Supporting Information

Ruthenium Catalyzed Hydrohydroxyalkylation of Isoprene with Heteroaromatic Secondary Alcohols: Isolation and Reversible Formation of the Putative Metallacycle Intermediate

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I. General Information: All reactions were run under an atmosphere of argon. Pressure tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14–959–35C) and were flame dried followed by cooling in a desiccator. Toluene was dried over sodium metal, benzophenone, and distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. Tricyclohexylphosphine was recrystallized prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F_{254}). Visualization was accomplished with UV light followed by dipping in Seebach's stain solution then heating. Purification of reactions was carried out by flash column chromatography using Silacycle silica gel (40–63 μm).

II. Spectroscopy, Spectrometry, and Data Collection: Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H or M+Na), or a suitable fragment ion. ^{1}H Nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in Hertz (Hz) for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.0 ppm). Melting points were taken on a Stuart SMP3 melting point apparatus.

III. Experimental Details and Spectral Data

a. General Procedure for Synthesis of Pyridyl Methanol 1a–1o:

2-Bromopyridine (0.48 mL, 5 mmol) was added to ^{i}PrMgCl (5 mmol) in THF (5 mL) at rt. After 2 hours, aldehyde (6 mmol) was added. After 2 hours at rt, water (25 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was subjected to by flash column chromatography (SiO_2, 25% EtOAc/hexanes) to furnish the title compounds **1a**,[1] **1b**,[2] **1c**,[3] **1e**,[2] **1f**,[1] **1h**,[4] **1j**,[5] **1k**,[6] **1l**,[5] **1n**[7] and **1o**.[8]

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[1] *J. Org. Chem*. **2009**, *74*, 3566.

[2] *Tetrahedron* **2012**, *68*, 7613.

[3] *Chem. Commun*. **2008**, *8*, 957.

[4] *J. Am. Chem. Soc*. **1949**, *71*, 887.

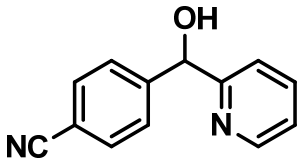
[5] *Angew. Chem. Int. Ed*. **1998**, *37*, 3279.

[6] *Tetrahedron* **1984**, *40*, 5185.

[7] *J. Med. Chem*. **1971**, *14*, 546.

[8] *Tetrahedron* **1994**, *50*, 275.

4-Cyanophenyl Pyridyl Methanol (1d).



In accordance with the general procedure, 2-bromopyridine (0.48 mL, 5 mmol) was added to ^{i}PrMgCl (5 mmol) in THF (5 mL) at rt. After 2 hours, 4-cyanobenzaldehyde (828.0 mg, 6 mmol) was added. After 2 hours at rt, water (25 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, 25% EtOAc/hexanes) to furnish the title compound (796.9 mg, 76% yield) as a brown solid.

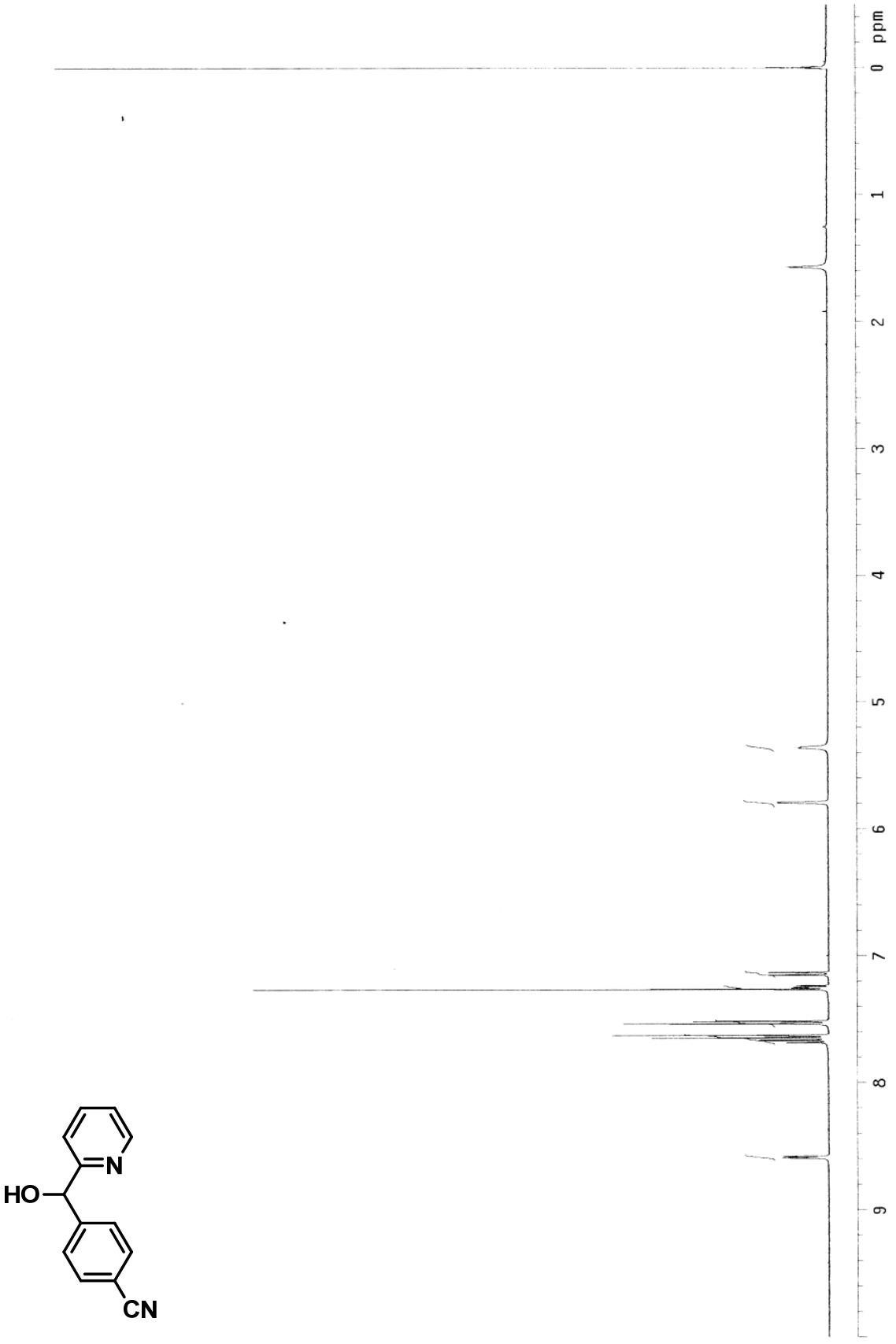
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60–8.58 (m, 1H), 7.69–7.62 (m, 3H), 7.54–7.52 (m, 2H), 7.26–7.23 (m, 1H), 7.15–7.13 (m, 1H), 5.79 (s, 1H), 5.36 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 148.5, 148.3, 137.3, 132.4, 127.6, 123.0, 121.2, 118.8, 111.5, 74.5.

LRMS (CI) Calcd. for $C_{13}H_{11}N_2O$ $[M+H]^+$: 211, Found: 211.

FTIR (neat): 3181, 2359, 2342, 2228, 1593, 1571, 1503, 1436, 1408, 1275, 1261, 1195, 1097, 1059, 1019, 1003, 870, 811, 764, 750, 668 cm^{-1}.

MP 76.0–77.0 ^{o}C.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8
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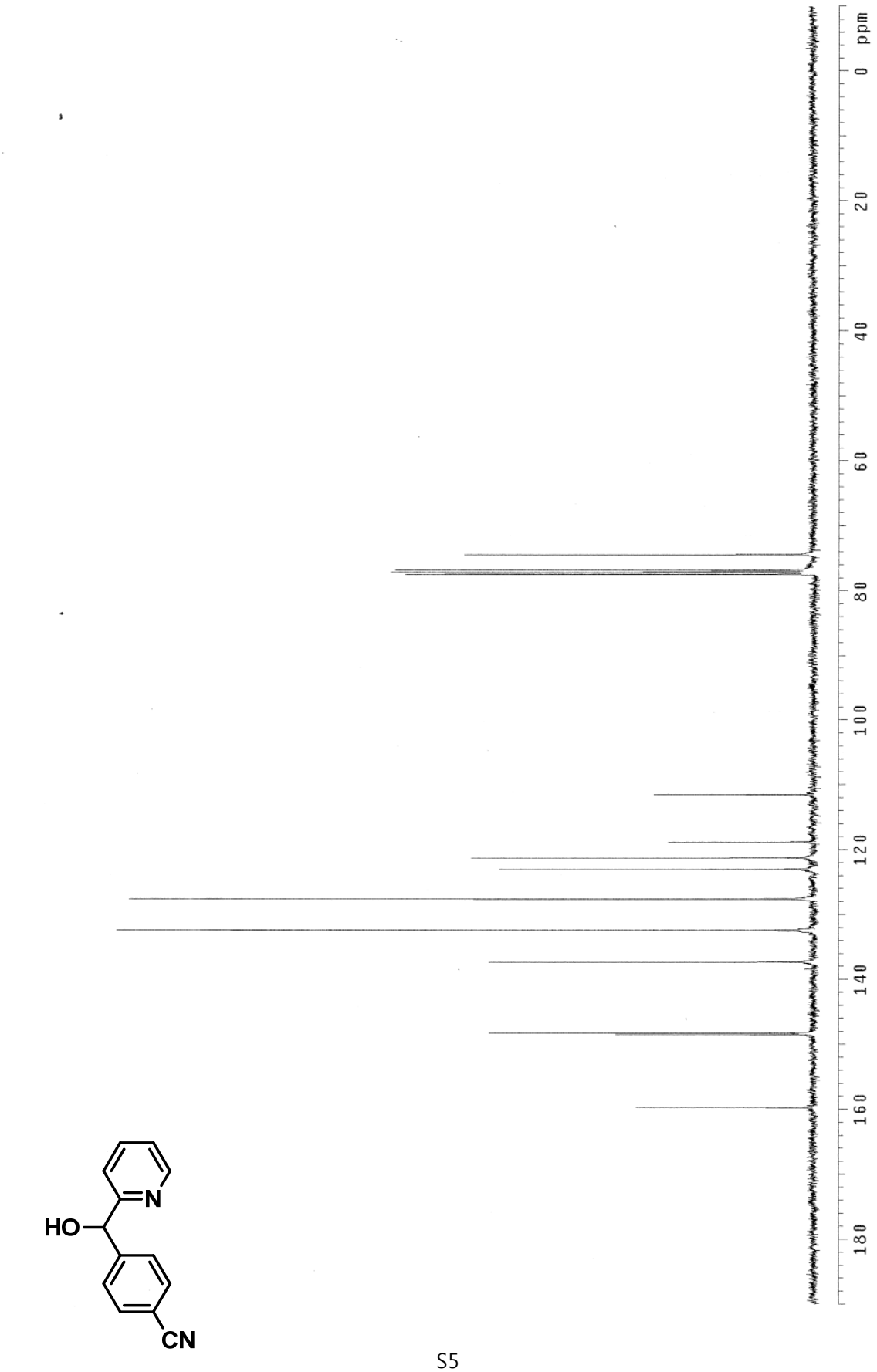
N
HO
CN


HO
N
CN
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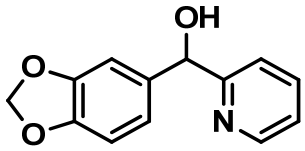
20
40
60
80
100
120
140
160
180

1,3-Benzodioxole Pyridyl Methanol (1g).



In accordance with the general procedure, 2-bromopyridine (0.48 mL, 5 mmol) was added to ^{i}PrMgCl (5 mmol) in THF (5 mL) at rt. After 2 hours, piperonal (910.0 mg, 6 mmol) was added. After 2 hours at rt, water (25 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, 25% EtOAc/hexanes) to furnish the title compound (861.4 mg, 75% yield) as a brown solid.

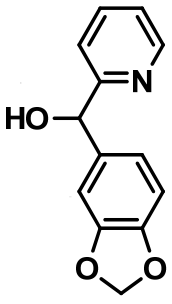
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.4 Hz, 1H), 7.64–7.60 (m, 1H), 7.21–7.18 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79–6.76 (m, 2H), 5.91 (dd, *J* = 4.0, 1.2 Hz, 2H), 5.66 (s, 1H), 5.31 (bs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 148.0, 147.9, 147.3, 137.4, 137.0, 122.5, 121.4, 120.8, 108.2, 107.5, 101.1, 74.8.

LRMS (CI) Calcd. for $C_{13}H_{12}NO_3$ $[M+H]^+$: 230, Found: 230.

FTIR (neat): 3148, 2891, 1593, 1571, 1503, 1487, 1470, 1436, 1372, 1334, 1293, 1248, 1214, 1187, 1124, 1102, 1055, 1038, 1003, 928, 869, 846, 802, 765, 742, 724, 716, 667 cm^{-1}.

MP 71.5–72.5 ^{o}C.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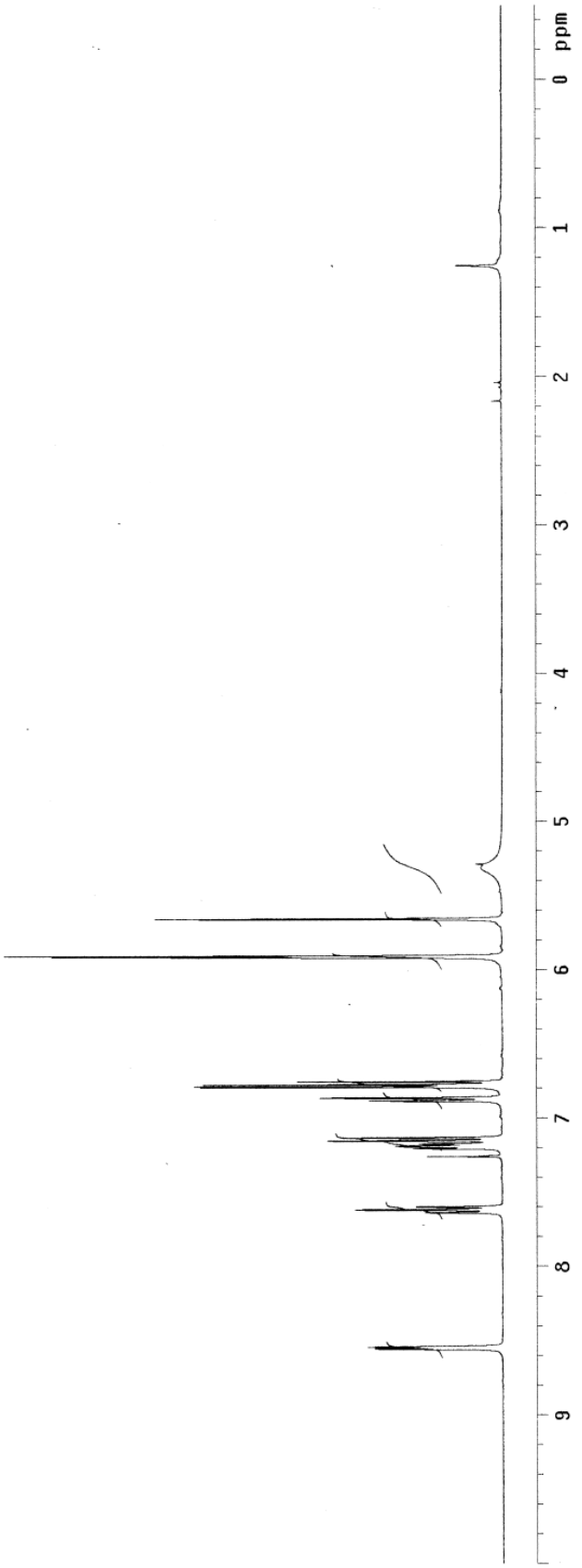
N
O
O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HO
N
O
O
0
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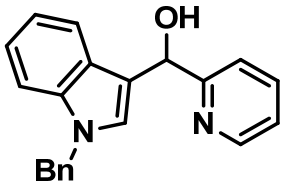
40
60
80
100
120
140
160
180
ppm

2-(*N*-Bn-indolyl) Pyridyl Methanol (1h).



In accordance with the general procedure, 2-bromopyridine (0.48 mL, 5 mmol) was added to ^{i}PrMgCl (5 mmol) in THF (5 mL) at rt. After 2 hours, N-benzyl-indole-3-carbaldehyde (1.4 g, 6 mmol) was added. After 2 hours at rt, water (25 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, 25% EtOAc/hexanes) to furnish the title compound (1.1 g, 72% yield) as a yellow solid.

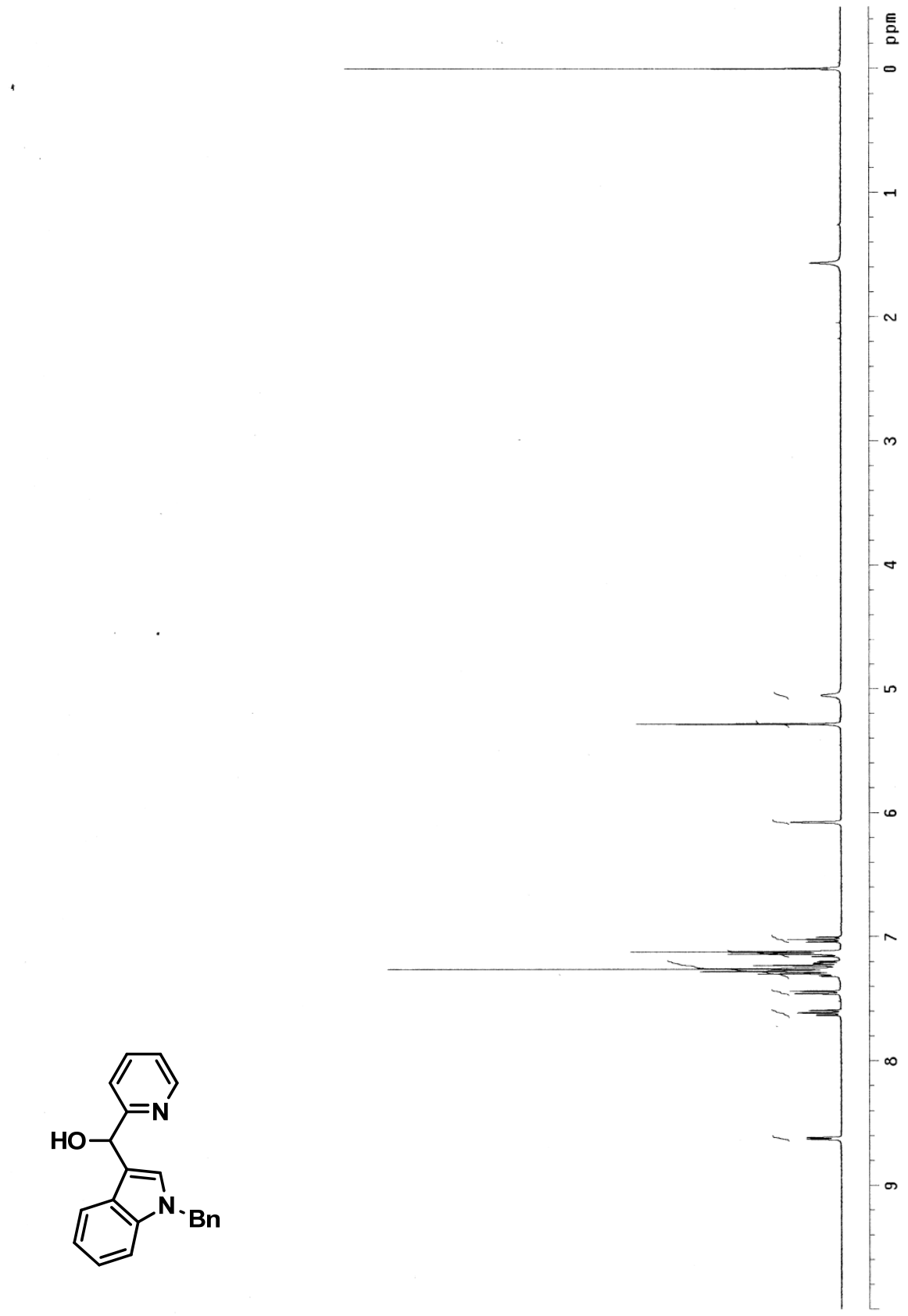
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63–8.61 (m, 1H), 7.61 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.32–7.20 (m, 7H), 7.16–7.14 (m, 3H), 7.04–7.00 (m, 1H), 6.08 (s, 1H), 5.28 (s, 2H), 5.04 (bs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 147.8, 137.3, 137.2, 136.8, 128.8, 127.7, 127.4, 126.9, 126.6, 122.4, 122.1, 121.4, 120.1, 119.7, 117.5, 109.9, 69.2, 50.1.

LRMS (CI) Calcd. for $C_{21}H_{19}N_2O$ $[M+H]^+$: 315, Found: 315.

FTIR (neat): 3115, 1593, 1572, 1544, 1494, 1465, 1452, 1437, 1397, 1351, 1334, 1307, 1238, 1171, 1095, 1046, 1025, 1001, 761, 733, 707, 693, 664 cm^{-1}.

MP 113.5–114.0 ^{o}C.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N
Bn
0 ppm
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3
4
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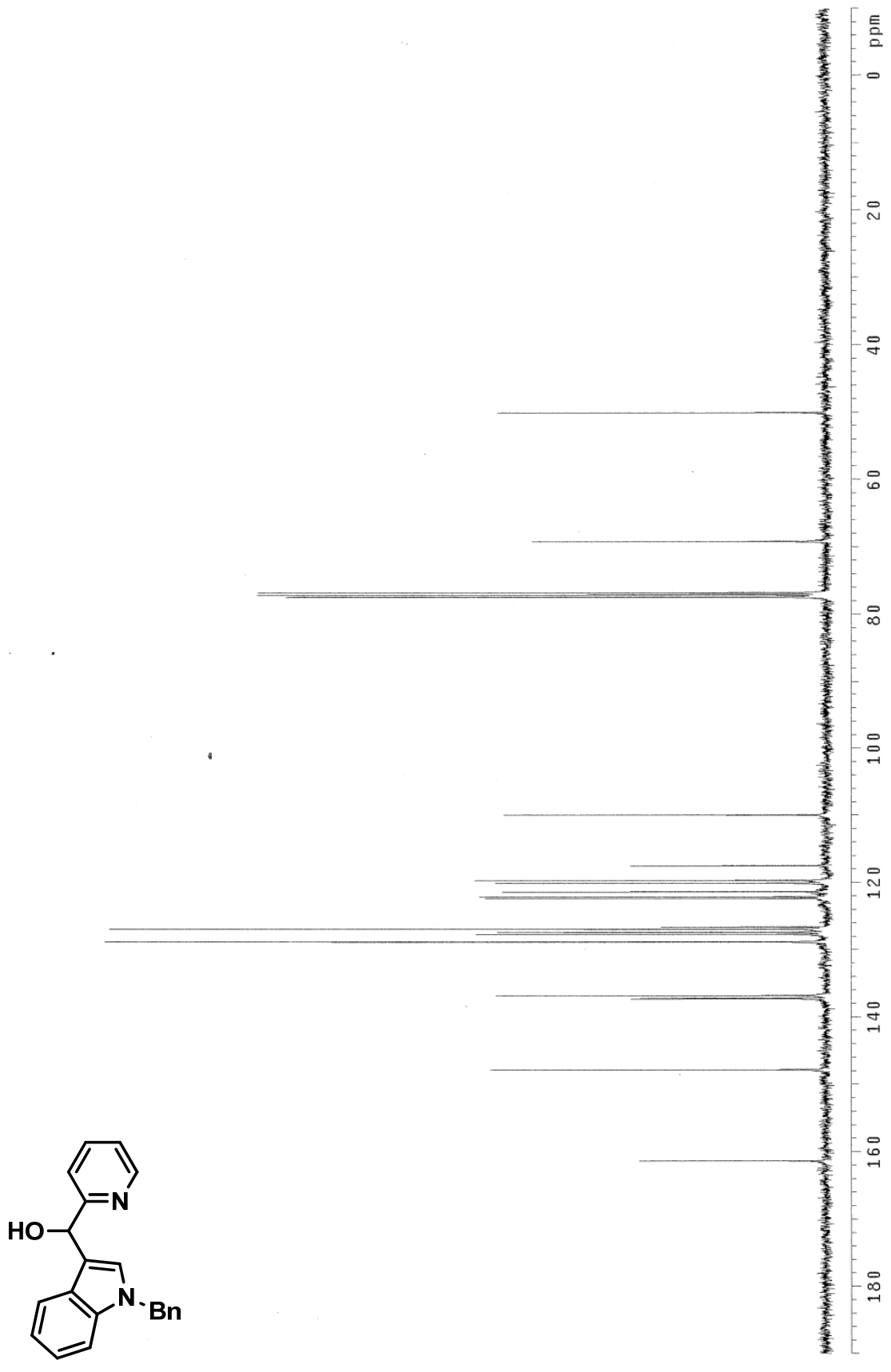
6
7
8
9


HO
N
N
Bn
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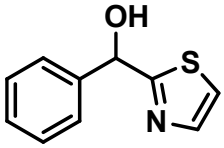
20
40
60
80
100
120
140
160
180
ppm

Thiazolyl Pyridyl Methanol (1o).



In accordance with the general procedure, 2-bromothiazole (0.46 mL, 5 mmol) was added to ^{i}PrMgCl (5 mmol) in THF (5 mL) at rt. After 2 hours, benzaldehyde (0.62 mL, 6 mmol) was added. After 2 hours at rt, water (25 mL) was added. The reaction mixture was extracted with dichloromethane (3 x 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, 25% EtOAc/hexanes) to furnish the title compound (621.0 mg, 65% yield) as a white solid.

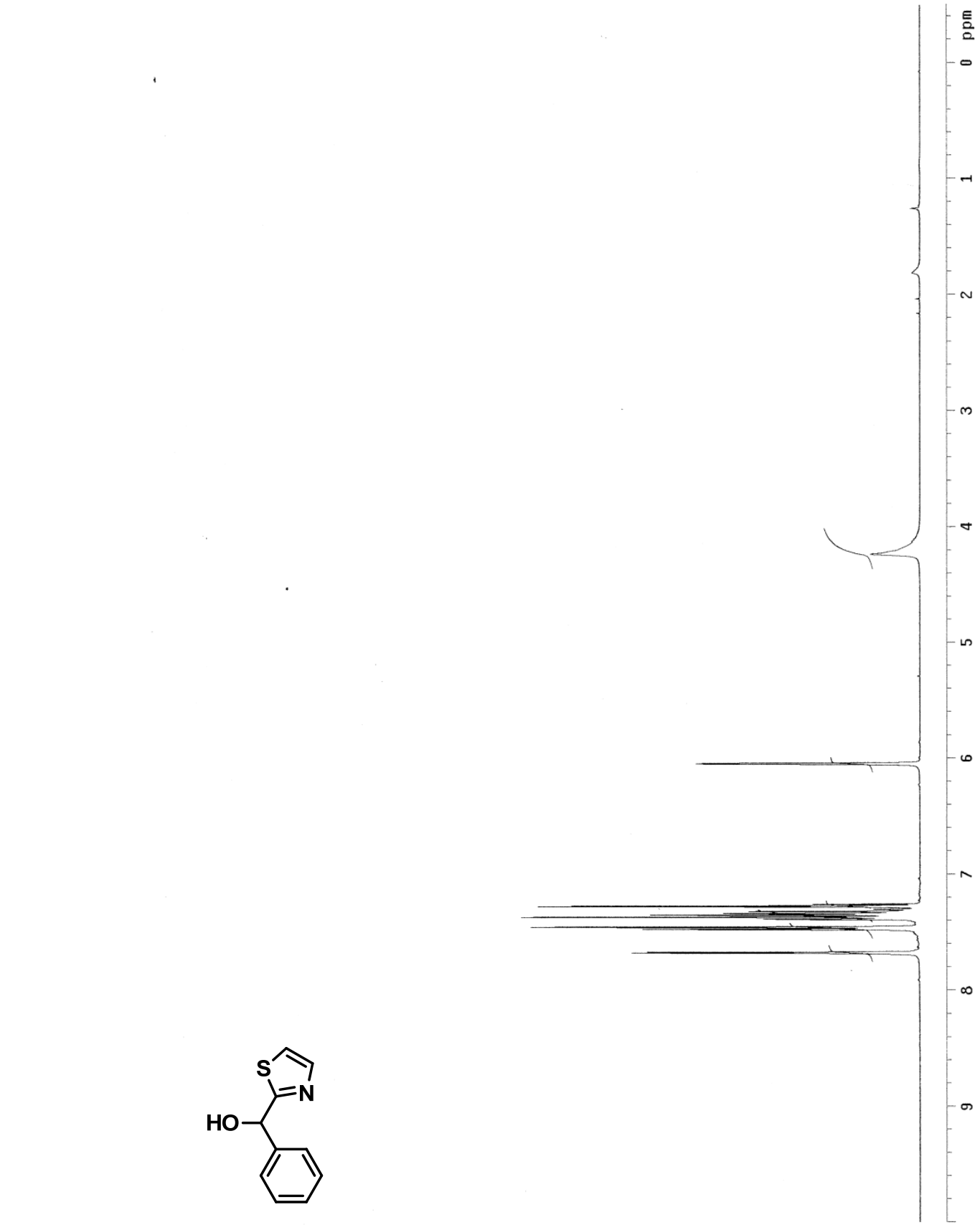
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 3.2 Hz 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.39–7.30 (m, 3H), 7.28 (d, *J* = 3.2 Hz, 1H), 6.04 (s, 1H), 4.23 (bs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 142.3, 141.5, 128.7, 128.5, 126.6, 119.6, 73.8.

LRMS (CI) Calcd. for $C_{10}H_9NaNOS$ $[M+H]^+$: 214, Found: 214.

FTIR (neat): 3124, 2853, 1738, 1509, 1495, 1454, 1341, 1282, 1249, 1196, 1183, 1141, 1088, 1064, 1049, 1027, 921, 831, 795, 770, 702, 662 cm^{-1}.

MP 108.5–109.5 ^{o}C.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6
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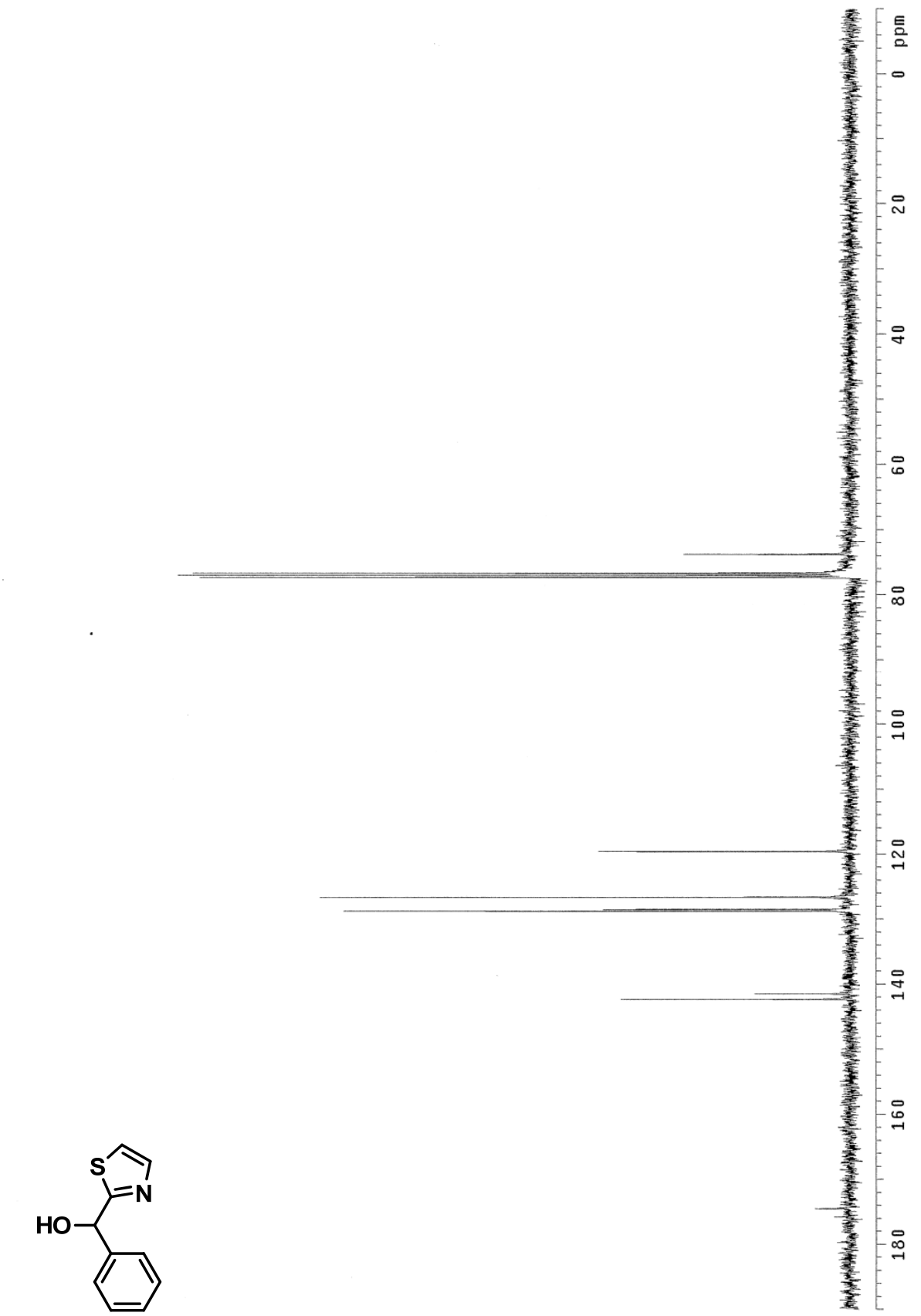
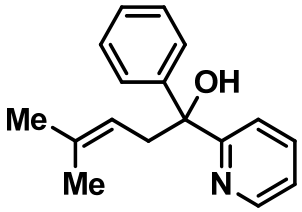
4
3
2
1
0 ppm


S
N
HO
0
20
40
60
80
100
120
140
160
180
ppm

b. General Procedure for the Coupling of Isoprene to Pyridyl Methanol 1a–1o:

To a pressure tube equipped with magnetic stir bar was added pyridyl methanol **1a**–**1o** (0.300 mmol, 100 mol%), $Ru_3(CO)_{12}$ (1.9 mg, 0.003 mmol, 1 mol%) and PCy_3 (4.2 mg, 0.015 mmol, 5 mol%). The tube was then sealed with a rubber septum, purged with argon. At this stage, PhMe (0.15 mL, 2.0 M concentration with respect to pyridyl methanol), and isoprene (60 μL, 0.600 mmol, 200 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 130 ^{o}C for the indicated time. The reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to furnish prenylated pyridyl methanols.

Phenyl Pyridyl Prenyl Methanol (3a).



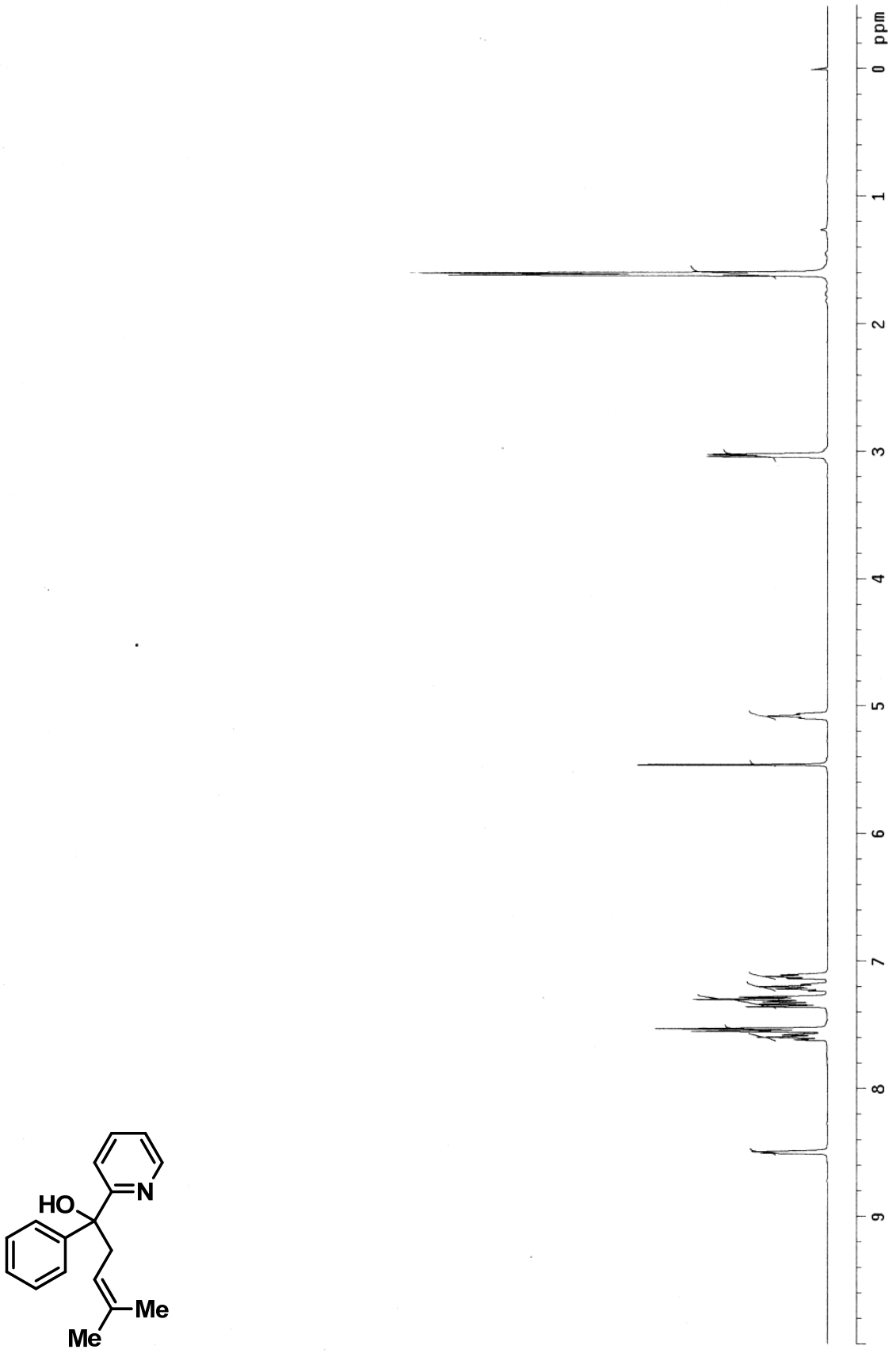
The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (68.6 mg, 90% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51–8.49 (m, 1H), 7.62–7.58 (m, 1H), 7.56–7.53 (m, 2H), 7.36–7.28 (m, 3H), 7.23–7.18(m, 1H), 7.14–7.11 (m, 1H), 5.46 (d, J = 1.6 Hz, 1H), 5.10–5.06 (m, 1H), 3.03 (d, J = 7.2 Hz, 2H), 1.62 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 144.4, 142.5, 138.8, 128.3, 127.4, 125.5, 119.5, 117.7, 78.3, 41.9, 26.2, 18.4.

LRMS (CI) Calcd. for $C_{17}H_{20}NO$ $[M+H]^+$: 254, Found: 254.

FTIR (neat): 3351, 2969, 2913, 1590, 1571, 1468, 1446, 1432, 1376, 1293, 1189, 1152, 1109, 1090, 1065, 998, 886, 838, 789, 748, 698, 665 cm^{-1}.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Me
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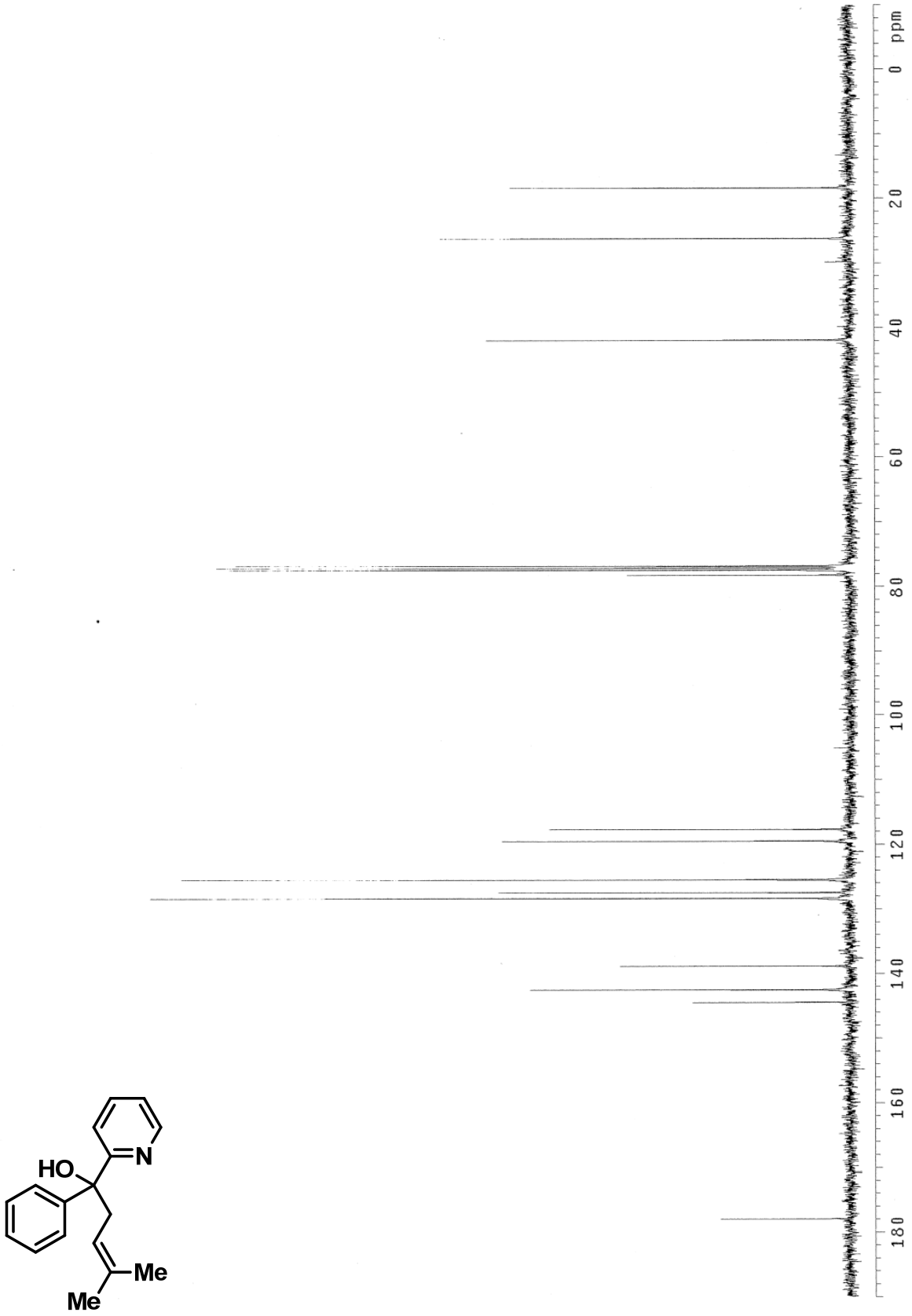
ppm


ppm
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80
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HO
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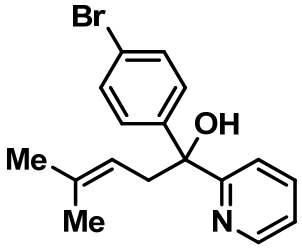
Me
Me

4-Bromophenyl Pyridyl Prenyl Methanol (3b).



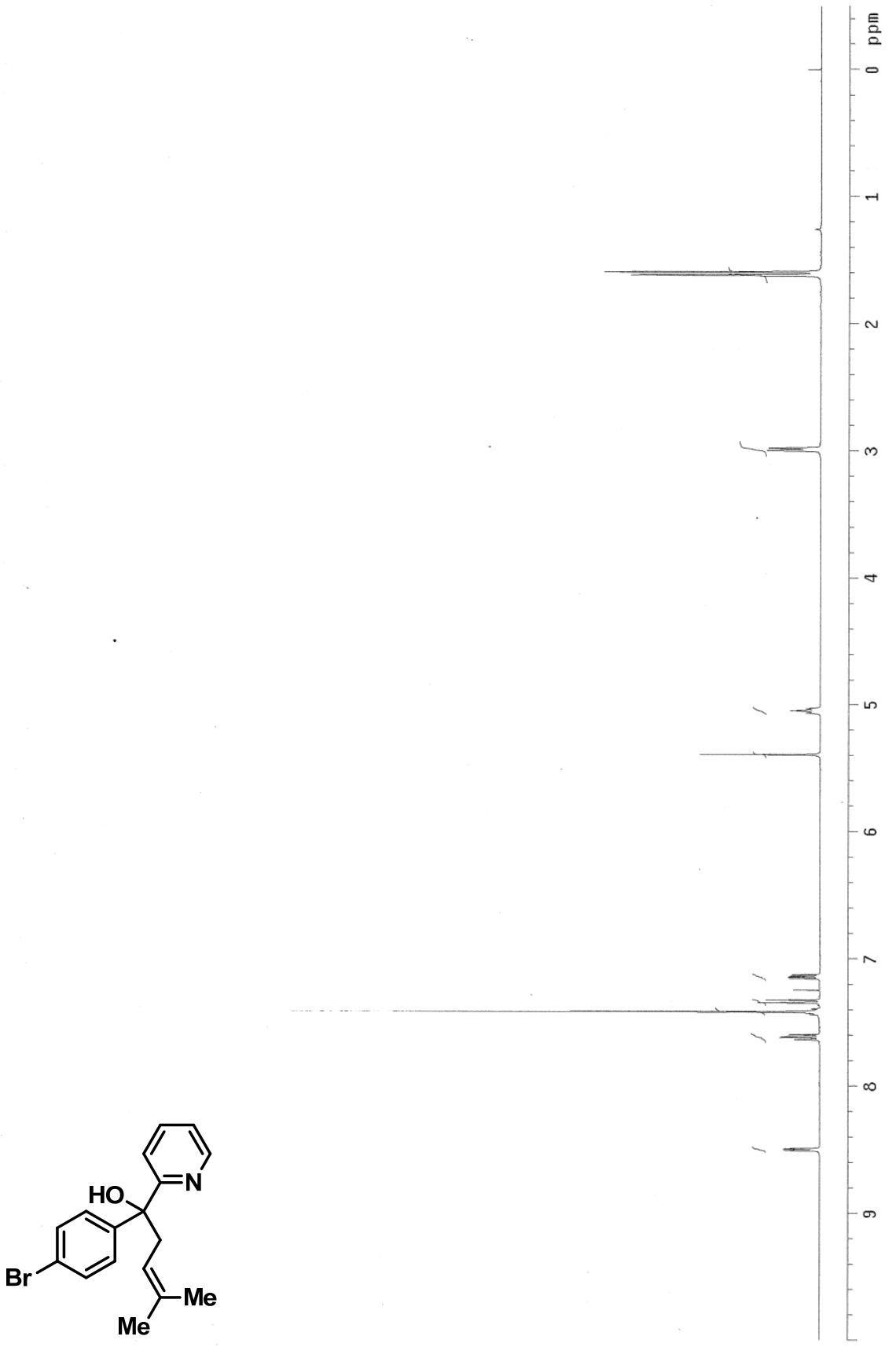
The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (91.7 mg, 92% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51–8.49 (m, 1H), 7.64–7.60 (m, 1H), 7.44–7.39 (m, 4H), 7.35–7.32 (m, 1H), 7.16–7.12 (m, 1H), 5.39 (s, 1H), 5.07–5.03 (m, 1H), 2.99 (dd, *J* = 6.8, 0.8 Hz, 2H), 1.62 (d, *J* = 1.6 Hz, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 147.6, 145.4, 137.0, 135.4, 131.2, 128.1, 122.2, 121.0, 120.5, 118.7, 40.0, 26.0, 18.3.

LRMS (CI) Calcd. for $C_{17}H_{19}BrNO$ $[M+H]^+$: 332, Found: 332.

FTIR (neat): 3375, 2969, 2912, 1738, 1590, 1570, 1485, 1468, 1433, 1393, 1375, 1291, 1216, 1152, 1102, 1072, 1052, 1008, 936, 886, 820, 781, 749, 735, 716, 669 cm^{-1}.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N
Br
Me
Me
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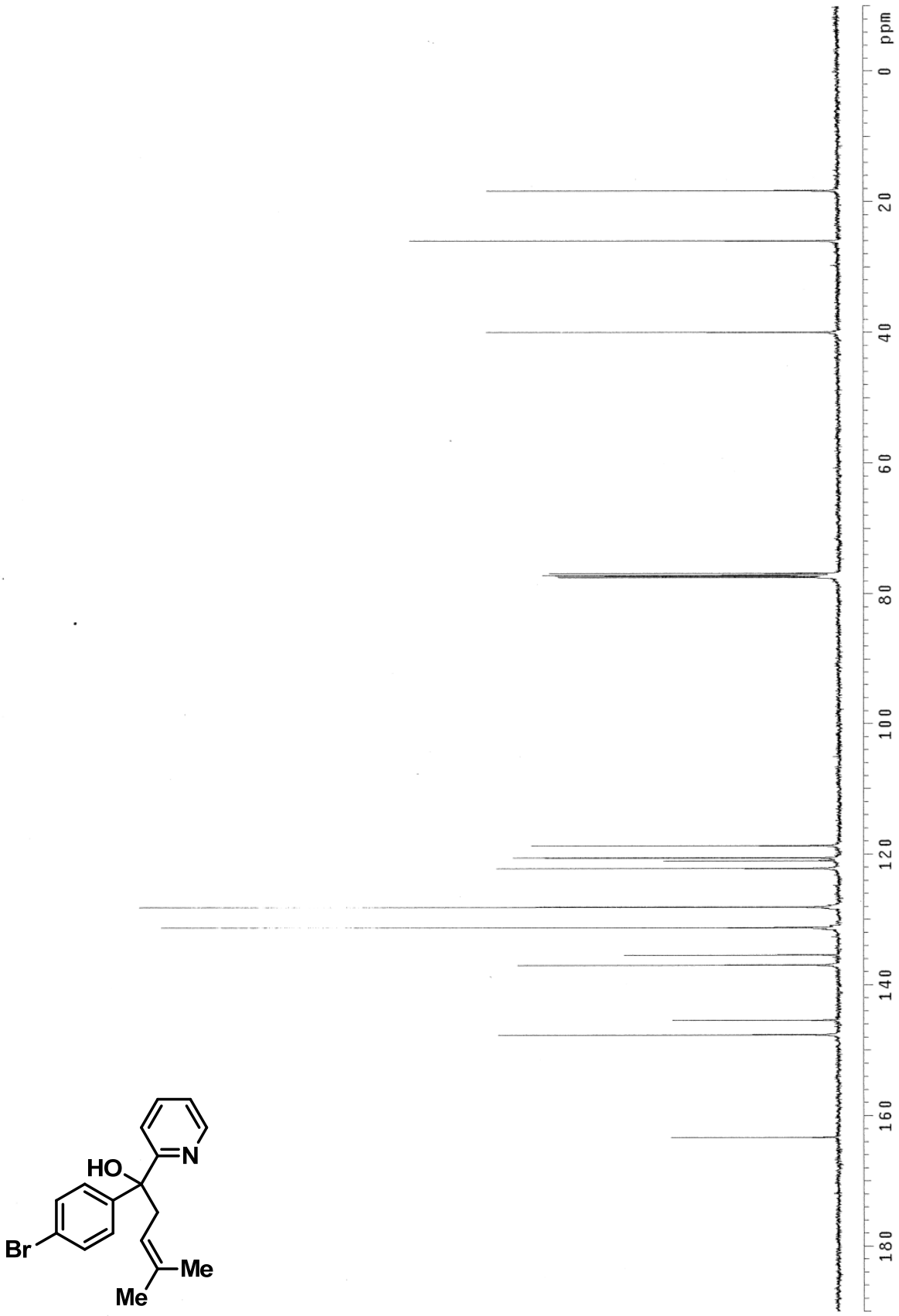
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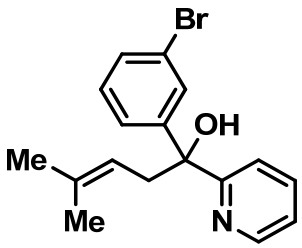
3-Bromophenyl Pyridyl Prenyl Methanol (3c).



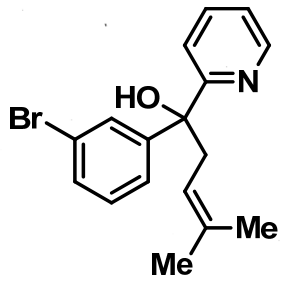
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) was employed. After 24 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (89.0 mg, 90% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53–8.51 (m, 1H), 7.71 (t, *J* = 2.0 Hz, 1H), 7.65 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.48–7.45 (m, 1H), 7.37–7.32 (m, 2H), 7.19–7.15 (m, 2H), 5.42 (s, 1H), 5.06–5.02 (m, 1H), 2.99 (d, *J* = 6.8 Hz, 2H), 1.63 (d, *J* =1.2 Hz, 3H), 1.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 148.8, 147.7, 137.1, 135.6, 130.1, 129.8, 129.5, 124.9, 122.6, 122.3, 120.7, 118.6, 40.0, 26.0, 18.4.

LRMS (CI) Calcd. for $C_{17}H_{19}BrNO$ $[M+H]^+$: 332, Found: 332.

FTIR (neat): 3352, 2970, 2913, 2355, 1738, 1588, 1568, 1467, 1433, 1416, 1375, 1294, 1169, 1112, 1096, 1072, 1052, 996, 892, 839, 792, 775, 749, 697, 683, 657 cm^{-1}.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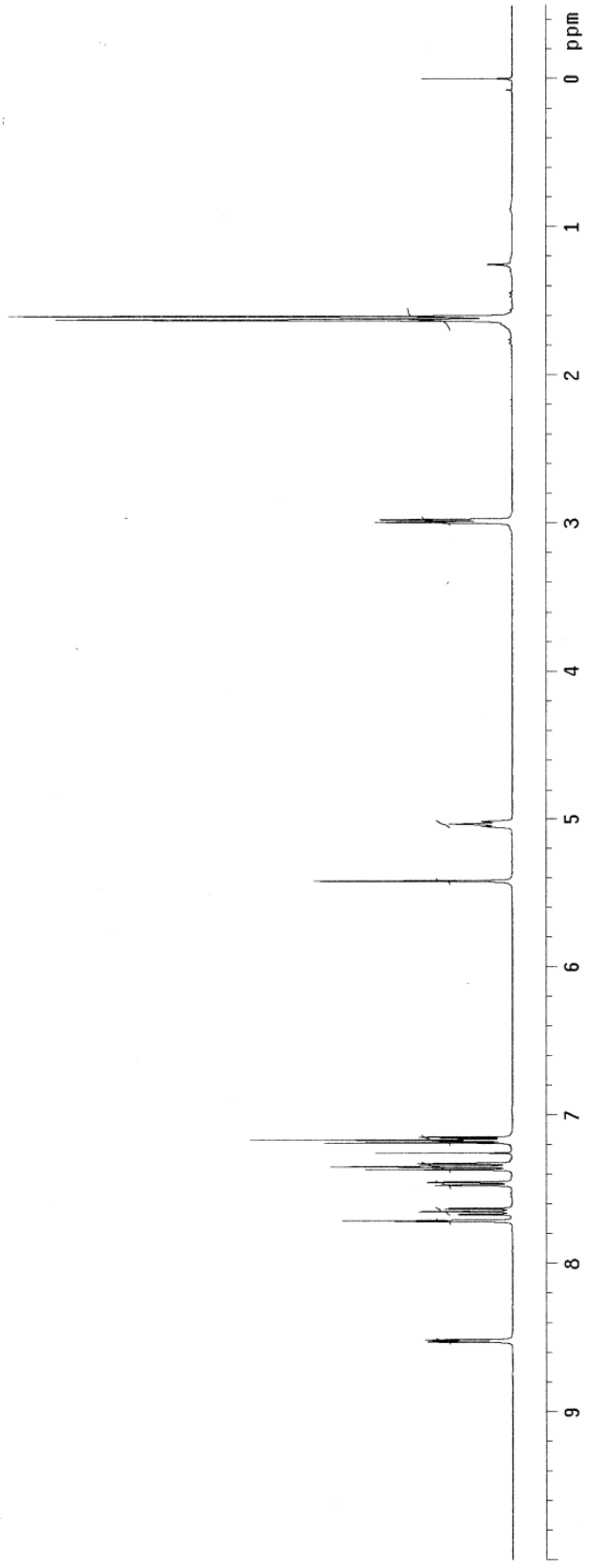
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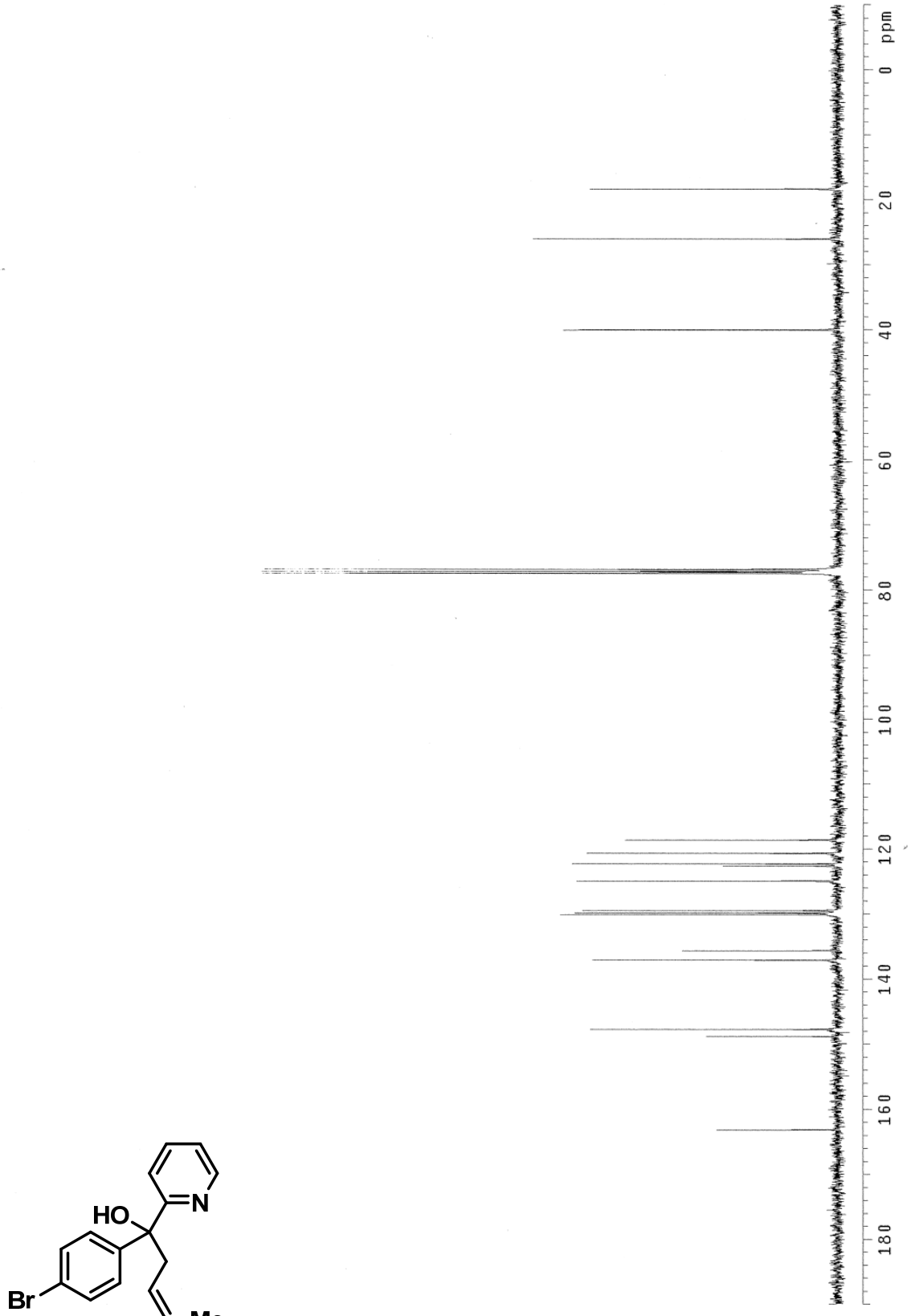
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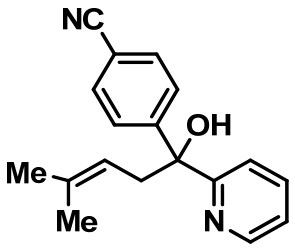
20
40
60
80
100
120
140
160
180

HO
N
Br
Me
Me

4-Cyanophenyl Pyridyl Prenyl Methanol (3d).



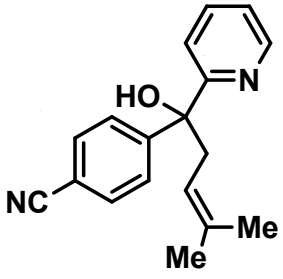
The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (83.0 mg, 99% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55–8.53 (m, 1H), 7.70–7.65 (m, 3H), 7.61–7.58 (m, 2H), 7.38 (dt, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.20 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1H), 5.31 (s, 1H), 5.03–4.99 (m, 1H), 3.01 (d, *J* = 7.2 Hz, 2H), 1.63 (d, *J* = 0.8 Hz, 3H), 1.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 151.5, 147.7, 137.0, 135.9, 131.9, 126.8, 122.3, 120.3, 118.8, 118.0, 110.5, 39.7, 25.8, 18.1.

LRMS (CI) Calcd. for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279, Found: 279.

FTIR (neat): 2915, 2227, 1606, 1589, 1573, 1504, 1469, 1454, 1434, 1403, 1384, 1292, 1191, 1153, 1105, 1079, 1052, 996, 888, 832, 787, 751, 710, 685 cm^{-1}.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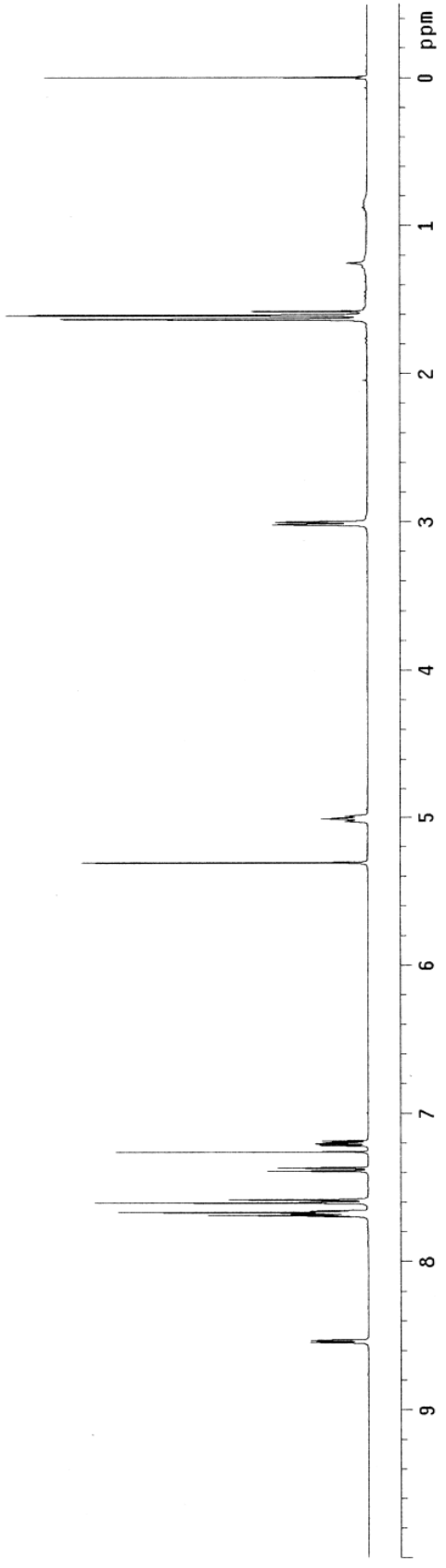
N
NC
Me
Me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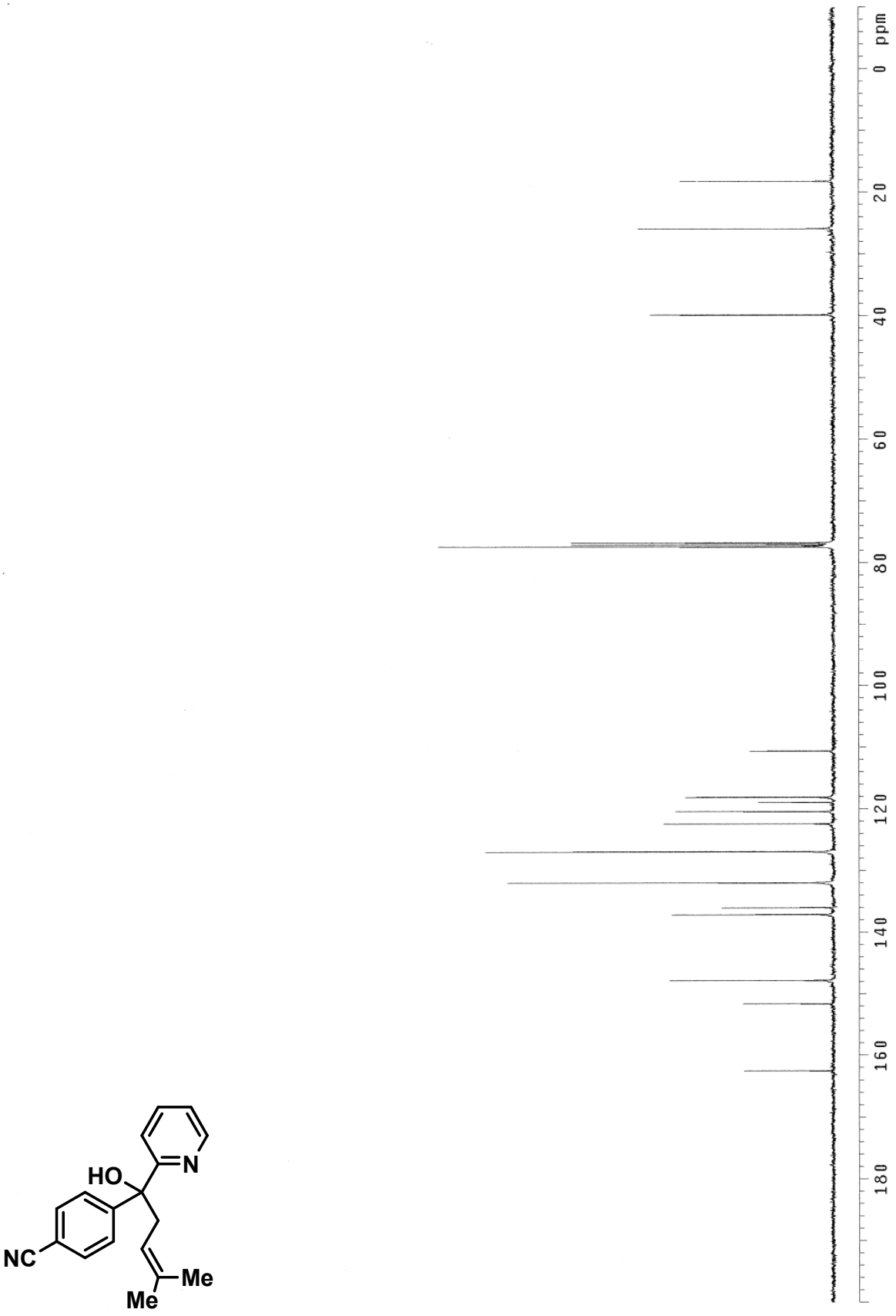
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N
NC
Me
Me
0 ppm
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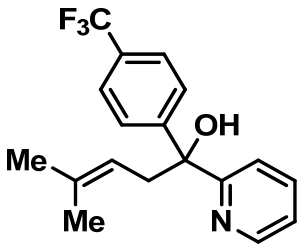
40
60
80
100
120
140
160
180

4-Trifluoromethylphenyl Pyridyl Prenyl Methanol (3e).



The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was purified flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (91.1 mg, 95% yield) as a yellow oil.

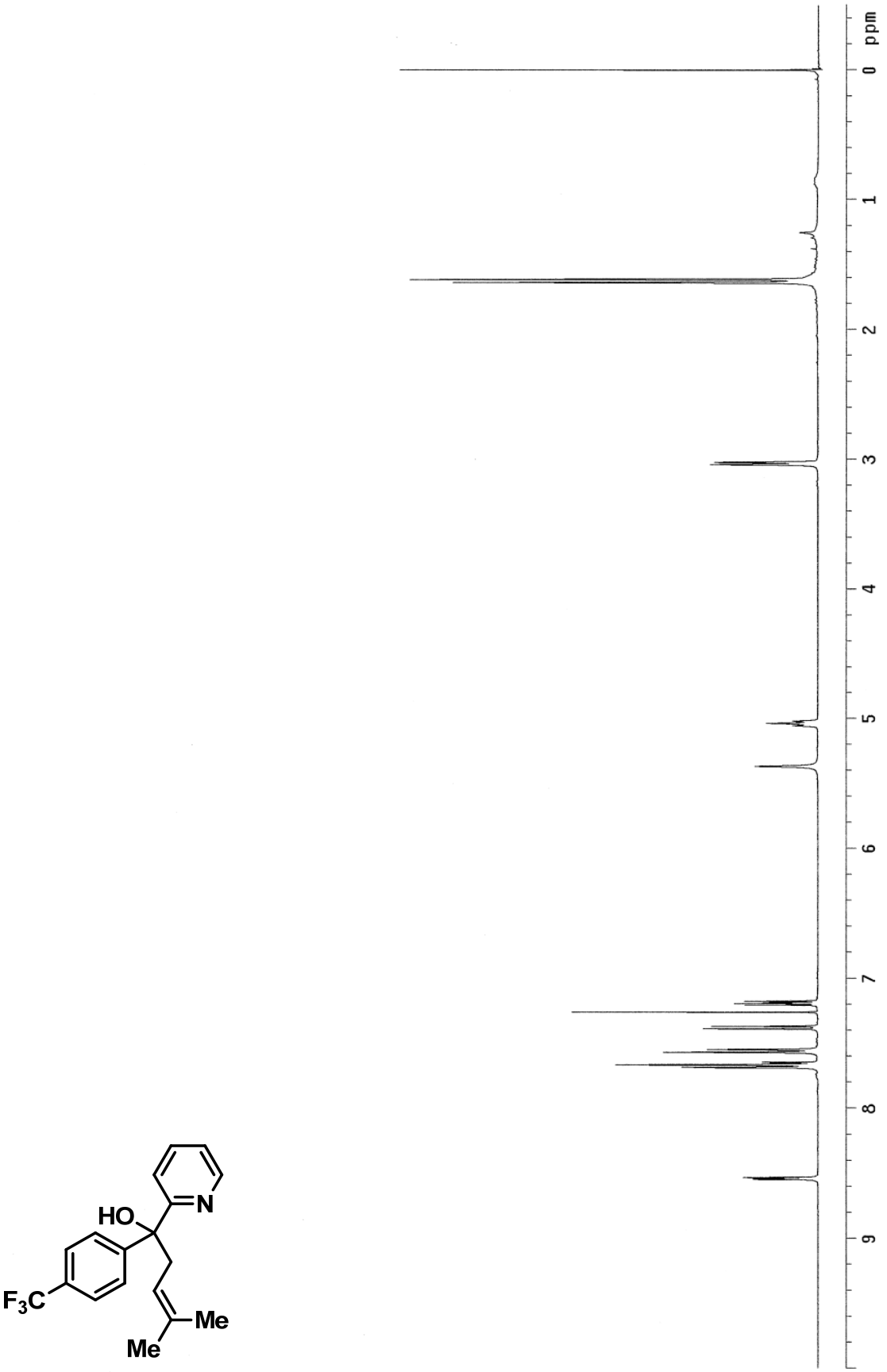
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55–8.53 (m, 1H), 7.69–7.65 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.39–7.37 (m, 1H), 7.21–7.17 (m, 1H), 5.37 (s, 1H), 5.06–5.02 (m, 1H), 3.03 (dd, *J* = 6.8, 1.2 Hz, 2H), 1.64 (d, *J* = 0.8 Hz, 3H), 1.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 150.2, 147.7, 137.0, 135.7, 129.0 (q, *J* = 32 Hz), 126.5, 125.1, 125.1, 124.2 (d, *J* = 270.8 Hz), 122.9, 122.2, 120.5, 118.4, 39.9, 25.9, 18.2.

^{19}F NMR (376 MHz, CDCl3): δ -62.4.

LRMS (CI) Calcd. for $C_{18}H_{19}F_3NO$ $[M+H]^+$: 322, Found: 322.

FTIR (neat): 3377, 2917, 1618, 1590, 1572, 1468, 1434, 1409, 1324, 1163, 1120, 1067, 1017, 999, 887, 835, 787, 751, 724, 670 cm^{-1}.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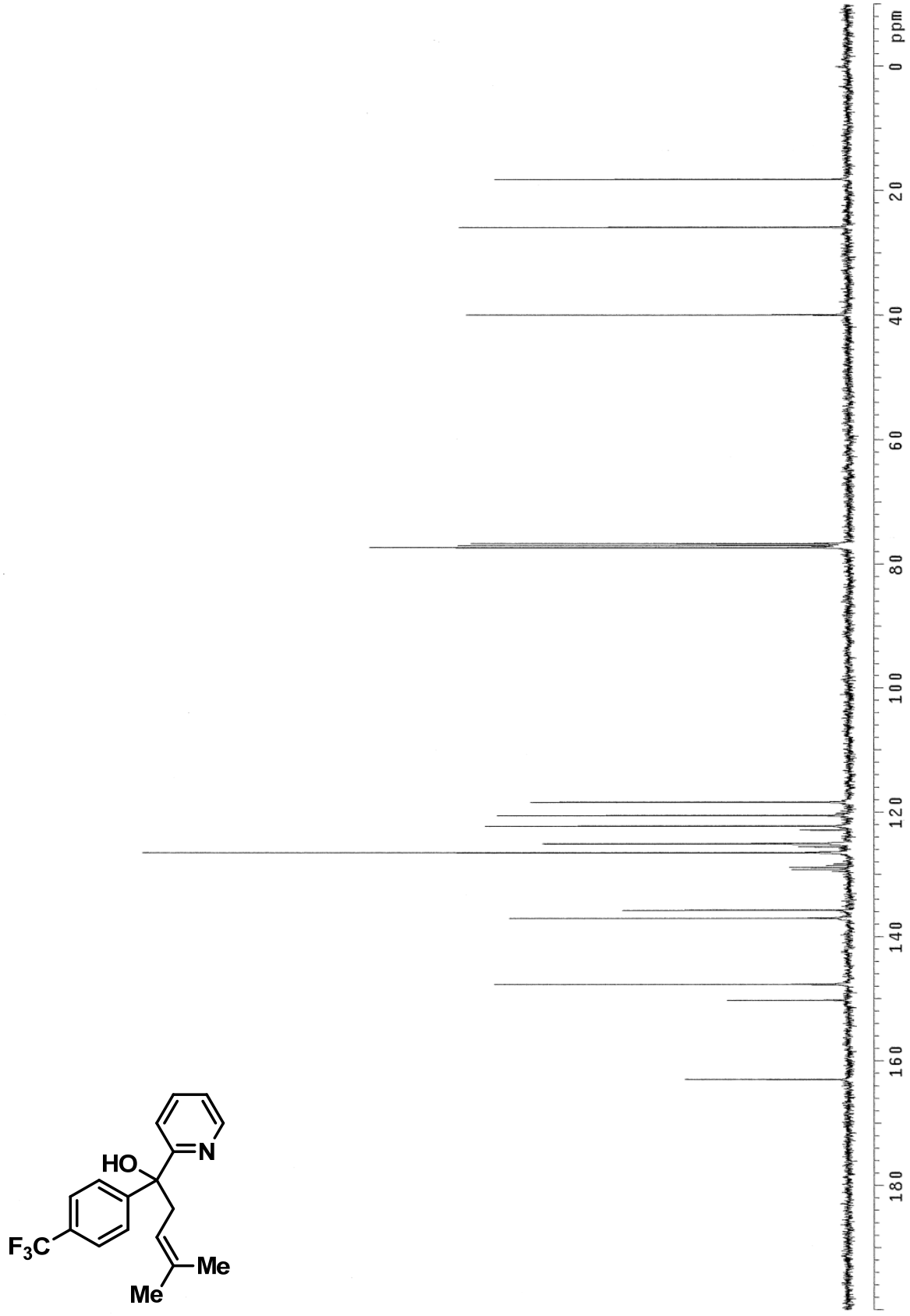
9

HO
N
F3C
Me
Me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N
F3C
Me
Me
0 ppm
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40
60
80
100
120
140
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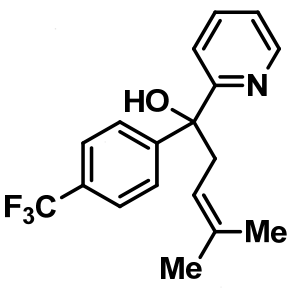
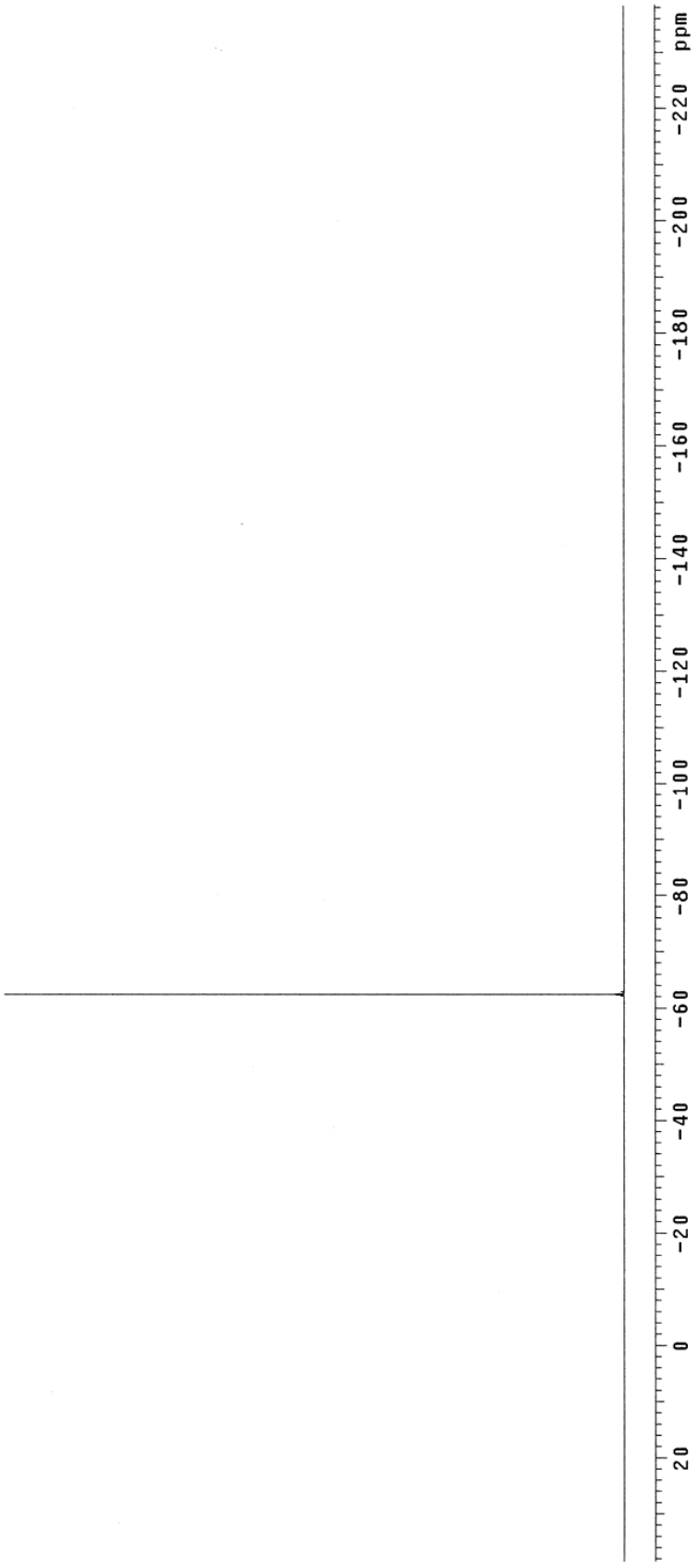
180


HO
N
F3C
Me
Me


20
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-40
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-80
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-140
-160
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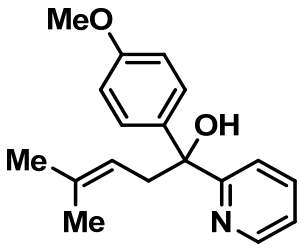
-200
-220
ppm

4-Methoxyphenyl Pyridyl Prenyl Methanol (3f).



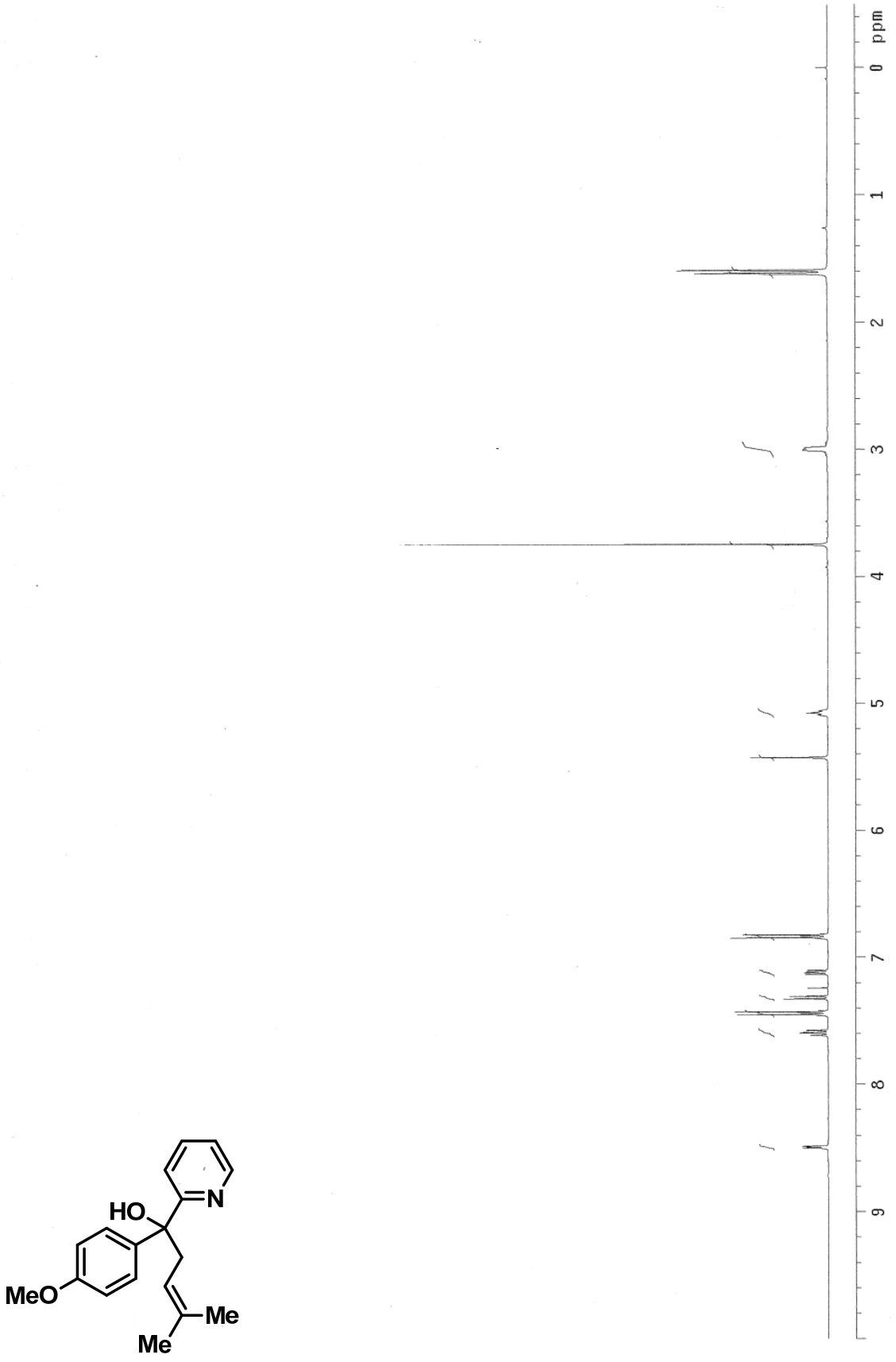
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) was employed. After 24 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 5% EtOAc/hexanes) to furnish the title compound (76.2 mg, 90% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50–8.48 (m, 1H), 7.60 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.46–7.42 (m, 2H), 7.32 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.12 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 6.85–6.82 (m, 2H), 5.43 (s, 1H), 5.10–5.06 (m, 1H), 3.75 (s, 3H), 3.01–2.99 (m, 2H), 1.62 (d, *J* = 1.2 Hz, 3H), 1.59 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 158.5, 147.4, 138.5, 136.8, 134.8, 127.4, 121.9, 120.7, 119.2, 113.5, 55.2, 40.1, 26.0, 18.3.

LRMS (CI) Calcd. for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284, Found: 284.

FTIR (neat): 3376, 2910, 2835, 1737, 1609, 1590, 1570, 1509, 1465, 1433, 1375, 1301, 1247, 1177, 1105, 1076, 1034, 998, 940, 887, 829, 797, 783, 750 cm^{-1}.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N
MeO
Me
Me
ppm
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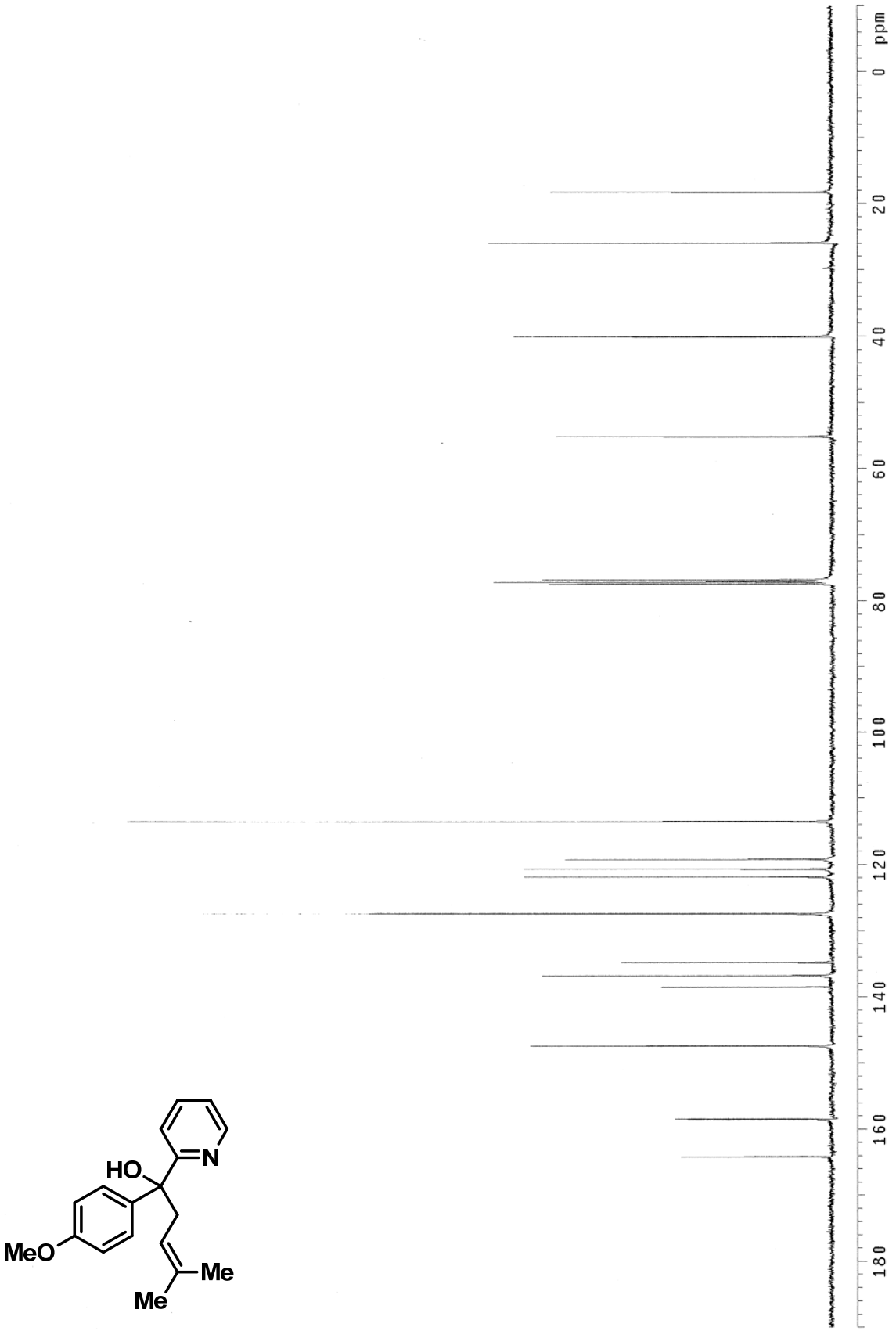
3
4
5
6
7
8
9


HO
N
MeO
Me
Me
ppm
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100
120
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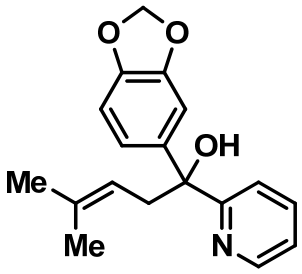
160
180

1,3-Benzodioxole Pyridyl Prenyl Methanol (3g).



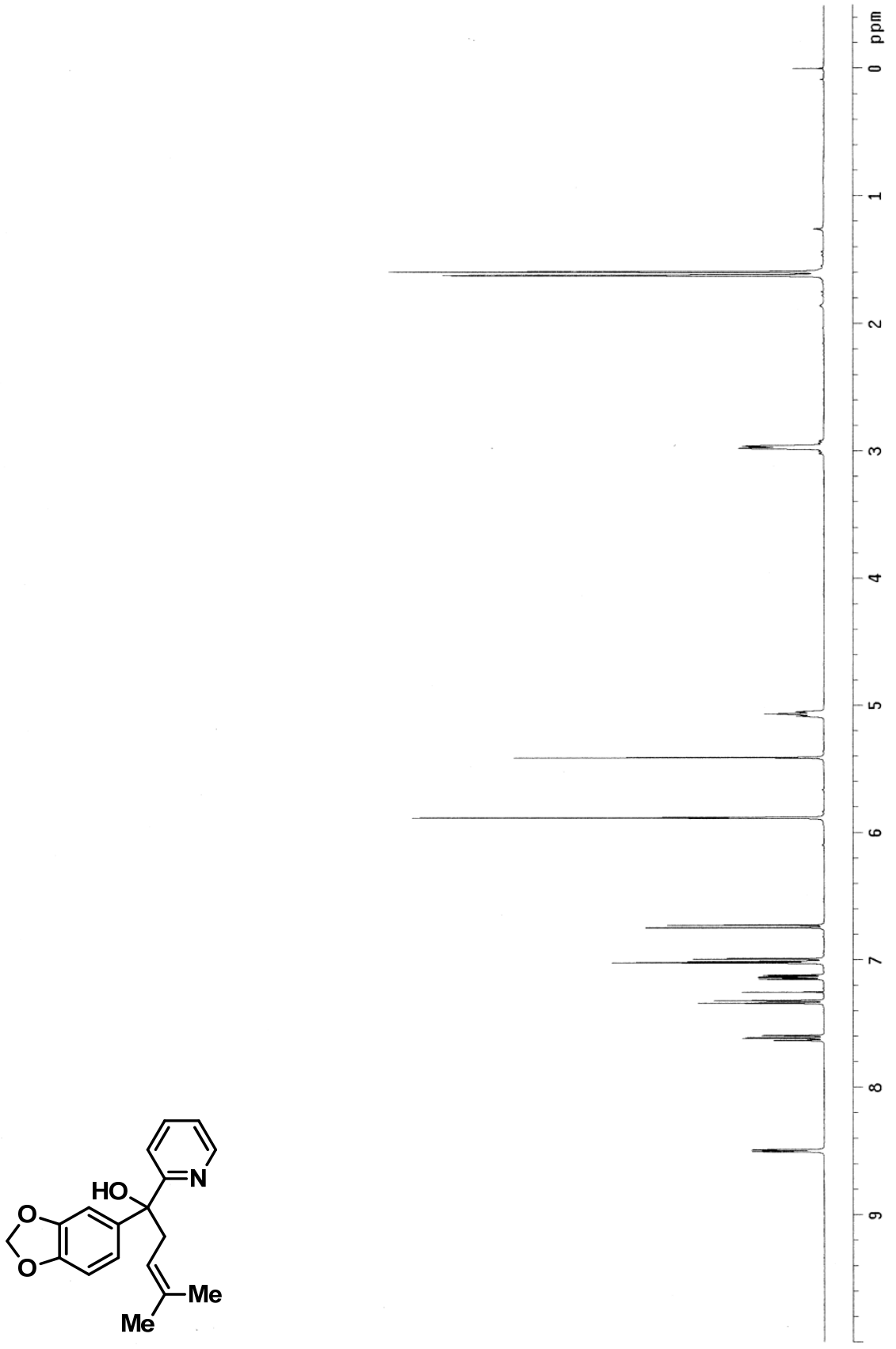
The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (76.0 mg, 85% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51–8.49 (m, 1H), 7.61 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.34–7.32 (m, 1H), 7.13 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 7.02–6.99 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.89–5.88 (m, 2H), 5.41 (s, 1H), 5.09–5.05 (m, 1H), 2.97 (d, *J* =6.8 Hz, 2H), 1.62 (d, *J* = 0.8 Hz, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 147.6, 147.5, 146.4, 140.6, 136.8, 135.0, 122.0, 120.6, 119.3, 119.0, 107.8, 107.3, 111.0, 40.1, 26.0, 18.3.

LRMS (CI) Calcd. for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298, Found: 298.

FTIR (neat): 3373, 2912, 1742, 1590, 1570, 1502, 1486, 1468, 1433, 1376, 1293, 1235, 1152, 1106, 1078, 1038, 998, 935, 912, 865, 812, 782, 750, 735, 715, 678 cm^{-1}.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Me
Me
0 ppm
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2
3
4
5
6
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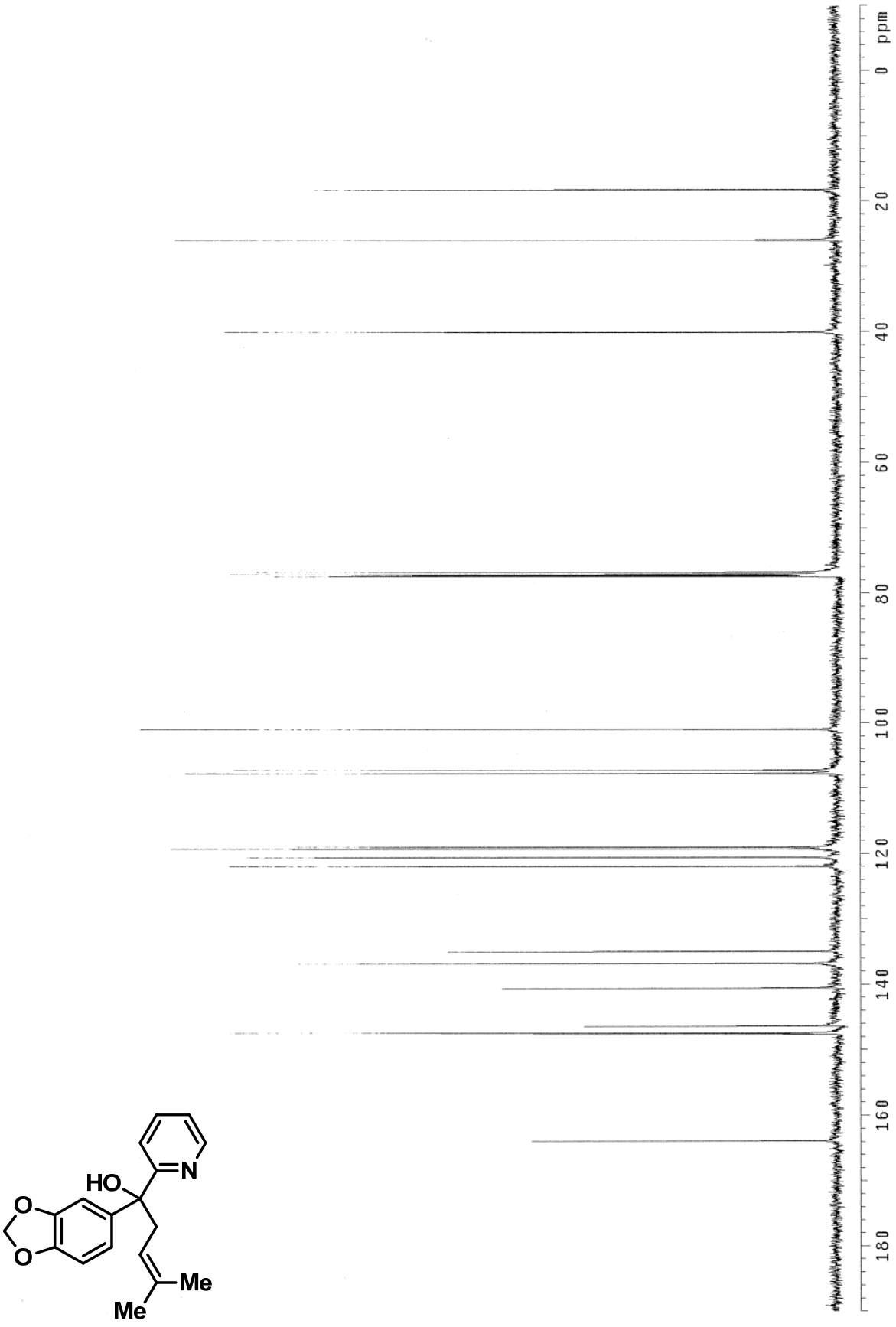
8
9


HO
N
O
O
Me
Me
0 ppm
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40
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80
100
120
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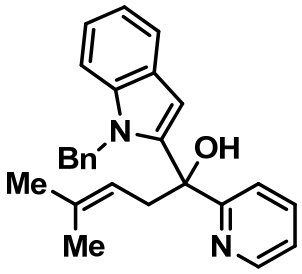
160
180

2-(*N*-Bn-indolyl) Pyridyl Prenyl Methanol (3h).



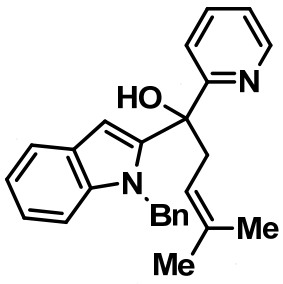
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) was employed. After 24 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 10% EtOAc/hexanes) to furnish the title compound (71.3 mg, 62% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.56–8.55 (m, 1H), 7.54 (td, J = 8.0, 2.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.30–7.17 (m, 6H), 7.14–7.05 (m, 4H), 6.96–6.92 (m, 1H), 5.59 (s, 1H), 5.27 (s, 2H), 5.18–5.14 (m, 1H), 3.15 (dd, J = 14.8, 6.8 Hz, 1H), 2.99 (dd, J = 14.8, 6.8 Hz, 1H), 1.61 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 147.2, 137.6, 137.3, 136.7, 134.4, 128.8, 127.7, 126.9, 126.6, 126.4, 121.9, 121.8, 121.4, 121.0, 120.8, 119.4, 109.7, 75.4, 50.1, 40.7, 26.0, 18.2.

LRMS (CI) Calcd. for $C_{26}H_{27}N_2O$ $[M+H]^+$: 383, Found: 383.

FTIR (neat): 3371, 2914, 1738, 1591, 1569, 1548, 1496, 1466, 1453, 1433, 1355, 1331, 1293, 1217, 1178, 1106, 1049, 1028, 1016, 998, 908, 872, 787, 733, 696 cm^{-1}.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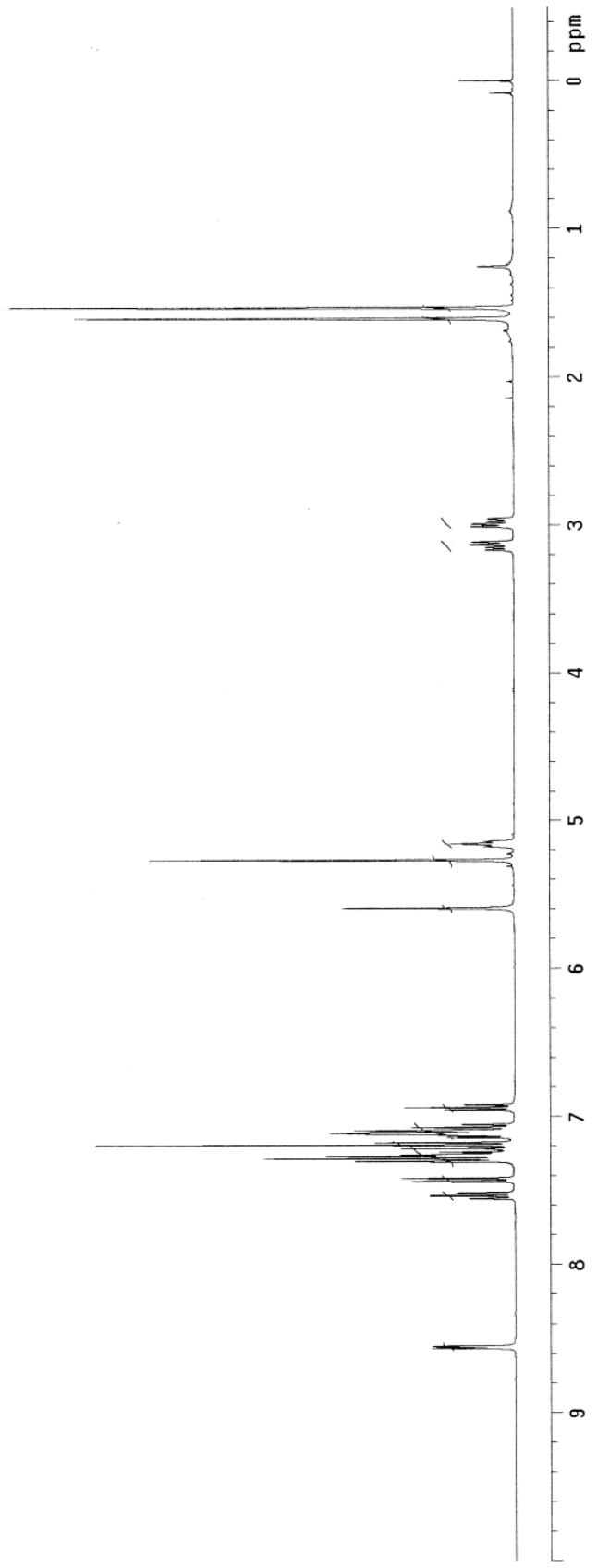
Bn
Me
Me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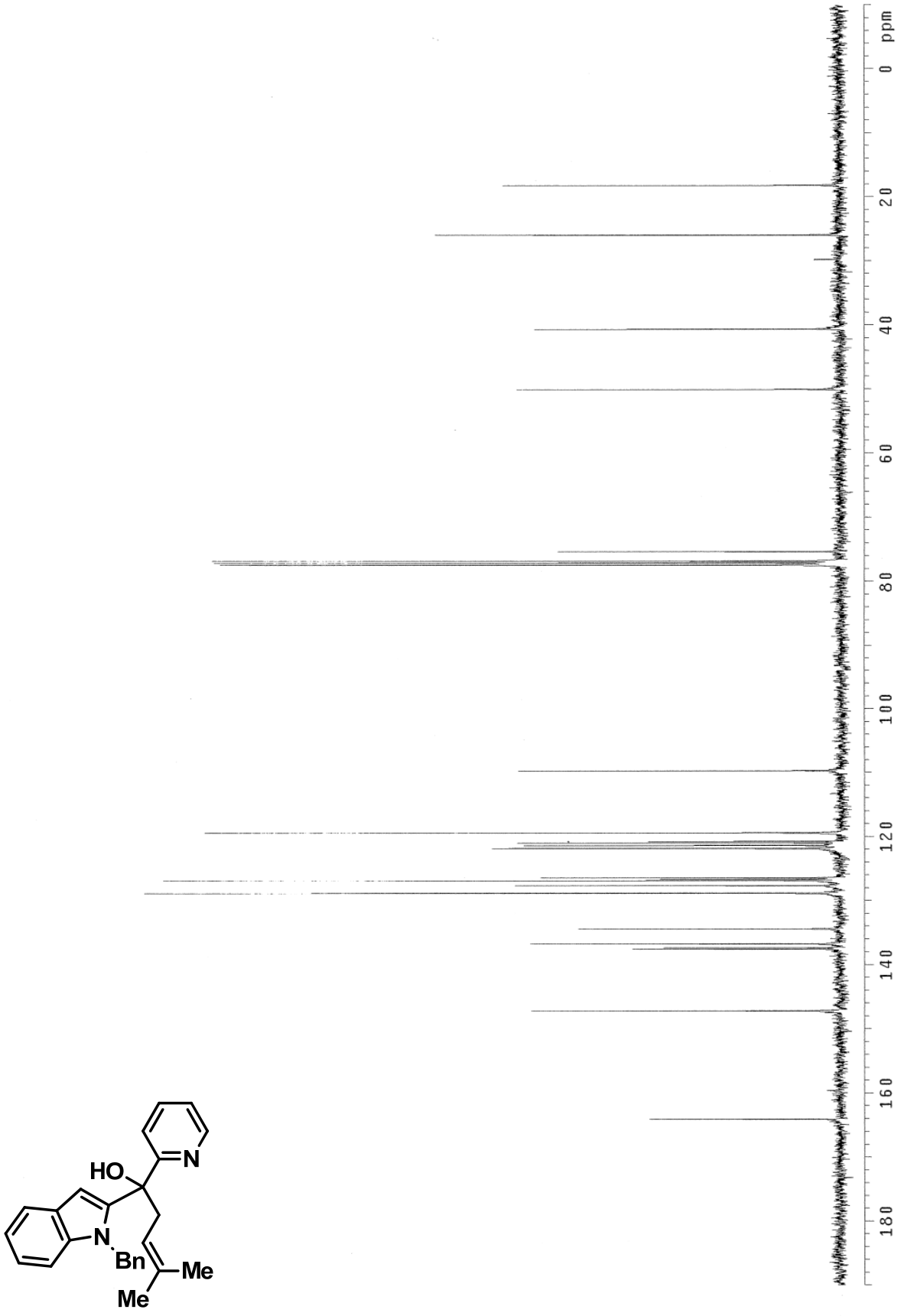
HO
N
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Bn
Me
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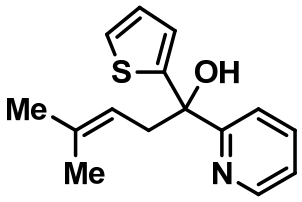
160
180

2-Thienyl Pyridyl Prenyl Methanol (3i).



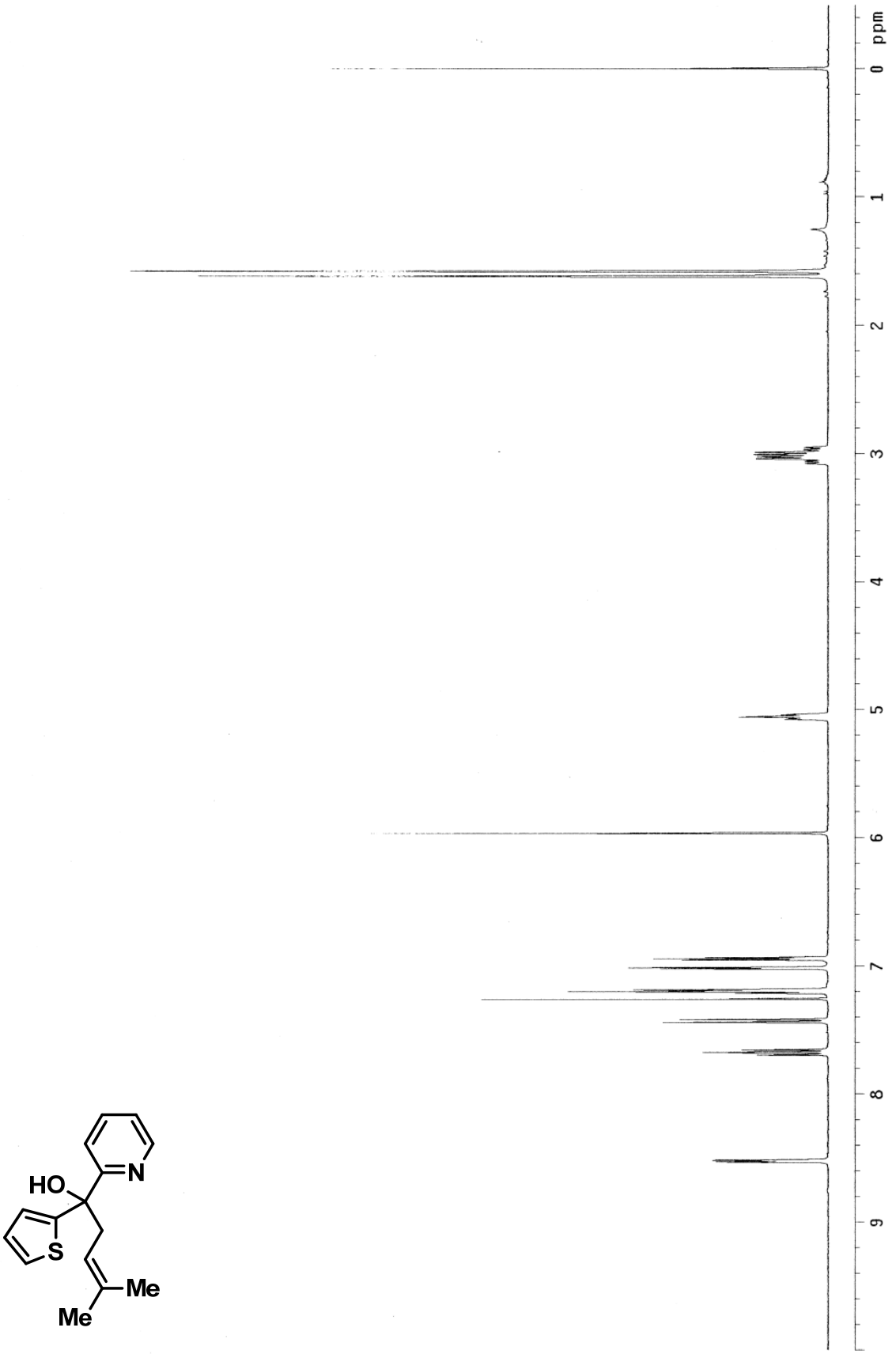
The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (63.0 mg, 90% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53–8.51 (m, 1H), 7.68 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.44–7.42 (m, 1H), 7.22–7.18 (m, 2H), 7.02–7.01 (m, 1H), 6.94 (dd, *J* = 5.0, 3.4 Hz, 1H), 5.97 (s, 1H), 5.08–5.04 (m, 1H), 3.05 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.98 (dd, *J* = 14.8, 2.4 Hz, 1H), 1.62 (s, 3H), 1.58 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 152.1, 147.1, 136.9, 135.1, 126.6, 124.6, 123.3, 122.2, 120.3, 118.4, 41.6, 25.8, 18.2.

LRMS (CI) Calcd. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260, Found: 260.

FTIR (neat): 3331, 2916, 1591, 1571, 1468, 1433, 1383, 1349, 1294, 1234, 1152, 1108, 1077, 1048, 999, 874, 848, 827, 781, 750, 697 cm^{-1}.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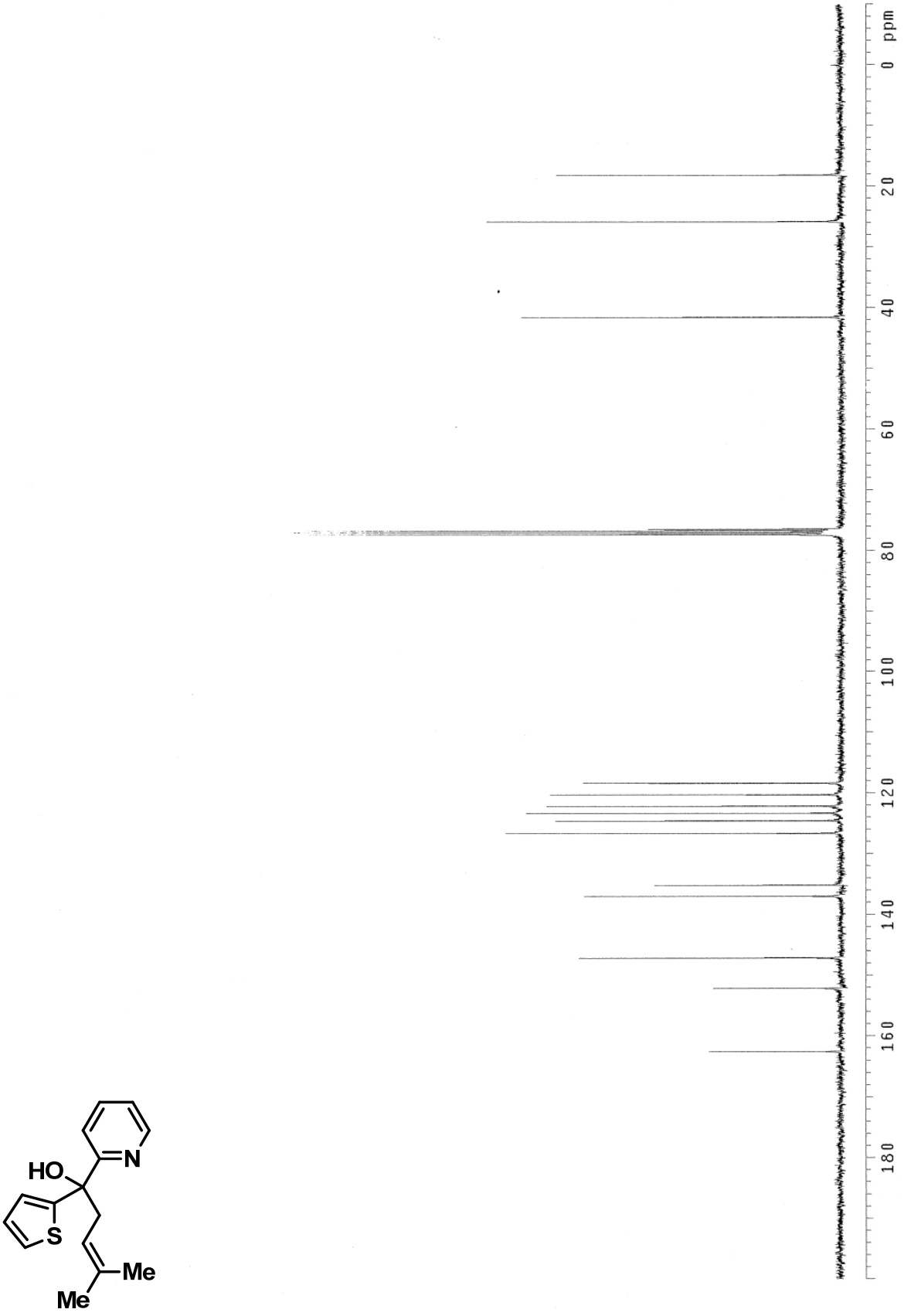
0 ppm
20
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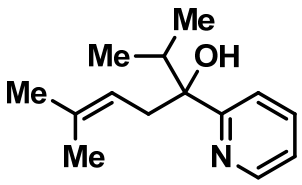
160
180

HO
N
S
Me
Me

Isopropyl Pyridyl Prenyl Methanol (3j).



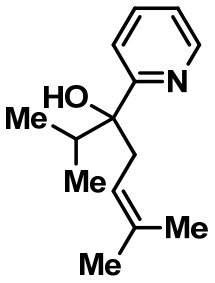
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) and PCy_3 (10 mol%) were employed. After 48 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (43.7 mg, 66% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51–8.49 (m, 1H), 7.64 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.15 (ddd, *J* = 6.0, 4.8, 1.4 Hz, 1H), 5.05 (s, 1H), 4.89–4.85 (m, 1H), 2.65 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.52 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.05 (heptet, *J* = 6.8 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.63 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 147.0, 136.2, 133.8, 121.5, 120.2, 119.4, 78.1, 37.7, 37.2, 25.8, 18.0, 17.3, 16.8.

LRMS (CI) Calcd. for $C_{14}H_{23}NO$ $[M+H]^+$: 220, Found: 220.

FTIR (neat): 3381, 2965, 2914, 2360, 1593, 1570, 1471, 1434, 1384, 1362, 1293, 1179, 1146, 1052, 1025, 999, 895, 838, 784, 751, 727 cm^{-1}.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Me
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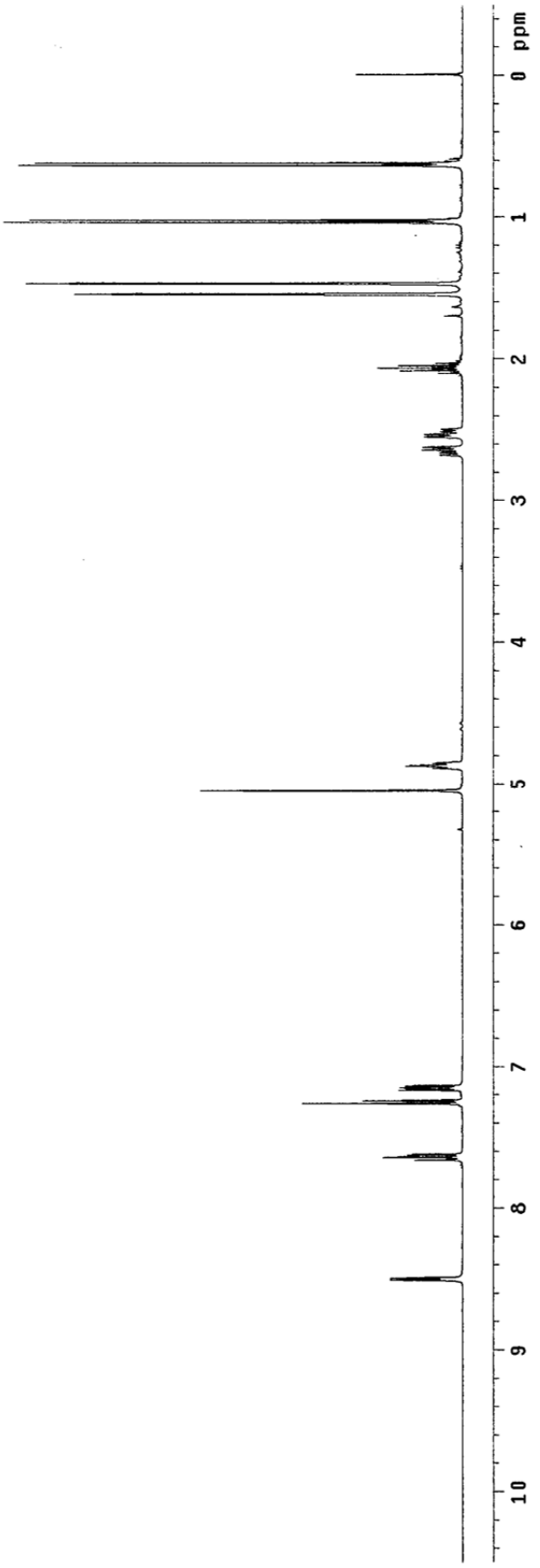
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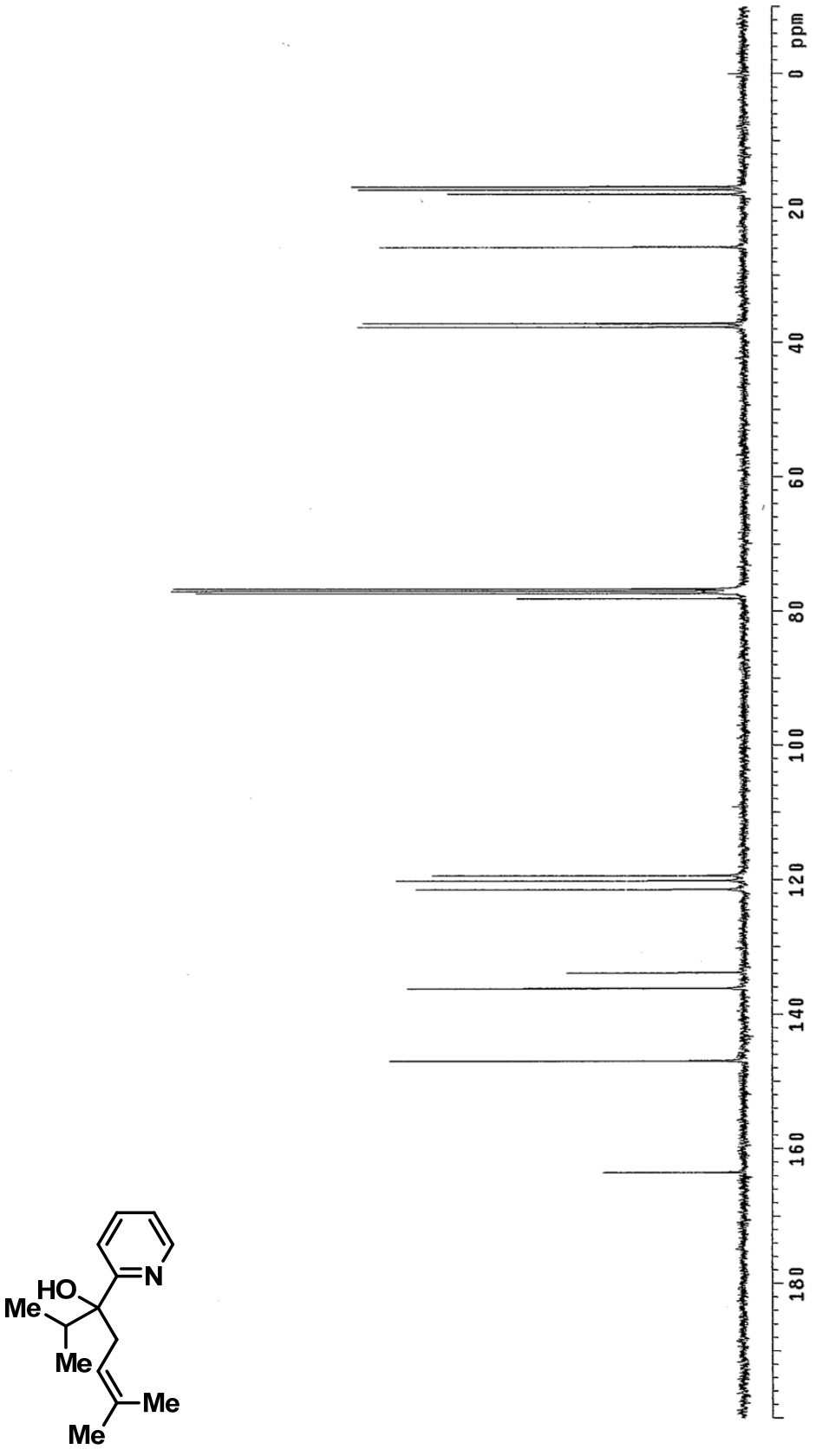
0 ppm
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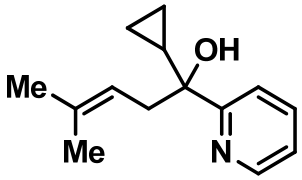
N
HO
Me
Me
Me
Me

Cyclopropyl Pyridyl Prenyl Methanol (3k).



In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) and PCy_3 (10 mol%) were employed. After 48 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (43.2 mg, 66%) as a yellow oil.

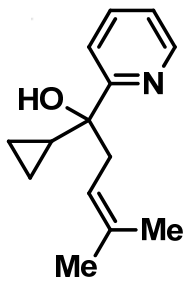
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49–8.48 (m, 1H), 7.71–7.67 (m, 1H), 7.39 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.19 (ddd, *J* = 4.8, 7.6, 1.2 Hz, 1H), 5.03–4.99 (m, 1H), 4.84 (s, 1H), 2.63 (d, *J* = 7.2 Hz, 2H), 1.60 (s, 3H), 1.53 (s, 3H), 1.26–1.19 (m, 1H), 0.68–0.62 (m, 1H), 0.47–0.40 (m, 1H), 0.32–0.26 (m, 1H), 0.20–0.13 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 147.2, 136.8, 134.3, 121.9, 120.1, 119.5, 74.0, 40.8, 26.1, 21.1, 18.2, 1.4.

LRMS (CI) Calcd. for $C_{14}H_{20}NO$ $[M+H]^+$: 218, Found: 218.

FTIR (neat): 3429, 3275, 3004, 2963, 2915, 1587, 1570, 1468, 1434, 1397, 1376, 1353, 1292, 1246, 1208, 1190, 1156, 1140, 1113, 1069, 1051, 1038, 1024, 1011, 999, 990, 915, 896, 836, 777, 751, 727 cm^{-1}.

MP 44–46 °C.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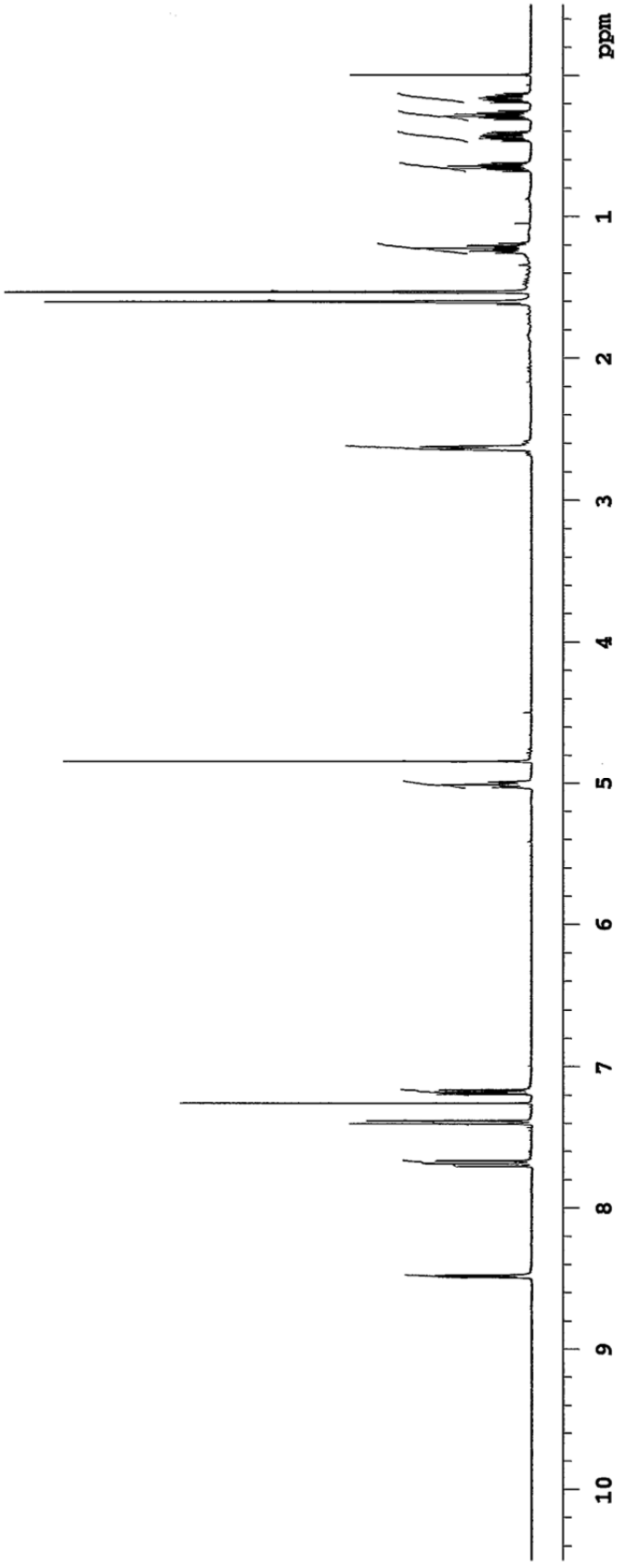
Me
Me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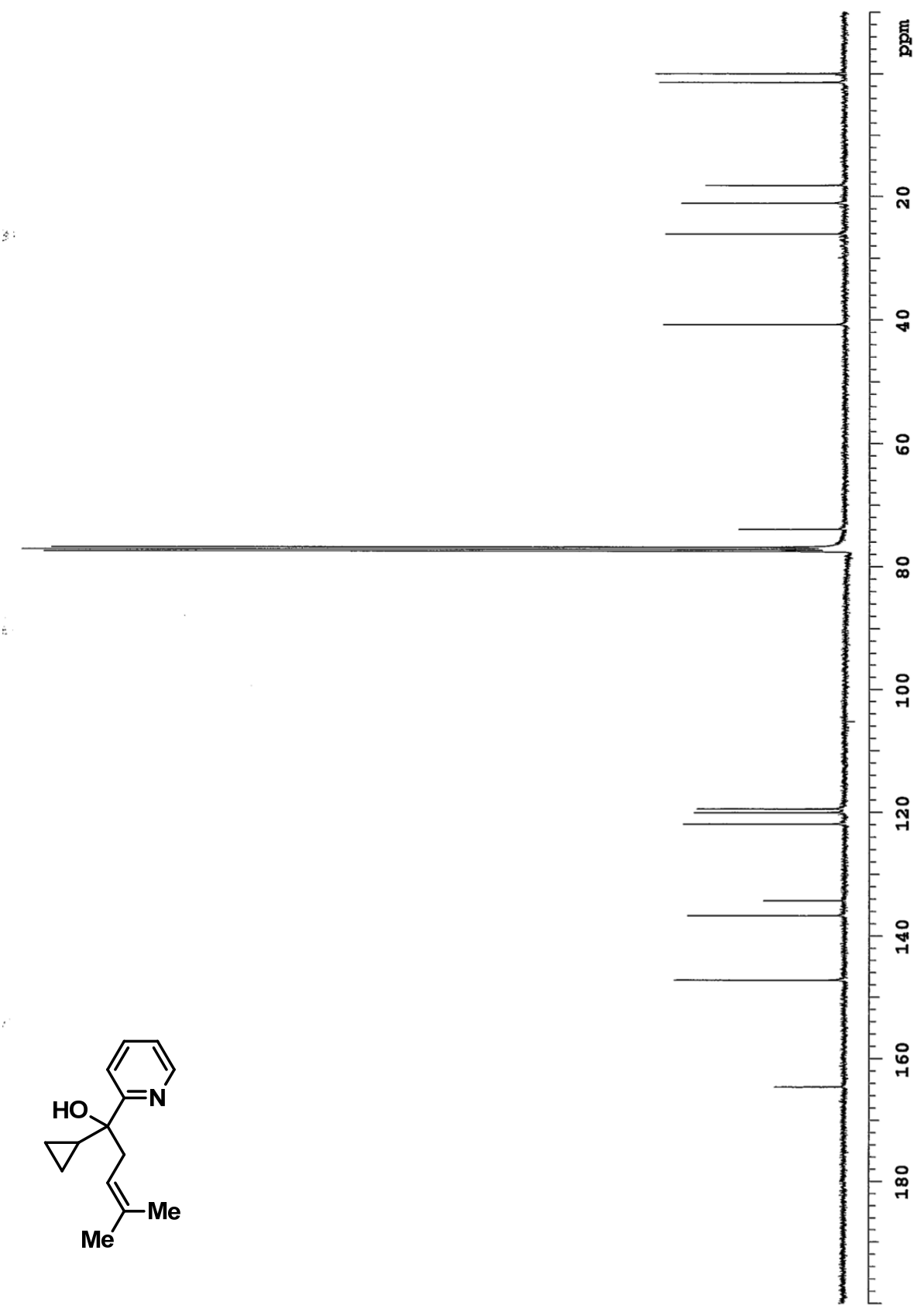
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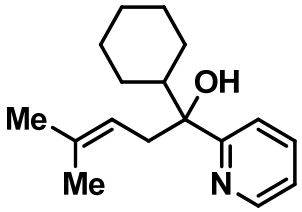
HO
N
Me
Me

Cyclohexyl Pyridyl Prenyl Methanol (3l).



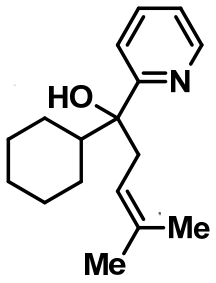
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) and PCy_3 (10 mol%) were employed. After 48 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (39.2 mg, 50% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.64 (dt, *J* = 6.4, 1.4 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 7.6, 5.6 Hz, 1H), 5.03 (s, 1H), 4.88–4.84 (m, 1H), 2.66 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.52 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.00–1.97 (m, 1H), 1.80–1.77 (m, 1H), 1.73-1.59 (m, 3H), 1.55 (s, 3H), 1.48 (s, 3H), 1.25–1.17 (m, 2H), 1.14–1.13 (m, 1H), 1.11–1.08 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 147.0, 136.2, 133.9, 121.4, 120.3, 119.4, 78.2, 47.4, 37.2, 27.2, 26.7, 26.6, 26.4, 25.9, 18.0.

LRMS (CI) Calcd. for $C_{17}H_{26}NO$ $[M+H]^+$: 260, Found: 260.

FTIR (neat): 2928, 2853, 2359, 1592, 1570, 1471, 1434, 1394, 1114, 1087, 777, 751, 667 cm^{-1}.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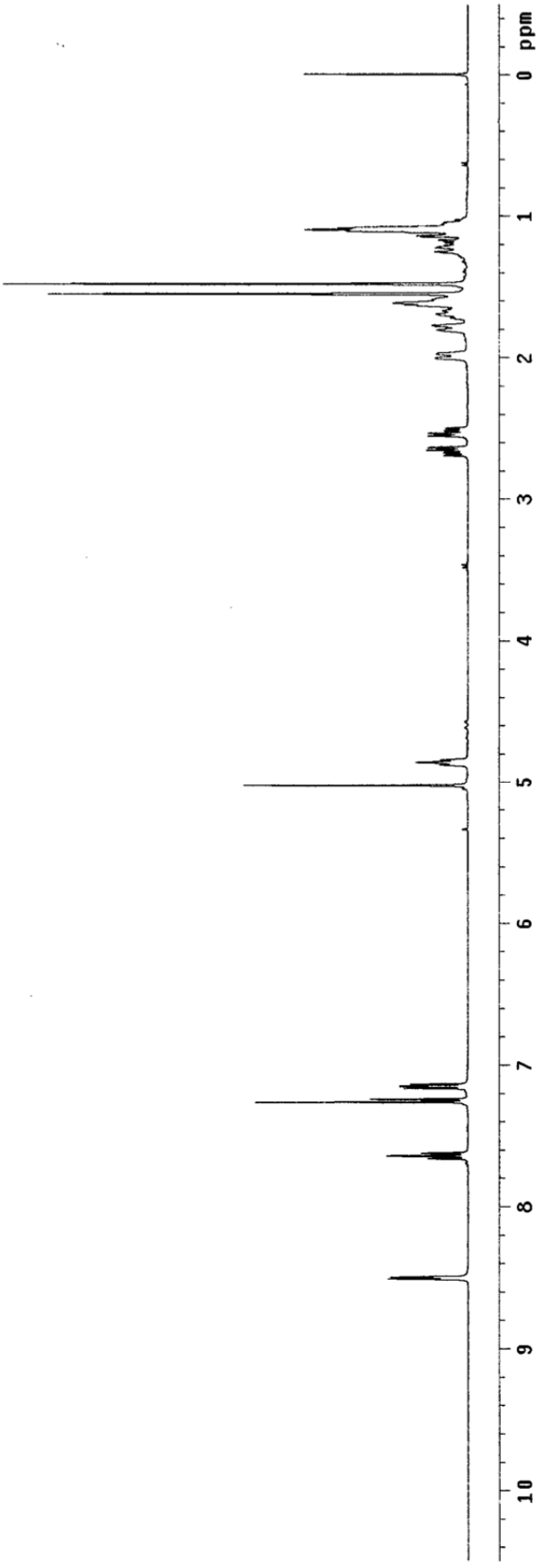
N
Me
Me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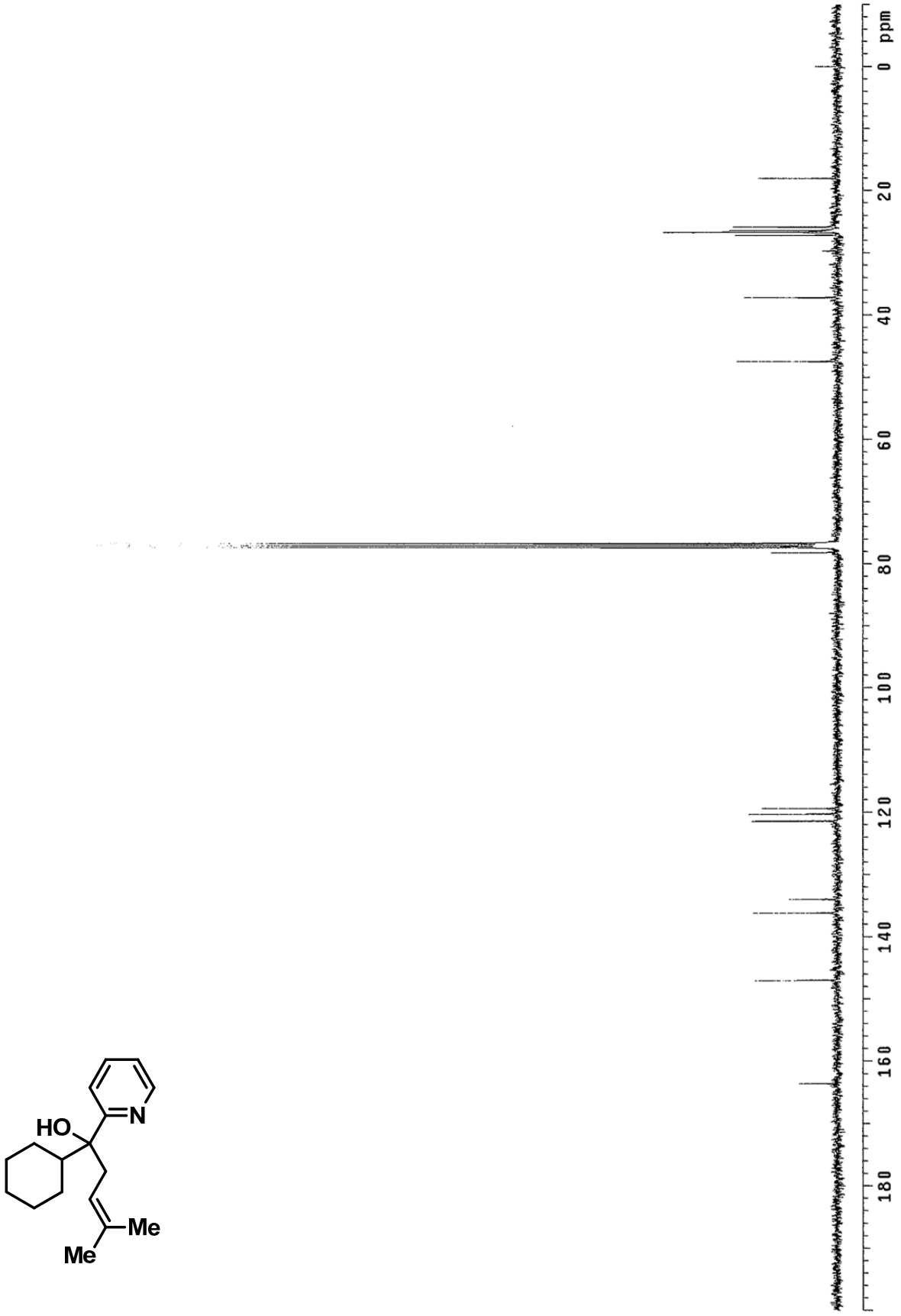
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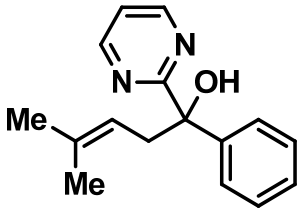
180

HO
N
Me
Me

Pyrimidinyl Pyridyl Prenyl Methanol (3m).



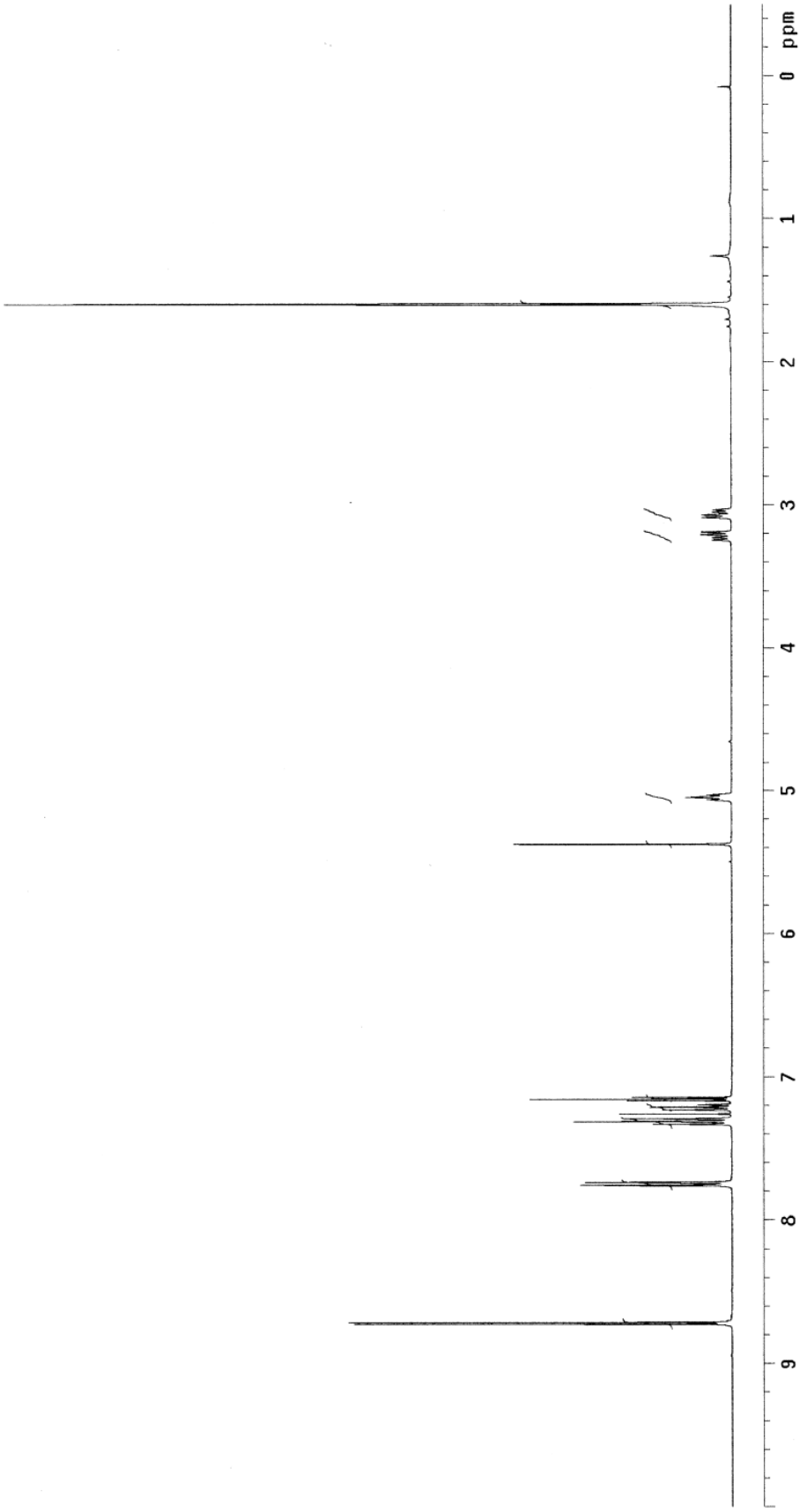
In a modification to the general procedure, the reaction was conducted at 120 ^{o}C. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (69.4 mg, 91% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 2H), 7.76–7.73 (m, 2H), 7.34–7.29 (m, 2H), 7.23–7.19 (m, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 5.37 (s, 1H), 5.07–5.02 (m, 1H), 3.22 (dd, *J* =14.4, 7.2 Hz, 1H), 3.06 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.60 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 156.8, 145.5, 134.7, 128.1, 127.0, 126.1, 119.1, 119.1, 78.7, 40.3, 26.0, 18.3.

LRMS (CI) Calcd. for $C_{16}H_{19}N_2O$ $[M+H]^+$: 255, Found: 255.

FTIR (neat): 3439, 2969, 2913, 1738, 1672, 1572, 1562, 1492, 1447, 1418, 1374, 1263, 1199, 1118, 1090, 1066, 1032, 997 cm^{-1}.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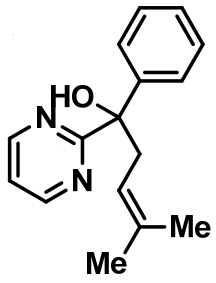
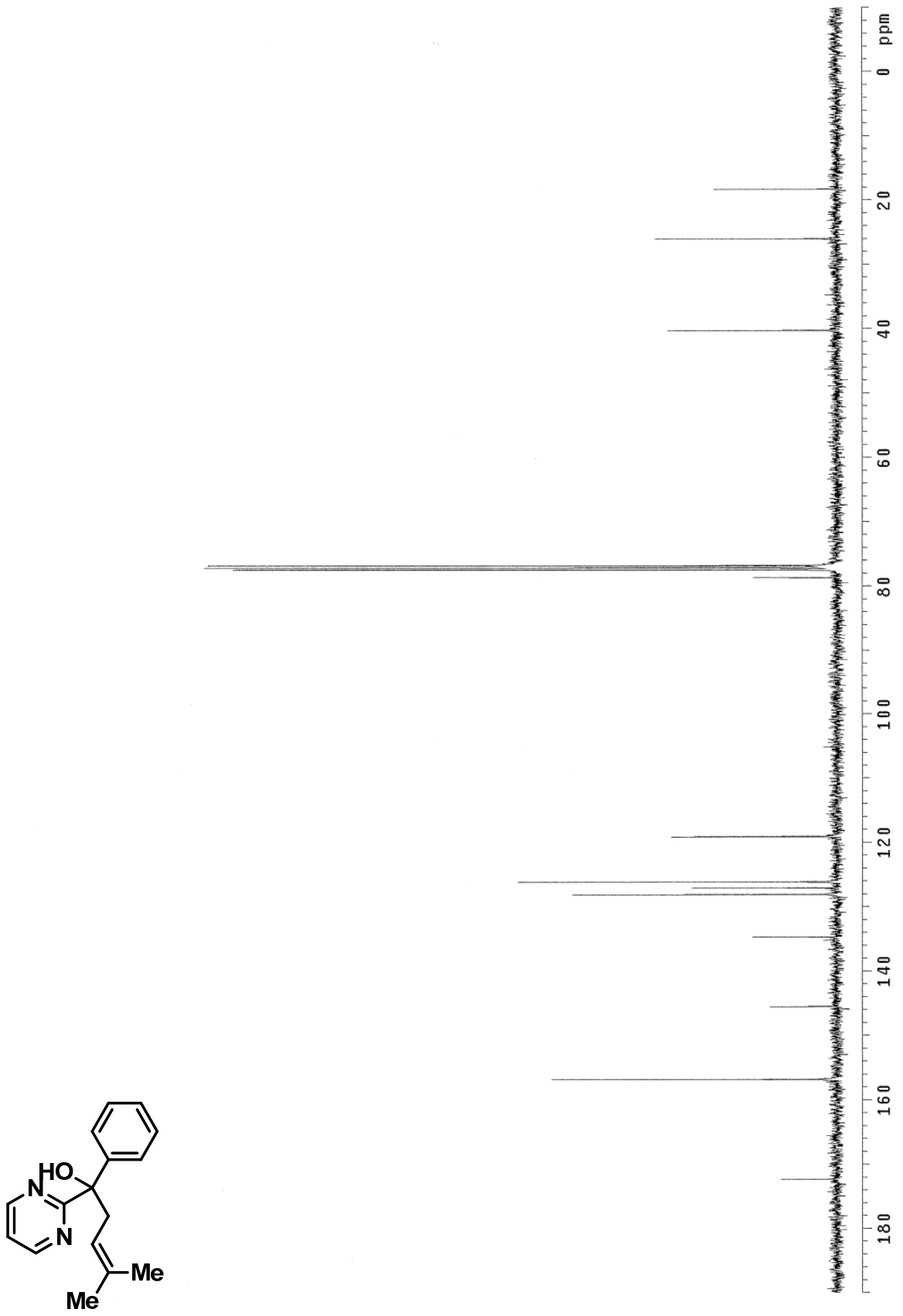

HO
N
N
Me
Me


HO
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N
Me
Me
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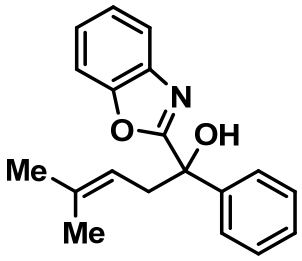
ppm

Benzoxazolyl Pyridyl Prenyl Methanol (3n).



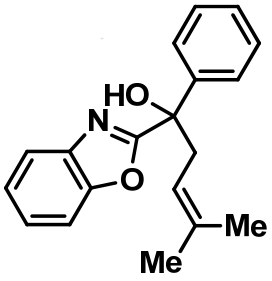
In a modification to the general procedure, $Ru_3(CO)_{12}$ (2 mol%) was employed. After 24 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (77.4 mg, 88% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 1H), 7.86–7.83 (m, 1H), 7.75–7.72 (m, 2H), 7.51–7.49 (m, 1H), 7.38–7.33 (m, 3H), 7.29–7.25 (m, 1H), 5.14–5.09 (m, 1H), 3.56 (s, 1H), 3.43 (dd, J = 14.4, 6.8 Hz, 1H), 3.10 (dd, J = 14.4, 8.0 Hz, 1H), 1.67 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 151.2, 142.4, 140.6, 138.1, 128.5, 128.4, 127.8, 125.4, 125.1, 124.6, 124.5, 120.2, 117.1, 110.9, 75.7, 40.1, 26.0, 18.2.

LRMS (ESI) Calcd. for $C_{19}H_{19}NaNO_2$ $[M+Na]^+$: 316, Found: 316.

FTIR (neat): 3414, 3058, 2914, 2357, 1610, 1560, 1494, 1474, 1454, 1376, 1241, 1159, 1096, 1069, 1033, 1003, 929, 908, 879, 840, 794, 761, 746, 726, 698, 667 cm^{-1}.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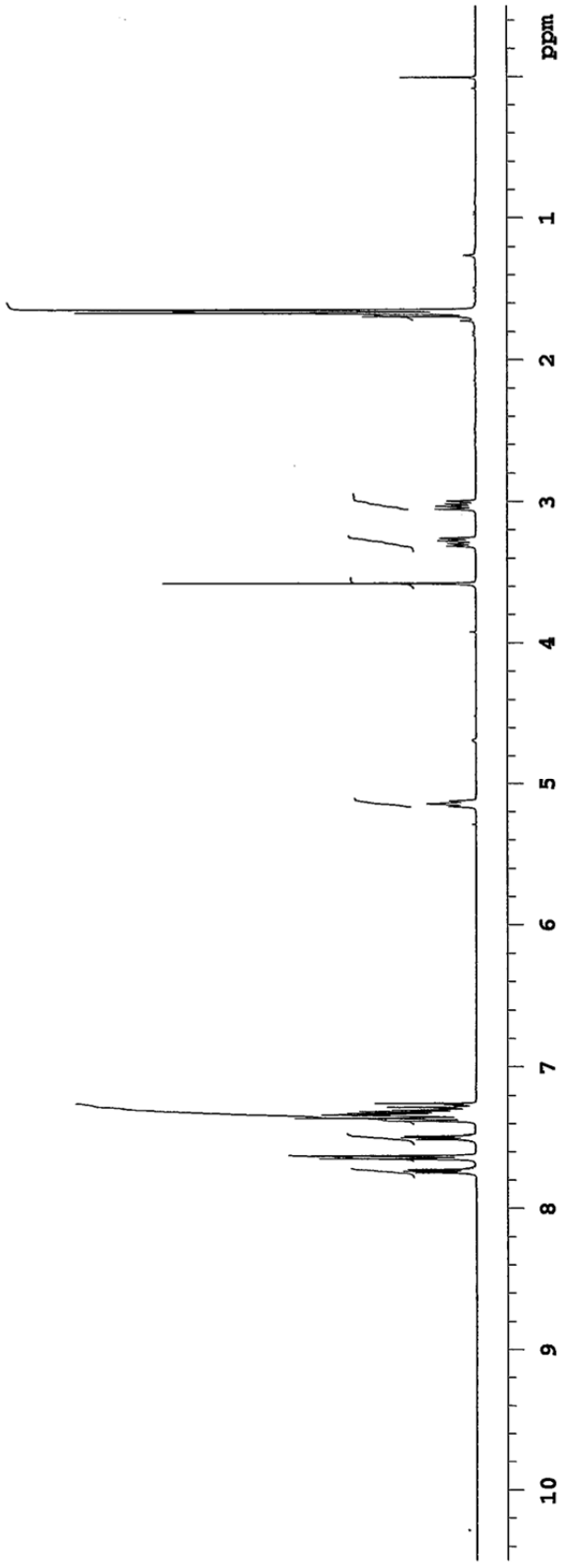
N
O
Me
Me


ppm
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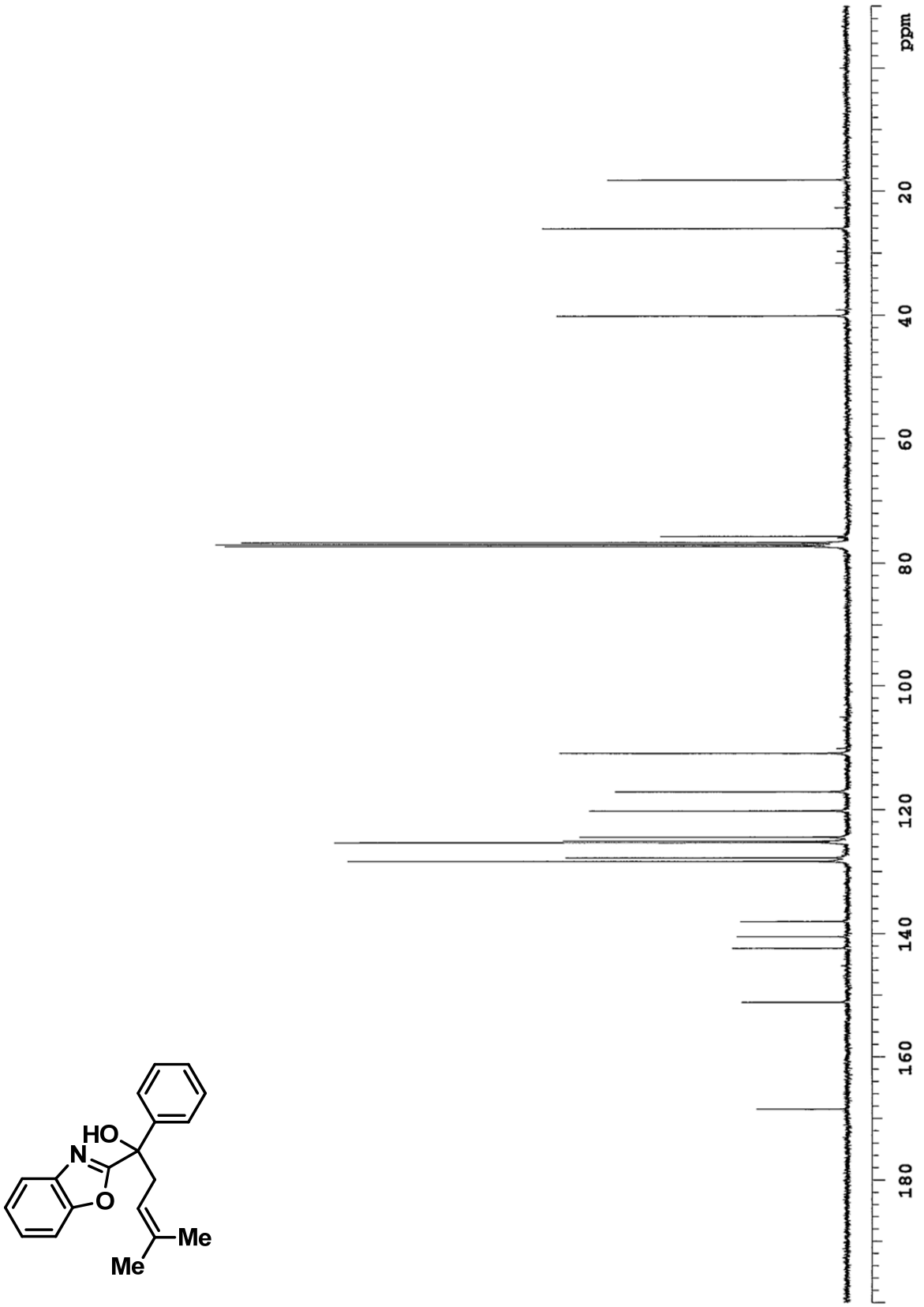
10


HO
N
O
Me
Me
ppm
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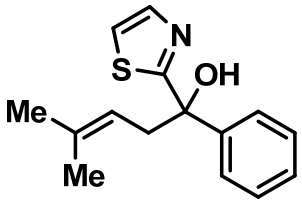
100
120
140
160
180

Thiazolyl Pyridyl Prenyl Methanol (3o).



The reaction was performed in accordance with the general procedure. After 18 hours, the reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (76.5 mg, 86% yield) as a brown solid.

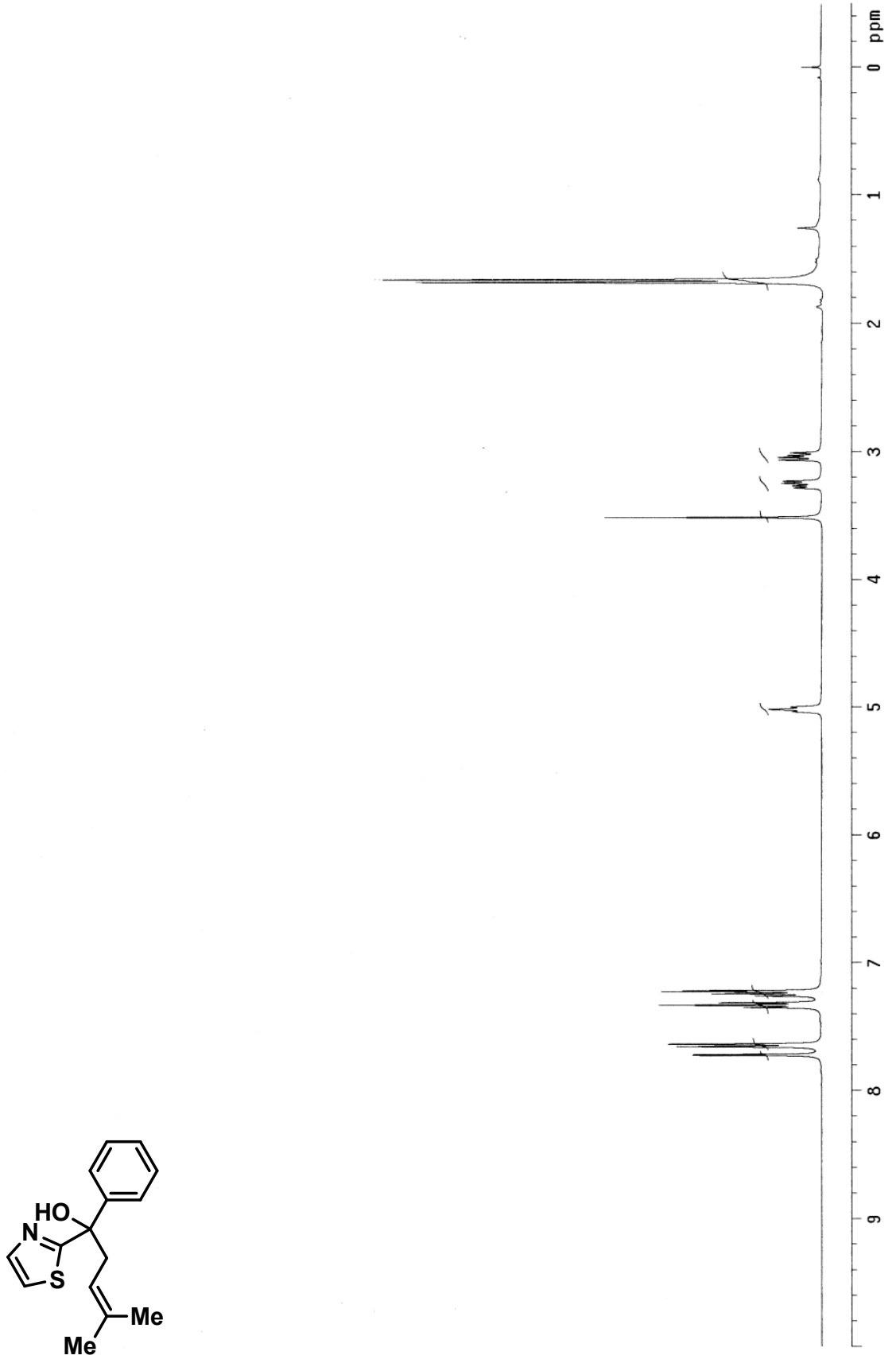
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 3.2 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 3.2 Hz, 1H), 5.02 (t, *J* = 6.8 Hz, 1H), 3.51 (s, 1H), 3.26 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.04 (dd, *J* = 14.4, 8.0 Hz, 1H), 1.68 (s, 3H), 1.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 144.4, 142.5, 138.8, 128.3, 127.4, 125.5, 119.5, 117.7, 78.2, 41.9, 26.2, 18.4.

LRMS (CI) Calcd. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260, Found: 260.

FTIR (neat): 3117, 2970, 2912, 2852, 1739, 1506, 1495, 1444, 1378, 1232, 1204, 1150, 1097, 1061, 984, 938, 918, 856, 821, 781, 765, 725, 696, 670 cm^{-1}.

MP 97.3–98.3 °C.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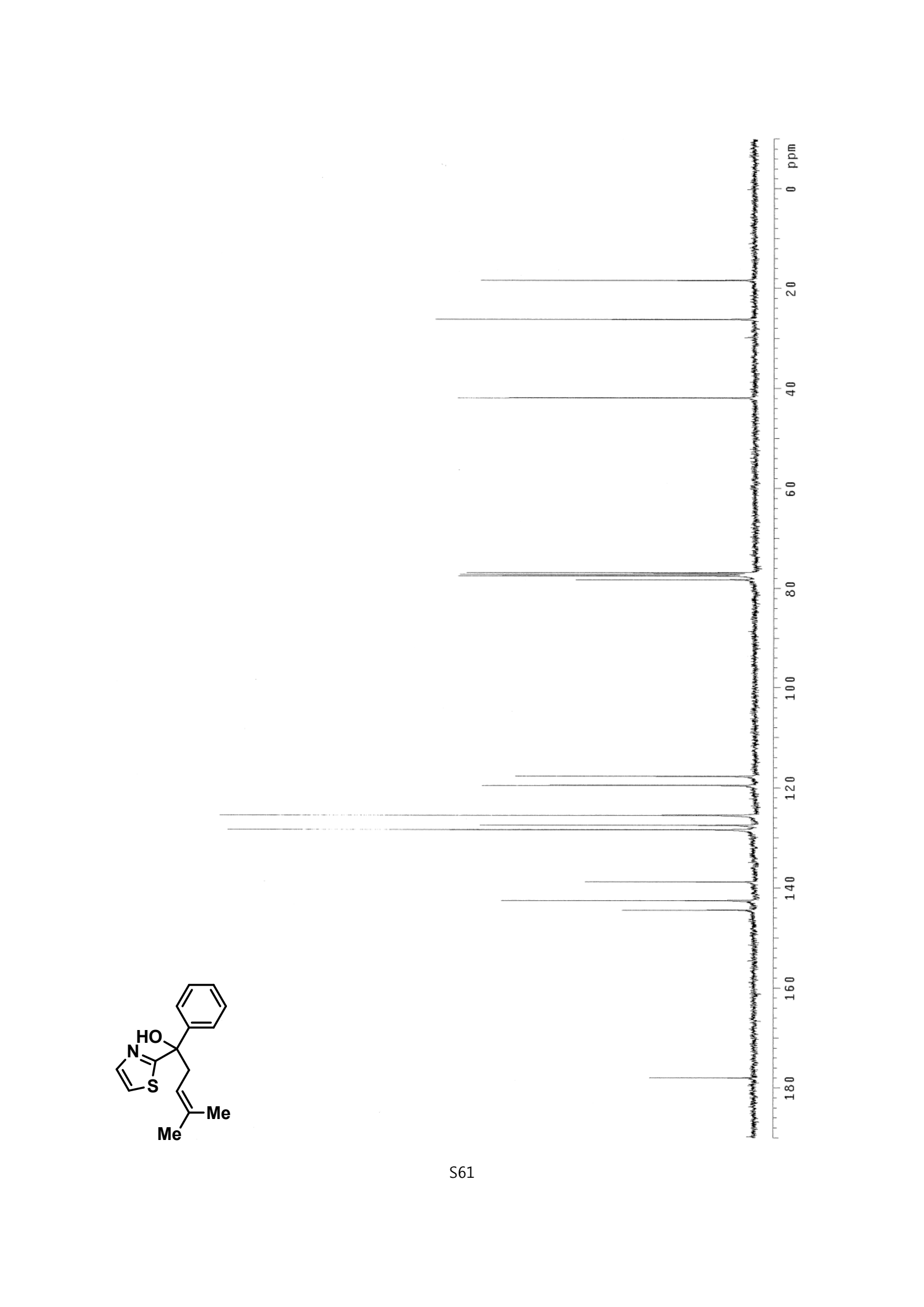
0 ppm


HO
N
S
Me
Me
0 ppm
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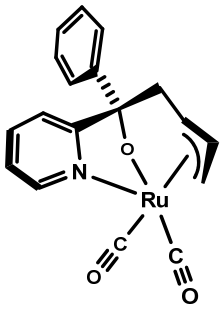
40
60
80
100
120
140
160
180

c. Charaterization of π-Allyl Oxaruthenacycle complex Derived from butadiene.

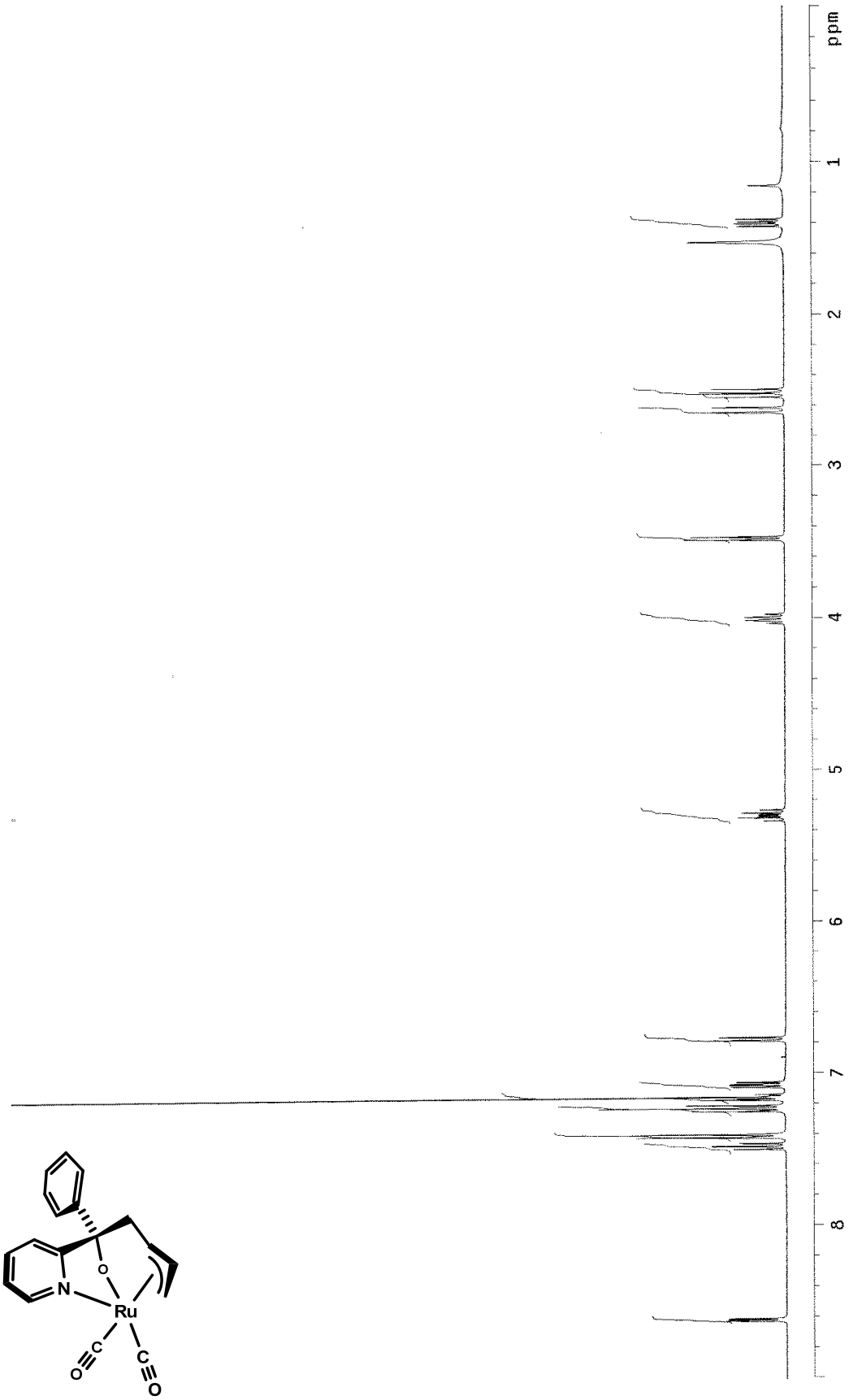


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63-8.61 (m, 1H), 7.48 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.43-7.40 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 1H), 7.09-7.06 (m, 1H), 6.78 (ddd, *J* = 8.0, 1.2, 1.2 Hz, 1H), 5.34-5.27 (m, 1H), 4.04-3.98 (m, 1H), 3.48 (ddd, *J* = 7.6, 1.2, 1.2 Hz, 1H), 2.65-2.61 (m, 1H), 2.52 (dd, *J* = 11.6, 8.4 Hz, 1H), 1.42-1.37 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 197.3, 172.1, 153.5, 147.2, 137.0, 128.3, 127.2, 122.5, 122.1, 105.0, 95.6, 80.3, 53.6, 45.5, 35.4.

HRMS (CI) Calcd. for $C_{19}H_{18}NO_3Ru$ $[M+H]^+$:396.0095, Found: 396.0181.

FTIR (neat): 2014, 1941 cm^{-1}.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O
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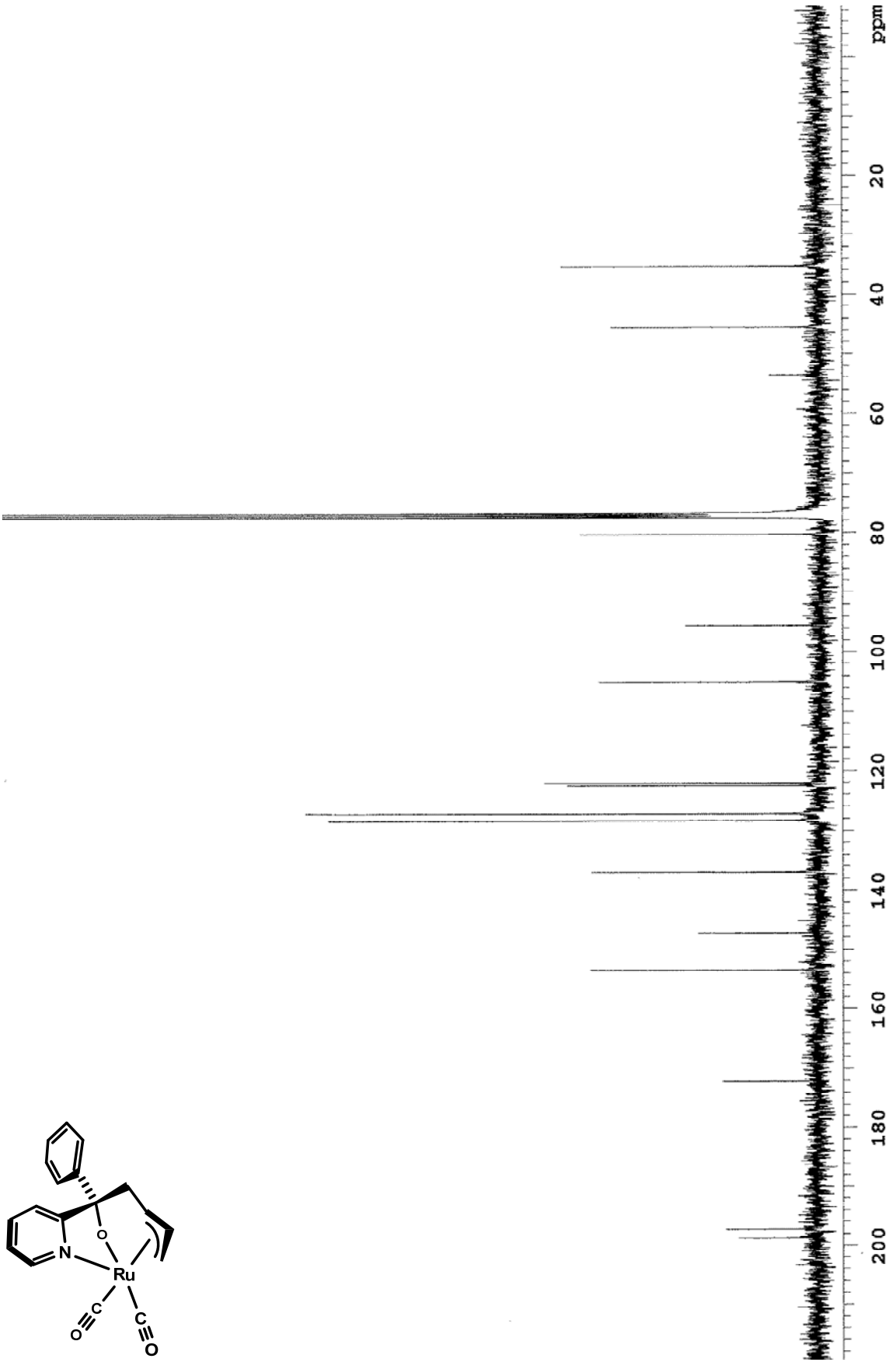
C
O
C
O


ppm
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40
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80
100
120
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N
Ru
C
O
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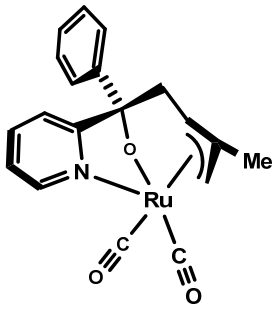
c. Charaterization of π-Allyl Oxaruthenacycle complex Derived from Isoprene.

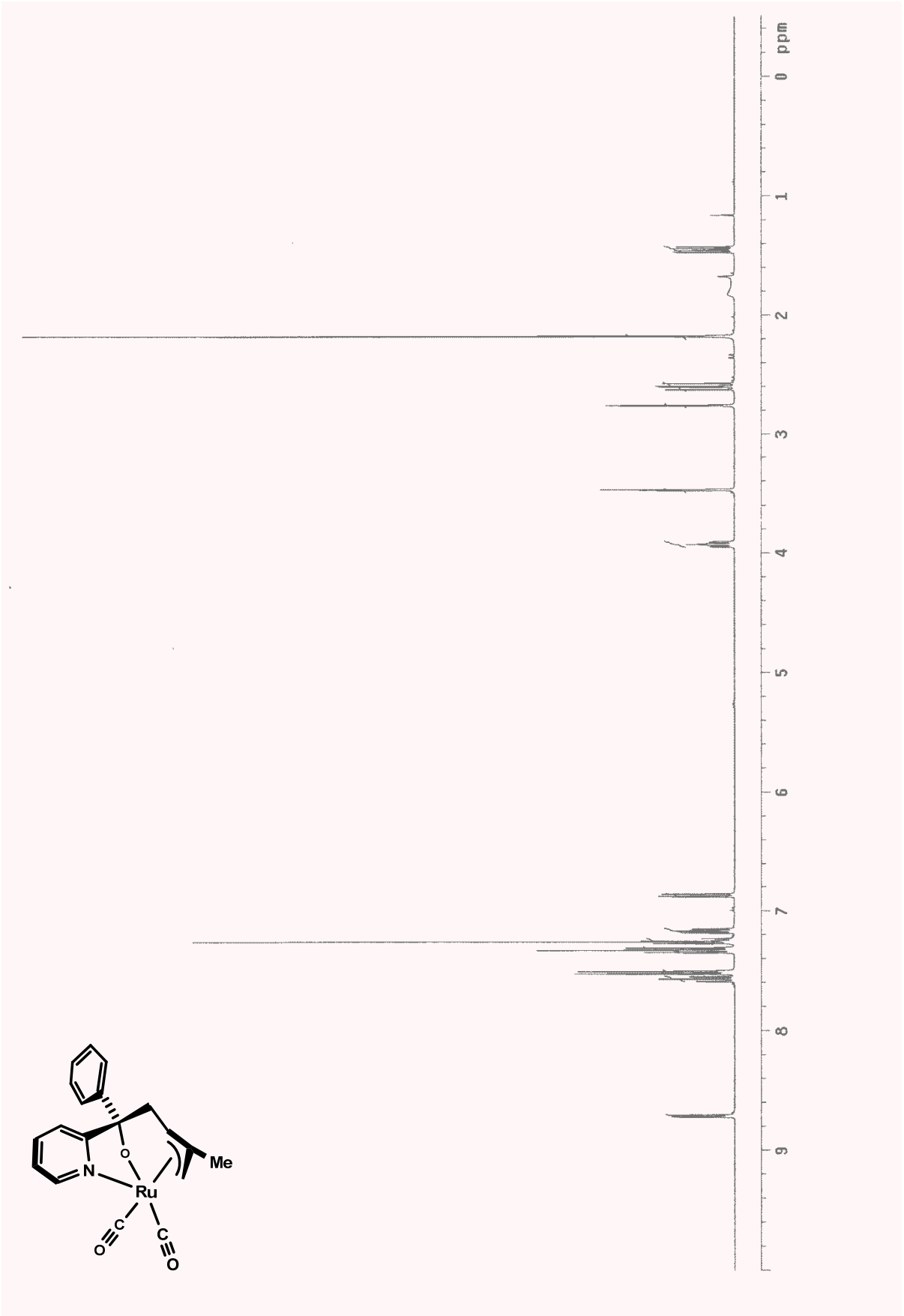


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (ddd, *J* = 5.2, 0.8, 0.8 Hz, 1H), 7.57 (td, *J* = 7.6, 1.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.23 (m, 1H), 7.19-7.15 (m, 1H), 6.88-6.86 (m, 1H), 3.95-3.91 (m, 1H), 3.47 (dd, *J* = 1.6, 1.6 Hz, 1H), 2.76 (dd, *J* = 1.2, 0.8 Hz, 1H), 2.60 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.18 (s, 3H), 1.45 (dd, *J* = 12.0, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 198.1, 172.0, 153.2, 147.0, 136.7, 128.1, 127.1, 127.0, 122.3, 121.8, 121.7, 94.9, 79.2, 47.1, 35.9, 28.5.

HRMS (CI) Calcd. for $C_{19}H_{18}NO_3Ru$ $[M+H]^+$: 410.0252, Found: 410.0340

FTIR (neat): 2008, 1929 cm^{-1}.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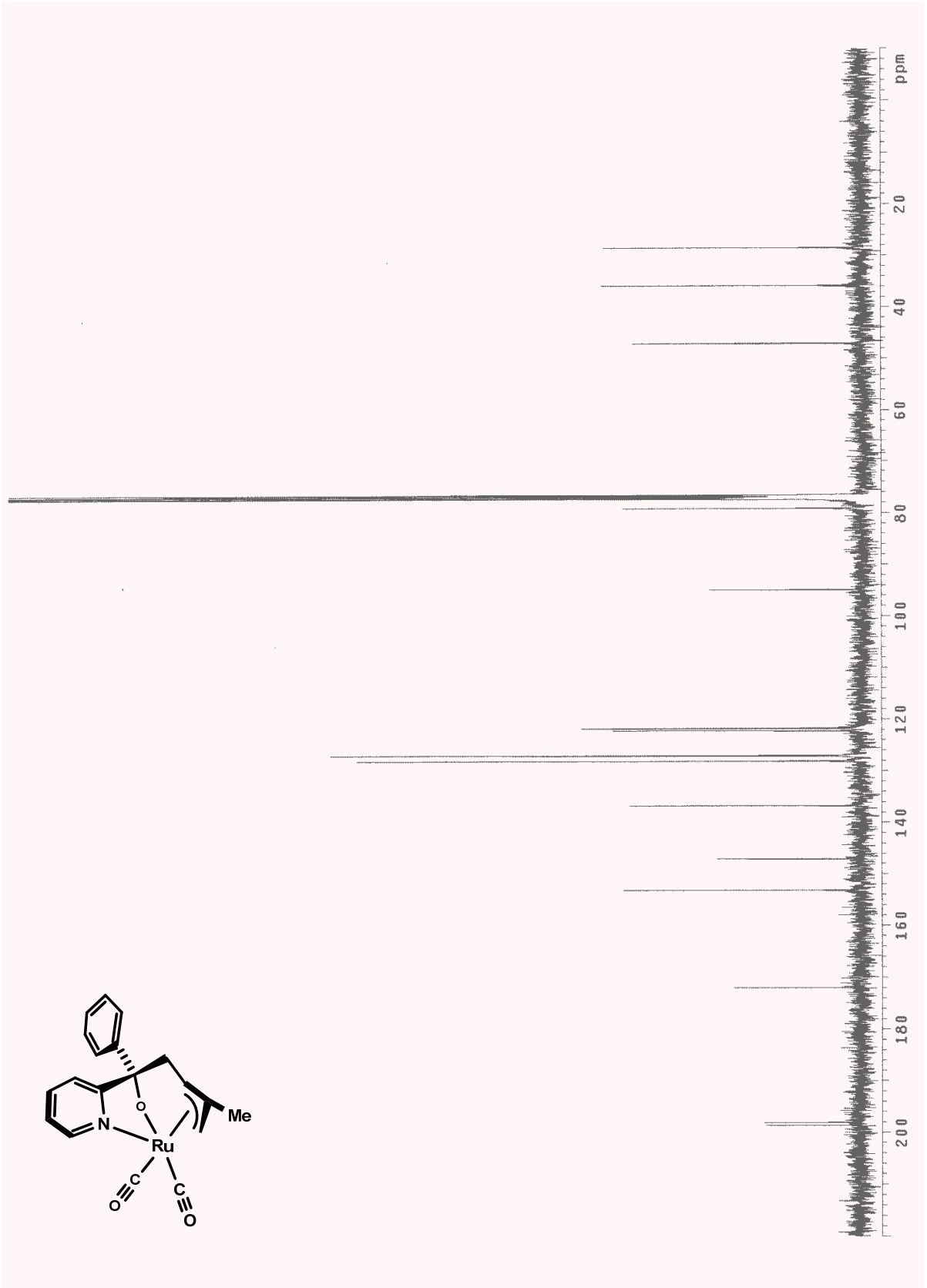
ppm
20
40
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140
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200
N
O
Ru
Me
C
O
C
O

Crystallographic Material for π-Allyl Oxaruthenacycle complex derived from isoprene.

X-ray Experimental.

Table 1. Crystallographic Data for π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 3. Bond Lengths (Å) and Angles (^{o}) for the non-hydrogen atoms of π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 5. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 6. Torsion Angles (^{o}) for the non-hydrogen atoms of π-Allyl Oxaruthenacycle complex derived from isoprene.

Table 1. Crystal data and structure refinement for π-Allyl Oxaruthenacycle complex derived from isoprene.

Identification code	shelxl	
Empirical formula	C19 H17.20 N O3.10 Ru	
Formula weight	410.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 8.0576(18) Å	a= 90°.
	b = 9.927(2) Å	b= 93.986(3)°.
	c = 21.084(5) Å	g = 90°.
Volume	1682.5(6) $Å^3$	
Z	4	
Density (calculated)	1.619 Mg/m^3	
Absorption coefficient	0.949 mm^{-1}	
F(000)	828	
Crystal size	0.24 x 0.05 x 0.04 mm^3	
Theta range for data collection	1.94 to 27.50°.	
Index ranges	-10<=h<=10, -12<=k<=12, -27<=l<=27	
Reflections collected	24210	
Independent reflections	3865 [R(int) = 0.0338]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.875	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3865 / 0 / 234	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0583	
R indices (all data)	R1 = 0.0279, wR2 = 0.0604	
Largest diff. peak and hole	0.829 and -0.620 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for π-Allyl Oxaruthenacycle complex derived from isoprene. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	-421(2)	4945(2)	1742(1)	15(1)
C2	-1423(2)	4892(2)	2249(1)	18(1)
C3	-693(2)	4591(2)	2848(1)	18(1)
C4	1022(2)	4398(2)	2924(1)	16(1)
C5	1970(2)	4512(2)	2402(1)	12(1)
C6	3880(2)	4405(2)	2403(1)	13(1)
C7	4713(2)	4811(2)	3046(1)	13(1)
C8	4892(2)	3913(2)	3556(1)	17(1)
C9	5635(3)	4311(2)	4140(1)	21(1)
C10	6231(2)	5615(2)	4223(1)	20(1)
C11	6073(2)	6513(2)	3718(1)	18(1)
C12	5320(2)	6119(2)	3135(1)	14(1)
C13	4357(2)	2953(2)	2211(1)	14(1)
C14	3657(2)	2600(2)	1550(1)	14(1)
C15	4428(2)	2724(2)	971(1)	16(1)
C16	5416(2)	3862(2)	844(1)	18(1)
C17	3940(3)	1742(2)	442(1)	22(1)
C18	3052(2)	6427(2)	807(1)	19(1)
C19	1657(3)	4069(2)	413(1)	20(1)
N1	1236(2)	4748(2)	1814(1)	12(1)
O1	4384(2)	5253(1)	1924(1)	12(1)
O2	3127(2)	7498(2)	619(1)	28(1)
O3	821(2)	3696(2)	-16(1)	34(1)
Ru1	3019(1)	4626(1)	1115(1)	12(1)
O1W	6490(20)	6941(17)	1280(8)	32(4)

Table 3. Bond lengths [Å] and angles [°] for π-Allyl Oxaruthenacycle complex derived from isoprene.

C1-N1	1.347(2)
C1-C2	1.385(3)
C1-H1	0.9500
C2-C3	1.388(3)
C2-H2	0.9500
C3-C4	1.393(3)
C3-H3	0.9500
C4-C5	1.387(3)
C4-H4	0.9500
C5-N1	1.356(2)
C5-C6	1.543(2)
C6-O1	1.397(2)
C6-C7	1.526(3)
C6-C13	1.553(3)
C7-C12	1.396(3)
C7-C8	1.395(3)
C8-C9	1.389(3)
C8-H8	0.9500
C9-C10	1.387(3)
C9-H9	0.9500
C10-C11	1.387(3)
C10-H10	0.9500
C11-C12	1.389(3)
C11-H11	0.9500
C12-H12	0.9500
C13-C14	1.508(3)
C13-H13A	0.9900
C13-H13B	0.9900
C14-C15	1.414(3)
C14-Ru1	2.255(2)
C14-H14	0.92(2)
C15-C16	1.418(3)
C15-C17	1.512(3)
C15-Ru1	2.2346(19)

C16-Ru1	2.1878(19)
C16-H16B	0.96(2)
C16-H16A	0.95(2)
C17-H17A	0.9800
C17-H17B	0.9800
C17-H17C	0.9800
C18-O2	1.139(3)
C18-Ru1	1.903(2)
C19-O3	1.150(2)
C19-Ru1	1.865(2)
N1-Ru1	2.1316(16)
O1-Ru1	2.0592(13)
O1-O1W	2.799(16)
O2-O1W	3.01(17)

N1-C1-C2	122.33(18)
N1-C1-H1	118.8
C2-C1-H1	118.8
C1-C2-C3	118.49(18)
C1-C2-H2	120.8
C3-C2-H2	120.8
C2-C3-C4	119.20(18)
C2-C3-H3	120.4
C4-C3-H3	120.4
C5-C4-C3	119.65(18)
C5-C4-H4	120.2
C3-C4-H4	120.2
N1-C5-C4	120.66(17)
N1-C5-C6	112.63(15)
C4-C5-C6	126.71(17)
O1-C6-C7	110.59(15)
O1-C6-C5	107.32(14)
C7-C6-C5	111.12(15)
O1-C6-C13	106.40(14)
C7-C6-C13	112.01(15)
C5-C6-C13	109.19(15)

C12-C7-C8	118.36(17)
C12-C7-C6	119.54(16)
C8-C7-C6	122.10(17)
C9-C8-C7	121.07(19)
C9-C8-H8	119.5
C7-C8-H8	119.5
C8-C9-C10	120.06(19)
C8-C9-H9	120.0
C10-C9-H9	120.0
C11-C10-C9	119.39(19)
C11-C10-H10	120.3
C9-C10-H10	120.3
C10-C11-C12	120.63(19)
C10-C11-H11	119.7
C12-C11-H11	119.7
C11-C12-C7	120.49(18)
C11-C12-H12	119.8
C7-C12-H12	119.8
C14-C13-C6	111.85(15)
C14-C13-H13A	109.2
C6-C13-H13A	109.2
C14-C13-H13B	109.2
C6-C13-H13B	109.2
H13A-C13-H13B	107.9
C15-C14-C13	128.30(17)
C15-C14-Ru1	70.87(11)
C13-C14-Ru1	103.24(12)
C15-C14-H14	113.5(13)
C13-C14-H14	114.3(13)
Ru1-C14-H14	116.8(13)
C14-C15-C16	121.21(18)
C14-C15-C17	118.26(18)
C16-C15-C17	119.70(17)
C14-C15-Ru1	72.41(11)
C16-C15-Ru1	69.52(11)
C17-C15-Ru1	122.46(13)

C15-C16-Ru1	73.10(11)
C15-C16-H16B	117.6(15)
Ru1-C16-H16B	123.6(14)
C15-C16-H16A	119.9(14)
Ru1-C16-H16A	98.9(14)
H16B-C16-H16A	115.7(19)
C15-C17-H17A	109.5
C15-C17-H17B	109.5
H17A-C17-H17B	109.5
C15-C17-H17C	109.5
H17A-C17-H17C	109.5
H17B-C17-H17C	109.5
O2-C18-Ru1	177.68(18)
O3-C19-Ru1	178.48(19)
C1-N1-C5	119.56(16)
C1-N1-Ru1	129.89(13)
C5-N1-Ru1	110.45(12)
C6-O1-Ru1	104.51(10)
C19-Ru1-C18	91.66(9)
C19-Ru1-O1	176.18(7)
C18-Ru1-O1	88.80(7)
C19-Ru1-N1	100.23(8)
C18-Ru1-N1	102.04(7)
O1-Ru1-N1	75.98(6)
C19-Ru1-C16	99.87(8)
C18-Ru1-C16	101.70(8)
O1-Ru1-C16	83.74(7)
N1-Ru1-C16	148.24(7)
C19-Ru1-C15	85.27(8)
C18-Ru1-C15	136.69(8)
O1-Ru1-C15	96.99(6)
N1-Ru1-C15	121.05(7)
C16-Ru1-C15	37.38(8)
C19-Ru1-C14	99.40(8)
C18-Ru1-C14	165.60(8)
O1-Ru1-C14	80.78(6)

N1-Ru1-C14	85.14(6)
C16-Ru1-C14	67.46(7)
C15-Ru1-C14	36.72(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for π-Allyl Oxaruthenacycle complex derived from isoprene. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	12(1)	16(1)	17(1)	-4(1)	-2(1)	1(1)
C2	12(1)	18(1)	24(1)	-4(1)	1(1)	-2(1)
C3	14(1)	21(1)	19(1)	-2(1)	5(1)	-3(1)
C4	15(1)	16(1)	16(1)	0(1)	0(1)	-2(1)
C5	11(1)	8(1)	15(1)	-1(1)	0(1)	-1(1)
C6	10(1)	14(1)	14(1)	1(1)	1(1)	0(1)
C7	9(1)	16(1)	13(1)	-1(1)	1(1)	1(1)
C8	18(1)	16(1)	17(1)	2(1)	-1(1)	-2(1)
C9	22(1)	25(1)	15(1)	5(1)	-2(1)	0(1)
C10	17(1)	28(1)	14(1)	-4(1)	-4(1)	1(1)
C11	16(1)	17(1)	20(1)	-4(1)	-2(1)	0(1)
C12	12(1)	16(1)	16(1)	1(1)	0(1)	2(1)
C13	14(1)	15(1)	14(1)	1(1)	0(1)	2(1)
C14	12(1)	13(1)	17(1)	-1(1)	-2(1)	2(1)
C15	13(1)	19(1)	17(1)	-3(1)	0(1)	8(1)
C16	13(1)	26(1)	16(1)	-2(1)	3(1)	4(1)
C17	21(1)	24(1)	22(1)	-8(1)	-1(1)	5(1)
C18	19(1)	22(1)	14(1)	-2(1)	3(1)	4(1)
C19	21(1)	18(1)	22(1)	-2(1)	-1(1)	8(1)
N1	11(1)	12(1)	14(1)	-2(1)	0(1)	-1(1)
O1	11(1)	15(1)	10(1)	0(1)	0(1)	-2(1)
O2	42(1)	21(1)	23(1)	4(1)	12(1)	4(1)
O3	38(1)	30(1)	30(1)	-13(1)	-20(1)	13(1)
Ru1	11(1)	15(1)	10(1)	-1(1)	0(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for π-Allyl Oxaruthenacycle complex derived from isoprene.

	x	y	z	U(eq)
H1	-919	5126	1330	18
H2	-2584	5059	2189	22
H3	-1355	4517	3202	22
H4	1539	4189	3330	19
H8	4499	3016	3502	21
H9	5736	3690	4483	25
H10	6742	5890	4621	24
H11	6483	7406	3772	21
H12	5218	6745	2794	17
H13A	5584	2871	2232	17
H13B	3933	2305	2518	17
H17A	4745	1001	450	33
H17B	3929	2207	32	33
H17C	2829	1382	502	33
H14	2820(30)	1960(20)	1537(10)	12(5)
H16B	5790(30)	3950(20)	425(11)	24(6)
H16A	6110(30)	4250(20)	1175(11)	20(6)

Table 6. Torsion angles [°] for π-Allyl Oxaruthenacycle complex derived from isoprene.

N1-C1-C2-C3	-1.7(3)
C1-C2-C3-C4	2.2(3)
C2-C3-C4-C5	0.1(3)
C3-C4-C5-N1	-3.0(3)
C3-C4-C5-C6	176.59(17)
N1-C5-C6-O1	31.7(2)
C4-C5-C6-O1	-147.92(18)
N1-C5-C6-C7	152.73(15)
C4-C5-C6-C7	-26.9(3)
N1-C5-C6-C13	-83.22(18)
C4-C5-C6-C13	97.1(2)
O1-C6-C7-C12	22.1(2)
C5-C6-C7-C12	-97.00(19)
C13-C6-C7-C12	140.57(17)
O1-C6-C7-C8	-157.97(16)
C5-C6-C7-C8	83.0(2)
C13-C6-C7-C8	-39.5(2)
C12-C7-C8-C9	0.8(3)
C6-C7-C8-C9	-179.13(18)
C7-C8-C9-C10	-0.7(3)
C8-C9-C10-C11	0.2(3)
C9-C10-C11-C12	0.3(3)
C10-C11-C12-C7	-0.2(3)
C8-C7-C12-C11	-0.4(3)
C6-C7-C12-C11	179.57(16)
O1-C6-C13-C14	-53.92(19)
C7-C6-C13-C14	-174.88(15)
C5-C6-C13-C14	61.61(19)
C6-C13-C14-C15	93.5(2)
C6-C13-C14-Ru1	17.61(17)
C13-C14-C15-C16	-40.4(3)
Ru1-C14-C15-C16	51.59(16)
C13-C14-C15-C17	150.04(19)
Ru1-C14-C15-C17	-117.96(17)

C13-C14-C15-Ru1	-92.00(19)
C14-C15-C16-Ru1	-52.88(16)
C17-C15-C16-Ru1	116.52(17)
C2-C1-N1-C5	-1.1(3)
C2-C1-N1-Ru1	174.79(14)
C4-C5-N1-C1	3.5(3)
C6-C5-N1-C1	-176.15(16)
C4-C5-N1-Ru1	-173.14(14)
C6-C5-N1-Ru1	7.20(17)
C7-C6-O1-Ru1	-176.35(11)
C5-C6-O1-Ru1	-55.00(14)
C13-C6-O1-Ru1	61.78(14)
C6-O1-Ru1-C19	52.1(11)
C6-O1-Ru1-C18	149.08(12)
C6-O1-Ru1-N1	46.36(11)
C6-O1-Ru1-C16	-109.01(12)
C6-O1-Ru1-C15	-73.97(11)
C6-O1-Ru1-C14	-40.90(11)
C1-N1-Ru1-C19	-25.08(18)
C5-N1-Ru1-C19	151.12(13)
C1-N1-Ru1-C18	68.85(18)
C5-N1-Ru1-C18	-114.95(13)
C1-N1-Ru1-O1	154.53(18)
C5-N1-Ru1-O1	-29.27(11)
C1-N1-Ru1-C16	-153.56(17)
C5-N1-Ru1-C16	22.6(2)
C1-N1-Ru1-C15	-115.70(17)
C5-N1-Ru1-C15	60.50(14)
C1-N1-Ru1-C14	-123.78(17)
C5-N1-Ru1-C14	52.42(12)
C15-C16-Ru1-C19	-68.57(13)
C15-C16-Ru1-C18	-162.35(12)
C15-C16-Ru1-O1	110.18(11)
C15-C16-Ru1-N1	59.99(18)
C15-C16-Ru1-C14	27.59(11)
C14-C15-Ru1-C19	-112.64(13)

C16-C15-Ru1-C19	113.05(13)
C17-C15-Ru1-C19	0.14(17)
C14-C15-Ru1-C18	159.97(12)
C16-C15-Ru1-C18	25.65(17)
C17-C15-Ru1-C18	-87.26(19)
C14-C15-Ru1-O1	64.27(11)
C16-C15-Ru1-O1	-70.05(12)
C17-C15-Ru1-O1	177.04(16)
C14-C15-Ru1-N1	-13.54(13)
C16-C15-Ru1-N1	-147.85(11)
C17-C15-Ru1-N1	99.24(16)
C14-C15-Ru1-C16	134.32(17)
C17-C15-Ru1-C16	-112.9(2)
C16-C15-Ru1-C14	-134.32(17)
C17-C15-Ru1-C14	112.8(2)
C15-C14-Ru1-C19	68.80(13)
C13-C14-Ru1-C19	-164.87(12)
C15-C14-Ru1-C18	-70.9(3)
C13-C14-Ru1-C18	55.4(3)
C15-C14-Ru1-O1	-115.06(11)
C13-C14-Ru1-O1	11.26(11)
C15-C14-Ru1-N1	168.39(12)
C13-C14-Ru1-N1	-65.29(12)
C15-C14-Ru1-C16	-28.05(11)
C13-C14-Ru1-C16	98.27(13)
C13-C14-Ru1-C15	126.32(17)

Symmetry transformations used to generate equivalent atoms:

X-ray Experimental for $(C_{17}H_{17}NO)Ru(CO)_2 - 0.1\ H_2O$: Crystals grew as clusters of large colorless needless by slow evaporation from toluene. The data crystal was cut from a cluster of crystals and had approximate dimensions; 0.24 x 0.05 x 0.04 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71075Å). A total of 1344 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] Most of the hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on the allylic carbon atoms were observed in a ΔF map and refined with isotropic displacement parameters. A small peak, 1.3 $e^-/Å^3$, persisted in the final ΔF map. This peak was within H-bonding distance to two oxygen atoms, O1 and O2. As a result, it was assumed to represent a small amount of water that co-crystallized along with the complex. The site occupancy factor for this atom, O1W, was refined while fixing a isotropic displacement parameter to 0.05 yielded an approximate occupancy of close to 10%.

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0343*P)^2 + (0.8933*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.0604, with R(F) equal to 0.0246 and a goodness of fit, S, = 1.00. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

References

1) CrystalClear 1.40 (2008). Rigaku Americas Corportion, The Woodlands, TX.

2) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. J. Appl. Cryst. 32, 115-119.

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4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

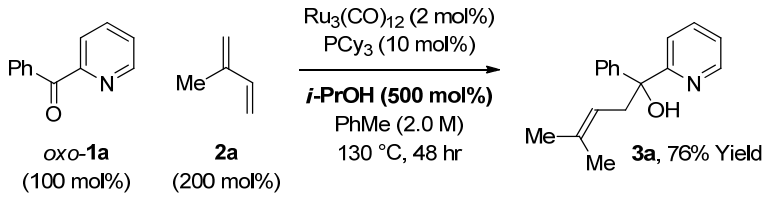
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.

6) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

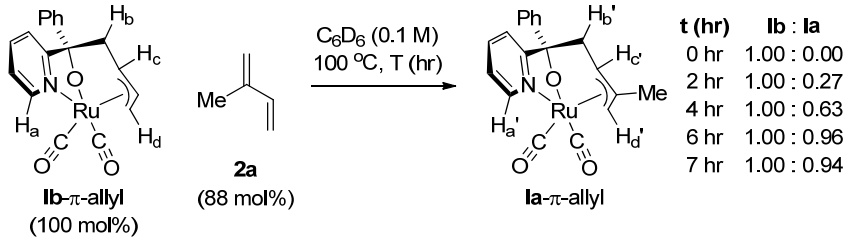
d. Ketone Oxidation Level Reaction.



oxo-**1a** (100 mol%) **2a** (200 mol%)

To a pressure tube equipped with magnetic stir bar was added benzoylpyridine (0.300 mmol, 100 mol%), $Ru_3(CO)_{12}$ (3.9 mg, 0.006 mmol, 2 mol%) and PCy_3 (8.4 mg, 0.030 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Toluene (0.15 mL, 2.0 M concentration with respect to benzoylpyridine), isopropanol (115 μL, 1.500 mmol, 500 mol%), and isoprene (60 μL, 0.600 mmol, 200 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 130 ^{o}C for 48 hr. The reaction mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, 2.5% EtOAc/hexanes) to furnish the title compound (57.9 mg, 90% yield) as a yellow oil.

e. ^{1}H NMR-Exchange Data.



t (hr)	Ib : Ia
0 hr	1.00 : 0.00
2 hr	1.00 : 0.27
4 hr	1.00 : 0.63
6 hr	1.00 : 0.96
7 hr	1.00 : 0.94

Procedure: To a pressure NMR tube was added **Ib**-π-allyl (0.060 mmol, 100 mol%). The tube was sealed with a rubber septum, purged with argon. At this stage, C_6D_6 (0.60 mL, 0.1 M concentration with respect to **Ib**-π-allyl), and isoprene (5.3 μL, 0.053 mmol, 88 mol%) were added. The rubber septum was quickly replaced with a screw cap. The reaction was heated to 100 °C and ^{1}H NMR were recorded every hour (at 25 °C).