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Helicate tris(aryl)carbinolates bearing pendant NR_2 donors – a new family of supporting ligands for the synthesis of Sc^{3+} alkyl complexes

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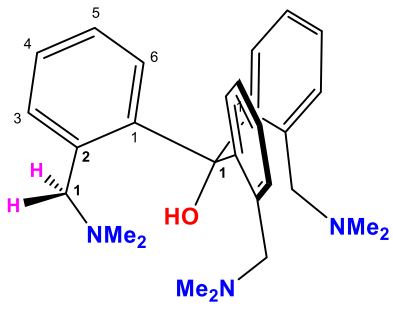
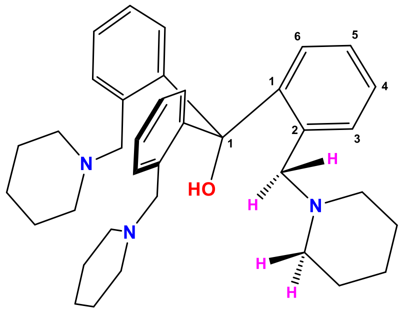
Experimental Section

General Procedures. All reactions were performed under a dry argon or nitrogen atmosphere using standard Schlenk techniques or under nitrogen atmosphere in a glovebox, unless indicated. Dry, oxygen-free solvents were used throughout. After being dried over KOH, THF and Et_2O was purified by distillation from sodium/benzophenone ketyl, hexane by distillation from sodium/potassium alloy prior to use. Benzene-d_6 and toluene-d_8 were heated at reflux over Na/K alloy, vacuum-transferred, and stored over 4 Å molecular sieves in a nitrogen-filled glovebox. $PhCH_2NMe_2$, BnCl, piperidine and $(MeO)_2CO$ were purchased from Aldrich. *n*-BuLi (2.5 M solution in hexane) was purchased from DalChem ltd. Aryllithium reagents *o*-$Me_2NCH_2C_6H_4Li$ and (2-(piperidin-1-yl-methyl)phenyl)lithium (*o*-piperidino$CH_2C_6H_4Li$) were prepared according to literature procedures.**[S1]** The corresponding N-benzylpiperidine was prepared by a slightly modified procedure from piperidine and benzyl chloride instead of benzyl bromide.**[S2]** Another reagents and solvents were used as purchased. NMR spectra were recorded on a Bruker DPX 300 or Bruker Avance DRX-400 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were referenced internally using the residual solvent resonances and are reported relative to TMS; coupling constants are given in Hz. The assignment of ^1H and $^{13}C\{^1H\}$ resonances was assisted with gHSQC and gHMBC spectra. IR spectra were recorded as Nujol mulls or KBr plates on FSM 1201 and Bruker Vertex 70 instruments. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexometric titration.**[S3]**



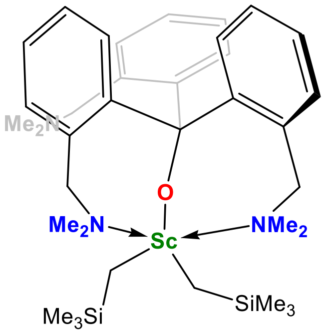
Tris[2-(dimethylaminomethyl)phenyl]methanol (1). Dimethyl carbonate (1.43 g, 15.90 mmol) was added to a intensively stirred suspension of *o*-$Me_2NCH_2C_6H_4Li$ (7.19 g, 51.00 mmol) in Et_2O (50 ml) at -30 ^{o}C, and the mixture was slowly brought to room temperature. The light yellow-green suspension was stirred at this temperature for 24 hours, then it was poured into an NH_4Cl-water-ice mixture. The solution was extracted with Et_2O (3×50 ml) and dried with $MgSO_4$, after this all volatiles were removed on a rotary evaporator. The solid beige residue was dried in vacuum for 2 hours and then re-dissolved in boiling hexane. Carbinol $[BnNMe_2]_3COH$ (**1**) was obtained as colorless X-ray suitable crystals in 74% yield (5.08 g) by slow concentration of the mother liquor in hexane. **^1H NMR (300 MHz, $CDCl_3$, 298 K)**: δ 9.84 (br. s, 1H, OH), 7.68 (d, 3H, 3-CH-aryl, $^3J_{HH}$= 7.5 Hz), 7.28 (t, 3H, 4-CH-aryl, $^3J_{HH}$= 7.5 Hz), 7.01 (t, 3H, 4-CH-aryl, $^3J_{HH}$= 7.5 Hz), 6.66 (br. s, 3H, 5-CH-aryl), 3.64 (br. s, 3H, diastereotopic -CH_2-), 3.28 (d, 3H, diastereotopic -CH_2-,$^2J_{HH}$= 14.7 Hz), 2.10 (s, 18H, NMe_2). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K):** δ 146.05 (s, *ipso*-C-aryl), 139.19 (s, *ipso*-C-aryl), 130.58 (s, CH-aryl), 129.15 (s, CH-aryl), 127.15 (s, CH-aryl), 125,79 (s, CH-aryl), 85.64 (s, COH), 62.80 (s, CH_2), 45.07 (s, NMe_2). **^1H NMR (300 MHz, C_7D_8, 223 K)**: δ 9.94 (s, 1H, OH), 7.98 (d, 3H, 3-CH-aryl, $^3J_{HH}$= 7.5 Hz), 7.26-7.18 (m, 3H, 4-CH-aryl), 6.94-6.79 (m, 6H, 4,5-CH-aryl), 4.12 (d, 3H, diastereotopic -CH_2-, $^2J_{HH}$= 14.7 Hz), 3.18 (d, 3H, diastereotopic -CH_2-, $^2J_{HH}$= 14.7 Hz), 2.02 (s, 18H, NMe_2). **^1H NMR (400 MHz, $CDCl_3$, 223 K)**: δ 10.49 (s, 1H, OH), 7.64 (d, 3H, 3-

CH-aryl, $^3J_{HH}$= 7.5 Hz), 7.32-7.25 (compl. m, 3H, 4-CH-aryl overlapping with $CDCl_3$), 6.98 (t, 3H, 4-CH-aryl, $^3J_{HH}$= 7.5 Hz), 6.48 (d, 3H, 5-CH-aryl, $^3J_{HH}$= 7.8 Hz), 3.78 (d, 3H, diastereotopic $-CH_2-$, $^2J_{HH}$= 14.5 Hz), 3.05 (d, 3H, diastereotopic $-CH_2-$, $^2J_{HH}$= 14.6 Hz), 2.06 (s, 18H, NMe_2). IR (KBr): 2763 (s), 1595 (m), 1316 (m), 1302 (m), 1254 (s), 1198 (m), 1173 (s), 1152 (m), 1096 (m), 1024 (s), 972 (m), 949 (m), 926 (m), 883 (m), 847 (s), 766 (s). Anal. Calcd for $C_{28}H_{37}N_3O$ (431.62 g/mol): C 77.92; H 8.64; N, 9.74. Found: C 77.89; H 8.60; N, 9.79. MS(EI): *m/z* 431.30 [M^+].



Tris[2-(piperidin-1-ylmethyl)phenyl]methanol (2).

Dimethyl carbonate (1.19 g, 13.30 mmol) was added to a intensively stirred suspension of *o*-piperidino$CH_2C_6H_4Li$ (7.70 g, 42.50 mmol) in Et_2O (50 ml) at -30 °C, and the mixture was slowly brought to room temperature. The light yellow-green suspension was stirred at this temperature for 24 hours, then it was poured into an NH_4Cl-water-ice mixture. The solution was extracted with toluene (3×70 ml) and dried with $MgSO_4$, after this all volatiles were removed on a rotary evaporator. The solid beige residue was dried in vacuum for another 2 hours and then re-dissolved in boiling hexane. Carbinol [BnPiperid]$_3$COH (**2**) was obtained as colorless X-ray suitable crystals in 61% yield (5.54 g) by slow concentration of the mother liquor in hexane. **^{1}H NMR (300 MHz, $CDCl_3$, 298 K)**: δ 9.91 (s, 1H, OH), 7.70 (br. s, 3H, 3-CH-aryl), 7.30-7.19 (m, 3H, 4-CH-aryl), 6.99 (br. s, 3H, 5-CH-aryl), 6.57 (br. s, 3H, 6-CH-aryl), 3.70 (br. s, 3H, diastereotopic $-CH_2-$), 3.24 (br. s, 3H, diastereotopic $-CH_2$), 2.31 (br. s, 6H, diastereotopic $-NCH_2$-piperidine), 2.15 (br. s, 6H, diastereotopic $-NCH_2$-piperidine), 1.50 (br. s, 12H, $-CH_2-$), 1.38 (br. s, 6H, $-CH_2-$).**^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K)**: δ 146.20 (s, *ipso*-C-aryl), 138.27 (s, *ipso*-C-aryl), 131.36 (s, CH-aryl), 129.38 (s, CH-aryl), 127.47 (s, CH-aryl), 126,39 (s, CH-aryl), 85.98 (s, COH), 62.04 (s, CH_2), 54.07 (s, NCH_2), 25.71 (s, CH_2), 24.16 (s, CH_2). **^{1}H NMR (300 MHz, C_6D_6, 298 K)**: δ 9.87 (s, 1H, OH), 7.94 (br. s, 3H, 3-CH-aryl), 7.21 (t, 3H, 4-CH-aryl, $^3J_{HH}$= 7.6 Hz), 6.92 (compl. m, 6H, 5,6-CH-aryl), 3.95 (br. s, 3H, diastereotopic $-CH_2-$), 3.40 (d, 3H, diastereotopic $-CH_2-$, $^2J_{HH}$= 13.5 Hz), 2.33 (br. s, 6H, diastereotopic $-NCH_2$-piperidine), 2.15 (br. s, 6H, diastereotopic $-NCH_2$-piperidine), 1.58-1.37 (m, 12H, $-CH_2-$), 1.24 (br. s, 6H, $-CH_2-$). **^{1}H NMR (400 MHz, pyridine-d_5, 353 K)**: δ 9.93 (s, 1H, OH), 7.92 (d, 3H, 3-CH-aryl, $^3J_{HH}$= 7.6 Hz), 7.36 (t, 3H, 4-CH-aryl, $^3J_{HH}$= 7.4 Hz), 7.10 (t, 3H, 5-CH-aryl, $^3J_{HH}$= 7.5 Hz), 6.95 (d, 3H, 6-CH-aryl, $^3J_{HH}$= 6.8 Hz), 3.83 (d, 3H, diastereotopic $-CH_2-$, $^2J_{HH}$= 14.2 Hz), 3.47 (d, 3H, diastereotopic $-CH_2-$, $^2J_{HH}$= 14.6 Hz), 2.33 (dt, 6H, diastereotopic $-NCH_2$-piperidine, $^2J_{HH}$= 10.7 Hz, $^3J_{HH}$= 5.2 Hz), 2.30-2.17 (compl. m, 6H, diastereotopic $-NCH_2$-piperidine, overlapping with toluene), 1.59-1.44 (m, 12H, $-CH_2-$), 1.41-1.30 (m, 6H, $-CH_2-$). IR (KBr): 3062 (m), 1744 (m), 1595 (m), 1347 (s), 1316 (m), 1298 (m), 1265 (s), 1246 (m), 1200 (m), 1155 (s), 1117 (s), 1098 (s), 1032 (s), 989 (m), 924 (m), 903 (w), 858 (s), 789 (s), 642 (s). Anal. Calcd for $C_{37}H_{49}N_3O$ (551.82 g/mol): C 80.53; H 8.95; N, 7.61. Found: C 80.56; H 8.90; N, 7.57. MS(EI): *m/z* 551.37 [M^+].



Synthesis of 3. To a precooled (0 °C) solution of $(Me_3SiCH_2)_3Sc(THF)_2$ (0.45 g, 1.00 mmol) in hexane (5 ml), compound **1** (0.44 g, 1.00 mmol) was added and stirred for 2 h at this temperature. Thereafter, the clear colorless solution was brought to room temperature and all volatiles together with THF were removed in vacuum. The next portion of fresh hexane (4 ml) was condensed, and the clear solution was placed in a refrigerator at -30 ºC. The colorless crystals of **3** were obtained by keeping the solution in the refrigerator for 24 hours. (0.49 g, 79%). **^{1}H NMR (400 MHz, C_6D_6, 298 K)**: δ 8.31 (d, 1H, CH-aryl, $^3J_{HH}$= 7.2 Hz), 7.22 (t, 1H, CH-aryl, $^3J_{HH}$= 7.0 Hz), 7.03-6.97 (compl. m, 3H, CH-aryl), 6.90-6.73 (compl. m, 4H, CH-aryl), 6.68 (d, 2H, CH-aryl, , $^3J_{HH}$= 7.5 Hz), 6.45 (d, 1H, CH-aryl, $^3J_{HH}$= 7.6 Hz), 4.57 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 13.0 Hz), 4.33 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 15.9 Hz), 3.96 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 12.2 Hz), 3.30 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 16.0 Hz), 2.85 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 13.1 Hz), 2.53 (s, 3H, NMe), 2.45 (s, 3H, NMe), 2.36 (s, 3H, NMe), 2.29 (d, 1H, diastereotopic -CH_2-, $^2J_{HH}$= 12.0 Hz), 2.19-2.02 (compl m, 9H, NMe), 0.27 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$), -0.20 (d, 1H, diastereotopic -CH_2SiMe_3, $^2J_{HH}$= 10.9 Hz), -0.40 (d, 1H, diastereotopic -CH_2SiMe_3, $^2J_{HH}$= 11.6 Hz), -0.94 (d, 1H, diastereotopic -CH_2SiMe_3, $^2J_{HH}$= 11.8 Hz), -1.02 (d, 1H, diastereotopic -CH_2SiMe_3, $^2J_{HH}$= 11.9 Hz),. **^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K)**: δ 152.23 (s, *ipso*-C-aryl), 149.08 (s, *ipso*-C-aryl), 148.11 (s, *ipso*-C-aryl), 140.28 (s, *ipso*-C-aryl), 135.94 (s, CH-aryl), 135.06 (s, CH-aryl), 134.72 (s, *ipso*-C-aryl), 134.20 (s, *ipso*-C-aryl), 129.76 (s, CH-aryl), 129.53 (s, CH-aryl), 127.99 (s, CH-aryl, overlapping with benzene), 127.67 (s, CH-aryl, overlapping with benzene), 127.53 (s, CH-aryl), 127.21 (s, CH-aryl), 127.12 (s, CH-aryl), 127.02 (s, CH-aryl), 126.66 (s, CH-aryl), 124.77 (s, CH-aryl), 88.51 (s, CO), 66.15 (s, CH_2), 62.71 (s, CH_2), 61.84 (s, CH_2), 50.98 (s, NMe), 49.21 (s, NMe), 48.01 (s, NMe), 45.81 (s, NMe), 45.70 (s, NMe), 45.61 (s, NMe), 36.42 (s, CH_2Si), 34.52 (s, CH_2Si), 4.23 (s, $SiMe_3$). IR (KBr): 1597 (s), 1250 (s), 1208 (m), 1169 (s), 1098 (s), 1045 (m), 1026 (s), 982 (m), 955 (w), 922 (m), 860 (s), 787 (m), 760 (s), 642 (s). Anal. Calcd for $C_{36}H_{58}N_3OScSi_2$ (650.01 g/mol): C 66.52; H 8.99; N, 6.46; Sc, 6.92. Found: C 66.58; H 8.91; N, 6.43; Sc, 6.97.

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S2. P. Zhao and Y.-W. Yin, *J. Heterocycl. Chem.*, 2004, **41**, 157.

S3. S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177.

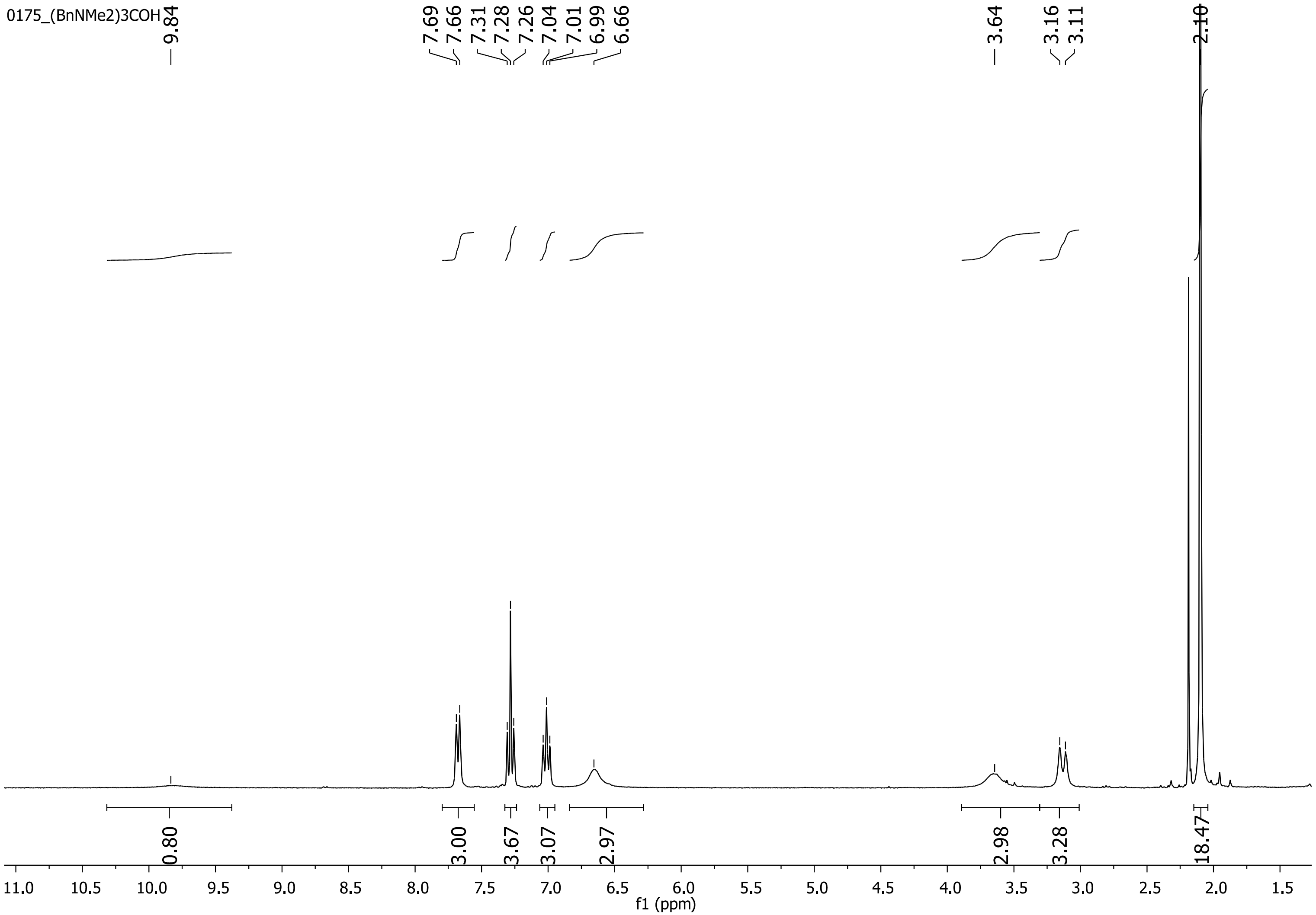

Figure S1. ^{1}H NMR spectrum of **1**. (300 MHz, $CDCl_3$, 298 K).

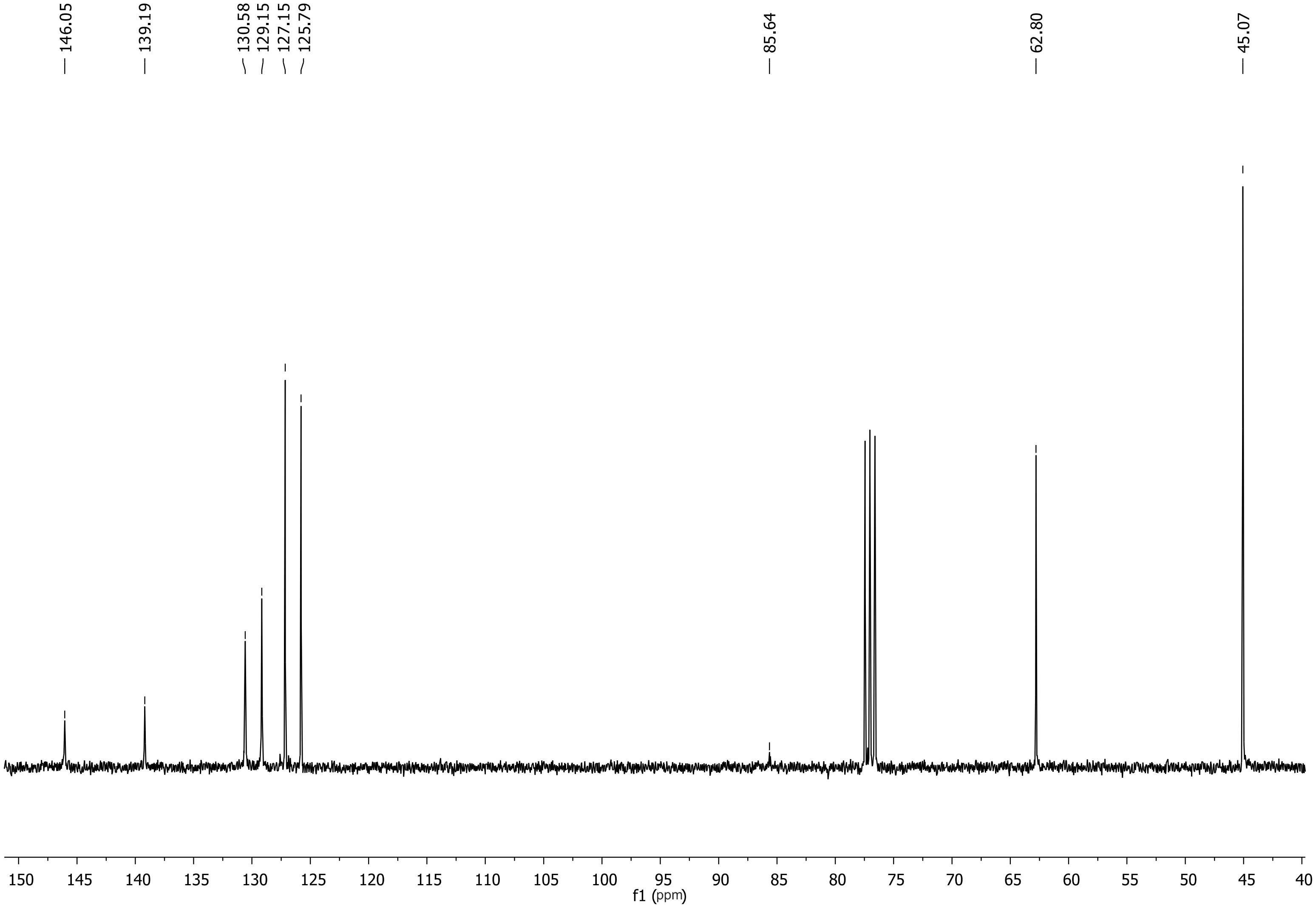

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1**. (75 MHz, $CDCl_3$, 298 K).

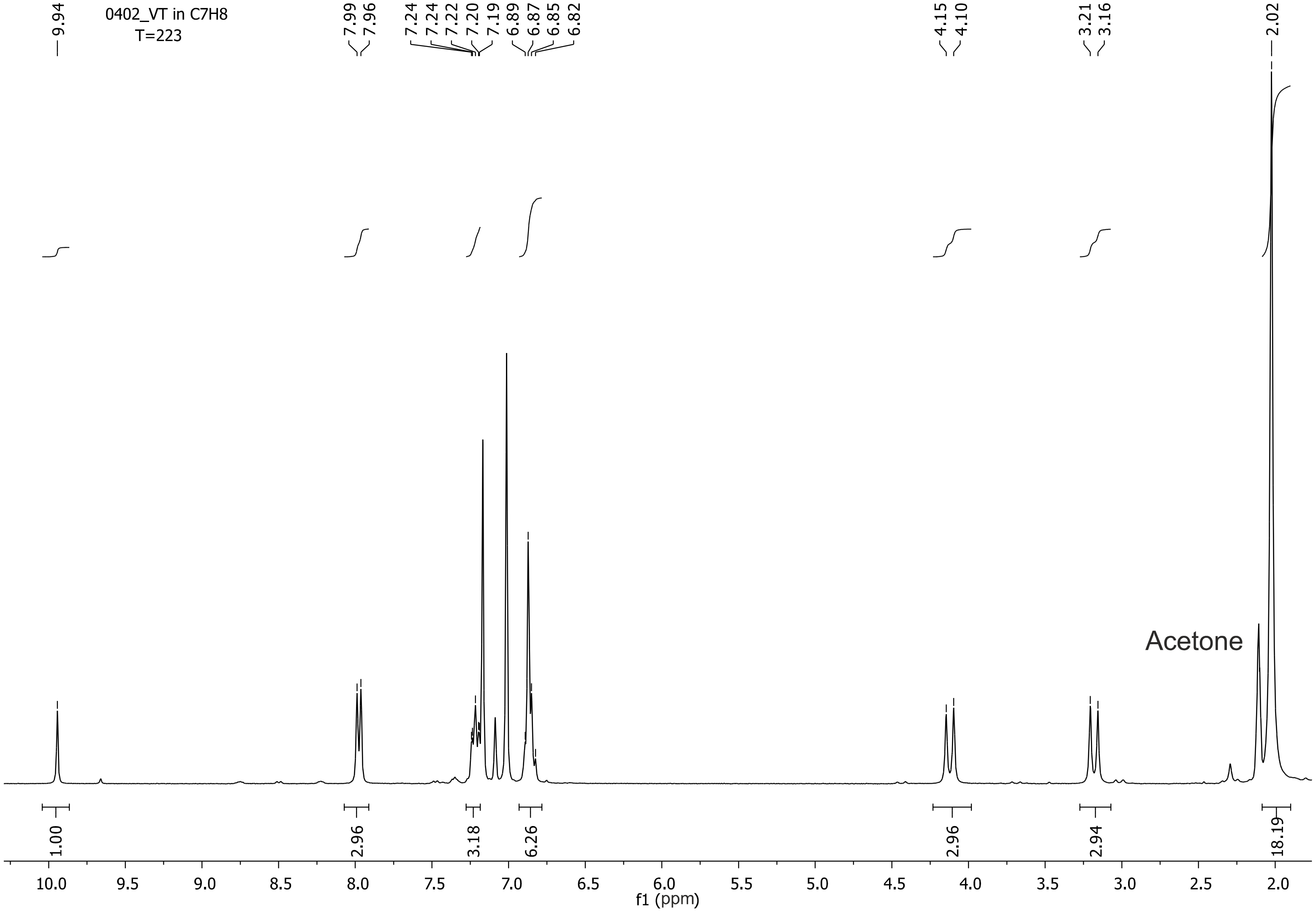

Figure S3. ^{1}H NMR spectrum of **1**. (300 MHz, C_7D_8, 223 K).

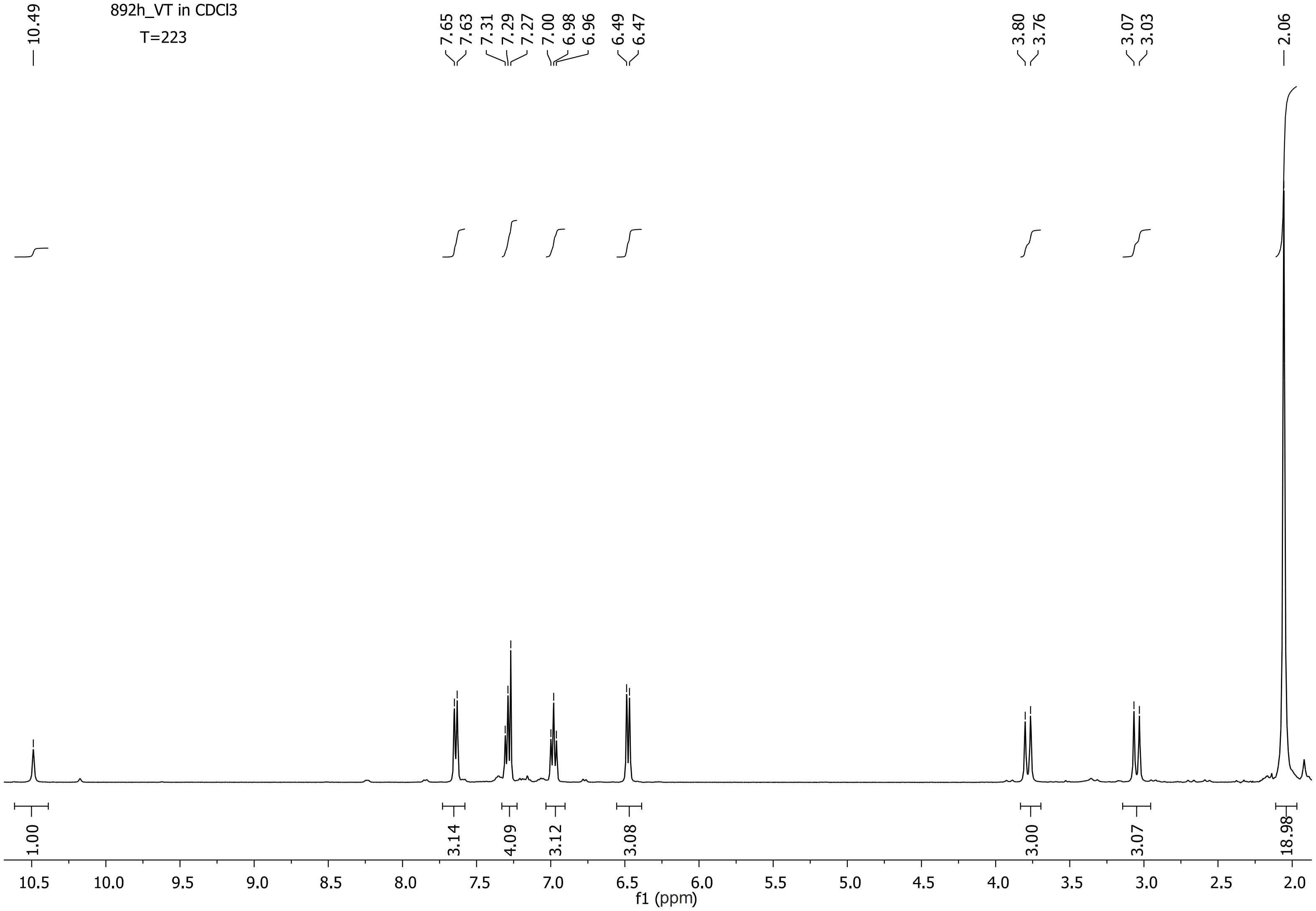

Figure S4. ^{1}H NMR spectrum of **1**. (400 MHz, $CDCl_3$, 223 K).

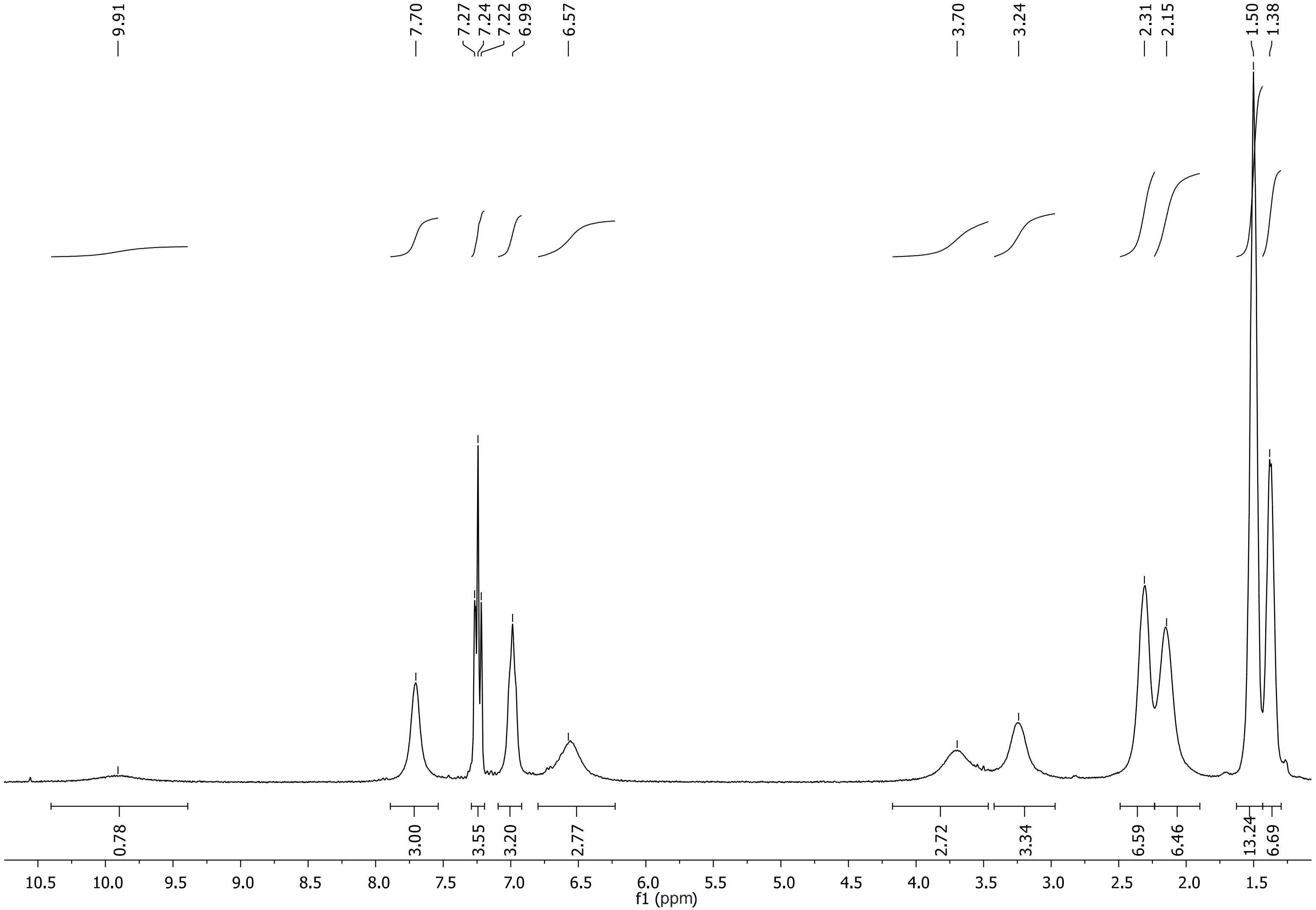

Figure S5. ^{1}H NMR spectrum of **2**. (300 MHz, $CDCl_3$, 298 K).

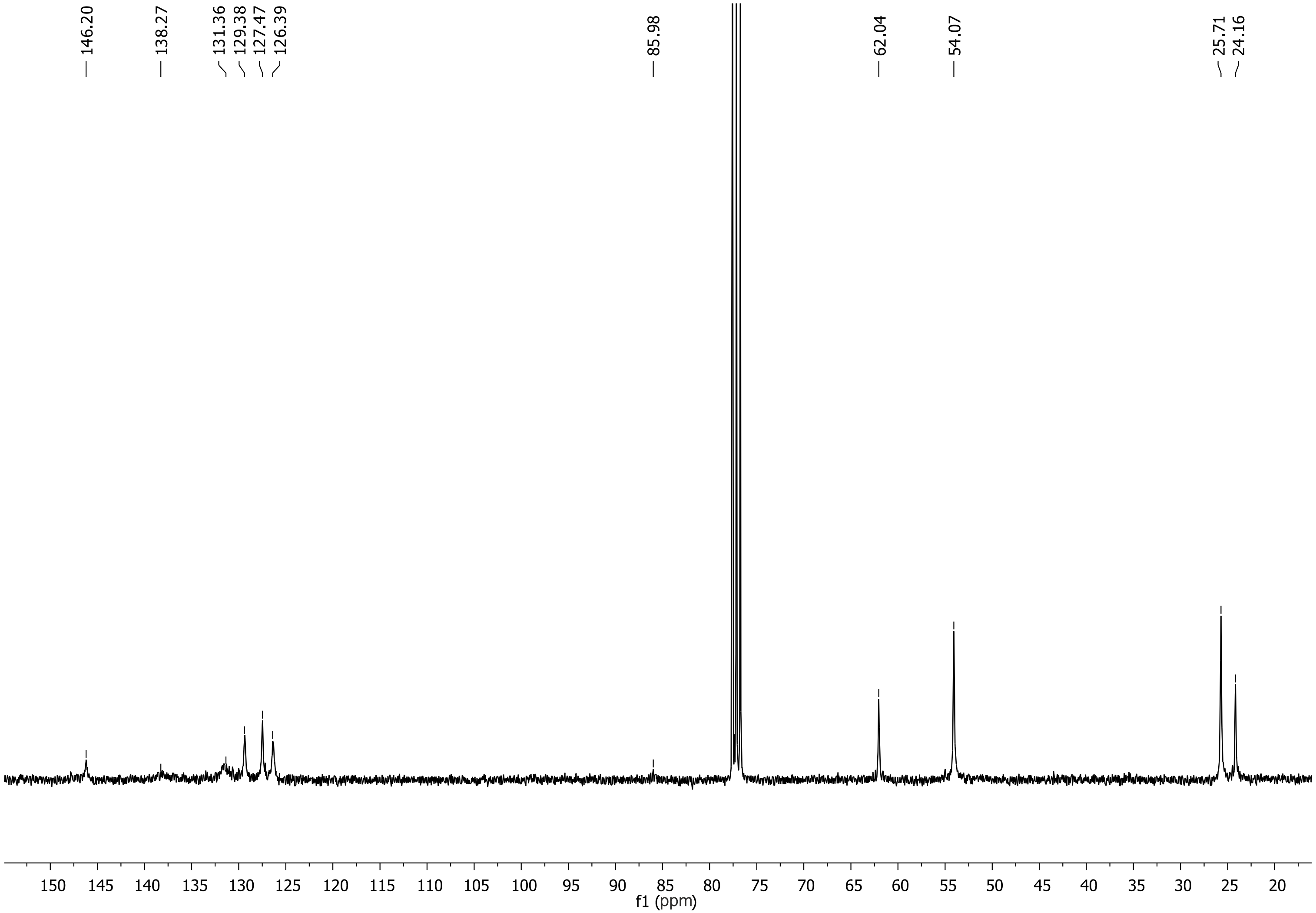

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2**. (75 MHz, $CDCl_3$, 298 K).

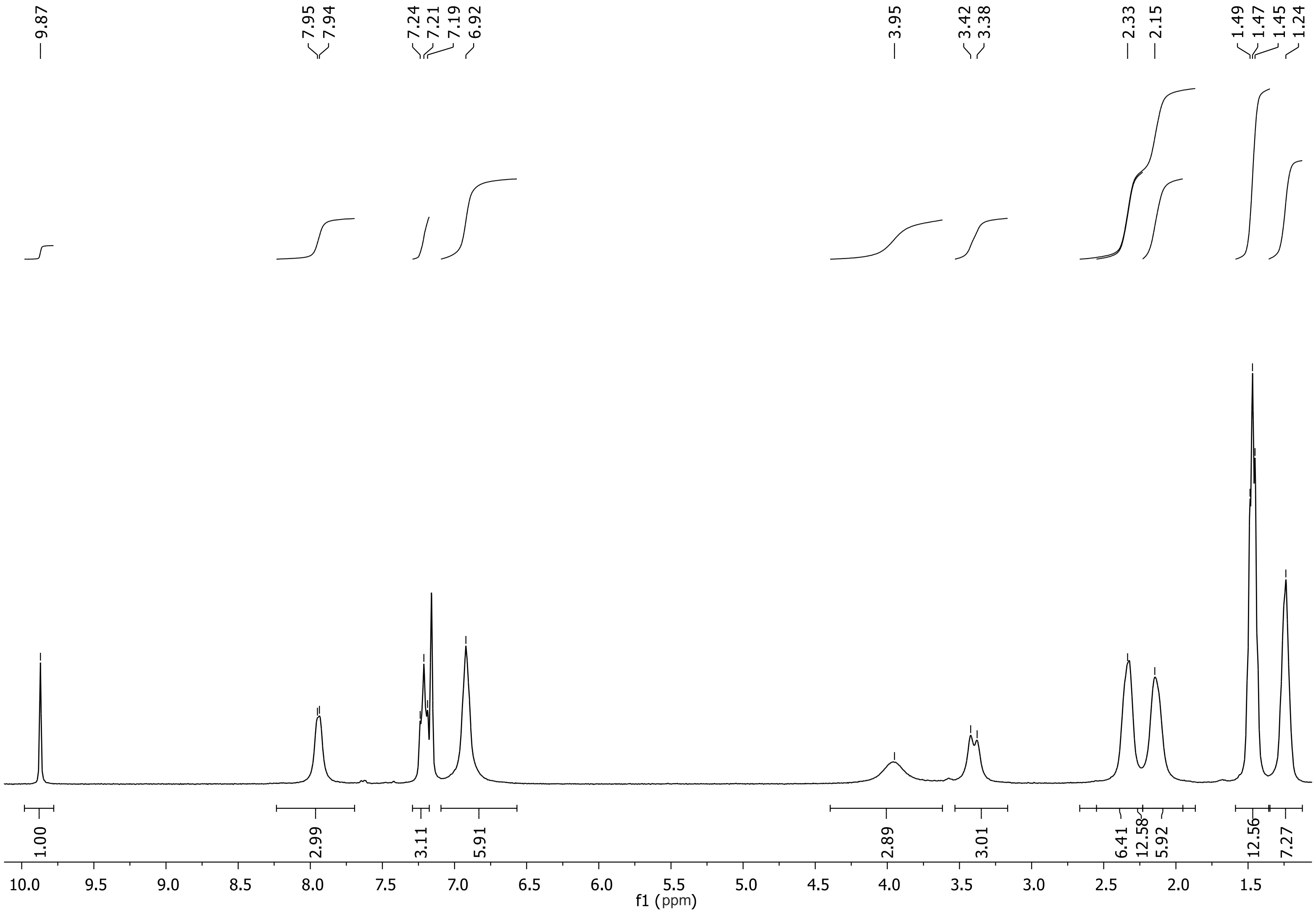

Figure S7. ^{1}H NMR spectrum of **2**. (300 MHz, C_6D_6, 298 K).

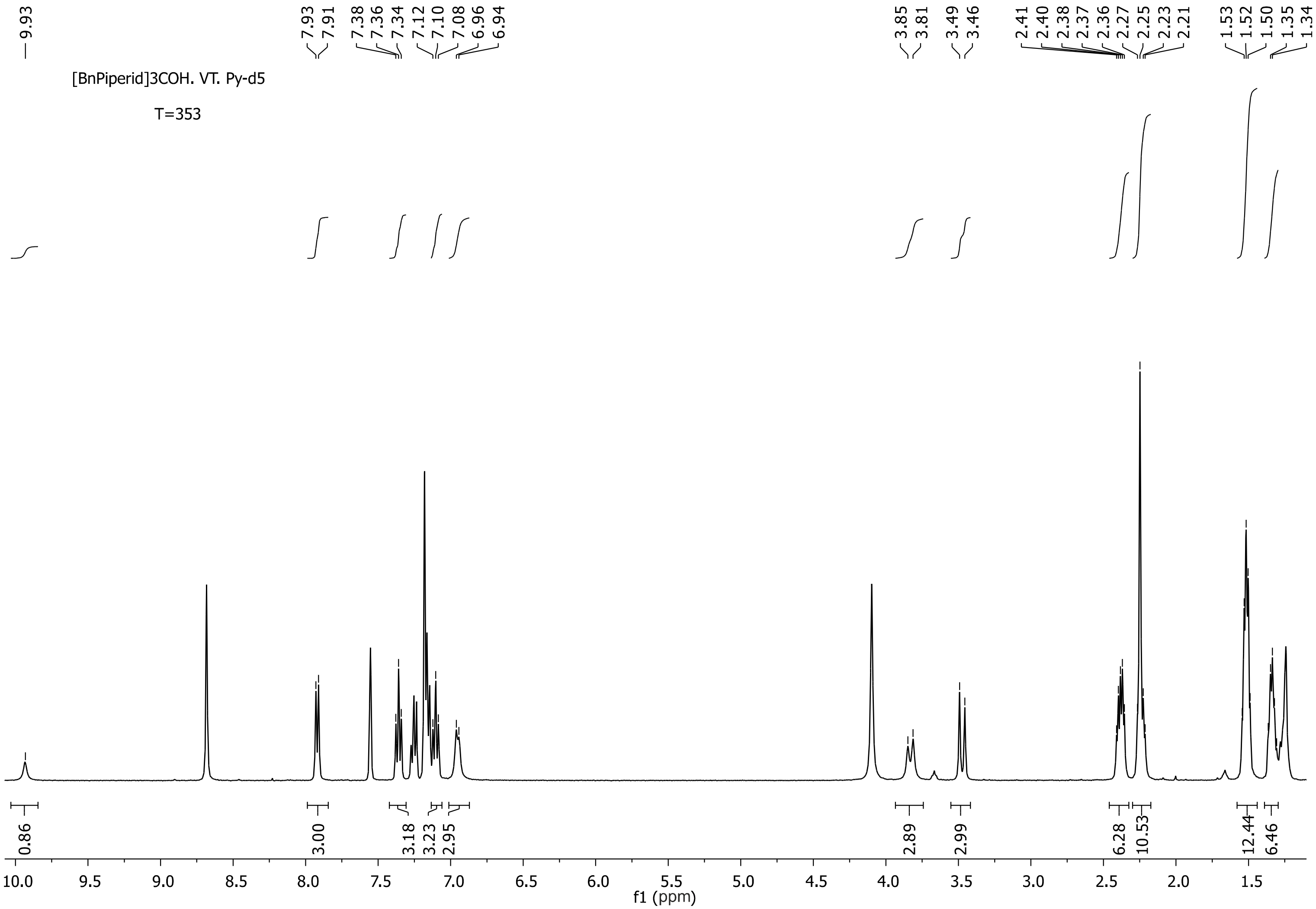

Figure S8. ^{1}H NMR spectrum of **2**. (400 MHz, C_5D_5N, 298 K).

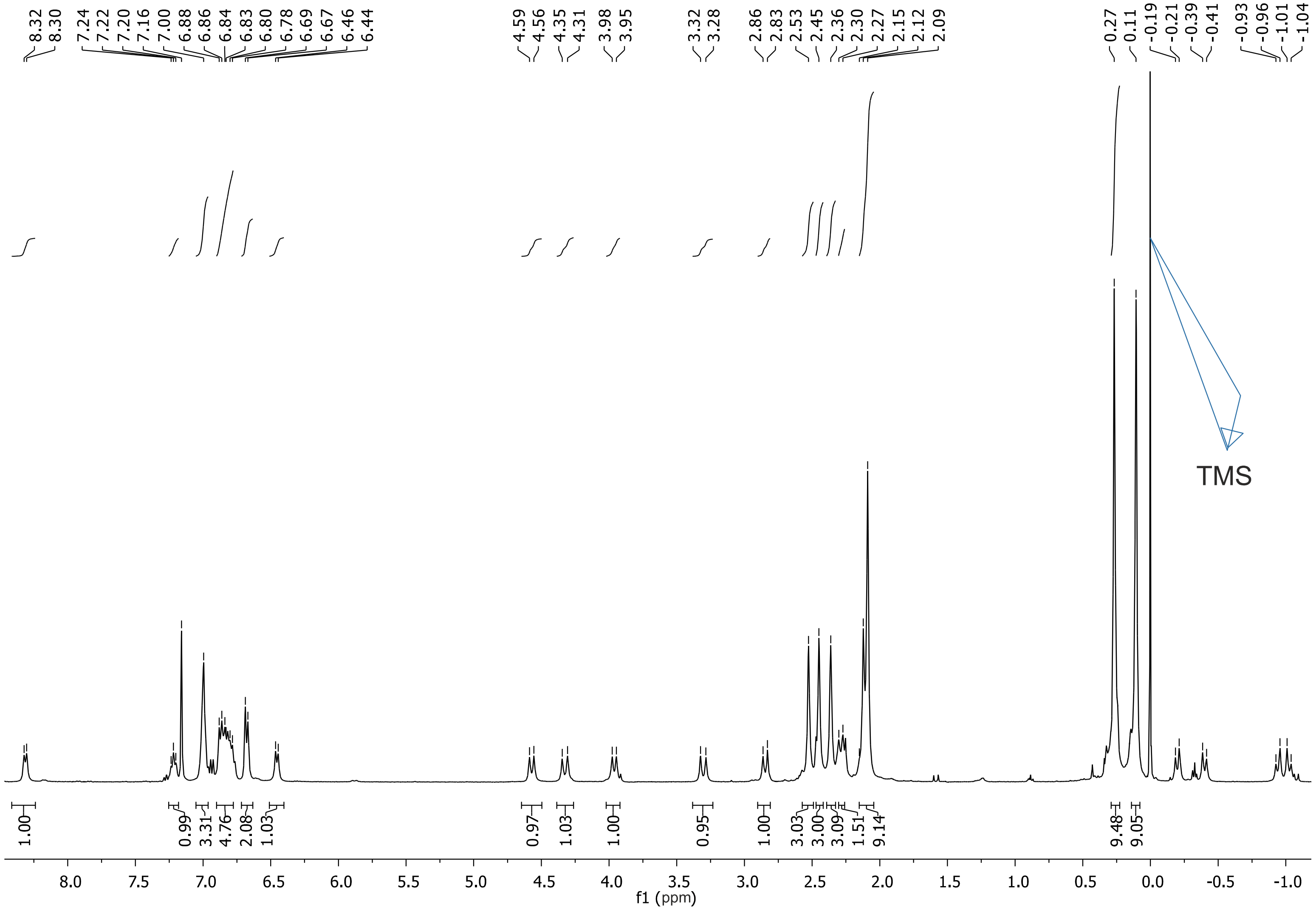

Figure S9. ^{1}H NMR spectrum of **3**. (400 MHz, C_6D_6, 298 K).

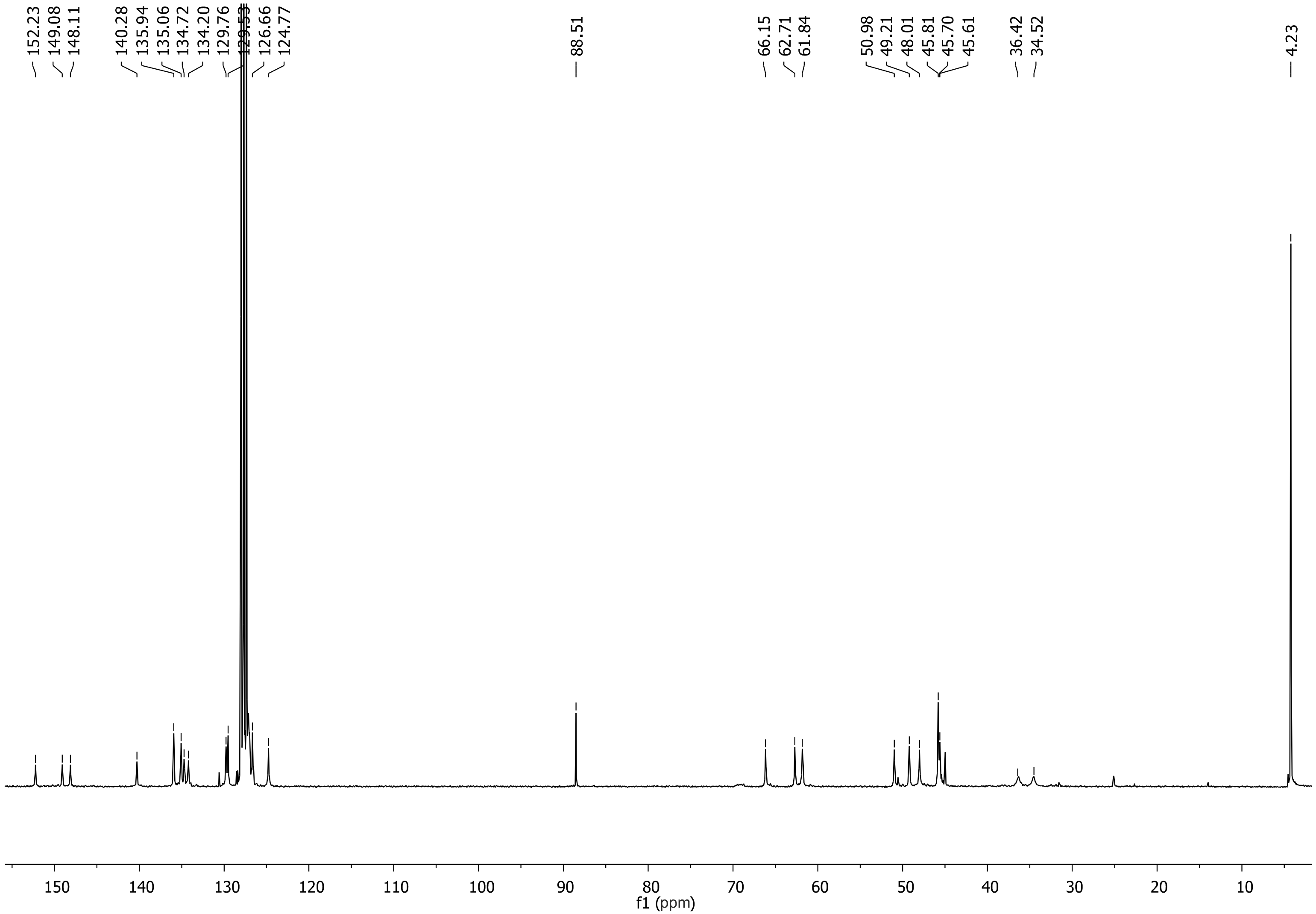

Figure S10. $^{13}C\{^1H\}$ NMR spectrum of **3**. (75 MHz, C_6D_6, 298 K).

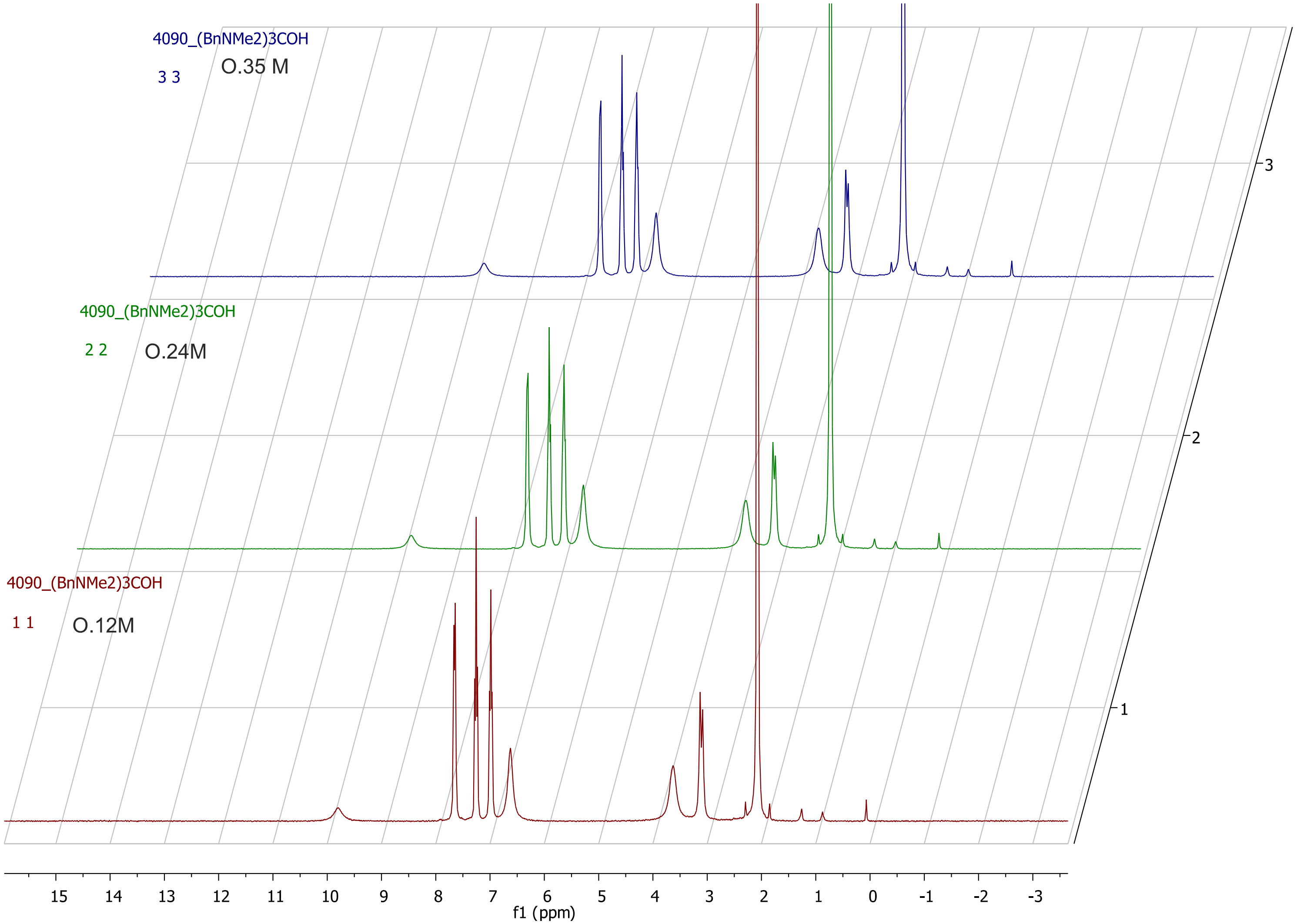

Figure S11. ^{1}H NMR spectrum of **1** at different concentrations (0.12-0.35 M). (300 MHz, $CDCl_3$, 298 K).

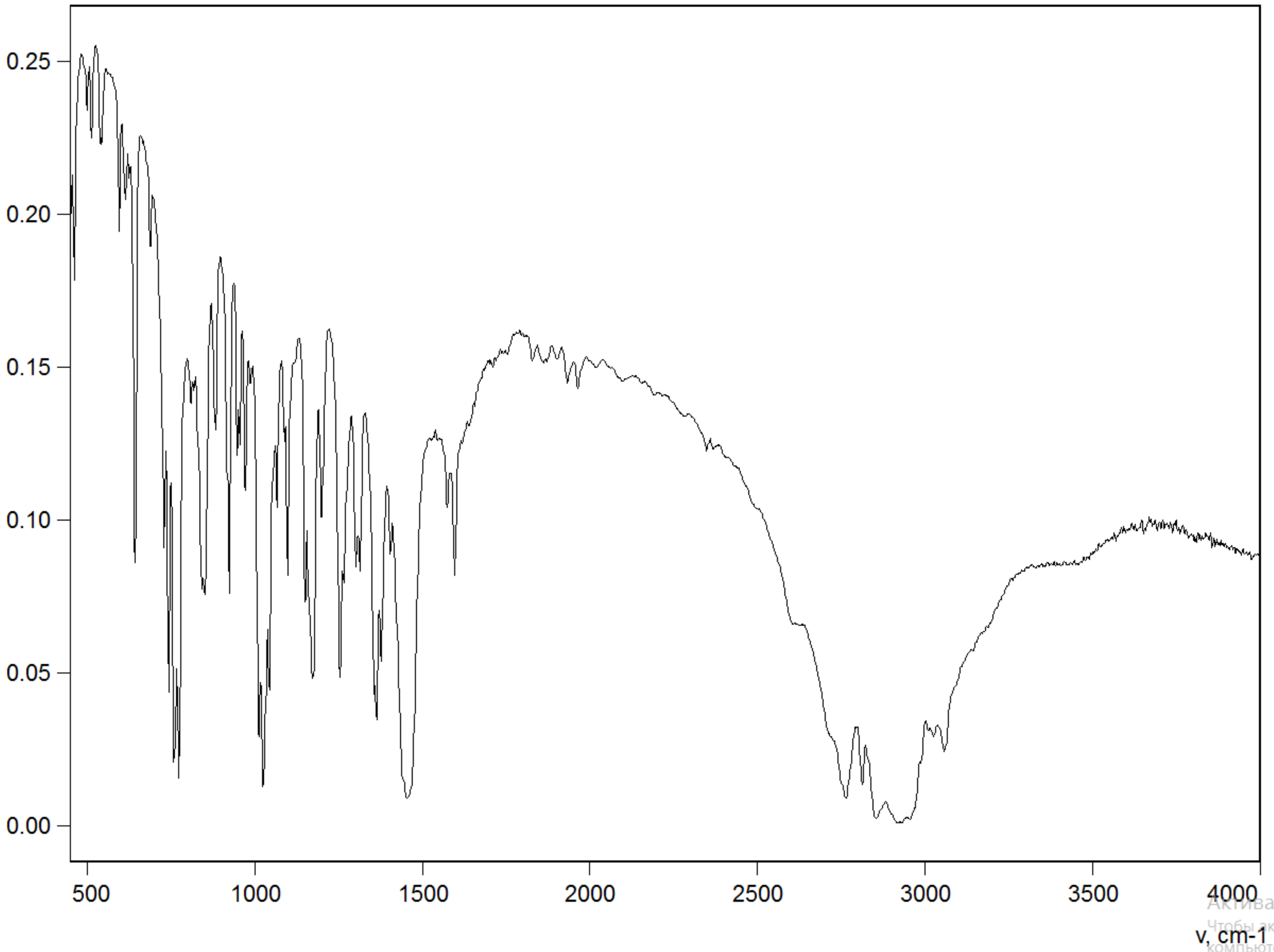

Figure S12. IR spectrum of **1** (KBr, Nujol).

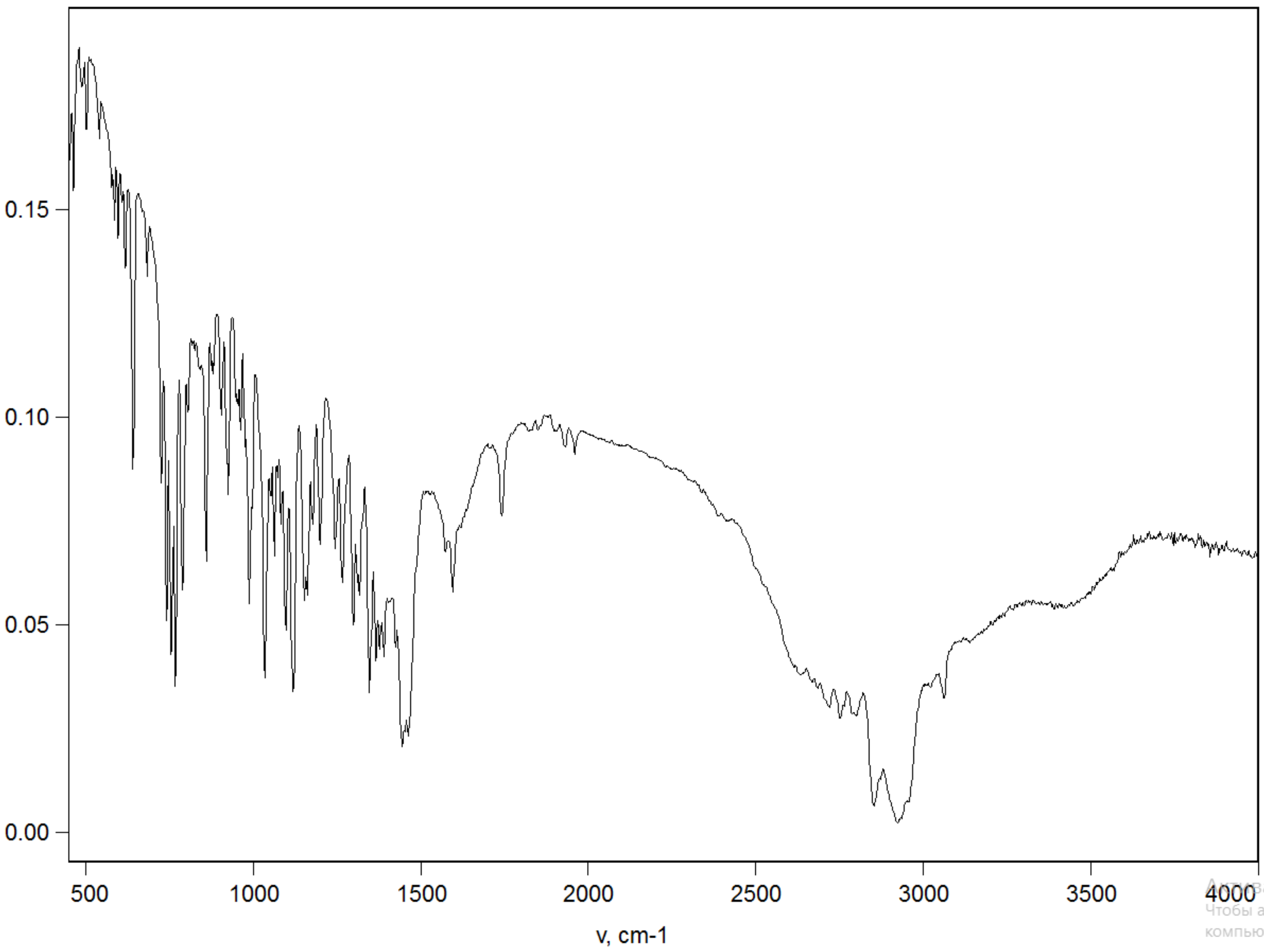

Figure S13. IR spectrum of **2** (KBr, Nujol).

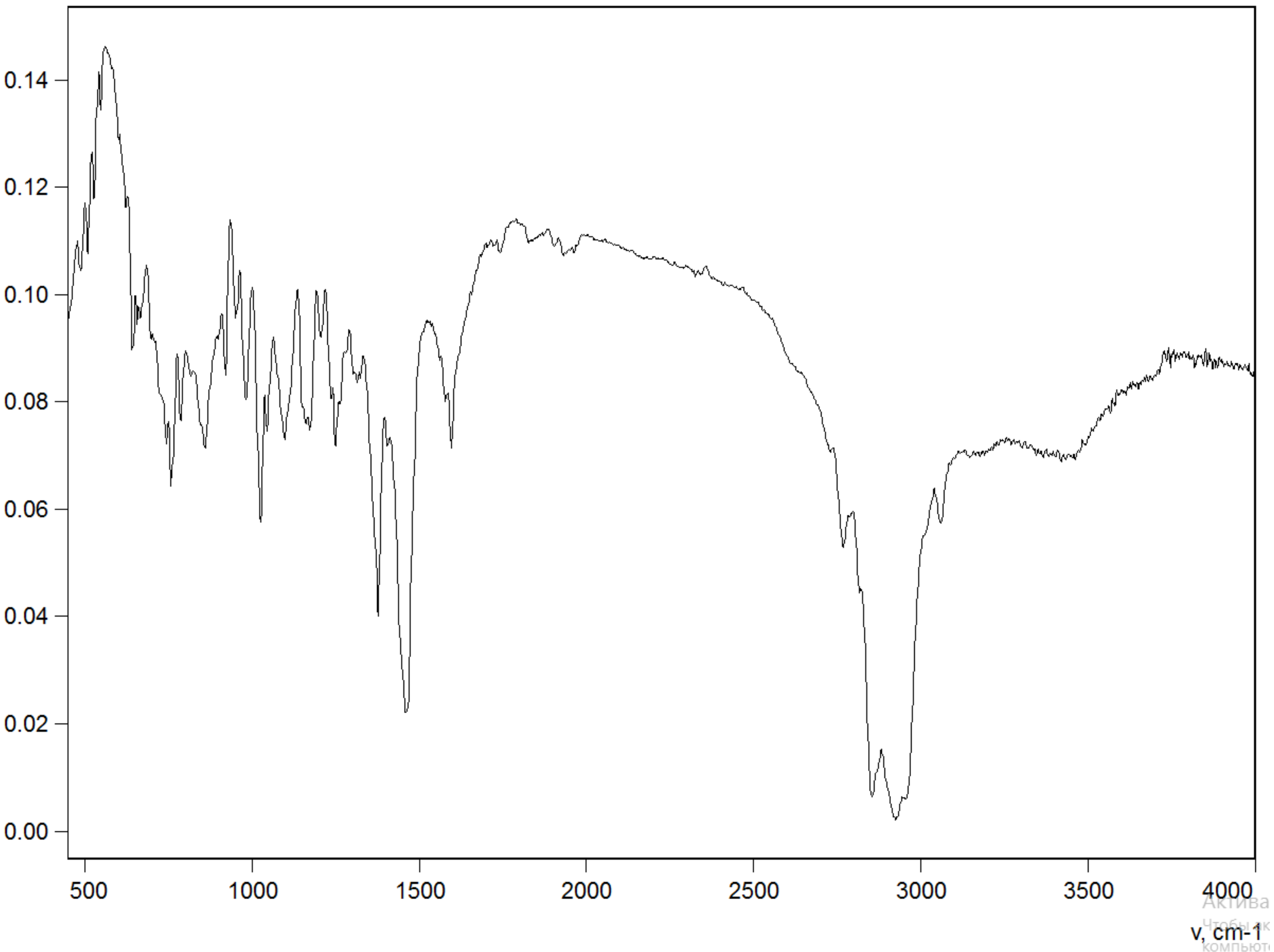

Figure S14. IR spectrum of **3** (KBr, Nujol).