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Heterogeneous Iron Catalyst for C(1)-H Functionalization of 2-Naphthols with Primary Aromatic Alcohols

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1. Physical measurements

All the characterizations and analysis were done by using the following analytical approaches to complete physical measurements. X-ray diffraction (XRD) of the sample was carried out in a Philips PANalytical Empyrean instrument, enabling low-angle measurement from 0-60° with a minimum step size (2θ) of 0.0001, and BRUKER AXS, D8 FOCUS instrument in the 2θ value range of 5-80°. The X-ray photoelectron spectroscopy (XPS) analyses were measured with KRATOS (ESCA AXIS 165) spectrometer using Mg K α (1253.6 eV) radiation as a source. The oven-dried samples (finely ground) were dusted on a graphite sheet (double stick) and mounted over the regular sample holder, before being transferred to an analysis chamber. The material was degassed overnight in a vacuum oven before recording the XPS. The binding energy values were corrected with reference to C 1s peak at 284.8 eV. The peaks were deconvoluted using Origin software (OriginPro 8.5). Energy dispersive X-ray (EDX) analysis were performed with JEOL, model No: 7582 (Oxford make), resolution: 137 eV at 5.9 KeV; Minimum weight % = .01%, sample size: 10mm dia, 1mm thick(max), dry and moisture free and Scanning electron microscopic (SEM) images were recorded with JEOL, JAPAN (Model: JSM 6390LV) with resolution: 3nm, magnification: 3,00,000X, applied voltage: 30 kV (max.). The transmission electron microscopic (TEM) images were recorded on a JEOL (JEM-2010) instrument equipped with a CCD camera (slow-scan) with a 200 kV accelerating voltage. A UV-visible diffuse reflectance spectrum (UV-DRS) analysis was performed in a DR apparatus equipped with an assimilating sphere having 60 mm inner diameter, (Hitachi U-3400 spectrophotometer). Thin Layer Chromatographic (TLC) plate (TLC Silica gel 60 F₂₅₄) was used for monitoring the progress of the reaction. The reactions were monitored through TLC by comparing the retention factor (R_f) of the reactant molecule with the reaction mixture. The isolated % yields are calculated after isolation of desired product using

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the following equation: % yield = [mole of isolated product/mole of limiting reactant] \times 100. ^1H NMR spectra are recorded on 400, 500 and 600 MHz spectrometers. ^{13}C NMR spectra were recorded on 101, 126 and 151 MHz. ^1H , and ^{13}C nuclear magnetic resonance (NMR) analyses were done by DRX-400 Varian, Bruker AVANCE III HD 600 MHz, 500 MHz and 400 MHz spectrometers. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane; spin-spin coupling constants (J) are expressed in hertz (Hz), and other data are reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet) q (quartet), br s (broad singlet), dd (doublet of doublet). Mass spectra (MS) were recorded in Thermo Scientific Q-Exactive, Accela 1250 pump. Perkin Elmer 20 CHN analyser was used for elemental analysis (wt% C, H) in the synthesized compounds.

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2. Synthesis of iron oxide supported on potassium exchanged zeolite-Y ($\text{Fe}_2\text{O}_3\text{-KY}$)

For synthesis of iron oxide supported on potassium exchanged zeolite-Y ($\text{Fe}_2\text{O}_3\text{-KY}$), 2 g of zeolite-HY (procured from Sigma-Aldrich.) was mixed in a round bottom flask in an aqueous solution and then 50 mL of 0.1 M potassium chloride (KCl) (purchased from SRL chemicals) was added to it. The suspension was stirred for 48 hours under refluxing condition at 60 °C. To the potassium exchanged zeolite-Y (KY), 50 mL of 0.1 M of sodium hydroxide (NaOH) solution and 0.01 M (0.135 g in 50 mL water) of iron (III) chloride (bought from Sigma-Aldrich) solution was added dropwise. It was then stirred for another 24 hours under refluxing condition at 60 °C. The resultant light yellowish solid material was collected by simple filtration method using Whatman 41 filter paper and washed several times with warm water. The light yellowish solid was washed several times with water until it gave negative silver nitrate (AgNO_3) (procured from Sigma Aldrich) test. The chloride free solid material was further calcination at 400 °C for 5 hours to get the zeolite-KY supported iron oxide nanocatalyst ($\text{Fe}_2\text{O}_3\text{-KY}$). The material was vacuum dried prior to its characterization.

3. Characterization of $\text{Fe}_2\text{O}_3\text{-KY}$

3.1 XRD analysis

In X-ray diffraction (XRD) pattern of $\text{Fe}_2\text{O}_3\text{-KY}$ a significant difference was observed in the intensities of the (440) and (533) planes at 2θ values of 18.7° and 20.4° (Fig. S1, black line) in comparison to neat zeolite-Y (Fig. S1, red line).¹ Comparison of the XRD patterns also indicated for the presence of weak signals for α -form of iron(III) oxide ($\alpha\text{-Fe}_2\text{O}_3$) at 2θ value of 33.2° (104) 35.6° (110) without affecting the other signal of neat zeolite-Y. These results provided an evident for the formation of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles on the surface of zeolite-Y, Fig. S1.²

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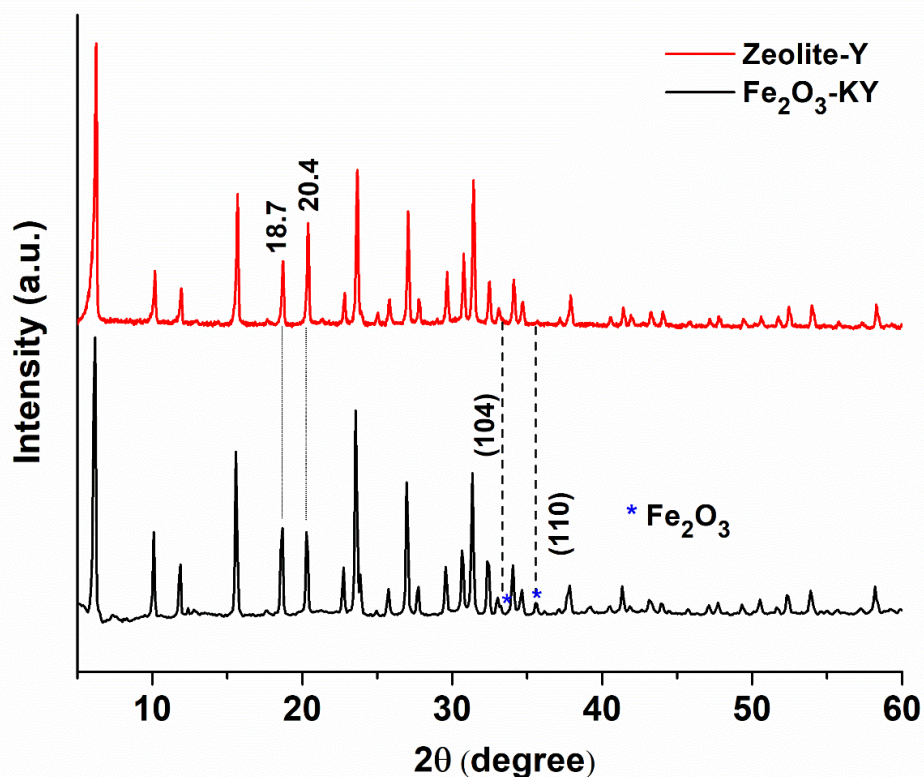


Fig. S1 a) XRD pattern of neat zeolite-Y (red), and Fe₂O₃-KY (black).

3.2 XPS analysis

All the elements viz Fe, Al, Si, and O present in the synthesised material, Fe₂O₃-KY was further confirmed from the XPS analysis, Fig. S2. The appearance of two prominent peaks at 711.2 eV and 724.9 eV corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively clearly signified the presence of Fe (III) species in the synthesized Fe₂O₃-KY material (Fig. S2a).³ A peak separation of more than 7 eV from Fe 2p_{3/2} level and satellite peak (719.0 eV) further confirmed the presence of Fe (III) species in the material.³ The binding energy values of 529.9, 530.9, and 531.8 eV in XPS spectrum of O 1s characteristic of Fe–O, Al–O, and Si–O bonds in the material, respectively (Fig. S2b).⁴ The XPS spectra of Al 2p and Si 2p showed peaks for aluminosilicates at 74.4 eV and 103.0 eV, respectively (Fig S2b-c).⁵ All of the above XPS peaks were fitted with respect to the C 1s peak having binding energy of 284.4 eV (C-C), 286.5 eV (C-O) and 289.0 eV (C=O), Fig. S2e.

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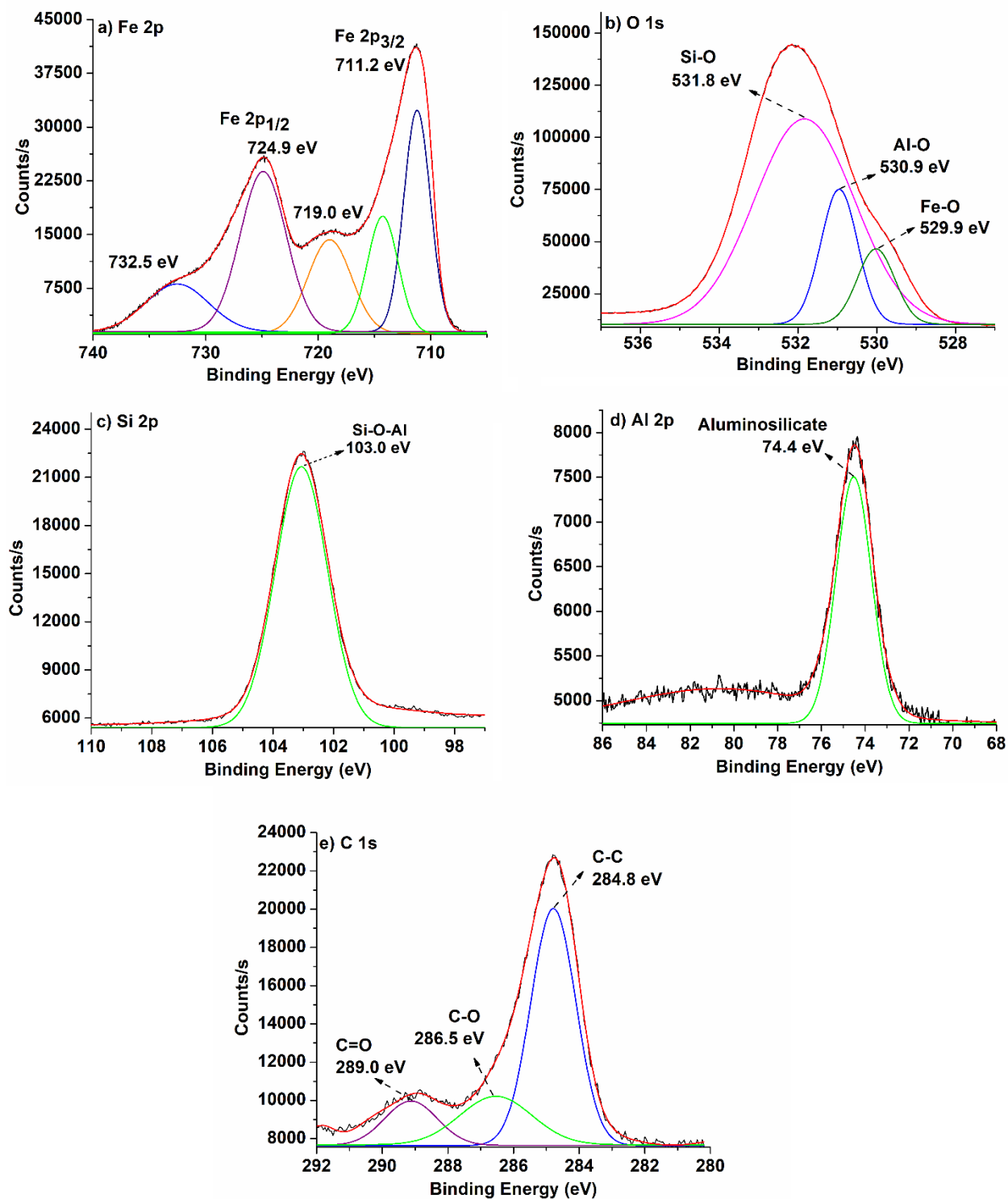


Fig. S2 The XPS spectra of (a) Fe 2p, (b) O 1s, (c) Si 2p, (d) Al 2p and (e) C 1s in Fe₂O₃-KY catalyst.

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3.3 EDX spectra of Fe₂O₃-KY

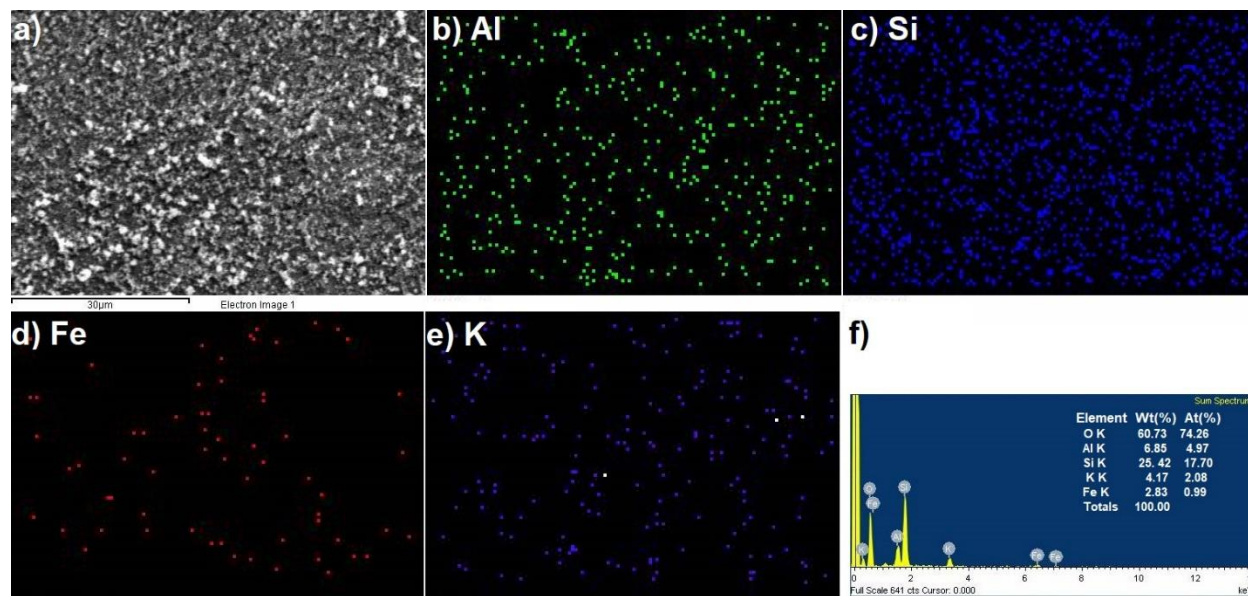


Fig. S3 a) SEM image of Fe₂O₃-KY considered for EDS elemental mapping of (b) Al, (c) Si, (d) Fe, (e) K and (f) EDX spectra showing the presence of all the elements in Fe₂O₃-KY material. The elemental amounts are given in weight% (wt%) and atomic% (At%).

3.4 SEM images of Fe₂O₃-KY

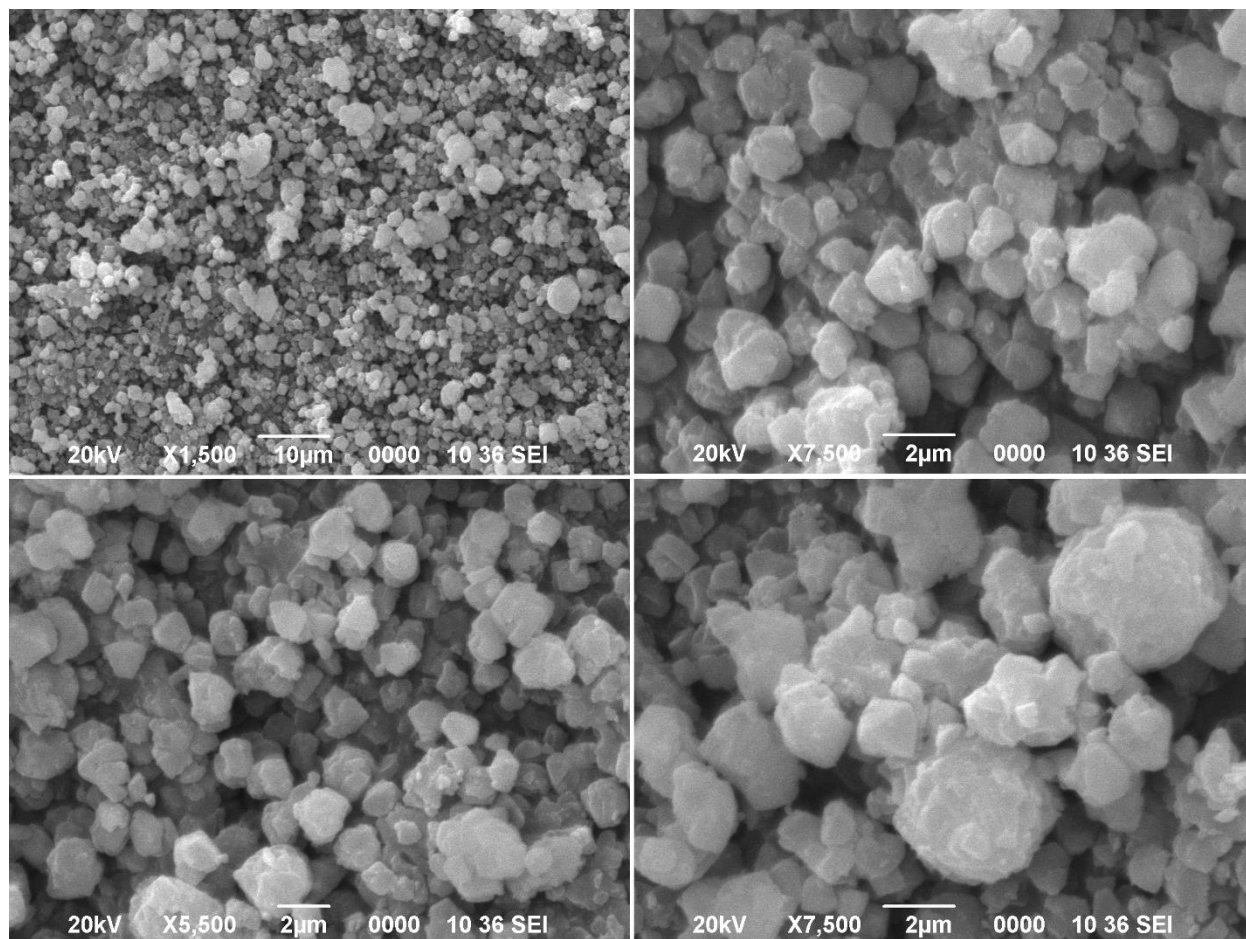


Fig. S4 SEM images of Fe₂O₃-KY in different magnifications

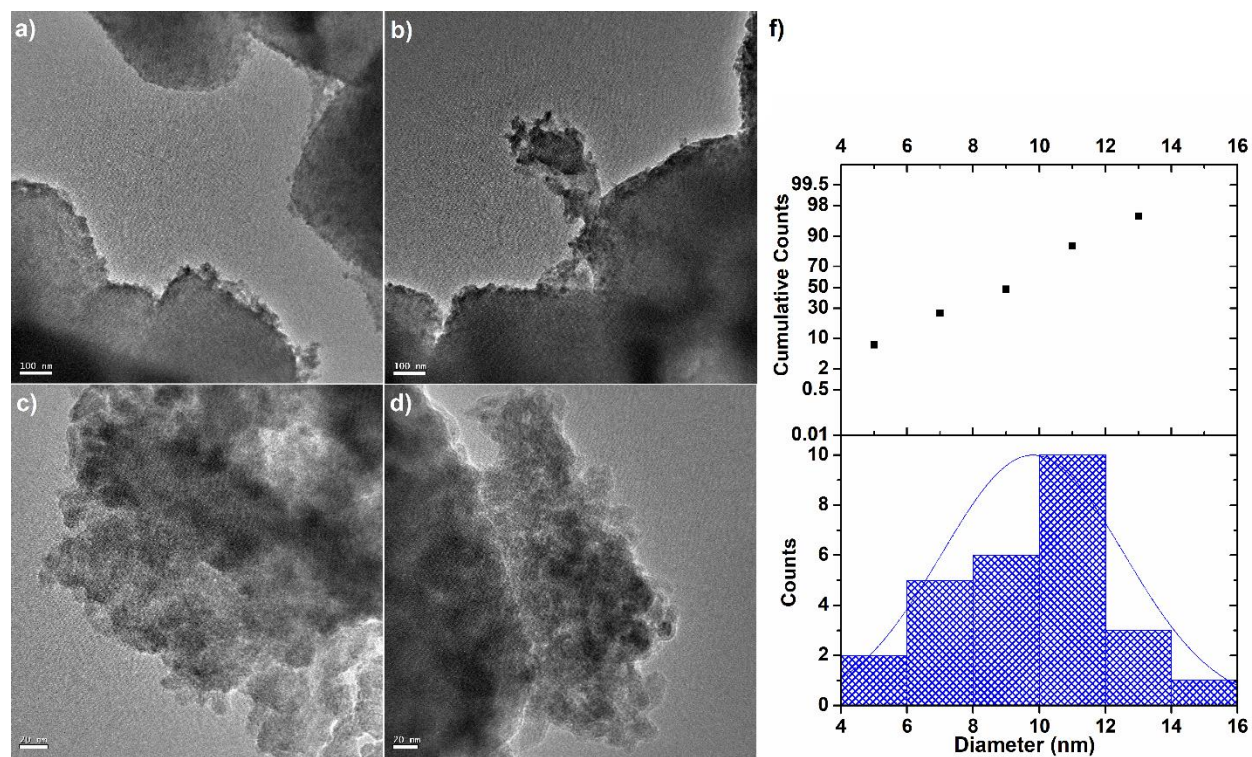
3.5 TEM images of Fe₂O₃-KY

Fig. S5 (a-b) TEM images of Fe₂O₃-KY showing the fine dispersion of Fe₂O₃ NPs on potassium exchanged zeolite-Y, f) particle size distribution of Fe₂O₃-KY from TEM images.

3.6 DRS Spectra of Fe₂O₃-KY

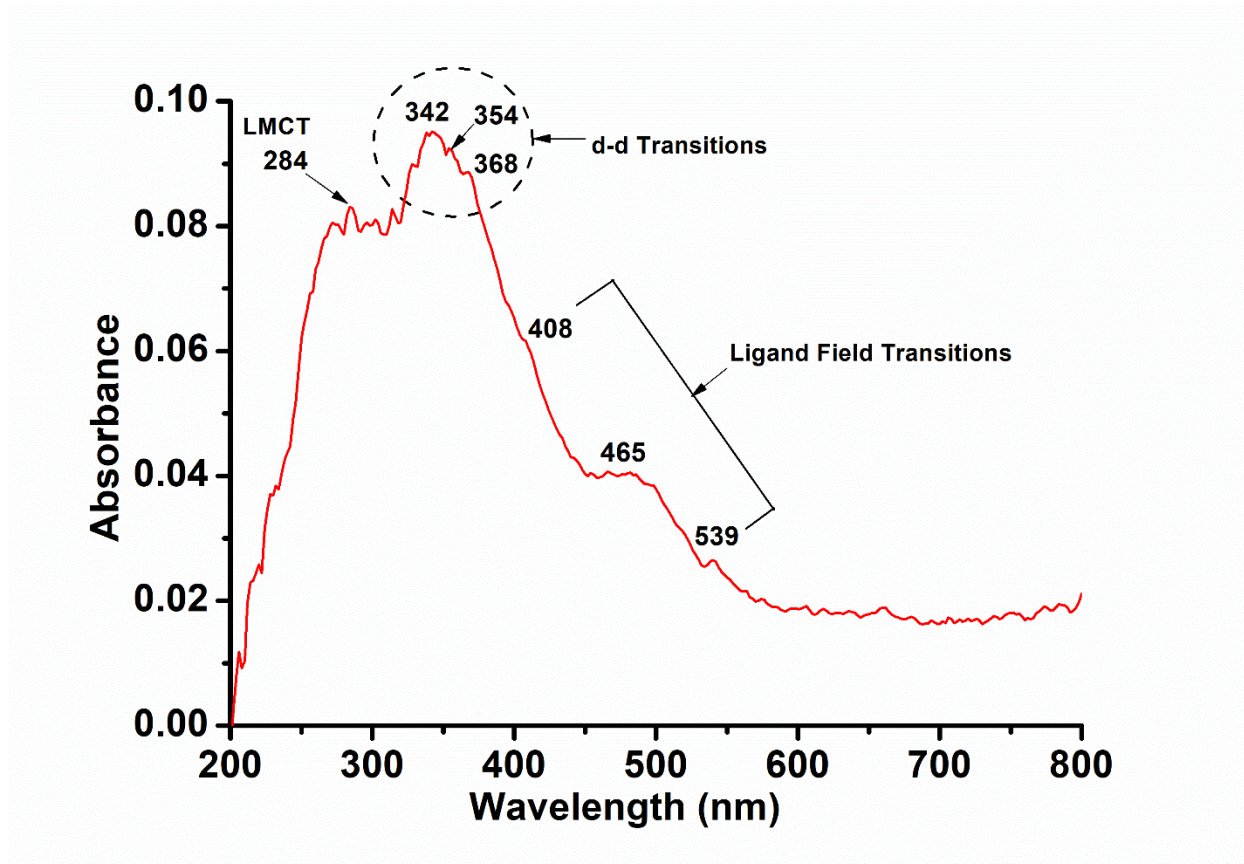


Fig. S6 UV-vis diffused reflectance spectrum of Fe₂O₃-KY.

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4 X-ray crystallography

X-ray diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using Mo K α ($\lambda = 0.71073$ Å) radiation⁶ and X-ray diffraction data for all crystals were collected using Bruker SMART software. This software is also used for indexing and determination of the unit cell parameters. Cell structures were solved by direct method and refined by full-matrix least squares against F² of all data, using SHELXTL software. All the non-H-atoms were refined by full-matrix least squares in anisotropic, all H-atoms in isotropic approximation, against F² of all reflections. Some hydrogen atoms attached to these atoms were treated as ‘riding’ in calculated positions. The crystallographic tables for the compound **3b**, **3h**, **3v** and **3z** are given in the table S1, which includes the crystal parameters and the refinement factor. The molecular structures were drawn at MERCURY.⁷

The CIF files containing complete information of the studied structures of compound **3b**, **3h**, **3v** and **3z** were deposited with CCDC, deposition number 2217708, 2217706, 2217707, and 2220406, respectively which are freely available upon request from the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; email:deposit@ccdc.cam.ac.uk) or from the following website: www.ccdc.cam.ac.uk/data_request/cif

The compound **3b** crystallizes in orthorhombic P2₁2₁2₁ space group and their asymmetric unit contain the whole molecule whereas compound **3h** and **3v** crystallize in monoclinic P2₁/c space group. The asymmetric of compound **3z** contains two molecules and crystallizes in triclinic P-1 space group.

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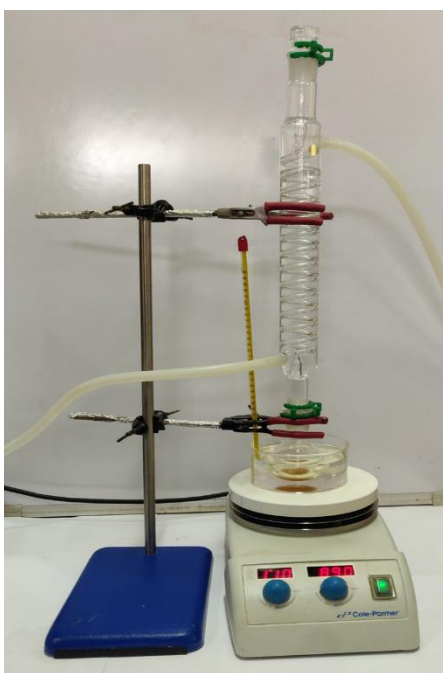
Table S1: Crystallographic data and refinement parameters for the compound **3h**, **3v**, **3b** and **3z**:

Compound name	Compound 3b	Compound 3h	Compound 3v	Compound 3z
chemical formula	C ₁₈ H ₁₆ O ₂	C ₁₈ H ₁₆ O ₃	C ₁₈ H ₁₅ BrO ₂	C ₂₀ H ₁₈ O ₄
CCDC deposition number	2217708	2217706	2217707	2220406
formula mass	264.31	280.31	343.20	322.34
crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
space group	<i>P 2₁ 2₁ 2₁</i>	<i>P21/c</i>	<i>P21/c</i>	<i>P-1</i>
a/Å	5.695(3)	8.3525(7)	15.974(7)	10.610(2)
b/Å	15.637(8)	11.4569(9)	5.729(3)	12.799(3)
c/Å	15.874(8)	14.7293(11)	18.827(11)	14.258(3)
α/°	90.00	90.00	90.00	63.537(5)
β/°	90.00	90.936(2)	119.690(11)	72.847(5)
γ/°	90.00	90.00	90.00	80.933(5)
V/Å ³	1413.6(13)	1409.31(19)	1496.8(13)	1655.5(6)
T/K	293(2)	296(2)	296(2)	296(2)
Density (g cm ⁻³)	1.242	1.321	1.523	1.293
Z	4	4	4	4
radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm-1	0.080	0.089	2.748	0.090
Total no. of reflections measured	4164	3584	3960	7833
Reflections, <i>I</i> > 2σ(<i>I</i>)	1239	2636	1847	4026
Complete to 2θ (%)	98.2	99.6	99.3	98.7
Ranges (h, k, l)	-7 ≤ h ≤ 7 -21 ≤ k ≤ 21 -21 ≤ l ≤ 22	-11 ≤ h ≤ 11 -15 ≤ k ≤ 15 -19 ≤ l ≤ 19	-21 ≤ h ≤ 21 -7 ≤ k ≤ 7 -25 ≤ l ≤ 25	-13 ≤ h ≤ 13 -16 ≤ k ≤ 16 -18 ≤ l ≤ 18
Data/ Restraints/Parameters	4164/1/235	3584/0/193	3960/0/192	7833/2/439
R indices [<i>I</i> > 2σ(<i>I</i>)]	0.0851	0.0446	0.0600	0.0570
R indices (all data)	0.2664	0.0659	0.1547	0.1257
wR(F ₂) (all data)	0.2597	0.0968	0.1955	0.1992
Goodness-of-fit	0.916	1.048	1.014	1.030

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5 General procedure for benzylation of 2-naphthols

The reaction was performed with various other substituted primary alcohols with different substituted naphthols, after optimizing the various reaction parameters *i.e.* solvent, catalyst amount, time and temperature. The reaction was performed in a 50 mL round bottom flask with appropriate amount of naphthols (1 mmol) and benzyl alcohols (1 mmol) immersed in oil bath at 110 °C under refluxing condition using 15 mg of F₂O₃-KY catalyst and 1 mL of dichloroethane (DCE) as solvent for 6 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (CH₃COOC₂H₅) and filtered. The heterogeneous catalyst was recovered and washed with ethanol and warm water several times for further use. The solvent was evaporated under reduced pressure, and the residue obtained was purified and isolated by column chromatography (hexane/ethyl acetate) on silica gel to get the desired benzylated product. Different isolated products are characterized by ¹H, ¹³C NMR. All the naphthol derivatives and alcohol derivatives are purchased from Merck and Sigma Aldrich, solvents used were of HPLC grade and were brought from E-Merck.



A photograph of reaction set-up.

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6 Characterization of the compound

❖ NMR Analysis of synthesized compounds

Compound 3a: 1-benzyl-naphthalen-2-ol

^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.26 – 7.12 (m, 5H), 7.09 (d, $J = 8.8$ Hz, 1H), 5.02 (s, 1H), 4.44 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.3, 140.1, 133.8, 129.6, 128.7, 128.7, 128.6, 128.3, 126.8, 126.2, 123.4, 118.3, 118.0, 30.8.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{O}$: 234.1045, found 234.1048.

The spectroscopic data were in accordance with literature.⁸

Compound 3b: 1-(4-methoxybenzyl)naphthalen-2-ol

The spectroscopic data were in consistent with literature.⁸

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 1H), 7.68 (d, $J = 8.1$ Hz, 1H), 7.58 (d, $J = 8.8$ Hz, 1H), 7.33 (dd, $J = 8.4, 6.8, 1.3$ Hz, 1H), 7.22 (t, $J = 7.0$ Hz, 1H), 7.00 (dd, $J = 17.0, 8.8$ Hz, 3H), 6.71 – 6.65 (m, 2H), 5.21 (s, 1H), 4.28 (s, 2H), 3.63 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.0, 151.3, 133.7, 132.1, 129.5, 129.2, 128.6, 126.7, 123.4, 118.6, 118.0, 114.1, 55.4, 29.9.

Compound 3c: 1-(4-methylbenzyl)naphthalen-2-ol

The spectroscopic data were in accordance with the literature.⁸

^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.5$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.32 (t, $J = 7.0$ Hz, 1H), 7.10 (dd, $J = 8.4, 4.7$ Hz, 3H), 7.05 (d, $J = 7.9$ Hz, 2H), 4.98 (s, 1H), 4.41 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.4, 136.9, 135.8, 133.8, 129.6, 129.5, 128.7, 128.6, 128.2, 123.5, 123.3, 118.5, 118.07, 30.4, 21.1.

Compound 3d: 1-(4-isopropylbenzyl)naphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 7.92 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.13 (d, $J = 7.5$ Hz, 2H), 7.09 (dd, $J = 7.5, 5.9$ Hz, 3H), 5.37 (s, 1H), 4.41 (s, 2H), 2.87 – 2.79 (m, 1H), 1.19 (d, $J = 6.9$ Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.5, 146.8, 137.3, 133.8, 129.6, 128.6, 128.5, 128.2, 126.7, 123.5, 123.2, 118.5, 118.1, 33.8, 30.4, 24.1.

Anal. calcd. For $\text{C}_{20}\text{H}_{20}\text{O}$: C, 86.92; H, 7.29; found C, 87.11; H, 7.36.

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Compound 3e: 1-(2-hydroxybenzyl)naphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.11 – 7.04 (m, 2H), 6.87 – 6.77 (m, 2H), 4.39 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 153.3, 150.5, 133.5, 131.1, 129.9, 128.9, 127.9, 126.8, 126.3, 123.4, 121.3, 118.3, 118.1, 115.9, 25.4.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 251.1067, found 251.1075.

Compound 3f: 1-(thiophen-2-ylmethyl)naphthalen-2-ol

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.14 – 7.03 (m, 2H), 6.87 – 6.82 (m, 1H), 6.77 (d, $J = 2.2$ Hz, 1H), 5.25 (s, 1H), 4.58 (s, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.1, 143.5, 133.3, 129.6, 128.9, 128.7, 126.9, 124.9, 123.8, 123.5, 123.2, 118.4, 118.0, 25.5.

The spectroscopic data were in consistant with literature.⁹

Compound 3g: 1-benzyl-naphthalene-2,7-diol

^1H NMR (400 MHz, MeOD) δ 7.49 (d, $J = 8.8$ Hz, 1H), 7.43 (d, $J = 8.7$ Hz, 1H), 7.08 (dt, $J = 15.0, 7.5$ Hz, 4H), 7.02 (d, $J = 1.5$ Hz, 1H), 6.97 (t, $J = 6.9$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 1H), 6.72 (dd, $J = 8.7, 2.2$ Hz, 1H), 4.23 (s, 2H).

^{13}C NMR (126 MHz, MeOD) δ 156.7, 154.2, 142.8, 136.9, 131.0, 129.4, 129.1, 128.8, 126.4, 125.4, 117.9, 115.8, 115.5, 106.4, 31.5.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 251.1067, found 251.1079.

Compound 3h: 1-(4-methoxybenzyl)naphthalene-2,7-diol

^1H NMR (400 MHz, MeOD) δ 7.48 (d, $J = 8.7$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 3H), 6.85 (d, $J = 8.9$ Hz, 1H), 6.71 (dd, $J = 8.7, 2.3$ Hz, 1H), 6.64 (d, $J = 8.6$ Hz, 2H), 4.15 (s, 2H), 3.61 (s, 3H).

^{13}C NMR (151 MHz, MeOD) δ 159.0, 156.6, 154.1, 136.8, 134.7, 130.9, 130.2, 128.7, 125.3, 118.2, 115.7, 115.5, 114.5, 106.4, 55.5, 30.6.

Anal. calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3$: C, 77.12; H, 5.75; found C, 77.23; H, 5.83.

Compound 3i: 1-(4-methylbenzyl)naphthalene-2,7-diol

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.17 (d, $J = 1.6$ Hz, 1H), 7.06 (q, $J = 8.1$ Hz, 4H), 6.93 (dd, $J = 13.0, 5.6$ Hz, 2H), 5.00 (d, $J = 17.8$ Hz, 2H), 4.31 (s, 2H), 2.28 (s, 3H).

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^{13}C NMR (101 MHz, CDCl_3) δ 154.5, 152.1, 136.8, 135.8, 135.3, 130.7, 129.5, 128.5, 128.2, 125.0, 116.9, 115.6, 115.0, 106.0, 30.5, 21.1.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 265.1223, found 265.1236.

Compound 3j: 1-(4-isopropylbenzyl)naphthalene-2,7-diol

^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.17 (s, 1H), 7.13 – 7.07 (m, 4H), 6.94 (dd, $J = 13.4, 8.8$ Hz, 2H), 5.21 (d, $J = 163.1$ Hz, 2H), 4.31 (s, 2H), 2.84 (dp, $J = 13.5, 6.7$ Hz, 1H), 1.20 (d, $J = 6.9$ Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 154.4, 152.1, 146.9, 137.1, 135.3, 130.6, 128.4, 128.2, 126.8, 125.0, 116.9, 115.6, 115.0, 106.0, 33.8, 24.1.

Anal. calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_2$: C, 82.16; H, 6.90; found C, 82.35; H, 6.99.

Compound 3k: 1-(thiophen-2-ylmethyl)naphthalene-2,7-diol

^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.7$ Hz, 1H), 7.57 (d, $J = 8.7$ Hz, 1H), 7.21 (d, $J = 1.8$ Hz, 1H), 7.05 (d, $J = 5.0$ Hz, 1H), 6.91 (dd, $J = 12.9, 5.6$ Hz, 2H), 6.84 – 6.78 (m, 1H), 6.72 (d, $J = 2.6$ Hz, 1H), 5.48 (d, $J = 70.7$ Hz, 2H), 4.45 (s, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 154.5, 151.7, 143.5, 134.9, 130.7, 128.8, 126.9, 124.9, 124.8, 124.7, 123.7, 116.9, 115.6, 115.2, 105.8, 25.6.

Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{S}$: C, 70.29; H, 4.72; found C, 70.41; H, 4.67.

Compound 3l: 1-(4-chlorobenzyl)naphthalene-2,7-diol

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.8$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.18 (d, $J = 8.3$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 3H), 6.97 – 6.87 (m, 2H), 5.11 (s, 2H), 4.31 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.6, 151.9, 138.8, 135.2, 131.8, 130.7, 129.7, 128.7, 125.0, 116.5, 115.5, 115.1, 105.9, 30.3.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 285.0677, found 285.0684.

Compound 3m: 1-benzyl-7-methoxynaphthalen-2-ol

^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.63 (m, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.22 (s, 1H), 7.21 – 7.11 (m, 5H), 6.97 (dd, $J = 8.9, 2.2$ Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 1H), 5.10 (d, $J = 30.3$ Hz, 1H), 4.38 (s, 2H), 3.80 – 3.75 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 151.9, 140.4, 135.1, 130.2, 128.7, 128.3, 126.2, 117.6, 115.4, 102.8, 55.3, 31.1.

The spectroscopic data were in accordance with the literature.⁹

Compound 3n: 7-methoxy-1-(4-methoxybenzyl)naphthalen-2-ol

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^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 8.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.25 (s, 1H), 7.15 (d, $J = 8.3$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 1H), 6.94 (s, 1H), 6.78 (d, $J = 8.3$ Hz, 2H), 5.05 (s, 1H), 4.33 (s, 2H), 3.82 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.5, 151.9, 135.1, 132.1, 130.2, 129.3, 128.2, 125.0, 117.8, 115.5, 115.4, 114.4, 114.2, 102.7, 55.4, 55.3, 30.2.

Anal. calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_3$: C, 77.53; H, 6.16; found C, 77.66; H, 6.25.

Compound 3o: 7-methoxy-1-(4-methylbenzyl)naphthalen-2-ol

^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.18 (s, 1H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.98 (dd, $J = 9.0, 2.3$ Hz, 1H), 6.94 (d, $J = 8.7$ Hz, 1H), 5.03 (s, 1H), 4.35 (s, 2H), 3.82 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.9, 137.1, 135.8, 135.2, 130.2, 129.4, 129.2, 128.3, 128.1, 127.3, 117.8, 115.5, 102.8, 55.3, 30.7, 21.1.

Anal. calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52; found C, 82.14; H, 6.68.

Compound 3p: 1-(4-isopropylbenzyl)-7-methoxynaphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, $J = 8.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.20 (s, 1H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.98 (dd, $J = 8.9, 2.0$ Hz, 1H), 6.95 (d, $J = 8.7$ Hz, 1H), 5.01 (s, 1H), 4.36 (s, 2H), 3.82 (s, 3H), 2.87 – 2.80 (m, 1H), 1.20 (d, $J = 6.9$ Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.50 (s), 151.9, 146.8, 137.3, 135.1, 130.4, 130.2, 128.3, 128.0, 126.8, 125.0, 117.8, 115.5, 115.5, 102.7, 55.3, 33.8, 30.7, 24.1.

Anal. calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_2$: C, 82.32; H, 7.24; found C, 82.44; H, 7.18.

Compound 3q: 1-(2-hydroxybenzyl)-7-methoxynaphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 7.64 (d, $J = 8.9$ Hz, 1H), 7.54 – 7.49 (m, 2H), 7.44 (d, $J = 7.5$ Hz, 1H), 7.07 (dd, $J = 14.6, 7.2$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 4.33 (s, 2H), 3.96 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.5, 153.6, 150.8, 134.9, 131.1, 130.4, 128.6, 128.0, 126.1, 125.3, 121.0, 117.2, 116.1, 115.6, 115.3, 102.9, 55.5, 26.1.

Anal. calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3$: C, 77.12; H, 5.75; found C, 77.29; H, 5.83.

Compound 3r: 7-methoxy-1-(thiophen-2-ylmethyl)naphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.03 – 7.00 (m, 2H), 6.95 (d, $J = 8.7$ Hz, 1H), 6.89 (dd, $J = 13.3, 8.5$ Hz, 1H), 5.77 (s, 1H), 4.58 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.7, 143.9, 134.7, 130.2, 128.5, 127.0, 126.9, 125.7, 124.8, 123.5, 117.6, 115.6, 102.4, 55.3, 25.7.

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Anal. calcd. for C₁₆H₁₄O₂S: C, 71.09; H, 5.22; found C, 71.26; H, 5.31.

Compound 3s: 1-([1,1'-biphenyl]-4-ylmethyl)-7-methoxynaphthalen-2-ol

¹H NMR (600 MHz, CDCl₃) δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 3H), 7.20 (s, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 5.11 (s, 1H), 4.44 (s, 2H), 3.82 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.4, 151.8, 141.0, 139.3, 139.0, 135.0, 130.1, 128.7, 128.3, 127.3, 127.0, 124.9, 117.4, 115.4, 102.6, 55.2, 30.7.

Anal. calcd. for C₂₄H₂₀O₂: C, 84.68; H, 5.92; found C, 84.81; H, 6.01.

Compound 3t: 1-(4-chlorobenzyl)-7-methoxynaphthalen-2-ol

¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.31 (t, *J* = 5.9 Hz, 1H), 7.17 (d, *J* = 9.4 Hz, 3H), 7.09 (s, 1H), 6.99 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.95 – 6.92 (m, 1H), 5.00 (s, 1H), 4.36 (s, 2H), 3.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.7, 139.0, 130.3, 129.7, 128.8, 128.7, 128.5, 128.4, 125.0, 117.2, 115.6, 115.3, 102.6, 55.3, 30.4.

Anal. calcd. for C₁₈H₁₅ClO₂: C, 72.36; H, 5.06; found C, 72.51; H, 5.22.

Compound 3u: 1-benzyl-6-bromonaphthalen-2-ol

¹H NMR (600 MHz, CDCl₃) δ 7.93 (s, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 9.1 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.17 (s, 2H), 7.12 (d, *J* = 8.9 Hz, 1H), 5.06 (s, 1H), 4.42 (s, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 151.6, 139.7, 132.4, 130.8, 130.5, 130.0, 128.8, 128.3, 127.7, 126.4, 125.4, 119.1, 118.7, 117.2, 30.8.

The spectroscopic data were in consistant with literature.⁹

Compound 3v: 6-bromo-1-(4-methoxybenzyl)naphthalen-2-ol

¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.48 (d, *J* = 10.8 Hz, 1H), 7.09 (dd, *J* = 12.2, 8.7 Hz, 3H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.11 (s, 1H), 4.34 (s, 2H), 3.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.7, 136.5, 136.0, 132.4, 130.8, 130.5, 130.0, 129.5, 128.1, 127.7, 125.4, 119.2, 118.9, 117.1, 30.4, 21.1.

Anal. calcd. for C₁₈H₁₅BrO₂: C, 62.99; H, 4.41; found C, 63.19; H, 4.53.

Compound 3w: 6-bromo-1-(4-methylbenzyl)naphthalen-2-ol

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.09 – 6.99 (m, 4H), 5.07 (s, 1H), 4.37 (s, 2H), 2.28 (s, 3H).

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^{13}C NMR (101 MHz, CDCl_3) δ 158.3, 151.7, 132.4, 131.7, 130.9, 130.6, 130.0, 129.2, 127.7, 125.4, 119.14, 119.07, 117.1, 114.3, 55.4, 30.0.

Anal. calcd. for $\text{C}_{18}\text{H}_{15}\text{BrO}$: C, 66.07; H, 4.62; found C, 66.17; H, 4.71.

Compound 3x: 6-bromo-1-(thiophen-2-ylmethyl)naphthalen-2-ol

^1H NMR (600 MHz, CDCl_3) δ 7.93 (s, 1H), 7.83 (d, $J = 9.1$ Hz, 1H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.52 (d, $J = 9.0$ Hz, 1H), 7.13 – 7.08 (m, 2H), 6.86 (t, $J = 4.2$ Hz, 1H), 6.75 (s, 1H), 5.16 (s, 1H), 4.56 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.3, 142.9, 131.9, 130.8, 130.6, 130.1, 128.0, 127.0, 125.1, 125.0, 124.0, 119.1, 118.7, 117.3, 25.5.

Anal. calcd. for $\text{C}_{15}\text{H}_{11}\text{BrOS}$: C, 56.44; H, 3.47; found C, 56.52; H, 3.45

Compound 3y: 1-([1,1'-biphenyl]-4-ylmethyl)naphthalene-2,7-diol

^1H NMR (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.7$ Hz, 1H), 7.64 (d, $J = 8.7$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 4H), 6.96 (d, $J = 5.8$ Hz, 1H), 5.00 (d, $J = 6.9$ Hz, 2H), 4.40 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 154.5, 152.0, 141.1, 139.3, 139.1, 135.3, 130.7, 128.84, 128.8, 128.7, 128.6, 128.6, 127.5, 127.49, 127.19, 127.16, 127.1, 125.1, 116.8, 115.6, 115.1, 106.0, 30.6.

Anal. calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_2$: C, 84.64; H, 5.56; found: C, 84.73; H, 5.63.

Compound 3z: methyl 6-hydroxy-5-(4-methoxybenzyl)-2-naphthoate

^1H NMR (600 MHz, MeOD) δ 8.48 (s, 1H), 7.89 (q, $J = 8.9$ Hz, 2H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 1H), 7.11 (d, $J = 8.3$ Hz, 2H), 6.75 (d, $J = 8.3$ Hz, 2H), 4.36 (s, 2H), 3.93 (s, 3H), 3.71 (s, 3H).

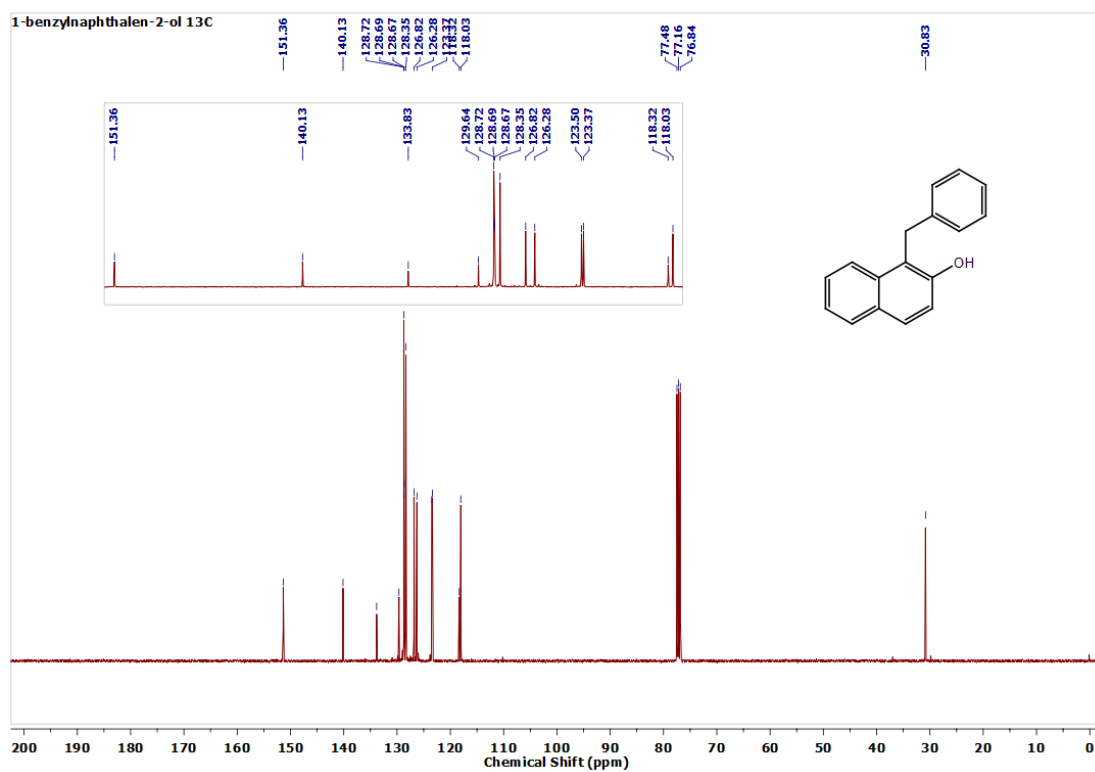
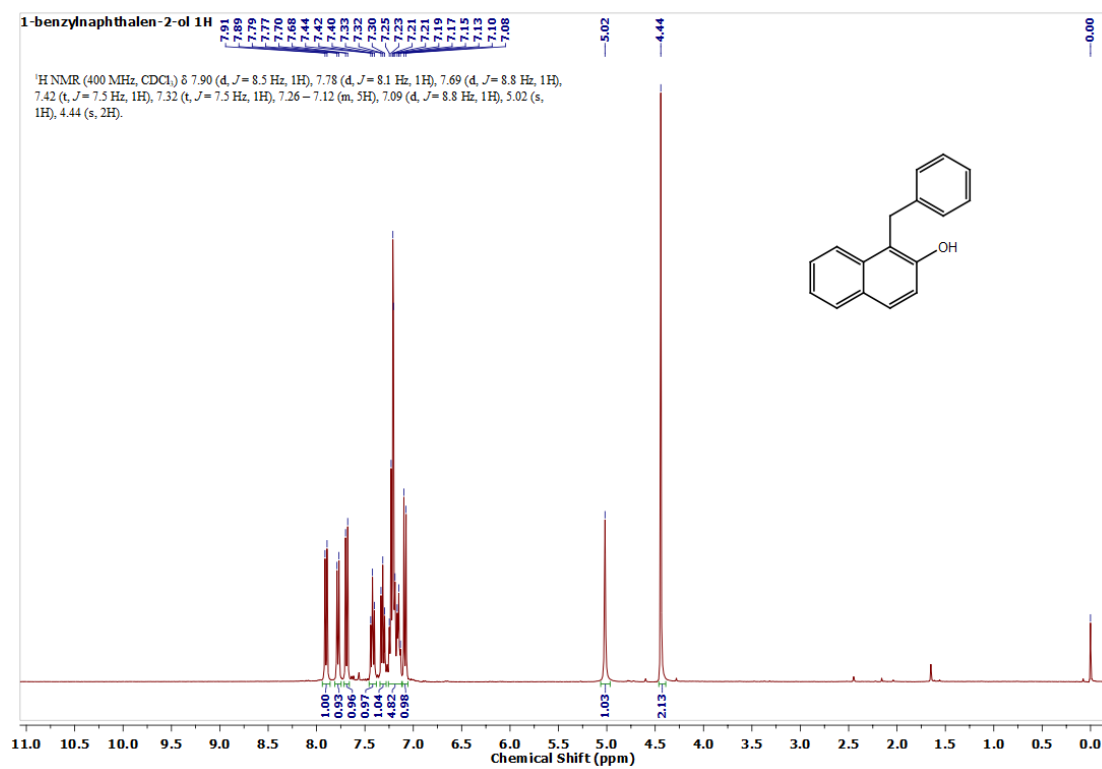
^{13}C NMR (151 MHz, MeOD) δ 169.0, 159.2, 156.3, 137.7, 134.4, 132.6, 130.6, 130.2, 129.2, 126.2, 124.9, 124.7, 120.4, 119.8, 114.6, 55.6, 52.5, 30.4.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_4$ $[\text{M}+\text{H}]^+$: 323.1278, found 323.1273.

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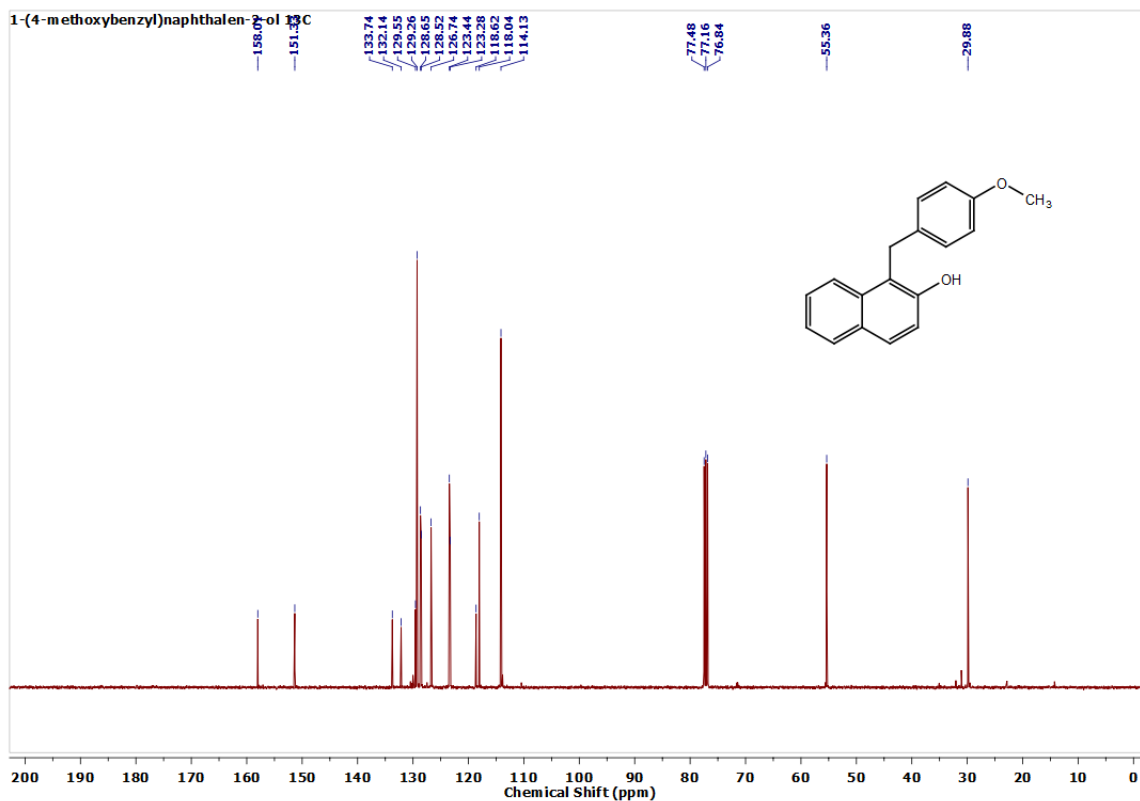
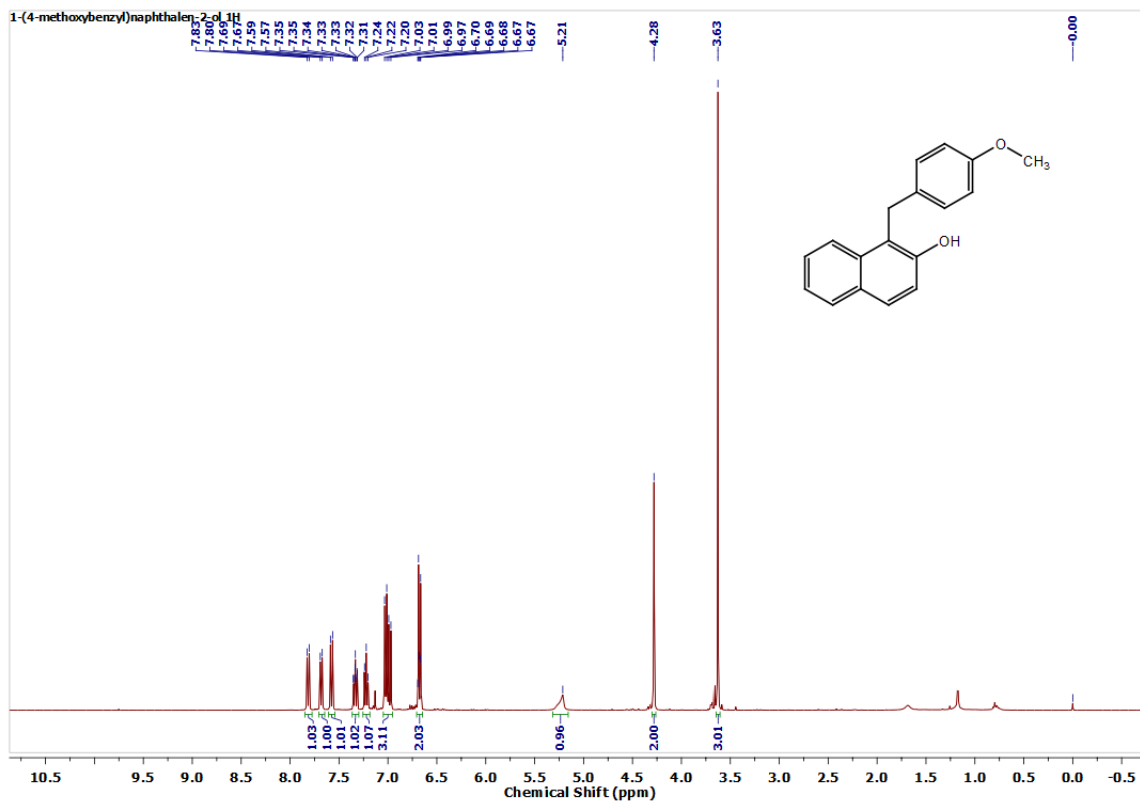
❖ NMR Spectra of Compounds

Compound 3a: 1-benzyl-naphthalen-2-ol



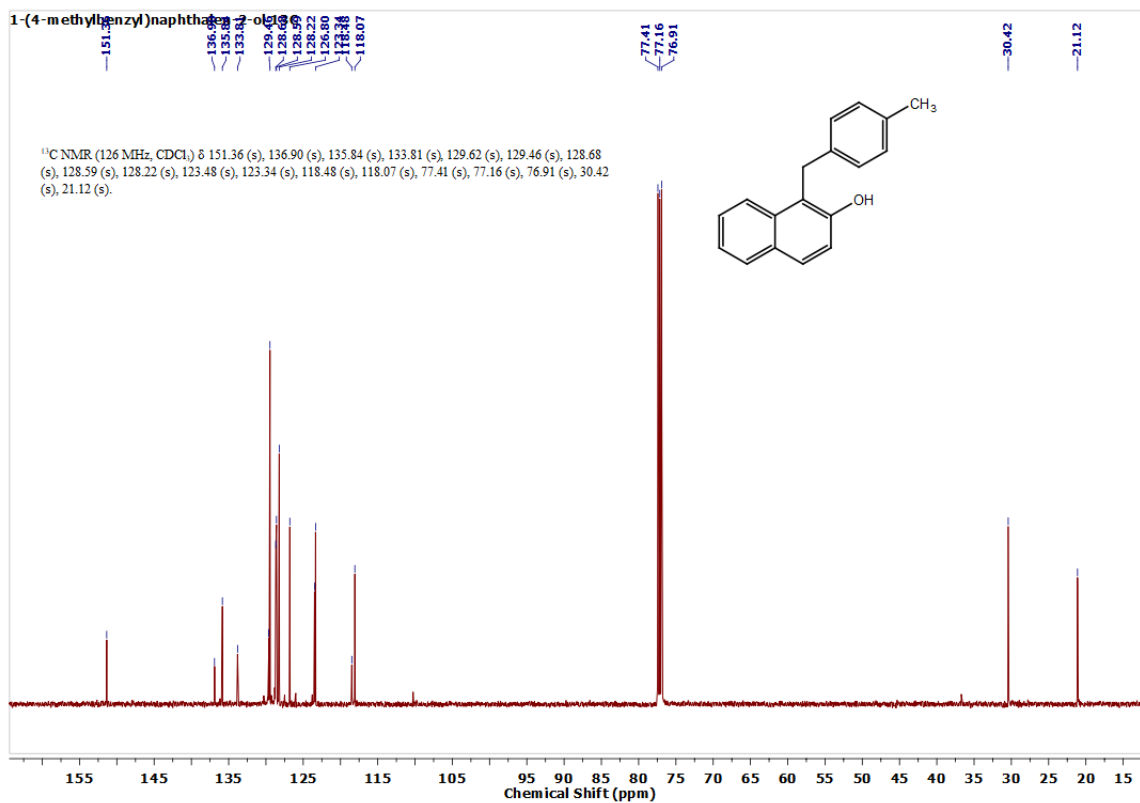
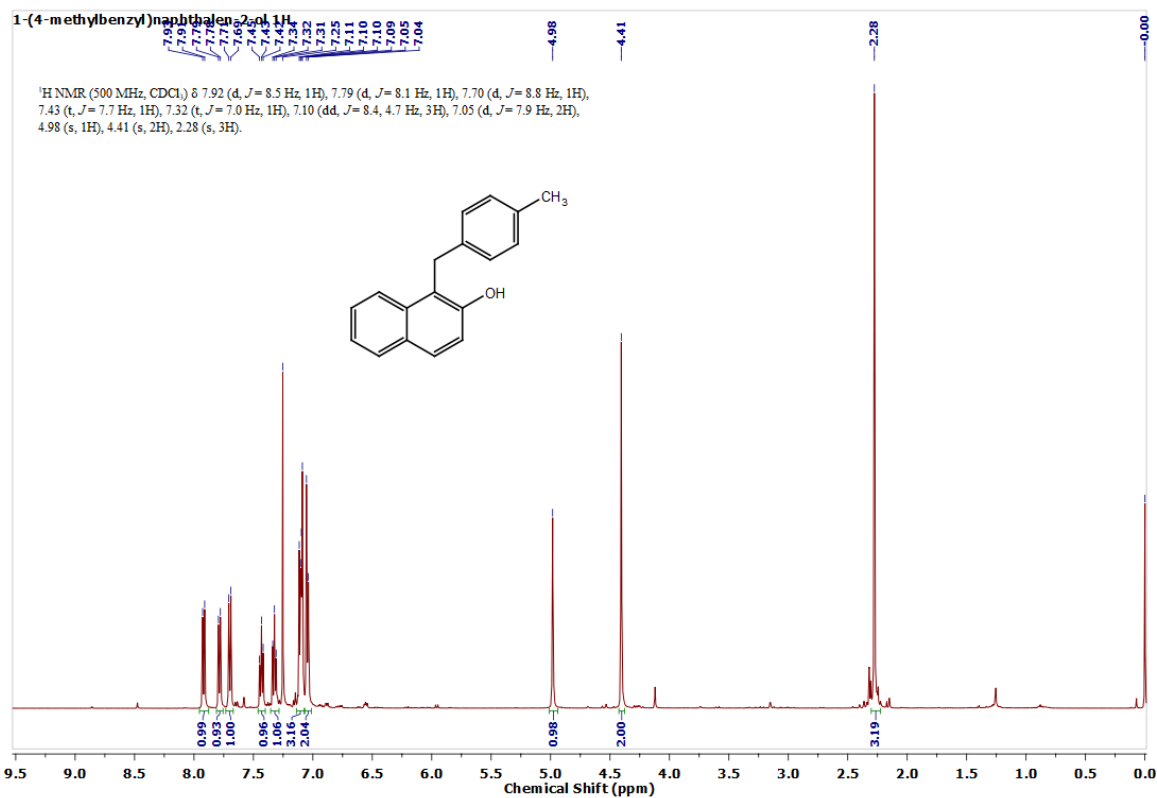
Electronic Supplementary Information

Compound 3b: 1-(4-methoxybenzyl)naphthalen-2-ol



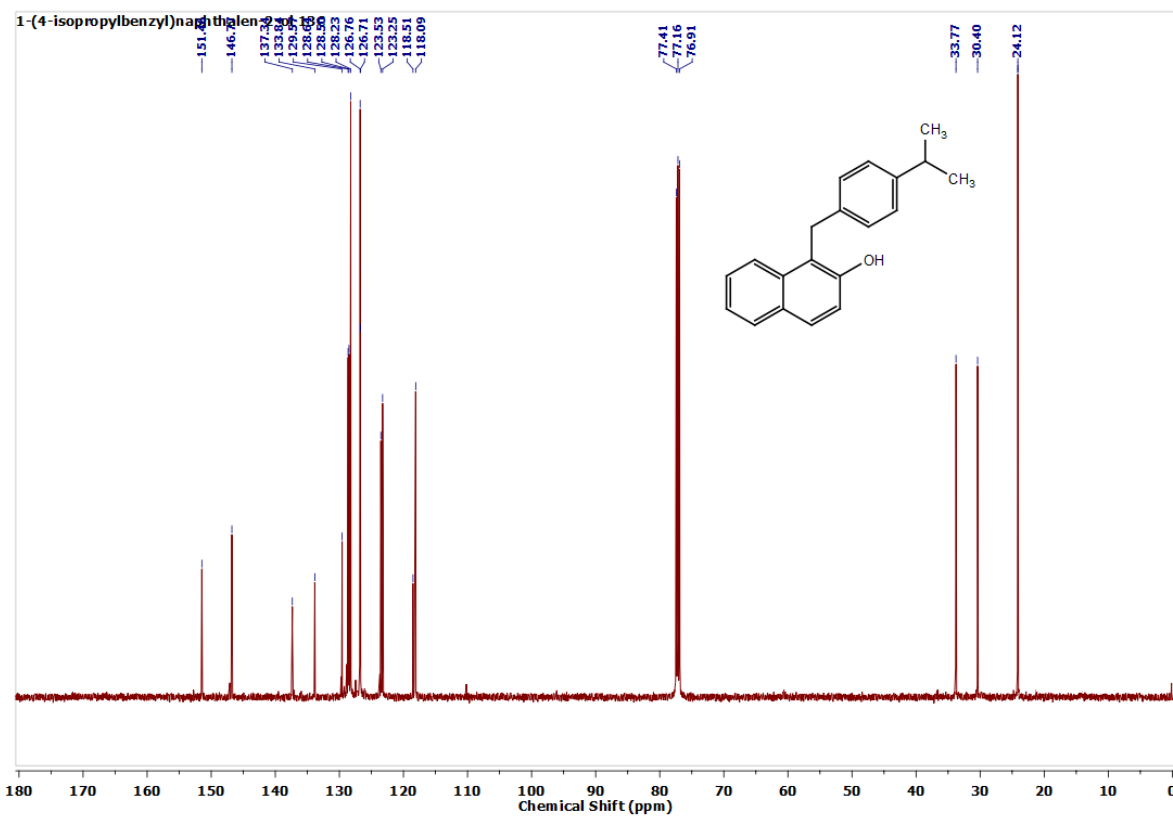
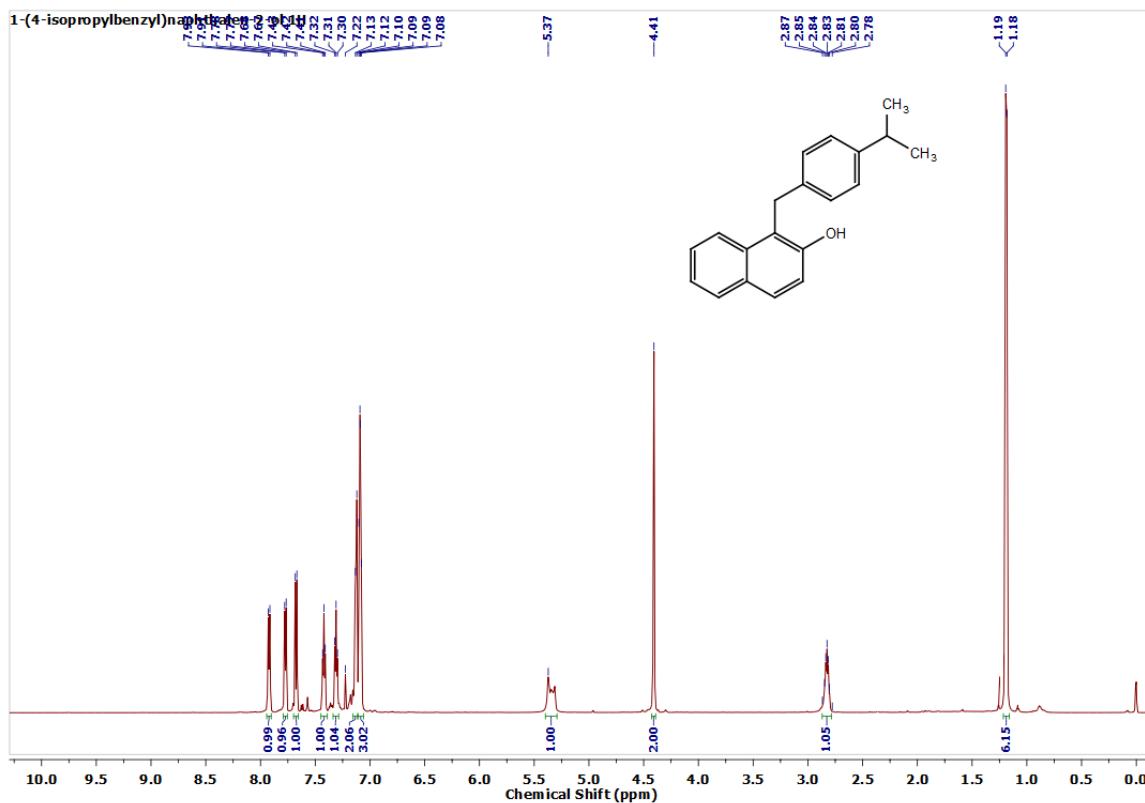
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Compound 3c: 1-(4-methylbenzyl)naphthalen-2-ol



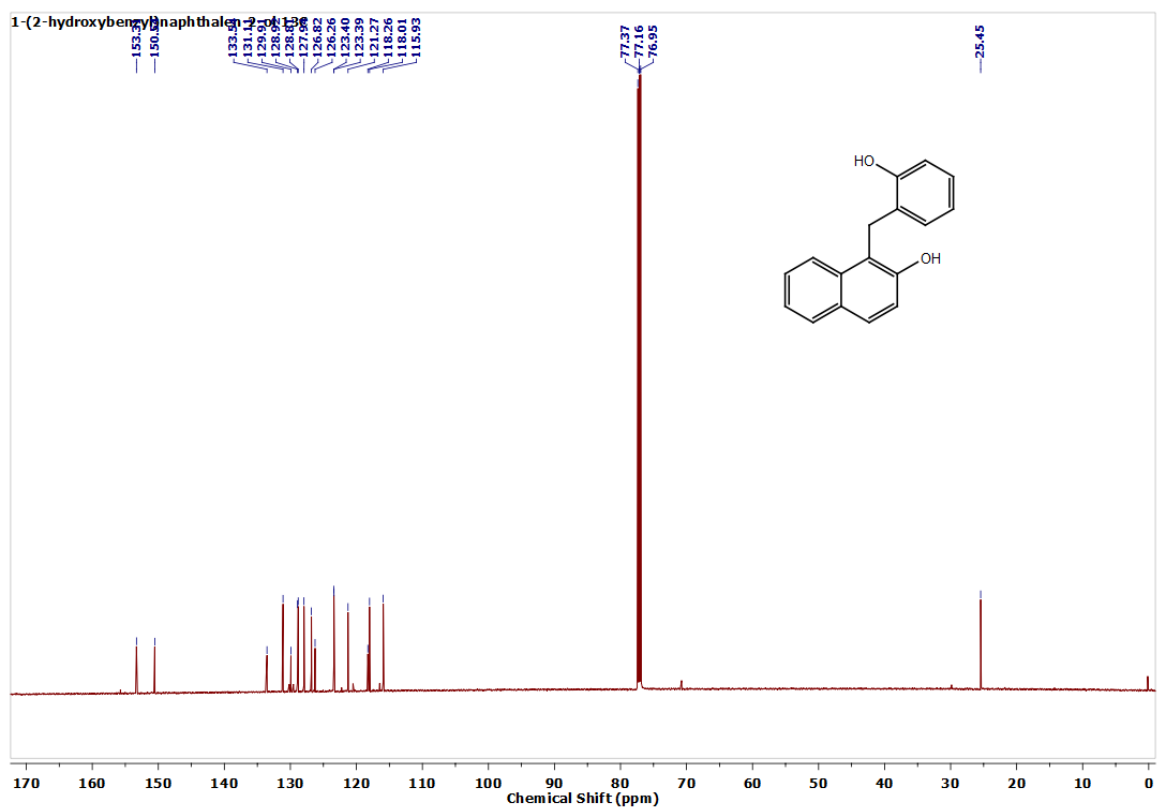
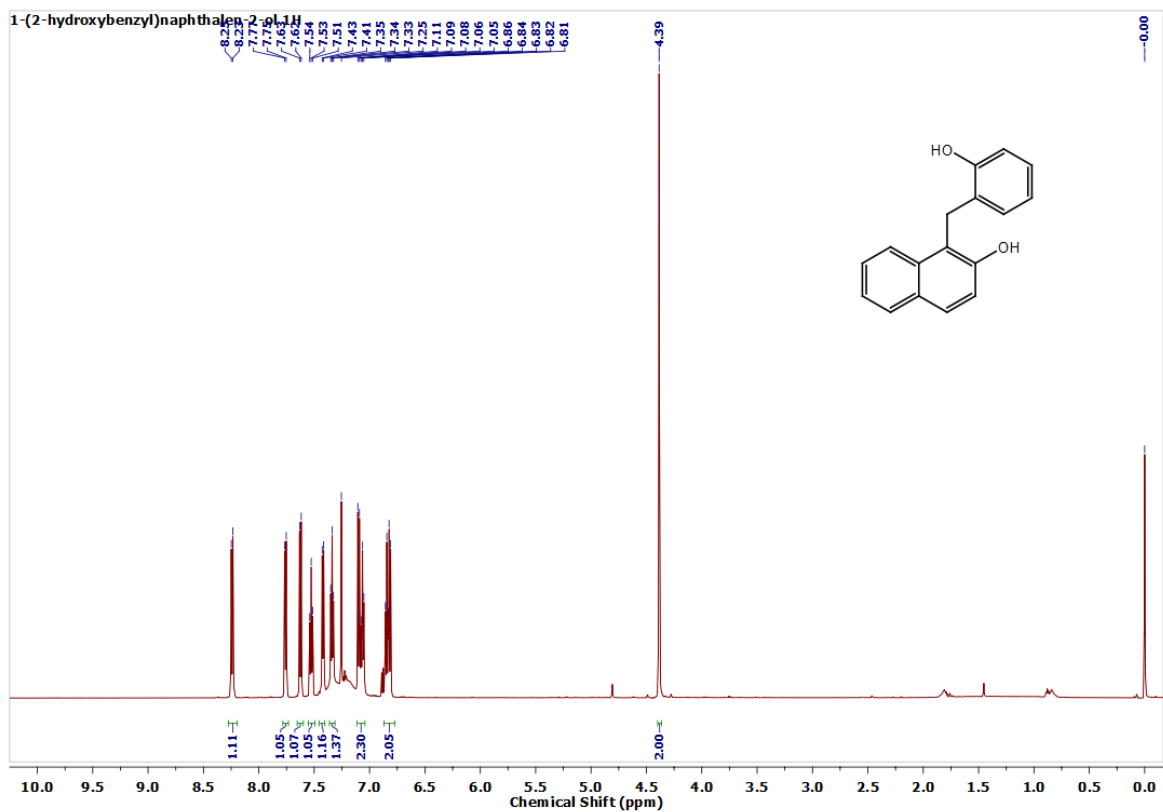
Electronic Supplementary Information

Compound 3d: 1-(4-isopropylbenzyl)naphthalen-2-ol



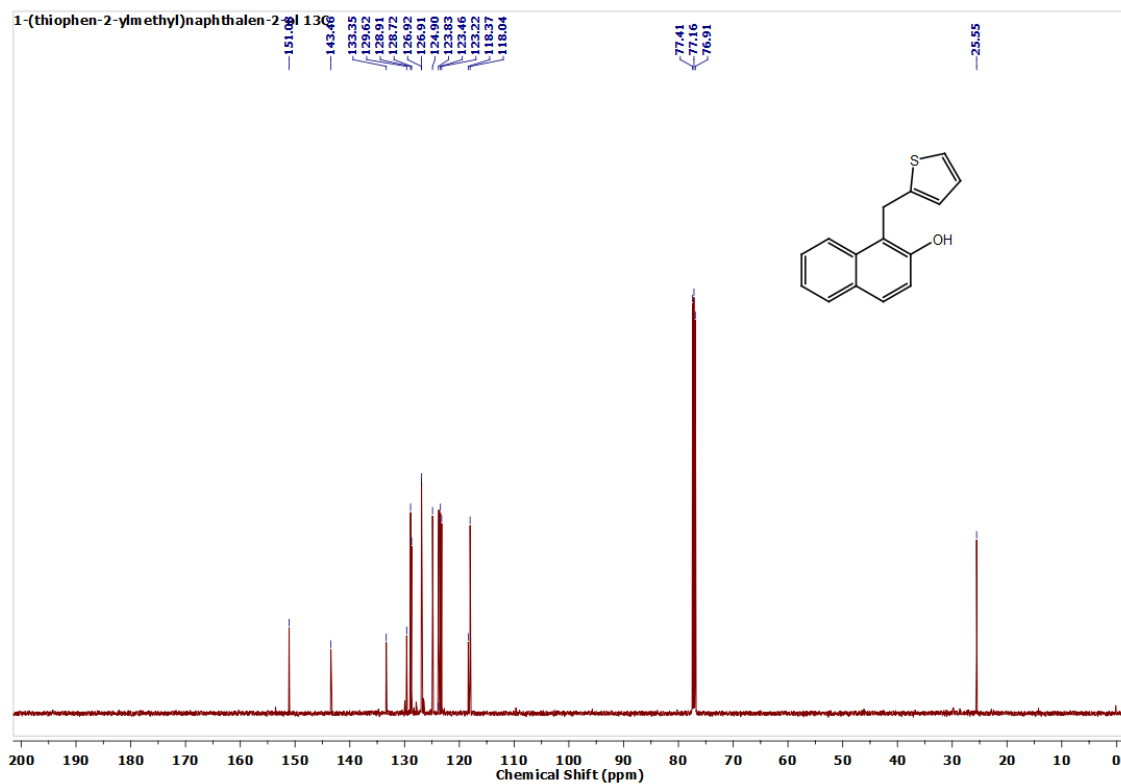
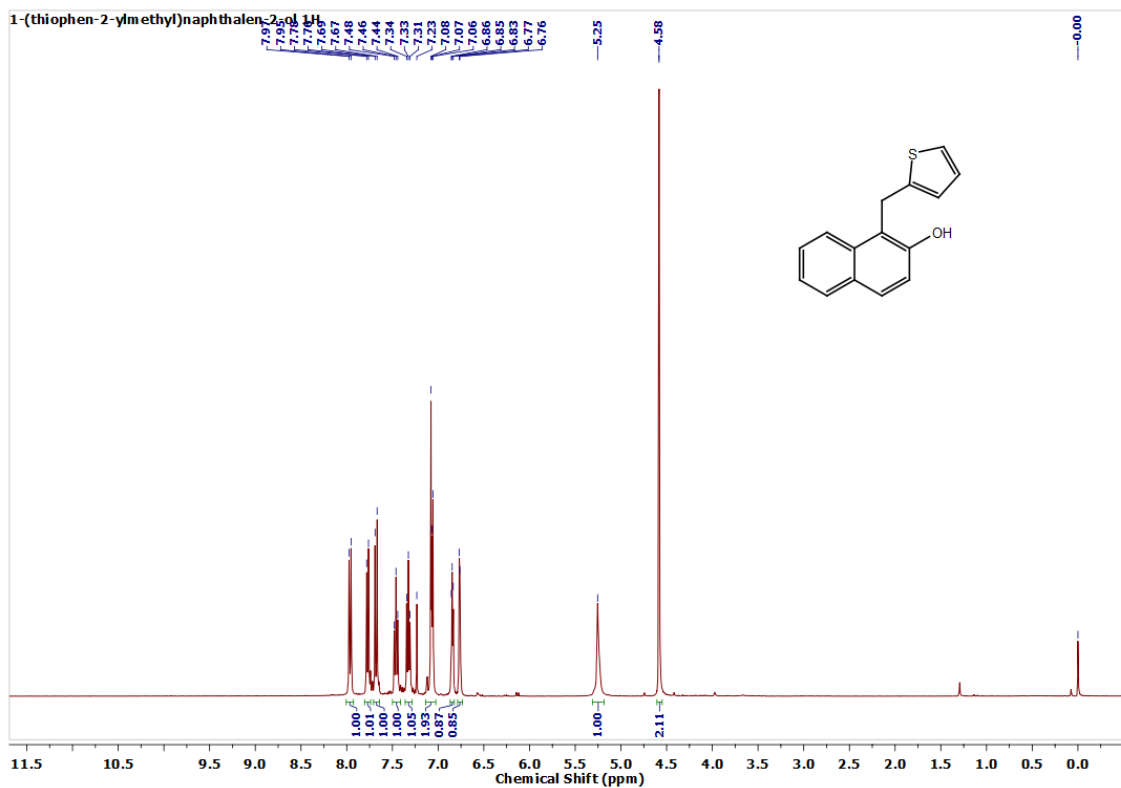
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Compound 3e: 1-(2-hydroxybenzyl)naphthalen-2-ol



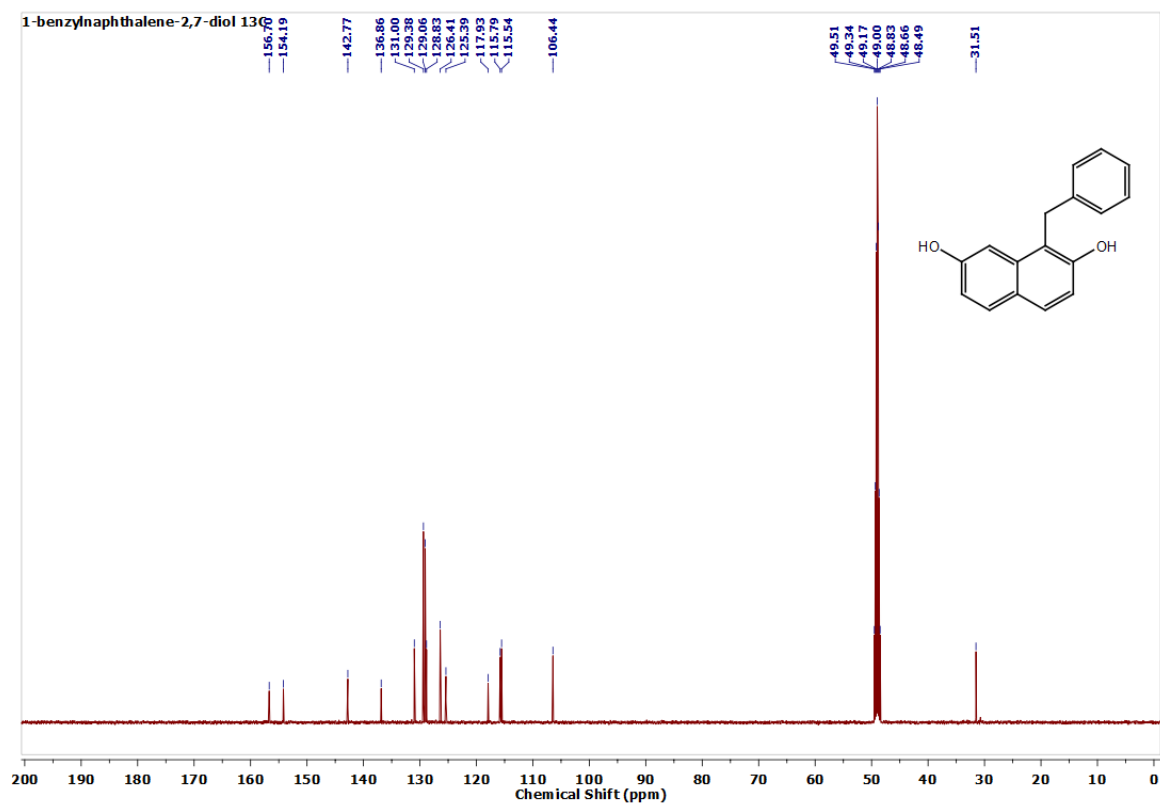
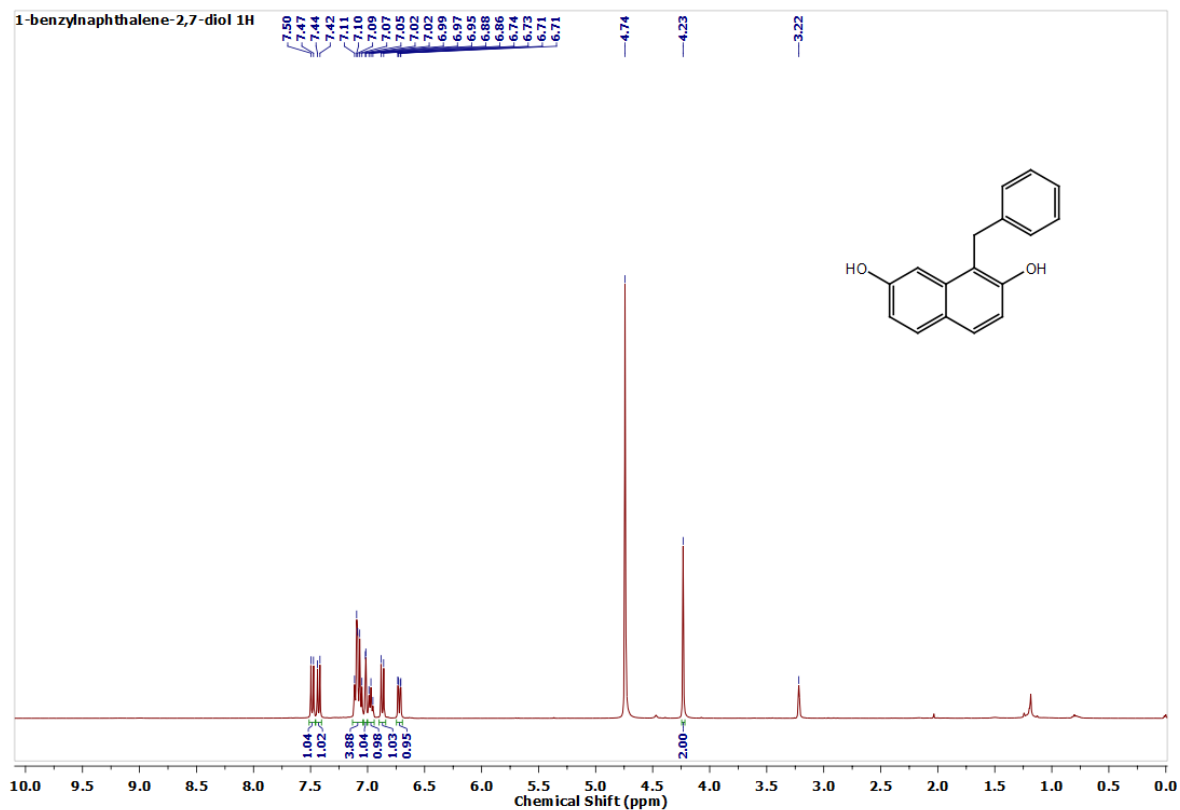
Electronic Supplementary Information

Compound 3f: 1-(thiophen-2-ylmethyl)naphthalen-2-ol



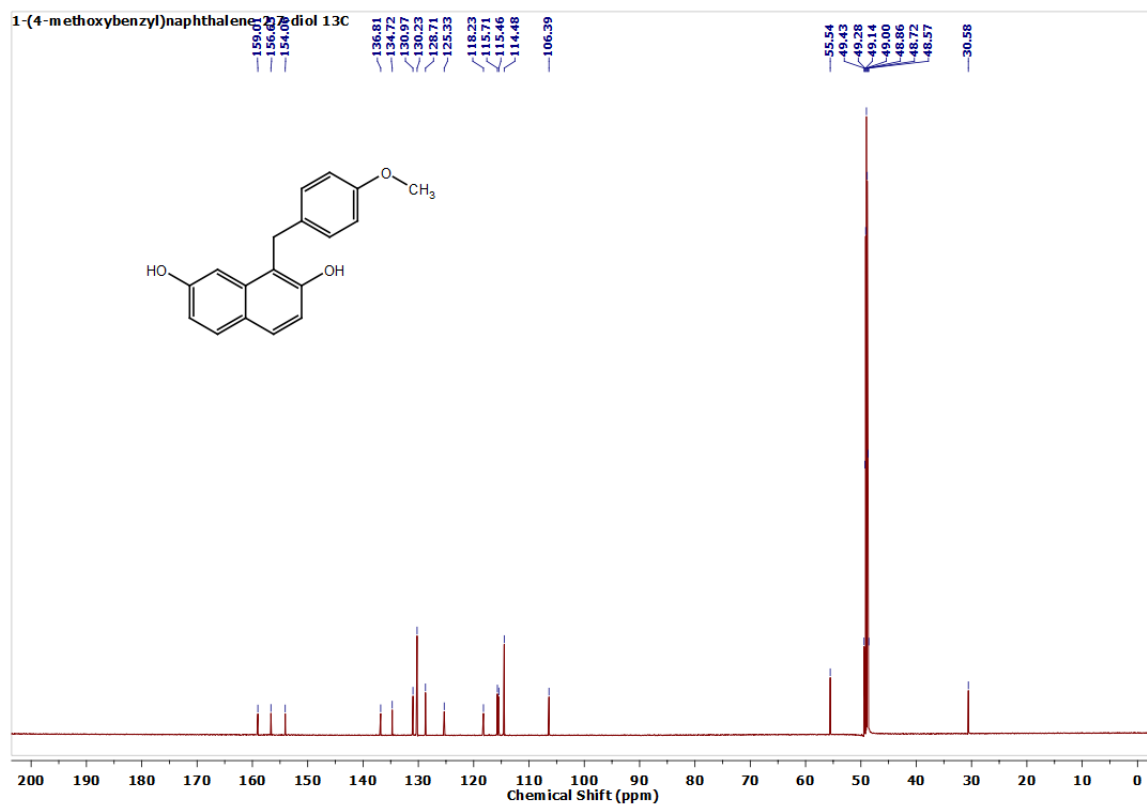
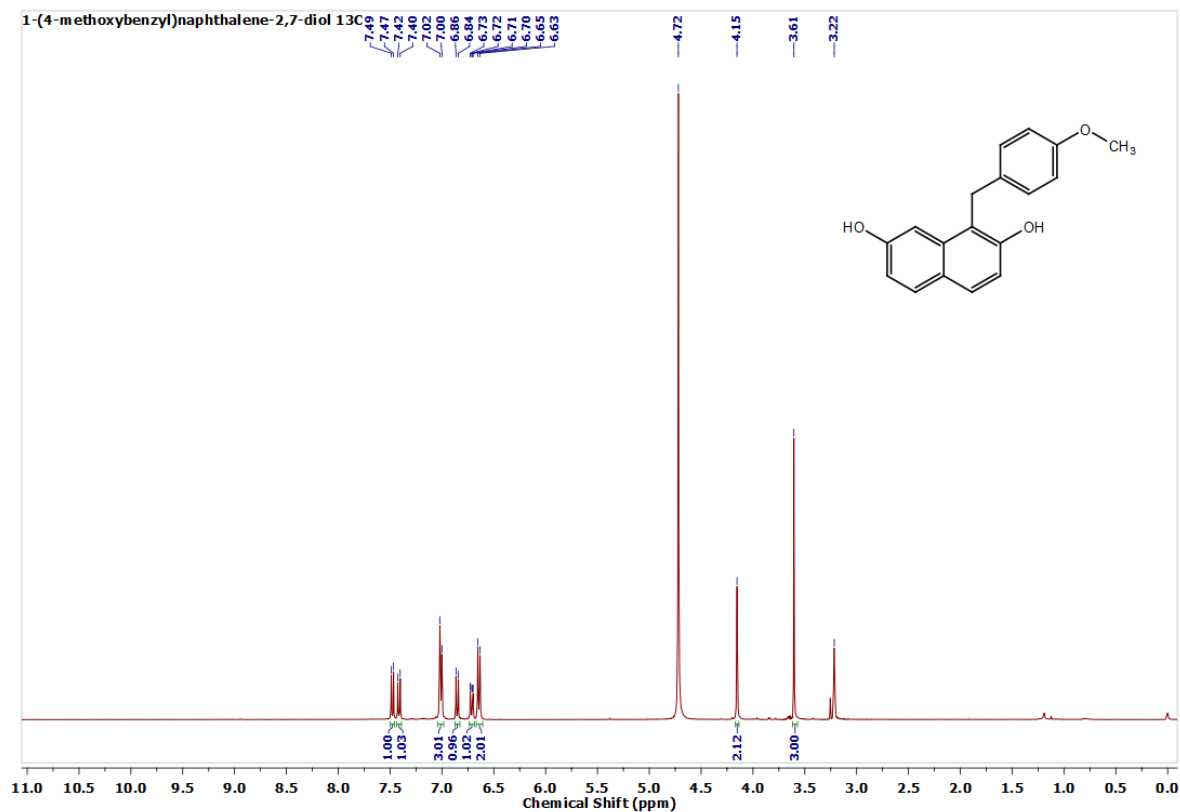
Electronic Supplementary Information

Compound 3g: 1-benzyl-naphthalene-2,7-diol



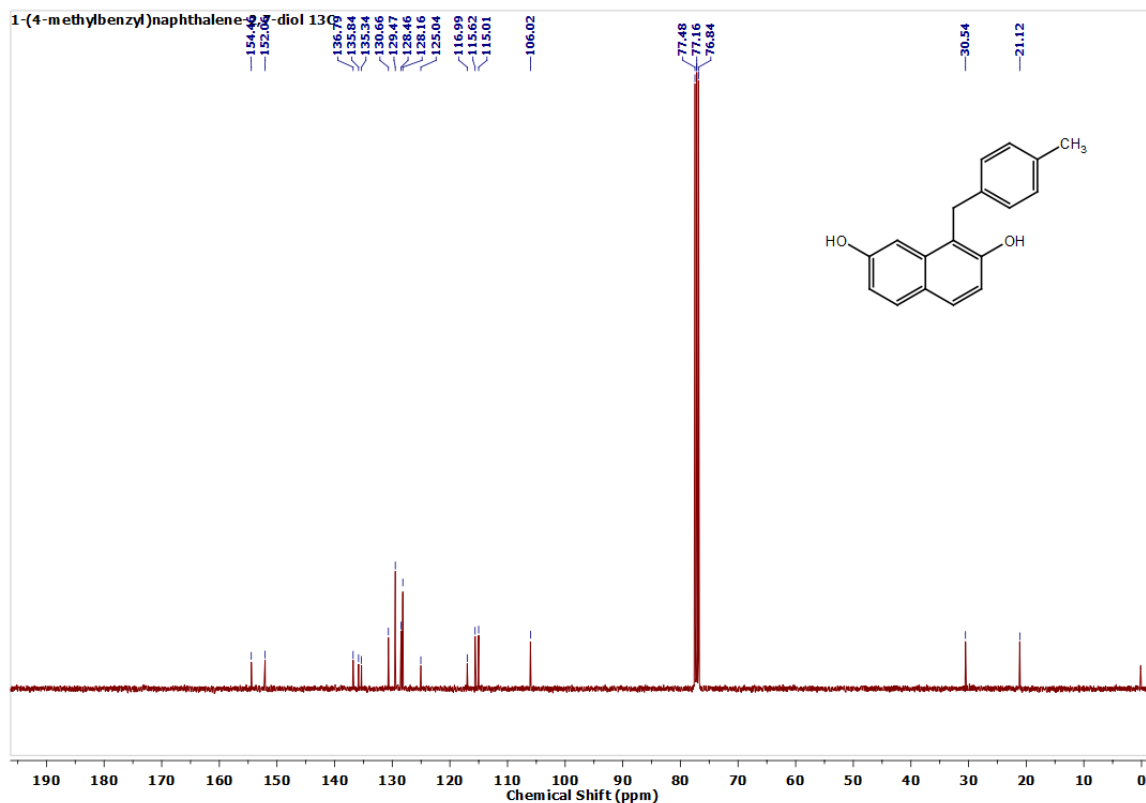
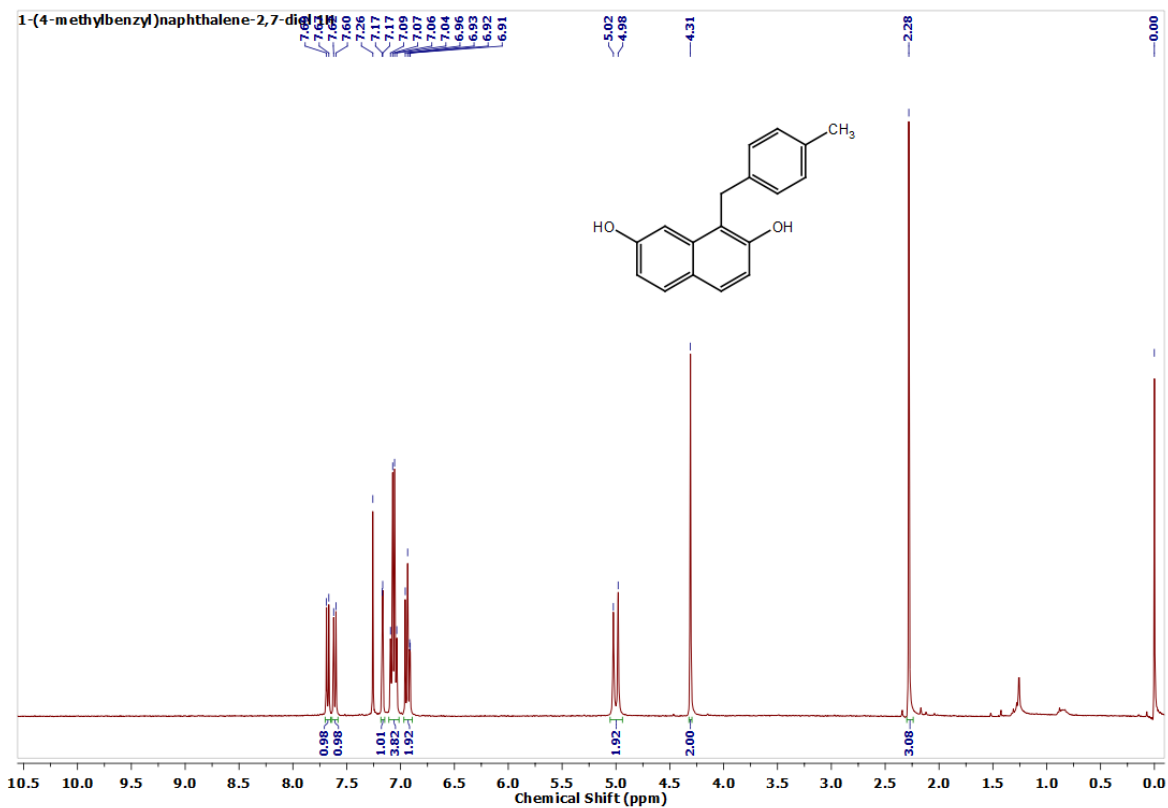
Electronic Supplementary Information

Compound 3h: 1-(4-methoxybenzyl)naphthalene-2,7-diol



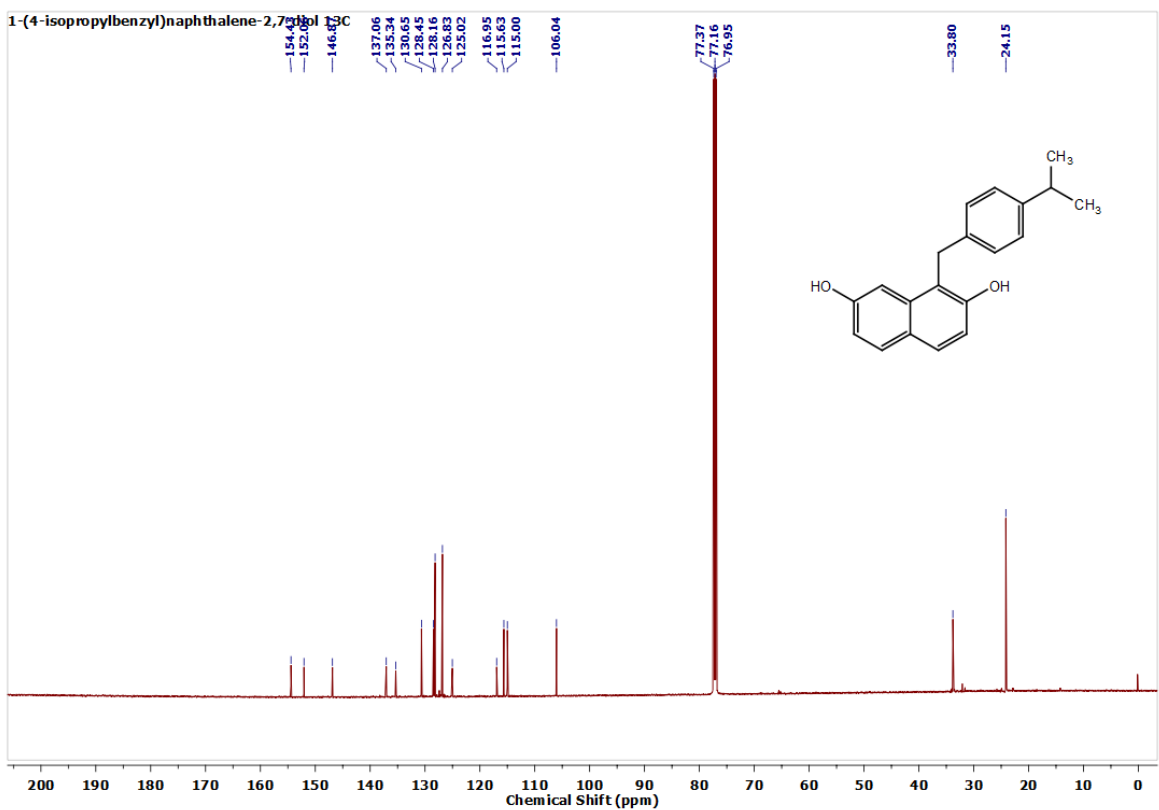
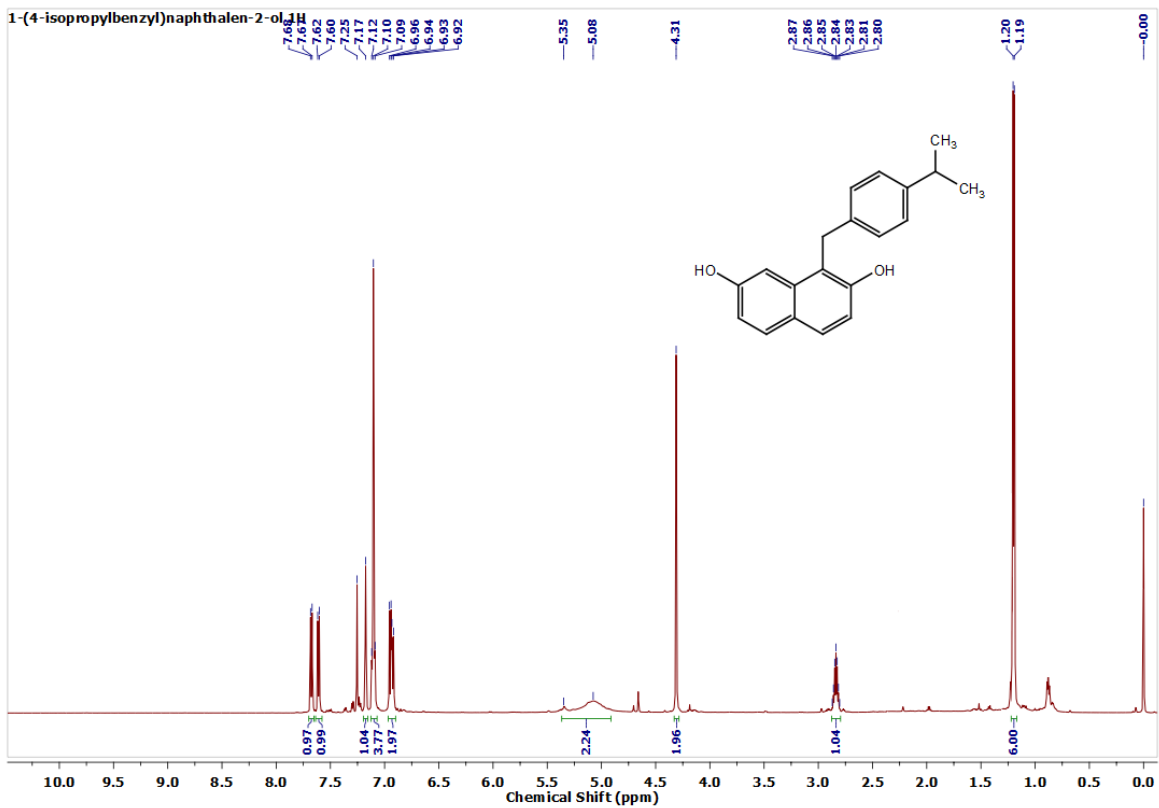
Electronic Supplementary Information

Compound 3i: 1-(4-methylbenzyl)naphthalene-2,7-diol



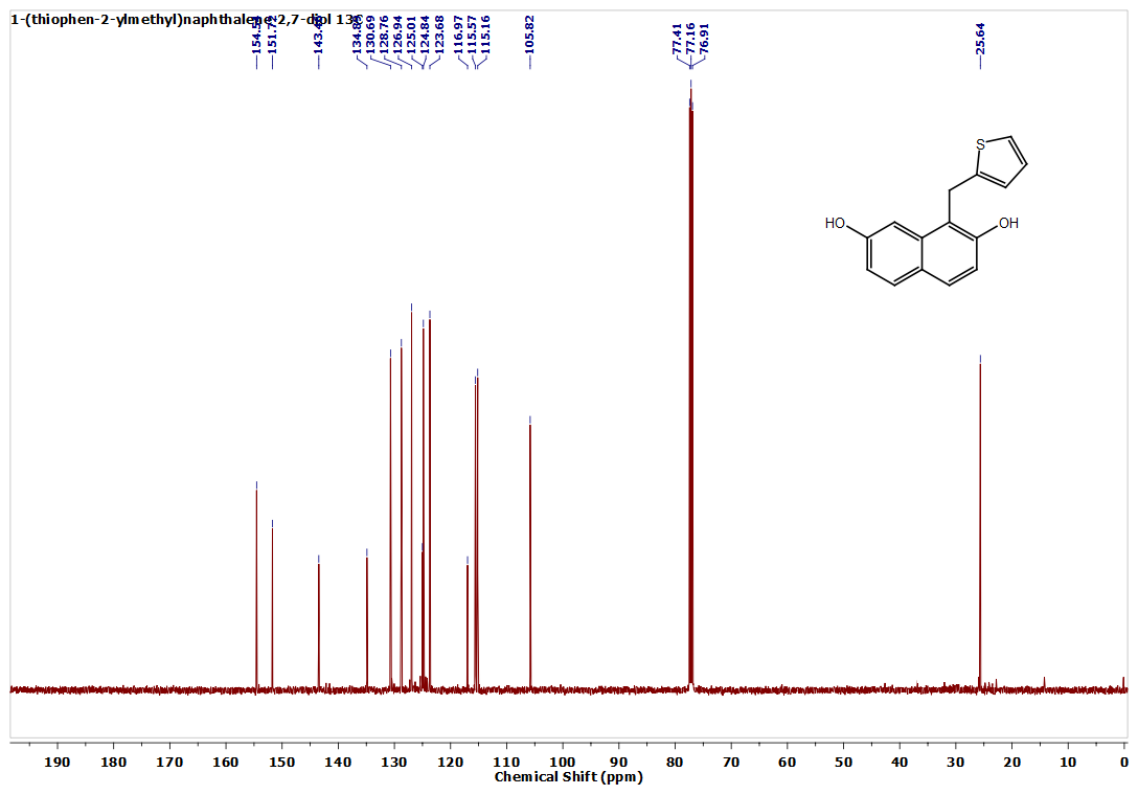
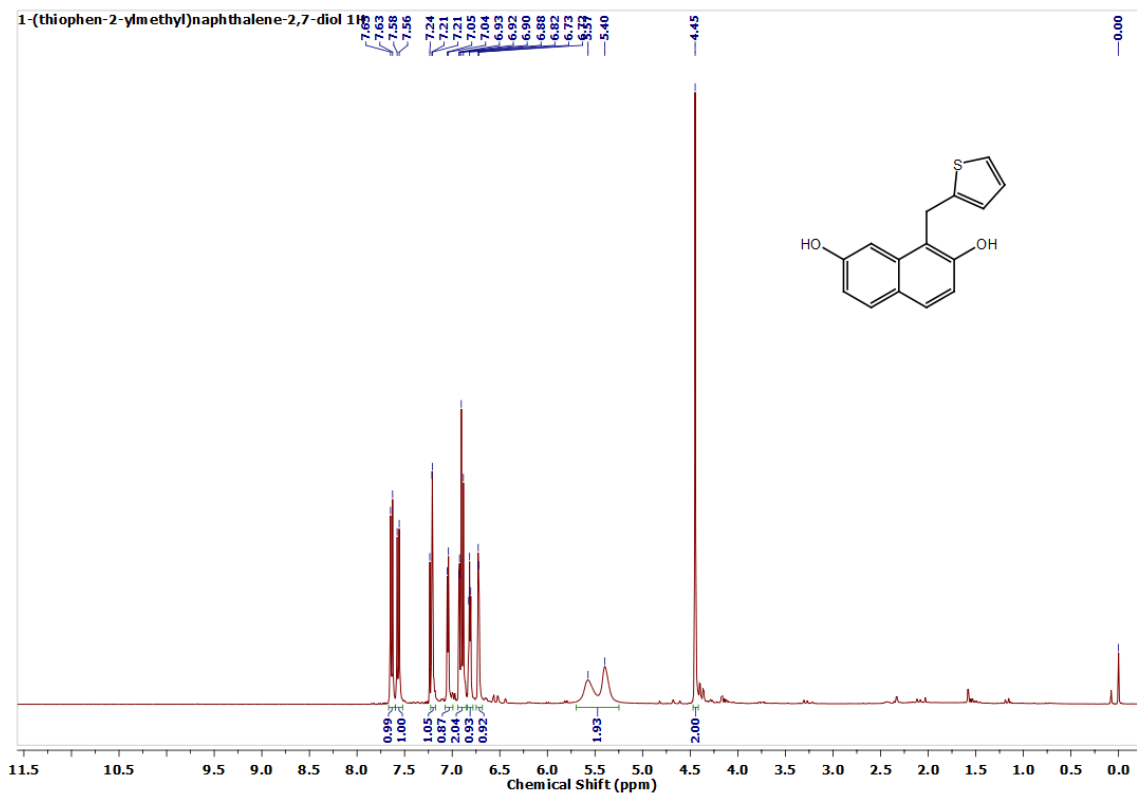
Electronic Supplementary Information

Compound 3j: 1-(4-isopropylbenzyl)naphthalene-2,7-diol



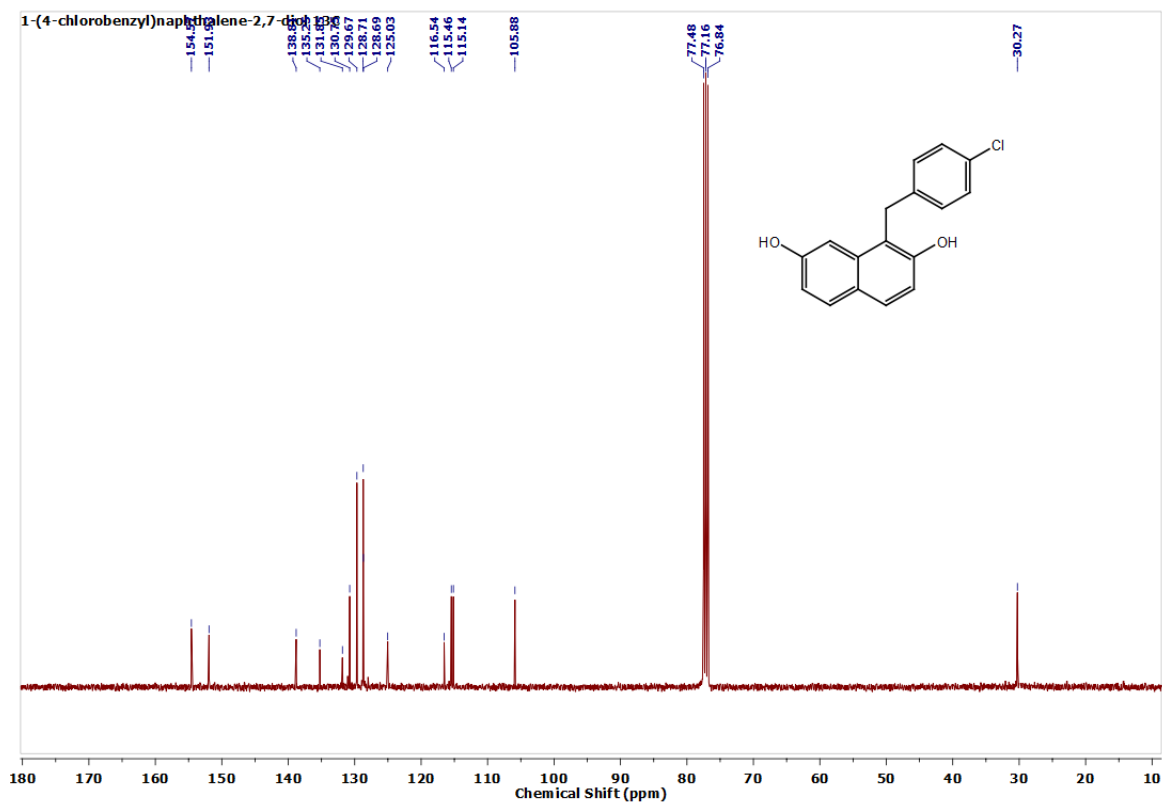
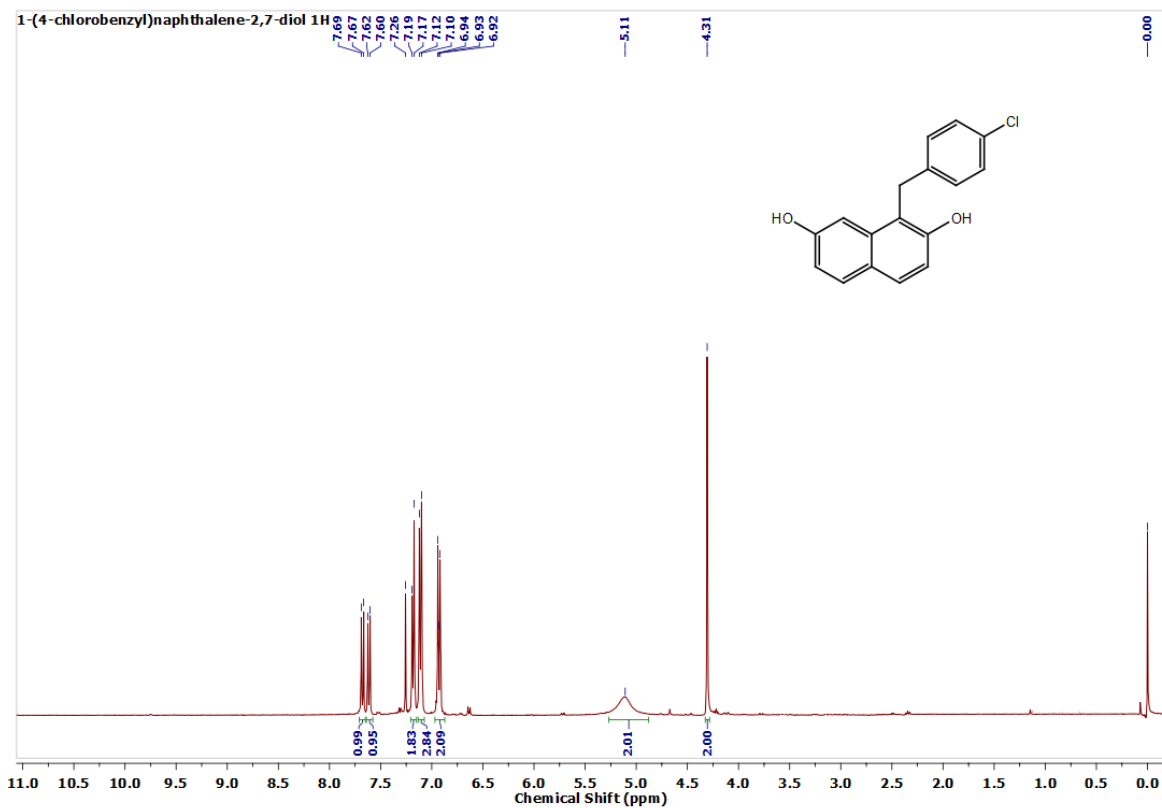
Electronic Supplementary Information

Compound 3k: 1-(thiophen-2-ylmethyl)naphthalene-2,7-diol



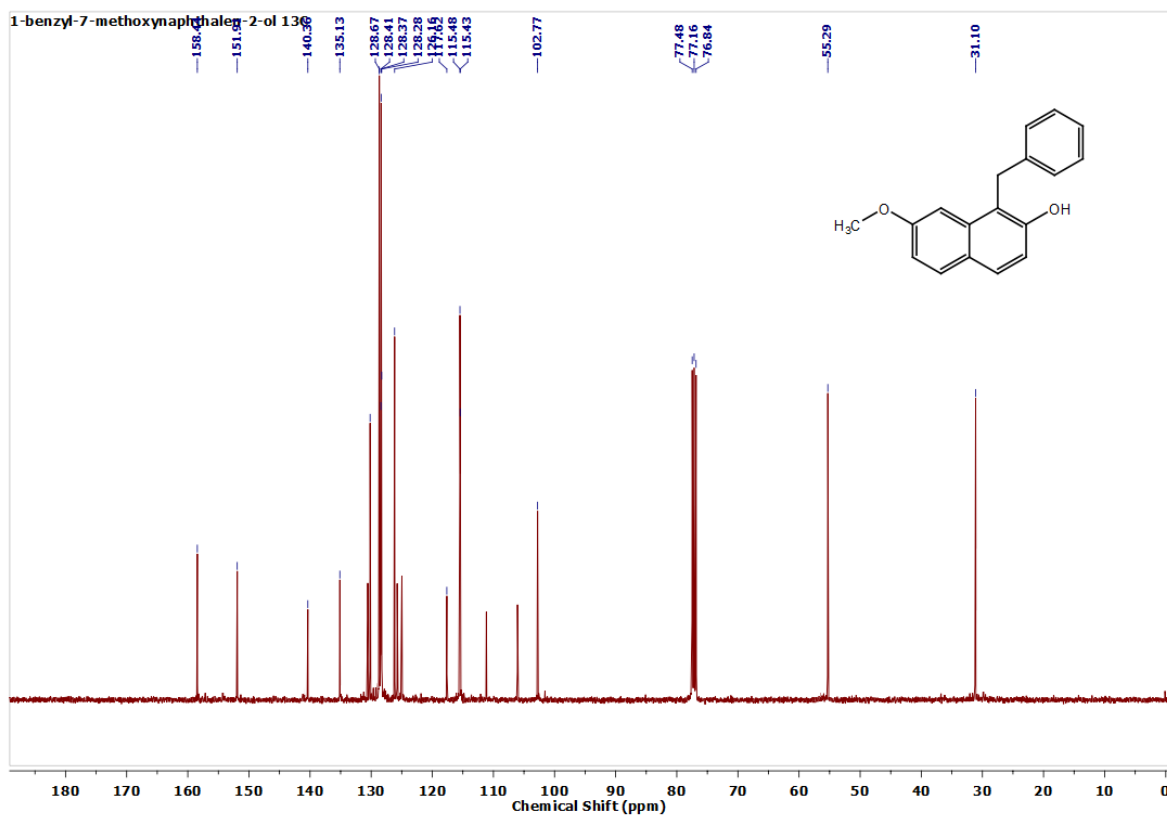
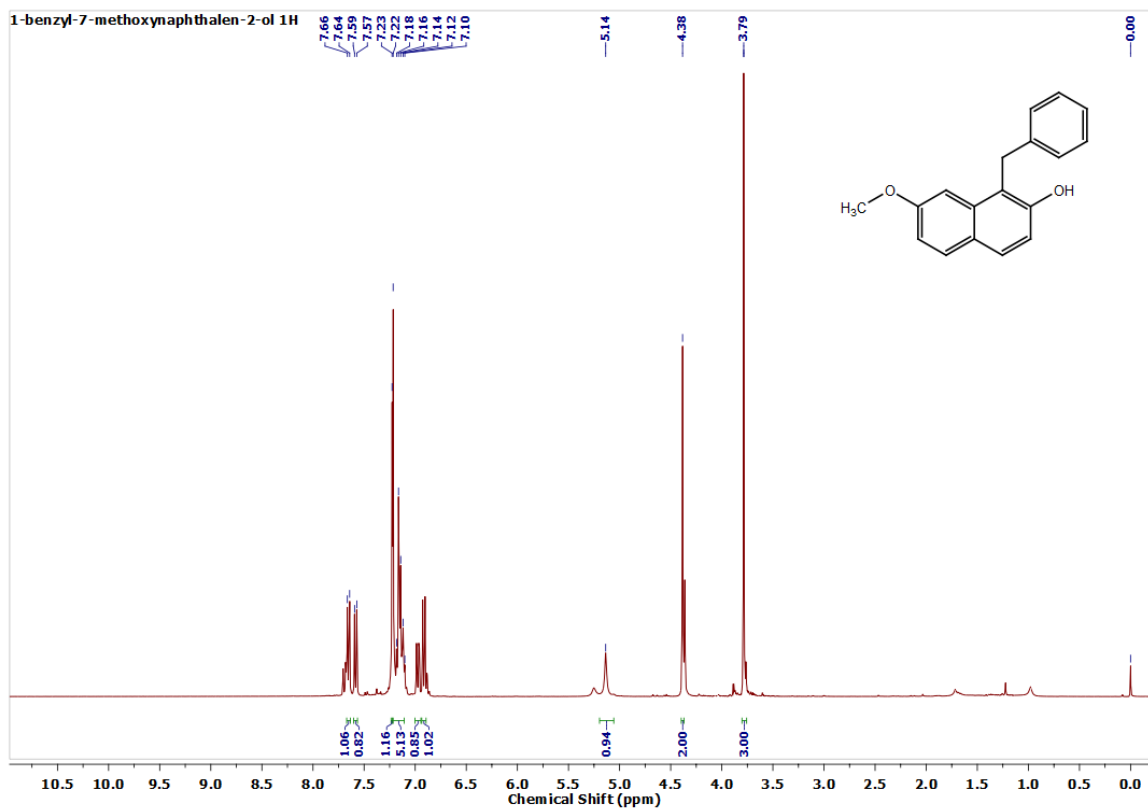
Electronic Supplementary Information

Compound 3l: 1-(4-chlorobenzyl)naphthalene-2,7-diol



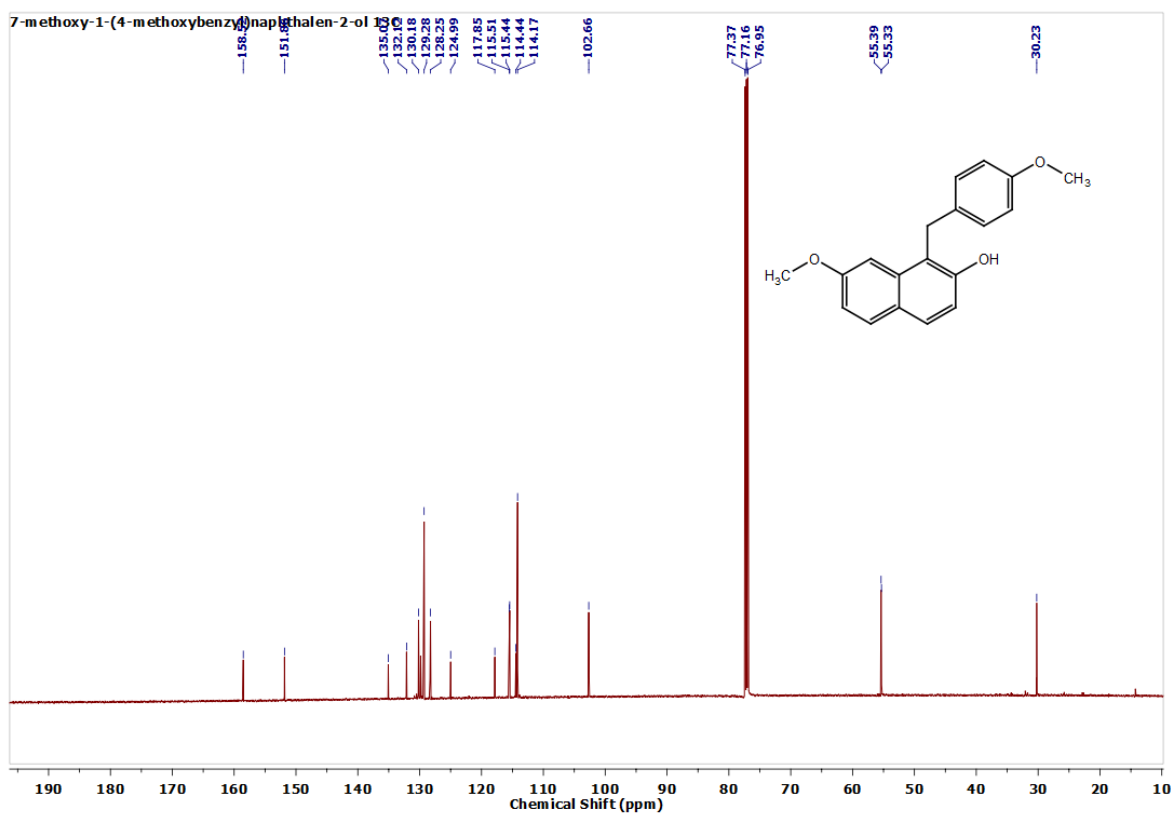
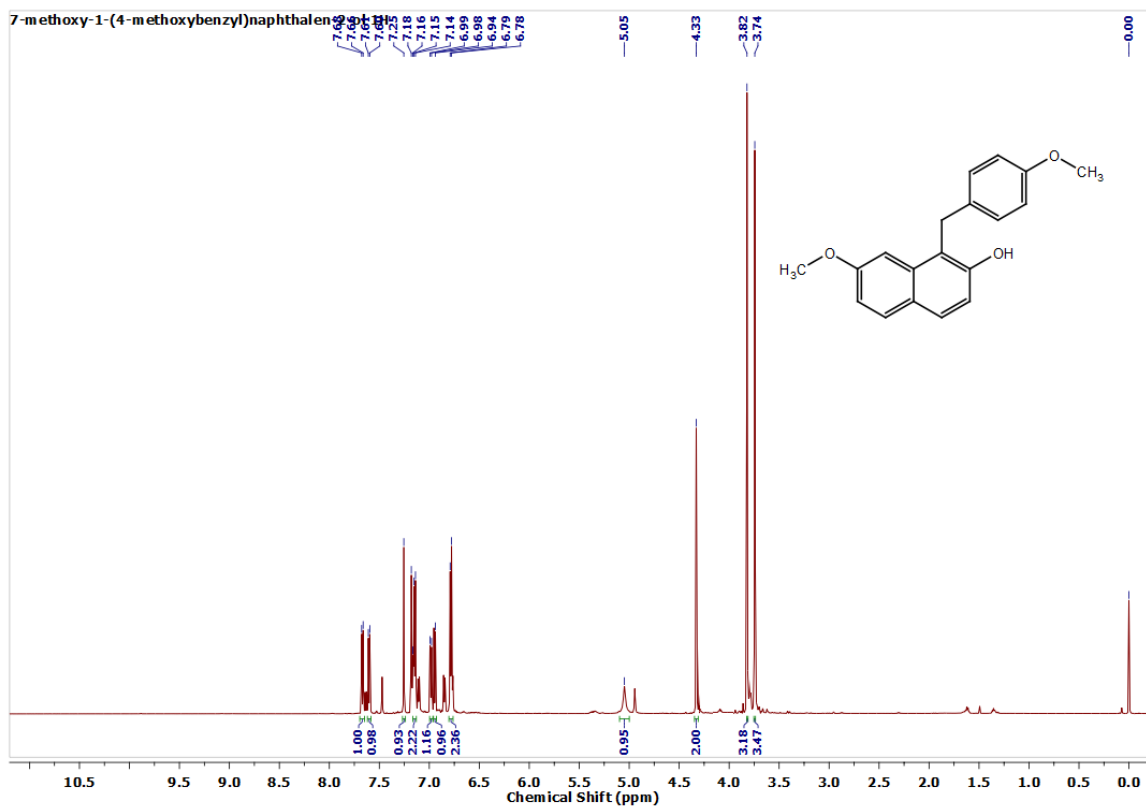
Electronic Supplementary Information

Compound 3m: 1-benzyl-7-methoxynaphthalen-2-ol



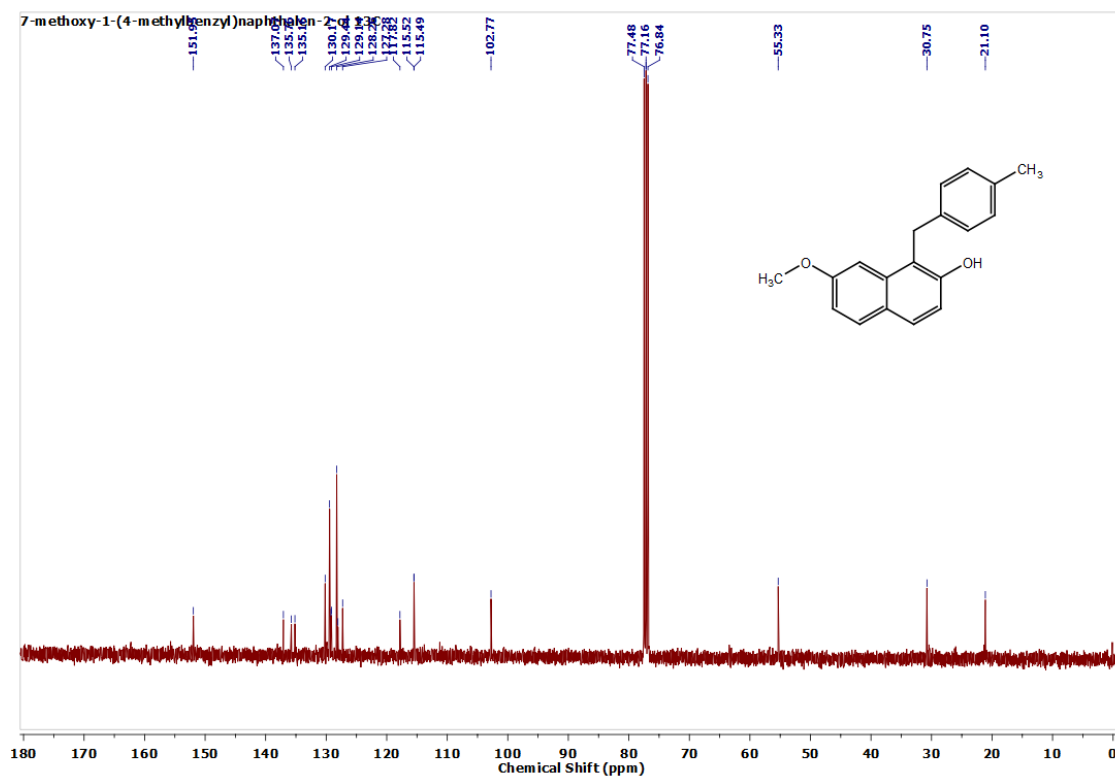
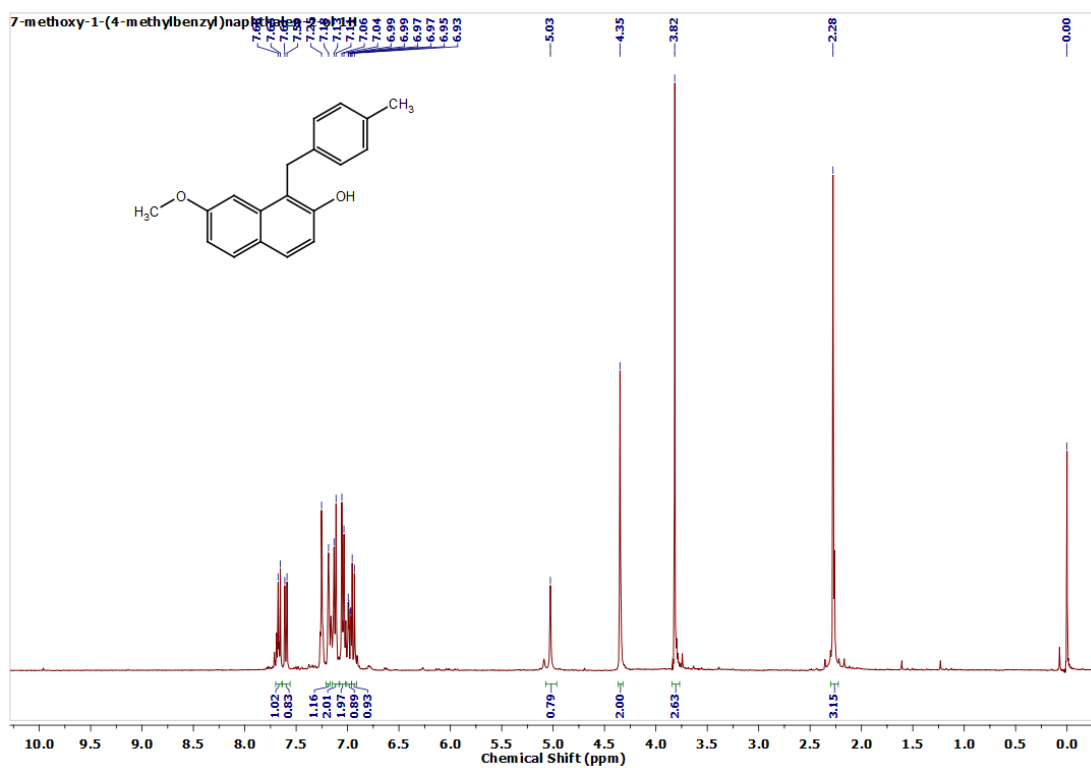
Electronic Supplementary Information

Compound 3n: 7-methoxy-1-(4-methoxybenzyl)naphthalen-2-ol



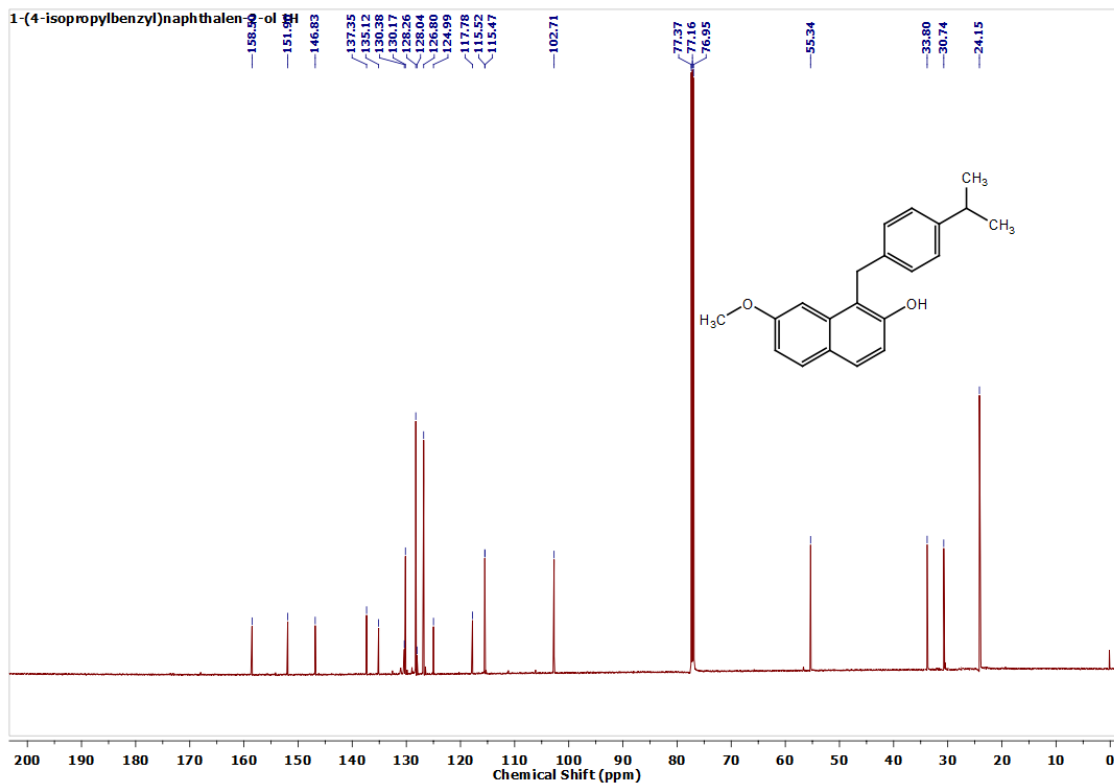
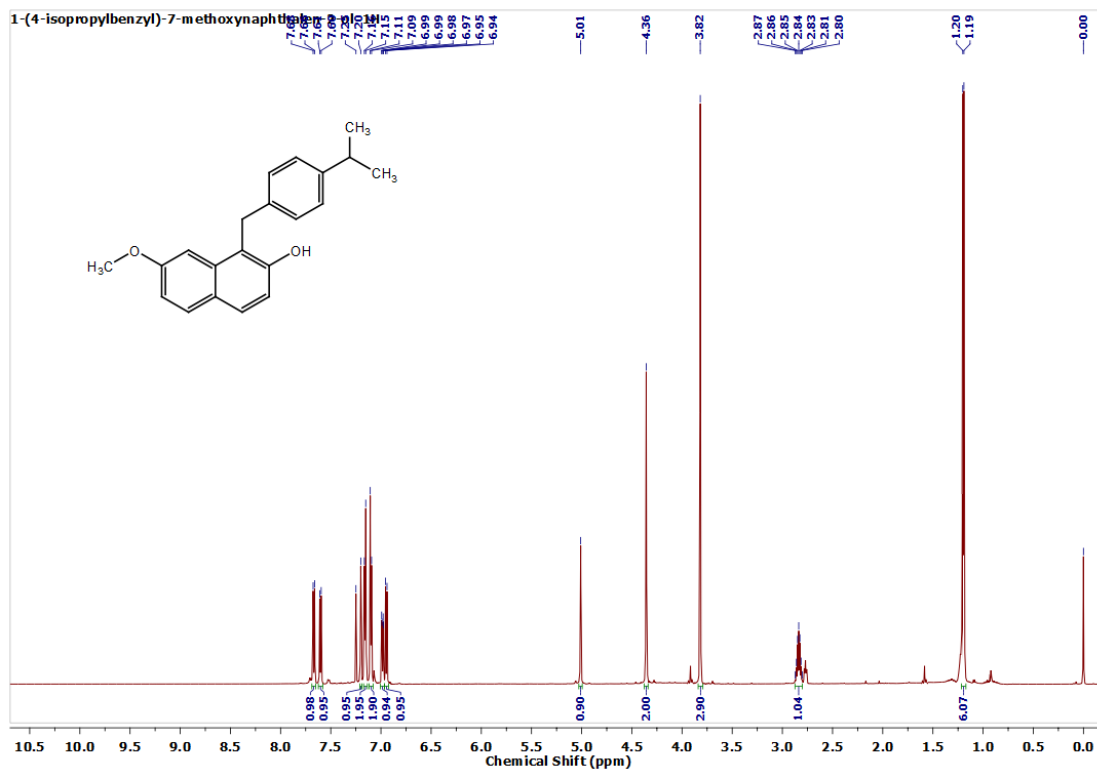
Electronic Supplementary Information

Compound 3o: 7-methoxy-1-(4-methylbenzyl)naphthalen-2-ol



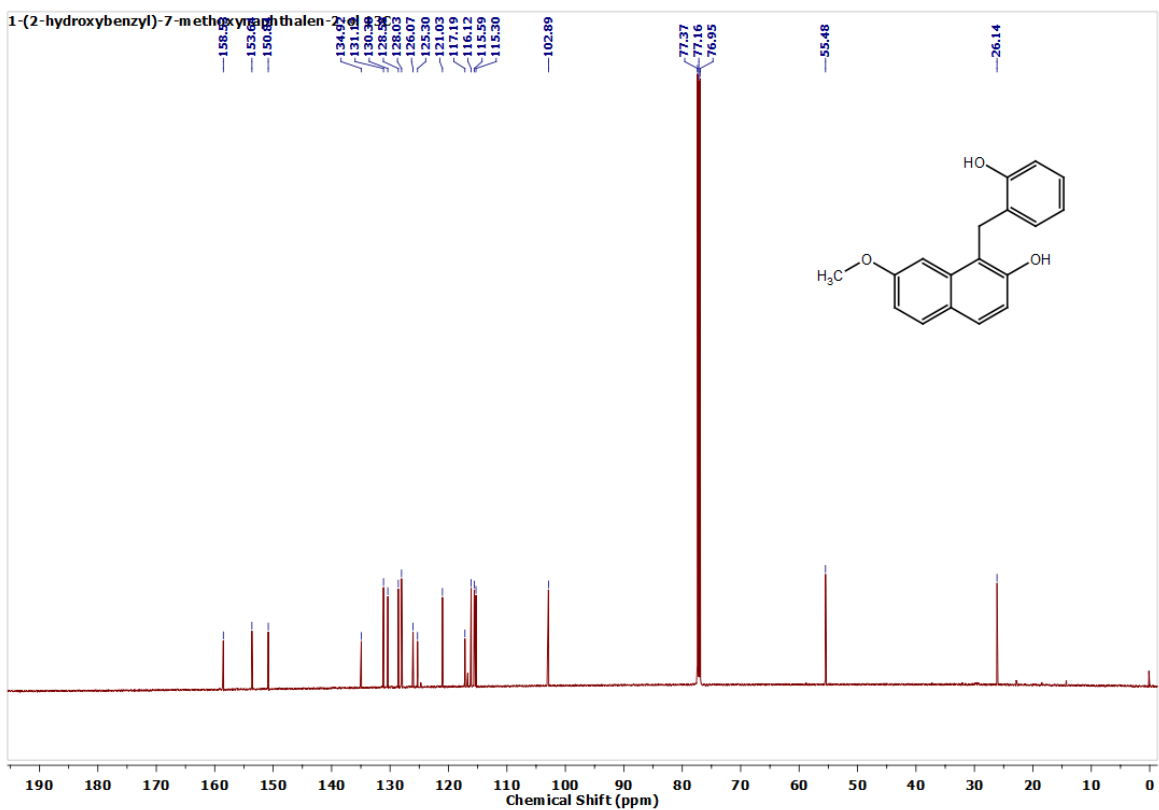
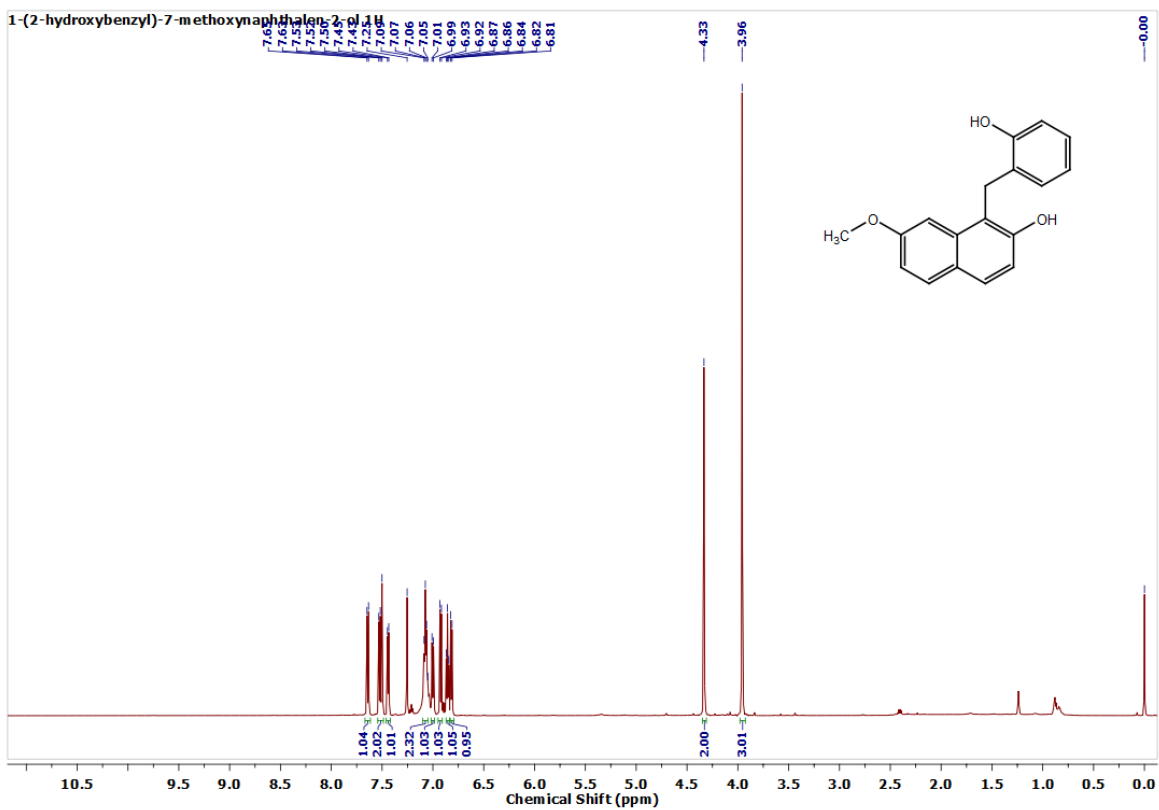
Electronic Supplementary Information

Compound 3p: 1-(4-isopropylbenzyl)-7-methoxynaphthalen-2-ol



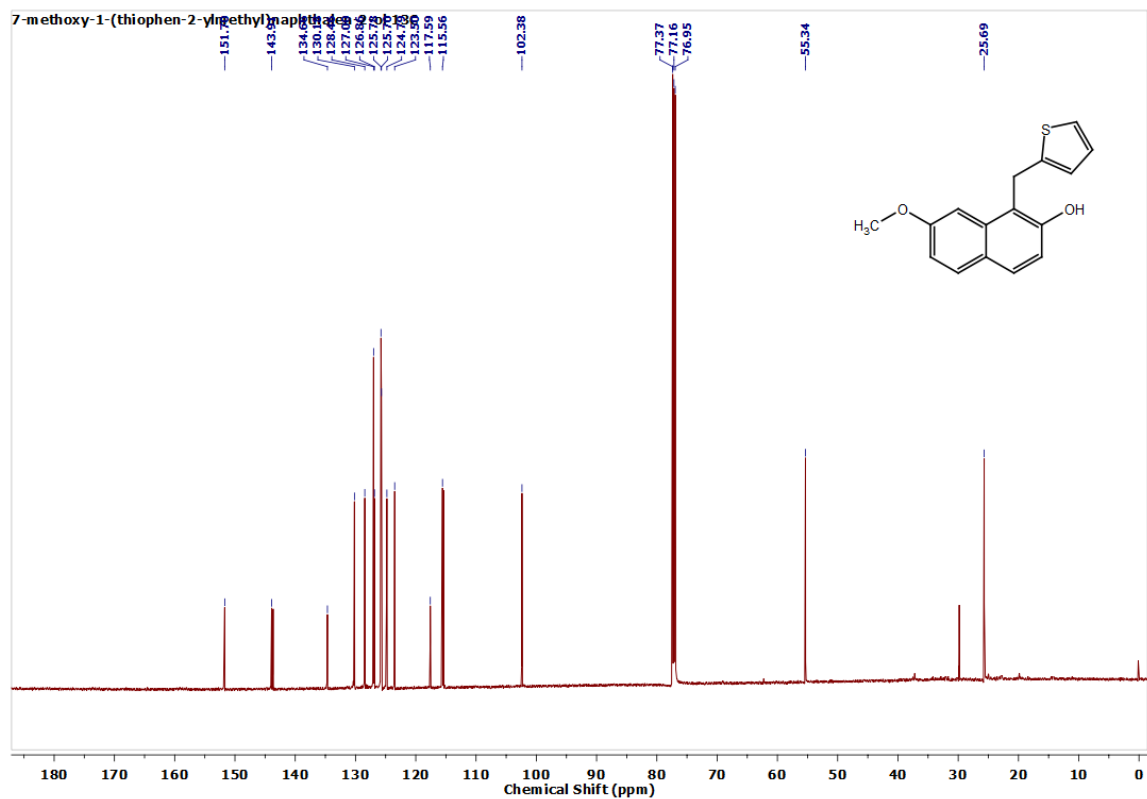
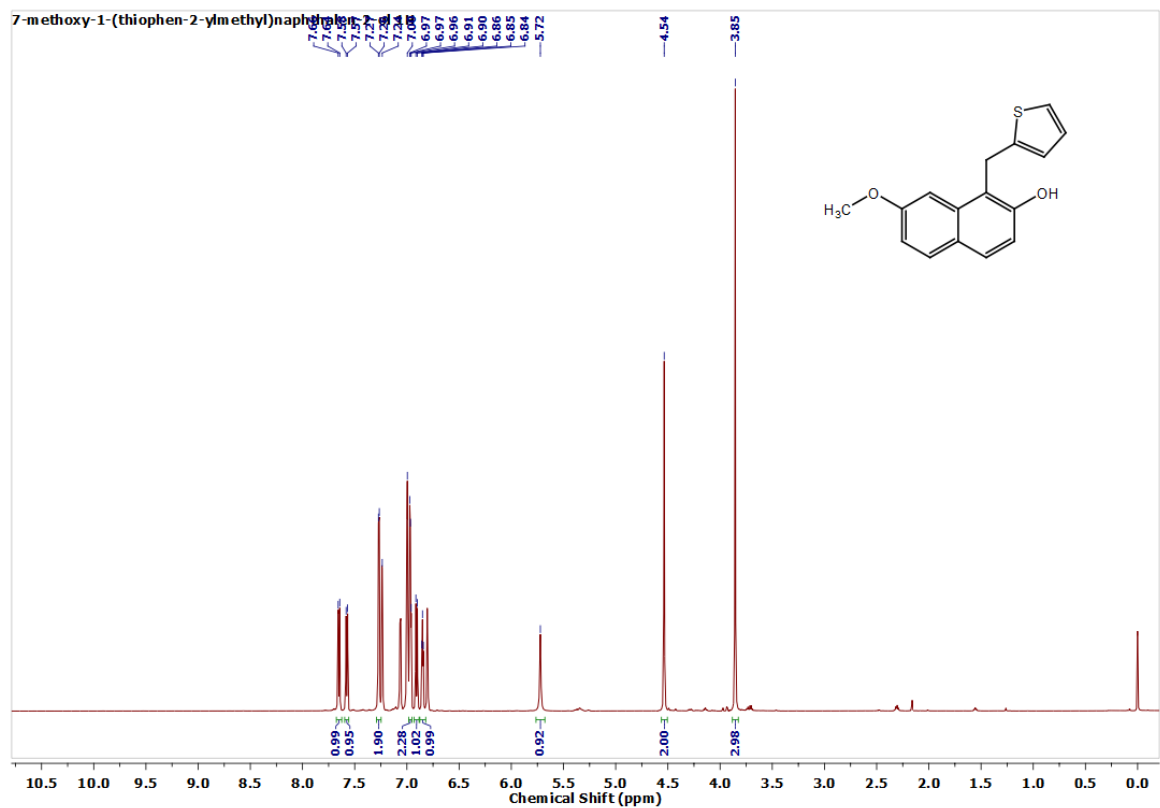
Electronic Supplementary Information

Compound 3q: 1-(2-hydroxybenzyl)-7-methoxynaphthalen-2-ol



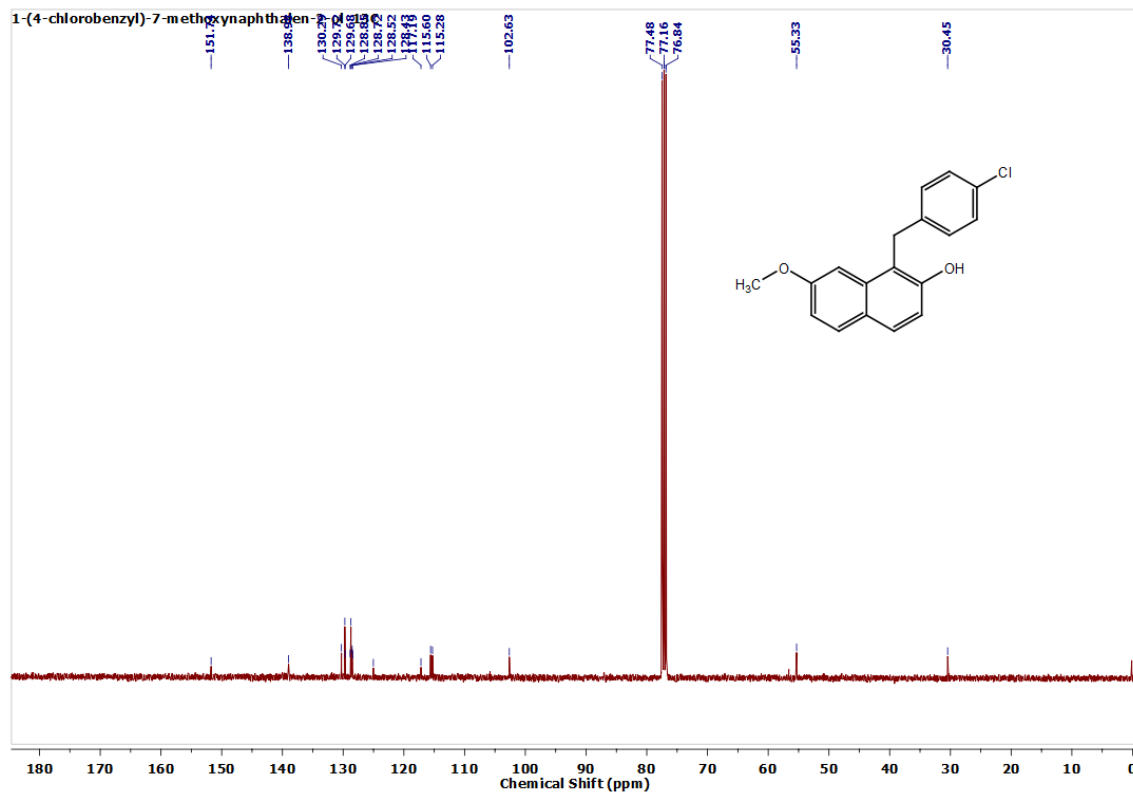
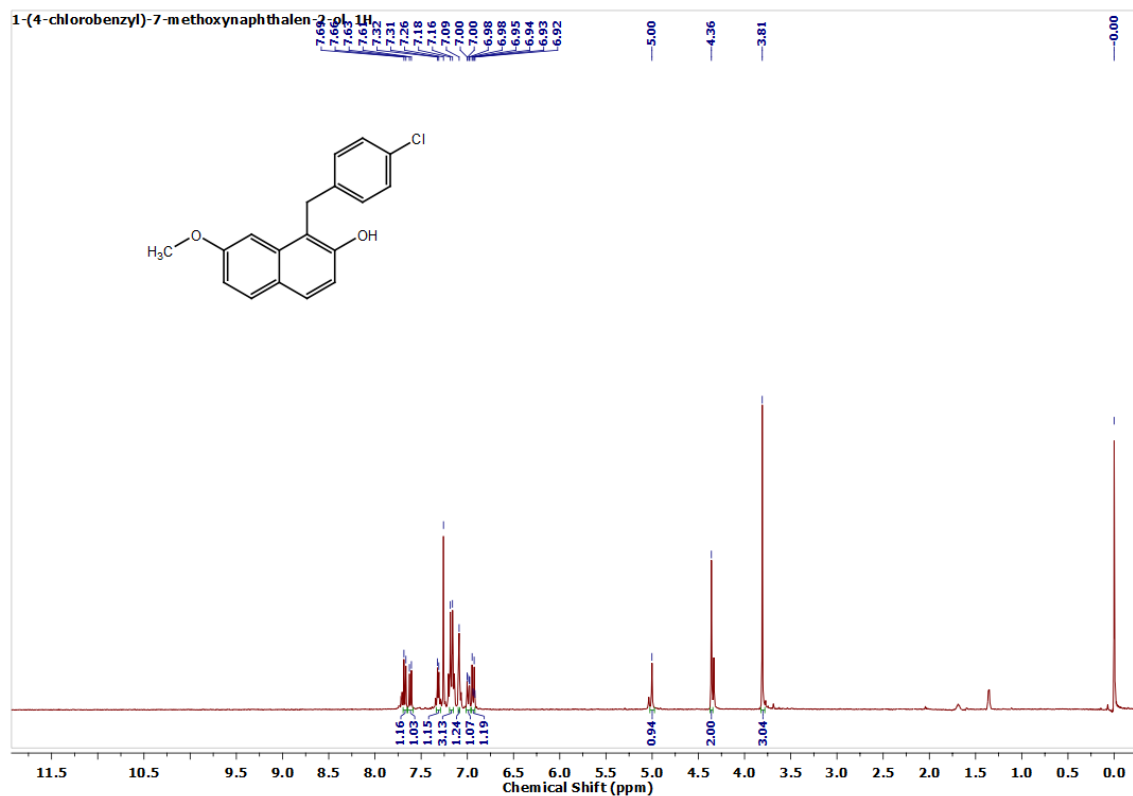
Electronic Supplementary Information

Compound 3r: 7-methoxy-1-(thiophen-2-ylmethyl)naphthalen-2-ol



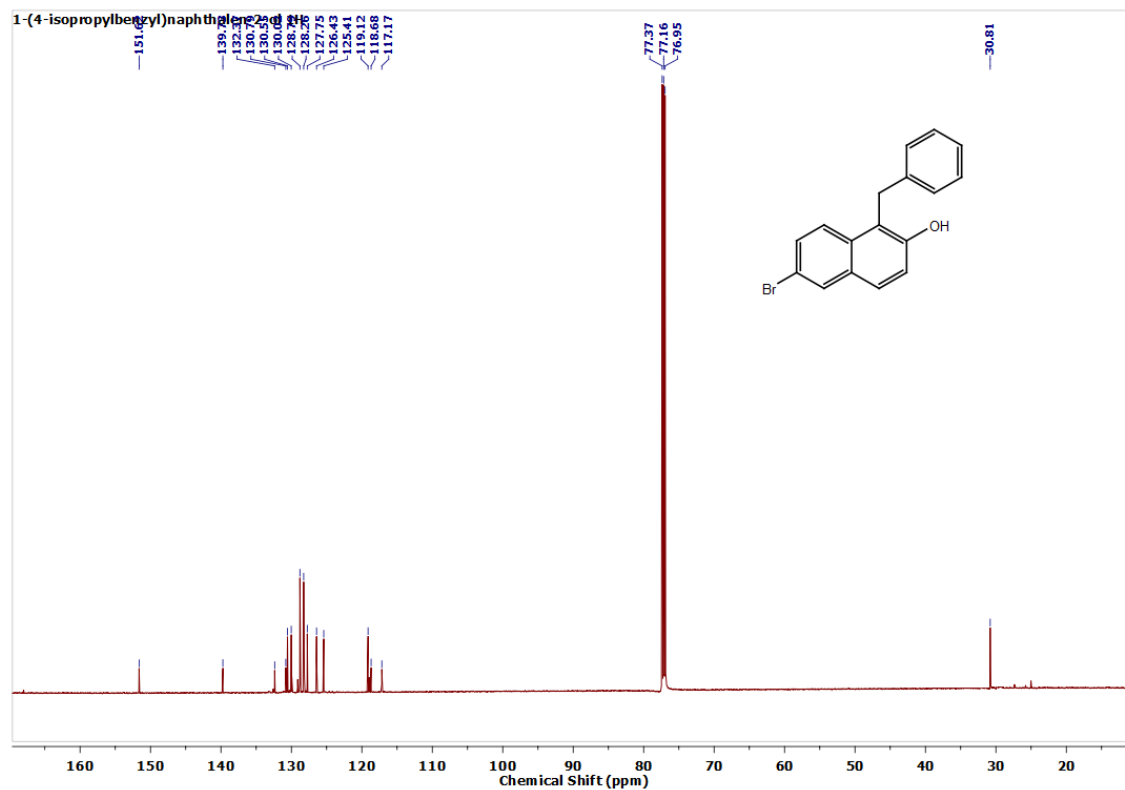
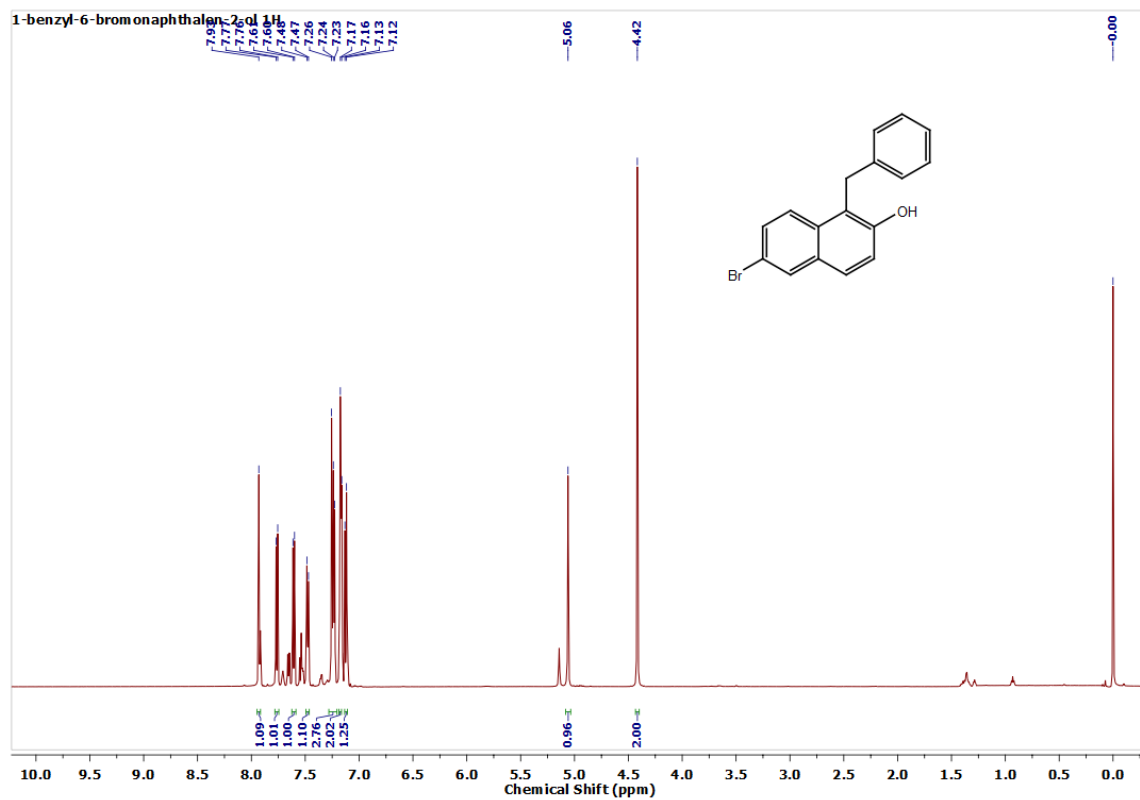
Electronic Supplementary Information

Compound 3t: 1-(4-chlorobenzyl)-7-methoxynaphthalen-2-ol



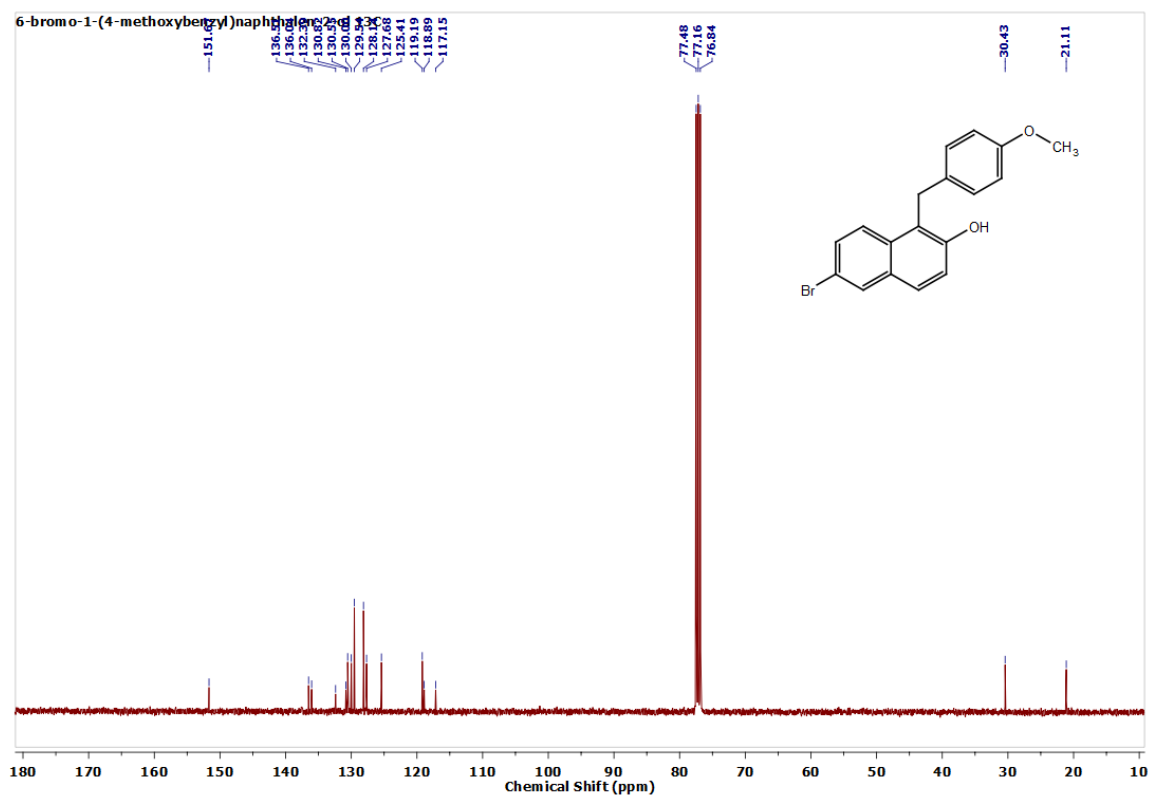
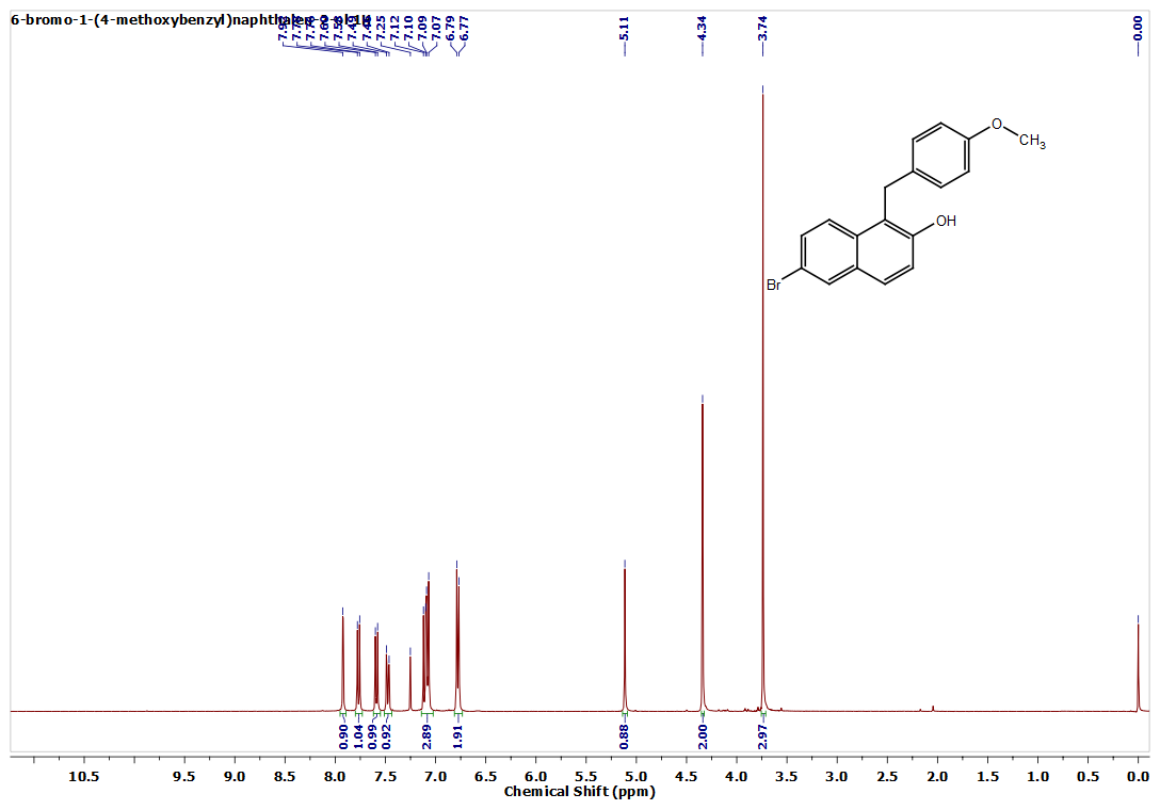
Electronic Supplementary Information

Compound 3u: 1-benzyl-6-bromonaphthalen-2-ol



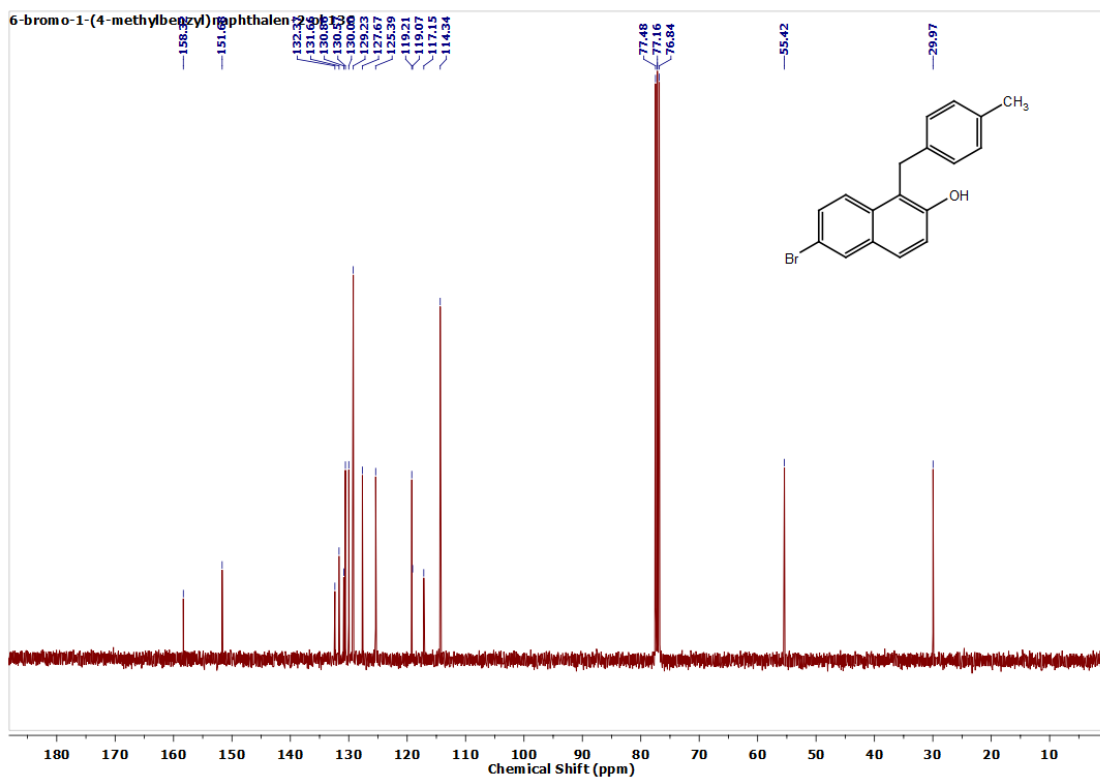
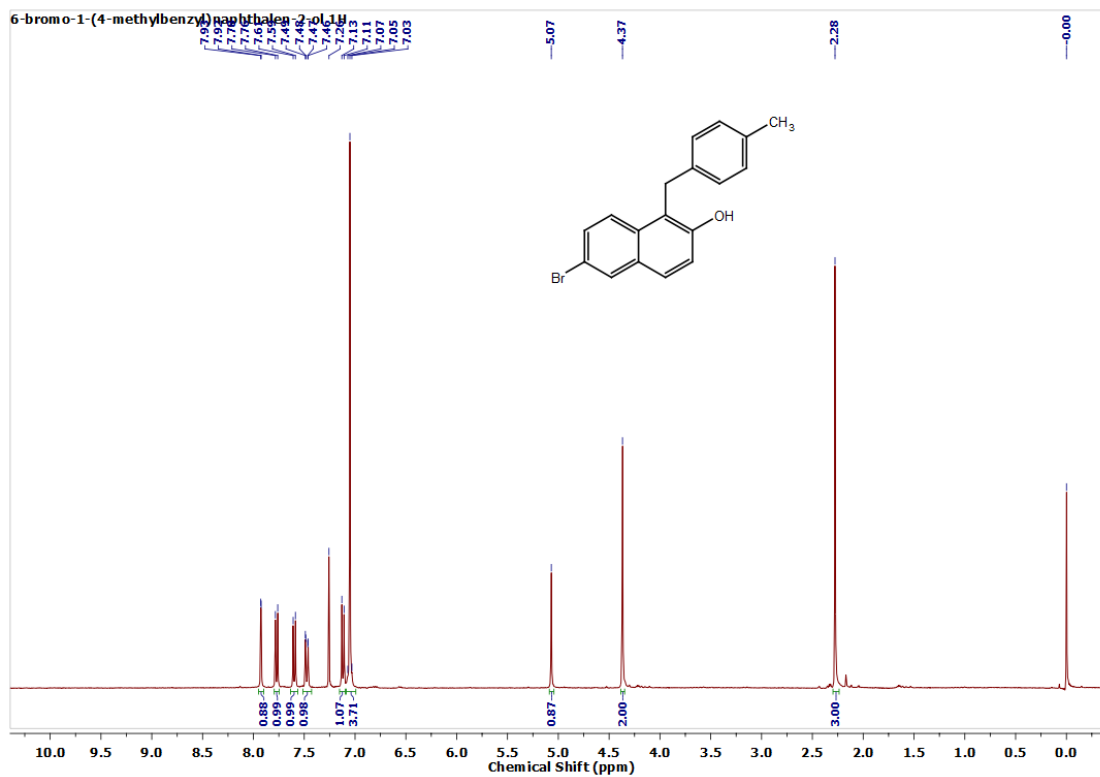
Electronic Supplementary Information

Compound 3v: 6-bromo-1-(4-methoxybenzyl)naphthalen-2-ol



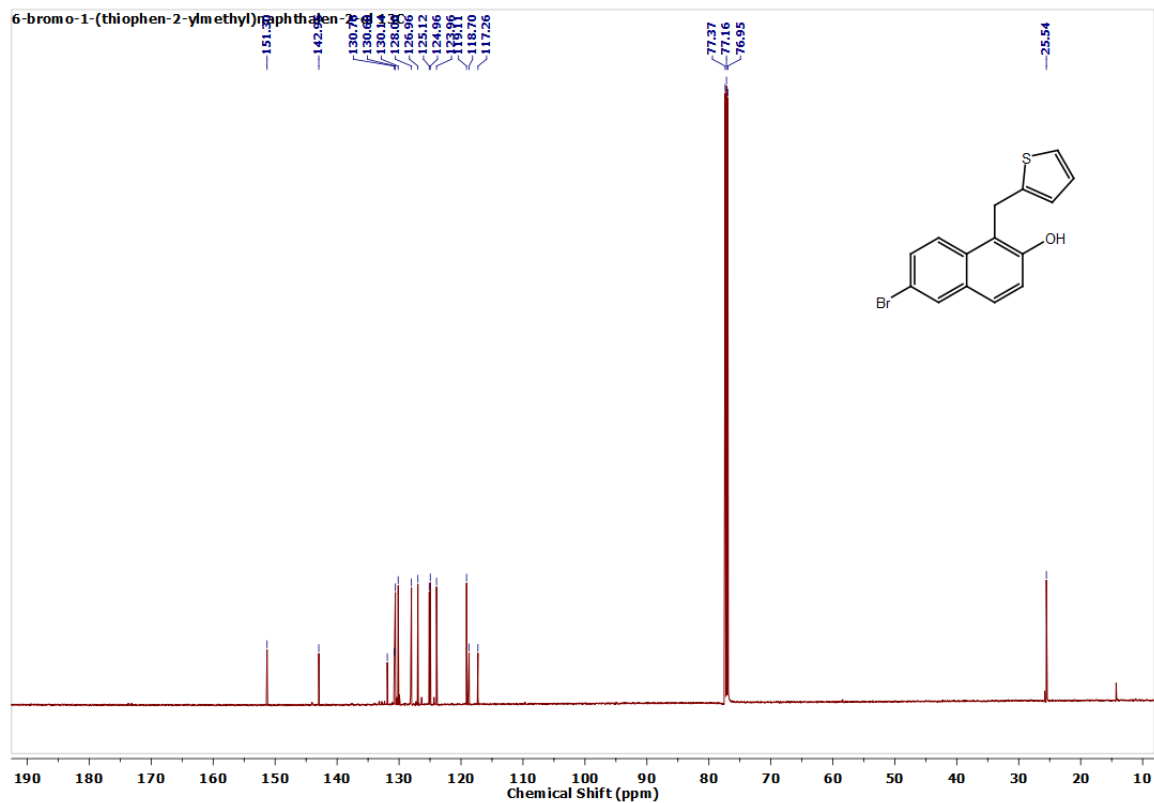
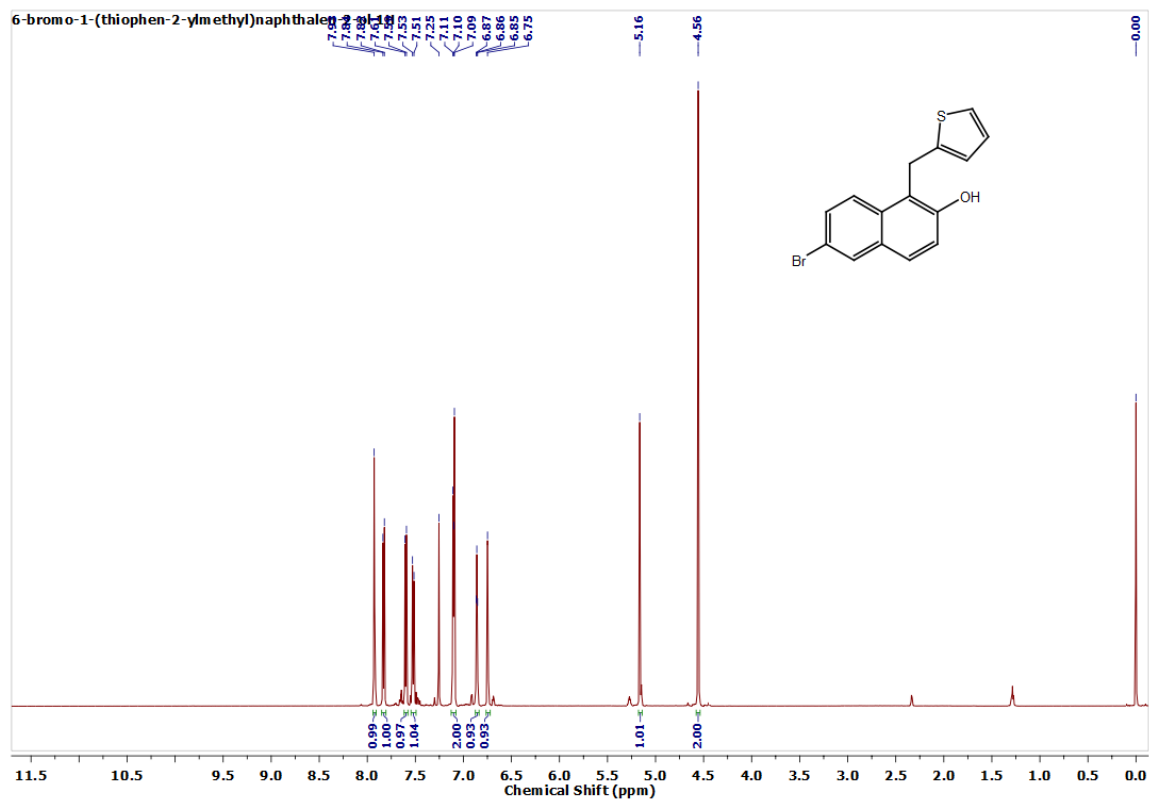
Electronic Supplementary Information

Compound 3w: 6-bromo-1-(4-methylbenzyl)naphthalen-2-ol



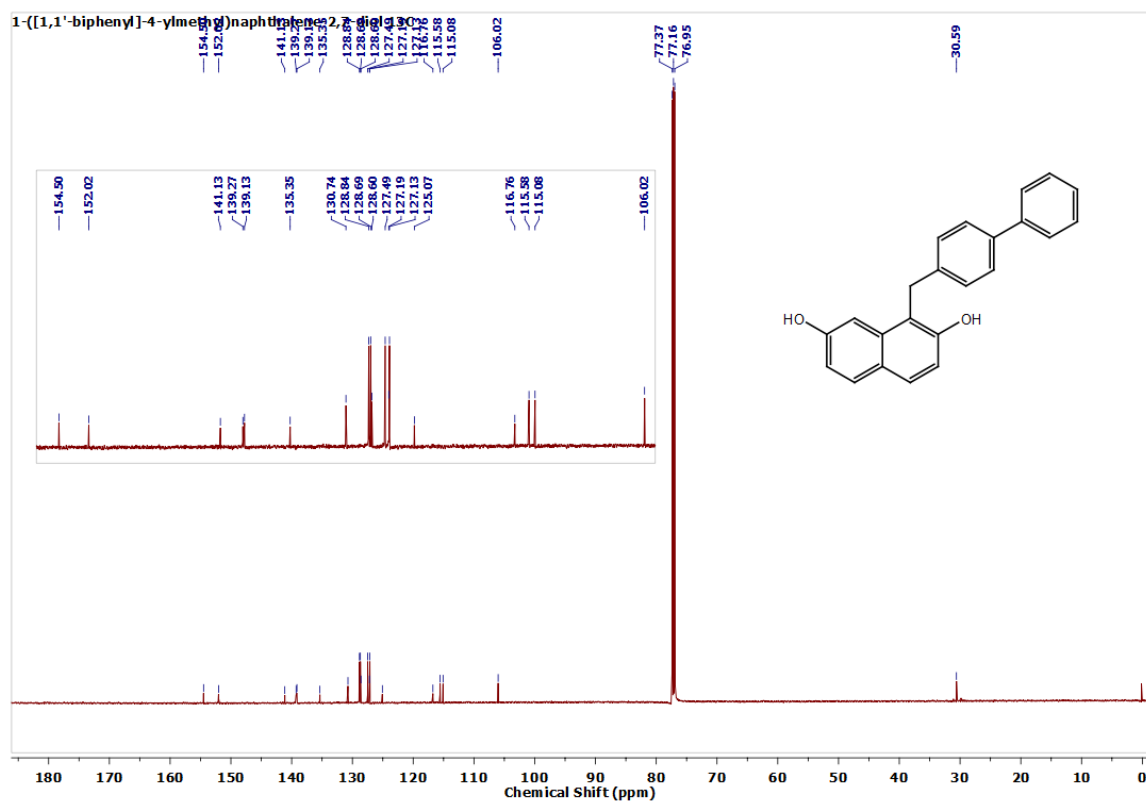
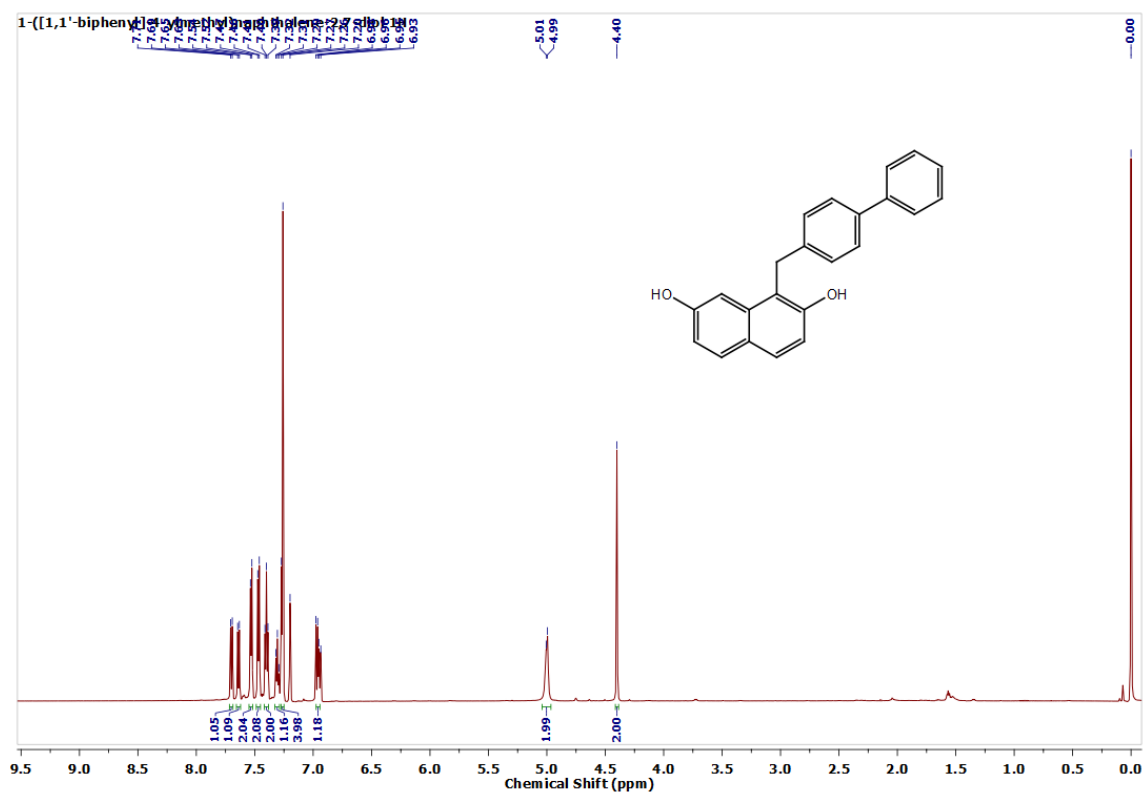
Electronic Supplementary Information

Compound 3x: 6-bromo-1-(thiophen-2-ylmethyl)naphthalen-2-ol



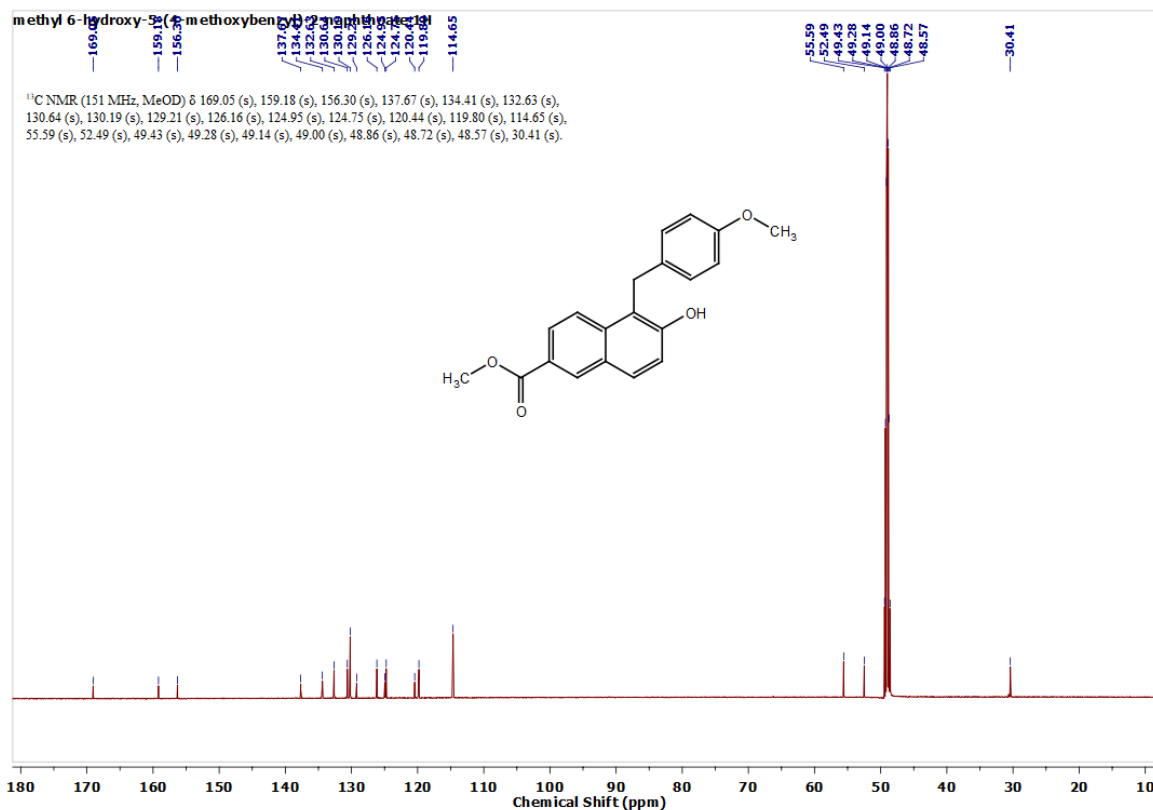
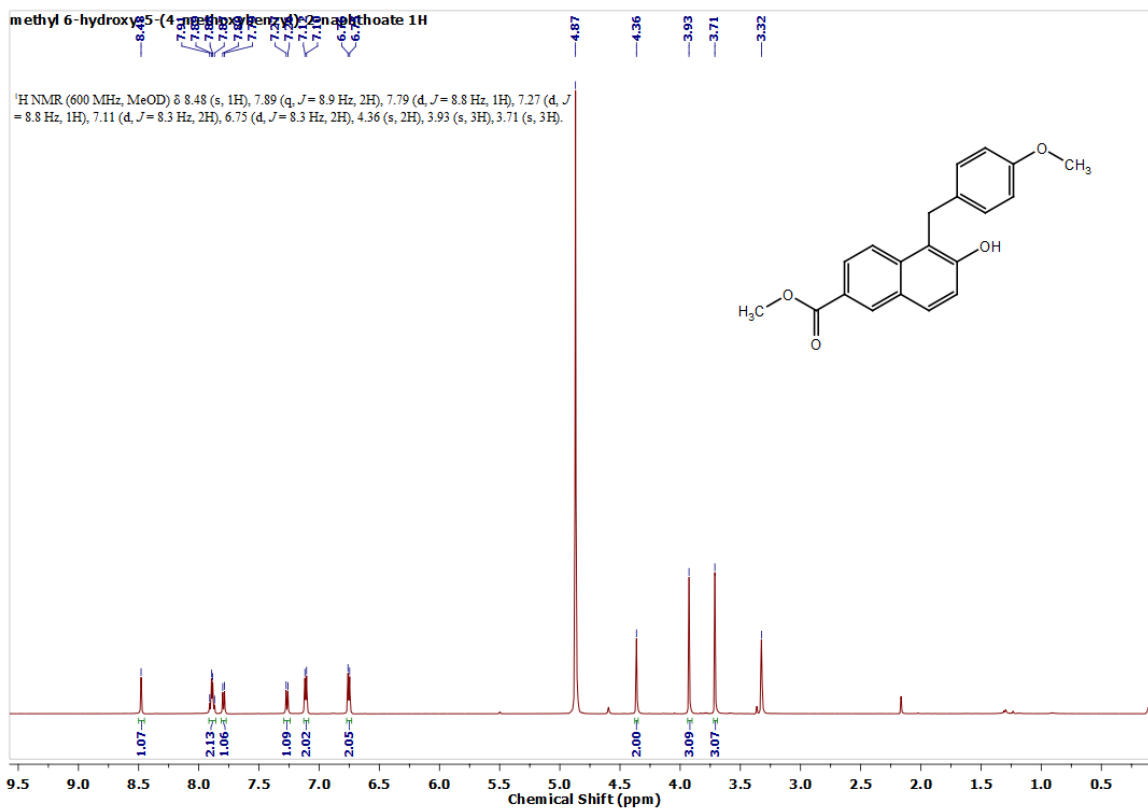
Electronic Supplementary Information

Compound 3y: 1-([1,1'-biphenyl]-4-ylmethyl)naphthalene-2,7-diol



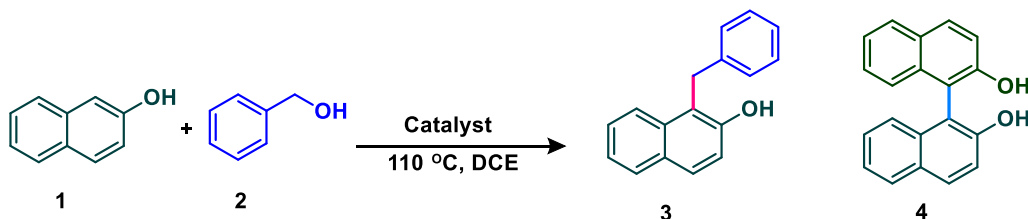
Electronic Supplementary Information

Compound 3z: methyl 6-hydroxy-5-(4-methoxybenzyl)-2-naphthoate



Electronic Supplementary Information

7 Table S2: Comparison of catalytic activities of different catalysts for C(1) benzylation of 2-naphthols with primary alcohols.^[a]



Entry	Catalyst	Yield (%)	
		3	4
1	-	-	-
2	HY	-	-
3	Na-Y	-	-
4	K-Y	-	-
5	Fe ₂ O ₃	-	-
6	FeCl ₃ (1 mol %)	35	47
7	Fe(NO ₃) ₃ (1 mol %)	31	38
8	FeSO ₄ (1 mol %)	26	30
9	Fe ₂ O ₃ -NaY	20	-
10	Fe ₂ O ₃ -HNT	16	-
11	Fe ₂ O ₃ -Al ₂ O ₃	trace	-
12	Fe ₂ O ₃ -SiO ₂	trace	-

^aReaction Conditions: 2-naphthol (1 mmol), benzyl alcohol (1 mmol), DCE (1 mL), catalyst (15 mg). Isolated yields are obtained after column chromatography.

Electronic Supplementary Information

8 Computational Details

All the structures were fully optimized without any symmetry constraints at TPSSh/def2-TZVP level of theory.^{10,11} Harmonic vibrational frequency calculations were performed at the same level of theory to understand the nature of the stationary states. All the intermediates were characterized by the presence of all real values of the Hessian matrix while the transition state was characterized by one imaginary value of the Hessian matrix. Since the transition state involved proton transfer, the imaginary frequency corresponded to the movement of the proton between the two oxygen atoms. Solvent corrections were taken into account using polarizable continuum model (PCM)¹¹ by performing single point calculations on the gas phase optimized geometries. Dichloromethane was used as the solvent. Zero point corrections were taken from gas phase calculations and solvent phase corrections were added to it. All calculations were performed using Gaussian 16 suite of program.¹²

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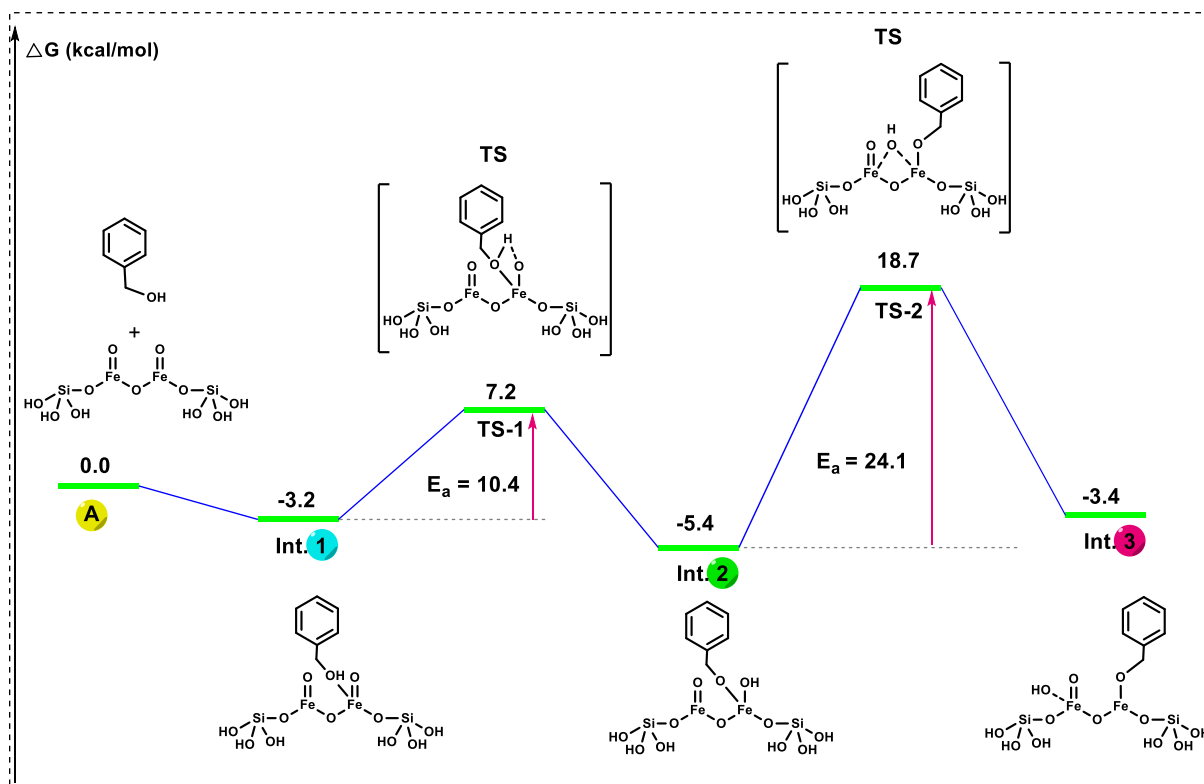


Fig. S7 Reaction energetic (kcal/mol) for the interaction of benzyl alcohol with the supported iron oxide.

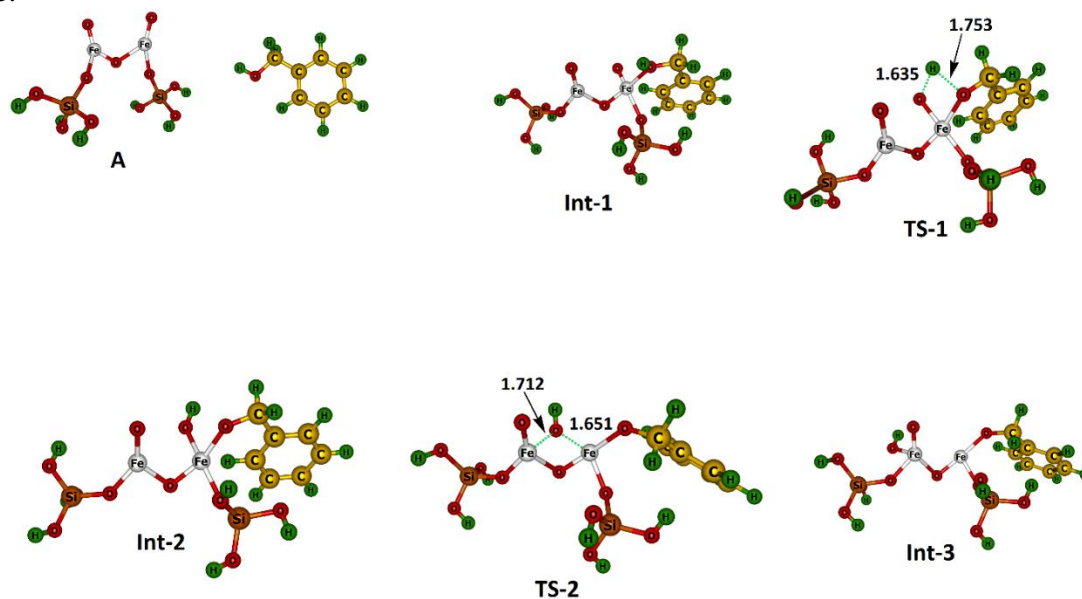


Fig. S8 The structures of the optimized geometries. Bond lengths are in Å.

Electronic Supplementary Information

8.1 Coordinates of the optimized geometries.

A

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Int-1

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TS-1

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Electronic Supplementary Information

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Int-2

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Electronic Supplementary Information

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Electronic Supplementary Information

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Electronic Supplementary Information

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Int-3

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Electronic Supplementary Information

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9. Catalytic Recyclability Study

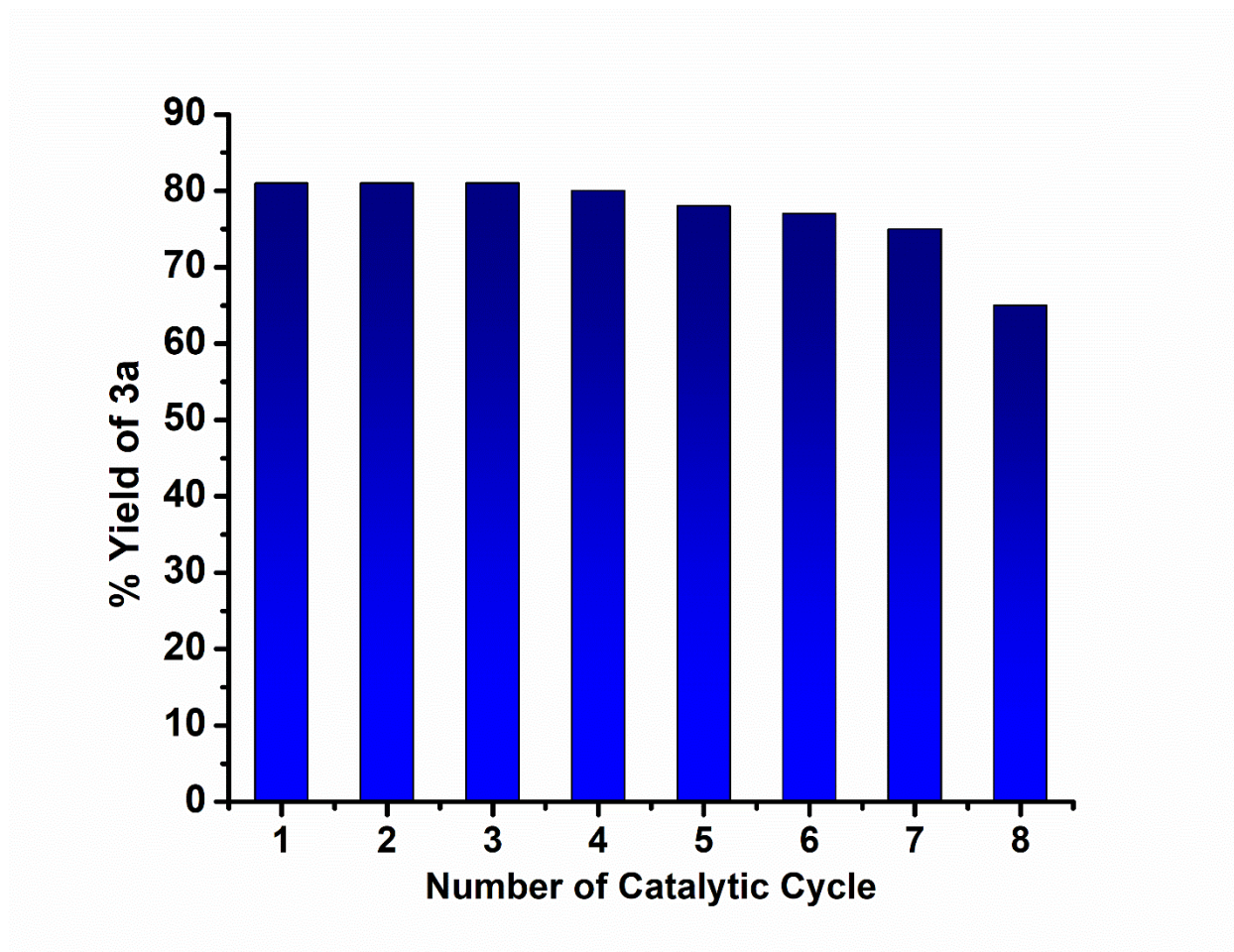


Fig. S9 Showing % yield of **3a** in each consecutive run of Fe₂O₃-KY.

Electronic Supplementary Information

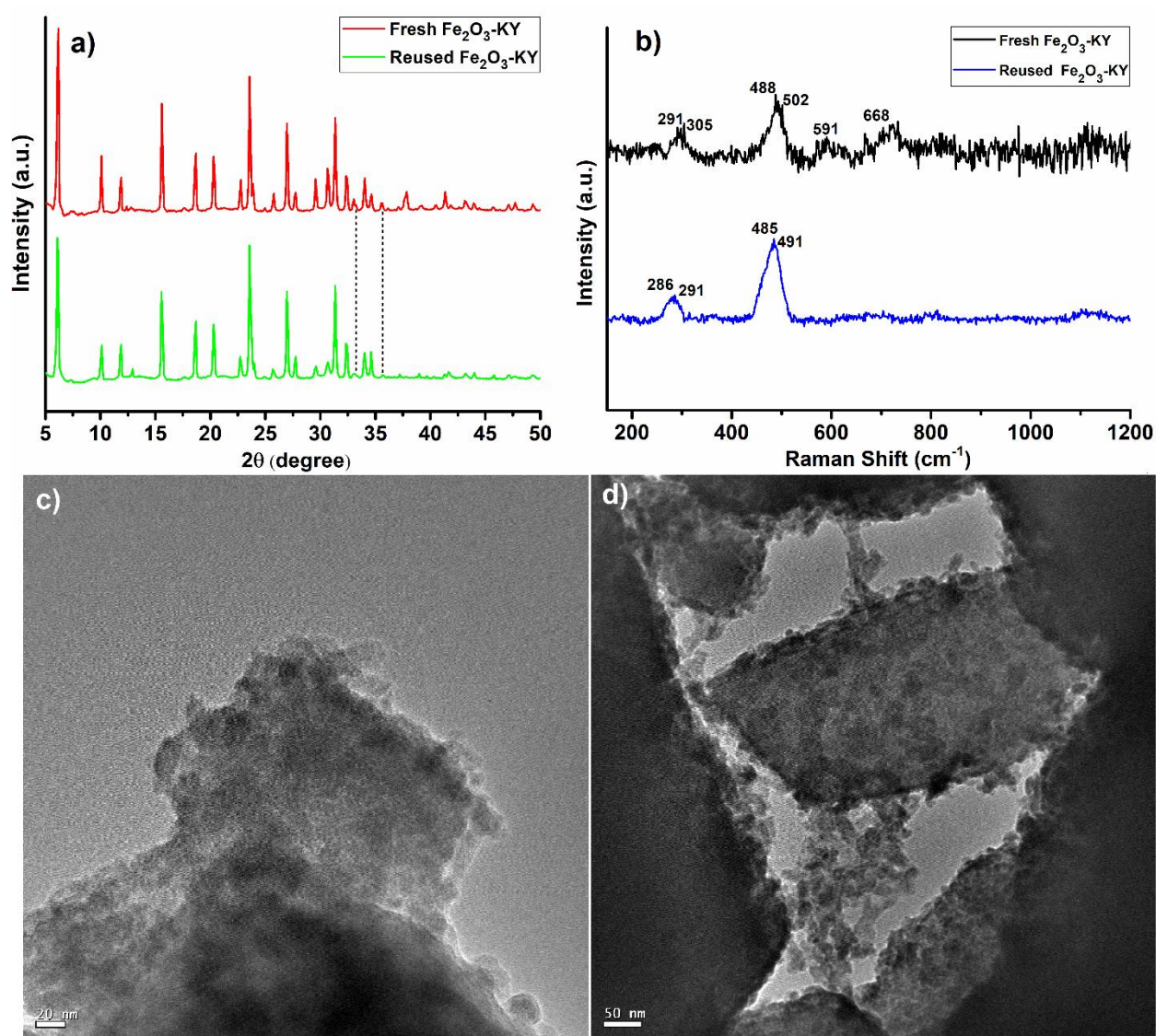


Fig. S10 a) XRD pattern of fresh (red line) and reused (green line) catalyst after 8th cycle, b) Raman spectra of fresh (black line) and reused (blue line) catalyst after 8th cycle, c-d) TEM images of reused Fe₂O₃-KY catalyst.

Electronic Supplementary Information

10. References

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