Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Oxidations with Air by Ascorbate-Driven Quinone Redox Cycling

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Materials and methods.

^{1}H NMR spectra were recorded at 600 and 500 MHz, ^{13}C NMR spectra were recorded at 150 and 125 MHz. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm (chloroform, 7.26 ppm; dimethyl sulfoxide-d_6 2.50 ppm, acetonitrile-d_3, 1.93 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sex = sextet, dd = double doublet, ddd = double double doublet, m =multiplet, dt = doublet triplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of $CDCl_3$ (77.0 ppm), dimethyl sulfoxide (39.5 ppm) and methanol (49.0 ppm) as the internal standard. Accurate mass (HRMS) were determined by electrospray ionization (ESI-TOF) and electronic impact (EI-TOF). Flash column chromatography was performed using silica gel, 60 Å and 0.2-0.5 mm with the indicated solvent system according to standard techniques. Compounds were visualized on TLC plates by use of UV light, or vanillin with acetic and sulfuric acid in ethanol with heating. Boronic acids were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. L-Sodium Ascorbate, BioXtra ≥99.0% from ALDRICH was employed. $NaHCO_3$ BioXtra, 99.5-100.5% from ALDRICH was employed. For detection of peroxymonocarbonate by NMR, $NaH^{13}CO_3$ 98 atom % ^{13}C from ALDRICH was employed. Reactions were performed protected from light. Anhydrous magnesium sulfate was used for drying solutions.

General Procedures

General procedure for oxidation (optimized conditions).

Arylboronic acid (1 mmol) (or arylboronic ester or potassium aryltrifluroborate salt or alkylboronic acid) and sodium ascorbate (2 mmol) were added to a mixture 1:1 (1M solution $NaHCO_3$/EtOH) at room temperature protected from light. Then the quinone (0.1 mmol) was added. The reaction was stirred open-flask at room temperature until the starting material disappeared. The progress of the reaction was monitored by TLC. The reaction mixture was poured into saturated aqueous NH_4Cl (10 mL, saturated solution) and extracted with ethyl acetate (4 × 20 mL). The combined extract was dried over

anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was chromatographed by silica gel to obtain the desired products.

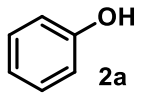
General Procedures for epoxidation of α,β-unsaturated aldehydes.

A mixture of α,*β*-unsaturated aldehyde (1 mmol) and sodium ascorbate (2 mmol) was stirred in a 1:1 mixture of solvents (1M solution $NaHCO_3$:EtOH). Then pyrrolidine (0.2 mmol) was added and finally menadione (0.1 mmol) was added. The reaction was stirred at room temperature protected from light. The progress of the reaction was monitored by TLC until the starting material disappeared. The mixture was poured into saturated NH_4Cl (10 mL, saturated solution) and extracted with ethyl acetate (4 × 20 mL). The combined extract was dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was chromatographed by silica gel to obtain the desired products.

For the over-oxidation to benzaldehyde: Similar procedure than above was followed, although 4mmol of ascorbate and 0.4mmol of menadione were employed.

Characterization of products

Benzaldehyde **5**, catechol **7** and benzoic acid **9**, were compared to commercial samples and they were completely identical.



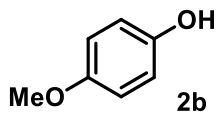
2a **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 7.19-7.16 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.77-6.75 (m, 2H), 4.82 (br, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 155.4, 129.7, 120.9, 115.4

LRMS (EI) *m/z* (relative intensity): 94.0 [M^+] (100.0) **HRMS (EI): m/z:** calcd for C_6H_6O [M^+]: 94.0419, found: 94.0415.

Column Chromatography: Gradient (95:5-80:20) (Hex-AcOEt)

Yield: 89 %



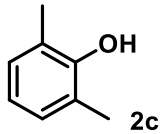
2b **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 6.81-6.77 (m, 4H), 5.45 (br, 1H), 3.77 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 153.5, 149.7, 116.3, 115.1, 56.0

LRMS (EI) *m/z* (relative intensity): 124.1 [M^+] (95.1); **HRMS (EI): m/z:** calcd for $C_7H_8O_2$ [M^+]: 124.0524, found: 124.0522.

Column Chromatography: Gradient (95:5-80:20) (Hex-AcOEt)

Yield: 99 %



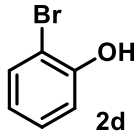
2c **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 7.00 (d, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 4.63 (br, 1H), 2.27 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 152.2, 128.6, 123.0, 120.2, 15.8

LRMS (EI) *m/z* (relative intensity): 122.1 [M^+] (10.4) **HRMS (EI): m/z: calcd for** $C_8H_{10}O$ [M^+] : 122.0732; found: 122.0732.

Column Chromatography: (99:1) (Hex:AcOEt)

Yield: 64 %

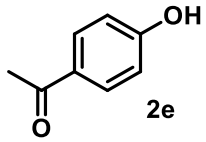


2d **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 7.45 (dd, J_1 = 1.1; J_2 = 8.0 Hz, 1H), 7.24-7.21 (m, 1H), 7.02 (dd, J_1 = 1.1; J_2 = 8.0 Hz, 1H) 5.49 (br, 1H)

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 152.3, 132.0, 129.2, 121.8, 116.1, 110.3

Column Chromatography: : (99:1) (Hex:AcOEt)

Yield: 90 %



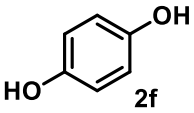
2e **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 7.91 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.56 (br, 1H), 2.56 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 198.8, 161.6, 131.2, 129.5, 115.6, 26.3

LRMS (EI) *m/z* (relative intensity): 136.0 [M^+] (46.0)**; HRMS (EI): m/z:** calcd for $C_8H_8O_2$ [M]$^+$: 136.0524, found: 136.0522.

Column Chromatography: Gradient (95:5-80:20) (Hex-AcOEt)

Yield: 98 %



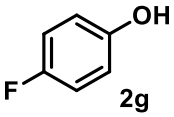
2f **^{1}H NMR (500 MHz, DMSO-*d*$_6$, 298 K): δ ppm** 6.55 (m, 4H)

^{13}C NMR (125 MHz, DMSO-*d*$_6$, 298 K): δ ppm 149.7, 115.6

LRMS (EI) *m/z* (relative intensity): 110.0 [M^+] (98.6) **HRMS (EI): m/z:** calcd for $C_6H_6O_2$ [$M]^+$: 110.0368; found: 110.0369.

Column Chromatography: Gradient (95:5-80:20) (Hex-AcOEt)

Yield: 86 %

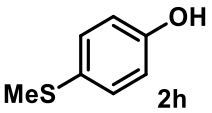


2g **^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ ppm** 6.92 (t, *J* = 8.4 Hz, 2H), 6.79-6.76 (m, 2H), 5.15 (br, 1H)

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ ppm 158.2, 156.4, 151.5, 151.5, 116.3, 116.2, 116.1, 115.8

Column Chromatography: (99:1) (Hex:AcOEt)

Yield: 95 %



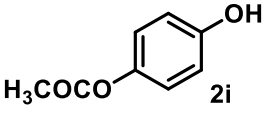
2h **^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ ppm** 7.21 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 5.27 (br, 1H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ ppm 154.1, 130.4, 128.9, 116.1, 18.1

LRMS (EI) *m/z* (relative intensity): 140.0 [M^+] (100.0); **HRMS (EI): m/z:** calcd for C_7H_8OS [$M]^+$: 140.0296; found: 140.0298.

Column Chromatography: (95:5) (Hex:AcOEt)

Yield: 89 %



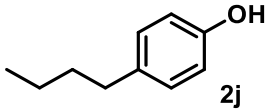
2i **^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ ppm** 7.94 (d, *J* = 8.6 Hz, 2H), 6.90 (d, 2H, *J* = 8.6 Hz), 3.90 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ ppm 167.5, 160.3, 131.9, 122.3, 115.3, 52.1.

LRMS (EI) *m/z* (relative intensity): 152.0 [M^+] (71.5); **HRMS (EI): m/z:** calcd for $C_8H_8O_3$ [M^+]: 152.0473; found: 152.0469.

Column Chromatography: (95:5) (Hex:AcOEt)

Yield: 98 %



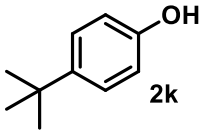
2j **^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm** 7.05 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 5.06 (br, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.57 (quin, *J* = 7.6 Hz, 2H), 1.36 (sex, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 153.4, 135.2, 129.5, 115.1, 34.7, 33.9, 22.3, 13.9.

LRMS (EI) *m/z* (relative intensity): 150.1 [M^+] (18.5) **HRMS (EI): m/z: calcd for** $C_{10}H_{14}O$ [M^+]: 150.1045; found: 152.1039.

Column Chromatography: (99:1) (Hex:AcOEt)

Yield: 76 %



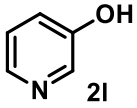
2k **^{1}H NMR (600 MHz, $CDCl_3$, 298 K)*: δ* ppm** 6.82 (d, 2H, *J* = 8.4 Hz), 5.11 (br, 1H), 1.33 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): *δ* ppm 153.1, 143.6, 126.5, 114.8, 34.1,31.6.

LRMS (EI) *m/z* (relative intensity): 149.1 [M - $1H^+$] (100.0) **HRMS (EI): *m/z:*** calcd for: $C_{10}H_{13}O$ [M – $1H^+$]: 149.0966; found: 149.0969.

Column Chromatography: gradient (99:1, 95:5) (Hex-AcOEt)

Yield: 85%



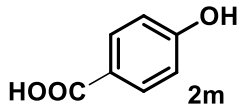
2l **^{1}H NMR (600 MHz, CD_3OD, 298 K)*: δ* ppm** 8.10 (s, 1H), 8.01 (d, 1H, *J* = 1.8 Hz), 7.26 (s, 2H), 5.08 (br, 1H).

^{13}C NMR (125 MHz, CD_3OD, 298 K): *δ* ppm 154.6, 139.4, 136.8, 124.5, 123.1.

LRMS (EI) *m/z* (relative intensity): 94.0 [M - $1H^+$] (100.0) **HRMS (EI): *m/z:*** calcd for: C_5H_5O [M – $1H^+$]: 94.0293; found: 94.0295.

Column Chromatography: gradient (80:20, 50:50, AcOEt) (Hex-AcOEt)

Yield: 83%

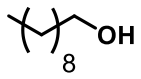


2m **^{1}H NMR (600 MHz, DMSO-*d*$_6$, 298 K): *δ* ppm** 7.79 (d, 2H, *J* = 8.4 Hz), 6.83 (d, 2H, *J* = 8.4 Hz), 3.41 (br, 1H).

^{13}C NMR (125 MHz, DMSO-*d6*, 298 K): *δ* ppm 167.6, 162.1, 132.0, 121.8, 115.6.

Column Chromatography: gradient (95:5, 75:25, 50:50) (Hex-AcOEt)

Yield: 98%

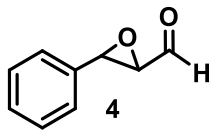


2n **^{1}H NMR (600 MHz, CDCl$_3$, 298 K): *δ* ppm** 3.61 (t, 2H, *J* = 6.7 Hz), 1.74 (br, 1H), 1.56-1.51 (m, 2H), 1.34-1.25 (m, 14H), 0.86 (t, 3H, *J* = 6.7 Hz).

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): *δ* ppm 63.0, 32.8, 31.9, 29.6, 29.5, 29.4, 29.3, 25.7, 22.6, 14.0.

Column Chromatography: (20:80) (Hex-AcOEt)

Yield: 83%

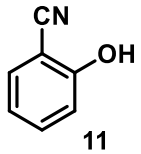


^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ ppm 3.45 (dt, 1H, *J* = 6.1, 2.1 Hz,), 4.19 (m, 1H), 7.29–7.40 (m, 5H), 9.21 (dd, *J* = 1.2, 6.0 Hz).

^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ ppm 56.6, 62.9, 125.7 (x 2), 128.8 (x 2), 129.2, 134.2, 196.8.

Column Chromatography: 95:5 (Hex-AcOEt)

Yield: 40%



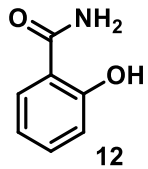
^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ ppm 7.50-7.44 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.46 (br, 1H)

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ ppm 159.0, 134.8, 133.0, 120.8, 116.7, 116.6, 99.3

LRMS (EI) *m/z* (relative intensity): 119.0 [M^+] (54.4); **HRMS (EI):** m/z: calcd for C_7H_5NO [M^+]: 119.0371; found: 119.0373.

Column Chromatography: Gradient (95:5-70:30) (Hex-AcOEt)

Yield: 50 %



12 **^{1}H NMR (500 MHz, CDCl$_3$-DMSO-*d*$_6$, 298 K): δ ppm** 12.9, (br, 1H), 8.27 (br, 1H), 7.79 (d, *J* = 7.00 Hz, 1H), 7.71 (br, 1H), 7.33 (t, *J* = 8.00 Hz, 1H), 6.83-6.78 (m, 2H)

^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ ppm 172.1, 161.2, 133.6, 127.9, 118.0, 117.2, 114.3.

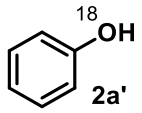
LRMS (EI) *m/z* (relative intensity): 137.0 [M^+] (38.8); **HRMS (EI): m/z:** calcd for: $C_7H_7NO_2$ [M^+]: 137.0477; found: 137.0482.

Column Chromatography: Gradient (95:5-70:30) (Hex-AcOEt)

Yield: 44 %

^{18}O Labelling experiment.

A mixture of phenylboronic acid (1 mmol) and sodium ascorbate (2 mmol) was stirred in a 1:1 mixture of solvents (1M solution $NaHCO_3$/EtOH) at room temperature protected from light. The reaction was stirred under nitrogen for 15 minutes and then menadione (0.1mmol) was added. The reaction was then stirred at room temperature under $^{18}O_2$ atmosphere. The progress of the reaction was monitored by TLC, until the starting material disappeared. The mixture was poured into saturated aqueous NH_4Cl (10 mL, saturated solution) and extracted with ethyl acetate (4 × 20 mL). The combined extract was dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was chromatographed by silica gel to obtain the desired product **2a'**.



2a'

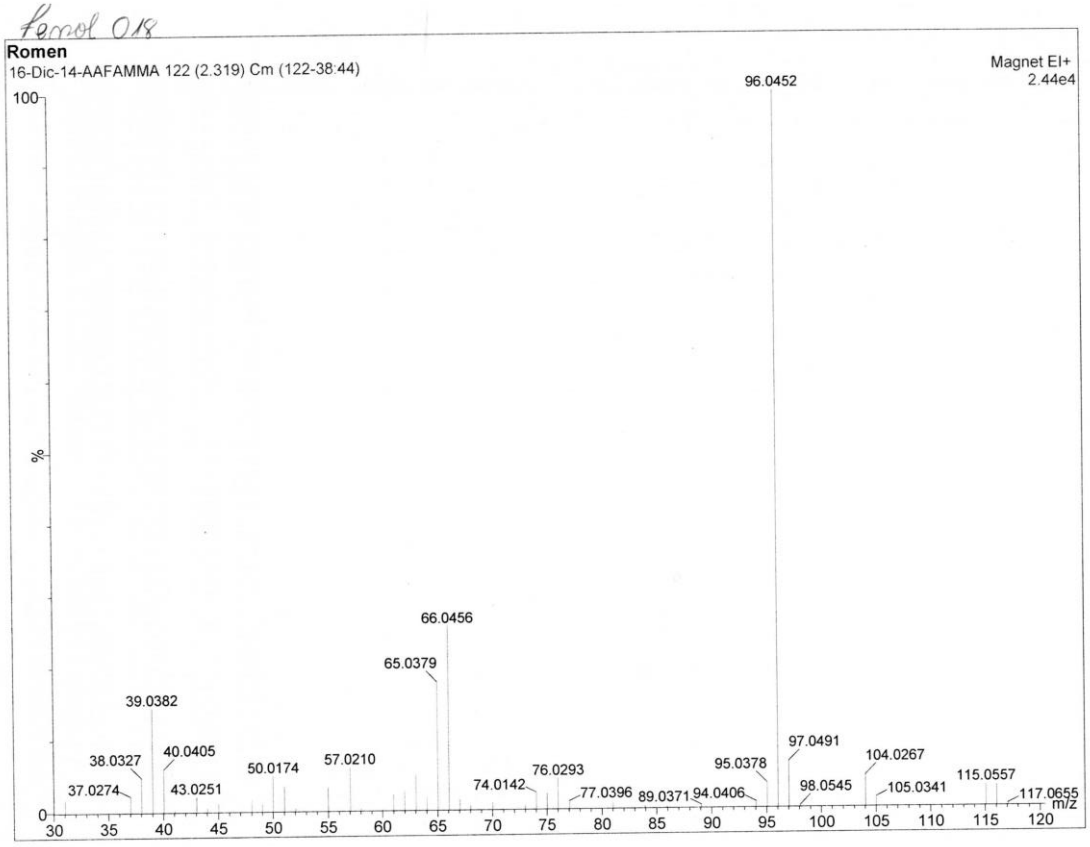
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ ppm 7.19-7.16 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.77-6.75 (m, 2H), 4.82 (br, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ ppm 155.4, 129.7, 120.9, 115.4

LRMS (EI) *m/z* (relative intensity): 96.0 [M^+] (100.0) **HRMS (EI): m/z:** calcd for C_6H_6 ^{18}O [M^+]: 96.0461, found: 96.0463.

Column Chromatography: Gradient (95:5-80:20) (Hex-AcOEt)

Yield: 89 %



Elemental Composition Report **Page 1**

Multiple Mass Analysis: 84 mass(es) processed - displaying only valid results
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
85 formula(e) evaluated with 14 results within limits (all results (up to 1000) for each mass)
Elements Used:
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Romen
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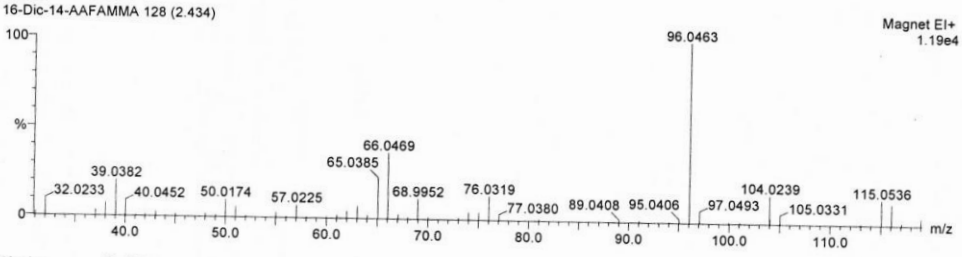

Minimum:	0.10				-1.5		
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77.0380	2.94	77.0391	-1.1	-14.3	4.5	5546123.0	C6 H5
76.0319	13.15	76.0313	0.6	7.9	5.0	2773100.0	C6 H4
75.0224	4.16	75.0235	-1.1	-14.7	5.5	949.5	C6 H3
74.0161	4.07	74.0157	0.4	5.4	6.0	352.0	C6 H2
73.0072	0.85	73.0078	-0.6	-8.2	6.5	502.5	C6 H
70.0303	0.92	70.0305	-0.2	-2.9	3.0	0.0	C4 H4 18O
66.0469	36.42	66.0470	-0.1	-1.5	3.0	2773024.3	C5 H6
65.0385	22.63	65.0391	-0.6	-9.2	3.5	2195.1	C5 H5
64.0325	1.50	64.0313	1.2	18.7	4.0	3732.2	C5 H4
63.0230	6.93	63.0235	-0.5	-7.9	4.5	1528.4	C5 H3
61.0069	1.64	61.0078	-0.9	-14.8	5.5	679.8	C5 H
57.0225	6.93	57.0226	-0.1	-1.8	2.5	0.3	C3 H3 18O
51.0237	5.84	51.0235	0.2	3.9	3.5	2773017.5	C4 H3

Figure S1

Detection of peroxymonocarbonate

The bicarbonate activated peroxide is a known method for activating H_2O_2. The actual oxidant is not hydrogen peroxide, but peroxymonocarbonate ion (HCO_4^-) formed by the equilibrium reaction between bicarbonate ion and H_2O_2:

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O$$

Peroxymonocarbonate ion is a reactive species but it can be detected by several techniques, such as ^{13}C NMR. We prepared a 1:1 solution of methanol-d_4 and sodium bicarbonate (1M) in deuterated water, analogous to the solution used in the reactions. We used 99% ^{13}C-enriched $NaHCO_3$ (SIGMA-Aldrich). Sodium ascorbate (100 mg) was added to 1 mL of the solvent mixture. Finally, 5 mg of menadione were added. After 10 minutes stirring under air, the ^{13}C NMR experiment at 25 °C was submitted. In the NMR spectrum it is clearly seen three peaks. The peak at 161.4 ppm was assigned to HCO_3^-, while the peak at 159.9 ppm corresponds to peroxymonocarbonate HCO_4^-. Primary alcohols, such as methanol, also react with bicarbonate to form alkyl carbonate esters, RCO_3^-, and a third peak at 161.1 ppm is observed in the NMR spectrum.

$$HCO_3^- + MeOH \rightleftharpoons MeOCO_2^- + H_2O$$

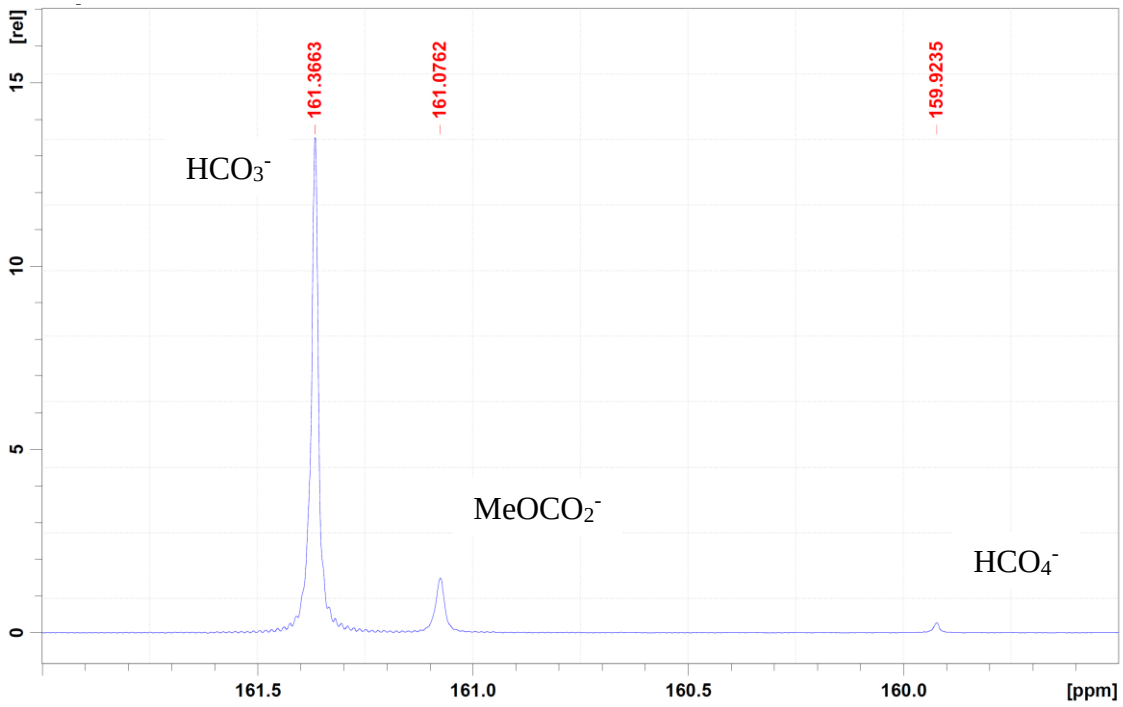

Figure S2

The small peak of peroxymonocarbonate is not only due to its intrinsically instable nature, but also because hydrogen peroxide is generated progressively in situ in small amounts, compared to previously reported experiments where a high concentration of peroxide is employed. Worth to mention, the experiment without ascorbate or menadione displays no peroxymonocarbonate peak.

NMR Spectra.

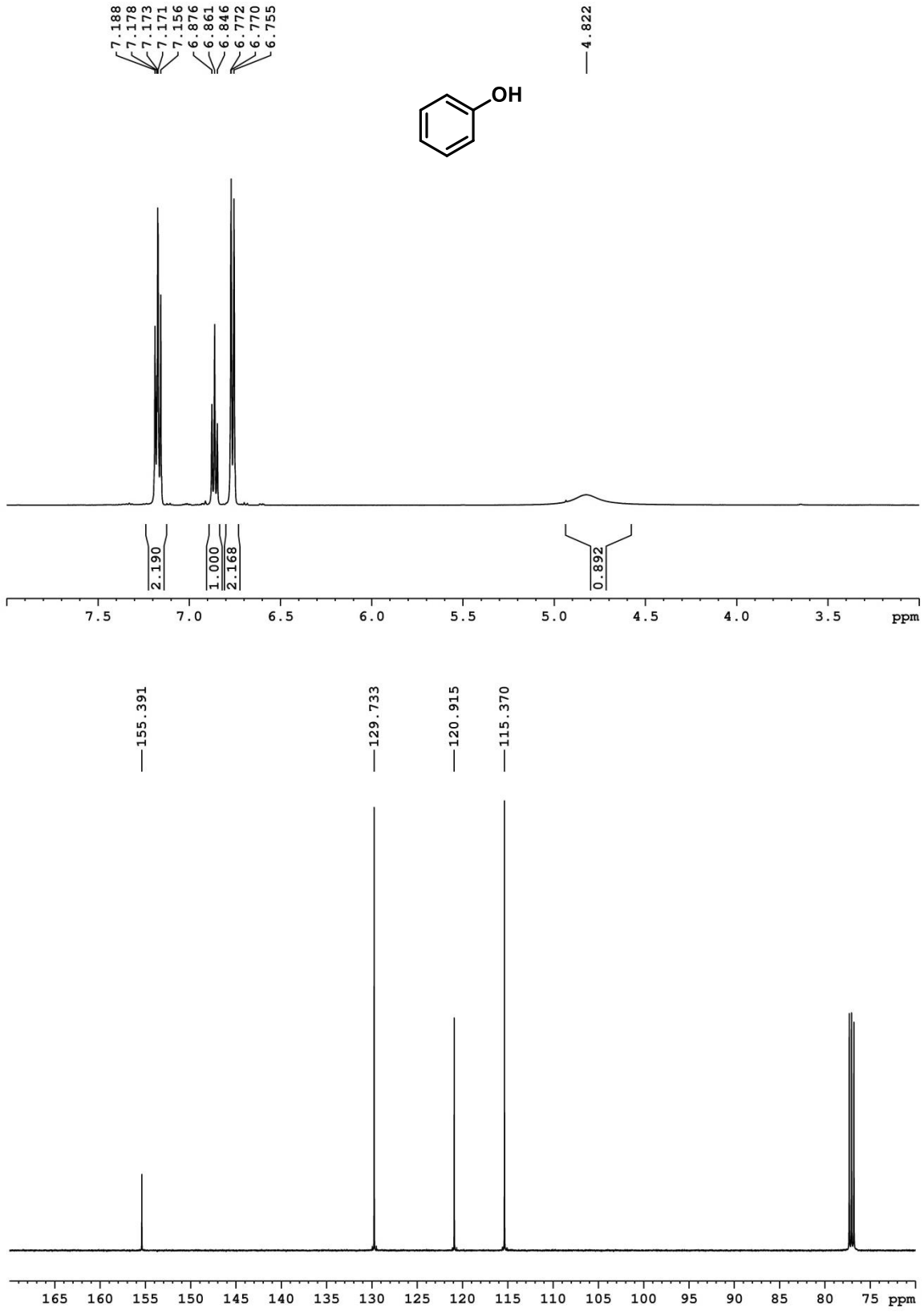

Figure S3. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2a** in $CDCl_3$

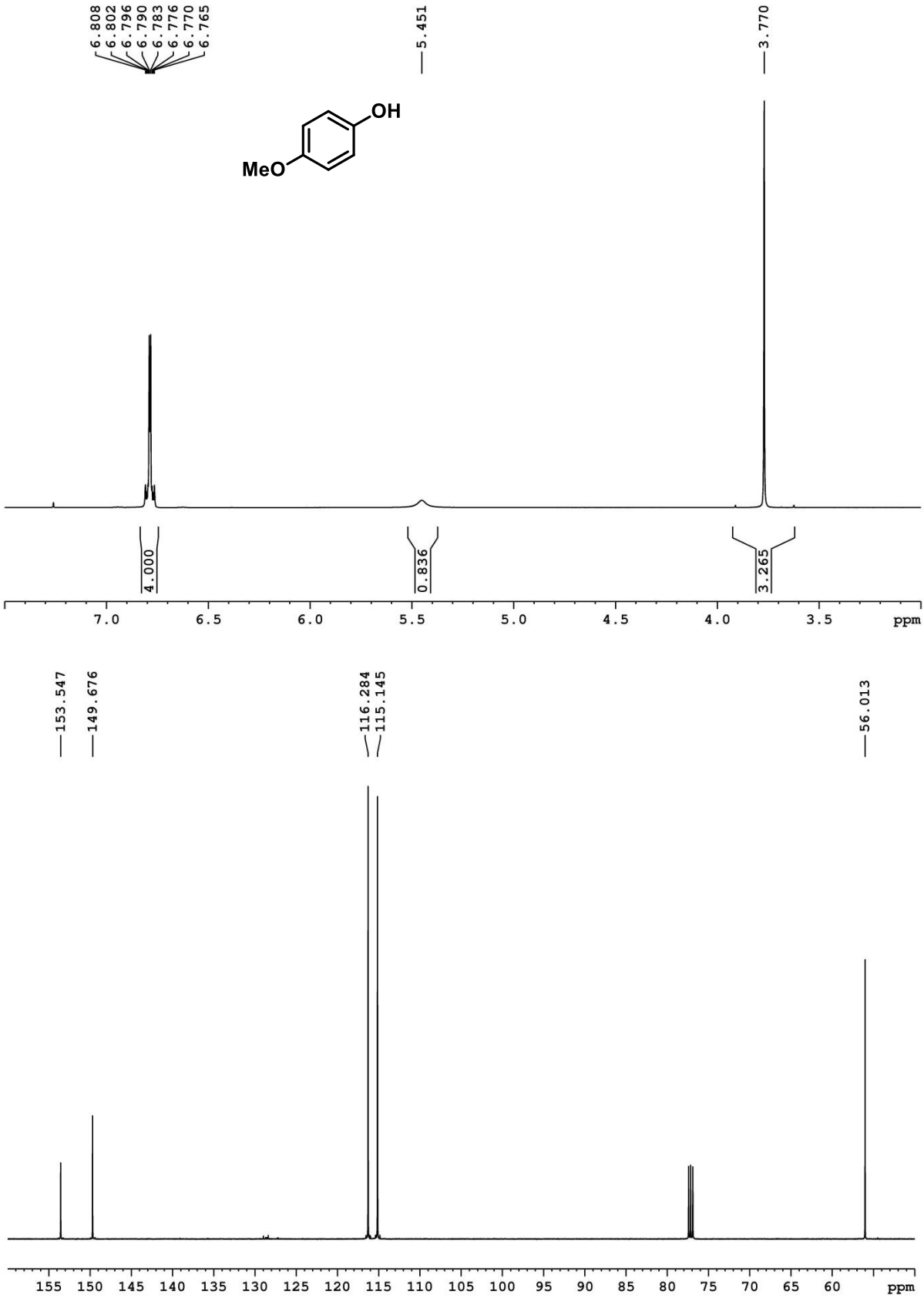

Figure S4. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2b** in $CDCl_3$.

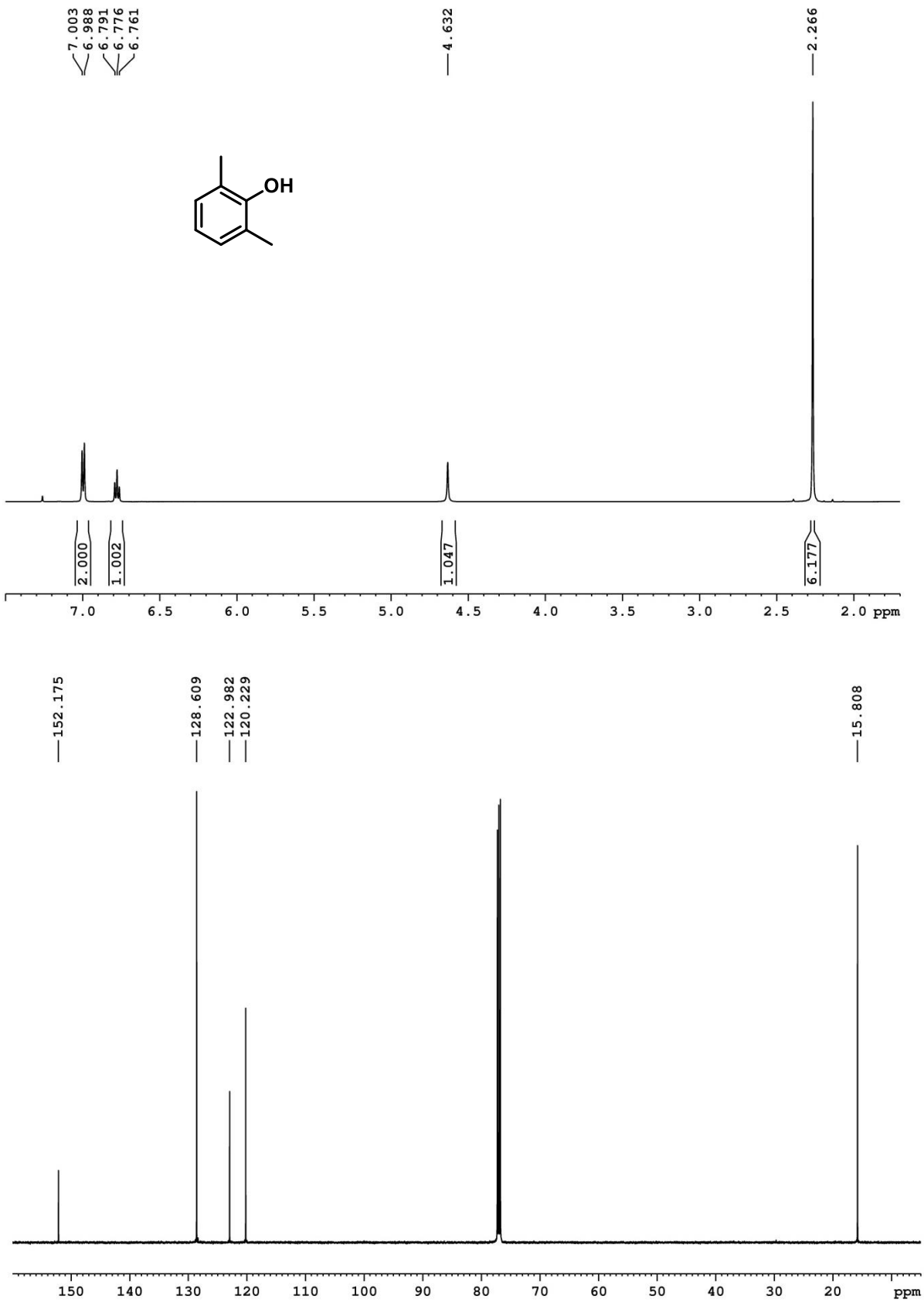

Figure S5. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2c** in $CDCl_3$

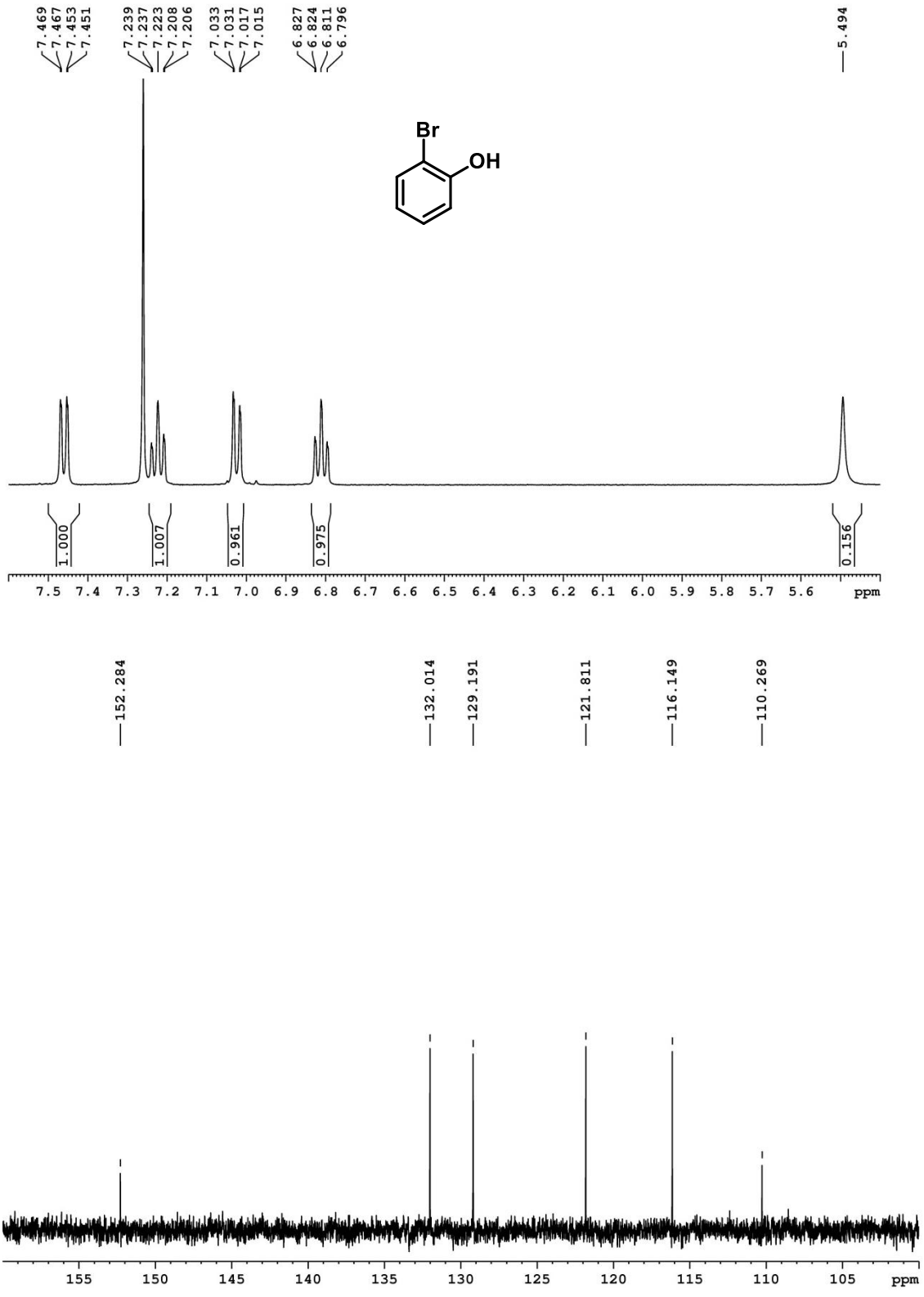

Figure S6. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2d** in $CDCl_3$

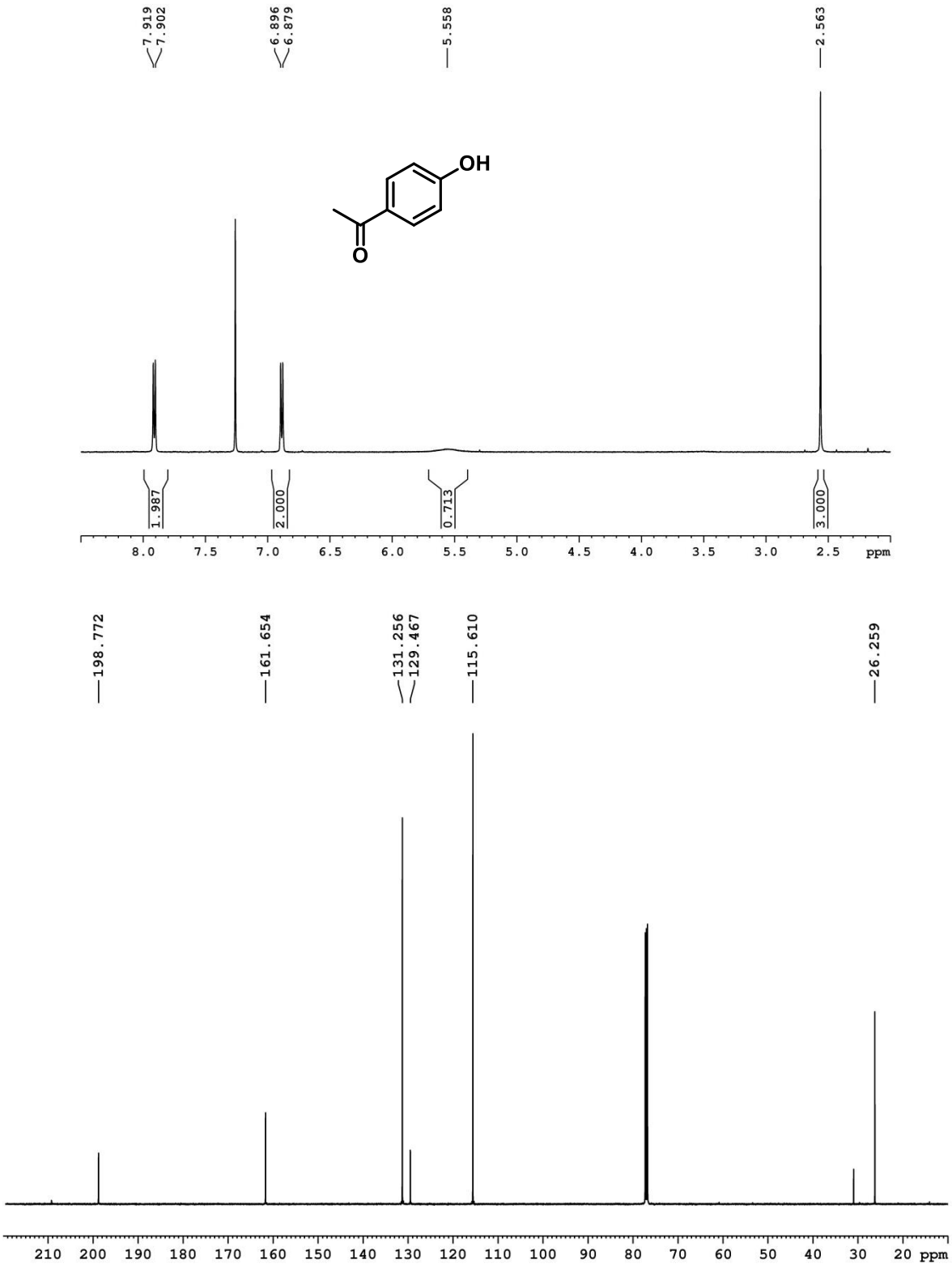

Figure S7. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2e** in $CDCl_3$

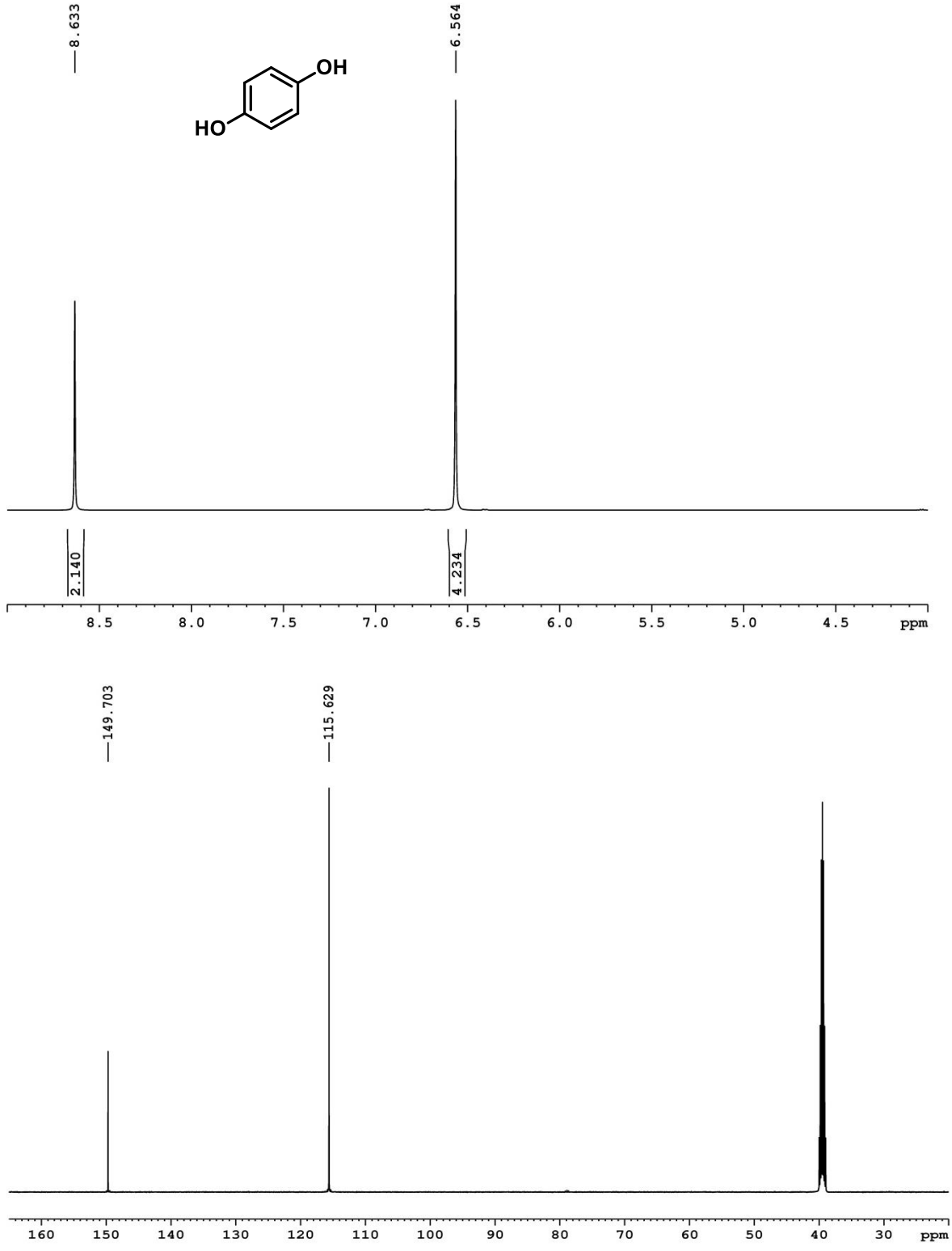

Figure S8. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2f** in DMSO-d_6

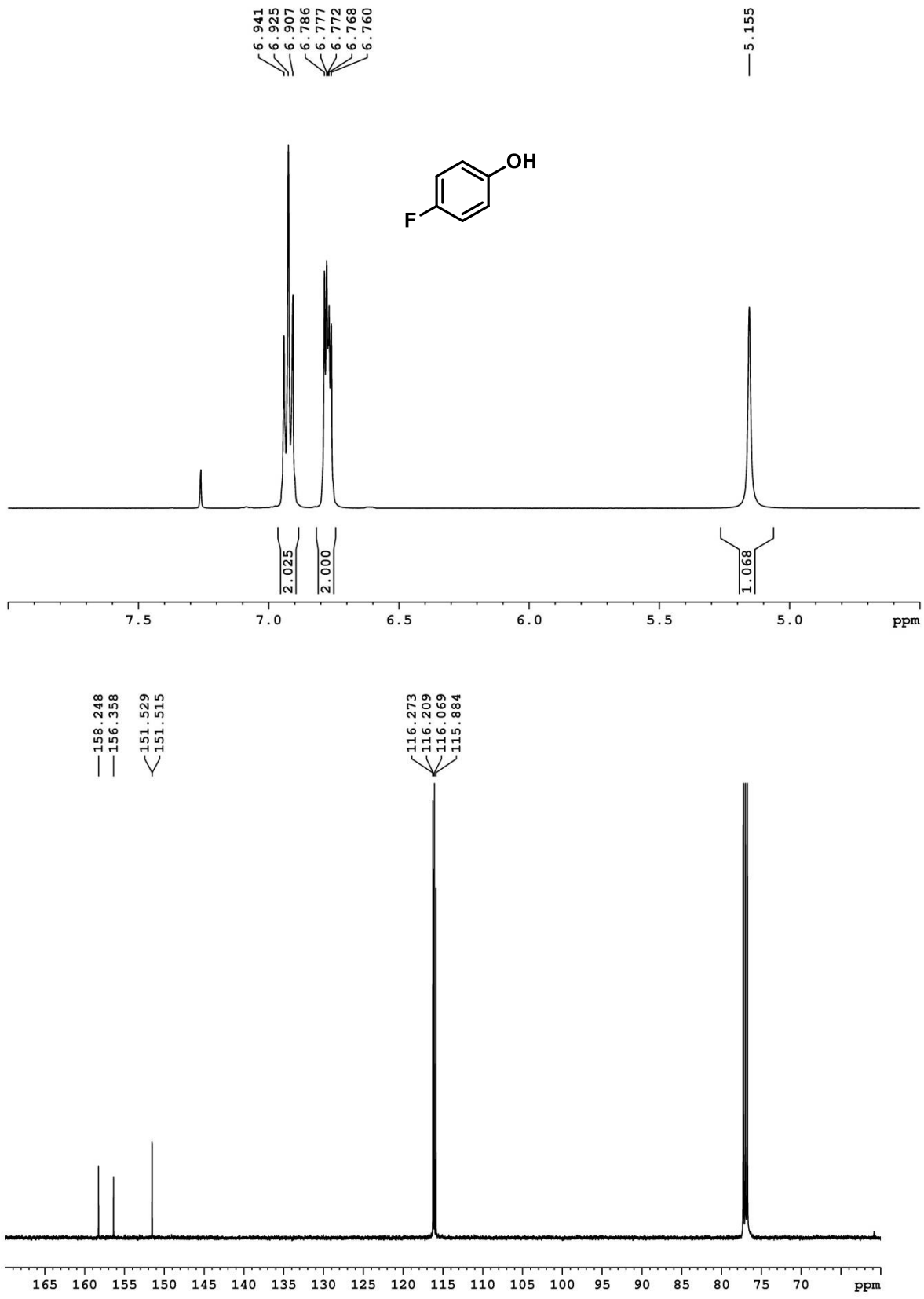

Figure S9. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2g** in $CDCl_3$

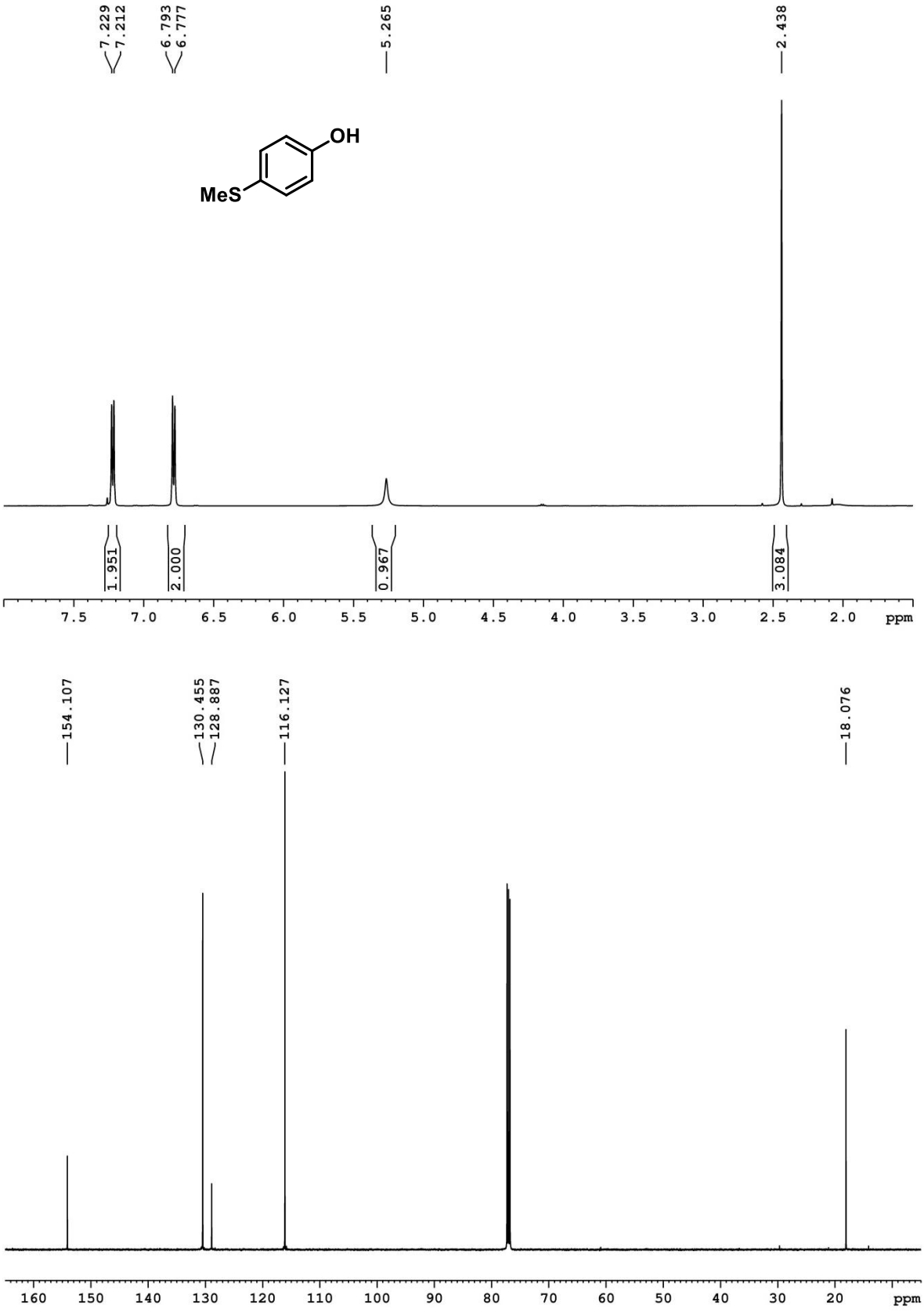

Figure S10. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2h** in $CDCl_3$

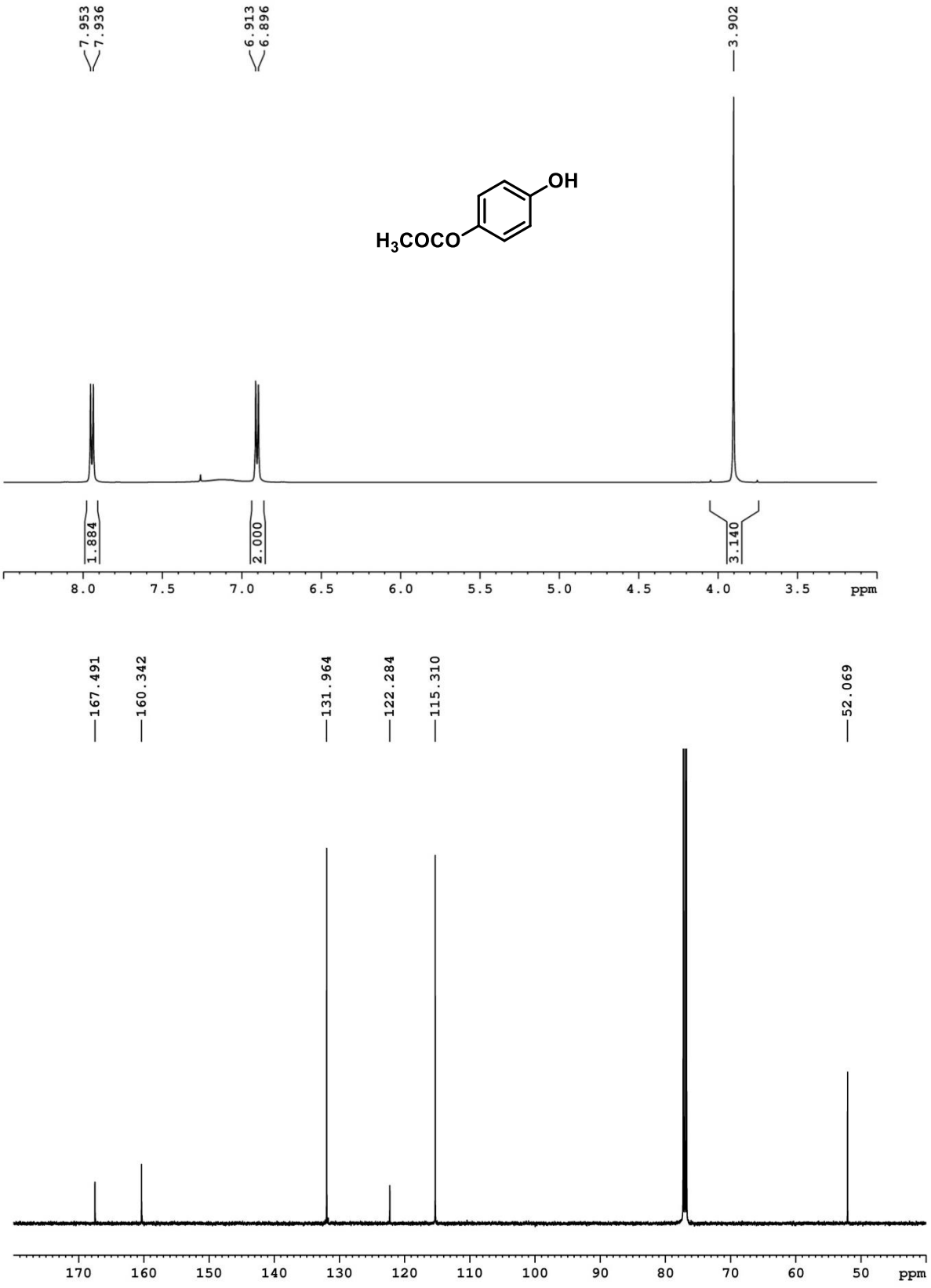

Figure S11. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2i** in $CDCl_3$

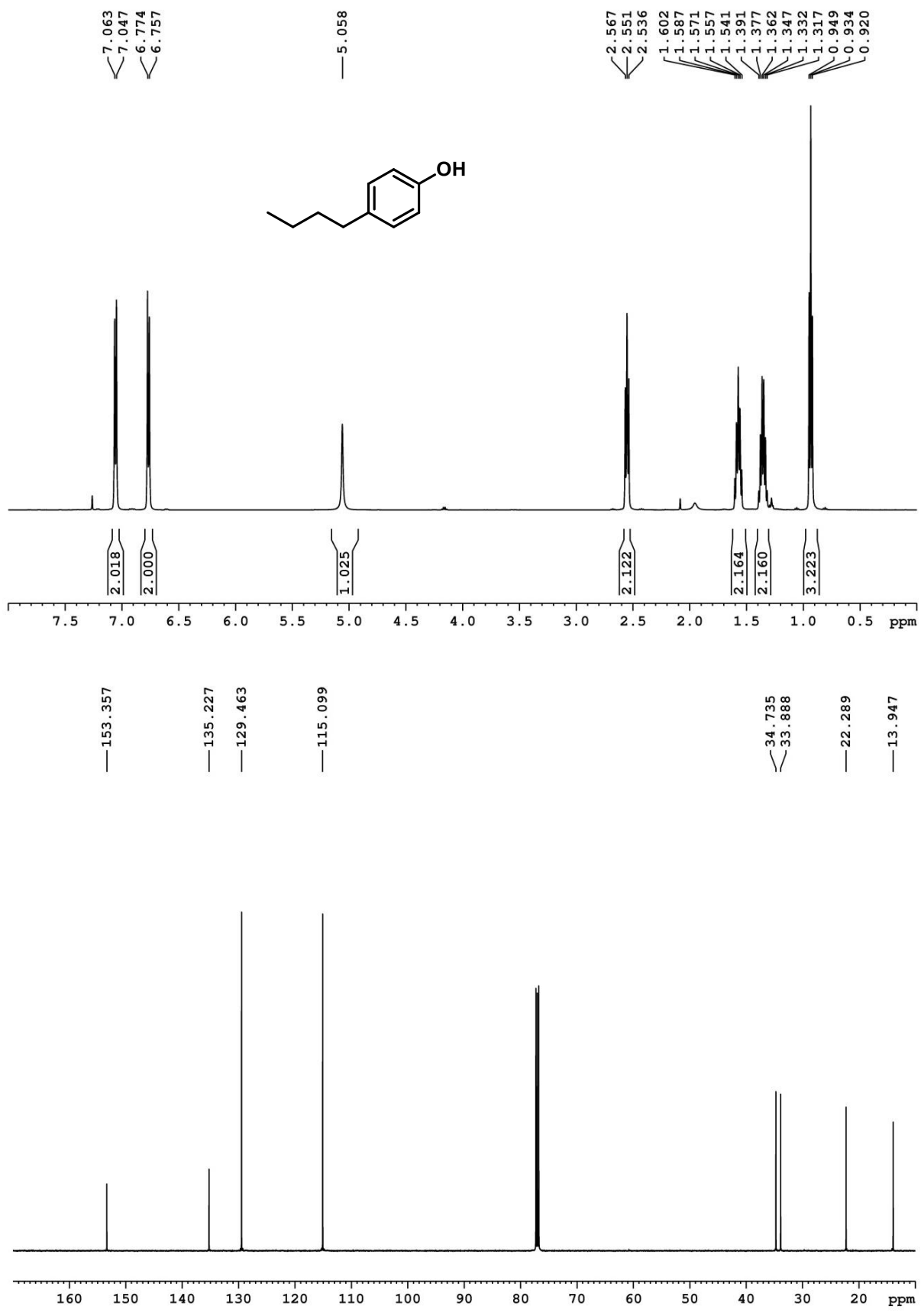

Figure S12. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2j** in $CDCl_3$

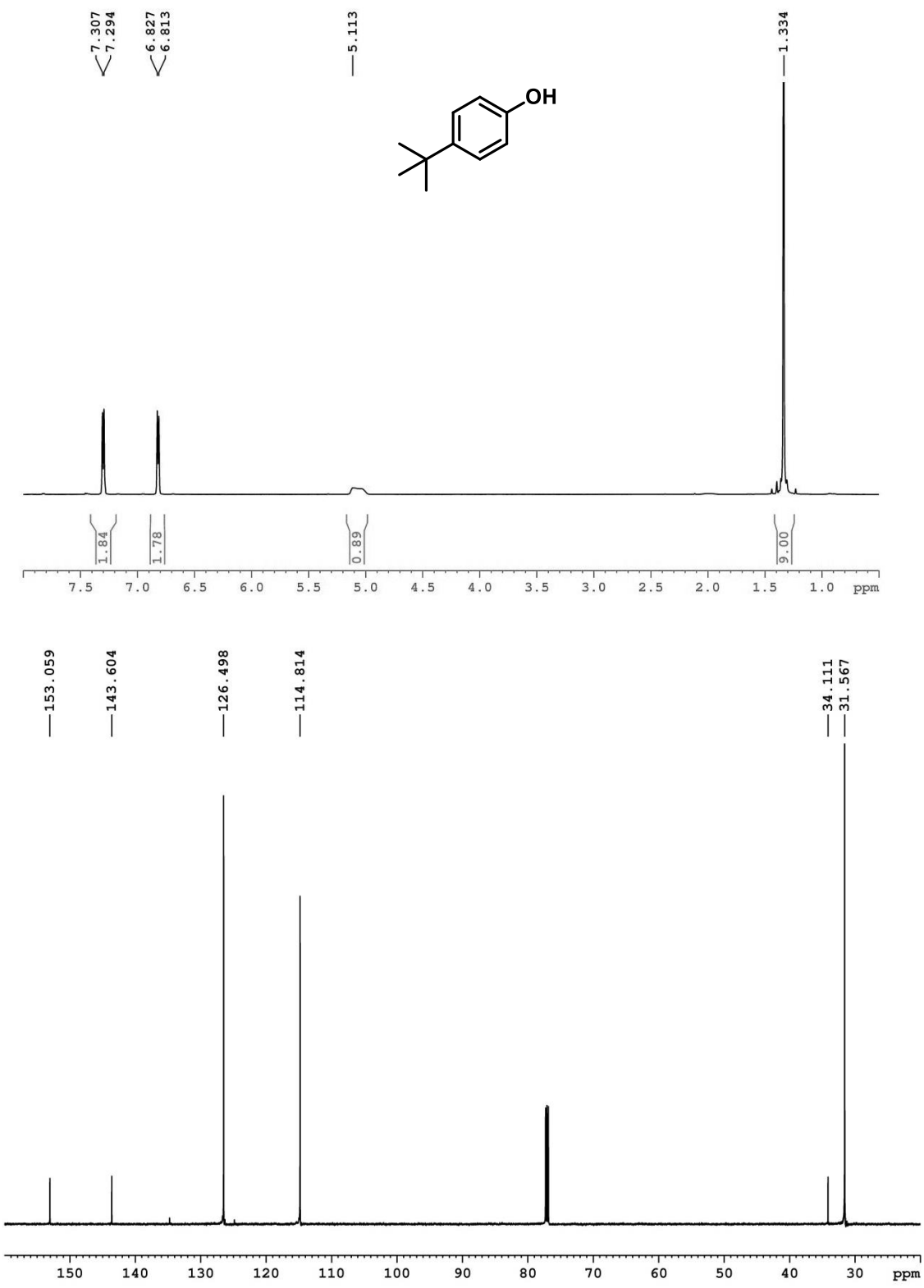

Figure S13. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2k** in $CDCl_3$

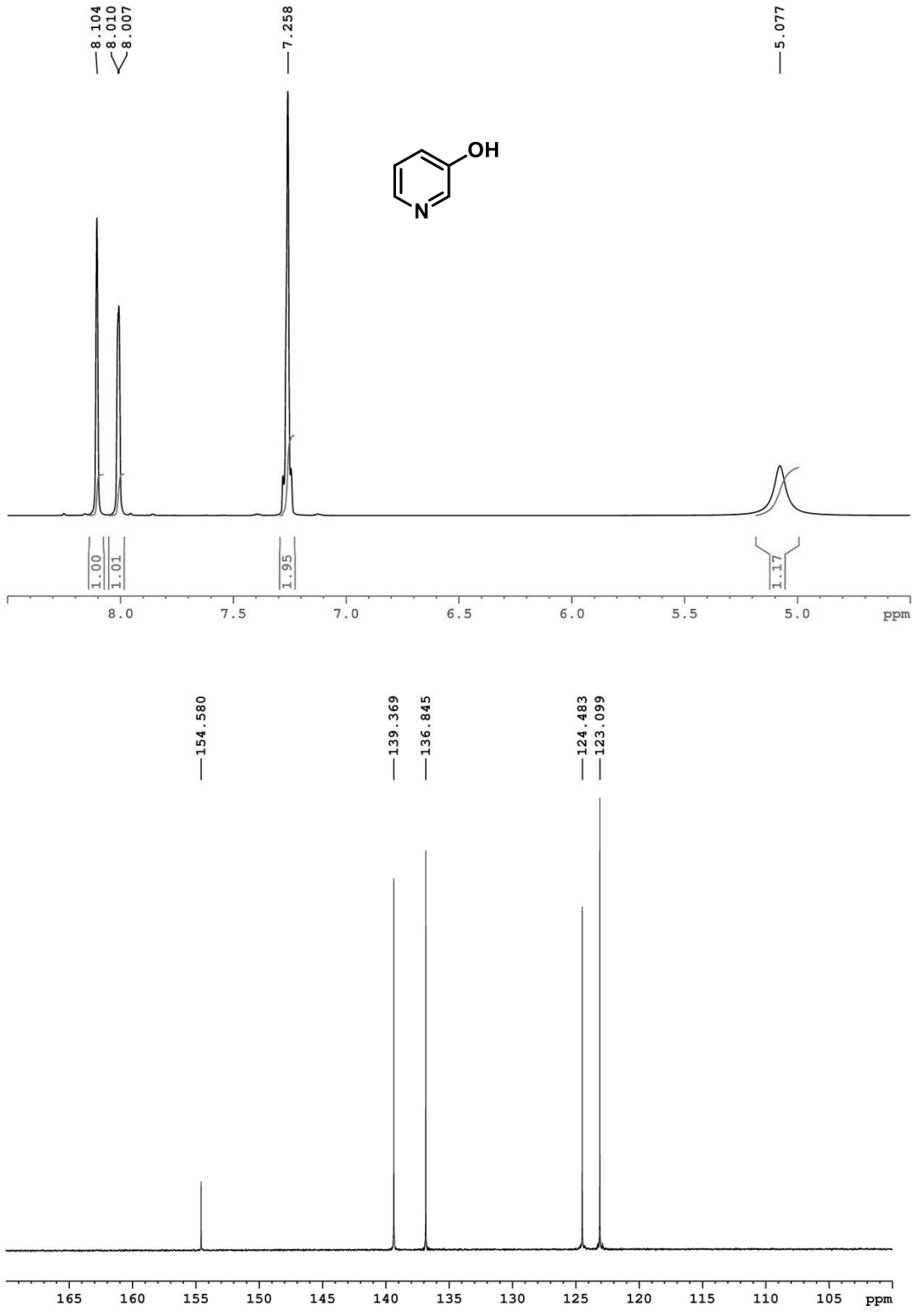

Figure S14. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2l** in CD_3OD

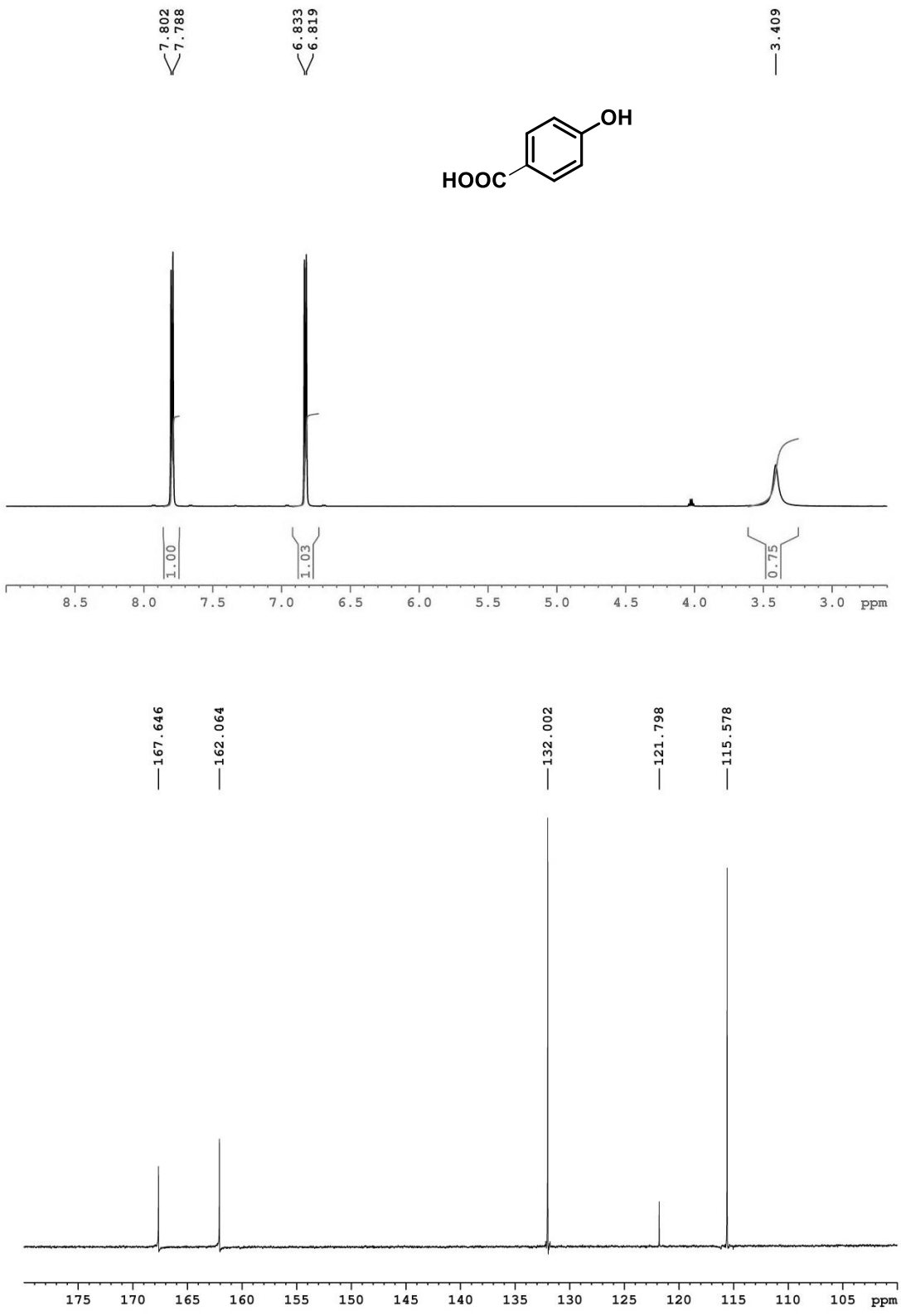

Figure S15. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **2m** in DMSO-d_6

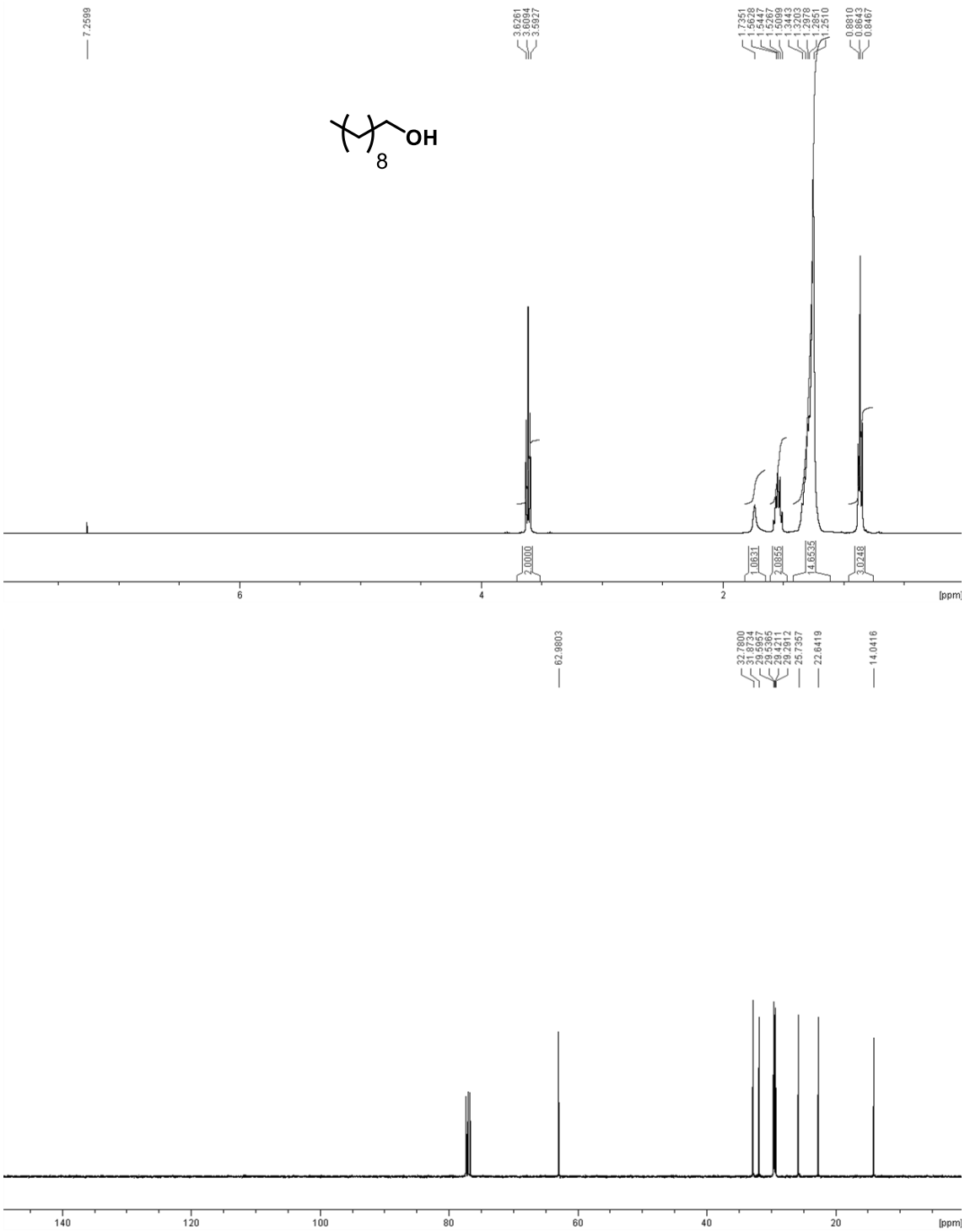

Figure S16. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **2n** in $CDCl_3$

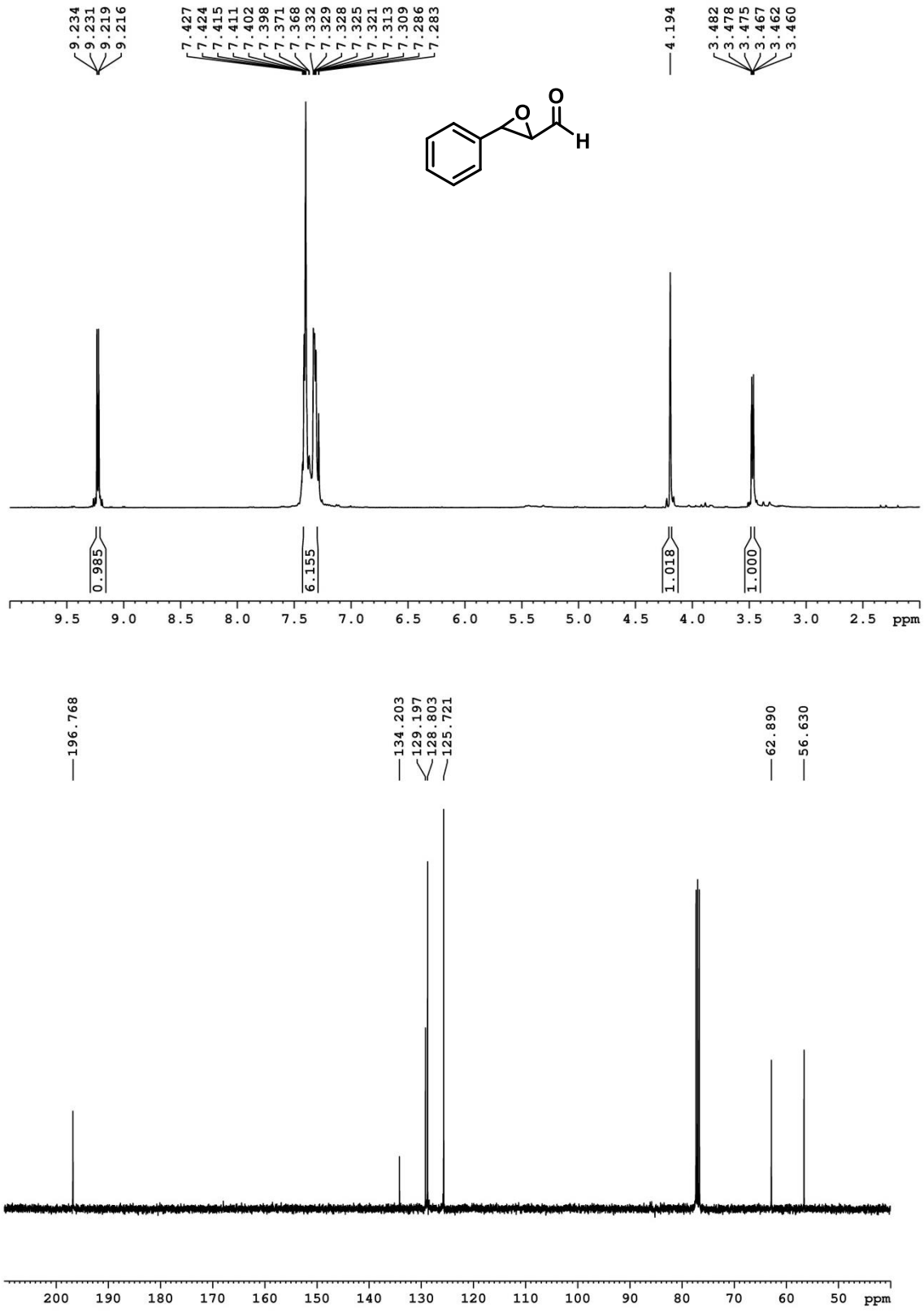

Figure S17. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **4** in $CDCl_3$

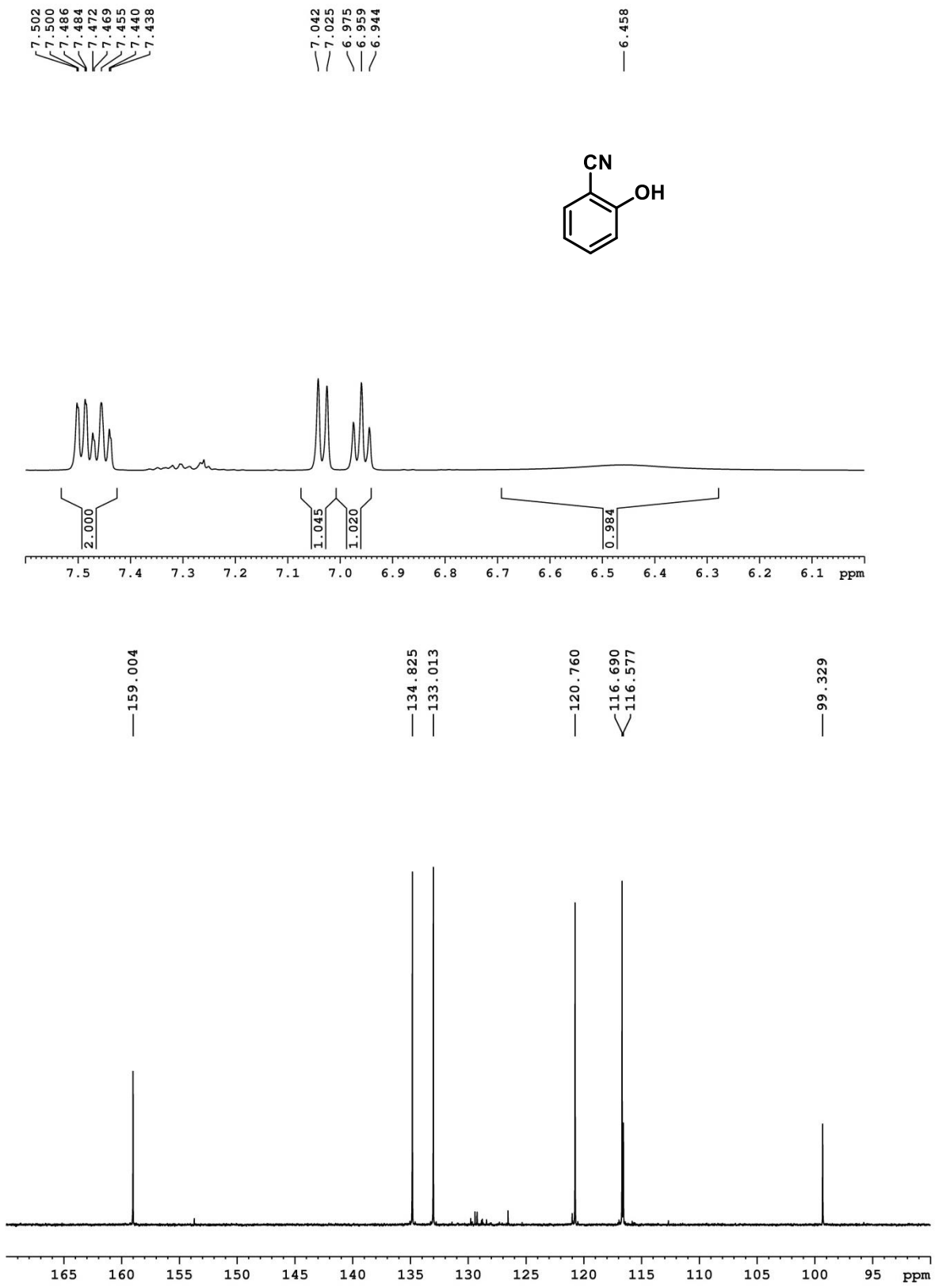

Figure S18. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **11** in $CDCl_3$

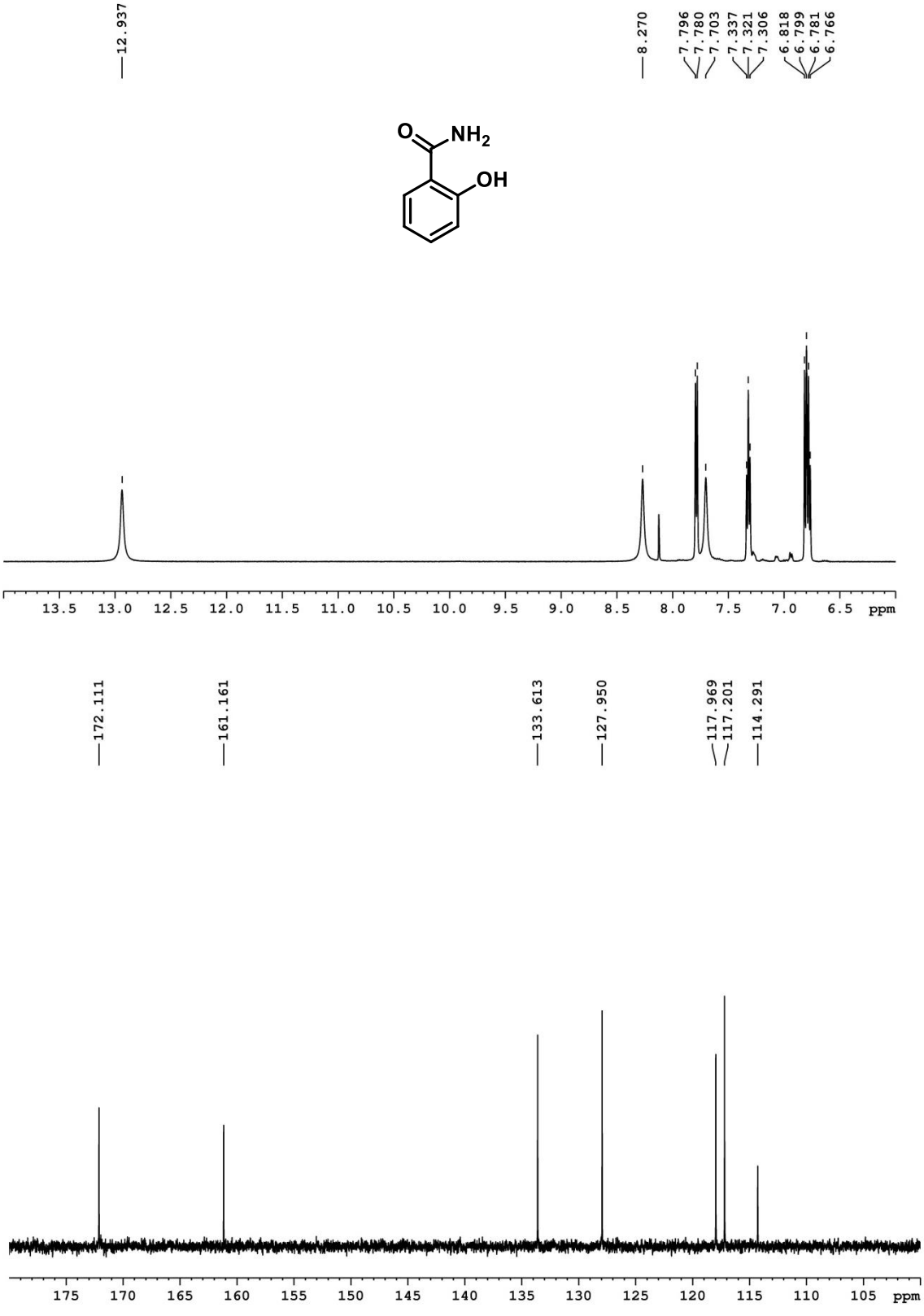

Figure S19. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of **12** in $CDCl_3$/DMSO-d_6