

Supporting Information

ZnI₂-Catalyzed Regioselective Cascade 1,4-Conjugate Addition/5-*exo-dig* Annulation Pathway for One-pot Access of Heterobiaryl Frameworks

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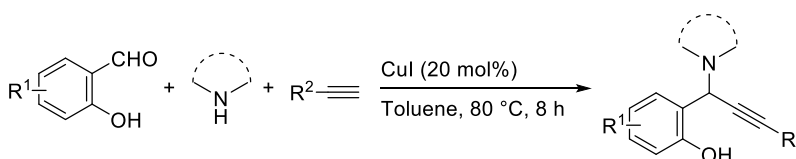
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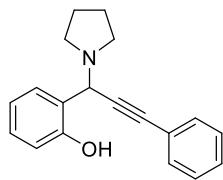
1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All cascade reactions were performed in a resealable screw-capped Schlenk flask (approximately 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4.5 mm × 12 mm). 1,4-Dioxane was distilled from sodium benzophenone ketyl under nitrogen.¹ Toluene and nitromethane were distilled from calcium hydride under nitrogen. Thin layer chromatography was performed on Merck precoated silica gel 60 F₂₅₄ plates. Silica gel (Merck, 230-400 mesh) was used for column chromatography. Melting points were measured on an uncorrected Büchi Melting Point B-545 instrument. ¹H NMR spectra were recorded on a Bruker (400 or 500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl₃ (δ 7.26 ppm), or DMSO (δ 2.50 ppm) or CD₃OD (δ 4.89 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ¹³C NMR spectra was recorded on a Bruker (100 or 125 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl₃ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on Bruker Solarix 9.4T FTMS mass spectrometer (APCI-DIP). Compounds described in the literatures were characterized by comparison of their ¹H, and/or ¹³C NMR spectra to the previously reported data.

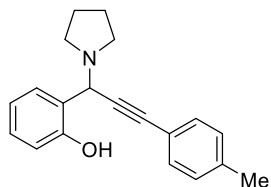
2. General procedure for the synthesis of propargylamines



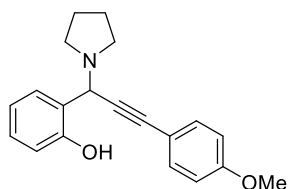
To a 25 mL round-bottom flask equipped with a magnetic stir bar were added amine (6.5 mmol), aldehyde (5.0 mmol), acetylene (6.5 mmol), copper (I) iodide (20 mol%) and toluene (10 mL). The mixture was degassed and backfilled with nitrogen, and then stirred in an oil bath preheated to 80 °C for 8 h (monitored by TLC). After the reaction completed (as determined using TLC), the reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (10 mL) and filtered through a thin pad of silica gel. The filter cake was washed with CH₂Cl₂, and the combined filtrate was concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to afford the corresponding propargylamines **1a-1z, 1a'-1c', 4**.

2-(3-Phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1a)²

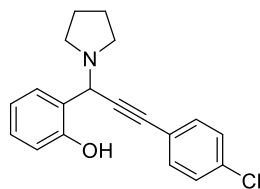
White solid; 80% yield; m.p. = 80–81 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.55–7.52 (m, 3H), 7.37–7.35 (m, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.87–6.84 (m, 2H), 5.29 (s, 1H), 2.92–2.87 (m, 2H), 2.83–2.79 (m, 2H), 1.91–1.85 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 157.6, 131.9, 129.3, 128.6, 128.4, 127.8, 122.5, 122.1, 118.9, 116.3, 89.0, 82.9, 57.0, 48.9, 23.8; HRMS (APCI) *m/z*: calcd for C₁₉H₁₉NO [M + H]⁺ 278.1539, found 278.1538.

2-(1-(Pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1b)

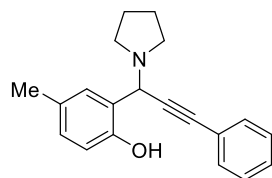
White solid; 79% yield; m.p. = 61–62 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.86–6.83 (m, 2H), 5.28 (s, 1H), 2.88 (s, 2H), 2.81–2.79 (m, 2H), 2.37 (s, 3H), 1.87 (s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 157.5, 138.7, 131.8, 129.3, 129.1, 127.9, 122.2, 119.4, 119.0, 116.3, 89.2, 82.1, 56.9, 48.9, 23.8, 21.5; HRMS (APCI) *m/z*: calcd for C₂₀H₂₁NO [M + H]⁺ 292.1695, found 292.1694.

2-(3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1c)

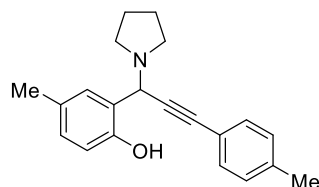
Yellow solid; 75% yield; m.p. = 97–98 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.54 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 1H), 6.88–6.86 (m, 4H), 5.27 (s, 1H), 3.83 (s, 3H), 2.88 (s, 2H), 2.81 (s, 2H), 1.87 (s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 159.8, 157.5, 133.3, 129.3, 127.9, 122.3, 118.9, 114.6, 114.0, 89.0, 81.3, 57.0, 55.3, 48.9, 23.8; HRMS (APCI) *m/z*: calcd for C₂₀H₂₁NO₂ [M + H]⁺ 308.1645, found 308.1642.

2-(3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1d)

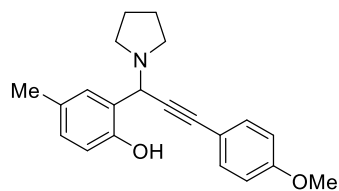
White solid; 72% yield; m.p. = 69–70 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 6.86–6.83 (m, 2H), 5.27 (s, 1H), 2.87 (s, 2H), 2.81–2.79 (m, 2H), 1.88 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.5, 134.8, 133.8, 133.2, 129.6, 129.0, 128.8, 127.9, 122.0, 119.2, 116.6, 88.0, 84.1, 57.1, 49.2, 23.9; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}$ [$\text{M} + \text{H}$] $^+$ 312.1149, found 312.1147.

4-Methyl-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1e)

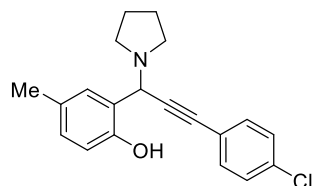
Yellow oil; 82% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.54–7.52 (m, 2H), 7.37–7.35 (m, 3H), 7.31 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 2.89–2.85 (m, 2H), 2.82–2.77 (m, 2H), 2.28 (s, 3H), 1.88–1.85 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.1, 131.9, 129.7, 128.5, 128.4, 128.3, 128.0, 122.6, 121.8, 116.0, 88.8, 83.1, 57.0, 48.9, 23.8, 20.7; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 292.1695, found 292.1696.

4-Methyl-2-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1f)

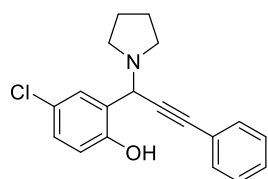
Yellow solid; 84% yield; m.p. = 67–68 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.43 (d, J = 8.0 Hz, 2H), 7.31 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 2.89–2.85 (m, 2H), 2.81–2.77 (m, 2H), 2.38 (s, 3H), 2.28 (s, 3H), 1.88–1.85 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.1, 138.7, 131.8, 129.7, 129.1, 128.3, 128.0, 121.9, 119.5, 116.0, 89.0, 82.3, 57.0, 48.9, 23.8, 21.5, 20.7; HRMS (APCI) m/z : calcd for $\text{C}_{21}\text{H}_{23}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 306.1852, found 306.1850.

2-(3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)-4-methylphenol (1g)

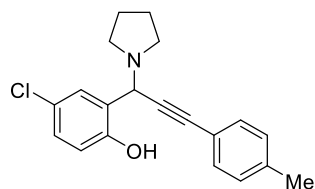
Brown oil; 81% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, J = 9.5 Hz, 2H), 7.31 (s, 1H), 7.02 (d, J = 9.5 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 8.5 Hz, 1H), 5.22 (s, 1H), 3.83 (s, 3H), 2.88-2.84 (m, 2H), 2.81-2.76 (m, 2H), 2.28 (s, 3H), 1.87-1.85 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 155.1, 133.3, 129.6, 128.3, 127.9, 122.0, 115.9, 114.7, 114.0, 88.7, 81.6, 57.0, 55.3, 48.9, 23.8, 20.7; HRMS (APCI) m/z : calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 322.1801, found 322.1799.

2-(3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)-4-methylphenol (1h)

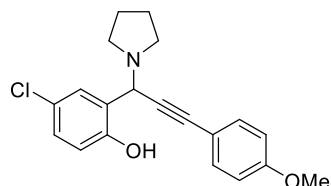
Yellow solid; 78% yield; m.p. = 79–80 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 5.20 (s, 1H), 2.84 (s, 2H), 2.79-2.77 (m, 2H), 2.28 (s, 3H), 1.87 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.0, 134.6, 133.1, 129.8, 128.7, 128.2, 128.1, 121.6, 121.0, 116.1, 87.7, 84.3, 57.1, 49.1, 23.8, 20.7; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{ClNO}$ $[\text{M} + \text{H}]^+$ 326.1306, found 326.1307.

4-Chloro-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1i)

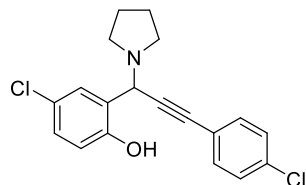
Yellow solid; 79% yield; m.p. = 61–62 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.54-7.52 (m, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.38-7.35 (m, 3H), 7.17 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 2.88 (s, 2H), 2.80-2.76 (m, 2H), 1.89-1.86 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 131.9, 129.1, 128.8, 128.4, 127.7, 123.6, 122.2, 117.5, 89.5, 82.0, 56.7, 48.9, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{ClNO}$ $[\text{M} + \text{H}]^+$ 312.1149, found 312.1146.

4-Chloro-2-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1j)

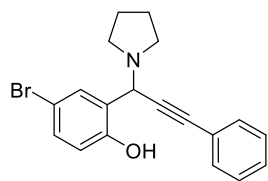
White solid; 80% yield; m.p. = 75–76 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.50 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.18–7.15 (m, 3H), 6.78 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 2.88 (s, 2H), 2.79–2.78 (m, 2H), 2.38 (s, 3H), 1.87 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 139.0, 131.8, 129.2, 129.1, 127.8, 123.7, 123.6, 119.1, 117.6, 89.7, 81.1, 56.6, 48.9, 23.8, 21.5; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{ClNO}$ $[\text{M} + \text{H}]^+$ 326.1306, found 326.1303.

4-Chloro-2-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1k)

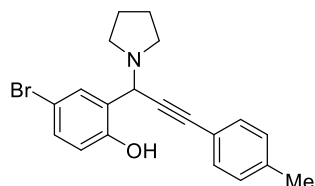
Yellow solid; 77% yield; m.p. = 68–69 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.49 (s, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 1H), 5.22 (s, 1H), 3.83 (s, 2H), 2.86 (s, 2H), 2.78–2.75 (m, 2H), 1.88–1.85 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.9, 156.3, 133.4, 129.1, 127.8, 123.8, 123.5, 117.5, 114.2, 114.0, 89.5, 80.4, 58.7, 55.3, 48.8, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{ClNO}_2$ $[\text{M} + \text{H}]^+$ 342.1255, found 342.1255.

4-Chloro-2-(3-(4-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1l)

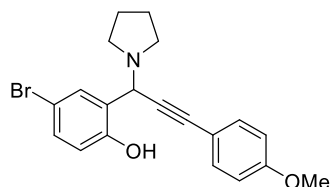
Yellow solid; 71% yield; m.p. = 94–95 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, J = 8.5 Hz, 3H), 7.34 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 5.21 (s, 1H), 2.85 (s, 2H), 2.78–2.76 (m, 2H), 1.88 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.2, 134.9, 133.7, 133.2, 128.9, 128.8, 127.6, 123.6, 123.4, 120.6, 117.7, 88.4, 83.1, 56.7, 49.0, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{NO}$ $[\text{M} + \text{H}]^+$ 346.0760, found 346.0757.

4-Bromo-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1m)

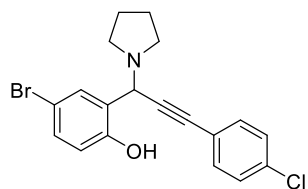
Yellow solid; 78% yield; m.p. = 47–48 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, J = 8.5 Hz, 1H), 7.57-7.55 (m, 2H), 7.41-7.38 (m, 3H), 7.34 (d, J = 8.5 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 2.90 (s, 2H), 2.84-2.79 (m, 2H), 1.92-1.89 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 132.1, 131.9, 130.6, 128.8, 128.4, 124.1, 122.2, 118.1, 110.8, 89.6, 81.9, 56.6, 48.9, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{BrNO}$ [$\text{M} + \text{H}$] $^+$ 356.0644, found 356.0640.

4-Bromo-2-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1n)

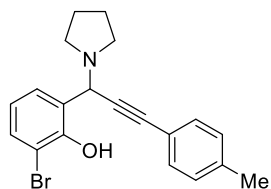
White solid; 82% yield; m.p. = 77–78 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.62 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.5 Hz, 1H), 5.22 (s, 1H), 2.86 (s, 2H), 2.78-2.76 (m, 2H), 2.38 (s, 3H), 1.87 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 139.0, 132.0, 131.8, 130.6, 129.2, 124.2, 119.1, 118.0, 110.7, 89.7, 81.2, 56.6, 48.8, 23.8, 21.5; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrNO}$ [$\text{M} + \text{H}$] $^+$ 370.0801, found 370.0796.

4-Bromo-2-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1o)

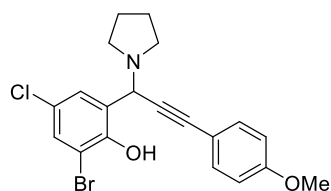
Yellow solid; 83% yield; m.p. = 84–85 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.65 (s, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 3.86 (s, 3H), 2.89 (s, 2H), 2.81-2.79 (m, 2H), 1.89 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.9, 156.8, 133.4, 132.0, 130.6, 124.3, 118.0, 114.2, 114.0, 110.7, 89.5, 80.4, 56.6, 55.3, 48.8, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrNO}_2$ [$\text{M} + \text{H}$] $^+$ 388.0732, found 388.0736.

4-Bromo-2-(3-(4-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1p)

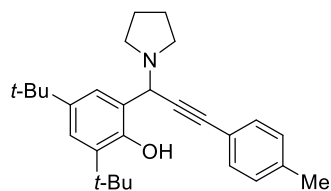
Pale yellow solid; 73% yield; m.p. = 91–92 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.57 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.35–7.31 (m, 3H), 6.75 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 2.89 (s, 2H), 2.80 (s, 2H), 1.89 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.6, 134.9, 133.2, 132.3, 130.5, 128.8, 120.5, 118.5, 111.0, 85.5, 82.9, 56.5, 49.1, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{17}\text{BrClNO}$ $[\text{M} + \text{H}]^+$ 392.0233, found 392.0233.

2-Bromo-6-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1q)

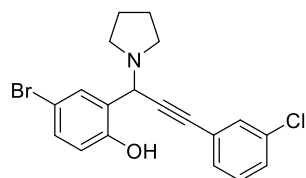
Yellow solid; 69% yield; m.p. = 86–87 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.49–7.45 (m, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 6.72 (t, J = 7.5 Hz, 1H), 5.28 (s, 1H), 2.92–2.90 (m, 2H), 2.81–2.80 (m, 2H), 2.37 (s, 3H), 1.88 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.6, 139.0, 132.7, 131.8, 129.2, 127.1, 123.3, 119.6, 119.1, 110.3, 89.7, 81.2, 57.1, 48.8, 23.8, 21.6; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrNO}$ $[\text{M} + \text{H}]^+$ 370.0801, found 370.0799.

2-Bromo-4-chloro-6-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1r)

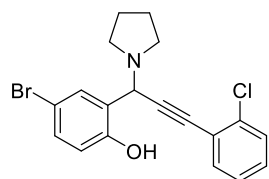
The general procedures were followed unless the reaction was carried out at room temperature for 12 hours. Yellow solid; 68% yield; m.p. = 86–87 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.47–7.45 (m, 4H), 6.89 (d, J = 8.5 Hz, 2H), 5.24 (s, 1H), 3.83 (s, 3H), 2.91–2.90 (m, 2H), 2.80–2.78 (m, 2H), 1.90–1.88 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.1, 153.5, 133.4, 131.9, 127.1, 124.2, 123.5, 114.1, 113.8, 110.6, 90.0, 79.6, 56.9, 55.3, 48.8, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{19}\text{BrClNO}_2$ $[\text{M} + \text{H}]^+$ 422.0339, found 422.0333.

2,4-Di-*tert*-butyl-6-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1s)

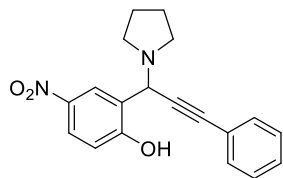
Yellow solid; 70% yield; m.p. = 74–75 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.51 (s, 1H), 7.43 (d, J = 6.5 Hz, 2H), 7.27 (s, 1H), 7.18 (d, J = 8.0 Hz, 2H), 5.26 (s, 1H), 2.88 (s, 2H), 2.80 (s, 2H), 2.38 (s, 3H), 1.87 (s, 4H), 1.45 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.0, 140.0, 138.5, 135.4, 131.7, 129.1, 123.3, 122.7, 121.4, 119.8, 89.0, 82.9, 57.4, 48.7, 34.9, 34.3, 31.6, 29.6, 24.0, 22.6, 21.5; HRMS (APCI) m/z : calcd for $\text{C}_{28}\text{H}_{37}\text{NO}$ $[\text{M} + \text{H}]^+$ 404.2947, found 404.2944.

4-Bromo-2-(3-(3-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1t)

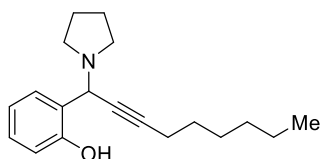
Yellow solid; 65% yield; m.p. = 74–75 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.57 (s, 1H), 7.51 (s, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.32–7.28 (m, 2H), 6.74 (d, J = 8.5 Hz, 1H), 5.22 (s, 1H), 2.85 (s, 2H), 2.79–2.75 (m, 2H), 1.90–1.87 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.7, 134.3, 132.2, 131.8, 130.4, 130.1, 129.7, 129.1, 123.8, 118.2, 110.8, 88.1, 83.3, 56.6, 49.0, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{17}\text{BrClNO}$ $[\text{M} + \text{H}]^+$ 392.0233, found 392.0234.

4-Bromo-2-(3-(2-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1u)

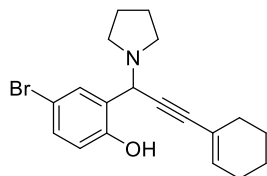
Yellow solid; 60% yield; m.p. = 64–65 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.75 (s, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.32–7.29 (m, 2H), 7.26 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 5.32 (s, 1H), 2.94–2.91 (m, 2H), 2.84–2.80 (m, 2H), 1.90–1.87 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.7, 136.1, 133.6, 132.2, 130.7, 129.8, 129.4, 126.6, 123.8, 122.2, 118.1, 110.9, 87.4, 86.3, 56.7, 48.9, 23.9; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{17}\text{BrClNO}$ $[\text{M} + \text{H}]^+$ 392.0233, found 392.0231.

4-Nitro-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1v)

The general procedures were followed unless the reaction was carried out at room temperature for 12 hours. Red solid; 58% yield; m.p. = 72–73 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.56 (s, 1H), 8.13 (d, J = 9.0 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.32–7.29 (m, 2H), 7.26–7.21 (m, 3H), 4.25 (s, 2H), 3.44 (s, 4H), 2.02 (s, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 147.2, 143.0, 138.1, 128.6, 128.3, 126.6, 126.1, 119.4, 119.2, 117.1, 111.6, 111.5, 52.1, 33.2, 25.3; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 323.1390, found 323.1386.

2-(1-(Pyrrolidin-1-yl)non-2-yn-1-yl)phenol (1w)

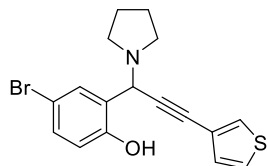
The general procedures were followed unless the reaction was carried out for 24 hours. Yellow oil, 55% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 6.84–6.81 (m, 2H), 5.03 (s, 1H), 2.81–2.77 (m, 2H), 2.73–2.68 (m, 2H), 2.34 (t, J = 7.5 Hz, 2H), 1.85–1.82 (m, 4H), 1.62–1.56 (m, 2H), 1.49–1.43 (m, 2H), 1.36–1.32 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.6, 129.1, 127.8, 122.7, 118.7, 116.0, 89.6, 73.3, 56.6, 48.6, 31.3, 28.8, 28.5, 23.8, 22.6, 18.7, 14.0; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{27}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 286.2165, found 286.2163.

4-Bromo-2-(3-(cyclohex-1-en-1-yl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1x)

Yellow solid, 84% yield; m.p. = 76–77 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.56 (s, 1H), 7.30 (d, J = 7.5 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.24 (s, 1H), 5.14 (s, 1H), 2.82 (s, 2H), 2.73 (s, 2H), 2.23 (s, 2H), 2.16 (s, 2H), 1.87 (s, 4H), 1.71 (s, 2H), 1.65 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 135.9, 131.9, 130.6, 124.4, 119.9, 118.0, 110.7, 91.5, 78.9, 56.5, 48.7, 29.4, 25.6, 23.8, 22.2, 21.4; HRMS (APCI) m/z : calcd for $\text{C}_{19}\text{H}_{22}\text{BrNO}$

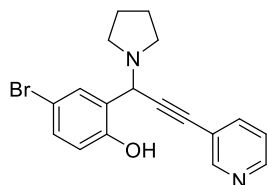
$[M + H]^+$ 360.0957, found 360.0953.

4-Bromo-2-(1-(pyrrolidin-1-yl)-3-(thiophen-3-yl)prop-2-yn-1-yl)phenol (1y)



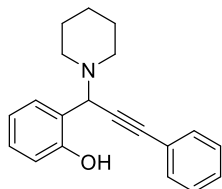
White solid, 86% yield; m.p. = 101–102 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.60 (s, 1H), 7.55 (s, 1H), 7.31 (s, 2H), 7.19 (s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 5.21 (s, 1H), 2.86 (s, 2H), 2.78 (s, 2H), 1.87 (s, 4H), 1.71 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 132.1, 130.6, 130.0, 129.6, 125.6, 124.1, 121.1, 118.1, 110.8, 84.6, 81.6, 56.7, 48.9, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{17}\text{H}_{16}\text{BrNOS}$ $[M + H]^+$ 364.0188, found 361.0189.

4-Bromo-2-(3-(pyridin-3-yl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1z)

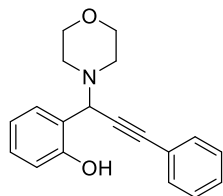


The general procedures were followed unless the reaction was carried out at room temperature for 12 hours. Brown solid, 54% yield; m.p. = 75–76 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.75 (s, 1H), 8.59 (d, J = 6.5 Hz, 1H), 7.82–7.80 (m, 1H), 7.56 (s, 1H), 7.32–7.29 (m, 2H), 6.75 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 2.89–2.86 (m, 2H), 2.81–2.76 (m, 2H), 1.90–1.87 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.6, 152.5, 149.2, 138.9, 132.3, 130.4, 123.6, 123.1, 119.3, 118.3, 110.9, 86.2, 85.6, 56.7, 49.1, 23.8; HRMS (APCI) m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{O}$ $[M + H]^+$ 357.0597, found 357.0605.

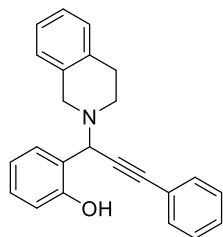
2-(3-Phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (1a')²



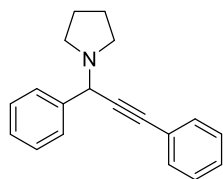
White solid, 82% yield; m.p. = 83–84 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.56–7.54 (m, 3H), 7.38–7.35 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 6.87–6.84 (m, 3H), 5.11 (s, 1H), 2.76–2.72 (m, 4H), 1.89 (br, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.6, 131.9, 129.4, 128.6, 128.5, 128.4, 122.6, 121.3, 119.0, 116.4, 89.8, 82.3, 61.0, 25.9, 23.9; HRMS (APCI) m/z : calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ $[M + H]^+$ 292.1695, found 292.1693.

2-(1-Morpholino-3-phenylprop-2-yn-1-yl)phenol (1b')²

Yellow solid, 73% yield; m.p. = 98–99 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.57–7.54 (m, 3H), 7.38–7.35 (m, 3H), 7.27–7.23 (m, 2H), 6.91–6.87 (m, 2H), 5.12 (s, 1H), 3.81 (s, 4H), 2.81 (s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 156.9, 131.9, 129.8, 128.8, 128.1, 122.1, 120.5, 119.5, 118.7, 90.5, 81.4, 66.7, 60.6; HRMS (APCI) m/z: calcd for C₁₉H₁₉NO₂ [M + H]⁺ 294.1488, found 294.1485.

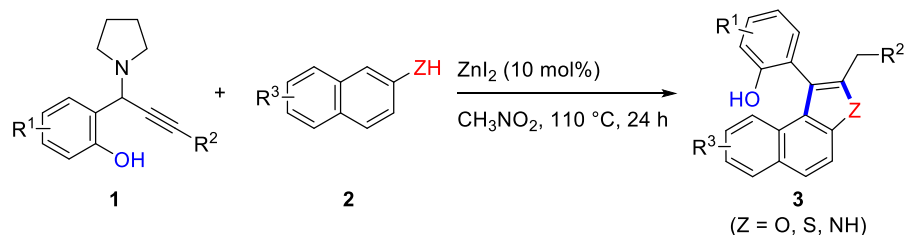
2-(1-(3,4-Dihydroisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-yl)phenol (1c')

White solid, 84% yield; m.p. = 112–113 °C, ¹H NMR (500 MHz, CDCl₃) δ 10.3 (s, 1H), 7.45–7.43 (m, 2H), 7.32–7.28 (m, 4H), 7.23–7.19 (m, 3H), 7.16–7.11 (m, 2H), 6.86–6.83 (m, 2H), 4.95 (s, 1H), 4.18 (dd, *J* = 14.0 Hz, *J* = 14.0 Hz, 2H), 3.19–3.14 (s, 1H), 3.12–3.06 (s, 1H), 2.96–2.92 (s, 1H), 2.88–2.84 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 157.9, 134.3, 133.1, 131.8, 129.2, 129.0, 128.4, 128.3, 127.8, 127.4, 126.2, 122.6, 121.1, 119.3, 116.2, 87.6, 85.6, 58.4, 54.2, 45.2, 28.6; HRMS (APCI) m/z: calcd for C₂₄H₂₁NO [M + H]⁺ 340.1695, found 340.1692.

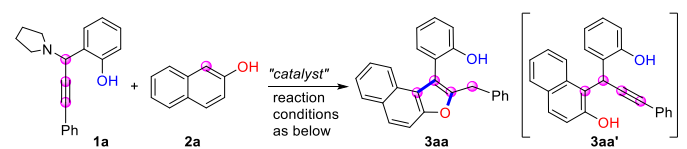
1-(1,3-Diphenylprop-2-yn-1-yl)pyrrolidine (4)³

Yellow oil, 80% yield; ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.51–7.50 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33–7.30 (m, 4H), 4.90 (s, 1H), 2.71–2.69 (m, 4H), 1.84–1.79 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 139.6, 131.8, 128.5, 128.2, 128.1, 128.0, 127.5, 123.2, 86.9, 86.7, 59.1, 50.3, 23.5; HRMS (APCI) m/z: calcd for C₁₉H₁₉N [M + H]⁺ 262.1596, found 262.1598.

3. General procedure for the synthesis of naphtho[2,1-*b*]furans derivatives



A mixture of propargylamines **1** (0.4 mmol), β -naphthol **2** (0.48 mmol), and ZnI_2 (0.04 mmol) were added to a resealable screw-capped Schlenk tube. Then nitromethane (4 mL) was added. The tube sealed with a Teflon-coated cap and the resulting mixture was stirred in an oil bath preheated to $110\text{ }^\circ\text{C}$ for 24 h (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified using flash column chromatography with a silica gel (230-400 mesh), using *n*-hexane and dichloromethane (1:1-4:1, v/v) as the elution solvent to afford the desired product **3**.

Table S1 Screening for optimal reaction conditions.^a


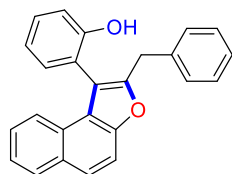
The reaction scheme shows the reaction of 1a (2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol) and 2a (2-naphthol) in the presence of a catalyst and reaction conditions to form products 3aa and 3aa' (2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)naphthalen-1-ol).

entry	catalyst	solvent	temp. (°C)	time (h)	yield (%) ^b
1	-	MeNO ₂	110	10	0
2	FeCl ₃	MeNO ₂	110	10	78 ^c
3	PdCl ₂	MeNO ₂	110	10	0
4	SnCl ₂	MeNO ₂	110	10	0
5	ZnBr ₂	MeNO ₂	110	10	68
6	ZnCl ₂	MeNO ₂	110	10	78
7	ZnI ₂	MeNO ₂	110	10	80
8	ZnCl ₂	DMF	110	10	trace
9	ZnCl ₂	DCE	110	10	50
10	ZnCl ₂	dioxane	110	10	48
11	ZnCl ₂	xylene	110	10	73
12	ZnI ₂	DCE	110	10	60
13	ZnI ₂	DMSO	110	10	67
14	ZnI ₂	<i>t</i> -BuOH	110	10	43
15	ZnI ₂	EtOH	110	10	trace
16 ^d	ZnI ₂	MeNO ₂	110	10	59
17 ^e	ZnI ₂	MeNO ₂	110	10	48
18 ^f	ZnI ₂	MeNO ₂	110	10	n.r.
19	ZnI ₂	MeNO ₂	90	10	52
20	ZnI ₂	MeNO ₂	130	10	80
21	ZnI ₂	MeNO ₂	110	8	75
22 ^g	ZnI ₂	MeNO ₂	110	24	72
23 ^h	ZnI ₂	MeNO ₂	110	24	87
24 ⁱ	ZnI ₂	MeNO ₂	110	24	86

^a Reaction conditions: 2-(3-Phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (**1a**) (0.4 mmol), 2-naphthol (**2a**) (0.4 mmol), and Lewis acid catalyst (50 mol% for initial trial) in solvent (3.0 mL). ^b Isolated yield. ^c Product **3aa'** was formed exclusively. ^d Morpholinyl group was used instead of pyrrolidinyl group in **1a**. ^e Piperidinyl group was used instead of pyrrolidinyl group in **1a**. ^f Dihydroisoquinolinyl group was used instead of pyrrolidinyl group in **1a**. ^g 5 mol% catalyst was used. ^h 10 mol% catalyst was used. ⁱ 20 mol% catalyst was used. n.r. = no reaction.

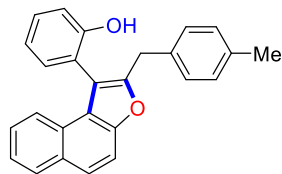
4. Characterization data for naphtho[2,1-*b*]furans derivatives

2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, Scheme 4b-f, compound 3aa)⁴

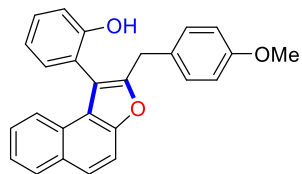


This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a white solid in 87% yield (121 mg); m.p. = 114–115 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 9.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.45 (t, J = 8.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 8.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.24–7.20 (m, 3H), 7.15 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 4.98 (s, 1H), 4.06 (dd, J = 16.0 Hz, J = 15.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 154.2, 152.3, 137.4, 131.6, 130.7, 130.3, 128.7, 128.6, 127.9, 126.7, 126.4, 125.6, 124.5, 122.5, 121.8, 121.0, 119.3, 115.7, 112.6, 112.3, 32.9; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{18}\text{O}_2$ [$\text{M} + \text{H}$]⁺ 351.1379, found 351.1376.

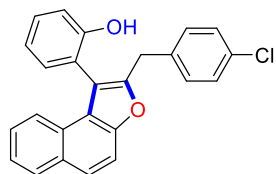
2-(2-(4-Methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ba)



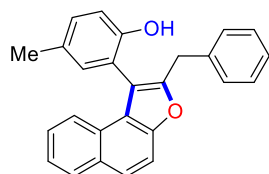
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 82% yield (119 mg); m.p. = 102–103 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.45 (t, J = 9.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 9.0 Hz, 2H), 7.20–7.17 (m, 3H), 7.16–7.12 (m, 3H), 5.06 (s, 1H), 4.07 (dd, J = 15.5 Hz, J = 17.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.0, 154.3, 152.3, 136.3, 134.4, 131.6, 130.7, 130.3, 129.3, 128.7, 128.5, 127.9, 126.4, 125.5, 124.5, 122.6, 121.8, 121.0, 119.4, 115.7, 112.4, 112.3, 32.5, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2$ [$\text{M} + \text{H}$]⁺ 365.1536, found 365.1531.

2-(2-(4-Methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ca)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford an orange solid in 88% yield (133 mg); m.p. = 109–110 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.63 (d, J = 9.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 3H), 7.10 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 5.01 (s, 1H), 4.00 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.3, 155.2, 154.2, 152.2, 131.6, 130.7, 130.3, 129.5, 128.7, 127.9, 126.4, 125.5, 124.5, 122.5, 121.8, 120.9, 119.4, 115.7, 114.0, 112.3, 112.2, 55.2, 32.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 381.1485, found 381.1482.

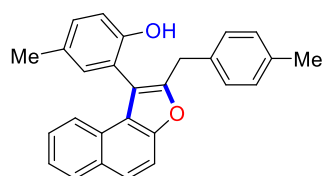
2-(2-(4-Chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3da)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 86% yield (132 mg); m.p. = 112–113 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 12.5 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.5 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 3H), 7.15 (d, J = 9.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 2H), 4.99 (s, 1H), 4.05 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.2, 154.0, 152.3, 135.9, 132.5, 131.5, 130.7, 130.4, 130.0, 128.7, 127.9, 126.5, 125.7, 124.6, 122.5, 121.7, 121.0, 119.1, 115.7, 112.8, 112.2, 32.3; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{17}\text{ClO}_2$ [$\text{M} + \text{H}$] $^+$ 385.0989, found 385.0988.

2-(2-(4-Methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ea)

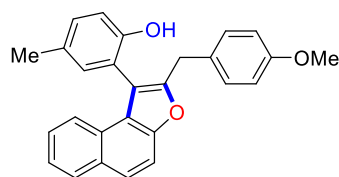
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 87% yield (126 mg); m.p. = 61–62 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 9.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.28–7.24 (m, 4H), 7.17 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 4.84 (s, 1H), 4.11 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 152.2, 152.0, 137.6, 131.8, 130.8, 130.6, 130.1, 128.7, 128.6, 127.9, 126.7, 126.4, 125.5, 124.4, 122.6, 121.8, 119.0, 115.4, 112.8, 112.3, 32.9, 20.6; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2$ $[\text{M} + \text{H}]^+$ 365.1536, found 365.1532.

4-Methyl-2-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3fa)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 85% yield (128 mg); m.p. = 62–63 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 6.0 Hz, 3H), 7.12 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 1H), 4.82 (s, 1H), 4.03 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.9, 152.2, 152.0, 136.2, 134.5, 131.8, 130.8, 130.6, 130.0, 129.3, 128.5, 127.9, 126.4, 125.5, 124.5, 122.7, 121.8, 119.1, 115.4, 112.6, 112.4, 32.5, 21.0, 20.6; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{22}\text{O}_2$ $[\text{M} + \text{H}]^+$ 379.1692, found 379.1690.

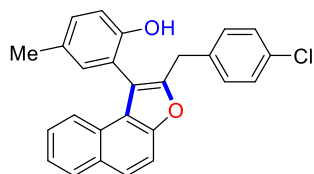
2-(2-(4-Methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenol (Scheme 2, compound 3ga)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford an orange solid in 86% yield (135 mg); m.p. = 65–66 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 9.0 Hz, 2H), 7.13 (s, 1H), 7.03 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 4.81 (s, 1H), 4.00 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H); ^{13}C

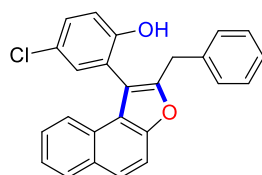
NMR (125 MHz, CDCl₃) δ 158.3, 155.1, 152.2, 152.0, 131.8, 130.8, 130.6, 130.0, 129.7, 129.6, 128.7, 127.9, 126.4, 125.4, 124.4, 122.6, 121.8, 119.0, 115.4, 114.0, 112.4, 112.3, 55.2, 32.0, 20.6; HRMS (APCI) m/z : calcd for C₂₇H₂₂O₃ [M + H]⁺ 395.1641, found 395.1640.

2-(2-(4-Chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenol (Scheme 2, compound 3ha)

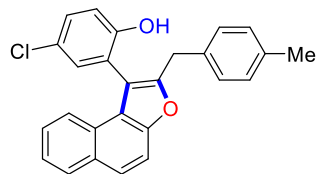


This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, *R_f* = 0.5) to afford a yellow solid in 88% yield (140 mg); m.p. = 80–81 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 9.5 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.27–7.23 (m, 3H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 4.80 (s, 1H), 4.04 (dd, *J* = 15.5 Hz, *J* = 16.0 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 154.0, 152.2, 152.0, 136.0, 132.5, 131.8, 130.7, 130.2, 130.0, 128.7, 127.9, 126.5, 125.7, 124.5, 122.6, 121.7, 118.9, 115.5, 113.1, 112.2, 32.3, 20.6; HRMS (APCI) m/z : calcd for C₂₆H₁₉ClO₂ [M + H]⁺ 399.1146, found 399.1147.

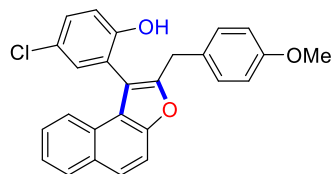
2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)-4-chlorophenol (Scheme 2, compound 3ia)



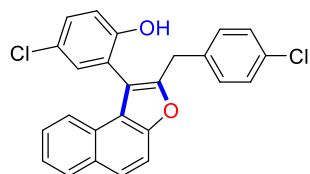
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, *R_f* = 0.5) to afford an orange solid in 86% yield (132 mg); m.p. = 62–63 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 9.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24–7.23 (m, 3H), 7.08 (d, *J* = 9.0 Hz, 1H), 4.96 (s, 1H), 4.07 (dd, *J* = 15.5 Hz, *J* = 15.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 155.0, 153.0, 152.3, 137.1, 131.0, 130.7, 130.3, 128.8, 128.7, 128.6, 127.7, 126.6, 125.8, 125.5, 124.6, 122.3, 121.3, 121.0, 117.0, 112.2, 111.4, 33.0; HRMS (APCI) m/z : calcd for C₂₅H₁₇ClO₂ [M + H]⁺ 385.0989, found 385.0987.

4-Chloro-2-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ja)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a white solid in 90% yield (143 mg); m.p. = 112–113 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.44 (t, J = 7.0 Hz, 1H), 7.41 (t, J = 6.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.11 (s, 4H), 7.08 (d, J = 8.5 Hz, 1H), 4.96 (s, 1H), 4.02 (dd, J = 16.0 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.3, 153.0, 152.2, 136.4, 134.0, 131.0, 130.7, 130.2, 129.4, 128.8, 128.5, 127.7, 126.6, 125.7, 125.5, 124.6, 122.3, 121.4, 121.0, 117.0, 112.3, 111.2, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{19}\text{ClO}_2$ [$\text{M} + \text{H}$] $^+$ 399.1146, found 399.1143.

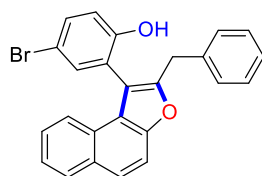
4-Chloro-2-(2-(4-methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ka)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1.5, R_f = 0.4) to afford a yellow solid in 89% yield (147 mg); m.p. = 61–62 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.41 (t, J = 6.5 Hz, 1H), 7.36 (t, J = 8.5 Hz, 1H), 7.32 (s, 1H), 7.15 (d, J = 9.0 Hz, 2H), 7.08 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 5.02 (s, 1H), 4.00 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.4, 155.5, 153.0, 152.6, 131.1, 130.7, 130.2, 129.6, 129.1, 128.8, 127.7, 126.6, 125.8, 125.5, 124.6, 122.4, 121.4, 121.1, 117.0, 114.1, 112.3, 111.1, 55.2, 32.1; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{19}\text{ClO}_3$ [$\text{M} + \text{H}$] $^+$ 415.1096, found 415.1097.

4-Chloro-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3la)

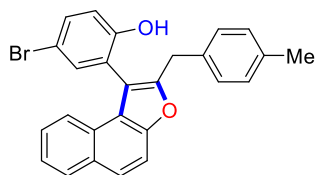
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1, R_f = 0.4) to afford a white solid in 71% yield (147 mg); m.p. = 100–101 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 7.0 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.31 (s, 1H), 7.27–7.25 (m, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 1H), 4.97 (s, 1H), 4.03 (dd, J = 15.5 Hz, J = 16.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.3, 153.0, 152.3, 135.5, 132.7, 131.0, 130.7, 130.3, 130.0, 128.8, 127.7, 126.7, 126.0, 125.6, 124.7, 122.3, 121.3, 120.8, 117.1, 112.2, 111.8, 32.4; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{16}\text{Cl}_2\text{O}_2$ [$M + H$] $^+$ 419.0600, found 419.0603.

2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)-4-bromophenol (Scheme 2, compound 3ma)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a white solid in 85% yield (146 mg); m.p. = 102–103 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.46 (s, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.24–7.21 (m, 3H), 7.03 (d, J = 8.5 Hz, 1H), 4.97 (s, 1H), 4.07 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.1, 153.5, 152.2, 137.1, 133.9, 133.2, 130.7, 128.8, 128.7, 128.6, 127.6, 126.8, 126.6, 125.8, 124.6, 122.3, 121.5, 121.3, 117.5, 112.7, 112.2, 111.3, 33.0; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{17}\text{BrO}_2$ [$M + H$] $^+$ 431.0467, found 431.0463.

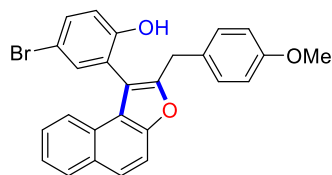
4-Bromo-2-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3na)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 88% yield (156 mg); m.p. = 106–107 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.11 (s, 4H), 7.03 (d, J = 8.5 Hz, 1H), 4.99 (s, 1H), 4.02 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.4, 153.5, 152.2,

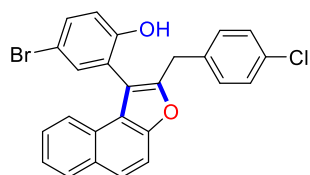
136.4, 134.0, 133.9, 133.1, 130.7, 128.8, 128.7, 127.7, 125.8, 124.6, 122.3, 121.6, 121.4, 117.4, 112.7, 112.3, 111.1, 32.6, 21.0; HRMS (APCI) m/z : calcd for $C_{26}H_{19}BrO_2$ $[M + H]^+$ 445.0624, found 445.0620.

4-Bromo-2-(2-(4-methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 30a)

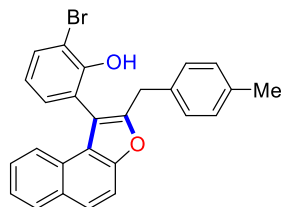


This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 87% yield (160 mg); m.p. = 72–73 °C, 1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.45 (s, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 9.0 Hz, 2H), 4.99 (s, 1H), 4.02 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 155.5, 153.5, 152.2, 133.9, 133.1, 130.7, 129.6, 128.8, 127.7, 126.6, 125.8, 124.6, 122.3, 121.6, 121.4, 117.4, 114.1, 112.7, 112.2, 111.0, 55.2, 32.2; HRMS (APCI) m/z : calcd for $C_{26}H_{19}BrO_3$ $[M + H]^+$ 461.0573, found 461.0575.

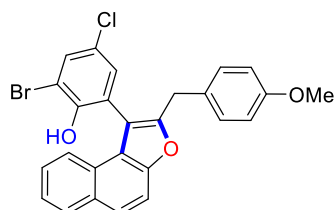
4-Bromo-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3pa)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 69% yield (128 mg); m.p. = 64–65 °C, 1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.5 Hz, 1H), 4.97 (s, 1H), 4.03 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 153.5, 152.3, 135.5, 133.8, 133.2, 132.7, 130.7, 130.0, 128.8, 127.7, 126.7, 126.0, 124.7, 122.3, 121.4, 121.3, 117.5, 112.8, 112.2, 111.6, 32.4; HRMS (APCI) m/z : calcd for $C_{25}H_{16}BrClO_2$ $[M + H]^+$ 465.0074, found 465.0069.

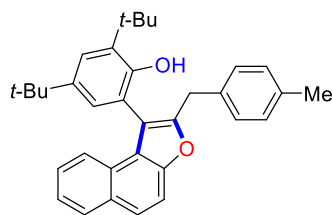
2-Bromo-6-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3qa)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 78% yield (138 mg); m.p. = 109–110 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.12–7.08 (m, 4H), 6.97 (t, J = 8.0 Hz, 1H), 5.57 (s, 1H), 4.04 (dd, J = 14.5 Hz, J = 16.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.2, 152.0, 151.0, 136.2, 134.3, 132.8, 131.5, 130.7, 129.3, 128.5, 127.9, 126.2, 125.3, 124.3, 122.6, 121.9, 121.8, 121.4, 113.5, 112.3, 110.4, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{19}\text{BrO}_2$ [$\text{M} + \text{H}$] $^+$ 445.0624, found 445.0621.

2-Bromo-4-chloro-6-(2-(4-methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ra)

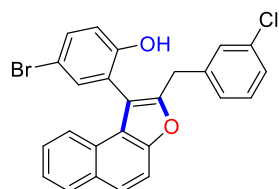
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1.5:1, R_f = 0.5) to afford a white solid in 75% yield (148 mg); m.p. = 119–120 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.83 (d, J = 7.5 Hz, 2H), 5.51 (s, 1H), 4.03 (dd, J = 16.0 Hz, J = 16.0 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.4, 154.7, 152.0, 150.0, 132.2, 131.1, 130.7, 129.6, 129.0, 128.9, 127.7, 126.4, 125.8, 125.5, 124.4, 122.5, 122.4, 121.6, 114.0, 112.3, 110.5, 55.2, 32.3; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{BrClO}_3$ [$\text{M} + \text{H}$] $^+$ 495.0180, found 495.0175.

2,4-Di-*tert*-butyl-6-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3sa)



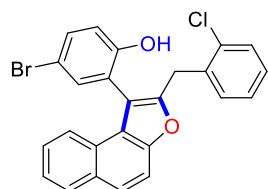
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 8:1, R_f = 0.5) to afford a yellow solid in 80% yield (152 mg); m.p. = 159–160 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.64 (t, J = 8.5 Hz, 2H), 7.47 (s, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.20 (s, 1H), 7.16 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.10 (s, 1H), 4.05 (dd, J = 15.5 Hz, J = 15.0 Hz, 2H), 2.31 (s, 3H), 1.50 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.2, 152.3, 150.3, 142.3, 136.2, 135.3, 134.5, 130.6, 129.3, 128.6, 128.0, 126.1, 125.9, 125.4, 124.4, 124.2, 122.8, 121.8, 119.0, 113.1, 112.3, 35.1, 34.4, 32.6, 31.7, 29.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{34}\text{H}_{36}\text{O}_2$ $[\text{M} + \text{H}]^+$ 477.2788, found 477.2782.

4-Bromo-2-(2-(3-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ta)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a white solid in 64% yield (118 mg); m.p. = 103–104 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.45–7.42 (m, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.23–7.20 (m, 3H), 7.08 (d, J = 6.0 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 5.01 (s, 1H), 4.04 (dd, J = 15.5 Hz, J = 16.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.0, 153.5, 152.3, 139.0, 134.5, 133.8, 133.3, 130.7, 129.9, 128.8, 127.7, 126.7, 126.1, 124.7, 122.3, 121.4, 121.3, 117.6, 112.8, 112.2, 111.9, 32.7; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{16}\text{BrClO}_2$ $[\text{M} + \text{H}]^+$ 465.0074, found 465.0069.

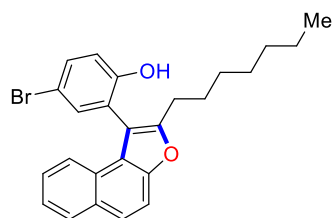
4-Bromo-2-(2-(2-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ua)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to

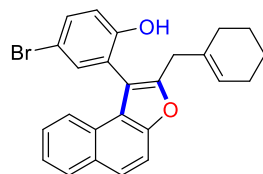
afford a yellow oil in 38% yield (70 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.38-7.31 (m, 3H), 7.18-7.17 (m, 2H), 6.97 (d, J = 8.5 Hz, 1H), 4.98 (s, 1H), 4.25 (dd, J = 16.0 Hz, J = 16.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 152.2, 134.5, 133.9, 133.7, 133.1, 130.7, 129.6, 128.8, 128.4, 127.7, 126.9, 126.7, 125.9, 124.7, 122.3, 121.4, 121.3, 117.4, 112.6, 112.2, 112.1, 30.9; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{16}\text{BrClO}_2$ $[\text{M} + \text{H}]^+$ 465.0074, found 465.0075.

4-Bromo-2-(2-heptylnaphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3wa)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow oil in 48% yield (68 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.47-7.40 (m, 2H), 7.35-7.32 (m, 2H), 7.15 (d, J = 8.5 Hz, 1H), 7.10 (d, J = 9.0 Hz, 1H), 5.07 (s, 1H), 2.78-2.68 (m, 2H), 1.78-1.72 (m, 2H), 1.34-1.26 (m, 8H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.1, 154.2, 152.0, 131.6, 130.7, 130.1, 128.7, 127.9, 126.3, 125.1, 124.4, 122.6, 121.9, 120.8, 119.6, 115.5, 121.1, 111.6, 31.7, 29.1, 28.9, 28.3, 26.5, 22.6, 14.1; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2$ $[\text{M} + \text{H}]^+$ 359.2005, found 359.2003.

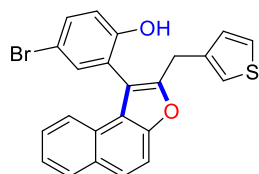
4-Bromo-2-(2-(cyclohex-1-en-1-ylmethyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3xa)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow oil in 88% yield (152 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.47 (s, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 5.45 (s, 1H), 5.05 (s, 1H), 3.37 (dd, J = 15.5

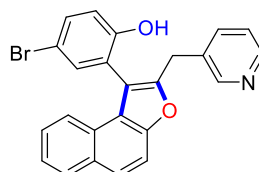
Hz, $J = 16.0$ Hz, 2H), 2.78-2.68 (m, 2H), 1.99 (s, 2H), 1.92 (s, 2H), 162-1.57 (m, 2H), 1.56-1.51 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.2, 153.5, 152.1, 133.9, 133.7, 132.9, 130.7, 128.8, 127.6, 126.6, 125.6, 124.6, 124.4, 122.4, 121.7, 121.4, 117.3, 112.5, 112.2, 111.5, 35.3, 28.3, 25.3, 22.7, 22.0; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{21}\text{BrO}_2$ $[\text{M} + \text{H}]^+$ 435.0780, found 435.0776.

4-Bromo-2-(2-(thiophen-3-ylmethyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3ya)

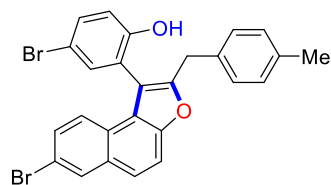


This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1.5:1, $R_f = 0.5$) to afford a yellow solid in 91% yield (158 mg); m.p. = 61–62 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 8.5$ Hz, 1H), 7.76 (d, $J = 9.0$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 8.5$ Hz, 1H), 7.46 (s, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.27-7.26 (m, 1H), 7.06 (s, 1H), 7.03 (d, $J = 8.5$ Hz, 1H), 6.99 (d, $J = 4.5$ Hz, 1H), 4.99 (s, 1H), 4.07 (dd, $J = 15.5$ Hz, $J = 16.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.6, 153.5, 152.2, 136.9, 133.8, 133.2, 130.7, 128.8, 128.0, 127.7, 126.7, 126.1, 125.9, 124.7, 122.4, 122.1, 121.5, 121.3, 117.5, 112.7, 112.2, 111.1, 27.7; HRMS (APCI) m/z : calcd for $\text{C}_{23}\text{H}_{15}\text{BrO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 437.0030, found 437.0030.

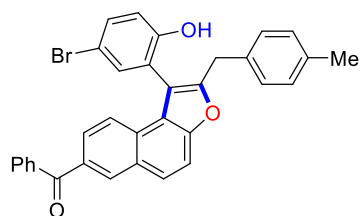
4-Bromo-2-(2-(pyridin-3-ylmethyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 2, compound 3za)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1.5:1, $R_f = 0.5$) to afford a white solid in 45% yield (77 mg); m.p. = 121–122 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.41 (s, 1H), 8.27 (s, 1H), 7.89 (d, $J = 7.5$ Hz, 1H), 7.71 (d, $J = 9.0$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.61-7.58 (m, 2H), 7.47 (d, $J = 9.0$ Hz, 1H), 7.43 (d, $J = 5.5$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 1H), 4.99 (s, 1H), 4.05 (dd, $J = 15.5$ Hz, $J = 16.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.5, 152.5, 152.1, 149.1, 146.8, 137.2, 134.0, 133.4, 133.0, 130.7, 128.7, 127.9, 126.5, 125.8, 124.5, 123.7, 122.6, 121.8, 121.7, 117.8, 113.6, 112.1, 112.0, 30.5; HRMS (APCI) m/z : calcd for $\text{C}_{24}\text{H}_{16}\text{BrNO}_2$ $[\text{M} + \text{H}]^+$ 432.0419, found 432.0418.

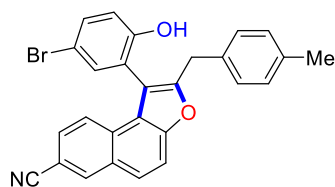
4-Bromo-2-(7-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3nb)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:2, R_f = 0.5) to afford a yellow solid in 89% yield (185 mg); m.p. = 67–68 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.67–7.61 (m, 2H), 7.55 (d, J = 8.5 Hz, 1H), 7.46–7.41 (m, 4H), 7.02 (d, J = 8.5 Hz, 1H), 4.92 (s, 1H), 4.02 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.9, 153.4, 152.2, 136.5, 133.8, 133.4, 132.0, 130.8, 130.7, 129.8, 129.4, 128.5, 126.1, 124.7, 124.0, 121.6, 121.2, 118.4, 117.5, 113.4, 112.8, 111.1, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 522.9727, found 522.9725.

(1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-7-yl)(phenyl)methanone (Scheme 3, compound 3nc)

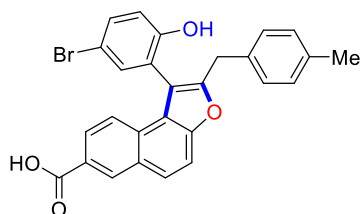
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:2, R_f = 0.5) to afford a yellow solid in 82% yield (179 mg); m.p. = 220–221 °C, ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 10.05 (s, 1H), 8.42 (s, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.75 (s, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.59–7.53 (m, 3H), 7.48 (s, 1H), 7.12–7.08 (m, 4H), 7.07 (d, J = 8.5 Hz, 1H), 4.04 (dd, J = 16.0 Hz, J = 16.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 196.0, 156.1, 154.5, 152.8, 137.8, 136.0, 134.8, 134.2, 133.2, 133.0, 132.6, 130.2, 130.1, 129.5, 129.0, 128.8, 126.9, 126.1, 123.3, 122.6, 122.3, 118.3, 115.2, 113.8, 110.5, 32.1, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{33}\text{H}_{23}\text{BrO}_3$ [$\text{M} + \text{H}$] $^+$ 549.0884, found 549.0880.

1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-7-carbonitrile (Scheme 3, compound 3nd)



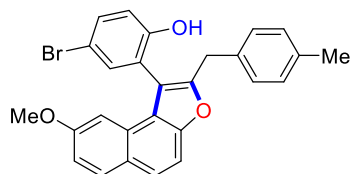
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:2.5, R_f = 0.5) to afford a white solid in 80% yield (150 mg); m.p. = 220–221 °C, ^1H NMR (500 MHz, DMSO- d_6) δ 10.06 (s, 1H), 8.65 (s, 1H), 7.96–7.92 (m, 2H), 7.74–7.69 (m, 2H), 7.55 (d, J = 9.0 Hz, 1H), 7.09 (s, 4H), 7.06 (d, J = 8.5 Hz, 1H), 4.03 (dd, J = 16.0 Hz, J = 16.0 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, DMSO- d_6) δ 156.0, 154.9, 152.9, 136.1, 135.4, 134.6, 134.2, 133.1, 129.8, 129.7, 129.5, 128.8, 127.2, 125.8, 124.1, 122.6, 122.0, 119.7, 118.3, 115.2, 114.6, 110.6, 107.1, 32.1, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{18}\text{BrNO}_2$ $[\text{M} + \text{H}]^+$ 470.0577, found 470.0572.

1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-7-carboxylic acid (Scheme 3, compound 3ne)



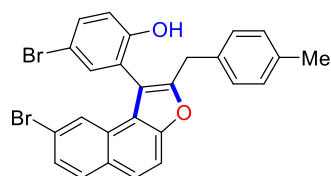
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1.5:1, R_f = 0.5) to afford a white solid in 89% yield (173 mg); m.p. = 223–224 °C, ^1H NMR (500 MHz, CD_3OD) δ 8.67 (s, 1H), 8.50 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.74–7.69 (m, 2H), 7.51 (d, J = 8.5 Hz, 1H), 7.37 (s, 1H), 7.17 (s, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 (J = 8.5 Hz, 1H), 4.06 (dd, J = 15.5 Hz, J = 16.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 168.9, 168.7, 157.5, 155.3, 154.4, 152.9, 137.6, 135.7, 134.4, 134.1, 132.2, 131.4, 130.6, 129.8, 128.7, 128.2, 127.2, 125.9, 125.8, 125.3, 124.9, 124.6, 122.7, 122.4, 118.8, 117.2, 114.4, 112.6, 110.7, 108.5, 31.9, 19.6; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{19}\text{BrO}_4$ $[\text{M} + \text{H}]^+$ 489.0523, found 489.0513.

4-Bromo-2-(8-methoxy-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3nf)



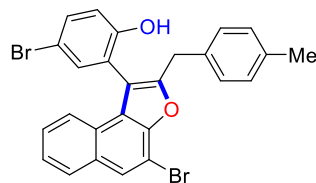
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1, R_f = 0.5) to afford an orange solid in 65% yield (123 mg); m.p. = 81–82 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.53–7.48 (m, 3H), 7.15–7.10 (m, 4H), 7.05 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 6.92 (s, 1H), 5.05 (s, 1H), 4.06 (dd, J = 15.5 Hz, J = 16.0 Hz, 2H), 3.55 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.1, 154.8, 153.6, 152.8, 136.5, 134.2, 134.0, 133.1, 130.2, 129.4, 128.8, 128.5, 125.6, 125.5, 121.6, 120.6, 117.3, 116.8, 112.5, 110.9, 101.4, 101.3, 54.8, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{21}\text{BrO}_3$ $[\text{M} + \text{H}]^+$ 475.0730, found 475.0730.

4-Bromo-2-(8-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3ng)

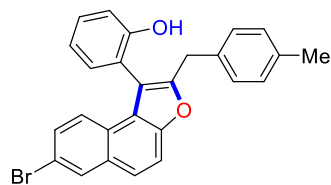


This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1.5:1, R_f = 0.5) to afford a white solid in 91% yield (189 mg); m.p. = 119–120 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, J = 8.5 Hz, 1H), 7.71 (s, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.45 (s, 1H), 7.11 (s, 4H), 7.04 (d, J = 8.5 Hz, 1H), 4.98 (s, 1H), 4.03 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.7, 153.4, 152.6, 136.5, 133.9, 133.8, 133.4, 130.3, 129.4, 129.1, 128.8, 128.5, 128.0, 125.5, 124.9, 120.9, 120.8, 120.7, 117.6, 112.8, 112.7, 111.2, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 522.9727, found 522.9727.

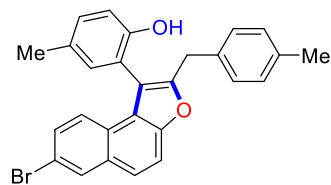
4-Bromo-2-(4-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3nh)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a white solid in 90% yield (187 mg); m.p. = 148–149 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.44–7.40 (m, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.14–7.10 (m, 4H), 7.01 (d, J = 8.5 Hz, 1H), 4.90 (s, 1H), 4.06 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.3, 153.4, 149.0, 136.5, 133.9, 133.6, 133.4, 131.7, 129.4, 128.5, 127.9, 127.7, 126.8, 125.4, 122.8, 122.5, 121.0, 117.6, 112.8, 112.0, 104.8, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 522.9727, found 522.9720.

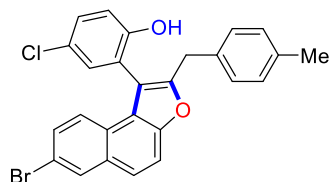
2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3bb):

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1, R_f = 0.5) to afford a yellow solid in 93% yield (165 mg); m.p. = 69–70 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 2H), 7.49–7.44 (m, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.14–7.08 (m, 6H), 4.94 (s, 1H), 4.02 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 154.2, 152.3, 136.4, 134.2, 132.0, 131.6, 130.6, 130.5, 129.6, 129.4, 128.5, 126.4, 124.4, 124.3, 122.0, 121.1, 119.0, 118.2, 115.8, 113.4, 112.3, 32.5, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{19}\text{BrO}_2$ $[\text{M} + \text{H}]^+$ 445.0624, found 445.0622.

2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenol (Scheme 3, compound 3fb)

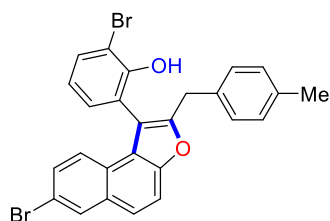
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1, R_f = 0.5) to afford a light yellow solid in 95% yield (174 mg); m.p. = 67–68 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.04 (s, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 9.0 Hz, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 9.0 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.15–7.10 (m, 5H), 7.03 (d, J = 8.0 Hz, 1H), 4.77 (s, 1H), 4.03 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.5, 152.2, 151.9, 136.3, 134.3, 131.9, 131.8, 131.0, 130.6, 130.2, 129.5, 129.3, 128.6, 126.4, 124.4, 124.3, 122.1, 118.7, 118.2, 115.5, 113.4, 112.5, 32.5, 21.0, 20.6; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{21}\text{BrO}_2$ $[\text{M} + \text{H}]^+$ 459.0778, found 459.0773.

2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)-4-chlorophenol (Scheme 3, compound 3jb)



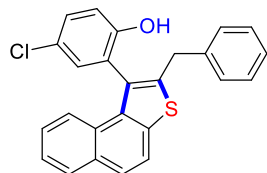
This compound was purified by column chromatography (*n*-hexane/dichloromethane = 1:1, R_f = 0.5) to afford a yellow solid in 91% yield (174 mg); m.p. = 68–69 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.63 (d, J = 9.0 Hz, 2H), 7.46–7.40 (m, 3H), 7.30 (s, 1H), 7.11 (s, 4H), 7.07 (d, J = 9.0 Hz, 1H), 4.92 (s, 1H), 4.02 (dd, J = 15.5 Hz, J = 15.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.9, 152.9, 152.2, 136.5, 133.8, 132.0, 131.0, 130.8, 130.4, 129.8, 129.4, 128.5, 126.1, 125.7, 124.7, 124.1, 121.6, 120.6, 118.4, 117.1, 113.4, 111.2, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{BrClO}_2$ [$\text{M} + \text{H}$] $^+$ 479.0231, found 479.0227.

2-Bromo-6-(7-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (Scheme 3, compound 3qb)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.5) to afford a yellow solid in 88% yield (183 mg); m.p. = 165–166 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (s, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 9.0 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.41 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.12–7.08 (m, 4H), 6.97 (t, J = 8.0 Hz, 1H), 5.58 (s, 1H), 4.05 (dd, J = 16.0 Hz, J = 16.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 152.0, 151.0, 136.3, 134.2, 132.9, 132.0, 131.6, 130.7, 129.3, 128.5, 126.4, 124.4, 124.1, 122.2, 121.9, 121.1, 118.0, 113.6, 113.4, 110.6, 32.6, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$ 522.9727, found 522.9733.

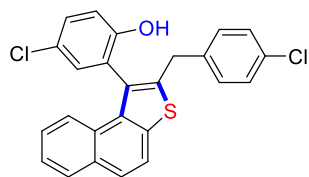
2-(2-Benzyl-6-(4-chlorophenyl)-5-hydroxy-1H-benzothiophen-1-yl)naphthalen-1-yl bromide (Scheme 3, compound 3ii)



This compound was purified by column chromatography (*n*-hexane/dichloromethane = 20:1, R_f = 0.6) to afford a yellow oil in 60% yield (96 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, J = 9.0 Hz, 1H), 7.73 (d, J =

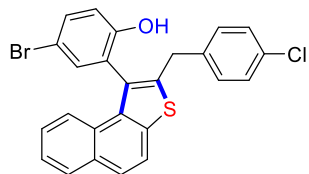
8.5 Hz, 1H), 7.62 (d, J = 7.0 Hz, 1H), 7.52 (s, 1H), 7.47-7.44 (m, 3H), 7.42 (d, J = 8.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.29-7.24 (m, 4H), 4.34 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.4, 152.9, 136.5, 133.7, 133.4, 131.8, 130.9, 129.1, 128.9, 128.7, 128.6, 127.7, 127.0, 126.9, 126.6, 125.6, 125.0, 124.9, 124.6, 119.6, 112.5, 105.3, 33.0; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{17}\text{ClOS}$ [$\text{M} + \text{H}$] $^+$ 401.0761, found 401.0757.

4-Chloro-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]thiophen-1-yl)phenol (Scheme 3, compound 3li):

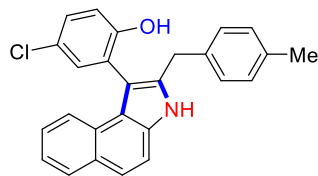


This compound was purified by column chromatography (n -hexane/dichloromethane = 15:1, R_f = 0.6) to afford a yellow solid in 84% yield (145 mg); m.p. = 97–98 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.44-7.41 (m, 3H), 7.40 (d, J = 8.5 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 7.21-7.19 (m, 4H), 4.26 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.7, 152.9, 134.9, 133.6, 133.2, 132.8, 131.6, 130.8, 130.2, 129.3, 128.8, 127.7, 127.0, 126.7, 125.7, 125.0, 124.9, 124.6, 119.7, 112.5, 105.6, 32.4; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{16}\text{Cl}_2\text{OS}$ [$\text{M} + \text{H}$] $^+$ 435.0371, found 435.0378.

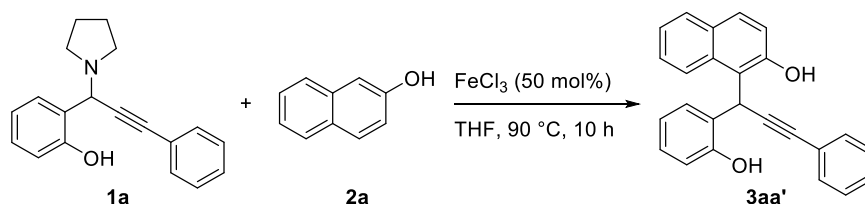
4-Bromo-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]thiophen-1-yl)phenol (Scheme 3, compound 3pi)



This compound was purified by column chromatography (n -hexane/dichloromethane = 15:1, R_f = 0.6) to afford a yellow solid in 89% yield (170 mg); m.p. = 108–109 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.46 (s, 1H), 7.45 (s, 1H), 7.43 (t, J = 6.0 Hz, 2H), 7.39 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 7.22-7.19 (m, 5H), 4.26 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.5, 153.3, 134.8, 133.6, 133.2, 132.8, 131.6, 131.4, 130.2, 128.8, 127.8, 127.7, 127.0, 126.7, 125.7, 124.8, 124.6, 122.7, 116.8, 112.9, 105.4, 32.4; HRMS (APCI) m/z : calcd for $\text{C}_{25}\text{H}_{16}\text{BrClOS}$ [$\text{M} + \text{H}$] $^+$ 480.9846, found 480.9851.

4-Chloro-2-(2-(4-methylbenzyl)-3H-benzo[e]indol-1-yl)phenol (Scheme 3, compound 3jj)

This compound was purified by column chromatography (*n*-hexane/dichloromethane = 2:1, R_f = 0.4) to afford a yellow solid in 34% yield (54 mg); m.p. = 133–134 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.34 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.38–7.31 (m, 4H), 7.15 (d, J = 7.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.24 (s, 1H), 3.98 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.4, 136.6, 135.4, 134.9, 132.2, 131.4, 129.7, 129.5, 128.6, 128.0, 126.1, 125.1, 123.9, 123.7, 123.6, 122.3, 120.5, 116.4, 112.3, 107.9, 32.0, 21.0; HRMS (APCI) m/z : calcd for $\text{C}_{26}\text{H}_{20}\text{ClNO}$ $[\text{M} + \text{H}]^+$ 398.1306, found 398.1304.

5. General procedure for the synthesis of intermediate 3aa'

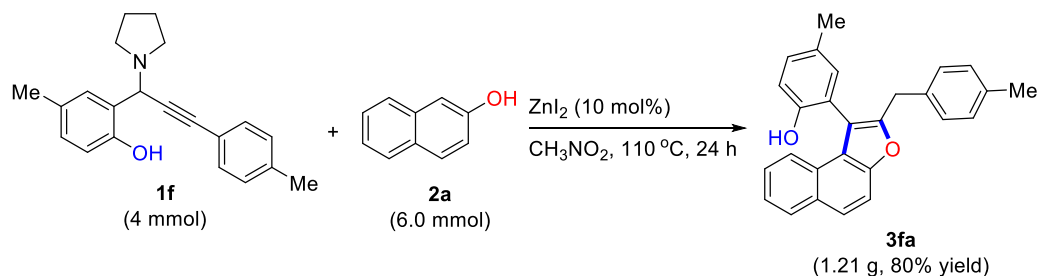
A mixture of propargylamines **1a** (1 mmol), β -naphthol (**2a**) (1.5 mmol), and FeCl_3 (0.5 mmol) were added to a resealable screw-capped Schlenk tube. Then tetrahydrofuran (5 mL) was added. The tube sealed with a Teflon-coated cap and the resulting mixture was stirred in an oil bath preheated to 90 °C for 10 h (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified using flash column chromatography with a silica gel (230–400 mesh), using *n*-hexane and ethyl acetate (3:1, v/v) as the elution solvent to afford the desired product **3aa'**.

1-(1-(2-Hydroxyphenyl)-3-phenylprop-2-yn-1-yl)naphthalen-2-ol (Scheme 4b-f, compound 3aa')

This compound was purified by column chromatography (*n*-hexane/ethyl acetate = 3:1, R_f = 0.4) to afford a white solid in 85% yield (119 mg); mp = 103–104 °C, ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.72 (s, 2H), 8.33 (d, J = 7.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 6.0 Hz, 1H), 7.36–7.31 (m, 5H), 7.25–7.21 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.74 (t, J = 7.5 Hz, 2H), 6.37 (s, 1H); ^{13}C NMR (125 MHz,

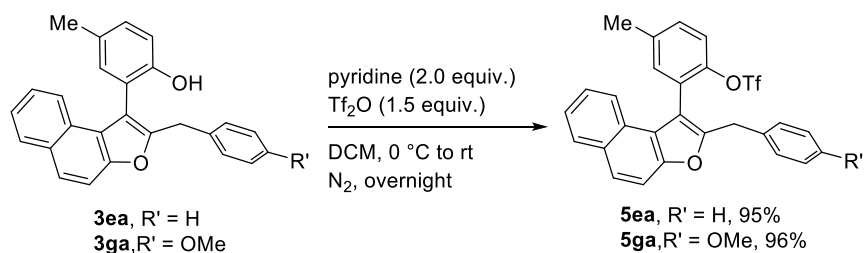
DMSO-*d*₆) δ 155.5, 152.8, 133.2, 131.6, 129.5, 129.1, 129.0, 128.9, 128.3, 128.1, 126.6, 125.8, 124.9, 123.8, 122.6, 118.8, 118.7, 117.6, 115.6, 92.2, 82.1, 28.9; HRMS (APCI) *m/z*: calcd for C₂₅H₁₈O₂ [M + H]⁺ 351.1379, found 351.1377.

6. Gram-scale synthesis of compound 3fa



A mixture of 4-methyl-2-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (**1f**) (1.22 g, 4 mmol), β -naphthol (**2a**) (0.86 g, 6.0 mmol), and ZnI₂ (127 mg, 0.4 mmol) were added to a resealable screw-capped Schlenk tube. Then nitromethane (20 mL) was added. The tube sealed with a Teflon-coated cap and the resulting mixture was stirred in an oil bath preheated to 110 °C for 24 h (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified using flash column chromatography with a silica gel (230-400 mesh), using *n*-hexane and dichloromethane (2:1, v/v) as the elution solvent to afford the desired product **3fa** in 80% yield (1.21 g).

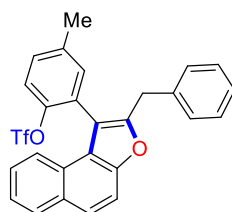
7. General procedure for the synthesis of compounds 5ea and 5ga



Compound **3** (**3ea** or **3ga**) (1.0 mmol), pyridine (2.0 equiv.) and dichloromethane (5.0 mL) were mixed in a reaction flask under a nitrogen atmosphere. Then the solution was cooled to 0 °C and a solution of trifluoromethanesulfonic anhydride (1.5 equiv.) in dichloromethane (2.0 mL) was added in a dropwise manner within 30 minutes. The reaction mixture was stirred overnight. After the completion of

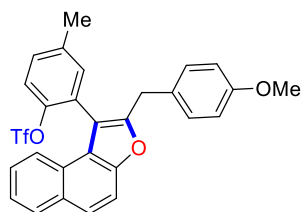
reaction, 25 mL of water was added to the mixture and stirred for 3 h. The mixture was extracted with ethyl acetate (~20 mL) and the organic layer was washed with water (~20 mL), 10% aqueous HCl (~10 mL) three times, water (~20 mL, twice), saturated aqueous NaHCO₃ (twice) and brine (10 mL, twice), and dried over Na₂SO₄. The organic layer was evaporated under vacuum, and the crude product was purified by flash column chromatography on silica gel (230-400 mesh), using *n*-hexane and EtOAc (5:1, v/v) as the elution solvent to afford the desired product **5ea** and **5ga** in 95% and 96% yield respectively.

2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenyl trifluoromethanesulfonate (Scheme 5, compound 5ea)



This compound was purified by column chromatography (*n*-hexane/ethyl acetate = 5:1, *R_f* = 0.4) to afford a light green solid in 95% yield (471 mg); m.p. = 86–88 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.47-7.43 (m, 3H), 7.41-7.27 (m, 7H), 4.22 (dd, *J* = 16.0 Hz, *J* = 16.0 Hz, 2H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.1, 152.0, 146.2, 138.8, 137.5, 133.9, 130.8, 128.9, 128.8, 128.6, 127.8 (d, *J_{C-F}* = 6.7 Hz), 126.6, 126.0, 125.4, 124.2, 122.6, 121.8, 116.7, 113.0, 112.3, 33.2, 21.0; HRMS (APCI) *m/z*: calcd for C₂₇H₂₀F₃O₄S [M + H]⁺ 497.1030, found 497.1029.

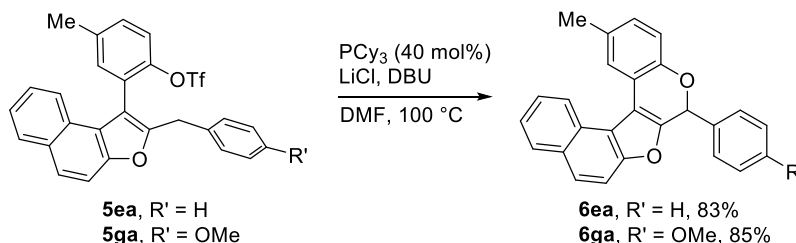
2-(2-(4-Methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenyl trifluoromethanesulfonate (Scheme 5, compound 5ga)



This compound was purified by column chromatography (*n*-hexane/ethyl acetate = 5:1, *R_f* = 0.4) to afford a light yellow solid in 96% yield (504 mg); m.p. = 113–115 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48-7.37 (m, 5H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.20 (dd, *J* = 16.0 Hz, *J* = 16.0 Hz, 2H), 3.83 (s, 3H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 154.5, 151.9, 146.2, 138.9, 133.9, 130.8, 129.8, 129.5, 128.9, 127.8, 126.0, 125.3, 124.2, 122.6,

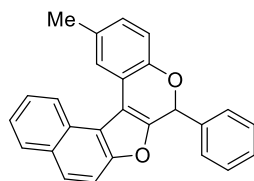
121.9, 121.8, 114.0, 112.8, 55.2, 32.3, 21.0; HRMS (APCI) m/z : calcd for $C_{28}H_{22}F_3O_5S$ $[M + H]^+$ 527.1133, found 527.1134.

8. General procedure for the synthesis of compounds 6ea and 6ga

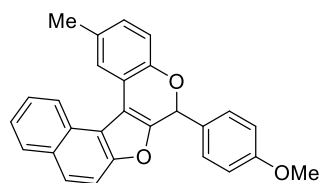


A mixture of compound **5** (**5ea** or **5ga**) (0.5 mmol), tricyclohexylphosphane (PCy_3) (40 mol%), and lithium chloride (5.0 equiv.) were added into a Schlenk tube in the presence of Teflon-coated magnetic stir bar. The tube was evacuated and re-filled with nitrogen for 3 cycles. Anhydrous DMF (dimethyl formamide) (2.0 mL) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (2.5 equiv.) were then added. The tube was placed into a preheated oil bath (100 °C) for 14 h. After the completion of reaction, the reaction was quenched by cooling to ambient temperature and EtOAc and water were added. The organic layer was separated and the aqueous layer was further extracted with EtOA (~10 mL $\times$ 3), and dried over Na_2SO_4 . The combined organic layer was evaporated under vacuum. The crude product was purified by flash column chromatography on silica gel (230-400 mesh), using *n*-hexane and EtOAc (10:1, v/v) as the elution solvent to afford the desired product **6ea** and **6ga** in 83% and 85% yield.

2-Methyl-6-phenyl-6*H*-naphtho[1',2':4,5]furo[2,3-*c*]chromene (**6ea**)



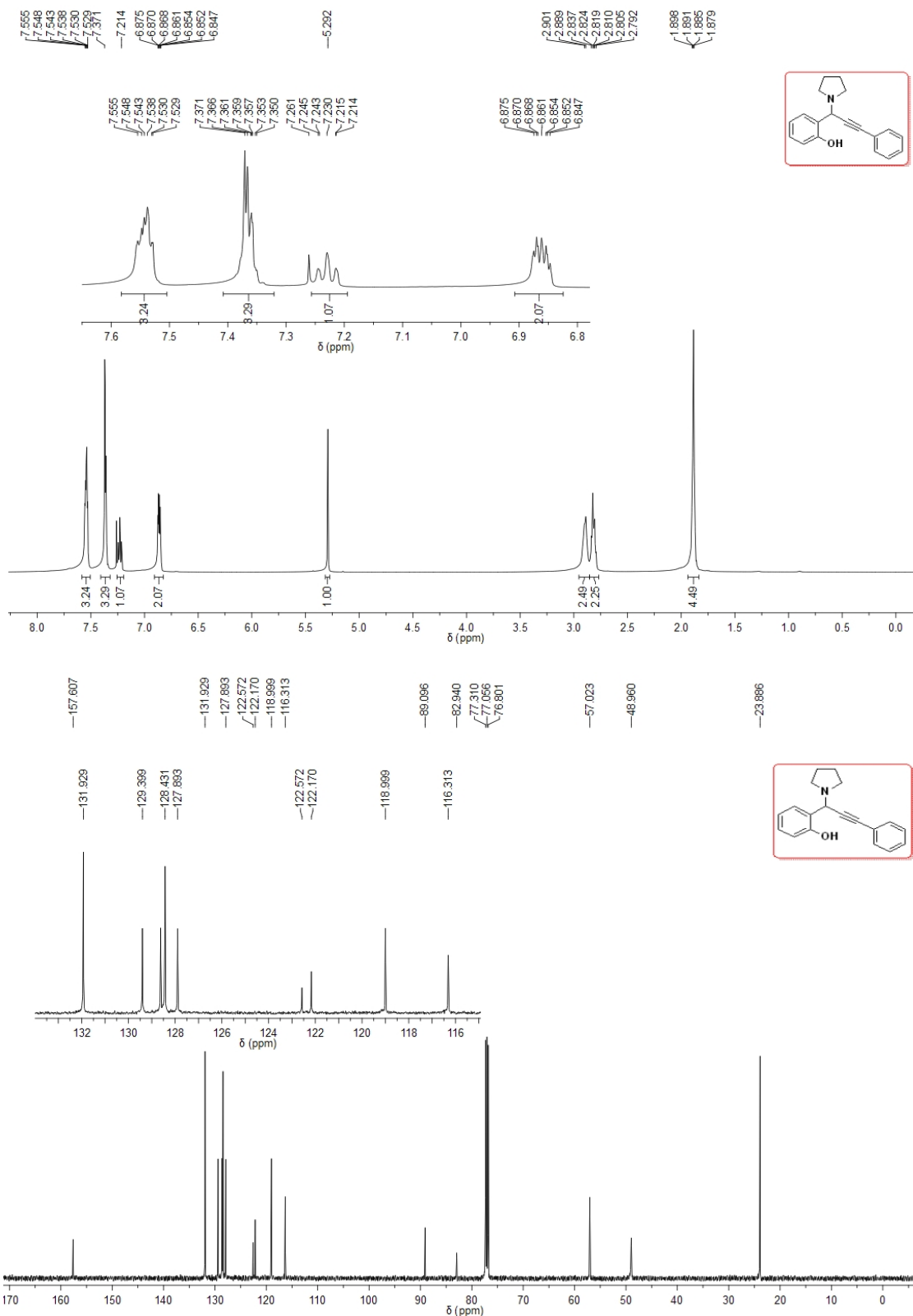
This compound was purified by column chromatography (*n*-hexane/ethyl acetate = 10:1, R_f = 0.4) to afford a light yellow solid in 83% yield (150 mg); m.p. = 146–148 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 6.4 Hz, 2H), 7.81 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 6.8 Hz, 2H), 7.45–7.41 (m, 3H), 7.08 (s, 2H), 6.45 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.7, 152.0, 149.7, 137.2, 131.8, 131.3, 129.2, 129.0, 128.7, 128.3, 128.1, 127.7, 126.1, 126.0, 125.8, 124.9, 124.6, 120.9, 119.3, 117.8, 113.3, 112.7, 75.8, 21.2; HRMS (APCI) m/z : calcd for $C_{26}H_{19}O_2$ $[M + H]^+$ 363.1375, found 363.1379.

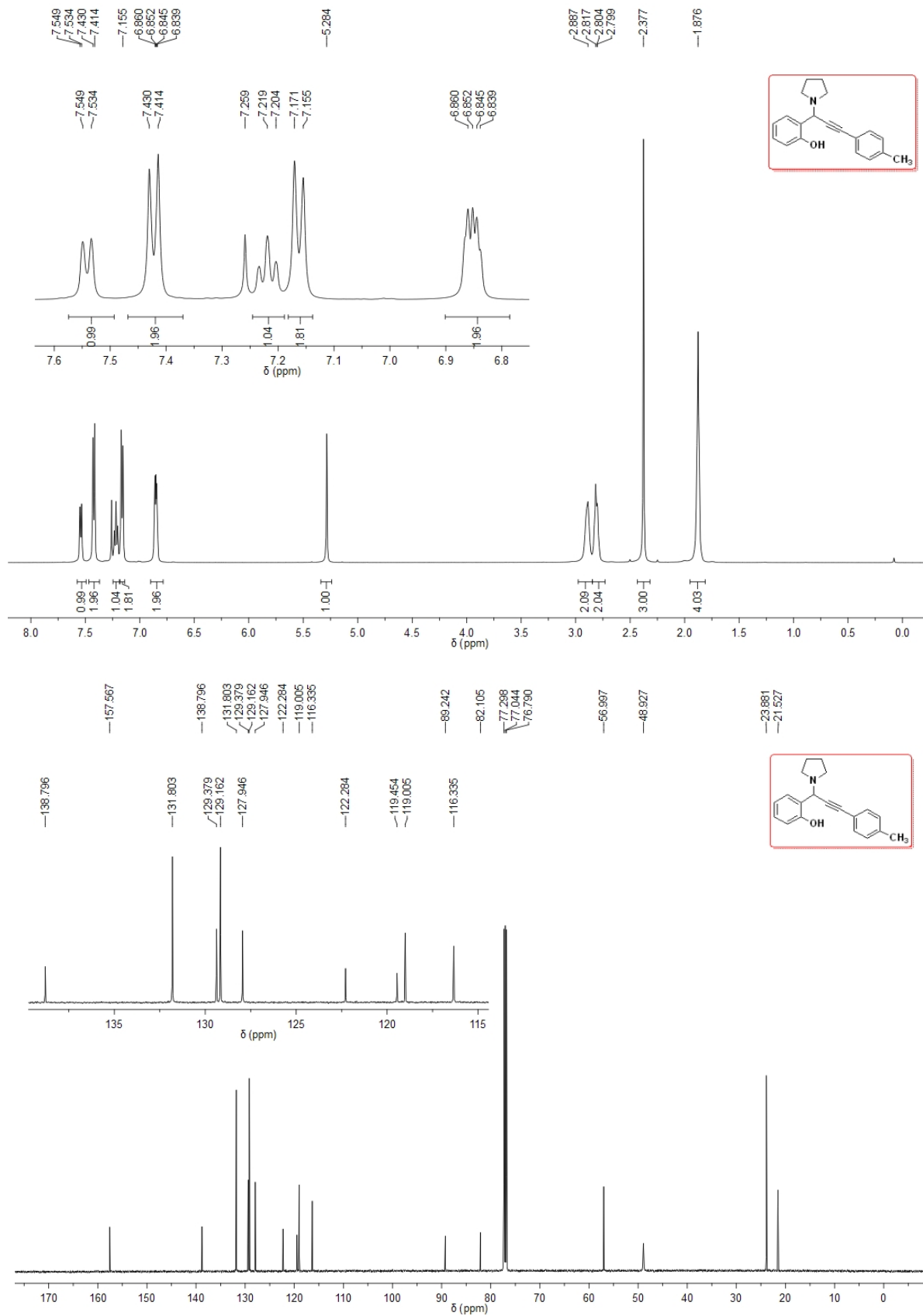
6-(4-Methoxyphenyl)-2-methyl-6H-naphtho[1',2':4,5]furo[2,3-c]chromene (6ga)

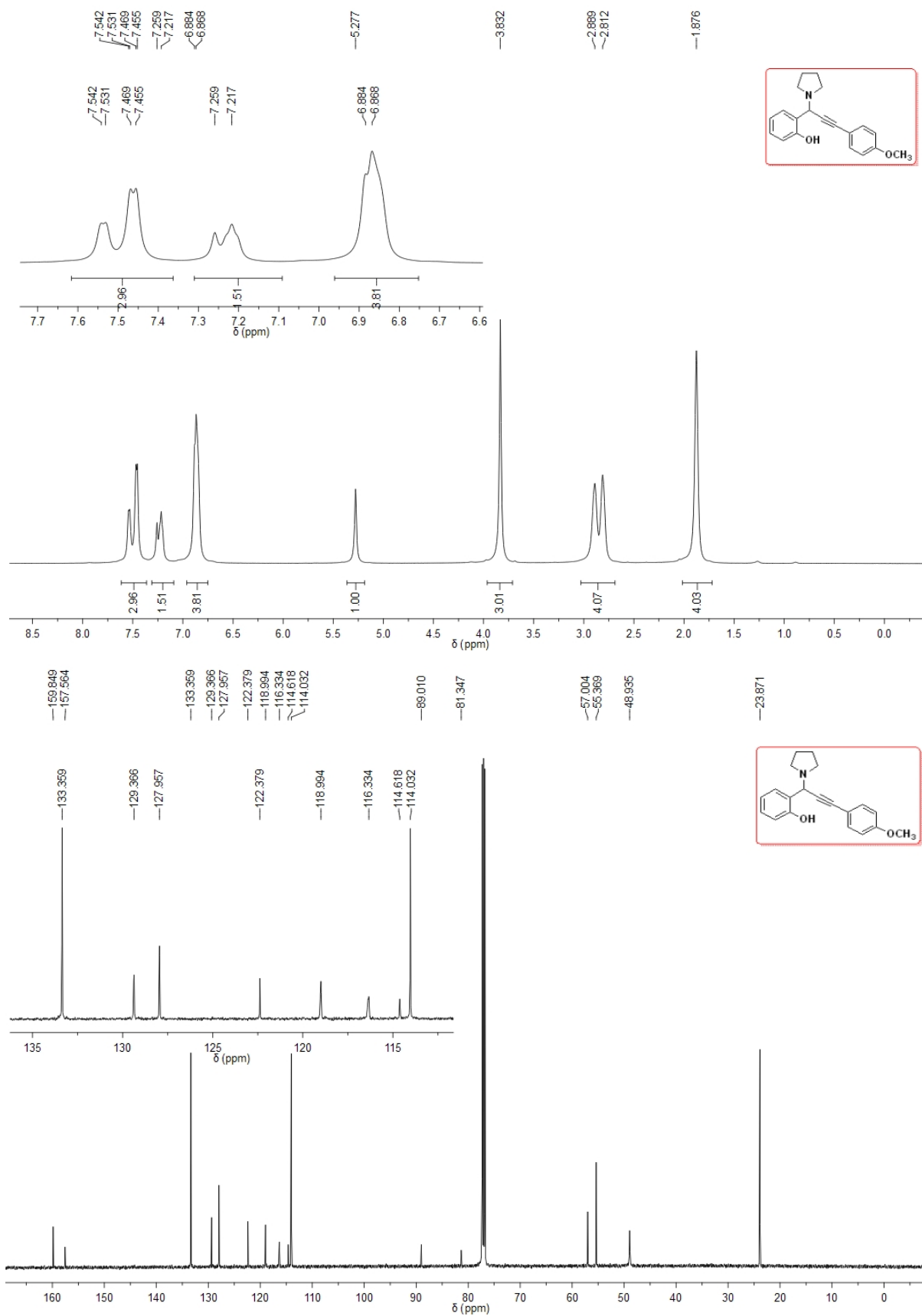
This compound was purified by column chromatography (*n*-hexane/ethyl acetate = 10:1, R_f = 0.4) to afford a light yellow solid in 85% yield (166 mg); m.p. = 160–161 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.80 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.97 (s, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.37 (d, J = 8.8 Hz, 2H), 7.00 (t, J = 8.4 Hz, 1H), 6.99 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 153.6, 152.2, 149.6, 131.7, 131.2, 129.3, 129.2, 129.1, 128.2, 128.0, 126.0, 125.7, 124.9, 124.6, 120.9, 119.3, 117.8, 114.1, 113.4, 112.7, 75.5, 55.2, 21.2; HRMS (APCI) m/z : calcd for $\text{C}_{27}\text{H}_{21}\text{O}_3$ $[\text{M} + \text{H}]^+$ 393.1481, found 393.1485.

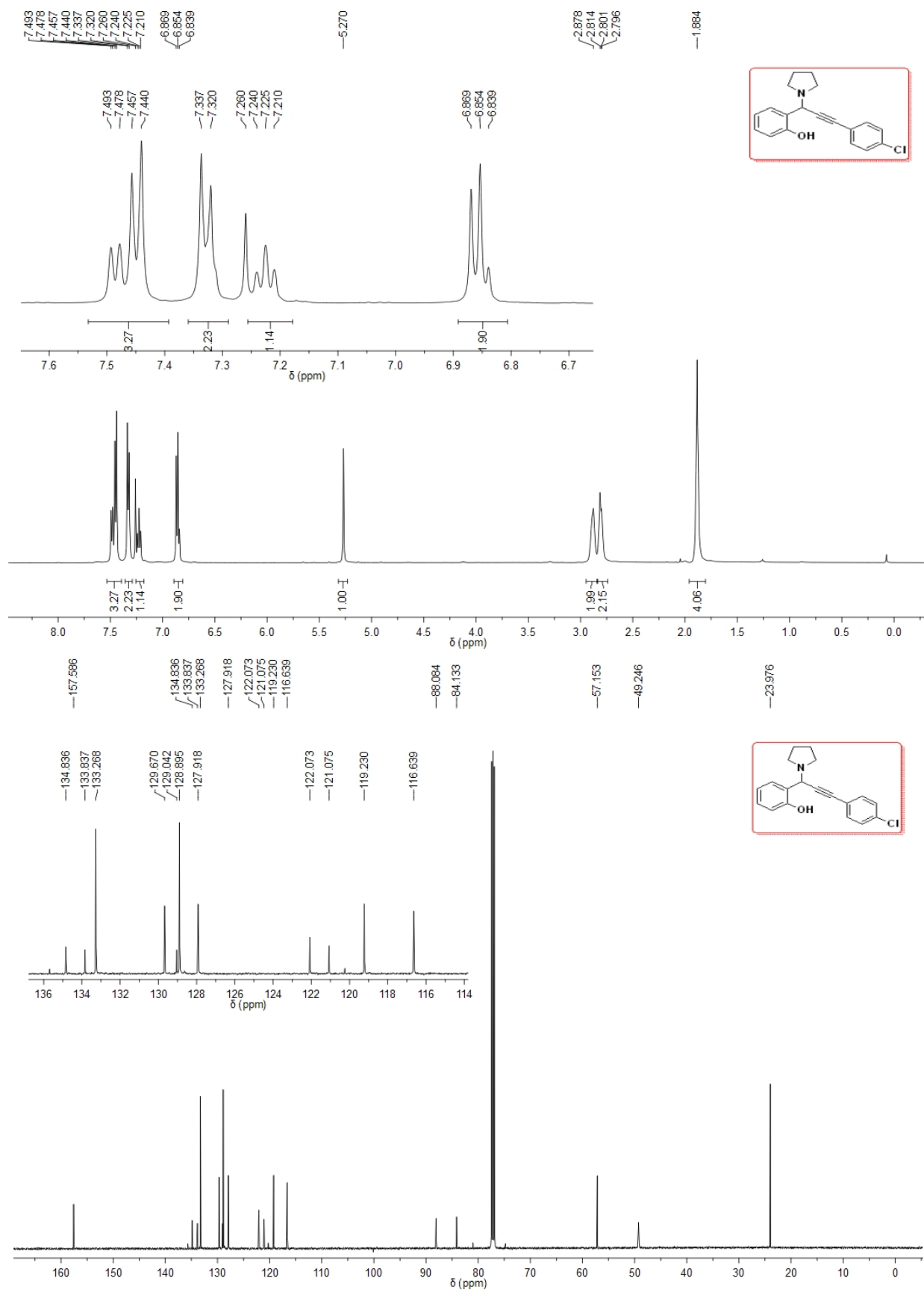
9. ^1H , and ^{13}C NMR spectra

2-(3-Phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1a)

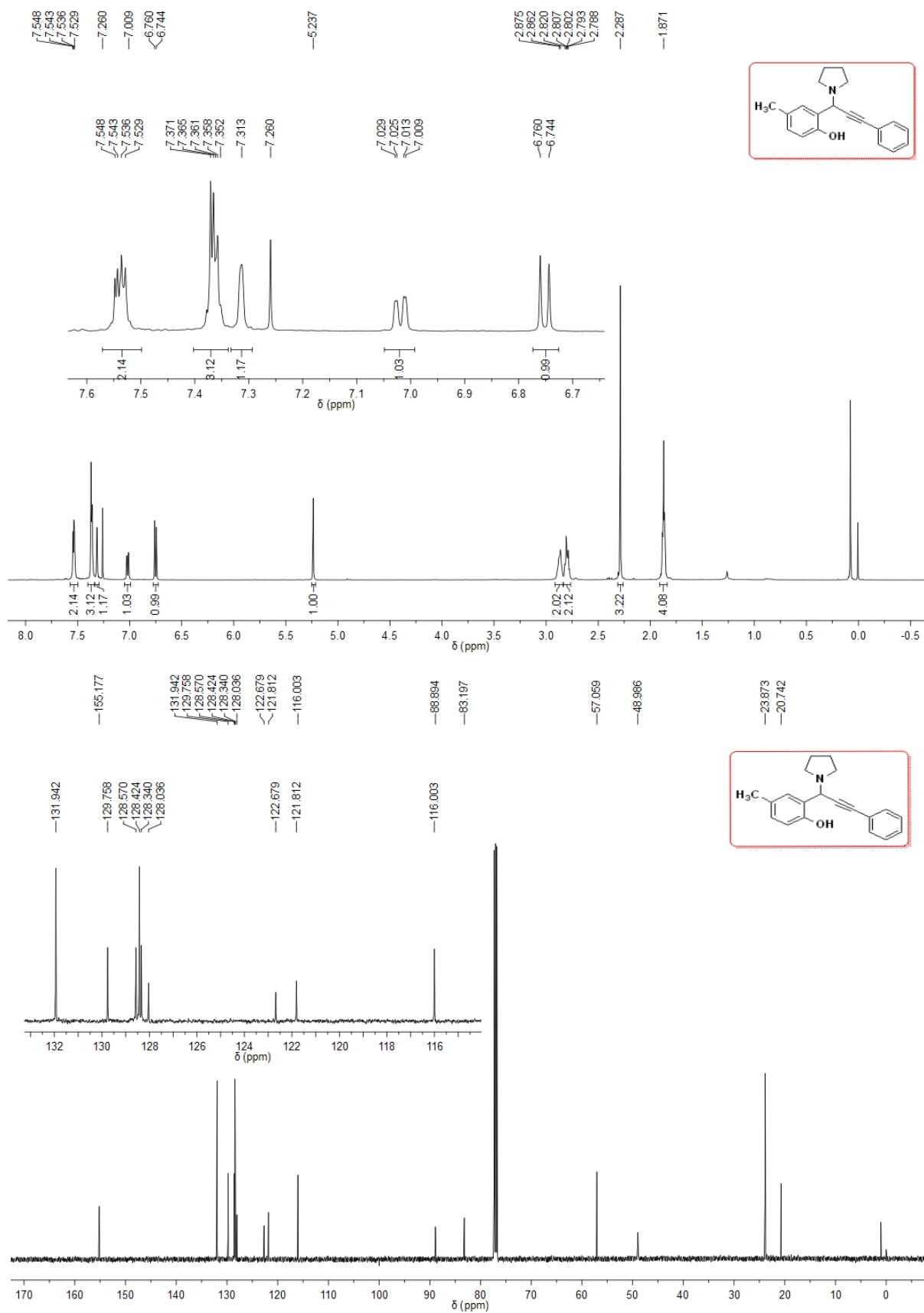


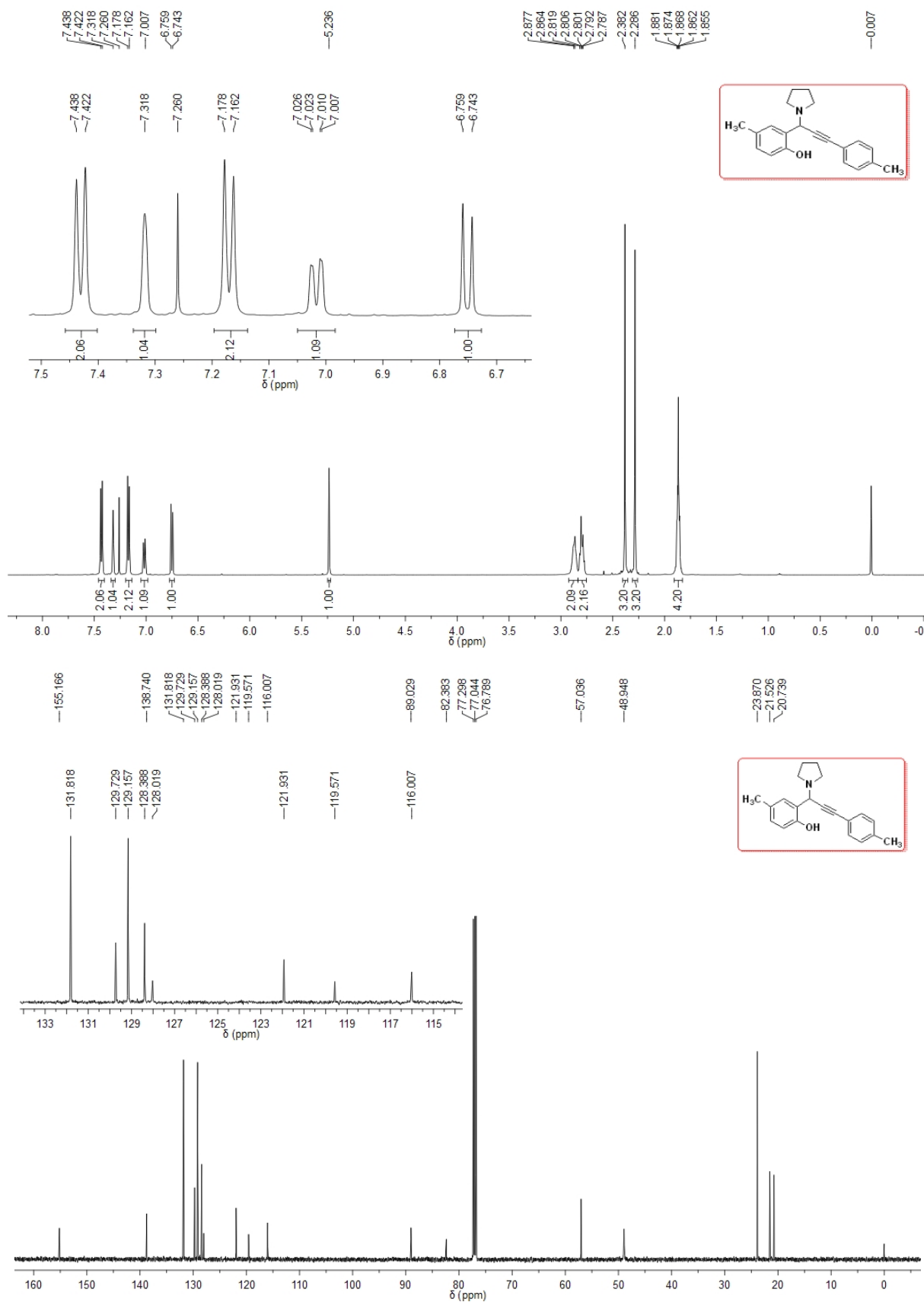
2-(1-(Pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1b)

2-(3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1c)

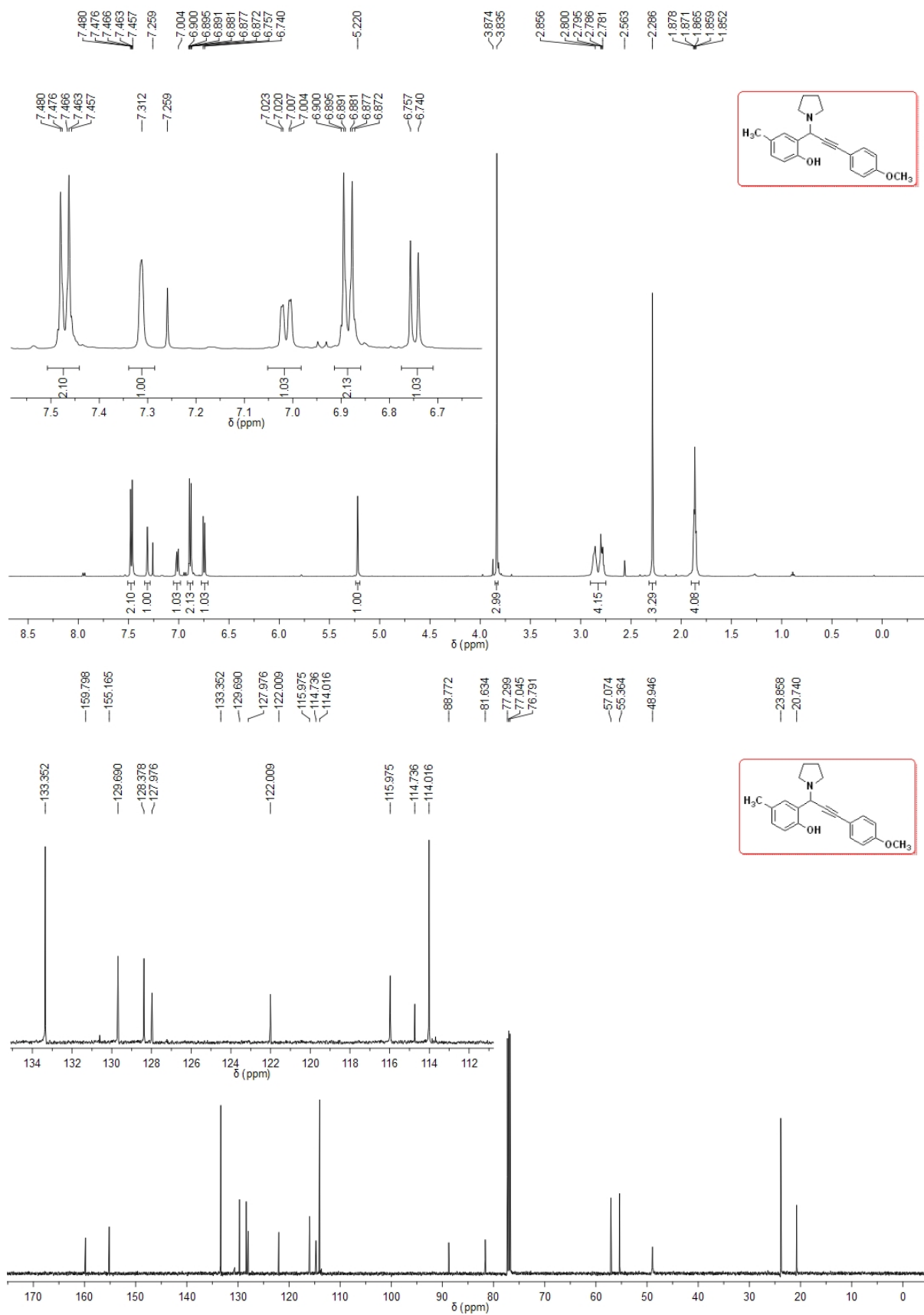
2-(3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1d)

4-Methyl-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1e)

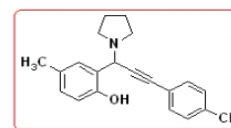
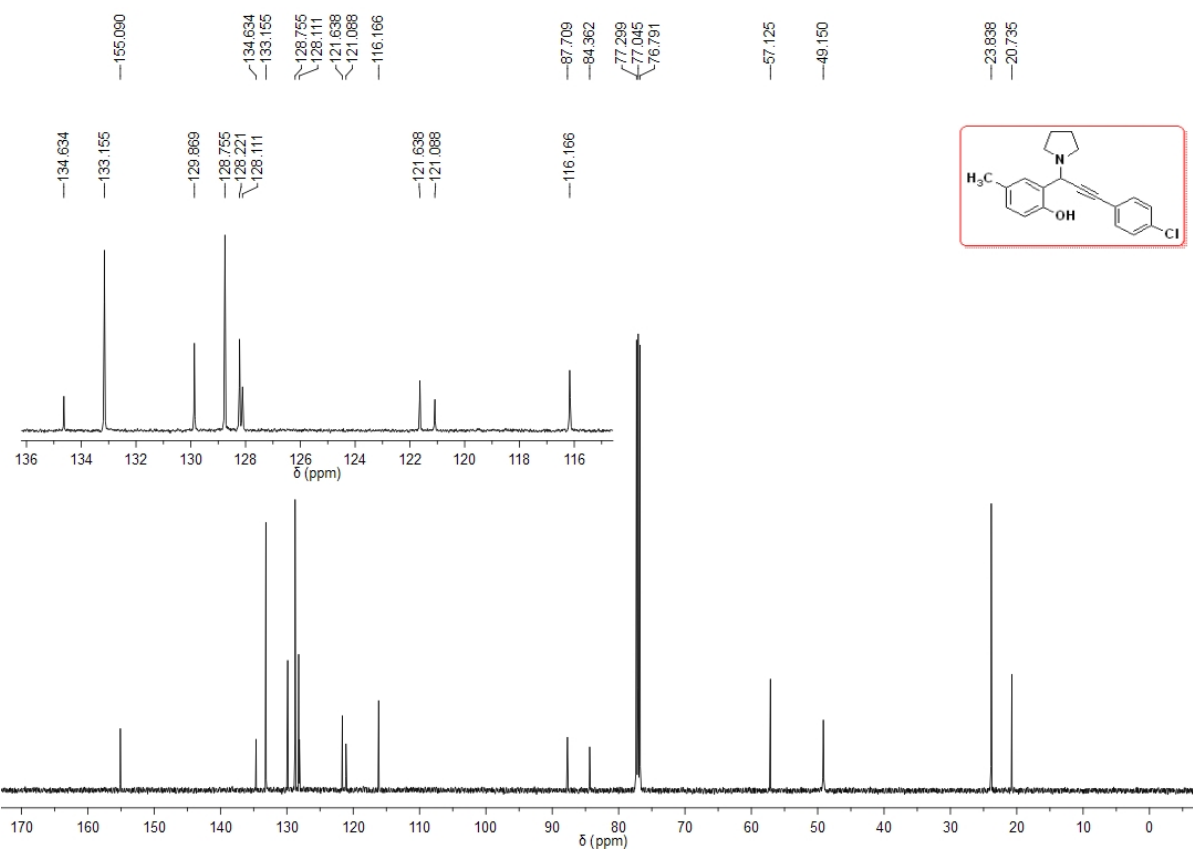
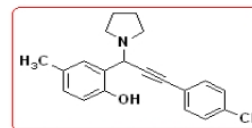
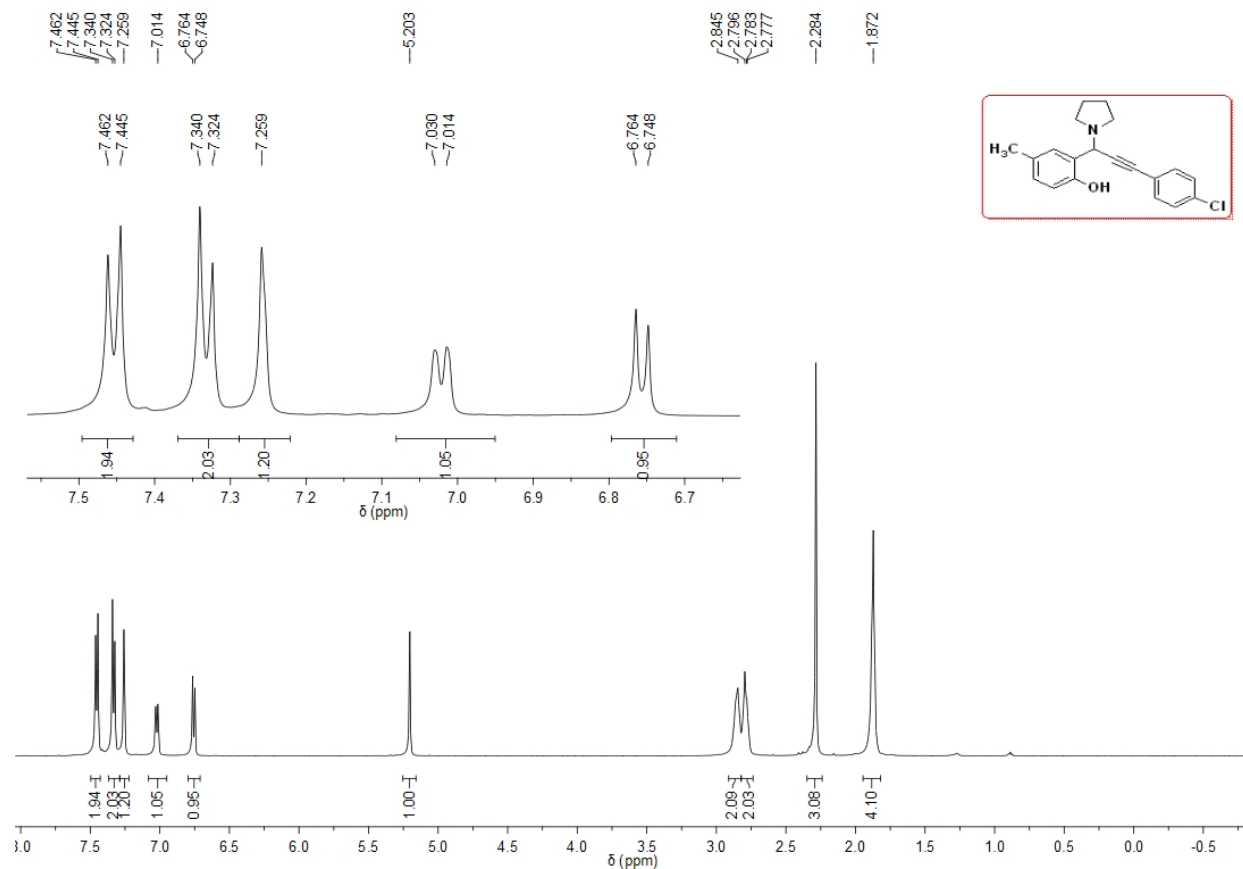


4-Methyl-2-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (**1f**)

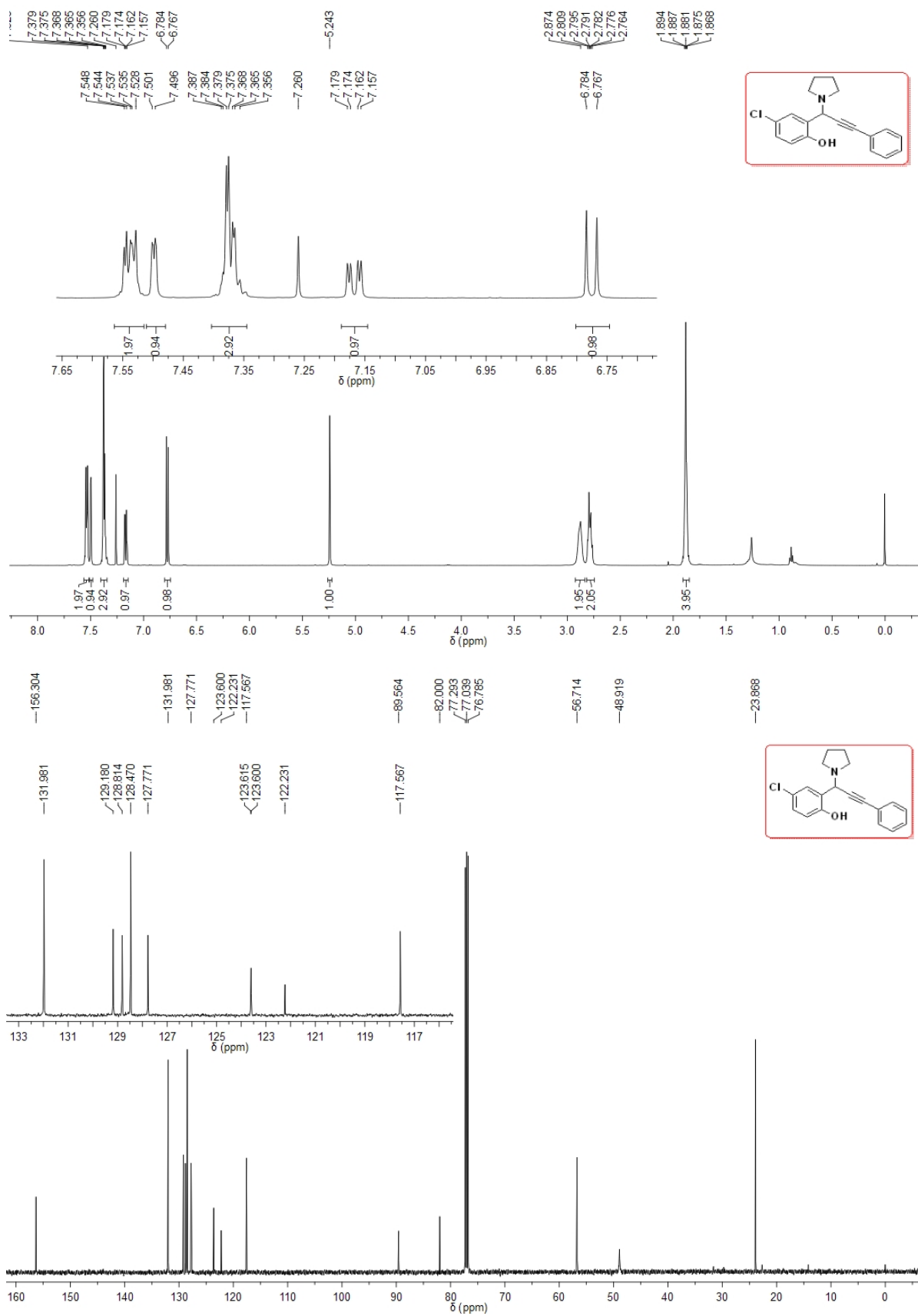
2-(3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)-4-methylphenol (1g)



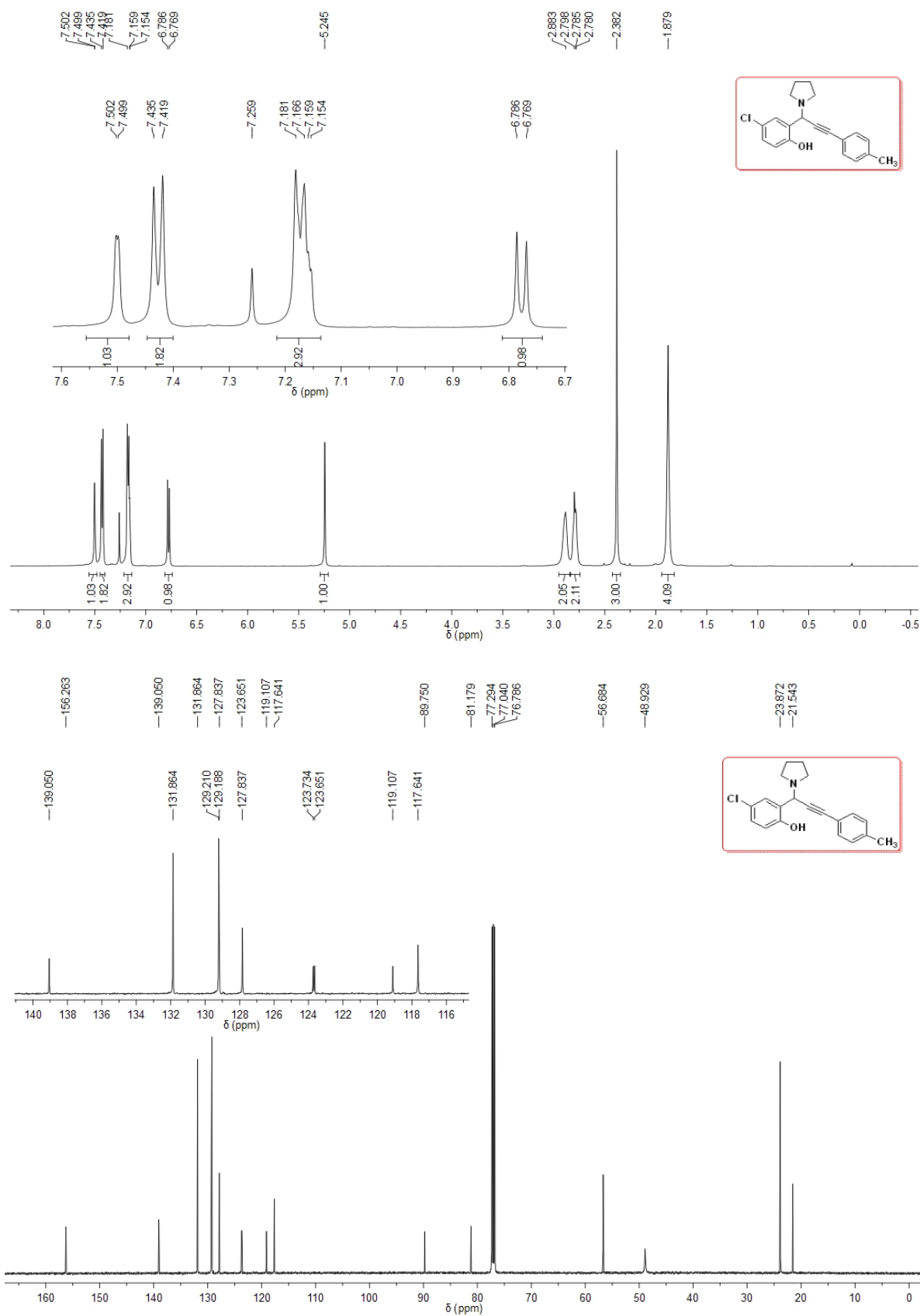
2-(3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)-4-methylphenol (1h)

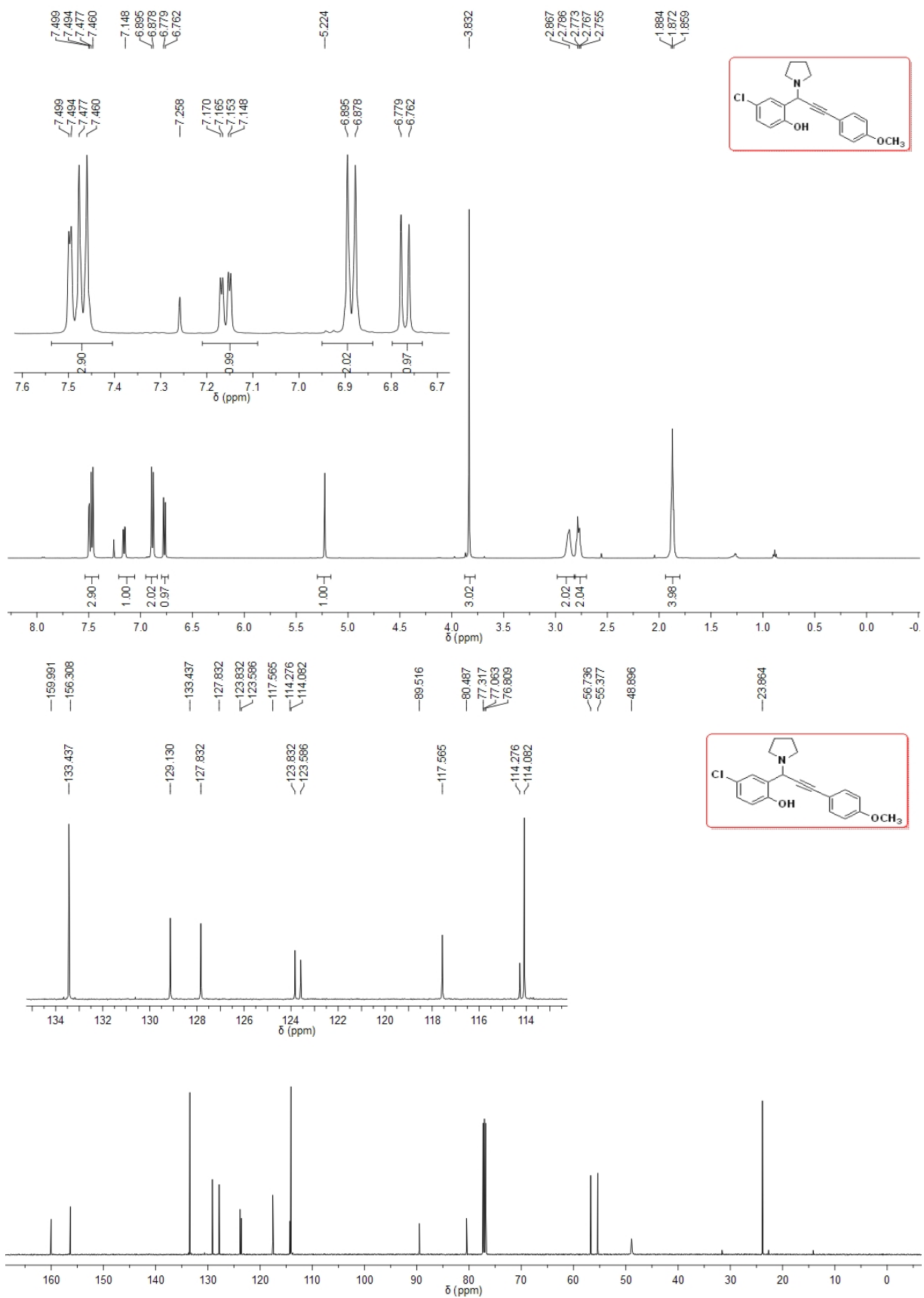


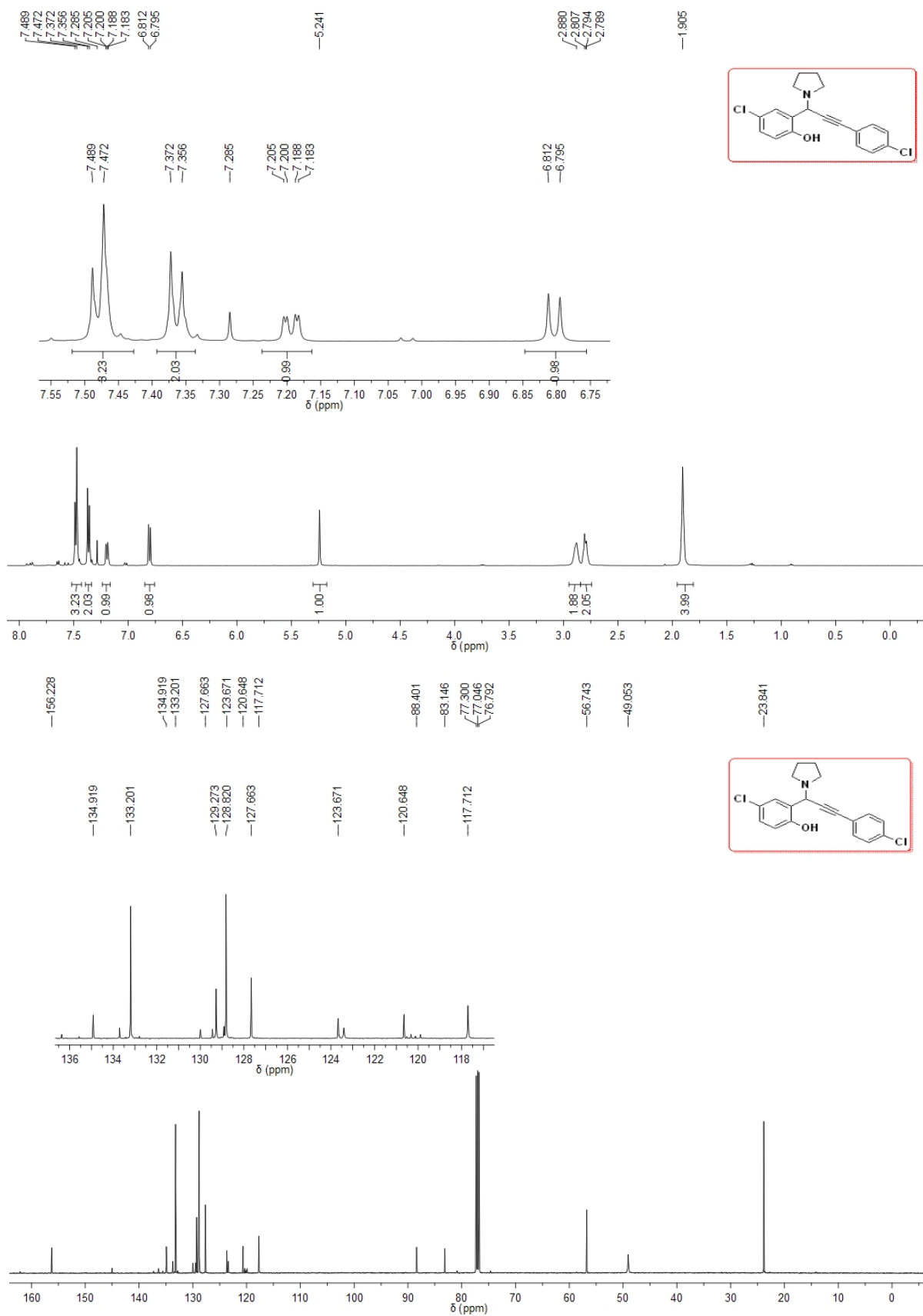
4-Chloro-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1i)



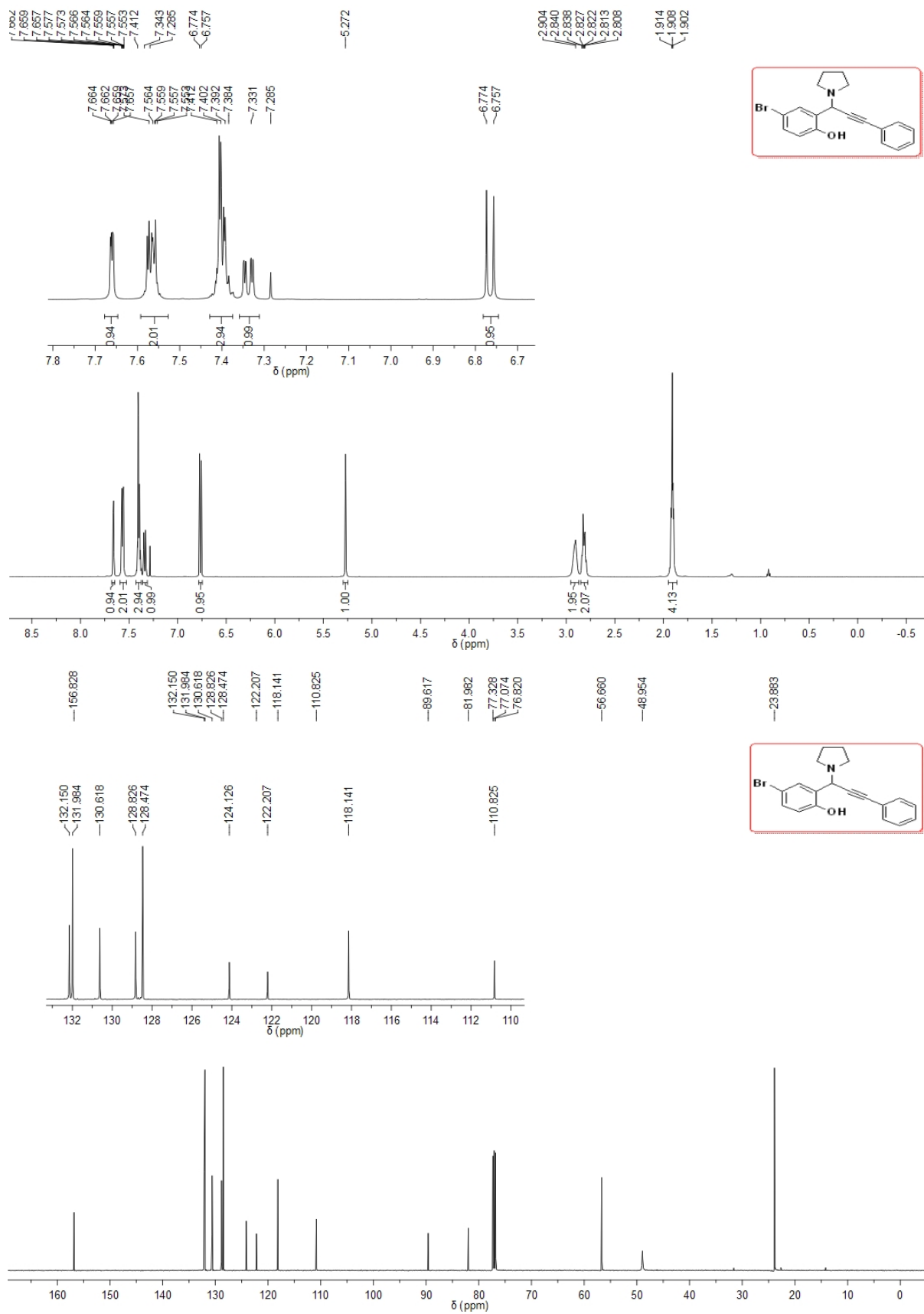
4-Chloro-2-(1-(pyrrolidin-1-yl)-3-(p-tolyl)prop-2-yn-1-yl)phenol (1j)



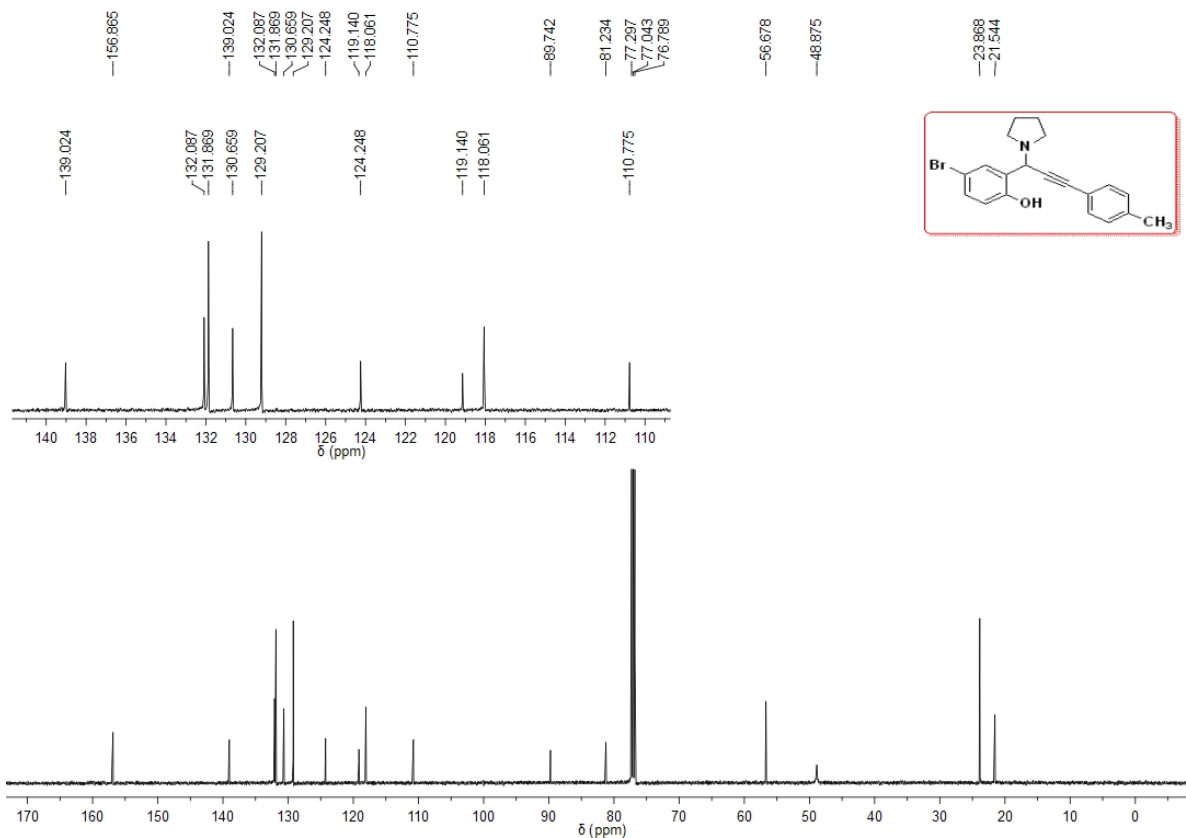
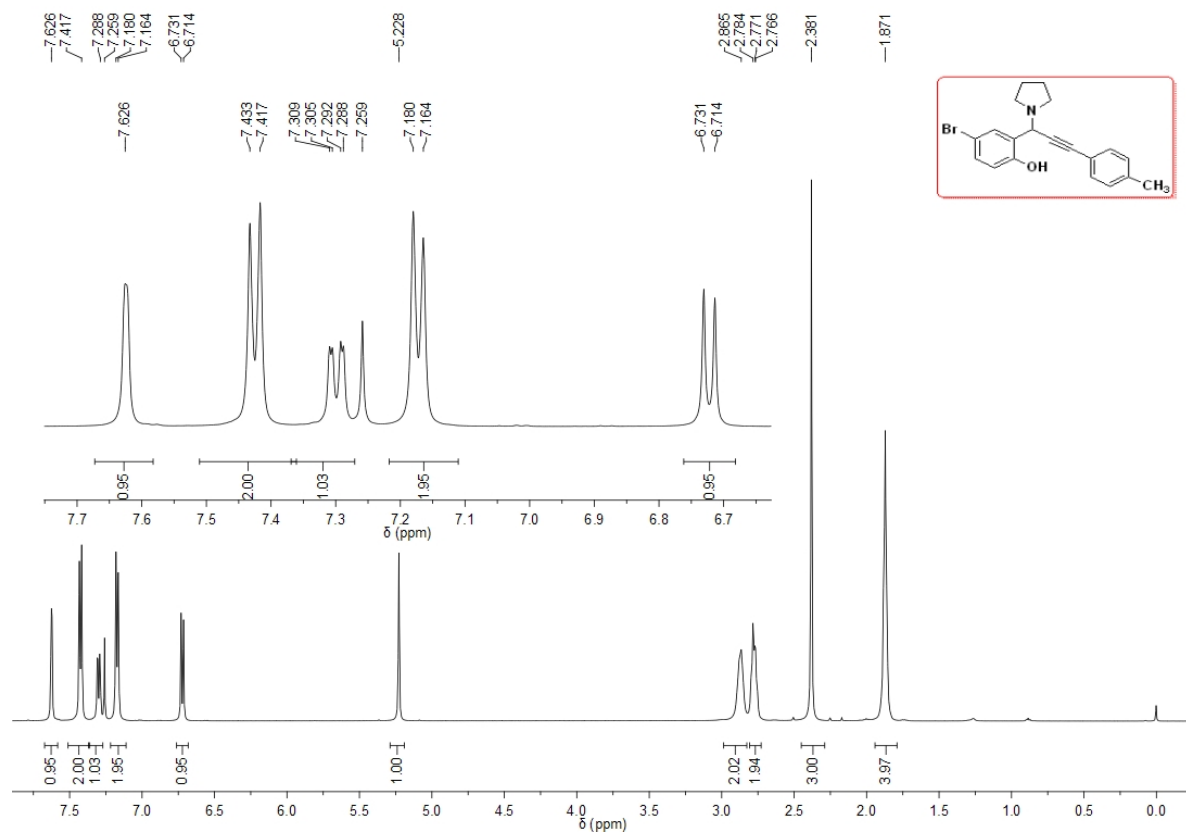
4-Chloro-2-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1k)

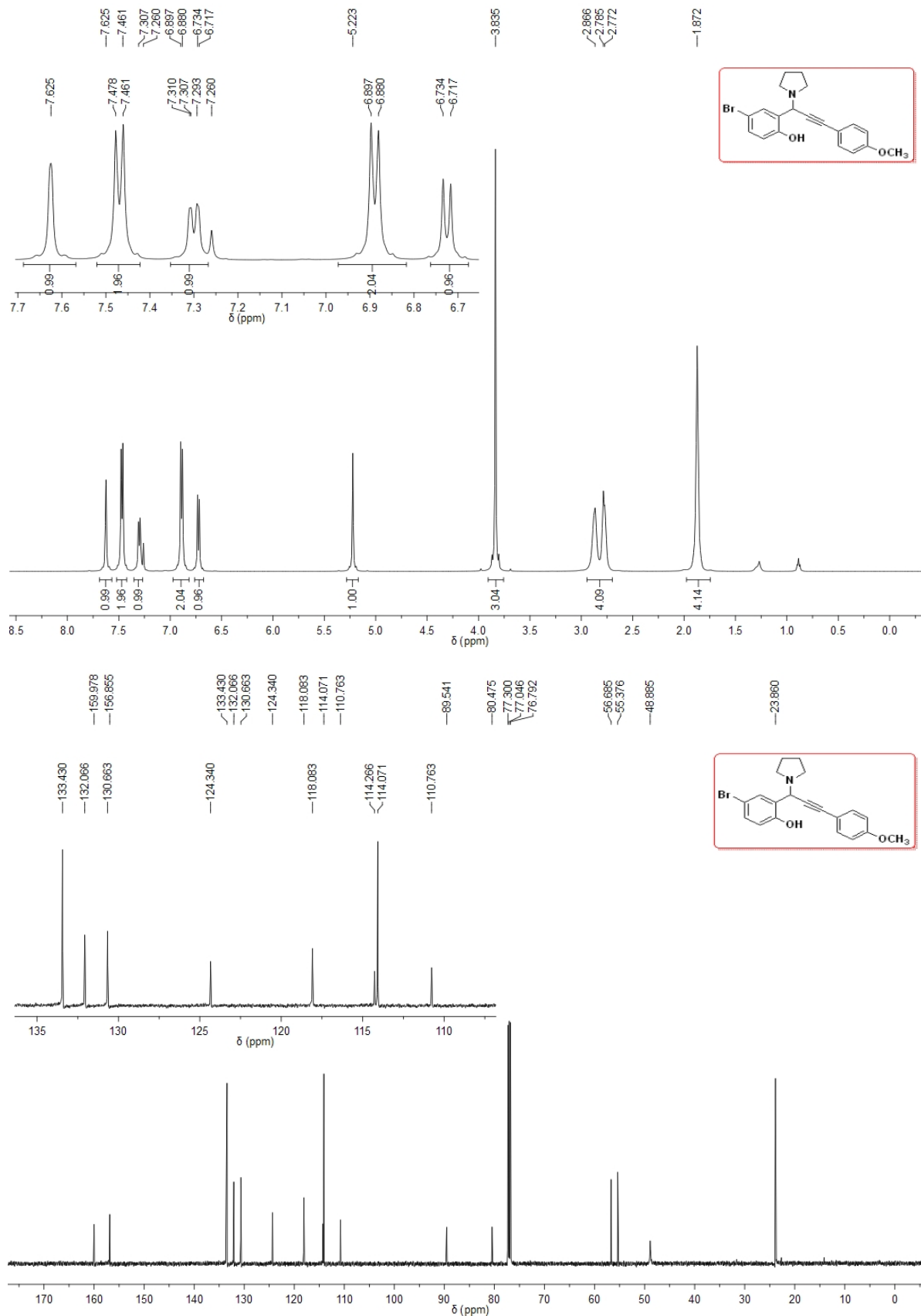
4-Chloro-2-(3-(4-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1I)

4-Bromo-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1m)

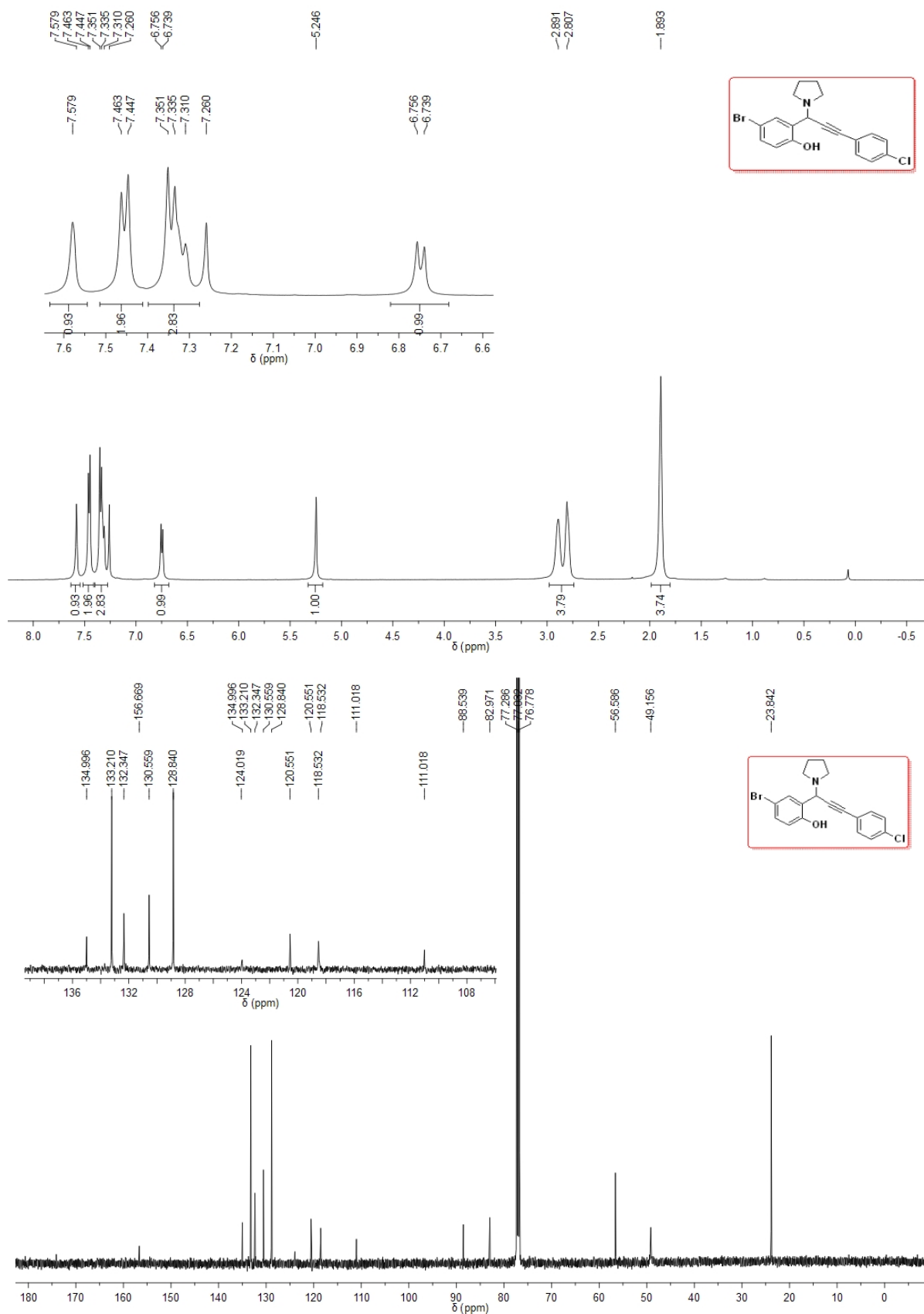


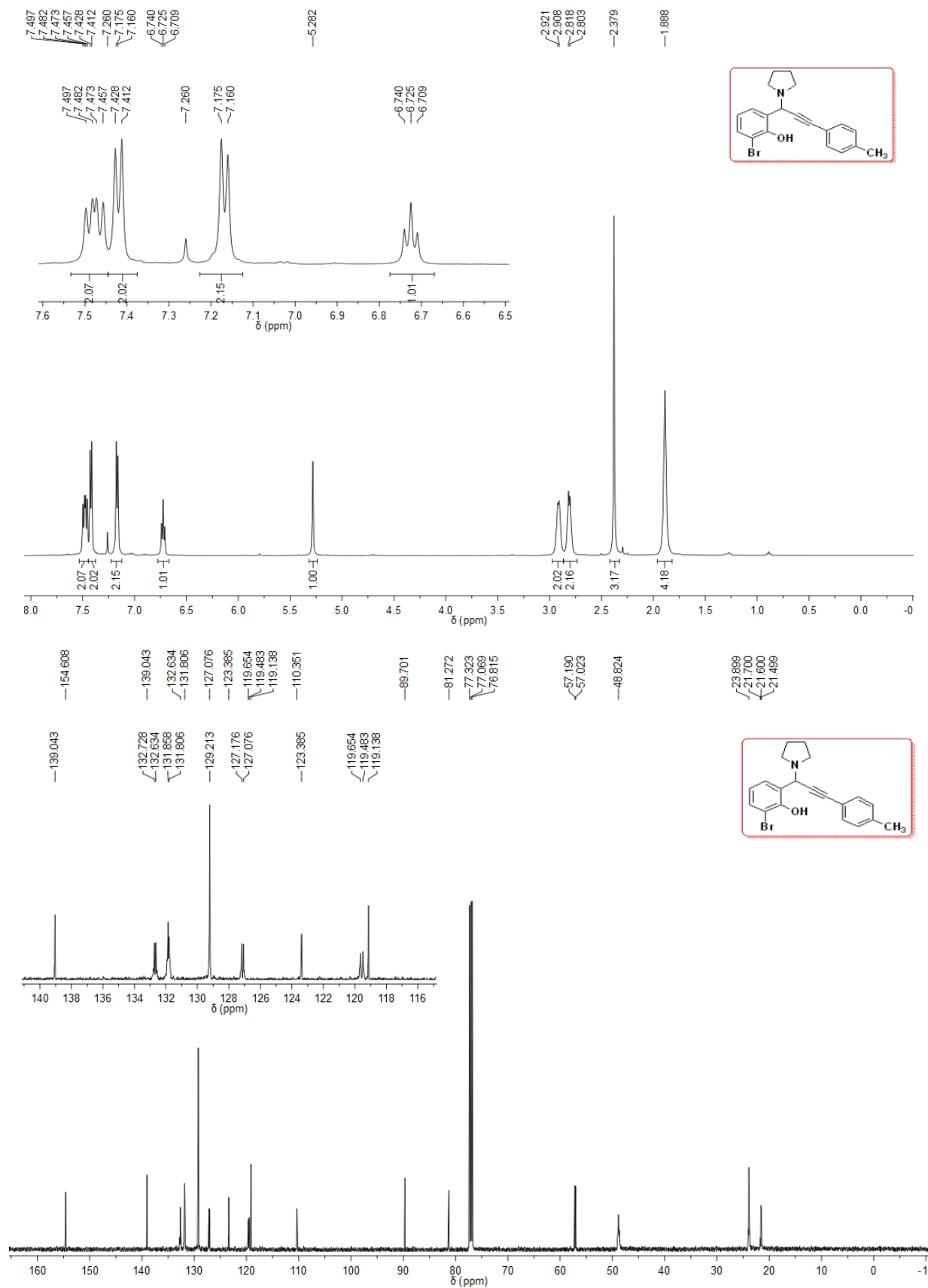
4-Bromo-2-(1-(pyrrolidin-1-yl)-3-(p-tolyl)prop-2-yn-1-yl)phenol (1n)



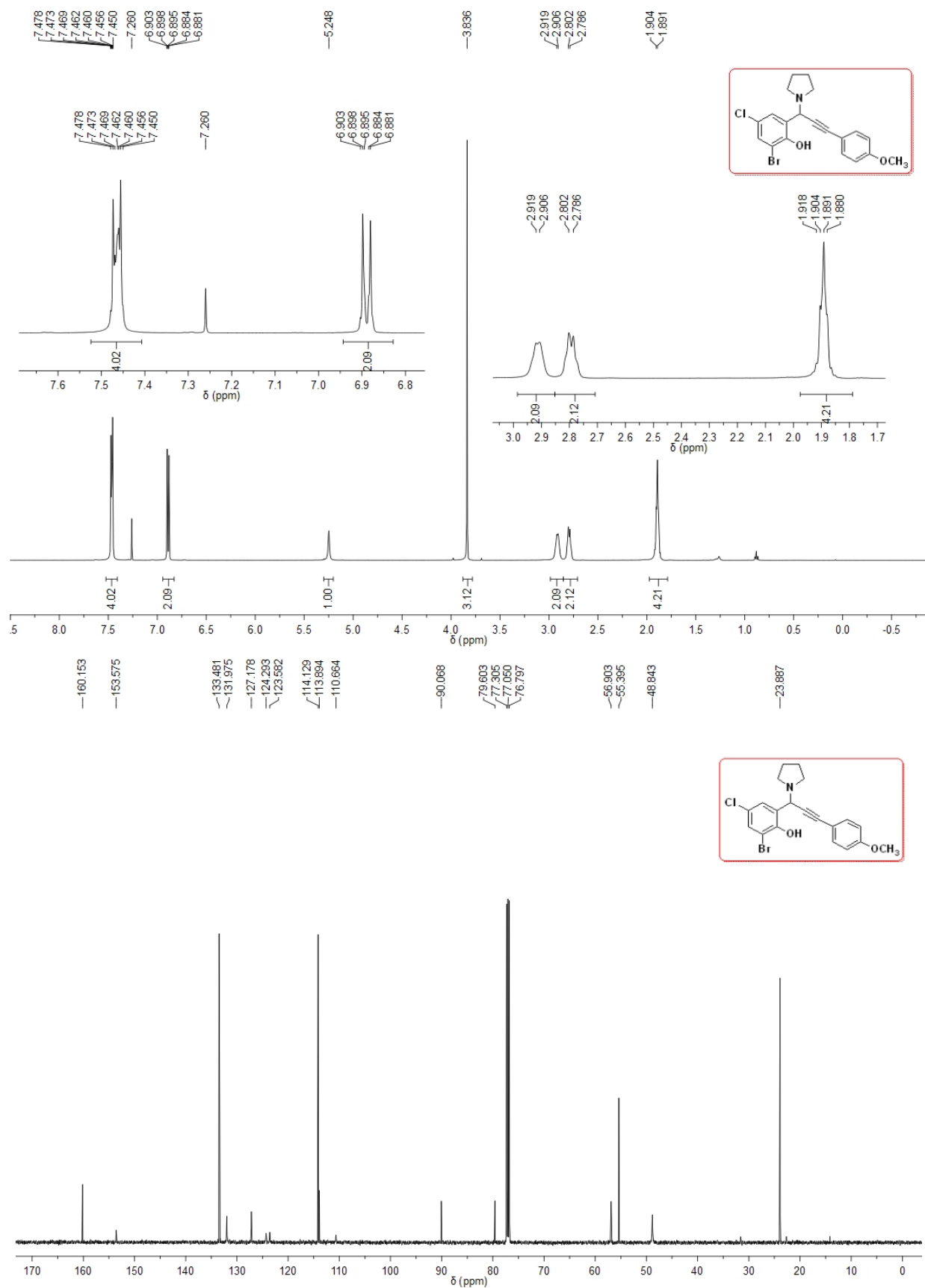
4-Bromo-2-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (**1o**)

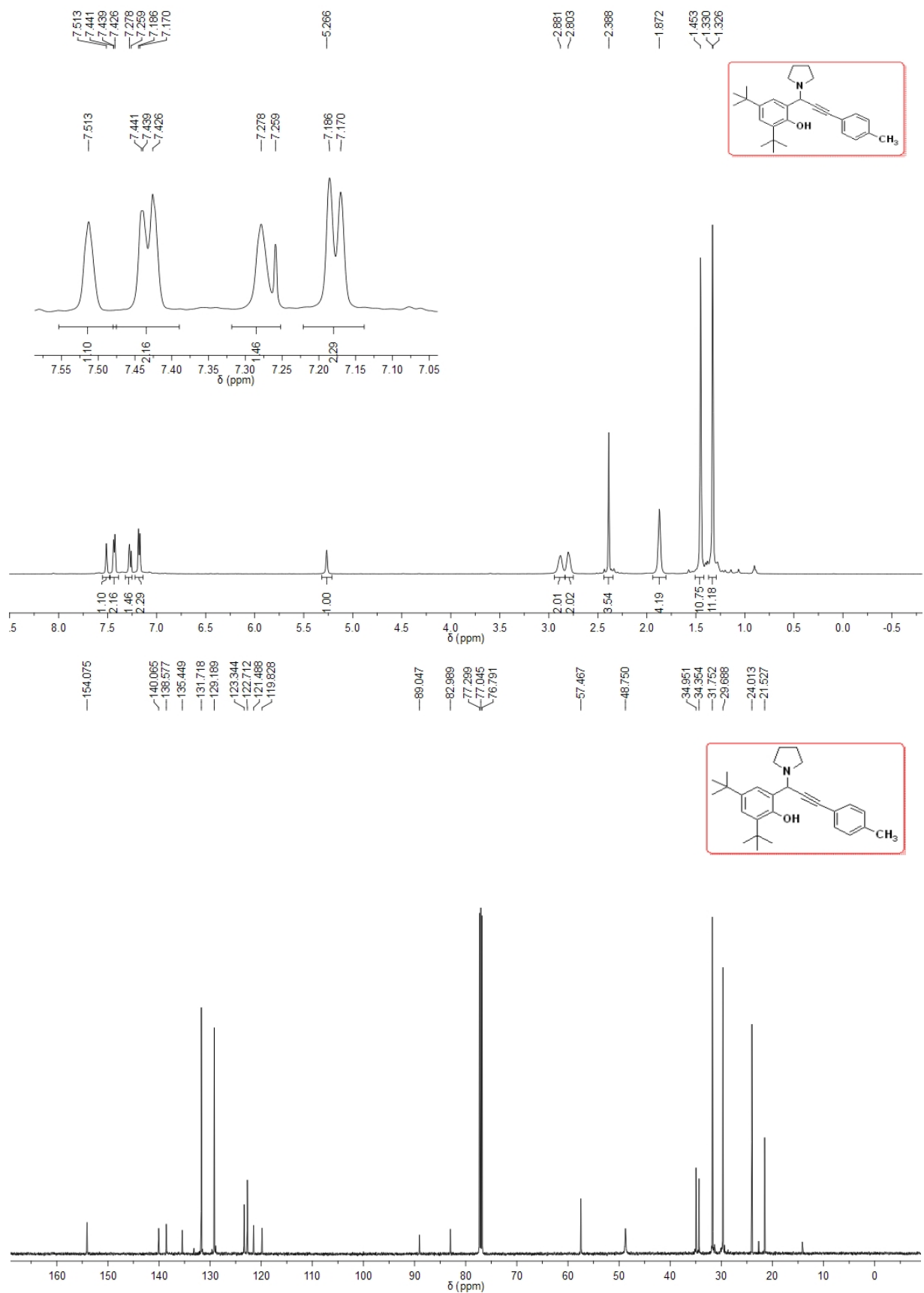
4-Bromo-2-(3-(4-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1p)



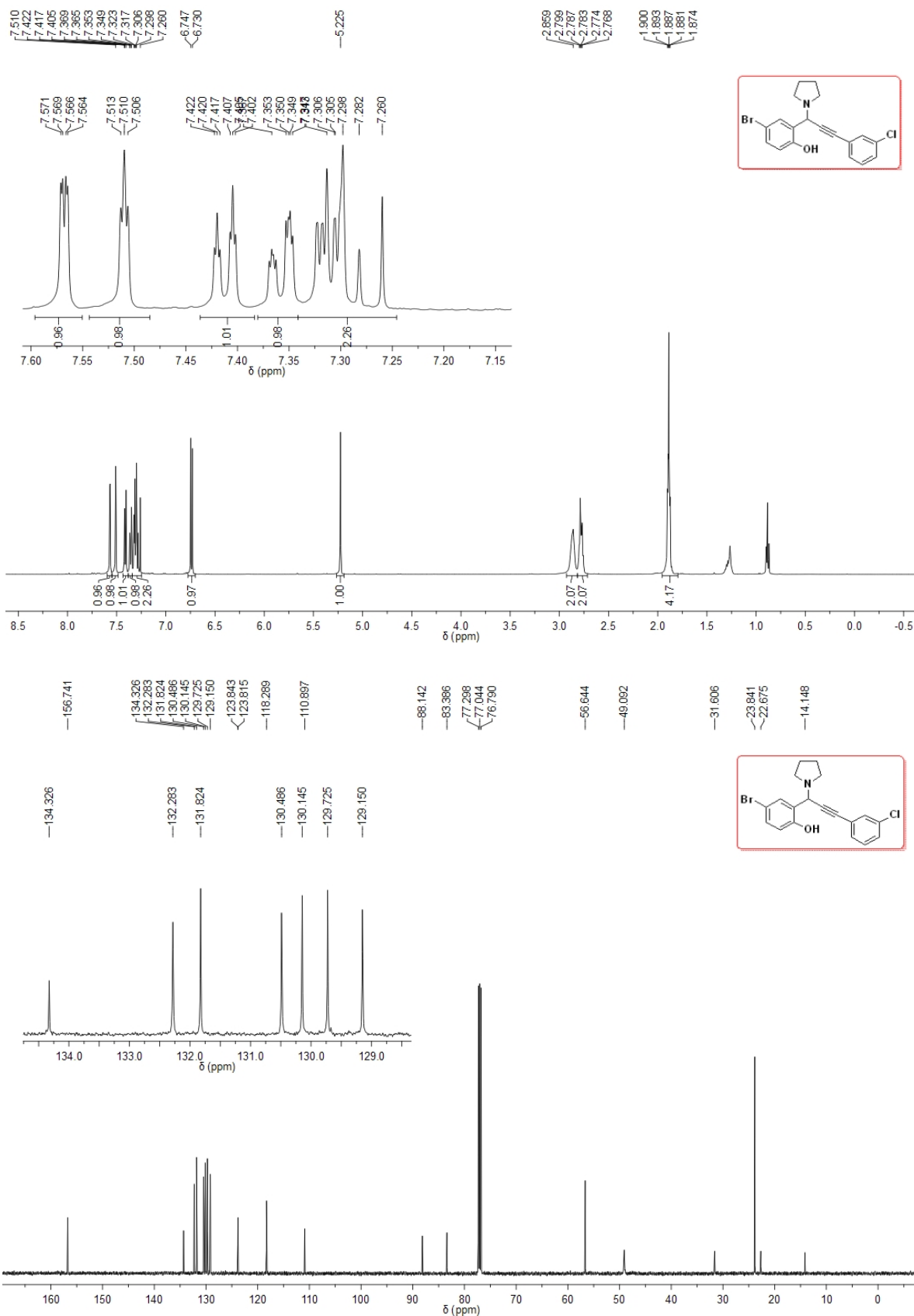
2-Bromo-6-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (1q)

2-Bromo-4-chloro-6-(3-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1r)

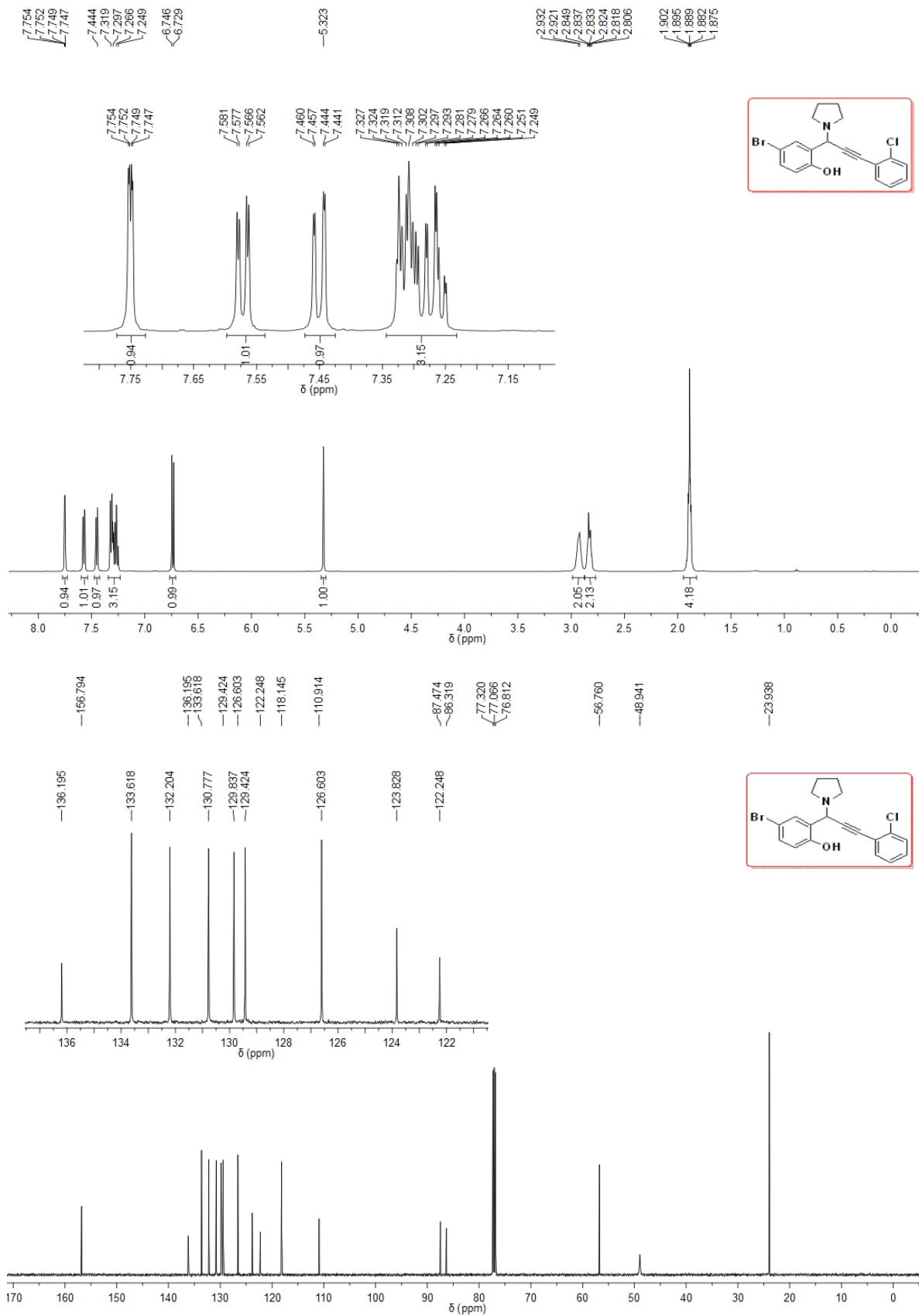


2,4-Di-*tert*-butyl-6-(1-(pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)phenol (**1s**)

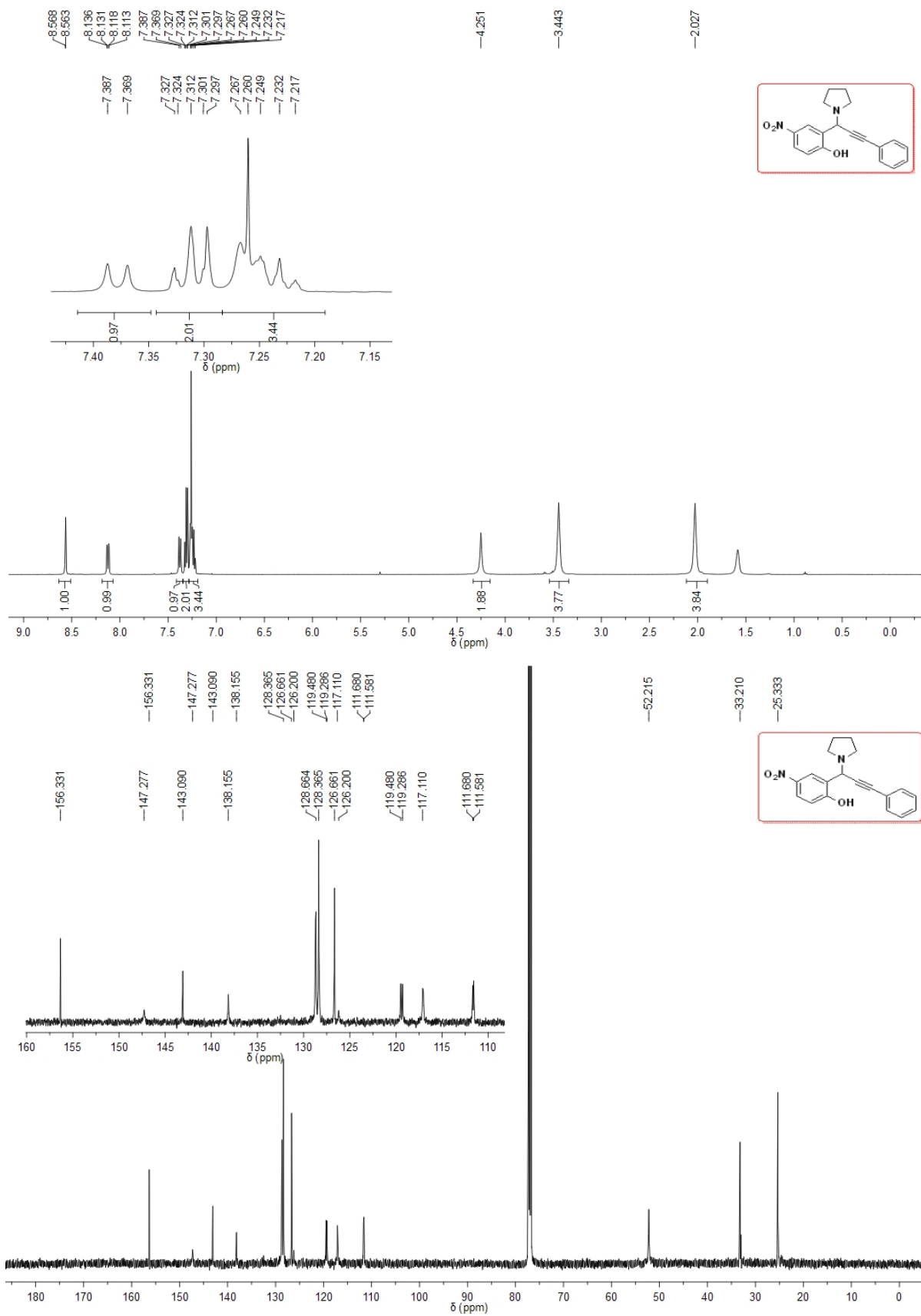
4-Bromo-2-(3-(3-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1t)



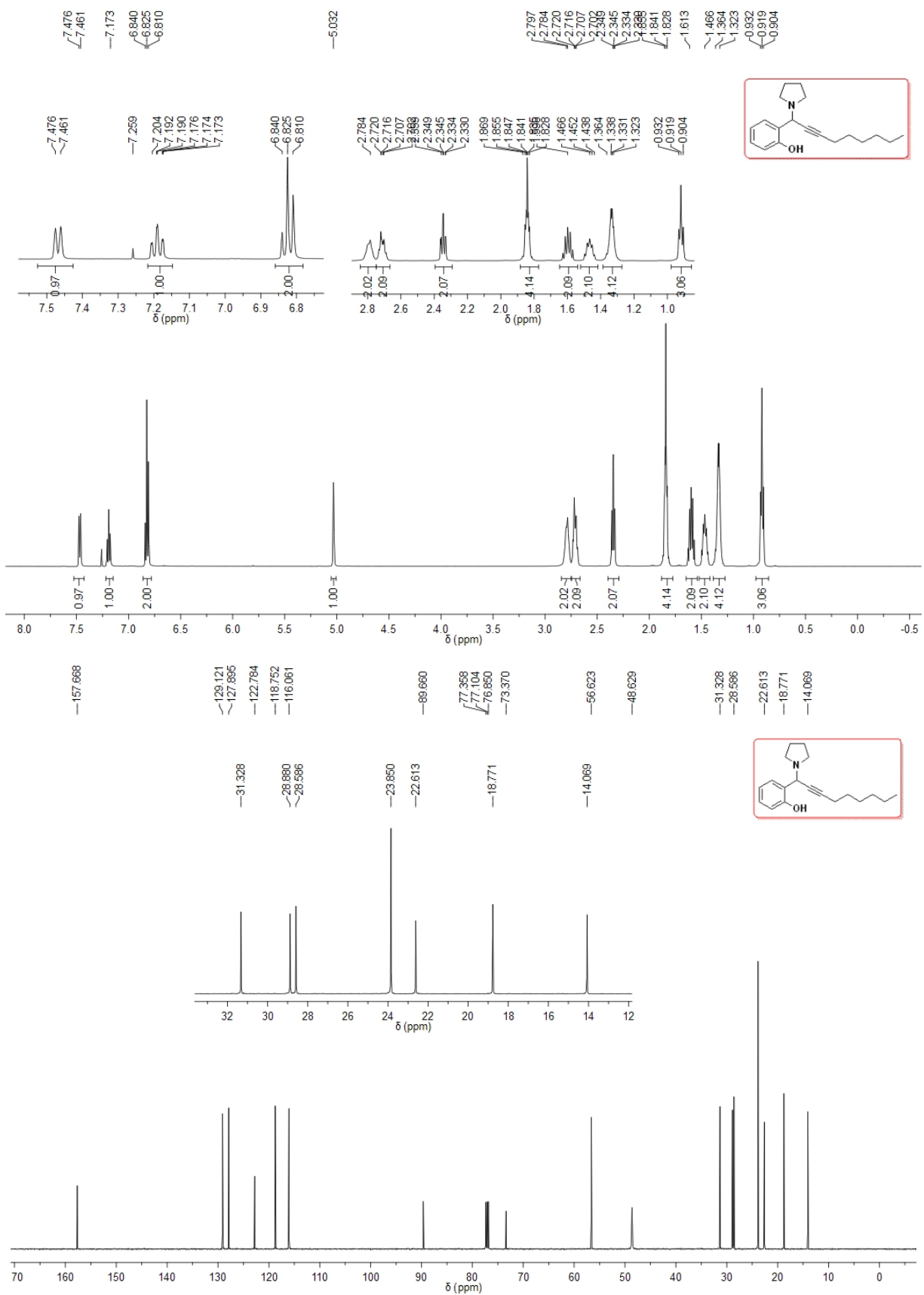
4-Bromo-2-(3-(2-chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1u)

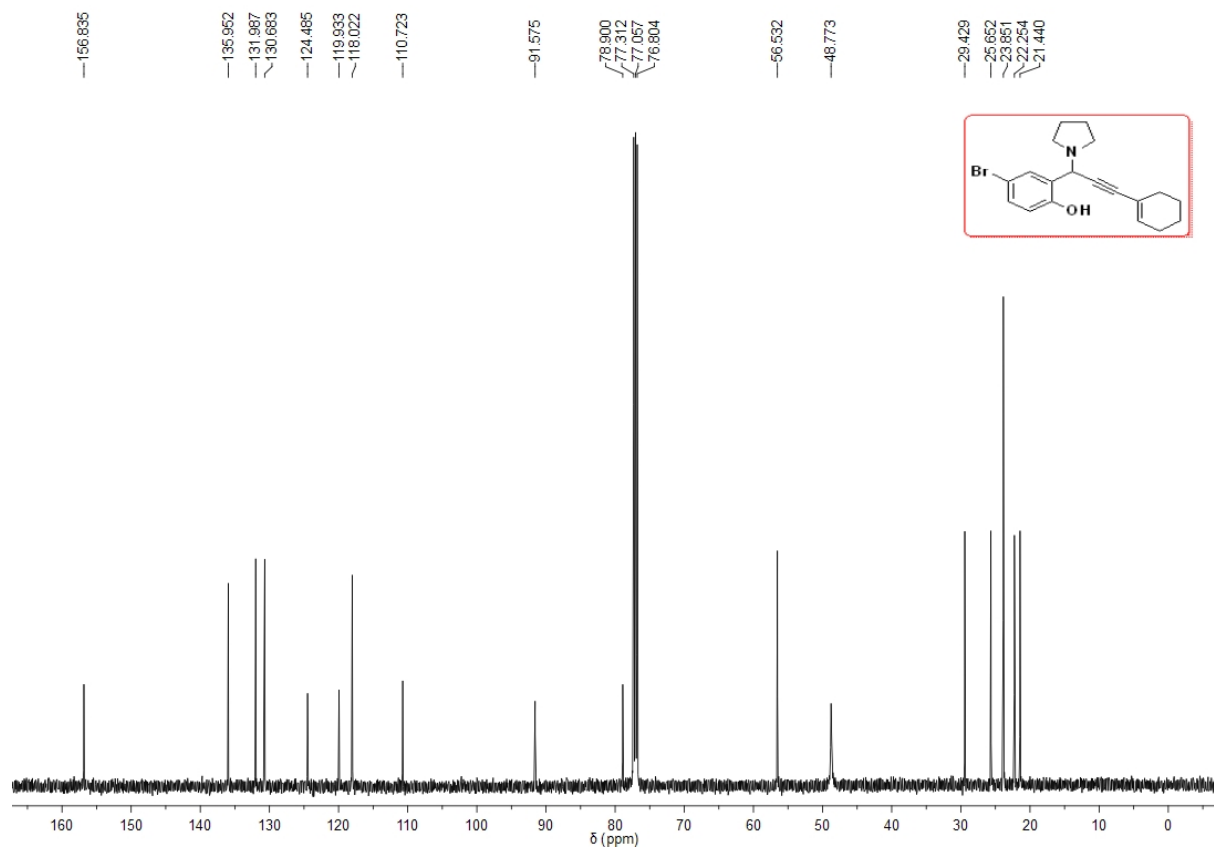
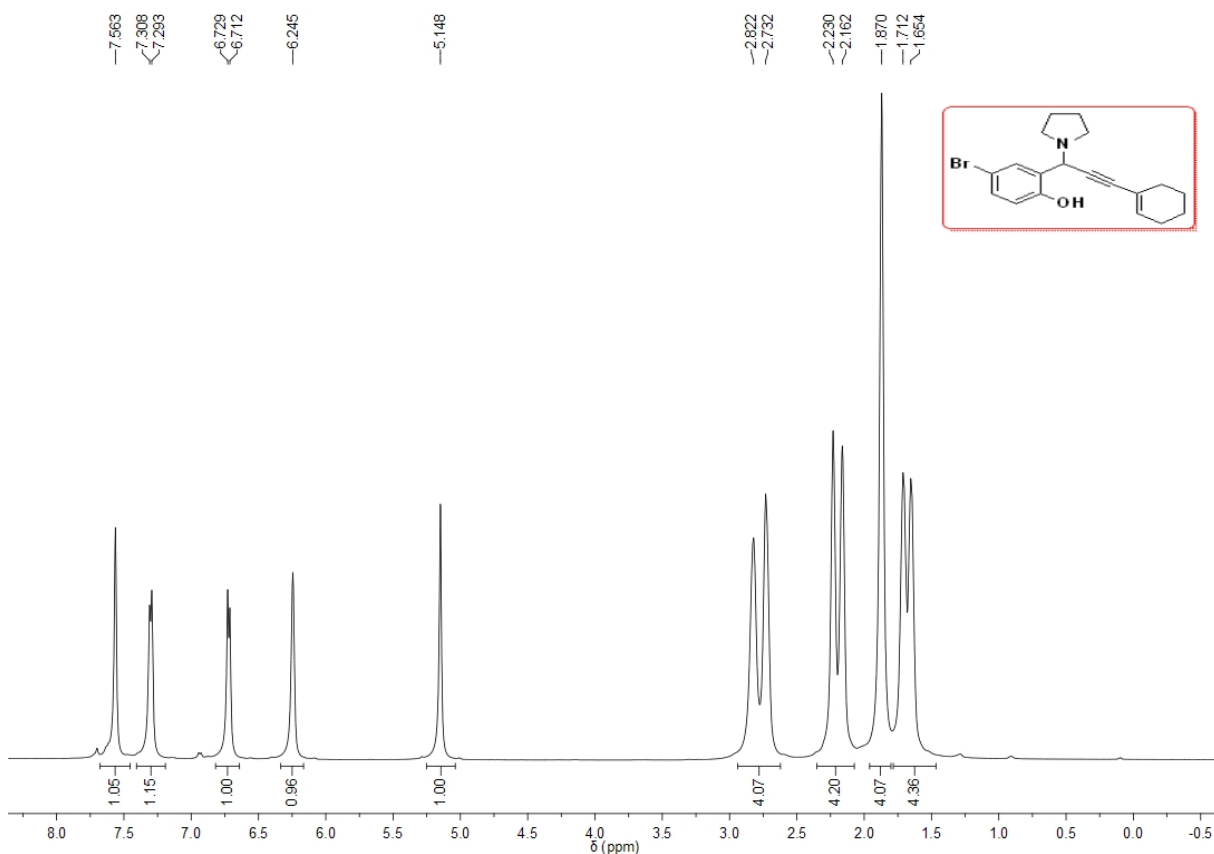


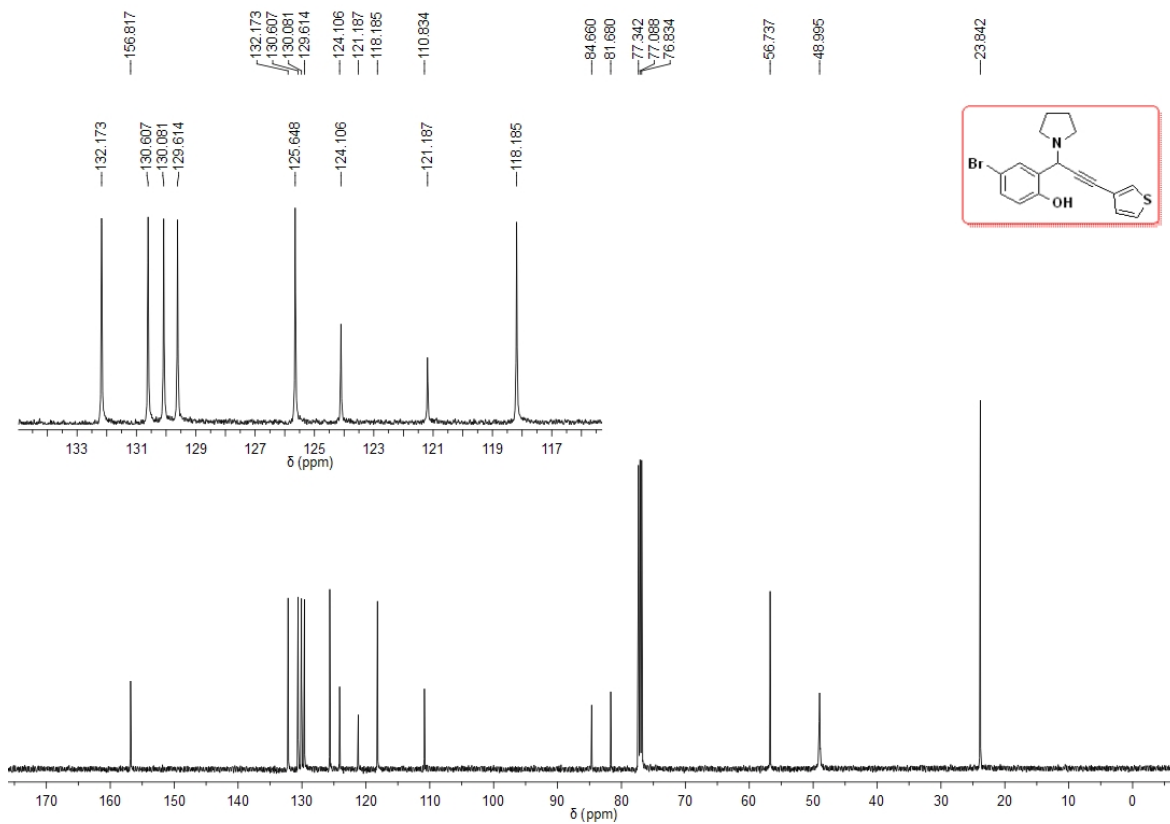
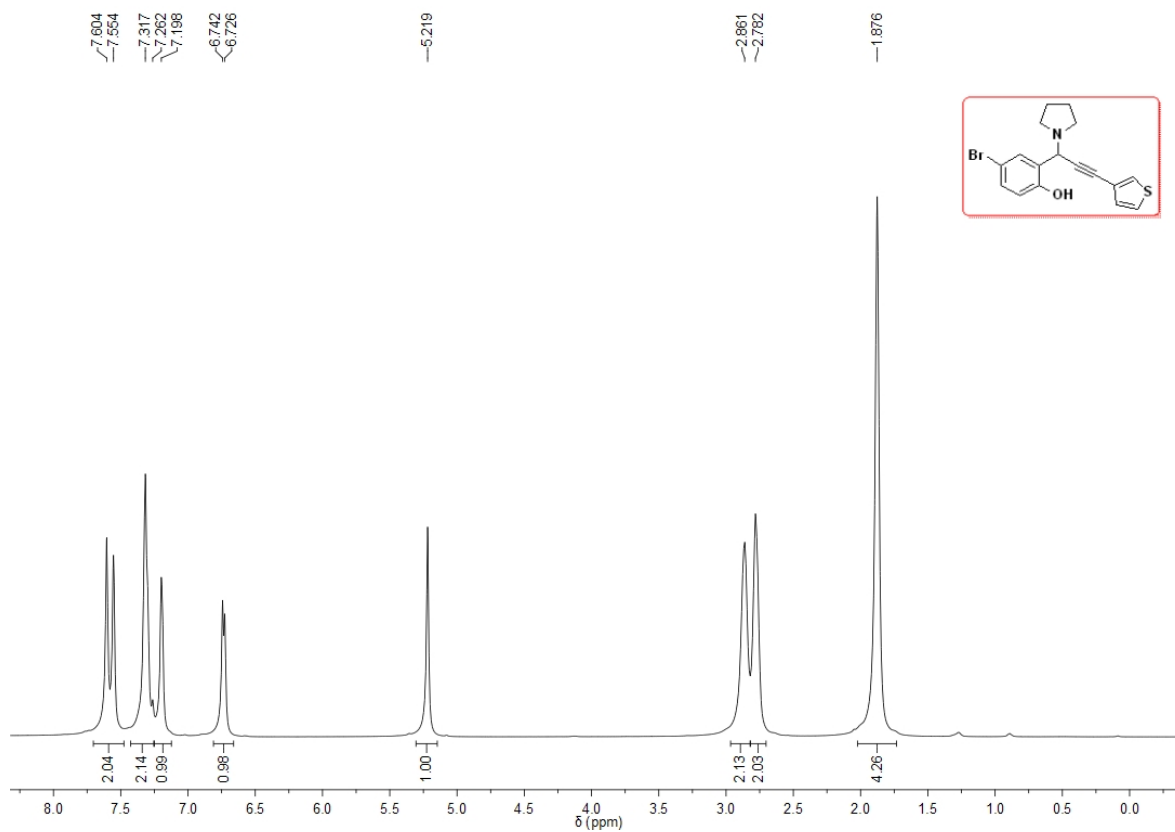
4-Nitro-2-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1v)



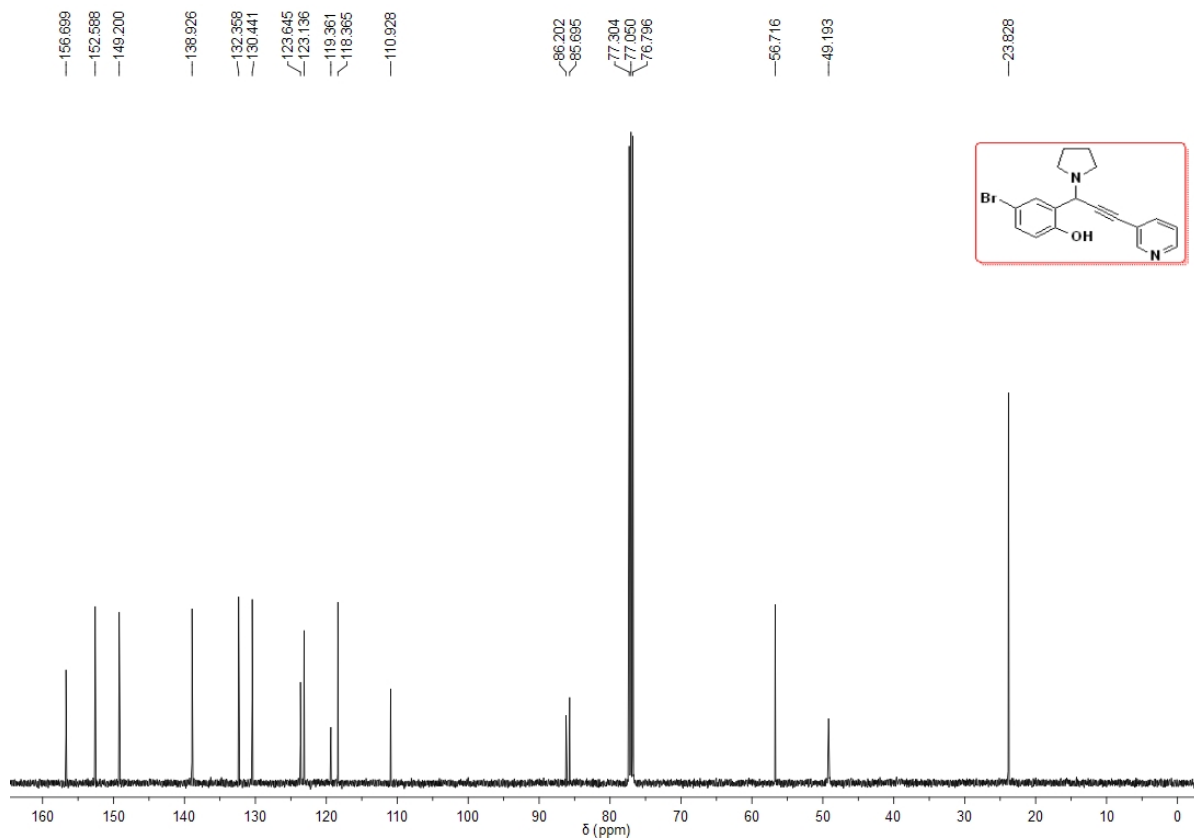
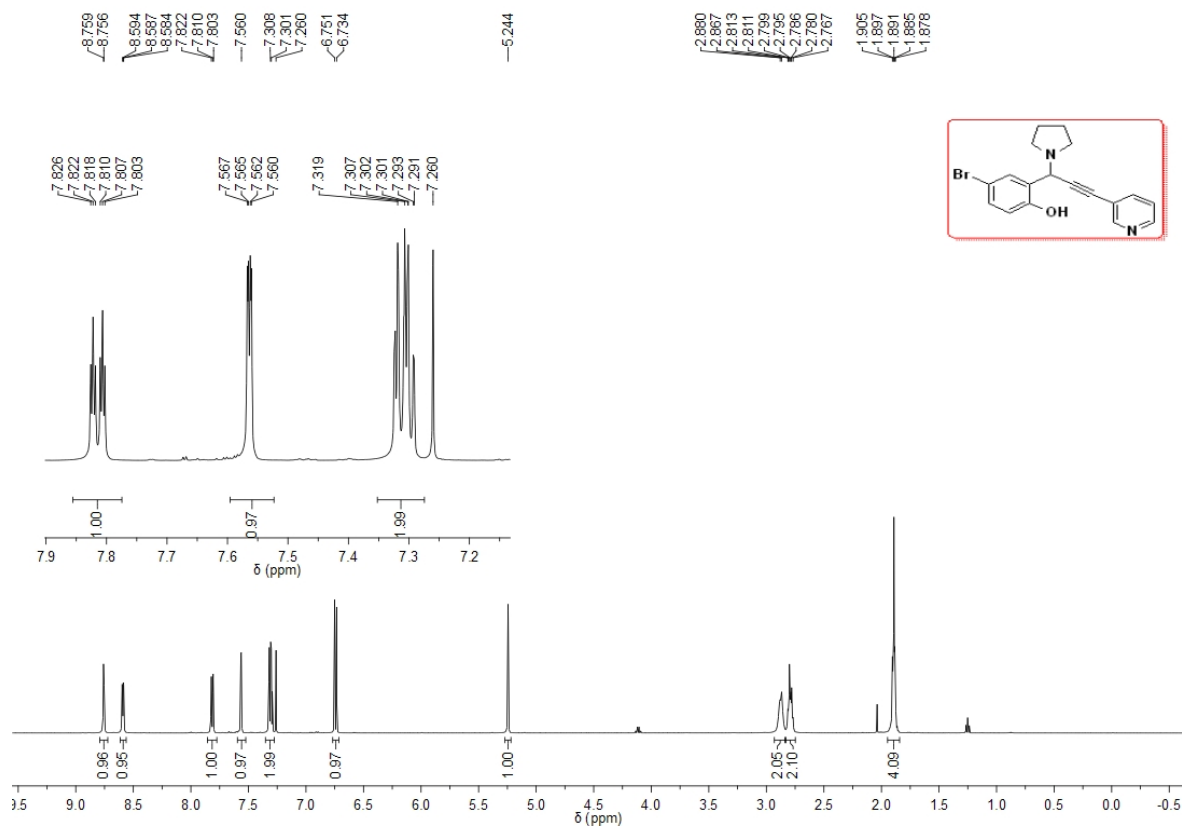
2-(1-(Pyrrolidin-1-yl)non-2-yn-1-yl)phenol (1w)



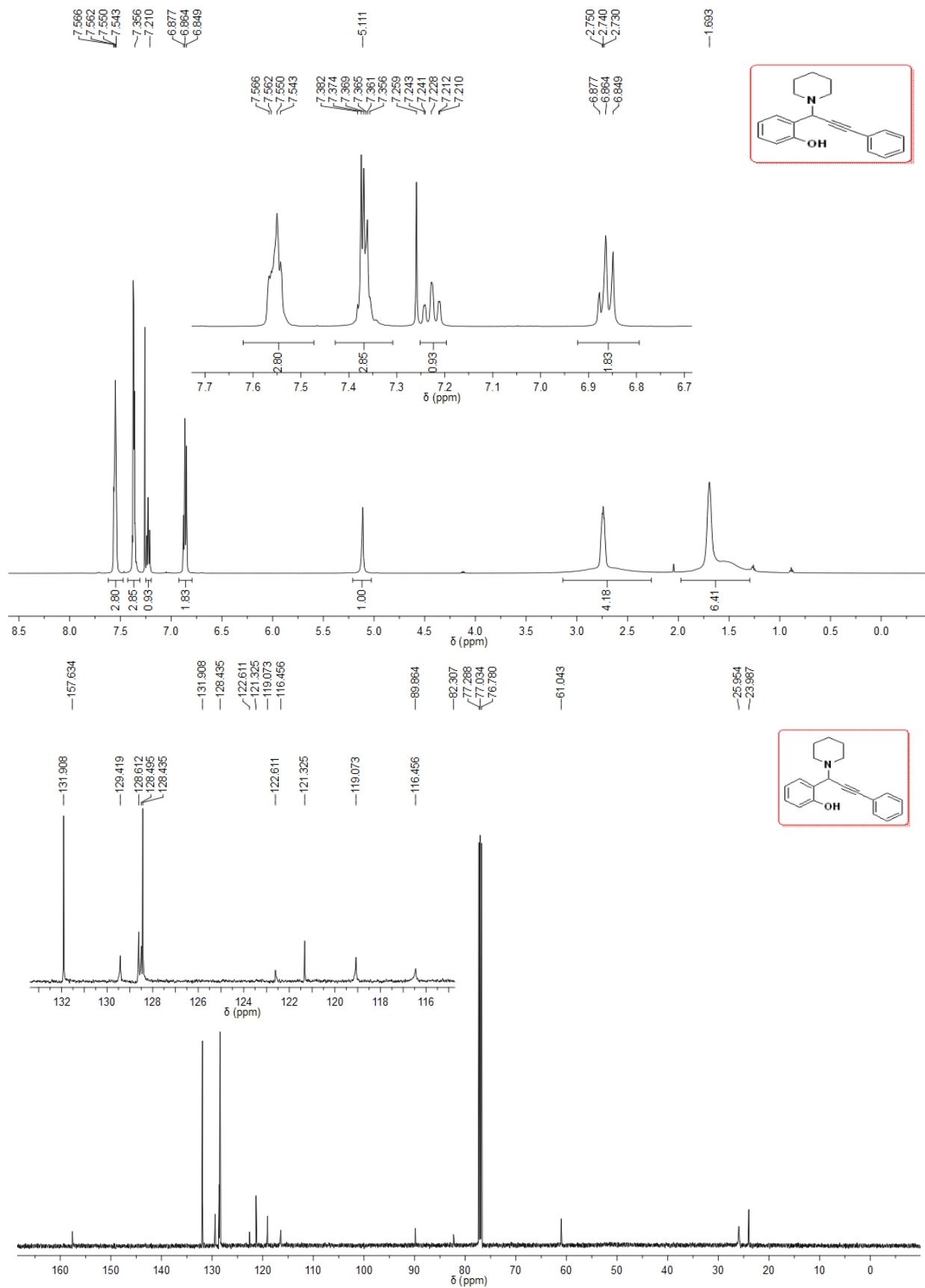
4-Bromo-2-(3-(cyclohex-1-en-1-yl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1x)

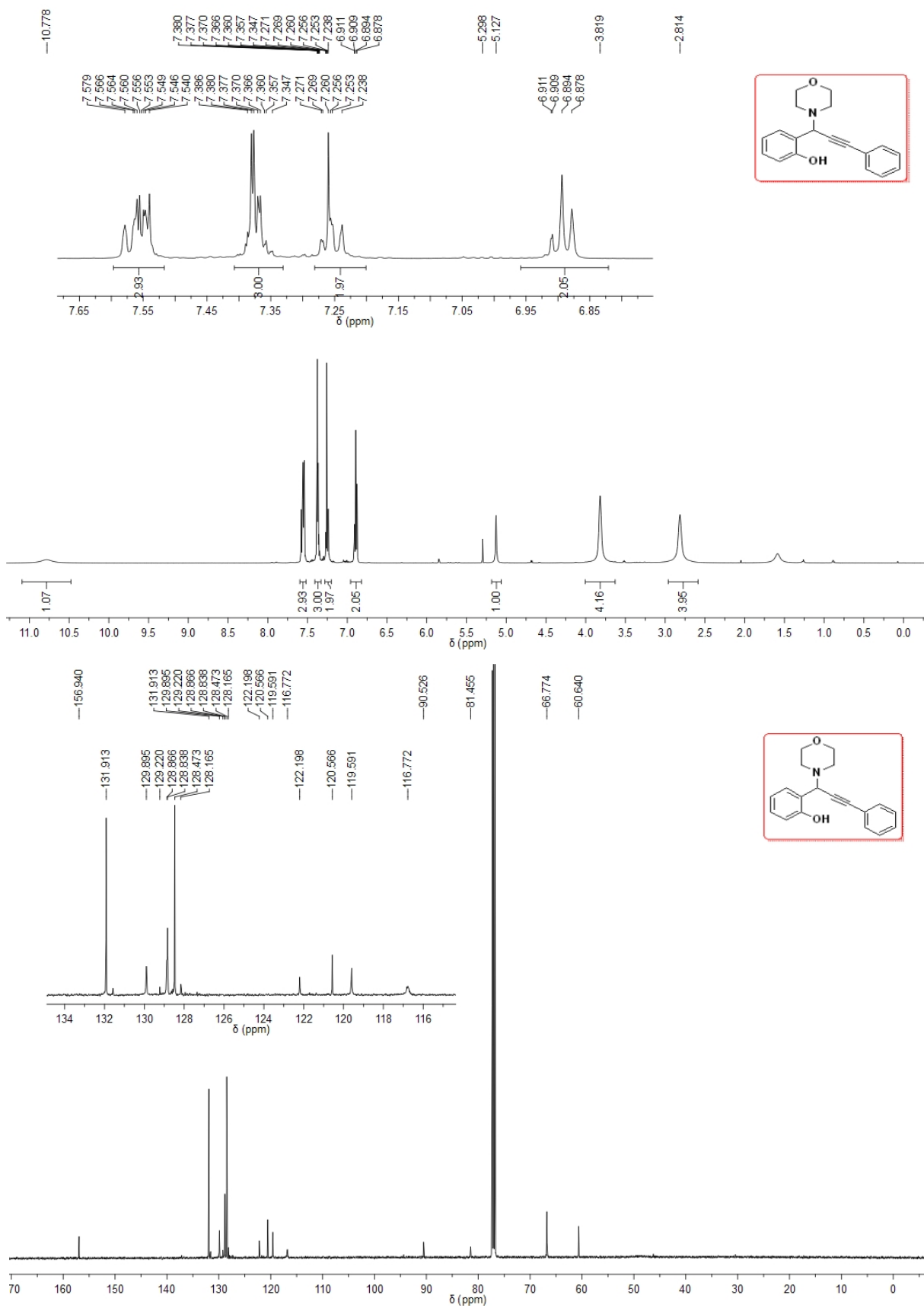
4-Bromo-2-(1-(pyrrolidin-1-yl)-3-(thiophen-3-yl)prop-2-yn-1-yl)phenol (1y)

4-Bromo-2-(3-(pyridin-3-yl)-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)phenol (1z)

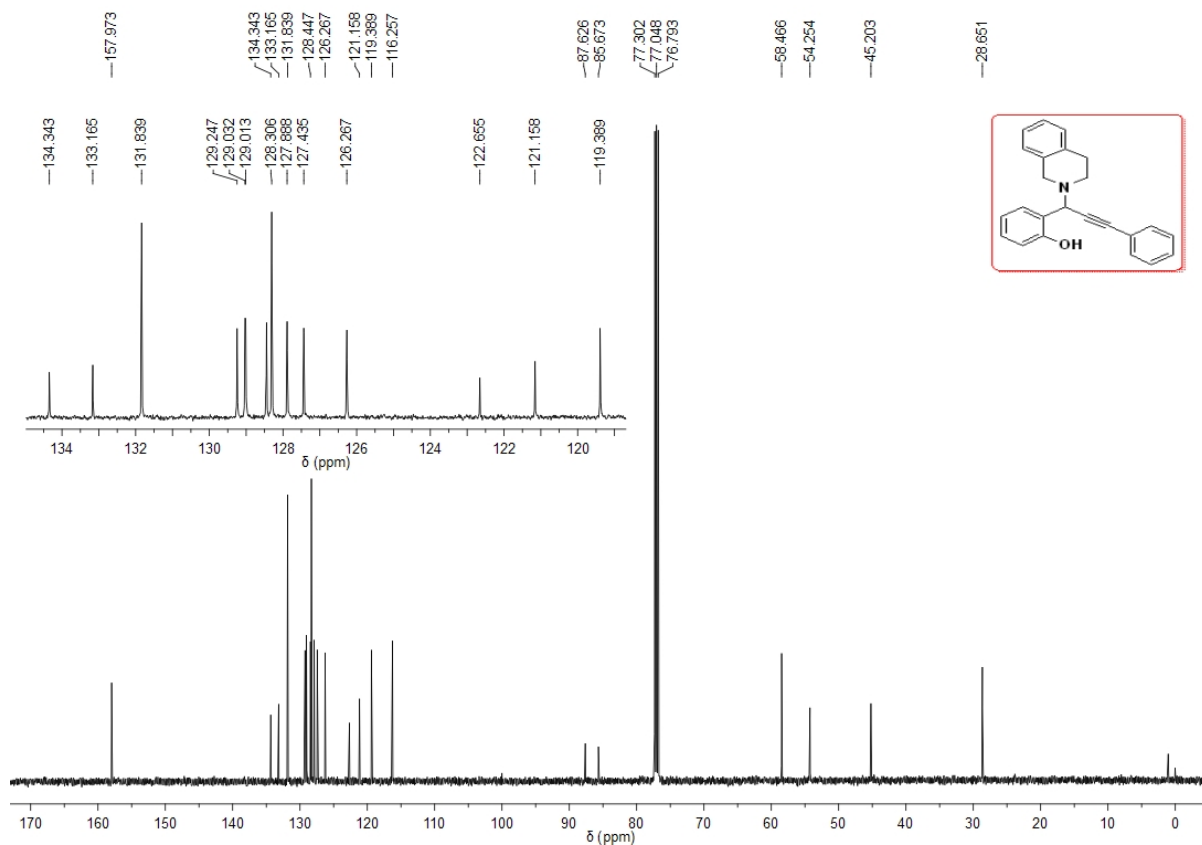
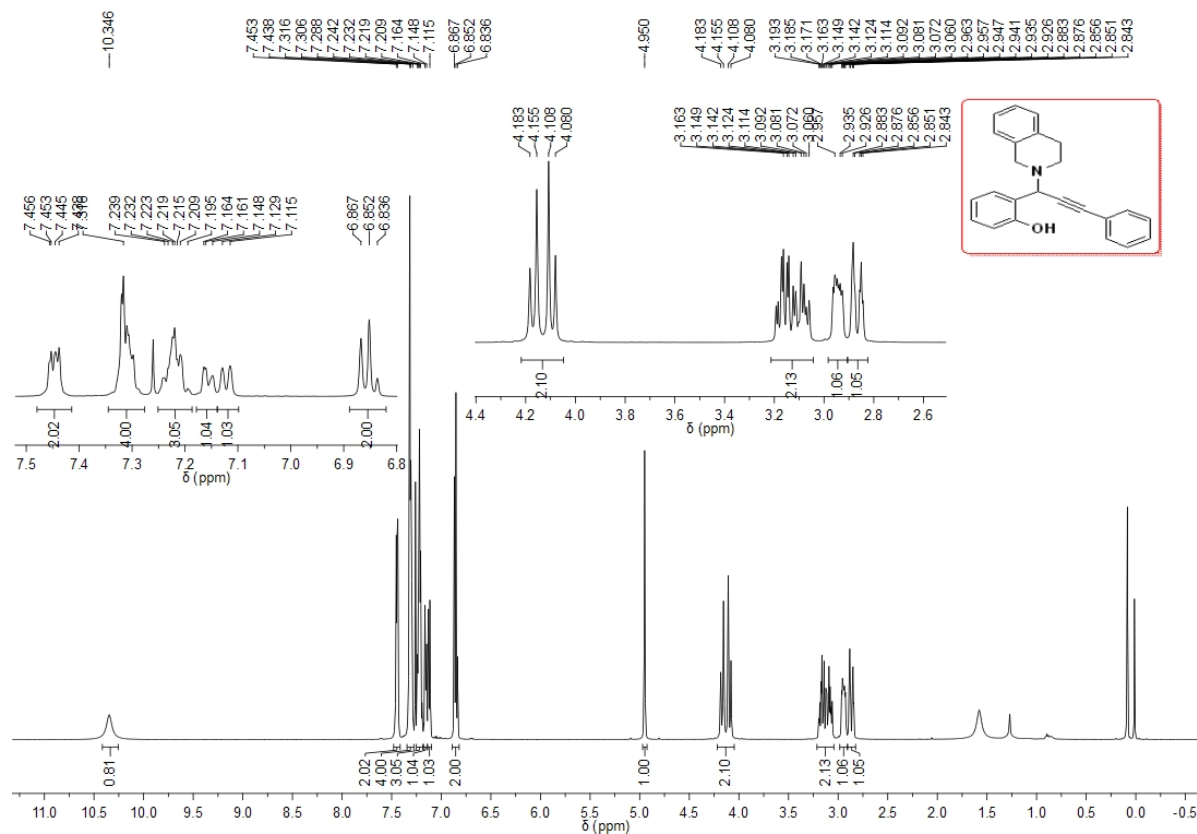


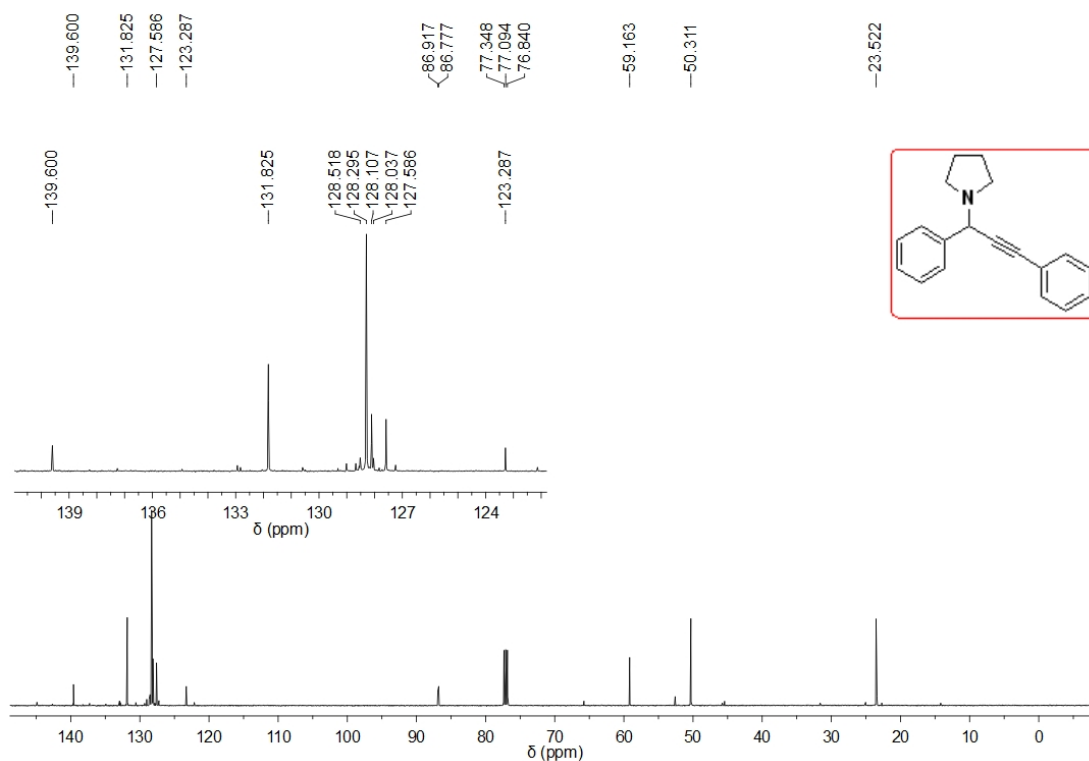
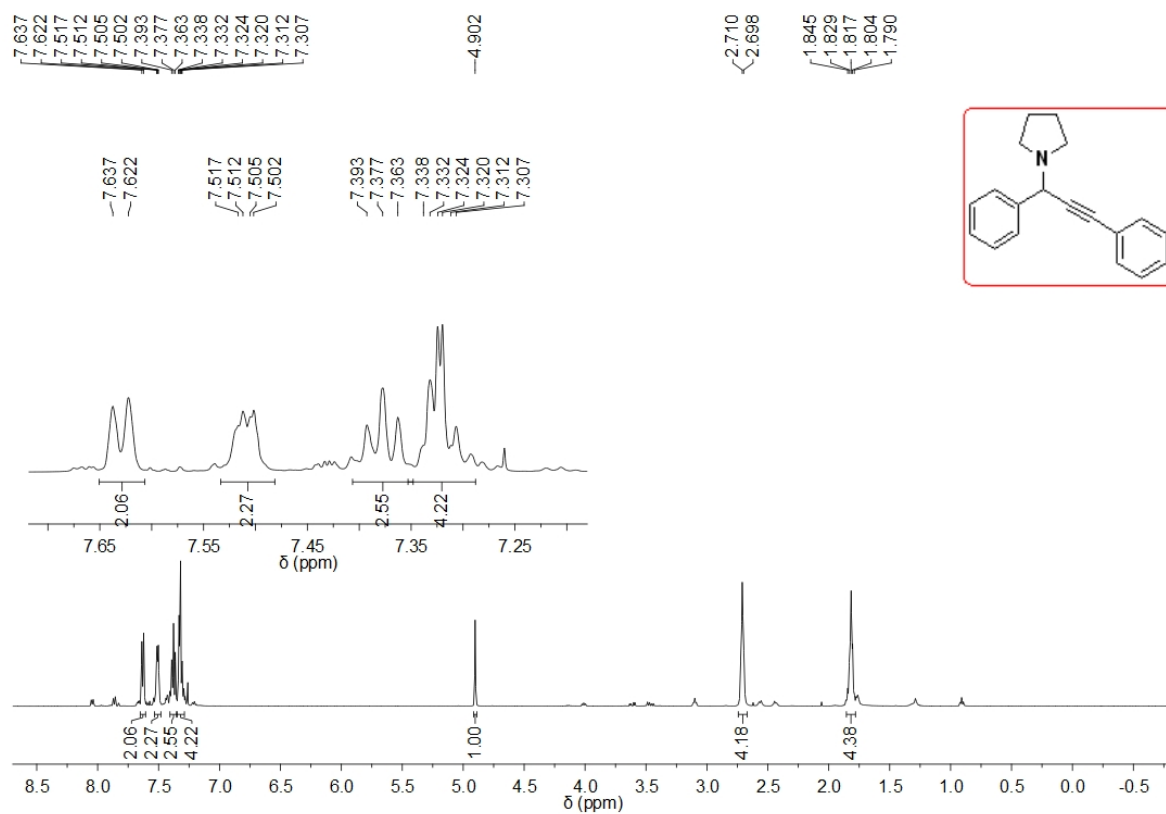
2-(3-Phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (1a')

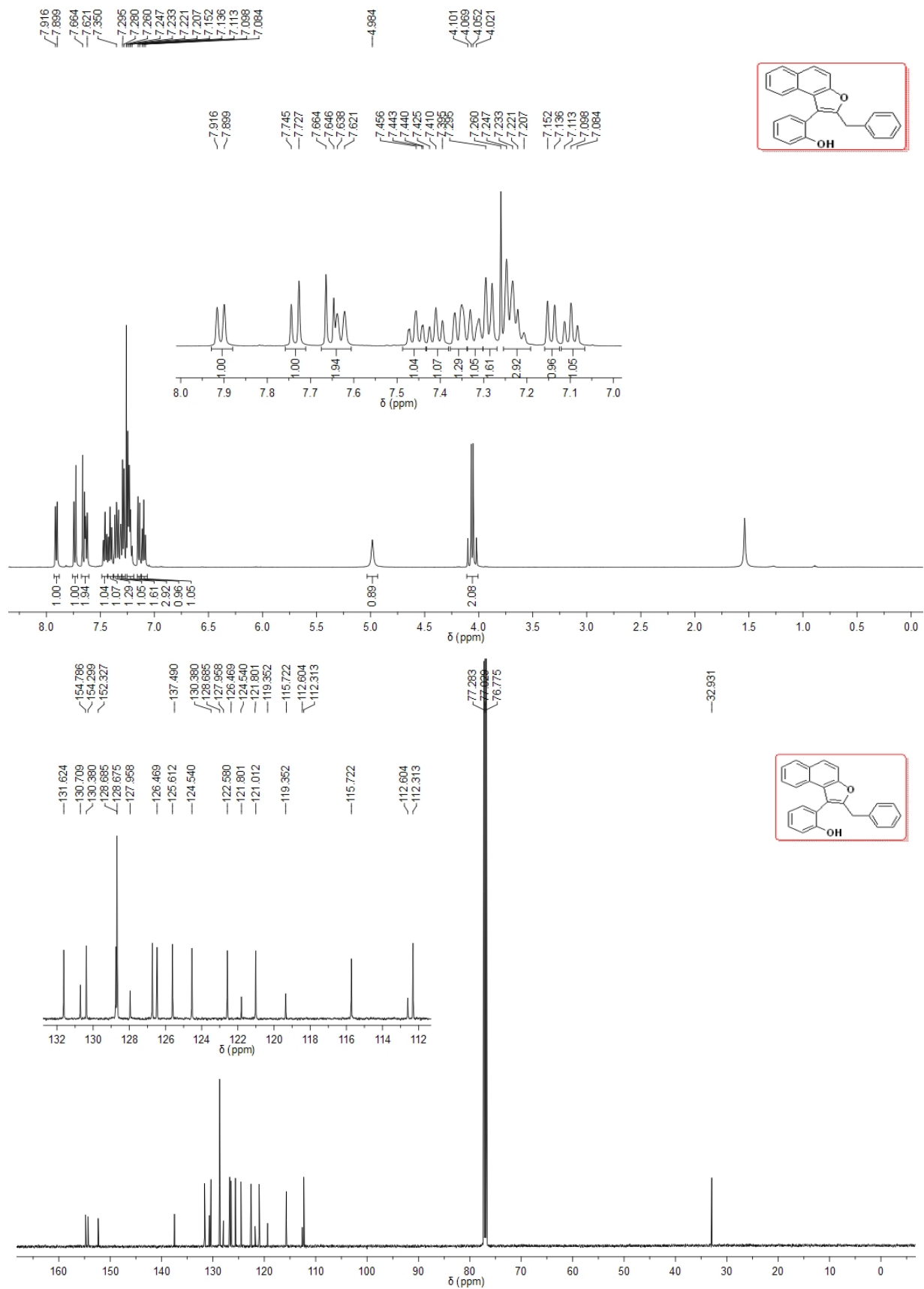


2-(1-Morpholino-3-phenylprop-2-yn-1-yl)phenol (1b')

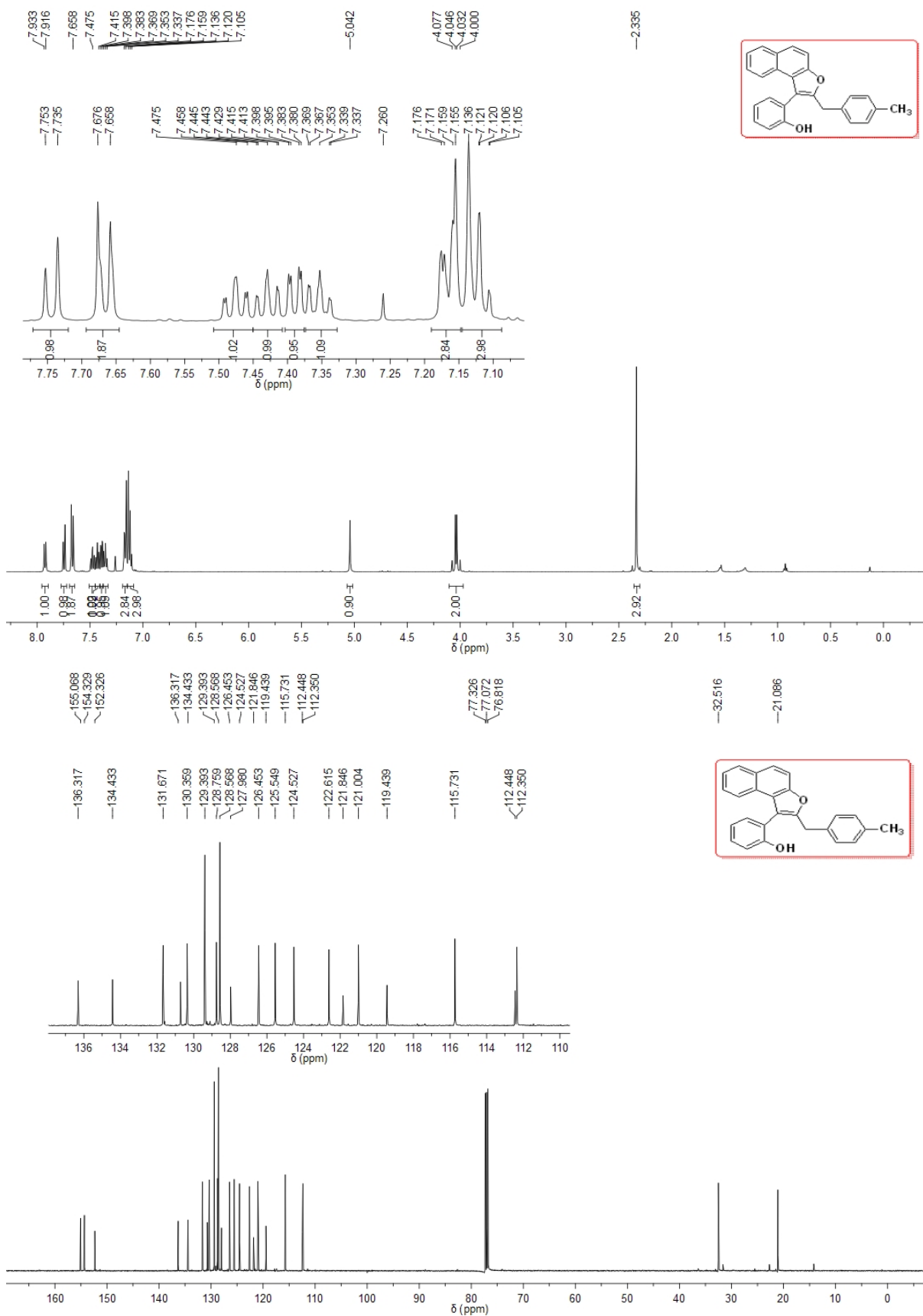
2-(1-(3,4-Dihydroisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-yl)phenol (1c')



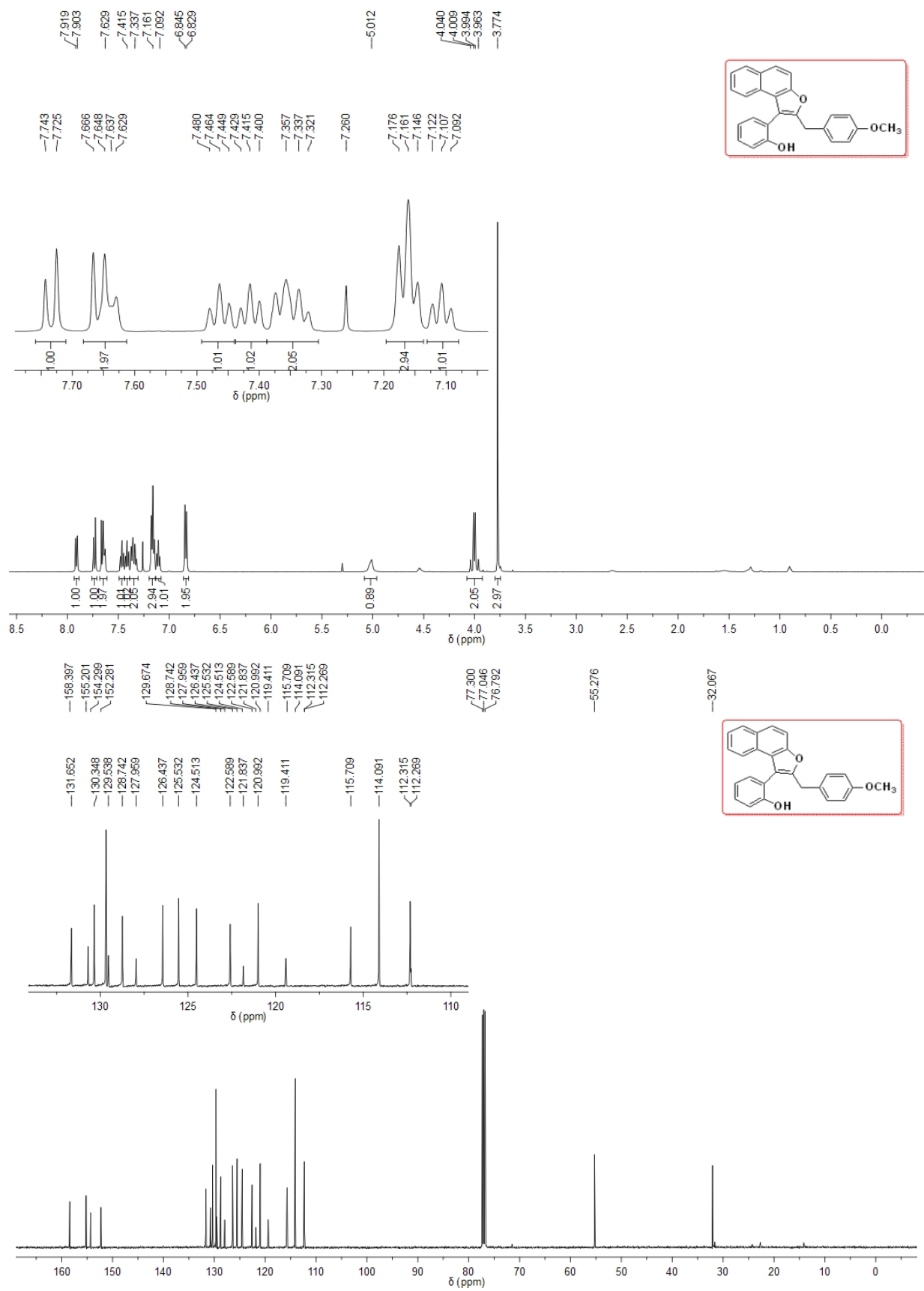
1-(1,3-Diphenylprop-2-yn-1-yl)pyrrolidine (4)

2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3aa)

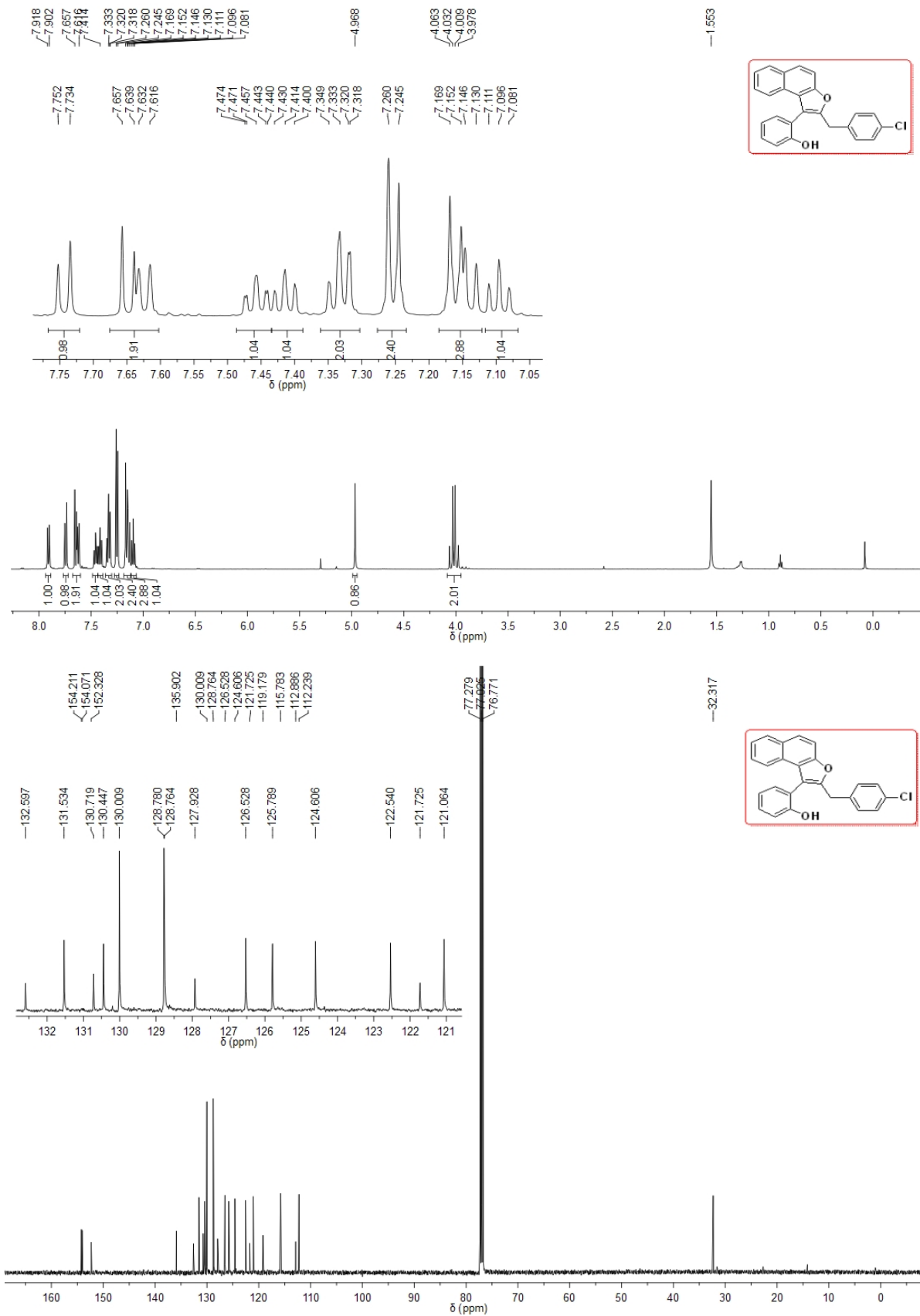
2-(2-(4-Methylbenzyl)naphtho[2,1-b]furan-1-yl)phenol (3ba)

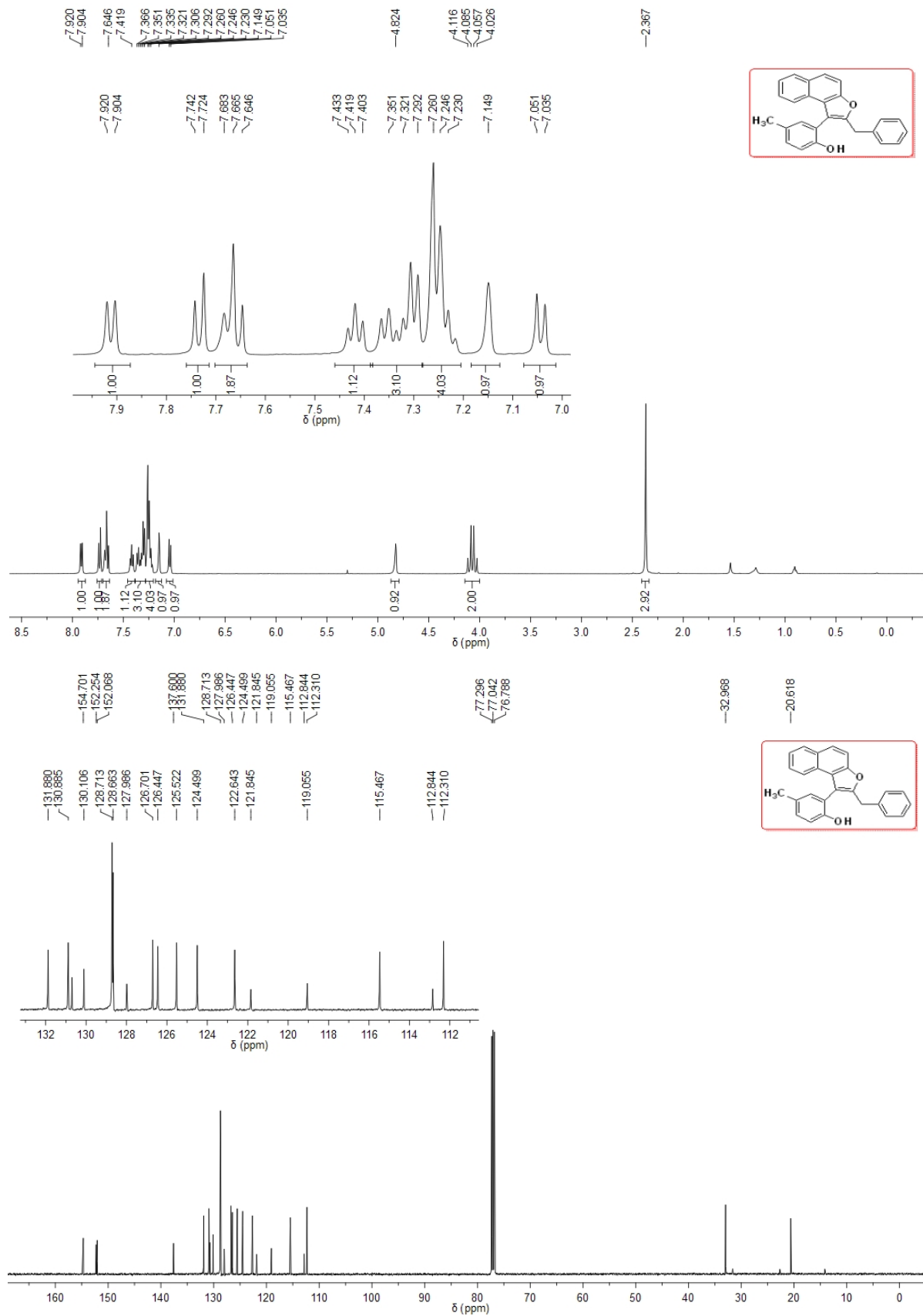


2-(2-(4-Methoxybenzyl)naphtho[2,1-b]furan-1-yl)phenol (3ca)

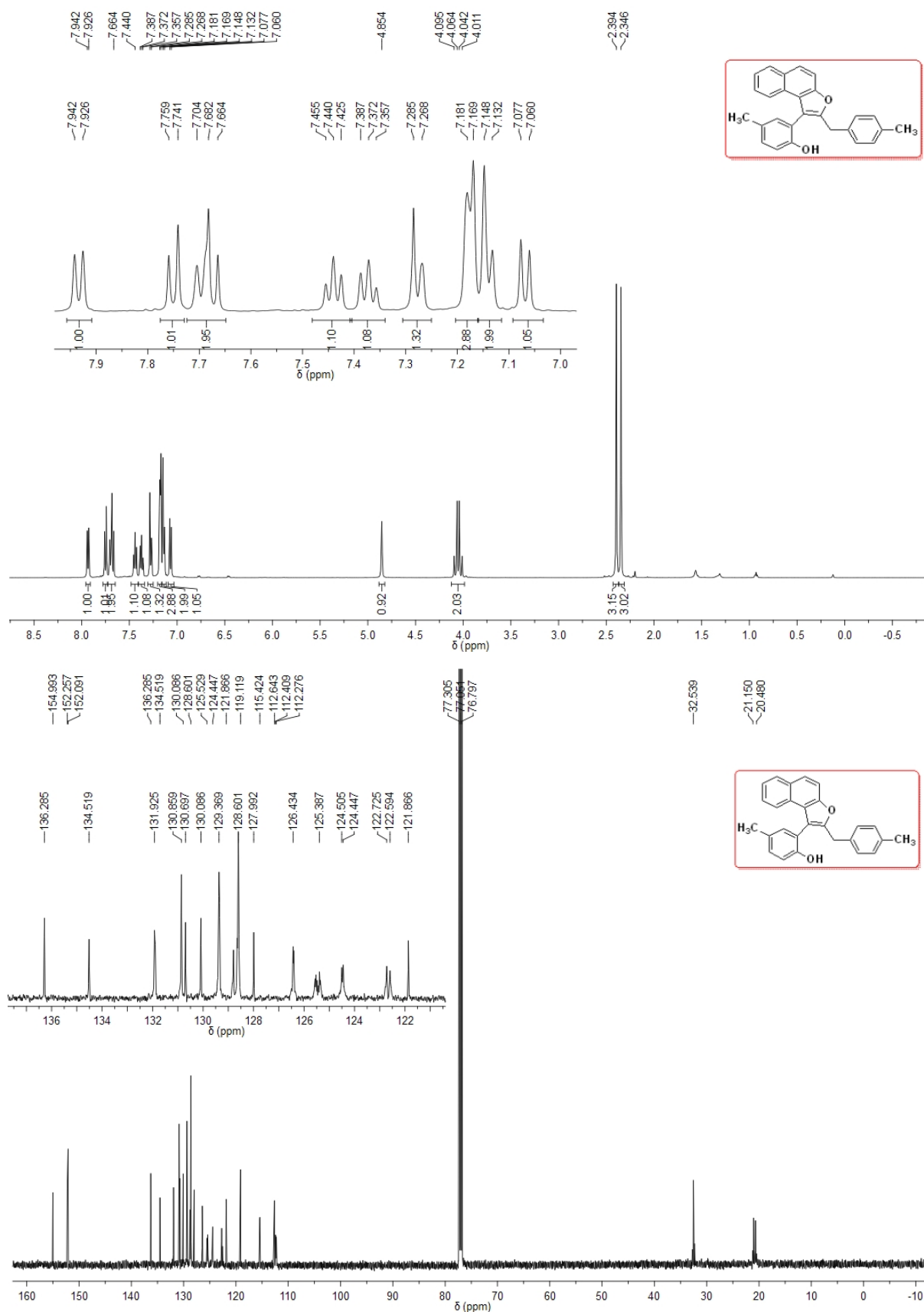


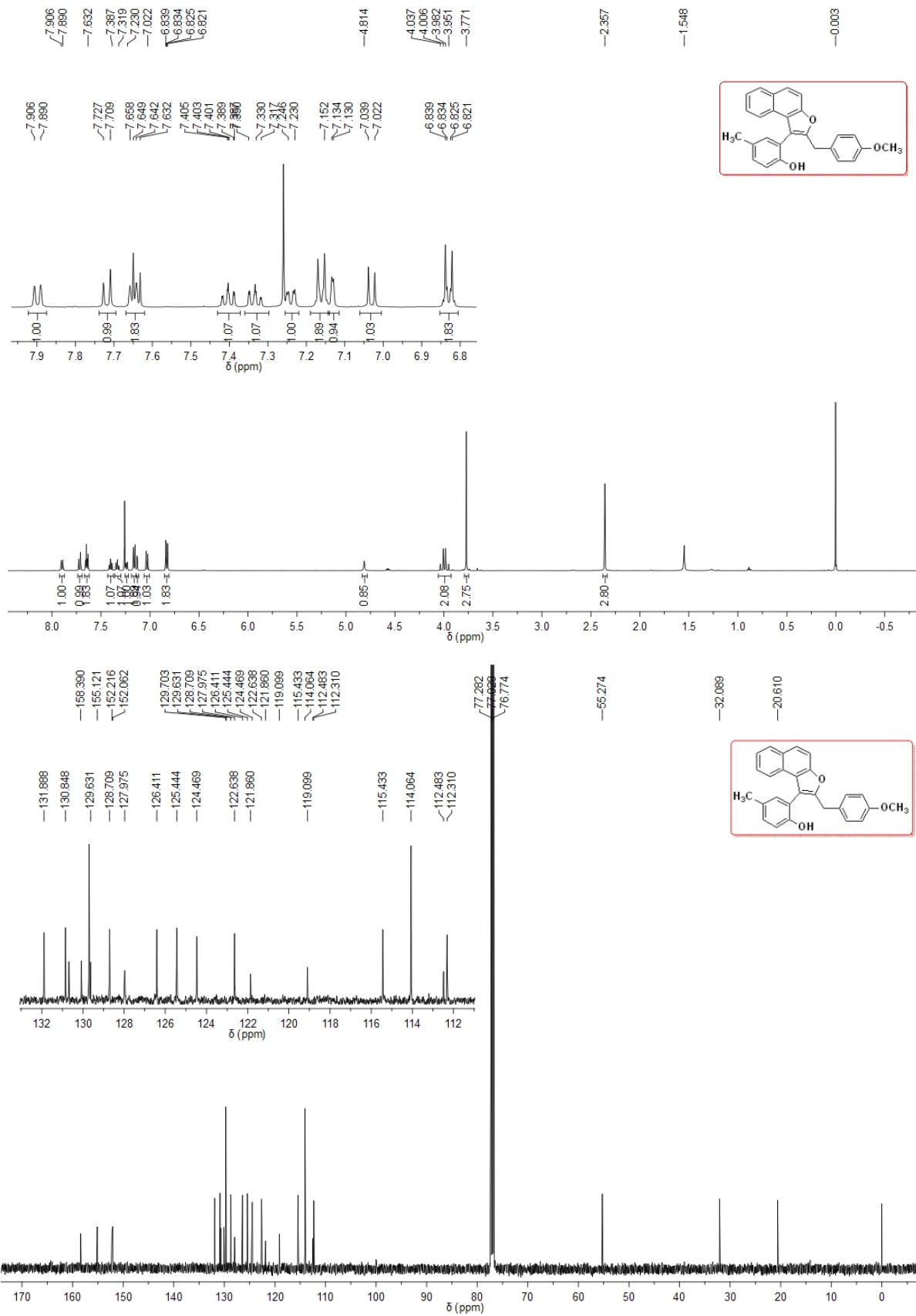
2-(2-(4-Chlorobenzyl)naphtho[2,1-b]furan-1-yl)phenol (3da)



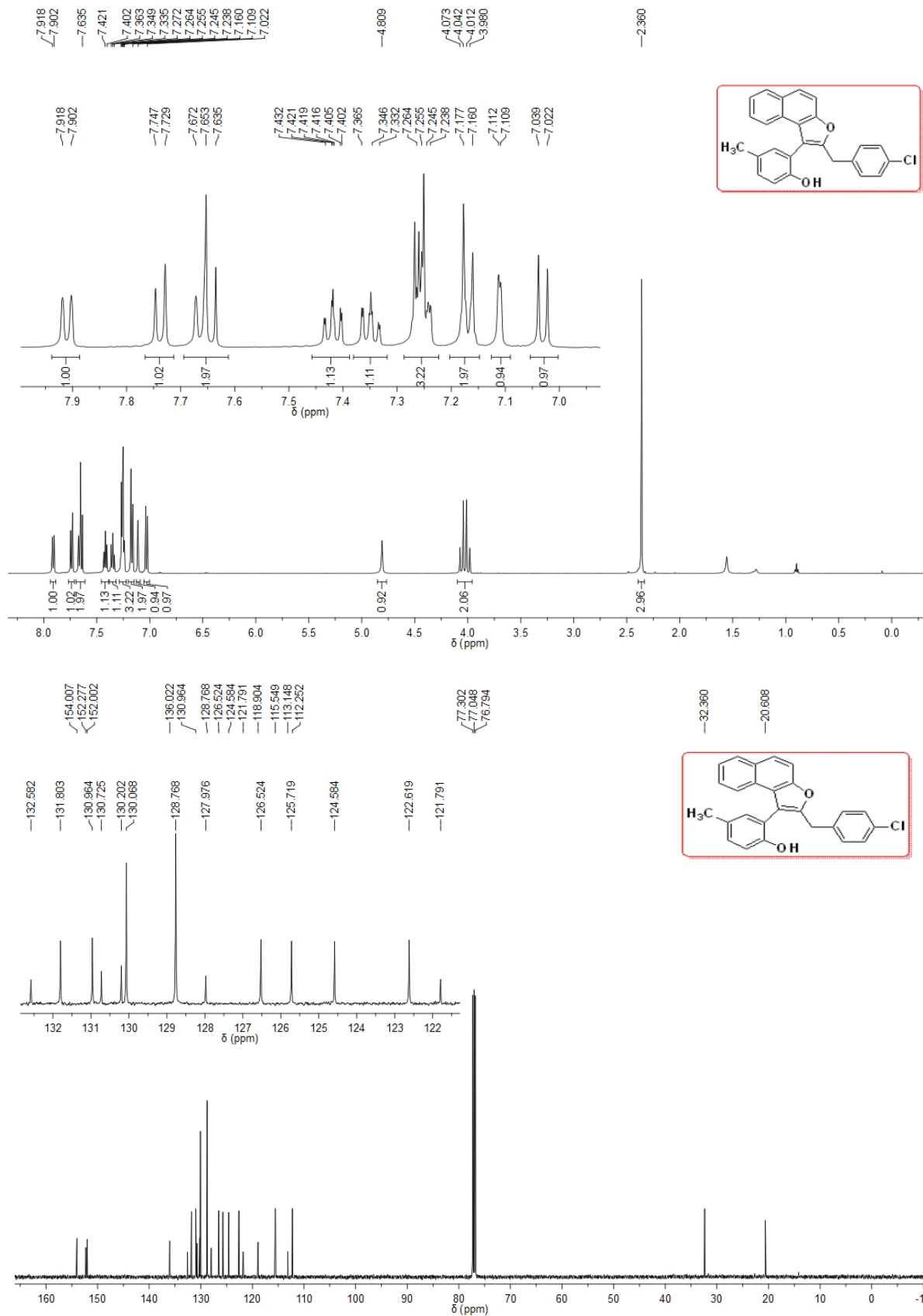
2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenol (3ea)

4-Methyl-2-(2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)phenol (3fa)



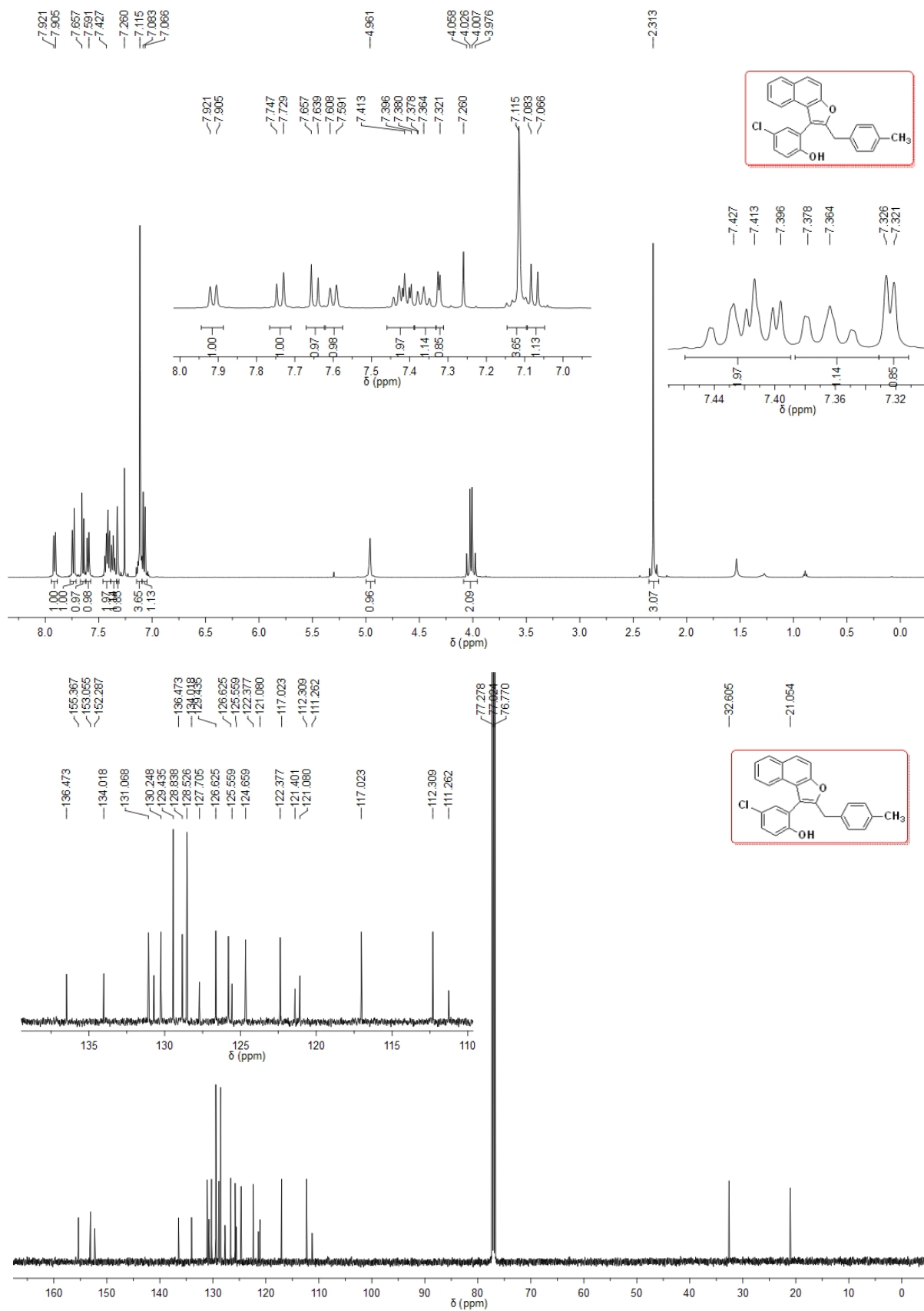
2-(2-(4-Methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenol (3ga)

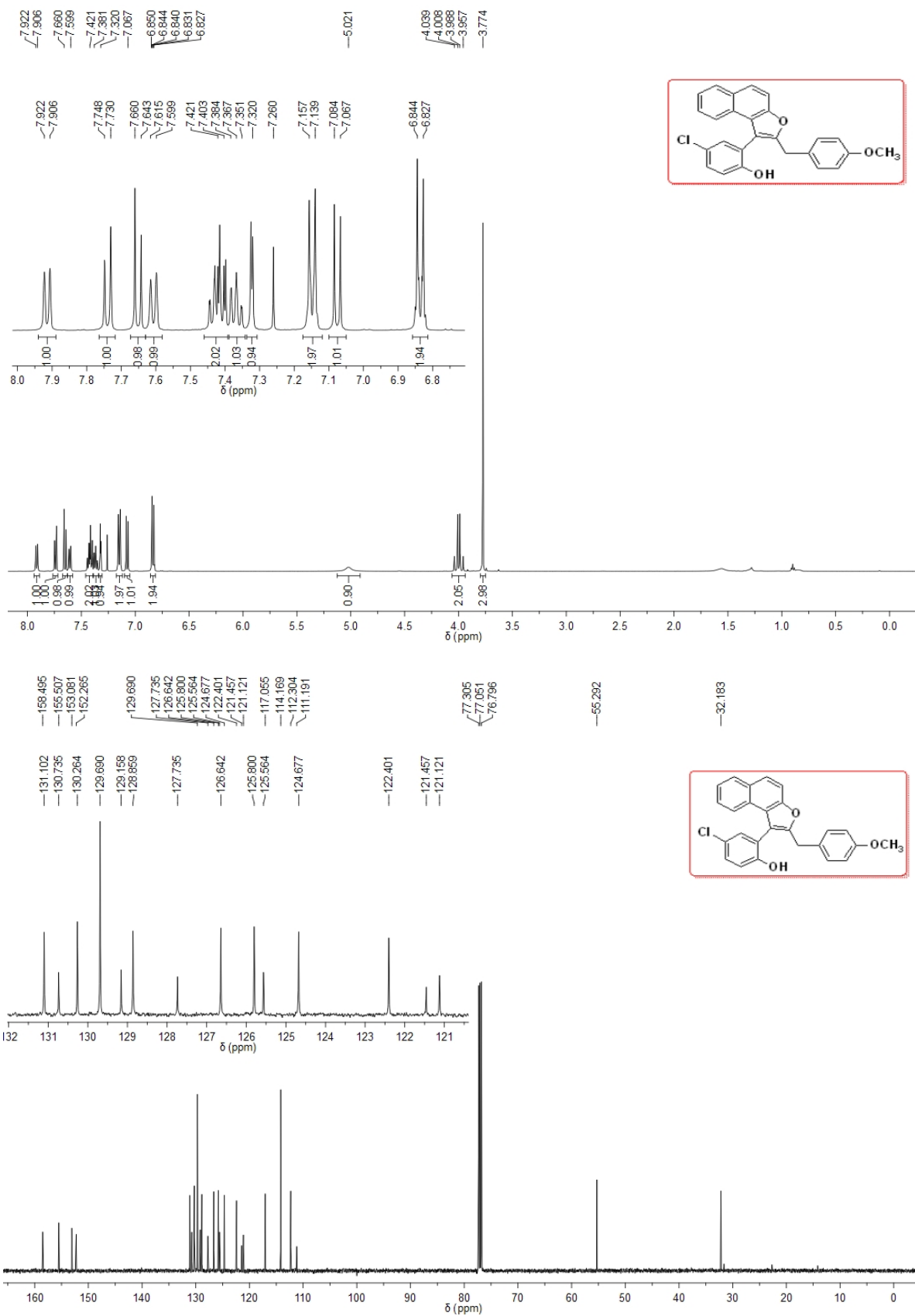
2-(2-(4-Chlorobenzyl)naphtho[2,1-b]furan-1-yl)-4-methylphenol (3ha)

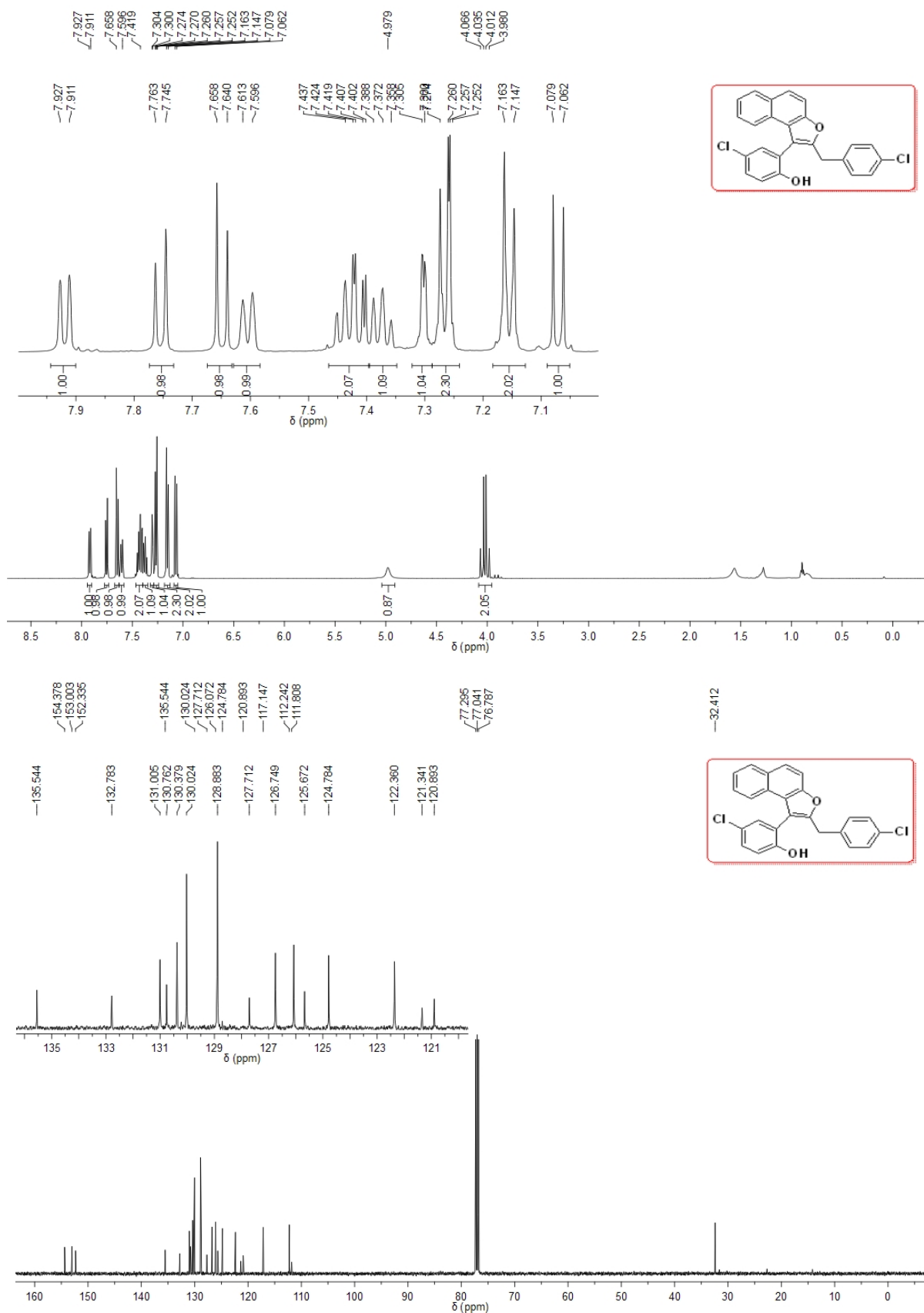


Oc1cc(Cl)ccc1C2=C(Cc3ccccc3)OC3=CC=CC=C32

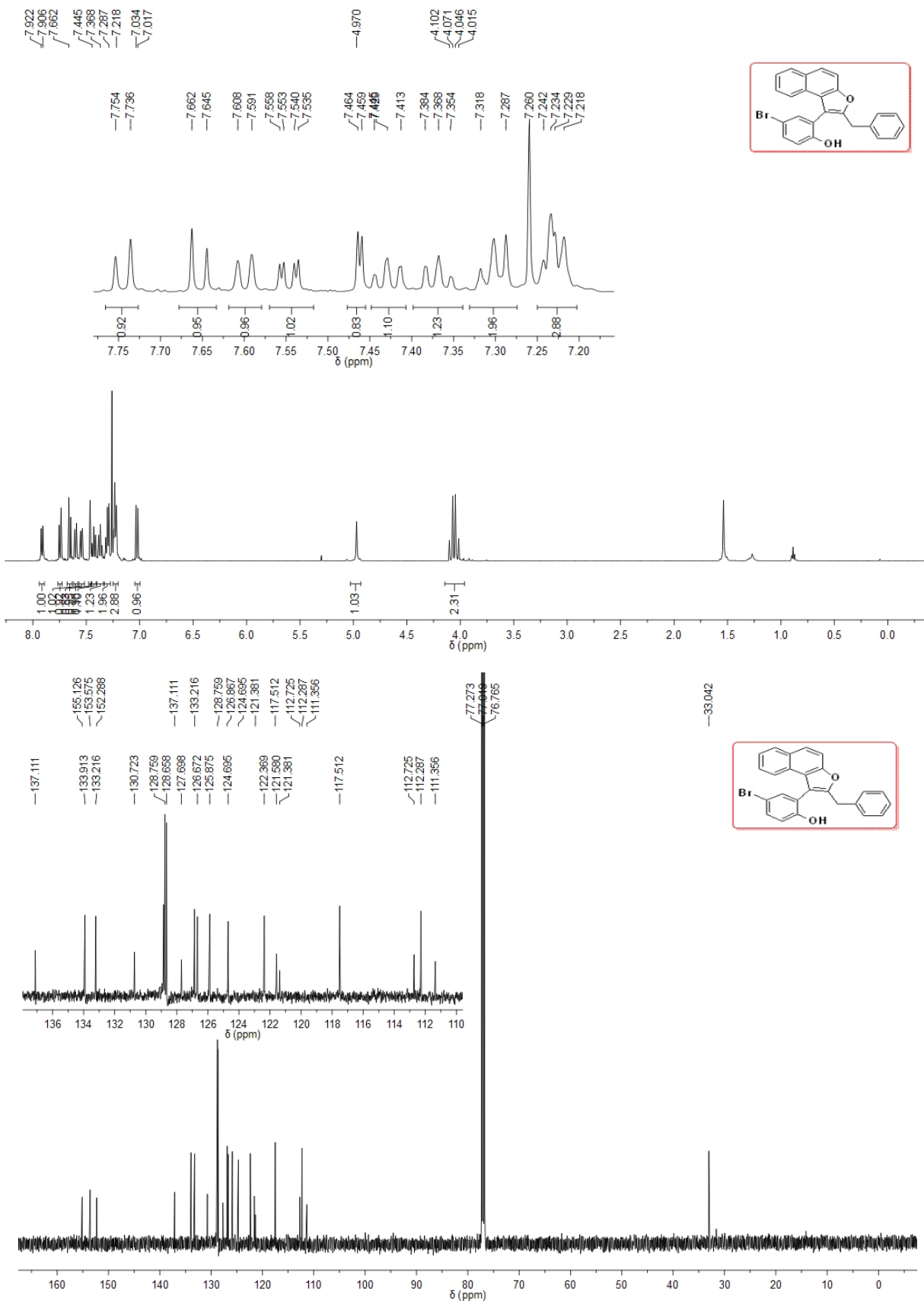
4-Chloro-2-(2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)phenol (3ja)



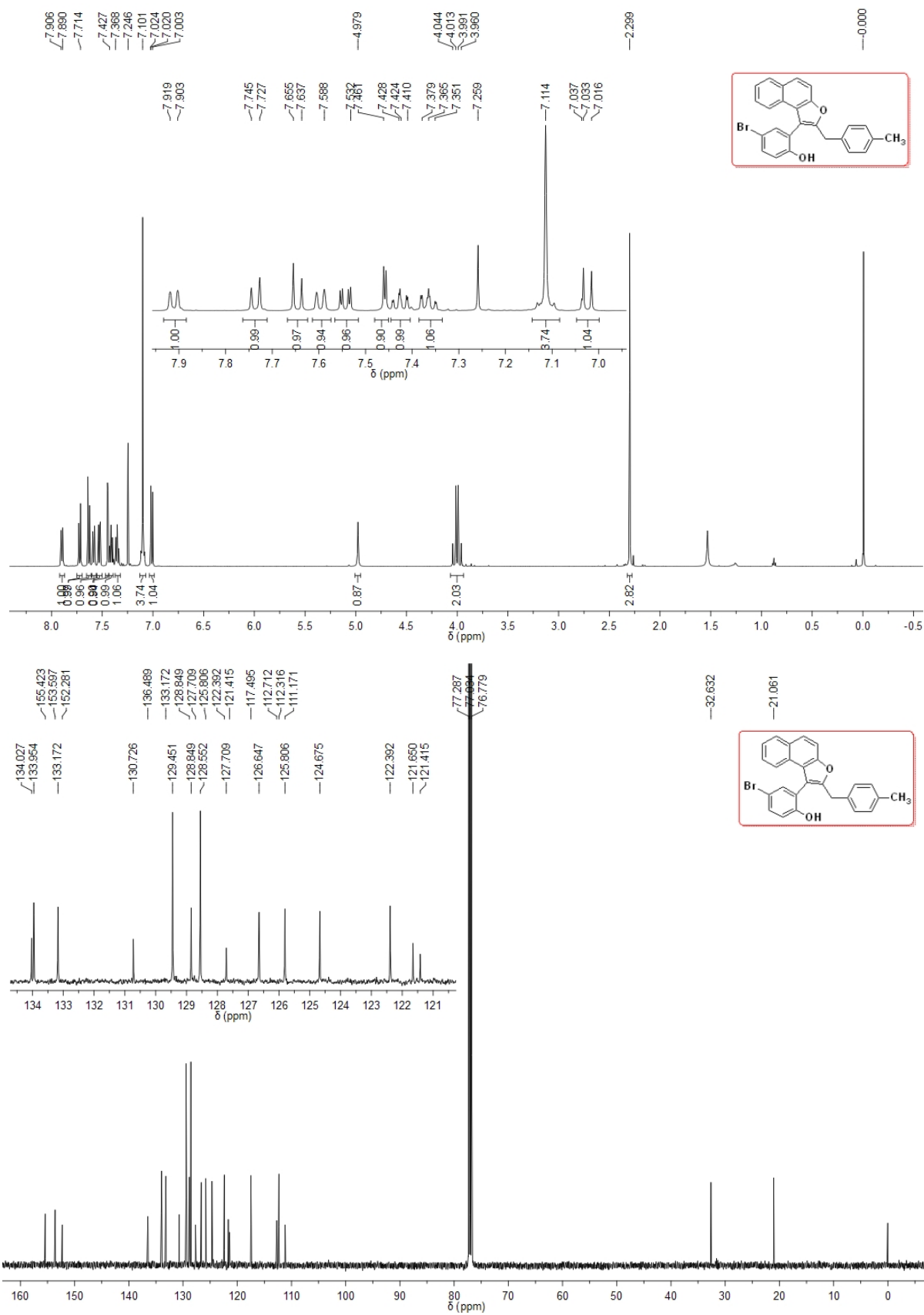
4-Chloro-2-(2-(4-methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3ka)

4-Chloro-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3la)

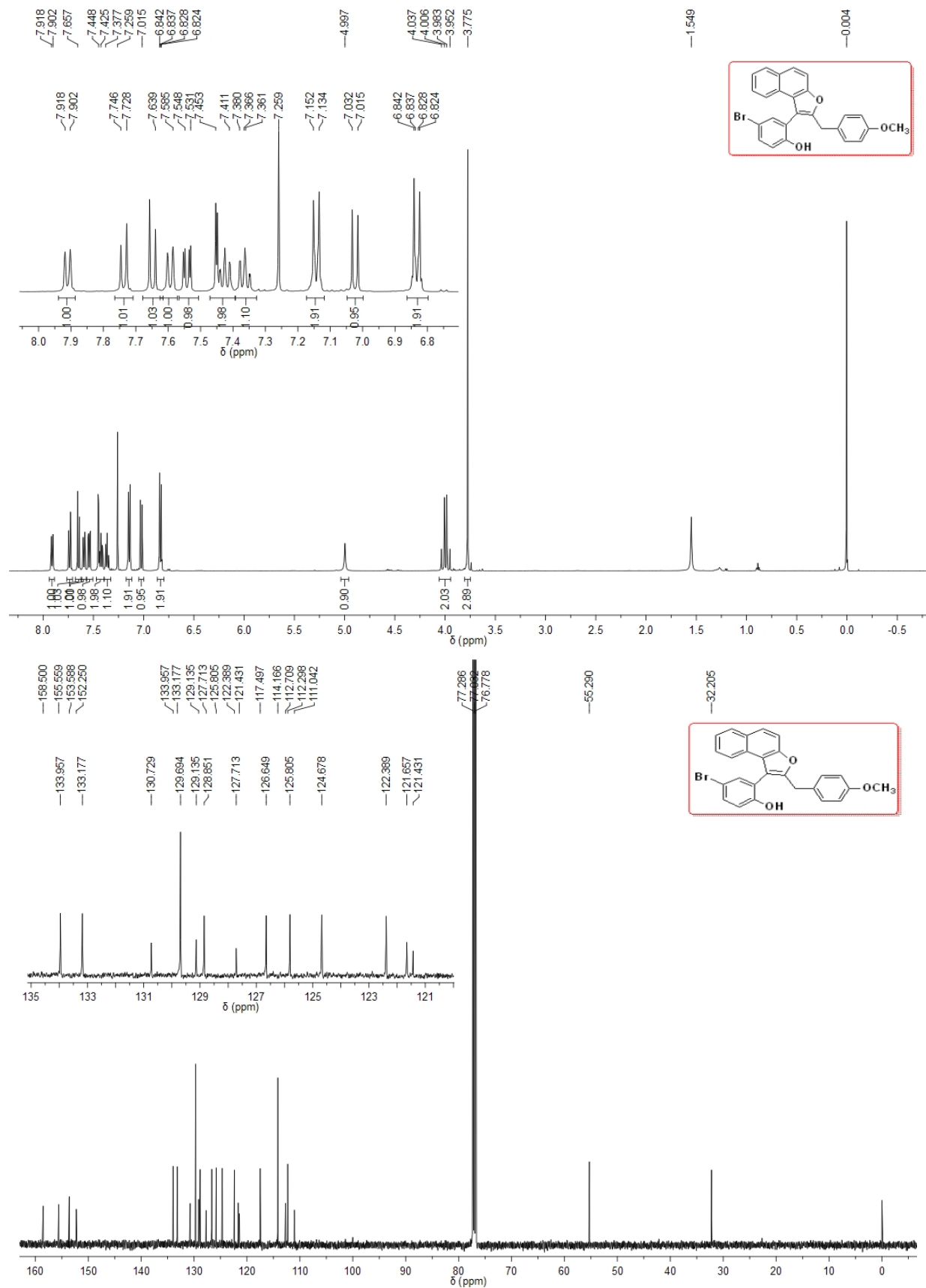
2-(2-Benzyl-4-bromophenyl)-4-hydroxy-1-benzofuran-3-yl (3ma)

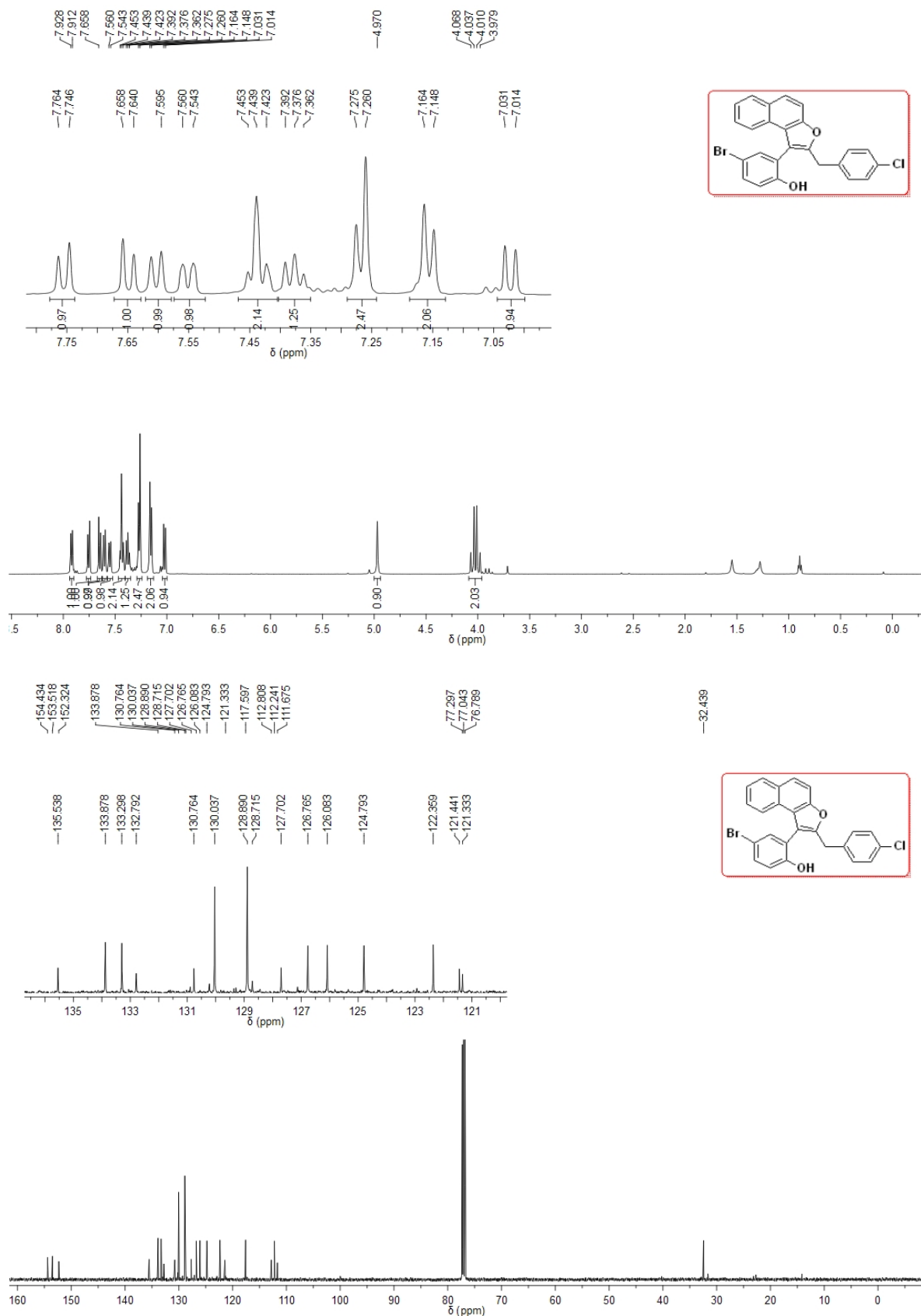


4-Bromo-2-(2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)phenol (3na)



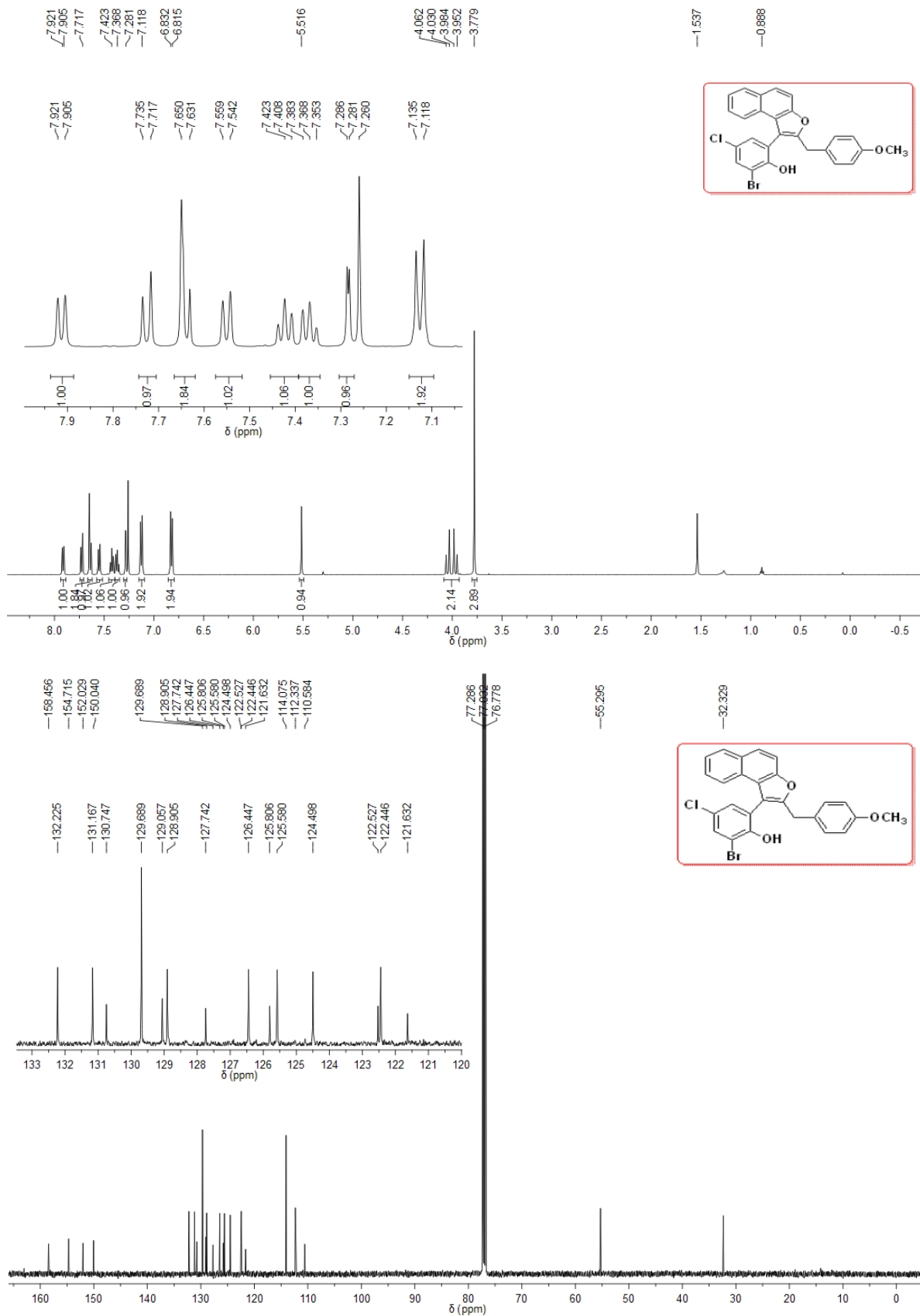
4-Bromo-2-(2-(4-methoxybenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (30a)

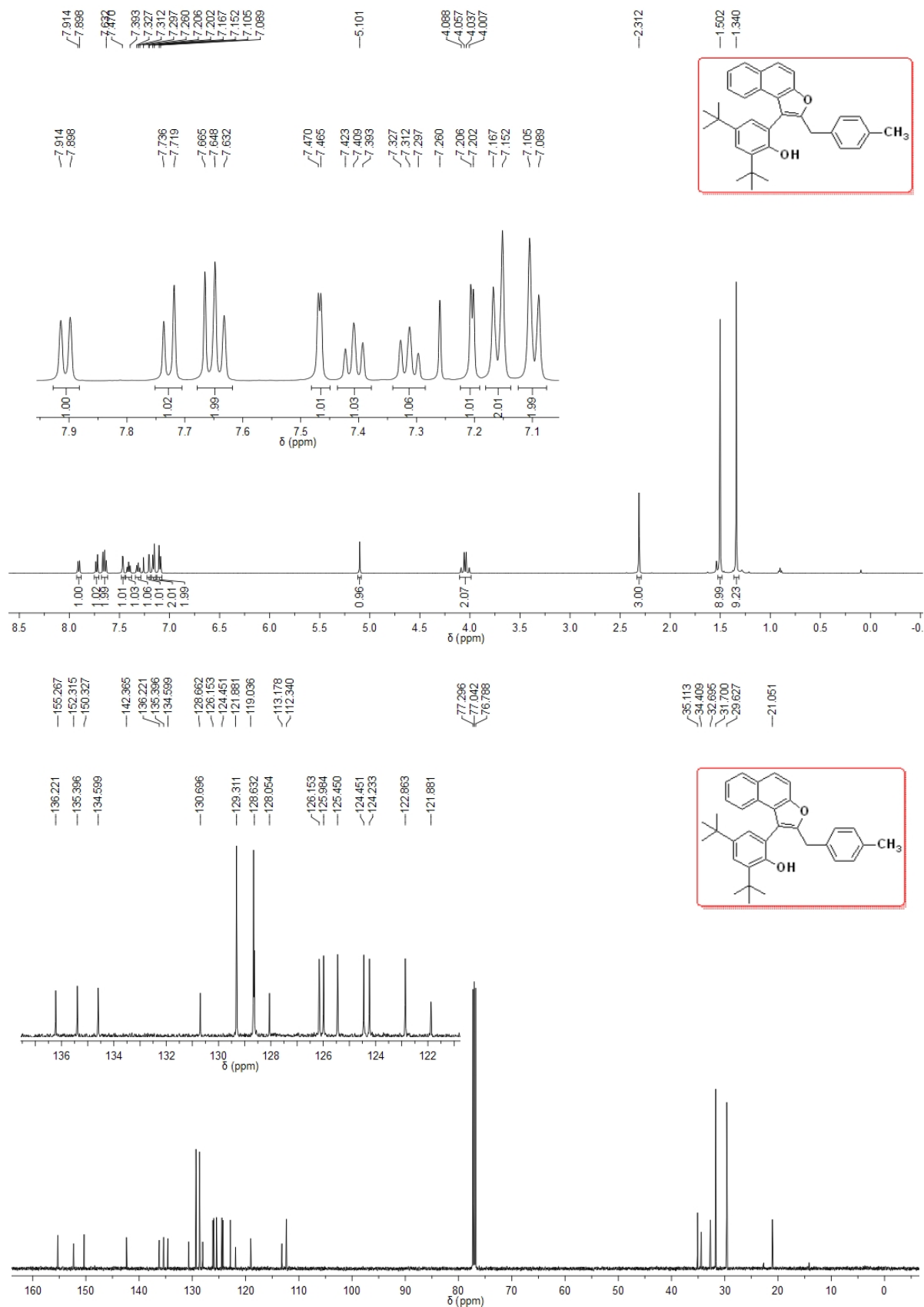


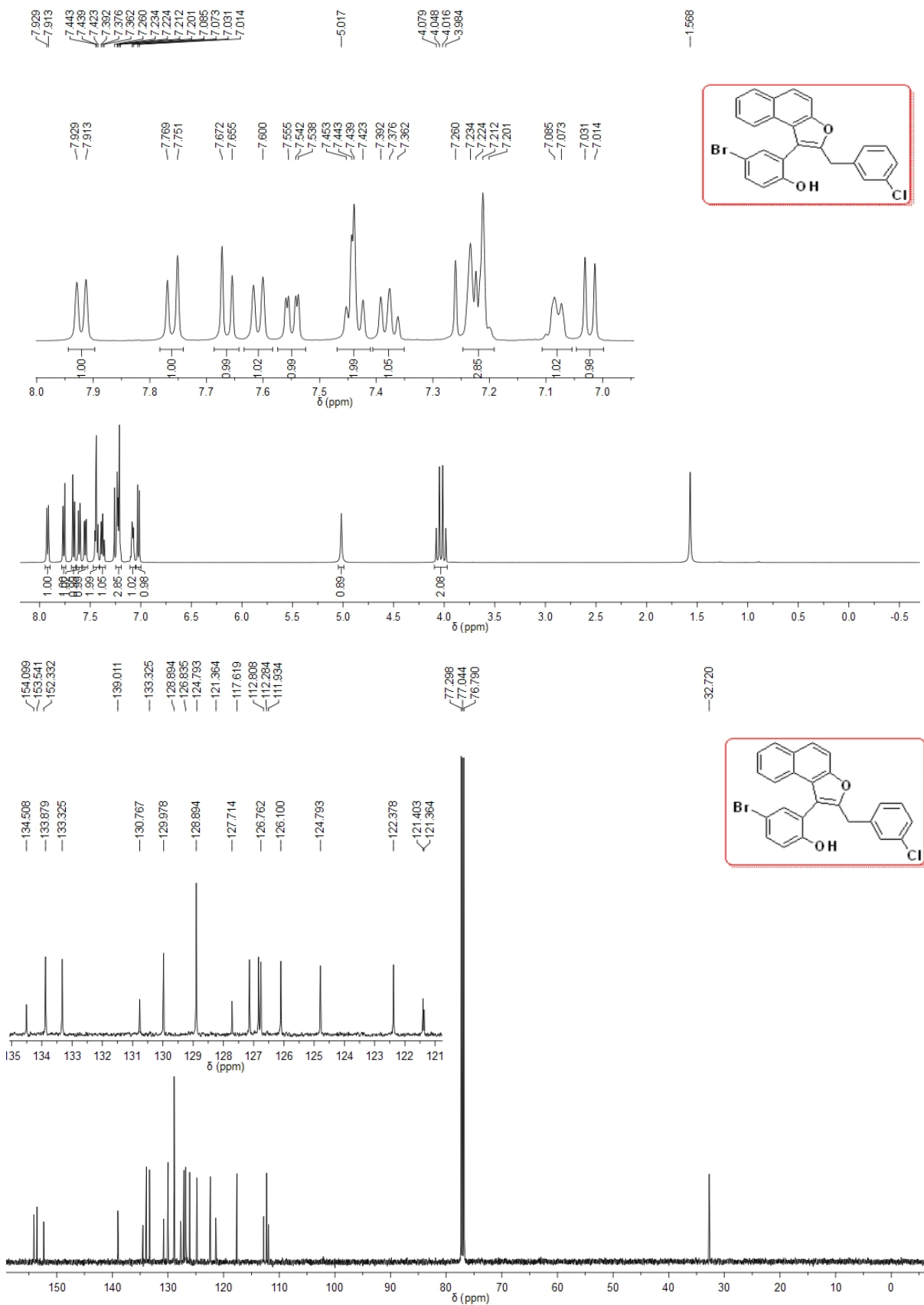
4-Bromo-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3pa)

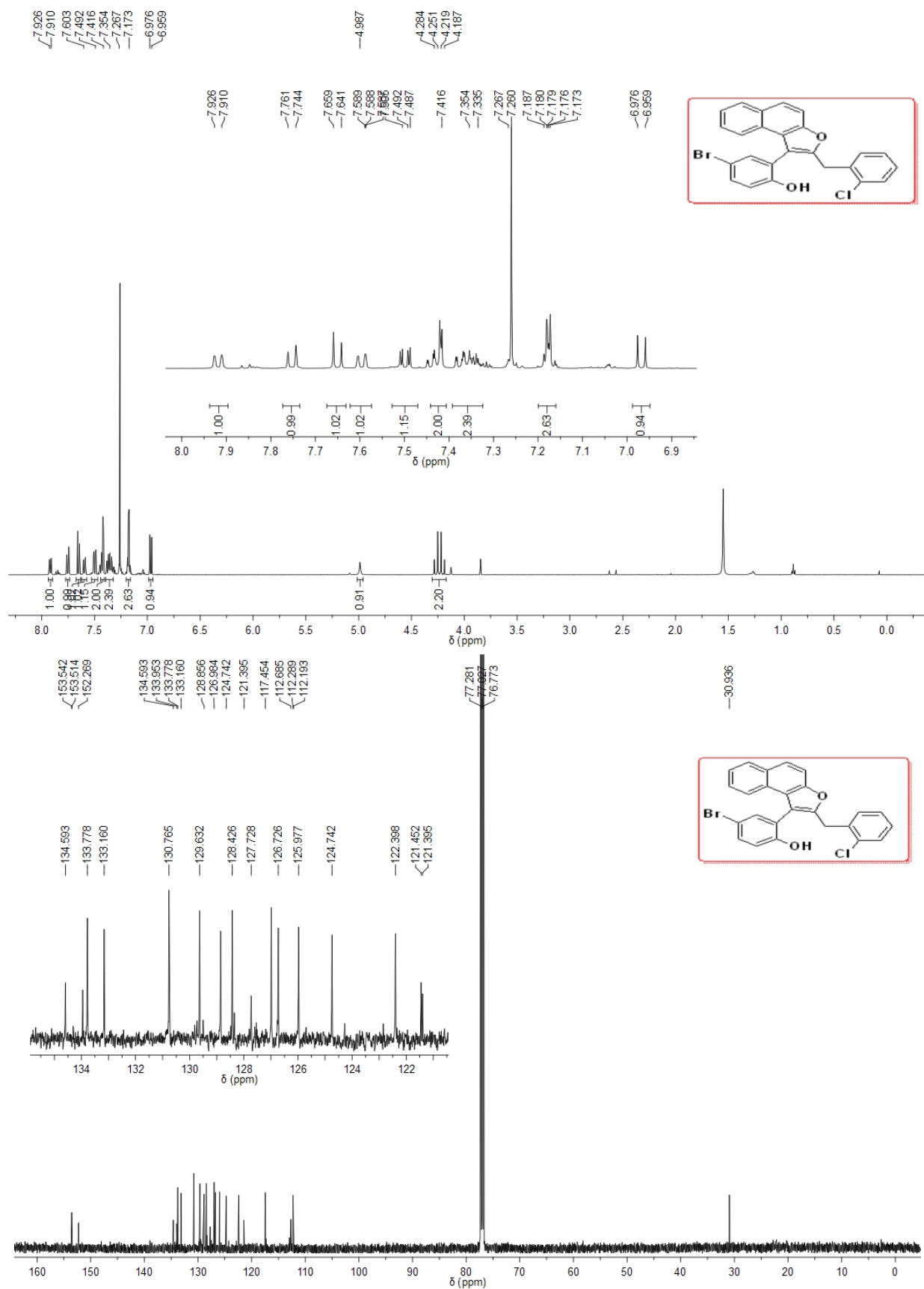


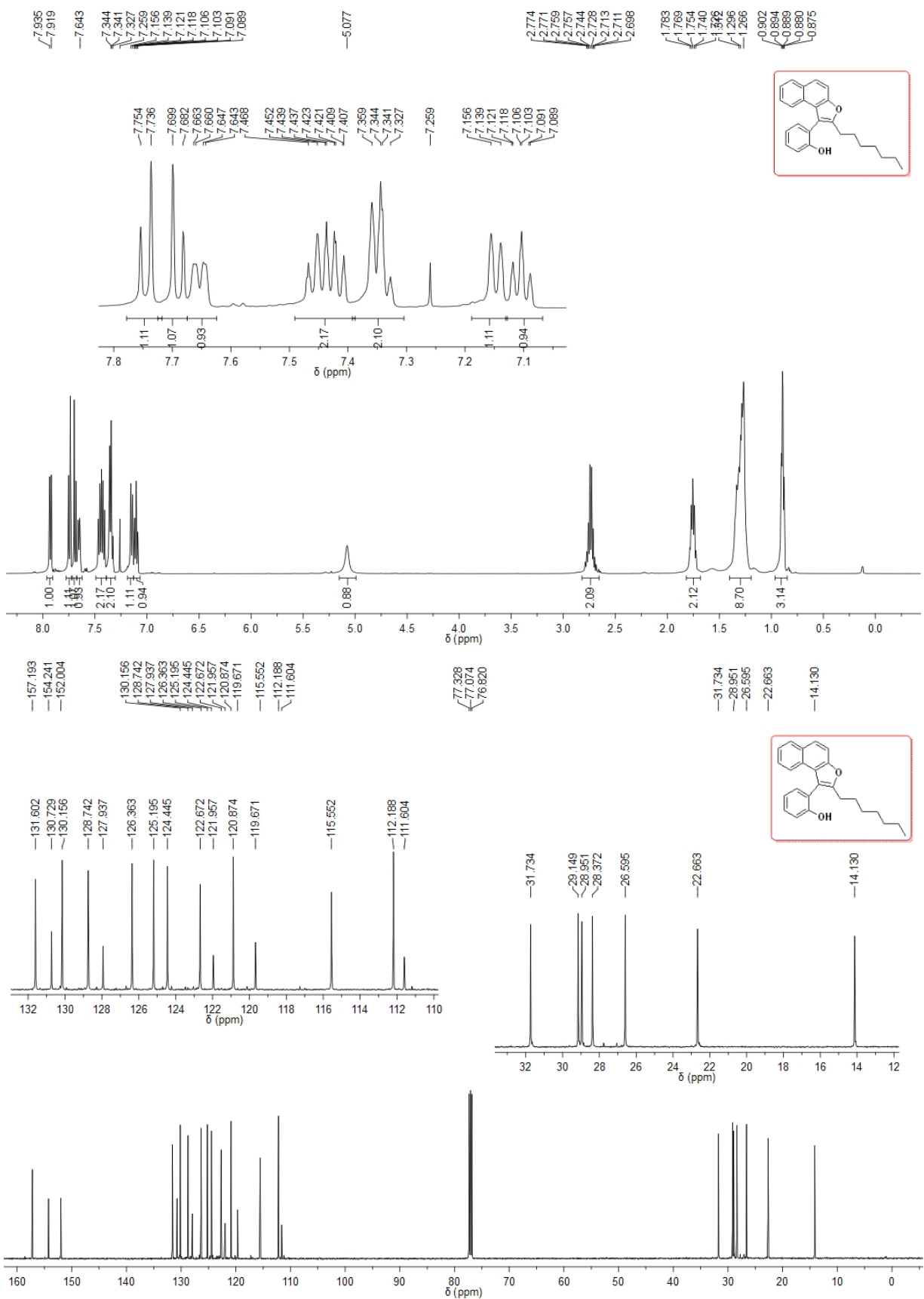
2-Bromo-4-chloro-6-(2-(4-methoxybenzyl)naphtho[2,1-b]furan-1-yl)phenol (3ra)



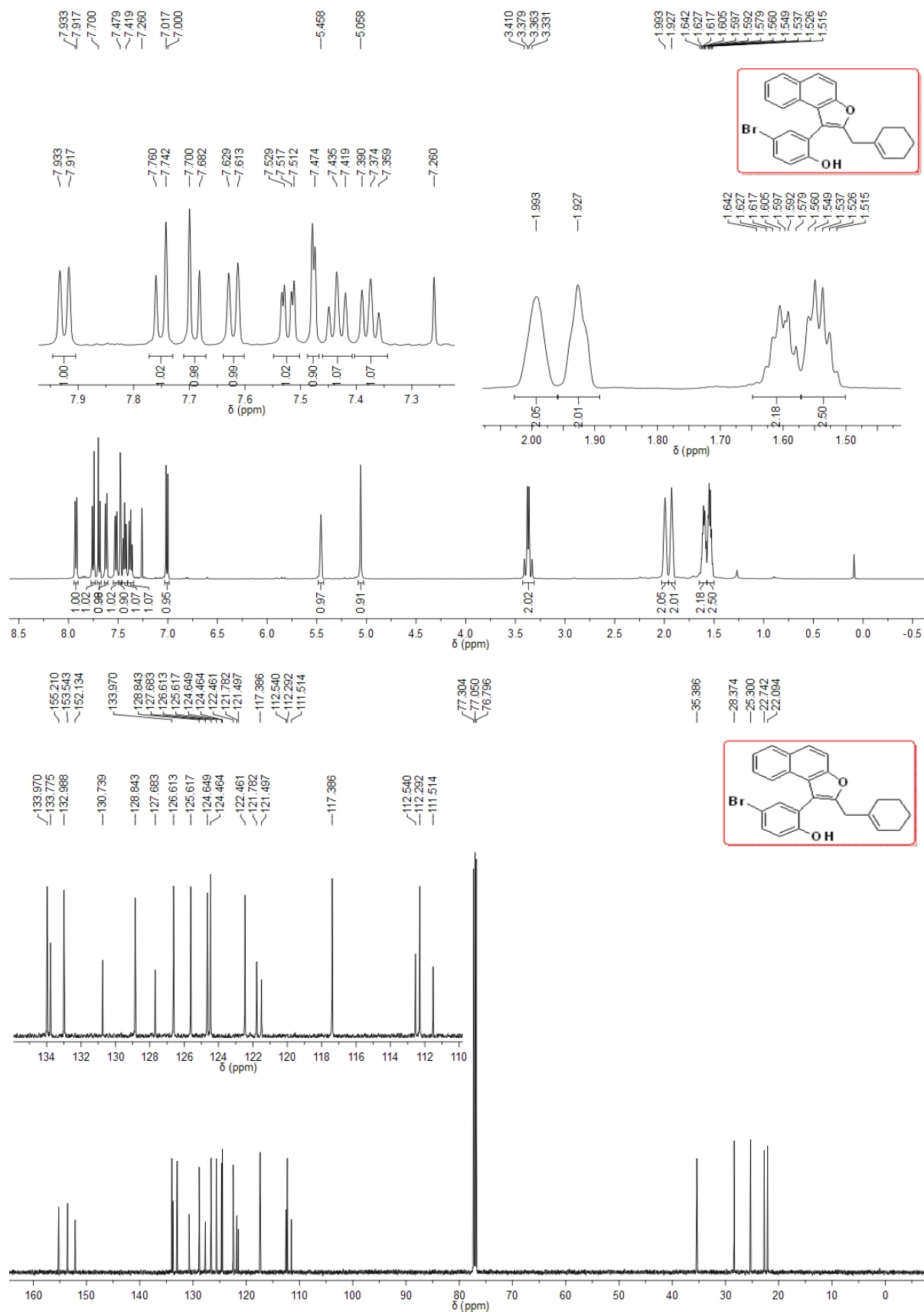
2,4-Di-*tert*-butyl-6-(2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3sa)

4-Bromo-2-(2-(3-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3ta)

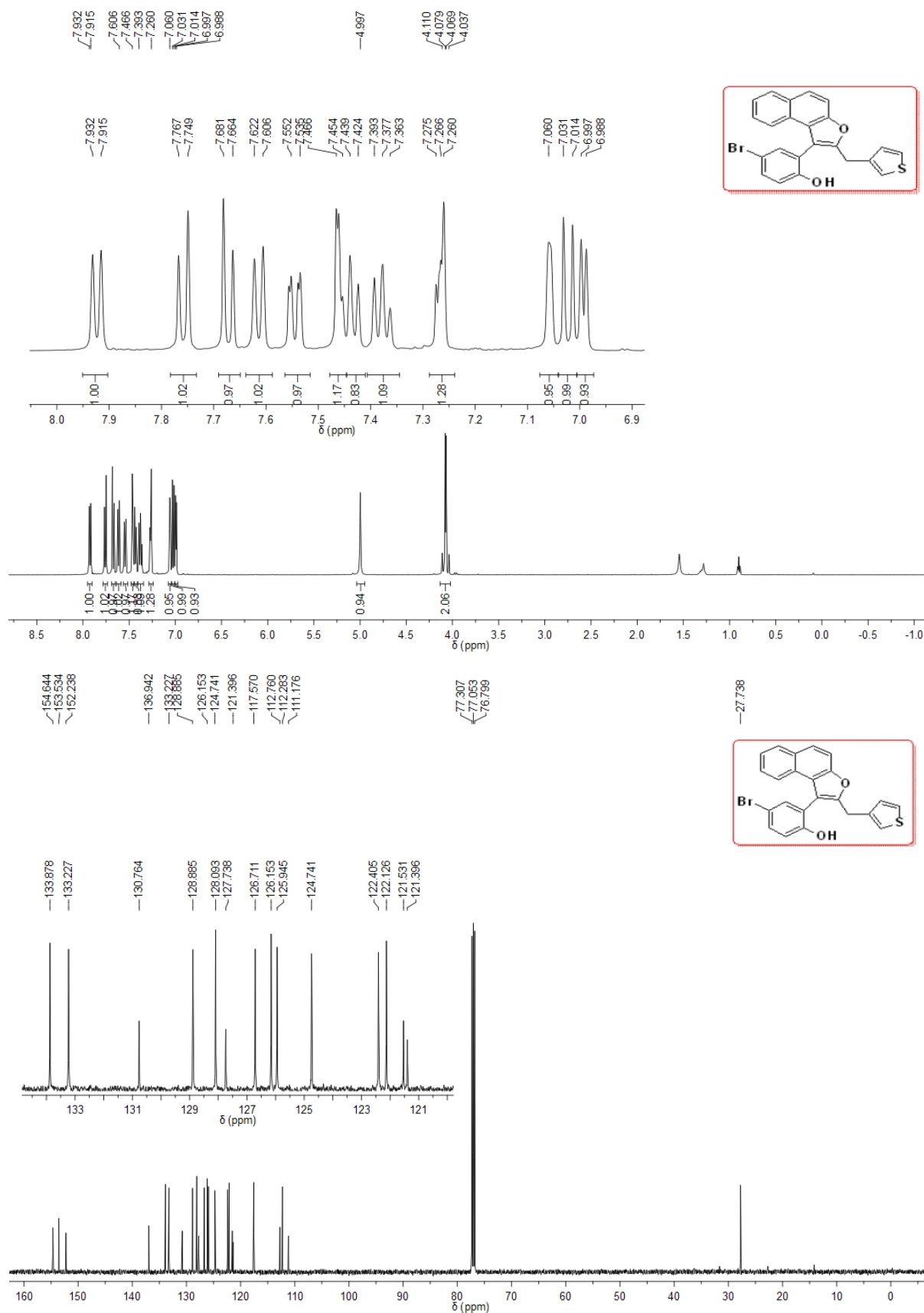
4-Bromo-2-(2-(2-chlorobenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3ua)

4-Bromo-2-(2-heptylnaphtho[2,1-*b*]furan-1-yl)phenol (3wa)

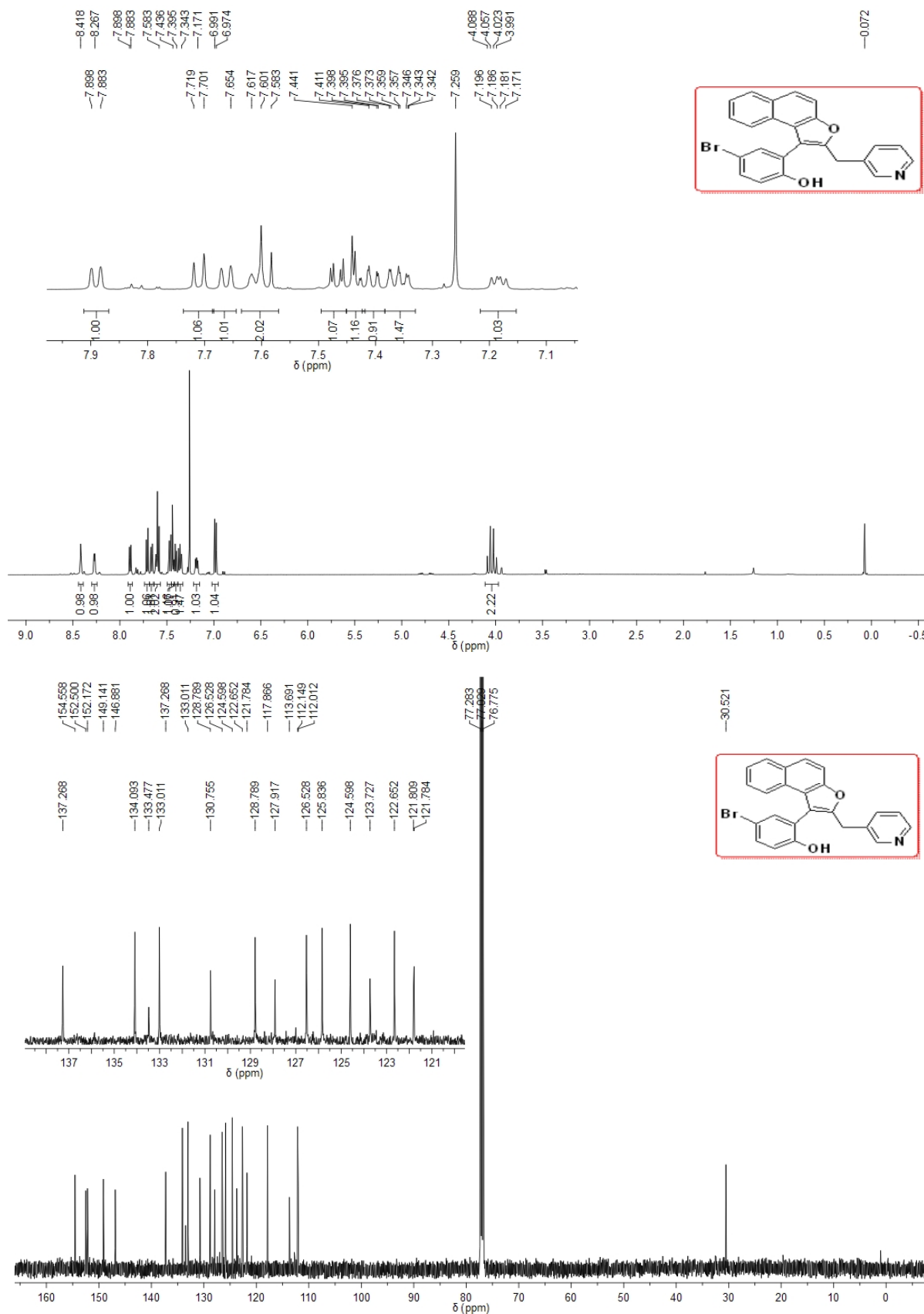
4-Bromo-2-(2-(cyclohex-1-en-1-ylmethyl)naphtho[2,1-b]furan-1-yl)phenol (3xa)

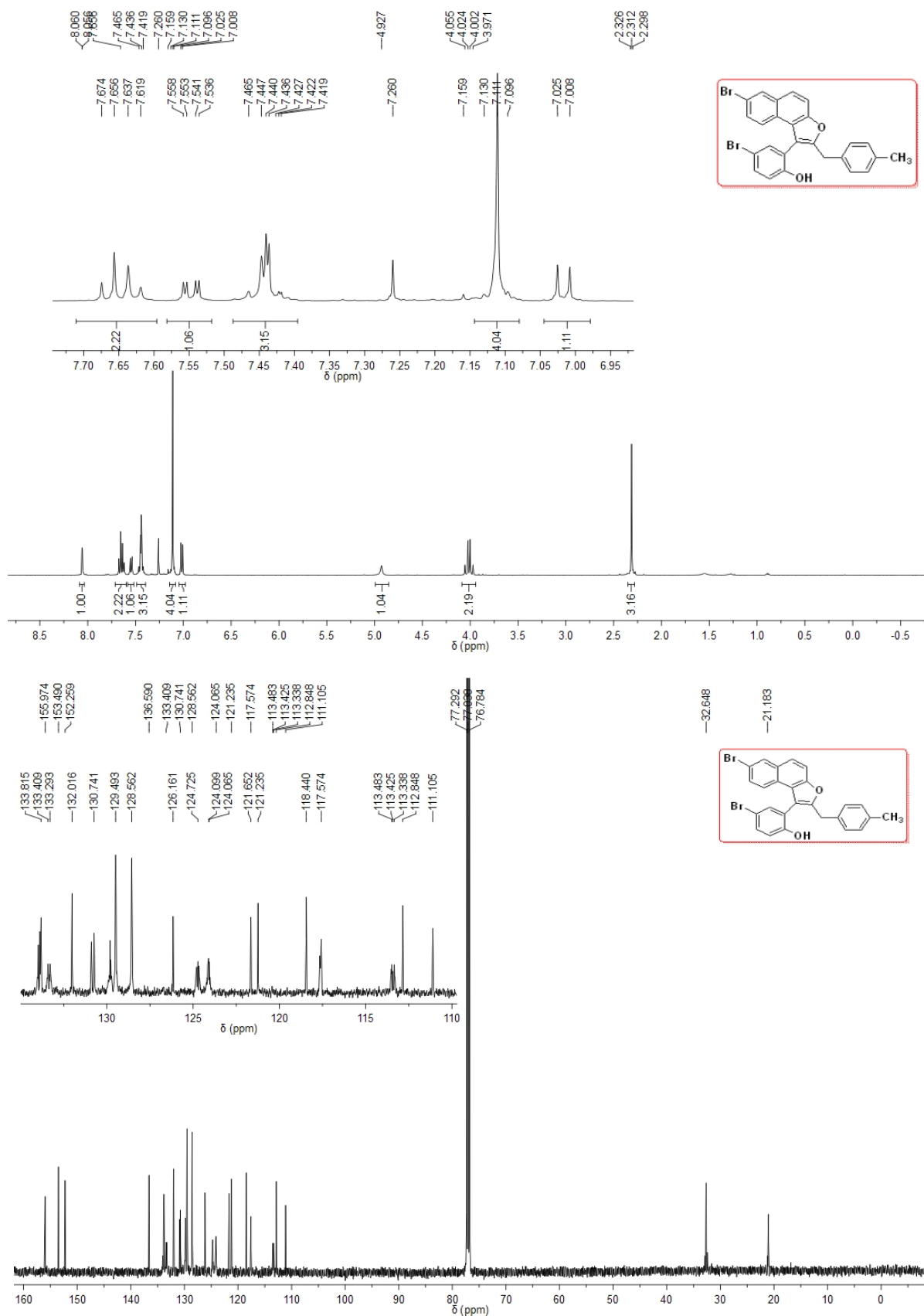


4-Bromo-2-(2-(thiophen-3-ylmethyl)naphtho[2,1-b]furan-1-yl)phenol (3ya)

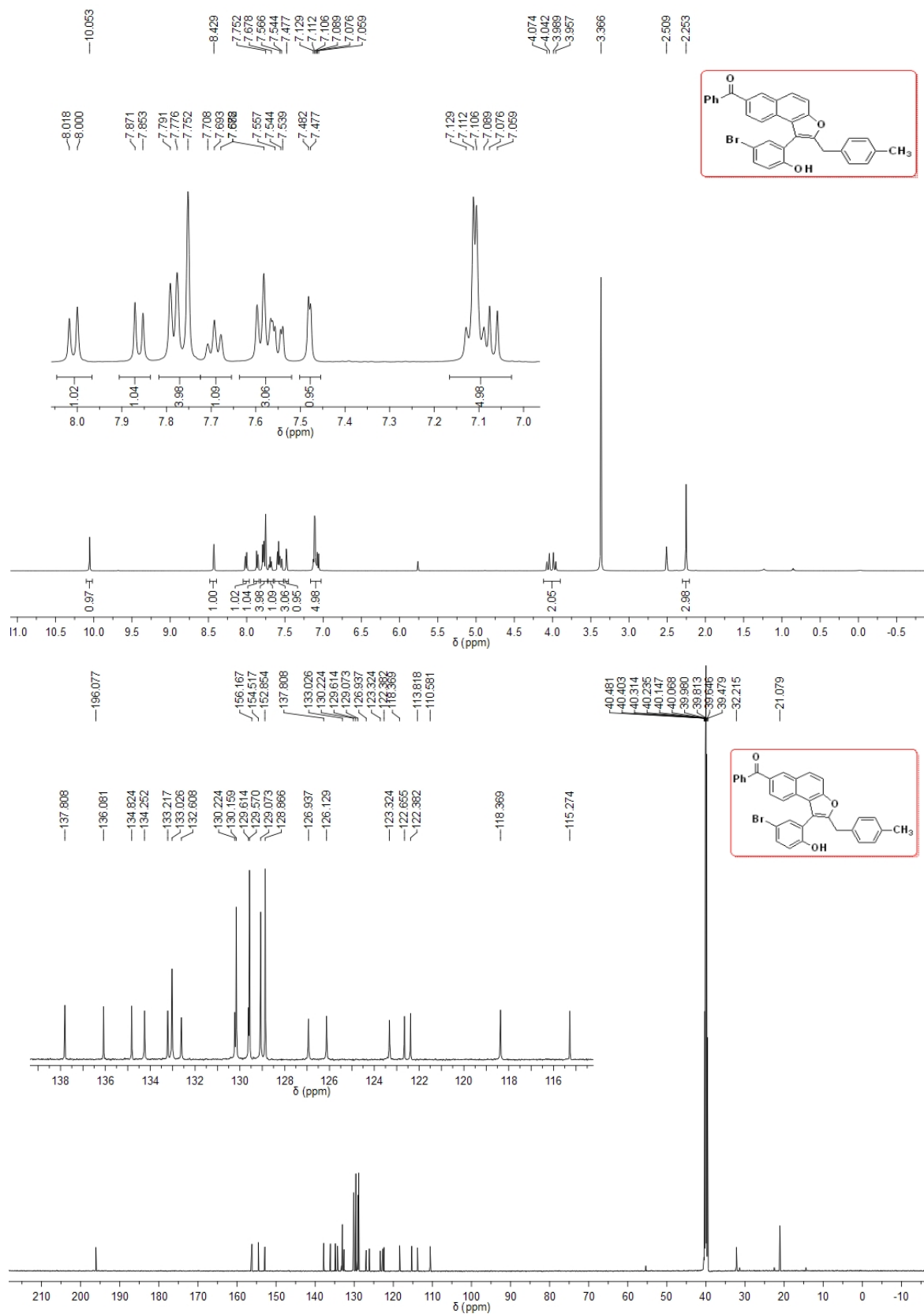


4-Bromo-2-(2-(pyridin-3-ylmethyl)naphtho[2,1-b]furan-1-yl)phenol (3a)



4-Bromo-2-(7-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3nb)

(1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-7-yl)(phenyl) methanone
(3nc)

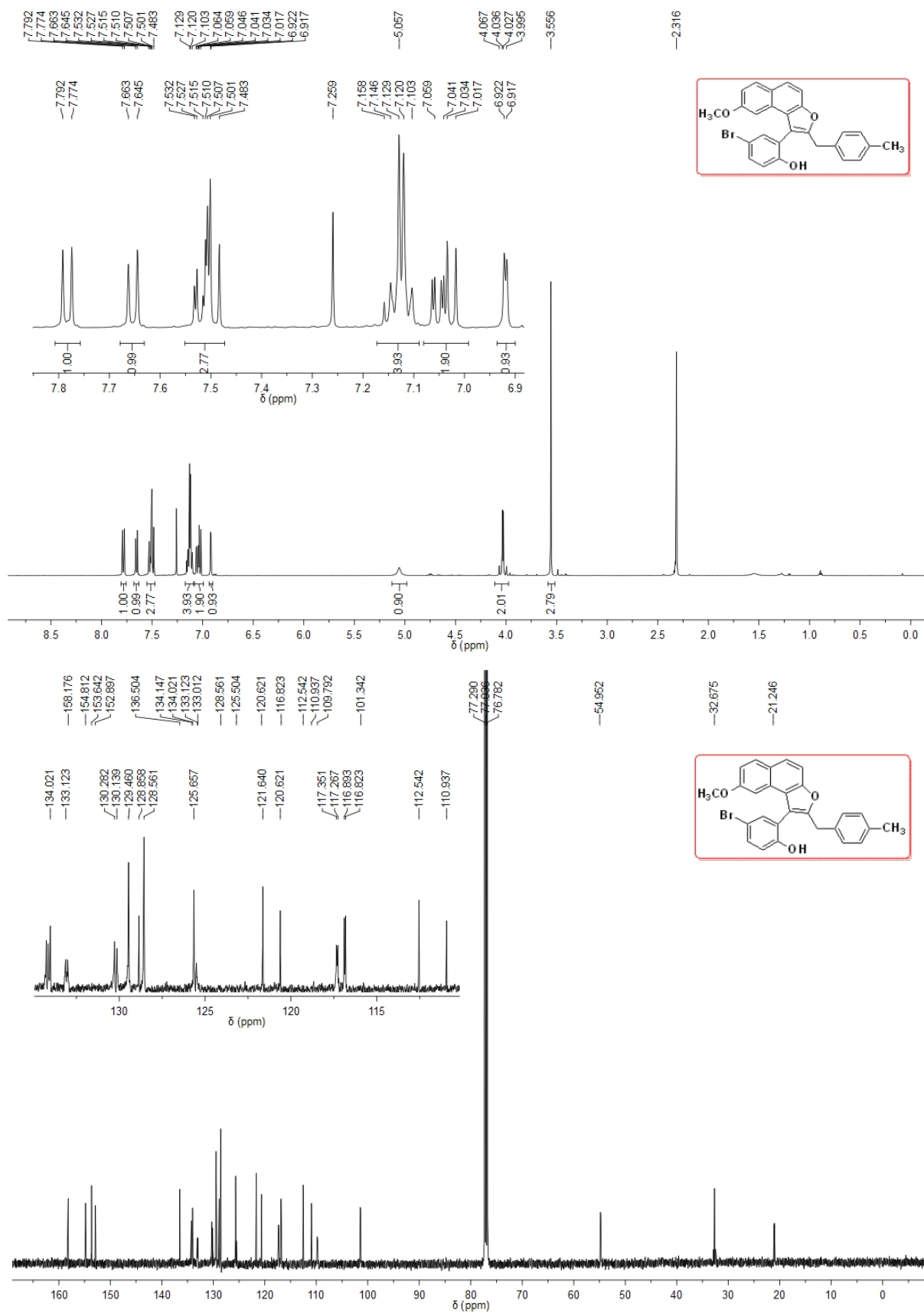


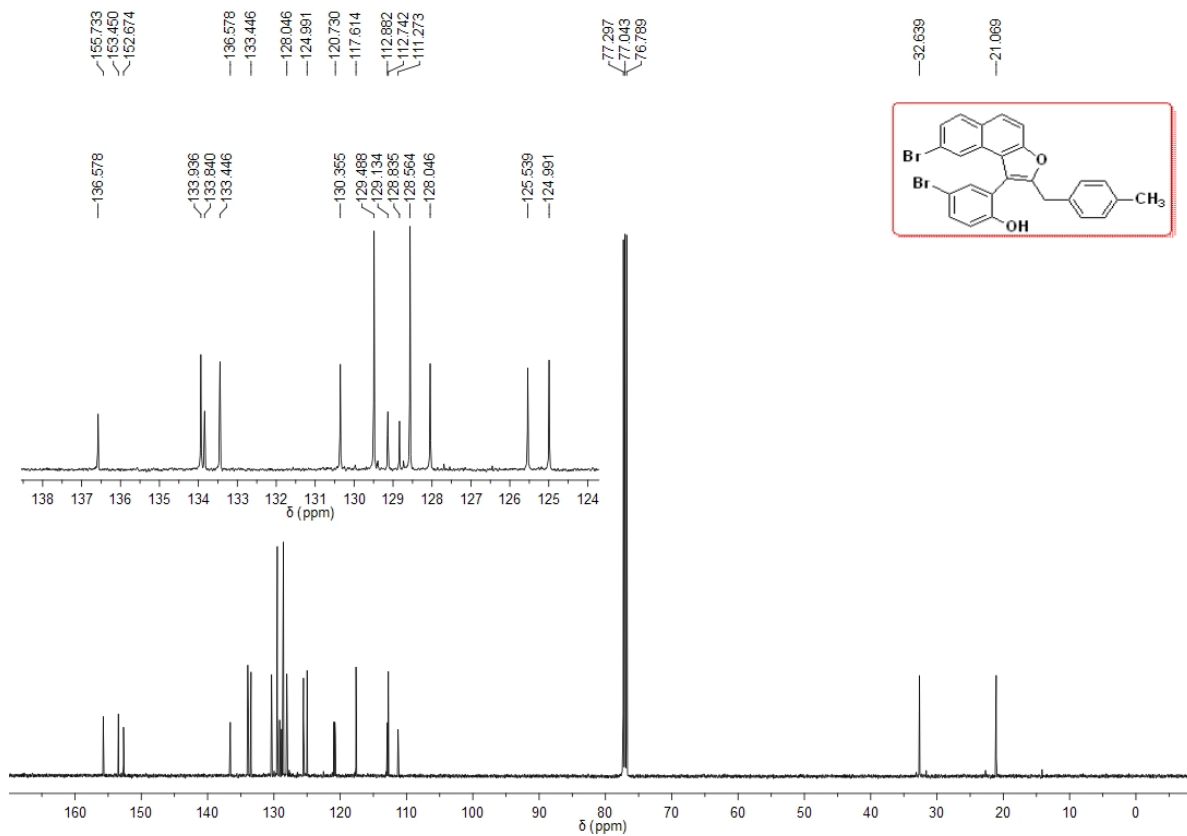
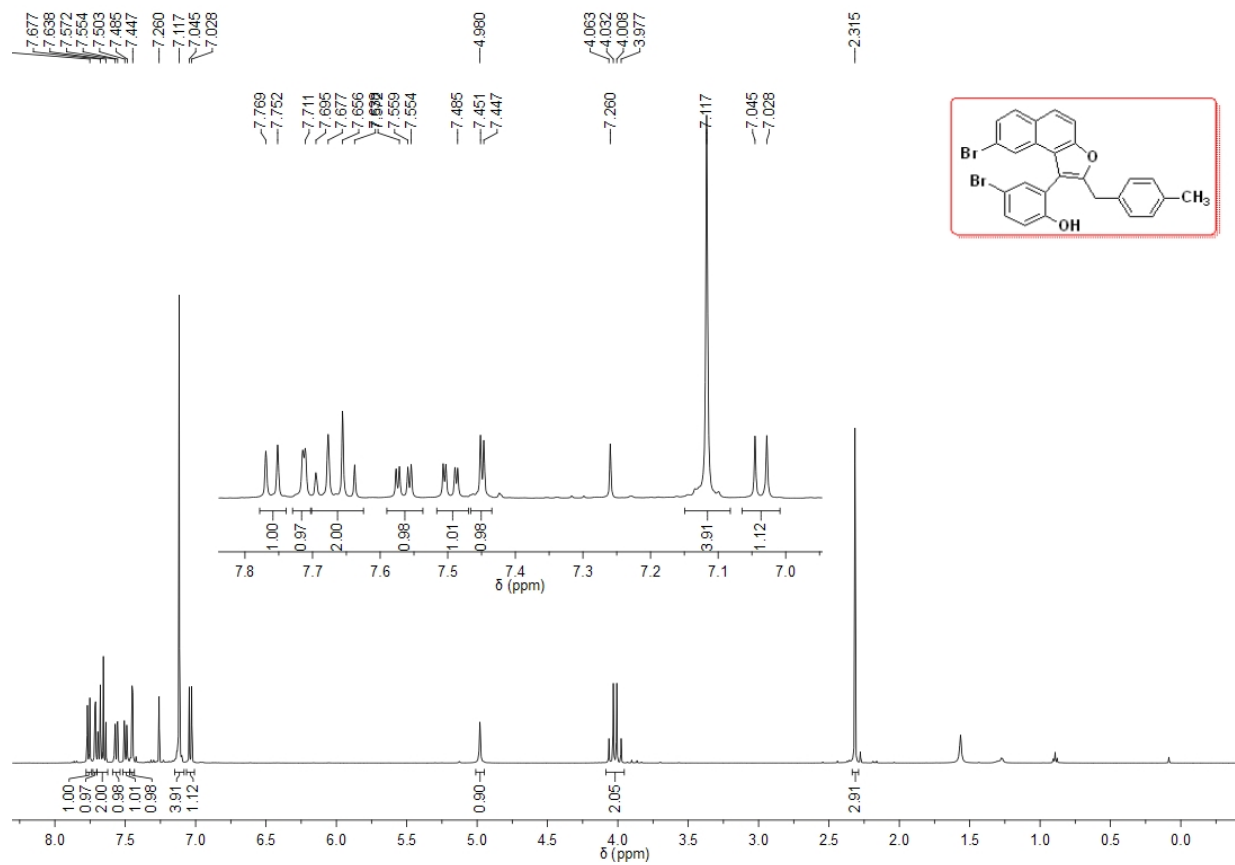
1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-b]furan-7-carbonitrile (3nd)

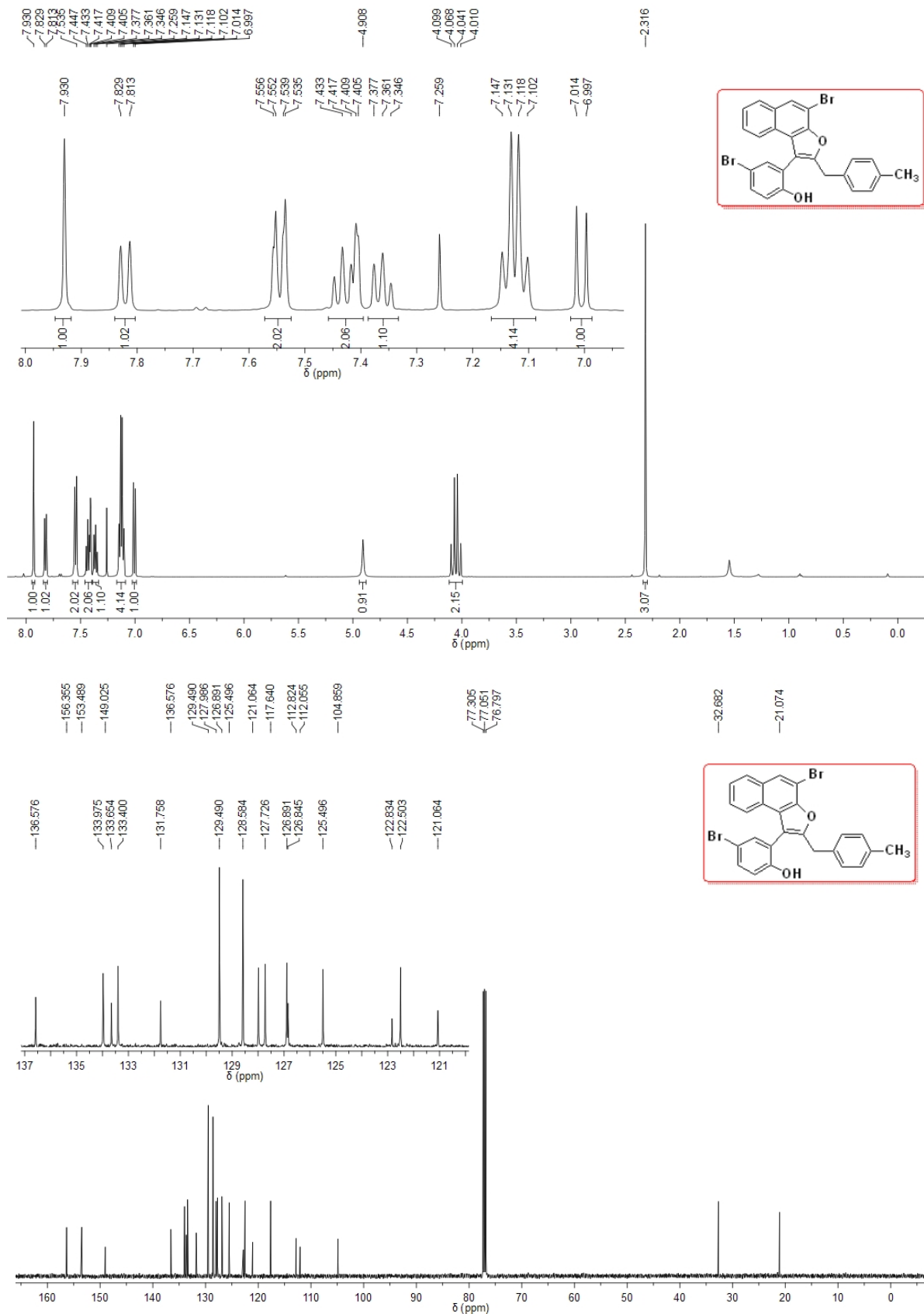


1-(5-Bromo-2-hydroxyphenyl)-2-(4-methylbenzyl)naphtho[2,1-b]furan-7-carboxylic acid (3ne)

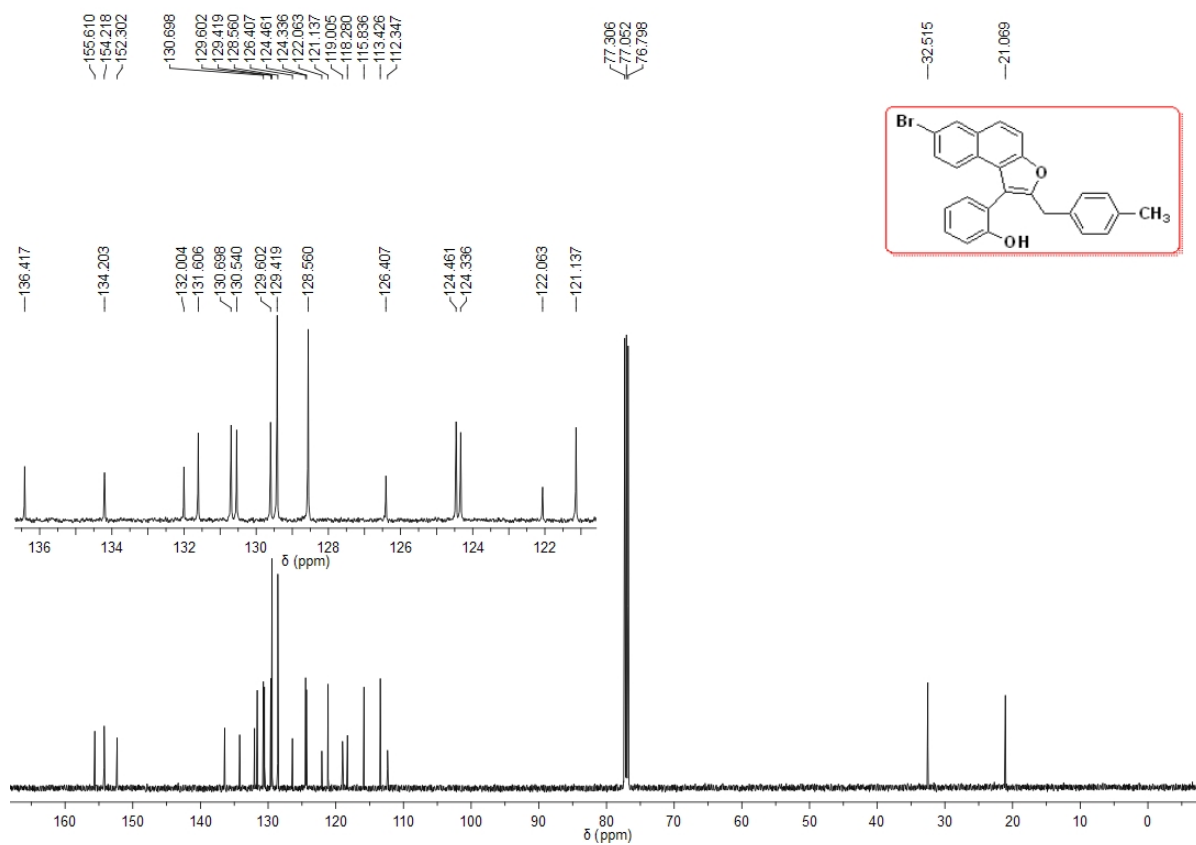
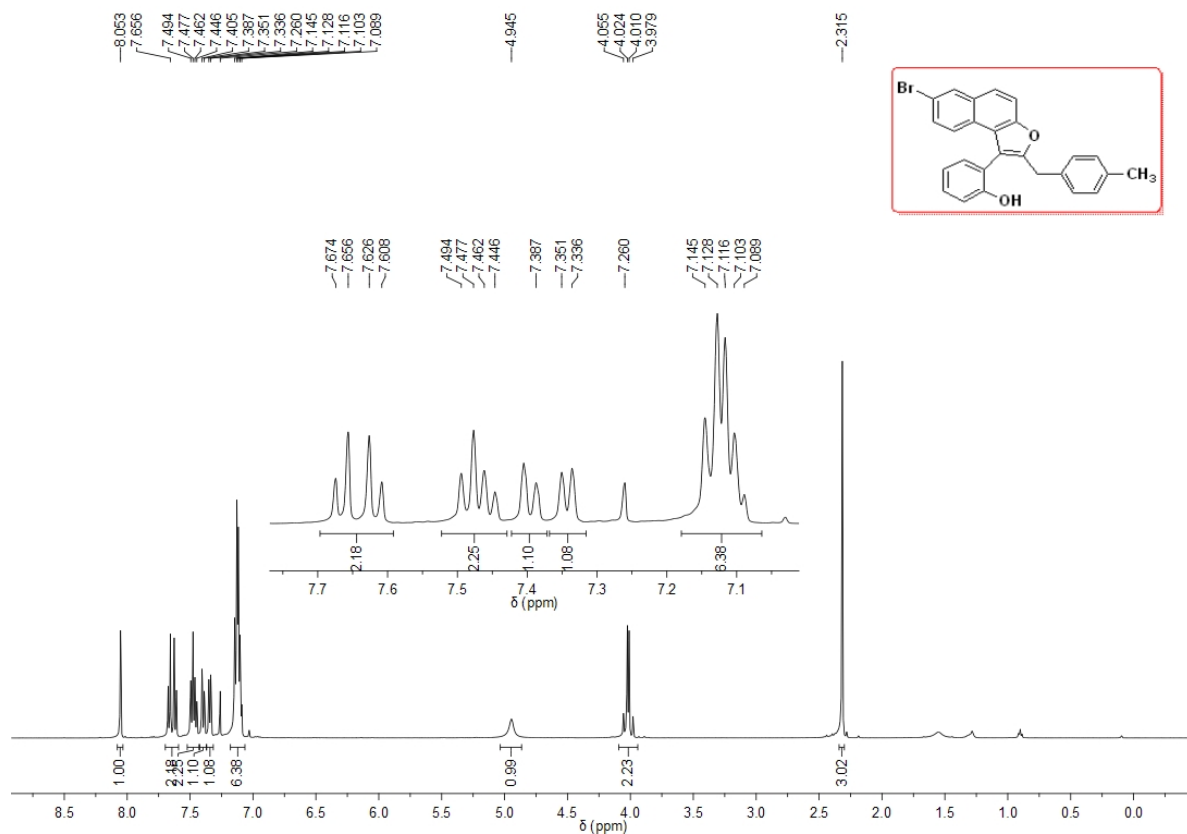


4-Bromo-2-(8-methoxy-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3nf)

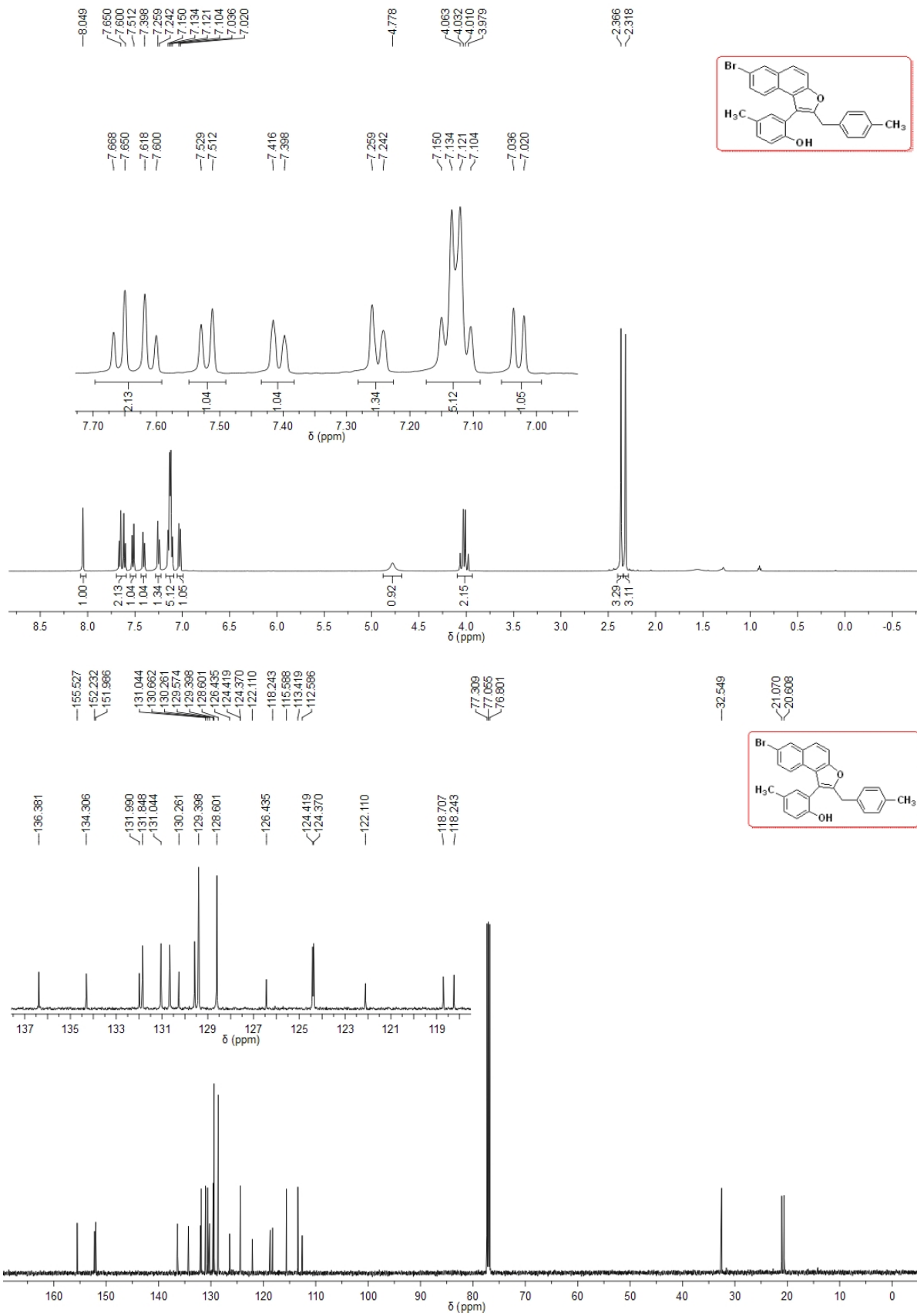
4-Bromo-2-(8-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3ng)

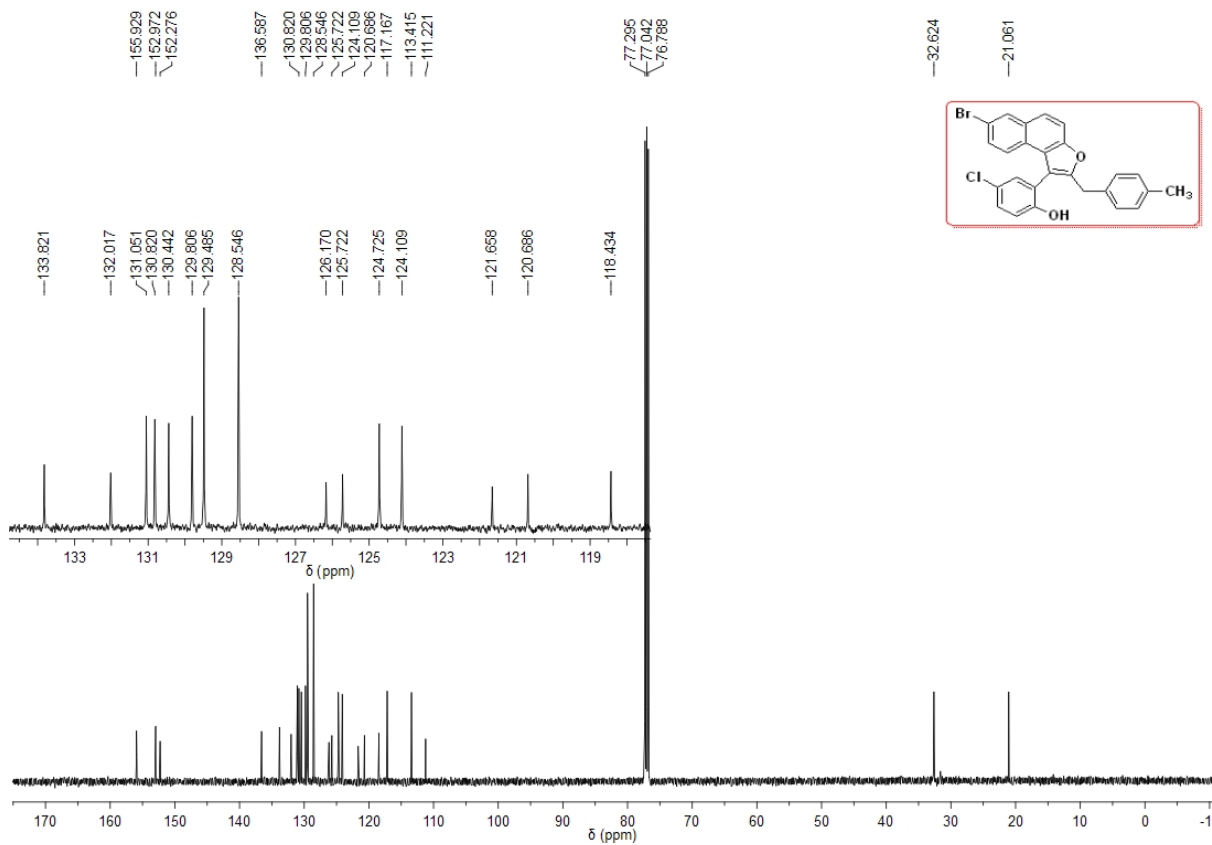
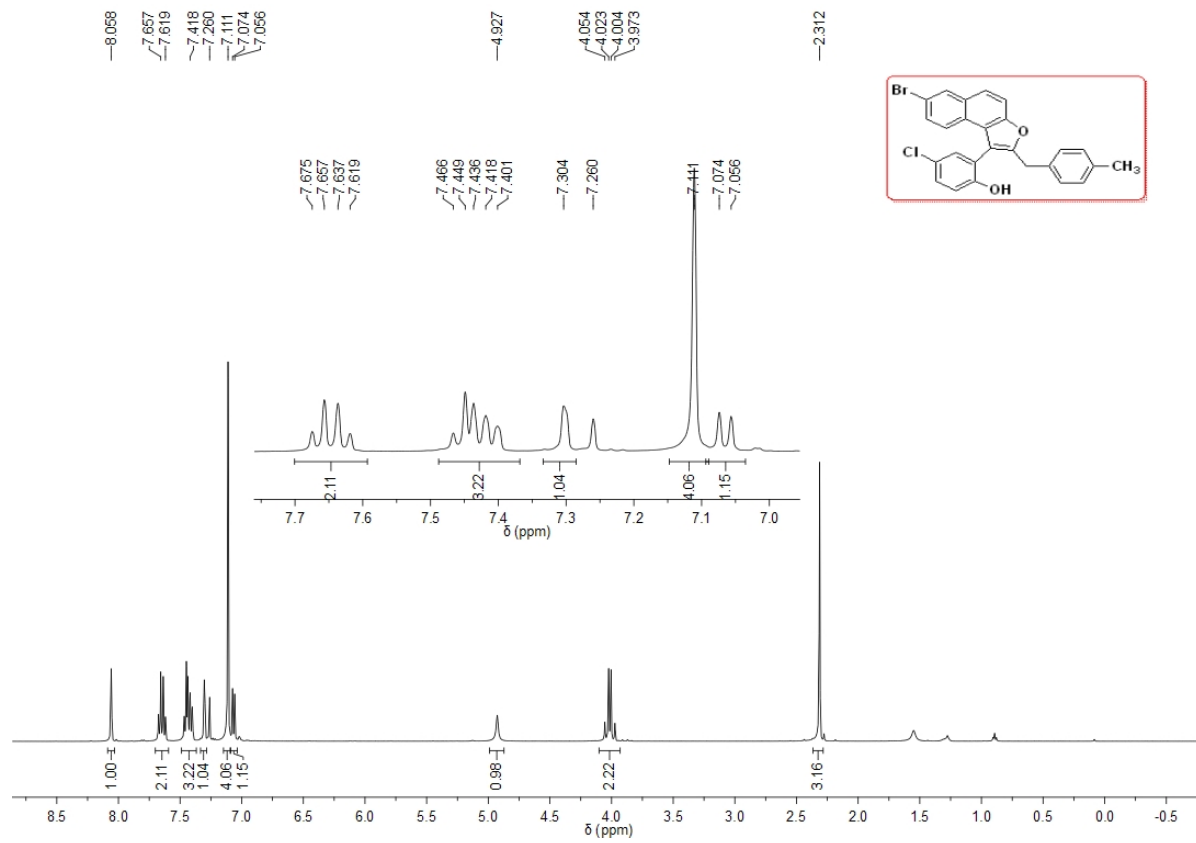
4-Bromo-2-(4-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3nh)

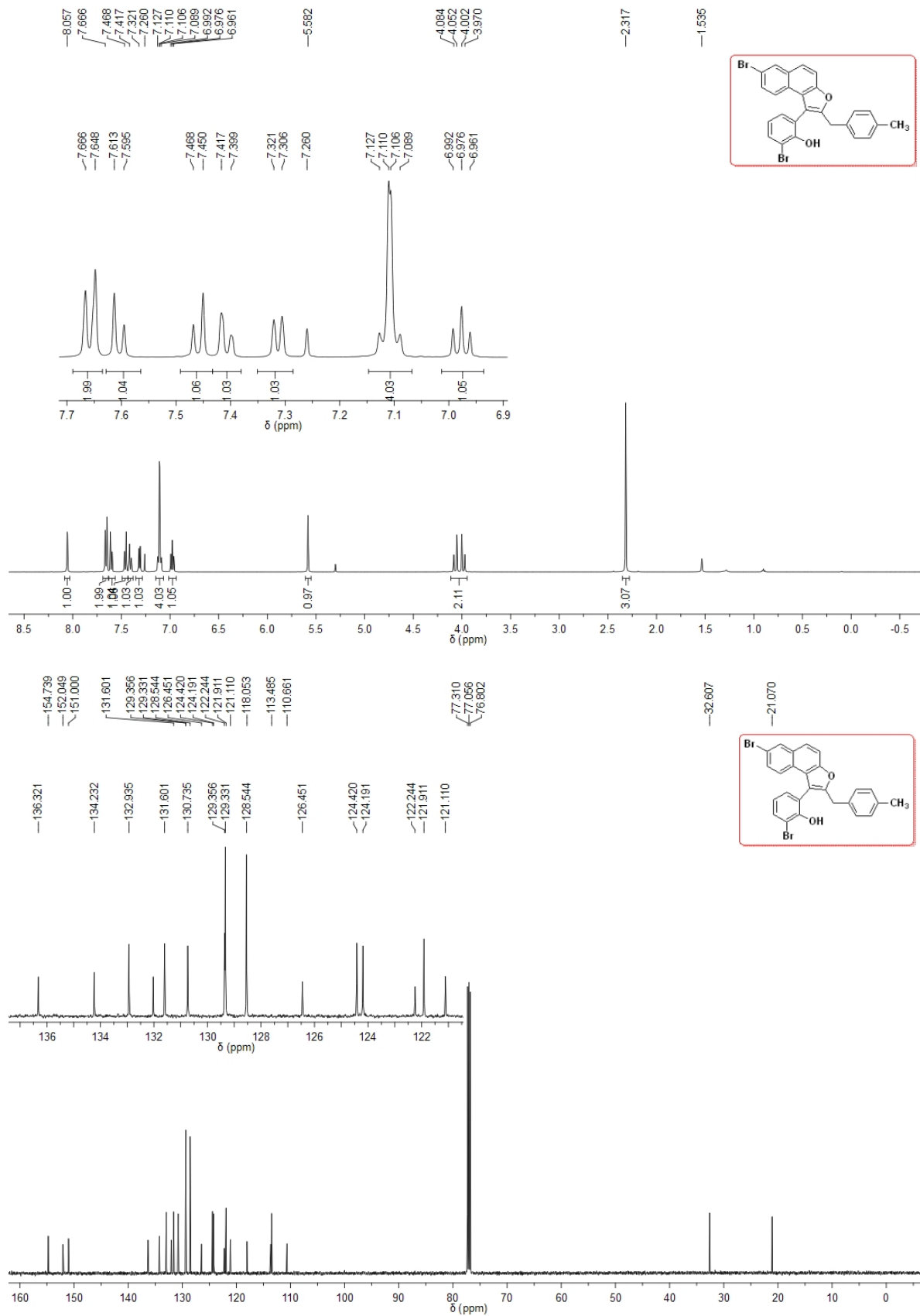
2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)phenol (3bb)



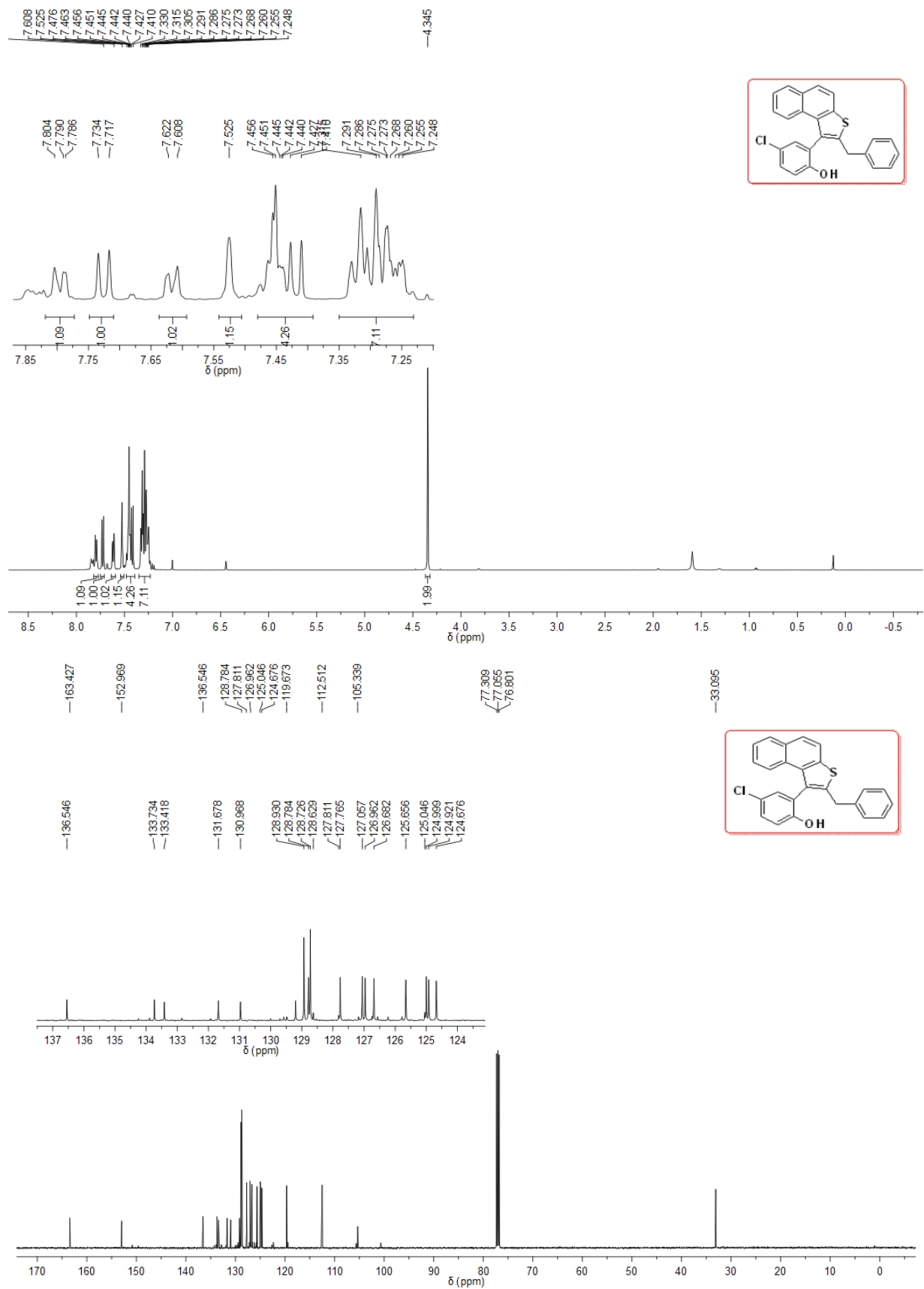
2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)-4-methylphenol (3fb)

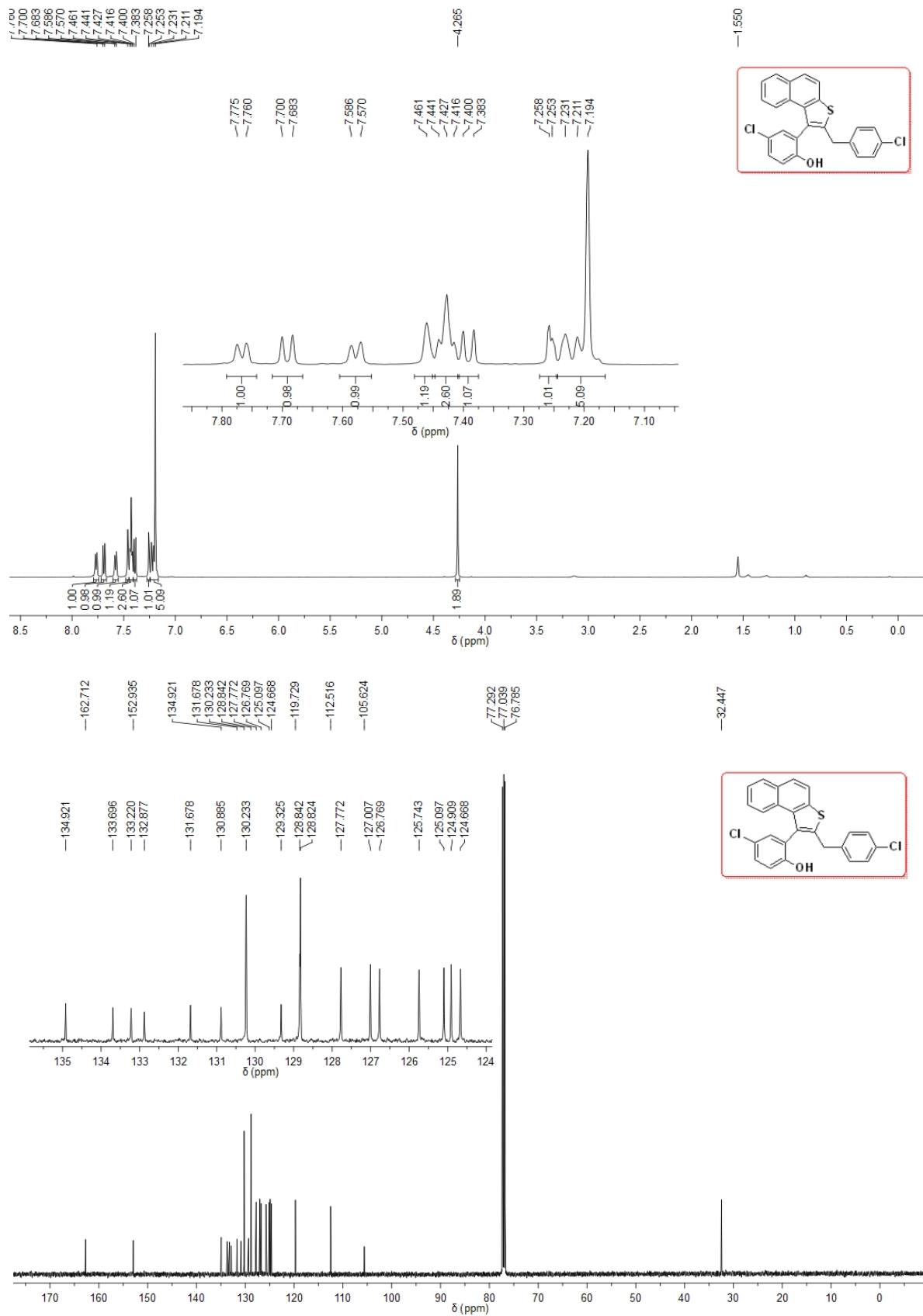


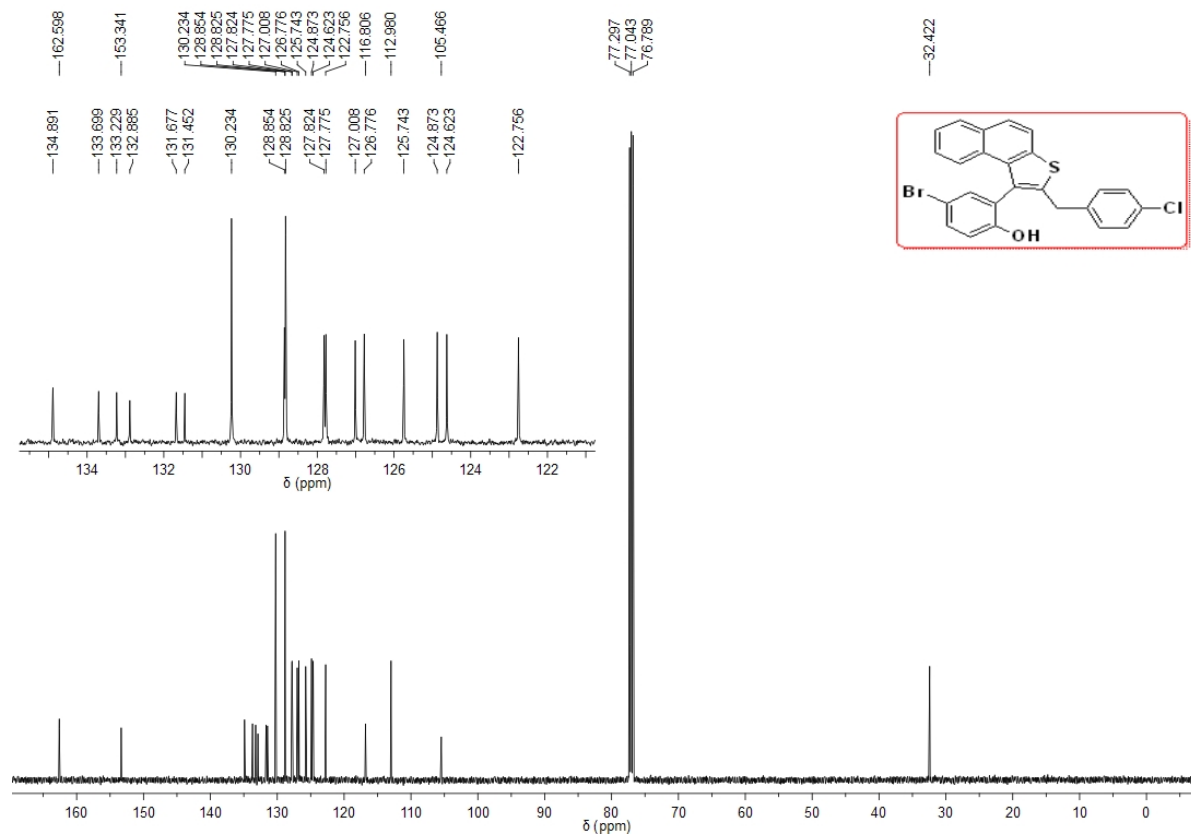
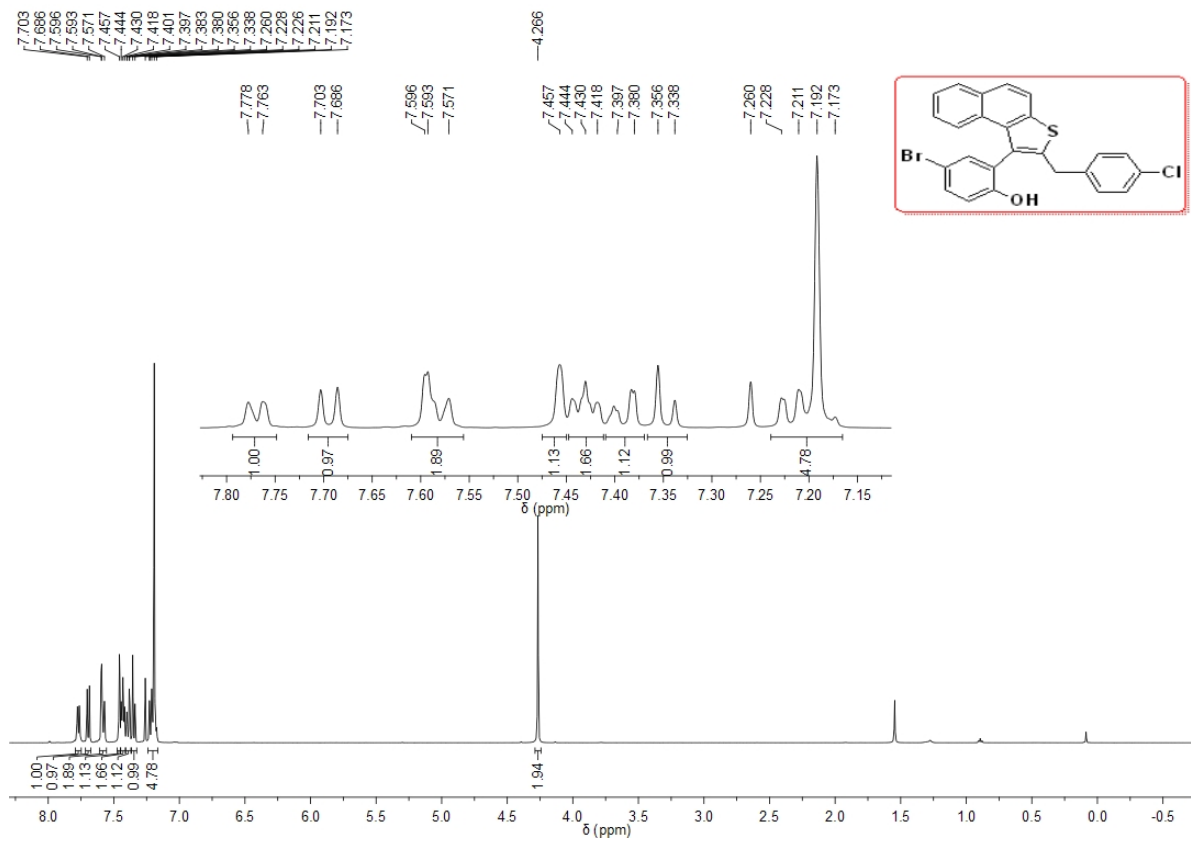
2-(7-Bromo-2-(4-methylbenzyl)naphtho[2,1-b]furan-1-yl)-4-chlorophenol (3jb)

2-Bromo-6-(7-bromo-2-(4-methylbenzyl)naphtho[2,1-*b*]furan-1-yl)phenol (3qb)

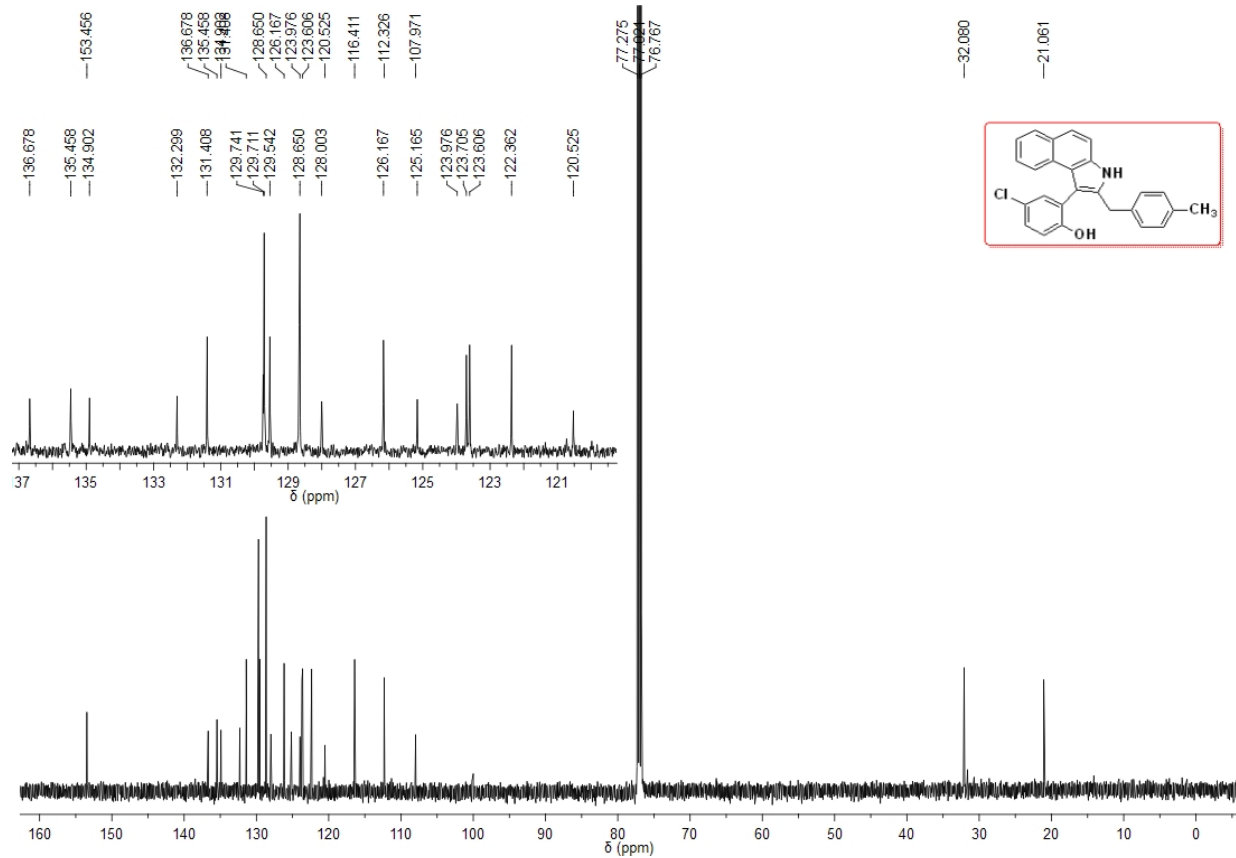
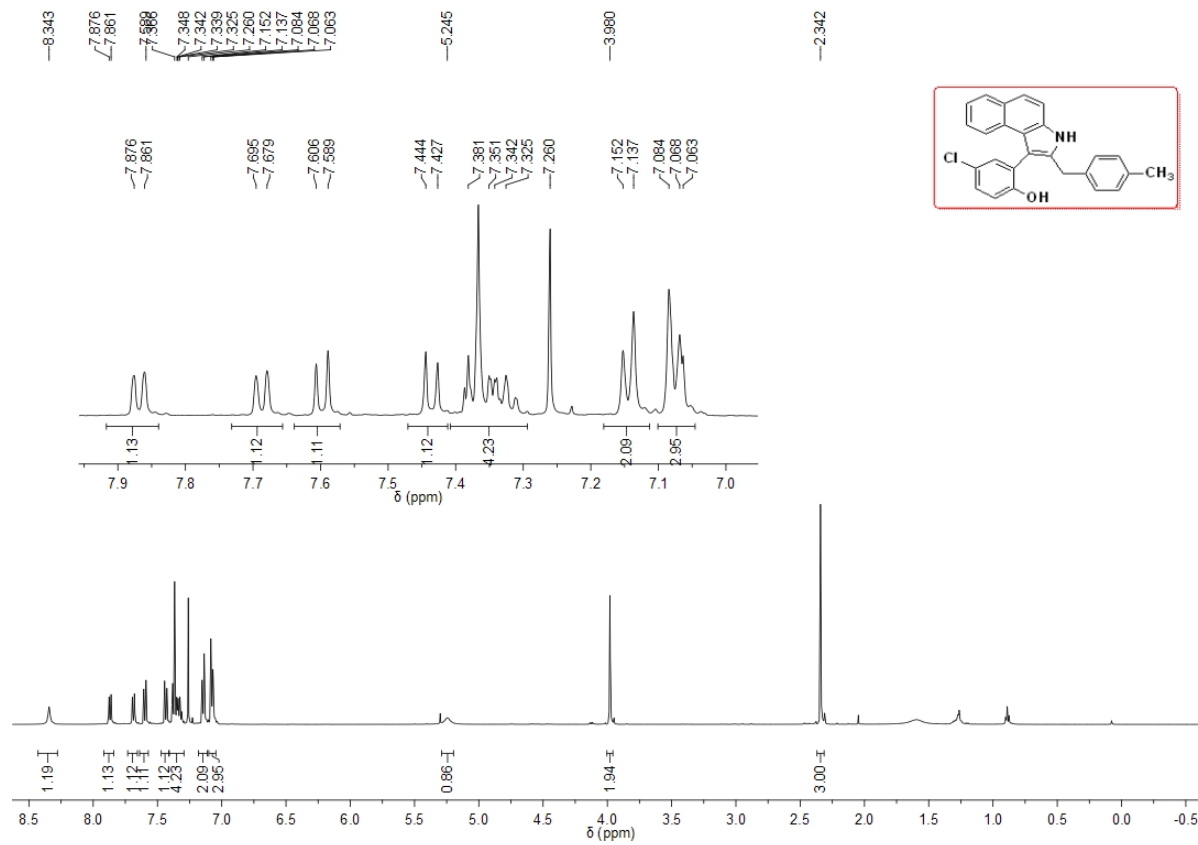
2-(2-Benzyl n aphtho[2,1- b]thiophen-1-yl)-4-chlorophenol (3ii)



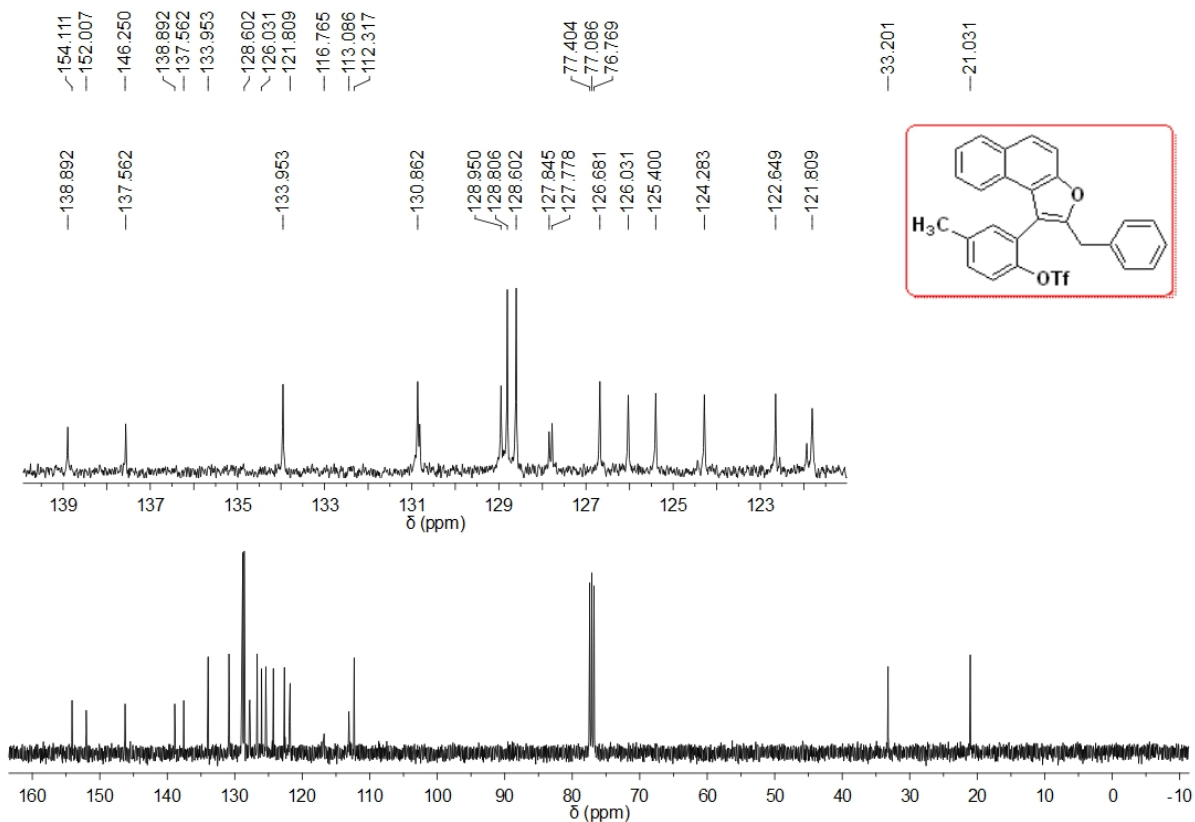
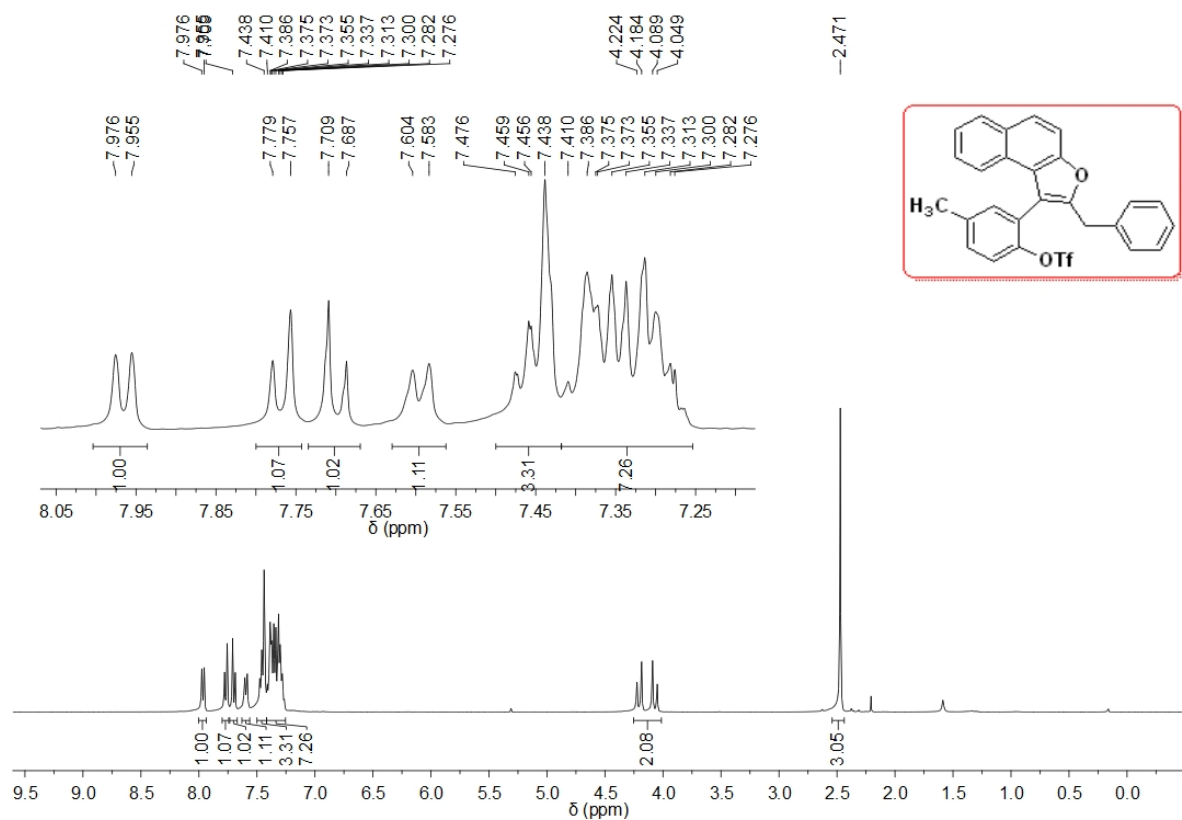
4-Chloro-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]thiophen-1-yl)phenol (3li)

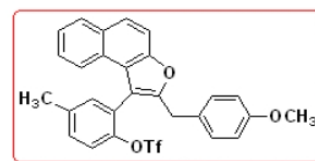
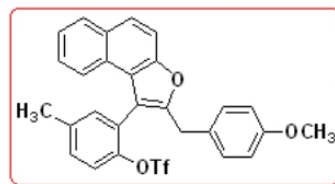
4-Bromo-2-(2-(4-chlorobenzyl)naphtho[2,1-*b*]thiophen-1-yl)phenol (3pi)

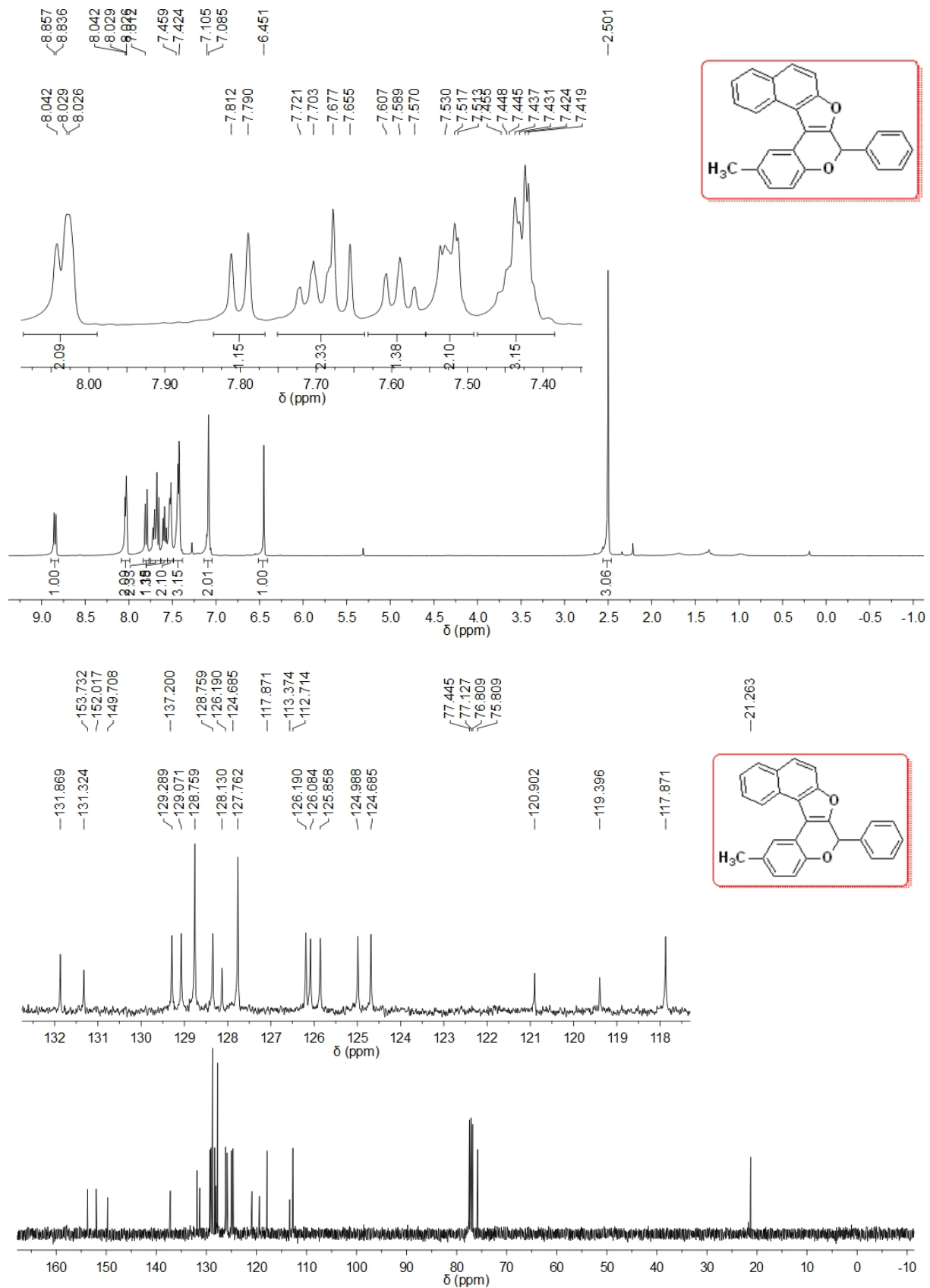
4-Chloro-2-(2-(4-methylbenzyl)-3H-benzo[e]indol-1-yl)phenol (3jj)

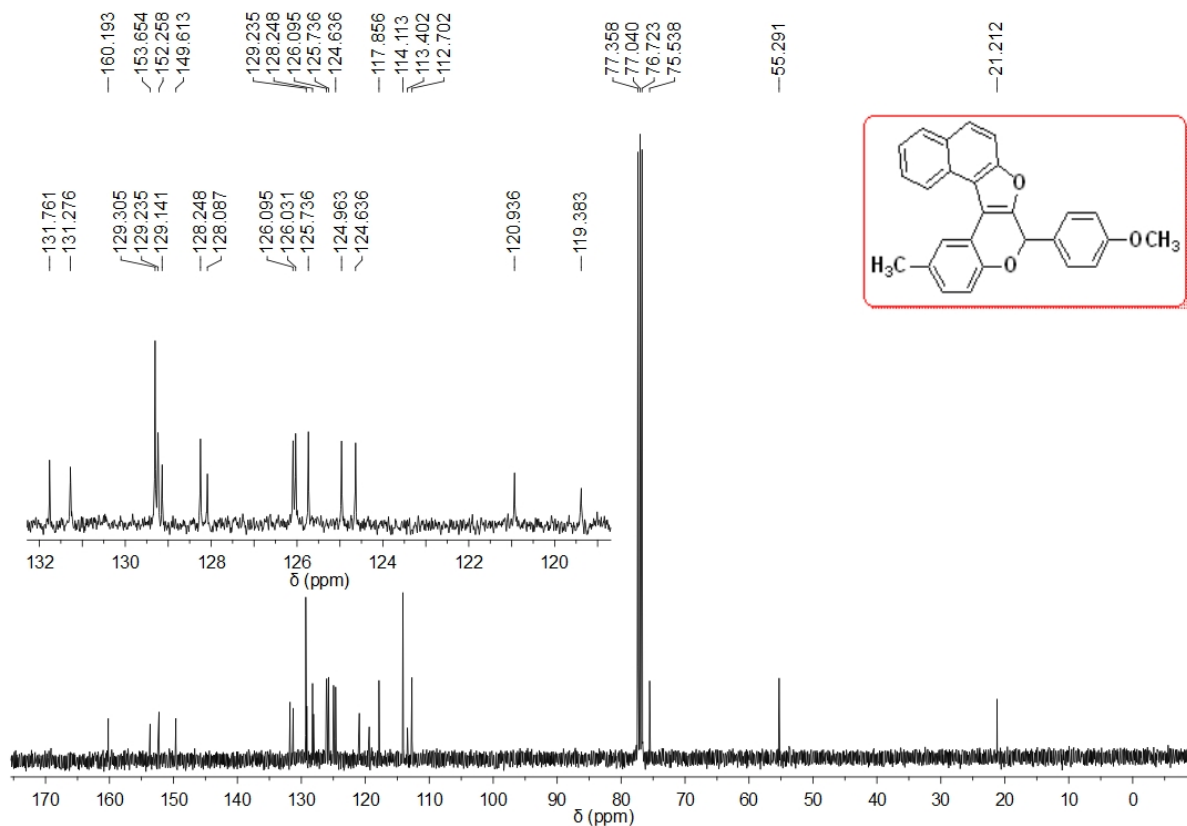
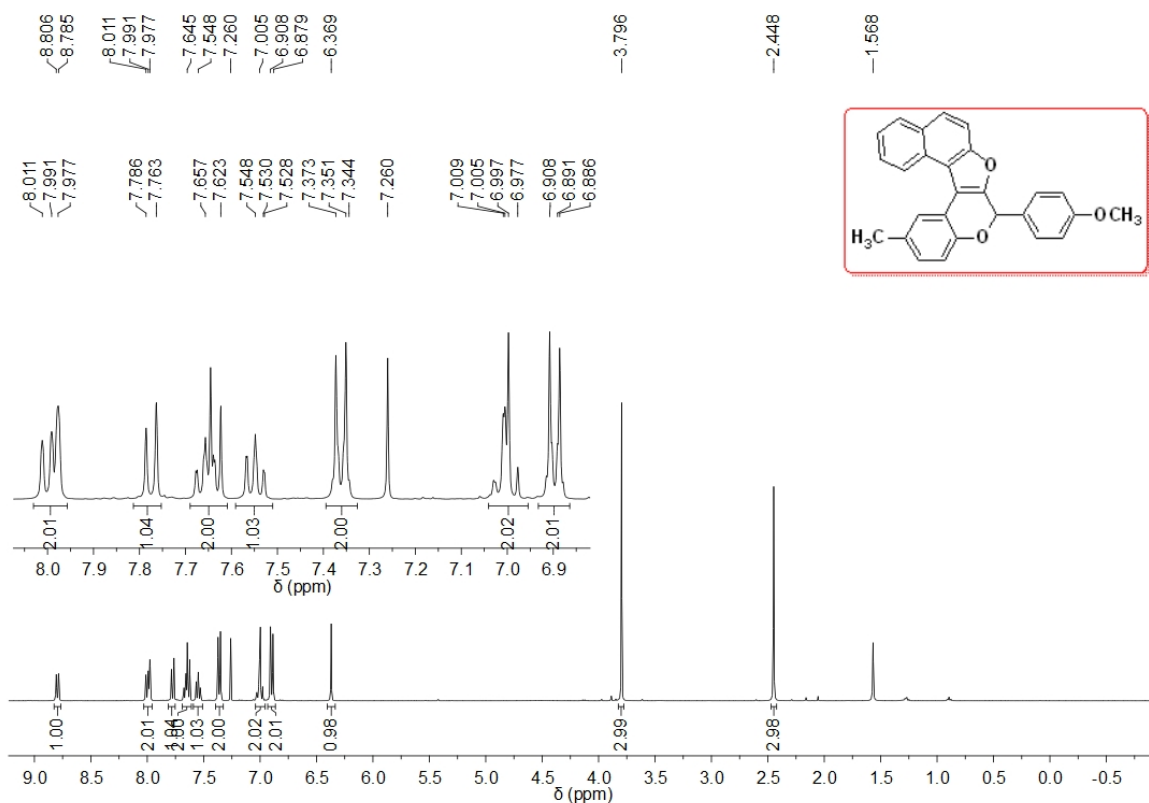




2-(2-Benzyl)naphtho[2,1-*b*]furan-1-yl)-4-methylphenyl trifluoromethanesulfonate (5ea)



2-Methyl-6-phenyl-6*H*-naphtho[1',2':4,5]furo[2,3-*c*]chromene (6ea)

6-(4-Methoxyphenyl)-2-methyl-6*H*-naphtho[1',2':4,5]furo[2,3-*c*]chromene (6a)

10. X-ray crystallographic data of compound 3ja

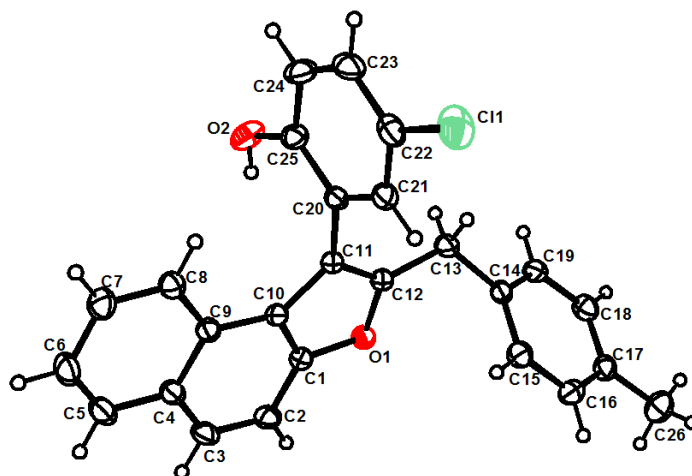
Figure S1. ORTEP drawing of compound **3ja** (30% probability for the thermal ellipsoid).

Table S1. Crystal data and structure refinement for mo_1510a_0m.

CCDC number	1945249
Identification code	mo_1510a_0m
Empirical formula	C ₂₆ H ₁₈ Cl O ₂
Formula weight	397.85
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 13.0387(8) Å α = 90°. b = 10.1877(6) Å β = 102.358(2)°. c = 15.2240(9) Å γ = 90°.
Volume	1975.4(2) Å ³
Z	4
Density (calculated)	1.338 Mg/m ³
Absorption coefficient	0.213 mm ⁻¹
F(000)	828
Crystal size	0.500 x 0.400 x 0.300 mm ³
Theta range for data collection	2.317 to 27.900°.
Index ranges	-17 ≤ h ≤ 17, -13 ≤ k ≤ 13, - 20 ≤ l ≤ 20

Reflections collected	57048
Independent reflections	4698 [R(int) = 0.0375]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6739
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4698 / 0 / 264
Goodness-of-fit on F ²	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1213
R indices (all data)	R1 = 0.0674, wR2 = 0.1318
Extinction coefficient	n/a
Largest diff. peak and hole	0.259 and -0.419 e.Å ⁻³

11. X-ray crystallographic data of compound 6ea

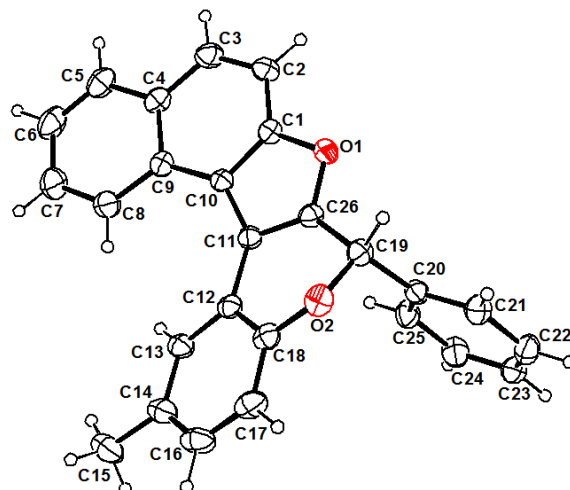
Figure S2. ORTEP drawing of compound **6ea** (30% probability for the thermal ellipsoid).

Table S2. Crystal data and structure refinement for lty642.

CCDC number	1945250
Identification code	lty642
Empirical formula	C ₂₆ H ₁₈ O ₂
Formula weight	362.40
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 5.6336(3) Å α = 90°. b = 19.4288(10) Å β = 94.477(2)°. c = 16.8408(9) Å γ = 90°.
Volume	1837.67(17) Å ³
Z	4
Density (calculated)	1.310 Mg/m ³
Absorption coefficient	0.082 mm ⁻¹
F(000)	760
Crystal size	0.400 x 0.300 x 0.200 mm ³
Theta range for data collection	3.207 to 25.248°.
Index ranges	-6 ≤ h ≤ 6, -23 ≤ k ≤ 23, -20 ≤ l ≤ 19

Reflections collected	28120
Independent reflections	3313 [R(int) = 0.0447]
Completeness to theta = 25.242°	99.7 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6987
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3313 / 0 / 253
Goodness-of-fit on F ²	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1061
R indices (all data)	R1 = 0.0649, wR2 = 0.1173
Extinction coefficient	n/a
Largest diff. peak and hole	0.168 and -0.194 e.Å ⁻³

12. References

- 1 W. L. F. Armarego and D. D. Perrin, *In Purification of Laboratory Chemicals*, 4th, Ed. Butterworth-Heinemann: Oxford UK: 1996.
- 2 N. Wongsas, U. Sommart, T. Ritthiwigrom, A. Yazici, S. Kanokmedhakul, K. Kanokmedhakul, A. C. Wills and S. G. Pyne, *J. Org. Chem.*, 2013, **78**, 1138.
- 3 C. Wei, Z. Li, and C.-J. Li, *Org. Lett.*, 2003, **5**, 4473.
- 4 S. Samanta, and A. Hajra, *Chem. Commun.*, 2018, **54**, 3379.