Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Regioselective Benzoyloxylative Dearomatization of Naphthols by Benzoyl Peroxide under Catalyst-Free Conditions

Hong-Wei Chen[a] and Qin-Hua Song*[a]

[a]Hefei National Laboratory for Physical Sciences at Microscale & Department of Chemistry, University of Science and Technology of China, Hefei 230026, China.

E-mail: qhsong@ustc.edu.cn

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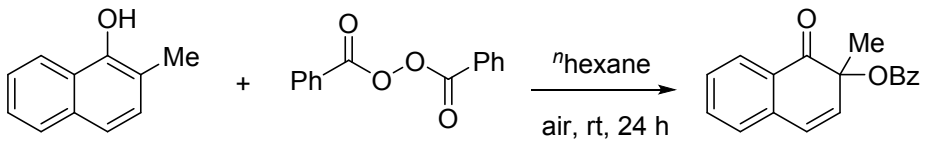
1. Methods and Materials.

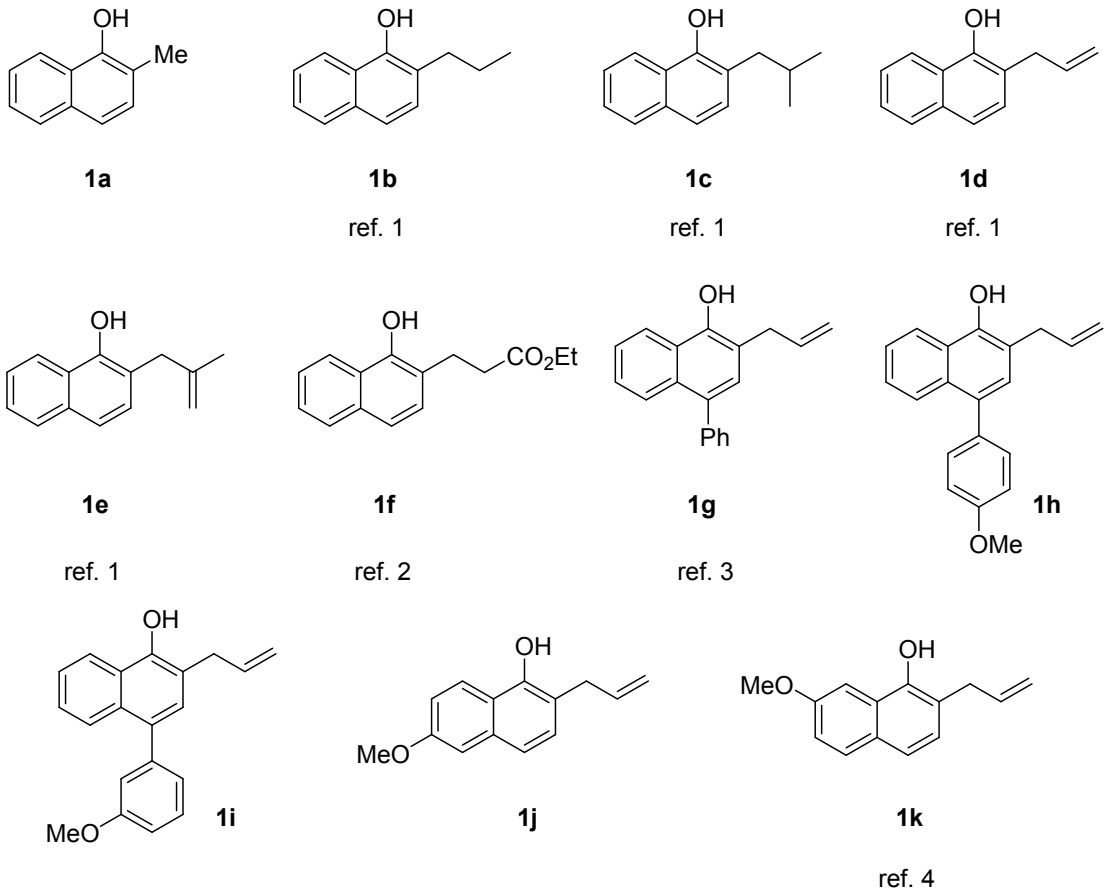
All reactions were carried out under argon atmosphere with dry solvents, unless otherwise noted. All the chemicals were purchased commercially and used without further purification. Anhydrous THF was distilled from sodium-benzophenone. Dichloromethane was distilled from calcium hydride. Dimethyl sulfoxide was purchased from Energy Chemical and used directly without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254). Flash column chromatography was performed on Tsingdao silica gel (200 - 300 mesh). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz) and reported relative to deuterated solvent signals or tetramethylsilane internal standard signals. Data for ^{1}H NMR spectra were reported as follows: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.), coupling constant (*J*/Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (100 or 125 MHz). Data for ^{13}C NMR spectra were reported in terms of chemical shift. ^{19}F NMR spectra were recorded on Bruker Spectrometers (376 MHz). High-resolution mass spectrometry (HRMS) was conducted on Bruker Apex IV RTMS.

2. General Procedure for the Preparation of Starting Materials



1a **2a** **3a**

To a mixture of **1a** (15.8 mg, 0.1 mmol) in hexane (1.0 mL) was added **2a** (29.0 mg, 0.12 mmol) at room temperature and the resultant mixture was stirred for 24 hours at room temperature. Upon completion, the mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give the desired product **3a** (26.7 mg, 96%) as a white solid.



1a **1b** **1c** **1d**

ref. 1 ref. 1 ref. 1

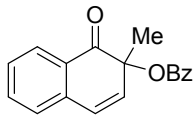
1e **1f** **1g** **1h**

ref. 1 ref. 2 ref. 3

1i **1j** **1k**

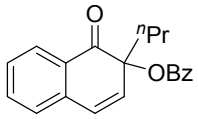
ref. 4

Scheme 1 Scope of α-naphthols



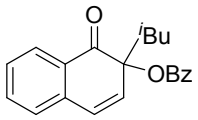
3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.55 (m, 2H), 7.45 – 7.40 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 1.64 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.2, 165.4, 137.0, 134.8, 134.7, 133.4, 130.0, 129.3, 129.1, 128.43, 128.38, 128.0, 127.6, 125.9, 78.5, 24.0. **HRMS (ESI):** m/z Calcd. for $[C_{18}H_{14}O_3Na, M+Na]^+$: 301.0835; Found: 301.0839.



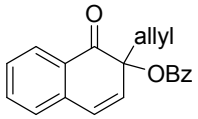
3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.62 - 7.55 (m, 2H), 7.45 -7.38 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 2.07 – 1.90 (m, 2H), 1.63 – 1.52 (m, 1H), 1.40 – 1.31 (m, 1H), 0.95 – 0.91 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.4, 165.3, 137.0, 134.6, 133.7, 133.2, 129.9, 129.7, 129.4, 128.3, 127.9, 127.2, 126.8, 81.1, 40.5, 16.2, 14.3. **HRMS (ESI):** m/z Calcd. for $[C_{20}H_{18}O_3Na, M+Na]^+$: 329.1148; Found: 329.1143.



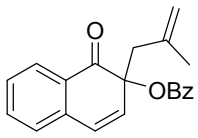
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.46 – 7.38 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 1.99 – 1.89 (m, 3H), 1.09 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.2, 165.3, 136.9, 134.5, 133.8, 133.2, 129.9, 129.5, 129.4, 128.3, 127.9, 127.4, 126.4, 81.5, 46.4, 24.6, 24.2. **HRMS (ESI):** m/z Calcd. for $[C_{21}H_{20}O_3Na, M+Na]^+$: 343.1305; Found: 343.1308.



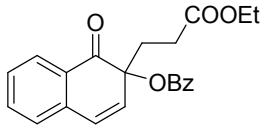
3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.46 – 7.38 (m, 3H), 7.30 (d, *J* =7 .6 Hz, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.21 – 5.12 (m, 2H), 2.80 – 2.68 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.7, 165.2, 137.0, 134.6, 133.3, 133.1, 130.1, 129.9, 129.6, 129.3, 128.45, 128.37, 128.0, 127.3, 127.0, 120.3, 80.2, 42.6. **HRMS (ESI):** m/z Calcd. for $[C_{20}H_{16}O_3Na, M+Na]^+$: 327.0992; Found: 327.0989.



3e

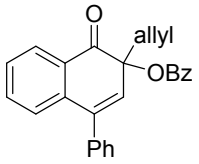
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.45 – 7.39 (m, 3H), 7.29 (d, *J* = 5.2 Hz, 1H), 6.74 (d, *J* = 6.4 Hz, 1H), 6.17 (d, *J* = 6.4 Hz, 1H), 4.95 (s, 1H), 4.84 (s, 1H), 2.75 (d, *J* = 9.2 Hz, 1H), 2.62 (d, *J* = 9.2 Hz, 1H), 1.92 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.6, 165.3, 139.0, 137.0, 134.6, 133.6, 133.3, 129.9, 129.51, 129.46, 128.4, 128.0, 127.4, 126.6, 117.1, 80.9, 45.7, 24.5. **HRMS (ESI):** m/z Calcd. for $[C_{21}H_{18}O_3Na, M+Na]^+$: 341.1148; Found: 341.1150.



3f

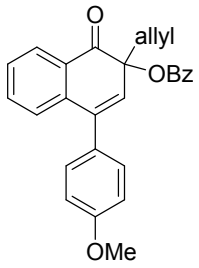
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.46 – 7.39 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 9.6 Hz, 1H), 6.14 (d, *J* = 9.6 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.55 – 2.47 (m, 2H), 2.43 – 2.36 (m, 1H), 2.32 – 2.27 (m, 1H), 1.25 – 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 172.4, 165.2, 136.8, 134.8, 133.4, 133.0, 129.9, 129.4, 129.2, 128.6, 128.4, 128.0, 127.4, 127.3, 79.8, 60.7, 32.6, 27.6, 14.1. **HRMS (ESI):** m/z

Calcd. for $[C_{22}H_{20}O_5Na, M+Na]^+$: 387.1203; Found: 387.1203.



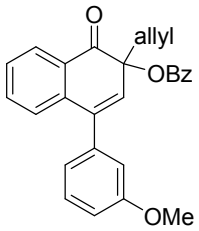
3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.46 – 7.38 (m, 8H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 1H), 5.98 – 5.88 (m, 1H), 5.28 – 5.18 (m, 2H), 2.90 – 2.79 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.5, 165.0, 138.6, 138.4, 137.5, 134.3, 133.2, 132.1, 130.2, 129.9, 129.6, 129.4, 129.1, 128.4, 128.32, 128.28, 127.9, 127.7, 127.1, 120.3, 80.4, 42.8. **HRMS (ESI):** m/z Calcd. for $[C_{26}H_{20}O_3Na, M+Na]^+$: 403.1305; Found: 403.1307.



3h

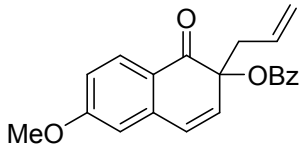
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.46 – 7.41 (m, 3H), 7.34 – 7.31 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 3.2 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 5.98 – 5.87 (m, 1H), 5.30 – 5.18 (m, 2H), 3.86 (s, 3H), 2.88 – 2.77 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.6, 165.0 , 159.4, 138.1, 137.8, 134.3, 133.2, 131.8, 130.7, 130.32, 130.26, 129.9, 129.6, 129.4, 128.3, 128.2, 127.7, 127.1, 120.2, 113.8, 80.5, 55.3, 42.8. **HRMS (ESI):** m/z Calcd. for $[C_{27}H_{22}O_4Na, M+Na]^+$: 433.1410; Found: 433.1407.



3i

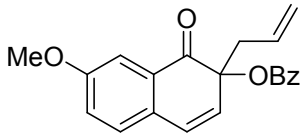
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H),

7.57 – 7.51 (m, 2H), 7.44 – 7.39 (m, 3H), 7.35 – 7.31 (m, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.08 (s, 1H), 5.95 – 5.85 (m, 1H), 5.27 –5.16 (m, 2H), 3.81 (s, 3H), 2.84 – 2.80 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 165.0, 159.5, 139.8, 138.4, 137.4, 134.3, 133.2, 132.0, 130.2, 129.8, 129.6, 129.44, 129.36, 128.31, 128.29, 127.6, 127.1, 121.5, 120.3, 114.7, 113.4, 80.3, 55.2, 42.8. **HRMS (ESI):** m/z Calcd. for $[C_{27}H_{22}O_4Na, M+Na]^+$: 433.1410; Found: 433.1412.



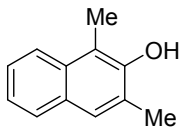
3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 3H), 7.58 – 7.54 (m, 1H), 7.45 – 7.41 (m, 2H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 9.6 Hz, 1H), 5.90 – 5.78 (m, 1H), 5.20 – 5.11 (m, 2H), 3.90 (s, 3H), 2.80 – 2.66 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.2, 165.1, 164.8, 139.2, 134.2, 133.3, 130.2, 129.9, 129.4, 128.3, 127.0, 123.2, 120.1, 114.2, 112.5, 80.0, 55.6, 42.8. **HRMS (ESI):** m/z Calcd. for $[C_{21}H_{18}O_4Na, M+Na]^+$: 357.1097; Found: 357.1097.



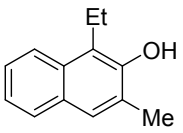
3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.49 – 7.45 (m, 2H), 7.28 (d, *J* = 6.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.75 (d, *J* = 10.0 Hz, 1H), 6.06 (d, *J* = 9.6 Hz, 1H), 5.93 – 5.82 (m, 1H), 5.20 – 5.15 (m, 2H), 3.91 (s, 3H), 2.84 – 2.71 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.9, 165.2, 159.7, 133.3, 130.8, 130.4, 130.3, 130.1, 129.9, 129.5, 129.3, 128.4, 126.7, 122.2, 109.8, 80.0, 56.0, 42.6. **HRMS (ESI):** m/z Calcd. for $[C_{21}H_{18}O_4Na, M+Na]^+$: 357.1097; Found: 357.1098.



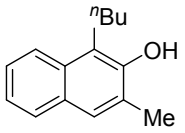
4a

ref. 5



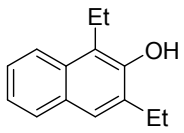
4b

ref. 5



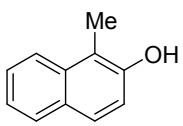
4c

ref. 5

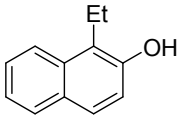


4d

ref.6

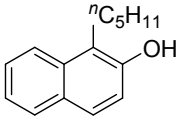


4e



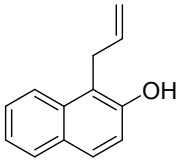
4f

ref. 7



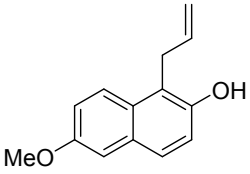
4g

ref. 7



4h

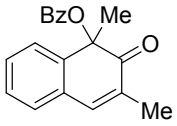
ref. 8



4i

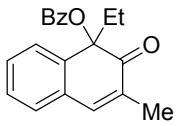
ref. 8

Scheme 2 Scope of *β*-naphthols



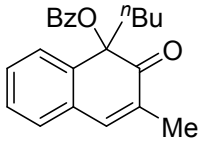
5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.45 – 7.39 (m, 3H), 7.33 (s, 1H), 7.29 – 7.25 (m, 3H), 2.08 (s, 1H), 1.70 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.8, 165.0, 143.1, 141.0, 133.3, 132.0, 130.0, 129.6, 129.4, 128.6, 128.4, 128.0, 123.9, 80.0, 28.3, 15.8. **HRMS (ESI):** m/z Calcd. for $[C_{19}H_{16}O_3Na, M+Na]^+$: 315.0992; Found: 315.0995.



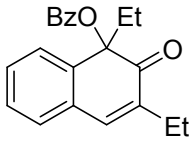
5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.55 (m, 1H), 7.45 – 7.42 (m, 2H), 7.37 – 7.35 (m, 1H), 7.30 – 7.26 (m, 4H), 2.25 – 2.15 (m, 1H), 2.12 – 2.02 (m, 4H), 0.82 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.9, 164.9, 141.6, 140.9, 133.2, 133.0, 130.6, 129.9, 129.7, 129.0, 128.41, 128.37, 128.0, 124.4, 82.8, 35.4, 16.0, 7.1. **HRMS (ESI):** m/z Calcd. for $[C_{20}H_{18}O_3Na, M+Na]^+$: 329.1148; Found: 329.1153.



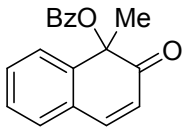
5c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.36 (m, 1H), 7.30 – 7.20 (m, 4H), 2.19 – 2.12 (m, 1H), 2.07 (s, 3H), 2.05 – 1.98 (m, 1H), 1.27 – 1.06 (m, 4H), 0.85 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.0, 164.9, 141.9, 140.9, 133.2, 132.9, 130.5, 129.9, 129.7, 129.0, 128.42, 128.37, 128.0, 124.4, 82.5, 42.0, 24.4, 22.8, 15.7, 13.8. **HRMS (ESI):** m/z Calcd. for $[C_{22}H_{22}O_3Na, M+Na]^+$: 357.1461; Found: 357.1464.



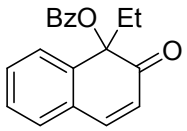
5d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.46 – 7.42 (m, 2H), 7.37 – 7.25 (m, 5H), 2.60 – 2.41 (m, 2H), 2.25 – 2.17 (m, 1H), 2.16 – 2.02 (m, 1H), 1.19 (t, *J* = 7.6 Hz, 1H), 0.83 (t, *J* = 7.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.5, 164.8, 141.5, 139.2, 138.4, 133.2, 130.5, 129.9, 129.7, 129.0, 128.6, 128.3, 128.0, 124.4, 82.9, 35.3, 22.2, 12.5, 7.1. **HRMS (ESI):** m/z Calcd. for $[C_{21}H_{20}O_3Na, M+Na]^+$: 343.1305; Found: 343.1309.



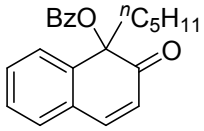
5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 2H), 7.55 – 7.26 (m, 5H), 6.33 (d, *J* = 10.0 Hz, 1H), 1.74(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.5, 164.9, 144.7, 143.9, 133.7, 133.4, 130.5, 130.2, 129.9, 129.5, 129.3, 129.0, 128.44, 128.38, 128.0, 124.3, 124.1, 79.9, 28.1. **HRMS (ESI):** m/z Calcd. for $[C_{18}H_{14}O_3Na, M+Na]^+$: 301.0835; Found: 301.0833.



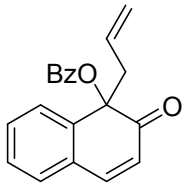
5f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 7.70 – 7.26 (m, 9H), 6.33 (d, *J* = 10.0 Hz, 1H), 2.25 – 2.20 (m, 1H), 2.12 – 2.07 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.6, 164.7, 144.6, 142.6, 133.7, 133.4, 130.2, 129.9, 129.6, 129.4, 128.5, 128.4, 128.1, 125.4, 124.7, 82.7, 35.2, 7.0. **HRMS (ESI):** m/z Calcd. for $[C_{19}H_{16}O_3Na, M+Na]^+$: 305.0992; Found: 305.0992.



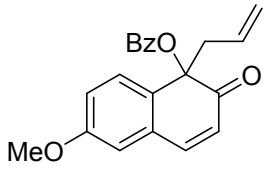
5g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.64 – 7.56 (m, 1H), 7.51 – 7.30 (m, 7H)， 6.32 (d, *J* = 10.0 Hz, 1H), 2.21 – 2.13 (m, 1H), 2.07 – 2.00 (m, 1H), 1.38 – 1.30 (m, 1H), 1.29 – 1.11 (m, 5H), 0.83 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 164.9, 144.6, 142.8, 133.3, 130.22, 130.16, 130.0, 129.9, 129.5, 129.4, 128.5, 128.4, 128.0, 125.3, 124.6, 82.5, 41.9, 31.7, 22.3, 21.8, 13.9. **HRMS (ESI):** m/z Calcd. for $[C_{22}H_{22}O_3Na, M+Na]^+$: 357.1461; Found: 357.1464.



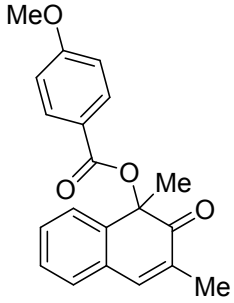
5h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 3.2 Hz, 1H), 8.07 (d, *J* = 3.6 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.50 – 7.41 (m, 5H), 7.38 – 7.26 (m, 3H), 6.31 (d, *J* = 9.6 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.08 – 5.00 (m, 1H), 2.90 – 2.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 171.8, 164.8, 144.8, 141.9, 133.8, 133.5, 130.22, 130.19, 130.02, 130.00, 129.5, 129.4, 129.3, 128.51, 128.50, 128.3, 125.1, 125.0, 46.1. **HRMS (ESI):** m/z Calcd. for $[C_{20}H_{16}O_3Na, M+Na]^+$: 327.0992; Found: 327.0988.



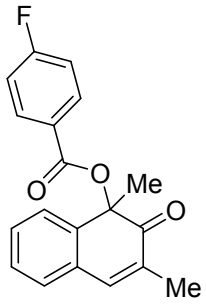
5i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.34 (d, *J* = 6.8 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.31 (d, *J* = 2.4 Hz, 1H)， 5.64 – 5.53 (m, 1H), 5.07 – 5.00 (m, 2H), 3.82 (s, 3H), 2.89 – 2.78 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.2, 164.7, 159.3, 144.6, 133.8, 133.4, 131.2, 130.2, 129.9, 129.5, 128.5, 128.4, 126.4, 125.8, 120.4, 115.8, 114.3, 81.4, 55.4, 46.2. **HRMS (ESI):** m/z Calcd. for $[C_{22}H_{22}O_3Na, M+Na]^+$: 357.1097; Found: 357.1098.



5j

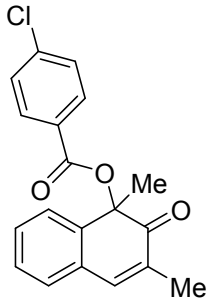
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.32 (m, 1H), 7.22 – 7.19 (m, 4H), 6.84 (d, *J* = 9.2 Hz, 1H), 3.79 (s, 3H), 2.02 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.9, 163.6, 162.6, 142.3, 139.9, 131.0, 130.9, 128.3, 127.6, 126.9, 122.9, 120.9, 78.6, 54.4, 27.3, 14.8. **HRMS (ESI):** m/z Calcd. for $[C_{20}H_{18}O_4Na, M+Na]^+$: 345.1097; Found: 345.1102.



5k

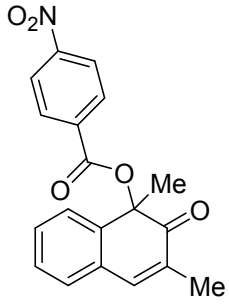
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.40 – 7.38 (m, 1H), 7.34 –

7.33(m, 1H), 7.30 – 7.25 (m, 3H), 7.13 – 7.08 (m, 2H), 2.08 (d, *J* = 0.8Hz, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.7, 167.2, 164.7, 163.9, 142.9, 141.1, 132.8, 132.6, 132.5, 131.9, 129.4, 129.3, 128.6, 128.0, 125.7, 125.7, 123.8, 115.6, 115.4, 80.1, 28.3, 15.7; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -104.8. **HRMS (ESI):** m/z Calcd. for $[C_{19}H_{15}O_3FNa, M+Na]^+$: 333.0897; Found: 333.0897.



5l

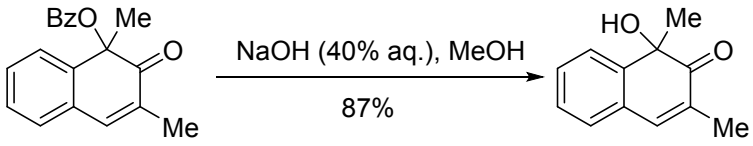
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 – 8.00 (m, 2H), 7.43 – 7.42 (m, 2H), 7.34 – 7.33 (m, 1H), 7.39 – 7.37 (m, 1H), 7.24 (s, 1H), 7.30 – 7.26 (m, 3H), 2.08 (d, *J* = 0.8 Hz, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 196.6, 163.1, 161.2, 141.8, 140.12, 140.07, 138.8, 130.9, 130.5, 130.3, 130.1, 128.4, 128.3, 127.7, 127.6, 127.1, 126.9, 122.81, 122.77, 79.3, 27.3, 14.7. **HRMS (ESI):** m/z Calcd. for $[C_{19}H_{15}O_3ClNa, M+Na]^+$: 349.0602; Found: 349.0603.



5m

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 – 8.24 (m, 4H), 7.39 – 7.37 (m, 2H), 7.34 – 7.30 (m, 3H), 2.09 (d, *J* = 1.2 Hz, 3H), 1.74 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.4, 163.1, 150.7, 142.3, 141.4, 134.8, 132.0, 131.1, 129.6, 129.4, 128.8, 128.4, 123.8, 123.6, 81.2, 28.4, 15.8. **HRMS (ESI):** m/z Calcd. for $[C_{19}H_{15}O_3NNa, M+Na]^+$: 360.0842; Found: 360.0843.

Synthesis of 6



5a **6**

To a solution of **5a** (29.2 mg, 0.1 mmol) in methanol (1.0 mL) was added 40% NaOH (0.33 mL) at room temperature and the reaction mixture was stirred for overnight at 60 ^{o}C. Upon completion, the mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with NH_4Cl, water and brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography to provide **6** (16.5 mg, 87%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 – 7.14 (m, 2H), 3.66 (s, 1H), 1.97 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 205.9, 144.1, 142.0, 130.3, 129.5, 128.6, 128.4, 127.8, 125.2, 76.9, 33.3, 15.4. **HRMS (ESI):** m/z Calcd. for. $[C_{12}H_{12}O_2Na, M+Na]^+$: 211.0730; Found: 211.0732.

Reference:

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3. Plausible Reaction Path

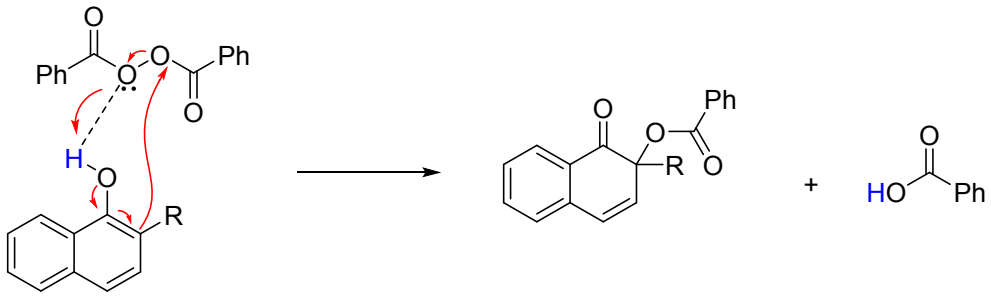
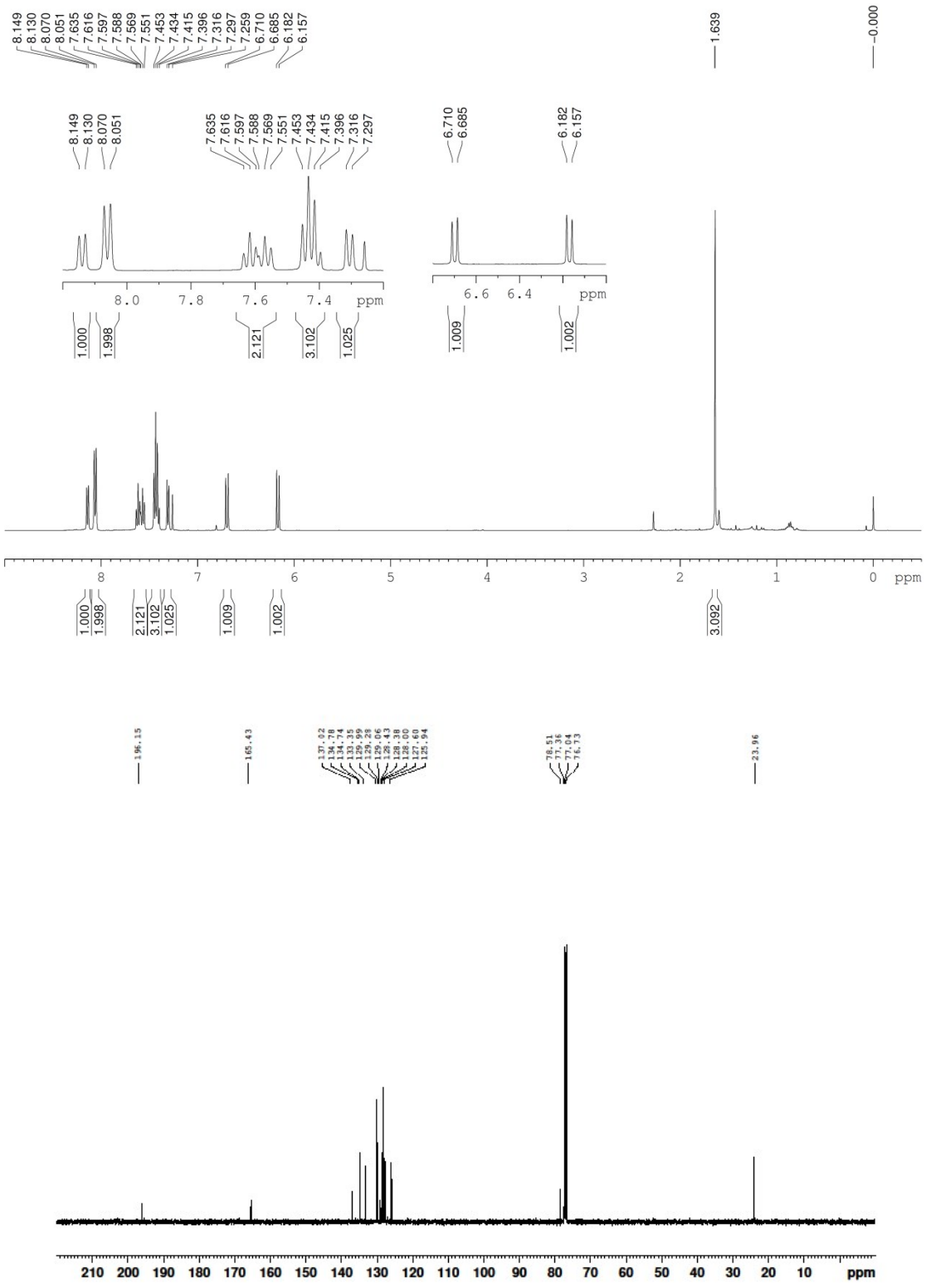


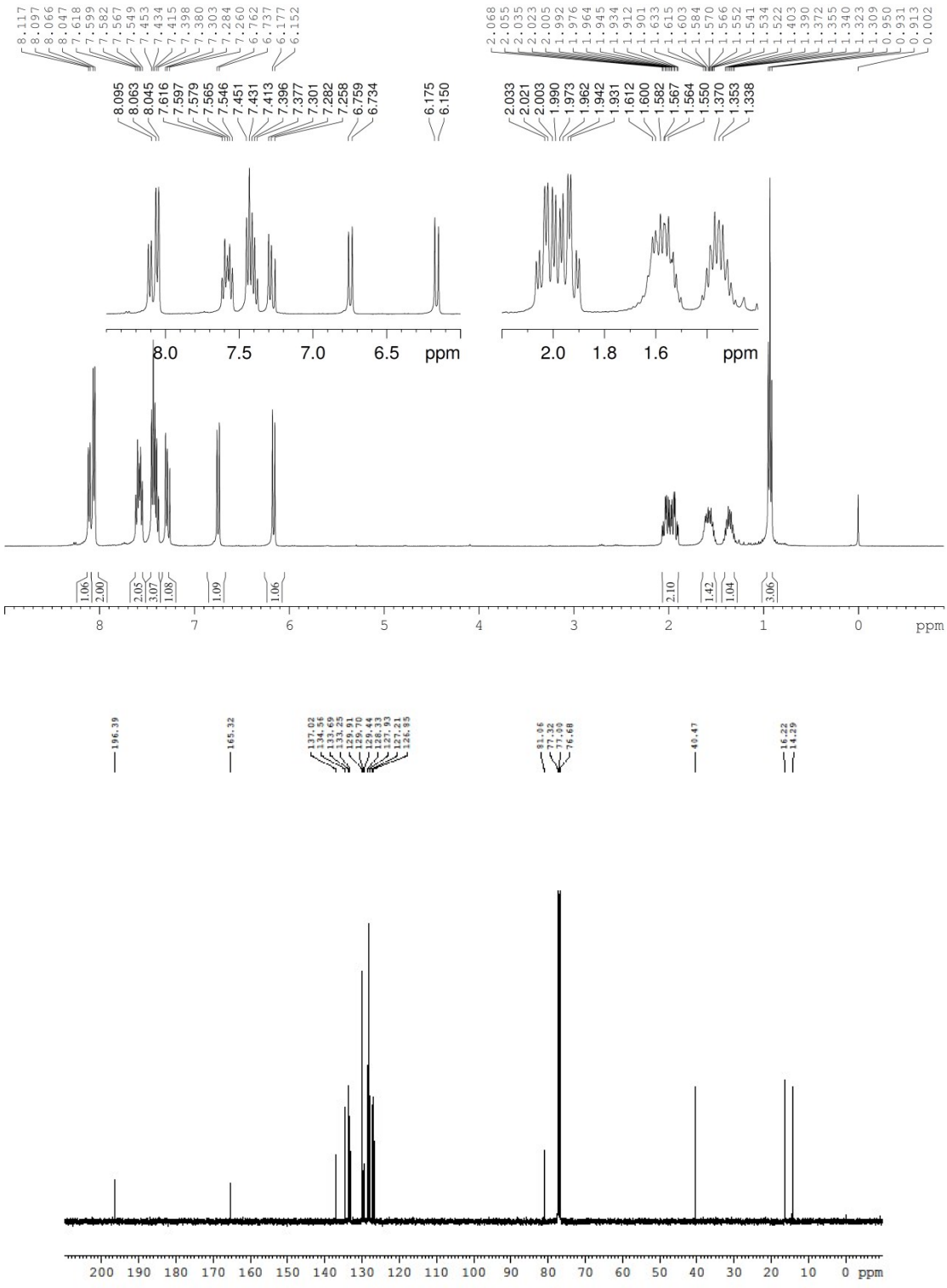
Figure S1

We propose that the hydroxyl group of naphthol activates the benzoyl peroxide through H-bonding interaction that increases the electrophilicity of benzoyl peroxide.

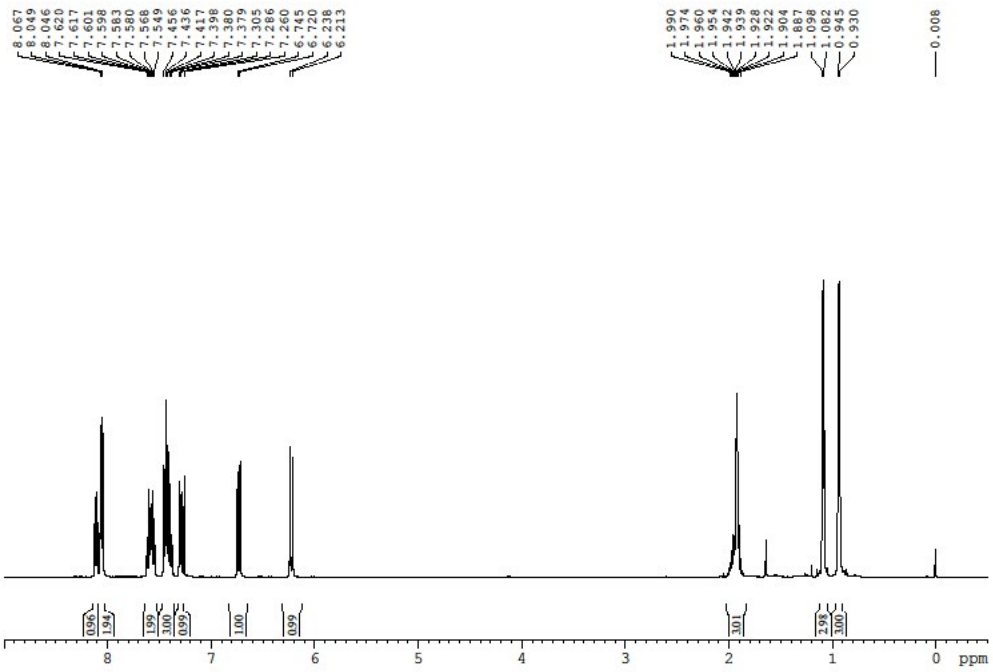
4. ^{1}H, ^{13}C and ^{19}F NMR Spectra for New Compounds.

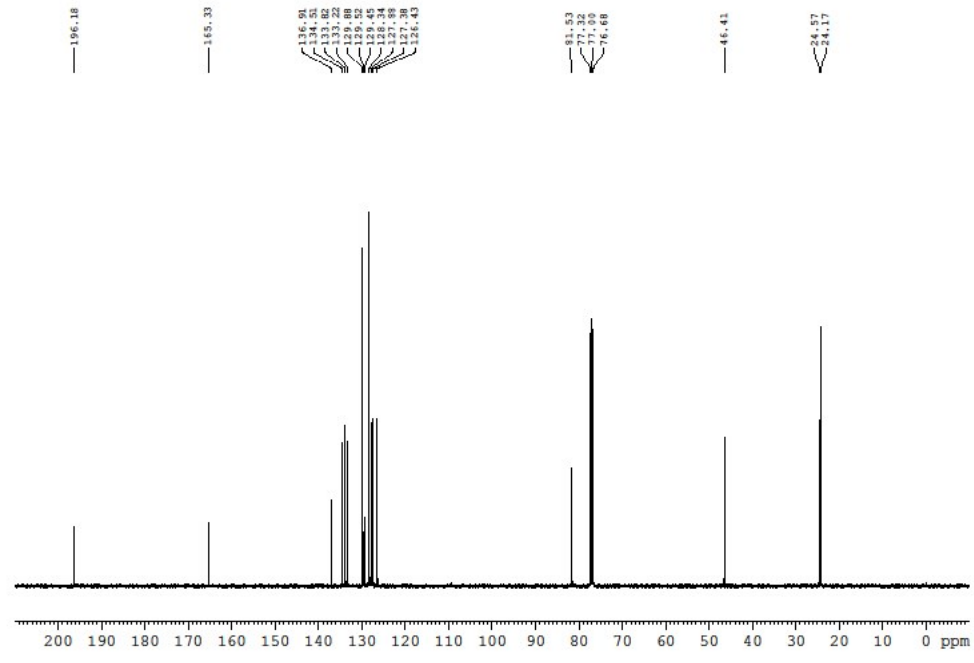


^{1}H NMR and ^{13}C NMR Spectrum of **3a**

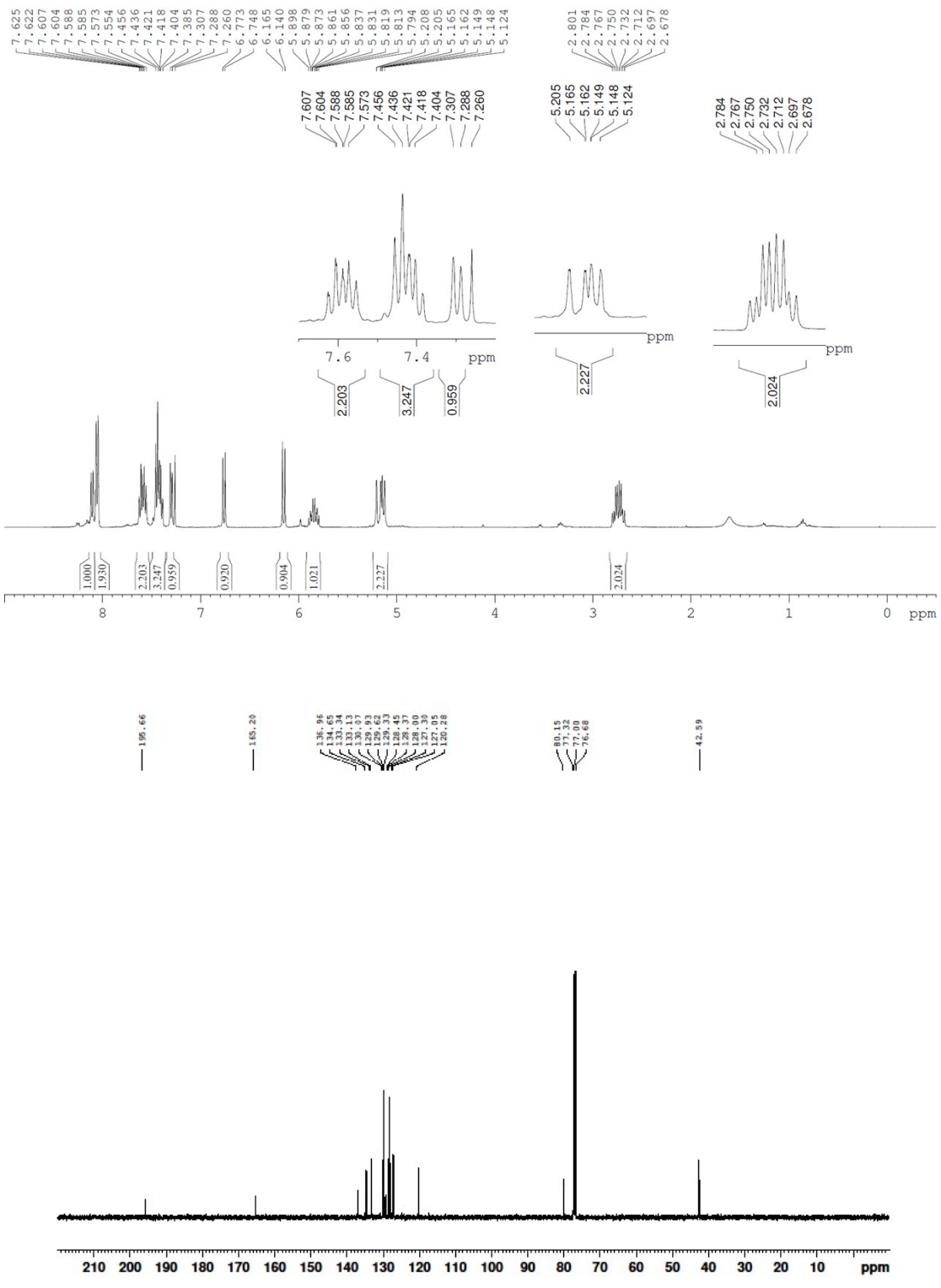


^{1}H NMR and ^{13}C NMR Spectrum of **3b**

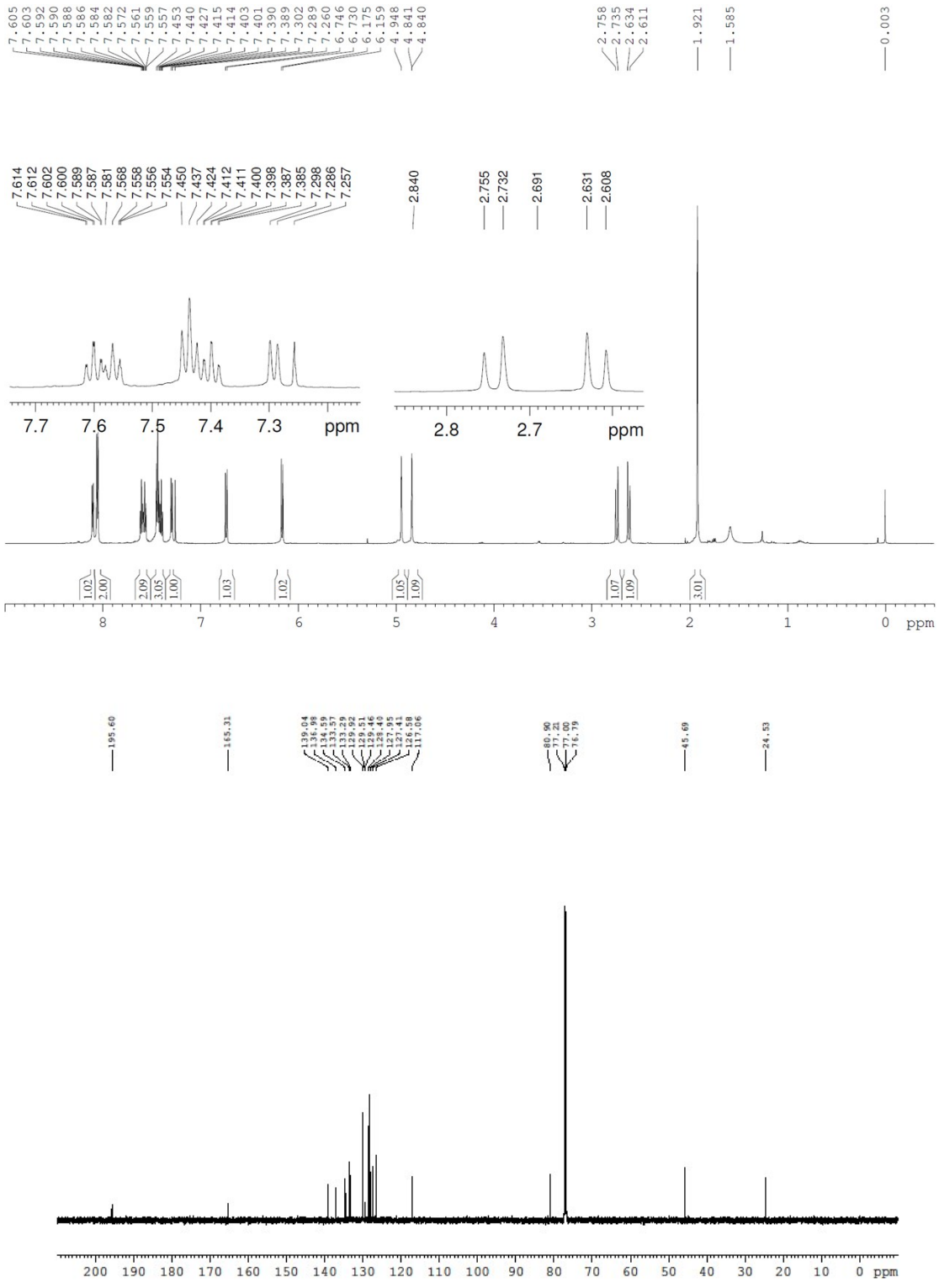




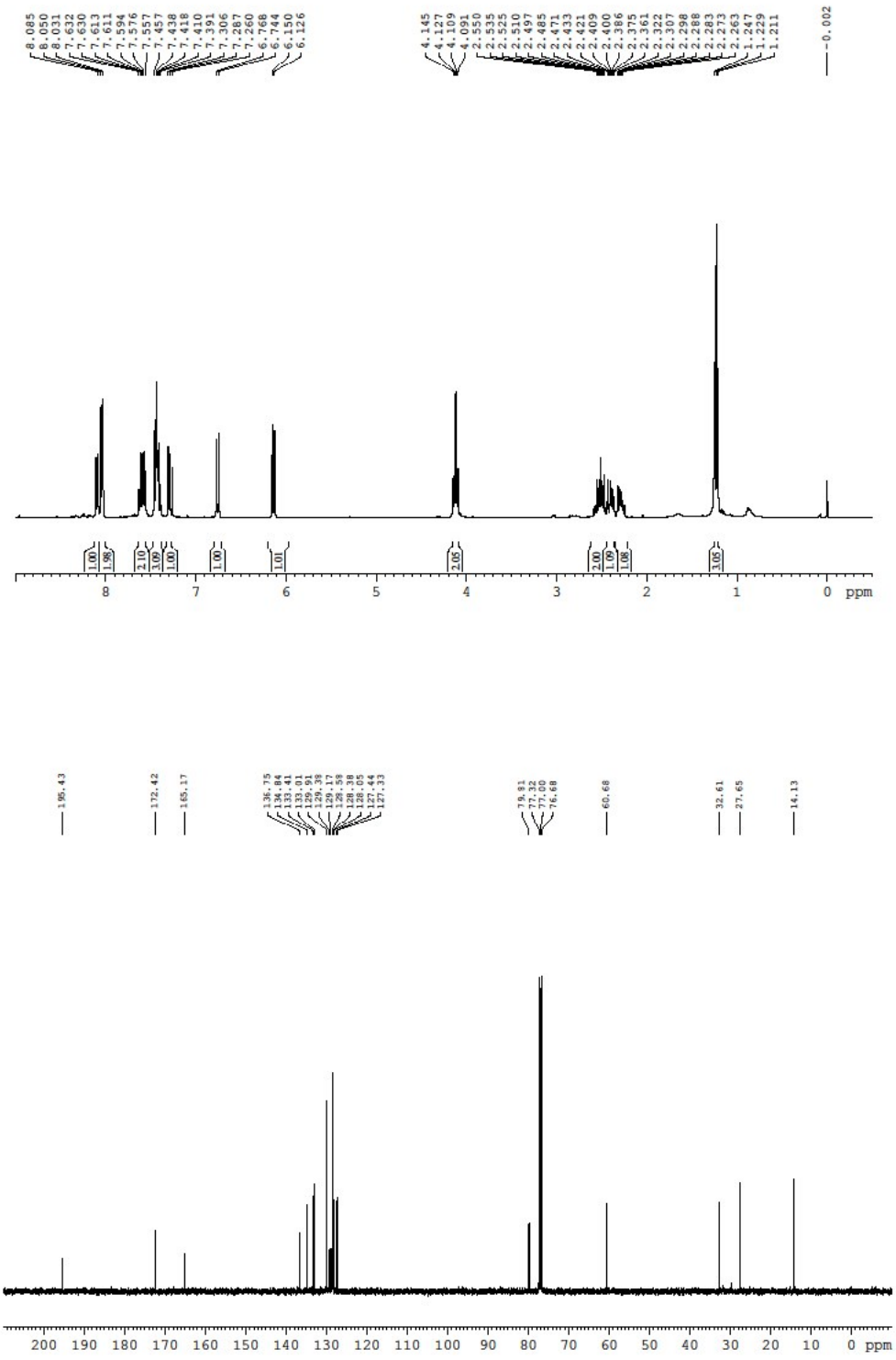
^{1}H NMR and ^{13}C NMR Spectrum of **3c**



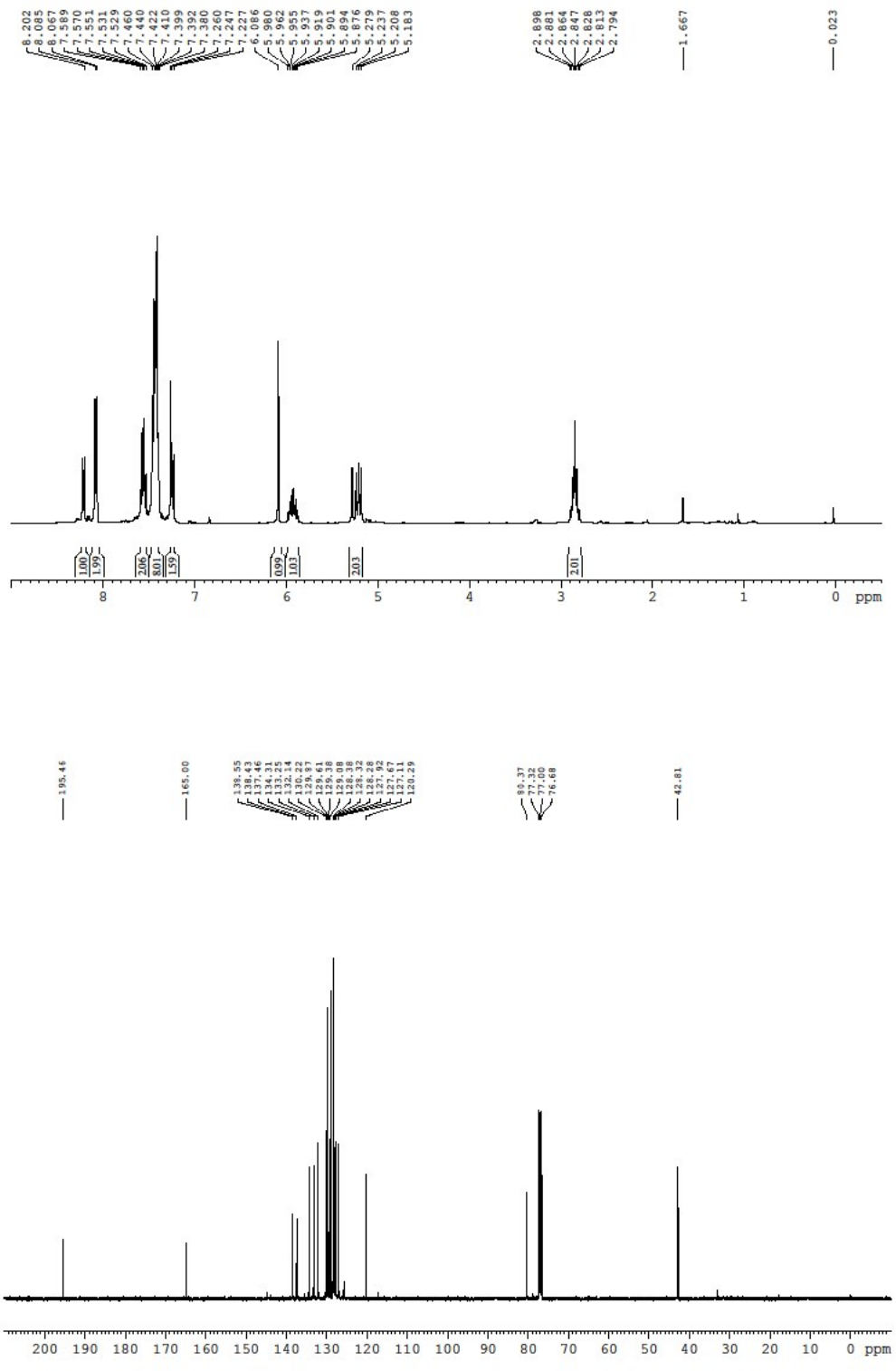
^{1}H NMR and ^{13}C NMR Spectrum of **3d**



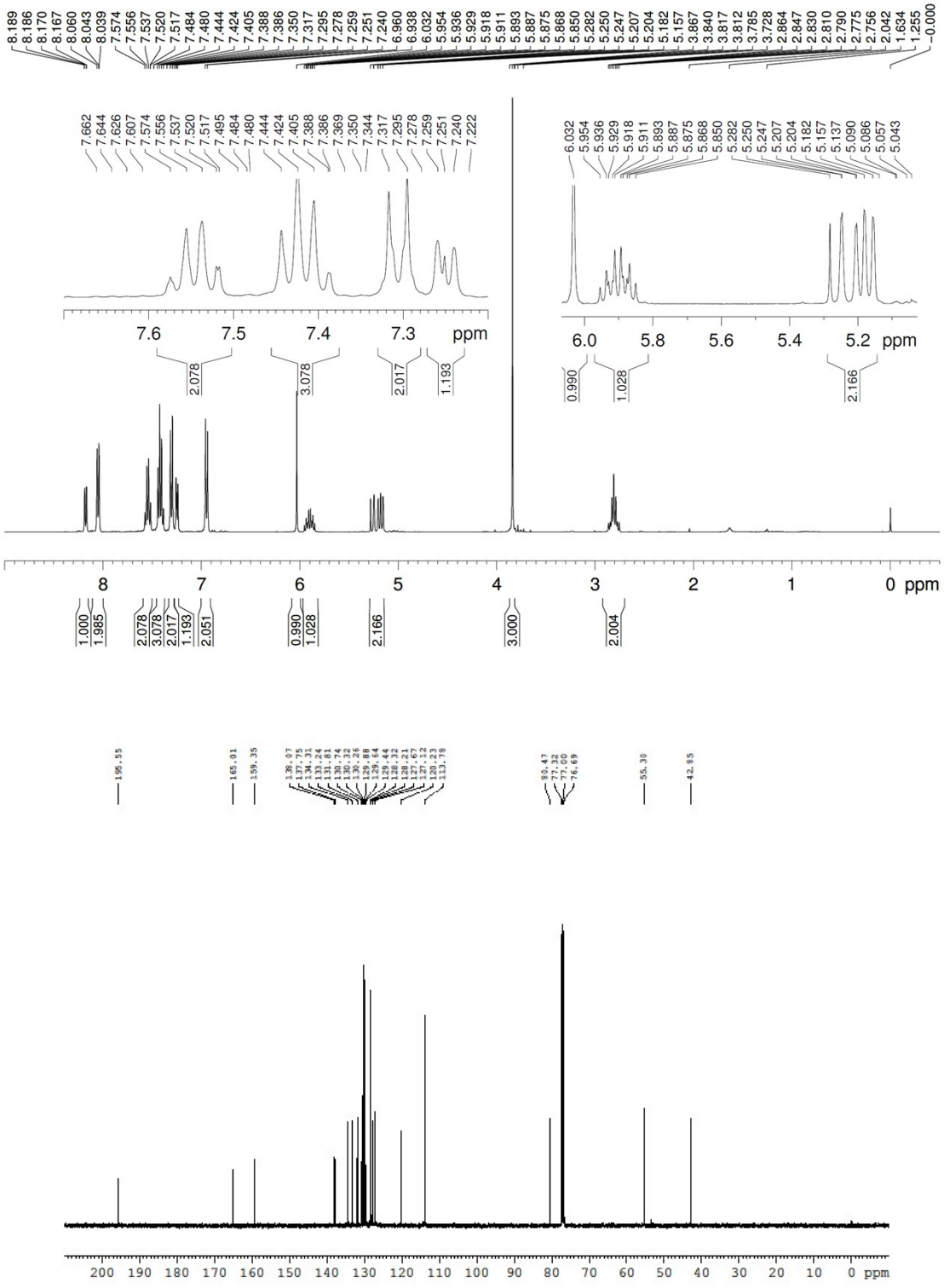
^{1}H NMR and ^{13}C NMR Spectrum of **3e**



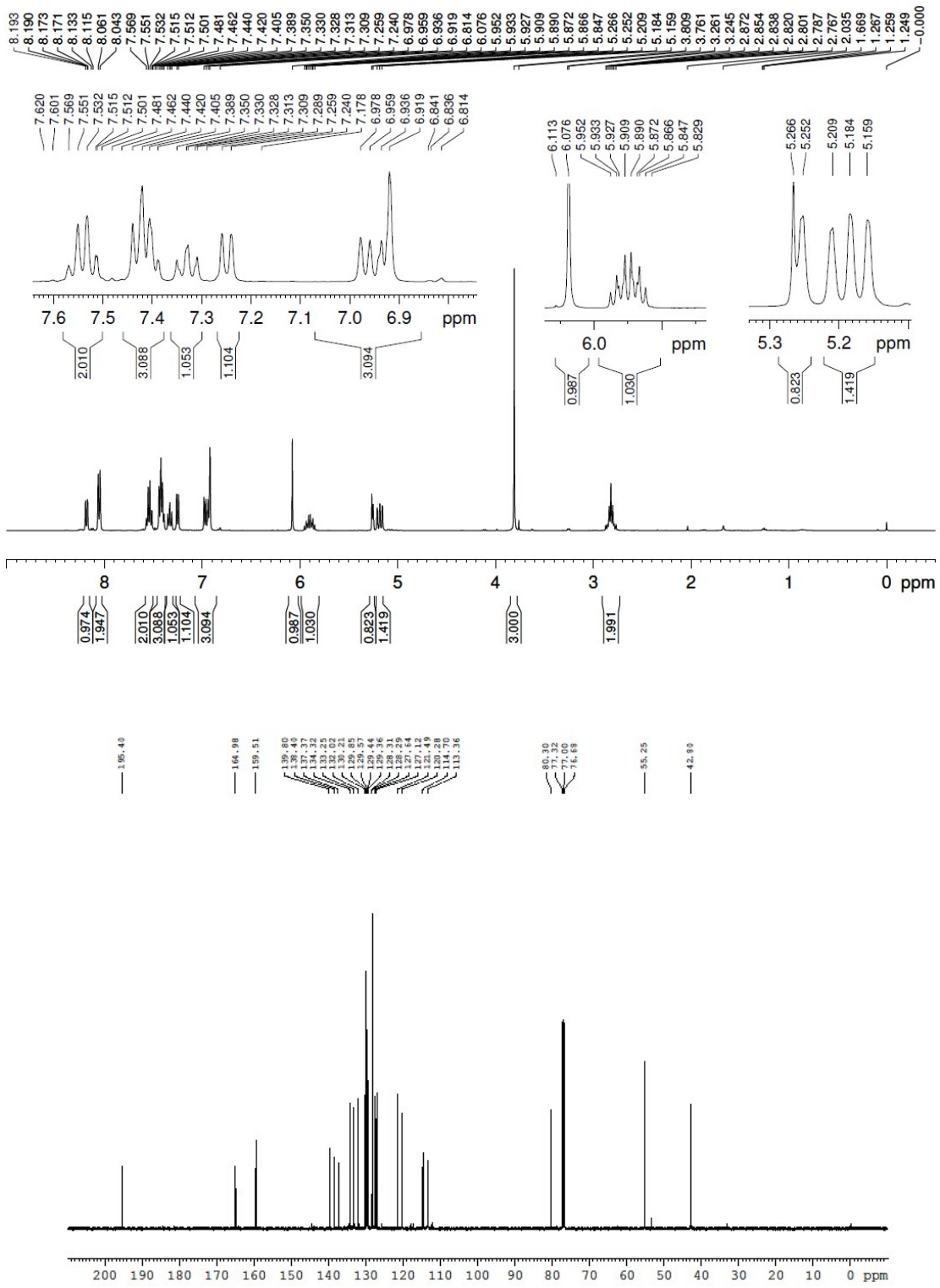
^{1}H NMR and ^{13}C NMR Spectrum of **3f**



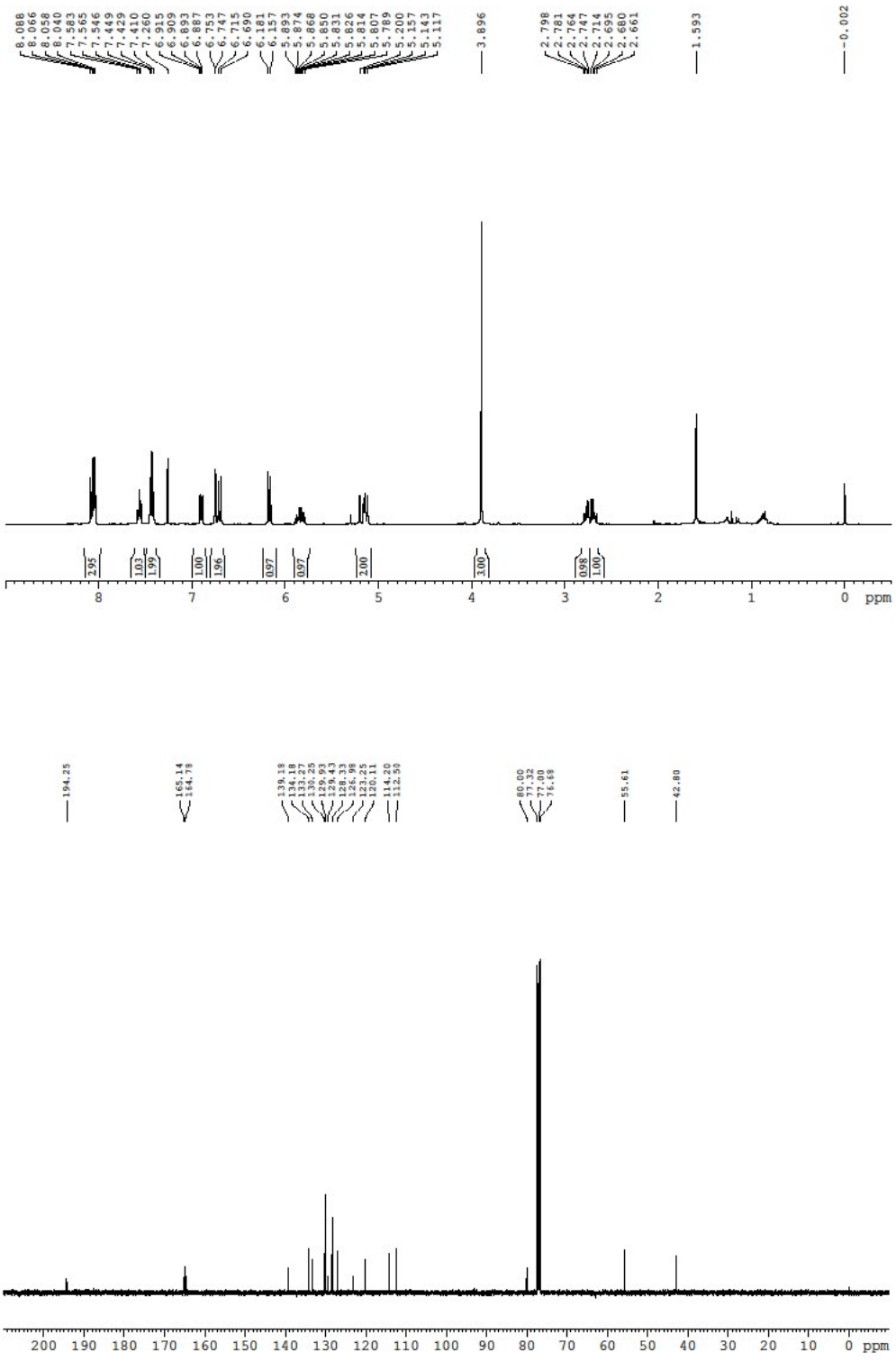
^{1}H NMR and ^{13}C NMR Spectrum of **3g**



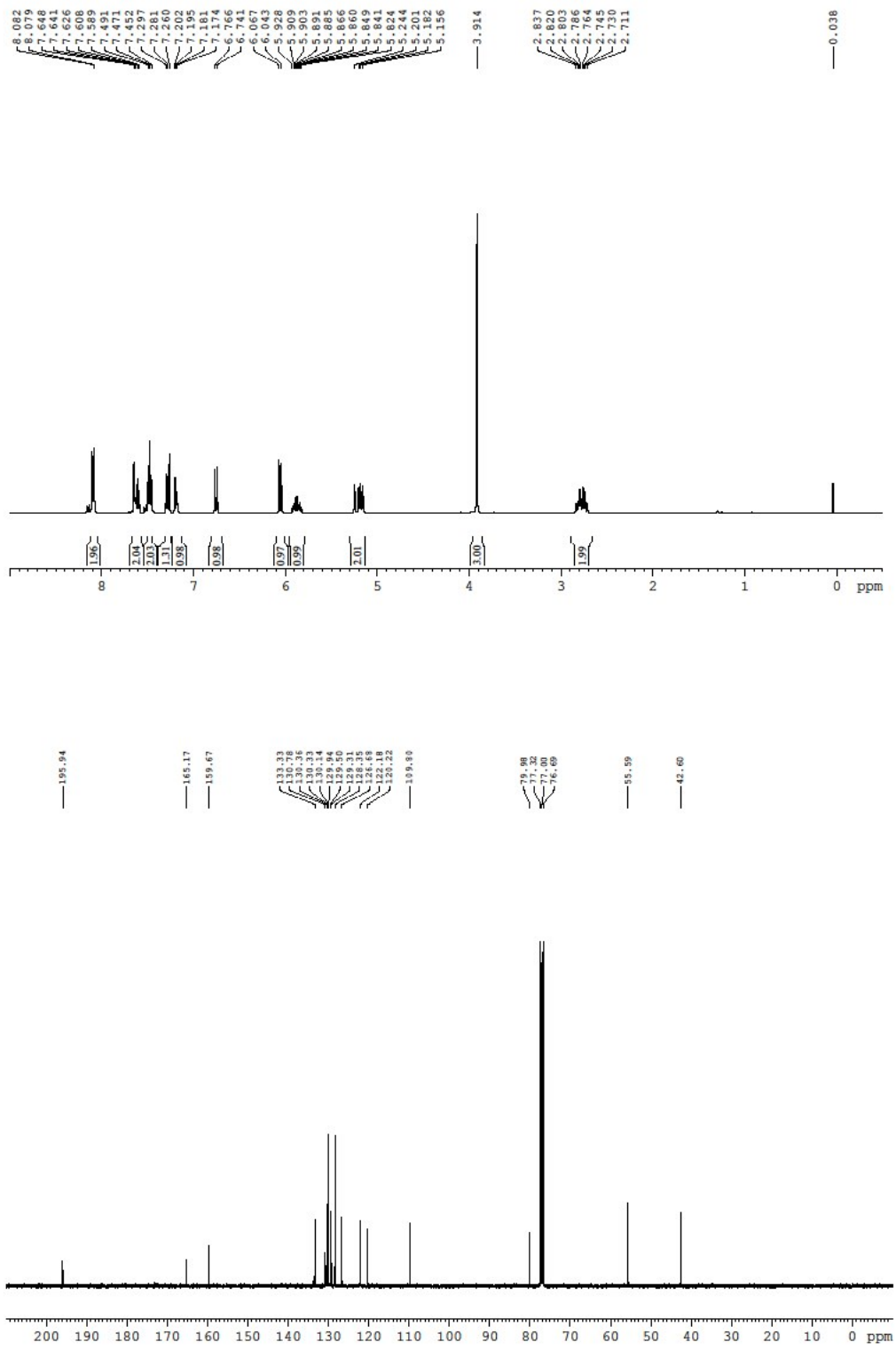
^{1}H NMR and ^{13}C NMR Spectrum of **3h**



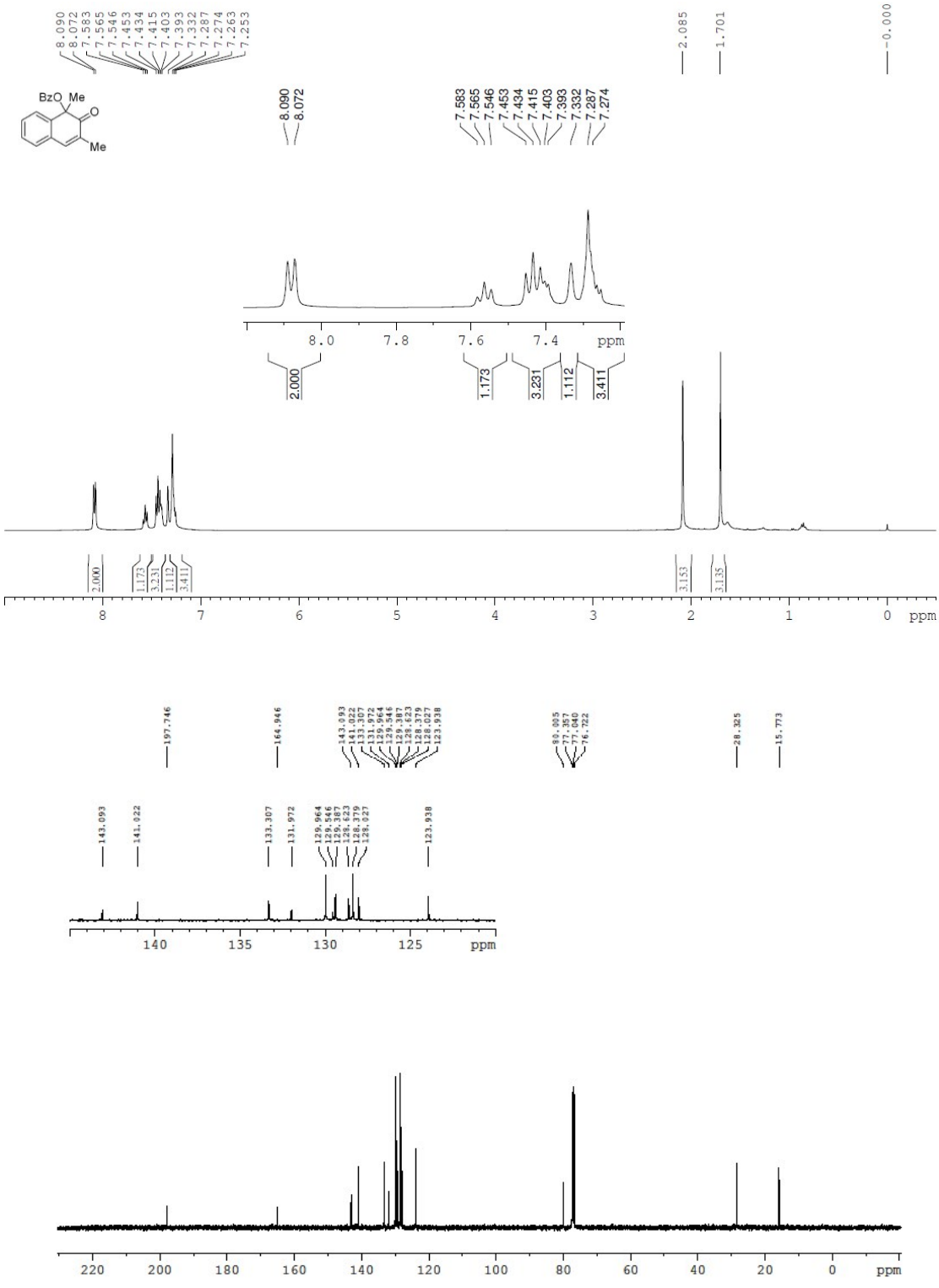
^{1}H NMR and ^{13}C NMR Spectrum of **3i**



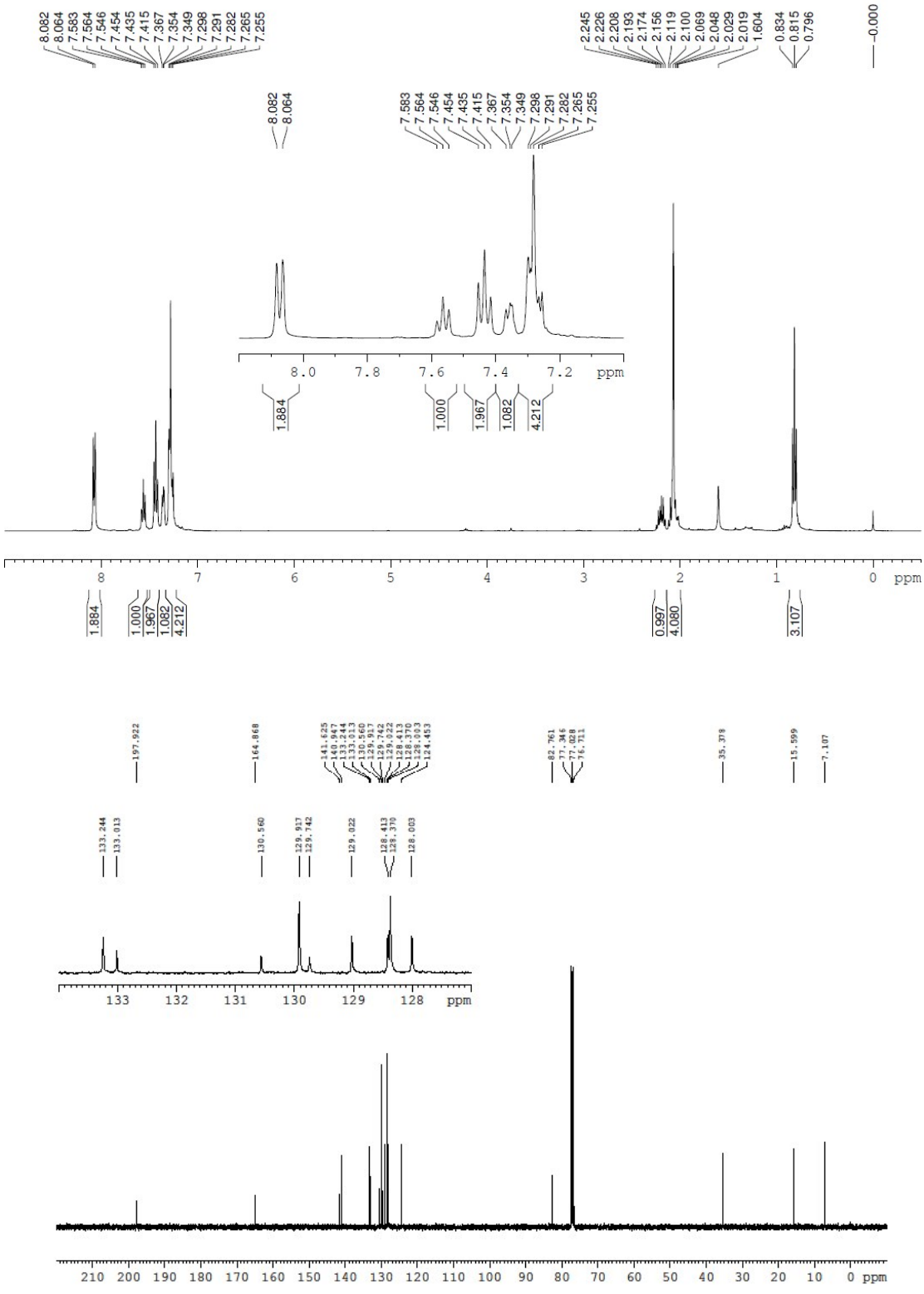
^{1}H NMR and ^{13}C NMR Spectrum of **3j**



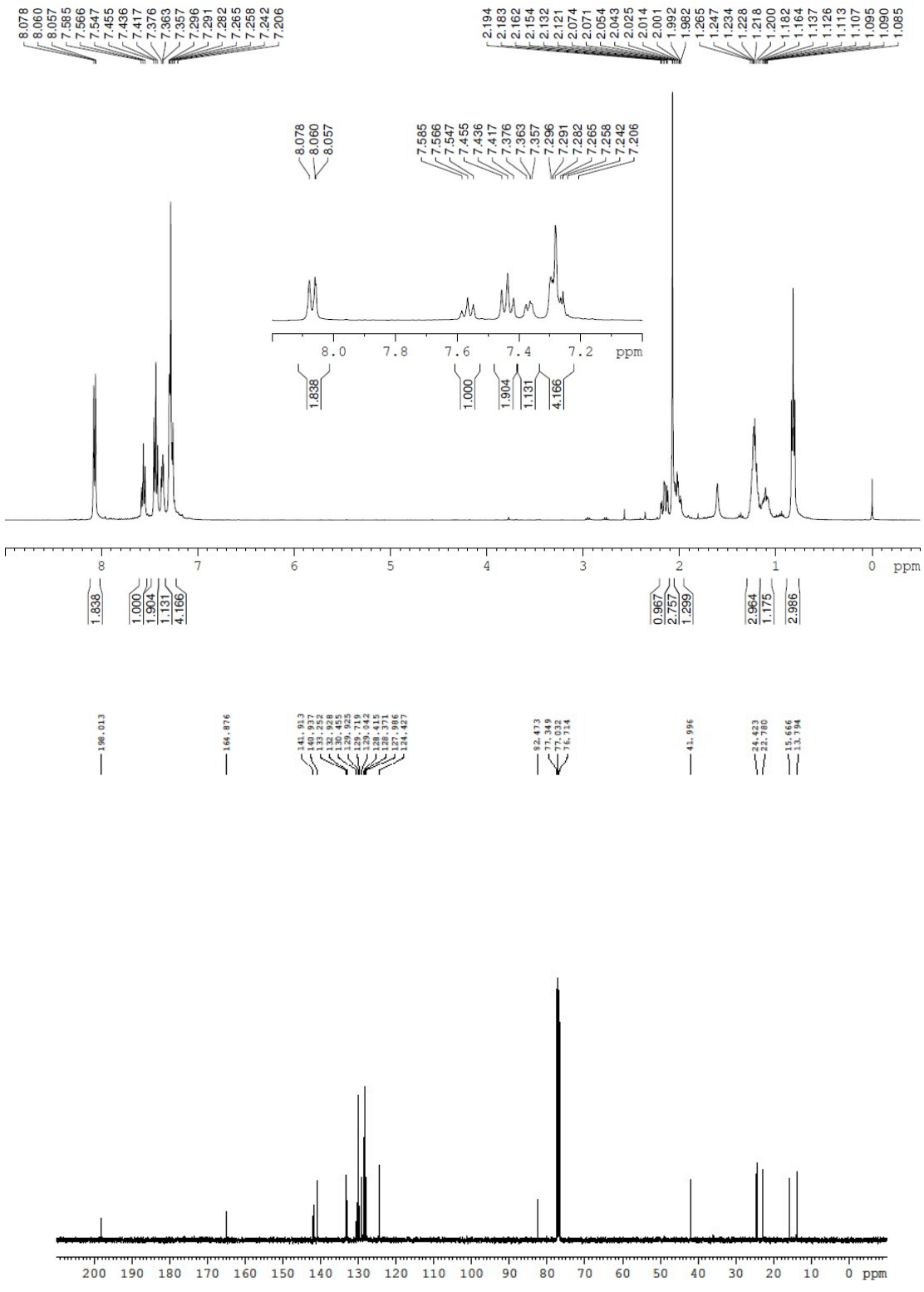
^{1}H NMR and ^{13}C NMR Spectrum of **3k**



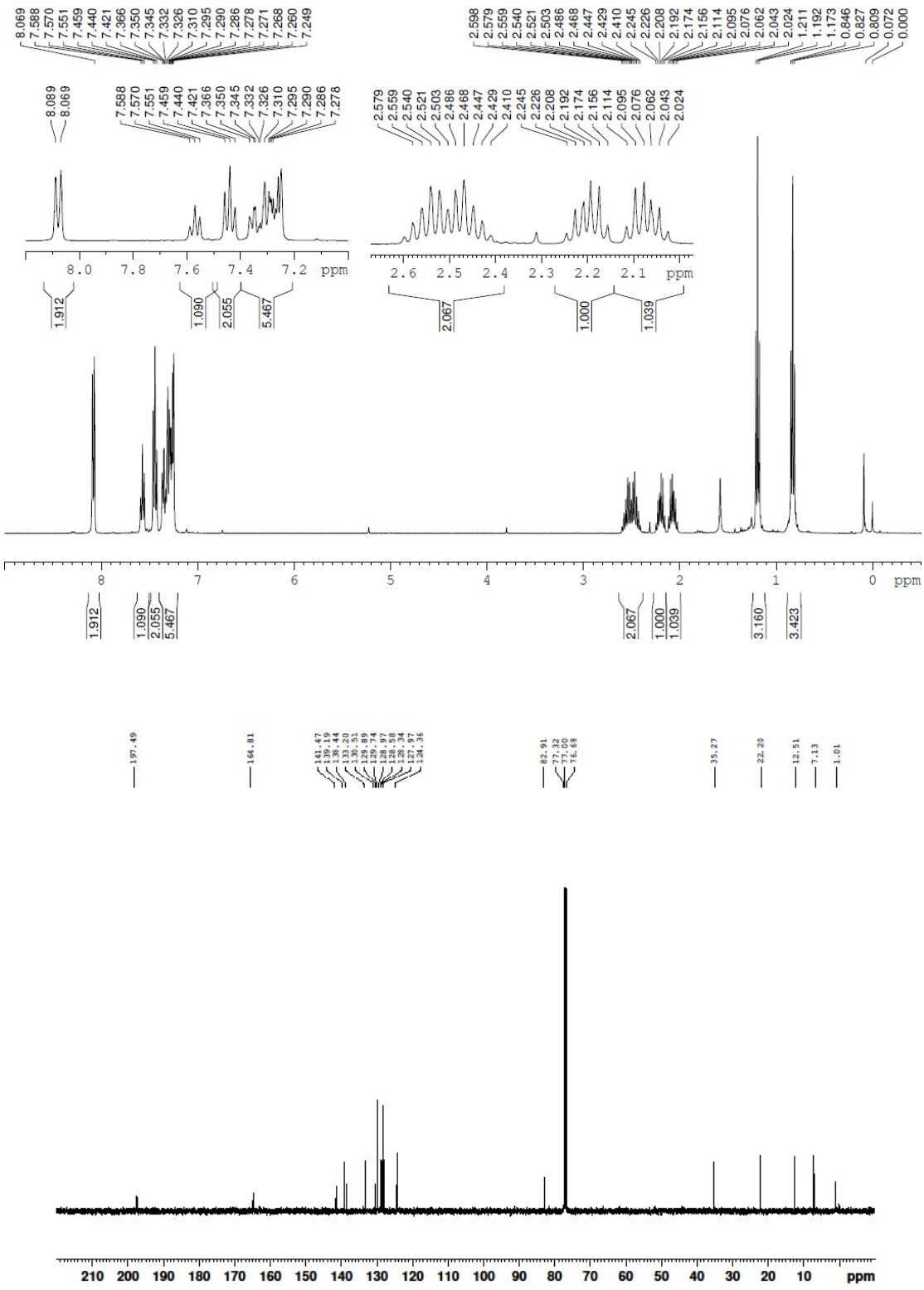
^{1}H NMR and ^{13}C NMR Spectrum of **5a**



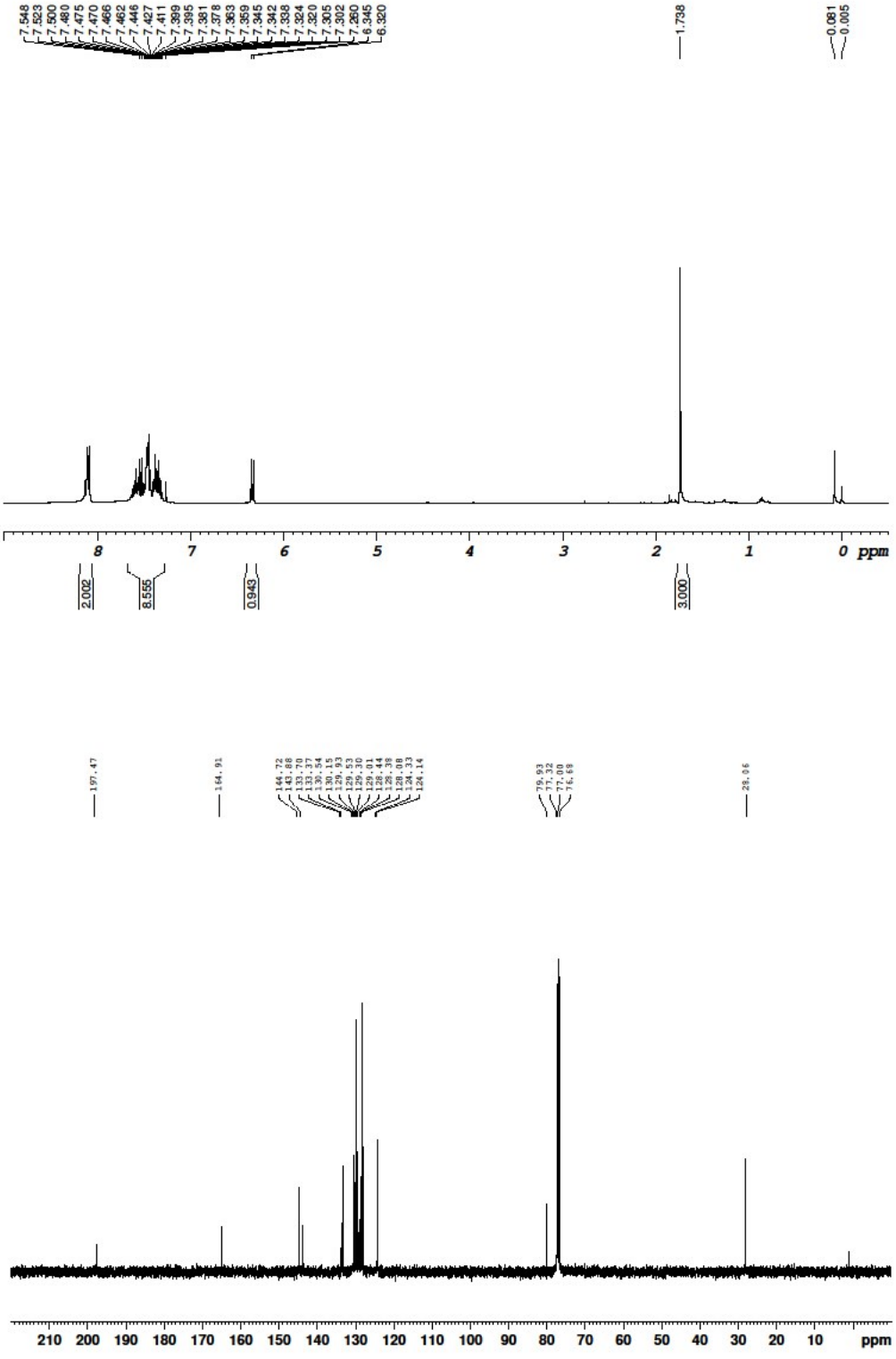
^{1}H NMR and ^{13}C NMR Spectrum of **5b**



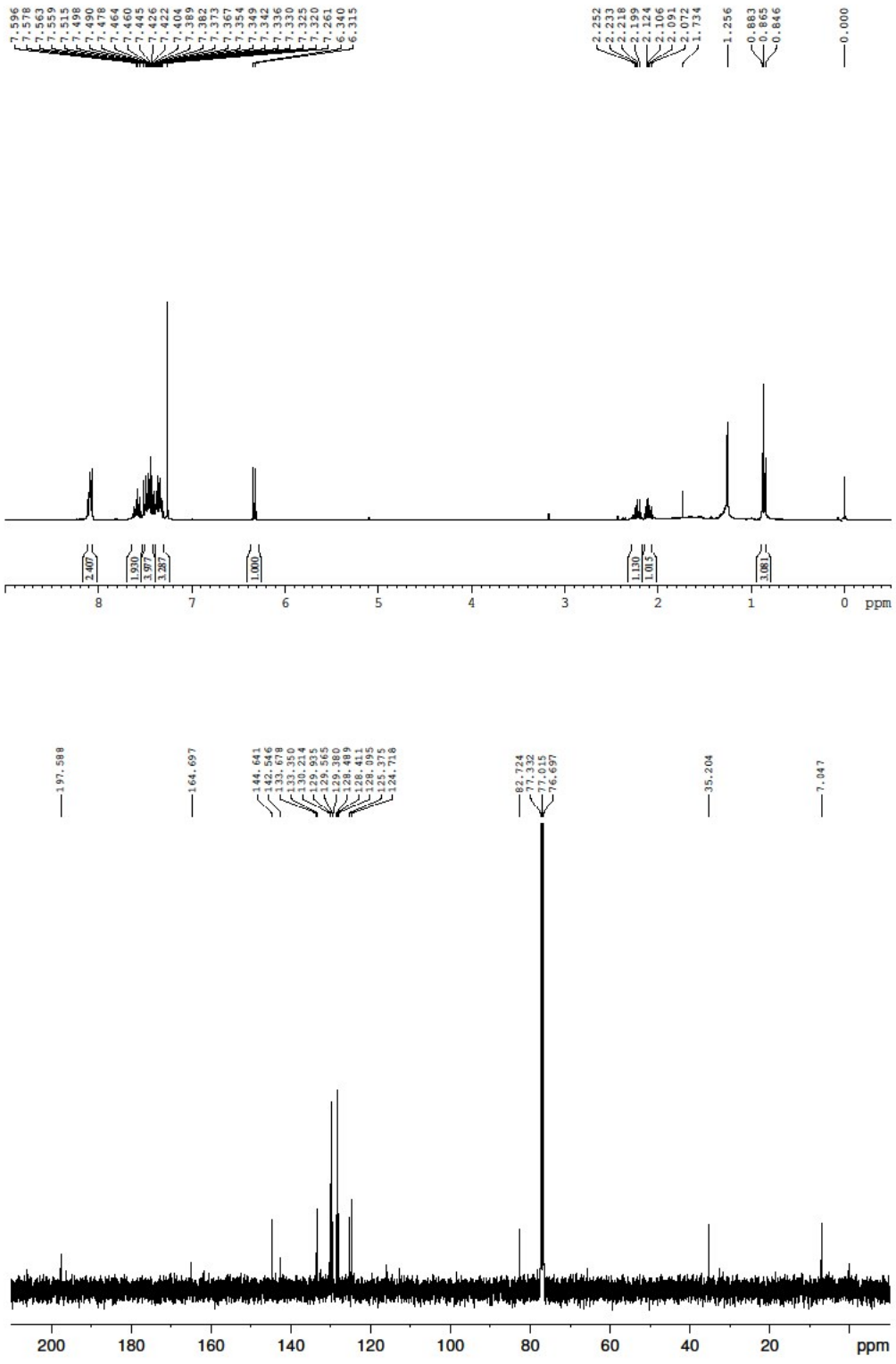
^{1}H NMR and ^{13}C NMR Spectrum of **5c**



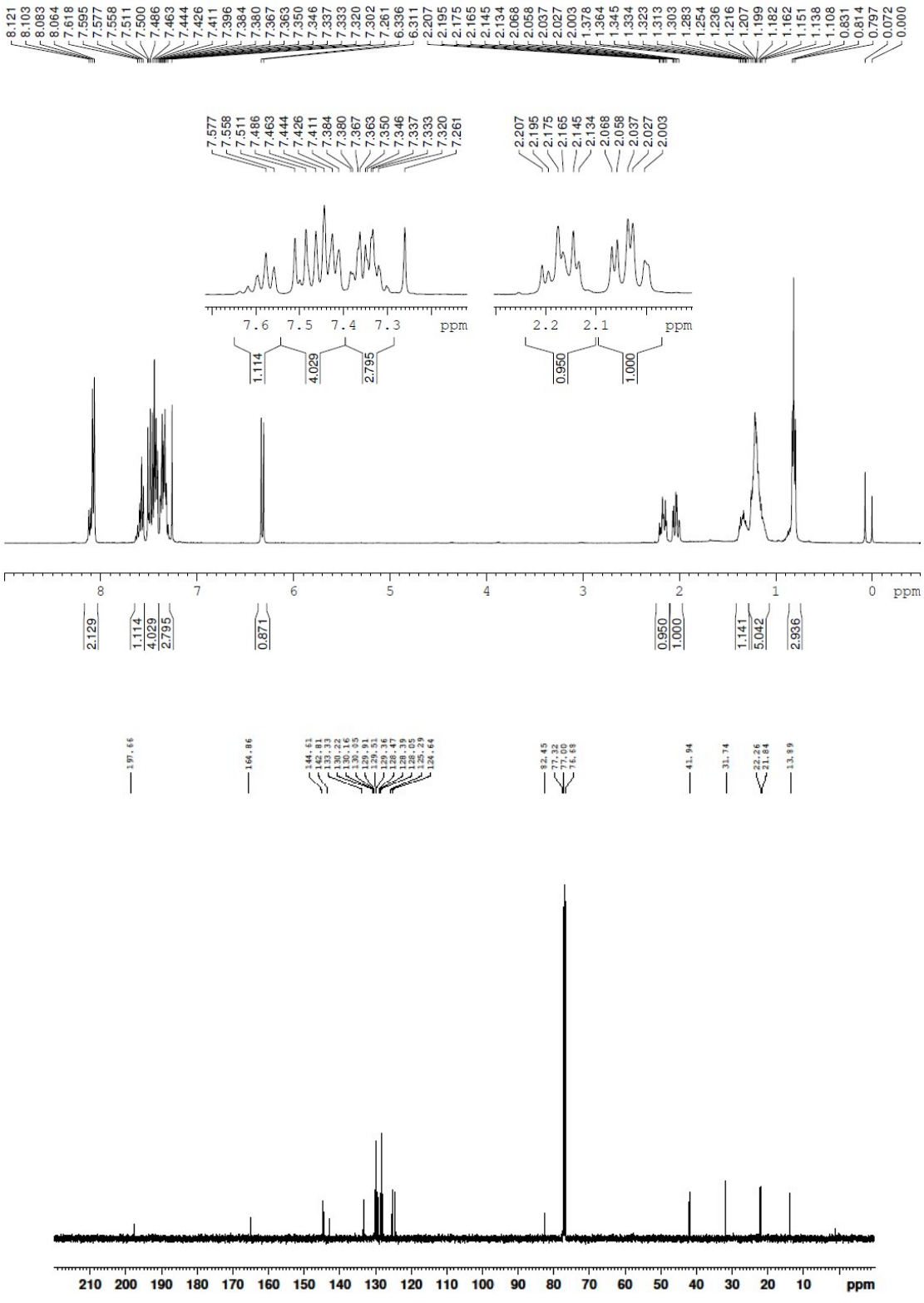
^{1}H NMR and ^{13}C NMR Spectrum of **5d**



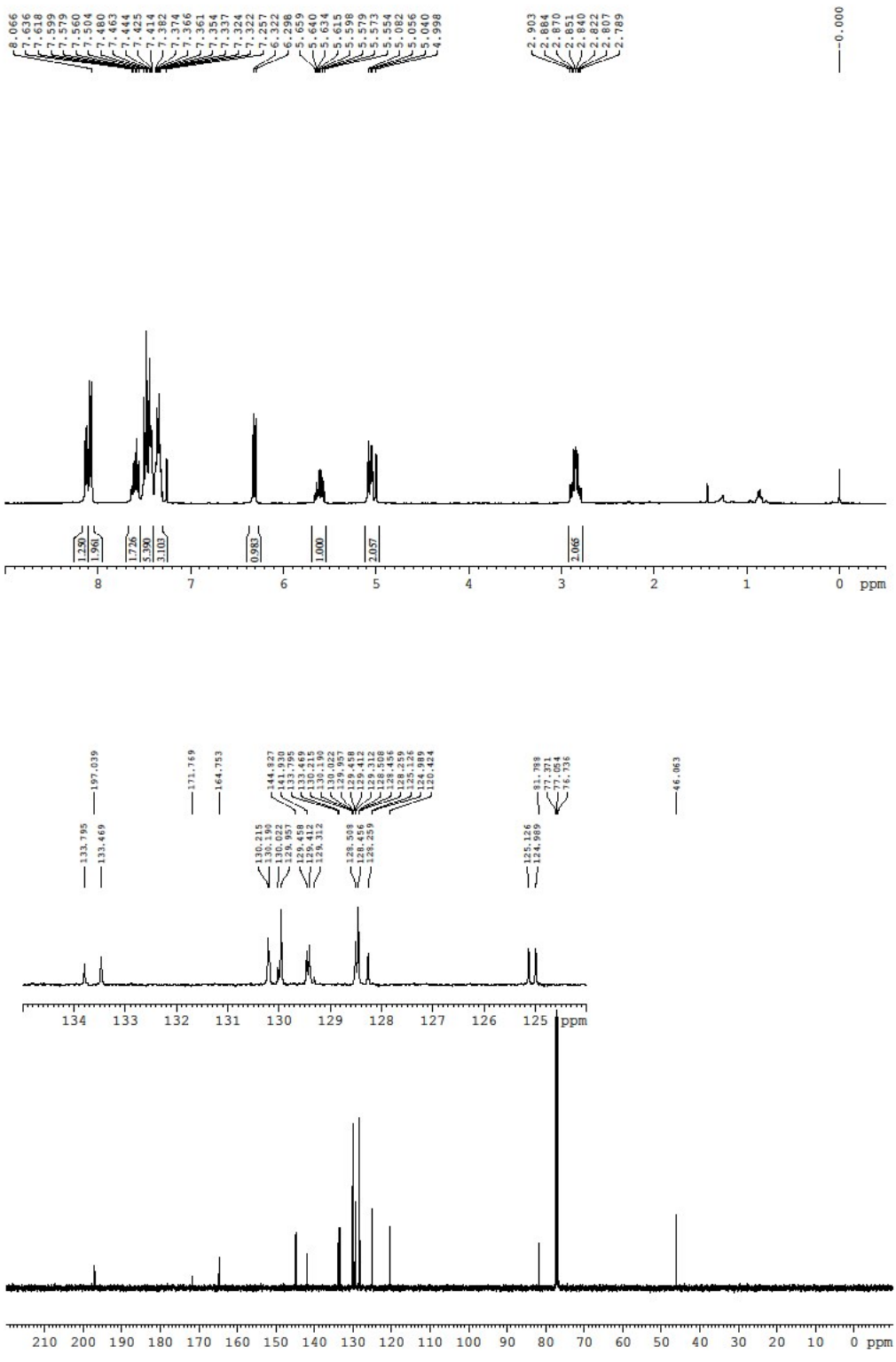
^{1}H NMR and ^{13}C NMR Spectrum of **5e**



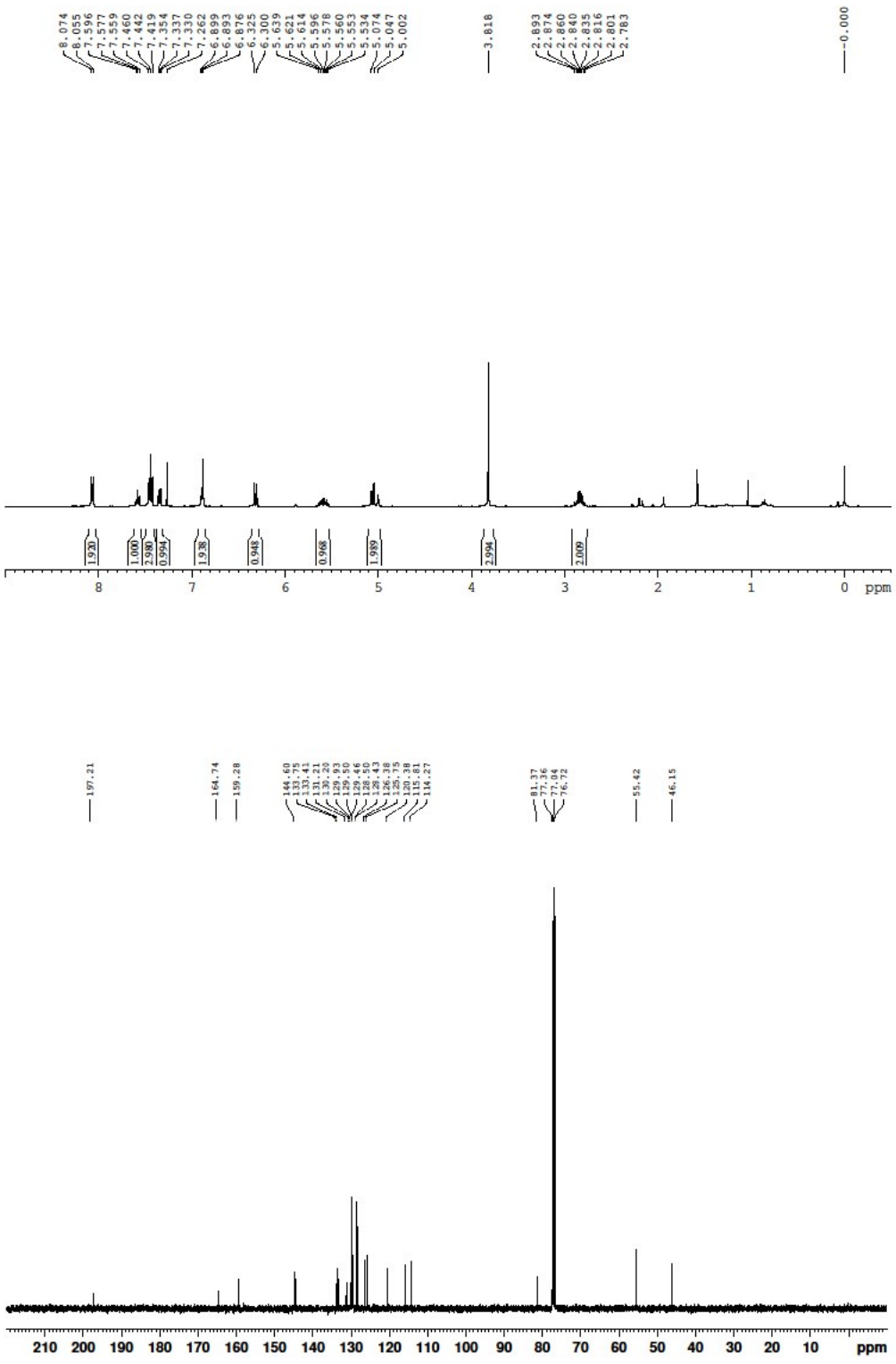
^{1}H NMR and ^{13}C NMR Spectrum of **5f**



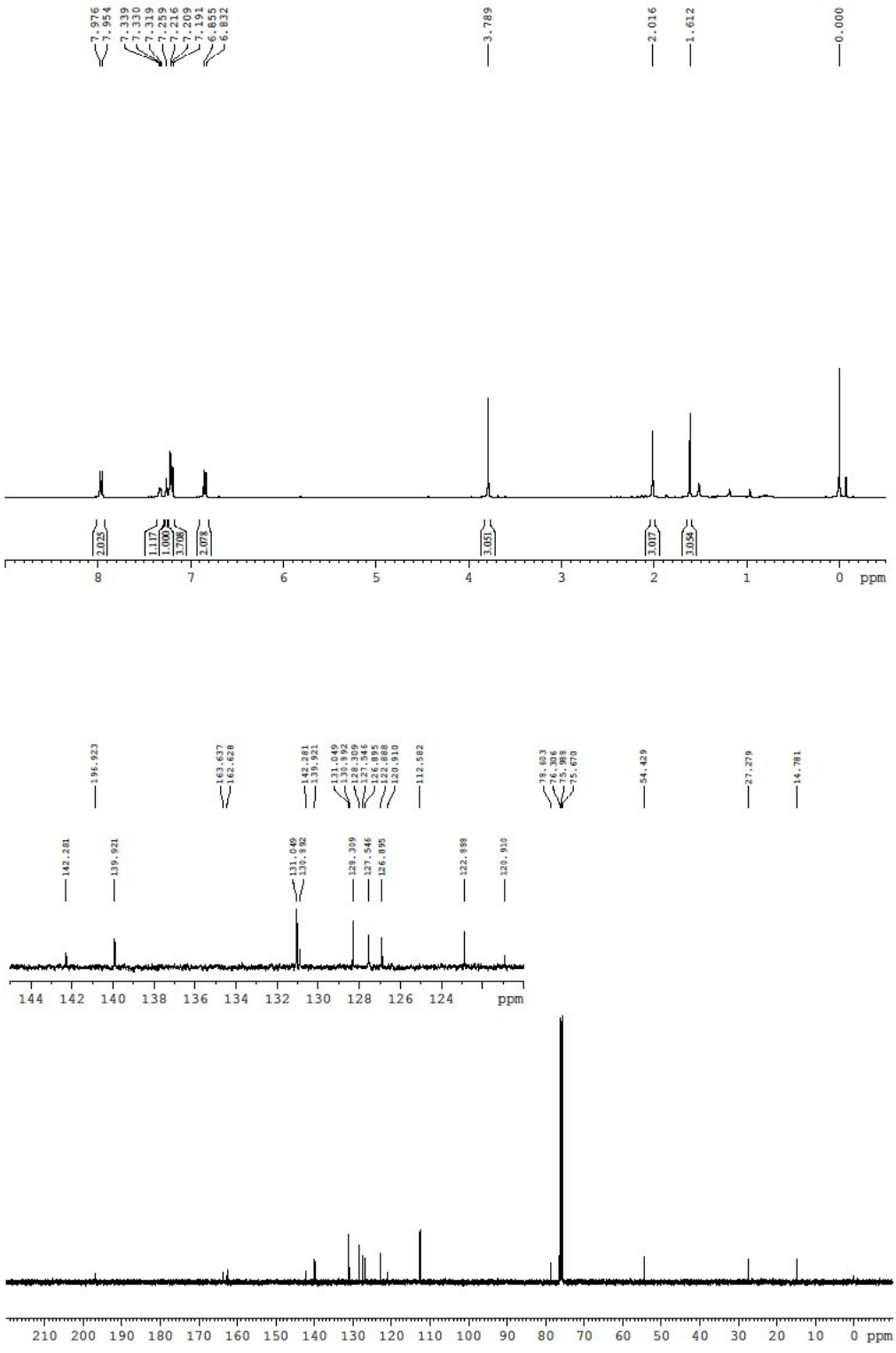
^{1}H NMR and ^{13}C NMR Spectrum of **5g**



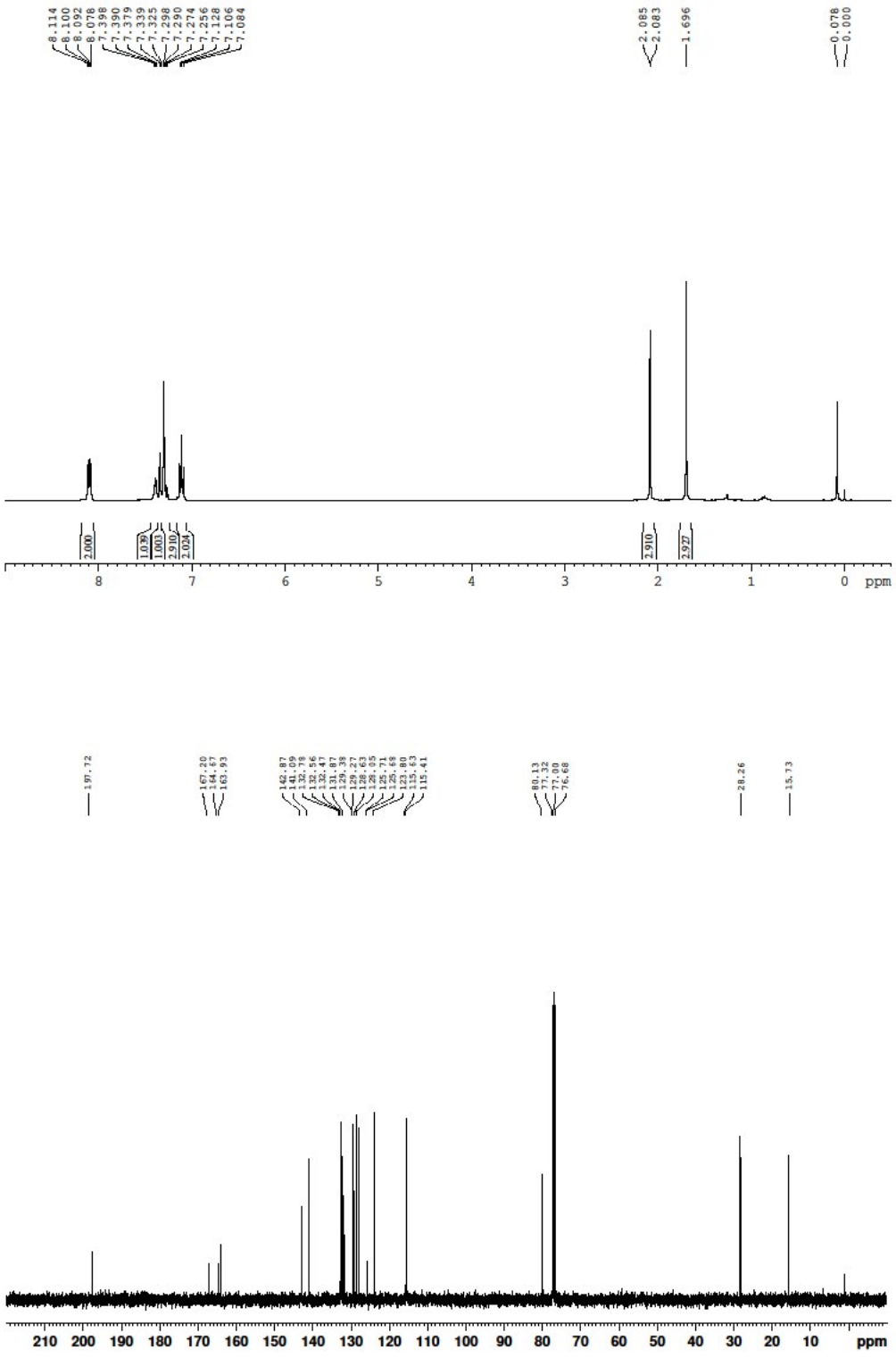
^{1}H NMR and ^{13}C NMR Spectrum of **5h**



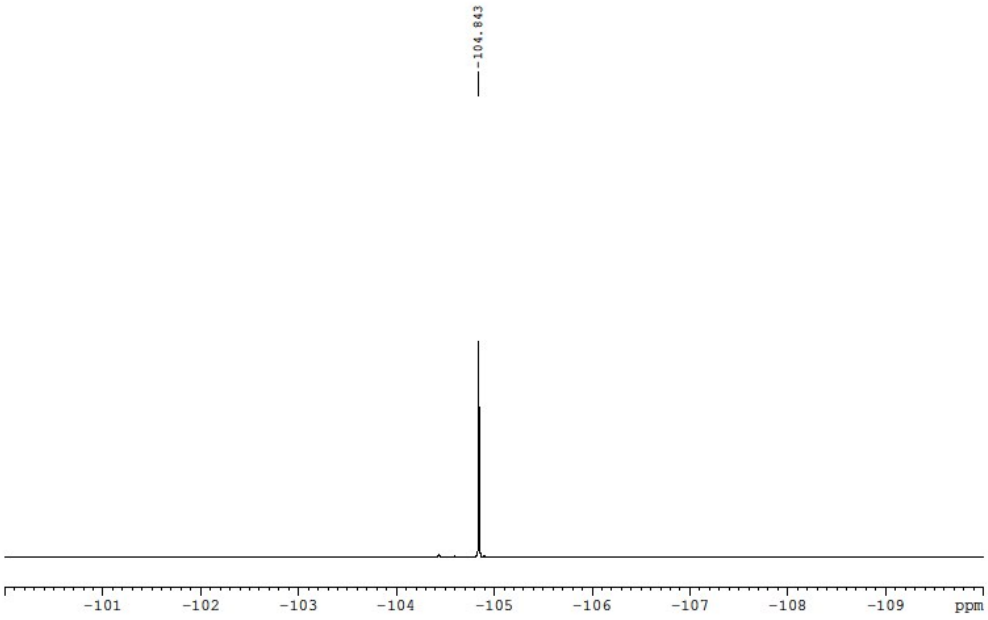
^{1}H NMR and ^{13}C NMR Spectrum of **5i**



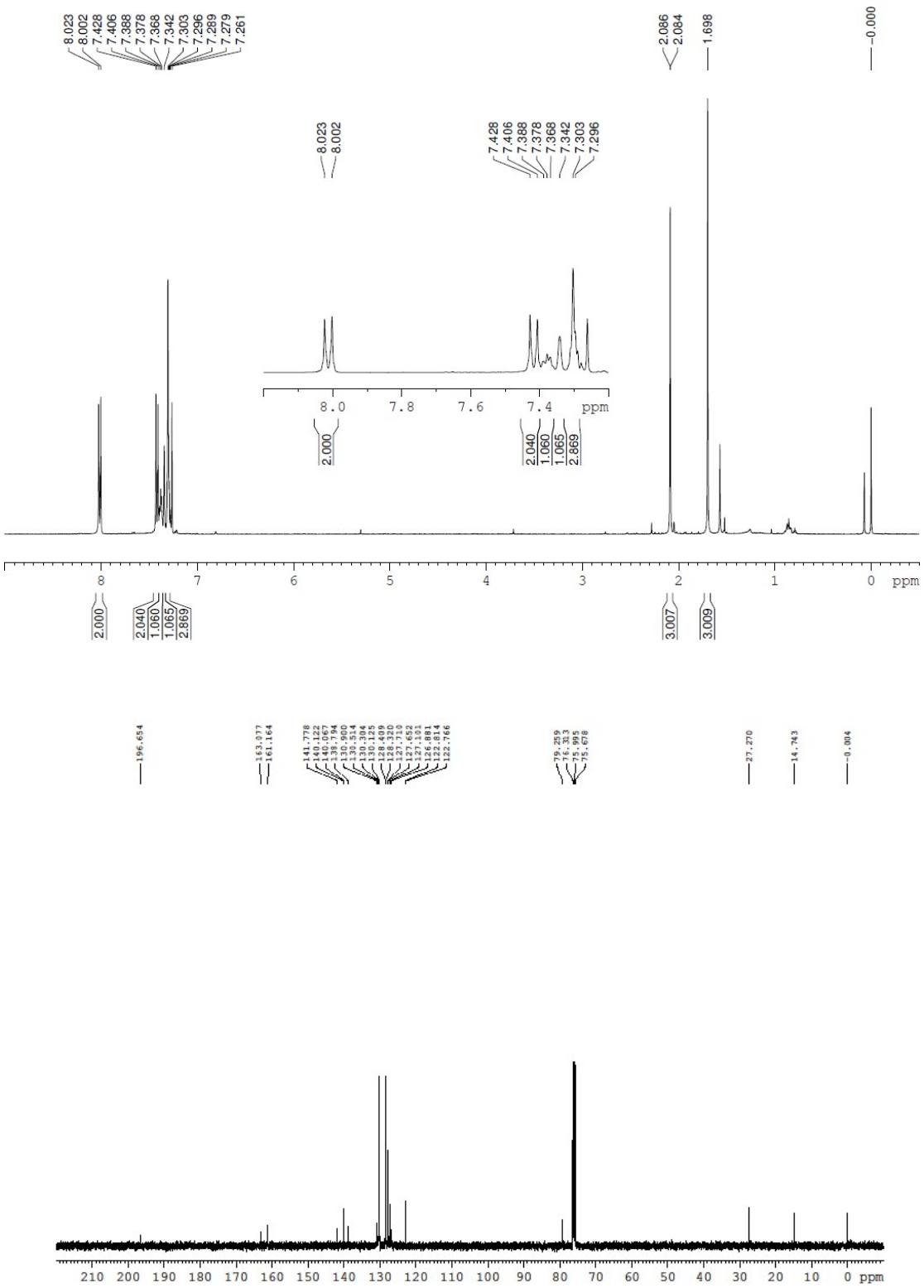
^{1}H NMR and ^{13}C NMR Spectrum of **5j**



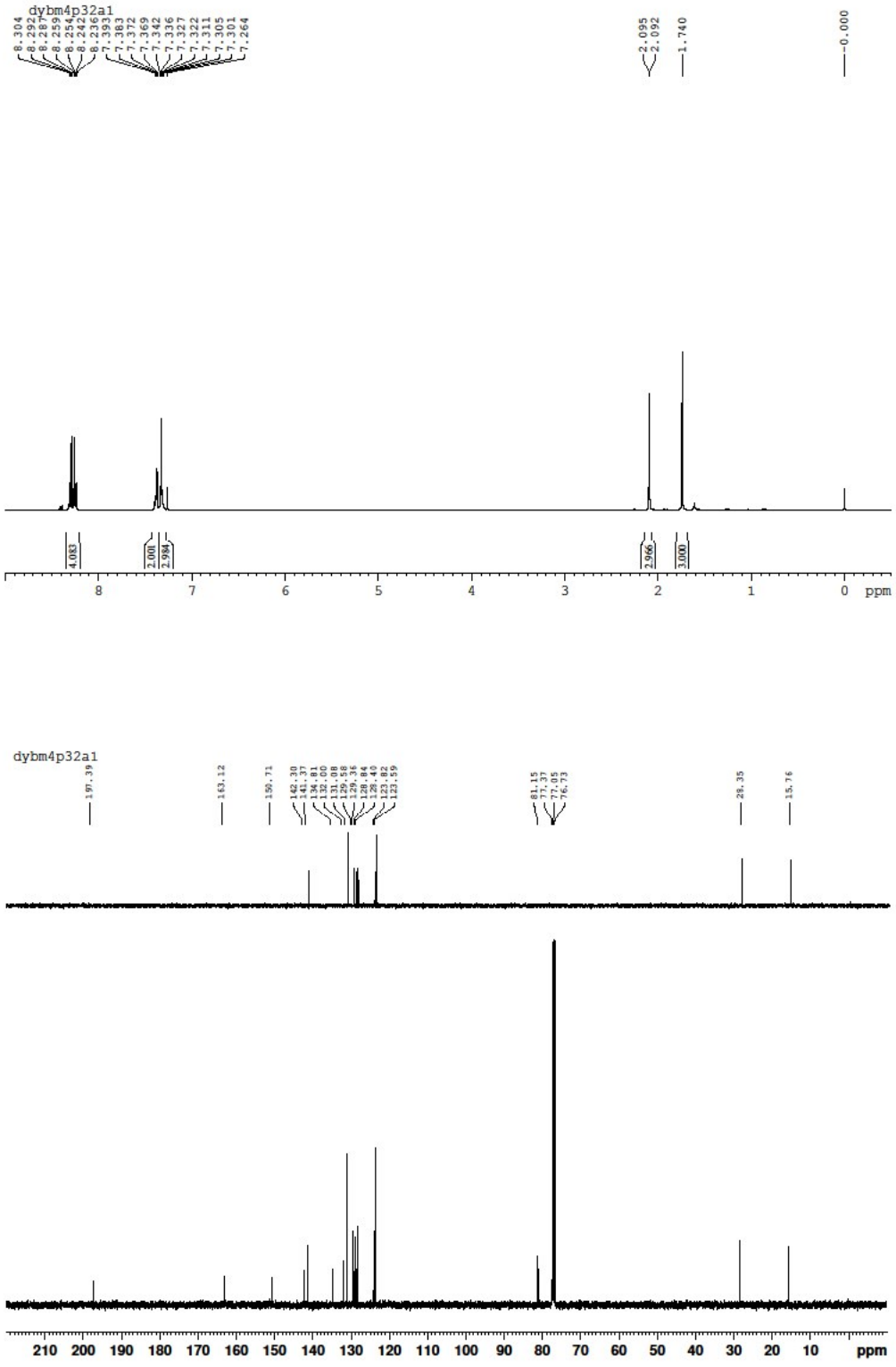
^{1}H NMR and ^{13}C NMR Spectrum of **5k**



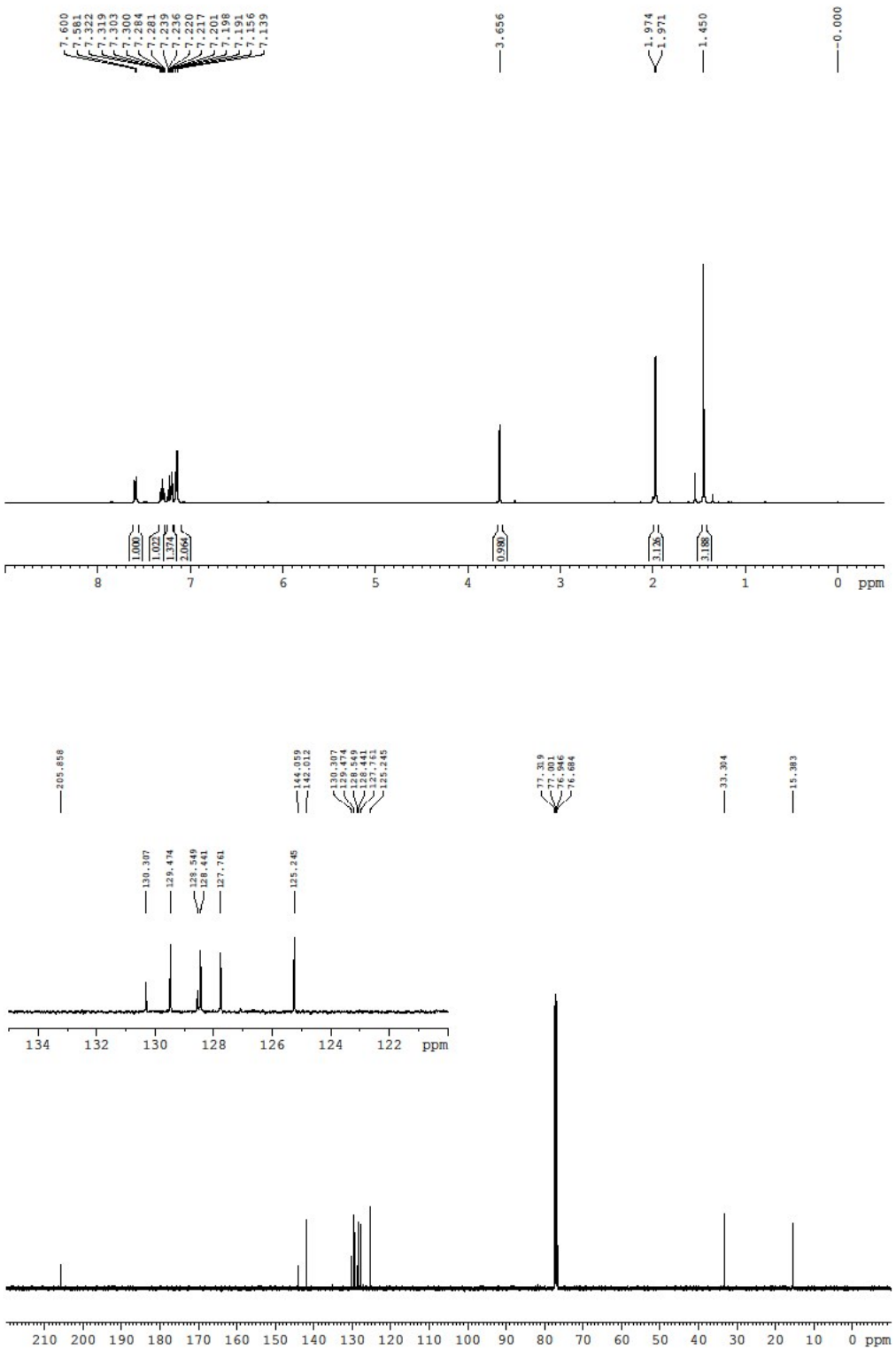
^{19}F NMR Spectrum of **5k**



^{1}H NMR and ^{13}C NMR Spectrum of **5l**



^{1}H NMR and ^{13}C NMR Spectrum of **5m**



^{1}H NMR and ^{13}C NMR Spectrum of **6**