Electronic supplementary materials *Mendeleev Commun.*, 2013, **23**, 356−357

Synthesis of 2-cyanoacryloyl chloride and its interaction with O- and S-nucleophiles

Valerie A. Dyatlov, Iskander R. Rustamov, Tatiana A. Grebeneva, Viktor I. Maleev, Yuri G. Gololobov and Vyacheslav V. Kireev

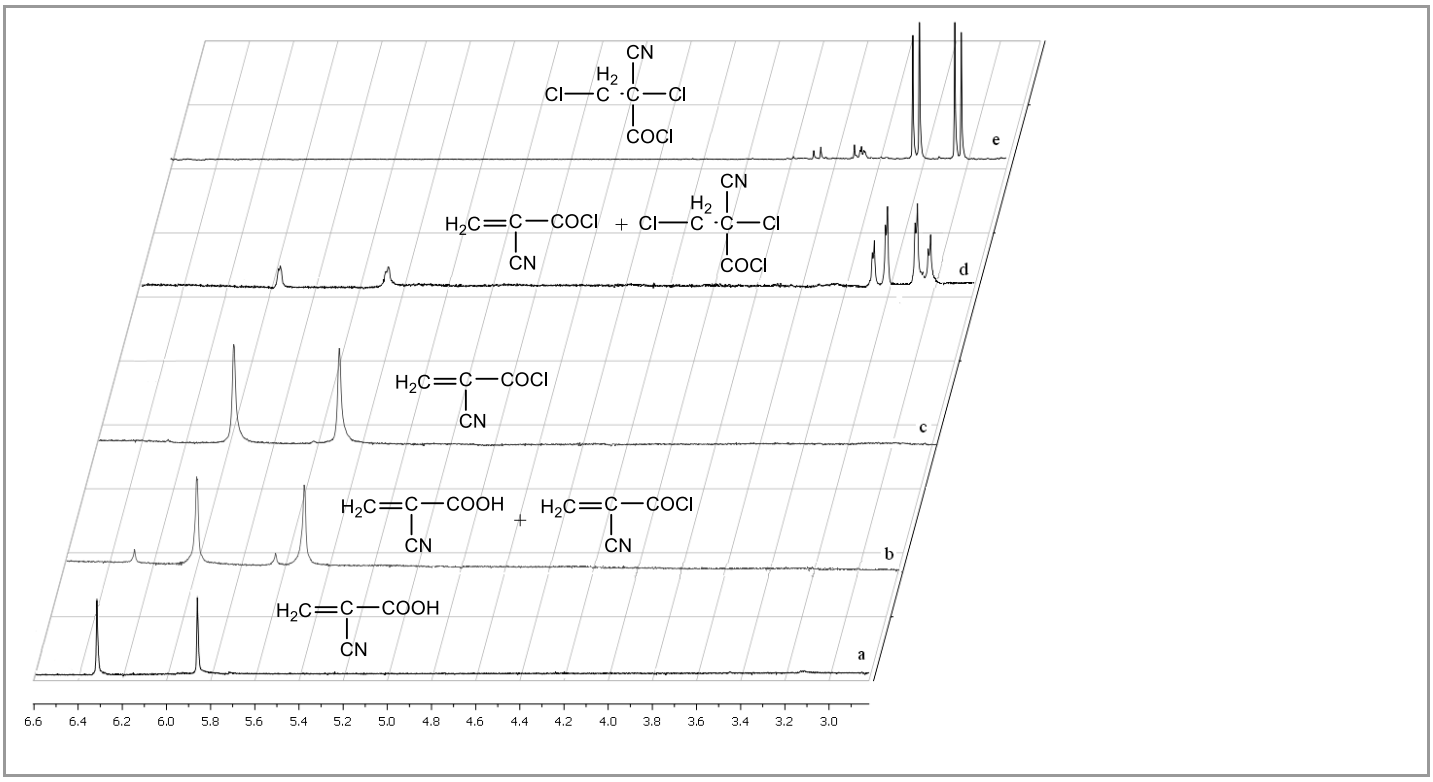


Figure S1 ^{1}H NMR spectra of: a – 2-cyanoacrylic acid; b – mixture of 2-cyanoacrylic acid and 2-cyanoacryloyl chloride; c – 2-cyanoacryloyl chloride; d – mixture of 2-cyanoacryloyl chloride and 2,3-dichloro-2-cyanopropanoyl chloride; e - 2,3-dichloro-2-cyanopropanoyl chloride.

Experimental section

Commercially available chemicals (Sigma, Aldrich) were used as purchased. All solvents were dried under P_2O_5 and distilled over Na-benzophenone system. NMR spectra were recorded on a Bruker Avance 600 (^{1}H) instrument at 25^{o}C.

2-Cyanoacrylic acid. Tube-type quartz pyrolysis reactor fitted with an addition funnel [filled with ethyl 2-cyanoacrylate (4.63 g, 37.04 mmol)] and a capillary tube for sparging SO_2 was heated up to 100 ^{o}C. Ethyl 2-

cyanoacrylate was added dropwise with a rate of approximately 3-4 droplets per min into the pyrolysis tube heated to 590–600 ^{o}C, with constant sparging of SO_2, at a flow rate of 0.5 ml/min., and at pressure of 0.01–0.1 mm Hg. Emerging vapours were cooled in a receiver yielding 2-cyanoacrylic acid (3.41 g, 35.19 mmol). The solid was recrystallized from toluene to give white crystals of 2-cyanoacrylic acid, M_p = 93-94 ^{o}C (3.23 g, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.73 and 7.11 (each 1H, s, H_aH_bC=C-), 10.29 (s, 1H, COOH); ^{13}C NMR ($CDCl_3$): δ 113.7, 116.1, 145.5, 165.3. Calcd for $C_4H_3NO_2$ (%): C, 49.48; H, 3.09; N, 14.44. Found (%): C, 49.45; H, 4.1; N, 14.48.

2,3-Dichloro-2-cyanopropanoyl chloride. Phosphorus pentachloride (1.29 g, 6.19 mmol) was added into a solution of 2-cyanoacrylic acid (0.5 g, 5.15 mmol) in toluene (5 ml) under intensive stirring. This solution was vigorously stirred for 15 min at 80 ^{o}C then a distillation was applied to remove $POCl_3$ and a portion of the solvent. The residual solution contained a pure 2,3-dichloro-2-cyanopropanoyl chloride and small residues of 2-cyanoacryloyl chloride that was fully converted to 2,3-dichloro-2-cyanopropanoyl chloride at room temperature. ^{1}H NMR (600 MHz, C_6D_6): δ 3.24 (2H, dd, J=1.8, H_aH_bClC-CCl); ^{13}C NMR (C_6D_6): δ 48.5, 65.8, 114.9, 166.7. Calcd for $C_4H_2NOCl_3$ (%): C, 25.74; H, 1.07; N, 7.51; Cl, 57.10. Found (%): C, 25.68; H, 1.1; N, 7.49; Cl, 57.15.

2-Cyanoacryloyl chloride. Oxalyl chloride (0.75 ml, 5 mmol) was added to 2-cyanoacrylic acid (0.25 g, 2.5 mmol) at room temperature with vigorous stirring. This suspension was vigorously stirred for 15 min at room temperature then heated to 40 ^{o}C. Acid slowly dissolved at this temperature within 5 min. Once the acid was completely dissolved then a stream of argon was bubbled through the solution and the reaction mixture was cooled down with liquid nitrogen. Obtained solid frozen mixture was slowly heated up to yield a mixture of excess oxalyl chloride with a solid precipitate. The liquid was decanted from precipitate that was dried in vacuum producing 0.24 g (2.1 mmol) of solid 2-cyanoacryloyl chloride, M_p=46–49 ^{o}C (83% yield). ^{1}H NMR (600 MHz, C_6D_6) δ 5.20 and 5.76 (each 1H, s, H_aH_bC=C-); ^{13}C NMR (C_6D_6): 112.8, 119.5, 146.0, 161.8. Calcd for C_4H_2NOCl (%): C, 41.56; H, 1.73; N, 12.12; Cl, 30.74. Found (%): C, 41.39; H, 1.75; N, 11.67; Cl, 31.40.

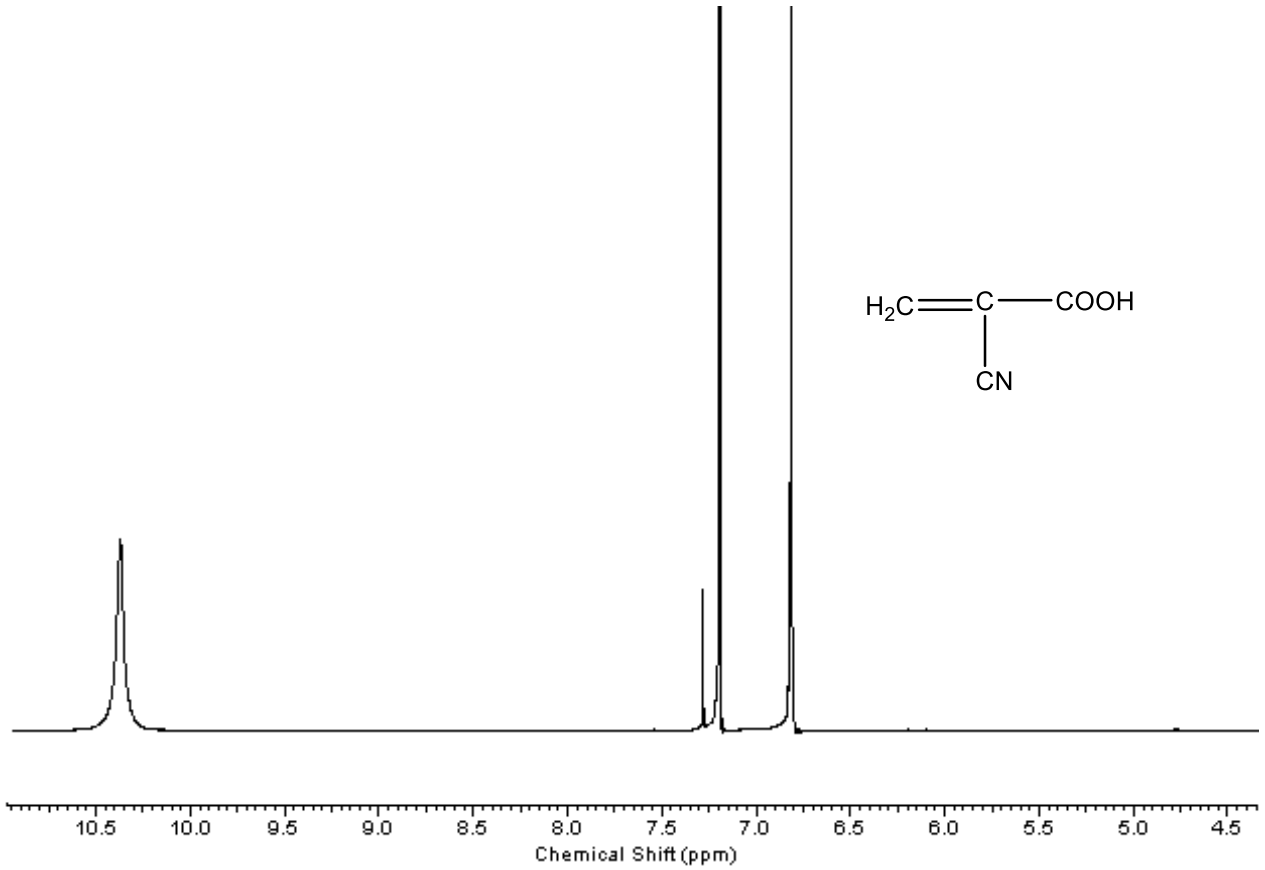
Pentafluorophenyl 2-cyanoprop-2-enoate. Oxalyl chloride (1.1659 g, 9.18 mmol) was added to a stirred solution of 2-cyanoacrylic acid (445 mg, 4.59 mmol) in benzene (5 ml). The mixture was refluxed for 1 h at 40 ^{o}C then it was cooled down to room temperature. Formation of 2-cyanoacryloyl chloride was controlled by ^{1}H NMR. When 2-cyanoacrylic acid was fully converted to 2-cyanoacryloyl chloride an equimolar amount of pentafluorophenol (845 mg, 4.59 mmol) was added. The mixture was refluxing for 10 min then it

was evaporated *in vacuo*. The residue was recrystallized from hexane producing white crystals (92% yield). Mp 75−77 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 6,25 (s, 1H, CH_2), 6,73 (s, 1H, CH_2); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -168,98 (tt, J=3,77, J=7,53, 1F, CF-p), -164,23 (td, J=3,77, J=11,29, 2F, CF-m), -163,20 (dd, J=3,77, J=11,29, 2F, CF-o); ^{13}C NMR ($CDCl_3$): δ 113.5, 115.6, 127.4, 127.7, 127.9, 145.1, 165.2. Calcd for $C_{10}H_2NO_2F_5$(%): C, 45.63; H, 0.76; N, 5.32; F, 36.12. Found (%): C, 45.59; H, 0.83; N, 5.29; F, 36.15.

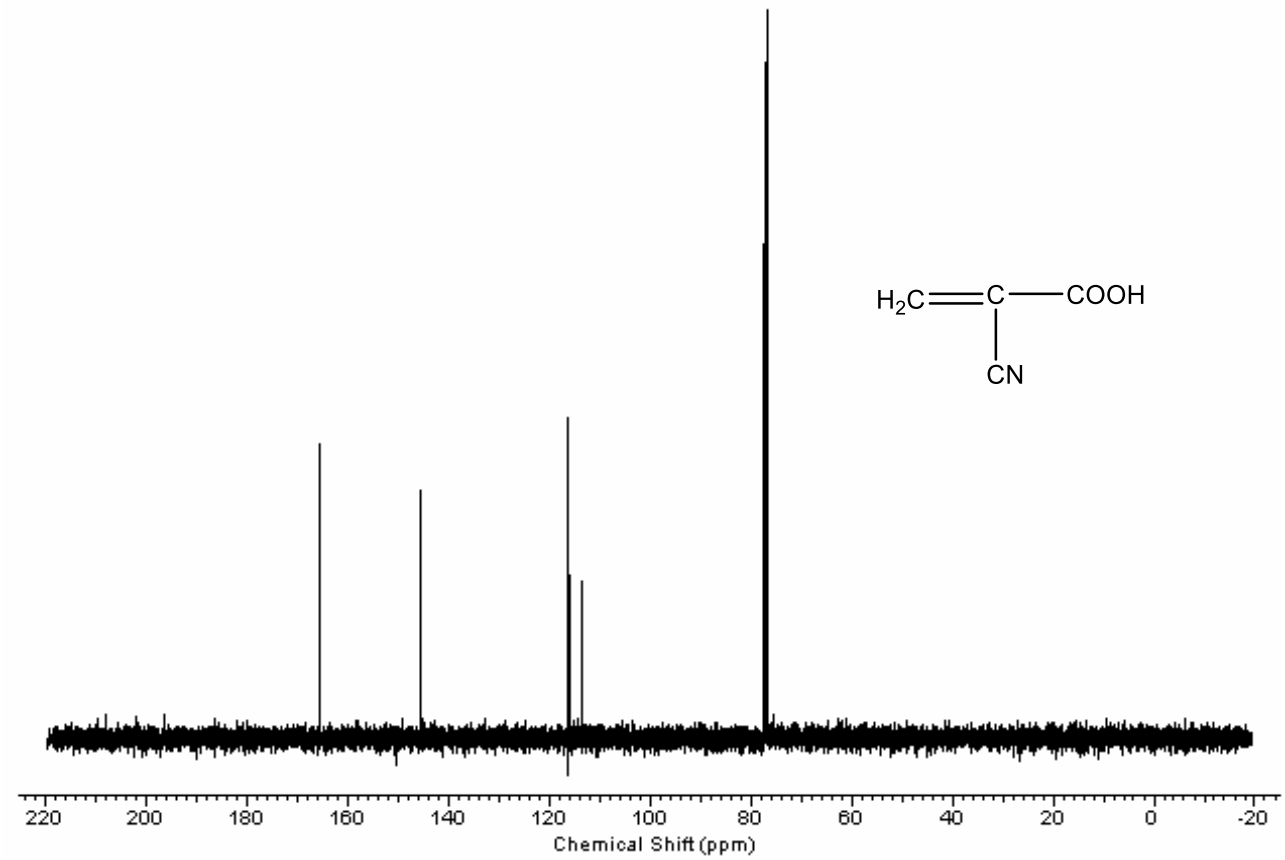
1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)butane-2,3-diyl bis(2-cyanoprop-2-enoate). Oxalyl chloride (1.3538 g, 10.66 mmol) was added to a stirred solution of 2-cyanoacrylic acid (517 mg, 5.33 mmol) in benzene (5 ml). The mixture was refluxing for 1 h at 40 ^{o}C then it was cooled down to room temperature. Formation of 2-cyanoacryloyl chloride was controlled by ^{1}H NMR. As soon 2-cyanoacrylic acid was fully converted to 2-cyanoacryloyl chloride then a solution of 1,1,1,4,4,4-hexafluoro-2,3-bis(trifluoromethyl)butane-2,3-diol (890 mg, 2.66 mmol) in benzene (5 ml) was added. After refluxing for 10 min, the mixture was evaporated *in vacuo*. The resulting residue turned out to be yellow oil (85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6,87 (d, J=1.92, 1H, CH_2), 7,085 (d, J=1.92, 1H, CH_2); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -70,12 (s, 12F, CF_3); ^{13}C NMR ($CDCl_3$): δ 161.9, 137.7, 120.1, 113.4, 112.3, 39.4. Calcd for $C_{14}H_4N_2O_4F_{12}$ (%): C, 34.15; H, 0.81; N, 5.69; F, 46.34. Found (%): C, 34.19; H, 0.84; N, 5.66; F, 46.37.

S-Decyl 2-cyanoprop-2-enethioate and decyl 2-cyanoprop-2-ene(dithioate). Solution of decanethiol (0.87 g, 4.99 mmol) in dry benzene (5 ml) was added to a stirred solution of 2-cyanoacryloyl chloride (0.5763 g, 4.99 mmol) in dry benzene (5 ml) at stoichiometric ratio. The mixture was let refluxing for 10 h at 25 ^{o}C in inert atmosphere then it was evaporated *in vacuo*. The obtained mixture in ratio 1:0.6 of S-decyl 2-cyanoprop-2-enethioate and decyl 2-cyanoprop-2-ene(dithioate) respectively was purified from hexane giving yellow oil (92% yield, 1.2 g). ^{1}H NMR (600 MHz, C_6D_6) δ 6.35 and 5.69 (each 1H, s, H_aH_bC=C-), 3.47 (2H, s, CH_2S), 2.73 (16H, m, $(CH_2)_8$), 2.35 (3H, s, CH_3). For $C_{14}H_{23}ONS$ ^{13}C NMR (C_6D_6) δ 14.2, 30.0, 33.5, 46.9, 115.1, 116.2, 139.0, 184.5. For $C_{14}H_{23}NS_2$ ^{13}C NMR (C_6D_6) δ 14.2, 30.0, 33.5, 46.9, 116.2, 122.2, 139.0, 191.7.

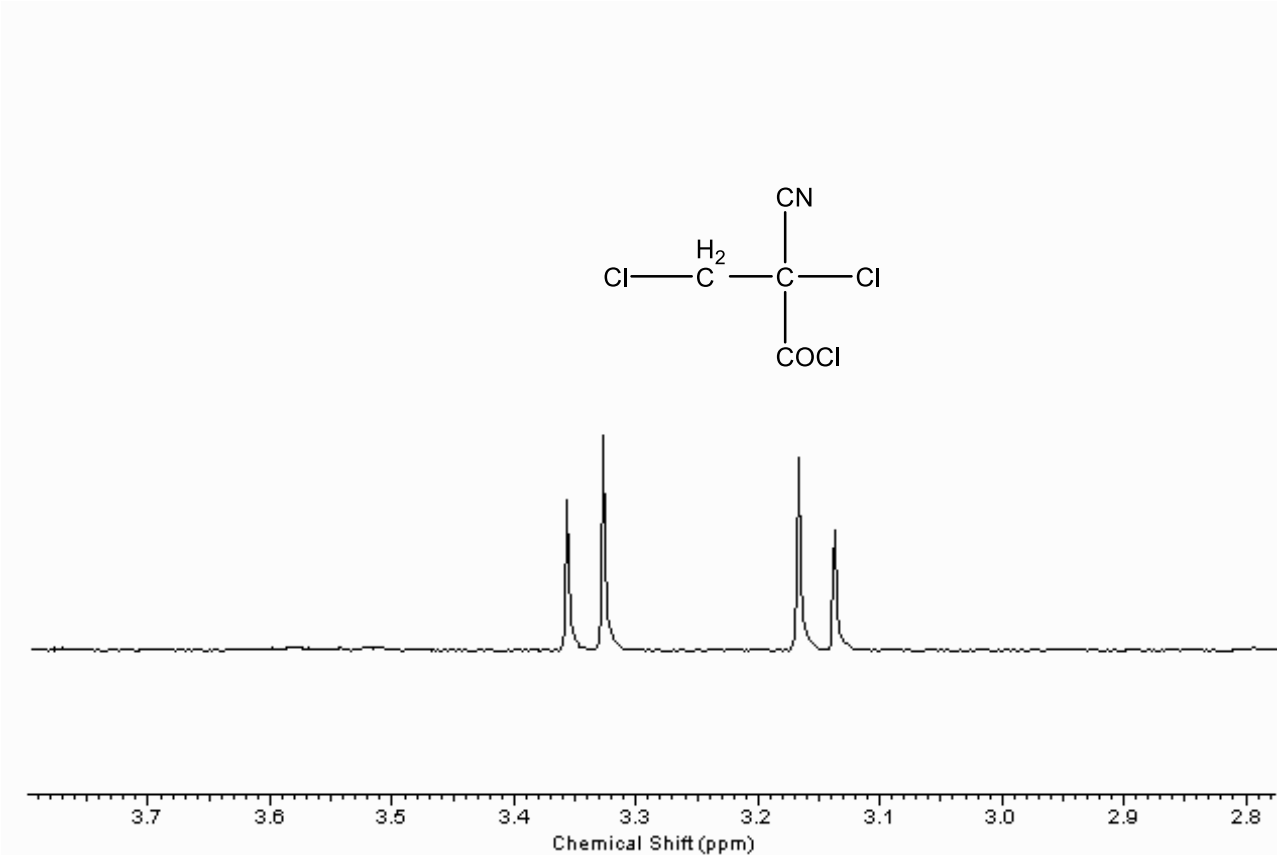
1. 2-Cyanoacrylic acid ^{1}H NMR ($CDCl_3$)



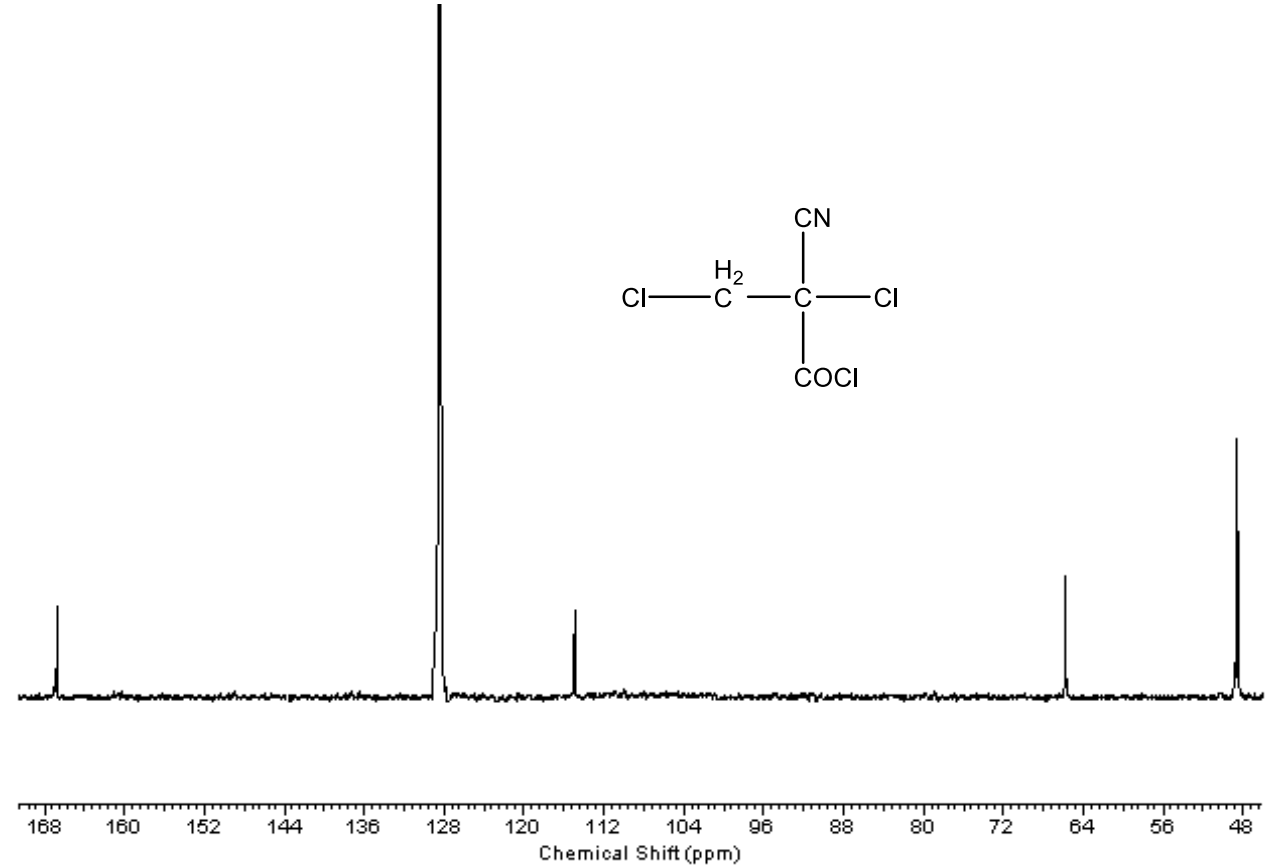
2. 2-Cyanoacrylic acid ^{13}C NMR ($CDCl_3$)



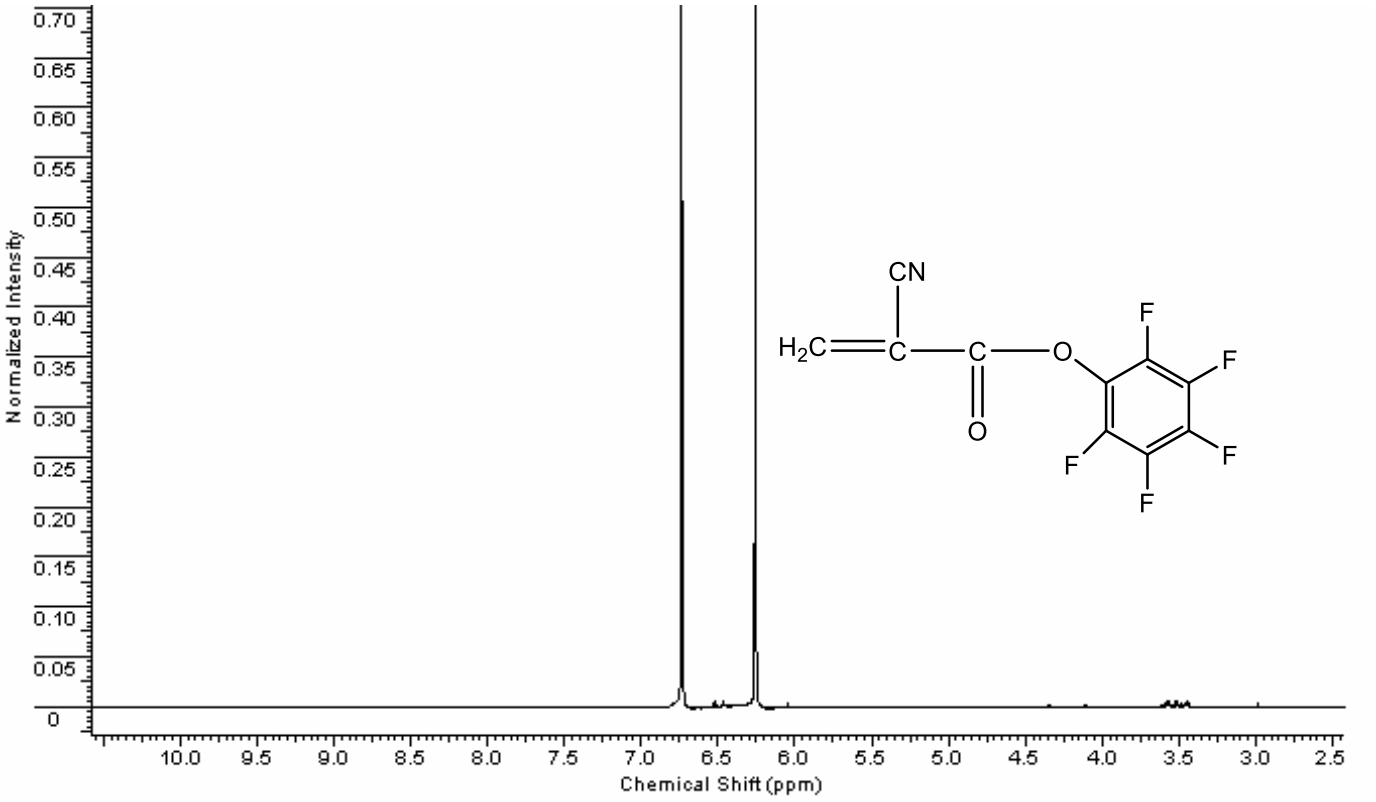
3. 2,3-Dichloro-2-cyanopropanoyl chloride ^{1}H NMR (C_6D_6)



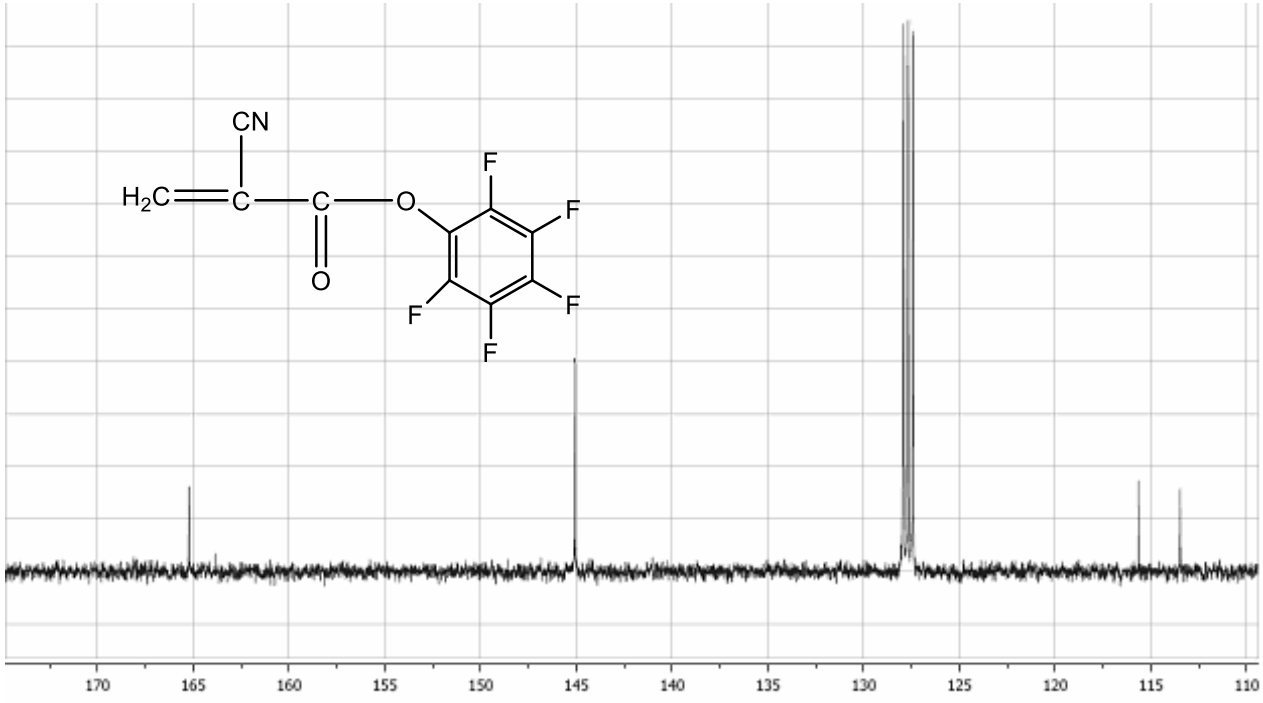
4. 2,3-Dichloro-2-cyanopropanoyl chloride ^{13}C NMR (C_6D_6)



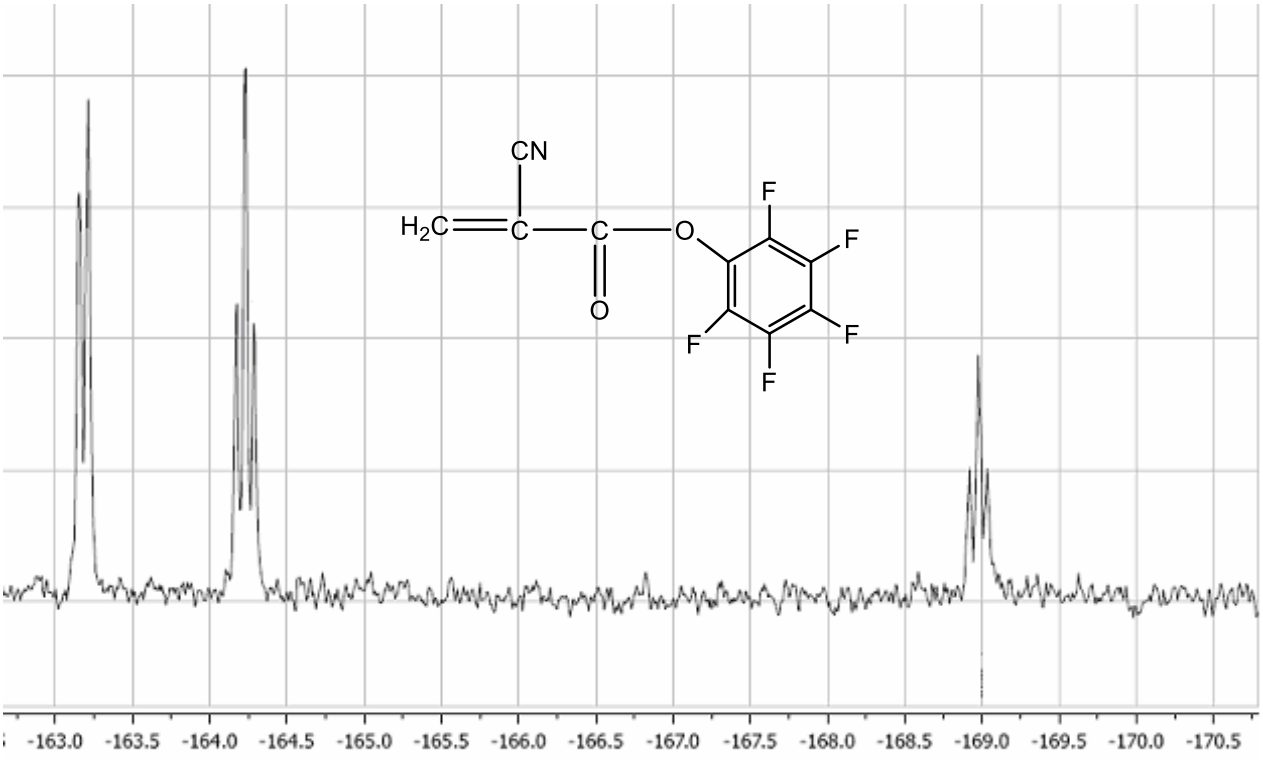
5. Pentafluorophenyl 2-cyanoprop-2-enoate ^{1}H NMR (C_6D_6)



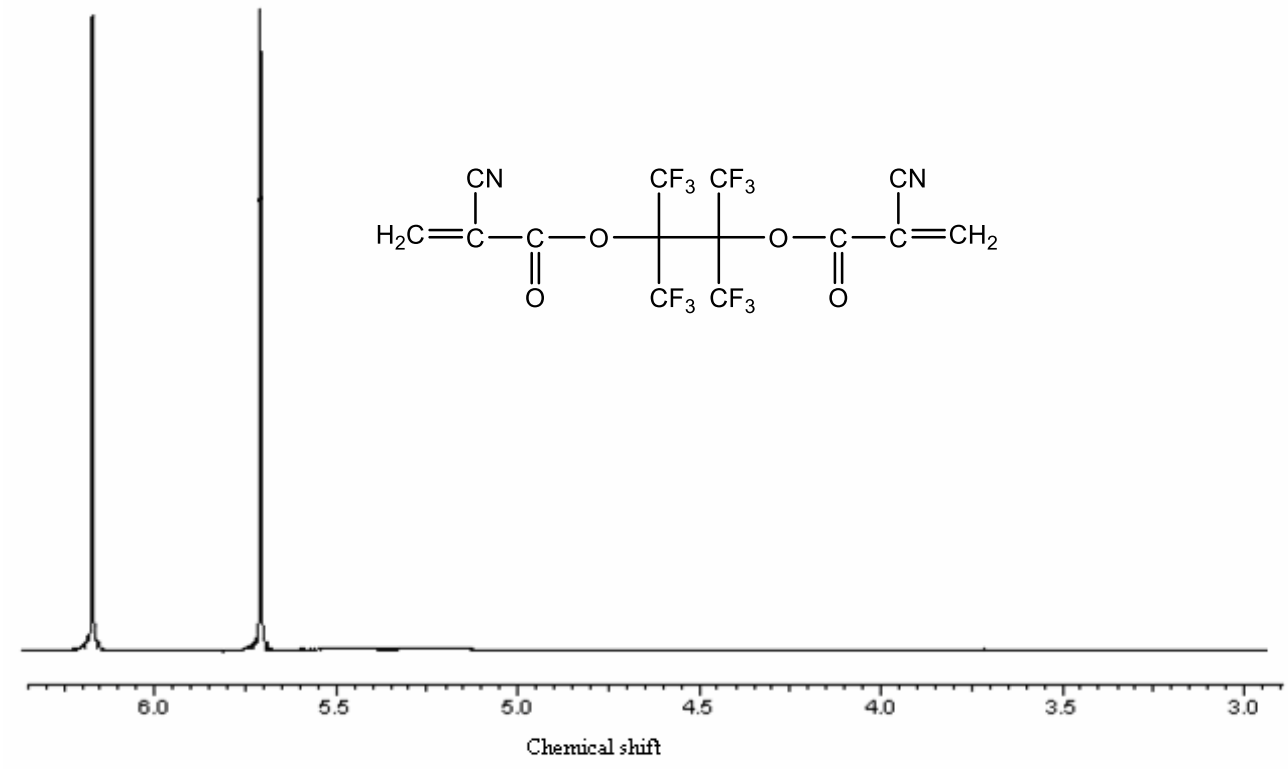
6. Pentafluorophenyl 2-cyanoprop-2-enoate ^{13}C NMR (C_6D_6)



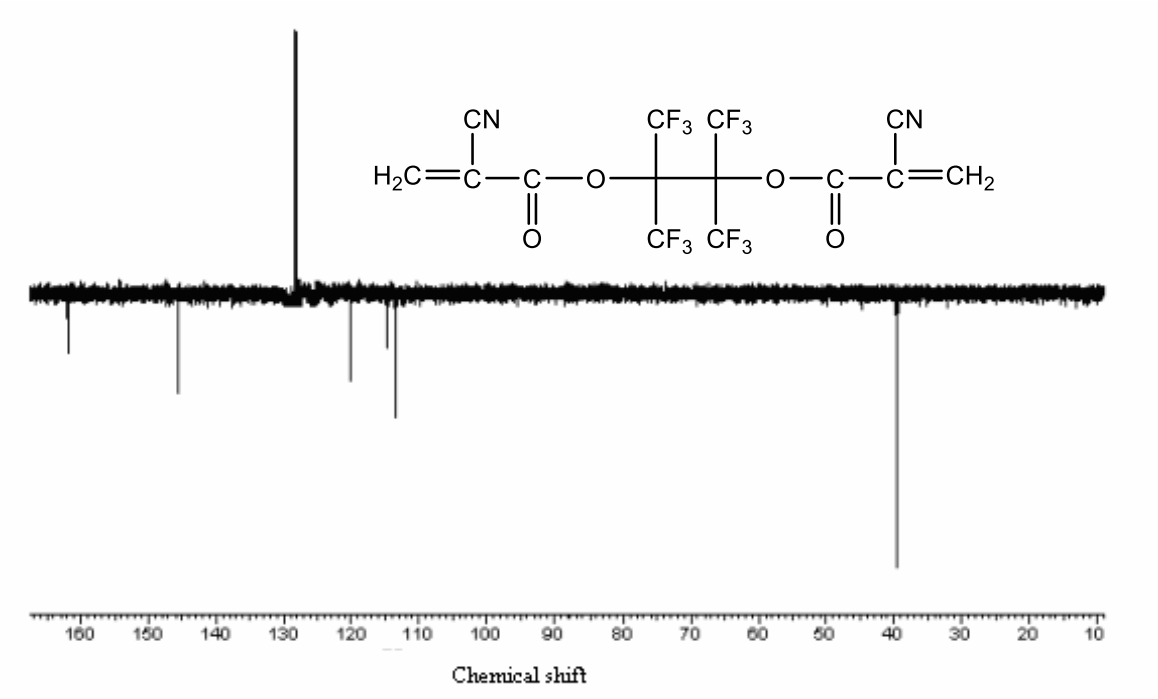
7. Pentafluorophenyl 2-cyanoprop-2-enoate ^{19}F NMR (C_6D_6)



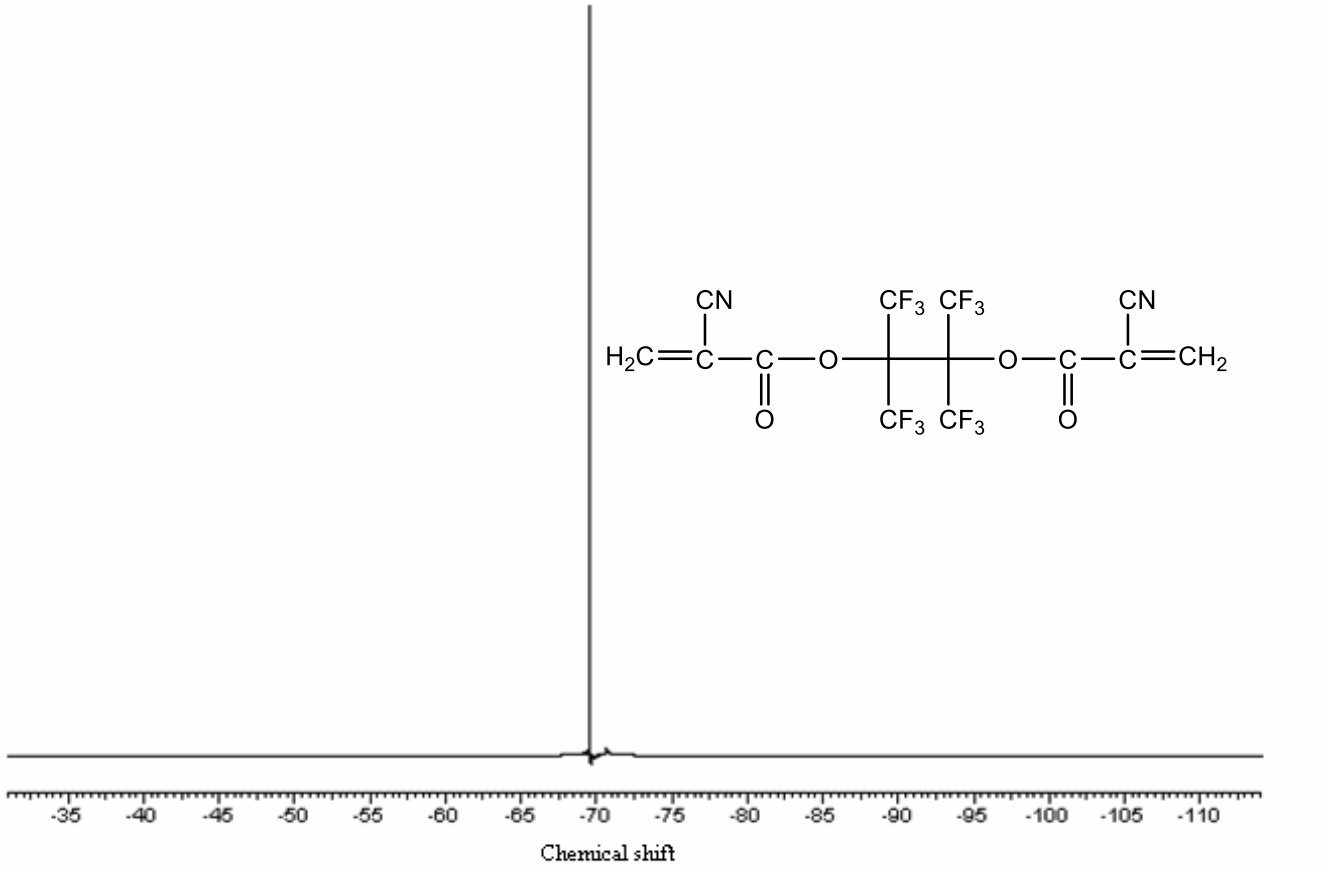
8. 1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)butane-2,3-diyl bis(2-cyanoprop-2-enoate) ^{1}H NMR (C_6D_6)



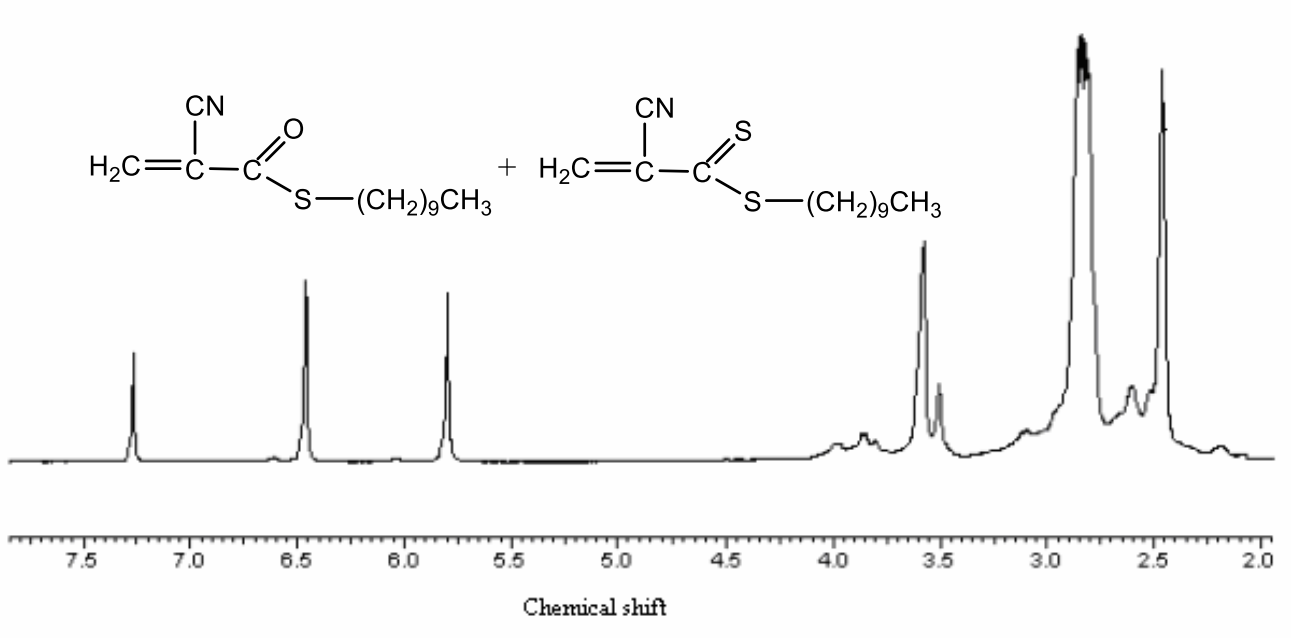
9. 1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)butane-2,3-diyl bis(2-cyanoprop-2-enoate) ^{13}C NMR (C_6D_6)



10. 1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)butane-2,3-diyl bis(2-cyanoprop-2-enoate) ^{19}F NMR (C_6D_6)



11. *S*-Decyl-2-cyanoprop-2-enethioate and decyl-2-cyanoprop-2-ene(dithioate) ^{1}H NMR (C_6D_6)



12. *S*-Decyl-2-cyanoprop-2-enethioate and decyl-2-cyanoprop-2-ene(dithioate) ^{13}C NMR (C_6D_6)