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The efficient synthesis of 3-hydroxyoxetane-3-carboxamides by the reaction of carbamoylsilanes with oxetan-3-one

Pengpeng Zhang, Shenghua Han and Jianxin Chen

I Experimental section

Toluene was freshly distilled from sodium and benzophenone as a moisture indicator under Ar atmosphere before use. Carbamoylsilane**s** was prepared according to our previous reported methods (see R. F. Cunico and J. X. Chen, *Synth. Commun*., 2003, **33**, 1963). Oxetan-3-one was obtained from J&K Scientific. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AR600 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Peak values are shown in δ (ppm). IR spectra were recorded on IMPACT-410 spectrophotometer. Elemental analysis was performed on a EA-1108 analyzer. Melting points were uncorrected. The monitoring of reaction and checking of purity of the product were done using pre-coated silica gel plates and visualization using iodine and/or UV lamp.

General procedure for the synthesis of 3,3-disubstituted oxetanes 3 or 4

A Schlenk tube fitted with a Teflon vacuum stopcock and a micro stirring bar was flame-heated under vacuum and refilled with argon. Oxetan-3-one (0.5 mmol), dry toluene (1.5 ml) and carbamoylsilane **2** (1.2 equiv.) were then added. The sealed reaction mixture was stirred at 60 °C until complete consumption of the carbamoylsilane (TLC). Volatiles were then removed under vacuum and the residue was chromatographed using light petroleum–EtOAc as the eluent to obtain 3,3-disubstituted oxetanes **3** (or **4**).

II ^{1}H and ^{13}C NMR, IR and elemental analysis data for compounds 4a,b and 3c-f.

Compound **4a**: Colourless solid, yield 85%, m.p. 70—71 ˚C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.02 (br s, 1H), 4.98, 4.70 (dd, J = 7.2 Hz, 4H), 3.14 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (151 MHz,

$CDCl_3$) δ: 170.7, 81.0, 74.7, 36.9, 36.6. IR (KBr, ν/cm^{-1}): 3274, 1617, 1516, 1386, 1329, 1191. Found (%): C, 49.60; H, 7.43; N, 9.41. Calc. for $C_6H_{11}NO_3$ (%): C, 49.65; H, 7.64; N, 9.65.

Compound **4b**: Yellowish liquid, yield 76 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.04—4.65 (m, 6H), 3.44—3.36 (m, 5H), 1.64—1.61 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.4, 81.3, 79.6, 75.7, 55.9, 55.5, 49.3, 48.4, 21.2, 11.2. IR (KBr, ν/cm^{-1}): 3359, 1638, 1467, 1382, 1187, 1094. Found (%): C, 53.42; H, 8.21; N, 6.68. Calc. for $C_{19}H_{17}NO_4$ (%): C, 53.19; H, 8.43; N, 6.89.

Compound **3c**: Yellowish liquid, yield 59 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.37–7.27 (m, 5H), 6.01, 5.24 (qq, J = 6.6 Hz, 1H), 5.15, 4.97 (dd, J = 7.2 Hz, 2H), 4.68–4.67 (m, 2H), 2.76, 2.55 (ss, 3H), 1.62, 1.53 (dd, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.6, 170.1, 140.1, 128.6, 128.5, 128.3, 127.5, 127.4, 126.6, 126.4, 81.2, 81.1, 80.9, 80.6, 54.6, 51.1, 28.7, 18.0, 15.0, 1.4, 1.0. IR (KBr, ν/cm^{-1}): 1643, 1613, 1500, 1443, 1394, 1077. Found (%): C, 62.60; H, 8.43; N, 4.41. Calc. for $C_{16}H_{25}NO_3Si$ (%): C, 62.50; H, 8.20; N, 4.56.

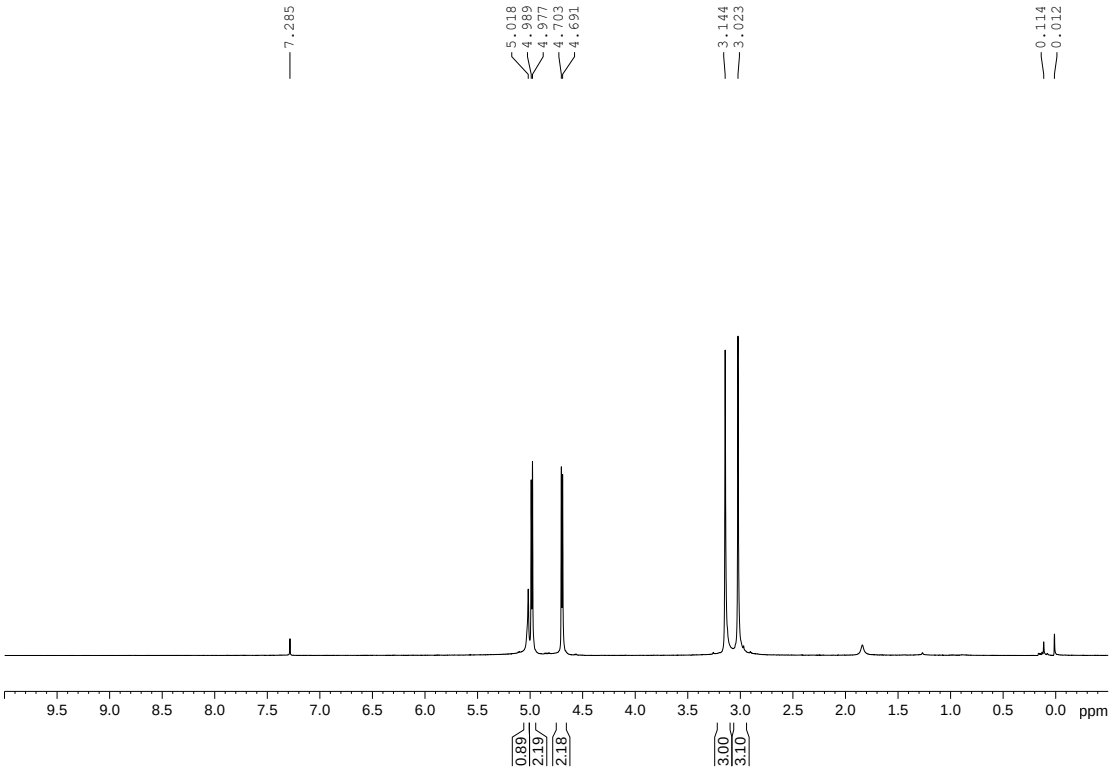
Compound **3d**: Colourless liquid, yield 80 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.09, 5.05 (dd, J = 6.6 Hz, 2H), 4.68, 4.64 (dd, J = 6.6 Hz, 2H), 4.82, 4.51 (ss, 2H), 3.35, 3.30 (ss, 3H), 3.00, 2.91 (ss, 3H), 0.15, 0.12 (ss, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.4, 171.2, 81.0, 80.9, 78.7, 56.2, 55.7, 33.2, 33.1, 0.9, 0.8. IR (KBr, ν/cm^{-1}):1658, 1459, 1394, 1252, 1098. Found (%): C, 48.32; H, 8.29; N, 5.48. Calc. for $C_{10}H_{21}NO_4Si$(%): C, 48.55; H, 8.56; N, 5.66.

Compound **3e**: Colourless solid, yield 68%, m.p. 69—70 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.14, 5.07 (dd, J = 6.6 Hz, 2H), 4.83, 4.49 (ss, 2H), 4.72, 4.62 (dd, J = 6.6 Hz, 2H), 4.09—4.06 (m, 1H), 3.39, 3.24 (ss, 3H), 1.83—1.15 (m, 10H), 0.30, 0.24 (ss, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.7, 171.1, 81.1, 80.6, 77.7, 76.4, 73.3, 56.8, 56.6, 55.2, 54.8, 32.3, 30.8, 26.1, 26.0, 25.6, 25.3, 1.3, 1.0. IR (KBr, ν/cm^{-1}): 1658, 1427, 1252, 996. Found (%): C, 57.30; H, 9.43; N, 4.41. Calc. for $C_{15}H_{29}NO_4Si$ (%): C, 57.11; H, 9.27; N, 4.44.

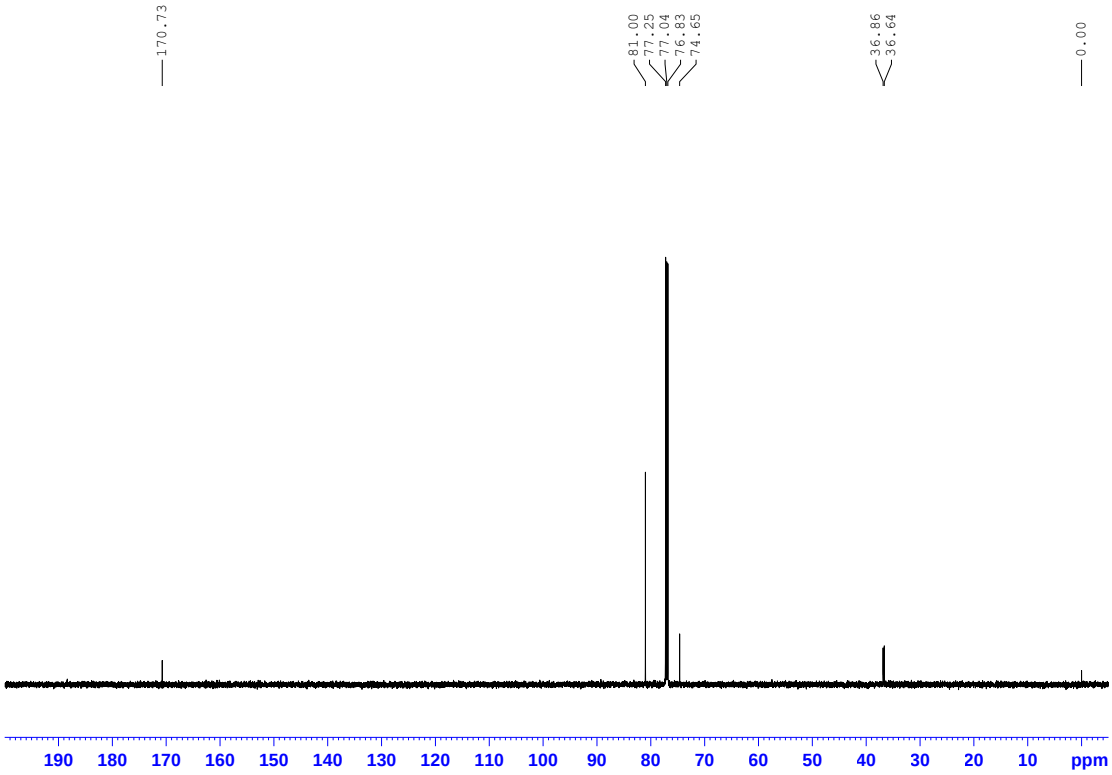
Compound **3f**: Colourless liquid, yield 62 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38—7.22 (m, 5H), 5.14, 5.10 (dd, J = 7.2 Hz, 2H), 4.80—4.67 (m, 4H), 4.51, 4.48 (ss, 2H), 3.36, 3.26 (ss, 3H), 0.21, 0.11 (ss, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 171.1, 136.8, 128.7, 128.5, 127.5, 127.3, 80.9, 80.7, 78.4, 55.5, 48.7, 47.9, 1.3, 1.0. IR (KBr, ν/cm^{-1}): 1642, 1597, 1516, 1414, 1252, 1077. Found (%): C, 59.65; H, 7.56; N, 4.30. Calc. for $C_{16}H_{25}NO_4Si$ (%): C, 59.41; H, 7.79; N, 4.33.

III ^{1}H NMR and ^{13}C NMR spectra for compounds 4a,b and 3c-f

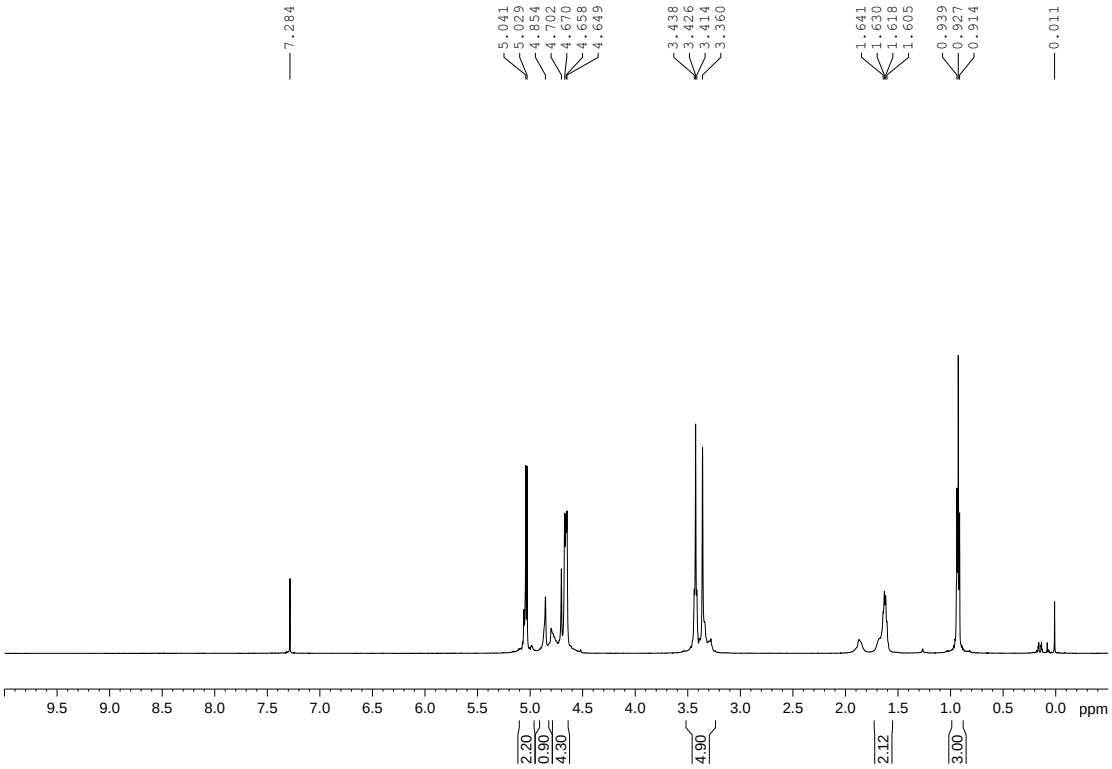
^{1}H NMR of **4a**



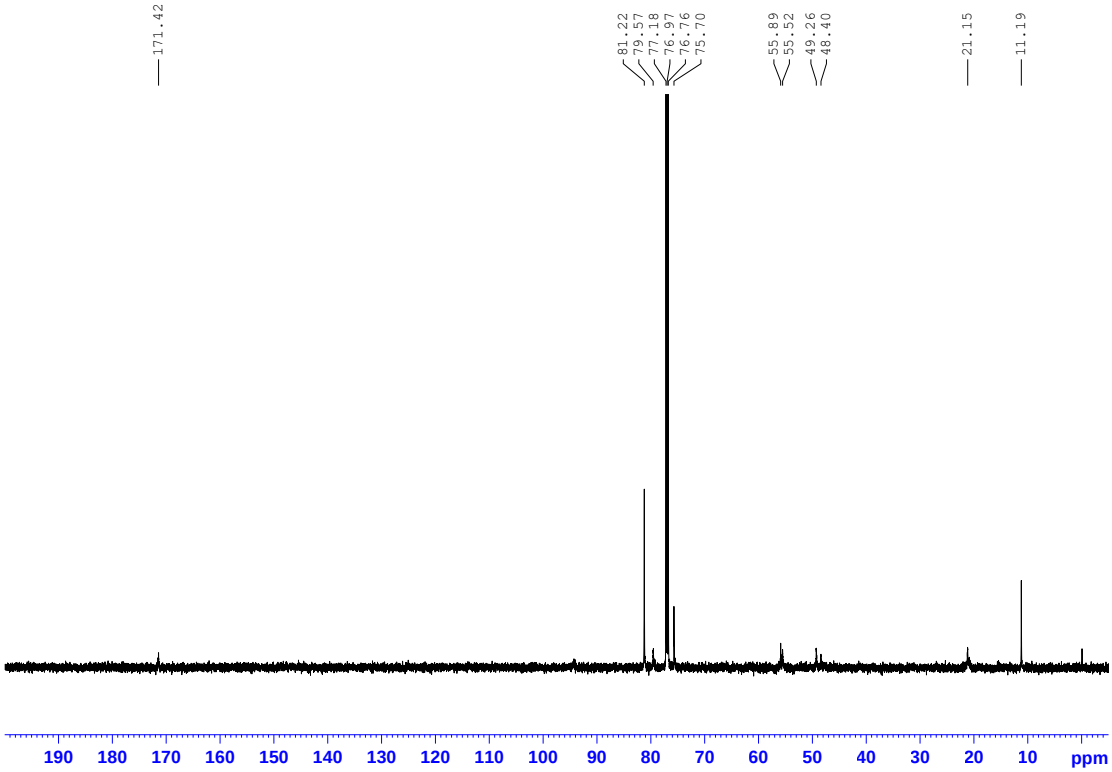
^{13}C NMR of **4a**



^{1}H NMR of **4b**



^{13}C NMR of **4b**



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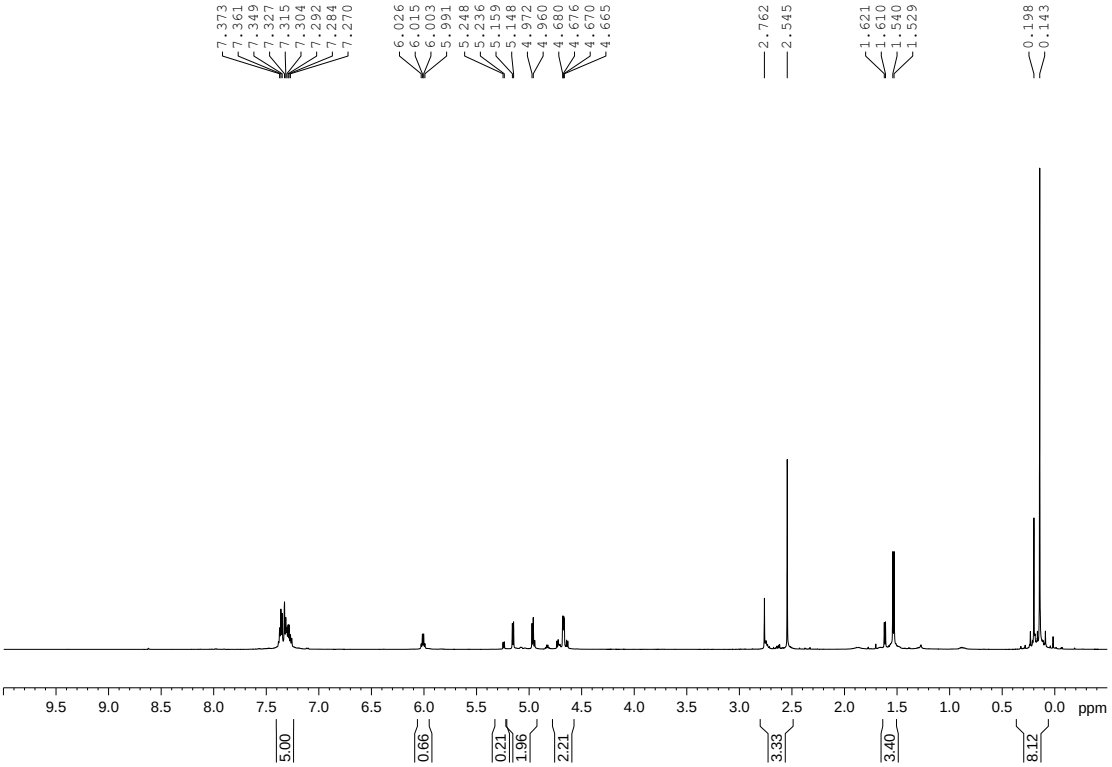
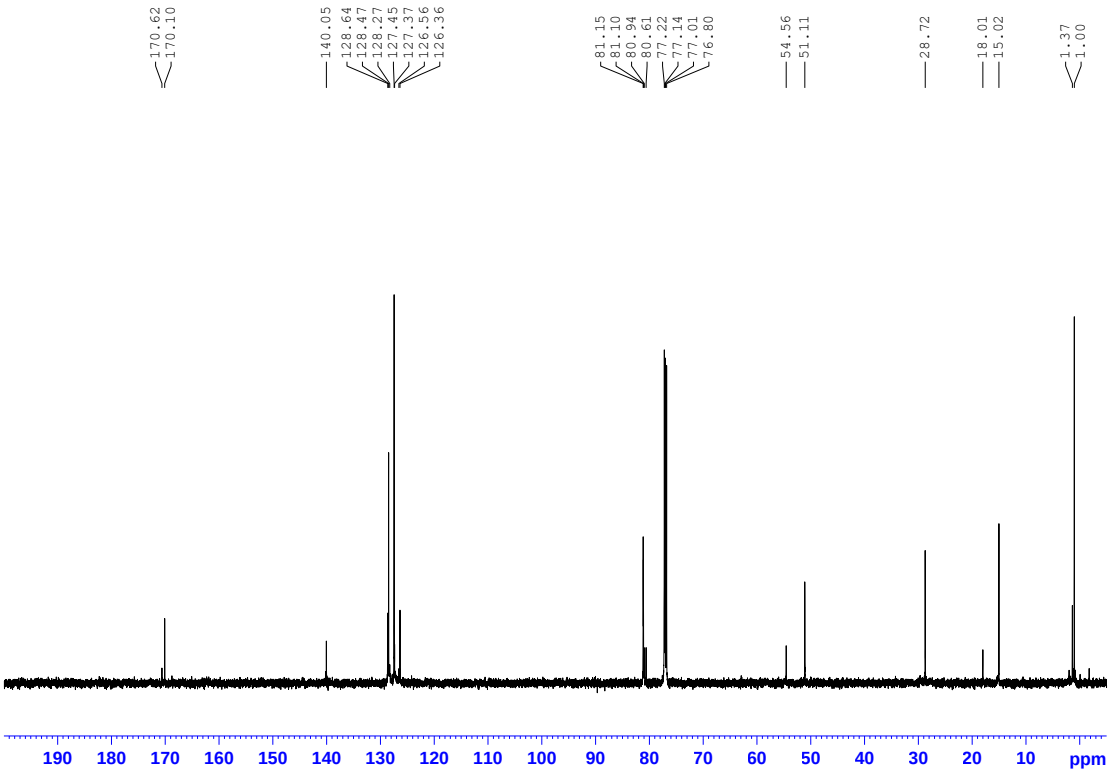


^{13}C NMR of **3c**



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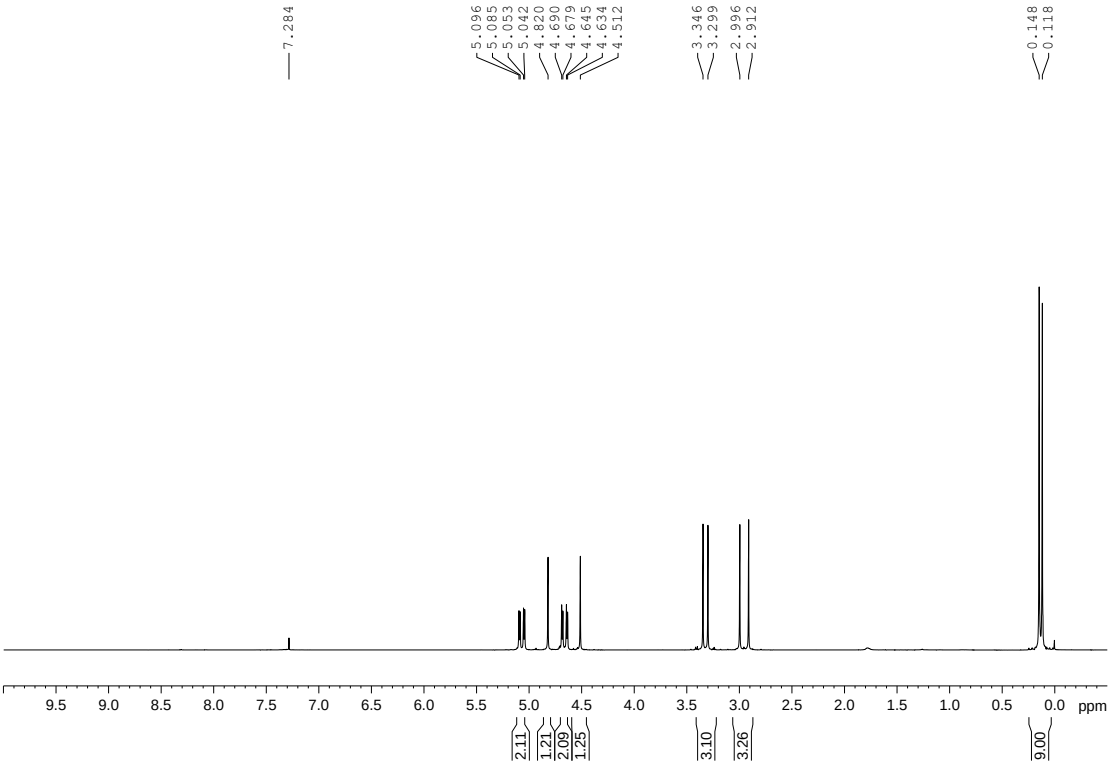
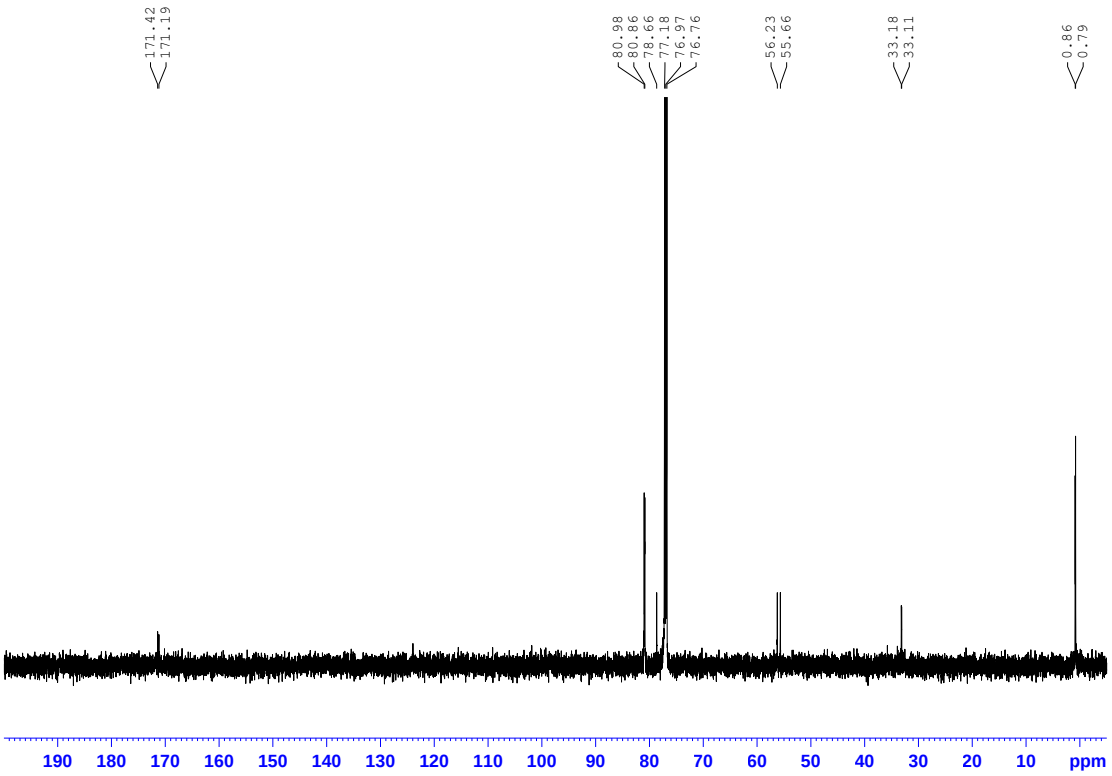
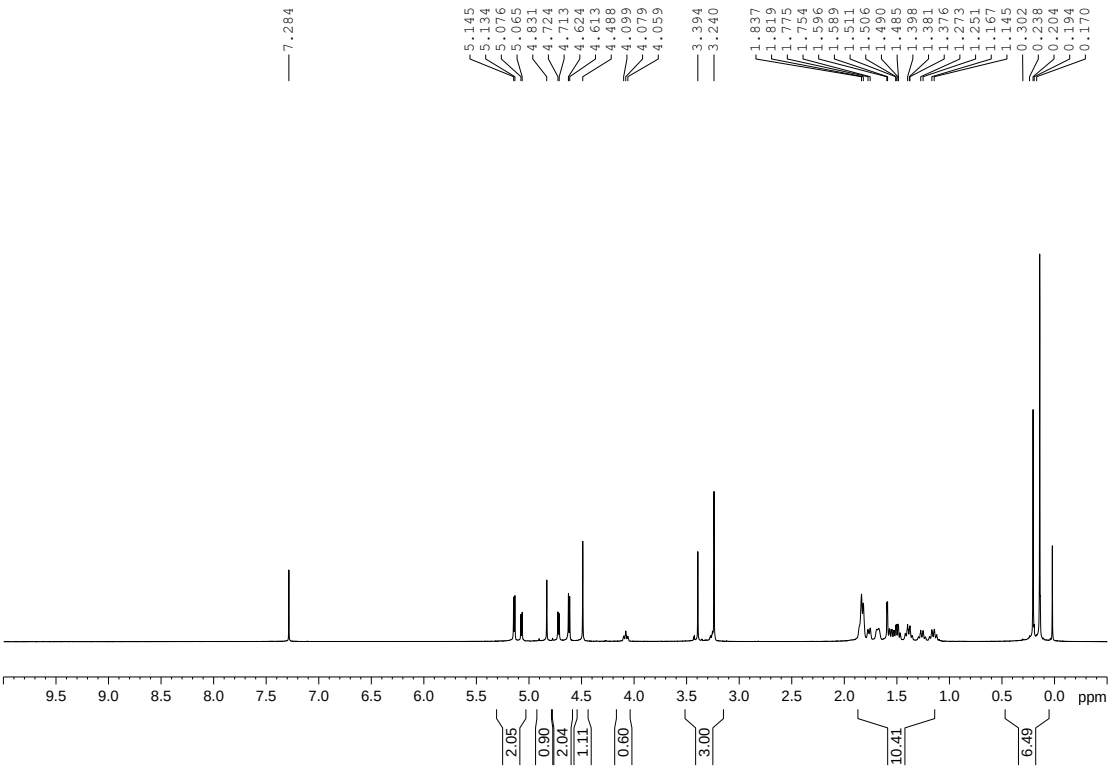


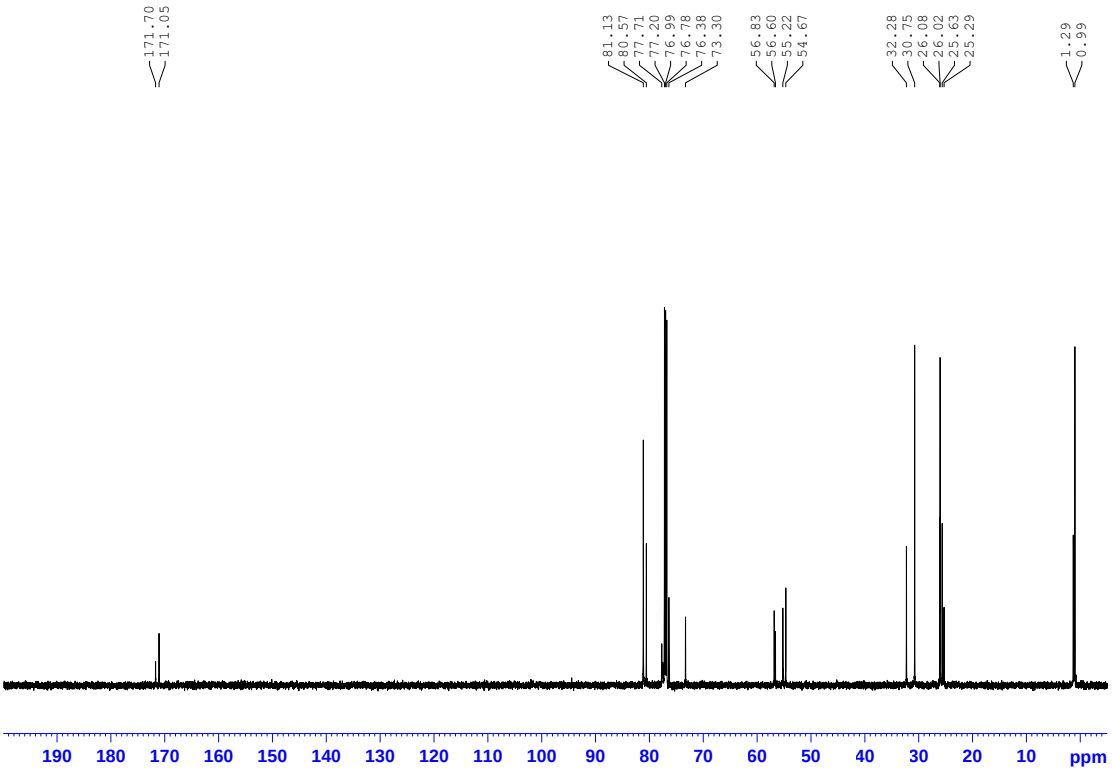
^{13}C NMR of **3d**



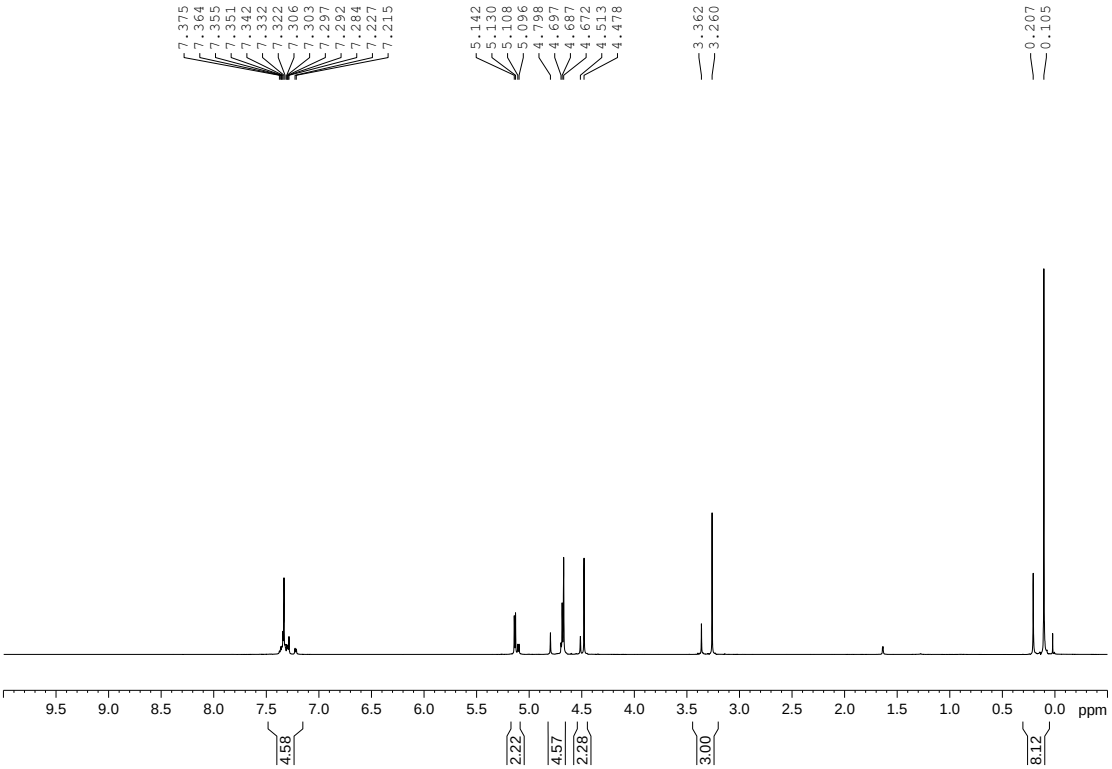
^{1}H NMR of **3e**



^{13}C NMR of **3e**



^{1}H NMR of **3f**



^{13}C NMR of **3f**