Supplementary Information

Preparations of spherical nanoparticles of chiral *Cinchona* alkaloid-based bridged silsesquioxanes and their use in heterogeneous catalysis of enantioselective reactions

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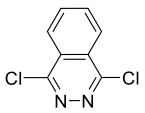
Contents:

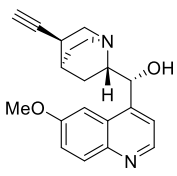
1. Syntheses of precursors

1,4-Dichlorophthalazine[1]



1,4-Dichlorophthalazine was synthesized from phthalic anhydride (12.0 g, 57 mmol) according to the literature procedure.[1] Crude product was purified by column chromatography (hexane/EtOAc 4:1). The product was obtained as a white solid in 46% yield (5.2 g, 26 mmol): Mp 165–167 °C; R_f 0.35 (hexane/EtOAc 4:1); ^{1}H NMR (300 MHz, d_6-DMSO): δ 8.40–8.31 (m, 2H), 8.30–8.18 (m, 2H); ^{13}C NMR (101 MHz, d_6-DMSO) δ 155.2, 136.1, 127.1, 126.1. NMR spectra were in accordance with literature data.[1]

10,11-Didehydroquinine[2] (3)

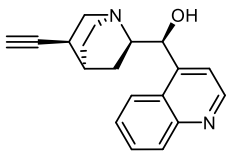


A solution of bromine (22.0 g, 138.5 mmol) in dichloromethane (80 mL) was added dropwise over 10 min to a cooled suspension (0 °C) of quinine (44.93 g, 138.5 mol) in dichloromethane (300 mL). The mixture was warmed to rt and stirred for 16 h. The solvent was evaporated in *vacuo* and crude 10,11-dibromoquinine was obtained as yellow solid. The crude dibromoderivative was dissolved in anhydrous THF (250 mL), Aliquat 336 (6.0 mL) and powdered KOH (23.5 g, 419 mmol) were added and the mixture was vigorously stirred at 60 °C for 5 h under an argon atmosphere. A second portion of KOH (23.5 g, 419 mmol) was added and the mixture was stirred at 60 °C overnight. The mixture was filtered and concentrated *in vacuo*. The crude product was purified twice by column chromatography using ethyl acetate/methanol (8:2) as an eluent and then vigorously stirred in a mixture of hexane/ethyl acetate (10:1). After filtration, 10,11-didehydroquinine was obtained as a pale yellow solid in 65% yield (29.0 g, 90.0 mmol): Mp 184–185 °C (ref.[2] 186-190 °C); R_f 0.25 (dichloromethane/ethanol 8:2); IR ν (cm^{-1}): 3301, 3161, 2939, 2870, 2108, 1622, 1591, 1509, 1472, 1453, 1431, 1242, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.6 Hz, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.50 (dd, J = 4.5, 0.7 Hz, 1H), 7.34 (dd, J = 9.2, 2.7 Hz, 1H), 7.25 (d, J = 2.8 Hz, 1H), 5.59–5.41 (m, 1H), 3.91 (s, 3H), 3.49–3.29 (m, 2H), 3.23–3.12 (m, 1H), 2.97–2.80 (m, 1H), 2.62 (td, J = 14.1, 12.3, 4.2 Hz, 1H), 2.55–2.44 (m, 1H), 2.06–1.98 (m, 1H), 1.96 (d, J = 2.5 Hz, 1H), 1.92–1.83 (m, 1H), 1.82–1.60 (m, 2H), 1.47–1.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6, 147.9, 147.3, 144.0, 131.2, 126.7, 121.5, 118.5, 101.4, 87.8, 71.8, 68.7, 59.4, 57.9, 55.6, 42.7, 27.5, 27.0, 26.1, 22.2; MS (ESI) m/z 355.2 ([M+H+MeOH]$^+$).

Note 1: Contrary to the published procedure,[2] only one equivalent of bromine was used in the first step. When two equivalents of bromine were used in accordance with literature,[2] bromination of the quinoline aromatic ring was observed.

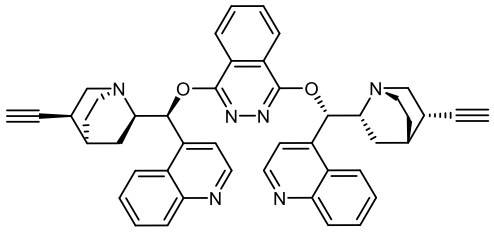
Note 2: ^{1}H NMR spectrum is concentration dependent due to the hydrogen bonding self-association.

10,11-Didehydrocinchonine[2] (4)



A solution of bromine (27.0 g, 0.169 mol) in CH_2Cl_2 (60 mL) was added dropwise over 10 min to a cooled suspension (0 °C) of cinchonine (24.9 g, 0.085 mol) in CH_2Cl_2 (300 mL). The mixture was warmed to rt and stirred for 16 h. The solvent was evaporated *in vacuo* and crude 10,11-dibromocinchonine was dissolved in anhydrous THF. Aliquat 336 (3.5 mL) and powdered KOH (28.5 g, 0.508 mol) were added and the mixture was vigorously stirred at 60 °C for 5 h. The mixture was concentrated *in vacuo*, extracted with water (150 mL) and CH_2Cl_2 (300 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 200 mL) and the combined organic phases were washed with brine (150 mL), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The crude product was recrystallized twice from ethyl acetate to provide 10,11-didehydrocinchonine as a white solid (5.96 g). The mother liquors were concentrated *in vacuo*, dissolved in CH_2Cl_2 and loaded onto a pad of silica gel. After column chromatography in a CH_2Cl_2/EtOH mixture (gradient from 20 to 30% EtOH), brown solid was obtained. It was recrystallized from ethyl acetate giving other portions of 10,11-didehydrocinchonine as a white solid. Overall yield 63% (15.66 g); Mp 210–211 °C (ref.[2] 205–209 °C); R_f 0.35 (CH_2Cl_2/EtOH 4:1); IR ν (cm^{-1}): 3300, 3065, 2934, 2877, 2707, 2113, 1612, 1506, 1455, 1264, 1109; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (d, J = 4.5 Hz, 1H), 8.09 (ddd, J = 12.2, 8.5, 1.3 Hz, 2H), 7.68 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.57 (dd, J = 4.5, 0.7 Hz, 1H), 7.52 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 5.66 (d, J = 5.8 Hz, 1H), 3.42–3.29 (m, 1H), 3.31 (br s, 1H), 3.16 (td, J = 8.9, 5.8 Hz, 1H), 3.01 (ddd, J = 13.7, 10.0, 1.4 Hz, 1H), 2.90–2.75 (m, 1H), 2.57–2.73 (m, 1H), 2.54–2.41 (m, 1H), 2.30–2.17 (m, 1H), 2.14 (d, J = 2.4 Hz, 1H), 2.01–1.95 (m, 1H), 1.54–1.35 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.8, 148.3, 130.3, 129.0, 126.6, 125.9, 123.1, 118.5, 87.2, 71.9, 69.2, 60.2, 50.3, 49.5, 27.99, 27.97, 25.1, 22.6; HRMS (ESI) for $C_{19}H_{21}N_2O$ ([M+H]$^+$) calcd. 293.1648, found 293.1649.

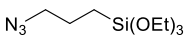
Dialkyne 6 [ref.3]



A suspension of 10,11-didehydrocinchonine (9.20 g, 31.4 mmol), 1,4-dichlorophthalazine (3.13 g, 15.7 mmol) and K_2CO_3 (3.20 g, 23.6 mmol) in anhydrous toluene (150 mL) was refluxed under an argon atmosphere with vigorous stirring for 10 min. Powdered KOH (1.30 g, 23.6 mmol) was added and the mixture was refluxed for 2 h, followed by addition of a fresh portion of the powdered KOH (1.30 g, 23.6 mmol). The mixture was refluxed for additional 16 h under an argon atmosphere and then approximately half of the volume of toluene was distilled off over the period of 2 h. After the 1,4-

dichlorophthalazine consumption (monitored by TLC), the mixture was cooled to rt, water (150 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. After filtration and solvent evaporation, the residual yellow solid was purified by column chromatography using a CH_2Cl_2/EtOH mixture (gradient from 10 to 20% EtOH). Dialkyne **4** was obtained as a light yellow solid in 81% yield (9.06 g, 12.74 mmol): Mp 272–273 °C; $[\alpha]_D^{25}$ -174.0 (c 1.00, CH_2Cl_2); R_f 0.4 (CH_2Cl_2/EtOH 4:1); IR ν (cm^{-1}) 3300, 3064, 2942, 2874, 2109, 1593, 1270, 1552, 1509, 1453, 1403, 1382, 1349; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (d, J = 4.5 Hz, 2H), 8.57 (dd, J = 6.1, 3.3 Hz, 2H), 8.26 (d, J = 7.8 Hz, 2H), 8.10 (dd, J = 8.5, 1.3 Hz, 2H), 7.91 (dd, J = 6.1, 3.3 Hz, 2H), 7.69 (ddd, J = 8.4, 6.8, 1.3 Hz, 2H), 7.56 (ddd, J = 8.3, 6.8, 1.4 Hz, 2H), 7.46 (d, J = 4.6 Hz, 2H), 7.13 (d, J = 5.2 Hz, 2H), 3.44–3.32 (m, 2H), 3.32–3.18 (m, 2H), 3.32–3.18 (m, 2H), 2.94 (dd, J = 13.8, 10.0 Hz, 2H), 2.87–2.70 (m, 2H), 2.67–2.50 (m, 2H), 2.51–2.29 (m, 4H), 2.05 (d, J = 2.4 Hz, 2H), 1.56–1.39 (m, 6H), 1.98 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 149.9, 148.5, 145.9, 132.1, 130.3, 129.0, 126.6, 126.1, 123.9, 123.4, 122.5, 118.1, 87.6, 76.5, 69.3, 59.9, 50.2, 49.6, 28.3, 28.1, 25.1, 23.1; HRMS (ESI) for $C_{46}H_{42}N_6O_2$ ($[M+H]^+$) calcd. 711.3442, found 711.3445.

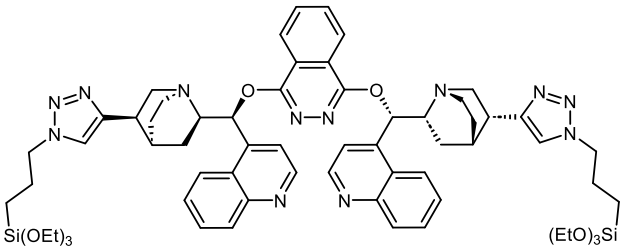
(3-Azidopropyl)triethoxysilane[4]



(3-Azidopropyl)triethoxysilane was prepared according to the literature procedure.[4] (3-Chloropropyl)triethoxysilane (30.0 g, 124.5 mmol, 30 mL) was added dropwise over 5 min to a suspension of NaN_3 (16.2 g, 249.2 mmol) in dry DMF (250 mL) under an argon atmosphere. The stirred mixture was heated to 95 °C for 2.5 h, then cooled to rt and stirred overnight. Solvent was evaporated *in vacuo*, diethyl ether (50 mL) was added to the viscous residue, the suspension was filtered through filter paper and the filter cake was washed twice with diethyl ether (2 × 50 mL). The filtrate was evaporated *in vacuo* and the crude product was purified by vacuum distillation. (3-Azidopropyl)triethoxysilane was obtained as colourless liquid in 75% yield (23.15 g): Bp 94–98 °C/700 Pa; IR ν (cm^{-1}): 2975, 2927, 2886, 2097, 1090, 1080. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (q, J = 7.0 Hz, 6H), 3.27 (t, J = 7.0 Hz, 2H), 1.89–1.58 (m, 2H), 1.23 (t, J = 7.0 Hz, 9H), 0.84–0.47 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 58.4, 53.8, 22.6, 18.2, 7.6. Analytical data were in accordance with literature data.[4]

Caution! Azides are potentially explosive chemicals. All operations should be performed behind a blast shield in a well-ventilated fume hood.

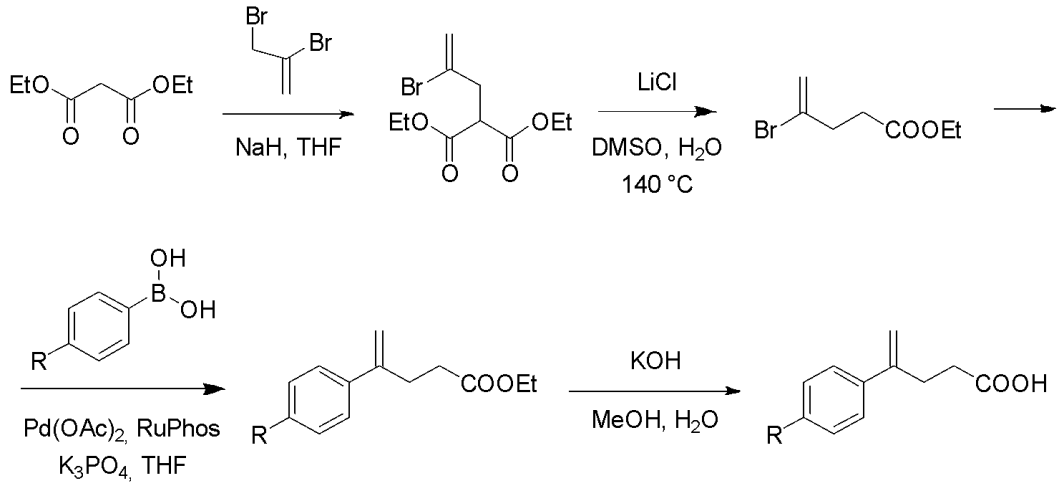
Bridged bis(triethoxysilane) 2 [ref.3]



A solution of (3-azidopropyl)triethoxysilane (1.35 g, 5.48 mmol) in anhydrous dioxane (10 mL) was added dropwise to a stirred mixture of dialkyne **4** (1.95 g, 2.74 mmol), Et_3N (0.4 mL) and Cu/C catalyst (650 mg) in anhydrous dioxane (60 mL). The mixture was stirred at 90 °C under an argon atmosphere for 16 h and then filtered through Celite. The filter cake was washed with $CHCl_3$ (2 × 20 mL), solvents from the filtrate were evaporated *in vacuo* and the residue was dried at 50 °C/0.2 kPa for 1 h. The obtained yellow solid was suspended in hexane (50 mL), vigorously stirred under an argon atmosphere for 30 min and filtered through PTFE membrane (0.45 µm). The solid was dried at 50 °C/0.2 kPa for 2 h. Bis(triethoxysilane) **2** was obtained as a light yellow solid in 88% yield (2.90 g, 2.41 mmol): Mp 165–170 °C; IR ν (cm^{-1}): 2972, 2938, 2879, 1551, 1386, 1349, 1165, 1084, 1077; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.75 (d, *J* = 4.5 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 2H), 8.17–8.06 (m, 2H), 7.90–7.80 (m, 2H), 7.71 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 4.5 Hz, 2H), 7.22 (s, 2H), 7.16–7.01 (m, 2H), 4.12 (ddt, *J* = 43.5, 13.8, 7.1 Hz, 4H), 3.78 (q, *J* = 7.0 Hz, 12H), 3.51 –3.31 (m, 4H), 3.14 (t, *J* = 11.8 Hz, 2H), 3.03–2.84 (m, 4H), 2.83–2.67 (m, 2H), 2.31–2.12 (m, 4H), 1.89 (dt, *J* = 15.4, 7.2 Hz, 4H), 1.69–1.44 (m, 4H), 1.19 (t, *J* = 7.0 Hz, 18H), 0.46–0.58 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 156.4, 149.9 (2C), 148.5, 146.0, 132.2, 130.3, 129.0, 126.6, 126.1, 124.0, 123.1, 122.4, 120.6, 118.3, 76.4, 60.3, 58.5, 52.3, 50.0, 49.7, 33.2, 27.6, 26.4, 24.2, 23.1, 18.3, 7.4; ^{29}Si NMR (80 MHz, $CDCl_3$) *δ* -46.9; HRMS (ESI) for $C_{64}H_{84}N_{12}O_8Si_2$ ($[M+H]^+$) calcd. 1205.6146, found 1205.6155.

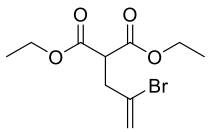
2. Syntheses of 4-arylpent-4-enoic acids

4-Arylpent-4-enoic acids were used as starting compounds in catalytic chlorolactonization experiments. They were prepared by the previously reported synthetic route (Scheme SI-1):



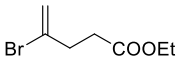
Scheme SI-1. Synthesis of 4-arylpent-4-enoic acids.

Diethyl 2-(2-bromoallyl)malonate[5]



A solution of diethyl malonate (25.62 g, 160 mmol) in anhydrous tetrahydrofuran (20 mL) was added dropwise over 10 min to a stirred suspension of NaH (4.22 g, 176 mmol) in anhydrous tetrahydrofuran (20 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 15 min and subsequently 60 min at 50 °C. The mixture was cooled to -10 °C and a solution of 2,3-dibromopropene (41.41 g, 148 mmol) in tetrahydrofuran (20 mL) was added dropwise over 10 min. The mixture was stirred at room temperature for 60 min. The reaction was quenched by addition of 4M HCl (35 mL) and the mixture was extracted with diethyl ether (3 × 45 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. Crude product was purified by column chromatography in hexane/EtOAc 9:1. The title compound was obtained as colourless oil in 63% yield (28.09 g; 101 mmol): R_f 0.45 (hexane/EtOAc, 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70–5.66 (m, 1H), 5.47 (dd, J = 1.9, 0.5 Hz, 1H), 4.21 (q, J = 7.1 Hz, 4H), 3.78 (t, J = 7.6 Hz, 1H), 3.01 (d, J = 7.5 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 129.5, 119.9, 61.9, 50.8, 40.5, 14.2. Analytical data were in accordance with literature data.[5]

Ethyl 4-bromopent-4-enoate[6,7]

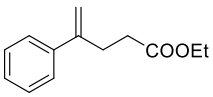


A solution of diethyl 2-(2-bromoallyl)malonate (2.98 g, 10.67 mmol) and LiCl (0.90 g, 21.20 mmol) in a mixture of DMSO (20 mL) and water (0.2 mL, 200 mg, 10.71 mmol) was stirred at 140 °C for 24 h. The reaction mixture was cooled to rt, diluted with water (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated *in vacuo*. Crude product was purified by vacuum distillation. The title compound was obtained as colourless oil in 60% yield (1.32 g, 6.37 mmol): Bp 38–40 °C/0.2 kPa, (ref.[6] 110 °C/4.4 kPa); R_f 0.7 (hexane/EtOAc 9:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.64 (dd, J = 1.3, 0.7 Hz, 1H), 5.43 (dd, J = 1.8, 0.5 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.82–2.67 (m, 2H), 2.67–2.43 (m, 2H), 1.26 (td, J = 7.1, 0.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 132.2, 117.6, 60.6, 36.6, 33.0, 14.2. Analytical data were in accordance with literature data.[6]

General procedure for Suzuki coupling

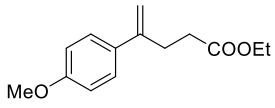
2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (81 mg, 0.17 mmol), $Pd(OAc)_2$ (20 mg, 0.08 mmol) and aryl boronic acid (2.07 mmol) were added to a solution of ethyl 4-bromopent-4-enoate (360 mg; 1.73 mmol) in tetrahydrofuran (7 mL). The flask was filled with argon and 1M solution of K_3PO_4 (5.2 mL, 5.2 mmol) was added using a syringe *via* a septum. The mixture was stirred at 60 °C for 1 h and then at rt overnight. The organic layer was separated and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, filtered and evaporated *in vacuo*. Crude product was purified by flash column chromatography using hexane/EtOAc (gradient from 5 to 11 %) as an eluent.

Ethyl 4-phenylpent-4-enoate[8]



Prepared from phenylboronic acid (252 mg) as colourless oil in 81% yield (248 mg; 1.4 mmol): R_f 0.38 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.37 (m, 2H), 7.36–7.26 (m, 3H), 5.35–5.24 (m, 1H), 5.09 (q, J = 1.3 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.89–2.78 (m, 2H), 2.53–2.41 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.1, 146.9, 140.6, 128.4, 127.6, 126.1, 112.8, 60.4, 33.3, 30.5, 14.2. Analytical data were in accordance with literature data.[8]

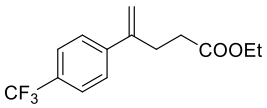
Ethyl 4-(4-methoxyphenyl)pent-4-enoate[9]



Prepared from 4-methoxyphenylboronic acid (315 mg) as colourless oil in 60% yield (243 mg, 1.0 mmol): R_f 0.44 (hexane/EtOAc 9:1); ^{1}H NMR (400

MHz, CDCl3): δ 7.34 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 5.28–5.17 (m, 1H), 5.00 (d, J = 1.3 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.81 (td, J = 7.6, 1.3 Hz, 2H), 2.52–2.38 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): 173.2, 159.2, 146.2, 133.0, 127.2, 113.7, 111.3, 60.4, 55.3, 33.3, 30.5, 14.2. Analytical data were in accordance with literature data.[9]

Ethyl 4-[4-(trifluoromethyl)phenyl]pent-4-enoate[10]

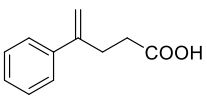


Prepared from 4-(trifluoromethyl)phenylboronic acid (393 mg) as pale yellow oil in 85% yield (400 mg, 1.5 mmol): R_f 0.4 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.2 Hz, 2H), 7.54–7.45 (m, 2H), 5.47–5.29 (m, 1H), 5.19 (q, J = 1.3 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.84 (td, J = 7.6, 1.3 Hz, 2H), 2.53–2.35 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.54. Analytical data were in accordance with literature data.[10]

General procedure for hydrolysis of ethyl 4-arylpent-4-enoates

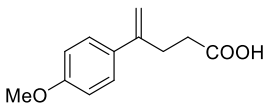
A solution of KOH (0.3 g, 5.34 mmol) in water (0.3 mL) was added to a stirred solution of ethyl 4-arylpent-4-enoate (1.21 mmol) in methanol (3 mL). The mixture was stirred at rt overnight. Methanol was evaporated *in vacuo* and concentrated HCl was added to adjust pH to 1. The mixture was diluted with water (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and evaporated *in vacuo*. Crude product was purified by column chromatography using hexane/EtOAc/AcOH (78:20:2) as an eluent.

4-Phenylpent-4-enoic acid[11]



Obtained as a white solid in 82% yield (176 mg, 1.0 mmol): Mp 94–96 °C; R_f 0.4 (hexane/EtOAc/AcOH 78:20:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.23 (m, 5H), 5.33 (s, 1H), 5.11 (d, J = 1.3 Hz, 1H), 2.90–2.81 (m, 2H), 2.58–2.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.5, 146.5, 140.4, 128.4, 127.7, 126.1, 113.0, 32.9, 30.1. Analytical data were in accordance with literature data.[11]

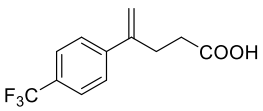
4-(4-Methoxyphenyl)pent-4-enoic acid[11]



Obtained as a white solid in 79% yield (197 mg, 0.96 mmol): Mp 138-140 °C (ref.[11] 95 °C, ref.[12] 145-146 °C); R_f 0.35 (hexane/EtOAc/AcOH 78:20:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 5.25 (d, J = 1.0 Hz, 1H), 5.02 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 2.86–2.74 (m, 2H), 2.60–2.45 (m, 2H); ^{13}C NMR

(101 MHz, $CDCl_3$): δ 179.0, 159.2, 145.8, 132.8, 127.2, 113.8, 111.4, 55.3, 33.0, 30.2. NMR spectra were in accordance with the reported spectra.[11]

4-[4-(Trifluoromethyl)phenyl]pent-4-enoic acid[12]



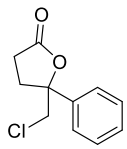
Obtained as a white solid in 75% yield (221 mg, 0.91 mmol): Mp 51-52 °C (ref.[12] 54-56 °C); R_f 0.35 (hexane/EtOAc/AcOH 78:20:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.55 (m, 2H), 7.54–7.45 (m, 2H), 5.39 (d, J = 0.8 Hz, 1H), 5.21 (q, J = 1.2 Hz, 1H), 2.90–2.81 (m, 2H), 2.58–2.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.3, 145.5, 144.0 (q, J = 1.4 Hz), 129.7 (q, J = 32.5 Hz), 126.4, 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 271.7 Hz), 114.9, 32.7, 29.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.56. Analytical data were in accordance with literature data.[12]

3. Syntheses of racemic standards of chlorolactones

General procedure for chlorolactonization

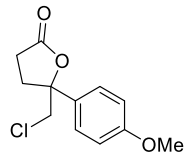
1,3-Dichloro-5,5-dimethylhydantoin (46 mg, 0.23 mmol) was added to a solution of 4-arylpent-4-enoic acid (0.19 mmol) in chloroform (3 mL) and the mixture was stirred at rt for 48 h. The mixture was diluted with chloroform (5 mL), 5% solution of $Na_2S_2O_3$ was added (8 mL), the layers were separated and the aqueous phase was extracted with chloroform (2 × 8 mL). The combined organic extracts were washed with brine (8 mL), dried over anhydrous $MgSO_4$, filtered and evaporated *in vacuo*. Crude product was purified by flash column chromatography using hexane/EtOAc (gradient from 7 to 22 %) as an eluent.

5-(Chloromethyl)-5-phenyldihydrofuran-2(3*H*)-one[13]



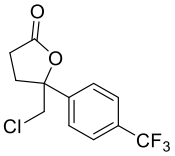
Obtained as colourless oil in 59% yield (23 mg, 0.11 mmol): R_f 0.6 (toluene/ethyl acetate 4:1, visualization by $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.28 (m, 5H), 3.84 (d, J = 12.1 Hz, 1H), 3.77 (d, J = 12.1 Hz, 1H), 2.92–2.73 (m, 2H), 2.63–2.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 140.7, 128.9, 128.7, 124.9, 87.1, 52.2, 31.4, 29.0. Analytical data were in accordance with literature data.[13] HPLC separation of enantiomers: column YMC Chiral ART Amylose-SA (250 × 4.6 mm; 5 µm); mobile phase: heptane/*i*-PrOH 98:2, flowrate 1.0 mL min^{-1}; UV detection at λ = 210 nm; $t_{(R)}$ = 15.3 min, $t_{(S)}$ = 17.6 min. Absolute configuration assignment was based on literature data.[13]

5-(Chloromethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one[11]



Obtained as colourless oil in 64% yield (29 mg, 0.12 mmol); R_f 0.5 (toluene/ethyl acetate 4:1, visualization by $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H), 3.81 (d, J = 12.0 Hz, 1H), 3.72 (d, J = 12.0 Hz, 1H), 2.90–2.66 (m, 2H), 2.64–2.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.8, 159.7, 132.5, 126.3, 114.1, 87.0, 55.4, 52.2, 31.2, 29.1. Analytical data were in accordance with literature data.[11] HPLC separation of enantiomers: column YMC Chiral ART Amylose-SA (250 × 4.6 mm; 5 µm); mobile phase: heptane/*i*-PrOH 98:2, flowrate 1.0 mL min^{-1}; UV detection at λ = 210 nm; t_1 = 25.5 min, t_2 = 31.3 min.

5-(Chloromethyl)-5-[4-(trifluoromethyl)phenyl]dihydrofuran-2(3*H*)-one[14]



Obtained as colourless oil in 58% yield (31 mg, 0.11 mmol); R_f 0.5 (toluene/ethyl acetate 4:1, visualization by $KMnO_4$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.64 (m, 2H), 7.61–7.50 (m, 2H), 3.83 (d, J = 12.1 Hz, 1H), 3.78 (d, J = 12.1 Hz, 1H), 2.93–2.74 (m, 2H), 2.66–2.42 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.80. Analytical data were in accordance with literature data.[14] HPLC separation of enantiomers: column YMC Chiral ART Amylose-SA (250 × 4.6 mm; 5 µm); mobile phase: heptane/*i*-PrOH 98:2, flowrate 1.0 mL min^{-1}; UV detection at λ = 210 nm; t_1 = 22.2 min, t_2 = 23.4 min.

4. Syntheses of racemic standards of diols (products of Sharpless dihydroxylation)

Racemic standards of Sharpless dihydroxylation products were synthesized by known methods. All synthetic procedures and characterizations of all diols are available in the Supporting Information for our previous paper.[3]

5. NMR spectra

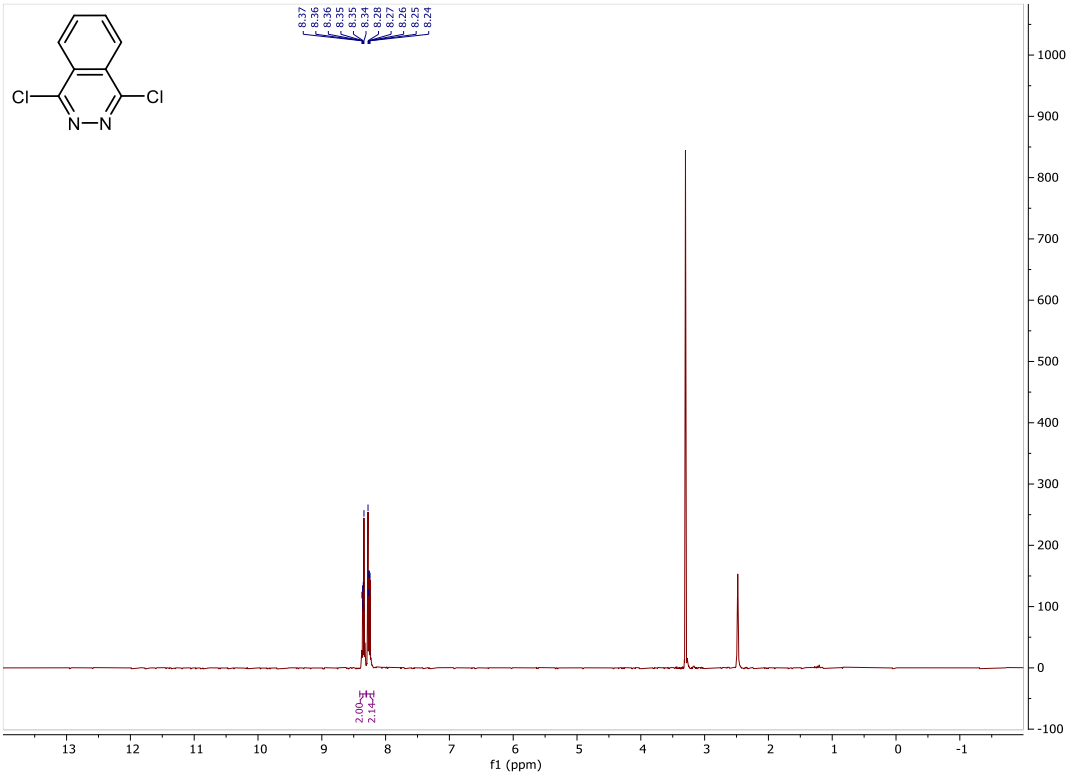


Figure SI-1. ^{1}H NMR spectrum of 1,4-dichlorophthalazine in d_6-DMSO.

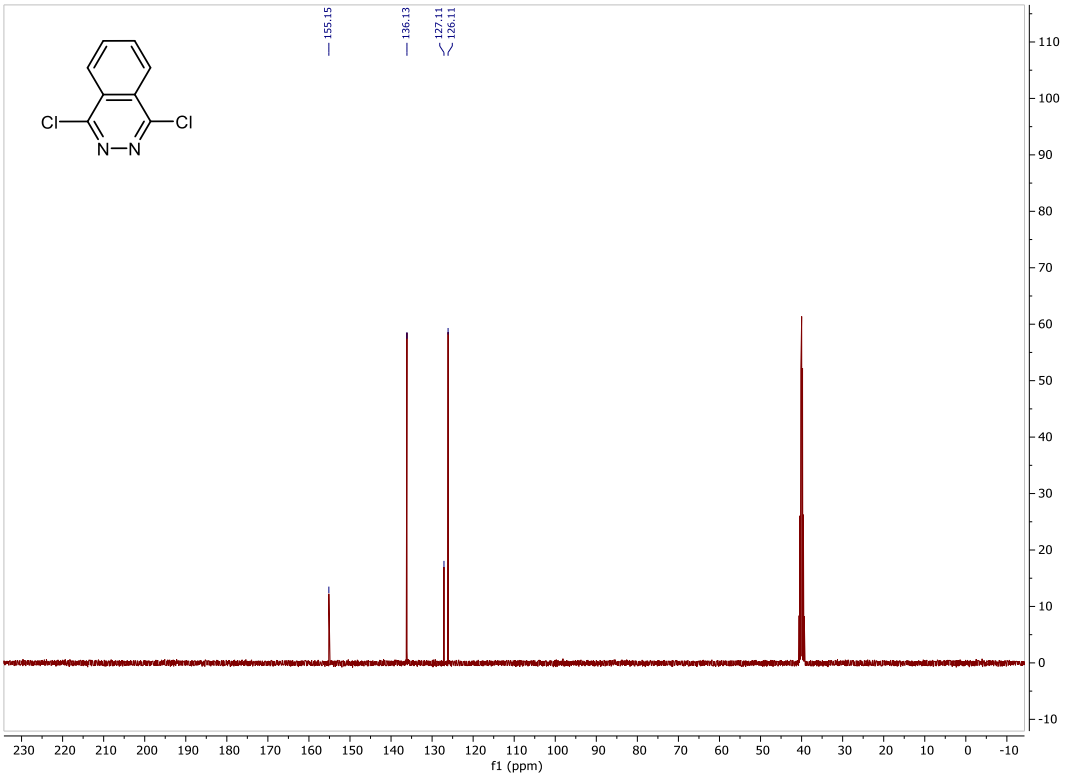


Figure SI-2. ^{13}C NMR spectrum of 1,4-dichlorophthalazine in d_6-DMSO.

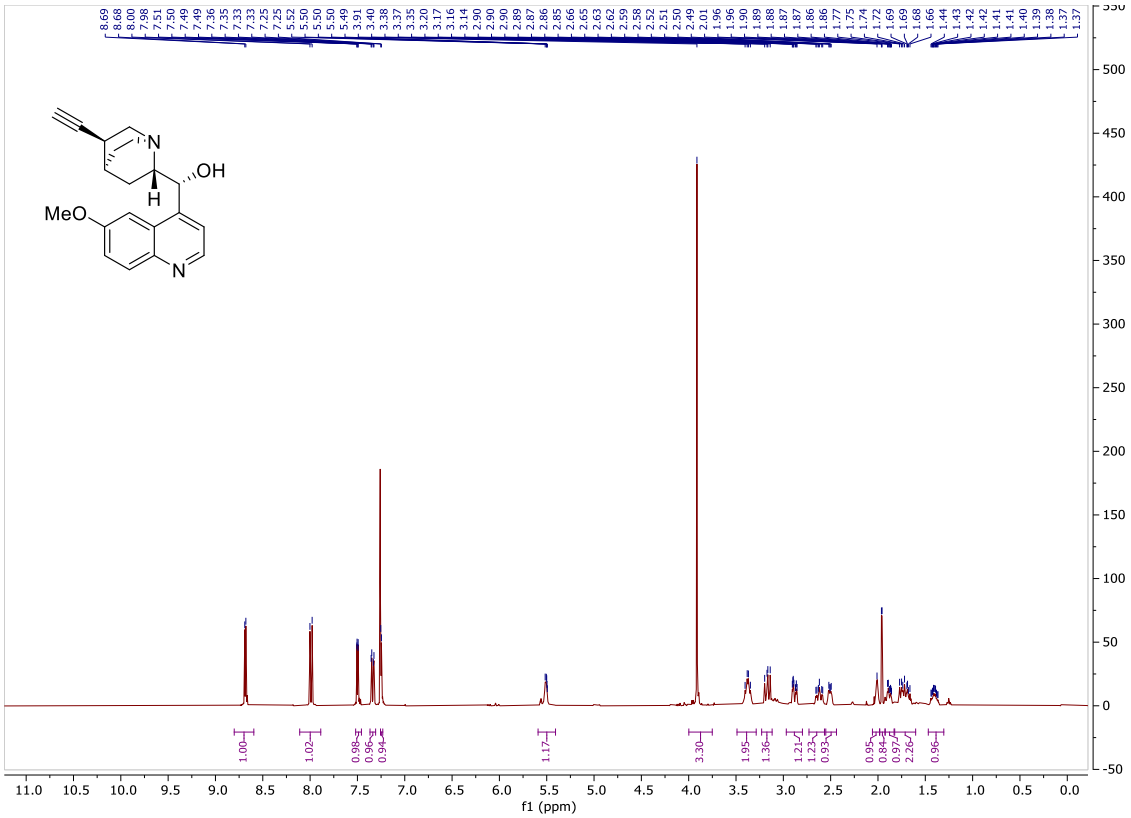


Figure SI-3. ^{1}H NMR spectrum of 10,11-didehydroquinine (**3**) in $CDCl_3$.

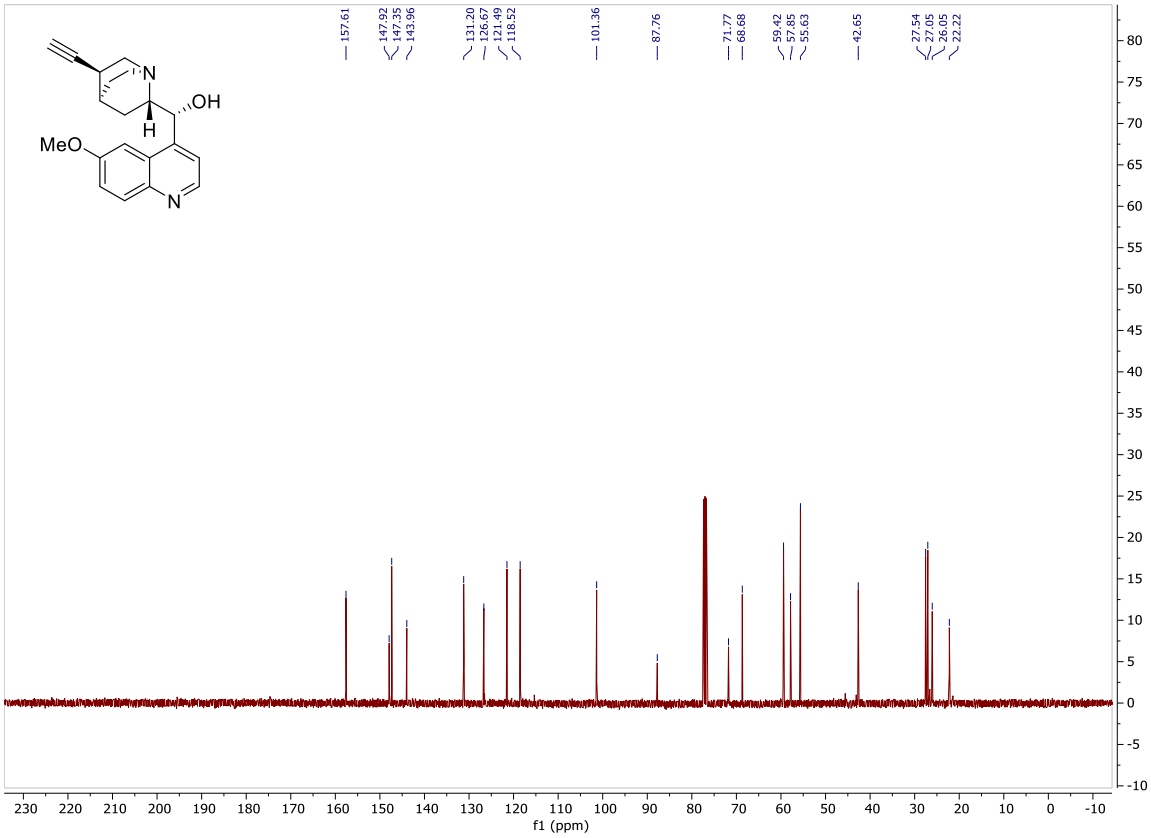


Figure SI-4. ^{13}C NMR spectrum of 10,11-didehydroquinine (**3**) in $CDCl_3$.

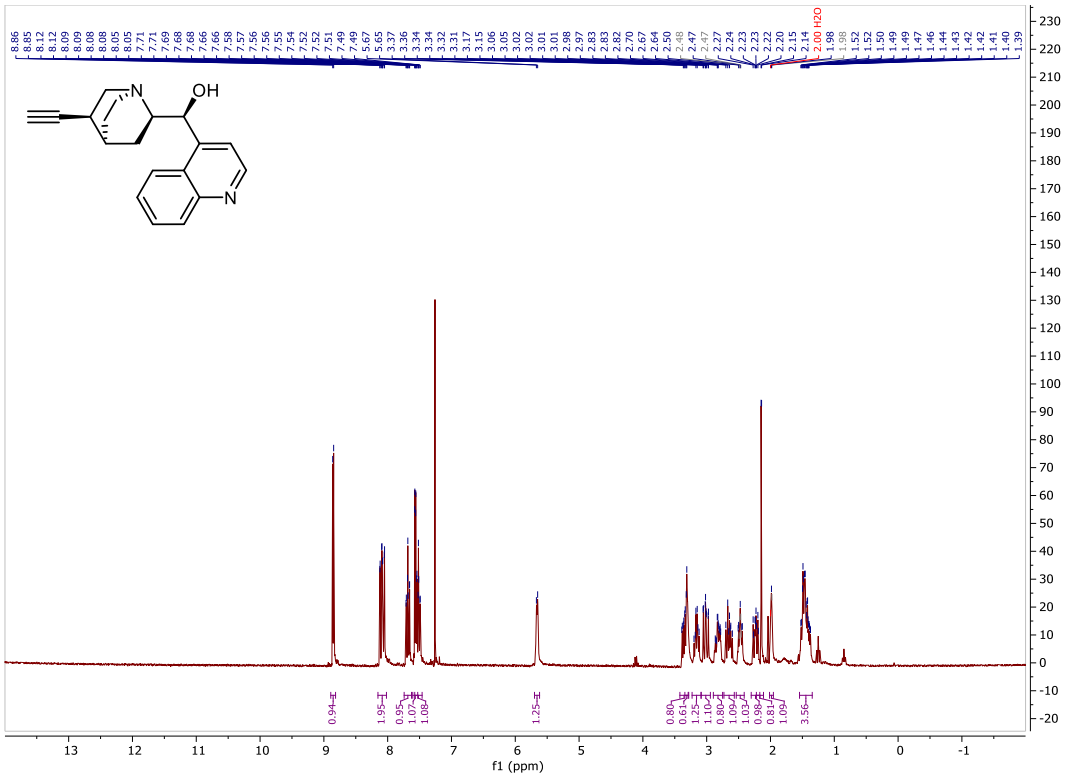


Figure SI-5. ^{1}H NMR spectrum of 10,11-didehydrocinchonine (**4**) in $CDCl_3$.

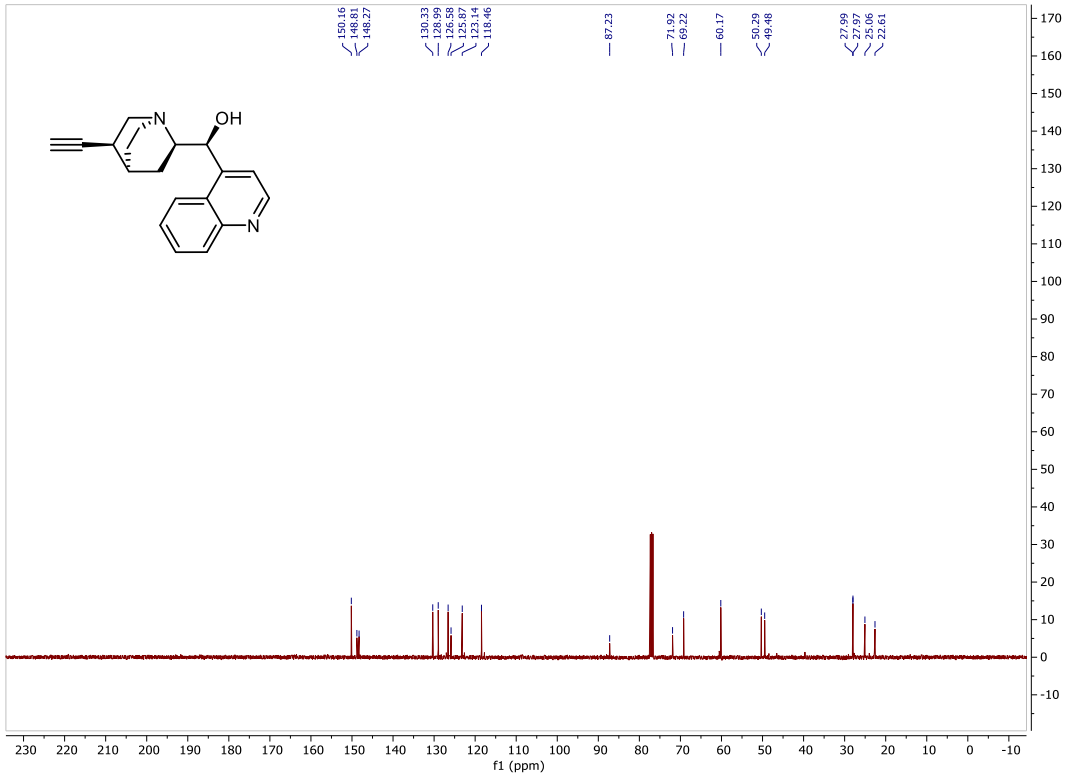


Figure SI-6. ^{13}C NMR spectrum of 10,11-didehydrocinchonine (**4**) in $CDCl_3$.

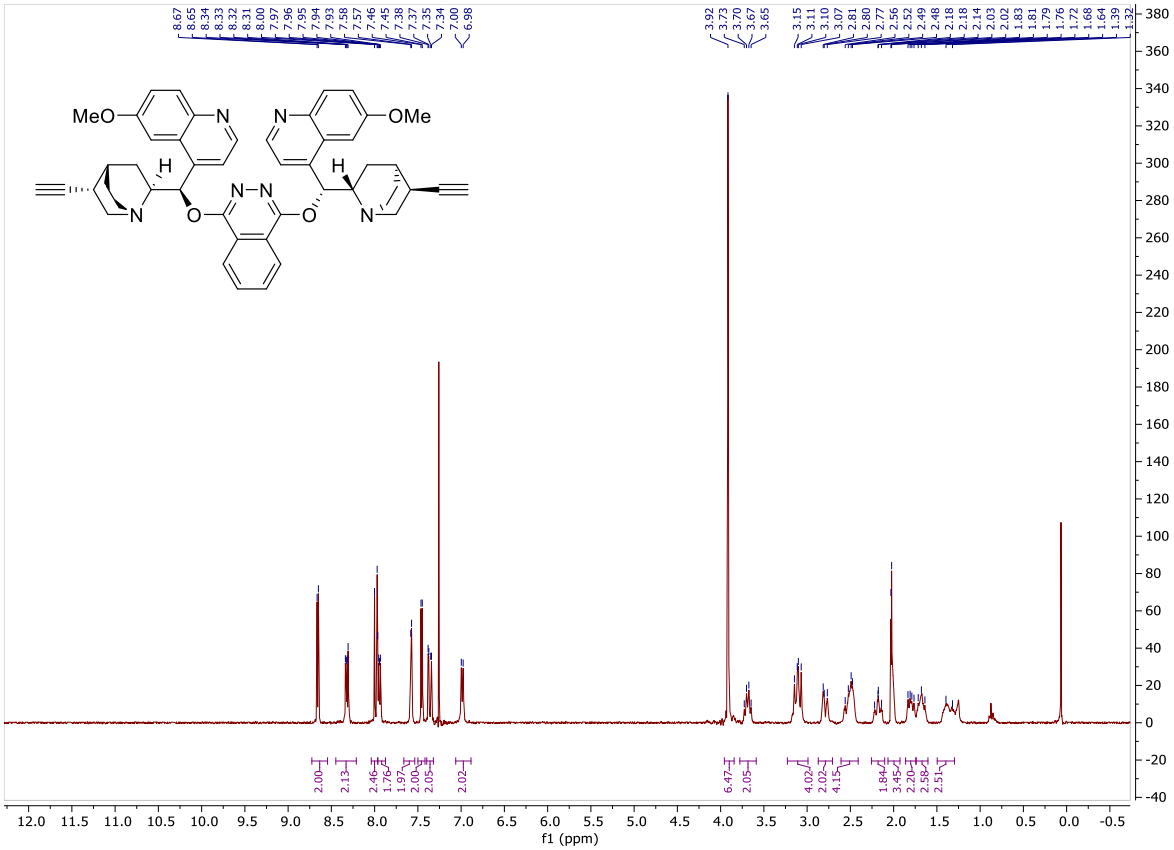


Figure SI-7. ^{1}H NMR spectrum of dialkyne **5** in $CDCl_3$.

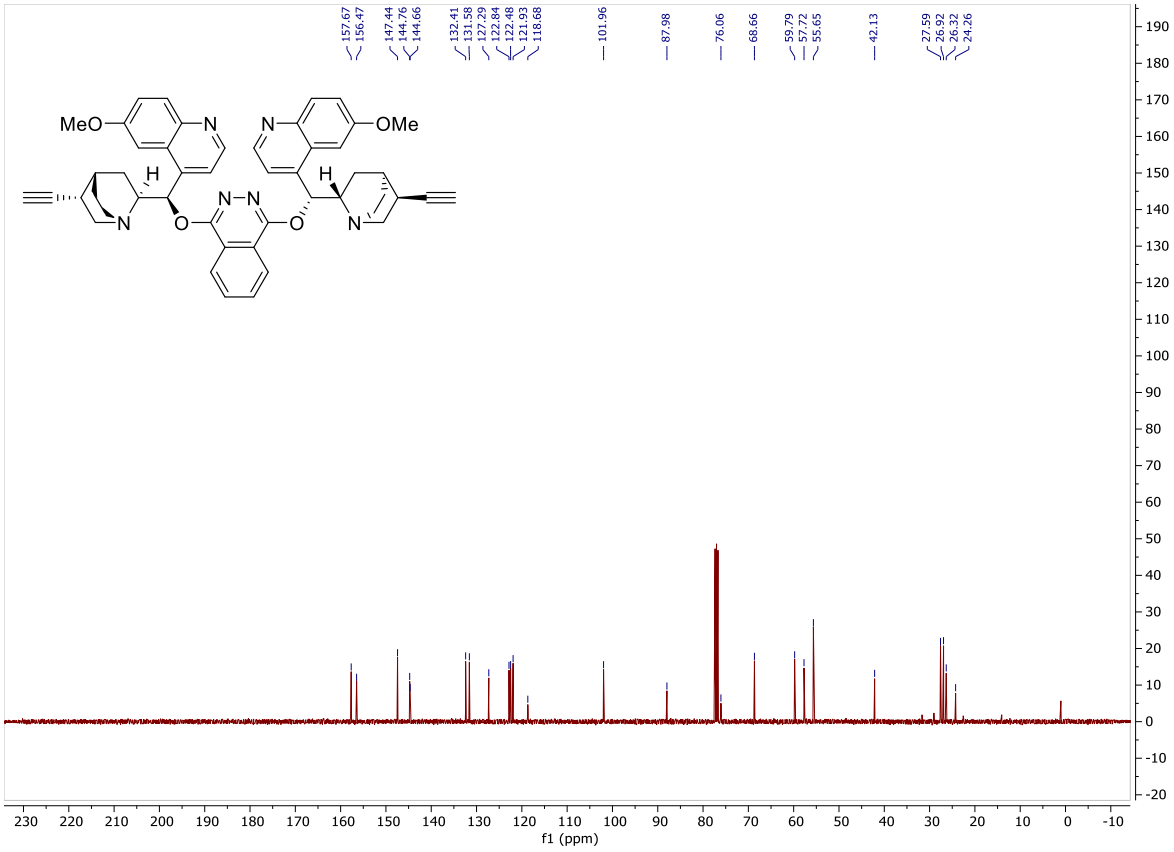


Figure SI-8. ^{13}C NMR spectrum of dialkyne **5** in $CDCl_3$.

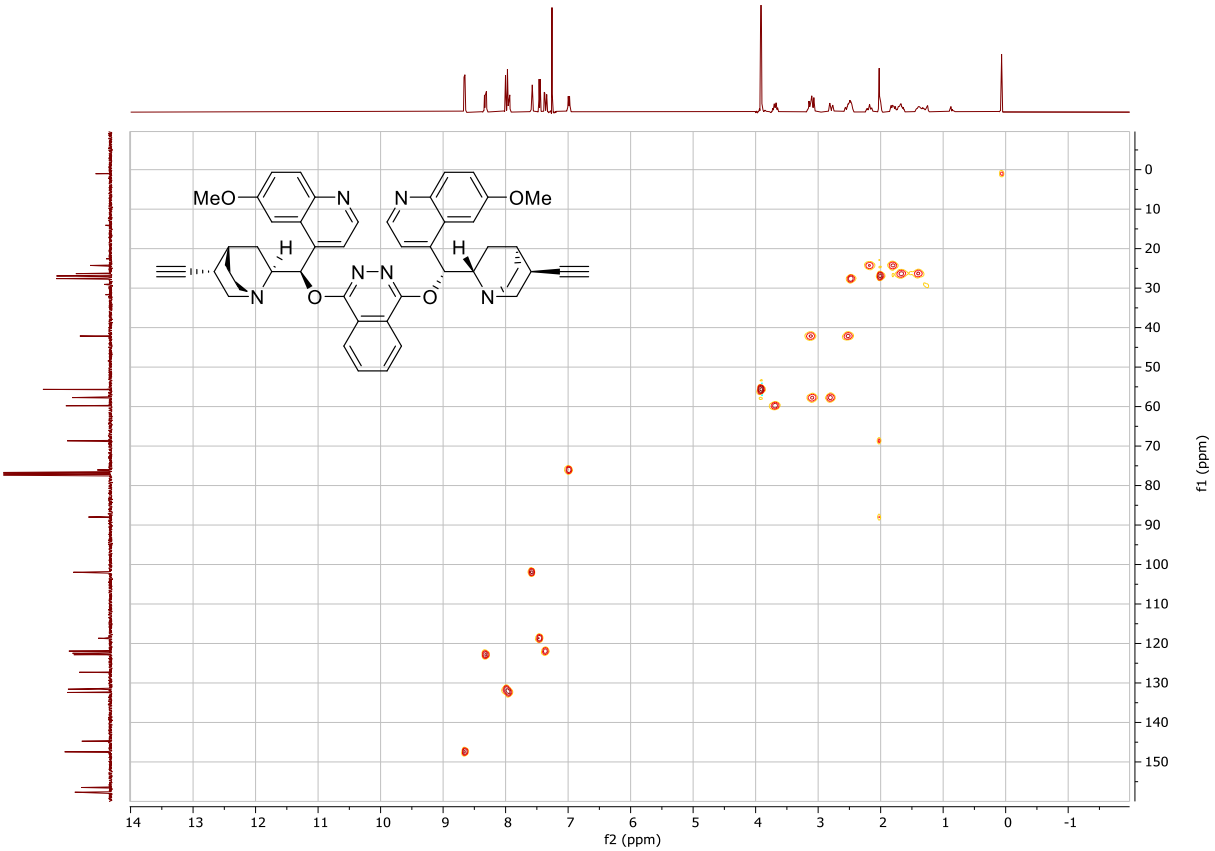


Figure SI-9. ^{1}H-^{13}C ASAPHMQC NMR spectrum of dialkyne **5** in $CDCl_3$.

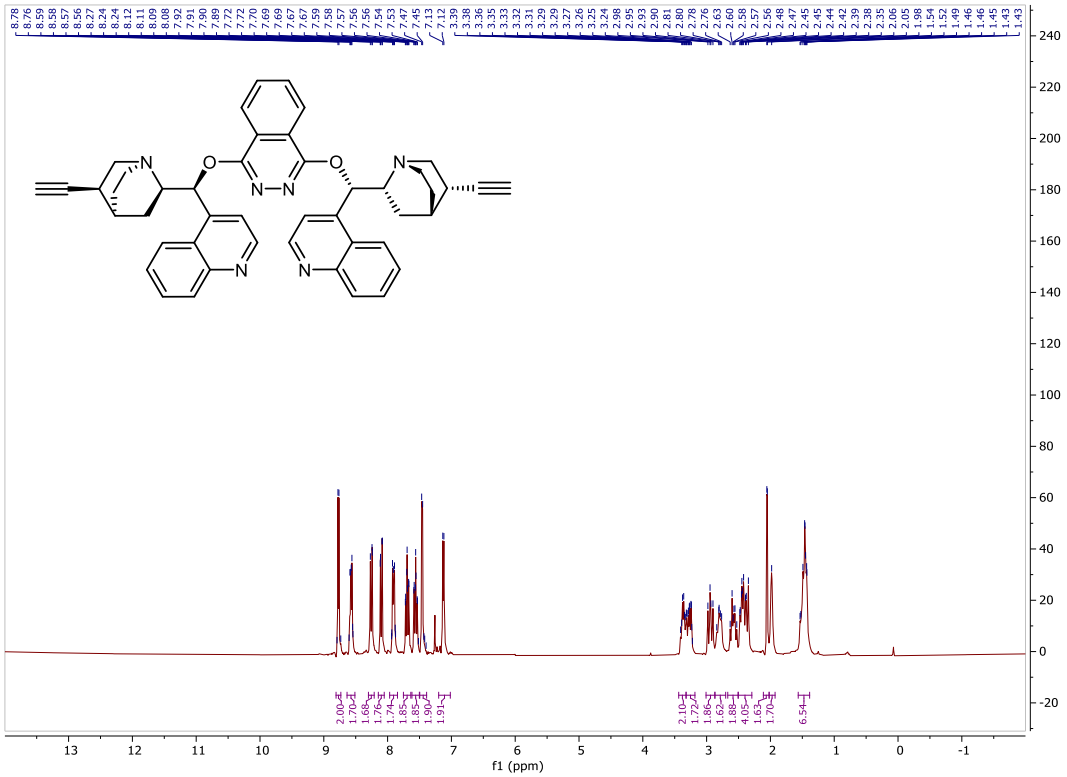


Figure SI-10. ^{1}H NMR spectrum of dialkyne **6** in $CDCl_3$.

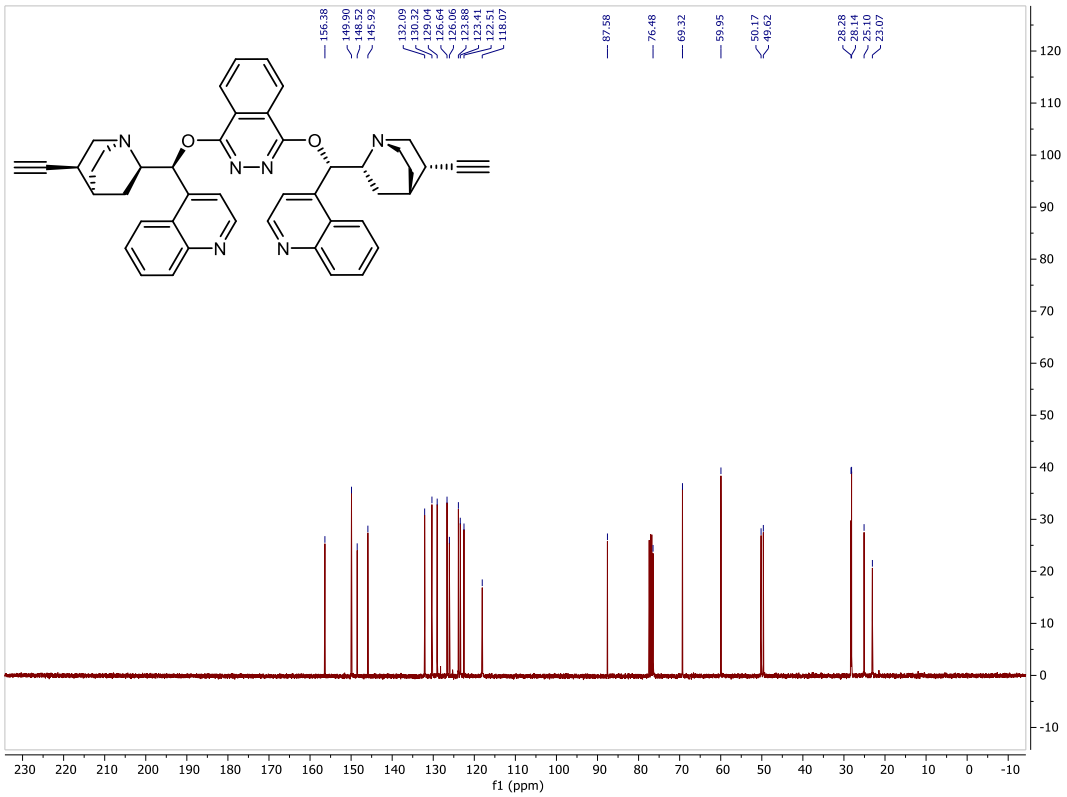


Figure SI-11. ^{13}C NMR spectrum of dialkyne **6** in $CDCl_3$.

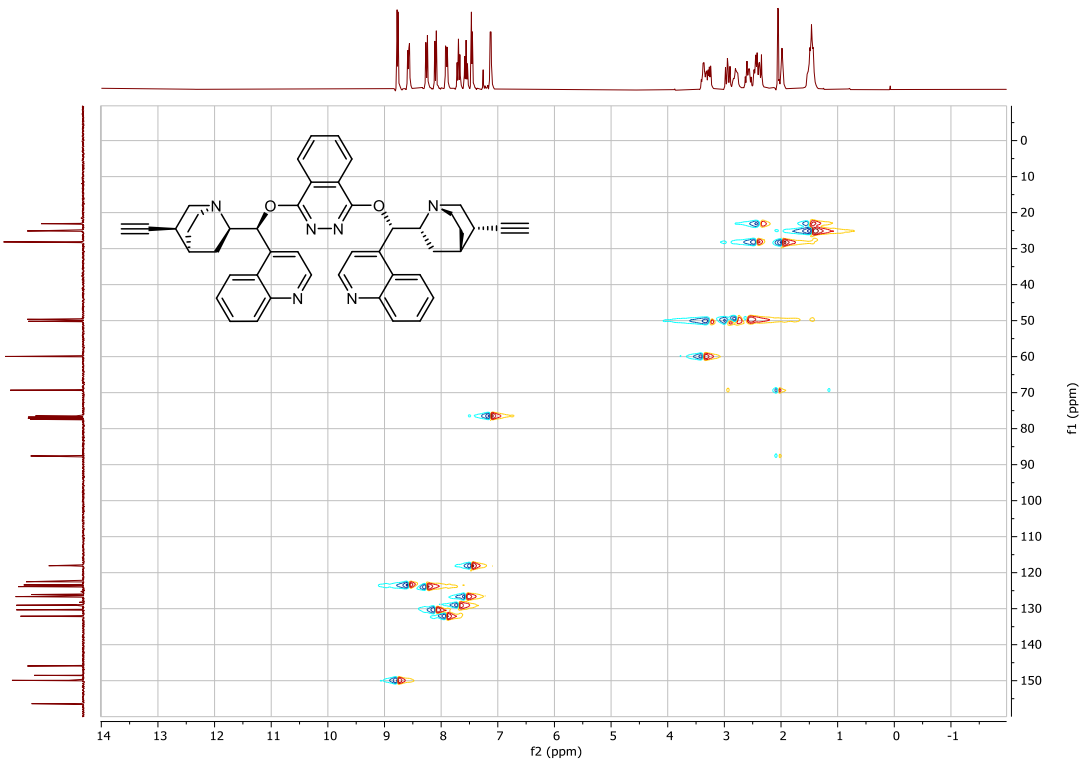


Figure SI-12. ^{1}H-^{13}C ASAP-HMQC NMR spectrum of dialkyne **6** in $CDCl_3$.

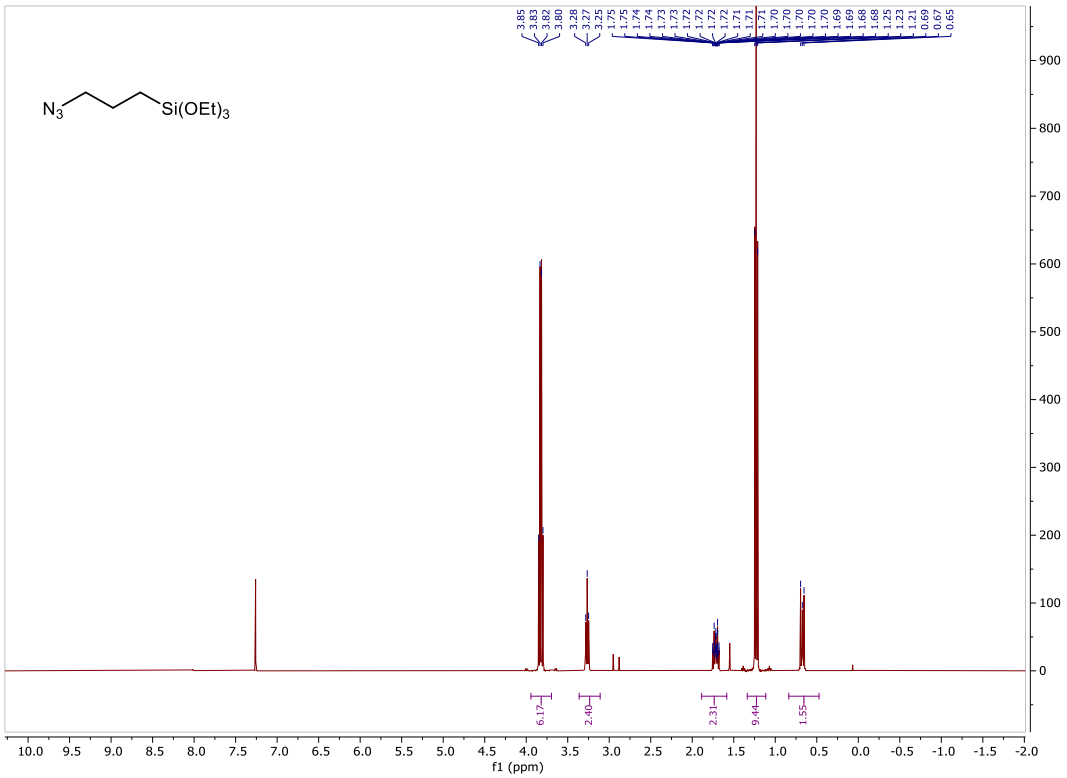


Figure SI-13. ^{1}H NMR spectrum of (3-azidopropyl)triethoxysilane in $CDCl_3$.

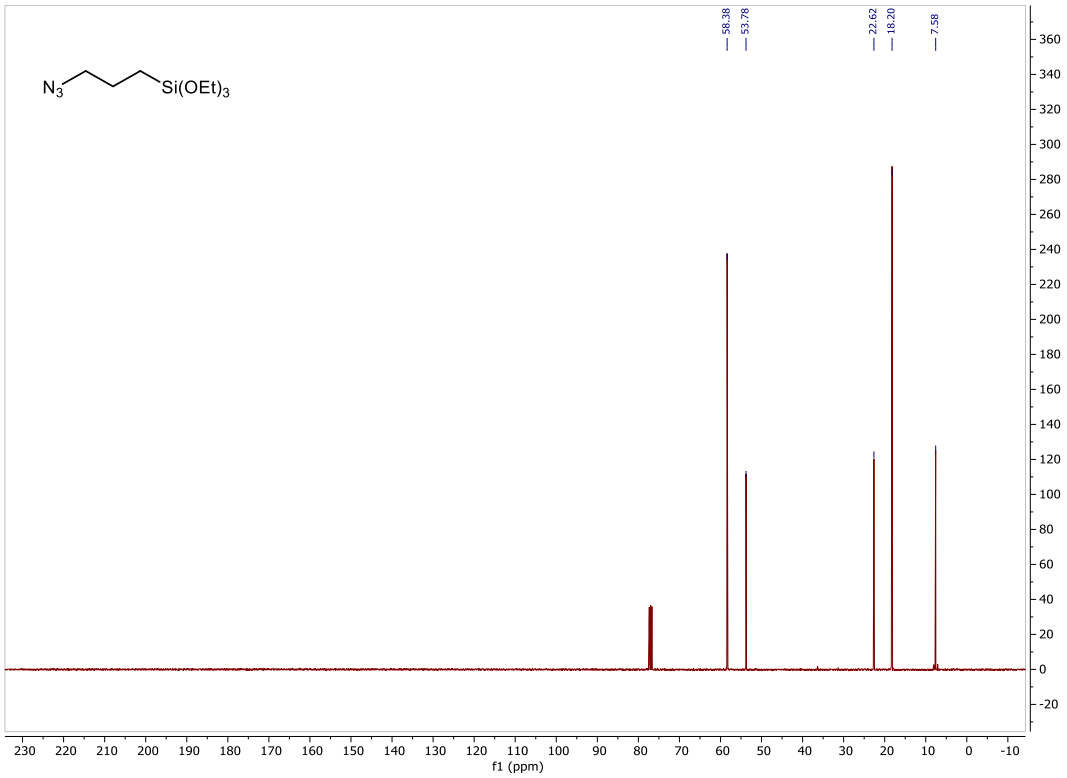


Figure SI-14. ^{13}C NMR spectrum of (3-azidopropyl)triethoxysilane in $CDCl_3$.

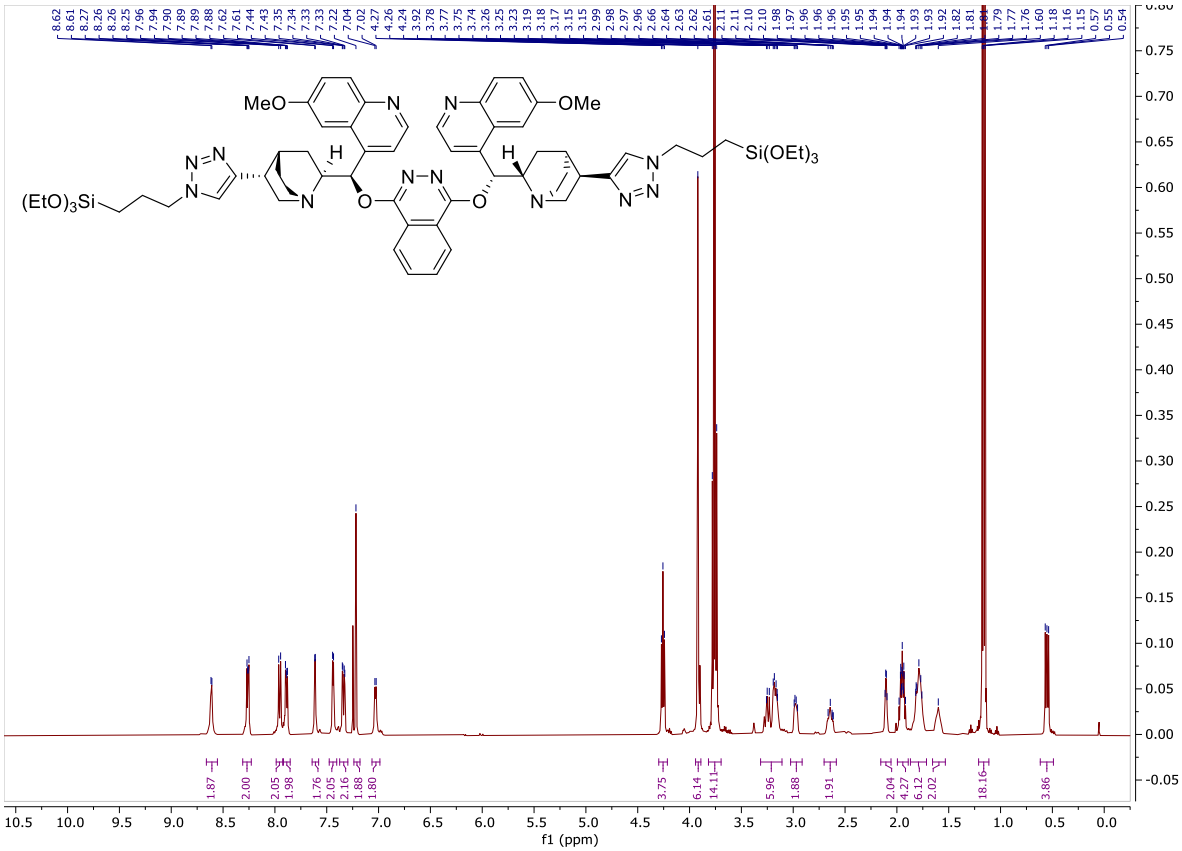


Figure SI-15. ^{1}H NMR spectrum of bis(triethoxysilane) **1** in $CDCl_3$.

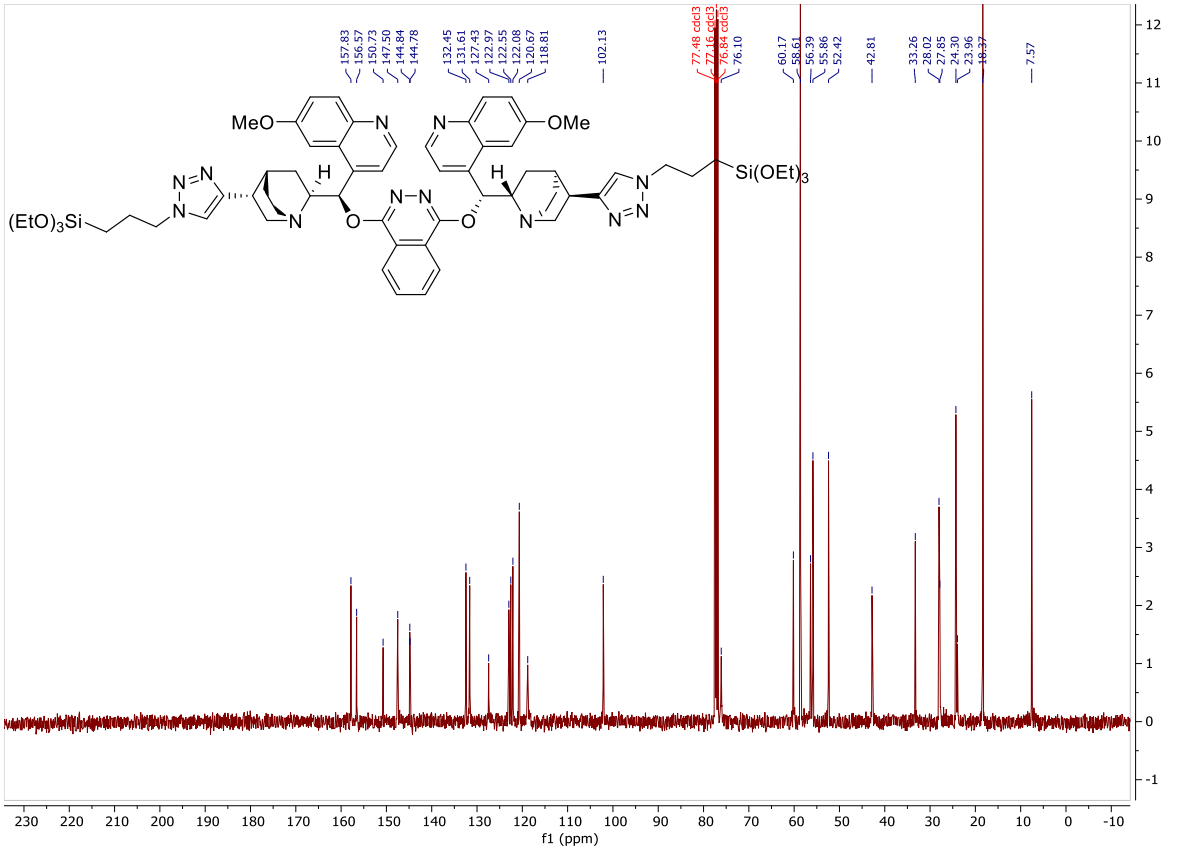


Figure SI-16. ^{13}C NMR spectrum of bis(triethoxysilane) **1** in $CDCl_3$.

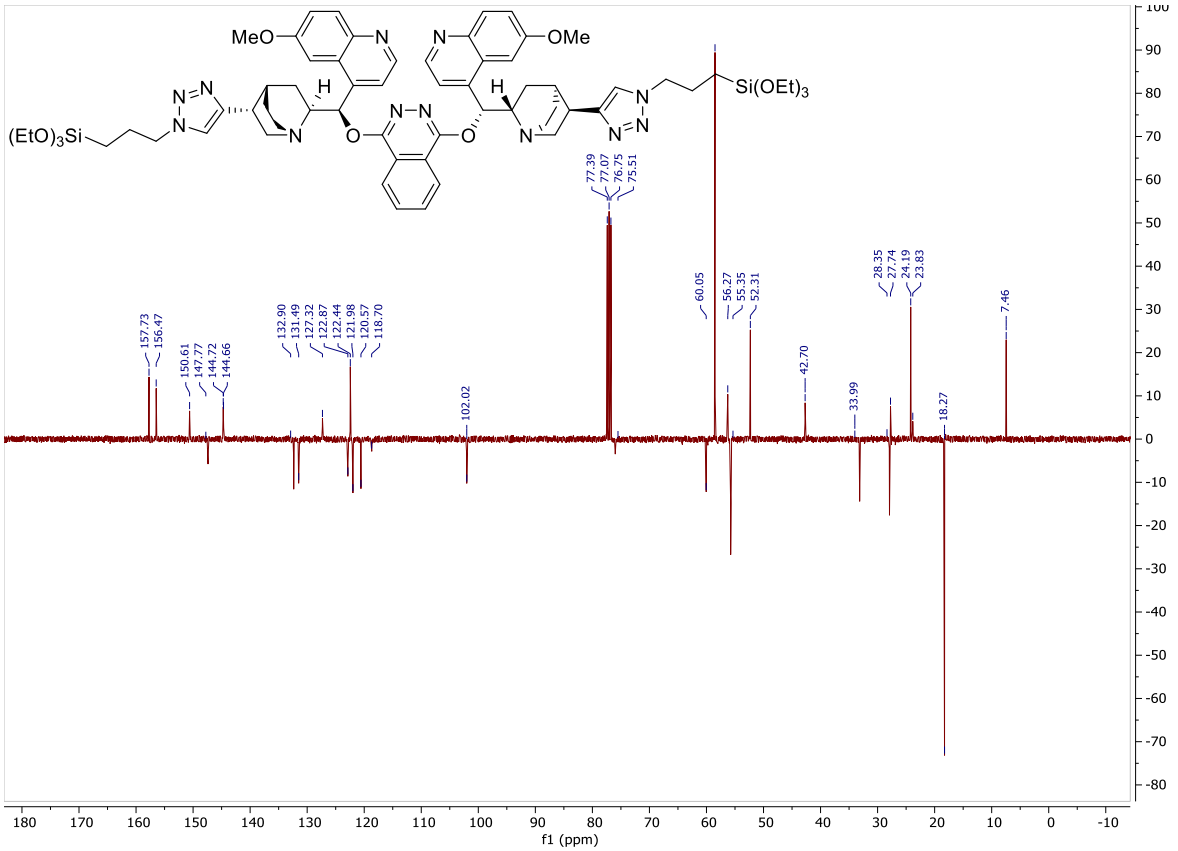


Figure SI-17. APT NMR spectrum of bis(triethoxysilane) **1** in $CDCl_3$; ↓CH,CH_3 ↑C,CH_2.

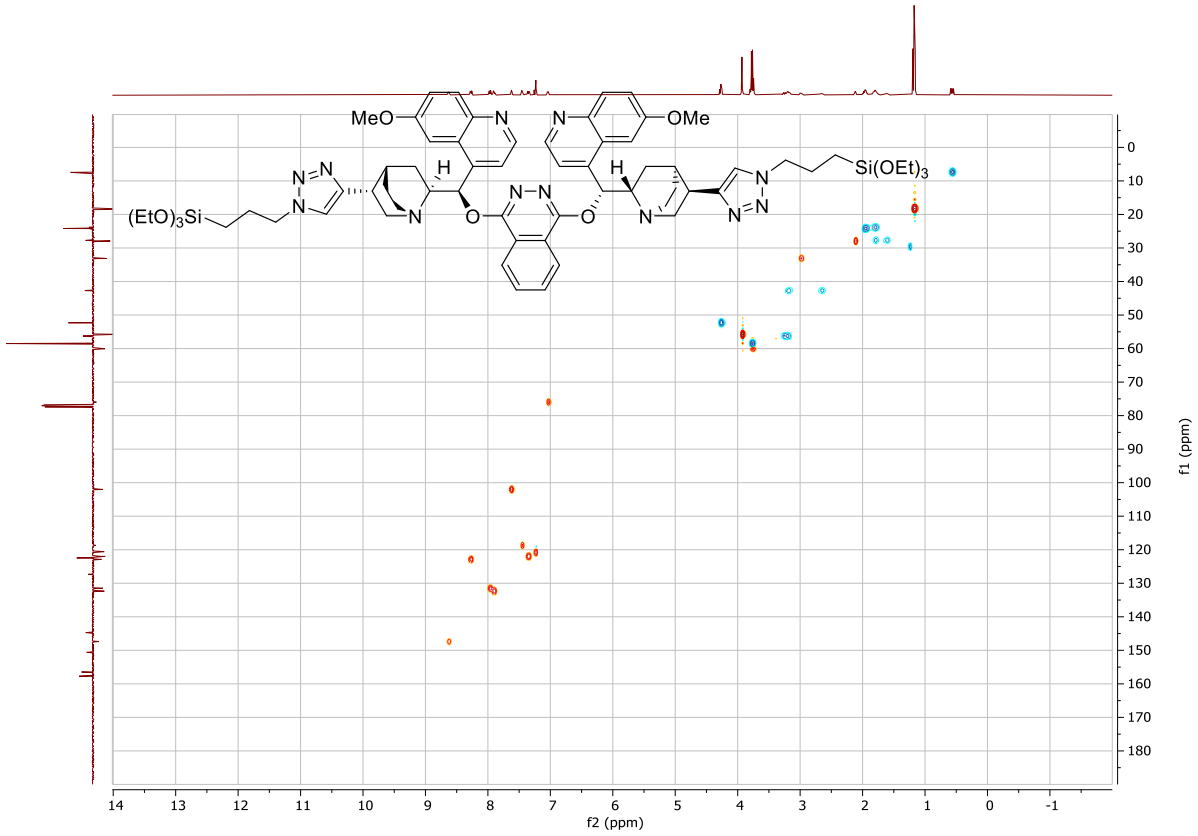


Figure SI-18. ^{1}H-^{13}C HSQC NMR spectrum of precursor **1** in $CDCl_3$; red CH,CH_3; blue C,CH_2.

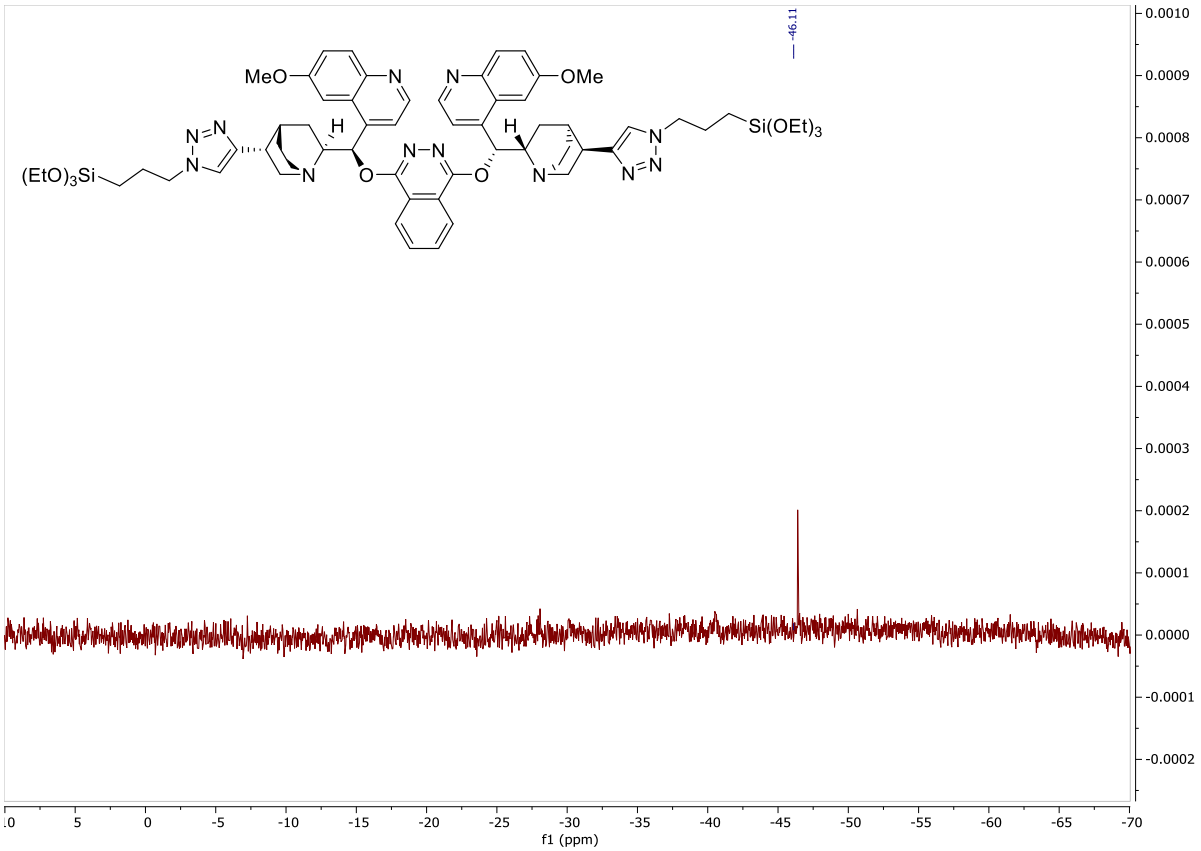


Figure SI-19. ^{29}Si NMR spectrum of bis(triethoxysilane) **1** in $CDCl_3$.

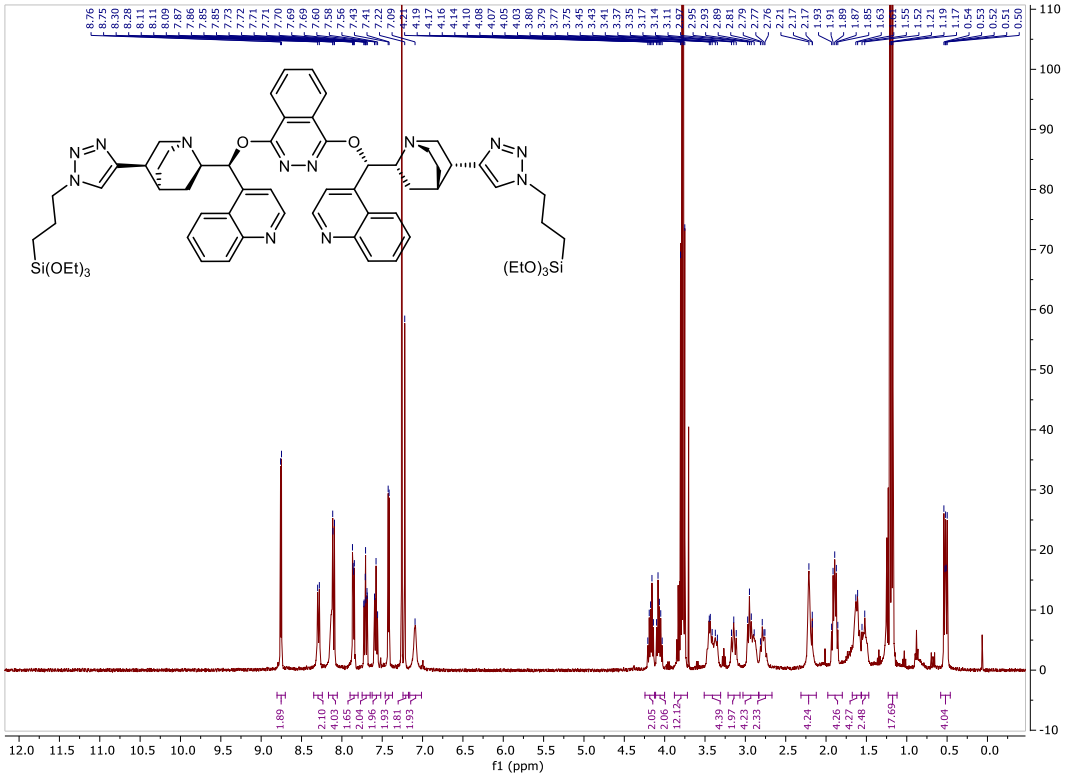


Figure SI-20. ^{1}H NMR spectrum of bis(triethoxysilane) **2** in $CDCl_3$.

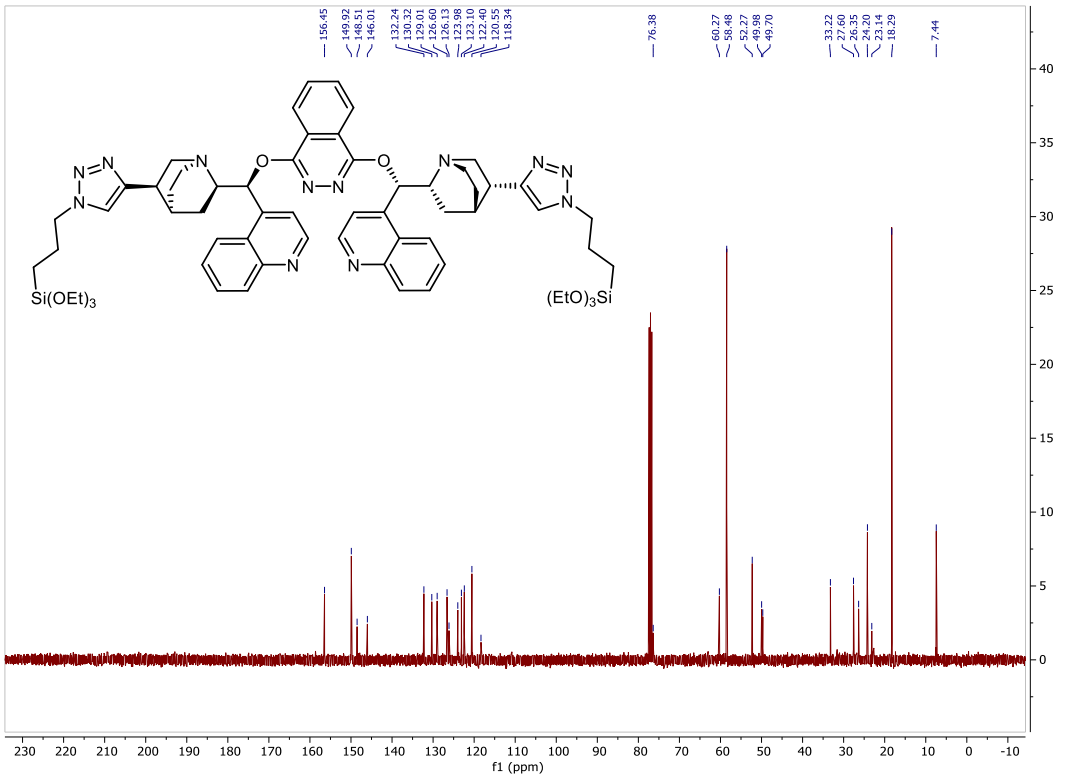


Figure SI-21. ^{13}C NMR spectrum of bis(triethoxysilane) **2** in $CDCl_3$.

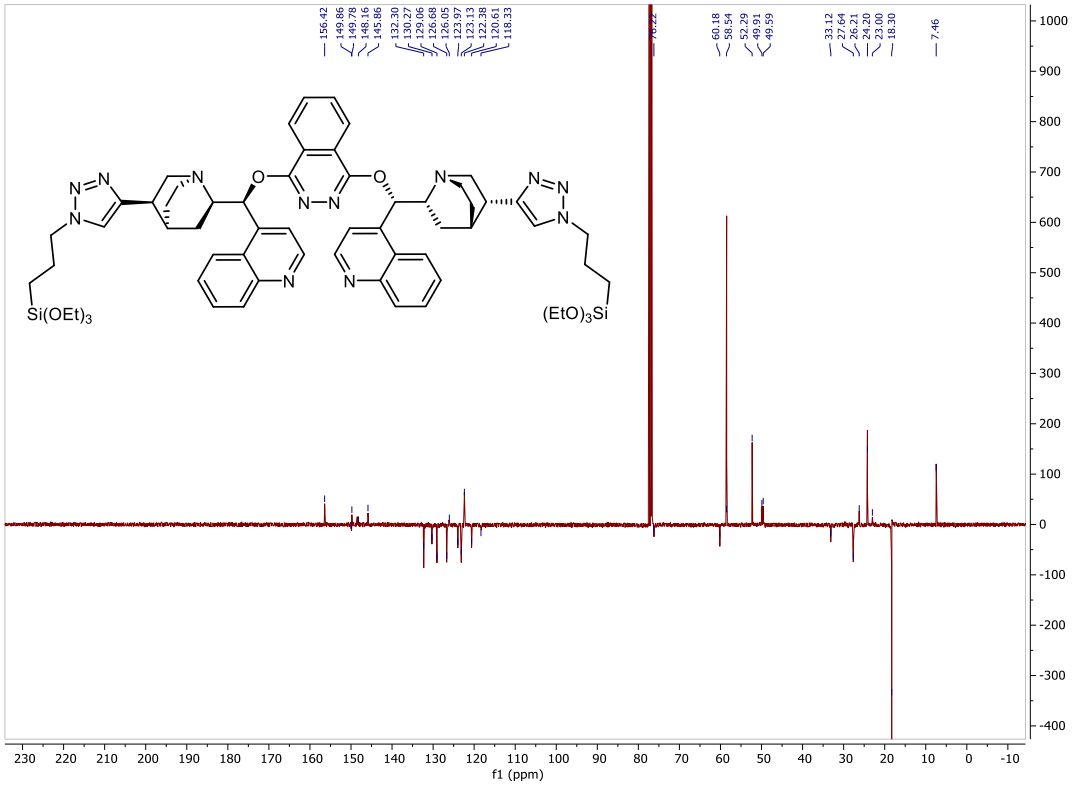


Figure SI-22. ^{13}C APT NMR spectrum of bis(triethoxysilane) **2** in $CDCl_3$.

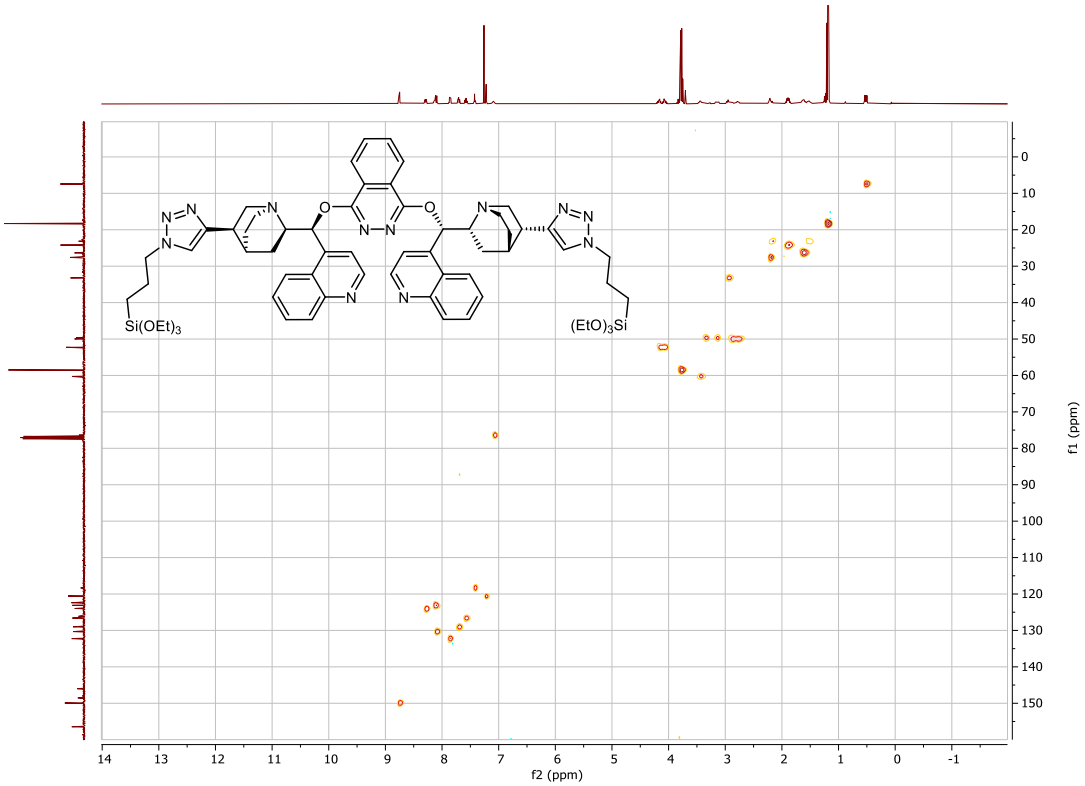


Figure SI-23. ^{1}H-^{13}C ASAP-HMQC spectrum of bis(triethoxysilane) **2** in $CDCl_3$.

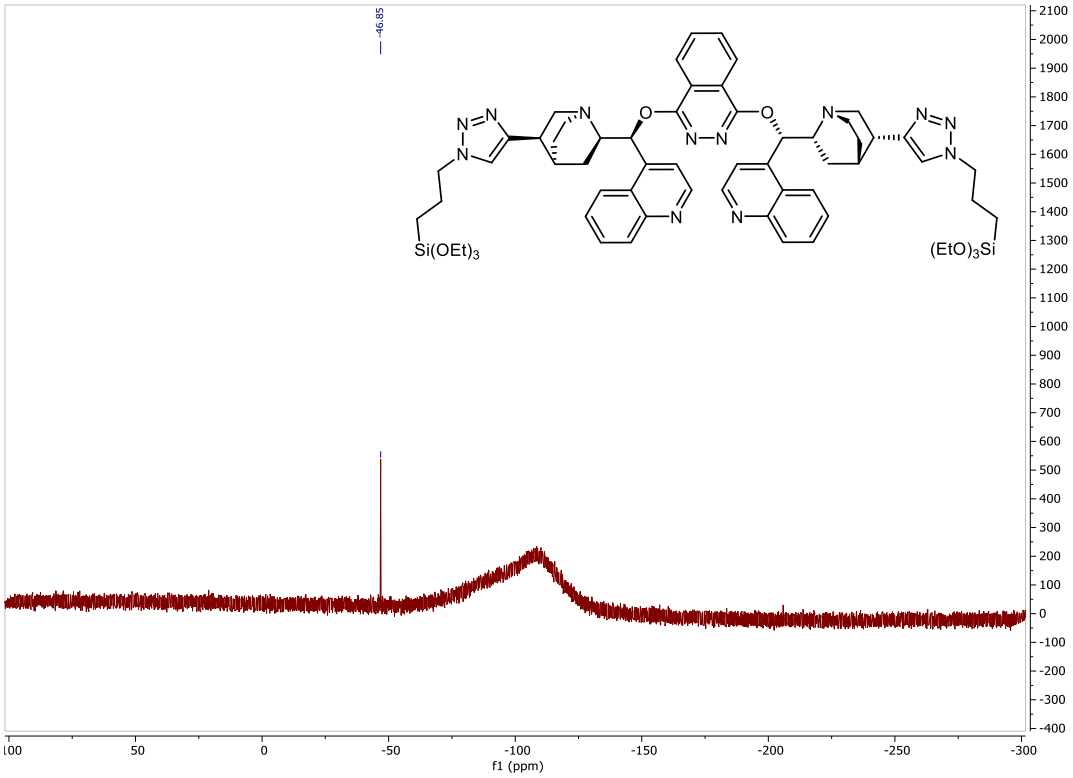


Figure SI-24. ^{29}Si NMR spectrum of bis(triethoxysilane) **2** in $CDCl_3$.

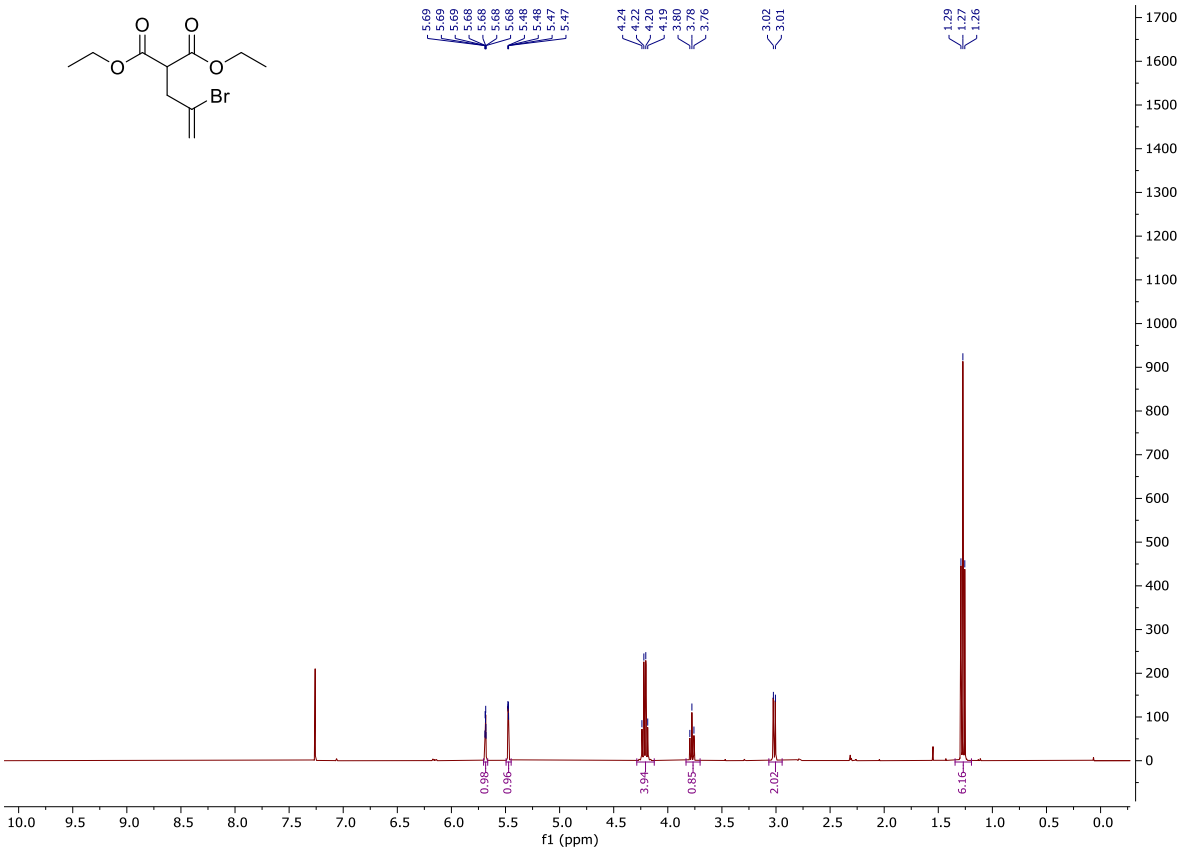


Figure SI-25. ^{1}H NMR spectrum of diethyl 2-(2-bromoprop-2-enyl)malonate in $CDCl_3$.

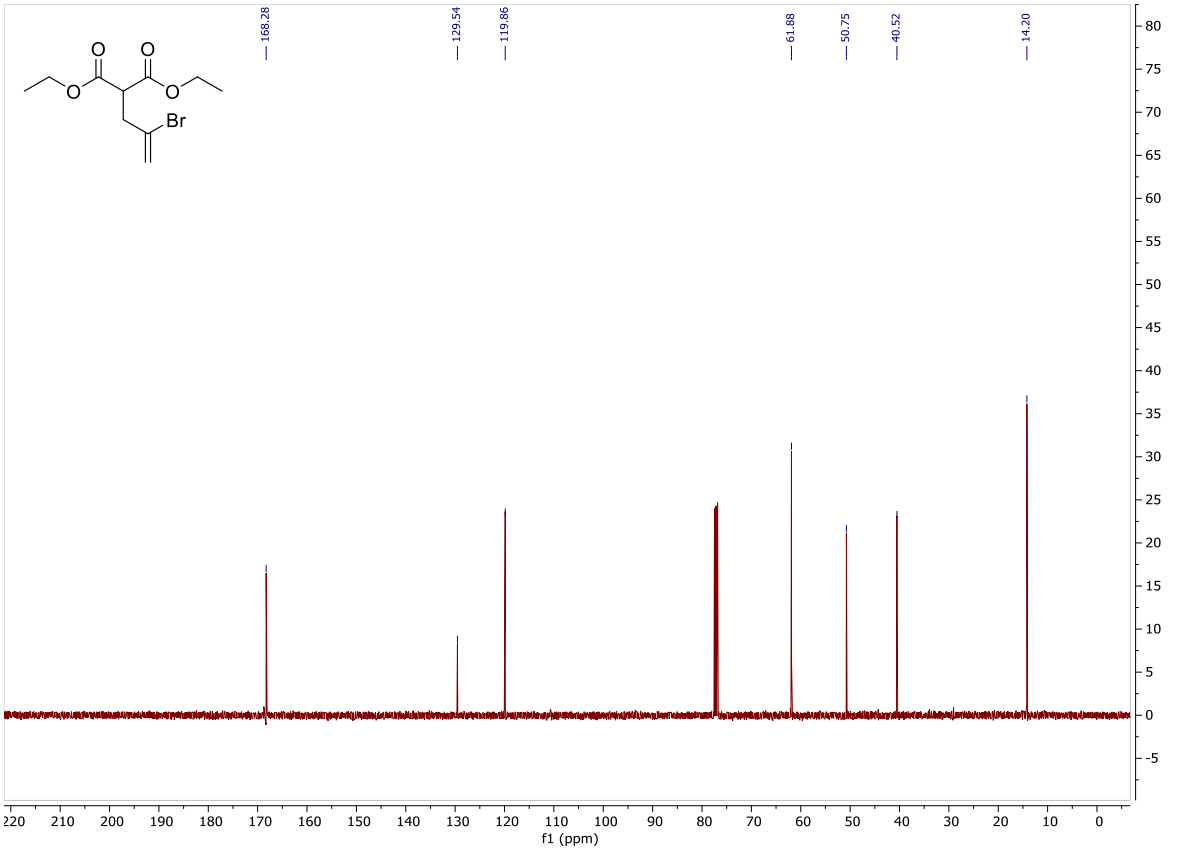


Figure SI-26. ^{13}C NMR spectrum of diethyl 2-(2-bromoprop-2-enyl)malonate in $CDCl_3$.

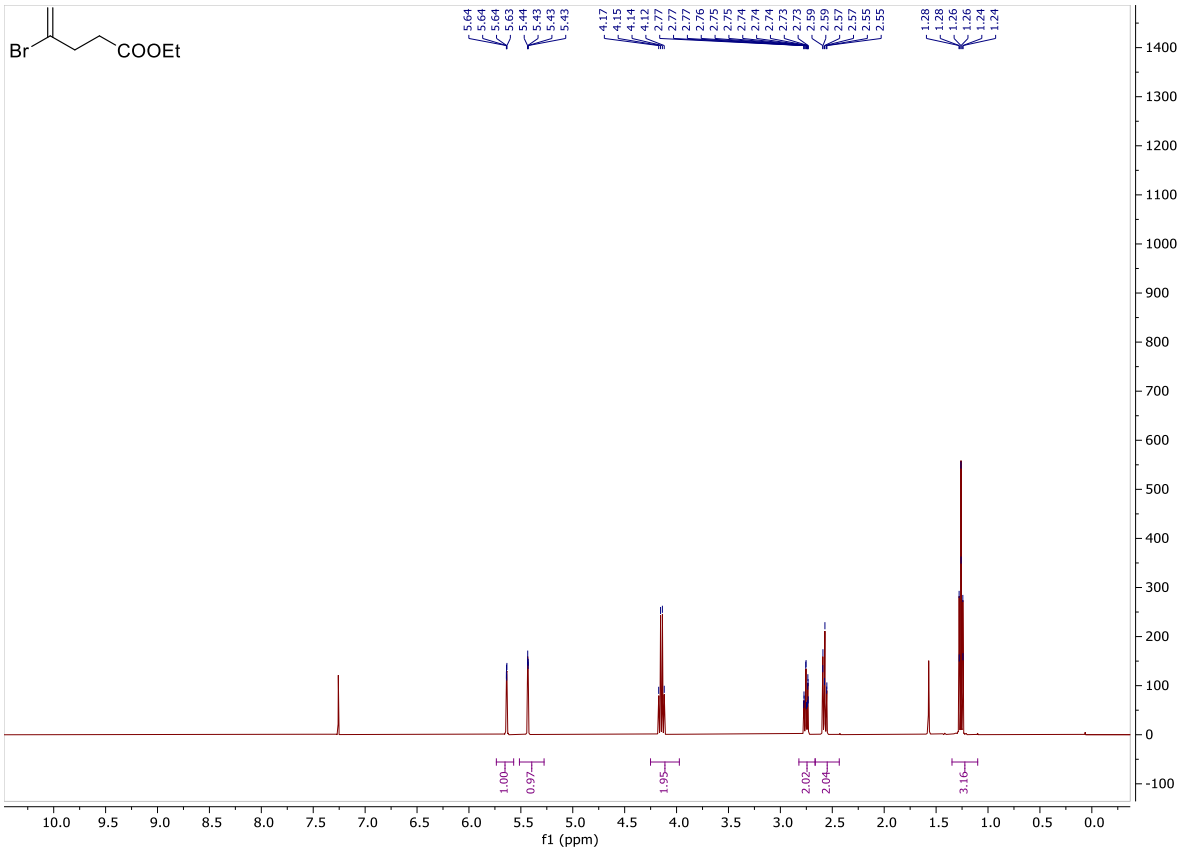


Figure SI-27. ^{1}H NMR spectrum of ethyl 4-bromopent-4-enoate in $CDCl_3$.

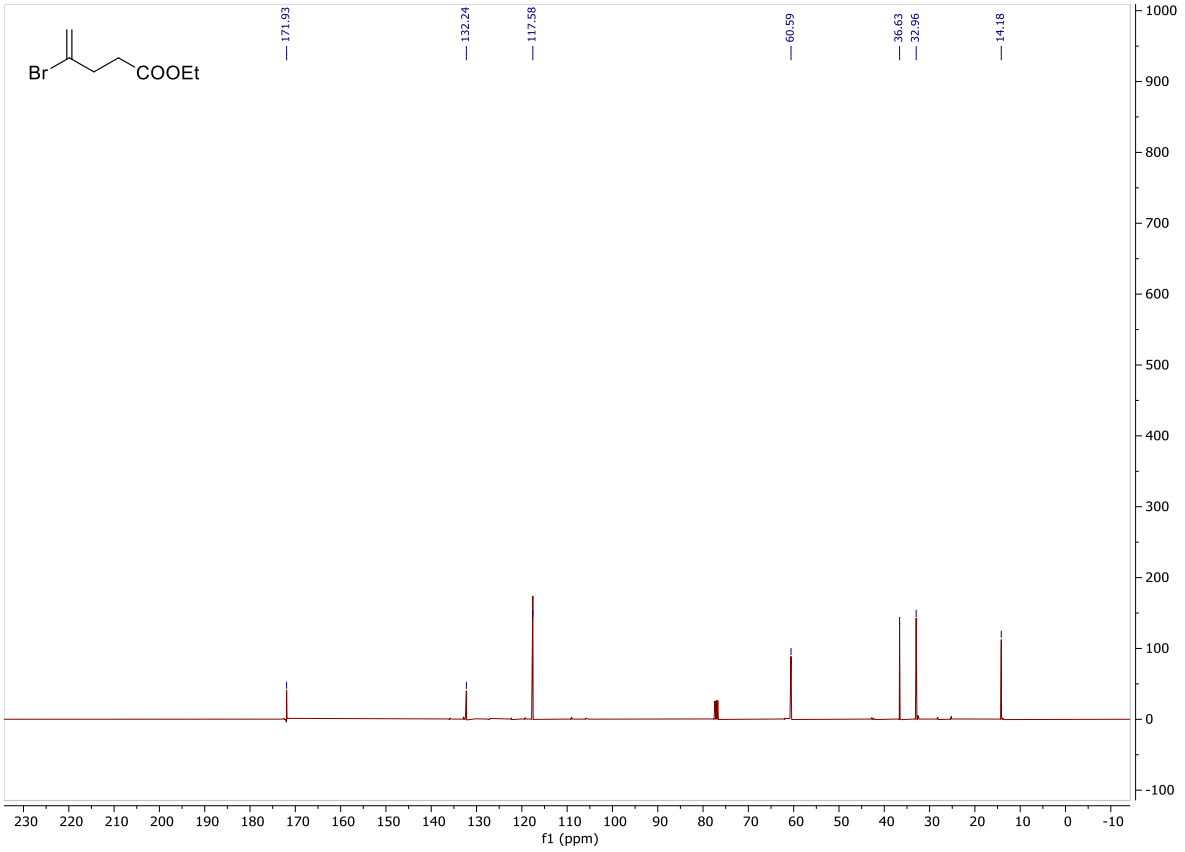


Figure SI-28. ^{13}C NMR spectrum of ethyl 4-bromopent-4-enoate in $CDCl_3$.

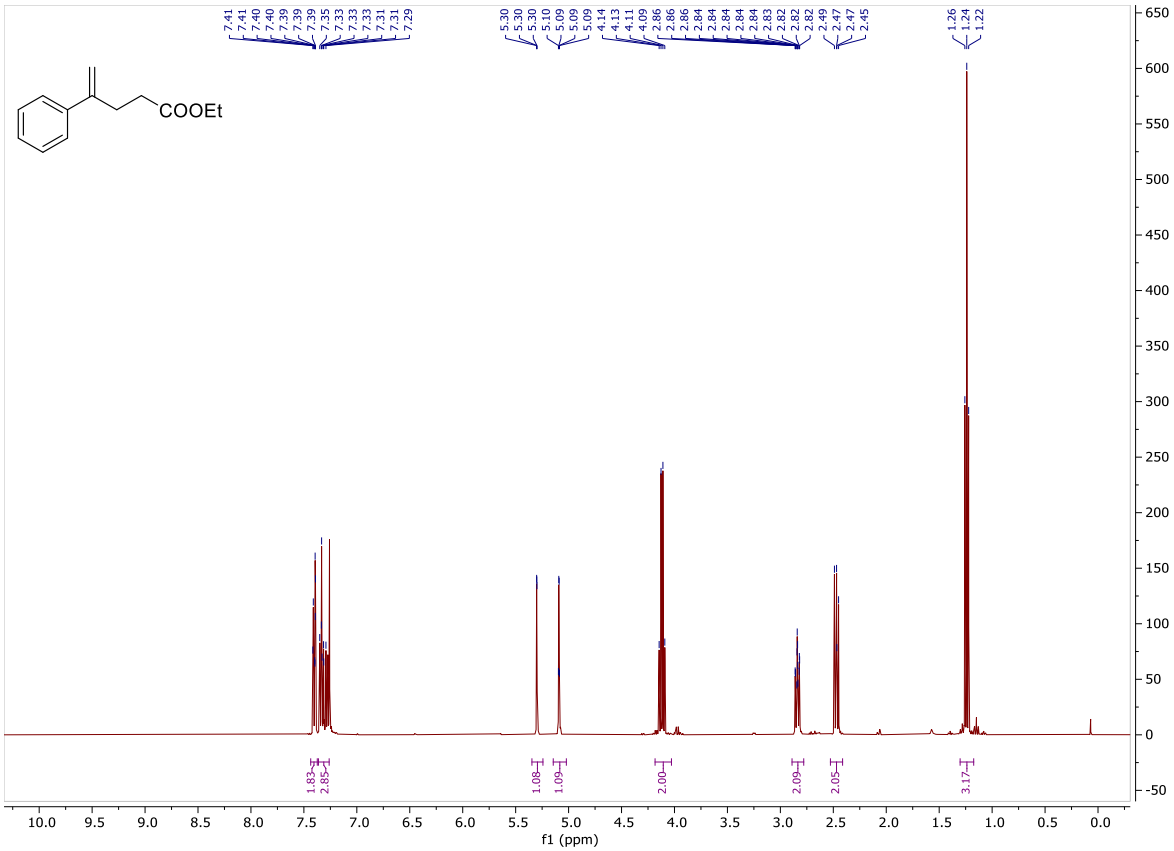


Figure SI-29. ^{1}H NMR spectrum of ethyl 4-phenylpent-4-enoate in $CDCl_3$.

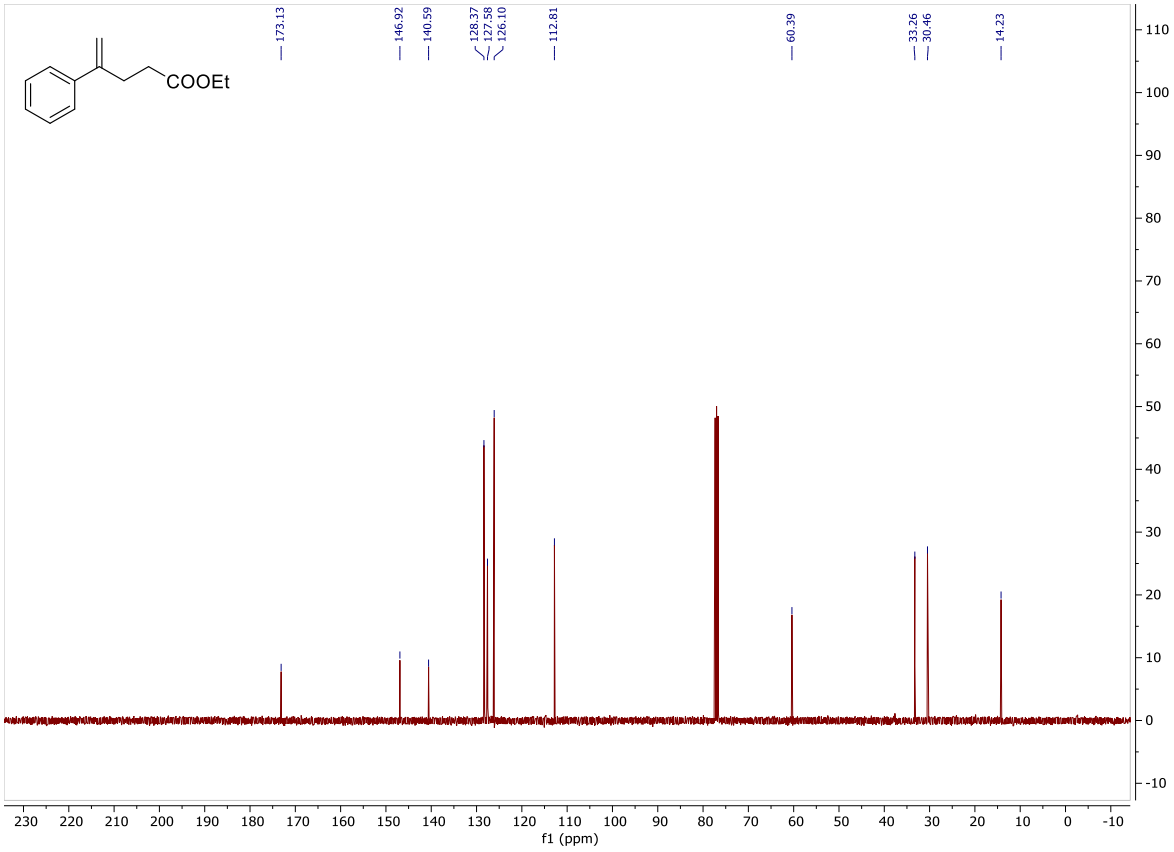


Figure SI-30. ^{13}C NMR spectrum of ethyl 4-phenylpent-4-enoate in $CDCl_3$.

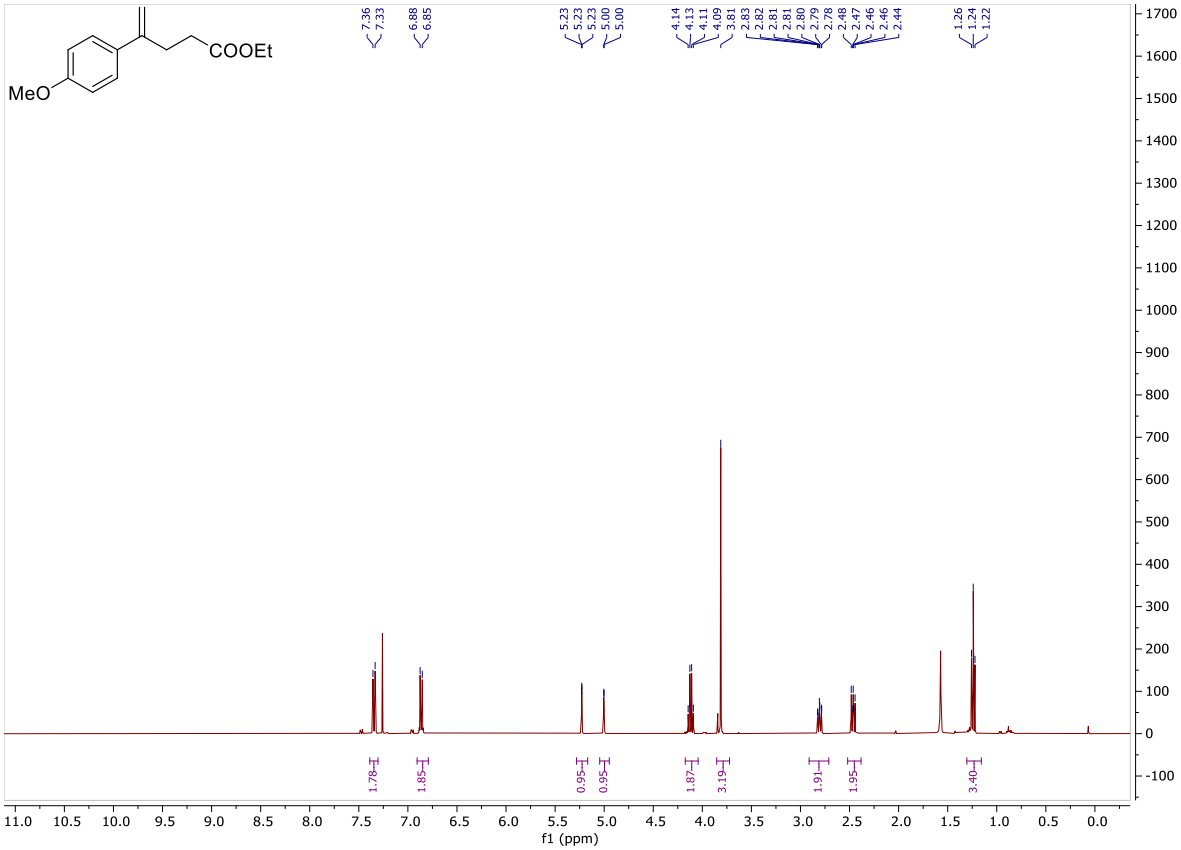


Figure SI-31. ^{1}H NMR spectrum of ethyl 4-(4-methoxyphenyl)pent-4-enoate in $CDCl_3$.

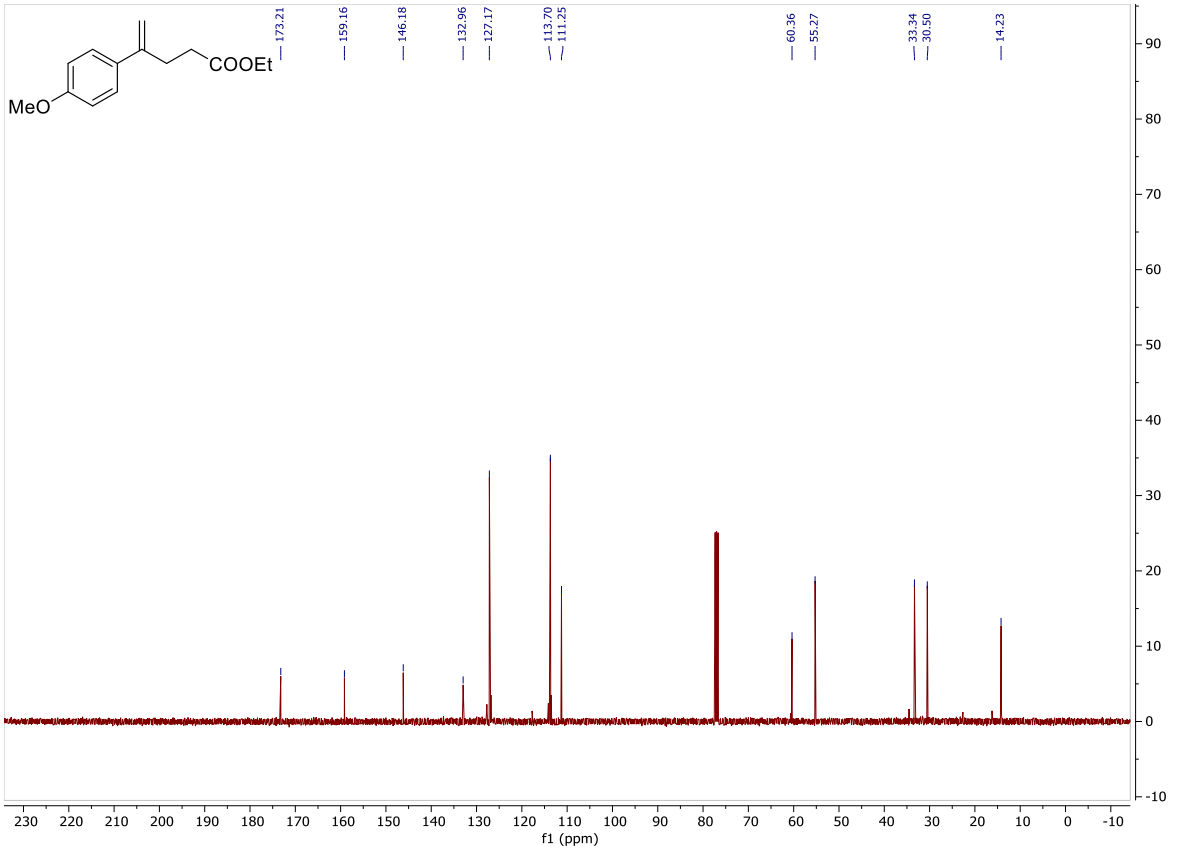


Figure SI-32. ^{13}C NMR spectrum of ethyl 4-(4-methoxyphenyl)pent-4-enoate in $CDCl_3$.

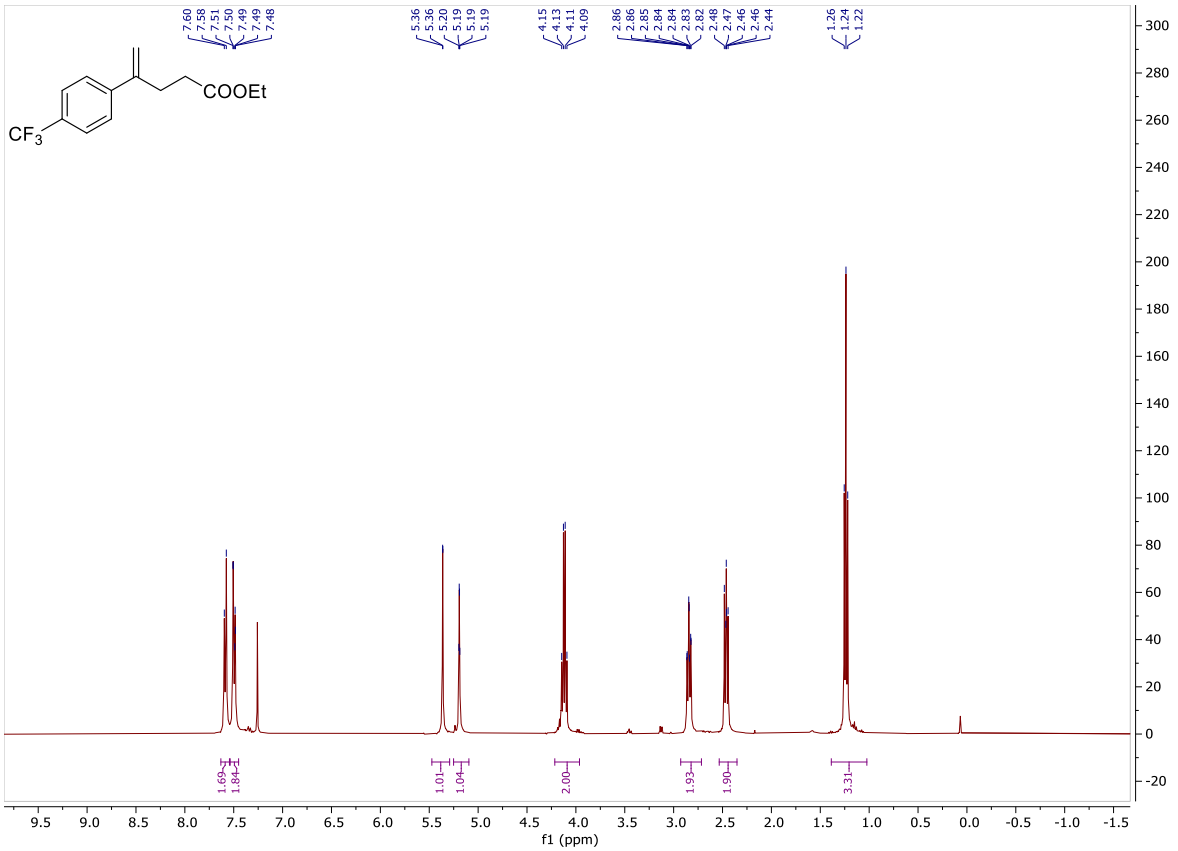


Figure SI-33. ^{1}H NMR spectrum of ethyl 4-[4-(trifluoromethyl)phenyl]pent-4-enoate in $CDCl_3$.

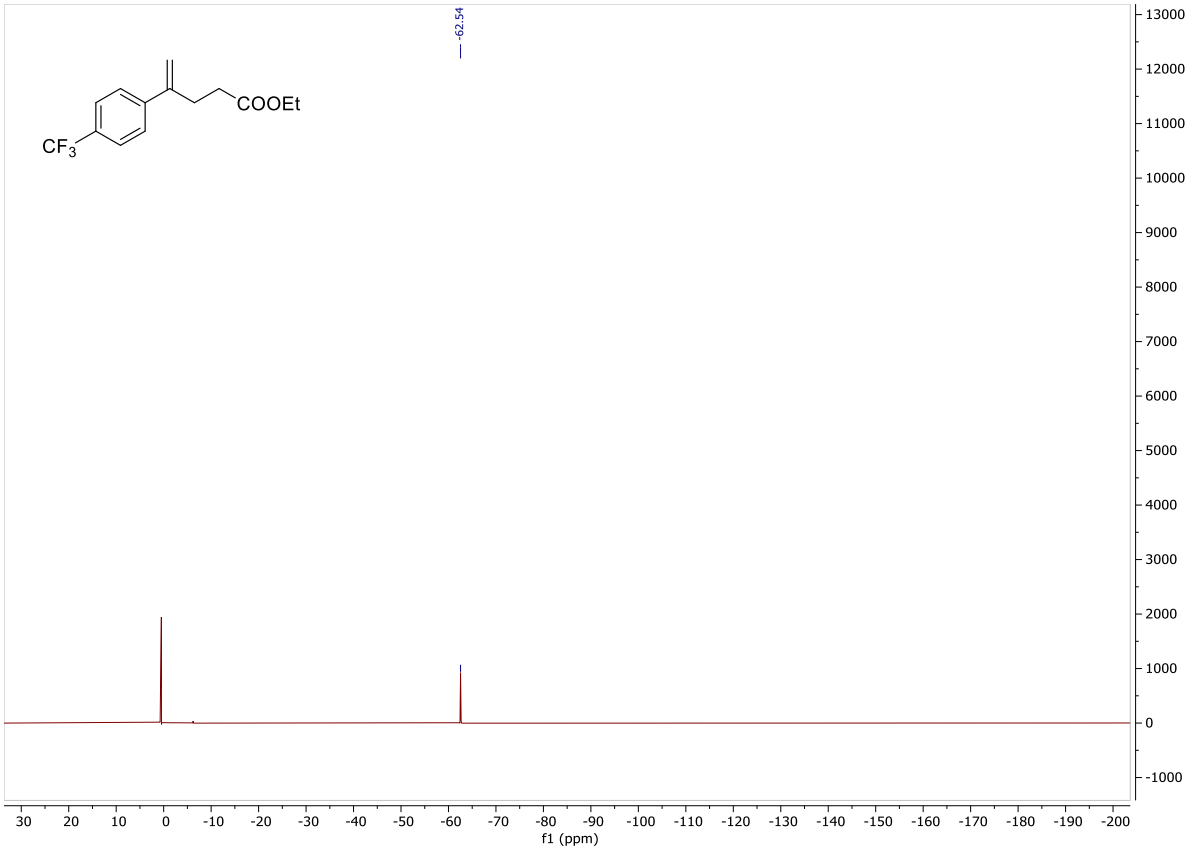


Figure SI-34. ^{19}F NMR spectrum of ethyl 4-[4-(trifluoromethyl)phenyl]pent-4-enoate in $CDCl_3$.

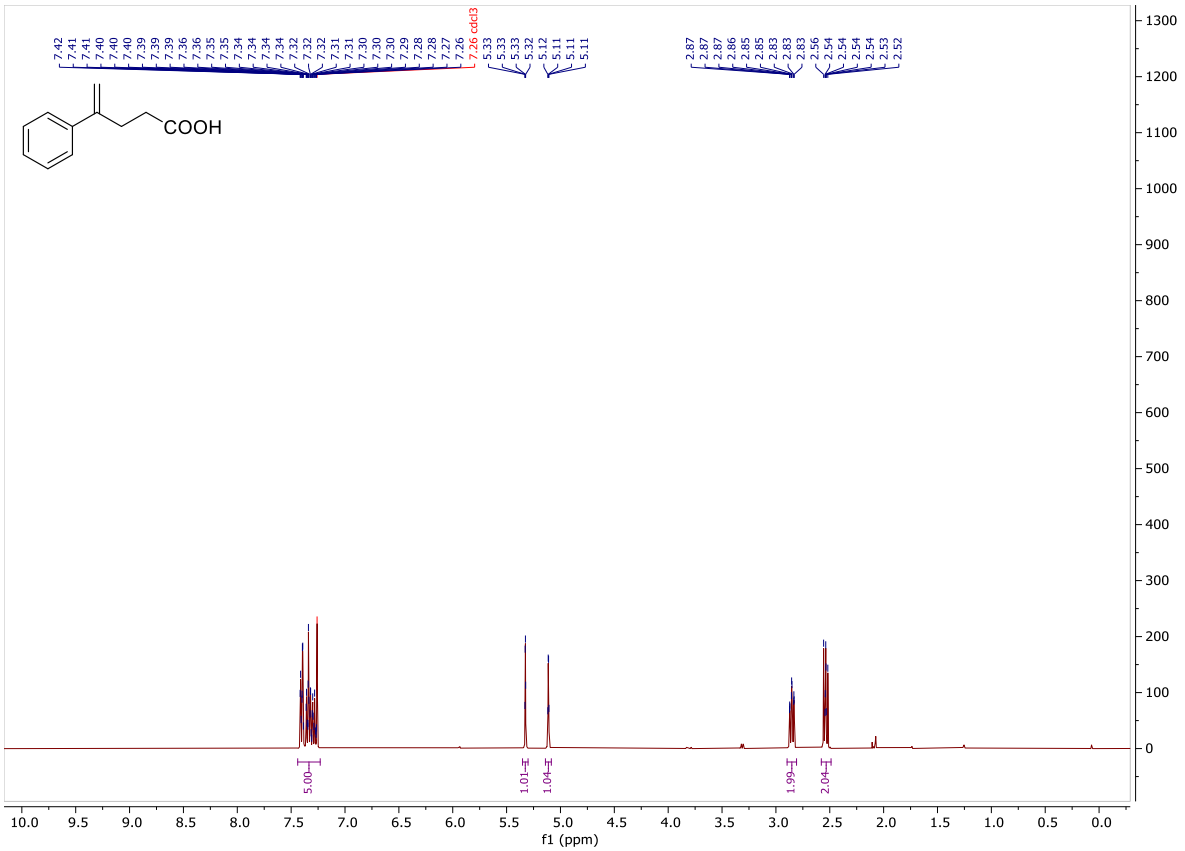


Figure SI-35. ^{1}H NMR spectrum of 4-phenylpent-4-enoic acid in $CDCl_3$.

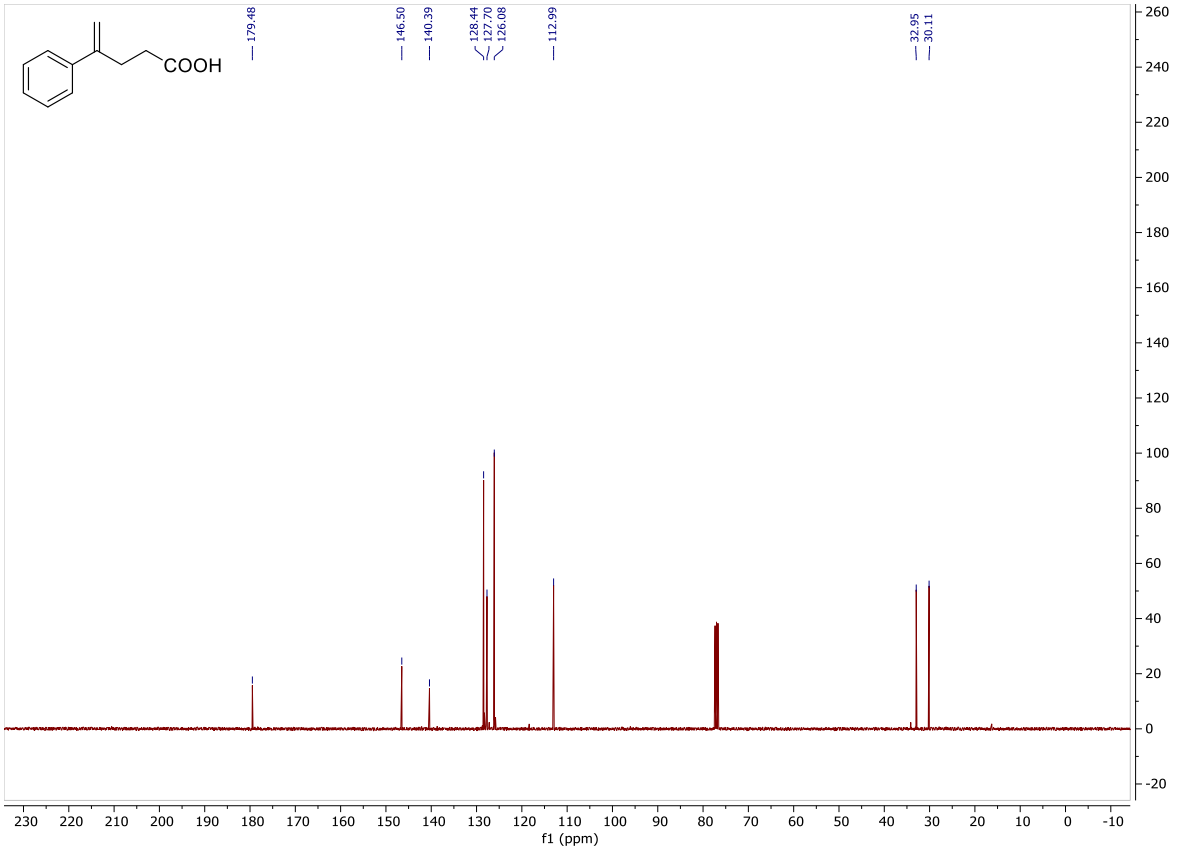


Figure SI-36. ^{13}C NMR spectrum of 4-phenylpent-4-enoic acid in $CDCl_3$.

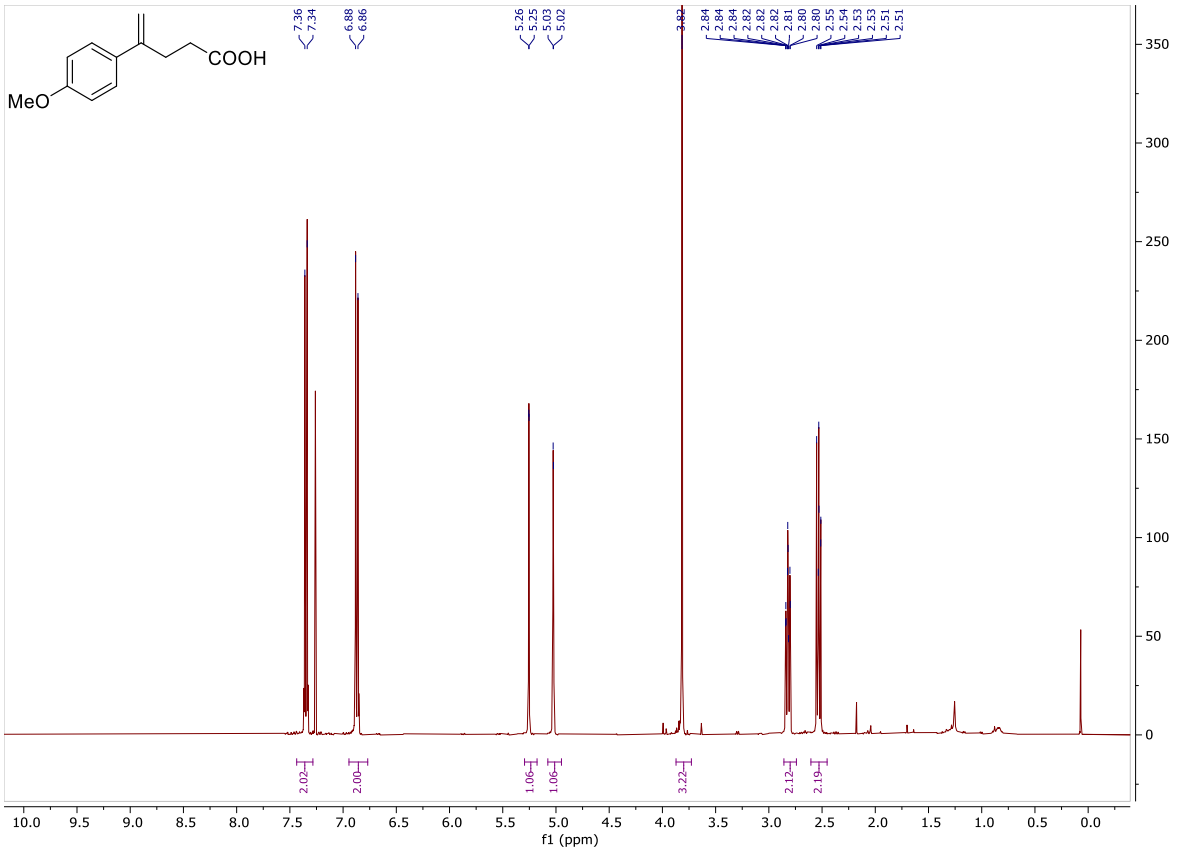


Figure SI-37. ^{1}H NMR spectrum of 4-(4-methoxyphenyl)pent-4-enoic acid in $CDCl_3$.

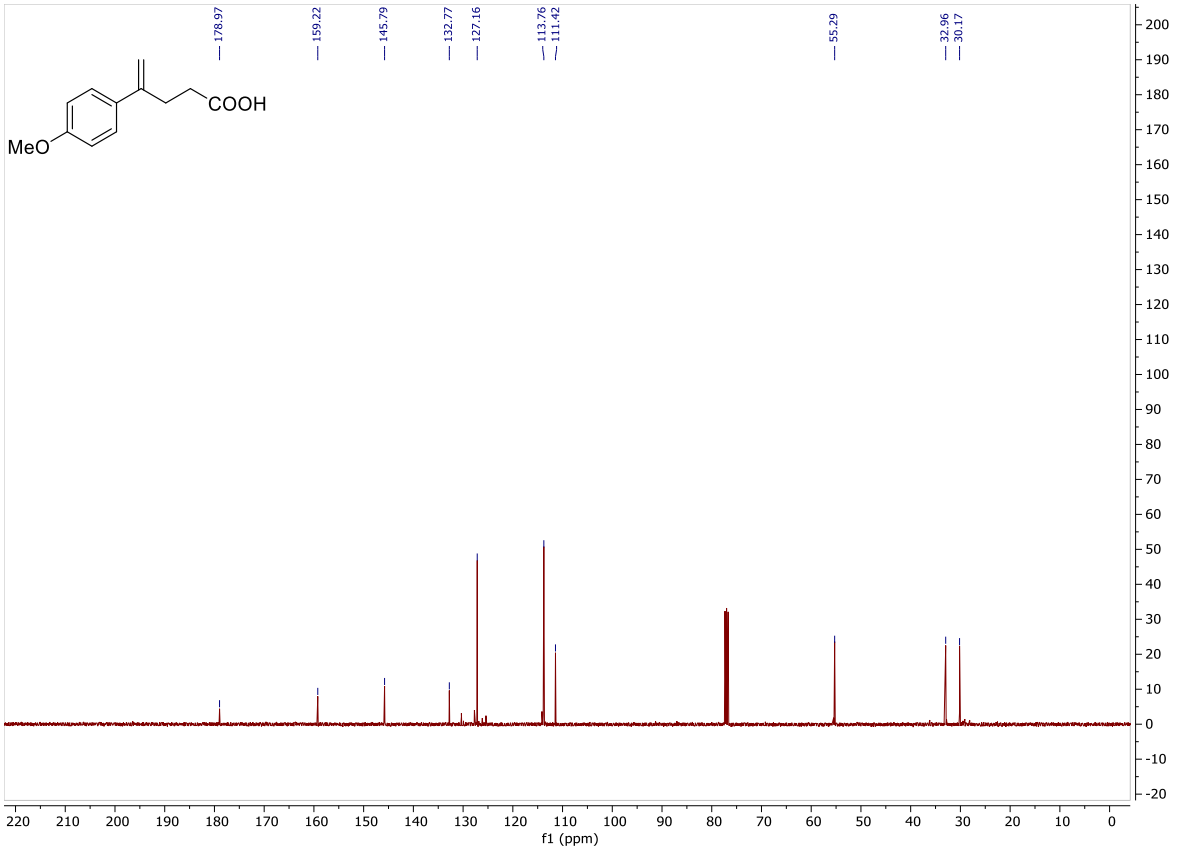


Figure SI-38. ^{13}C NMR spectrum of 4-(4-methoxyphenyl)pent-4-enoic acid in $CDCl_3$.

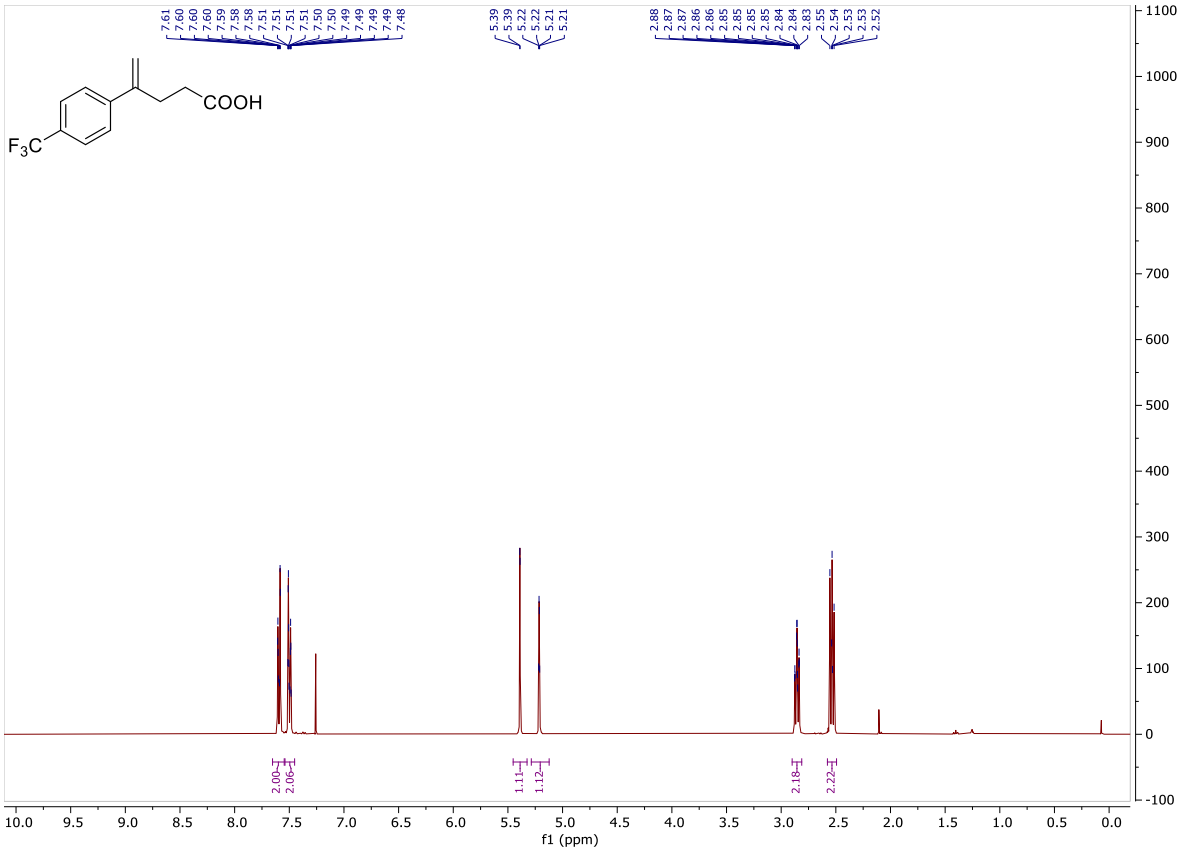


Figure SI-39. ^{1}H NMR spectrum of 4-[4-(trifluoromethyl)phenyl]pent-4-enoic acid in $CDCl_3$.

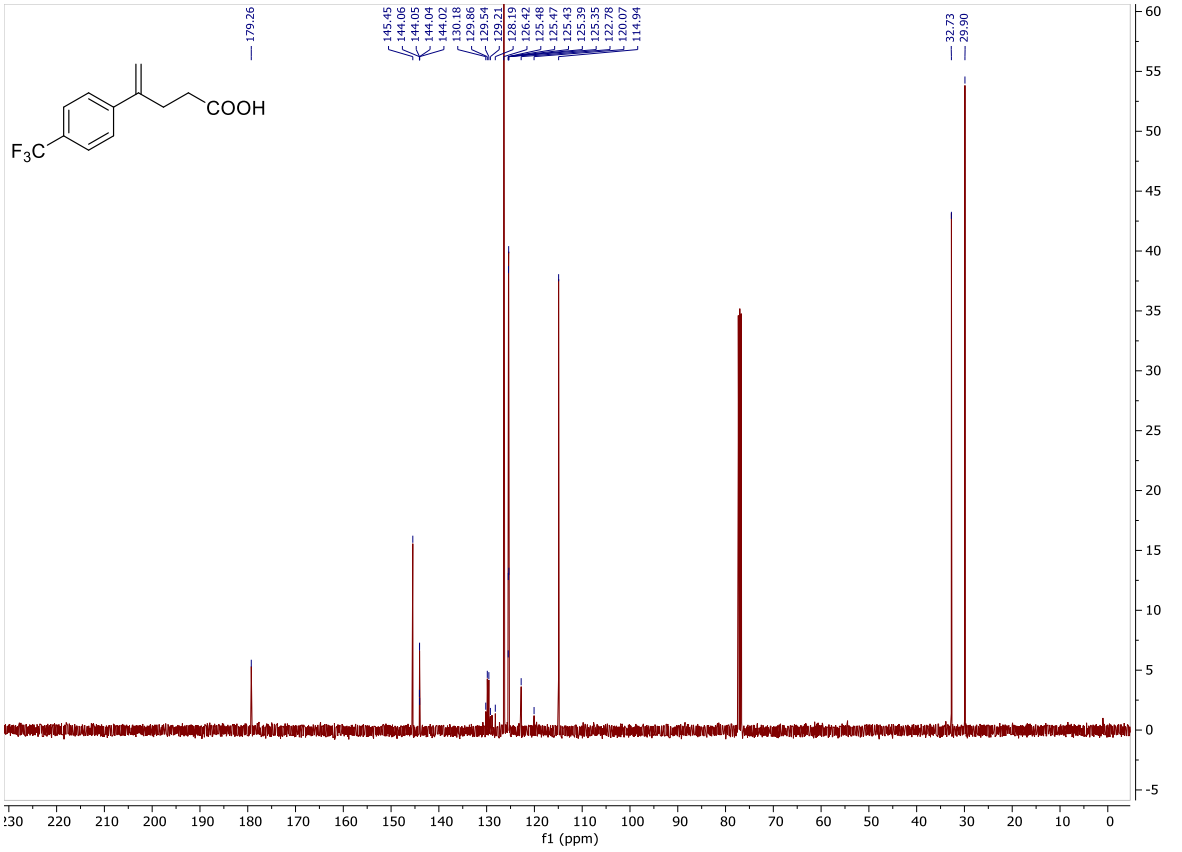


Figure SI-40. ^{13}C NMR spectrum of 4-[4-(trifluoromethyl)phenyl]pent-4-enoic acid in $CDCl_3$.

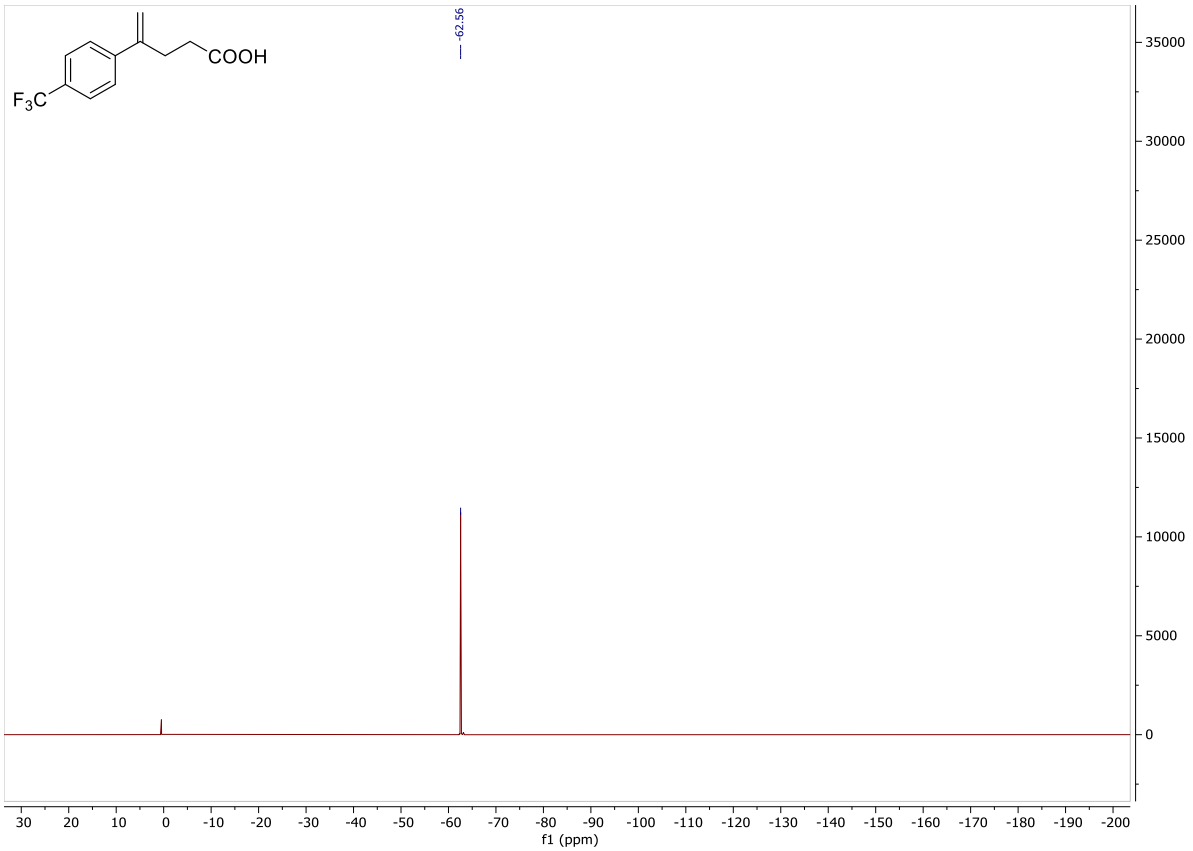


Figure SI-41. ^{19}F NMR spectrum of 4-[4-(trifluoromethyl)phenyl]pent-4-enoic acid in $CDCl_3$.

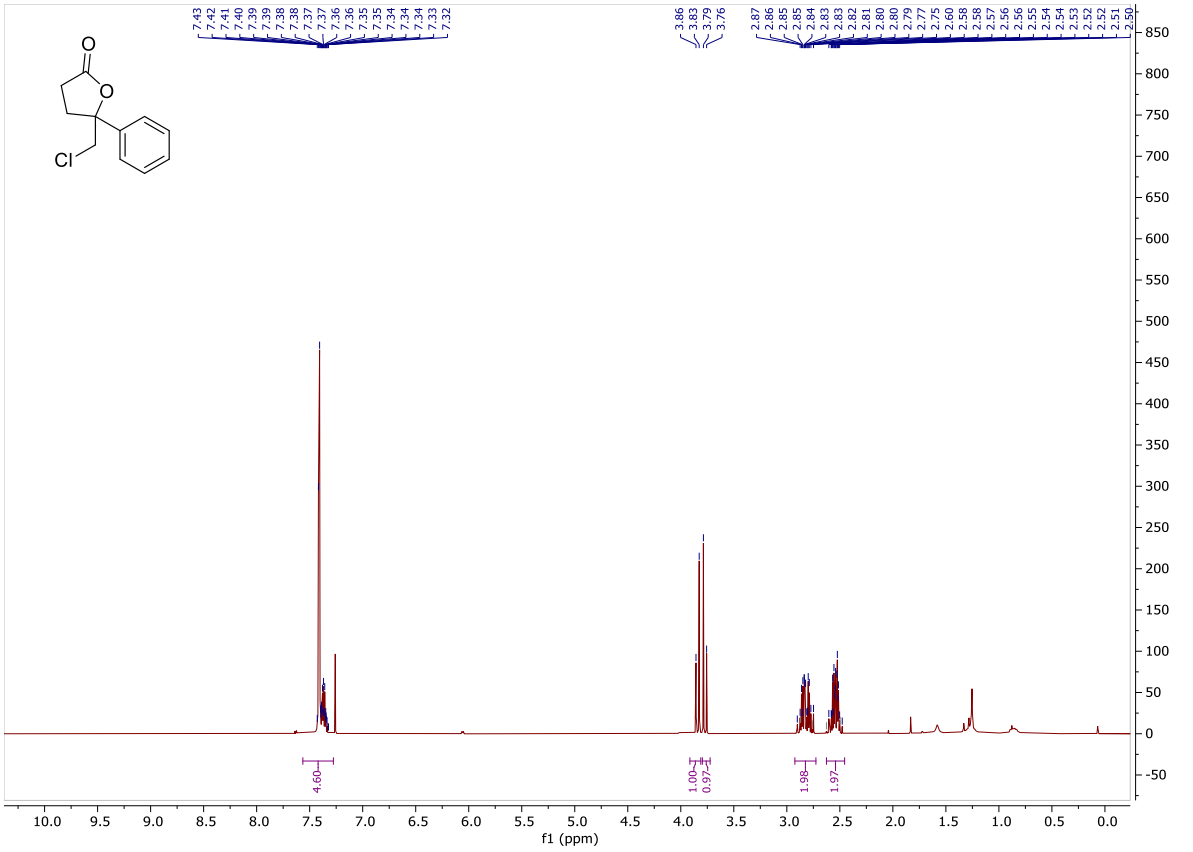


Figure SI-42. ^{1}H NMR spectrum of 5-(chloromethyl)-5-phenyldihydrofuran-2(3*H*)-one in $CDCl_3$.

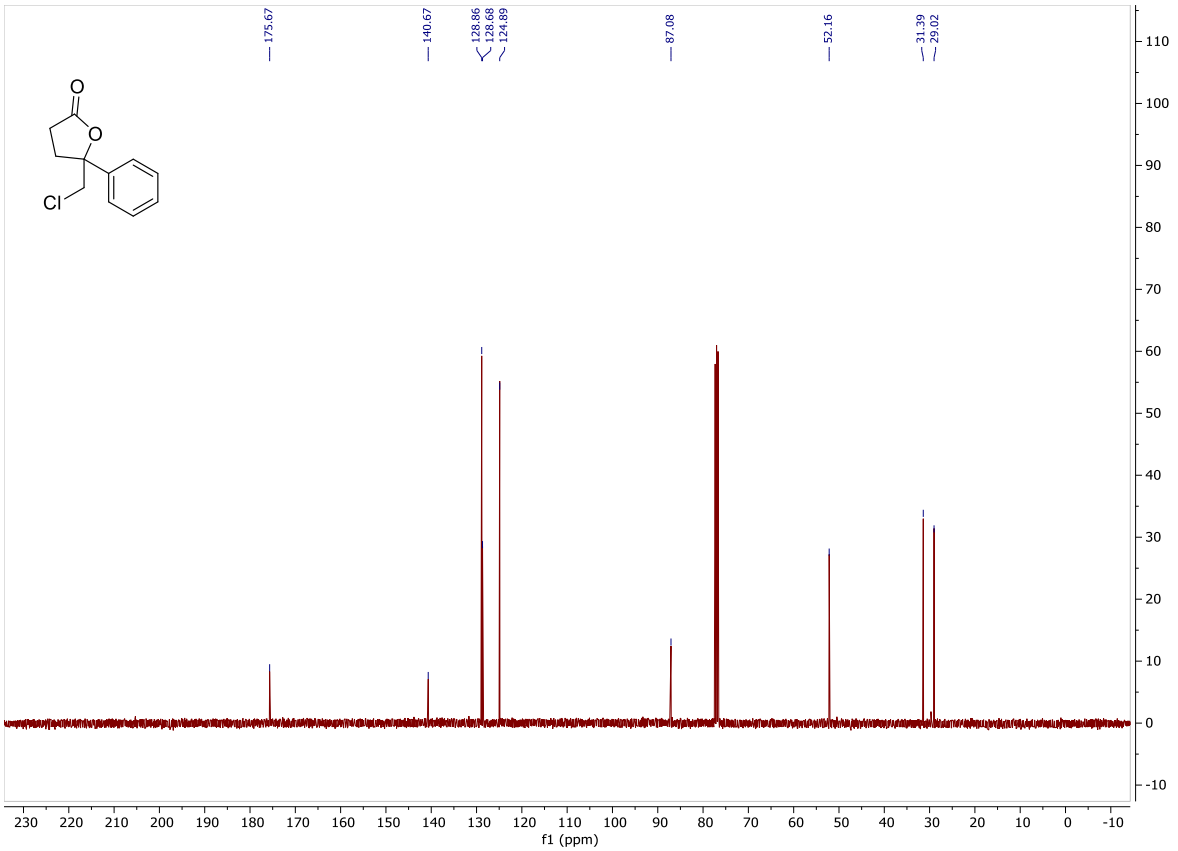


Figure SI-43. ^{13}C NMR spectrum of 5-(chloromethyl)-5-phenyldihydrofuran-2(3*H*)-one in $CDCl_3$.

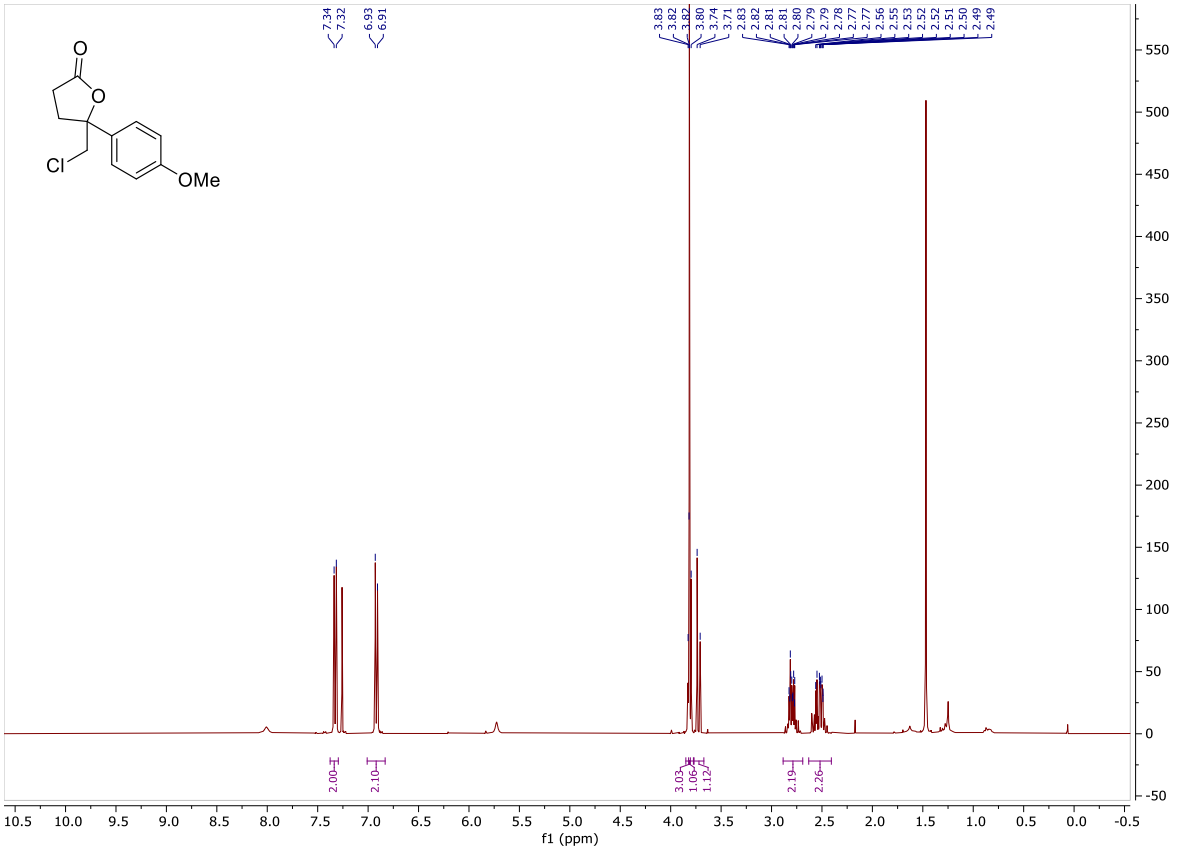


Figure SI-44. ^{1}H NMR spectrum of 5-(chloromethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one in $CDCl_3$.

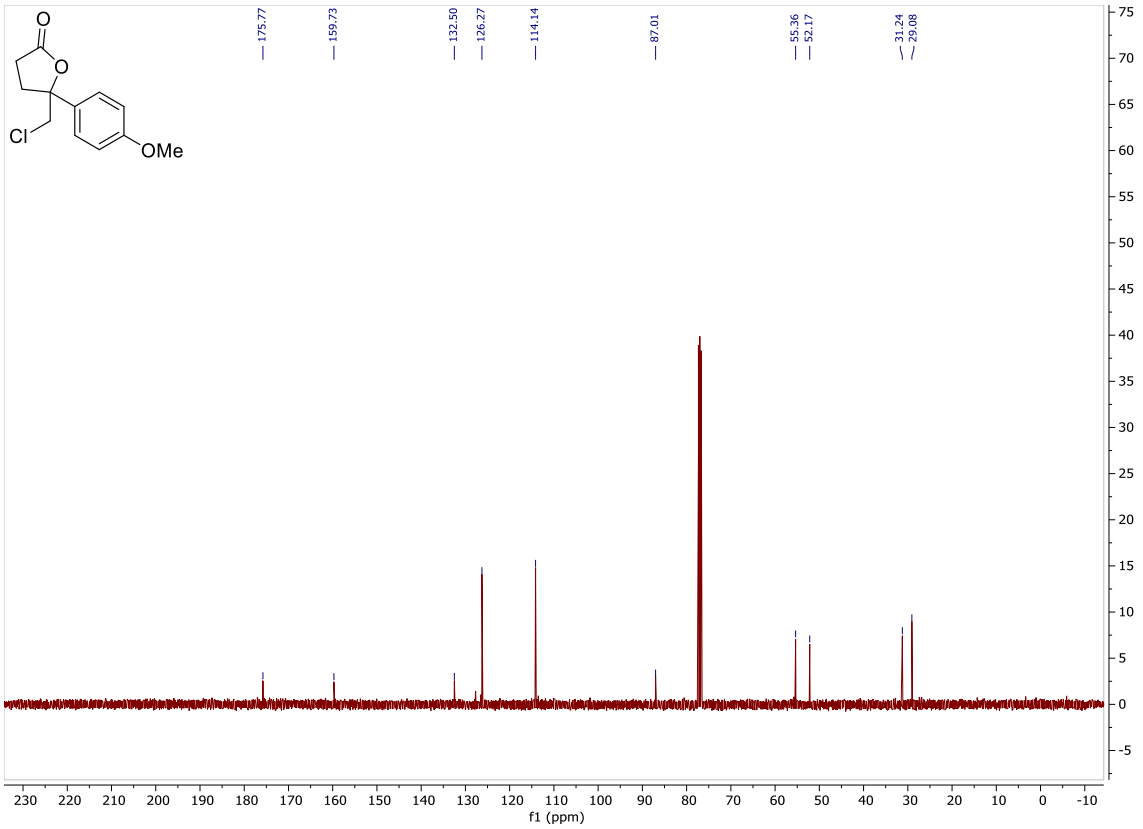


Figure SI-45. ^{13}C NMR spectrum of 5-(chloromethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one in $CDCl_3$.

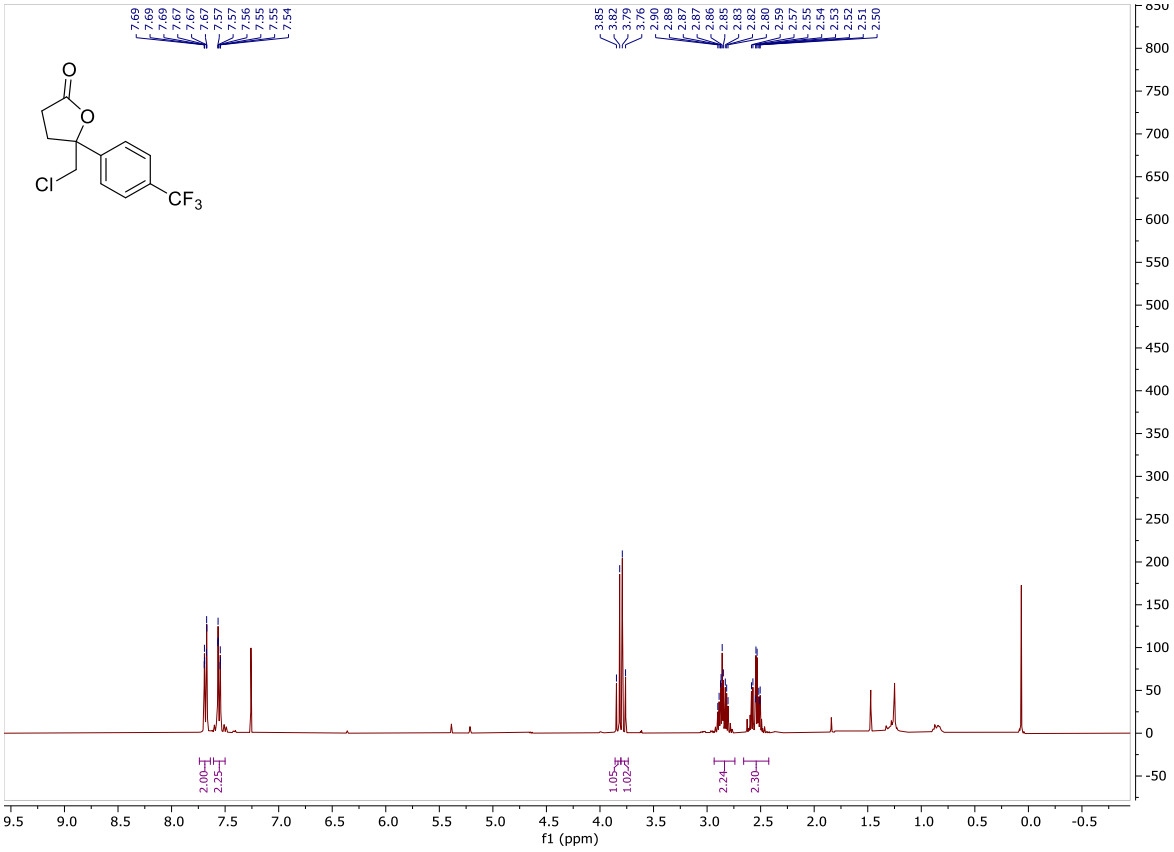


Figure SI-46. ^{1}H NMR spectrum of 5-(chloromethyl)-5-[4-(trifluoromethyl)phenyl]dihydrofuran-2(3*H*)-one in $CDCl_3$.

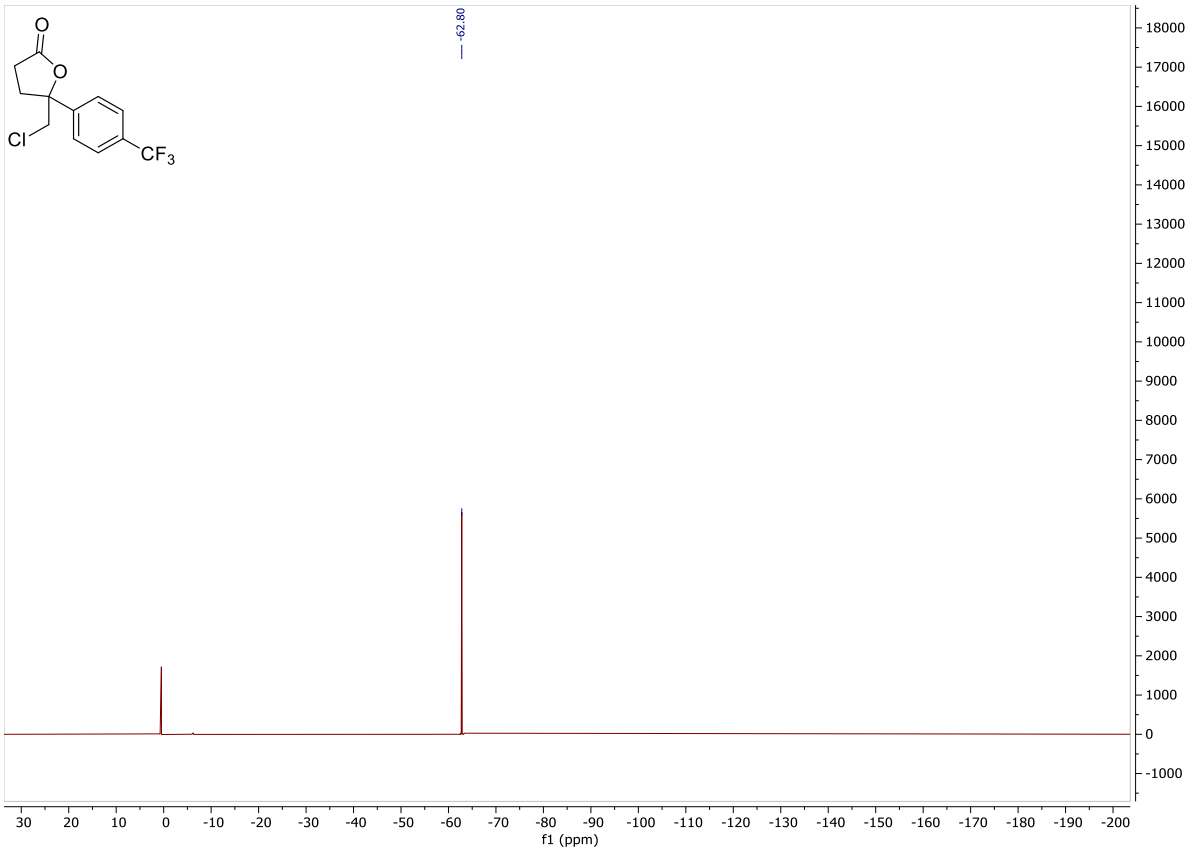


Figure SI-47. ^{19}F NMR spectrum of 5-(chloromethyl)-5-[4-(trifluoromethyl)phenyl]dihydrofuran-2(3*H*)-one in $CDCl_3$.

6. Infrared spectra

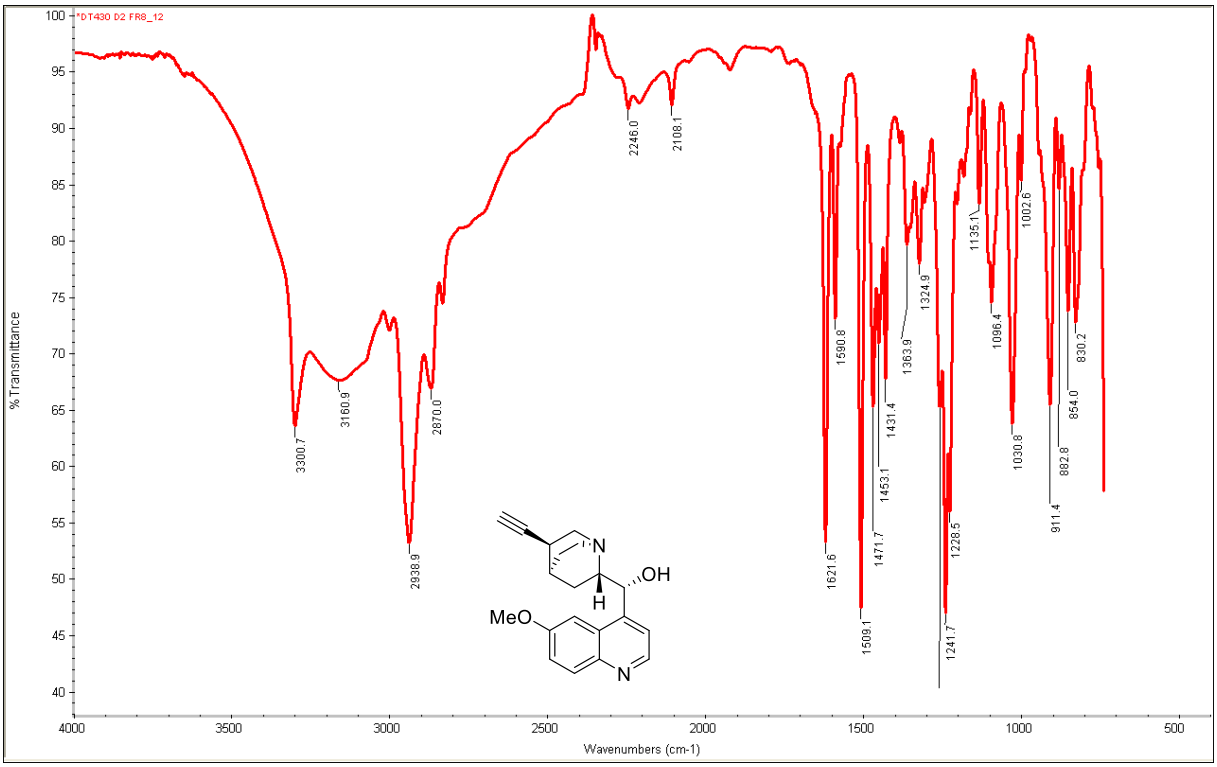


Figure SI-48. Infrared spectrum of 10,11-didehydroquinine (**3**).

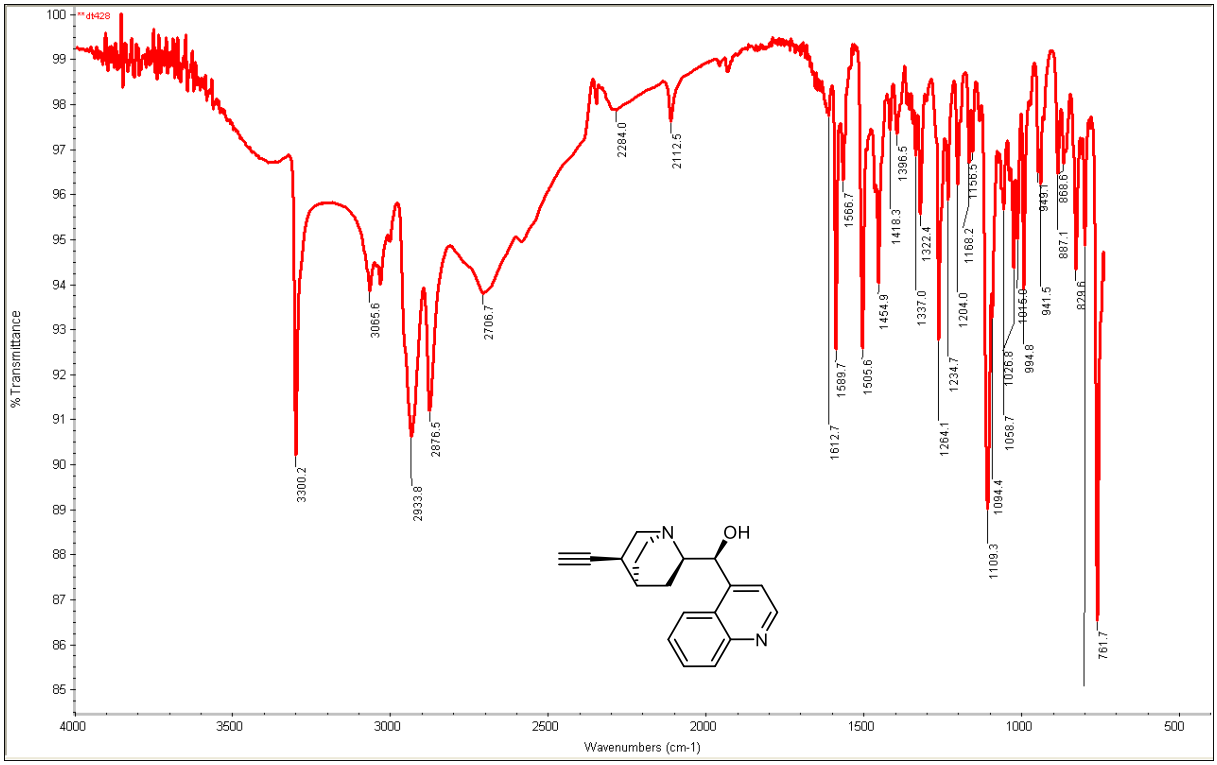


Figure SI-49. Infrared spectrum of 10,11-didehydrocinchonine (**4**).

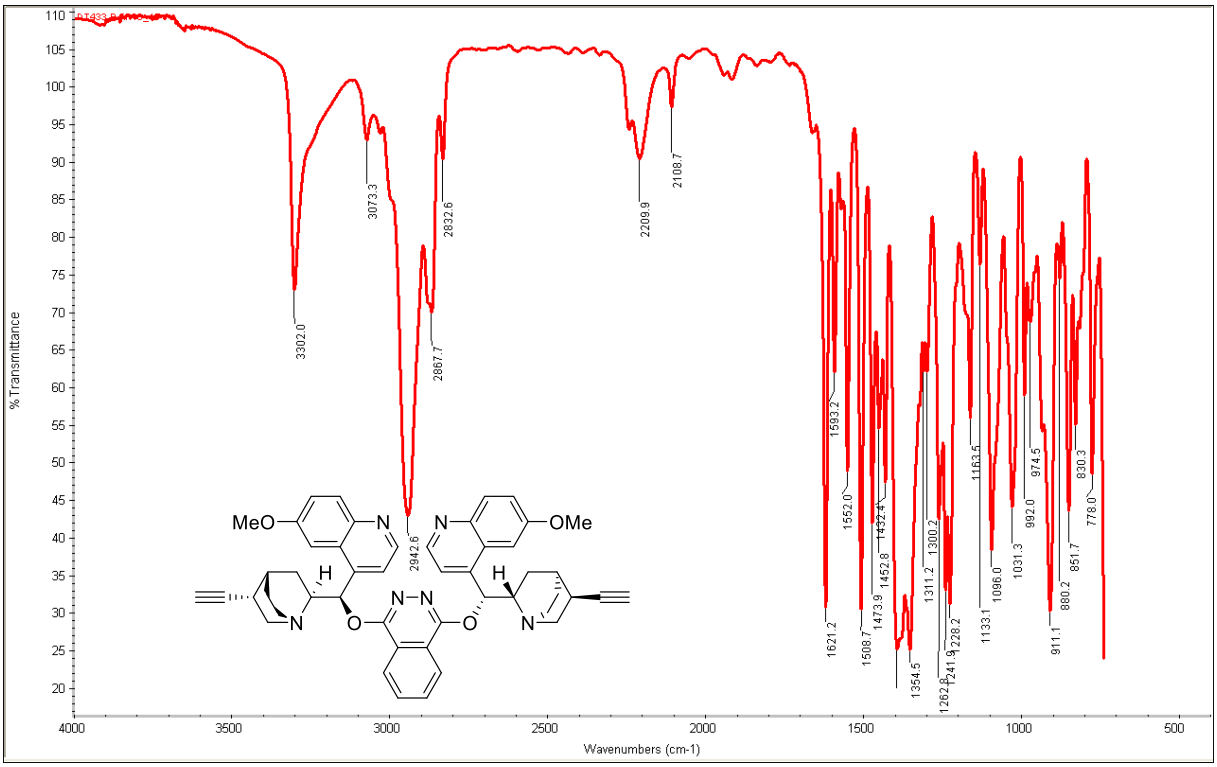


Figure SI-50. Infrared spectrum of dialkyne **5**.

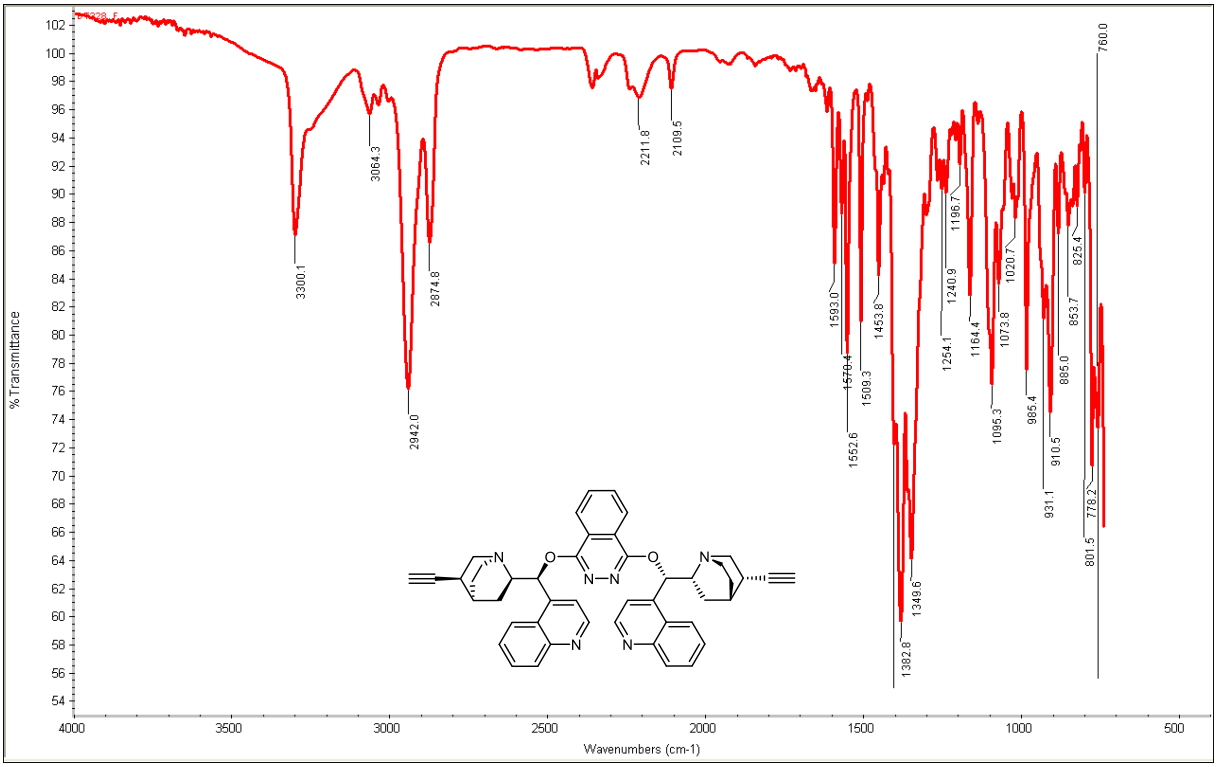


Figure SI-51. Infrared spectrum of dialkyne **6**.

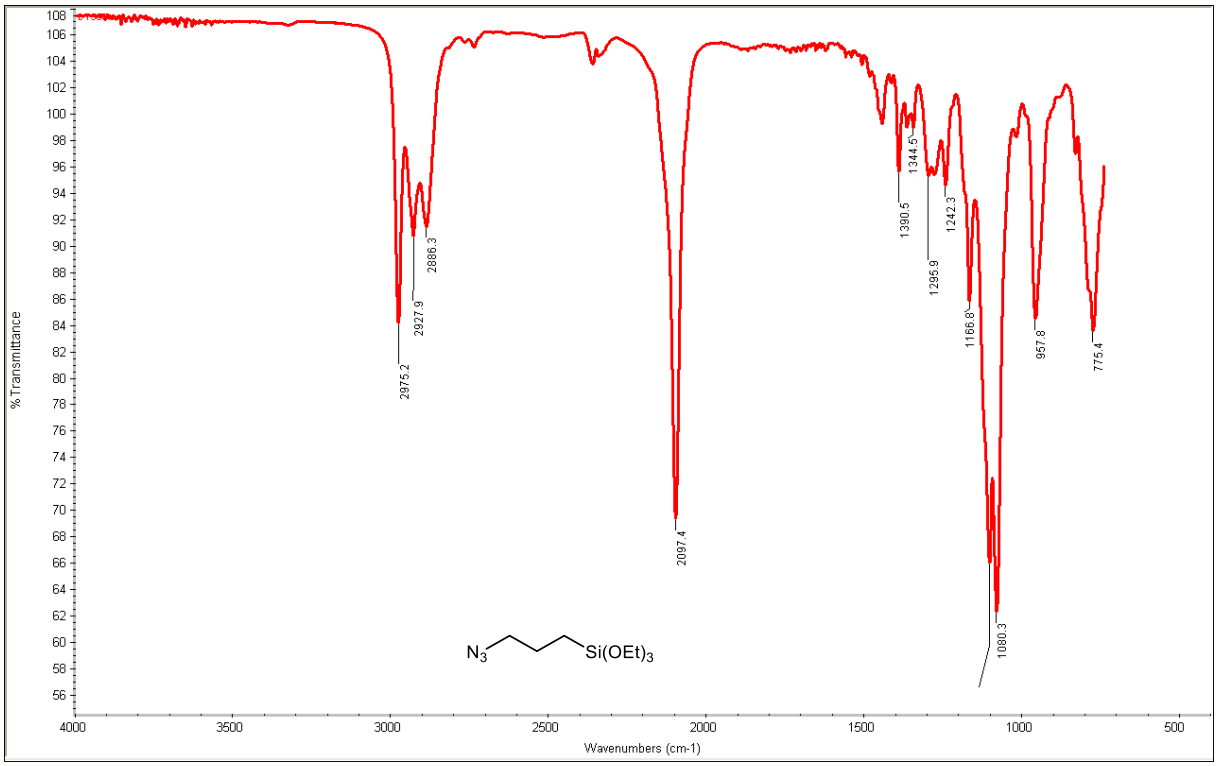


Figure SI-52. Infrared spectrum of (3-azidopropyl)triethoxysilane.

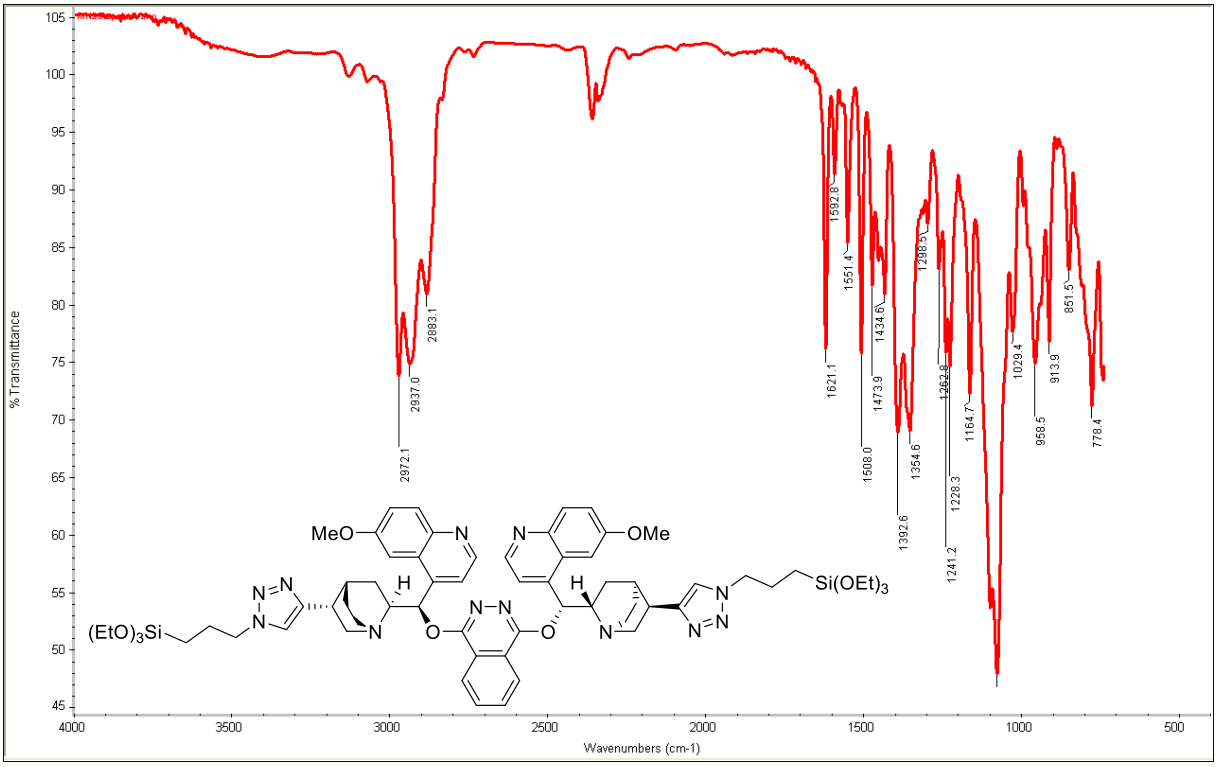


Figure SI-53. Infrared spectrum of bis(triethoxysilane) **1**.

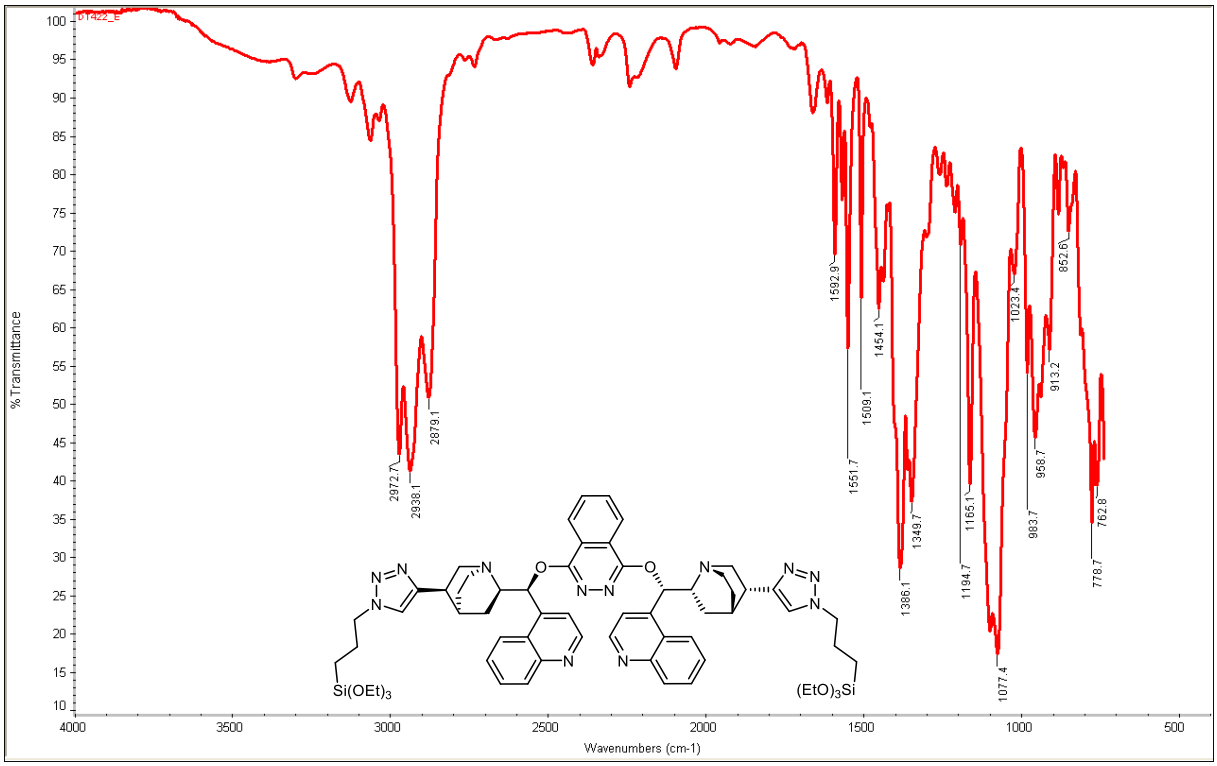


Figure SI-54. Infrared spectrum of bis(triethoxysilane) **2**.

7. MS spectra

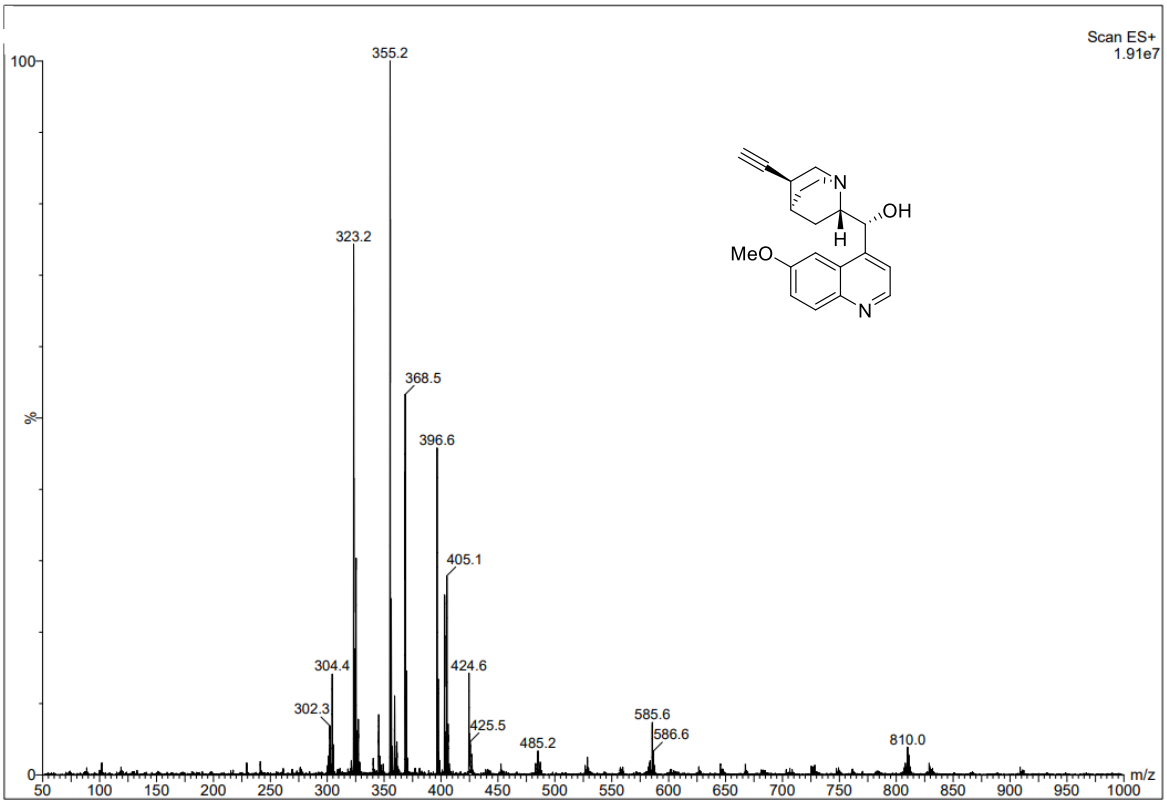


Figure SI-55. ESI-MS spectrum of 10,11-didehydroquinine (**3**).

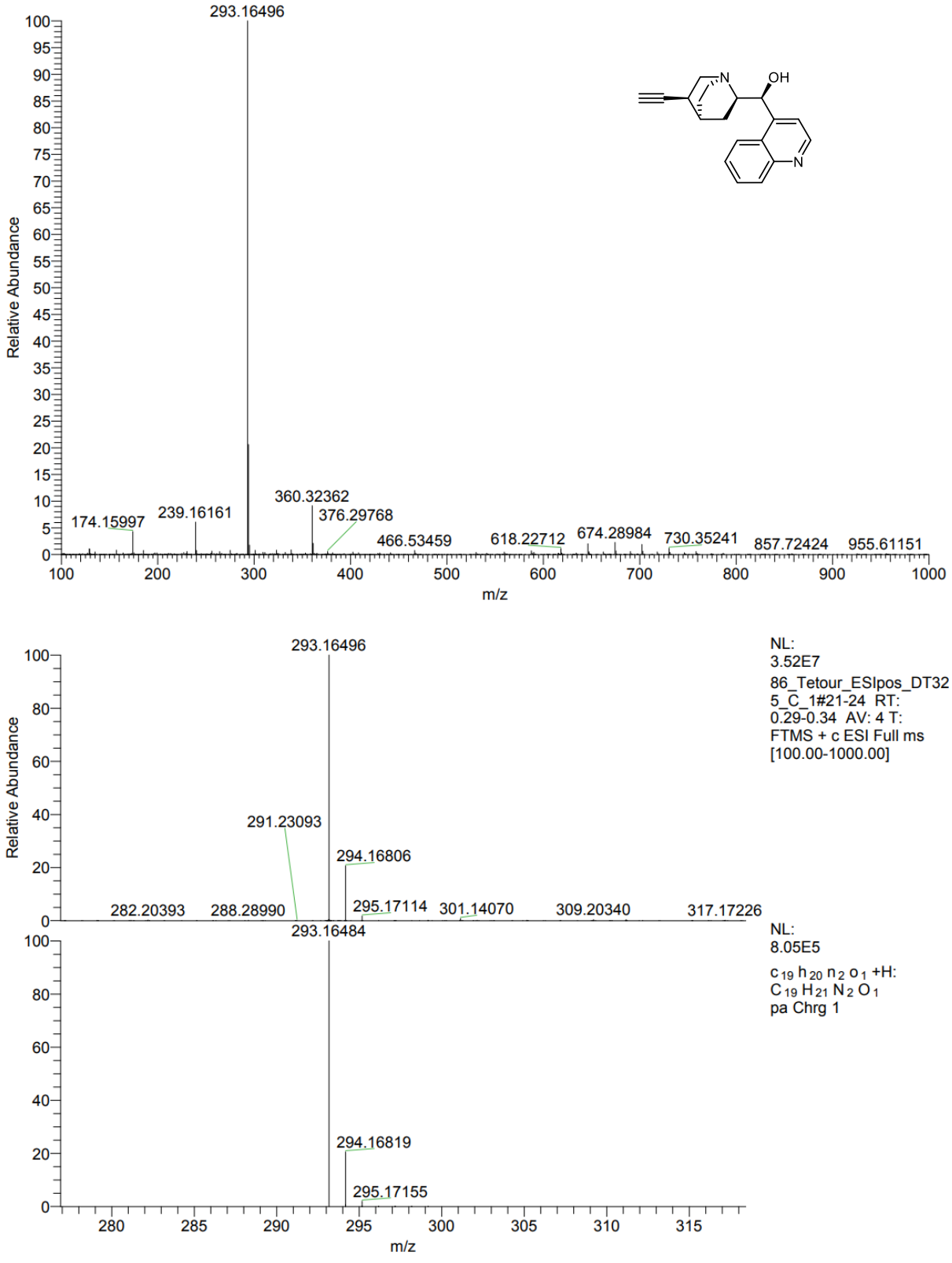


Figure SI-56. ESI-HRMS spectrum of 10,11-didehydrocinchonine (**4**).

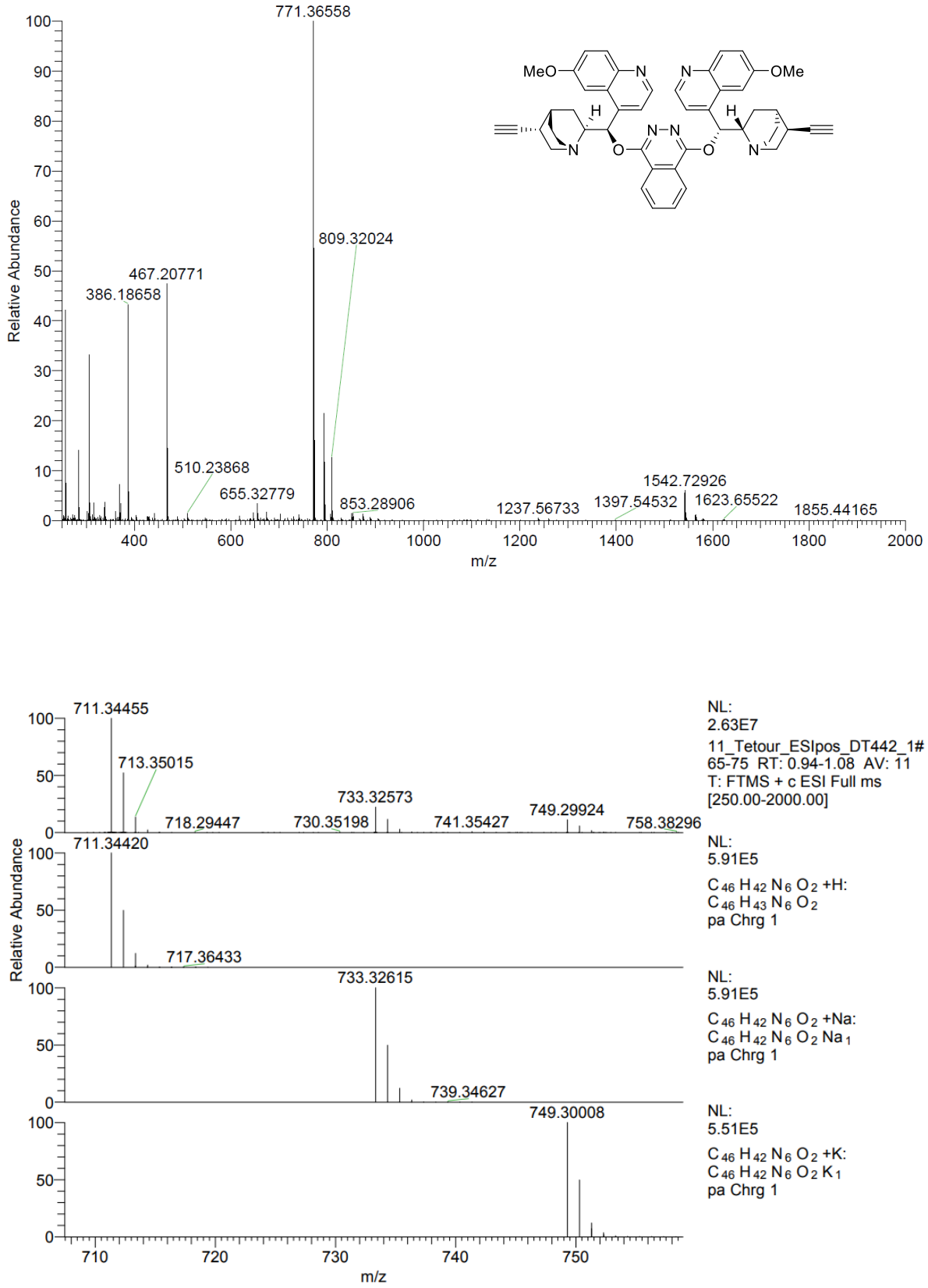


Figure SI-57. ESI-HRMS spectrum of dialkyne **5**.

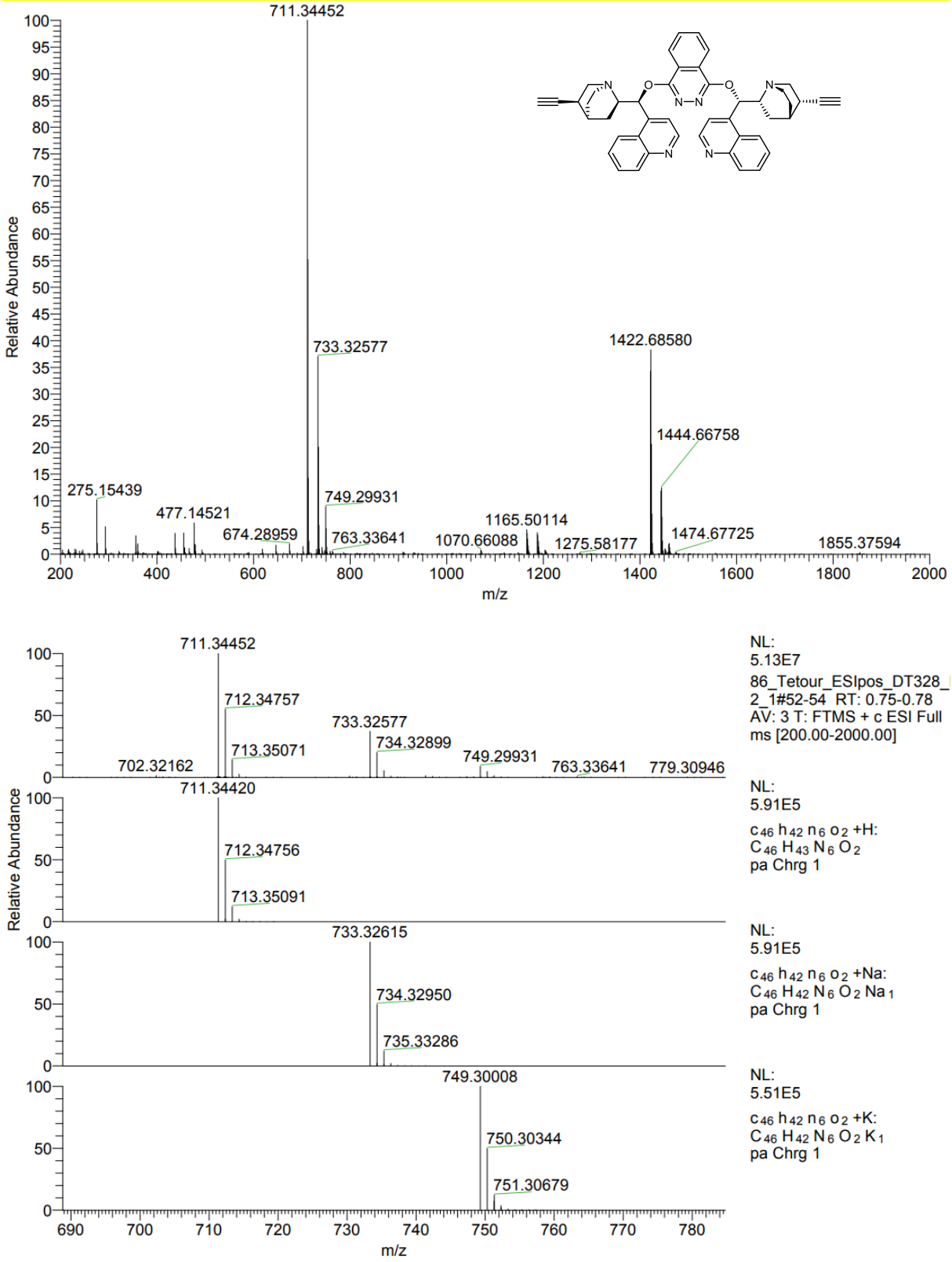


Figure SI-58. ESI-HRMS spectrum of dialkyne **6**.

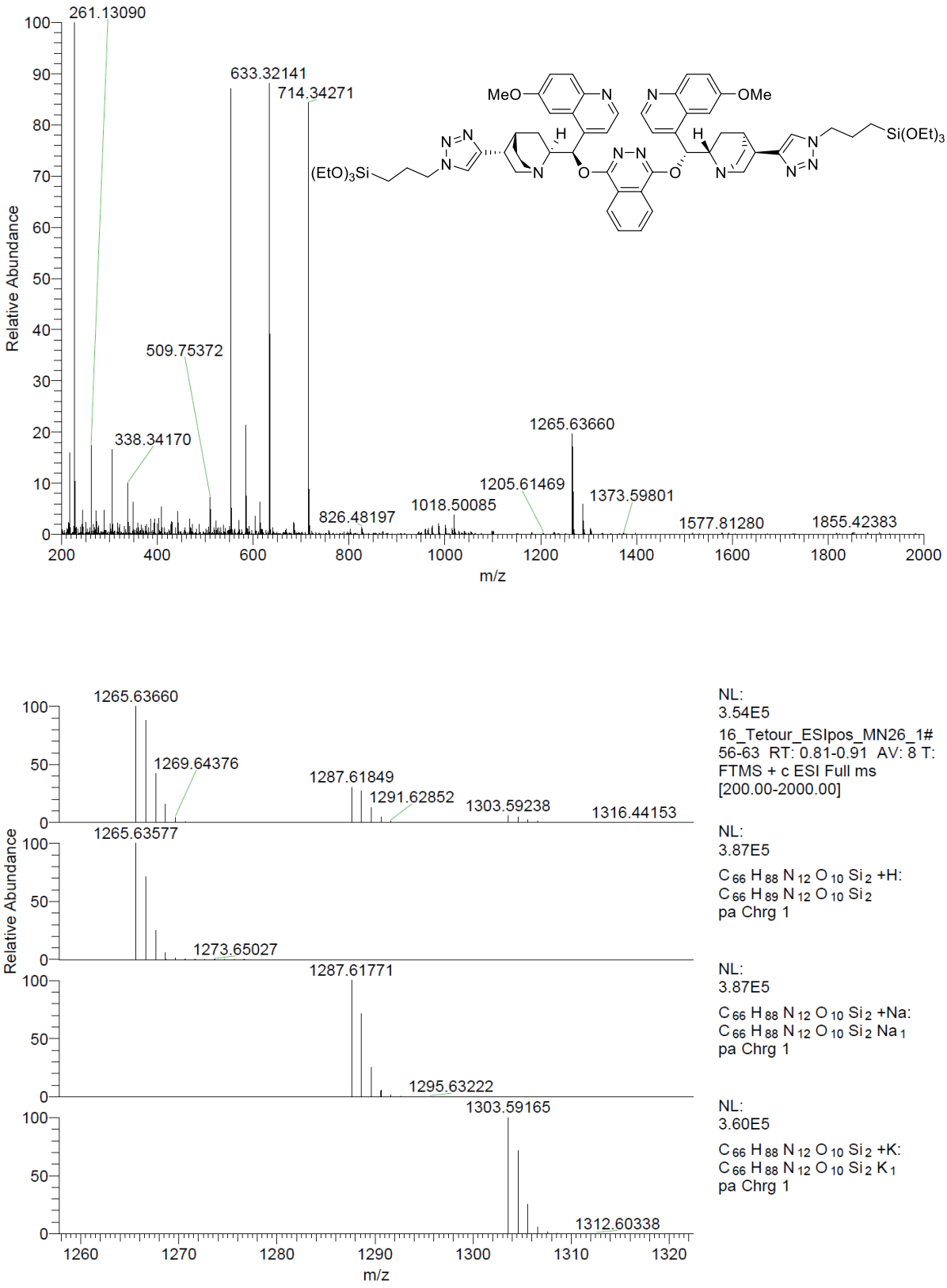


Figure SI-59. ESI-HRMS spectrum of bis(triethoxysilane) **1**.

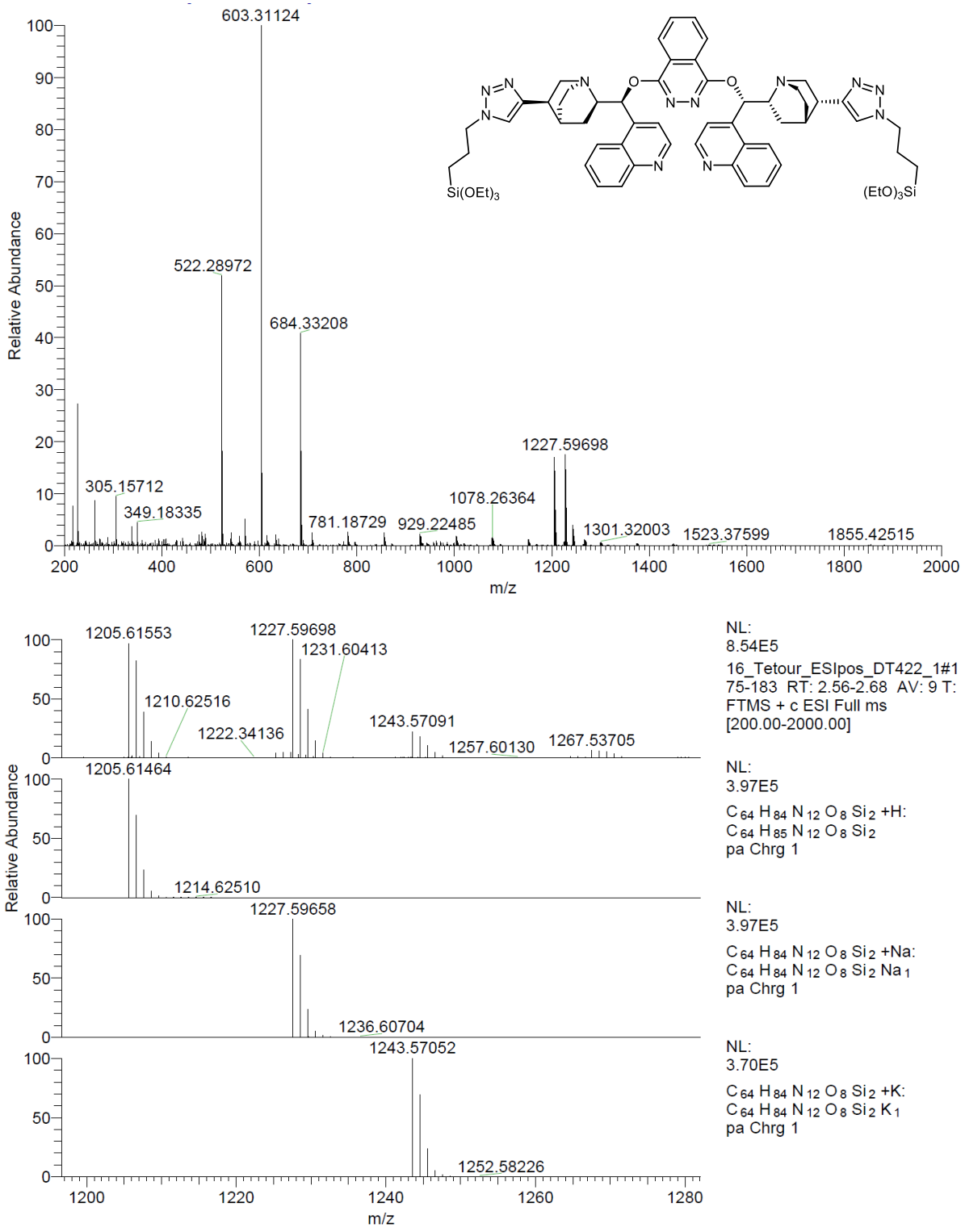
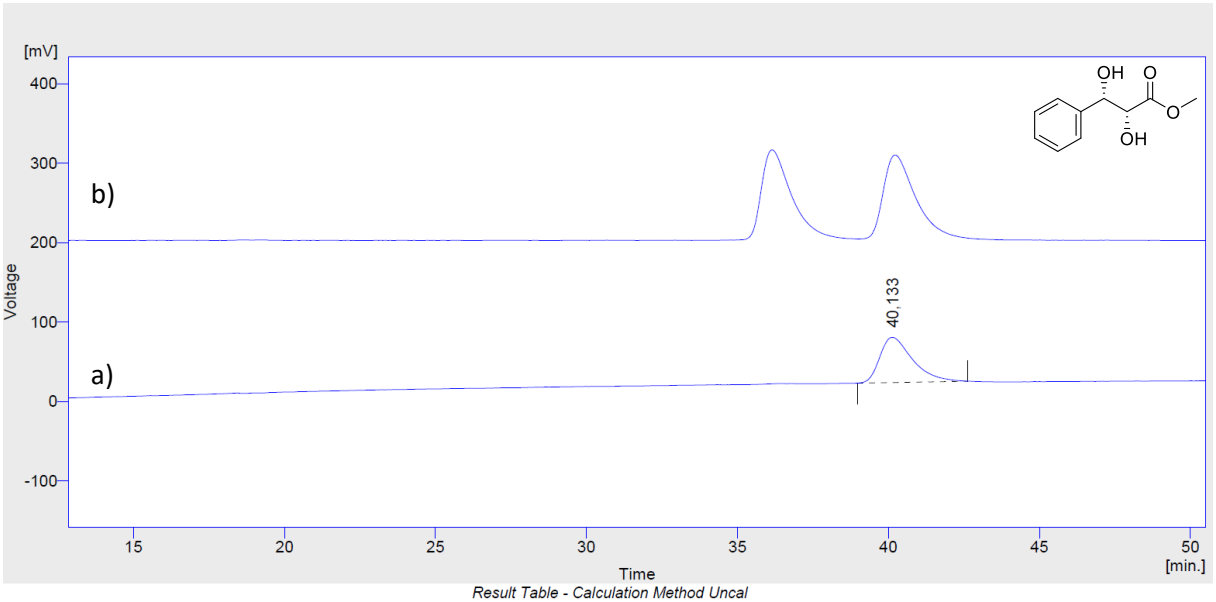


Figure SI-60. ESI-HRMS spectrum of bis(triethoxysilane) **2**.

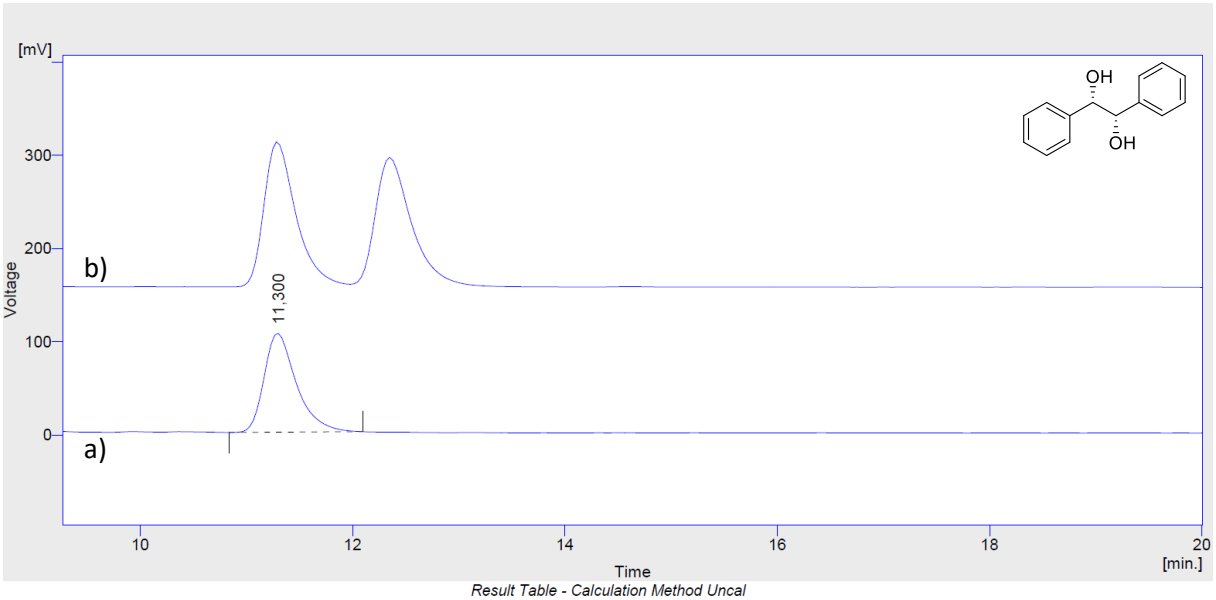
8. HPLC analyses



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
40,133	4284,225	56,958	100,0	100,0	1,17
Total	4284,225	56,958	100,0	100,0	

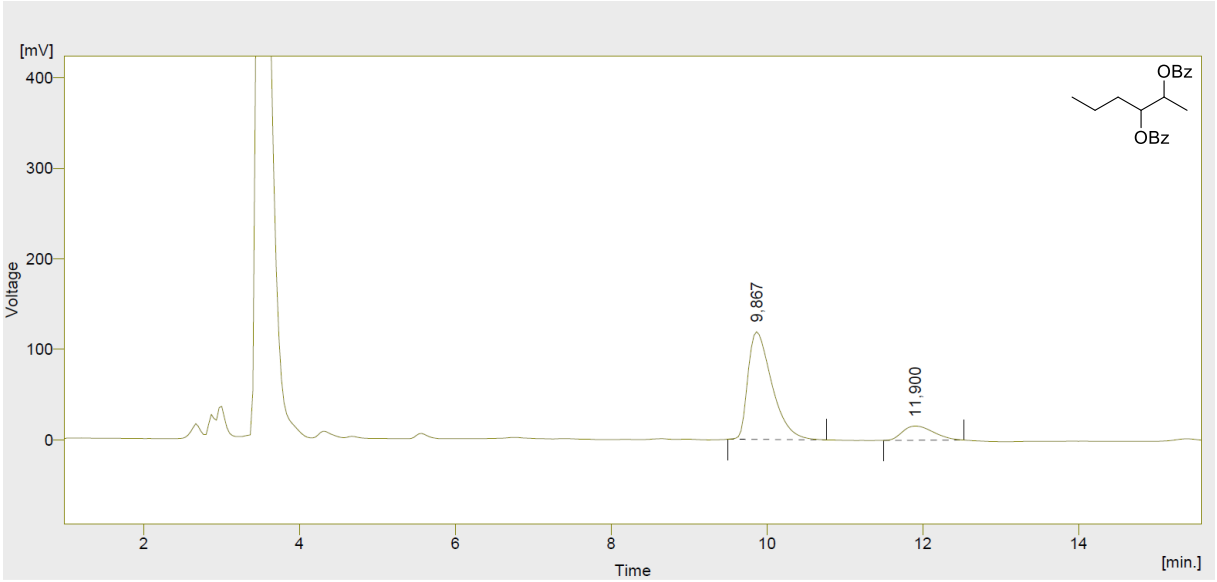
Figure SI-61. HPLC chromatogram of methyl *syn*-2,3-dihydroxy-3-phenylpropanoate on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (95:5) 1.0 mL min^{-1} at λ = 210 nm, a) product obtained under catalysis with material **M1** (Table 1, Entry 1 in the main text), b) racemate.



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
11,300	2235,052	105,975	100,0	100,0	0,37
Total	2235,052	105,975	100,0	100,0	

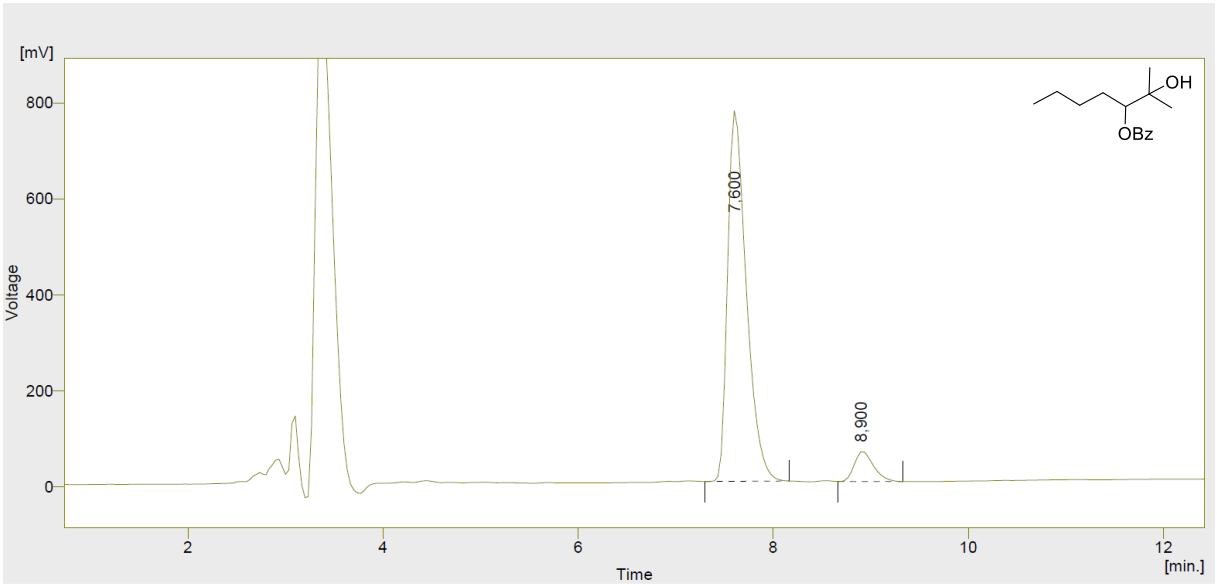
Figure SI-62. HPLC chromatograms of *syn*-1,2-diphenylethane-1,2-diol on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (9:1) 1.0 mL min^{-1} at λ = 210 nm, a) product obtained under catalysis with material **M1** (Table 1, Entry 2 in the main text), b) racemate.



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
9,867	2539,815	118,840	85,4	88,3	0,37
11,900	433,767	15,679	14,6	11,7	0,47
Total	2973,583	134,519	100,0	100,0	

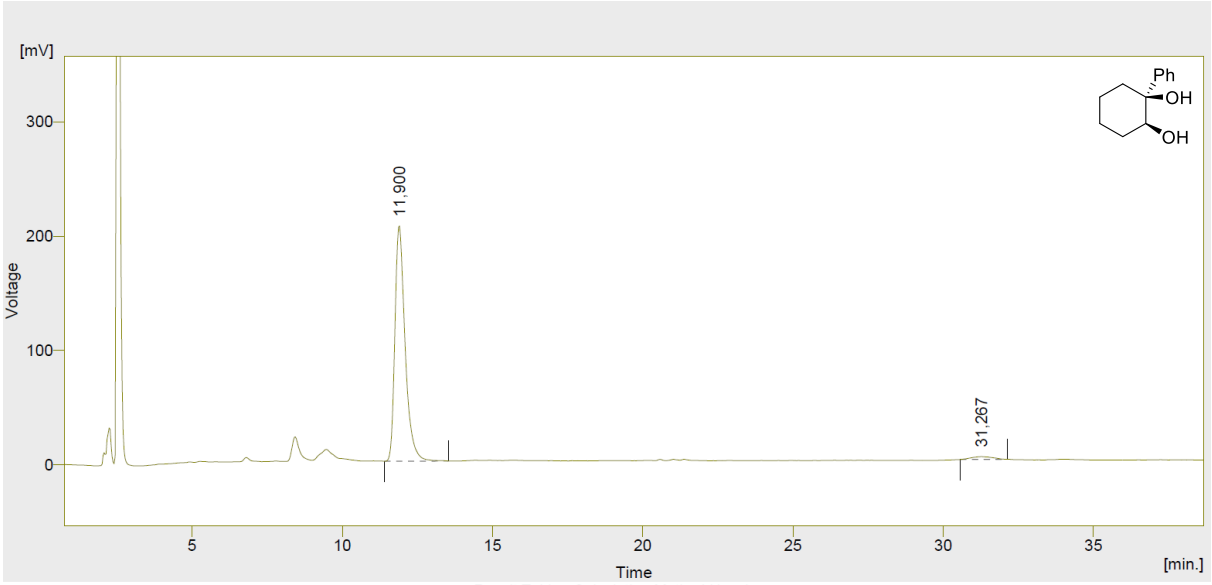
Figure SI-63. HPLC chromatogram of hexane-2,3-diyl dibenzoate on the YMC Chiral Cellulose-SB column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (99.8:0.2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 3 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
7,600	10278,044	771,334	92,3	92,6	0,23
8,900	851,678	61,897	7,7	7,4	0,23
Total	11129,722	833,231	100,0	100,0	

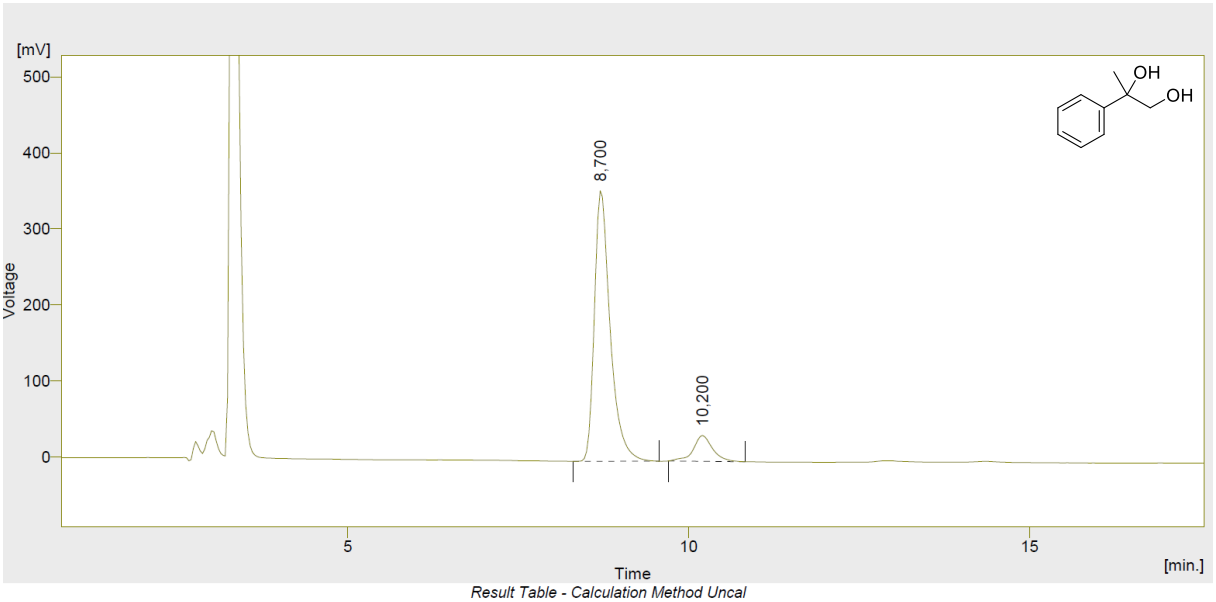
Figure SI-64. HPLC chromatograms of 2-hydroxy-2-methylheptan-3-yl benzoate on the YMC Chiral Cellulose-SB column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (98:2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 4 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
11,900	4844,622	205,624	97,6	98,8	0,37
31,267	119,438	2,453	2,4	1,2	0,87
Total	4964,059	208,077	100,0	100,0	

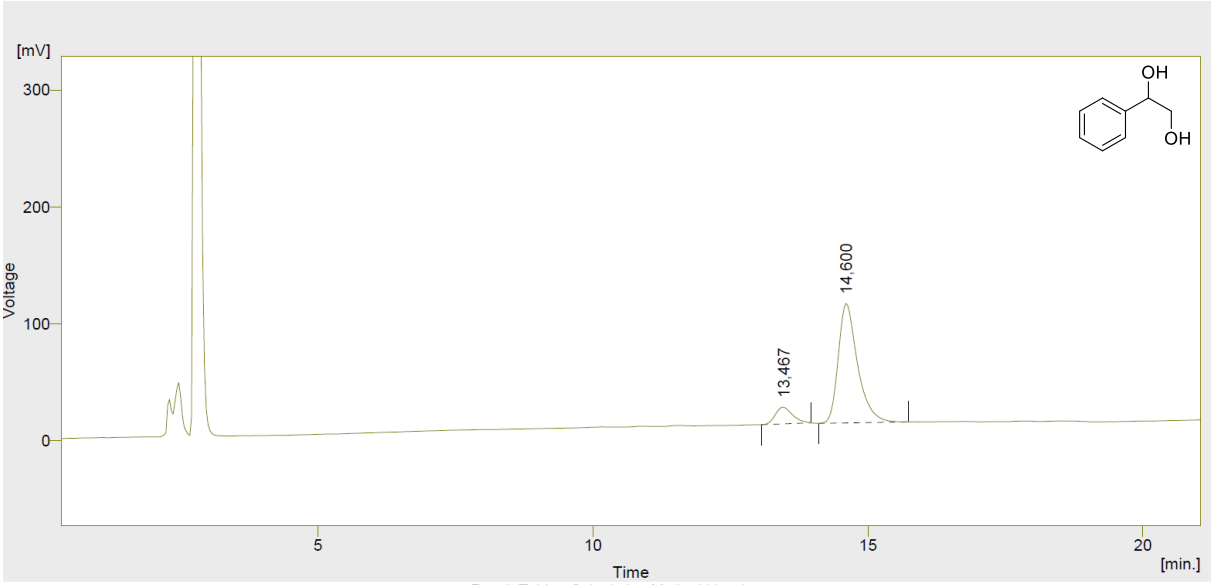
Figure SI-65. HPLC chromatograms of *cis*-1-phenylcyclohexane-1,2-diol-1,2-diol on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (95:5) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 5 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
8,700	5740,126	355,839	89,6	91,3	0,27
10,200	668,365	34,035	10,4	8,7	0,30
Total	6408,491	389,874	100,0	100,0	

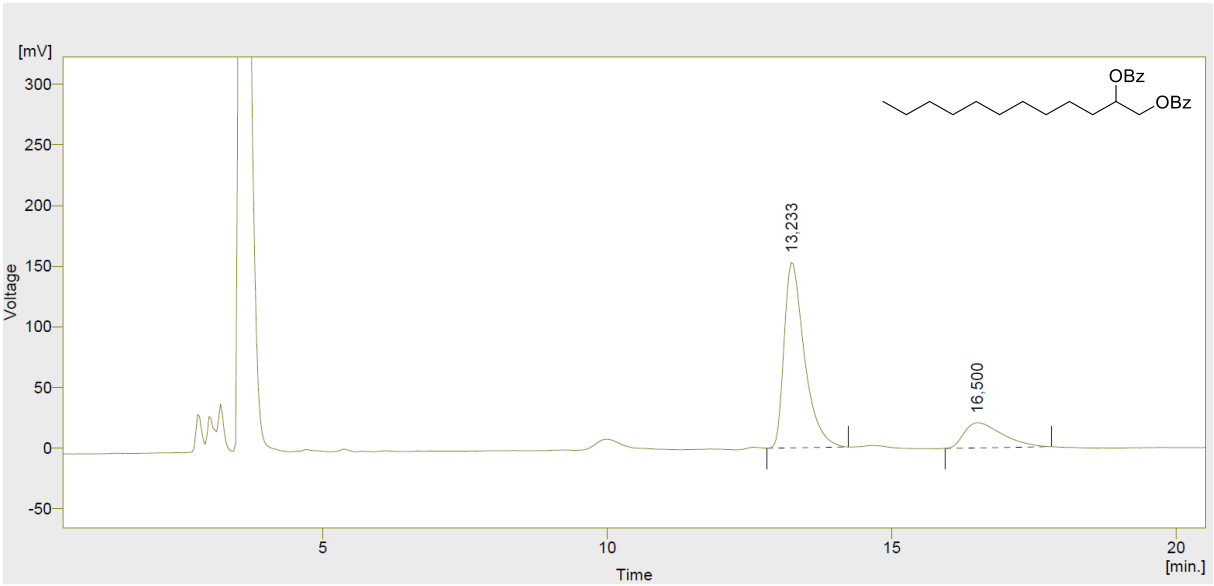
Figure SI-66. HPLC chromatograms of 2-phenylpropane-1,2-diol on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (92:8) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 6 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
13,467	307,039	14,272	11,0	12,2	0,37
14,600	2488,736	102,236	89,0	87,8	0,40
Total	2795,775	116,508	100,0	100,0	

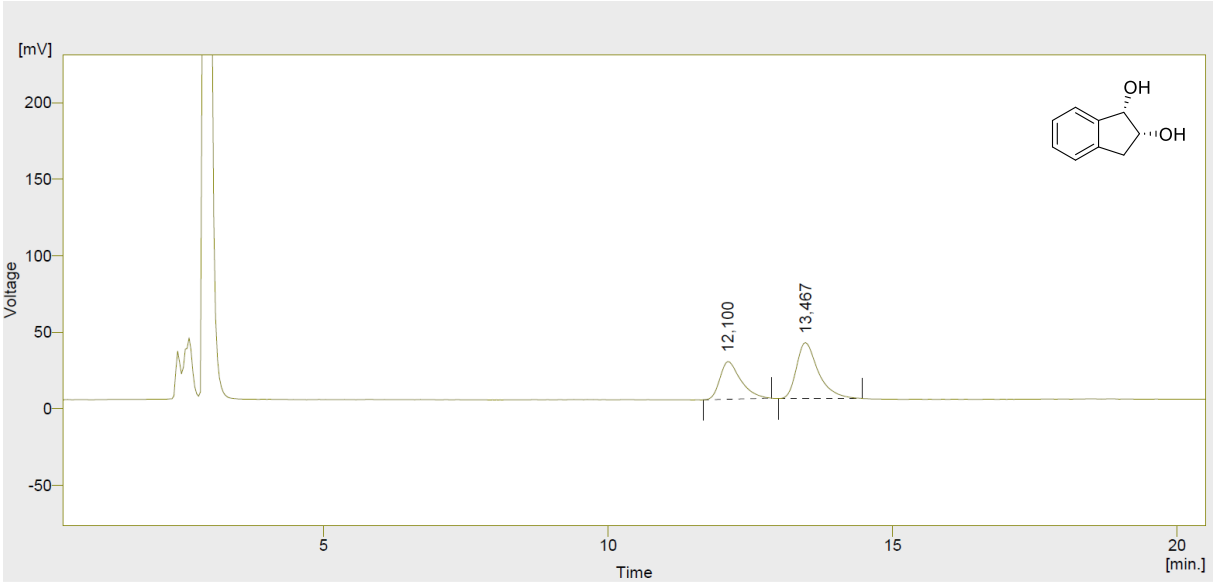
Figure SI-67. HPLC chromatograms of 1-phenylethane-1,2-diol on the YMC Chiral Cellulose-SB column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (95:5) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 7 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
13,233	3798,392	152,982	79,7	88,0	0,40
16,500	967,040	20,834	20,3	12,0	0,77
Total	4765,432	173,815	100,0	100,0	

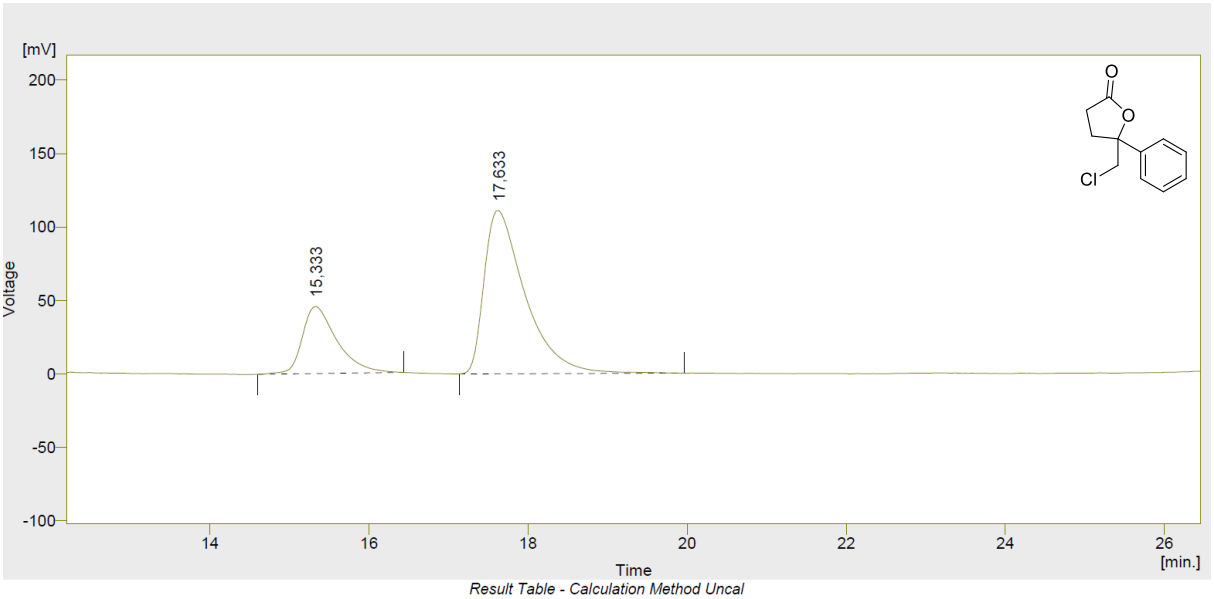
Figure SI-68. HPLC chromatograms of dodecane-1,2-diyl dibenzoate on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (99.8:0.2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 8 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
12,100	621,225	24,617	39,0	40,2	0,40
13,467	973,631	36,588	61,0	59,8	0,43
Total	1594,855	61,205	100,0	100,0	

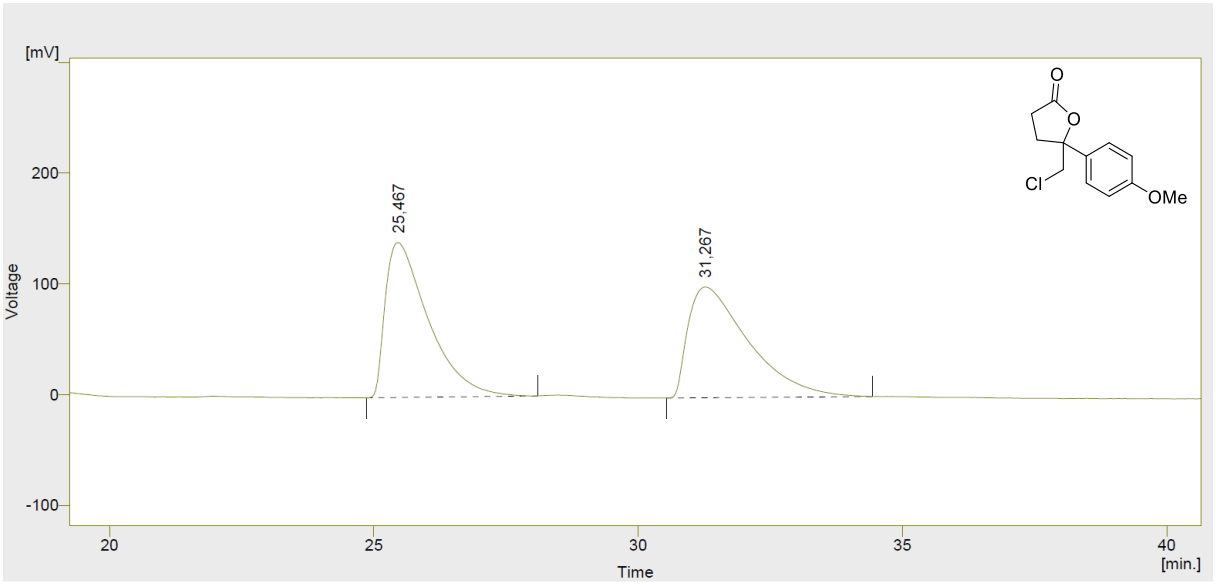
Figure SI-69. HPLC chromatograms of *cis*-2,3-dihydro-1*H*-indene-1,2-diol on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (95:5) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 1, Entry 9 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
15,333	1372,581	45,701	25,6	29,1	0,47
17,633	3982,875	111,129	74,4	70,9	0,57
Total	5355,455	156,830	100,0	100,0	

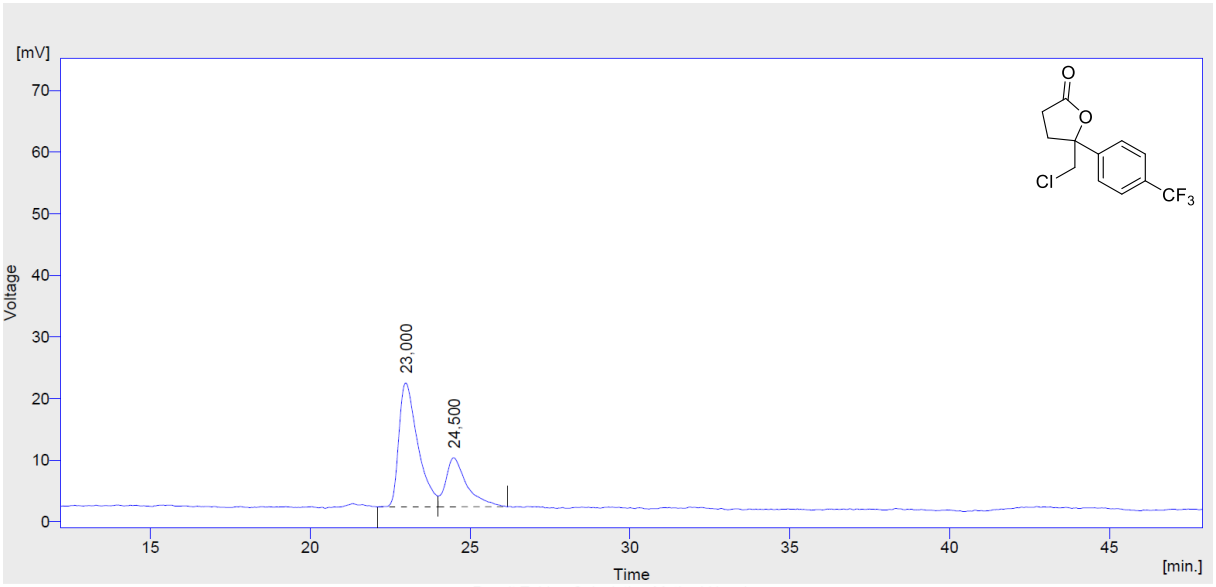
Figure SI-70. HPLC chromatogram of 5-(chloromethyl)-5-phenyldihydrofuran-2(3*H*)-one on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (98:2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material with material **M1** (Table 2, Entry 1 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
25,467	7932,026	139,966	50,0	58,3	0,90
31,267	7934,197	99,998	50,0	41,7	1,27
Total	15866,223	239,964	100,0	100,0	

Figure SI-71. HPLC chromatogram of 5-(chloromethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (98:2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 2, Entry 2 in the main text).



Result Table - Calculation Method Uncal

Reten. Time	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
23,000	828,817	20,104	69,2	71,6	0,67
24,500	368,286	7,959	30,8	28,4	0,67
Total	1197,102	28,062	100,0	100,0	

Figure SI-72. HPLC chromatograms of 5-(chloromethyl)-5-(4-(trifluoromethyl)phenyl)dihydrofuran-2(3*H*)-one on the YMC Chiral ART Amylose-SA column (250 x 4.6 mm; 5 µm) in heptane/*i*-PrOH (98:2) 1.0 mL min^{-1} at λ = 210 nm. Product obtained under catalysis with material **M1** (Table 2, Entry 3 in the main text).

9. Characterization of materials

In addition to SEM and ^{29}Si NMR shown in the main text, the materials were also characterized by TEM, ^{13}C NMR, FTIR, TGA and CD:

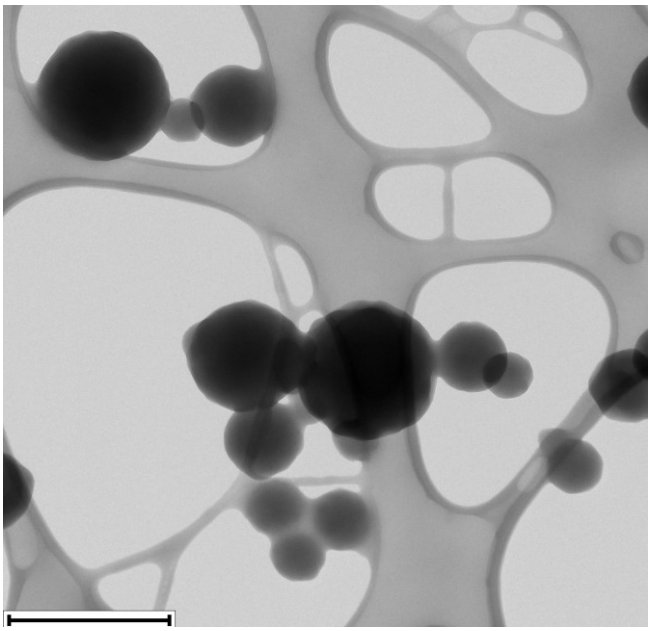


Figure SI-73. TEM image of material **M1**. Scale bar 500 nm.

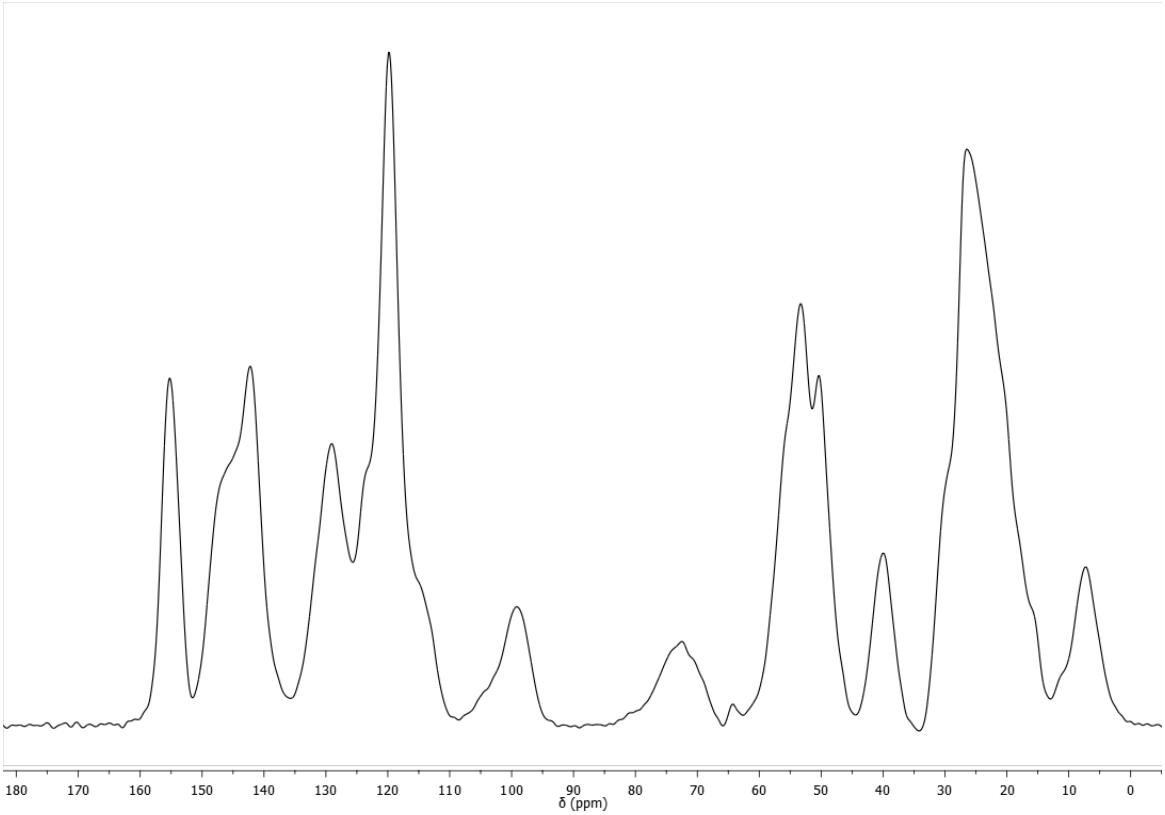


Figure SI-74. ^{13}C CP-MAS NMR spectrum of material **M1**.

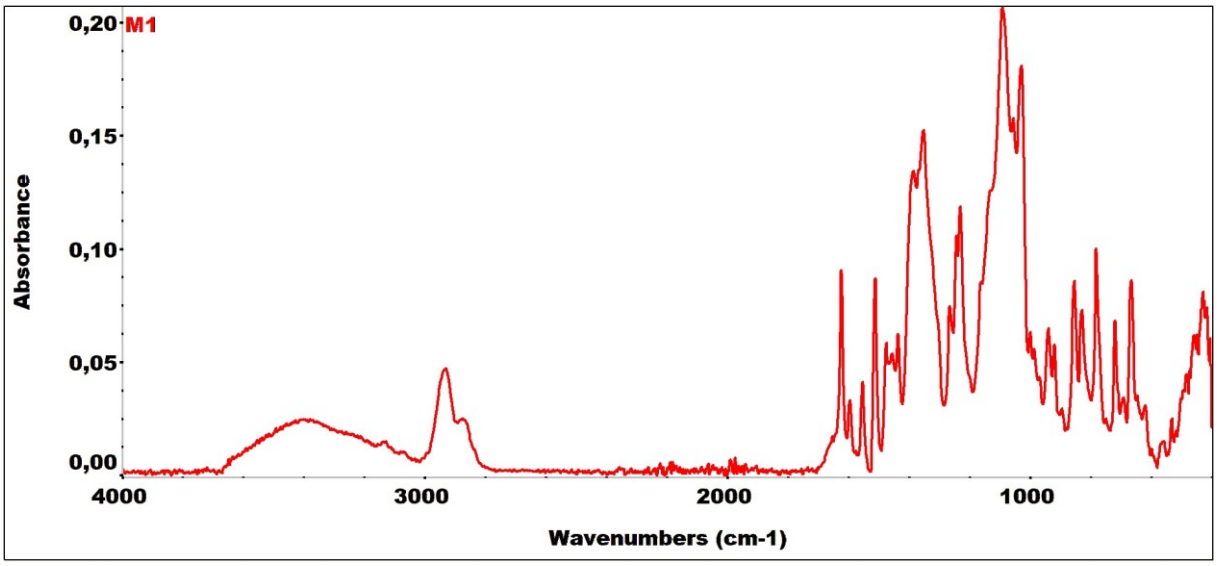


Figure SI-75. FTIR spectrum of material **M1**.

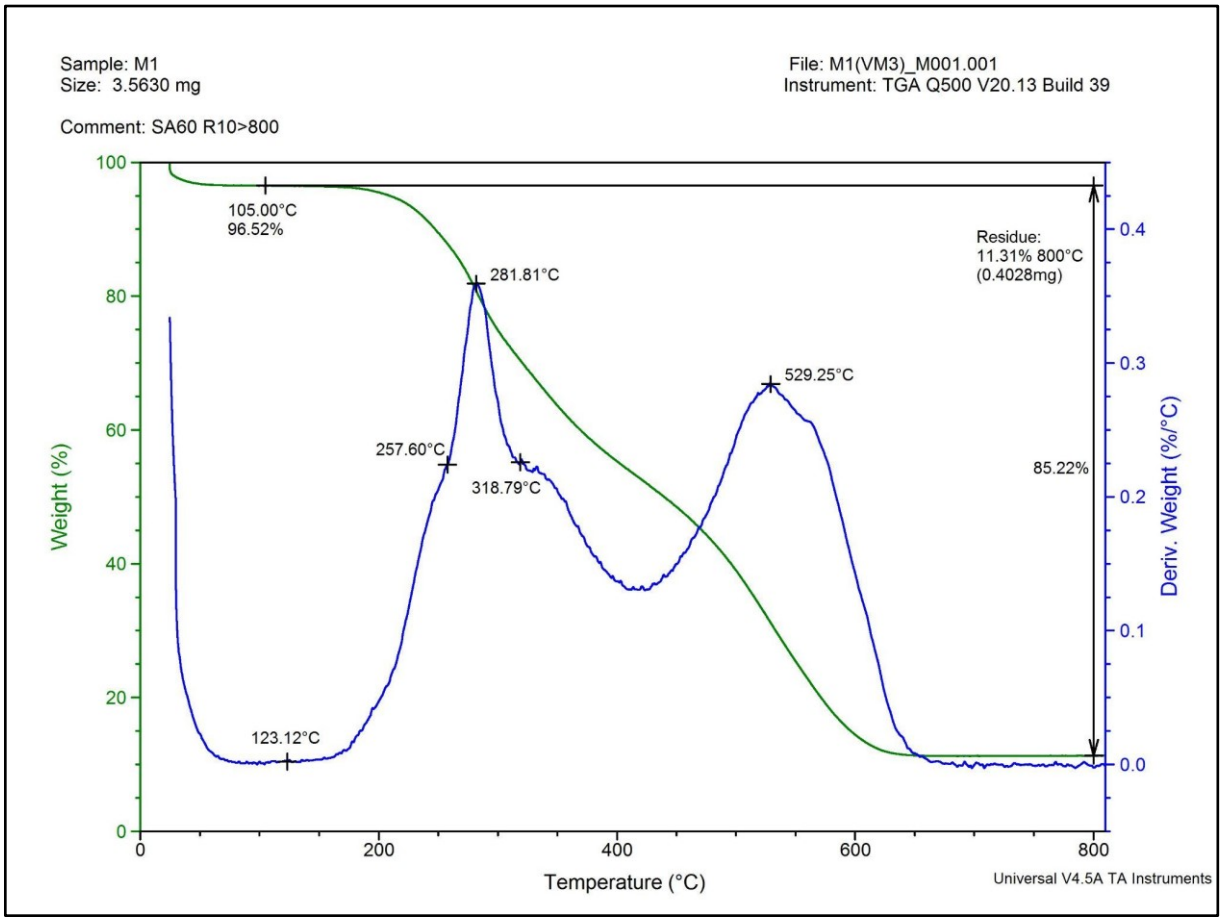


Figure SI-76. TGA analysis of material **M1**.

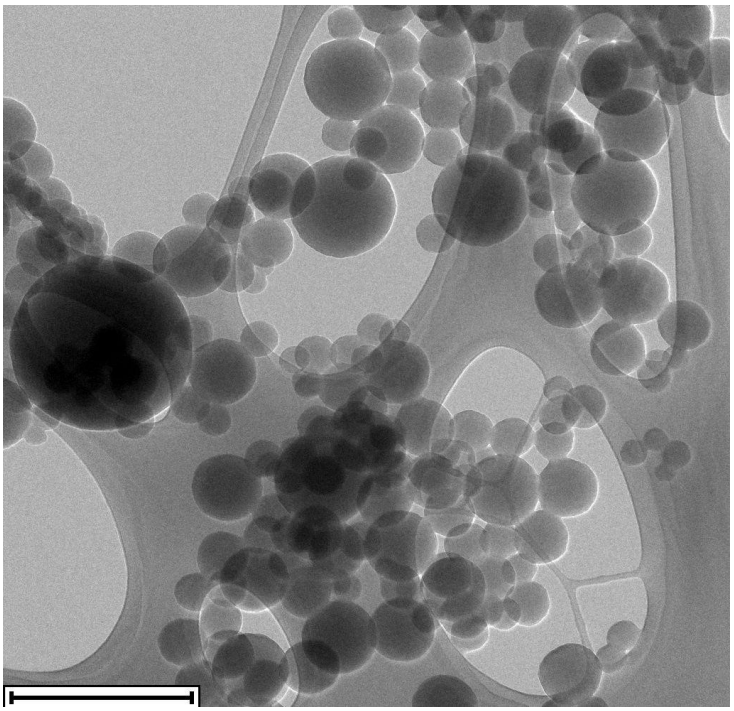


Figure SI-77. TEM image of material **M2**. Scale bar 500 nm.

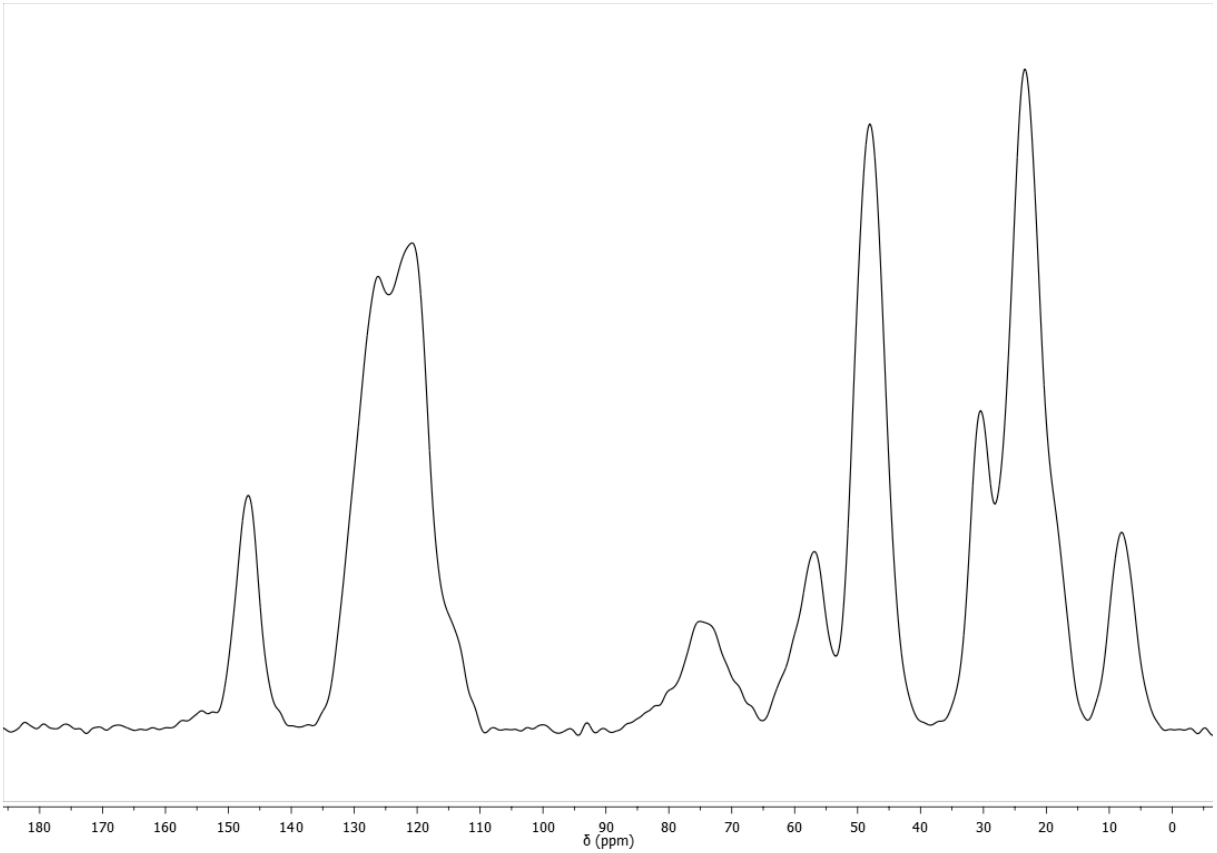


Figure SI-78. ^{13}C CP-MAS NMR spectrum of material **M2**.

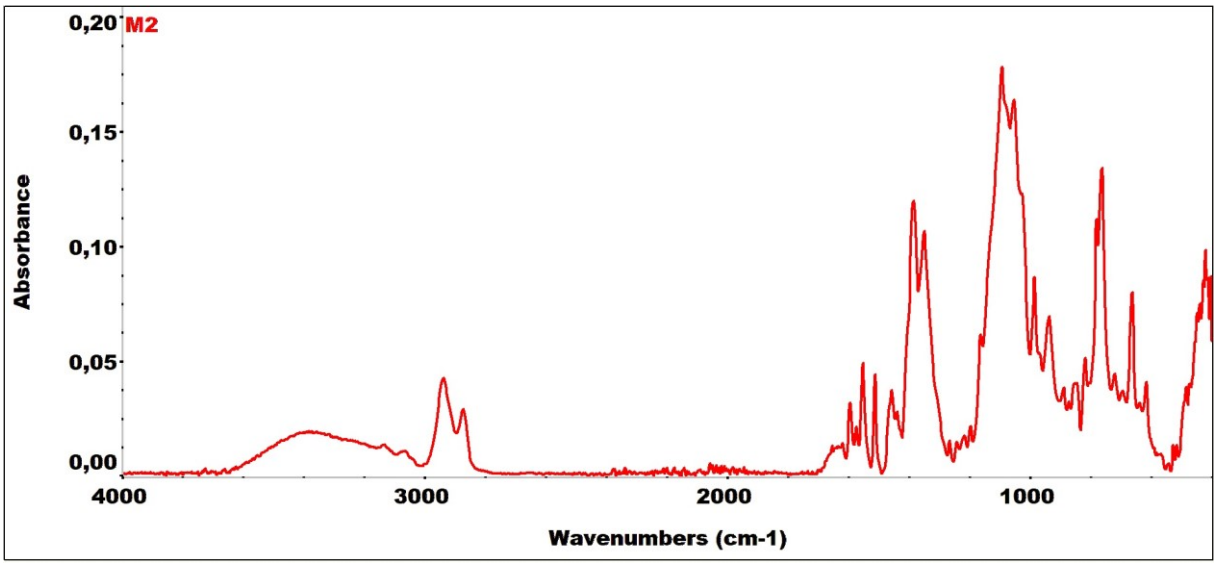


Figure SI-79. FTIR spectrum of material **M2**.

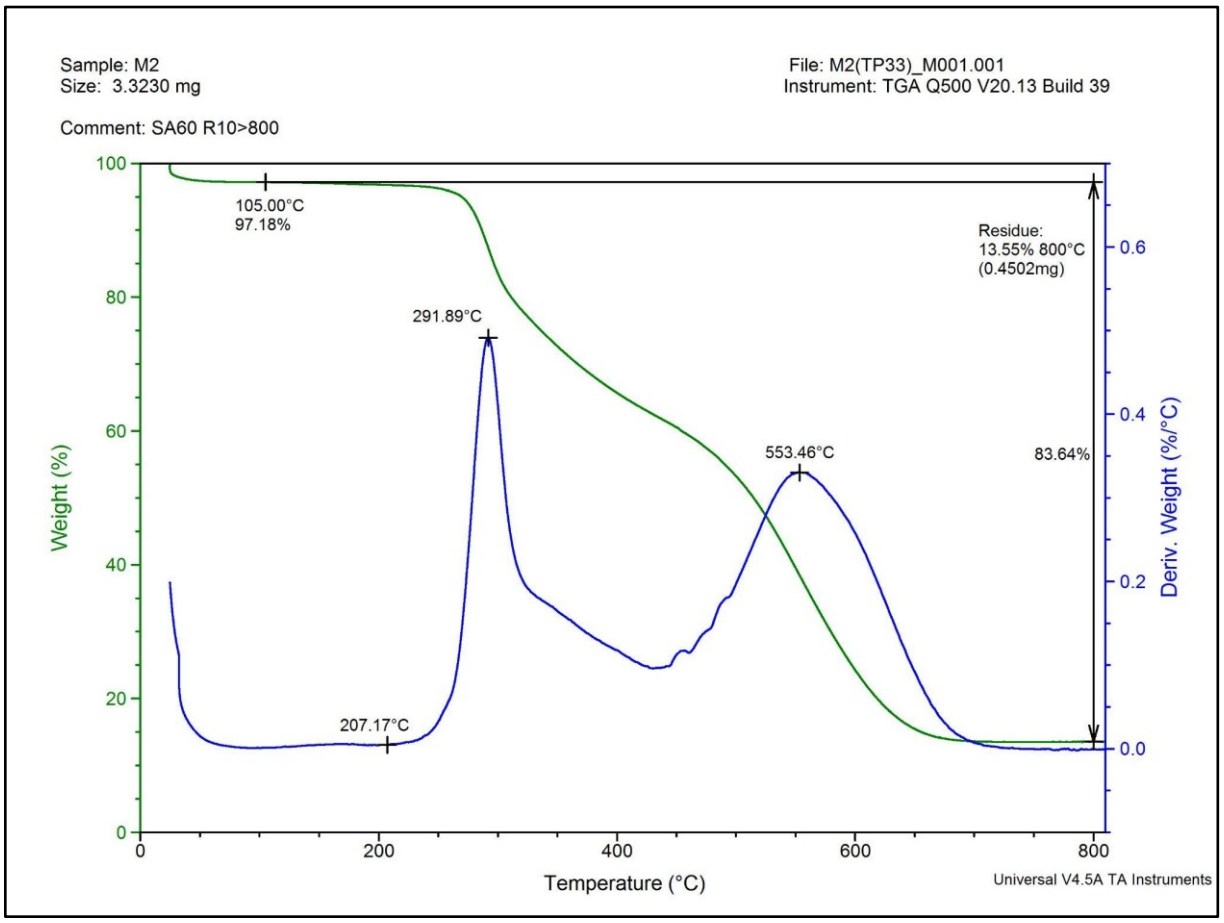


Figure SI-80. TGA analysis of material **M2**.

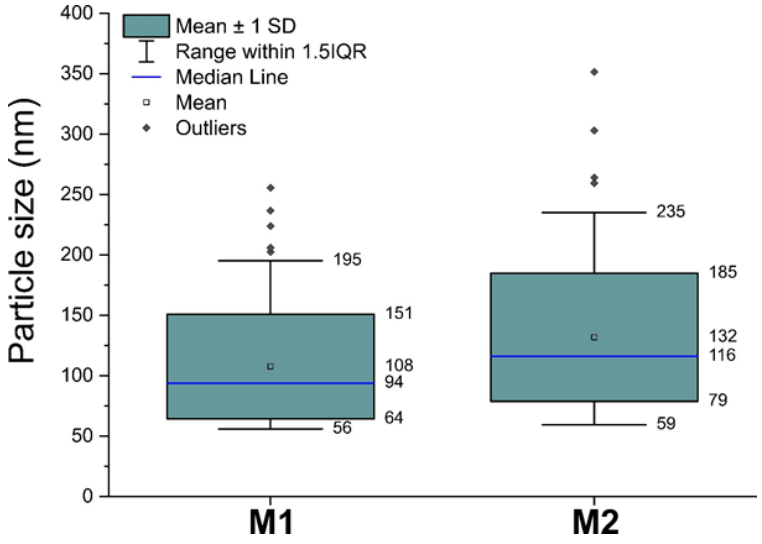


Figure SI-81. Statistical analysis of diameters of materials **M1** and **M2**.

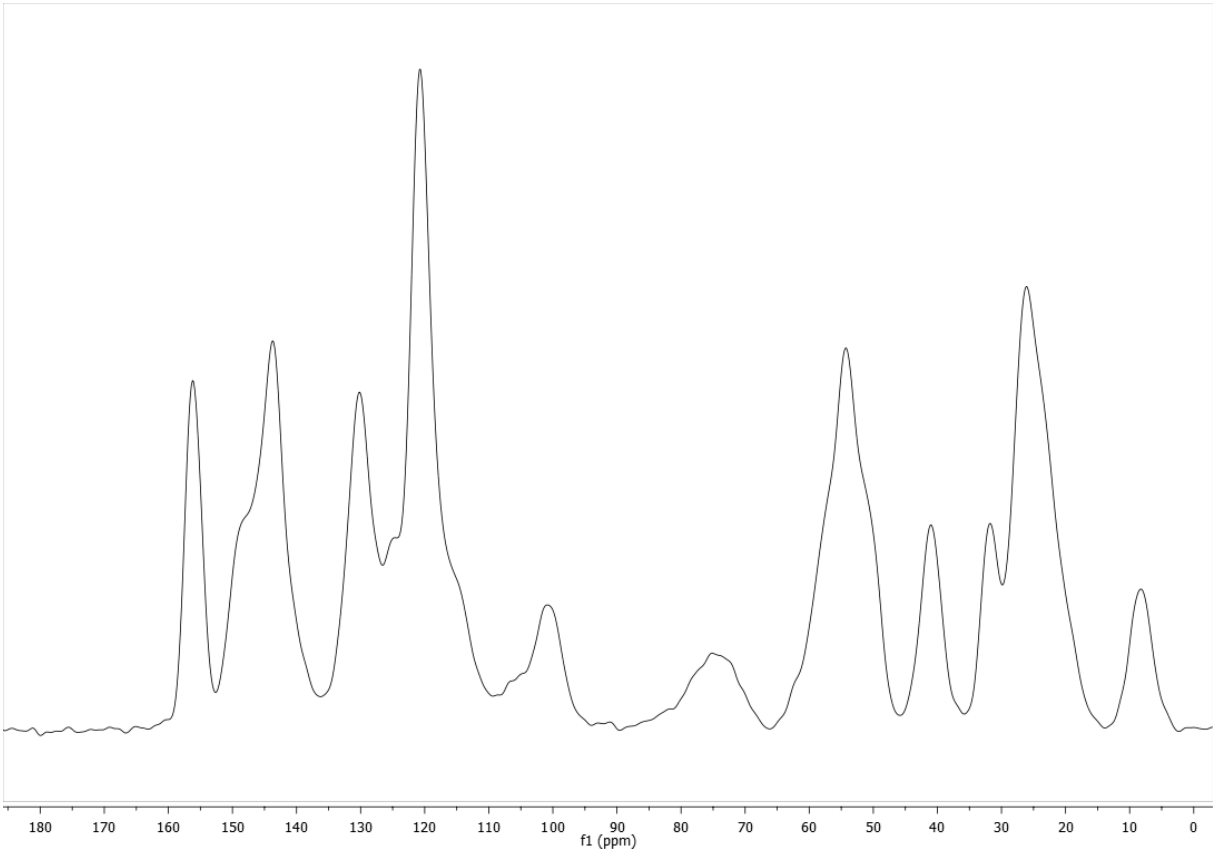


Figure SI-82. ^{13}C CP-MAS NMR spectrum of material **M3**.

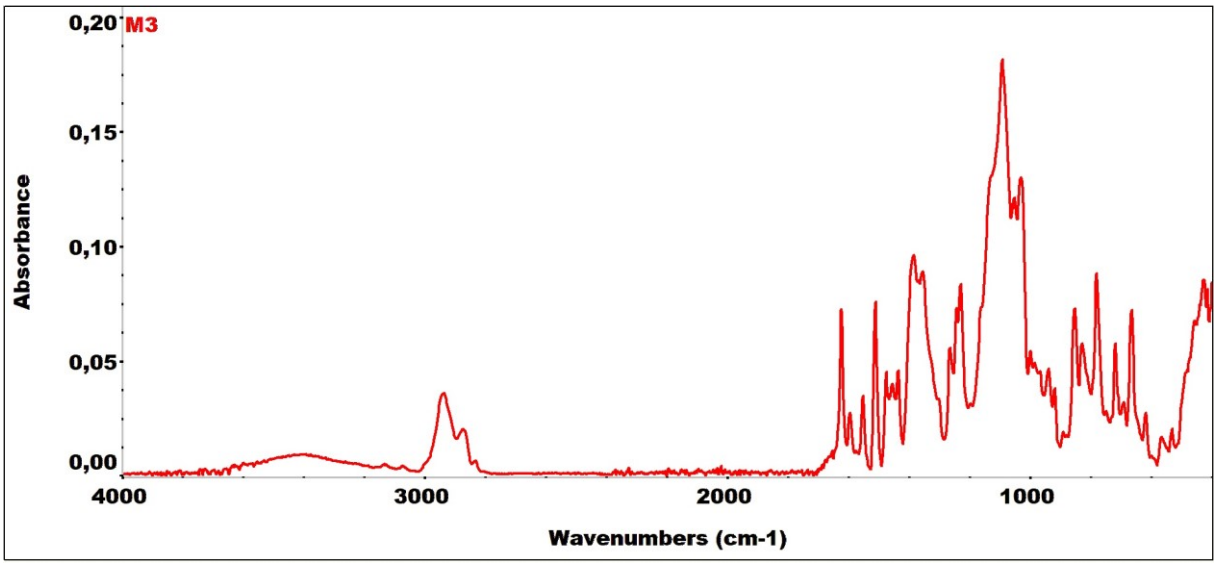


Figure SI-83. FTIR spectrum of material **M3**.

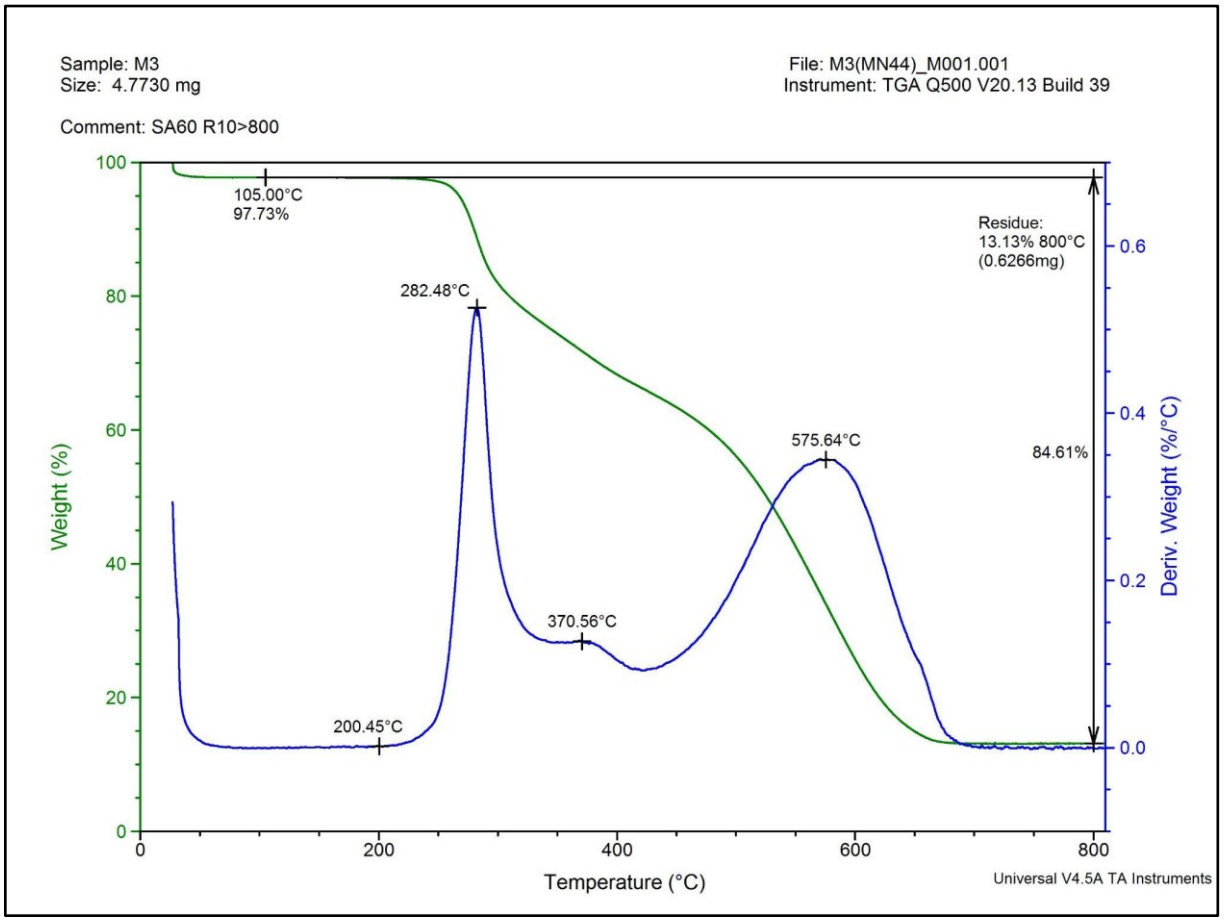


Figure SI-84. TGA analysis of material **M3**.

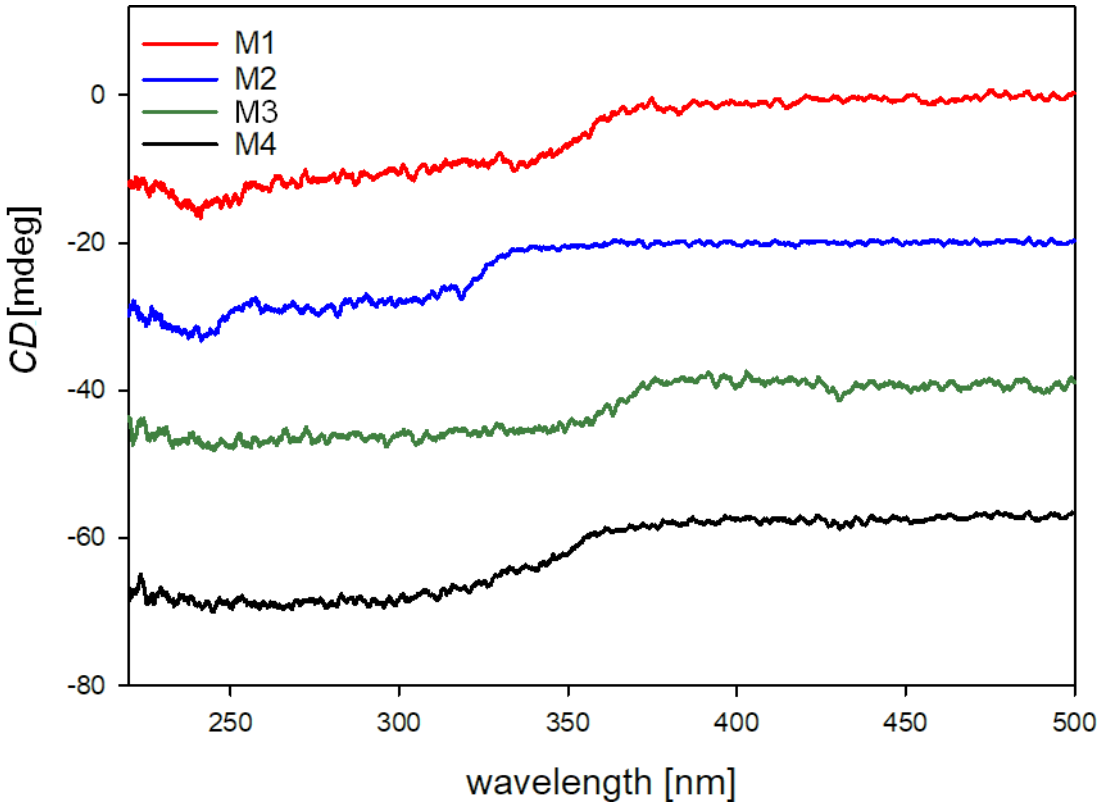


Figure SI-85. The experimental ECD spectra of **M1** (red), **M2** (blue), **M3** (green) and **M4** (black) in solid-state recorded in the spectral range of 220–500 nm (offset for clarity).

10. References

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