Supporting Information

Oxidative [4+2] Annulation of 1-Naphthols with Alkynes Accelerated by an Electron-Deficient Rhodium(III) Catalysts

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1. General

Materials: Anhydrous CH_2Cl_2 (No. 041-32345) and 1,4-dioxane (No. 042-31655) were obtained from Wako and used as received. Anhydrous $(CH_2Cl)_2$ (No. 284505) and *o*-xylene (No. 294780) were obtained from Aldrich and used as received. Anhydrous *t*-AmOH (P0059) was obtained from TCI and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4Å (Wako) prior to use. Rh(III) complex $[Cp^ERhCl_2]_2$,[1] 1-naphthols **1b**[2] and **1c**[3], and alkynes **2b**,[4] **2c**,[5] **2d–f**,[4] **2g**[6], **2j**,[7] and **2k**,[8] were already reported. All other reagents were obtained from commercial sources and used as received. Preparative thin-layer chromatography was performed with silica gel 60 from Merck.

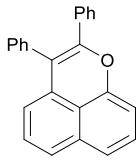
Instrumentation: ^1H, ^{13}C, and ^{19}F NMR spectra were collected on a Bruker AVANCE III HD 400 spectrometer at room temperature. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. ESI and APCI mass spectra were measured on a Bruker micrOTOF Focus II spectrometer. UV–vis absorption and fluorescence spectra were recorded on JASCO V-630 and JASCO FP-6200 spectrophotometers, respectively. Fluorescence quantum yields were obtained on a Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System, C11347-01. Melting points were determined with a Mettler Toledo MP50 One Click Melting Point System and are uncorrected. Single crystal X-ray diffraction measurements were made on XtaLAB mini II diffractometer using graphite monochromated Mo-Kα radiation. All reactions were carried out in oven-dried glassware with magnetic stirring.

2. Rhodium-Catalyzed Oxidative Annulation of 1-Naphthols with Internal Alkynes

Representative procedure for rhodium-catalyzed oxidative annulation of 1-naphthols with internal alkynes (3aa, Figure 2a): To a Schlenk flask were added $[Cp^ERhCl_2]_2$ (2.1 mg, 0.0025 mmol), $Cu(OAc)_2·H_2O$ (4.0 mg, 0.020 mmol), AgOAc (3.3 mg, 0.020 mmol), 1-naphthol (**1a**, 28.8 mg, 0.200 mmol), diphenylacetylene (**2a**, 17.8 mg, 0.100 mmol) and CH_2Cl_2 (2.0 mL). The mixture was stirred at room temperature under air for 2 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. To the residue were added dimethyl sulfone (as an internal standard) and $CDCl_3$. Then NMR yield was analyzed by ^1H NMR. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (PTLC, hexane/EtOAc = 10:1) to give **3aa** [21.8 mg (92 wt% purity), 0.0623 mmol, 62% yield] as a pale yellow solid.

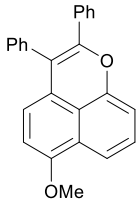
The reaction using $[Cp^ERhCl_2]_2$ (6.4 mg, 0.0075 mmol), $Cu(OAc)_2·H_2O$ (12.0 mg, 0.060 mmol), AgOAc (10.0 mg, 0.060 mmol), 1-naphthol (**1a**, 86.5 mg, 0.600 mmol), diphenylacetylene (**2a**, 53.5 mg, 0.300 mmol) and CH_2Cl_2 (6.0 mL) at room temperature under air for 16 h gave **3aa** [63.6 mg, 0.199 mmol, 66% yield].

2,3-Diphenylbenzo[*de*]chromene (3aa, Figure 2a)[9]



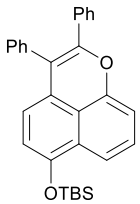
^1H NMR (400 MHz, $CDCl_3$, after repeated purification by PTLC) δ 7.40–7.10 (m, 14H), 6.86 (dd, J = 7.4, 1.2 Hz, 1H), 6.44 (dd, J = 7.2, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.6, 135.7, 134.9, 134.4, 132.1, 131.1, 129.2, 129.1, 128.5, 127.81, 127.80, 127.7, 127.6, 123.8, 123.1, 119.3, 117.7, 115.8, 107.1.

6-Methoxy-2,3-diphenylbenzo[*de*]chromene (3ba, Figure 2a)[9]



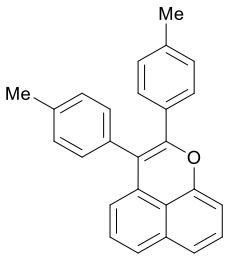
Pale yellow solid; 32.5 mg, 0.0927 mmol, 93% yield, purified by PTLC (hexane/EtOAc = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 1H), 7.40–7.20 (m, 8H), 7.20–7.13 (m, 3H), 6.91 (d, J = 7.7 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.7, 147.4, 136.0, 134.5, 131.1, 129.2, 129.0, 128.2, 127.8, 127.6, 127.3, 126.8, 124.8, 123.7, 117.7, 115.7, 113.9, 108.2, 105.2, 55.6.

tert-Butyl((2,3-diphenylbenzo[*de*]chromen-6-yl)oxy)dimethylsilane (3ca, Figure 2a)



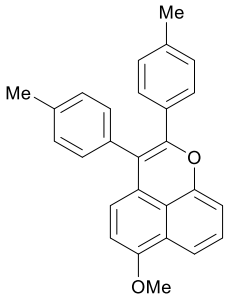
Pale yellow solid; 29.1 mg, 0.0646 mmol, 65% yield, purified by PTLC (hexane/EtOAc = 10:1); reaction at 40 °C for 24 hours, 0.2 mmol scale: 75.7 mg, 0.168 mmol, 84% yield; Mp 104.1–105.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 1H), 7.40–7.22 (m, 8H), 7.21–7.13 (m, 3H), 6.88 (d, J = 7.6 Hz, 1H), 6.60 (d, J = 7.9 Hz, 1H), 6.34 (d, J = 7.9 Hz, 1H), 1.07 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 148.8, 147.6, 135.9, 134.5, 131.1, 129.24, 129.15, 129.0, 128.2, 127.8, 127.6, 127.1, 125.4, 124.3, 117.8, 116.0, 114.5, 114.2, 107.7, 26.0, 18.6, -4.1; HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{31}SiO_2$ 451.2088; Found 451.2099.

2,3-Di-*p*-tolylbenzo[*de*]chromene (3ab, Figure 2a)[10]



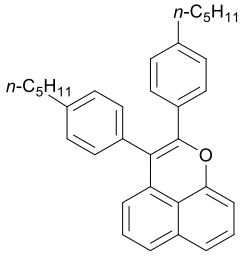
Pale green solid; 20.2 mg, 0.0580 mmol, 58% yield, purified by PTLC (hexane/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.4, 0.5 Hz, 1H), 7.32–7.15 (m, 6H), 7.32–7.15 (m, 3H), 6.99 (m, 2H), 6.84 (dd, J = 7.5, 1.1 Hz, 1H), 6.43 (dd, J = 7.3, 0.4 Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.5, 138.4, 137.2, 134.9, 132.8, 132.5, 131.6, 130.9, 129.9, 128.9, 128.5, 127.8, 127.5, 123.5, 123.0, 119.2, 117.1, 115.6, 107.0, 21.5, 21.4.

6-Methoxy-2,3-di-p-tolylbenzo[*de*]chromene (3bb, Figure 2a)



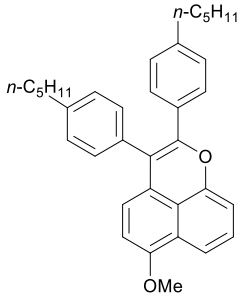
Pale yellow solid; 36.2 mg, 0.0956 mmol, 96% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 175.9–177.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.4, 0.9 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.23–7.15 (m, 4H), 7.15–7.10 (m, 2H), 7.01–6.95 (m, 2H), 6.89 (dd, J = 7.7, 0.9 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.5, 147.3, 138.0, 137.1, 133.0, 131.8, 130.9, 129.9, 128.8, 128.5, 127.2, 126.8, 125.1, 123.7, 117.0, 115.5, 113.7, 108.1, 105.2, 55.6, 21.5, 21.4; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{22}O_2$ 378.1614; Found 378.1599.

2,3-Bis(4-pentylphenyl)benzo[*de*]chromene (3ac, Figure 2a)



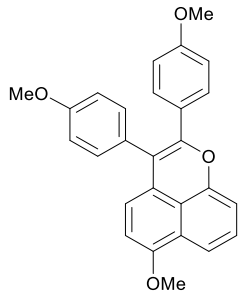
Yellow viscous liquid; 25.0 mg, 0.0543 mmol, 54% yield, purified by PTLC (hexane/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.5, 0.7 Hz, 1H), 7.32–7.22 (m, 2H), 7.21–7.10 (m, 7H), 6.99–6.94 (m, 2H), 6.84 (d, J = 7.5 Hz, 1H), 6.46 (d, J = 7.3 Hz, 1H), 2.63 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 1.64 (quint, J = 7.5 Hz, 2H), 1.55 (quint, J = 7.6 Hz, 2H), 1.41–1.21 (m, 8H), 0.91 (t, J = 7.0 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.5, 143.4, 142.2, 135.0, 133.0, 132.5, 131.8, 130.9, 129.2, 128.9, 127.81, 127.78, 127.5, 123.5, 123.0, 119.2, 117.2, 115.7, 107.0, 35.83, 35.79, 31.61, 31.55, 31.1, 30.9, 22.7, 22.6, 14.24, 14.15; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{36}O$ 460.2761; Found 460.2761.

6-Methoxy-2,3-bis(4-pentylphenyl)benzo[*de*]chromene (3bc, Figure 2a)



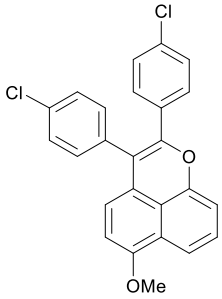
Pale yellow solid; 39.4 mg, 0.0803 mmol, 80% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 133.9–135.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.3, 0.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.21–7.12 (m, 6H), 6.99–6.93 (m, 2H), 6.90 (dd, J = 7.6, 0.6 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.63 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 1.65 (quint, J = 7.4 Hz, 2H), 1.55 (quint, J = 7.4 Hz, 2H), 1.42–1.21 (m, 8H), 0.91 (t, J = 7.0 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.5, 147.3, 143.0, 142.2, 133.2, 131.9, 130.9, 129.2, 128.7, 127.7, 127.2, 126.8, 125.2, 123.7, 117.1, 115.6, 113.7, 108.1, 105.2, 55.6, 35.83, 35.78, 31.6, 31.5, 31.2, 31.0, 22.7, 22.6, 14.24, 14.15; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{35}H_{38}O_2$ 490.2866; Found 490.2866.

6-Methoxy-2,3-bis(4-methoxyphenyl)benzo[*de*]chromene (3bd, Figure 2a)



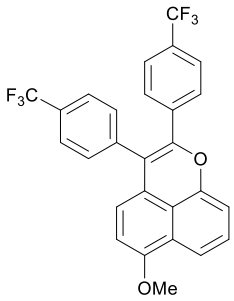
Yellow solid; 37.5 mg, 0.0914 mmol, 91% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 178.4–179.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.25–7.20 (m, 2H), 7.18–7.12 (m, 2H), 6.94–6.85 (m, 3H), 6.73–6.67 (m, 2H), 6.54 (d, J = 7.8 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.9, 152.8, 152.5, 147.2, 132.2, 130.3, 128.3, 127.2, 127.1, 126.8, 125.3, 123.6, 116.1, 115.3, 114.7, 113.7, 113.2, 108.1, 105.2, 55.6, 55.4, 55.3; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{22}NaO_4$ 410.1513; Found 410.1513.

2,3-Bis(4-chlorophenyl)-6-methoxybenzo[*de*]chromene (3be, Figure 2a)



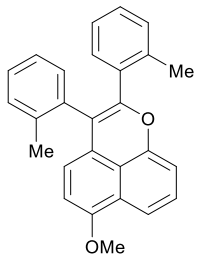
Reaction at 60 °C for 16 h; Pale yellow solid; 15.4 mg, 0.0503 mmol, 50% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 180.5–182.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 1H), 7.40–7.31 (m, 3H), 7.22–7.13 (m, 6H), 6.90 (d, J = 7.7, 0.8 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 152.4, 146.5, 134.3, 134.2, 133.7, 132.7, 132.5, 130.2, 129.7, 128.2, 127.4, 126.8, 124.0, 123.5, 117.0, 115.8, 114.2, 108.4, 105.0, 55.6; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{25}H_{16}Cl_2O_2$ 418.0522; Found 418.0522.

6-Methoxy-2,3-bis(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bf, Figure 2a)



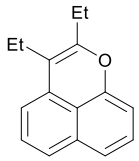
Reaction at 60 °C for 16 h; Yellow solid; 15.8 mg, 0.0325 mmol, 33% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 201.3–202.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 2H), 7.62 (dd, J = 8.4, 0.6 Hz, 1H), 7.47–7.42 (m, 2H), 7.41–7.34 (m, 5H), 6.93 (dd, J = 7.7, 0.6 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 152.3, 146.3, 139.4 (d, J = 1.4 Hz), 137.5 (d, J = 1.4 Hz), 131.5, 130.32 (q, J = 32.6 Hz), 130.26 (q, J = 32.6 Hz), 129.2, 127.5, 126.9, 126.4 (q, J = 3.7 Hz), 125.0 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 124.0 (q, J = 272.1 Hz), 123.6, 123.5, 118.0, 116.3, 114.5, 108.6, 105.0, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5, -62.8; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{16}F_6O_2$ 486.1049; Found 486.1043.

6-Methoxy-2,3-di-o-tolylbenzo[*de*]chromene (3bg, Figure 2a)



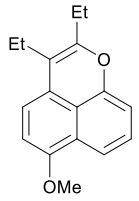
Reaction at 60 °C for 16 h; Pale brown solid; 25.1 mg, 0.0663 mmol, 66% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 137.8–139.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.4, 0.7 Hz, 1H), 7.34 (t, J = 8.1 Hz, 1H), 7.17–7.01 (m, 7H), 6.95–6.89 (m, 1H), 6.87 (dd, J = 7.7, 0.7 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.15 (d, J = 7.9 Hz, 1H), 3.92 (s, 3H), 2.48 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.7, 148.8, 137.7, 137.4, 134.7, 134.0, 131.3, 130.30, 130.26, 130.2, 128.8, 127.7, 127.2, 127.0, 126.1, 125.2, 123.9, 123.7, 117.8, 115.3, 114.0, 108.2, 105.2, 55.6, 20.3, 19.7; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{22}O_2$ 378.1614; Found 378.1614.

2,3-Diethylbenzo[*de*]chromene (3ah, Figure 2a)[10]



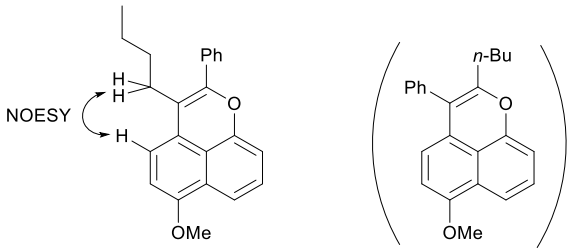
Yellow viscous liquid; 10.3 mg, 0.0459 mmol, 46% yield, purified by PTLC (hexane/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.3, 0.8 Hz, 1H), 7.27–7.21 (m, 2H), 7.18 (dd, J = 8.2, 1.1 Hz, 1H), 6.76 (dd, J = 7.1, 0.8 Hz, 1H), 6.72 (dd, J = 7.4, 1.2 Hz, 1H), 2.46 (dd, J = 7.5, 2.9 Hz, 2H), 2.42 (dd, J = 7.5, 2.8 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H), 1.15 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 152.9, 135.2, 130.7, 127.8, 127.2, 123.3, 122.7, 118.8, 112.9, 112.3, 106.6, 24.0, 19.7, 13.0, 12.6.

2,3-Diethyl-6-methoxybenzo[*de*]chromene (3bh, Figure 2a)



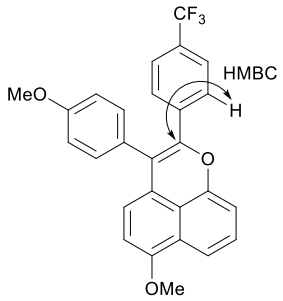
Pale brown solid, 20.5 mg (88 wt% purity due to instability under air), 0.0710 mmol, 71% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 116.3–118.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, after repeated purification by PTLC) δ 7.51 (dd, J = 8.4, 0.8 Hz, 1H), 7.31–7.26 (m, 1H), 6.77 (dd, J = 7.7, 0.7 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H), 2.45 (d, J = 7.5 Hz, 2H), 2.41 (d, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 151.9, 150.9, 127.1, 126.9, 123.9, 123.2, 113.2, 112.6, 111.9, 107.7, 105.3, 55.6, 23.8, 19.6, 13.1, 12.7; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}O_2$ 254.1301; Found 254.1313.

3-Butyl-6-methoxy-2-phenylbenzo[*de*]chromene (3bi, Figure 2a)



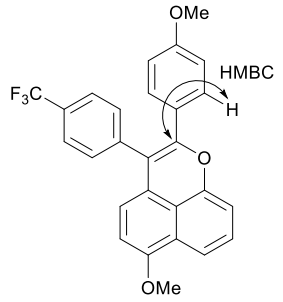
Yellow viscous liquid; 13.4 mg, 0.0422 mmol, 42% yield, purified by PTLC (hexane/EtOAc = 10:1); The regioisomer, 2-butyl-6-methoxy-3-phenylbenzo[*de*]chromene was observed on crude ^{1}H NMR in very low yield and was not isolated; Regioisomer structure determined based on NOESY NMR as shown; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 8.4, 0.9 Hz, 1H), 7.56–7.52 (m, 2H), 7.48–7.37 (m, 3H), 7.31 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.82 (dd, J = 7.7, 0.9 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.98 (s, 3H), 2.45–2.38 (m, 2H), 2.65–2.56 (m, 2H), 1.34 (sextet, J = 7.4 Hz, 2H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.8, 152.5, 148.0, 135.2, 129.1, 128.8, 128.4, 127.02, 126.99, 124.0, 123.2, 114.2, 113.6, 113.4, 108.0, 105.2, 55.6, 30.5, 27.1, 23.0, 14.0; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{23}H_{22}O_2$ 330.1614; Found 330.1596.

6-Methoxy-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj, Figure 2a)



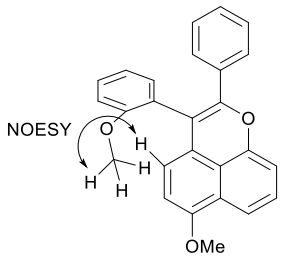
Yellow solid; 20.5 mg, 0.0457 mmol, 46% yield, purified by PTLC (hexane/EtOAc = 10:1); 174.6 °C (decomposition); Regioisomer structure determined based on HMBC NMR as shown; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.4, 0.9 Hz, 1H), 7.45–7.37 (m, 4H), 7.37–7.32 (m, 1H), 7.17–7.11 (m, 2H), 6.96–6.90 (m, 2H), 6.91 (dd, J = 7.7, 0.9 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 153.1, 152.5, 145.7, 138.2 (d, J = 1.3 Hz), 132.0, 129.7 (q, J = 32.4 Hz), 129.1, 127.4, 127.3, 126.8, 124.7 (q, J = 3.8 Hz), 124.5, 124.1 (q, J = 272.1 Hz), 123.7, 118.8, 116.5, 114.9, 114.1, 108.3, 105.1, 55.6, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{19}F_3O_3$ 448.1281; Found 448.1281.

6-Methoxy-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj', Figure 2a)

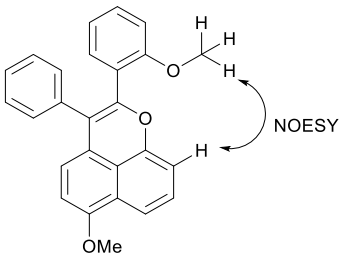


Pale orange solid; 11.8 mg, 0.0263 mmol, 26% yield, purified by PTLC (hexane/EtOAc = 10:1); Mp 199.8–200.6 °C; Regioisomer structure determined based on HMBC NMR as shown; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 8.4, 0.8 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 8.1 Hz, 1H), 7.21–7.15 (m, 2H), 6.91 (dd, J = 7.7, 0.9 Hz, 1H), 6.74–6.68 (m, 2H), 6.54 (d, J = 8.0 Hz, 1H), 6.29 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.7, 152.6, 147.9, 140.4 (d, J = 1.3 Hz), 131.7, 130.4, 129.6 (q, J = 32.4 Hz), 127.4, 126.9, 126.4, 126.2 (q, J = 3.7 Hz), 124.34 (q, J = 272.0 Hz), 124.3, 123.5, 115.6, 115.1, 114.1, 113.4, 108.4, 105.1, 55.6, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{27}H_{19}F_3O_3$ 448.1281; Found 448.1288.

6-Methoxy-3-(2-methoxyphenyl)-2-phenylbenzo[*de*]chromene/6-methoxy-2-(2-methoxyphenyl)-3-phenylbenzo[*de*]chromene (3bk/3bk', Figure 2a)



3bk major



3bk' minor

Yellow viscous liquid; 33.7 mg, 0.0886 mmol, 89% yield, purified by PTLC (hexane/EtOAc = 10:1); Isolated as a mixture of both regioisomers; Major product (**3bk**)/minor product (**3bk'**) ratio calculated with ^{1}H NMR spectra; Regioisomer structure determined based on NOESY NMR as shown; **3bk** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 8.4, 0.9 Hz, 1H), 7.36–7.13 (m, 7H), 7.11–7.07 (m, 1H), 6.96–6.88 (m, 3H), 6.55 (d, J = 8.0 Hz, 1H), 6.25 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.66 (s, 3H); **3bk'** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.4, 0.9 Hz, 1H), 7.36–7.13 (m, 8H), 6.84 (dd, J = 7.7, 0.9 Hz, 1H), 6.80 (td, J = 11.2, 1.0 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 3.64 (s, 3H); **3bk /3bk'** mixture ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.4, 153.3, 152.9, 152.6, 152.5, 147.8, 146.2, 135.9, 134.9, 132.5, 131.8, 130.5, 130.3, 129.3, 128.3, 128.22, 128.20, 127.7, 127.2, 127.10, 127.08, 127.0, 126.9, 124.9, 124.6, 124.3, 124.1, 123.7, 121.4, 120.2, 119.0, 115.2, 114.9, 114.1, 113.8, 113.7, 111.5, 111.1, 108.3, 108.1, 105.4, 105.0, 55.7, 55.59, 55.55, 55.5; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{26}H_{20}O_3$ 380.1407; Found 380.1407.

3. Single-Crystal X-Ray Diffraction Analysis of 3bd

Details of the crystal data and the summaries of the intensity data collection parameters for **3bd** are listed in Table S1 (CCDC Deposition Number: 2108408).

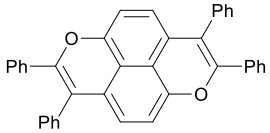
Table S1: Crystallographic data and structure refinement details for **3bd**.

formula	C56H46O6
formula weight	814.93
crystal color, shape	colorless block
crystal system	triclinic
space group	*P*-1
a (Å)	9.6823(4)
b (Å)	10.4434(4)
c (Å)	11.6367(5)
α (deg)	82.076(4)
β (deg)	78.416(4)
γ (deg)	65.109(4)
V (Å^3)	1043.73(8)
Z	1
d_{calc} (g/cm^3)	1.306
μ (Cu Kα) (mm^{-1})	0.083
F_{000}	430.0
crystal size (mm)	0.2×0.2×0.4
temperature (K)	210
θ range (deg)	2.216–30.339
number of independent reflections	5933
number of parameters	283
R_1, wR_2 [I>2σ(I)]	0.0464, 0.1312
R_1, wR_2 (all data)	0.0594, 0.1404
S	1.062
largest difference peak and hole (eÅ^{-3})	0.26, -0.24

4. One-step Synthesis of 2,3,7,8-Tetraphenyl-1,6-dioxapyrene

Representative procedure for rhodium-catalyzed oxidative annulation of naphthalene-1,5-diol with diphenylacetylene (3da, Figure 2b): To a Schlenk flask were added $[Cp^ERhCl_2]_2$ (2.1 mg, 0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (119.6 mg, 0.600 mmol), AgOAc (3.3 mg, 0.020 mmol), naphthalene-1,5-diol **1d** (16.0 mg, 0.100 mmol), diphenylacetylene **2a** (53.4 mg, 0.300 mmol) and acetone (2.0 mL). The mixture was stirred at 60 °C under an Ar atmosphere for 2 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with CH_2Cl_2/EtOAc. To the residue were added dimethyl terephthalate (as an internal standard) and $CDCl_3$. Then NMR yield was analyzed by ^1H NMR. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (PTLC, hexane/EtOAc = 10:1) to give **3da** (7.6 mg, 0.0148 mmol, 15% yield) as an orange solid. Under the above PTLC conditions, product **3da** was a little unstable, and pure **3da** was isolated with considerable product loss.

2,3,7,8-Tetraphenylchromeno[6,5,4-*def*]chromene (3da, Figure 2b)

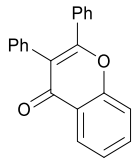


271.6 °C (decomposition); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 6H), 7.21–7.09 (m, 14H), 6.25 (d, J = 8.0 Hz, 2H), 6.08 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.3, 149.2, 135.8, 134.6, 131.2, 129.4, 129.1, 128.7, 127.7, 127.4, 126.1, 125.7, 118.8, 118.3, 108.5; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{38}H_{24}O_2$ 512.1771; Found 512.1776.

5. Rhodium-Catalyzed Oxidative Annulation of Salicylaldehyde with Internal Alkynes

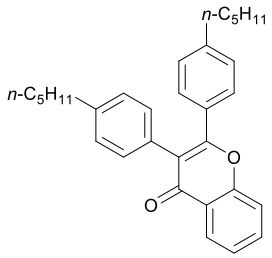
Representative procedure for rhodium-catalyzed oxidative annulation of salicylaldehyde with internal alkynes (5a, Figure 2c): To a Schlenk flask were added $[Cp^ERhCl_2]_2$ (2.1 mg, 0.0025 mmol), $Cu(OAc)_2·H_2O$ (4.0 mg, 0.020 mmol), salicylaldehyde **4** (24.4 mg, 0.200 mmol), diphenylacetylene **2a** (17.8 mg, 0.100 mmol) and $(CH_2Cl)_2$ (2.0 mL). The mixture was stirred under air at 80 ºC for 20 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. To the residue were added dimethyl sulfone (as an internal standard) and $CDCl_3$. Then NMR yield was analyzed by ^1H NMR. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (PTLC, hexane/EtOAc = 10:1) to give **5a** (28.9 mg, 0.0962 mmol, 96% yield) as a colorless solid.

2,3-Diphenyl-4H-chromen-4-one (5a, Figure 2c)[11]



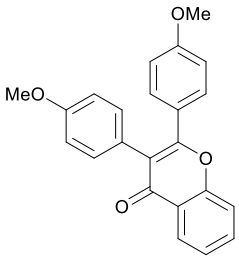
^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, J = 8.0, 1.5 Hz, 1H), 7.74–7.68 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.46–7.39 (m, 3H), 7.37–7.26 (m, 6H), 7.24–7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 161.6, 156.2, 133.8, 133.5, 133.0, 131.4, 130.2, 129.7, 128.4, 128.2, 127.8, 126.6, 125.2, 123.7, 123.1, 118.1.

2,3-Bis(4-pentylphenyl)-4H-chromen-4-one (5c, Figure 2c)



Yellow viscous liquid; 40.1 mg, 0.0914 mmol, 91% yield, purified by PTLC (hexane/EtOAc = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.0, 1.4 Hz, 1H), 7.70–7.64 (m, 1H), 7.51 (dd, J = 8.4, 0.5 Hz, 1H), 7.43–7.37 (m, 1H), 7.33–7.29 (m, 2H), 7.15–7.09 (m, 4H), 7.08–7.04 (m, 2H), 2.58 (q, J = 8.1 Hz, 4H), 1.67–1.16 (m, 4H), 1.39–1.22 (m, 8H), 0.89 (q, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 161.6, 156.2, 145.4, 142.3, 133.6, 131.1, 130.8, 130.3, 129.6, 128.5, 128.2, 126.5, 125.0, 123.7, 122.7, 118.0, 35.9, 35.8, 31.6 (2C), 31.0, 30.8, 22.7, 22.6, 14.2, 14.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{34}NaO_2$ 461.2451; Found 461.2451.

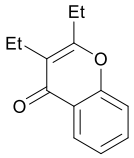
2,3-Bis(4-methoxyphenyl)-4H-chromen-4-one (5d, Figure 2c)[11]



Colorless solid; 33.6 mg, 0.0938 mmol, 94% yield, purified by PTLC (hexane/EtOAc = 10:1); ^1H

NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.0, 1.6 Hz, 1H), 7.71–7.65 (m, 1H), 7.52 (dd, J = 8.4, 0.5 Hz, 1H), 7.43–7.35 (m, 3H), 7.19–7.14 (m, 2H), 6.90–6.85 (m, 2H), 6.82–6.77 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 161.2, 161.0, 159.1, 156.1, 133.6, 132.5, 131.4, 126.5, 125.8, 125.5, 125.0, 123.6, 121.8, 118.0, 114.1, 113.7, 55.5, 55.3.

2,3-Diethyl-4H-chromen-4-one (5h, Figure 2c)[12]



Yellow oil; 9.7 mg, 0.0480 mmol, 48% yield, purified by PTLC (hexane/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 8.0, 1.6 Hz, 1H), 7.65–7.56 (m, 1H), 7.39 (dd, J = 8.4, 05 Hz, 1H), 7.37–7.31 (m, 1H), 2.74 (q, J = 7.6 Hz, 2H), 2.58 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H), 1.13 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 166.4, 156.1, 133.0, 126.0, 124.5, 123.1, 122.3, 117.7, 25.3, 18.0, 14.0, 12.1.

6. Photophysical Experiments

Uv-vis absorption and fluorescence spectra were measured for the naphtho[1,8-bc]pyran derivates **3aa**, **3ba**, **3bd**, **3bf**, and **3da** in $CHCl_3$ solution.

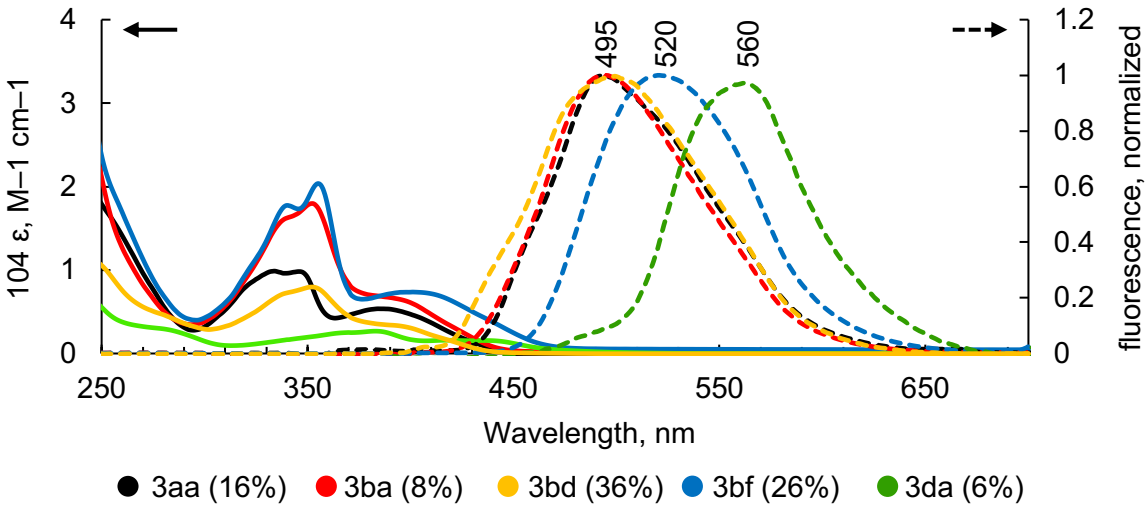


Figure S1: Uv-vis absorption (solid line) and fluorescence (dotted line) spectra for compounds **3aa**, **3ba**, **3bd**, **3bf**, and **3da** in $CHCl_3$ (5×10^{-5} M). Maximum quantum yields observed for each compound shown in parenthesis.

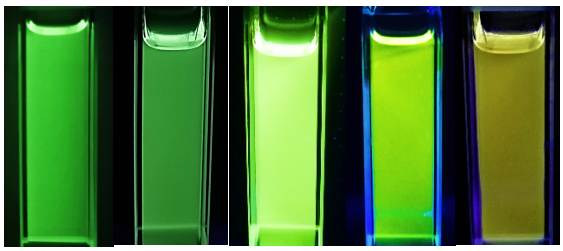


Figure S2: Emission images of 5×10^{-5} M $CHCl_3$ solution under UV light (365 nm). From left to right: **3aa**, **3ba**, **3bd**, **3bf**, and **3da**.

7. Mechanistic Experiments

Rhodium-catalyzed oxidative annulation of 1-naphthol with internal diphenylacetylene in the presence of CD_3CO_2D (Figure 4b): To a Schlenk flask were added $[Cp^ERhCl_2]_2$ (2.1 mg, 0.0025 mmol), $Cu(OAc)_2{\cdot}H_2O$ (4.0 mg, 0.020 mmol), AgOAc (3.3 mg, 0.020 mmol), 1-naphthol **1a** (28.8 mg, 0.200 mmol), diphenylacetylene **2a** (17.8 mg, 0.100 mmol), CH_2Cl_2 (2.0 mL), and CD_3CO_2D (ca. 0.4 mmol). The mixture was stirred at room temperature under air for 1 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (PTLC, hexane/EtOAc = 10:1) to recover unreacted **1a** (0% D)**.** Deuteration was analyzed through ^{1}H NMR.

Competitive rhodium-catalyzed oxidative annulation of 1-naphthol and 5-methoxy-1-naphthol with diphenylacetylene (Figure 4c): To a Schlenk flask were added $[Cp^ERhCl_2]_2$ (2.1 mg, 0.0025 mmol), $Cu(OAc)_2{\cdot}H_2O$ (4.0 mg, 0.020 mmol), AgOAc (3.3 mg, 0.020 mmol), 1-naphthol **1a** (14.4 mg, 0.100 mmol), 5-methoxy-1-naphthol **1b** (17.4 mg, 0.100 mmol), diphenylacetylene **2a** (17.8 mg, 0.100 mmol), and CH_2Cl_2 (2.0 mL). The mixture was stirred at room temperature under air for 1.5 h. The resulting mixture was diluted with hexane, filtered through a silica gel pad, and washed with diethyl ether. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (PTLC, hexane/EtOAc = 10:1) to afford a mixture of both annulation products (19.3 mg) **3aa** (0.0043 mmol, 4% yield) and **3ba** (0.048 mmol, 48% yield)**.**

8. Computational Study

All calculations were carried with the Gaussian 16 program package.[13] The hybrid density functional method based on M06 [14–17] with a standard 6-31g* basis set (LANL2DZ basis set for Rh) was used for geometry optimizations. Geometry optimization and vibrational analysis were performed at the same level. All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.[18–21]

Table S2. Gibbs-free energies and imaginary frequencies for **Figure 5**.

	G (hartree) (M06/6-31g* & LANL2DZ)	Imaginary Frequency (cm^{-1})
AcOH	-228.9240950	
1a	-538.8792420	
Cp*Rh IM1	-1187.508618	
Cp*Rh TS1	-1187.474517	-1553.58
Cp*Rh IM2	-1187.494065	
Cp*Rh IM3	-1497.435843	
Cp*Rh TS2	-1497.415190	-258.50
Cp*Rh IM4	-1497.448448	
Cp*Rh IM4'	-1497.448233	
Cp*Rh TS3	-1497.414835	-403.05
Cp*Rh IM5	-1497.462721	
Cp^{E}Rh IM1	-1564.422951	
Cp^{E}Rh TS1	-1564.396155	-1478.37
Cp^{E}Rh IM2	-1564.411376	
Cp^{E}Rh IM3	-1874.360846	
Cp^{E}Rh TS2	-1874.340909	-264.39
Cp^{E}Rh IM4	-1874.371204	
Cp^{E}Rh IM4'	-1874.372683	
Cp^{E}Rh TS3	-1874.344379	-402.57
Cp^{E}Rh IM5	-1874.402904	

AcOH

Sum of electronic and zero-point Energies = -228.897155

Sum of electronic and thermal Free Energies = -228.924095

C	-2.338380	0.150984	-0.023715
H	-1.650964	-0.529503	-0.538781
H	-2.733064	0.886543	-0.727123
H	-3.155092	-0.459914	0.377310
C	-1.626597	0.850196	1.092034
O	-1.495177	2.041587	1.220414
O	-1.125406	-0.035555	1.978802
H	-0.683902	0.496673	2.663756

1a

Sum of electronic and zero-point Energies = -538.839468

Sum of electronic and thermal Free Energies = -538.879242

C	-0.958879	-0.333142	0.000059
C	0.254689	-0.332680	-0.000211
C	-2.385543	-0.332912	0.000094
C	-3.095739	0.874998	0.044288
C	-3.096557	-1.540306	-0.044170
C	-4.483553	0.871718	0.044155
H	-2.541928	1.811420	0.078591
C	-4.484377	-1.536021	-0.044013
H	-2.543429	-2.477130	-0.078465
C	-5.181422	-0.331916	0.000083
H	-5.025092	1.815462	0.078715
H	-5.026562	-2.479395	-0.078545
H	-6.270003	-0.331564	0.000075
C	1.681368	-0.332649	-0.000128
C	2.391934	-0.292297	-1.207954
C	2.392026	-0.372735	1.207626
C	3.779748	-0.292236	-1.204237
H	1.838412	-0.261161	-2.144657
C	3.779843	-0.372440	1.203778
H	1.838609	-0.403999	2.144386
C	4.477254	-0.332254	-0.000250
H	4.321575	-0.260737	-2.147923
H	4.321741	-0.403817	2.147428
H	5.565835	-0.332090	-0.000273

Cp*Rh IM1

Sum of electronic and zero-point Energies = -1187.451002

Sum of electronic and thermal Free Energies = -1187.508618

Rh	-1.051535	0.008892	-0.180721
C	-2.368773	-1.587736	0.403039
C	-2.370811	-0.595931	1.433325
C	-1.021015	-2.100725	0.260659
C	-1.012956	-0.479038	1.918122
C	-0.193838	-1.438893	1.232419
O	0.411578	0.504663	-1.519210
C	-0.564597	-3.164947	-0.670764
H	0.415367	-2.912072	-1.100374
H	-0.462684	-4.127659	-0.148425
H	-1.268108	-3.303910	-1.499410
C	-2.075638	2.125471	-1.216569
O	-2.354268	0.981774	-1.685297
O	-1.396388	2.227752	-0.153061
C	-2.521056	3.356742	-1.945539
H	-3.437403	3.163053	-2.511350
H	-2.665987	4.188127	-1.248924
H	-1.735849	3.641595	-2.656776
C	1.620055	0.007981	-1.363159
C	2.508975	0.566962	-0.377229
C	2.080381	-1.045011	-2.149576
C	2.092519	1.636497	0.447945
C	3.813142	0.017885	-0.210594
C	3.383580	-1.555246	-1.994738
H	1.405448	-1.445178	-2.906432
C	2.920828	2.122729	1.433489
H	1.103711	2.064577	0.279257
C	4.641452	0.546269	0.810260
C	4.236441	-1.048304	-1.042603
H	3.713520	-2.370773	-2.638361
C	4.205195	1.566486	1.619923
H	2.592406	2.948753	2.063667
H	5.637730	0.121895	0.942643
H	5.240121	-1.453605	-0.913669
H	4.855489	1.957555	2.401639
C	-0.550489	0.497999	2.938549
H	-0.777326	0.140339	3.953278
H	0.529855	0.669420	2.865780
H	-1.046636	1.467006	2.801635
C	-3.522263	-1.983356	-0.446766
H	-3.956638	-2.930815	-0.097176
H	-4.308474	-1.221170	-0.438406
H	-3.210964	-2.116481	-1.490011
C	-3.526683	0.229276	1.878421
H	-4.026921	-0.213980	2.751232
H	-3.203244	1.240849	2.150914
H	-4.270461	0.332533	1.079181
C	1.236212	-1.747107	1.488163
H	1.768456	-0.910213	1.955013
H	1.312406	-2.616073	2.158632
H	1.763910	-1.995450	0.558759

Cp*Rh TS1

Sum of electronic and zero-point Energies = -1187.418338

Sum of electronic and thermal Free Energies = -1187.474517

Rh	-0.745887	0.022005	-0.080534
C	-2.361249	-1.311181	-0.707024
C	-2.512612	-1.025115	0.704120
C	-1.114256	-1.990074	-0.883199
C	-1.354489	-1.502165	1.385139
C	-0.455528	-2.066996	0.394290
O	0.452360	0.522652	-1.729395
C	-0.537477	-2.399187	-2.192295
H	0.322419	-3.065423	-2.062719
H	-1.284947	-2.916725	-2.806798
H	-0.191543	-1.506635	-2.738107
C	-1.171184	2.968550	-0.159669
O	-1.775812	1.882832	-0.394392
O	-0.025502	3.060890	0.353299
C	-1.869376	4.247638	-0.538102
H	-2.942857	4.087624	-0.670037
H	-1.682093	5.017557	0.216762
H	-1.448278	4.604258	-1.486063

C	1.722320	0.336947	-1.430259
C	2.114893	0.406298	-0.056881
C	2.692343	0.022509	-2.377156
C	1.105493	0.738096	0.895188
C	3.442517	0.102585	0.340523
C	4.015240	-0.242737	-1.974526
H	2.405756	-0.029376	-3.426770
C	1.437910	0.725482	2.243097
H	0.420530	1.809259	0.602096
C	3.721298	0.109204	1.729717
C	4.399465	-0.220820	-0.651693
H	4.750284	-0.493024	-2.739866
C	2.746457	0.408303	2.657937
H	0.693393	1.014792	2.987694
H	4.735314	-0.125380	2.057652
H	5.421568	-0.456612	-0.356475
H	2.995851	0.420440	3.718741
C	-1.123545	-1.480987	2.855250
H	-1.539374	-2.384926	3.323722
H	-0.054409	-1.440823	3.092211
H	-1.597939	-0.611424	3.326184
C	-3.335408	-0.963766	-1.776655
H	-4.116127	-1.732739	-1.877122
H	-3.829276	-0.008422	-1.561817
H	-2.833138	-0.860712	-2.745963
C	-3.681324	-0.318768	1.295216
H	-4.597350	-0.915666	1.181253
H	-3.539069	-0.120716	2.363180
H	-3.841995	0.644561	0.793247
C	0.862153	-2.711951	0.652907
H	1.326119	-2.323606	1.567183
H	0.756278	-3.801279	0.761884
H	1.565588	-2.517425	-0.167710

Cp*Rh IM2

Sum of electronic and zero-point Energies = -1187.436501

Sum of electronic and thermal Free Energies = -1187.494065

Rh	-0.715800	0.028452	-0.060135
C	-2.991511	-0.052688	-0.446168
C	-2.640178	-0.325886	0.948329
C	-2.350786	-1.001421	-1.250067
C	-1.859962	-1.515406	0.993116
C	-1.562213	-1.873695	-0.374294
O	0.588378	0.165167	-1.696836
C	-2.292694	-1.069571	-2.734860
H	-2.586926	-2.064320	-3.097710
H	-2.950265	-0.329364	-3.204005
H	-1.265286	-0.873188	-3.076132
C	0.315292	3.065196	0.152778
O	-0.637925	2.293550	0.139631
O	1.571587	2.706276	0.294632
C	0.154361	4.544181	0.006298
H	-0.904255	4.811260	-0.000057
H	0.675175	5.061828	0.819087
H	0.620635	4.864327	-0.933018
C	1.827046	-0.164380	-1.399558
C	2.136413	-0.378853	-0.021897
C	2.852867	-0.279061	-2.333208
C	1.055386	-0.265097	0.896956
C	3.464412	-0.649101	0.410744
C	4.157749	-0.576586	-1.900100
H	2.634609	-0.116202	-3.387427
C	1.316291	-0.374227	2.247970
H	1.637406	1.724141	0.378677
C	3.678082	-0.775020	1.806396
C	4.478067	-0.755559	-0.569340
H	4.945830	-0.656393	-2.649676
C	2.637549	-0.626349	2.693706
H	0.515828	-0.272357	2.983813
H	4.686779	-0.979525	2.167711
H	5.501842	-0.968390	-0.262118
H	2.828097	-0.707674	3.764342
C	-1.439929	-2.277619	2.200049
H	-2.094061	-3.150219	2.342591
H	-0.408411	-2.639212	2.115933
H	-1.502552	-1.668567	3.109533
C	-3.812017	1.113201	-0.875543
H	-4.828277	1.059840	-0.458604
H	-3.364378	2.056125	-0.532210
H	-3.898293	1.167872	-1.966297
C	-3.139332	0.468596	2.104545
H	-4.188156	0.229396	2.336871
H	-2.543981	0.282744	3.006669
H	-3.083693	1.543668	1.889940
C	-0.771354	-3.048289	-0.833775
H	-0.027450	-3.342215	-0.083530
H	-1.418323	-3.916229	-1.032615
H	-0.228446	-2.811821	-1.757589

Cp*Rh IM3

Sum of electronic and zero-point Energies = -1497.372835

Sum of electronic and thermal Free Energies = -1497.435843

Rh	0.353851	-0.324213	-0.577261
C	2.338502	-0.166654	-1.815288
C	1.221527	0.501245	-2.465932
C	1.986648	-1.516096	-1.642649
C	0.240414	-0.481210	-2.803716
C	0.652978	-1.716651	-2.200973
O	0.324430	-1.684280	1.031350
C	2.746712	-2.580060	-0.933687
H	2.922389	-3.444216	-1.589842
H	3.718319	-2.220355	-0.576664
H	2.169919	-2.929129	-0.063329
C	-0.895161	-2.004543	1.422742
C	-1.984037	-1.398217	0.737544
C	-1.165902	-2.894189	2.455929
C	-1.670301	-0.491751	-0.303226
C	-3.331854	-1.673510	1.096932
C	-2.502193	-3.169472	2.802063
H	-0.340212	-3.363696	2.988439
C	-2.684961	0.147586	-0.976667
C	-4.350880	-1.003922	0.373452
C	-3.569374	-2.584843	2.153533
H	-2.693046	-3.868729	3.616871
C	-4.032199	-0.120302	-0.630071
H	-2.473820	0.894525	-1.744452
H	-5.393159	-1.197797	0.630705
H	-4.595235	-2.810133	2.445294
H	-4.826945	0.399307	-1.166690
C	-0.944384	-0.291022	-3.682510

H	-0.707193	-0.621767	-4.704487
H	-1.810580	-0.864727	-3.334074
H	-1.246539	0.761553	-3.741418
C	3.617649	0.490224	-1.427607
H	4.326880	0.488075	-2.268604
H	3.463339	1.536851	-1.136140
H	4.099303	-0.009598	-0.577911
C	1.193437	1.940898	-2.845961
H	1.719896	2.121361	-3.795098
H	0.162226	2.300086	-2.959102
H	1.676994	2.560694	-2.078639
C	-0.046869	-3.029002	-2.278448
H	-1.123967	-2.896495	-2.434162
H	0.344467	-3.645710	-3.101703
H	0.080538	-3.592618	-1.345450
C	0.012548	1.617736	0.689857
C	1.093120	1.089960	1.005932
C	-1.180512	2.409372	0.645362
C	-2.244612	2.117081	1.509169
C	-1.305583	3.460822	-0.271444
C	-3.412871	2.862501	1.448884
H	-2.151208	1.280354	2.199924
C	-2.479588	4.200929	-0.327277
H	-0.473449	3.687762	-0.937513
C	-3.535913	3.901133	0.529376
H	-4.239503	2.618188	2.113544
H	-2.570888	5.016653	-1.042787
H	-4.457234	4.479202	0.479671
C	2.398273	0.937701	1.591177
C	2.855787	-0.299428	2.064625
C	3.235378	2.060653	1.667087
C	4.135571	-0.402655	2.594999
H	2.185227	-1.155844	1.997168
C	4.512949	1.945810	2.199229
H	2.869971	3.018645	1.297324
C	4.967568	0.713361	2.661172
H	4.486788	-1.365201	2.964070
H	5.156950	2.822132	2.252300
H	5.969847	0.623535	3.077062

Cp*Rh TS2

Sum of electronic and zero-point Energies = -1497.350350

Sum of electronic and thermal Free Energies = -1497.415190

Rh	-0.46292351	-1.586466	0.746729
C	-1.95310315	-2.351106	4.659175
C	0.74992613	-2.705773	4.569240
C	-3.04202974	-4.068761	2.915385
C	1.28846585	-4.865303	2.978065
C	-1.01168097	-5.635109	1.875806
O	-2.27787405	-1.851800	-2.852739
C	-5.76577057	-4.406996	2.294987
H	-6.56566996	-6.048201	3.290434
H	-6.88277775	-2.740387	2.815345
H	-6.02118939	-4.721119	0.260293
C	-0.67493608	-1.662532	-4.736119
C	1.9154326	-1.146331	-4.183684
C	-1.36017024	-2.020749	-7.255586
C	2.59251917	-0.574607	-1.644654
C	3.79980186	-1.307599	-6.097649
C	0.49637545	-2.041163	-9.150756
H	-3.33600139	-2.378747	-7.704655
C	5.11966186	-0.415276	-0.991195
C	6.36457322	-1.090365	-5.345702
C	3.0309232	-1.737498	-8.619010
H	-0.09142283	-2.369246	-11.098314
C	7.00273898	-0.721673	-2.852666
H	5.66458891	0.114983	0.927750
H	7.83116578	-1.243240	-6.785876
H	4.45319991	-1.852491	-10.103818
H	8.98414696	-0.583951	-2.308336
C	3.85448793	-5.927838	2.531742
H	4.6758318	-6.655849	4.296064
H	3.80578156	-7.483860	1.166848
H	5.15308104	-4.493098	1.772570
C	-3.30100842	-0.419018	6.201886
H	-3.71484603	-1.133222	8.108783
H	-2.16044483	1.302565	6.416974
H	-5.09638137	0.149348	5.331018
C	2.65278074	-1.349458	6.140559
H	2.93207504	-2.296152	7.971509
H	4.49662336	-1.275864	5.194134
H	2.0700261	0.601680	6.532207
C	-1.42803556	-7.642724	-0.049710
H	0.35611555	-8.479041	-0.684908
H	-2.62553118	-9.167976	0.697583
H	-2.37483183	-6.850553	-1.719858
C	0.76802191	2.393127	-0.207567
C	-1.59644519	2.086393	0.253592
C	2.65273131	4.397546	0.008571
C	4.03973244	5.223904	-2.085409
C	2.99830773	5.589142	2.342835
C	5.71386945	7.227261	-1.845486
H	3.77536294	4.280513	-3.895696
C	4.70071639	7.578863	2.582908
H	1.91758009	4.923819	3.968873
C	6.0551373	8.403743	0.487399
H	6.76692813	7.876405	-3.489306
H	4.96395746	8.487568	4.410306
H	7.38160033	9.966320	0.668222
C	-4.07401102	3.112877	0.734132
C	-6.23194353	1.906137	-0.218949
C	-4.34986912	5.269487	2.247475
C	-8.61712272	2.830560	0.366941
H	-5.96336289	0.261161	-1.428518
C	-6.74401624	6.177288	2.829569
H	-2.66592605	6.213020	2.966599
C	-8.88116438	4.954390	1.902273
H	-10.28666313	1.889890	-0.383797
H	-6.94244221	7.846779	4.016093
H	-10.75583112	5.664513	2.366457

Cp*Rh IM4

Sum of electronic and zero-point Energies = -1497.383943

Sum of electronic and thermal Free Energies = -1497.448448

Rh	0.746221	0.688773	-0.025752
C	1.000838	2.654355	-0.975891
C	1.782132	1.684025	-1.669989
C	1.462901	2.658294	0.388423
C	2.854403	1.224619	-0.778875
C	2.663214	1.819254	0.470795

O	0.485496	-0.212293	1.912721
C	0.949592	3.501139	1.500517
H	1.539492	4.425172	1.600335
H	-0.098923	3.781470	1.340643
H	1.008033	2.961623	2.454909
C	1.1182	-1.338231	1.707827
C	1.050424	-1.946613	0.389367
C	1.964697	-1.913632	2.652818
C	0.045872	-1.574024	-0.576760
C	2.072356	-2.875518	0.008474
C	2.866729	-2.925624	2.287041
H	1.983094	-1.478735	3.651214
C	0.221955	-1.962717	-1.905693
C	2.162653	-3.267294	-1.345916
C	2.966511	-3.370890	0.988624
H	3.54475	-3.321594	3.043484
C	1.286551	-2.784061	-2.295364
H	-0.546008	-1.681556	-2.627936
H	2.951817	-3.965317	-1.629060
H	3.72073	-4.100224	0.695225
H	1.384181	-3.088416	-3.336605
C	3.866268	0.200389	-1.157027
H	4.581439	0.598443	-1.891929
H	4.431179	-0.149969	-0.285245
H	3.391672	-0.684338	-1.608294
C	-0.093004	3.495979	-1.530165
H	0.292223	4.477578	-1.842507
H	-0.560276	3.026303	-2.404551
H	-0.888397	3.666409	-0.792969
C	1.658097	1.292247	-3.101120
H	2.372346	1.844343	-3.730455
H	1.856512	0.220466	-3.234536
H	0.648958	1.489571	-3.482888
C	3.391768	1.555659	1.741102
H	4.18791	0.814751	1.607299
H	3.8414	2.473840	2.145378
H	2.697523	1.156502	2.496058
C	-1.312325	-0.987647	-0.238717
C	-1.255176	0.339836	-0.080612
C	-2.456346	-1.914975	-0.147824
C	-2.253062	-3.298935	-0.255218
C	-3.765112	-1.462507	0.083933
C	-3.311661	-4.192046	-0.142035
H	-1.248054	-3.686152	-0.422825
C	-4.820909	-2.356422	0.191006
H	-3.95776	-0.396908	0.187641
C	-4.603582	-3.727324	0.076498
H	-3.121133	-5.261266	-0.225209
H	-5.826191	-1.976351	0.369027
H	-5.434445	-4.425998	0.160921
C	-2.227467	1.391448	0.159820
C	-2.298786	2.015874	1.415009
C	-3.057739	1.856241	-0.871017
C	-3.17835	3.070662	1.627471
H	-1.653381	1.650219	2.214233
C	-3.934562	2.913098	-0.653949
H	-3.006272	1.367448	-1.845104
C	-3.995575	3.527197	0.594428
H	-3.230078	3.539438	2.609518
H	-4.574097	3.259858	-1.464653
H	-4.681194	4.355806	0.764091

Cp*Rh IM4’

Sum of electronic and zero-point Energies = -1497.384784

Sum of electronic and thermal Free Energies = -1497.448233

Rh	0.954638	-0.489625	-0.021484
C	1.433137	-1.943525	1.538798
C	2.359884	-0.863791	1.607037
C	1.581076	-2.536667	0.230401
C	3.214184	-0.902218	0.422522
C	2.732395	-1.912121	-0.417528
O	0.349947	0.219980	-1.941987
C	0.857141	-3.725723	-0.292121
H	1.402292	-4.652446	-0.054840
H	-0.150996	-3.805215	0.133551
H	0.746423	-3.672130	-1.382599
C	1.058213	1.261321	-1.593563
C	0.736018	2.068863	-0.402849
C	2.217408	1.576908	-2.334400
C	-0.495122	2.003534	0.352443
C	1.688565	3.093571	-0.036216
C	3.085391	2.588253	-1.955006
H	2.393311	0.974782	-3.224647
C	-0.716202	2.905706	1.372651
C	1.424598	3.944728	1.069976
C	2.845515	3.318032	-0.802835
H	3.966202	2.801633	-2.560543
C	0.242871	3.864927	1.750221
H	-1.657271	2.841314	1.918145
H	2.173277	4.693282	1.330804
H	3.519134	4.120604	-0.502604
H	0.034313	4.540031	2.578957
C	4.342276	0.039085	0.184988
H	5.130223	-0.097294	0.940393
H	4.793895	-0.107920	-0.802530
H	4.017208	1.089237	0.235280
C	0.533877	-2.404330	2.631321
H	1.085832	-3.031500	3.346637
H	0.106589	-1.559660	3.187262
H	-0.298391	-3.000045	2.239897
C	2.521048	0.099726	2.730763
H	3.340801	-0.199599	3.401875
H	2.747434	1.107309	2.356419
H	1.603751	0.170935	3.327592
C	3.183611	-2.247343	-1.795592
H	4.003099	-1.598379	-2.123806
H	3.526183	-3.289877	-1.863256
H	2.357853	-2.121979	-2.510928
C	-1.516954	0.932161	0.182389
C	-1.082261	-0.338221	0.157013
C	-2.931318	1.360653	0.064087
C	-3.249376	2.443065	-0.768470
C	-3.974297	0.727020	0.748079
C	-4.564015	2.859257	-0.930984
H	-2.446527	2.953409	-1.301048
C	-5.290971	1.144992	0.588324
H	-3.746732	-0.097639	1.420636
C	-5.592932	2.210546	-0.252925
H	-4.787048	3.696065	-1.591735
H	-6.085750	0.637494	1.133669
H	-6.624099	2.538411	-0.375899
C	-1.862981	-1.549474	-0.104264

C	-2.016807	-1.979302	-1.432006
C	-2.433616	-2.323101	0.915864
C	-2.719039	-3.142198	-1.722393
H	-1.568842	-1.377411	-2.222257
C	-3.131351	-3.491372	0.622190
H	-2.339732	-1.986670	1.949573
C	-3.274185	-3.907458	-0.698291
H	-2.837662	-3.454237	-2.759465
H	-3.574513	-4.073274	1.429667
H	-3.823231	-4.818982	-0.929267

Cp*Rh TS3

Sum of electronic and zero-point Energies = -1497.352912

Sum of electronic and thermal Free Energies = -1497.414835

Rh	1.070615	-0.474114	-0.039369
C	1.004668	-1.320233	1.992640
C	2.048547	-0.351332	1.864284
C	1.320622	-2.361313	1.061756
C	3.129265	-0.922021	1.046352
C	2.682763	-2.142652	0.559989
O	0.101103	-0.078991	-2.015641
C	0.536402	-3.601689	0.814323
H	0.888184	-4.421222	1.460019
H	-0.533613	-3.453290	1.005078
H	0.636528	-3.934485	-0.226778
C	1.015285	0.896073	-1.798259
C	0.816164	1.928510	-0.798914
C	2.196072	0.844754	-2.553178
C	-0.461927	2.162502	-0.145004
C	1.874910	2.897096	-0.650705
C	3.214411	1.763558	-2.331861
H	2.282132	0.058219	-3.300460
C	-0.647735	3.371939	0.505027
C	1.657336	4.037444	0.165294
C	3.066170	2.762465	-1.382934
H	4.129024	1.702126	-2.920036
C	0.412022	4.279982	0.686155
H	-1.624898	3.604374	0.923179
H	2.473985	4.746241	0.300374
H	3.848533	3.508586	-1.241985
H	0.231372	5.191323	1.255536
C	4.398403	-0.206997	0.741135
H	4.961350	0.022428	1.657818
H	5.049701	-0.798695	0.087382
H	4.204744	0.749367	0.229663
C	-0.206467	-1.196224	2.850280
H	0.032104	-1.361572	3.911145
H	-0.656374	-0.196013	2.759826
H	-0.973917	-1.925045	2.562532
C	2.133360	0.945463	2.591620
H	2.669986	0.830306	3.546241
H	2.663221	1.702508	1.998449
H	1.134026	1.342698	2.811761
C	3.363705	-3.060845	-0.393145
H	4.335003	-2.667341	-0.713550
H	3.532866	-4.051788	0.053745
H	2.756366	-3.215968	-1.296564
C	-1.443434	1.108484	-0.231572
C	-0.942824	-0.126084	-0.605364
C	-2.883753	1.342509	0.010455
C	-3.828807	1.095020	-0.994087
C	-3.354457	1.775367	1.258789
C	-5.187487	1.269736	-0.761051
H	-3.478979	0.754694	-1.969002
C	-4.712692	1.964674	1.490172
H	-2.638301	1.937259	2.066109
C	-5.636618	1.710866	0.480820
H	-5.901531	1.066935	-1.558458
H	-5.052341	2.298301	2.470246
H	-6.701058	1.852152	0.662070
C	-1.705110	-1.378649	-0.722811
C	-1.539082	-2.274549	-1.788549
C	-2.602659	-1.727617	0.300665
C	-2.249938	-3.468919	-1.829476
H	-0.851177	-2.021704	-2.590643
C	-3.306810	-2.923954	0.256454
H	-2.756264	-1.041282	1.131913
C	-3.134472	-3.803894	-0.809166
H	-2.110887	-4.143410	-2.673557
H	-4.001694	-3.165624	1.059608
H	-3.689576	-4.739832	-0.845732

Cp*Rh IM5

Sum of electronic and zero-point Energies = -1497.400185

Sum of electronic and thermal Free Energies = -1497.462721

Rh	1.737553	-0.530730	-0.304684
C	1.502170	-0.318266	1.946575
C	2.743167	0.214123	1.426902
C	1.509658	-1.690775	1.625186
C	3.604167	-0.906502	1.020582
C	2.835541	-2.062371	1.111941
O	-0.325275	-0.133979	-1.886740
C	0.407603	-2.673857	1.825469
H	0.624781	-3.362909	2.656523
H	-0.547231	-2.177837	2.039513
H	0.253942	-3.289208	0.926310
C	0.665602	0.779430	-1.494232
C	0.232259	2.041742	-0.965266
C	1.938499	0.623598	-2.133496
C	-1.074759	2.150696	-0.450717
C	1.138740	3.121821	-0.944044
C	2.810721	1.770764	-2.105527
H	2.050611	-0.109051	-2.935574
C	-1.479261	3.378151	0.071249
C	0.701892	4.332764	-0.378487
C	2.446179	2.944486	-1.521961
H	3.786997	1.685993	-2.583964
C	-0.587471	4.454967	0.111248
H	-2.489285	3.497298	0.459128
H	1.387376	5.180325	-0.346794
H	3.131346	3.792732	-1.508847
H	-0.917728	5.403548	0.531976
C	5.021083	-0.757158	0.587234
H	5.683517	-0.540237	1.440243
H	5.395026	-1.665850	0.100482
H	5.134379	0.068884	-0.127839
C	0.407265	0.480021	2.568305
H	0.606762	0.701709	3.628226
H	0.266865	1.443179	2.052610
H	-0.551400	-0.055161	2.517595

C	3.207943	1.619502	1.575574
H	3.784069	1.742914	2.506263
H	3.852148	1.921414	0.739693
H	2.364685	2.321706	1.606491
C	3.227754	-3.458911	0.771803
H	4.180336	-3.492679	0.229809
H	3.337002	-4.078869	1.675632
H	2.473678	-3.947734	0.139992
C	-1.903306	0.939901	-0.456832
C	-1.461407	-0.173179	-1.102481
C	-3.214994	0.964251	0.232519
C	-4.391380	0.713519	-0.480222
C	-3.306921	1.233251	1.603439
C	-5.622829	0.696386	0.163668
H	-4.326091	0.515072	-1.549713
C	-4.538337	1.215015	2.248910
H	-2.396586	1.444784	2.165634
C	-5.699723	0.940963	1.531631
H	-6.527891	0.492461	-0.406396
H	-4.590857	1.413209	3.318500
H	-6.663826	0.925080	2.037395
C	-2.019662	-1.536553	-1.077330
C	-1.751943	-2.406653	-2.143693
C	-2.726876	-2.035929	0.026427
C	-2.196042	-3.722779	-2.117799
H	-1.187797	-2.040261	-2.997986
C	-3.162938	-3.353625	0.051320
H	-2.920328	-1.394063	0.883928
C	-2.904050	-4.203150	-1.020887
H	-1.983290	-4.377846	-2.961267
H	-3.701610	-3.721636	0.923115
H	-3.247364	-5.236162	-0.998070

$Cp^{E}Rh$ IM1

Sum of electronic and zero-point Energies = -1564.358525

Sum of electronic and thermal Free Energies = -1564.422951

Rh	-0.811540	0.286298	-0.315373
C	-1.901369	-1.496450	-0.878024
C	-2.367941	-1.052685	0.419444
C	-0.513962	-1.855011	-0.761205
C	-1.256796	-1.062574	1.325936
C	-0.113329	-1.564253	0.592345
O	0.660900	1.292413	-1.289882
C	0.333069	-2.427955	-1.837759
H	0.636329	-3.449349	-1.572776
H	-0.202617	-2.465290	-2.791500
H	1.254953	-1.847091	-1.971206
C	-1.739216	2.651769	-0.200438
O	-2.048380	1.864896	-1.150951
O	-1.028920	2.223096	0.752538
C	-2.187015	4.077674	-0.235475
H	-3.103444	4.181730	-0.823832
H	-2.336565	4.454625	0.780732
H	-1.402435	4.679021	-0.711010
C	1.896467	0.839302	-1.346569
C	2.775751	0.973201	-0.213381
C	2.399145	0.288549	-2.521867
C	2.316136	1.508623	1.010740
C	4.138397	0.575346	-0.335162
C	3.745697	-0.106813	-2.623986
H	1.722355	0.207504	-3.372430
C	3.167111	1.624213	2.086080
H	1.282162	1.847293	1.078013
C	4.991708	0.727336	0.784984
C	4.603473	0.030515	-1.558695
H	4.109379	-0.518457	-3.565133
C	4.517454	1.232474	1.971754
H	2.801152	2.032297	3.026913
H	6.036736	0.428824	0.686840
H	5.649730	-0.266347	-1.639497
H	5.185357	1.338223	2.825606
C	-3.710041	-0.516591	0.745151
O	-3.960759	0.218123	1.671794
O	-4.636935	-0.962806	-0.115765
C	-5.953137	-0.462391	0.111775
H	-5.965906	0.629689	0.032716
H	-6.579877	-0.910899	-0.661045
H	-6.305034	-0.749075	1.108228
C	1.195773	-1.829280	1.234806
O	1.371981	-1.806515	2.431056
O	2.138638	-2.135228	0.341164
C	3.423808	-2.417730	0.897747
H	4.089023	-2.555216	0.042993
H	3.762798	-1.577984	1.513710
H	3.377414	-3.325202	1.510299
C	-1.240813	-0.606056	2.738969
H	-1.168779	-1.474001	3.407503
H	-0.348671	0.002685	2.925391
H	-2.138566	-0.028777	2.967314
C	-2.698566	-1.536603	-2.132970
H	-3.373009	-2.403085	-2.134048
H	-3.318015	-0.638629	-2.225527
H	-2.048181	-1.595396	-3.011314

$Cp^{E}Rh$ TS1

Sum of electronic and zero-point Energies = -1564.330557

Sum of electronic and thermal Free Energies = -1564.396155

Rh	-0.496812	0.084896	-0.364257
C	-1.957366	-1.498211	-0.954270
C	-2.088337	-1.171553	0.460312
C	-0.639554	-1.987724	-1.161474
C	-0.875187	-1.516524	1.136691
C	0.053930	-1.946859	0.118253
O	0.934045	0.657899	-1.755891
C	-0.040373	-2.361391	-2.470534
H	0.471235	-3.327635	-2.402165
H	-0.802552	-2.423403	-3.253466
H	0.706814	-1.611253	-2.764014
C	-1.415845	2.859783	-0.893088
O	-1.723917	1.647106	-1.103805
O	-0.459891	3.248402	-0.180030
C	-2.260945	3.902075	-1.575507
H	-3.238896	3.498189	-1.850962
H	-2.370241	4.778882	-0.930442
H	-1.745201	4.220777	-2.489621
C	2.106225	0.861368	-1.185608
C	2.136820	1.096482	0.218972
C	3.314871	0.815139	-1.873371
C	0.878425	1.225486	0.882382
C	3.361552	1.170690	0.926149

C	4.528596	0.940665	-1.170511
H	3.305495	0.654835	-2.950249
C	0.864410	1.355859	2.265847
H	0.138489	2.125882	0.348649
C	3.283608	1.307800	2.333807
C	4.575354	1.091287	0.199656
H	5.460788	0.892015	-1.733748
C	2.071208	1.392080	2.987610
H	-0.087779	1.472201	2.786774
H	4.212780	1.352737	2.903810
H	5.525529	1.158954	0.728563
H	2.049361	1.509545	4.070208
C	-3.245010	-0.530036	1.126650
O	-3.194198	0.071369	2.175811
O	-4.374670	-0.690263	0.423209
C	-5.521568	-0.051323	0.979222
H	-5.361024	1.029824	1.048630
H	-6.345812	-0.274174	0.299295
H	-5.731418	-0.441755	1.980488
C	1.473031	-2.261645	0.406498
O	1.941708	-2.341114	1.519471
O	2.186871	-2.407669	-0.714756
C	3.593770	-2.551227	-0.518363
H	4.021651	-2.649069	-1.517887
H	3.997837	-1.660969	-0.021289
H	3.808572	-3.438406	0.086791
C	-0.644396	-1.517881	2.605378
H	-0.771173	-2.548626	2.968366
H	0.379499	-1.226909	2.848991
H	-1.365549	-0.874735	3.114172
C	-2.987006	-1.273761	-2.005219
H	-3.822610	-1.976353	-1.893173
H	-3.395624	-0.260084	-1.928604
H	-2.560503	-1.390102	-3.006492

Cp^ERh IM2

Sum of electronic and zero-point Energies = -1564.347266

Sum of electronic and thermal Free Energies = -1564.411376

Rh	-0.425302	0.013435	-0.326707
C	-2.259174	-1.307850	-0.931072
C	-2.283158	-0.875586	0.472665
C	-1.081157	-2.033873	-1.133169
C	-1.171157	-1.443841	1.164289
C	-0.349029	-2.047351	0.141282
O	1.159131	0.172750	-1.643831
C	-0.566584	-2.573031	-2.421394
H	-0.238605	-3.613200	-2.308846
H	-1.332526	-2.535700	-3.203018
H	0.304427	-1.989827	-2.749173
C	-0.649845	2.992750	-1.289143
O	-1.216407	1.910489	-1.147892
O	0.493880	3.315027	-0.736016
C	-1.223632	4.085351	-2.129445
H	-2.220048	3.809920	-2.480198
H	-1.262076	5.018421	-1.557167
H	-0.565082	4.257901	-2.988998
C	2.307776	0.407834	-1.037213
C	2.246155	0.812238	0.327092
C	3.552091	0.314962	-1.648071
C	0.953301	0.854647	0.913698
C	3.408486	1.184113	1.051516
C	4.707442	0.653014	-0.914876
H	3.616785	0.005016	-2.689787
C	0.807250	1.330716	2.199384
H	0.822449	2.561064	-0.184996
C	3.219610	1.644606	2.378390
C	4.659212	1.081099	0.395979
H	5.674735	0.580753	-1.412892
C	1.958460	1.732378	2.922574
H	-0.175977	1.386750	2.669444
H	4.091977	1.941515	2.961727
H	5.569630	1.349740	0.931217
H	1.836736	2.108193	3.938487
C	-3.309577	-0.040546	1.133960
O	-3.149763	0.575622	2.164267
O	-4.469105	-0.043092	0.455856
C	-5.497557	0.760266	1.026770
H	-5.180656	1.807079	1.086305
H	-6.359283	0.657359	0.364507
H	-5.744161	0.410954	2.035000
C	0.982057	-2.633098	0.433389
O	1.382150	-2.885069	1.546951
O	1.709273	-2.796233	-0.677088
C	3.074332	-3.144937	-0.454358
H	3.521120	-3.237869	-1.445939
H	3.575378	-2.349536	0.110454
H	3.149632	-4.087267	0.098623
C	-0.922319	-1.465437	2.630732
H	-1.091294	-2.485357	3.002679
H	0.117815	-1.219873	2.862702
H	-1.592392	-0.775346	3.148602
C	-3.249222	-0.918100	-1.974233
H	-4.220308	-1.399790	-1.804480
H	-3.420145	0.165256	-1.958349
H	-2.895384	-1.188638	-2.974539

Cp^ERh IM3

Sum of electronic and zero-point Energies = -1874.289020

Sum of electronic and thermal Free Energies = -1874.360846

Rh	0.086028	-0.329395	-0.268825
C	1.617090	-1.249894	-1.751853
C	1.723818	0.163048	-1.805998
C	0.262566	-1.589271	-2.117109
C	0.459256	0.738114	-2.222013
C	-0.422718	-0.371096	-2.450339
O	-0.254778	-2.017583	0.938663
C	-0.236695	-2.991954	-2.144350
H	-1.198774	-3.071776	-2.652248
H	0.491678	-3.643241	-2.645772
H	-0.360587	-3.357229	-1.112984
C	-1.497603	-2.088699	1.384449
C	-2.379129	-1.027758	1.044588
C	-1.981881	-3.138999	2.153665
C	-1.855164	0.025917	0.265387
C	-3.734726	-1.019361	1.470542
C	-3.325618	-3.127773	2.574347
H	-1.317034	-3.958732	2.421730
C	-2.649946	1.083157	-0.101325
C	-4.533216	0.086517	1.081974
C	-4.193448	-2.105810	2.252558

H	-3.686044	-3.961591	3.177415
C	-4.004615	1.101510	0.319457
H	-2.266900	1.918845	-0.689149
H	-5.575834	0.120075	1.400856
H	-5.228683	-2.120933	2.593098
H	-4.629144	1.948226	0.033091
C	2.910272	0.975455	-1.458735
O	2.882121	2.099720	-1.004773
O	4.046960	0.323103	-1.738277
C	5.245125	1.039708	-1.452972
H	5.323210	1.242102	-0.378934
H	6.062394	0.393540	-1.778168
H	5.263203	1.989908	-1.996978
C	-1.832903	-0.185575	-2.862094
O	-2.260697	0.844221	-3.332984
O	-2.581406	-1.270111	-2.630935
C	-3.985542	-1.085286	-2.798225
H	-4.436367	-2.062296	-2.615431
H	-4.348392	-0.356579	-2.062586
H	-4.214843	-0.732438	-3.809172
C	0.203452	2.169105	-2.553752
H	0.044068	2.282891	-3.633535
H	-0.707573	2.541469	-2.070670
H	1.045879	2.793040	-2.243162
C	2.634864	-2.249193	-1.318712
H	3.170272	-2.670325	-2.182094
H	3.380357	-1.805470	-0.650021
H	2.149024	-3.074312	-0.782409
C	0.439612	1.240454	1.370622
C	1.260030	0.309747	1.482633
C	-0.275624	2.474125	1.494010
C	0.167414	3.586072	0.763468
C	-1.414541	2.576242	2.302519
C	-0.529441	4.784633	0.843164
H	1.055045	3.483539	0.137976
C	-2.099268	3.781020	2.379315
H	-1.766218	1.697510	2.842003
C	-1.662296	4.883125	1.648169
H	-0.187060	5.647232	0.273977
H	-2.987899	3.855705	3.003513
H	-2.208017	5.823675	1.704993
C	2.467442	-0.385528	1.839493
C	2.476176	-1.734443	2.217507
C	3.675104	0.329847	1.786574
C	3.679138	-2.351416	2.537239
H	1.532730	-2.275898	2.222681
C	4.870438	-0.299381	2.109231
H	3.653293	1.378347	1.488500
C	4.875972	-1.641148	2.483580
H	3.681729	-3.399674	2.831490
H	5.803115	0.263052	2.075984
H	5.814134	-2.131981	2.737520

Cp^ERh TS2

Sum of electronic and zero-point Energies = -1874.271133

Sum of electronic and thermal Free Energies = -1874.340909

Rh	0.014895	-0.681600	0.005749
C	1.197468	-2.563806	-0.392458
C	1.523121	-1.604728	-1.396688
C	-0.213801	-2.871715	-0.523359
C	0.322533	-1.270453	-2.127362
C	-0.730660	-2.114873	-1.609448
O	-0.402812	-0.911734	2.068998
C	-0.909361	-3.834231	0.376020
H	-1.913425	-4.068356	0.019467
H	-0.331210	-4.764295	0.460610
H	-0.998341	-3.402180	1.384167
C	-1.537805	-0.341503	2.415543
C	-2.259988	0.389740	1.428641
C	-2.092060	-0.460385	3.687319
C	-1.651080	0.605367	0.161967
C	-3.587976	0.837650	1.673786
C	-3.374237	0.053342	3.944834
H	-1.539746	-1.000418	4.454448
C	-2.396417	1.117408	-0.882080
C	-4.307550	1.395490	0.585968
C	-4.128970	0.669928	2.969131
H	-3.793302	-0.072290	4.943411
C	-3.738355	1.495578	-0.663179
H	-1.941533	1.298944	-1.856169
H	-5.331102	1.732473	0.754587
H	-5.140967	1.017663	3.174830
H	-4.311869	1.906577	-1.493636
C	2.809406	-0.889176	-1.547936
O	2.942112	0.220228	-2.019716
O	3.834945	-1.613003	-1.079193
C	5.095217	-0.945225	-1.079825
H	5.045321	-0.044367	-0.456943
H	5.809002	-1.659214	-0.664554
H	5.380573	-0.663184	-2.098819
C	-2.135552	-1.970106	-2.041686
O	-2.474982	-1.475828	-3.094223
O	-3.002092	-2.408059	-1.116564
C	-4.374682	-2.166745	-1.413334
H	-4.936426	-2.585917	-0.576576
H	-4.555767	-1.088351	-1.489485
H	-4.659988	-2.649089	-2.354666
C	0.231007	-0.372797	-3.313210
H	0.224863	-0.975079	-4.232589
H	-0.707747	0.188907	-3.316223
H	1.079619	0.314696	-3.344947
C	2.077139	-3.213074	0.620307
H	2.485238	-4.157832	0.231563
H	2.922987	-2.576216	0.892695
H	1.506265	-3.441042	1.529033
C	0.126549	1.547860	0.213982
C	1.078263	0.886086	0.769846
C	-0.046365	2.818215	-0.481420
C	0.827679	3.124573	-1.531392
C	-1.018775	3.745519	-0.092235
C	0.726765	4.349804	-2.182998
H	1.574573	2.385240	-1.828113
C	-1.101586	4.972068	-0.735711
H	-1.699541	3.492725	0.720011
C	-0.233410	5.274190	-1.784136
H	1.402755	4.581994	-3.004360
H	-1.849891	5.697527	-0.421171
H	-0.308151	6.234766	-2.291586
C	2.372554	0.844025	1.402332
C	2.686111	-0.158877	2.329581
C	3.341861	1.799461	1.061753
C	3.954098	-0.209386	2.894758
H	1.904683	-0.866190	2.605648

C	4.603408	1.747557	1.641796
H	3.094053	2.572773	0.335484
C	4.914706	0.740198	2.553093
H	4.190968	-0.988499	3.617768
H	5.349240	2.495708	1.377239
H	5.905726	0.699833	3.002568

Cp^ERh IM4

Sum of electronic and zero-point Energies = -1874.301767

Sum of electronic and thermal Free Energies = -1874.371204

Rh	-0.288510	-0.600838	0.148713
C	0.173320	-2.702582	0.526127
C	0.215934	-2.478891	-0.894053
C	-1.196920	-2.473924	0.957149
C	-1.090254	-2.055590	-1.325090
C	-1.978102	-2.130526	-0.185789
O	-0.665844	0.537989	1.912575
C	-1.638367	-2.551842	2.376577
H	-2.644159	-2.973245	2.451981
H	-0.948288	-3.159815	2.971579
H	-1.668197	-1.539222	2.808461
C	-1.605687	1.362632	1.512772
C	-1.614244	1.764479	0.125800
C	-2.665537	1.762731	2.319550
C	-0.447602	1.599354	-0.709047
C	-2.834132	2.223309	-0.453760
C	-3.800911	2.369738	1.752525
H	-2.641001	1.495160	3.374868
C	-0.606896	1.671439	-2.095014
C	-2.910535	2.324982	-1.860588
C	-3.923268	2.550584	0.393205
H	-4.631899	2.636198	2.406207
C	-1.839036	2.002989	-2.669171
H	0.275892	1.536037	-2.721672
H	-3.852059	2.651329	-2.303586
H	-4.840987	2.937017	-0.048764
H	-1.934300	2.060958	-3.752033
C	1.395448	-2.579119	-1.777931
O	1.572640	-1.944607	-2.794554
O	2.271258	-3.488600	-1.318185
C	3.449635	-3.640663	-2.102348
H	3.984725	-2.687785	-2.187327
H	4.063004	-4.376892	-1.579102
H	3.199299	-3.992803	-3.108866
C	-3.360872	-1.630336	-0.230521
O	-3.944786	-1.307077	-1.243122
O	-3.911704	-1.546656	0.992578
C	-5.206761	-0.954574	1.024561
H	-5.499553	-0.940159	2.076703
H	-5.165457	0.067511	0.628905
H	-5.917159	-1.543712	0.434031
C	-1.488288	-1.706388	-2.714599
H	-2.116182	-2.508813	-3.126018
H	-2.106963	-0.802154	-2.723302
H	-0.607895	-1.567826	-3.346911
C	1.273151	-3.166539	1.414783
H	1.297164	-4.265103	1.461587
H	2.248862	-2.830224	1.050332
H	1.140939	-2.779766	2.432158
C	0.984726	1.672635	-0.204069
C	1.414402	0.486997	0.227281
C	1.690330	2.963774	-0.287114
C	3.071004	3.065266	-0.060825
C	0.978403	4.136637	-0.573482
C	3.710264	4.295747	-0.115473
H	3.649502	2.168742	0.155242
C	1.620639	5.367654	-0.622266
H	-0.095832	4.085864	-0.753699
C	2.990143	5.454487	-0.395626
H	4.783930	4.349576	0.059782
H	1.044056	6.265457	-0.840419
H	3.494775	6.418327	-0.438785
C	2.633425	-0.046426	0.804254
C	2.811718	-0.037277	2.195494
C	3.621595	-0.623560	-0.006933
C	3.957937	-0.586822	2.756465
H	2.032356	0.404150	2.816214
C	4.766306	-1.170781	0.562092
H	3.479206	-0.618794	-1.089599
C	4.937021	-1.156346	1.944594
H	4.090774	-0.569116	3.837300
H	5.533762	-1.606486	-0.077460
H	5.834187	-1.584589	2.388563

Cp^ERh IM4'

Sum of electronic and zero-point Energies = -1874.300883

Sum of electronic and thermal Free Energies = -1874.372683

Rh	0.744312	0.159387	0.052088
C	1.857487	-0.093980	1.949637
C	2.896975	0.312992	1.027494
C	1.347497	-1.353565	1.505217
C	2.961172	-0.639187	-0.010221
C	1.953635	-1.667045	0.229893
O	0.267339	0.943795	-1.846541
C	0.583289	2.057169	-1.231742
C	-0.245823	2.639791	-0.169146
C	1.798759	2.693271	-1.581180
C	-1.536395	2.149380	0.241944
C	0.236747	3.855677	0.436757
C	2.228108	3.852615	-0.961239
H	2.383178	2.214492	-2.364211
C	-2.285878	2.891661	1.131769
C	-0.559038	4.535113	1.398451
C	1.461312	4.422666	0.043878
H	3.168699	4.312509	-1.261184
C	-1.805103	4.078749	1.719366
H	-3.263746	2.510627	1.423623
H	-0.159906	5.445406	1.846186
H	1.776761	5.351195	0.520086
H	-2.424571	4.613933	2.436988
C	1.508692	0.657100	3.187142
H	0.584669	0.275196	3.628063
H	2.315016	0.577539	3.932334
H	1.374439	1.724542	2.963012
C	3.693025	1.553423	1.222888
H	4.412624	1.699107	0.414788
H	3.037466	2.438490	1.254112
H	4.222234	1.513086	2.186092
C	1.690223	-2.880163	-0.591466
H	1.740605	-2.643209	-1.658138

H	2.443180	-3.654285	-0.384981
H	0.703274	-3.294577	-0.364957
C	-2.061593	0.810883	-0.123373
C	-1.239809	-0.252411	-0.138757
C	-3.513211	0.710733	-0.424324
C	-4.068422	1.543563	-1.403842
C	-4.352351	-0.187809	0.240347
C	-5.416768	1.461208	-1.726991
H	-3.422674	2.255462	-1.918772
C	-5.703707	-0.268178	-0.079833
H	-3.937390	-0.818979	1.024701
C	-6.240074	0.552711	-1.066126
H	-5.828113	2.110135	-2.499101
H	-6.342323	-0.972718	0.451354
H	-7.298162	0.489917	-1.316045
C	-1.572839	-1.605789	-0.595723
C	-1.482774	-1.885344	-1.968222
C	-1.958283	-2.634018	0.274123
C	-1.771096	-3.155206	-2.451555
H	-1.180642	-1.082684	-2.640292
C	-2.246981	-3.904468	-0.215051
H	-2.044231	-2.418891	1.340857
C	-2.151015	-4.171646	-1.577679
H	-1.703987	-3.353022	-3.520636
H	-2.560460	-4.690393	0.472588
H	-2.379675	-5.165878	-1.958397
C	0.428256	-2.182698	2.314305
O	-0.360718	-1.763197	3.131657
O	0.622539	-3.490030	2.083281
C	-0.184897	-4.367801	2.860081
H	-1.248913	-4.177664	2.679426
H	0.080619	-5.377459	2.540842
H	0.019666	-4.233984	3.927880
C	3.815504	-0.487889	-1.201635
O	4.388757	0.532369	-1.522625
O	3.915214	-1.628648	-1.904063
C	4.710510	-1.539820	-3.081519
H	4.689611	-2.534435	-3.531116
H	4.295224	-0.798190	-3.772281
H	5.737647	-1.252119	-2.832464

Cp^ERh TS3

Sum of electronic and zero-point Energies = -1874.273823

Sum of electronic and thermal Free Energies = -1874.344379

Rh	1.55467588	0.562487	0.491276
C	0.44146143	4.014663	2.385824
C	3.10065437	3.804627	3.050932
C	-0.89036732	2.001599	3.614321
C	3.42054815	1.582613	4.470948
C	0.97337168	0.319531	4.666143
O	2.52976799	-2.466809	-2.195436
C	3.52290569	-0.288506	-3.087011
C	1.9840884	1.659494	-4.248480
C	6.13799398	0.061393	-2.776326
C	-0.67018227	1.340891	-4.831558
C	3.27998006	3.877903	-5.141132
C	7.29152994	2.280217	-3.562878
H	7.20053639	-1.454153	-1.879962
C	-1.81447605	3.073843	-6.412330
C	1.92093169	5.701866	-6.568671
C	5.88397704	4.164283	-4.720950
H	9.312926	2.527982	-3.274991
C	-0.53779896	5.261812	-7.239565
H	-3.77784375	2.785609	-6.952600
H	2.90943411	7.398194	-7.190003
H	6.80534198	5.873674	-5.409034
H	-1.54555528	6.622338	-8.409855
C	-0.63604937	6.158777	0.914575
H	-2.30803638	5.554815	-0.140729
H	-1.20721372	7.711909	2.175620
H	0.76939236	6.905440	-0.415462
C	5.03416821	5.675620	2.240032
H	6.86817595	5.276564	3.096877
H	5.29630038	5.615273	0.173122
H	4.42491228	7.602574	2.719590
C	0.47095542	-2.134758	5.947984
H	2.04400769	-3.444451	5.660014
H	0.2617072	-1.849113	7.995378
H	-1.26848692	-2.996143	5.238821
C	-1.98423435	-0.763551	-3.672926
C	-0.80528246	-1.895747	-1.676205
C	-4.50809018	-1.603261	-4.553599
C	-4.83395431	-3.978016	-5.665880
C	-6.63349953	-0.062090	-4.212914
C	-7.21382609	-4.789689	-6.428452
H	-3.18910638	-5.193616	-5.913569
C	-9.01102687	-0.865739	-4.992628
H	-6.40284004	1.749093	-3.254597
C	-9.30821974	-3.231747	-6.104982
H	-7.43304153	-6.647515	-7.287195
H	-10.6457954	0.351789	-4.704497
H	-11.17152988	-3.865160	-6.707065
C	-1.68836613	-4.041833	-0.161306
C	-0.17591843	-6.150807	0.366350
C	-4.1374322	-3.952438	0.855775
C	-1.10022454	-8.115417	1.844116
H	1.72629164	-6.236436	-0.400663
C	-5.05122376	-5.927827	2.321781
H	-5.32486318	-2.314138	0.462503
C	-3.53741555	-8.019804	2.827093
H	0.09933627	-9.744550	2.222147
H	-6.96579589	-5.830484	3.074295
H	-4.25558291	-9.567043	3.977541
C	-3.65266196	1.703600	3.513139
O	-5.04639715	2.740842	2.015101
O	-4.51213727	0.181000	5.360536
C	-7.17661738	-0.155046	5.409505
H	-7.86663847	-0.868531	3.590900
H	-7.54442889	-1.526199	6.907897
H	-8.12938915	1.637805	5.816933
C	5.90312035	0.618105	5.253198
O	7.91852961	1.326250	4.415241
O	5.72569547	-1.156592	7.070297
C	8.07707665	-2.170219	7.888240
H	7.61832699	-3.563120	9.339857
H	9.07717849	-3.068116	6.313245
H	9.28280696	-0.679744	8.669206

Cp^ERh IM5

Sum of electronic and zero-point Energies = -1874.334276

Sum of electronic and thermal Free Energies =

-1874.402904

Rh	1.460455	0.348119	-0.429675
C	1.614155	0.964471	1.675417
C	2.940237	0.847577	1.073846
C	1.058840	-0.344701	1.754053
C	3.203942	-0.543757	0.836337
C	1.968893	-1.244076	1.074436
O	-0.418670	0.291497	-2.082613
C	0.137742	1.467408	-1.576666
C	-0.724457	2.421581	-0.950649
C	1.427719	1.807505	-2.073493
C	-2.010796	2.016135	-0.543134
C	-0.239534	3.726653	-0.728789
C	1.872190	3.153700	-1.817490
H	1.854688	1.251664	-2.909150
C	-2.836980	2.963418	0.055324
C	-1.098197	4.645917	-0.100777
C	1.090587	4.057790	-1.166783
H	2.859183	3.446126	-2.174781
C	-2.375377	4.266854	0.272083
H	-3.841835	2.686454	0.367624
H	-0.747105	5.661817	0.080981
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H	-3.035267	4.990177	0.748262
C	1.022660	2.224822	2.200829
H	-0.038843	2.304602	1.941975
H	1.080753	2.242960	3.298833
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C	3.891036	1.985767	0.940873
H	4.654134	1.770341	0.189483
H	3.360391	2.907587	0.670732
H	4.407271	2.163740	1.896396
C	1.678985	-2.670046	0.739491
H	2.257406	-2.985465	-0.132453
H	1.952147	-3.330007	1.575415
H	0.610680	-2.813816	0.542766
C	-2.368278	0.607259	-0.735320
C	-1.529728	-0.215030	-1.419355
C	-3.649099	0.107078	-0.181817
C	-4.616618	-0.436776	-1.031486
C	-3.908571	0.164271	1.193085
C	-5.807096	-0.940141	-0.519795
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C	-6.050572	-0.897783	0.849723
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H	-5.284902	-0.303632	2.775513
H	-6.981847	-1.293609	1.251978
C	-1.552270	-1.682098	-1.539485
C	-0.920202	-2.297170	-2.629459
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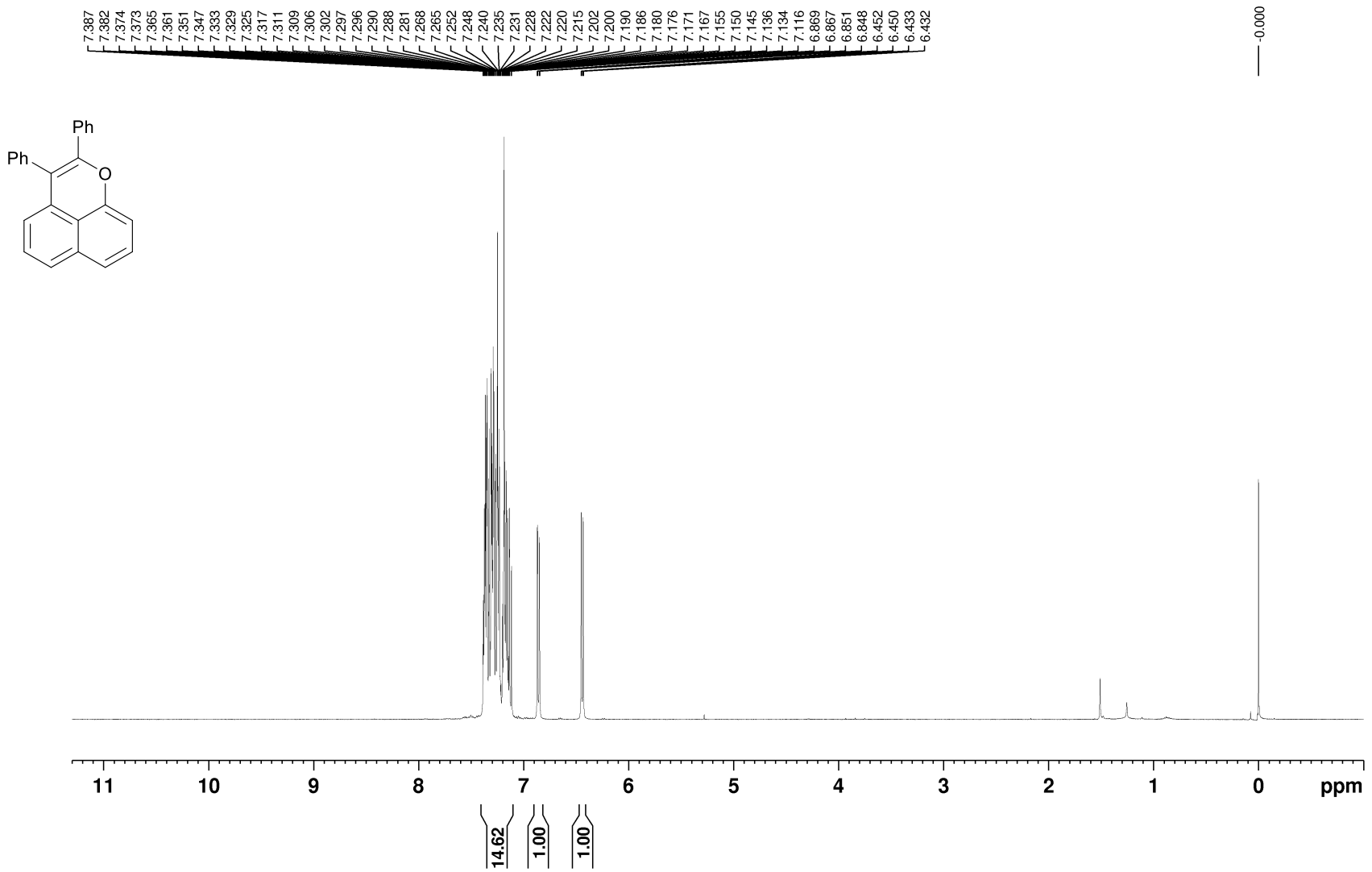
H	5.936706	-2.536149	-1.297580
H	6.533086	-2.691014	0.369732

9. References

1 Y. Shibata and K. Tanaka, *Angew. Chem. Int. Ed.*, 2011, **50**, 10917–10921.
2 S. Kamila, C. Mukherjee and A. De, *Tetrahedron Lett.*, 2001, **42**, 5955–5957.
3 F. Wendler, K. R. A. Schneider, B. Dietzek and F. H. Schacher, *Polym. Chem.*, 2017, **8**, 2959.
4 M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199–3202.
5 E. Kudo, Y. Shibata, M. Yamazaki, K. Masutomi, Y. Miyauchi, M. Fukui, H. Sugiyama, H. Uekusa, T. Satoh, M. Miura and K. Tanaka, *Chem. Eur. J.*, 2016, **22**, 14190–14194.
6 L. E. Sattler and G. Hilt, *Chem. Eur. J.*, 2021, **27**, 605–608.
7 V. Weingand, T. Wurm, V. Vethacke, M. C. Dietl, D. Ehjeij, M. Rudolph, F. Rominger, J. Xie and A. S. K. Hashmi, *Chem. Eur. J.*, 2018, **24**, 3725–3728.
8 M. N. A. Fetzer, G. Tavakoli, A. Klein and M. H. G. Prechtl, *ChemCatChem*, 2021, **13**, 1317–1325.
9 S. Mochida, M. Shimizu, K. Hirano, T. Satoh and M. Miura, *Chem. Asian J.*, 2010, **5**, 847–851.
10 V. S. Thirunavukkarasu, M. Donati and L. Ackermann, *Org. Lett.*, 2012, **14**, 3416–3419.
11 M. Shimizu, H. Tsurugi, T. Satoh and M. Miura, *Chem. Asian J.*, 2008, **3**, 881–886.
12 S. Baruah, P. P. Kaishap and S. Gogoi, *Chem. Commun.*, 2016, **52**, 13004–13007.
13 C.01 Gaussian 16 Revision, CT Gaussian Inc. Wallingford, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016.
14 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
16 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.
17 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
18 K. Ishida, K. Morokuma and A. Komornicki, *J. Chem. Phys.*, 1976, **66**, 2153–2156.
19 C. Gonzalez, H. B. Schlegel and I. Introduction, 1989, **48202**, 2154–2161.
20 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368.
21 C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523–5527.

10. ^{1}H, ^{13}C, ^{19}F, NMR Spectra

^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-diphenylbenzo[*de*]chromene (3aa)



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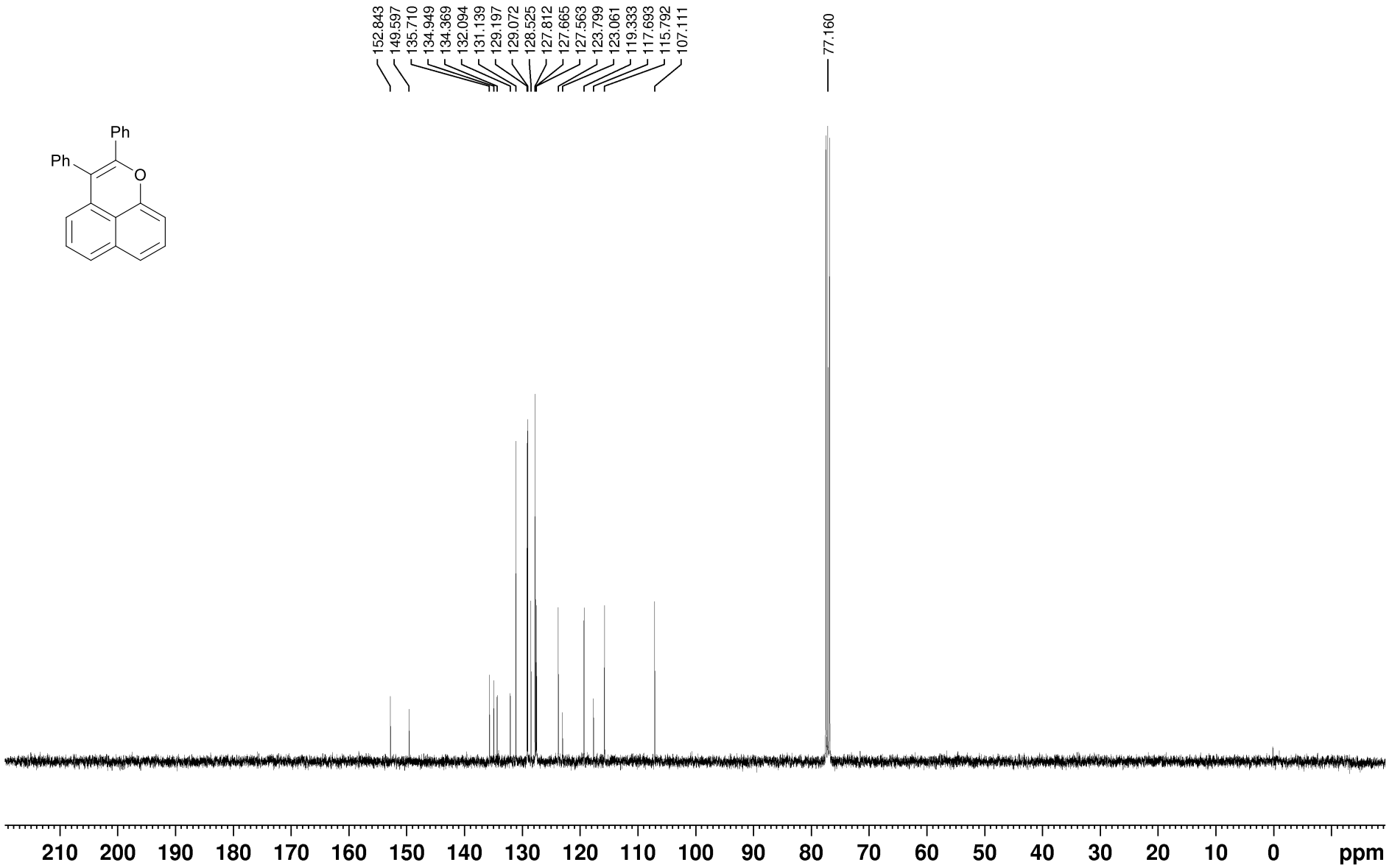

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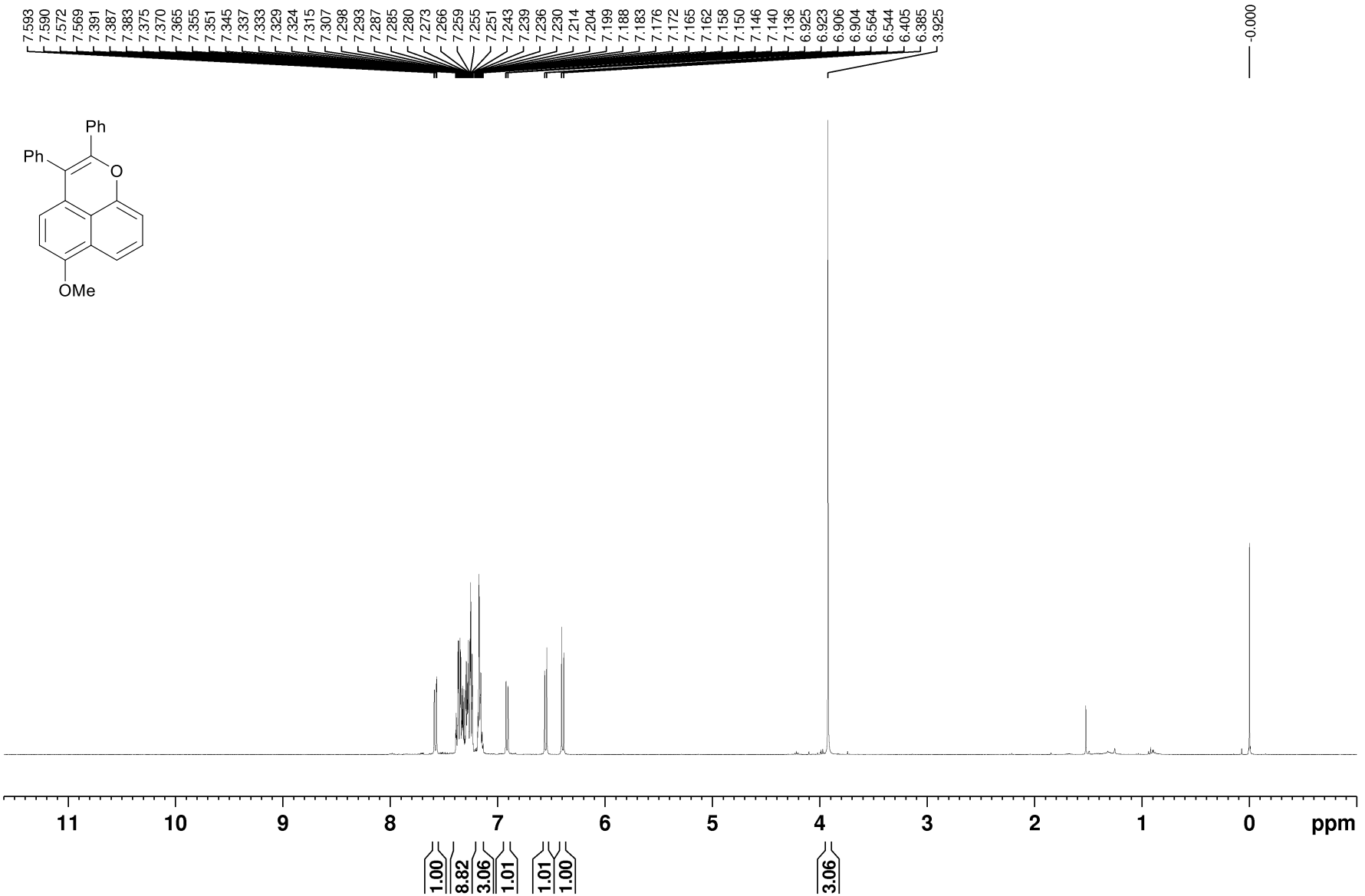

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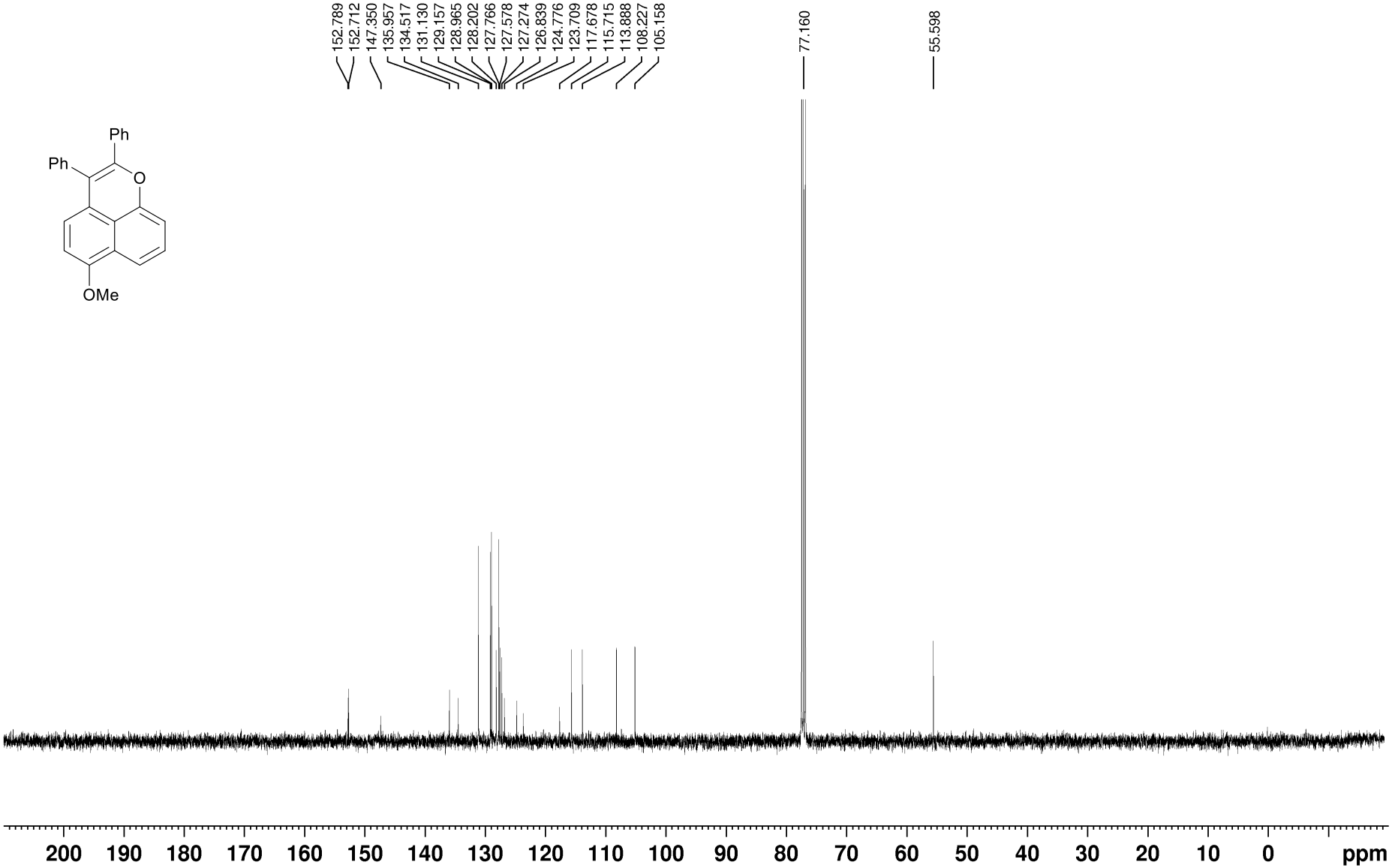
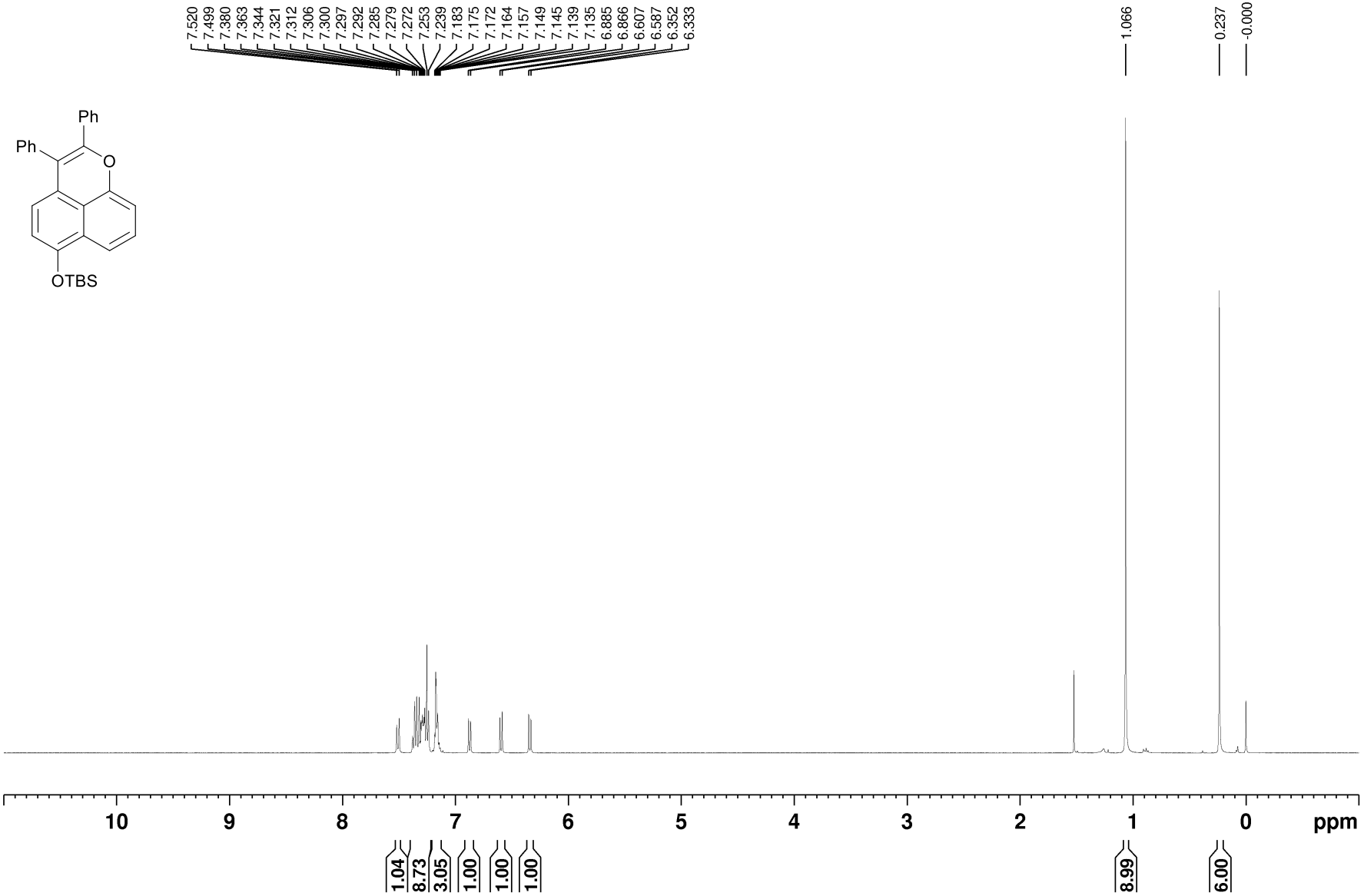
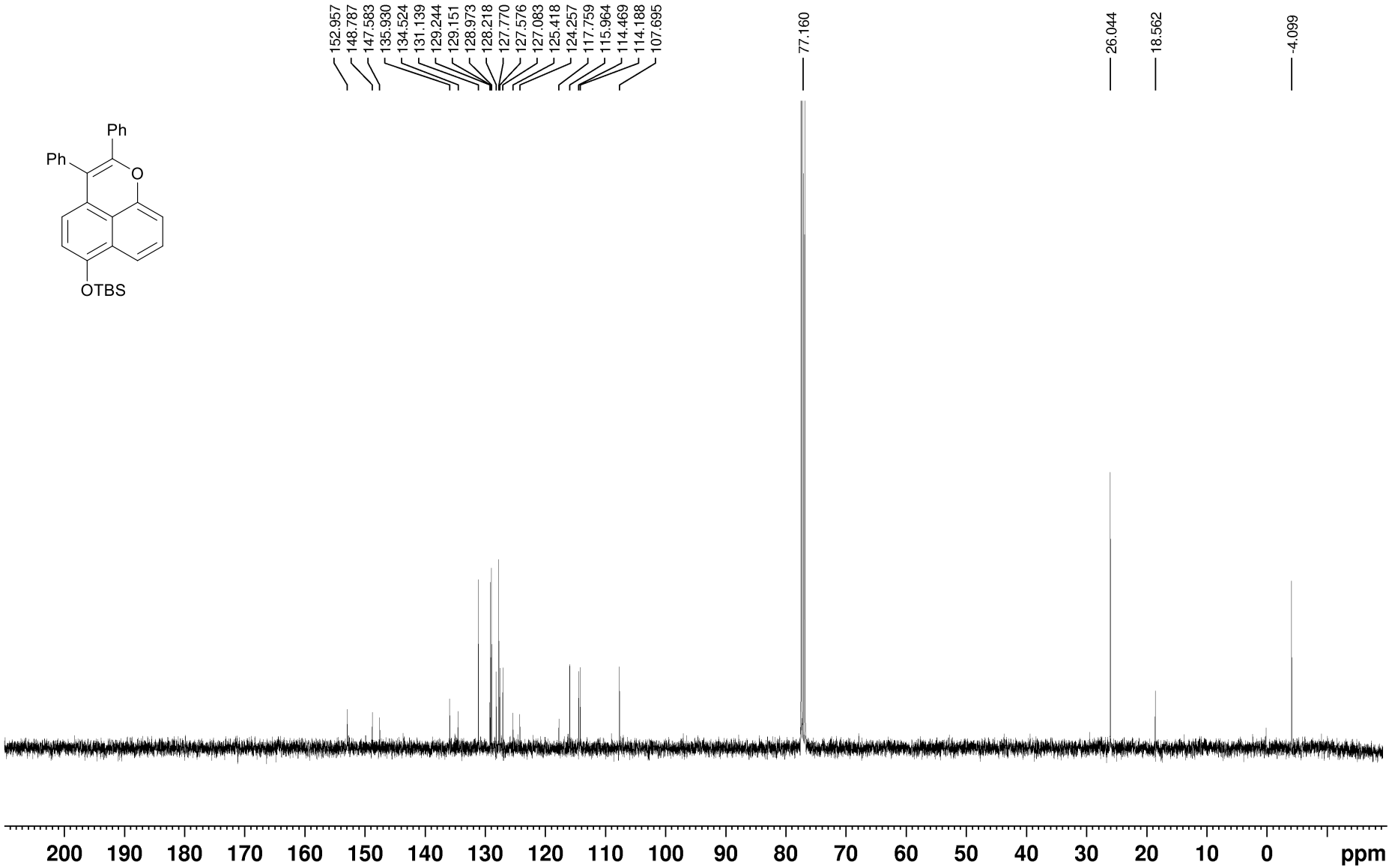


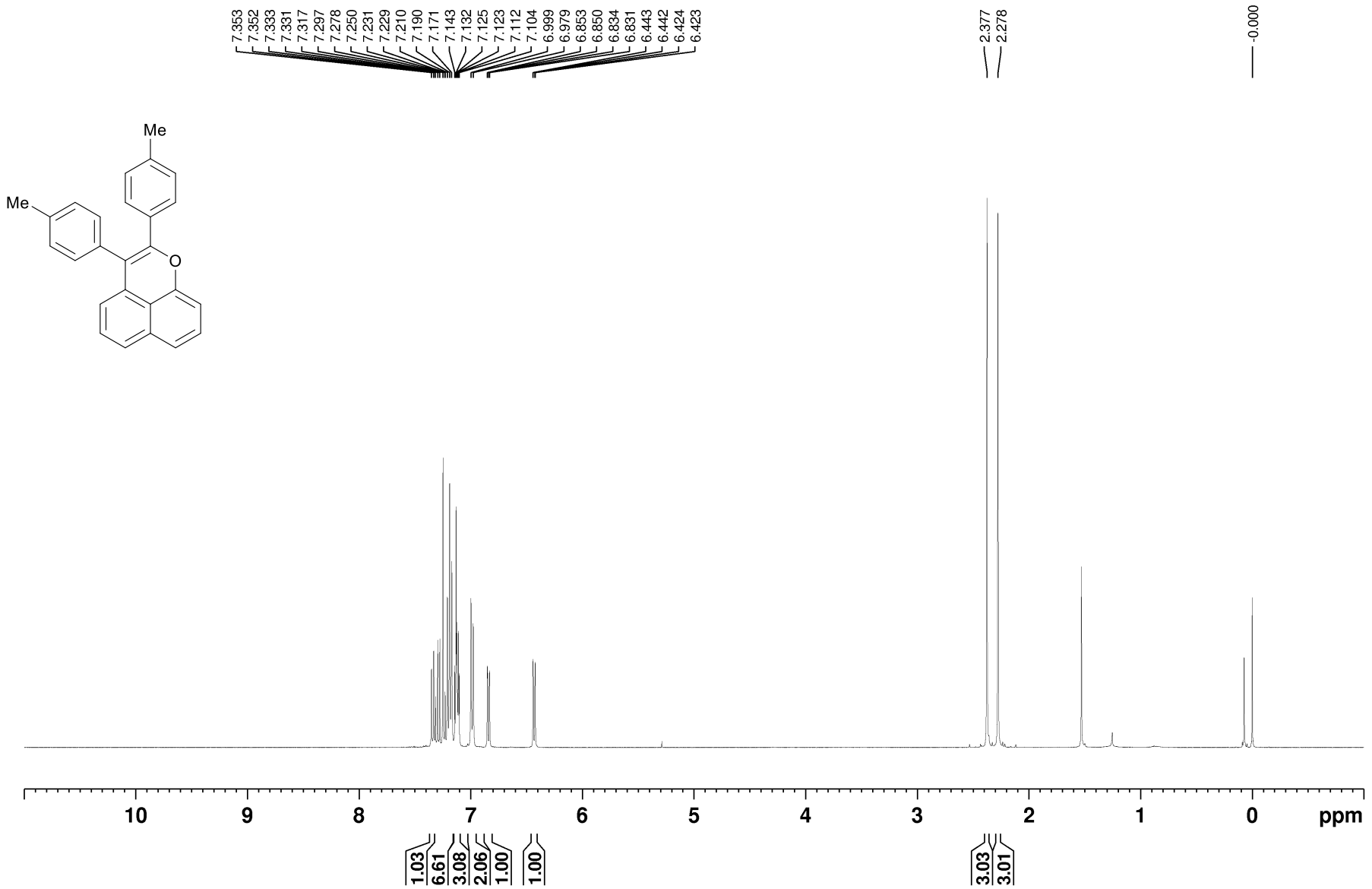
^{1}H NMR ($CDCl_3$, 400 MHz) of tert-butyl((2,3-diphenylbenzo[*de*]chromen-6-yl)oxy)dimethylsilane (3ca)



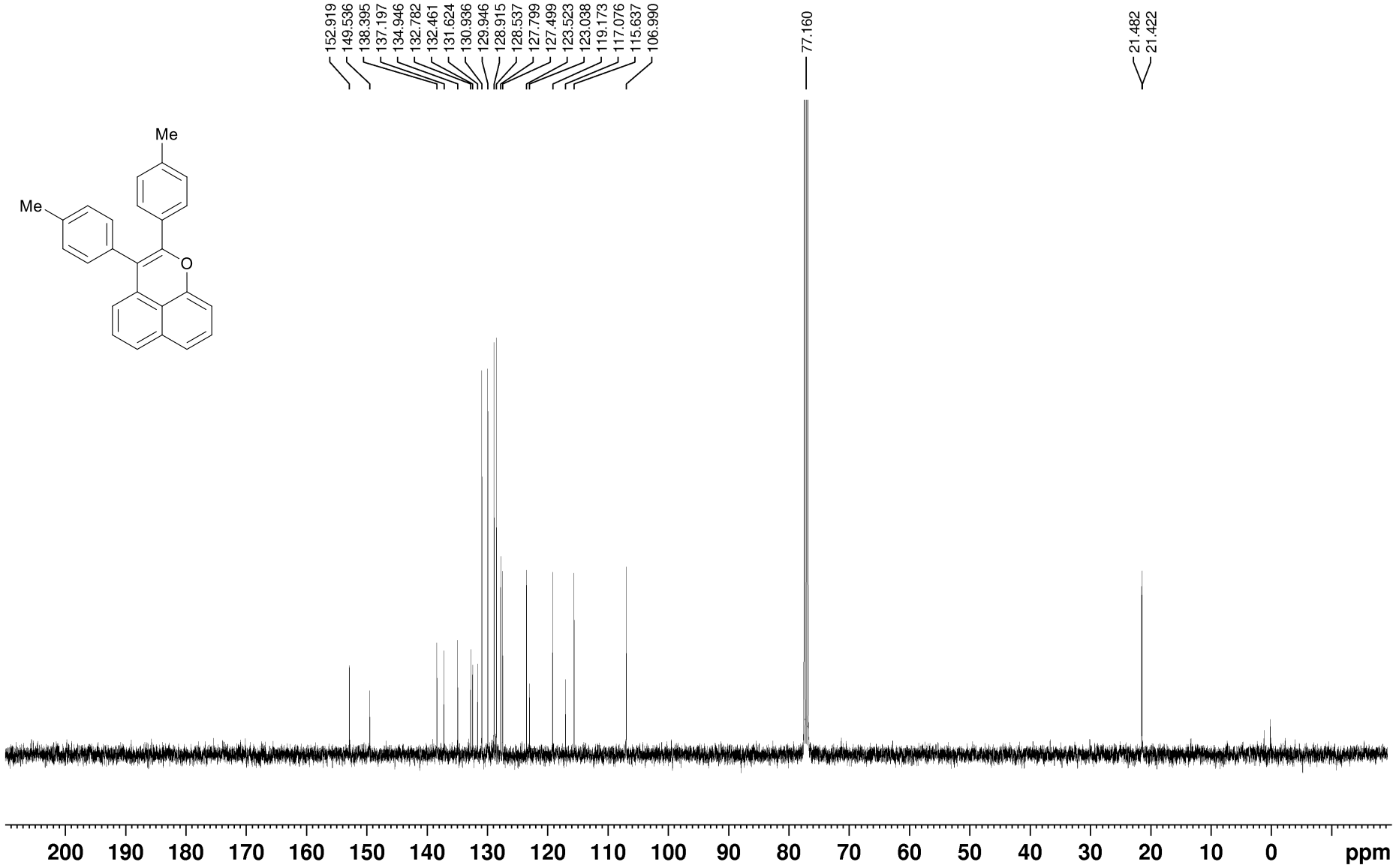
^{13}C NMR ($CDCl_3$, 100 MHz) of tert-butyl((2,3-diphenylbenzo[*de*]chromen-6-yl)oxy)dimethylsilane (3ca)



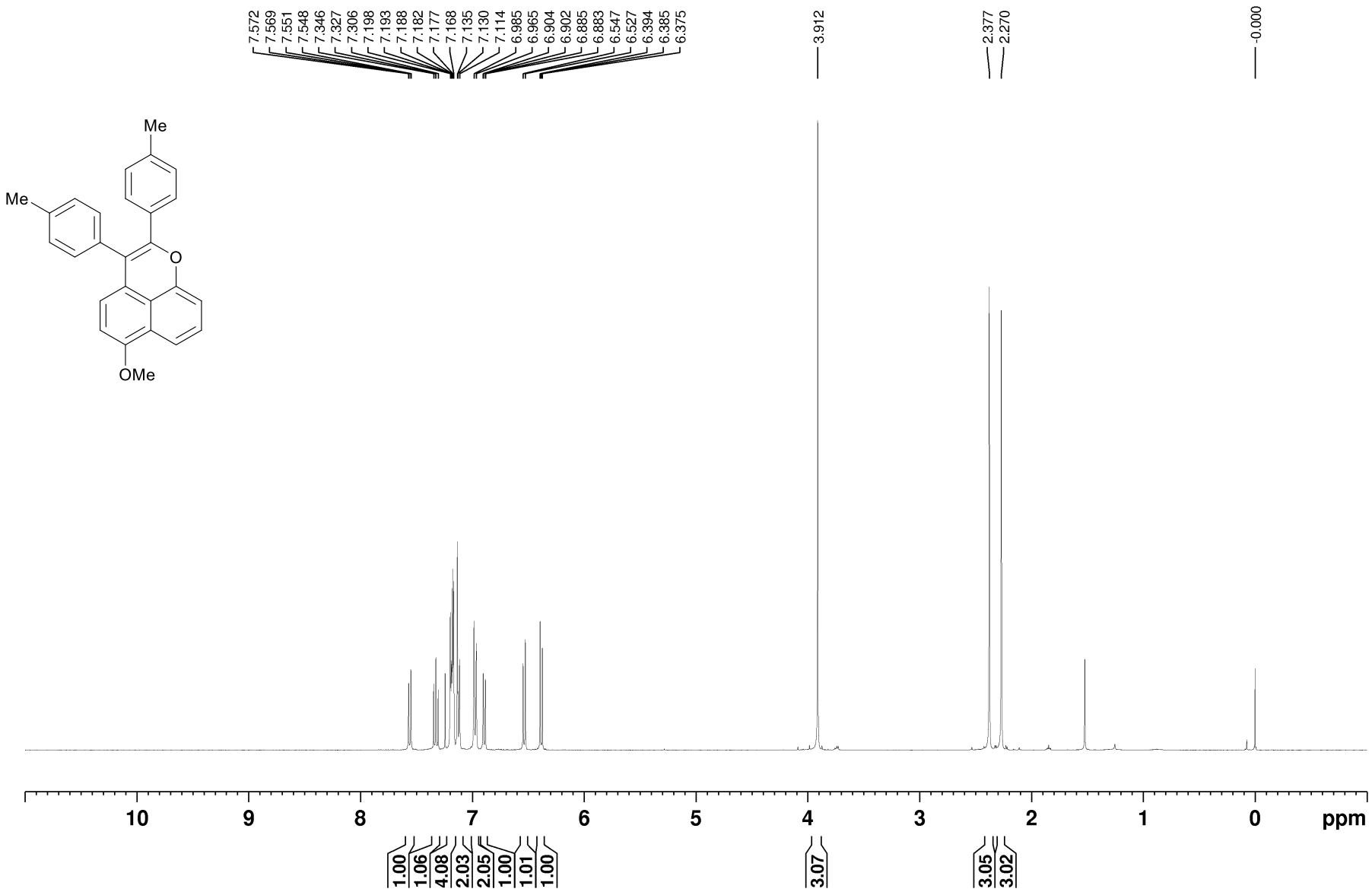
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-di-p-tolylbenzo[*de*]chromene (3ab)



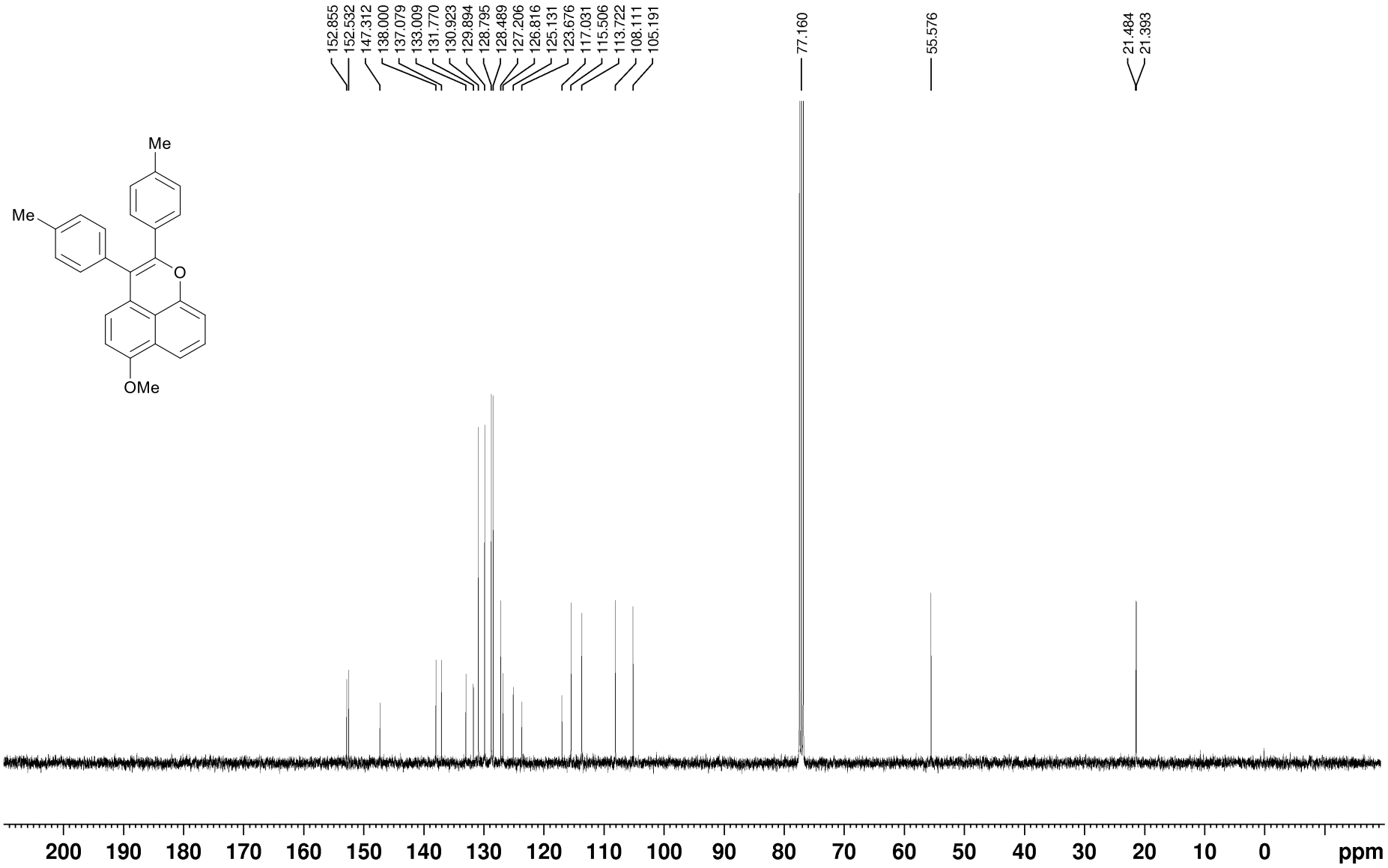
^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-di-p-tolylbenzo[*de*]chromene (3ab)



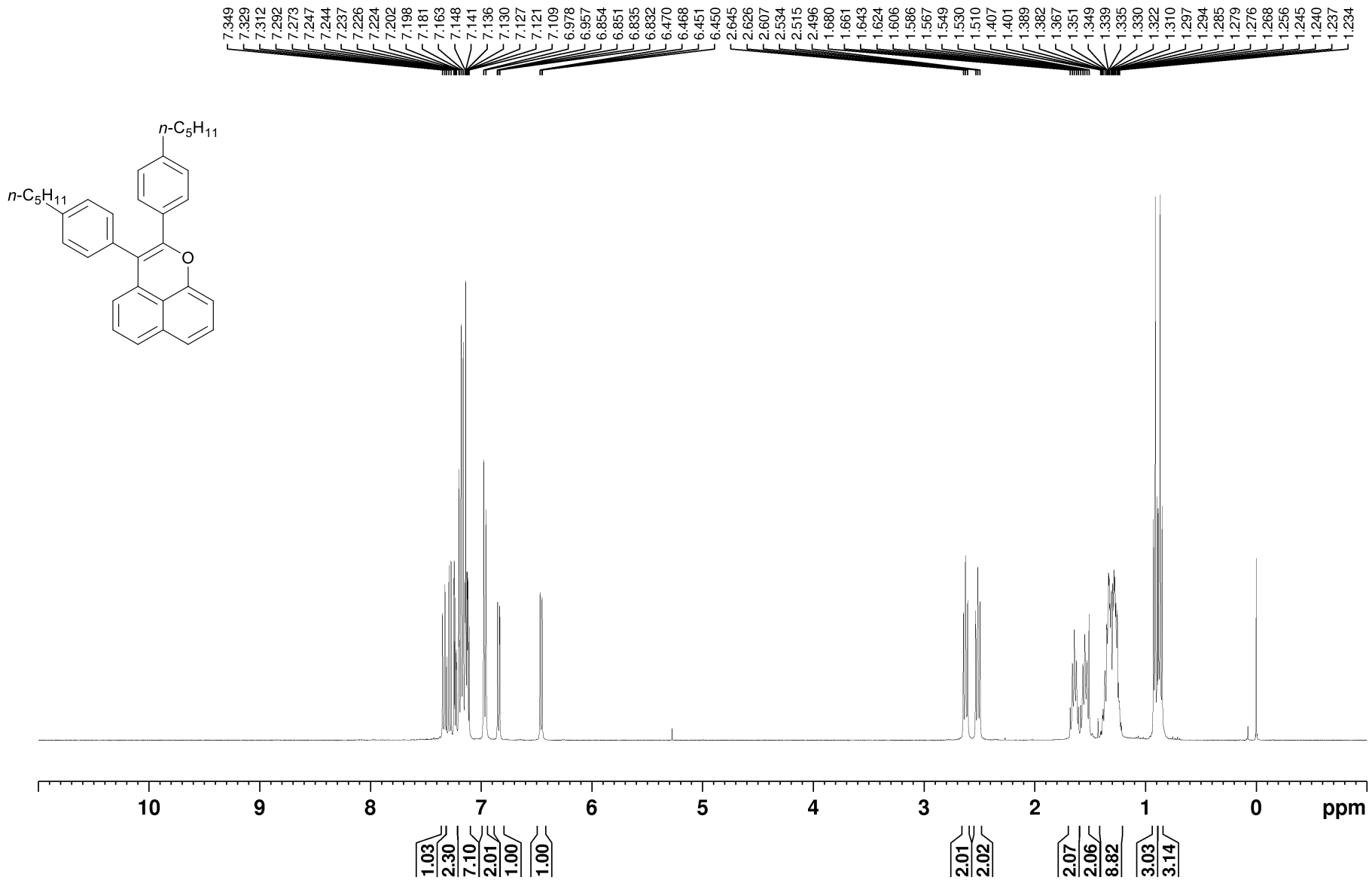
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2,3-di-p-tolylbenzo[*de*]chromene (3bb)



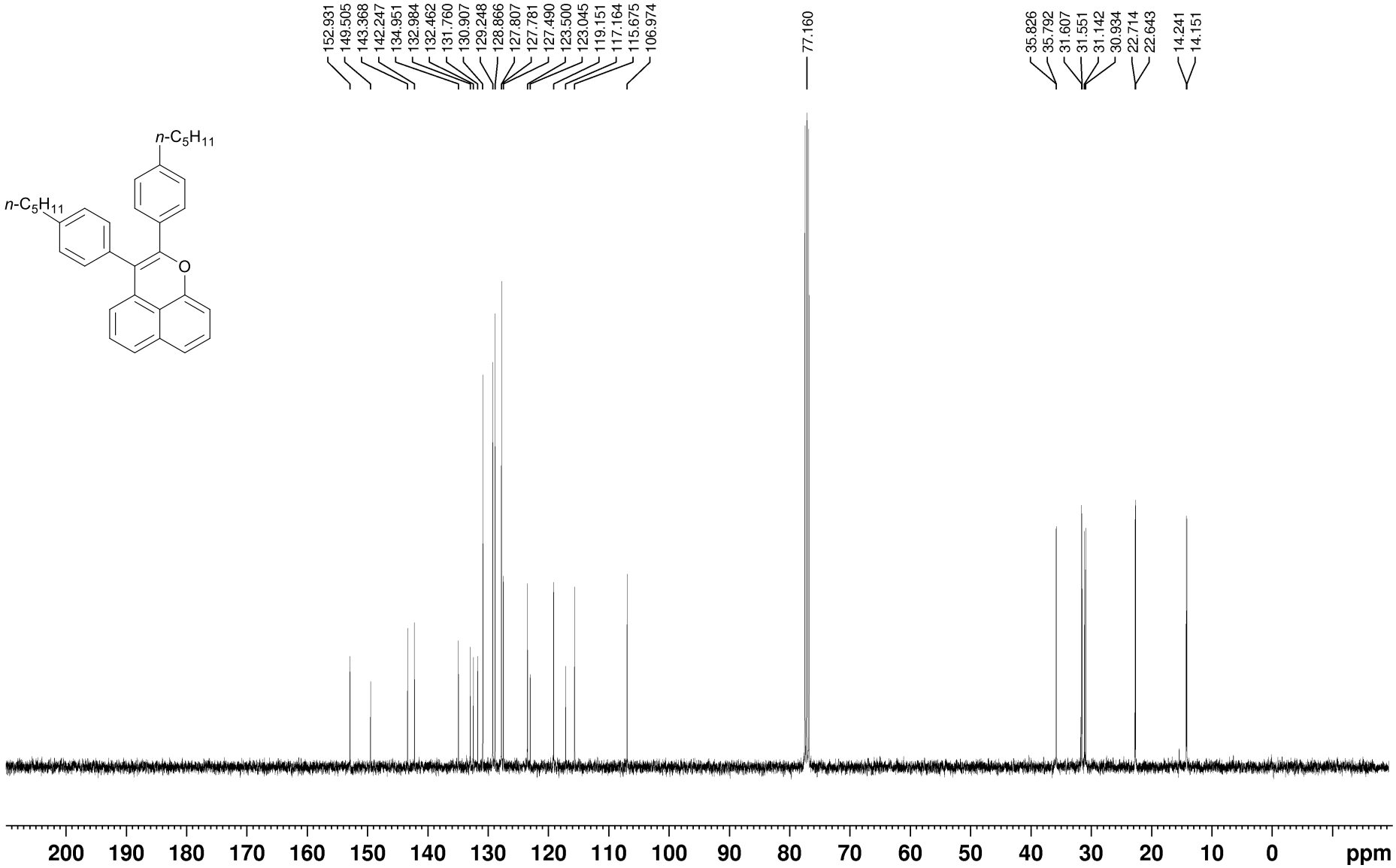
^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-2,3-di-p-tolylbenzo[*de*]chromene (3bb)



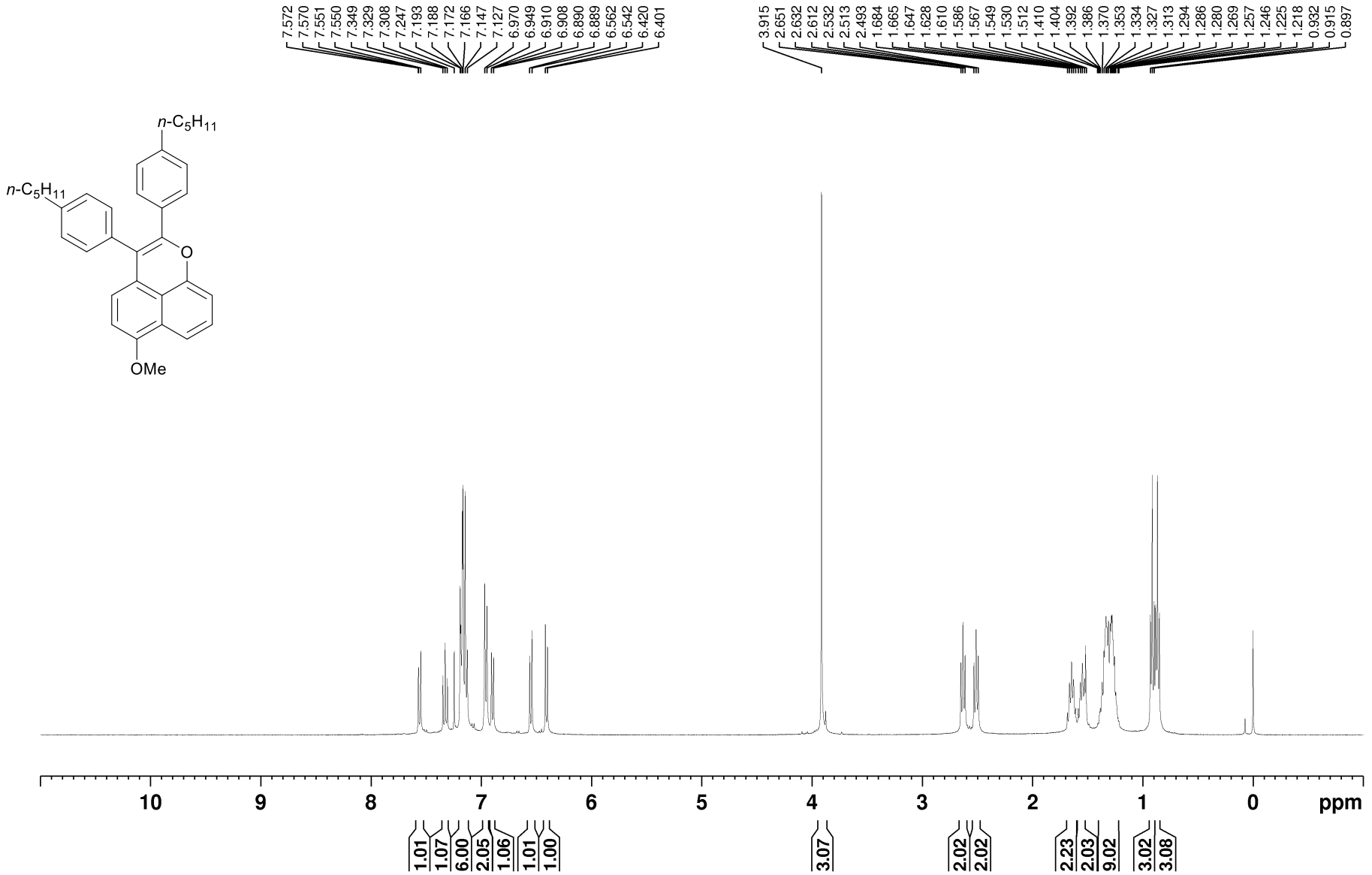
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-bis(4-pentylphenyl)benzo[*de*]chromene (3ac)



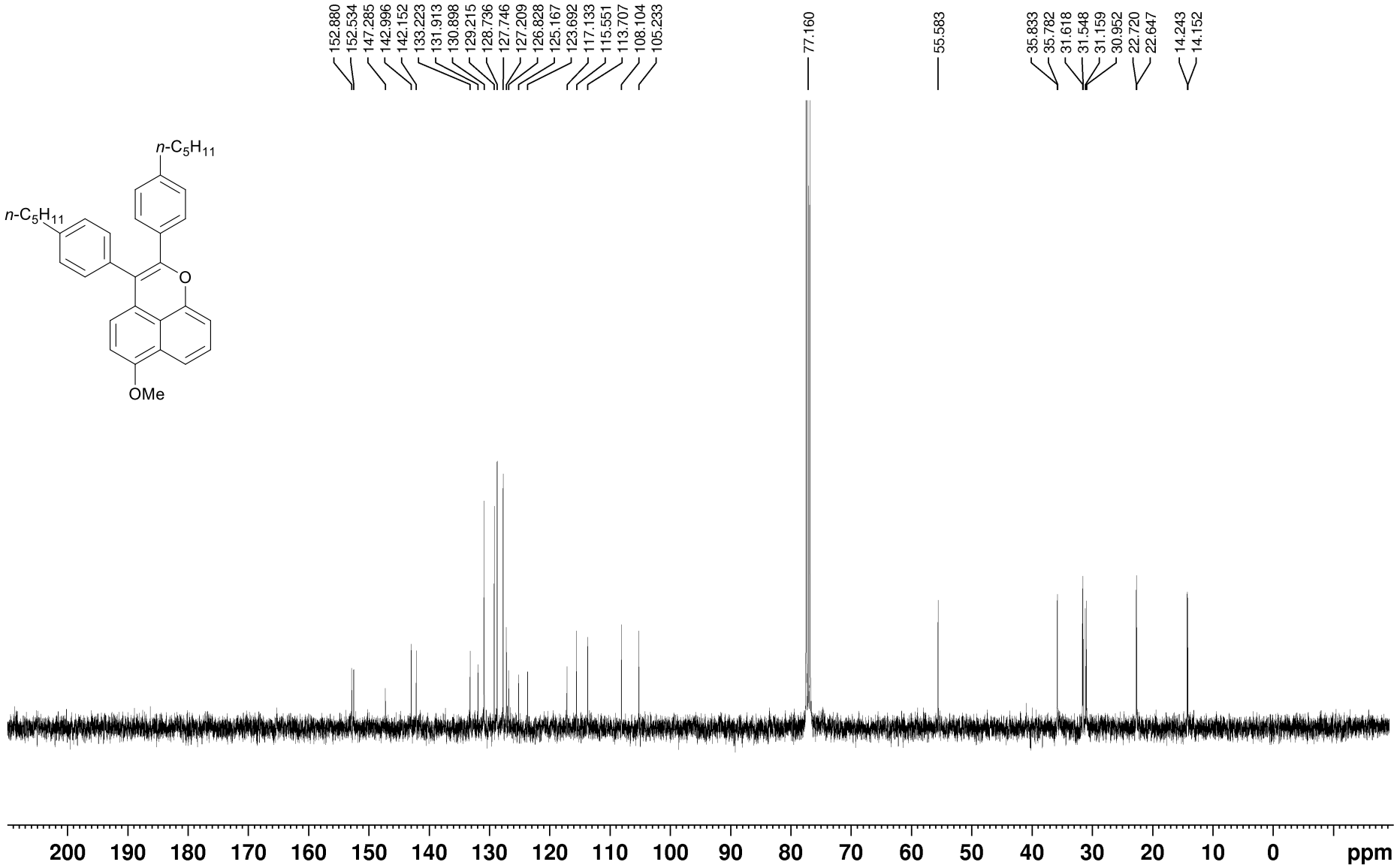
^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-bis(4-pentylphenyl)benzo[*de*]chromene (3ac)



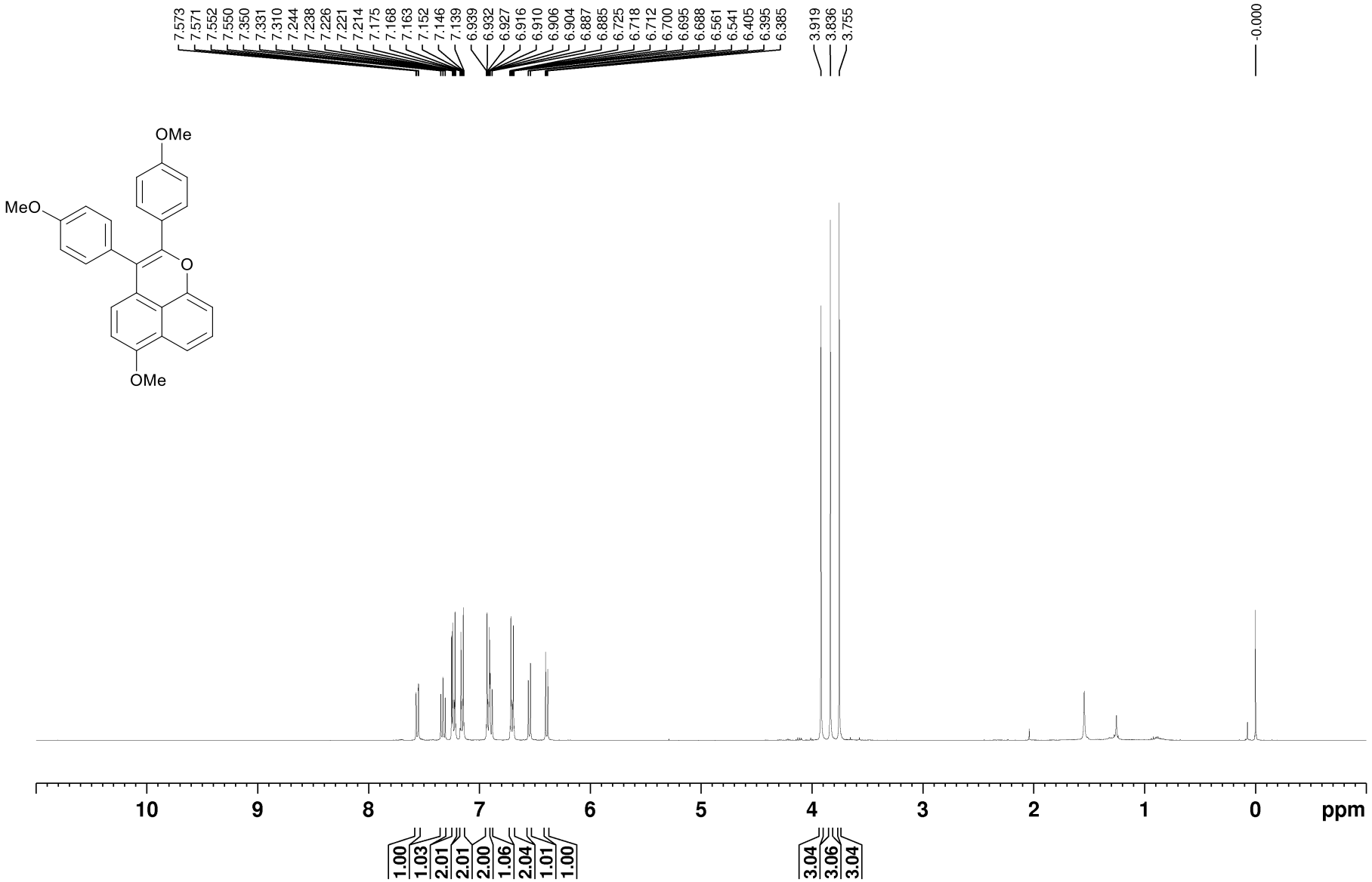
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2,3-bis(4-pentylphenyl)benzo[*de*]chromene (3bc)



^{13}C NMR ($CDCl_3$, 100 MHz) of of 6-methoxy-2,3-bis(4-pentylphenyl)benzo[*de*]chromene (3bc)



^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2,3-bis(4-methoxyphenyl)benzo[*de*]chromene (3bd)



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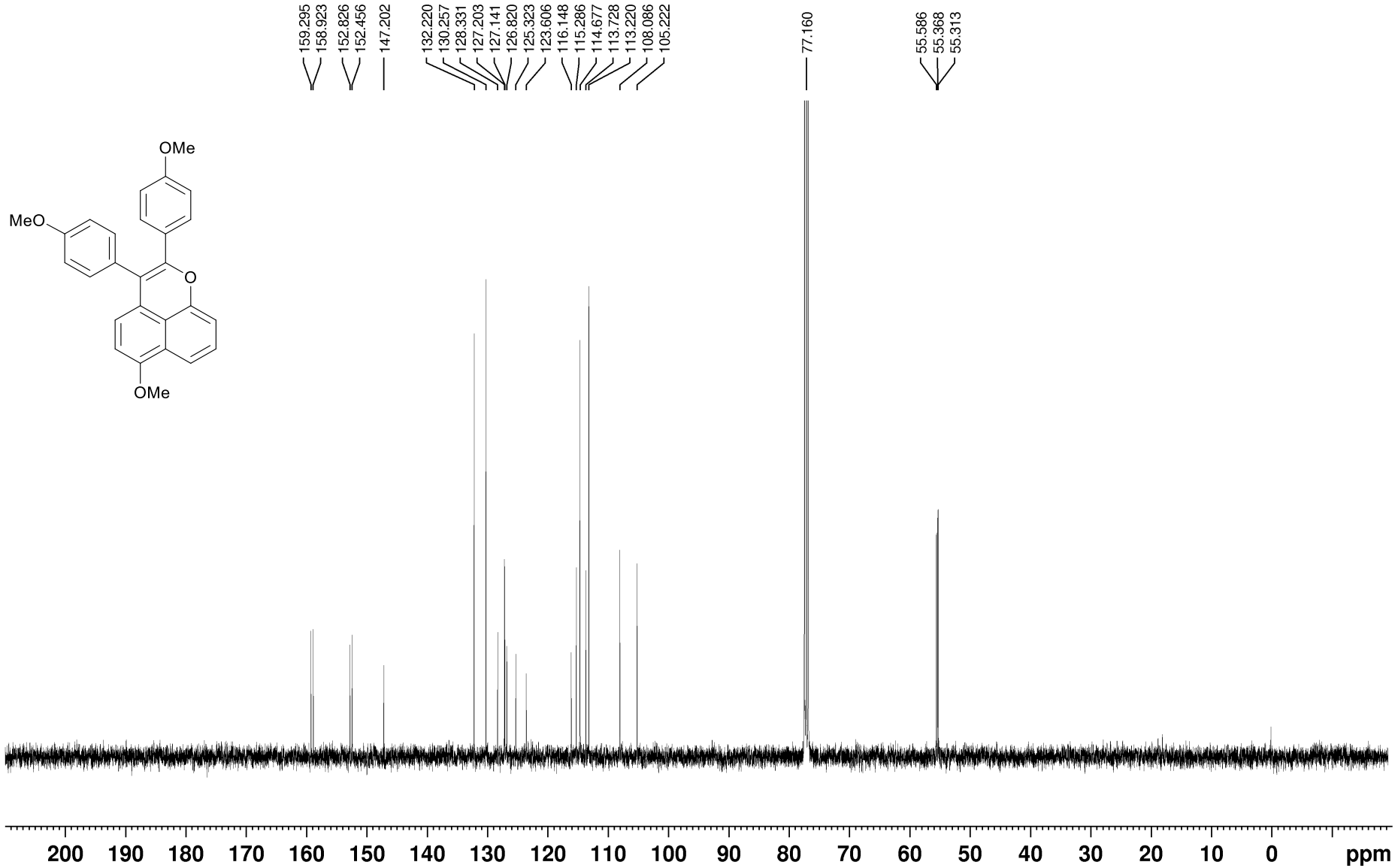
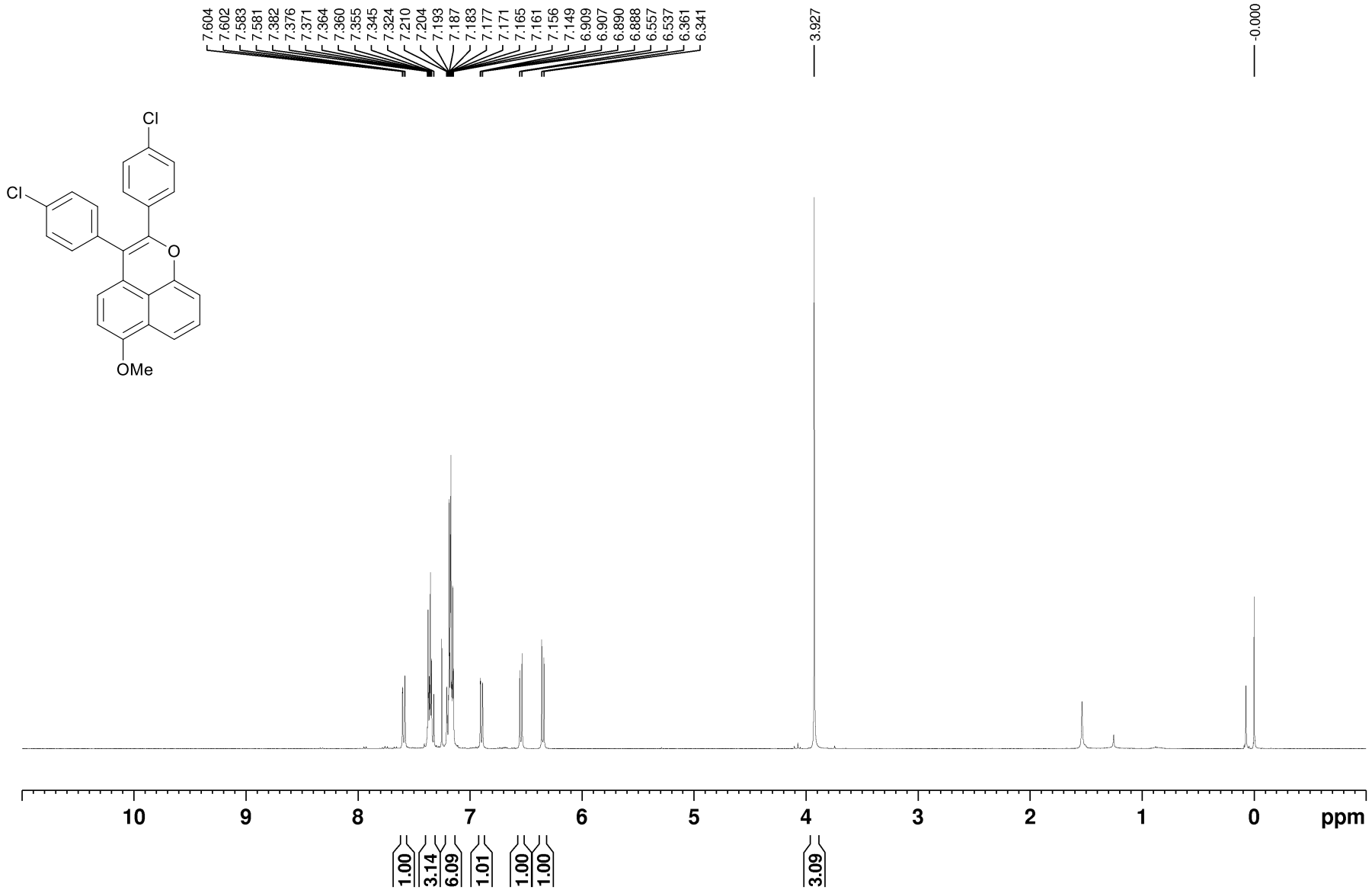
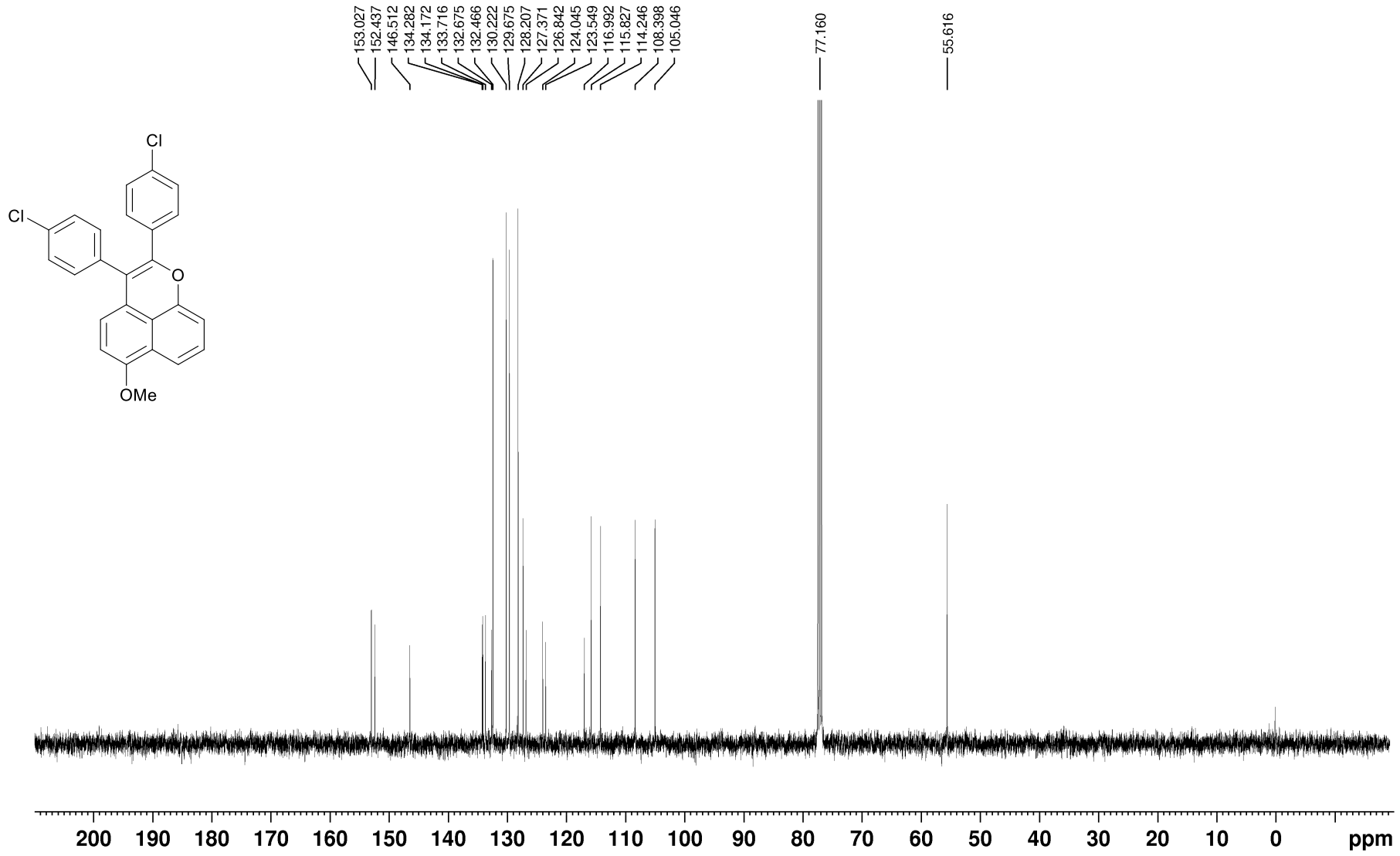


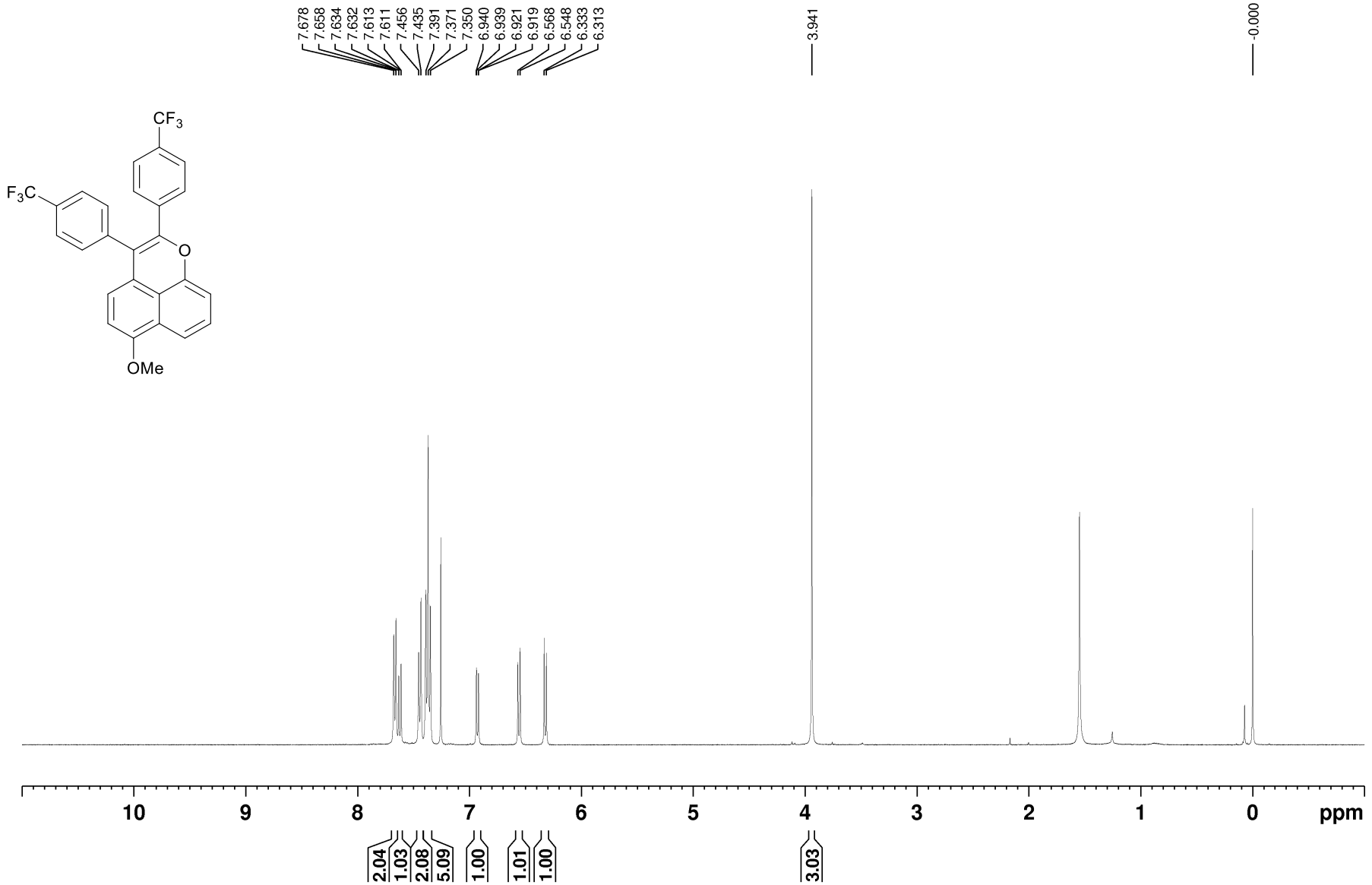
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-bis(4-chlorophenyl)-6-methoxybenzo[*de*]chromene (3be)



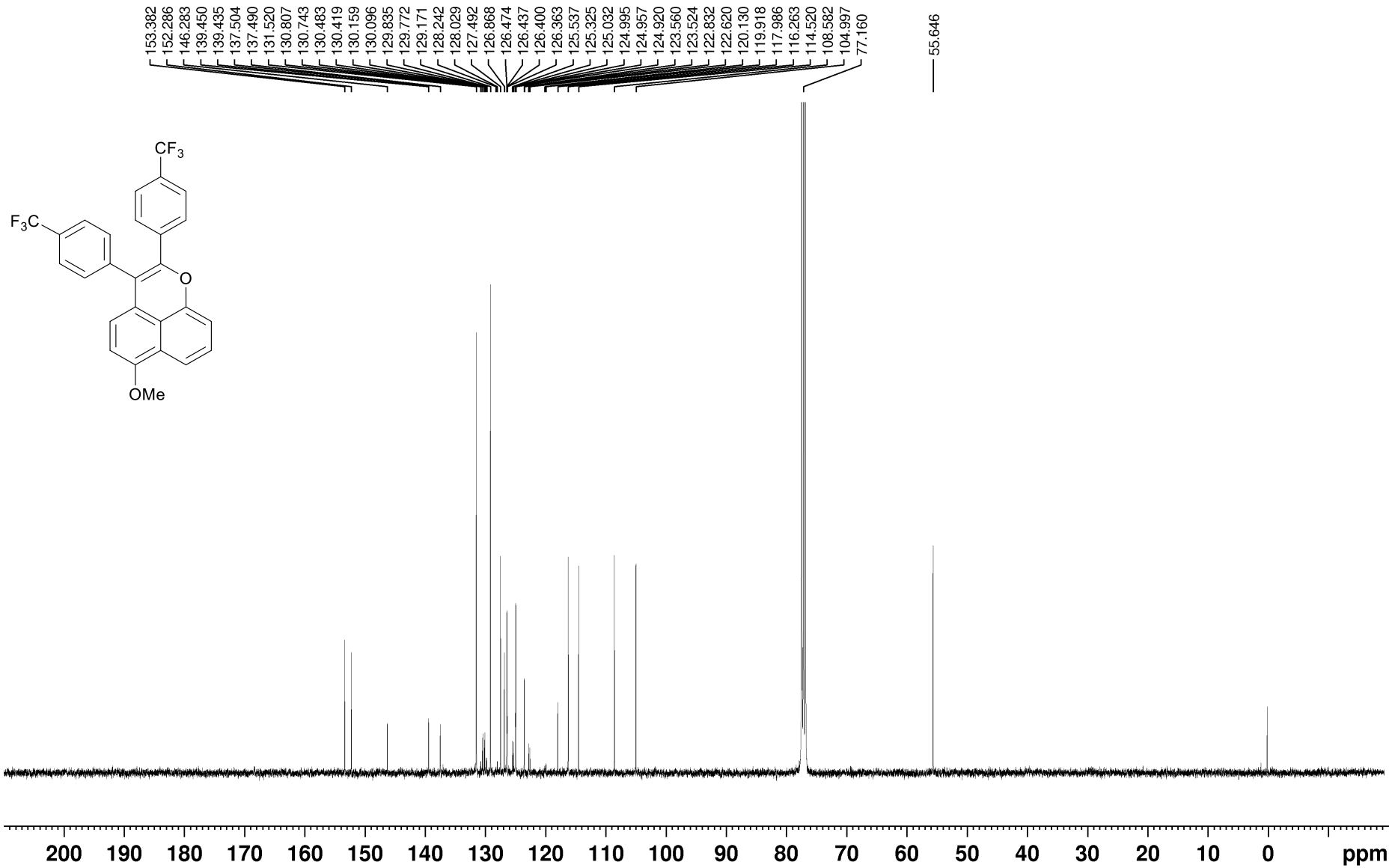
^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-bis(4-chlorophenyl)-6-methoxybenzo[*de*]chromene (3be)



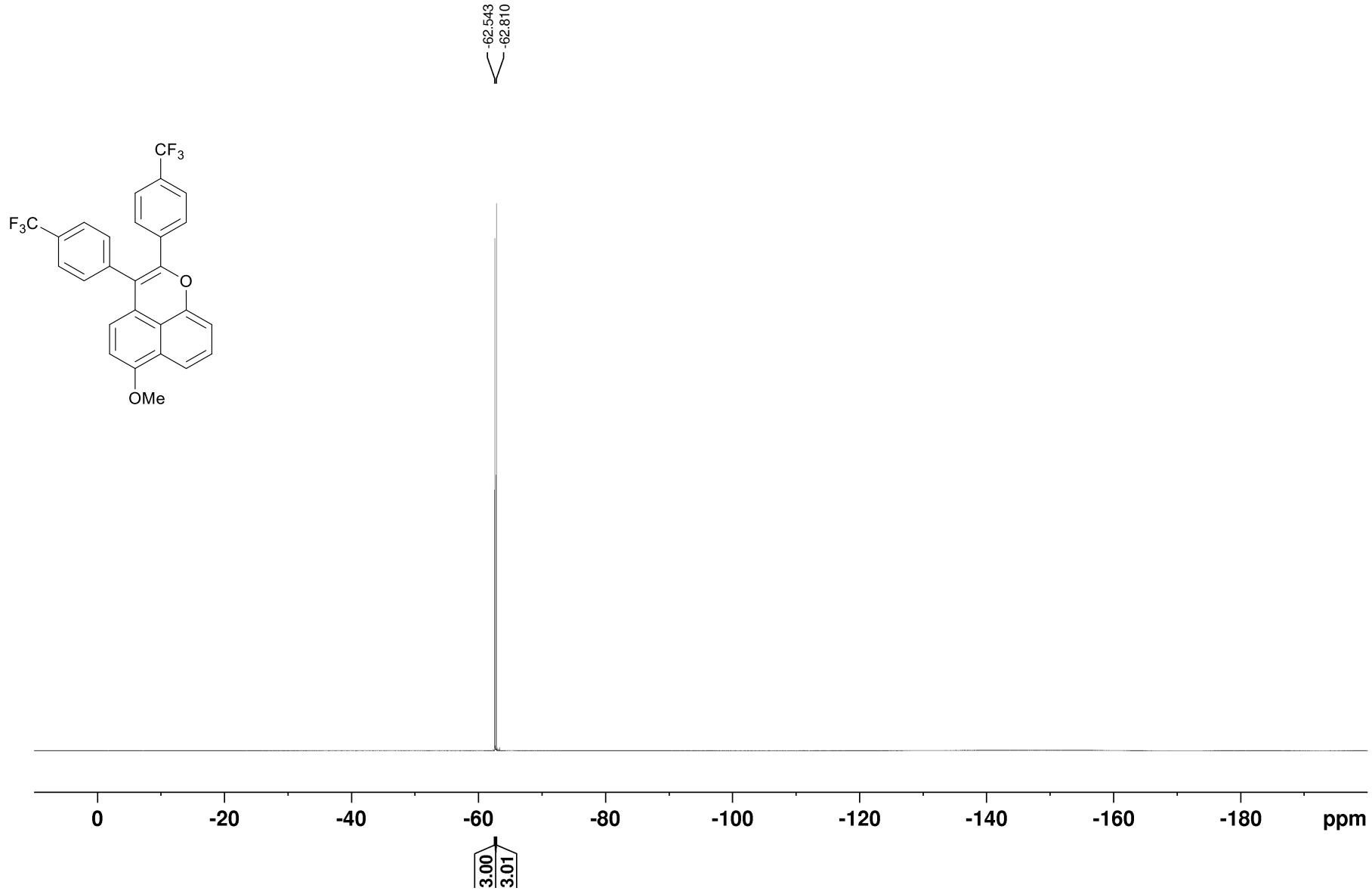
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bf)



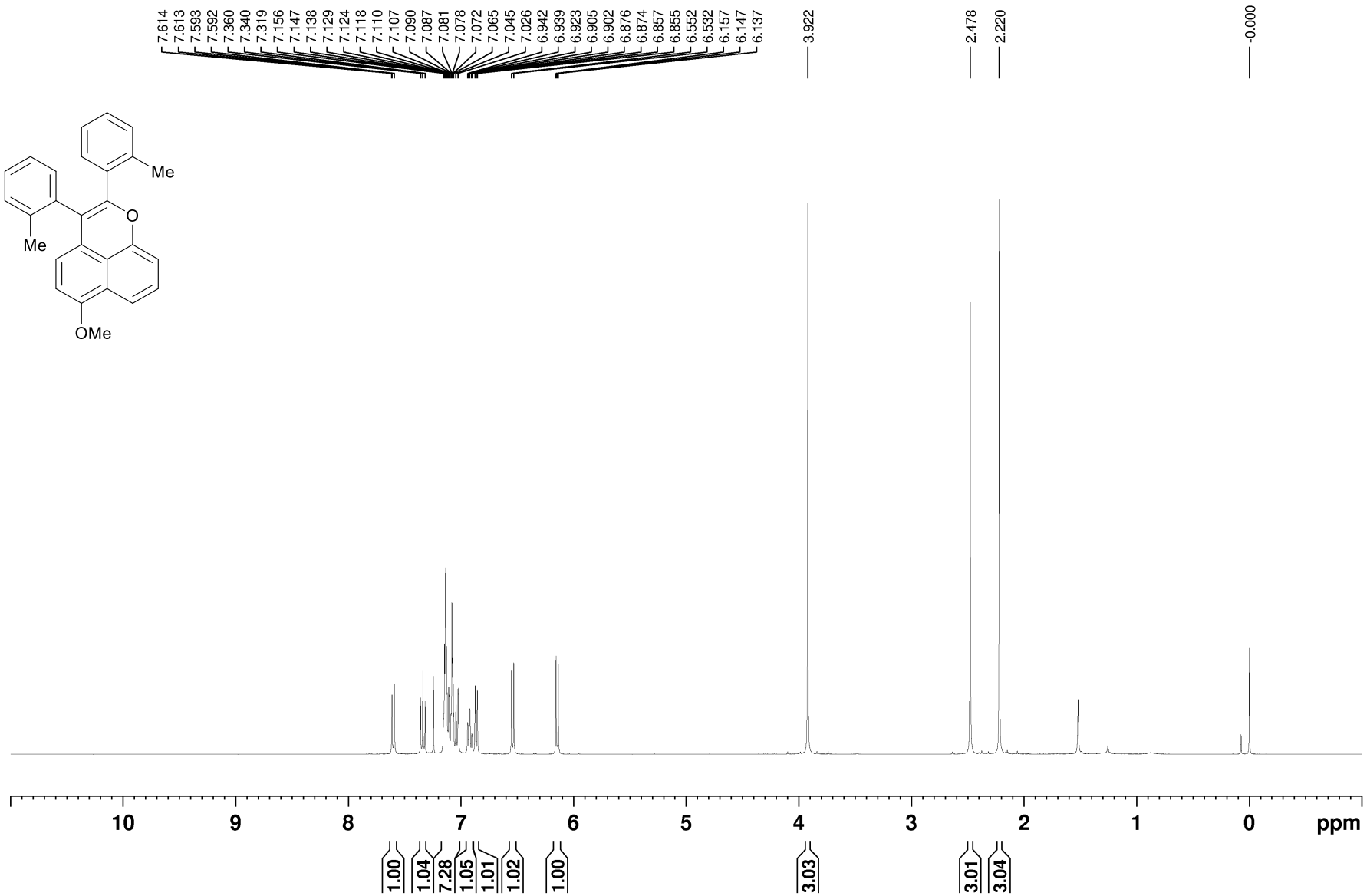
^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bf)



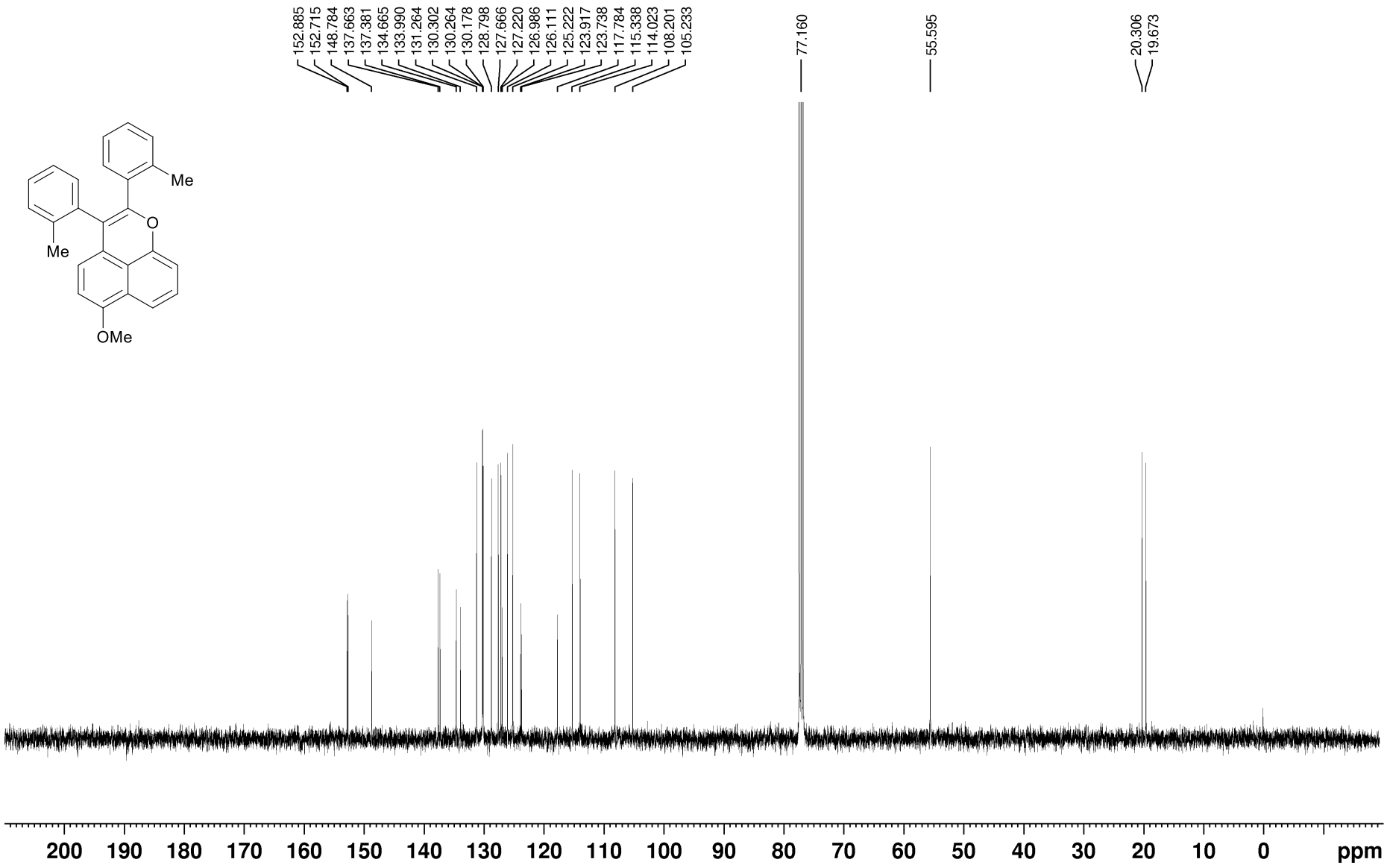
^{19}F NMR ($CDCl_3$, 376 MHz) of 6-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bf)



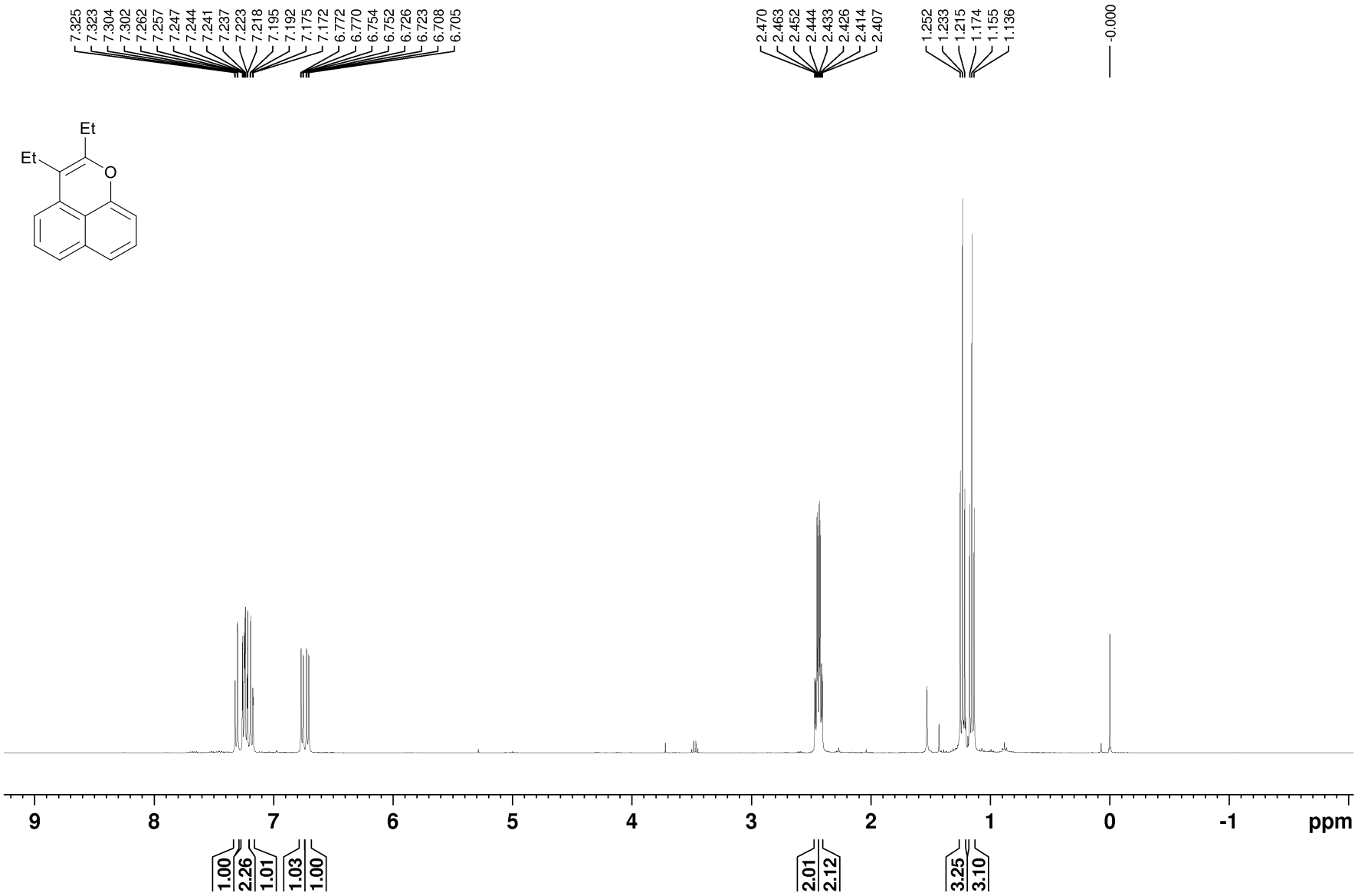
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2,3-di-o-tolylbenzo[*de*]chromene (3bg)



^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-2,3-di-o-tolylbenzo[*de*]chromene (3bg)



^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-diethylbenzo[*de*]chromene (3ah)



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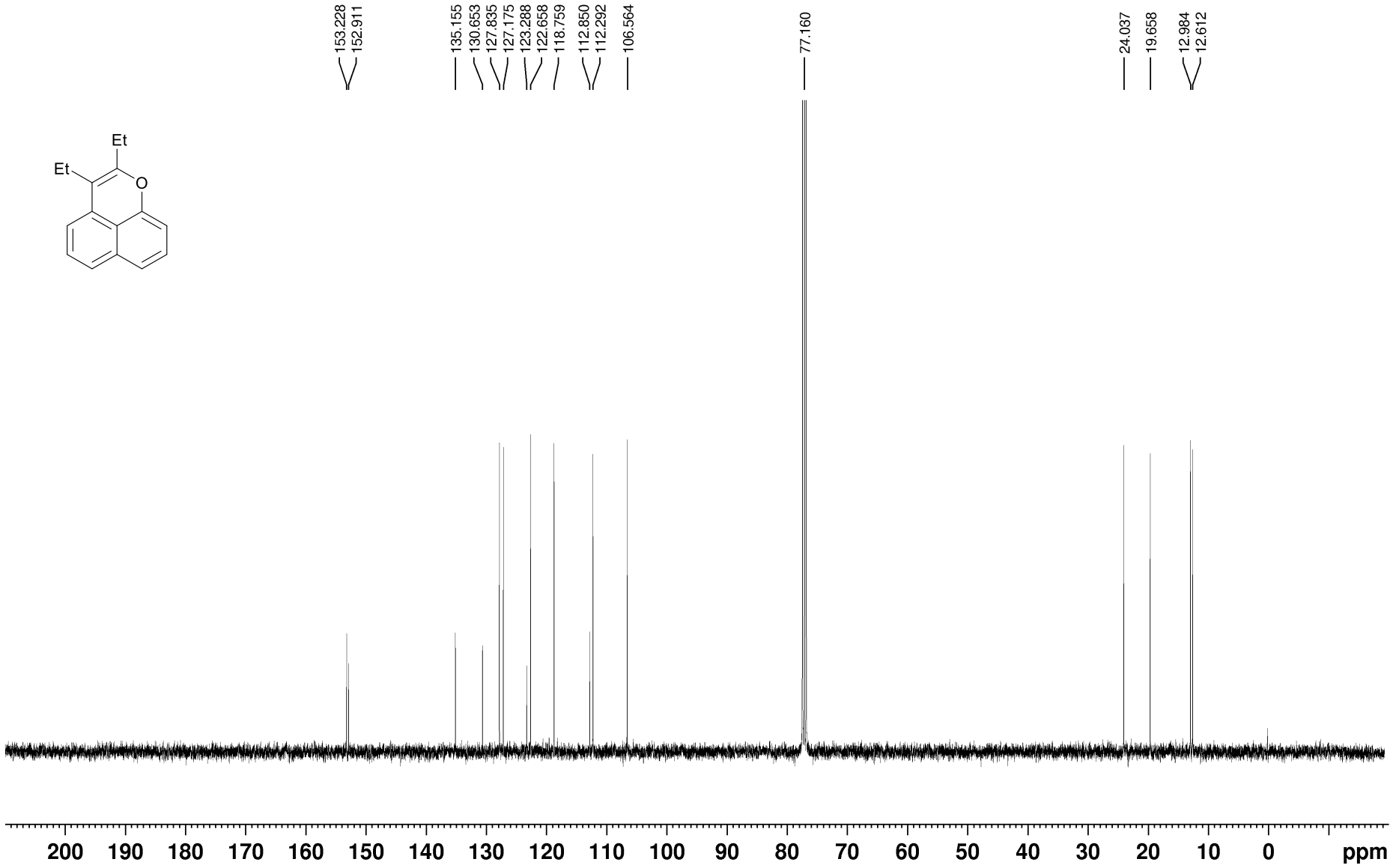

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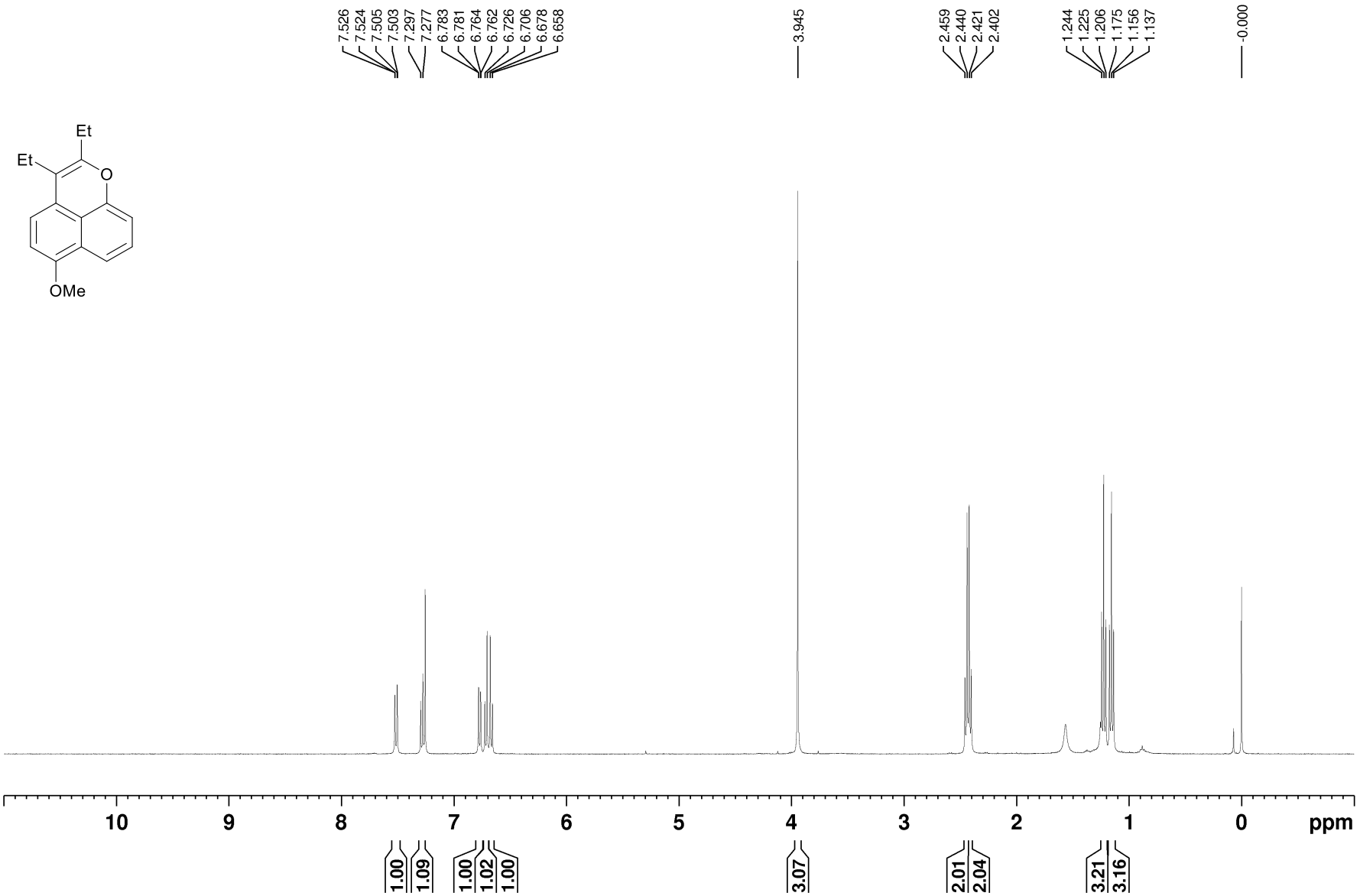
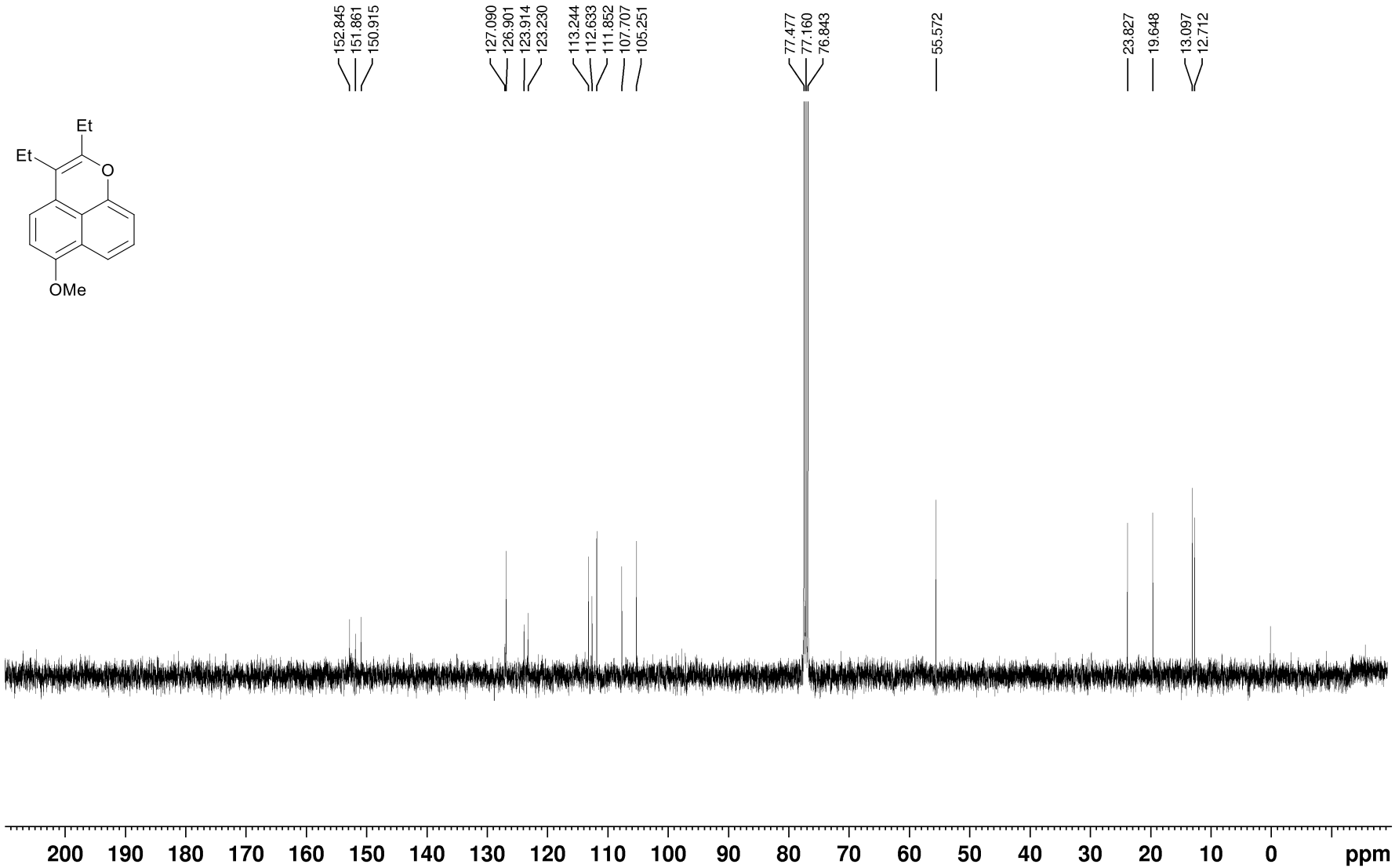
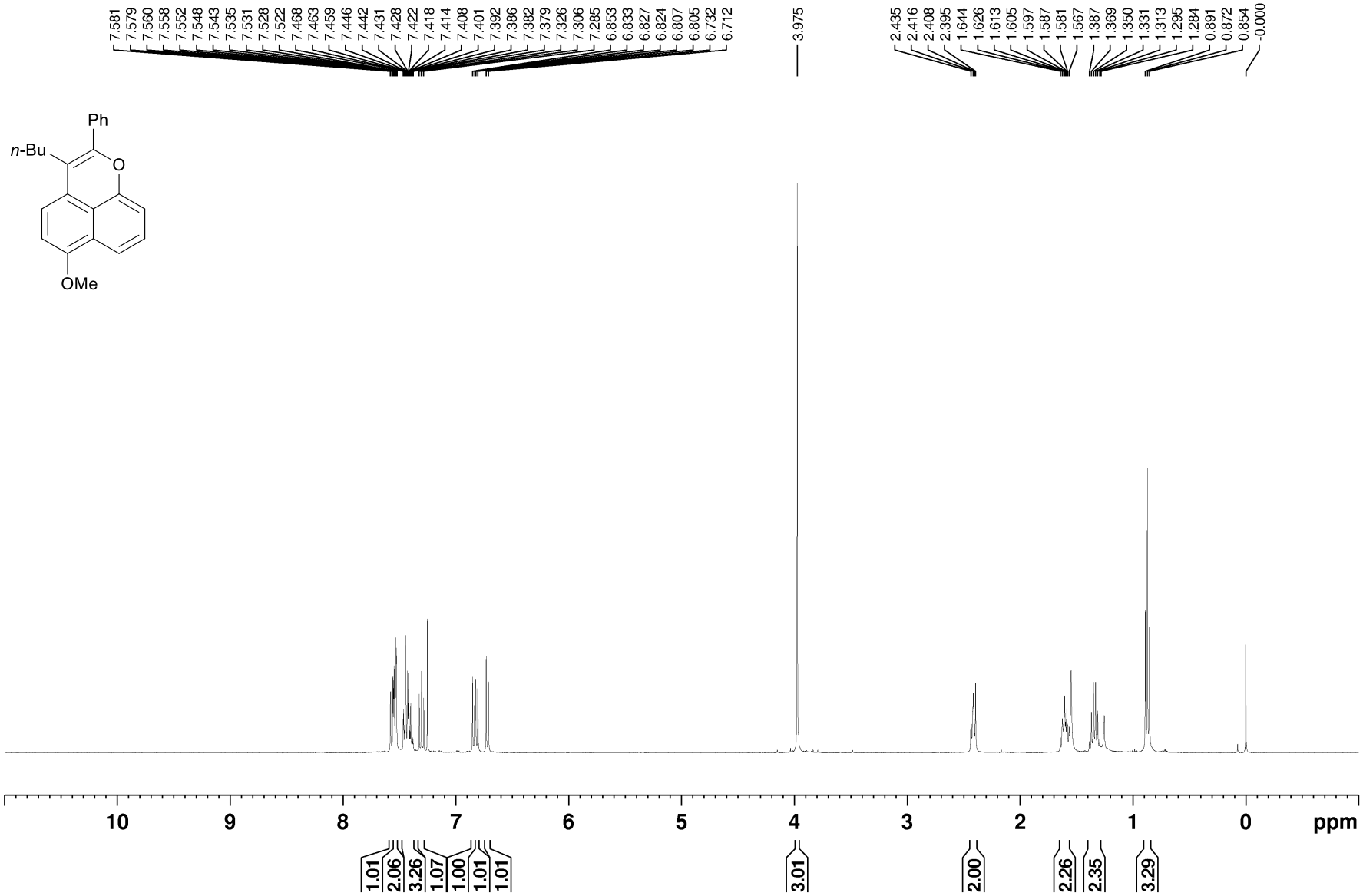


^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-diethyl-6-methoxybenzo[*de*]chromene (3bh)



^{1}H NMR ($CDCl_3$, 400 MHz) of 3-butyl-6-methoxy-2-phenylbenzo[*de*]chromene (3bi)



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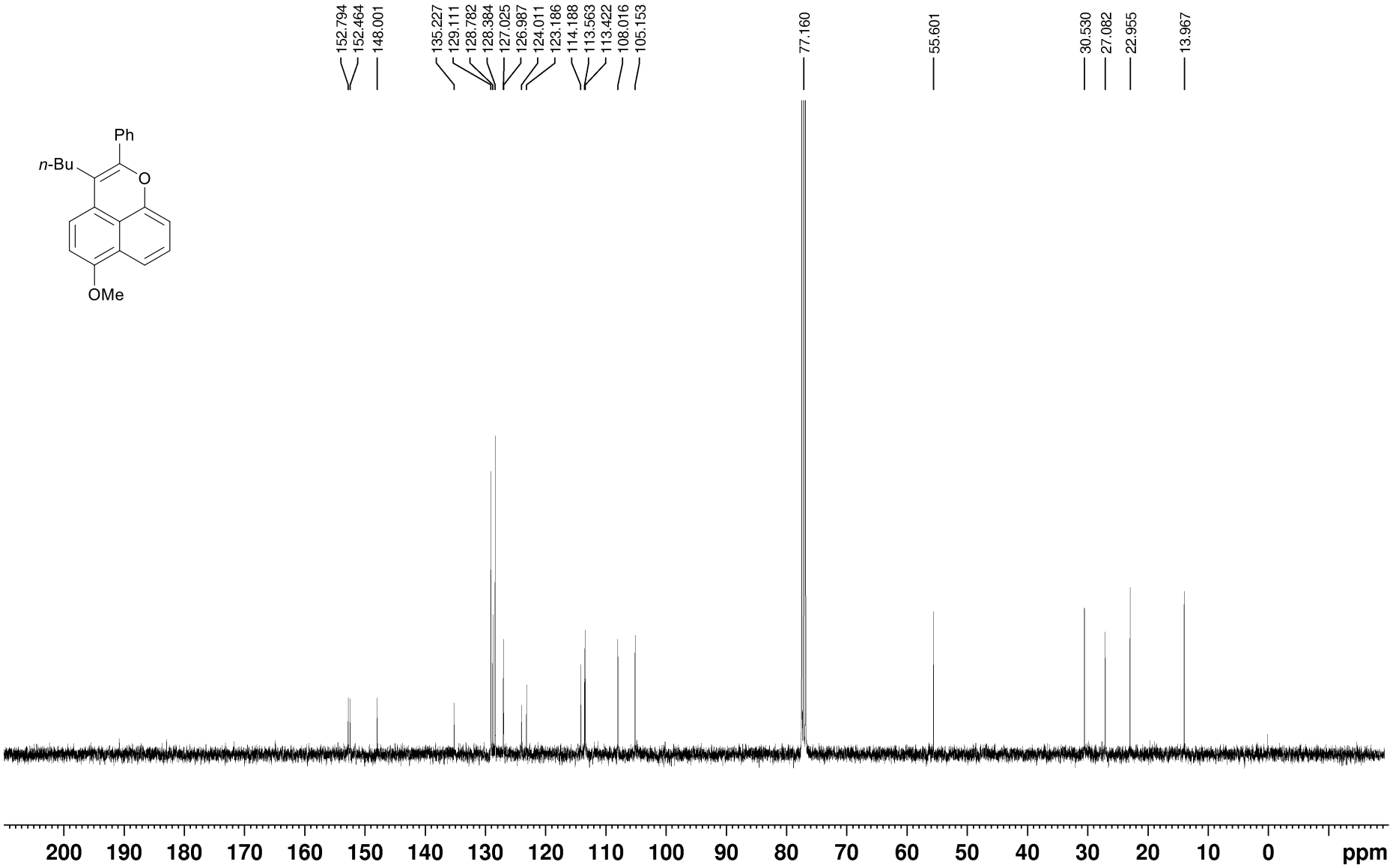
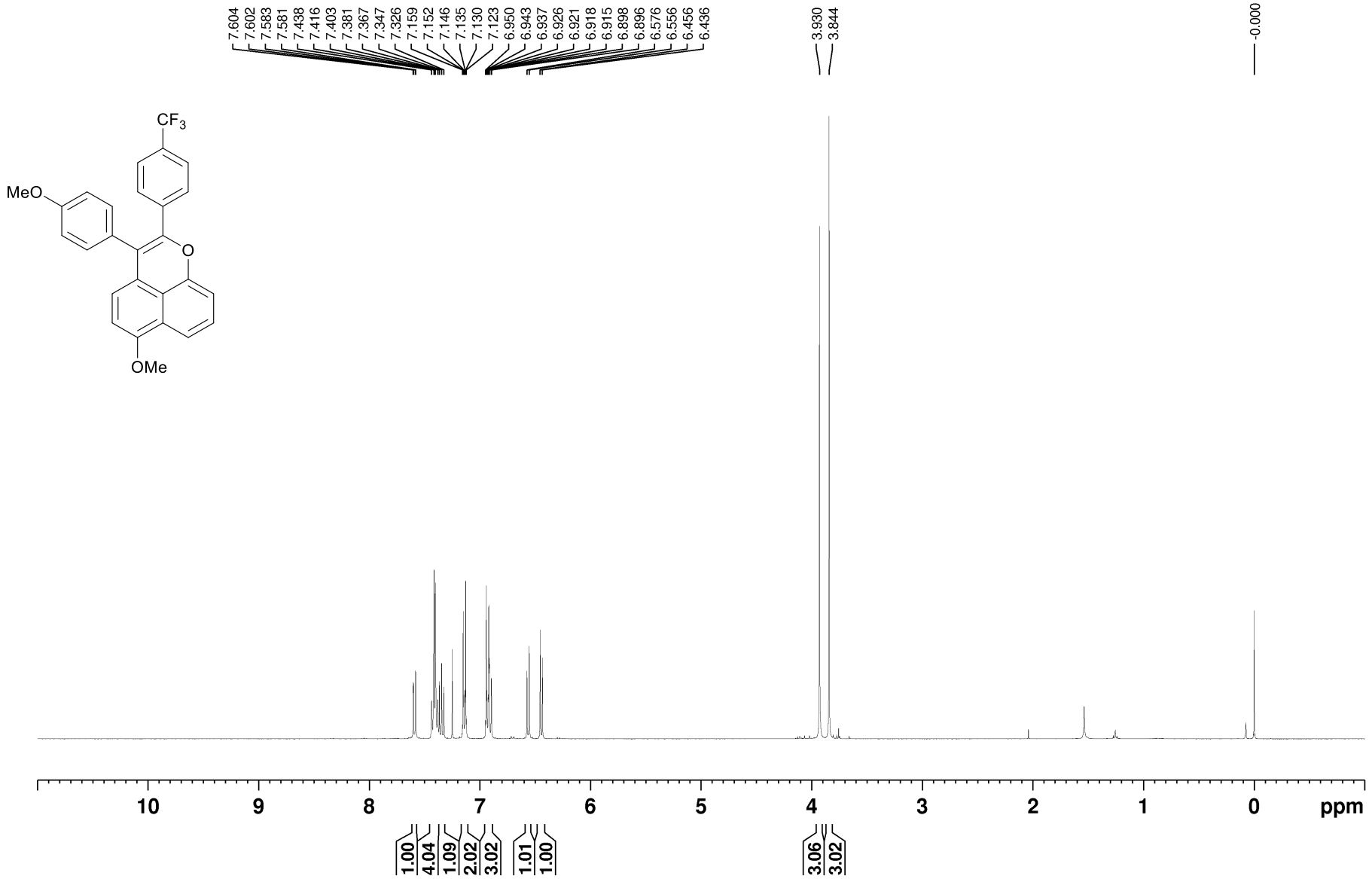
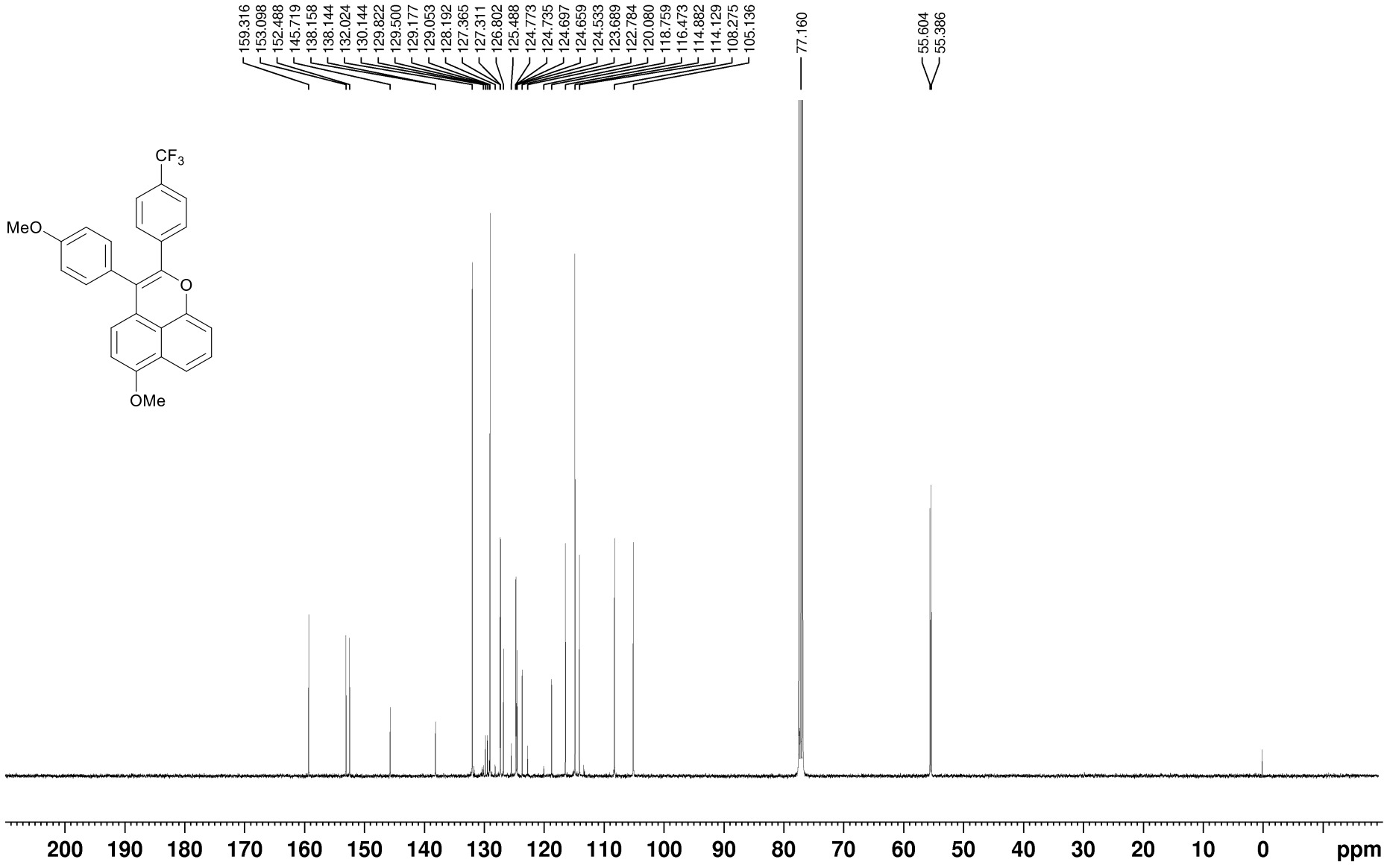


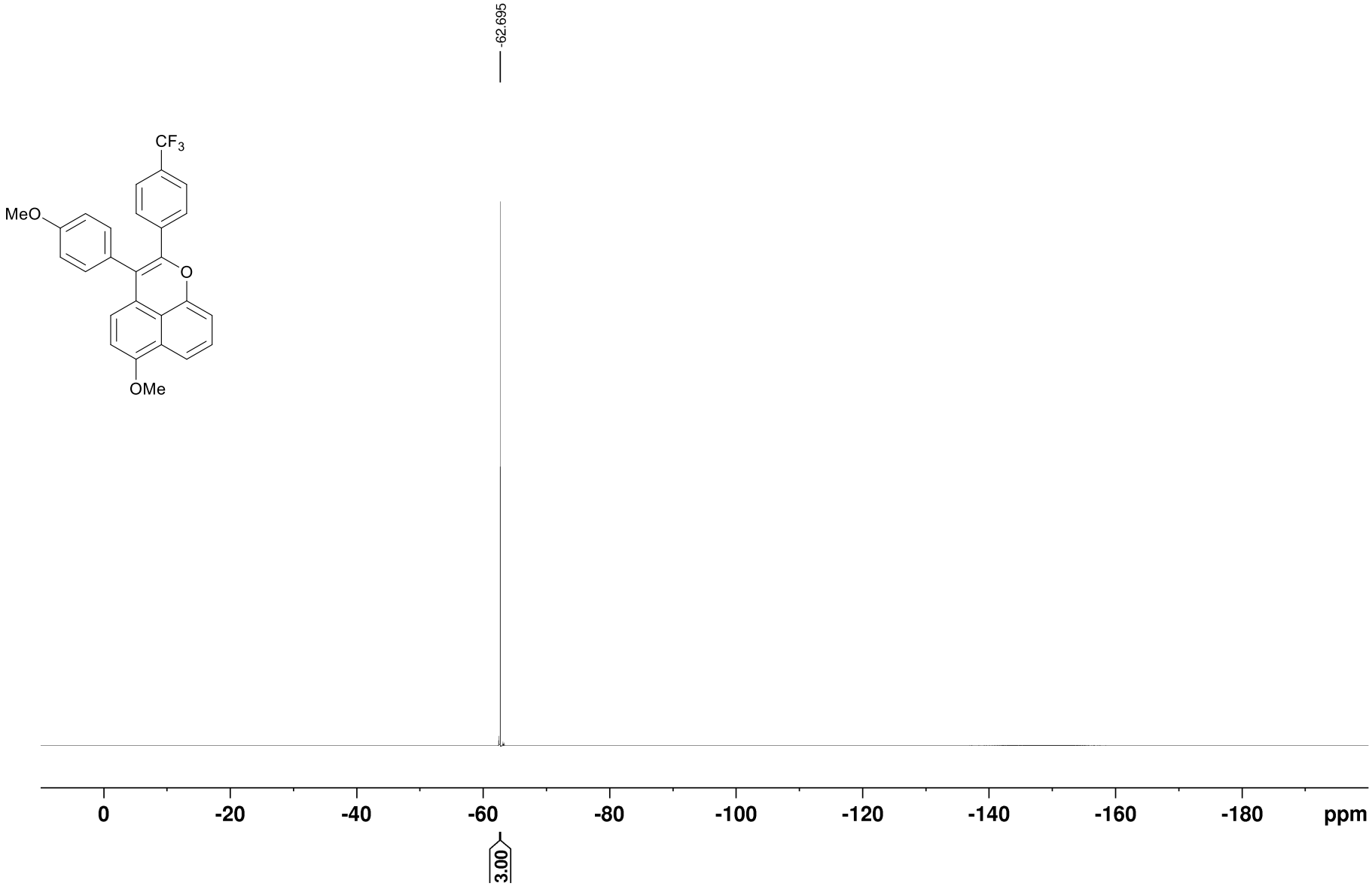
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



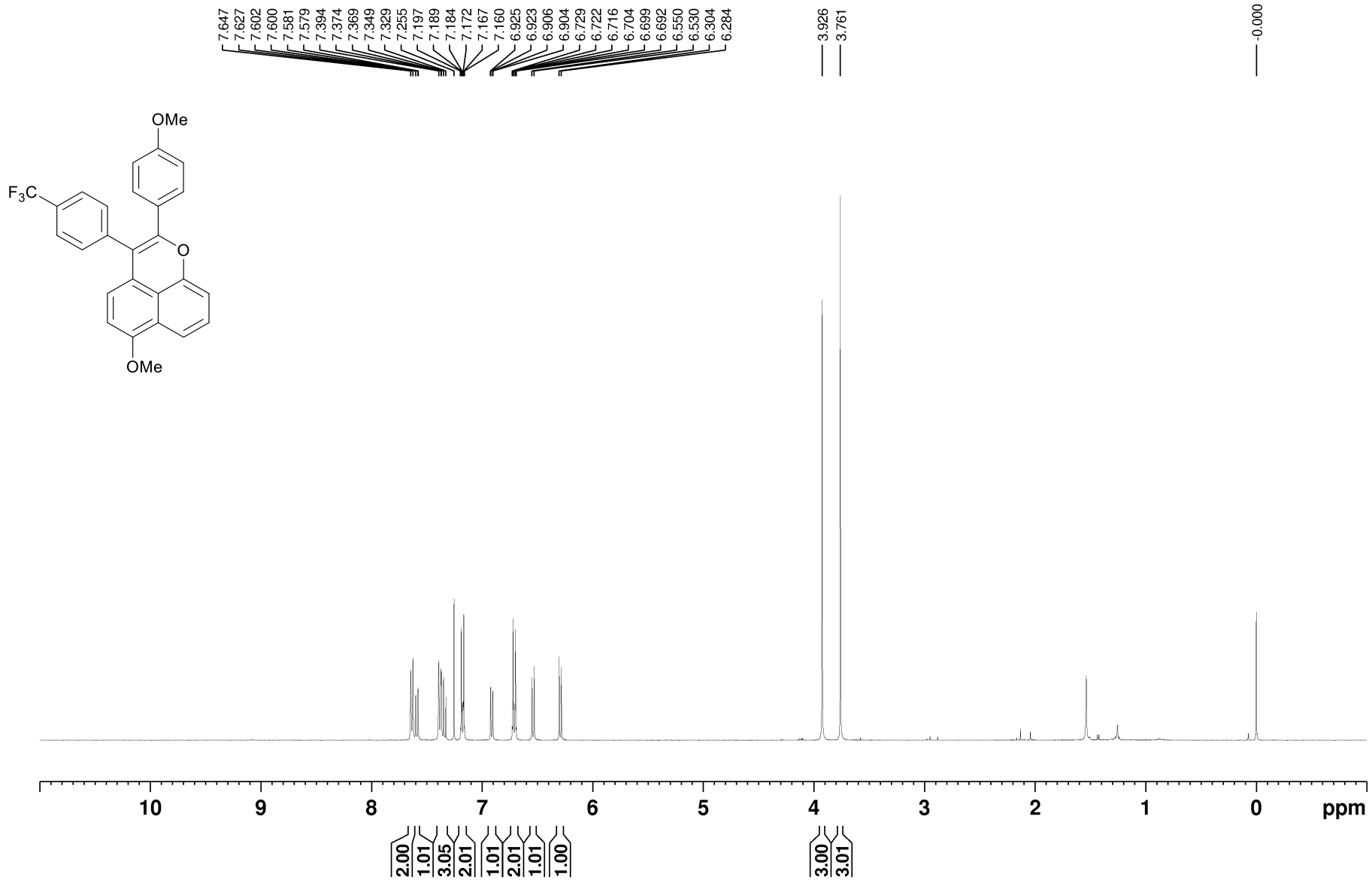
^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



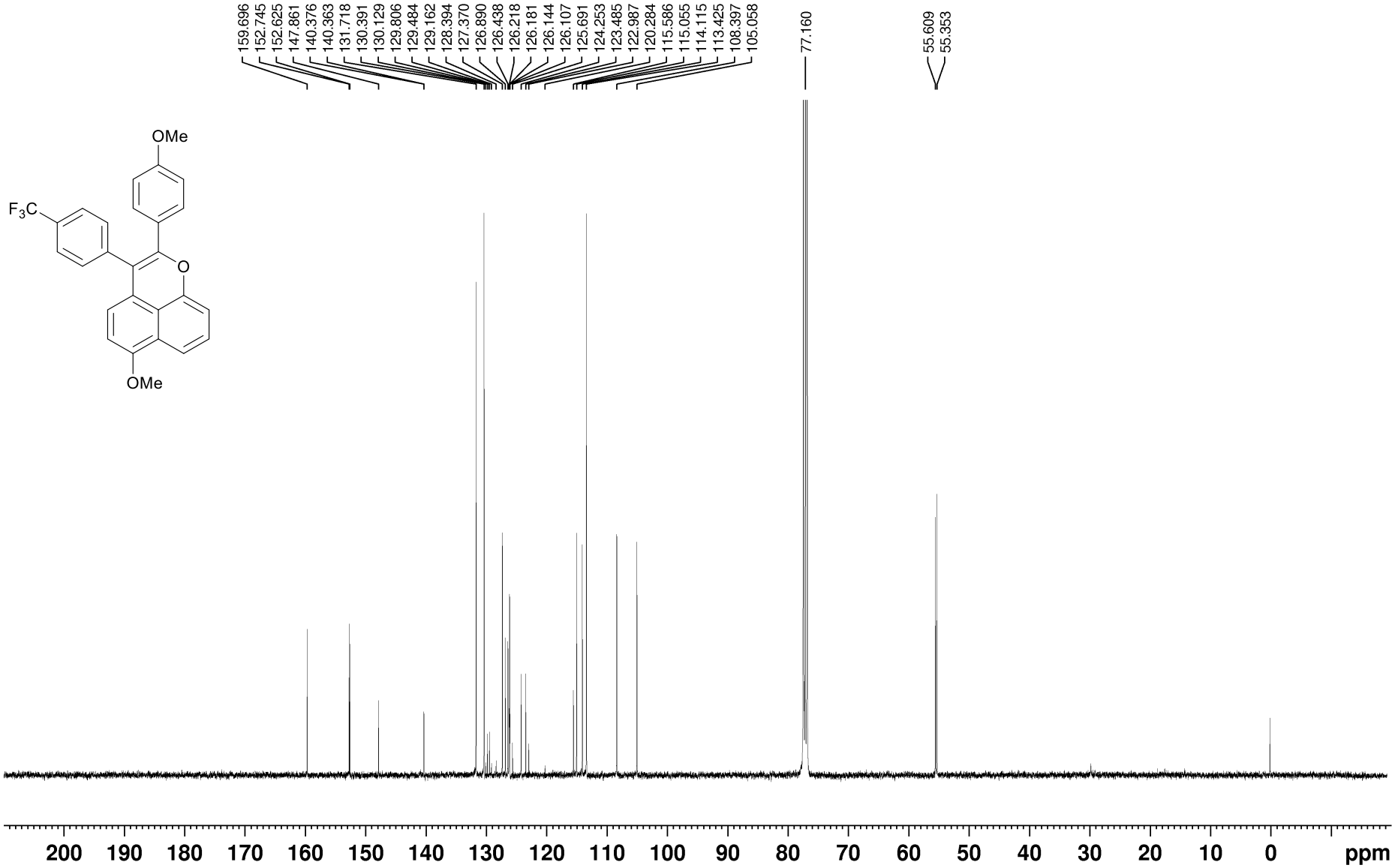
^{19}F NMR ($CDCl_3$, 376 MHz) of 6-methoxy-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



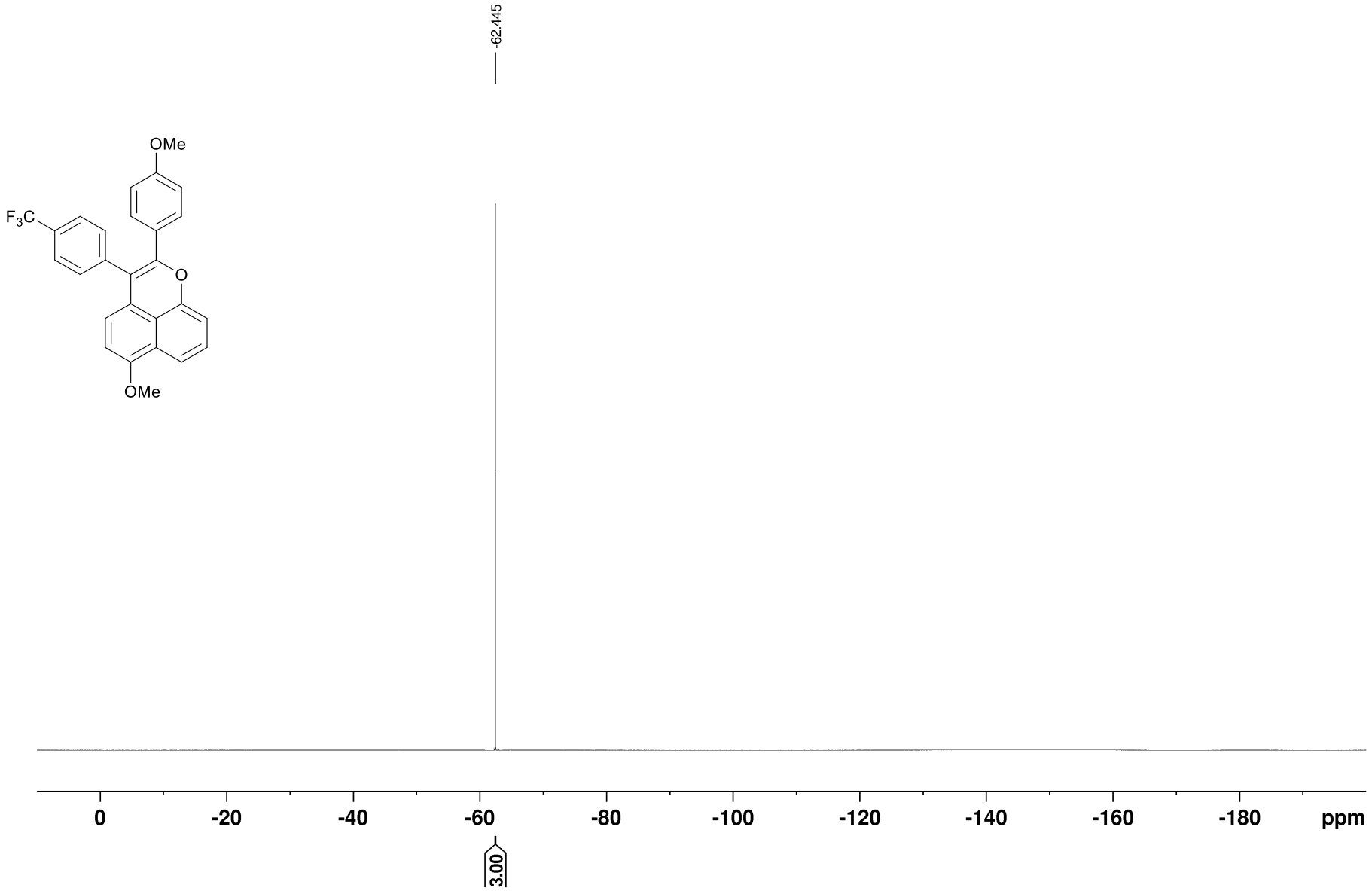
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



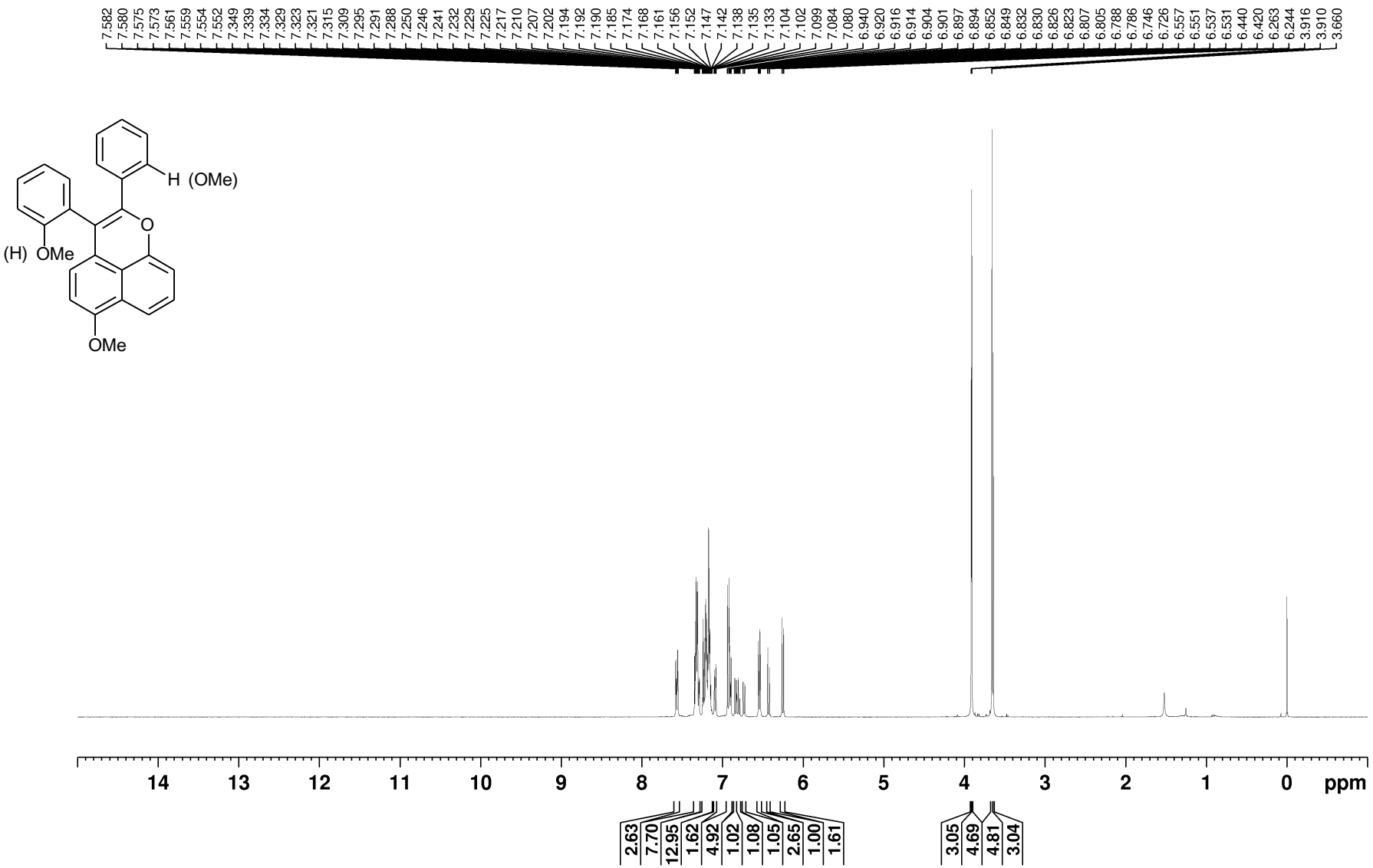
^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



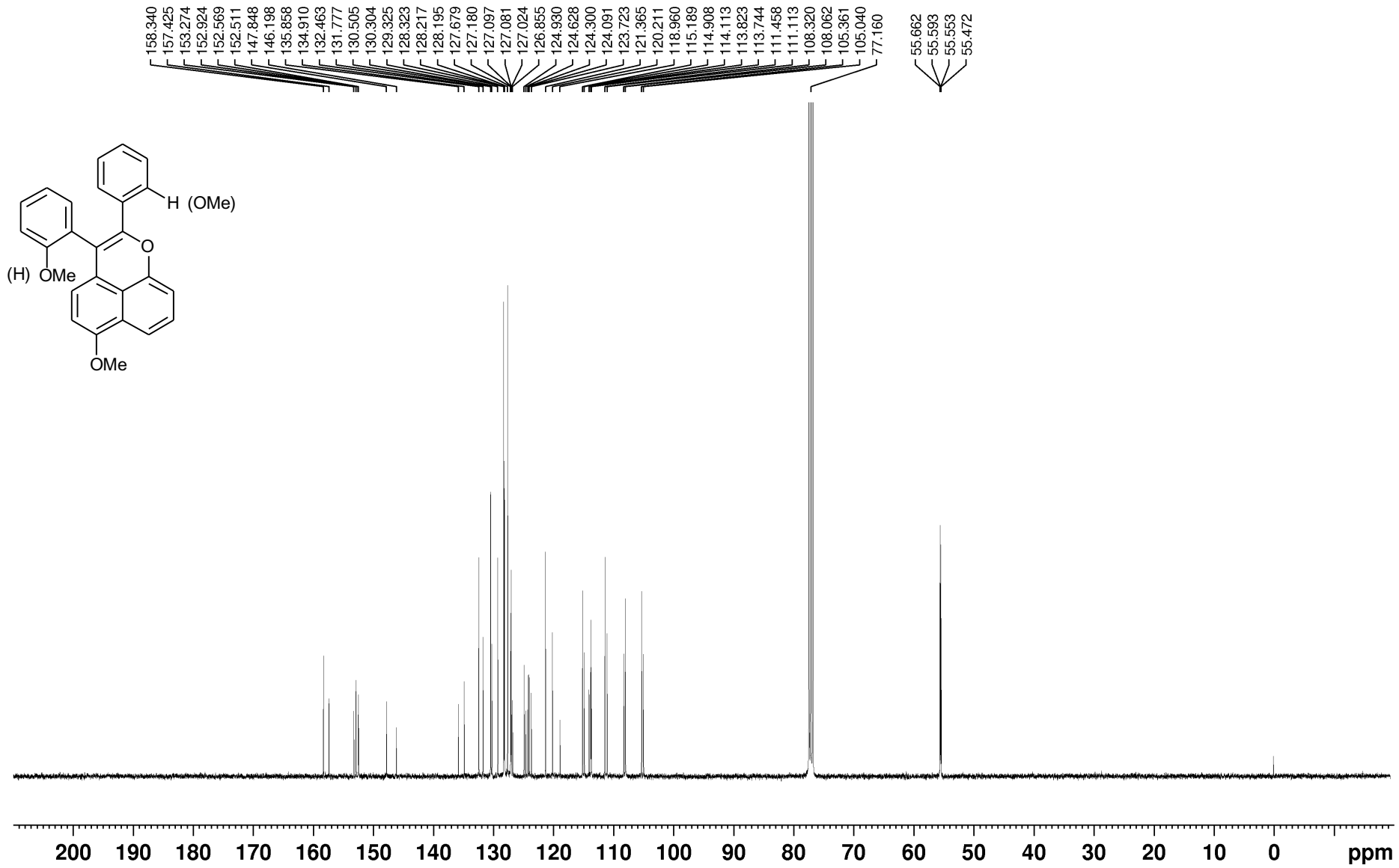
^{19}F NMR ($CDCl_3$, 376 MHz) of 6-methoxy-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)benzo[*de*]chromene (3bj)



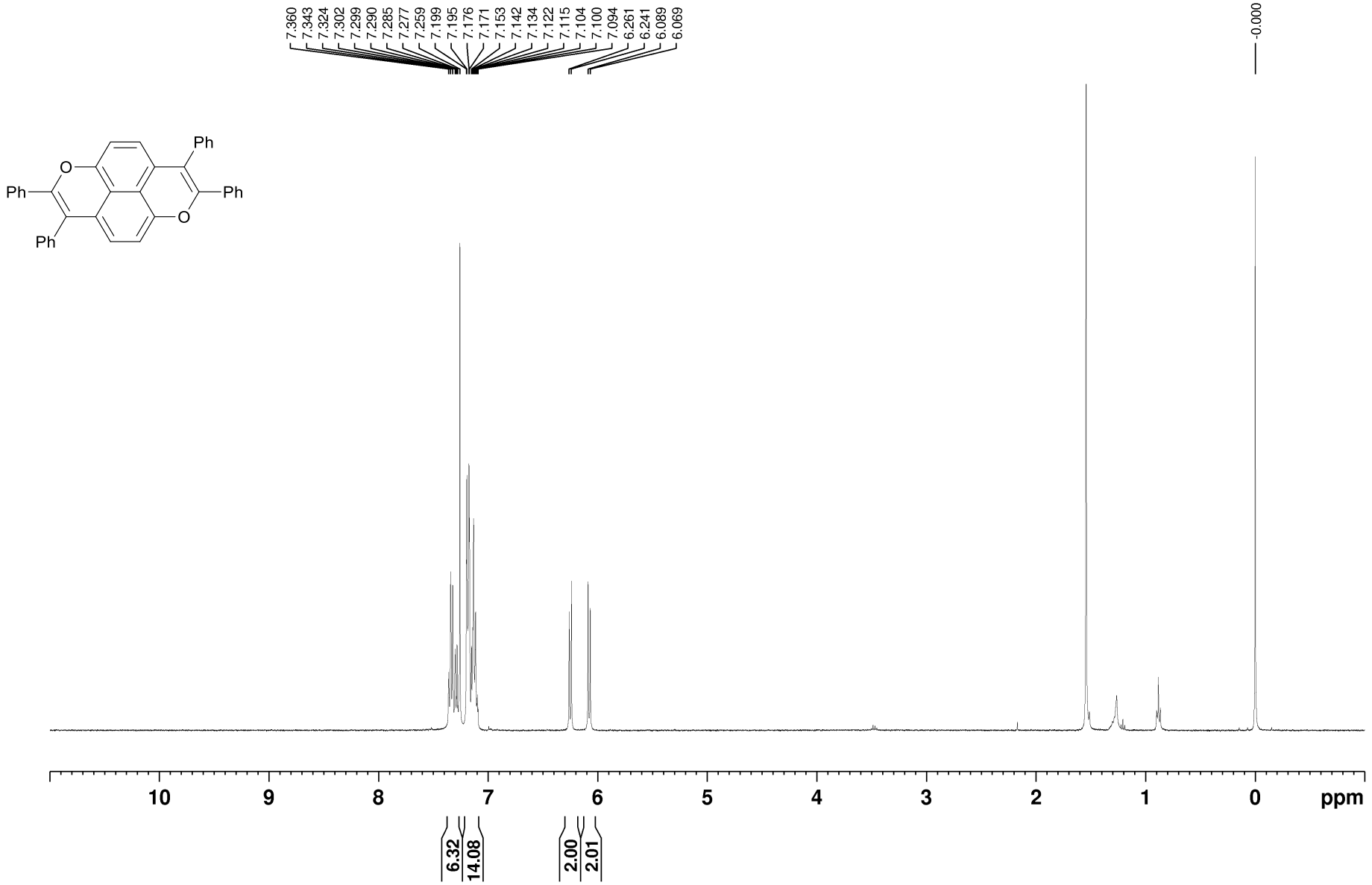
^{1}H NMR ($CDCl_3$, 400 MHz) of 6-methoxy-3-(2-methoxyphenyl)-2-phenylbenzo[*de*]chromene/6-methoxy-2-(2-methoxyphenyl)-3-phenylbenzo[*de*]chromene mixture (3bk/3bk')



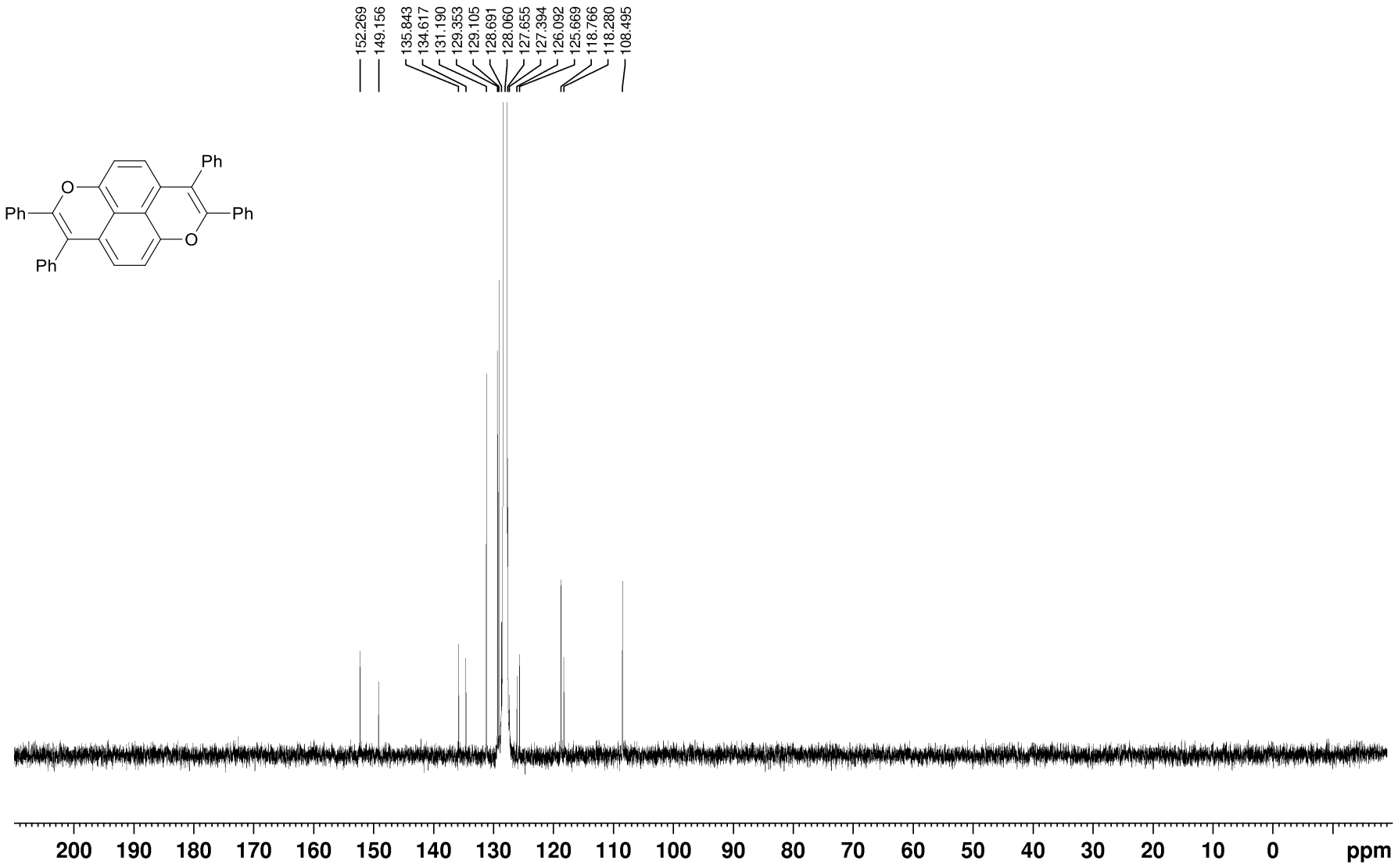
^{13}C NMR ($CDCl_3$, 100 MHz) of 6-methoxy-3-(2-methoxyphenyl)-2-phenylbenzo[*de*]chromene/6-methoxy-2-(2-methoxyphenyl)-3-phenylbenzo[*de*]chromene mixture (3bk/3bk')



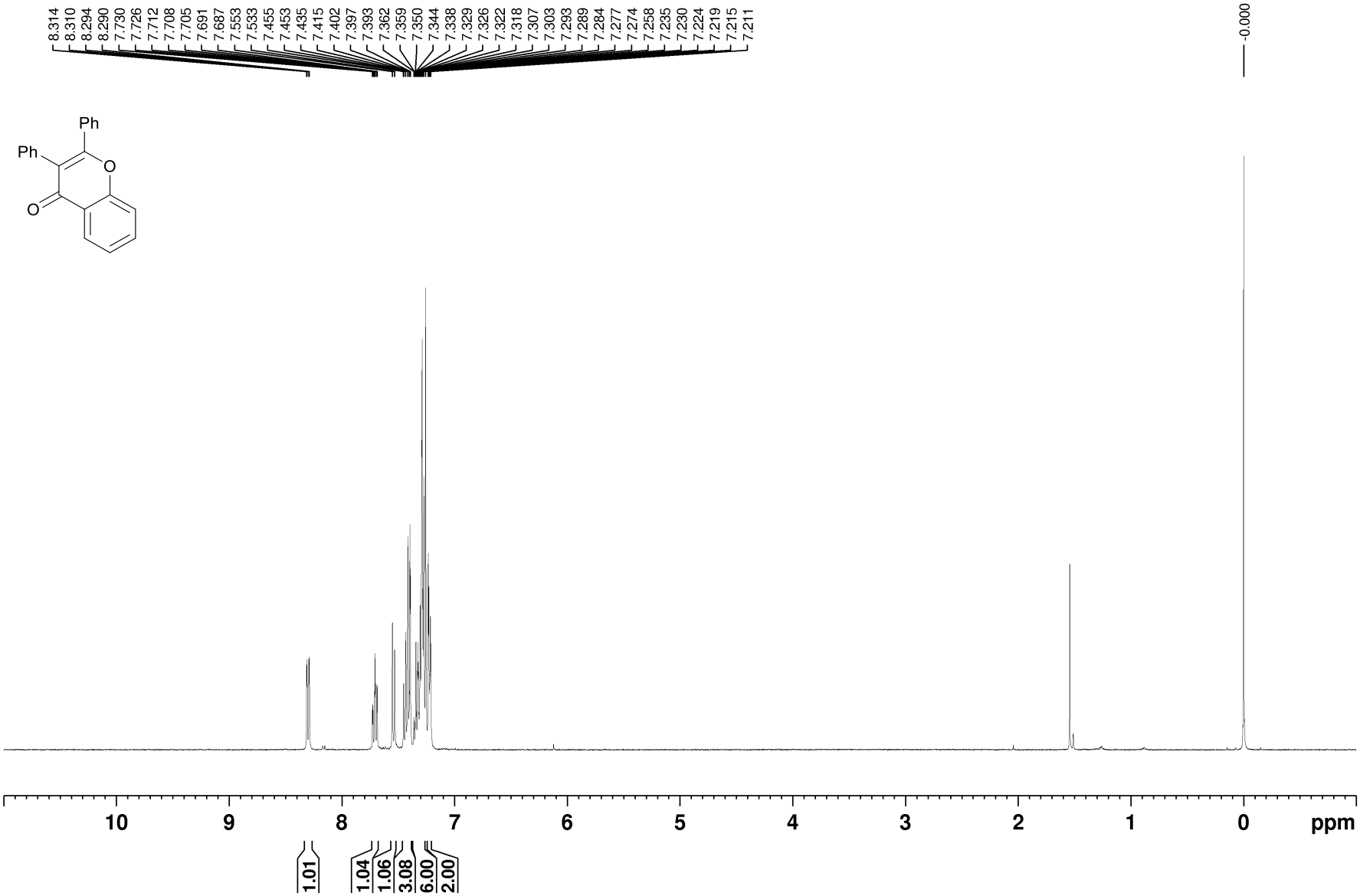
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3,7,8-tetraphenylchromeno[6,5,4-*def*]chromene (3da)



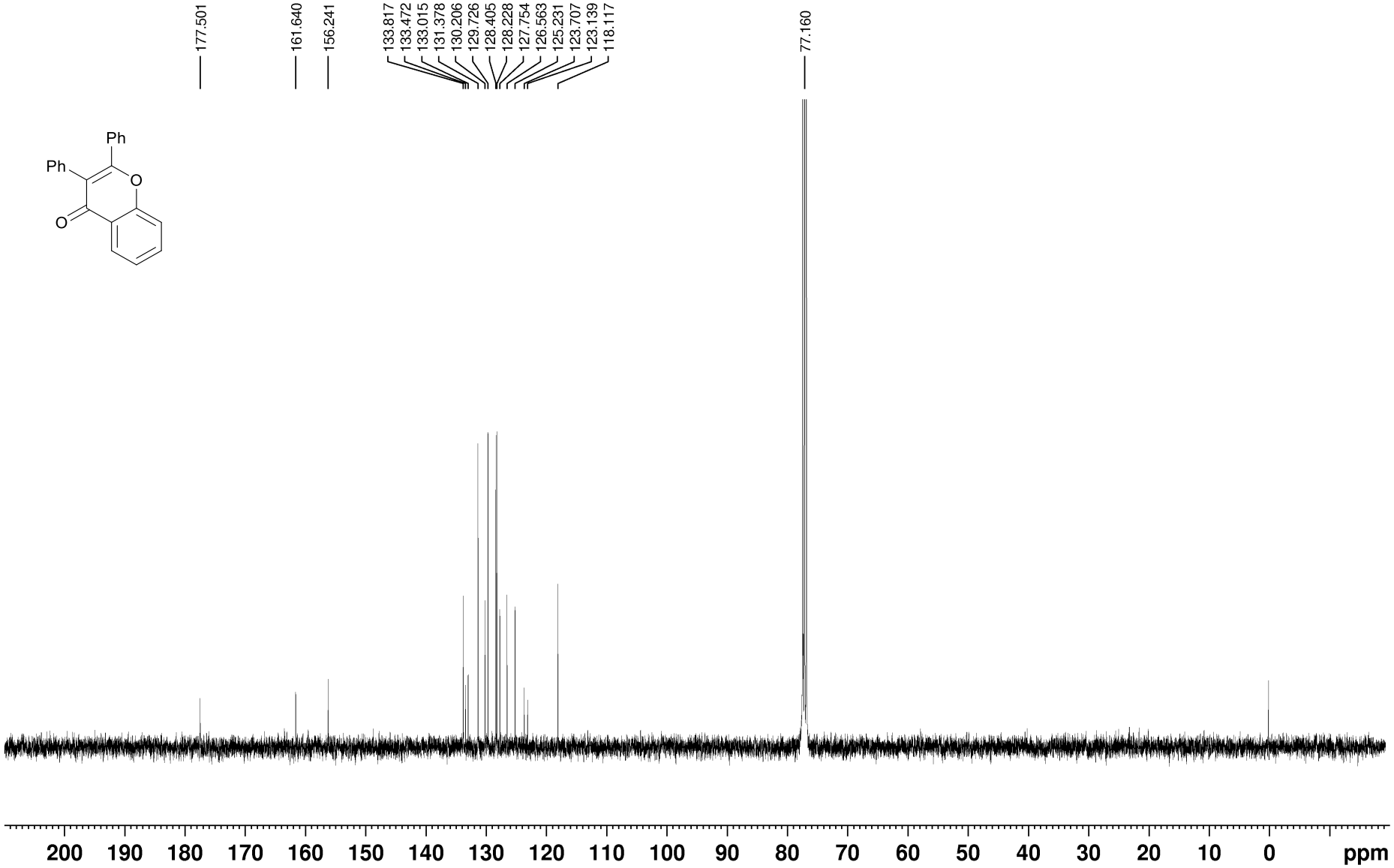
^{13}C NMR (C_6D_6, 100 MHz) of 2,3,7,8-tetraphenylchromeno[6,5,4-*def*]chromene (3da)



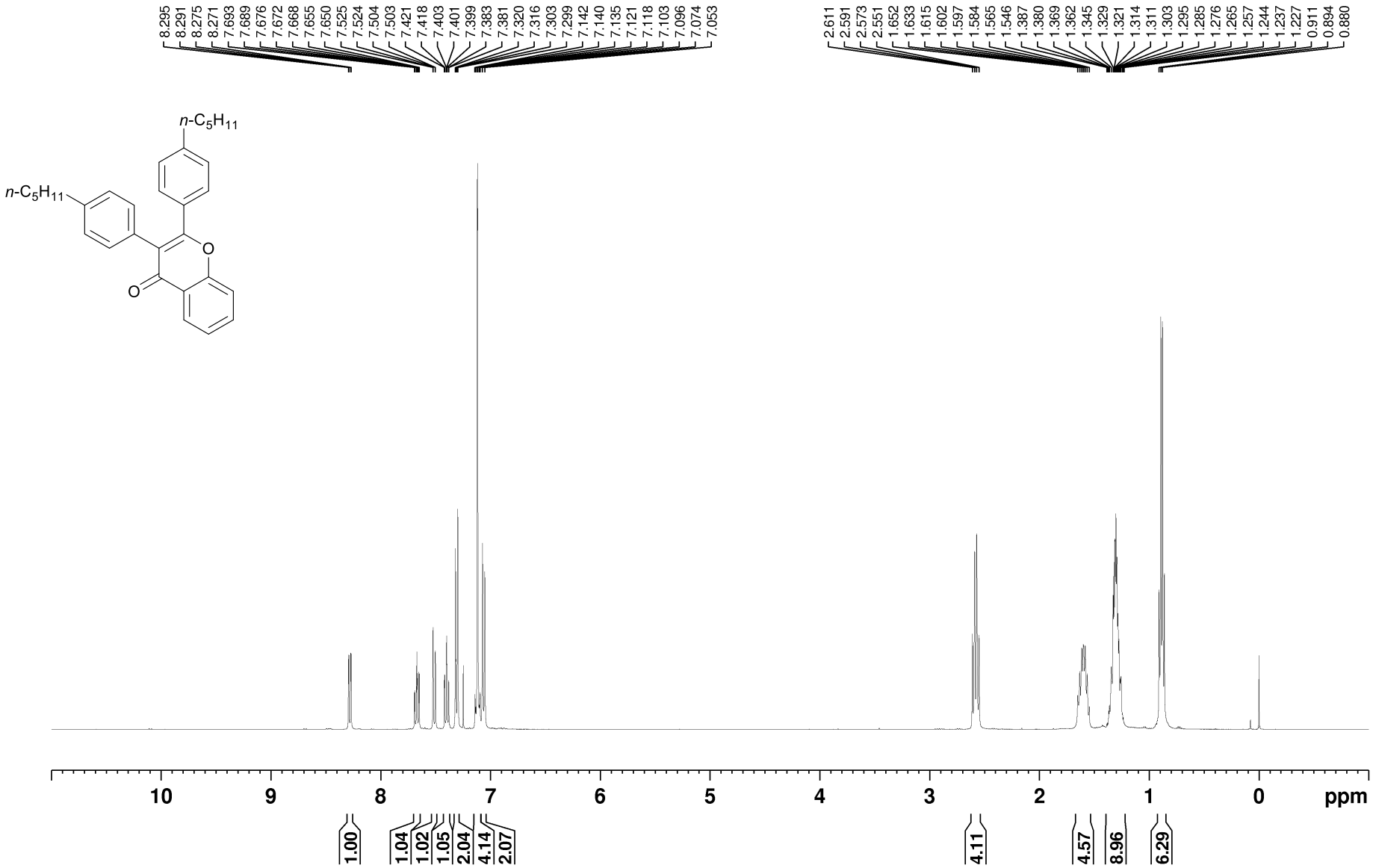
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-diphenyl-4H-chromen-4-one (5a)



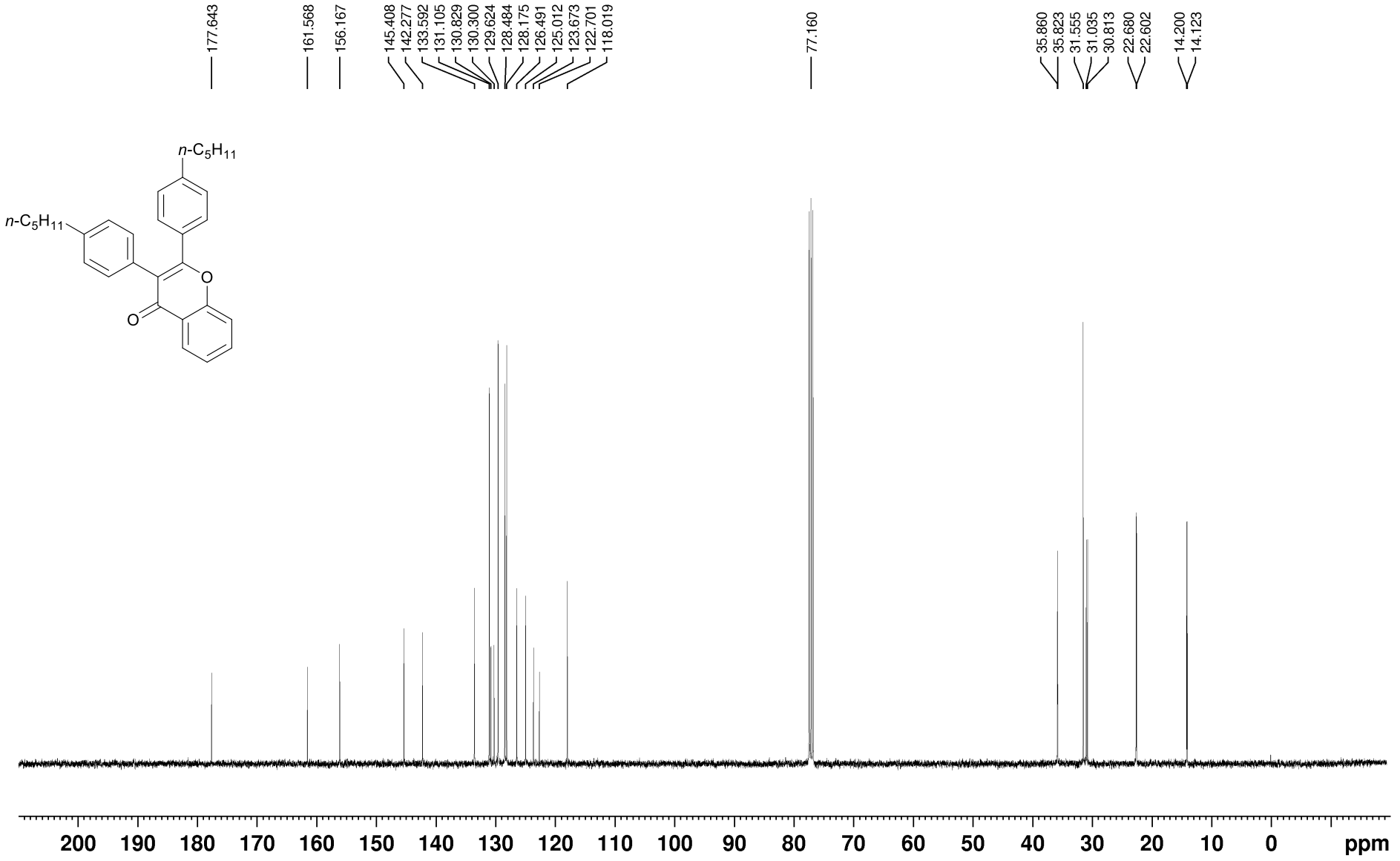
^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-diphenyl-4H-chromen-4-one (5a)



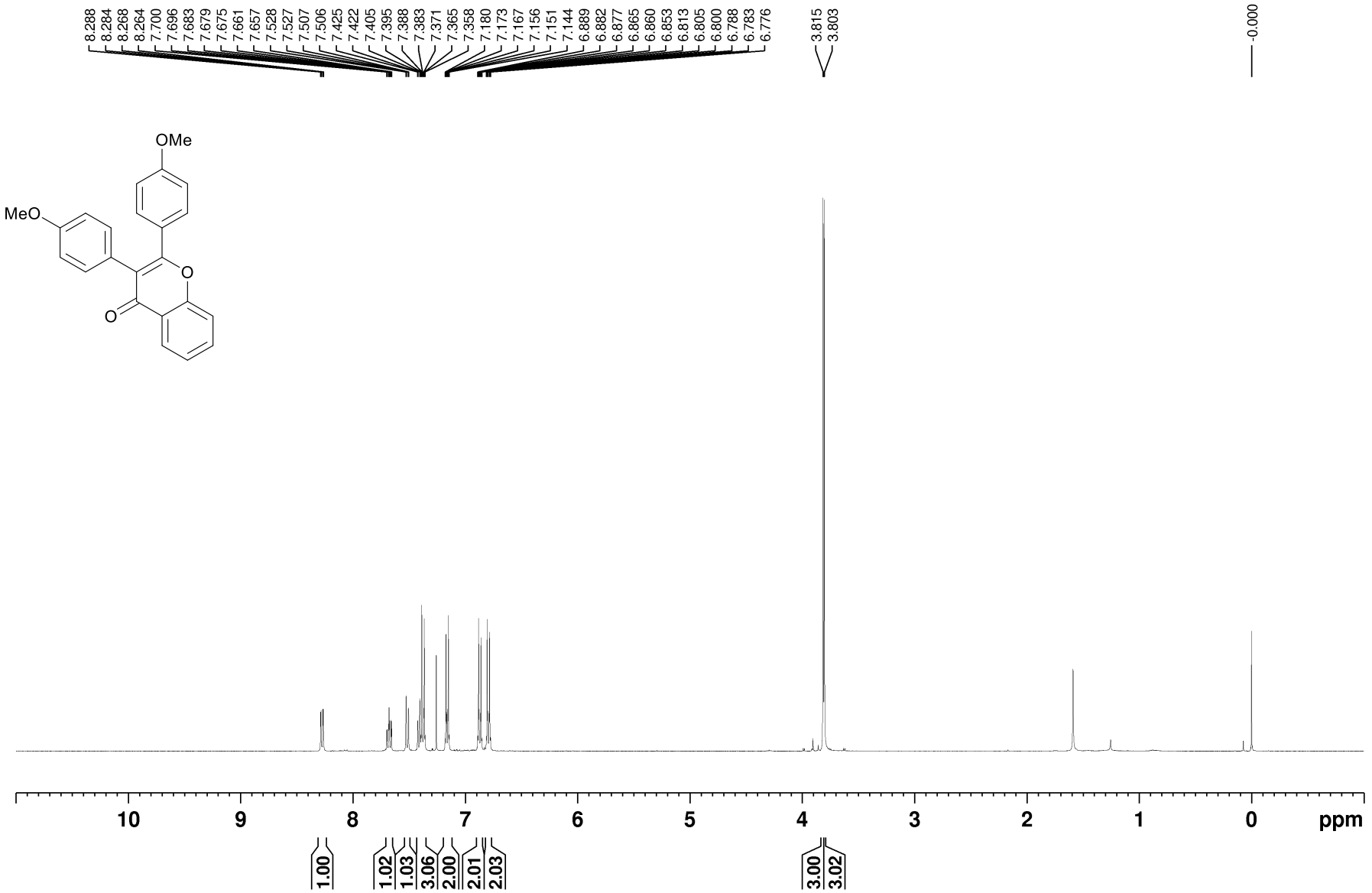
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-bis(4-pentylphenyl)-4H-chromen-4-one (5c)



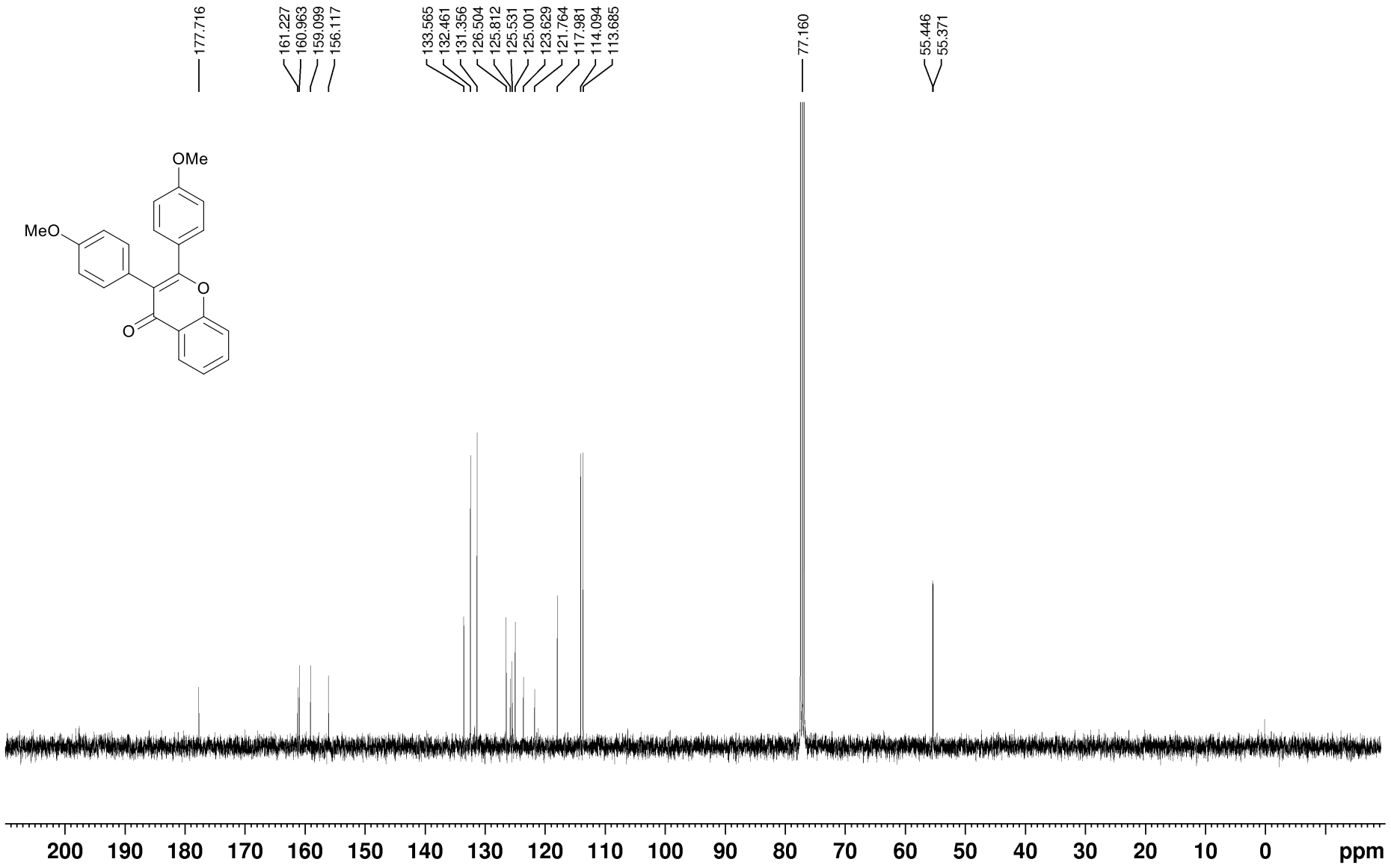
^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-bis(4-pentylphenyl)-4H-chromen-4-one (5c)



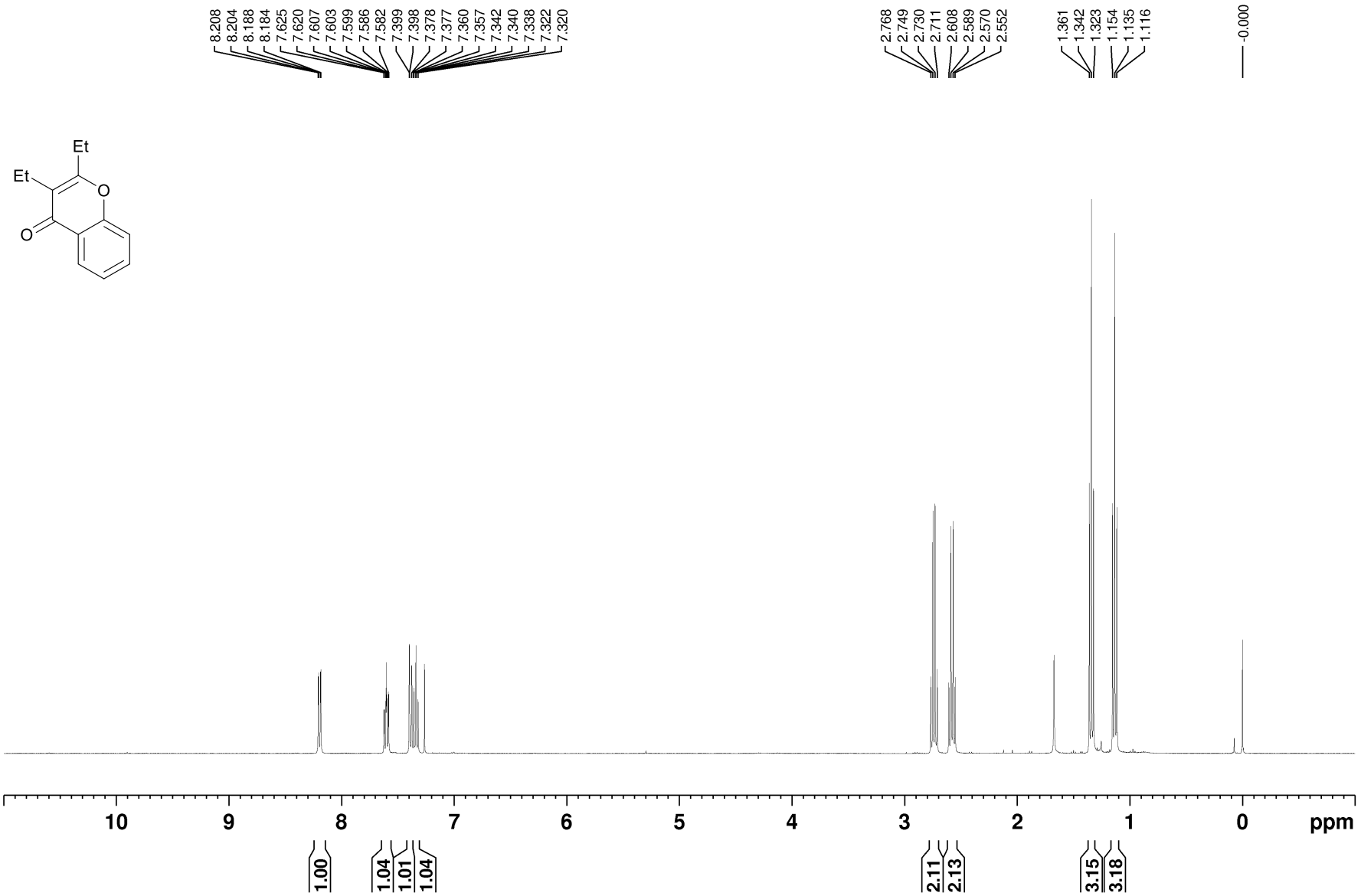
^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-bis(4-methoxyphenyl)-4H-chromen-4-one (5d)



^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-bis(4-methoxyphenyl)-4H-chromen-4-one (5d)



^{1}H NMR ($CDCl_3$, 400 MHz) of 2,3-diethyl-4H-chromen-4-one (5h)



^{13}C NMR ($CDCl_3$, 100 MHz) of 2,3-diethyl-4H-chromen-4-one (5h)