

Supplementary Information

for

**Photoinduced vitamin B₁₂-catalysis for deprotection of
(allyloxy)arenes**

Maciej Giedyk, Joanna Turkowska, Sandra Lepak, Marcin Marculewicz,
and Dorota Gryko

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1. General Information

All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification. Photoreactions (method A) were carried out using Rayonet RPR-200 photoreactor equipped with RPR-2537A lamps (254 nm). High resolution mass spectra were recorded on a Waters AutoSpec Premier and SYNAPT spectrometer. ^1H and ^{13}C NMR spectra were recorded at rt on Bruker 400 MHz instruments with TMS as an internal standard. Thin layer chromatography (TLC) was performed using Merck Silica Gel GF254, 0.20 mm thickness. Chromatography was performed using DCVC method¹ on Merck Silica Gel 60 H.

Vitamin B₁₂ (**1a**, cyanocobalamin, (CN)Cbl) and hydroxocobalamin (**1b**, (OH)Cbl) were purchased from Carbosynth (MV16892 and FH23894). TiO₂ used in method A was a nanopowder mixture of anatase and rutile and was purchased from Sigma-Aldrich (718467). ND₄Cl used in deuterium experiment was purchased from Sigma-Aldrich (175676). Cby(II) used in mechanistic investigation was synthesized according to the reported procedure.²

Zn was used in its activated form. Activation process comprised: 1) grinding in 10% HCl, 2) washing with water, acetone, MeOH and Et₂O, 3) grinding, 4) drying *in vacuo*. It was stored under argon for maximum 7 days. We observed that the use of freshly activated Zn was important for reaction reproducibility.

0.05 M solution of HCl in MeOH was prepared by diluting 37% aqueous HCl in MeOH.

2. Description of general synthetic procedures

2.1 Optimization of the reaction conditions

Table 1. Optimization: the influence of TiO₂.^a

entry	TiO ₂ form	TiO ₂ (equiv)	1a (mol %)	yield (%)
1	nanopowder ^b	1.5	10	53
2	nanopowder ^b	1	10	55
3	anatase	1	10	57
4	rutile	1	10	59
5	nanopowder^b	0.5	10	59
6	nanopowder ^b	0.5	2	51
7	nanopowder ^b	0.25	2	44
8	nanopowder ^b	0.1	2	40

^aReaction conditions: 2-(allyloxy)naphthalene (**4a**, 0.5 mmol), TiO₂ (equiv indicated in the table.), (CN)Cbl (**1a**, mol % indicated in the table), MeOH (2 mL), 20 h, UV light (254 nm). ^bcommercially available TiO₂ nanopowder - a mixture of anatase and rutile was used.

Table 2. Optimization: the influence of the catalyst.^a

entry	catalyst	loading (mol %)	<i>c</i> (M)	yield (%) ^b
1	(1a)	10	0.25	59
2	(1a)	6	0.25	58 (23) ^d
3 ^c	(1a)	6	0.25	22 (12) ^d
4	(1a)	4	0.25	50
5	(1a)	2	0.25	51
6	(1a)	10	0.125	61
7	(1b)	10	0.25	23

^aReaction conditions: 2-(allyloxy)naphthalene (**4a**, 0.5 mmol), TiO₂ (0.5 equiv), catalyst (form and mol % indicated in the table), MeOH, 20 h, UV light (254 nm). ^bIsolated yields. ^cEtOH was used instead of MeOH. ^dValues in brackets – (vinylxy)naphthalene (**6a**) was formed additionally.

2.2 General procedure for photo-reductive system (method A):

Step 1: A 10 mL quartz tube equipped with a stirring bar was charged with (allyloxy)benzene (0.5 mmol), vitamin B₁₂ (**1a**, 42 mg, 6 mol %) and TiO₂ (20 mg). MeOH (2 mL) was added and the mixture was degassed by bubbling argon and sonication for 15 min. The reaction vessel was sealed with a septa. The septa was additionally covered with parafilm and alumina foil. The reaction was irradiated and stirred vigorously under UV light (254 nm) for 20 h. It was then diluted with Et₂O (20 mL), filtered through a 2 cm silica plug and concentrated *in vacuo*.

Step 2 (only if partial isomerization to (vinylloxy)benzene was observed): The crude mixture was dissolved in methanolic solution of HCl (0.05 M, 10 mL) and stirred at 50 °C. The reaction progress was monitored by thin layer chromatography (TLC). When the reaction was completed, it was diluted with Et₂O/*n*-hexane (1:1, 50 mL), washed with water, dried over Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by DCVC chromatography (AcOEt in hexane or DCM in hexane).

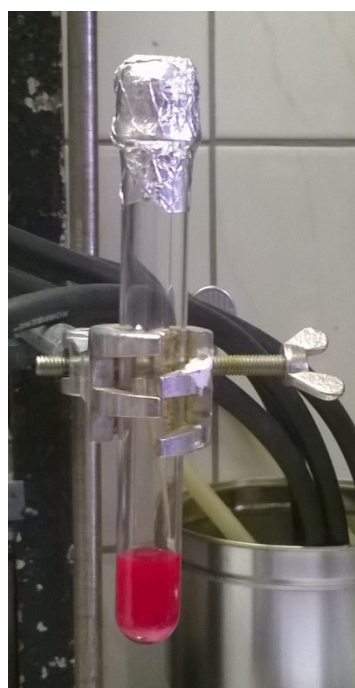


Fig. 1 Standard set-up for method A

2.3 General procedure for Zn, NH₄Cl-reductive system (method B):

A 10 mL glass reaction tube equipped with a stirring bar was charged with (allyloxy)benzene (0.5 mmol), vitamin B₁₂ (**1a**, 42 mg, 6.0 mol %), Zn (196 mg, 3.0 mmol) and NH₄Cl (90 mg, 1.7 mmol). MeOH (2 mL) was added and the mixture was degassed by bubbling argon and sonication for 15 min. The reaction vessel was sealed with a septa, which was additionally covered with parafilm. The reaction was stirred vigorously at 60 °C for 20 h. It was then diluted with Et₂O (20 mL), filtered through a 2 cm silica plug and concentrated *in vacuo*. The crude product was purified by DCVC chromatography (AcOEt in hexane or DCM in hexane).



Fig. 2 Standard set-up for method **B**

2.4 Catalyst recovery

After the reaction was finished, it was diluted with Et₂O filtered through a sintered funnel. The precipitate, consisting of cobalamin (**1a**) and TiO₂, stayed on the sinter. It was then scratched off, dried and used in a next reaction.



Fig. 3 Filtering crude mixture through a Schott funnel.

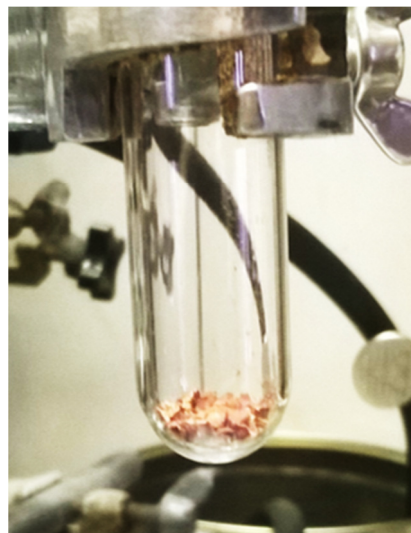


Fig. 4 Recovered catalysts prepared for the next reaction.

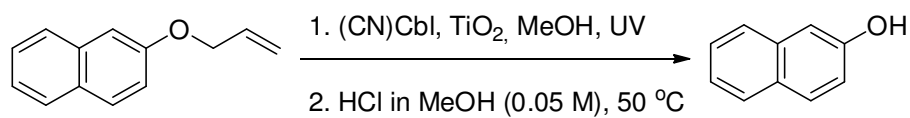
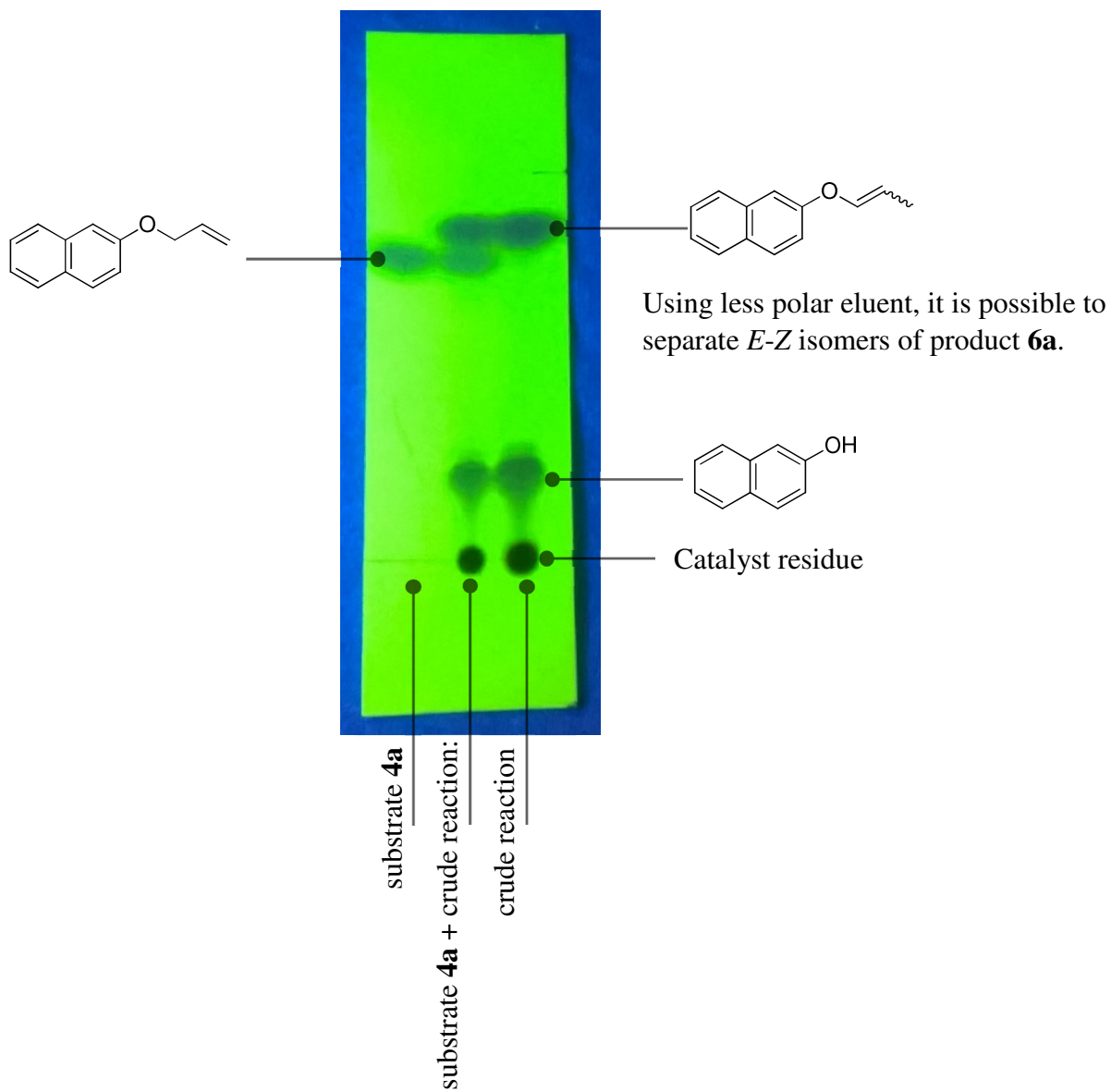


Table 1 Yields of the reactions with the recovered catalyst.

cycle	yield (%)
1	83
2	72
3	66
4	29

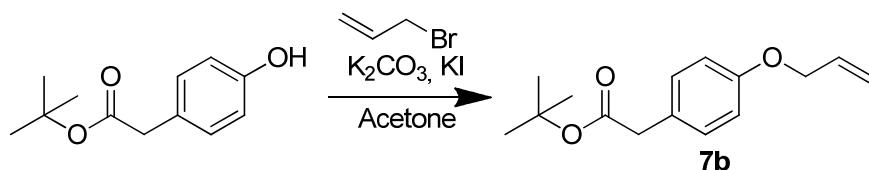
2.5 TLC of a crude reaction mixture

Eluent – hexane : AcOEt 10:1.



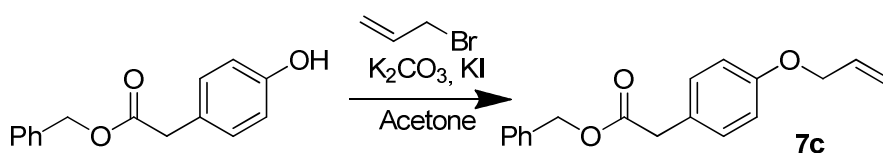
3 Specific synthetic procedures

Procedure for the synthesis of *tert*-butyl 2-(4-(allyloxy)phenyl)acetate (**7b**)



A 50 mL round-bottom flask equipped with a stirring bar was charged with *tert*-butyl 4-hydroxyphenyl acetate³ (415 mg, 2.0 mmol), K_2CO_3 (413 mg, 3.0 mmol) and KI (7 mg, 0.2 mmol). Substrates were dissolved in acetone (20 mL) at 0 °C. Subsequently, allyl bromide (0.27 mL, 3.0 mmol) was added under argon. The resulting mixture was stirred at reflux for 18 h. It was then filtrated through cotton wool, diluted with AcOEt (60 mL) and washed with brine and H_2O . The organic layer was dried over Na_2SO_4 , filtered through cotton wool and concentrated *in vacuo*. The crude product (**7b**) was purified by DCVC chromatography¹ (hexane:DCM:AcOEt 10:1:0-0.2) to give a pale-yellow oil. Yield = 82%. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3$: C 72.55, H 8.12, found: C 72.31, H 8.13. HRMS ESI calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 271.1310, found: 271.1306. ^1H NMR (CDCl_3 , 400 MHz): δ 7.19 – 7.12 (m, 2H), 6.88 – 6.81 (m, 2H), 6.04 (ddt, 1H, $J = 17.2, 10.5, 5.3$ Hz), 5.39 (dq, 1H, $J = 17.3, 1.6$ Hz), 5.26 (dq, 1H, $J = 10.5, 1.4$ Hz), 4.51 (dt, 2H, $J = 5.3, 1.5$ Hz), 3.44 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.2, 157.6, 133.4, 130.2, 127.0, 117.5, 114.7, 80.6, 68.8, 41.7, 28.0.

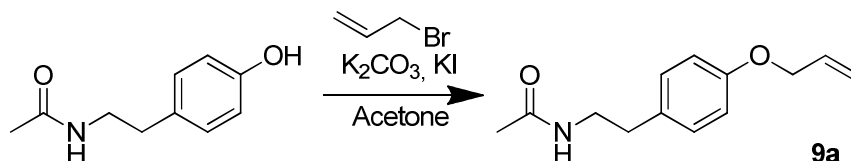
Procedure for the synthesis of phenyl 2-(4-(allyloxy)phenyl)acetate (**7c**)



A 100 mL round-bottom flask equipped with a stirring bar was charged with benzyl 2-(4-hydroxyphenyl)acetate⁴ (1.2 g, 5.0 mmol), K_2CO_3 (1.04 g, 7.5 mmol) and KI (15 mg, 0.4 mmol). Substrates were dissolved in acetone (30 mL) at 0 °C. Subsequently, allyl bromide (0.67 mL, 7.5 mmol) was added under argon. The resulting mixture was stirred at reflux for 18 h. It was then filtrated through cotton wool, diluted with AcOEt (90 mL) and washed with brine and H_2O . The organic layer was dried over Na_2SO_4 , filtered through cotton wool and concentrated *in vacuo*. The crude product **7c** was purified by DCVC chromatography¹ (hexane:DCM:AcOEt 2:1:0-0.2) to give pale-yellow oil. Yield = 77%. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C 76.57, H 6.43, found: C 76.54, H 6.65. HRMS ESI calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$

283.1334, found: 283.1325. ^1H NMR (CDCl_3 , 400 MHz): δ 7.41 – 7.26 (m, 5H), 7.22 – 7.15 (m, 2H), 6.92 – 6.80 (m, 2H), 6.05 (ddt, 1H, J = 17.3, 10.5, 5.3 Hz), 5.41 (dq, 1H, J = 17.3, 1.6 Hz), 5.28 (dq, 1H, J = 10.5, 1.4 Hz), 5.13 (s, 2H), 4.53 (dt, 2H, J = 5.3, 1.5 Hz), 3.61 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.7, 157.8, 135.9, 133.3, 130.3, 128.5, 128.2, 128.1, 126.2, 117.6, 114.9, 68.9, 66.5, 40.5.

Procedure for synthesis of *N*-(4-(allyloxy)phenethyl)acetamide (**9a**)



A 50 mL round-bottom flask equipped with a stirring bar was charged with *N*-(4-hydroxyphenethyl)acetamide⁵ (602 mg, 3.4 mmol), K₂CO₃ (463 mg, 3.4 mmol) and KI (11 mg, 0.3 mmol). Substrates were dissolved in acetone (20 mL) at 0 °C. Subsequently, allyl bromide (0.3 mL, 3.4 mmol) was added under argon. The resulting mixture was stirred at reflux for 48 h. It was then filtrated through cotton wool, diluted with AcOEt (60 mL) and washed with brine and H₂O. The organic layer was dried over Na₂SO₄, filtered through cotton wool and concentrated *in vacuo*. The crude product **9a** was purified by DCVC chromatography¹ (DCM:AcOEt 4:1) to give white solid. Yield = 60%. mp 84-85 °C. Anal. calcd for C₁₃H₁₇NO₂: C 71.21, H 7.81, N 6.39, found: C 71.27, H 7.86, N 6.33. HRMS EI calcd for C₁₃H₁₇NO₂Na [M+Na]⁺ 242.1157, found: 242.1151. ^1H NMR (CDCl_3 , 400 MHz): δ 7.13 – 7.05 (m, 2H), 6.90 – 6.83 (m, 2H), 6.05 (ddt, 1H, J = 17.2, 10.6, 5.3 Hz), 5.51 (s, 1H), 5.41 (dq, 1H, J = 17.3, 1.6 Hz), 5.28 (dq, 1H, J = 10.5, 1.4 Hz), 4.52 (dt, 2H, J = 5.3, 1.5 Hz), 3.47 (dd, 2H, J = 12.9, 6.9 Hz), 2.75 (t, 2H, J = 7.0 Hz), 1.93 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.0, 157.3, 133.3, 131.0, 129.6, 117.6, 114.9, 68.9, 40.8, 34.7, 23.3.

4-(Allyloxy)benzaldehyde (**4l**) was purchased from Sigma-Aldrich (544396).

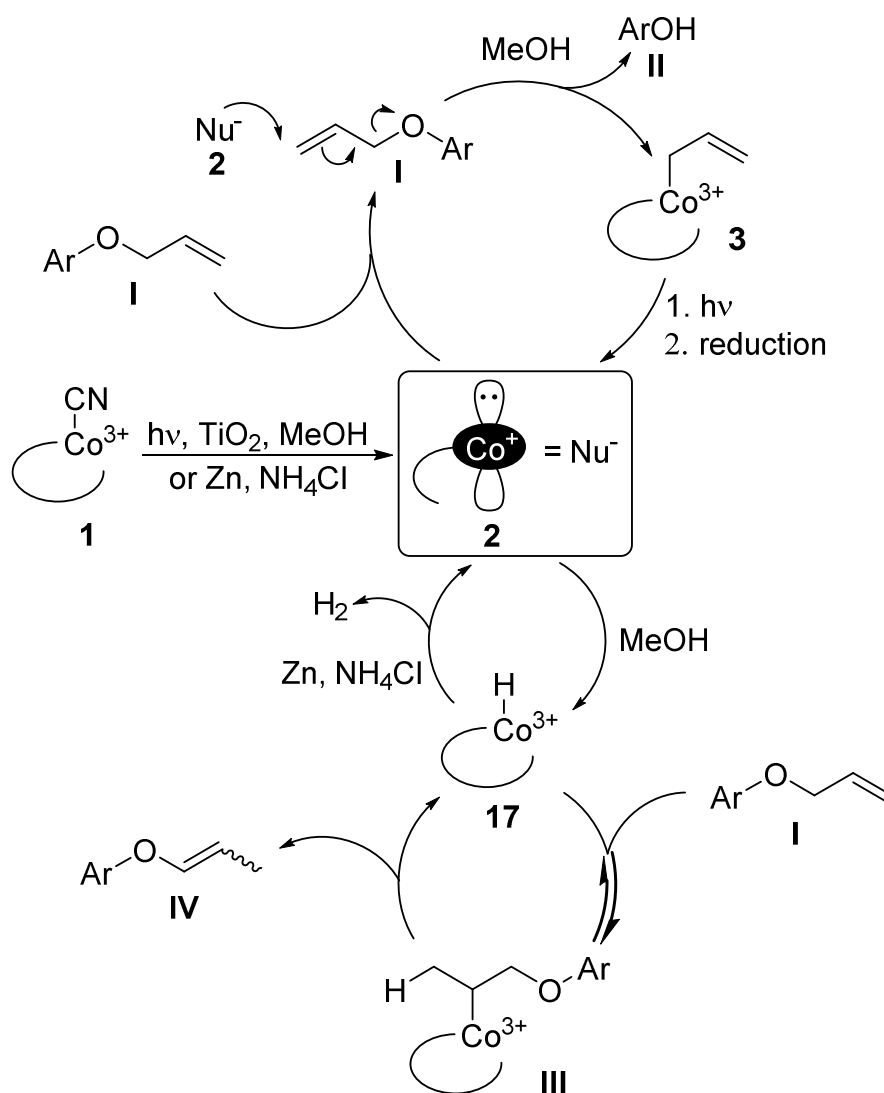
Other (allyloxy)derivatives were synthesized according to the reported procedures:

2-(allyloxy)naphthalene (**4a**),⁶ 1-(allyloxy)naphthalene (**4b**),⁷ allyloxybenzene (**4c**),⁸ 2-(allyloxy)-1,3,5-trimethylbenzene (**4d**),⁹ 1-(allyloxy)-4-(*tert*-butyl)benzene (**4e**),¹⁰ 1-(allyloxy)-3-bromobenzene (**4f**),⁹ 1-(allyloxy)-4-methoxybenzene (**4g**),⁷ 1-(allyloxy)-3-methoxybenzene (**4h**),¹¹ 4-(allyloxy)benzonitrile (**4i**),¹² 3-(allyloxy)benzonitrile (**4j**),¹² 2-(allyloxy)benzonitrile (**4k**),¹³

1-(allyloxy)-4-nitrobenzene (**4m**),¹⁴ methyl 2-(allyloxy)-4-methoxybenzoate (**4n**),¹⁵
4-(allyloxy)-3-methoxybenzaldehyde (**4o**),¹⁶ (3-(allyloxy)propyl)benzene (**4p**),¹⁷
methyl 2-(4-(allyloxy)phenyl)acetate (**7a**),¹⁸ *tert*-butyl 4-(allyloxy)phenethylcarbamate (**9b**),¹⁹
methyl 2-acetamido-3-(4-(allyloxy)phenyl)propanoate (**11a**),²⁰
methyl 3-(4-(allyloxy)phenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (**11b**),²¹
(*E*)-2-(but-2-en-1-yloxy)naphthalene (**13**),²²
2-((2-methylallyl)oxy)naphthalene (**15**),²³

4. Mechanistic considerations

4.1 Proposed mechanism

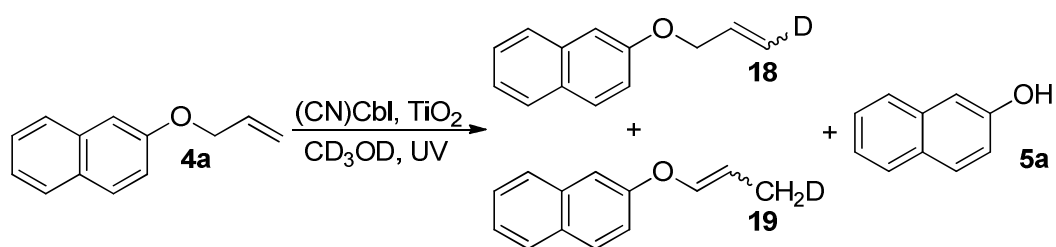


The existence of the cobalt-hydride form of vitamin B_{12} was proposed as early as 1962 by Müller and Müller^{24a} and was further studied by Smith,^{24b} Dolphin,^{24c} Bernhauer^{24d} and Schrauzer.^{24e} In 1984 Pratt and Chemaly reported a UV-Vis spectra of hydridocobalamin in solution, which they described as an unstable, yellow complex.^{24f} Other Co(III)-H species have been generally accepted as a key intermediate e.g. in the cobalt-catalyzed evolution of hydrogen.^{25,26} On the contrary, Peters and Norton postulated that the reactive hydrogen atom may be attached to the ligand not the cobalt ion.^{27a,27b}

While the debate concerned mainly cobaloxime as the most commonly used cobalt complex, vitamin B_{12} arouses far less controversies. Recently Hisaeda and Shimakoshi

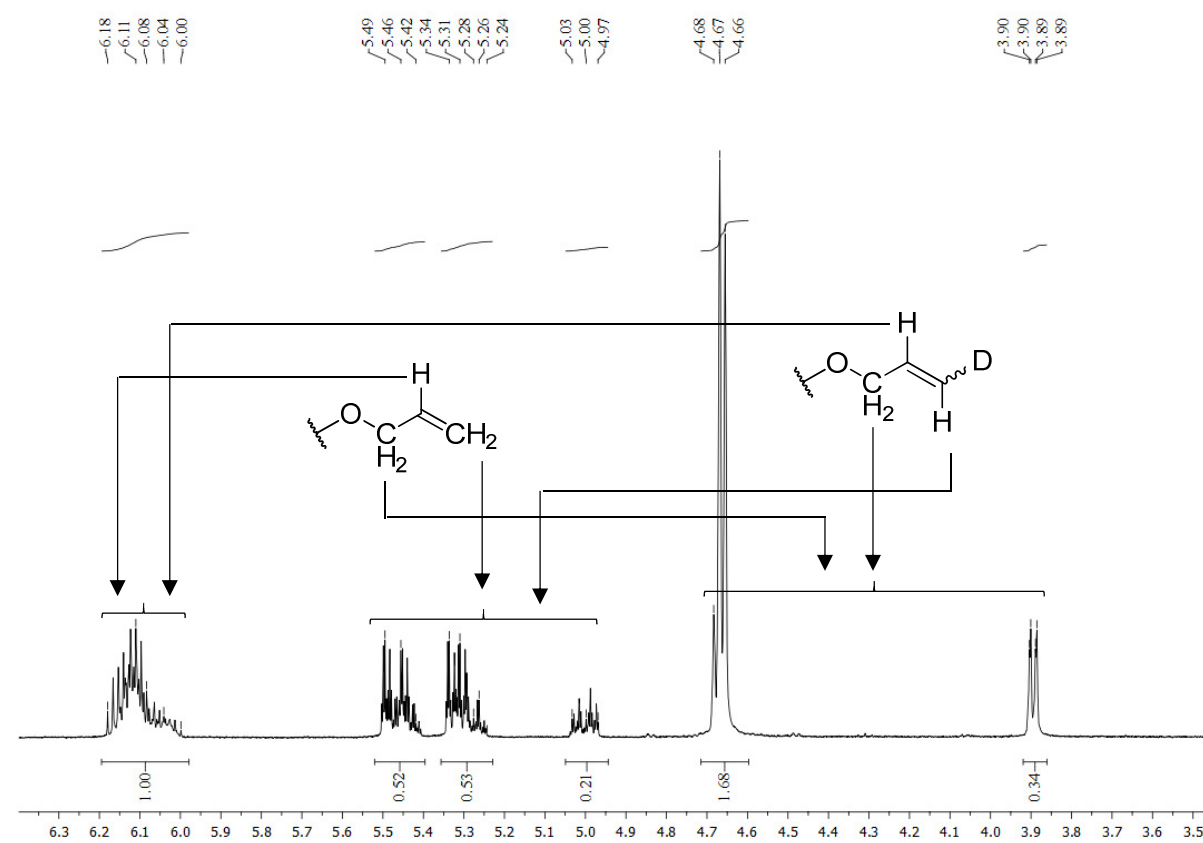
proposed a mechanism of hydrogen evolution in which vitamin B₁₂-derived cobyrinic acid hydride is involved in either bimetallic or monometallic mode.²⁸

4.2 Experiments in CD₃OD



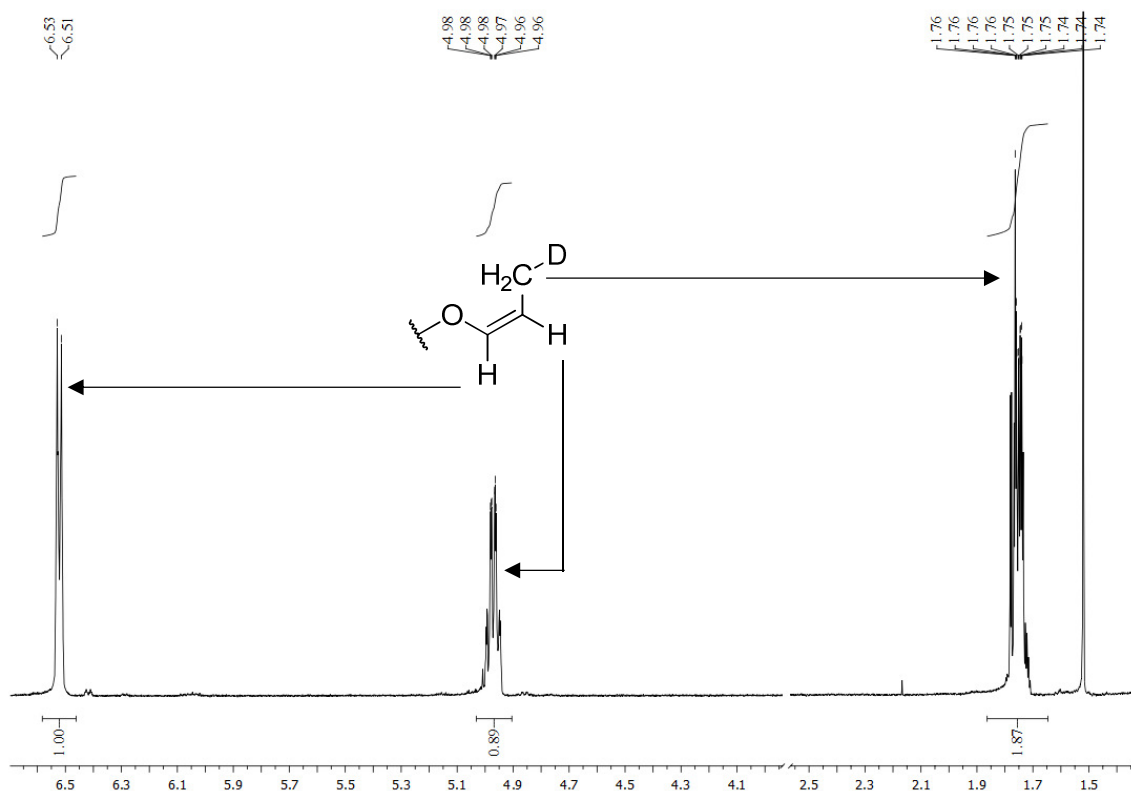
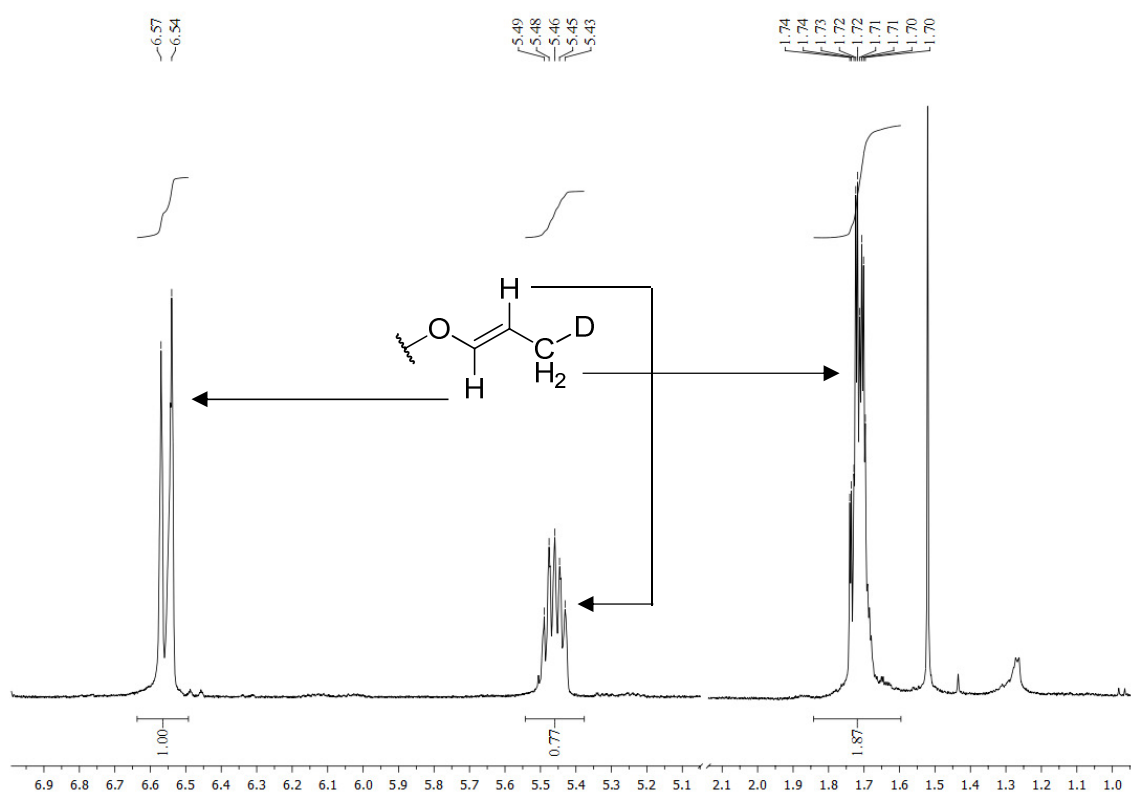
Conditions: 2-(allyloxy)naphthalene (**4a**, 0.5 mmol), TiO₂ (20 mg, 0.5 equiv), (CN)Cbl (42 mg, 6 mol %), CD₃OD (2 mL), 20 h, UV light (254 nm).

¹H NMR of **18**



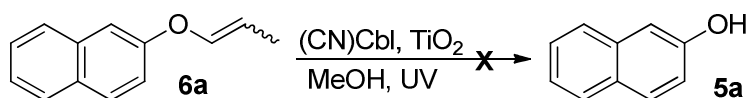
To prove the hypothesis of the external hydrocobaltation of the double bond, the experiment in CD₃OD was performed. The overall integration 1.26 for the signals at 5-5.5 ppm demonstrates that the deuterated substrate is present in the mixture in a 3:1 ratio to the original, protonated substrate.

^1H NMR of **19** – (*E*)- and (*Z*)- isomers



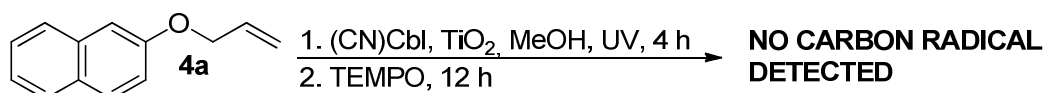
These results support the proposed mechanism, in which hydrocobaltation-dehydrocobaltation occurs leading either to starting material **I** or isomerized ether **IV**.

4.3 Verification of (vinyloxy)arene-intermediate mechanism



2-(Vinyloxy)naphthalene **6a** was isolated and subsequently subjected to our model, vitamin B₁₂-catalysed reaction conditions. No conversion was observed (compound **6a** was recovered), thus excluding the vinyloxy-intermediate pathway from the considered reaction mechanism.

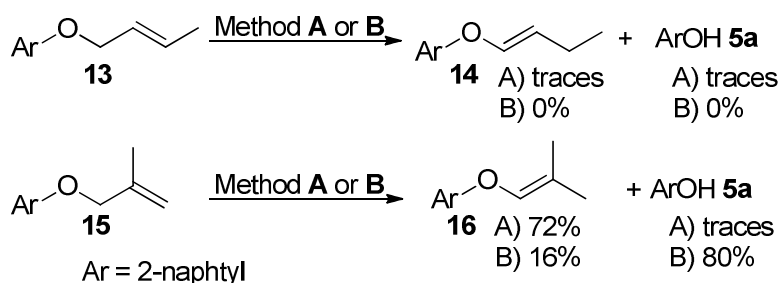
5d. Radical trapping



Conditions: 1. 2-(allyloxy)naphthalene (**4a**, 0.5 mmol), TiO₂ (20 mg, 0.5 equiv), (CN)Cbl (42 mg, 6 mol %), MeOH (2 mL), 4 h, UV light (254 nm); 2. TEMPO (0.5 mmol), 12 h, UV light (254 nm).

The reaction was set-up in standard method A conditions for 4 h. Then TEMPO was added under argon and the mixture was stirred for additional 12 h. The mixture was analyzed using TLC, GC MS and LR MS, but no carbon radical trapping was observed. This result suggests a non-radical pathway and supports the proposed mechanism.

5e. Experiments with substituted allyloxy- derivatives **13** and **15**



Conditions: method A: (allyloxy)arene (0.5 mmol), TiO₂ (20 mg, 0.5 equiv), (CN)Cbl (**1a**, 42 mg, 6 mol %), MeOH (2 mL), 20 h, UV light (254 nm); method B: (allyloxy)arene (0.5 mmol), Zn (6 equiv), NH₄Cl (3.4 equiv), (CN)Cbl (**1a**, 6 mol %), MeOH, 20 h, 60 °C.

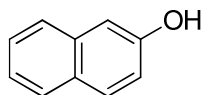
Reactions with substituted (allyloxy)derivatives **13** and **15** were performed. Substitution at position 3 (compound **13**) decreased the reactivity of the group in both methods **A** and **B**. It suggests that the steric hindrance around of the terminal C=C atom is critical for any reaction to occur. In the case of compound **15** possessing the methyl substituent at position 2, rapid isomerization to trisubstituted olefin **16** was observed under photochemical conditions (method A). As soon as a stronger reducing system (method B) was used, deprotection yielding naphthol **5a** predominated. Such conditions should reduce the stability of Co-H intermediate **17**, which led us to the conclusion that it is compound **17** that is responsible for the isomerization reaction, while the attack of supernucleophilic species **2** catalyzes desired deprotection.

5. Scope and the analytical data

References to known compounds are given for comparison.

Naphthalen-2-ol (5a)²⁹

The title product was obtained as a white solid (**method A**: 58 mg, 81%; **method B**: 63 mg; 87%). For the reaction conducted on a scale 0.5 mg the following results were obtained: **method A**: 286 mg, 73%; **method B**: 329 mg, 84%.

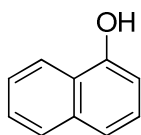


¹H NMR (CDCl₃, 400 MHz): δ 7.75 (t, 2H, *J* = 7.6 Hz), 7.67 (d, 1H, *J* = 8.8 Hz), 7.42 (t, 1H, *J* = 6.9 Hz), 7.32 (t, 1H, *J* = 6.9 Hz), 7.16 – 7.05 (m, 2H), 4.92 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 153.3, 134.6, 129.9, 129.0, 127.8, 126.6, 126.4, 123.7, 117.7, 109.5.

Naphthalen-1-ol (5b)²⁹

The title product was obtained as a white solid (**method A**: 63 mg, 88%).

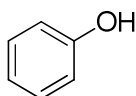


¹H NMR (CDCl₃, 400 MHz): δ 8.17 (d, 1H, *J* = 9.7 Hz), 7.85 – 7.77 (m, 1H), 7.52 – 7.46 (m, 2H), 7.44 (d, 1H, *J* = 8.3 Hz), 7.33 – 7.27 (m, 1H), 6.81 (dd, 1H, *J* = 7.4, 0.9 Hz), 5.18 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 151.3, 134.8, 127.7, 126.4, 125.8, 125.3, 124.3, 121.5, 120.7, 108.6.

Phenol (5c)²⁹

The title product was obtained as a white solid (**method A**: 35 mg, 75%).

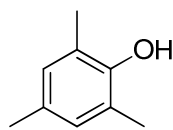


¹H NMR (CDCl₃, 400 MHz): δ 7.31 – 7.19 (m, 2H), 6.93 (t, 1H, *J* = 7.4 Hz), 6.83 (dd, 2H, *J* = 8.6, 1.0 Hz), 4.87 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 155.4, 129.7, 120.8, 115.3.

2,4,6-Trimethylphenol (**5d**)³⁰

The title product was obtained as a pale-yellow solid (**method A**: 58 mg, 85%).

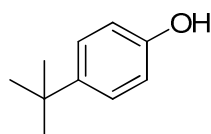


¹H NMR (CDCl₃, 400 MHz): δ 6.78 (d, 2H, J = 0.4 Hz), 4.43 (s, 1H), 2.21 (s, 3H), 2.20 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 149.9, 129.3, 129.1, 122.8, 20.4, 15.8.

4-(*tert*-Butyl)phenol (**5e**)²⁹

The title product was obtained as a white solid (**method A**: 62 mg, 82%).

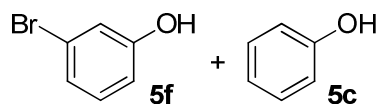


¹H NMR (CDCl₃, 400 MHz): δ 7.29 – 7.21 (m, 2H), 6.80 – 6.70 (m, 2H), 4.89 (s, 1H), 1.29 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 153.1, 143.6, 126.5, 34.1, 31.5.

A crude mixture of 3-bromophenol (**5f**) and phenol (**5c**)²⁹

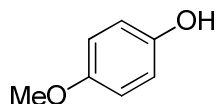
Method B: A yield of 3-bromophenol was calculated based on the ¹H NMR spectrum of the mixture. Combined yield of the mixture of product **5f** and debrominated phenol **5c** was 76% (57 mg) including 56% (48 mg) of **5f** and 20% (9 mg) of **5c**.



¹H NMR (CDCl₃, 400 MHz): δ 7.27 – 7.21 (m, 2H, **5c**), 7.12 – 7.04 (m, 5.3H, **5f**), 7.01 (dd, 2.7H, **5f**, J = 2.3, 1.7 Hz), 6.93 (tt, 1H, **5c**, J = 7.6, 1.1 Hz), 6.87 – 6.80 (m, 2H, **5c**), 6.76 (ddd, 2.7H, **5f**, J = 7.6, 2.4, 1.6 Hz), 5.28 (s, 3H, **5c** + **5f**).

4-Methoxyphenol (**5g**)²⁹

The title product was obtained as a white solid (**method A**: 51 mg, 83%).

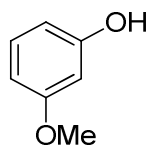


¹H NMR (CDCl₃, 400 MHz): δ 6.85 – 6.70 (m, 4H), 4.75 (s, 1H), 3.76 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 153.8, 149.5, 116.1, 114.9, 55.8.

3-Methoxyphenol (5h)³¹

The title product was obtained as a pale-yellow solid (**method A**: 40 mg, 65%; **method B**: 51 mg; 82%).

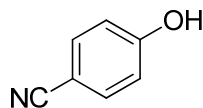


¹H NMR (CDCl₃, 400 MHz): δ 7.16 – 7.08 (m, 1H), 6.52 – 6.47 (m, 1H), 6.45 – 6.39 (m, 2H), 5.47 (s, 1H), 3.77 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 160.9, 156.7, 130.2, 107.8, 106.5, 101.6, 55.3.

4-Hydroxybenzonitrile (5i)²⁹

The title product was obtained as a white solid (**method A**: 21 mg, 36%; **method B**: 52 mg; 87%).

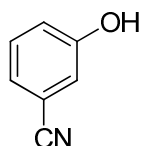


¹H NMR (CDCl₃, 400 MHz): δ 7.55 (d, 2H, *J* = 8.9 Hz), 6.93 (d, 2H, *J* = 8.9 Hz), 6.33 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 160.0, 134.3, 119.2, 116.4, 103.3.

3-Hydroxybenzonitrile (5j)³²

The title product was obtained as a pale-yellow solid (**method A**: 42 mg, 71%; **method B**: 48 mg; 80%).

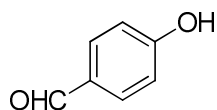


¹H NMR (CDCl₃, 400 MHz): δ 7.33 (t, 1H, *J* = 7.9 Hz), 7.24 – 7.19 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 (ddd, 1H, *J* = 8.2, 2.6, 1.0 Hz), 6.20 (s, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 156.3, 130.6, 124.5, 120.9, 118.8, 118.6, 112.7.

4-Hydroxybenzaldehyde (5k)³³

The title product was obtained as a white solid (**method A**: 45 mg, 73%).

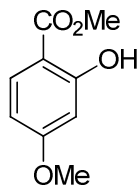


¹H NMR ((CD₃)₂CO, 400 MHz): δ 9.85 (s, 1H), 9.31 (s, 1H), 7.83 – 7.75 (m, 2H), 7.04 – 6.96 (m, 2H).

^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 190.1, 162.9, 131.9, 129.6, 115.8.

Methyl 2-hydroxy-4-methoxybenzoate (**5m**)³⁴

The title product was obtained as a yellow solid (**method B**: 79 mg; 87%).

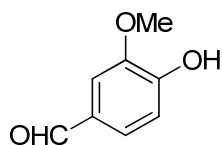


^1H NMR (CDCl_3 , 400 MHz): δ 10.98 (s, 1H), 7.77 – 7.69 (m, 1H), 6.44 (q, 2H, J = 2.1 Hz), 3.91 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 170.4, 165.6, 163.8, 131.2, 107.6, 105.5, 100.7, 55.5, 52.0.

4-Hydroxy-3-methoxybenzaldehyde (**5n**)³⁵

The title product was obtained as a white solid (**method A**: 58 mg, 76%).

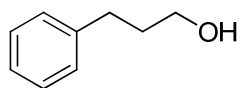


^1H NMR (CDCl_3 , 400 MHz): δ 9.83 (s, 1H), 7.42 (dt, 2H, J = 5.6, 1.8 Hz), 7.08 – 7.01 (m, 1H), 6.24 (s, 1H), 3.97 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 190.8, 151.7, 147.2, 129.9, 127.5, 114.4, 108.8, 56.1.

3-Phenylpropan-1-ol (**5o**)³⁶

The title product was obtained as a colourless oil (**method A**: 52 mg, 76%; **method B**: 50 mg; 74%).

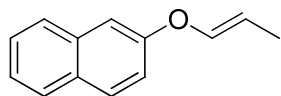


^1H NMR (CDCl_3 , 400 MHz): δ 7.22 (dq, 5H, J = 30.8, 7.9 Hz), 3.64 (dd, 2H, J = 11.4, 6.3 Hz), 2.73 – 2.64 (m, 2H), 1.93 – 1.81 (m, 2H), 1.49 (t, 1H, J = 5.0 Hz).

^{13}C NMR (CDCl_3 , 100 MHz): δ 141.8, 128.42, 128.40, 125.9, 62.3, 34.2, 32.1.

(E)-2-(prop-1-en-1-yloxy)naphthalene (E-6a)³⁷

The title product was obtained as a pale-yellow oil (6 mg, 7%).

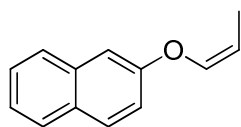


¹H NMR (CDCl₃, 400 MHz): δ 7.82 – 7.71 (m, 3H), 7.45 (ddd, 1H, J = 8.2, 6.9, 1.3 Hz), 7.36 (ddd, 1H, J = 8.1, 6.9, 1.2 Hz), 7.27 (d, 1H, J = 2.4 Hz), 7.20 (dd, 1H, J = 8.9, 2.5 Hz), 6.55 (dd, 1H, J = 12.1, 1.7 Hz), 5.52 – 5.39 (m, 1H), 1.72 (dd, 3H, J = 6.9, 1.7 Hz).

¹³C NMR (CDCl₃, 100 MHz): δ 155.3, 141.8, 134.3, 129.8, 129.6, 127.7, 126.9, 126.5, 124.2, 118.6, 110.3, 108.9, 12.3.

(Z)-2-(prop-1-en-1-yloxy)naphthalene (Z-6a)³⁷

The title product was obtained as a pale-yellow oil (13 mg, 14%).

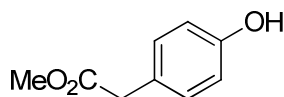


¹H NMR (CDCl₃, 400 MHz): δ 7.74 (dd, 3H, J = 19.4, 8.5 Hz), 7.39 (dt, 2H, J = 15.0, 7.0 Hz), 7.29 – 7.19 (m, 2H), 6.50 (d, 1H, J = 6.0 Hz), 4.96 (m, 1H), 1.76 (d, 3H, J = 6.9 Hz).

¹³C NMR (CDCl₃, 100 MHz): δ 155.4, 140.8, 134.4, 129.8, 129.7, 127.7, 127.0, 126.5, 124.2, 118.6, 110.1, 108.1, 9.5.

Methyl 2-(4-hydroxyphenyl)acetate (8a)³⁸

The title product was obtained as a pale-yellow solid (**method A**: 61 mg, 73%; **method B**: 56 mg; 67%).

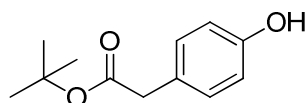


¹H NMR (CDCl₃, 400 MHz): δ 7.16 – 7.03 (m, 2H), 6.79 – 6.67 (m, 2H), 5.88 (s, 1H), 3.70 (s, 3H), 3.55 (s, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ 173.2, 155.0, 130.4, 125.6, 115.6, 52.2, 40.3.

tert-Butyl 2-(4-hydroxyphenyl)acetate (8b)³⁹

The title product was obtained as a white solid (**method B**: 92 mg; 88%).

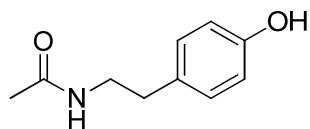


¹H NMR (CDCl₃, 400 MHz): δ 7.07 (d, 2H, J = 8.6 Hz), 6.71 (d, 2H, J = 8.6 Hz), 5.95 (s, 1H), 3.45 (s, 2H), 1.44 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 172.1, 154.9, 130.3, 126.3, 115.5, 81.1, 41.8, 28.0.

***N*-(4-hydroxyphenethyl)acetamide (10a)⁴⁰**

The title product was obtained as a white solid (**method A**: 45 mg, 50%; **method B**: 62 mg; 69%).

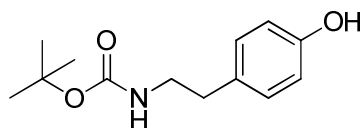


^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ 8.39 (s, 1H), 7.22 (s, 1H), 7.05 – 6.98 (m, 2H), 6.79 – 6.69 (m, 2H), 3.40 – 3.28 (m, 2H), 2.71 – 2.63 (m, 2H), 1.86 (s, 3H).

^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 169.6, 155.9, 130.1, 129.6, 115.2, 41.0, 34.8, 22.0.

***tert*-butyl 4-hydroxyphenethylcarbamate (10b)⁴¹**

The title product was obtained as a white solid (**method A**: 49 mg, 41%; **method B**: 107 mg; 90%).

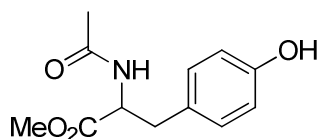


^1H NMR (CDCl_3 , 400 MHz): δ 7.04 (d, 2H, J = 8.4 Hz), 6.83 – 6.72 (m, 2H), 5.15 (s, 1H), 4.54 (s, 1H), 3.33 (d, 2H, J = 6.4 Hz), 2.71 (t, 2H, J = 7.0 Hz), 1.44 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 156.3, 154.8, 130.3, 129.8, 115.5, 79.6, 42.1, 35.3, 28.4.

Methyl 2-acetamido-3-(4-hydroxyphenyl)propanoate (12a)⁴²

The title product was obtained as a white solid (**method A**: 50 mg, 42%; **method B**: 89 mg; 75%).

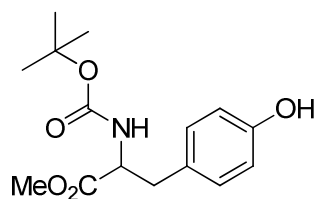


^1H NMR (CDCl_3 , 400 MHz): δ 6.98 – 6.91 (m, 2H), 6.77 – 6.72 (m, 2H), 6.71 (s, 1H), 6.05 (d, 1H, J = 8.0 Hz), 4.87 (dt, 1H, J = 8.1, 5.9 Hz), 3.74 (s, 3H), 3.09 (dd, 1H, J = 14.1, 5.7 Hz), 2.98 (dd, 1H, J = 14.1, 6.2 Hz), 1.99 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 172.3, 170.2, 155.5, 130.3, 127.1, 115.6, 53.3, 52.4, 37.2, 23.0.

Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-hydroxyphenyl)propanoate (12b)⁴³

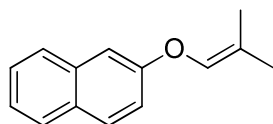
The title product was obtained as a white solid (**method A**: 58 mg, 39%; **method B**: 99 mg; 67%).



¹H NMR (CDCl₃, 400 MHz): δ 6.95 (d, 2H, J = 8.4 Hz), 6.73 (d, 2H, J = 7.9 Hz), 6.24 (s, 1H), 5.04 (d, 1H, J = 7.8 Hz), 4.53 (d, 1H, J = 6.7 Hz), 3.71 (s, 3H), 2.99 (qd, 2H, J = 14.1, 6.1 Hz), 1.42 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.7, 155.4, 155.2, 130.3, 127.4, 115.5, 80.3, 54.7, 52.3, 37.6, 28.3.

2-((2-methylprop-1-en-1-yl)oxy)naphthalene (16) – for mechanistic studies



¹H NMR (CDCl₃, 400 MHz): δ 7.79 – 7.69 (m, 3H), 7.42 (t, 1H, J = 7.5 Hz), 7.33 (t, 1H, J = 7.5 Hz), 7.26 – 7.18 (m, 2H), 6.38 – 6.29 (m, 1H), 1.75 (d, 6H, J = 8.2 Hz).

6. References

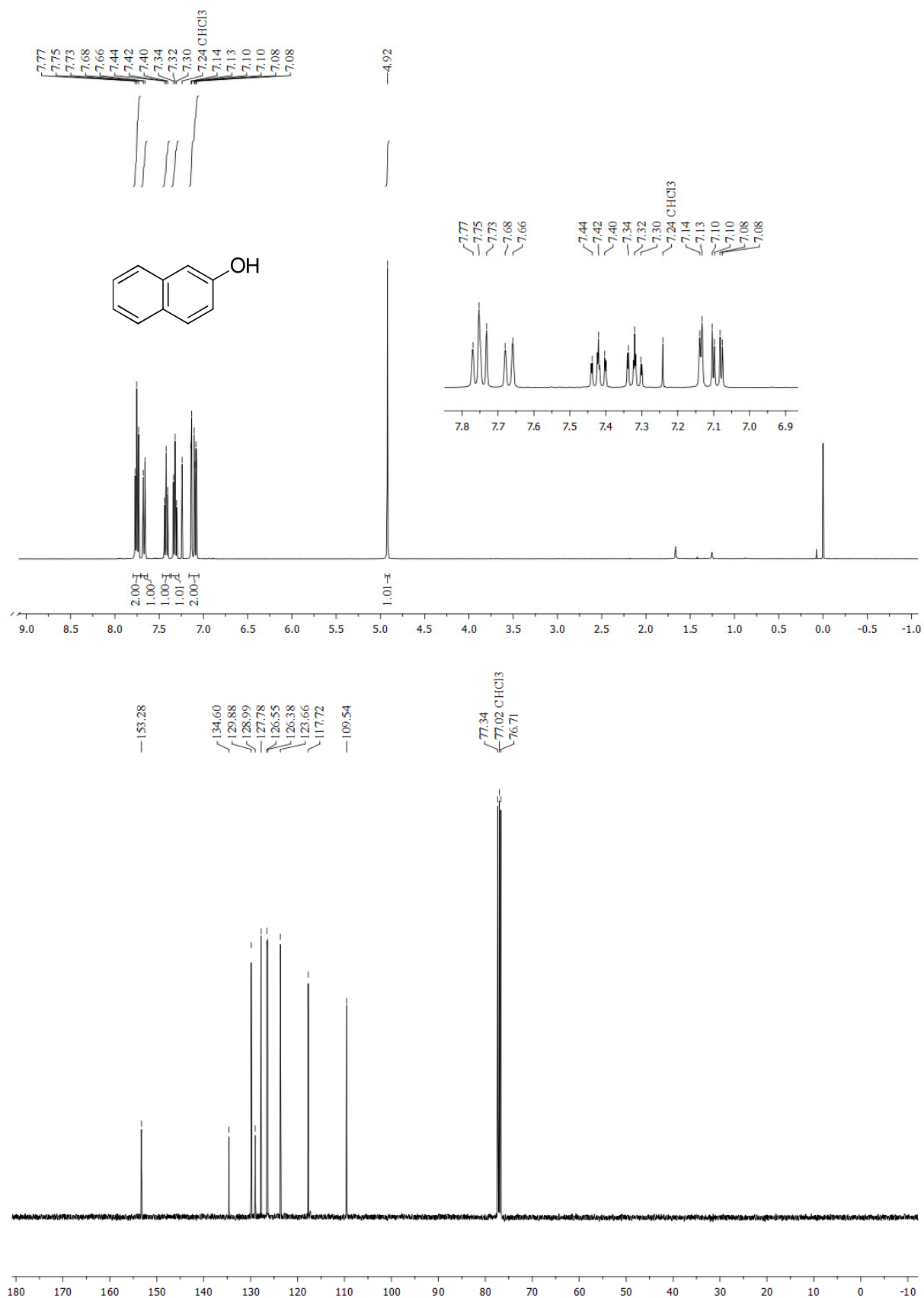
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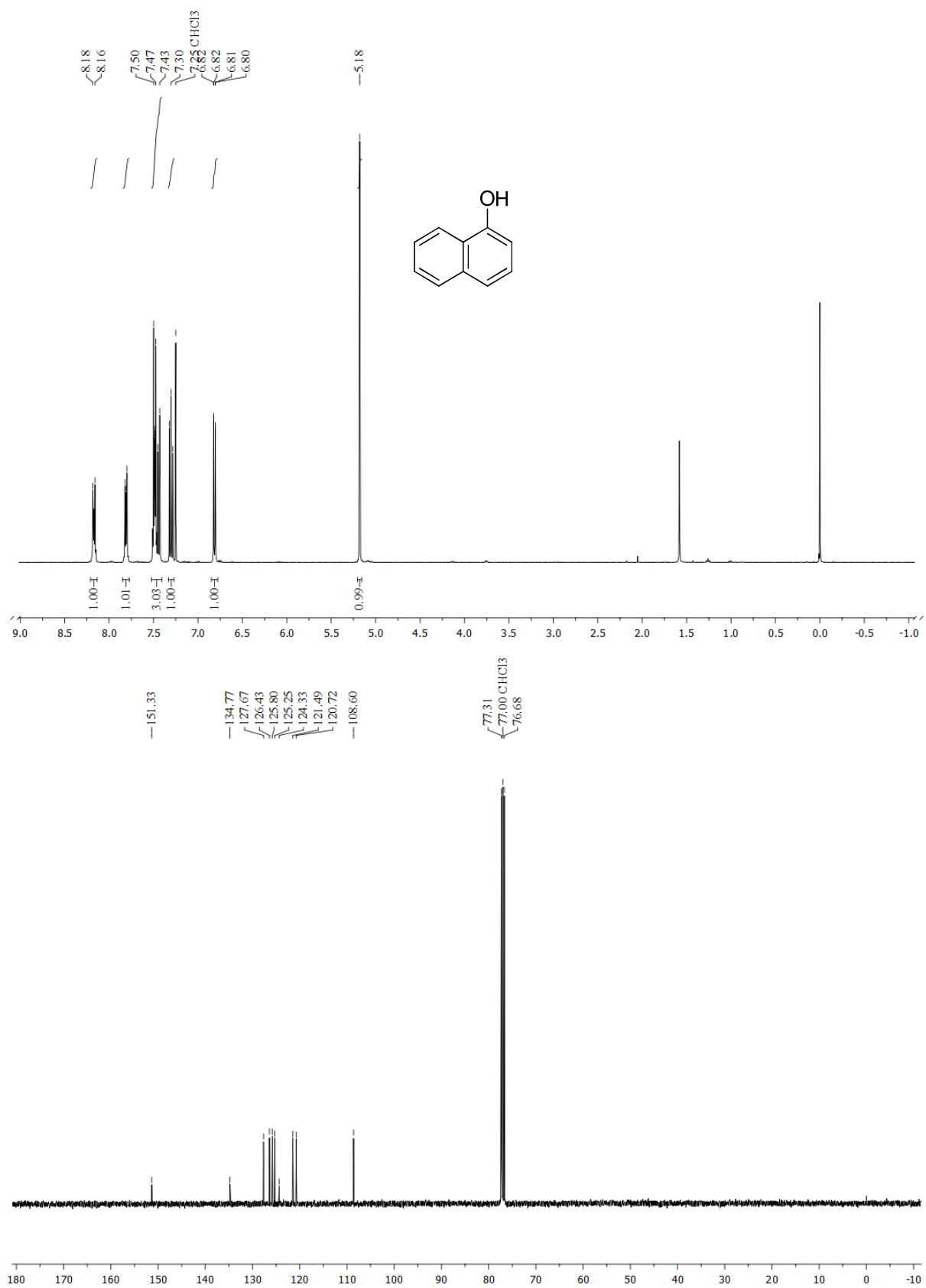
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7. ^1H and ^{13}C NMR spectra

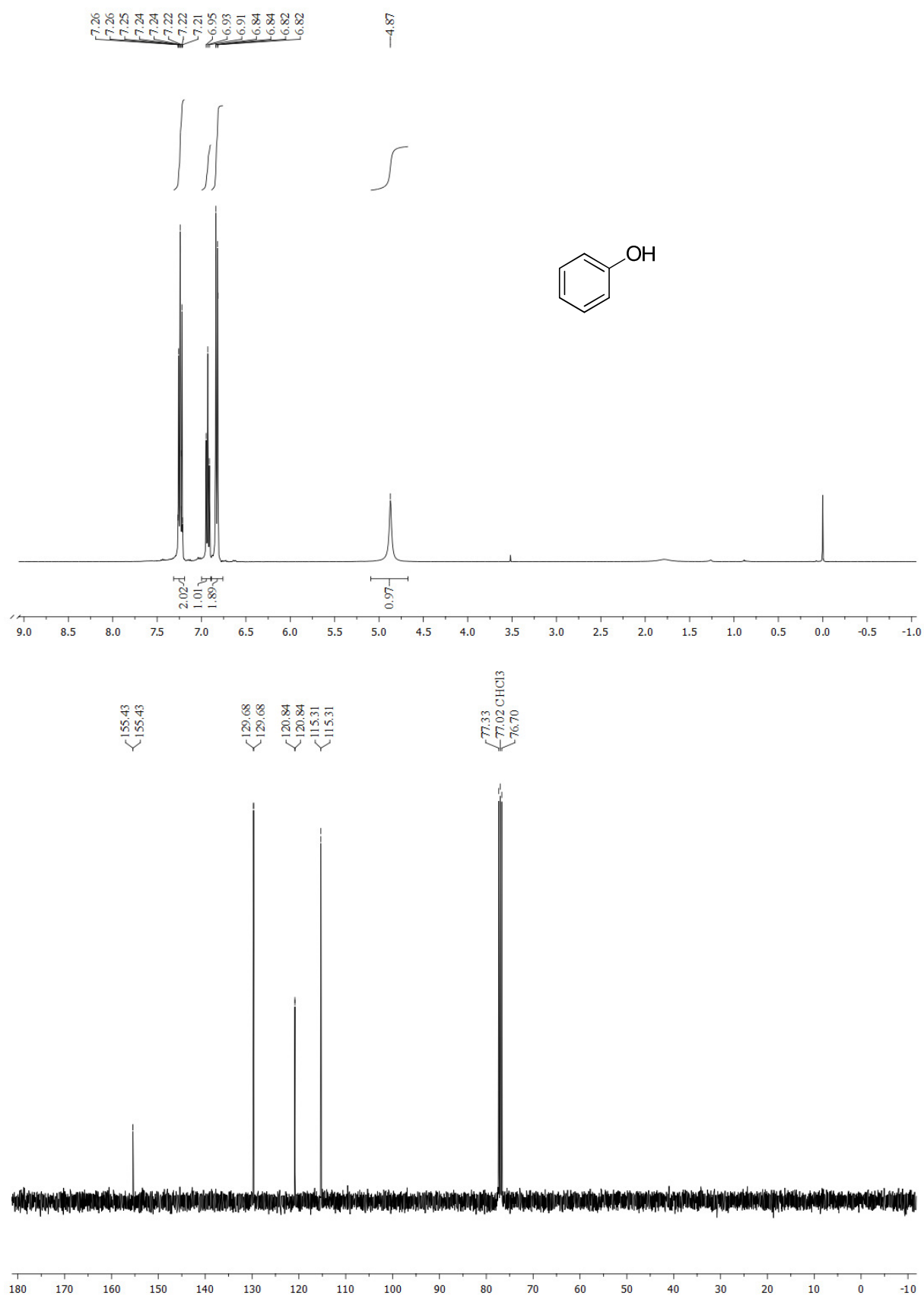
Naphthalen-2-ol (5a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



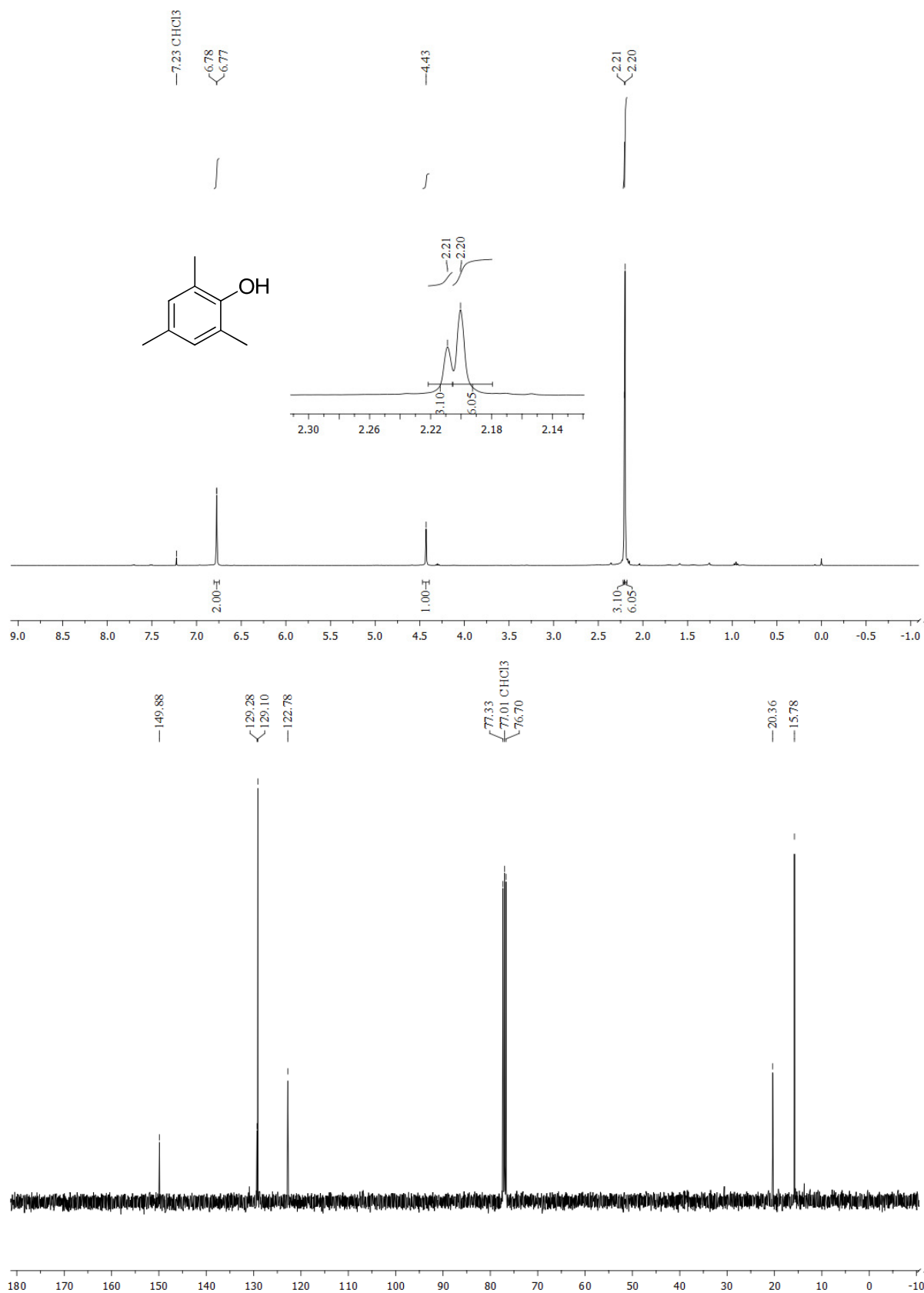
Naphthalen-1-ol (5b) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



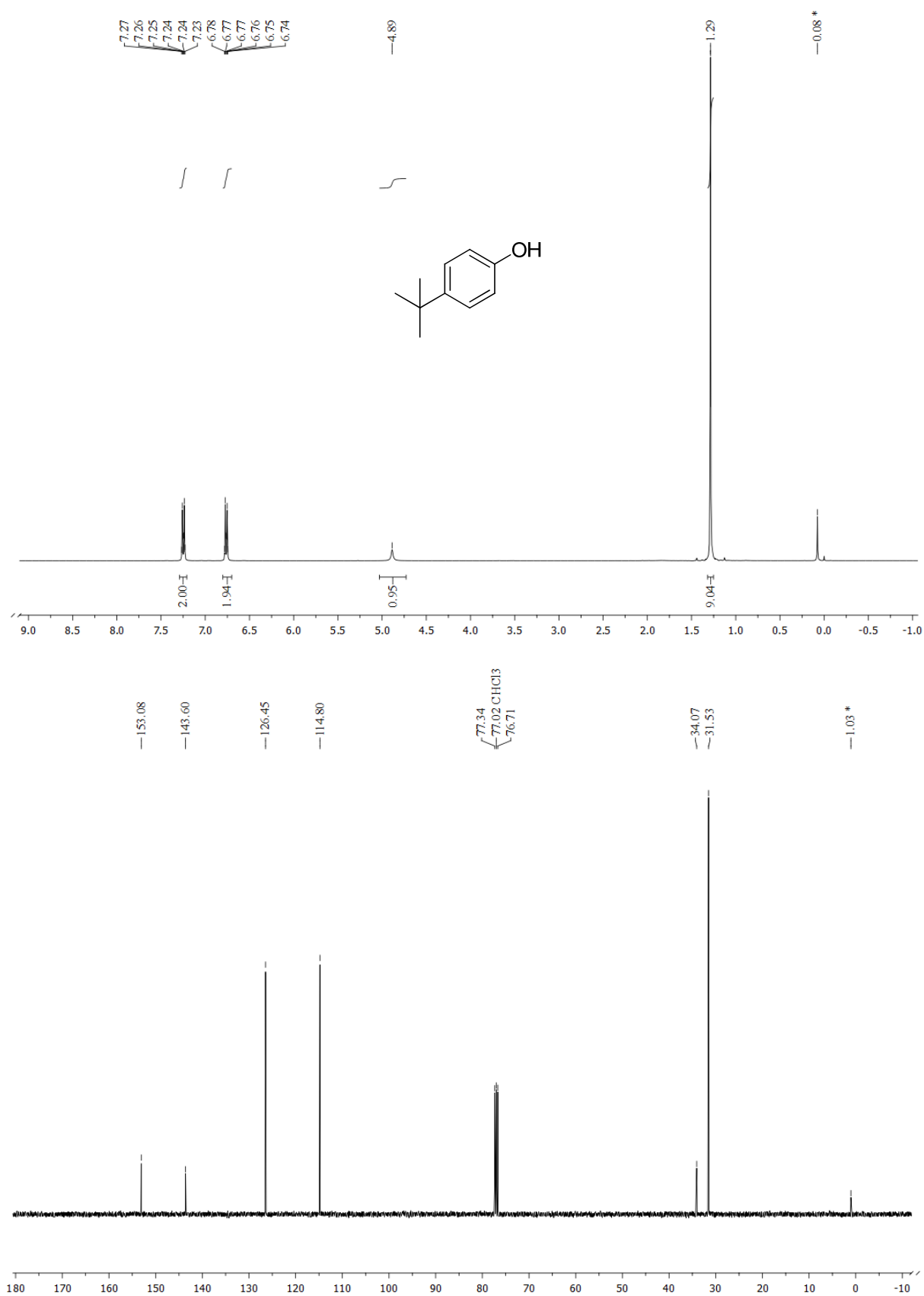
Phenol (5c) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



2,4,6-Trimethylphenol (5d) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)

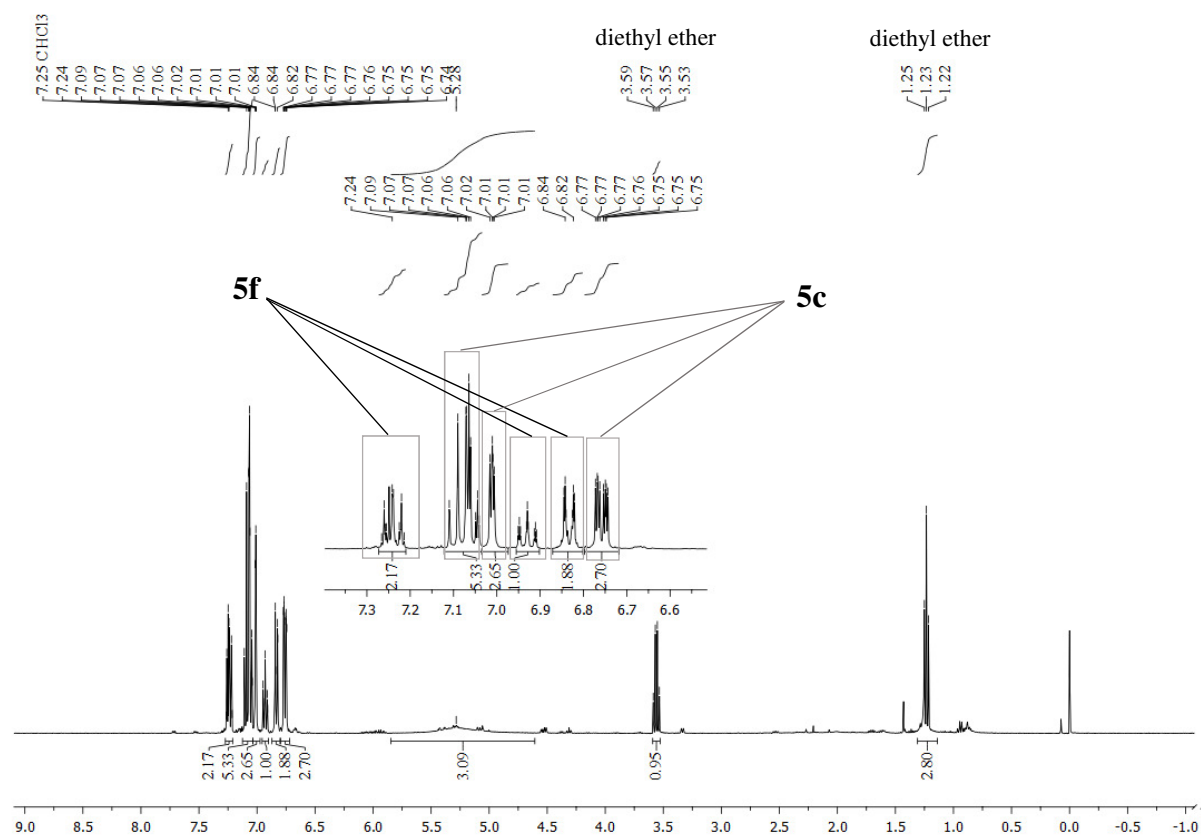


4-(*tert*-Butyl)phenol (5e) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



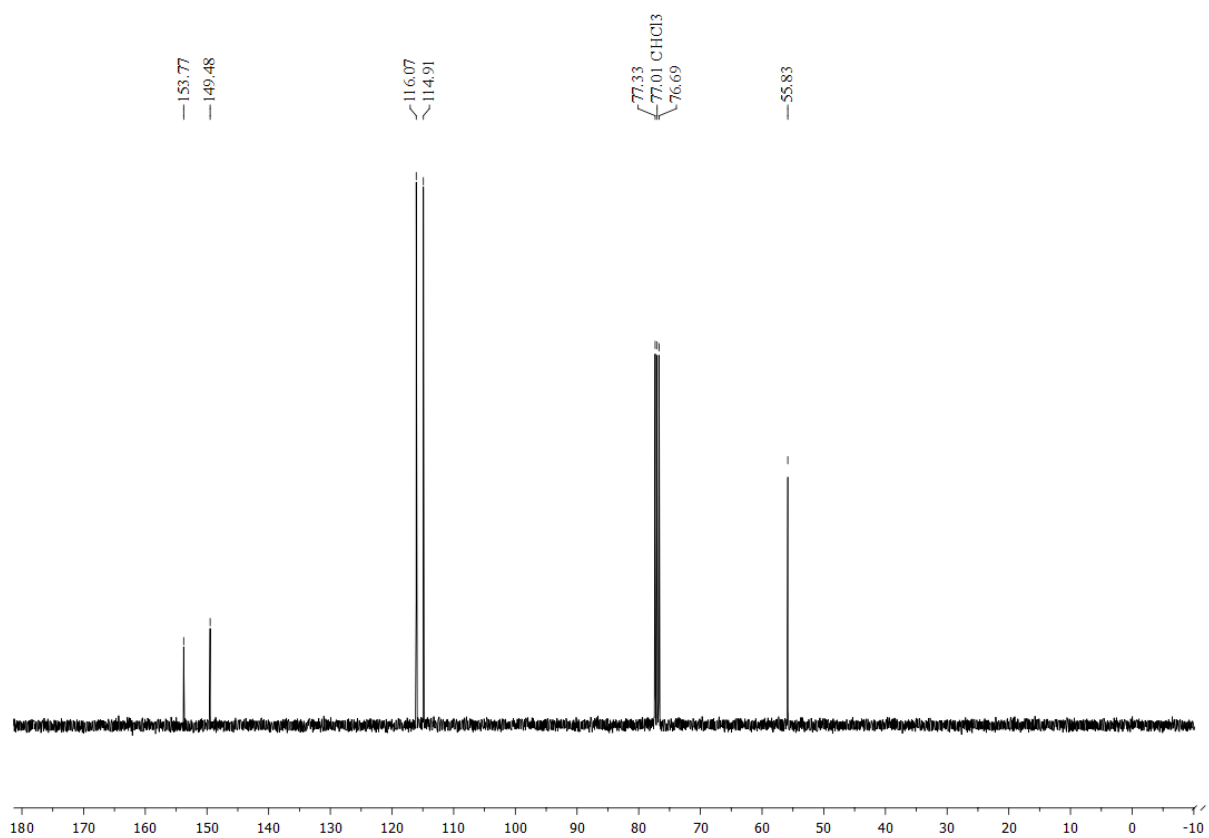
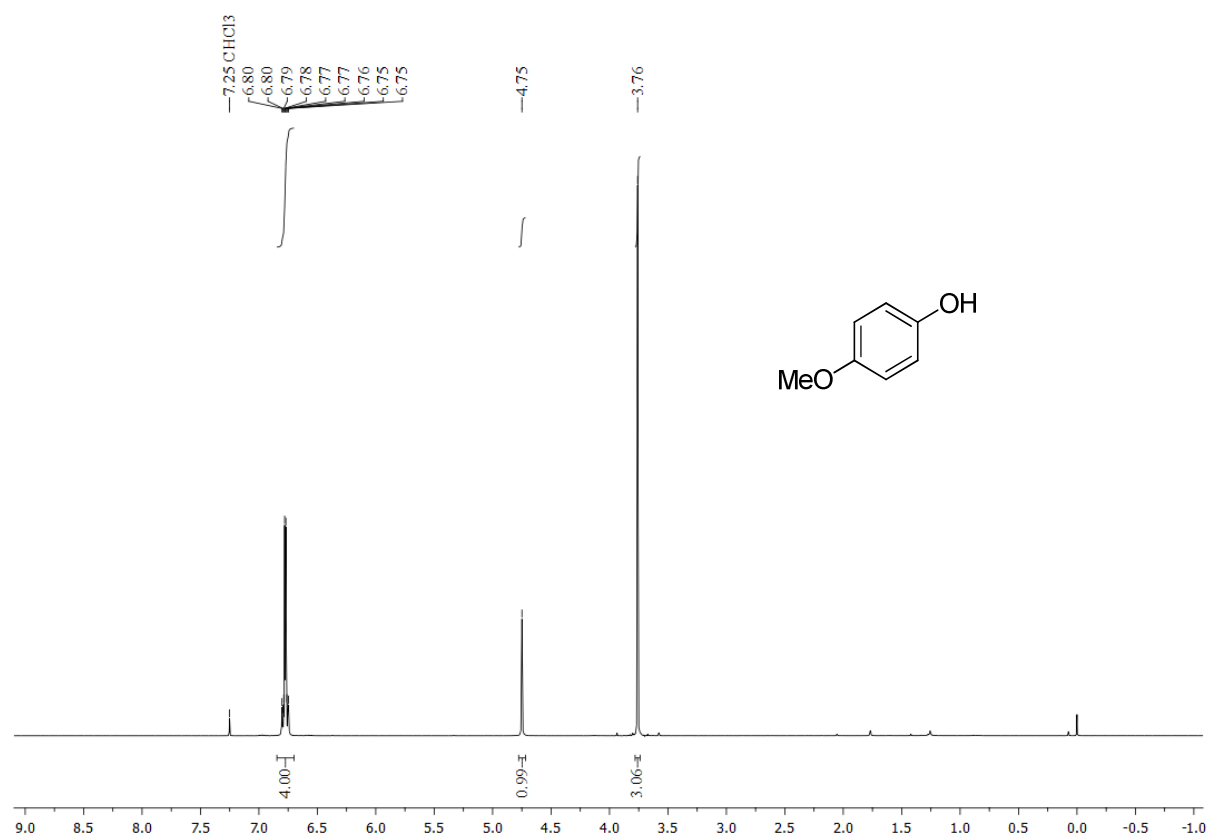
* Silicone grease (poly(dimethylsiloxane))

Crude mixture of 3-bromophenol (5f) and phenol (5c) – ^1H NMR (CDCl_3 , 400 MHz)

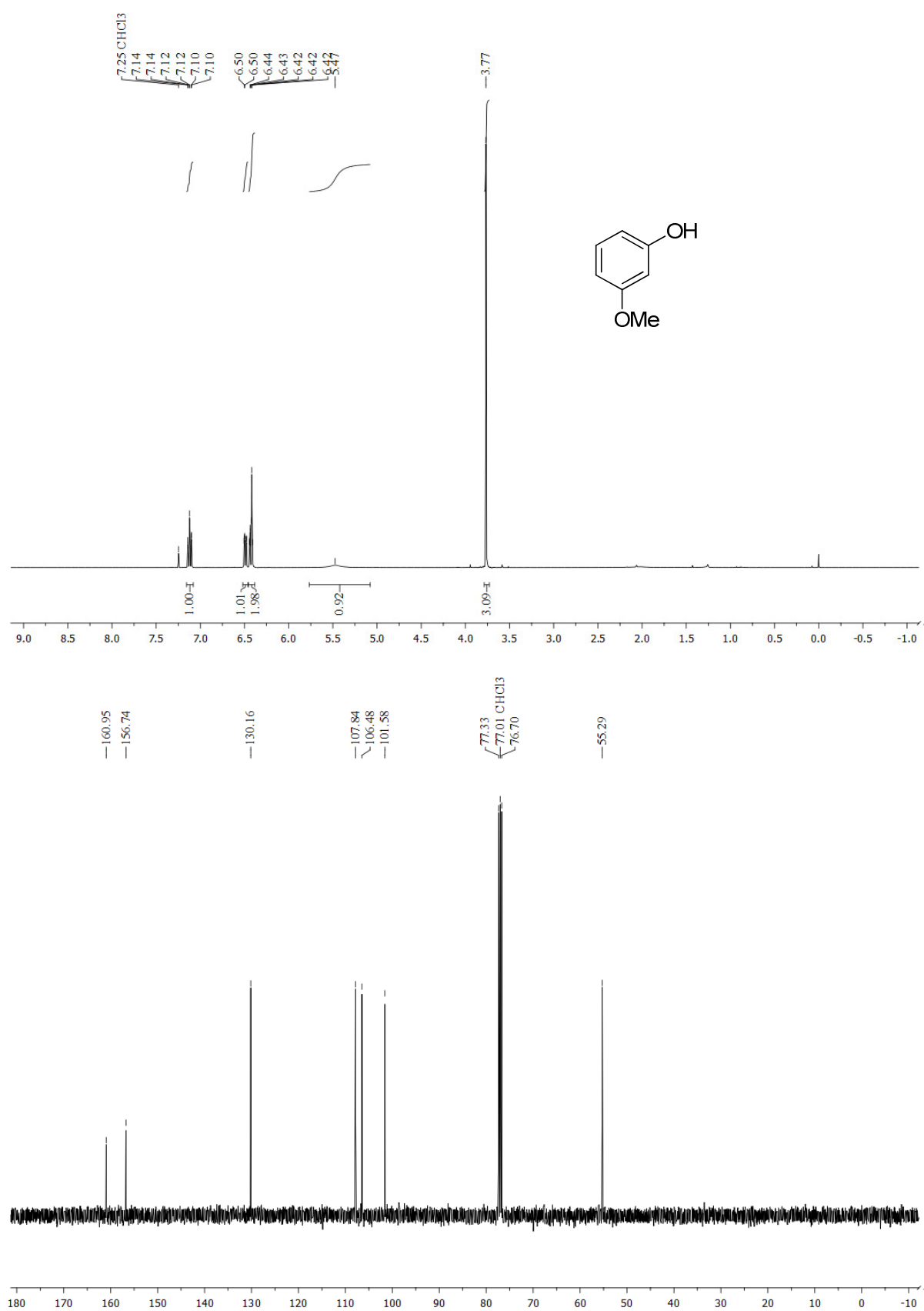


The spectrum was used to calculate the 3-bromophenol to phenol ratio. Et_2O contribution, showed on the spectrum, was eliminated in calculating the reaction yield.

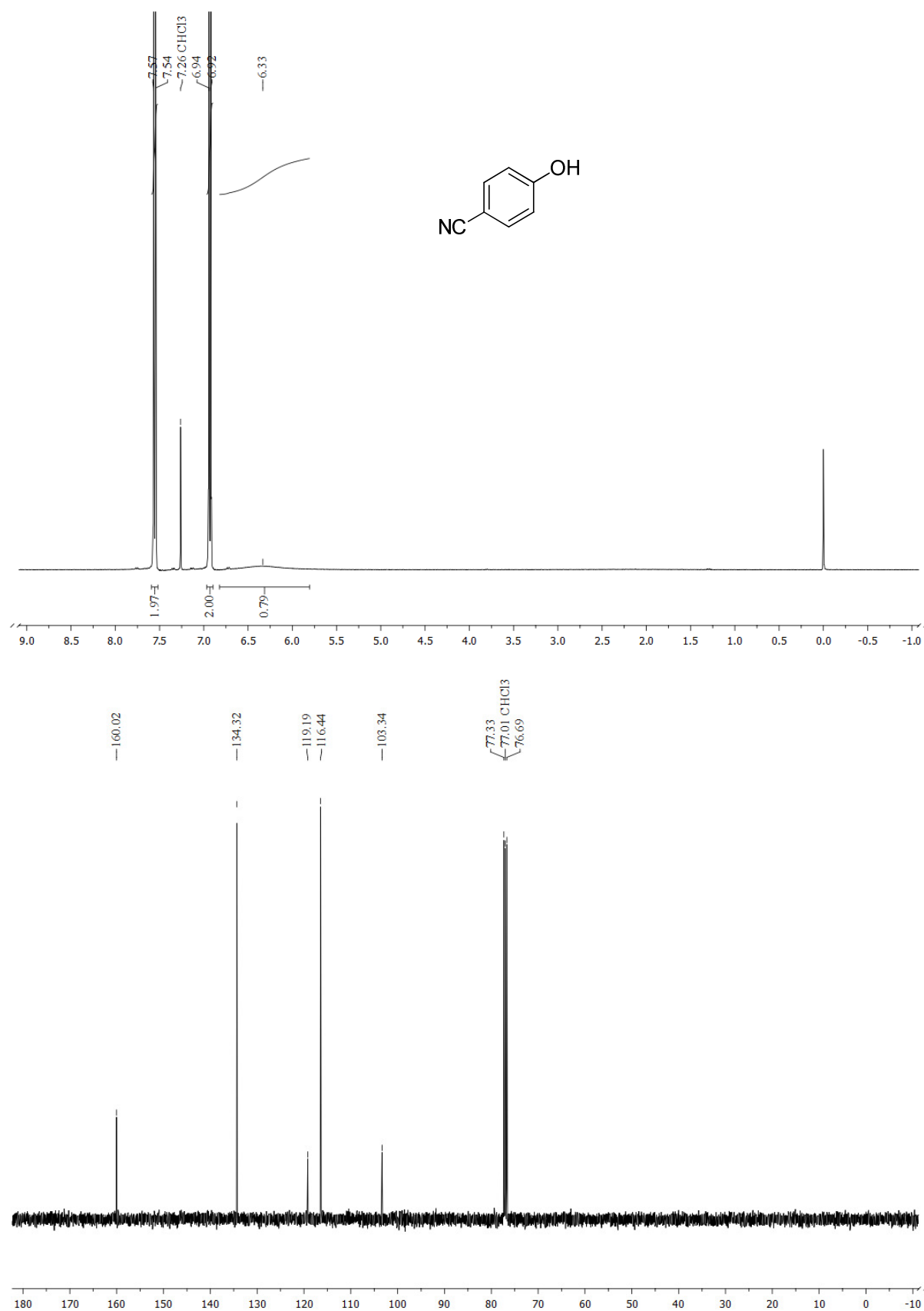
4-Methoxyphenol (5g) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



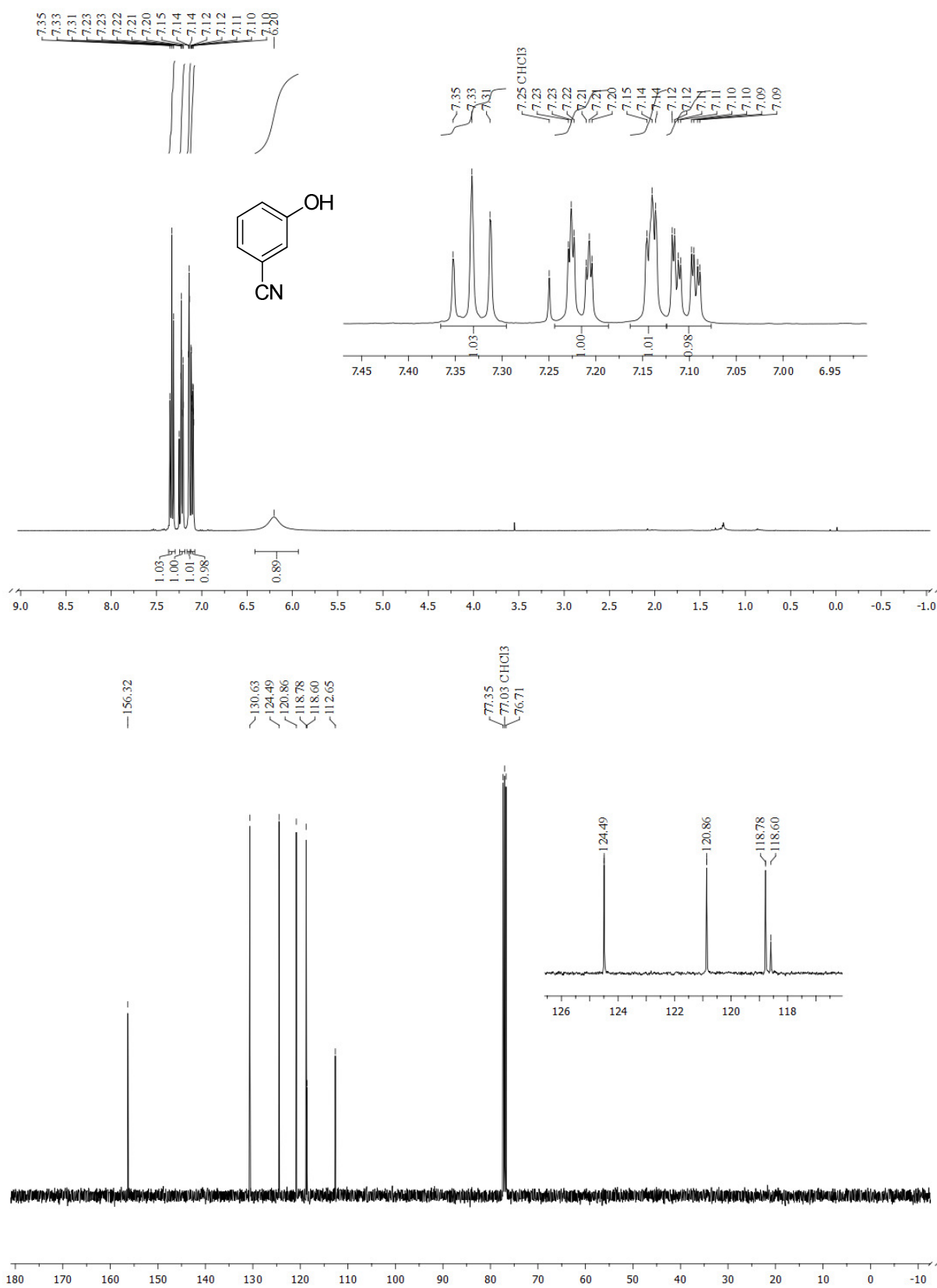
3-Methoxyphenol (5h) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



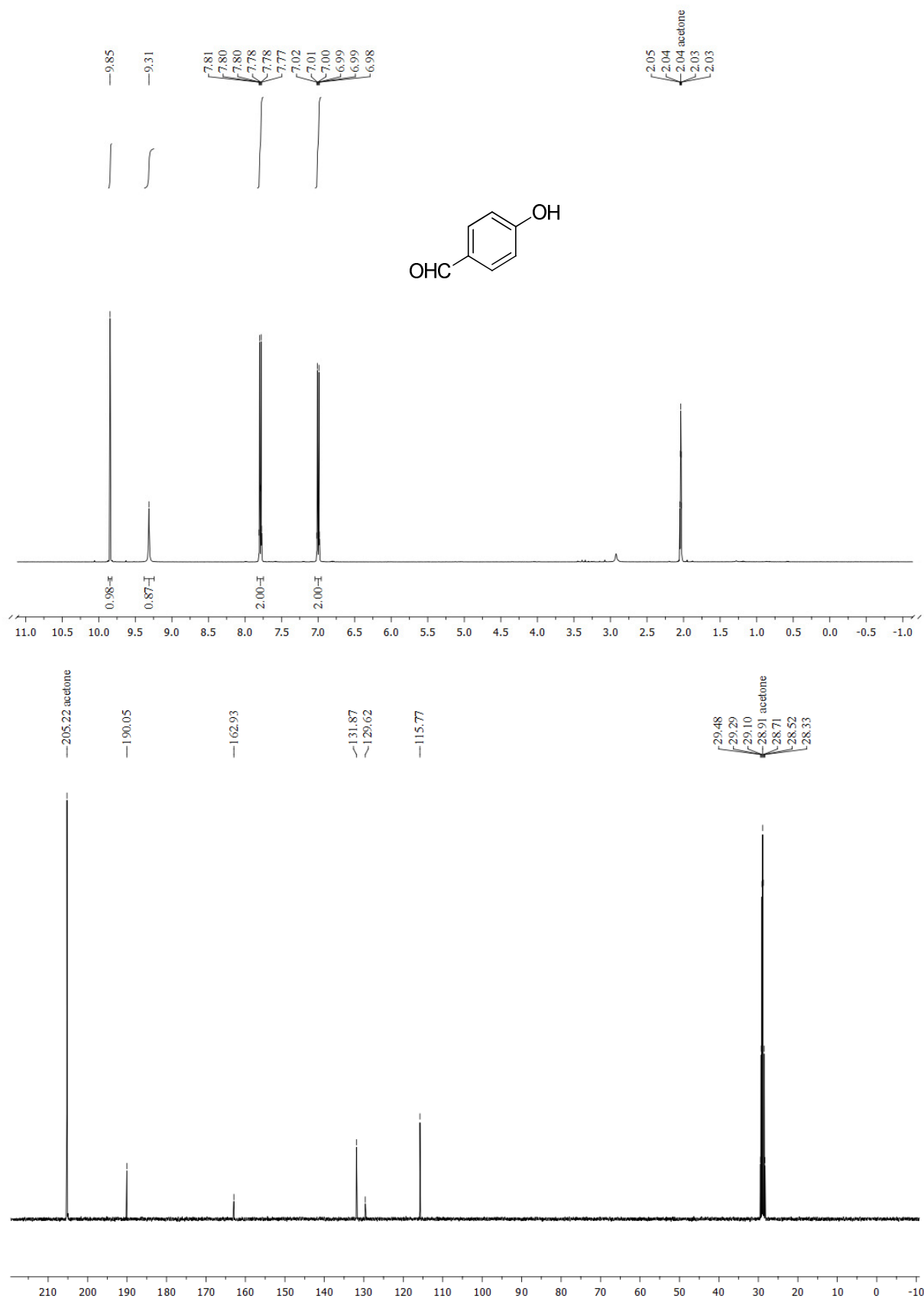
4-Hydroxybenzonitrile (5i) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



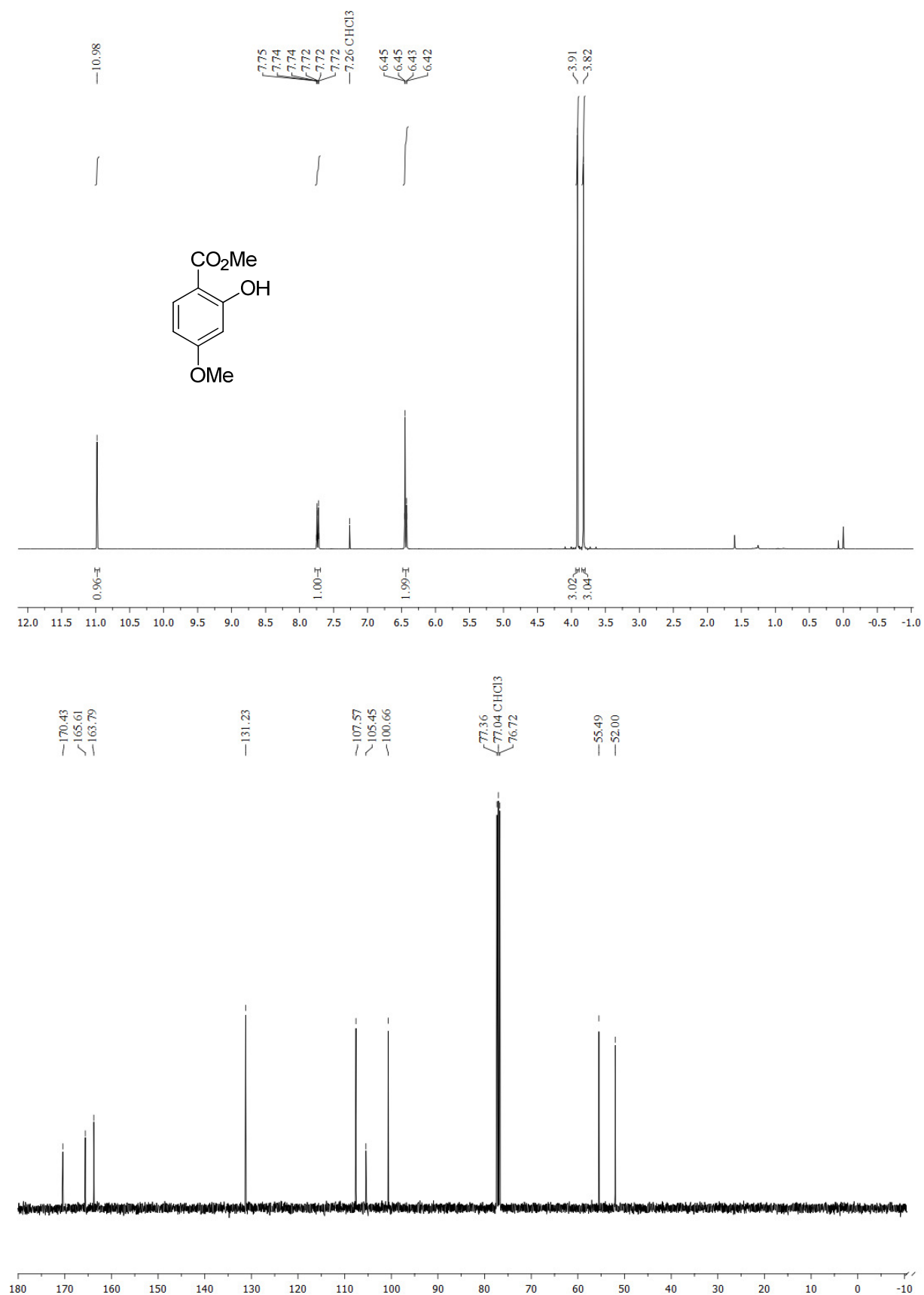
3-Hydroxybenzonitrile (5j) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



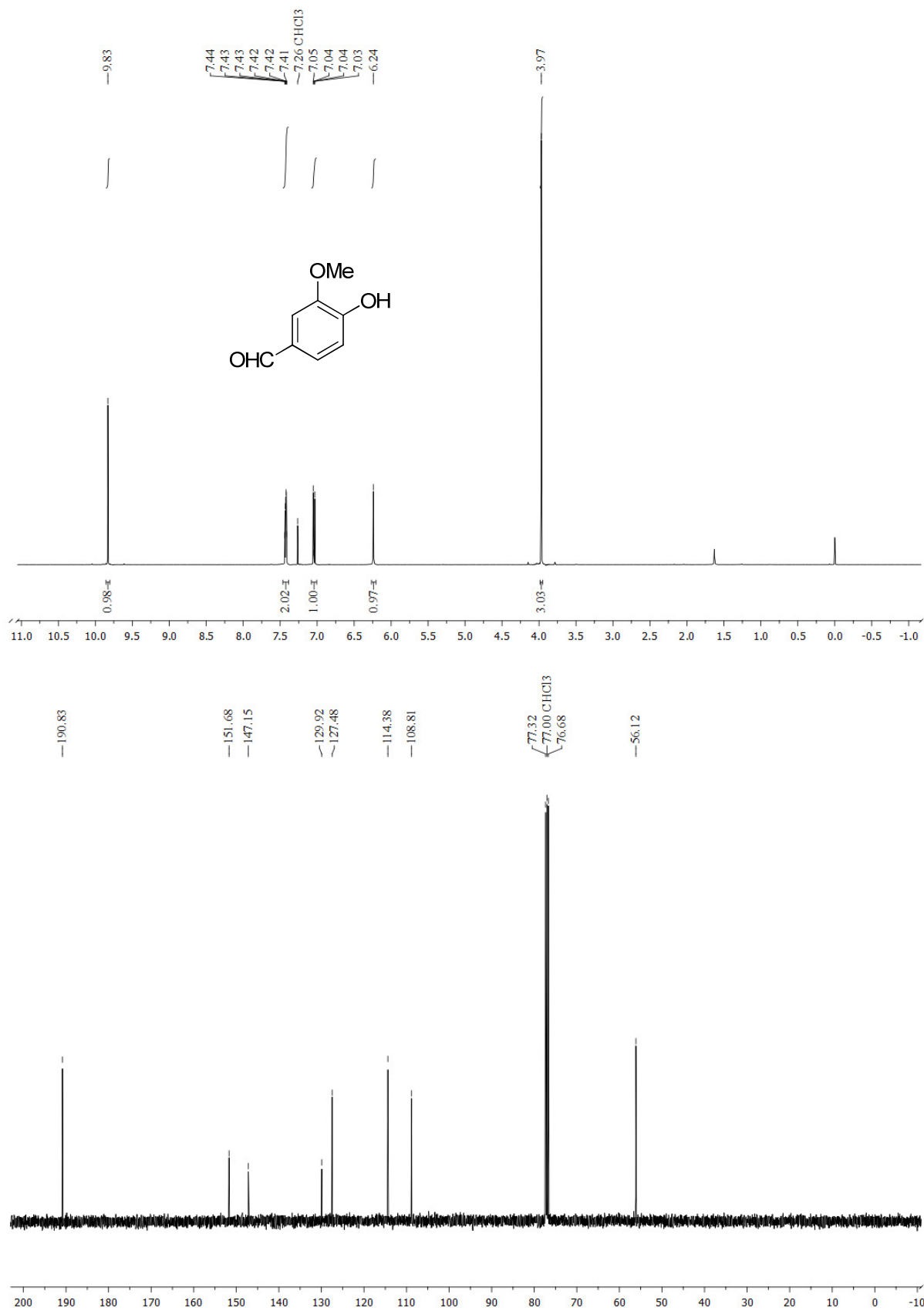
4-Hydroxybenzaldehyde (5k) – ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz) and ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz)



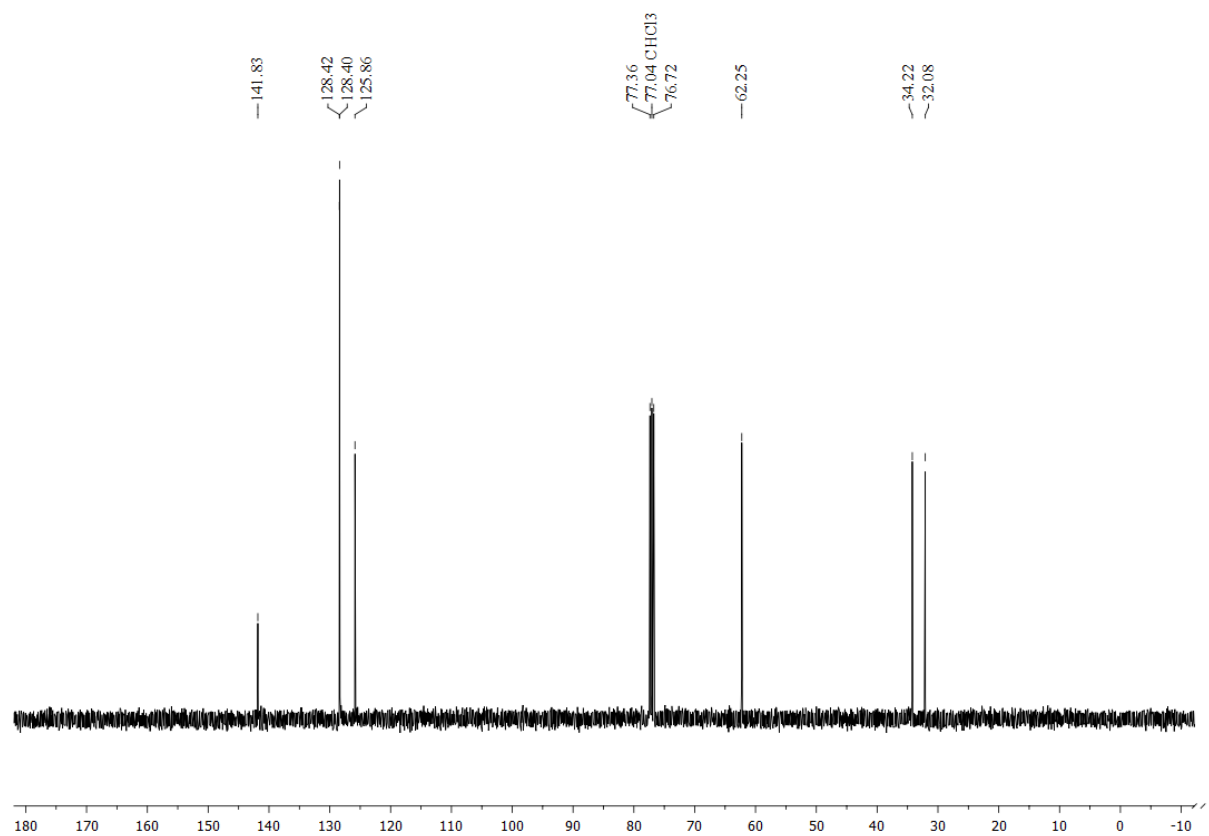
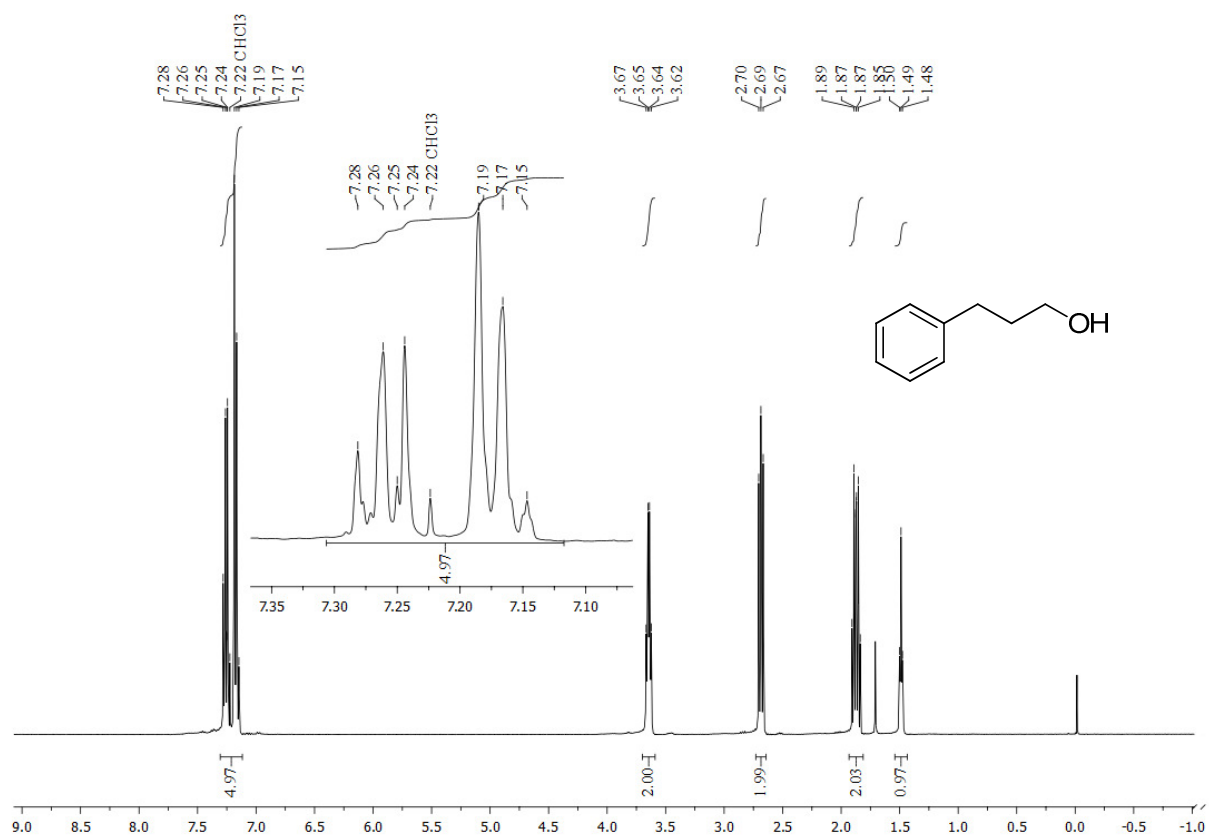
Methyl 2-hydroxy-4-methoxybenzoate (5m) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



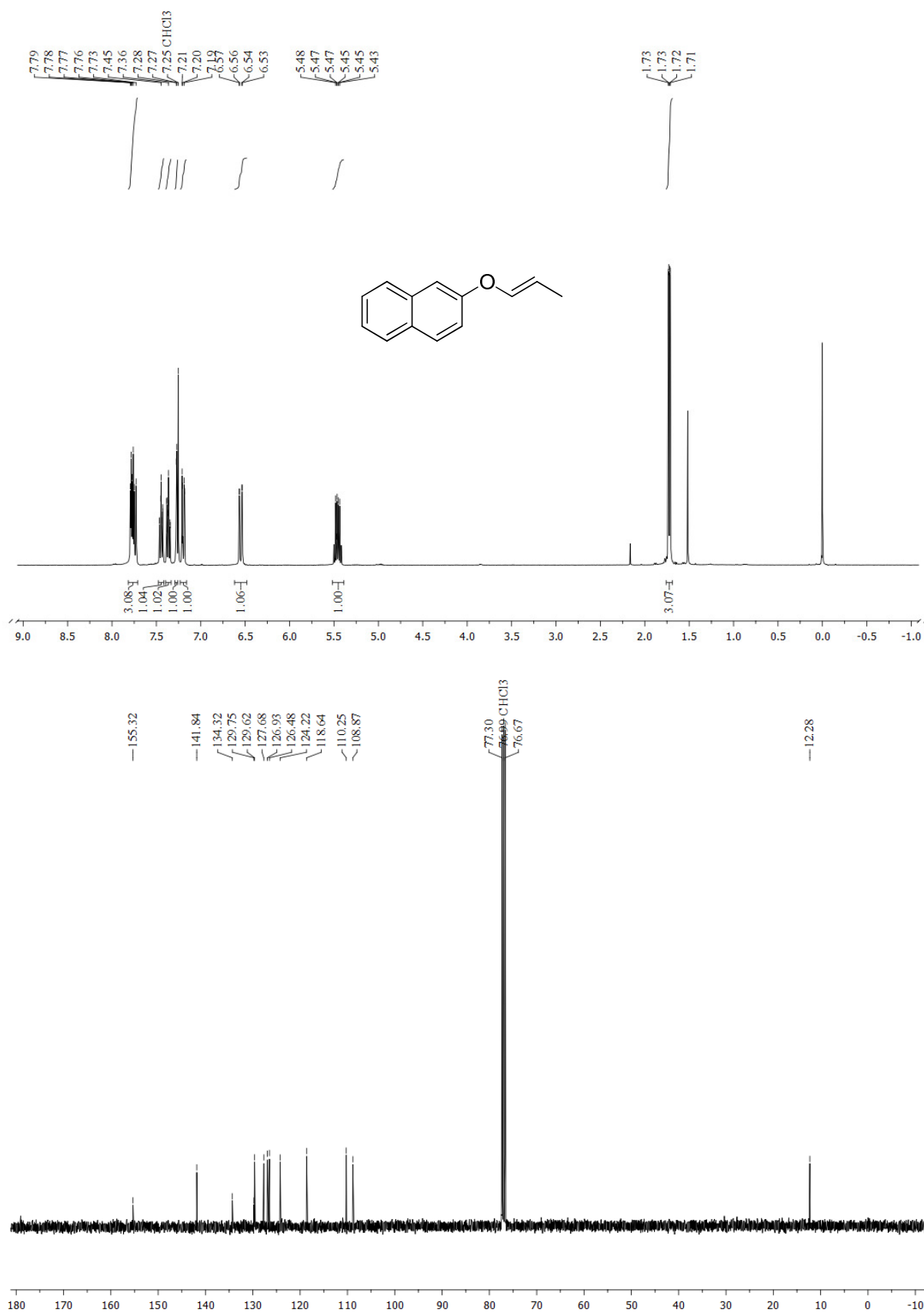
4-Hydroxy-3-methoxybenzaldehyde (5n) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



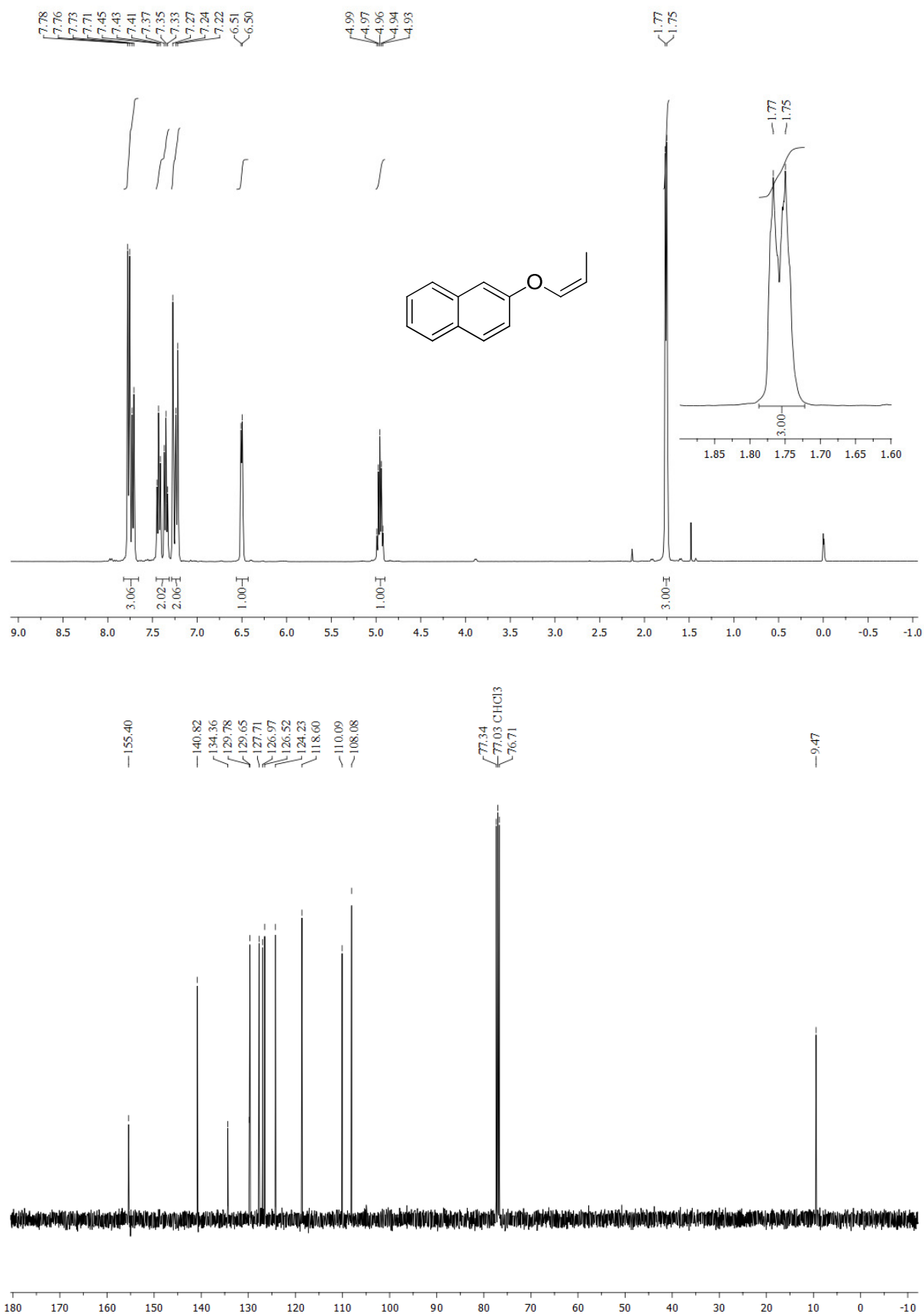
3-Phenylpropan-1-ol (5o) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



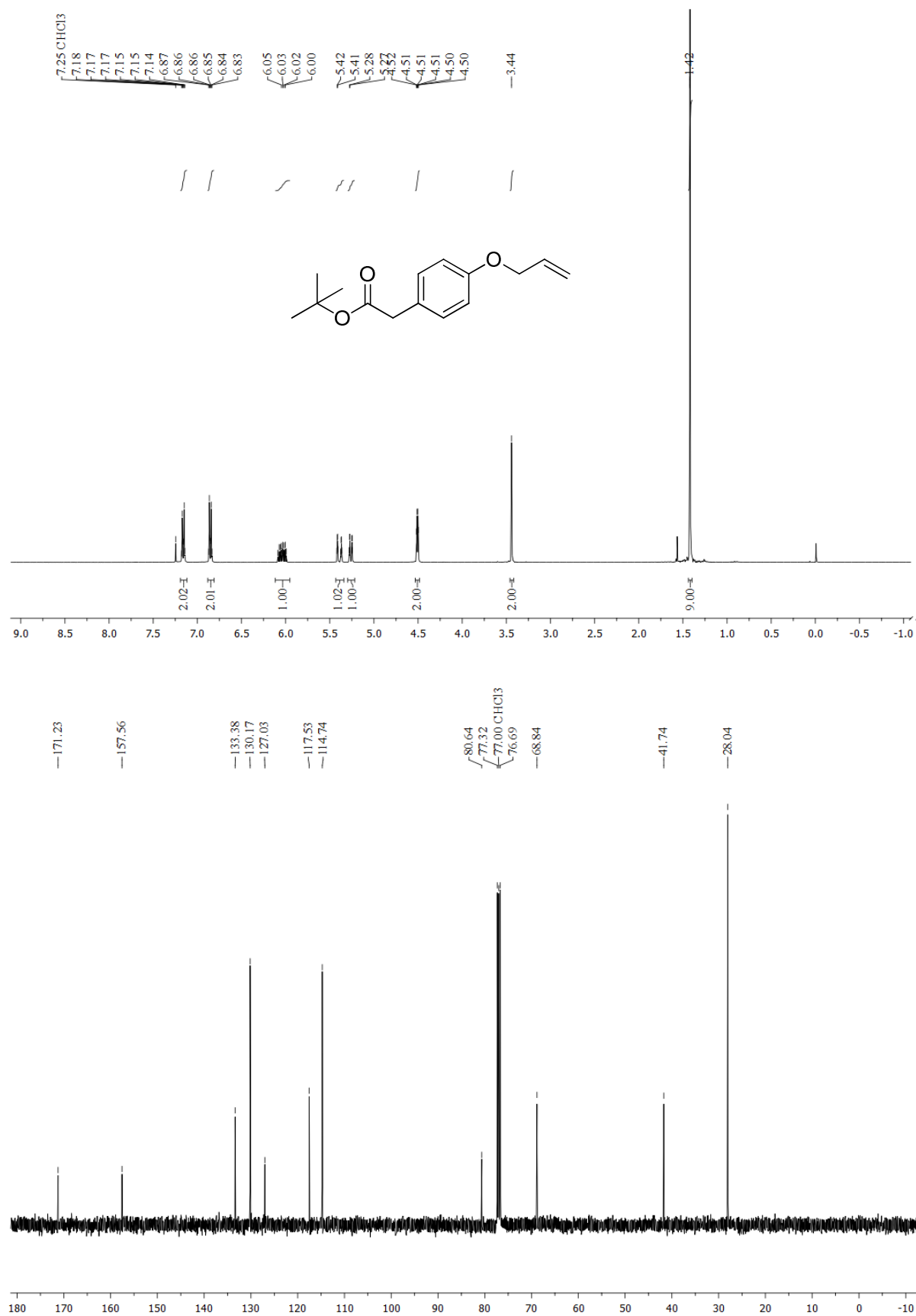
(*E*)-2-(prop-1-en-1-yloxy)naphthalene (*E*-6a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



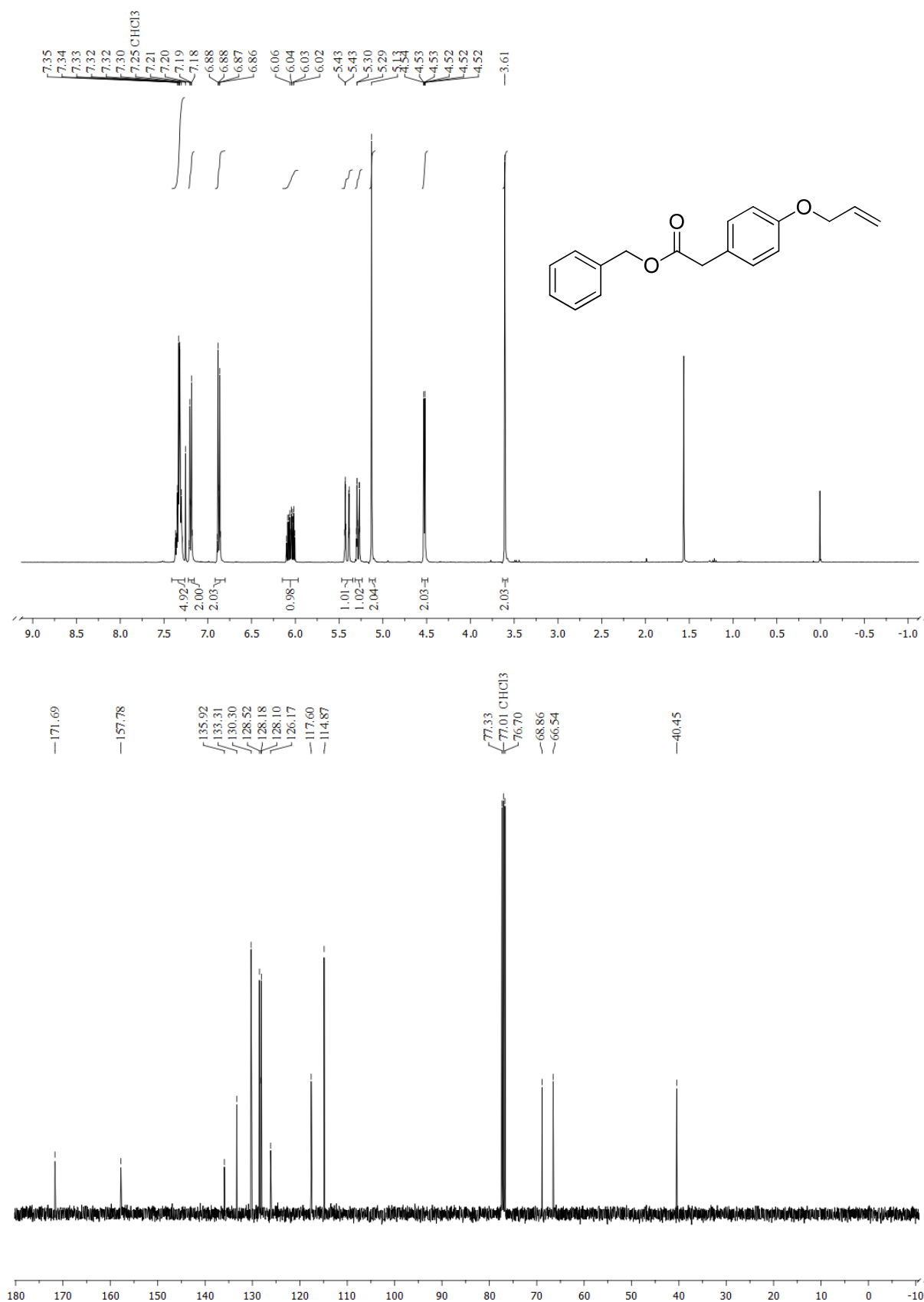
(Z)-2-(prop-1-en-1-yloxy)naphthalene (Z-6a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



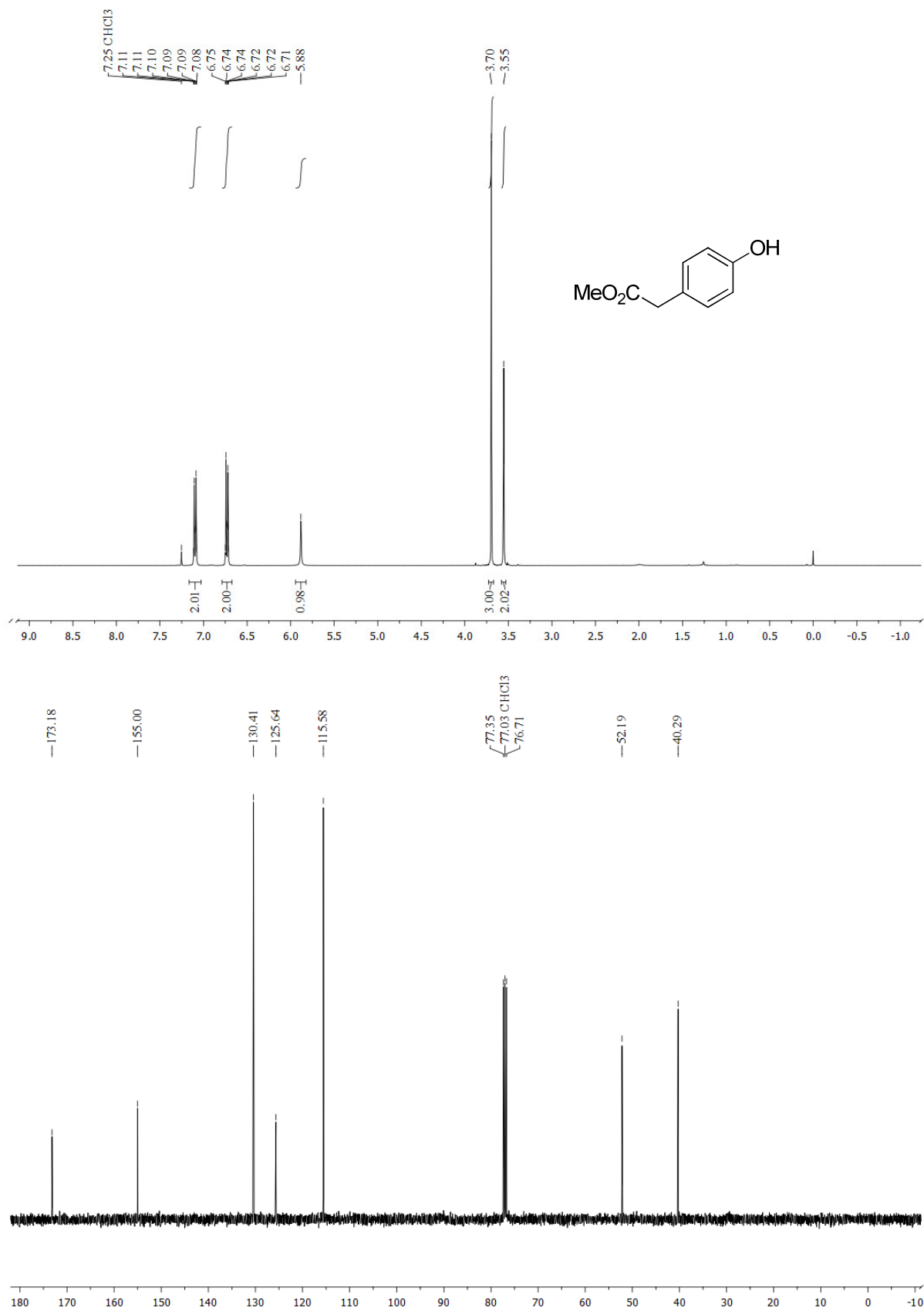
***tert*-Butyl 2-(4-hydroxyphenyl)acetate (7b) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)**



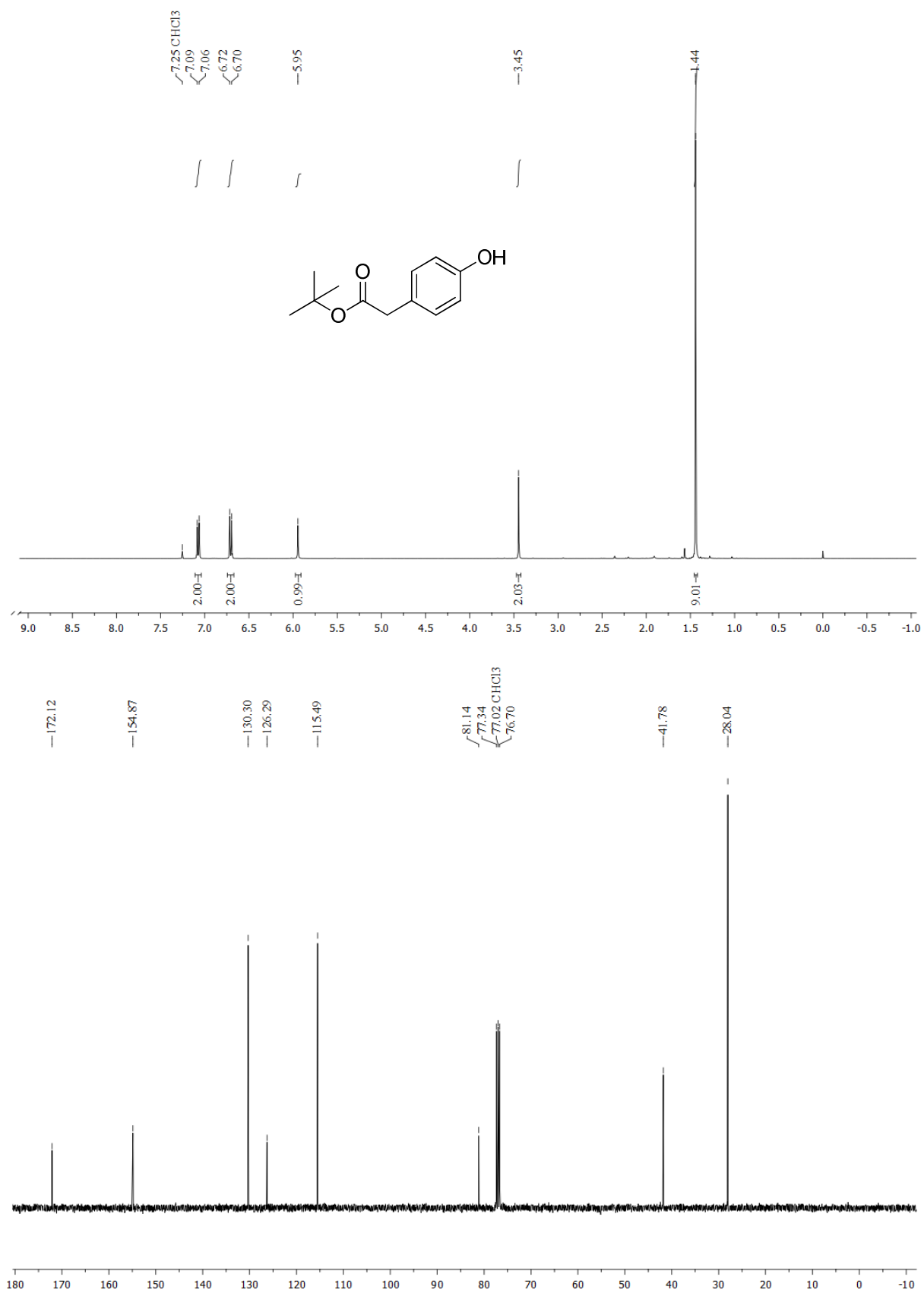
Benzyl 2-(4-(allyloxy)phenyl)acetate (7c) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



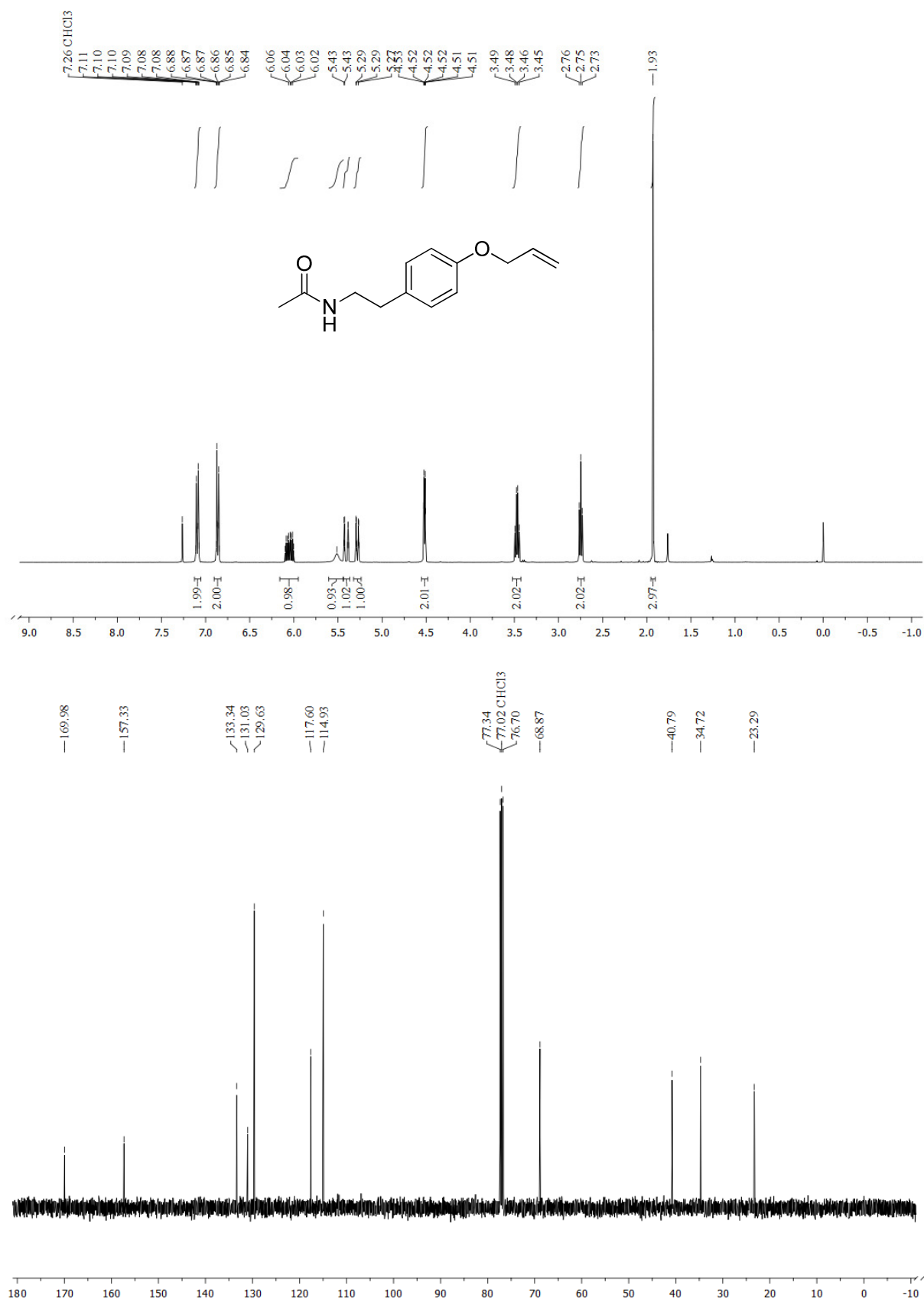
Methyl 2-(4-hydroxyphenyl)acetate (8a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



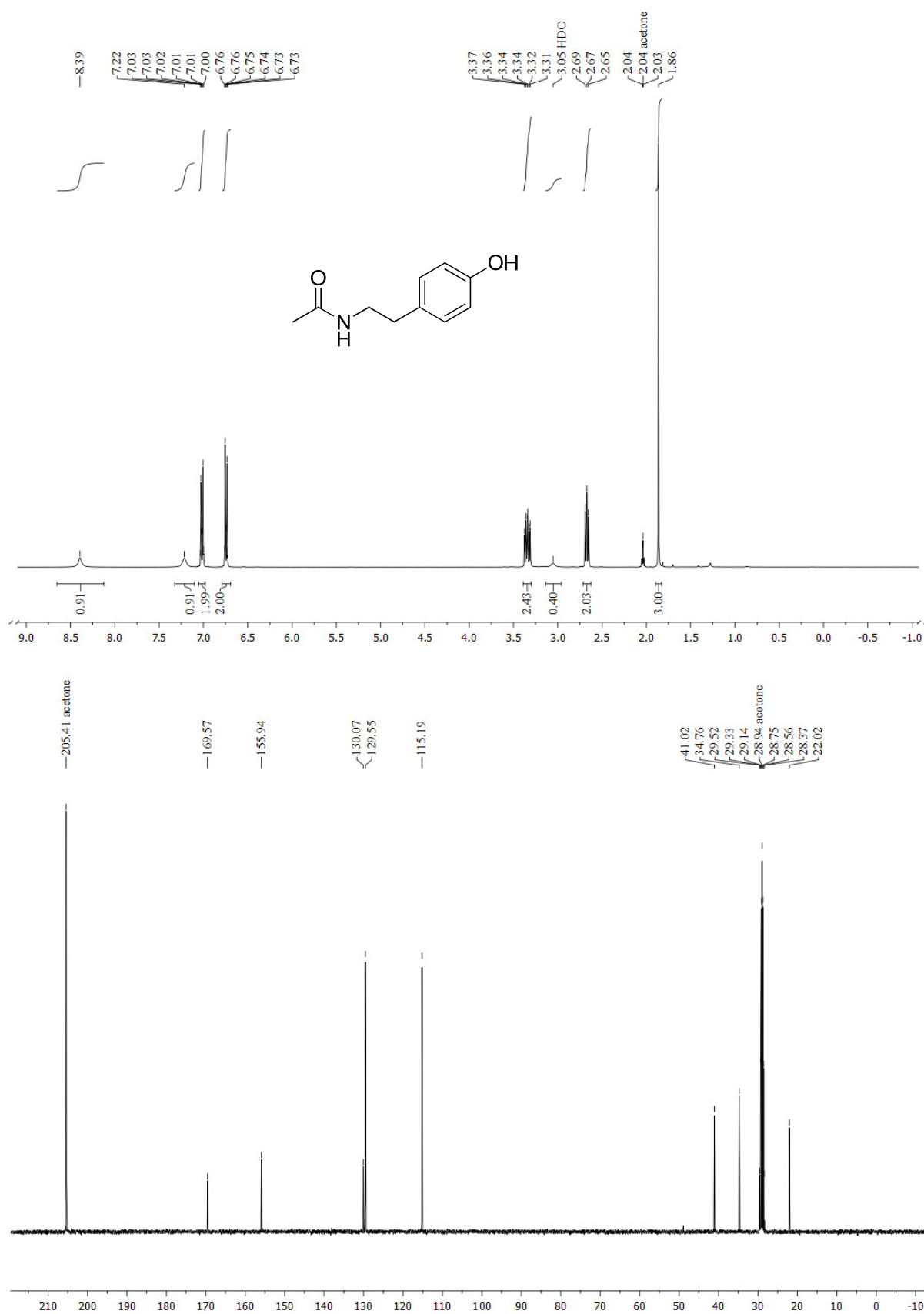
***tert*-Butyl 2-(4-hydroxyphenyl)acetate (8b) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)**



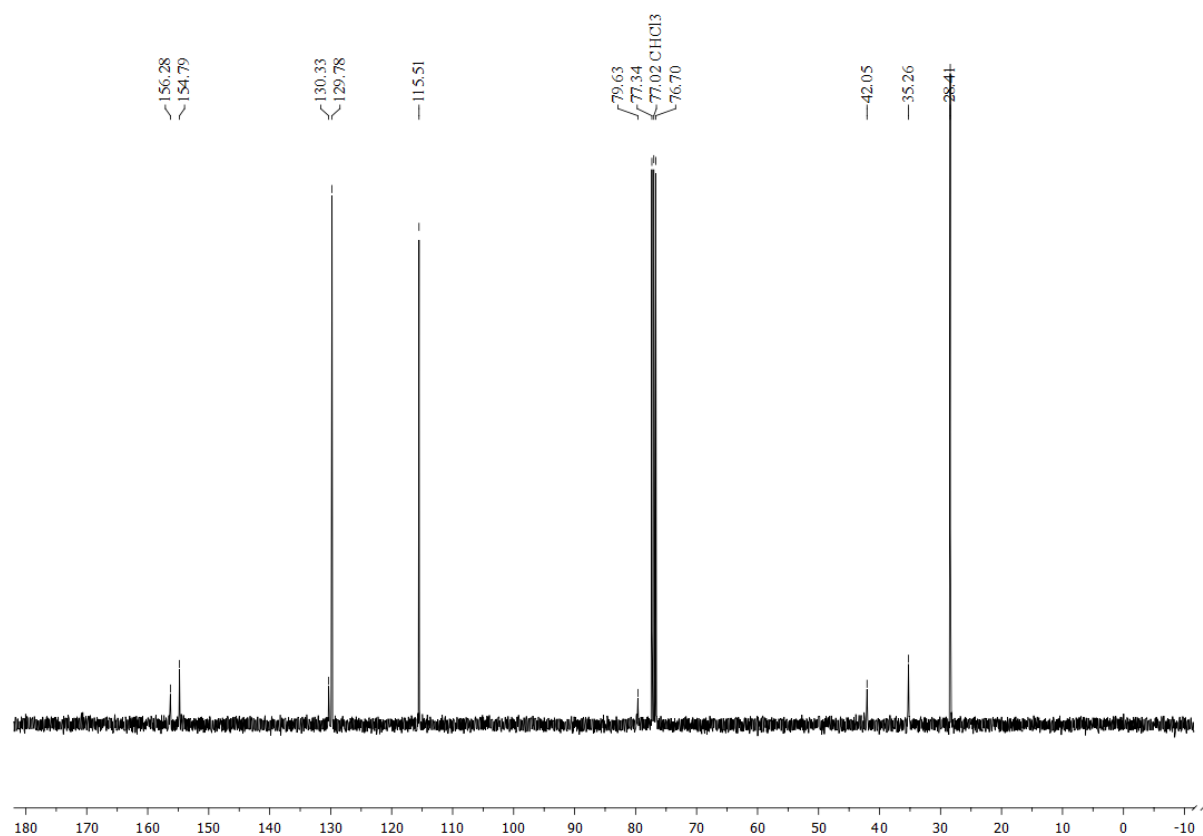
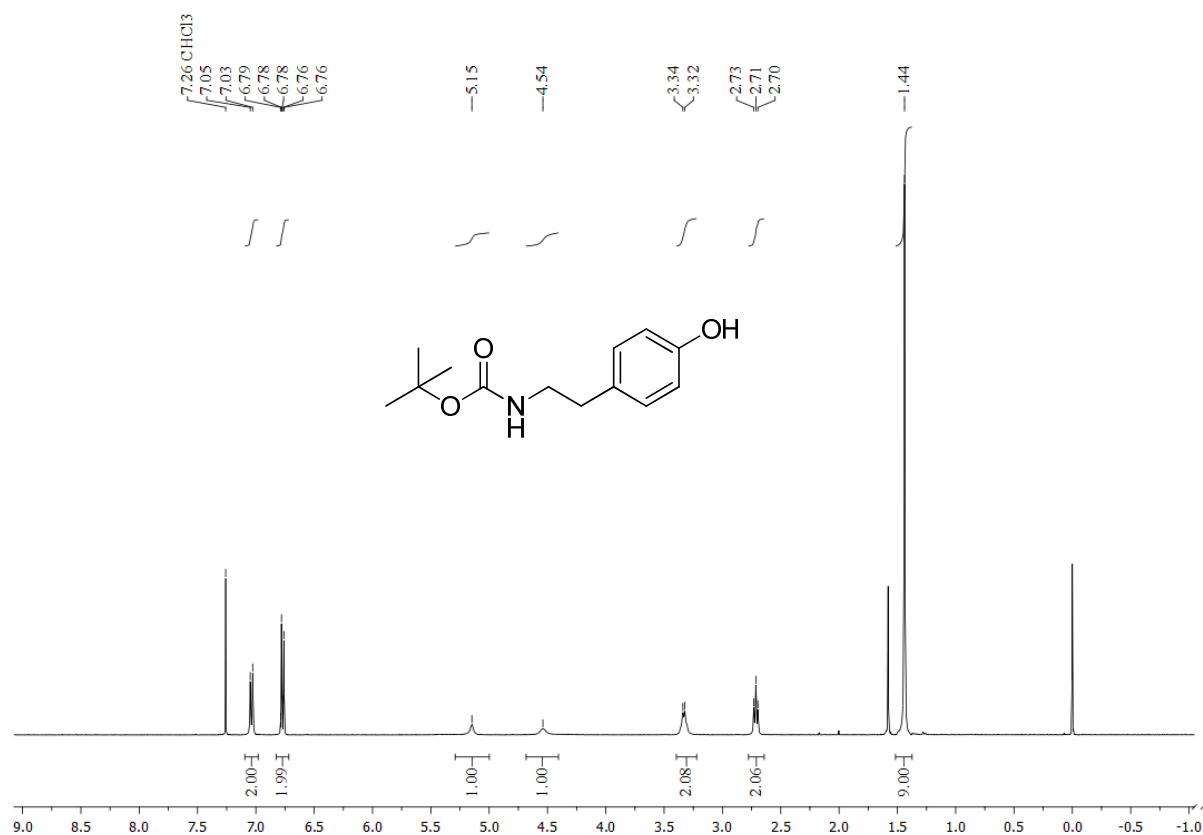
***N*-(4-(allyloxy)phenethyl)acetamide (9a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)**



***N*-(4-hydroxyphenethyl)acetamide (10a) – ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz) and ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz)**



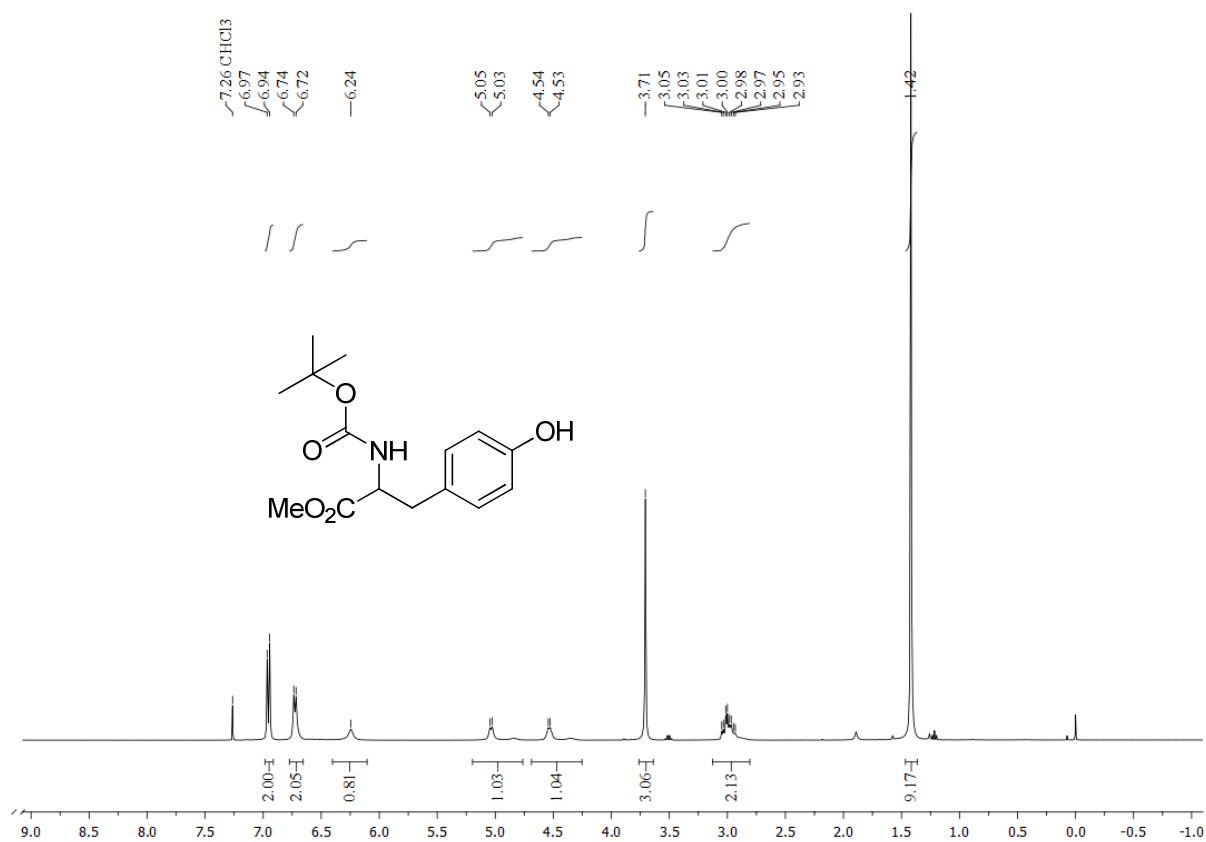
***tert*-Butyl 4-hydroxyphenethylcarbamate (10b) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)**



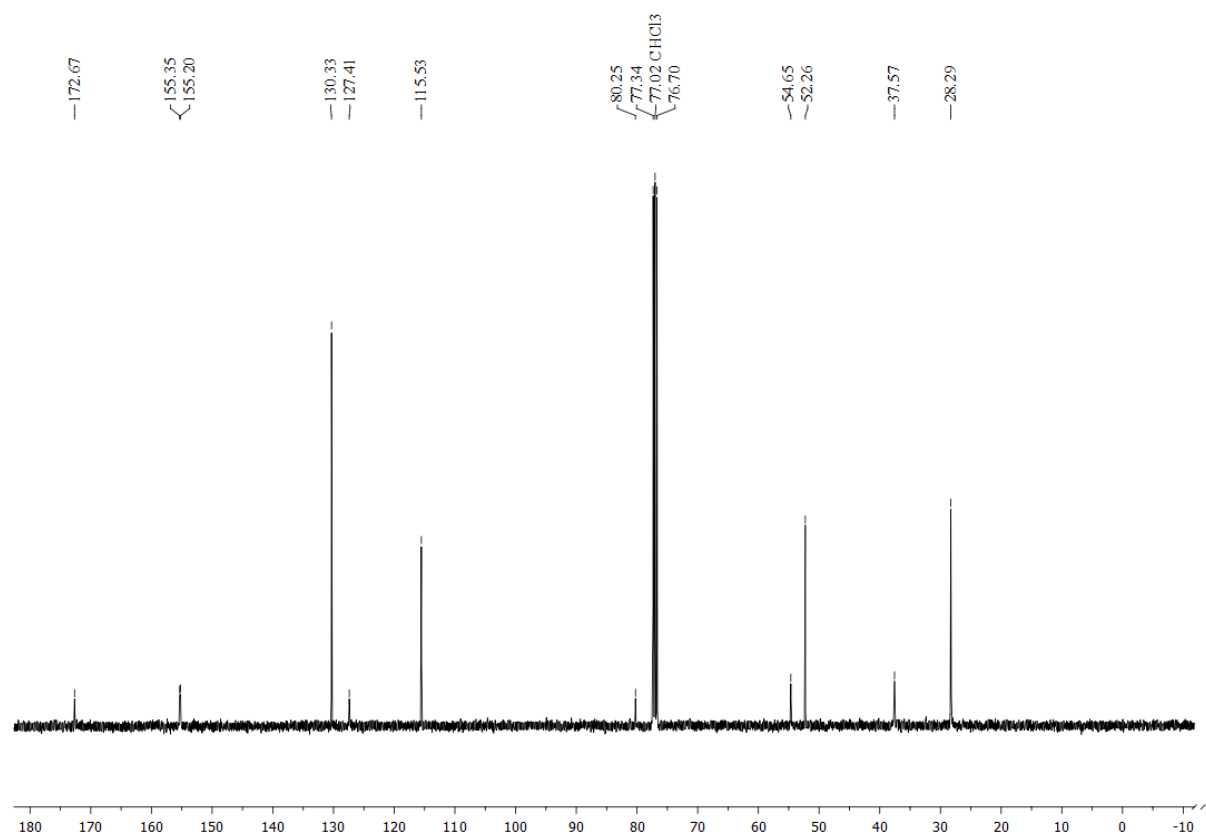
Methyl 2-acetamido-3-(4-hydroxyphenyl)propanoate (12a) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-hydroxyphenyl)propanoate (12b) – ^1H NMR (CDCl_3 , 400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz)



* Signals splitting may come from rotation barrier around C-N bond.



2-((2-methylprop-1-en-1-yl)oxy)naphthalene (16) – ^1H NMR (CDCl_3 , 400 MHz) – for mechanistic studies

