Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Synthesis of N-Functionalized 2,3 - Disubstituted Benzofurans/Naphthofurans from *para*-Quinone Methides and Isocyanides via [4 +1] Annulation Pathway

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1. General Information

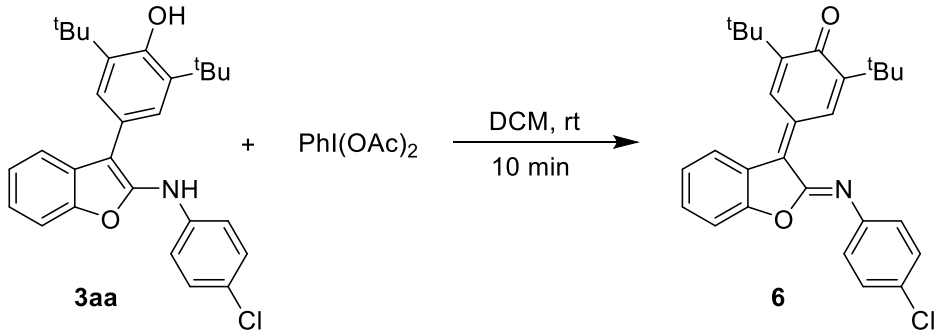
Unless otherwise stated, all commercially available reagents were used as received without further purification. All reactions were carried out using flame-dried glassware with magnetic stirring. All the solvents were distilled prior to use. Thin layer chromatography (TLC) was performed on precoated 0.25 mm silica gel plates 60 F254 and was visualized by exposure to ultraviolet light or $KMnO_4$/DNP/Ninhydrin stain. Column chromatography was performed on silica gel (230-400 mesh) by using Teledyne Isco combi *flash RF+*. ^1H, ^{13}C NMR spectra were recorded on 400 MHz or 500 MHz Bruker/JEOL spectrometers using TMS as an internal standard. $CDCl_3$ was purchased from Merck ($CDCl_3$ at 7.26 ppm for ^1H and 77.16 ppm for ^{13}C), (DMSO-d_6 at 2.50 ppm for ^1H and 39.51 ppm for ^{13}C) Chemical shifts (δ) are given in ppm. All the NMR spectra were processed in either MestReNova or Bruker software. The following abbreviations are used to explain multiplicities: s = singlet, d = doublet, t = triplet and m = multiplet. High Resolution Mass Spectroscopy (HRMS) was recorded on Qexcative-orbitrap spectrometer with electrospray ionization as ionization source. Elemental analyses were recorded on a Thermo-Finnigan Flash EA 1112 analyzer. Melting points were recorded on Buchi B-540 instrument.

Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. The *para*-quinone methides and isocyanide derivatives were prepared following the literature procedures.[1-2]

2. General Procedure for Synthesis of Benzofurans 3 & Naphthofurans 5

In an oven-dried round bottom flask *p*-QM[1] (0.1 mmol, 1eq), Isocyanide[2] (1eq) were dissolved in Toluene (0.5 mL) to this mixture $Sc(OTf)_3$ (10 mol%) was added and the reaction mixture was stirred for 15 min to 2 h at 30 °C. The progress of the reaction was monitored by TLC and was purified by using column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate.

3. General Procedure for Synthesis ofCompound6



To a solution of Benzofuran**3aa**(0.1 mmol)in dichloromethane (DCM) (1 mL),(diacetoxyiodo)benzene (1 eq) was added. The reaction mixture was stirred at 30 °C for 10 min, the progress of the reaction was monitored by TLC and was purified by using column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate = 97:3 to afford 43.7 mg (88%) of the title compound

4. General Procedure for Synthesis of Compound 7a and 7b

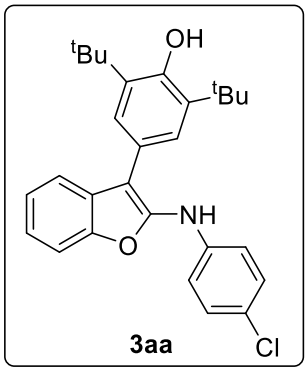
In an oven dry round bottom flask $AlCl_3$ (5 equiv.) and Benzofuran **3aa** (0. 15 mmol) in anhy. Toluene (2mL/mmol) stirred under nitrogen atmosphere at 30 °C, reaction progress monitored by TLC. After of the completion of reaction, the mixture was cooled to 0 °C and ice water was added to quench the $AlCl_3$. The mixture was extracted with EtOAc and the combined organic layers dried over Na_2SO_4 and evaporated under vacuum and was purified by using column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate (5-15%). (For compound **7a** reaction stirred for 15 min and for compound **7b** for 6 hrs)

5. General Procedure for Synthesis of Compound 9

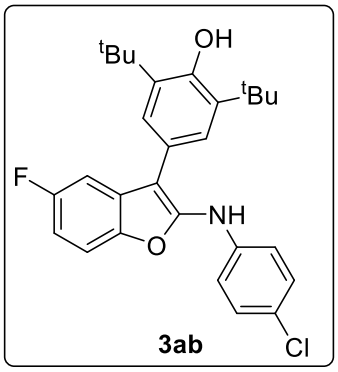
In an oven dry Schlenck tube*o*-hydroxybenzhydryl alcohol **8** (0.2mmol), isocyanide **2a**(0.2 mmol)), were dissolved in Toluene (1 mL) to this mixture $Sc(OTf)_3$ (10 mol%) was added and the reaction mixture was stirred for 30 min and then solvent of reaction mixture evaporated

under reduced pressure. The mixture of compound purified by using column chromatography on silica gel with a gradient eluent of ethyl acetate and petroleum ether (5-15%).

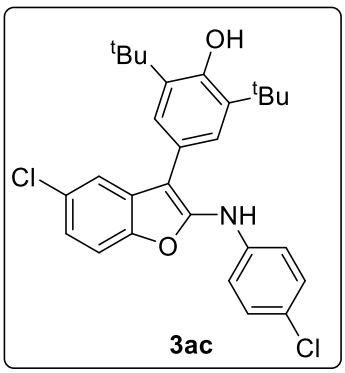
6. Characterization of Compounds



(3aa): Reaction time: (15 min); Brown solid (43.9 mg, 98%); mp 170-171 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 1H), 7.50 – 7.43 (m, 1H), 7.38 (s, 2H), 7.23 – 7.18 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.07 (s, 1H), 5.29 (s, 1H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.09, 151.20, 147.06, 141.67, 136.68, 129.33, 128.97, 125.71, 125.05, 123.30, 123.18, 122.89, 119.28, 116.93, 110.97, 106.64, 34.56, 30.39; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{30}ClNO_2[M+H]^+$ 448.2038 found 448.2025.

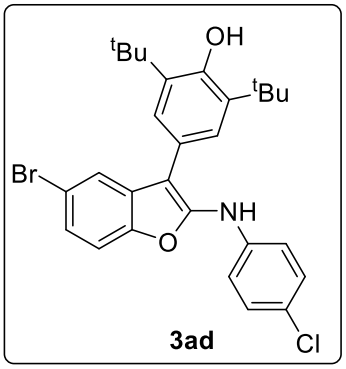


(3ab): Reaction time: (30 min); Brown solid (35.3 mg, 76%); mp 171-172 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.30 (s, 2H), 7.27 – 7.22 (m, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.98 – 6.88 (m, 3H), 6.14 (s, 1H), 5.30 (s, 1H), 1.44 (s, 18H);^{13}C NMR (126 MHz, $CDCl_3$) δ 159.80 (d, *J* = 237.9 Hz), 153.21, 148.95, 147.07, 140.78, 136.89, 130.16 (d, *J* = 10.1 Hz), 129.36, 126.18, 124.88, 122.46, 117.38, 111.39 (d, *J* = 9.6 Hz), 110.15 (d, *J* = 26.2 Hz), 105.26, 104.90 (d, *J* = 25.8 Hz), 34.58, 30.39; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.21; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{29}ClFNO_2[M+H]^+$466.1944 found 466.1930.

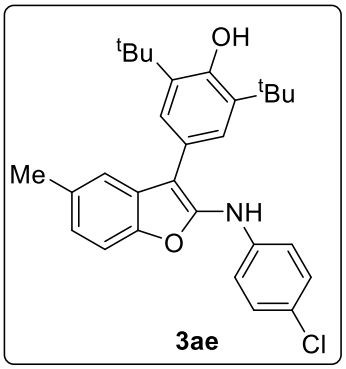


(3ac): Reaction time: (20 min); Sticky liquid (39.1 mg, 81%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.23 – 7.13 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.14 (s, 1H), 5.29 (s, 1H), 1.43 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 149.30, 148.71, 140.68, 136.94, 130.71, 129.37, 128.93,

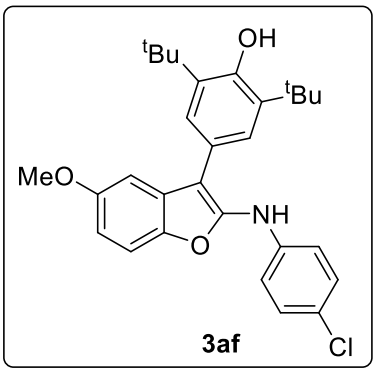
126.28, 125.01, 122.93, 122.27, 118.65, 117.47, 111.75, 104.62, 34.58, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{29}Cl_2NO_2$ $[M+H]^+$ 482.1648 found 482.1641.



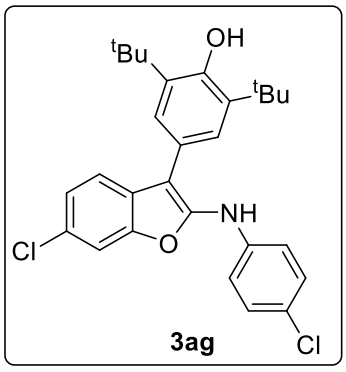
(3ad): Reaction time: (20 min); Sticky liquid (49.7 mg, 94%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.27 (s, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.14 (s, 1H), 5.30 (s, 1H), 1.43 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 149.69, 148.58, 140.64, 136.95, 131.31, 129.37, 126.31, 125.65, 125.03, 122.23, 121.65, 117.49, 116.46, 112.23, 104.41, 34.58, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{29}BrClNO_2$ $[M+H]^+$ 526.1148 found 526.1144.



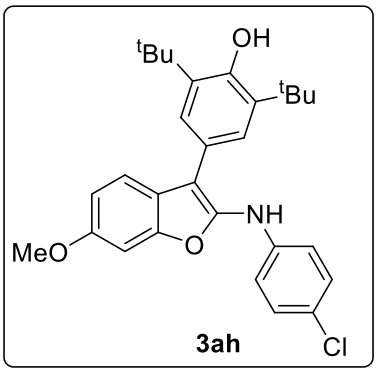
(3ae): Reaction time: (20 min); Brown solid (39.3 mg, 85%); mp 131-132 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.36 –7.31 (m, 3H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.02 (s, 1H), 5.27 (s, 1H), 2.46 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.06, 149.52, 147.18, 141.80, 136.64, 132.62, 129.32, 128.99, 125.63, 125.10, 124.37, 122.99, 119.26, 116.87, 110.51, 106.55 , 34.57, 30.39, 21.74; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{32}ClNO_2$ $[M+H]^+$ 462.2194 found 462.2184.



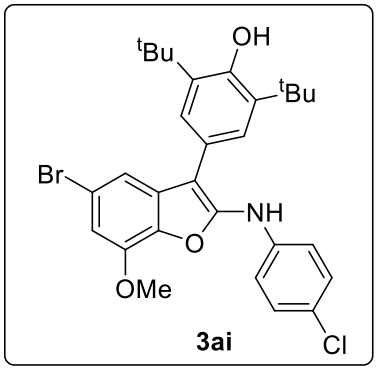
(3af): Reaction time: (20 min); Sticky liquid (40.2 mg, 84%); R_f = 0.7 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.07 (s, 1H), 5.27 (s, 1H), 3.84 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.25, 152.92, 147.80, 145.82, 141.37, 136.62, 129.43, 129.20, 125.63, 124.82, 122.84, 116.89, 111.24, 111.00, 106.20, 102.35, 55.89, 34.46, 30.28; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{32}ClNO_3$ $[M+H]^+$ 478.2143 found 478.2142.



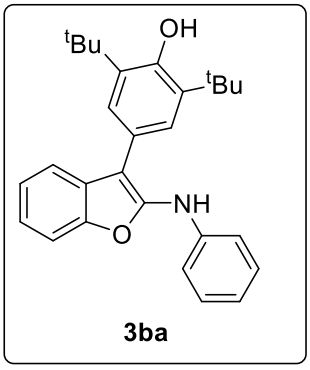
(3ag): Reaction time: (20 min); liquid (38.2 mg, 79%); R_f = 0.7 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.1 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.28 (s, 2H), 7.23 – 7.12 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.14 (s, 1H), 5.30 (s, 1H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.28, 149.29, 148.69, 140.66, 136.91, 130.69, 129.36, 128.91, 126.26, 125.00, 122.92, 122.25, 118.63, 117.44, 111.75, 104.59, 34.57, 30.38; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{29}Cl_2NO_2$ $[M+H]^+$ 482.1648 found 482.1644.



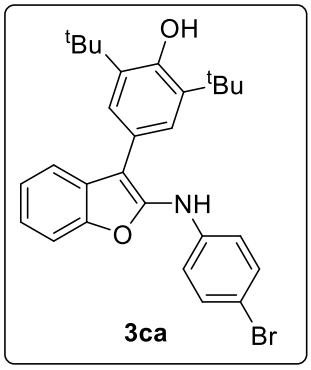
(3ah): Reaction time: (15 min); Brown solid (40.1 mg, 84%); mp 188-189 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 1H), 7.37 (s, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 1.6 Hz, 1H), 6.94 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.88 (s, 1H), 5.28 (s, 1H), 3.88 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.76, 153.15, 152.38, 145.41, 142.88, 136.56, 129.35, 125.25, 124.98, 122.90, 121.88, 120.00, 116.25, 111.60, 109.56, 96.30, 55.93, 34.54, 30.35; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{32}ClNO_3$ $[M]^+$ 477.2071 found 477.2067.



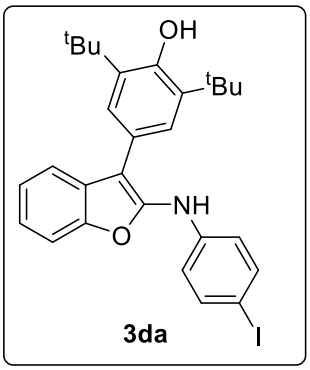
(3ai): Reaction time: (25 min); Brown solid (37.9 mg, 68%); mp187-189 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 1.7 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 1.7 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.07 (s, 1H), 5.28 (s, 1H), 4.00 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 147.99, 145.36, 141.02, 138.87, 136.80, 132.00, 129.29, 126.00, 125.06, 122.19, 117.17, 116.35, 114.62, 109.63, 106.15, 56.53, 34.55, 30.37; Analysis Calculated for C, 62.54; H, 5.61; N, 2.52; Found C,61.96; H, 6.21; N, 1.51.



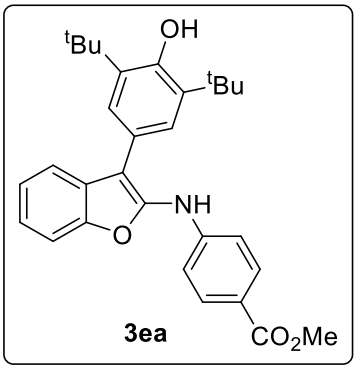
(3ba): Reaction time: (20 min); Brown solid (29.4 mg, 71%); mp 156-157 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 4.6, 2.4 Hz, 1H), 7.48 (d, *J* = 6.5 Hz, 1H), 7.42 (s, 2H), 7.36 – 7.25 (m, 4H), 7.08 – 6.87 (m, 3H), 6.11 (s, 1H), 5.29 (s, 1H), 1.45 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.97, 151.18, 147.81, 143.04, 136.64 , 129.45, 129.11, 125.06, 123.18, 123.06, 123.00, 120.97, 119.10, 115.82, 110.94, 105.98, 34.57, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{31}NO_2$ $[M+H]^+$ 414.2428 found 414.2422.



(3ca): Reaction time: (20 min); liquid (41.1 mg, 83%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 1H), 7.38 – 7.31 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 5.96 (s, 1H), 5.18 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.12, 151.23, 146.95, 142.18, 136.72, 132.24, 128.96, 125.06, 123.34, 123.19, 122.88, 119.31, 117.36, 112.97, 110.99, 106.81, 34.58, 30.41; Analysis calcd for C, 68.29; H, 6.14; N, 2.84; Found C, 67.64; H, 6.94; N, 1.82.

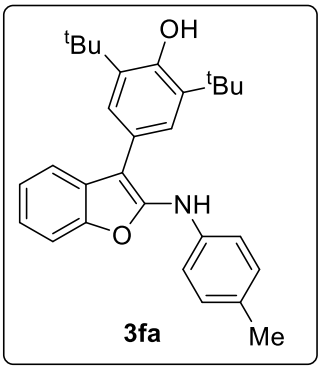


(3da): Reaction time: (20 min); liquid (41.1 mg, 76%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.35 (s, 2H), 7.29 – 7.24 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 5.27 (s, 1H), 1.42 (s, 18H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.12, 151.23, 146.79, 142.86, 138.14, 136.70, 128.93, 125.06, 123.37, 123.19, 122.84, 119.33, 117.83, 111.00, 106.93, 82.59, 34.58, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{30}INO_2$ $[M]^+$ 539.1321 found 539.1318.



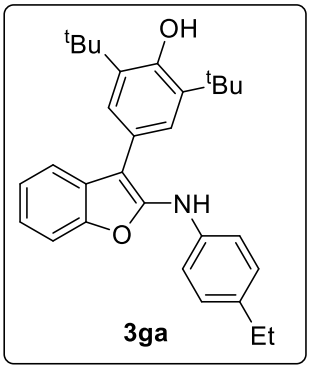
3ea

(3ea): Reaction time: (20 min); liquid (36.5 mg, 77%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.77 – 7.61 (m, 1H), 7.49 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.38 (s, 2H), 7.35 – 7.27 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.33 (s, 1H), 5.30 (s, 1H), 3.89 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.09, 153.25, 151.45, 147.62, 145.77, 136.70, 131.57, 128.63, 125.06, 123.83, 123.24, 122.59, 122.07, 119.67, 114.43, 111.17, 108.86, 51.93, 34.55, 30.35; HRMS (ESI+) (*m/z*) calcd for $C_{30}H_{33}NO_4$ $[M]^+$ 471.2404 found 471.2402.



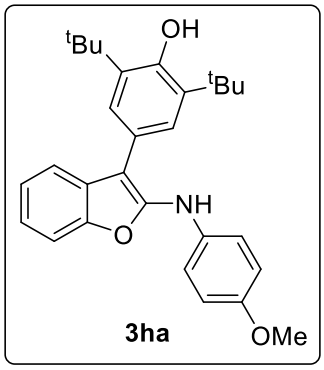
3fa

(3fa): Reaction time: (20 min); Brown solid (37.1 mg, 87%); mp 177-179 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.41 (s, 2H), 7.33 – 7.16 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.07 (s, 1H), 5.27 (s, 1H), 2.31 (s, 3H), 1.46 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.85, 151.01, 148.51, 140.18, 136.63, 130.51, 129.89, 129.32, 125.04, 123.36, 123.03, 122.61, 118.78, 116.30, 110.81, 104.37, 34.57, 30.42, 20.74; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{33}NO_2$ $[M+H]^+$ 428.2584 found 428.2578.

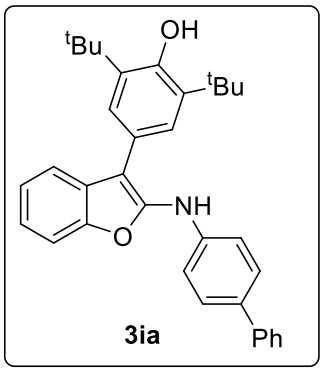


3ga

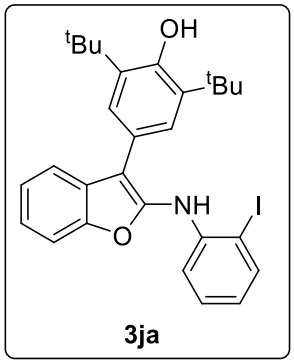
(3ga): Reaction time: (20 min); Brown solid (34.9 mg, 79%); mp 113-114 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.42 (s, 2H), 7.32 – 7.23 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 5.28 (s, 1H), 2.62 (q, *J* = 14.04 Hz, 2H), 1.47 (s, 18H), 1.24 (t, *J* = 7.3 Hz, 3H);^{13}C NMR (126 MHz, $CDCl_3$) δ 152.86, 151.03, 148.49, 140.44, 137.11, 136.64, 129.33, 128.75, 125.06, 123.36, 123.03, 122.64, 118.82, 116.30, 110.83, 104.55, 34.59, 30.43, 28.25, 16.04; HRMS (ESI+) (*m/z*) calcd for $C_{30}H_{35}NO_2$ $[M+H]^+$ 442.2741 found 442.2732.



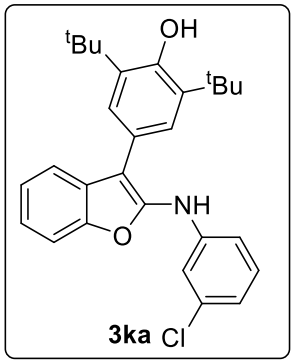
(3ha): Reaction time: (20 min); Brown solid (40.1 mg, 90%); mp114-115 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.39 (s, 2H), 7.30 – 7.20 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.03 (s, 1H), 5.27 (s, 1H), 3.80 (s, 3H), 1.46 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.71, 152.80, 150.86, 149.07, 136.65, 135.93, 129.50, 127.96, 125.00, 123.43, 123.05, 122.37, 118.57, 118.18, 114.79, 110.70, 103.18, 55.80, 34.58, 30.44; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{33}NO_3$ $[M+H]^+$ 444.2533 found 444.2525.



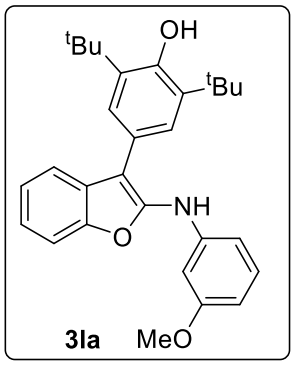
(3ia): Reaction time: (20 min); liquid (38.2 mg, 78%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 1H), 7.49 – 7.45 (m, 2H), 7.44 – 7.37 (m, 3H), 7.35 – 7.30 (m, 1H), 7.28 (s, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 7.02 – 6.90 (m, 2H), 6.17 (s, 1H), 5.18 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.99, 151.33, 147.15, 140.33, 138.78, 136.42, 130.60, 129.49, 129.22, 129.11, 129.08, 128.66, 127.80, 124.94, 123.32, 122.98, 120.78, 119.43, 115.33, 110.97, 108.11, 34.50, 30.36; HRMS (ESI+) (*m/z*) calcd for $C_{34}H_{35}NO_2$ $[M+H]^+$ 490.2746 found 490.2740.



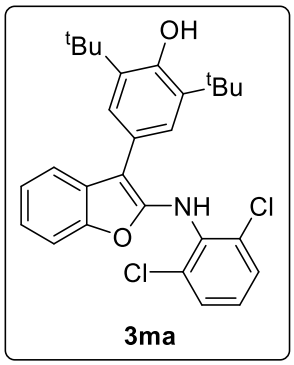
(3ja): Reaction time: (20 min); Brown solid (42.1 mg, 78%); mp 149-150 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.54 – 7.45 (m, 1H), 7.40 (s, 2H), 7.31 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.20 – 7.03 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.67 – 6.59 (m, 1H), 6.54 (s, 1H), 5.27 (s, 1H), 1.45 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.16, 151.39, 146.46, 143.09, 139.14, 136.56, 129.45, 128.80, 124.94, 123.60, 123.17, 122.65, 122.19, 119.64, 115.29, 111.09, 108.35, 85.82, 34.58, 30.42; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{30}INO_2$ $[M+H]^+$ 540.1394 found 540.1383.



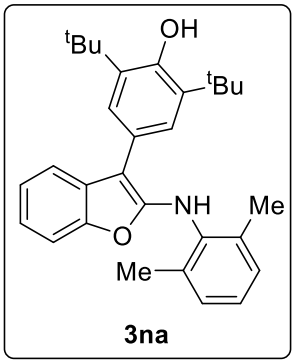
(3ka): Reaction time: (20 min); liquid (42.1 mg, 94%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 1H), 7.50 – 7.42 (m, 1H), 7.34 (s, 2H), 7.31 – 7.23 (m, 1H), 7.17 – 7.10 (m, 1H), 6.94 – 6.88 (m, 1H), 6.86 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 6.78 (ddd, *J* = 8.2, 2.2, 0.8 Hz, 1H), 6.06 (s, 1H), 5.26 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.16, 151.31, 146.54, 144.33, 136.68, 135.21, 130.38, 128.92, 125.09, 123.50, 123.19, 122.78, 120.81, 119.45, 115.62, 113.88, 111.08, 107.48, 34.57, 30.39; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{30}ClNO_2$ $[M]^+$ 447.1960 found 447.1954.



(3la): Reaction time: (20 min); liquid (34.5 mg, 78%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 1H), 7.48 – 7.42 (m, 1H), 7.39 (s, 2H), 7.31 – 7.21 (m, 2H), 7.17 – 7.11 (m, 1H), 6.66 – 6.37 (m, 3H), 6.10 (s, 1H), 5.25 (s, 1H), 3.67 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.77, 152.94, 151.17, 147.47, 143.97, 136.56, 130.14, 129.15, 125.10, 123.15, 123.06, 123.05, 119.16, 110.91, 108.62, 106.61, 105.86, 101.78, 55.28, 34.55, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{33}NO_3$ $[M]^+$ 443.2455 found 443.2456.

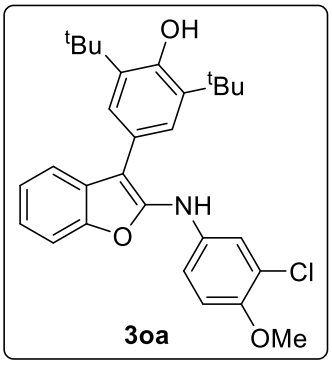


(3ma): Reaction time: (40 min); Brown solid (38.8 mg, 80%); mp 139-140 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 1H), 7.46 – 7.32 (m, 3H), 7.27 – 7.15 (m, 4H), 6.96 – 6.77 (m, 1H), 6.38 (s, 1H), 5.19 (s, 1H), 1.45 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.84, 150.79, 146.84, 136.12, 135.93, 129.89, 128.81, 127.23, 125.48, 123.67, 123.01, 122.87, 122.78, 119.06, 110.78, 105.29, 34.54, 30.44; HRMS (ESI+) (*m/z*) calcd for $C_{28}H_{29}Cl_2NO_2$ $[M+H]^+$ 482.1648 found 482.1643.



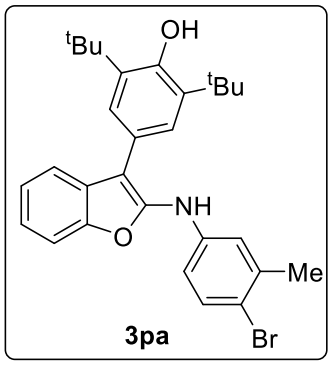
3na

(3na): Reaction time: (20 min); liquid (33.6 mg, 76%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.45 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.12 – 7.04 (m, 4H), 5.88 (s, 1H), 5.24 (s, 1H), 2.31 (s, 6H), 1.52 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.26, 151.43, 150.07, 136.45, 134.13, 130.87, 128.67, 127.81, 125.61, 124.91, 123.97, 123.01, 120.76, 117.37, 110.21, 95.91, 34.61, 30.48, 18.75; HRMS (ESI+) (*m/z*) calcd for $C_{30}H_{35}NO_2[M]^+$441.2662 found 441.2664.



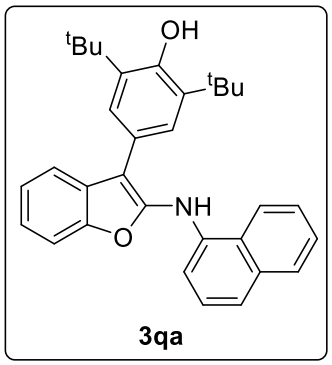
3oa

(3oa): Reaction time: (20 min); Brown solid (35.8 mg, 75%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.34 (s, 2H), 7.30 – 7.21 (m, 2H), 7.02 (s, 1H), 6.83 (s, 2H), 5.97 (s, 1H), 5.26 (s, 1H), 3.85 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.97, 150.98, 149.94, 147.86, 136.63, 129.29, 125.04, 123.28, 123.15, 123.01, 122.88, 118.94, 118.76, 115.72, 113.39, 110.84, 104.76, 56.84, 34.56, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{32}ClNO_3$ $[M]^+$ 477.2065 found 477.2065.



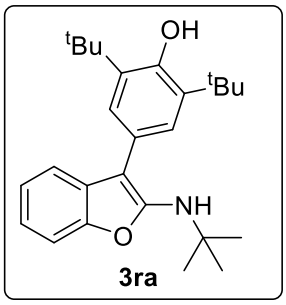
3pa

(3pa): Reaction time: (20 min); liquid (43.0 mg, 85%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 9.1 Hz, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.07 (s, 1H), 5.27 (s, 1H), 3.84 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.38, 153.05, 147.93, 145.95, 141.50, 136.74, 129.56, 129.33, 124.95, 117.02, 111.37, 111.13, 106.33, 102.48, 56.02, 34.59, 30.40; HRMS of oxidized product of **3pa** (ESI+) (*m/z*) calcd for $C_{29}H_{32}BrNO_2$ $[M+H]^+$ 504.1333 found 504.1546.



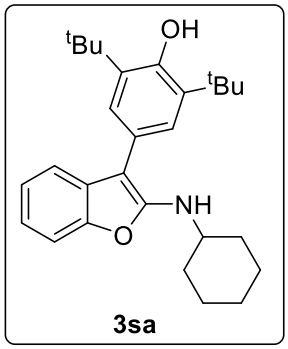
3qa

(3qa): Reaction time: (20 min); Brown solid (32.8 mg, 71%); mp 180-181 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 1H), 7.87 – 7.78 (m, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.37 (s, 2H), 7.33 – 7.19 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.58 (s, 1H), 5.18 (s, 1H), 1.31 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.97, 151.32, 148.44, 138.14, 136.64, 134.52, 129.31, 128.89, 126.20, 126.13, 125.80, 124.93, 124.87, 123.22, 123.12, 122.97, 121.85, 120.41, 119.09, 112.17, 110.97, 105.91, 34.50, 30.30; HRMS (ESI+) (*m/z*) calcd for $C_{32}H_{33}NO_2$ $[M+H]^+$ 464.2584 found 464.2575.



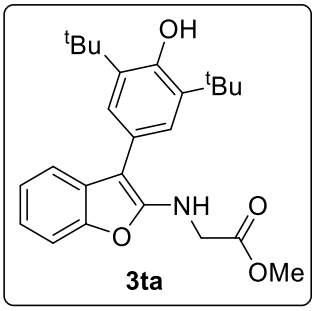
3ra

(3ra): Reaction time: (20 min); liquid (26.4 mg, 67%); mp 147-149 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 3H), 7.18 (dd, *J* = 11.0, 3.9 Hz, 1H), 7.12 – 7.07 (m, 1H), 5.23 (s, 1H), 4.30 (s, 1H), 1.52 (s, 18H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.91, 152.19, 150.61, 136.72, 130.02, 124.63, 122.80, 120.54, 117.20, 110.06, 98.08, 53.40, 34.71, 30.73, 30.57; HRMS (ESI+) (*m/z*) calcd for $C_{26}H_{35}NO_2$ $[M]^+$ 393.2662 found 393.2661.



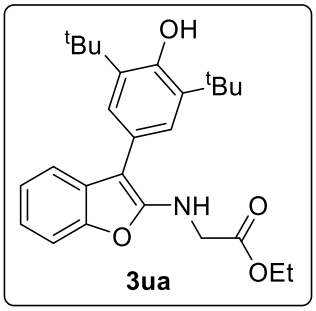
3sa

(3sa): Reaction time: (20 min); Brown solid (26.8 mg, 64%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 1H), 7.34 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.03 – 6.96 (m, 1H), 5.18 (s, 1H), 4.23 (d, *J* = 8.6 Hz, 1H), 3.79 – 3.24 (m, 1H), 2.07 (d, *J* = 12.1 Hz, 2H), 1.74 (d, *J* = 13.6 Hz, 2H), 1.62 (d, *J* = 15.9 Hz, 2H), 1.48 (s, 18H), 1.42 – 1.37 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.57, 151.97, 150.18, 136.71, 130.80, 124.74, 124.48, 122.88, 119.92, 116.70, 109.80 , 94.19, 52.83, 34.70, 34.50, 30.54, 25.82, 25.05; HRMS of **3sa**(ESI+) (*m/z*) calcd for $C_{28}H_{37}NO_2$ $[M+H]^+$420.2897 found 420.2887.



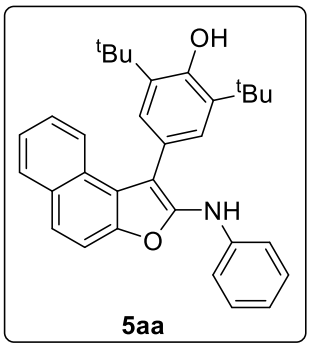
3ta

(3ta): Reaction time: (120 min); liquid (24.7 mg, 60%); R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.10 – 7.04 (m, 1H), 5.24 (s, 1H), 4.99 (t, *J* = 5.8 Hz, 1H), 4.20 (d, *J* = 5.9 Hz, 2H), 3.79 (s, 3H), 1.52 (s, 18H);^{13}C NMR (126 MHz, $CDCl_3$) δ 171.29, 153.25, 152.26, 150.10, 136.81, 130.64, 124.52, 124.02, 123.12, 120.43, 117.30, 109.98, 94.75, 52.51, 45.39, 34.68, 30.52; HRMS (ESI+) (*m/z*) calcd for $C_{25}H_{31}NO_4$ $[M+H]^+$ 410.2326 found 410.2325.



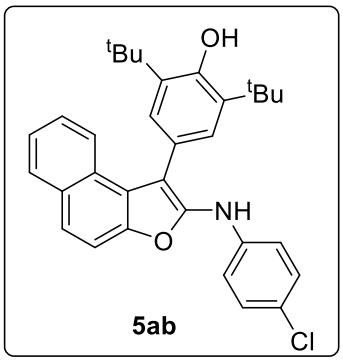
3ua

(3ua): Reaction time: (120 min); Yellow solid (30.4 mg, 72%); mp136-137 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.42 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.11 – 7.04 (m, 1H), 5.24 (s, 1H), 5.01 (t, *J* = 5.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.19 (d, *J* = 5.8 Hz, 2H), 1.52 (s, 18H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.76, 153.37, 152.23, 150.10, 136.79, 130.63, 124.49, 124.07, 123.10, 120.39, 117.28, 109.95, 94.66, 61.60, 45.59, 34.68, 30.52, 14.31; HRMS (ESI+) (*m/z*) calcd for $C_{31}H_{34}N_2O_2$ $[M+H]^+$424.2488 found 424.2484; HRMS (ESI+) (*m/z*) calcd for $C_{26}H_{33}NO_4$ $[M+H]^+$ 424.2482 found 424.2483.

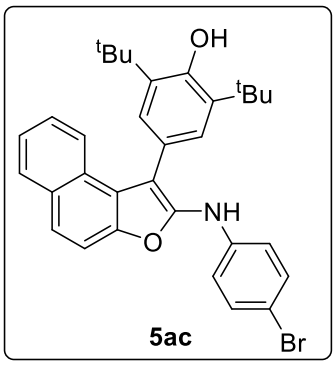


5aa

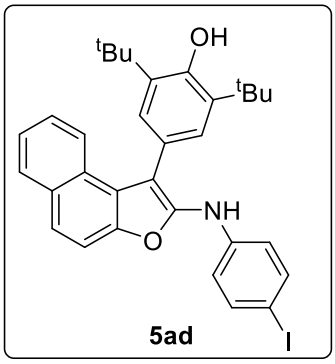
(5aa): Reaction time: (20 min); Brown solid (35.3 mg, 76%); mp 162-163 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.93 – 6.88 (m, 1H), 5.95 (s, 1H), 5.31 (s, 1H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.56, 148.50, 148.04, 143.78, 136.38, 131.10, 129.45, 129.05, 127.91, 127.23, 125.34, 124.24, 123.77, 123.70, 123.54, 122.72, 120.88, 115.81, 112.13, 108.77, 34.59, 30.51; HRMS (ESI+) (*m/z*) calcd for $C_{32}H_{33}NO_2$ $[M]^+$ 463.2506 found 463.2507.



(5ab): Reaction time: (20 min); liquid (43.8 mg, 88%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.37 – 7.30 (m, 3H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.95 (s, 1H), 5.35 (s, 1H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.66, 148.13, 147.79, 142.45, 136.45, 131.10, 129.34, 129.08, 127.94, 127.16, 125.63, 125.47, 124.35, 124.13, 123.64, 123.30, 122.60, 116.92, 112.09, 109.48, 34.59, 30.50; HRMS of oxidized product of **5ab** (ESI+) (*m/z*) calcd for $C_{32}H_{32}ClNO_2$ $[M+H]^+$ 496.2038 found 496.2035.

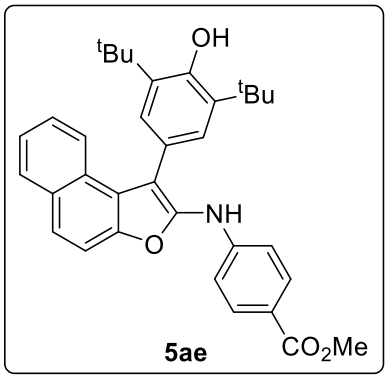


(5ac): Reaction time: (20 min); liquid (46.7 mg, 86%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.42 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.36 – 7.32 (m, 5H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.96 (s, 1H), 5.34 (s, 1H), 1.43 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.67, 148.16, 147.65, 142.96, 136.46, 132.24, 131.11, 129.09, 127.95, 127.16, 125.49, 124.36, 124.18, 123.64, 123.28, 122.58, 117.33, 112.84, 112.10, 109.65, 34.60, 30.51; HRMS of oxidized product of **5ac** (ESI+) (*m/z*) calcd for $C_{32}H_{32}BrNO_2$ $[M+H]^+$ 540.1533 found 540.1535.



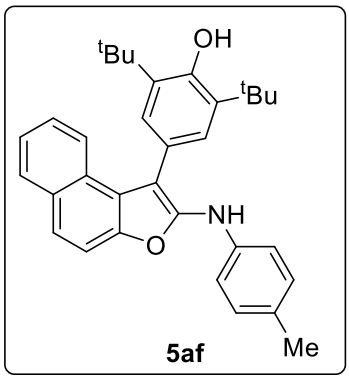
(5ad): Reaction time: (20 min); liquid (51.4 mg, 87%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.38 (d, *J* = 11.7 Hz, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.99 (s, 1H), 5.38 (s, 1H), 1.47 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.66, 148.17, 147.48, 143.61, 138.12, 136.44, 131.09,

129.08, 127.94, 127.15, 125.49, 124.35, 124.21, 123.62, 123.25, 122.55, 117.79, 112.09, 109.80, 82.43, 34.58, 30.50; HRMS of oxidized product of **5ad** (ESI+) (*m/z*) calcd for $C_{32}H_{32}INO_2$ $[M+H]^+$ 588.1395 found 588.1398.



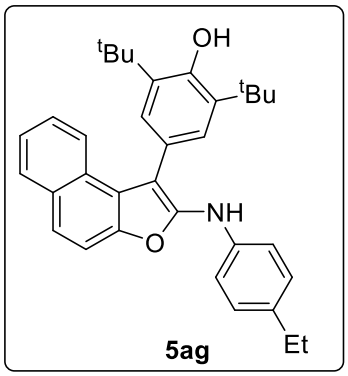
5ae

(5ae): Reaction time: (20 min); Brown solid (35.5 mg, 68%); mp207-208 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 6.9 Hz, 3H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.47 – 7.32 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 5.36 (s, 1H), 3.89 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.10, 153.74, 148.50, 148.28, 146.44, 136.44, 131.56, 131.08, 129.12, 128.05, 127.08, 125.63, 124.73, 124.44, 123.60, 123.04, 122.32, 121.95, 114.39, 112.18, 111.56, 51.92, 34.57, 30.47; HRMS (ESI+) (*m/z*) calcd for $C_{34}H_{35}NO_4$ $[M+H]^+$ 522.2639 found 522.2633.

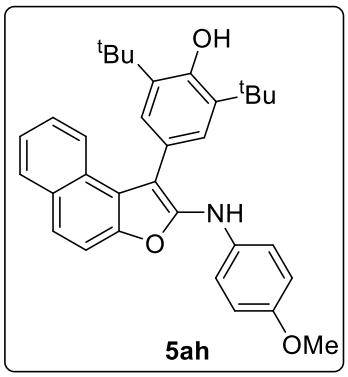


5af

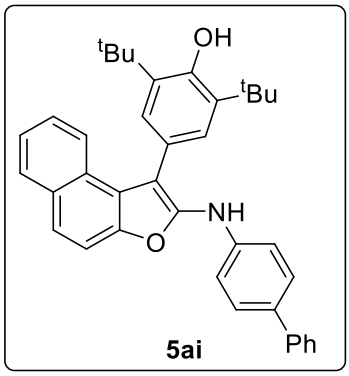
(5af): Reaction time: (20 min); liquid (41.7 mg, 87%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.40 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.35 (s, 2H), 7.31 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.93 (s, 1H), 5.32 (s, 1H), 2.29 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.50, 149.21, 147.78, 140.90, 136.39, 131.12, 130.43, 129.91, 129.58, 129.01, 127.80, 127.28, 125.21, 124.17, 123.72, 123.31, 122.92, 116.30, 112.06, 107.20, 34.59, 30.53, 20.74; HRMS (ESI+) (*m/z*) calcd for $C_{33}H_{35}NO_2$ $[M]^+$477.2662 found 477.2654.



(5ag): Reaction time: (20 min); liquid (37.4 mg, 76%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.65 (q, *J* = 8.8 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.38 – 7.30 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 5.95 (s, 1H), 5.32 (s, 1H), 2.59 (q, *J* = 7.5 Hz, 2H), 1.44 (s, 18H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.49, 149.17, 147.80, 141.18, 137.01, 136.38, 131.11, 129.02, 128.75, 128.42, 127.82, 127.28, 125.22, 124.17, 123.72, 123.35, 122.91, 116.27, 112.07, 107.40, 34.59, 30.52, 28.25, 16.06; HRMS of oxidized product of **5ag** (ESI+) (*m/z*) calcd for $C_{34}H_{37}NO_2$ $[M+H]^+$ 490.2741 found 490.2741.

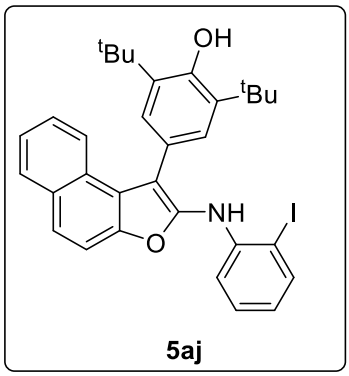


(5ah): Reaction time: (20 min); liquid (36.1 mg, 73%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 (s, 2H), 7.32 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.91 (s, 1H), 5.34 (s, 1H), 3.79 (s, 3H), 1.47 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.66, 153.47, 149.78, 147.57, 136.66, 136.42, 131.13, 129.00, 127.72, 127.30, 125.15, 124.15, 123.73, 123.08, 123.04, 118.21, 114.81, 111.98, 106.04, 55.80, 34.59, 30.53; HRMS (ESI+) (*m/z*) calcd for $C_{33}H_{35}NO_3$ $[M]^+$ 493.2611 found 493.2611.



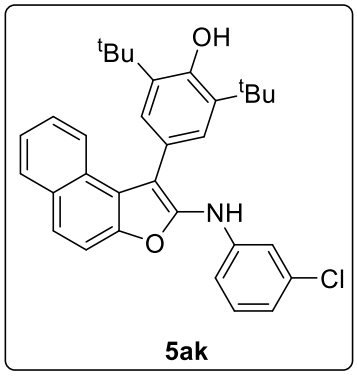
(5ai): Reaction time: (20 min); liquid (49.3 mg, 91%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.58 (dd, *J* = 21.2, 8.3 Hz, 2H), 7.35 – 7.20 (m, 7H), 7.17 – 7.06 (m, 5H), 6.87 (s, 1H), 6.04 (s, 1H), 5.18 (s, 1H), 1.29 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.50, 148.23, 148.17, 141.16, 138.78, 136.17, 131.02, 130.53, 129.38, 129.13, 129.03, 128.95, 128.75,

128.70, 127.99, 127.67, 126.97, 125.40, 124.25, 124.06, 123.71, 123.39, 122.70, 120.64, 115.25, 112.18, 110.64, 77.41, 77.16, 76.91, 34.49, 30.45; HRMS (ESI+) (*m/z*) calcd for $C_{38}H_{37}NO_2$ $[M+H]^+$ 540.2902 found 540.2905.



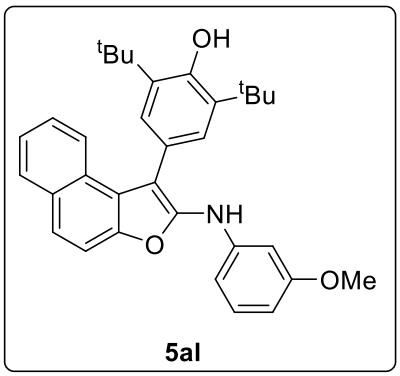
5aj

(5aj): Reaction time: (20 min); liquid (50.1 mg, 85%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 11.1, 3.8 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.23 – 7.19 (m, 1H), 7.16 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.65 – 6.60 (m, 1H), 6.51 (s, 1H), 5.32 (s, 1H), 1.46 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.58, 148.29, 147.48, 143.58, 139.10, 136.31, 131.09, 129.49, 129.08, 128.02, 126.92, 125.50, 124.38, 124.33, 123.78, 123.07, 122.43, 122.14, 115.37, 112.13, 110.45, 85.92, 77.41, 77.16, 76.91, 34.58, 30.51; HRMS (ESI+) (*m/z*) calcd for $C_{32}H_{32}INO_2$ $[M]^+$ 589.1472 found 589.1481.



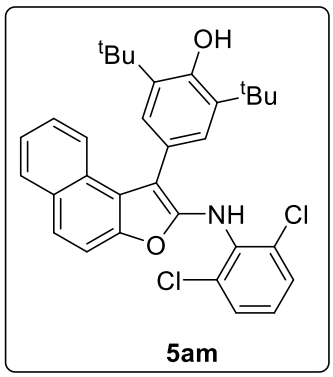
5ak

(5ak): Reaction time: (20 min); liquid (36.6 mg, 73%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.36 – 7.33 (m, 1H), 7.32 (s, 2H), 7.17 – 7.13 (m, 1H), 6.98 – 6.96 (m, 1H), 6.87 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.96 (s, 1H), 5.33 (s, 1H), 1.42 (s, 17H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.69, 148.32, 147.23, 145.20, 136.44, 135.21, 131.11, 130.40, 129.11, 128.14, 128.03, 127.13, 125.55, 124.39, 123.64, 123.22, 122.51, 120.71, 115.52, 113.80, 112.19, 110.48, 34.60, 30.50; HRMS (ESI+) (*m/z*) calcd for $C_{32}H_{32}ClNO_2$ $[M]^+$ 497.2116 found 497.2117.



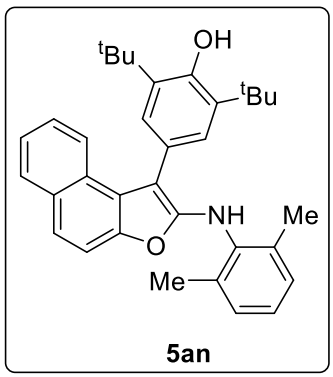
5al

(5al): Reaction time: (20 min); Brown solid (40.5 mg, 82%); mp192-194 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* = 19.8, 8.8 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.40 – 7.31 (m, 3H), 7.20 – 7.13 (m, 1H) 6.59 (d, *J* = 9.0 Hz, 2H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.97 (s, 1H), 5.33 (s, 1H), 3.78 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.85, 153.57, 148.23, 148.13, 145.14, 136.35, 131.09, 130.22, 129.06, 127.94, 127.22, 125.36, 124.25, 123.89, 123.70, 123.48, 122.64, 112.16, 109.18, 108.55, 106.15, 101.89, 55.38, 34.59, 30.51; HRMS (ESI+) (*m/z*) calcd for $C_{33}H_{35}NO_3$ $[M]^+$ 494.2690 found 494.2664.



5am

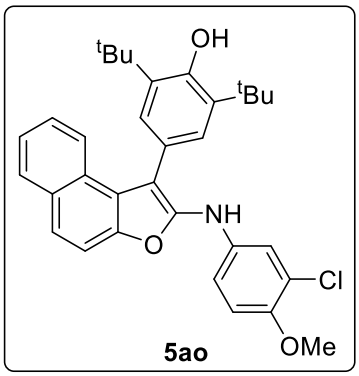
(5am): Reaction time: (20 min); Brown solid (35.8 mg, 67%); mp175-176 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.79 – 6.72 (m, 1H), 6.27 (s, 1H), 5.17 (s, 1H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.27, 147.75, 146.99, 136.08, 135.68, 131.03, 128.95, 128.61, 128.15, 127.03, 126.98, 125.55, 125.42, 124.16, 123.88, 123.57, 123.28, 123.03, 112.09, 109.39, 34.43, 30.42; HRMS (ESI+) (*m/z*) calcd for $C_{32}H_{31}Cl_2NO_2$ $[M]^+$ 531.1726 found 531.1735.



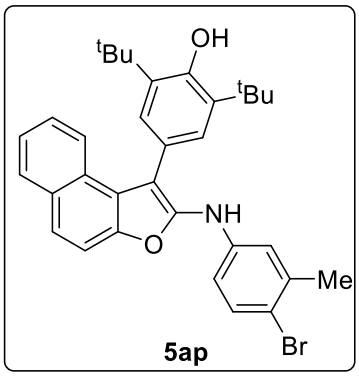
5an

(5an): Reaction time: (20 min); liquid (33.4 mg, 68%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.7, 5.7 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.39 – 7.33 (m,3H), 7.29 – 7.25 (m, 1H), 7.05 – 7.00 (m, 3H), 5.69 (s, 1H), 5.27 (s, 1H), 2.28 (s, 6H), 1.48 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.13, 152.00, 146.50, 137.26, 136.17, 134.10, 131.19, 128.83, 128.62, 127.87, 127.29, 125.46, 124.78, 124.40, 124.10, 123.93,

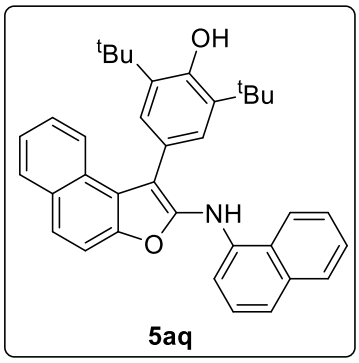
123.76, 121.32, 111.65, 99.67, 34.54, 30.53, 18.72; HRMS (ESI+) (*m/z*) calcd for $C_{34}H_{37}NO_2$ $[M]^+$ 491.2819 found 491.2827.



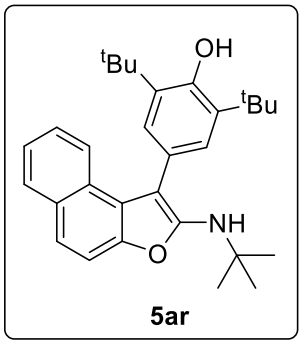
(5ao): Reaction time: (20 min); liquid(32.8 mg, 62%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 19.7, 8.9 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.34 (d, *J* = 5.0 Hz, 3H), 7.08 (d, *J* = 2.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.86 (s, 1H), 5.34 (s, 1H), 3.86 (s, 3H), 1.45 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.47, 149.78, 148.47, 147.74, 137.43, 136.32, 131.01, 128.94, 127.74, 127.09, 125.24, 124.16, 123.56, 123.31, 123.19, 122.74, 121.74, 118.60, 115.57, 113.38, 111.93, 107.71, 56.76, 34.47, 30.40; HRMS (ESI+) (*m/z*) calcd for $C_{33}H_{34}ClNO_3$ $[M+H]^+$ 528.2300 found 528.2298.



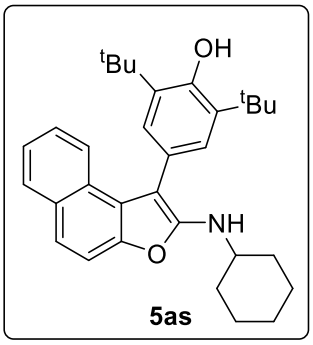
(5ap): Reaction time: (20 min); Brown solid (33.8 mg, 61%); mp193-194 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.34 (s, 3H), 6.85 (d, *J* = 2.7 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.89 (s, 1H), 5.34 (s, 1H), 2.33 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.62, 148.13, 147.86, 143.03, 138.73, 136.40, 132.92, 131.10, 129.08, 127.95, 127.17, 125.46, 124.33, 124.08, 123.65, 123.35, 122.65, 117.99, 115.54, 114.98, 112.12, 109.47, 34.59, 30.50, 23.19; HRMS (ESI+) (*m/z*) calcd for $C_{33}H_{34}BrNO_2$ $[M+H]^+$556.1846 found 556.1847.



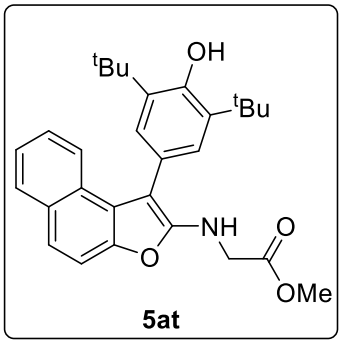
(5aq): Reaction time: (20 min); Brown solid (36.1 mg, 70%); mp 189-190 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.52 – 7.46 (m, 3H), 7.46 – 7.42 (m, 1H), 7.37 (dd, *J* = 17.1, 9.0 Hz, 4H), 6.56 (s, 1H), 5.29 (s, 1H), 1.39 (s, 18H^{13}C NMR (126 MHz, $CDCl_3$) δ 153.51, 149.27, 148.06, 138.70, 136.40, 134.47, 131.15, 129.07, 128.85, 127.88, 126.99, 126.27, 126.10, 125.73, 125.33, 124.99, 124.27, 123.78, 123.62, 123.59, 122.89, 121.83, 120.48, 112.35, 112.14, 108.21, 34.52, 30.44; HRMS (ESI+) (*m/z*) calcd for $C_{36}H_{35}NO_2$ $[M+H]^+$ 514.2741found 514.2745.



(5ar): Reaction time: (20 min); liquid (35.2 mg, 79%); mp 147-149 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 17.9, 8.2 Hz, 2H), 7.58 (dd, *J* = 20.6, 8.7 Hz, 2H), 7.41 – 7.32 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 1H), 5.32 (s, 1H), 4.00 (s, 1H), 1.51 (s, 18H), 1.41 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.32, 153.18, 147.24, 136.50, 131.11, 128.83, 127.36, 127.31, 124.71, 124.60, 123.84, 123.77, 123.46, 121.39, 111.73, 102.68, 53.60, 34.66, 30.65; HRMS (ESI+) (*m/z*) calcd for $C_{30}H_{37}NO_2$ $[M]^+$ 443.2819 found 443.2821.

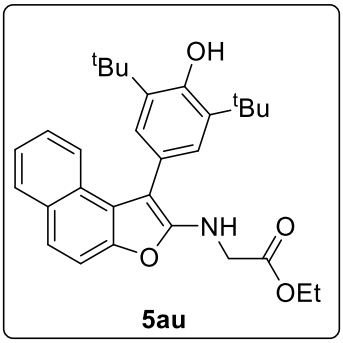


(5as): Reaction time: (20 min); Brown solid (35.8 mg, 76%); mp 166-168 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 29.8, 8.4 Hz, 2H), 7.33 (s, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 5.28 (s, 1H), 3.99 (s, 1H), 3.56 (s, 1H), 2.06 (d, *J* = 10.0 Hz, 2H), 1.73 (d, *J* = 11.4 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.48 (s, 18H), 1.41 – 1.30 (m, 3H), 1.25 – 1.13 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.08, 153.03, 146.58, 136.44, 131.21, 128.80, 127.45, 127.13, 124.65, 124.47, 124.35, 123.89, 123.78, 120.50, 111.43, 98.13, 53.41, 34.65, 34.43, 30.64, 25.84, 25.10; HRMS of **5as**(ESI+) (*m/z*) calcd for $C_{32}H_{39}NO_2$ $[M]^+$ 469.2975 found 469.2963.



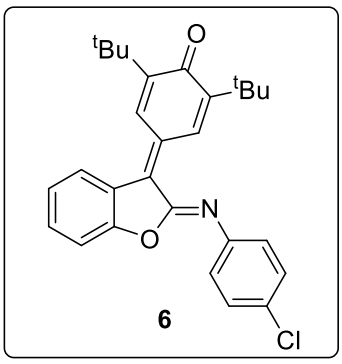
5at

(5at): Reaction time: (20 min); Yellow solid (27.8 mg, 60%); mp184-185 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.43 – 7.31 (m, 3H), 7.29 – 7.22 (m, 1H), 5.30 (s, 1H), 4.75 (s, 1H), 4.16 (d, *J* = 4.7 Hz, 2H), 3.76 (s, 3H), 1.49 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.41, 153.74, 153.19, 146.48, 136.67, 136.51, 131.26, 128.82, 127.34, 124.64, 124.33, 123.99, 123.94, 123.92, 120.95, 111.42, 97.82, 52.45, 45.62, 34.64, 30.61; HRMS (ESI+) (*m/z*) calcd for $C_{29}H_{33}NO_4$ $[M+H]^+$ 460.2482found 460.2481.



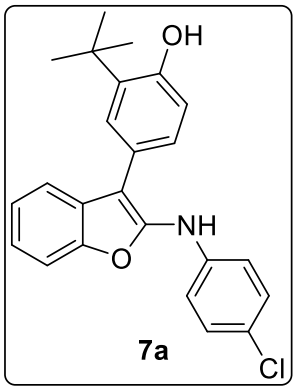
5au

(5au): Reaction time: (20 min); liquid (33.8 mg, 71%); R_f = 0.4 (petroleum ether/ethyl acetate = 95/05); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 – 7.32 (m, 3H), 7.27 – 7.22 (m, 1H), 5.30 (s, 1H), 4.77 (s, 1H), 4.21 (q, *J* = 6.82, 2H), 4.15 (d, *J* = 5.7 Hz, 2H), 1.49 (s, 18H), 1.26 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.90, 153.85, 153.16, 146.47, 136.49, 131.26, 128.82, 127.31, 124.60, 124.33, 124.04, 123.93, 120.88, 111.41, 97.70, 61.51, 45.79, 34.64, 30.61, 14.33; HRMS (ESI+) (*m/z*) calcd for $C_{30}H_{35}NO_4$ $[M+H]^+$ 474.2639 found 474.2635.



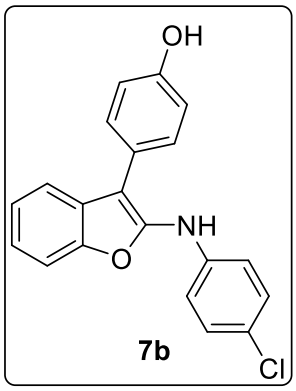
6

(6): Reaction time: (10 min); Maroon liquid (39.6 mg, 88%); R_f = 0.4 (petroleum ether/ethyl acetate = 97/03); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 2.3 Hz, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.25 – 7.20 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 1.39 (d, *J* = 12.3 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.86, 156.91, 154.43, 150.83, 150.62, 143.49, 135.62, 132.11, 131.51, 130.43, 129.66, 129.16, 128.06, 126.18, 125.86, 124.60, 124.38, 111.47, 36.32, 36.21, 29.97, 29.96; HRMS of **6** (ESI+) (*m/z*) calcd for $C_{28}H_{28}BrNO_2$ $[M+H]^+$ 446.1881 found 446.1867.



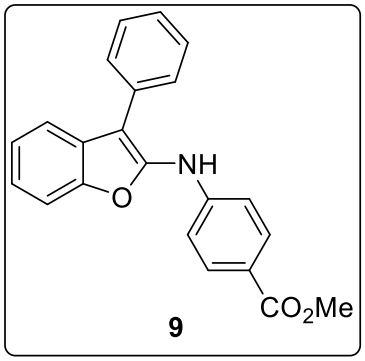
7a

(7a): Reaction time: (30 min); liquid (Quantitative); R_f = 0.5 (petroleum ether/ethyl acetate = 80/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.44 (s, 2H), 7.29 – 7.24 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 1H), 4.96 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.46, 151.09, 147.20, 141.38, 136.96, 129.36, 128.93, 127.44, 126.70, 125.85, 124.04, 123.29, 123.22, 119.10, 117.28, 117.08, 110.94, 105.71, 34.80, 29.64; HRMS **7a** (ESI+) (*m/z*) calcd for $C_{24}H_{22}ClNO_2$ $[M]^+$ 391.1334 found 391.1330.



7b

(7b): Reaction time: (6 h); Green liquid (44.4 mg, 84%); R_f = 0.5 (petroleum ether/ethyl acetate = 80/20; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.47 – 7.41 (m, 3H), 7.28 (s, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.93 (dd, J = 8.6, 2.9 Hz, 4H), 6.04 (s, 1H), 5.18 (s, 1H).); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.01, 147.33, 141.26, 129.99, 129.69, 129.56, 129.40, 128.93, 128.83, 125.95, 124.32, 123.33, 123.24, 118.97, 117.36, 117.15, 116.20, 115.48, 110.93, 105.16; HRMS of oxidized product of **7b** (ESI+) (*m/z*) calcd for $C_{20}H_{14}ClNO_2$ $[M+H]^+$ 334.0629 found 334.0634 [Note: the product spectra contain visible amount of solvent peaks. We could not remove it even after repeated attempts].

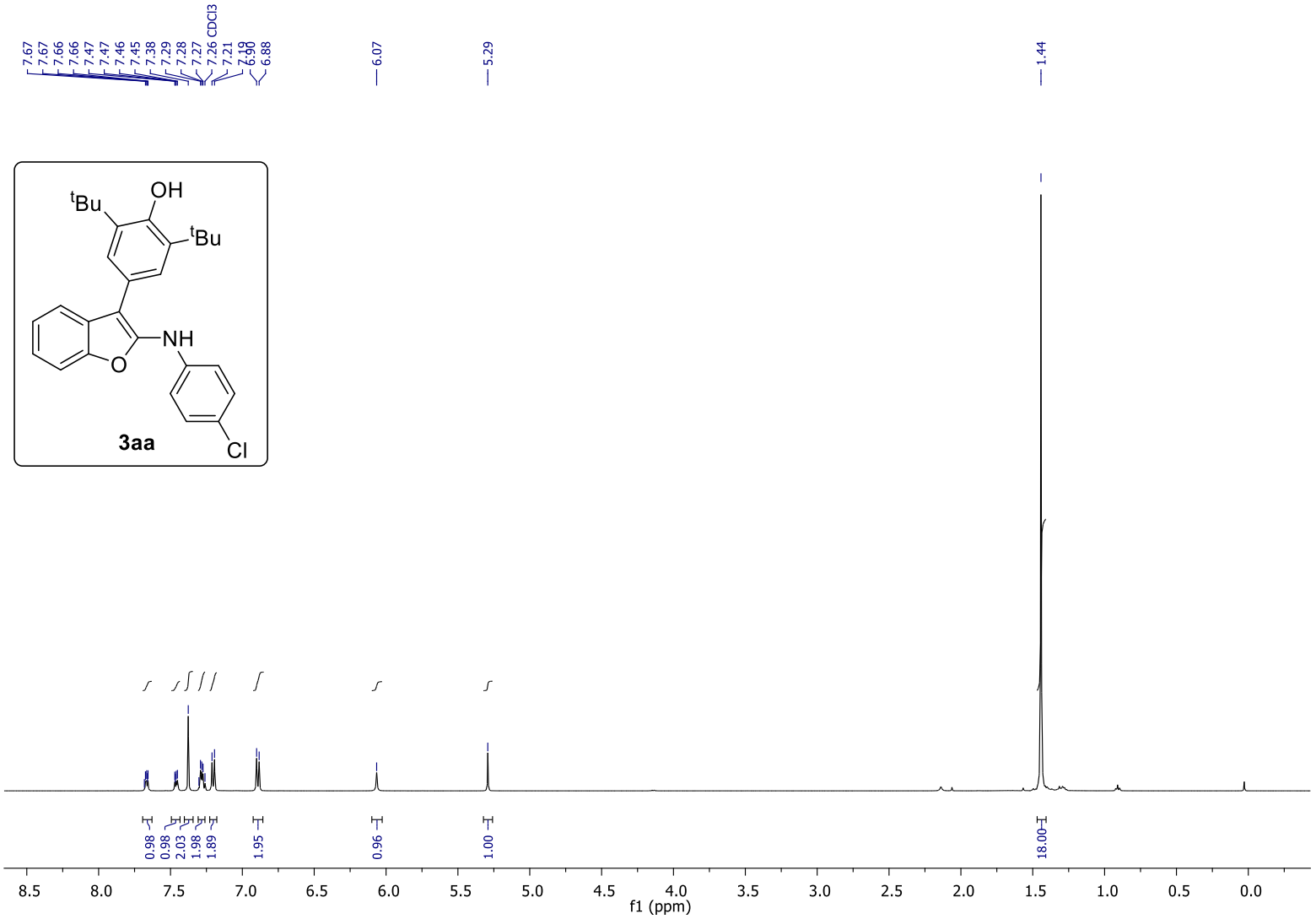


9

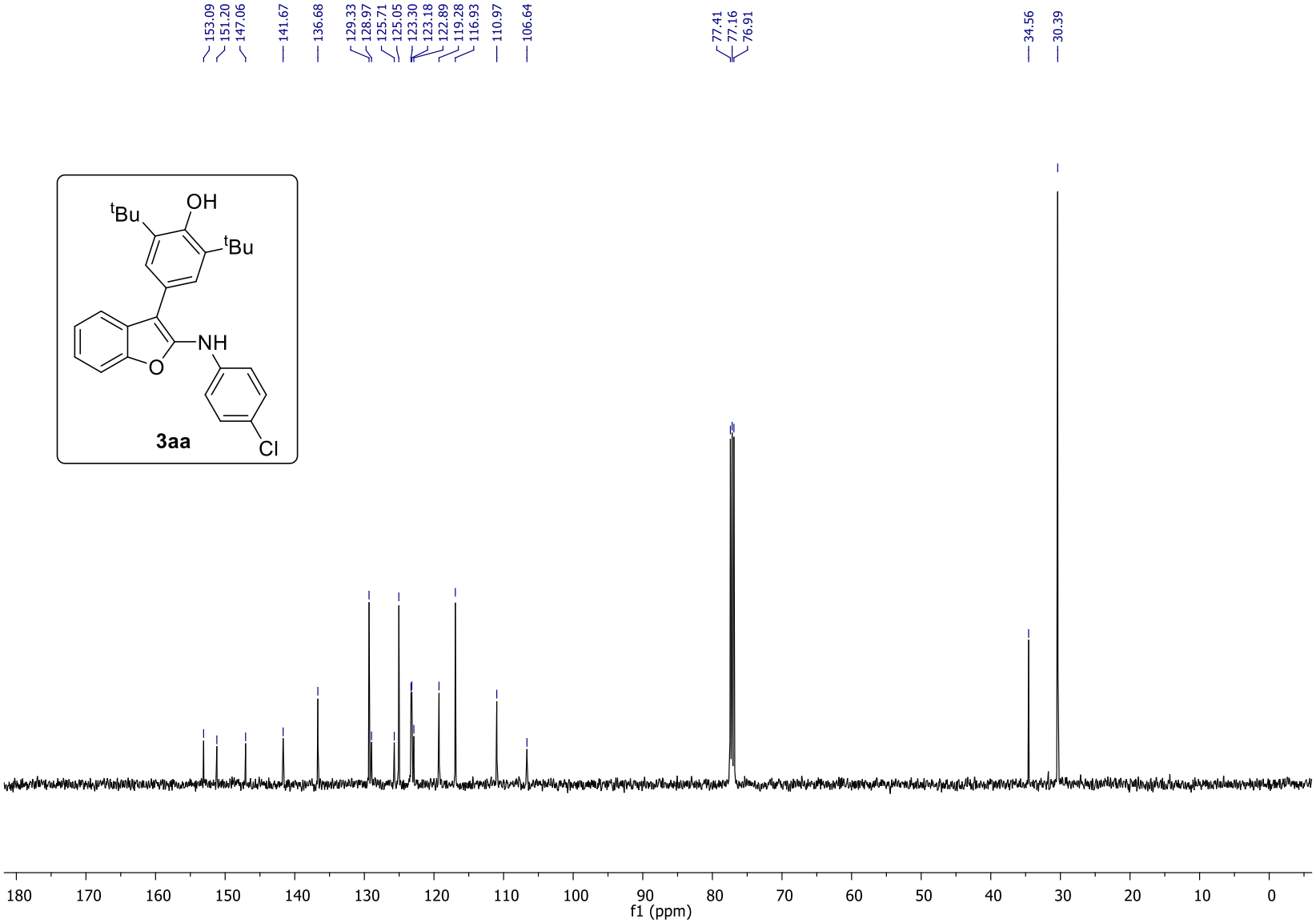
(9): Reaction time: (30 min); liquid (50.1 mg, 73%); R_f = 0.5 (petroleum ether/ethyl acetate = 80/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.67 (dd, *J* = 5.4, 1.3 Hz, 1H), 7.57 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.37 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.37 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.02, 151.19, 146.69, 131.81, 131.53, 129.27, 128.39, 128.29, 127.36, 123.75, 123.41, 122.39, 119.25, 114.86, 111.08, 106.60, 51.96; HRMS **9** (ESI+) (*m/z*) calcd for $C_{22}H_{17}NO_2$ $[M]^+$ 343.1203 found 343.1199.

7. ^{1}H NMR, ^{13}C NMR, Mass Spectra of Compounds

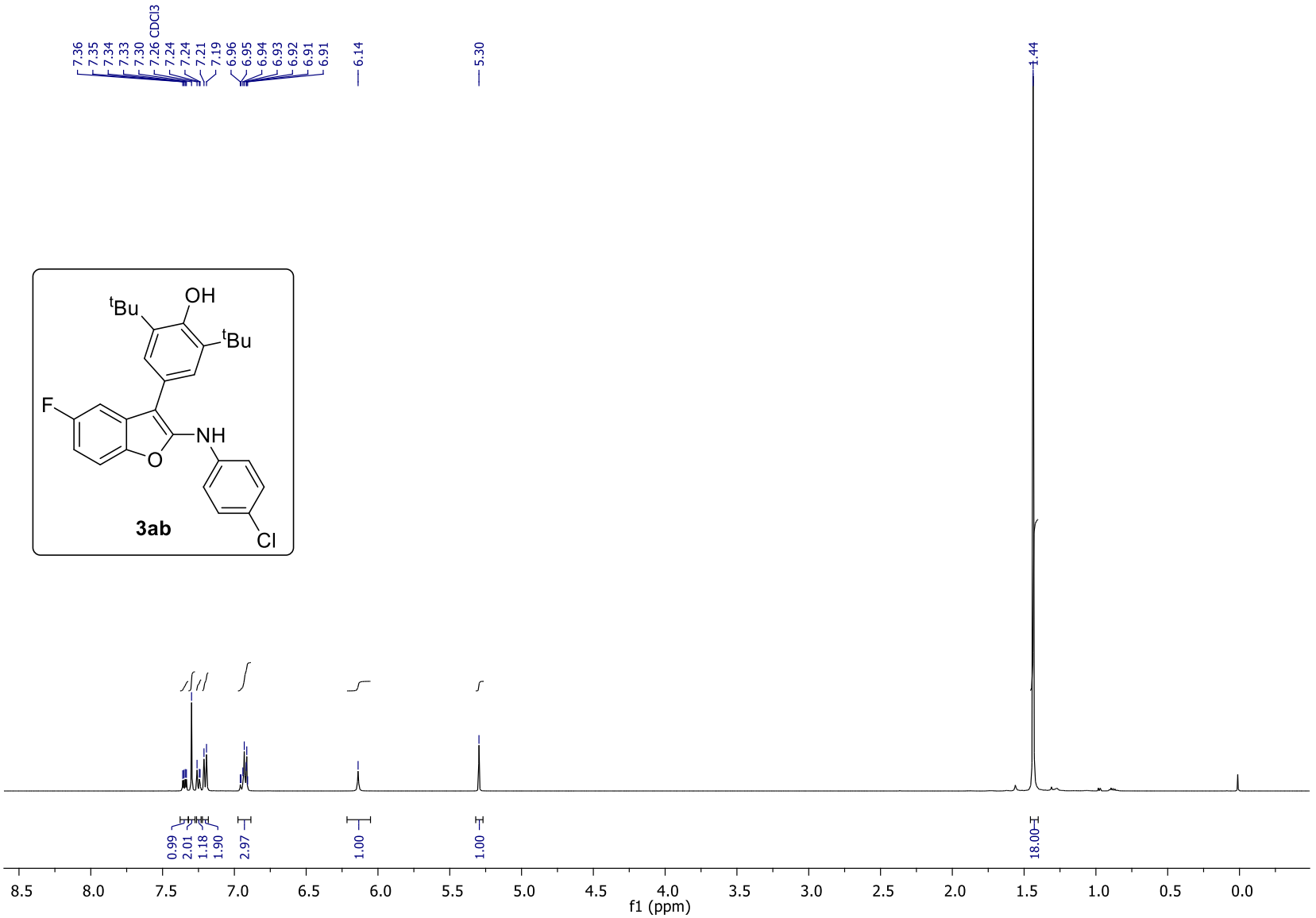
^{1}H NMR of compound **3aa** in $CDCl_3$



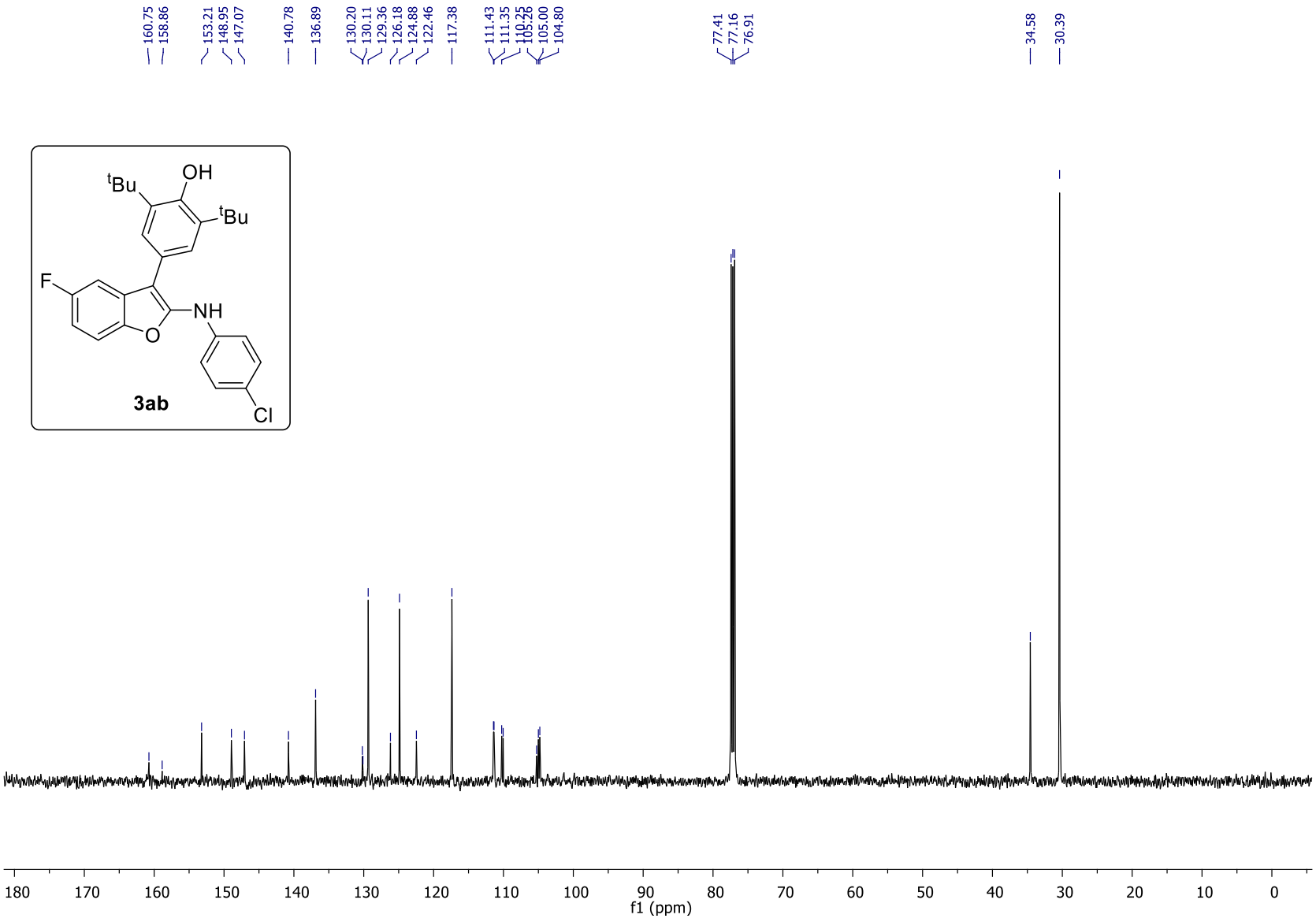
^{13}C NMR of compound **3aa** in $CDCl_3$



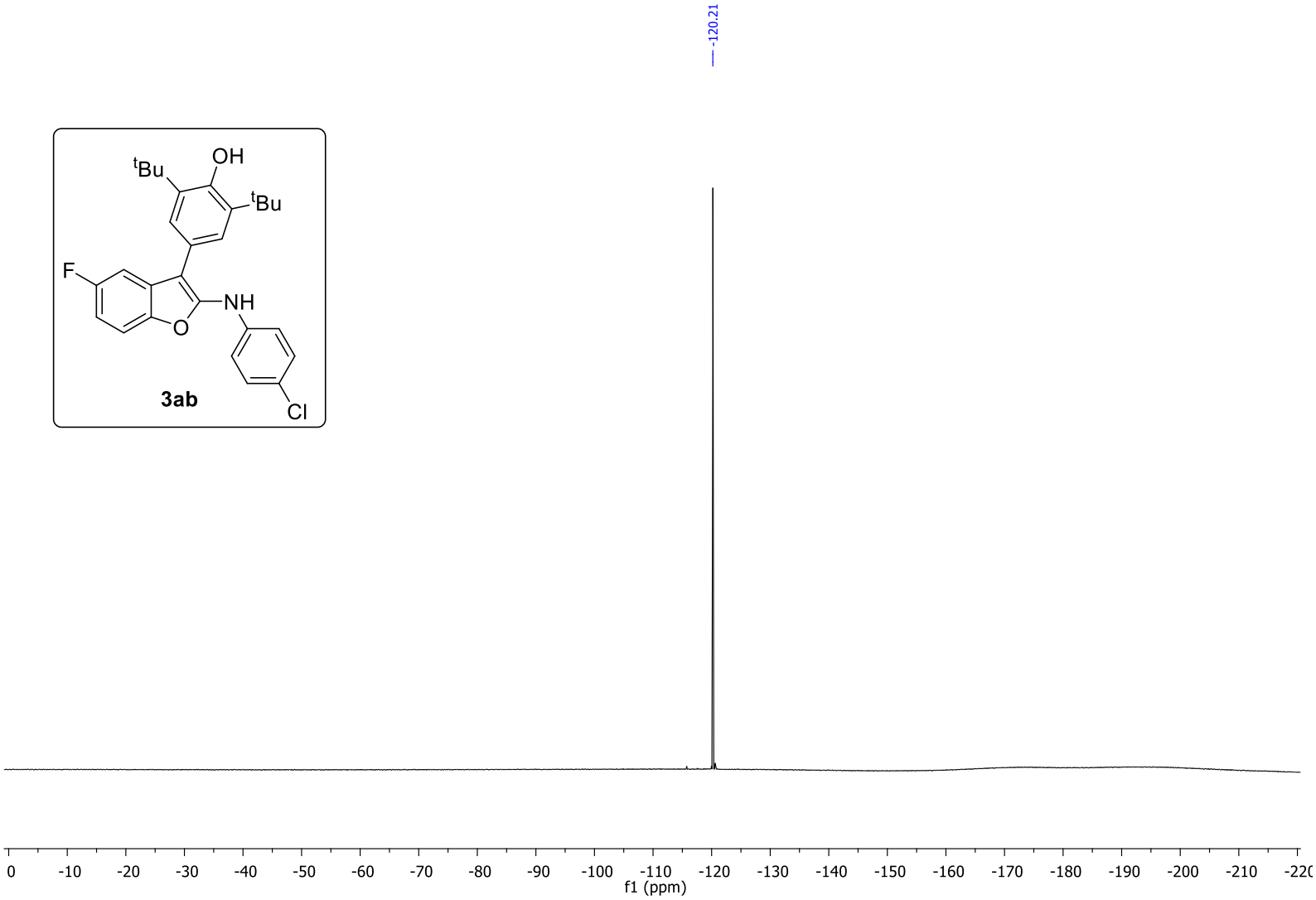
^{1}H NMR of compound **3ab** in $CDCl_3$



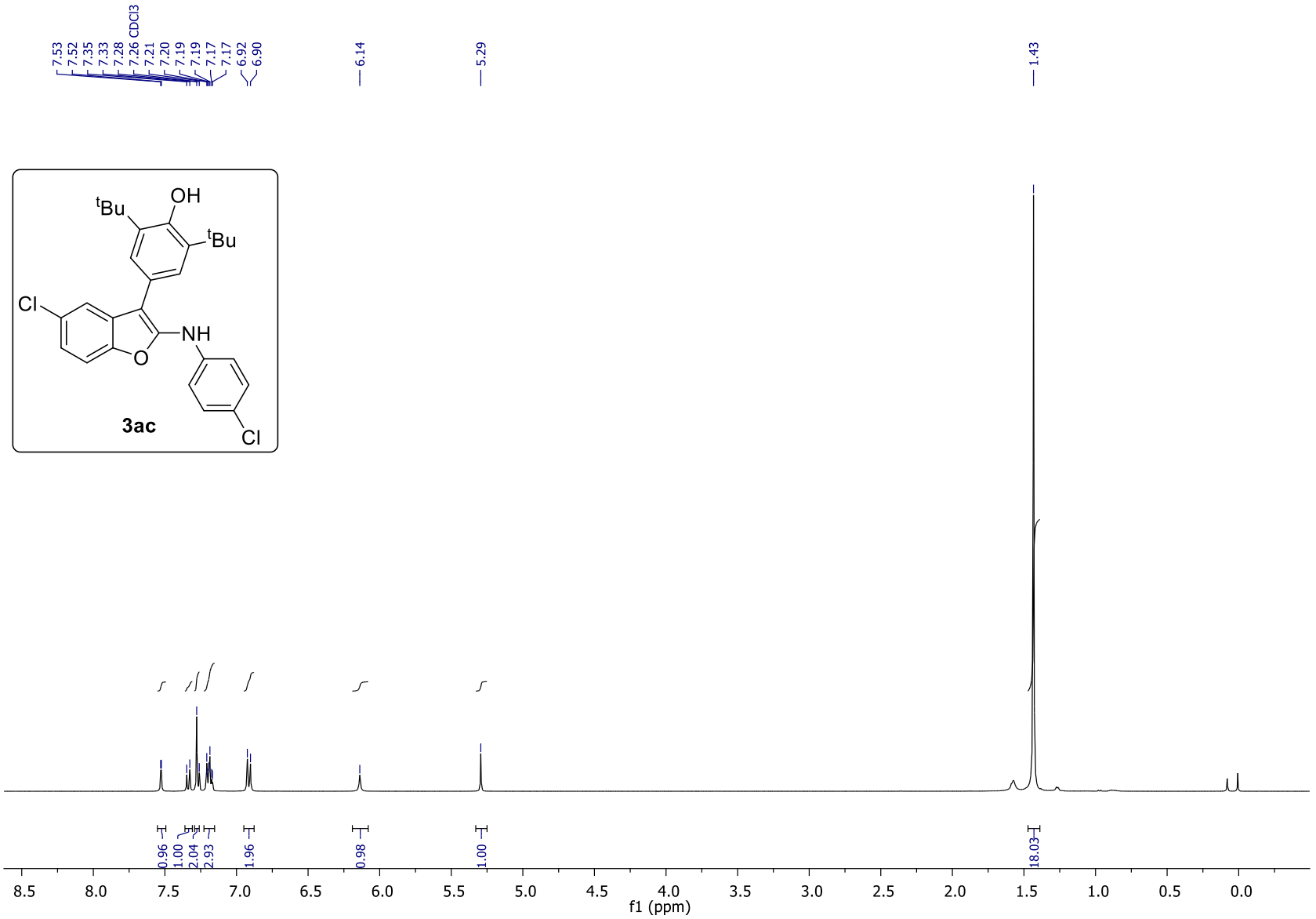
^{13}C NMR of compound **3ab** in $CDCl_3$



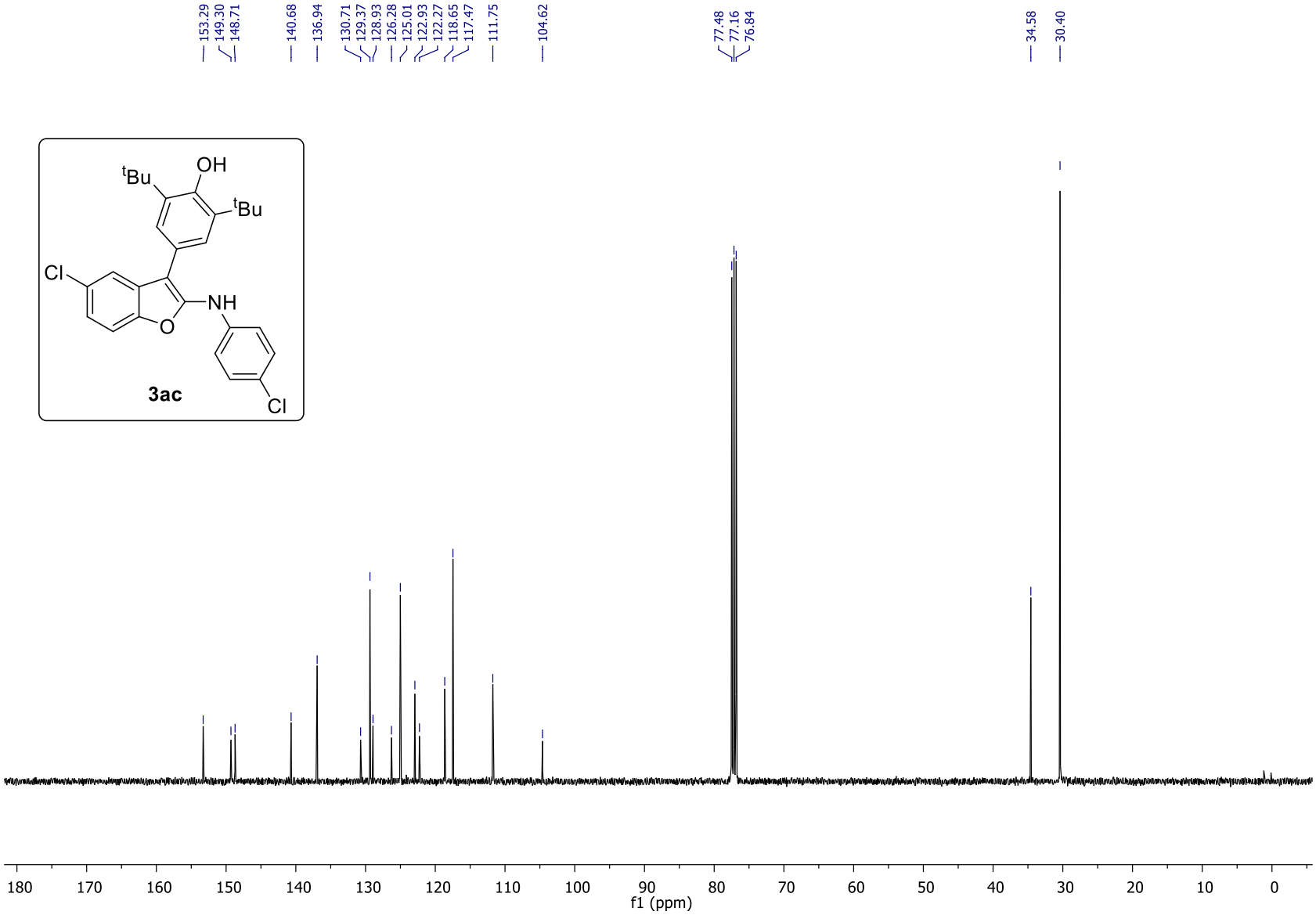
^{19}F NMR of compound **3ab** in $CDCl_3$



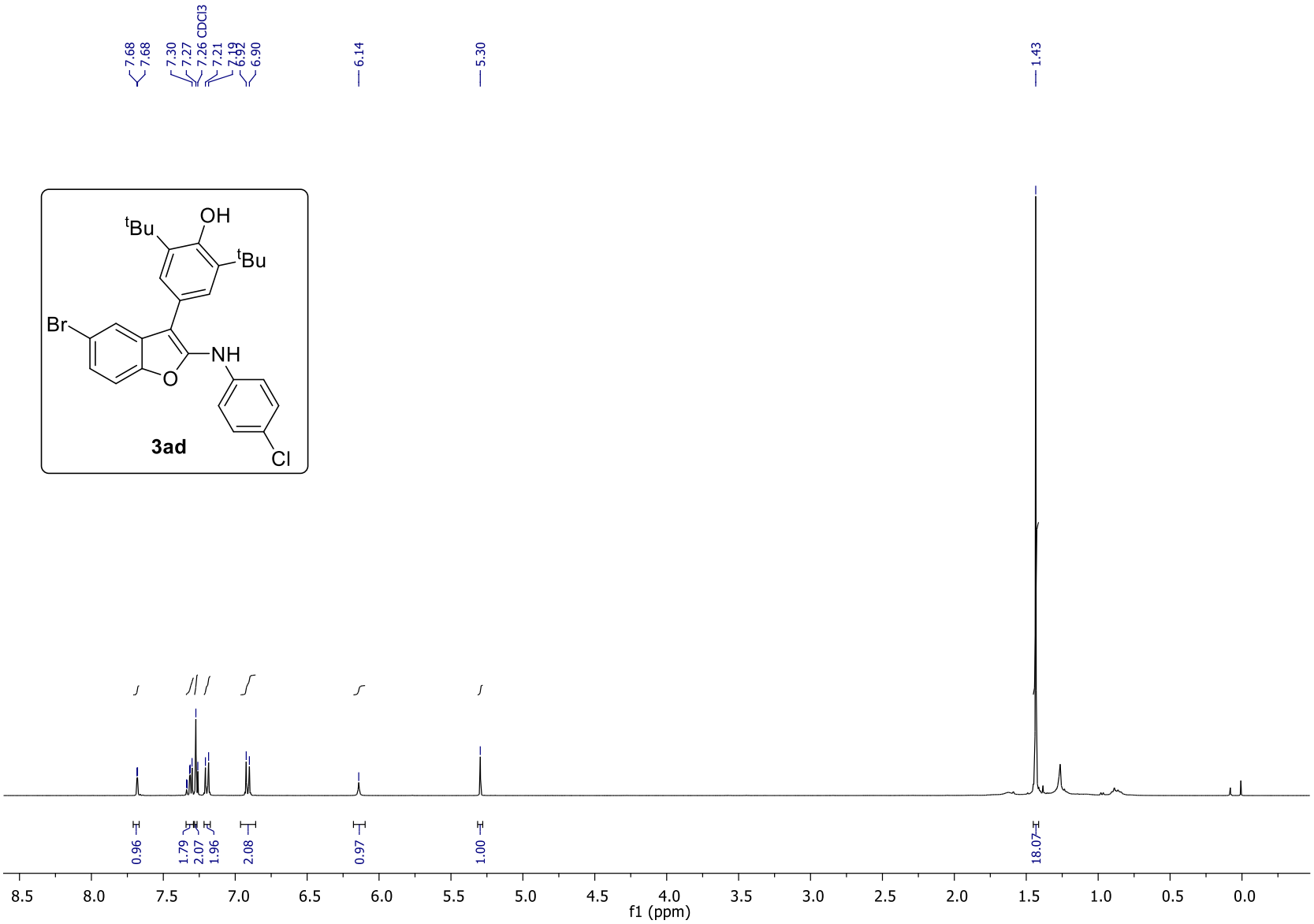
^{1}H NMR of compound **3ac** in $CDCl_3$



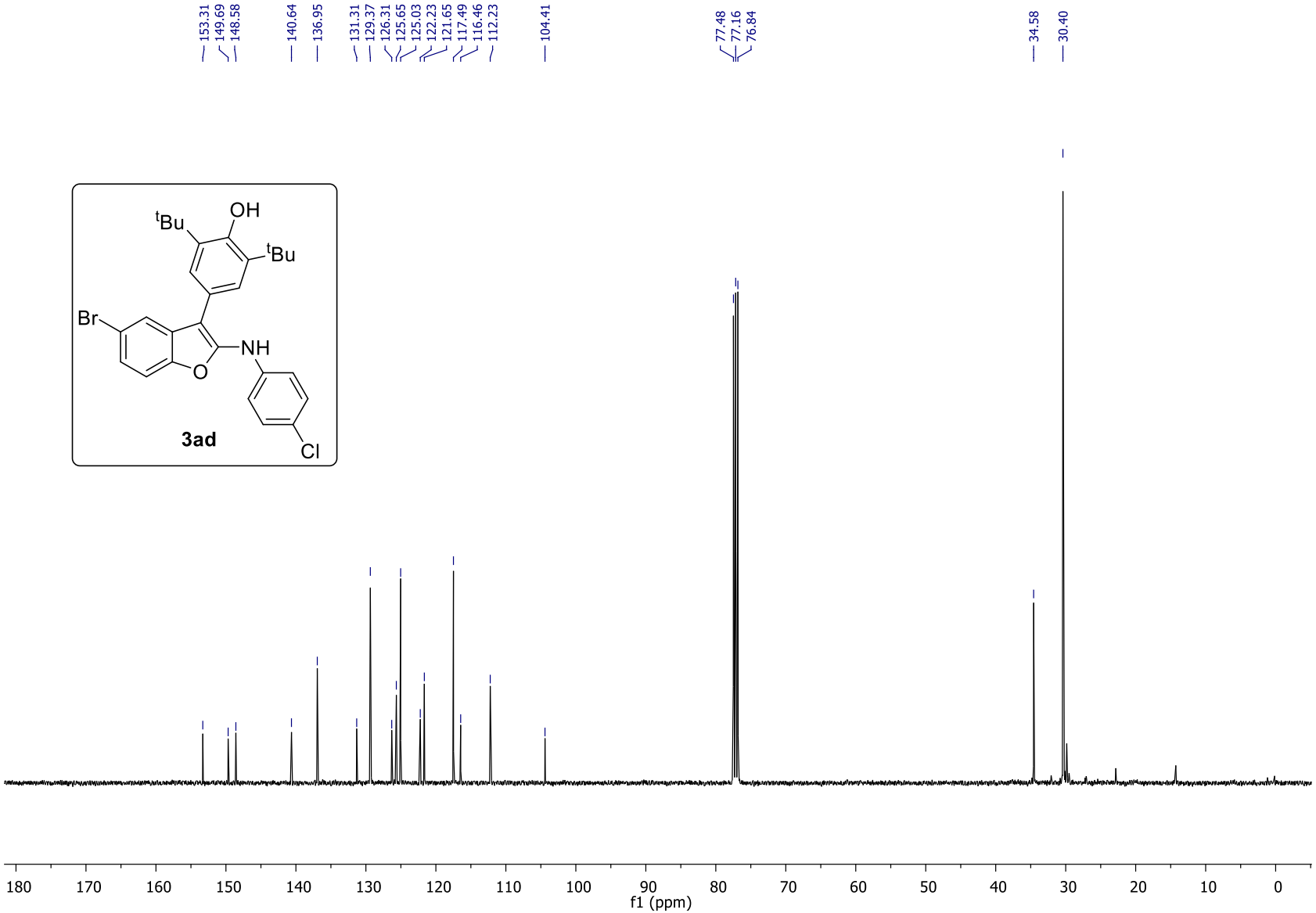
^{13}C NMR of compound **3ac** in $CDCl_3$



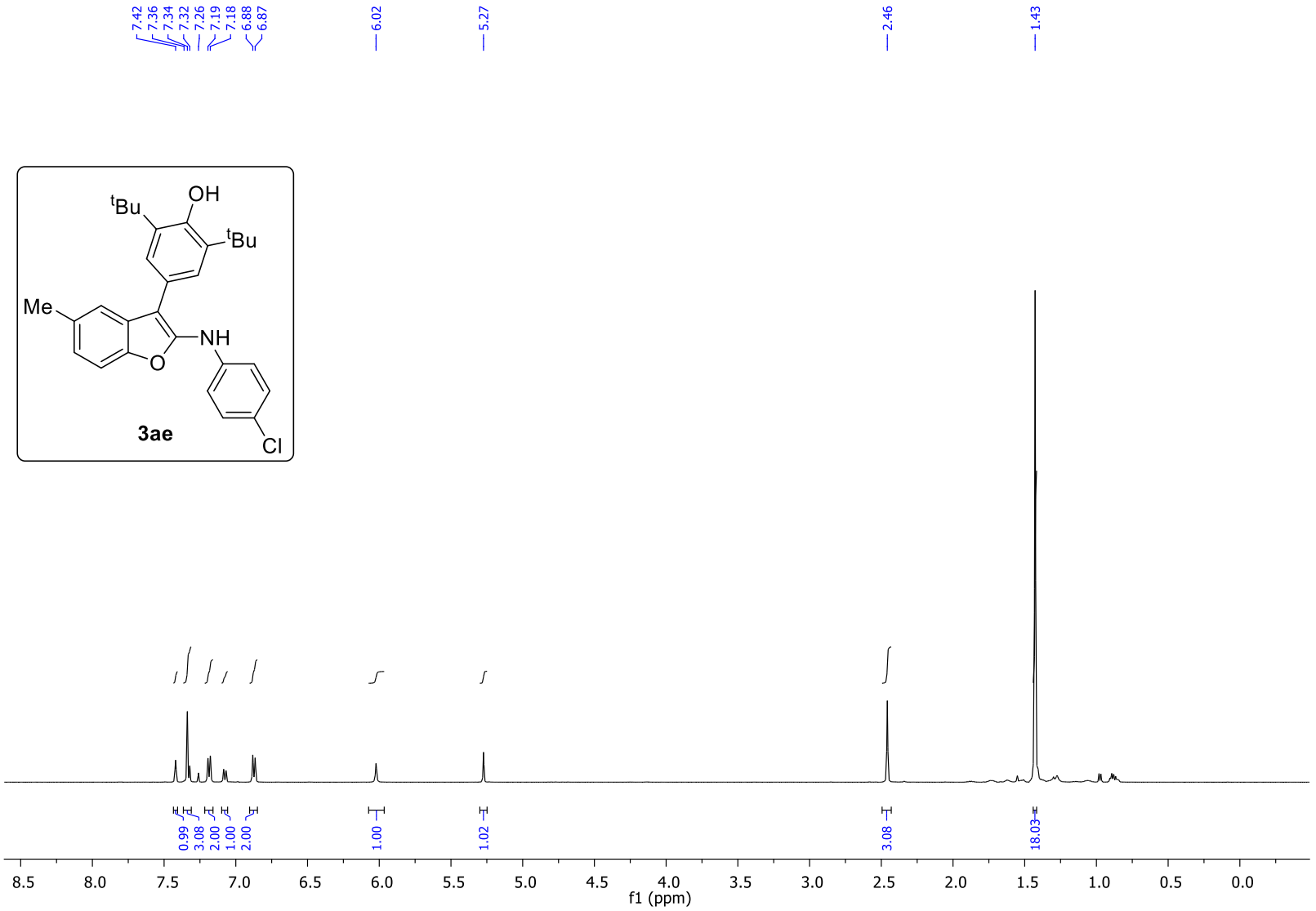
^{1}H NMR of compound **3ad** in $CDCl_3$



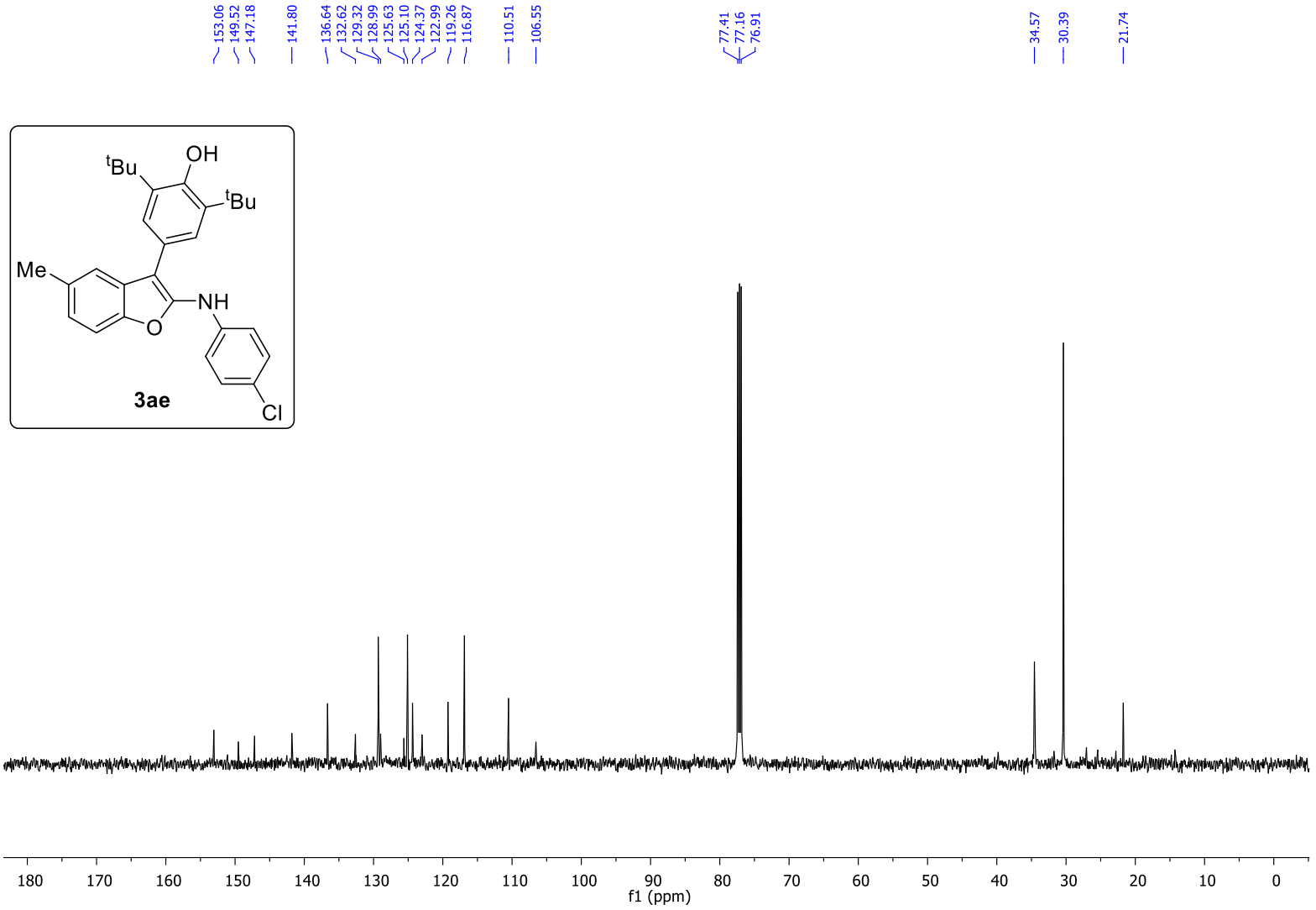
^{13}C NMR of compound **3ad** in $CDCl_3$



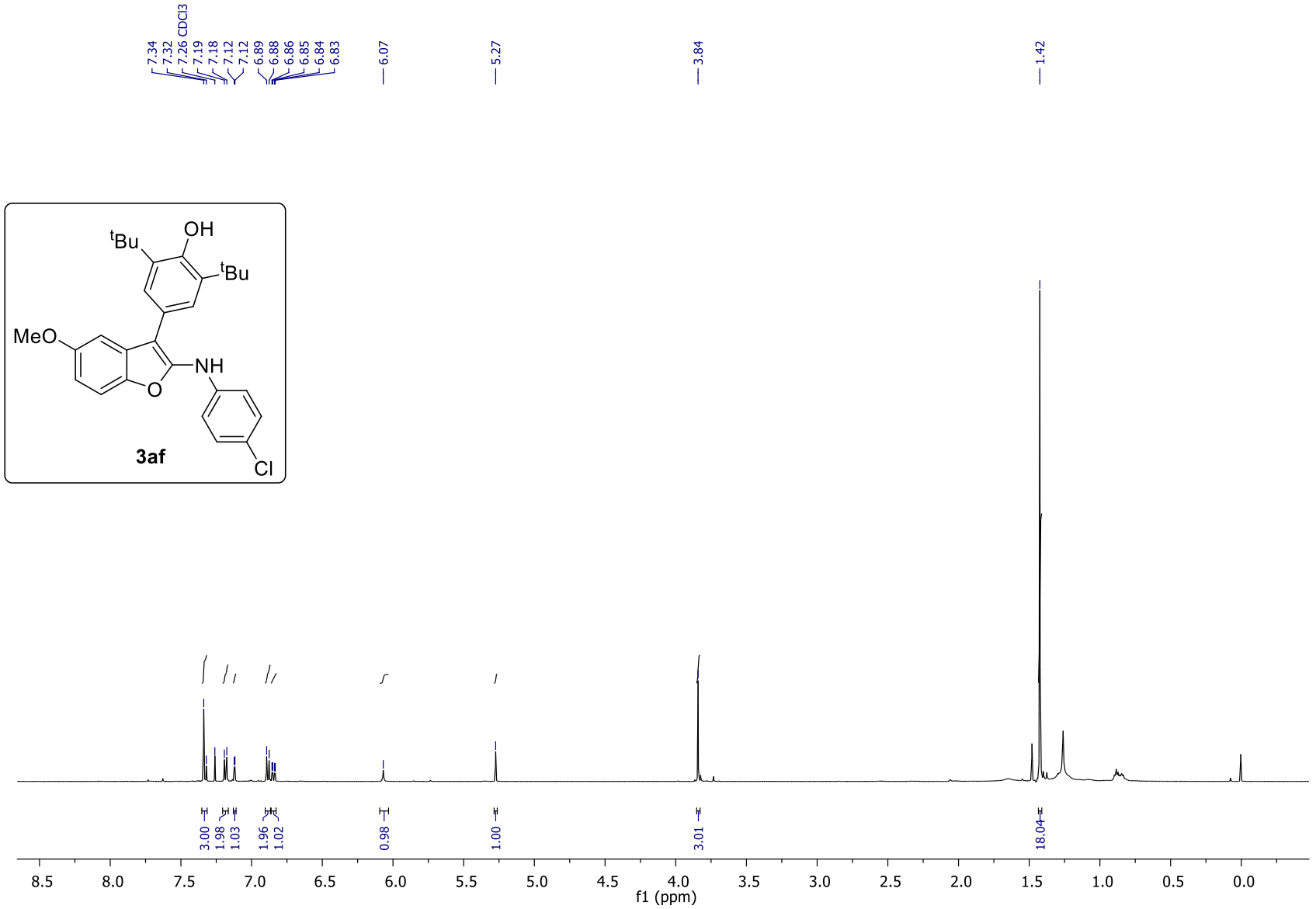
^{1}H NMR of compound **3ae** in $CDCl_3$



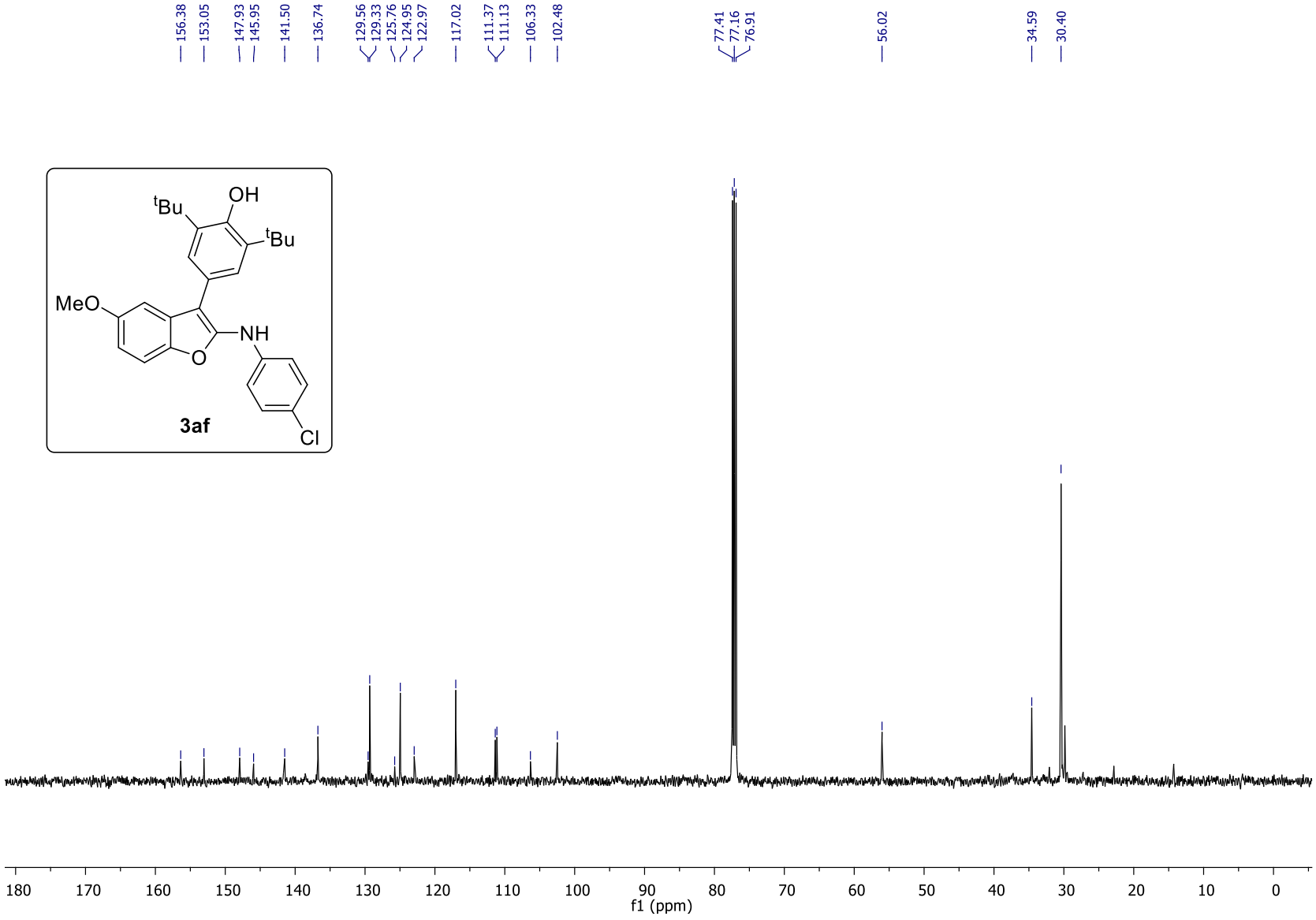
^{13}C NMR of compound **3ae** in $CDCl_3$



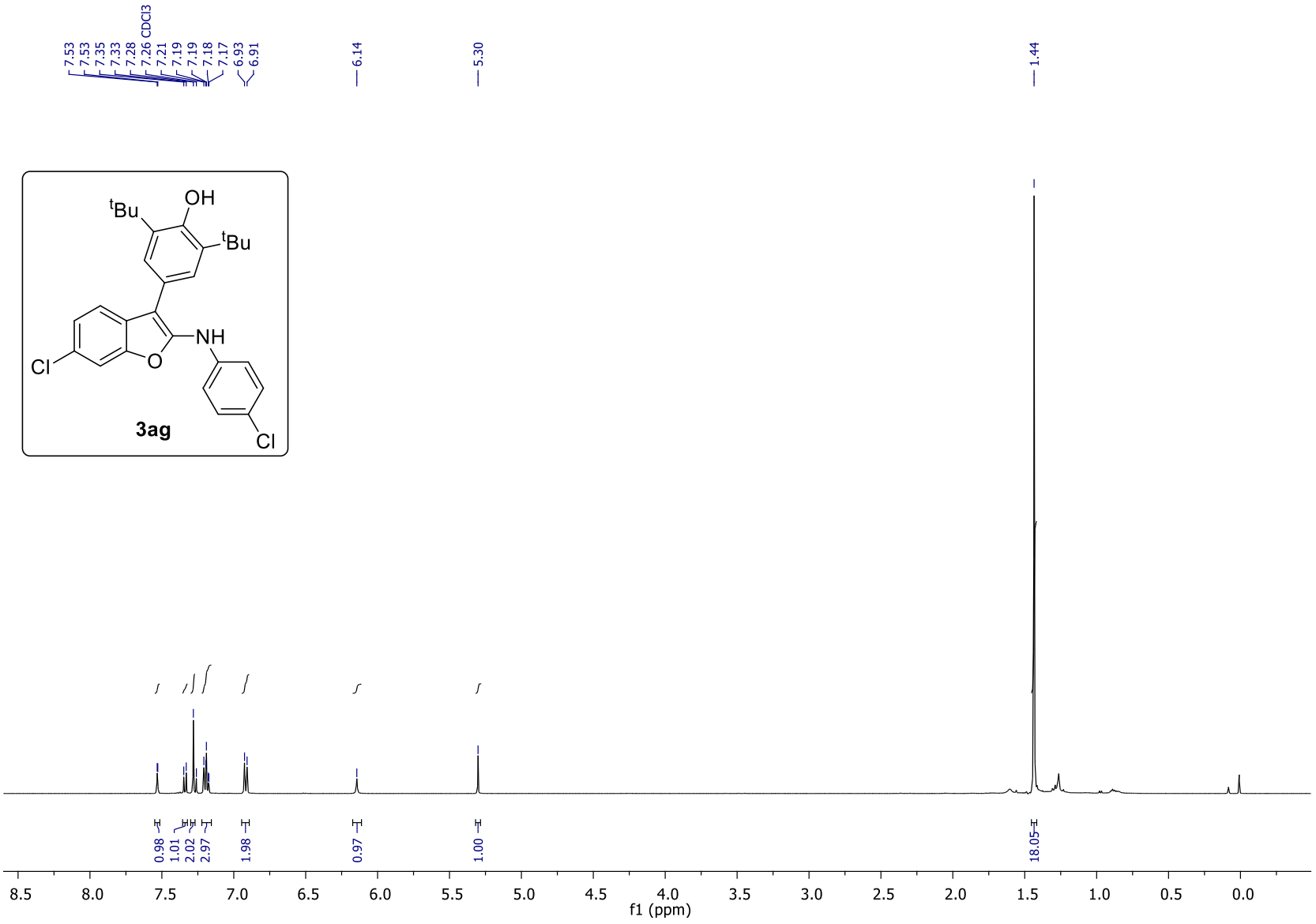
^{1}H NMR of compound **3af** in $CDCl_3$



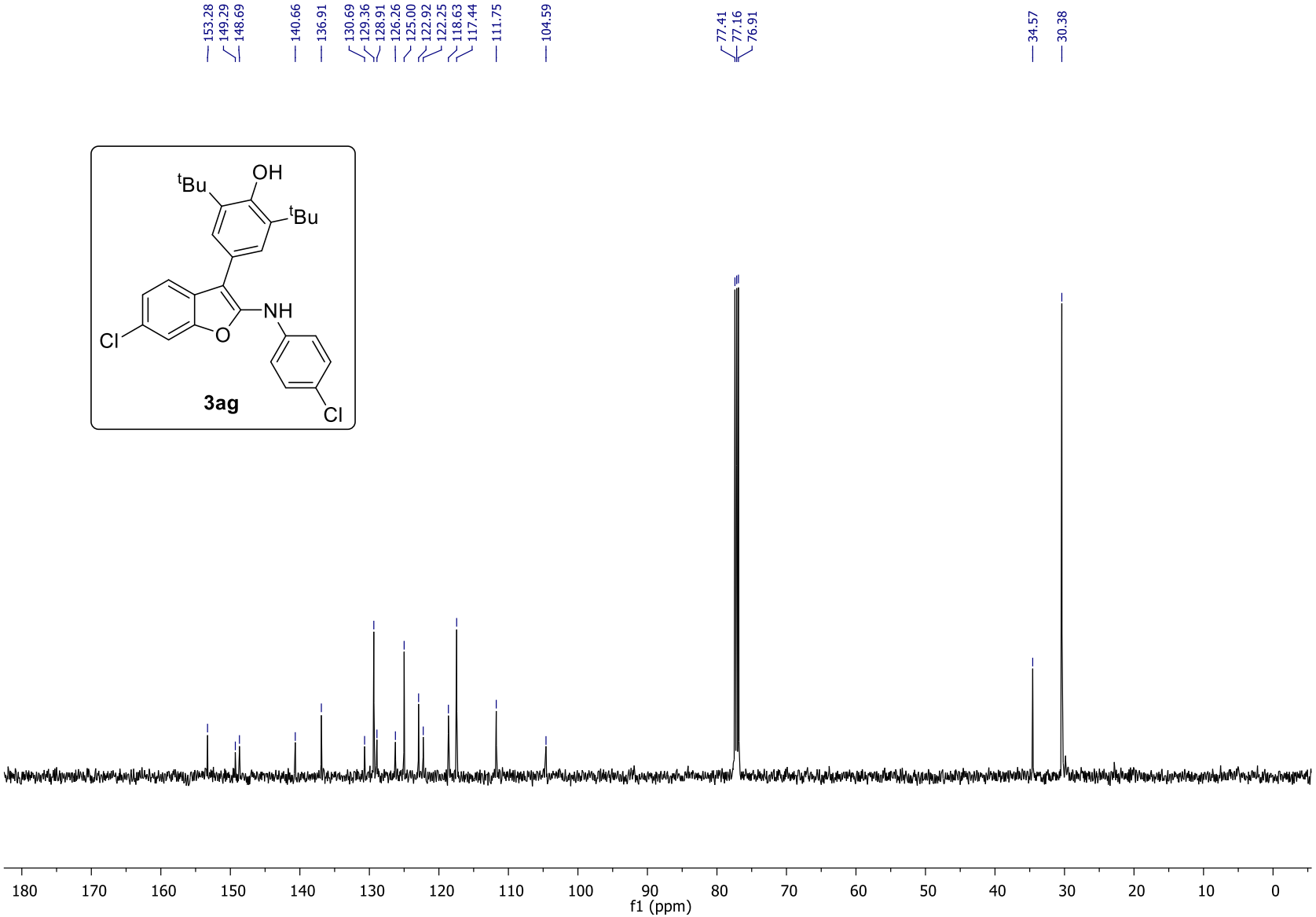
^{13}C NMR of compound **3af** in $CDCl_3$



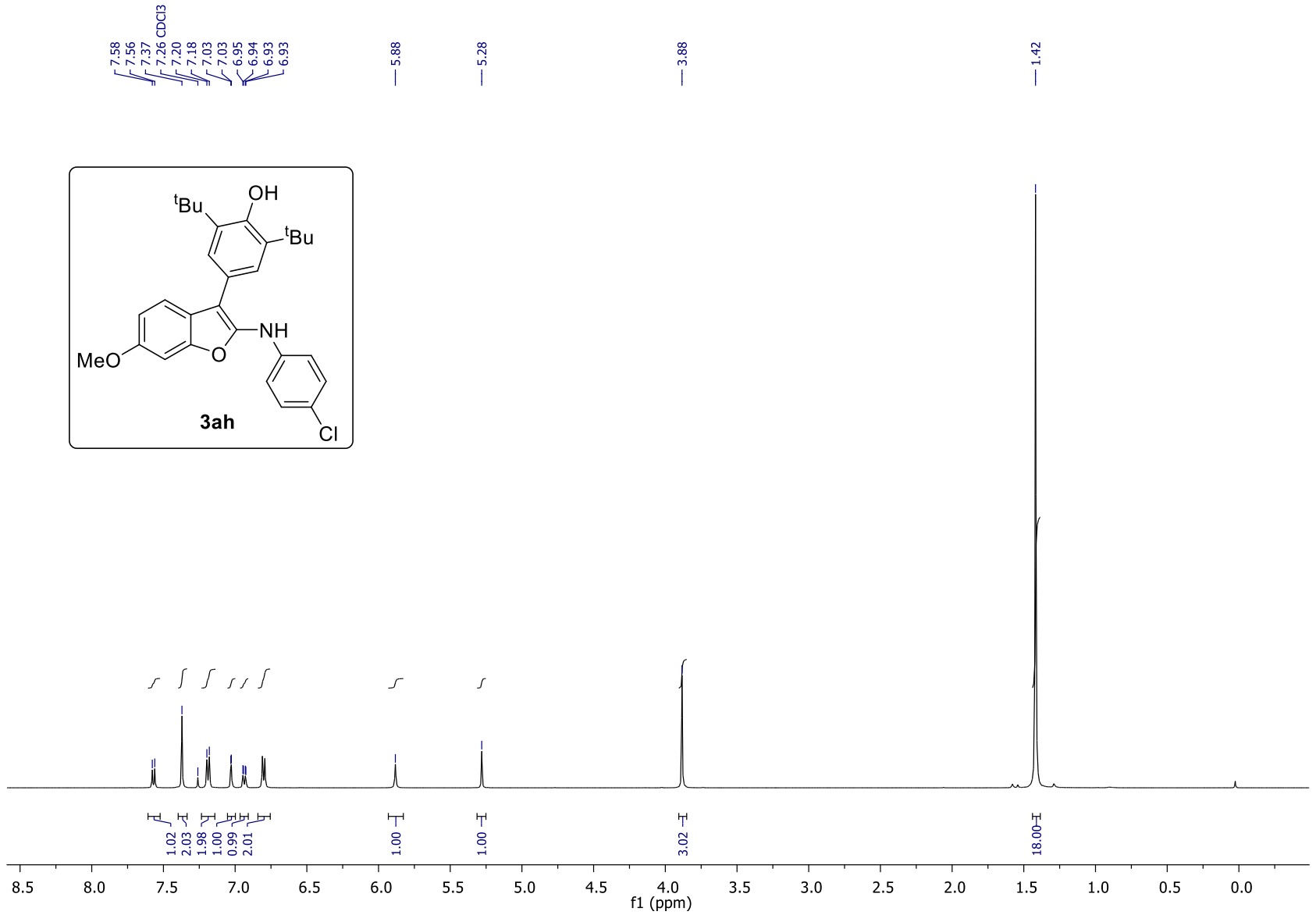
^{1}H NMR of compound **3ag** in $CDCl_3$



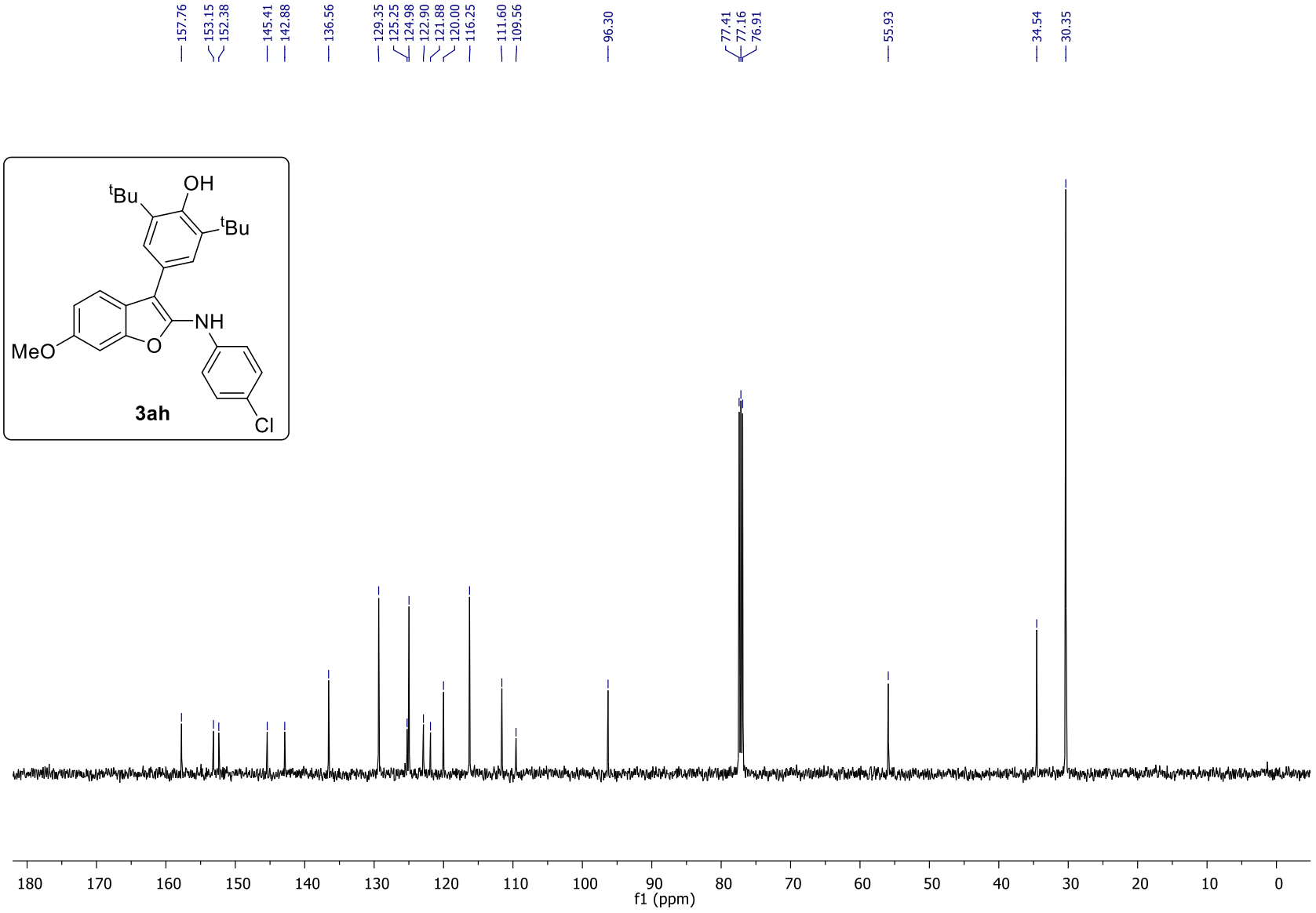
^{13}C NMR of compound **3ag** in $CDCl_3$



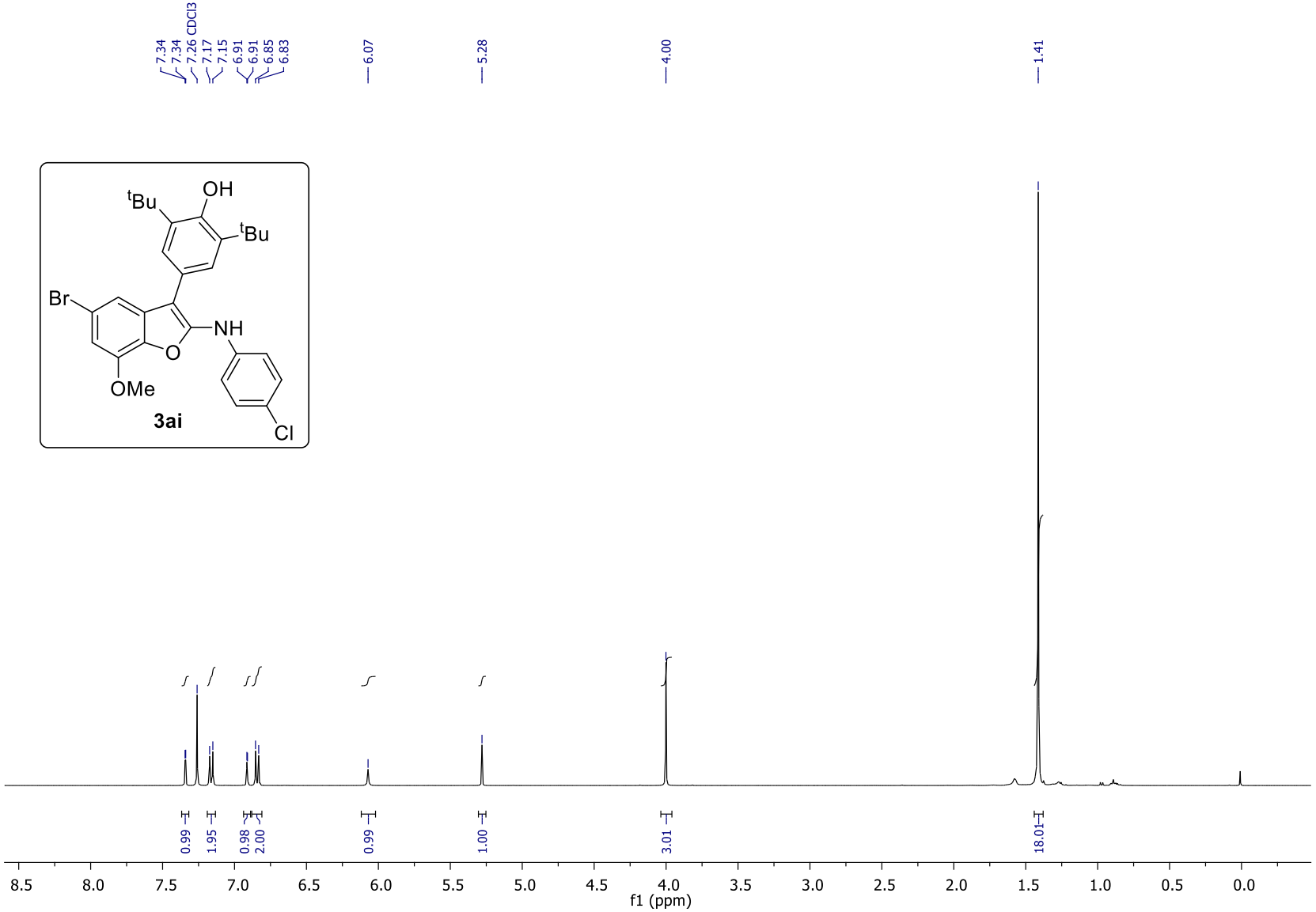
^{1}H NMR of compound **3ah** in $CDCl_3$



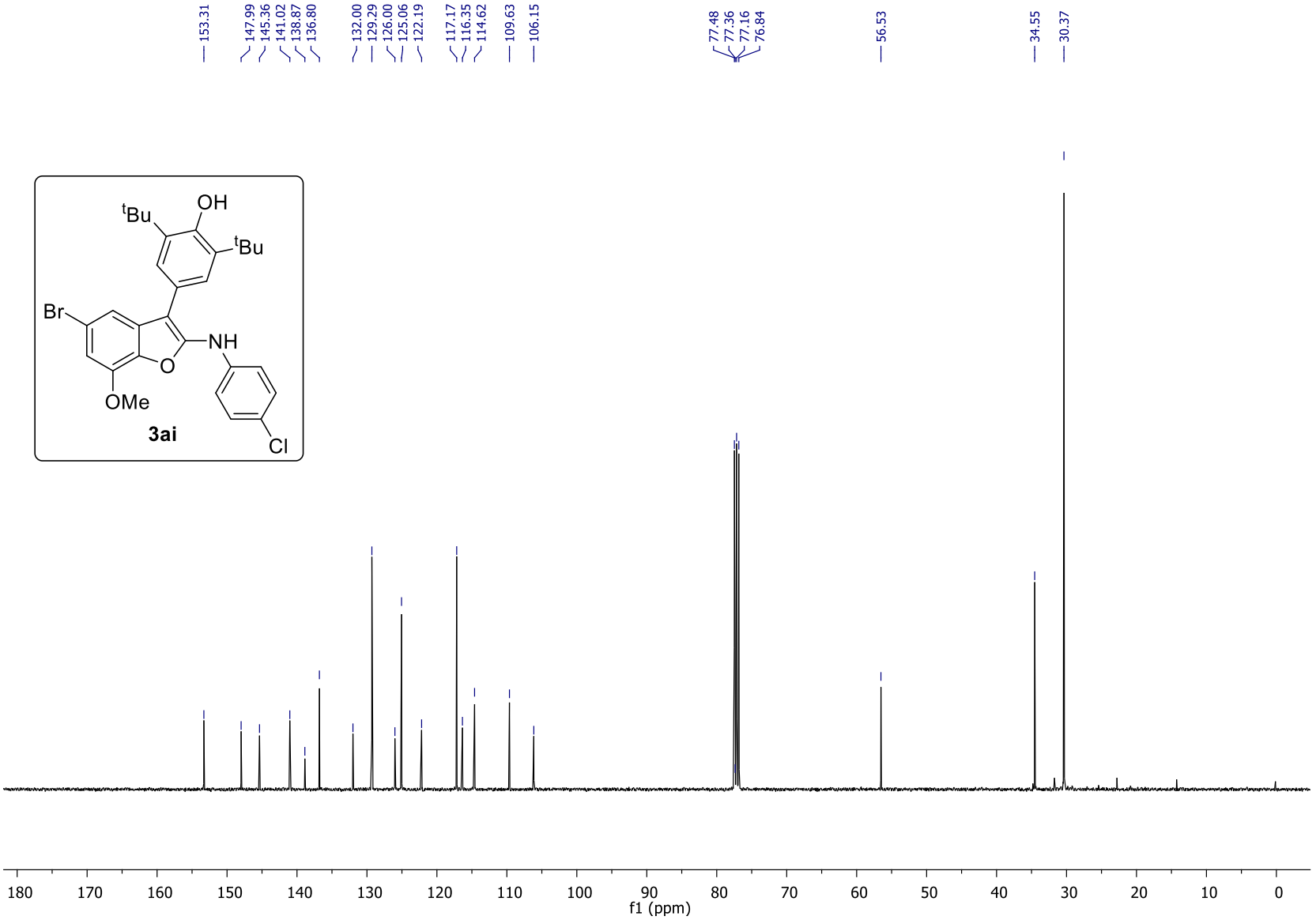
^{13}C NMR of compound **3ah** in $CDCl_3$



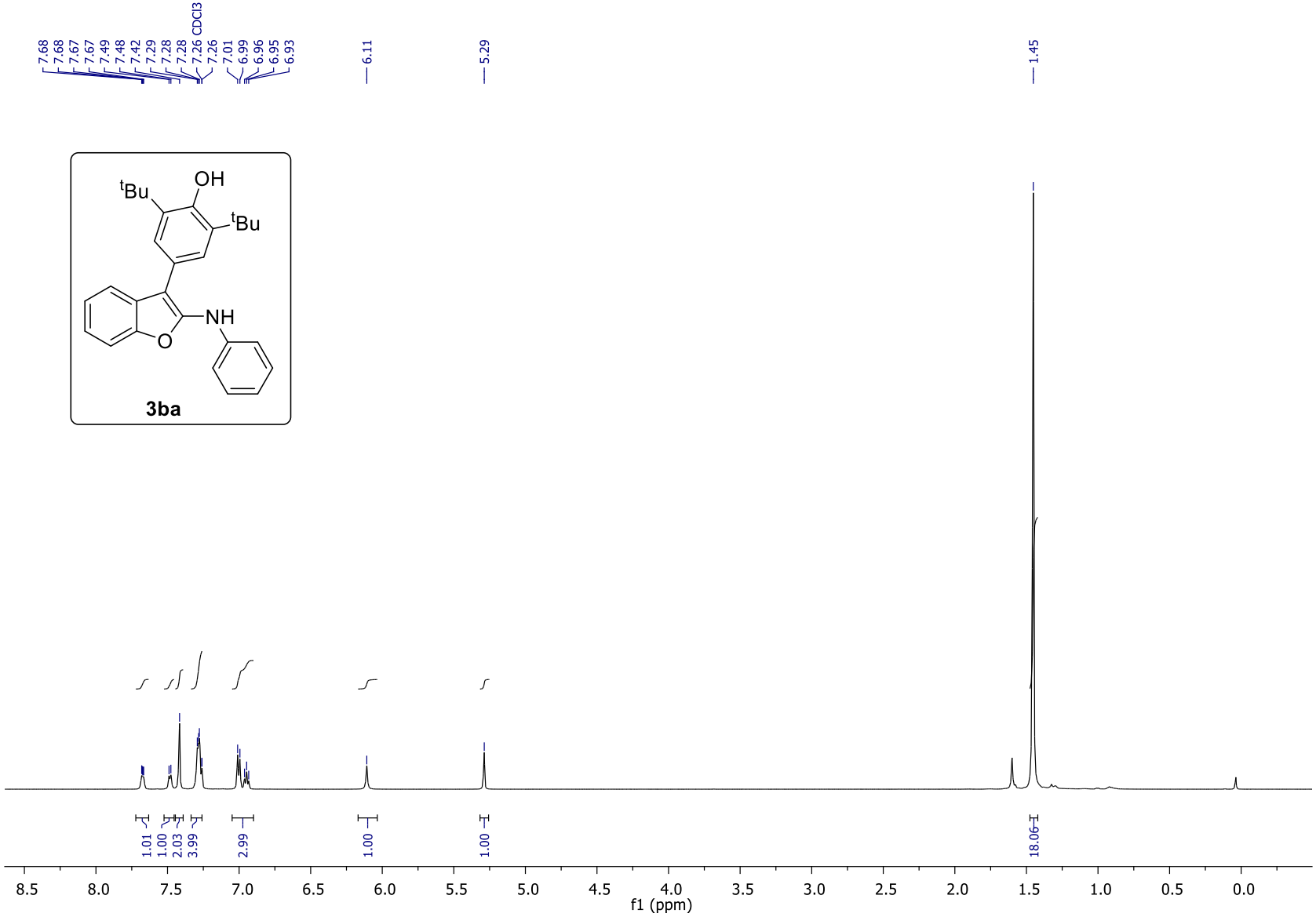
^{1}H NMR of compound **3ai** in $CDCl_3$



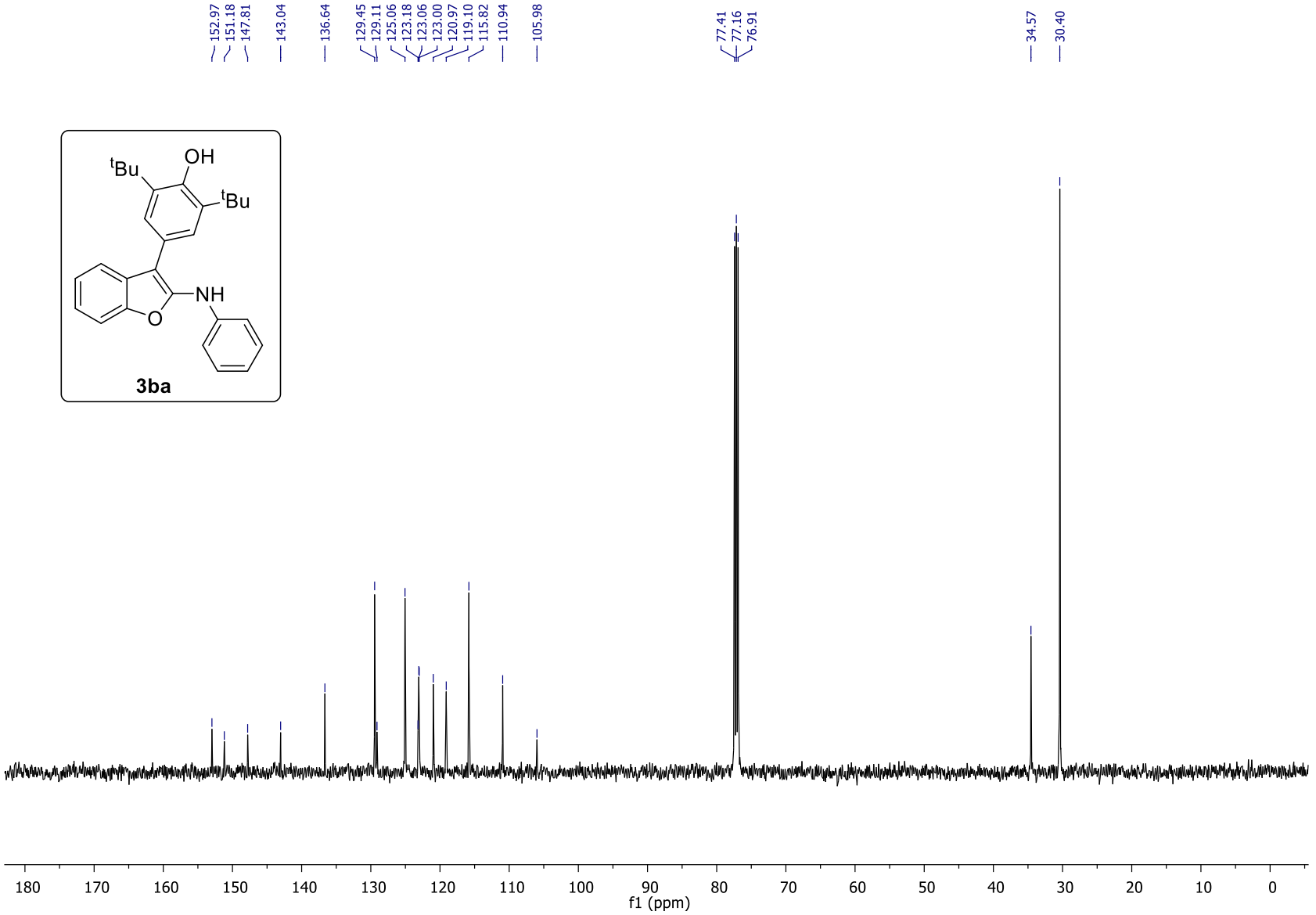
^{13}C NMR of compound **3ai** in $CDCl_3$



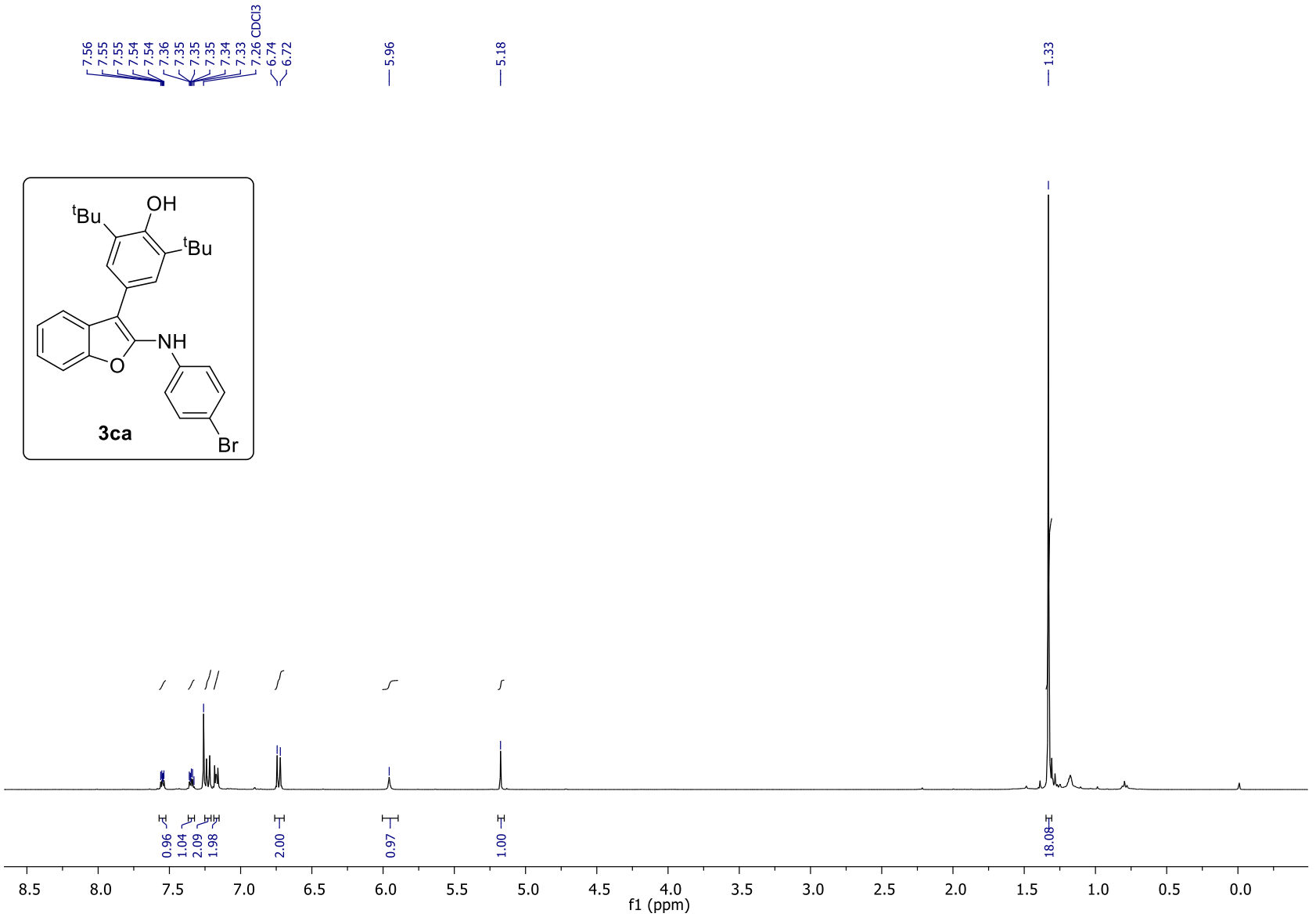
^{1}H NMR of compound **3ba** in $CDCl_3$



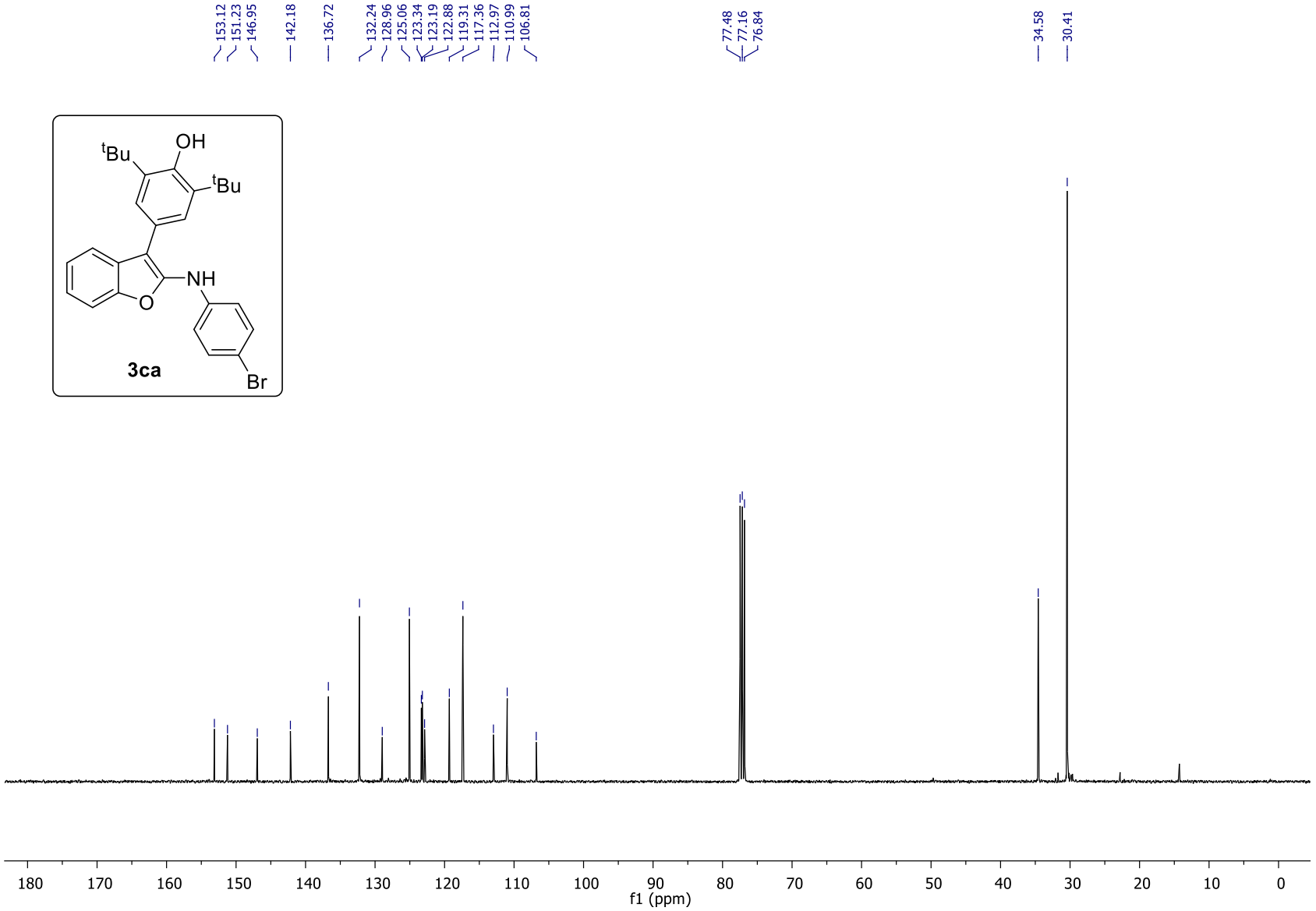
^{13}C NMR of compound **3ba** in $CDCl_3$



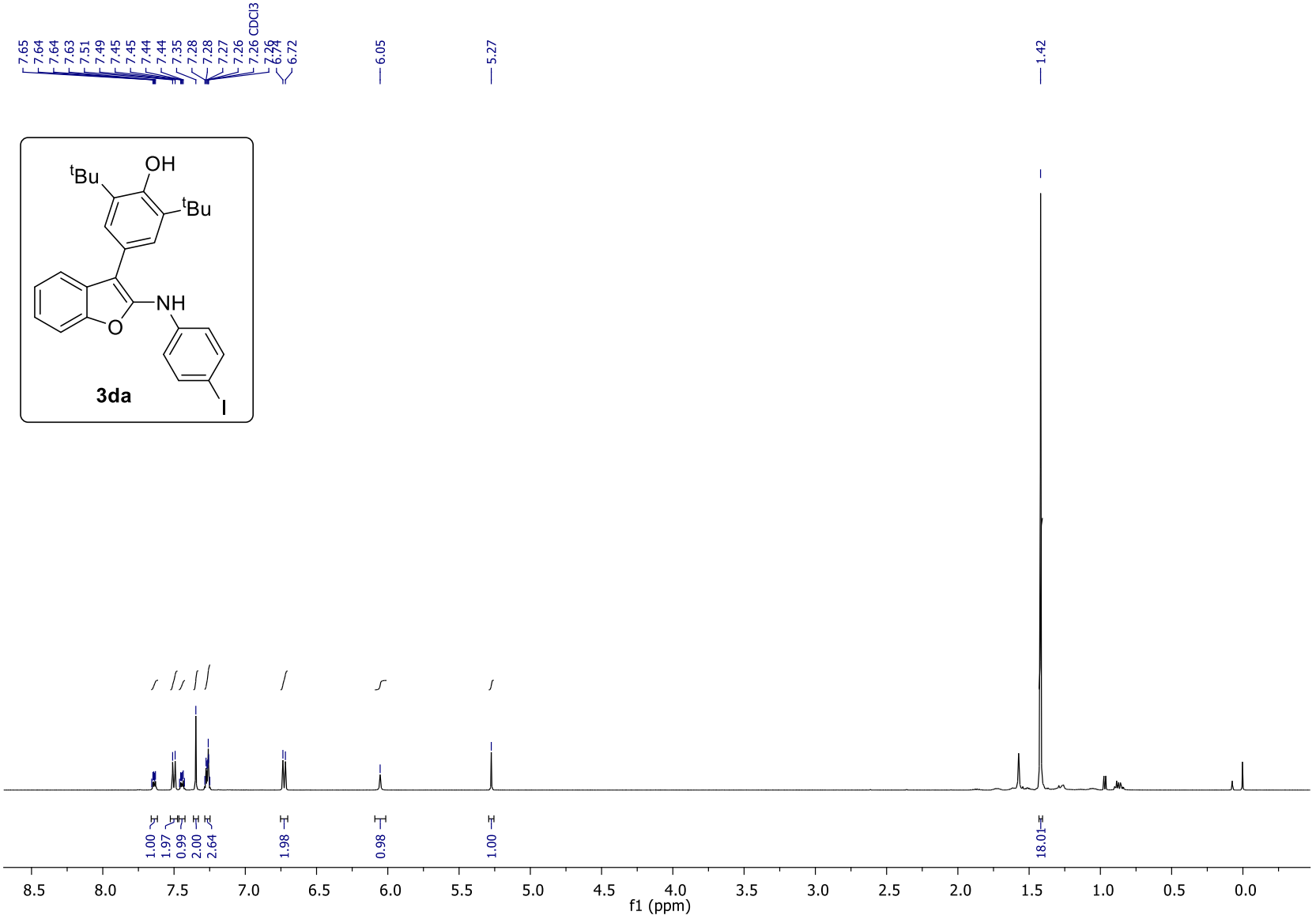
^{1}H NMR of compound **3ca** in $CDCl_3$



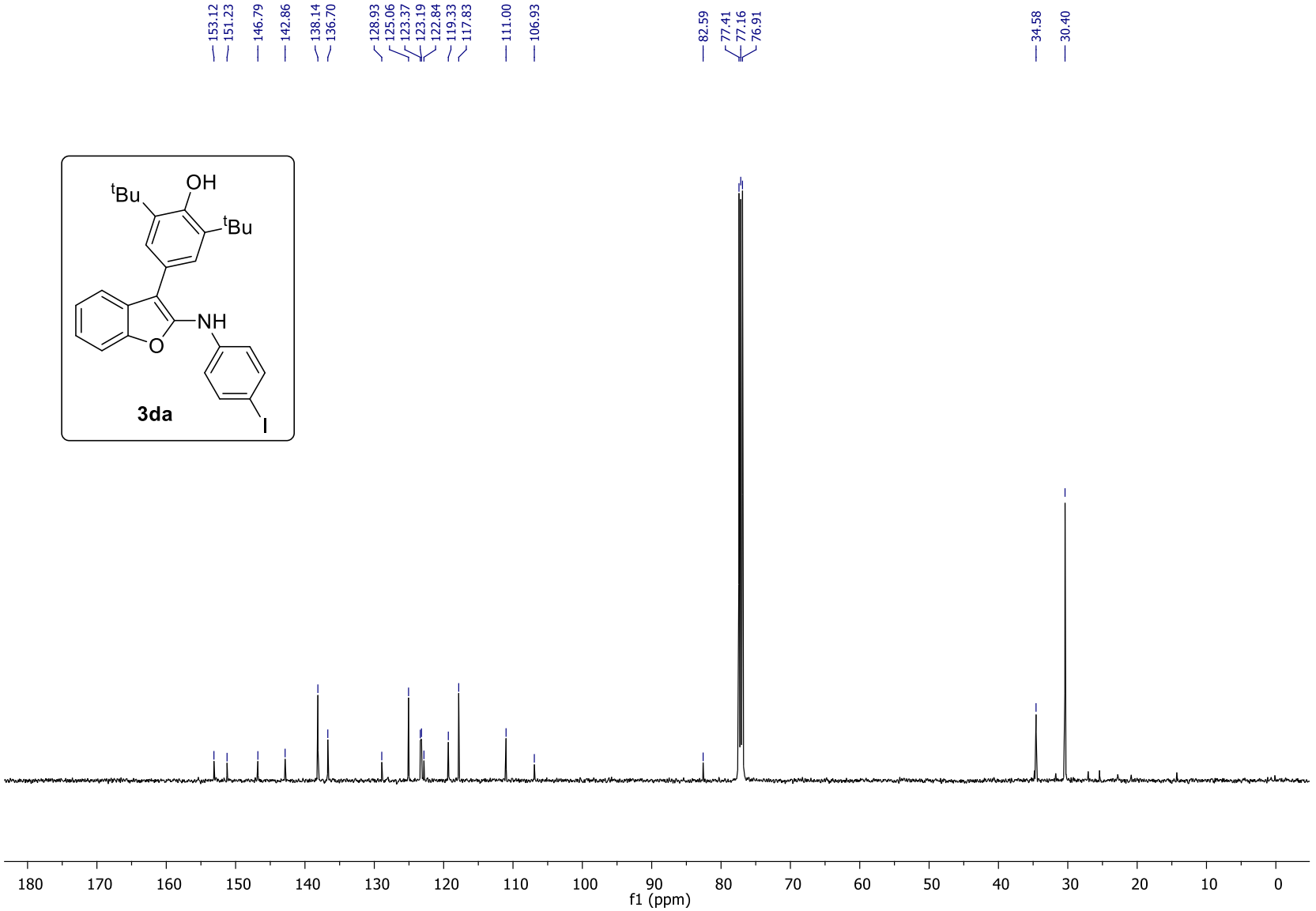
^{13}C NMR of compound **3ca** in $CDCl_3$



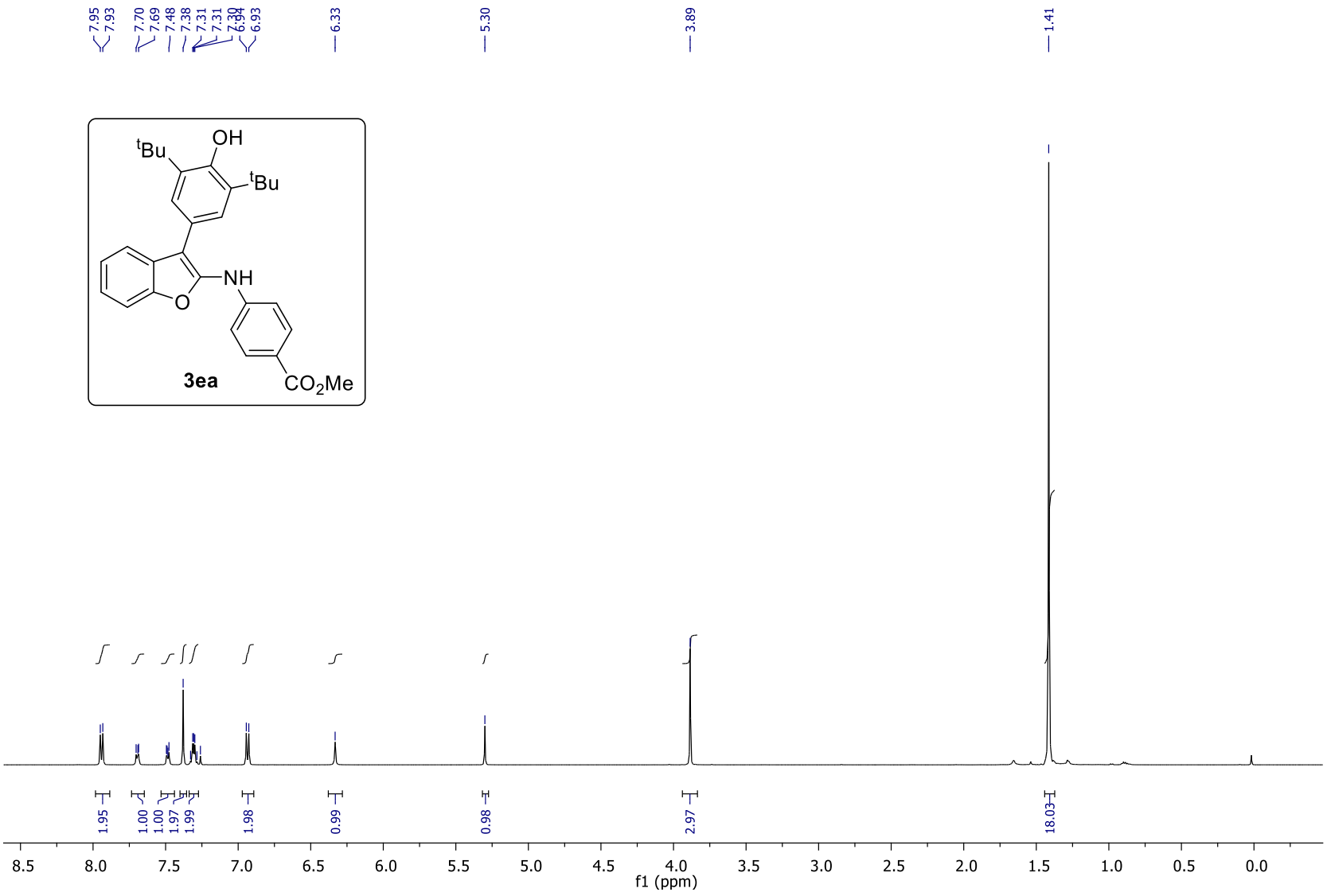
^{1}H NMR of compound **3da** in $CDCl_3$



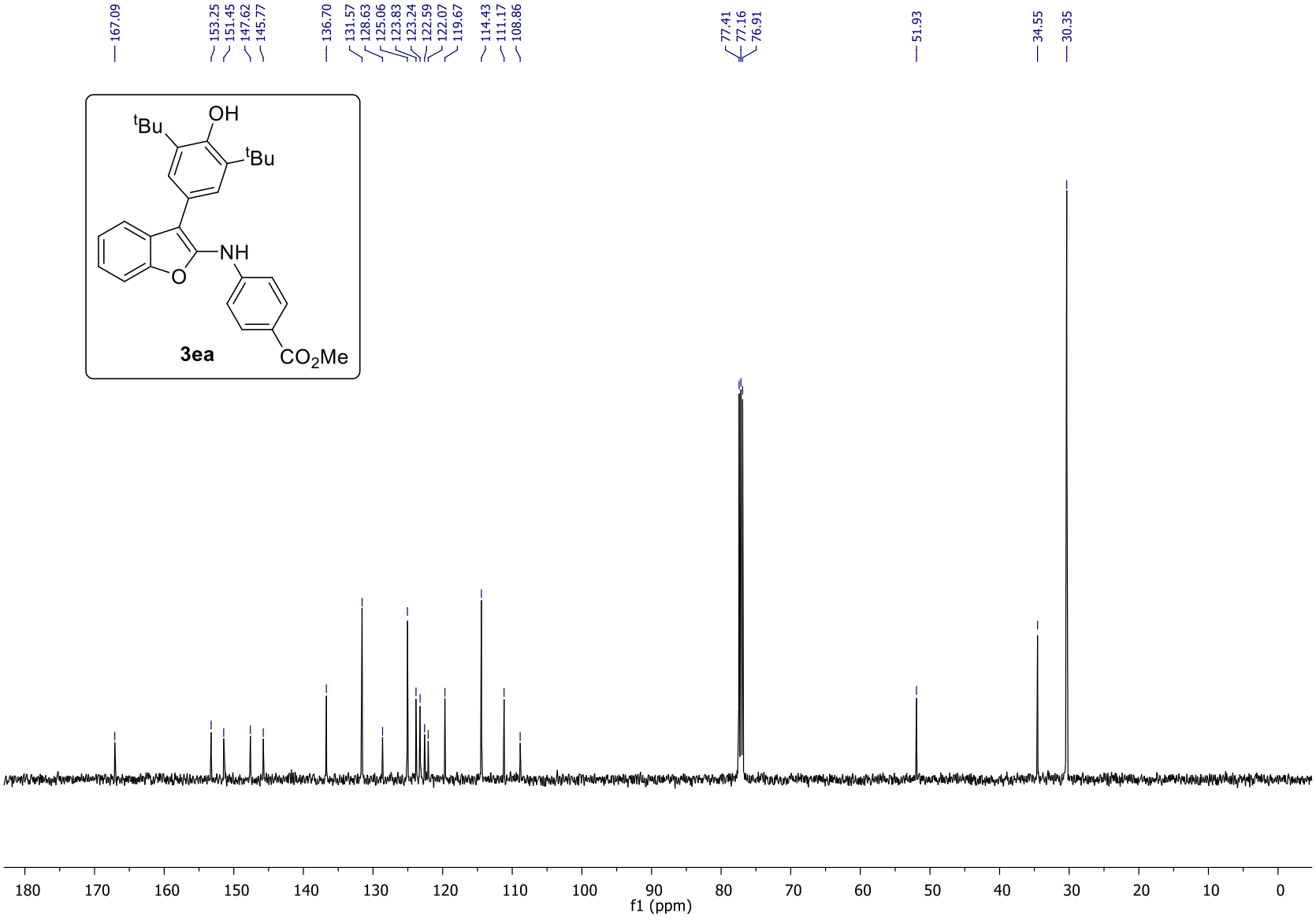
^{13}C NMR of compound **3da** in $CDCl_3$



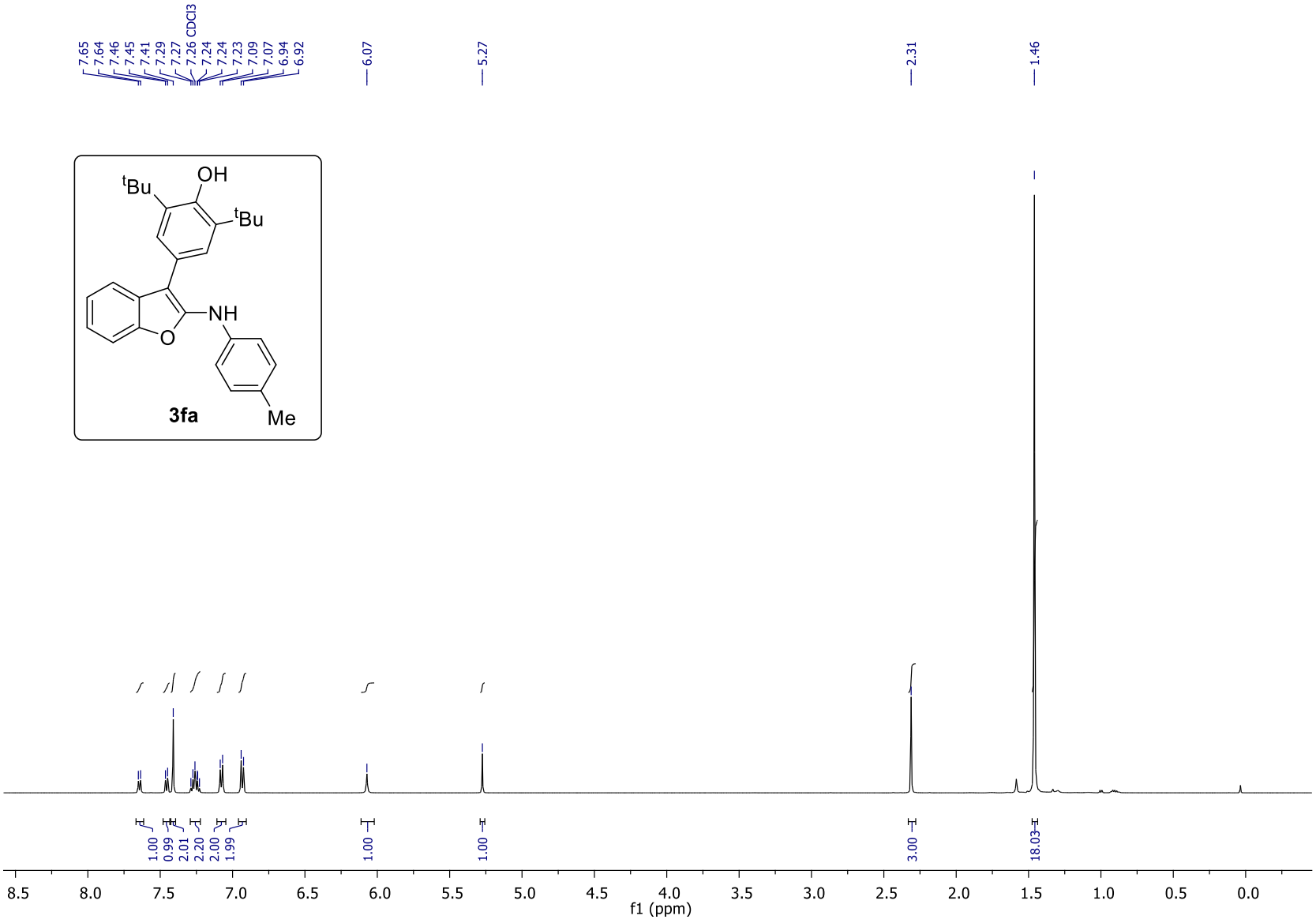
^{1}H NMR of compound **3ea** in $CDCl_3$



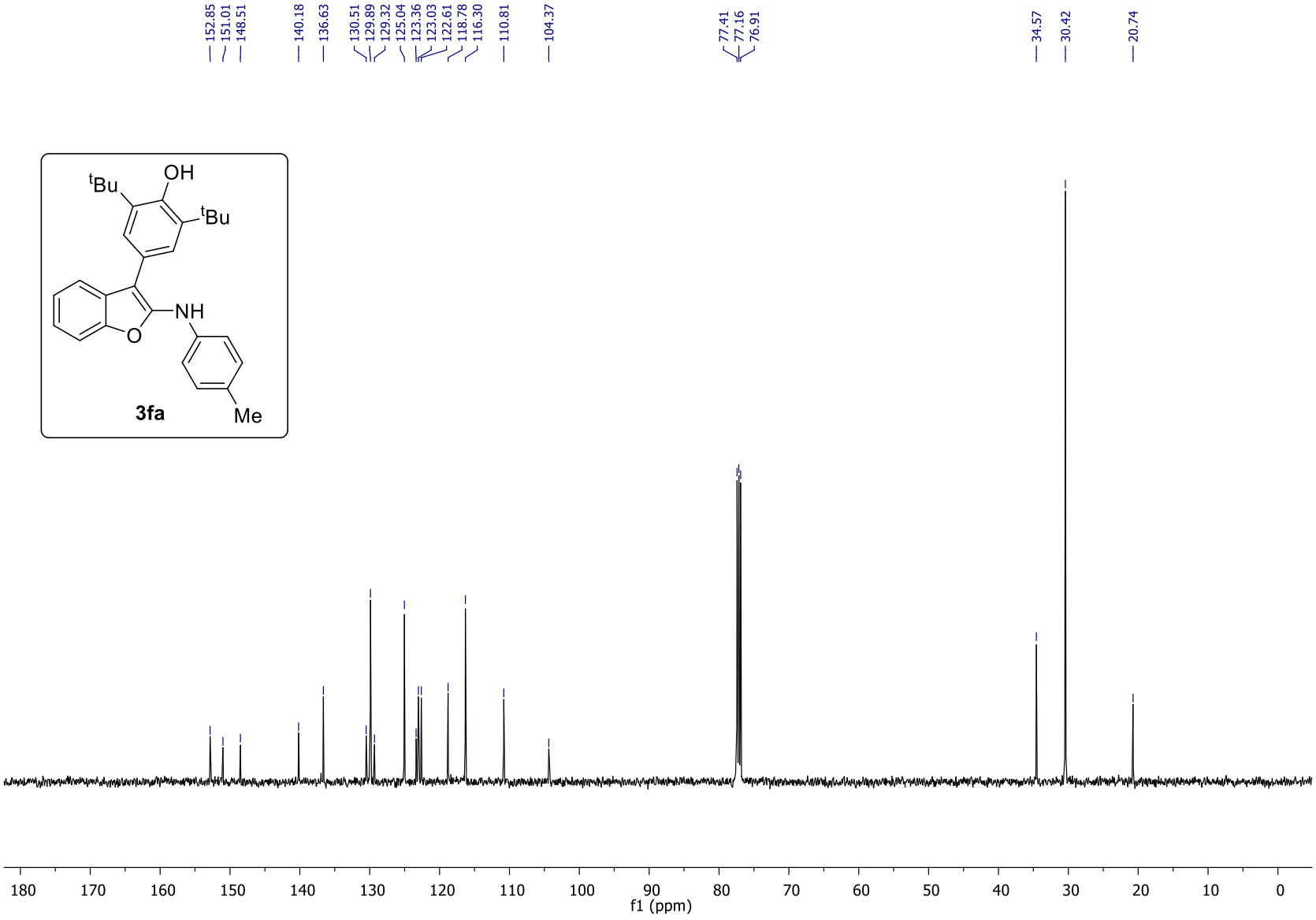
^{13}C NMR of compound **3ea** in $CDCl_3$



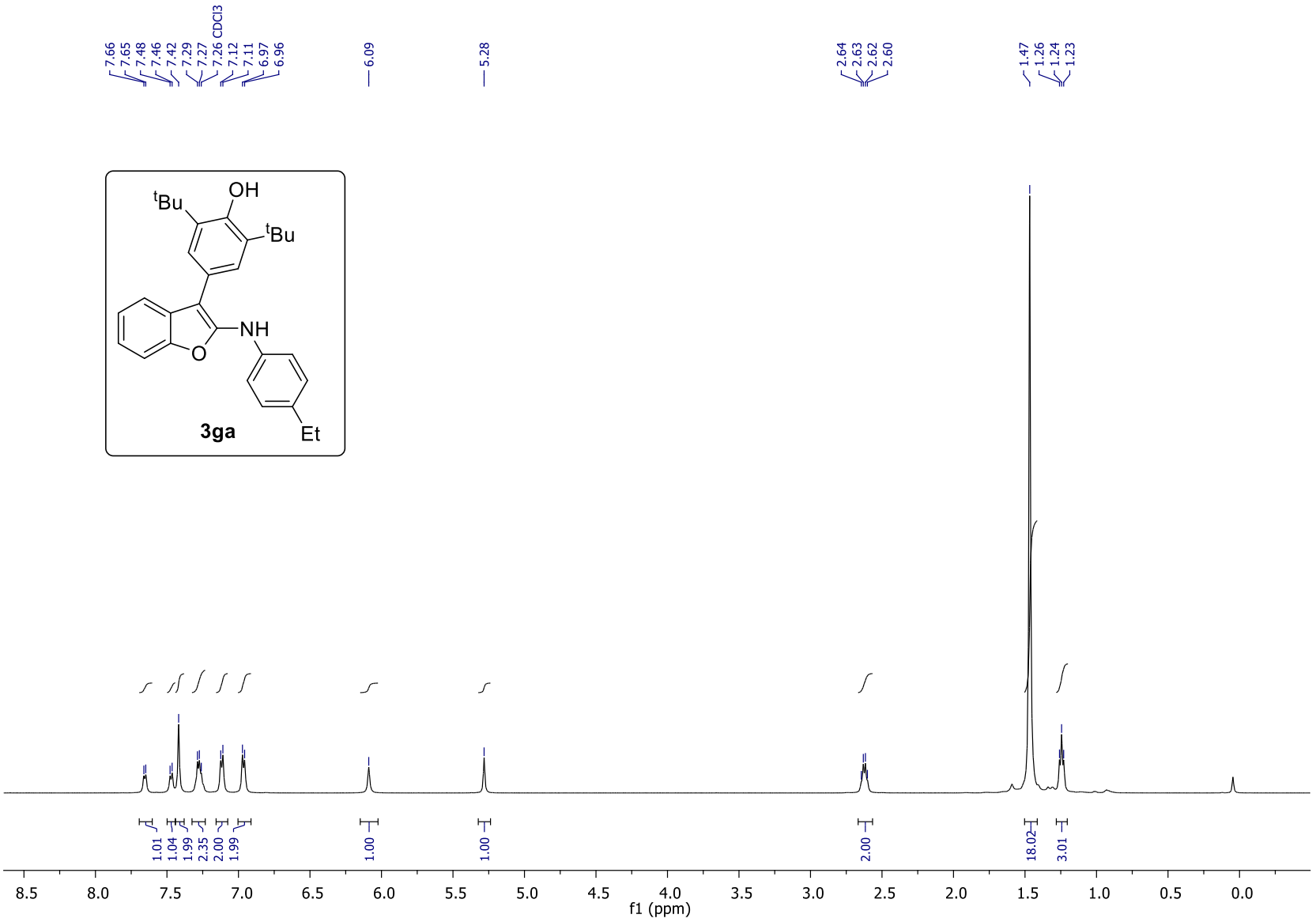
^{1}H NMR of compound **3fa** in $CDCl_3$



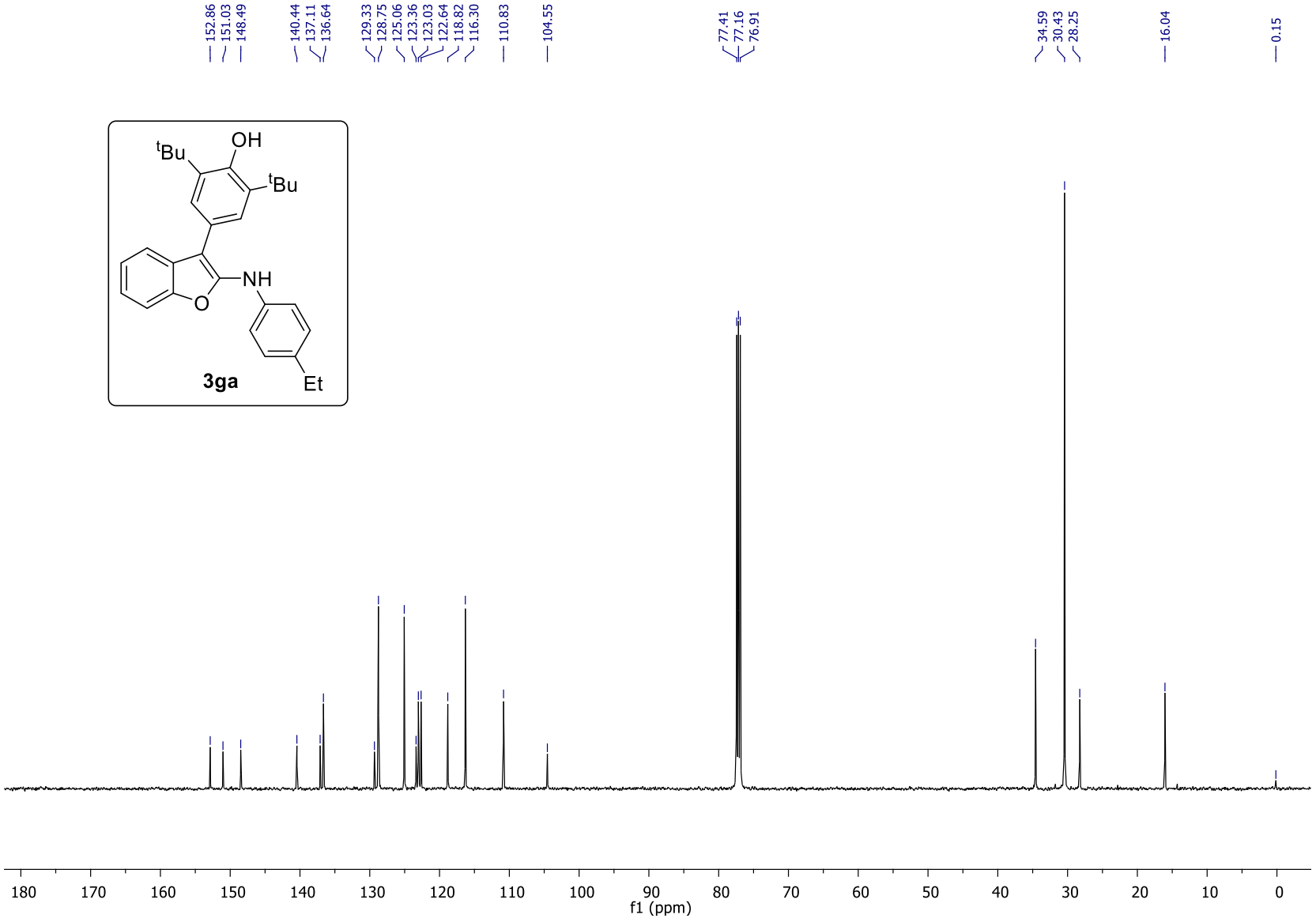
^{13}C NMR of compound **3fa** in $CDCl_3$



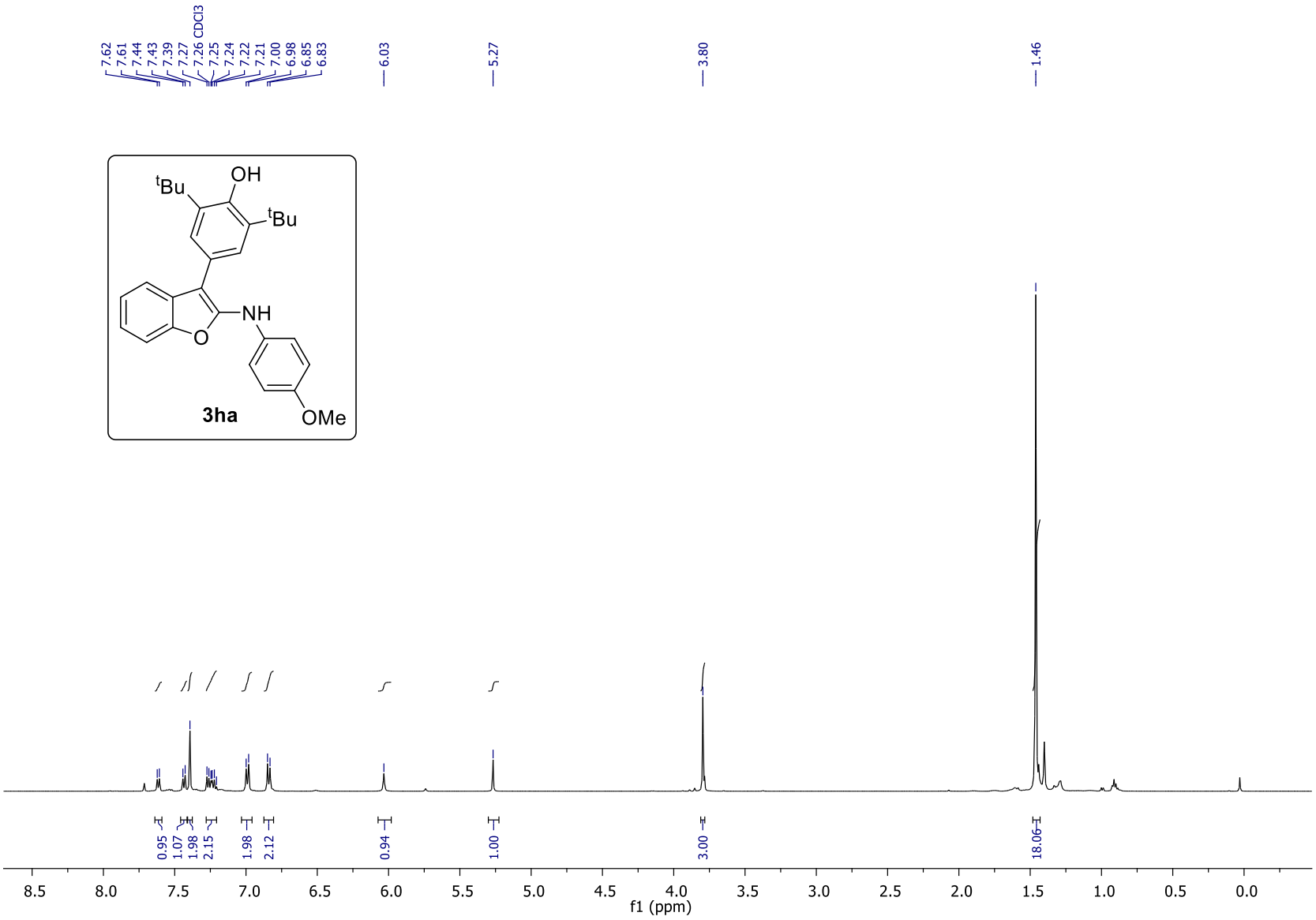
^{1}H NMR of compound **3ga** in $CDCl_3$



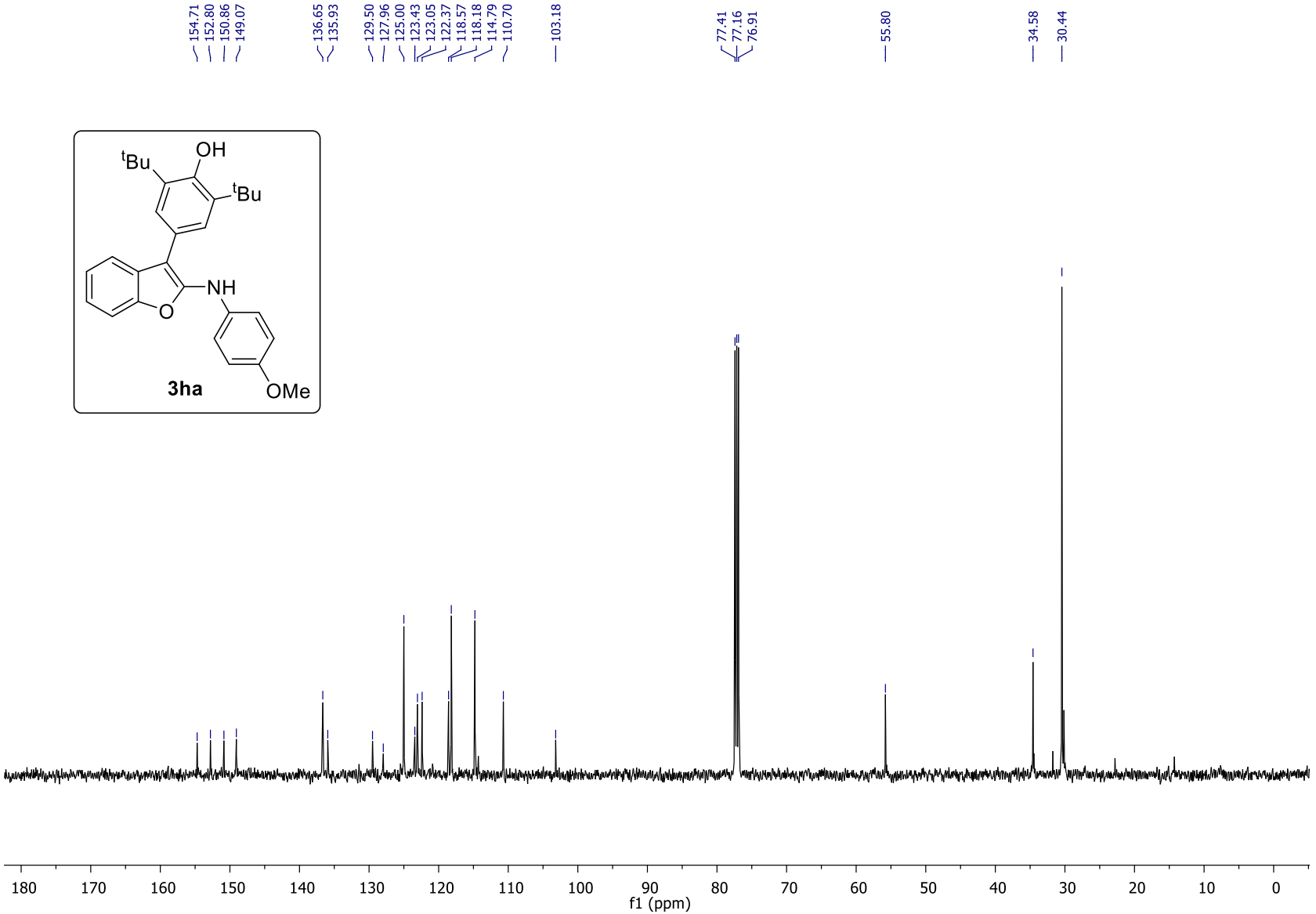
^{13}C NMR of compound **3ga** in $CDCl_3$



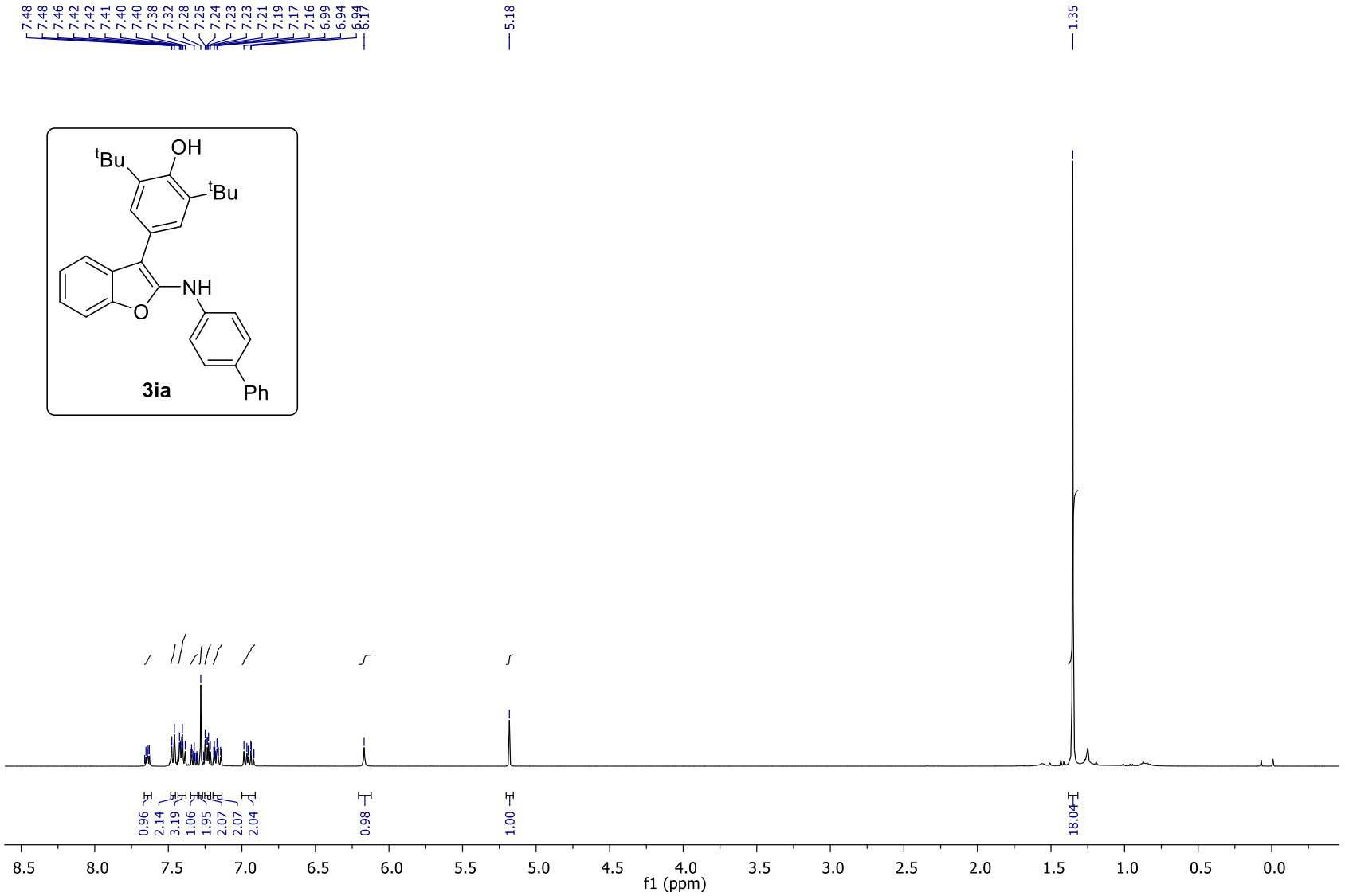
^{1}H NMR of compound **3ha** in $CDCl_3$



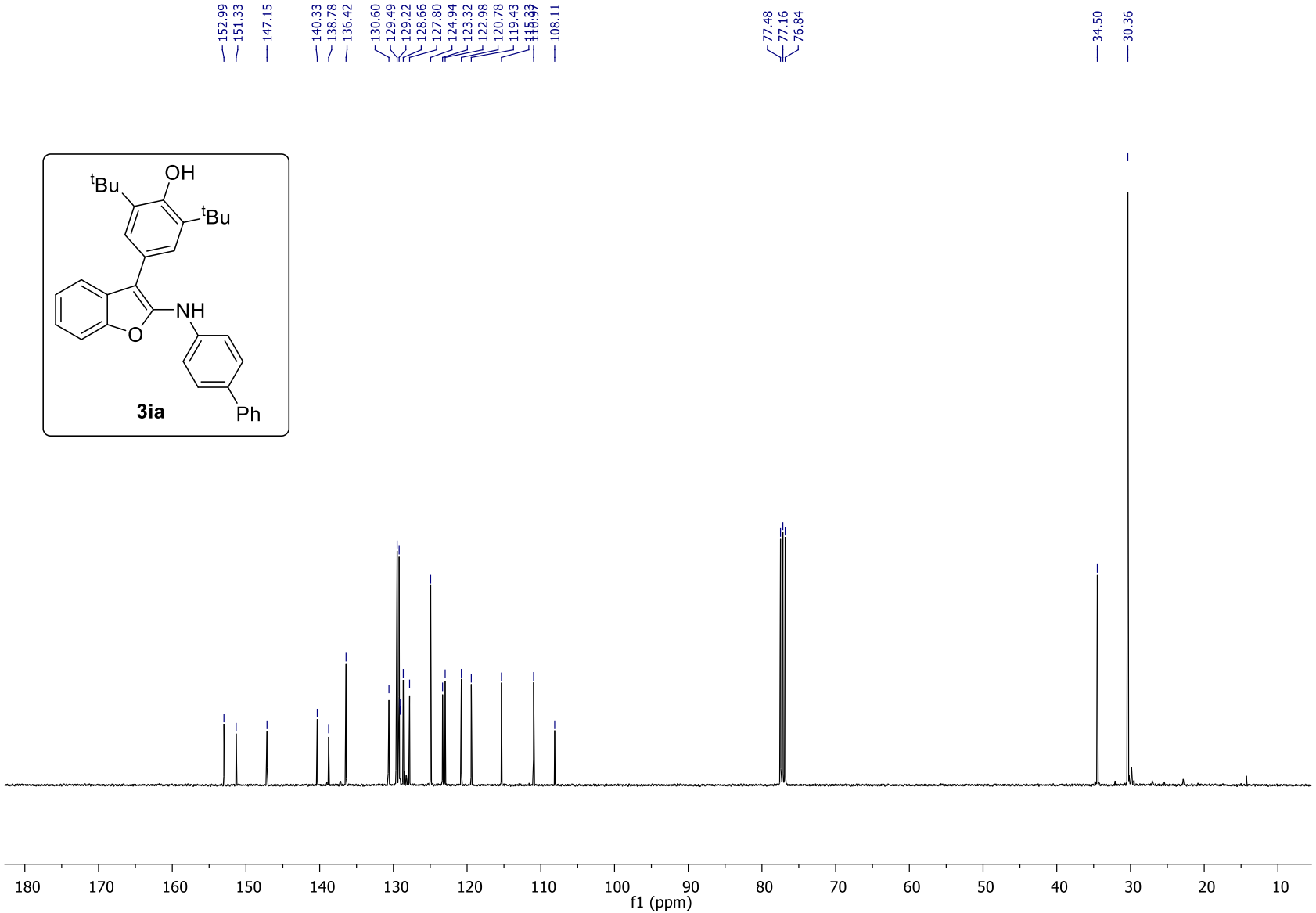
^{13}C NMR of compound **3ha** in $CDCl_3$



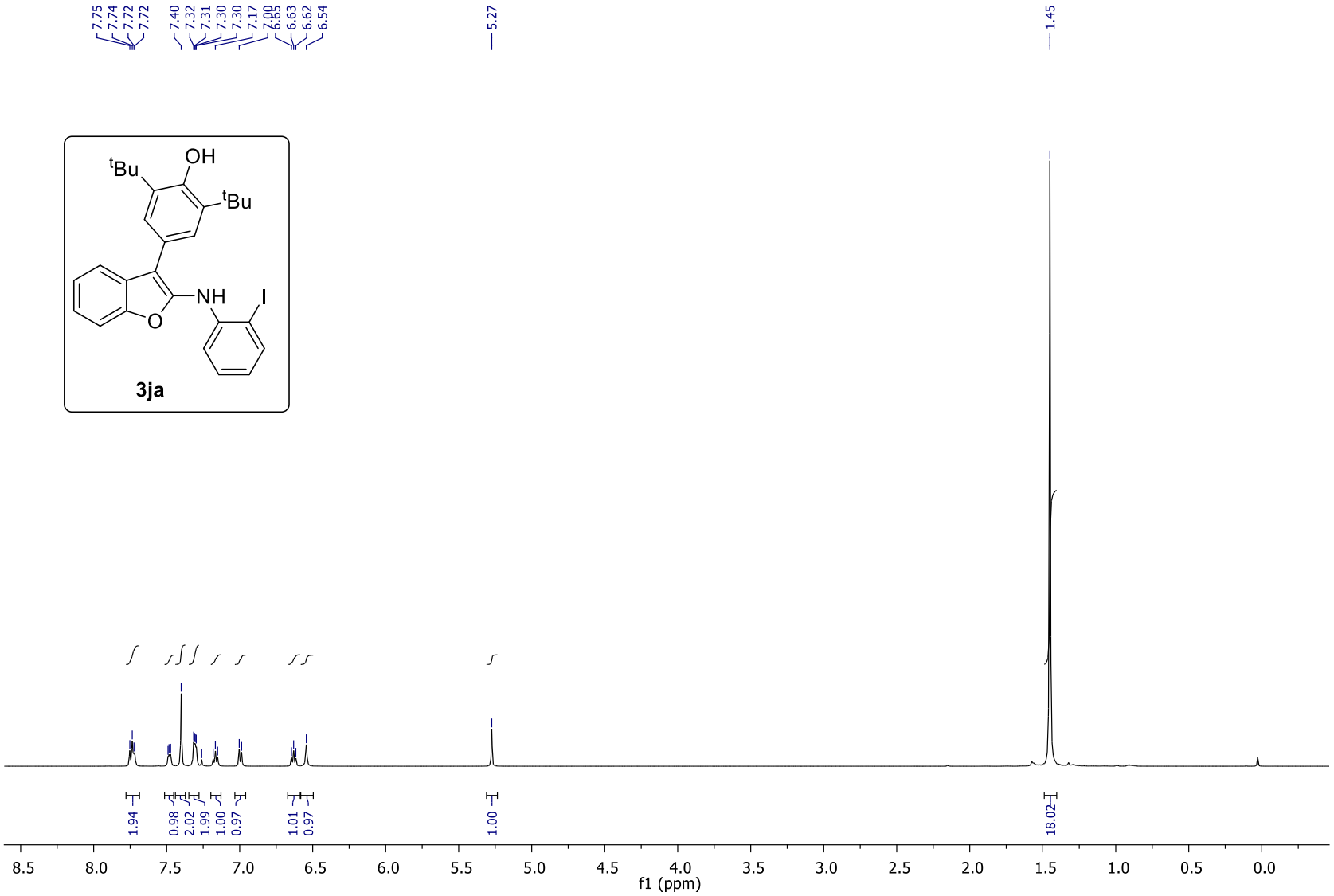
^{1}H NMR of compound **3ia** in $CDCl_3$



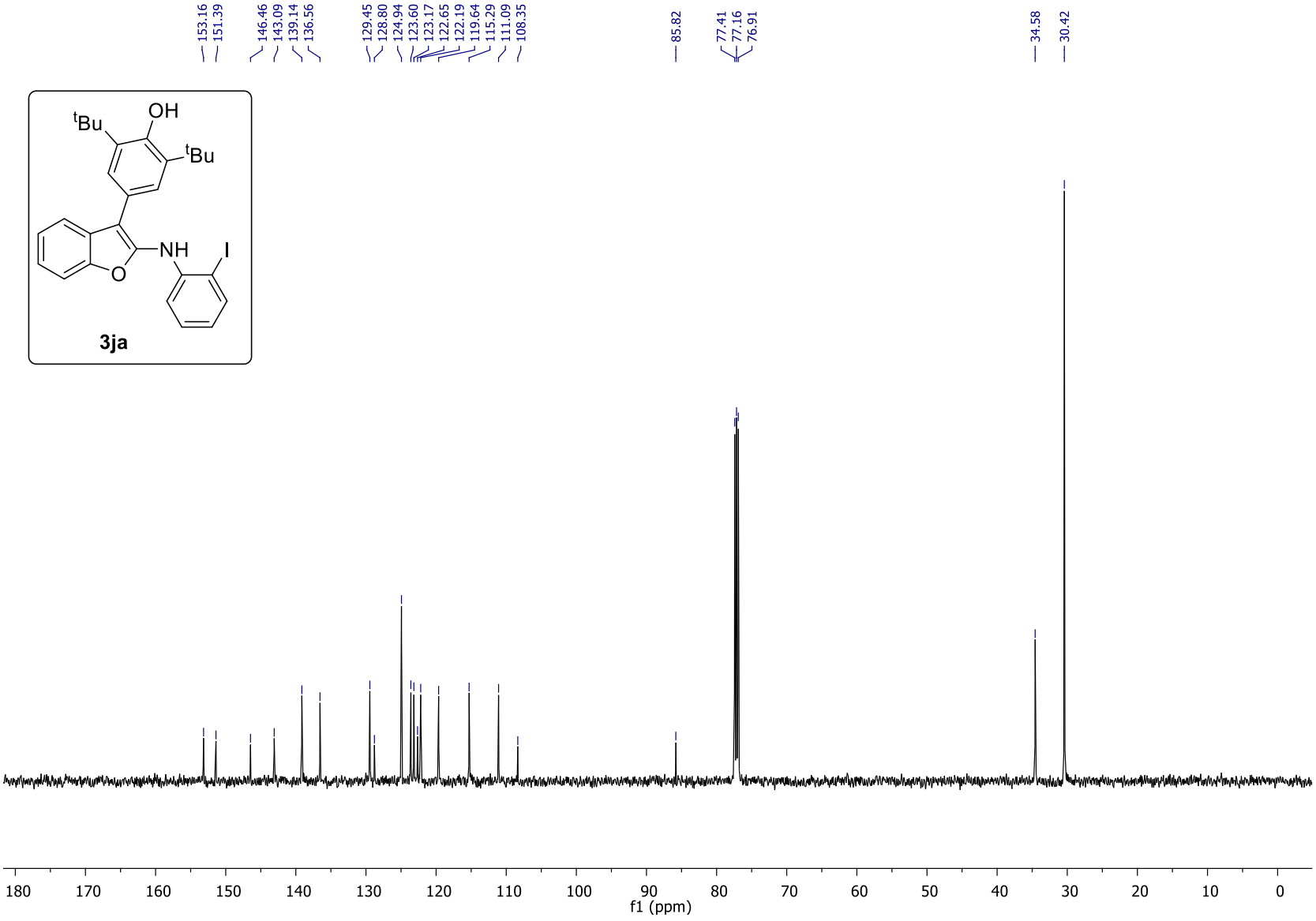
^{13}C NMR of compound **3ia** in $CDCl_3$



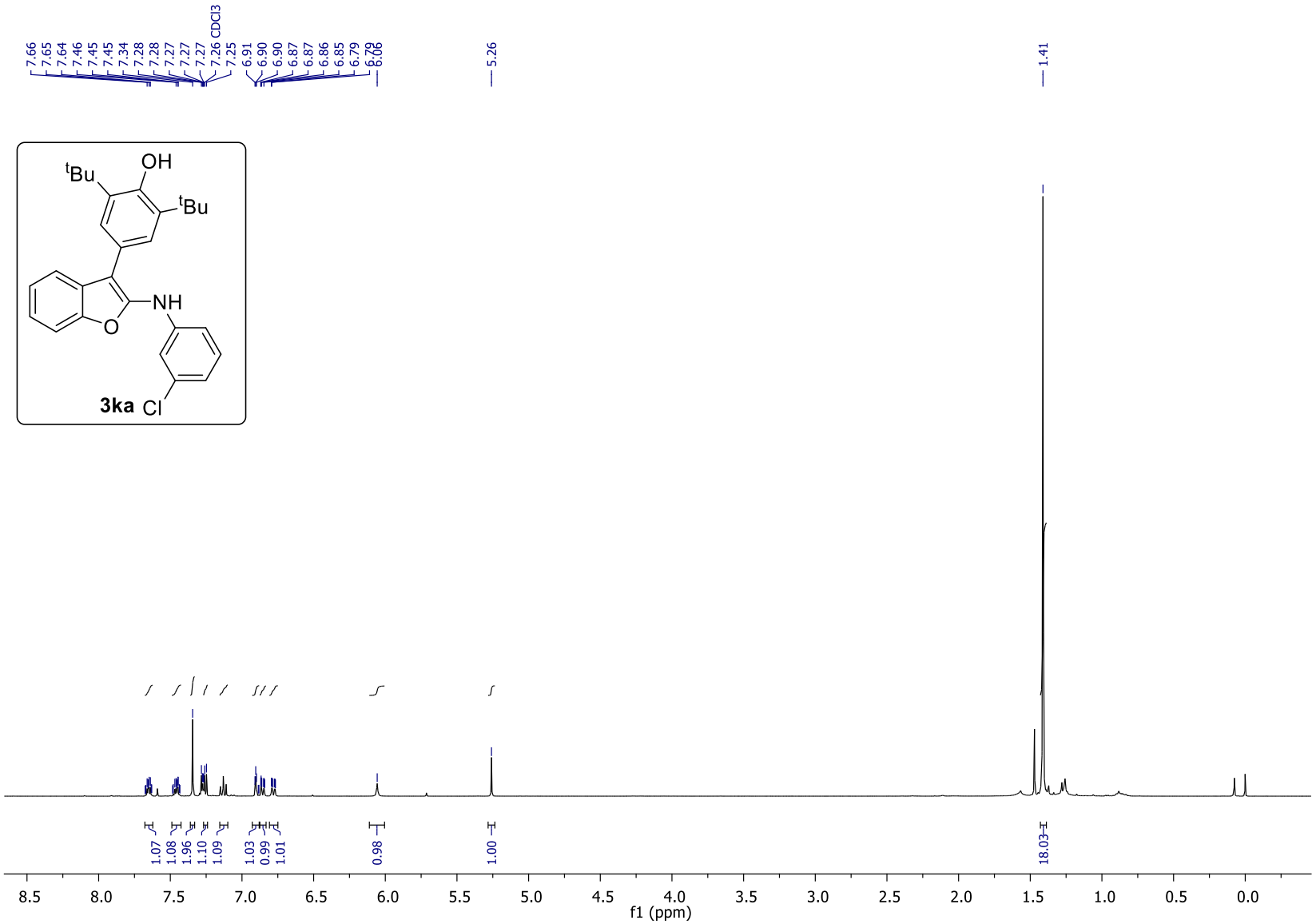
^{1}H NMR of compound **3ja** in $CDCl_3$



^{13}C NMR of compound **3ja** in $CDCl_3$



^{1}H NMR of compound **3ka** in $CDCl_3$



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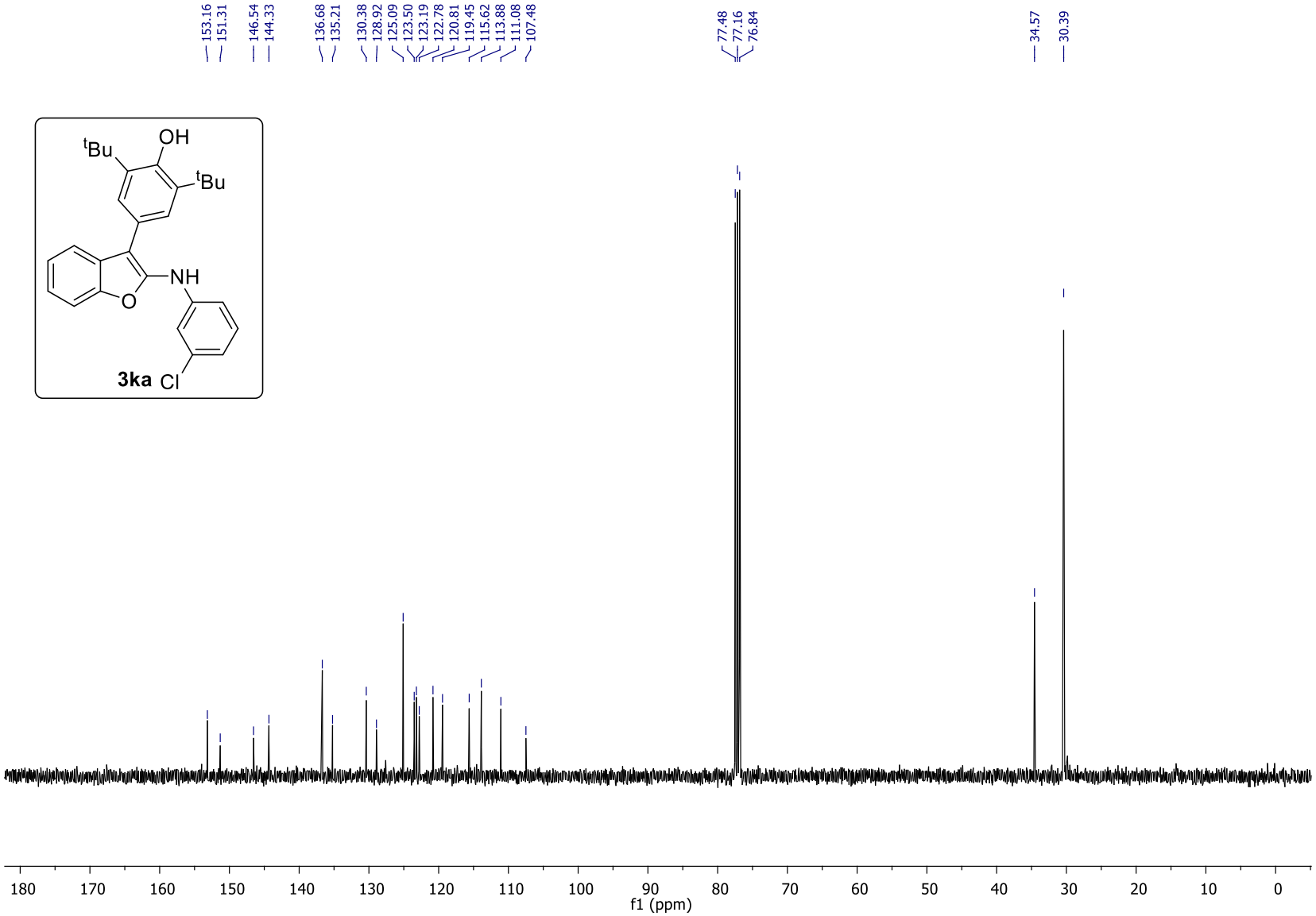
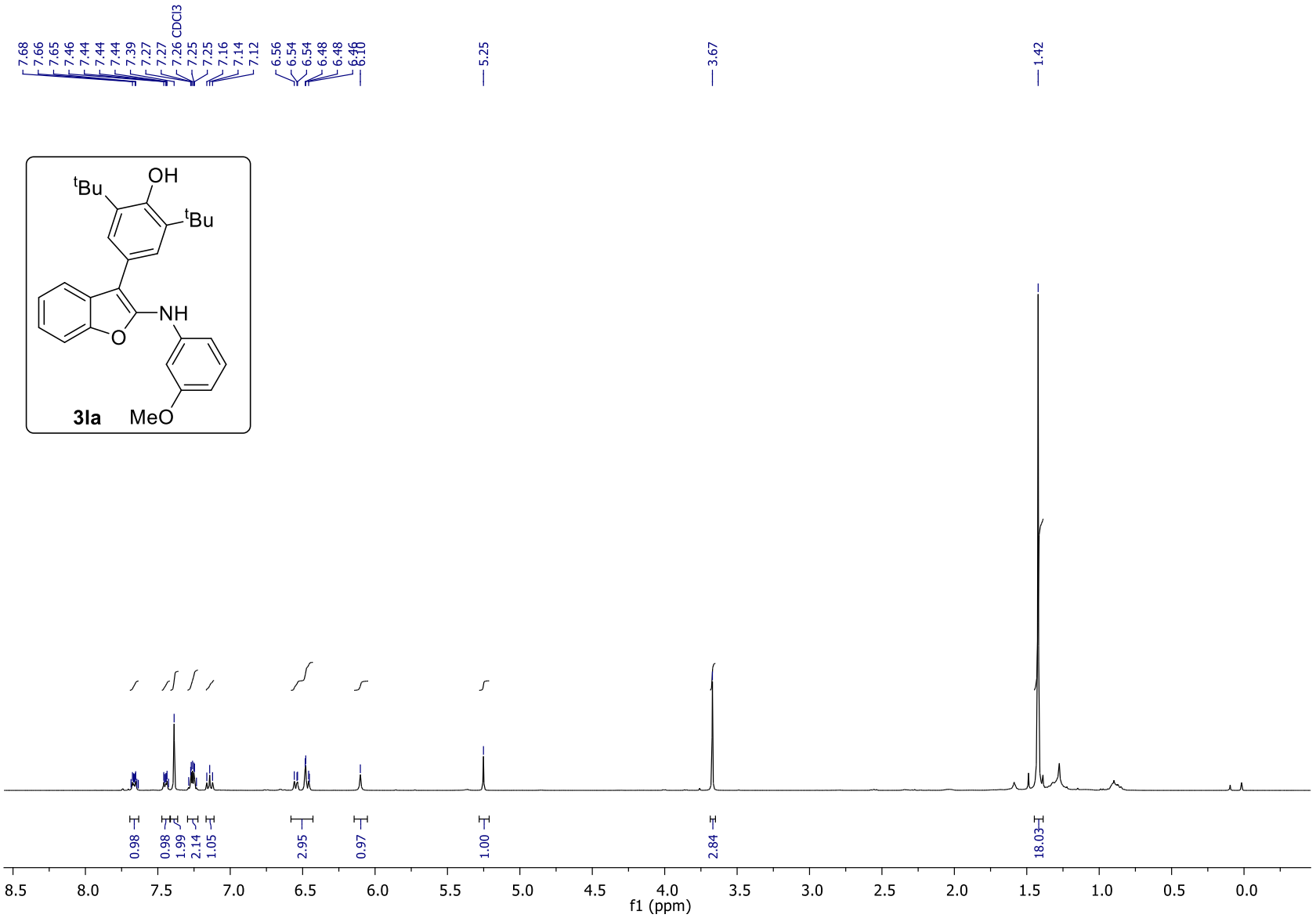
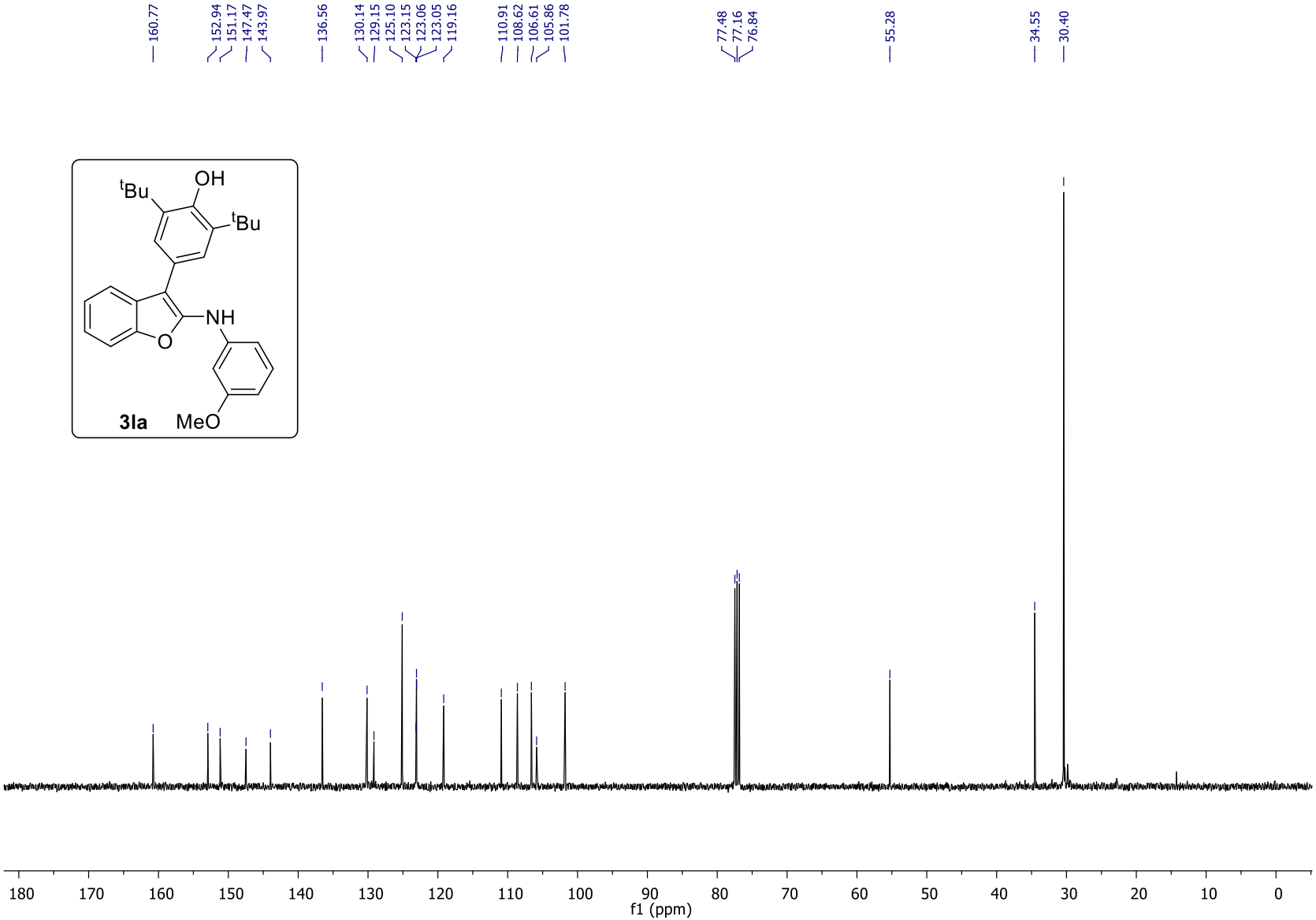


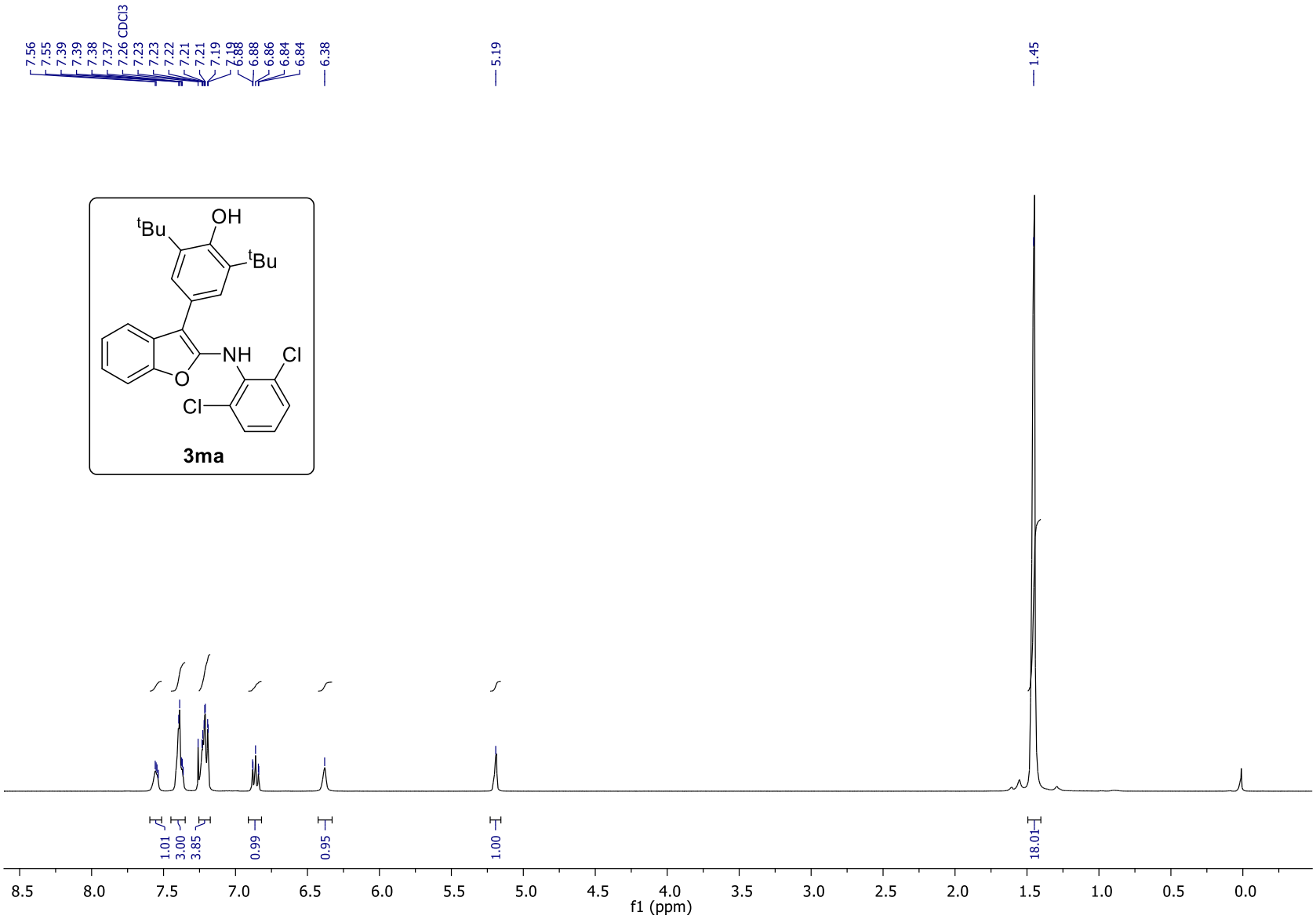
^{1}H NMR of compound **3la** in $CDCl_3$



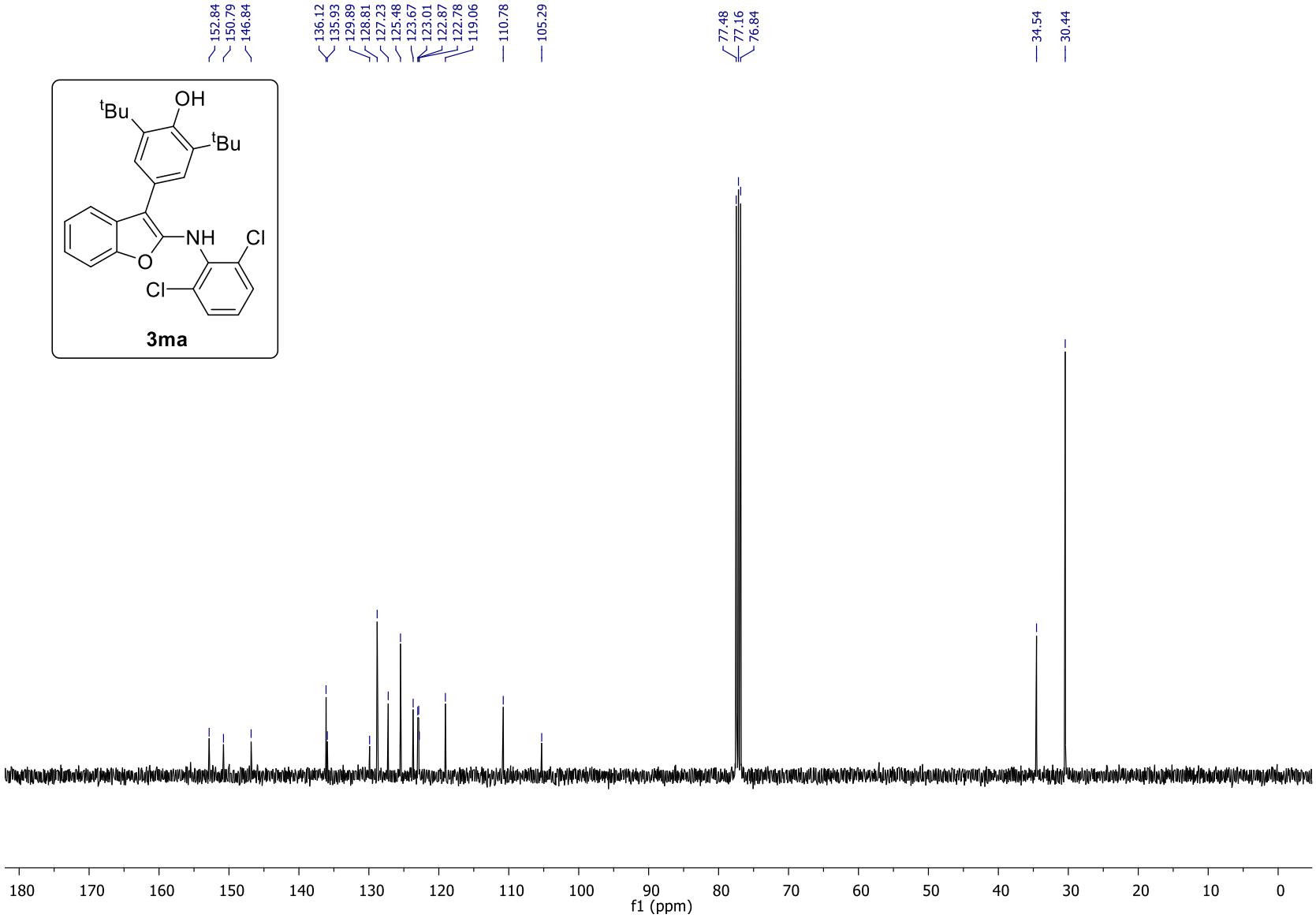
^{13}C NMR of compound **3la** in $CDCl_3$



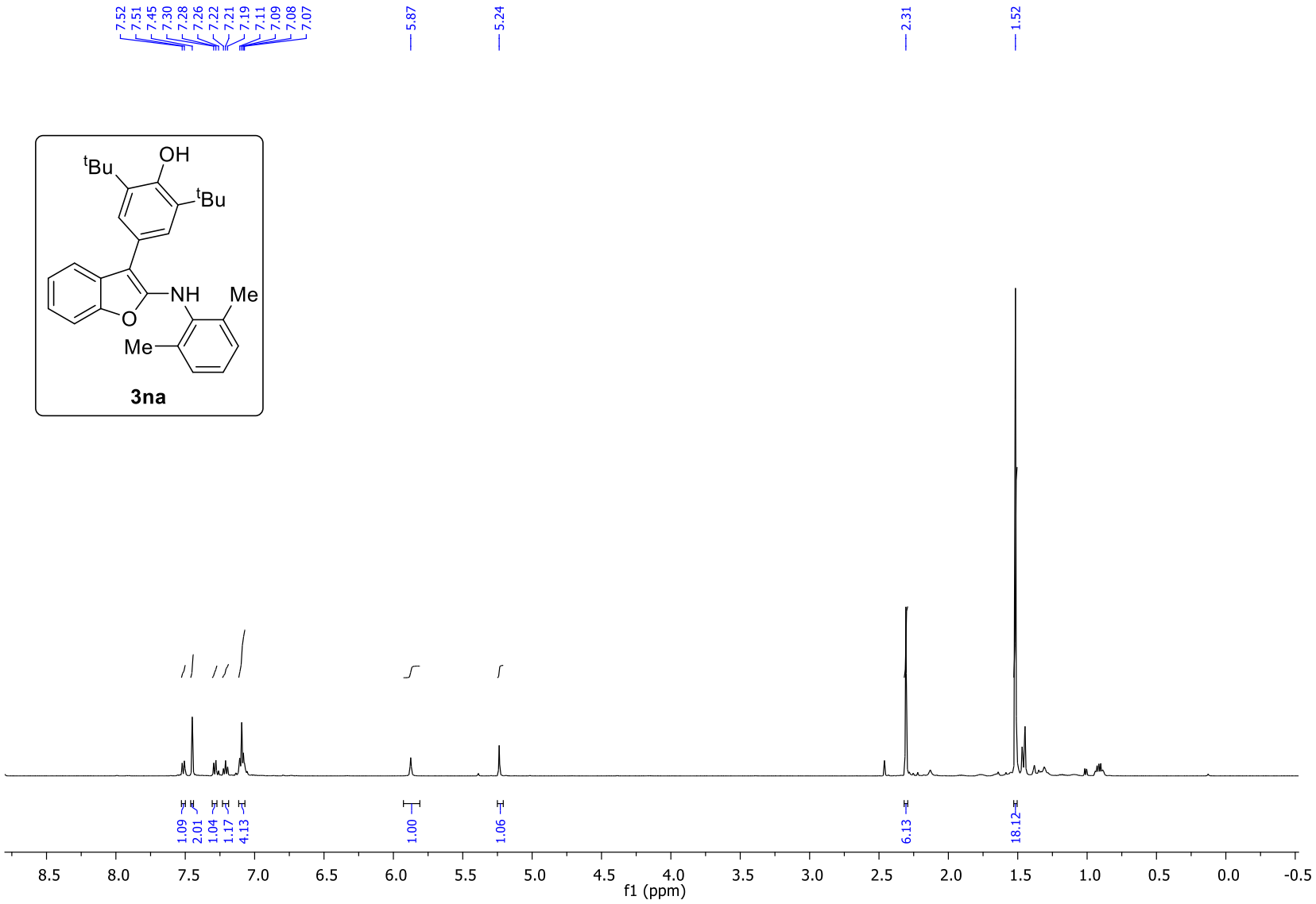
^{1}H NMR of compound **3ma** in $CDCl_3$



^{13}C NMR of compound **3ma** in $CDCl_3$



^{1}H NMR of compound **3na** in $CDCl_3$



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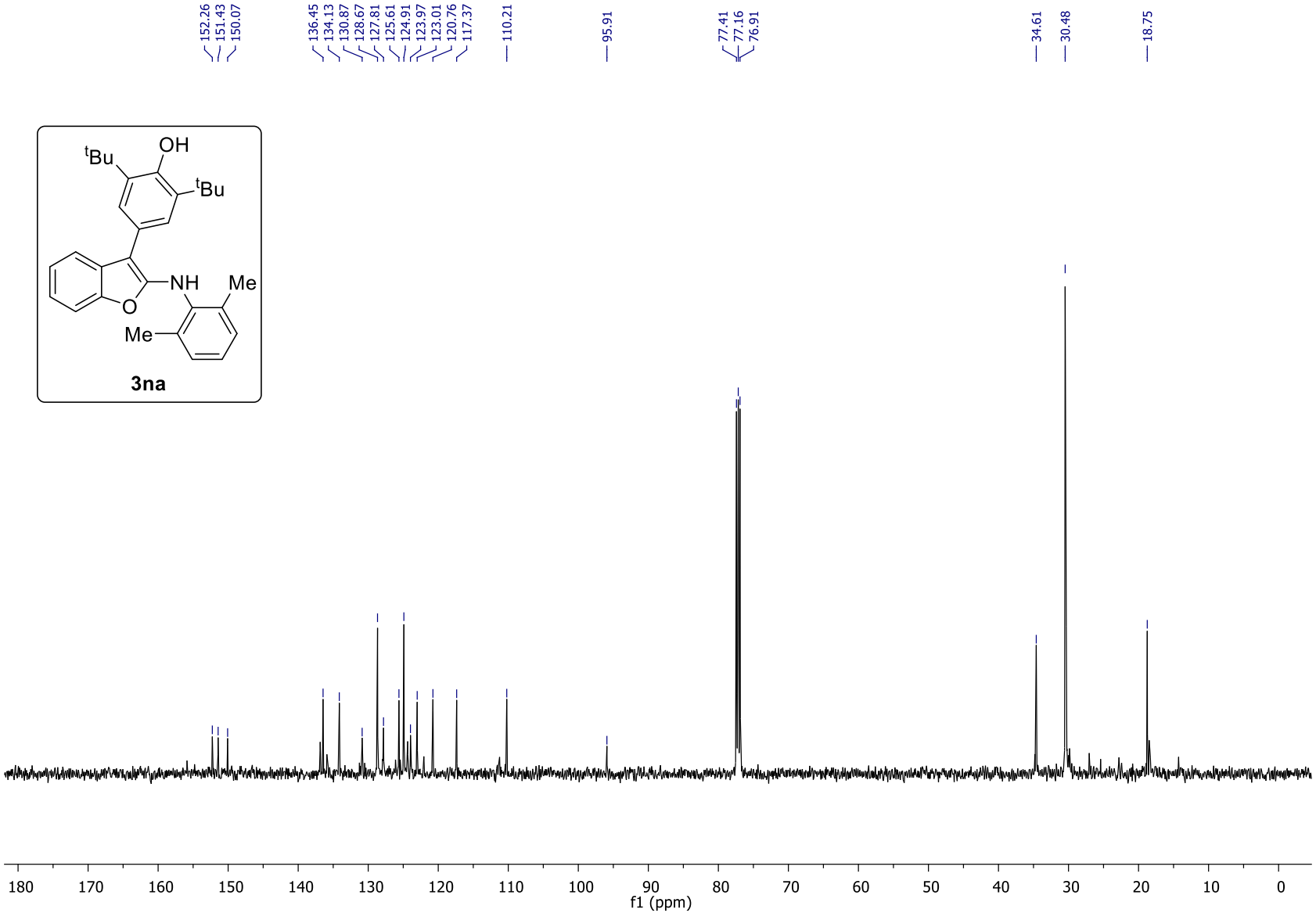
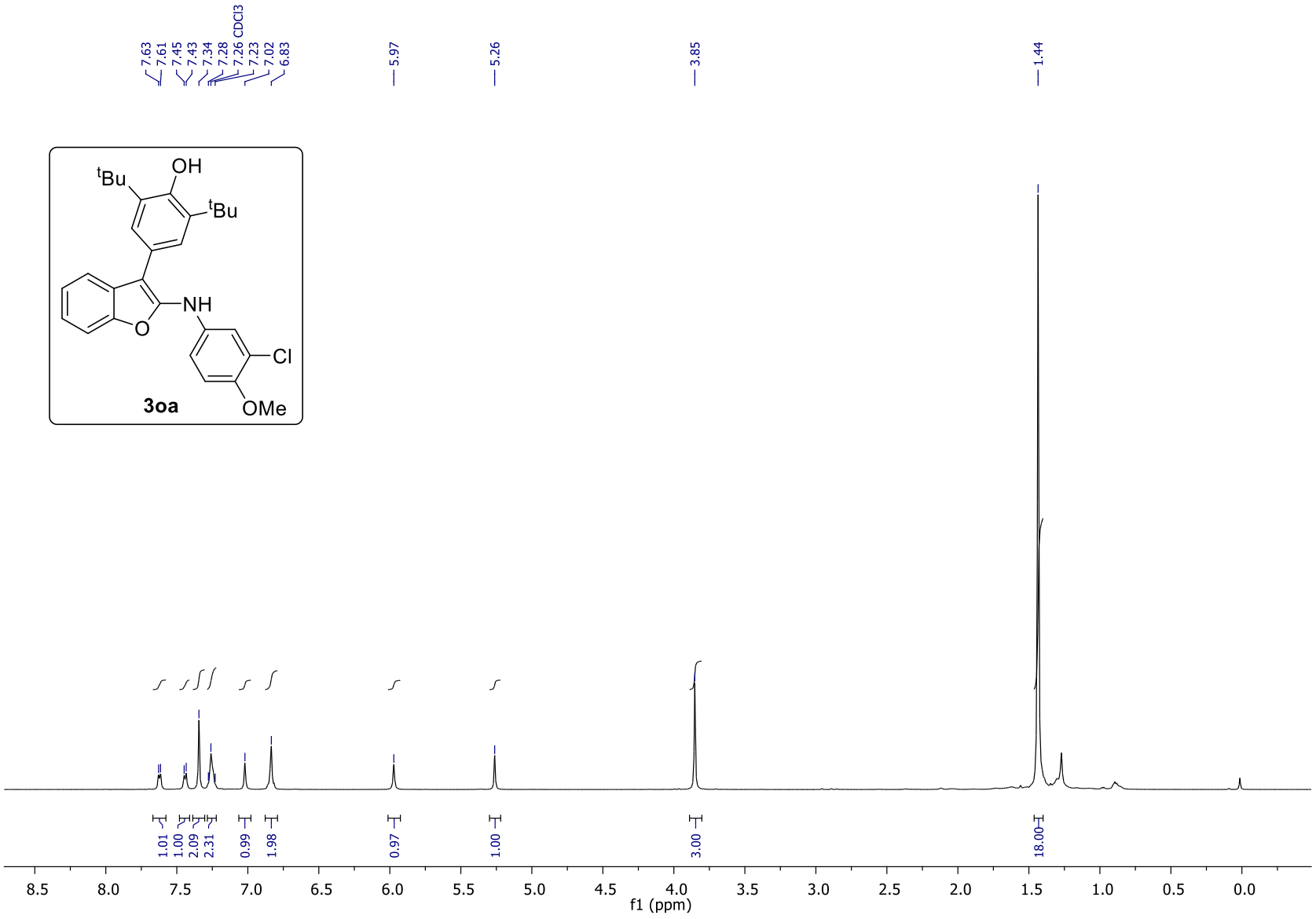
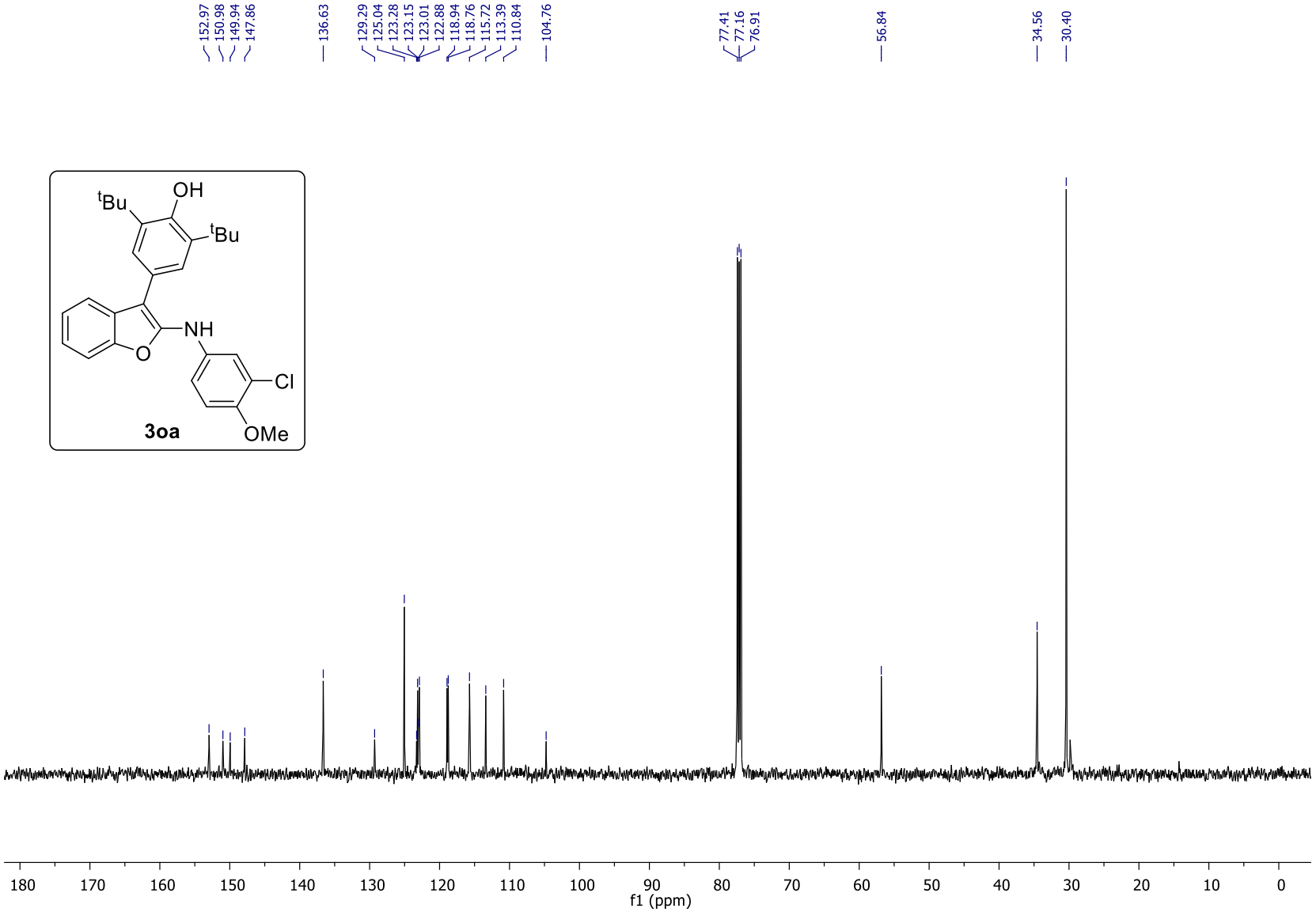


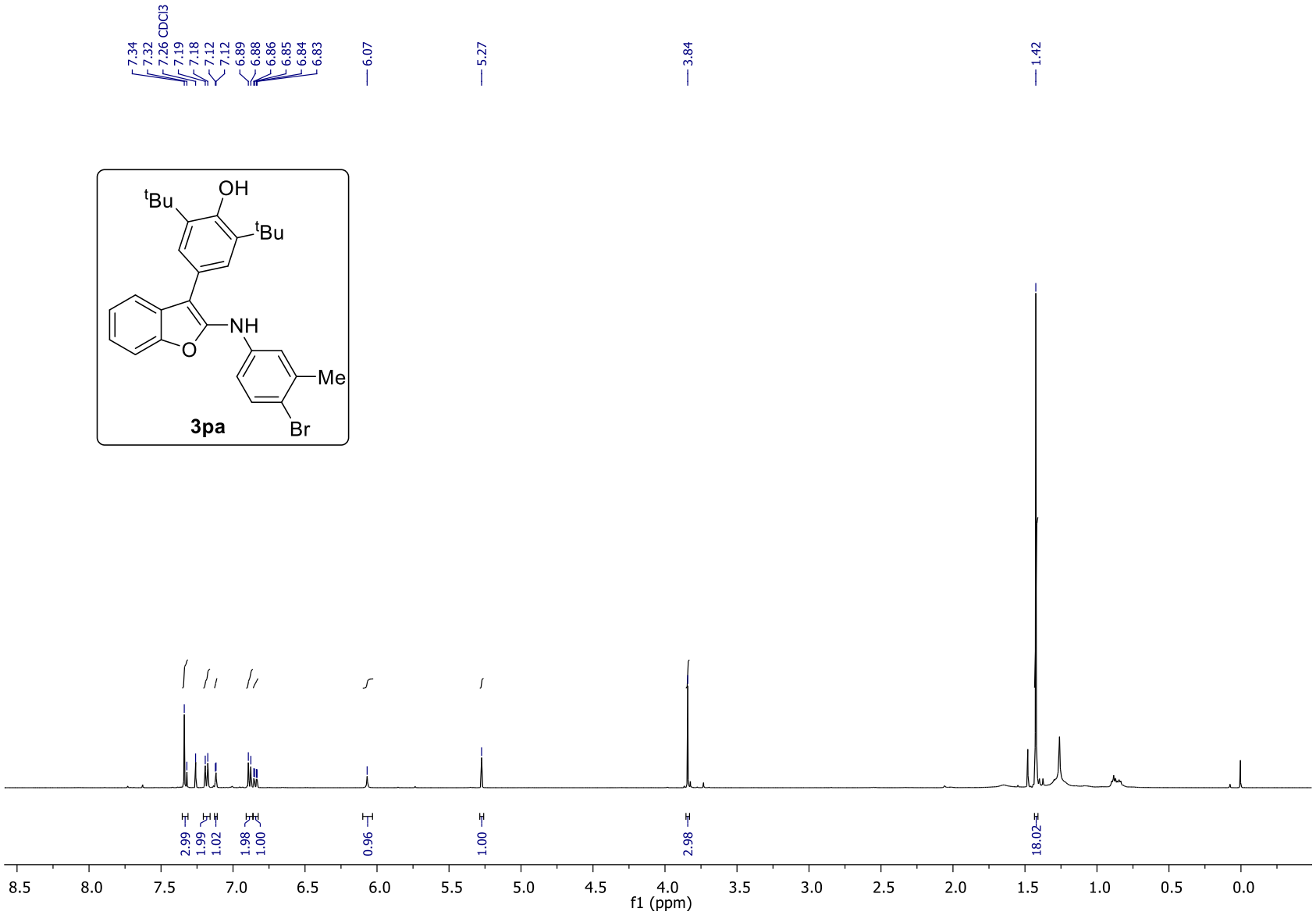
^{1}H NMR of compound **3oa** in $CDCl_3$



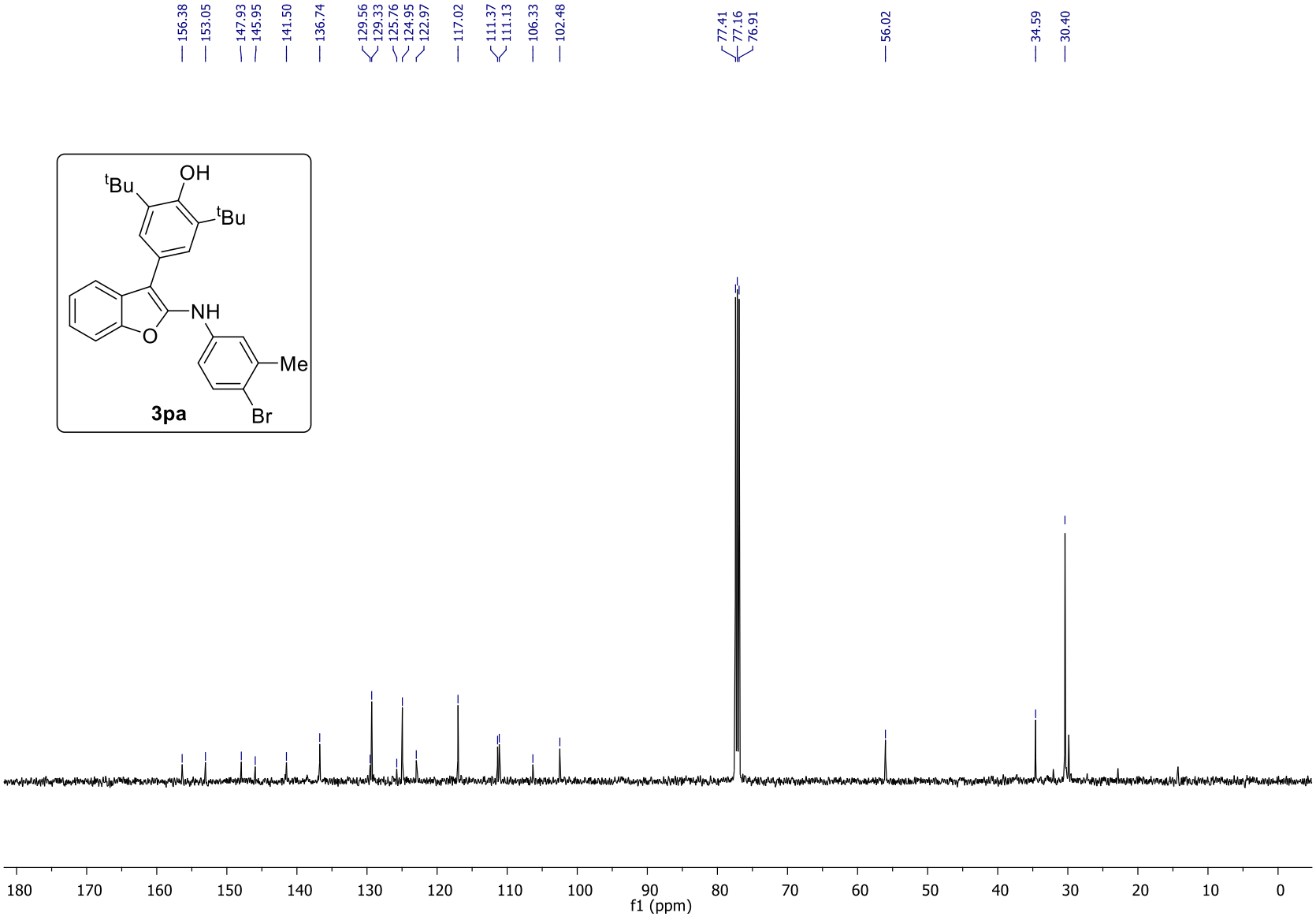
^{13}C NMR of compound **3oa** in $CDCl_3$



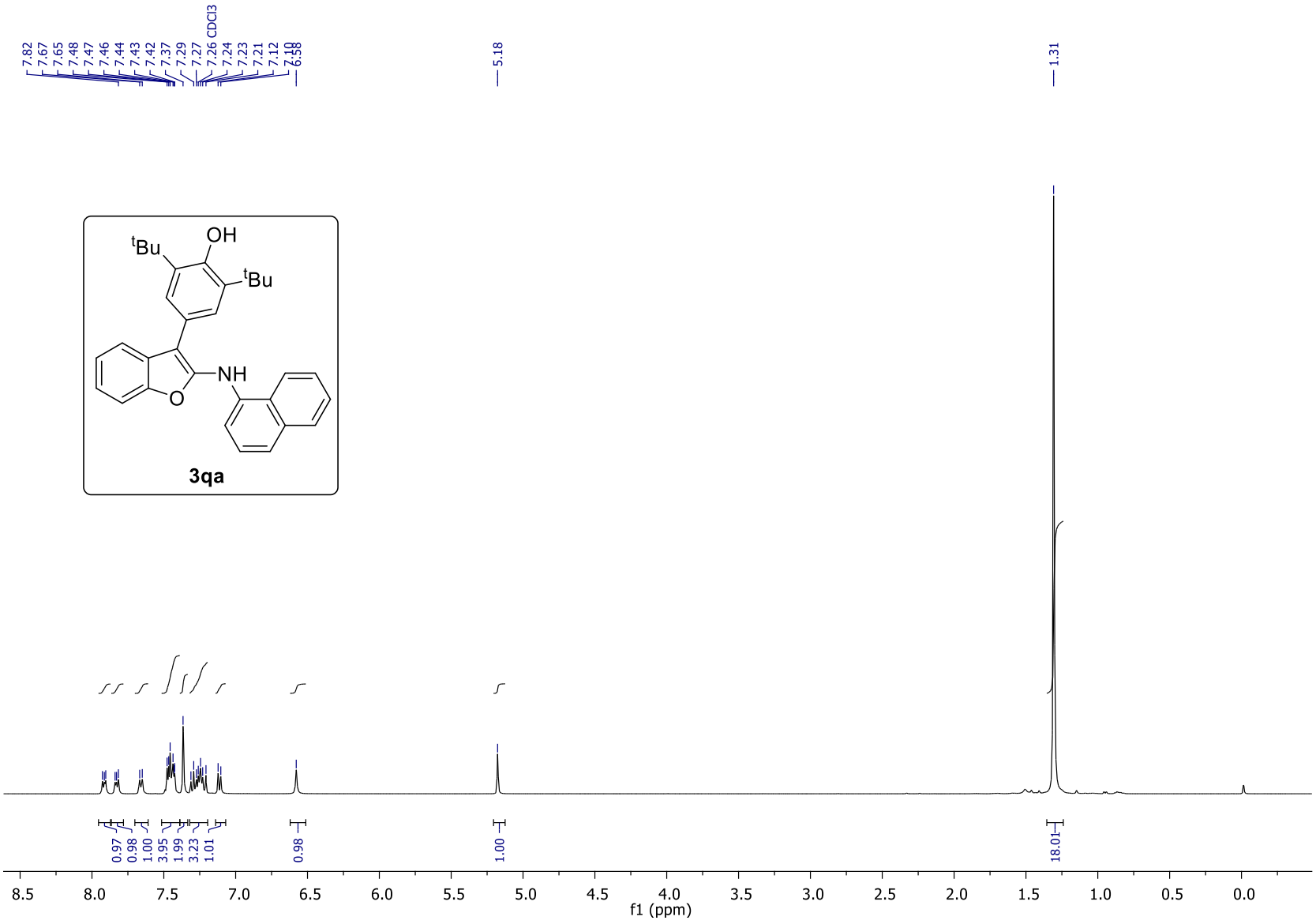
^{1}H NMR of compound **3pa** in $CDCl_3$



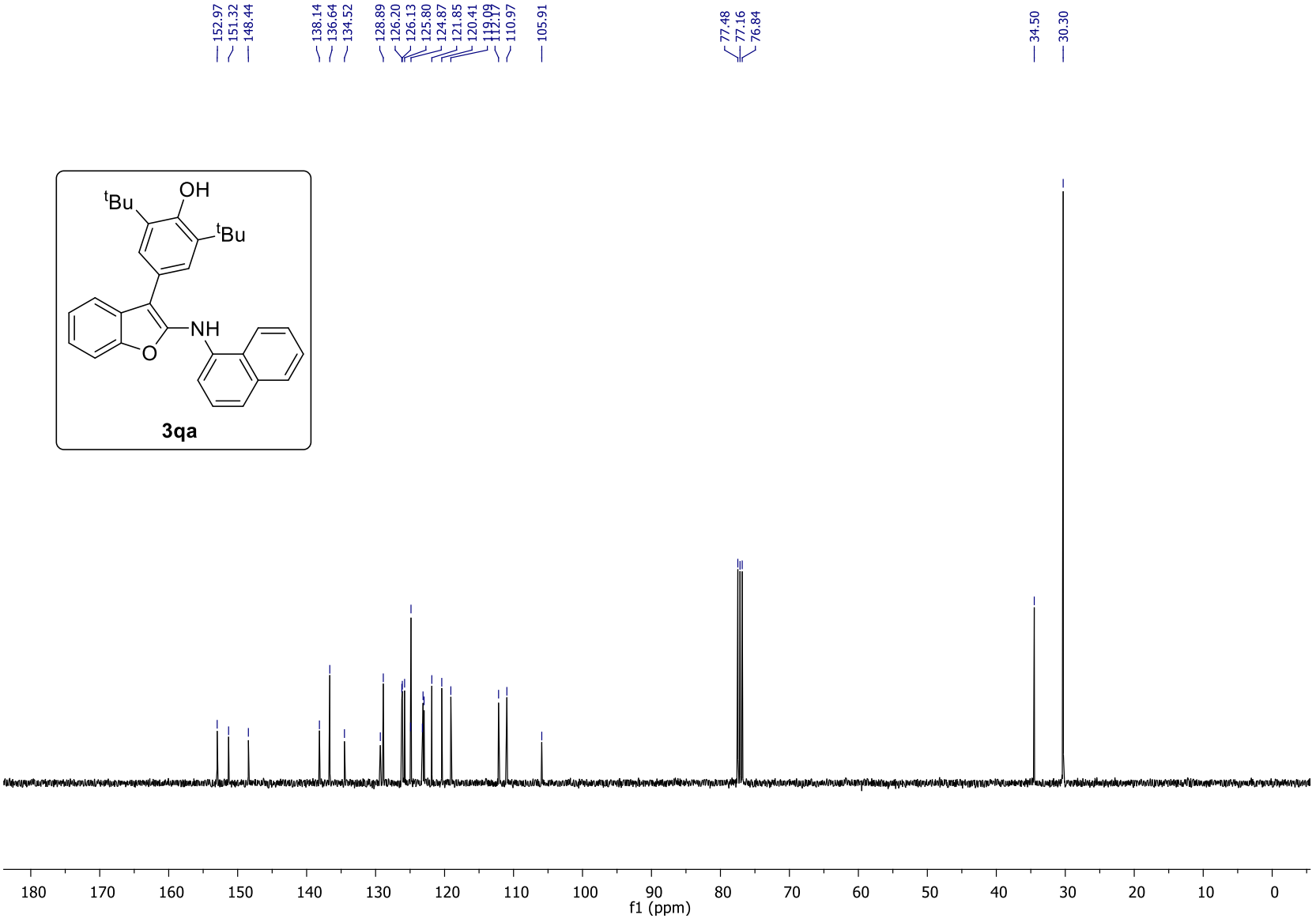
^{13}C NMR of compound **3pa** in $CDCl_3$



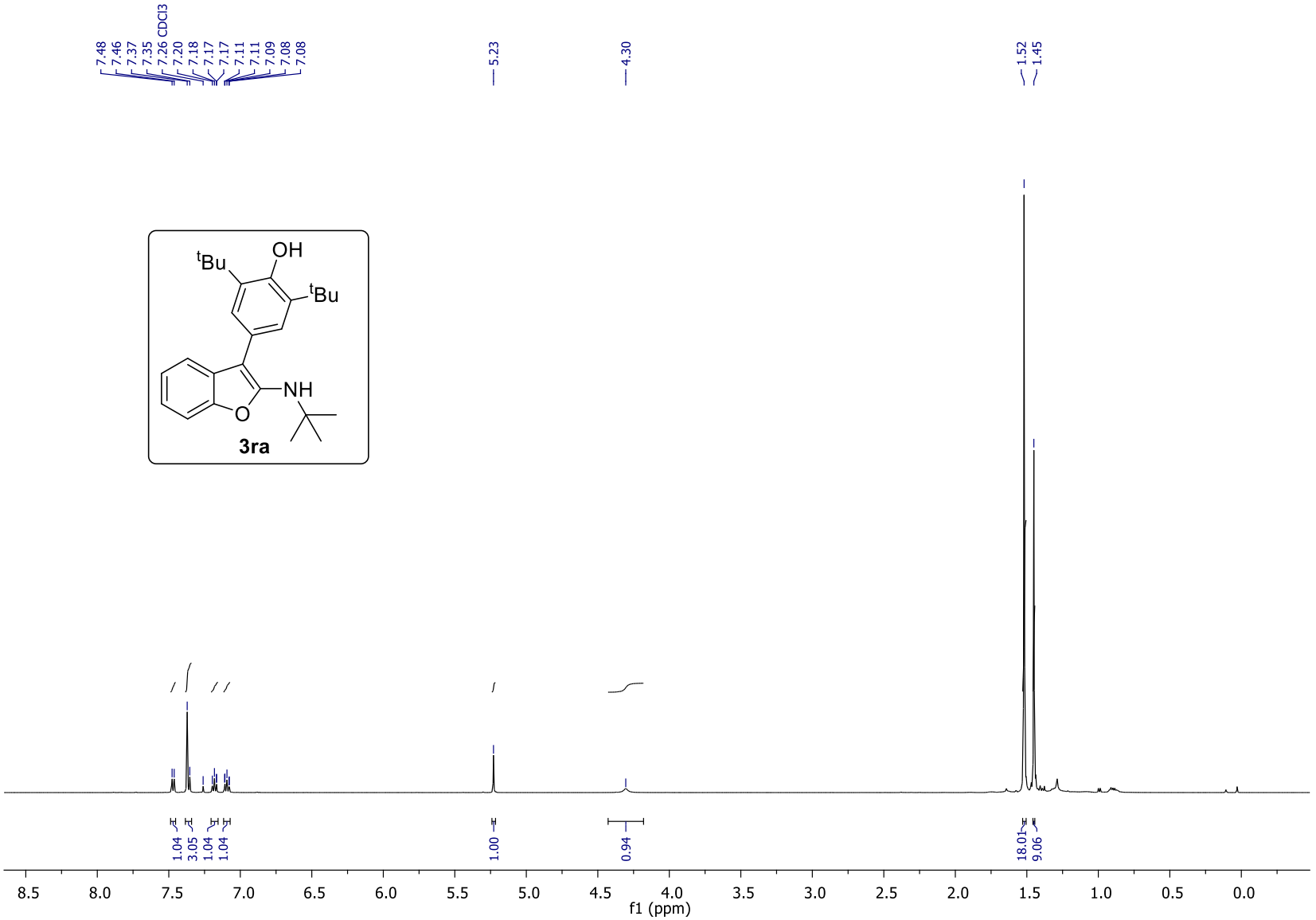
^{1}H NMR of compound **3qa** in $CDCl_3$



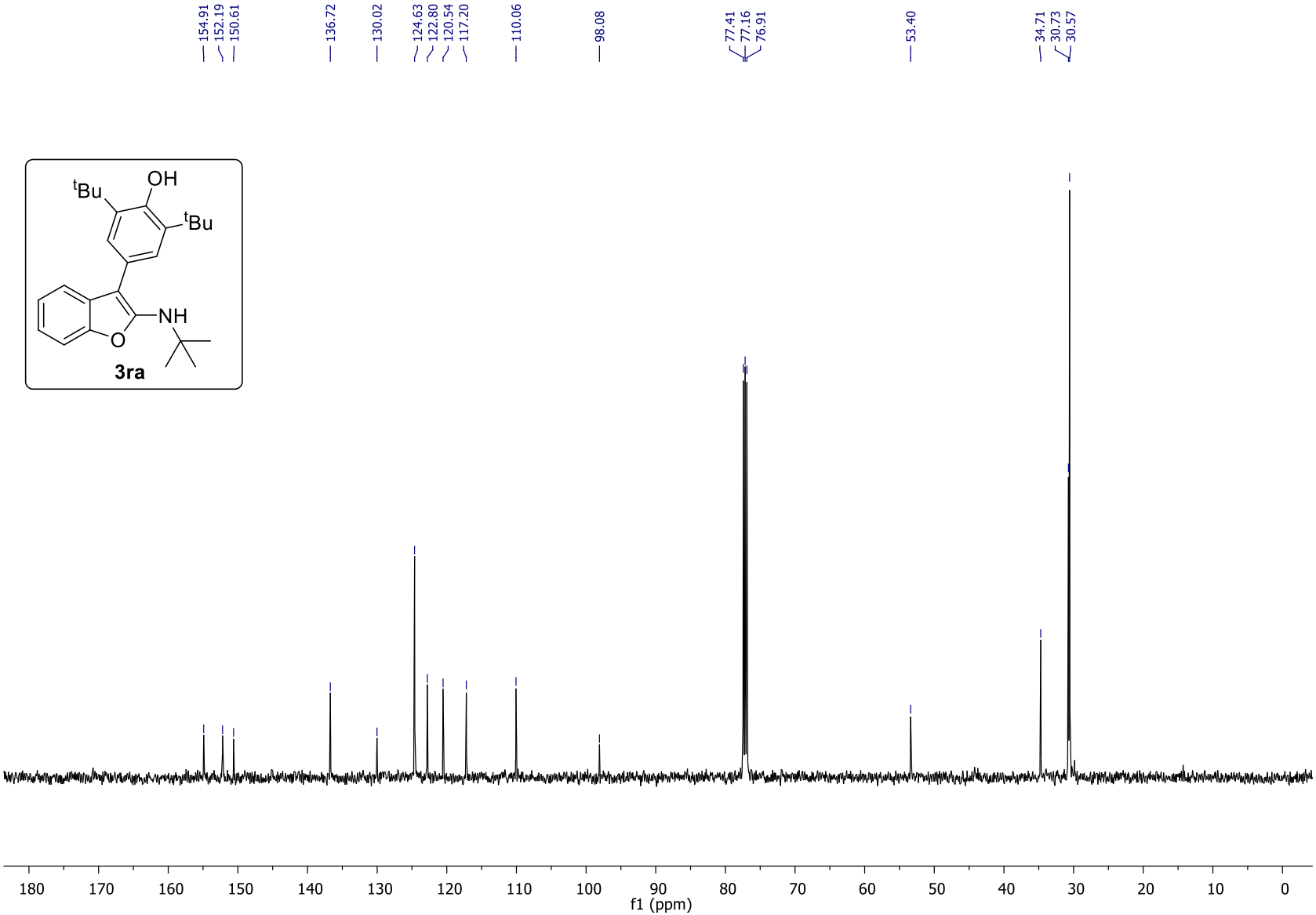
^{13}C NMR of compound **3qa** in $CDCl_3$



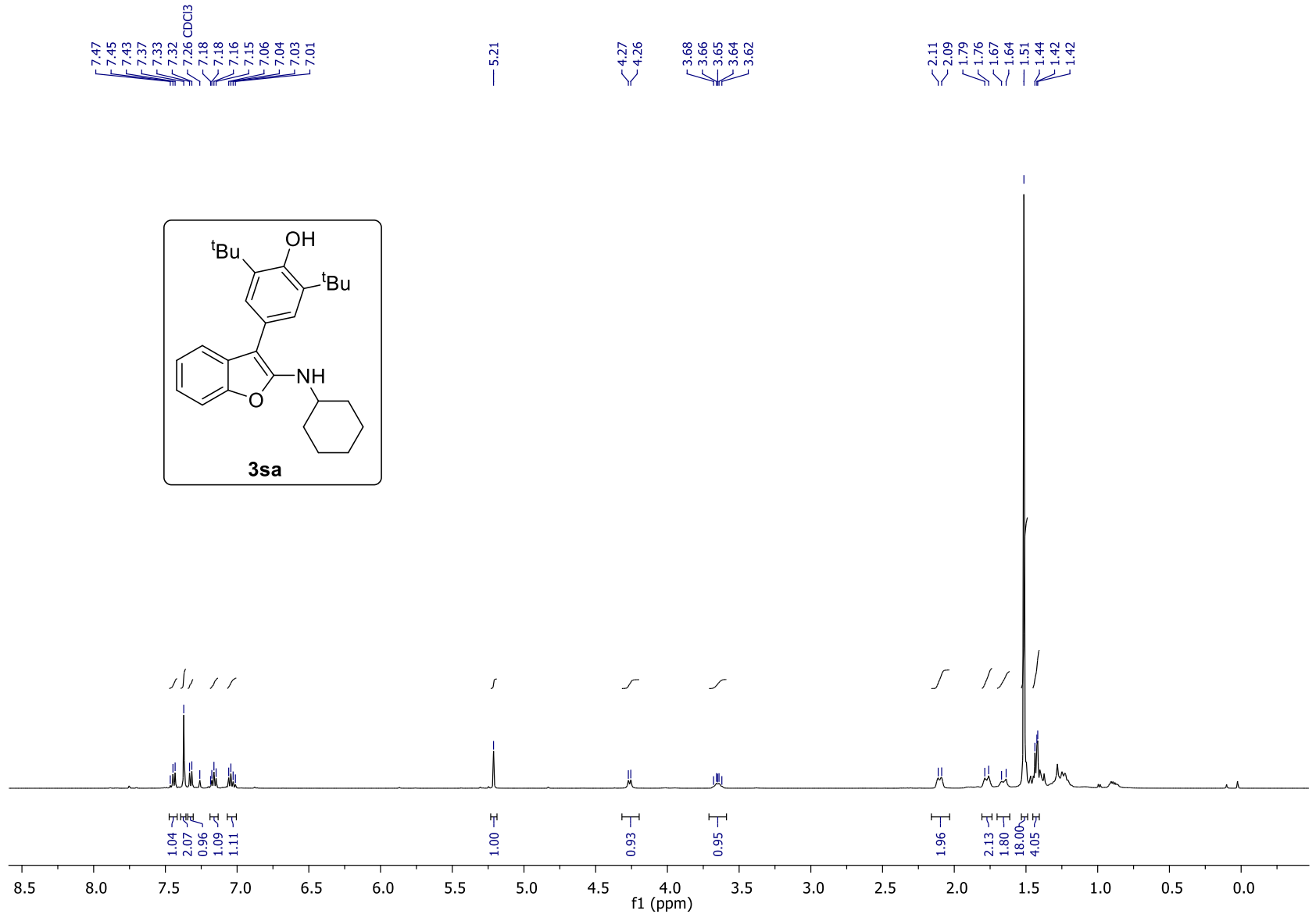
^{1}H NMR of compound **3ra** in $CDCl_3$



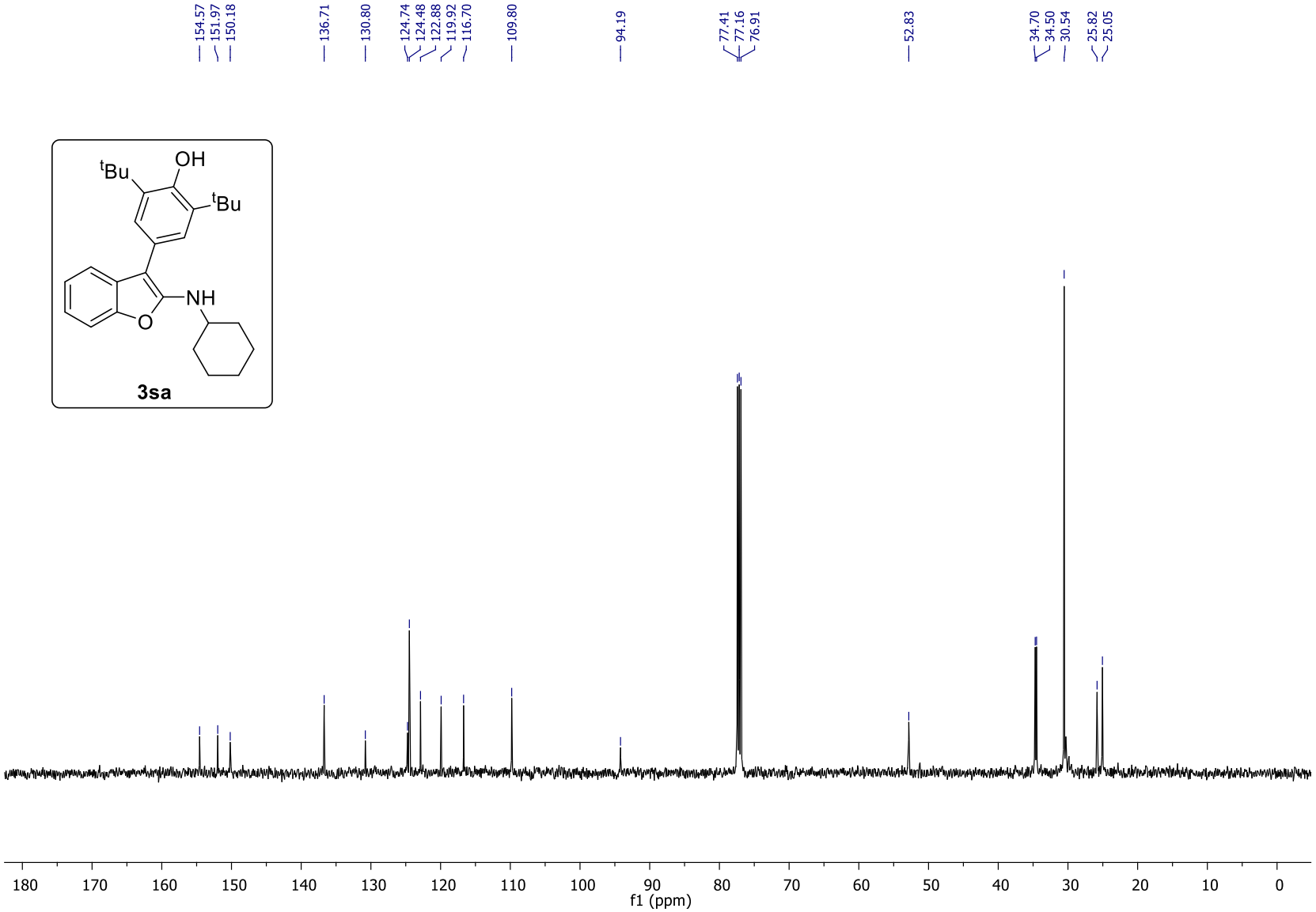
^{13}C NMR of compound **3ra** in $CDCl_3$



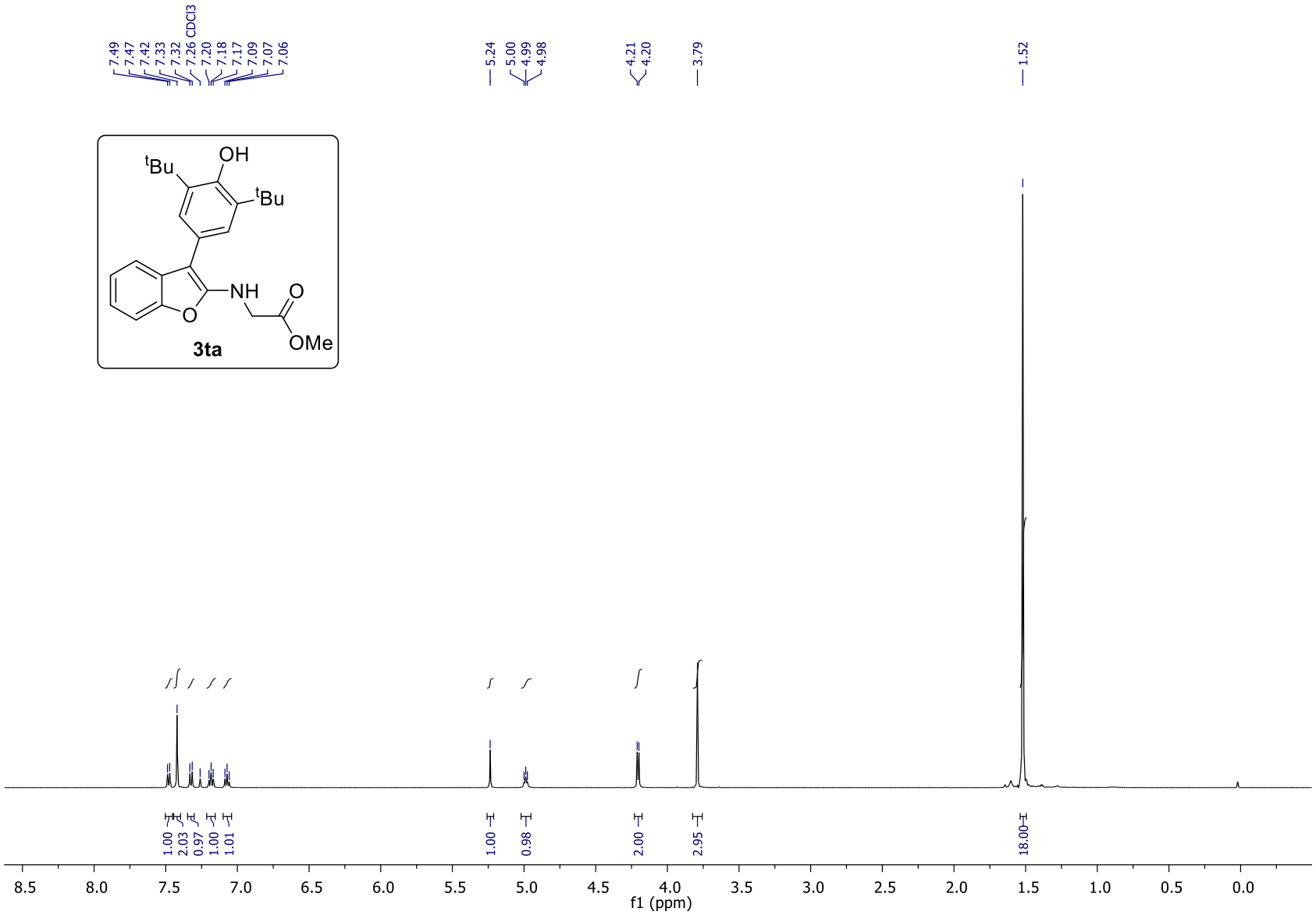
^{1}H NMR of compound **3sa** in $CDCl_3$



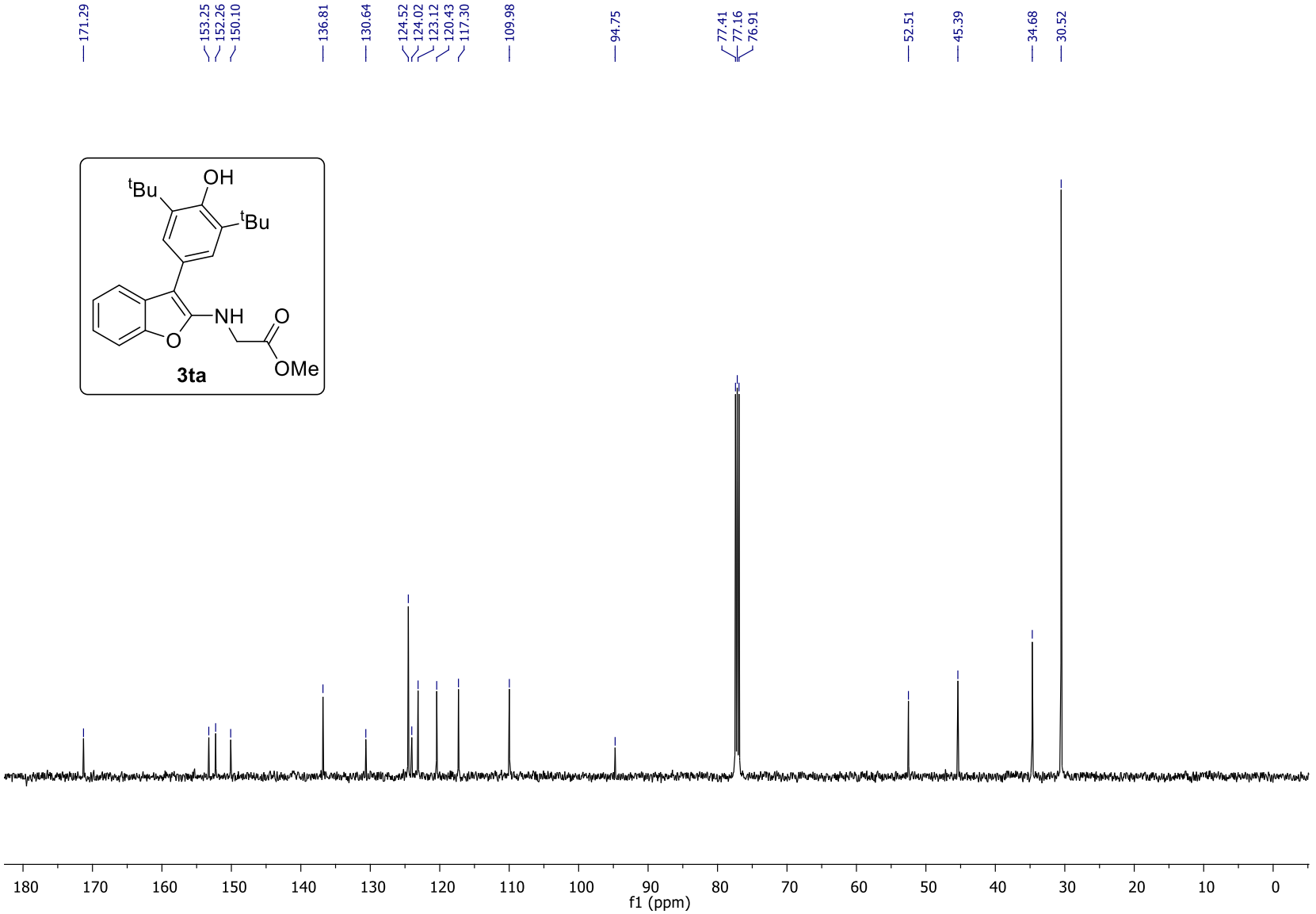
^{13}C NMR of compound **3sa** in $CDCl_3$



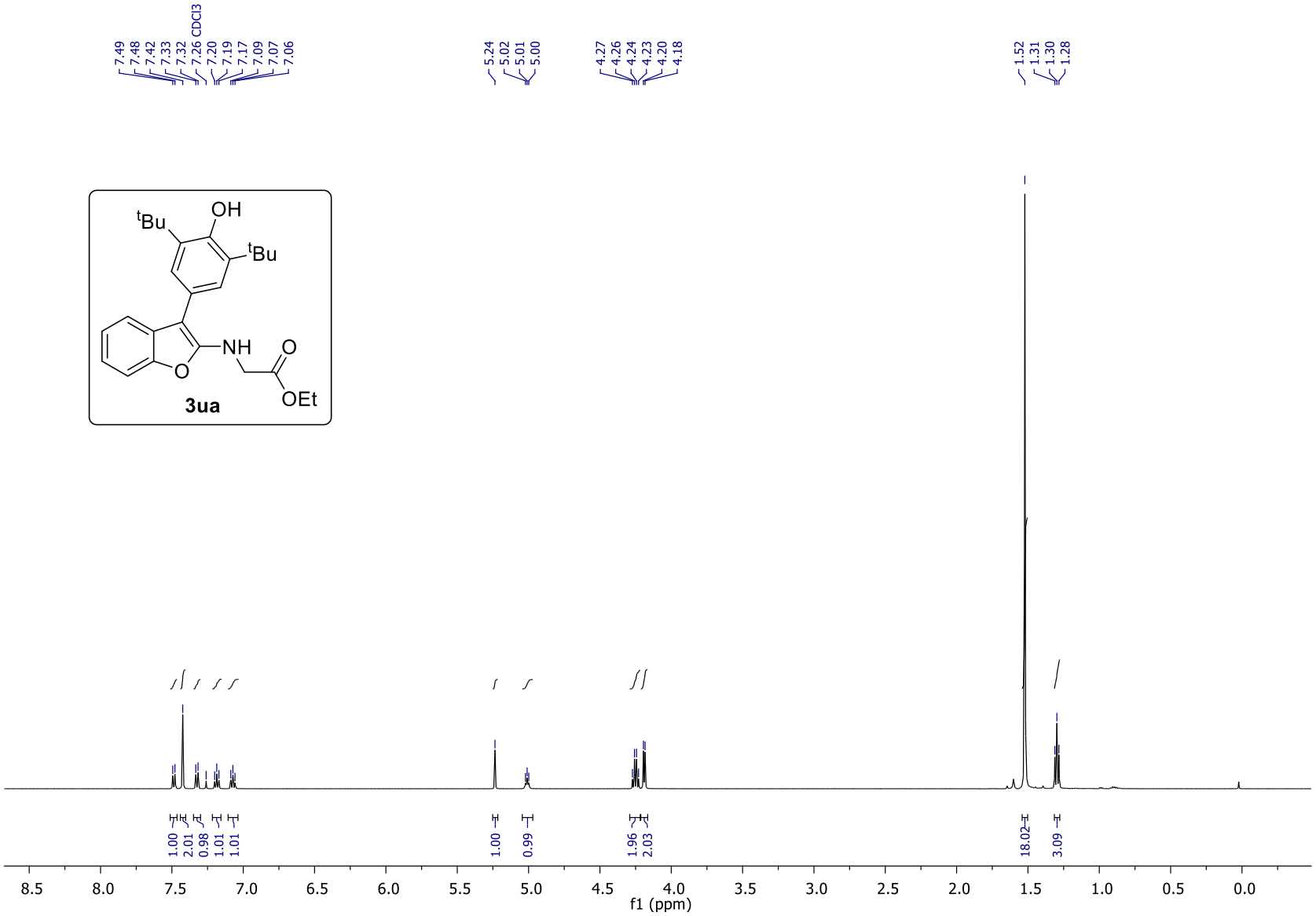
^{1}H NMR of compound **3ta** in $CDCl_3$



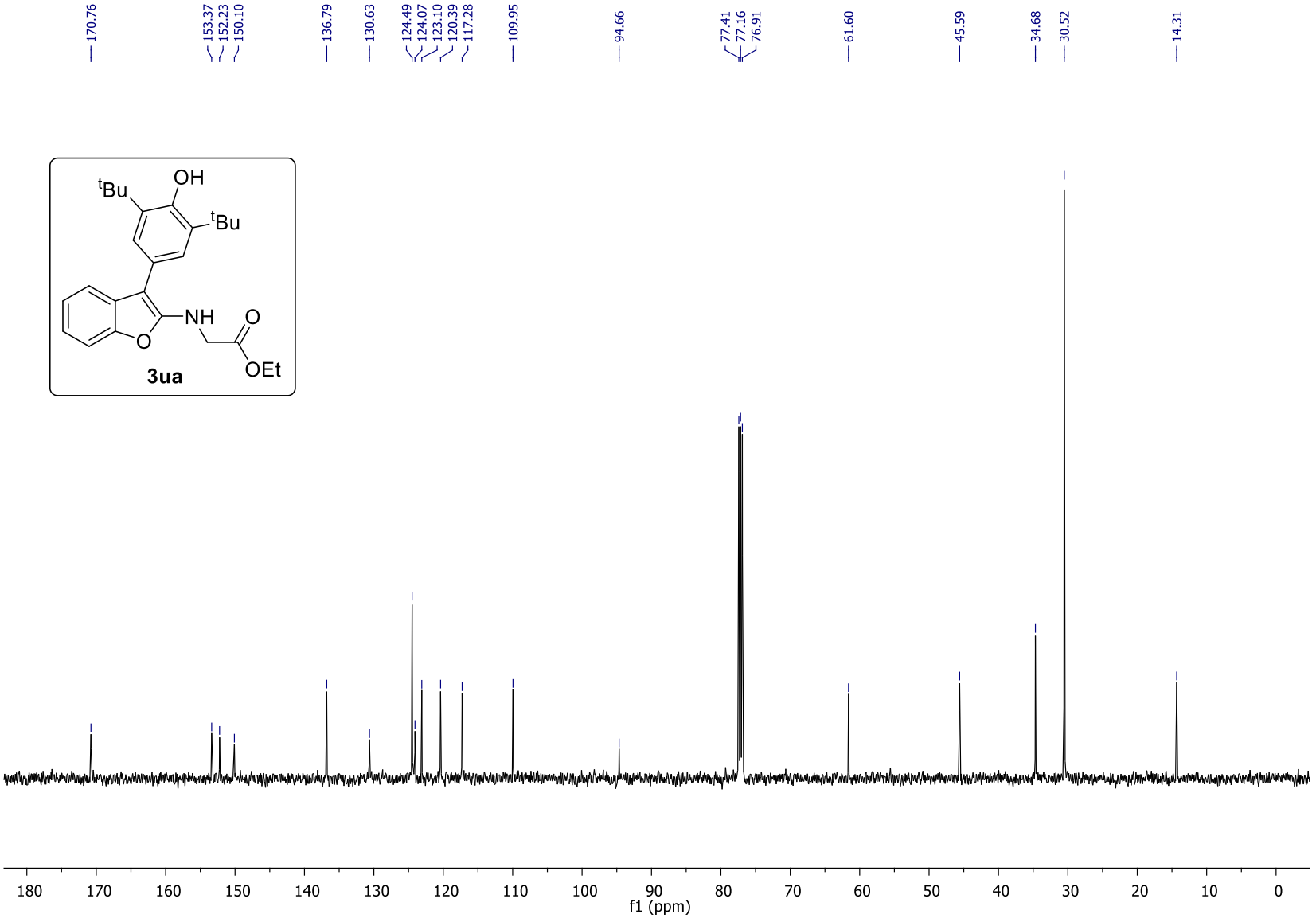
^{13}C NMR of compound **3ta** in $CDCl_3$



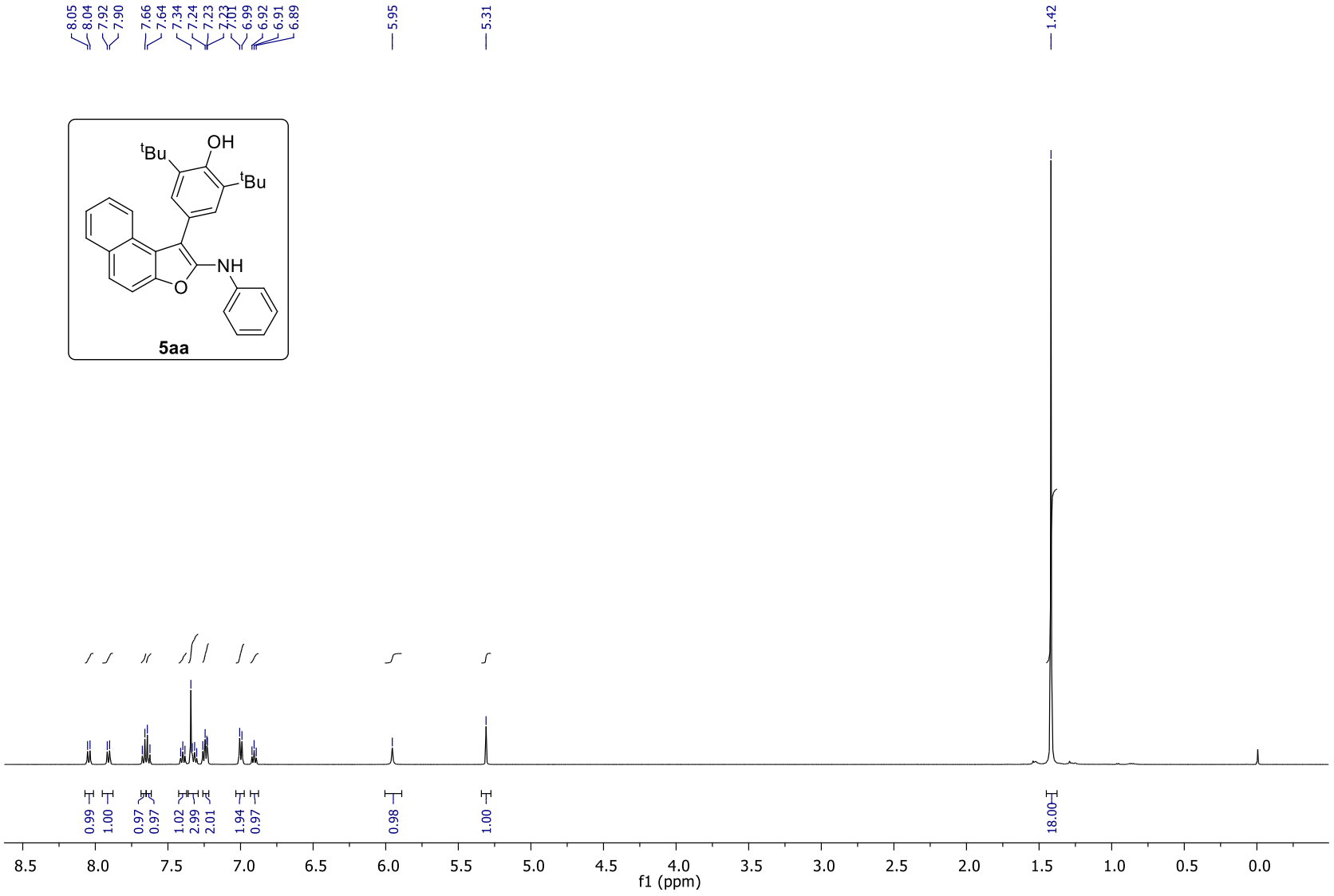
^{1}H NMR of compound **3ua** in $CDCl_3$



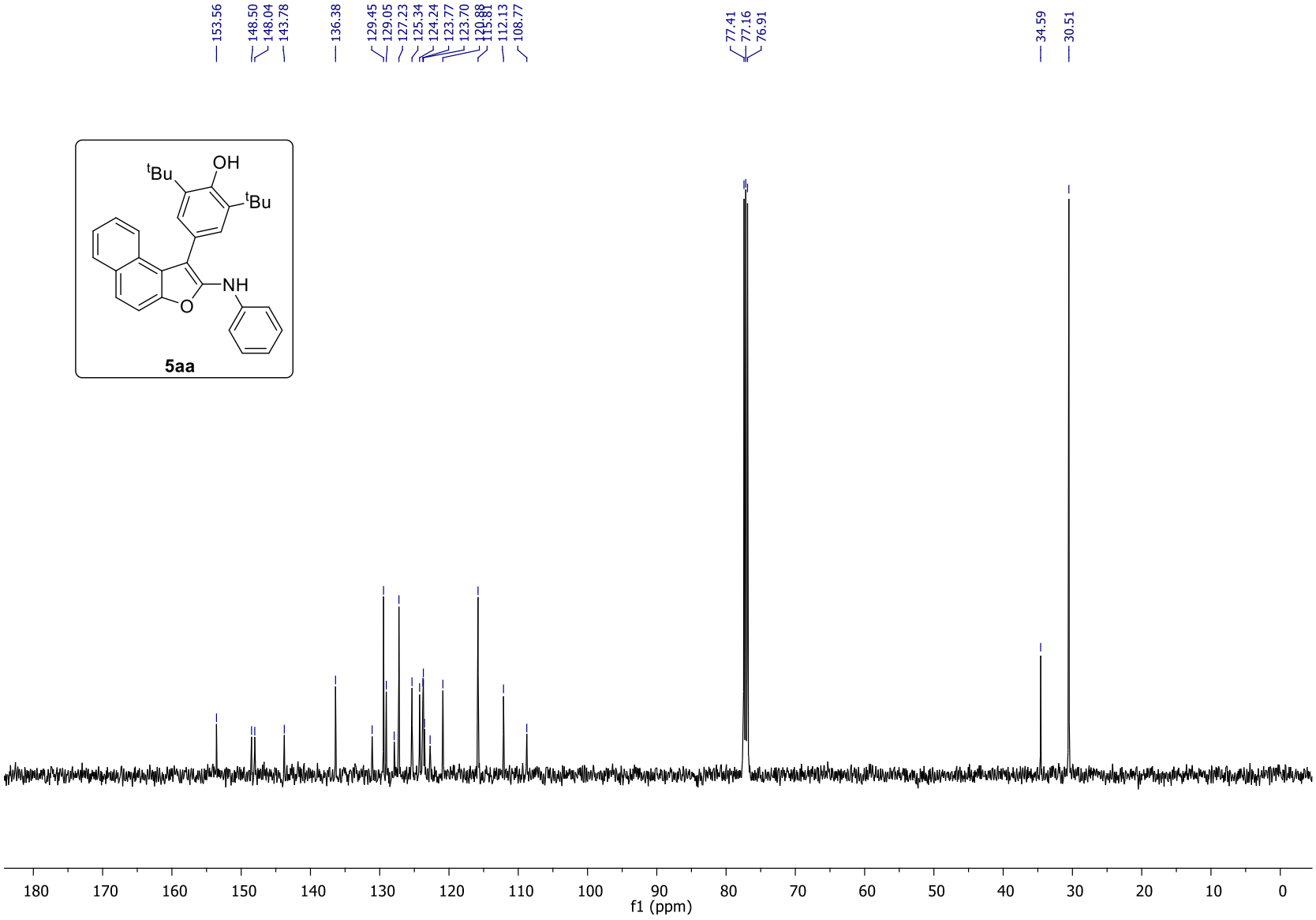
^{13}C NMR of compound **4ua** in $CDCl_3$



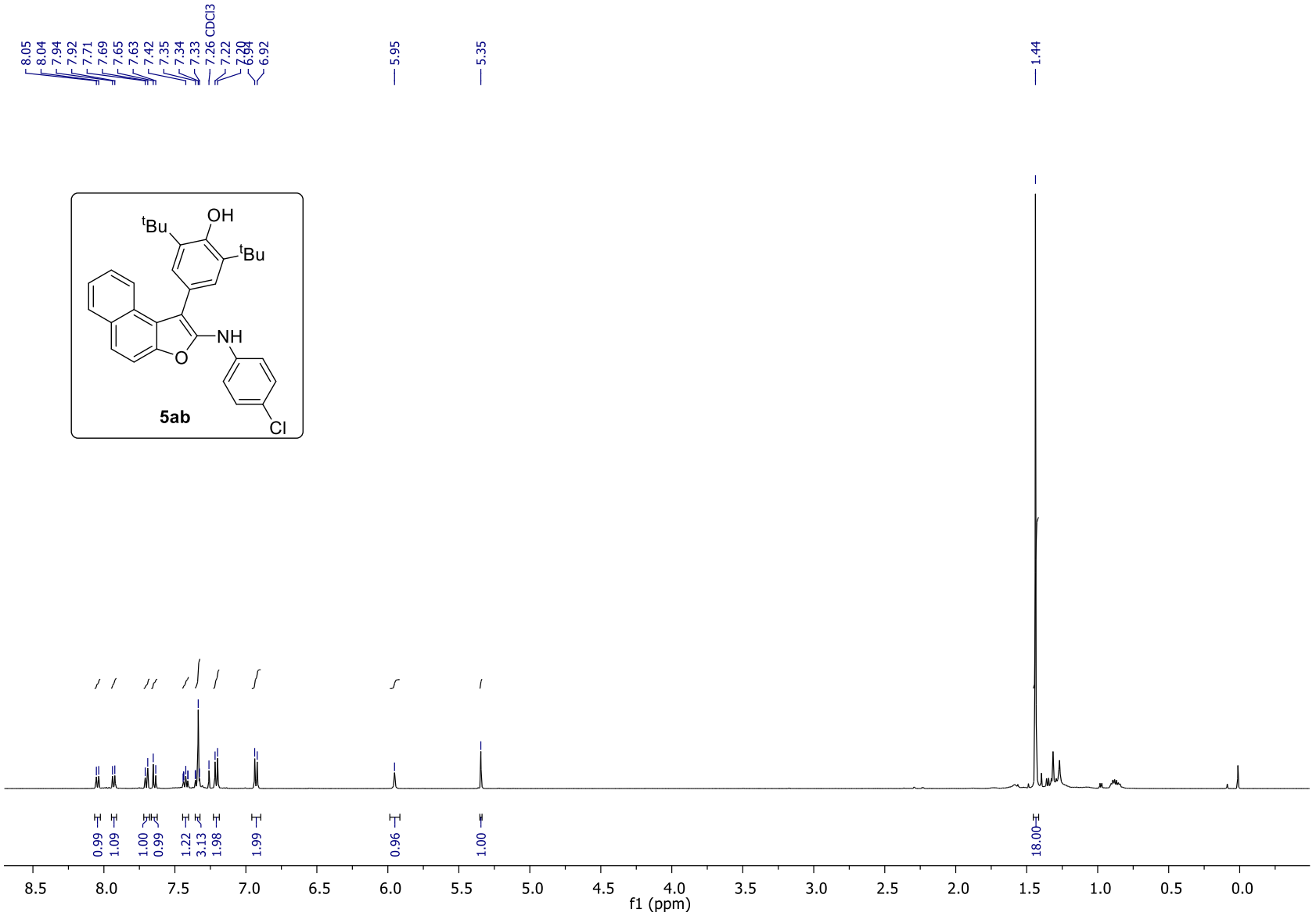
^{1}H NMR of compound **5aa** in $CDCl_3$



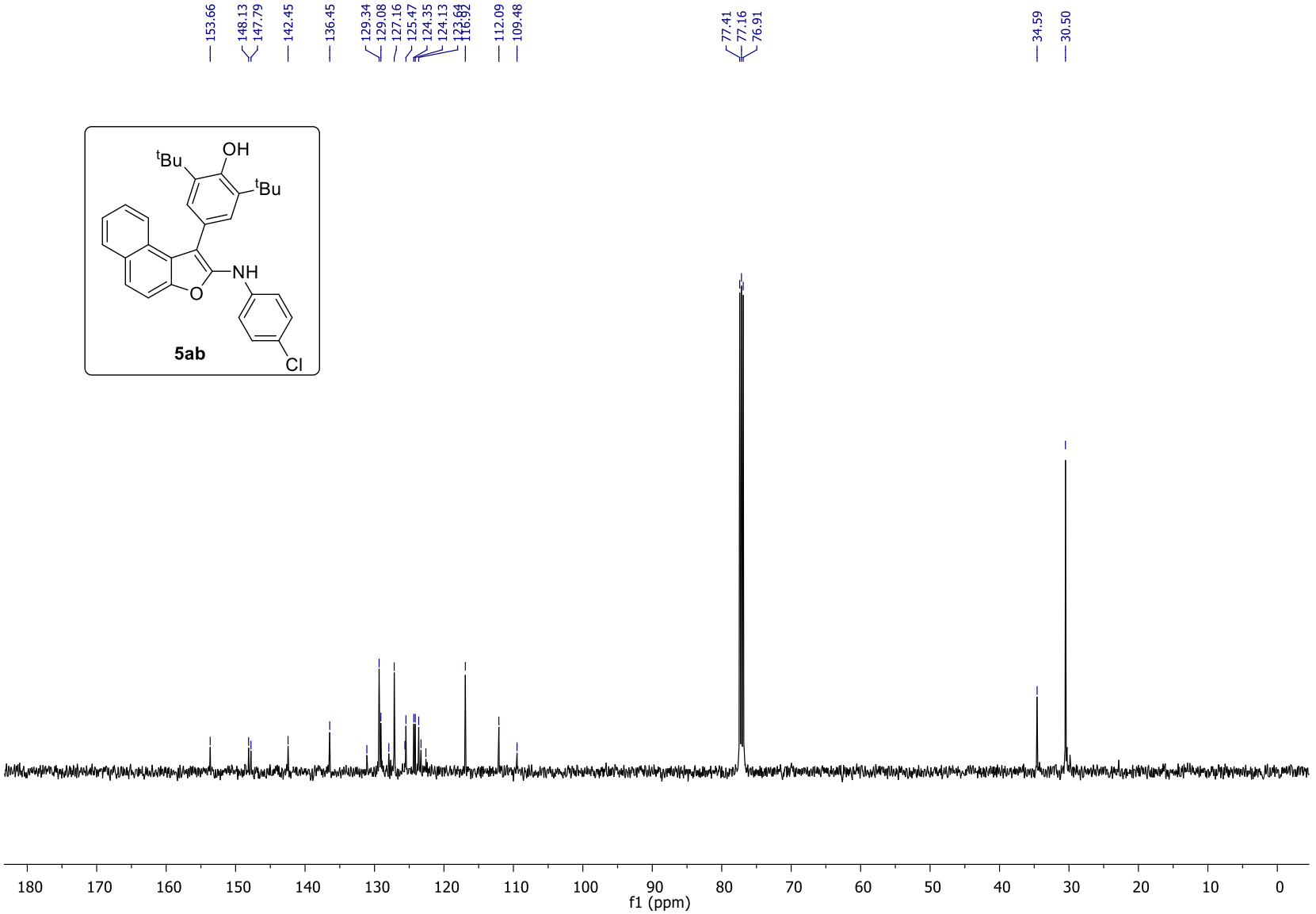
^{13}C NMR of compound **5aa** in $CDCl_3$



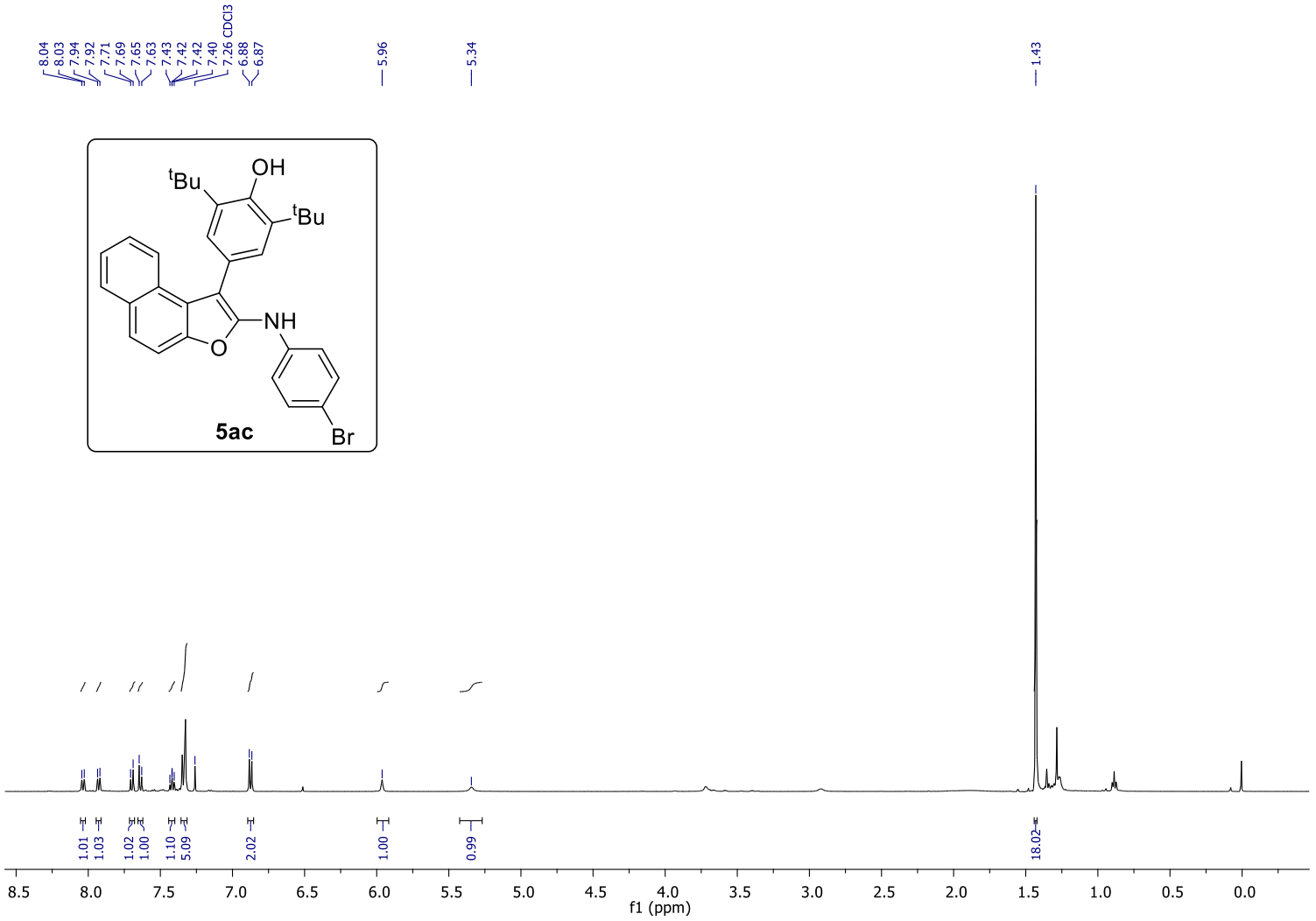
^{1}H NMR of compound **5ab** in $CDCl_3$



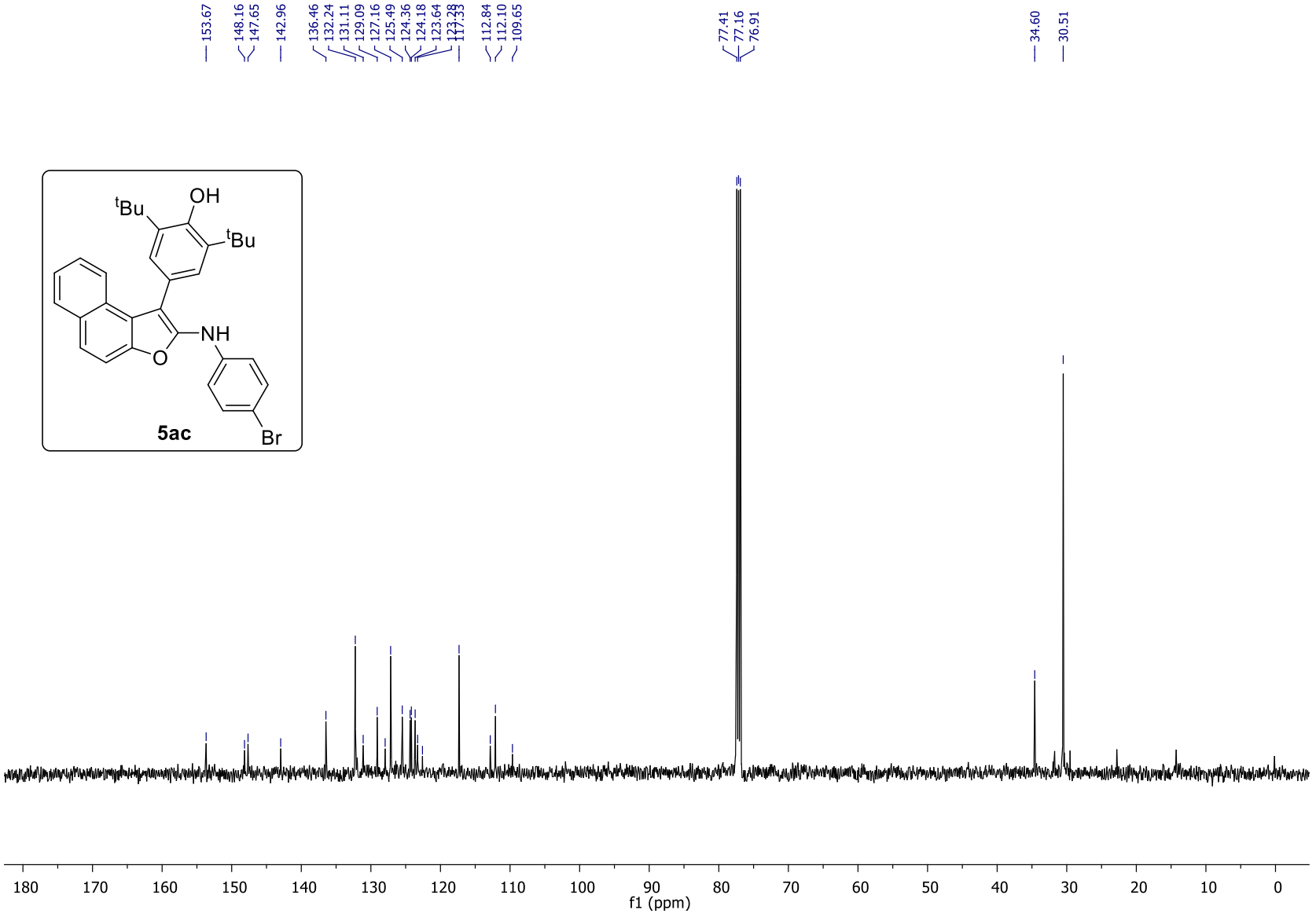
^{13}C NMR of compound **5ab** in $CDCl_3$



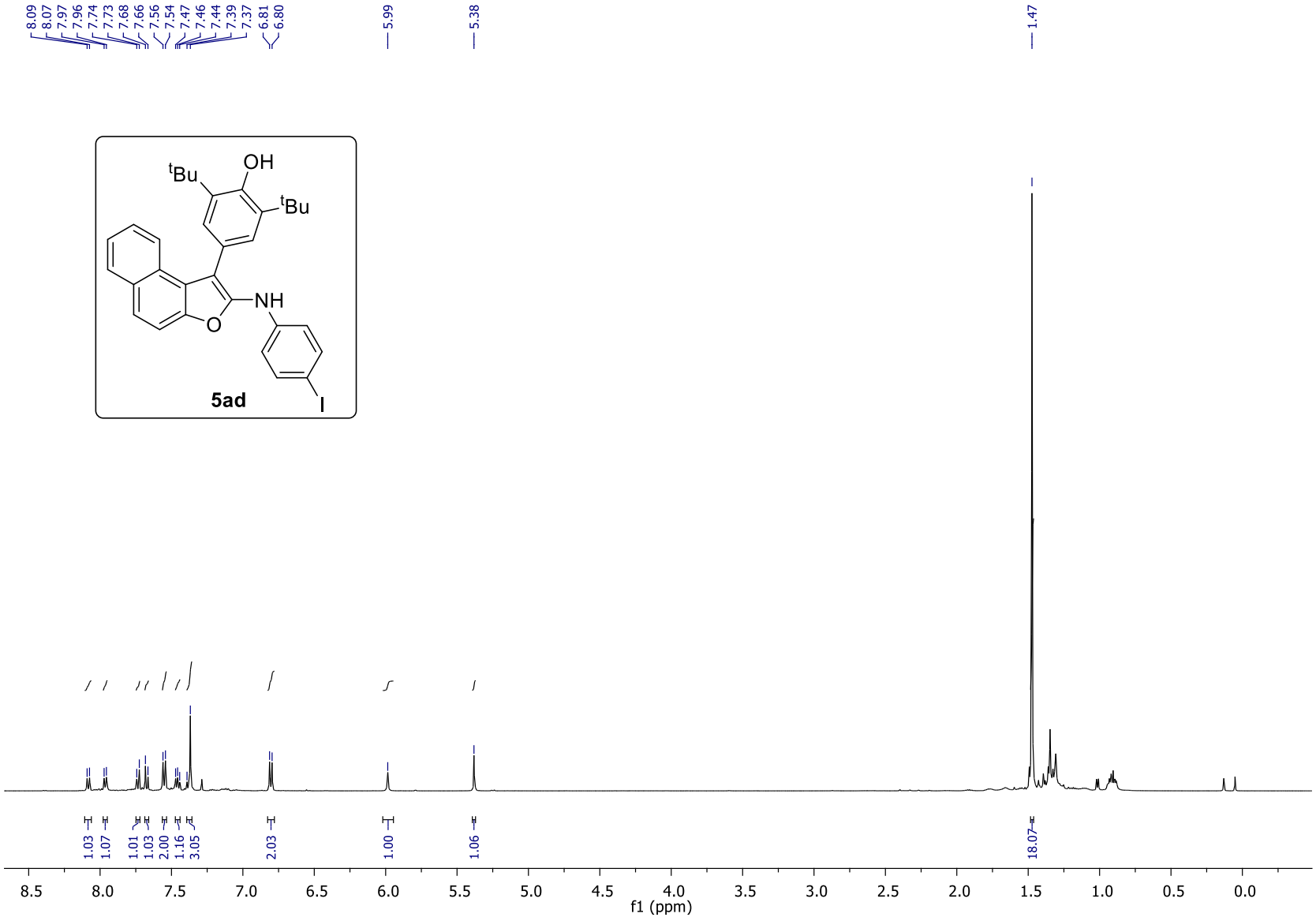
^{1}H NMR of compound **5ac** in $CDCl_3$



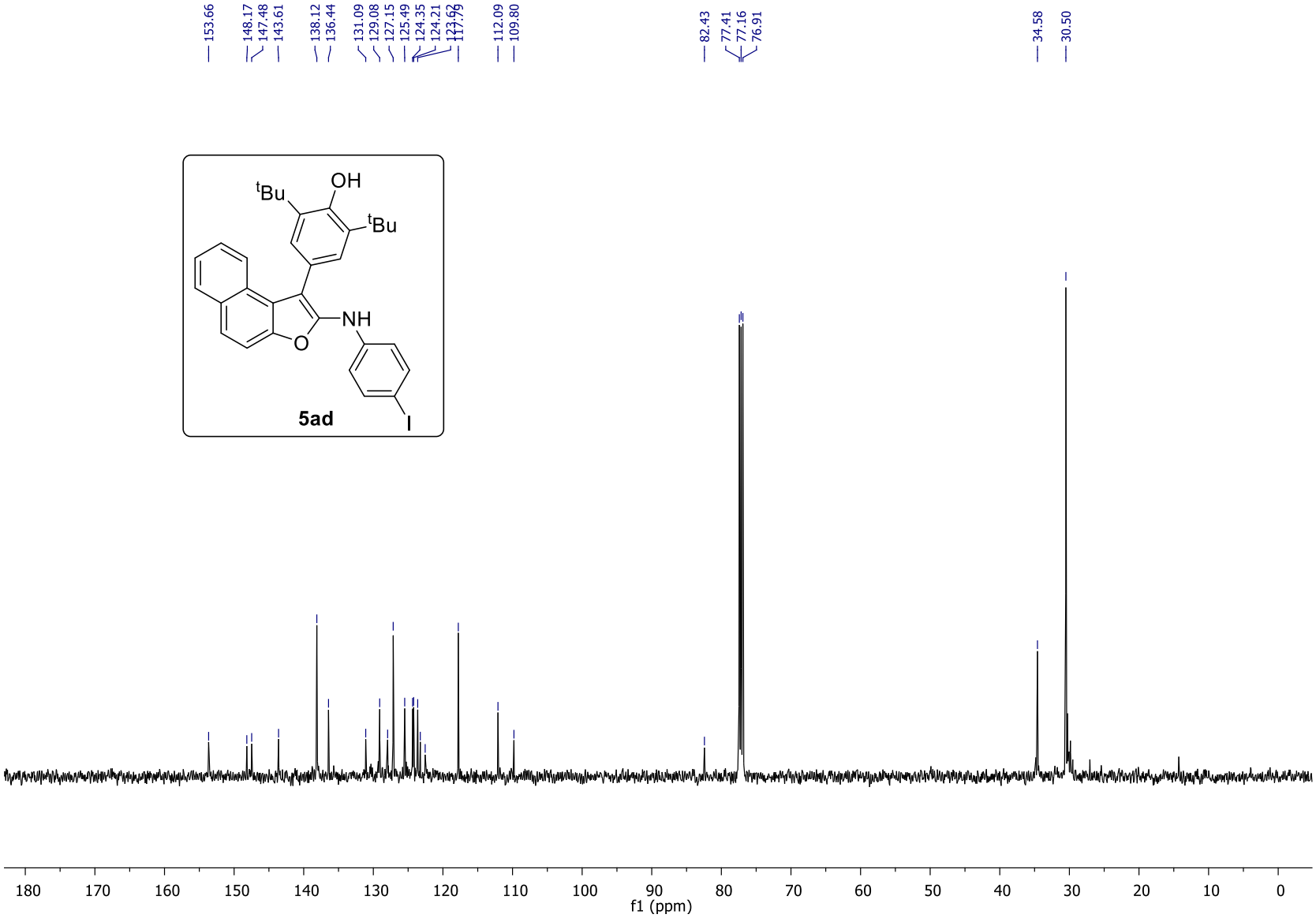
^{13}C NMR of compound **5ac** in $CDCl_3$



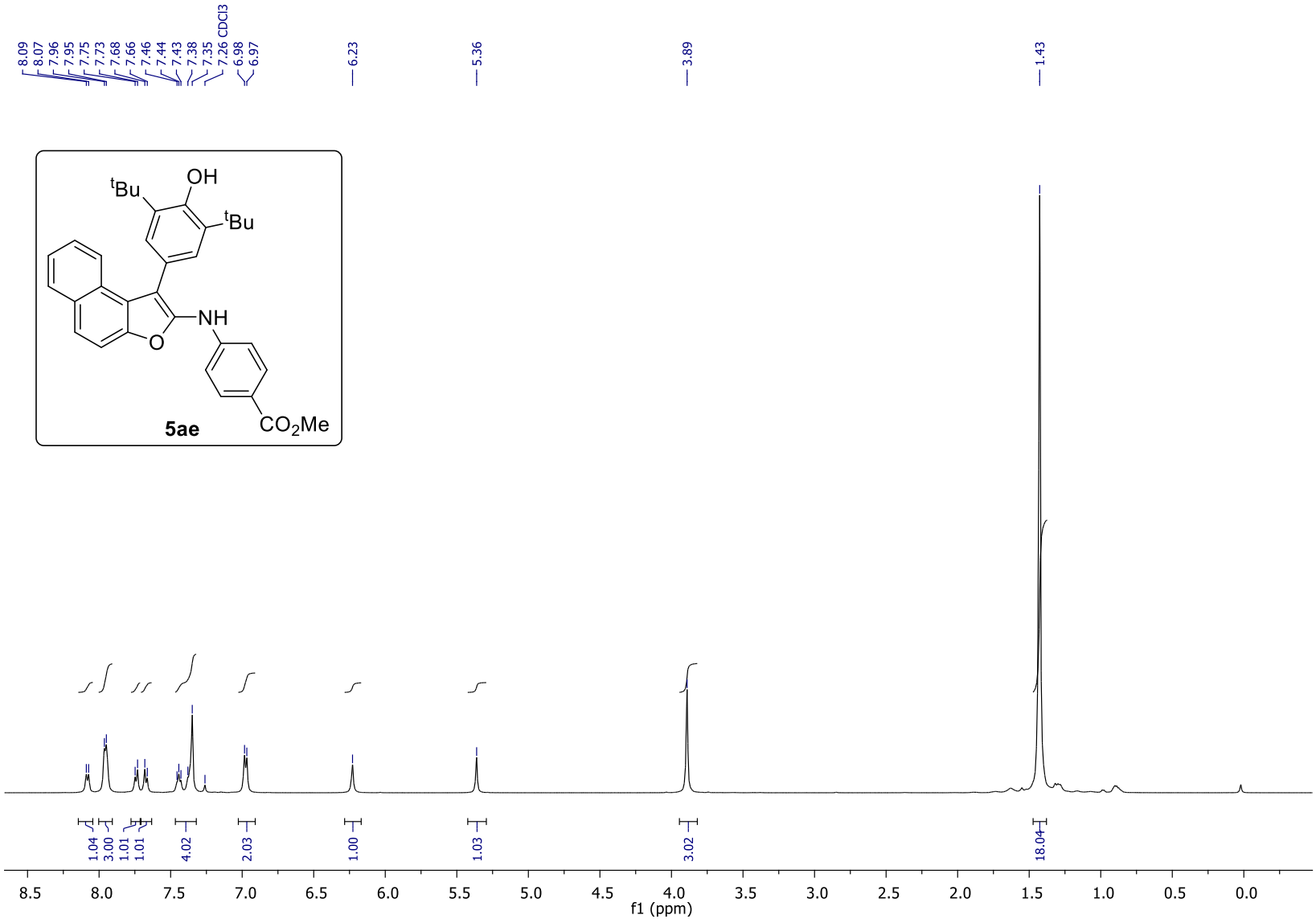
^{1}H NMR of compound **5ad** in $CDCl_3$



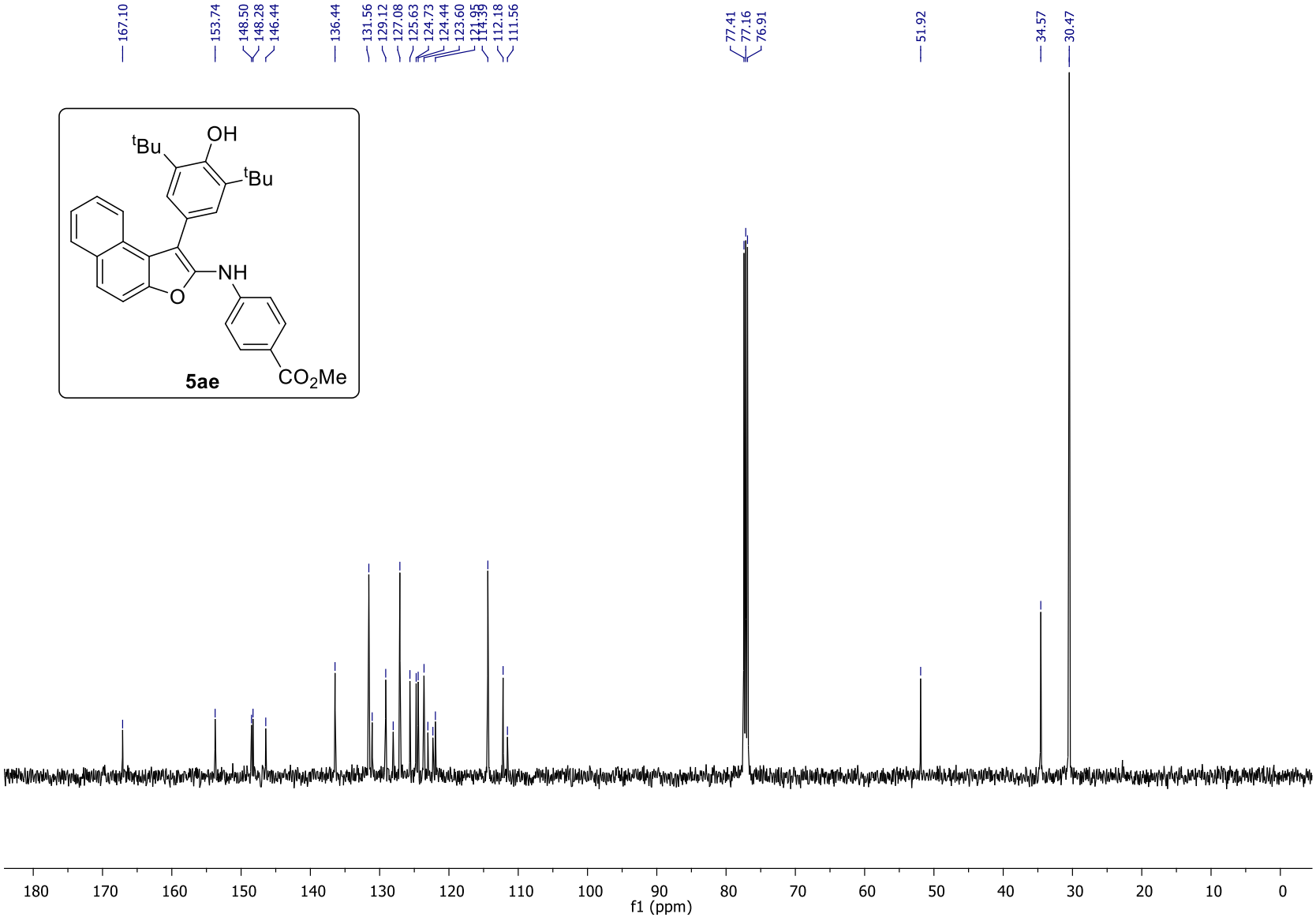
^{13}C NMR of compound **5ad** in $CDCl_3$



^{1}H NMR of compound **5ae** in $CDCl_3$



^{13}C NMR of compound **5ae** in $CDCl_3$



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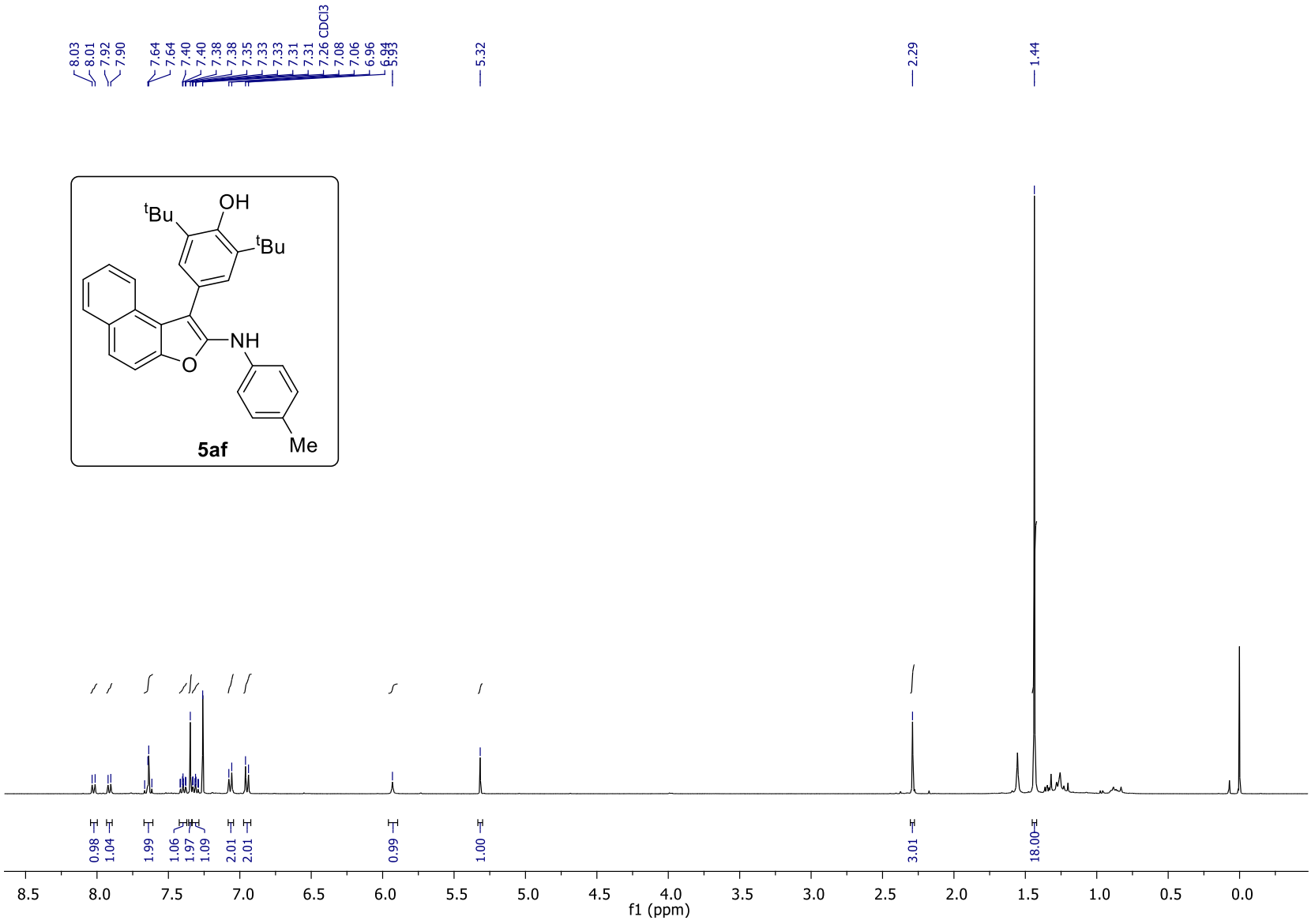
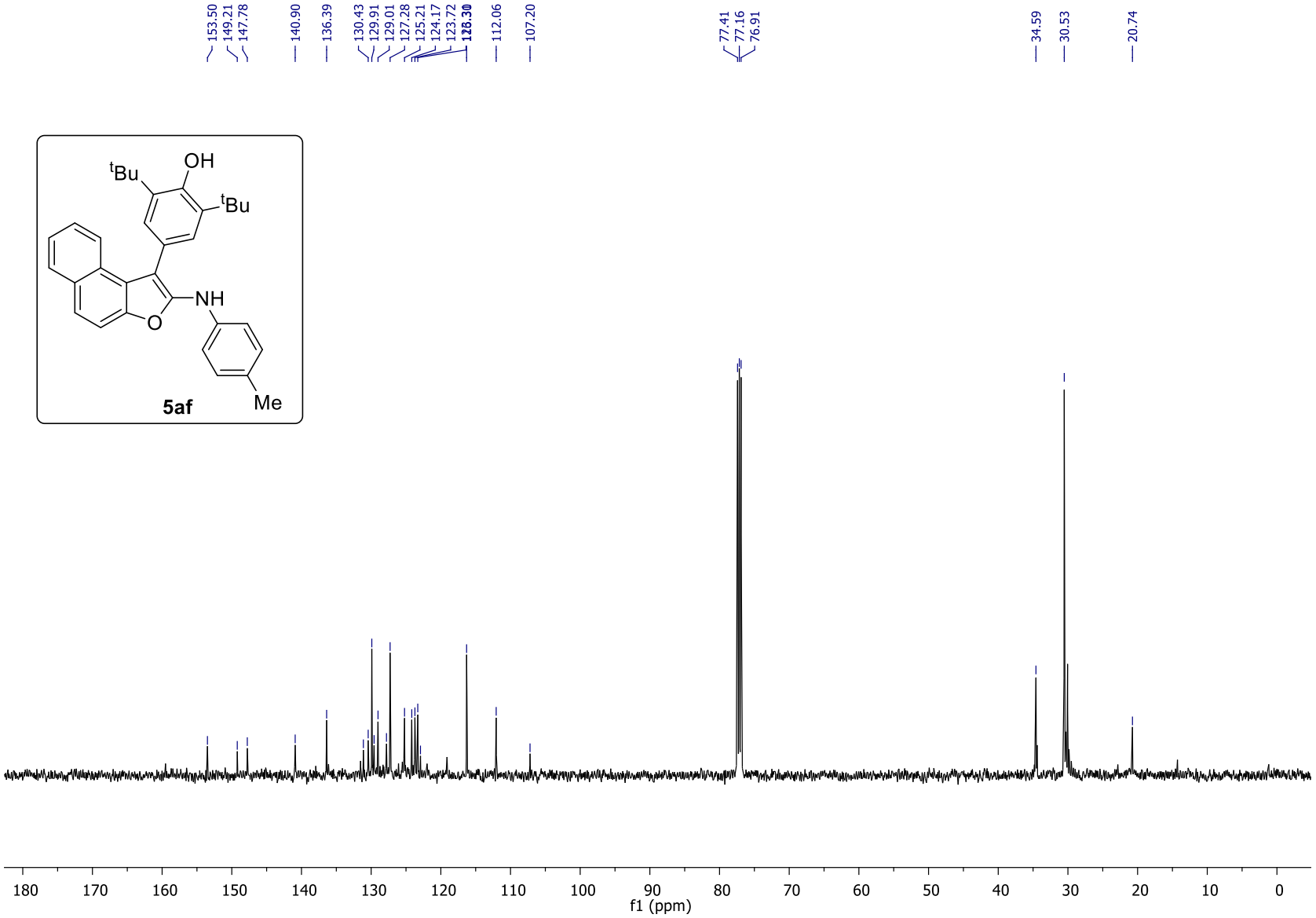
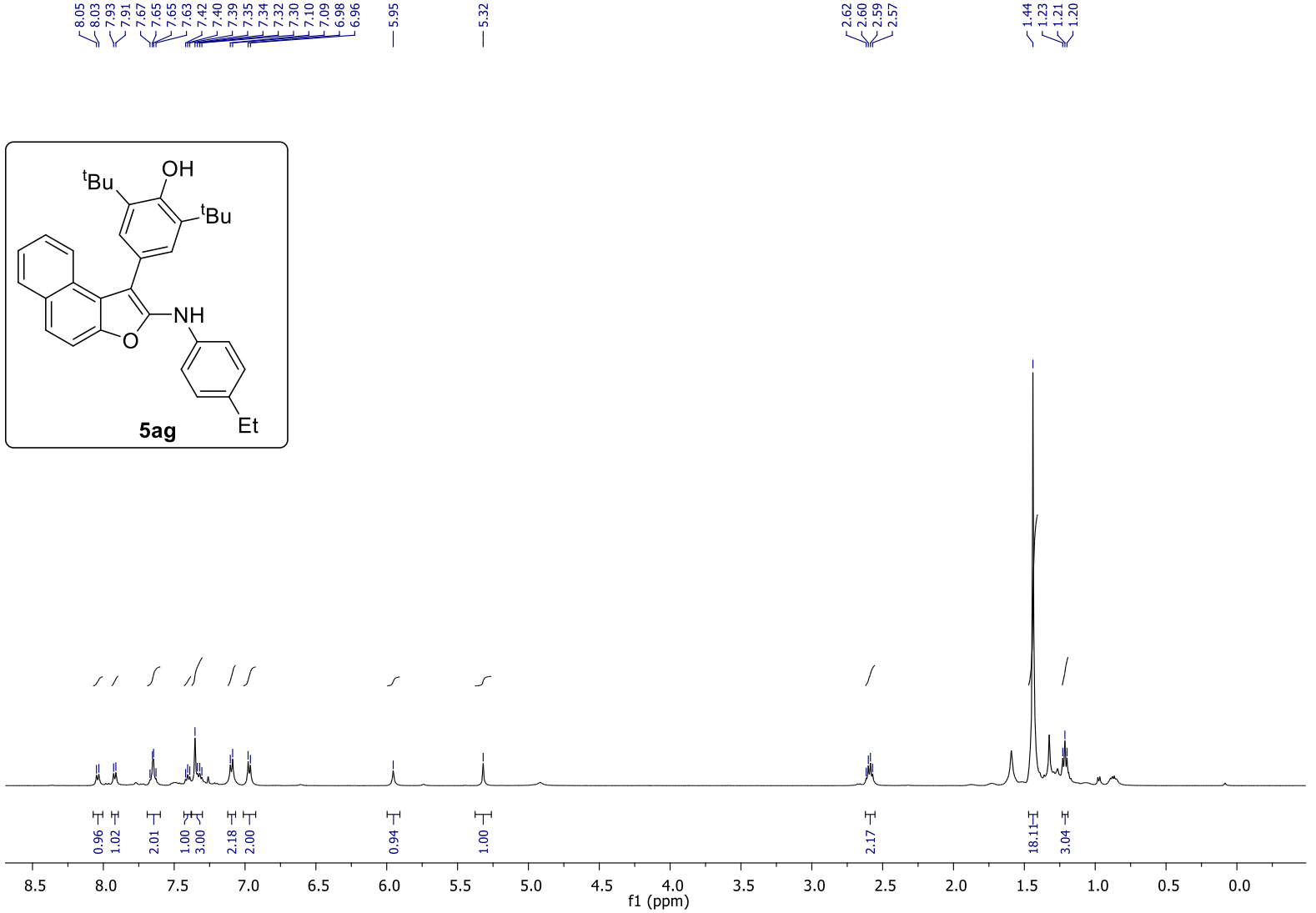


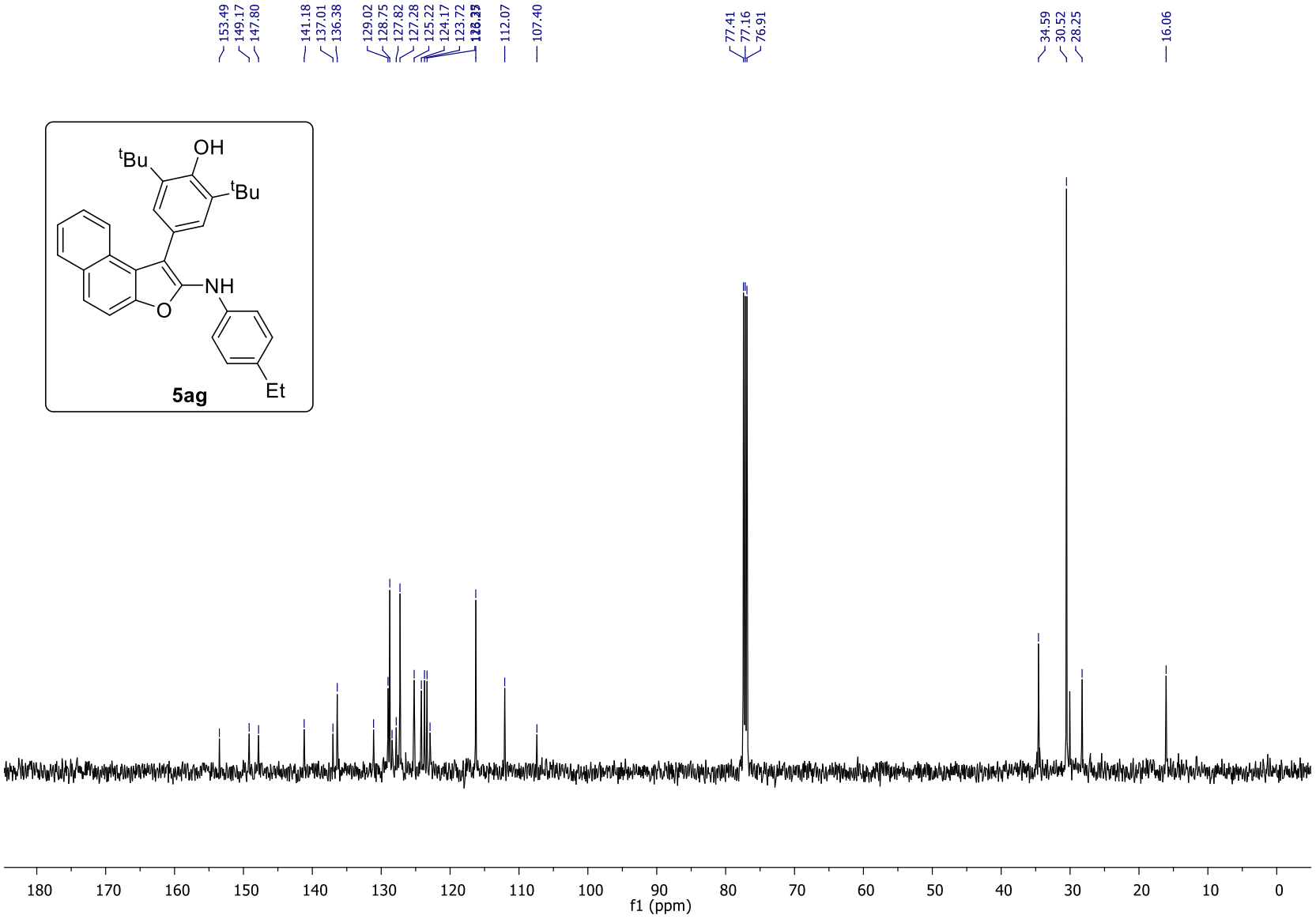
^{13}C NMR of compound **5af** in $CDCl_3$



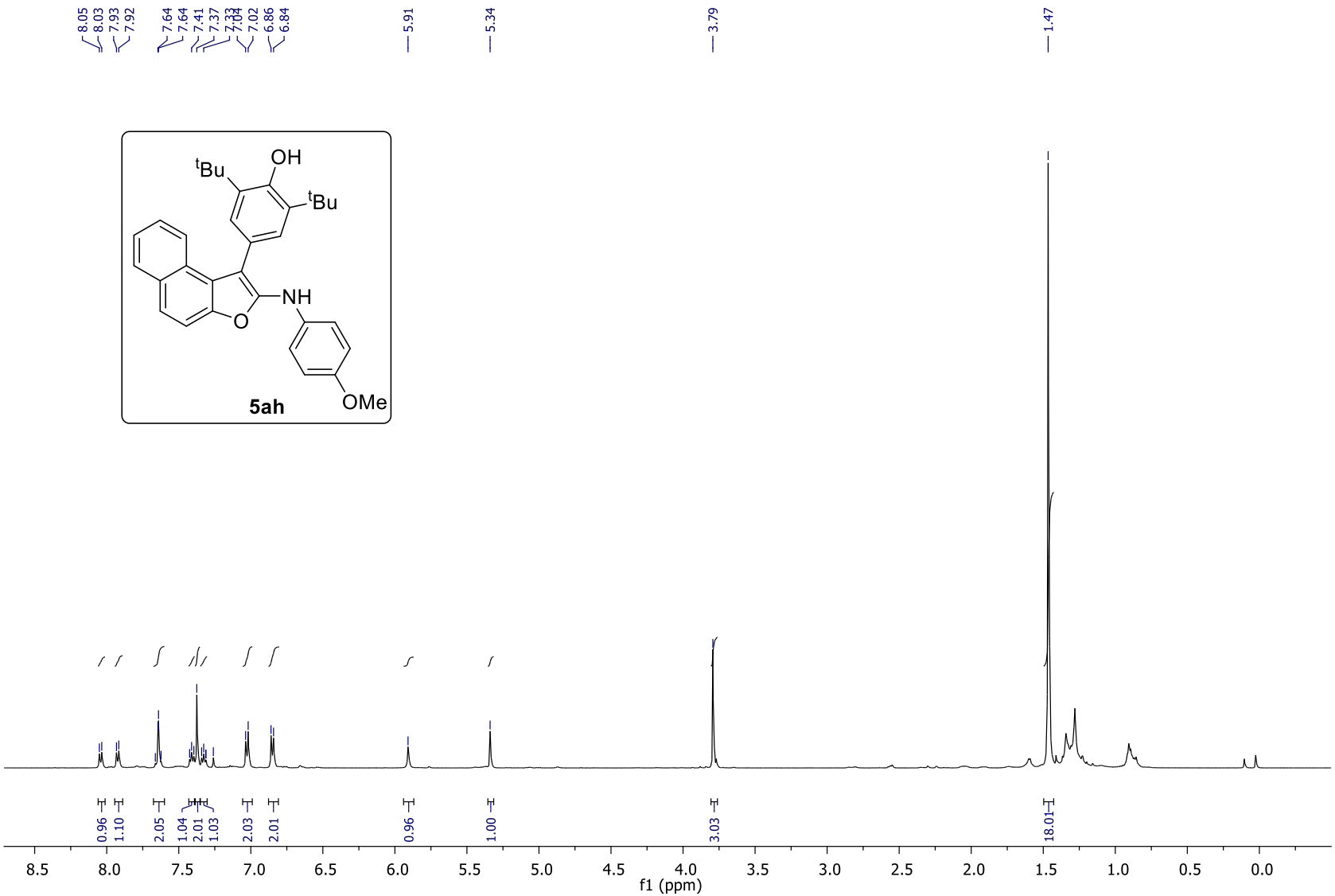
^{1}H NMR of compound **5ag** in $CDCl_3$



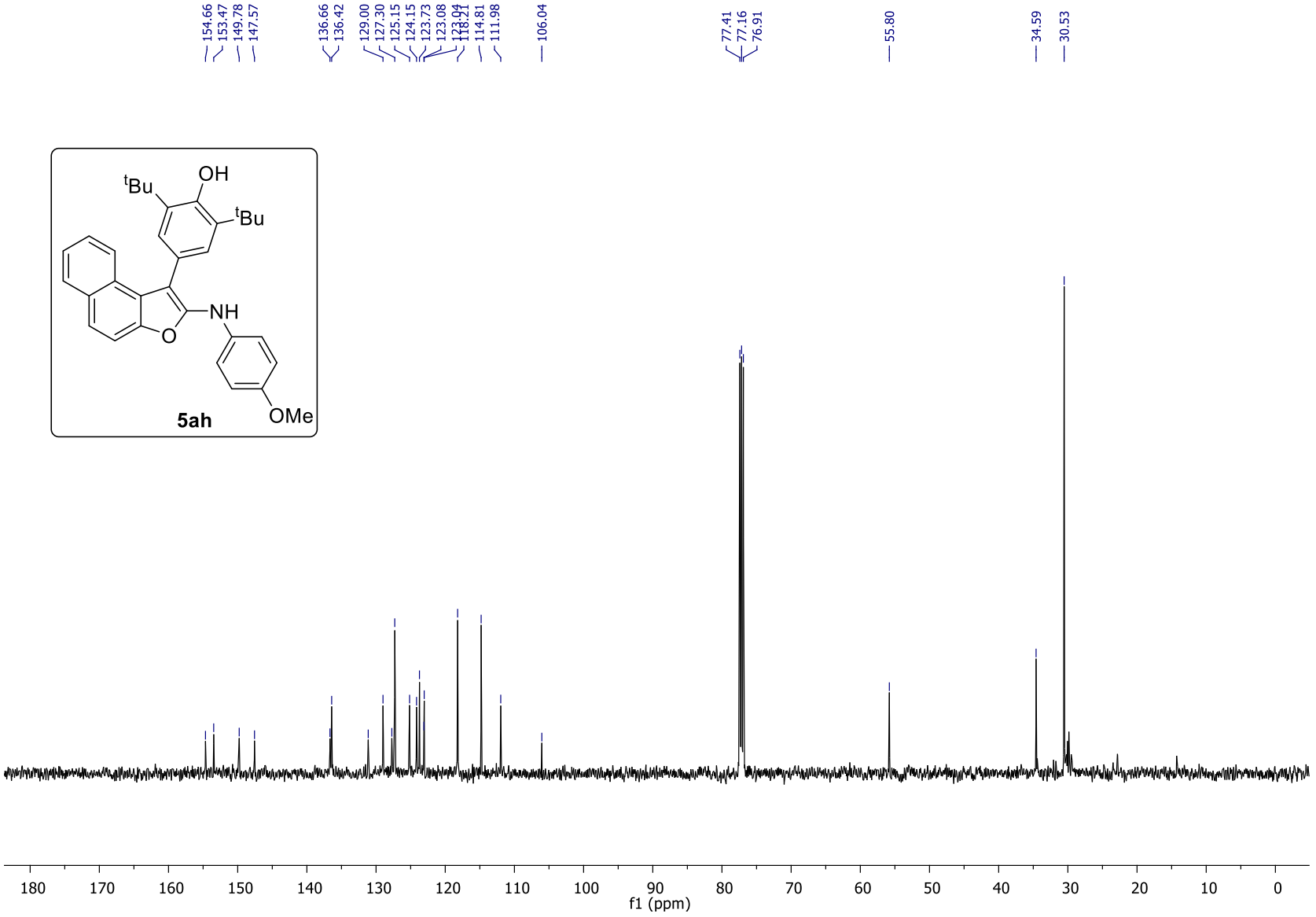
^{13}C NMR of compound **5ag** in $CDCl_3$



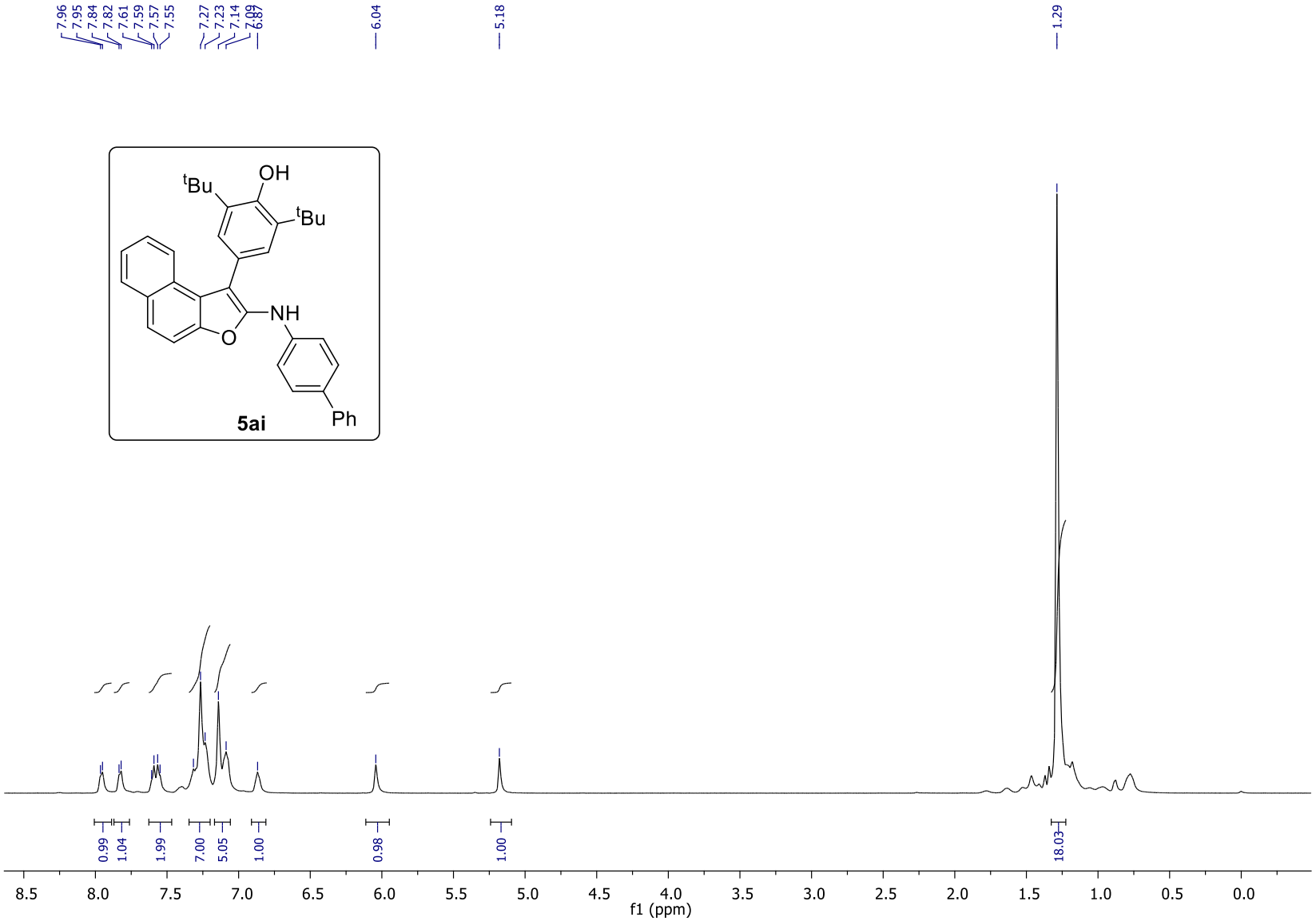
^{1}H NMR of compound **5ah** in $CDCl_3$



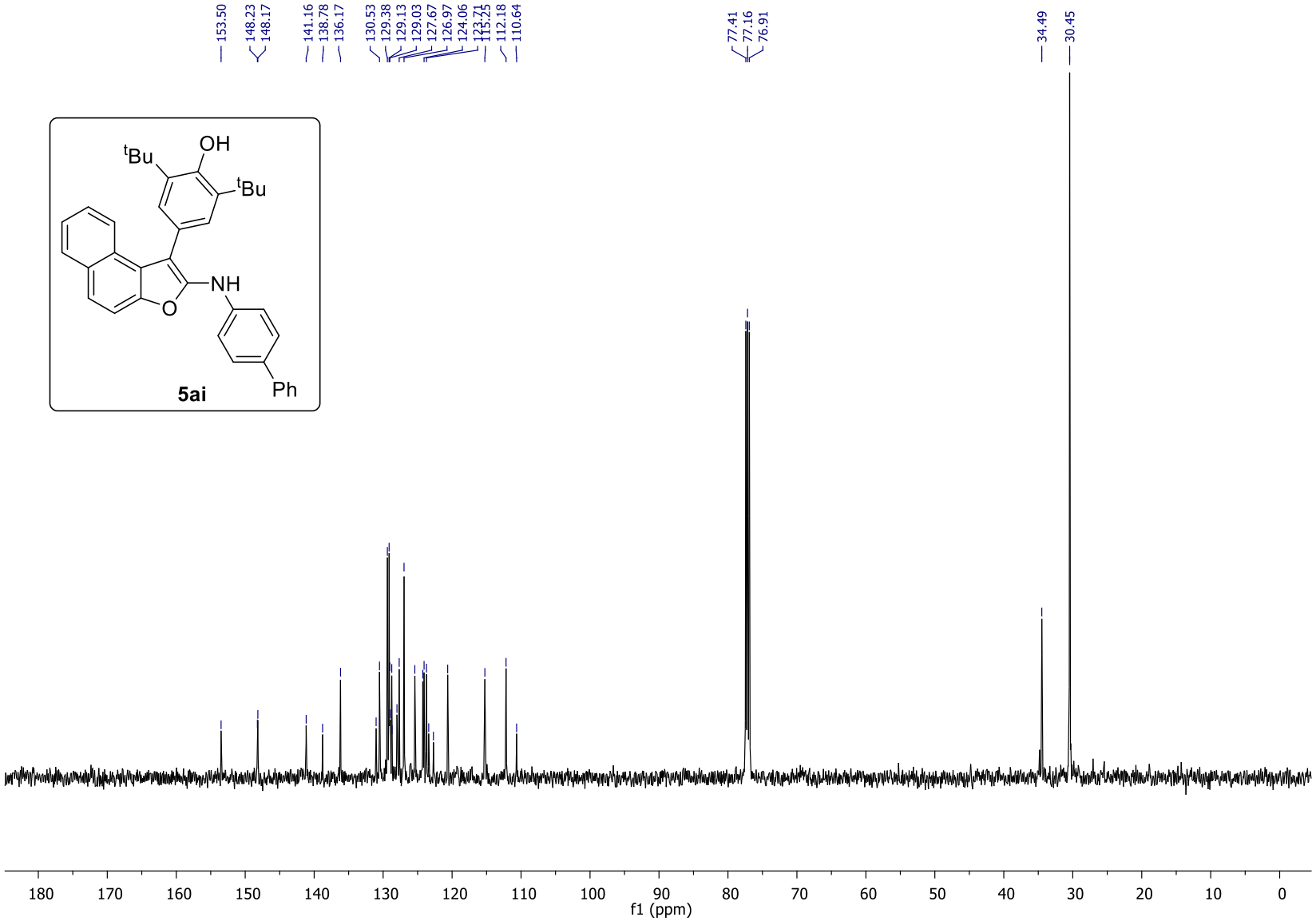
^{13}C NMR of compound **5ah** in $CDCl_3$



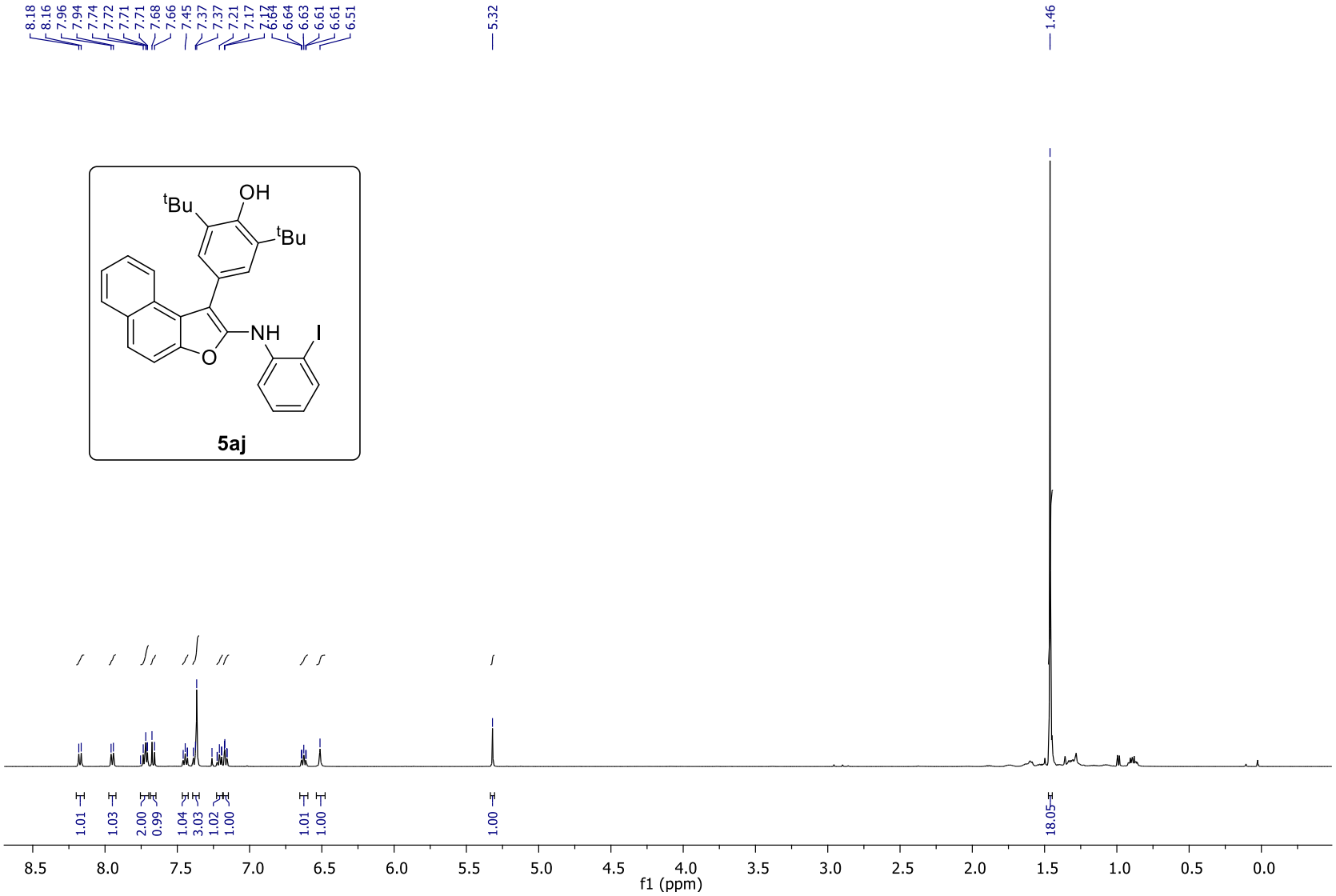
^{1}H NMR of compound **5ai** in $CDCl_3$



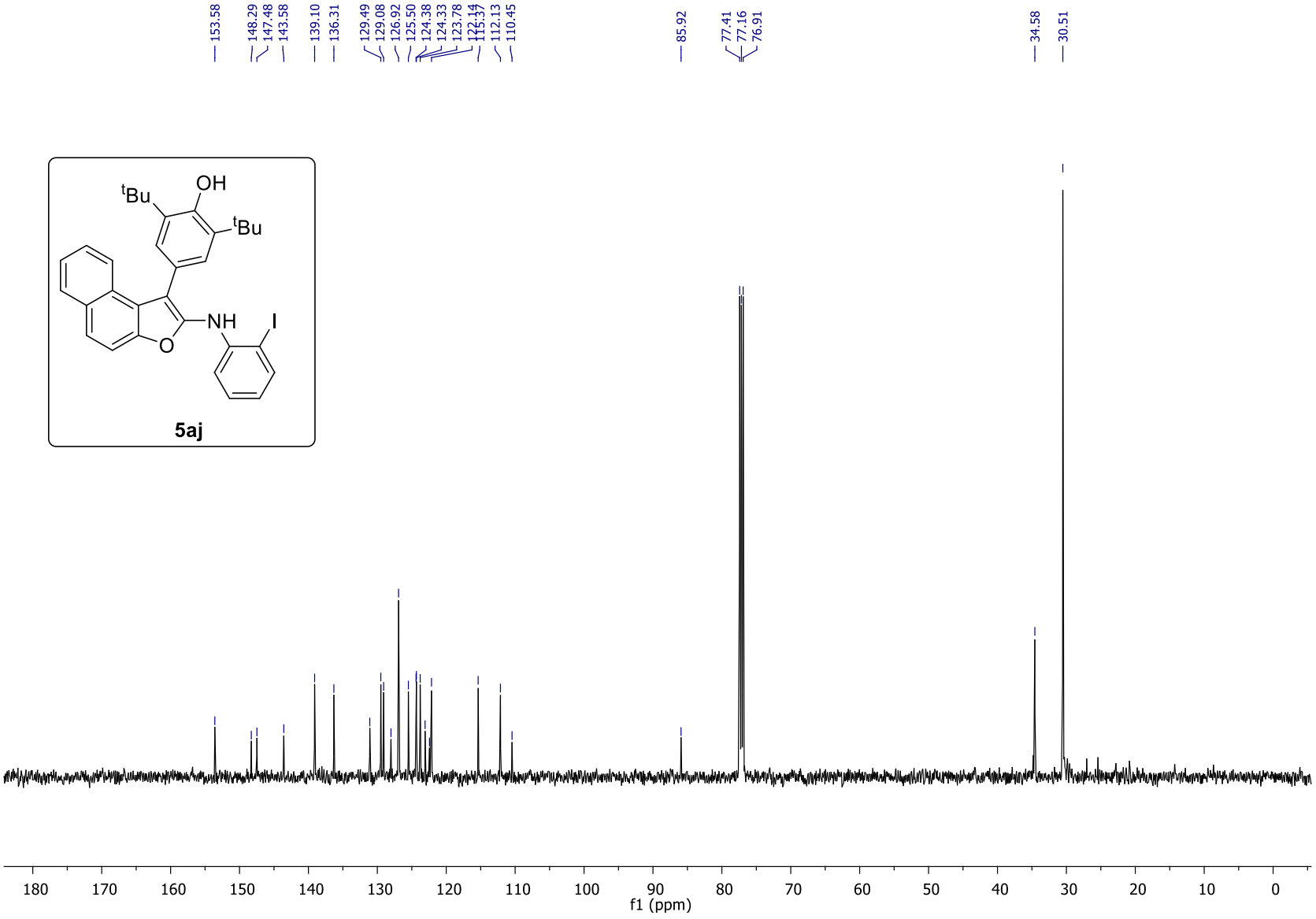
^{13}C NMR of compound **5ai** in $CDCl_3$



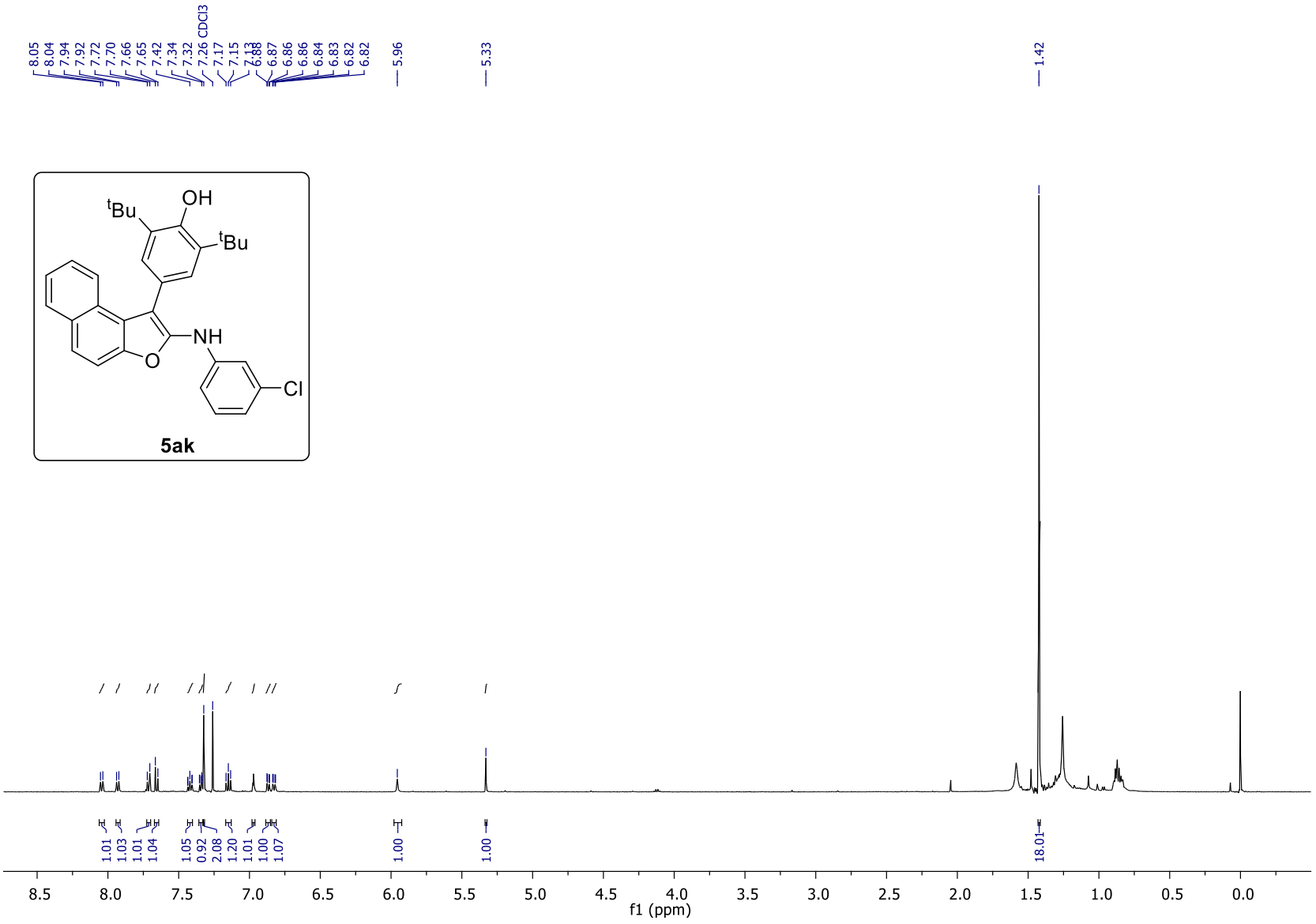
^{1}H NMR of compound **5aj** in $CDCl_3$



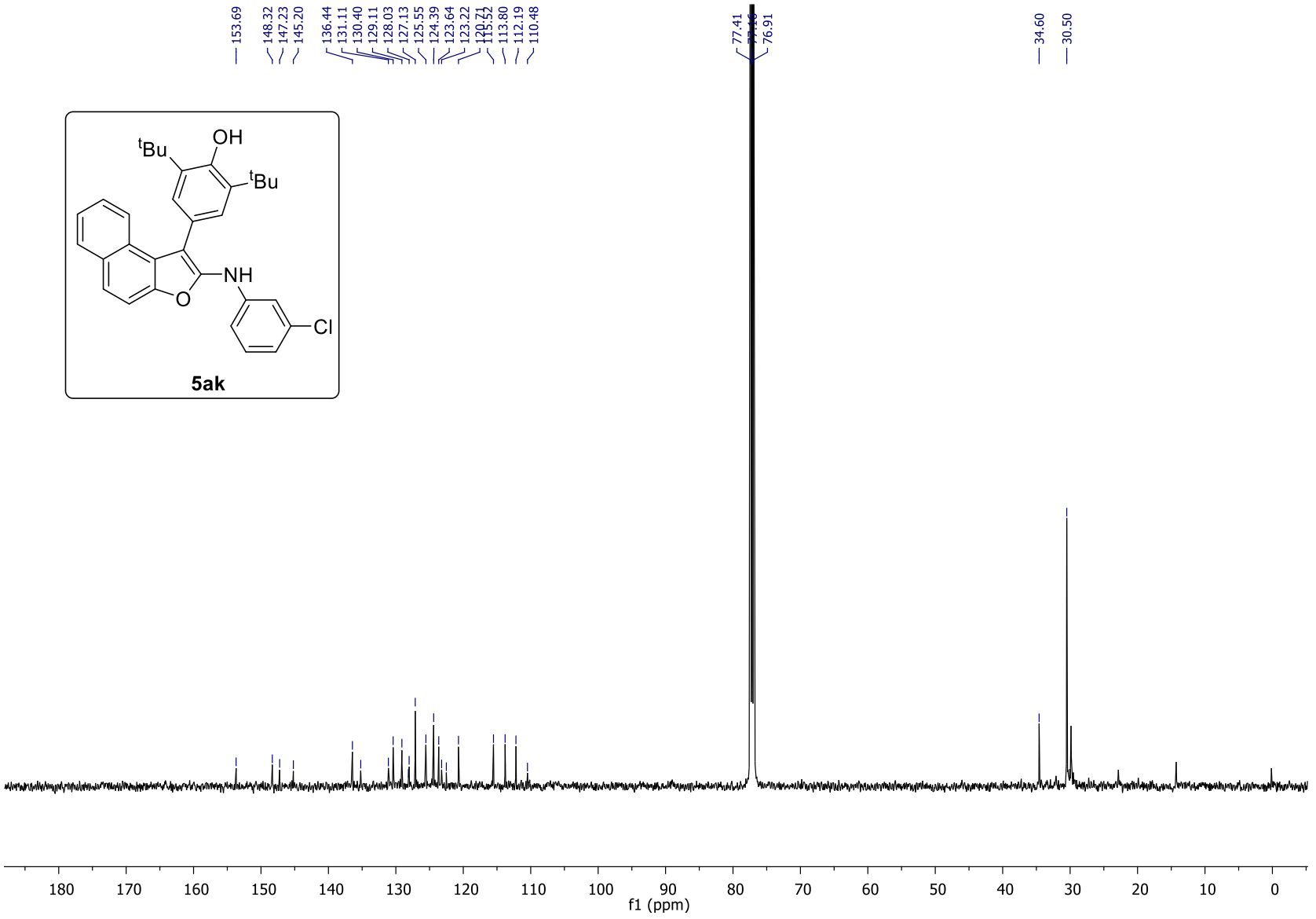
^{13}C NMR of compound **5aj** in $CDCl_3$



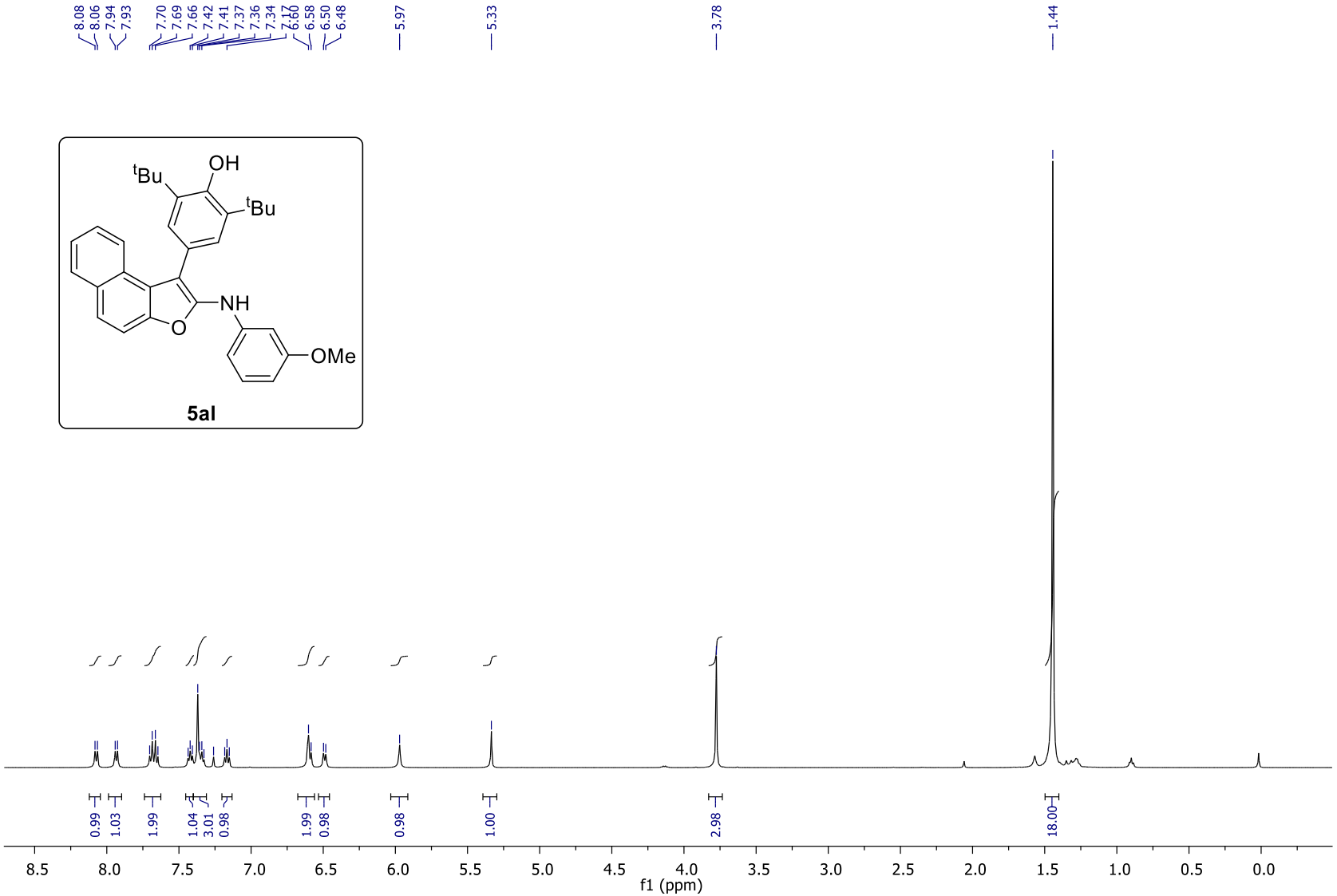
^{1}H NMR of compound **5ak** in $CDCl_3$



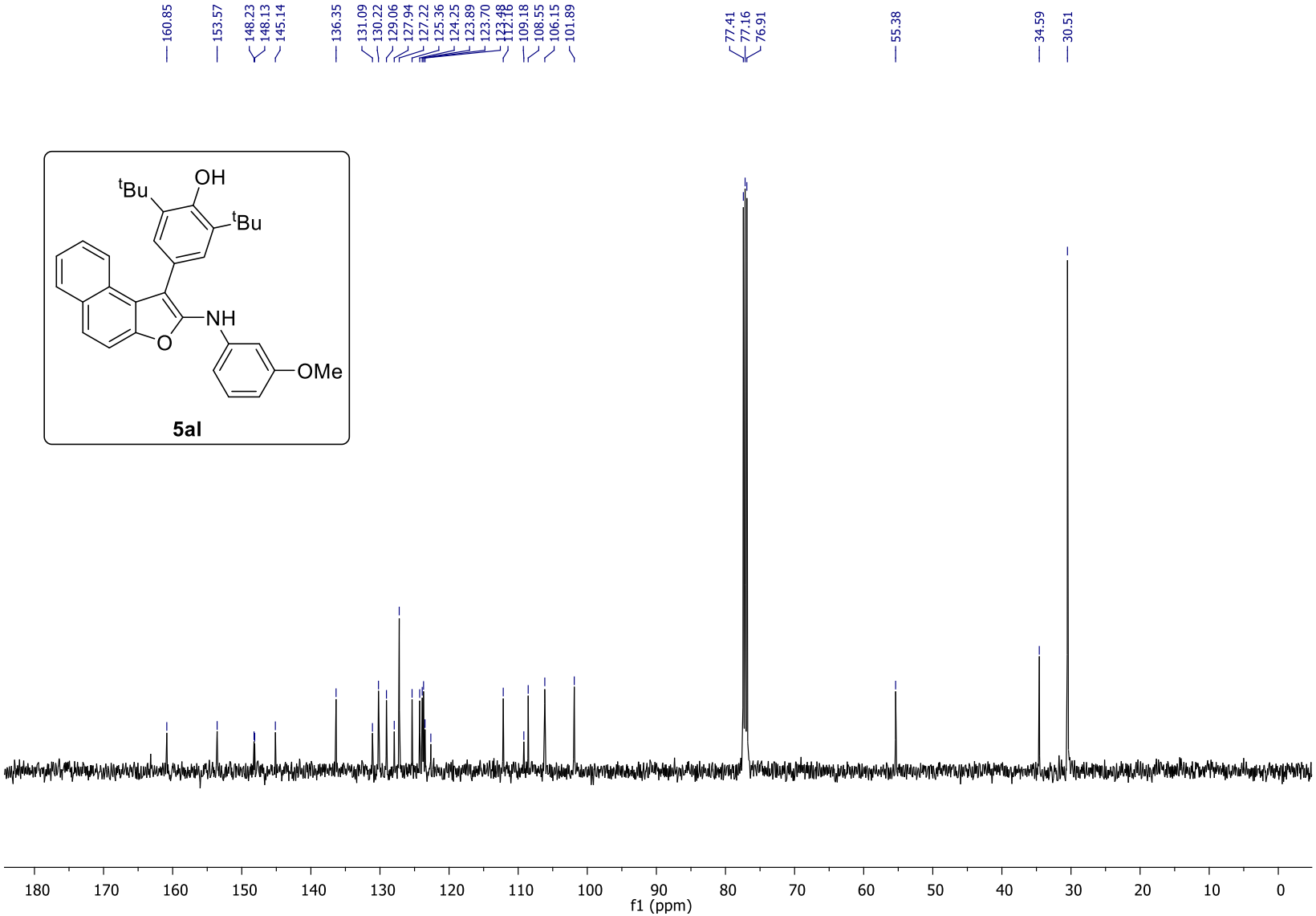
^{13}C NMR of compound **5ak** in $CDCl_3$



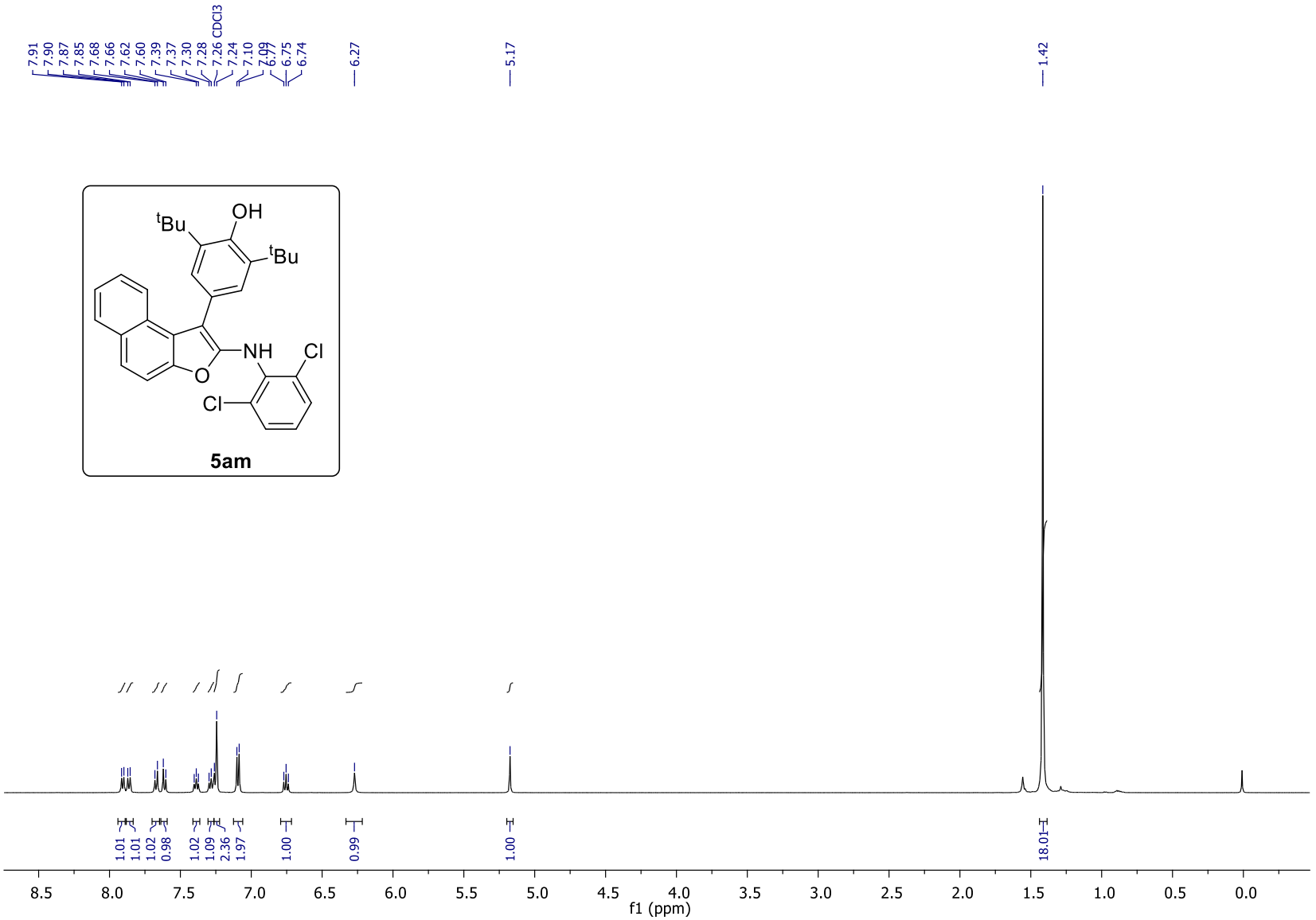
^{1}H NMR of compound **5al** in $CDCl_3$



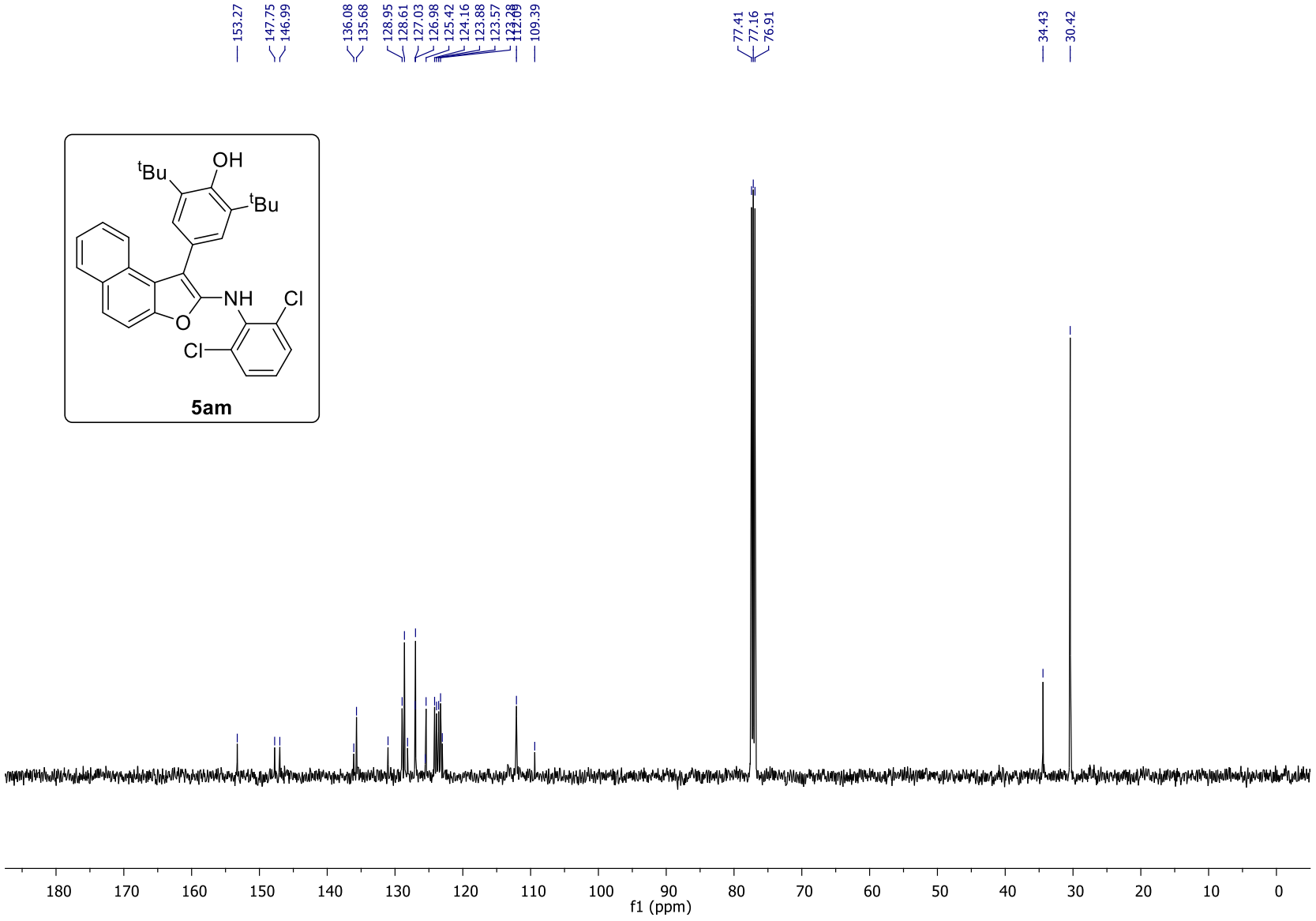
^{13}C NMR of compound **5al** in $CDCl_3$



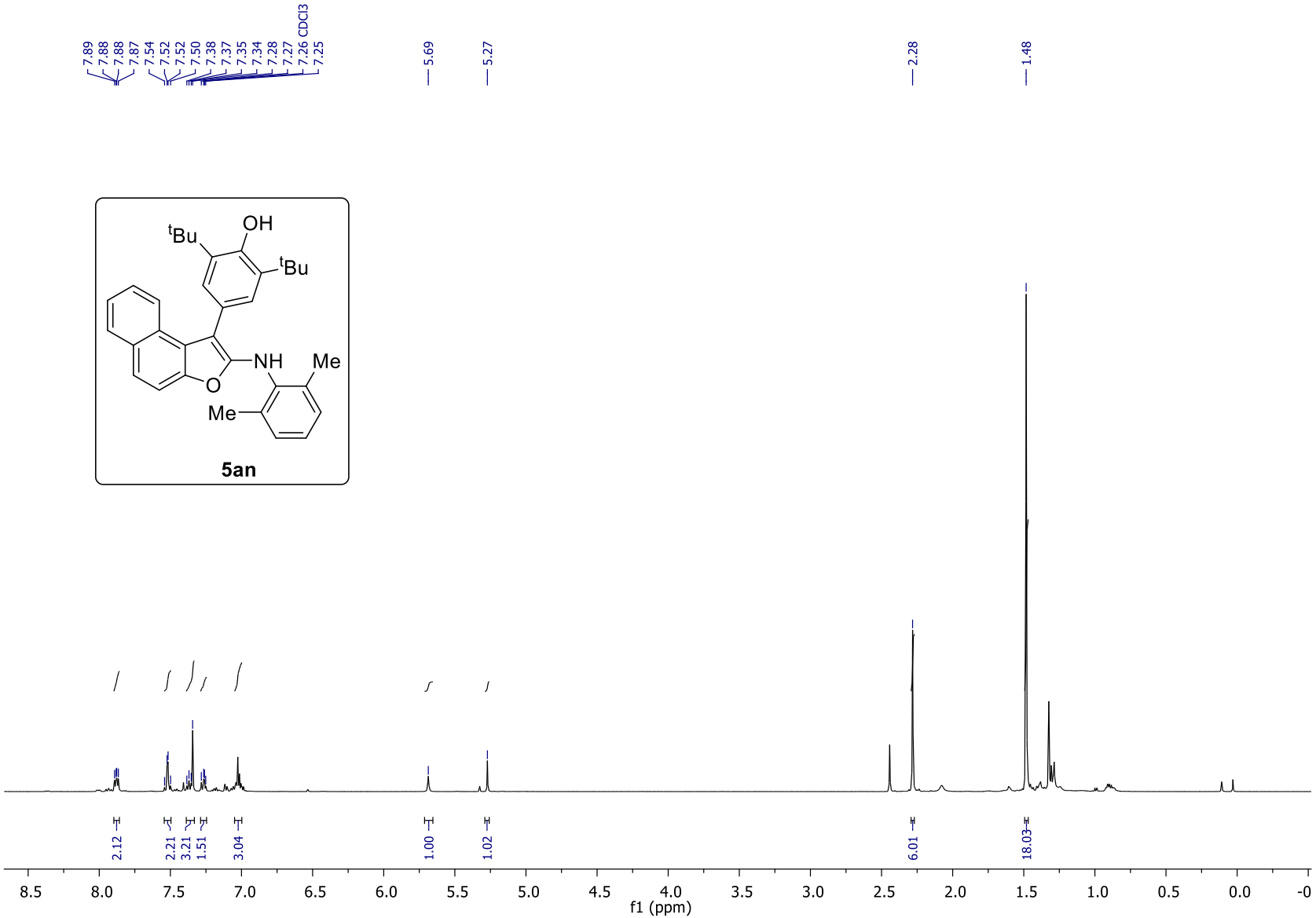
^{1}H NMR of compound **5am** in $CDCl_3$



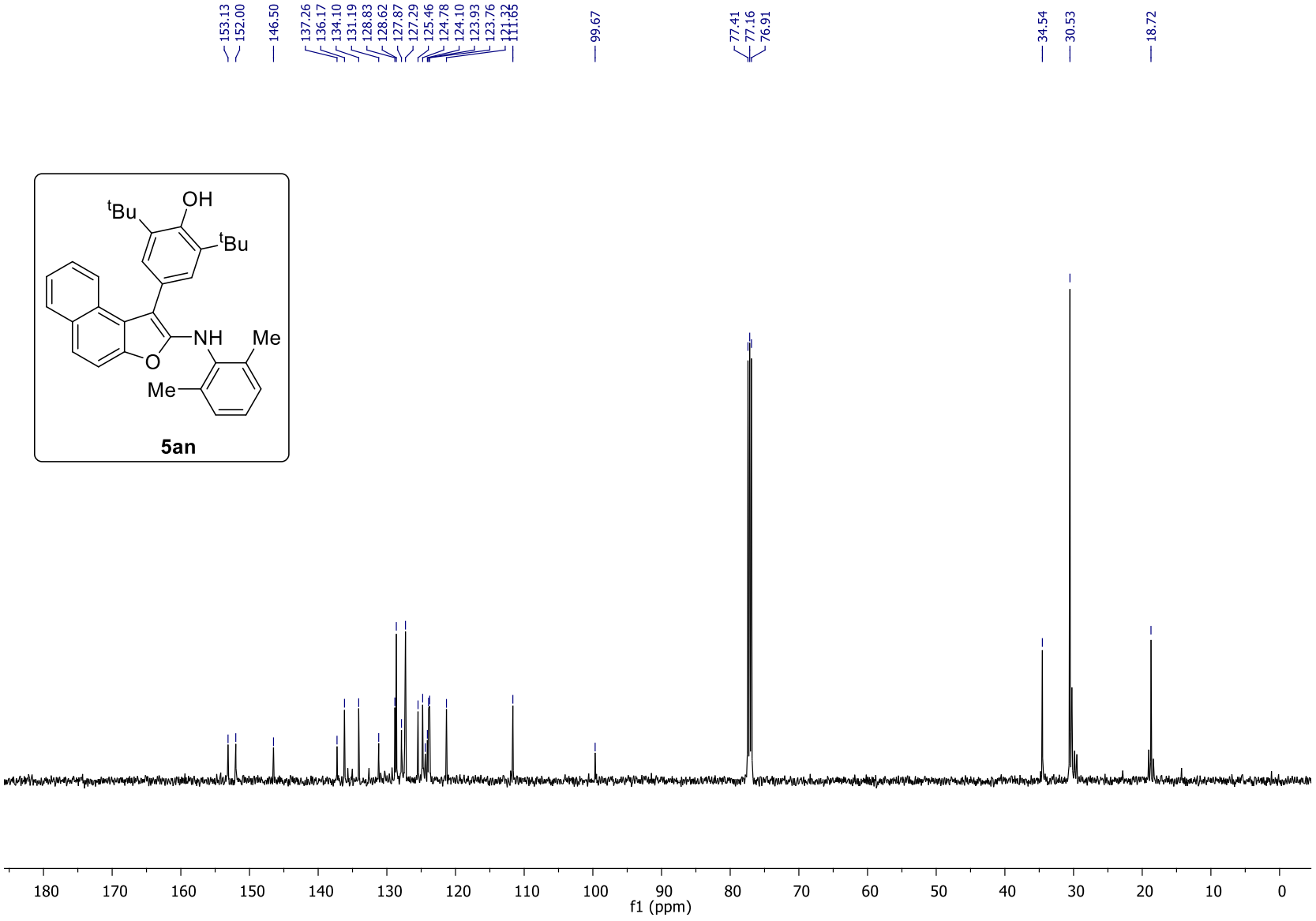
^{13}C NMR of compound **5am** in $CDCl_3$



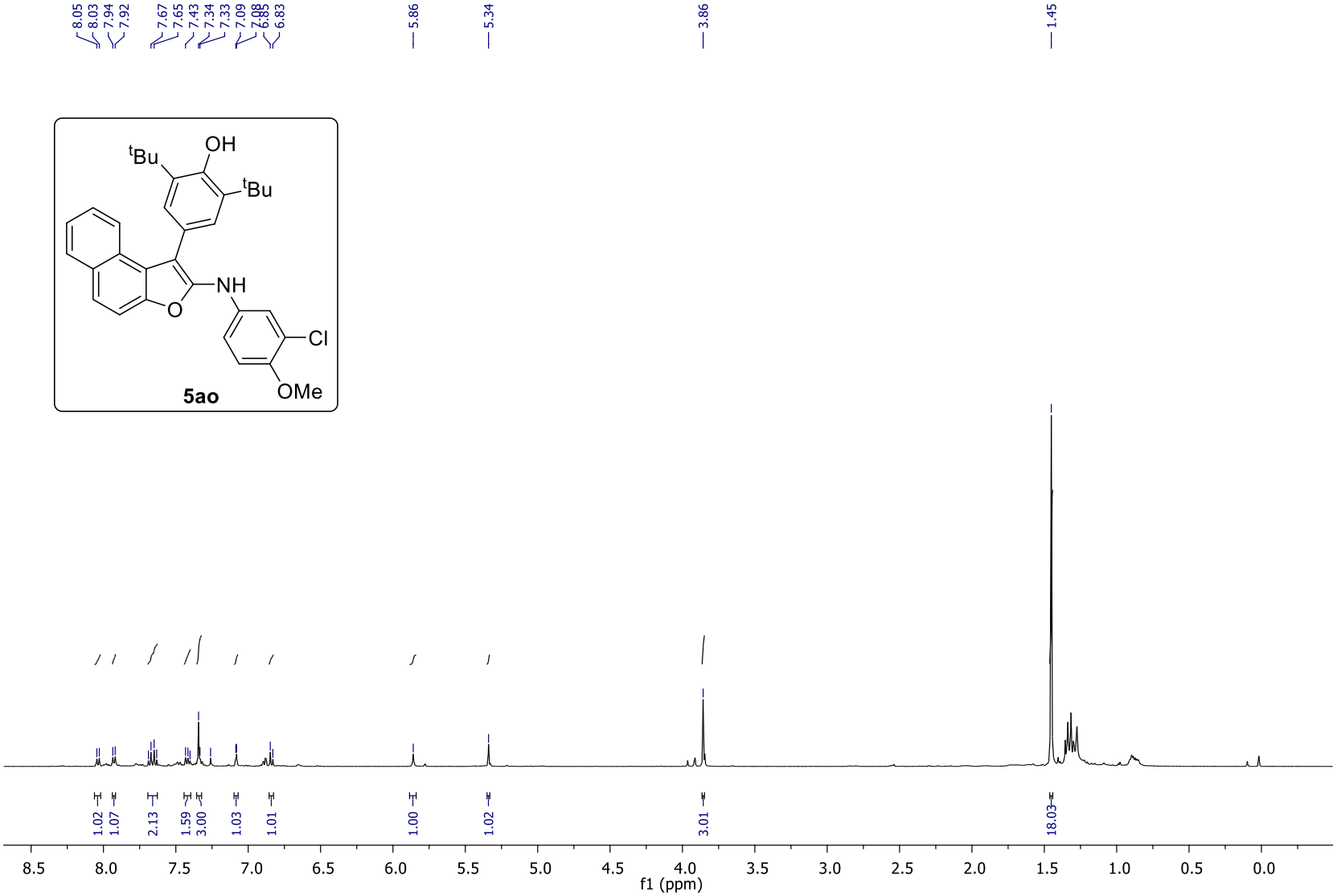
^{1}H NMR of compound **5an** in $CDCl_3$



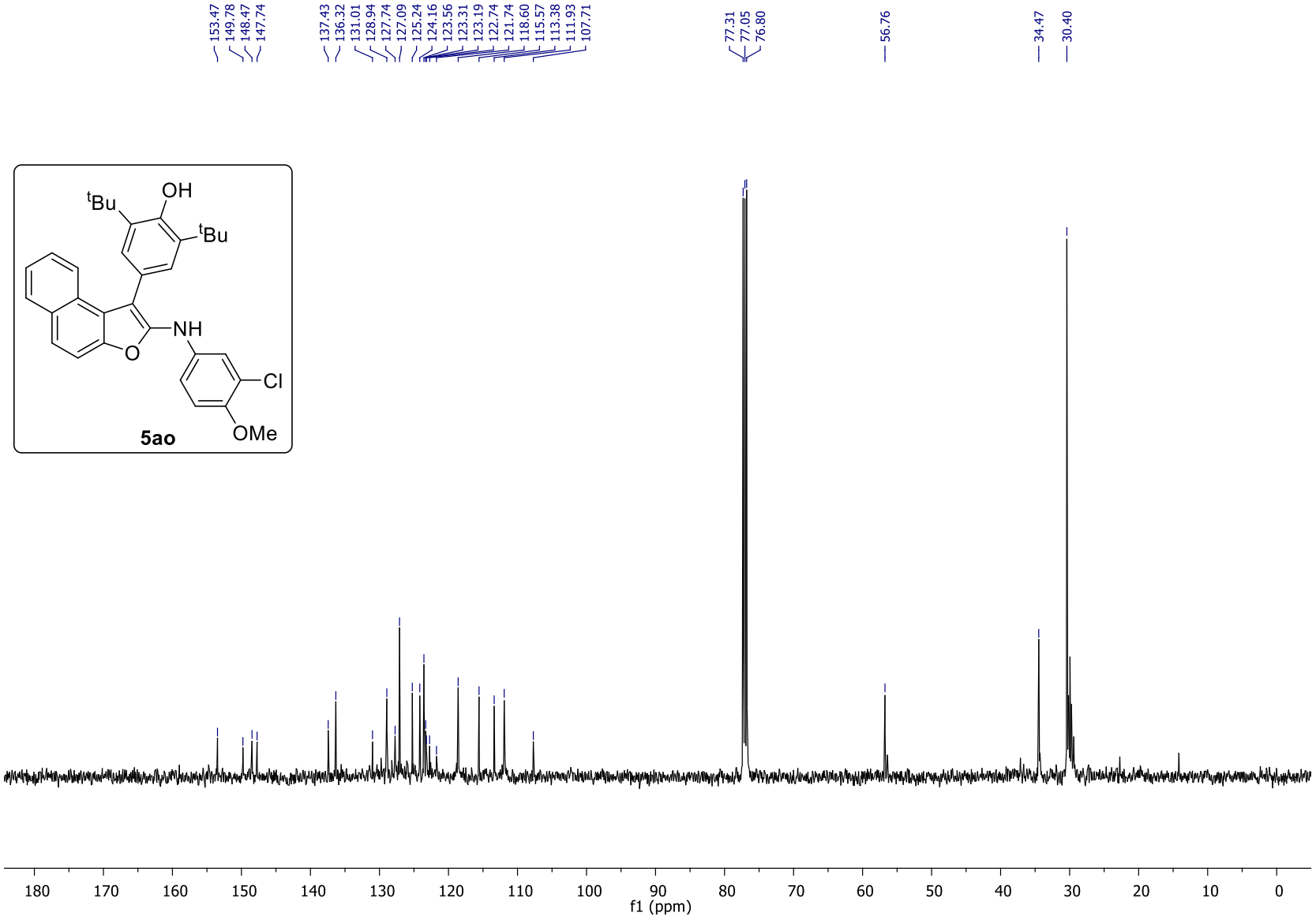
^{13}C NMR of compound **5an** in $CDCl_3$



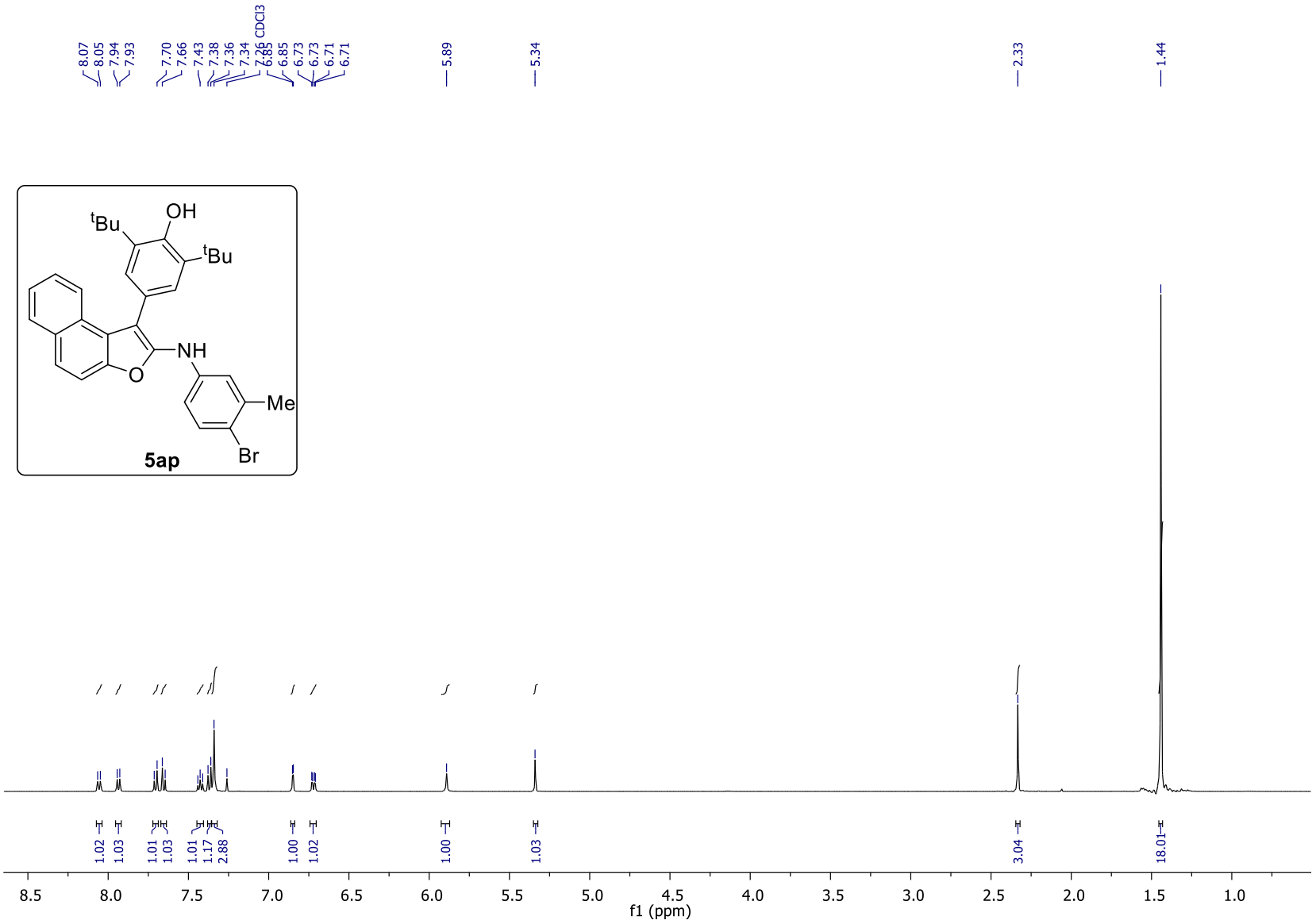
^{1}H NMR of compound **5ao** in $CDCl_3$



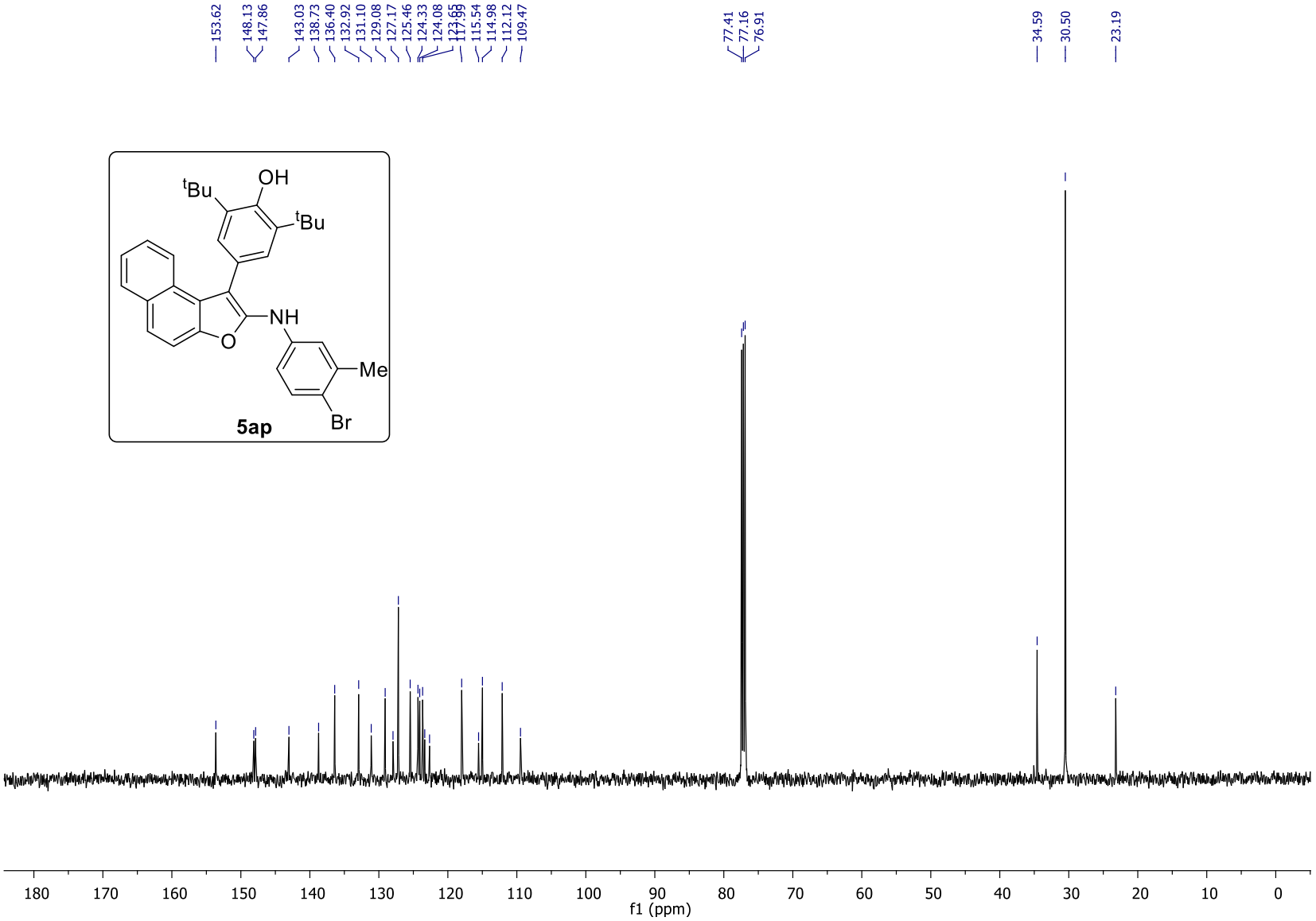
^{13}C NMR of compound **5ao** in $CDCl_3$



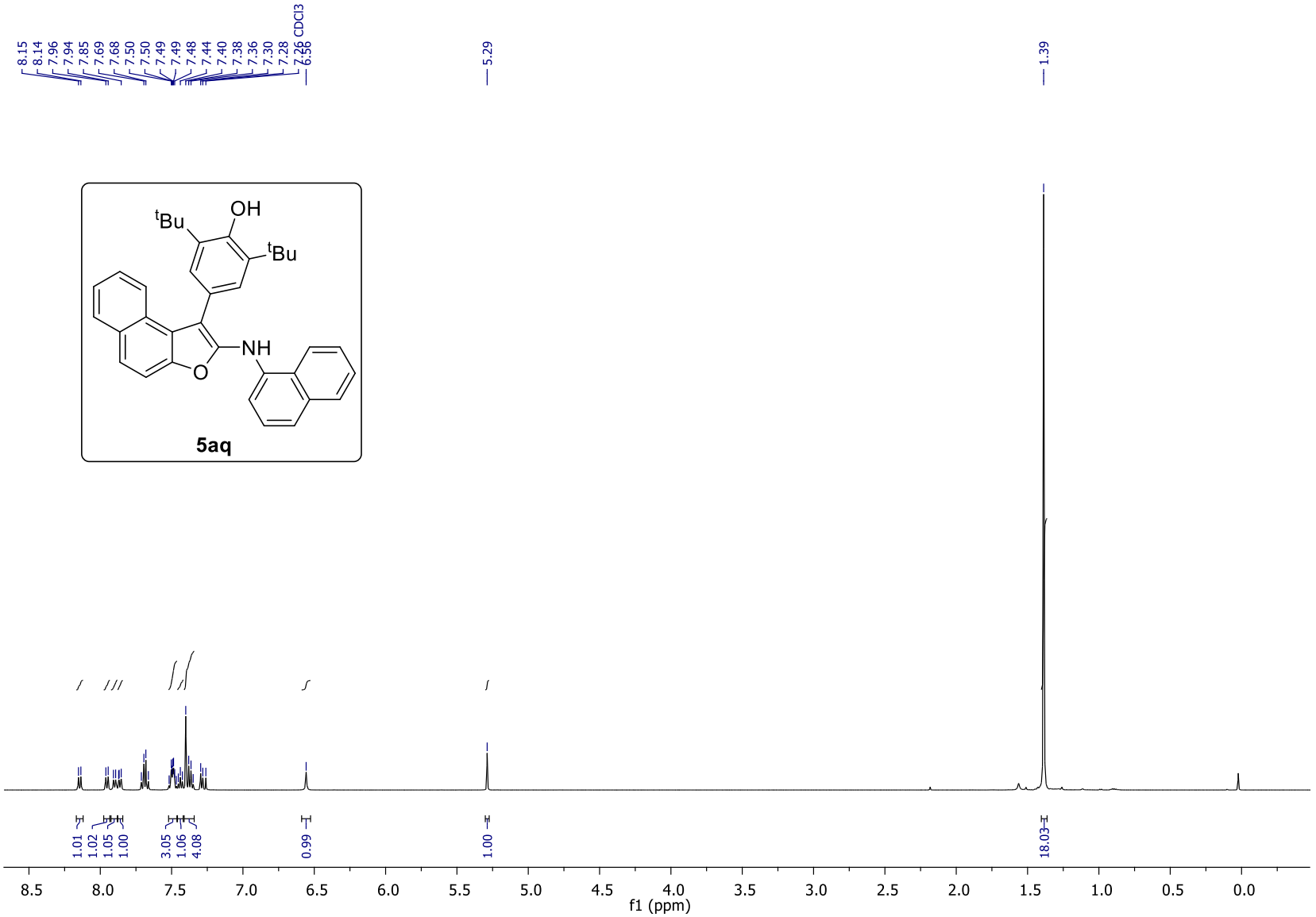
^{1}H NMR of compound **5ap** in $CDCl_3$



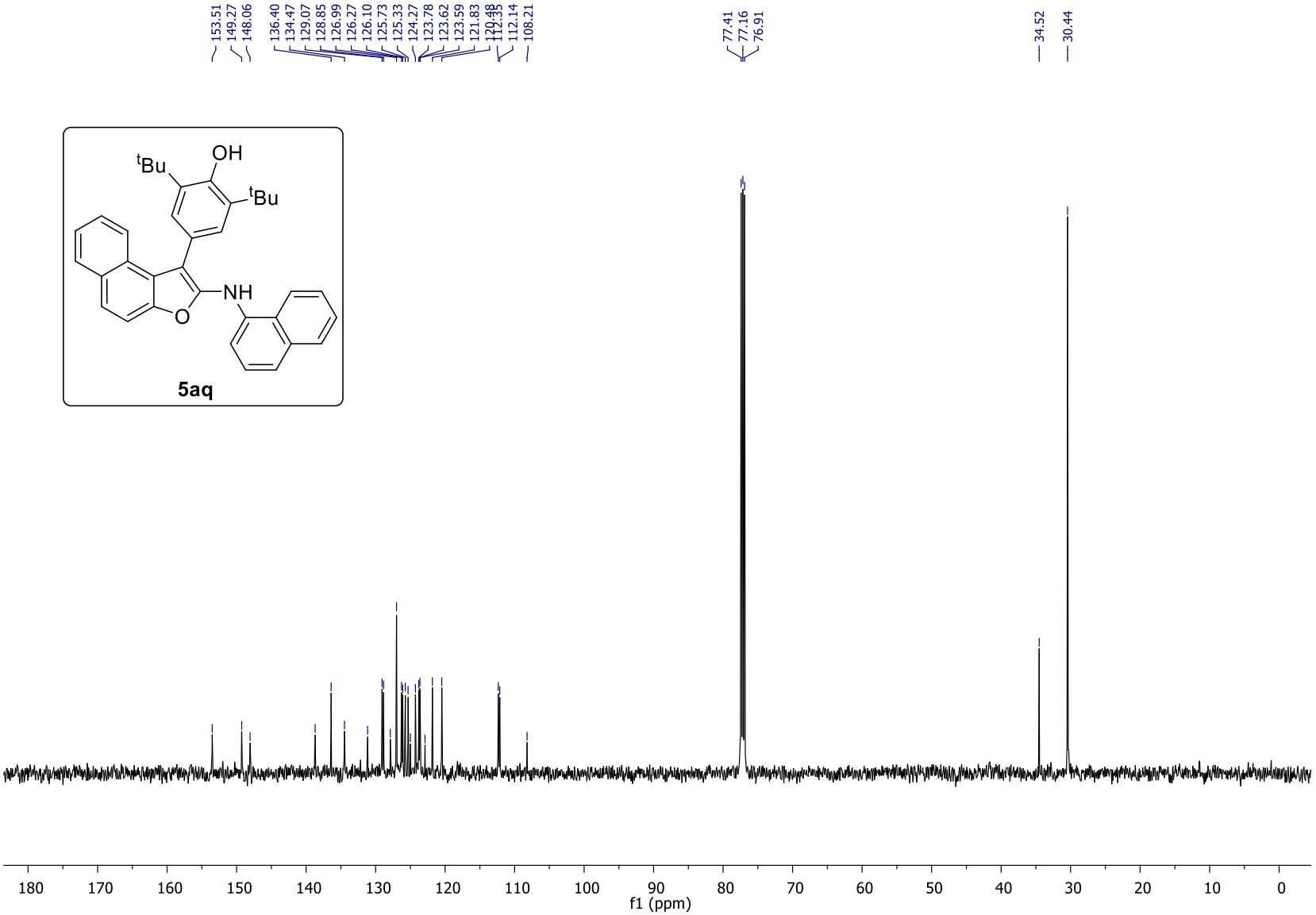
^{13}C NMR of compound **5ap** in $CDCl_3$



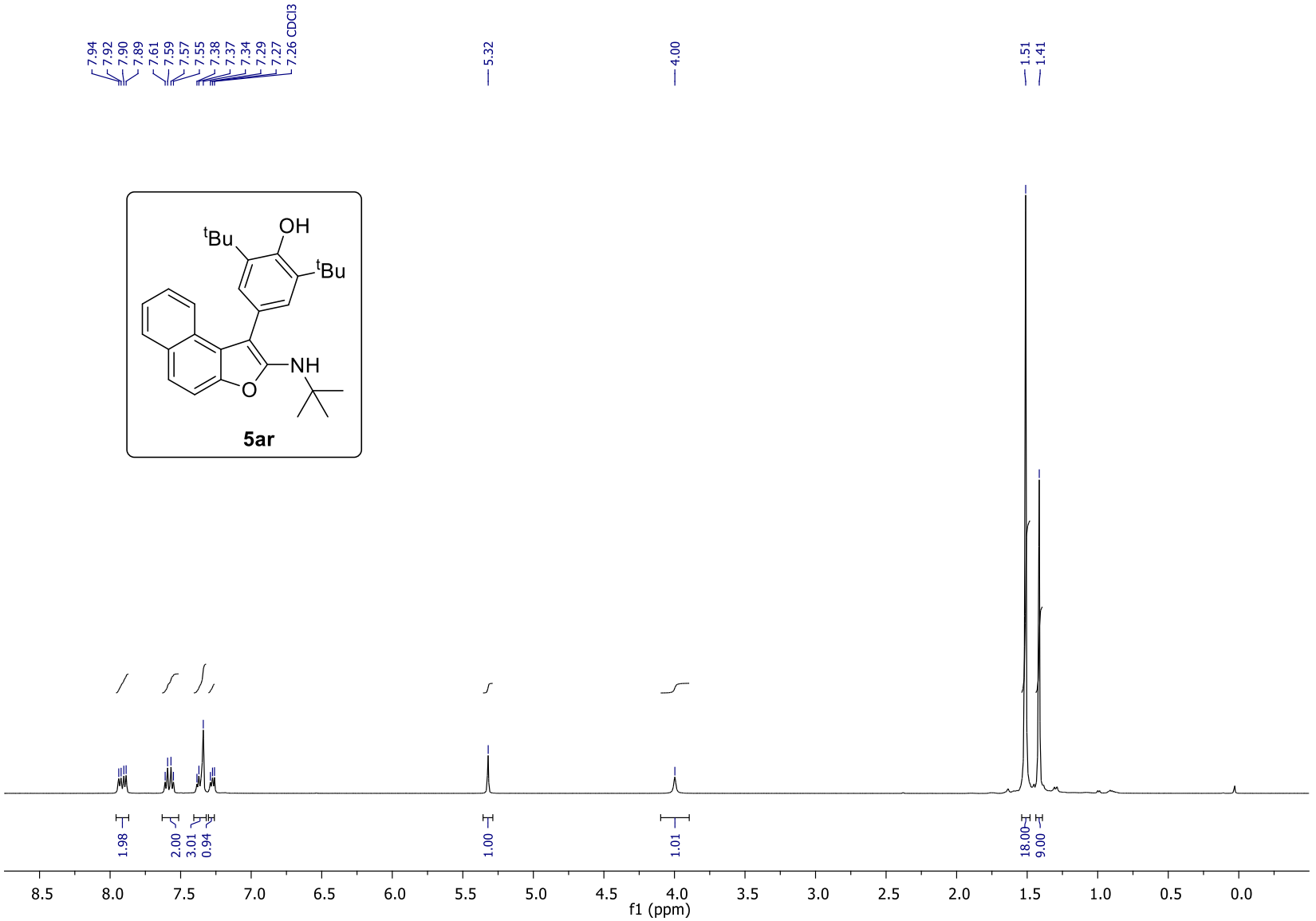
^{1}H NMR of compound **5aq** in $CDCl_3$



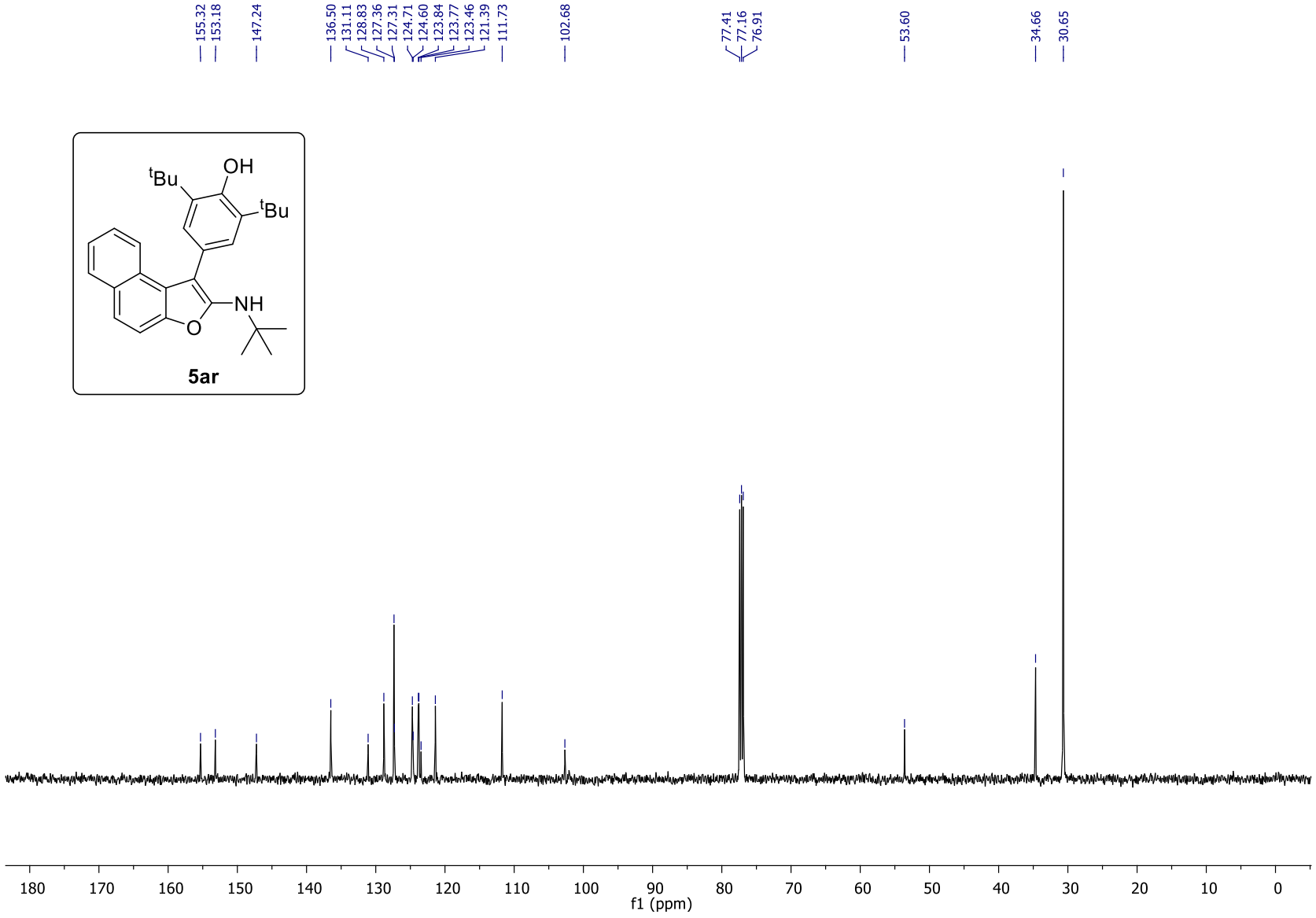
^{13}C NMR of compound **5aq** in $CDCl_3$



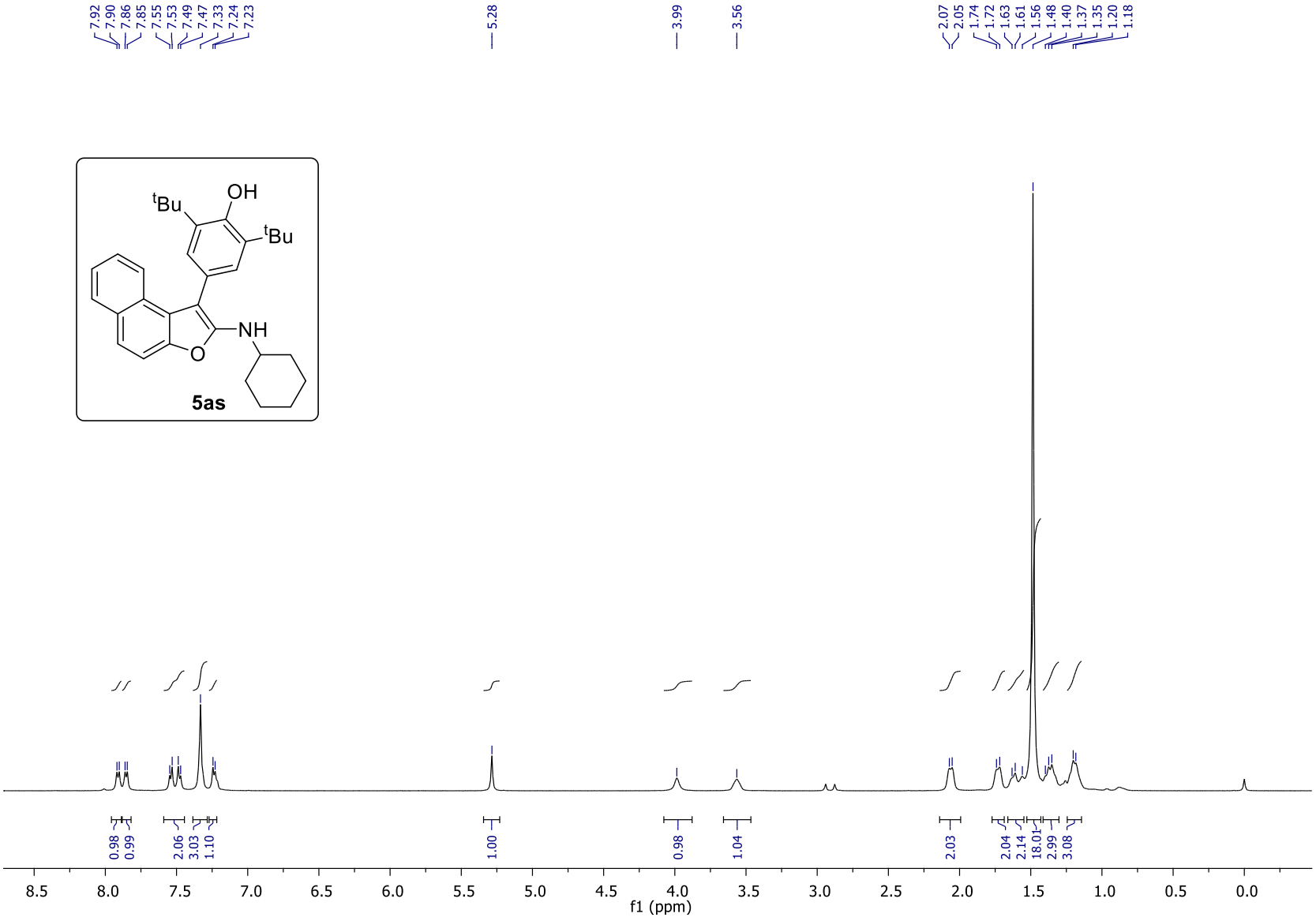
^{1}H NMR of compound **5ar** in $CDCl_3$



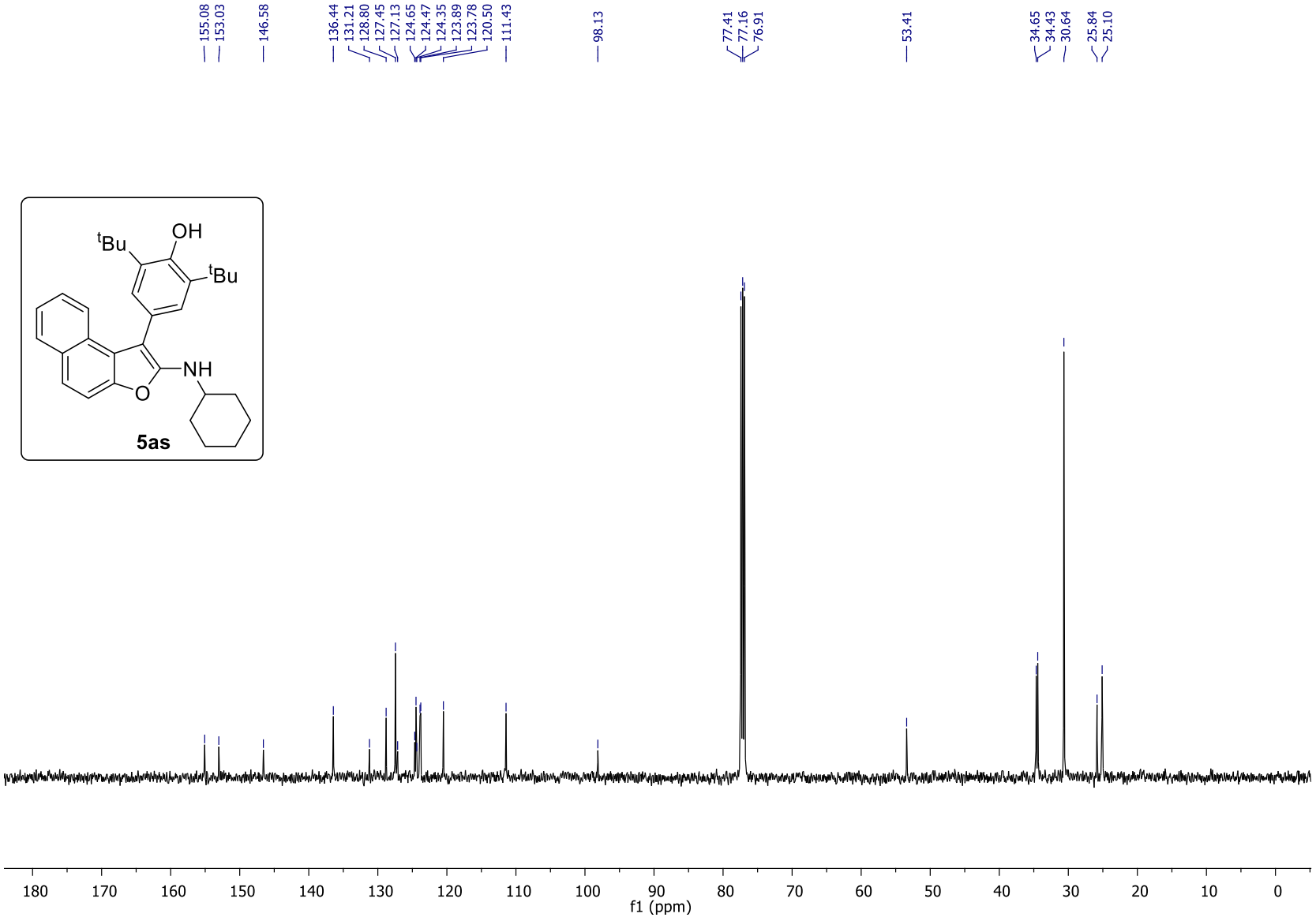
^{13}C NMR of compound **5ar** in $CDCl_3$



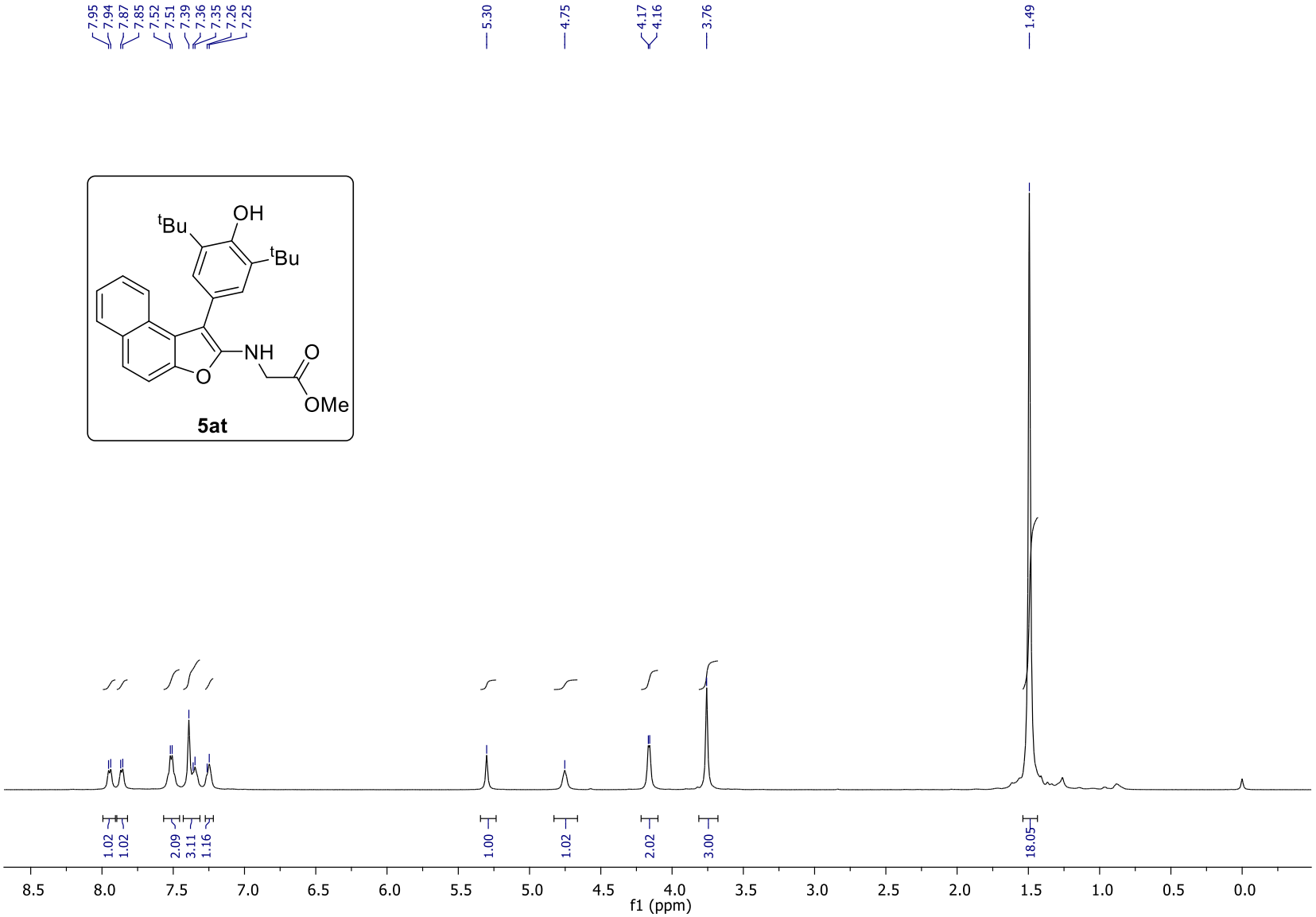
^{1}H NMR of compound **5as** in $CDCl_3$



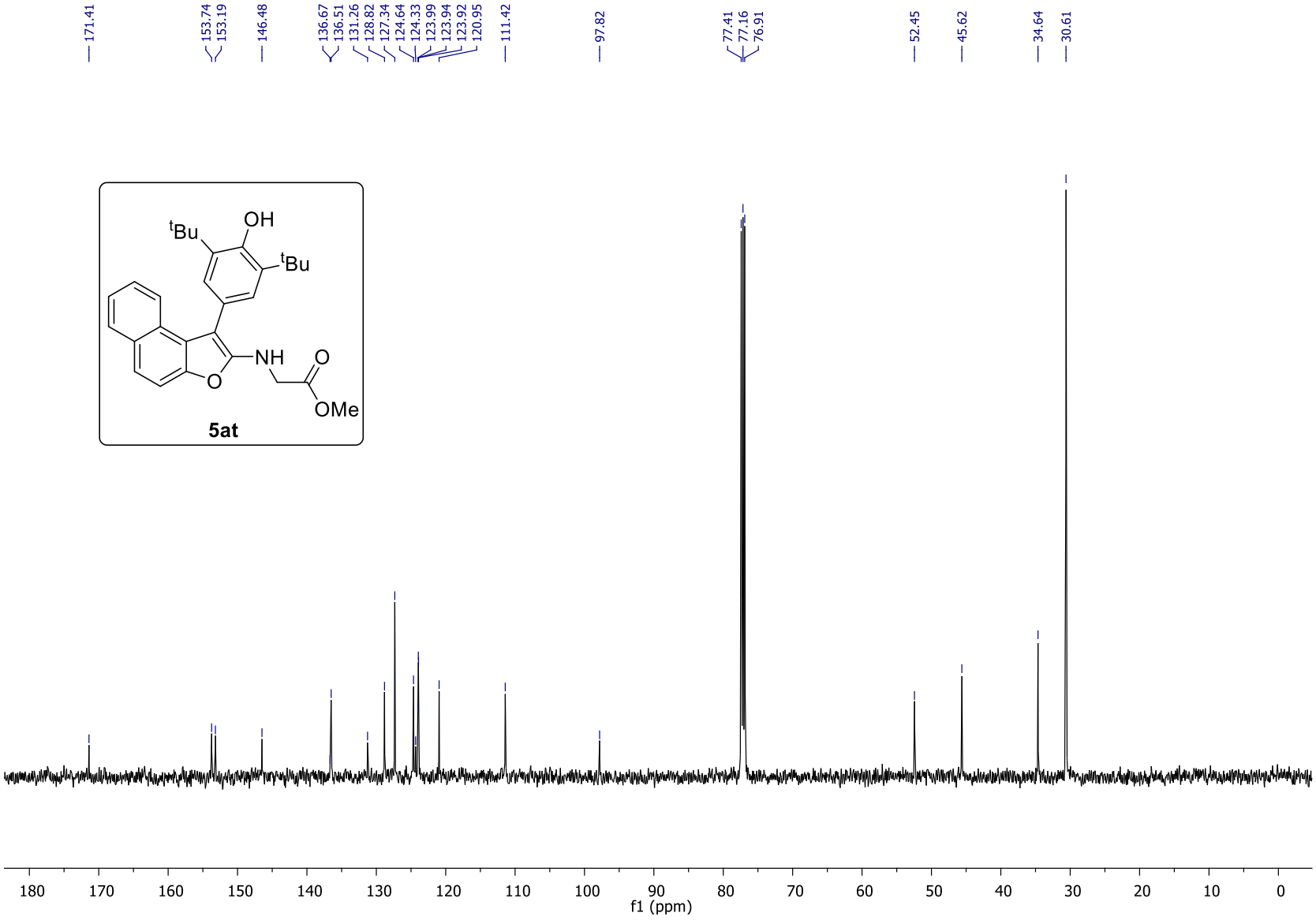
^{13}C NMR of compound **5as** in $CDCl_3$



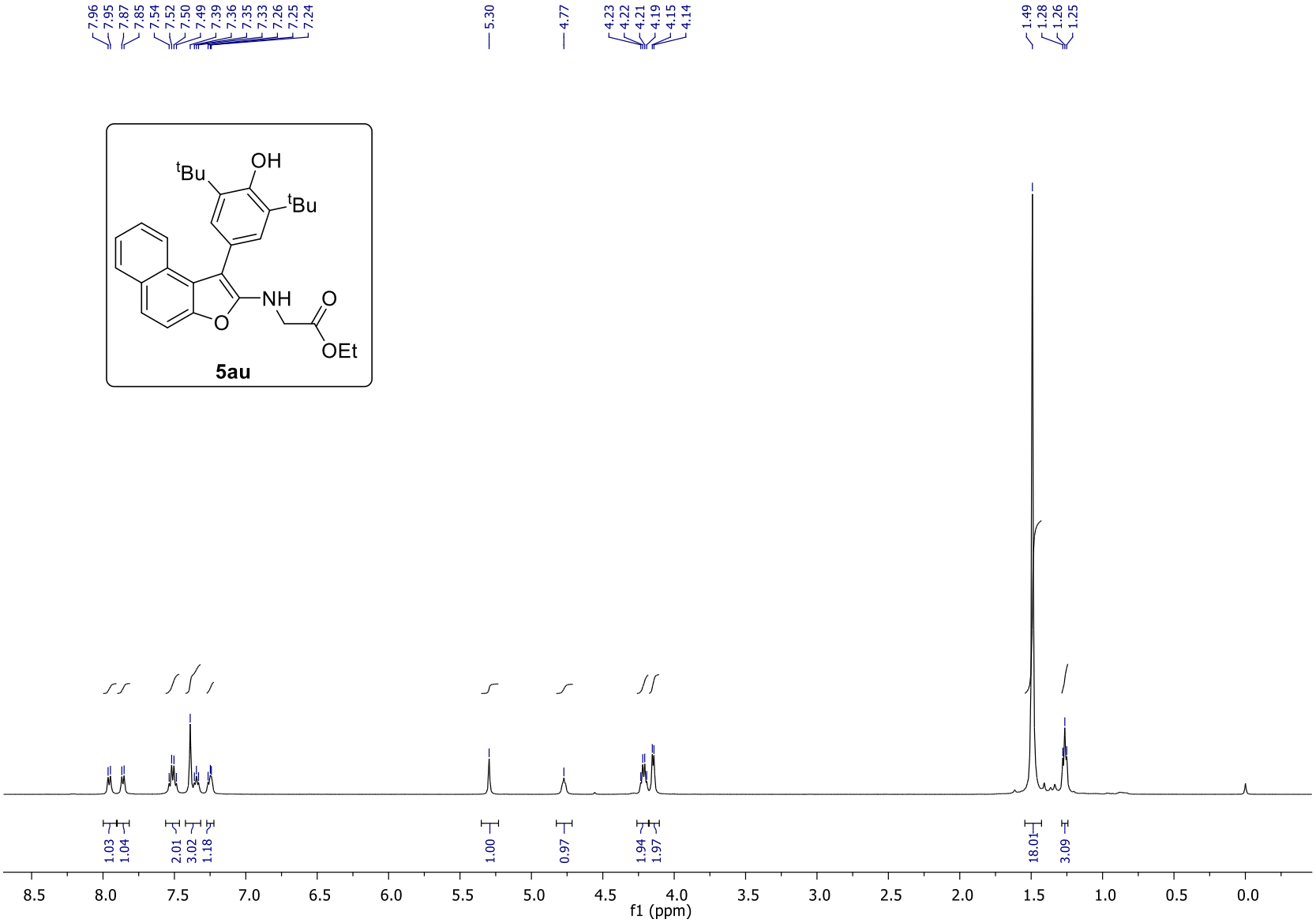
^{1}H NMR of compound **5at** in $CDCl_3$



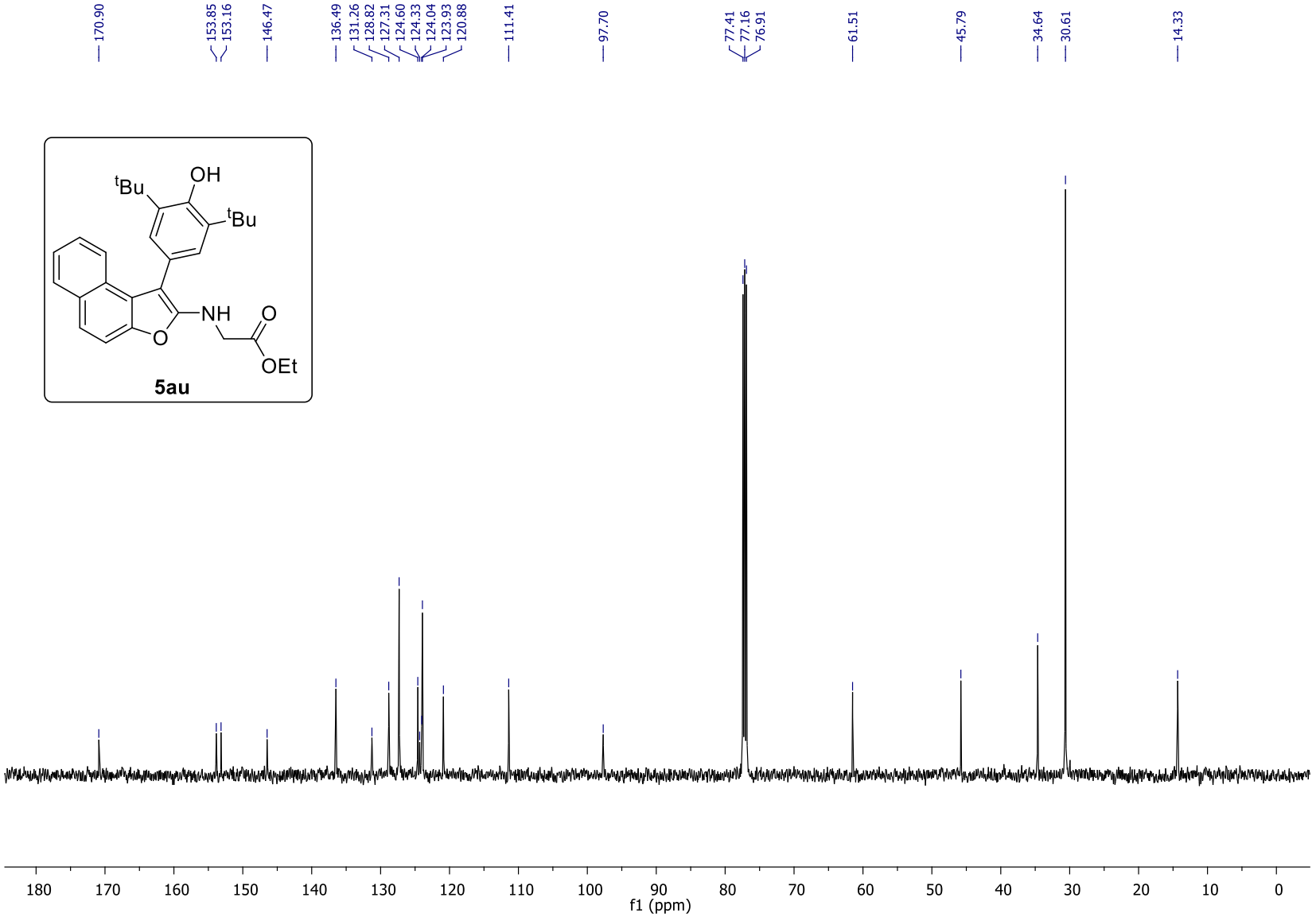
^{13}C NMR of compound **5at** in $CDCl_3$



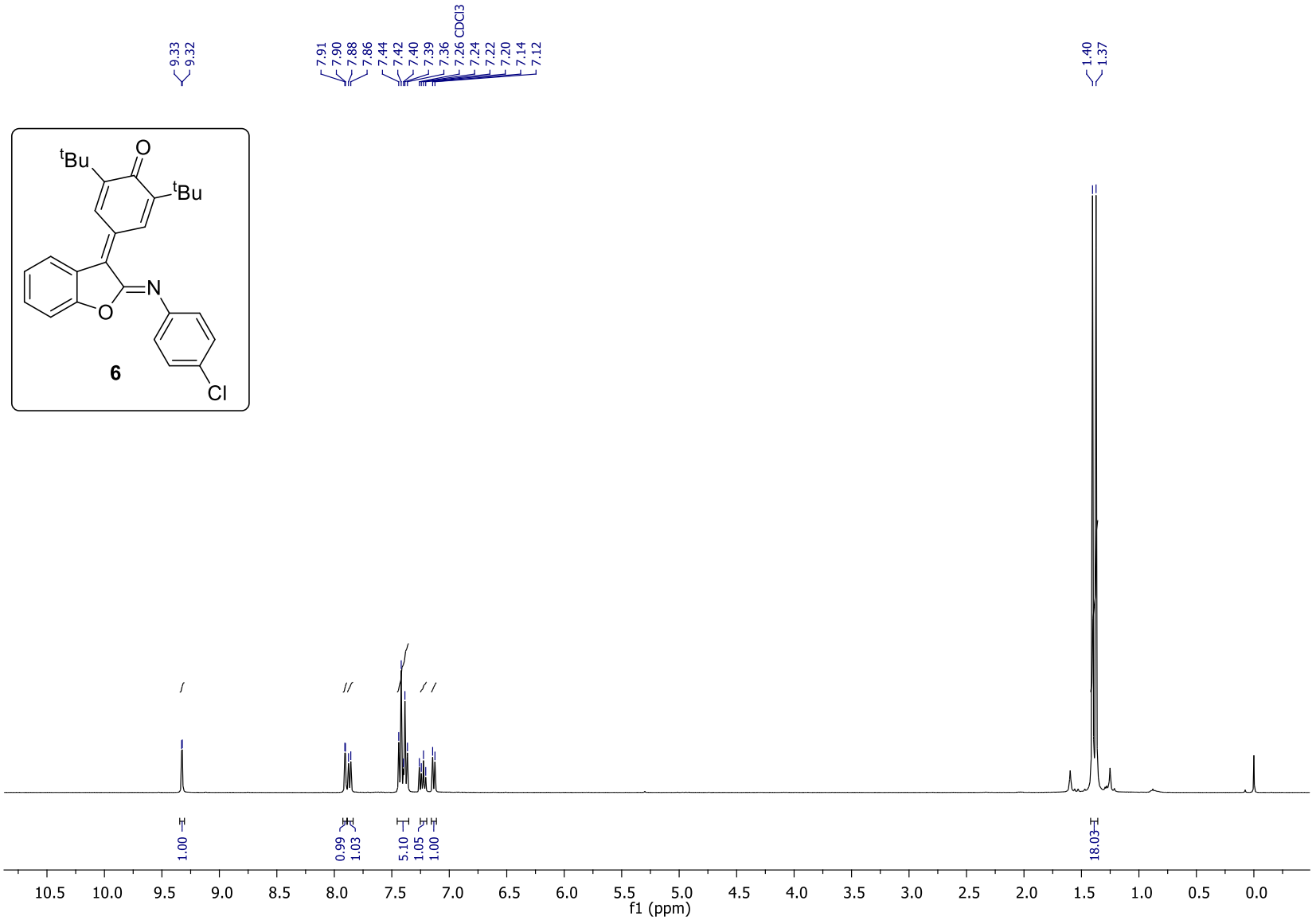
^{1}H NMR of compound **5au** in $CDCl_3$



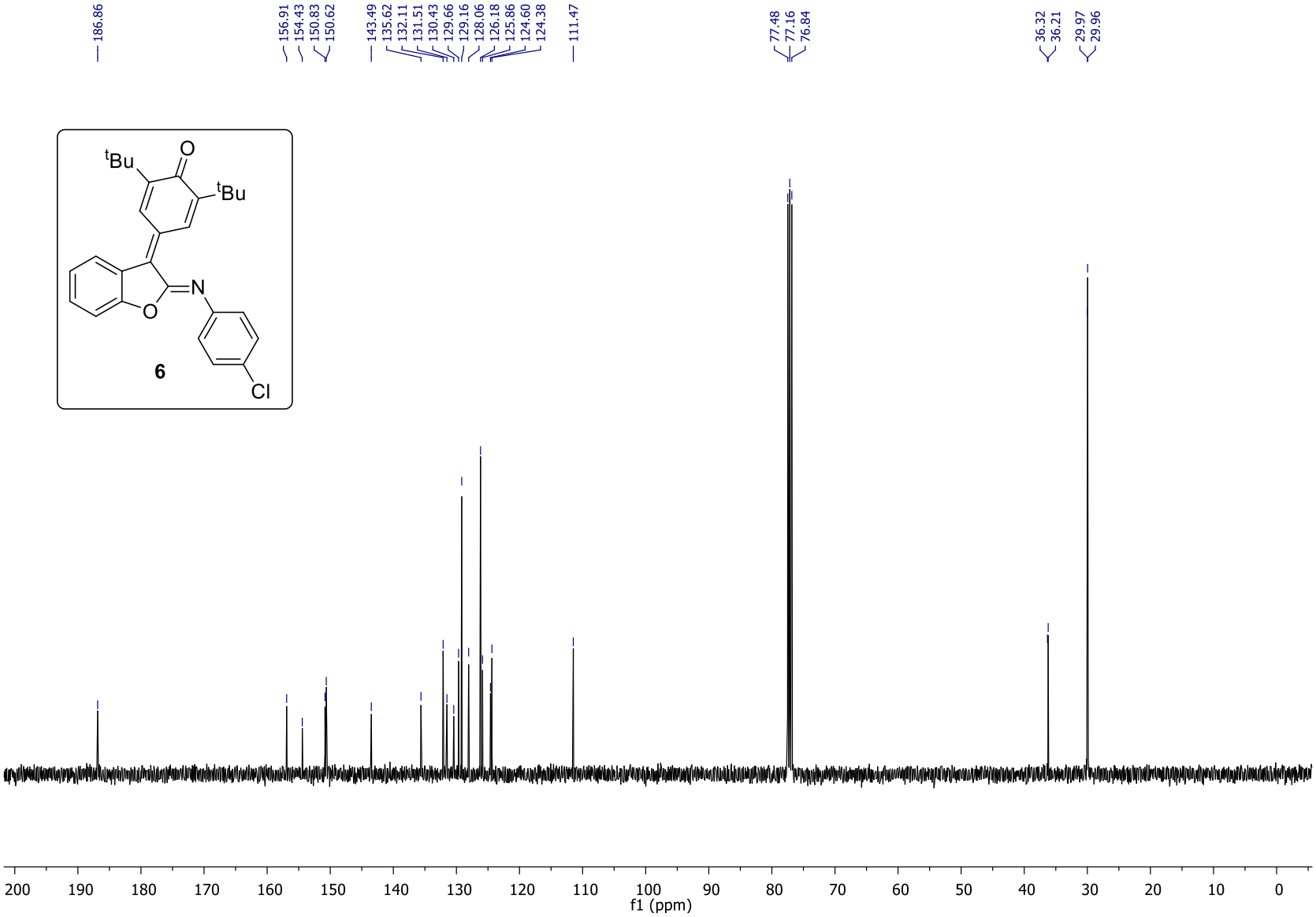
^{13}C NMR of compound **5au** in $CDCl_3$



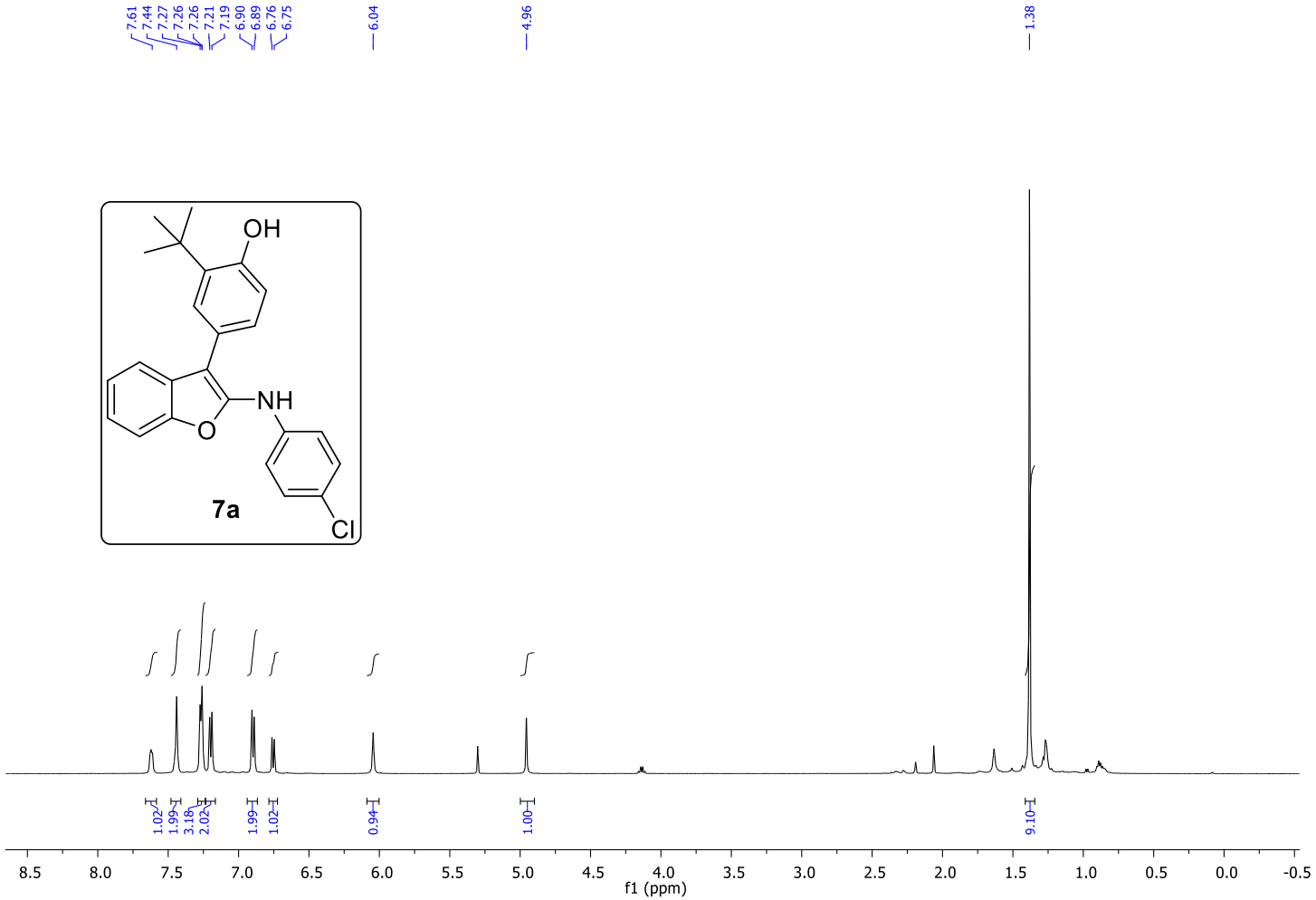
^{1}H NMR of compound **6** in $CDCl_3$



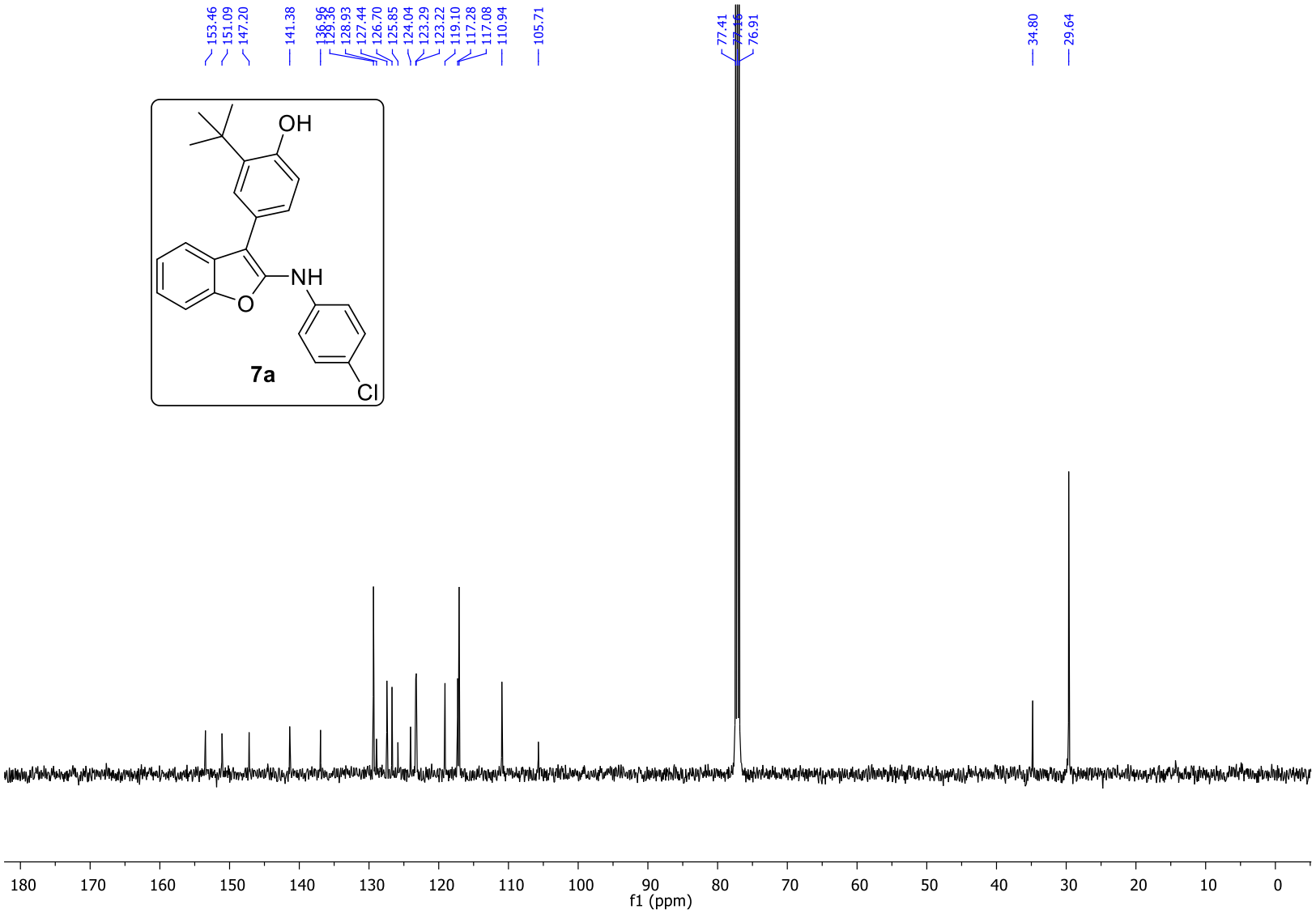
^{13}C NMR of compound **6** in $CDCl_3$



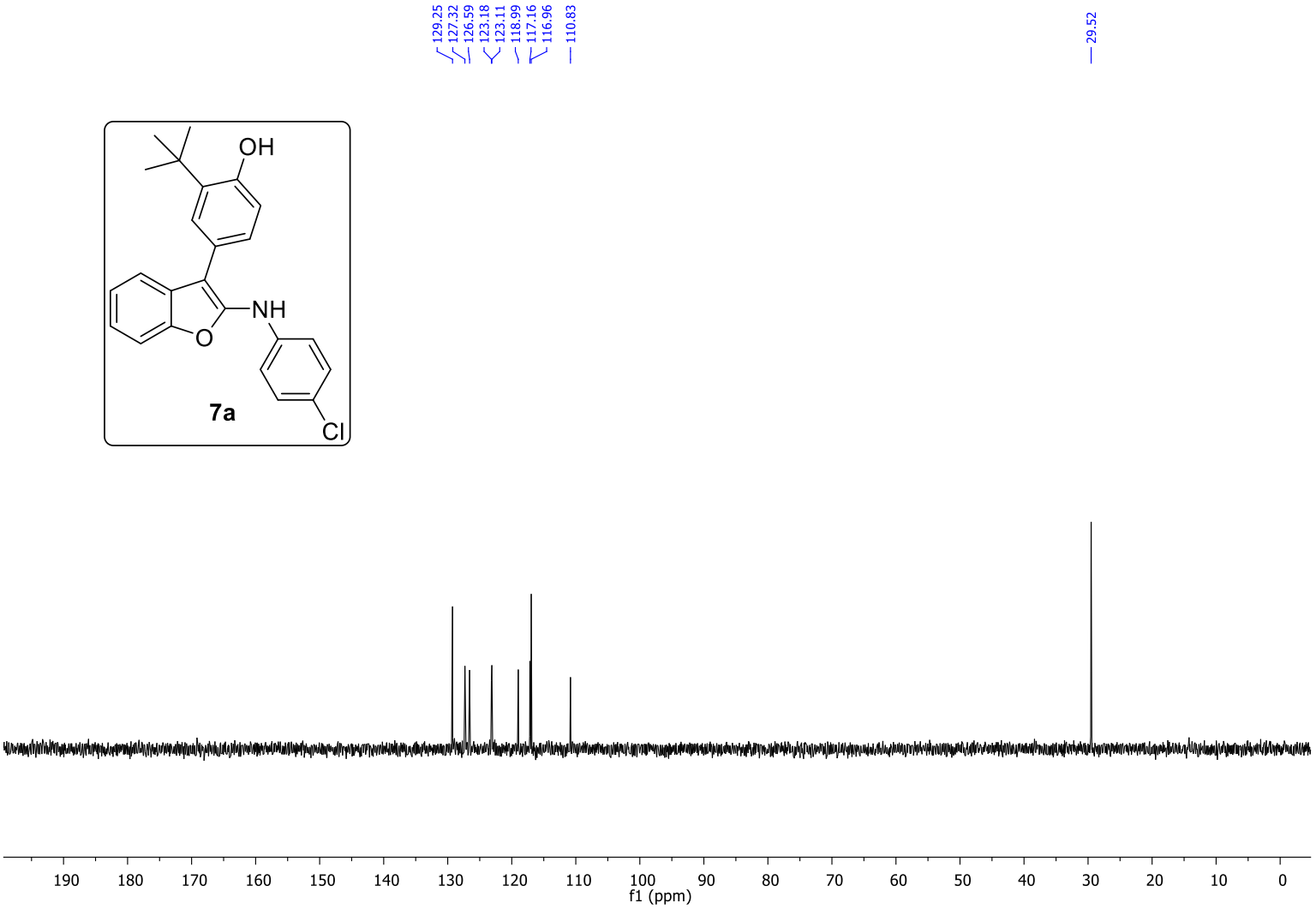
^{1}H NMR of compound **7a** in $CDCl_3$



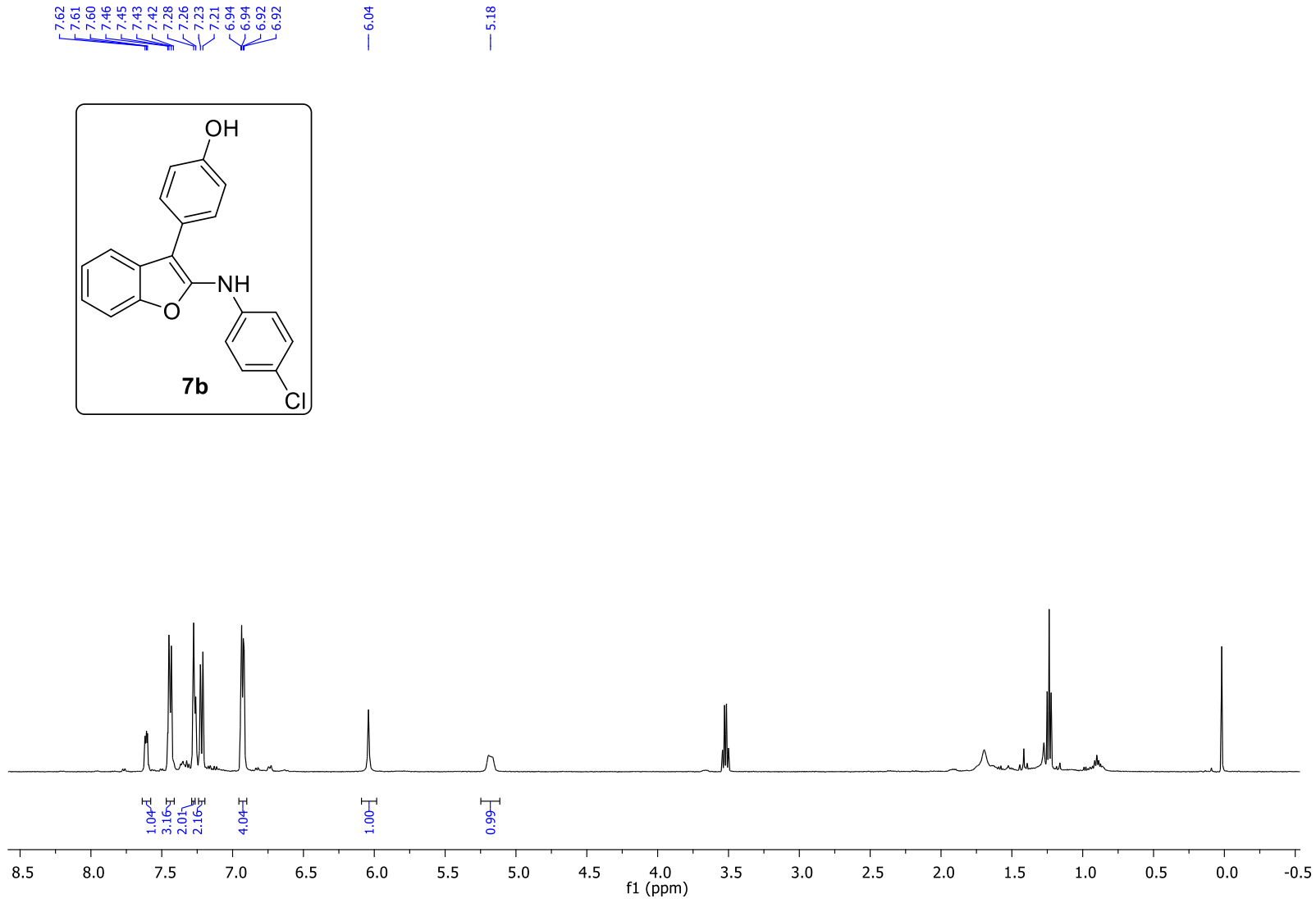
^{13}C NMR of compound **7a** in $CDCl_3$



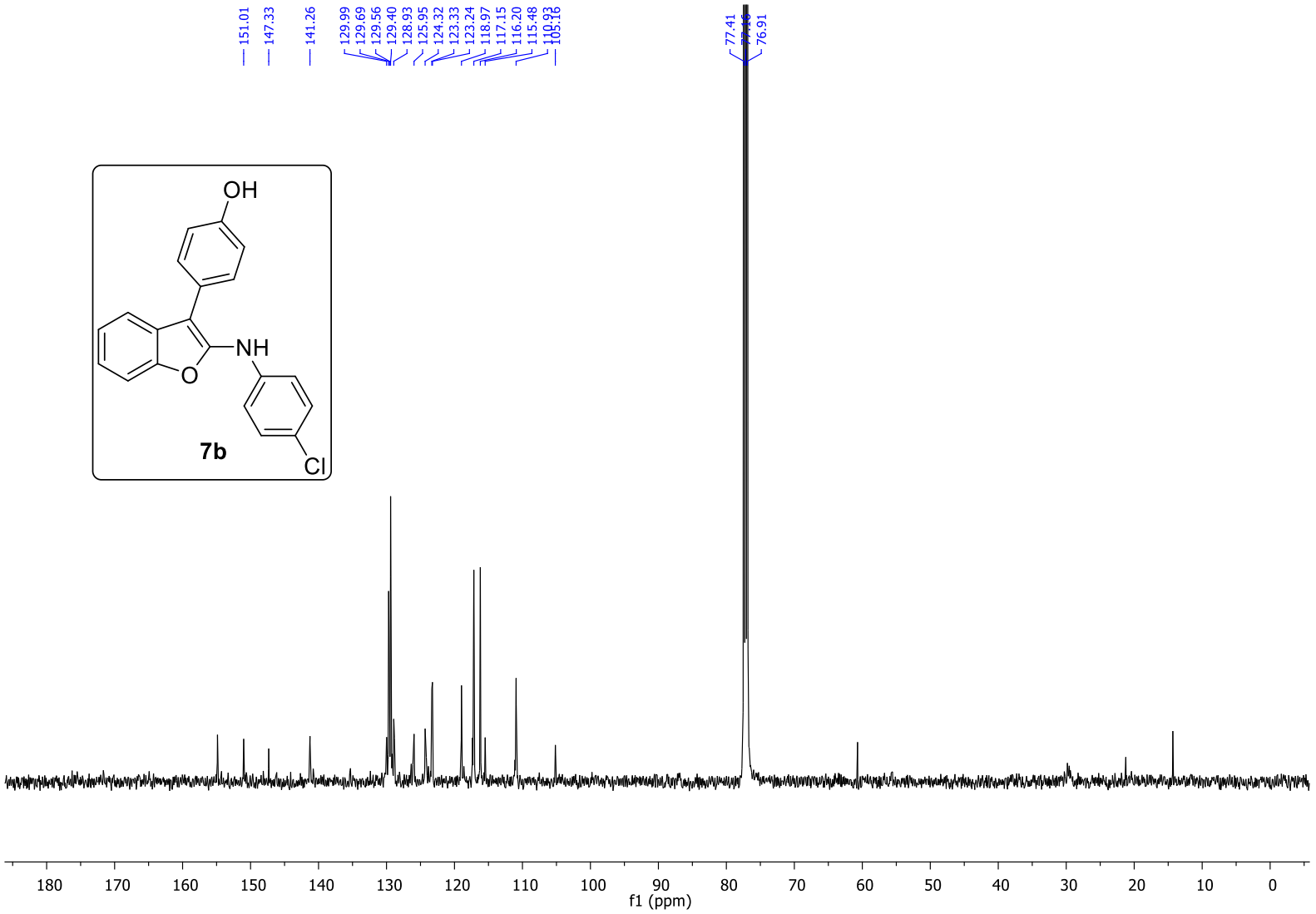
DEPT 135NMR of compound **7a** in $CDCl_3$



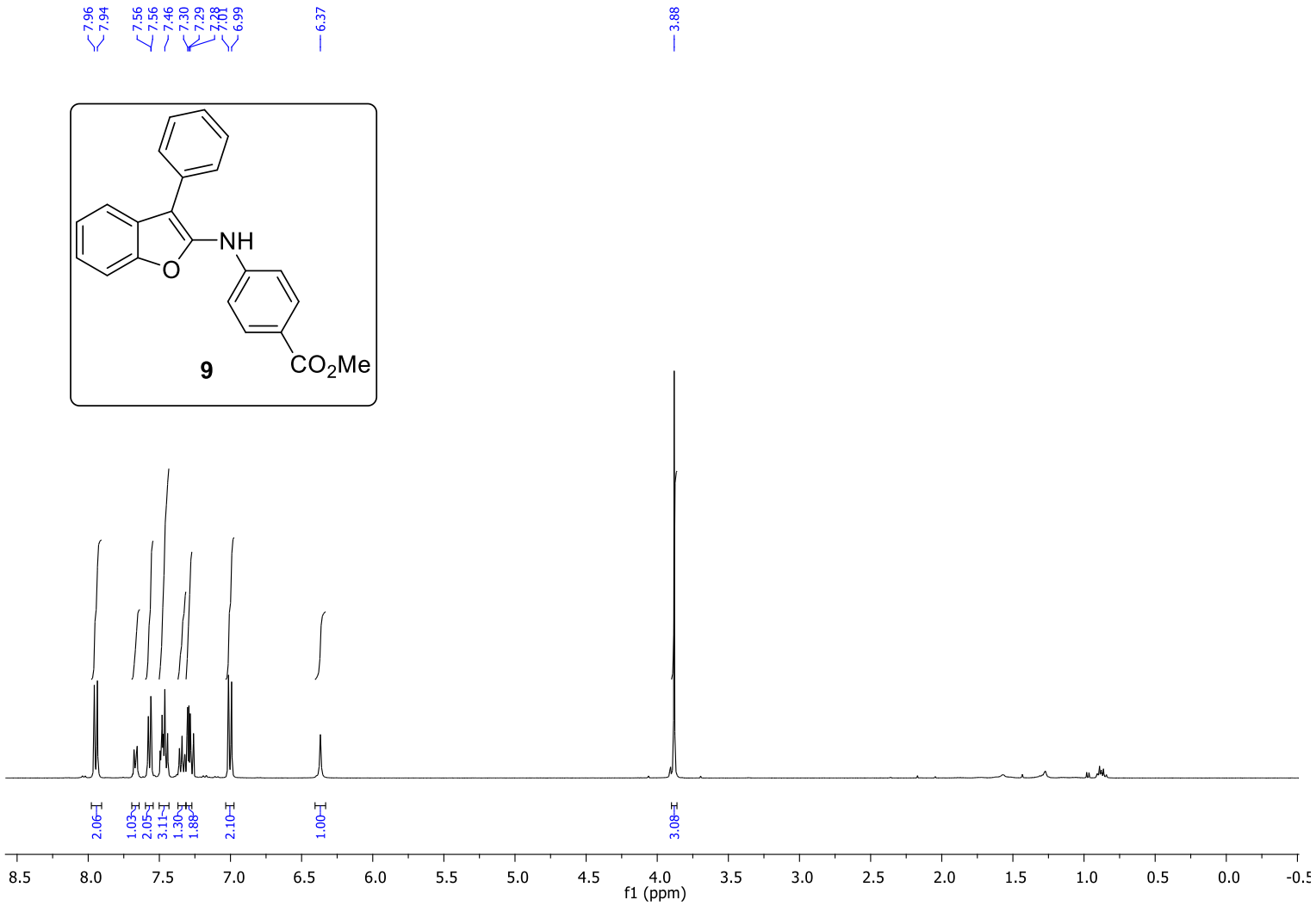
^{1}H NMR of compound **7b** in $CDCl_3$



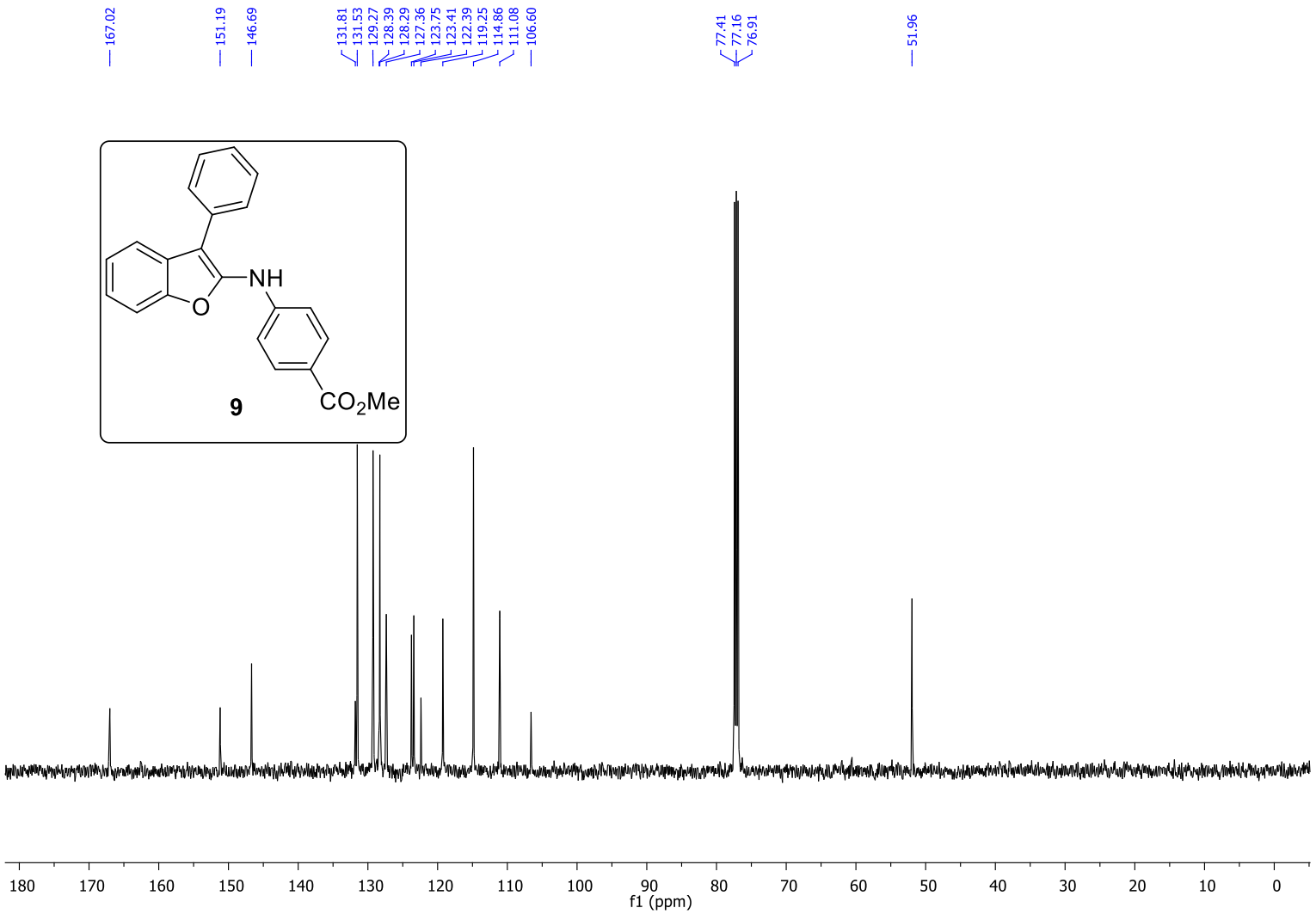
^{13}C NMR of compound **7b** in $CDCl_3$



^{1}H NMR of compound **9** in $CDCl_3$

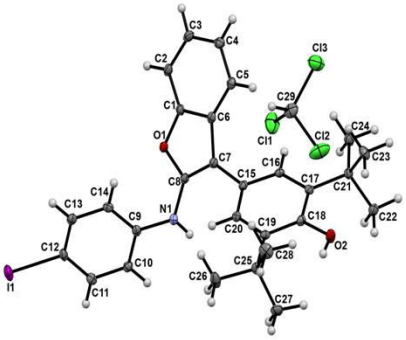


^{13}C NMR of compound **9** in $CDCl_3$

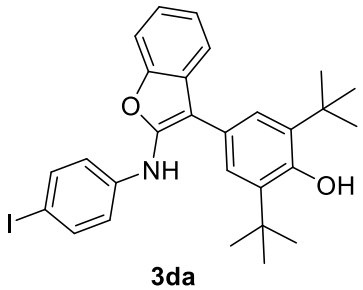

167.02
151.19
146.69
131.81
131.53
129.27
128.39
128.29
127.36
123.75
123.41
122.39
119.25
114.86
111.08
106.60
77.41
77.16
76.91
51.96
NH
O
CO2Me
9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8. X-Ray Crystal Data

X-Ray Crystal Data of Compound 3da



3da,CCDC: **2231953**

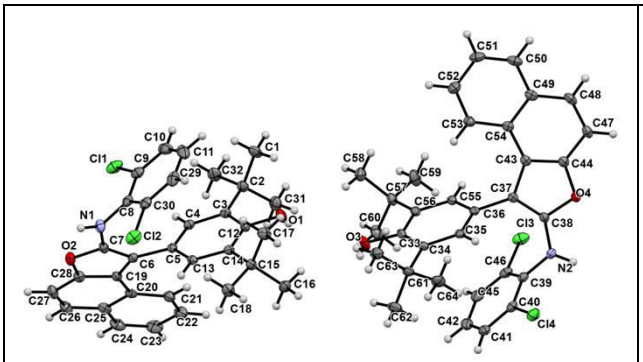


3da

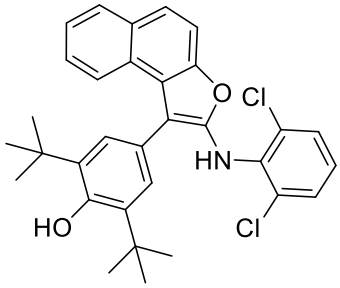
Bond precision:	C-C = 0.0020 A		Wavelength=0.71073
Cell:	a=9.7428(8)	b=12.0230(12)	c=12.5462(12)
	alpha=91.228(3)	beta=94.255(3)	gamma=108.270(3)
Temperature:	100 K		
	Calculated		Reported
Volume	1390.2(2)		1390.2(2)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C28 H30 I N O2, C H Cl3		C28 H30 I N O2, C H Cl3
Sum formula	C29 H31 Cl3 I N O2		C29 H31 Cl3 I N O2
Mr	658.80		658.80
Dx,g cm-3	1.574		1.574
Z	2		2
Mu (mm-1)	1.468		1.468
F000	664.0		664.0
F000'	664.15		
h,k,lmax	12,15,16		12,15,16
Nref	6080		5967
Tmin,Tmax	0.824,0.876		0.614,0.746
Tmin'	0.735		

Correction method= # Reported T Limits: Tmin=0.614 Tmax=0.746
AbsCorr = MULTI-SCAN
Data completeness= 0.981 Theta(max)= 27.000
R(reflections)= 0.0201(5821) wR2(reflections)=0.0510(5967)
S = 1.069 Npar= 351

X-Ray Crystal Data of Compound 5am



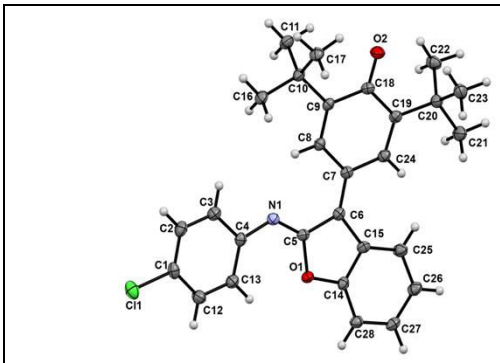
5am,CCDC: **2231951**



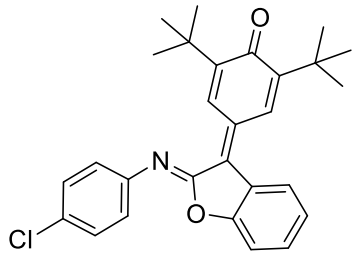
5am

Bond precision:	C-C = 0.0021 A	Wavelength=0.71073	
Cell:	a=12.4014(18)	b=26.842(4)	c=16.599(3)
	alpha=90	beta=98.868(6)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	5459.4(15)	5459.4(14)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C32 H31 Cl2 N O2	?	
Sum formula	C32 H31 Cl2 N O2	C64 H62 Cl4 N2 O4	
Mr	532.48	1064.95	
Dx,g cm-3	1.296	1.296	
Z	8	4	
Mu (mm-1)	0.268	0.268	
F000	2240.0	2240.0	
F000'	2243.18		
h,k,lmax	15,34,21	15,34,21	
Nref	11928	11921	
Tmin,Tmax	0.968,0.976	0.678,0.746	
Tmin'	0.950		
Correction method= # Reported T Limits: Tmin=0.678 Tmax=0.746			
AbsCorr = MULTI-SCAN			
Data completeness=	0.999	Theta(max)= 26.998	
R(reflections)=	0.0367(10505)	wR2(reflections)=0.0943(11921)	
S = 1.025	Npar= 685		

X-Ray Crystal Data of Compound 6



6,CCDC: **2231952**



6

Bond precision:	C-C = 0.0019 A	Wavelength=0.71073	
Cell:	a=8.5276(9)	b=15.1024(13)	c=17.9533(17)
	alpha=90	beta=93.727(4)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2307.3(4)	2307.3(4)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C28 H28 Cl N O2	?	
Sum formula	C28 H28 Cl N O2	C28 H28 Cl N O2	
Mr	445.96	445.96	
Dx,g cm-3	1.284	1.284	
Z	4	4	
Mu (mm-1)	0.191	0.191	
F000	944.0	944.0	
F000'	944.95		
h,k,lmax	10,19,22	10,19,22	
Nref	5027	5022	
Tmin,Tmax	0.975,0.983	0.678,0.746	
Tmin'	0.961		
Correction method= # AbsCorr = MULTI-SCAN	Reported T Limits: Tmin=0.678 Tmax=0.746		
Data completeness=	0.999	Theta(max)= 26.999	
R(reflections)=	0.0338(4304)	wR2(reflections)=0.0873(5022)	
S = 1.068	Npar= 296		

9. References

(1) (a) Zhao, K.; Zhi, Y.; Shu, T.; Valkonen, A.; Rissanen, K.; Enders, D.; *Angew. Chem. Int. Ed*. **2016**, *55*, 12104.(b) Chu, W.-D.; Zhang, L.-F.; Bao, X.; Zhao, X.- H.; Zeng, C.; Du, J.-Y.; Zhang, G.-B.; Wang, F.-X.; Ma, X.-Y.; Fan, C.- A.; *Angew. Chem. Int. Ed*. **2013**, *52*, 9229.

(2)Škoch, K.; Císařová, I.; Štěpnička, P.; *Chem. - Eur. J.*, **2018**, *24*, 13788-13791.