Supporting Information of

Gold-Catalyzed Tandem Reaction of 2-Alkynylanilines, followed by 1,6-Conjugate Addition to *para*-Quinone Methides: An efficient access to unsymmetrical Diarylindolylmethanes

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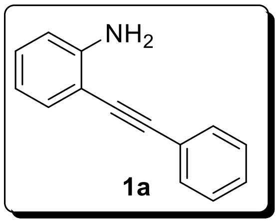
General Information

All reactions were carried in an oven dried reaction tubes. Triethylamine and dichloromethane were dried over calcium hydride, distilled and stored with molecular sieves. Melting points were recorded on SMP20 melting point apparatus and are uncorrected. Most of the reagents and starting materials were purchased from commercial sources and used as such. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ (400 and 100 MHz respectively) on Bruker FT-NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS and the coupling constants (J) are reported in Hz. High resolution mass spectra were recorded on ESI-Q-TOF mass spectrometer (Bruker Daltonics Inc., Germany) at Organic Chemistry Research Center of Sogang University, Seoul, Korea. Spectrometer. FT-IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer. Thin layer chromatography was performed on Merck silica gel 60 F254 TLC plates. Column chromatography was carried out through silica gel (100-200 mesh) using EtOAc/hexane as an eluent.

General procedure for the synthesis of *o*-alkynyl anilines (1a-i)

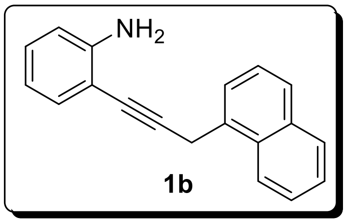
To a stirred solution of 2-iodo-aniline (1 equiv), $PdCl_2(PPh_3)_2$ (0.05 equiv), and CuI (0.05 equiv), in triethylamine (0.2 M) at room temperature was added Terminal acetylene (1.1 equiv) under argon atmosphere. After completion of the reaction (by TLC), triethylamine was removed under reduced pressure and the reaction mixture was then diluted with dichloromethane and water. Organic layer was separated and the aqueous layer was extracted with DCM (x2). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was purified through silica gel column chromatography using hexane/EtOAc to obtain pure 2-alkynyl aniline derivatives.

2-(phenylethynyl) aniline (1a):



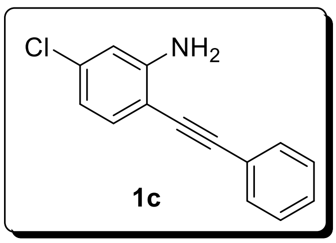
The reaction was performed at 9.13 mmol of *o*-iodo aniline: Yield 96% (1691.6 mg), colorless solid, m.p. 88-89 °C; R_f = 0.6 (hexanes/EtOAc = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.37-7.34 (m, 4H), 7.14 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 8.4 Hz, 2H), 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 132.3, 131.6, 129.9, 128.6, 128.4, 123.5, 118.2, 114.5, 108.1, 94.9, 86.0; IR (KBr, cm^{-1}) 3432, 3312, 3052, 1466, 1256, 1156, 986; HRMS (ESI) $[M + Na]^+$ calculated for $C_{14}H_{11}NNa^+$: 216.0789, found 216.0793.

2-(3-(naphthalen-1-yl) prop-1-yn-1-yl) aniline (1b):



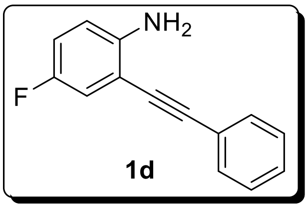
The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 97% (222.2 mg), pale yellow solid, m.p. 86-87 °C; R_f = 0.6 (hexanes/EtOAc = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.61-7.52 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.13-7.09 (m, 1H), 6.72-6.67 (m, 2H), 4.30 (s, 2H), 4.13 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 133.8, 132.7, 132.2, 131.4, 129.2, 128.9, 127.7, 126.3, 125.8, 125.7, 123.4, 117.9, 114.2, 108.5, 92.6, 80.2, 24.0; IR (KBr, cm^{-1}) 3462, 3322, 3042, 1446, 1266, 1110, 824; HRMS (ESI) $[M + Na]^+$ calculated for $C_{29}H_{15}NNa^+$: 280.1102, found 280.1106.

5-chloro-2-(phenylethynyl) aniline (1c):



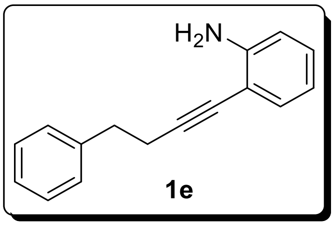
The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 93% (194 mg), white solid, R_f = 0.3 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53, 7.39-7.37 (m, 3H), 7.39-7.29 (m, 1H), 6.75-6.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 135.3, 133.0, 131.5, 128.5, 123.0, 118.2, 114.0, 106.5, 95.4, 84.9; IR (KBr, cm^{-1}) 3432, 3302, 3022, 1466, 1256, 1110, 824, 737; HRMS (ESI) $[M + Na]^+$ calculated for C14H10ClNNa$^+$: 250.0399, found 250.0394.

4-fluoro-2-(phenylethynyl)aniline (1d):



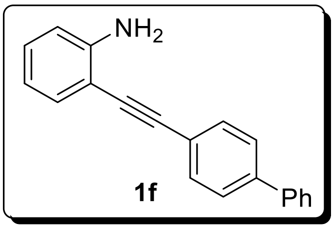
The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 85% (165.15 mg), Brown solid, R_f = 0.4 (hexanes/EtOAc = 9:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.37-7.35 (m, 3H), 7.10-7.07 (m, 1H), 6.90-6.85 (m, 1H), 6.67-6.64 (m, 1H), 4.15 (bs, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 154.1, 144.2, 131.6, 129.1, 128.6, 128.5, 122.8, 117.9, 117.7, 117.0, 116.8, 115.4, 115.3, 108.8, 108.7, 95.4, 85.0; IR (KBr, cm^{-1}) 3468, 3379, 2934, 2845, 2214, 1621, 1498, 1435, 735; HRMS (ESI) $[M + Na]^+$ calculated for $C_{14}H_{10}FNNa^+$: 234.0695, found 234.0670.

2-(4-phenylbut-1-yn-1-yl) aniline (1e):



The reaction was performed at 0.91 mmol of *o*-iodo aniline: Yield 95% (192.6 mg), block liquid, R_f = 0.60 (hexanes/EtOAc = 9:1): ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 7.17-7.13 (m, 1H), 6.75-6.69 (m, 2H), 4.04 (bs, 2H), 3.01 (t, J = 7.2 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.7, 132.0, 129.0, 128.6, 128.5, 126.4, 117.8, 114.2, 108.6, 35.2, 21.8; IR (KBr, cm^{-1}) 3432, 3342, 3042, 2935, 2846, 1436, 1256, 1110, 824, 777; HRMS (ESI) $[M + Na]^+$ calculated for $C_{16}H_{15}NNa^+$: 244.1102, found 244.1106.

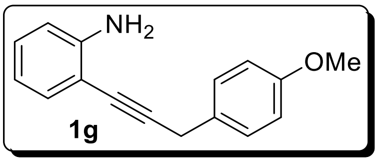
2-([1, 1'-biphenyl]-4-ylethynyl) aniline (1f):



1f

The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 88% (217.7 mg), block liquid, R_f = 0.6 (hexanes/EtOAc = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42-7.38 (m, 2H), 7.18-7.04 (m, 1H), 6.76-6.73 (m, 2H), 4.30 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.9, 140.3, 135.2, 133.0, 132.3, 131.9, 130.3, 129.8, 128.9, 127.7, 127.2, 127.1, 127.0, 122.2, 118.0, 114.4, 108.0, 94.7, 86.6; IR (KBr, cm^{-1}) 3472, 3302, 3062, 1426, 667; HRMS (ESI) [M + Na]$^+$ calculated for $C_{20}H_{15}NNa^+$: 292.1102, found 292.1106.

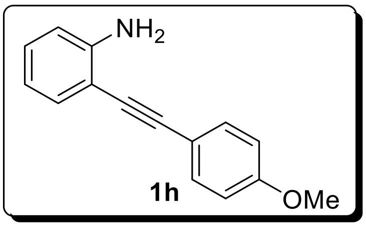
2-(3-(4-methoxyphenyl) prop-1-yn-1-yl) aniline (1g):



1g

The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 90% (196.48 mg), block liquid, R_f = 0.3 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.8 Hz, 2H), 7.33-7.28 (m, 1H), 7.14-7.10 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.72-6.68 (m, 2H), 4.23 (bs, 2H), 3.86 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 147.8, 132.2, 129.1, 128.9, 128.8, 117.8, 114.2, 114.0, 108.6, 93.4, 78.9, 55.3, 25.2; IR (Thin film, cm^{-1}) 3471, 3373, 2946, 2923, 2212, 1612, 1545, 1269, 750; HRMS (ESI) [M + Na]$^+$ calculated for $C_{16}H_{15}NNaO^+$: 260.1051, found 260.1055.

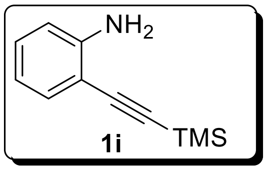
2-((4-methoxyphenyl) ethynyl) aniline (1h):



1h

The reaction was performed at 0.92 mmol of *o*-iodo aniline: Yield 95% (192.85 mg), Brown solid, m.p. 98-100 °C; R_f = 0.6 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.38-7.35 (m, 1H), 7.15-7.11 (m, 1H), 6.91-6.87 (m, 2H), 6.74-6.70 (m, 2H), 4.27 (bs, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.6, 132.9, 132.0, 129.4, 118.0, 115.5, 114.3, 114.0, 108.4, 94.6, 86.7, 55.4; IR (KBr, cm^{-1}) 3462, 3332, 3062, 1446, 1255, 112, 824, 757; HRMS (ESI) $[M + Na]^+$ calculated for $C_{15}H_{13}NNaO^+$: 246.0894, found 246.0898.

2-((trimethylsilyl)ethynyl)aniline (1i):



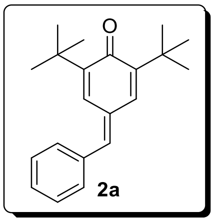
The reaction was performed at 1.2 mmol of *o*-iodo aniline: Yield 96% (217.72 mg), block liquid, R_f = 0.6 (hexanes/EtOAc = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 1H), 7.13-7.09 (m, 1H), 6.69-6.64 (m, 2H), 4.23 (bs, 2H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 132.3, 129.9, 114.2, 107.8, 101.8, 99.8, 0.17; IR (Thin film, cm^{-1}) 3482, 3412, 3062, 1436, 1216, 1110, 814, 757; HRMS (ESI) $[M + Na]^+$ calculated for $C_{20}H_{15}NNaSi^+$: 212.0871, found 212.0876.

General procedure for the synthesis of p-quinone methides (2a-k)

In a Dean-Stark apparatus, a mixture of 2,6-di-tert-butylphenol (1 equiv.) and aldehyde (1 equiv.) in toluene (0.25 M) was placed and refluxed. Piperidine (2 equiv.) was added to this reaction mixture in a drop-wise manner within an hour and the resultant mixture was stirred at reflux temperature for 12 h. The reaction mixture was cooled to 100 °C and acetic anhydride (2 equiv.) was added and the resulting solution was stirred for 30 more minutes at the same temperature. The reaction mixture was then cooled to room temperature and poured in to ice cold water (50 mL) and extracted with dichloromethane (50 mL X 2). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to obtain a pure p-quinone methide.

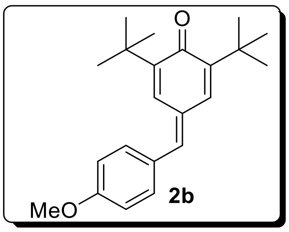
Characterization data for p-quinone methides (2a-c & 2e-k)

4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (2a):



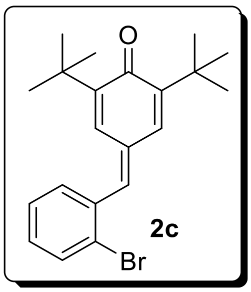
The reaction was performed at 3 mmol of *o*-iodo aniline: Yield 70% (617.2 mg), yellow solid, m.p. 77-79 °C; R_f = 0.6 (hexanes/EtOAc = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 5H), 7.21 (s, 2H), 7.05 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 186.8, 149.4, 147.8, 124.5, 135.9, 135.1, 131.9, 130.4, 129.1, 128.8, 127.8, 35.5, 35.0, 29.6, 29.5; IR (KBr, cm^{-1}) 2945, 2826, 1599, 1525, 1540, 1265, 1172, 1012, 812; HRMS (ESI) $[M + Na]^+$ calculated for $C_{21}H_{26}NaO^+$: 317.1881, found 317.1885.

2,6-di-tert-butyl-4-(4-methoxybenzylidene)cyclohexa-2,5-dien-1-one (2b):



The reaction was performed at 1.0 mmol of *o*-iodo aniline: Yield 79% (255.9 mg), yellow solid, m.p. 108-110 °C; R_f = 0.53 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.15 (s, 1H), 7.02-6.99 (s, 3H), 3.89 (d, *J* = 3.6 Hz, 3H), 1.35 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 186.5, 160.6, 149.0, 147.2, 142.7, 142.6, 135.4, 130.5, 128.6, 127.8, 112.3, 55.4, 35.4, 34.9, 29.6, 29.5; IR (KBr, cm^{-1}) 2954, 2862, 1599, 1552, 1504, 1256, 1172, 1021, 821; HRMS (ESI) $[M + Na]^+$ calculated for $C_{22}H_{28}NaO_2^+$: 347.1987, found 347.1992.

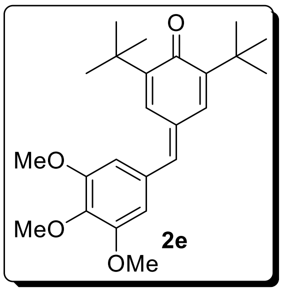
4-(2-bromobenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (2c):



The reaction was performed at 1.2 mmol of *o*-iodo aniline: Yield 78% (348.1 mg), yellow solid, R_f = 0.60 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.41

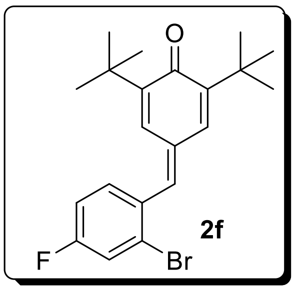
(d, J = 4.4 Hz, 2H), 7.30 (d, J = 2.4 Hz, 1H), 7.30-7.28 (m, 1H), 7.25 (s, 1H), 7.09 (d, J = 2.4 Hz, 1H), 1.36 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 149.7, 148.3, 140.8, 135.8, 134.6, 133.2, 132.6, 132.3, 130.3, 127.6, 127.2, 125.0, 35.3, 35.1, 29.5; IR (KBr, cm^{-1}) 2963, 2930, 2855, 1612, 1556, 1557, 1369, 942; HRMS (ESI) $[M + Na]^+$ calculated for $C_{21}H_{25}BrNaO^+$: 395.0986, found 395.0991.

2,6-di-tert-butyl-4-(3,4,5-trimethoxybenzylidene)cyclohexa-2,5-dien-1-one (2e):



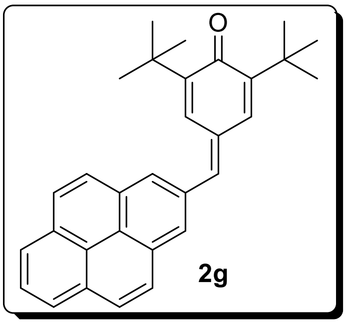
The reaction was performed at 1.2 mmol of *o*-iodo aniline: Yield 60% (293.04 mg), yellow solid, m.p. 124-126 °C; R_f = 0.51 (hexanes/EtOAc = 4:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 2 HZ, 1H), 7.14 (s, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.73 (s, 2H), 3.94 (s, 3H), 3.92 (s, 6H), 1.35 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 153.3, 149.2, 147.6, 142.5, 139.2, 135.1, 131.5, 131.3, 127.7, 107.7, 61.0, 56.1, 35.5, 35.0, 29.6, 29.5; IR (KBr, cm^{-1}): 2967, 2857, 1625, 1610, 1466, 1350, 1215, 1145; HRMS (ESI) $[M + Na]^+$ calculated for $C_{24}H_{32}NaO_4^+$: 407.2198, found 407.2194.

4-(2-bromo-4-fluorobenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (2f):



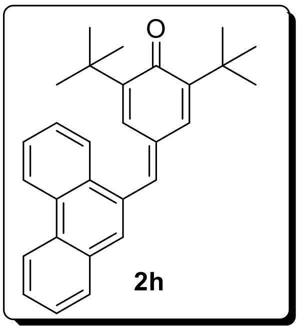
The reaction was performed at 2.0 mmol of *o*-iodo aniline: Yield 62% (483.0 mg), yellow solid, m.p. 138-140 °C; R_f = 0.63 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 2H), 7.21 (d, J = 2.4 Hz, 1H), 7.14-7.10 (m, 2H), 7.05 (d, J = 2.4 Hz, 1H), 1.33 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 163.6, 161.1, 149.9, 148.4, 139.4, 134.4, 133.2, 133.1, 132.7, 132.1, 132.0, 127.3, 125.4, 125.3, 120.8, 120.5, 114.8, 114.6, 35.5, 35.1, 29.5; IR (KBr, cm^{-1}) 3011, 2961, 2923, 2855, 1606, 1591, 1442, 1352, 1235, 768; HRMS (ESI) [M + Na]$^+$ calculated for $C_{21}H_{24}BrFNaO^+$: 413.0892, found 413.0897.

2,6-di-tert-butyl-4-(pyren-2-ylmethylene)cyclohexa-2,5-dien-1-one (2g):



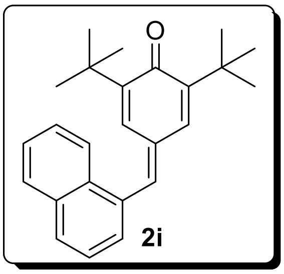
The reaction was performed at 0.82 mmol of *o*-iodo aniline: Yield 80% (274.2 mg), red solid, R_f = 0.60 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.49 (m, 10H), 7.30 (s, 1H), 7.29 (s, 1H), 1.43 (d, *J* = 3.6 Hz, 9H), 1.27 (d, *J* = 3.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 149.7, 147.9, 140.9, 134.9, 133.1, 132.0, 131.3, 130.8, 130.0, 128.9, 128.6, 128.4, 127.3, 126.4, 126.0, 125.9, 124.9, 124.5, 123.8, 35.5, 35.2, 29.6, 29.5; IR (KBr, cm^{-1}) 3012, 2963, 2842, 1681, 1456, 1246, 1120, 814, 767; HRMS (ESI) [M + Na]$^+$ calculated for $C_{31}H_{30}NaO^+$: 441.2194, found 441.2199

2,6-di-tert-butyl-4-(phenanthren-9-ylmethylene)cyclohexa-2,5-dien-1-one (2h):



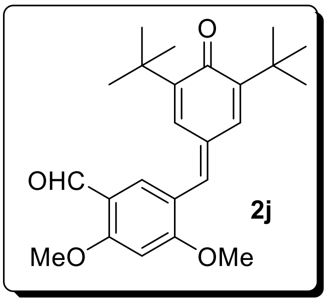
The reaction was performed at 1.2 mmol of *o*-iodo aniline: Yield 55% (211.2 mg), yellow solid, m.p. 146-148 °C; R_f = 0.60 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74-8.66 (m, 2H), 8.05-8.03 (m, 1H), 7.88 (s, 1H), 7.87-7.59 (m, 5H), 7.54 (d, *J* = 2.4 HZ, 1H), 7.21 (s, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 1.35 (s, 9H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 149.2, 148.0, 140.6, 134.6, 133.6, 131.5, 131.2, 130.9, 130.8, 130.7, 130.5, 129.2, 128.5, 127.7, 127.3, 127.2, 127.1, 125.5, 122.7, 35.4, 35.1, 29.6, 29.5; IR (KBr, cm^{-1}): 3002, 2956, 2865, 1613, 1567; HRMS (ESI) [M + Na]$^+$ calculated for $C_{29}H_{30}NaO^+$: 407.2194, found 407.2199.

2,6-di-tert-butyl-4-(naphthalen-1-ylmethylene)cyclohexa-2,5-dien-1-one (2i):



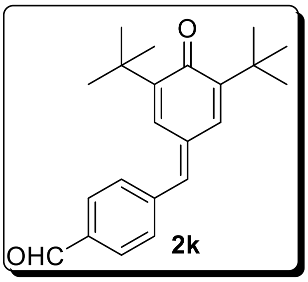
The reaction was performed at 1.0 mmol of *o*-iodo aniline: Yield 90% (330.1 mg), red solid, m.p. 115-116 °C; R_f = 0.60 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 1H), 7.93-7.90 (m, 2H), 7.77 (s, 1H), 7.59-7.53 (m, 3H), 7.48 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 1.38 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 149.3, 148.0, 140.4, 134.7, 133.6, 133.3, 132.0, 129.7, 129.3, 128.8, 128.5, 126.8, 126.5, 125.3, 124.6, 35.4, 35.1, 29.6, 29.5; IR (KBr, cm^{-1}) 2946, 2855, 1602, 1547; HRMS (ESI) [M + Na]$^+$ calculated for $C_{25}H_{28}NaO^+$: 367.2037, found 367.2042.

5-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-2,4-dimethoxybenzaldehyde (2j):



The reaction was performed at 1.2 mmol of *o*-iodo aniline: Yield 58% (265.8 mg), pale yellow solid, m.p. 194-196 °C; R_f = 0.51 (hexanes/EtOAc = 4:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.99 (d, J = 2.8 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 6.0 Hz, 1H), 7.05 (s, 1H), 6.51 (s, 1H), 4.03 (d, J = 2.8 Hz, 3H), 4.01 (d, J = 2.4 Hz, 3H), 1.34 (d, J = 2.0 Hz, 9H), 1.31 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 186.5, 164.5, 164.3, 149.1, 147.4, 136.4, 134.9, 132.5, 131.6, 127.8, 118.5, 118.1, 94.3, 56.1, 56.0, 35.4, 35.0, 29.5, 29.5; IR (KBr, cm^{-1}) 2942, 2854, 2921, 1786, 1617, 1484, 1358, 764; HRMS (ESI) [M + Na]$^+$ calculated for $C_{24}H_{30}NaO_4^+$: 405.2041, found 405.2046.

4-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzaldehyde (2k):

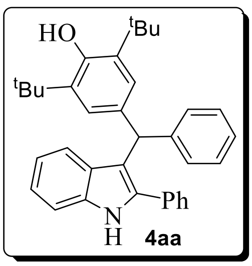


The reaction was performed at 2 mmol of *o*-iodo aniline: Yield 28% (167.4 mg), yellow solid, m.p. 115-116 °C; R_f = 0.52 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.93 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 2.4 Hz, 1H), 6.99 (s, 1H), 6.98 (s, 1H), 1.30 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 186.5, 150.2, 148.7, 141.8, 139.9, 135.9, 134.7, 133.8, 130.7, 129.9, 127.1, 35.5, 35.1, 29.6, 29.5; IR (KBr, cm^{-1}) 3052, 1776, 1456, 1246, 1020, 767; HRMS (ESI) [M + Na]$^+$ calculated for $C_{22}H_{26}NaO_2^+$: 322.1932, found 322.1936.

General procedure for the synthesis of unsymmetrical diarylindolylmethanes (4aa-4ak & 4ba-4ia): A mixture of o-alkynyl aniline (1 equiv.), p-quinone methide (1.2 equiv.) and $NaAuCl_4.2H_2O$ (0.02 equiv.) in dichloromethane (0.04 M) was heated to 50 °C the progress was monitored by TLC. After completion of the reaction, solvent was removed under reduced pressure and the residue was directly loaded on a silica gel column and eluted using 10-20% EtOAc/hexane mixture to obtain pure diarylindolylmethane derivatives.

Characterization data for the diarylindolylmethanes:

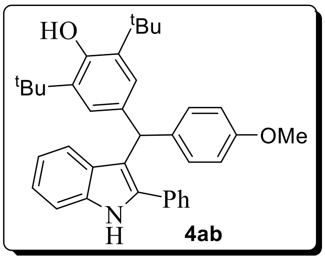
2,6-di-tert-butyl-4-(phenyl(2-phenyl-1H-indol-3-yl)methyl)phenol (4aa):



Yield 90% (87.7 mg), yellow solid, m.p. 161-163 °C; R_f = 0.2 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (bs, 1H), 7.53-7.51 (m, 2H), 7.46-7.42 (m, 2H), 7.40-7.38 (m, 2H), 7.28-7.13 (m, 7H), 7.10 (s, 2H), 6.96-6.92 (m, 1H), 5.76 (bs, 1H), 5.05 (s, 1H), 1.35 (s, 18H); ^{13}C

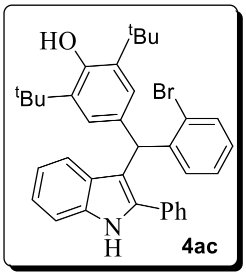
NMR (100 MHz, $CDCl_3$) δ 151.9, 144.9, 136.2, 135.5, 135.3, 134.3, 133.3, 129.0, 128.8, 128.6, 128.3, 127.9, 127.8, 126.0, 125.7, 121.8, 121.8, 119.4, 116.2, 110.6, 47.7, 34.3, 30.3; IR (KBr, cm^{-1}) 3629, 3400, 2969, 2926, 2863, 1445, 1224, 762; HRMS (ESI) $[M + Na]^+$ calculated for $C_{35}H_{37}NNaO^+$: 510.2772, found 510.2777.

2,6-di-tert-butyl-4-((4-methoxyphenyl)(2-phenyl-1H-indol-3-yl)methyl)phenol (4ab):



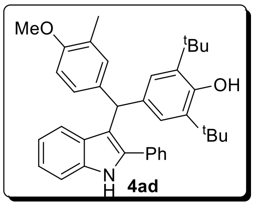
Yield 79% (81.7 mg), yellow solid, m.p. 162-163 °C; R_f = 0.14 (hexanes/EtOAc = 9:1): ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (bs, 1H), 7.53 (d, J = 3.2 Hz, 2H), 7.51-7.42 (m, 2H), 7.41-7.36 (m, 2H), 7.21-7.17 (m, 1H), 7.16-7.11 (m, 5H), 6.97-6.94 (m, 1H), 6.82 (d, J = 6.2 Hz, 2H), 5.72 (bs, 1H), 5.06 (s, 1H), 3.80 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 151.8, 137.1, 136.2, 135.4, 135.3, 134.6, 133.3, 129.9, 128.8, 128.5, 128.3, 127.8, 125.9, 121.8, 121.7, 119.3, 116.5, 113.3, 110.6, 55.2, 46.9, 34.3, 30.4; IR (KBr, cm^{-1}) 3637, 3417, 2943, 2863, 1466, 1425, 762; HRMS (ESI) $[M + Na]^+$ calculated for $C_{36}H_{39}NNaO_2^+$: 540.2878, found 540.2883.

4-((2-bromophenyl)(2-phenyl-1H-indol-3-yl)methyl)-2,6-di-tert-butylphenol (4ac):



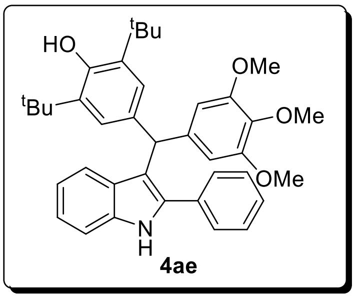
Yield 68% (76.8 mg), yellow solid, m.p. 188-190 °C; R_f = 0.14 (hexanes/EtOAc = 9:1): ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (bs, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.42-7.37 (m, 7H), 7.24-7.20 (m, 1H), 7.18-7.14 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.99 (s, 2H), 6.95 (t, J = 8.0 Hz, 1H), 6.02 (s, 1H), 5.08 (bs, 1H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.0, 136.2, 136.0, 135.4, 133.3, 133.0, 132.9, 132.8, 131.4, 128.9, 128.6, 128.5, 127.7, 127.7, 127.1, 125.9, 125.5, 121.7, 121.1, 119.5, 114.5, 110.7, 47.9, 34.3, 30.4; IR (KBr, cm^{-1}) 3647, 3427, 2963, 2843, 1426, 1415, 801; HRMS (ESI) [M + Na]$^+$ calculated for $C_{35}H_{36}BrNNaO^+$: 588.1878, found 588.1882.

2,6-di-tert-butyl-4-((4-methoxy-3-methylphenyl)(2-phenyl-1H-indol-3-yl)methyl)phenol (4ad):



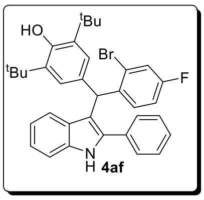
Yield 90% (95.7 mg), brown semi solid, R_f = 0.14 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (bs, 1H), 7.57-7.55 (m, 2H), 7.48-7.41 (m, 3H), 7.36 (d, J = 8Hz, 1H), 7.30 (d, J = 8 Hz, 1H), 7.18 (d, J = 4 Hz, 1H), 7.17 (s, 2H), 7.07-7.01 (m, 3H), 6.76 (d, J = 8.4 Hz, 1H), 5.77 (s, 1H), 5.11 (s, 1H), 3.84 (s, 3H), 2.02 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 151.8, 136.5, 136.2, 135.3, 135.3, 134.8, 133.4, 131.5, 128.9, 128.6, 128.5, 127.8, 127.1, 126.0, 125.8, 121.9, 121.8, 119.3, 116.6, 110.7, 109.4, 55.3, 46.9, 34.4, 30.5, 20.5; IR (KBr, cm^{-1}) 3639, 3417, 2908, 28112, 1456, 1425, 1435, 1217, 700; HRMS (ESI) [M + Na]$^+$ calculated for $C_{37}H_{41}NNaO_2^+$: 554.3035, found 554.30399.

2,6-di-tert-butyl-4-(phenyl(2-(3,4,5-trimethoxyphenyl)-1H-indol-3-yl)methyl)phenol (4ae):



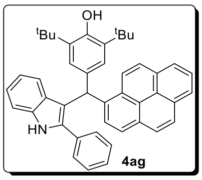
Yield 76% (87.7 mg), yellow solid, m.p. 234-236 ^{o}C; R_f = 0.23 (hexanes/EtOAc = 4:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (bs, 1H), 7.54-7.51 (m, 2H), 7.45-7.35 (m, 4H), 7.25 (d, J = 8 Hz, 1H), 7.17-7.13 (m, 1H), 7.11 (s, 2H), 6.99-6.95 (m, 1H), 6.47 (s, 1H), 5.72 (s, 1H), 5.08 (s, 1H), 3.85 (s, 3H), 3.66 (s, 6H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.9, 140.7, 136.2, 136.0, 135.6, 135.4, 134.1, 133.4, 128.9, 128.5, 128.3, 127.8, 125.9, 121.8, 121.5, 119.4, 115.9, 110.7, 106.6, 60.9, 56.0, 47.8, 34.4, 30.4; IR (KBr, cm^{-1}) 3647, 3438, 2966, 2915, 2938, 1519, 1417, 1204, 714; HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{43}NNaO_4^+$: 600.3089, found 600.3093.

4-((2-bromo-4-fluorophenyl)(2-phenyl-1H-indol-3-yl)methyl)-2,6-di-tert-butylphenol (4af):



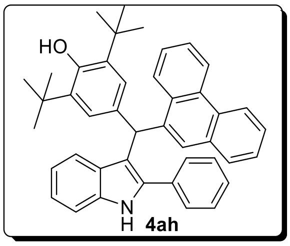
Yield 88% (94.2 mg), yellow solid, m.p. 182-184 °C; R_f = 0.20 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (bs, 1H), 7.53-7.41 (m, 5H), 7.30-7.20 (m, 5H), 7.08 (s, 2H), 6.90-6.88 (m, 1H), 6.81-6.78 (m, 1H), 5.75 (s, 1H), 5.11 (s, 1H), 1.38 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.4, 152.0, 144.7, 137.3, 135.5, 133.9, 132.9, 132.7, 129.0, 128.7, 128.6, 128.1, 125.9, 116.4, 111.2, 110.3, 110.2, 106.6, 106.3, 47.6, 34.4, 30.3; IR (KBr, cm^{-1}) 3657, 3410, 3012, 2965, 2834, 1453, 1368, 1335; HRMS (ESI) [M + Na]$^+$ calculated for $C_{35}H_{35}BrFNNaO^+$: 606.1783, found 606.1789.

2,6-di-tert-butyl-4-((2-phenyl-1H-indol-3-yl)(pyren-1-yl)methyl)phenol (4ag):



Yield 85% (104.0 mg), white solid, m.p. 168-170 °C; R_f = 0.15 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 1H), 8.13-8.10 (m, 4H), 8.07-8.04 (m, 3H), 7.97 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 9.6 HZ, 1H), 7.46-7.44 (m, 2H), 7.35-7.33 (m, 4H), 7.18 (d, J = 8.4 Hz, 1H), 7.13 (s, 2H), 7.11 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.78 (s, 1H), 5.11 (s, 1H), 1.32 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.01, 139.00, 136.2, 135.5, 135.2, 134.5, 133.3, 131.5, 130.9, 130.0, 129.2, 129.1, 128.7, 128.6, 127.9, 127.7, 127.6, 127.1, 126.7, 126.4, 125.1, 125.0, 124.8, 124.7, 124.7, 124.1, 121.9, 121.4, 119.5, 116.4, 110.6, 45.1, 34.4, 30.4; IR (KBr, cm^{-1}) 3621, 2958, 2924, 2873, 1595, 1434, 1362, 1236, 1147, 911, 843; HRMS (ESI) [M + Na]$^+$ calculated for $C_{25}H_{41}NNaO^+$: 634.3085, found 634.3090.

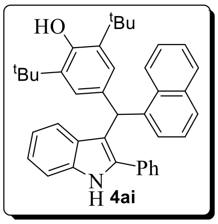
2,6-di-tert-butyl-4-(phenanthren-9-yl(2-phenyl-1H-indol-3-yl)methyl)phenol (4ah):



4ah

Yield 89% (104.6 mg), yellow solid, m.p. 158-160 °C; R_f = 0.2 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 8.0, 6.8 Hz, 2H), 8.13 (bs, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.65 (s, 2H), 7.65-7.61 (m, 2H), 7.58-7.55 (m, 2H), 7.48-7.46 (m, 5H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.37 (s, 2H), 7.34 (t, *J* = 6.0 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 5.10 (s, 1H), 1.34 (18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 138.9, 136.2, 135.4, 135.2, 134.0, 133.2, 131.7, 131.6, 130.7, 129.8, 129.2, 128.8, 128.6, 128.5, 128.1, 127.8, 126.4, 126.3, 126.1, 125.8, 125.4, 122.9, 122.4, 121.8, 121.3, 119.5, 115.6, 110.6, 45.2, 34.3, 30.4; IR (KBr, cm^{-1}) 3664, 3321, 2966, 2934, 2845, 1519, 1468, 1425, 1236, 733; HRMS (ESI) $[M + Na]^+$ calculated for $C_{43}H_{41}NNaO^+$: 610.3085, found 610.3089.

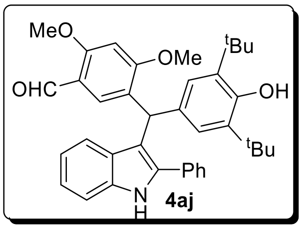
2,6-di-tert-butyl-4-(naphthalen-1-yl(2-phenyl-1H-indol-3-yl)methyl)phenol (4ai):



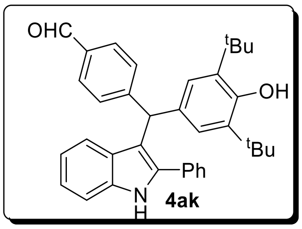
4ai

Yield 86% (92.4 mg), brown gummy liquid; R_f = 0.20 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (bs, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.47-7.39 (m, 8H), 7.35-7.26 (m, 4H), 7.12 (s, 2H), 6.93 (t, 1H), 5.11 (s, 1H), 5.10 (s, 1H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 140.8, 136.2, 135.4, 135.1, 134.3, 133.9, 133.3, 132.2, 129.1, 128.6, 128.6, 127.8, 127.2, 127.0, 126.3, 125.6, 125.3, 125.1, 124.6, 121.7, 121.4, 119.4, 115.9, 110.6, 44.8, 34.3, 30.4; IR (KBr, cm^{-1}) 3616, 3402, 2937, 2904, 2865,1425, 717; HRMS (ESI) $[M + Na]^+$ calculated for $C_{39}H_{39}NNaO^+$: 560.2929, found 560.2934.

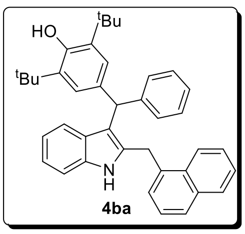
5-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-phenyl-1H-indol-3-yl)methyl)-2,4-dimethoxybenzaldehyde (4aj):

 Yield 95% (109.3 mg), yellow solid, m.p. 152-154 °C; R_f = 0.06 (hexanes/EtOAc = 4:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.06 (bs, 1H), 7.78 (s, 1H), 7.46-7.35 (m, 5H), 7.30 (d, J = 8 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.12-7.08 (m, 1H), 7.06 (s, 2H), 6.96-6.92 (m, 1H), 6.29 (s, 1H), 5.94 (s, 1H), 5.07 (s, 1H), 3.86 (s, 3H), 3.57 (s, 3H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 163.7, 162.4, 151.9, 136.0, 135.6, 135.2, 133.8, 132.9, 130.7, 128.6, 128.5, 128.3, 127.5, 126.5, 125.8, 121.6, 121.2, 119.4, 117.6, 114.6, 110.6, 94.0, 55.6, 55.4, 40.7, 34.3, 30.4; IR (KBr, cm^{-1}) 3645, 3426, 3052, 2956, 2859, 1756, 1452; HRMS (ESI) [M + Na]$^+$ calculated for $C_{38}H_{41}NNaO_4^+$: 598.2933, found 598.2938.

4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-phenyl-1H-indol-3-yl)methyl)benzaldehyde (4ak):

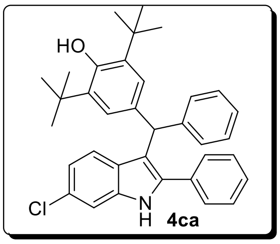
 Yield 96% (98.8 mg), yellow solid, m.p. 118-120 °C; R_f = 0.20 (hexanes/EtOAc = 4:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.25 (bs, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.47-7.36 (m, 6H), 7.19-7.12 (m, 4H), 6.96 (t, J = 7.2 Hz, 1H), 5.82 (s, 1h0, 5.14 (bs, 1H), 1.37 (s, 18hH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 152.7, 152.2, 136.2, 135.9, 135.7, 134.3, 133.2, 133.0, 128.1, 127.9, 122.0, 121.3, 119.6, 115.0, 110.9, 48.1, 34.4, 30.4; IR (KBr, cm^{-1}) 3665, 3424, 3062, 2935, 2885, 1736, 1412; HRMS (ESI) [M + Na]$^+$ calculated for $C_{36}H_{37}NNaO_2^+$: 538.2722, found 538.2726.

2,6-di-tert-butyl-4-((2-(naphthalen-1-ylmethyl)-1H-indol-3-yl)(phenyl)methyl)phenol (4ba):

 Yield 91% (100.4 mg), yellow solid, m.p. 179-181 °C; R_f = 0.25 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz,

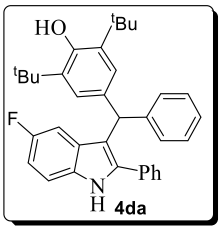
1H), 7.58-7.54 (m, 1H), 7.54-7.50 (m, 4H), 7.50-7.42 (m, 3H), 7.40-7.39 (m, 2H), 7.29 (s, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.14-7.12 (m, 2H), 7.05-7.03 (m, 1H), 6.00 (s, 1H), 5.20 (bs, 1H), 4.46 (dd, *J* = 16.4, 12.0 Hz, 2H) 1.45 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 144.6, 135.7, 135.6, 134.5, 134.2, 134.0, 133.9, 132.1, 129.3, 128.7, 128.55, 128.3, 127.8, 127.2, 126.5, 126.1, 126.0, 125.7, 124.0, 121.0, 120.4, 119.2, 115.1, 110.5, 48.0, 34.5, 30.5, 22.1; IR (KBr, cm^{-1}) 3649, 3413, 2967, 2915, 2866, 2208. 1446, 1425, 780; HRMS (ESI) [M + Na]$^+$ calculated for $C_{40}H_{41}NNaO^+$: 574.3085, found 574.3089.

2,6-di-tert-butyl-4-((6-chloro-2-phenyl-1H-indol-3-yl)(phenyl)methyl)phenol (4ca):



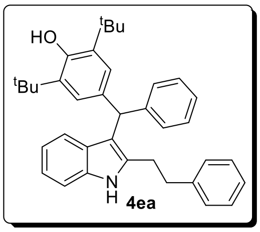
Yield 82% (85.6 mg), white solid, m.p. 178-180 °C; R_f = 0.26 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (bs, 1H), 7.54-7.52 (m, 2H), 7.48-7.42 (m, 3H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.23-7.20 (m, 3H), 7.12 (s, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.95 (dd, *J* = 2.0, 6.8 Hz, 1H), 5.78 (s, 1H), 5.13 (bs, 1H), 1.39 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 144.7, 136.6, 136.2, 135.6, 134.0, 132.7, 129.0, 128.8, 128.7, 128.1, 128.0, 127.6, 127.0, 126.0, 125.9, 122.5, 120.1, 116.4, 110.7, 48.6, 34.4, 30.4; IR (KBr, cm^{-1}) 3636, 3424, 2957, 2923, 2862, 1466, 1445, 1244, 732; HRMS (ESI) [M + Na]$^+$ calculated for $C_{36}H_{36}ClNNaO^+$: 5444.2383, found 544.2388.

2,6-di-tert-butyl-4-((5-fluoro-2-phenyl-1H-indol-3-yl)(phenyl)methyl)phenol (4da):



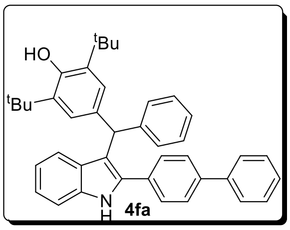
Yield 79% (79.8 mg), yellow solid, m.p. 178-180 °C; R_f = 0.19 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (bs, 1H), 7.41-7.31 (m, 6H), 7.33-7.29 (m, 2H), 7.18-7.16 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.97-6.93 (m, 5H), 5.94 (s, 1H), 5.09 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 159.5, 152.0, 140.1, 140.0, 136.2, 136.1, 135.5, 133.3, 132.8, 132.1, 132.0, 128.7, 128.6, 128.5, 127.8, 125.8, 125.2, 125.0, 121.8, 120.9, 120.0, 119.6, 114.2, 114.1, 113.9, 110.7, 47.3, 34.3, 30.4; IR (KBr, cm^{-1}) 3648, 3401, 2947, 2935, 2961, 1497, 1466, 1445, 919, 728; HRMS (ESI) [M + Na]$^+$ calculated for $C_{35}H_{36}FNNaO^+$: 528.2678, found 528.2683.

4-((2-benzyl-1H-indol-3-yl)(phenyl)methyl)-2,6-di-tert-butylphenol (4ea):



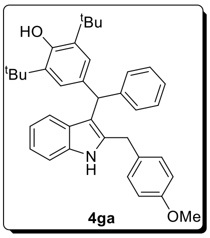
Yield 81% (83.5 mg), yellow solid, m.p. 247-249 °C; R_f = 0.21 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (bs, 1H), 7.40-7.29 (m, 9H), 7.24-7.20 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07-7.03 (m, 1H), 5.86 (s, 1H), 5.22 (bs, 1H), 2.98 (t, *J* = 2.4 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.48 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 151.9, 145.1, 136.0, 135.5, 135.4, 134.5, 130.1, 129.1, 128.4, 128.0, 126.1, 125.8, 125.7, 121.6, 119.3, 115.6, 114.0, 110.6, 55.4, 47.8, 35.9, 34.5, 30.5, 28.9; IR (KBr, cm^{-1}) 3583, 3416, 3047, 2981, 2935, 2859, 1491, 1464, 1205, 1161, 741; HRMS (ESI) [M + Na]$^+$ calculated for $C_{37}H_{41}NNaO^+$: 538.7301, found 538.7305.

4-((2-([1,1'-biphenyl]-4-yl)-1H-indol-3-yl)(phenyl)methyl)-2,6-di-tert-butylphenol (4fa):

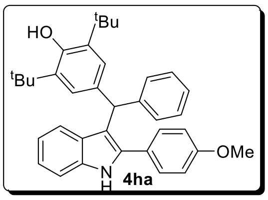


Yield 85% (95.8 mg), gummy brown liquid, R_f = 0.20 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (bs, 1H), 7.68-7.65 (m, 4H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.41-7.38 (m, 2H), 7.28-7.25 (m, 4H), 7.17 (d, *J* = 7.6 Hz, 3H), 7.13 (s, 2H), 7.97-6.93 (m, 1H), 5.84 (s, 1H), 5.07 (s, 1H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.9, 140.6, 140.5, 136.3, 135.4, 134.2, 132.2, 129.0, 128.9, 128.5, 128.0, 127.5, 127.3, 127.0, 126.0, 125.7, 121.9, 121.7, 119.4, 116.5, 110.6, 47.8, 34.3, 30.4; IR (KBr, cm^{-1}) 3622, 3346, 3051, 2923, 2869, 1436, 1253, 1167, 745; HRMS (ESI) [M + Na]$^+$ calculated for $C_{41}H_{41}NNaO^+$: 586.3085, found 586.3089.

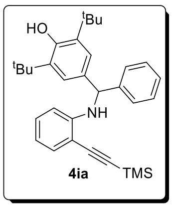
2,6-di-tert-butyl-4-((2-(4-methoxybenzyl)-1H-indol-3-yl)(phenyl)methyl)phenol (4ga):

 Yield 90% (95.7 mg), yellow solid, m.p. 72-74 ^{o}C; R_f = 0.14 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (bs, 1H), 7.32 (d, *J* = 4.4 HZ, 4H), 7.26-7.22 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.99-6.97 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.83 (s, 1H), 5.14 (bs, 1H), 3.94 (s, 2H), 3.83 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 152.0, 144.7, 135.6, 135.5, 134.6, 134.2, 130.8, 129.8, 129.2, 128.4, 128.1, 126.0, 125.9, 121.0, 120.3, 119.0, 115.5, 114.1, 110.3, 55.3, 47.7, 34.4, 31.7, 30.4; IR (KBr, cm^{-1}) 3583, 3411, 3046, 3014, 2931, 1477, 1461, 1186, 723; HRMS (ESI) $[M + Na]^+$ calculated for $C_{37}H_{41}NNaO_2^+$: 554.3035, found 554.3039.

2,6-di-tert-butyl-4-((2-(4-methoxyphenyl)-1H-indol-3-yl)(phenyl)methyl)phenol (4ha):

 Yield 85% (88.0 mg), semi-solid, R_f = 0.14 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (bs, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.10-7.06 (m, 3H), 7.03-7.01 (m, 3H), 6.96 (s, 3H), 6.80-6.78 (m, 3H), 5.59 (s, 1H), 4.90 (s, 1H), 3.70 (s, 3H), 1.21 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 151.9, 145.1, 136.0, 135.5, 135.4, 134.5, 130.1, 129.1, 128.4, 128.0, 126.1, 125.8, 125.7, 121.6, 119.3, 115.6, 114.0, 110.6, 55.4, 47.8, 34.4, 30.4; IR (KBr, cm^{-1}) 3636, 3402, 2945, 1455, 729; HRMS (ESI) $[M + Na]^+$ calculated for $C_{36}H_{39}NNaO_2^+$: 540.2878, found 540.2882.

2,6-di-tert-butyl-4-(phenyl((2-((trimethylsilyl)ethynyl)phenyl)amino)methyl)phenol (4ia):

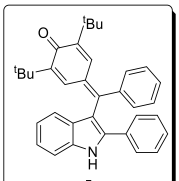
Yield 95% (91.9 mg), yellow solid, m.p. 56-58 ^{o}C; R_f = 0.16 (hexanes/EtOAc = 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.46-7.34 (m, 3H), 3.31-7.27 (m, 1H), 7.16 (s, 2H), 7.11-7.07 (m, 1H), 6.64-6.60 (m, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 5.58 (d, *J* = 4.8 HZ, 1H), 5.28 (d, *J* = 4.4

Hz, 1H), 5.20 (s, 1H), 1.45 (s, 18H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 148.9, 142.8, 136.0, 133.8, 131.6, 130.0, 128.6, 127.1, 127.0, 124.3, 116.3, 111.0, 107.6, 102.5, 100.5, 62.8, 34.4, 30.3, 0.1; IR (KBr, cm^{-1}) 3642, 3422, 3012, 2958, 2842, 1465, 1202; HRMS (ESI) $[M + Na]^+$ calculated for $C_{32}H_{41}NNaOSi^+$: 506.2855, found 506.2859.

General Procedure for oxidation product of 4aa to 5a.

2,6-di-tert-butyl-4-(phenyl(2-phenyl-1H-indol-3-yl)methyl)phenol (4aa) (100 mg, 0.2 mmol), $Pd(OAc)_2$ (3.4 mg, 0.020 mmol), $Cu(OAc)_2$ (37.21 mg, 0.2 mmol) and TFA (0.05 ml) were combined in a 2ml DMF at 10 mL tube equipped with a magnetic stir bar. The reaction was stirred at 120 °C for 16 h. after that reaction mixture was then extracted with Ethyl acetate (20 mL X 2). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to obtain a pure p-quinone indolyl methide **5a**.

2,6-di-tert-butyl-4-(phenyl(2-phenyl-1H-indol-3-yl)methylene)cyclohexa-2,5-dien-1-one (5a):



5a

Yield 85% (82.4 mg), red semi solid, R_f = 0.3 (hexanes/EtOAc = 9:1): ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (bs, 1H), 7.38-7.31 (m, 5H), 7.27-7.22 (m, 4H), 7.19-7.12 (m, 5H), 6.94 (d, J = 1.2 Hz, 1H), 6.94-6.90 (m, 1H), 6.85 (d, J = 8.0 Hz, 1H), 1.17 (s, 9H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 149.6, 146.6, 146.5, 140.3, 136.0, 132.8, 132.0, 131.7, 131.5, 129.8, 129.2, 128.7, 128.4, 128.0, 127.9, 123.1, 121.0, 120.9, 114.2, 111.1, 35.2, 34.9, 29.6, 29.3; IR (KBr, cm^{-1}) 3058, 2977, 2866, 1675, 1620, 1456, 1352, 1245, 1135; HRMS (ESI) $[M + Na]^+$ calculated for $C_{35}H_{35}NNaO^+$: 508.2616, found 508.2620.

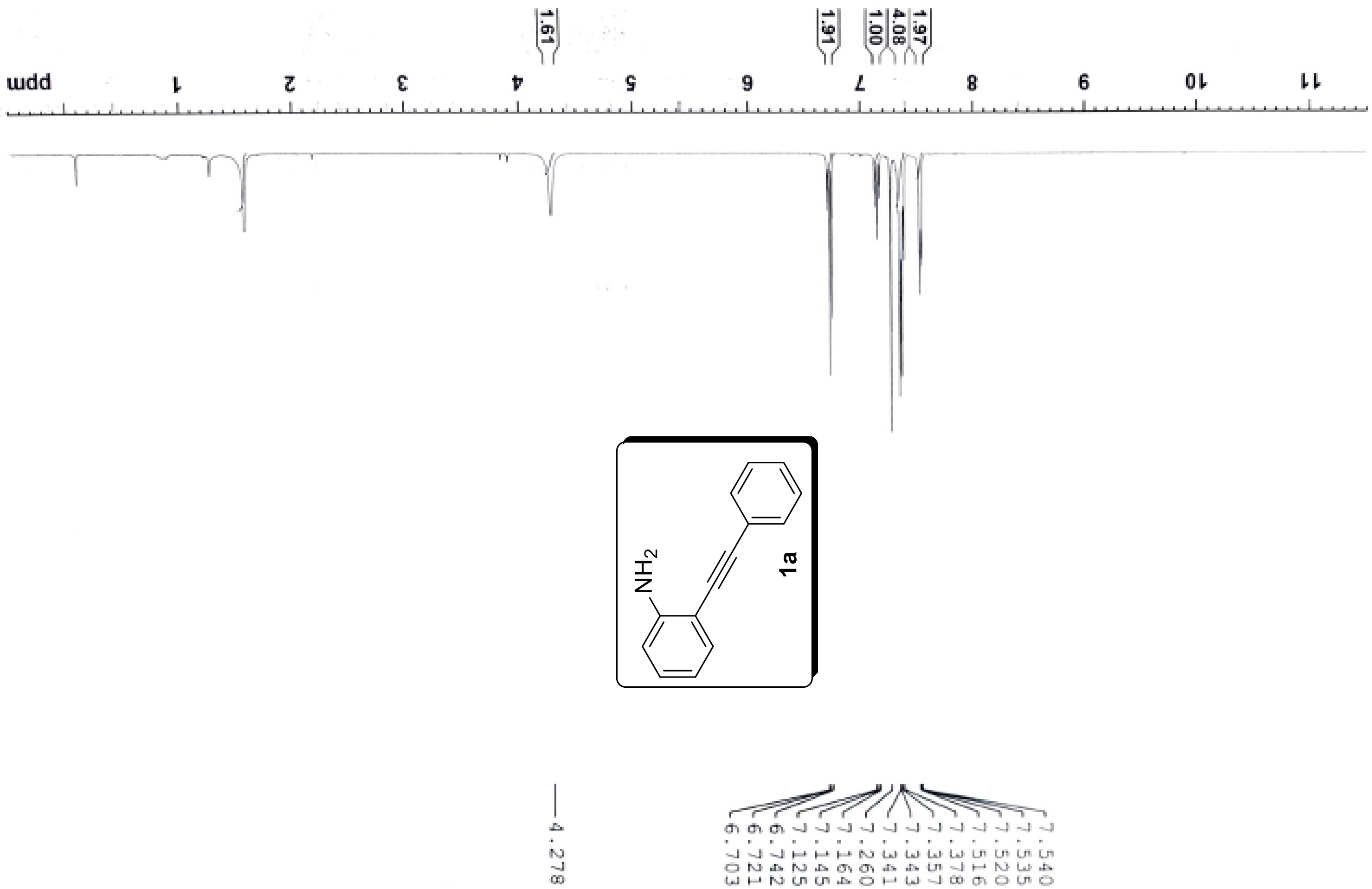


Figure S01. ^{1}H-NMR spectrum of compound **1a**($CDCl_3$, 400 MHz)

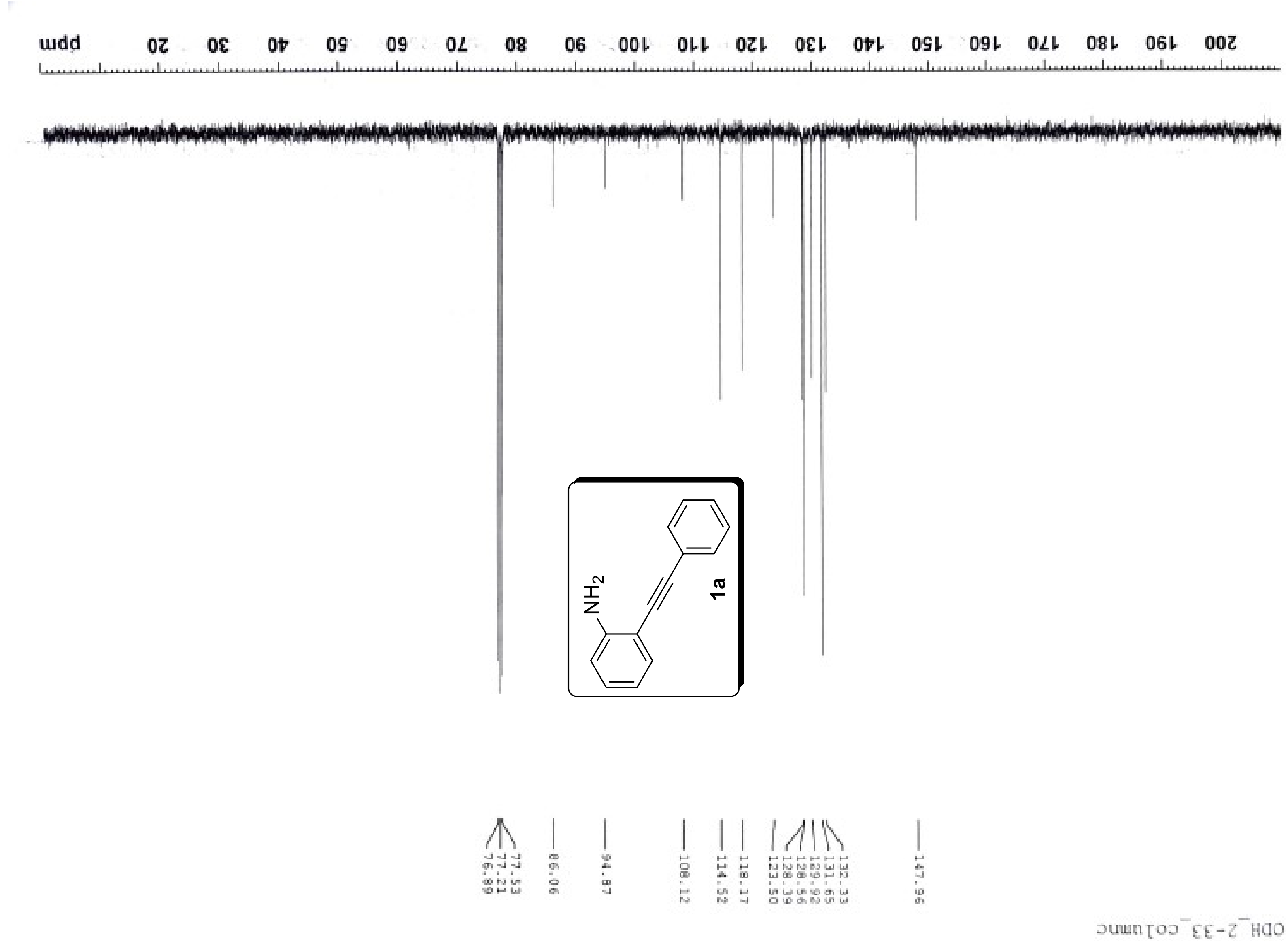


Figure S02. ^{13}C-NMR spectrum of compound **31**($CDCl_3$, 100 MHz)

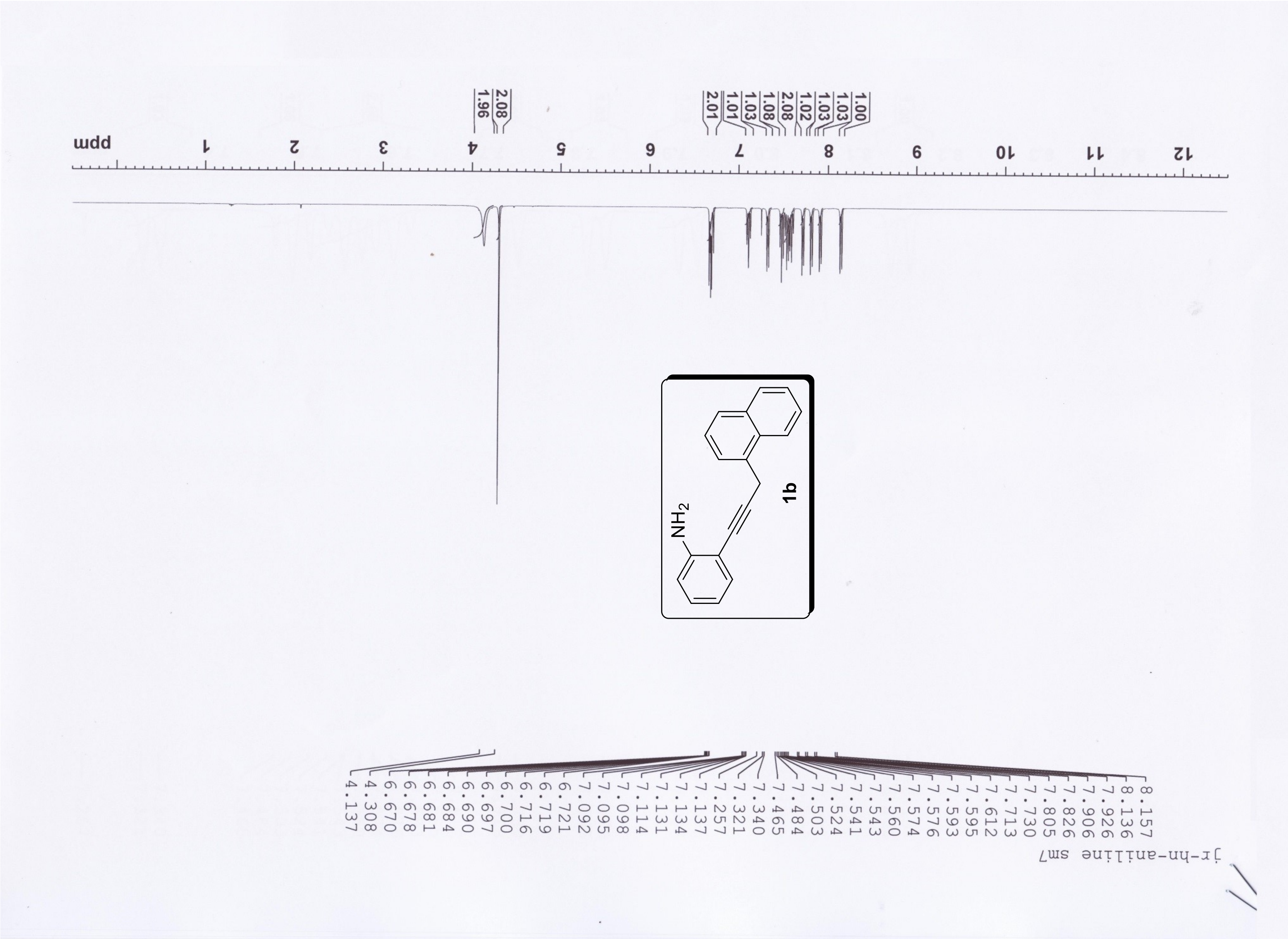


Figure S03. ^{1}H-NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz)

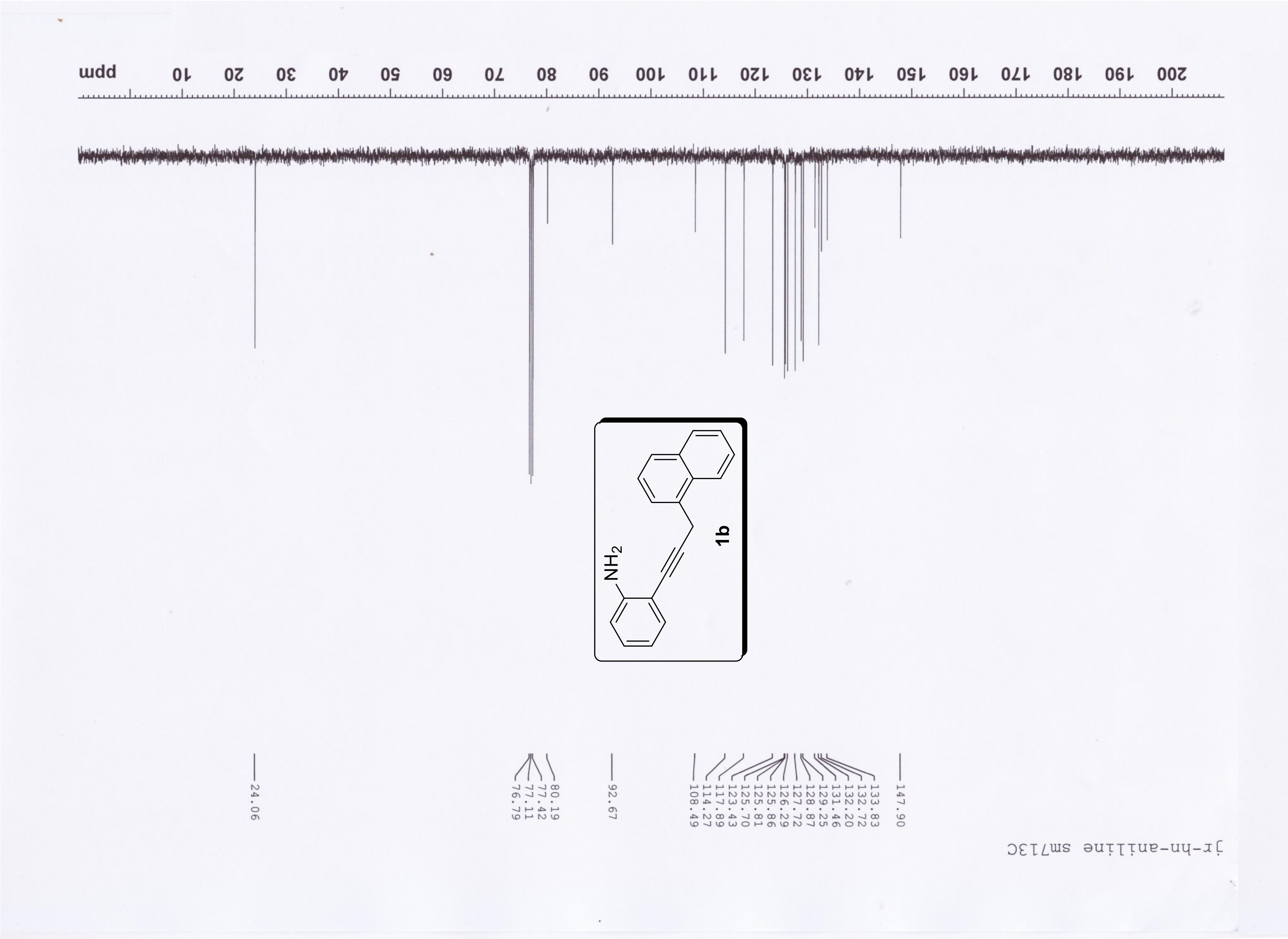


Figure S04. ^{13}C-NMR spectrum of compound **1b** ($CDCl_3$,100 MHz)

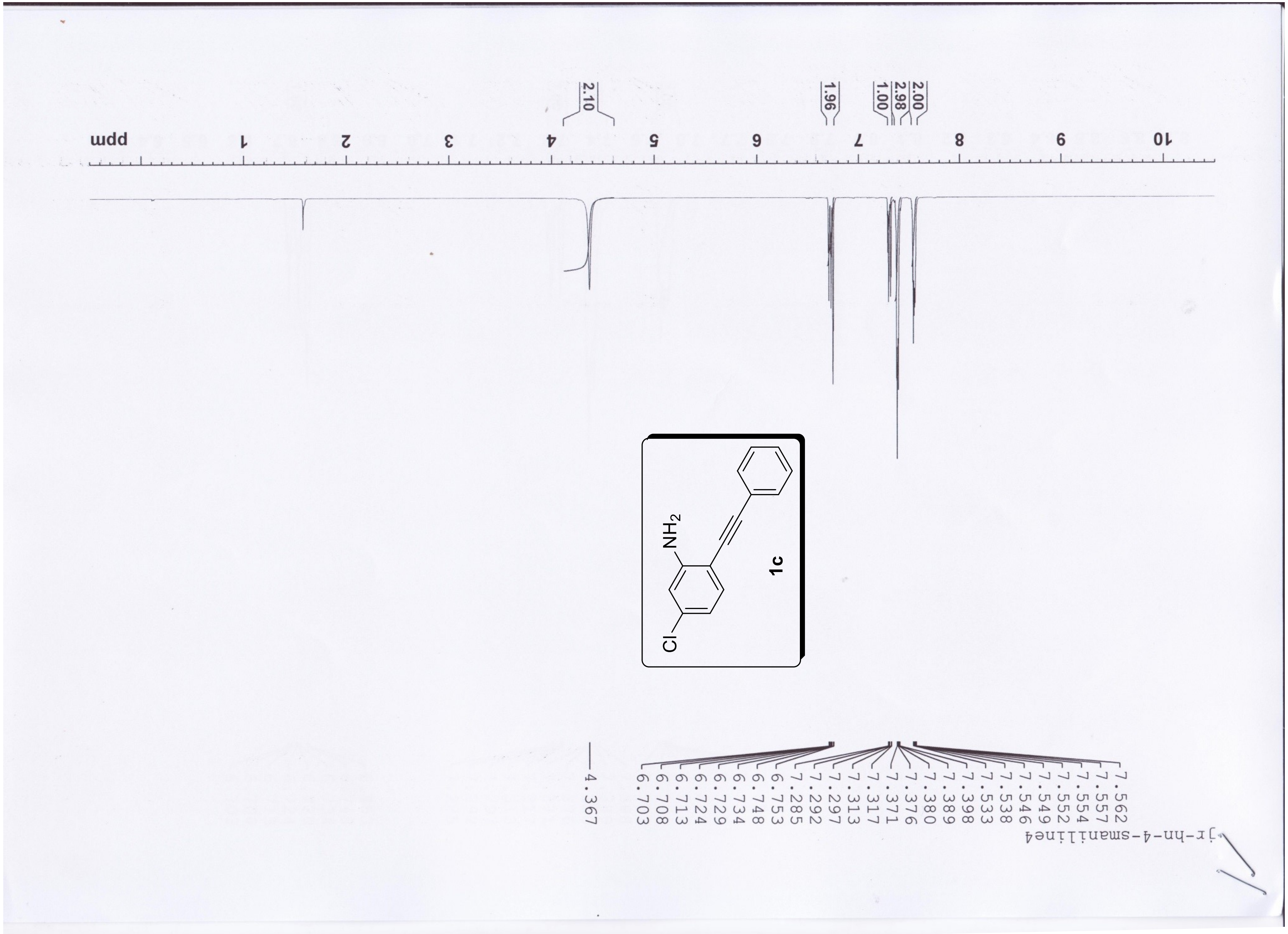


Figure S05. ^{1}H-NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz)

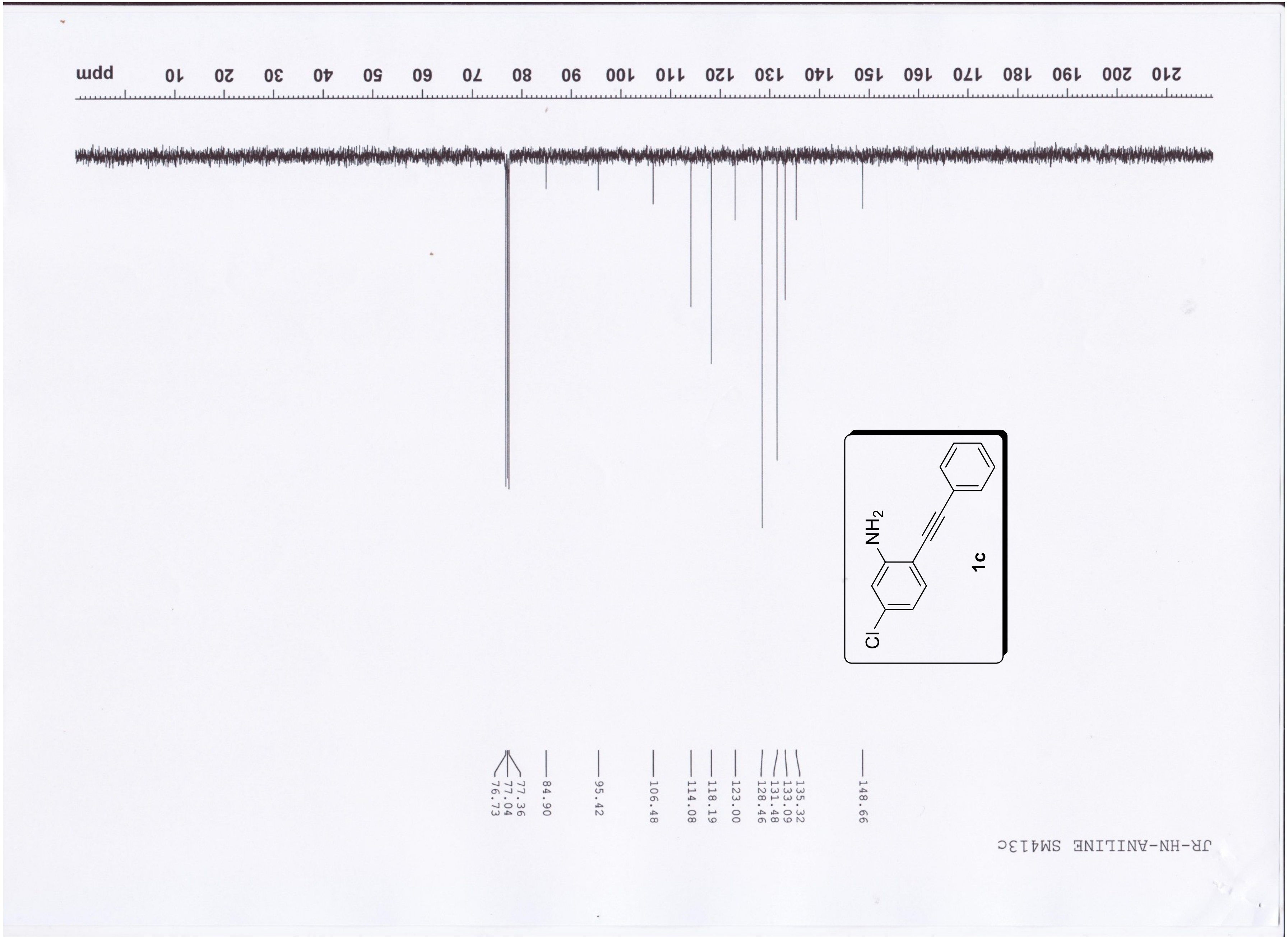


Figure S06. ^{13}C-NMR spectrum of compound **1c** ($CDCl_3$, 100 MHz)

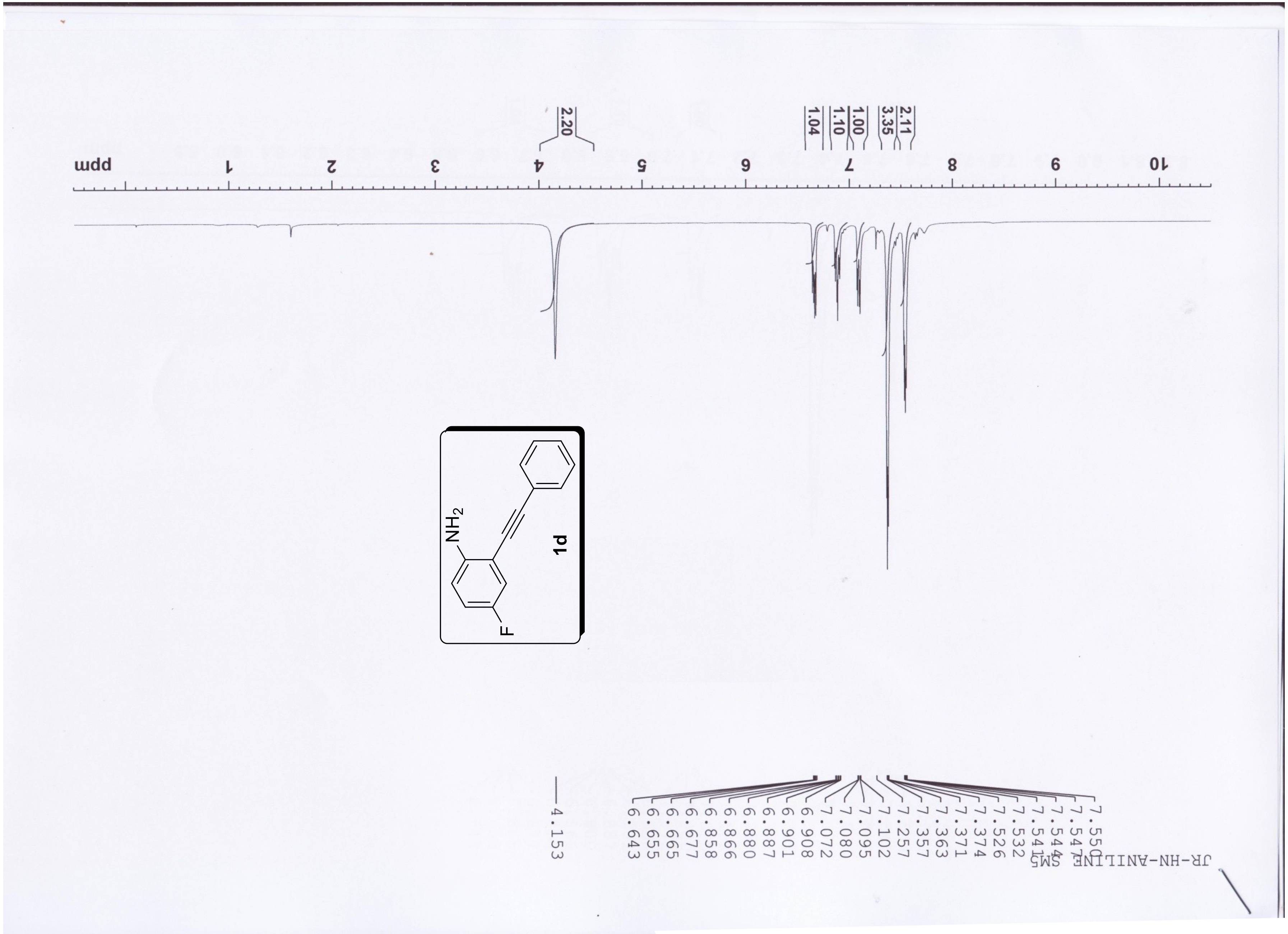


Figure S07. ^{1}H-NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)

Figure S08. ^{13}C-NMR spectrum of compound **1d**($CDCl_3$, 100 MHz)

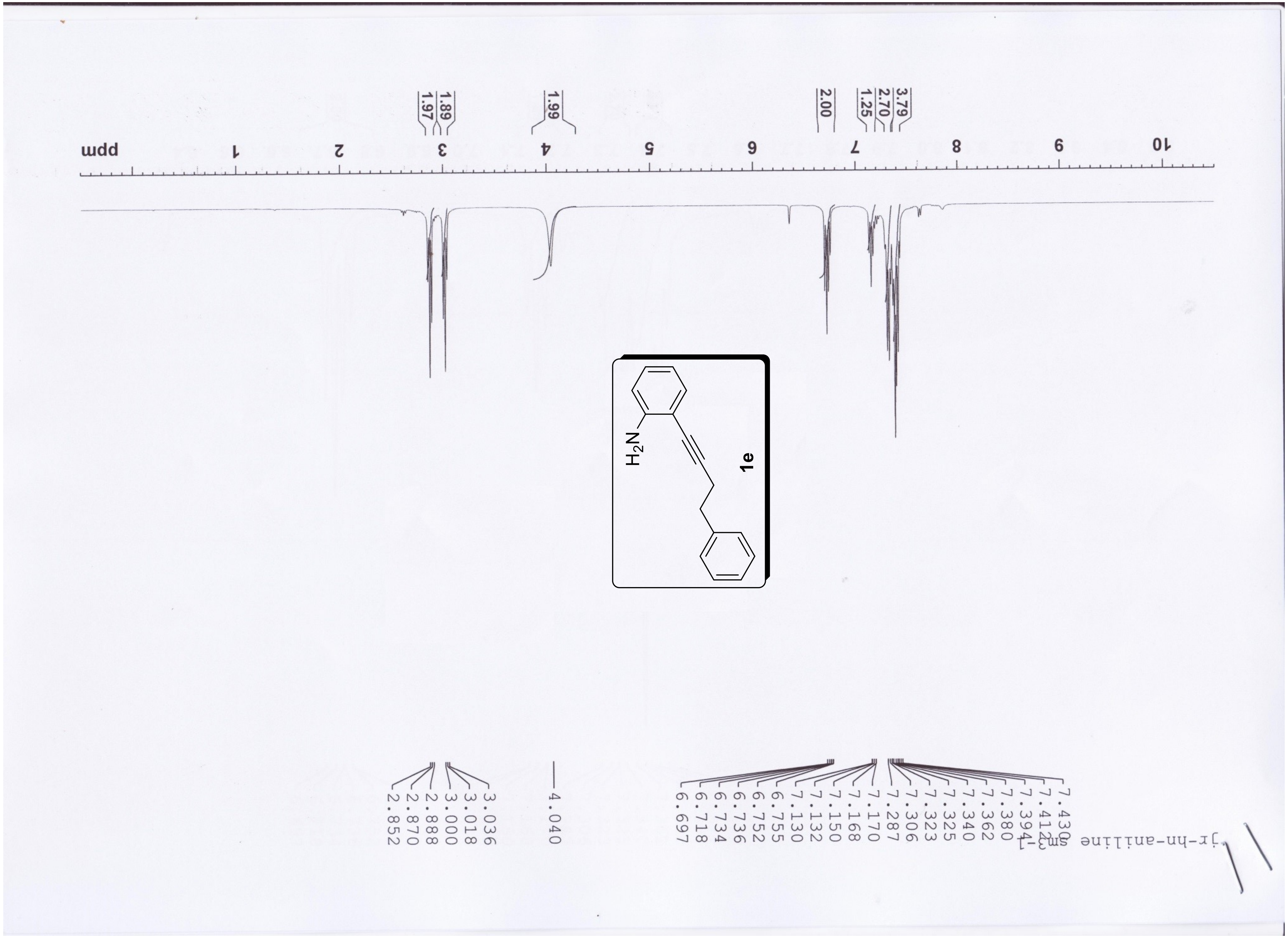


Figure S09. ^{1}H-NMR spectrum of compound **1e**($CDCl_3$, 400 MHz)

Figure S10. ^{13}C-NMR spectrum of compound **1e**($CDCl_3$, 100 MHz)

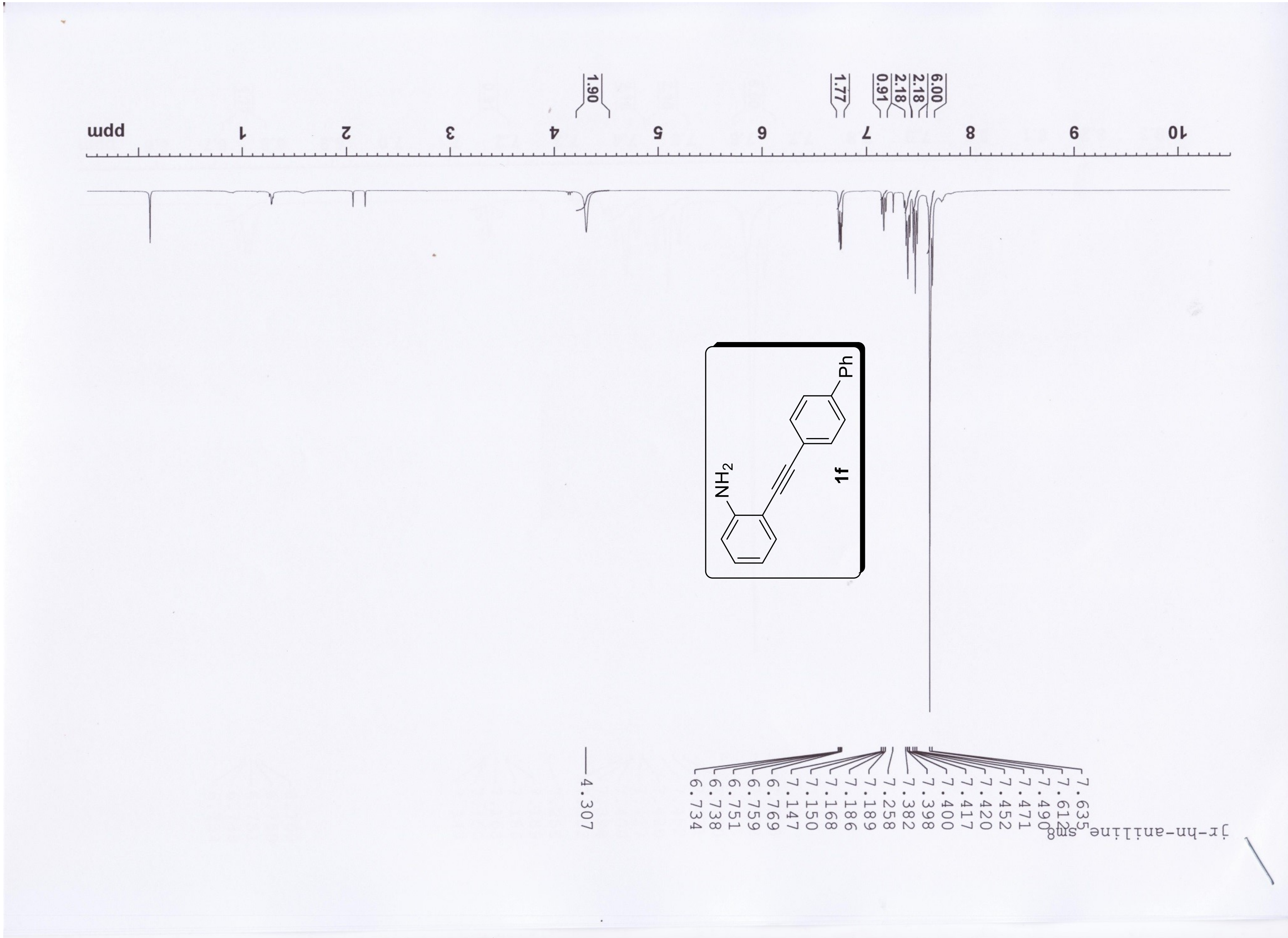


Figure S11. ^{1}H-NMR spectrum of compound **1f**($CDCl_3$, 400 MHz)

Figure Figure S12. ^{13}C-NMR spectrum of compound **1f**($CDCl_3$, 100 MHz)

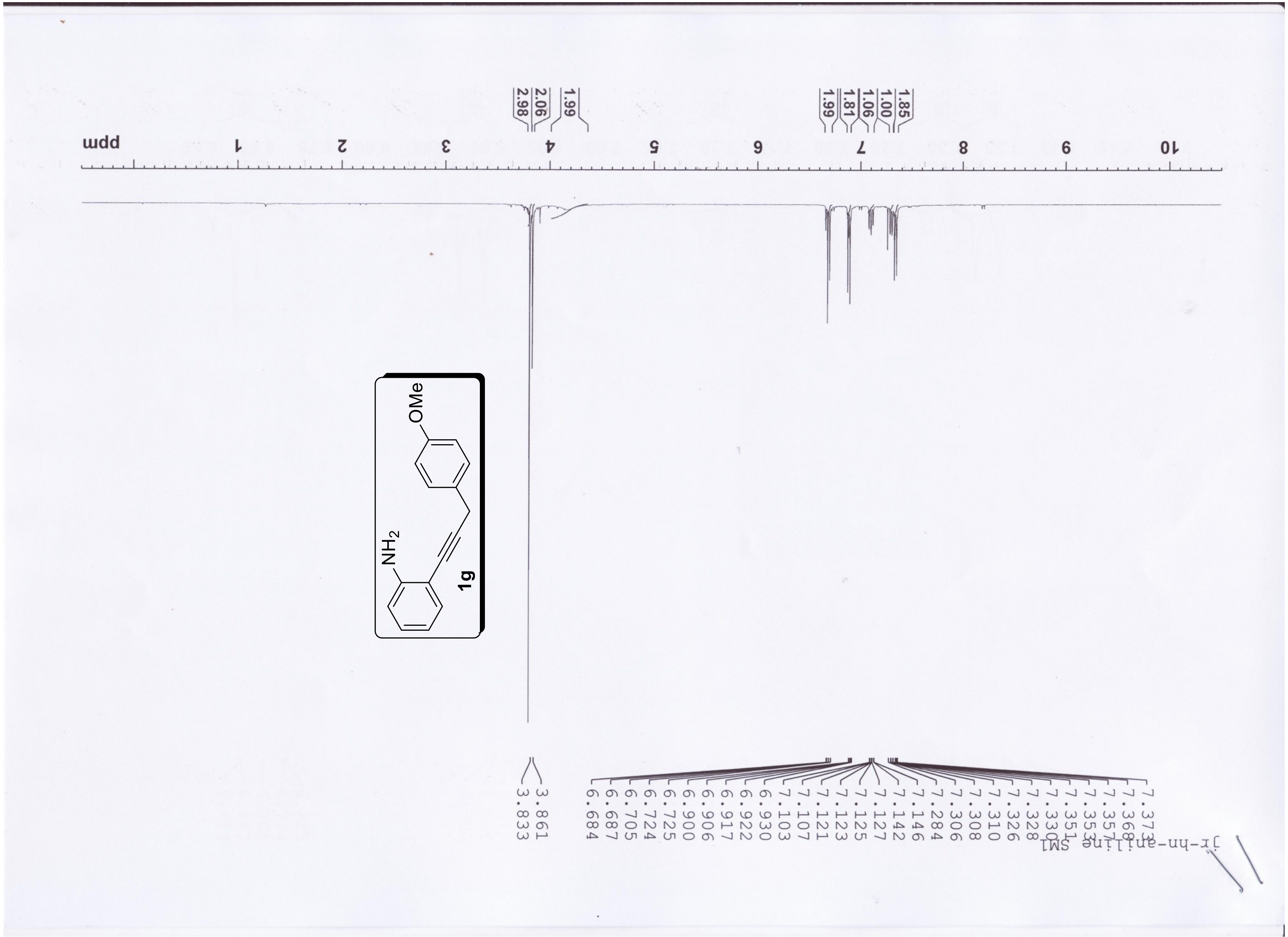


Figure Figure S13. ^{1}H-NMR spectrum of compound **1g**($CDCl_3$, 400 MHz)

Figure S14. ^{13}C-NMR spectrum of compound **1g**($CDCl_3$, 400 MHz)

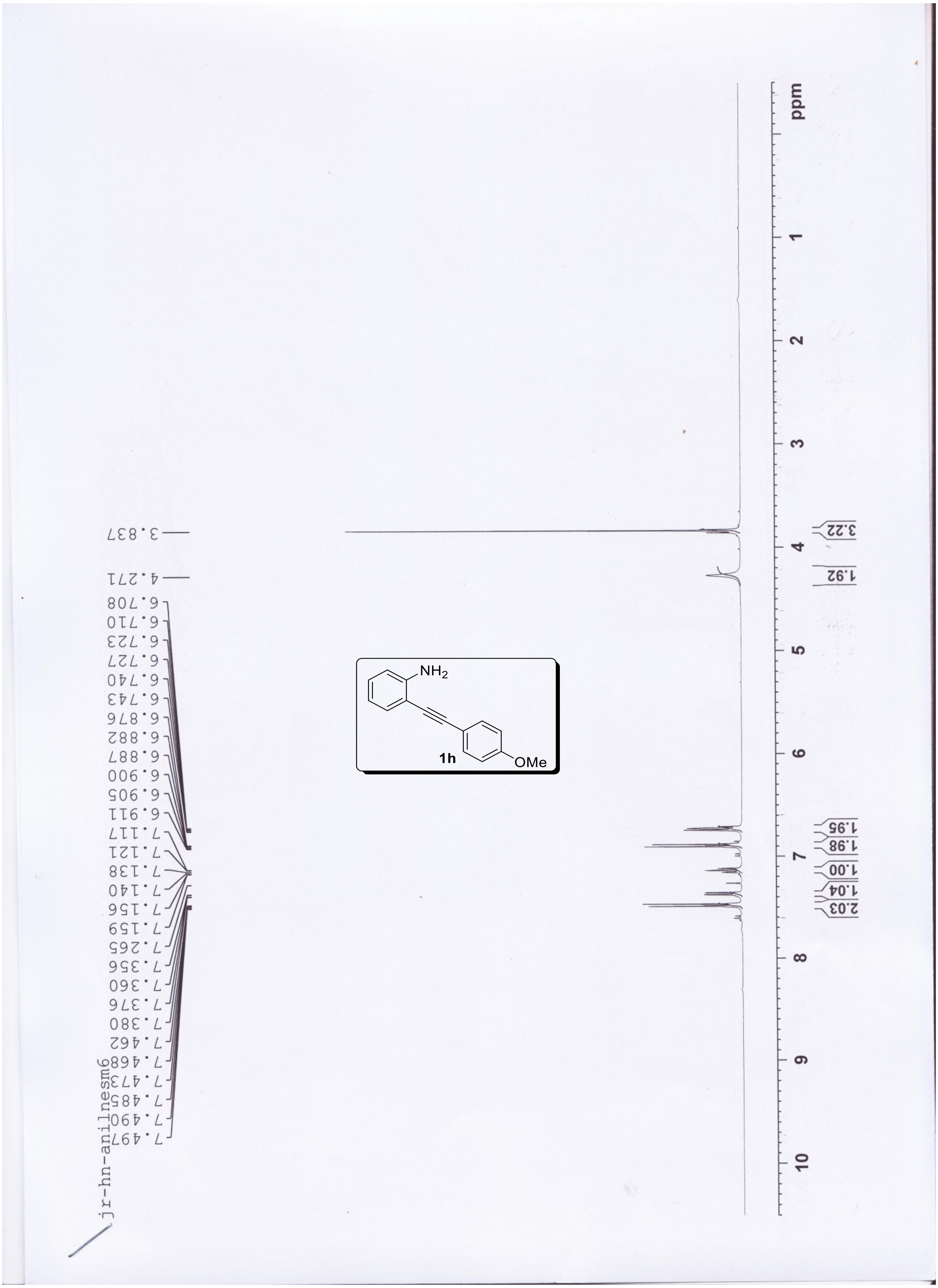


Figure S15. ^{13}H-NMR spectrum of compound **1h**($CDCl_3$, 400 MHz)

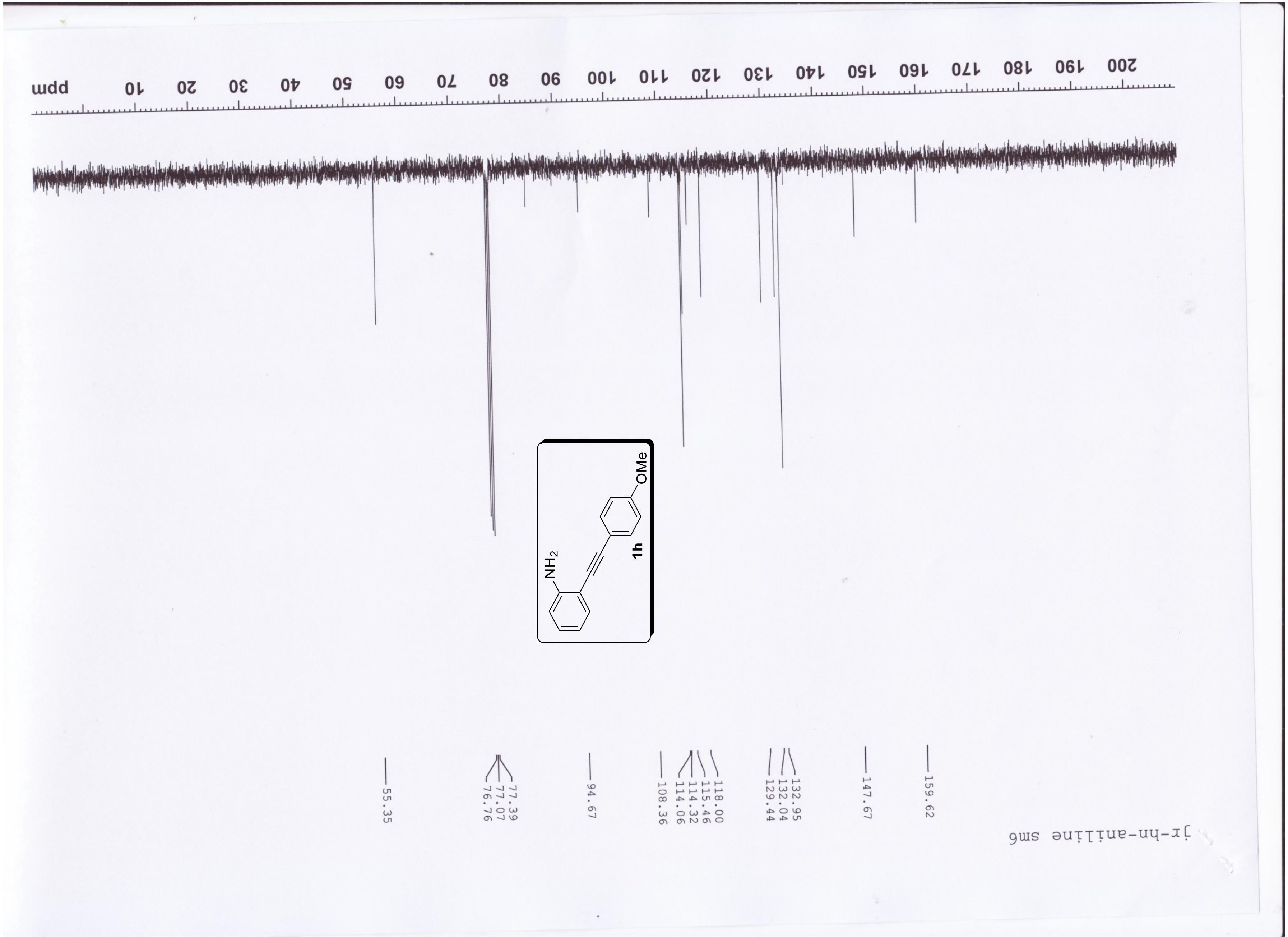


Figure S16. ^{13}C-NMR spectrum of compound **1h**($CDCl_3$, 100 MHz)

Figure S17. [1]H-NMR spectrum of compound **1i**($CDCl_3$, 400 MHz)

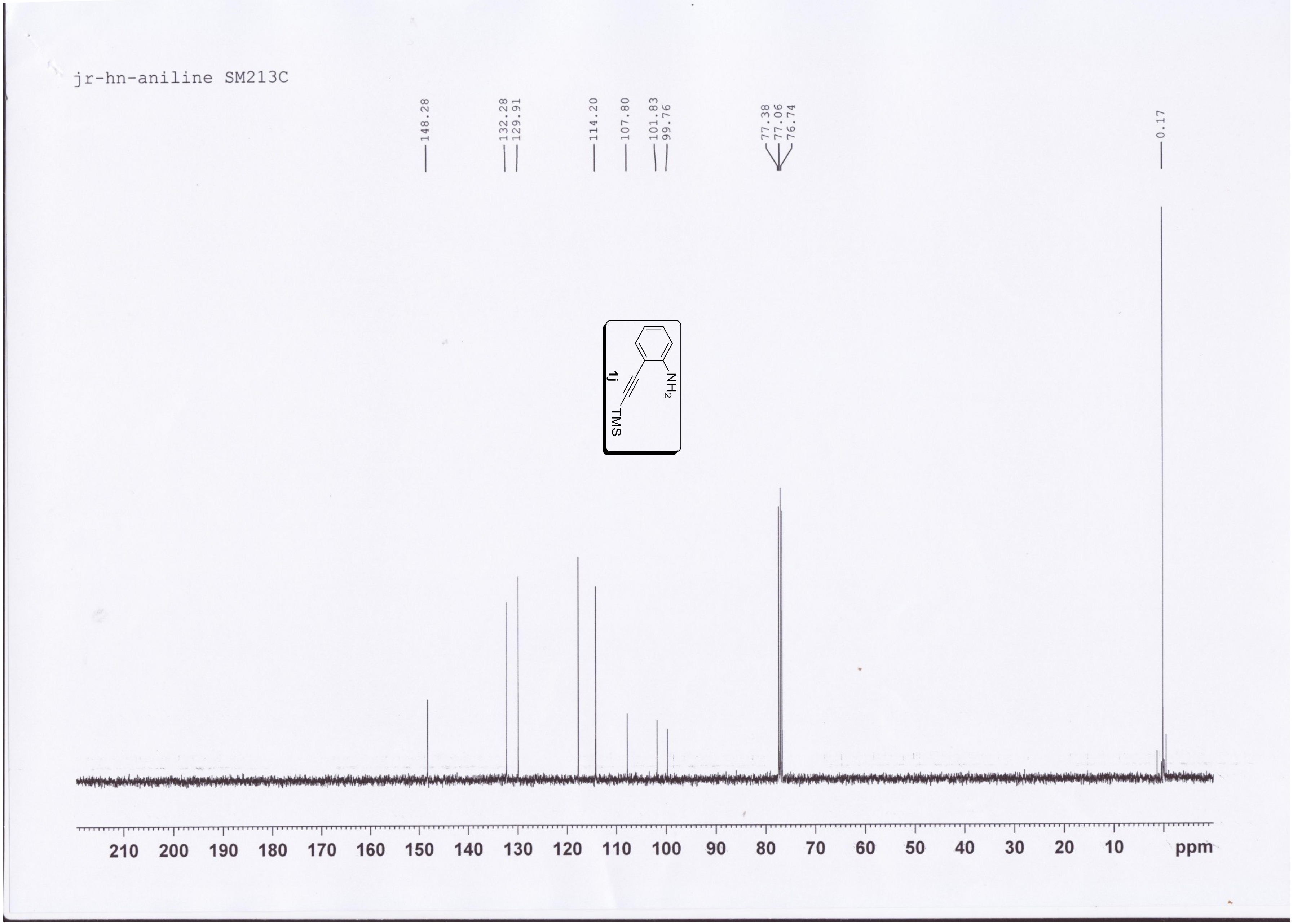


Figure S18. ^{13}C-NMR spectrum of compound **1i**($CDCl_3$, 100 MHz)

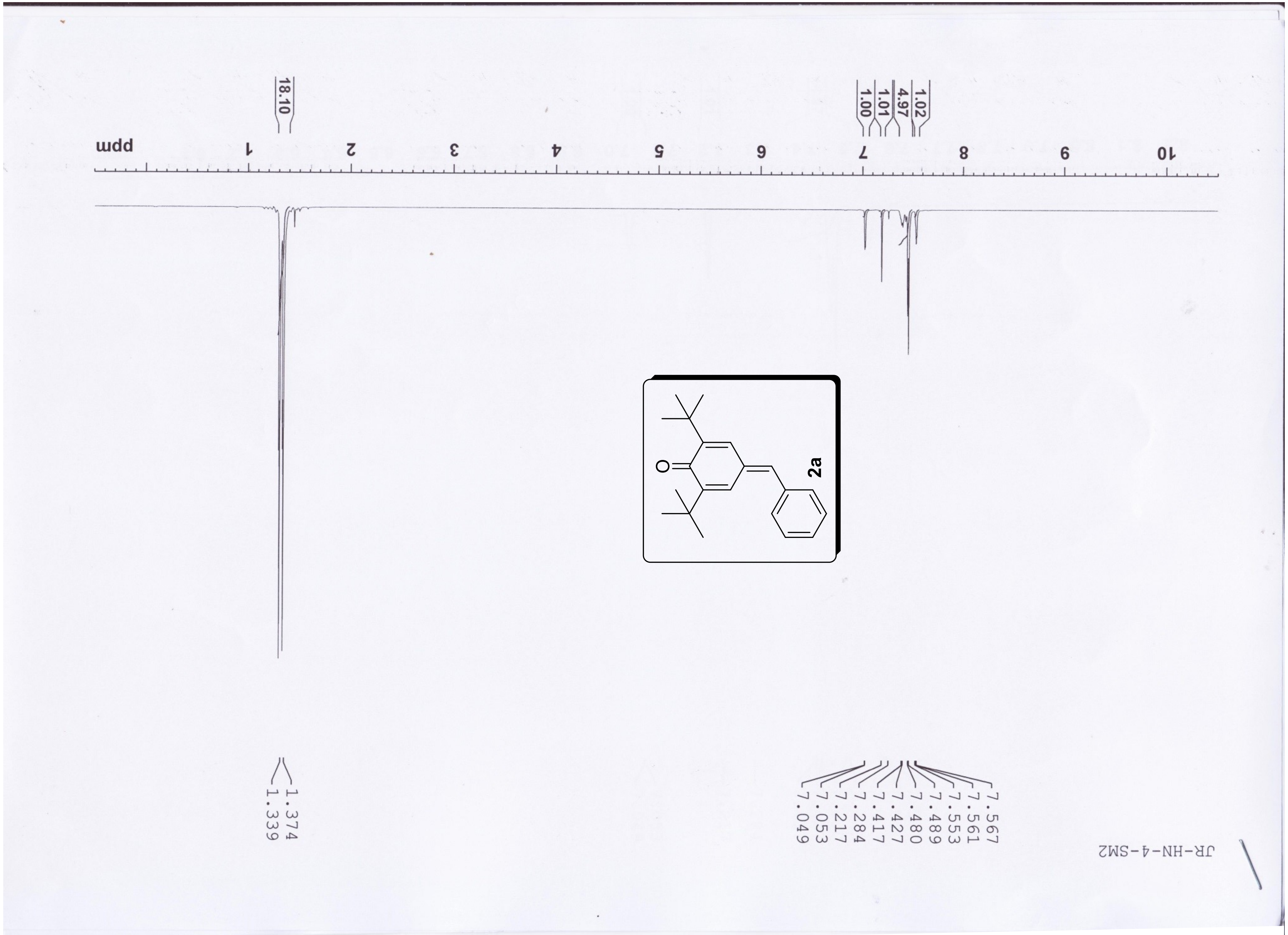


Figure S19. ^{1}H-NMR spectrum of compound **2a**(DMSO-d6, 400 MHz)

Figure S20. ^{13}C-NMR spectrum of compound **2a**(DMSO-d6, 100 MHz)

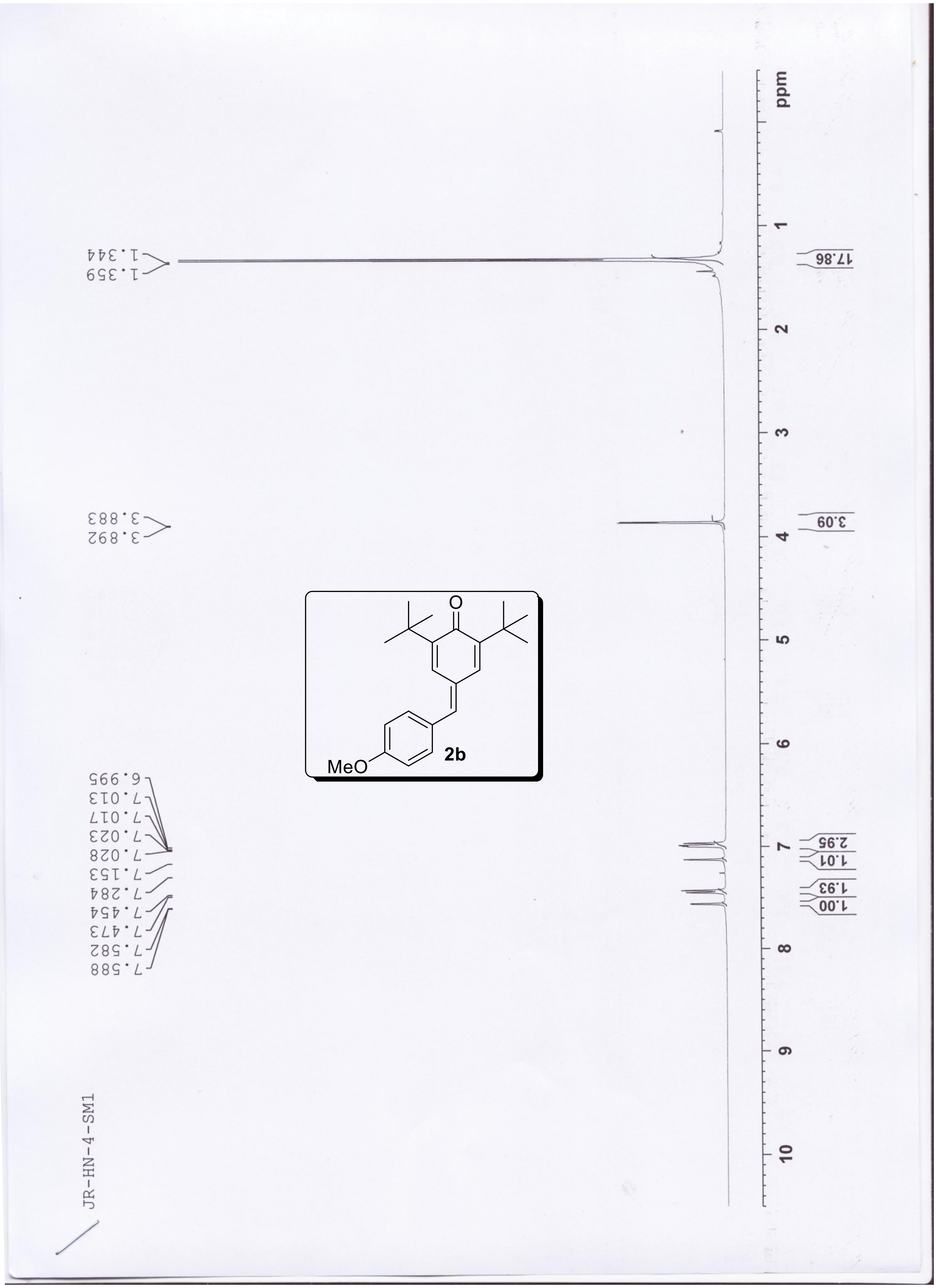


Figure S21. ^{1}H-NMR spectrum of compound **2b**($CDCl_3$, 400 MHz)

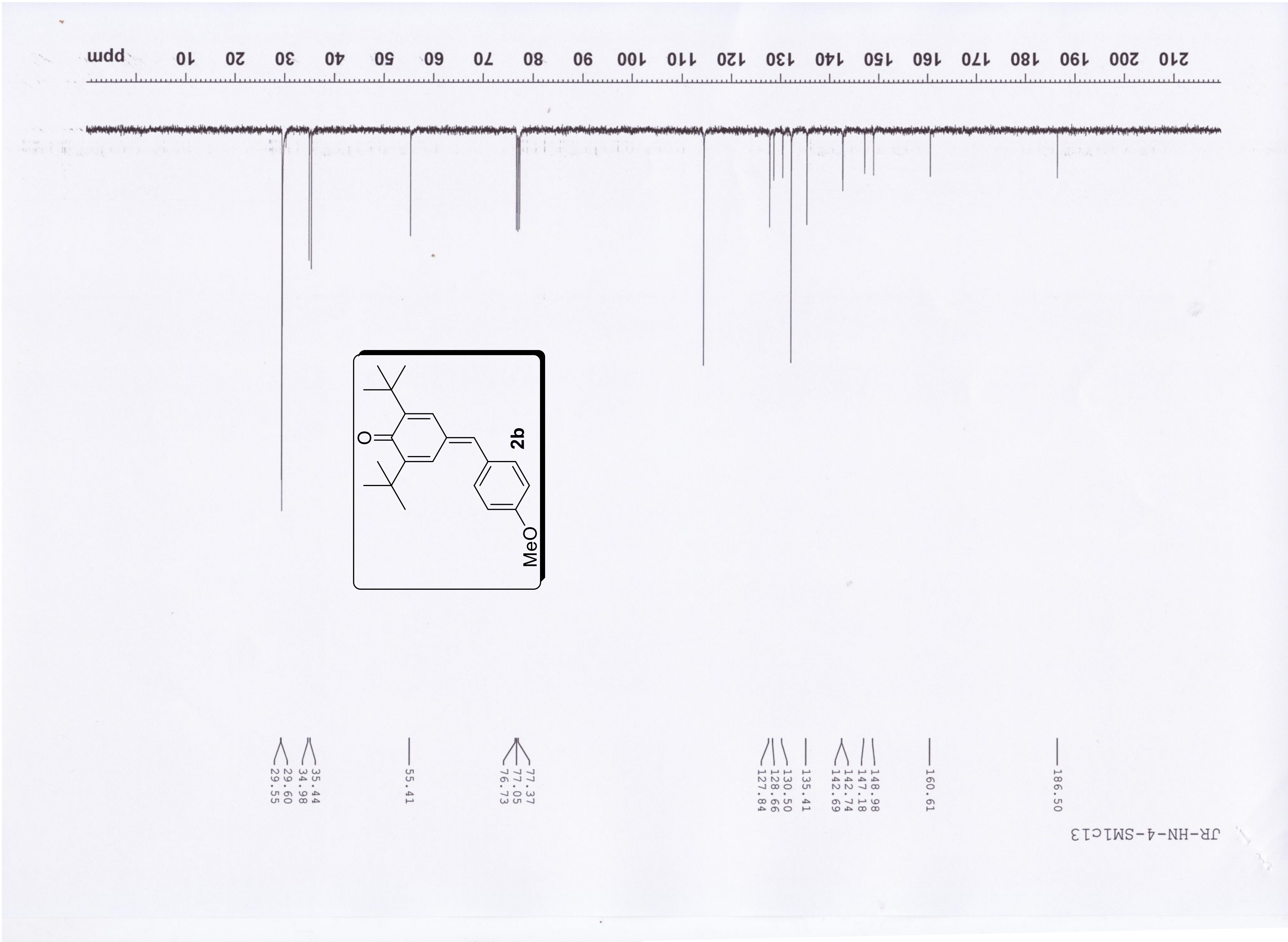


Figure S22. ^{13}C-NMR spectrum of compound **2b**($CDCl_3$, 100 MHz)

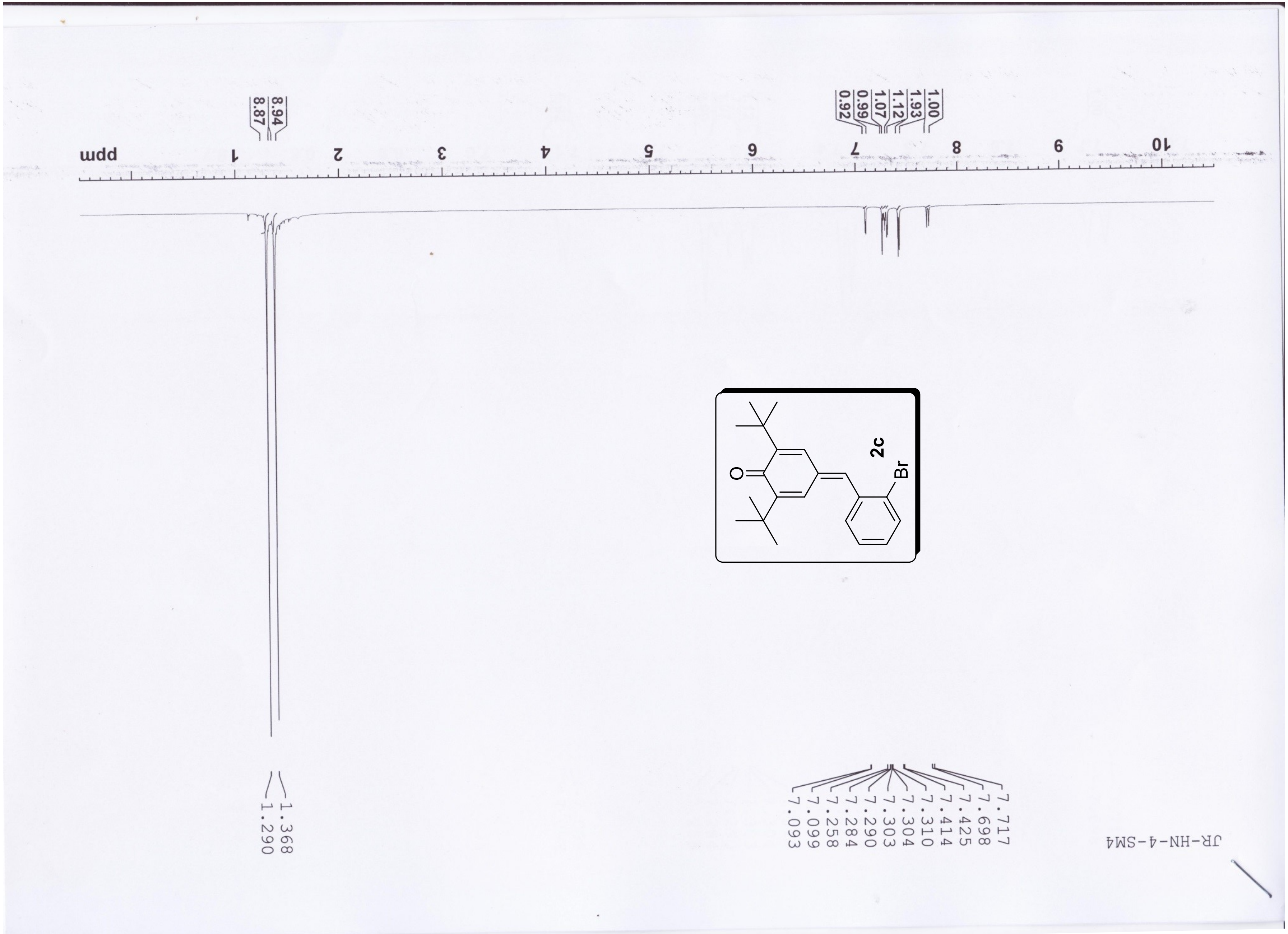


Figure S23. ^{1}H-NMR spectrum of compound **2c**($CDCl_3$, 400 MHz)

Figure S24. ^{13}C-NMR spectrum of compound **2c**($CDCl_3$, 100 MHz)

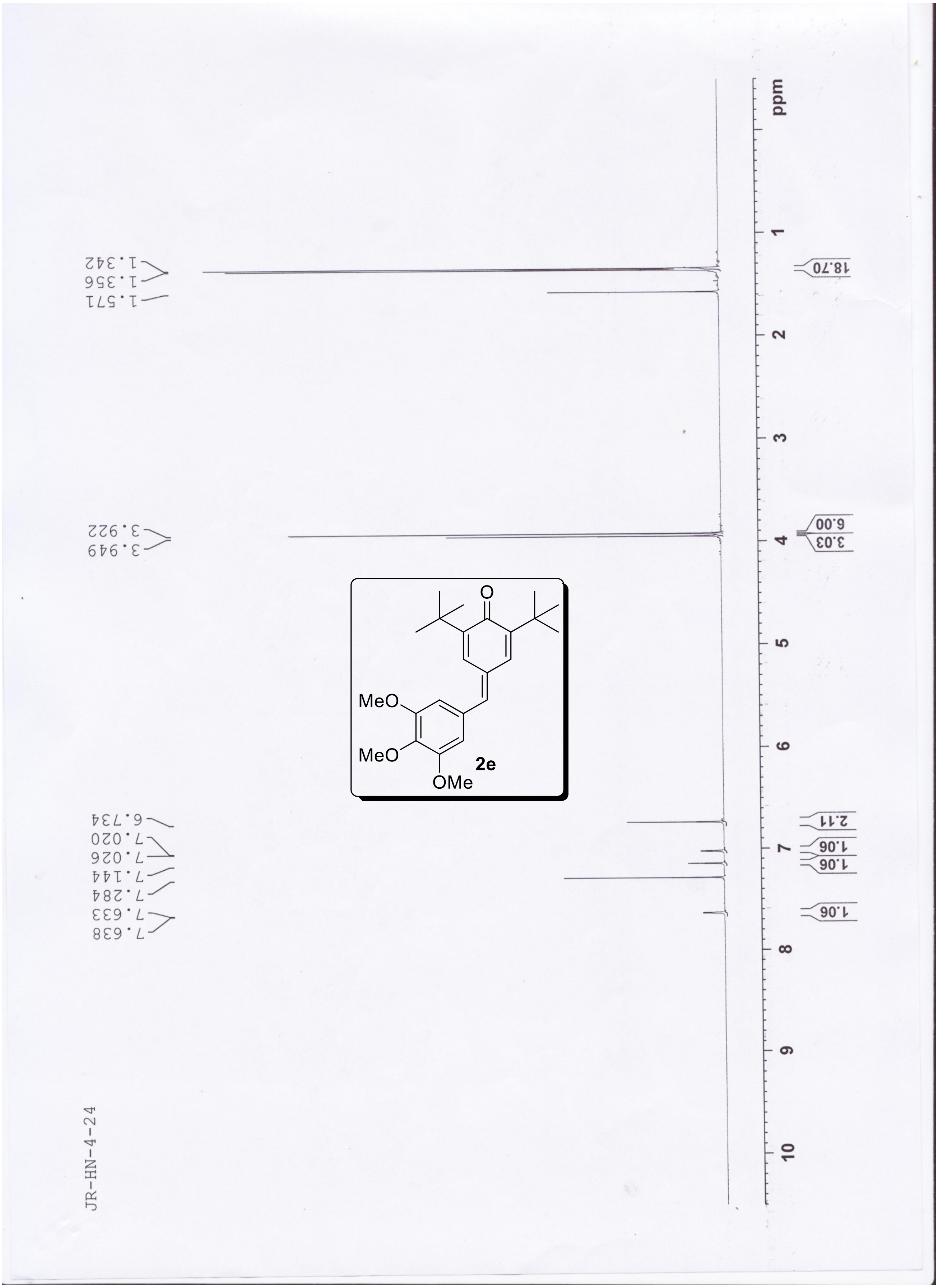


Figure S25. ^{1}H-NMR spectrum of compound **2e**(acetone-d$_6$, 400 MHz)

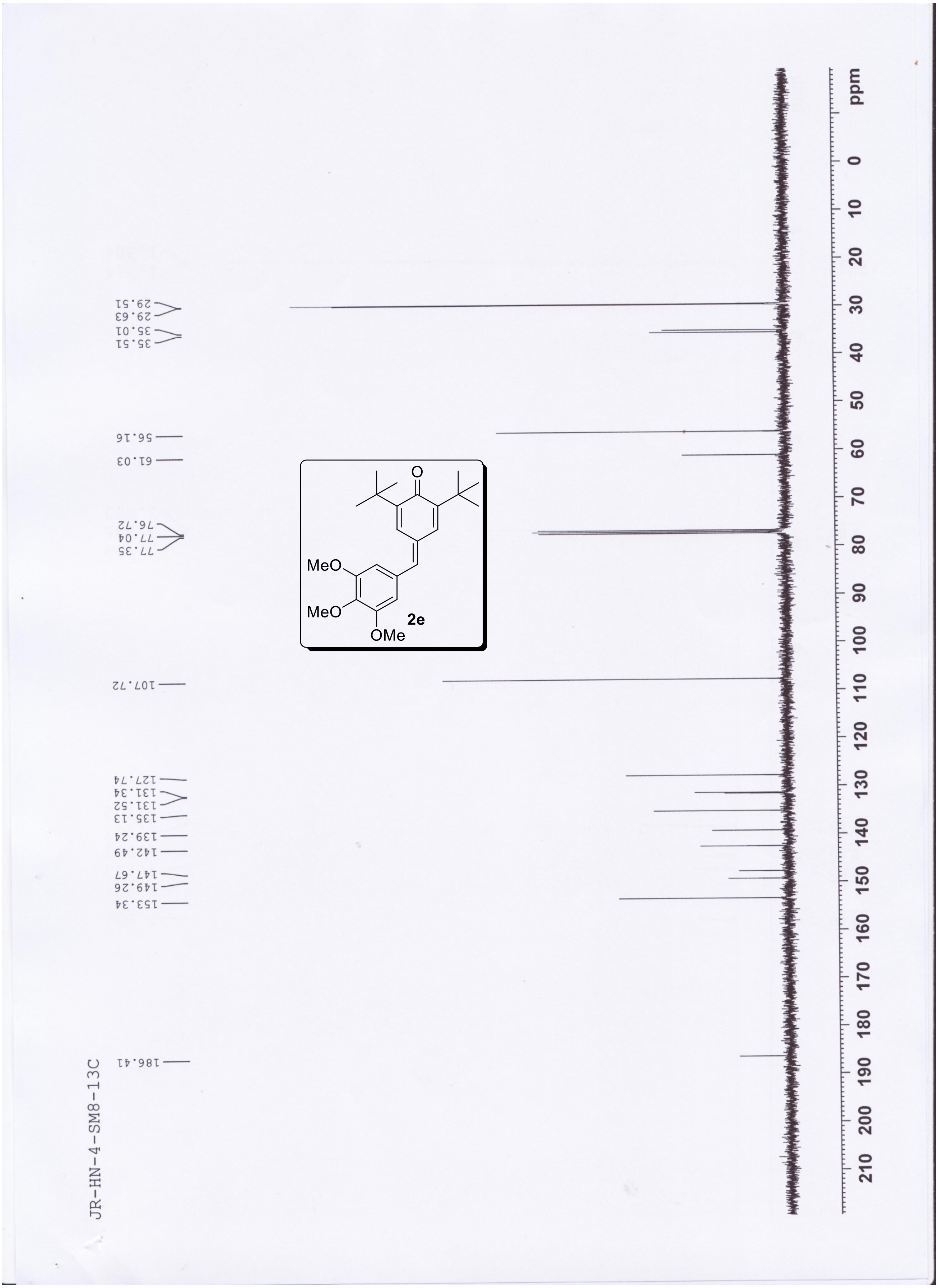


Figure S26. ^{13}C-NMR spectrum of compound **2e**(acetone-d$_6$, 100 MHz)

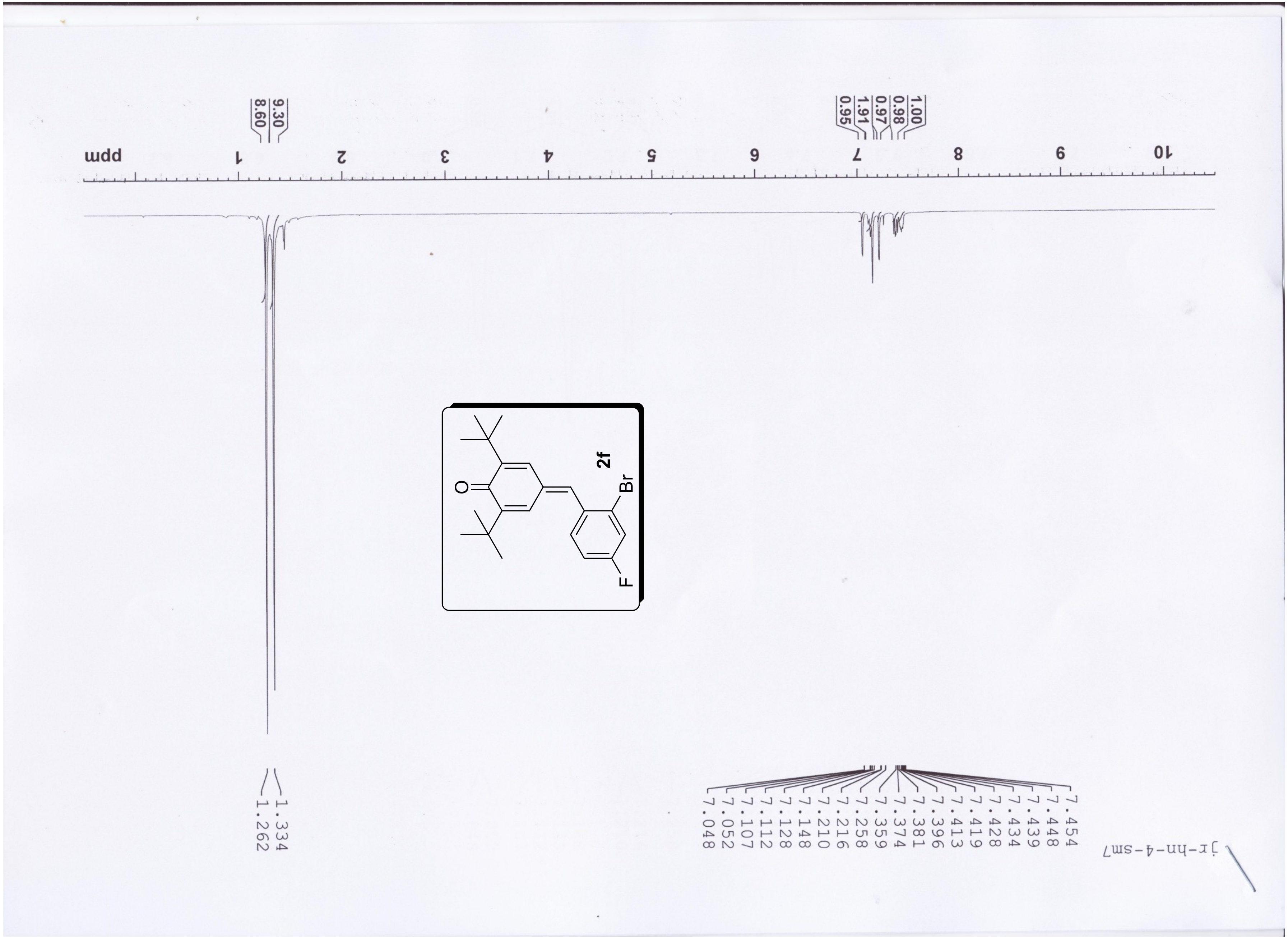


Figure S27. ^{1}H-NMR spectrum of compound **2f**($CDCl_3$, 400 MHz)

Figure S28. ^{1}H-NMR spectrum of compound **2f**($CDCl_3$, 100 MHz)

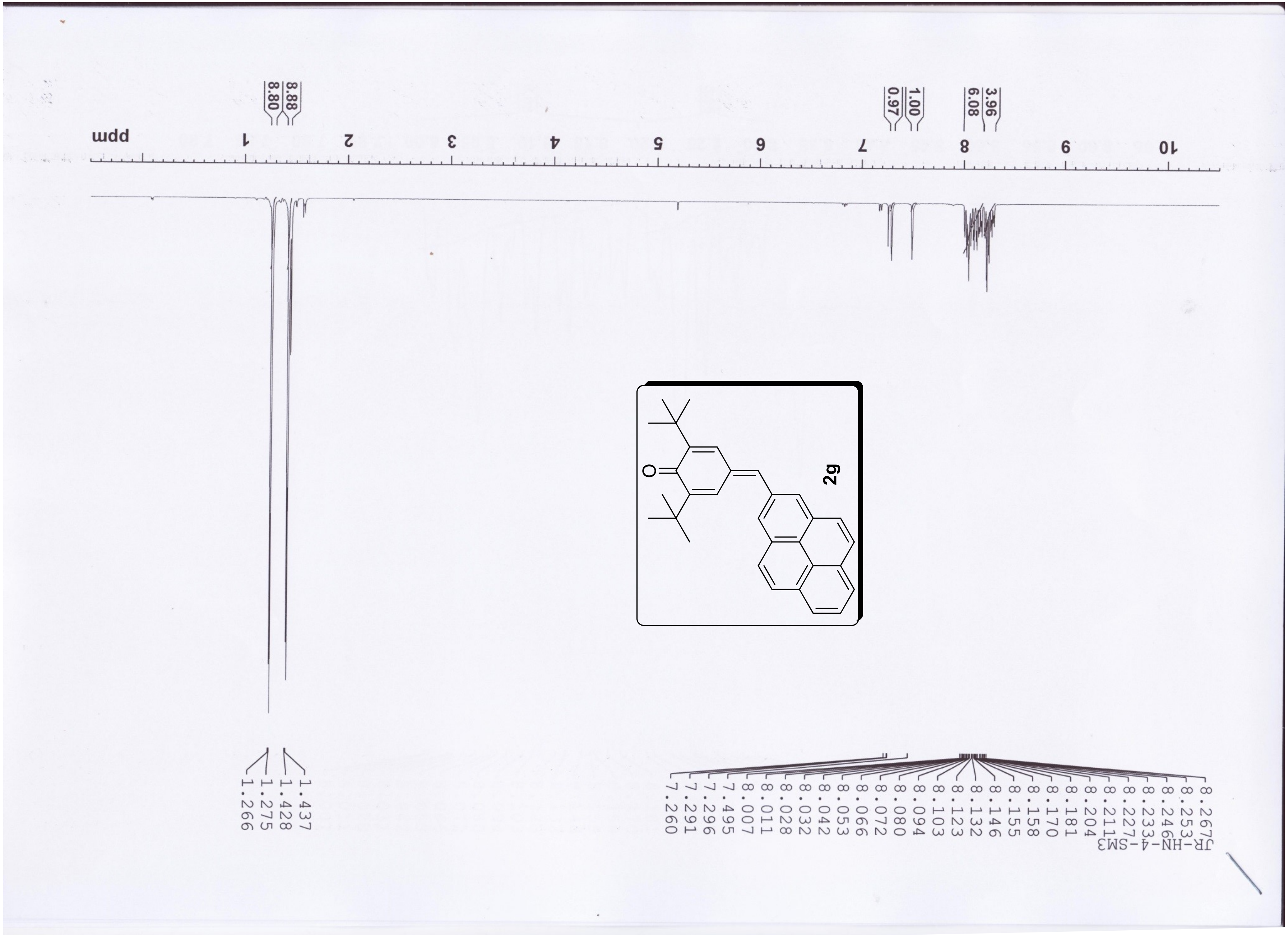


Figure S29. ^{1}H-NMR spectrum of compound **2g**($CDCl_3$, 400 MHz)

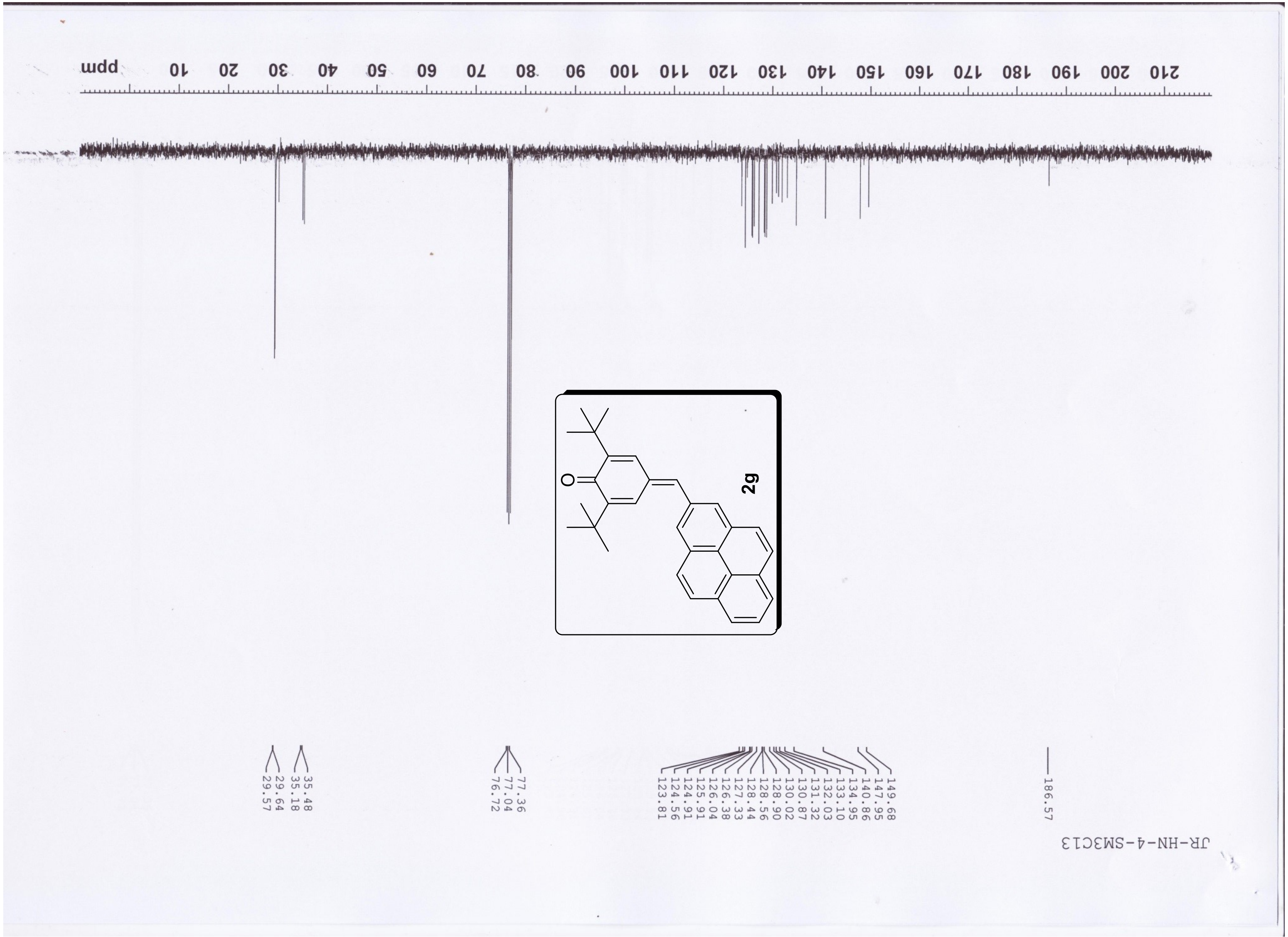


Figure S30. ^{13}C-NMR spectrum of compound **2g**($CDCl_3$, 100 MHz)

Figure S31. ^{1}H-NMR spectrum of compound **2h**($CDCl_3$, 400 MHz)

Figure S32. ^{13}C-NMR spectrum of compound **2h**(DMSO-d_6, 100 MHz)

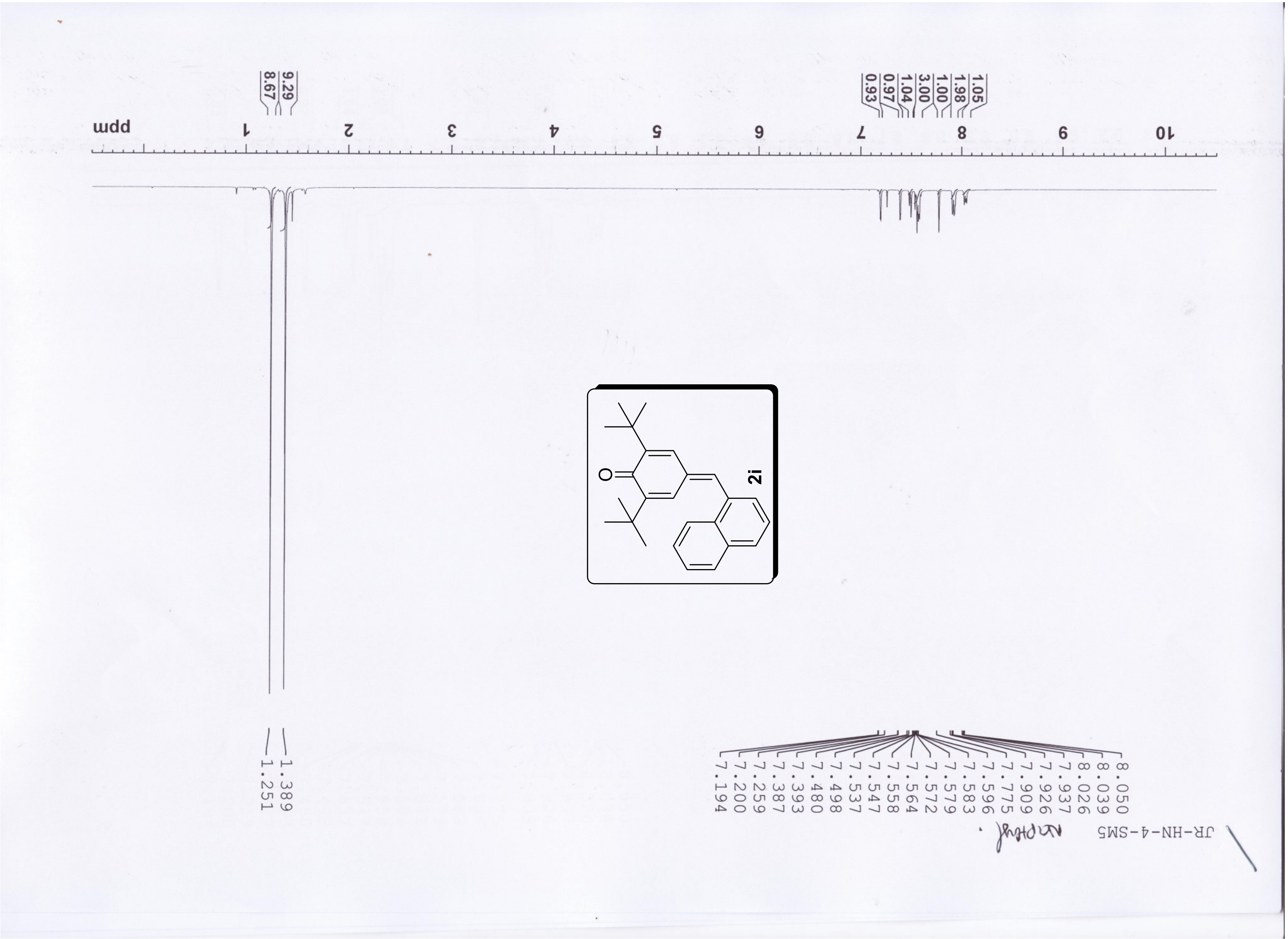


Figure S33. ^{1}H-NMR spectrum of compound **2i**(acetone-d_6, 400 MHz)

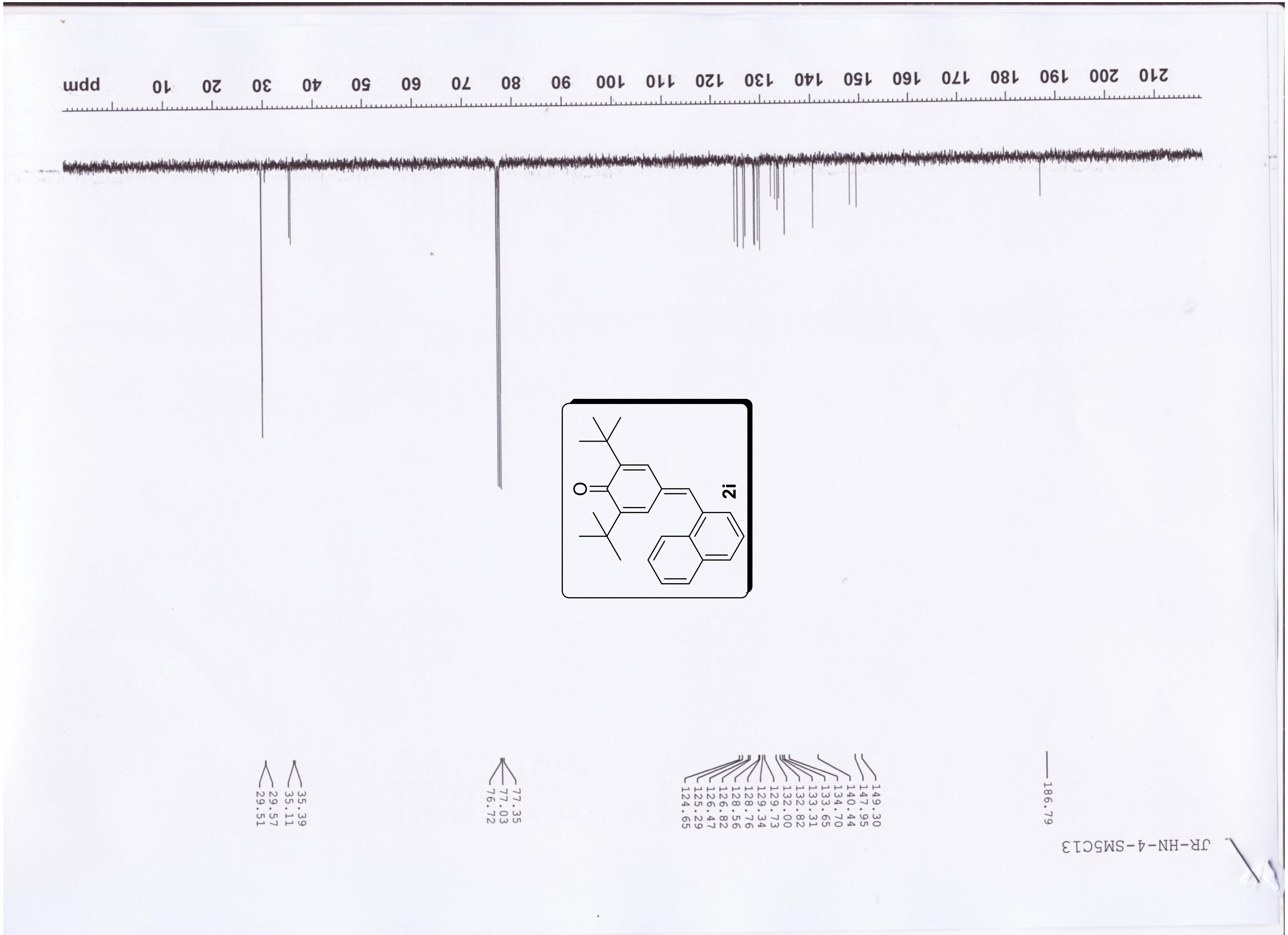


Figure S34. ^{13}C-NMR spectrum of compound **2i**(acetone-d_6, 100 MHz)

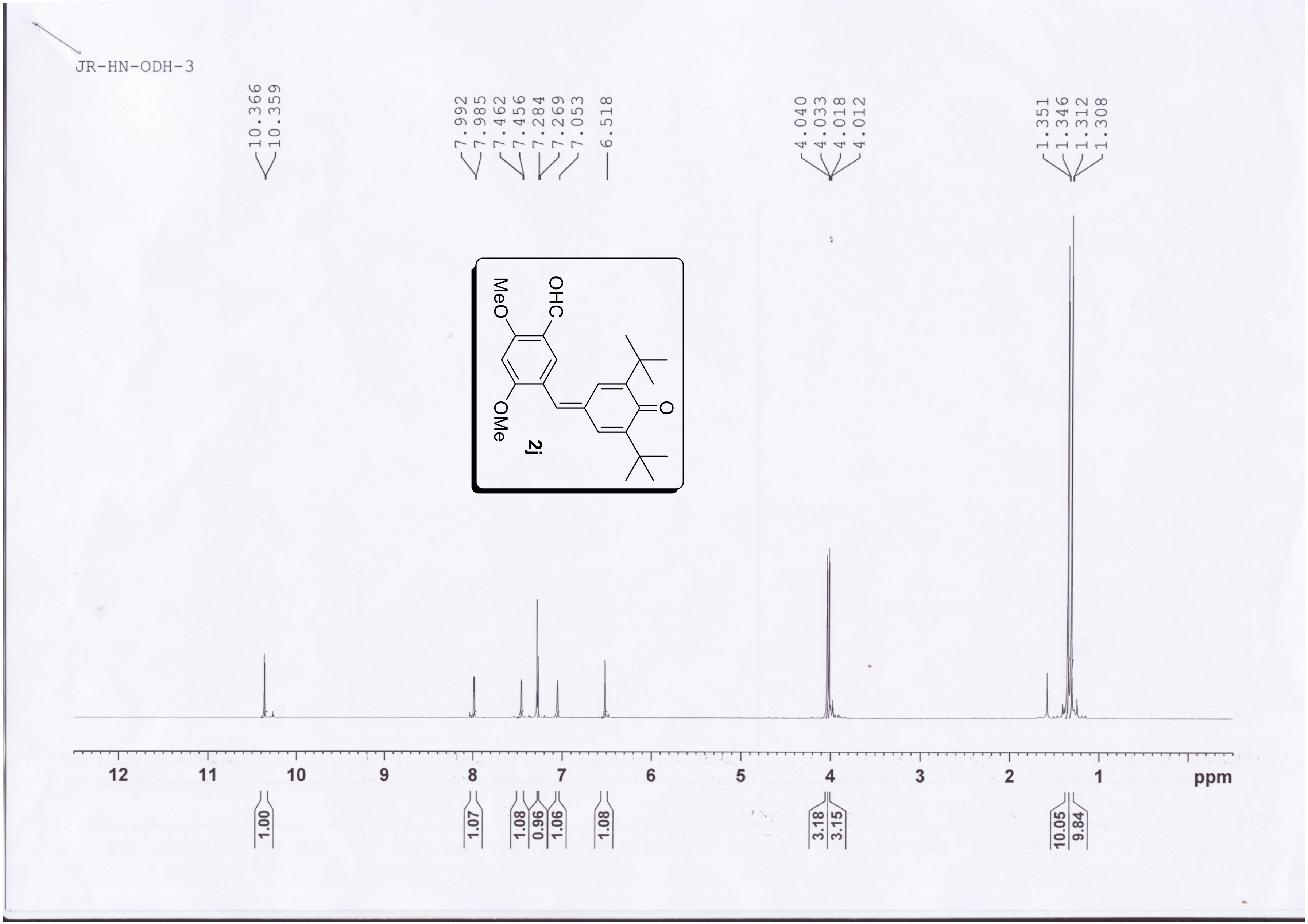


Figure S35. ^{1}H-NMR spectrum of compound **2j**($CDCl_3$, 400 MHz)

Figure S36. ^{13}C-NMR spectrum of compound **2j**($CDCl_3$, 100 MHz)

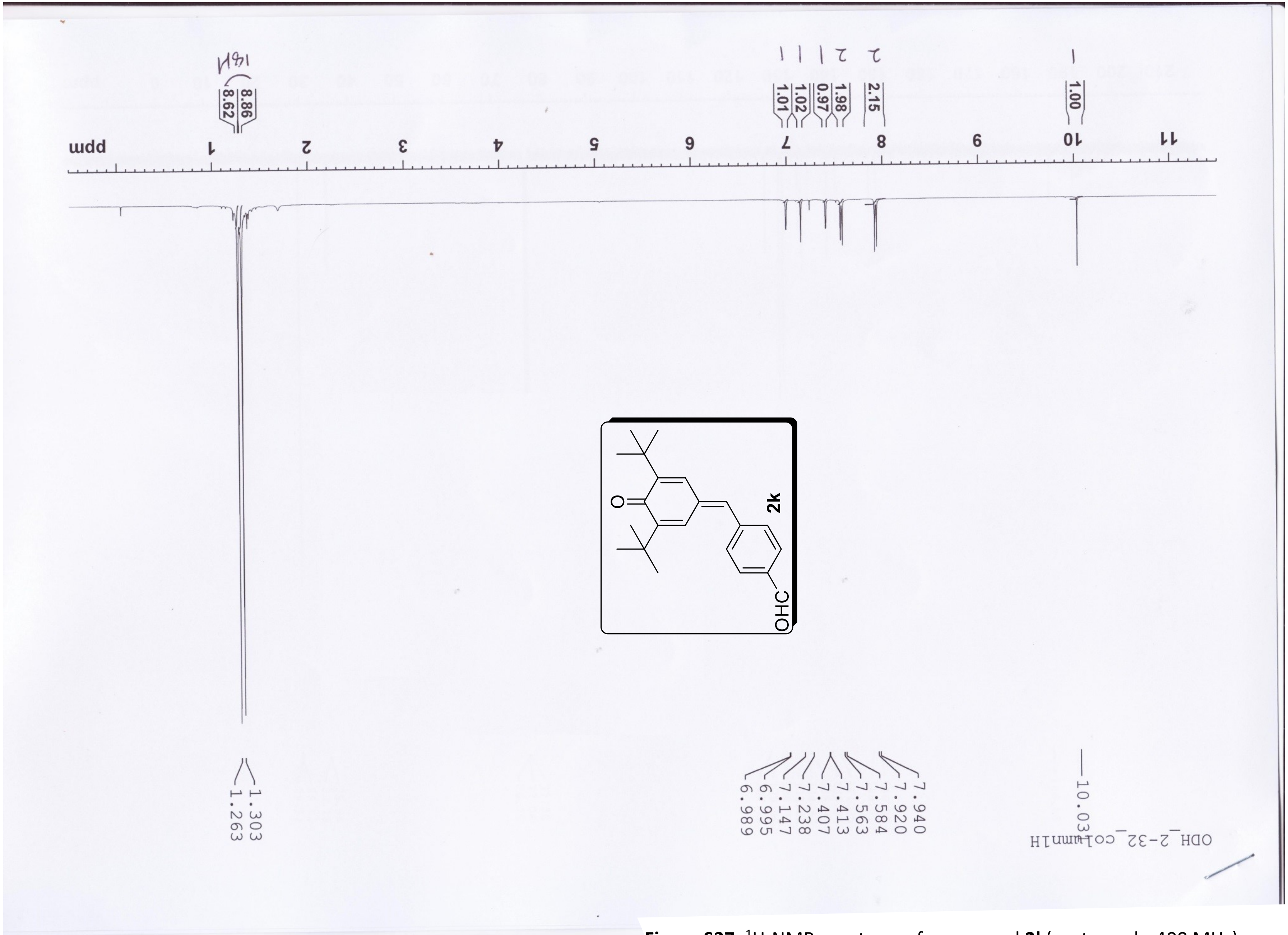


Figure S37. ^{1}H-NMR spectrum of compound **2k**(acetone-d_6, 400 MHz)

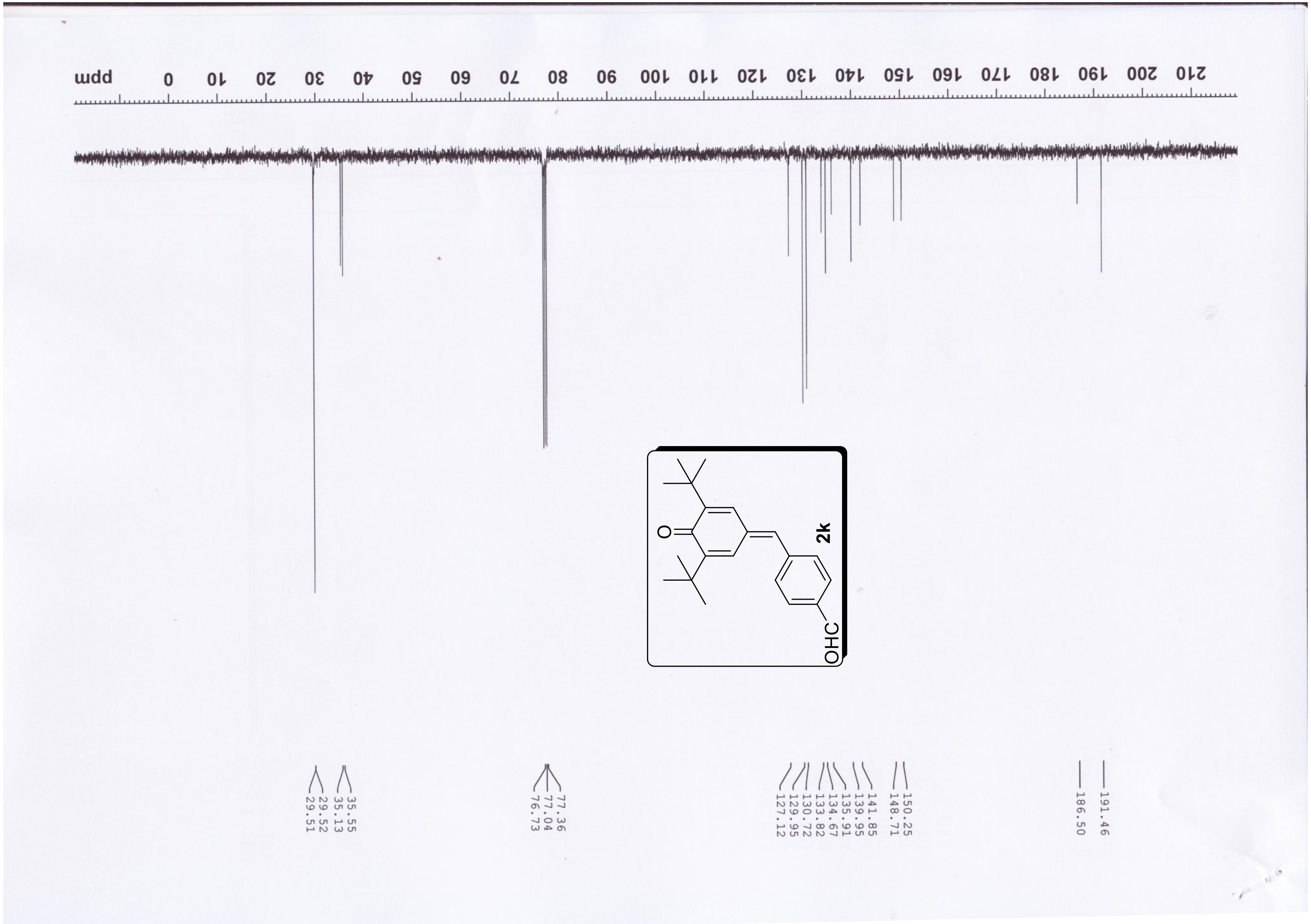


Figure S39. ^{1}H-NMR spectrum of compound **2k**(acetone-d_6, 400 MHz)

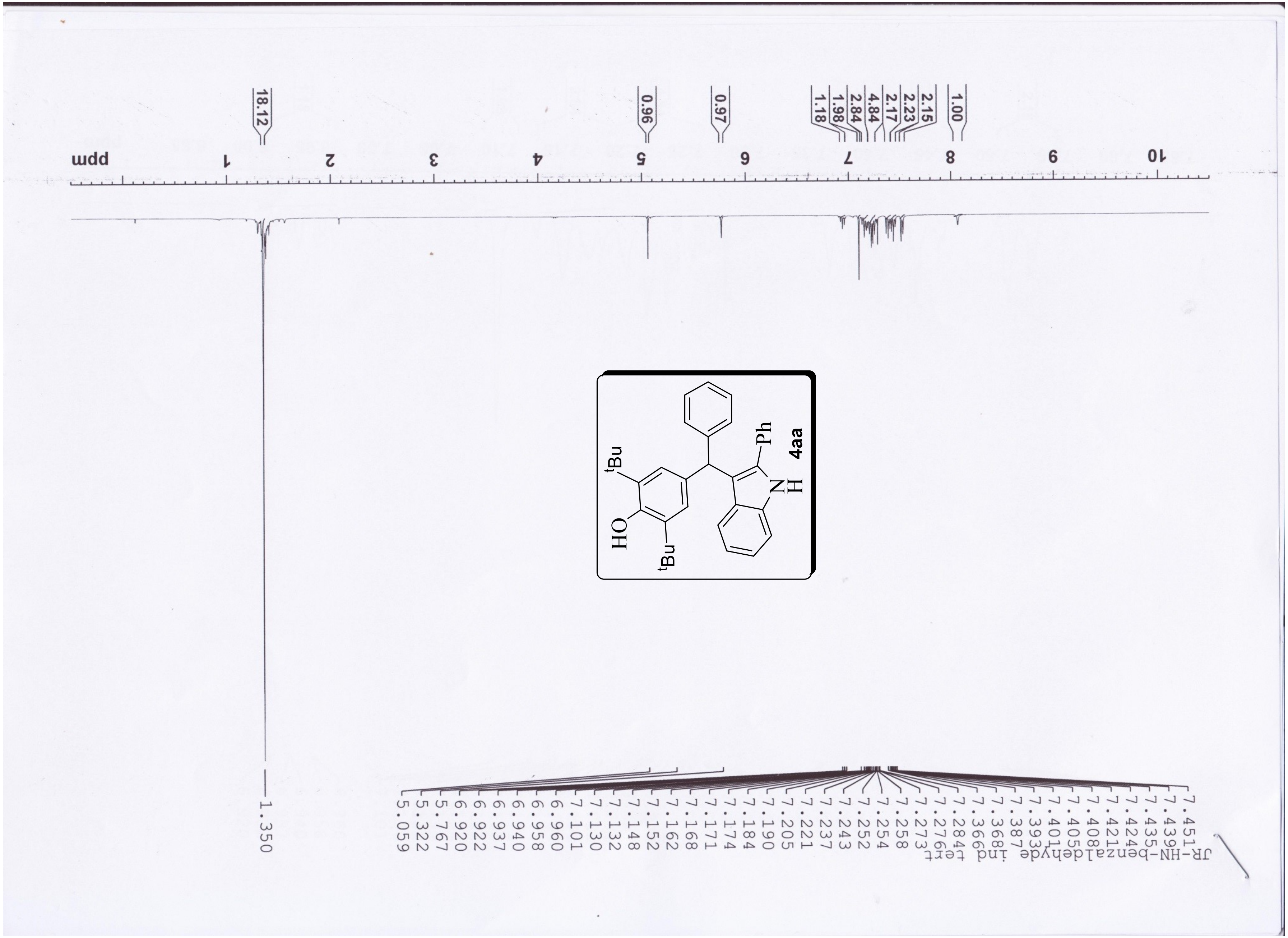


Figure S40. ^{1}H-NMR spectrum of compound **4aa**($CDCl_3$, 400 MHz)

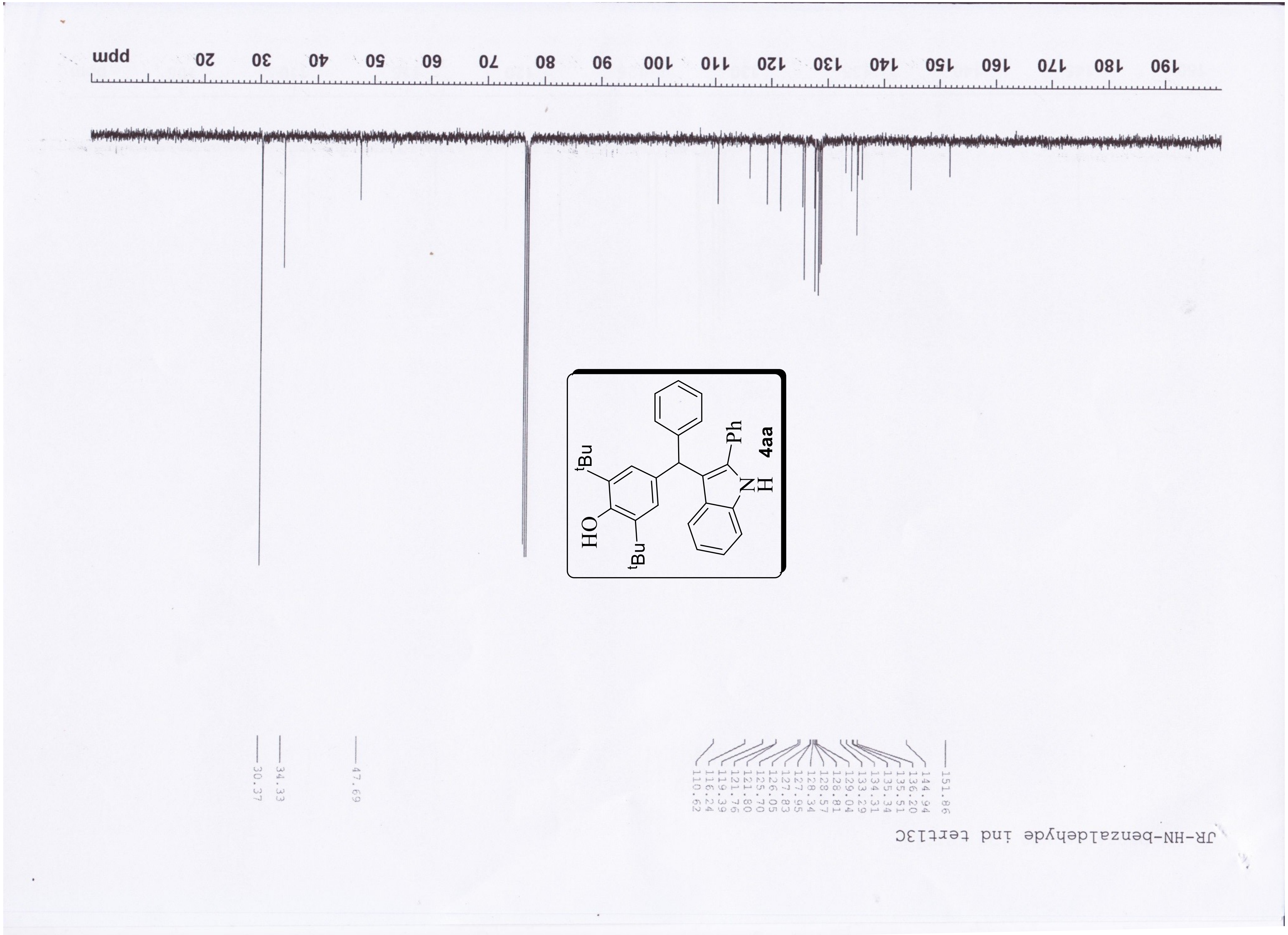


Figure S41. ^{13}C-NMR spectrum of compound **4aa** ($CDCl_3$, 100 MHz)

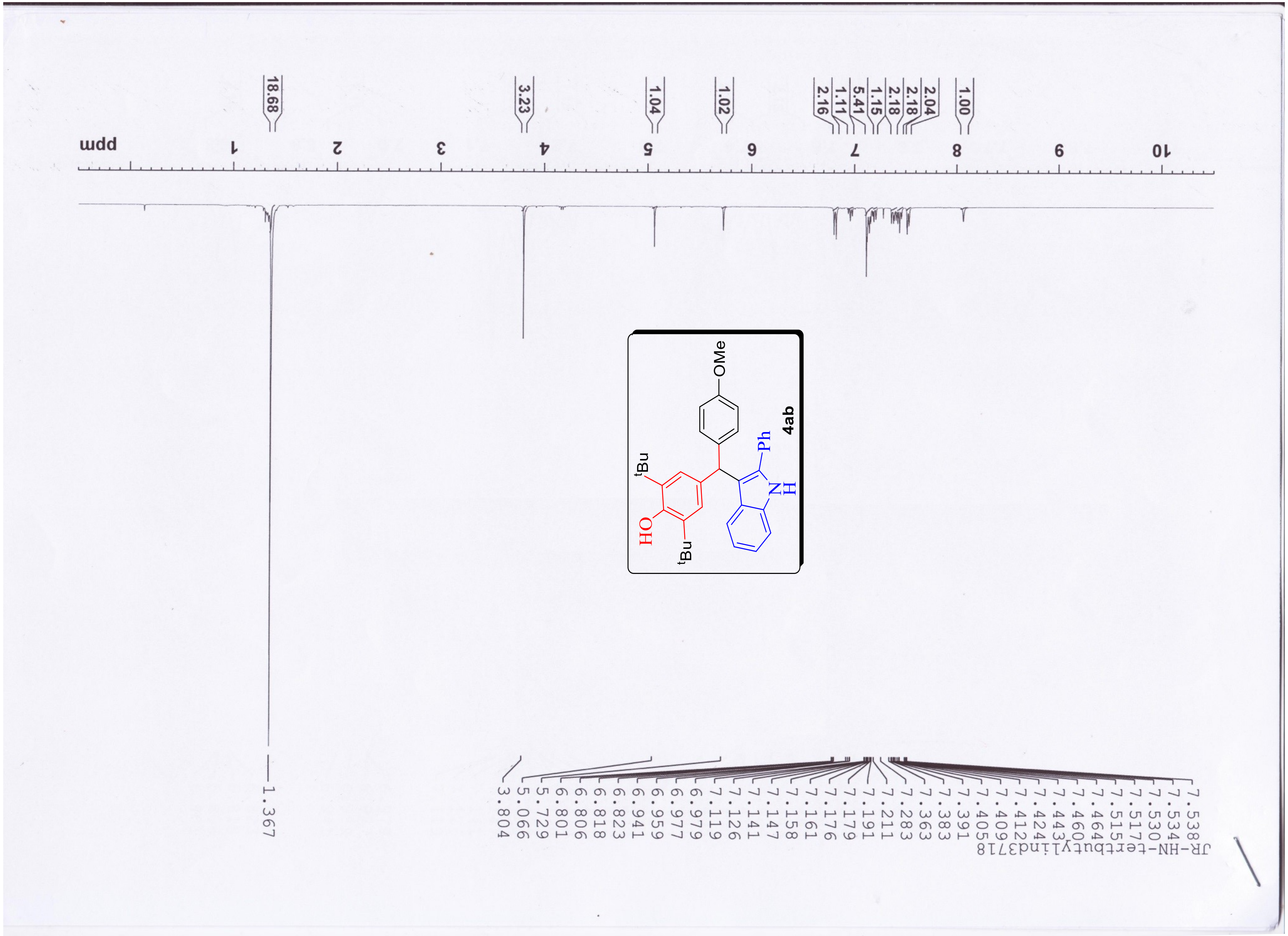


Figure S42. ^{1}H-NMR spectrum of compound **4ab**($CDCl_3$, 400 MHz)

Figure S43. ^{13}C-NMR spectrum of compound **4ab**($CDCl_3$,100 MHz)

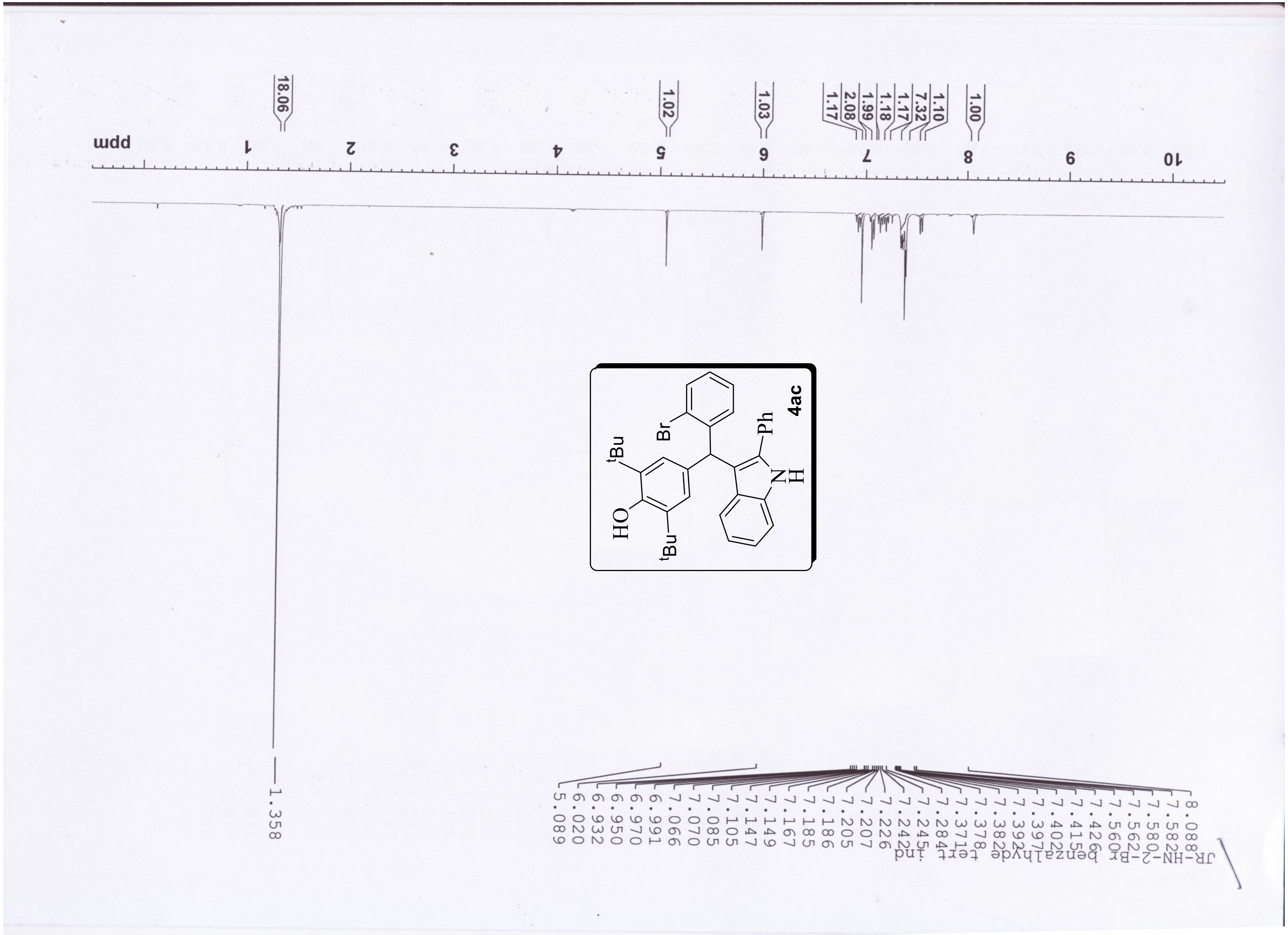


Figure S44. ^{1}H-NMR spectrum of compound **4ac**($CDCl_3$, 400 MHz)

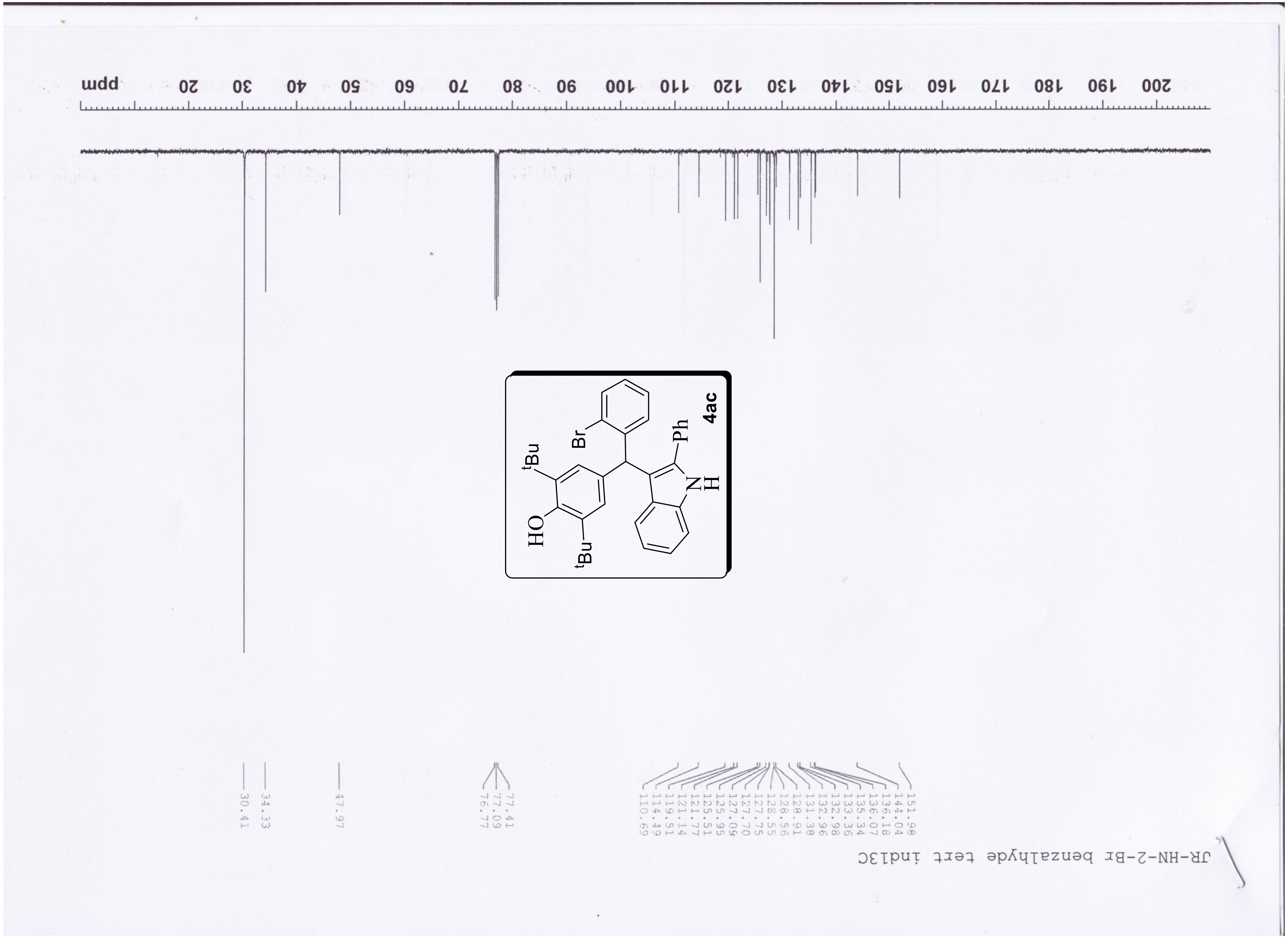


Figure S45. ^{13}C-NMR spectrum of compound **4ac**($CDCl_3$, 100 MHz)

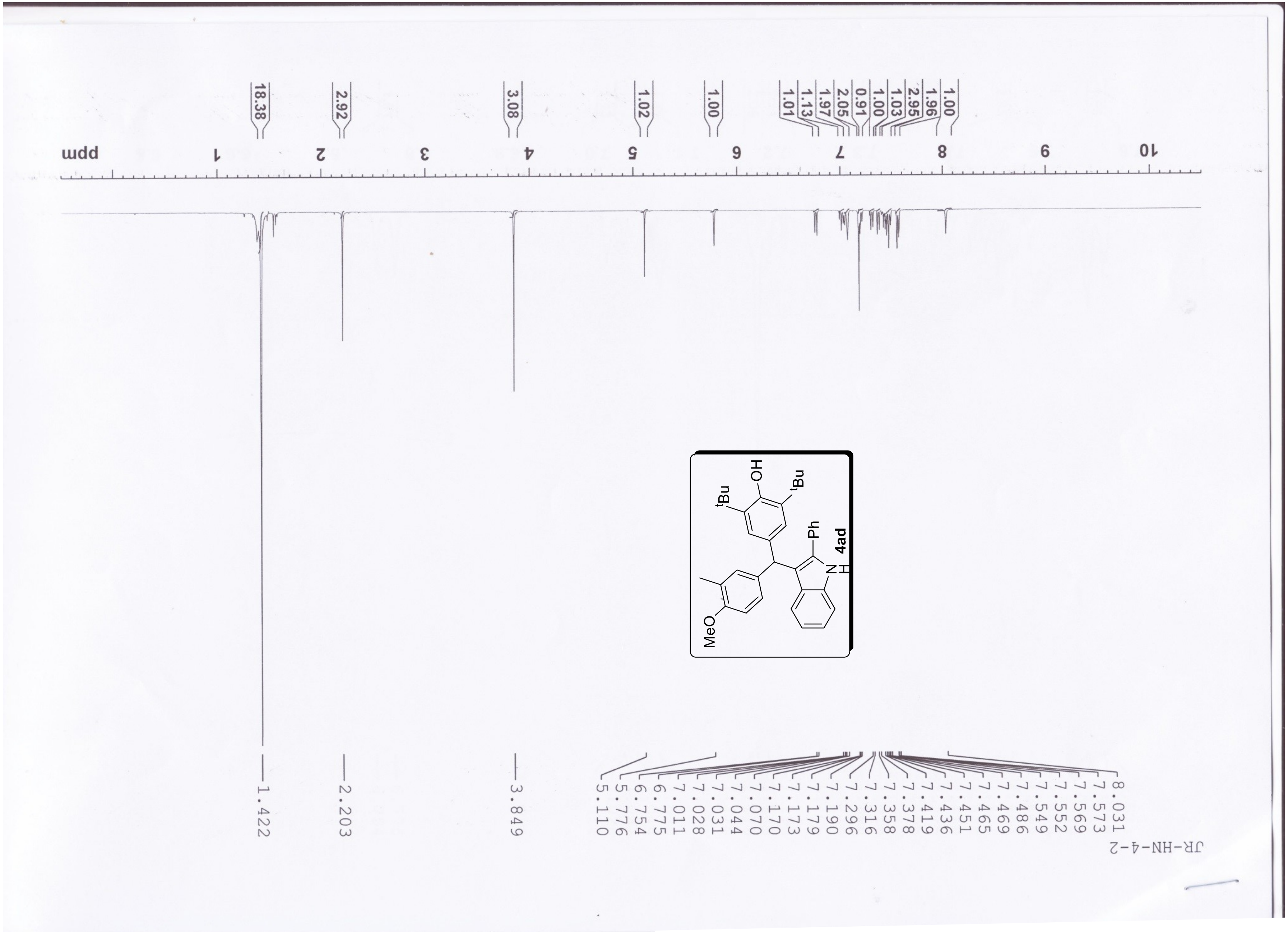


Figure S46. ^{1}H-NMR spectrum of compound **4ad**($CDCl_3$, 400 MHz)

Figure S47. ^{13}C-NMR spectrum of compound **4ad**($CDCl_3$, 100 MHz)

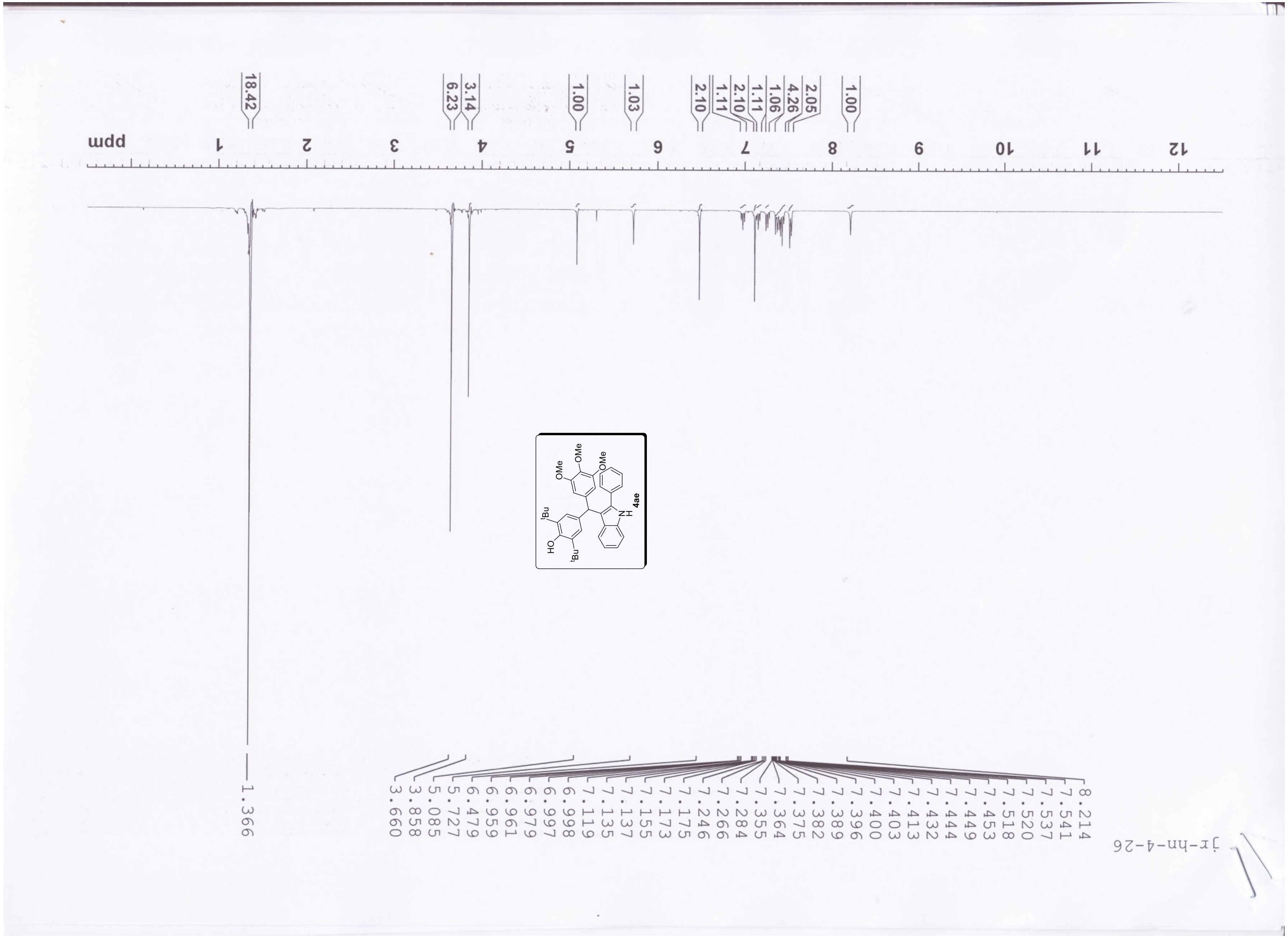


Figure S48. ^{1}H-NMR spectrum of compound **4ae**($CDCl_3$, 400 MHz)

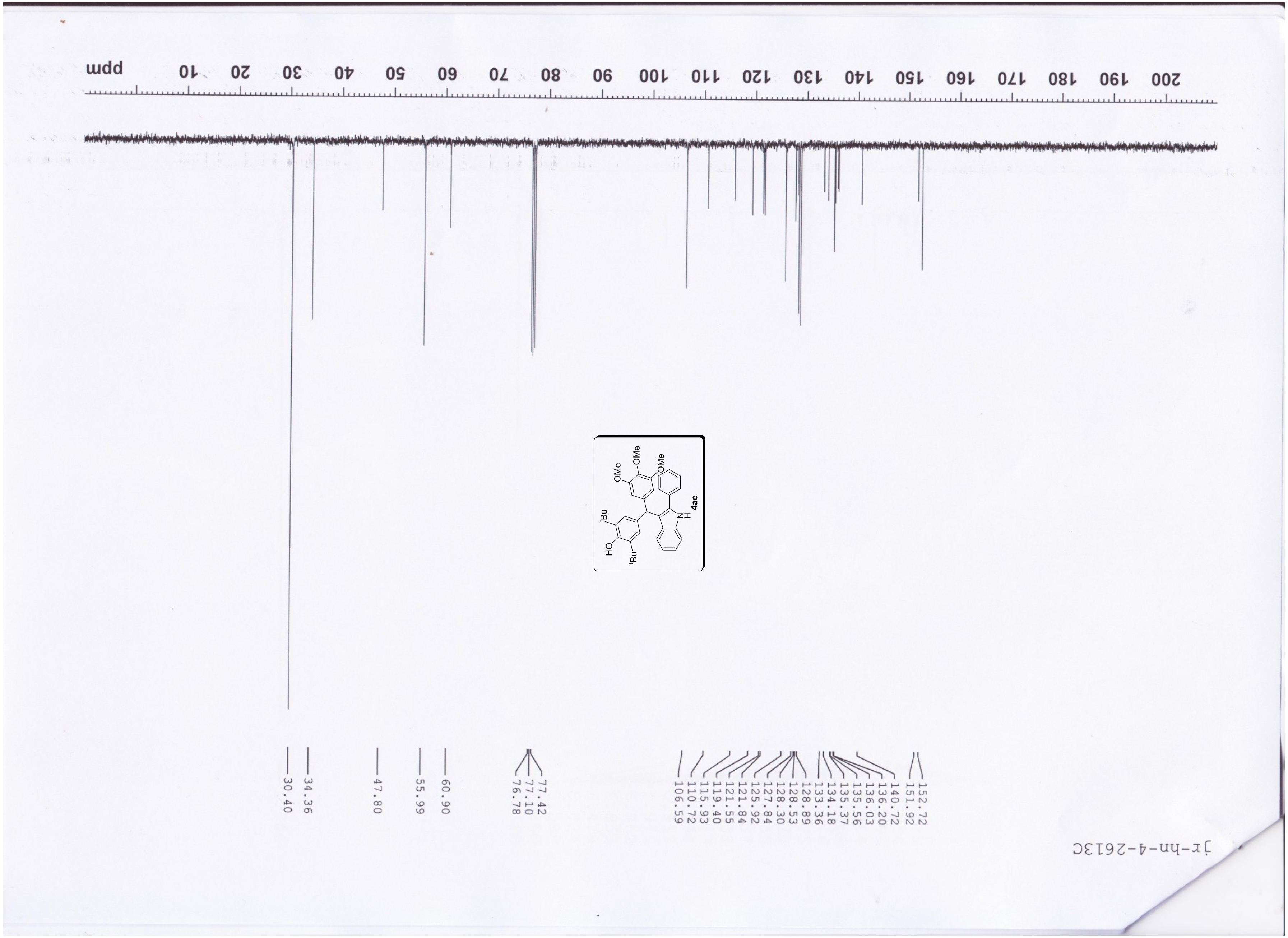


Figure S49. ^{13}C-NMR spectrum of compound **4ae**(($CDCl_3$, 100 MHz)

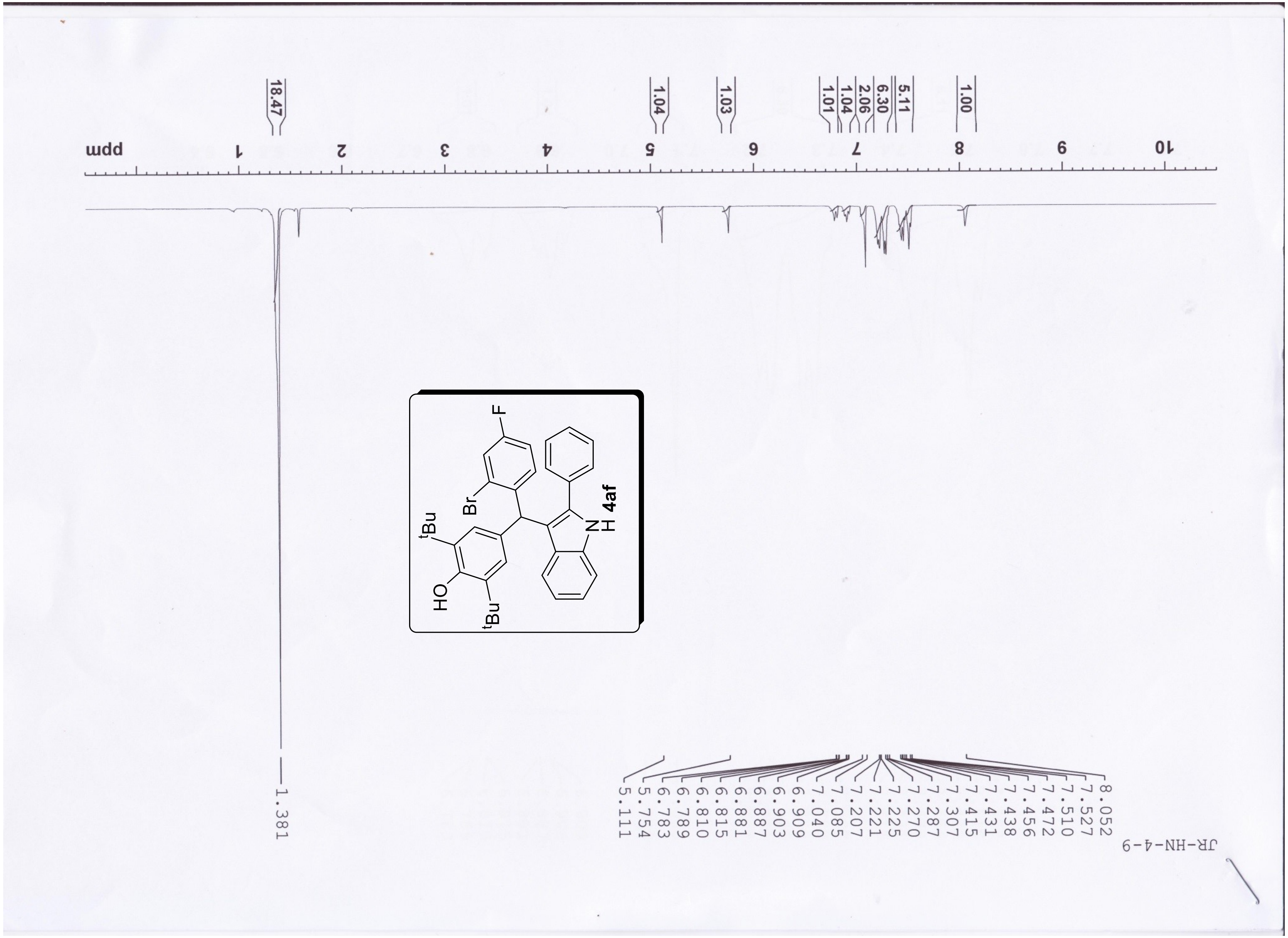


Figure S50. ^{1}H-NMR spectrum of compound **4af**($CDCl_3$, 400 MHz)

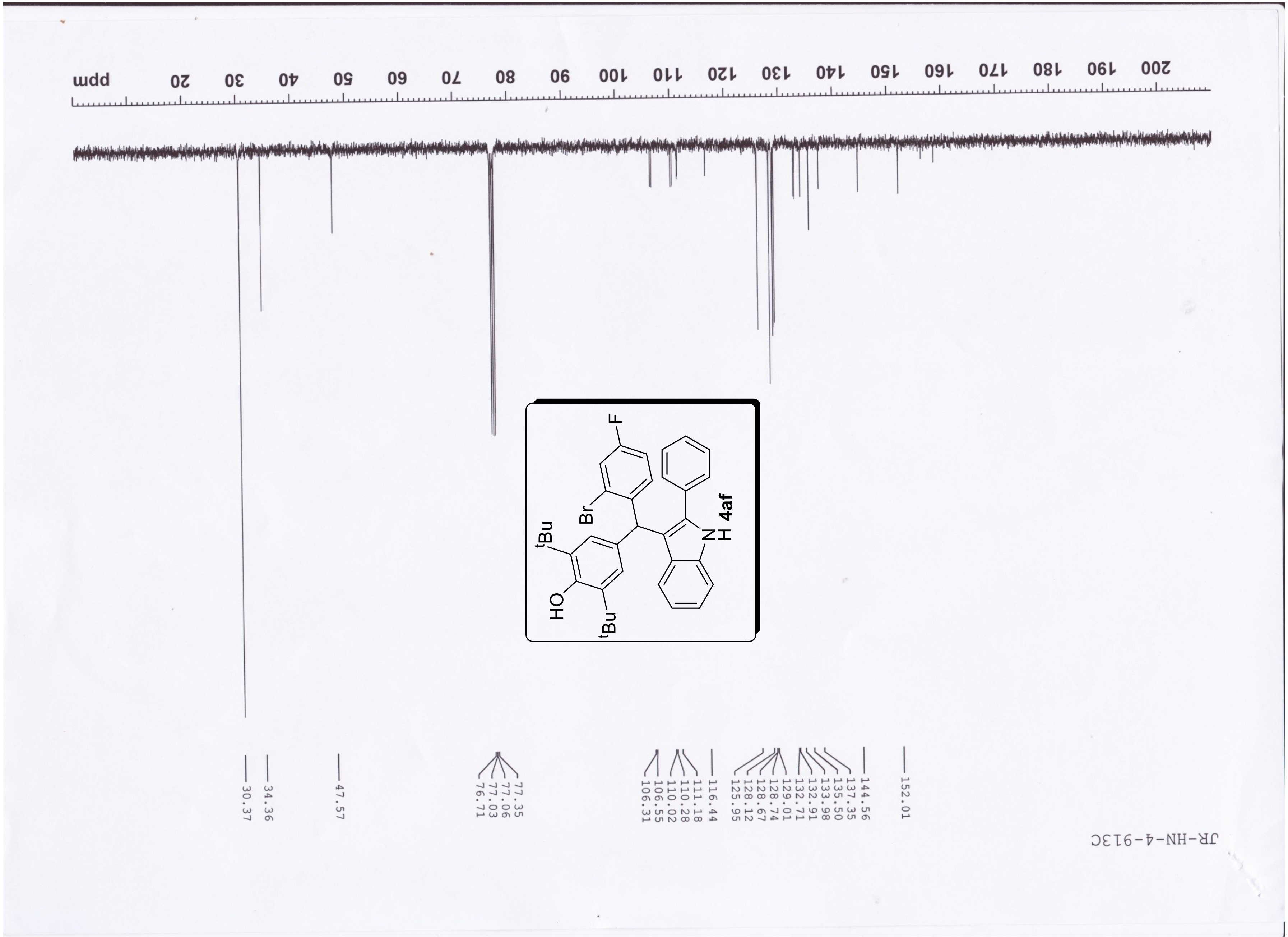


Figure **Figure S51.** ^{13}C-NMR spectrum of compound **4af**($CDCl_3$, 100 MHz)

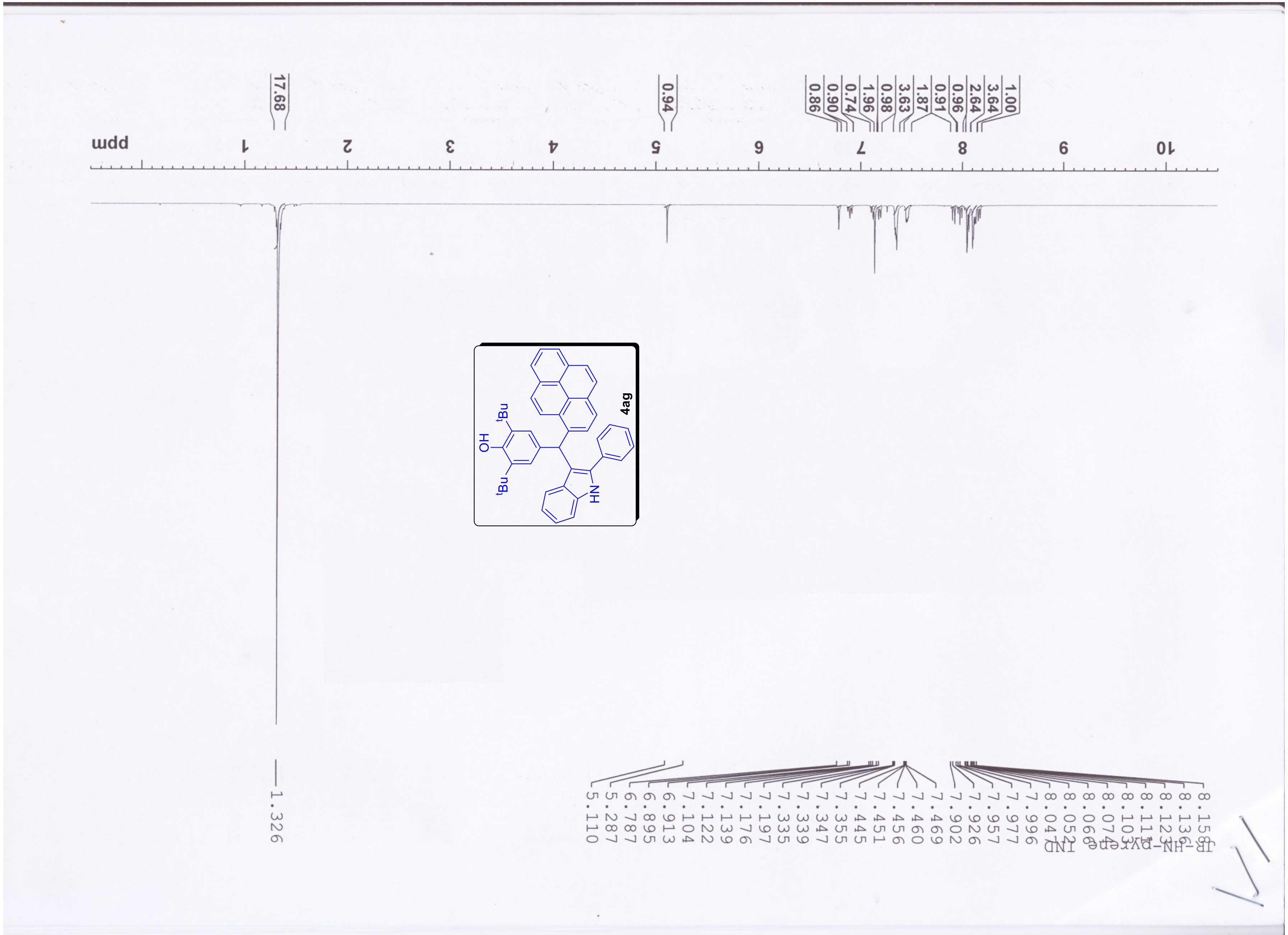


Figure Figure S52. ^{1}H-NMR spectrum of compound **4ag**($CDCl_3$, 400 MHz)

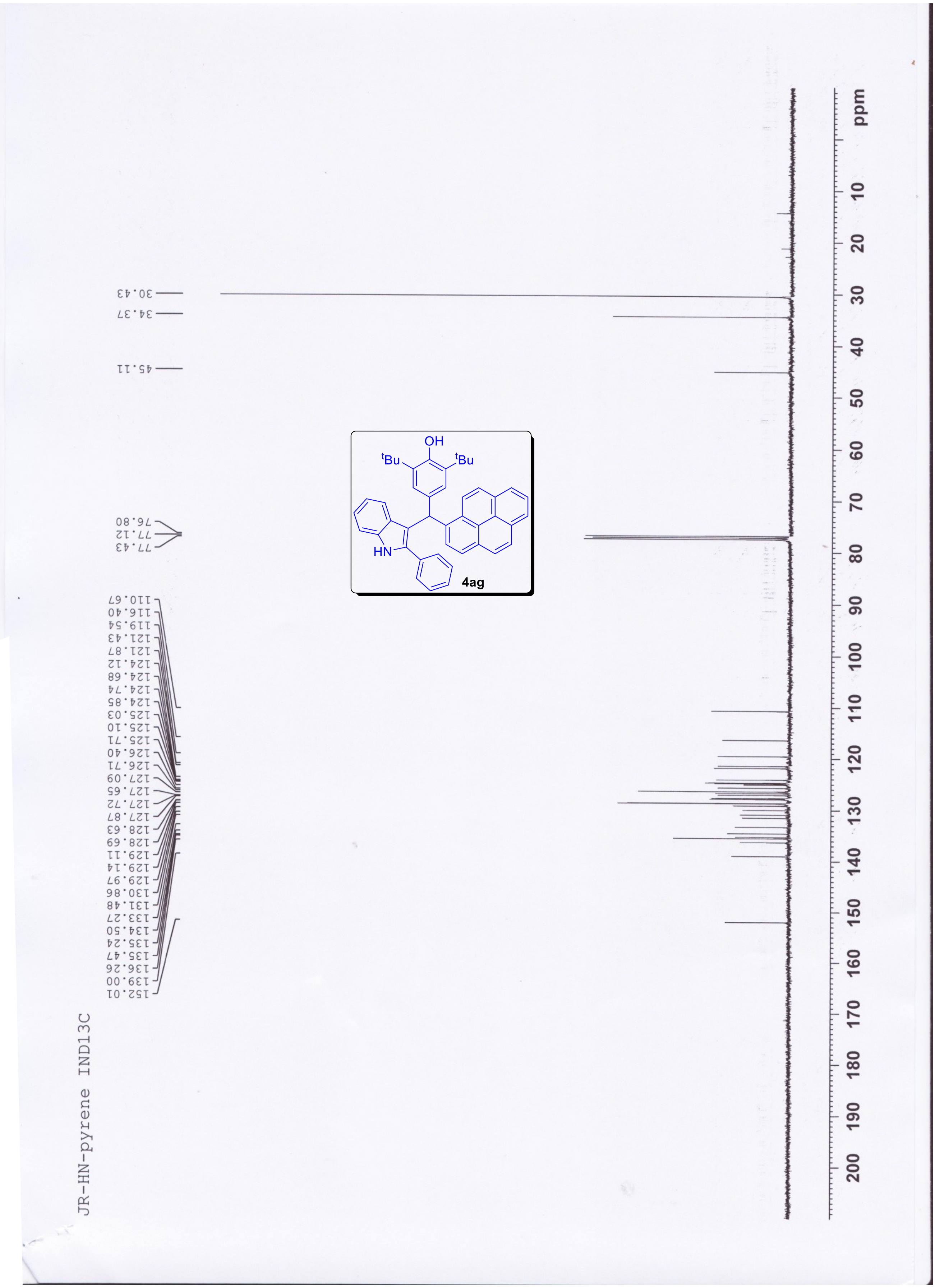


Figure S53. ^{13}C-NMR spectrum of compound **4ag**($CDCl_3$, 400 MHz)

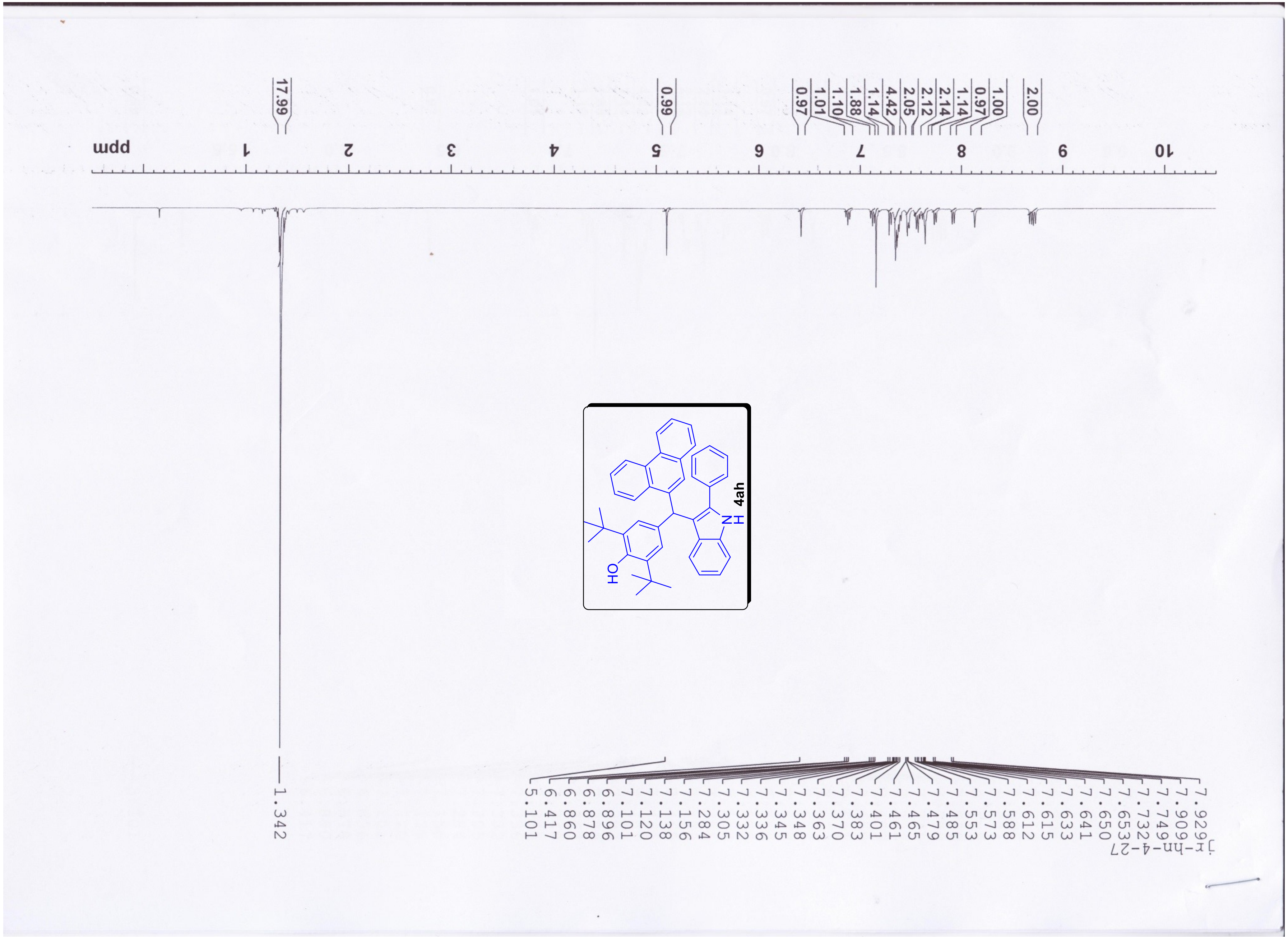


Figure S54. ^{13}H-NMR spectrum of compound **4ah**($CDCl_3$, 400 MHz)

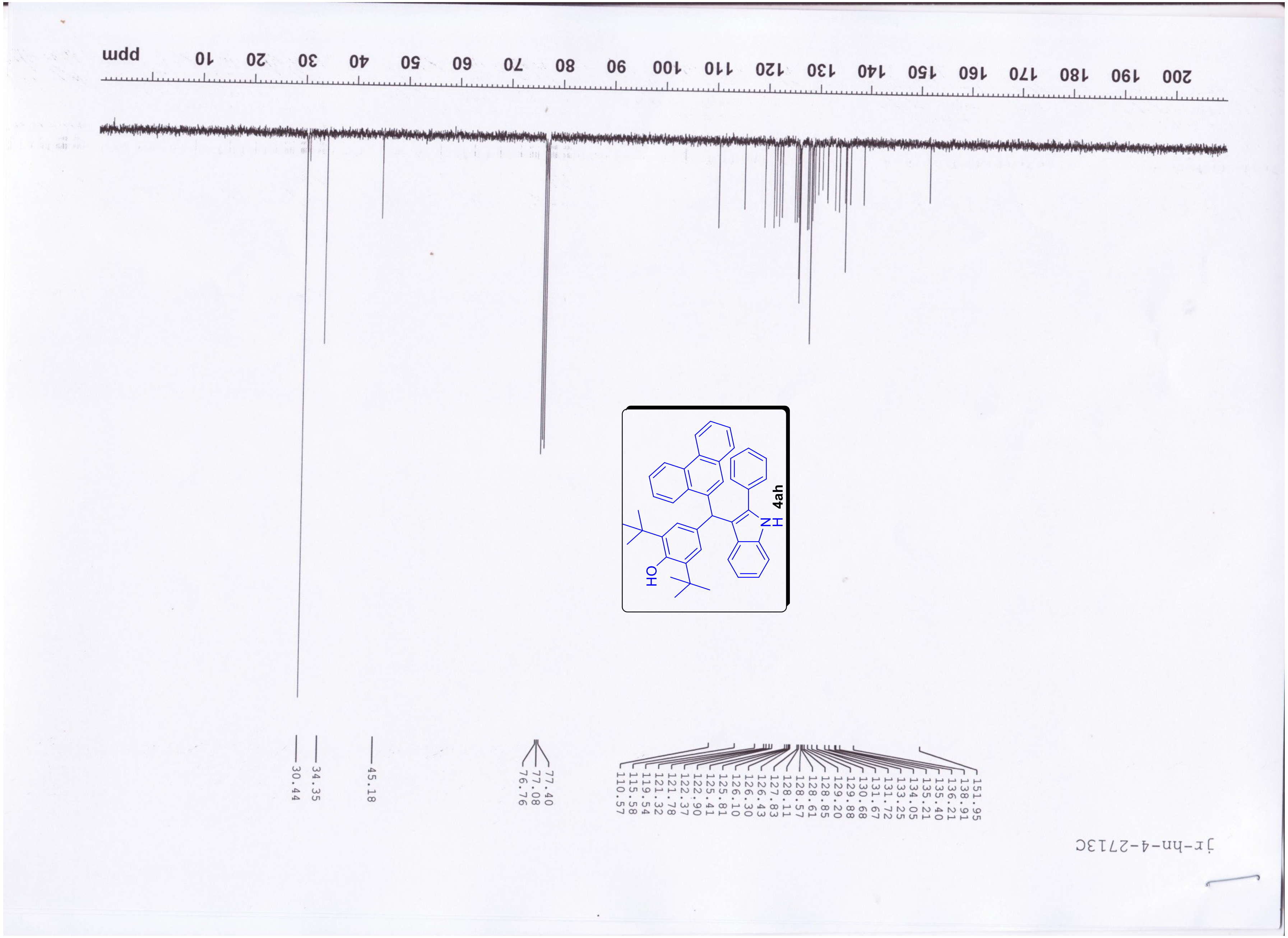


Figure S55. ^{13}C-NMR spectrum of compound **4ah**($CDCl_3$, 100 MHz)

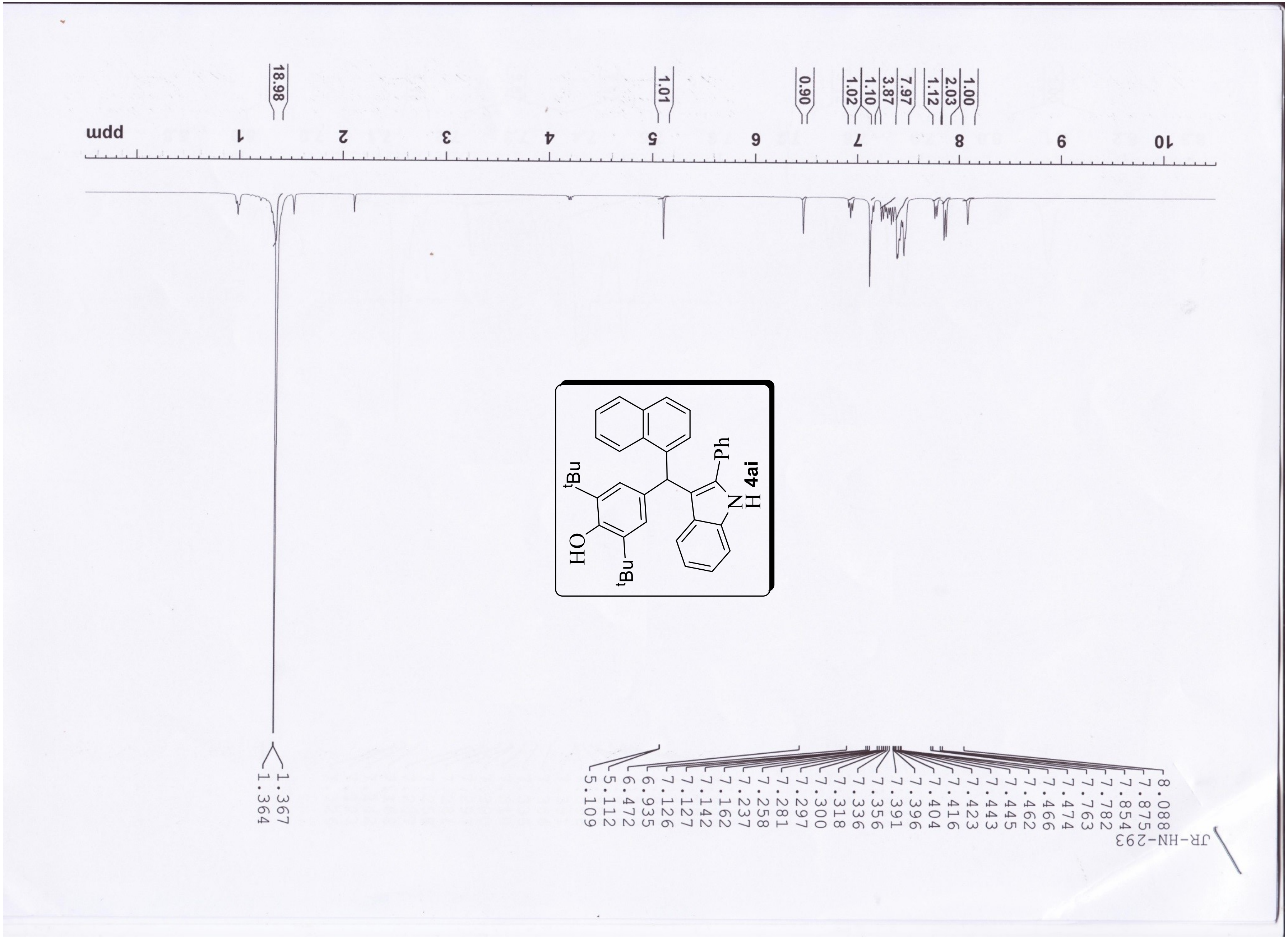


Figure S56. ^{1}H-NMR spectrum of compound **4ai**($CDCl_3$, 400 MHz)

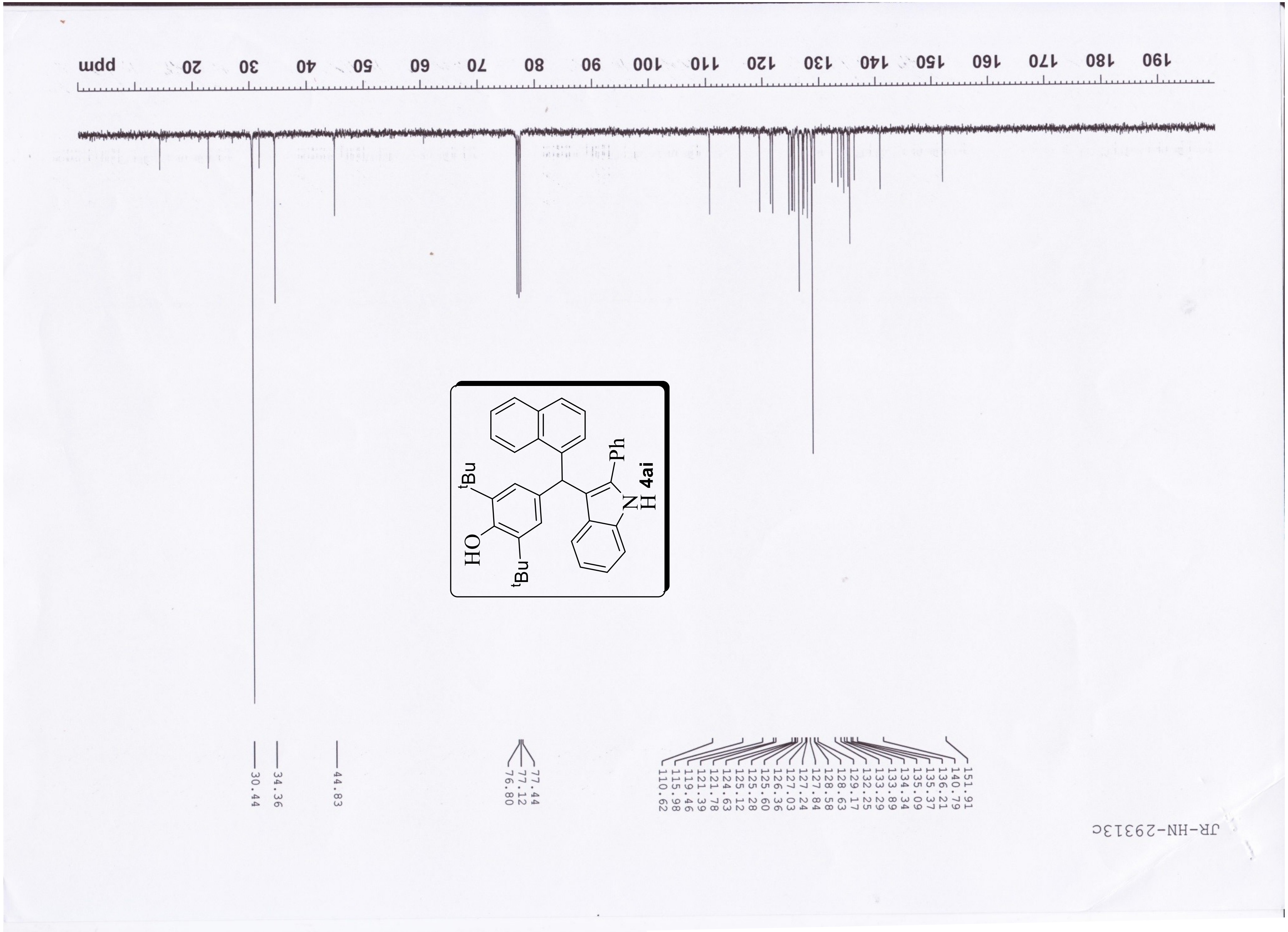


Figure S57. ^{13}C-NMR spectrum of compound **4ai**($CDCl_3$, 100 MHz)

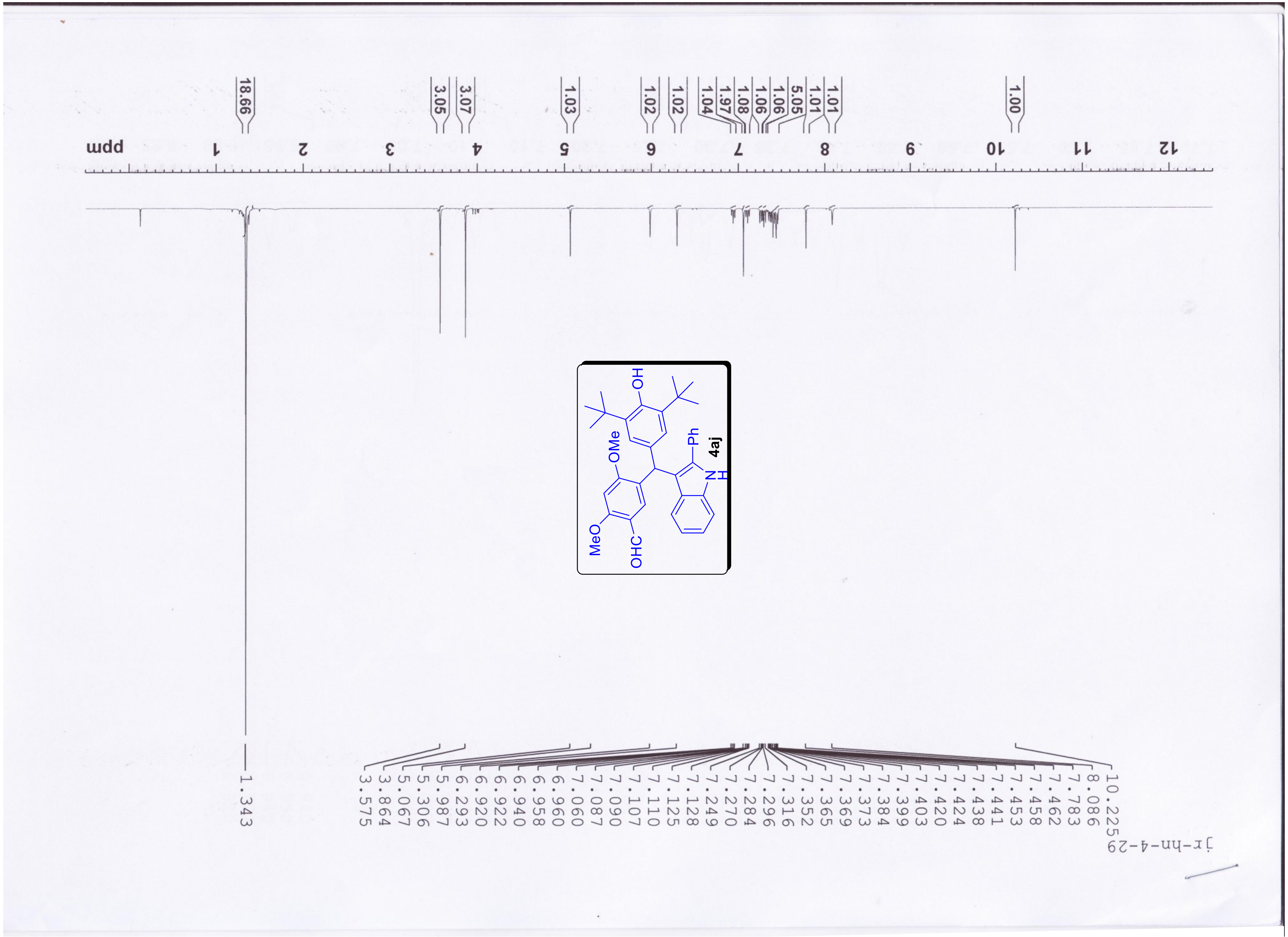


Figure S58. ^{1}H-NMR spectrum of compound **4aj**($CDCl_3$, 400 MHz)

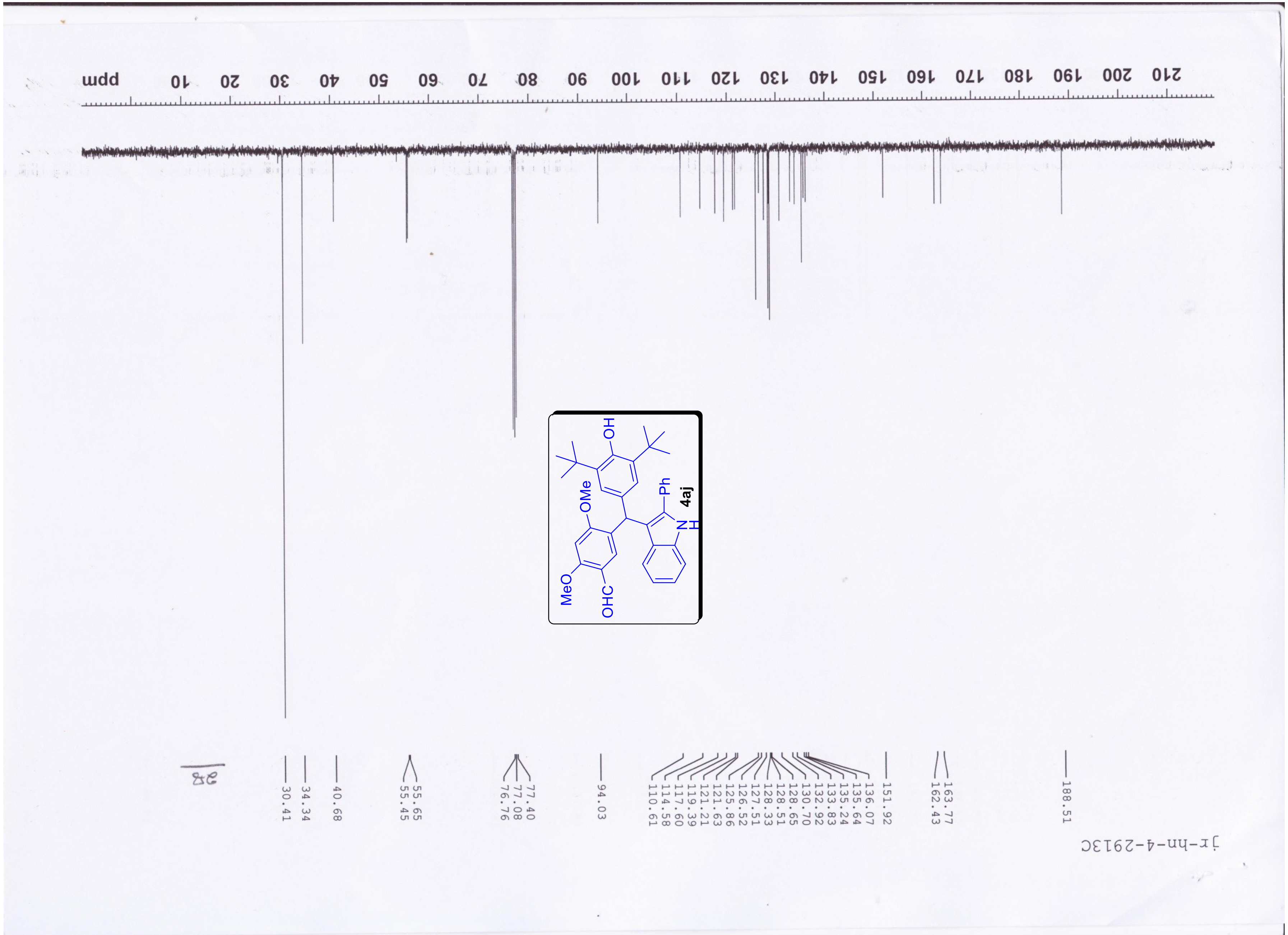


Figure S59. ^{13}C-NMR spectrum of compound **4aj**($CDCl_3$, 100 MHz)

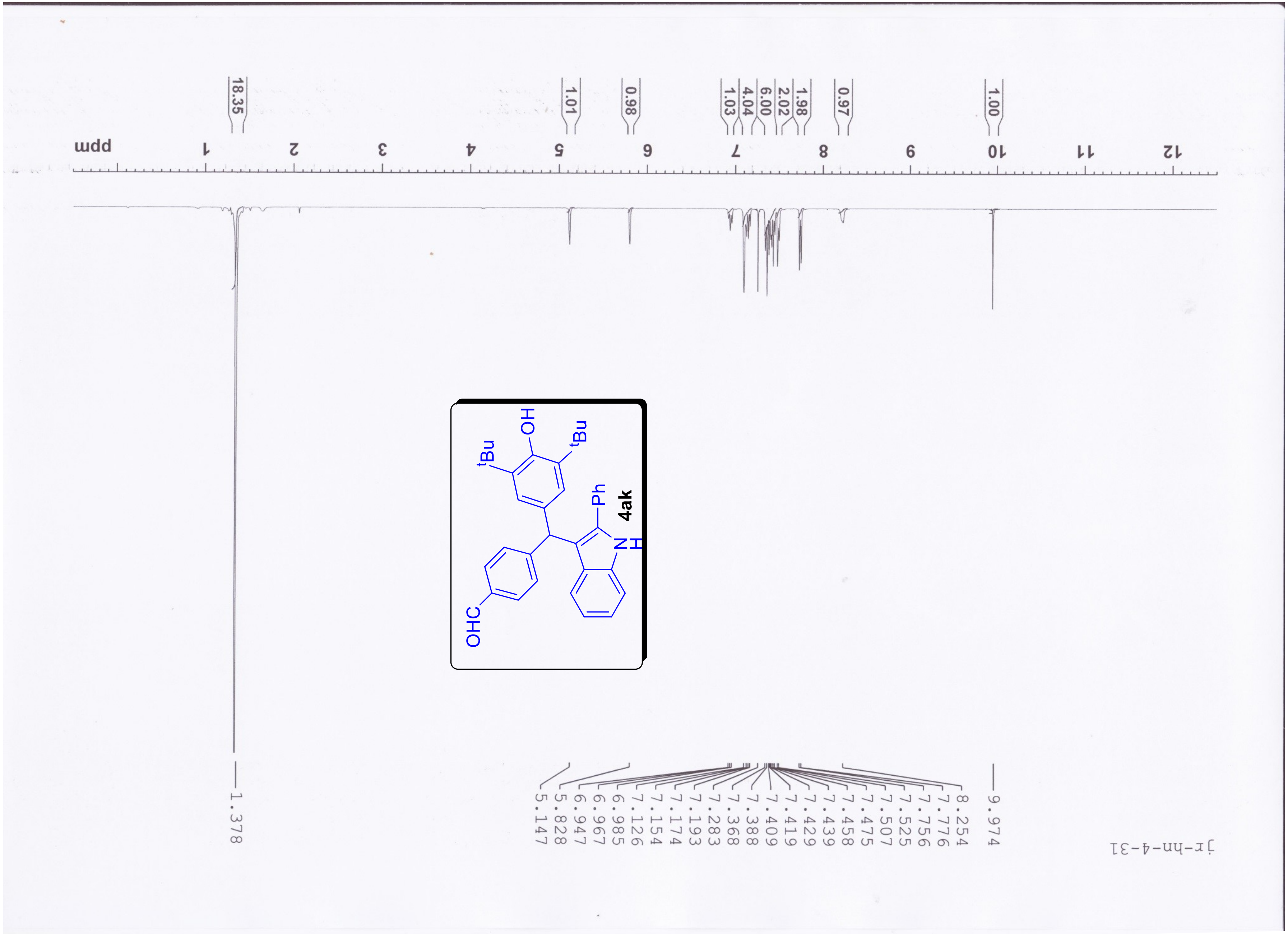


Figure S60. ^{1}H-NMR spectrum of compound **4ak**($CDCl_3$, 400 MHz)

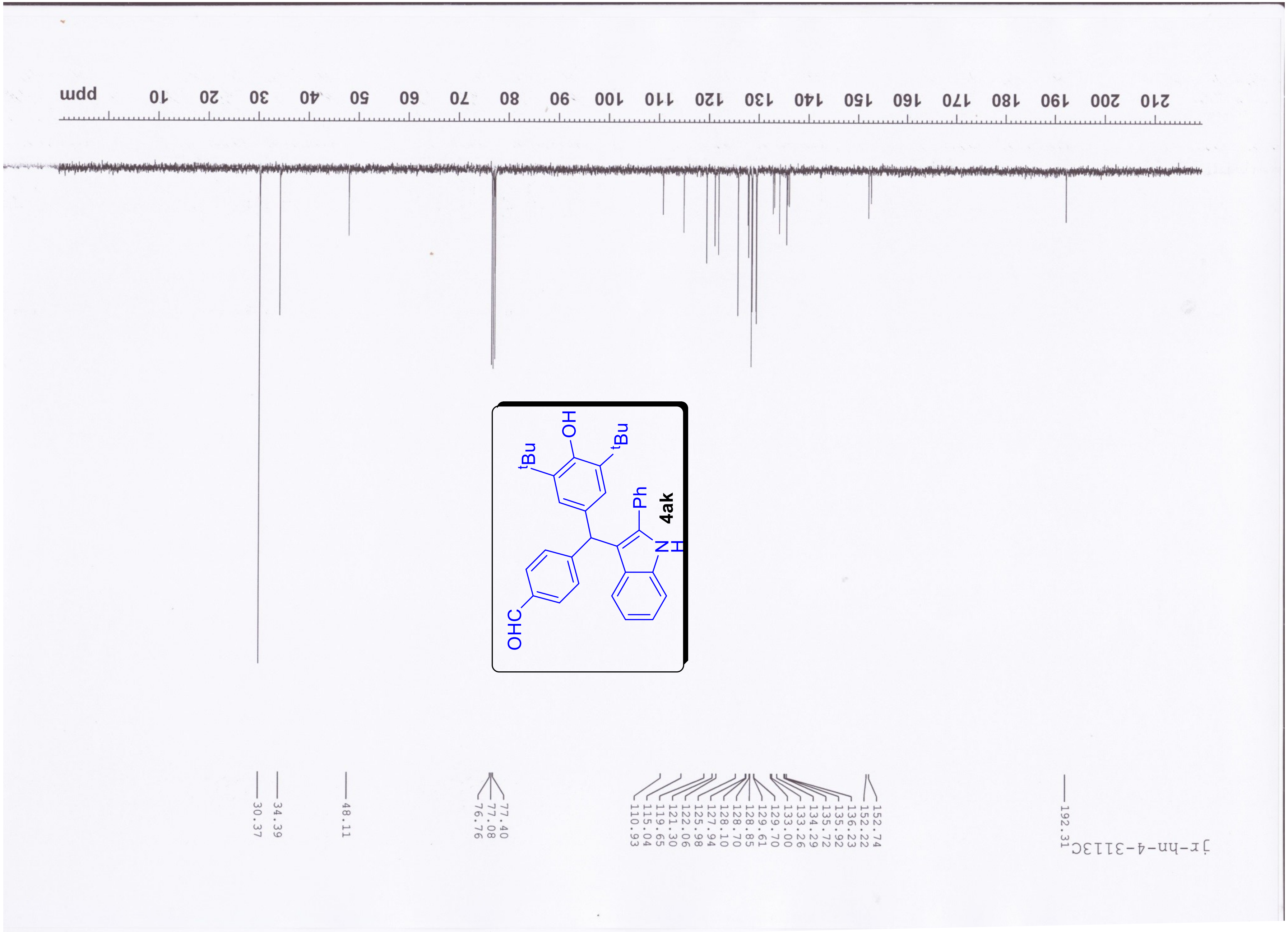


Figure S61. ^{13}C-NMR spectrum of compound **4ak**($CDCl_3$, 100 MHz)

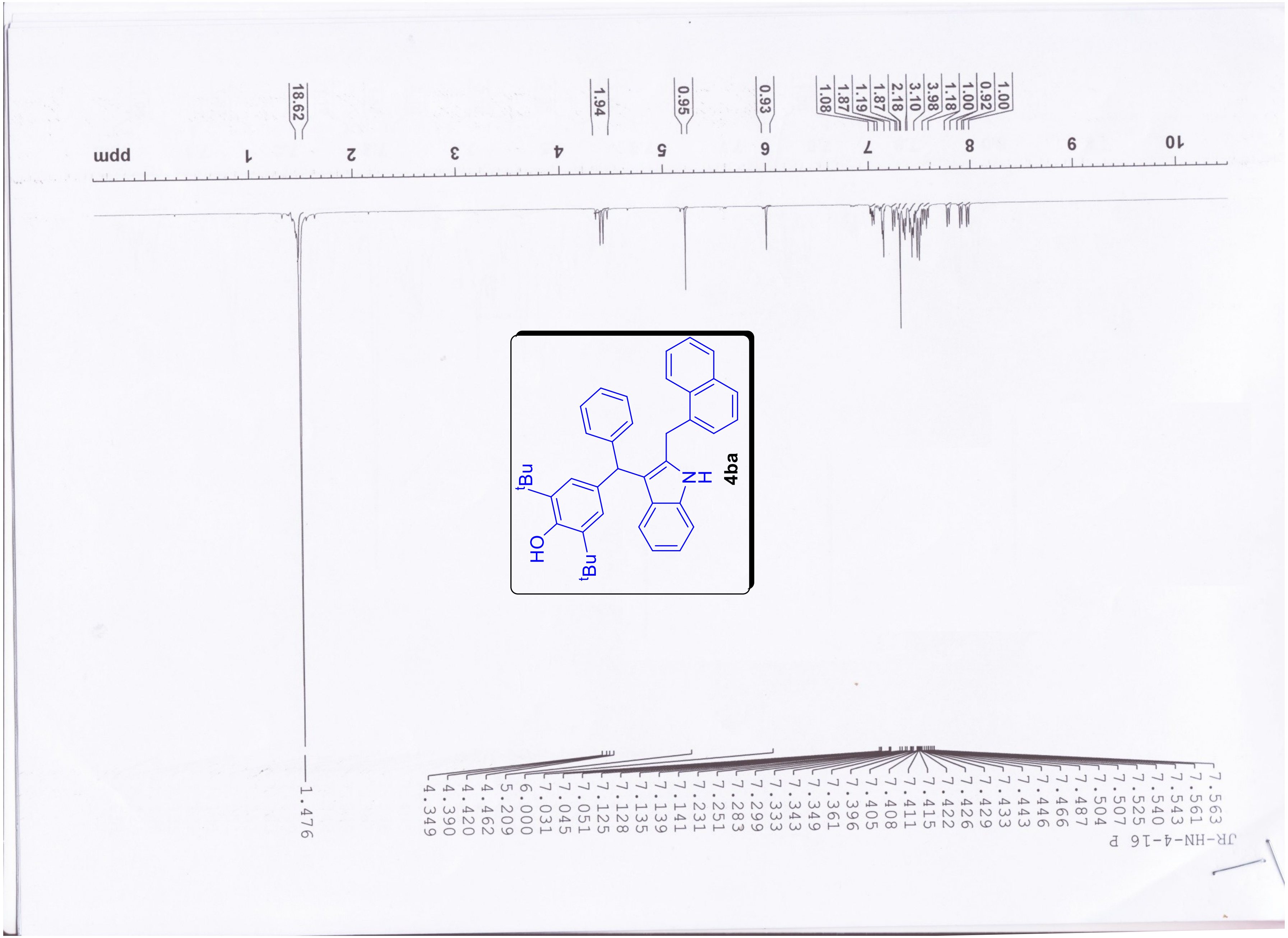


Figure S62. ^{1}H-NMR spectrum of compound **4ba**($CDCl_3$, 400 MHz)

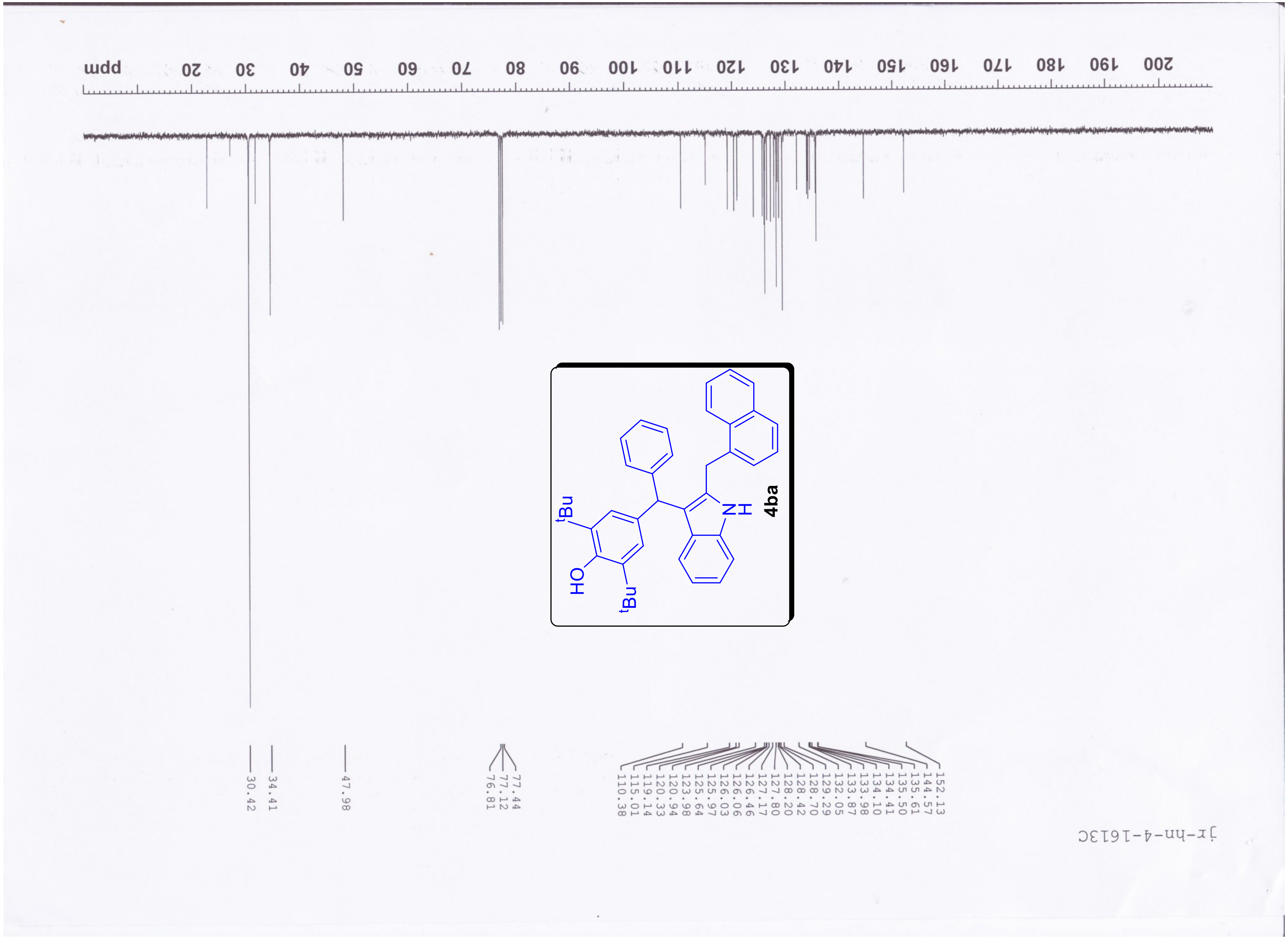


Figure S63. ^{13}C-NMR spectrum of compound **4ba**($CDCl_3$, 100 MHz)

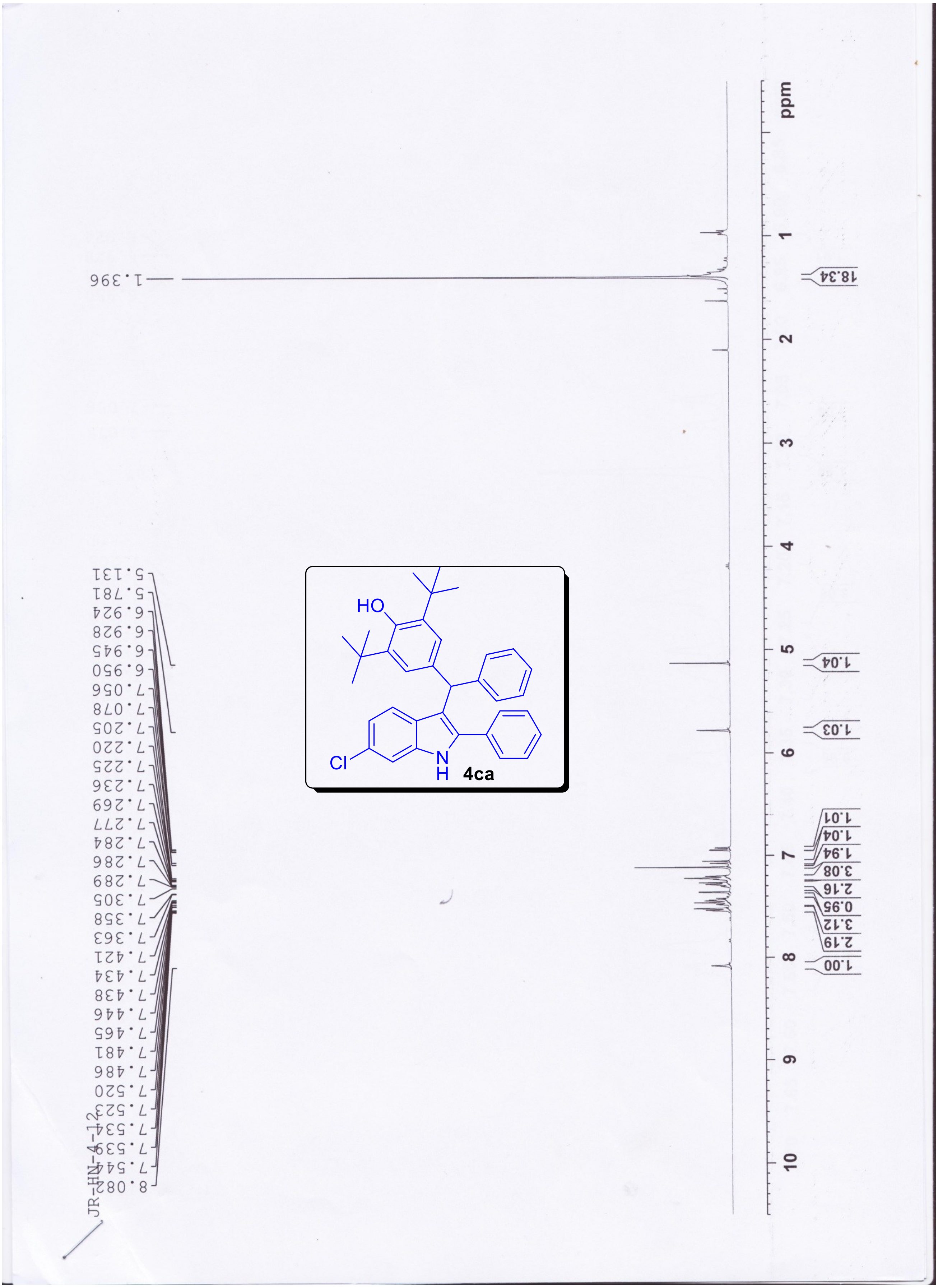


Figure S64. ^{1}H-NMR spectrum of compound **4ca**($CDCl_3$, 400 MHz)

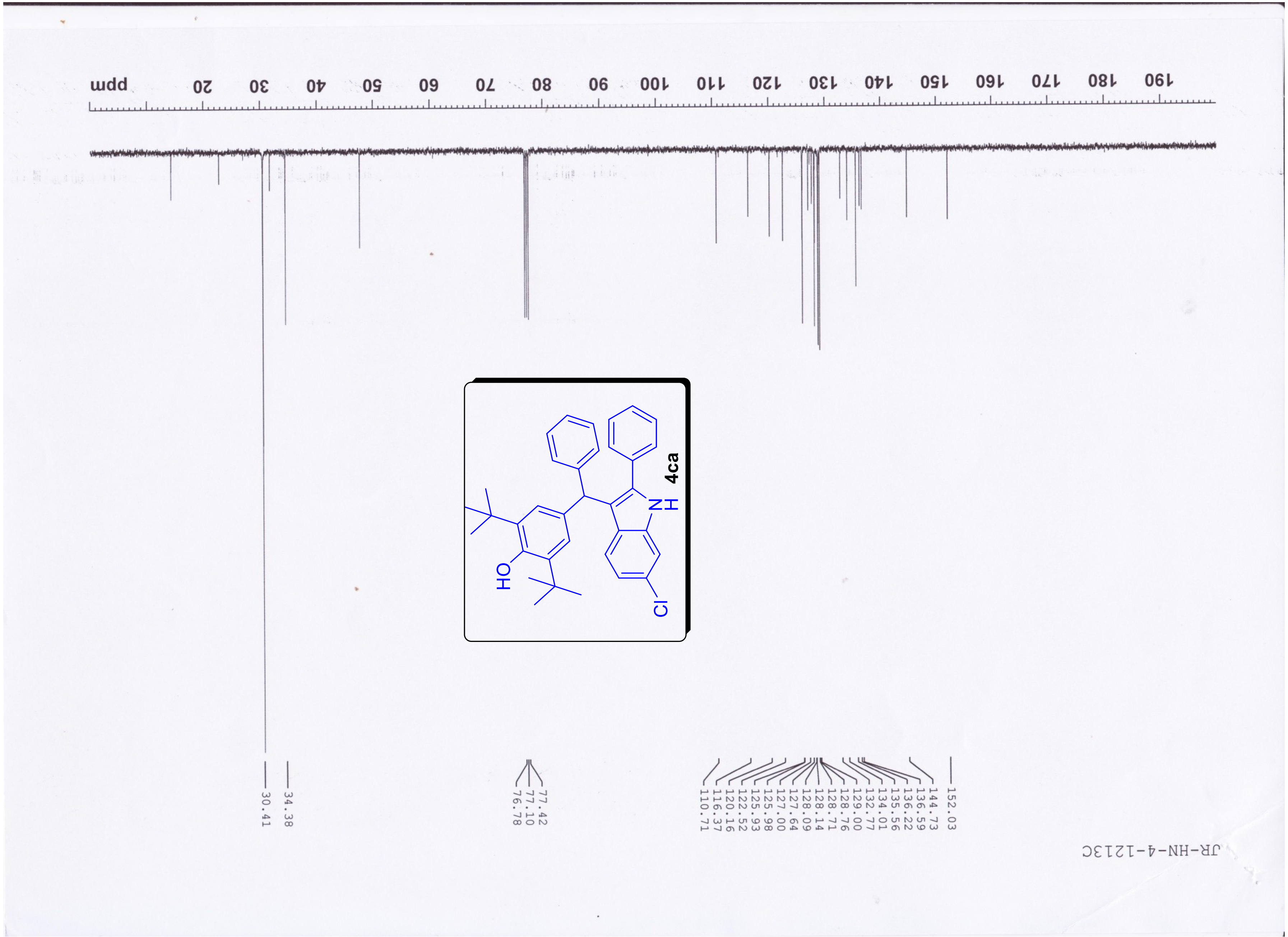


Figure S65. ^{13}C-NMR spectrum of compound **4ca**($CDCl_3$, 100 MHz)

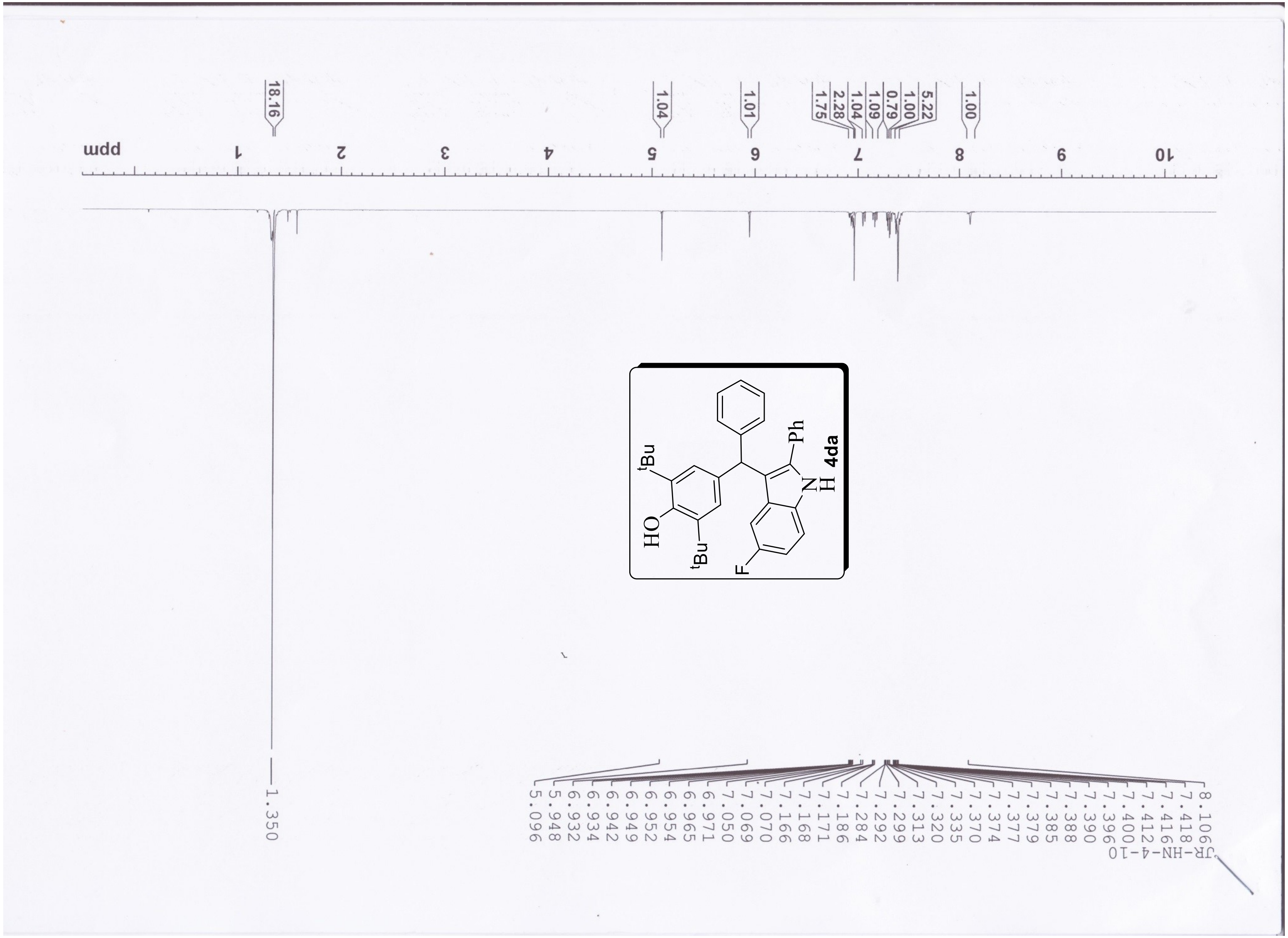


Figure S66. ^{1}H-NMR spectrum of compound **4da**($CDCl_3$, 400 MHz)

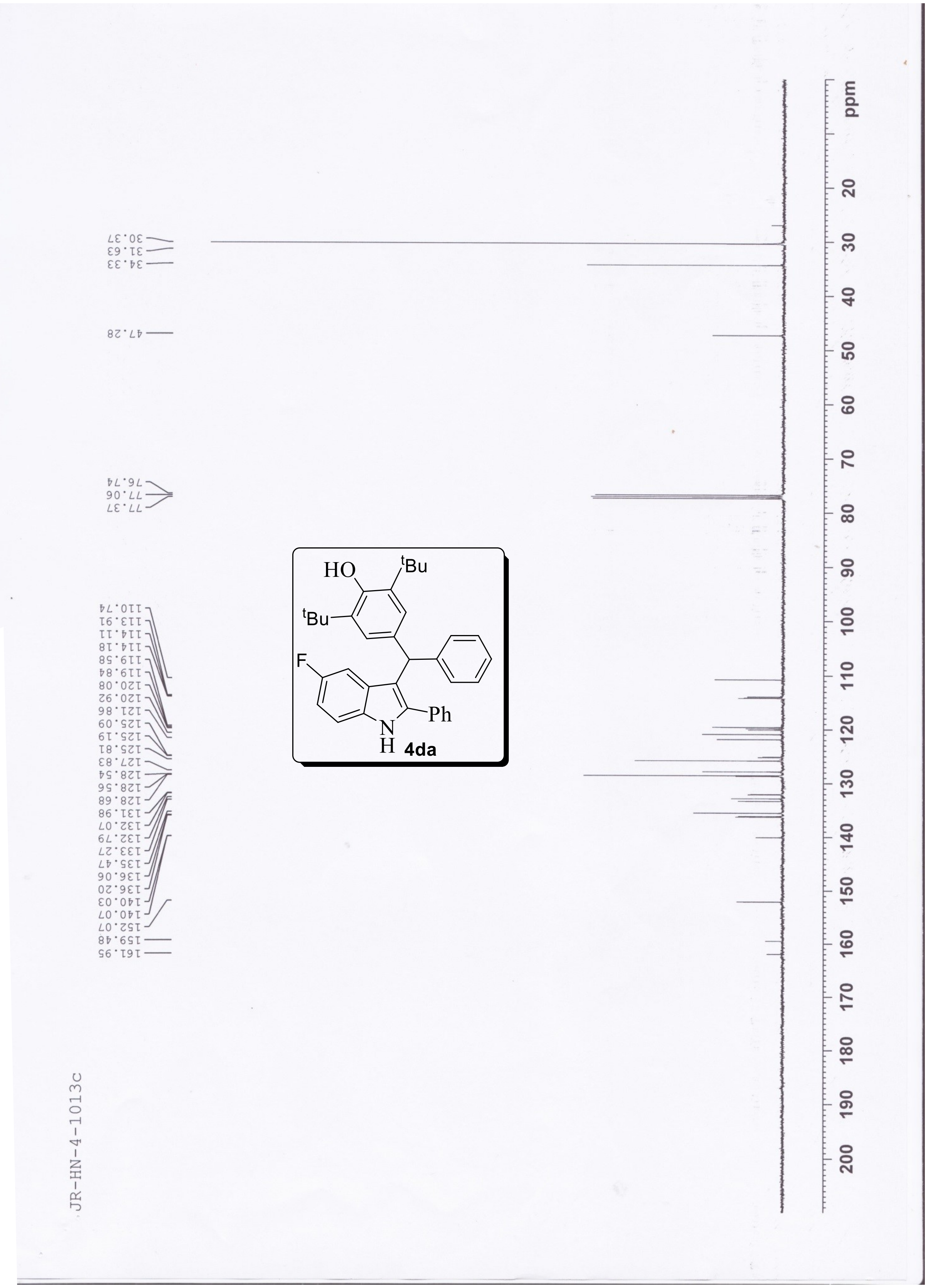


Figure S67. ^{1}H-NMR spectrum of compound **4da**(CDCl$_3$, 100 MHz)

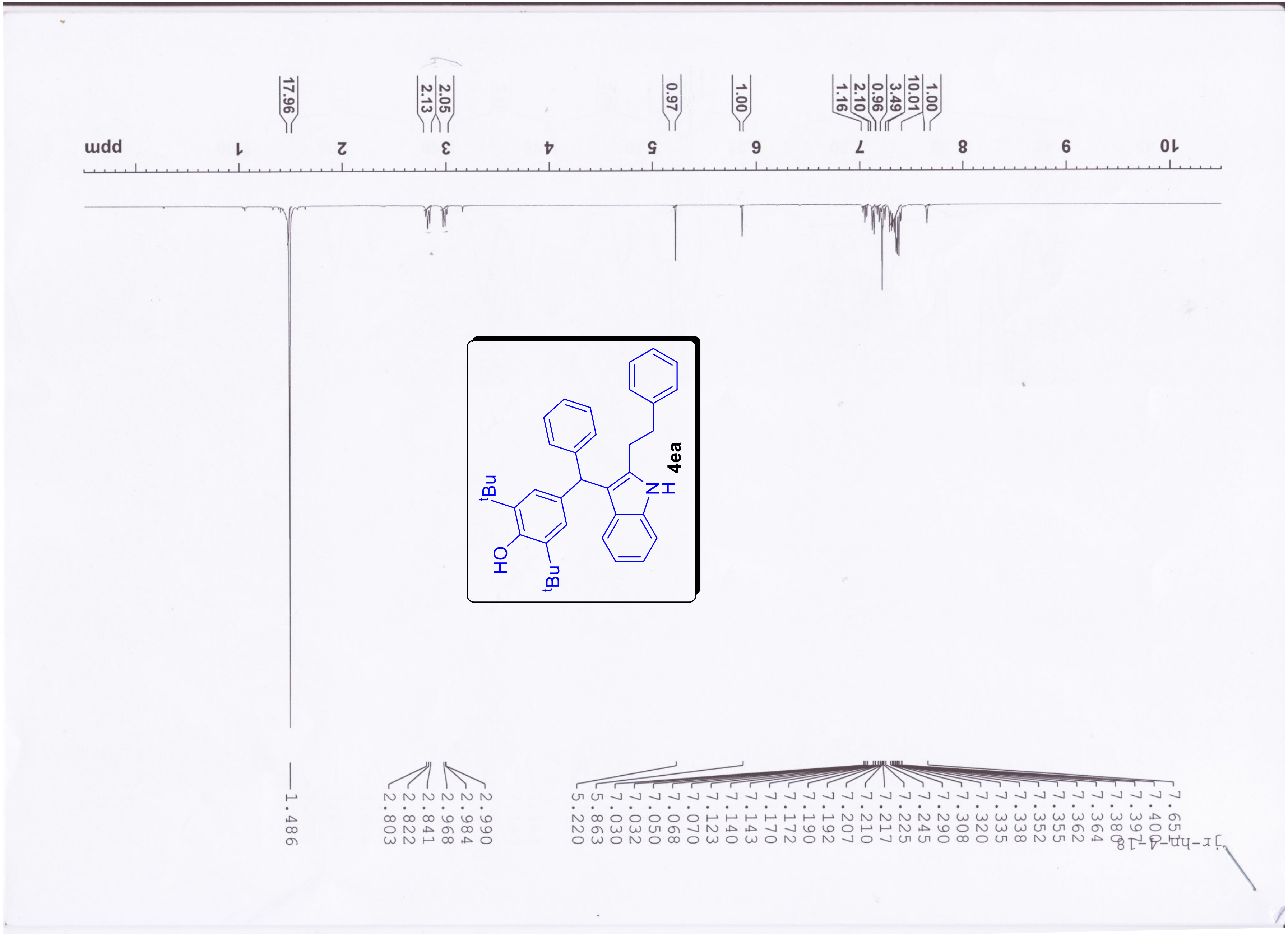


Figure S68. ^{1}H-NMR spectrum of compound **4ea**($CDCl_3$, 400 MHz)

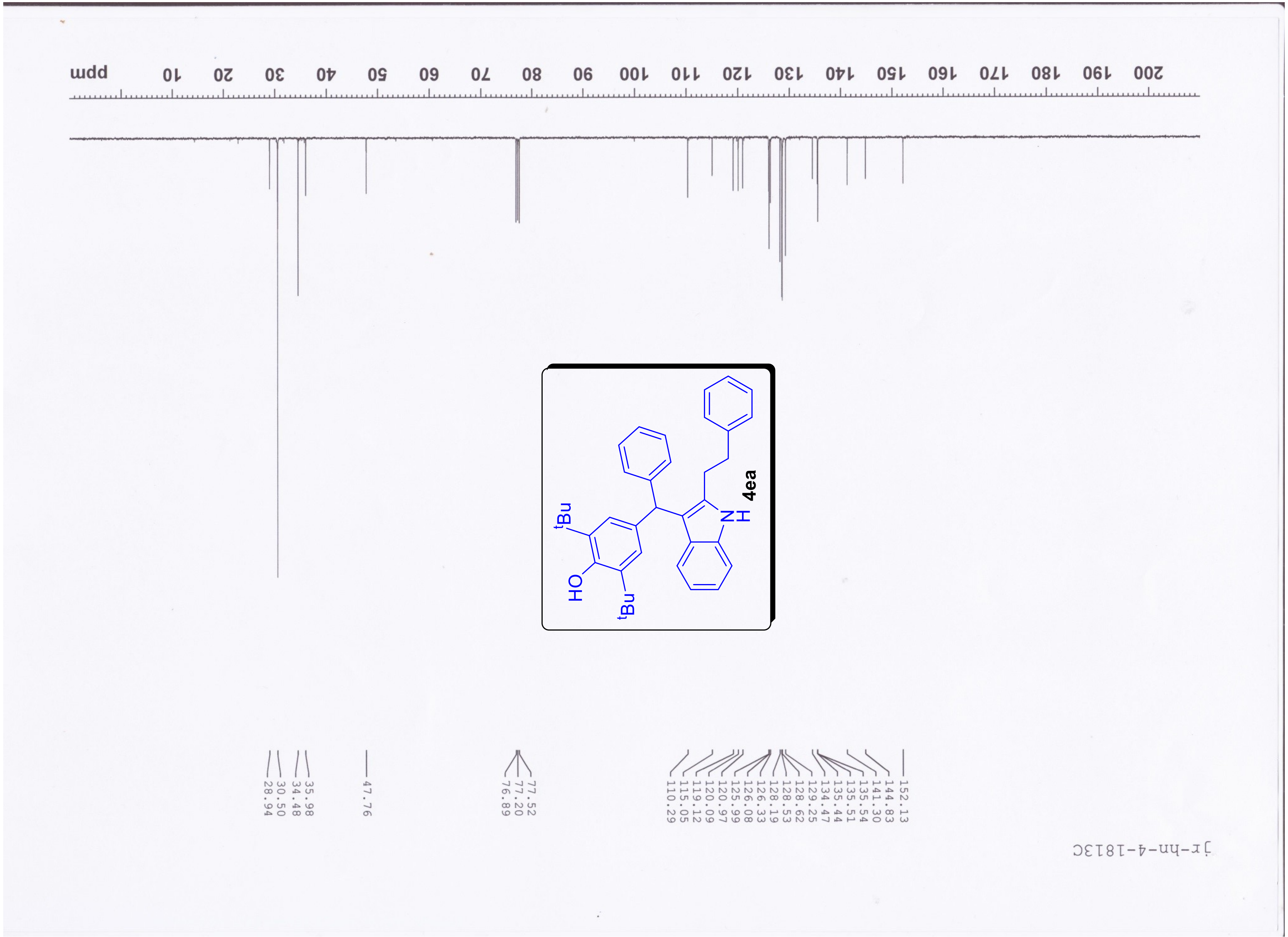


Figure S69. ^{13}C-NMR spectrum of compound **4ea**($CDCl_3$, 100 MHz)

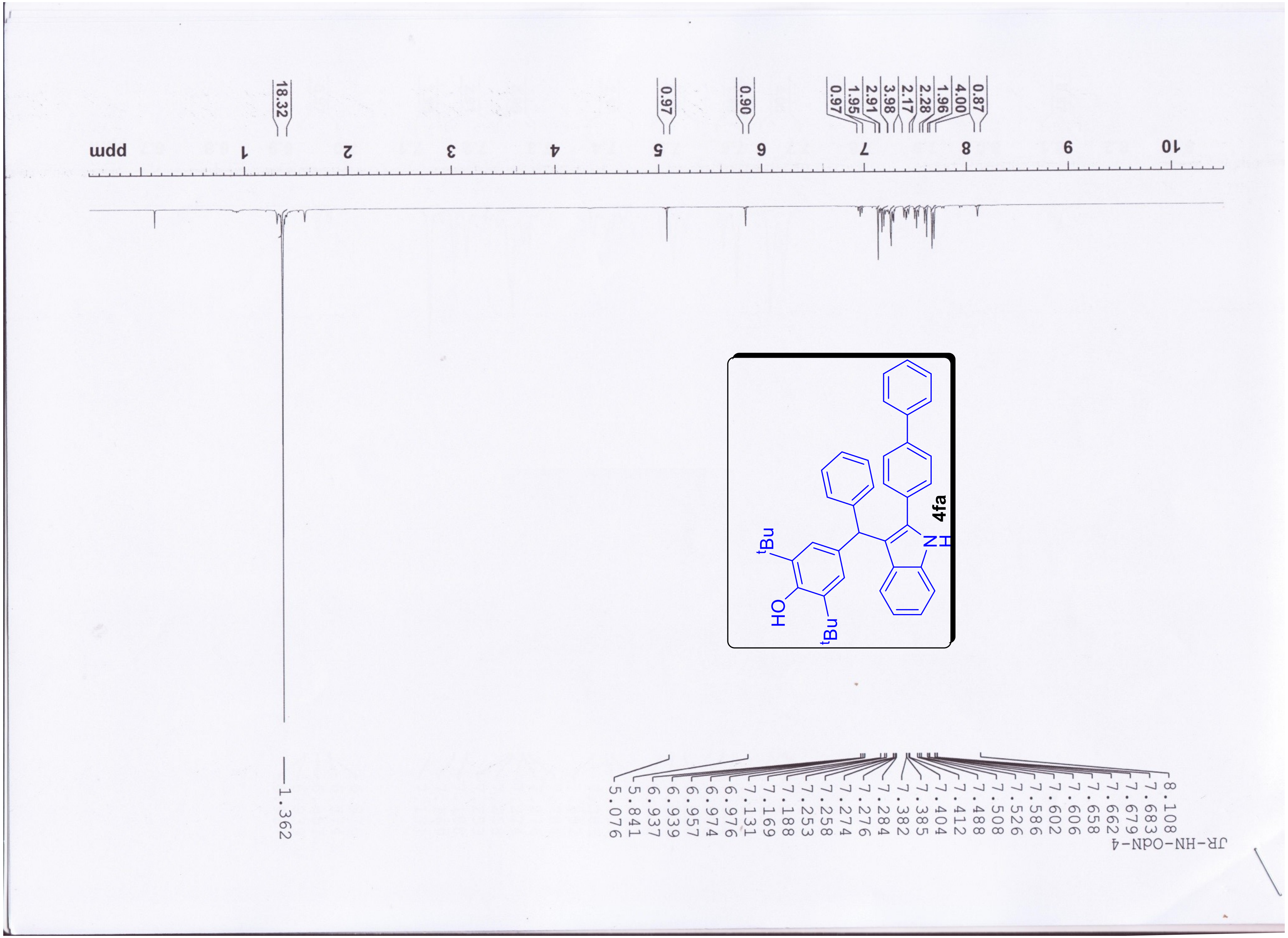


Figure S70. ^{1}H-NMR spectrum of compound **4fa**($CDCl_3$, 400 MHz)

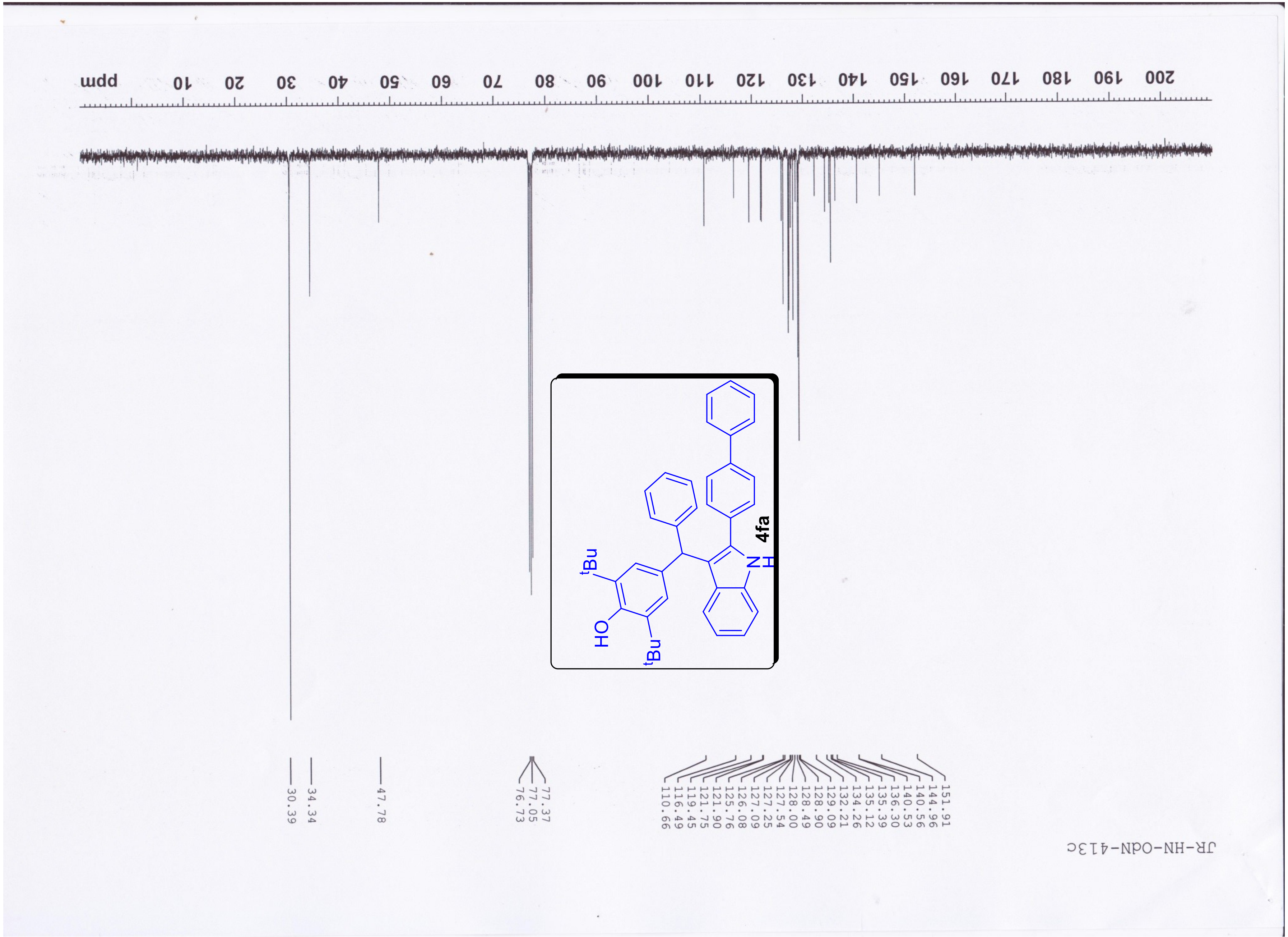


Figure S71. ^{13}C-NMR spectrum of compound **4fa**($CDCl_3$, 100 MHz)

Figure S72. ^{1}H-NMR spectrum of compound **4ga**($CDCl_3$, 400 MHz)

Figure S73. ^{13}C-NMR spectrum of compound **4ga**($CDCl_3$, 100 MHz)

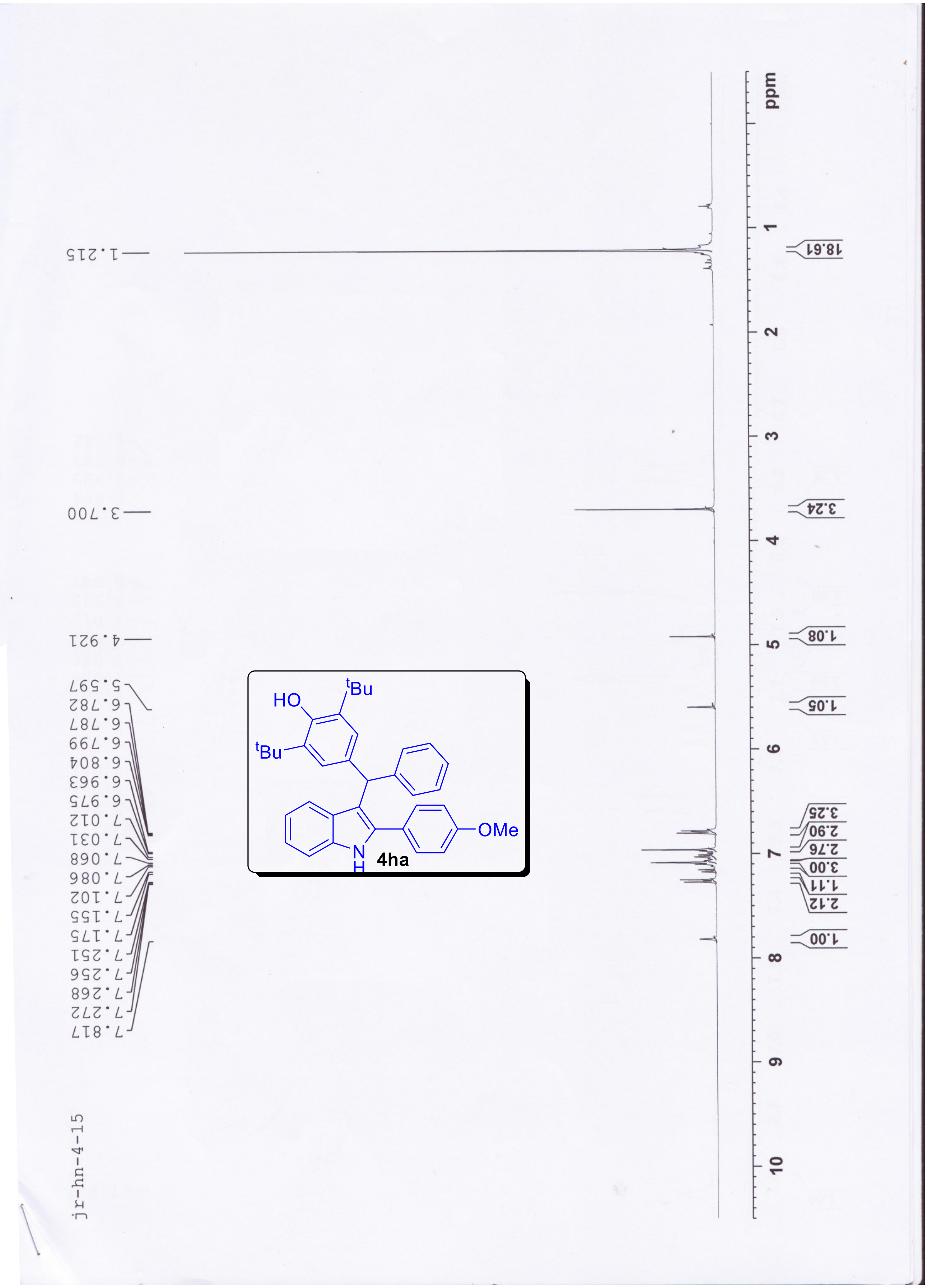


Figure S74. ^{1}H-NMR spectrum of compound **4ha**($CDCl_3$, 400 MHz)

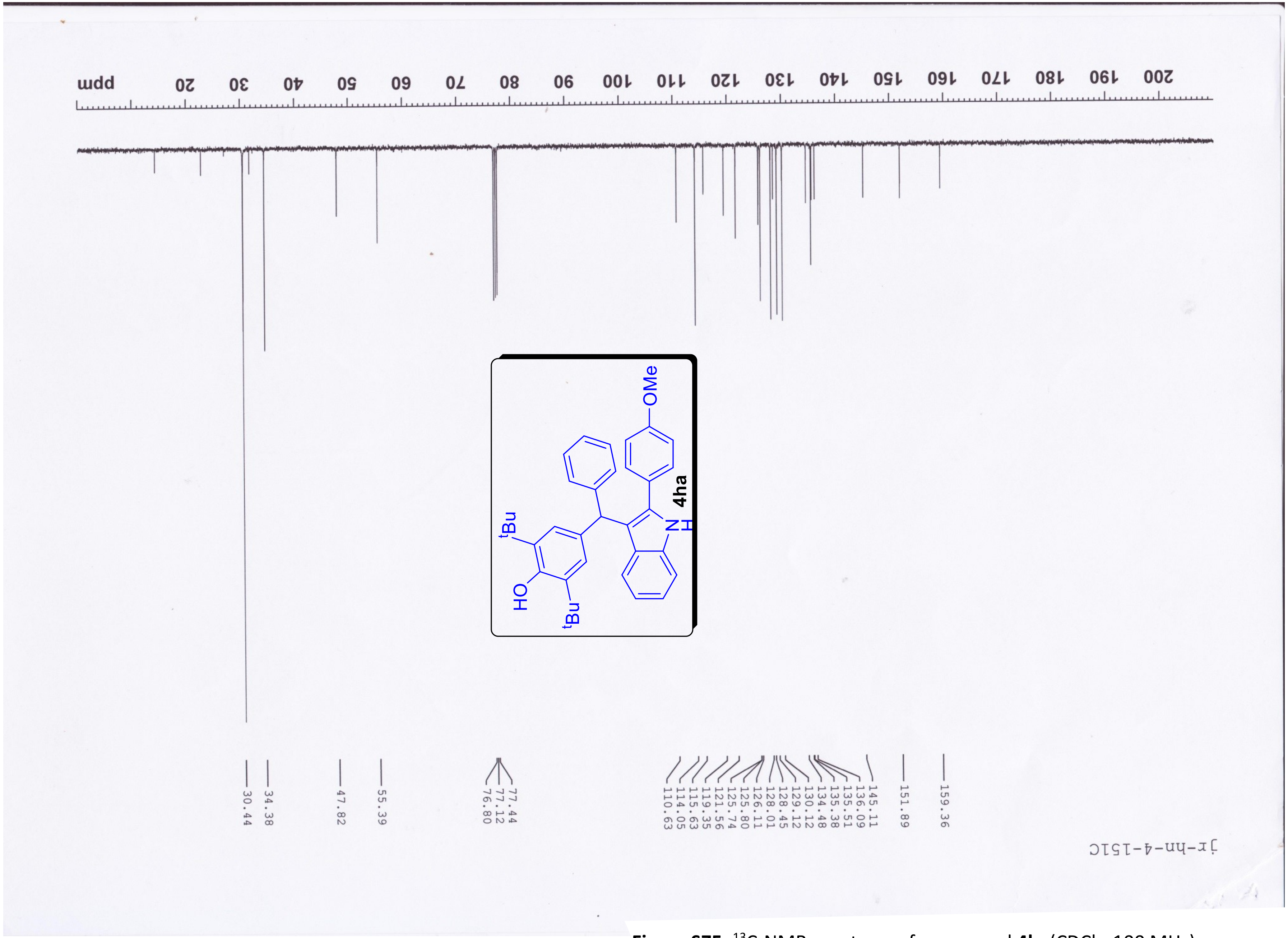


Figure S75. ^{13}C-NMR spectrum of compound **4ha**($CDCl_3$, 100 MHz)

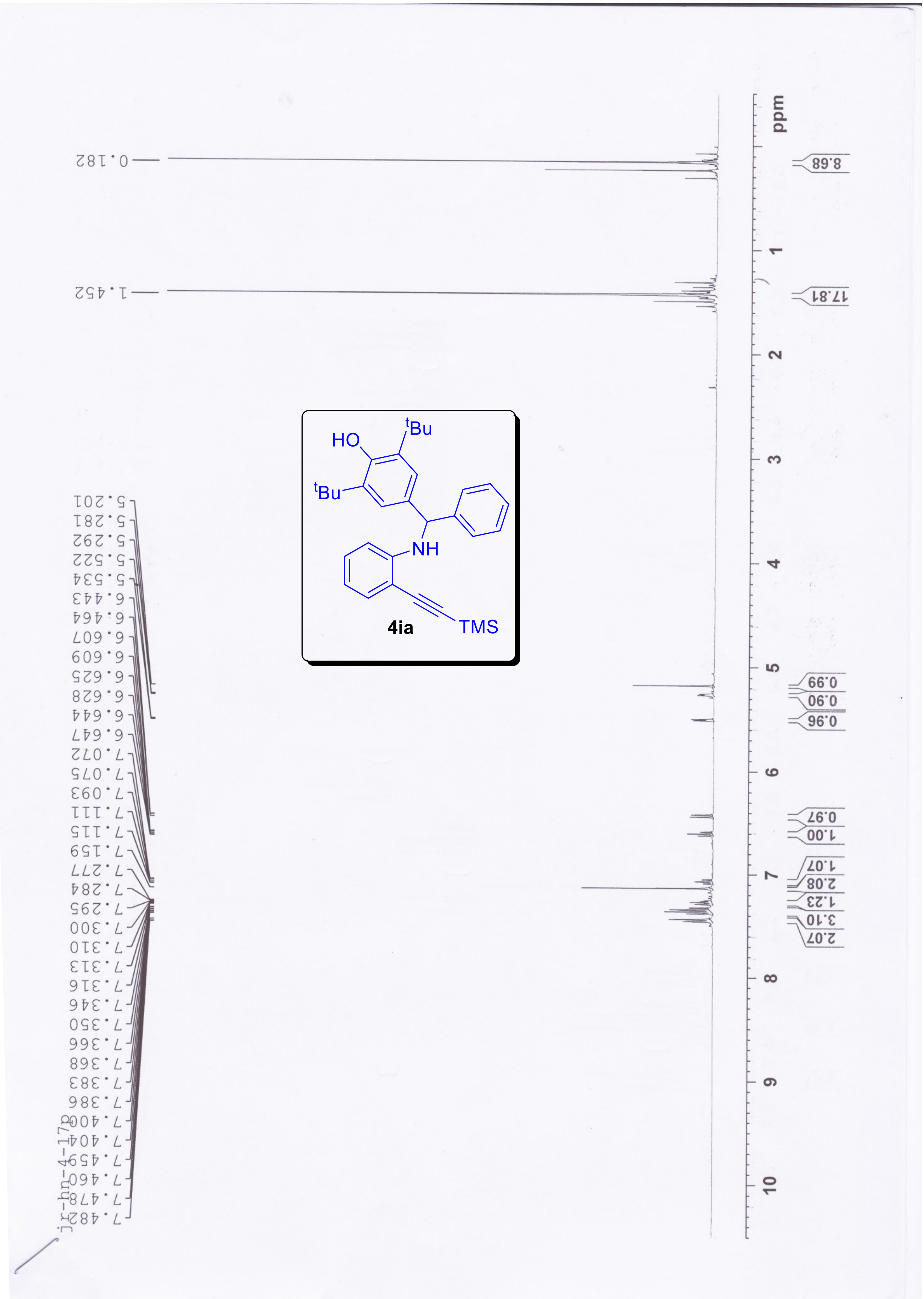


Figure S76. ^{1}H-NMR spectrum of compound **4ia**($CDCl_3$, 400 MHz)

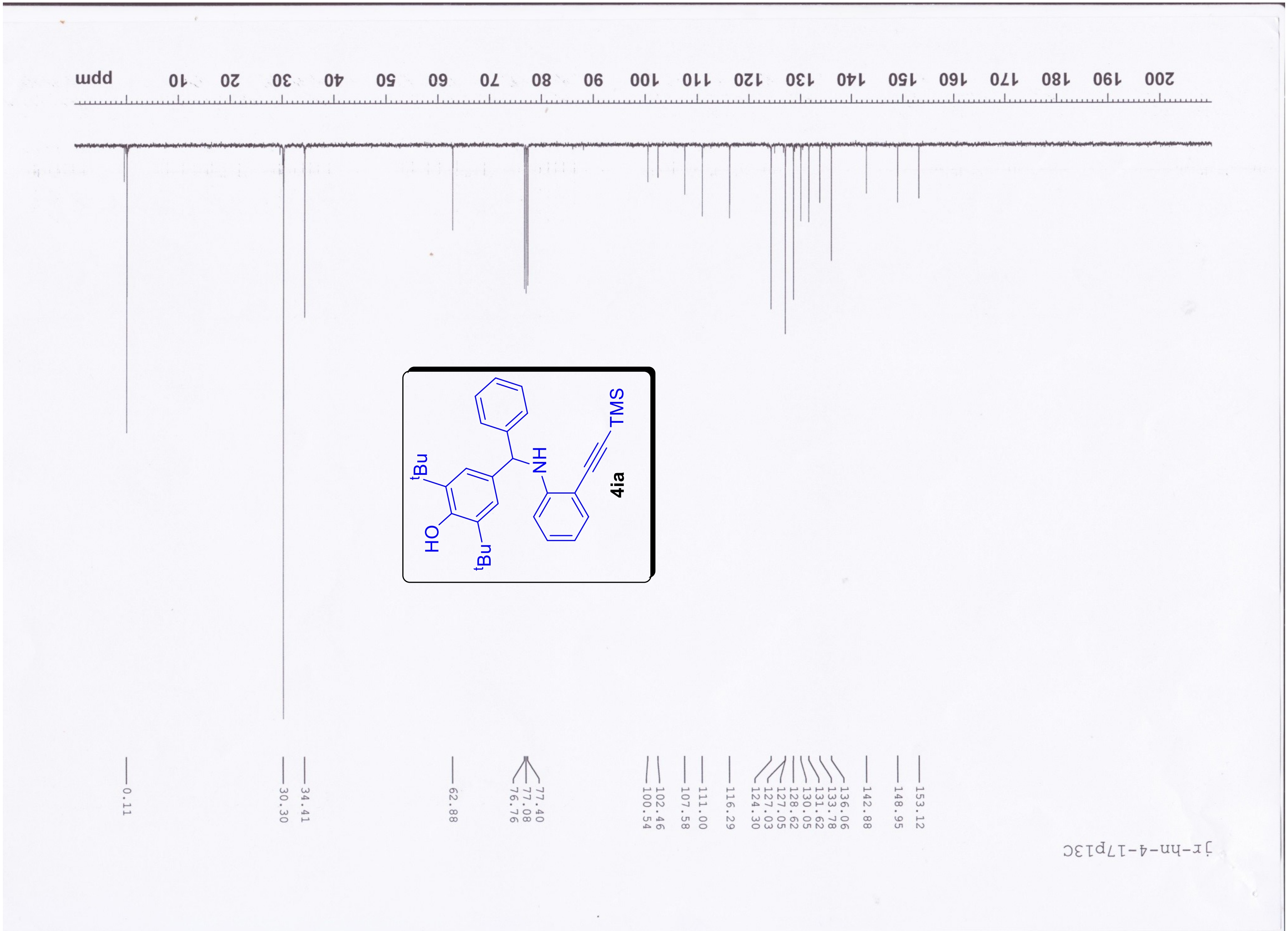


Figure S77. ^{13}C-NMR spectrum of compound **4ia**($CDCl_3$, 100 MHz)

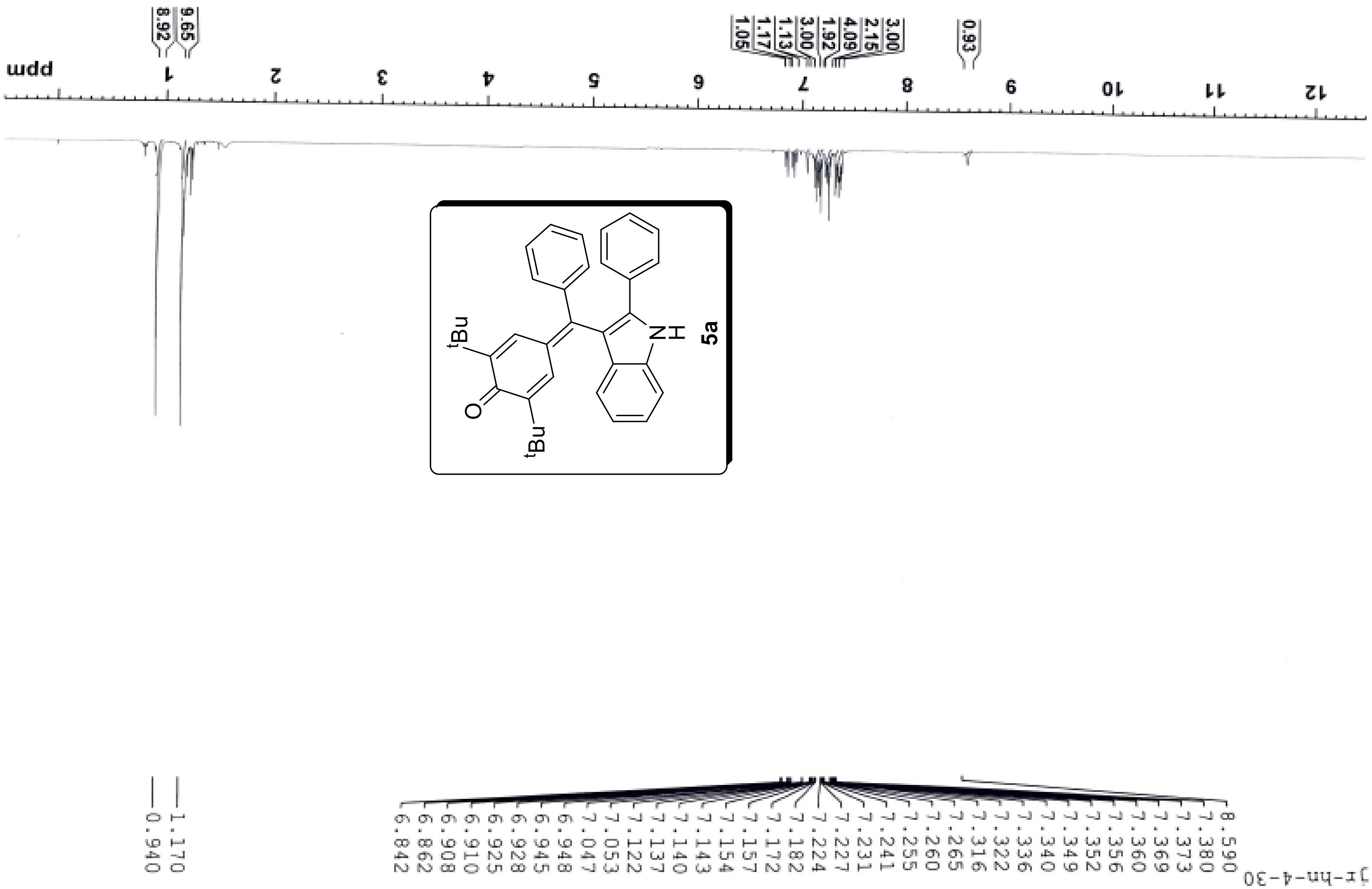


Figure S78. ^{1}H-NMR spectrum of compound **5a**($CDCl_3$, 400 MHz)

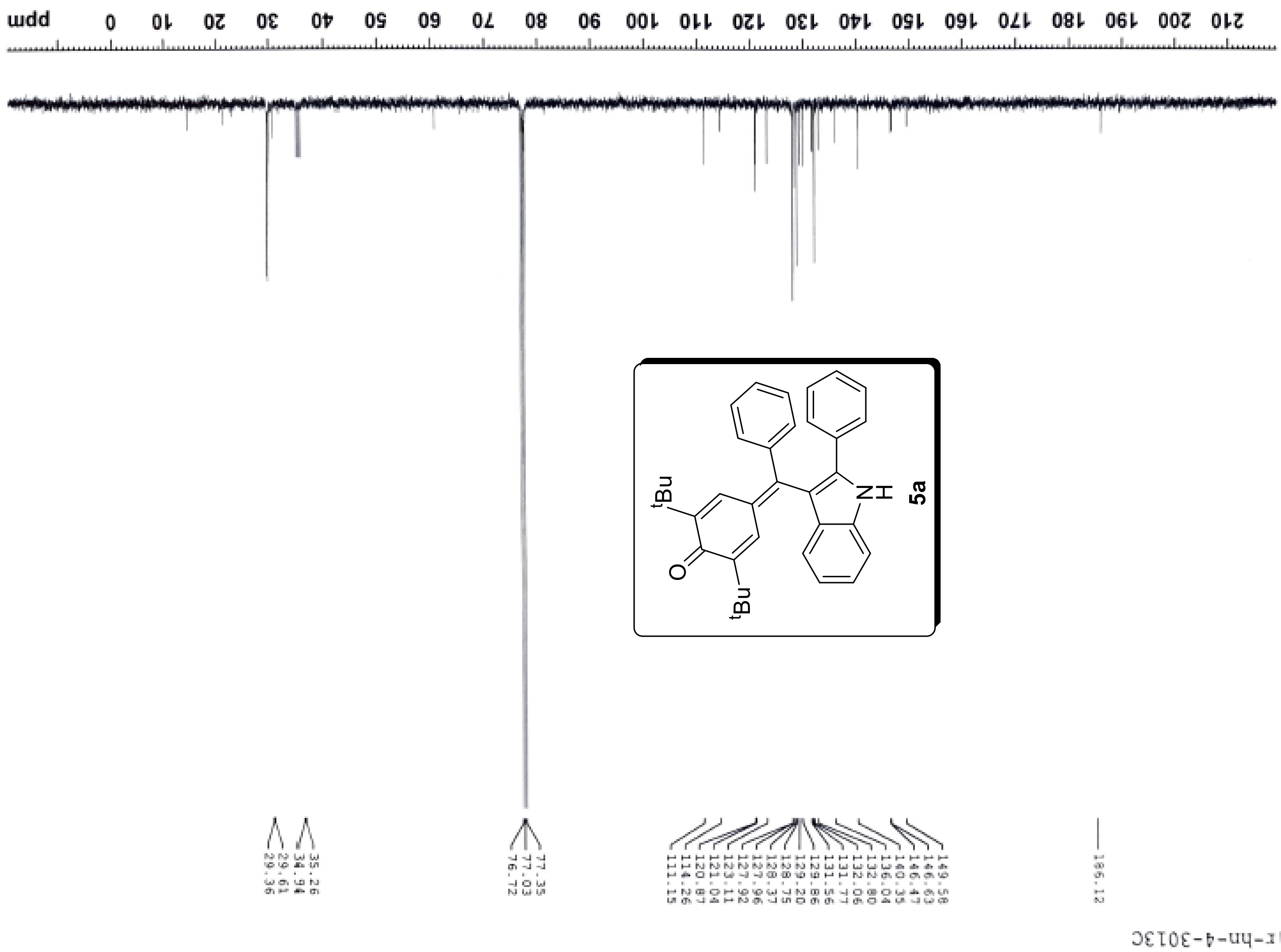


Figure S79. ^{13}C-NMR spectrum of compound **5j**($CDCl_3$, 100 MHz)