

SUPPORTING INFORMATION

Title: A Practical Route to Regiospecifically Substituted (*R*)- and (*S*)-Oxazolylphenols

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Supporting Information

A Practical Route to Regiospecifically Substituted (R)- and (S)-Oxazolylphenols

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IR spectra were recorded on a Nicolet 205 FT-IR spectrometer for liquid films between NaCl plates and are reported in wavenumbers (cm^{-1}). NMR spectra were measured using dilute solutions on a Bruker ARX 400 (^1H at 400.13 MHz, ^{13}C at 100.61 MHz) spectrometer. Chemical shifts are reported in ppm on the δ scale from tetramethylsilane (TMS) which is used as an internal standard. Elemental analyses were performed by ICSN in Gif-Sur-Yvette or at the Institut für Organische Chemie in Erlangen. Low resolution mass spectra were carried out at the Institut für Organische Chemie in Erlangen. High-resolution mass spectra (HRMS) were obtained under electronic impact at 70 eV from a Varian MAT 311 spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (Rennes).

Detailed characterization data are given for the described compounds. Selected ^1H and ^{13}C NMR spectra are shown for twelve of them.

Methyl 3,5-di-*tert*-butyl-2-hydroxybenzoate 1

IR (Nujol, NaCl): $\tilde{\nu}$ 3095, 1806 (small, aromatic harmonic), 1675 (C=O), 1608 (C=C), 1602 (C=C), 1463, 1457, 1440, 1362, 1343, 1276, 1247, 1216, 1199, 1115, 985, 896, 824, 802, 760, 741, 724, 641 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 11.35 (s, 1H, OH), 7.71 (d, 1H, $J = 2.6$ Hz, CH aromatic), 7.52 (d, 1H, $J = 2.6$ Hz, CH aromatic), 3.94 (s, 3H, CO_2CH_3), 1.43 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.30 (s, 9H, $\text{C}(\text{CH}_3)_3$).

^{13}C NMR (100 MHz, CDCl_3): δ 171.74 (1C, CO_2CH_3), 158.97 (1C, $\text{C}_{\text{ipso}} \alpha$ to OH), 140.42 (1C, $\text{C}_{\text{ipso}} \alpha$ to $\text{C}(\text{CH}_3)_3$), 137.17 (1C, $\text{C}_{\text{ipso}} \alpha$ to $\text{C}(\text{CH}_3)_3$), 130.42 (1C, CH aromatic), 123.59 (1C, CH aromatic),

111.31 (1C, C_{ipso} α to CO₂CH₃), 52.19 (1C, CO₂C_H3), 35.13 (1C, C(CH₃)₃), 34.27 (1C, C(CH₃)₃), 31.41 (3C, C(CH₃)₃), 29.38 (3C, C(CH₃)₃).

MS (EI, 70 eV) *m/z* (rel intens) 264 (49) [M]⁺, 249 (93) [M - CH₃]⁺, 232 (21) [M - CH₃OH]⁺, 217 (100) [M - CH₃ - CH₃OH]⁺, 175 (36) [M - C₄H₉ - CH₃OH]⁺, 87 (24), 57 (24), 41 (24).

3,5-Di-*tert*-butyl-2-hydroxybenzoic acid 7

IR (Nujol, NaCl): $\tilde{\nu}$ 3425 (broad, OH), 1649 (C=O), 1606 (C=C), 1437, 1364, 1294, 1279, 1234, 1190, 1118, 804, 709 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): *d* 11.05 (broad s, 1H, OH), 7.80 (d, 1H, *J* = 2.5 Hz, CH aromatic), 7.59 (d, 1H, *J* = 2.5 Hz, CH aromatic), 6.90-5.40 (broad s, 1H, CO₂H), 1.44 (s, 9H, C(CH₃)₃), 1.32 (s, 9H, C(CH₃)₃).

¹³C NMR (100 MHz, CDCl₃): *d* 175.79 (1C, CO₂H), 159.71 (1C, C_{ipso} α to OH), 140.86 (1C, C_{ipso} α to C(CH₃)₃), 137.41 (1C, C_{ipso} α to C(CH₃)₃), 131.73 (1C, CH aromatic), 124.57 (1C, CH aromatic), 110.35 (1C, C_{ipso} α to CO₂H), 35.16 (1C, C(CH₃)₃), 34.29 (1C, C(CH₃)₃), 31.34 (3C, C(CH₃)₃), 29.38 (3C, C(CH₃)₃).

MS (EI, 70 eV) *m/z* (rel intens) 250 (26) [M]⁺, 235 (41) [M - CH₃]⁺, 217 (100) [M - CH₃ - H₂O]⁺, 175 (33) [M - C₄H₉ - H₂O]⁺, 87 (26), 57 (20), 41 (16).

Methyl 3-*tert*-butyl-2-hydroxy-5-nitrobenzoate 3

IR (Nujol, NaCl): $\tilde{\nu}$ 3106, 1822 (small, aromatic harmonic), 1687 and 1674 (C=O), 1615, 1583, 1531, 1453, 1359, 1336, 1249, 1206, 1151, 1098, 980, 926, 805, 739, 707 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 12.26 (s, 1H, OH), 8.70 (d, 1H, $J = 2.5$ Hz, CH aromatic), 8.34 (d, 1H, $J = 2.5$ Hz, CH aromatic), 4.03 (s, 3H, CO_2CH_3), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$).

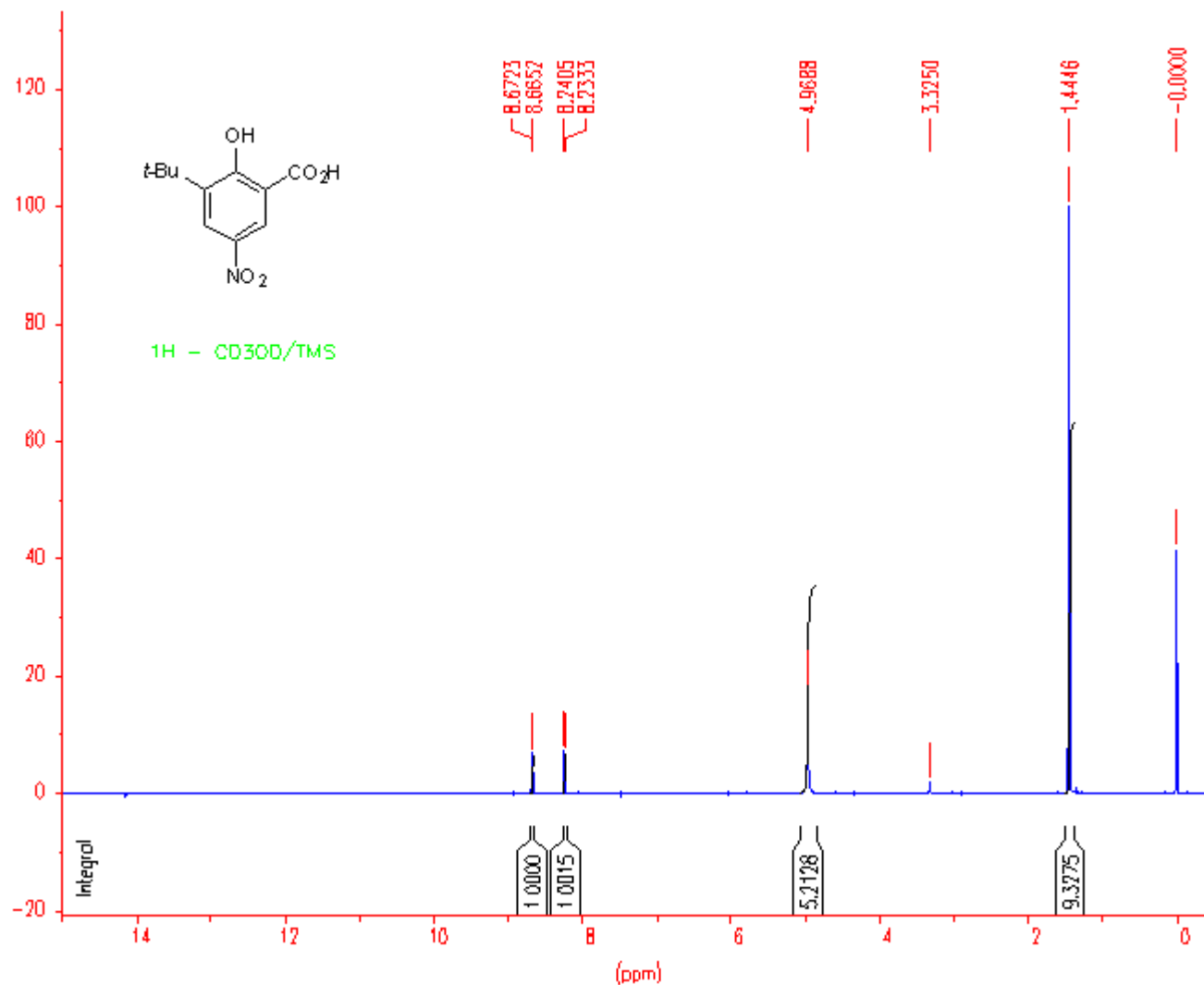
^{13}C NMR (100 MHz, CDCl_3): δ 170.39 (1C, $\text{C}=\text{O}$), 165.88 (1C, $\text{C}_{\text{ipso}} \alpha$ to OH), 139.90 and 139.21 (2C, $\text{C}_{\text{ipso}} \alpha$ to $\text{C}(\text{CH}_3)_3$ and $\text{C}_{\text{ipso}} \alpha$ to NO_2), 127.51 (1C, CH aromatic), 124.49 (1C, CH aromatic), 111.87 (1C, $\text{C}_{\text{ipso}} \alpha$ to CO_2CH_3), 53.14 (1C, CO_2CH_3), 35.42 (1C, $\text{C}(\text{CH}_3)_3$), 28.94 (3C, $\text{C}(\text{CH}_3)_3$).

MS (EI, 70 eV) m/z (rel intens) 253 (15) $[\text{M}]^+$, 238 (56) $[\text{M} - \text{CH}_3]^+$, 206 (100) $[\text{M} - \text{CH}_3 - \text{CH}_3\text{OH}]^+$, 160 (26) $[\text{M} - \text{CH}_3 - \text{CH}_3\text{OH} - \text{NO}_2]^+$.

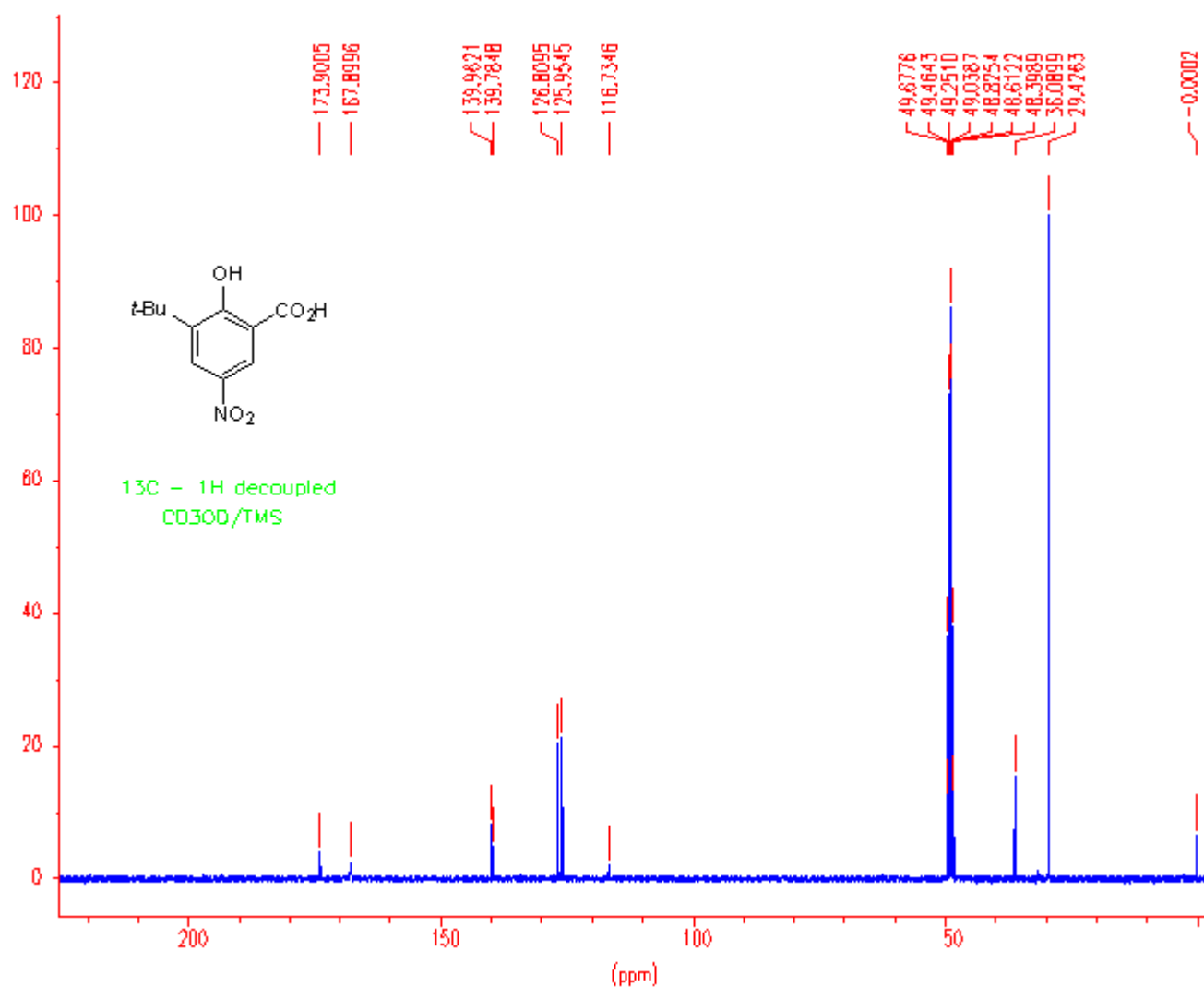
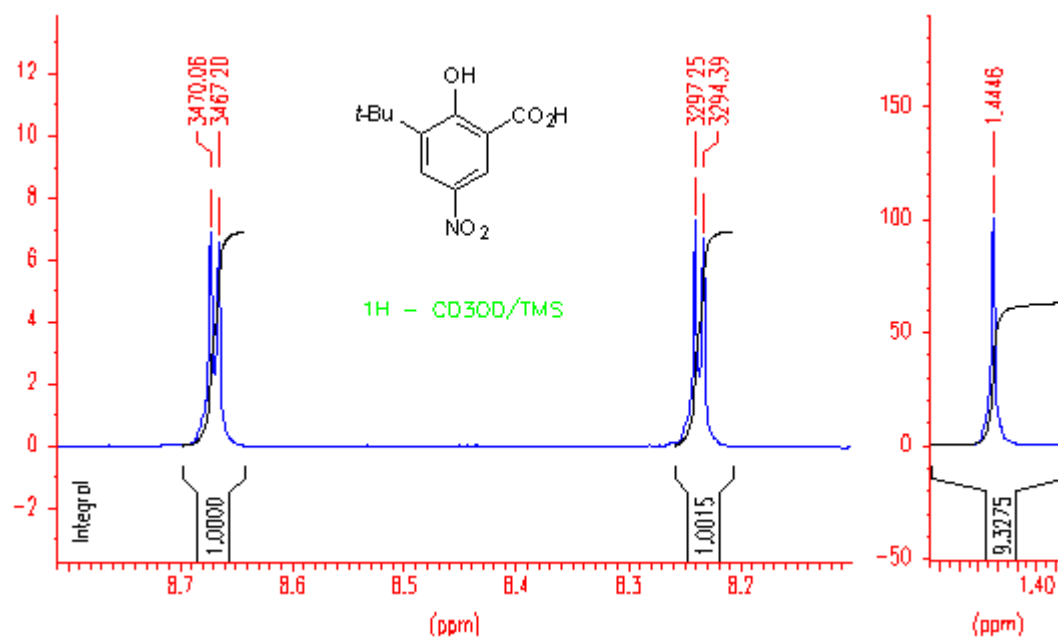
Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 57.28; H, 6.17; N, 5.46.

3-*tert*-Butyl-2-hydroxy-5-nitrobenzoic acid 5

IR (HCB, NaCl): $\tilde{\nu}$ 3640-2390 (broad envelope, OH), 3103, 2965, 2915, 2876, 1742, 1666, 1453, 1442, 1341, 1238, 1159, 1099, 1047, 937, 740, 697, 654 cm^{-1} .

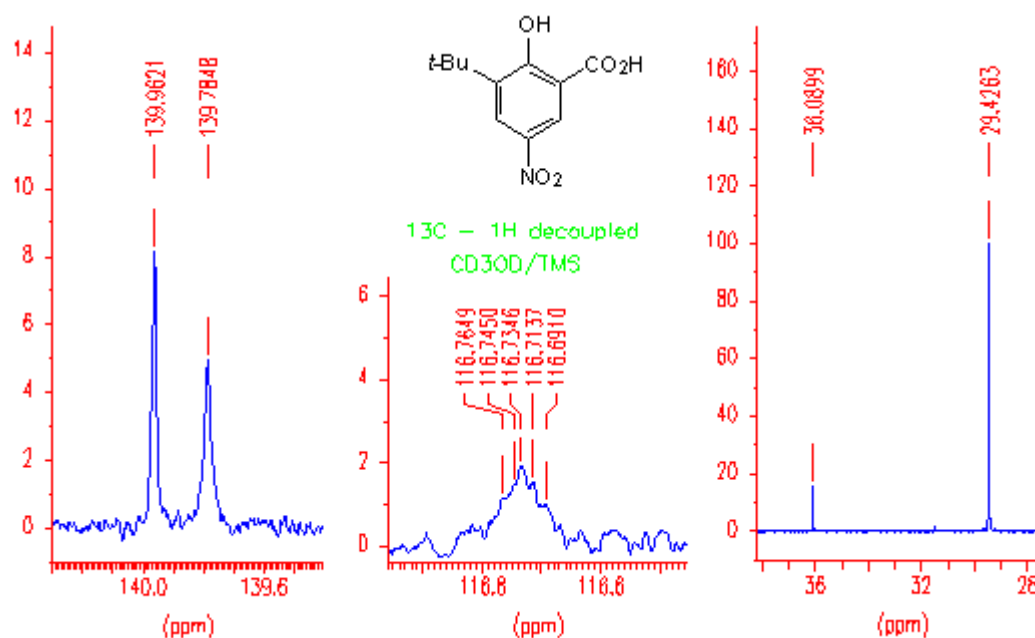
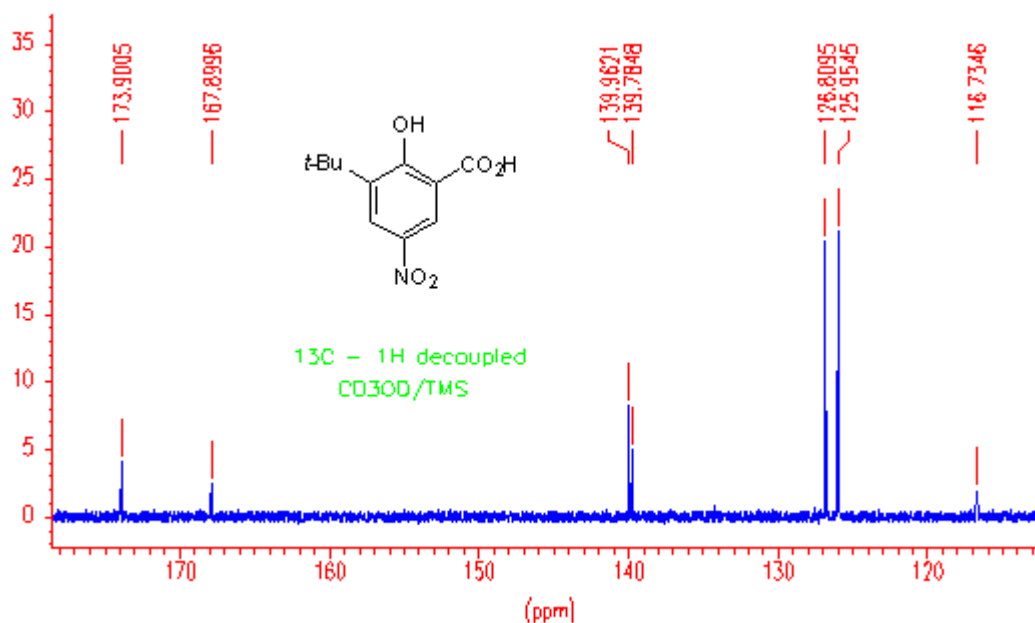


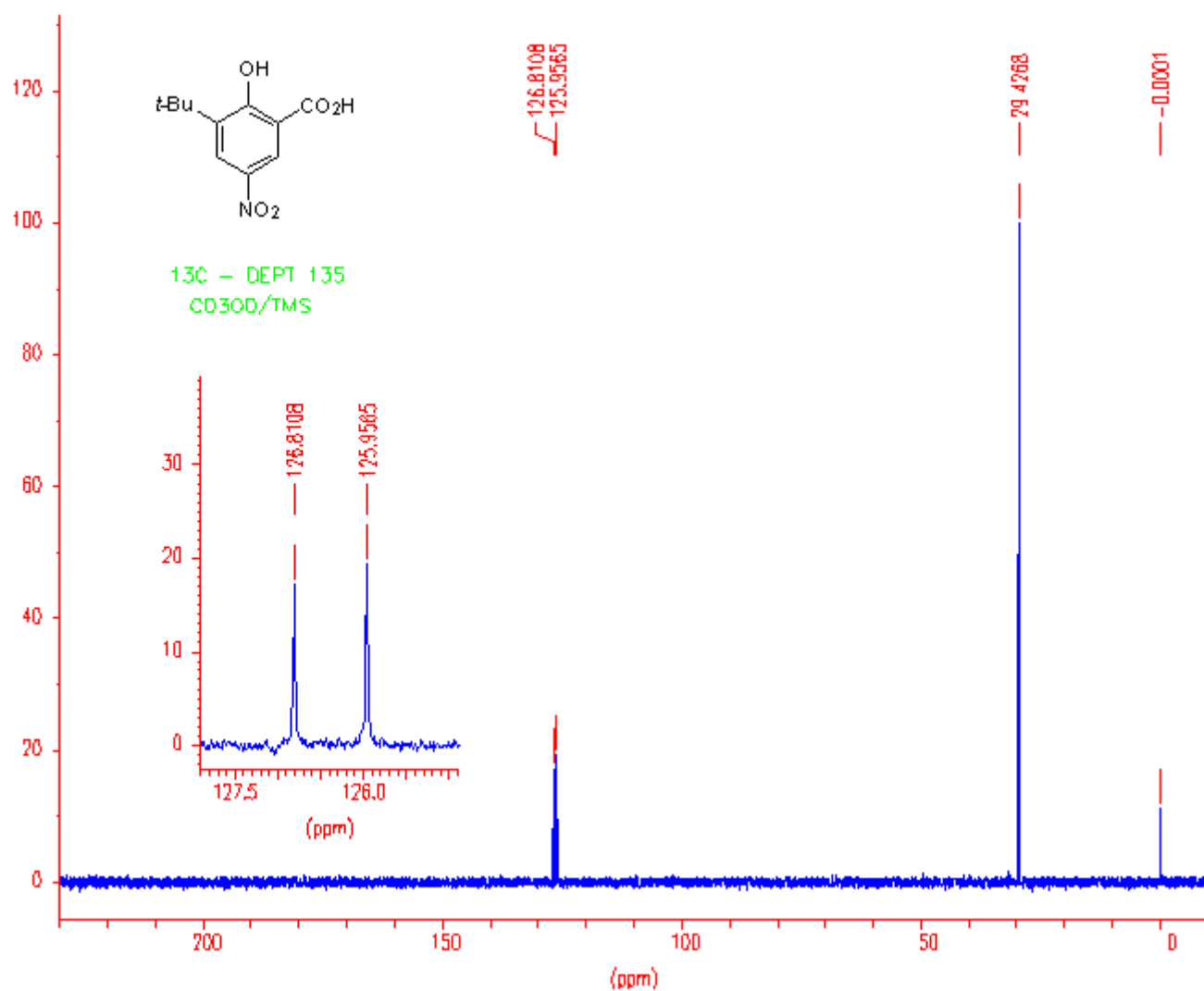
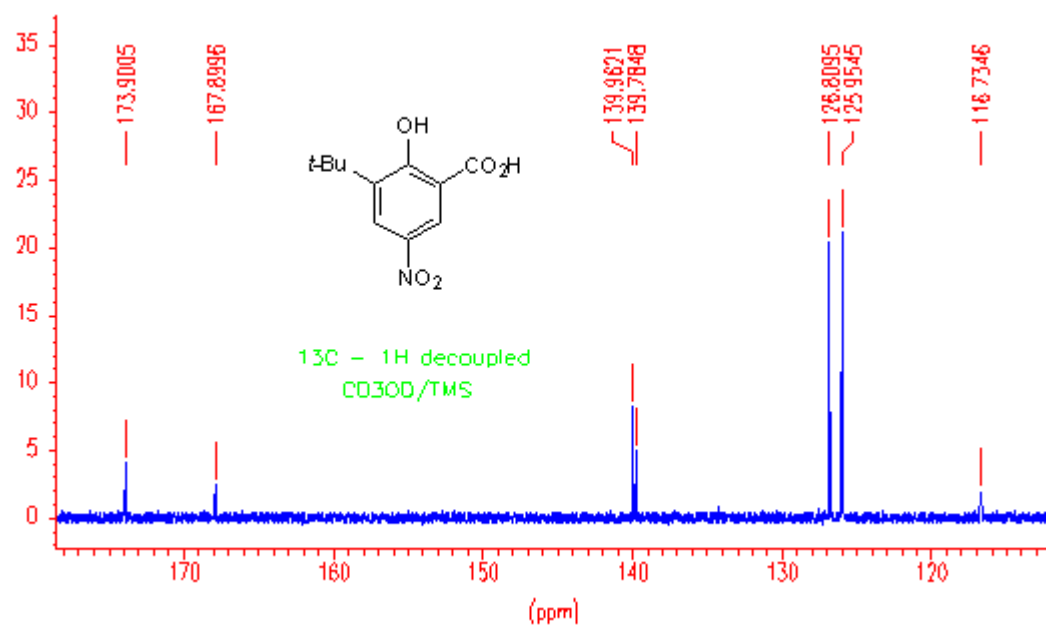
^1H NMR (400 MHz, CD_3OD): δ 8.67 (d, 1H, $J = 2.9$ Hz, CH aromatic), 8.24 (d, 1H, $J = 2.9$ Hz, CH aromatic), 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$).



^{13}C NMR (100 MHz, CD_3OD): δ 173.90 (1C, $\text{C}=\text{O}$), 167.90 (1C, C_{ipso} α to OH), 139.96 and 139.78 (2C, C_{ipso} α to $\text{C}(\text{CH}_3)_3$ and C_{ipso} α to NO_2), 126.81 (1C, CH aromatic), 125.95 (1C, CH aromatic), 116.74 (broad, 1C, C_{ipso} α to $\text{C}=\text{O}$), 36.09 (1C, $\text{C}(\text{CH}_3)_3$), 29.43 (3C, $\text{C}(\text{CH}_3)_3$).

MS (EI, 70 eV) m/z (rel intens) 239 (21) $[\text{M}]^+$, 224 (69) $[\text{M} - \text{CH}_3]^+$, 206 (100) $[\text{M} - \text{CH}_3 - \text{H}_2\text{O}]^+$, 160 (39) $[\text{M} - \text{CH}_3 - \text{H}_2\text{O} - \text{NO}_2]^+$.





3,5-Di-*tert*-butyl-2-hydroxybenzonitrile 4

IR (Nujol, NaCl): $\tilde{\nu}$ 3300 (OH), 2998, 2870, 2233 (C $\equiv$ N), 1819 and 1787 (very small, aromatic harmonics), 1752 (small, aromatic harmonic), 1603 (C=C), 1480, 1466, 1448, 1409, 1389, 1364, 1331, 1252, 1220, 1202, 1158, 1124, 937, 902, 879 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, 1H, J = 2.4 Hz, CH aromatic), 7.30 (d, 1H, J = 2.4 Hz, CH aromatic), 6.12 (broad s, 1H, OH), 1.41 (s, 9H, C(CH₃)₃), 1.29 (s, 9H, C(CH₃)₃).

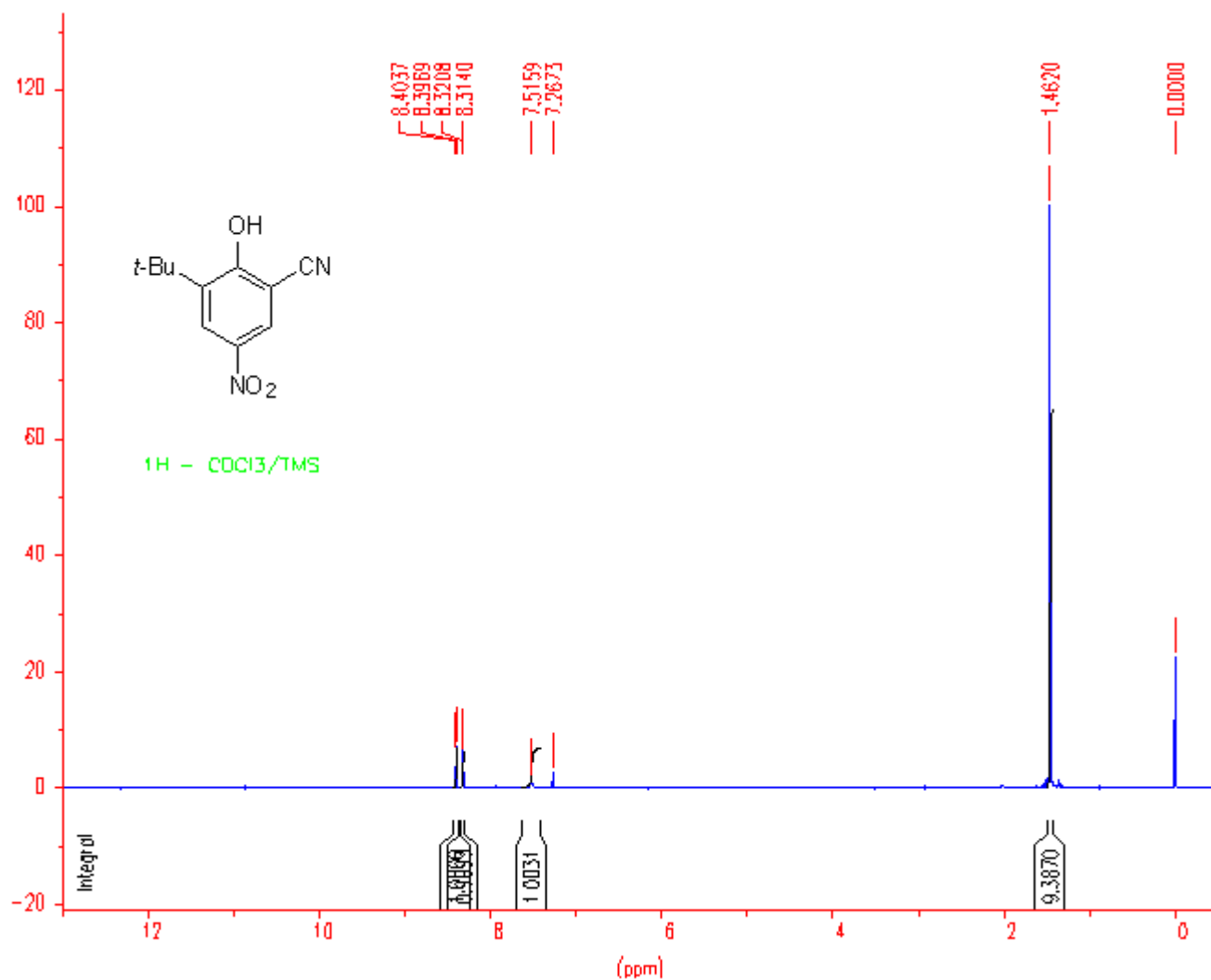
¹³C NMR (100 MHz, CDCl₃): δ 154.97 (1C, C_{ipso} α to OH), 143.51 (1C, C_{ipso} α to C(CH₃)₃), 137.17 (1C, C_{ipso} α to C(CH₃)₃), 129.79 (1C, CH aromatic), 126.07 (1C, CH aromatic), 117.41 (1C, CN), 99.48 (1C, C_{ipso} α to CN), 35.16 (1C, C(CH₃)₃), 34.42 (1C, C(CH₃)₃), 31.23 (3C, C(CH₃)₃), 29.34 (3C, C(CH₃)₃).

MS (EI, 70 eV) m/z (rel intens) 231 (18) [M]⁺, 216 (100) [M - CH₃]⁺, 188 (10) [M - CH₃ - CO]⁺, 57 (20) [C₄H₉]⁺.

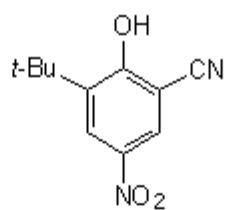
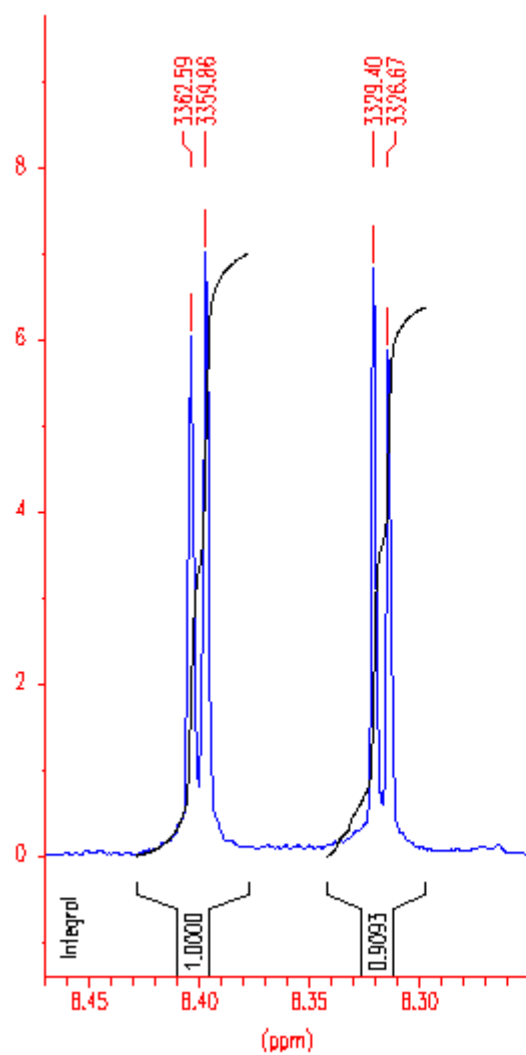
Anal. Calcd for C₁₅H₂₁NO: C, 77.88; H, 9.12; N, 6.06. Found: C, 80.84; H, 9.45; N, 6.18.

3-*tert*-Butyl-2-hydroxy-5-nitrobenzonitrile **6**

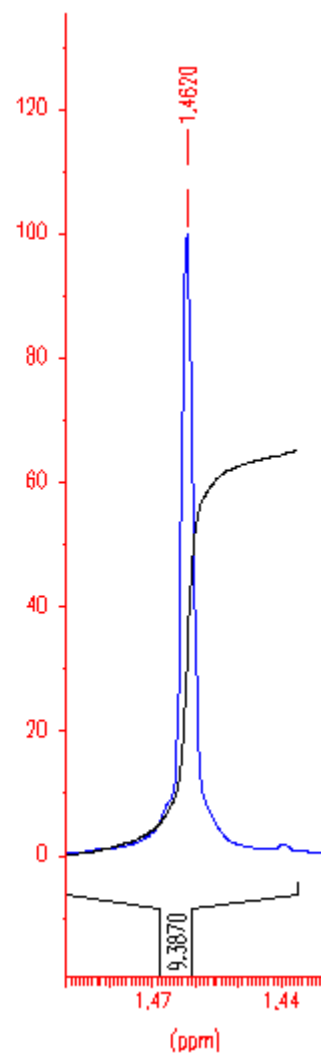
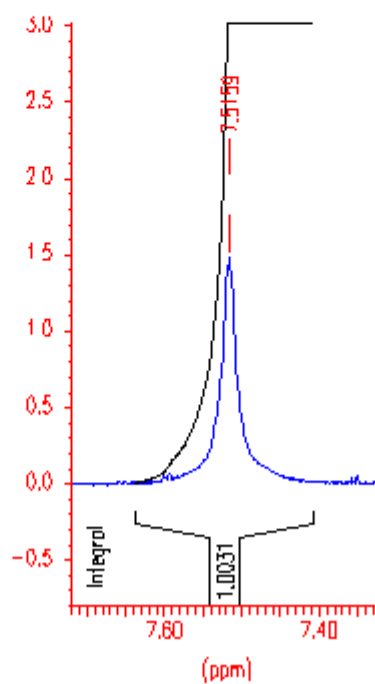
IR (Nujol, NaCl): $\tilde{\nu}$ 3300 (broad, OH), 3094, 2243 (C $\equiv$ N), 1611 (C=C), 1583 (C=C), 1527, 1347, 1245, 1159, 1106, 900 cm⁻¹.

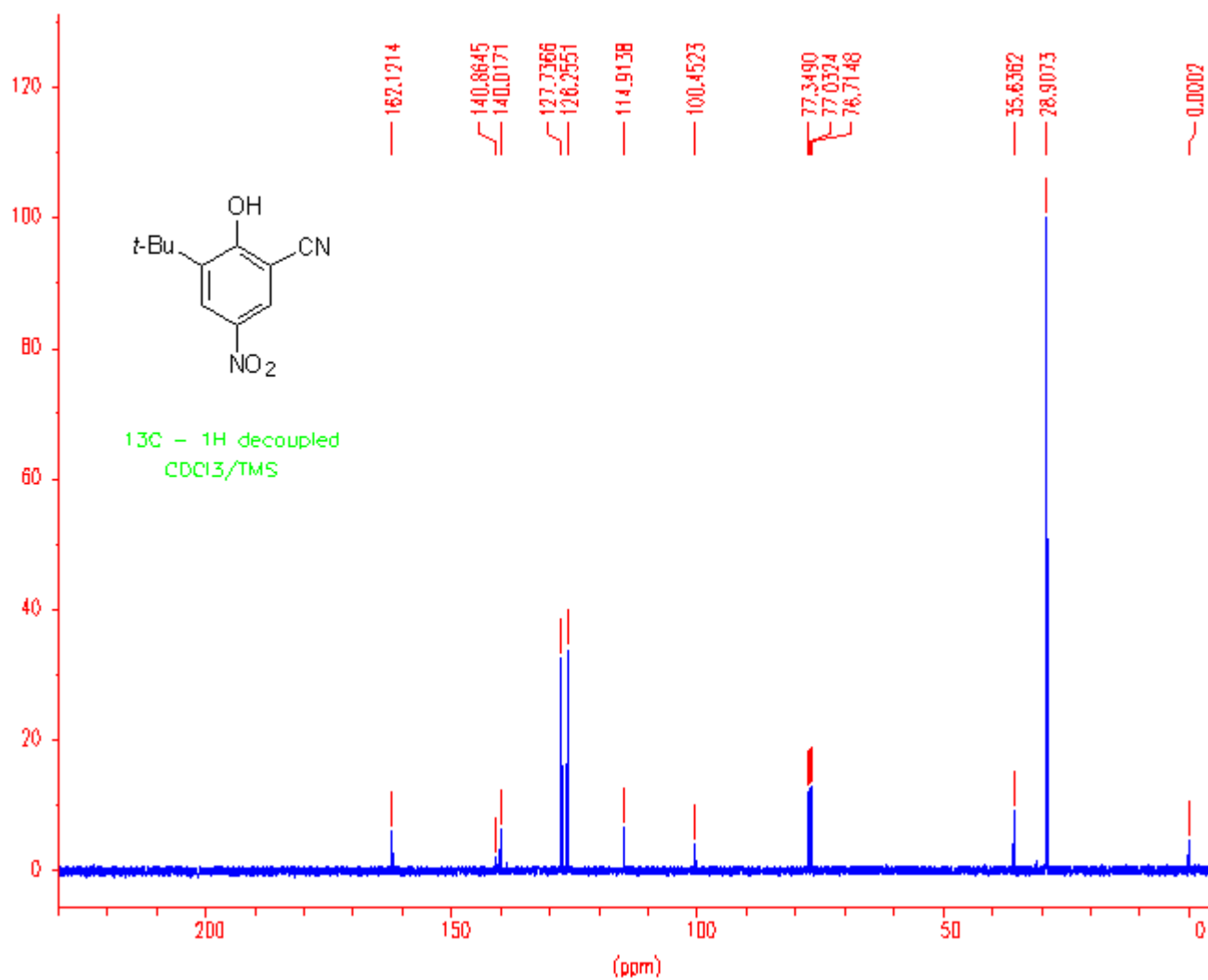


¹H NMR (400 MHz, CDCl₃): δ 8.40 (d, 1H, J = 2.7 Hz, CH aromatic), 8.32 (d, 1H, J = 2.7 Hz, CH aromatic), 7.52 (broad s, 1H, OH), 1.46 (s, 9H, C(CH₃)₃).

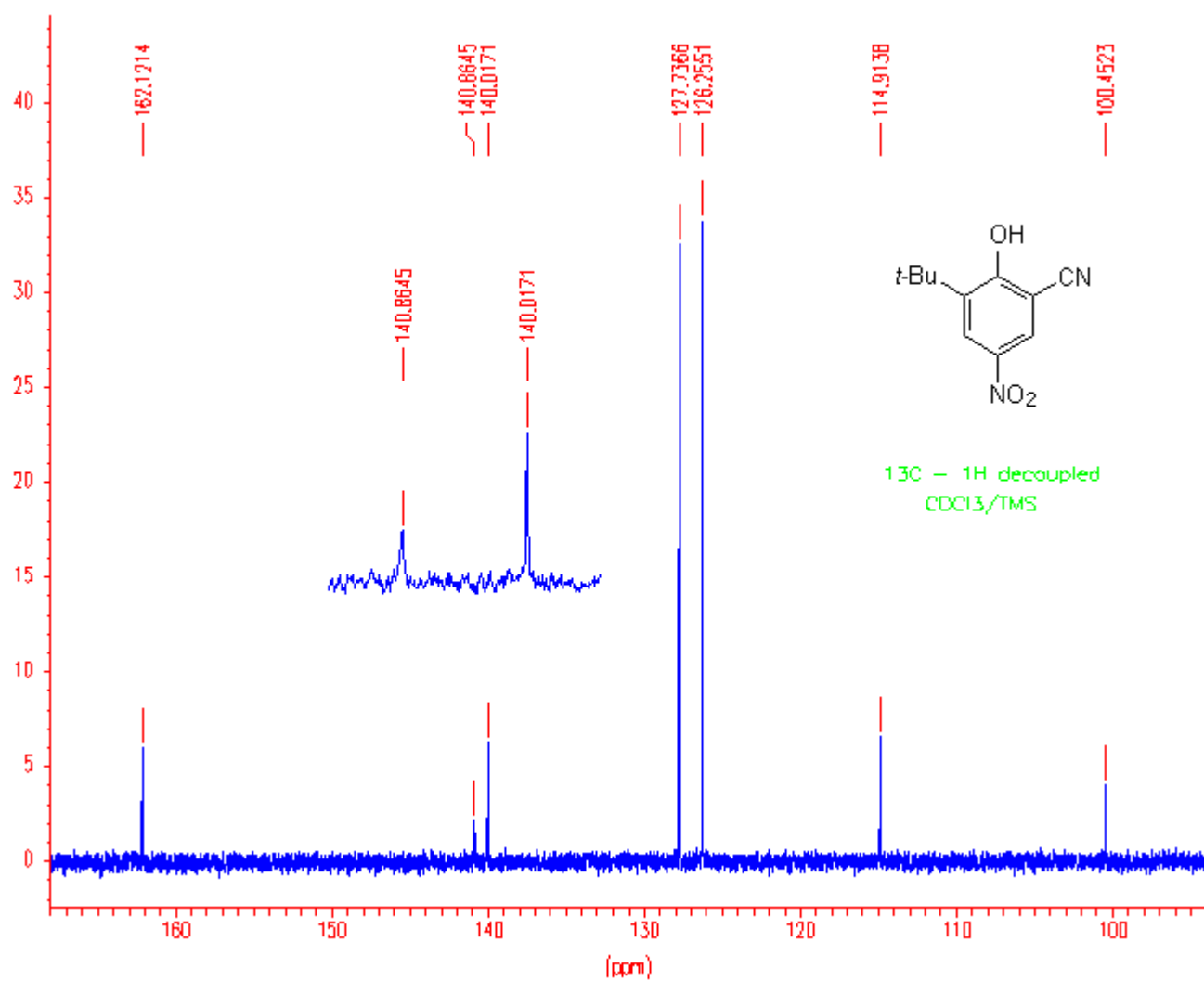


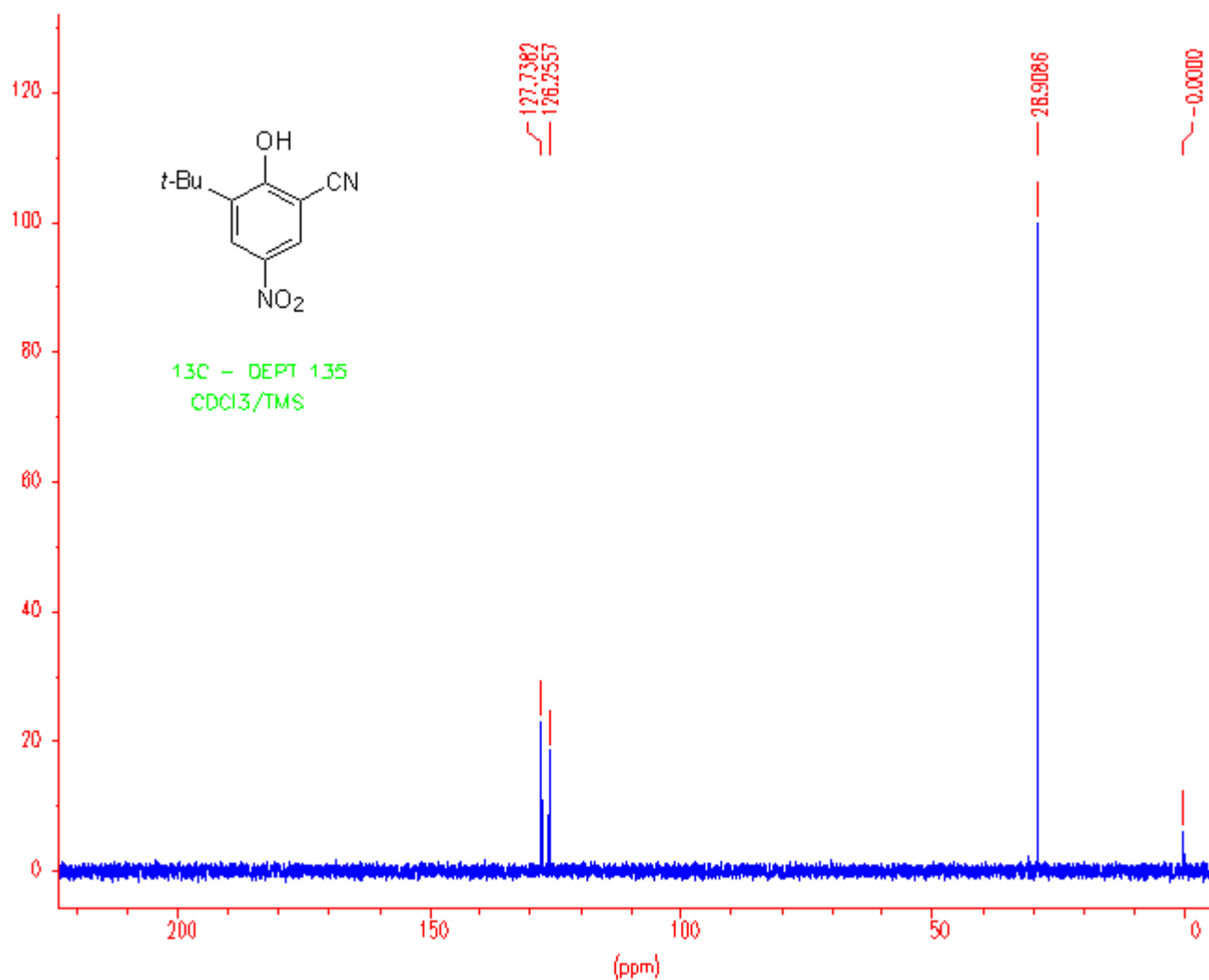
^1H - CDCl_3/TMS





¹³C NMR (100 MHz, CDCl₃): *d* 162.12 (1C, C_{ipso} α to OH), 140.86 and 140.02 (2C, C_{ipso} α to C(CH₃)₃ and C_{ipso} α to NO₂), 127.74 (1C, CH aromatic), 126.25 (1C, CH aromatic), 114.91 (1C, CN), 100.45 (1C, C_{ipso} α to CN), 35.64 (1C, C(CH₃)₃), 28.91 (3C, C(CH₃)₃).





MS (EI, 70 eV) m/z (rel intens) 220 (26) $[M]^+$, 205 (100) $[M - CH_3]^+$, 177 (54) $[M - CH_3 - CO]^+$, 159 (12) $[M - CH_3 - NO_2]^+$, 131 (15) $[M - CH_3 - CO - NO_2]^+$.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.22; H, 5.69; N, 12.47.

***N*-(Benzyloxycarbonyl)-D-serine (R)-9**

IR (Nujol, NaCl): $\tilde{\nu}$ 3443 (broad, OH), 3338 (NH), 3318 (NH), 3205 (broad, NH), 3062, 3029, 1748 (CO of acid), 1691 (CO of carbamate), 1537, 1478, 1455, 1401, 1350, 1306, 1249, 1061, 1030, 966, 912, 840, 786, 750, 731, 697 cm^{-1} .

^1H NMR (400 MHz, CD_3COCD_3): δ 7.42-7.26 (m, 5H, Ph), 6.42 (d, 1H, $J = 8.1$ Hz, NH), 5.90-4.20 (broad s, 2H, CO_2H and OH), 5.10 (s, 2H, OCH_2Ph), 4.34 (ddd, 1H, $J = 8.1, 4.6, 3.9$ Hz, CH_2CH), 3.97 (dd, 1H, $J = 11.1, 4.6$ Hz, CH_2CH), 3.89 (dd, 1H, $J = 11.1, 3.9$ Hz, CH_2CH).

^{13}C NMR (100 MHz, CD_3COCD_3): δ 172.31 (1C, CO_2H), 157.04 (1C, NHCO), 138.03 (1C, C_{ipso} aromatic), 129.18 (2C, CH aromatic), 128.63 and 128.62 (3C, CH aromatic), 66.83 (1C, CH_2Ph), 62.95 (1C, CH_2CH), 57.16 (1C, CH_2CH).

MS (EI, 70 eV) m/z (rel intens) 239 (3) $[\text{M}]^+$, 148 (5) $[\text{M} - \text{C}_7\text{H}_7]^+$, 108 (74) $[\text{PhCH}_2\text{OH}]^+$, 91 (100) $[\text{C}_7\text{H}_7]^+$, 86 (34), 79 (54), 77 (30) $[\text{C}_6\text{H}_5]^+$, 65 (24) $[\text{C}_5\text{H}_5]^+$, 42 (25).

***N*-(Benzyloxycarbonyl)-D-serine methyl ester (R)-10**

IR (Nujol, NaCl): $\tilde{\nu}$ 3390 (broad, OH, NH), 1715 (CO of carbamate) with a shoulder at 1750 (CO of ester), 1526, 1345, 1215, 1063, 1029, 740, 699 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.40-7.26 (m, 5H, Ph), 5.93 (d, 1H, $J = 7.9$ Hz, NH), 5.10 (s, 2H, OCH_2Ph), 4.42 (ddd, 1H, $J = 7.9, 3.6, 3.4$ Hz, CH_2CH), 3.96 (dd, 1H, $J = 11.3, 3.6$ Hz, CH_2CH), 3.86 (dd, 1H, $J = 11.3, 3.4$ Hz, CH_2CH), 3.74 (s, 3H, CO_2CH_3), 2.98 (broad s, 1H, OH).

^{13}C NMR (100 MHz, CDCl_3): δ 171.18 (1C, CO_2CH_3), 156.33 (1C, NHCO), 136.06 (1C, C_{ipso} aromatic), 128.53 (2C, CH_{meta} aromatic), 128.23 (1C, CH_{para} aromatic), 128.11 (2C, CH_{ortho} aromatic), 67.17 (1C, CH_2Ph), 63.05 (1C, CH_2CH), 56.06 (1C, CH_2CH), 52.71 (1C, CO_2CH_3).

MS (EI, 70 eV) m/z (rel intens) 253 (3) $[\text{M}]^+$, 223 (2) $[\text{M} - \text{CH}_2\text{OH}]^+$, 194 (3) $[\text{M} - \text{CO}_2\text{CH}_3]^+$, 162 (10) $[\text{M} - \text{C}_7\text{H}_7]^+$, 150 (8) $[\text{M} - \text{HOCH}_2\text{CO}_2\text{CH}_3]^+$, 132 (4), 108 (59) $[\text{PhCH}_2\text{OH}]^+$, 91 (100) $[\text{C}_7\text{H}_7]^+$, 65 (26) $[\text{C}_5\text{H}_5]^+$.

$[\alpha]_{\text{D}}^{23} = -5.4$, $[\alpha]_{578}^{23} = -5.7$, $[\alpha]_{546}^{23} = -6.6$, $[\alpha]_{436}^{23} = -12.1$, $[\alpha]_{365}^{23} = -20.9$ ($c = 6.0$, CHCl_3), starting from L-serine: $[\alpha]_{\text{D}}^{24} = +6.3$, $[\alpha]_{578}^{24} = +6.4$, $[\alpha]_{546}^{24} = +7.4$, $[\alpha]_{436}^{24} = +12.9$, $[\alpha]_{365}^{24} = +22.0$ ($c = 6.0$, CHCl_3).

(R)-N-(Benzyloxycarbonyl)-2-amino-3-methyl-1,3-butanediol (R)-11

IR (neat, NaCl): $\tilde{\nu}$ 3404 (broad, OH), 3330 (broad, NH), 3090, 3066, 3035, 2977, 2892, 1700 (C=O), 1534, 1456, 1379, 1337, 1258, 1157, 1057, 738, 699 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.39-7.28 (m, 5H, Ph), 5.80 (d, 1H, $J = 9.1$ Hz, NH), 5.10 (d, 2H, $J = 12.5$ Hz, CH_2Ph), 5.09 (d, 2H, $J = 12.5$ Hz, CH_2Ph), 3.96 (dd, 1H, $J = 11.4, 2.8$ Hz, CH_2CH), 3.78 (dd, 1H, $J = 11.4, 2.3$ Hz, CH_2CH), 3.51 (ddd, 1H, $J = 9.1, 2.8, 2.3$ Hz, CH_2CH), 3.40-3.34 (broad s, 1H, OH), 3.27 (s, 1H, OH), 1.32 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.21 (s, 3H, $\text{C}(\text{CH}_3)_2$).

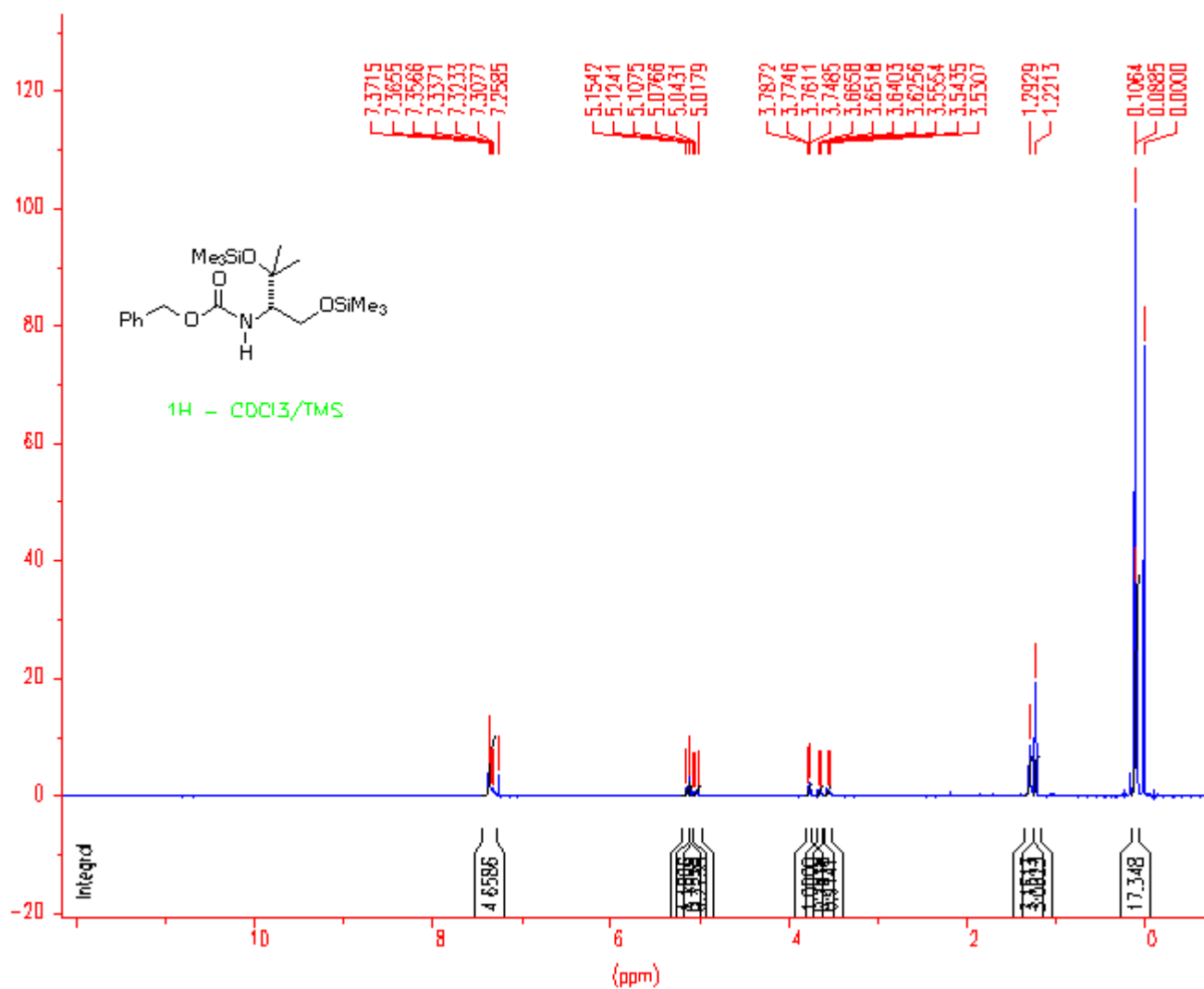
^{13}C NMR (100 MHz, CDCl_3): δ 156.92 (1C, NHCO), 136.36 (1C, C_{ipso} aromatic), 128.54 (2C, CH_{meta} aromatic), 128.17 and 128.03 (3C, 2 CH_{ortho} and 1 CH_{para} aromatic), 73.54 (1C, $\text{C}(\text{CH}_3)_2$), 66.91 (1C, CH_2Ph), 63.13 (1C, CH_2CH), 58.30 (1C, CH_2CH), 27.44 (1C, $\text{C}(\text{CH}_3)_2$), 27.26 (1C, $\text{C}(\text{CH}_3)_2$).

MS (EI, 70 eV) m/z (rel intens) 253 (1) $[\text{M}]^+$, 235 (1) $[\text{M} - \text{H}_2\text{O}]^+$, 222 (4) $[\text{M} - \text{CH}_2\text{OH}]^+$, 194 (2) $[\text{M} - \text{C}(\text{CH}_3)_2\text{OH}]^+$, 177 (22) $[\text{M} - \text{C}_6\text{H}_5]^+$, 132 (13), 91 (100) $[\text{C}_7\text{H}_7]^+$, 65 (34) $[\text{C}_5\text{H}_5]^+$, 60 (41).

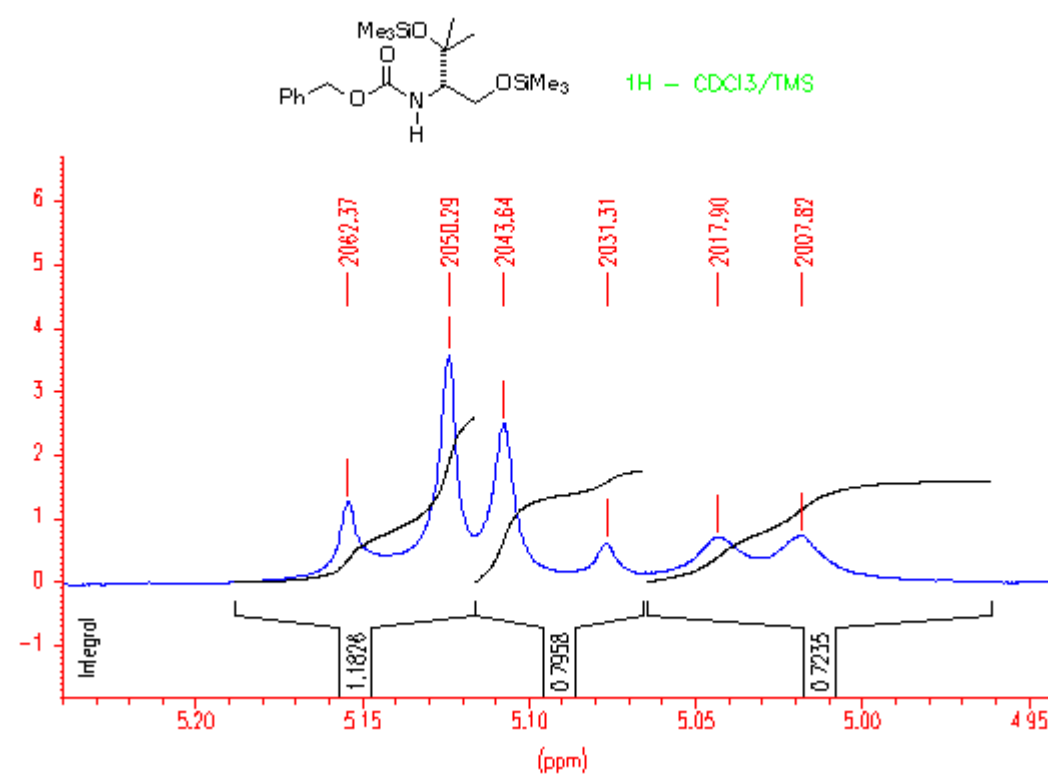
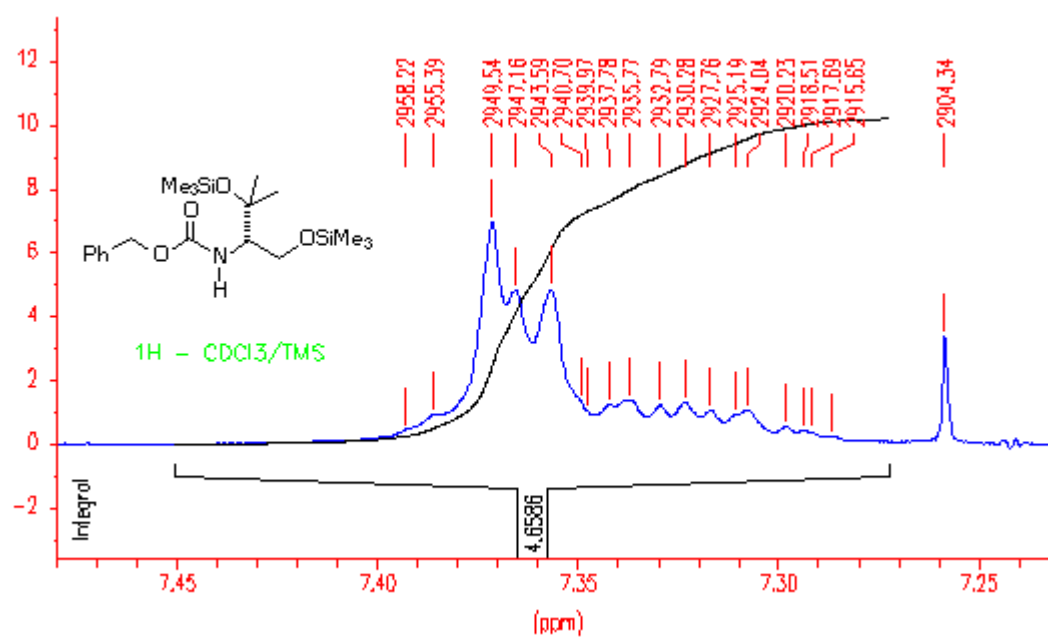
$[\alpha]_{\text{D}}^{23} = -28.8$, $[\alpha]_{578}^{23} = -30.0$, $[\alpha]_{546}^{23} = -34.1$, $[\alpha]_{436}^{23} = -58.5$, $[\alpha]_{365}^{23} = -92.6$ ($c = 6.0$, CHCl_3), starting from L-serine: $[\alpha]_{\text{D}}^{24} = +29.1$, $[\alpha]_{578}^{24} = +30.4$, $[\alpha]_{546}^{24} = +34.4$, $[\alpha]_{436}^{24} = +59.0$, $[\alpha]_{365}^{24} = +93.4$ ($c = 6.0$, CHCl_3).

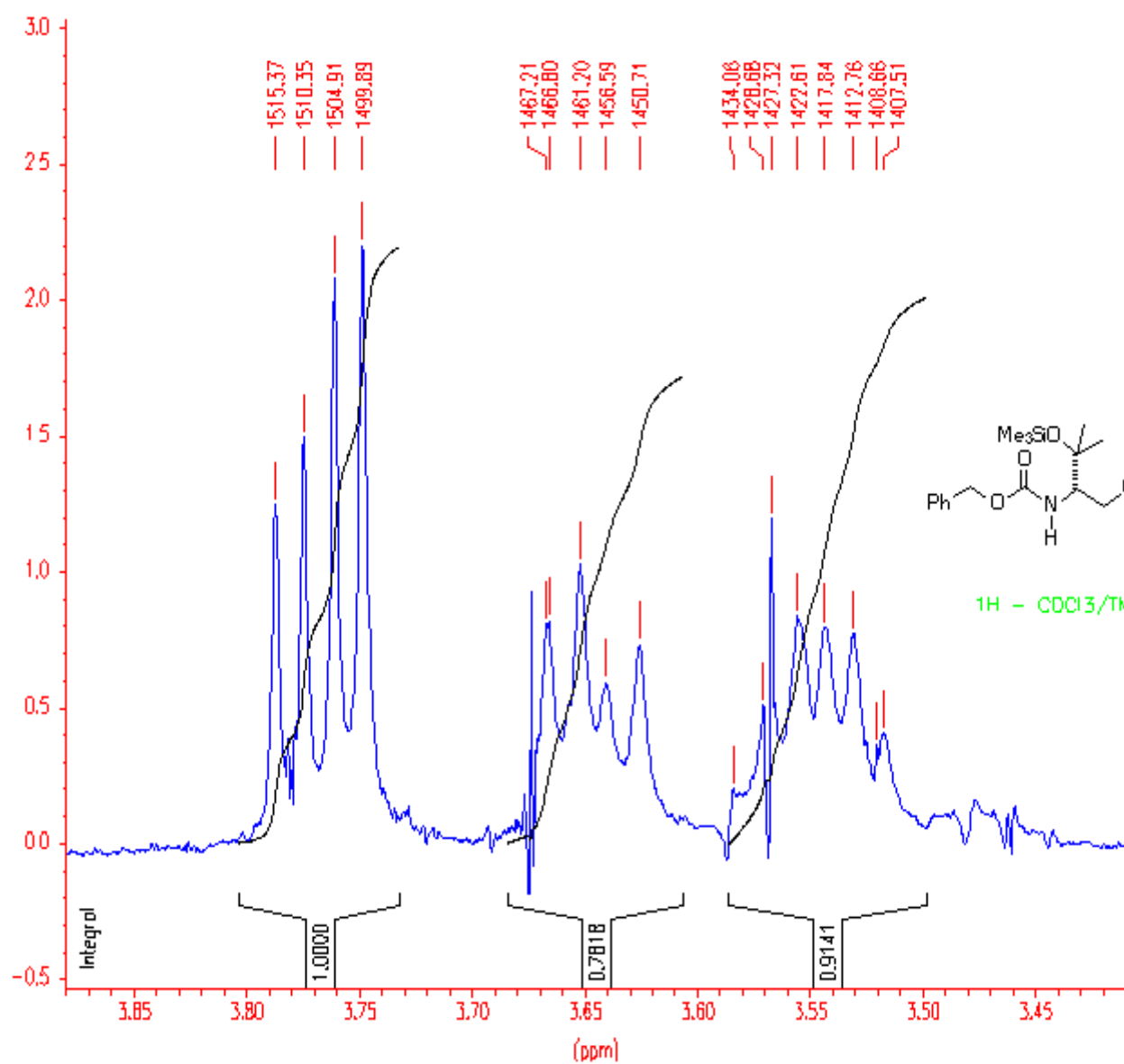
(R)-N-(Benzyloxycarbonyl)-2-amino-3-methyl-1,3-bis(trimethylsilyloxy)butane (R)-12

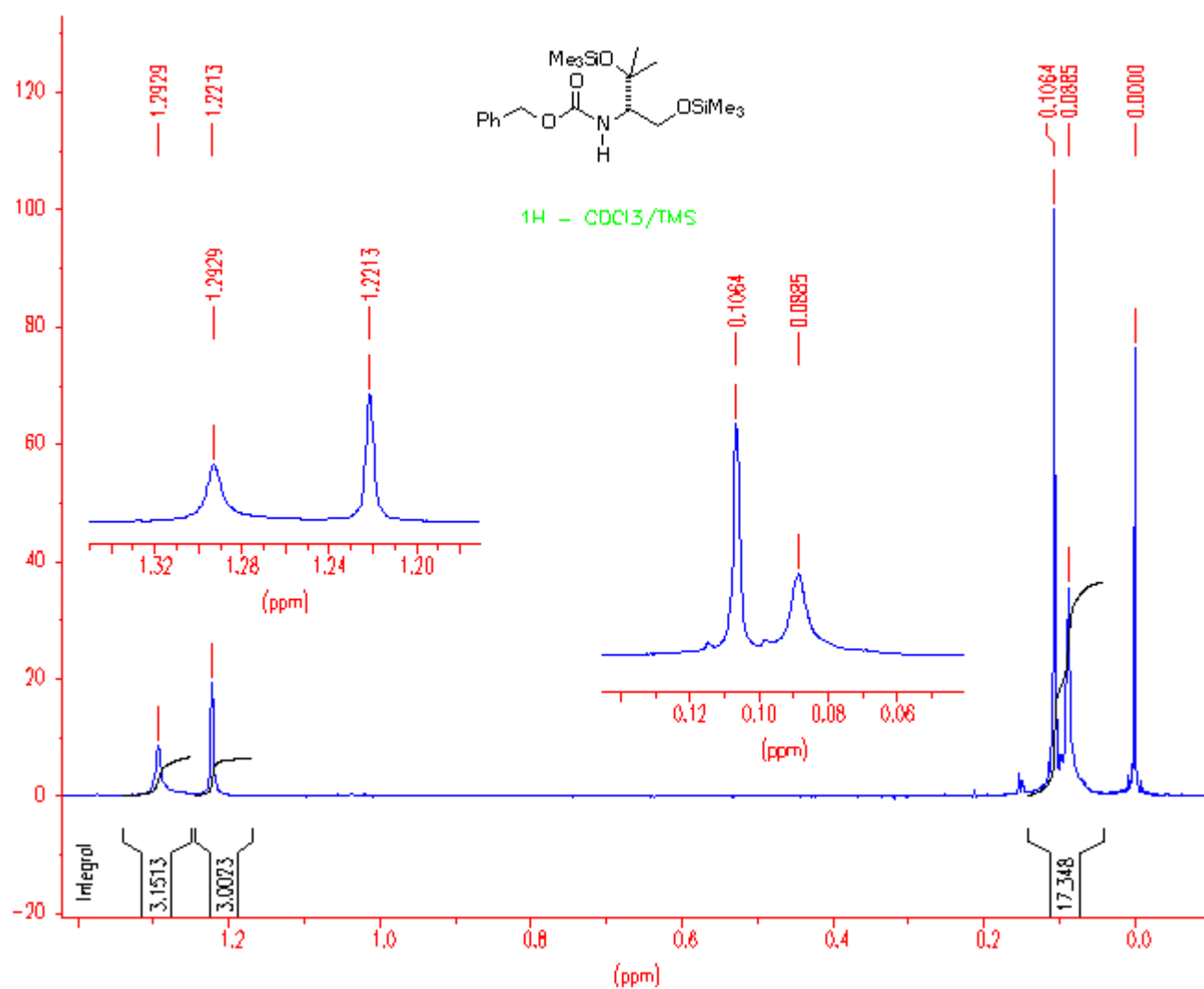
IR (neat, NaCl): $\tilde{\nu}$ 3446, 3342 (broad, NH), 3091, 3067, 3035, 2958, 2899, 2251 (small, aromatic harmonic), 1726 (C=O), 1504, 1339, 1252, 1171, 1037, 842, 752, 735, 697 cm^{-1} .

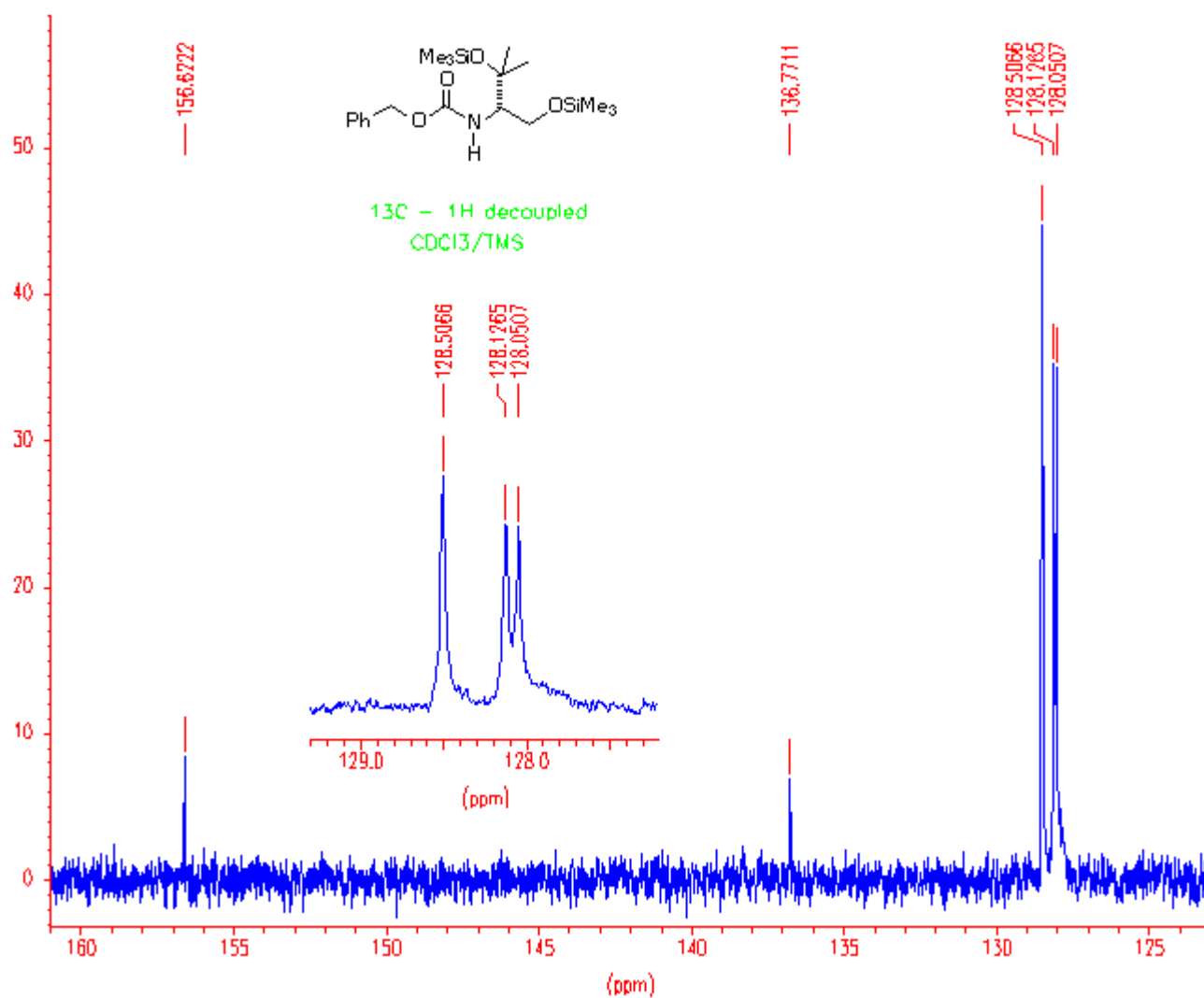


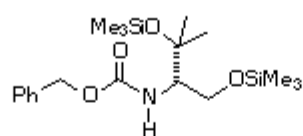
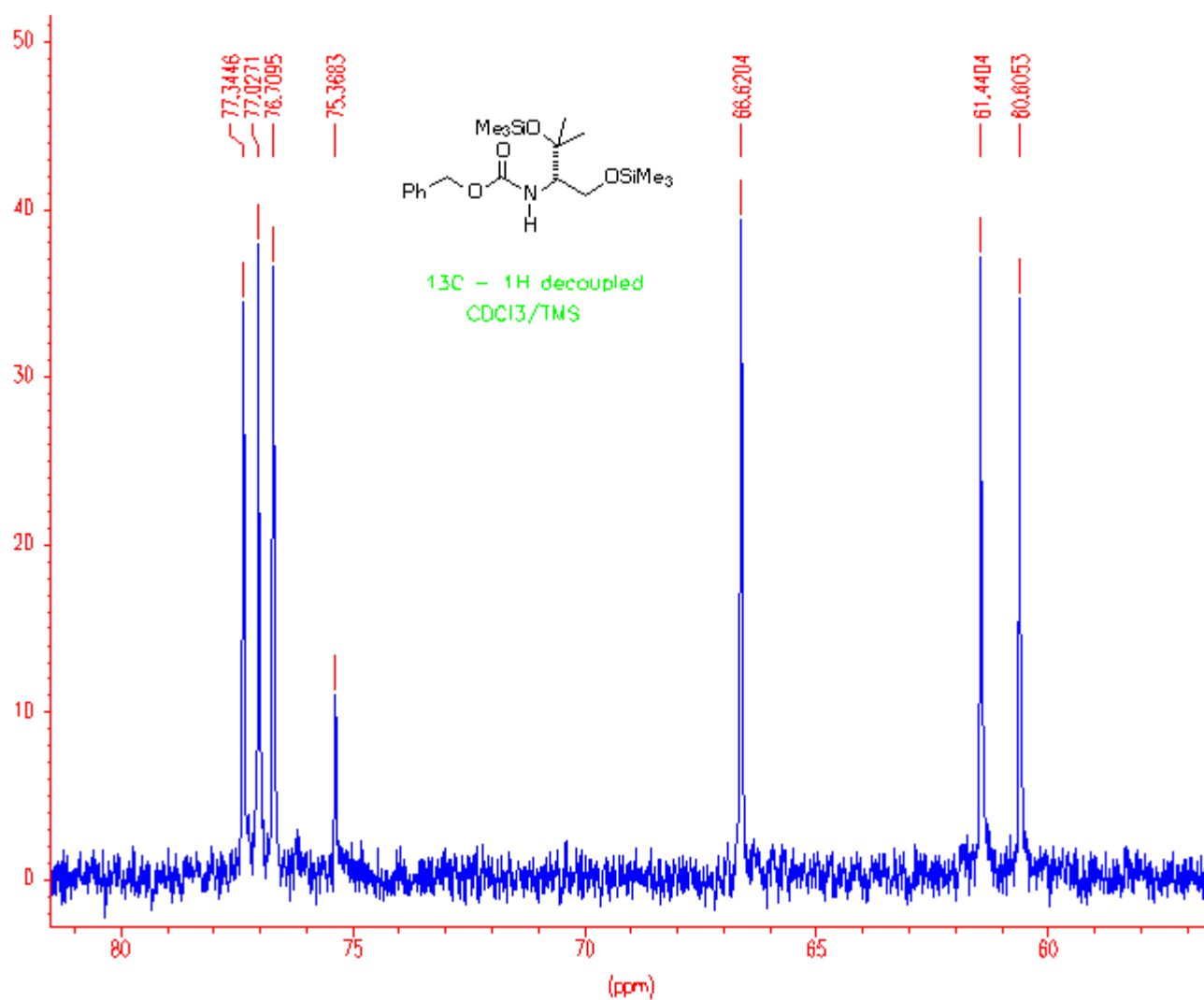
^1H NMR (400 MHz, CDCl_3): δ 7.40 - 7.28 (m, 5H, Ph), 5.13 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 5.10 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 5.03 (d, 1H, $J = 10.1$ Hz, NH), 3.77 (dd, 1H, $J = 10.5, 5.0$ Hz, CH_2CH), 3.65 (dd, 1H, $J = 10.5, 5.8$ Hz, CH_2CH), 3.54 (ddd, 1H, $J = 10.1, 5.8, 5.0$ Hz, CH_2CH), 1.29 (broad s, 3H, $\text{C}(\text{CH}_3)_2$), 1.22 (s, 3H, $\text{C}(\text{CH}_3)_2$), 0.11 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.09 (broad s, 9H, $\text{Si}(\text{CH}_3)_3$).

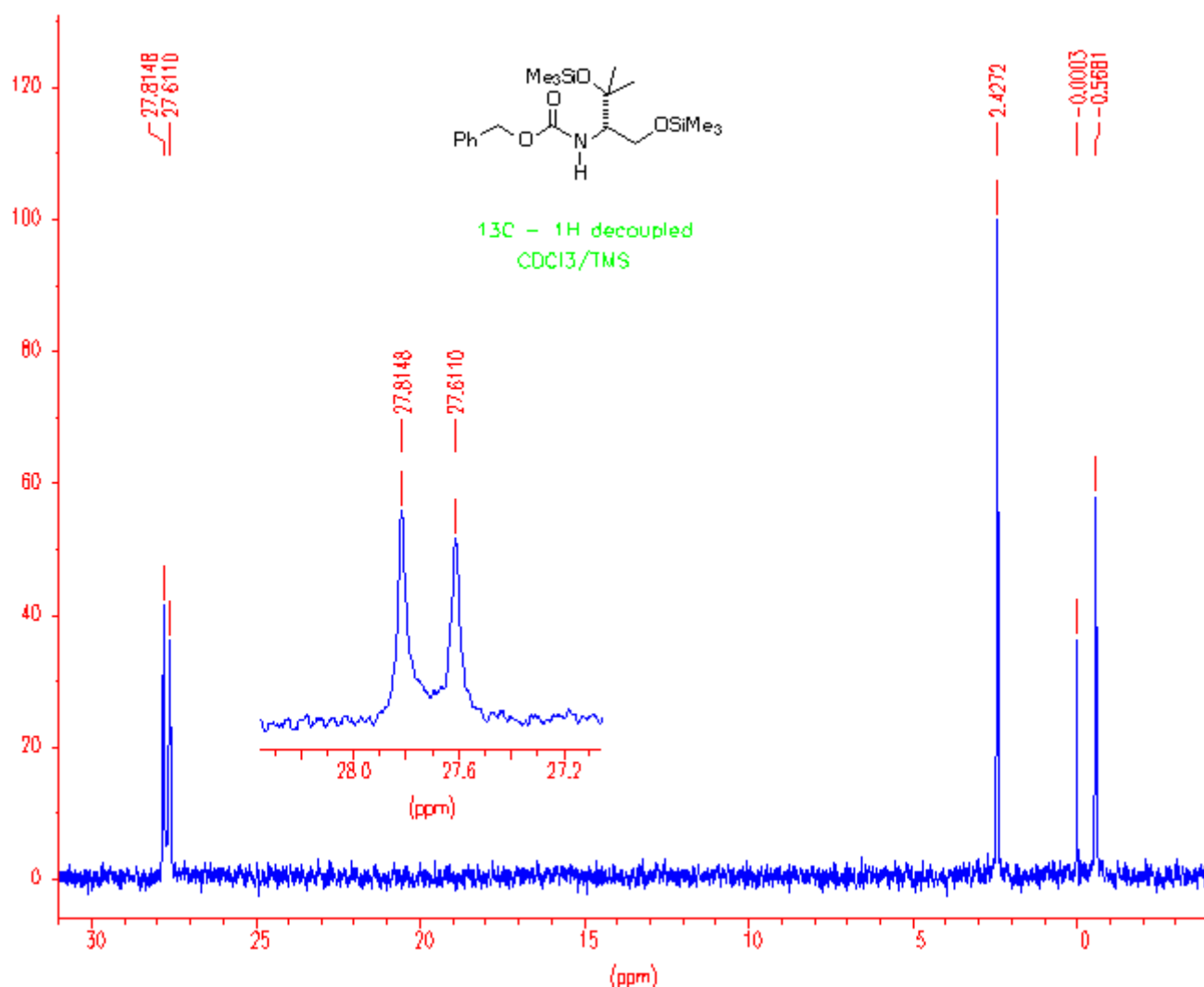












HRMS (EI, 70 eV) m/z (%): calcd for $C_{18}H_{32}NO_4Si_2$ 382.1870 $[M - Me]^+$, found 382.1869 (1.7), 294 (2.0) $[M - CH_2OSiMe_3]^+$, 248 (34) $[M - Me - CO_2CHPh]^+$, 204 (4.6) $[M - CH_2OSiMe_3 - Me_3SiOH]^+$, 131 (100) $[CMe_2OSiMe_3]^+$, 91 (57) $[C_7H_7]^+$, 75 (6.7) $[Me_2Si=OH]^+$, 73 (62) $[Me_3Si]^+$.

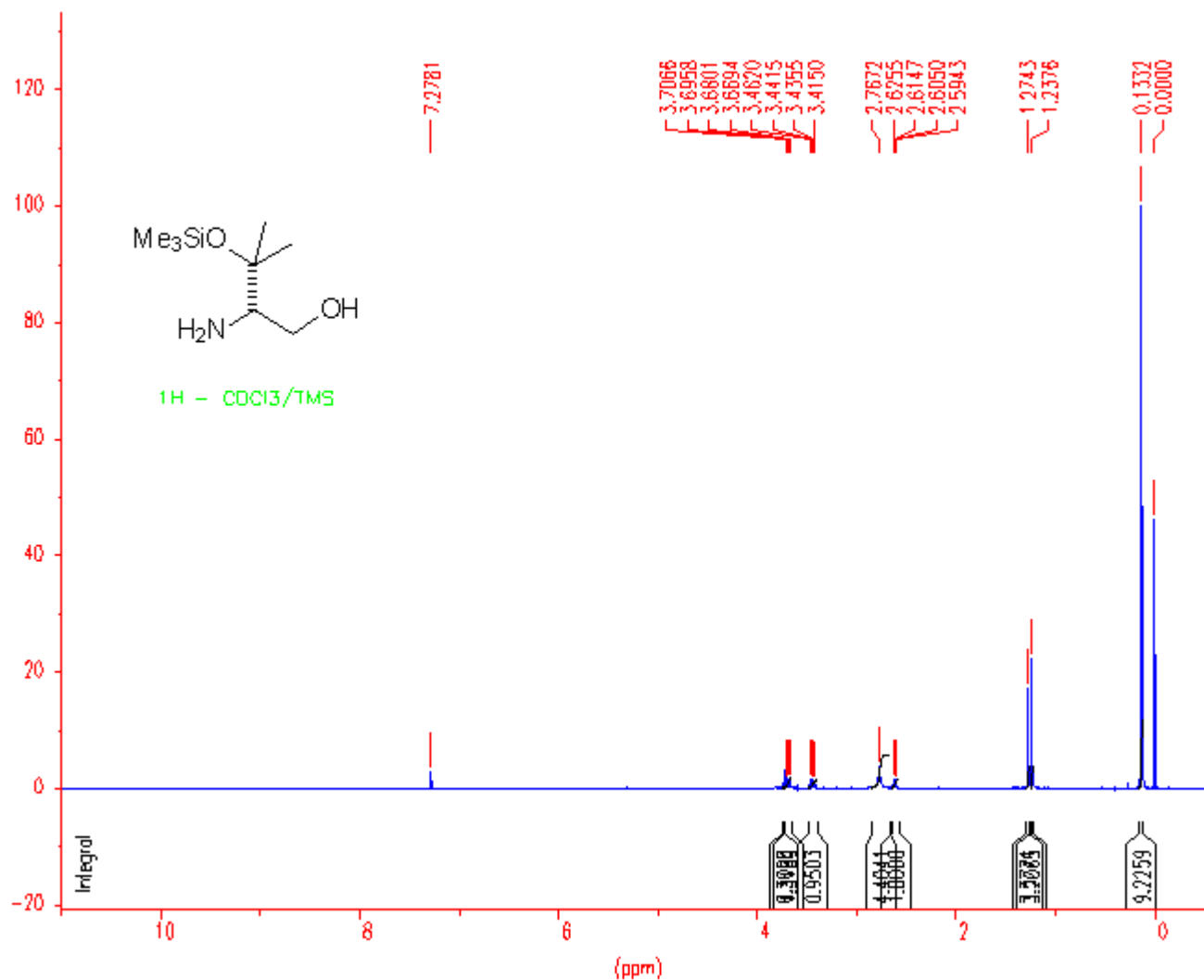
MS (FAB, *m*-nitrobenzylic alcohol matrix) m/z (%) Calcd for $C_{19}H_{35}NO_4Si_2$ 397.2 $[M]^+$, found 470 (97) $[M + SiMe_3]^+$, 398 (54) $[M + H]^+$, 382 (59) $[M - CH_3]^+$, 308 (100) $[M - OSiMe_3]^+$.

$[\alpha]_D^{27} = -3.0$, $[\alpha]_{578}^{27} = -3.1$, $[\alpha]_{546}^{27} = -3.4$, $[\alpha]_{436}^{27} = -6.8$, $[\alpha]_{365}^{27} = -11.9$ ($c = 4.4$, $CHCl_3$), starting from L-serine: $[\alpha]_D^{23} = +3.2$, $[\alpha]_{578}^{23} = +3.3$, $[\alpha]_{546}^{23} = +3.9$, $[\alpha]_{436}^{23} = +7.3$, $[\alpha]_{365}^{23} = +13.2$ ($c = 4.3$, $CHCl_3$).

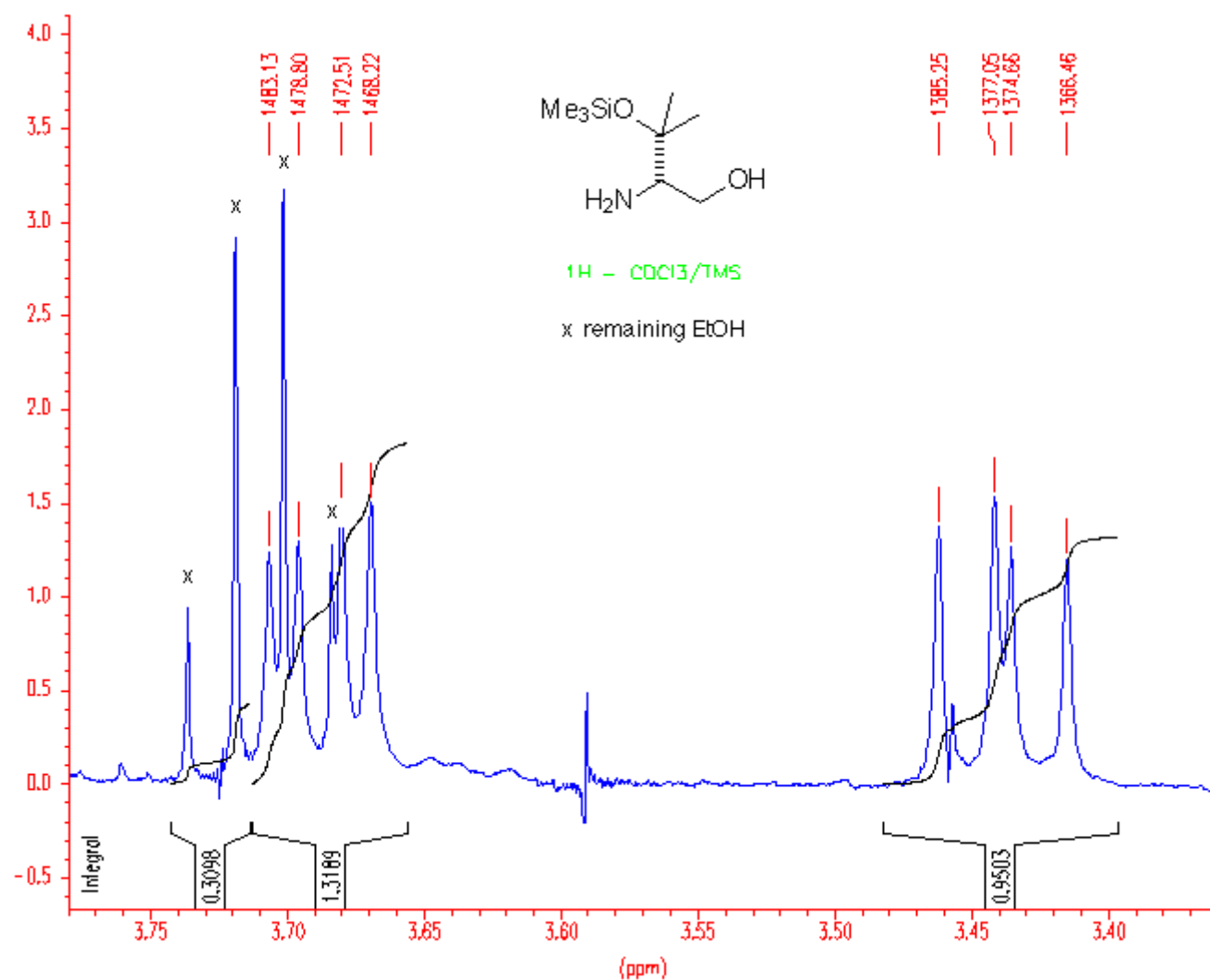
Anal. Calcd for $C_{19}H_{35}NO_4Si_2$: C, 57.39; H, 8.87; N, 3.52. Found: C, 56.96; H, 8.32; N, 3.62.

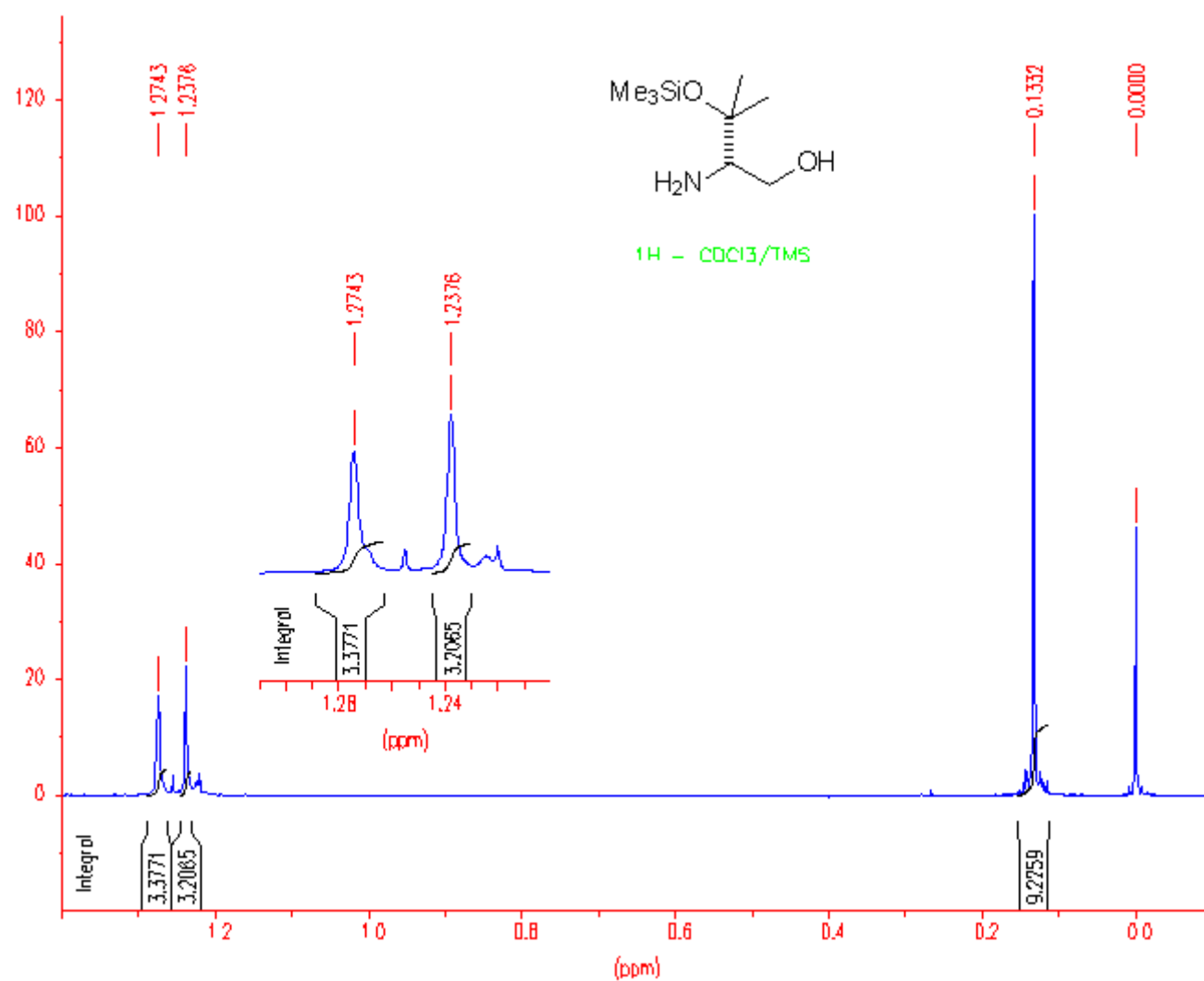
(R)-2-Amino-3-methyl-3-(trimethylsilyloxy)butan-1-ol (R)-13a

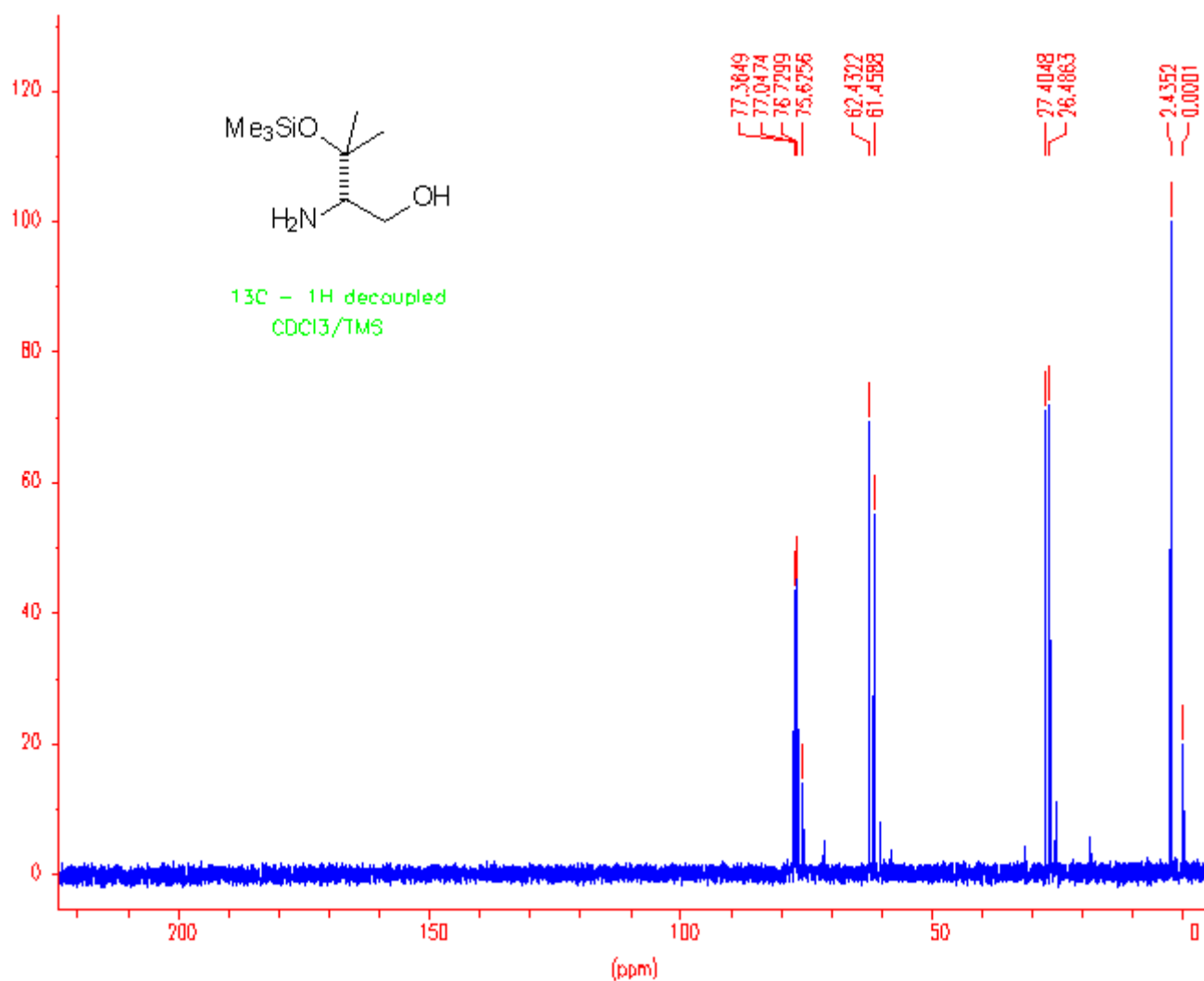
IR (neat, NaCl): $\tilde{\nu}$ 3360 (broad, OH), 3296 (broad, NH), 2960, 2899, 1585, 1465, 1385, 1367, 1251, 1158, 1033, 889, 840, 754 cm^{-1} .



^1H NMR (400 MHz, CDCl_3): δ 3.69 (dd, 1H, $J = 10.6, 4.3$ Hz, CH_2CH), 3.44 (dd, 1H, $J = 10.6, 8.2$ Hz, CH_2CH), 2.77 (broad s, 3H, NH_2 and OH), 2.61 (dd, 1H, $J = 8.2, 4.3$ Hz, CH_2CH), 1.27 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.24 (s, 3H, $\text{C}(\text{CH}_3)_2$), 0.13 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

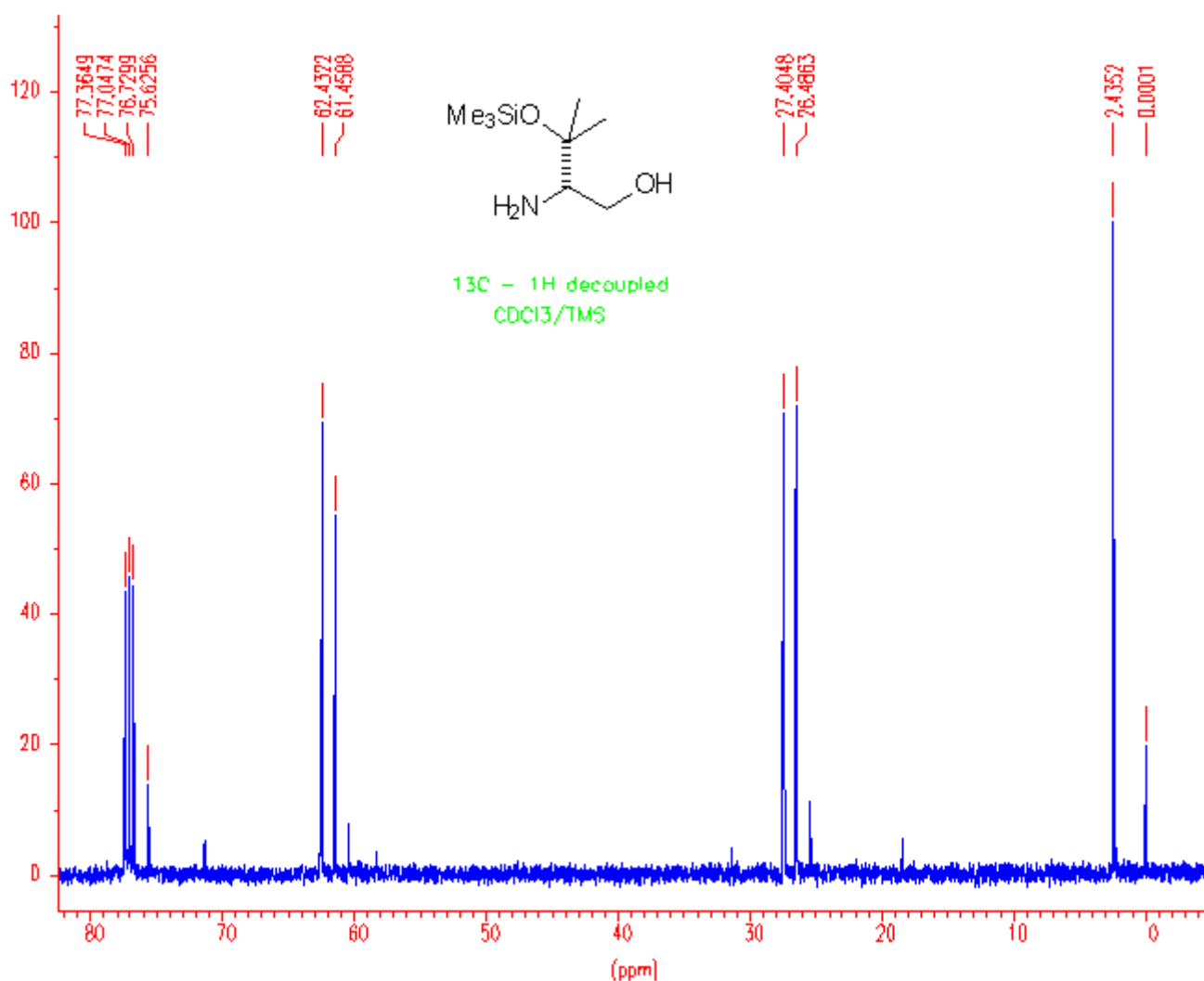






¹³C NMR (100 MHz, CDCl₃): *d* 75.63 (1C, C(CH₃)₂), 62.43 (1C, CH₂CH), 61.46 (1C, CH₂CH), 27.41 (1C, C(CH₃)₂, correlates with protons at 1.27 ppm), 26.49 (1C, C(CH₃)₂, correlates with protons at 1.24 ppm), 2.44 (3C, Si(CH₃)₃).

As a remark, this compound proved to be highly sensitive to the acidity of CDCl₃ which resulted in the apparition of extra peaks due to some degradation during recording the ¹³C NMR spectrum.

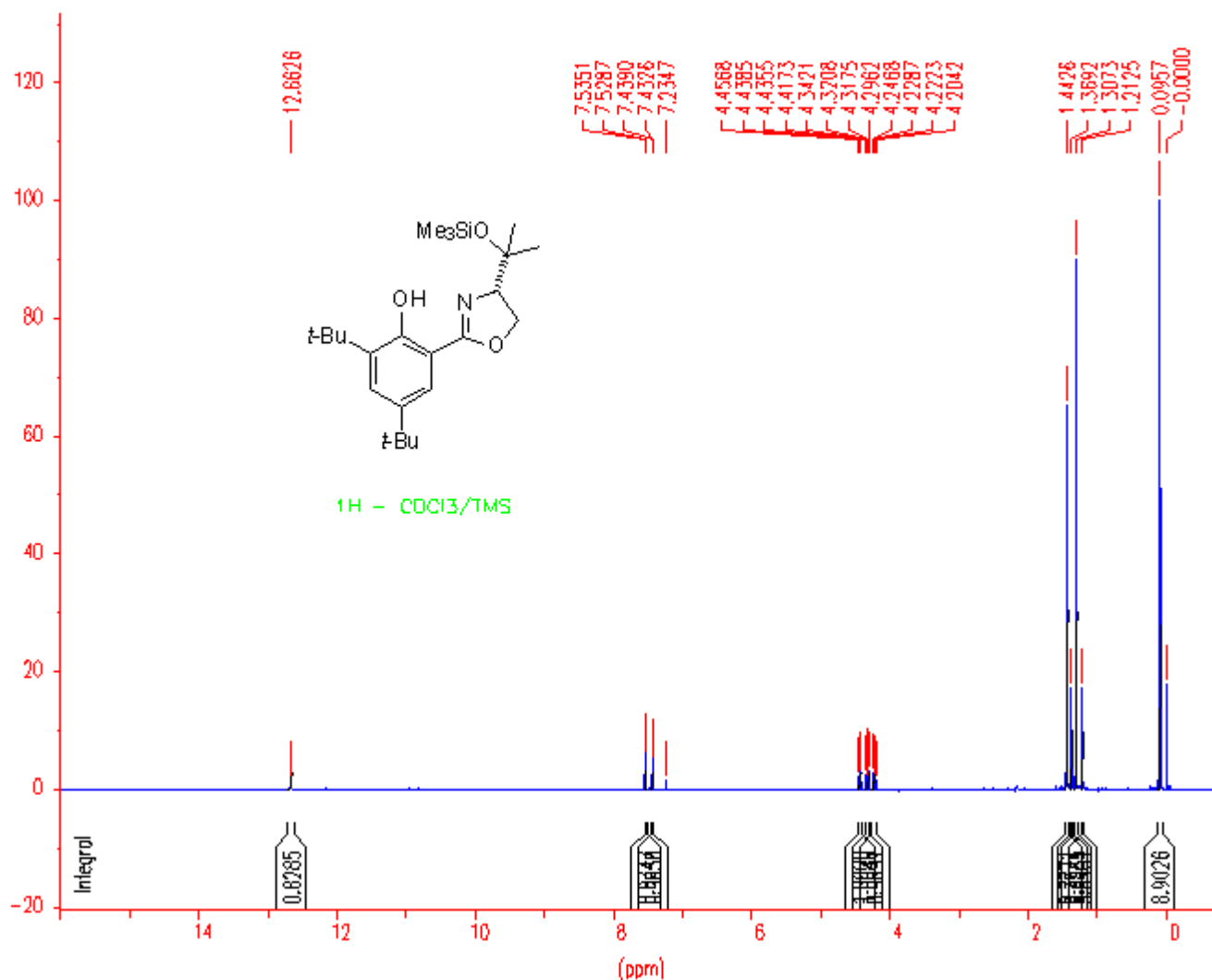


MS (EI, 70 eV) m/z (rel intens) 192 (1) $[M + H]^+$, 176 (4) $[M - CH_3]^+$, 160 (18) $[M - CH_2OH]^+$, 131 (100) $[M - HOCH_2CHNH_2 \text{ e.g. } Me_3SiOC(CH_3)_2]^+$, 116 (14) $[M - C_2H_7OSi]^+$, 105 (16), 85 (56), 73 (90) $[SiMe_3]^+$, 60 (70) $[HOCH_2CHNH_2]^+$.

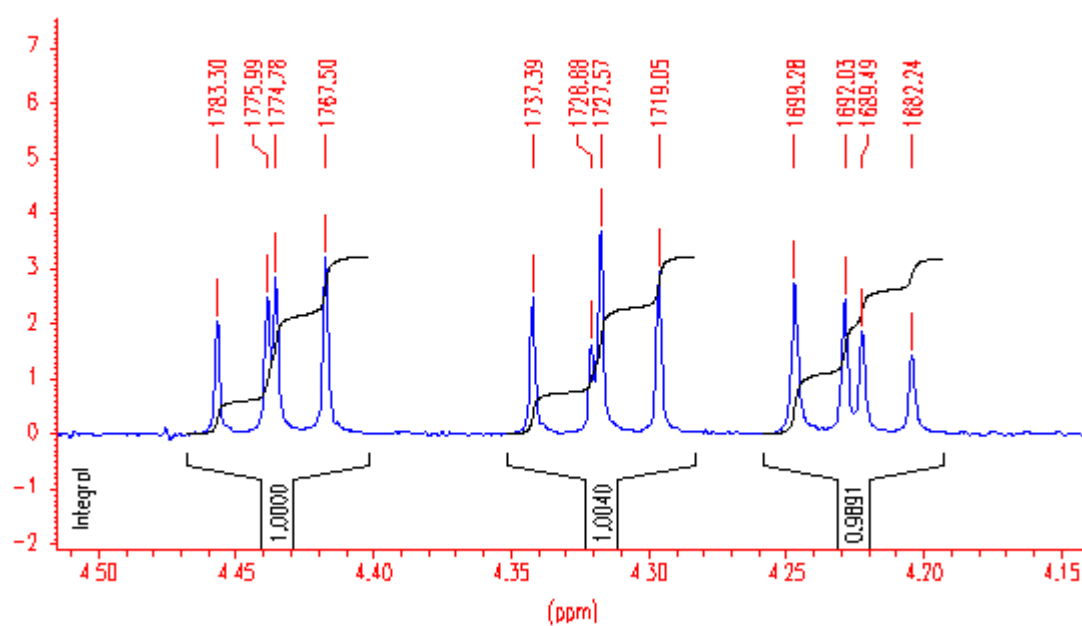
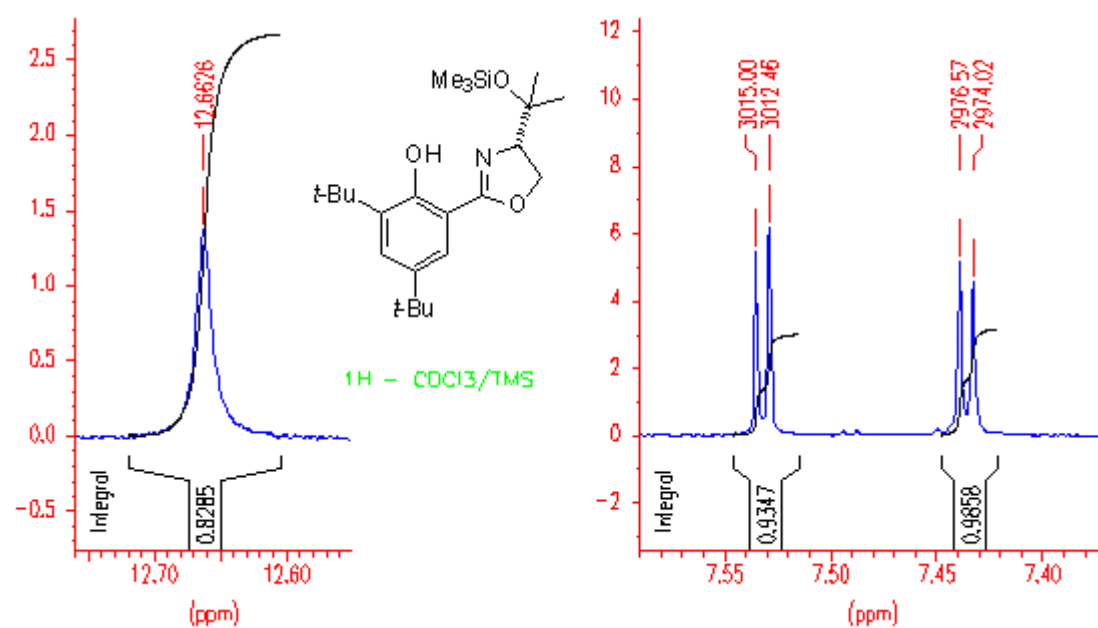
$[\alpha]_D^{23} = +14.8$, $[\alpha]_{578}^{23} = +15.3$, $[\alpha]_{546}^{23} = +17.3$, $[\alpha]_{436}^{23} = +28.3$, $[\alpha]_{365}^{23} = +42.4$ ($c = 3.4$, $CHCl_3$), starting from L-serine: $[\alpha]_D^{24} = -15.3$, $[\alpha]_{578}^{24} = -15.8$, $[\alpha]_{546}^{24} = -17.6$, $[\alpha]_{436}^{24} = -28.3$, $[\alpha]_{365}^{24} = -41.7$ ($c = 2.5$, $CHCl_3$).

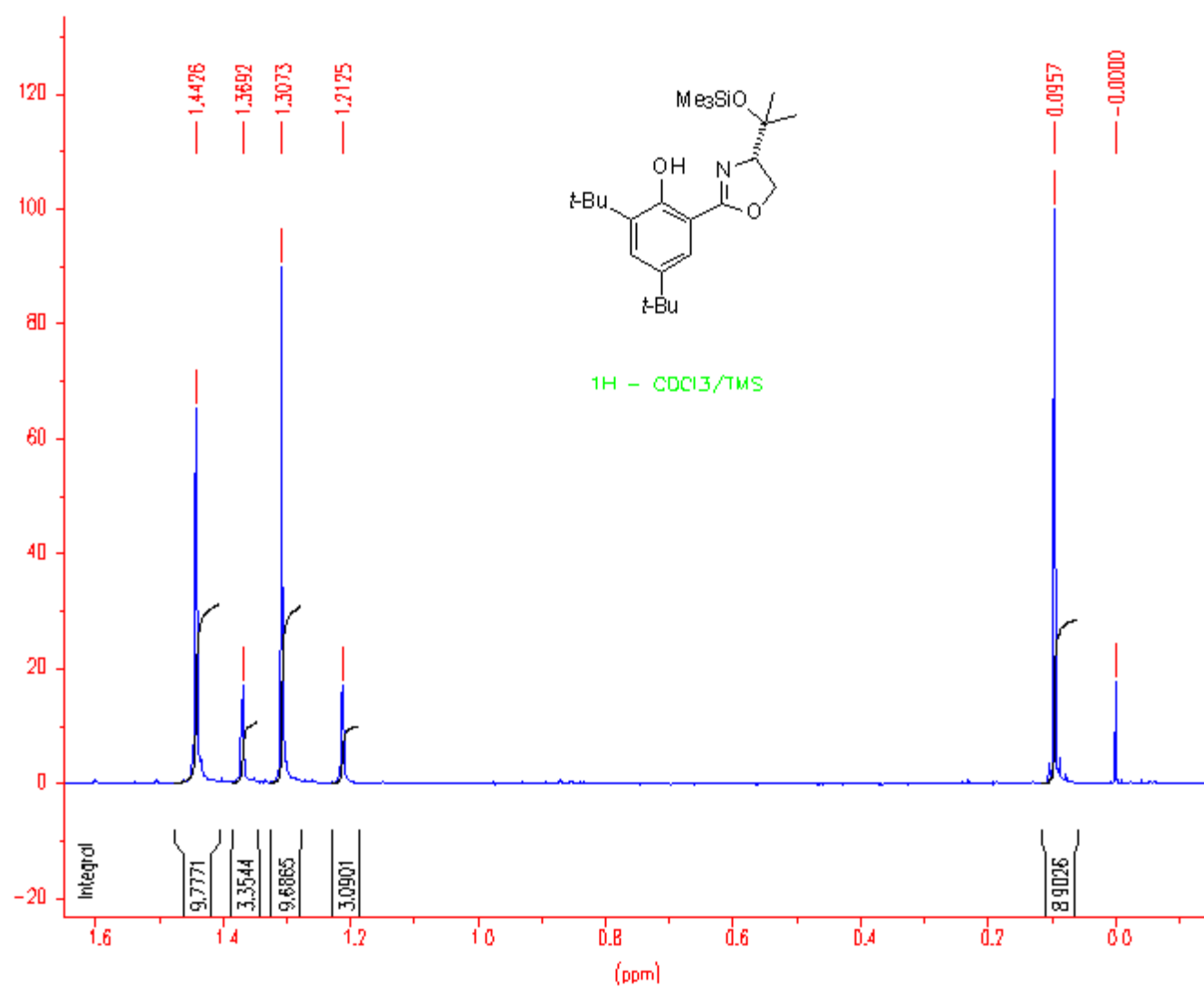
(R)-2,4-Di-*tert*-butyl-6-[4-(1-methyl-1-trimethylsilyloxyethyl)-4,5-dihydro-2-oxazolyl]-phenol (R)-14a

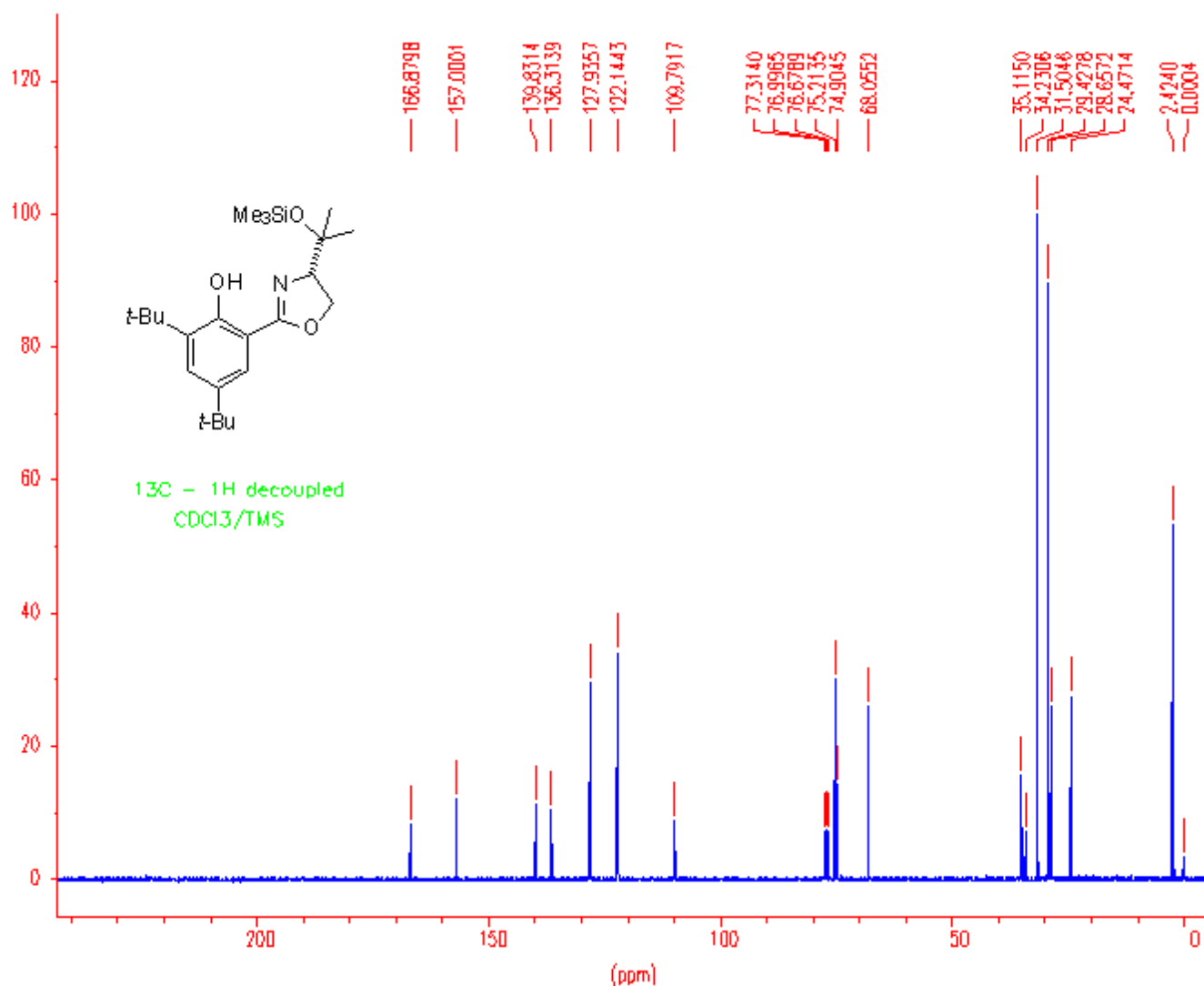
IR (Nujol, NaCl): $\tilde{\nu}$ 1635 (C=N), 1598 (C=C), 1444, 1252, 1189, 1165, 1106, 1059, 977, 840 cm^{-1} .



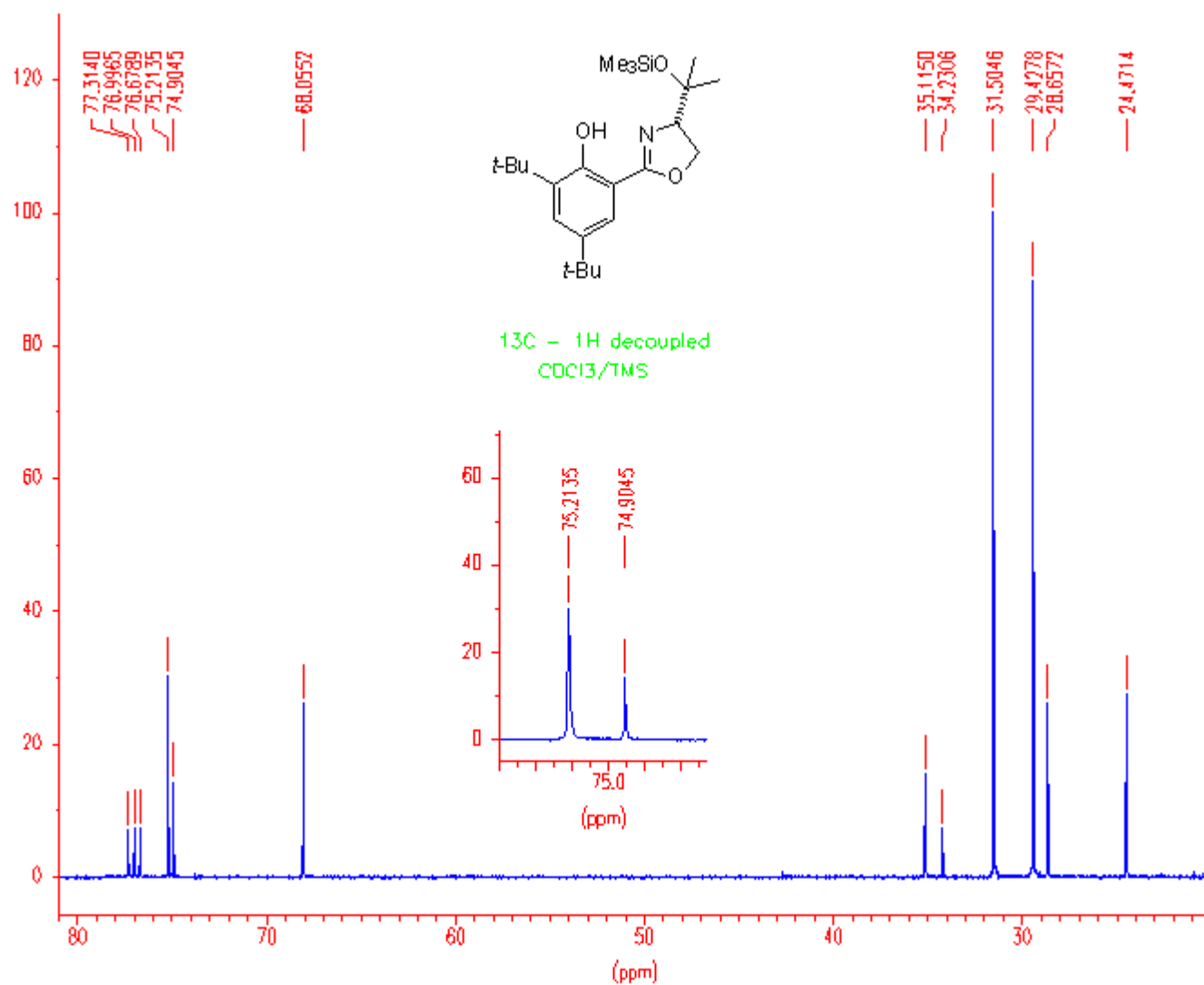
^1H NMR (400 MHz, CDCl_3): δ 12.66 (broad s, 1H, OH), 7.53 (d, 1H, $J = 2.5$ Hz, CH aromatic), 7.44 (d, 1H, $J = 2.5$ Hz, CH aromatic), 4.44 (dd, 1H, $J = 8.5, 7.3$ Hz, CH_2CH), 4.32 (dd, 1H, $J = 9.8, 8.5$ Hz, CH_2CH), 4.23 (dd, 1H, $J = 9.8, 7.3$ Hz, CH_2CH), 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.37 (s, 3H, $\text{C}(\text{CH}_3)_2\text{O}$), 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.21 (s, 3H, $\text{C}(\text{CH}_3)_2\text{O}$), 0.10 (s, 9H, $\text{OSi}(\text{CH}_3)_3$).

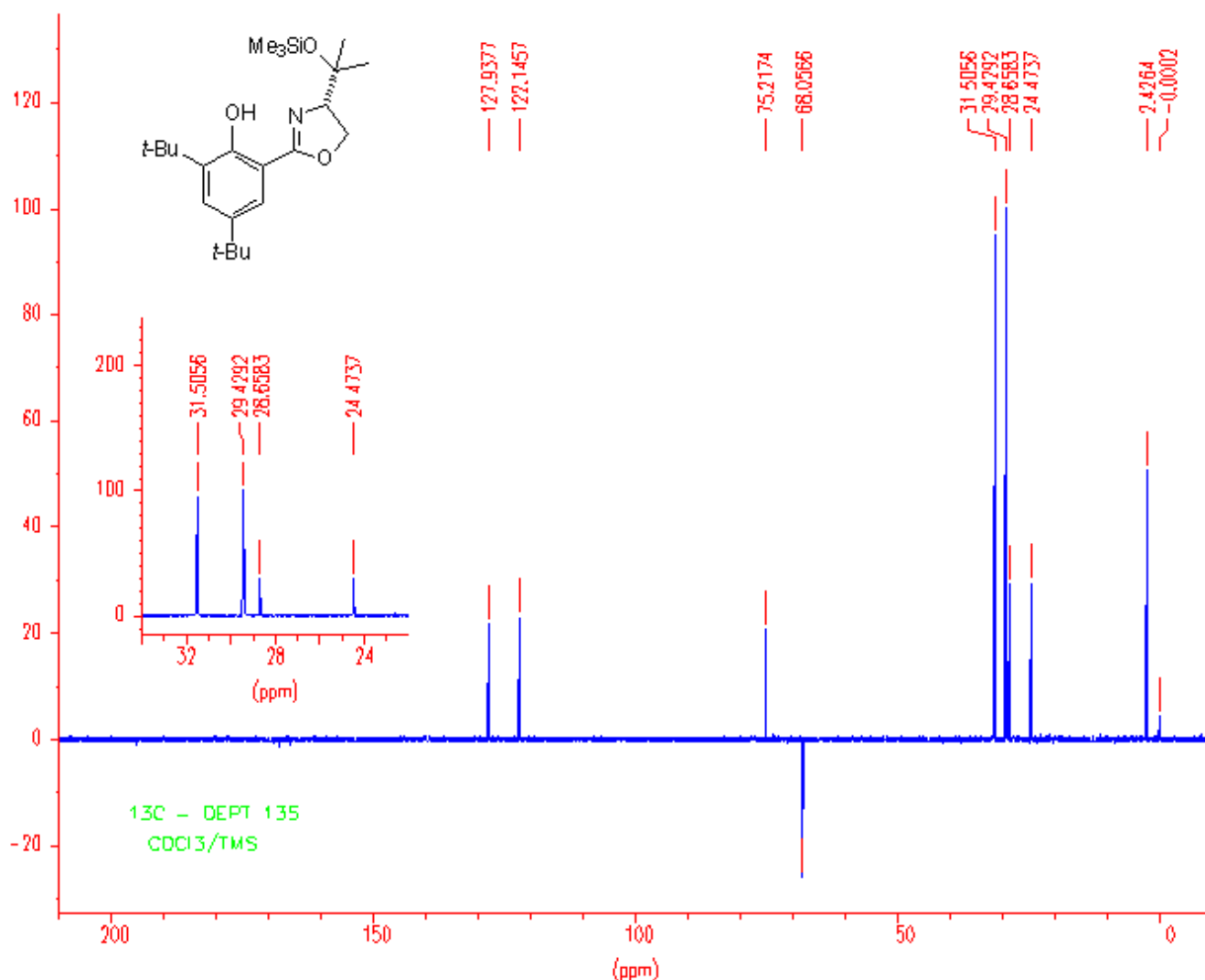






¹³C NMR (100 MHz, CDCl₃): *d* 166.88 (1C, O=C=N), 157.00 (1C, C_{ipso} α to OH), 139.83 (1C, C_{ipso} α to C(CH₃)₃), 136.32 (1C, C_{ipso} α to C(CH₃)₃), 127.94 (1C, CH aromatic, correlates with proton at 7.44 ppm), 122.14 (1C, CH aromatic, correlates with proton at 7.53 ppm), 109.80 (1C, C_{ipso} α to oxazoline), 75.22 (1C, CH₂CH), 74.91 (1C, C(CH₃)₂O), 68.06 (1C, CH₂CH), 35.12 (1C, C(CH₃)₃), 34.24 (1C, C(CH₃)₃), 31.51 (3C, C(CH₃)₃, correlates with protons at 1.31 ppm), 29.43 (3C, C(CH₃)₃, correlates with protons at 1.44 ppm), 28.66 (1C, C(CH₃)₂O, correlates with protons at 1.37 ppm), 24.47 (1C, C(CH₃)₂O, correlates with protons at 1.21 ppm), 2.43 (3C, OSi(CH₃)₃).





HRMS (EI, 70 eV) m/z (%): calcd for C₂₃H₃₉NO₃Si 405.2699 [M]⁺, found 405.2676 (18), 390 (3) [M - Me]⁺, 131 (100) [CMe₂OSiMe₃]⁺, 75 (3) [Me₂Si=OH]⁺, 73 (13) [Me₃Si]⁺.

MS (FAB, *m*-nitrobenzyl alcohol matrix) m/z (rel intens): Calcd for C₂₃H₃₉NO₃Si 405.3 [M]⁺, found 405 (100) [M]⁺, 390 (33) [M - CH₃]⁺, 316 (7) [M - OSi(CH₃)₃]⁺.

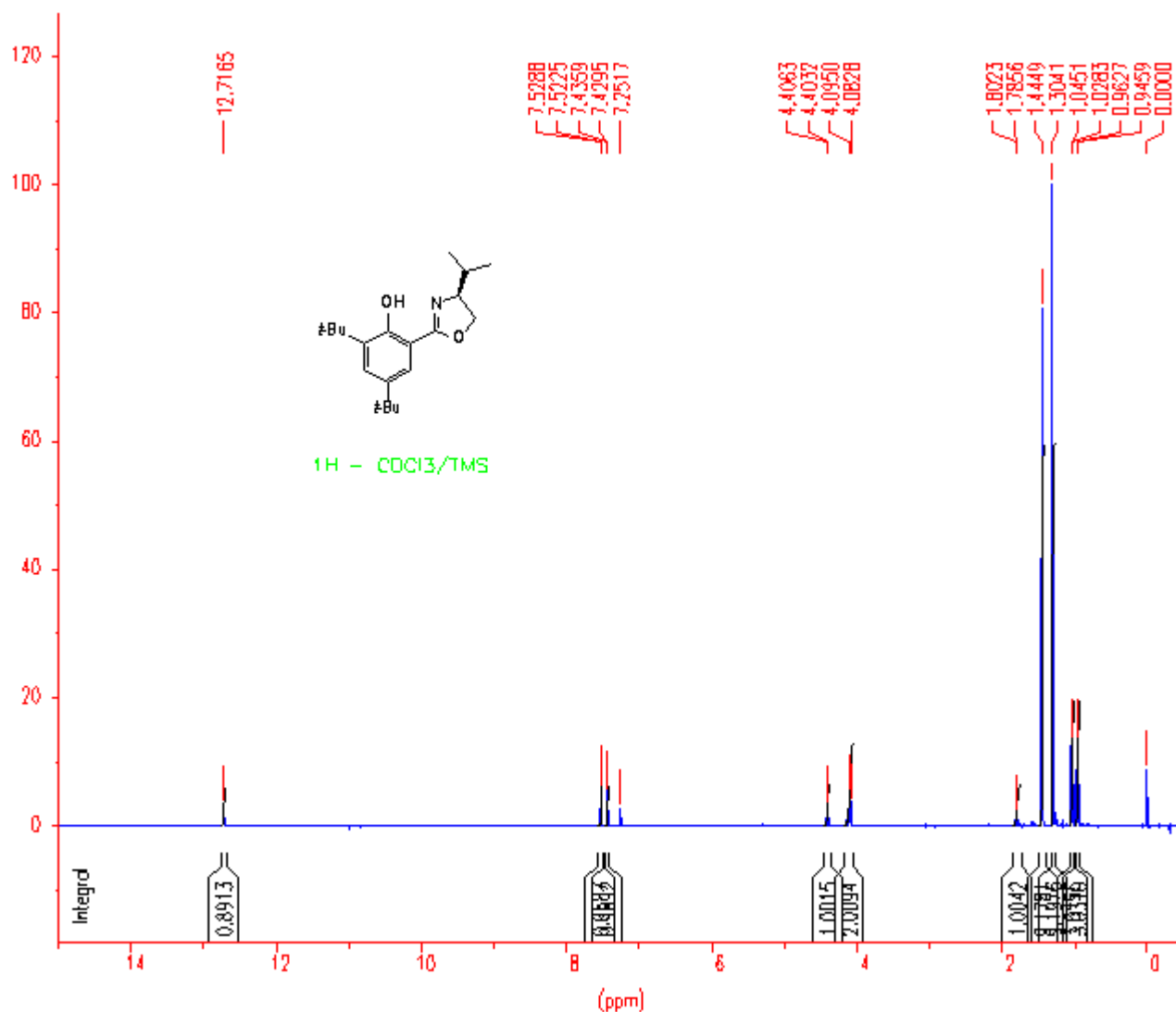
Starting from D-serine: $[\alpha]_D^{24} = +6.7$, $[\alpha]_{578}^{24} = +7.6$, $[\alpha]_{546}^{24} = +9.3$, $[\alpha]_{436}^{24} = +30.8$ ($c = 2.7$, CHCl₃).

Starting from L-serine: $[\alpha]_D^{27} = -6.8$, $[\alpha]_{578}^{27} = -7.4$, $[\alpha]_{546}^{27} = -9.3$, $[\alpha]_{436}^{27} = -32.0$ ($c = 1.0$, CHCl₃).

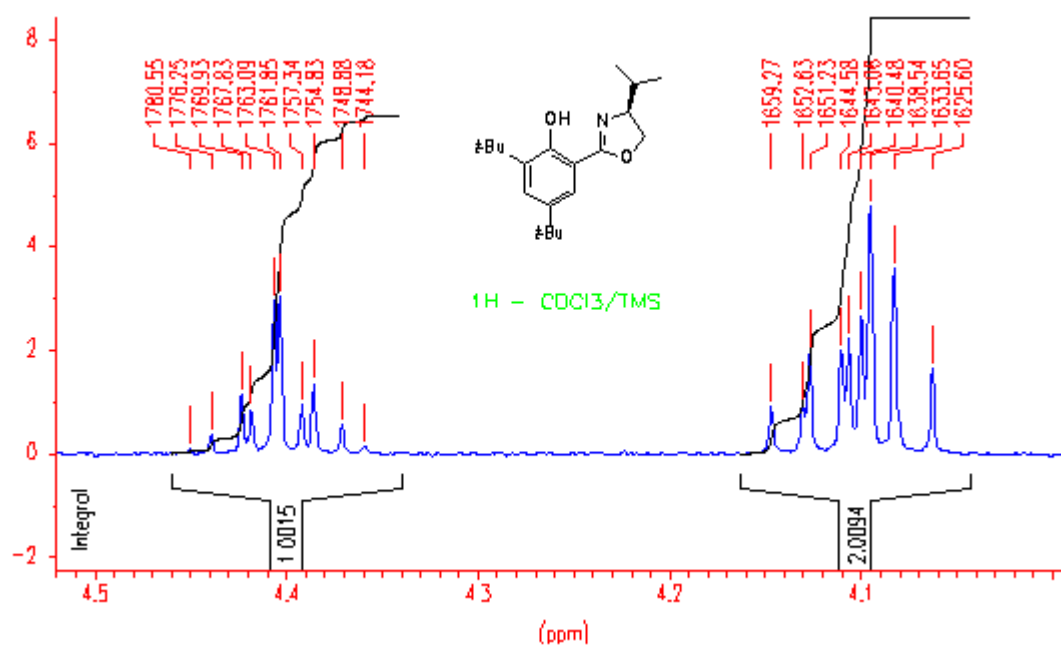
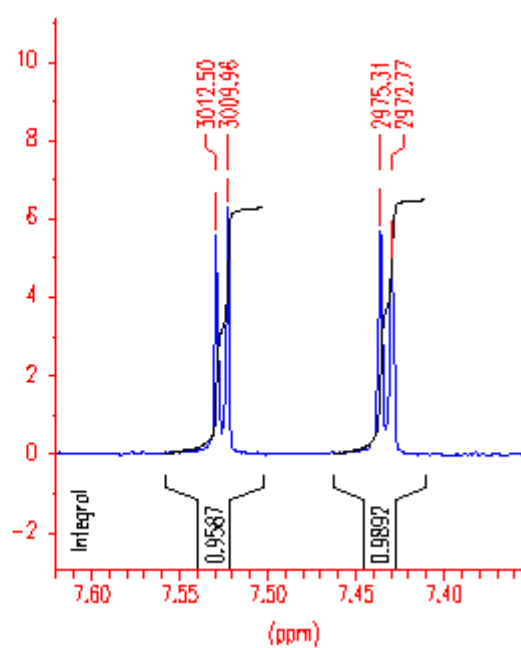
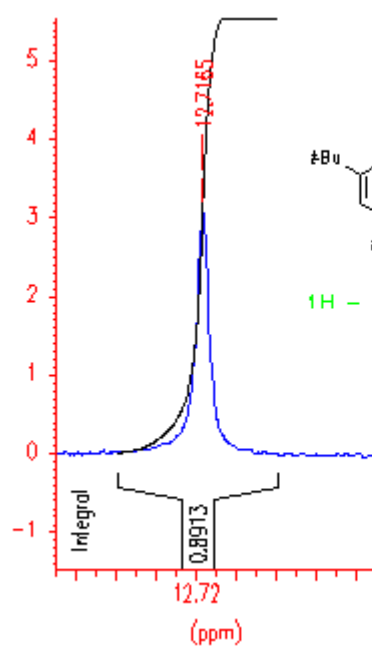
Anal. Calcd for C₂₃H₃₉NO₃Si: C, 68.10; H, 9.69; N, 3.45. Found: C, 68.16; H, 9.48; N, 3.56.

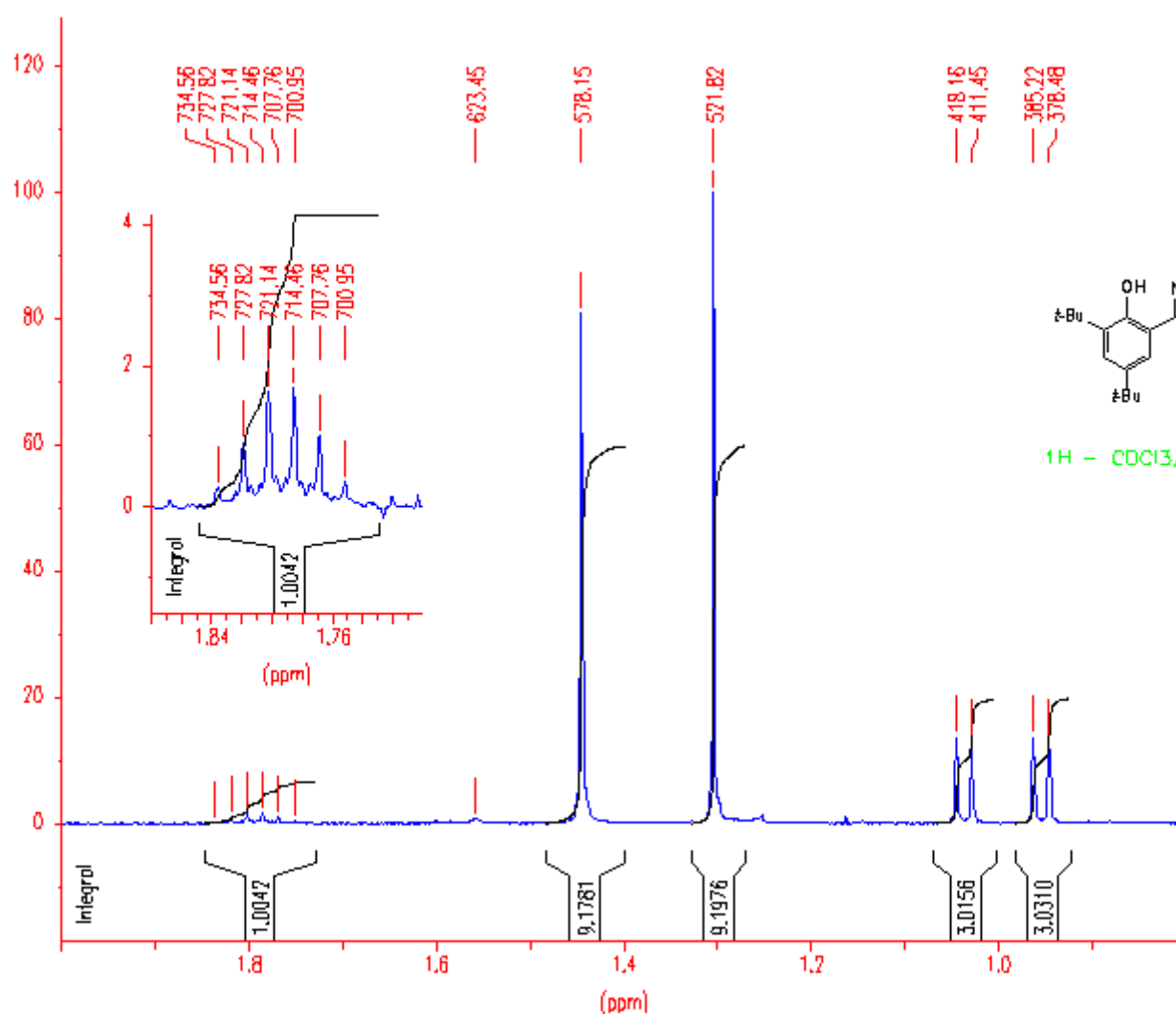
(S)-2,4-Di-*tert*-butyl-6-[4-*i*-propyl-4,5-dihydro-2-oxazolyl]-phenol (S)-14b

IR (neat, NaCl): $\tilde{\nu}$ 2960, 2909, 2873, 1795 (small, aromatic harmonic), 1637 (C=N), 1598 (C=C), 1469, 1440, 1392, 1255, 1219, 1103, 1047, 979, 890, 786 cm^{-1} .

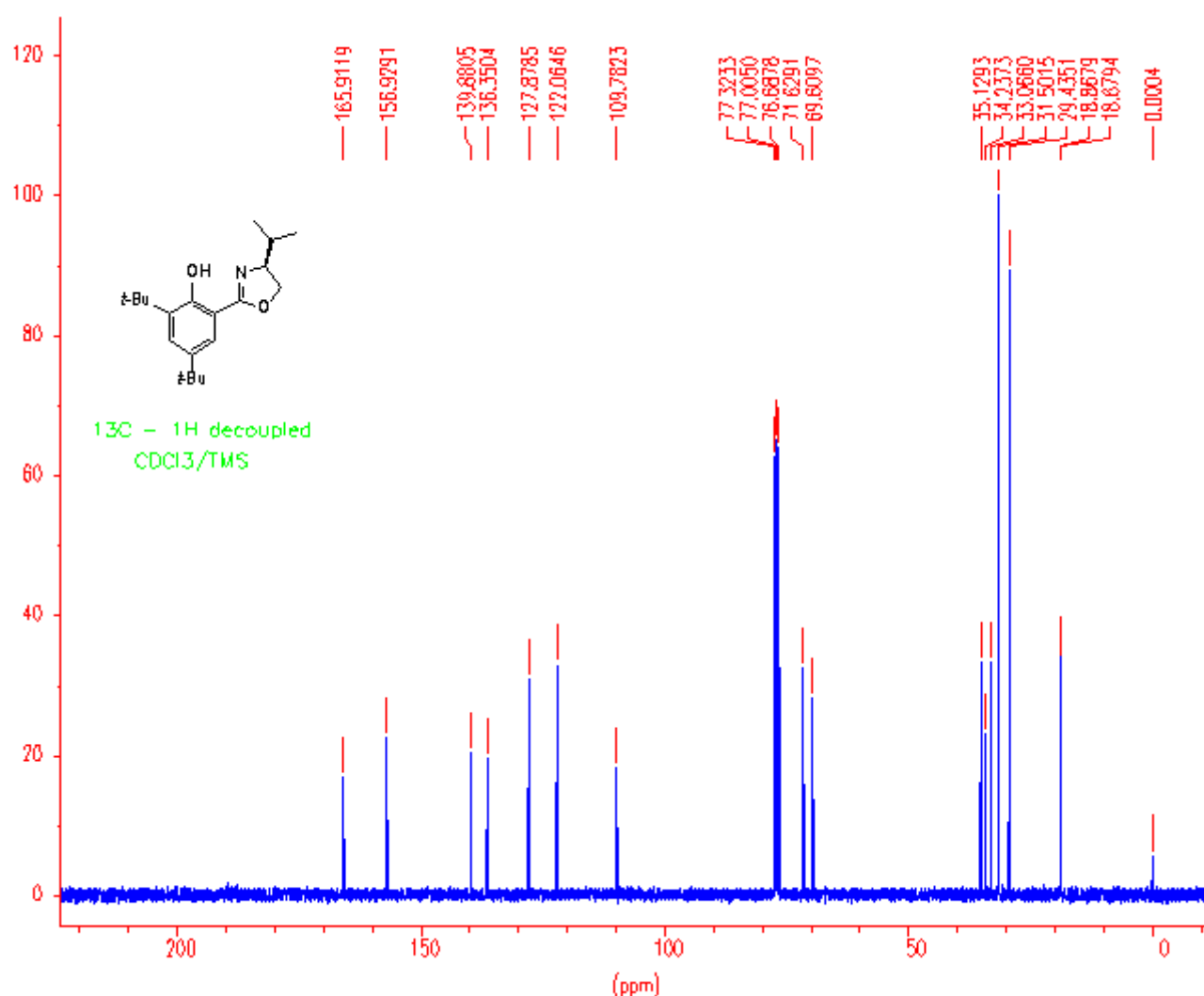


^1H NMR (400 MHz, CDCl_3): δ 12.71 (broad s, 1H, OH), 7.53 (d, 1H, $J = 2.5$ Hz, CH aromatic), 7.44 (d, 1H, $J = 2.5$ Hz, CH aromatic), 4.44-4.34 (m, 1H, CH_2CH), 4.14-4.05 (m, 2H, CH_2CH and CH_2CH), 1.79 (dq, 1H, $J = 6.9, 6.7, 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.03 (d, 1H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, 1H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$).

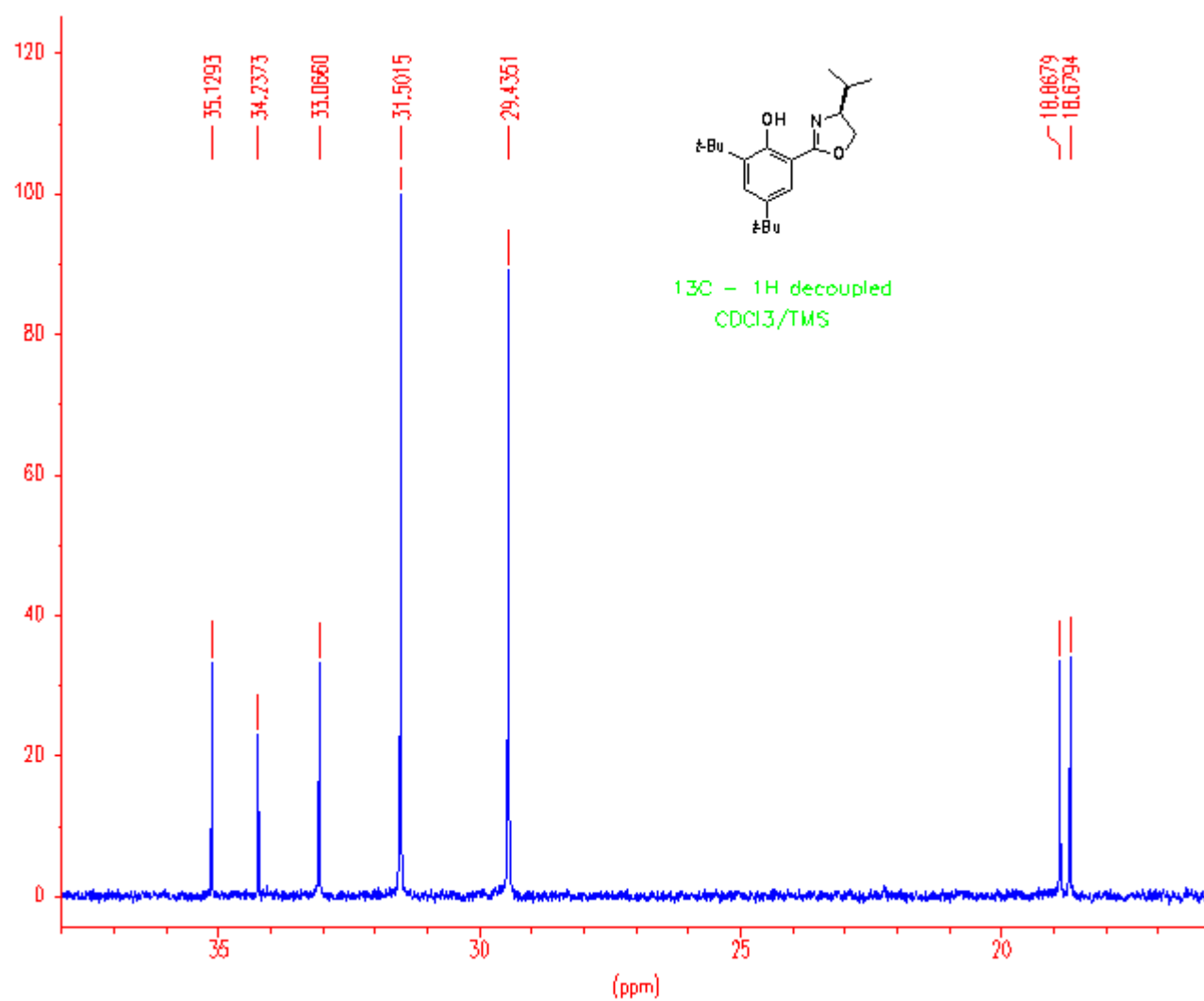


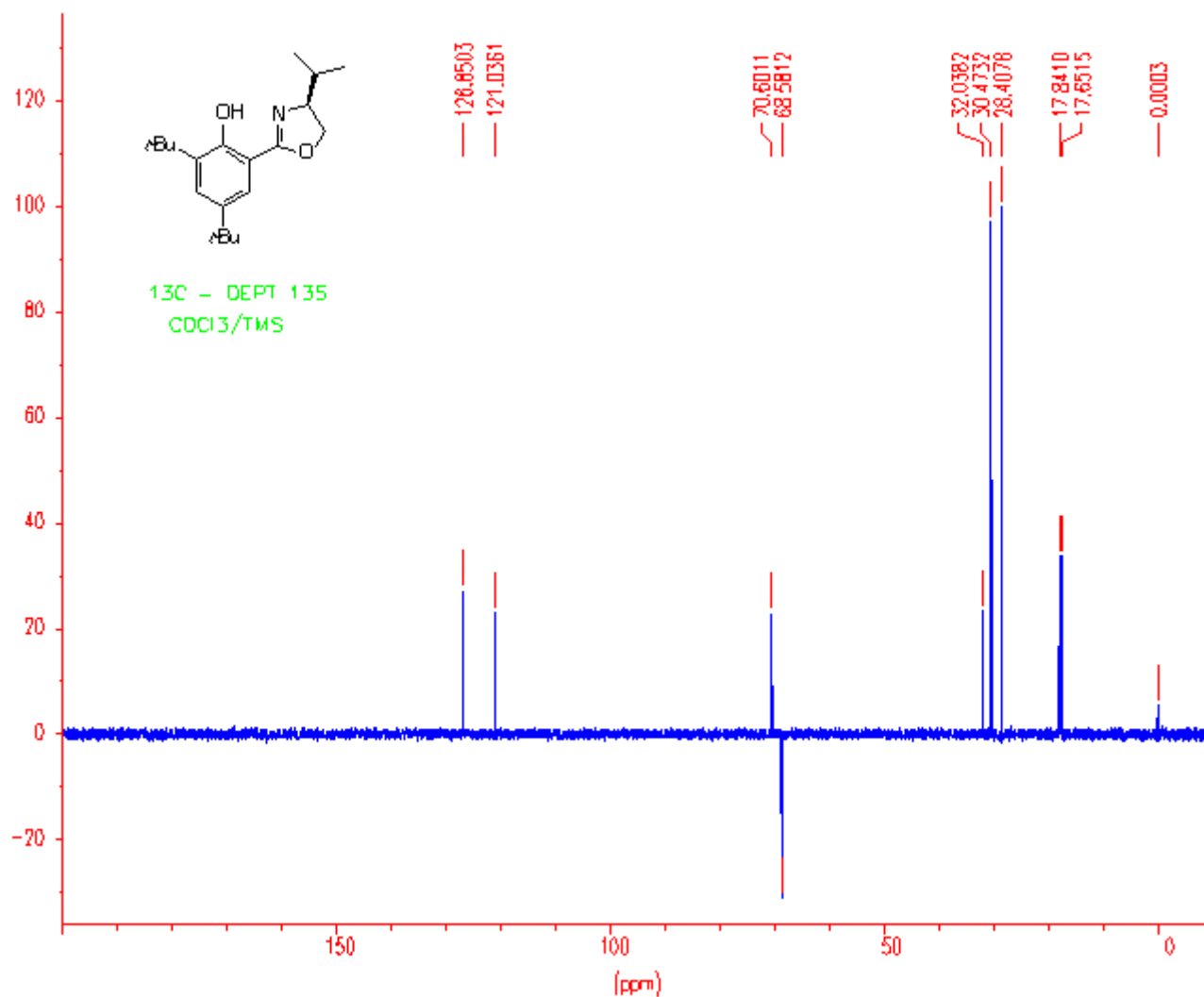


1H - CDCl₃/TMS



¹³C NMR (100 MHz, CDCl₃): *d* 165.92 (1C, O=C=N), 156.95 (1C, C_{ipso} α to OH), 139.88 (1C, C_{ipso} α to C(CH₃)₃), 136.35 (1C, C_{ipso} α to C(CH₃)₃), 127.87 (1C, CH aromatic, correlates with proton at 7.44 ppm), 122.08 (1C, CH aromatic, correlates with proton at 7.53 ppm), 109.79 (1C, C_{ipso} α to oxazoline), 71.63 (1C, CH₂CH), 69.60 (1C, CH₂CH), 35.13 (1C, C(CH₃)₃), 34.23 (1C, C(CH₃)₃), 33.07 (1C, CH(CH₃)₂), 31.50 (3C, C(CH₃)₃, correlates with protons at 1.31 ppm), 29.45 (3C, C(CH₃)₃, correlates with protons at 1.45 ppm), 18.86 (1C, CH(CH₃)₂, correlates with protons at 1.03 ppm), 18.67 (1C, CH(CH₃)₂, correlates with protons at 0.95 ppm).





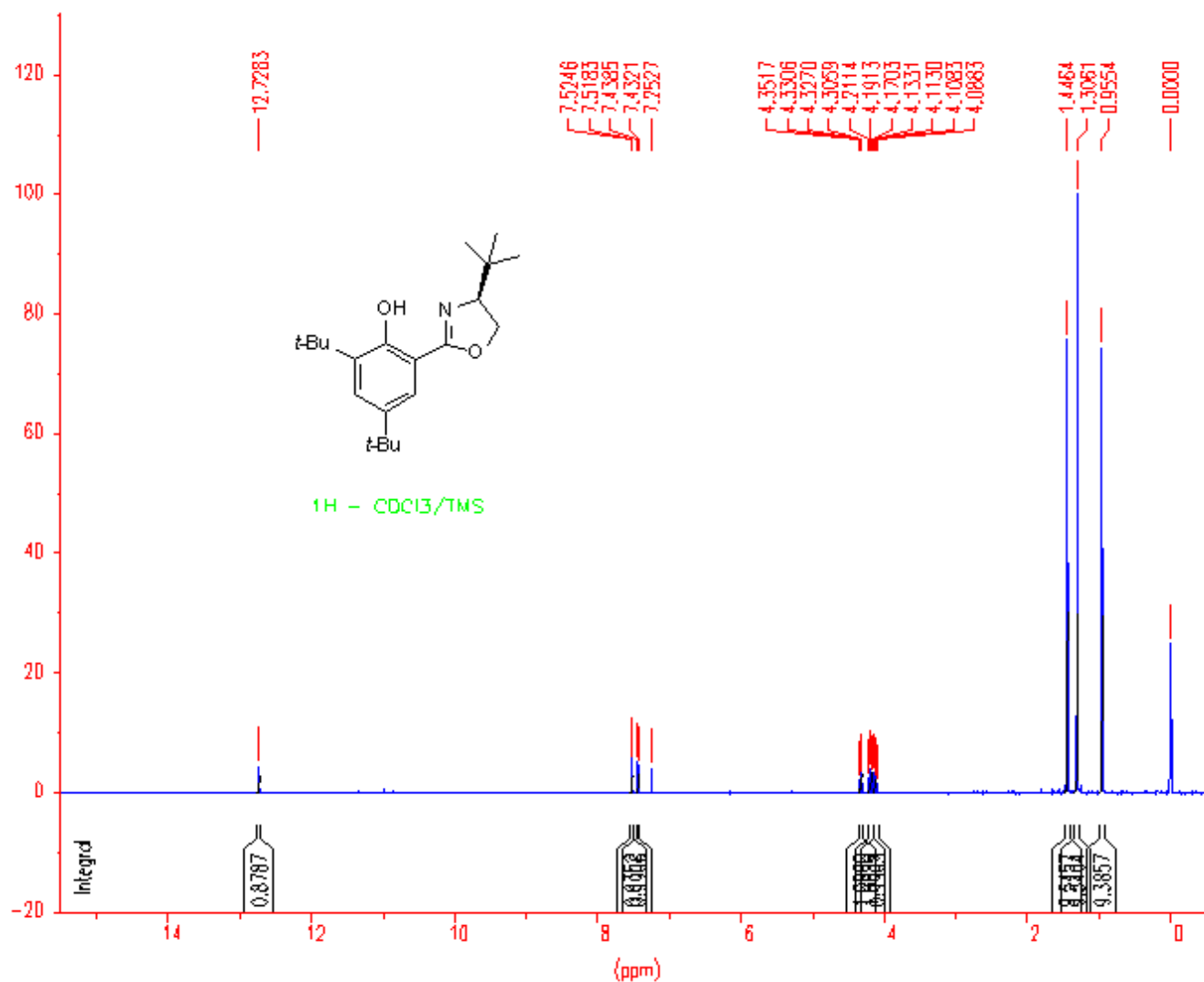
MS (EI, 70 eV) m/z (rel intens) 317 (41) $[M]^+$, 302 (72) $[M - CH_3]^+$, 274 (36) $[M - C_3H_7]^+$, 260 (14) $[M - C_4H_9]^+$, 216 (31), 57 (27) $[C_4H_9]^+$, 41 (24), 28 (100).

$[\alpha]_D^{24} = -24.9$, $[\alpha]_{578}^{24} = -26.0$, $[\alpha]_{546}^{24} = -29.5$, $[\alpha]_{436}^{24} = -44.0$ ($c = 1.4$, $CHCl_3$).

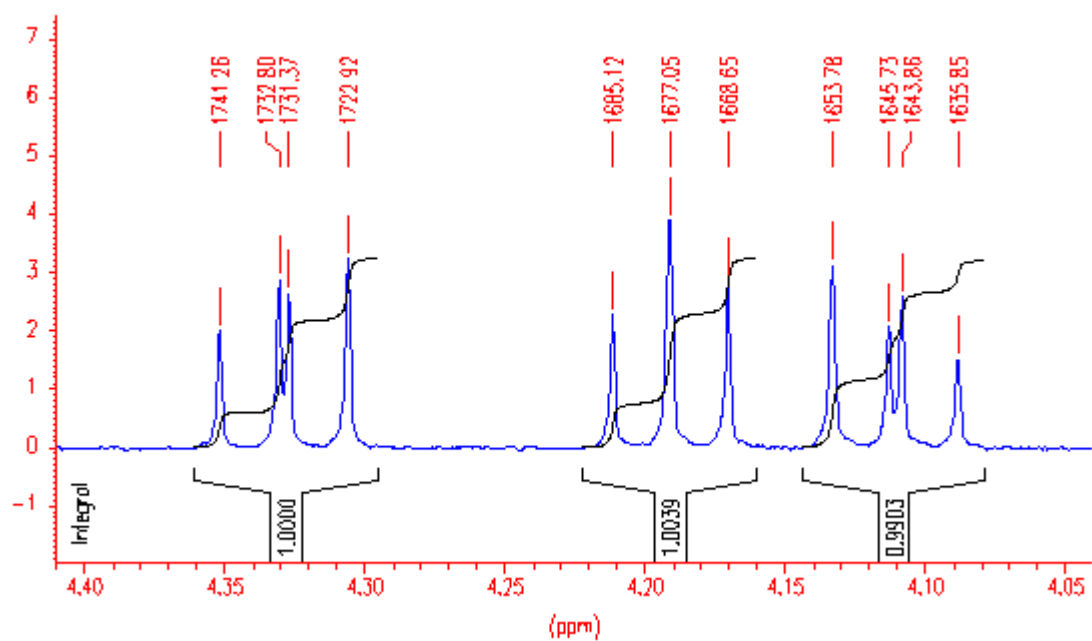
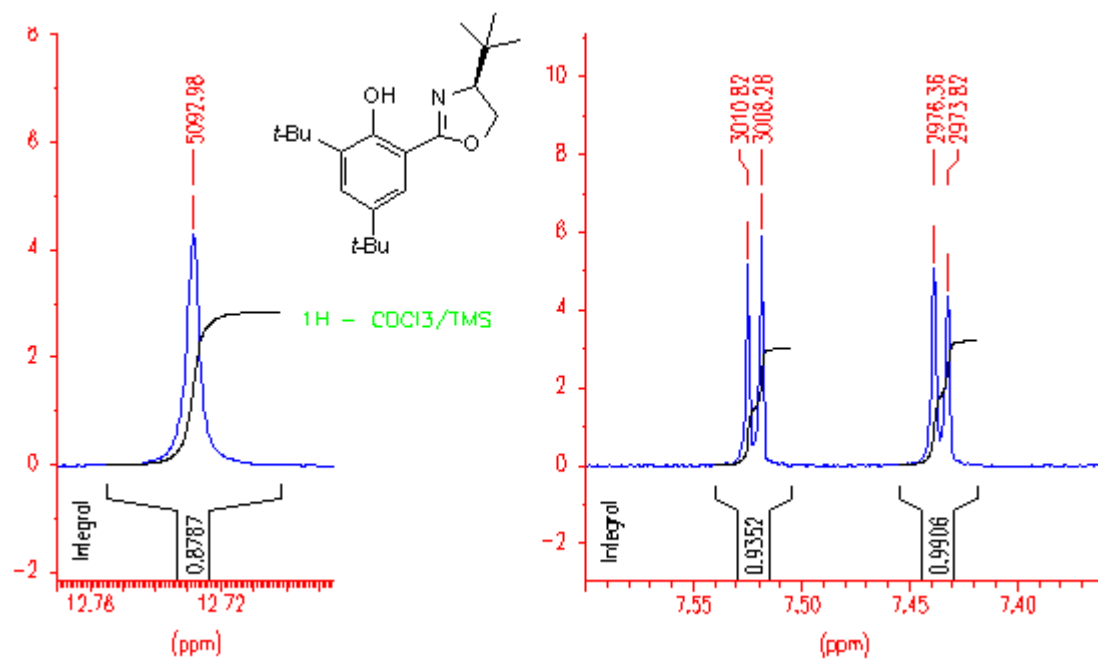
Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.79; H, 9.87; N, 4.45.

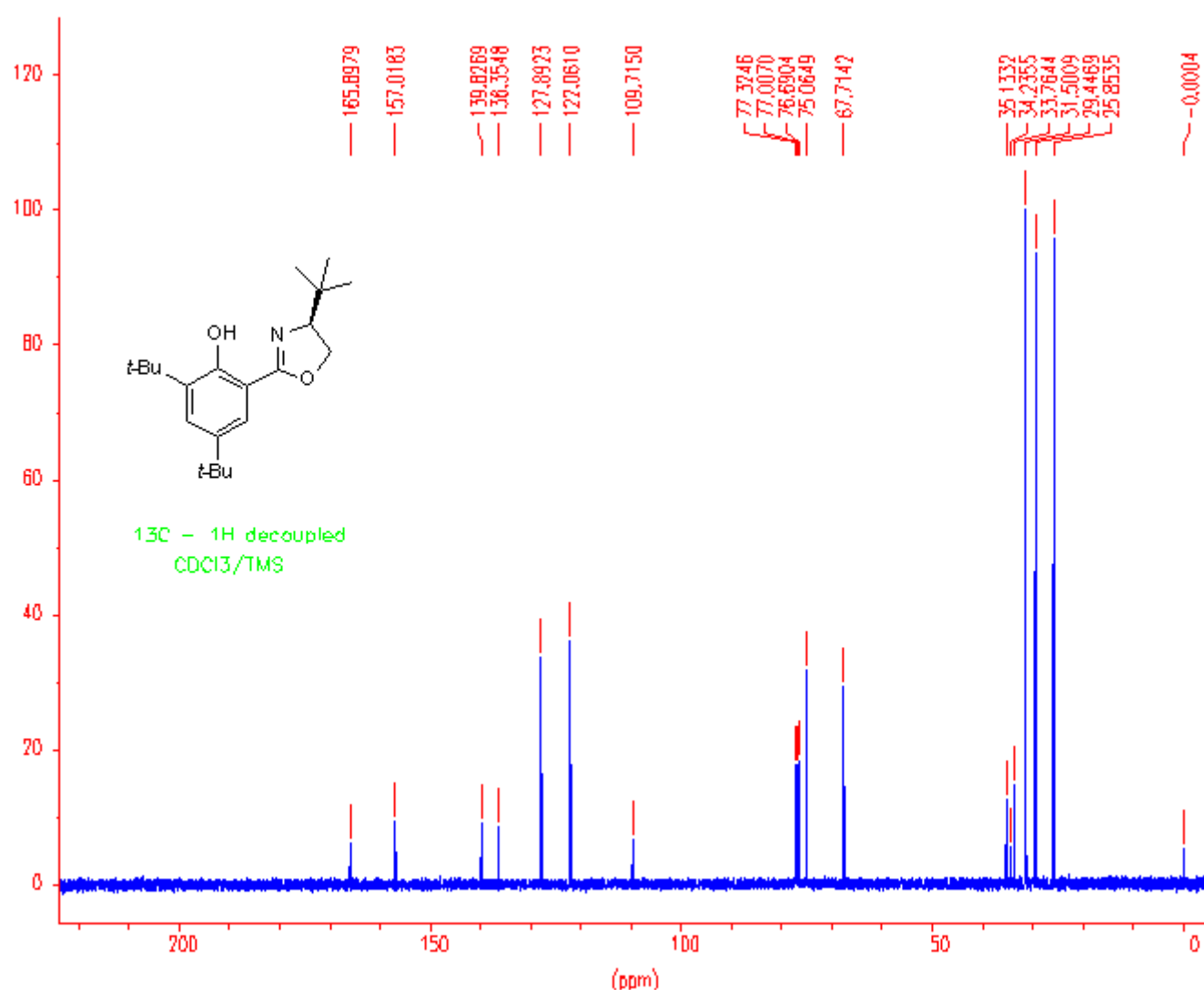
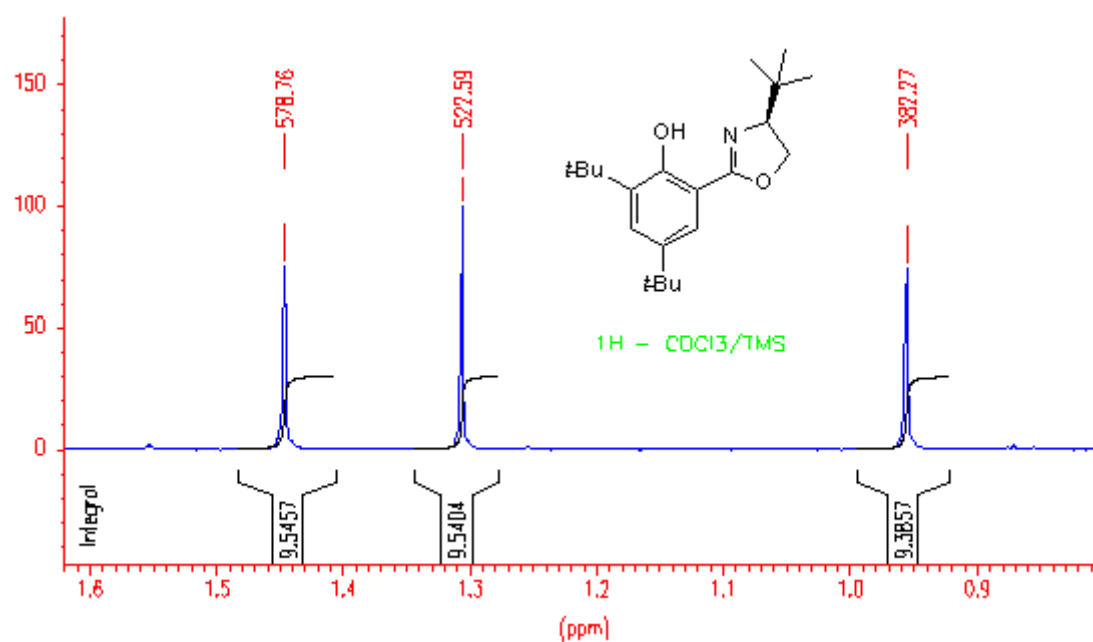
(S)-2,4-Di-*tert*-butyl-6-[4-*tert*-butyl-4,5-dihydro-2-oxazolyl]-phenol (S)-14c

IR (Nujol, NaCl): $\tilde{\nu}$ 1797 (small, aromatic harmonic), 1635 (C=N), 1596 (C=C), 1440, 1366, 1289, 1255, 1106, 1028, 981, 786 cm^{-1} .

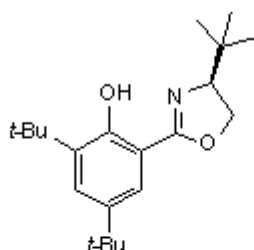


^1H NMR (400 MHz, CDCl_3): δ 12.74 (broad s, 1H, OH), 7.52 (d, 1H, $J = 2.5$ Hz, CH aromatic), 7.44 (d, 1H, $J = 2.5$ Hz, CH aromatic), 4.33 (dd, 1H, $J = 9.8, 8.5$ Hz, CH_2CH), 4.19 (dd, 1H, $J = 8.5, 8.1$ Hz, CH_2CH), 4.11 (dd, 1H, $J = 9.8, 8.1$ Hz, CH_2CH), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.95 (s, 9H, $\text{C}(\text{CH}_3)_3$).

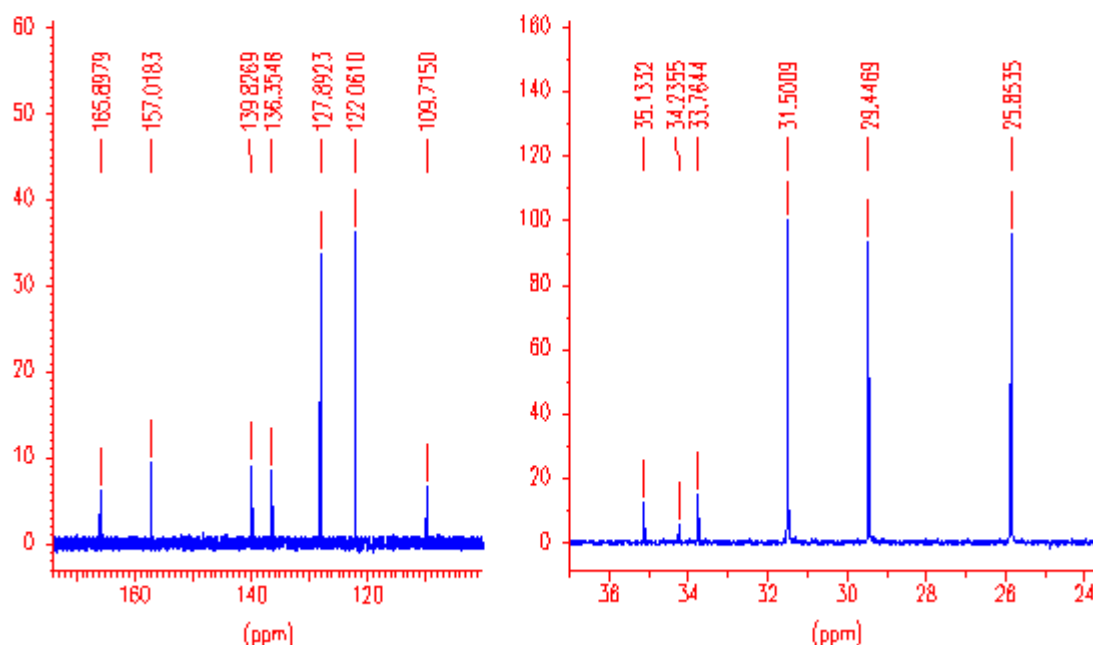




^{13}C NMR (100 MHz, CDCl_3): δ 165.90 (1C, O-C=N), 157.02 (1C, C_{ipso} α to OH), 139.83 (1C, C_{ipso} α to $\text{C}(\text{CH}_3)_3$), 136.36 (1C, C_{ipso} α to $\text{C}(\text{CH}_3)_3$), 127.89 (1C, CH aromatic, correlates with proton at 7.44 ppm), 122.07 (1C, CH aromatic, correlates with proton at 7.52 ppm), 109.72 (1C, C_{ipso} α to oxazoline), 75.07 (1C, CH_2CH), 67.72 (1C, CH_2CH), 35.14 (1C, $\text{C}(\text{CH}_3)_3$), 34.24 (1C, $\text{C}(\text{CH}_3)_3$), 33.77 (1C, $\text{C}(\text{CH}_3)_3$ of oxazoline), 31.50 (3C, $\text{C}(\text{CH}_3)_3$, correlates with protons at 1.31 ppm), 29.45 (3C, $\text{C}(\text{CH}_3)_3$, correlates with protons at 1.45 ppm), 25.86 (3C, $\text{C}(\text{CH}_3)_3$ of oxazoline).



^{13}C - ^1H decoupled
 CDCl_3/TMS



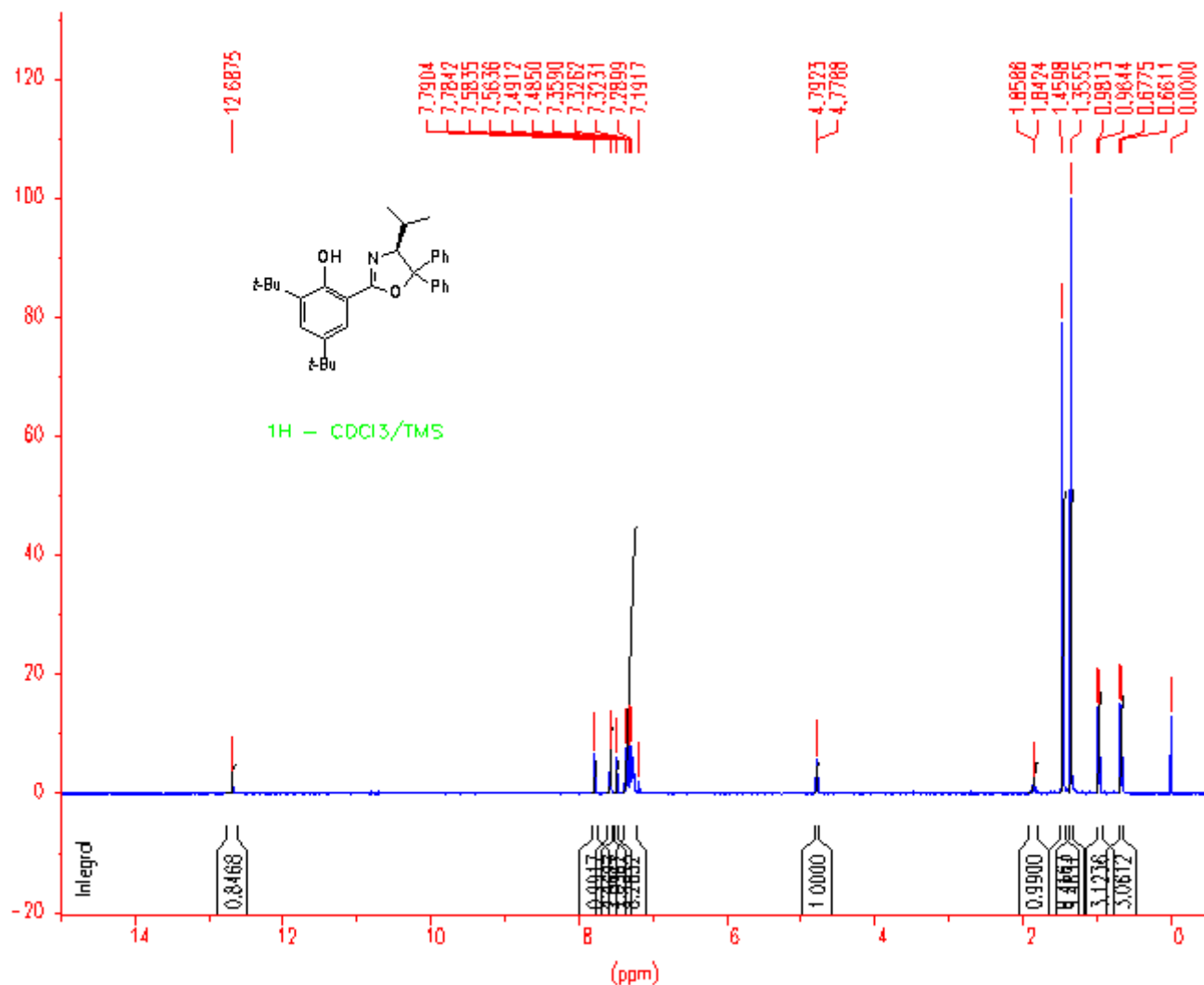
MS (EI, 70 eV) m/z (rel intens) 331 (43) $[\text{M}]^+$, 316 (59) $[\text{M} - \text{CH}_3]^+$, 288 (40) $[\text{M} - \text{C}_3\text{H}_7]^+$, 274 (32) $[\text{M} - \text{C}_4\text{H}_9]^+$, 216 (25), 57 (18) $[\text{C}_4\text{H}_9]^+$, 28 (100).

$[\alpha]_{\text{D}}^{24} = -13.7$, $[\alpha]_{578}^{24} = -14.0$, $[\alpha]_{546}^{24} = -15.5$, $[\alpha]_{436}^{24} = -18.6$ ($c = 2.6$, CHCl_3).

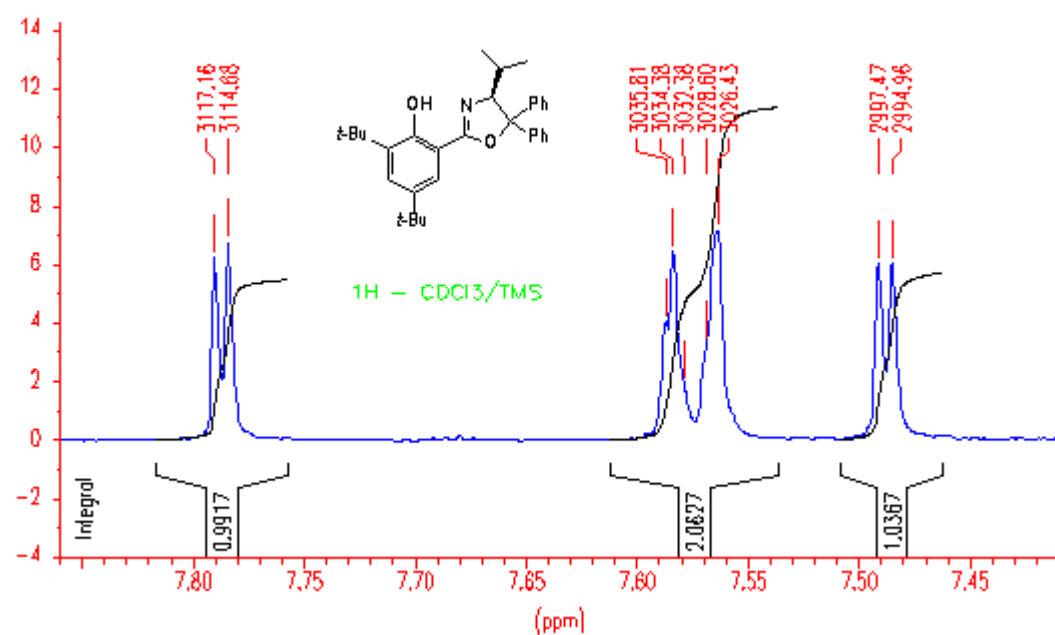
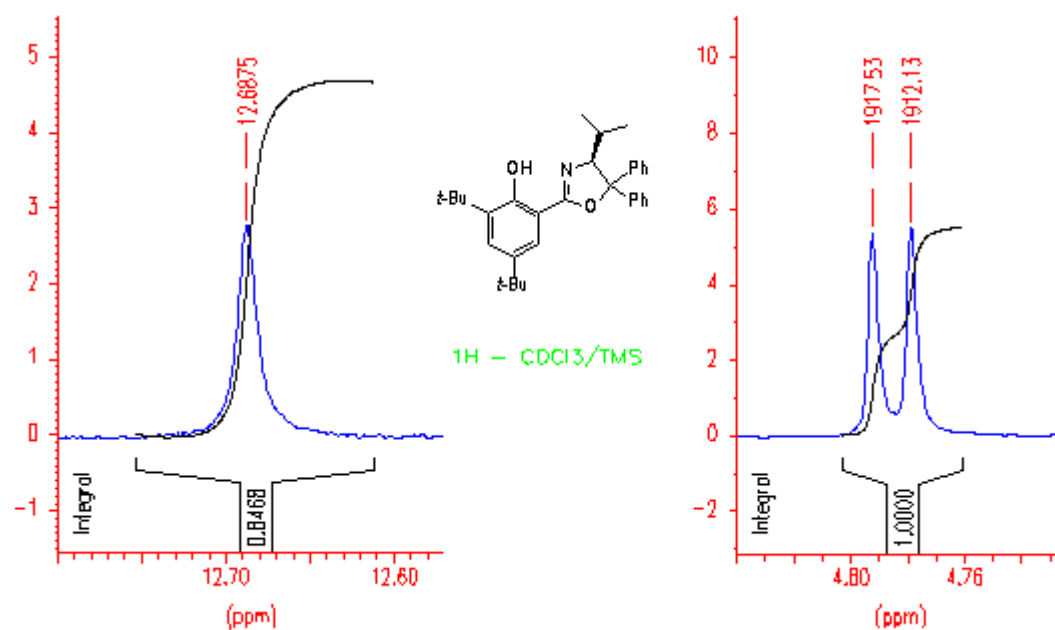
Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{NO}_2$: C, 76.09; H, 10.03; N, 4.23. Found: C, 76.01; H, 10.11; N, 4.14.

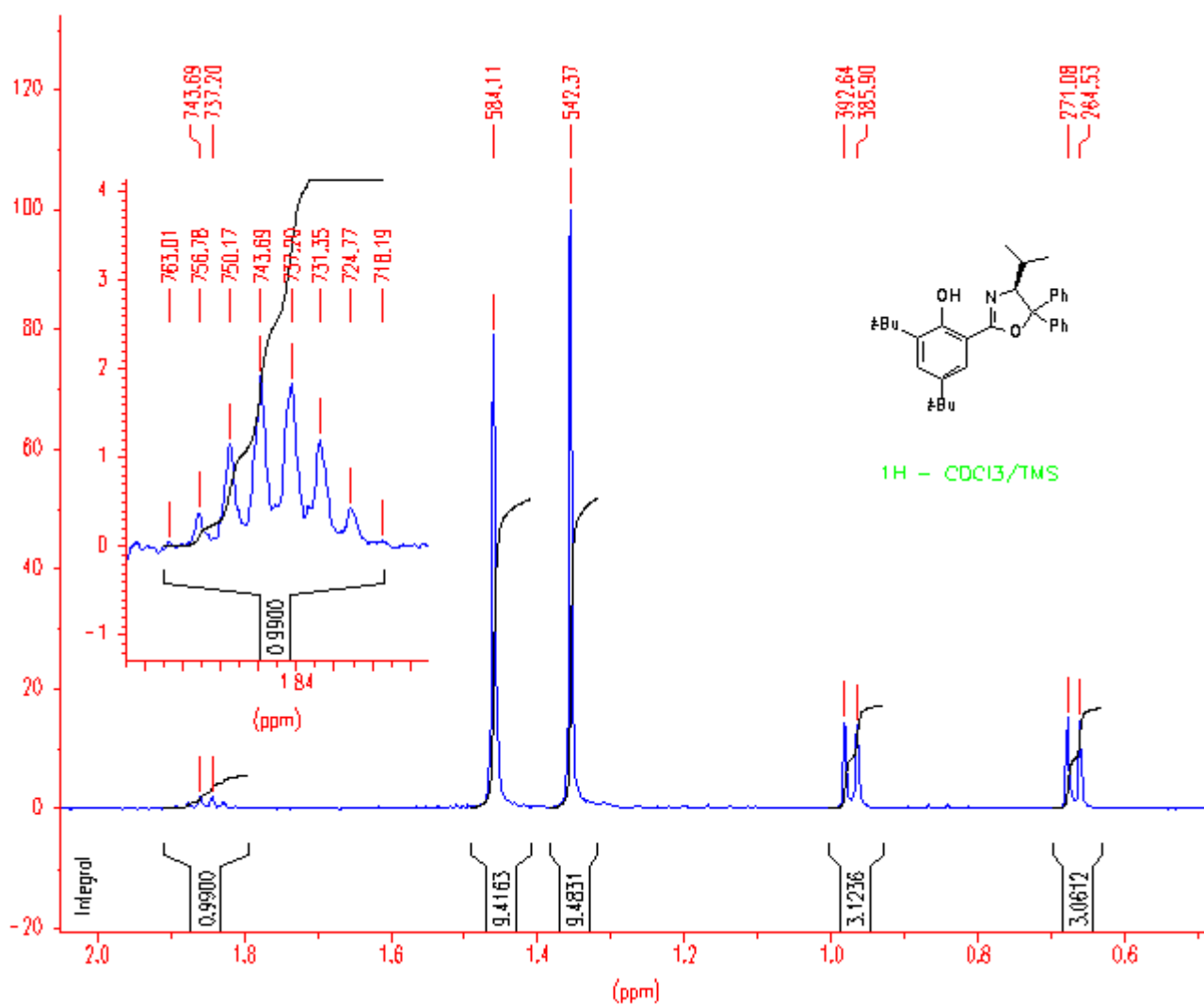
(S)-2,4-Di-*tert*-butyl-6-[5,5-diphenyl-4-*i*-propyl-4,5-dihydro-2-oxazolyl]-phenol (S)-14d

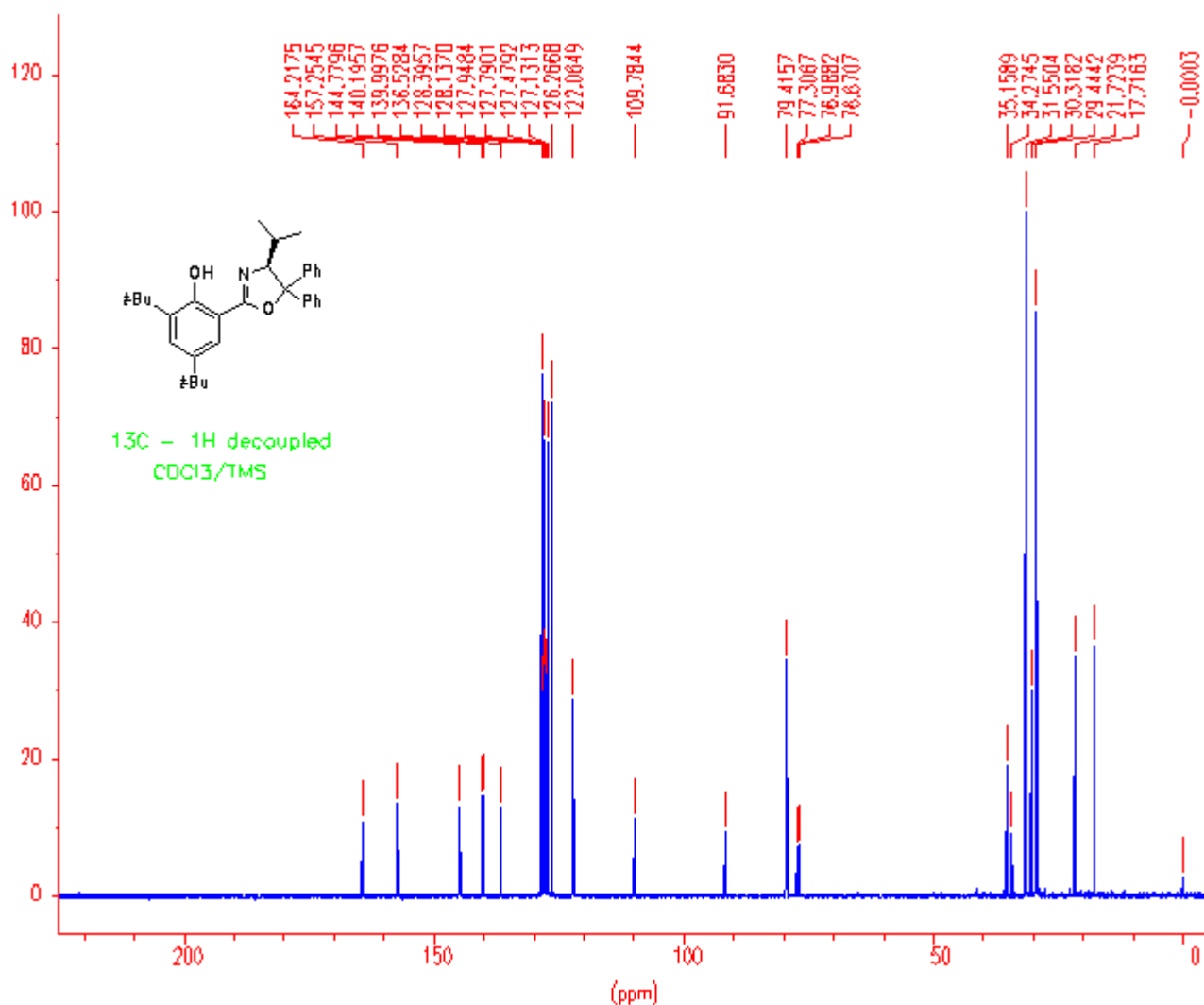
IR (neat, NaCl): $\tilde{\nu}$ 3089, 3062, 3029, 2959, 2929, 2872, 1644 (C=N), 1600, 1467, 1440, 1391, 1369, 1280, 1254, 1220, 1190, 1109, 977, 804, 700 cm^{-1} .



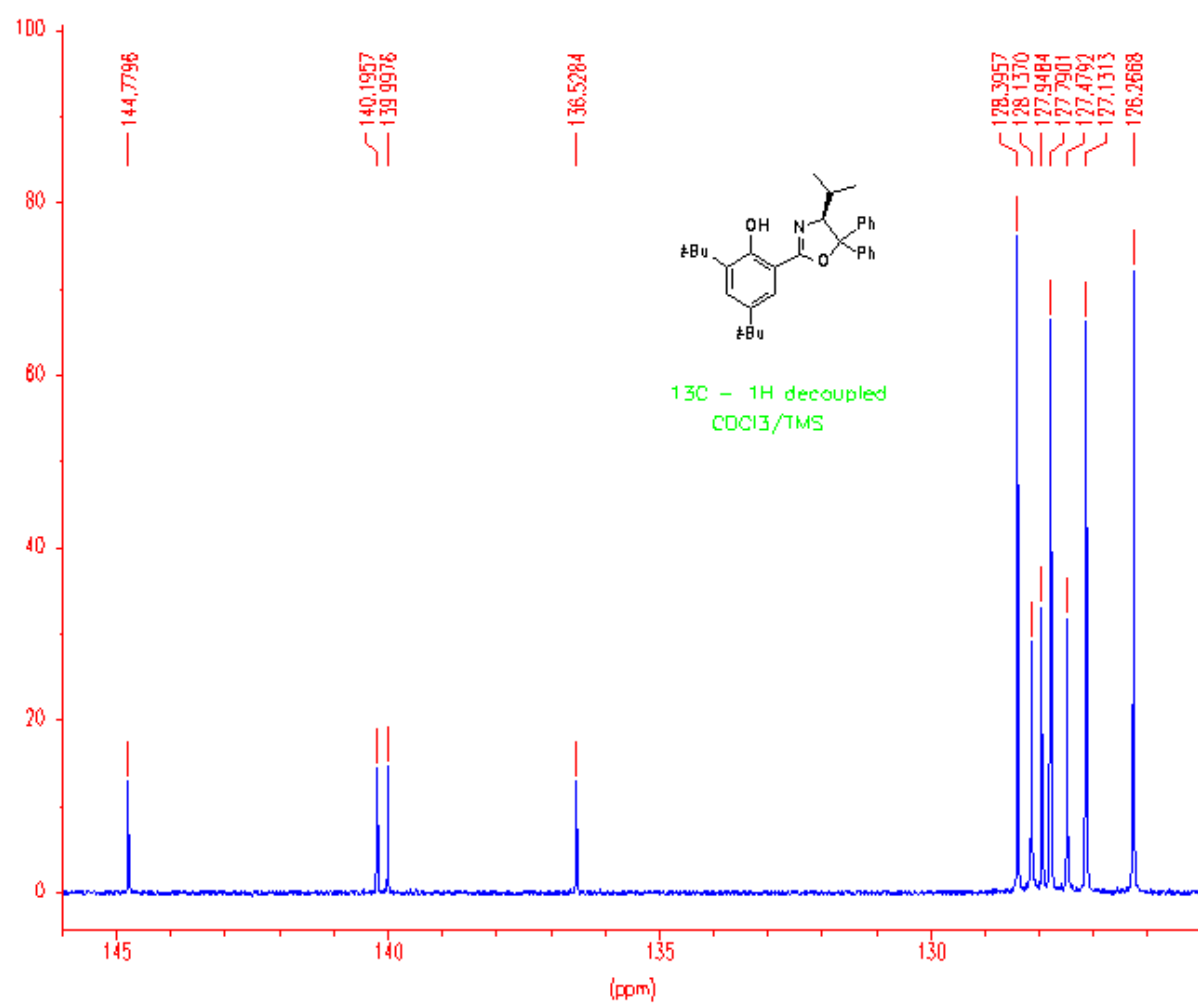
^1H NMR (400 MHz, CDCl_3): δ 12.68 (s, 1H, OH), 7.78 (d, 1H, J = 2.5 Hz, CH of phenol), 7.60-7.55 (m, 2H, CH of CPh_2), 7.48 (d, 1H, J = 2.5 Hz, CH of phenol), 7.40-7.21 (m, 8H, CH of CPh_2), 4.78 (d, 1H, J = 5.4 Hz, CPh_2CH), 1.85 (qqd, 1H, J = 6.7, 6.5, 5.4 Hz, $\text{CH}(\text{CH}_3)_2$), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.35 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.97 (d, 3H, J = 6.7 Hz, $\text{CH}(\text{CH}_3)_2$), 0.67 (d, 3H, J = 6.5 Hz, $\text{CH}(\text{CH}_3)_2$).

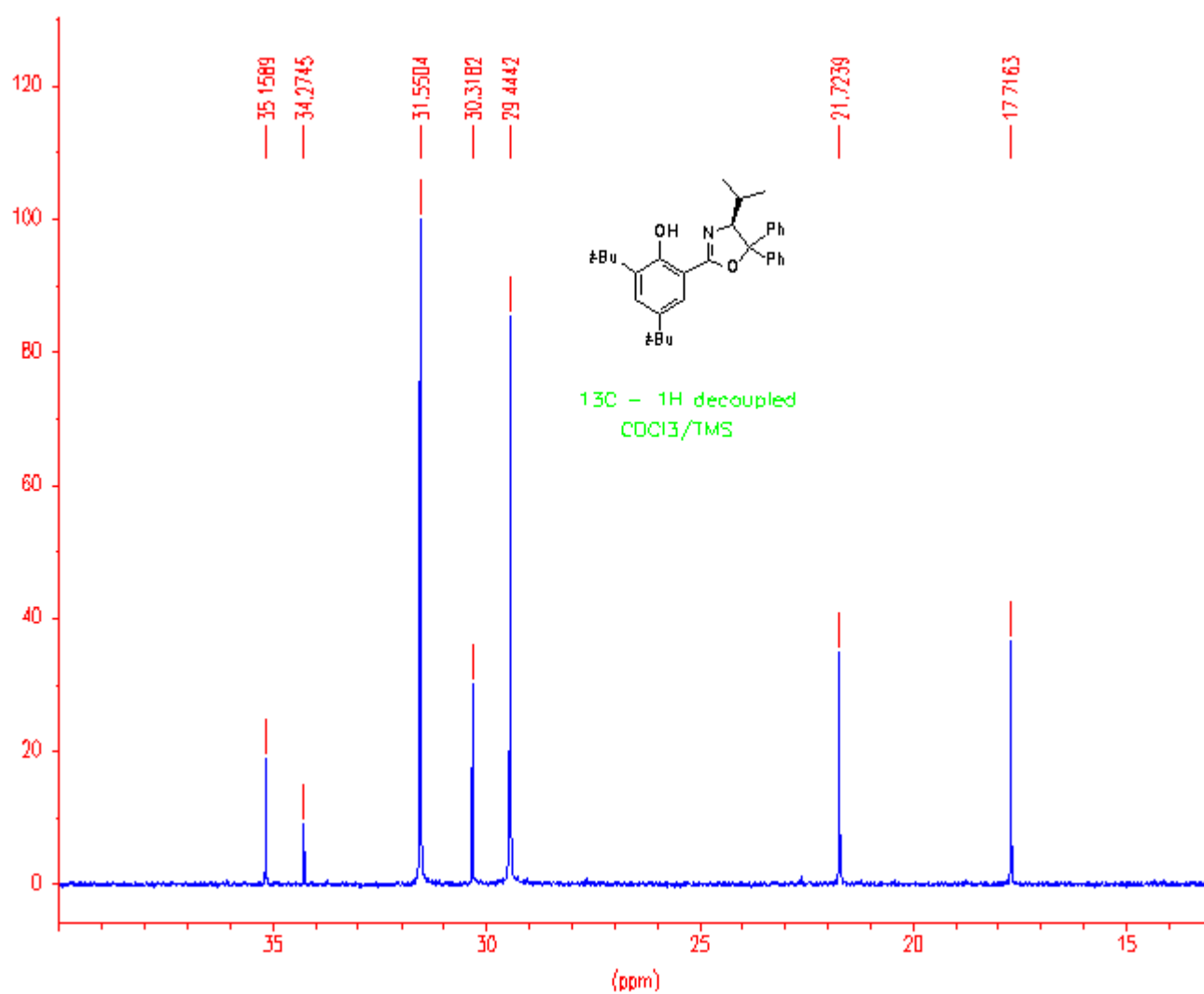


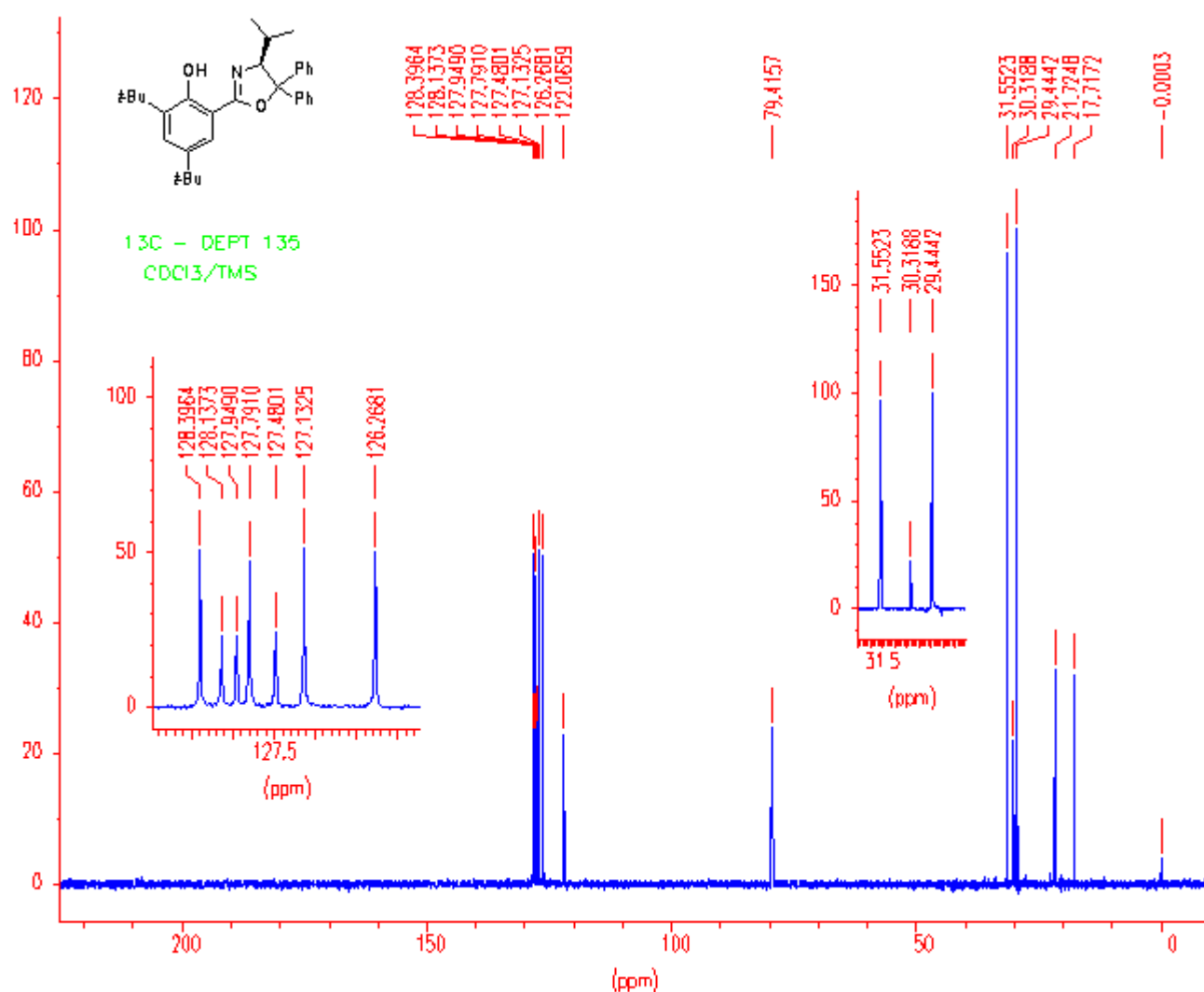




¹³C NMR (100 MHz, CDCl₃): *d* 164.21 (1C, O-C=N), 157.23 (1C, C_{ipso} α to OH), 144.79 (1C, C_{ipso} of phenyl), 140.20 and 140.00 (2C, C_{ipso} α to C(CH₃)₃ and C_{ipso} of phenyl), 136.52 (1C, C_{ipso} α to C(CH₃)₃), 128.40 (2C, C_{Hmeta} of phenyl), 128.15 (1C, C_{Hpara} of phenyl), 127.96 (1C, C_{Hpara} of phenyl), 127.80 (2C, C_{Hmeta} of phenyl), 127.49 (1C, C_H of phenol), 127.14 (2C, C_{Hortho} of phenyl), 126.28 (2C, C_{Hortho} of phenyl), 122.07 (1C, C_H of phenol), 109.78 (1C, C_{ipso} α to oxazoline), 91.68 (1C, C(Ph)₂CH), 79.42 (1C, C(Ph)₂CH), 35.16 (1C, C(CH₃)₃), 34.29 (1C, C(CH₃)₃), 31.55 (3C, C(CH₃)₃), 30.32 (1C, CH(CH₃)₂), 29.43 (3C, C(CH₃)₃), 21.73 (1C, CH(CH₃)₂), 17.72 (1C, CH(CH₃)₂).







HRMS (EI, 70 eV) m/z (%): calcd for C₃₂H₃₉NO₂ 469.2981 [M]⁺, found 469.2982 (15), 302 (11) [M - Ph₂CH]⁺, 237 (100) [C₁₇H₁₉N]⁺.

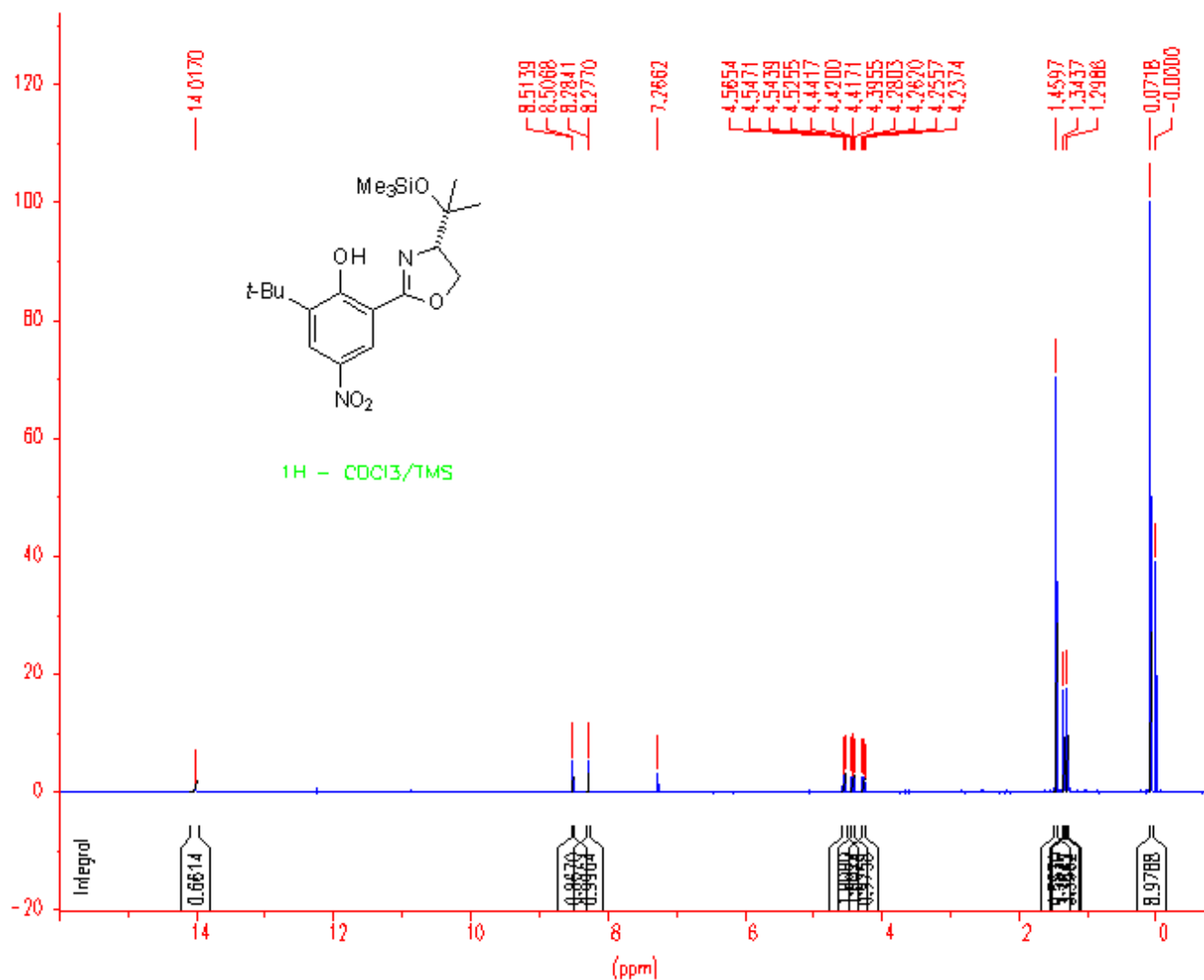
MS (FAB, *m*-nitrobenzylic alcohol matrix) m/z (rel intens): Calcd for C₃₂H₃₉NO₂ 469.3 [M]⁺, found 469 (81) [M]⁺, 302 (17), 260 (7), 237 (100).

[α]_D²⁸ = -206.6, [α]₅₇₈²⁸ = -216.4, [α]₅₄₆²⁸ = -249.5, [α]₄₃₆²⁸ = -460.0, [α]₃₆₅²⁸ = -809.4 (c = 1.0, CHCl₃).

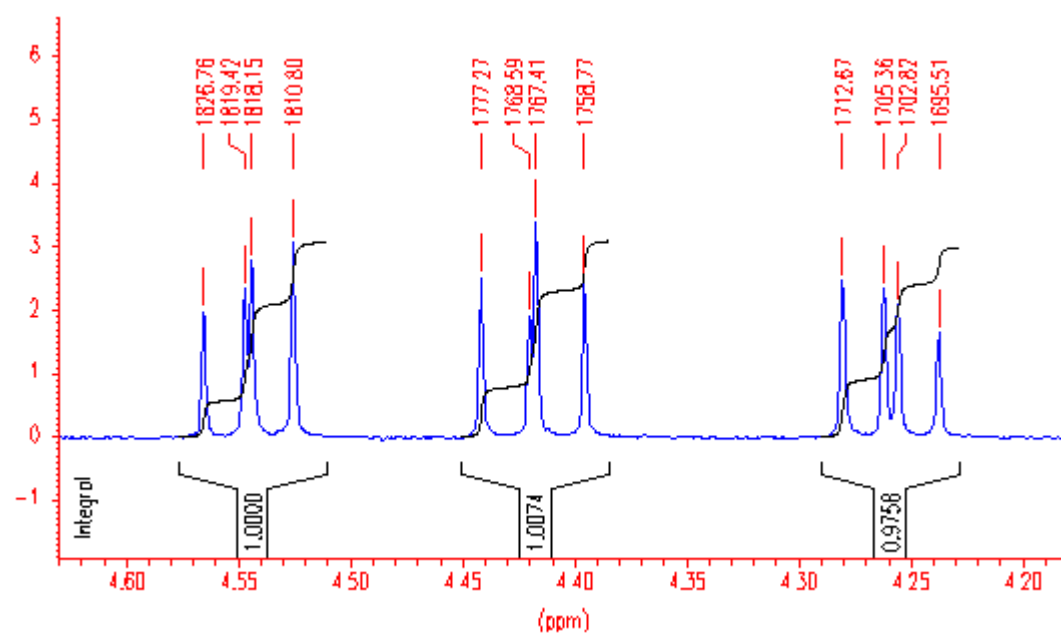
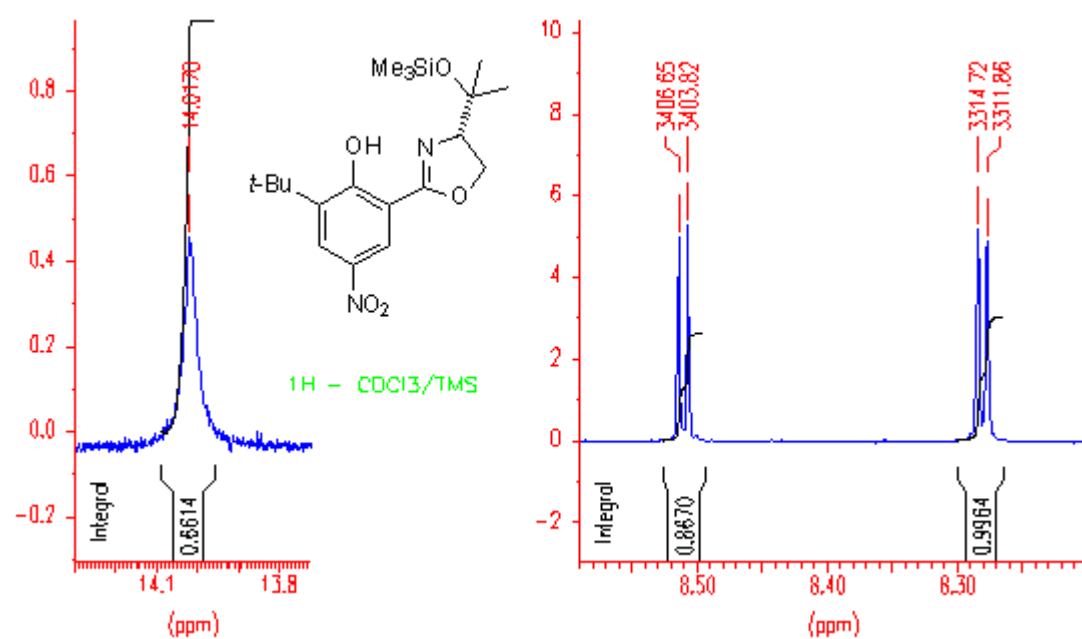
Anal. Calcd for C₃₂H₃₉NO₂: C, 81.83; H, 8.37; N, 2.98. Found: C, 81.75; H, 8.17; N, 2.91.

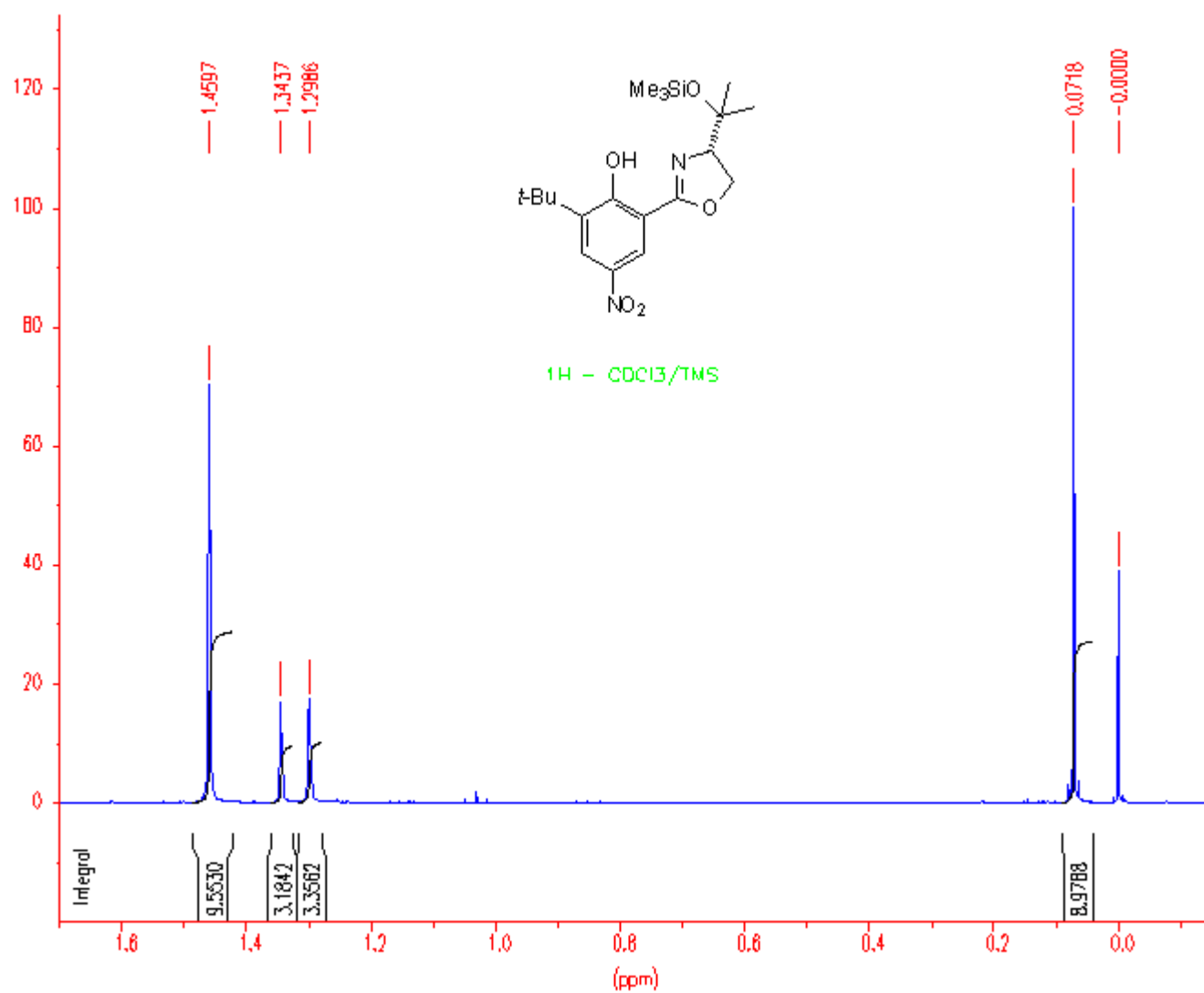
**(R)-2-tert-Butyl-6-[4-(1-methyl-1-trimethylsilyloxyethyl)-4,5-dihydro-2-oxazolyl]-4-nitrophenol
(R)-15a**

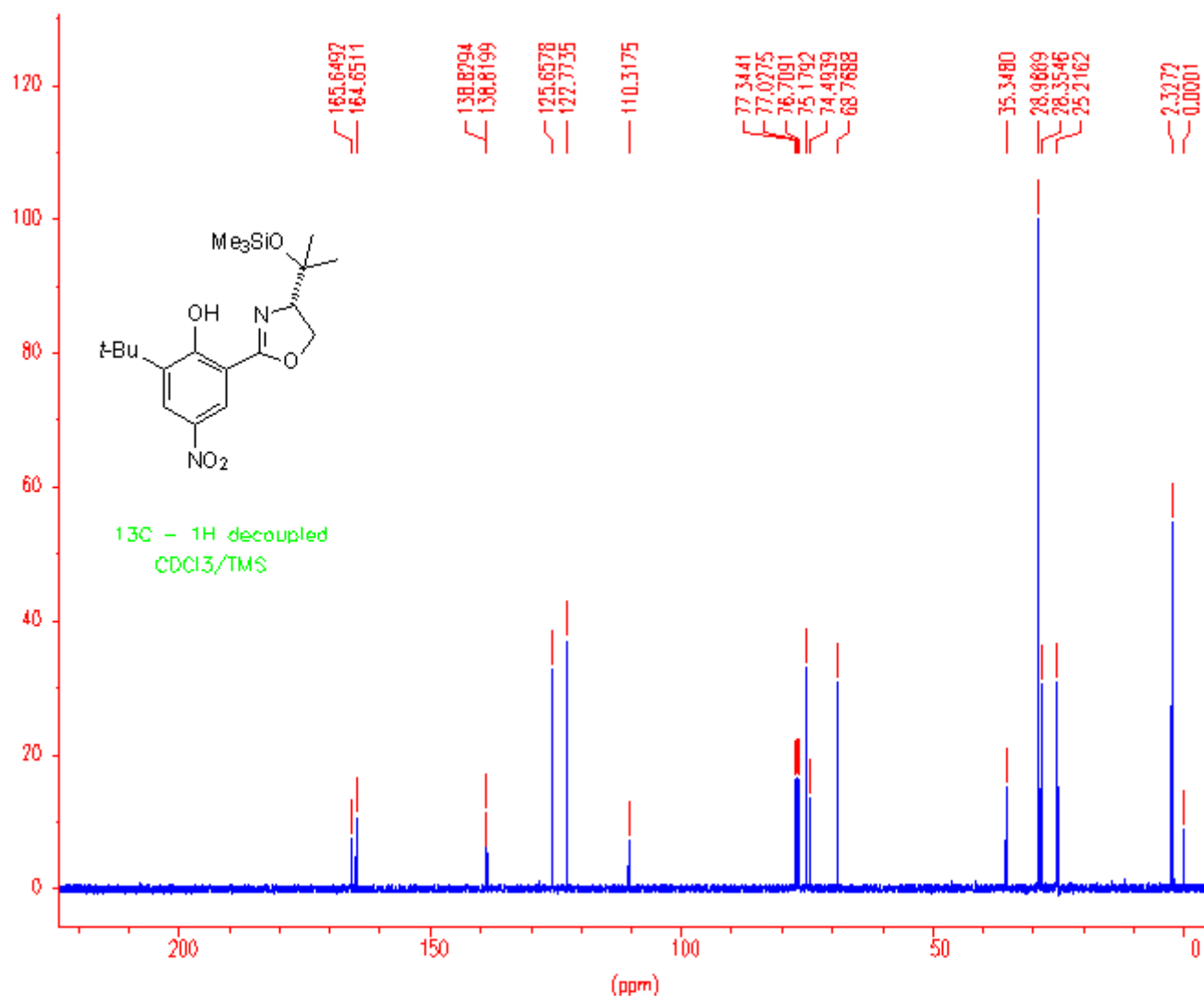
IR (neat, NaCl): $\tilde{\nu}$ 3107, 2964, 2919, 2876, 1819 (small, aromatic harmonic), 1642 (C=N), 1530, 1481, 1471, 1435, 1367, 1337, 1246, 1171, 1140, 1094, 1056, 974, 908, 842, 750, 708 cm^{-1} .



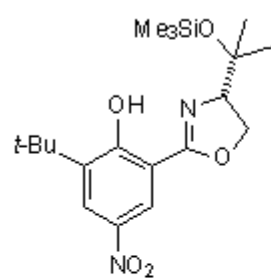
¹H NMR (400 MHz, CDCl₃): δ 14.02 (broad s, 1H, OH), 8.51 (d, 1H, J = 2.8 Hz, CH aromatic), 8.28 (d, 1H, J = 2.8 Hz, CH aromatic), 4.55 (dd, 1H, J = 8.6, 7.3 Hz, CH₂CH), 4.42 (dd, 1H, J = 9.9, 8.6 Hz, CH₂CH), 4.26 (dd, 1H, J = 9.9, 7.3 Hz, CH₂CH), 1.46 (s, 9H, C(CH₃)₃), 1.34 (s, 3H, C(CH₃)₂O), 1.30 (s, 3H, C(CH₃)₂O), 0.07 (s, 9H, OSi(CH₃)₃).



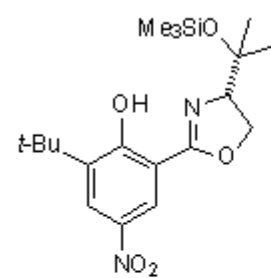
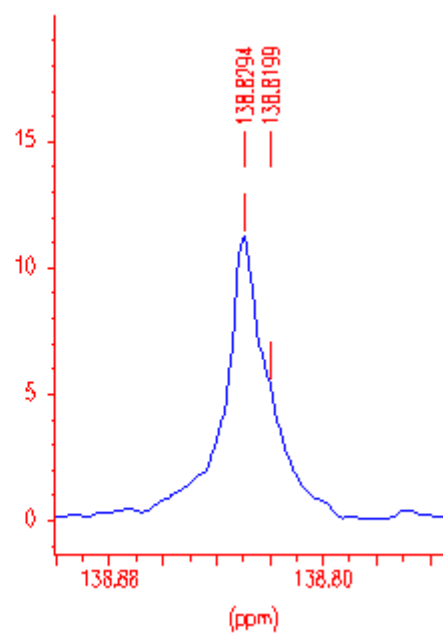
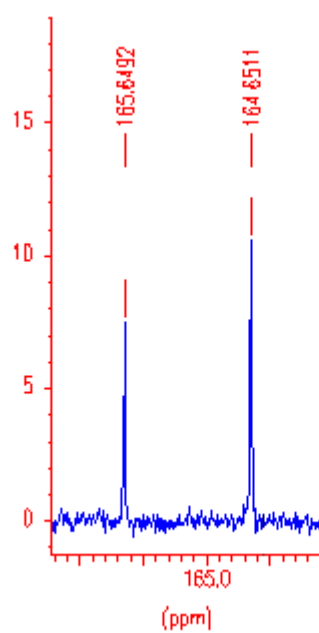




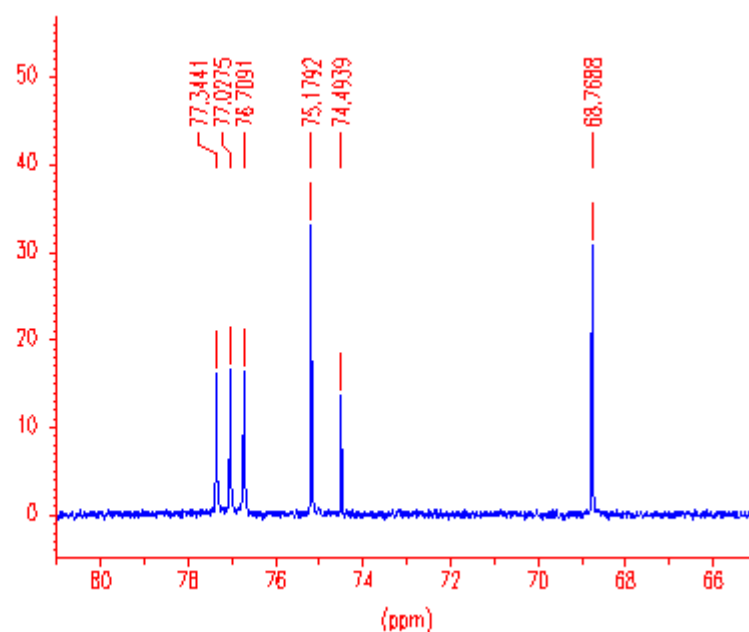
¹³C NMR (100 MHz, CDCl₃): *d* 165.65 (1C, O=C=N), 164.65 (1C, C_{ipso} α to OH), 138.83 and 138.82 (2C, C_{ipso} α to C(CH₃)₃ and C_{ipso} α to NO₂), 125.66 (1C, CH aromatic, correlates with proton at 8.28 ppm), 122.77 (1C, CH aromatic, correlates with proton at 8.51 ppm), 110.32 (1C, C_{ipso} α to oxazoline), 75.18 (1C, CH₂CH), 74.50 (1C, C(CH₃)₂O), 68.77 (1C, CH₂CH), 35.35 (1C, C(CH₃)₃), 28.97 (3C, C(CH₃)₃), 28.36 (1C, C(CH₃)₂O, correlates with protons at 1.34 ppm), 25.22 (1C, C(CH₃)₂O, correlates with protons at 1.30 ppm), 2.33 (3C, OSi(CH₃)₃).

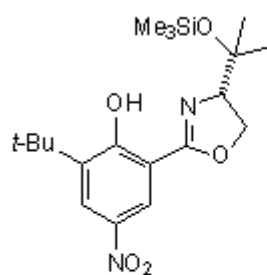
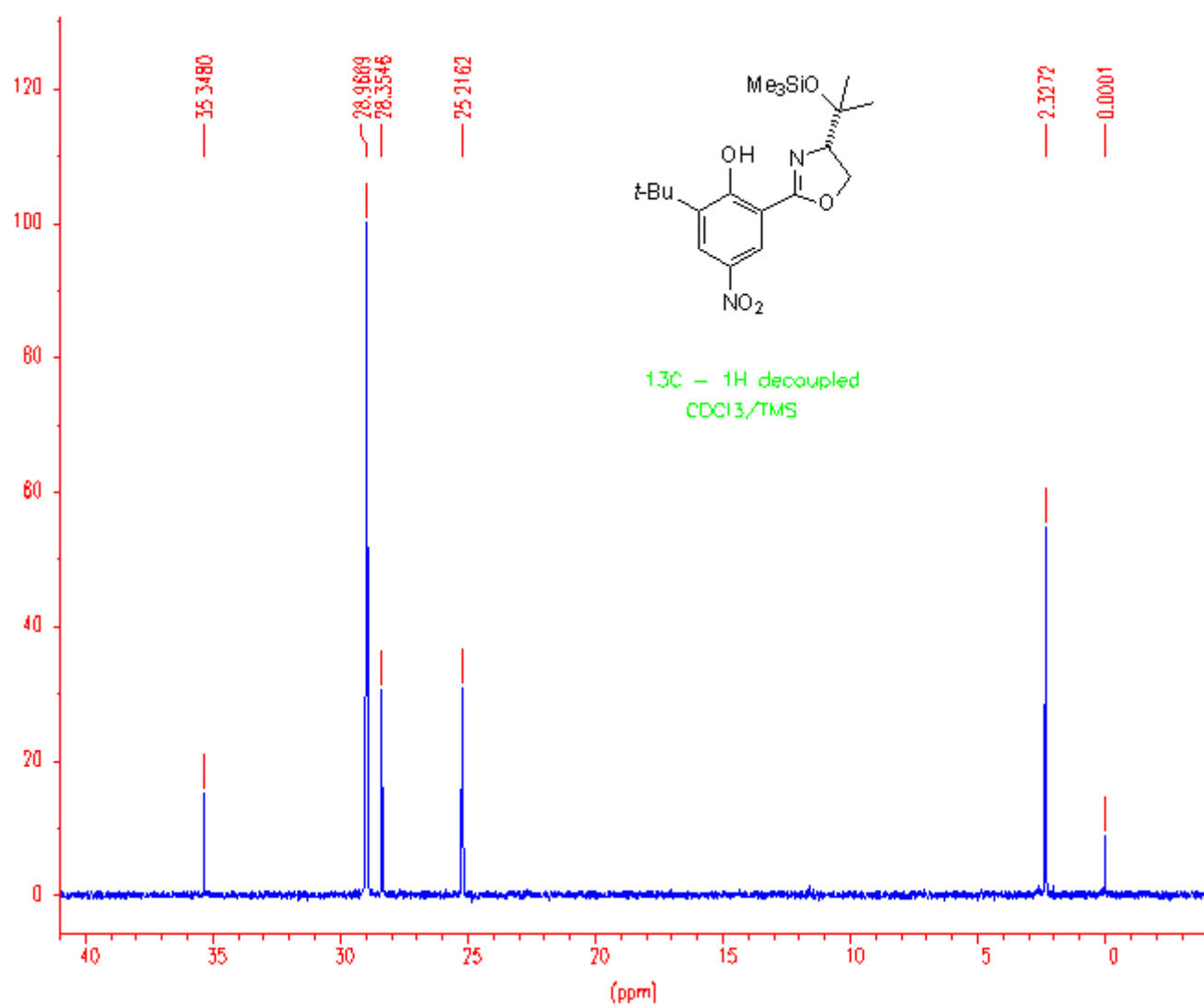


$^{13}\text{C} - ^1\text{H}$ decoupled
 CDCl_3/TMS



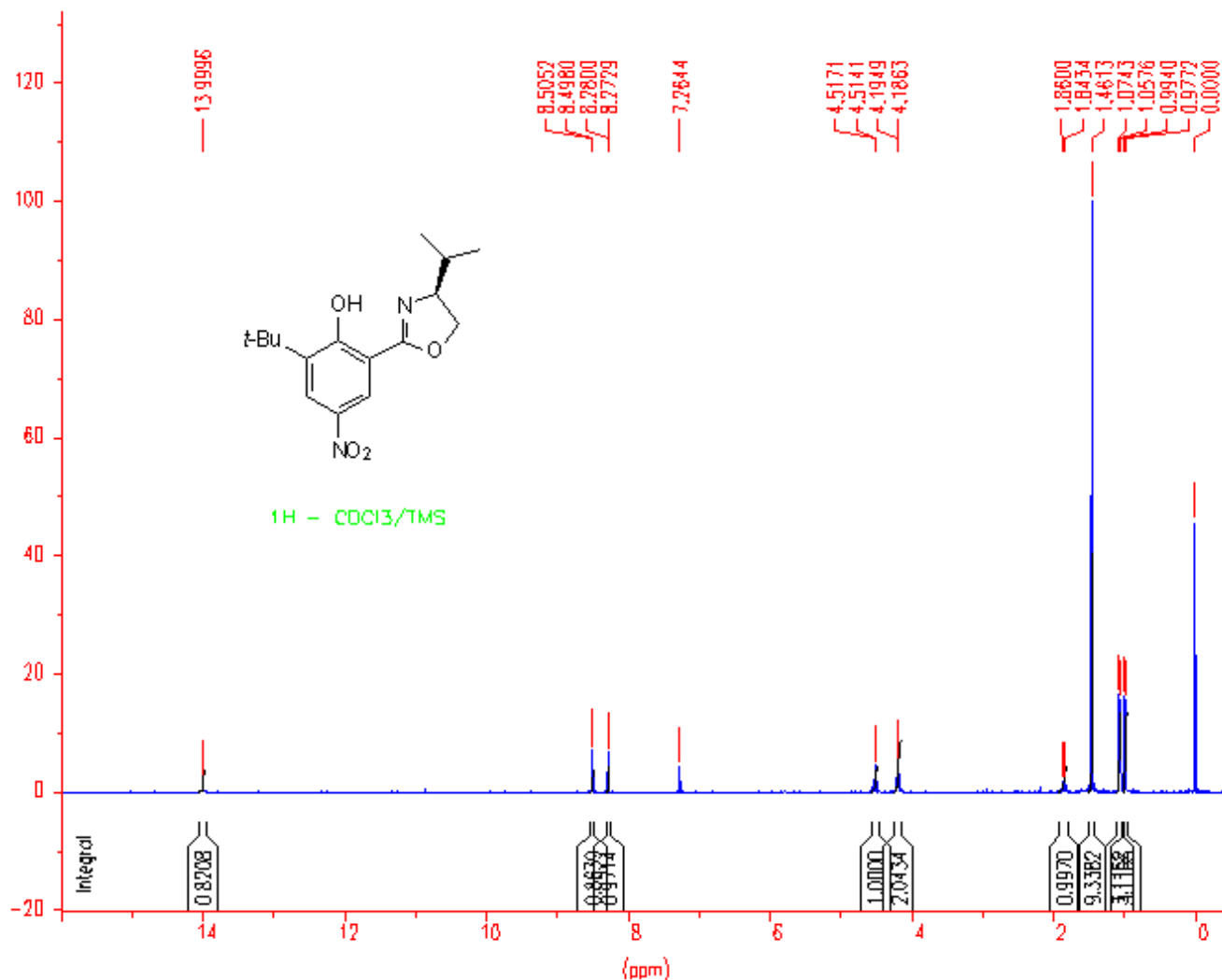
$^{13}\text{C} - ^1\text{H}$ decoupled
 CDCl_3/TMS



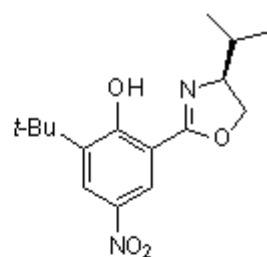


(S)-2-*tert*-Butyl-6-[4-*i*-propyl-4,5-dihydro-2-oxazolyl]-4-nitrophenol (S)-15b

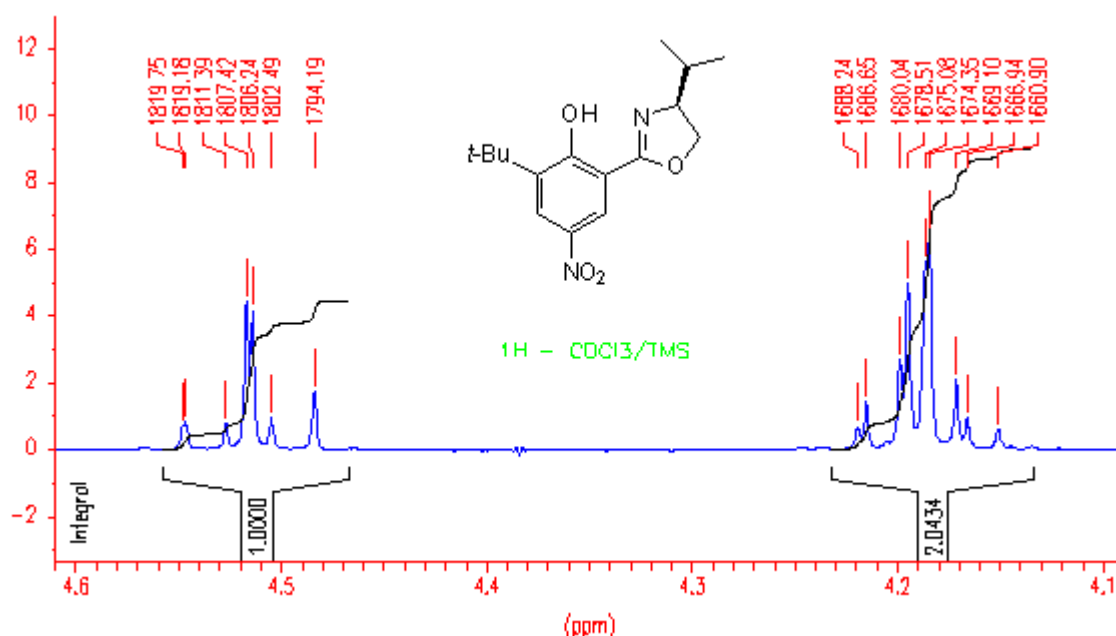
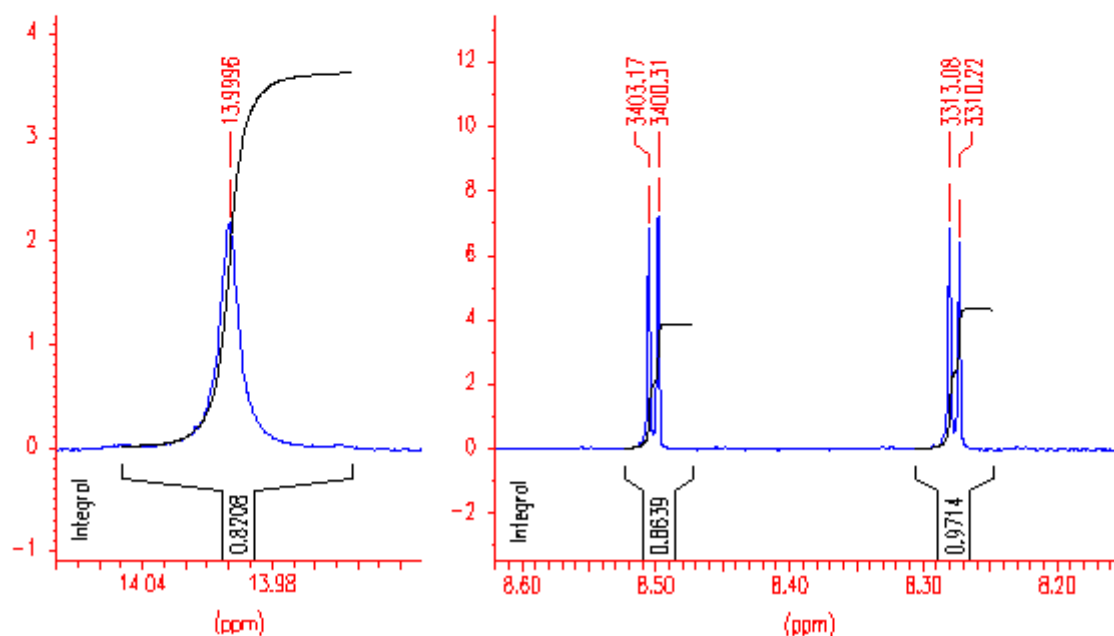
IR (Nujol, NaCl): $\tilde{\nu}$ 3104, 1816 (small, aromatic harmonic), 1640 (C=N), 1580, 1530, 1487, 1435, 1335, 1244, 1132, 1090, 1047, 969, 939, 867, 748, 705 cm^{-1} .

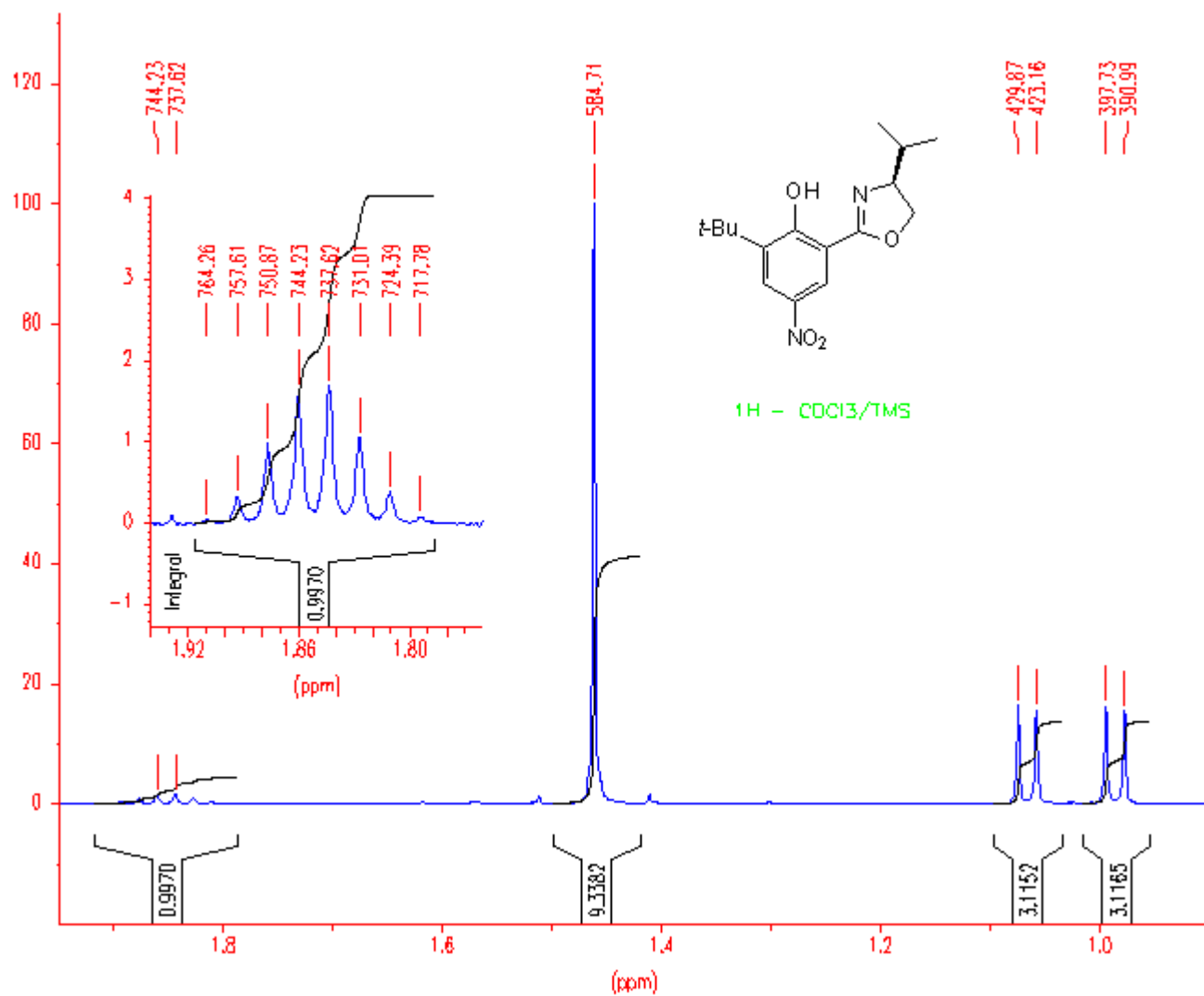


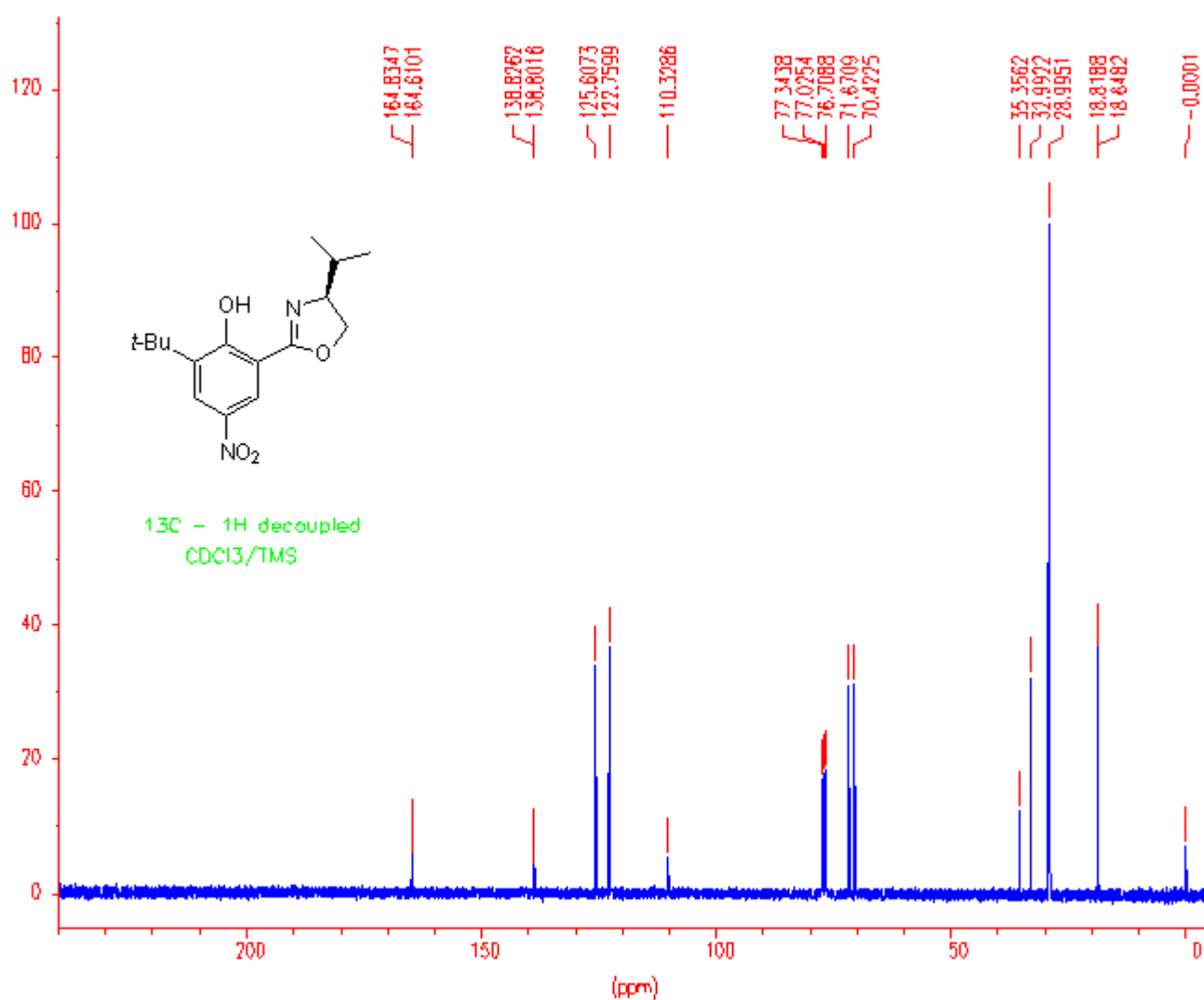
^1H NMR (400 MHz, CDCl_3): δ 14.00 (broad s, 1H, OH), 8.50 (d, 1H, $J = 2.8$ Hz, CH aromatic), 8.28 (d, 1H, $J = 2.8$ Hz, CH aromatic), 4.55-4.48 (m, 1H, CH_2CH), 4.23-4.14 (m, 2H, CH_2CH and CH_2CH), 1.85 (qqd, 1H, $J = 6.7, 6.7, 6.3$ Hz, $\text{CH}(\text{CH}_3)_3$), 1.46 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.07 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.99 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$).



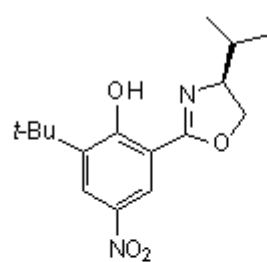
$^1\text{H} - \text{CDCl}_3/\text{TMS}$



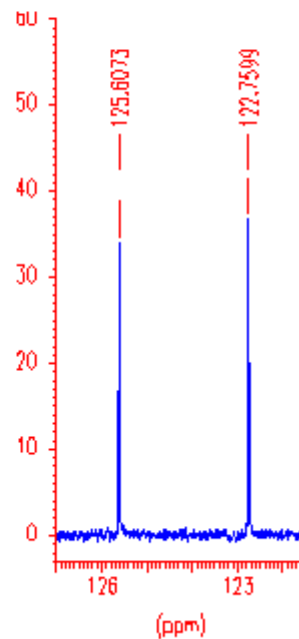
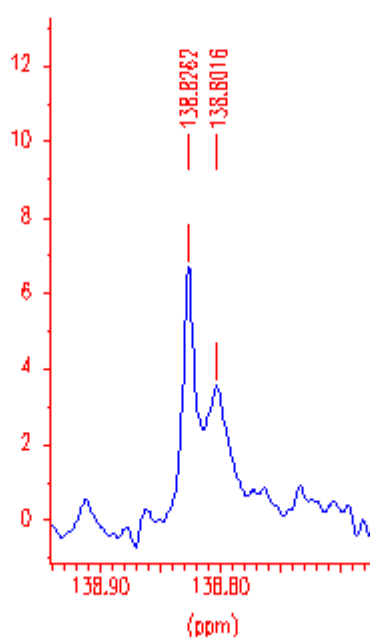
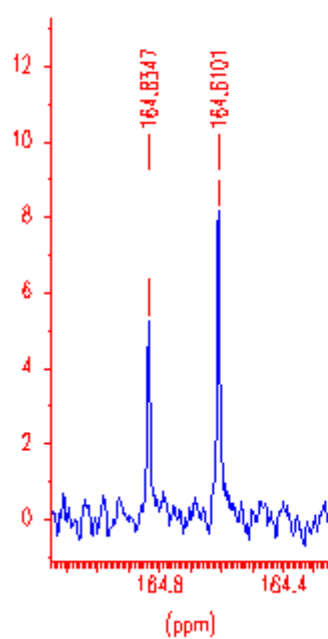


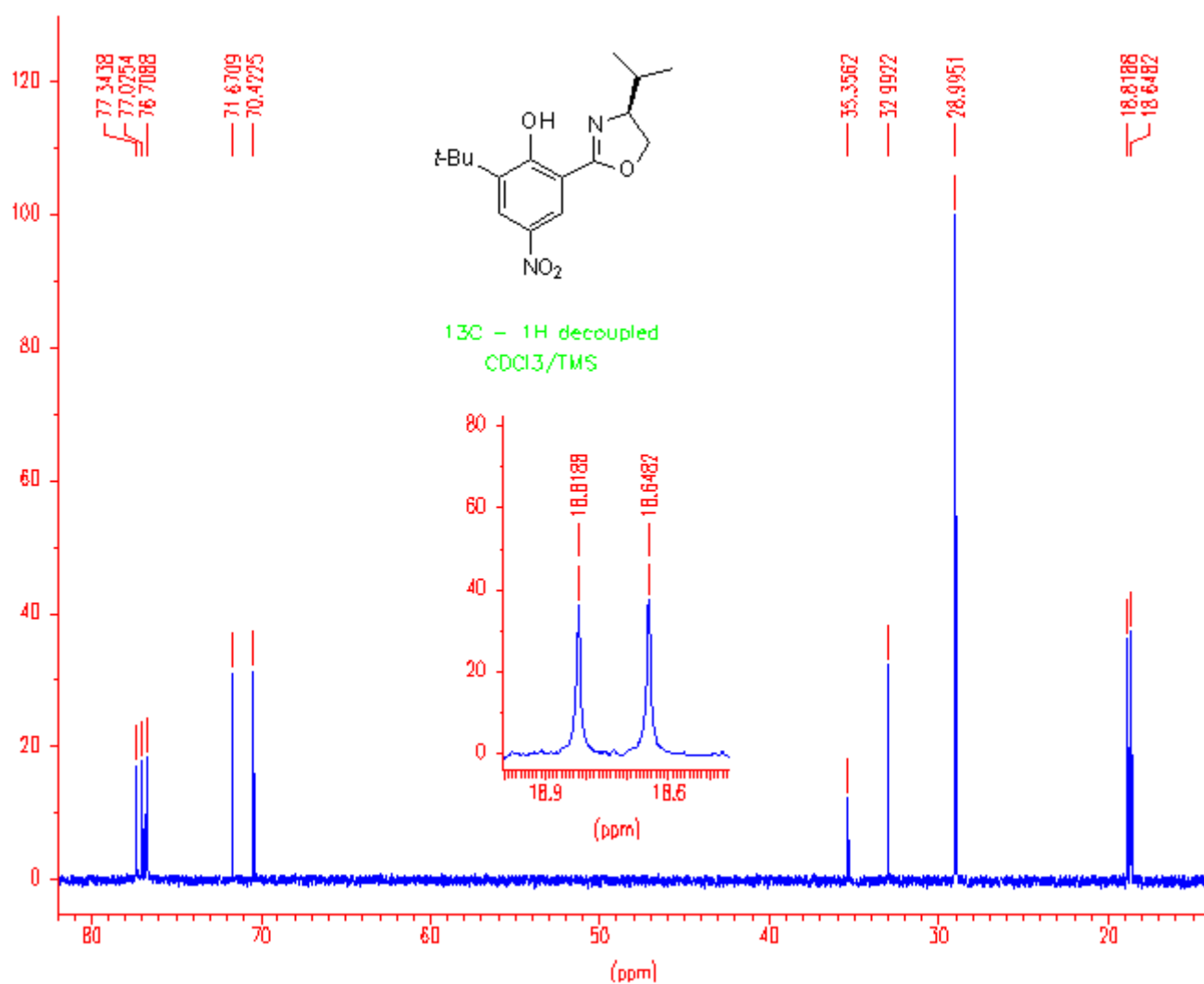


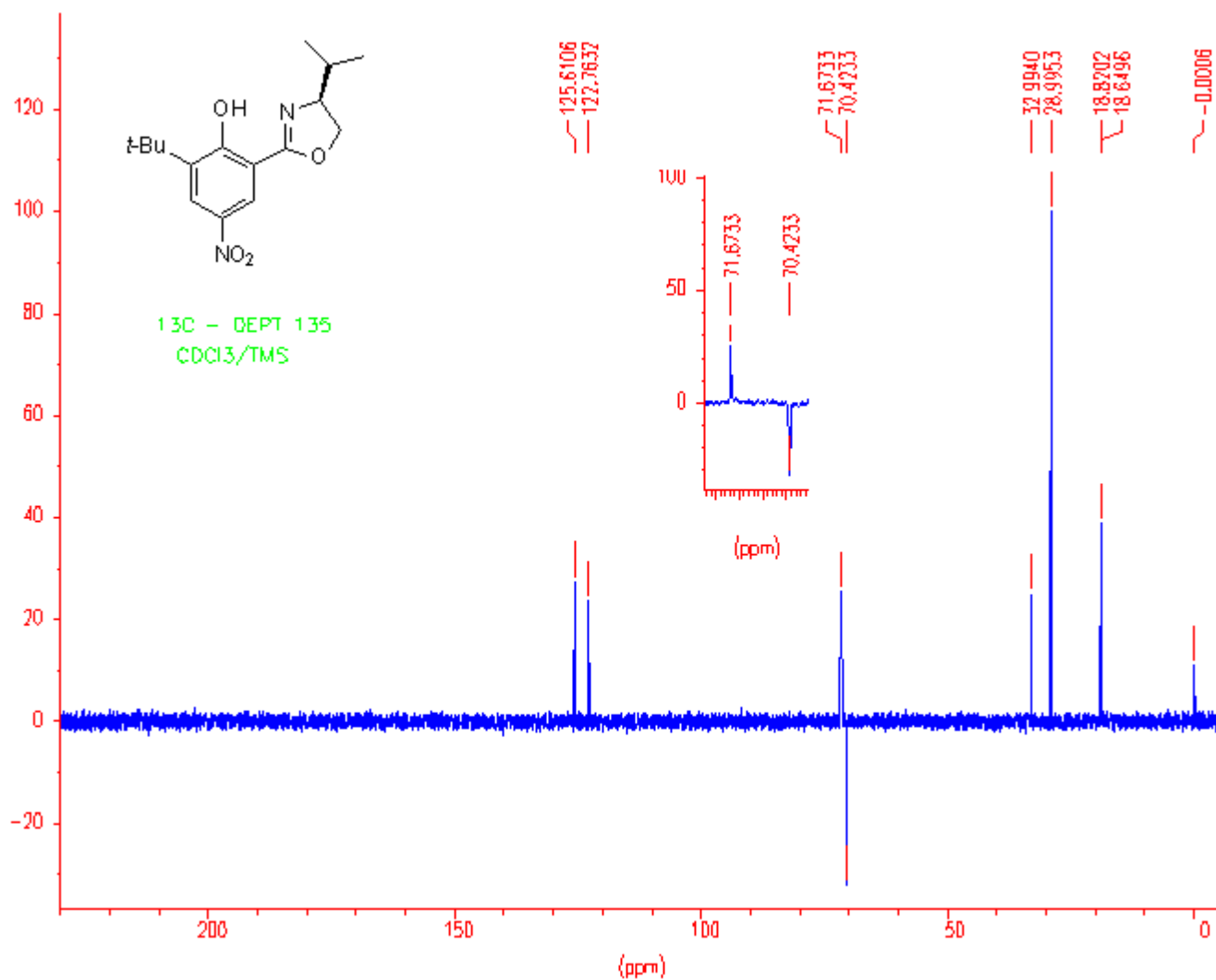
¹³C NMR (100 MHz, CDCl₃): *d* 164.84 and 164.61 (2C, O-C=N and C_{ipso} α to OH), 138.83 and 138.80 (2C, C_{ipso} α to C(CH₃)₃ and C_{ipso} α to NO₂), 125.61 (1C, CH aromatic, correlates with proton at 8.28 ppm), 122.76 (1C, CH aromatic, correlates with proton at 8.50 ppm), 110.33 (1C, C_{ipso} α to oxazoline), 71.67 (1C, CH₂CH), 70.42 (1C, CH₂CH), 35.36 (1C, C(CH₃)₃), 32.99 (1C, CH(CH₃)₂), 29.00 (3C, C(CH₃)₃), 18.82 (1C, CH(CH₃)₂, correlates with protons at 1.07 ppm), 18.65 (1C, CH(CH₃)₂, correlates with protons at 0.99 ppm).



¹³C - ¹H decoupled
CDCl₃/TMS







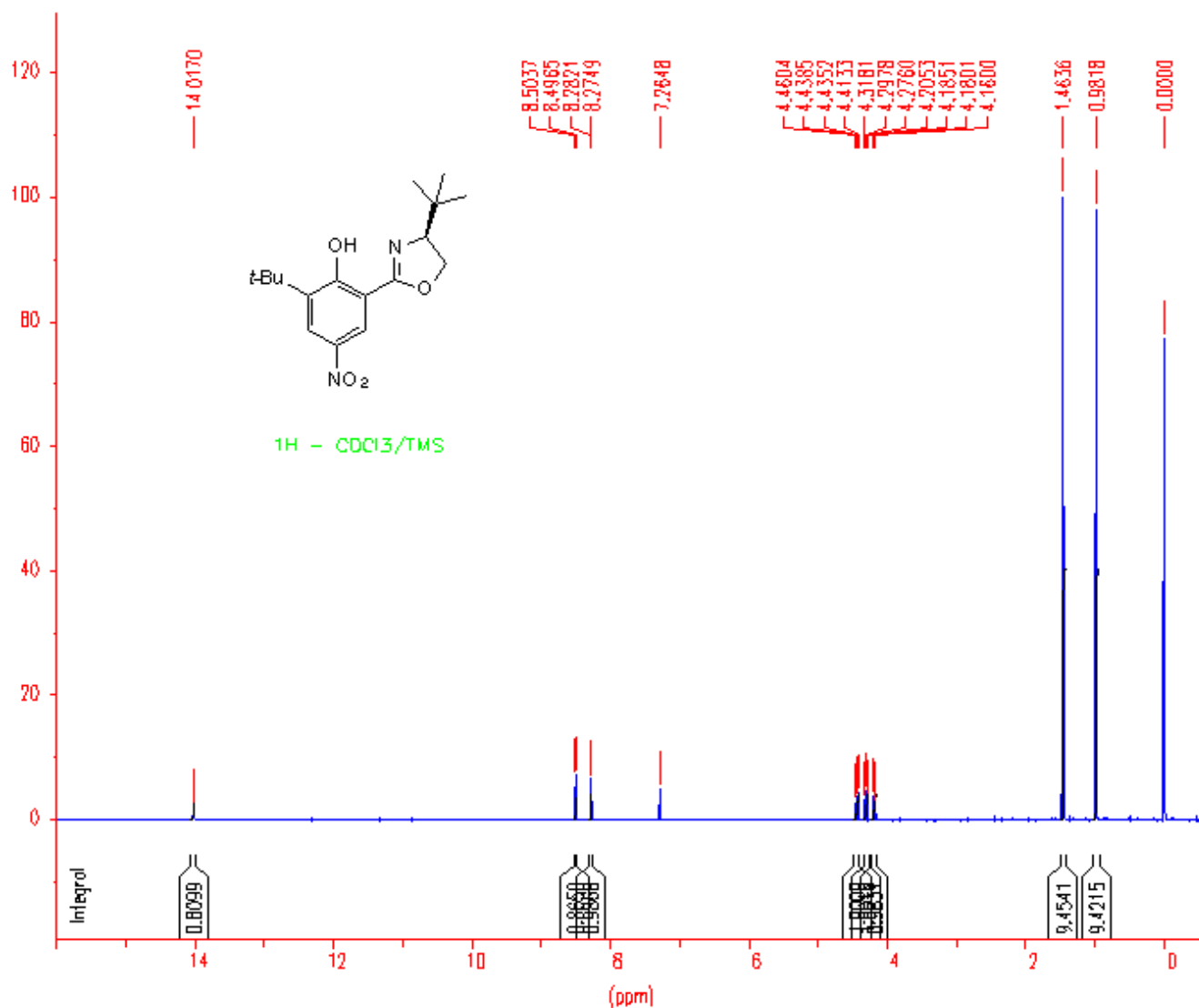
MS (EI, 70 eV) m/z (rel intens) 306 (44) $[M]^+$, 291 (100) $[M - CH_3]^+$, 264 (79), 263 (80) $[M - C_3H_7]^+$, 221 (30), 206 (23) $[M - C_3H_7 - C_4H_9]^+$, 177 (16), 160 (16), 131 (39), 85 (61), 73 (37), 57 (28), 41 (47).

$[\alpha]_D^{24} = -44.8$, $[\alpha]_{578}^{24} = -47.1$, $[\alpha]_{546}^{24} = -54.7$ ($c = 2.6$, $CHCl_3$).

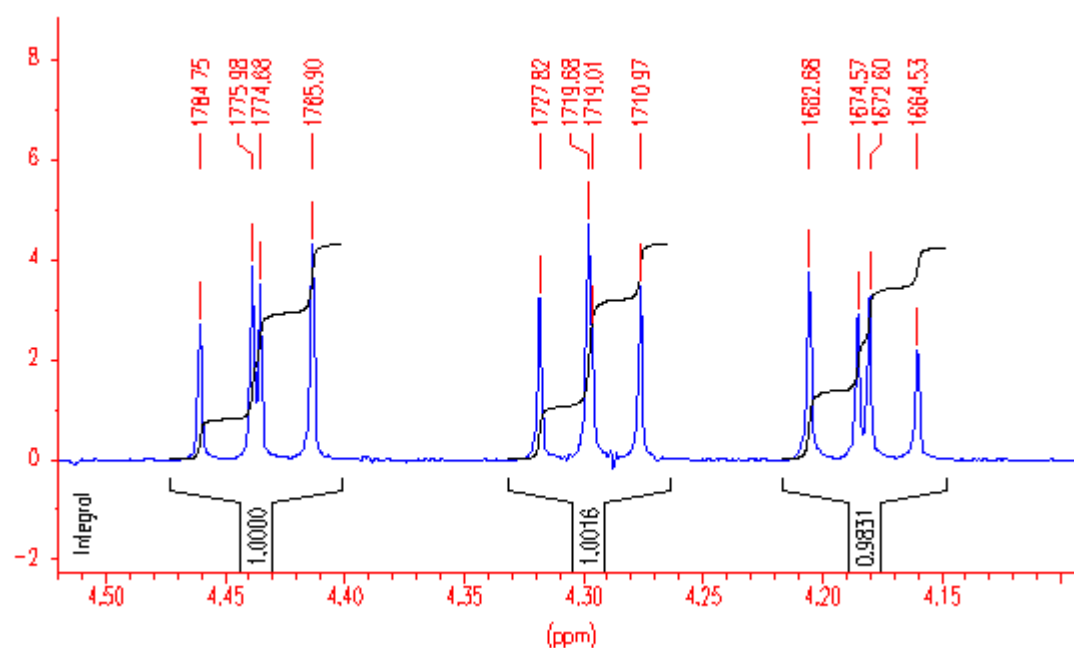
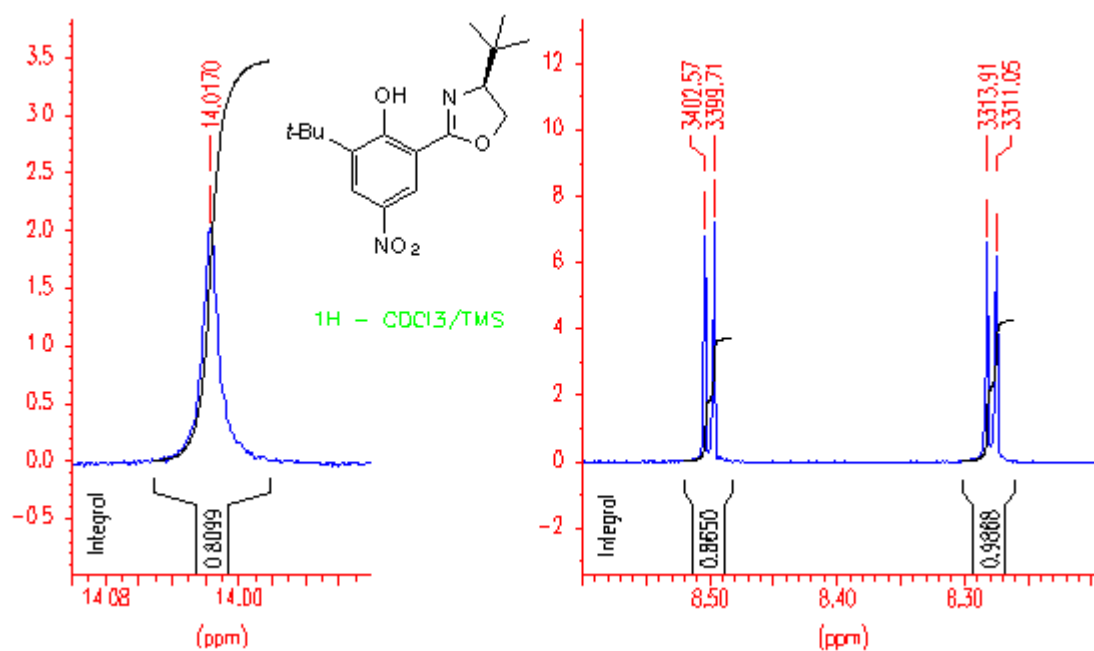
Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.69; H, 7.33; N, 9.13.

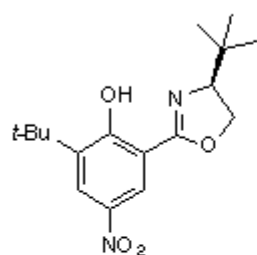
(S)-2-tert-Butyl-6-[4-tert-butyl-4,5-dihydro-2-oxazolyl]-4-nitrophenol (S)-15c

IR (Nujol, NaCl): $\tilde{\nu}$ 3109, 1825 (very small, aromatic harmonic), 1815 and 1804 (small, aromatic harmonics), 1642 (C=C), 1617, 1530, 1443, 1365, 1333, 1299, 1274, 1242, 1136, 1091, 1029, 977, 840, 748, 705 cm^{-1} .

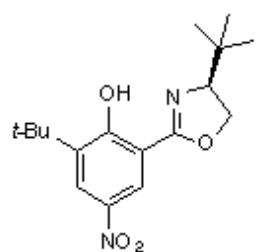
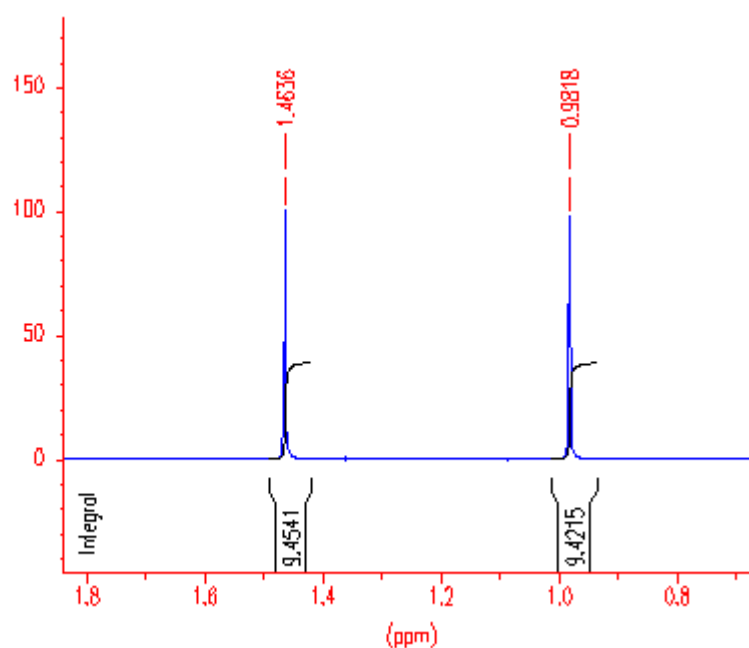


^1H NMR (400 MHz, CDCl_3): 14.01 (broad s, 1H, OH), 8.50 (d, 1H, $J = 2.8$ Hz, CH aromatic), 8.28 (d, 1H, $J = 2.8$ Hz, CH aromatic), 4.44 (dd, 1H, $J = 10.0, 8.8$ Hz, CH₂CH), 4.30 (dd, 1H, $J = 8.8, 8.1$ Hz, CH₂CH), 4.18 (dd, 1H, $J = 10.0, 8.1$ Hz, CH₂CH), 1.46 (s, 9H, C(CH₃)₃), 0.98 (s, 9H, C(CH₃)₃).

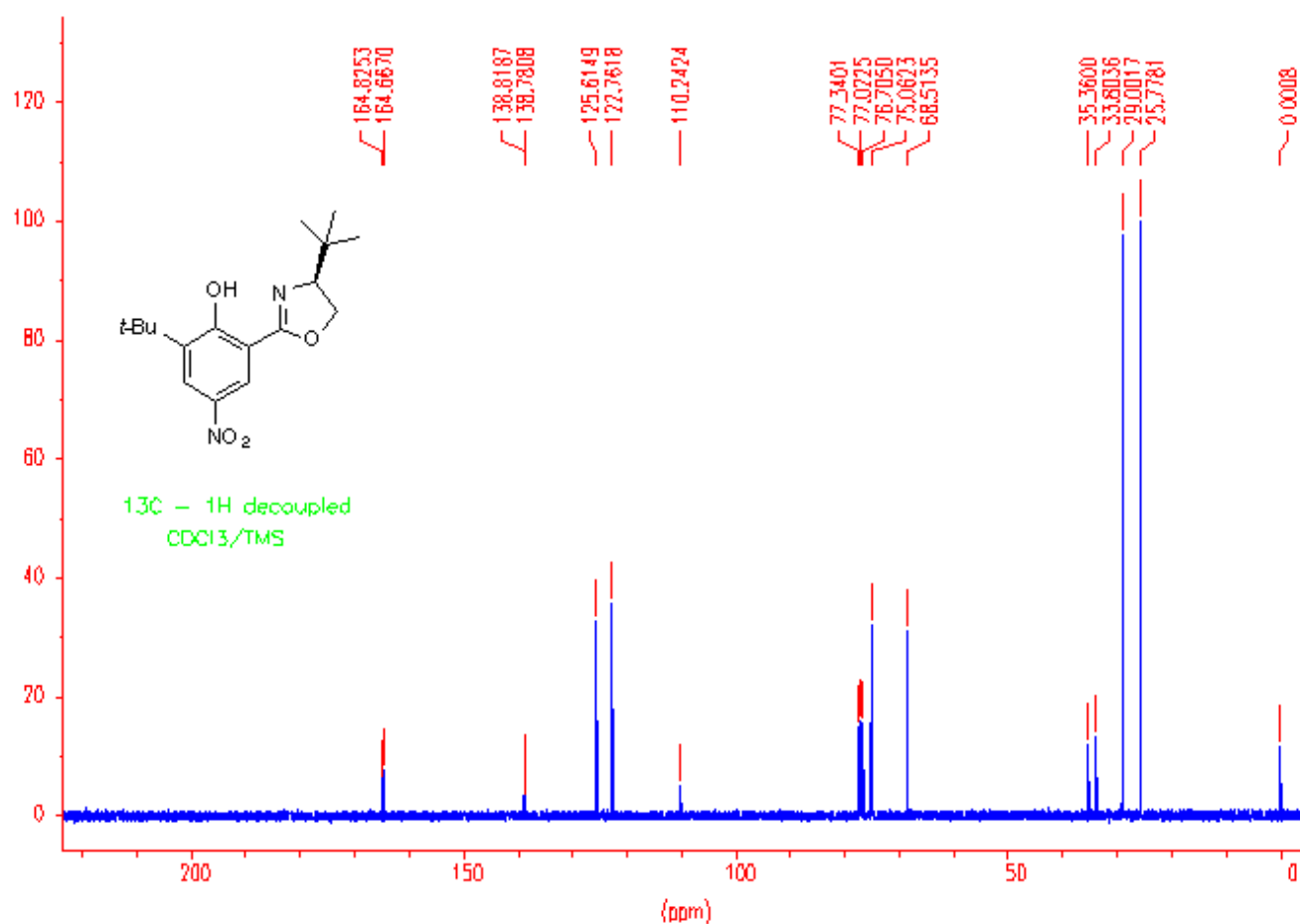




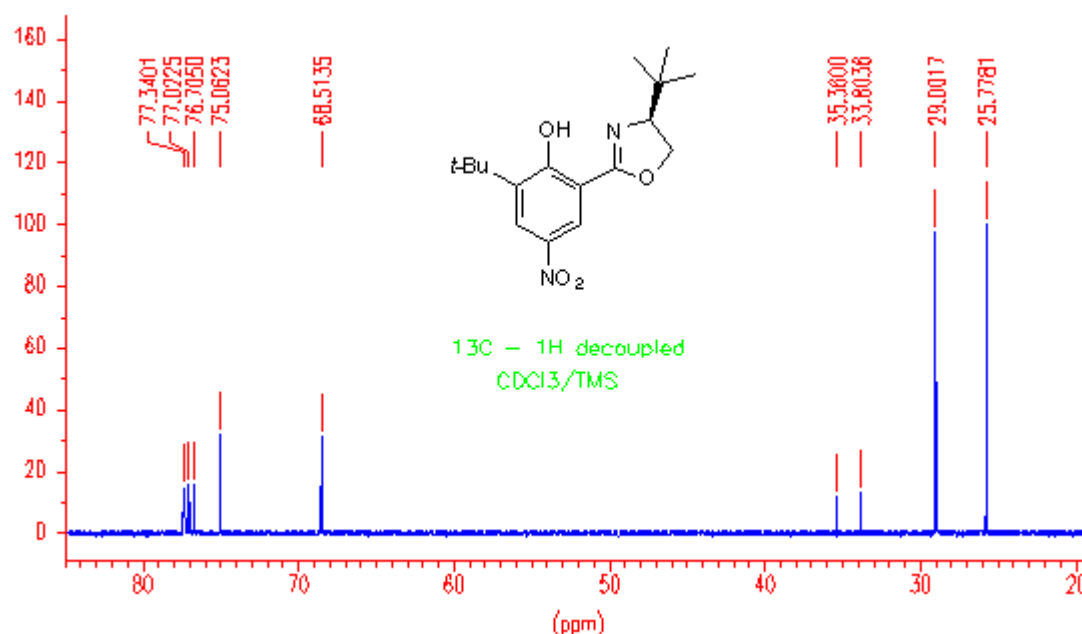
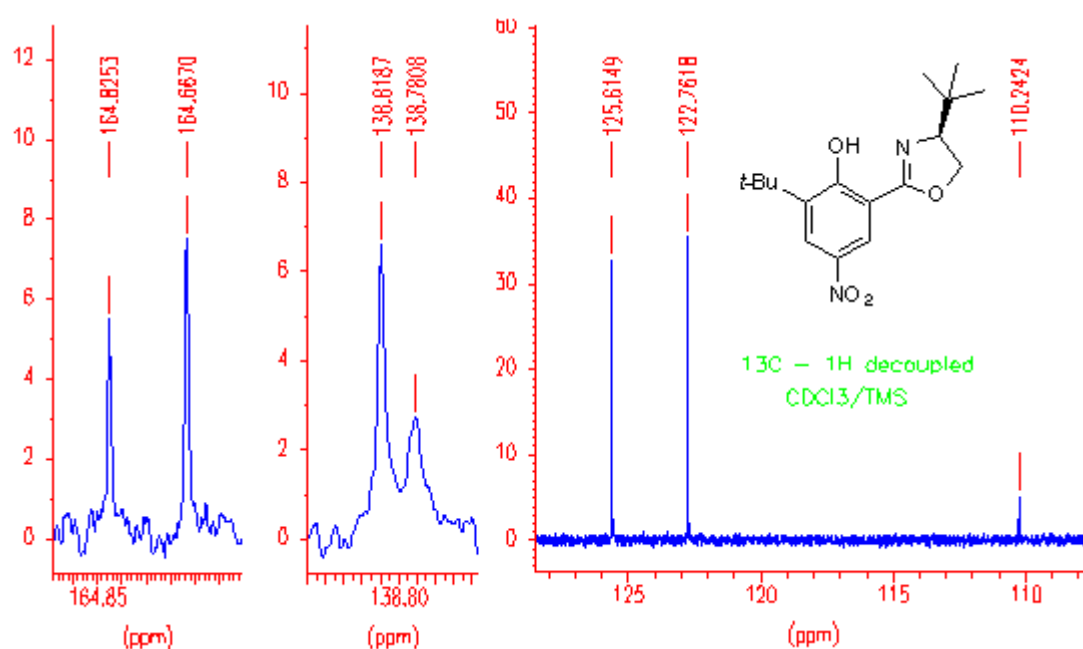
¹H - CDCl₃/TMS

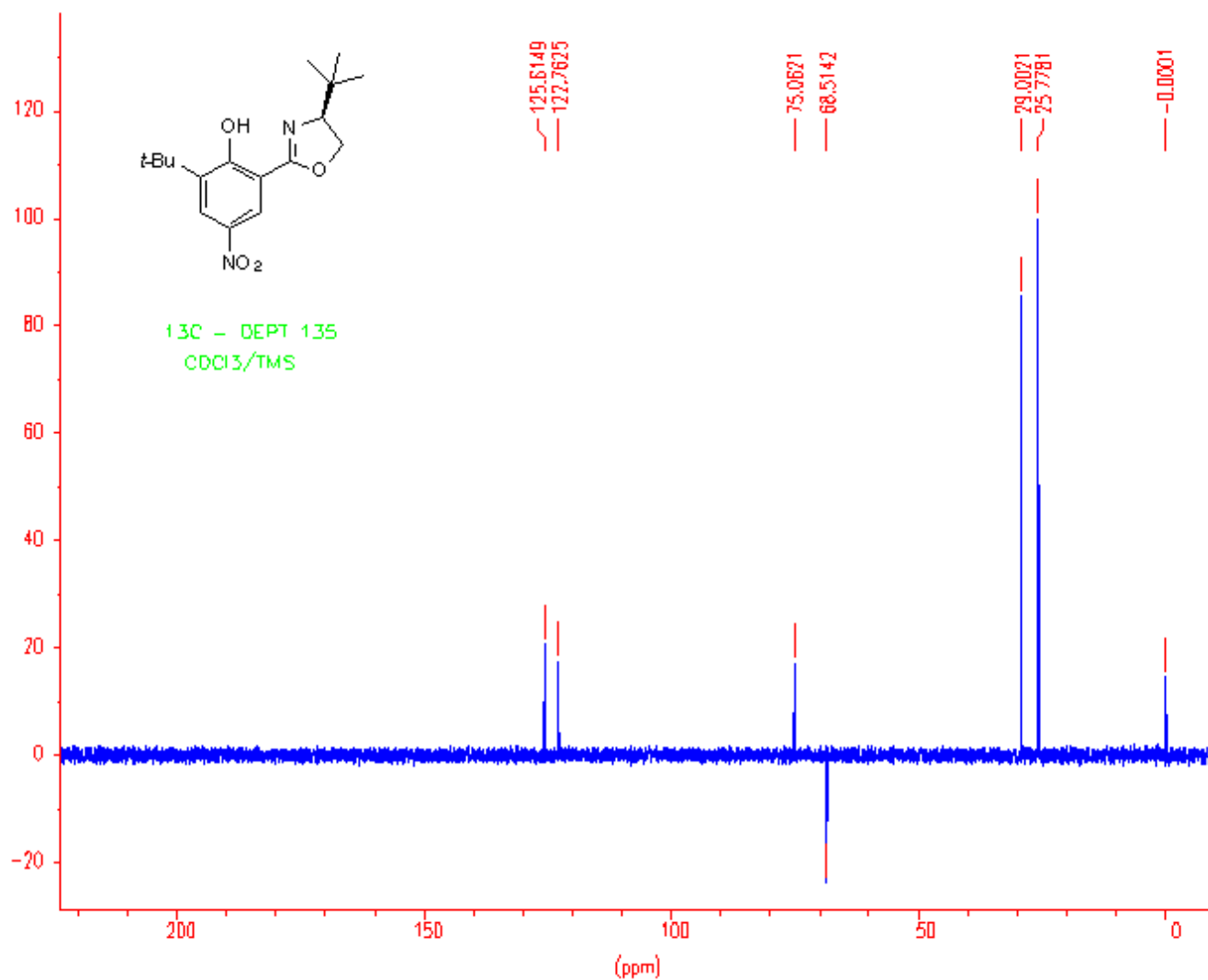


¹³C - ¹H decoupled
CDCl₃/TMS



^{13}C NMR (100 MHz, CDCl_3): δ 164.84 and 164.67 (1C, $\text{O}-\text{C}=\text{N}$ and $1\text{C}_{\text{ipso}} \alpha$ to OH), 138.83 and 138.80 (2C, $\text{C}_{\text{ipso}} \alpha$ to $\text{C}(\text{CH}_3)_3$ and $\text{C}_{\text{ipso}} \alpha$ to NO_2), 125.62 (1C, CH aromatic, correlates with proton at 8.28 ppm), 122.76 (1C, CH aromatic, correlates with proton at 8.50 ppm), 110.25 (1C, $\text{C}_{\text{ipso}} \alpha$ to oxazoline), 75.07 (1C, CH_2CH), 68.52 (1C, CH_2CH), 35.36 (1C, $\text{C}(\text{CH}_3)_3$), 33.81 (1C, $\text{C}(\text{CH}_3)_3$), 29.01 (3C, $\text{C}(\text{CH}_3)_3$), 25.78 (3C, $\text{C}(\text{CH}_3)_3$ of oxazoline).





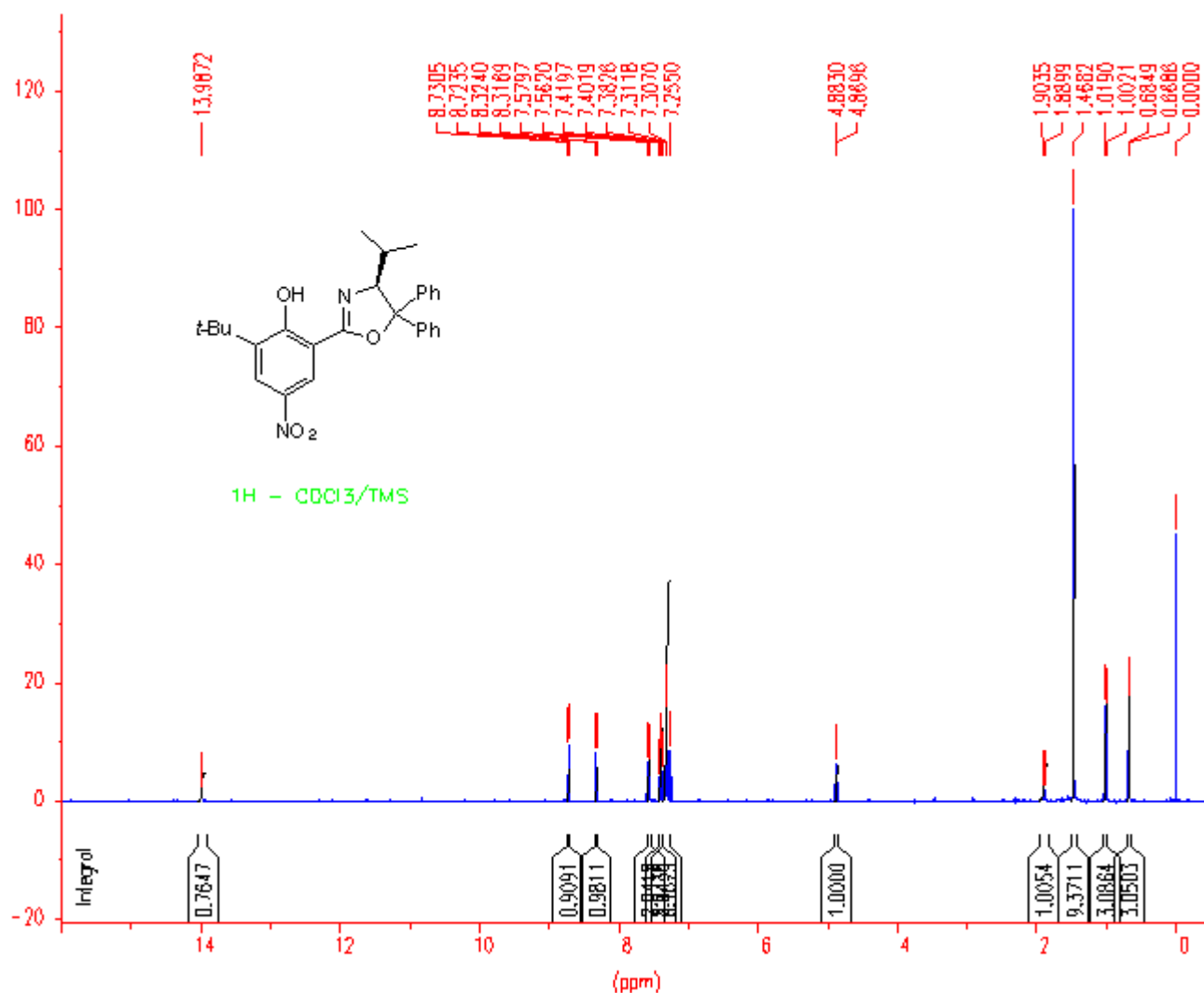
MS (EI, 70 eV) m/z (rel intens) 320 (45) $[M]^+$, 305 (100) $[M - CH_3]^+$, 277 (64) $[M - C_3H_7]^+$, 263 (18) $[M - C_4H_9]^+$, 247 (16), 235 (10), 221 (21), 206 (27), 177 (13), 160 (17), 85 (34), 57 (52) $[C_4H_9]^+$, 41 (49).

$[\alpha]_D^{27} = -32.4$, $[\alpha]_{578}^{27} = -34.0$, $[\alpha]_{546}^{27} = -39.5$ ($c = 2.2$, $CHCl_3$).

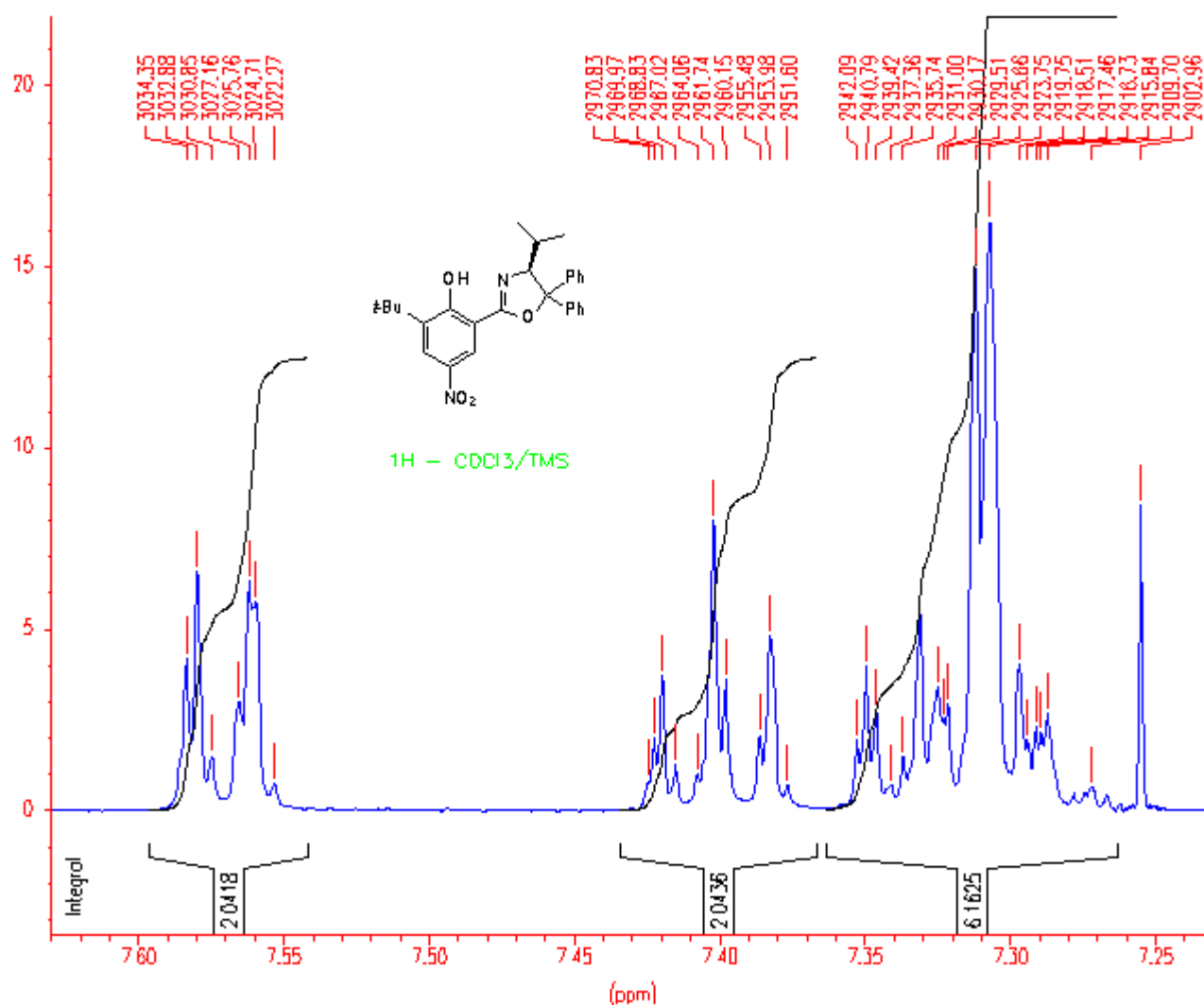
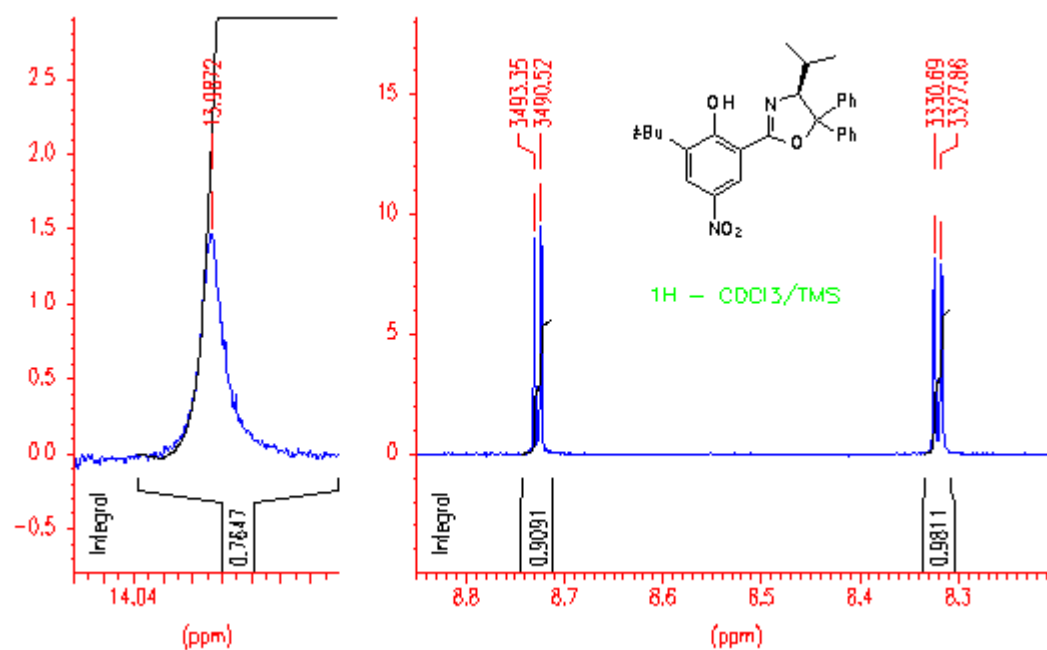
Anal. Calcd for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74. Found: C, 63.95; H, 7.36; N, 8.87.

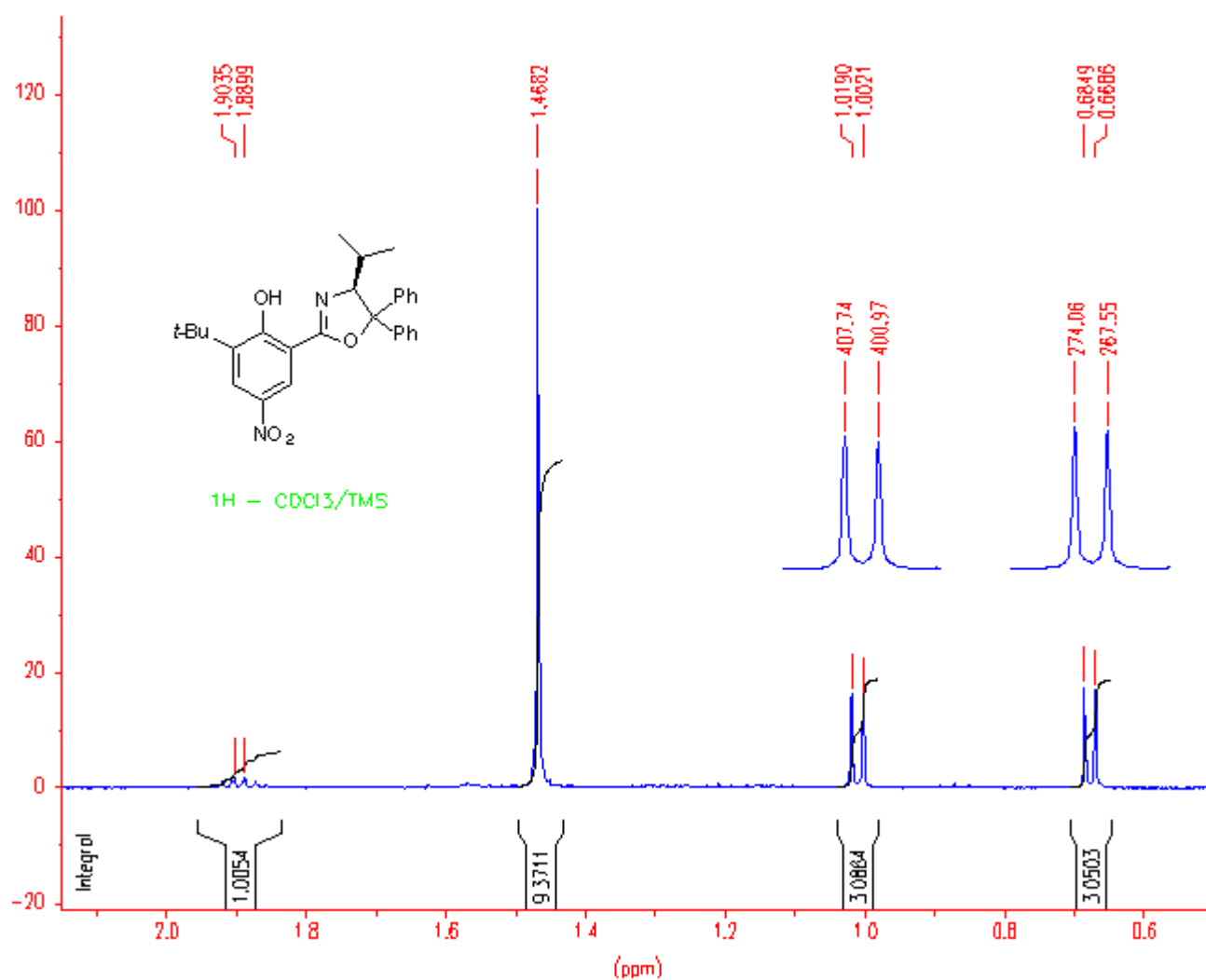
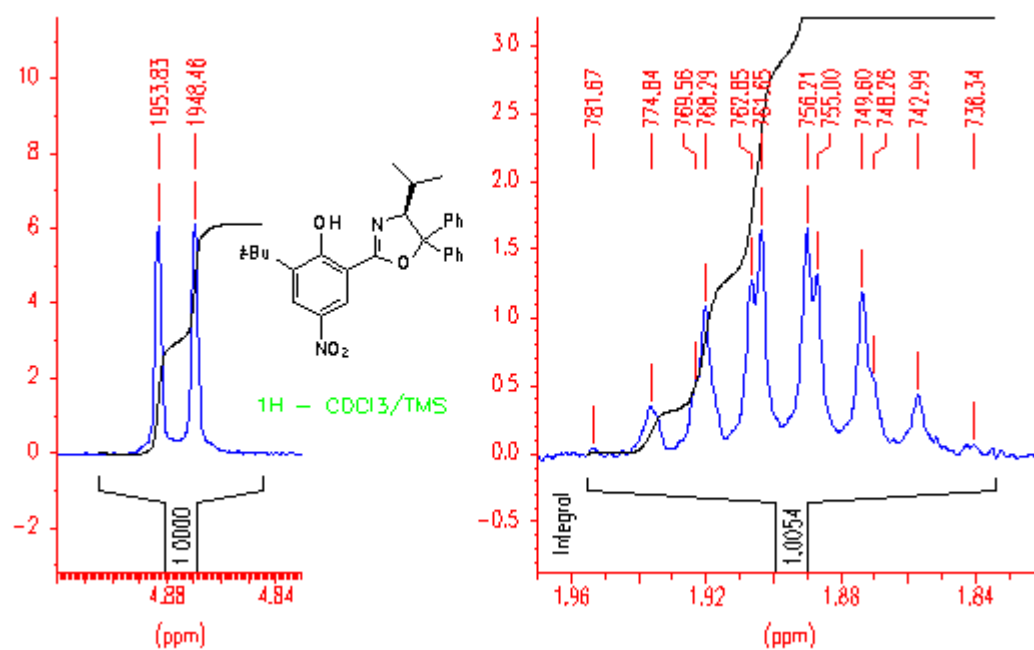
(S)-2-*tert*-butyl-6-[5,5-diphenyl-4-*i*-propyl-4,5-dihydro-2-oxazolyl]-4-nitrophenol (S)-15d

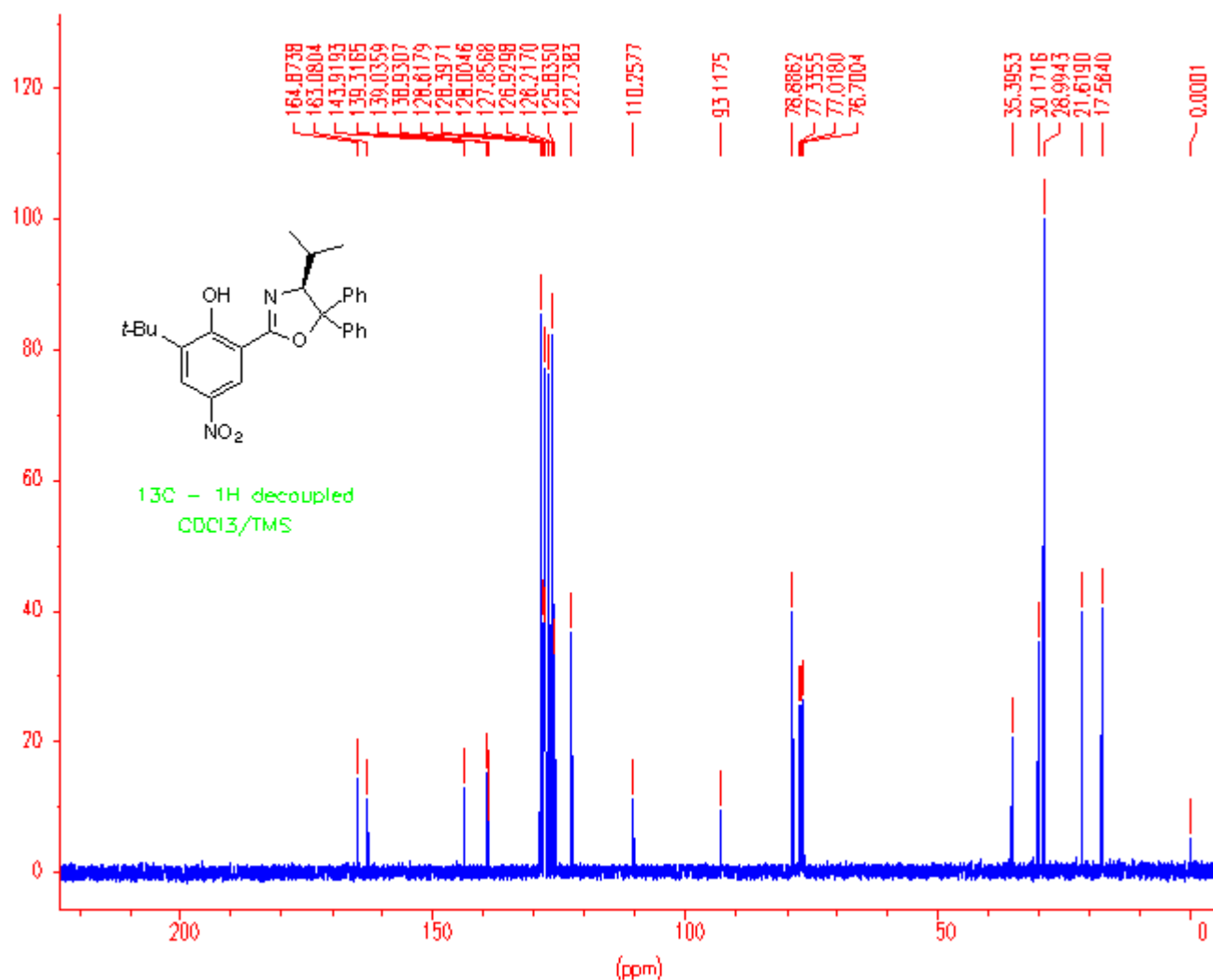
IR (Nujol, NaCl): $\tilde{\nu}$ 3092, 3062, 3029, 1952 (small, aromatic harmonic), 1889 and 1873 (very small, aromatic harmonics), 1815 (small, aromatic harmonic), 1648 (C=N), 1621, 1587, 1530, 1370, 1336, 1279, 1247, 1210, 1188, 1144, 1091, 972, 918, 839, 749, 701 cm^{-1} .



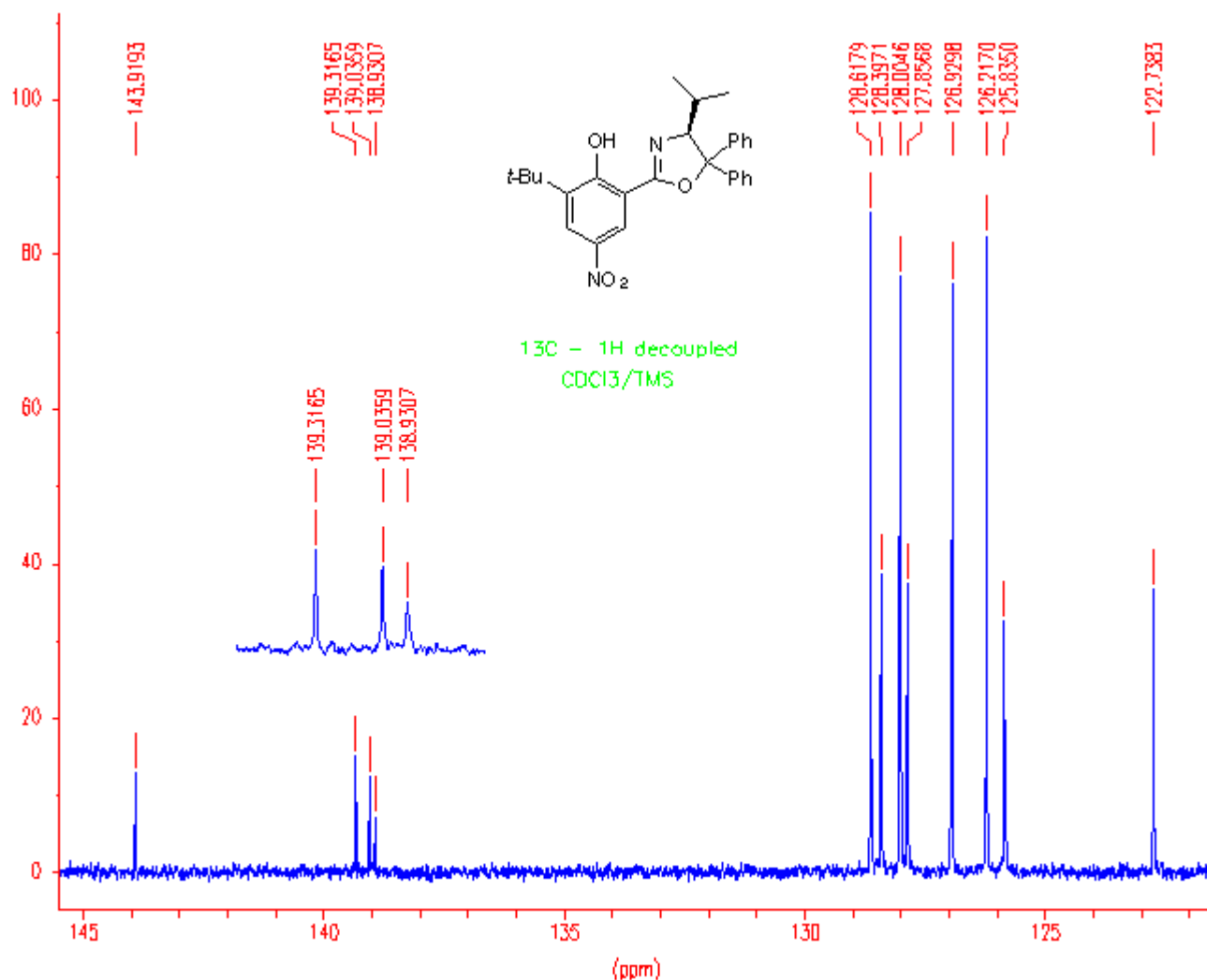
^1H NMR (400 MHz, CDCl_3): δ 13.99 (broad s, 1H, OH), 8.73 (d, 1H, $J = 2.8$ Hz, CH of phenol), 8.32 (d, 1H, $J = 2.8$ Hz, CH of phenol), 7.60-7.54 (m, 2H of phenyl), 7.43-7.37 (m, 2H of phenyl), 7.36-7.26 (m, 6H of phenyl), 4.88 (d, 1H, $J = 5.4$ Hz, $\text{C}(\text{Ph})_2\text{CH}$), 1.90 (qqd, 1H, $J = 6.7, 6.5, 5.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.47 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.01 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.68 (d, 3H, $J = 6.5$ Hz, $\text{CH}(\text{CH}_3)_2$).





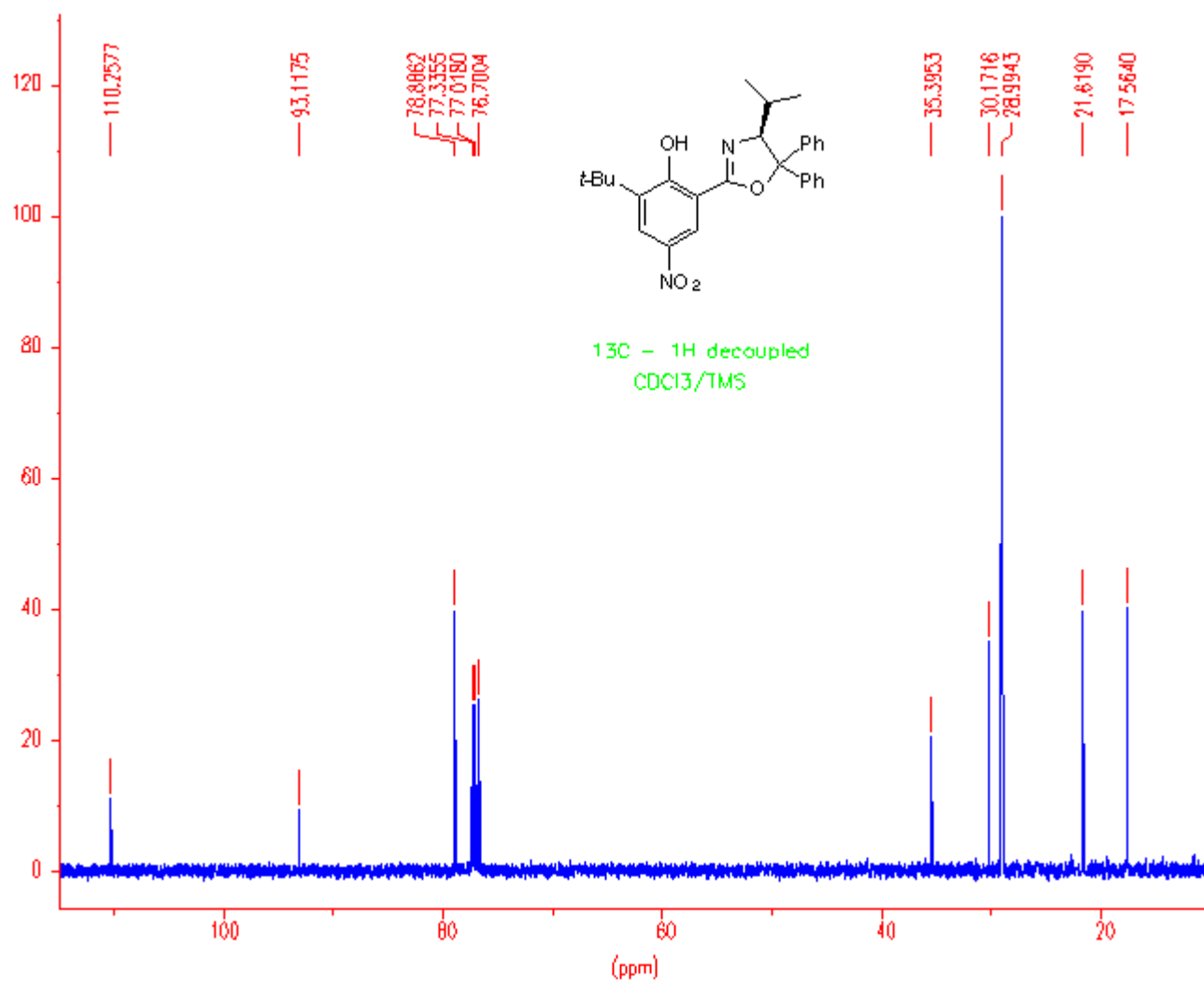


¹³C NMR (100 MHz, CDCl₃): *d* 164.87 (1C, O-C=N), 163.08 (1C, C_{ipso} α to OH), 143.92 (1C, C_{ipso} of phenyl), 139.32, 139.03 and 138.93 (3C, C_{ipso} of phenyl, C_{ipso} α to C(CH₃)₃ and C_{ipso} α to NO₂), 128.62 (2C, CH_{meta} of phenyl), 128.40 (1C, CH_{para} of phenyl), 128.01 (2C, CH_{meta} of phenyl), 127.86 (1C, CH_{para} of phenyl), 126.93 (2C, CH_{ortho} of phenyl), 126.22 (2C, CH_{ortho} of phenyl), 125.84 (1C, CH of phenol, correlates with proton at 8.32 ppm), 122.74 (1C, CH of phenol, correlates with proton at 8.73 ppm), 110.26 (1C, C_{ipso} α to oxazoline), 93.12 (1C, C(Ph)₂CH), 78.88 (1C, C(Ph)₂CH), 35.40 (1C, C(CH₃)₃), 30.17 (1C, CH(CH₃)₂), 29.00 (3C, C(CH₃)₃), 21.62 (1C, CH(CH₃)₂, correlates with protons at 1.01 ppm), 17.56 (1C, CH(CH₃)₂, correlates with protons at 0.68 ppm).



HRMS (EI, 70 eV) m/z (%): calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$ 458.2205 $[\text{M}]^+$, found 458.2184 (42), 443 (3) $[\text{M} - \text{Me}]^+$, 291 (7) $[\text{M} - \text{Ph}_2\text{CH}]^+$, 276 (6) $[\text{M} - \text{Ph}_2\text{CO}]^+$, 261 (12) $[\text{M} - \text{Ph}_2\text{CO} - \text{Me}]^+$, 237 (100) $[\text{C}_{17}\text{H}_{19}\text{N}]^+$, 222 (37) $[\text{C}_6\text{H}_2(\text{NO}_2)(t\text{-Bu})(\text{OH})\text{CO}]^+$, 220 (23.5), 207 (23) $[\text{C}_6\text{H}_2(\text{NO}_2)(t\text{-Bu})(\text{OH})\text{CO} - \text{Me}]^+$, 195 (28) $[\text{C}_{14}\text{H}_{11}\text{O} \text{ e.g. } \text{Ph}_2\text{COCH}]^+$, 194 (21), 105 (12), 91 (29), 43 (25) $[i\text{-Pr}]^+$.

MS (FAB, *m*-nitrobenzylic alcohol matrix) m/z (rel intens): Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$ 458.2 $[\text{M}]^+$, found 458 (100) $[\text{M}]^+$, 276 (5), 237 (38).



$[\alpha]_{\text{D}}^{28} = -219.3$, $[\alpha]_{578}^{28} = -229.6$, $[\alpha]_{546}^{28} = -264.2$ ($c = 3.3$, CHCl_3).

Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.56; H, 6.66; N, 5.97.