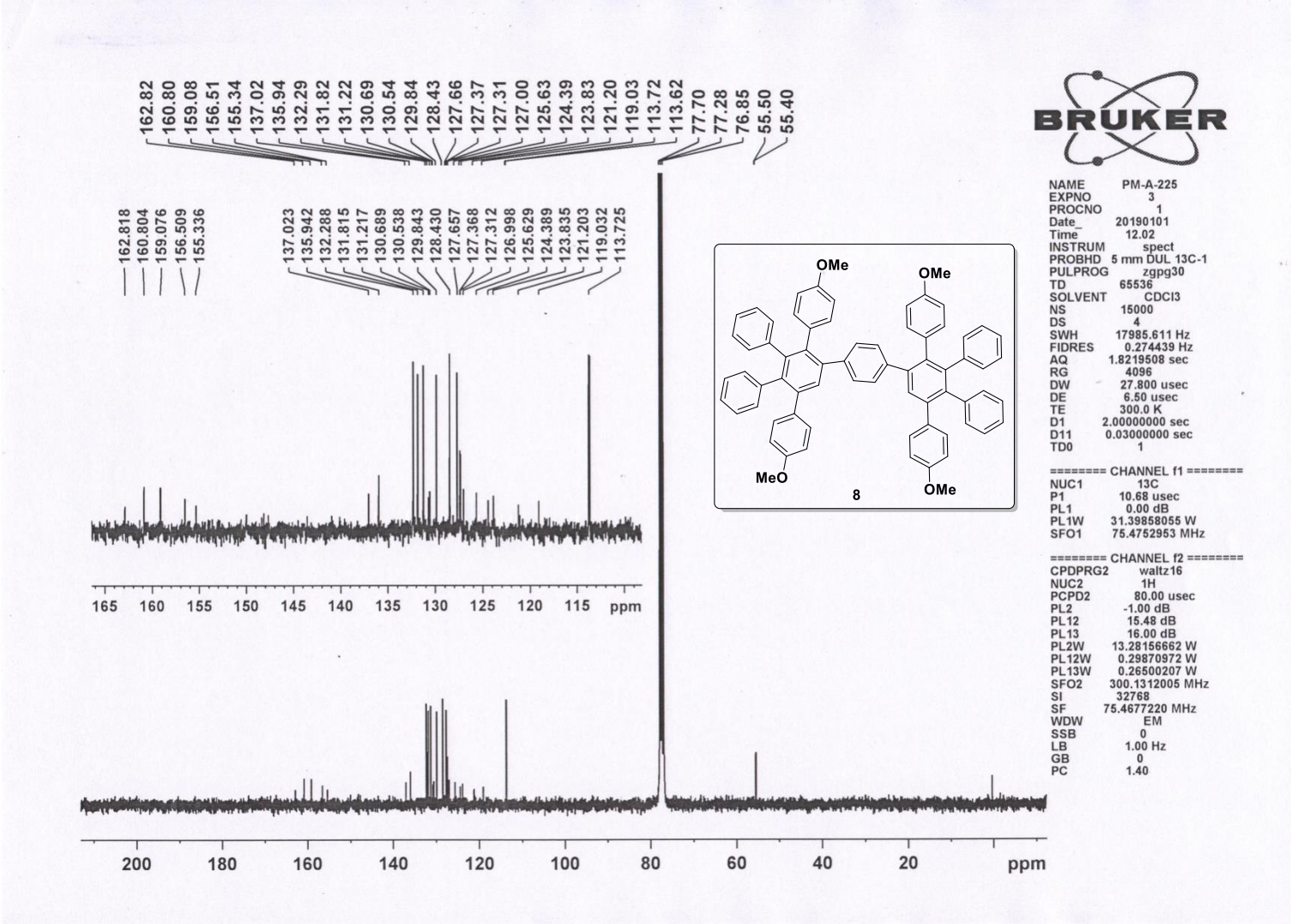
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **7**



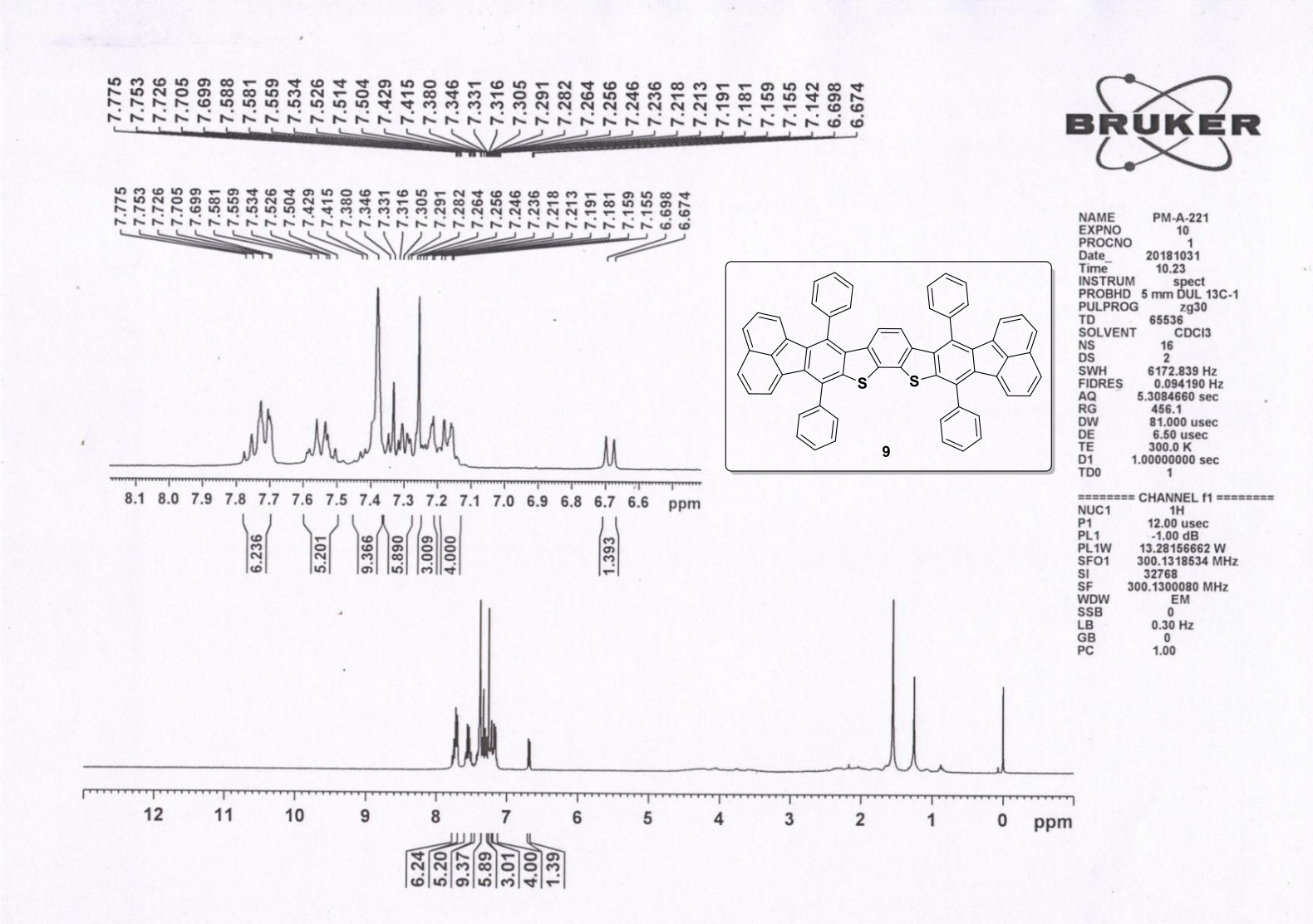
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **7**



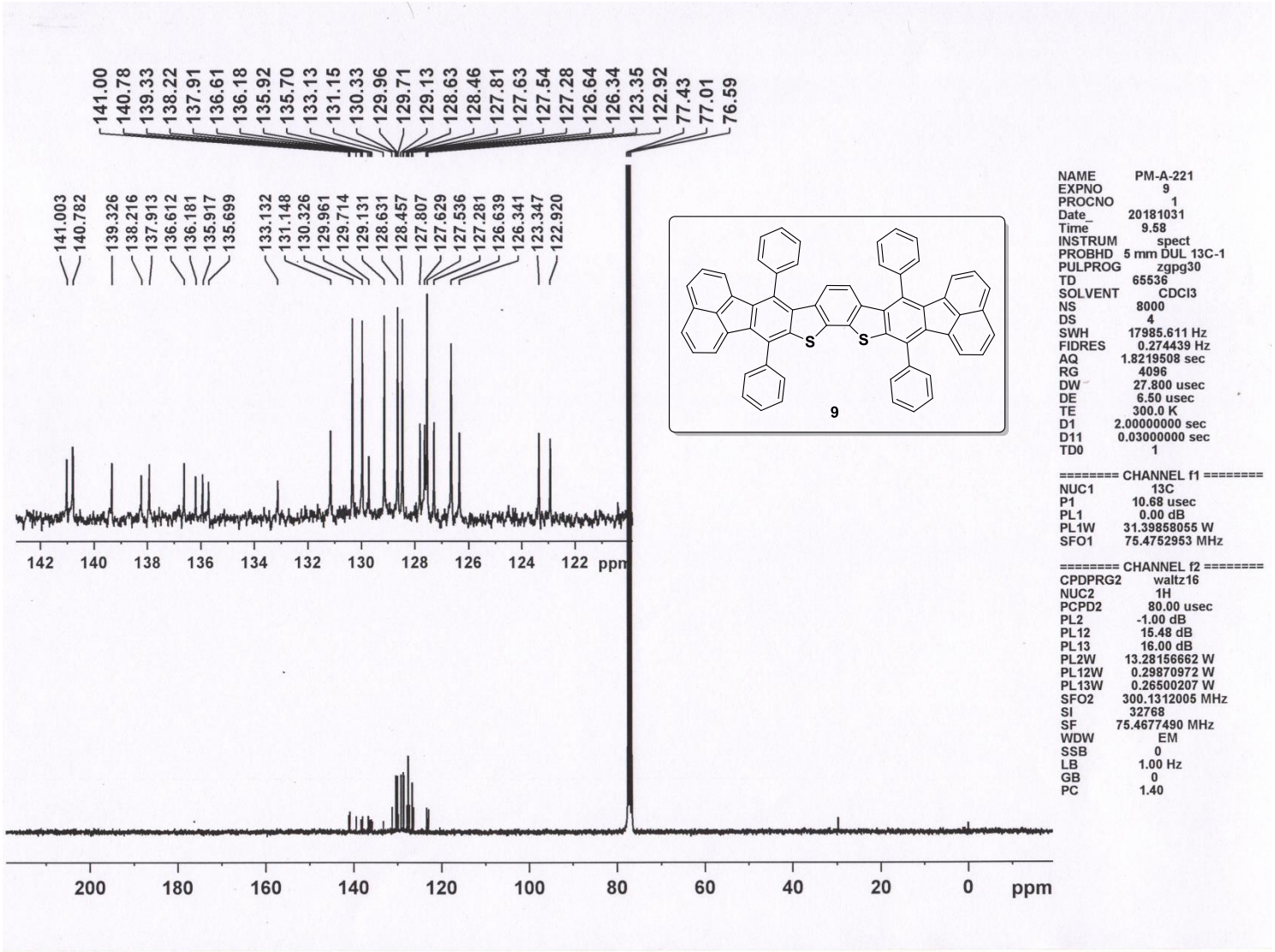
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **8**



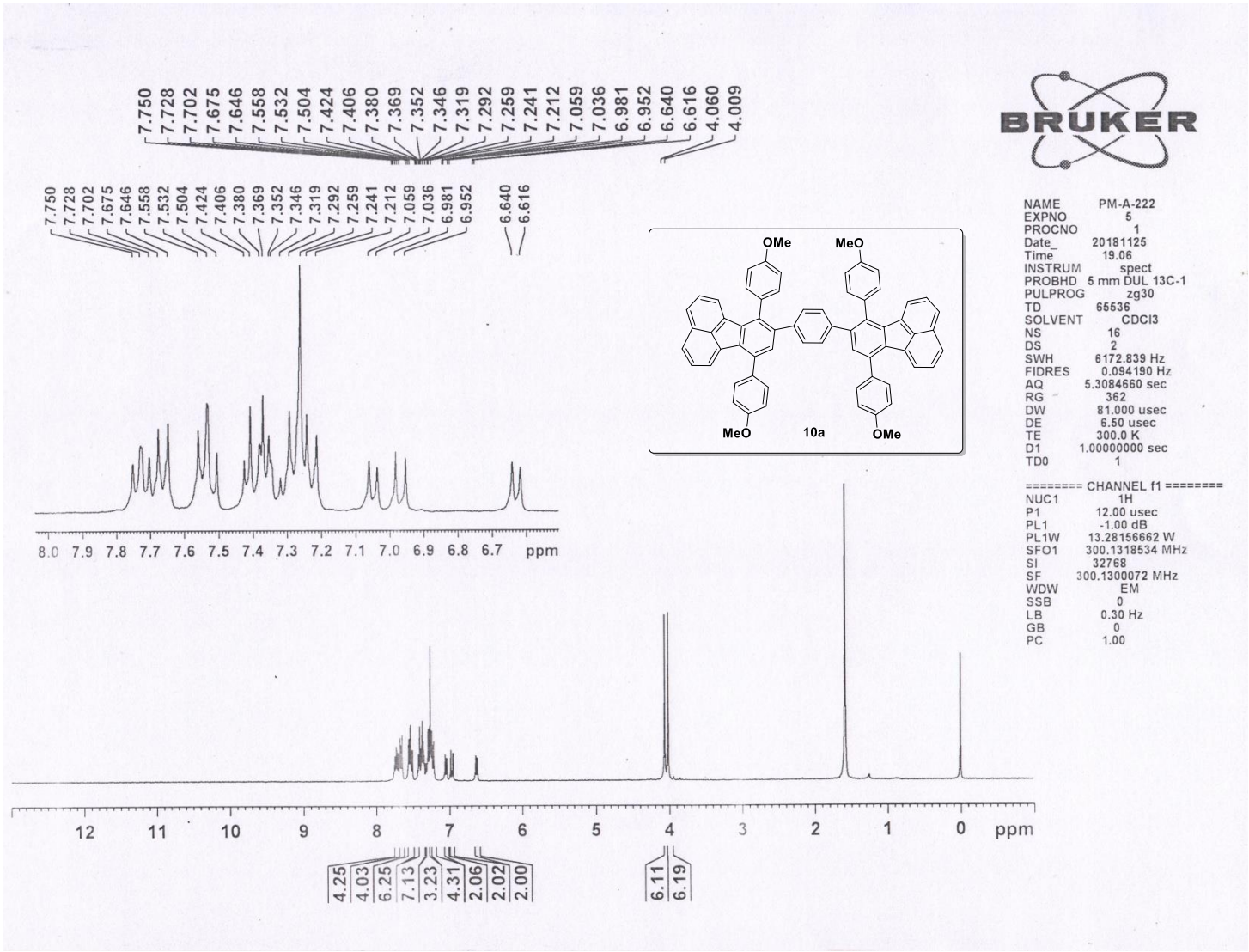
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **8**



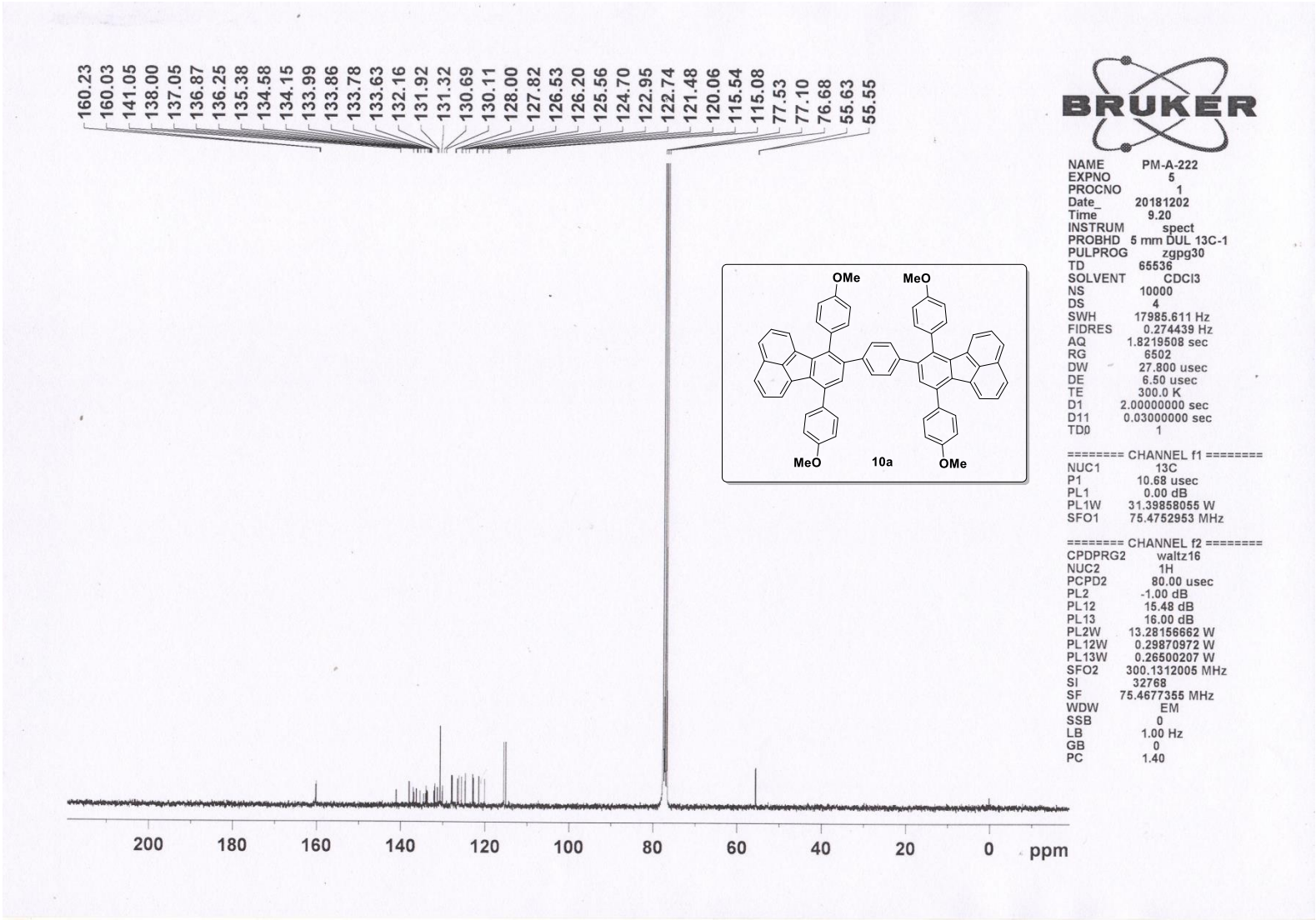
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **9**



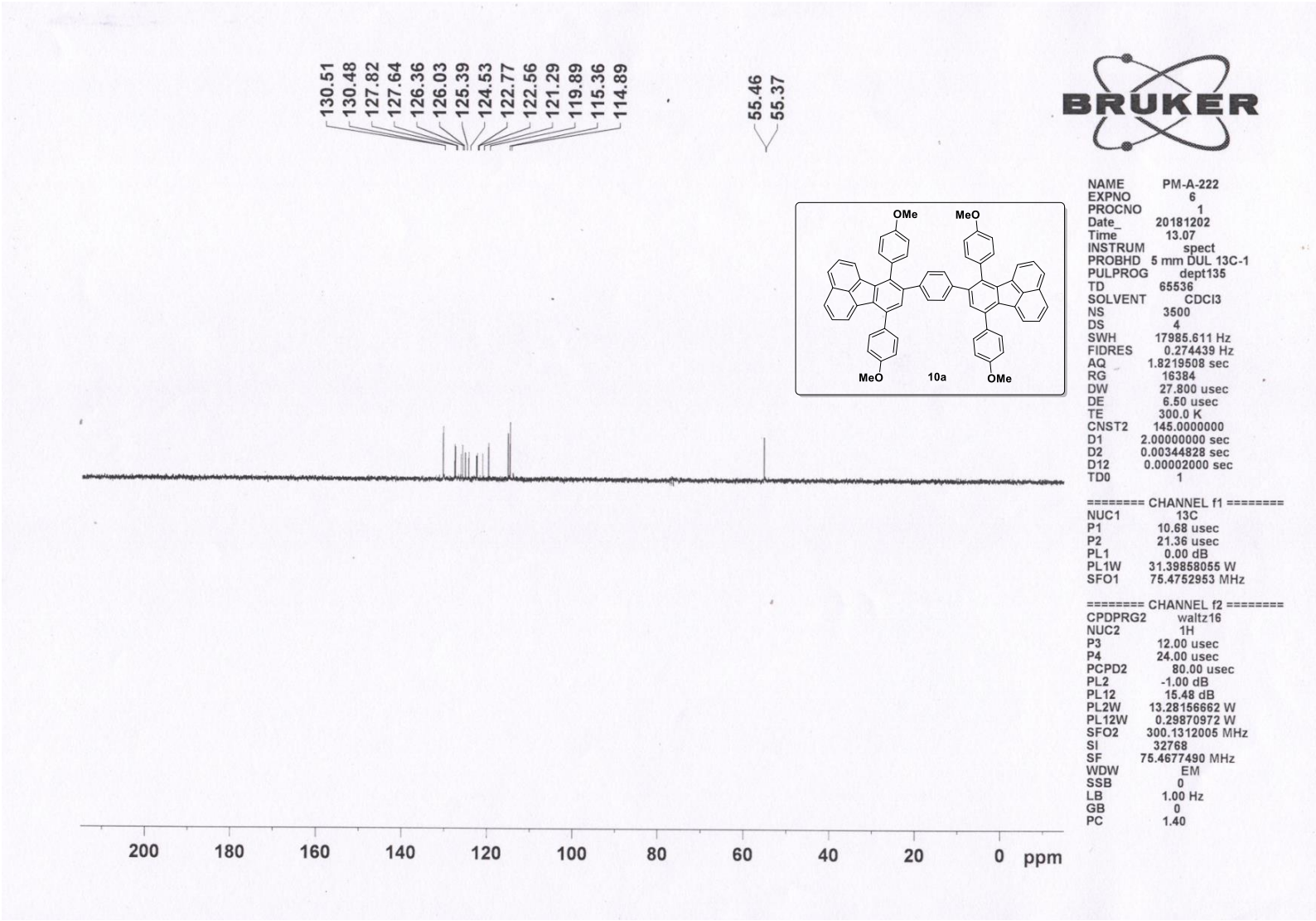
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **9**



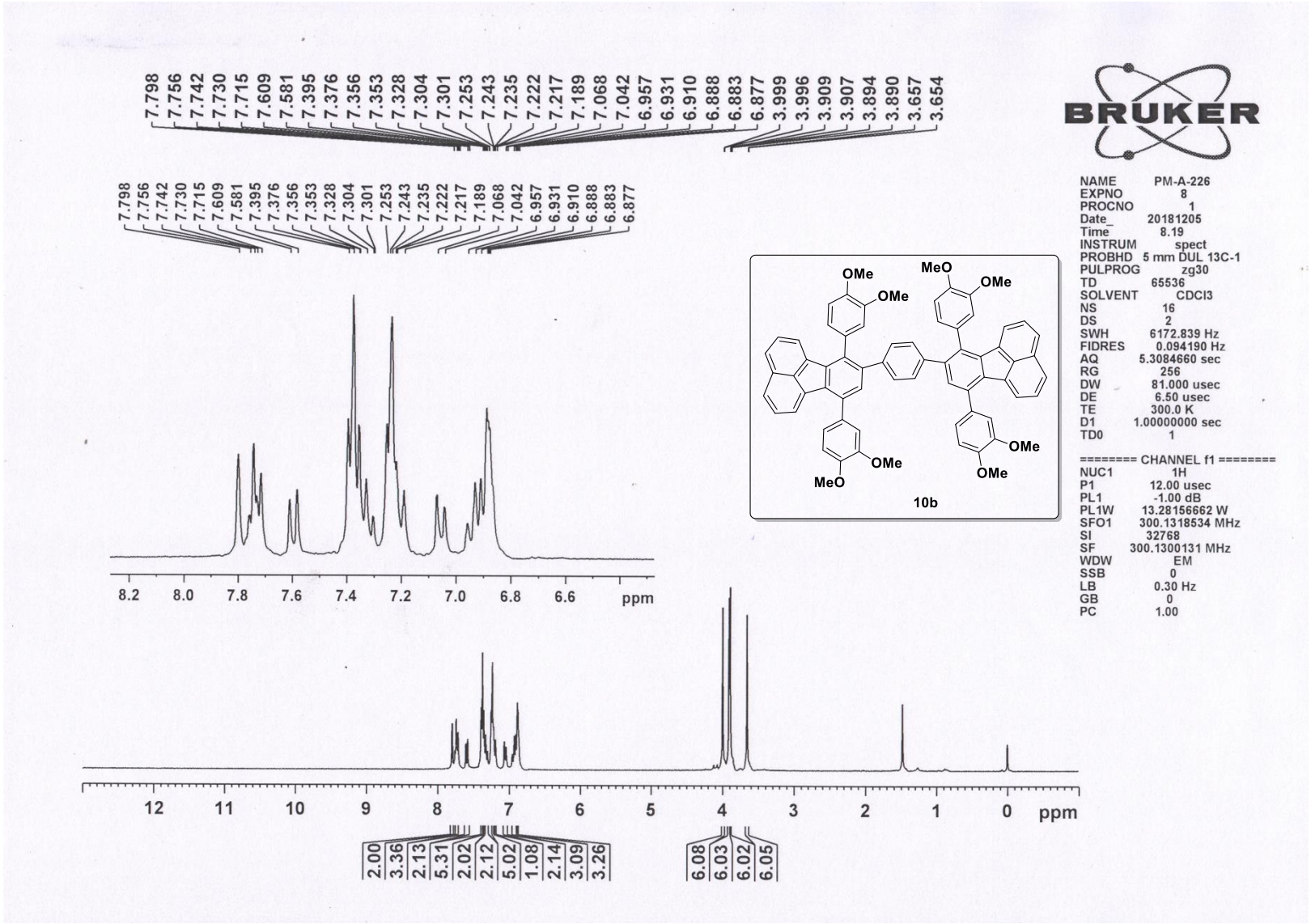
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **10a**



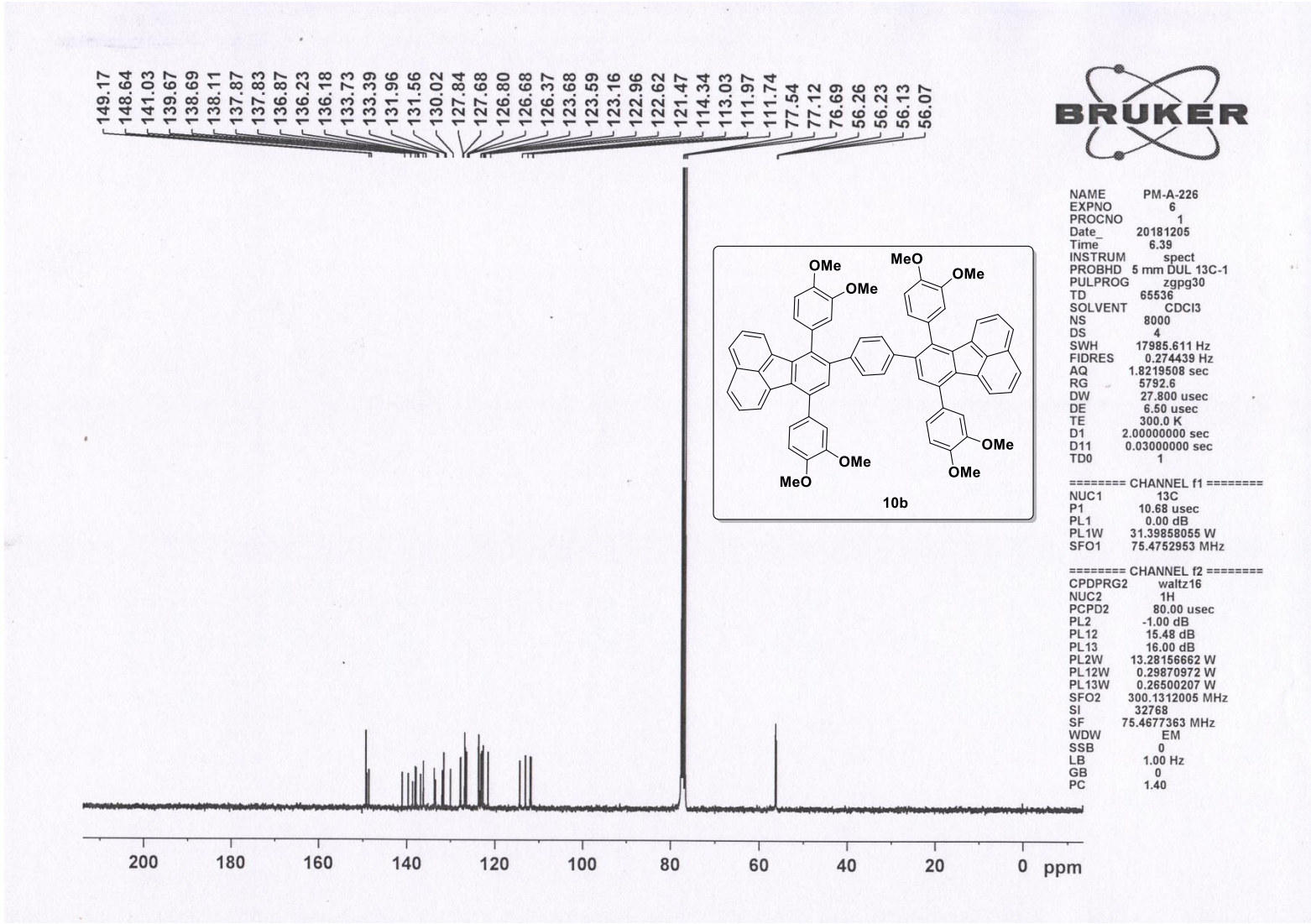
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **10a**



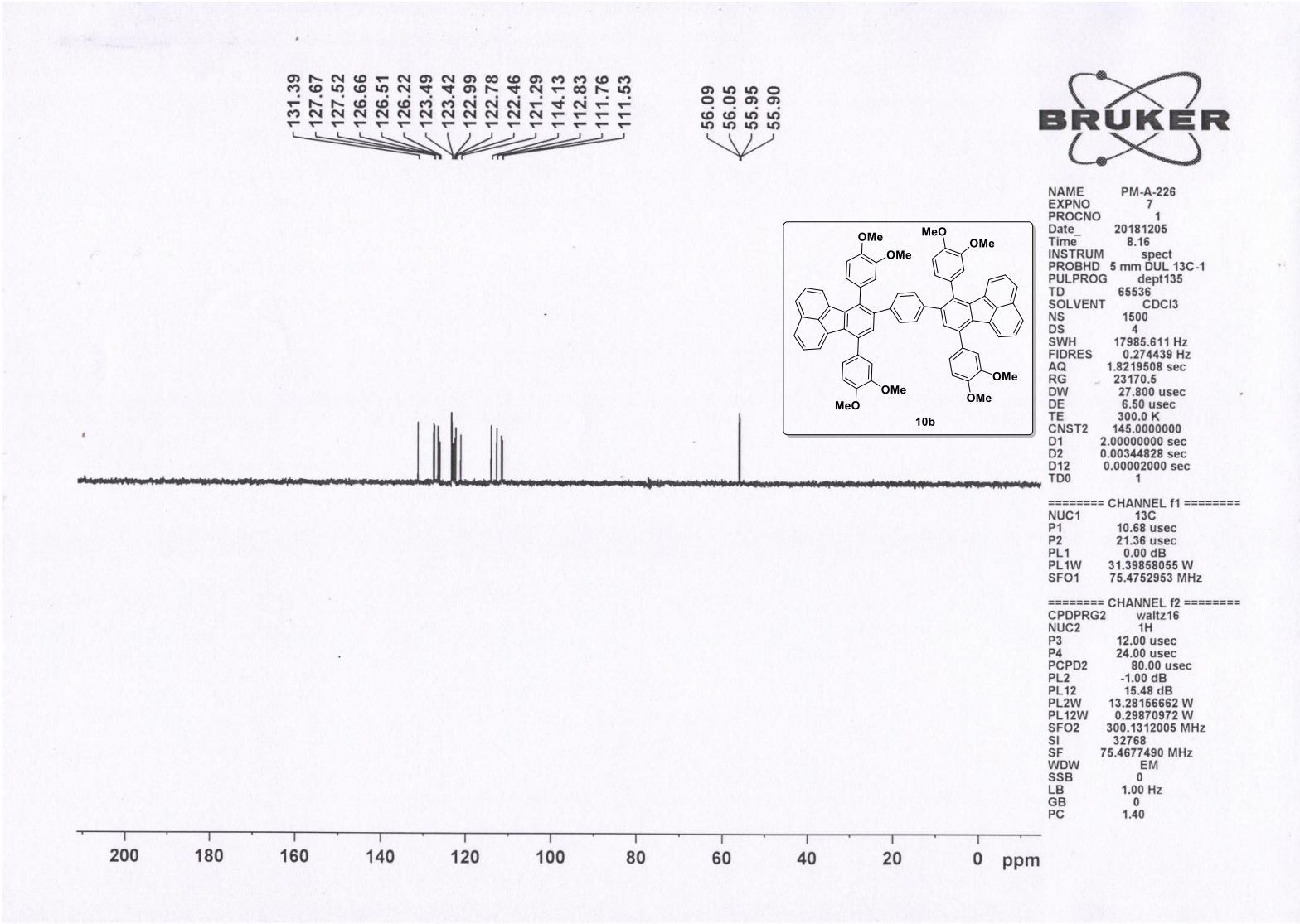
DEPT-135NMR (75 MHz, $CDCl_3$) spectrum of compound **10a**



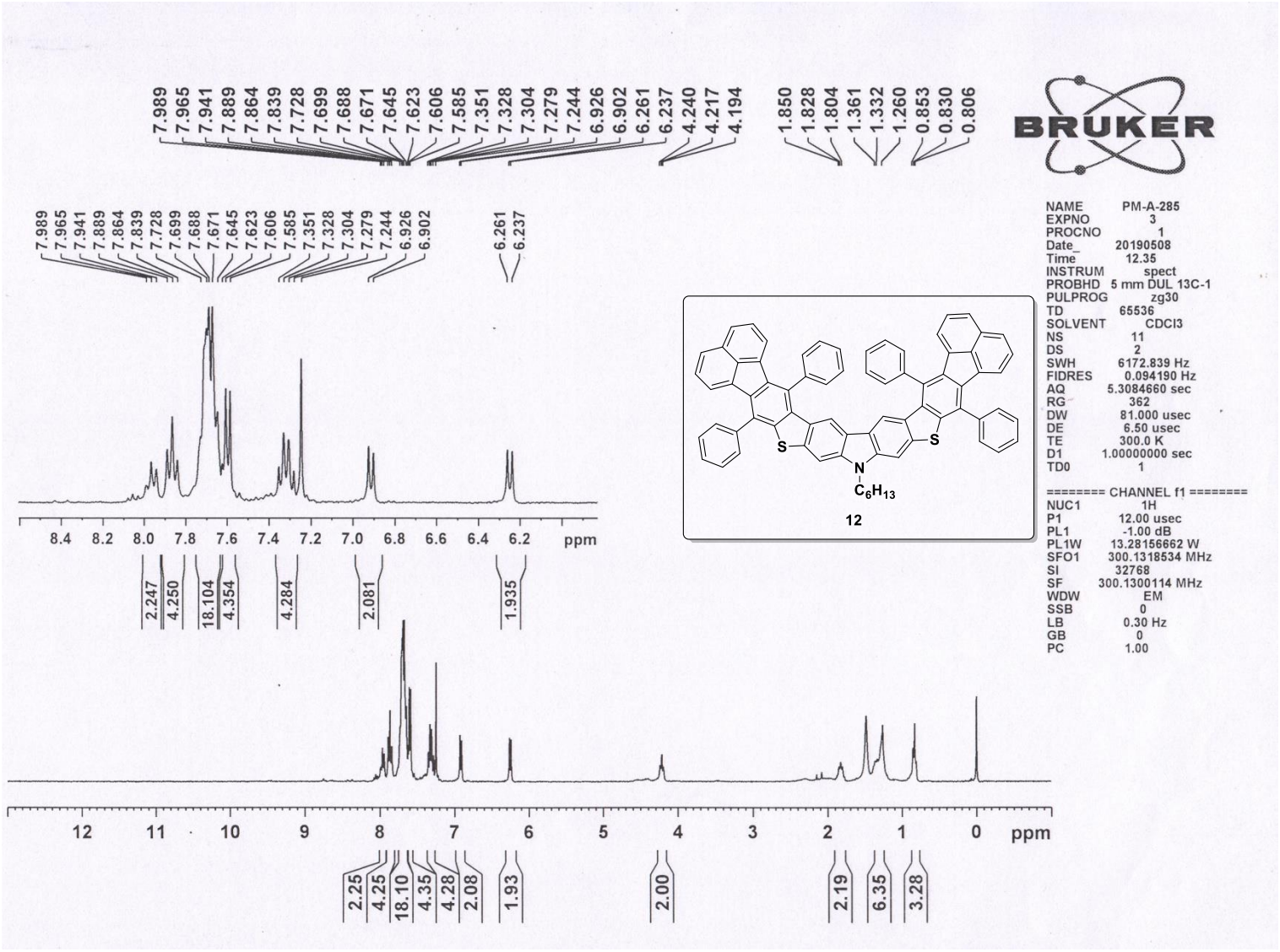
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **10b**



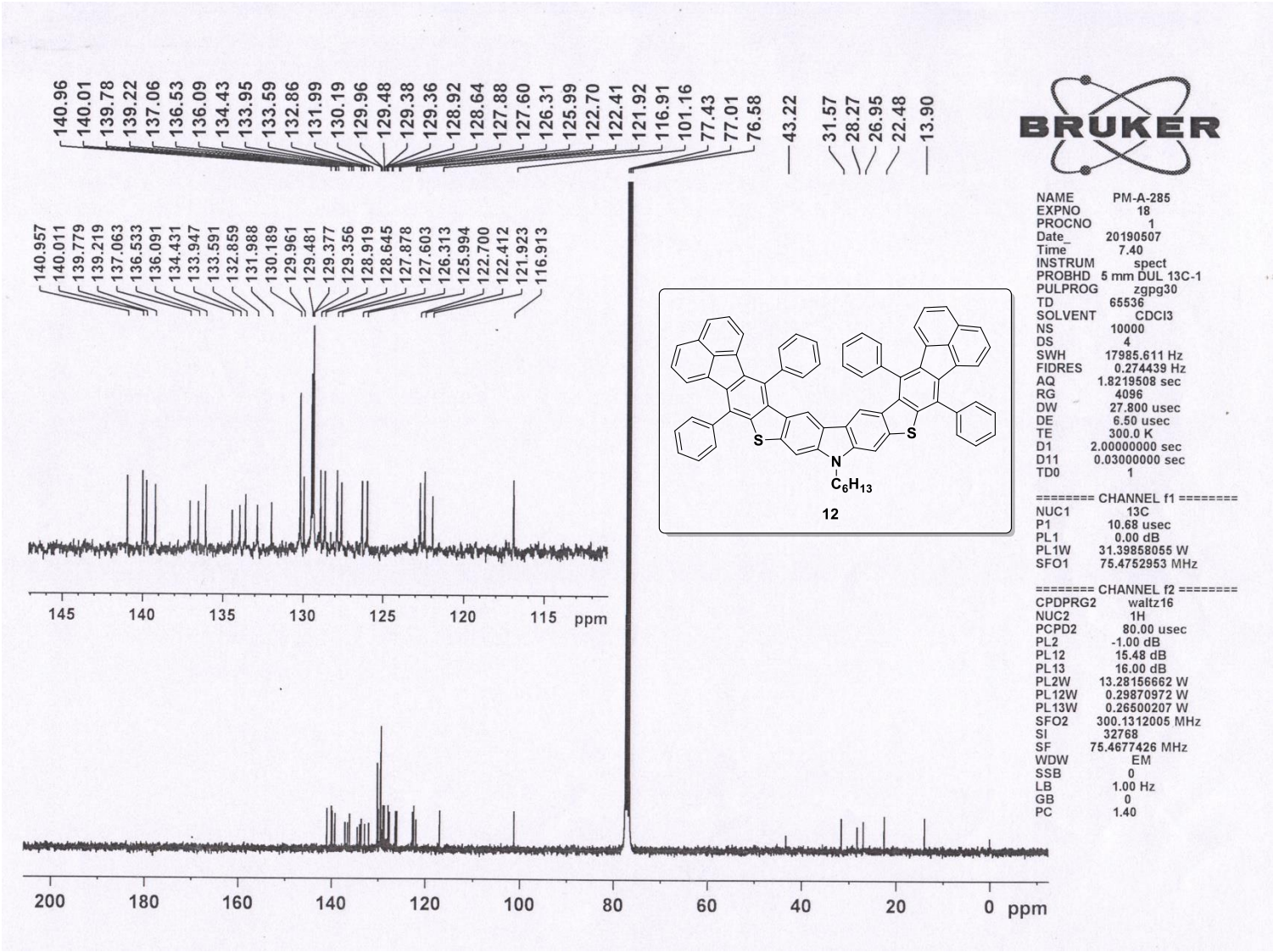
^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **10b**



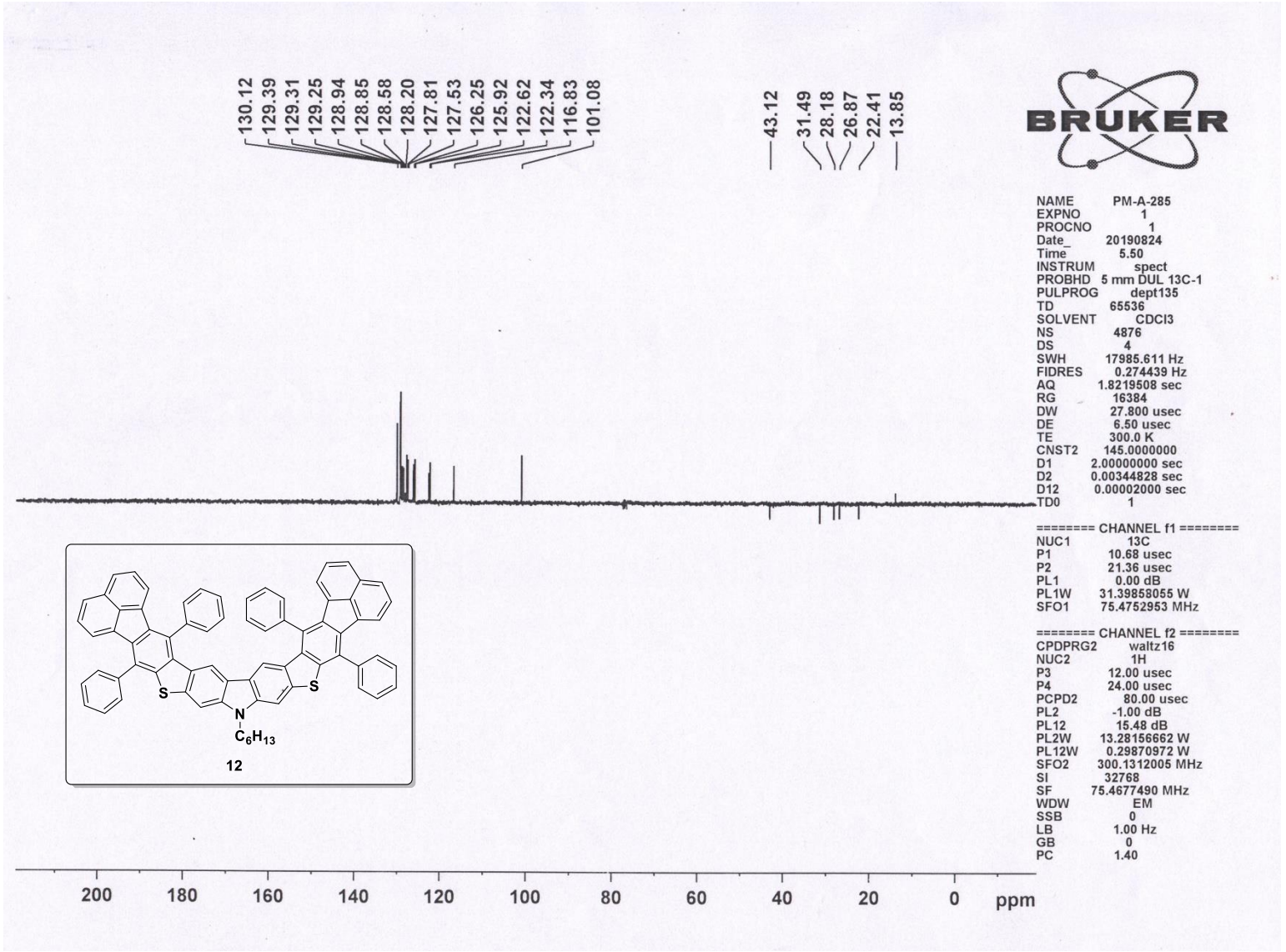
DEPT-135 NMR (75 MHz, $CDCl_3$) spectrum of compound **10b**



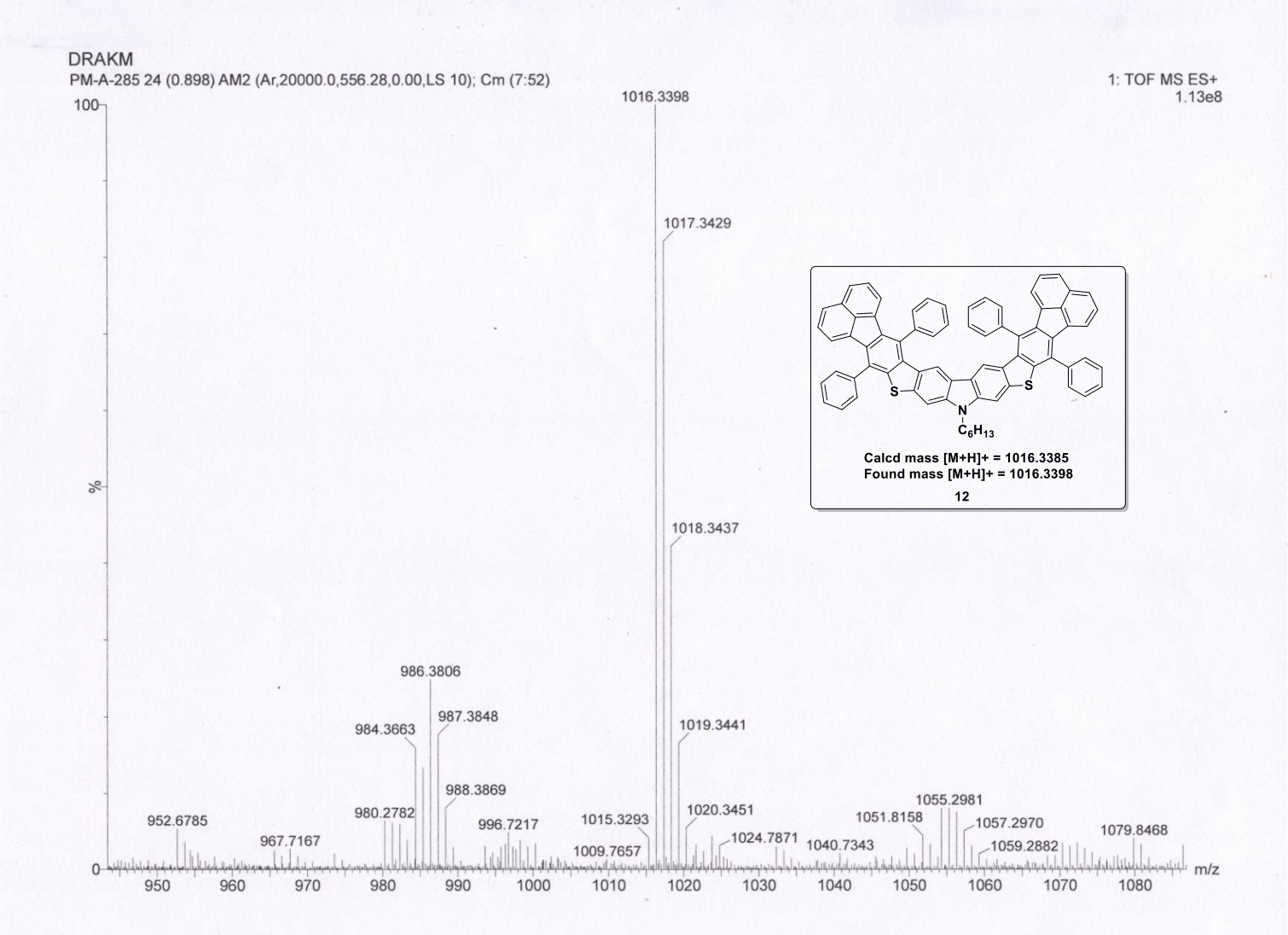
^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of compound **12**



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **12**



DEPT-135 (75 MHz, $CDCl_3$) NMR spectrum of compound **12**

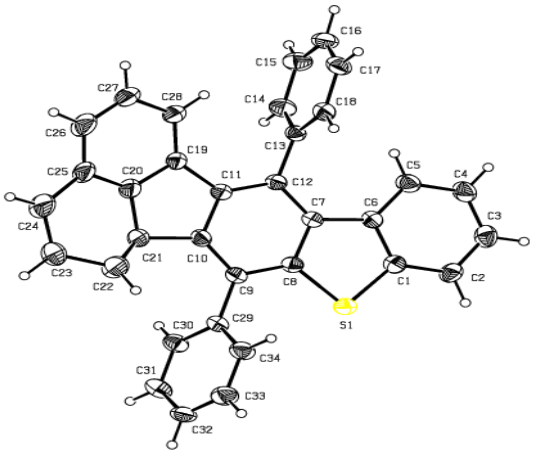


HRMS spectrum of compound **12**

5. X-Ray Structure & Crystallographic data of 3e, 4a and 4c

Crystallographic data of 7,13-diphenylbenzo[*d*]fluorantheno[8,9-*b*]thiophene 3e:

CCDC Number is **1891300**.



Computing Details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2*/*SAINT* (Bruker, 2012); data reduction: *SAINT*/*XPREP* (Bruker, 2012); program(s) used to solve structure: *SHELXS1997* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014*/7 (Sheldrick, 2014).

7,13-Diphenylbenzo[*d*]fluorantheno[8,9-*b*]thiophene 3e

Experimental

Crystal data	
$C_{34}H_{20}S$	$F(000) = 960$
$M_r = 460.56$	$D_x = 1.266$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.7856$ (6) Å	Cell parameters from 26342 reflections
$b = 24.1392$ (14) Å	$\theta = 2.4$–$22.5°$
$c = 9.3144$ (6) Å	$\mu = 0.16$ mm^{-1}
$\beta = 94.959$ (2)°	$T = 293$ K
$V = 2416.0$ (2) Å^3	BLOCK, colorless
$Z = 4$	0.25 × 0.20 × 0.15 mm
Data collection	

Bruker Kappa APEXII CCD diffractometer	2838 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.050$
ω and φ scan	$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan *SADABS2012*/1	$h = -13 \rightarrow 13$
$T_{min} = 0.888$, $T_{max} = 0.945$	$k = -29 \rightarrow 29$
25863 measured reflections	$l = -11 \rightarrow 10$
4727 independent reflections	

Refinement

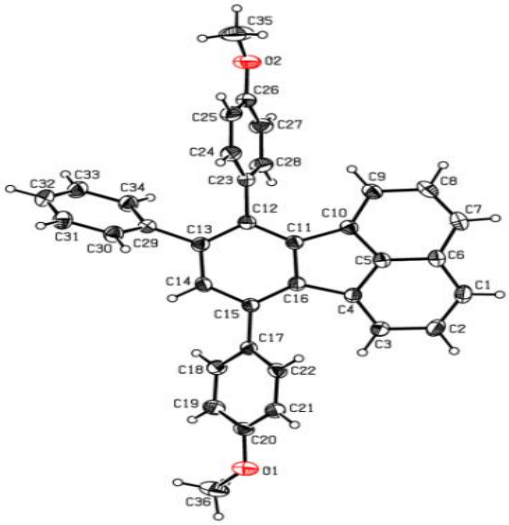
Refinement on F^2	6 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.201$	$w = 1/[\sigma^2(F_o^2) + (0.0971P)^2 + 1.4204P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
4727 reflections	$\Delta\rho_{max} = 0.79$ e Å^{-3}
316 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Crystallographic data of 7,10-bis(4-methoxyphenyl)-8-phenylfluoranthene 4a:

CCDC Number is **1960428.**



Computing Details

Data collection: SHELXS97 (Sheldrick, 1990), SHELXL97 (Sheldrick, 1997).

7,10-Bis(4-methoxyphenyl)-8-phenylfluoranthene 4a

Experimental

Crystal data

$C_{36}H_{26}O_2$	Z = 2
M_r = 490.57	F(000) = 516
Triclinic, P1	D_x = 1.251 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.4170 (3) Å	Cell parameters from 5383 reflections
b = 11.3442 (4) Å	θ = 2.0–26.5°
c = 12.5770 (4) Å	μ = 0.08 mm^{-1}
α = 108.867 (2)°	T = 296 K
β = 105.293 (3)°	Block, colourless
γ = 99.814 (4)°	0.35 × 0.30 × 0.25 mm
V = 1302.26 (7) Å^3	

Data collection

Bruker Kappa ApexII CCD diffractometer	5383 independent reflections
Radiation source: fine-focus sealed tube	3166 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.041$
ω & φ scans	$\theta_{max} = 26.5°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan *SADABS* (Bruker, 2008)	$h = -13 \rightarrow 12$
$T_{min} = 0.974$, $T_{max} = 0.981$	$k = -14 \rightarrow 14$
26328 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.143$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.1956P]$ where $P = (F_o^2 + 2F_c^2)/3$
5383 reflections	$(\Delta/\sigma)_{max} < 0.001$
345 parameters	$\Delta\rho_{max} = 0.17$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}

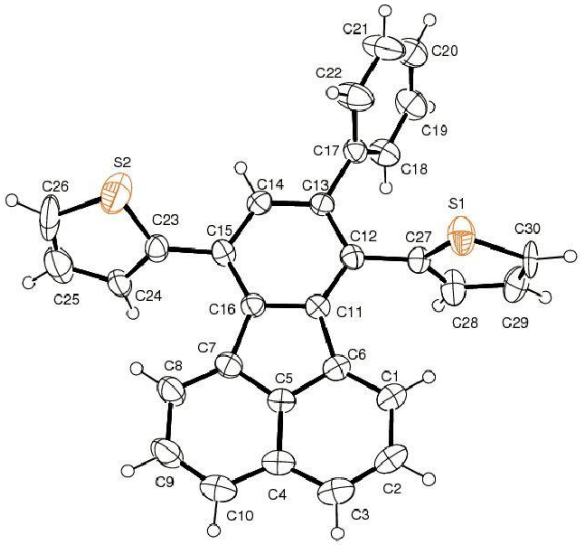
Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Crystallographic data of 2,2'-(8-phenylfluorathene-7,10-diyl)dithiophene 4c:

CCDC Number is **1891974.**



Computing Details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*/*SAINT* (Bruker, 2004); data reduction: *SAINT*/*XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXT2014*/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL2014*/7 (Sheldrick, 2014).

2,2'-(8-Phenylfluorathene-7,10-diyl)dithiophene 4c

Experimental

Crystal data

$C_{30}H_{18}S_2$	$F(000) = 920$
$M_r = 442.56$	$D_x = 1.330$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.7855$ (11) Å	Cell parameters from 4488 reflections
$b = 9.5702$ (7) Å	$\theta = 2.5–21.8°$
$c = 19.7443$ (17) Å	$\mu = 0.26$ mm^{-1}
$\beta = 96.996$ (4)°	$T = 296$ K

V = 2210.4 (3) Å^3	Block, colourless
Z = 4	0.15 × 0.15 × 0.10 mm

Data collection

Bruker axs kappa apex2 CCD Diffractometer	3883 independent reflections
Radiation source: fine-focus sealed tube	2074 reflections with $I > 2\sigma(I)$
Graphite monochromator	R_{int} = 0.076
ω and φ scan	θ_{max} = 25.0°, θ_{min} = 2.1°
Absorption correction: multi-scan *SADABS* (Bruker, 2004)	h = −14→14
T_{min} = 0.696, T_{max} = 0.745	k = −11→11
28725 measured reflections	l = −23→23

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.102P)^2 + 0.2976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.194	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.03	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
3883 reflections	$\Delta\rho_{min}$ = −0.37 e Å^{-3}
327 parameters	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
131 restraints	Extinction coefficient: 0.0031 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

6. Computational studies

To gain insights into relative stabilities of the different radical species proposed in plausible mechanisms for deoxygenation and sulfur dioxide extrusion, DFT calculations were performed on radical species **II** and **III**. It is clearly evident from the **Figure S1**, radical **III** is more stable radical structure than **II** (total electronic energies of **III** is lower than **II** in both gas and solvent phase) and radical **II** was found to be ~30 kcal/mol (both gas and solvent phase) less stable than the radical species **III**, which was attributed to the inability of radical delocalization in **II** when compared to **III**. To further understand the plausible mechanisms, the detailed DFT calculations were performed and the results (optimized geometries of transition states and Gibbs free energy profile) are given the in the **Figure S1** and **S2**.

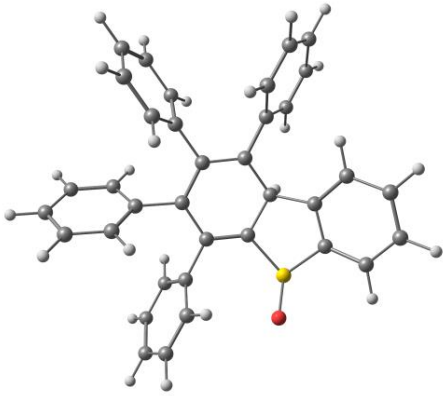
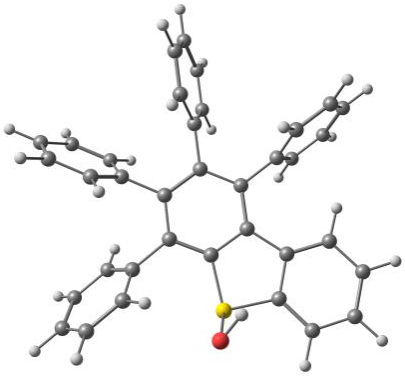
 **II**	 **III**
E= -1860.196925 (gas phase) E=-1860.204035 (solvent phase) RE=0 kcal/mol (gas phase) RE=0 kcal/mol (solvent phase)	E= -1860.244517 (gas phase) E=-1860.250972 (solvent phase) RE=-29.9 kcal/mol (gas phase) RE=-29.5 kcal/mol (solvent phase)

Figure S1: Optimized geometries, electronic energies (in a.u.) and relative energies (RE) of radical species **II** and **III** at the B3LYP/6-31G* level of theory in gas and solvent phase (xylene).

The reaction is initiated with a 1,3-H shift of **5a** leading to the formation of **I** through the transition state, **TS1**, with an activation barrier of 23.20 kcal/mol. At this particular step, elimination of $OH^{\cdot}$

to form **II**. Further reaction from **II** occurs 1,5 H· shift to form **III** through transition state, **TS2**, with an activation barrier of 22.4 kcal/mol. Whereas radical **III** leads to formation of an 3a elimination of OH· an activation barrier of -18.3 kcal/mol confirm this path id thermodynamically feasible path.

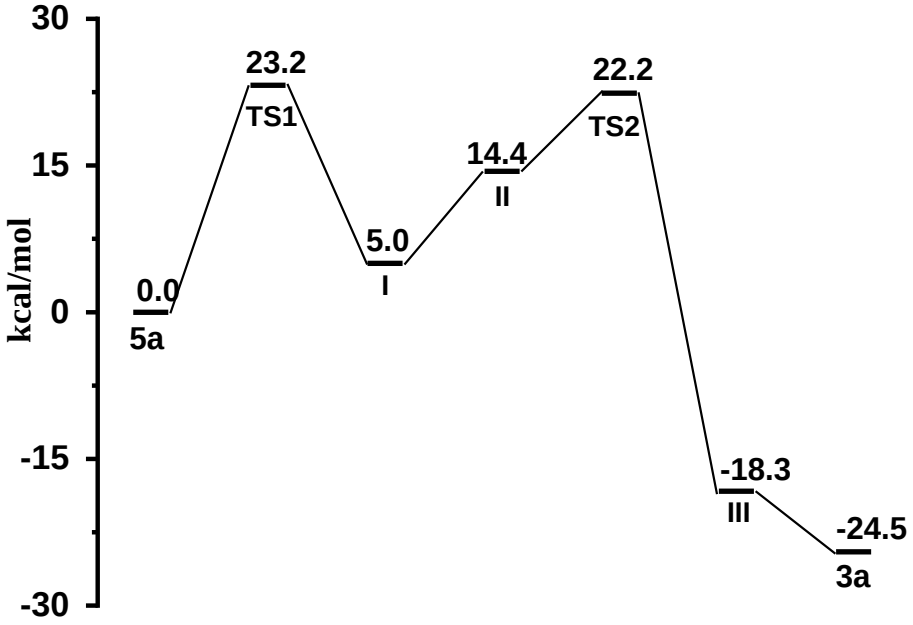
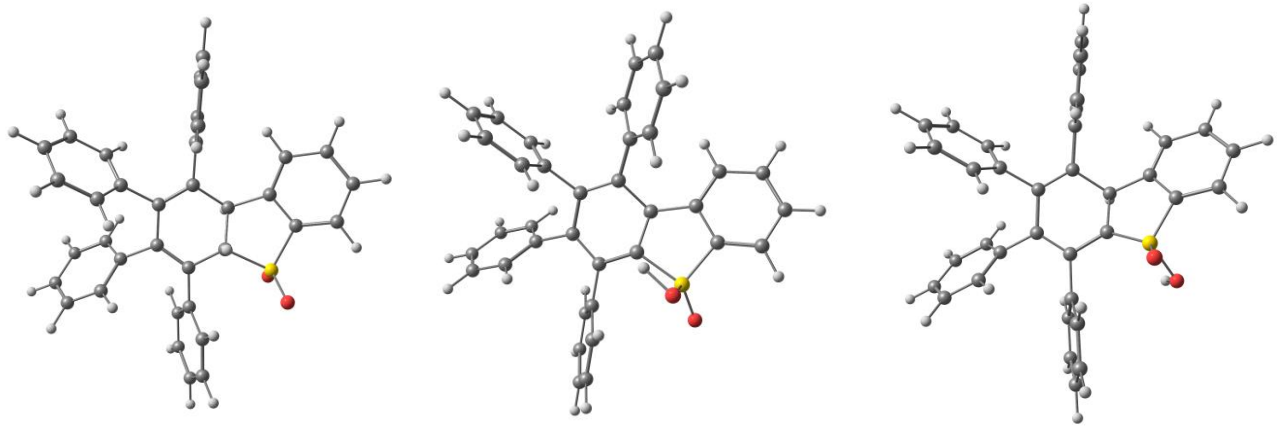


Figure S2: Gibbs free energy profile (kcal/mol) obtained at the B3LYP/6-31G* level of theory in xylene solvent.



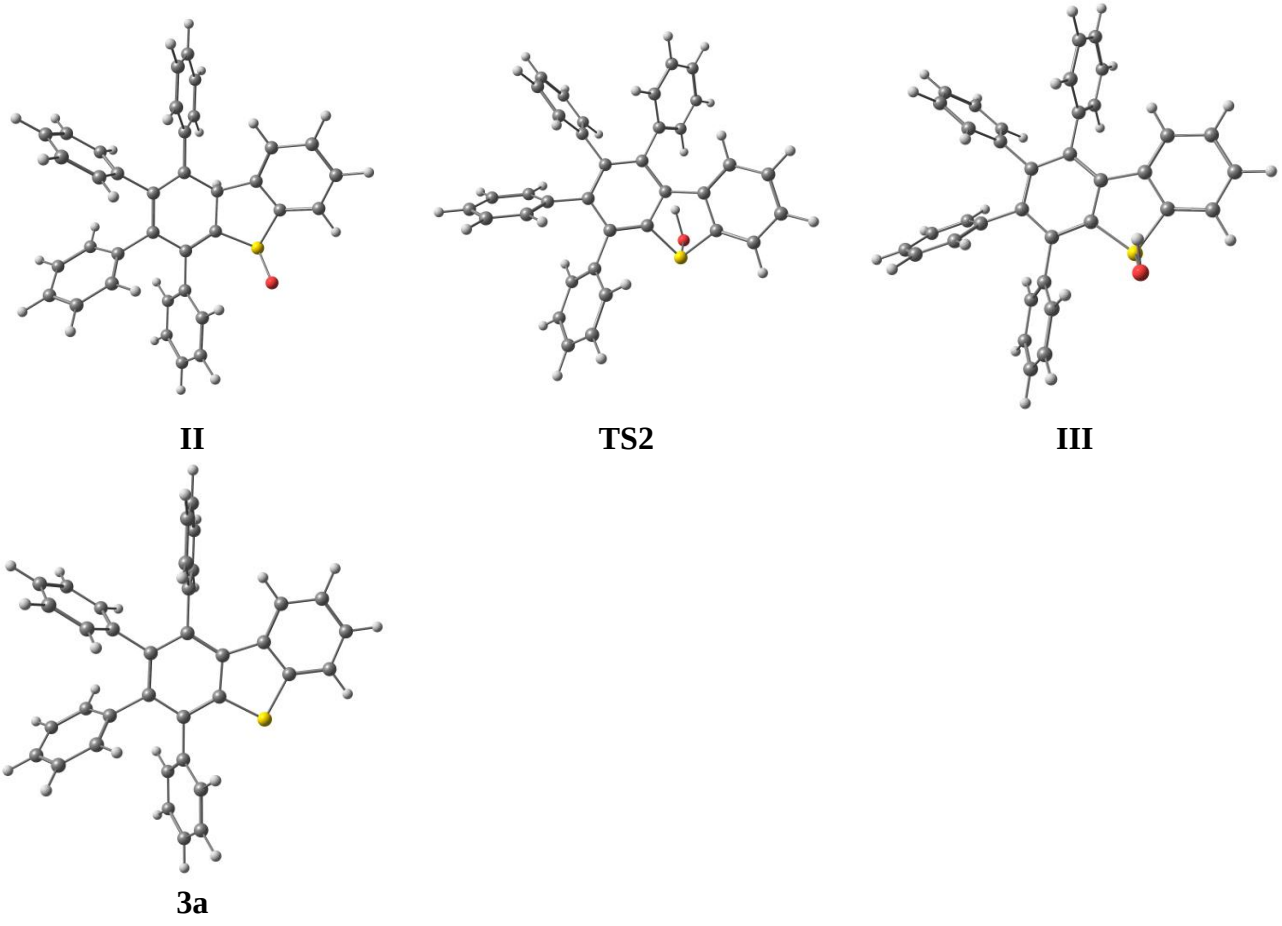


Figure S3: Optimized structure of the substrates, transition states and intermediates.

Computational Details:

In support of experimental study density functional theory (DFT) calculations were carried out using Gaussian 03 program.[1] The ground state geometries of all the studies molecules and intermediates were optimized by DFT at the B3LYP/6-31G* level of theory.[2,3] All the optimized structures were characterized by a frequency analysis and were shown to be all positive frequencies. All the transition states (TSs) structures were optimized at the same level of theory and presence of one imaginary frequency criteria was used for the characterization of TSs. Furthermore, the intrinsic reaction coordinate (IRC)[4,5] calculations were performed to verify whether the TSs were connected with corresponding two minima (reactant and product). Based on gas phase optimized geometries, a single point calculation was performed in xylene using Polarizable Continuum Model (PCM) for solvent correction. The energy profiles of the reaction

pathways are presented as Gibbs free energy changes (ΔG's) involving zero-point vibrational energy and thermal corrections obtained at 298.15 K and 1 atm pressure.

References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03; Gaussian, Inc.: Wallingford, CT, 2004.
2. A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648.
3. B. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
4. Gonzalez, C.; Schlegel, H. B. J. Chem. Phys. 1989, 90, 2154.
5. Gonzalez, C.; Schlegel, H. B. J. Phys. Chem. 1990, 94, 5523.

7. Absorption and Emission spectra of representative compounds 3a, 3a', 3a", 3e, 3f, 3i, 4a, 4c, 4f, 7, 10b &12

UV-vis Spectra of 3a, 3a', 3a", 3e, 3f, 3i, 4a, 4c, 4f, 7, 10b & 12

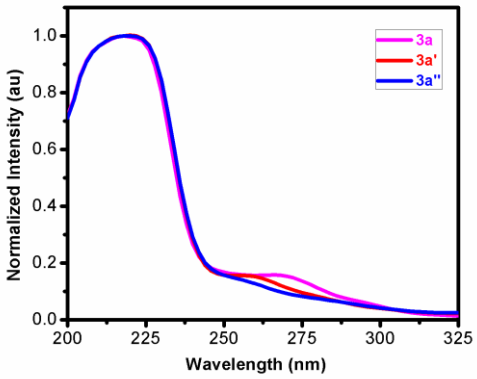


Figure 1a

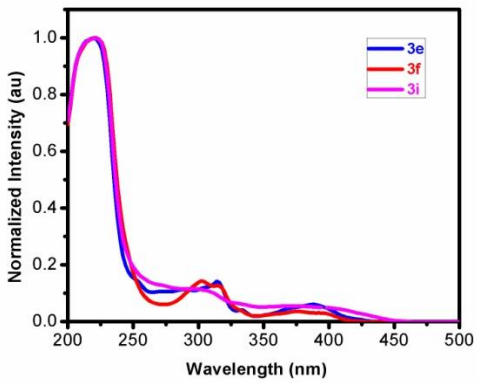


Figure 1b

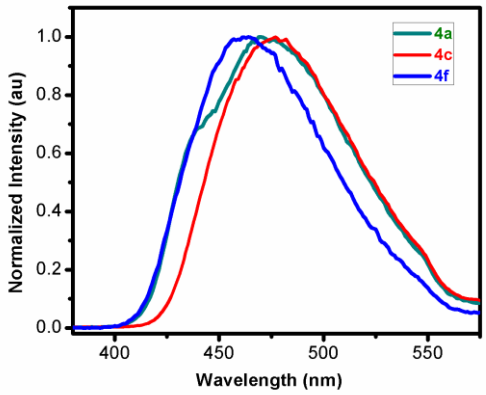


Figure 1c

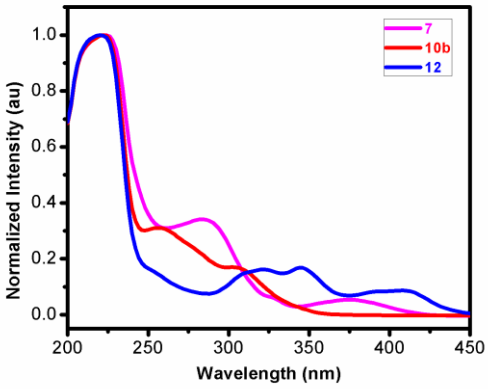


Figure 1d

Fluorescence Spectra of 3a, 3a', 3a'', 3e, 3f, 3i, 4a, 4c, 4f, 7, 10b & 12

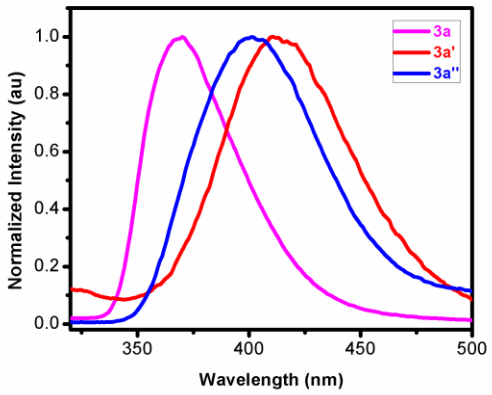


Figure 2a

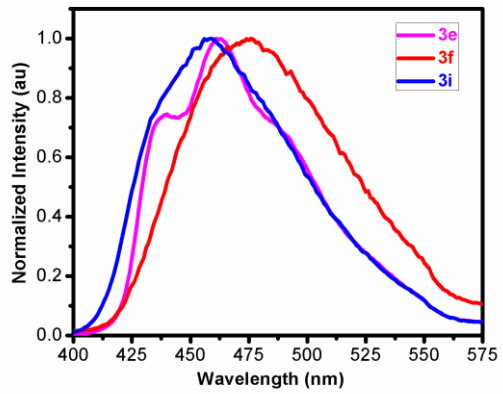


Figure 2b

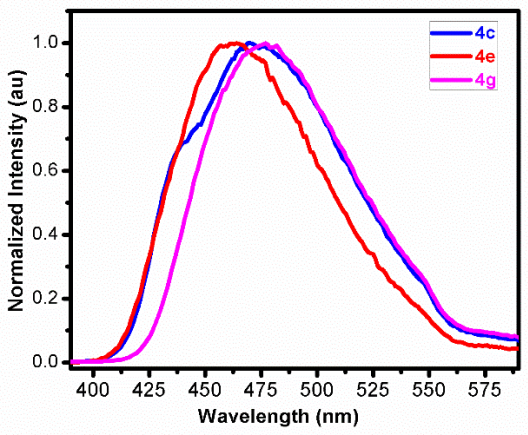


Figure 2c

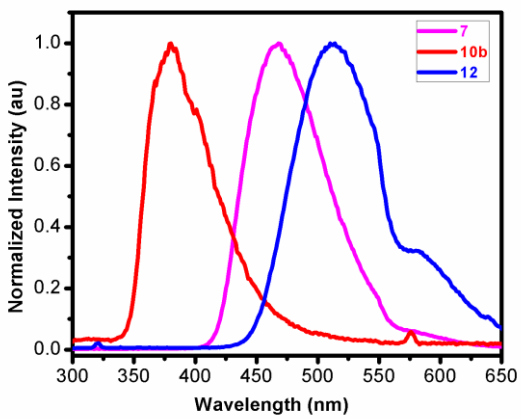


Figure 2d

Table 1: Photophysical data of polycyclic aromatic compounds 3a, 3a', 3a", 3e, 3f, 3i, 4a, 4c, 4f, 7, 10b & 12

entry	product	absorption[a] $\lambda_{max\ (abs)}$ (nm)	Emission[a,b] $\lambda_{max\ (em)}$ (nm)	Stokes[c] Shift (cm^{-1})	Quantum yield (φ)[d]
1	**3a**	218, 266	370	18845	0.0146
2	**3e**	220, 290, 388	443, 461	23763	**0.0801**
3	**3f**	222, 316, 380	459	23259	0.0321
4	**3i**	222, 296	476	24037	0.0179
5	**4a**	220, 304, 402	470	24178	0.0396
6	**4c**	220, 296	464	23903	0.0214
7	**4f**	220, 314, 390	477	24490	0.0268
8	**7**	222, 256, 302	380	18729	0.0028
9	**10b**	224, 284, 376	468	23275	0.0191
10	**12**	220, 348, 408	510, 576	25847	0.0251
11	**3a"**	220	401	20517	0.0262
12	**3a'**	222, 256	411, 521	20714	0.0454

[a]Recorded in EtOH at 25 ^{o}C.[b]Excited at the longest wavelength of the absorption maximum.[c]Stokes shift = $\lambda_{max(abs)}$-$\lambda_{max(emi)}$(cm^{-1}). [d] Fluorescence quantum yield was calculated using the anthracene as a standard (Φ_{std}= 0.29 in ethanol).

The optical properties of representative dibenzothiophenes (**3a, 3e, 3f, 3i, 3a"** and **3a'**), triarylfluoranthenes (**4a, 4c, 4f** and **10b**) and non-planar heteroacenes (**7** and **12**) were investigated by UV-visible absorption and fluorescence spectroscopy (**Figures 1** and**2**).The absorption spectra of tetraphenyl dibenzothiophene analogues **3a, 3a'**and **3a"**showed a strong absorption band at around 220 nm due to the π-π* transition. Except **3a"**, the dibenzothiophenes **3a** and **3a'** showed a less intense shoulder peak at ~260nm due to the n-π*transition (**Figure 1a**). Acenaphthylene fused dibenzothiophenes **3e, 3f** and **3i** exhibit one intense and two weak absorptions bands in the region of 200-400 nm owing to the dibenzothiophene and diarylfluoranthene groups (**Figure 1b**). The remaining triarylfluoranthenes**4 a, 4c** and **4f** as well as highly conjugated acenes **7**, **10b** and **12** displayed absorption bands in the region of 200-420 nm (**Figures 1c** & **1d**). The fluorescence spectra of tetraphenyl dibenzothiophenes **3a, 3a"**and **3a'** show broad emission band in the region of 350-475 nm (**Figure 2a**). The dibenzothiophene *S*-oxide **3a'** showed higher emission value

compared to that of thiophene as well as sulfone counterparts (**3a**, **3a"**) possibly due to the higher charge mobility. Further, benzo[*b*]thienofluoranthenes (**3e**, **3f**, **3i**) as well as triarylfluoranthenes (**4a**, **4c, 4f**) displayed strong emission band in the region of 425-550 nm (**Figures 2b & 2c**). Lastly, the π-extended acenes **7**, **10b** and **12** show (**Figure 2d**) discrete sharp emission peaks from the region of 350 to 600 nm. Relatively, the higher π-conjugation of **12** ensured its longer wavelength emission value than acenes **7** and **10b**.

Among twelve polycyclic aromatic compounds **3a, 3a', 3a", 3e, 3f, 3i, 4a, 4c, 4f, 7, 10b** and **12**, the undecacene **12** show slightly higher stokes shift value (**Table 1**). The oxygenated homologs of tetraphenyl dibenzothiophenes **3a"**and **3a'** exhibited higher quantum efficiency (**Table 1**) than that of the parent dibenzothiophene **3a**. The incorporation of bromineas well as methylenedioxy substituentson acenaphthylene fused dibenzothiophene (**3e, 3f, 3i**) decreased the fluorescence quantum yields. The presence of aryl or heteroaryl substituents on fluoranthenes (**4a, 4c, 4f**) is not showing any appreciable influence on their quantum yield. Among acenes (**7**, **10b, 12**), the *N*-hexylcarbazole based undecacene **12** displayed higher quantum yield value (**Table 1**).