Supporting Information for

A bipyridine ligand embedded in polysiloxane gel which soaks up CuCl to form a reusable gel-catalyst active for ATRC

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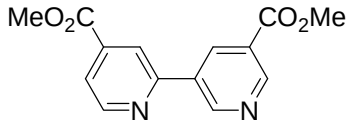
1. General Methods

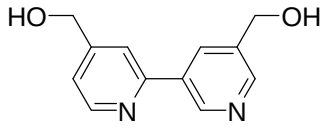
Karstedt's catalyst in 0.1 M xylene solution was purchased from Aldrich. . Polymethylhydrosiloxane (PMHS, n = 25) was purchased from AZmax Co. Ltd. Chemical shifts for ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured on JEOL ECA 400 (396 MHz) and ECA 600 (600 MHz) spectrometers. Chemical shifts for ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.1), unless otherwise noted. Chemical shifts for ^{29}Si NMR were described in parts per million downfield from tetramethylsilane as an external standard. IR spectra were measured on JASCO FT/IR-550 and 4200 spectrometers. ICP-MS and HRMS analyses were performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide (Merck, aluminum oxide 150 F_{254}, neutral) and glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid.

2. Preparation of 2,2'-Bipyridine Derivatives

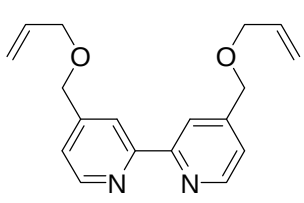
4,4'-Di(methoxycarbonyl)-2,2'-bipyridine.[1] This compound was prepared from 2,2'-bipyridine-4,4'-dicarboxylic acid (1.16 g, 4.75 mmol) and conc. H_2SO_4 (2.3 mL) in methanol (20 mL) according to the literature method;[1] 1.11 g (86%); Mp 209.2-210.4 °C; IR (KBr): ν 1731, 1558, 1466, 1437, 1359, 1295, 1246, 1191, 1126, 959, 758 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 4.00 (s, 6H), 7.91 (d, *J* = 4.8 Hz, 2H), 8.87 (d, *J* = 4.8 Hz, 2H), 8.97 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 52.9, 120.7, 123.4, 138.7, 150.3, 156.6, 165.7. This compound was used in the next step without further purification.



4,4'-Bis(hydoroxymethyl)-2,2'-bipyridine.[1,2] This compound was prepared from 4,4'-di(methoxycarbonyl)-2,2'-bipyridine (1.11 g, 4.07 mmol) and $NaBH_4$ (3.34 g, 88.3 mmol) in ethanol (81 mL) according to the literature method;[1,2] 725 mg (82%); Mp 170.6-171.4 °C; IR (KBr): ν 3366, 3064, 2883, 1601, 1557, 1456, 1388, 1060, 997, 816 cm^{-1}; ^{1}H NMR (396 MHz, CD_3OD): δ 4.79 (s, 4H), 7.48 (d, *J* = 4.8 Hz, 2H), 8.31 (bs, 2H), 8.63 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (150 MHz, CD_3OD): δ 63.6, 120.2, 122.7, 150.1, 154.4, 157.2. This compound was used in the next step without further purification.



4,4'-Bis[(2-propenyloxy)methyl]-2,2'-bipyridine (DABipy). To a suspension of NaH (60 wt%; 523 mg, 8.7 mmol) in DMF(5 mL) was added a solution of 4,4'-bis(hydroxymethyl)-2,2'-bipyridine (725 mg, 3.35 mmol) in DMF (11 mL) at 0 °C. After it was stirred at that temperature for 40 min, allyl bromide (760 μL, 8.71 mmol) was added and the resultant mixture was stirred at room temperature overnight. Purification by silica gel chromatography ($CHCl_3$/MeOH = 20:1) gave **2** in 77% yield (770 mg); IR (neat) ν 2855, 1597, 1557, 1459, 1367, 1105, 1092, 991, 926, 826 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 4.11 (d, *J* = 5.3 Hz, 4H), 4.64 (s, 4H), 5.25 (d, *J* = 10.1 Hz, 2H), 5.35 (d, *J* = 16.9 Hz, 2H), 5.98 (ddd, *J* = 16.9, 10.1, 5.3 Hz, 2H), 7.39 (d, *J* = 4.8 Hz, 2H), 8.38 (bs, 2H), 8.67 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 70.6, 71.9, 117.7, 119.4, 122.0, 134.4, 148.8, 149.5, 156.2; HRMS (FAB) calcd for $C_{18}H_{20}N_2O_2$+H 297.1603, found 297.1603.



3. Synthesis of [Cu/bipy]@Si

[bipy]@Si: To a stirred solution of DABipy (**2**) (14.8 mg, 0.05 mmol) and PMHS (M_w = 1500–1900; n = 25.6 (average); 140 μL, Si–H = 2 mmol) in tetrahydropyran (0.5 mL) was added a xylene solution of Karstedt's catalyst (0.1 *M* solution, 100 μL, 0.01 mmol). After it was stirred for 30 min, 1,5-hexadiene (180 μL, 1.5 mmol) was added to the solution. Hydrosilylation proceeded at 40 °C and [bipy]@Si was formed as a wet gel within 2 h. Finally, the formed wet gel was treated with ethylene (balloon) in ether (2 mL) for 1 h for complete consumption of the unreacted Si–H moieties in the gel. The resultant wet gel was washed with ether (20 mL) and then dried under reduced pressure to afford the dry gel. ^{29}Si NMR (CP/MAS; 10 kHz) δ 9.9 (Me_3SiO–), -21.0 [–$CH_2SiMe(O–)_2$].

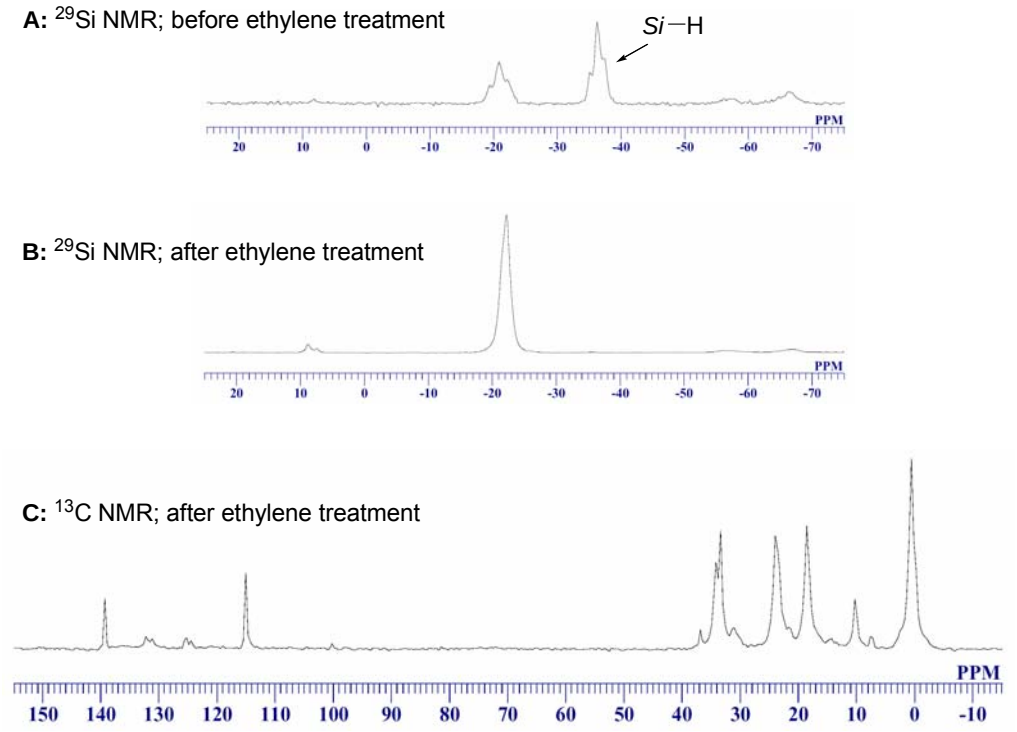


Figure S1. ^{29}Si NMR (CP/MAS; 10 kHz) (**A** and **B**) and ^{13}C NMR (CP/MAS; 10 kHz) spectra (**C**) of [bipy]@Si.

[Cu/bipy]@Si: CuCl (2.0 mg, 0.02 mmol and [Pt]@$Si_{C6\text{-}Dabipy}$ obtained as above were measured into a flask, and the atmosphere was replaced by argon. Then freshly distilled, carefully degassed dichloromethane (1.5 mL) was added. After it was stirred for 1 h at ambient temperature, the resultant wet gel was washed with dichloromethane (20 mL) and then dried under reduced pressure to afford [Cu]@$Si_{C6\text{-}DABipy}$ as a dry gel. ICP-MS analysis revealed that the dichloromethane solution contained 102 μg of copper; which means that 92% of the charged CuCl was entrapped in the gel.

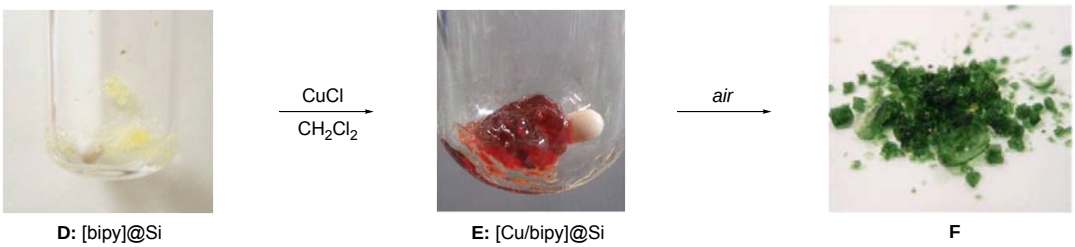
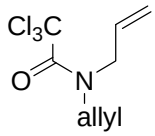


Figure S2. Photos of [bipy]@Si (**D**), [Cu/bipy]@Si (**E:** as prepared; **F:** exposure to air).

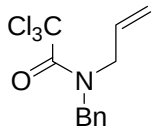
4. Spectral Dada of the Substrates

***N,N*-Diallyl- α,α,α-trichloroacetamide (1a):**[3] IR (neat): ν 3084, 2986, 1681, 1435, 1409, 1232, 1183, 992, 929,



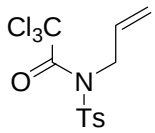
844, 810, 670 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 4.01 (bs, 2H), 4.32 (bs, 2H), 5.10-5.39 (m, 4H), 5.80 (bs, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 49.6, 51.5, 92.9, 117.9, 119.2, 130.9, 131.8, 160.0.

***N*-Allyl-*N*-benzyl-α,α,α-trichloroacetamide (1b):**[3] mp: 43.9-44.6 °C; IR (KBr): ν 3065, 2986, 1678, 1496, 1414,



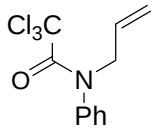
1229, 991, 937, 847, 738 cm^{-1}. Spectroscopic data of this amide were obtained as a mixture of two rotational isomers. ***major isomer*:** ^1H NMR (396 MHz, $CDCl_3$): δ 4.28 (bs, 2H), 4.67 (bs, 2H), 5.26 (bd, *J* = 17.4 Hz, 1H), 5.35 (bd, *J* = 9.7 Hz, 1H), 5.84 (bs, 1H), 7.21-7.41 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 49.9, 51.1, 93.0, 119.7, 127.7, 127.8, 128.7, 131.8, 135.7, 160.6; ***minor isomer*:** ^1H NMR (396 MHz, $CDCl_3$): δ 3.94 (bs, 2H), 4.98 (bs, 2H), 5.13 (bd, *J* = 16.9 Hz, 1H), 5.23 (bd, *J* = 9.2 Hz, 1H), 5.77 (bs, 1H), 7.21-7.41 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 49.9, 52.2, 93.0, 118.3, 127.0, 127.8, 128.7, 130.7, 135.0, 160.6.

***N*-Allyl-*N*-tosyl-α,α,α-trichloroacetamide (1c):**[3] mp: 72.5-73.0 °C; IR (KBr): ν 3057, 2988, 1712, 1596, 1365,



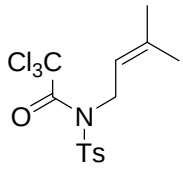
1322, 1267, 1222, 1173, 1086, 840, 817, 674 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.92 (dm, *J* = 5.3 Hz, 2H), 5.38 (dm, *J* = 10.6 Hz, 1H), 5.46 (dm, *J* = 17.4 Hz, 1H), 5.96 (ddt, *J* = 17.4, 10.6, 5.3 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.8, 51.2, 92.1, 119.6, 129.5, 129.6, 132.3, 134.7, 145.7, 159.0.

***N*-Allyl-*N*-phenyl-α,α,α-trichloroacetamide (1d):**[4] IR (neat): ν 3082, 2934, 1683, 1594, 1493, 1385, 1258, 930,



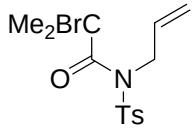
835, 699 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 4.38 (bs, 2H), 5.13 (dm, *J* = 16.9 Hz, 1H), 5.21 (dm, *J* = 10.1 Hz, 1H), 5.93 (ddt, *J* = 16.9, 10.1, 6.3 Hz, 1H), 7.28-7.43 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 57.8, 93.1, 119.6, 128.6, 128.8, 129.6, 131.1, 141.1, 160.1.

***N*-Prenyl-*N*-tosyl-α,α,α-trichloroacetamide (1e):** mp: 99.7-100.3 °C; IR (KBr): ν 3061, 2975, 1709, 1596, 1446,



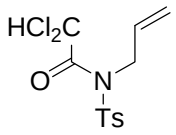
1365, 1311, 1171, 1085, 844, 814, 704 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 1.78 (bs, 3H), 1.80 (bs, 3H), 2.45 (s, 3H), 4.90 (d, *J* = 6.3 Hz, 2H), 5.22 (m, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 18.3, 21.8, 25.8, 47.9, 92.3, 119.3, 129.4, 129.6, 135.2, 137.4, 145.5, 159.3; HRMS (FAB) calcd for $C_{14}H_{16}NO_3Cl_3S$+H 383.9995, found 383.9995.

***N*-Allyl-*N*-tosyl-α,α-dimethyl-α-bromoacetamide (1f):**[5] mp: 83.2-84.6 °C; IR (KBr): ν 2982, 2934, 1682, 1596,



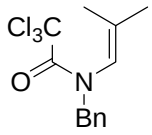
1458, 1392, 1352, 1317, 1240, 1168, 1086, 927, 813, 775, 716 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): 1.89 (s, 6H), 2.44 (s, 3H), 4.96 (dm, *J* = 4.8 Hz, 2H), 5.32 (dm, *J* = 10.6 Hz, 1H), 5.42 (dm, *J* = 16.9 Hz, 1H), 5.99 (ddt, *J* = 16.9, 10.6, 4.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.7, 32.0, 50.6, 57.0, 118.2, 128.9, 129.2, 133.6, 136.1, 144.7, 170.4.

***N*-Allyl-*N*-tosyl-α,α-dichloroacetamide (1g):**[6] mp: 95.3-96.0 °C; IR (KBr): ν 3057, 2986, 1715, 1596, 1366, 1266, 1172, 1087, 811, 739 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 2.47 (s, 3H), 4.42 (dm, *J* = 5.3 Hz, 2H), 5.21-



5.28 (m, 2H), 5.80 (ddt, *J* = 17.4, 10.1, 5.3 Hz, 1H), 6.88 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.7, 49.0, 64.7, 119.0, 128.2, 130.0, 131.2, 134.6, 146.0, 163.5; HRMS (EI) calcd for $C_{12}H_{13}NO_3Cl_2$ 320.9993, found 320.9992.

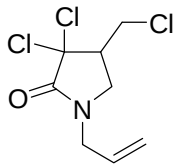
***N*-Benzyl-*N*-(2-methyl-1-propenyl)-α,α,α-trichloroacetamide (1h):**[7] mp: 44.8-45.7 °C; IR (KBr): ν 3061, 2982,



1685, 1667, 1496, 1455, 1387, 1265, 1245, 949, 864, 816 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 1.59 (bs, 3H), 1.71 (bs, 3H), 4.72 (s, 2H), 6.10 (bs, 1H), 7.26-7.36 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 18.6, 21.8, 56.1, 93.3, 123.2, 127.8, 128.4, 128.6, 136.0, 137.8, 160.7.

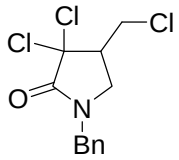
5. Spectral Dada of the Products

3,3-Dichloro-4-chloromethyl-1-allylpyrroridin-2-one (2a):[3] IR (neat): ν 2923, 1728, 1482, 1446, 1418, 1273,



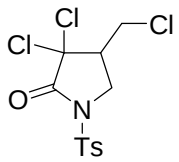
956, 916, 835 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 3.11 (m, 1H), 3.22 (dd, *J* = 10.1, 8.2 Hz, 1H), 3.58 (dd, *J* = 10.1, 7.2 Hz, 1H), 3.74 (dd, *J* = 10.6, 10.1 Hz, 1H), 3.92-4.05 (m, 3H), 5.27 (dm, *J* = 16.9 Hz, 1H), 5.30 (dm, *J* = 10.1 Hz, 1H), 5.74 (ddt, *J* = 16.9, 10.1, 6.3 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 41.1, 46.4, 47.4, 51.6, 83.7, 119.7, 130.4, 165.7.

3,3-Dichloro-4-chloromethyl-1-benzylpyrroridin-2-one (2b):[3] mp: 129.3-130.0 °C; IR (KBr): ν 3030, 2927,



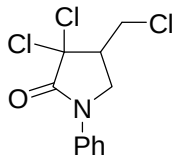
1725, 1482, 1446, 1430, 1360, 1273, 957, 911, 834, 701 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 3.03-3.14 (m, 2H), 3.47 (m, 1H), 3.68 (dd, *J* = 11.1, 9.7 Hz, 1H), 3.98 (dd, *J* = 11.1, 3.9 Hz, 1H), 4.45 (d, *J* = 14.5 Hz, 1H), 4.64 (d, *J* = 14.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.31-7.40 (m, 3H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 41.1, 47.3, 47.9, 51.6, 83.7, 128.3, 128.4, 129.1, 134.5, 166.1.

3,3-Dichloro-4-chloromethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2c):[3] mp: 159.5-160.9 °C; IR (KBr): ν



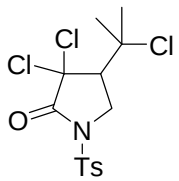
3054, 1763, 1376, 1265, 1176, 985, 748, 730 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 2.46 (s, 3H), 3.08 (dddd, *J* = 10.1, 8.7, 6.8, 4.3 Hz, 1H), 3.56 (dd, *J* = 10.1, 8.7 Hz, 1H), 3.66 (dd, *J* = 11.1, 10.1 Hz, 1H), 3.94 (dd, *J* = 11.1, 4.3 Hz, 1H), 4.25 (dd, *J* = 10.1, 6.8 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.9, 40.2, 47.5, 50.7, 82.7, 128.3, 130.1, 133.3, 146.5, 163.1.

3,3-Dichloro-4-chloromethyl-1-phenylpyrroridin-2-one (2d):[8] mp: 139.9-140.8 °C; IR (KBr): ν 3060, 2965,



1710, 1593, 1494, 1409, 1305, 1184, 1123, 1052, 817, 761, 684 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 3.26 (dddd, *J* = 10.6, 8.7, 7.2, 4.3 Hz, 1H), 3.74 (dd, *J* = 10.1, 8.7 Hz, 1H), 3.85 (dd, *J* = 11.1, 10.6 Hz, 1H), 4.09 (dd, *J* = 11.1, 4.3 Hz, 1H), 4.10 (dd, *J* = 10.1, 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 7.7, 7.2 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 41.0, 49.1, 51.1, 84.1, 120.3, 126.3, 129.3, 137.9, 164.4.

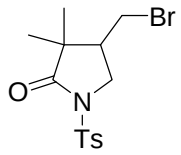
3,3-Dichloro-4-[(1-chloro-1-methyl)ethyl]-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2e): mp: 118.6-119.5 °C; IR



(KBr): ν 3054, 2987, 1762, 1375, 1265, 1176, 1129, 971, 749, 729, 704 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$): δ 1.87 (s, 3H), 1.89 (s, 3H), 2.47 (s, 3H), 3.10 (dd, *J* = 10.1, 7.2 Hz, 1H), 3.88 (t, *J* = 10.1 Hz, 1H), 4.25 (dd, *J* = 10.1, 7.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.9, 30.2, 33.7, 45.9, 58.3, 67.8, 81.9, 128.4, 130.1,

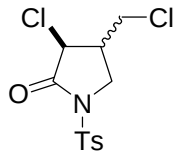
133.5, 146.5, 163.3; HRMS (FAB) calcd for $C_{14}H_{16}NO_3Cl_3S$+H 383.9995, found 383.9997.

3,3-Dimethylo-4-bromoomethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2f):[5] mp: 130.9-131.2 °C; IR (KBr): ν



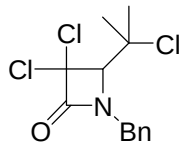
3057, 2973, 1736, 1366, 1266, 1173, 1115, 744 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 0.89 (s, 3H), 1.16 (s, 3H), 2.43 (s, 3H), 2.44 (dddd, *J* = 10.1, 8.7, 7.2, 4.8 Hz, 1H), 3.20 (t, *J* = 10.1 Hz, 1H), 3.43 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.46 (dd, *J* = 10.1, 8.7 Hz, 1H), 4.14 (dd, *J* = 10.1, 7.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 17.8, 21.7, 23.4, 29.9, 45.0, 45.4, 48.8, 128.0, 129.8, 134.8, 145.4, 176.9.

3-Chloro-4-chloromethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2g):[6] mp: 125.3-126.9 °C; IR (KBr): ν 3055,



1753, 1372, 1265, 1174, 1129, 1089, 964, 741 cm^{-1}; *trans*-**4h**: ^1H NMR (396 MHz, $CDCl_3$): δ 2.46 (s, 3H), 2.83 (m, 1H), 3.69-3.81 (m, 3H), 4.11 (dd, *J* = 10.6, 7.7 Hz, 1H), 4.35 (d, *J* = 8.7 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.8, 42.3, 44.2, 46.9, 56.1, 128.3, 130.01, 134.2, 146.1, 166.7. *cis*-**4h**: ^1H NMR (396 MHz, $CDCl_3$): δ 2.46 (s, 3H), 2.95 (m, 1H), 3.53 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.63-3.74 (m, 2H), 4.13 (dd, *J* = 10.1, 7.3 Hz, 1H), 4.44 (d, *J* = 6.3 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 21.8, 40.3, 41.1, 47.9, 57.5, 128.2, 129.96, 134.0, 146.0, 166.8.

3,3-Dichloro-4-[(1-chloro-1-methyl)ethyl]-1-benzylazetidin-2-one (2h): mp: 89.6-90.3 °C; IR (KBr): ν 3064,



2937, 1792, 1394, 1265, 1111, 805, 739 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$): δ 1.75 (s, 3H), 1.81 (s, 3H), 4.23 (s, 1H), 4.33 (d, *J* = 15.0 Hz, 1H), 5.00 (d, J = 15.0 Hz, 1H), 7.29-7.40 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$): δ 26.3, 29.1, 46.3, 68.6, 81.2, 128.4, 128.6, 129.0, 134.0, 161.8; HRMS (FAB) calcd for $C_{13}H_{14}NOCl_3$+H 306.0219, found 306.0219.

6. References

1) D. Miyoshi, H. Karimata, Z.-M. Wang, K. Koumoto and N. Sugimoto, *J. Am. Chem. Soc*., 2007, **129**, 5919.

2) I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu and G. J. Meyer, *Inorg. Chem*., 2001, **40**, 6073.

3) H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama and K. Itoh, *J. Org. Chem*., 1993, **58**, 464.

4) C. K. Tseng, E. G. Teach and R. W. Simons, *Synth. Commun*., 1984, **14**, 1027.

5) A. J. Clark, R. P. Filik, D. M. Haddleton, A. Radigue, C. J. Sanders, G. H. Thomas and M. E. Smith, *J. Org. Chem*., 1999, **64**, 8954.

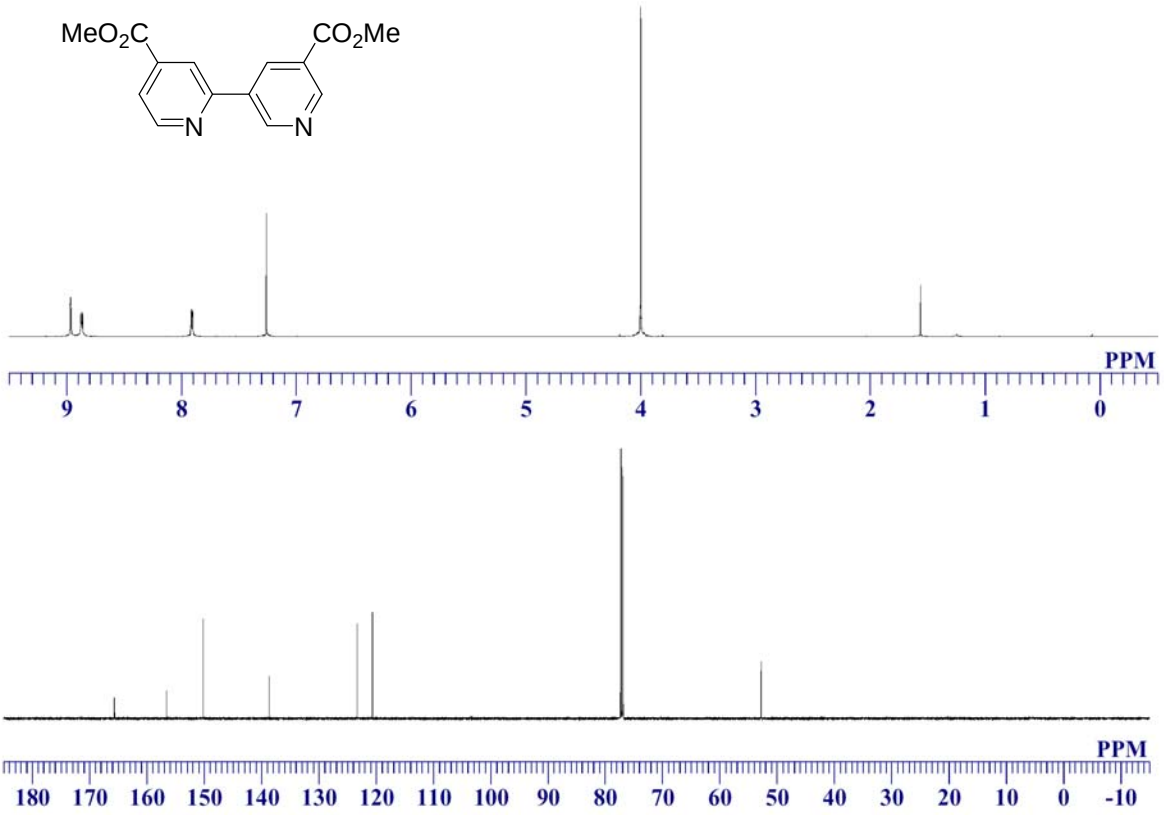
6) M. A. Rachita and G. A. Slough, *Tetrahedron Lett*., 1993, **34**, 6821.

7) J. Cassayre, B. Quiclet-Sire, J.-B. Saunier and S. Z. Zard, *Tetrahedron*, 1998, **54**, 1029.

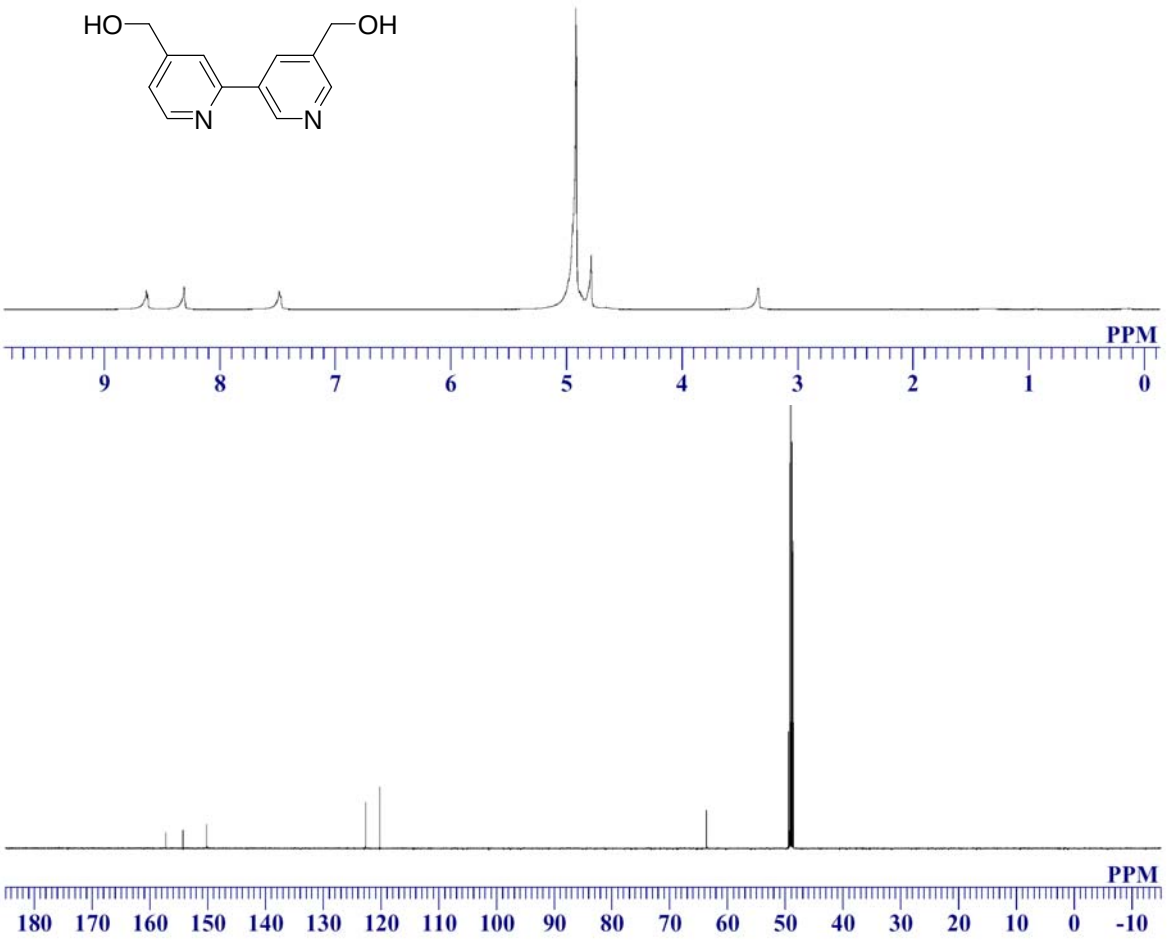
8) Y. Motoyama, S. Hanada, S. Niibayashi, K. Shimamoto, N. Takaoka and H. Nagashima, *Tetrahedron*, 2005, **61**, 10216.

7. NMR Spectra of Pyridine Derivatives

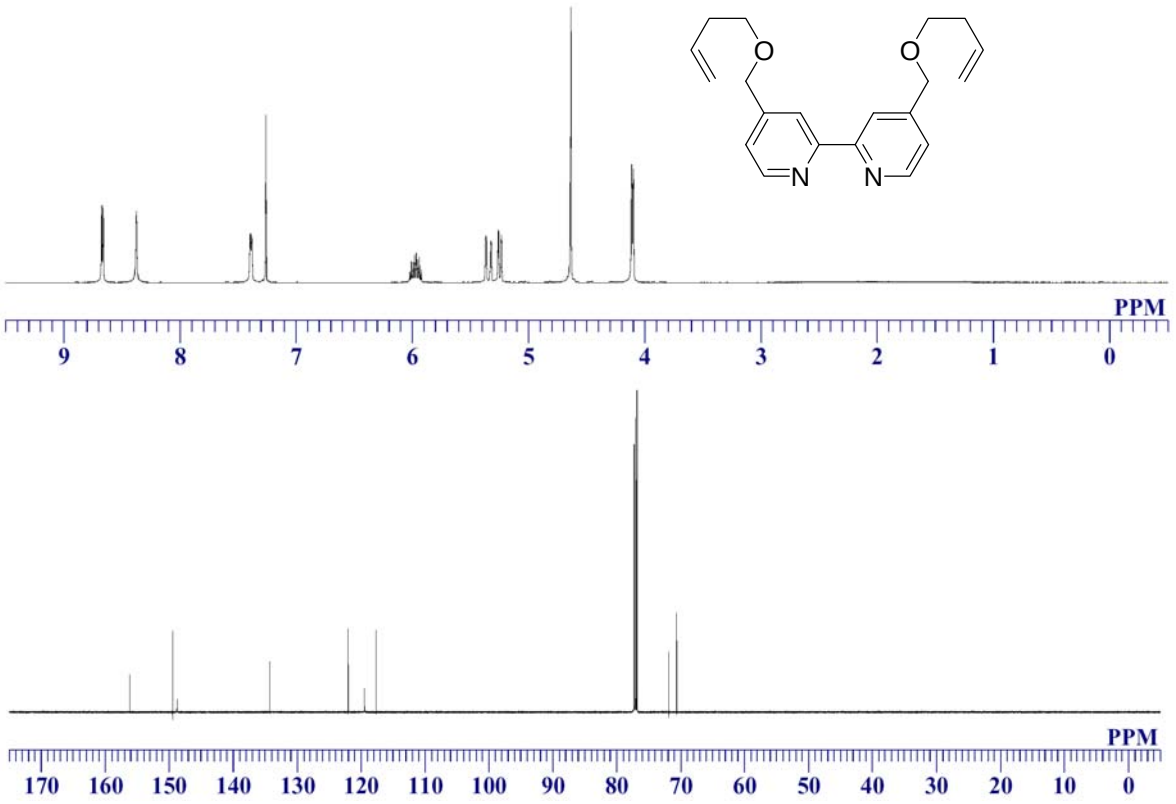
4,4'-Di(methoxycarbonyl)-2,2'-bipyridine



4,4'-Bis(hydoroxymethyl)-2,2'-bipyridine

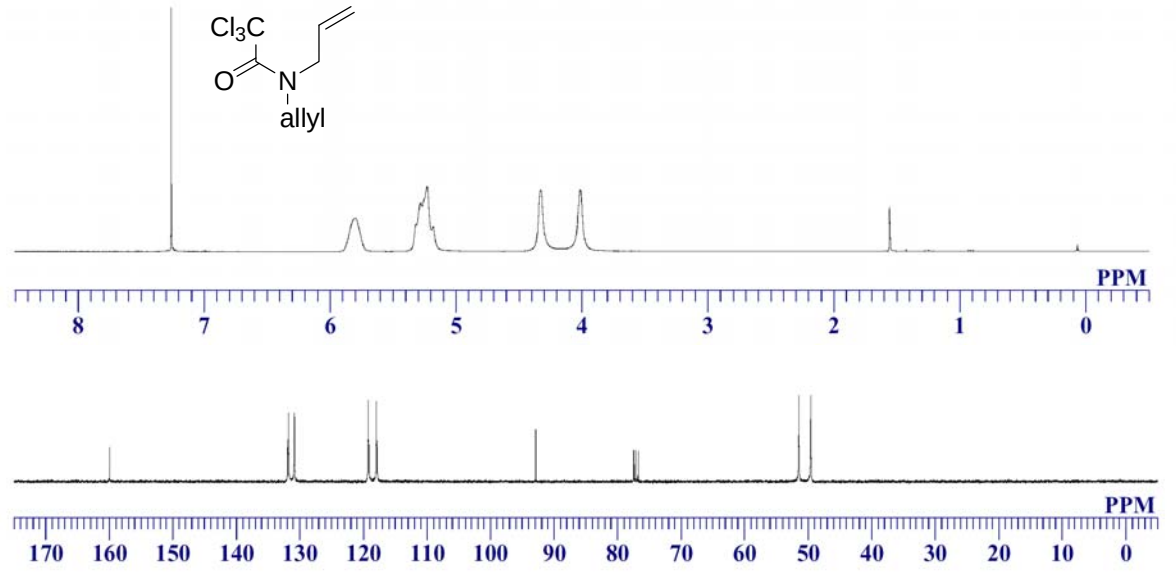


4,4'-Bis(2-propenoxymethyl)-2,2'-bipyridine (DABipy)

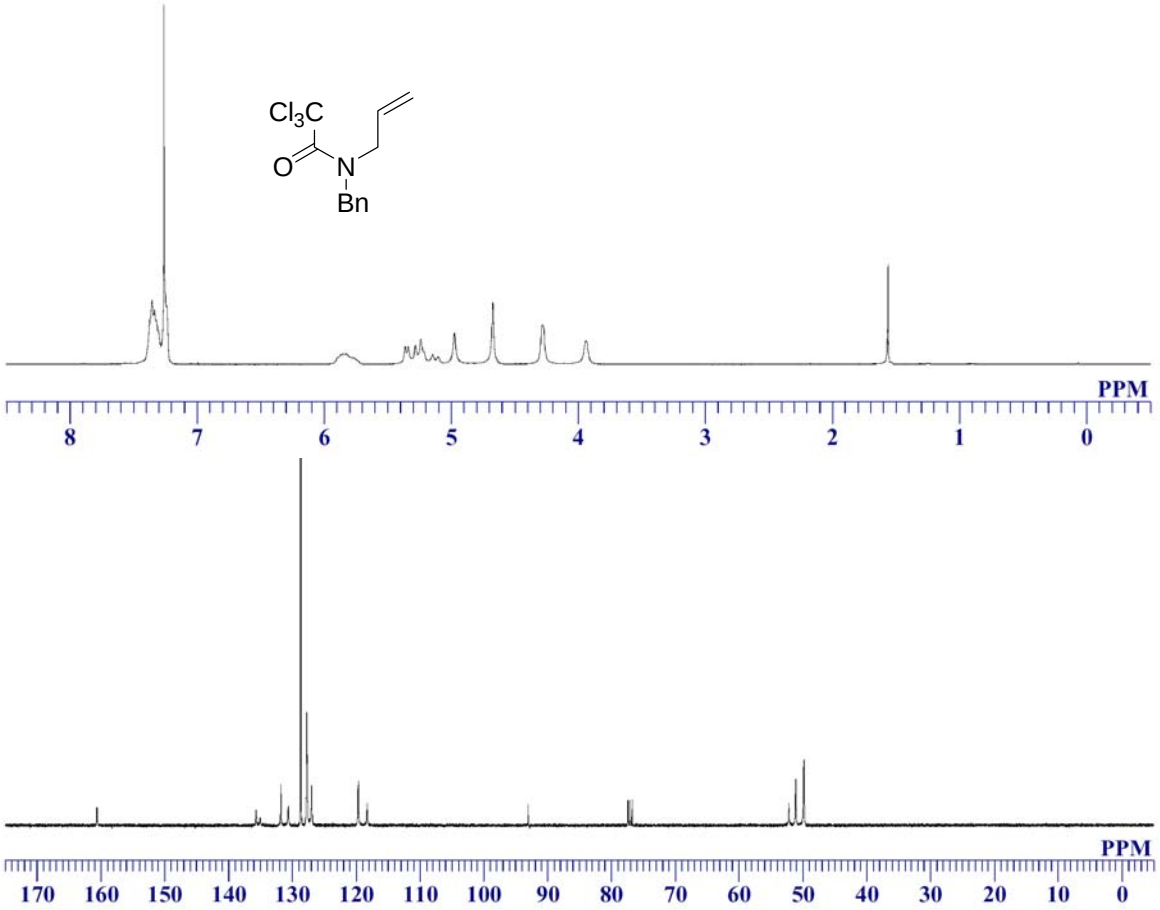


NMR Spectra of the Substrates

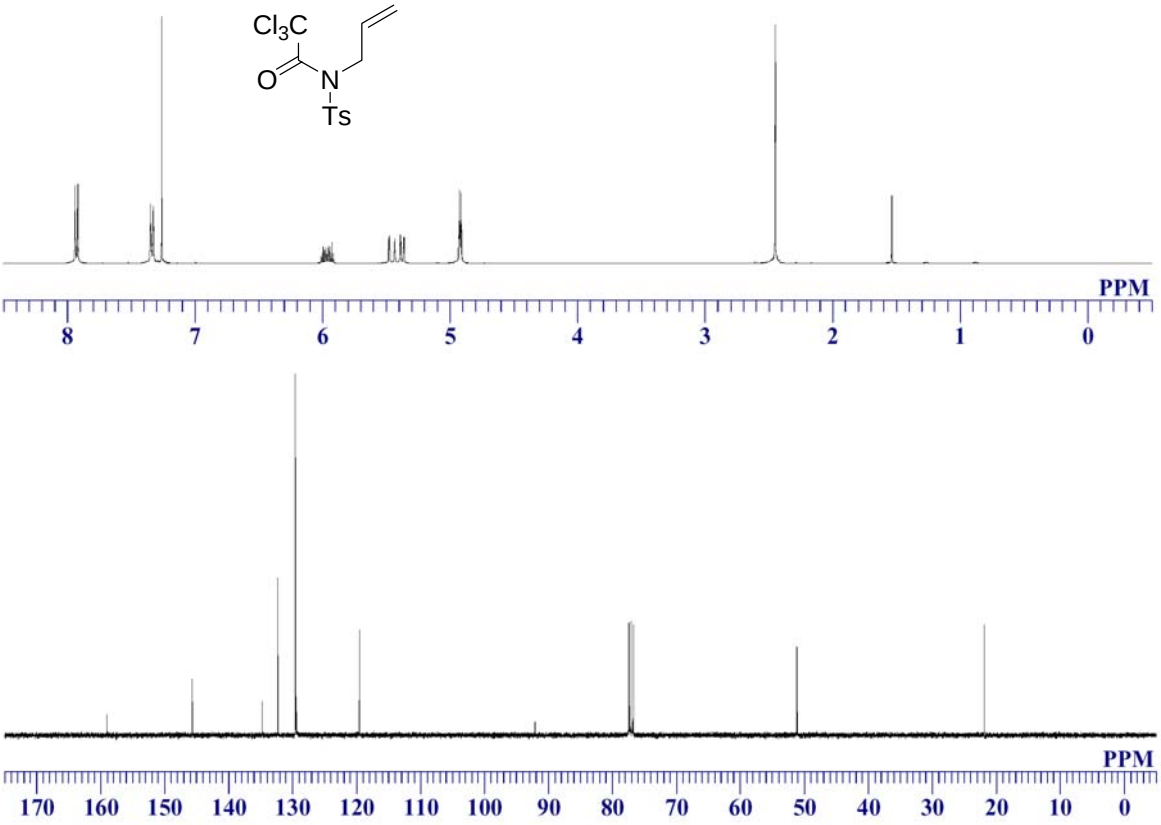
***N,N*-Diallyl- α,α,α-trichloroacetamide (1a)**



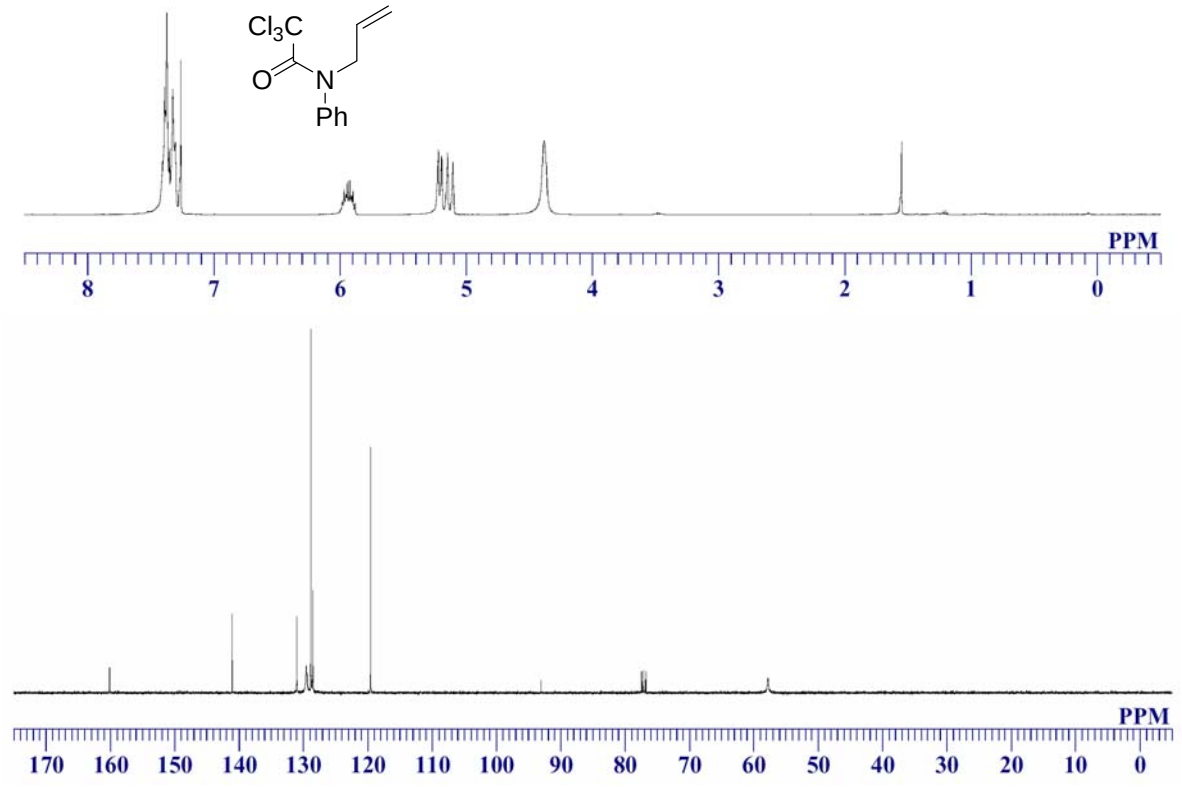
_N_-Allyl-_N_-benzyl-α,α,α-trichloroacetamide (1b)



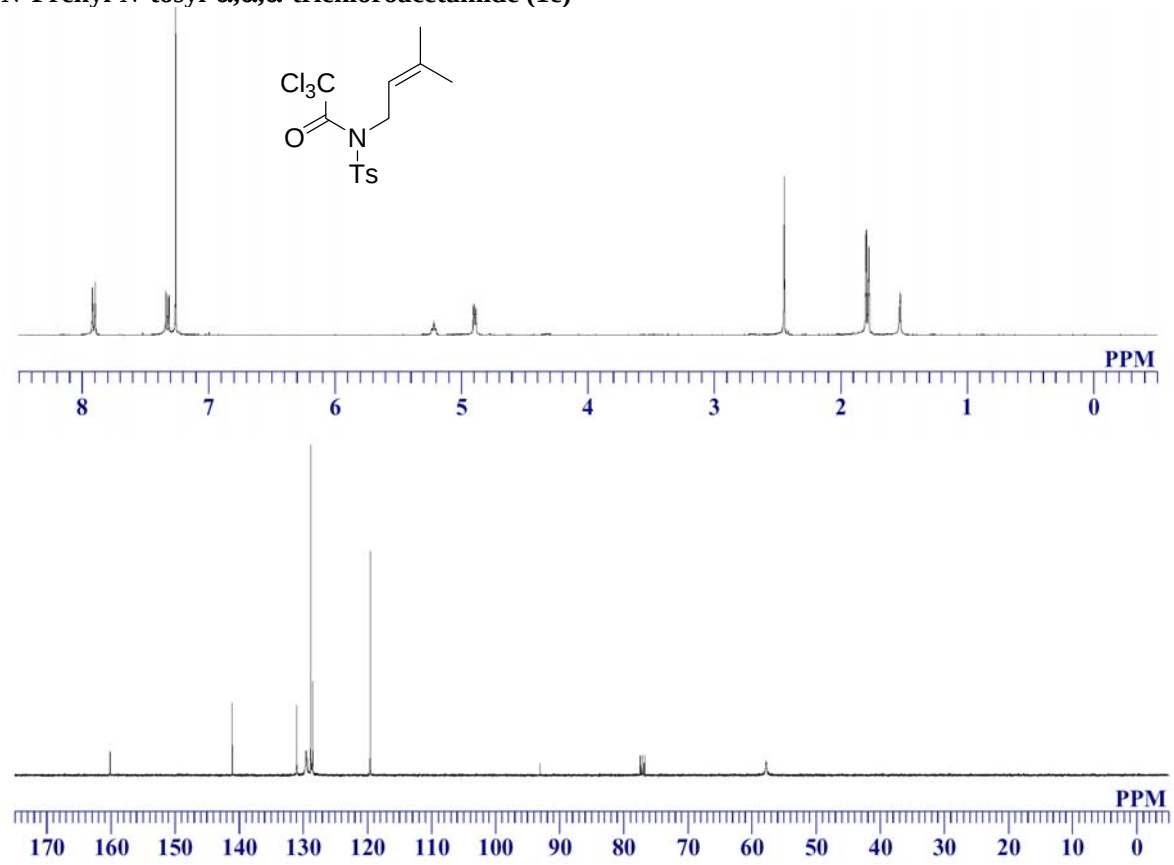
_N_-Allyl-_N_-tosyl-α,α,α-trichloroacetamide (1c)



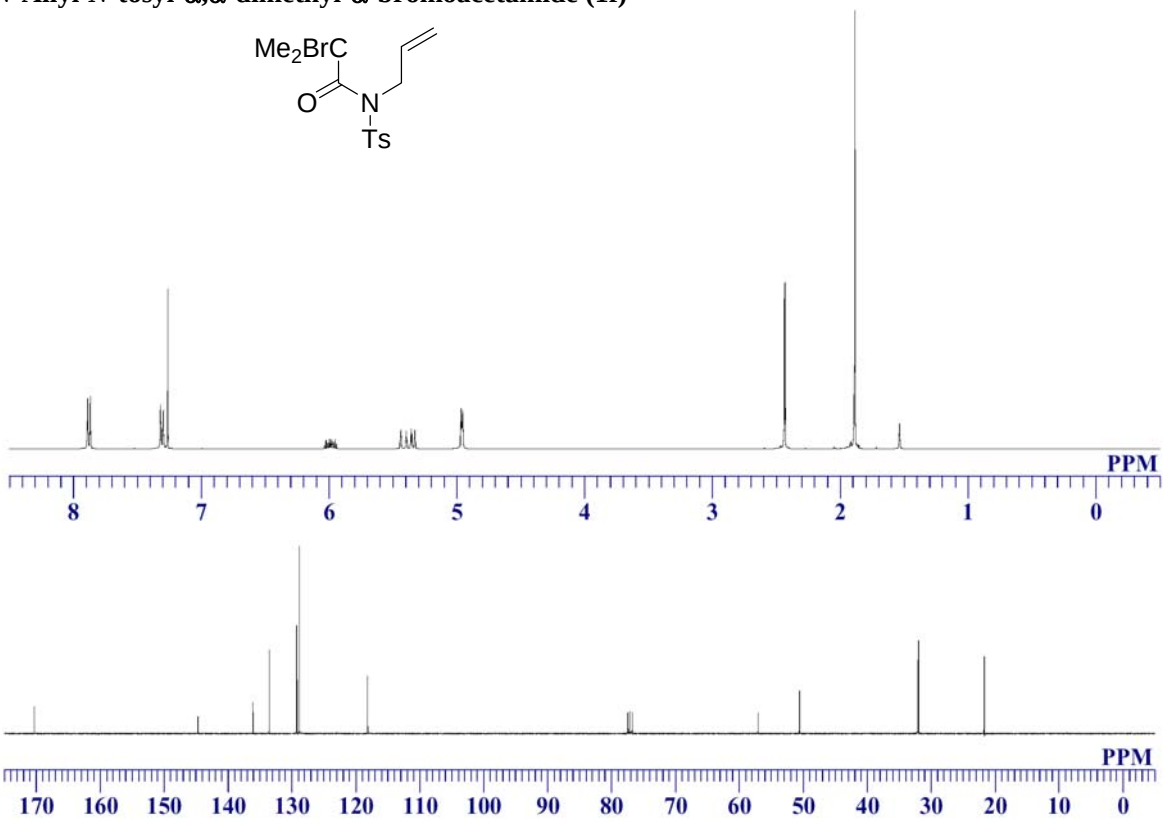
_N_-Allyl-_N_-phenyl-α,α,α-trichloroacetamide (1d)



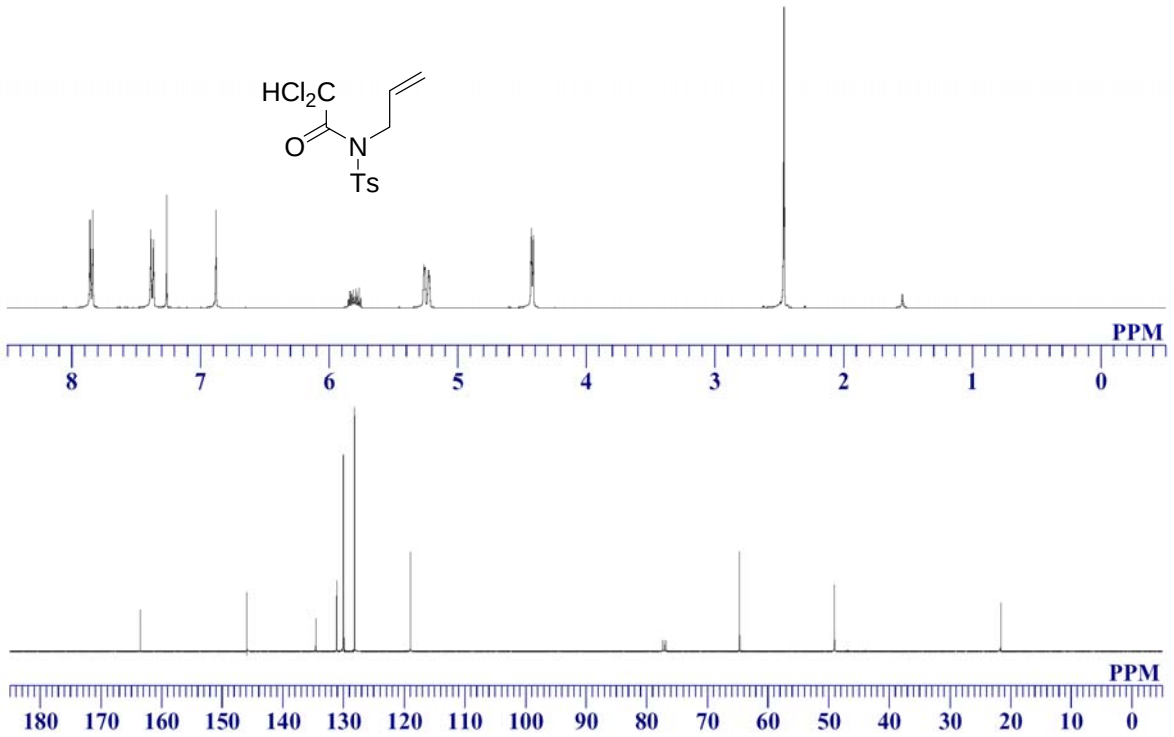
_N_-Prenyl-_N_-tosyl-α,α,α-trichloroacetamide (1e)



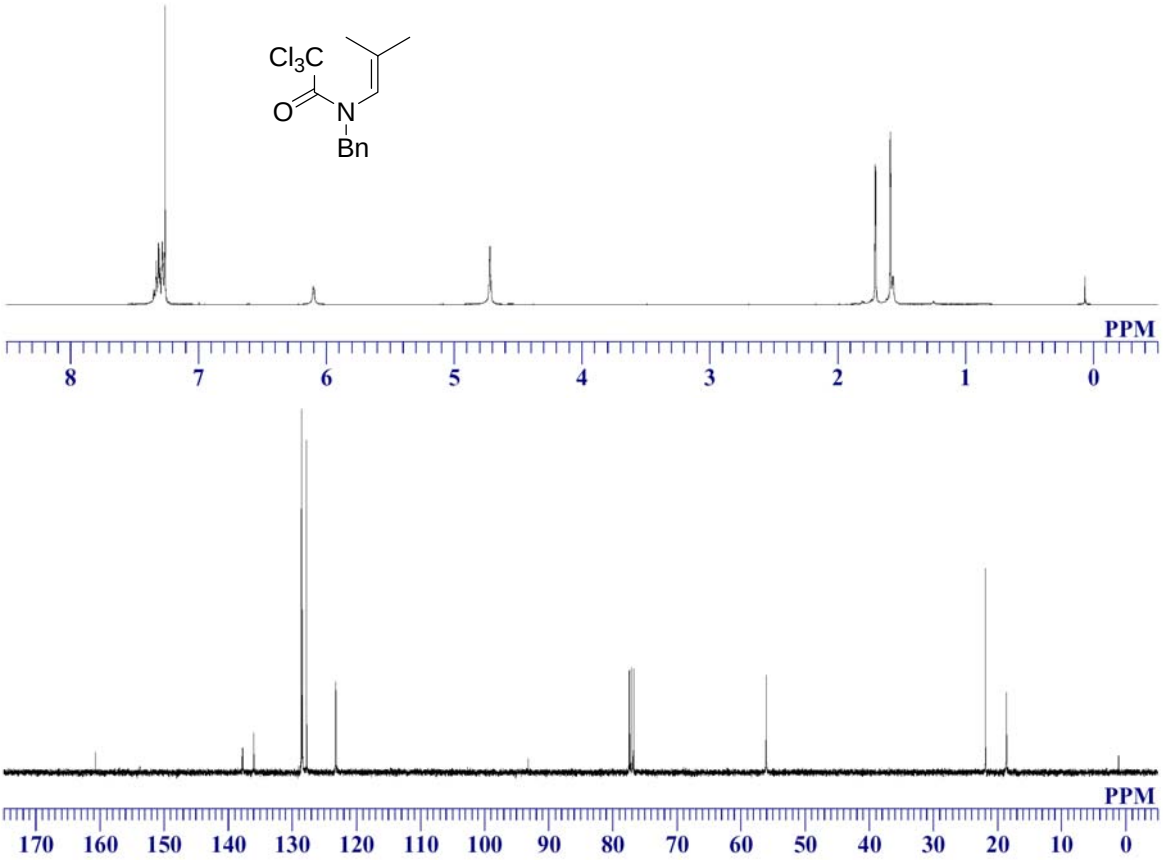
_N_-Allyl-_N_-tosyl-α,α-dimethyl-α-bromoacetamide (1f)



_N_-Allyl-_N_-tosyl-α,α-dichloroacetamide (1g)

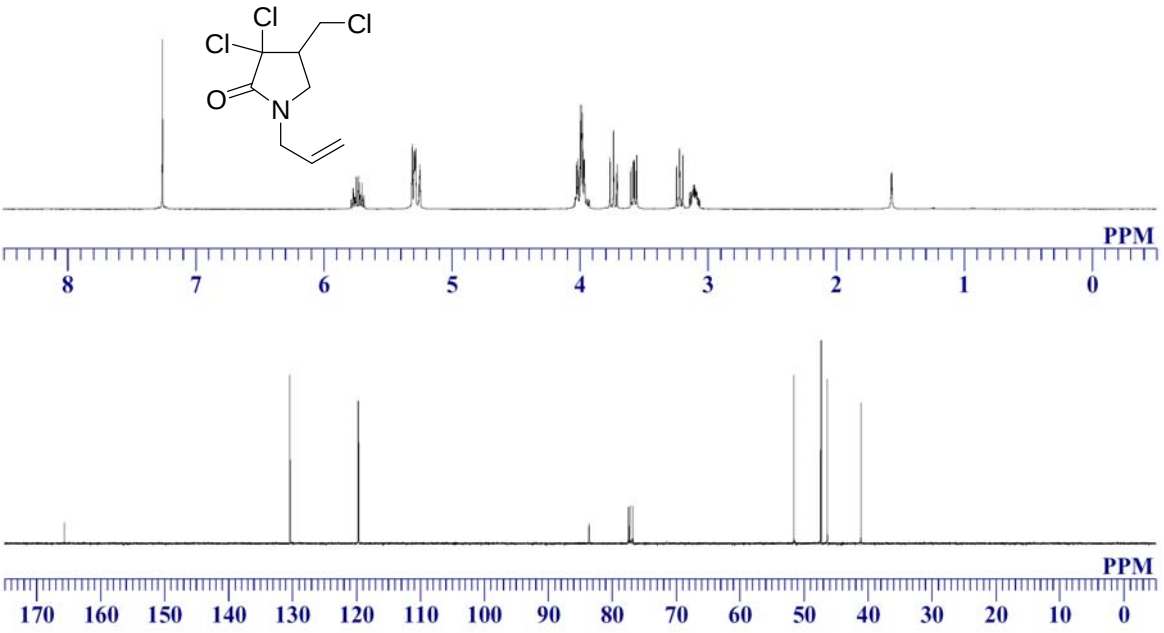


_N_-Benzyl-_N_-(2-methyl-1-propenyl)-α,α,α-trichloroacetamide (1h)

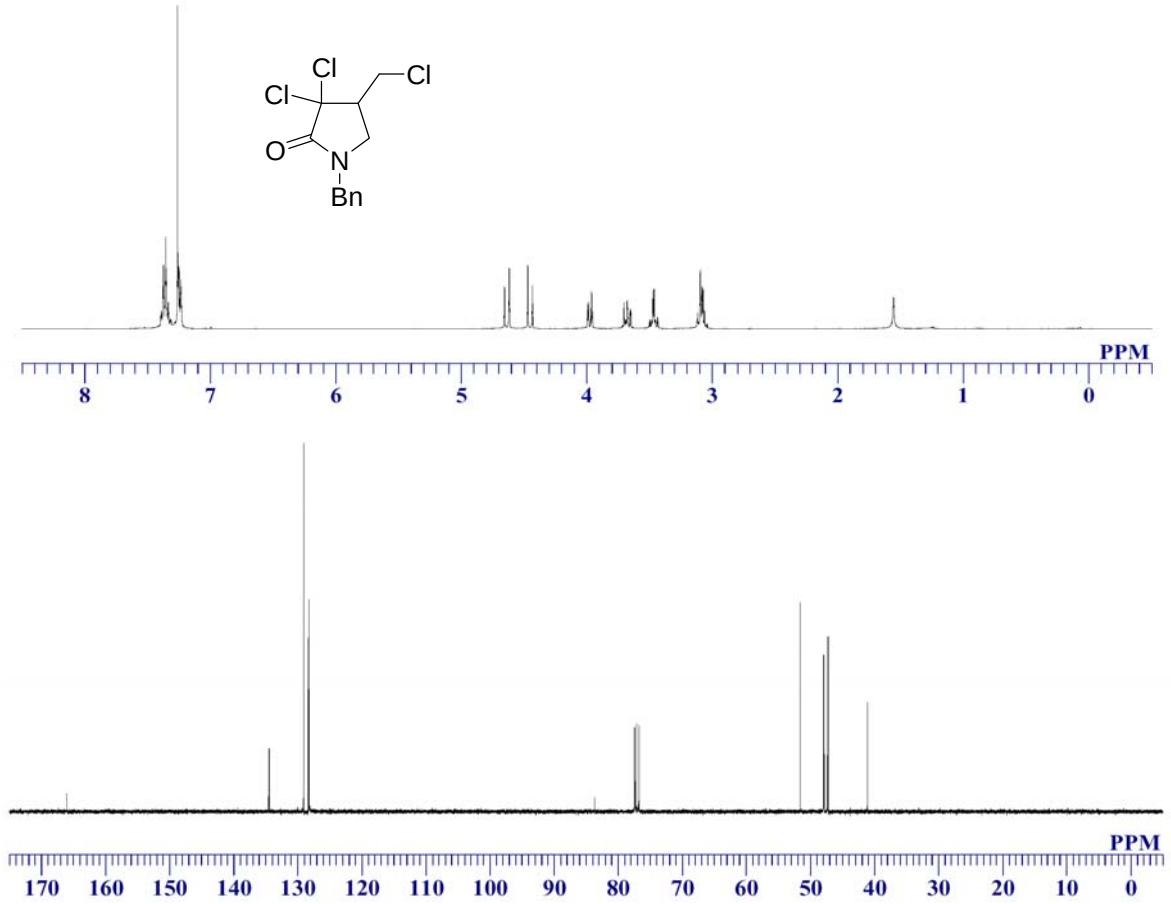


NMR Spectra of the Products

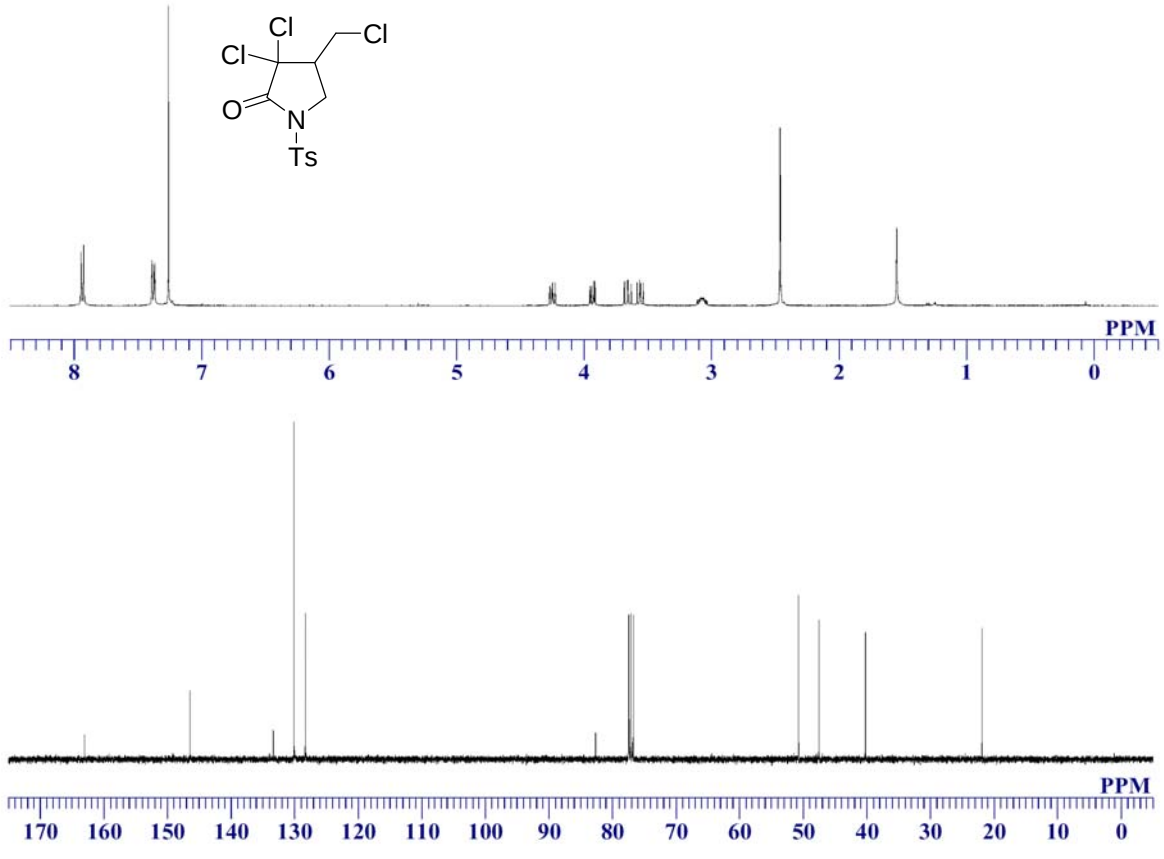
3,3-Dichloro-4-chloromethyl-1-allylpyrroridin-2-one (2a)



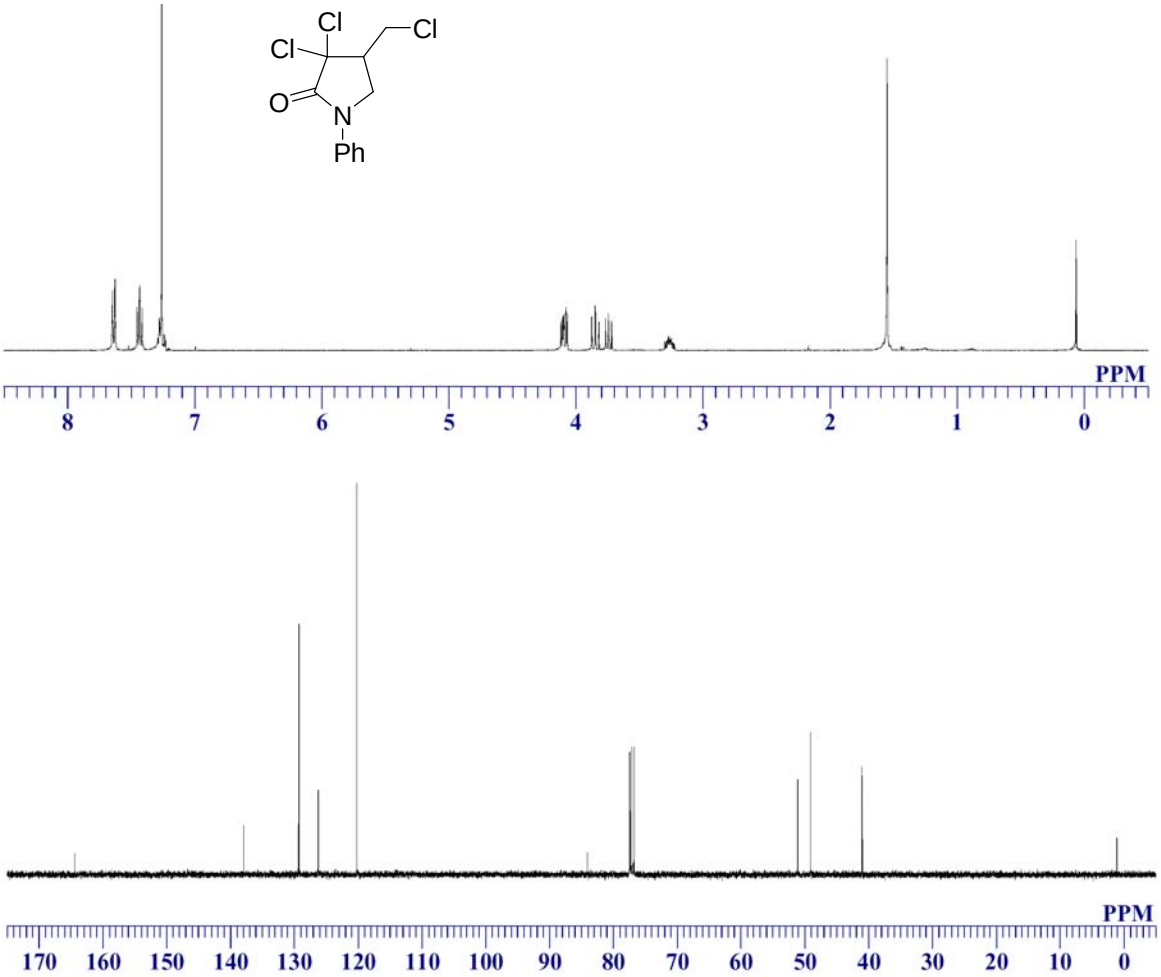
3,3-Dichloro-4-chloromethyl-1-benzylpyrroridin-2-one (2b)



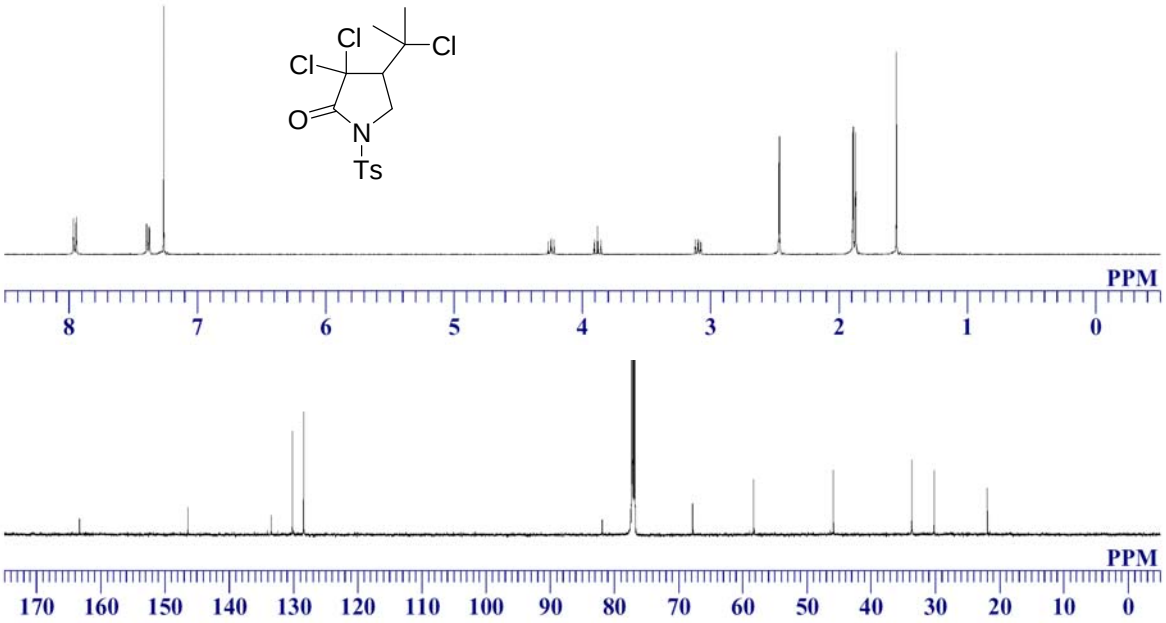
3,3-Dichloro-4-chloromethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2c)



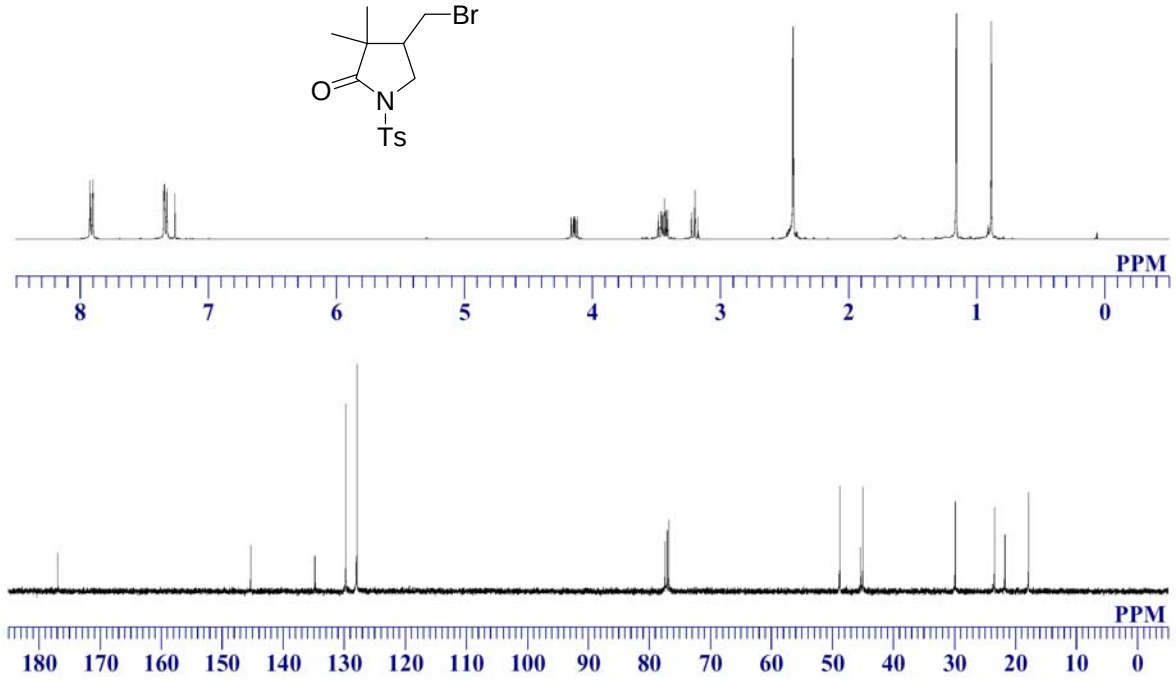
3,3-Dichloro-4-chloromethyl-1-phenylpyrroridin-2-one (2d)



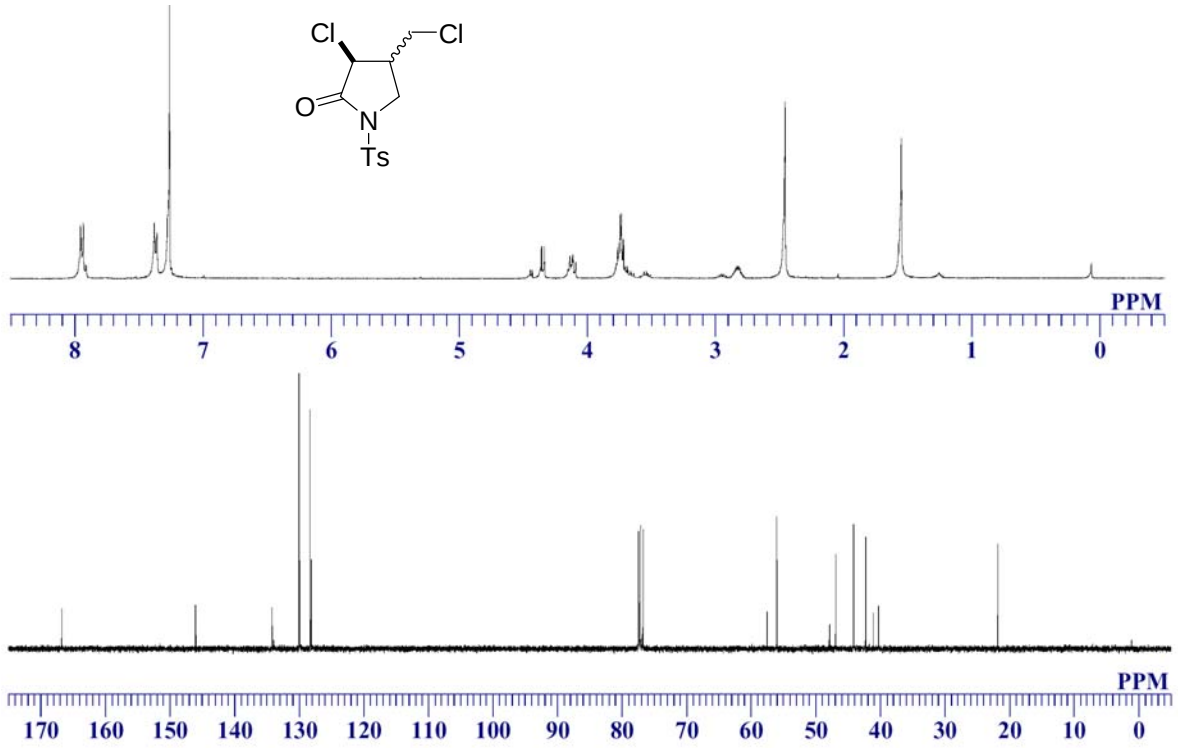
3,3-Dichloro-4-[(1-chloro-1-methyl)ethyl]-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2e)



3,3-Dimethylo-4-bromoomethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2f)



3-Chloro-4-chloromethyl-1-(*p*-toluenesulfonyl)pyrroridin-2-one (2g)



3,3-Dichloro-4-[(1-chloro-1-methyl)ethyl]-1-benzylazetidin-2-one (2h)