Palladium Catalyzed Bicyclization of 1,8-Diiodonaphthalene and Tertiary Propargylic Alcohols to Phenalenones and Their Applications as Fluorescent Chemosensor for Fluoride Anion

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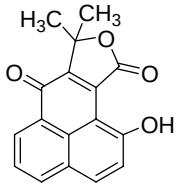
Supporting Information

General:

Melting points were recorded on a BÜCHI 535. NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR in $CDCl_3$. All electron impact mass spectra were recorded on Agilent 5973N MSD instrument and all high-resolution mass spectra (HRMS) were recorded on Waters Micromass GCT instrument. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254.

Triethylamine, diisopropylamine, N,N-diisopropylethylamine, pyrrolidine, piperidine, tetrahydrofuran (THF), dichloromethane, ethyl acetate, hexane, 1,8-dibromonaphthalene, tetrabutylammonium fluoride(1M in THF, contain 5%H_2O) (acros), tetrabutylammonium chloride (acros), tetrabutylammonium bromide (acros), tetrabutylammonium hydroxide(1M in H_2O) (acros), 2-methylbut-3-yn-2-ol (**2a**) (acros), 3-methylpent-1-yn-3-ol (**2b**) (acros), 1-ethynylcyclohexanol (**2f**) (acros), prop-2-yn-1-ol (**2k**), $Pd(PPh_3)_2Cl_2$ (acros), $Pd(OAc)_2$ (acros), $Pd(PPh_3)_4$ (acros) were used as received. 1,8-Diiodonaphthalene (**1**), 3-methylhex-1-yn-3-ol (**2c**), 3-ethylpent-1-yn-3-ol (**2d**), 1-ethynylcyclopentanol (**2e**), 3,5-dimethylhex-1-yn-3-ol (**2g**), hex-1-yn-3-ol (**2h**), non-1-yn-3-ol (**2i**), 1-phenylprop-2-yn-1-ol (**2j**) were synthesized employing published procedures.[1,2]

1. 1-hydroxy-8,8-dimethyl-7H-phenaleno[1,2-c]furan-7,10(8H)-dione **(3a):**



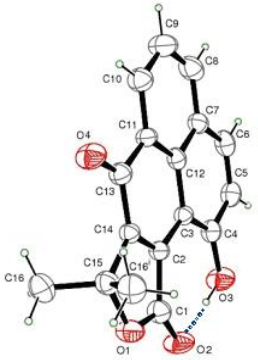
(a) General Procedure for $Pd(PPh_3)_2Cl_2$/CuI-catalyzed bicyclization of 1,8-diiodonaphthalene (**1**) and 2-methylbut-3-yn-2-ol (**2a**): To a solution of **1** (380 mg, 1 mmol) and **2a** (336 mg, 4 mmol) in Et_3N (40 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) were added at ambient temperature. The reaction mixture is purged with nitrogen for 10 min. Then water (10 μL) and air (5 mL) was mixed in by syringe and the sealed flask was heated at 80 ^{o}C for about 10 h. After complete consumption of starting material as tracked by TLC, Et_3N was removed under redeuced pressure and the residue was dissolved with ether, washed with water, and dried over Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified via flash chromatography on silica gel (dichloromethane/hexane = 1:2). **3a** (179 mg, 64%) was obtained.

(b) Under the reaction conditions claimed above, **5a** (336 mg, 1 mmol) and **2a** (168 mg, 2 mmol) in 20 mL of Et_3N also afforded **3a** (190 mg) in yield of 68%.

3a:

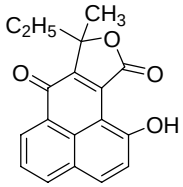
orange solid, m.p. 232.8-234.4 °C.

Crystal structure of **3a**:



^{1}H-NMR (Figure S1): δ 13.28 (s, 1H), 8.74 (d, J = 7.60 Hz, 1H), 8.18 (d, J = 7.60 Hz, 1H), 8.00 (d, J = 9.10 Hz, 1H), 7.70 (dd, J_1 = J_2 = 7.60 Hz, 1H), 7.23 (d, J = 9.10 Hz, 1H), 1.87 (s, 6H);
^{13}C-NMR (Figure S2): δ 25.2, 91.2, 104.5, 122.5, 125.4, 128.7, 130.2, 130.6, 131.9, 132.5, 137.1, 137.6, 152.7, 163.2, 175.5, 178.9;
EIMS: *m/z* 280 (M^+, 41.24), 237 (100);
HRMS: cacld. for $C_{17}H_{12}O_4$ [M^+], 280.0685; found, 280.0695.

2. 8-ethyl-1-hydroxy-8-methyl-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3b):**



(a) The reaction of **1** (380 mg, 1 mmol), **2b** (392 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **3b** (182 mg) in yield of 62%.

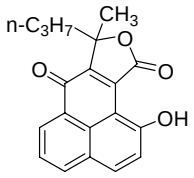
(**b)** The reaction of **5a** (336 mg, 1 mmol), **2b** (196 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 mL of Et_3N also afforded **3b** (191 mg) in yield of 65%.

3b:

orange solid, m.p. 165.8-167.2 °C.

^{1}H-NMR (Figure S3): δ 13.33 (s, 1H), 8.75 (d, J = 7.60 Hz, 1H), 8.20 (d, J = 7.60 Hz, 1H), 8.03 (d, J = 9.00 Hz, 1H), 7.72 (dd, J_1 = J_2 = 7.60 Hz, 1H), 7.26 (d, J = 9.00 Hz, 1H), 2.31 (q, J = 7.40 Hz, 2H), 1.85 (s, 3H), 0.82 (t, J = 7.40 Hz, 3H);
^{13}C-NMR (Figure S4): δ 8.2, 24.0, 30.5, 94.0, 104.5, 122.6, 125.4, 128.8, 130.3, 130.5, 132.1, 133.4, 137.1, 137.6, 151.6, 163.2, 175.8, 178.9;
EIMS: *m/z* 294 (M^+, 47.36), 266 (100);
HRMS: cacld. for $C_{18}H_{14}O_4$ [M^+], 294.0892; found, 294.0887.

3. 1-hydroxy-8-methyl-8-propyl-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3c):**



(a) The reaction of **1** (380 mg, 1 mmol), **2c** (448 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **3c** (179 mg) in yield of 58%.

(**b)** The reaction of **5a** (336 mg, 1 mmol), **2c** (224 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 mL of Et_3N also afforded **3c** (191 mg) in yield of 62%.

3c:

orange solid, m.p. 109.5-110.8 ^{o}C.

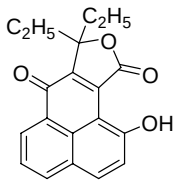
^{1}H-NMR (Figure S5): δ 13.32 (s, 1H), 8.74 (d, J = 7.50 Hz, 1H), 8.19 (d, J = 7.50 Hz, 1H), 8.01 (d, J = 9.00 Hz, 1H), 7.71 (dd, $J_1 = J_2$ = 7.50 Hz, 1H), 7.24 (d, J = 9.00 Hz, 1H), 2.27-2.20 (m, 2H), 1.85 (s, 3H), 1.36-1.30 (m, 1H), 1.14-1.08 (m, 1H), 0.88 (t, J = 7.50 Hz, 1H);

^{13}C-NMR (Figure S6): δ 14.1, 17.3, 24.2, 39.4, 93.7, 104.5, 122.5, 125.4, 128.7, 130.2, 130.3, 132.0, 133.1, 137.1, 137.6, 151.8, 163.2, 175.7, 178.9;

EIMS: *m/z* 308 (M^+, 12.94), 266 (100);

HRMS: cacld. for $C_{19}H_{16}O_4$ [M^+], 308.1049; found, 308.1053.

4. 8,8-diethyl-1-hydroxy-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3d):**



(a) The reaction of **1** (380 mg, 1 mmol), **2d** (448 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **3d** (138 mg) in yield of 45%.

(**b)** The reaction of **5a** (336 mg, 1 mmol), **2d** (224 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 mL of Et_3N also afforded **3d** (132 mg) in yield of 43%.

3d:

orange solid, m.p. 105.8-107.3 °C.

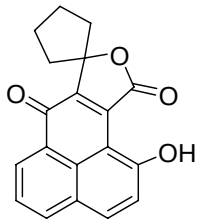
^{1}H-NMR (Figure S7): δ 13.36 (s, 1H), 8.75 (d, *J* = 8.00 Hz, 1H), 8.21 (d, *J* = 8.00 Hz, 1H), 8.04 (d, *J* = 9.50 Hz, 1H), 7.72 (dd, J_1 = J_2 = 8.00 Hz, 1H), 7.27 (d, *J* = 9.50 Hz, 1H), 2.38 (m, 2H), 2.27(m, 2H), 0.78 (t, *J* = 8.50 Hz, 6H);

^{13}C-NMR (Figure S8): δ 8.0, 29.6, 97.1, 104.6, 122.6, 125.4, 128.8, 130.2, 130.3, 132.1, 133.6, 137.1, 137.6, 150.0, 163.1, 176.0, 178.8;

EIMS: *m/z* 308 (M^+, 46.29), 280 (100);

HRMS: cacld. for $C_{19}H_{16}O_4$ [M^+], 308.1049; found, 308.1046.

5. 8,8-cyclopentyl-1-hydroxy-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3e):**



(a) The reaction of **1** (380 mg, 1 mmol), **2e** (440 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **3e** (180 mg) in yield of 59%.

(**b)** The reaction of **5a** (336 mg, 1 mmol), **2e** (220 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 mL of Et_3N also afforded **3e** (187 mg) in yield of 61%.

3e:

yellow solid, m.p. 166.0-167.1 °C.

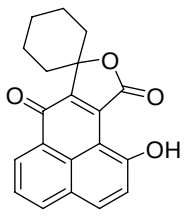
^{1}H-NMR (Figure S9): δ 13.34 (s, 1H), 8.75 (d, *J* = 7.60 Hz, 1H), 8.20 (d, *J* = 7.60 Hz, 1H), 8.01 (d, *J* = 9.00 Hz, 1H), 7.71 (dd, J_1 = J_2 = 7.60 Hz, 1H), 7.25 (d, *J* = 9.00 Hz, 1H), 2.72-2.66 (m, 2H), 2.10 (m, 4H),2.00-1.95 (m, 2H);

^{13}C-NMR (Figure S10): δ 25.4, 39.9, 101.2, 104.6, 122.5, 125.4, 128.7, 130.2, 130.4, 131.9, 133.1, 137.1, 137.5, 149.9, 163.1, 175.6, 179.1;

EIMS: *m/z* 306 (M^+, 43.06), 265 (100);

HRMS: cacld. for $C_{19}H_{14}O_4$ [M^+], 306.0892; found, 306.0898.

6. 8,8-cyclohexyl-1-hydroxy-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3f):**



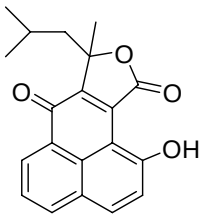
(a) The reaction of **1** (380 mg, 1 mmol), **2f** (496 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in

40 ml of Et_3N afforded **3f** (192 mg) in yield of 60%.

(b) The reaction of **5a** (336 mg, 1 mmol), **2f** (248 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 ml of Et_3N also afforded **3f** (192 mg) in yield of 60%.

3f :
orange solid, m.p. 242.5-243.8 °C.
^{1}H-NMR (Figure S11): δ 13.40 (s, 1H), 8.73 (d, J = 7.60 Hz, 1H), 8.18 (d, J = 7.60 Hz, 1H), 8.00 (d, J = 9.00 Hz, 1H), 7.70 (dd, $J_1 = J_2$ = 7.60 Hz, 1H), 7.24 (d, J = 9.00 Hz, 1H), 2.61-2.54 (m, 2H), 1.89-1.72 (m, 5H),1.70 (m, 2H), 1.46 (m, 1H);
^{13}C-NMR (Figure S12): δ 22.3, 24.5, 33.6, 93.1, 104.6, 122.6, 125.3, 128.7, 130.1, 130.7, 132.0, 132.6, 137.0, 137.5, 152.8, 163.2, 175.8, 179.0;
EIMS: *m/z* 320 (M^+,56.32), 265 (100);
HRMS: cacld. for $C_{20}H_{16}O_4$ [M^+], 320.1049; found, 320.1049.

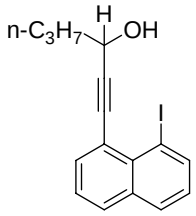
7. 1-hydroxy-8-isobutyl-8-methyl-7H-phenaleno[1,2-c]furan-7,10(8H)**-dione (3g):**



(a) The reaction of **1** (380 mg, 1 mmol), **2g** (504 mg, 4 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 ml of Et_3N afforded **3g** (174 mg) in yield of 54%.
(b) The reaction of **5a** (336 mg, 1 mmol), **2g** (252 mg, 2 mmol), water (10 μL), air(5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 20 ml of Et_3N also afforded **3g** (182 mg) in yield of 55%.

3g:
orange solid, m.p. 274.5-275.8 °C.
^{1}H-NMR (Figure S13): δ 13.36 (s, 1H), 8.75 (d, J = 7.60 Hz, 1H), 8.20 (d, J = 7.60 Hz, 1H), 8.02 (d, J = 9.00 Hz, 1H), 7.72 (dd, $J_1 = J_2$ = 7.60 Hz, 1H), 7.27 (d, J = 9.00 Hz, 1H), 2.23 (dd, $J_1 = J_2$ = 5.75 Hz, 2H), 2.16 (dd, $J_1 = J_2$ = 6.60 Hz, 2H), 1.84(s, 3H), 1.60 (m, 1H), 0.93 (d, J = 7.15 Hz , 3H), 0.83 (d, J = 7.15 Hz , 3H);
^{13}C-NMR (Figure S14): δ 24.0, 23.4, 24., 24.8, 45.6, 93.8, 104.5, 122.5, 125.3, 128.7, 130.2, 130.4, 132.1, 133.0, 137.1, 137.6, 152.2, 163.2, 175.8, 179.0;
EIMS: *m/z* 322 (M^+, 2.06), 266 (100);
HRMS: cacld. for $C_{20}H_{18}O_4$ [M^+], 322.1205; found, 322.1206.

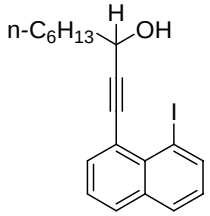
8. 1-(8-iodonaphthalen-1-yl)hex-1-yn-3-ol (5h):



The reaction of **1** (380 mg, 1 mmol), **2h** (392 mg, 4 mmol), water (10μL), air (5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **5h** (262 mg) in yield of 75%.

5h: colorless oil.
^{1}H-NMR (Figure S15): δ 8.27 (dd, J_1 = 7.32 Hz and J_2 = 1.20 Hz, 1H), 7.82-7.78 (m, 3H), 7.40 (dd, $J_1 = J_2$ = 7.67 Hz, 1H), 7.09 (dd, $J_1 = J_2$ = 7.72 Hz, 1H), 4.72 (t, J = 6.58, 1H), 1.99 (br, 1H), 1.91-1.86 (m, 2H), 1.64-1.60 (m, 2H), 1.00 (t, J = 7.45 Hz, 3H);
^{13}C-NMR (Figure S16): δ 14.1, 18.8, 39.4, 63.8, 84.6, 93.1, 101.8, 122.3, 125.6, 127.3, 130.4, 130.7, 132.1, 135.0, 136.4, 142.9;
EIMS: *m/z* 350 (M^+, 11.82), 152 (100);
HRMS: cacld. for $C_{16}H_{15}OI$ [M^+], 350.0168; found, 350.0166.

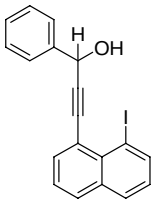
9. 1-(8-iodonaphthalen-1-yl)non-1-yn-3-ol (5i):



The reaction of **1** (380 mg, 1 mmol), **2i** (560 mg, 4 mmol), water (10 μL), air (5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **5i** (290 mg) in yield of 74%.

5i: colorless oil.
^{1}H-NMR (Figure S17): δ 8.25 (dd, J_1 = 7.32 Hz and J_2 = 1.00 Hz, 1H), 7.80-7.74 (m, 3H), 7.37 (dd, $J_1 = J_2$ = 7.67 Hz, 1H), 7.06 (dd, $J_1 = J_2$ = 7.70 Hz, 1H), 4.70 (t, J = 6.60 Hz, 1H), 2.17 (br, 1H), 1.92-1.86 (m, 2H), 1.58-1.55 (m, 2H), 1.38-1.29 (m, 6H), 0.88 (t, J = 6.90, 3H);
^{13}C-NMR (Figure S18): δ 14.3, 22.8, 25.5, 29.3, 32.0, 37.3, 64.0, 84.6, 93.1, 101.9, 122.4, 125.6, 127.3, 130.4, 130.7, 132.1, 135.0, 136.4, 142.9;
EIMS: *m/z* 392 (M^+, 12.29), 152 (100);
HRMS: cacld. for $C_{19}H_{21}OI$ [M^+], 392.0637; found, 392.0638.

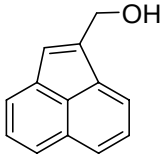
10. 3-(8-iodonaphthalen-1-yl)-1-phenylprop-2-yn-1-ol (5j):



The reaction of **1** (380 mg, 1 mmol), **2j** (528 mg, 4 mmol), water (10 μL), air (5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol),CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **5j** (274 mg) in yield of 72%.

5j: colorless oil.
^{1}H-NMR (Figure S19): δ 8.25 (dd, J_1 = 7.32 Hz and J_2 = 0.86 Hz, 1H), 7.86 (d, J = 7.22 Hz, 1H), 7.80 (dd, J_1 = J_2 = 7.05 Hz, 2H), 7.67 (d, J = 7.46 Hz, 2H), 7.43-7.34 (m, 4H), 5.80 (d, J = 4.80 Hz, 1H), 2.50 (d, J = 5.30, 1H);
^{13}C-NMR (Figure S20): δ 66.2, 86.4, 93.0, 100.1, 122.1, 125.6, 127.2, 127.4, 128.6,128.9, 130.4, 131.0, 132.2, 135.1, 136.6, 140.3, 142.9;
EIMS: *m/z* 384 (M^+, 50.18), 257 (100);
HRMS: cacld. for $C_{19}H_{13}OI$ [M^+], 380.0011; found, 380.0012.

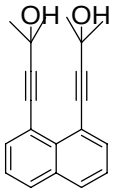
11. acenaphthylen-1-ylmethanol[3] (6):



The reaction of **1** (380 mg, 1 mmol), **2k** (224 mg, 4 mmol), water (10 μL), air (5 mL), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol),CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) in 40 mL of Et_3N afforded **6** (138 mg) in yield of 76%.

6: yellow solid, m.p. 52.6-55.5 ^{o}C (Lit.[3], 49-50 ^{o}C)
^{1}H-NMR (Figure S21): δ 7.77 (d, J = 8.15 Hz, 1H), 7.73 (d, J = 9.20 Hz, 1H), 7.71 (d, J = 6.75 Hz, 1H), 7.57 (d, J = 6.75 Hz, 1H), 7.51-7.46 (m, 2H), 6.89 (s, 1H), 4.88 (s, 2H), 1.94 (s, 1H);
^{13}C-NMR (Figure S22): δ 60.1, 123.1, 124.1, 125.9, 127.2, 127.7, 128.0, 128.3, 129.3, 138.6, 139.0, 143.4;
EIMS: *m/z* 181 (M^+, 85.93), 153 (100);
HRMS: cacld. for $C_{13}H_{10}O$ [M^+], 182.0732; found, 182.0732.

12. 4,4'-(naphthalene-1,8-diyl)bis(2-methylbut-3-yn-2-ol)[4] (4a):

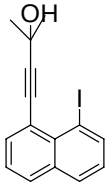


General Procedure for $Pd(PPh_3)_2Cl_2$/CuI-catalyzed Sonogashira coupling reaction of

1,8-diiodonaphthalene (**1**) and 2-methylbut-3-yn-2-ol (**2a**): To a solution of **1** (380 mg, 1 mmol) and **2a** (336 mg, 4 mmol) in 40 mL of Et_3N, $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol), CuI (19.1 mg, 0.10 mmol) and PPh_3 (26.2 mg, 0.10 mmol) were added at ambient temperature. The reaction mixture is purged with nitrogen for 10 min. Then the sealed flask was heated at 80 ^oC for about 20 h. After complete consumption of starting material as determined by TLC, Et_3N was removed and the residue was dissolved with ether, washed with water, and dried by Na_2SO_4. After filtration, the filtrate was distilled under reduced pressure and the residue was purified via flash chromatography on silica gel (ethyl acetate/ hexane = 1:4). **4a** (276 mg, 94%) was obtained.

4a:
white solid, m.p. 119.4-120.6 ^oC (Lit[4] 120-121 ^oC)
^{1}H-NMR (Figure S23): δ 7.75 (d, J = 8.25 Hz, 2H), 7.66 (d, J = 7.20 Hz, 2H), 7.37 (dd, $J_1 = J_2$ = 7.64 Hz, 2H), 4.52 (s, 2H), 1.68 (s, 12H);
^{13}C-NMR (Figure S24): δ 31.8, 66.1, 82.4, 100.6, 120.7, 125.6, 129.6, 131.2, 134.2, 135.2.

13. 4-(8-iodonaphthalen-1-yl)-2-methylbut-3-yn-2-ol[4] (5a):



The reaction of **1** (1140 mg, 3 mmol), **2a** (168 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.05 mmol), CuI (38.2 mg, 0.10 mmol) and PPh_3 (52.4mg, 0.10 mmol) in 40 mL of Et_3N, afforded **5a** (618 mg, 92%).

5a: colorless oil.
^{1}H-NMR (Figure S25): δ 8.26 (d, J=7.35 Hz, 1H), 7.81-7.76 (m, 3H), 7.38 (dd, $J_1 = J_2$ = 7.68 Hz, 1H), 7.08 (dd, $J_1 = J_2$ = 7.72 Hz, 1H), 2.13 (br, 1H), 1.68 (s, 6H);
^{13}C-NMR (Figure S26): δ 30.9, 66.1, 81.5, 93.1, 104.6, 122.4, 125.5, 127.1, 130.3, 130.52, 131.9, 134.9, 136.5, 142.6.

Figure S1 ^{1}H-NMR spectrum of **3a**.

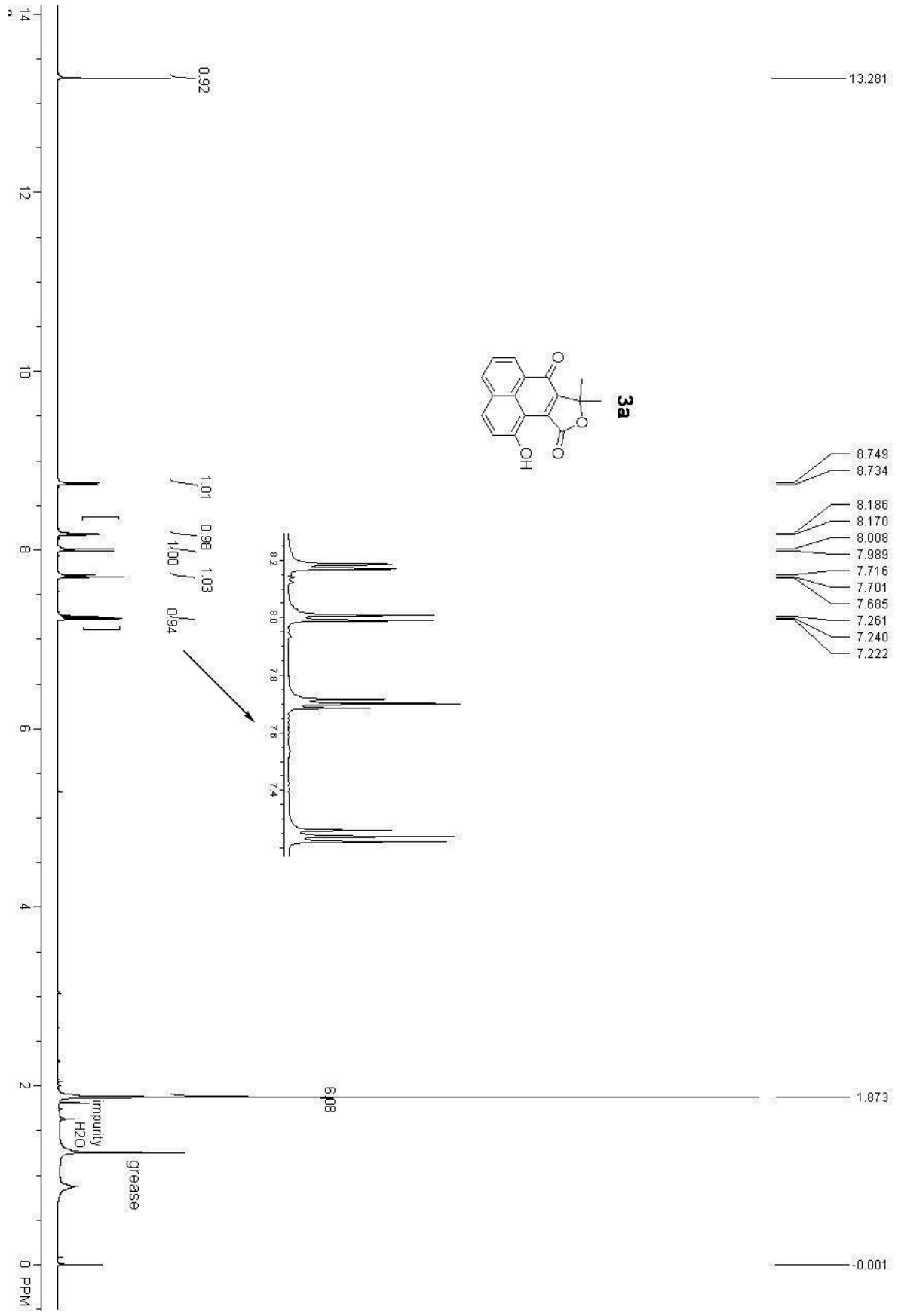

3a
OH
O
O
O
13.281
8.749
8.734
8.186
8.170
8.008
7.989
7.716
7.701
7.685
7.261
7.240
7.222
1.873
-0.001
0.92
1.01
0.98
1.03
1.00
0.94
6.08
impurity
H2O
grease
PPM

Figure S2 ^{13}C-NMR spectrum of **3a**.

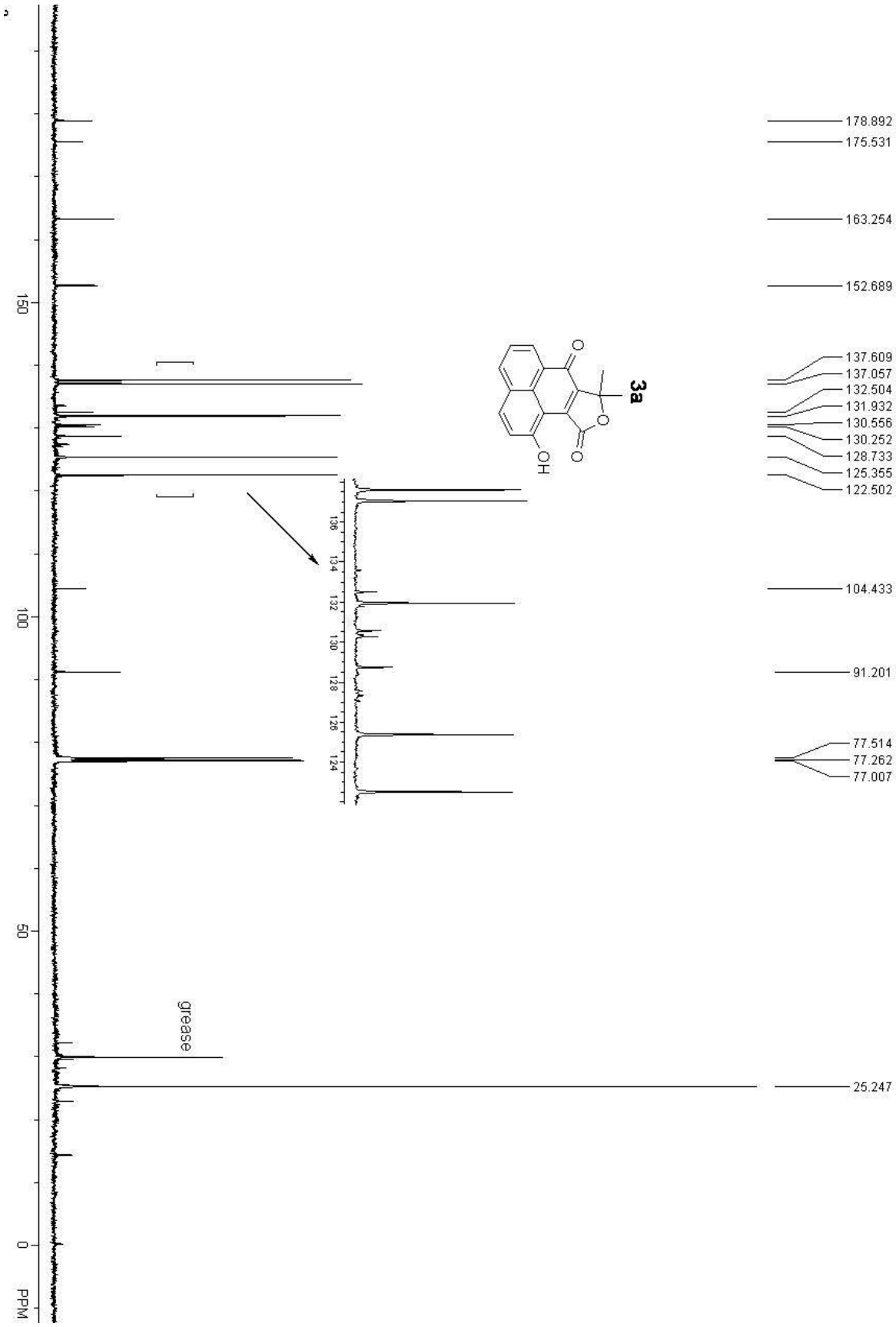


Figure S3 ^{1}H-NMR spectrum of **3b**.

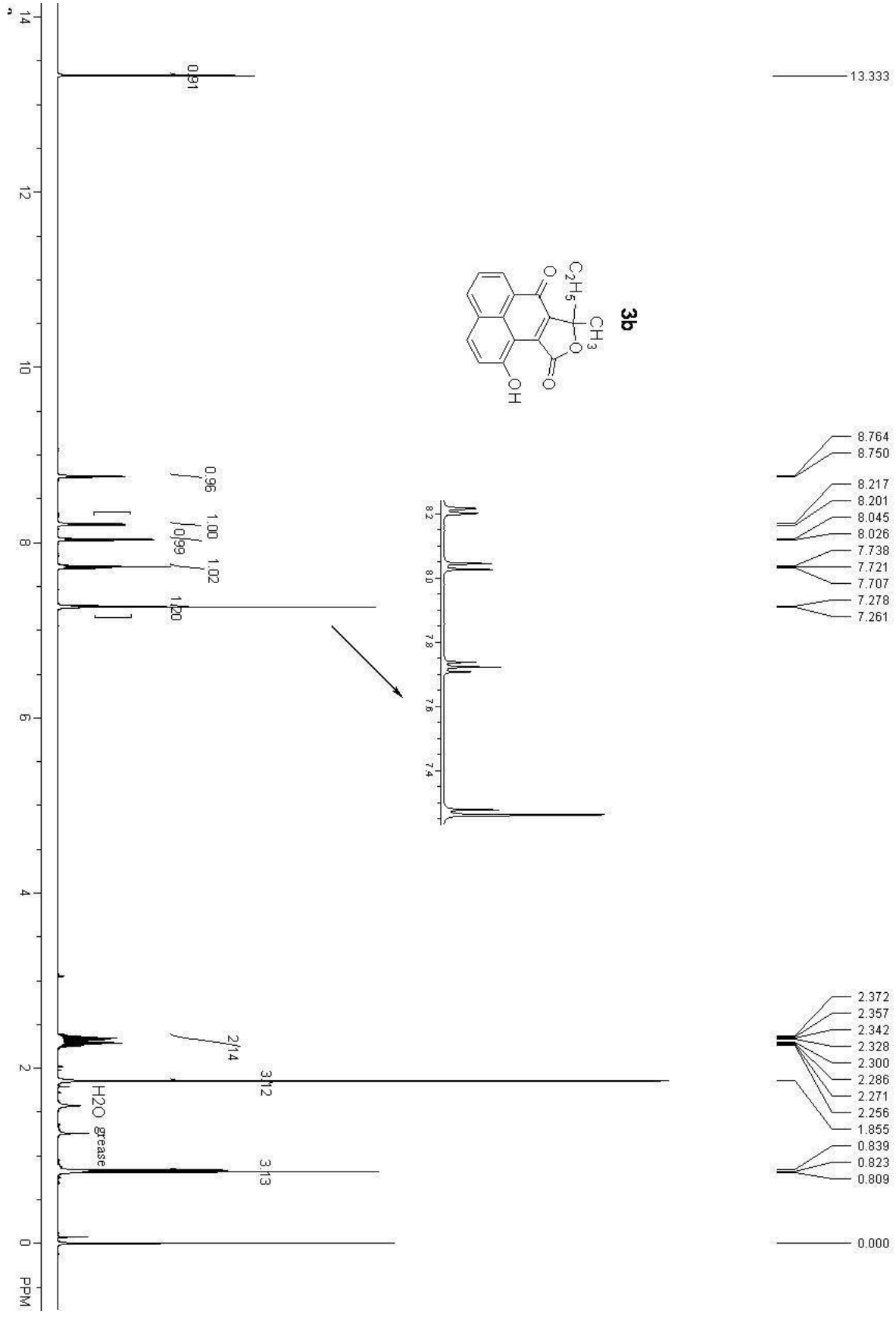


Figure S4 ^{13}C-NMR spectrum of **3b**.

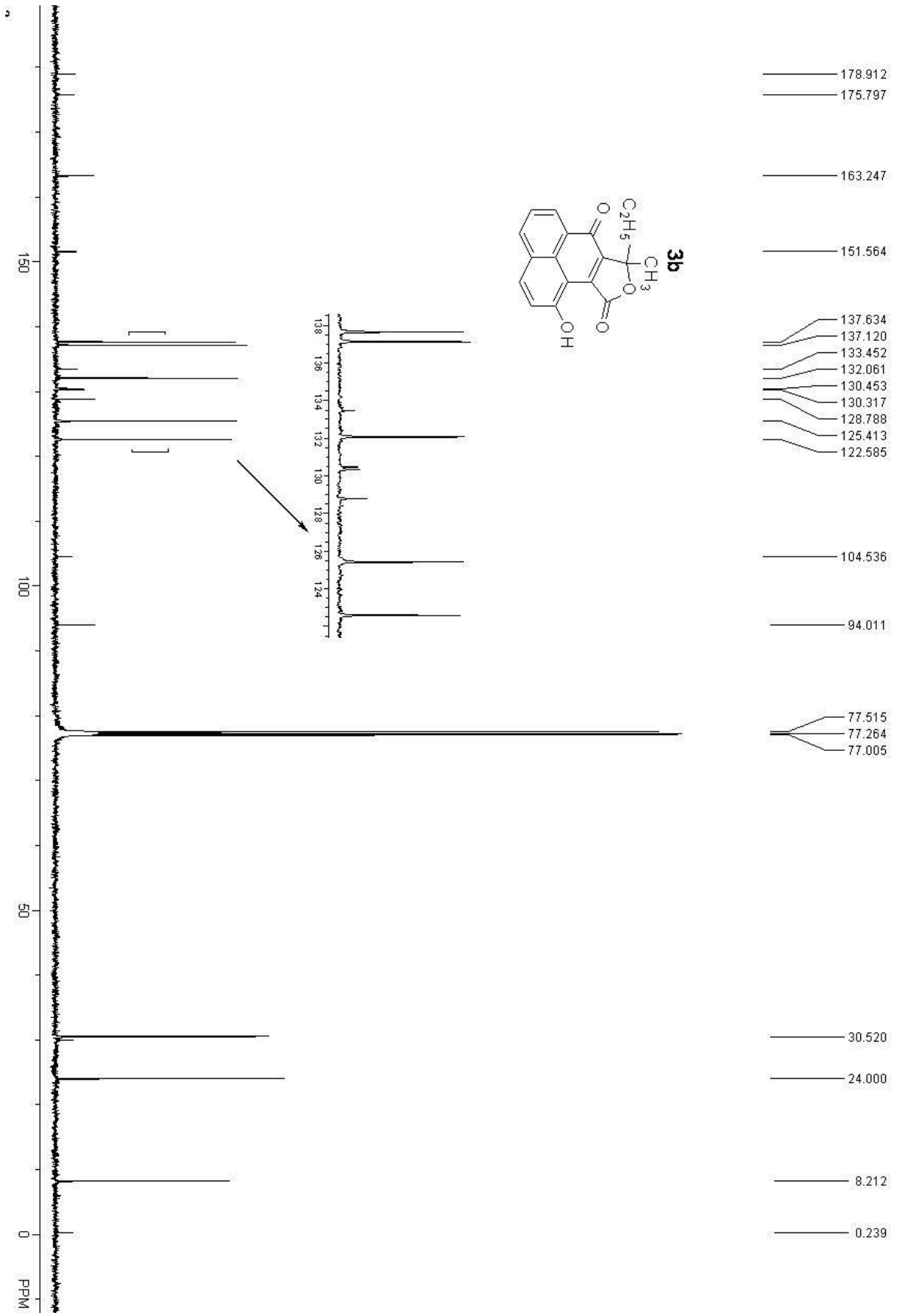


Figure S5 ^{1}H-NMR spectrum of **3c**.

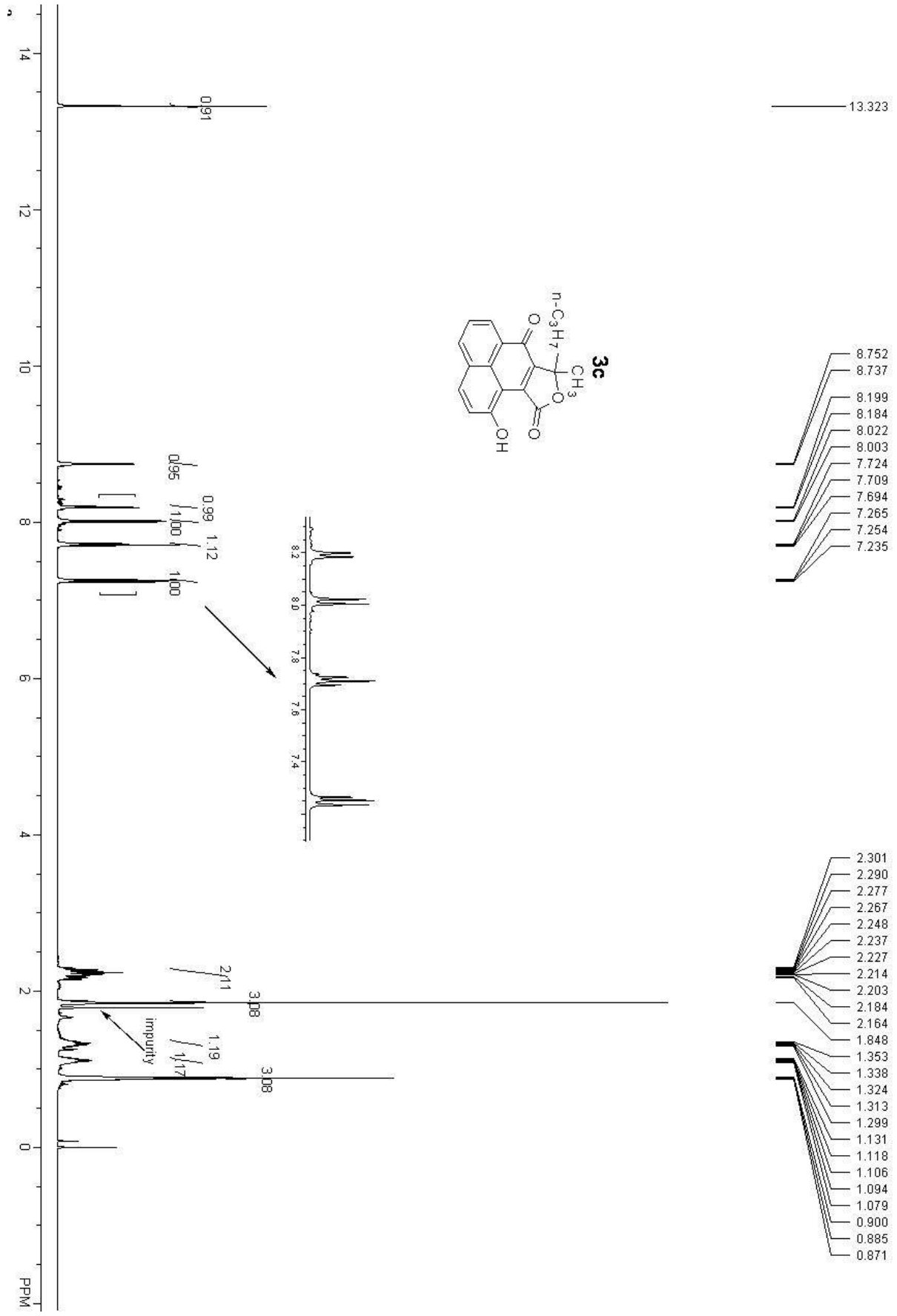


Figure S6 ^{13}C-NMR spectrum of **3c**.

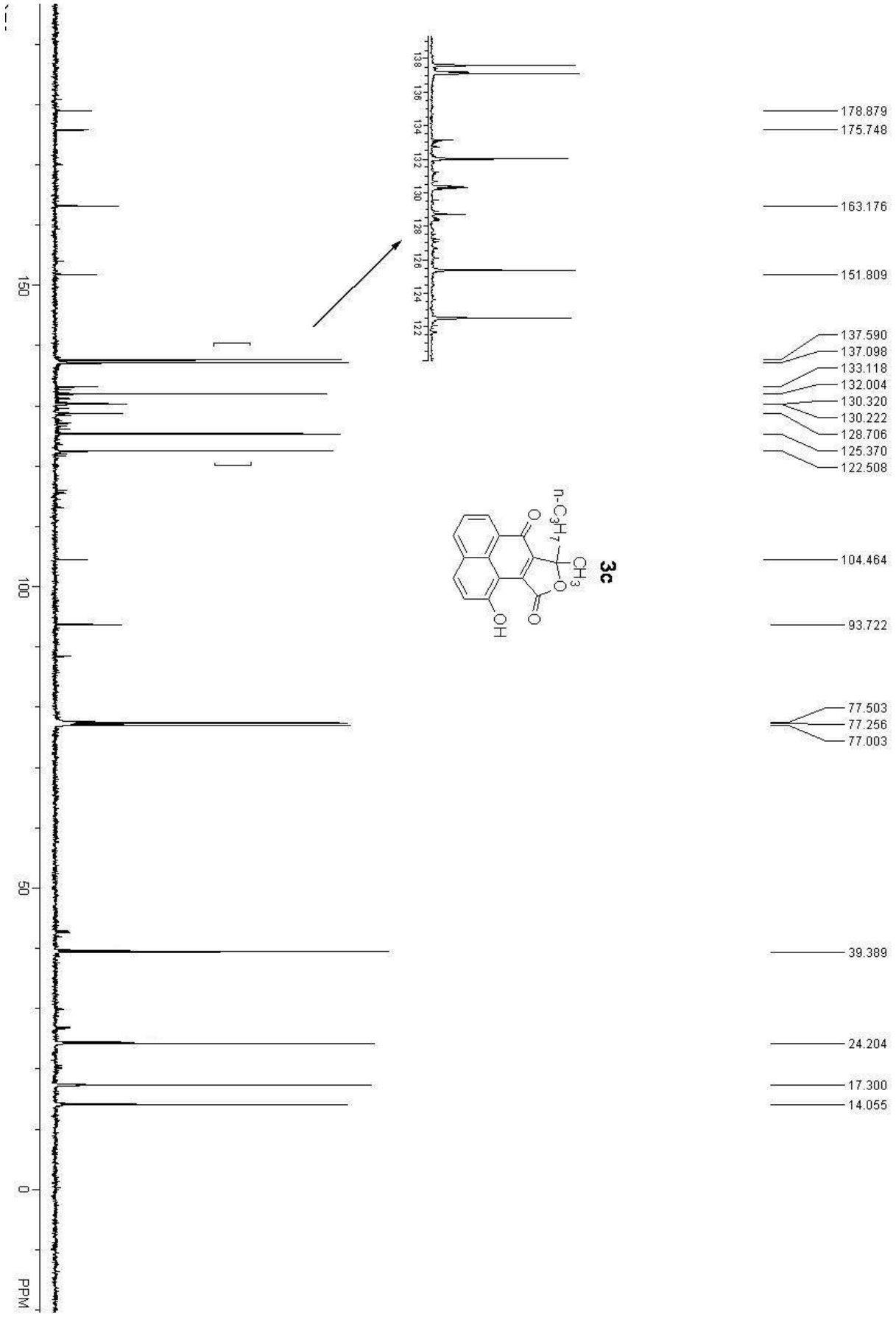


Figure S7 ^{1}H-NMR spectrum of **3d**.

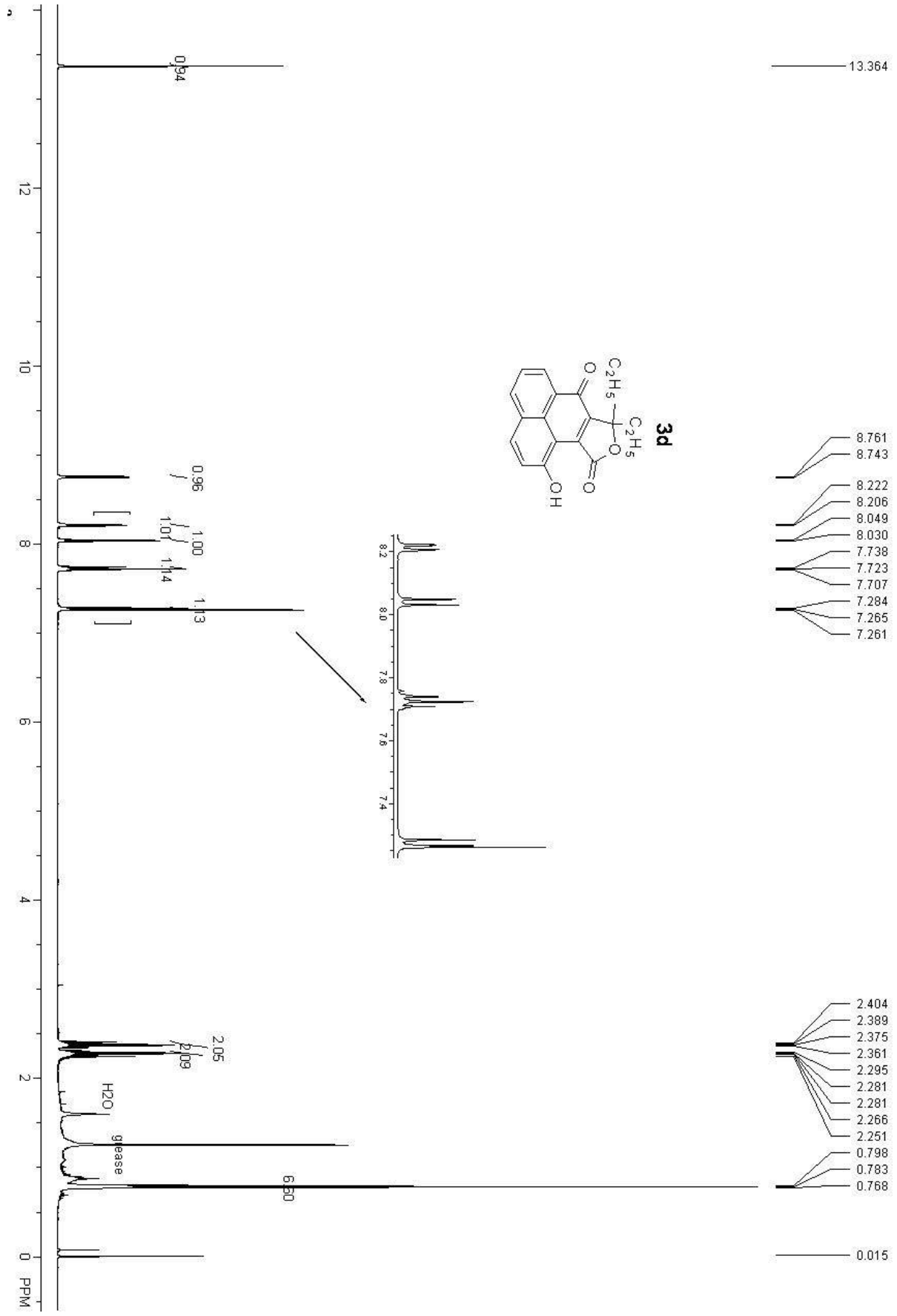


Figure S8 ^{13}C-NMR spectrum of **3d**.

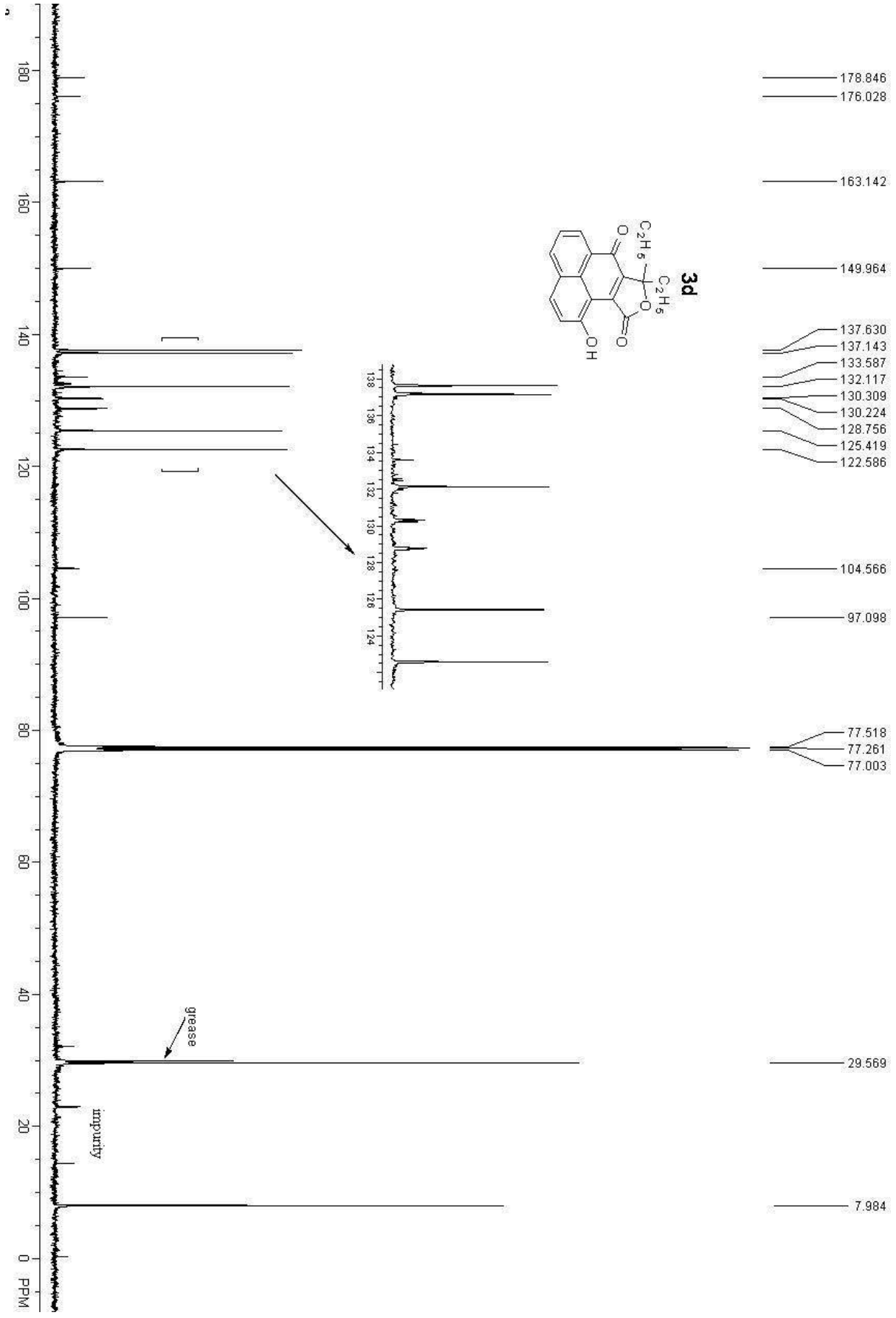


Figure S9 ^{1}H-NMR spectrum of **3e**.

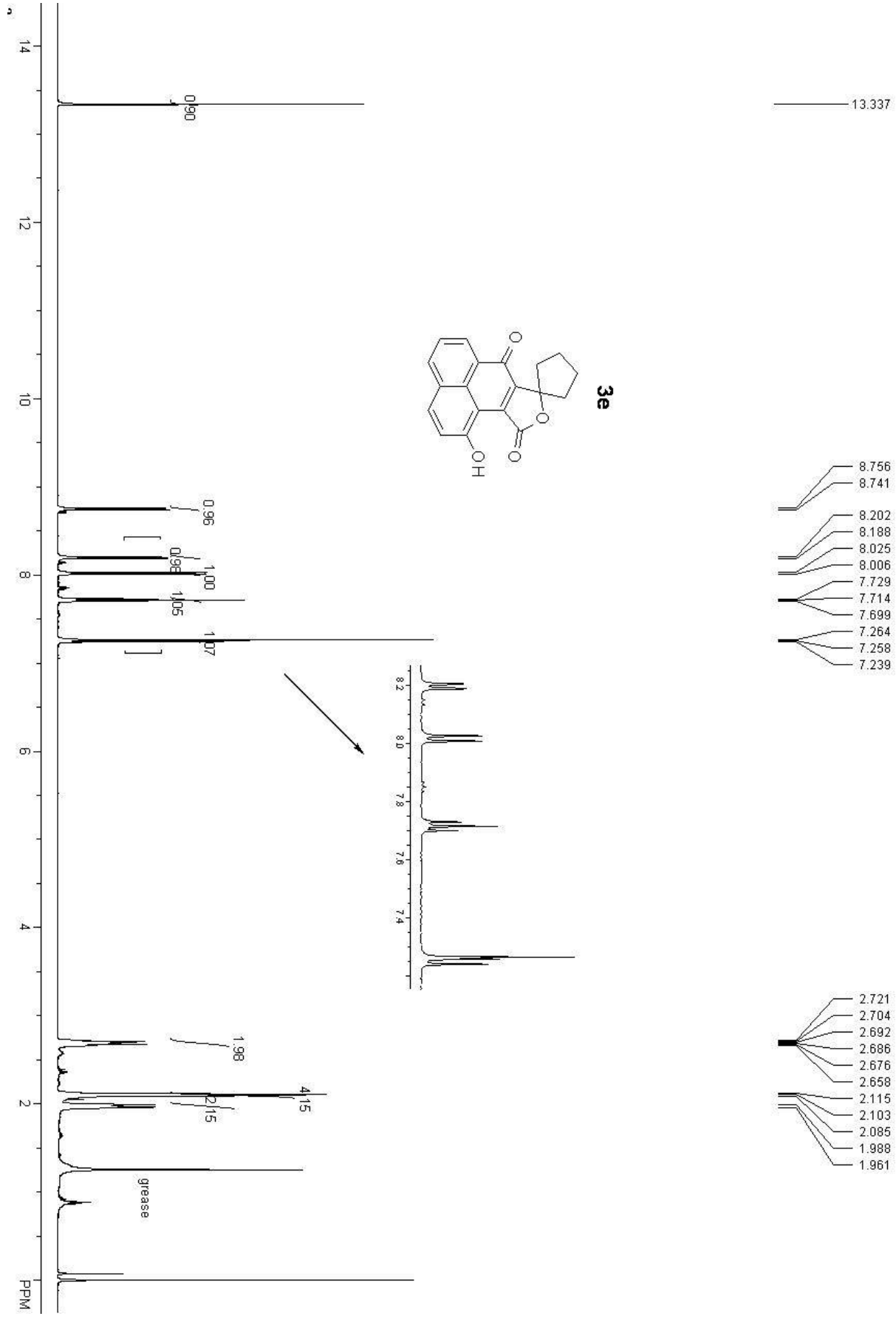


Figure S10 ^{13}C-NMR spectrum of **3e**.

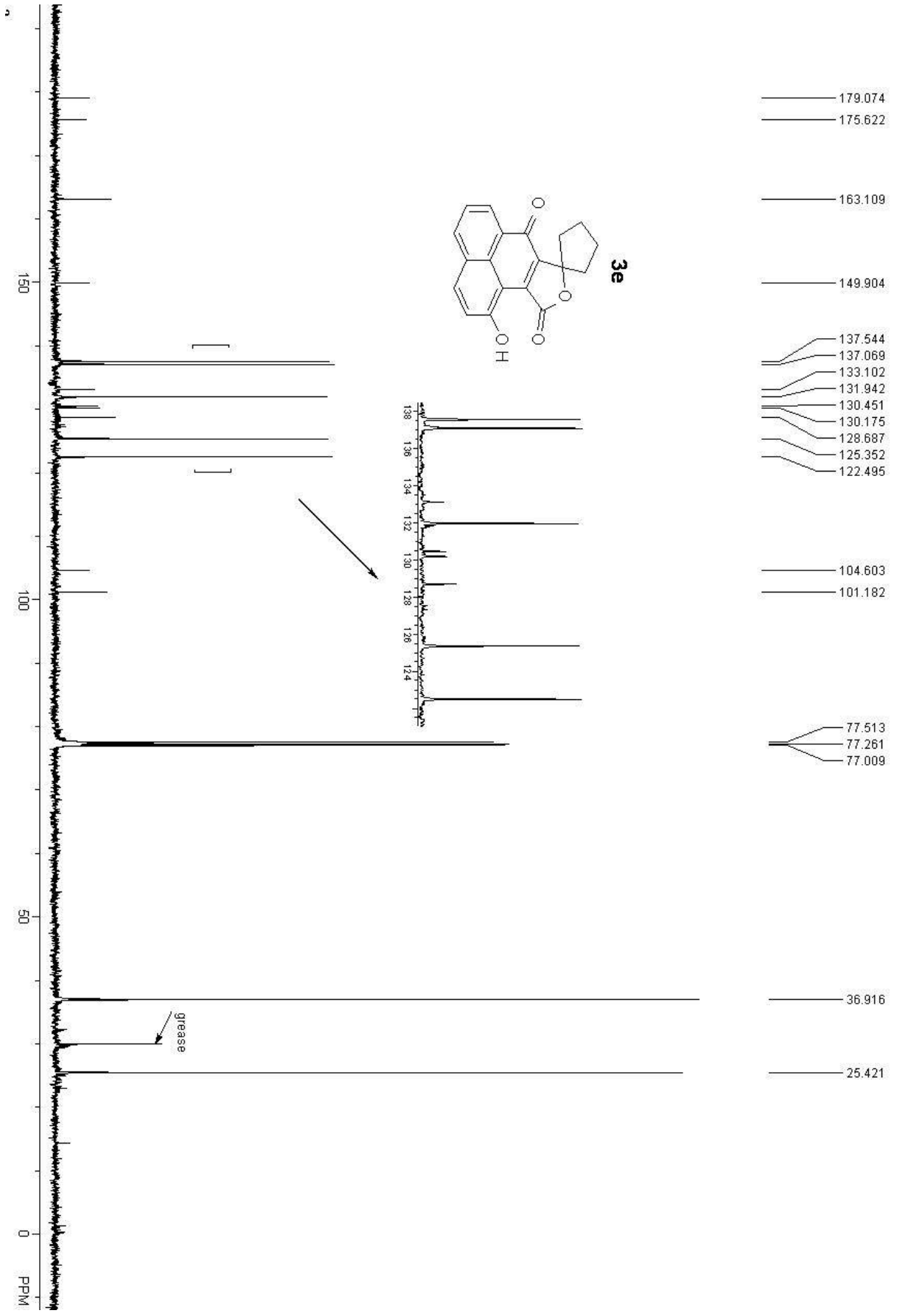


Figure S11 ^{1}H-NMR spectrum of **3f**.

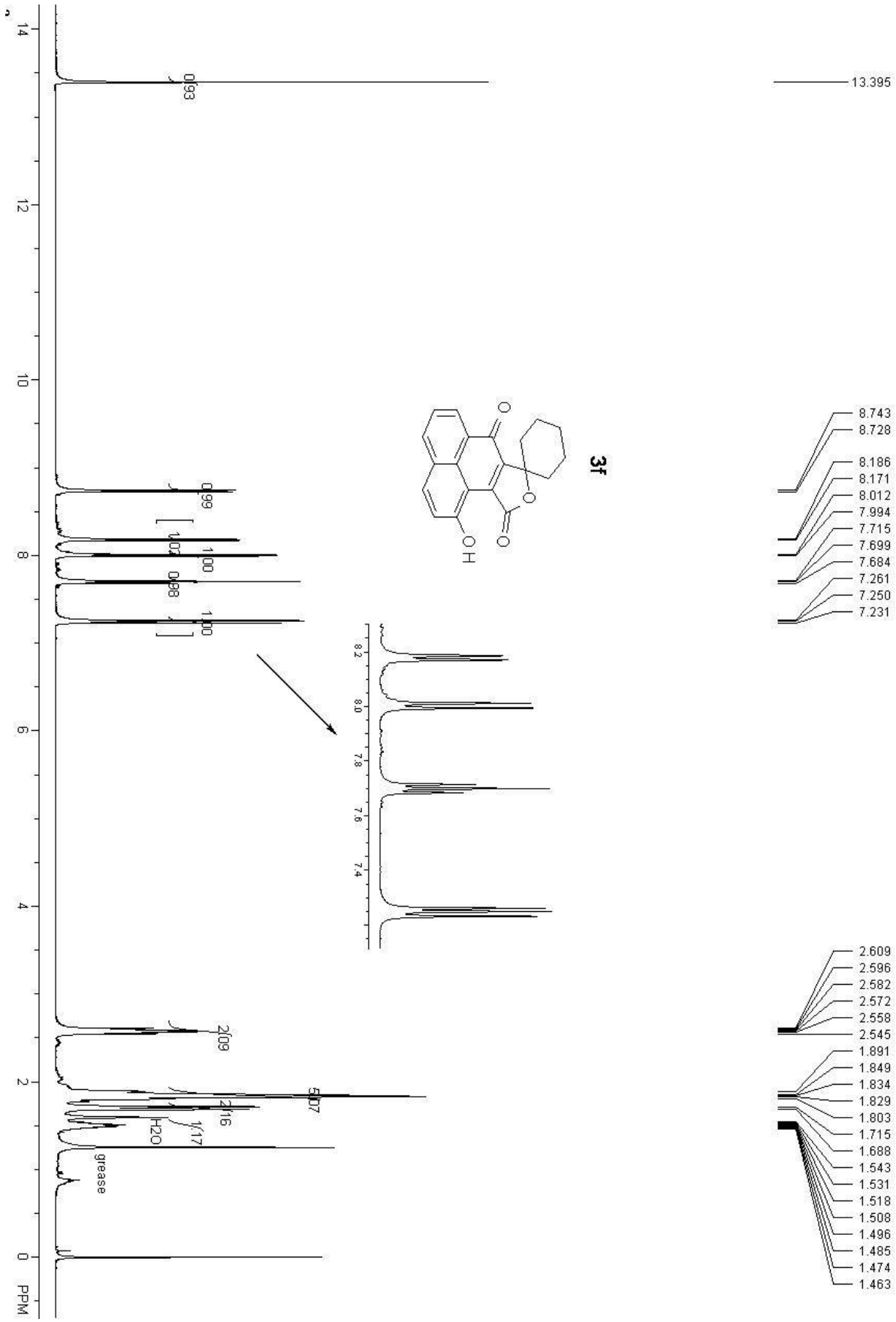


Figure S12 ^{13}C-NMR spectrum of **3f**.

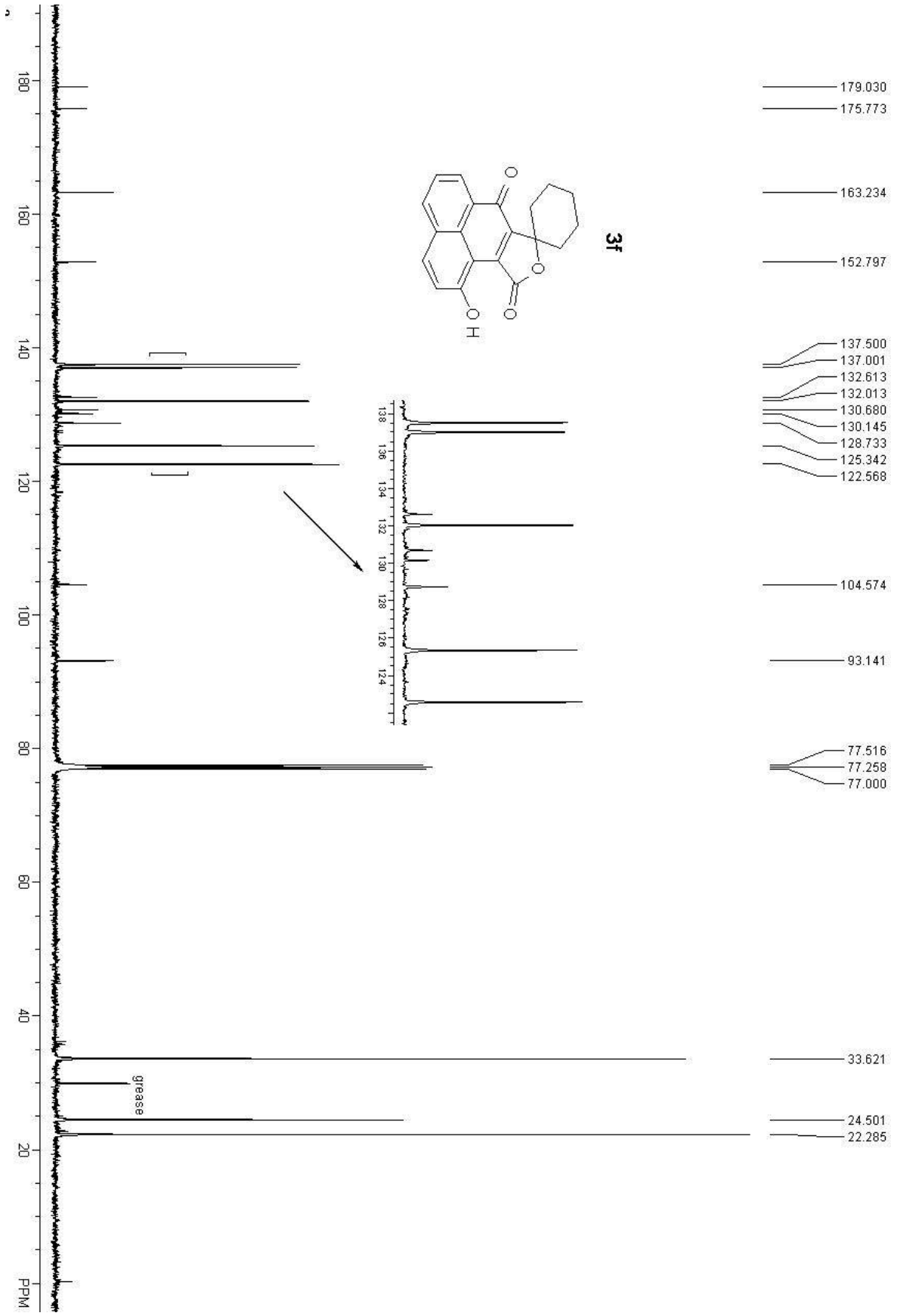


Figure S13 ^{1}H-NMR spectrum of **3g**.

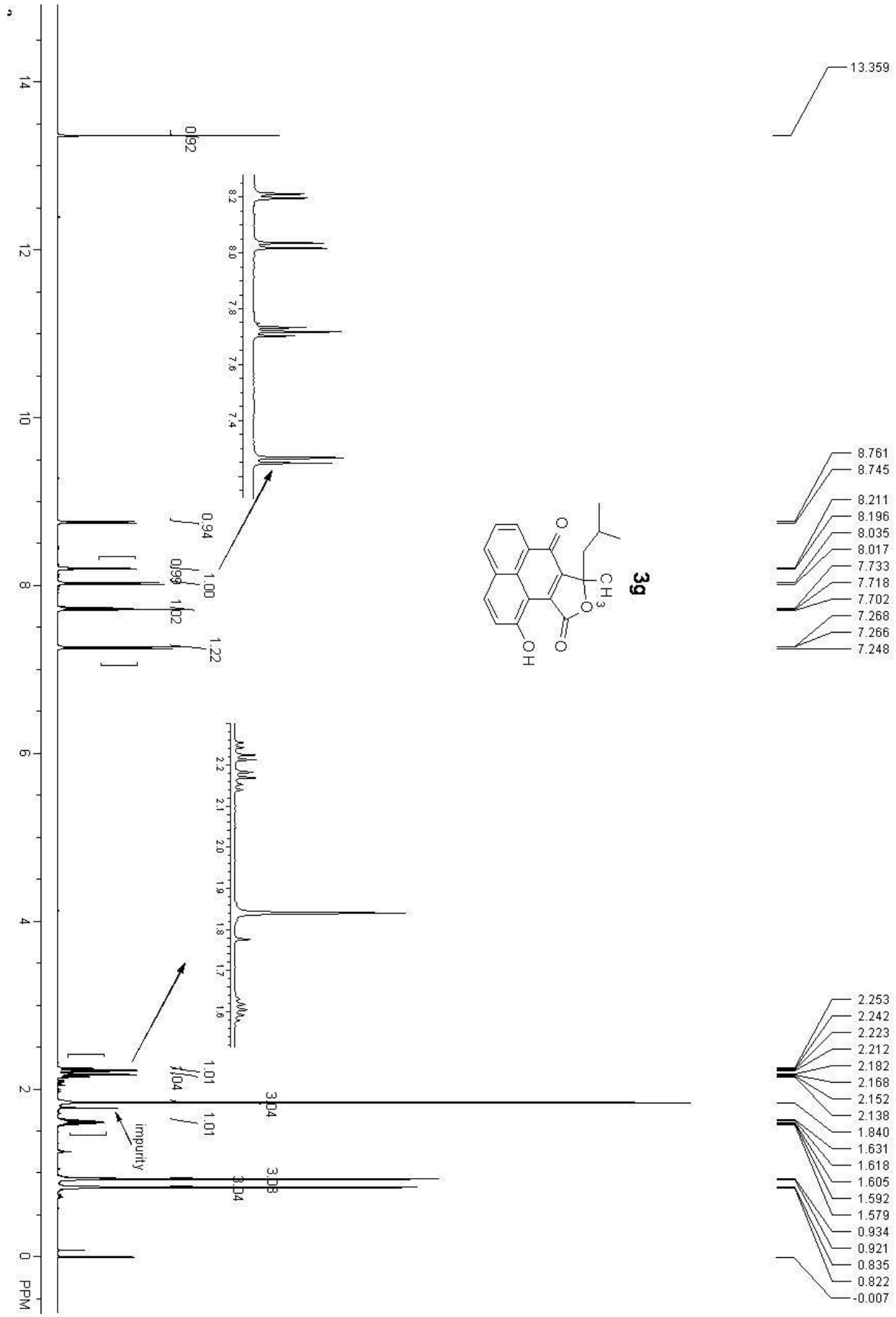


Figure S14 ^{13}C-NMR spectrum of **3g**.

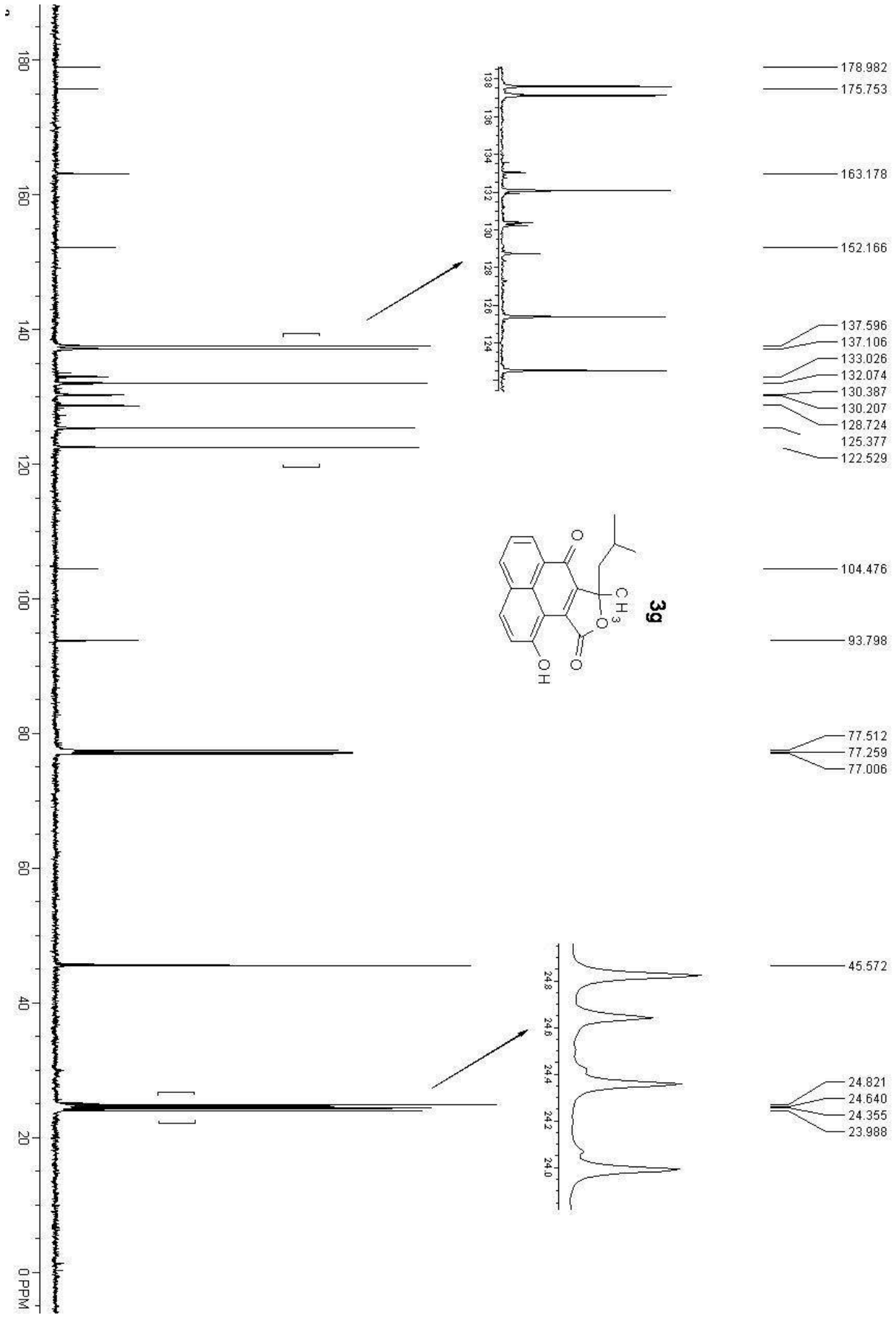


Figure S15 ^{1}H-NMR spectrum of **5h**.

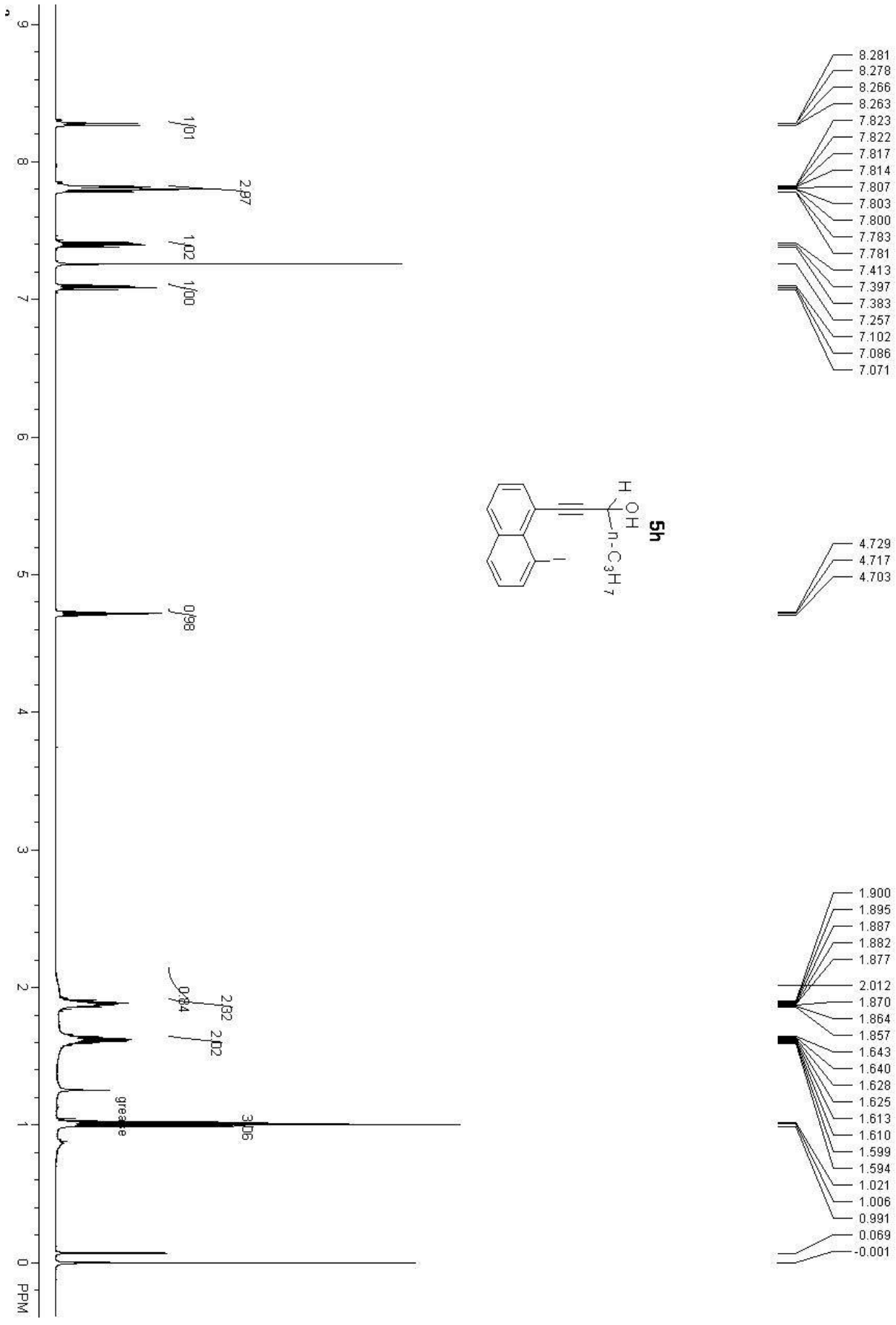


Figure S16 ^{13}C-NMR spectrum of **5h**.

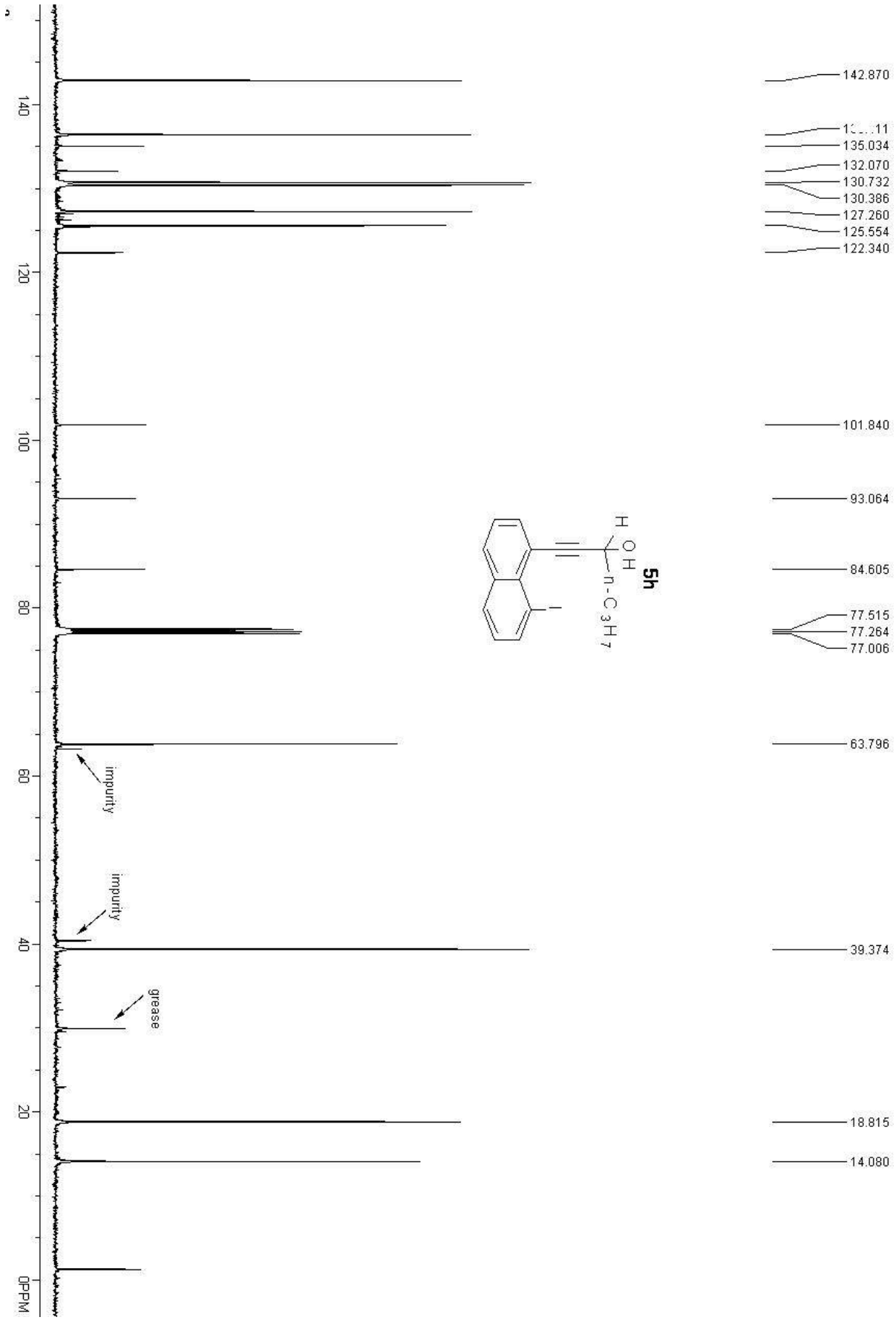


Figure S17 ^{1}H-NMR spectrum of **5i**.

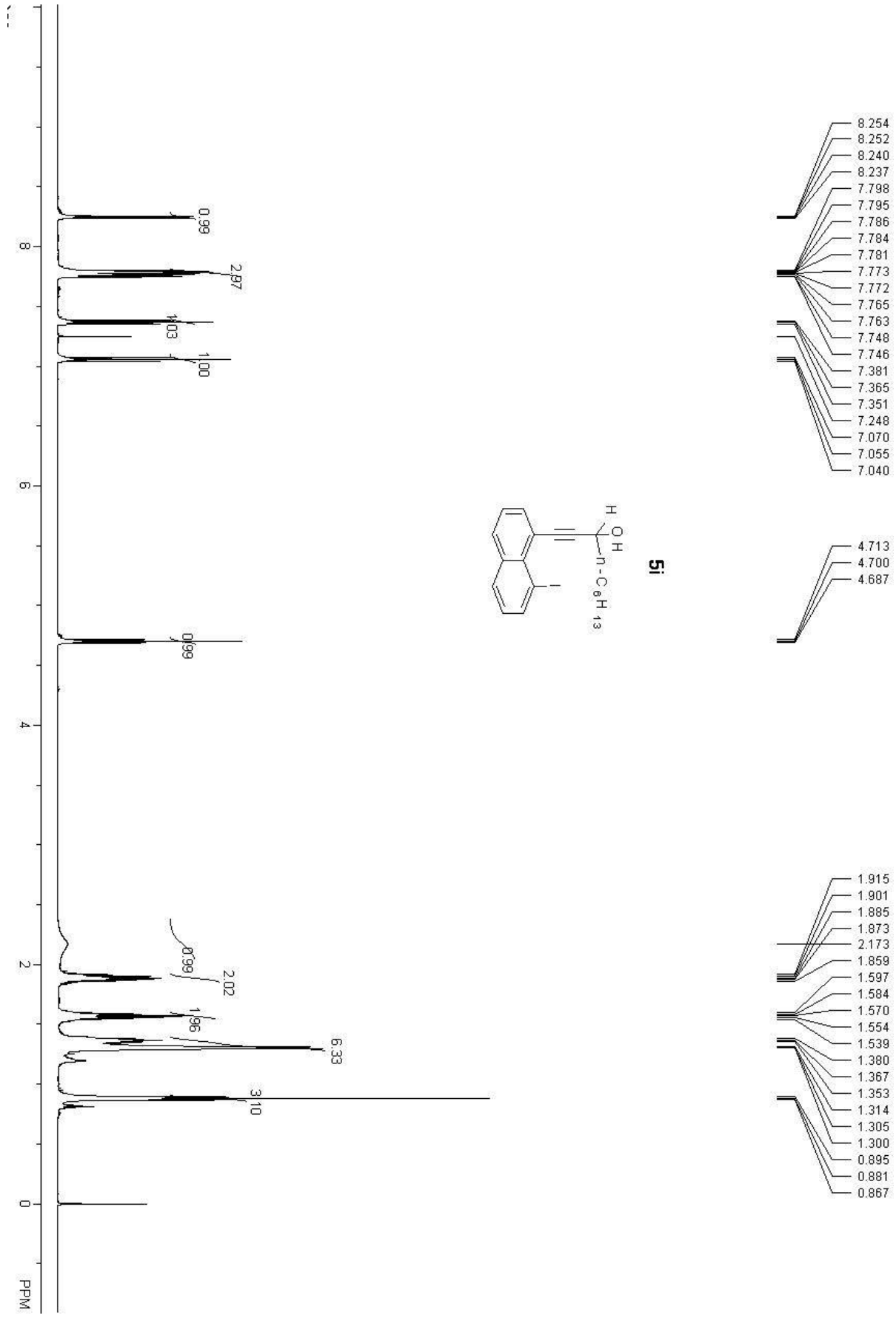


Figure S18 ^{13}C-NMR spectrum of **5i**.

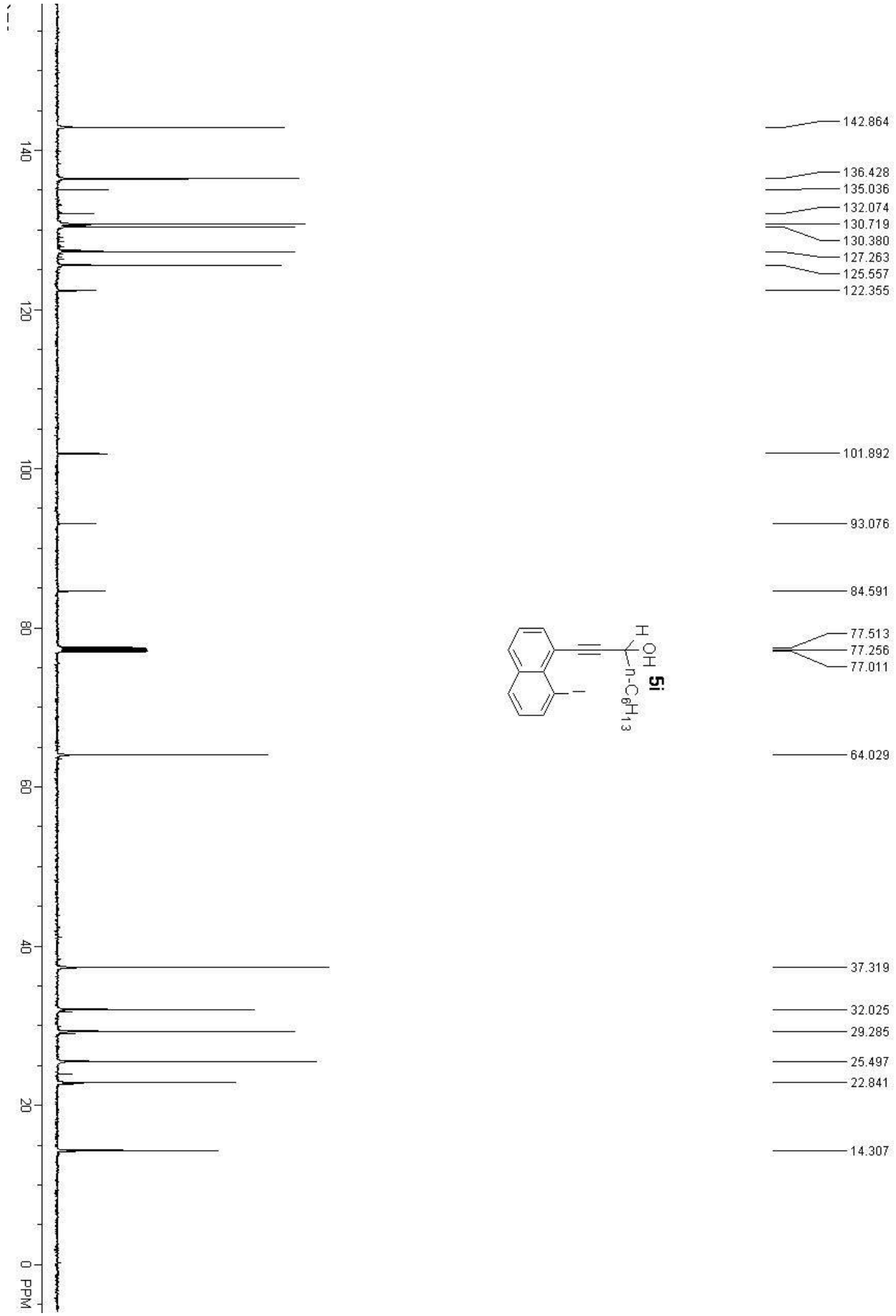


Figure S19 ^{1}H-NMR spectrum of **5j**.

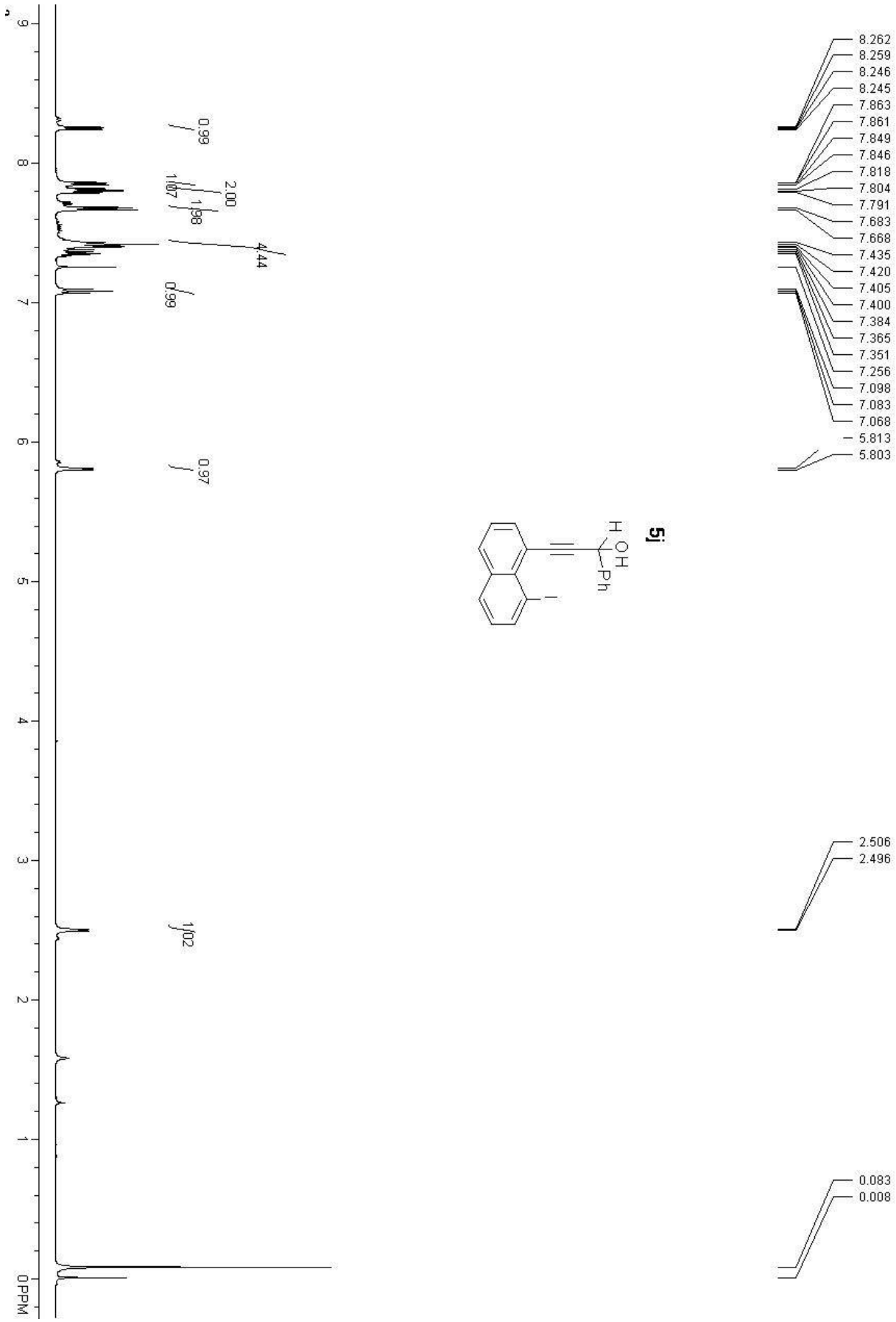


Figure S20 ^{13}C-NMR spectrum of **5j**.

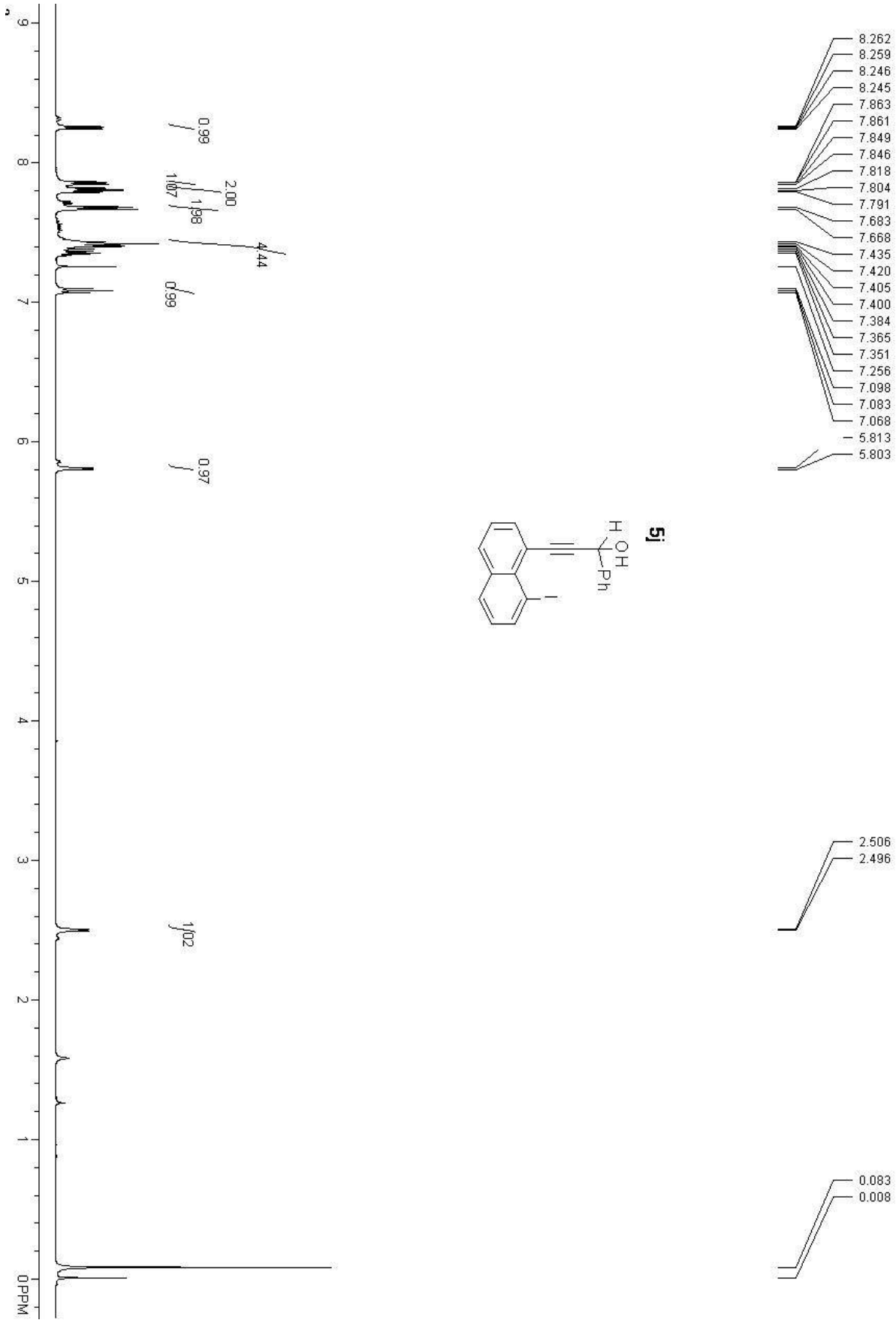


Figure S21 ^{1}H-NMR spectrum of **6**.

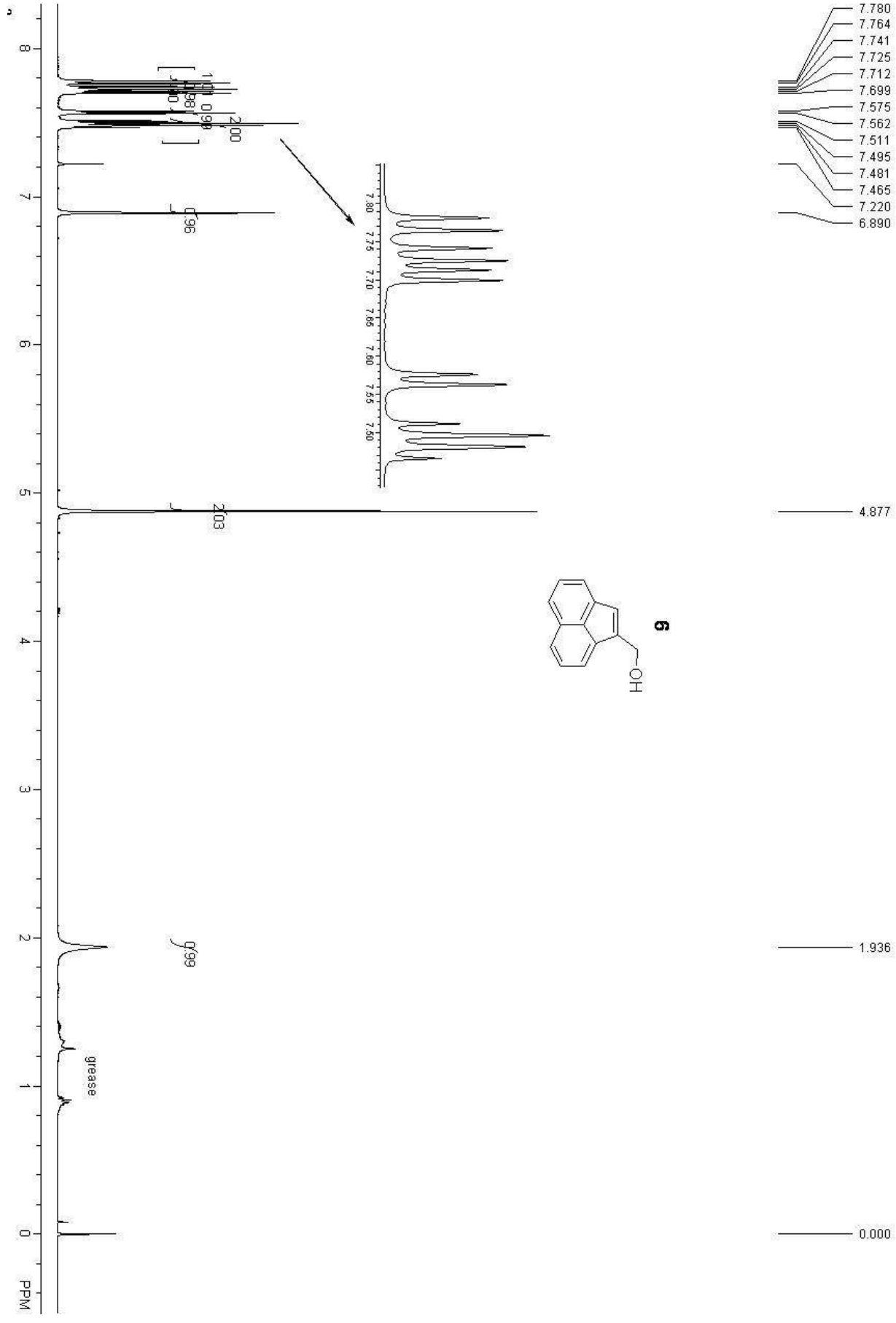

7.780
7.764
7.741
7.725
7.712
7.699
7.575
7.562
7.511
7.495
7.481
7.465
7.220
6.890
4.877
1.936
0.000
grease
PPM
OH
6

Figure S22 ^{13}C-NMR spectrum of **6**.

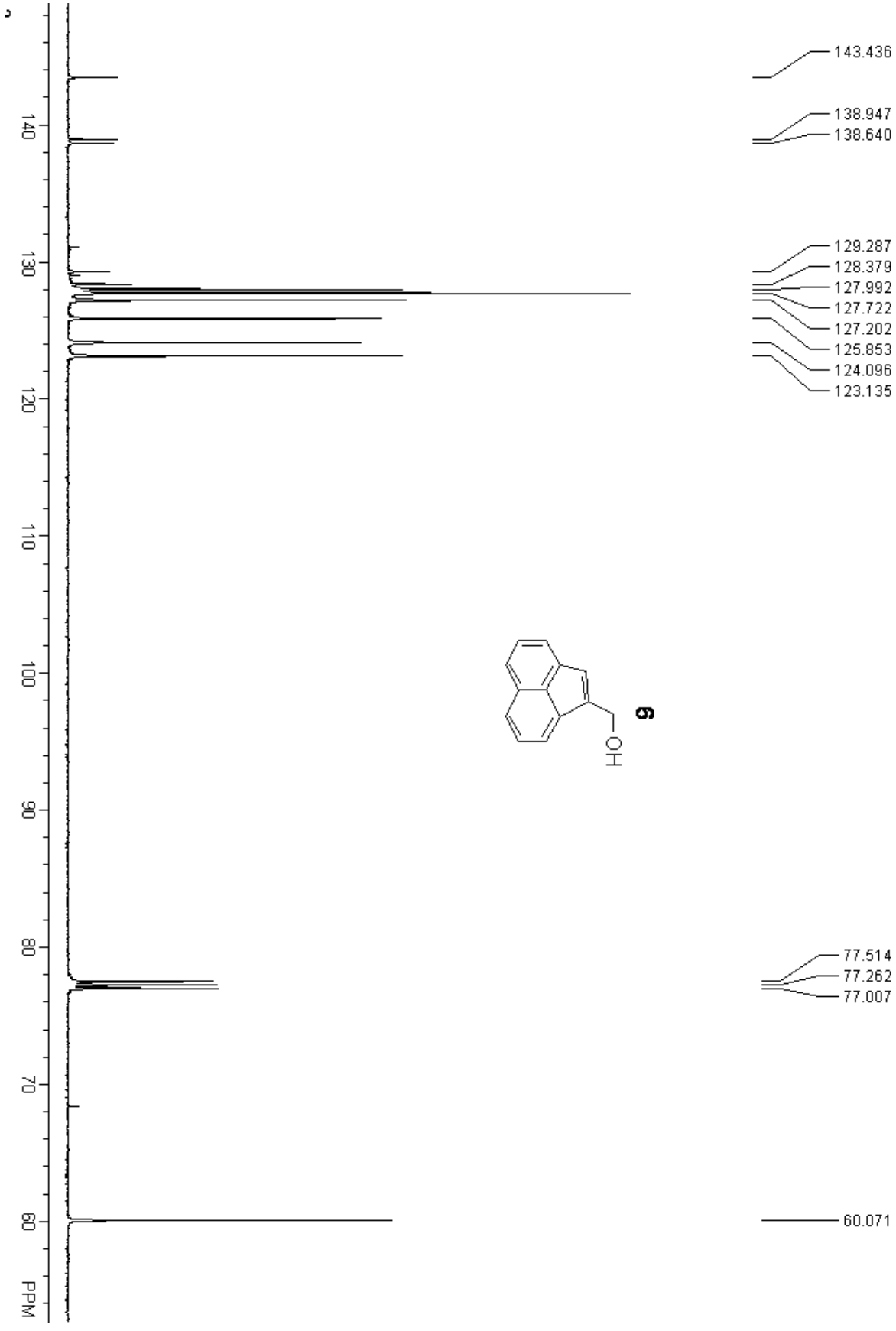


Figure S23 ^{1}H-NMR spectrum of **4a**.

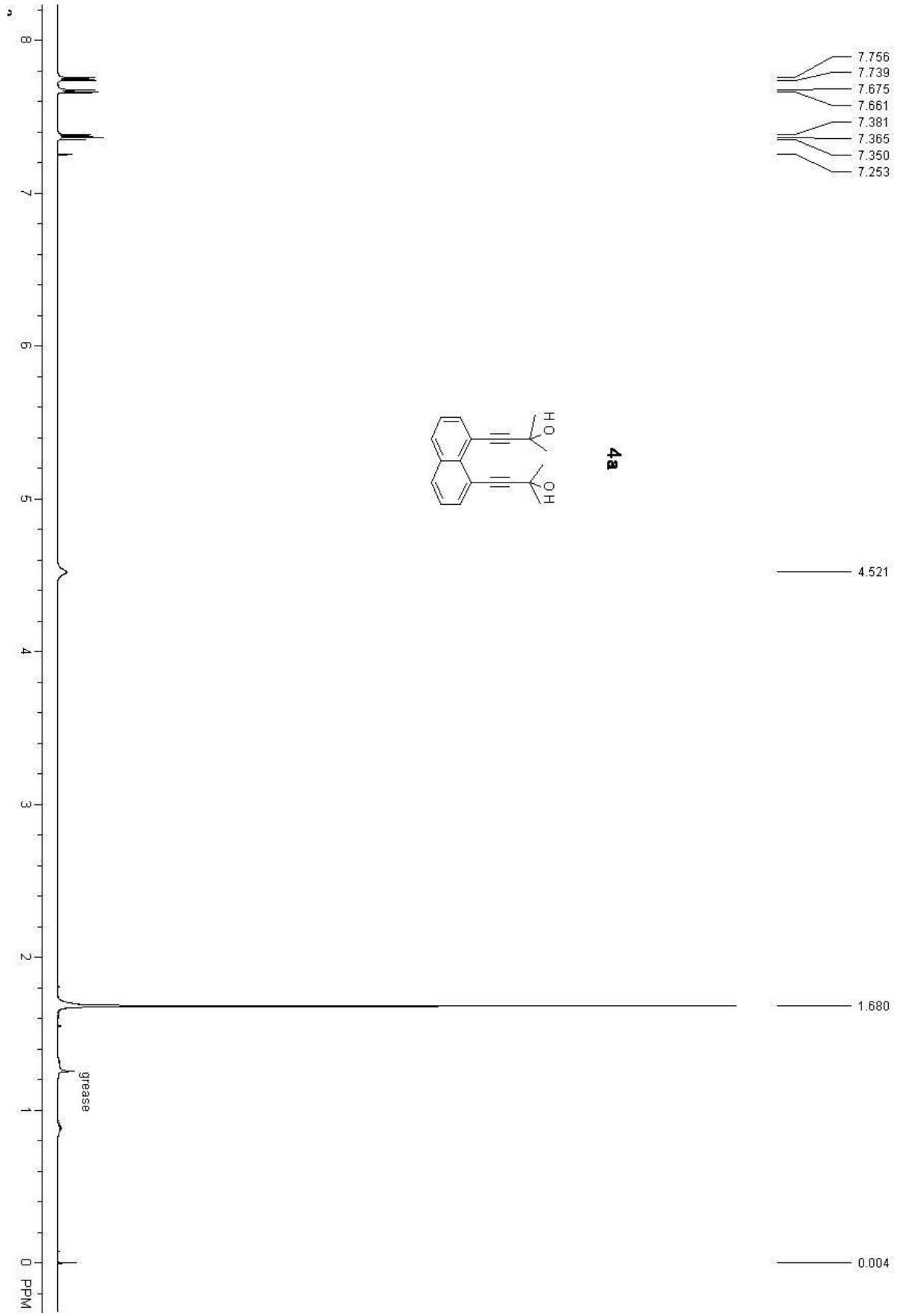


Figure S24 ^{13}C-NMR spectrum of **4a**.

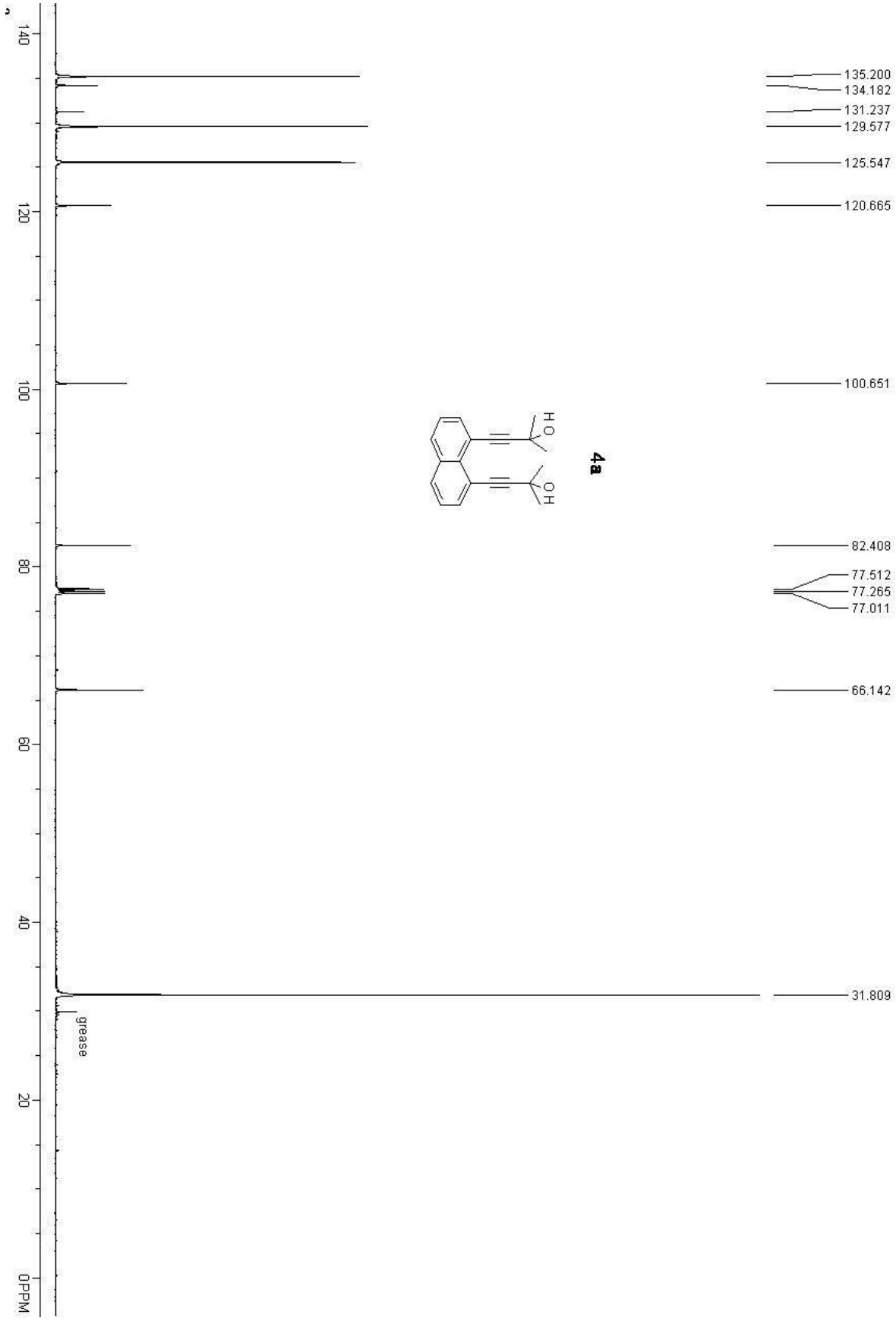


Figure S25 ^{1}H-NMR spectrum of **5a**.

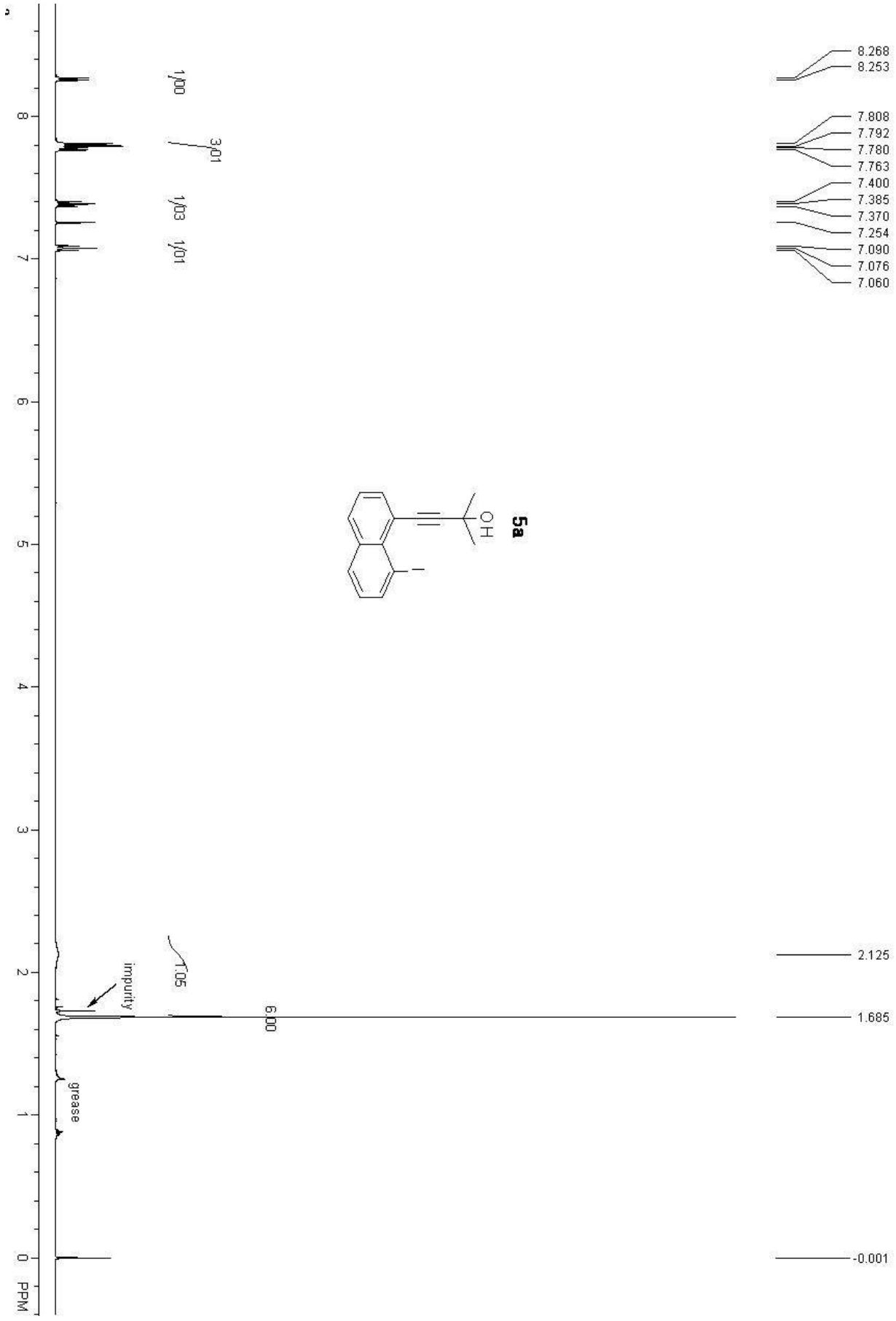


Figure S26 ^{13}C-NMR spectrum of **5a**.

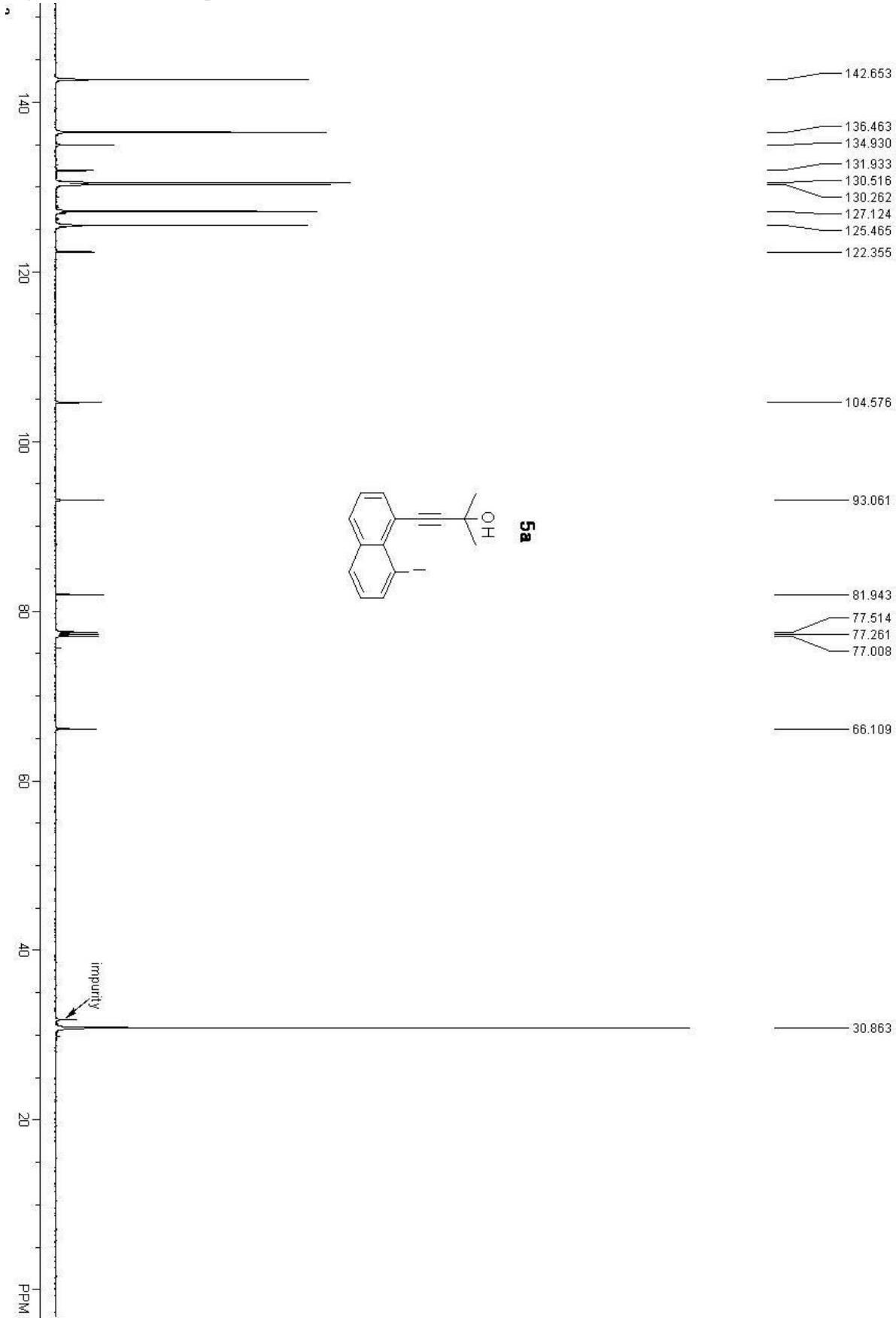


Figure S27 The Color of **3a** (1×10^{-5} M in THF) exposed to daylight before (left, canary yellow) and after (right, orange) titration with F^-.

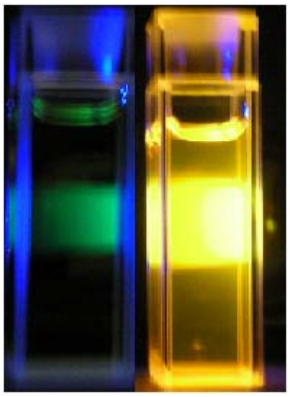


Figure S28 The color of **3a** (1×10^{-5} M in THF) excited at 454 nm before (left, dark green) and after (right, bright yellow) titration with F^-.

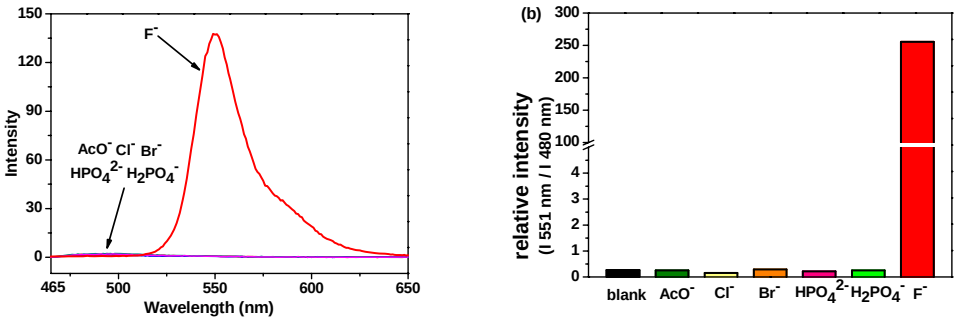
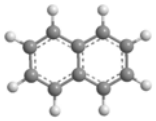
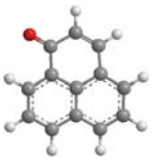
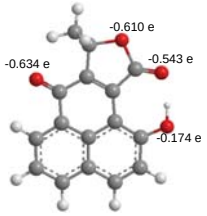


Figure S29 (a) The fluorescent spectra of **3a** (1×10^{-5} M) in THF with various anions. (b) The selectivity of **3a** with various anions : Its relative fluorescence intensities (from left to right: blank, AcO^-, Cl^-, Br^-, HPO_4^{2-}, $H_2PO_4^-$ and F^-).

Table S1 the computational orbital energy of naphthalene, phenalenone and **3a** (all in eV at B3LYP/6-31G* level) using Gaussian 03 programs.[5]

compound	naphthalene	phenalenone	**3a**
sturcture			
LUMO (eV)	-1.11	-2.61	-3.00
HOMO (eV)	-5.90	-6.19	-6.00
Eg (eV)	4.79	3.58	3.00

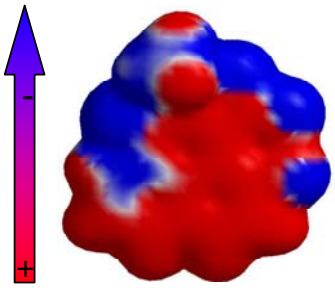


Figure S30 Total charge density of **3a**

References:

1 For the synthesis of 1,8-diiodonaphthalene, see: H. House, D. Koepsell and W. J . Campbell, *J. Org. Chem*. 1972, **37**, 1003.

2 For the synthesis of propynols, see: Z. Lu and S. Ma, *J. Org. Chem*. 2006, **71**, 2655; J. –J. Liu, F. Konzelmann, K. –C. Luk, *Tetrahedron Lett.* 2003, **44**, 3901.

3 N. Haddad and E. A. –Shqara, *J. Org. Chem*. 1994, **59**, 6090.

4 J. J. González, A. Francesch, D. J. Cárdenas and A. M. Echavarren, *J. Org. Chem.* 1998, **63**, 2854.

5 I. V. Alabugin and M. Manoharan, *J. Am. Chem. Soc.* 2005, **127**, 9534.