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SUPPORTING INFORMATION FOR:

Synthesis and properties of novel chiral imidazolium-based ionic liquids derived from carvone

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Electronic Supplementary Information

Experimental Section

General Procedures

^{1}H and ^{13}C NMR spectra were recorded at 400.1621 and 100.6314 MHz respectively using a Brüker DPX400 in $CDCl_3$ referenced to the solvent for both proton and carbon spectra. Chemical shifts (δ) were reported in parts per million (ppm), and referenced to residual deuterated solvent ($CDCl_3$: 7.26 ppm (1H), 77.0 ppm (^{13}C); D_2O: 4.79 ppm (1H); CD_3OD: 3.31 ppm (1H), 49.0 ppm (^{13}C)). Mass spectra were recorded on a FISON VG using 3-nitrobenzyl alcohol as matrix while ESI mass spectra were recorded on an APEX-Qe spectrometer. IR spectra were recorded on a MIDAC Prospect JASCO FT-IR and FT/I(R)-6100 type A spectrophotometers. All optical rotations α were measured on a JASCO P-2000 polarimeter. Elemental analyses (CHNS) were performed with a Fisons EA 1108 Carlo Erba. All chemicals used in the synthesis were purchased from ACROS or ALDRICH and were used without any further pretreatment or pre-purification, except methanol and dichloromethane which were dried with a suitable drying agents and distilled under argon prior to use. Reactions progress was monitored by TLC on 25 Aluminium sheets (TLC Silica gel 60 F254) from Merck KGaA. The chromatograms were developed in mixtures of hexane/ethyl acetate or ethyl acetate/methanol in different proportions and visualized by UV lamp (254 nm) using standard visualizing agents. Column chromatographies were performed using silica gel 60 (particle size: 0.063-0.200 mm). In order to prove the absence of chloride or bromide anions as impurities, the obtained ILs were washed several times with 30 mL of distilled water until no Cl^- or Br^- was detected as indicated by a solution of AgNO3/HNO3.

General procedure for the synthesis of (1R,5R)-2-methyl-5-(isopropenyl)-2-cyclohexen-1-ol (R-2) and (1S,5S)-2-methyl-5-(isopropenyl)-2-cyclohexen-1-ol (S-2).

A solution of (R) or (S)-carvone and $CeCl_3 \cdot 7\ H_2O$ (1.2 equiv) in dry methanol (30 mL) was introduced into a round flask under inert atmosphere. The mixture was cooled to -78 °C with a dry ice–acetone bath and $NaBH_4$ (1.2 equiv) was then added. After stirring for 10 min, the reaction mixture was allowed to gradually warm up to rt and stirred for 1 h. The reaction progress was monitored by TLC (hexane/ethyl acetate 7/3). The reaction was worked up by adding water (5 mL) and extracted with diethyl ether (2 x 10 mL). The combined organic extracts were washed with brine (2 x 10 mL) and dried with anhyd Na_2SO_4. The solvent was removed on the rotary evaporator and the residue was further purified by column chromatography to afford the desired products **R-2** and **S-2** (97% and 96%, respectively) as colourless oils.

R-2 colourless oil (2.9 g, 97%); R_f 0.6 (Hexane/ethyl acetate 7/3), $[\alpha]^{18}_D$ -34 (*c* 4, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53 (s, 1H), 4.77 (s, 2H), 4.22 (m, 1H), 2.3 (t, *J* = 11.6 Hz, 1H), 2.19 (m, 1H), 2.08 (m, 1H), 2.01 (d, *J* = 12.8 Hz, 1H), 1.79 (s, 3H), 1.77 (s, 3H), 1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 136.1, 123.8, 109.1, 70.9, 40.4, 37.9, 31, 20.6, 18.9; IR (KBr) ν (cm^{-1}):3324.68, 3079.76, 2967.91, 2928.98, 2917.77, 2886.92, 2856.06, 1644.98, 1448.28, 1375, 1324.86, 1286.29, 1079.94, 1035.59, 1000.87, 914.09, 889.02, 809.95; ESI-HRMS *m/z* [M^+] calcd for $C_{10}H_{16}NaO$ 175.1934, found 175.1953.

S-2 colourless oil (2.8 g, 96%); R_f 0.6 (Hexane/ethyl acetate 7/3), $[\alpha]^{18}_D$ 31 (*c* 12.7, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (s, 1H), 4.75 (s, 2H), 4.2 (m, 1H), 2.28 (t, *J* = 10.3 Hz, 1H), 2.19 (m, 1H), 2.08 (m, 1H), 2.01 (d, *J* = 12.8 Hz, 1H),1.79 (s, 3H), 1.77 (s, 3H), 1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 136.1, 123.8, 109.1, 70.9, 40.4, 37.9, 31, 20.6, 18.9; IR (KBr) ν (cm^{-1}): 3338.18, 3079.76, 2967.91, 2938.98, 2915.84, 2886.92, 2856.06, 1644.98, 1448.28, 1375, 1324.86, 1286.29, 1079.94, 1035.59, 1000.87, 914.09, 889.02, 809.95.

General procedure for the synthesis of (1R,2R,4S,6S)-1-methyl-4-(isopropenyl)-7-oxabicyclo[4.1.0]heptan-2-ol (R-3) and (1S,2S,4R,6R)-1-methyl-4-(isopropenyl)-7-oxabicyclo[4.1.0]heptan-2-ol (S-3).

A solution of **R-2** or **S-2** in dry dichloromethane (30 mL) was introduced into a round flask under inert atmosphere. The mixture was cooled to -78 °C with a dry ice–acetone bath and *m*-CPBA(1 equiv) was then added. After stirring for 10 min, the reaction mixture was allowed to gradually warm up to -36 °C and stirred for 20 h. The reaction progress was monitored by TLC using hexane/ethyl acetate (7/3) as eluent. The reaction was worked up by adding sodium bicarbonate (10 mL of a saturated solution) and extracted with dichloromethane (2 x 10 mL). The combined organic extracts were washed with brine (2 x 10 mL) and dried with anhyd Na_2SO_4. The solvent was removed on the rotary evaporator and the residue was further purified by column chromatography to afford the desired products **R-3** and **S-3** (86% and 82%, respectively) as colourless liquids.

R-3 colourless liquid (2.8 g, 86%); R_f 0.3 (Hexane/ethyl acetate 7/3), $[\alpha]^{19}_D$ -21 (*c* 1.2, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (d, *J* = 5.6, 2H), 3.89 (dt, J_1 = 10.2, J_2 = 5.5 Hz, 1H), 3.19 (d, *J* = 4.9 Hz, 1H), 2.03 (m, 2H), 1.79 (m, 1H), 1.68 (s, 3H), 1.48 (s, 3H), 1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 109.7, 72.2, 62.3,60.3, 40.4, 33.9, 29.1, 20.1, 19.1; IR (KBr) ν (cm^{-1}): 3432.67, 3079.76, 2973.7, 2937.06, 2883.06, 1644.98,1442.49, 1376.93, 1295.93, 1243.86, 1085.73, 1051.01, 1006.66, 890.95, 846.59, 688.46; ESI-HRMS *m/z* [M^+] calcd for $C_{10}H_{16}NaO_2$ 191.1425, found 191.1506.

S-3 colourless liquid (2.3 g, 82%); R_f 0.3 (Hexane/ethyl acetate 7/3), $[\alpha]^{20}_D$ 24 (*c* 8.2, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.7 (d, *J* = 5.4 Hz, 2H), 3.86 (dt, J_1 = 10.2 Hz, J_2 = 5.5 Hz, 1H), 3.17 (d, *J* = 4.9 Hz, 1H), 1.99 (m, 2H), 1.78 (m, 1H), 1.69 (s, 3H), 1.46 (s, 3H), 1.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 109.7, 72.2, 62.3, 60.3, 40.4, 34, 29.1, 20.1, 19.1; IR (KBr) ν (cm^{-1}): 3426.89, 3077.83, 2971.77, 2935.13, 1644.98, 1442.49,1376.93, 1297.86, 1257.36, 1232.29, 1168.65, 1085.73, 1052.94, 1006.66, 958.44,889.02, 846.59, 775.24, 688.46, 630.61, 592.03, 541.89, 522.61, 497.54, 437.72.

General procedure for the synthesis of (1S,2R,4R,6R)-6-(imidazol-1-yl)-1-methyl-4-isopropenylcyclohexane-1,2-diol (R-4) and (1R,2S,4S,6S)-6-(imidazol-1-yl)-1-methyl-4-isopropenylcyclohexane-1,2-diol (S-4).

R-3 or S-3 and imidazole (0.5 equiv) were stirred at 60 °C. The reaction progress was monitored by TLC using ethyl acetate as eluent. After 24 h, the formed viscous reaction mixture was dissolved in dichloromethane and purified by column chromatography to obtain the desired products **R-4** and **S-4** (97% and 99%, respectively) as white solids.

R-4 White solid (1.2 g, 97%); mp: 60.4-61.0ºC*;* R_f 0 (ethyl acetate), $[\alpha]^{20}_D$ -50 (*c* 3.3, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.06 (s, 1H), 7.02 (s, 1H), 4.83 (d, *J* = 6 Hz, 2H), 4.43 (t, *J* = 5.2 Hz, 1H), 3.91 (dd, J_1 = 8.4 Hz, J_2 = 4.7 Hz, 1H), 2.53 (s, 1H), 2.29 (m, 1H), 1.96 (m, 3H), 1.79 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 137.7, 129.1, 119.2, 109.9, 73.1, 73, 60.9, 38.5, 32.9, 31.7, 21.8, 21.3; IR (KBr) ν (cm^{-1}): 3363.25, 3116.4, 2971.77, 2944.77, 2883.06, 1469.49, 1450.21, 1114.65, 1085.73, 1058.73, 755.95, 665.32; EI-HRMS *m/z* [M^+] calcd for $C_{13}H_{21}N_2O_2$ 237.15975, found 237.15885.

S-4 White solid (1.4 g, 99%); mp: 60.1-60.8ºC*;* R_f 0 (ethyl acetate), $[\alpha]^{19}_D$ 42 (*c* 1, CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.07 (s, 1H), 7.02 (s, 1H), 4.83 (d, *J* = 6.2 Hz, 2H), 4.4

(t, *J* = 5.3 Hz, 1H), 3.9 (m, 1H), 2.53 (s, 1H), 2.29 (m, 1H), 1.95 (m, 3H), 1.79 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 137.7, 128.9, 119.2, 109.9, 73, 72.9, 60.8, 38.4, 32.7, 31.6, 21.7, 21.3; IR (KBr) ν (cm^{-1}): 3363.25, 3116.4, 2971.77, 2944.77, 2883.06, 1496.49, 1450.21, 1230.36, 1114.65, 1085.73, 1058.73, 892.88, 755.95, 665.32.

General procedure for the synthesis of 3-butyl-1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium chloride (R-5a) and 3-butyl-1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium chloride (S-5a).

To **R-4** or **S-4**, 1-chlorobutane (30 equiv) was added. The resulting mixture was stirred at 100 °C for 5 d. The reaction progress was monitored by TLC (ethyl acetate) . The reaction crude was washed with diethyl ether and dried under high vacuum to afford the desired products **R-5a** and **S-5a** (66% and 90%, respectively) as white solids.

R-5a White solid (1.2 g, 66%); mp: 215.1-215.5ºC; $[\alpha]^{21}_D$ -43 (*c* 4.7, CH_3OH); elem. anal. found: C, 62.38; H, 9.01; N, 8.60; calcd for $C_{17}H_{29}ClN_2O_2$: C, 62.08; H, 8.89; N, 8.52%; ^{1}H NMR (400 MHz, D_2O): δ 8.82 (s, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 4.85 (s, 2H), 4.68 (dd, J_1 = 7.8 Hz, J_2 = 4.5 Hz, 1H), 4.23 (t, *J* = 7.1 Hz, 2H), 3.89 (c, *J* = 3.6 Hz, 1H), 2.62 (m, 1H), 2.35 (m, 1H), 2.15 (m, 1H), 2.03 (m, 1H), 1.97 (m, 1H), 1.86 (td, J_1= 14.8 Hz, J_2 = 7.2 Hz, 2H), 1.8 (s, 3H), 1.3 (m, 2H), 1.06 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 148.3, 122.5, 121.9, 108.6, 72.8, 72.7, 62.7, 49.3, 37, 31.1, 31, 29.5, 20.7, 19.3, 18.6, 12.5; IR (KBr) ν (cm^{-1}): 3322.75, 2950.55, 1639.2, 1558.2, 1446.35, 1388.5, 1243.86, 1141.65, 1066.44, 894.81, 750.17, 655.67, 561.18; EI-HRMS *m/z* [M^+] calcd for $C_{34}H_{58}ClN_4O_4$ 621.41411, found 621.41334. Calcd for $C_{17}H_{29}N_2O_2$ 293.22235, found 293.22185.

S-5a White solid (1.6 g, 90%); mp: 214.8-215.3ºC; $[\alpha]^{20}_D$ 42 (*c* 4.5, CH_3OH); elem. anal. found: C, 62.40; H, 9.07; N, 8.64; calcd for $C_{17}H_{29}ClN_2O_2$: C, 62.08; H, 8.89; N, 8.52%; ^{1}H NMR (400 MHz, D_2O): δ 8.9 (s, 1H), 7.6 (t, *J* = 1.7 Hz, 1H), 7.51 (t, *J* = 1.6 Hz, 1H), 4.76 (d, *J* = 5 Hz, 2H), 4.61 (dd, J_1 = 7.7 Hz, J_2 = 4.6 Hz, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 3.82 (q, *J* = 3.7 Hz, 1H), 2.54 (m, 1H), 2.27 (m, 1H), 2.07 (m, 1H), 1.95 (m, 1H), 1.91 (m, 1H), 1.79 (dt, J_1= 14.7 Hz, J_2 = 7.1 Hz, 2H), 1.72 (s, 3H), 1.23 (m, 2H), 1 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H);^{13}C NMR (100 MHz, D_2O): δ 148.5, 135.6, 122.7, 122.2, 108.8, 72.8, 72.8, 63, 49.5, 37.2, 31.4, 31.2, 29.7, 20.9, 19.6, 18.8, 12.7; IR (KBr) ν (cm^{-1}): 3251.4, 3131.83, 3081.69, 2960.2, 2953.13, 2871.49, 1644.98, 1558.2, 1525.42, 1455.99, 1373.07, 1351.86, 1326.79, 1195.65, 1160.94, 1130.08, 1058.73, 939.16, 890.95, 757.88. 659.53, 615.18.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium chloride (R-5b) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium chloride (S-5b).

To **R-4** or **S-4**, 1-chlorohexane (20 equiv) was added. The resulting mixture was stirred at 80 °C for 3 d. The reaction progress was monitored by TLC using ethyl acetate as eluent. The reaction crude was washed with ethyl acetate and further purified by column chromatography using gradient elution (starting with ethyl acetate to ethyl acetate/methanol 9/1) to afford the desired products **R-5b** and **S-5b** (61% and 45%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-5b liquid (1.2 g, 97%); $[\alpha]^{20}_D$ -27 (*c* 2.8, CH_3OH); elem. anal. found: C, 64.08; H, 9.33; N, 8.08; calcd for $C_{19}H_{33}ClN_2O_2$: C, 63.93; H, 9.32; N, 7.85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.58 (s, 1H), 7.4 (s, 1H), 5.03 (s, 1H), 4.79 (s, 2H), 4.37 (t, *J* = 7.4 Hz, 2H), 3.94 (m, 1H), 2.56

(m, 1H), 2.4 (m, 1H), 2.2 (m, 2H), 1.92 (m, 3H), 1.84 (s, 3H), 1.32 (s, 6H), 1.16 (s, 3H), 0.87 (t, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 137.2, 122.2, 121.3, 109.1, 73.7, 73.3, 62.2, 50.1, 37.4, 30.2, 30.1, 29, 28.9, 26.2, 22.5, 22.1, 20.1, 14; IR (KBr) ν (cm^{-1}): 3363.25, 3116.4, 2971.77, 2944.77, 2883.06, 1496.49, 1450.21, 1230.36, 1114.65, 1085.73, 1058.73, 892.88, 755.95, 665.32; EI-HRMS *m/z* [M^+] calcd for $C_{38}H_{66}ClN_4O_4$ 677.47671, found 677.47448. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25310.

S-5b liquid (1 g, 45%); $[\alpha]^{22}_D$ 28 (*c* 2.9, CH_3OH); elem. anal. found: C, 64.18; H, 9.35; N, 8.05; calcd for $C_{19}H_{33}ClN_2O_2$: C, 63.93; H, 9.32; N, 7.85%; ^{1}H NMR (400 MHz, D_2O): δ 8.88 (s, 1H), 7.61 (s, 1H), 7.51 (s, 1H), 4.8 (d, *J* = 9.7 Hz, 2H), 4.63 (s, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.84 (m, 1H), 2.56 (m, 1H), 2.3 (m, 1H), 2.09 (m, 1H), 1.98 (m, 2H), 1.83 (m, 2H), 1.75 (s, 3H), 1.23 (s, 6H), 1.02 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 135.6, 122.7, 122.1, 108.8, 72.9, 72.8, 63, 49.7, 37.2, 31.3, 30.2, 29.7, 29, 24.9, 21.7, 20.8, 19.6, 13.1; IR (KBr) ν (cm^{-1}): 3222.47, 3129.9, 3079.76, 3039.26, 2926.13, 2933.2, 2861.84, 1452.14, 1376.93, 1159.01, 1062.59, 890.95, 755.95.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium chloride (R-5c) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium chloride (S-5c).

To **R-4** or **S-4**, 1-chlorooctane (20 equiv) was added. The resulting mixture was stirred at 100 °C for 4 d. The reaction progress was monitored by TLC using ethyl acetate as eluent. The reaction crude was washed with ethyl acetate and further purified by column chromatography using gradient elution (starting with ethyl acetate to ethyl acetate/methanol 9/1) to afford the desired products **R-5c** and **S-5c** (76% and 62%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-5c liquid (0.6 g, 76%); $[\alpha]^{22}_D$ -28 (*c* 3.5, CH_3OH); elem. anal. found: C, 65.80; H, 9.93; N, 7.50; calcd for $C_{21}H_{37}ClN_2O_2$: C, 65.52; H, 9.69; N, 7.28%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.62 (s, 1H), 7.45 (s, 1H), 4.95 (d, *J* = 4.9 Hz, 1H), 4.74 (s, 2H), 4.34 (t, *J* = 7.2 Hz, 2H), 3.89 (m, 1H), 2.53 (m, 1H), 2.35 (m, 1H), 2.14 (m, 2H), 1.86 (m, 3H), 1.78 (s, 3H), 1.21 (m, 10H), 1.06 (s, 3H), 0.83 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 137.2, 122.4, 121.3, 109, 73.7, 73.3, 62.2, 50, 37.4, 31.6, 31.6, 30.2, 30.1, 29, 28.9, 26.2, 22.5, 22.1, 20.1, 14; IR (KBr) ν (cm^{-1}): 3226.33, 3126.04, 3077.83, 3039.26, 2958.27, 2927.41, 2857.99, 1644.98, 1567.84, 1544.7, 1452.14, 1376.93, 1322.93, 1261.22, 1201.43, 1159.01, 1128.15, 8892, 757.88; EI-HRMS *m/z* [M^+] calcd for $C_{42}H_{74}ClN_4O_4$ 733.53931, found 733.53795. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.2846.

S-5c liquid (1.2 g, 62%); $[\alpha]^{21}_D$ 27 (*c* 3.3, CH_3OH); elem. anal. found: C, 65.75; H, 9.98; N, 7.55; calcd for $C_{21}H_{37}ClN_2O_2$: C, 65.52; H, 9.69; N, 7.28%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 1.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 4.83 (d, *J* = 13.1 Hz, 2H), 4.74 (m, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 3.82 (m, 1H), 2.63 (m, 1H), 2.42 (m, 1H), 2.11 (m, 2H), 1.93 (m, 3H), 1.84 (s, 3H), 1.42 (m, 10H), 1.07 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 122.8, 121.9, 108.2, 72.5, 72, 63.6, 49.5, 37.7, 32, 31.4, 29.9, 29.7, 28.8, 28.6, 25.8, 22.3, 20.5, 19.6, 13; IR (KBr) ν (cm^{-1}): 3226.33, 3124.12, 3077.83, 3039.26, 2958.27, 2927.41, 2857.99, 1565.92, 1548.56, 1455.99, 1375, 1321, 1259.29, 1232.29, 1203.36, 1159.01, 1130.08, 1064.51, 939.16, 890.95, 755.95, 661.46.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium chloride (R-11a) and 3-hexyl-1-

((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium chloride (S-11a).

To **R-4** or **S-4**, 1-chlorohexane (20 equiv) was added. The resulting mixture was stirred at 100 °C for 9 d. The reaction progress was monitored by TLC using ethyl acetate as eluent. The crude reaction was washed with ethyl acetate (2 x 20 mL), dissolved in methanol and filtered through celite and activated charcoal affording **R-11a** and **S-11a** (79% and 40%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-11a liquid (1.1 g, 79%); $[\alpha]^{19}_{D}$ -51 (*c* 2.5, CH_3OH); elem. anal. found: C, 64.20; H, 9.48; N, 8.05; calcd for $C_{19}H_{33}ClN_2O_2$: C, 63.93; H, 9.32; N, 7.85%; ^{1}H NMR (400 MHz, D_2O): δ 8.9 (s, 1H, H-2), 7.6 (s, 1H), 7.54 (s, 1H), 4.66 (s, 1H), 4.2 (t, *J* = 6.9 Hz, 2H), 4.08 (d, *J* = 6.5 Hz, 1H), 2.42 (m, 1H), 2.27 (m, 2H), 2.12 (m, 1H), 1.86 (m, 3H), 1.41 (s, 3H), 1.24 (s, 9H), 0.83 (s, 3H), 0.78 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 135.1, 122.5, 121.9, 83.9, 83.7, 74.8, 64.4, 49.8, 41, 32.9, 30.3, 29.1, 29.1, 28.9, 25, 21.8, 21.7, 18.9, 13.3; IR (KBr) ν (cm^{-1}): 3338.18, 3133.76, 3073.98, 2931.27, 2863.77, 1459.85, 1369.21, 1232.29, 1164.79, 1139.72, 1043.3, 752.1, 661.46; EI-HRMS *m/z* [M^+] calcd for $C_{38}H_{66}ClN_4O_4$ 677.47671, found 677.47548. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25302.

S-11a liquid (0.2 g, 40%); $[\alpha]^{20}_{D}$ 50 (*c* 2.6, CH_3OH); elem. anal. found: C, 64.24; H, 9.50; N, 8.12; calcd for $C_{19}H_{33}ClN_2O_2$: C, 63.93; H, 9.32; N, 7.85%; ^{1}H NMR (400 MHz, D_2O): δ 8.82 (s, 1H), 7.52 (t, *J* = 1.7 Hz, 1H), 7.47 (t, *J* = 1.7 Hz, 1H), 4.63 (dd, J_1 = 12.8 Hz, J_2= 6.2 Hz, 1H), 4.14 (t, *J* = 6.9 Hz, 2H), 4.03 (d, *J* = 6.5 Hz, 1H), 2.38 (m, 1H), 2.23 (m, 2H), 2.12 (dt, J_1 = 13.9 Hz, J_2= 1.7 Hz, 1H), 1.81 (m, 3H), 1.36 (s, 3H), 1.19 (s, 9H), 0.79 (s, 3H), 0.74 (m, 3H); ^{13}C NMR (100 MHz, D_2O): δ 135, 122.4, 121.8, 83.9, 83.6, 74.8, 64.3, 49.7, 40.8, 32.8, 30.2, 29.1, 29, 28.9, 24.9, 21.7, 21.6, 18.7, 13.1; IR (KBr) ν (cm^{-1}): 3397.96, 2931.27, 2861.84, 1560.13, 1459.85, 1371.14, 1232.29, 1162.87, 1137.8, 1045.23, 7543, 644.1, 547.68.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium bromide (R-11b) and 3-hexyl-1-((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium bromide (S-11b).

To **R-4** or **S-4**, 1-bromohexane (20 equiv) was added. The resulting mixture was stirred at 100 °C for 5 d. The reaction progress was monitored by TLC using ethyl acetate as eluent. The reaction crude was washed with ethyl acetate (2 x 20 mL) and dried under high vacuum to afford **R-11b** and **S-11b** (91% and 74%, respectively) as liquids.

R-11b liquid (2.1 g, 91%); $[\alpha]^{19}_{D}$ -52 (*c* 2.2, CH_3OH); elem. anal. found: C, 57.10; H, 8.48; N, 7.15; calcd for $C_{19}H_{33}BrN_2O_2$: C, 56.85; H, 8.29; N, 6.98%; ^{1}H NMR (400 MHz, D_2O): δ 8.84 (s, 1H), 7.53 (s, 1H), 7.48 (s, 1H), 4.63 (dd, J_1 = 12.8 Hz, J_2 = 6.2 Hz, 1H), 4.15 (t, *J* = 7 Hz, 2H), 4.01 (d, *J* = 6.5 Hz, 1H), 2.38 (s, 1H), 2.22 (s, 2H), 2.07 (t, *J* = 12.2 Hz, 1H), 1.8 (m, 3H), 1.36 (s, 3H), 1.19 (s, 9H), 0.79 (s, 3H), 0.74 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 135, 122.4, 121.8, 83.9,83.6, 74.8, 64.3, 49.7, 40.8, 32.8, 30.2,29.1, 29, 28.8, 24.9, 21.7, 21.6, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3353.6, 3127.97, 3068.19, 2933.2, 2863.77, 1558.2, 1459.85, 1369.21, 1232.29, 1164.79, 1137.8, 1045.23, 989.3, 752.1, 661.46; EI-HRMS *m/z* [M^+] calcd for $C_{38}H_{66}BrN_4O_4$ 721.42620, found 721.42488. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25328.

S-11b liquid (1.5 g, 74%); $[\alpha]^{20}_{D}$ 50 (*c* 2.2, CH_3OH); elem. anal. found: C, 57.14; H, 8.50; N, 7.10; calcd for $C_{19}H_{33}BrN_2O_2$: C, 56.85; H, 8.29; N, 6.98%;^{1}H NMR (400 MHz, CD_3OD): δ 7.57 (d, *J* = 1.5 Hz, 1H), 7.52 (d, *J* = 1.5 Hz, 1H), 4.66 (m, 1H), 4.18 (t, *J* = 7 Hz, 2H), 4.05 (d, *J* = 6.5 Hz, 1H), 2.41 (m,1H), 2.28 (m, 2H), 2.11 (t, *J* = 13.1 Hz, 1H), 1.84 (m, 3H), 1.39 (s, 3H), 1.22 (s, 9H), 0.82 (s, 3H), 0.78 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 122.4, 121.8, 84, 83.6, 74.8, 64.3, 49.8, 40.9, 32.9, 30.2, 29.1, 29, 28.9, 24.9, 21.8, 21.7, 18.9, 13.3; IR (KBr) ν (cm^{-1}): 3357.46, 3124.12, 3066.26, 2933.2, 2863.77, 1558.2, 1459.85, 1369.21, 1232.29, 1162.87, 1137.8, 1045.23, 987.37, 931.45, 752.1.

General procedure for the synthesis of 1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium chloride (R-11c) and 1-((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium chloride (S-11c).

To **R-4** or **S-4**, 1-chlorooctane (20 equiv) was added. The resulting mixture was stirred at 100 °C for 9 d. The reaction progress was monitored by TLC using ethyl acetate as eluent. The reaction crude was washed with ethyl acetate (2 x 20 mL) and further purified by column chromatography using gradient elution (starting with ethyl acetate to ethyl acetate/methanol 9/1). The resulting fractions were combined and the solvent removed under reduced pressure to afford **R-11c** and **S-11c** (79% both of them) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-11c liquid (1.1 g, 79%); $[\alpha]^{23}_{D}$ -53 (*c* 3, CH_3OH); elem. anal. found: C, 65.68; H, 9.80; N, 7.50; calcd for $C_{21}H_{37}ClN_2O_2$: C, 65.52; H, 9.69; N, 7.28%; ^{1}H NMR (400 MHz, CD_3OD): δ 9.01 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 4.05 (d, *J* = 6 Hz, 1H), 2.41 (m, 1H), 2.25 (m, 2H), 2.14 (m, 1H), 1.82 (m, 3H), 1.4 (s, 3H), 1.23 (m, 13H), 0.82 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 135.2, 122.7, 121.9, 83.8, 83.7, 74.8, 64.5, 49.8, 41, 33, 31.3, 29.4, 29.1, 29, 28.6, 28.4, 25.5, 22.2,21.8, 19, 13.7; IR (KBr) ν (cm^{-1}): 3388.32, 3141.47, 2929.34, 2857.99, 1639.2, 1459.85, 1162.87, 1137.8, 752.1, 661.46, 547.68; EI-HRMS *m/z* [M^+] calcd for $C_{42}H_{74}ClN_4O_4$ 733.53931, found 733.53767. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28433.

S-11c liquid (1.1 g, 79%); $[\alpha]^{23}_{D}$ 52 (*c* 3.1, CH_3OH); elem. anal. found: C, 65.70; H, 9.85; N, 7.54; calcd for $C_{21}H_{37}ClN_2O_2$: C, 65.52; H, 9.69; N, 7.28%; ^{1}H NMR (400 MHz, CD_3OD): δ 9.01 (s, 1H), 7.63 (s, 1H), 7.55 (s, 1H), 4.21 (t, *J* = 6.9 Hz, 2H), 4.03 (d, *J* = 6.5 Hz, 1H), 2.39 (m, 1H), 2.22 (m, 2H), 2.14 (m, 1H), 1.81 (m, 3H), 1.38 (s, 3H), 1.21 (m, 13H), 0.79 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, D_2O): δ 135, 122.4, 121.8, 83.9, 83.6, 74.7, 64.3, 49.7, 40.8, 32.8, 30.8, 29, 28.9, 28.7, 28.1, 27.8, 25.1, 21.9, 21.5, 18.7, 13.3; IR (KBr) ν (cm^{-1}): 3401.82, 2929.34, 2857.99, 1643.05, 1560.13, 1459.85, 1162.87, 1137.8, 754.03.

General procedure for the synthesis of 3-butyl-1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium tetrafluoroborate (R-6a) and 3-butyl-1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium tetrafluoroborate (S-6a).

To a stirred solution of **R-5a** or **S-5a** in acetone (10 mL), sodium tetrafluoroborate (1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent

by rotatory evaporation, the residue was dissolved in dichloromethane and kept al -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6a** and **S-6a** (78% and 84%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6a liquid (0.4 g, 78%); $[\alpha]^{23}_{D}$ -35 (*c* 3.6, CH_3OH); elem. anal. found: C, 53.94; H, 7.93; N, 7.50; calcd for $C_{17}H_{29}BF_4N_2O_2$: C, 53.70; H, 7.69; N, 7.37%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 7.38 (t, *J* = 1.7 Hz, 1H), 4.9 (d, *J* = 16.7 Hz, 2H), 4.75 (dd, J_1 = 11.5 Hz, J_2 = 3.9 Hz, 1H), 4.27 (t, *J* = 7.5 Hz, 2H), 3.83 (dd, J_1 = 4.8 Hz, J_2 = 3.1 Hz, 1H), 2.6 (m, 1H), 2.48 (m, 1H), 2.23 (m, 3H), 1.89 (m, 2H), 1.85 (s, 3H), 1.38 (m, 2H), 1.03 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147, 136.4, 122, 121, 110.1, 74.9, 73.2, 61.8, 50.1, 36.9, 31.9, 30.4, 29.4, 22.3, 19.4, 18.7, 13.3; IR (KBr) ν (cm^{-1}): 3509.81, 3369.03, 3153.04, 2960.2, 2933.2, 2873.42, 1558.2, 1455.99, 1378.85, 1249.65, 1162.87, 1062.59, 943.02, 892.88, 755.95, 661.46. EI-HRMS *m/z* [M^+] calcd for $C_{34}H_{58}BF_4N_4O_4$ 673.44878, found 673.44676. Calcd for $C_{17}H_{29}N_2O_2$ 293.22235, found 293.22179.

S-6a liquid (0.4 g, 84%); $[\alpha]^{23}_{D}$ 33 (*c* 3.2, CH_3OH); elem. anal. found: C, 53.96; H, 7.95; N, 7.48; calcd for $C_{17}H_{29}BF_4N_2O_2$: C, 53.70; H, 7.69; N, 7.37%; ^{1}H NMR (400 MHz, D_2O): δ 8.82 (s, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 4.76 (d, *J* = 16.7 Hz, 2H), 4.6 (dd, J_1 = 7.8 Hz, J_2 = 4.5 Hz, 1H), 4.14 (t, *J* = 7.5 Hz, 2H), 3.81 (dd, J_1 = 7.4 Hz, J_2 = 3.7 Hz, 1H), 2.53 (m, 1H), 2.27 (m, 1H), 2.06 (m, 3H), 1.78 (m, 2H), 1.72 (m, 3H), 1.22 (m, 2H), 0.99 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 148.5, 135.6, 122.6, 122.1, 108.7, 72.9, 72.8, 63, 49.5, 37.2, 31.3, 31.1, 29.6, 20.8, 19.5, 18.7, 12.5; IR (KBr) ν (cm^{-1}): 3523.31, 3153.04, 2956.34, 2925.48, 2856.06, 1556.27, 1457.92, 1376.93, 1160.94, 1052.94, 750.17.

General procedure for the synthesis of 3-butyl-1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium bis(trifluoromethanesulfonyl)imide (R-6b) and 3-butyl-1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium bis(trifluoromethanesulfonyl)imide (S-6b).

To a stirred solution of **R-5a** or **S-5a** in methanol (10 mL), lithium bis(trifluoromethanesulfonyl)imide (1 equiv) was added. After stirring at rt for 24 h, deionized water was added and the resulting aqueous solution was extracted with dichloromethane. The combined organic extracts were dried with anhyd Na_2SO_4 and the solvent was removed on the rotary evaporator to give **R-6b** and **S-6b** (69% and 78%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6b liquid (0.5 g, 69%); $[\alpha]^{22}_{D}$ -22 (*c* 4.9, CH_3OH); elem. anal. found: C, 39.94; H, 5.33; N, 7.50; S, 11.24; calcd for $C_{19}H_{29}F_6N_3O_6S_2$: C, 39.79; H, 5.10; N, 7.33; S, 11.18%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.43 (t, *J* = 1.8 Hz, 1H), 7.29 (t, *J* = 1.7 Hz, 1H), 4.9 (d, *J* = 16.7 Hz, 2H), 4.75 (dd, J_1 = 11.6 Hz, J_2 = 3.9 Hz, 1H), 4.23 (t, *J* = 7.5 Hz, 2H), 3.83 (dd, J_1 = 4.7 Hz, J_2= 3.1 Hz, 1H), 2.61 (m, 1H), 2.48 (m, 1H), 2.32 (m, 1H), 2.2 (m, 1H), 1.94 (m, 1H), 1.88 (m, 2H), 1.86 (s, 3H), 1.38 (m, 2H), 1 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 135.9, 122.2, 121.3, 119.7 (q, J_{CF} = 320.4 Hz), 110.3, 74.9, 73.2, 61.8, 50.1, 36.8, 31.9, 30.3, 29.4, 22.2, 19.3, 18.6, 13.2; IR (KBr) ν (cm^{-1}): δ 3507.88, 3149.19, 3104.83, 2962.13, 2931.27, 2877.27, 1558.2, 1455.99, 1349.93, 1195.65, 1137.8, 1056.8, 894.81, 742.46, 655.67, 615.18, 570.82, 512.97; EI-HRMS *m/z* [M^+] calcd for $C_{36}H_{58}F_6N_5O_8S_2$ 866.36255, found 866.3612. Calcd for $C_{17}H_{29}N_2O_2$ 293.22235, found 293.22186.

S-6b liquid (0.5 g, 78%); $[\alpha]^{21}_D$ 21 (*c* 4.3, CH_3OH); elem. anal. found: C, 39.98; H, 5.38; N, 7.55; S, 11.30; calcd for $C_{19}H_{29}F_6N_3O_6S_2$: C, 39.79; H, 5.10; N, 7.33; S, 11.18%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.51 (s, 1H), 7.36 (s, 1H), 4.86 (d, *J* = 16.7 Hz, 2H), 4.74 (dd, J_1 = 11.2 Hz, J_2 = 3.6 Hz, 1H), 4.2 (t, *J* = 7.5 Hz, 2H), 3.8 (s, 1H), 2.58 (m, 1H), 2.41 (m, 1H), 2.25 (m, 2H), 1.86 (m, 3H), 1.84 (s, 3H), 1.31 (m, 2H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 147, 135.5, 122.5, 121.6, 121.3 (q, J_{CF} = 321.4 Hz), 109.7, 74.7, 73.2, 61.6, 49.9, 36.8, 31.8, 30.4, 29.4, 22.2, 19.3, 18.7, 13.2; IR (KBr) ν (cm^{-1}): 3507.88, 3151.11, 3102.9, 2965.98, 2942.84, 2877.27, 1556.27, 1454.06, 1349.93, 1195.65, 1137.8, 1056.8, 746.31, 655.67, 615.18, 572.75, 512.97.

General procedure for the synthesis of 3-butyl-1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium methyl sulfate (R-6c) and 3-butyl-1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]imidazolium methyl sulfate (S-6c).

To a stirred solution of **R-5a** or **S-5a** in methanol (10 mL), sodium methyl sulfate (1.4 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6c** and **S-6c** (70% and 65%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6c liquid (0.4 g, 70%); $[\alpha]^{22}_D$ -32 (*c* 3.6, CH_3OH); elem. anal. found: C, 53.56; H, 8.23; N, 7.12; S, 8.00; calcd for $C_{18}H_{32}N_2O_6S$: C, 53.44; H, 7.97; N, 6.93; S, 7.93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.56 (s, 1H), 7.42 (s, 1H), 4.78 (d, *J* = 6.1 Hz, 1H), 4.71 (s, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 3.81 (s,1H), 3.64 (s, 3H), 2.49 (m, 1H), 2.32 (m, 1H), 2.14 (m, 2H), 1.84 (m, 3H), 1.76 (s, 3H), 1.31 (m, 2H), 1 (s, 3H), 0.9 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 136.5, 122.7, 121.4, 108.8, 73.7, 72.9, 62, 54.4, 49.6, 37.2, 31.9, 31.1, 29.7, 22, 19.5, 19.3, 13.3; IR (KBr) ν (cm^{-1}): 3394.1, 3137.62, 3097.12, 2958.27, 2929.34, 2871.49, 1558.2, 1455.99, 1376.93, 1247.72, 1224.58, 1162.87, 1128.15, 1060.66, 1010.52, 754.03, 661.46, 611.32, 580.46, 555.39; EI-HRMS *m/z* [M^+] calcd for $C_{35}H_{61}N_4O_8S$ 697.42046, found 697.41952. Calcd for $C_{17}H_{29}N_2O_2$ 293.22235, found 293.22183.

S-6c liquid (0.4 g, 65%); $[\alpha]^{22}_D$ 31 (*c* 3.5, CH_3OH); elem. anal. found: C, 53.60; H, 8.25; N, 7.20; S, 8.10; calcd for $C_{18}H_{32}N_2O_6S$: C, 53.44; H, 7.97; N, 6.93; S, 7.93%; ^{1}H NMR (400 MHz, D_2O): δ 8.87 (s, 1H), 7.62 (t, *J* = 1.7 Hz, 1H), 7.53 (t, *J* = 1.7 Hz, 1H), 4.79 (d, *J* = 6.1 Hz, 2H), 4.63 (dd, J_1 = 7.6 Hz, J_2= 4.5 Hz, 1H), 4.18 (t, *J* = 7.1 Hz, 2H), 3.83 (dd, J_1 = 7.4 Hz, J_2 = 3.7 Hz, 1H), 3.66 (s, 3H), 2.56 (m, 1H), 2.29 (m, 1H), 2.09 (m, 1H), 1.97 (m, 1H), 1.93 (m, 1H), 1.81 (m, 2H), 1.74 (s, 3H), 1.25 (m, 2H), 1.02 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): 148.4, 135.7, 122.7, 122.2, 108.9, 72.9, 72.8, 63, 55.3, 49.5, 37.3, 31.4, 31.2, 29.7, 20.9, 19.6, 18.8, 12.7; IR (KBr) ν (cm^{-1}): 3397.96, 3137.62, 3097.12, 2962.13, 2937.06, 2873.42, 1533.13, 1459.85, 1253.5, 1216.86, 1164.79, 1137.8, 1060.66, 1012.45, 894.81, 757.88, 615.18, 576.61.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium trifluoroacetate (R-6d) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium trifluoroacetate (S-6d).

To a stirred solution of **R-5b** or **S-5b** in methanol (5 mL), sodium trifluoroacetate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6d** and **S-6d** (41% and 60%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6d liquid (0.1 g, 41%); $[\alpha]^{20}_{D}$ -26 (*c* 0.9, CH_3OH); elem. anal. found: C, 58.26; H, 7.78; N, 6.60; calcd for $C_{21}H_{33}F_3N_2O_4$: C, 58.05; H, 7.66; N, 6.45%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.51 (s, 1H), 7.39 (s, 1H), 4.73 (dd, J_1 = 8.8 Hz, J_2 = 4.2 Hz, 1H), 4.69 (d, *J* = 3.9 Hz, 2H), 4.19 (t, *J* =7.4 Hz, 2H), 3.75 (dd, J_1 = 6.6 Hz, J_2 = 3.4 Hz, 1H), 2.45 (m, 1H), 2.29 (m, 1H), 2.01 (m, 2H), 1.81 (m, 3H), 1.71 (s, 3H), 1.22 (m, 6H), 0.96 (s, 3H), 0.77 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (q, J_{CF} = 33.3 Hz), 147, 137.6, 121.5, 121.1, 116.9 (q, J_{CF} = 292.5 Hz), 108.9, 74, 73.1, 61.3, 50, 37.2, 31.2, 30.9, 29.9, 29.7, 25.8, 22.2, 22.1, 19.3, 13.8; IR (KBr) ν (cm^{-1}): 3378.67, 3139.54, 3093.26, 2958.27, 2933.2, 2865.7, 1679.69, 1562.06, 1452.14, 1428.99, 1378.85, 1201.43, 1176.36, 1133.94, 1072.23, 892.88, 8339, 802.24, 721.24, 659.53, 553.47, 518.75; EI-HRMS *m/z* [M^+] calcd for $C_{40}H_{66}F_3N_4O_6$ 755.49290, found 755.49139. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25320.

S-6d liquid (0.3 g, 60%); $[\alpha]^{23}_{D}$ 27 (*c* 0.9, CH_3OH); elem. anal. found: C, 58.30; H, 7.80; N, 6.64; calcd for $C_{21}H_{33}F_3N_2O_4$: C, 58.05; H, 7.66; N, 6.45%; ^{1}H NMR (400 MHz, CD_3OD): δ 7.84 (d, *J* = 2 Hz, 1H), 7.75 (d, *J* = 2 Hz, 1H), 4.81 (d, *J* = 17.5 Hz, 2H), 4.76 (dd, J_1 = 7.4 Hz, J_2 = 4.6 Hz, 1H), 4.29 (t, *J* = 7.3 Hz, 2H), 3.85 (dd, J_1 = 7.6 Hz, J_2 = 3.5 Hz, 1H), 2.61 (m, 1H), 2.39 (m, 1H), 2.11 (m, 2H), 1.92 (m, 3H), 1.82 (s, 3H), 1.35 (m, 6H), 1.07 (s, 3H), 0.91 (t, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 161.5 (q, J_{CF} = 34 Hz), 147.4, 122.8, 122, 116.9 (q, J_{CF} = 293.5 Hz), 108.3, 72.1, 63.6, 63.6, 49.5, 37.7, 32.1, 30.8, 29.9, 29.7, 25.5, 22.1, 20.6, 19.6, 13. IR (KBr) ν (cm^{-1}): 3394.1, 3137.62, 3085.55, 3014.19, 2954.41, 2931.27, 2859.92, 1529.27, 1455.99, 1378.85, 1216.86, 1162.87, 1132.01, 1058.73, 1012.45, 892.88, 765.6, 665.32, 611.32, 580.46.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium bis(trifluoromethanesulfonyl)imide (R-6e) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium bis(trifluoromethanesulfonyl)imide (S-6e).

To a stirred solution of **R-5b** or **S-5b** in methanol (5 mL), lithium bis(trifluoromethanesulfonyl)imide (1.1 equiv) was added. After stirring at rt for 24 h, the formed solid was filtered and the filtrate was evaporated by rotary evaporation to give **R-6e** and **S-6e** (89% and 79%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6e liquid (0.1 g, 89%); $[\alpha]^{21}_{D}$ -15 (*c* 4.3, CH_3OH); elem. anal. found: C, 42.20; H, 5.78; N, 7.12; S, 10.83; calcd for $C_{21}H_{33}F_6N_3O_6S_2$: C, 41.92; H, 5.53; N, 6.98; S, 10.66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.52 (s, 1H), 7.36 (s, 1H), 4.83 (d, *J* = 9.2 Hz, 2H), 4.79 (dd, J_1 = 10.9 Hz, J_2 = 3.2 Hz, 1H), 4.2 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 1H,), 2.57 (m, 1H), 2.4 (m, 1H), 2.25 (m, 2H), 1.88 (m, 3H), 1.84 (m, 3H), 1.31 (s, 6H), 1.02 (s, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147, 135.7, 122.4, 121.6, 119.7 (c, J_{CF} = 321.3 Hz), 109.6, 74.5, 73.3, 61.6, 50.2, 36.9, 30.9, 30.6, 29.9, 29.5, 25.7, 22.3, 22.2, 18.9, 13.7; IR (KBr) ν (cm^{-1}): 3494.38, 3149.19, 2958.27, 2953.13, 2865.7, 1556.27, 1454.06, 1351.86, 1195.65, 1137.8, 1056.8, 894.81, 790.67, 738.61,

653.75, 615.18, 570.82, 512.97; EI-HRMS *m/z* [M^+] calcd for $C_{40}H_{66}F_6N_5O_8S_2$ 922.42357, found 922.42307. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25316.

S-6e liquid (0.5 g, 79%); $[\alpha]^{22}_D$ 14 (*c* 4.6, CH_3OH); elem. anal. found: C, 42.24; H, 5.80; N, 7.15; S, 10.86; calcd for $C_{21}H_{33}F_6N_3O_6S_2$: C, 41.92; H, 5.53; N, 6.98; S, 10.66%; ^{1}H NMR (400 MHz, CD_3OD): δ 9.08 (s, 1H), 7.77 (d, *J* = 1.5 Hz, 1H), 7.67 (d, *J* = 1.5 Hz, 1H), 4.81 (d, *J* = 19.4 Hz, 2H), 4.72 (dd, J_1 = 7.4 Hz, J_2 = 4.4 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.81 (dd, J_1 = 10.9 Hz, J_2 = 3.2 Hz, 1H), 2.6 (m, 1H), 2.37 (m, 1H), 2.12 (m, 2H), 1.91 (m, 3H), 1.82 (s, 3H), 1.34 (s, 6H), 1.06 (s, 3H), 0.9 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 147.3, 136.1, 122.8, 122, 119.7 (q, *J* = 320.4 Hz), 108.3, 72.7, 72.1, 63.4, 49.6, 37.5, 31.8, 30.7, 29.8, 29.6, 25.4, 22, 20.6, 19.5, 12.9; IR (KBr) ν (cm^{-1}): 3504.02, 3153.04, 2958.27, 2935.13, 2867.63, 1454.06, 1349.93, 1197.58, 1137.8, 1058.73, 792.6, 740.53, 653.75, 617.1, 572.75, 512.97, 404.97.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium methyl sulfate (R-6f) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-hexylimidazolium methyl sulfate (S-6f).

To a stirred solution of **R-5b** or **S-5b** in methanol (5 mL), sodium methyl sulfate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6f** and **S-6f** (60% and 91%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6f liquid (0.05 g, 60%); $[\alpha]^{22}_D$ -26 (*c* 3.5, CH_3OH); elem. anal. found: C, 55.70; H, 8.58; N, 6.65; S, 7.63; calcd for $C_{20}H_{36}N_2O_6S$: C, 55.53; H, 8.39; N, 6.48; S, 7.41%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.47 (s, 1H), 7.33 (s, 1H), 4.89 (dd, J_1 = 9.7 Hz, J_2 = 3.5 Hz, 1H), 4.83 (d, *J* = 7 Hz, 2H), 4.31 (dd, J_1 = 7.4 Hz, J_2 = 4.4 Hz, 2H), 3.88 (d, *J* = 1.8 Hz, 1H), 3.72 (s, 3H), 2.56 (m, 1H), 2.42 (m, 1H), 2.2 (m, 2H), 1.91 (m, 3H), 1.85 (s, 3H), 1.34 (m, 6H), 1.09 (s, 3H), 0.89 (t, 3H, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 137.2, 121.9, 121.2, 109.4, 74.1, 73, 62.1, 54.6, 50.2, 37.3, 31.1, 31, 30, 29.9, 25.9, 22.3, 22.1, 19.4, 13.9; IR (KBr) ν (cm^{-1}): 3421.1, 3137.62, 2929.34, 2859.92, 1455.99, 1226.5, 1162.87, 1060.66, 1008.59, 755.95, 611.32, 582.39; EI-HRMS *m/z* [M^+] calcd for $C_{39}H_{69}N_4O_8S$ 753.48306, found 753.48742. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25328.

S-6f liquid (0.4 g, 91%); $[\alpha]^{20}_D$ 25 (*c* 3.1, CH_3OH); elem. anal. found: C, 55.73; H, 8.60; N, 6.70; S, 7.65; calcd for $C_{20}H_{36}N_2O_6S$: C, 55.53; H, 8.39; N, 6.48; S, 7.41%; ^{1}H NMR (400 MHz, CD_3OD): δ 9.15 (t, *J* = 1.5 Hz, 1H), 7.82 (t, *J* = 1.9 Hz, 1H), 7.72 (t, *J* = 1.9 Hz, 1H), 4.82 (d, *J* = 13.2 Hz, 2H), 4.72 (dd, J_1 = 7.8, J_2 = 4.5 Hz, 1H), 4.27 (t, *J* = 7.3 Hz, 2H), 3.8 (dd, J_1 = 7.4 Hz, J_2 = 3.5 Hz, 1H), 3.7 (s, 3H), 2.62 (m, 1H), 2.4 (m, 1H), 2.11 (m, 2H), 1.93 (m, 3H), 1.84 (s, 3H), 1.37 (m, 6H), 1.05 (s, 3H), 0.92 (t, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 147.5, 136.3, 122.9, 122, 108.3, 72.5, 72, 63.6, 53.8, 49.5, 37.7, 32, 30.8, 29.9, 29.7, 25.5, 22.1, 20.5, 19.6, 12.9; IR (KBr) ν (cm^{-1}): 3345.89, 3139.54, 3091.33, 2958.27, 2933.2, 2865.7, 1681.62, 1562.06, 1531.2, 1454.06, 1427.07, 1378.85, 1321, 1201.43, 1174.44, 1132.01, 1072.23, 892.88, 831.16, 802.24, 757.88, 721.24, 661.46.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium trifluoroacetate (R-6g) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium trifluoroacetate (S-6g).

To a solution of **R-5c** or **S-5c** in methanol (10 mL), sodium trifluoroacetate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6g** and **S-6g** (88% and 55%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6g liquid (0.2 g, 88%); $[\alpha]^{22}_{D}$ -34 (*c* 1.7, CH_3OH); elem. anal. found: C, 59.86; H, 8.18; N, 6.25; calcd for $C_{23}H_{37}F_3N_2O_4$: C, 59.72; H, 8.06; N, 6.06%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.5 (s, 1H), 7.33 (s, 1H), 4.93 (dd, J_1 = 10.1 Hz, J_2 = 3.7 Hz, 1H), 4.74 (d, J = 4.3 Hz, 2H), 4.18 (dt, J_1 = 6.9 Hz, J_2 = 3.1 Hz, 2H), 3.86 (s, 1H), 2.5 (m, 1H), 2.36 (m, 1H), 2.16 (m, 2H), 1.84 (m, 3H), 1.78 (s, 3H), 1.27 (m, 10H), 1.03 (s, 3H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (q, J_{CF} = 33.6 Hz), 147.1, 137.4, 121.8, 121.2, 117 (q, J_{CF} = 295.1 Hz), 108.8, 73.8, 73, 61.7, 50, 37.3, 31.5, 31.4, 29.9, 29.8, 28.9, 28.8, 26.1, 22.5, 22, 19.5, 13.9; IR (KBr) ν (cm^{-1}): 3363.25, 3139.54, 3091.33, 2929.34, 2859.92, 1679.69, 1562.06, 1454.06, 1428.99, 1378.85, 1201.43, 1174.44, 1132.01, 1072.23, 892.88, 831.16, 802.24, 723.17, 661.46; EI-HRMS *m/z* [M^+] calcd for $C_{44}H_{74}F_3N_4O_6$ 811.55550, found 811.55409. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28466.

S-6g liquid (0.3 g, 55%); $[\alpha]^{22}_{D}$ 33 (*c* 1.4, CH_3OH); elem. anal. found: C, 59.90; H, 8.28; N, 6.30; calcd for $C_{23}H_{37}F_3N_2O_4$: C, 59.72; H, 8.06; N, 6.06%; ^{1}H NMR (400 MHz, CD_3OD): δ 7.82 (d, J = 2 Hz, 1H), 7.73 (d, J = 2 Hz, 1H), 4.82 (d, J = 15.7 Hz, 2H), 4.74 (dd, J_1 = 7.4 Hz, J_2 = 4.5 Hz, 1H), 4.27 (t, J = 7.2 Hz, 2H), 3.83 (dd, J_1 = 7.6 Hz, J_2 = 3.5 Hz, 1H), 2.61 (m, 1H), 2.39 (m, 1H), 2.1 (m, 2H), 1.91 (m, 3H), 1.83 (s, 3H), 1.3 (m, 10H), 1.06 (s, 3H), 0.9 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 161.5 (q, J_{CF} = 34.6 Hz), 147.4, 122.8, 121.9, 116.9 (q, J_{CF} = 279.1 Hz), 108.2, 72.5, 72, 63.5, 49.5, 37.6, 32, 31.4, 29.8, 29.7, 28.8, 28.6, 25.8, 22.2, 20.5, 19.5, 13; IR (KBr) ν (cm^{-1}): 3289.96, 3135.69, 3091.33, 2929.34, 2857.99, 1681.62, 1563.99, 1454.06, 1376.93, 1201.43, 1174.44, 1132.01, 1076.08, 890.95, 833.09, 802.24, 721.24.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (R-6h) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (S-6h).

To a solution of **R-5c** or **S-5c** in methanol (10 mL), lithium bis(trifluoromethanesulfonyl)imide (1.1 equiv) was added. After stirring at rt for 24 h, the solvent was removed and the residue was dissolved in dichloromethane (10 mL) and kept at -20 ºC for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to give **R-6h** and **S-6h** (66% and 87%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6h liquid (0.2 g, 66%); $[\alpha]^{23}_{D}$ -14 (*c* 1.1, CH_3OH); elem. anal. found: C, 44.12; H, 6.18; N, 6.84; S, 10.28; calcd for $C_{23}H_{37}F_6N_3O_6S_2$: C, 43.87; H, 5.92; N, 6.67; S, 10.18%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.5 (s, 1H), 7.34 (s, 1H), 4.9 (d, J = 16.8 Hz, 2H), 4.82 (dd, J_1 = 11.3 Hz, J_2 = 3.7 Hz, 1H), 4.19 (t, J = 7.4 Hz, 2H), 3.89 (s, 1H), 2.59 (m, 1H), 2.41 (m, 1H), 2.28 (m, 1H), 2.18 (m, 1H), 1.89 (m, 3H), 1.84 (s, 3H), 1.27 (m, 10H), 1.06 (s, 3H), 0.88 (t, J = 6.9 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7 (C-13), 135.6, 122.2, 121.7, 119.6 (q, J_{CF} = 320.8 Hz), 110.2, 74.9, 73.6, 61.4, 50.3, 36.7, 31.5, 30.4, 29.9, 29.5, 28.9, 28.7, 26.1, 22.5, 22.1, 18.6, 13.9; IR (KBr) ν (cm^{-1}): 3505.95, 3151.11, 3104.83, 2931.27, 2861.84, 1643.05, 1554.34, 1455.34, 1351.86, 1197.58, 1137.8, 1058.73, 896.73, 790.67, 740.53, 653.75, 617.11, 572.75, 512.97; EI-HRMS *m/z* [M^+] calcd for $C_{44}H_{74}F_6N_5O_8S_2$ 978.48775, found 978.48661. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.2847.

S-6h liquid (0.4 g, 87%); $[\alpha]^{22}_D$ 15 (*c* 1.3, CH_3OH); elem. anal. found: C, 44.15; H, 6.20; N, 6.88; S, 10.30; calcd for $C_{23}H_{37}F_6N_3O_6S_2$: C, 43.87; H, 5.92; N, 6.67; S, 10.18%; ^{1}H NMR (400 MHz, CD_3OD): δ 7.75 (d, *J* = 2 Hz, 1H), 7.65 (d, *J* = 2 Hz, 1H), 4.79 (s, 2H), 4.71 (dd, J_1 = 7.8 Hz, J_2 = 4.4 Hz, 1H), 4.26 (t, *J* = 7.3 Hz, 2H), 3.81 (dd, J_1 = 7.4 Hz, J_2 = 3.5 Hz, 1H), 2.59 (m, 1H), 2.38 (m, 1H), 2.11 (m, 2H), 1.91 (m, 3H), 1.81 (s, 3H), 1.34 (m, 10H), 1.05 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 147.3, 122.7, 121.9, 119.7 (q, J_{CF} = 320.4 Hz), 108.3, 72.7, 72.1, 63.4, 49.6, 37.5, 31.8, 31.4, 29.8, 29.6, 28.7, 28.5, 25.8, 22.2, 20.6, 19.4, 13; IR (KBr) ν (cm^{-1}): 3505.95, 3153.04, 2931.27, 2861.84, 1349.93, 1328.71, 1197.58, 1139.72, 1058.73, 653.75, 615.18, 572.75, 512.97.

General procedure for the synthesis of 1-[(1R,2S,3R,5R)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium methyl sulfate (R-6i) and 1-[(1S,2R,3S,5S)-2,3-dihydroxy-2-methyl-5-isopropenylcyclohexyl]-3-octylimidazolium methyl sulfate (S-6i).

To a stirred solution of **R-5c** or **S-5c** in methanol (10 mL), sodium methyl sulfate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-6i** and **S-6i** (65% and 83%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-6i liquid (0.1 g, 65%); $[\alpha]^{23}_D$ -20 (*c* 1.3, CH_3OH); elem. anal. found: C, 57.52; H, 8.90; N, 6.34; S, 7.18; calcd for $C_{22}H_{40}N_2O_6S$: C, 57.36; H, 8.75; N, 6.08; S, 6.96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.59 (s, 1H), 7.42 (s, 1H), 4.8 (dd, J_1 = 9.3 Hz, J_2 = 3.9 Hz, 2H), 4.73 (s, 1H), 4.23 (t, *J* = 7.3 Hz, 2H), 3.82 (s, 1H), 3.63 (s, 3H), 2.49 (m, 1H), 2.31 (m, 1H), 2.13 (m, 2H), 1.84 (m, 3H), 1.76 (s, 3H), 1.24 (m, 10H), 1.01 (s, 3H), 0.82 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 136.6, 122.8, 121.6, 109, 73.7, 73, 62.2, 54.4, 50, 37.3, 31.6, 31.4, 30.1, 29.9, 29, 28.9, 26.2, 22.5, 22, 19.7, 14; IR (KBr) ν (cm^{-1}): 3411.46, 3137.62, 3097.12, 2929.34, 2857.99, 1643.05, 1556.27, 1455.99, 1376.93, 1251.58, 1224.58, 1162.87, 1130.08, 1060.66, 1012.45, 914.09, 890.95, 750.17, 611.32, 580.46, 553.47; EI-HRMS *m/z* [M^+] calcd for $C_{43}H_{77}N_4O_8S$ 809.54566, found 809.5446. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28474.

S-6i liquid (0.4 g, 83%); $[\alpha]^{22}_D$ 21 (*c* 1.4, CH_3OH); elem. anal. found: C, 57.58; H, 8.95; N, 6.40; S, 7.20; calcd for $C_{22}H_{40}N_2O_6S$: C, 57.36; H, 8.75; N, 6.08; S, 6.96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 7.59 (s, 1H), 7.42 (s, 1H), 4.82 (m, 1H), 4.76 (s, 2H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.85 (m, 1H), 3.67 (s, 3H), 2.52 (m, 1H), 2.35 (m, 1H), 2.13 (m, 2H), 1.87 (m, 3H), 1.79 (s, 3H), 1.24 (m, 10H), 1.04 (s, 3H), 0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 136.7, 122.6, 121.5, 109.1, 73.6, 73, 62.3, 54.5, 50, 37.4, 31.6, 31.4, 30.2, 30, 29, 28.9, 26.2, 22.5, 22, 19.7, 14; IR (KBr) ν (cm^{-1}): 3384.46, 3135.69, 3089.4, 2929.34, 2857.99, 1643.05, 1560.13, 1457.92, 1376.93, 1249.65, 1226.5, 1160.94, 1132.01, 1060.66, 1012.45, 889.02, 752.1, 661.46, 611.32, 580.46, 555.39.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium tetrafluoroborate (R-12a) and 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium tetrafluoroborate (S-12a).

To a solution of **R-11b** or **S-11b** in methanol (5 mL), sodium tetrafluoroborate (1.1 equiv) was added. The resulting mixture was stirred at rt for 72 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation. The residue was dissolved in methanol and filtered through celite and activated charcoal affording **R-12a** and **S-12a** (89% and 90%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12a liquid (0.5 g, 89%); $[\alpha]^{22}_{D}$ -53 (*c* 5.8, CH_3OH); elem. anal. found: C, 56.12; H, 8.40; N, 6.98; calcd for $C_{19}H_{33}BF_4N_2O_2$: C, 55.89; H, 8.15; N, 6.86%; ^{1}H NMR (400 MHz, CD_3OD): δ 7.54 (s, 1H), 7.49 (s, 1H), 4.64 (dd, J_1 = 12.8 Hz, J_2 = 6.2 Hz, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 4.02 (d, *J* = 6.5 Hz, 1H), 2.38 (s, 1H), 2.23 (s, 2H), 2.07 (t, *J* = 12.2 Hz, 1H), 1.82 (m, 3H), 1.37 (s, 3H), 1.2 (s, 9H), 0.79 (s, 3H), 0.74 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 122.4, 121.8, 83.9, 83.6, 74.8, 64.3, 49.7, 40.9, 32.9, 30.2, 29.1, 29, 28.8, 24.9, 21.7, 21.7, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3365.17, 3151.11, 3075.9, 2933.2, 2863.77, 1560.13, 1459.85, 1369.21, 1297.86, 1232.29, 1162.87, 1137.8, 1066.44, 931.45, 754.03; EI-HRMS *m/z* [M^+] calcd for $C_{38}H_{66}BF_4N_4O_4$ 729.51144, found 729.5973. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25326.

S-12a liquid (0.5 g, 90%); $[\alpha]^{20}_{D}$ 52 (*c* 5.5, CH_3OH); elem. anal. found: C, 56.15; H, 8.43; N, 6.96; calcd for $C_{19}H_{33}BF_4N_2O_2$: C, 55.89; H, 8.15; N, 6.86%; ^{1}H NMR (400 MHz, CD_3OD): δ 8.84 (s, 1H), 7.56 (t, *J* = 1.8 Hz, 1H), 7.5 (t, *J* = 1.7 Hz, 1H), 4.66 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 4.16 (t, *J* = 7 Hz, 2H), 4.04 (d, *J* = 6.5 Hz, 1H), 2.41 (s, 1H), 2.25 (s, 2H), 2.08 (t, *J* = 12.2 Hz, 1H), 1.84 (m, 3H), 1.39 (s, 3H), 1.22 (s, 9H), 0.81 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 135, 122.4, 121.9, 83.9, 83.6, 74.8, 64.3, 49.8, 40.92, 32.9, 30.2, 29.1, 29, 28.8, 24.9, 21.7, 21.6, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3359.39, 3141.47, 3070.12, 2931.27, 2863.77, 1560.13, 1531.2, 1459.85, 1369.21, 1297.86, 1230.36, 1162.87, 1137.8, 1047.16, 989.3, 931.45, 754.03, 522.61.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium trifluoroacetate (R-12b) and 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium trifluoroacetate (S-12b).

To a stirred solution of **R-11b** or **S-11b** in methanol (10 mL), sodium trifluoroacetate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation and purified by column chromatography using gradient elution (starting with ethyl acetate to ethyl acetate/methanol 9/1) to afford **R-12b** and **S-12b** (71% and 76%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12b liquid (0.4 g, 71%); $[\alpha]^{23}_{D}$ -42 (*c* 2.8, CH_3OH); elem. anal. found: C, 58.24; H, 7.94; N, 6.68; calcd for $C_{21}H_{33}F_3N_2O_4$: C, 58.05; H, 7.66; N, 6.45%; ^{1}H NMR (400 MHz, D_2O): δ 8.85 (s, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 4.64 (dd, J_1 = 12.8 Hz, J_2 = 6.1 Hz, 1H), 4.14 (t, *J* = 7 Hz, 2H), 4.01 (d, *J* = 6.6 Hz, 1H), 2.37 (s, 1H), 2.2 (s, 2H), 2.05 (t, *J* = 12.2 Hz, 1H), 1.8 (m, 3H), 1.35 (s, 3H), 1.18 (s, 9H), 0.78 (s, 3H), 0.72 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 162.6 (q, J_{CF} = 35.2 Hz), 135, 122.4, 121.8, 116.4 (q, J_{CF} = 291.9 Hz), 83.8, 83.6, 74.7, 64.3, 49.7,

40.9, 32.8, 30.2, 29.1, 28.9, 28.8, 24.9, 21.7, 21.6, 18.8, 13.2. IR (KBr) ν (cm^{-1}): 3378.67, 3133.76, 3095.19, 2958.27, 2935.13, 2865.7, 1685.48, 1558.2, 1459.85, 1417.42, 1388.5, 1373.07, 1201.43, 1170.58, 1133.94, 1072.23, 1045.23, 987.37, 827.31, 800.31, 719.31, 646.03; EI-HRMS *m/z* [M^+] calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25320.

S-12b liquid (0.4 g, 76%); $[\alpha]^{23}_D$ 41 (*c* 2.6, CH_3OH); elem. anal. found: C, 58.30; H, 7.98; N, 6.70; calcd for $C_{21}H_{33}F_3N_2O_4$: C, 58.05; H, 7.66; N, 6.45%; ^{1}H NMR (400 MHz, D_2O): δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.5 (d, *J* = 1.9 Hz, 1H), 4.66 (m, 1H), 4.17 (t, *J* = 7 Hz, 2H), 4.04 (d, *J* = 6.5 Hz, 1H), 2.4 (s, 1H), 2.24 (s, 2H), 2.08 (t, *J* = 12.2 Hz, 1H), 1.83 (m, 3H), 1.38 (s, 3H), 1.22 (s, 9H), 0.81 (s, 3H), 0.76 (t, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 162.7 (q, *J* = 35.3 Hz), 122.4, 121.8, 116.4 (q, *J* = 292.1 Hz), 83.9, 83.6, 74.8, 64.3, 49.7, 40.9, 32.9, 30.2, 29.1, 29, 28.8, 24.9, 21.7, 21.6, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3392.17, 3139.54, 3093.26, 2958.27, 2935.13, 2865.7, 1683.55, 1560.13, 1459.85, 1421.28, 1388.5, 1373.07, 1201.43, 1172.51, 1135.87, 829.24, 802.24, 719.31, 646.03.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium bis(trifluoromethanesulfonyl)imide (R-12c) and 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium bis(trifluoromethanesulfonyl)imide (S-12c).

To a solution of **R-11b** or **S-11b** in methanol (10 mL), lithium bis(trifluoromethanesulfonyl)imide (1.1 equiv) was added. After stirring at rt for 72 h, the formed solid was filtered and the filtrate was evaporated by rotary evaporation and purified by column chromatography to afford **R-12c** and **S-12c** (90% and 88%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12c liquid (0.7 g, 90%); $[\alpha]^{22}_D$ -56 (*c* 5.8, CH_3OH); elem. anal. found: C, 42.12; H, 5.84; N, 7.12; S, 10.94; calcd for $C_{21}H_{33}F_6N_3O_6S_2$: C, 41.92; H, 5.53; N, 6.98; S, 10.66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.56 (s, 1H), 7.33 (s, 1H), 4.7 (dd, J_1 = 12.6 Hz, J_2 = 6.1 Hz, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 4.06 (d, *J* = 6.5 Hz, 1H), 2.4 (s, 1H), 2.21 (m, 3H), 1.84 (m, 3H), 1.41 (s, 3H), 1.24 (s, 9H), 0.82 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1,121.5, 121.2, 119.5 (q, J_{CF} = 320.6 Hz), 83.7, 83.5, 75.1, 65.3, 50.3, 41.2, 33, 30.8, 29.9, 29.6, 29.1, 25.6, 22.3, 22.2, 18.7, 13.7; IR (KBr) ν (cm^{-1}): 3498.24, 3153.04, 2958.27, 2937.06, 2867.63, 1556.27, 1461.78, 1349.93, 1195.65, 1137.8, 1056.8, 985.44, 925.66, 825.44, 790.67, 740.53, 649.89, 615.18, 572.75, 512.97; EI-HRMS *m/z* [M^+] calcd for $C_{40}H_{66}F_6N_5O_8S_2$ 922.42515, found 922.42319. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25317.

S-12c liquid (0.5 g, 88%); $[\alpha]^{22}_D$ 54 (*c* 5.8, CH_3OH); elem. anal. found: C, 42.20; H, 5.90; N, 7.20; S, 10.98; calcd for $C_{21}H_{33}F_6N_3O_6S_2$: C, 41.92; H, 5.53; N, 6.98; S, 10.66%;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.57 (s, 1H), 7.33 (s, 1H), 4.74 (dd, J_1 = 12.8 Hz, J_2 = 6.4 Hz, 1H), 4.2 (t, *J* = 7.4 Hz, 2H), 4.09 (d, *J* = 6.5 Hz, 1H), 2.44 (s, 1H), 2.25 (s, 2H), 2.14 (1H, m), 1.88 (m, 3H), 1.45 (s, 3H), 1.28 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 122.4, 121.7, 119.6 (q, J_{CF} = 320.8 Hz), 83.9, 83.6, 75.1, 64.9, 50.1, 41.2, 32.8, 30.8, 29.8, 29.5, 29, 25.6, 22.1, 22.1, 18.7, 13.6; IR (KBr) ν (cm^{-1}): 3504.02, 3153.04, 2958.27, 2937.06, 2867.63, 1629.55, 1556.27, 1461.78, 1349.93, 1137.8, 1058.73, 985.44, 925.66, 894.8, 858.16, 825.38, 790.67, 740.53, 651.82, 512.97, 430.04, 404.97.

General procedure for the synthesis of 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium methyl sulfate (R-12d) and 3-hexyl-1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)imidazolium methyl sulfate (S-12d).

To a stirred solution of **R-11b** or **S-11b** in methanol (10 mL), sodium methyl sulfate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-12d** and **S-12d** (73% and 65%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12d liquid (0.4 g, 73%); $[\alpha]^{22}_{D}$ -53 (*c* 3.3, CH_3OH); elem. anal. found: C, 55.72; H, 8.64; N, 6.70; S, 7.64; calcd for $C_{20}H_{36}N_2O_6S$: C, 55.53; H, 8.39; N, 6.48; S, 7.41%; ^{1}H NMR (400 MHz, D_2O): δ 7.53 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 4.63 (dd, J_1 = 12.8 Hz, J_2 = 6.2 Hz, 1H), 4.14 (t, *J* = 7 Hz, 2H), 4.01 (d, *J* = 6.5 Hz, 1H), 3.25 (s, 3H), 2.37 (m, 1H), 2.25 (m, 2H), 2.06 (t, *J* = 12.3 Hz), 1.8 (m, 3H), 1.36 (s, 3H), 1.19 (s, 9H), 0.79 (s, 3H), 0.74 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 122.4, 121.8, 83.9, 83.6, 74.8, 64.3, 55.2, 49.7, 40.8, 32.8, 30.2, 29.1, 29, 28.8, 24.9, 21.7, 21.6, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3380.6, 3133.76, 3070.12, 2933.2, 2863.77, 1558.2, 1459.85, 1369.21, 1228.43, 1164.79, 1137.8, 1045.23, 1012.45, 750.17; EI-HRMS *m/z* [M^+] calcd for $C_{39}H_{69}N_4O_8S$753.48306, found 753.48145. Calcd for $C_{19}H_{33}N_2O_2$ 321.25365, found 321.25332.

S-12d liquid (0.4 g, 65%); $[\alpha]^{23}_{D}$ 55 (*c* 3.1, CH_3OH); elem. anal. found: C, 55.80; H, 8.70; N, 6.75; S, 7.70; calcd for $C_{20}H_{36}N_2O_6S$: C, 55.53; H, 8.39; N, 6.48; S, 7.41%; ^{1}H NMR (400 MHz, D_2O): δ 7.55 (d, *J* = 1.9 Hz, 1H), 7.5 (d, *J* = 1.9 Hz, 1H), 4.66 (dd, J_1 = 12.9 Hz, J_2 = 6.2 Hz, 1H), 4.17 (t, *J* = 7 Hz, 2H), 4.04 (d, *J* = 6.6 Hz, 1H), 3.65 (s, 3H), 2.4 (m, 1H), 2.25 (m, 2H), 2.08 (t, *J* = 12.3 Hz, 1H), 1.83 (m, 3H), 1.38 (s, 3H), 1.21 (s, 9H), 0.81 (s, 3H), 0.76 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, D_2O): δ 122.4, 121.8, 83.9, 83.6, 74.8, 64.3, 55.3, 49.7, 40.9, 32.9, 30.2, 29.1, 29, 28.8, 24.9, 21.7, 21.7, 18.8, 13.2; IR (KBr) ν (cm^{-1}): 3384.46, 3129.9, 3064.33, 2933.2, 2863.77, 1558.2, 1459.85, 1384.64, 1369.21, 1297.86, 1228.43, 1160.94, 1139.72, 1045.23, 1012.45, 931.45, 752.1, 661.46, 578.54, 551.54.

General procedure for the synthesis of 1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium trifluoroacetate (R-12e) and 1-((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium trifluoroacetate (S-12e).

To a stirred solution of **R-11c** or **S-11c** in methanol (5 mL), sodium trifluoroacetate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-12e** and **S-12e** (88% and 19%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12e liquid (0.2 g, 88%); $[\alpha]^{23}_{D}$ -42 (*c* 1.1, CH_3OH); elem. anal. found: C, 59.94; H, 8.34; N, 6.30; calcd for $C_{23}H_{37}F_3N_2O_4$: C, 59.72; H, 8.06; N, 6.06%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81(s, 1H), 7.72 (s, 1H), 7.33 (s, 1H), 4.93 (dd, J_1 = 11.8 Hz, J_2 = 6.8 Hz, 1H), 4.14 (m, 2H), 3.97 (d, *J* = 6.2 Hz, 1H), 2.29 (m, 1H), 2.15 (m, 3H), 1.8 (m, 3H), 1.34 (s, 3H), 1.16 (m, 13H), 0.77 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (q, *J* = 33 Hz) 137.1, 122.3, 120.9, 117 (q, *J* = 295 Hz), 83.6, 82.8, 74.4, 64.2, 49.9, 41.4, 33.1, 31.5, 29.9, 29.8, 29.2, 28.8, 28.7, 26, 22.4, 22.1, 19.6, 13.9; IR (KBr) ν (cm^{-1}): 3355.53, 3137.62, 3095.19, 2931.27, 2859.92, 1685.48, 1562.06, 1461.78, 1419.35, 1375, 1301.72, 1201.43, 1172.51, 1133.94, 1074.16, 1045.23, 987.37, 829.24, 800.31, 754.03, 719.31, 647.96; EI-HRMS *m/z* [M^+] calcd for $C_{44}H_{74}F_3N_4O_6$ 811.55550, found 811.55279. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28431.

S-12e liquid (0.06 g, 19%); $[\alpha]^{22}_{D}$ 43 (*c* 1.2, CH_3OH); elem. anal. found: C, 59.95; H, 8.40; N, 6.35; calcd for $C_{23}H_{37}F_3N_2O_4$: C, 59.72; H, 8.06; N, 6.06%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 7.58 (s, 1H), 7.26 (s, 1H), 4.92 (dd, J_1 = 11.1 Hz, J_2 = 8.2 Hz, 1H), 4.27 (dt, J_1 = 7.2 Hz, J_2 = 3.9 Hz, 2H), 4.07 (d, *J* = 6.5 Hz, 1H), 2.4 (m, 1H), 2.26 (m, 2H), 2.22 (m, 1H), 1.89 (m, 3H), 1.44 (s, 3H), 1.26 (m, 13H), 0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (q, *J* = 30 Hz,), 137.4, 122.3, 120.8, 117 (q, *J* = 295 Hz), 83.7, 82.9, 74.7, 65, 50, 41.4, 33.2, 31.6, 30, 29.8, 29.5, 28.9, 28.8, 26.1, 22.5, 22.4, 19.3, 14; IR (KBr) ν (cm^{-1}): 3409.53, 3143.4, 2931.27, 2859.92, 1681.62, 1560.13, 1461.78, 1428.99, 1388.5, 1301.72, 1203.36, 1135.87, 1074.16, 1045.23, 8339, 802.24, 721.24, 6463.

General procedure for the synthesis of 1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (R-12f) and 1-((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (S-12f).

To a stirred solution of **R-11c** or **S-11c** in methanol (5 mL), lithium bis(trifluoromethanesulfonyl)imide (1.1 equiv) was added and the resulting mixture was stirred at rt for 24 h. After removing the solvent by rotatory evaporation, the residue was dissolved in dichloromethane and kept at -20 °C for 12 h. The formed solid was filtered and the filtrate was evaporated by rotary evaporation to afford **R-12f** and **S-12f** (96% and 62%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12f liquid (0.37 g, 96%); $[\alpha]^{19}_{D}$ -20 (*c* 2.9, CH_3OH); elem. anal. found: C, 44.12; H, 6.14; N, 6.80; S, 10.28; calcd for $C_{23}H_{37}F_6N_3O_6S_2$: C, 43.87; H, 5.92; N, 6.67; S, 10.18%; ^{1}H NMR (400 MHz, CD_3OD): δ 8.95 (s, 1H), 7.71 (t, *J* = 1.7 Hz, 1H), 7.64 (t, *J* = 1.7 Hz, 1H), 4.78 (m, 1H), 4.25 (t, *J* = 7.3 Hz, 2H), 4.04 (d, *J* = 6.5 Hz, 1H), 2.44 (m, 1H), 2.32 (m, 1H), 2.24 (m, 2H), 1.93 (m, 3H), 1.47 (s, 3H), 1.29 (m, 13H), 0.91 (t, *J* = 6.9 Hz, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 135.4, 122.5, 121.6, 119.8 (q, *J* = 320.6 Hz), 83.8, 82.7, 74.2, 64.9, 49.6, 41.4, 32.8, 31.4, 29.7, 28.9, 28.8, 28.7, 28.5, 25.8, 22.2, 21.5, 18.7, 13; IR (KBr) ν (cm^{-1}): 3511.74, 3149.19, 3112.55, 2931.27, 2859.92, 1562.06, 1535.06, 1461.78, 1351.86, 1195.65, 1137.8, 1058.73, 987.37, 927.59, 786.81, 761.74, 740.53, 653.75, 615.18, 570.82, 512.97; EI-HRMS *m/z* [M^+] calcd for $C_{44}H_{74}F_6N_5O_8S_2$ 978.48775, found 978.48555. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28419.

S-12f liquid (0.21 g, 62%); $[\alpha]^{22}_{D}$ 19 (*c* 2.8, CH_3OH); elem. anal. found: C, 44.15; H, 6.20; N, 6.84; S, 10.30; calcd for $C_{23}H_{37}F_6N_3O_6S_2$: C, 43.87; H, 5.92; N, 6.67; S, 10.18%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 1 Hz, 1H), 7.58 (t, *J* = 1.6 Hz, 1H), 7.33 (s, 1H), 4.72 (m, 1H), 4.19 (t, *J* = 7.5 Hz, 2H), 4.06 (d, *J* = 6.5 Hz, 1H), 2.43 (m, 1H), 2.24 (m, 1H), 2.14 (m, 2H), 1.86 (m, 3H), 1.43 (s, 3H), 1.27 (m, 13H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.81 (s, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 122.4, 121.6, 119.6 (q, *J* = 320.7 Hz), 84.1, 83.6, 75.3, 65, 50.2, 41.2, 32.8, 31.5, 30, 29.5, 29.1, 28.8, 28.7, 26, 22.5, 22.2, 18.6, 13.9; IR (KBr) ν (cm^{-1}): 3493.38, 3153.04, 2931.27, 2859.92, 1635.34, 1558.2, 1461.78, 1351.86, 1197.58, 1137.8, 1058.73, 985.44, 790.67, 740.53, 651.82, 617.1, 572.75, 512.97.

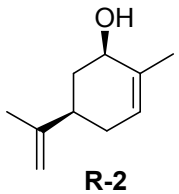
General procedure for the synthesis of 1-((1R,3R,4S,5R)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium methyl sulfate (R-12g) and 1-((1S,3S,4R,5S)-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-yl)-3-octylimidazolium methyl sulfate (S-12g).

To a stirred solution of **R-11c** or **S-11c** in methanol (5 mL), sodium methyl sulfate (1.1 equiv) was added. The resulting mixture was stirred at rt for 24 h. After removing the formed solid by filtration, the filtrate was evaporated by rotary evaporation to afford **R-12g** and **S-12g** (91% and 40%, respectively) as liquids which were dried by heating at 70 °C and stirring under high vacuum (2 x 10^{-1} Pa) for 48 h.

R-12g liquid (0.30 g, 91%); $[\alpha]^{23}_{D}$ -29 (*c* 1.8, CH_3OH); elem. anal. found: C, 57.58; H, 8.94; N, 6.30; S, 7.15; calcd for $C_{22}H_{40}N_2O_6S$: C, 57.36; H, 8.75; N, 6.08; S, 6.96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.72 (s, 1H), 7.35 (s, 1H), 4.74 (dd, J_1 = 12.1 Hz, J_2= 5.8 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 3.9 (d, *J* = 6.1 Hz, 1H), 3.55 (s, 3H), 2.22 (m, 2H), 2.05 (m, 2H), 1.79 (m, 3H), 1.31 (s, 3H), 1.09 (m, 13H), 0.71 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 123, 121.3, 83.6, 82.5, 74.5, 64.9, 54.2, 49.8, 41.5, 33.1, 31.5, 30.1, 29.9, 29.2, 28.9, 28.8, 26, 22.5, 22.4, 19.2, 13.9; IR (KBr) ν (cm^{-1}): 3405.67, 3137.62, 3100.97, 2929.34, 2857.99, 1562.06, 1533.13, 1461.78, 1371.14, 1249.65, 1226.5, 1137.8, 1106.94, 1060.66, 1014.37, 748.24, 611.32, 578.54, 553.47; EI-HRMS *m/z* [M^+] calcd for $C_{44}H_{77}N_4O_8S$ 809.54566, found 809.54292. Calcd for $C_{21}H_{37}N_2O_2$ 349.28495, found 349.28434.

S-12g liquid (0.15 g, 40%); $[\alpha]^{22}_{D}$ 30 (*c* 1.9, CH_3OH); elem. anal. found: C, 57.60; H, 8.98; N, 6.35; S, 7.10; calcd for $C_{22}H_{40}N_2O_6S$: C, 57.36; H, 8.75; N, 6.08; S, 6.96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.6 (s, 1H), 7.72 (d, *J* = 1.1 Hz, 1H), 7.36 (d, *J* = 1.3 Hz, 1H), 4.82 (dd, J_1 = 12.6 Hz, J_2 = 6.3 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 6.5 Hz, 1H), 3.71 (s, 3H), 2.34 (m, 2H), 2.21 (m, 2H), 1.95 (d, *J* = 6.8 Hz, 1H), 1.87 (m, 2H), 1.44 (s, 3H), 1.24 (m, 13H), 0.86 (t, *J* = 6.1 Hz, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 123, 121.2, 83.6, 82.6, 74.6, 65.2, 54.3, 49.9, 41.5, 33.2, 31.6, 30.1, 29.9, 29.3, 29, 28.9, 26.1, 22.6, 22.5, 19.2, 14; IR (KBr) ν (cm^{-1}): 3419.17, 3137.62, 3100.97, 2929.34, 2857.99, 2244.74, 1643.05, 1560.13, 1461.78, 1371.14, 1338.36, 1224.58, 1164.79, 1139.72, 1060.66, 1012.45, 921.8, 827.31, 740.53, 646.03, 611.32, 578.54, 553.47, 431.97.

NMR Spectra



R-2

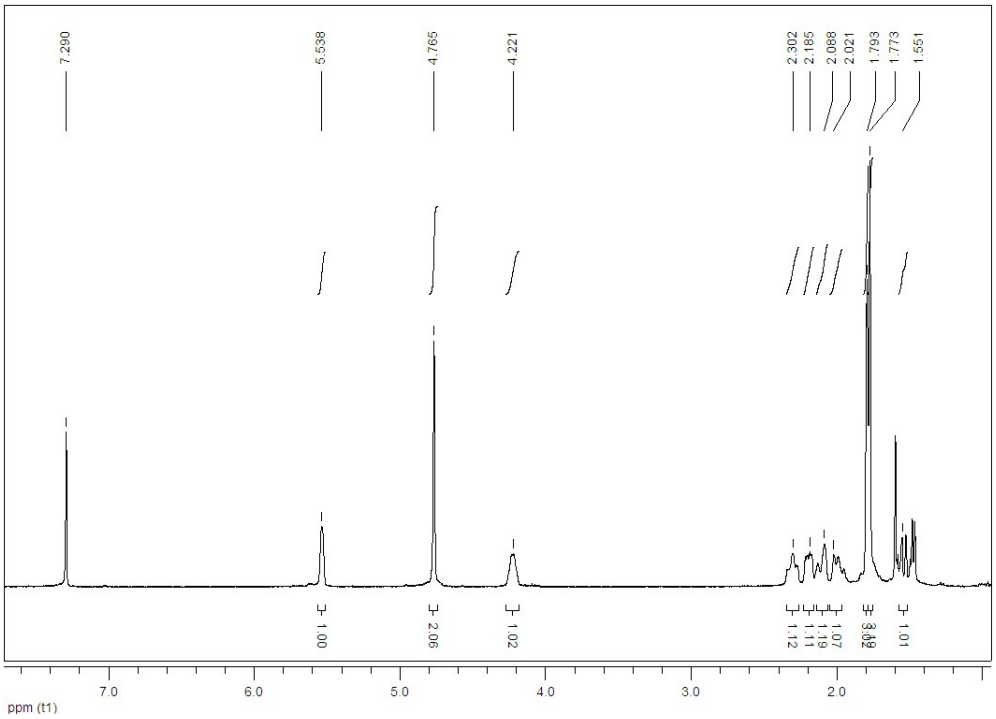


Figure S1- ^{1}H NMR spectrum of compound R-2

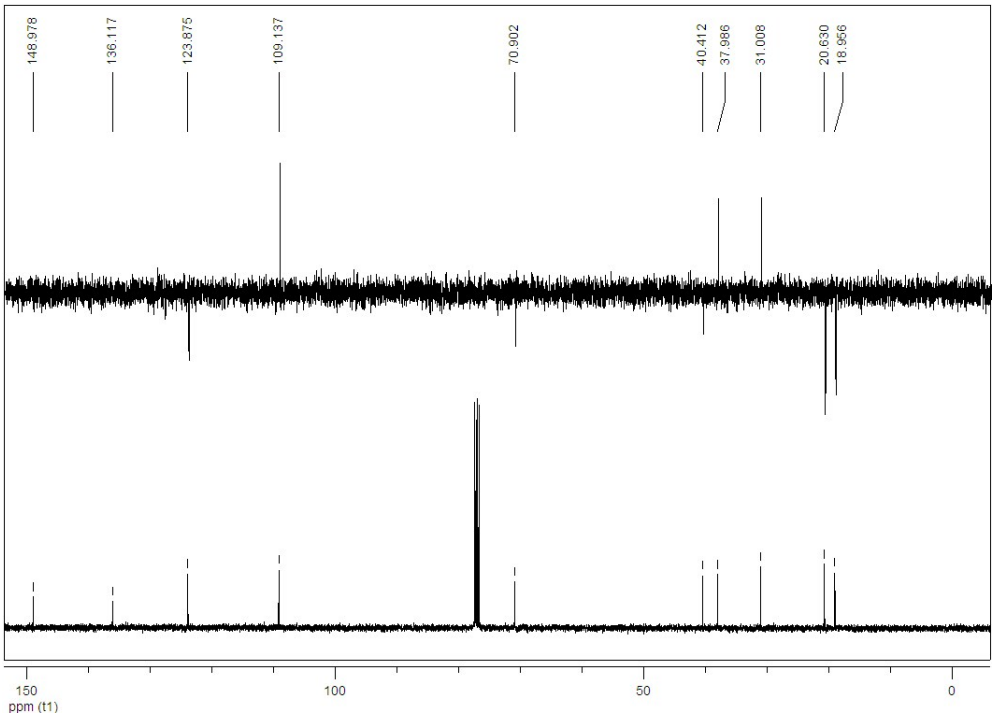
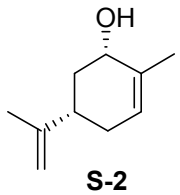


Figure S2- ^{13}C NMR and DEPT spectrum of compound R-2



S-2

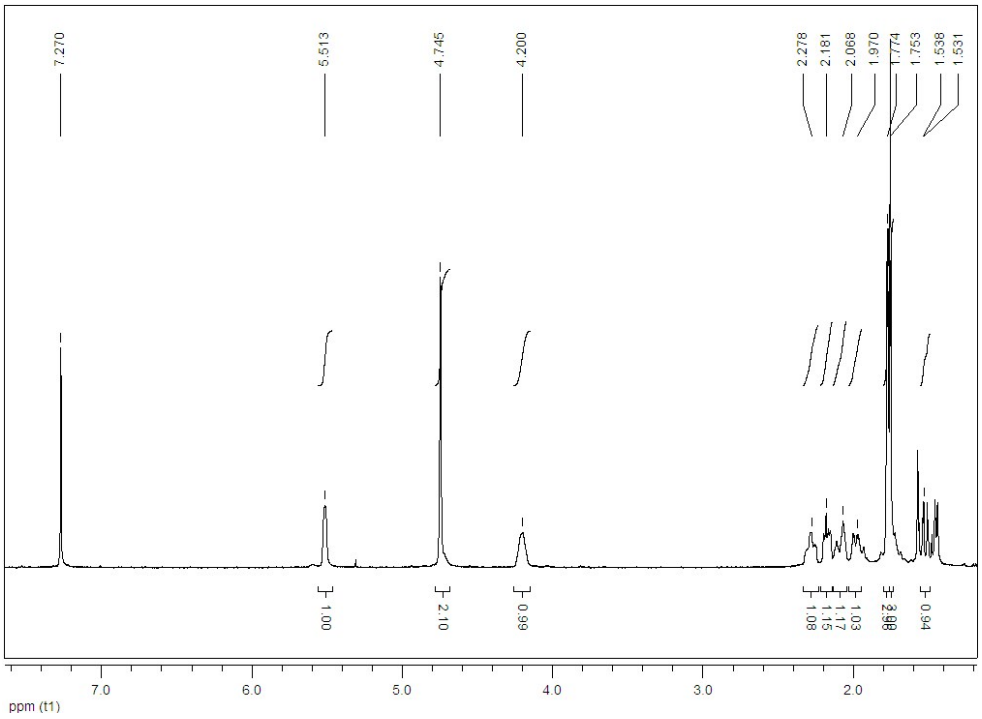


Figure S3- ^{1}H NMR spectrum of compound S-2

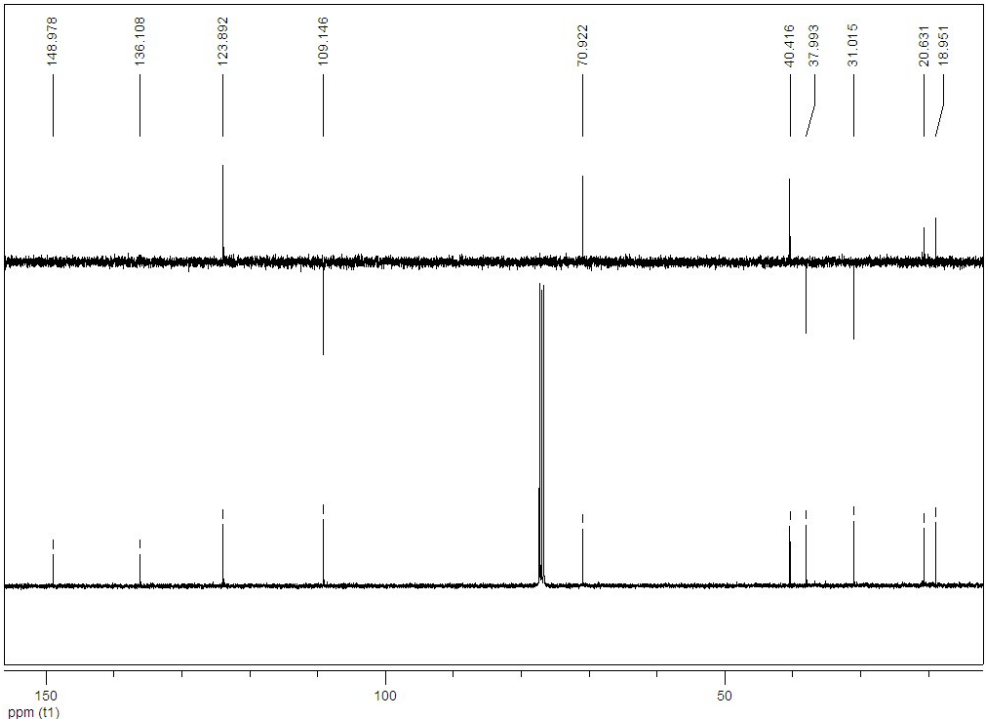
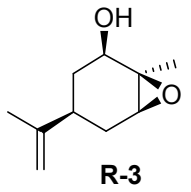


Figure S4- ^{13}C NMR and DEPT spectrum of compound S-2



R-3

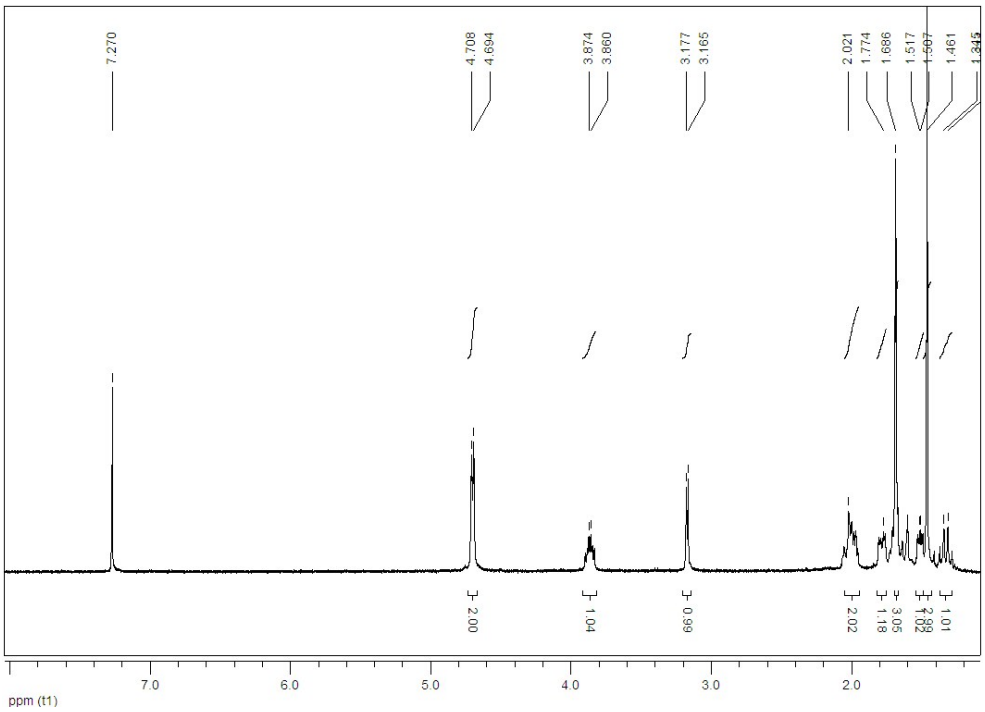


Figure S5- ^{1}H NMR spectrum of compound R-3

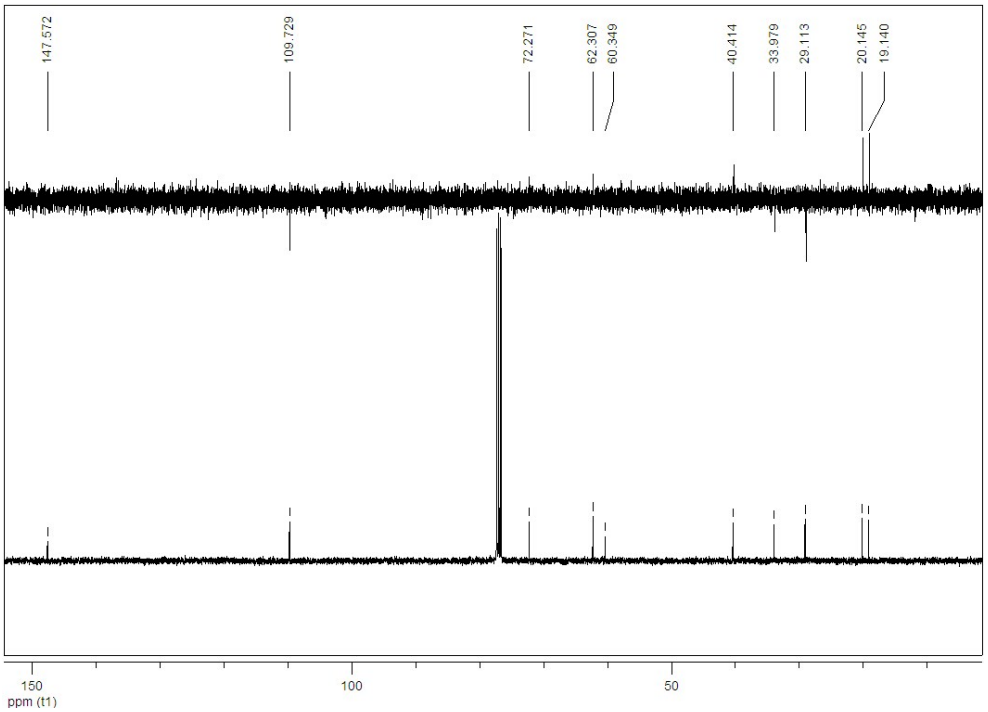
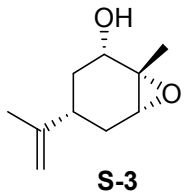


Figure S6- ^{13}C NMR and DEPT spectrum of compound R-3



S-3

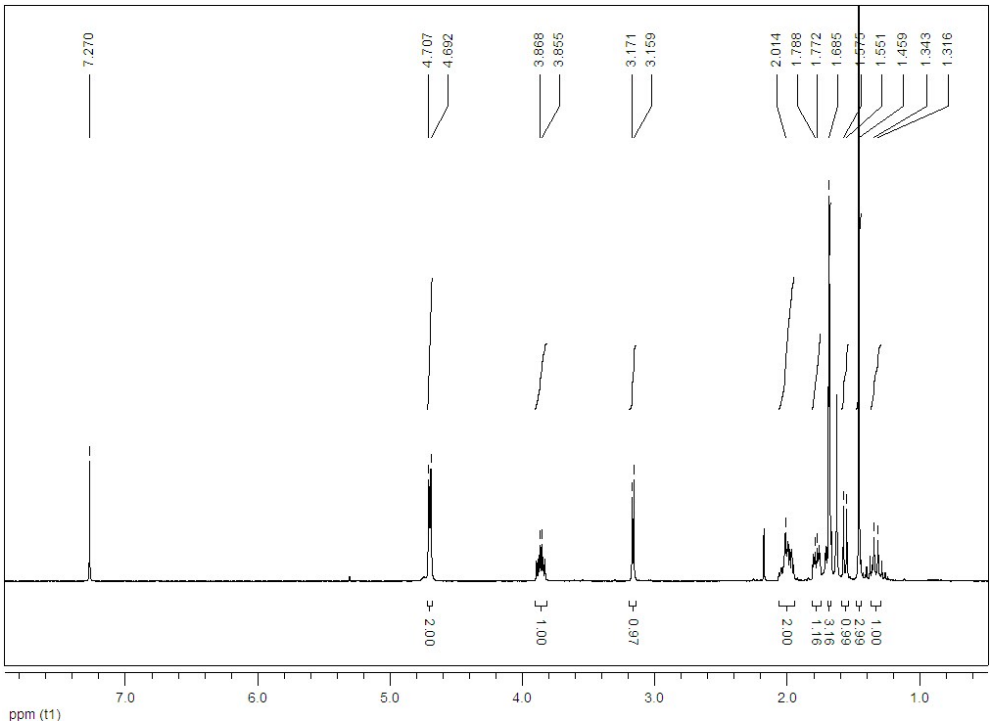


Figure S7- ^{1}H NMR spectrum of compound S-3

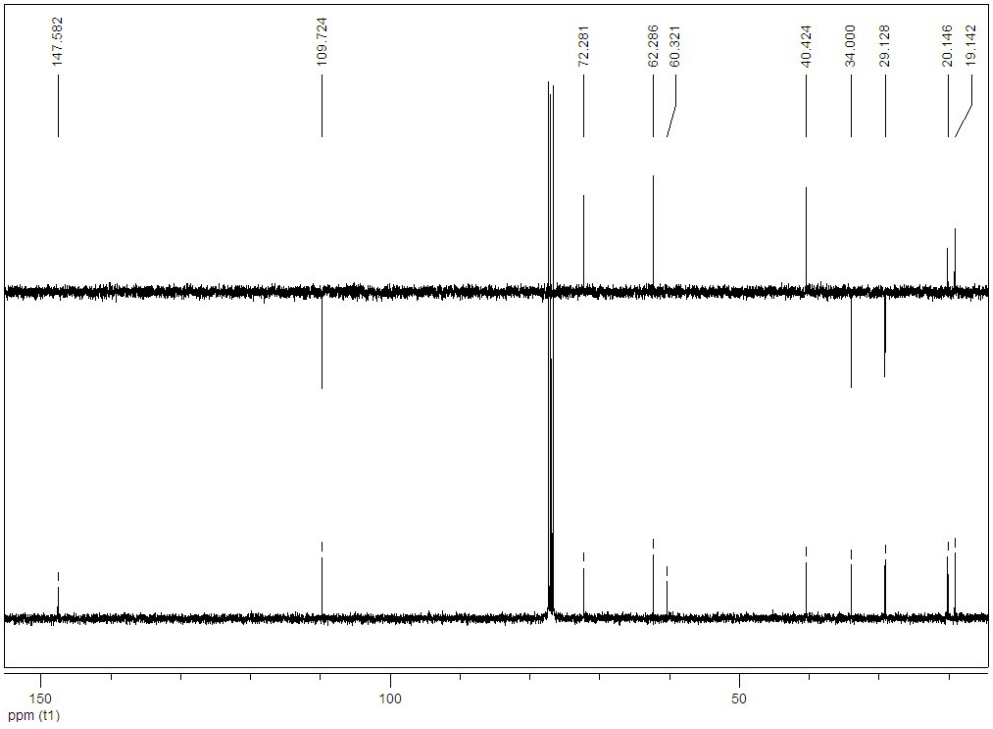
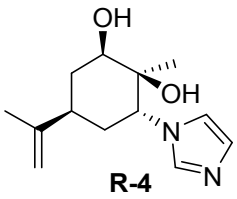


Figure S8- ^{13}C NMR and DEPT spectrum of compound S-3



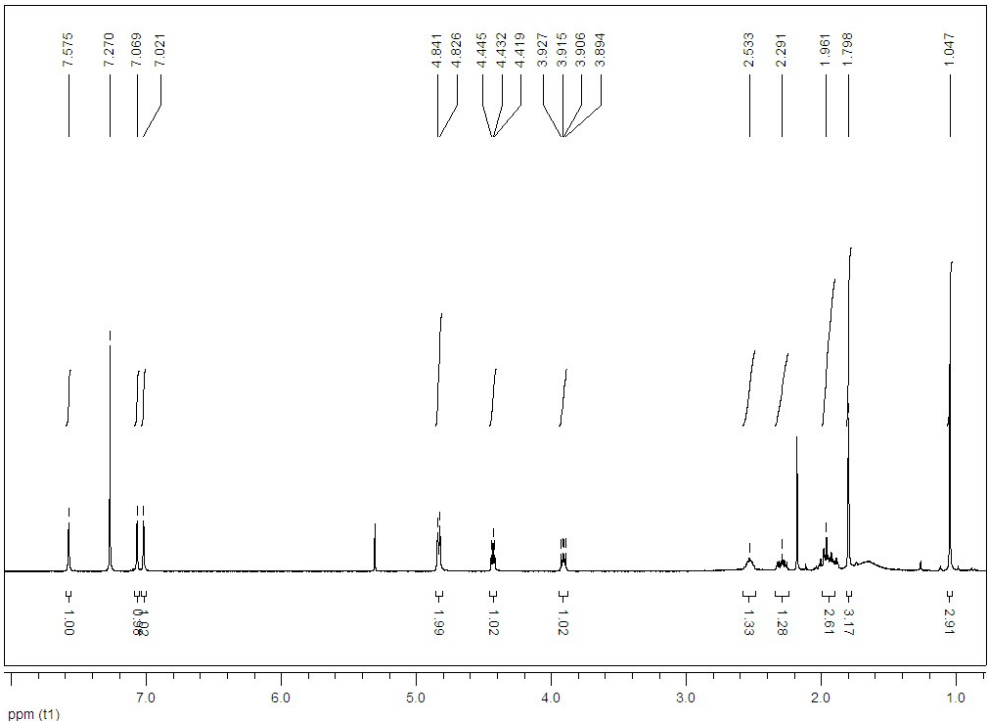


Figure S9- ^{1}H NMR spectrum of compound R-4

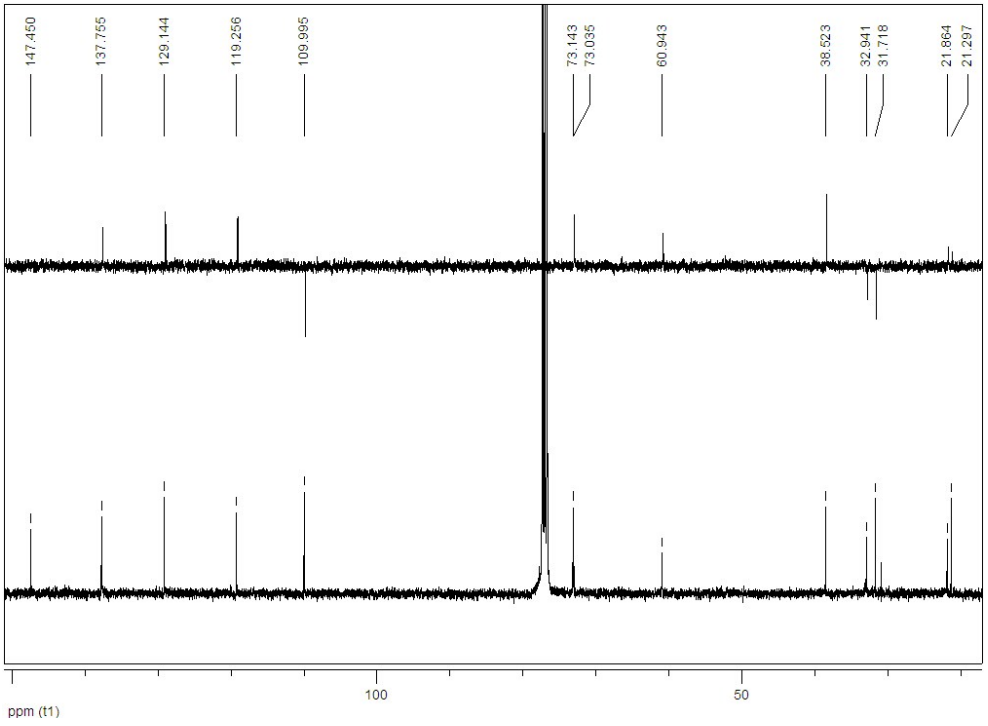
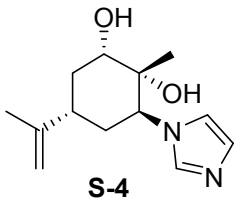


Figure S10- ^{13}C NMR and DEPT spectrum of compound R-4



S-4

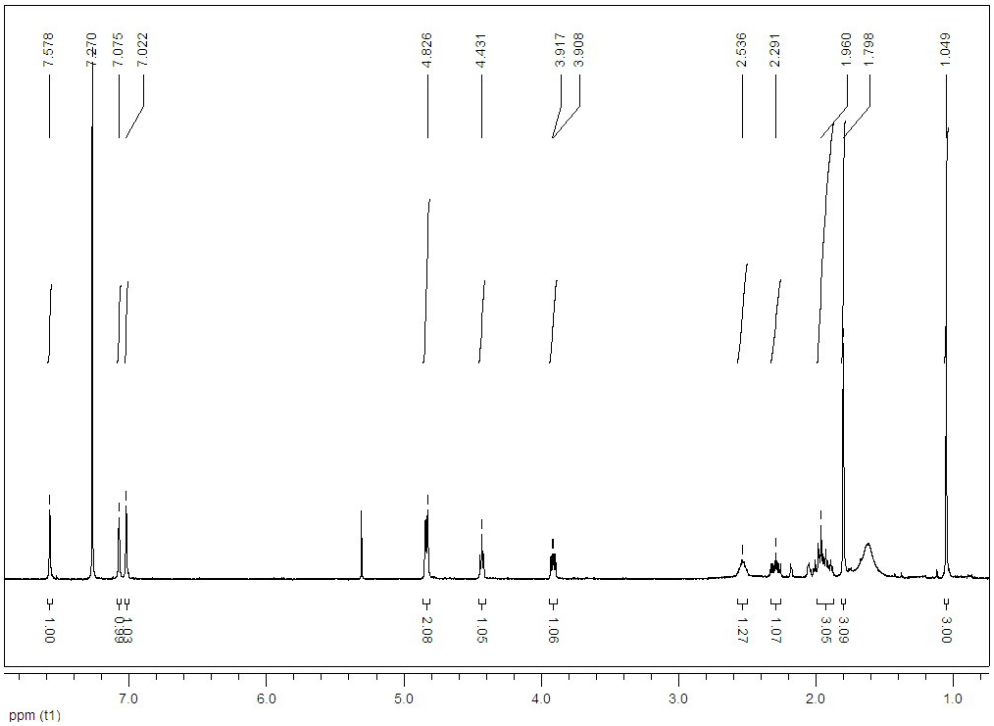


Figure S11- ^{1}H NMR spectrum of compound S-4

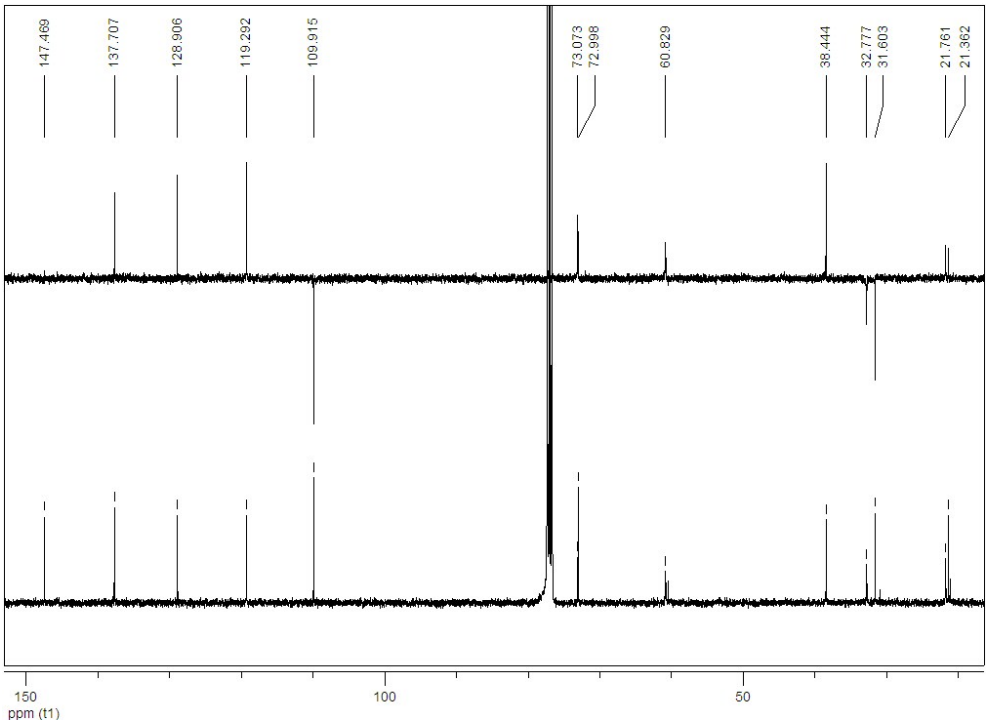
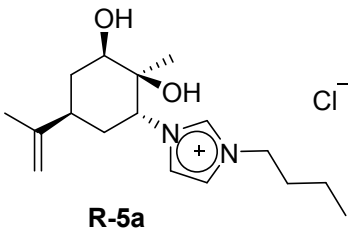


Figure S12- ^{13}C NMR and DEPT spectrum of compound S-4



R-5a

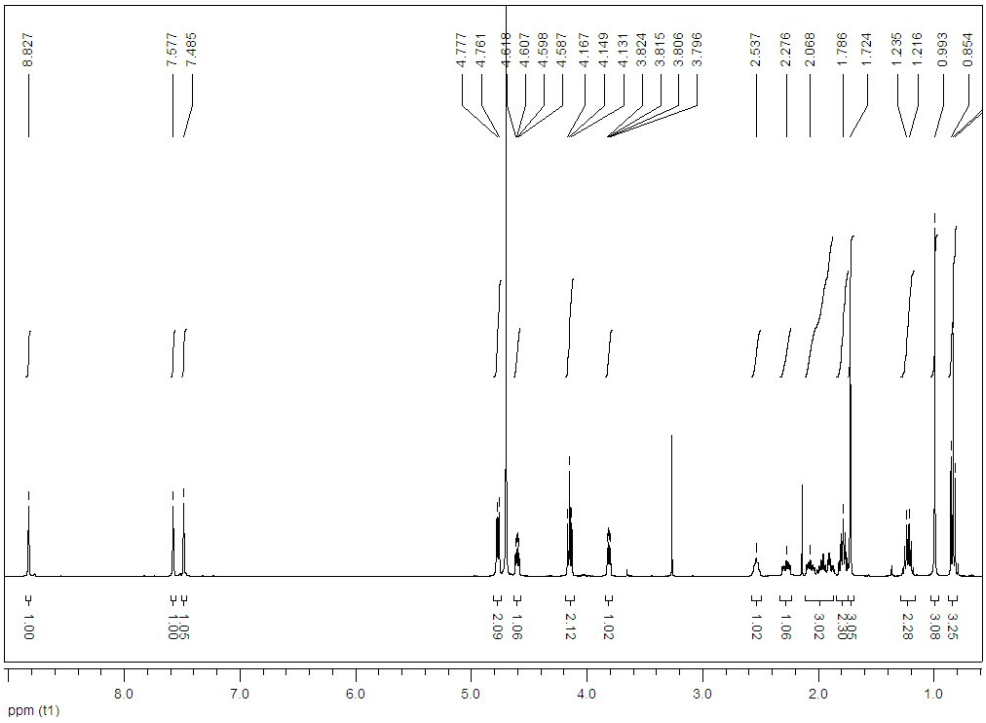


Figure S13- ^{1}H NMR spectrum of compound R-5a

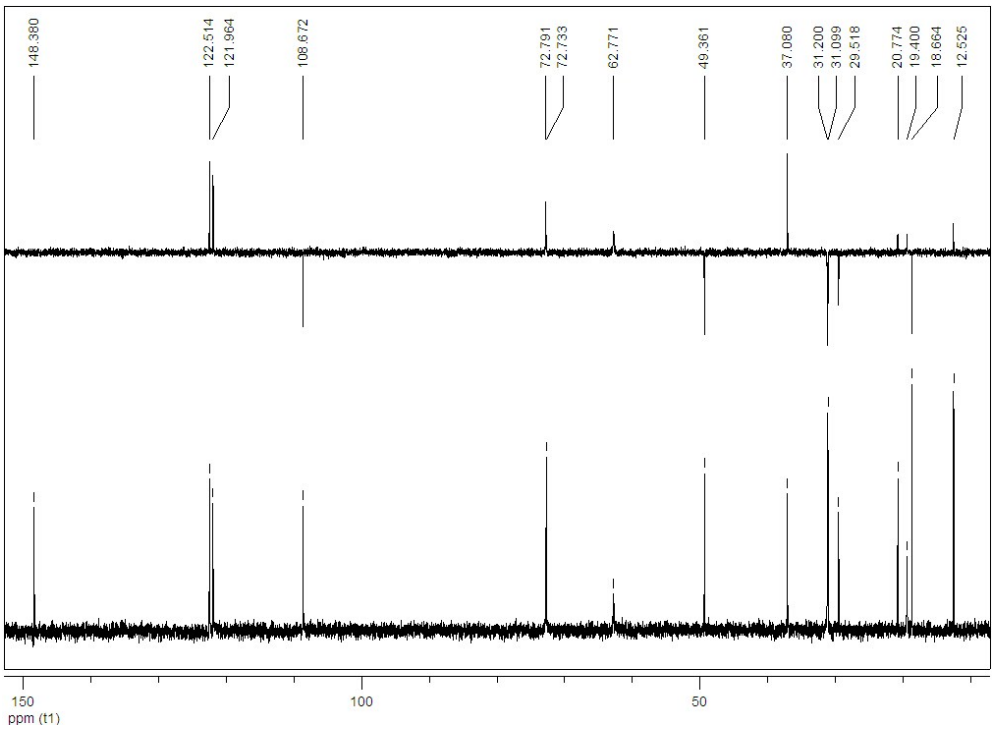


Figure S14- ^{13}C NMR and DEPT spectrum of compound R-5a

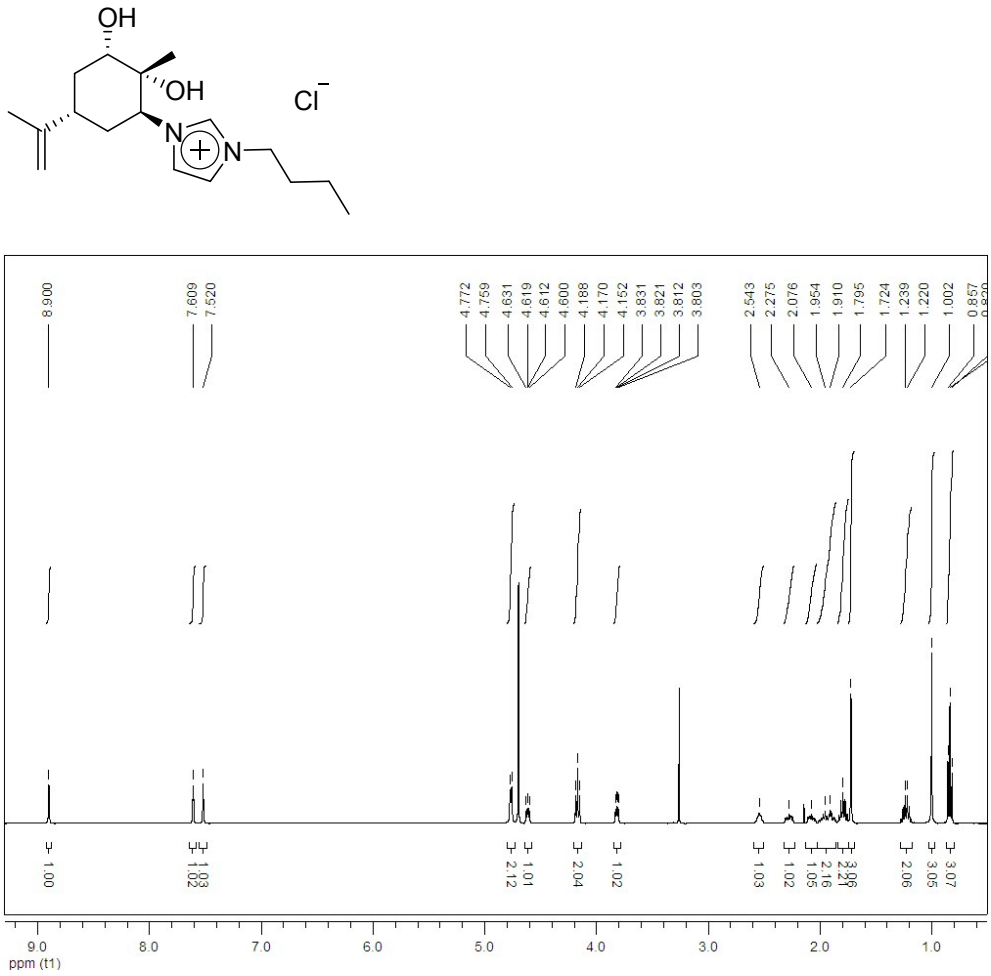


Figure S15- ^{1}H NMR spectrum of compound S-5a

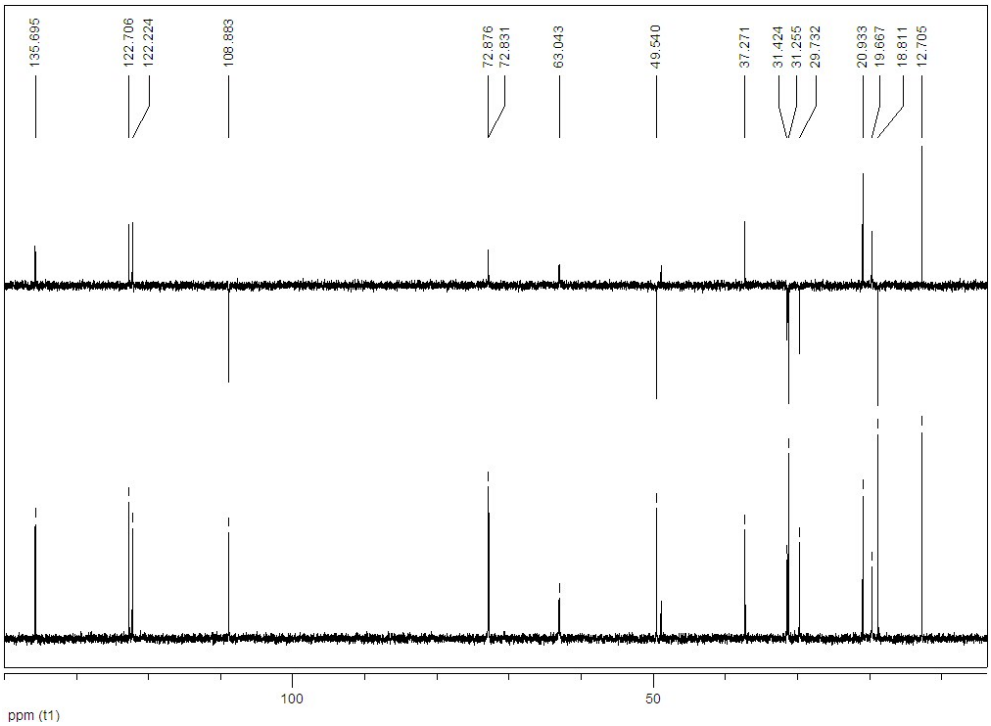
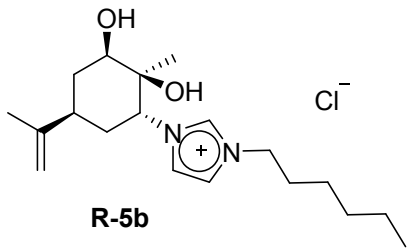


Figure S16- ^{13}C NMR and DEPT spectrum of compound S-5a



R-5b

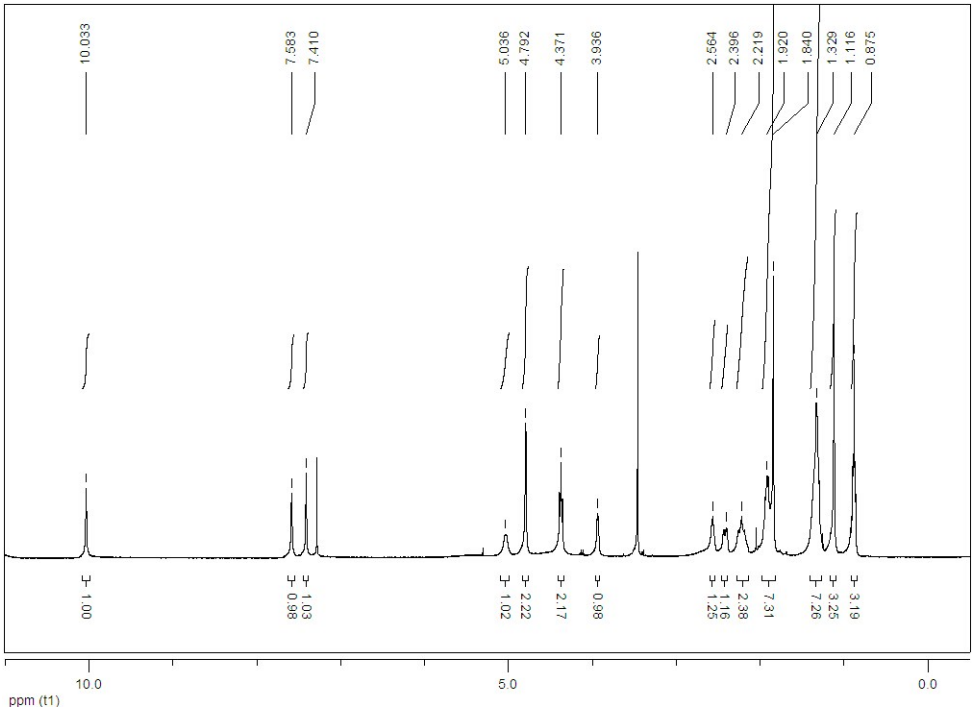


Figure S17- ^{1}H NMR spectrum of compound R-5b

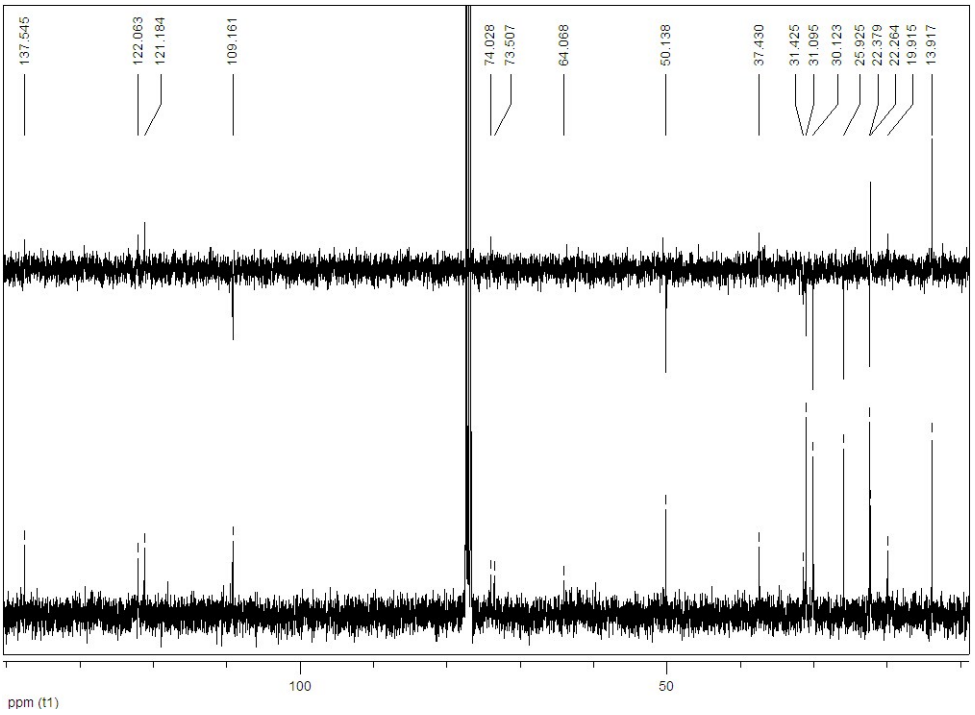
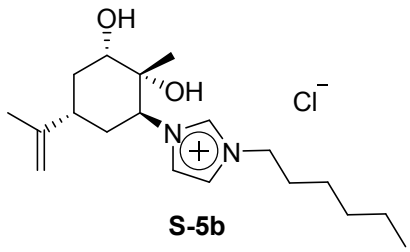


Figure S18- ^{13}C NMR and DEPT spectrum of compound R-5b



S-5b

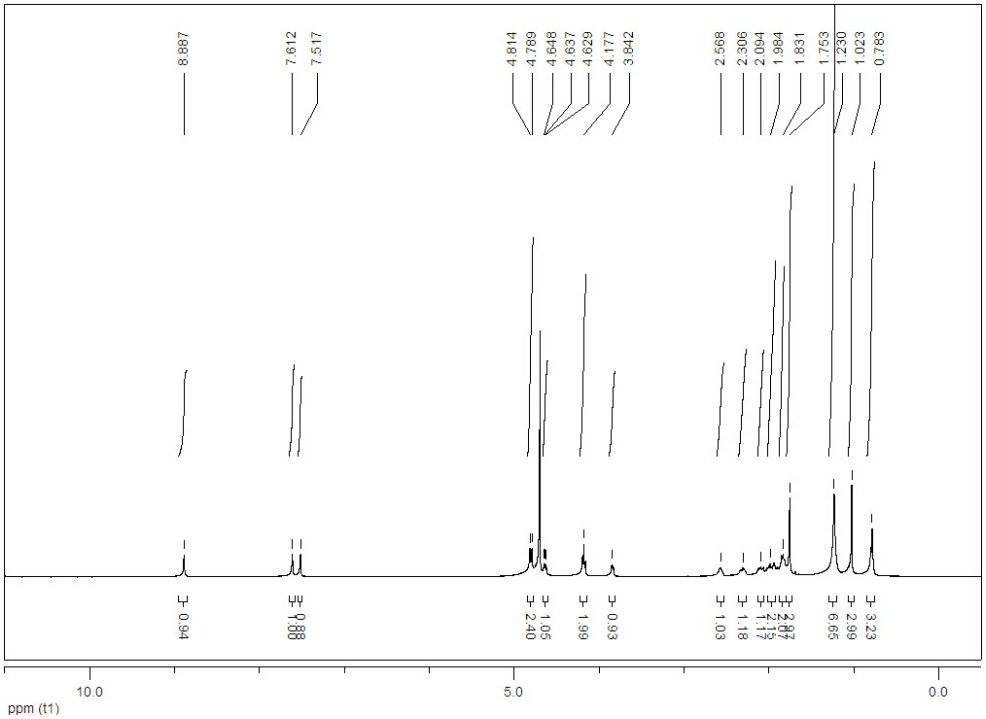


Figure S19- ^{1}H NMR spectrum of compound S-5b

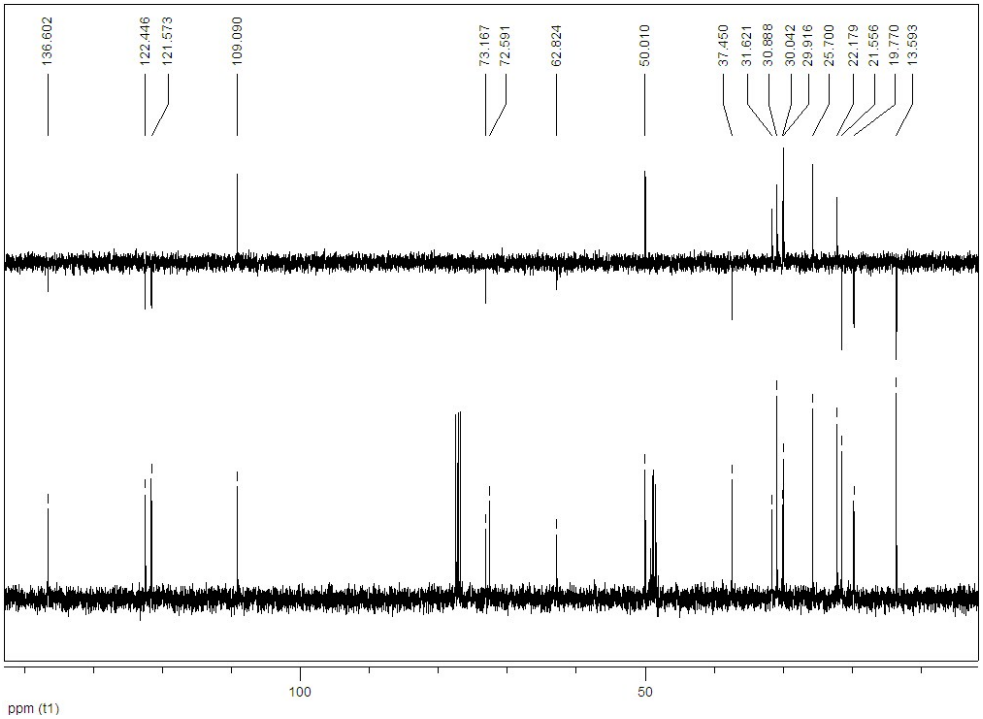
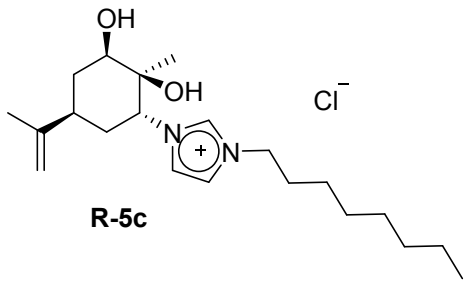


Figure S20- ^{13}C NMR and DEPT spectrum of compound S-5b



R-5c

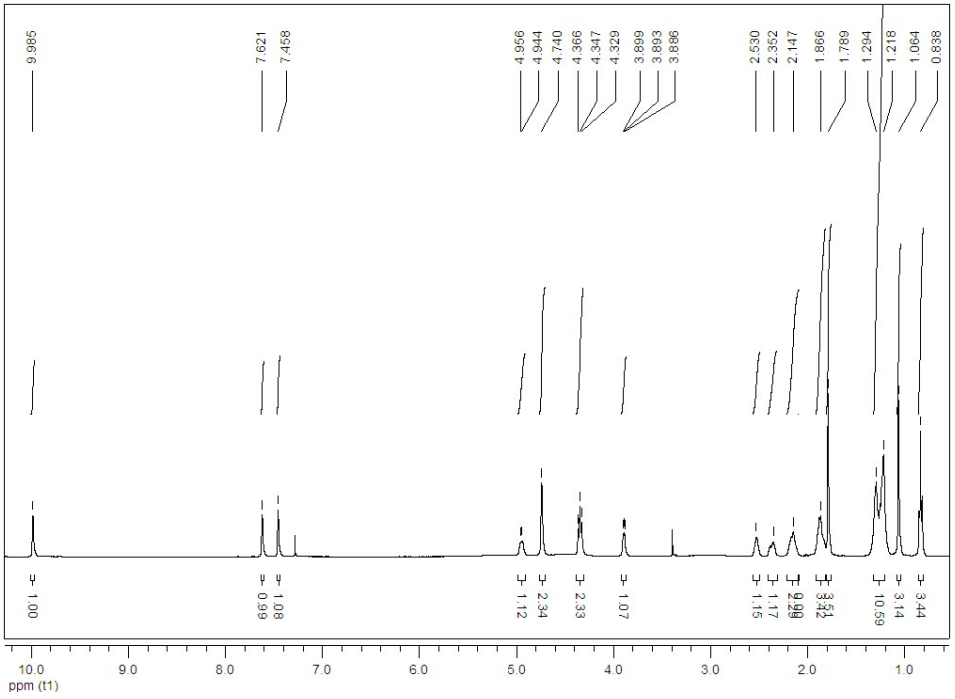


Figure S21- ^{1}H NMR spectrum of compound R-5c

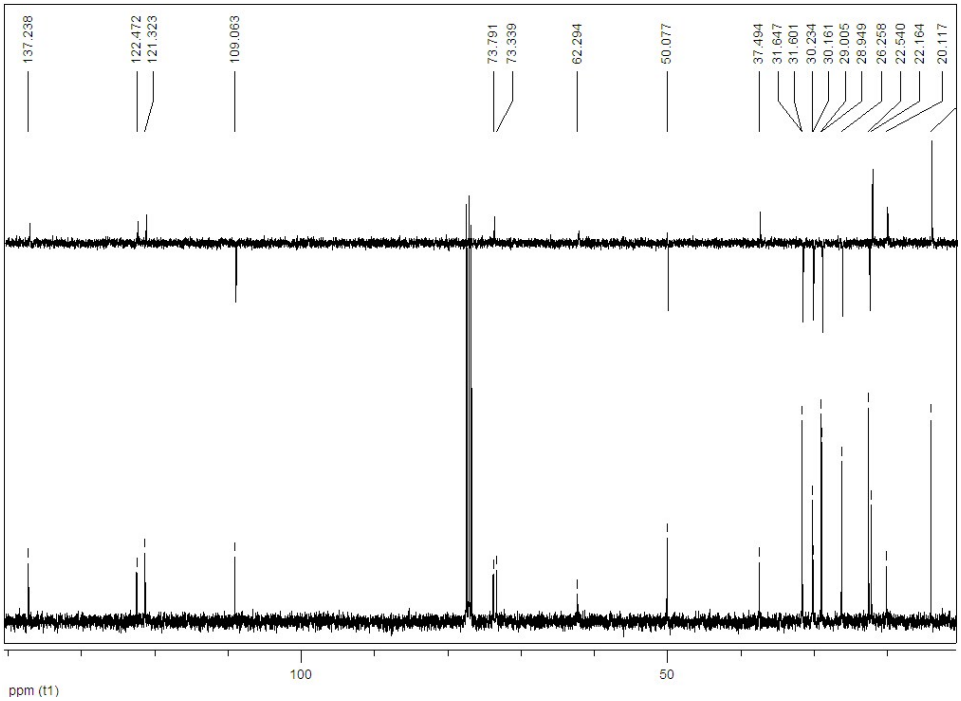
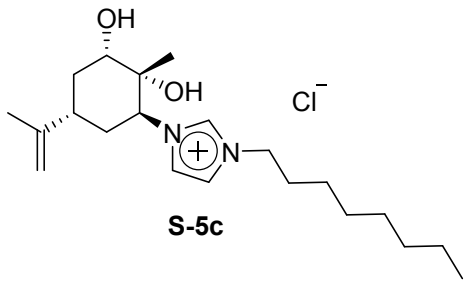


Figure S22- ^{13}C NMR and DEPT spectrum of compound R-5c



S-5c

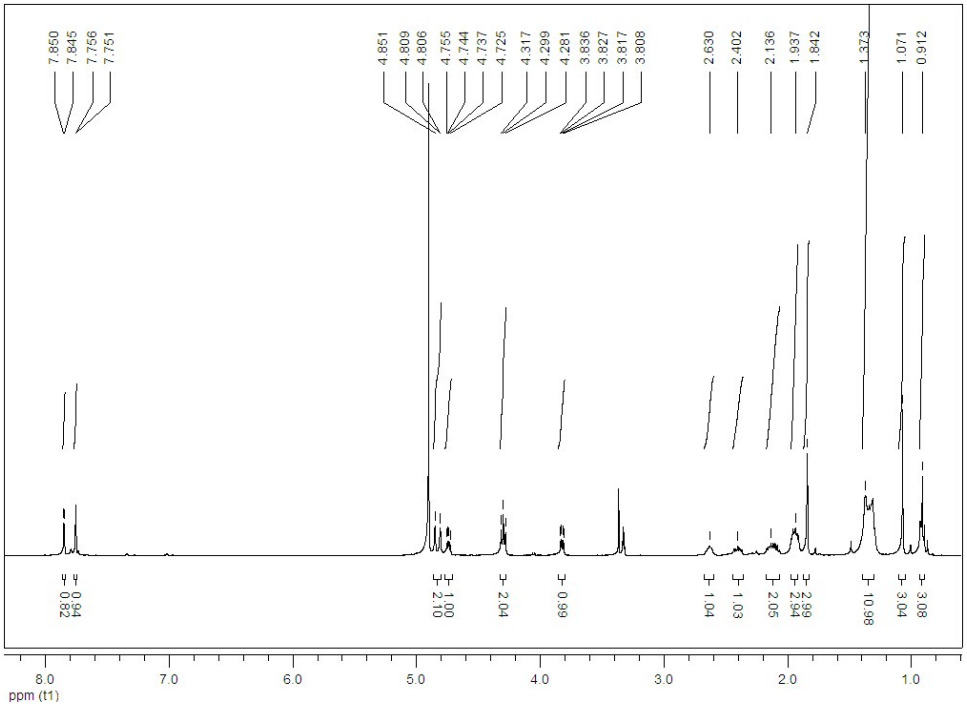


Figure S23- ^{1}H NMR spectrum of compound S-5c

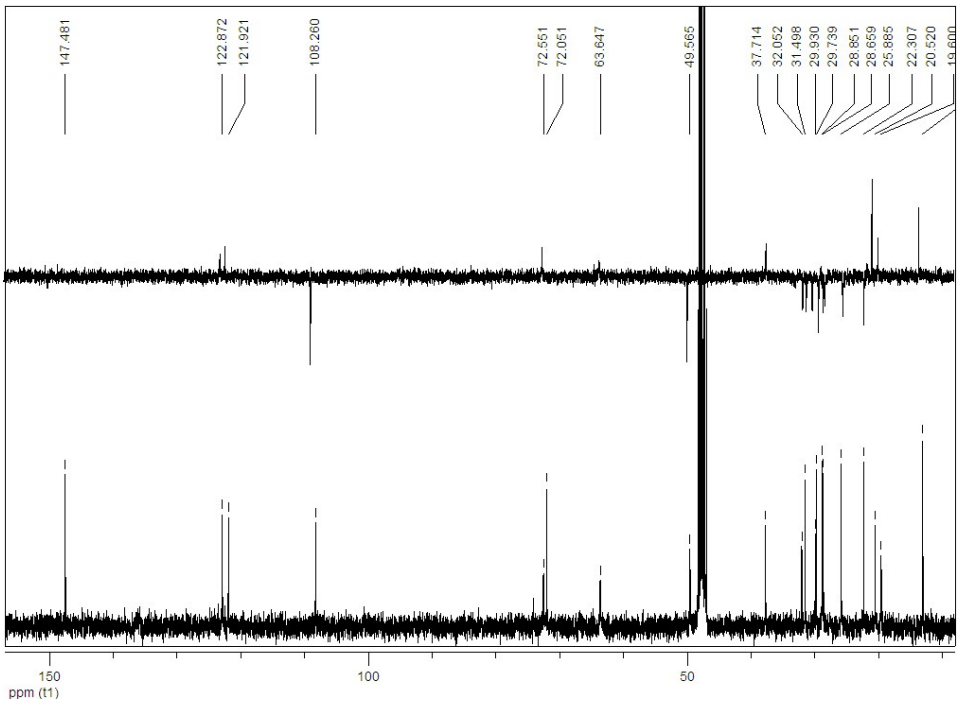
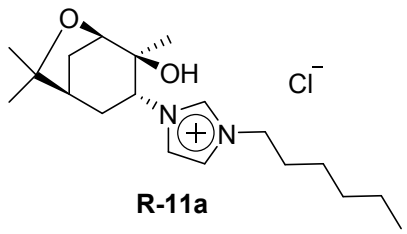


Figure S24- ^{13}C NMR and DEPT spectrum of compound S-5c



R-11a

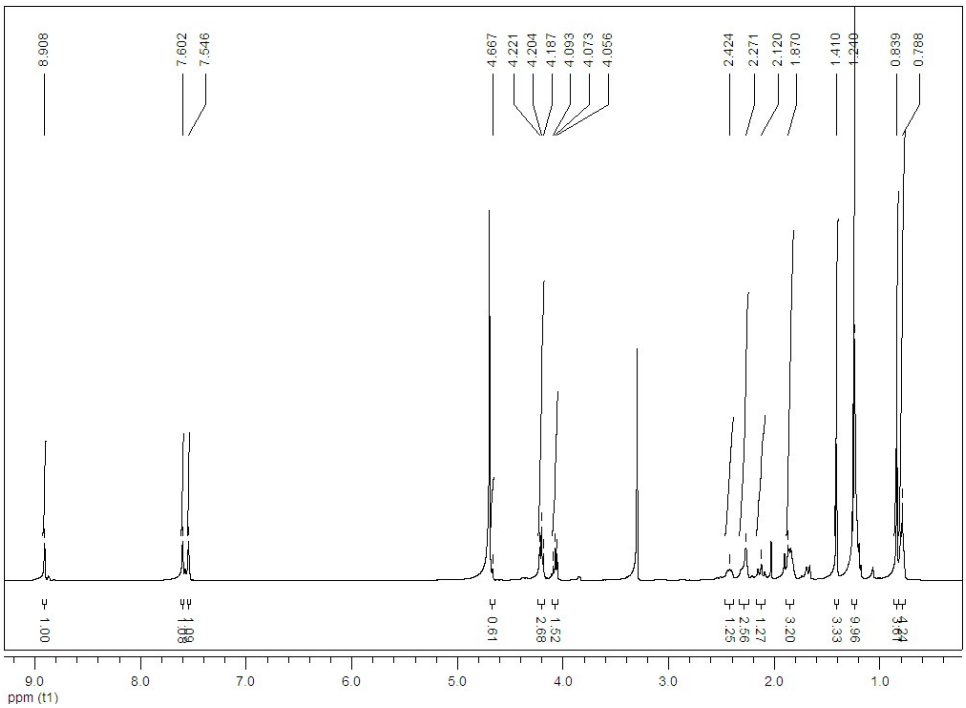


Figure S25- ^{1}H NMR spectrum of compound R-11a

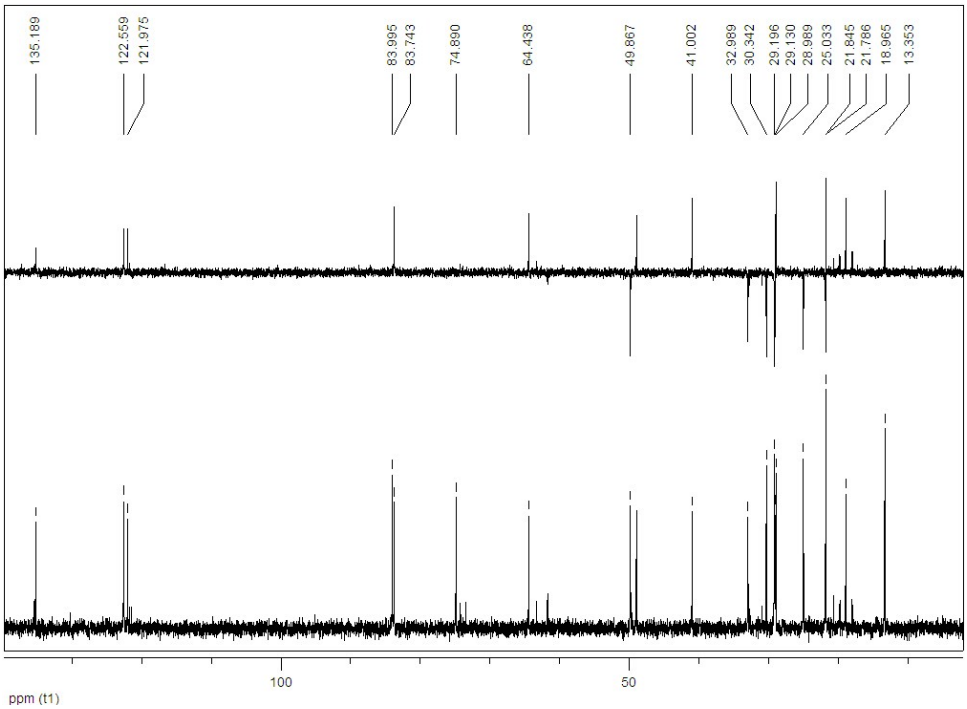
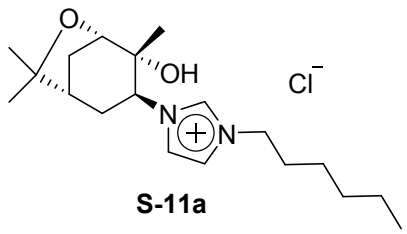


Figure S26- ^{13}C NMR and DEPT spectrum of compound R-11a



S-11a

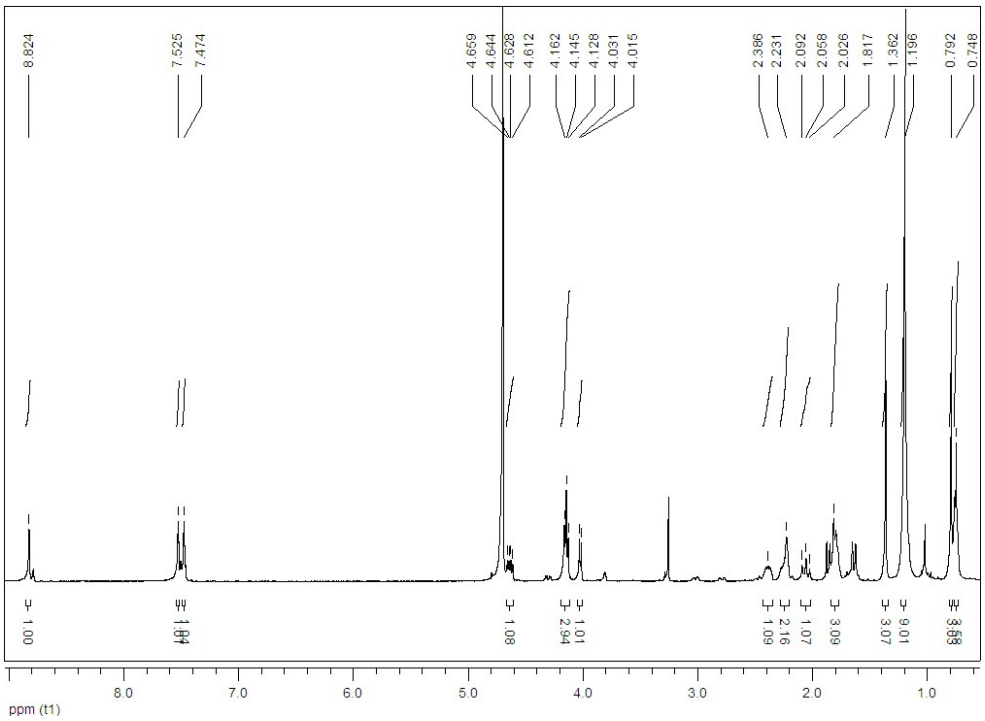


Figure S27- ^{1}H NMR spectrum of compound S-11a

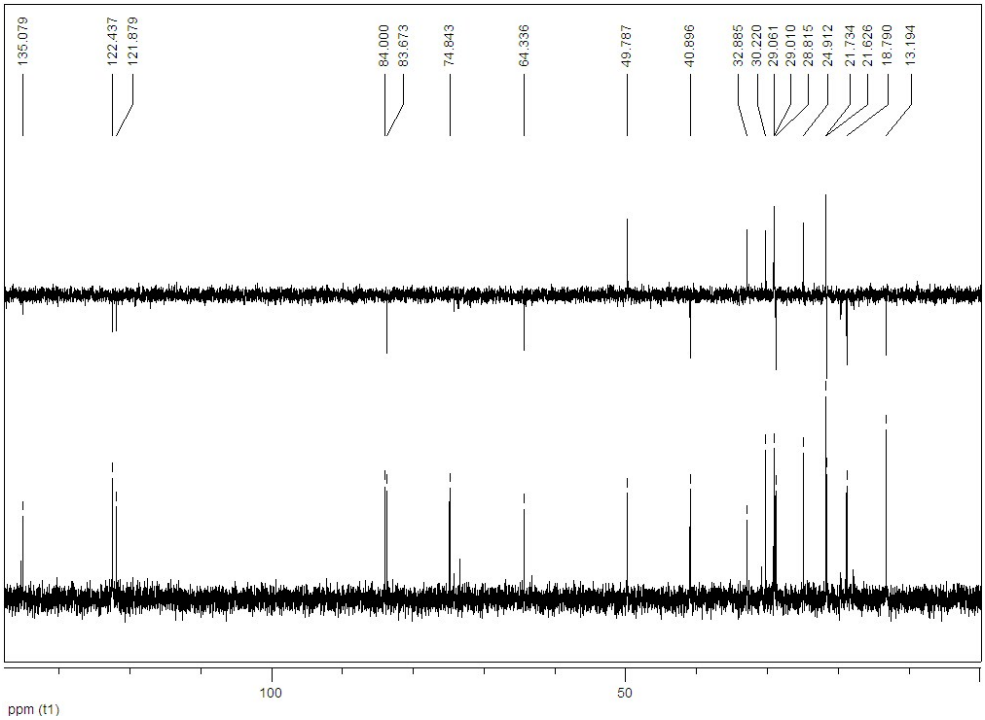
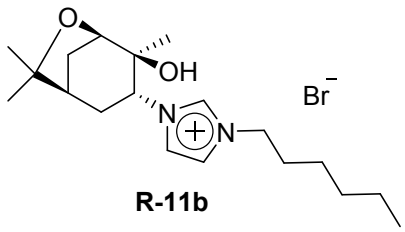


Figure S28- ^{13}C NMR and DEPT spectrum of compound S-11a



R-11b

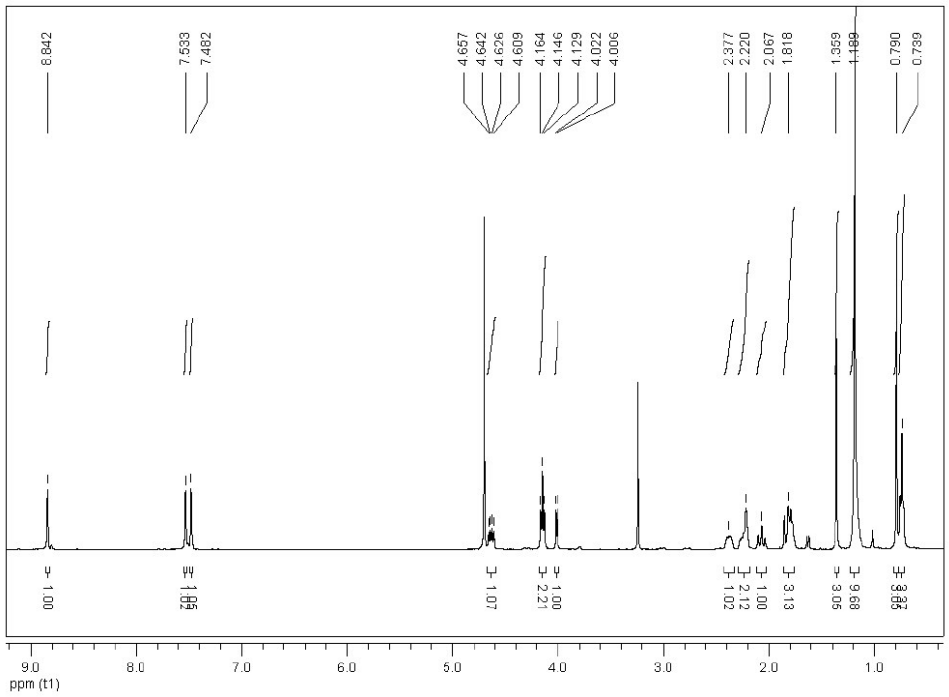


Figure S29- ^{1}H NMR spectrum of compound R-11b

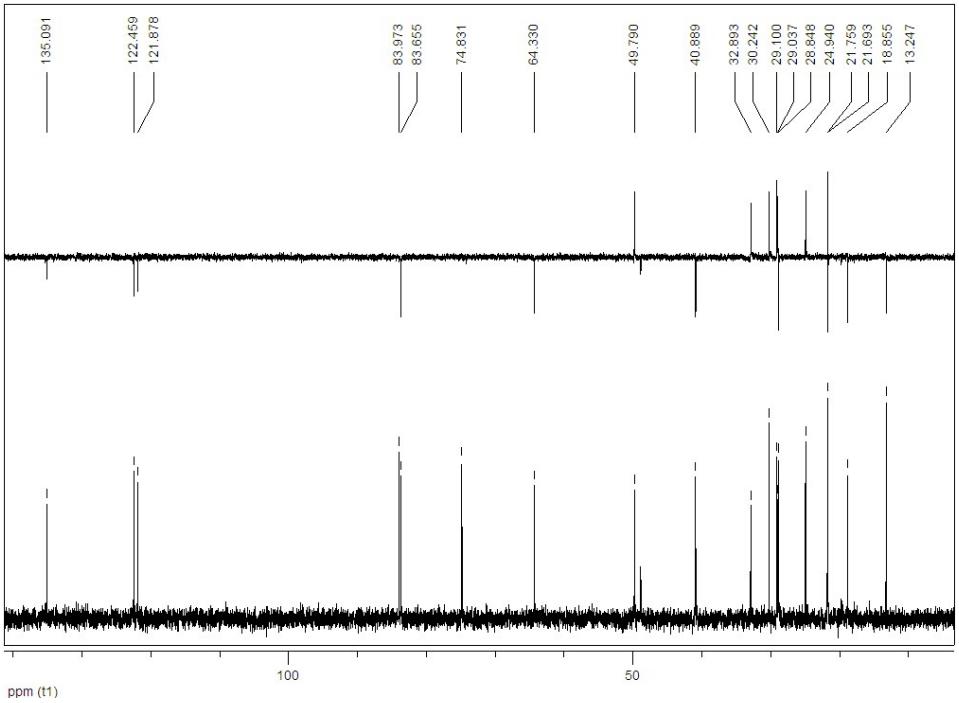
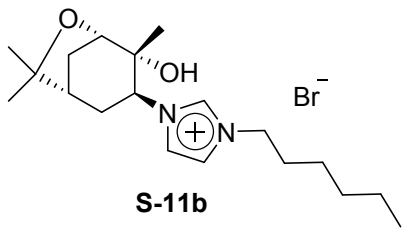


Figure S30- ^{13}C NMR and DEPT spectrum of compound R-11b



S-11b

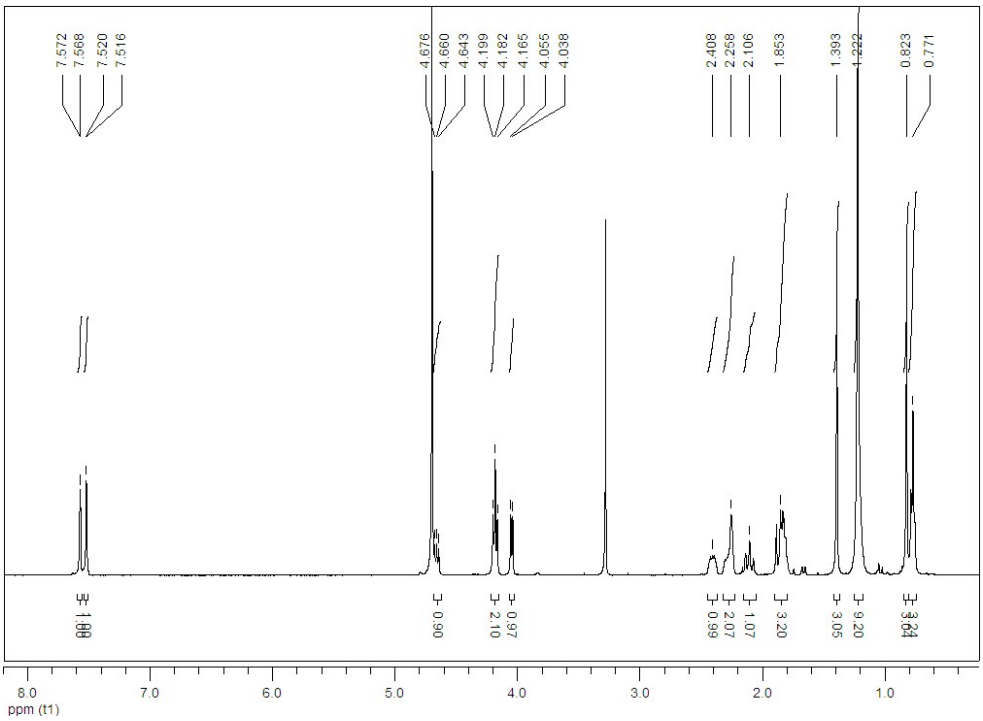


Figure S31- ^{1}H NMR spectrum of compound S-11b

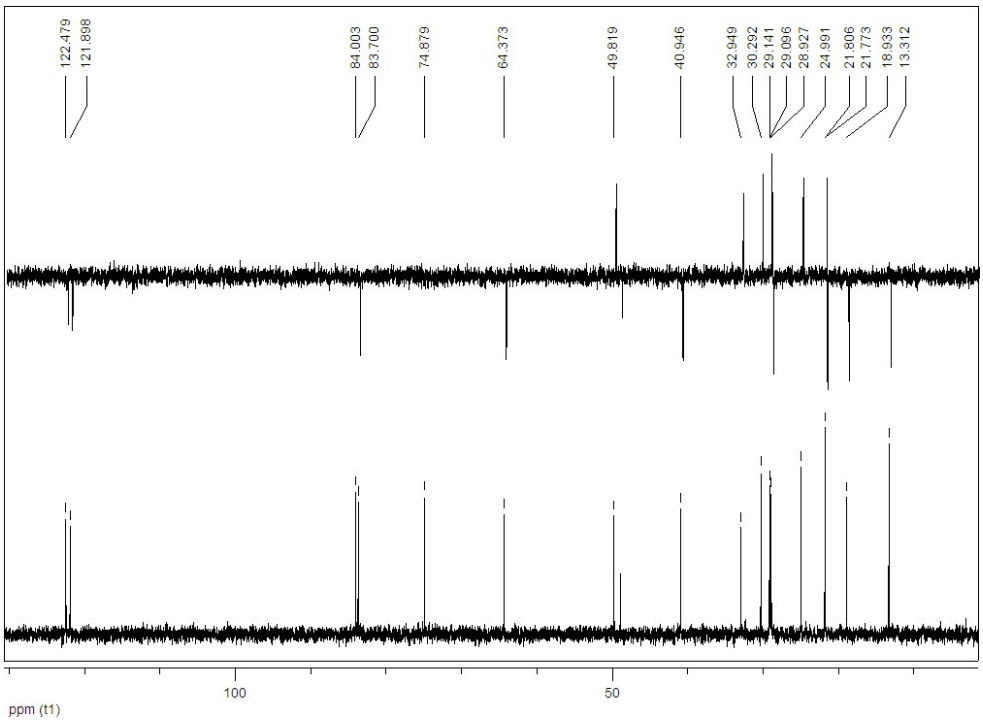
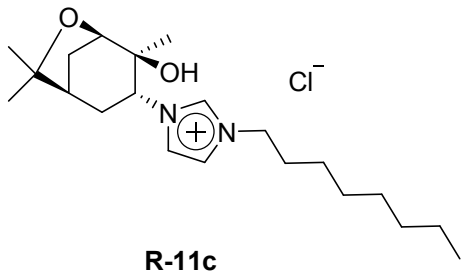


Figure S32- ^{13}C NMR and DEPT spectrum of compound S-11b



R-11c

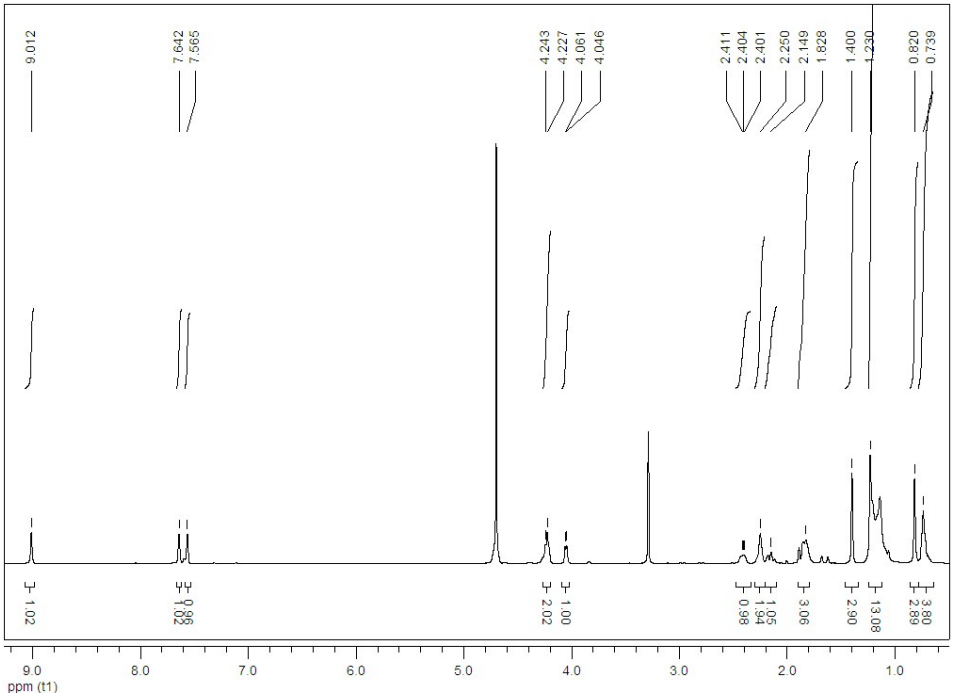


Figure S33- ^{1}H NMR spectrum of compound R-11c

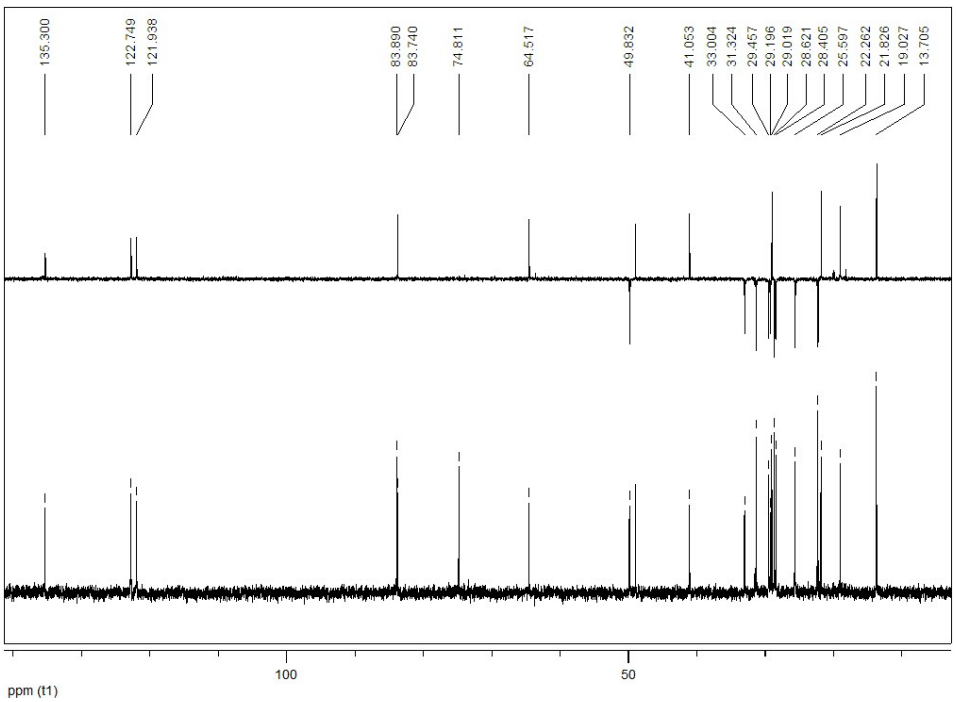
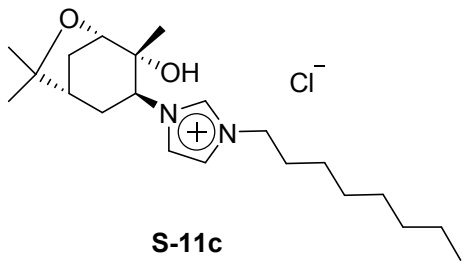


Figure S34- ^{13}C NMR and DEPT spectrum of compound R-11c



S-11c

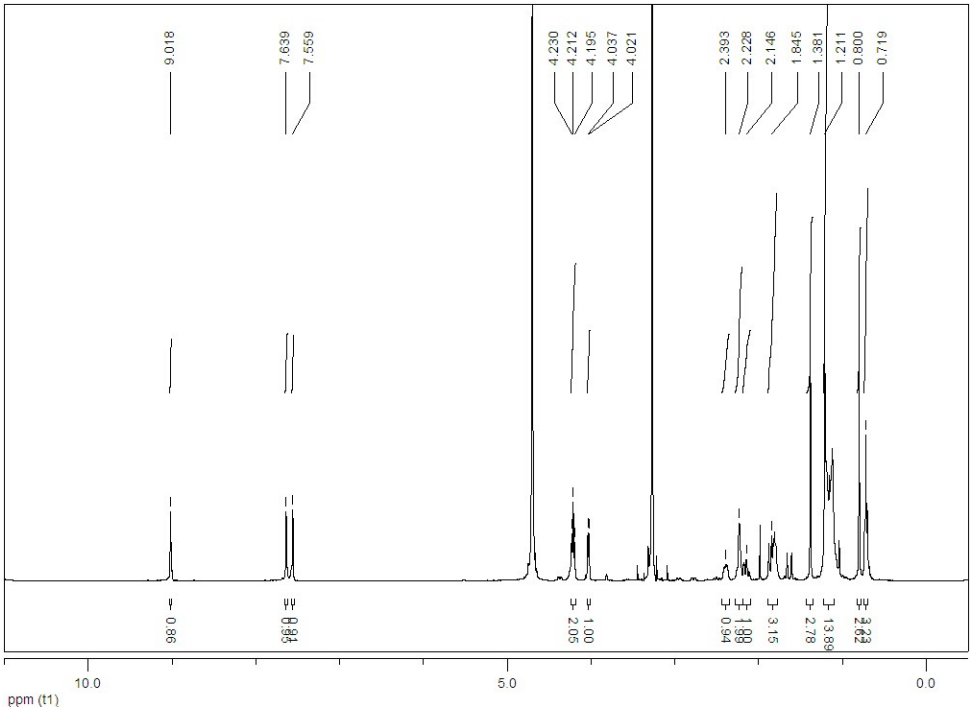


Figure S35- ^{1}H NMR spectrum of compound S-11c

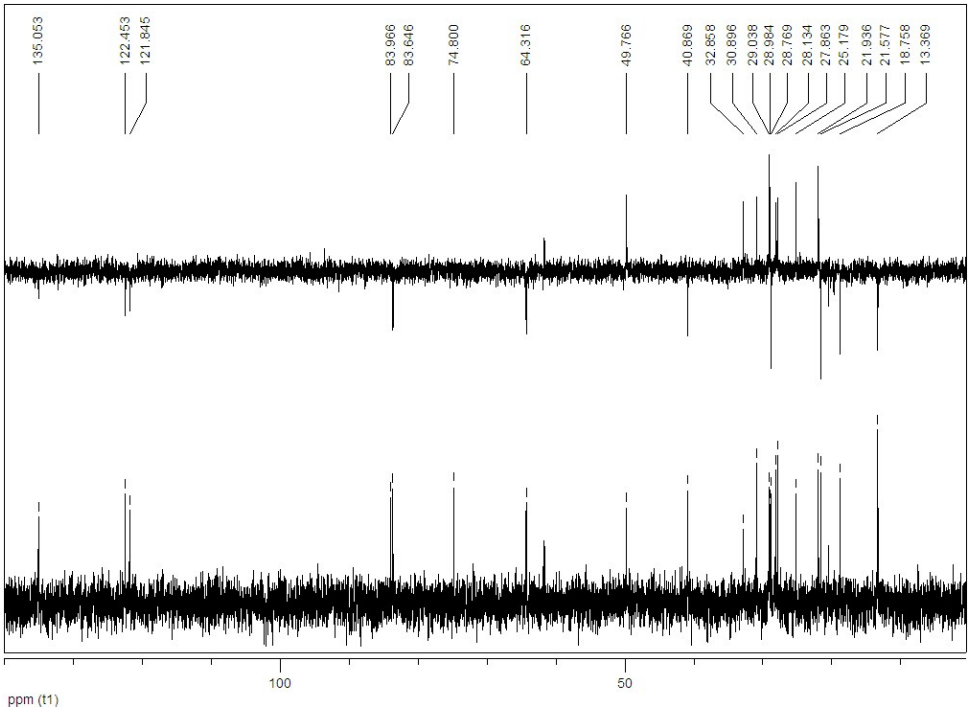
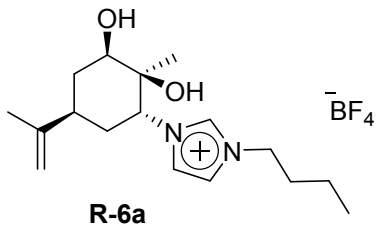


Figure S36- ^{13}C NMR and DEPT spectrum of compound S-11c



R-6a

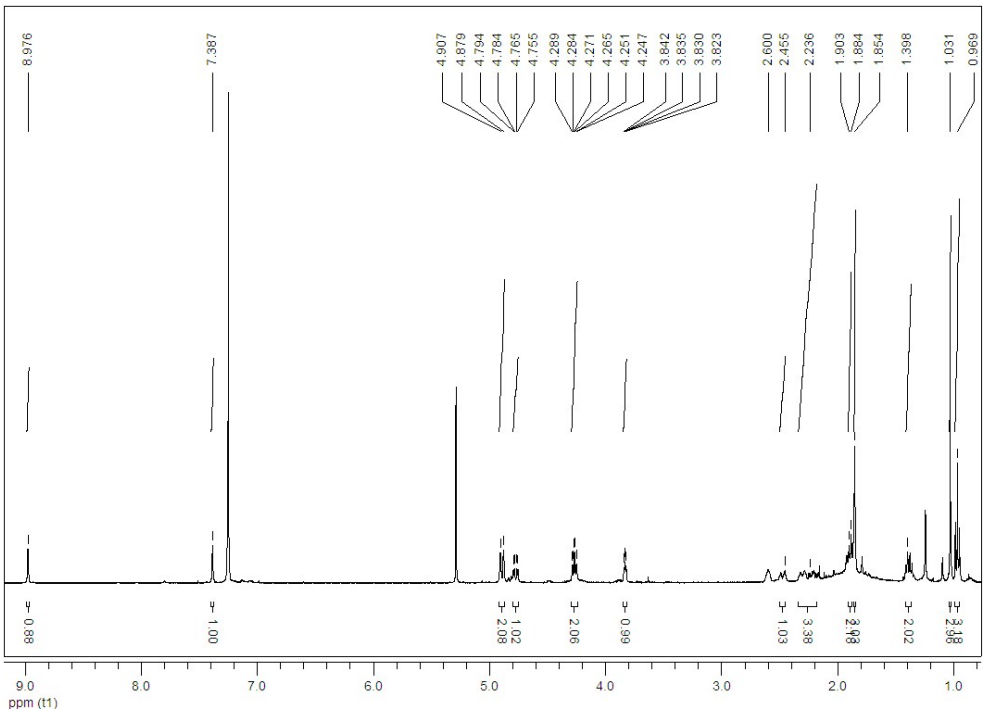


Figure S37- ^{1}H NMR spectrum of compound R-6a

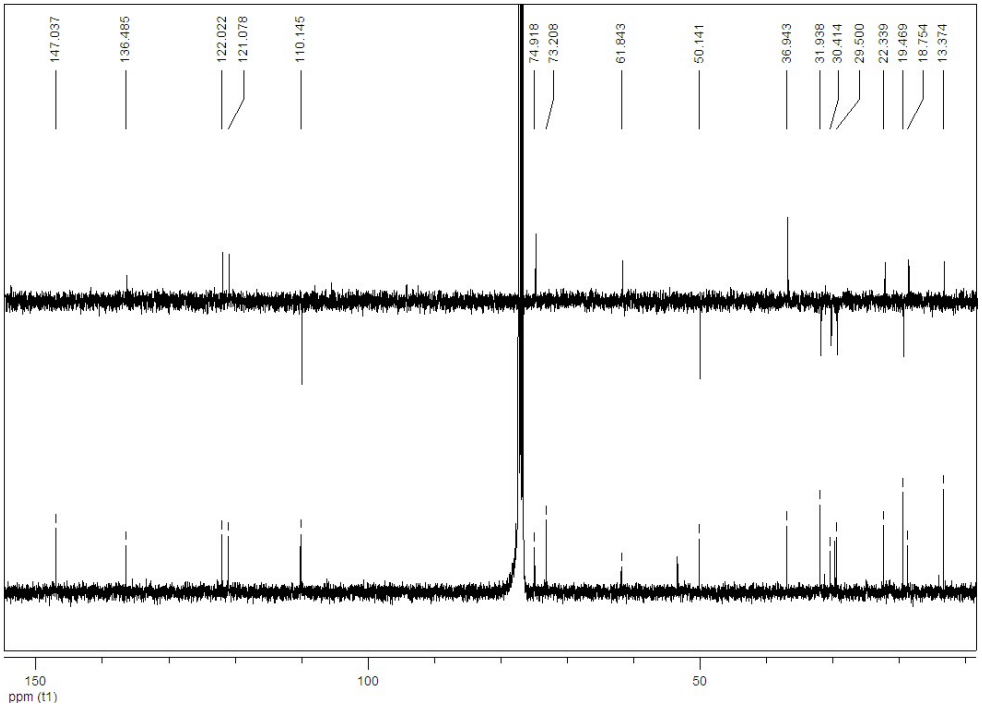
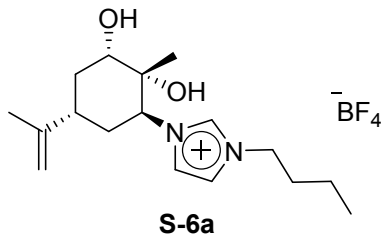


Figure S38- ^{13}C NMR and DEPT spectrum of compound R-6a



S-6a

Figure S39- ^{1}H NMR spectrum of compound S-6a

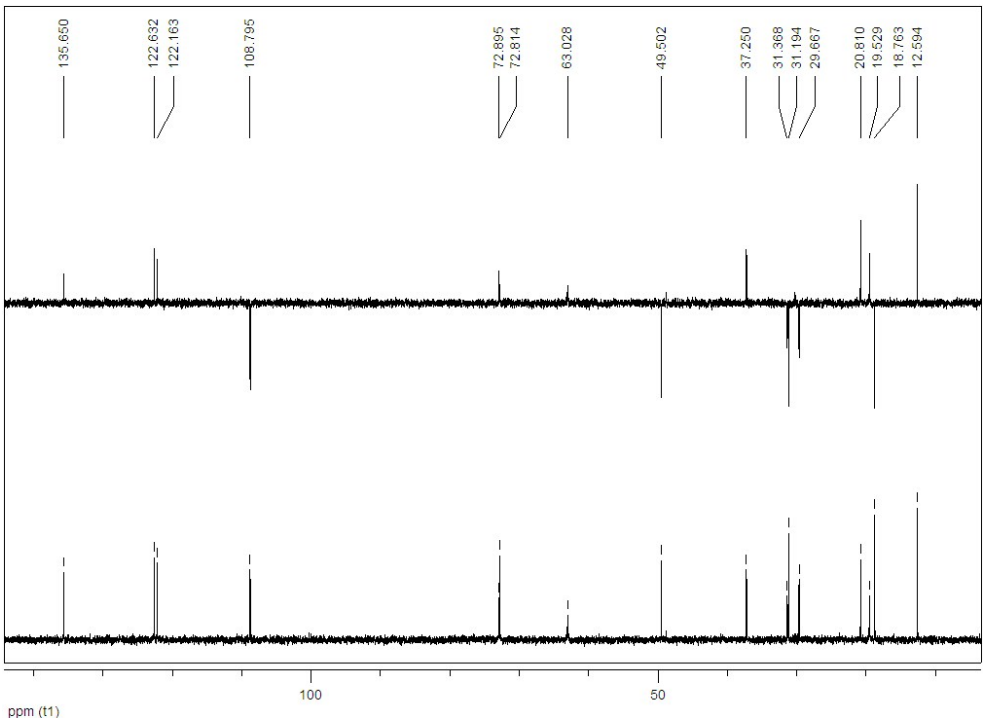
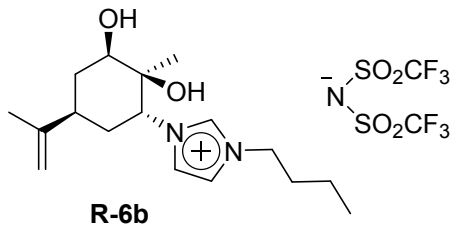


Figure S40- ^{13}C NMR and DEPT spectrum of compound S-6a



R-6b

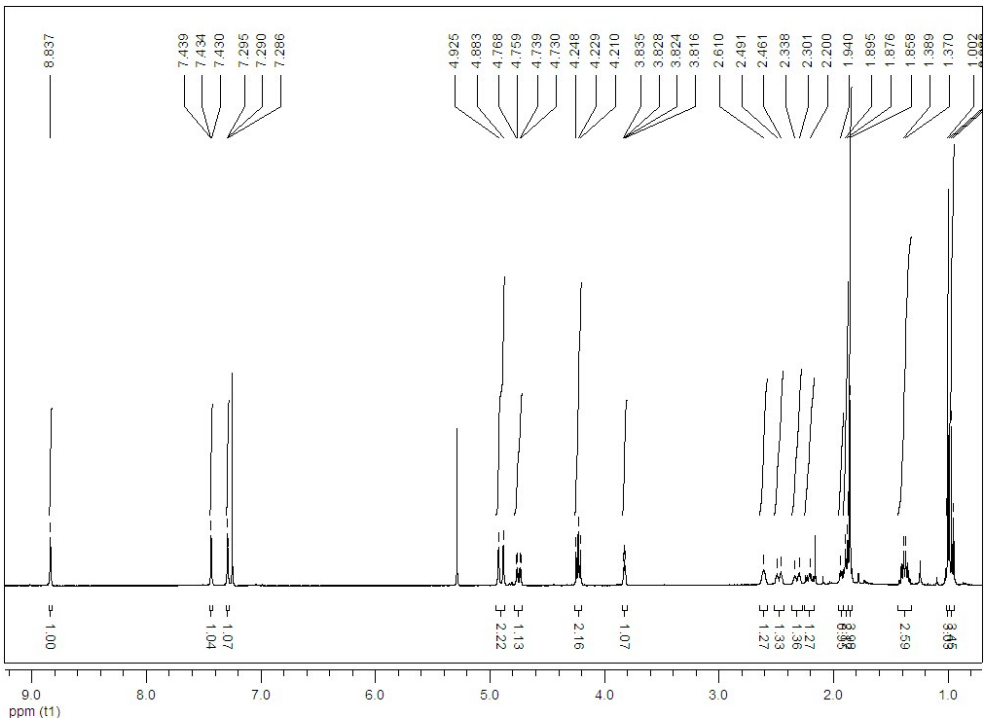


Figure S41- ^{1}H NMR spectrum of compound R-6b

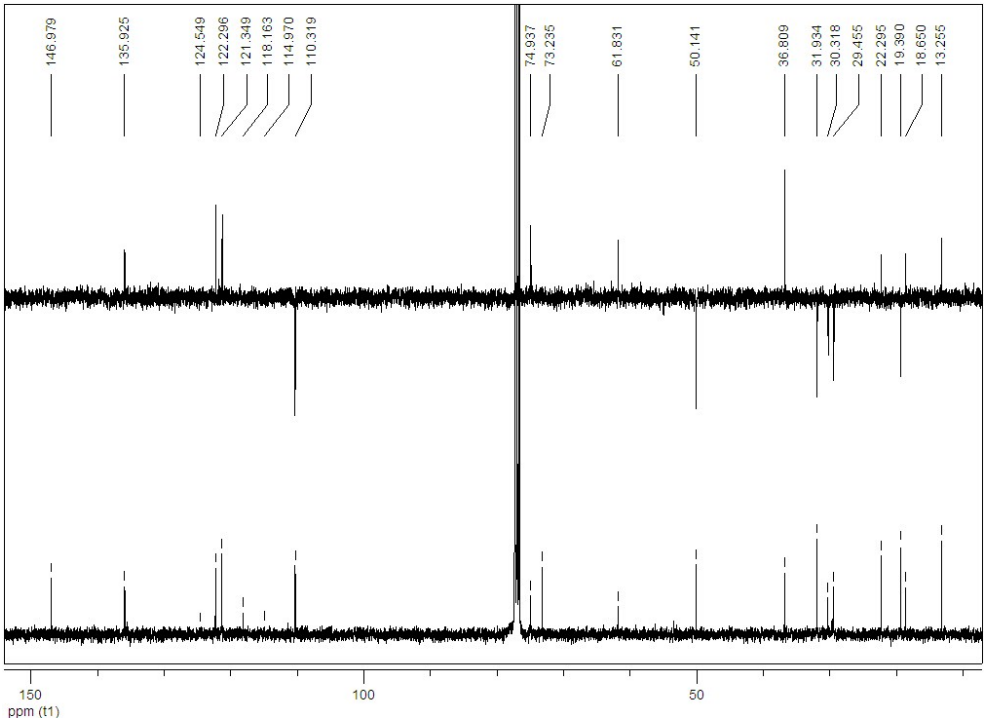
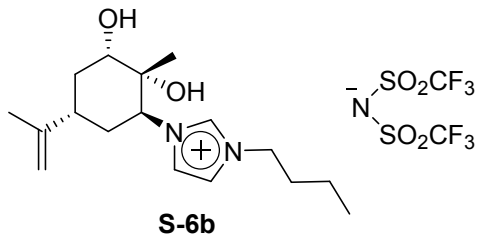


Figure S42- ^{13}C NMR and DEPT spectrum of compound R-6b



S-6b

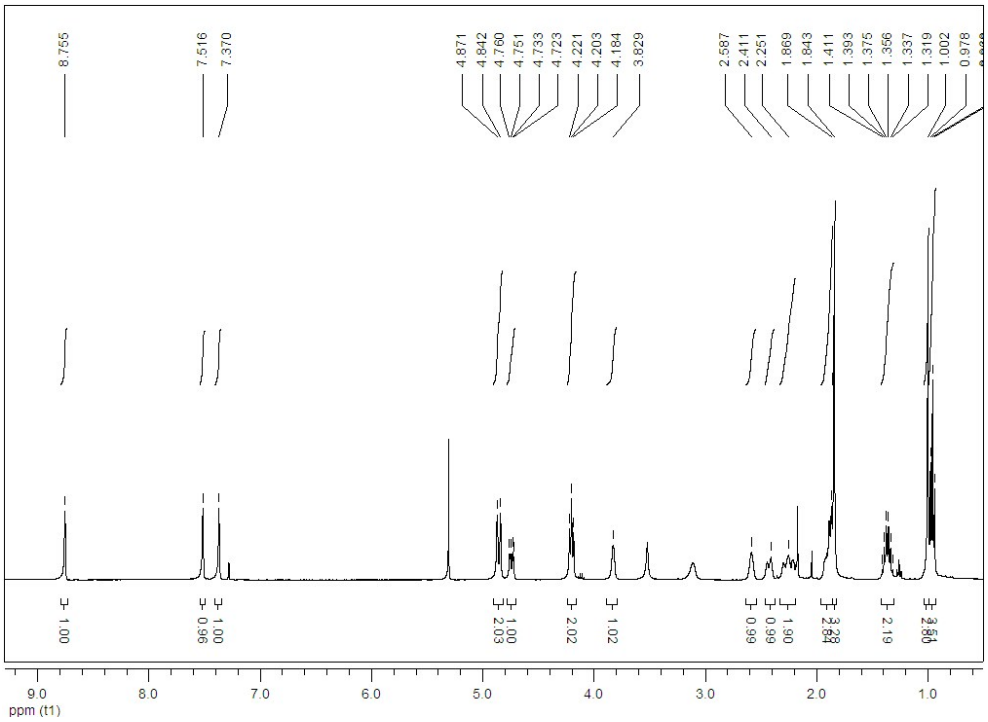


Figure S43- ^{1}H NMR spectrum of compound S-6b

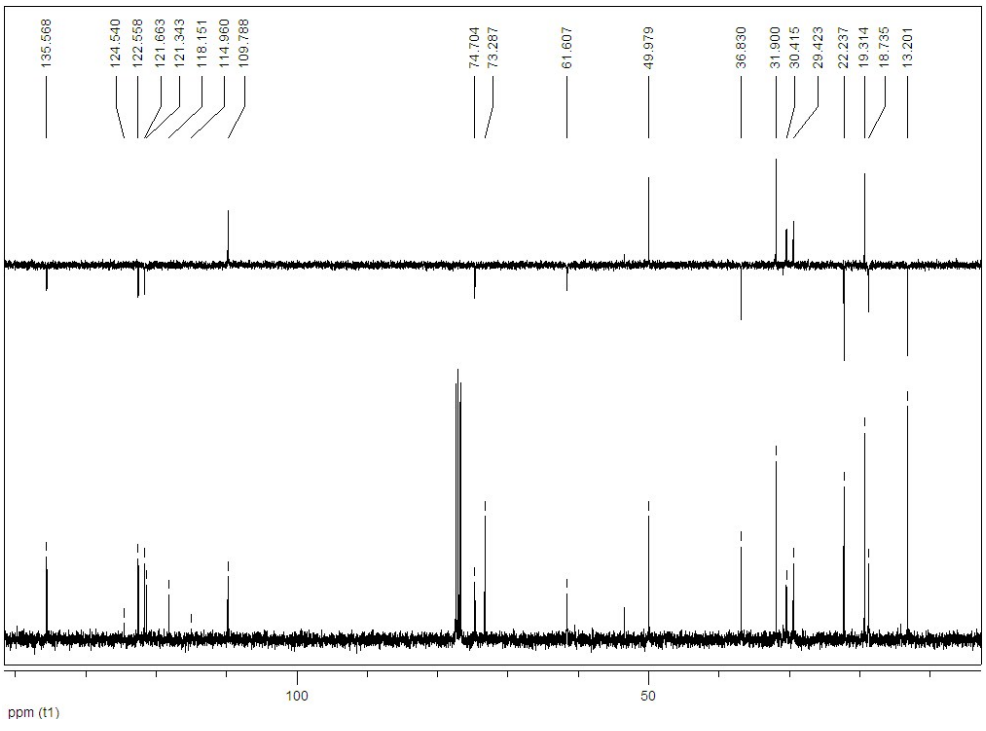
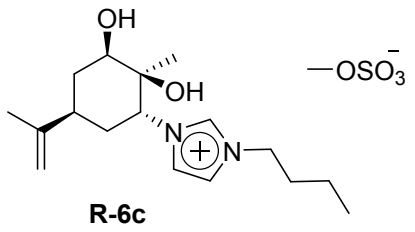


Figure S44- ^{13}C NMR and DEPT spectrum of compound S-6b



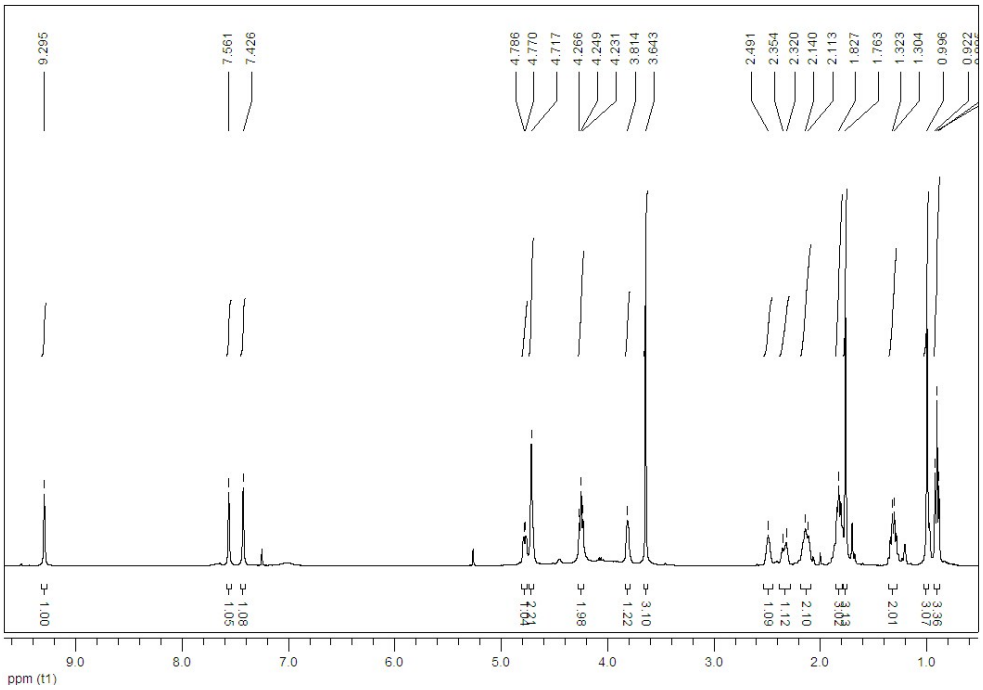


Figure S45- ^{1}H NMR spectrum of compound R-6c

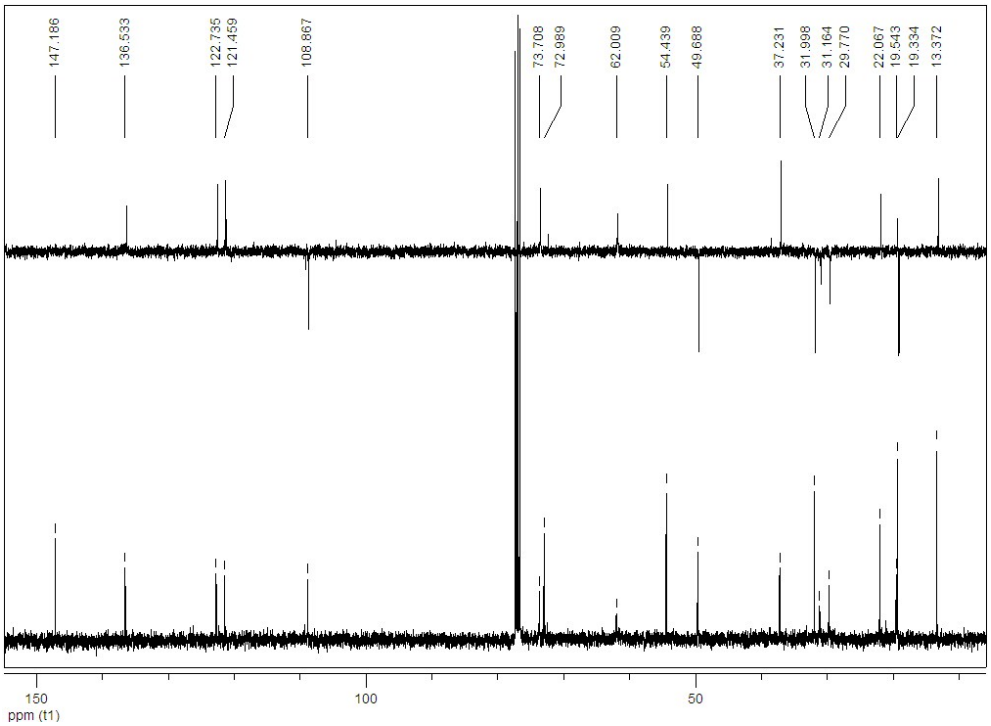
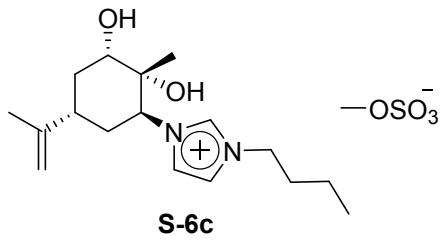


Figure S46- ^{13}C NMR and DEPT spectrum of compound R-6c



S-6c

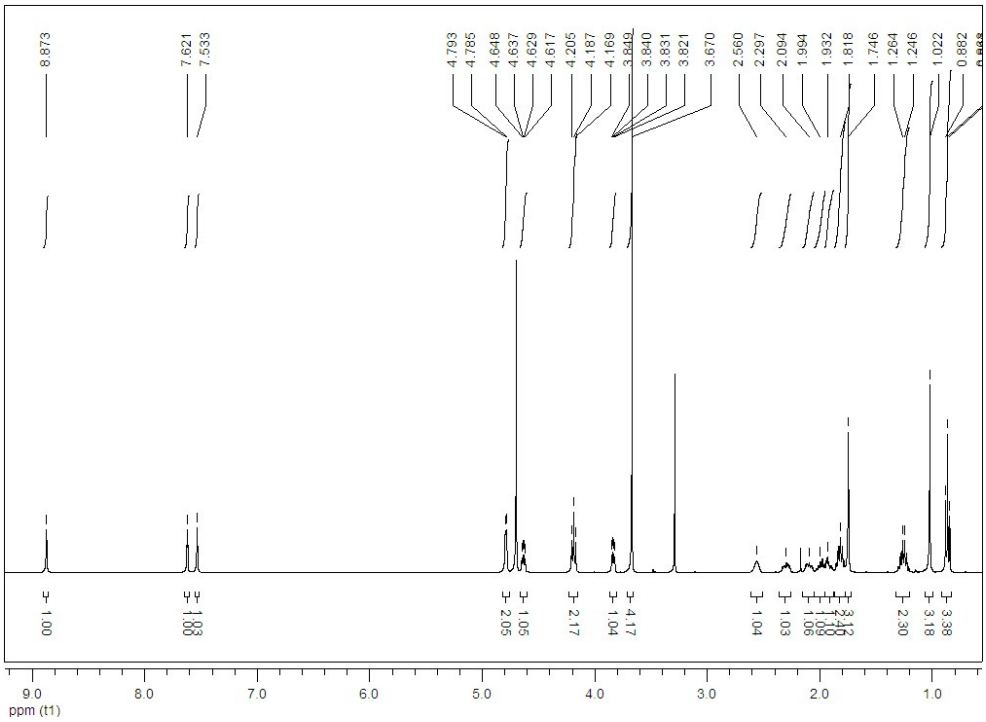


Figure S47- ^{1}H NMR spectrum of compound S-6c

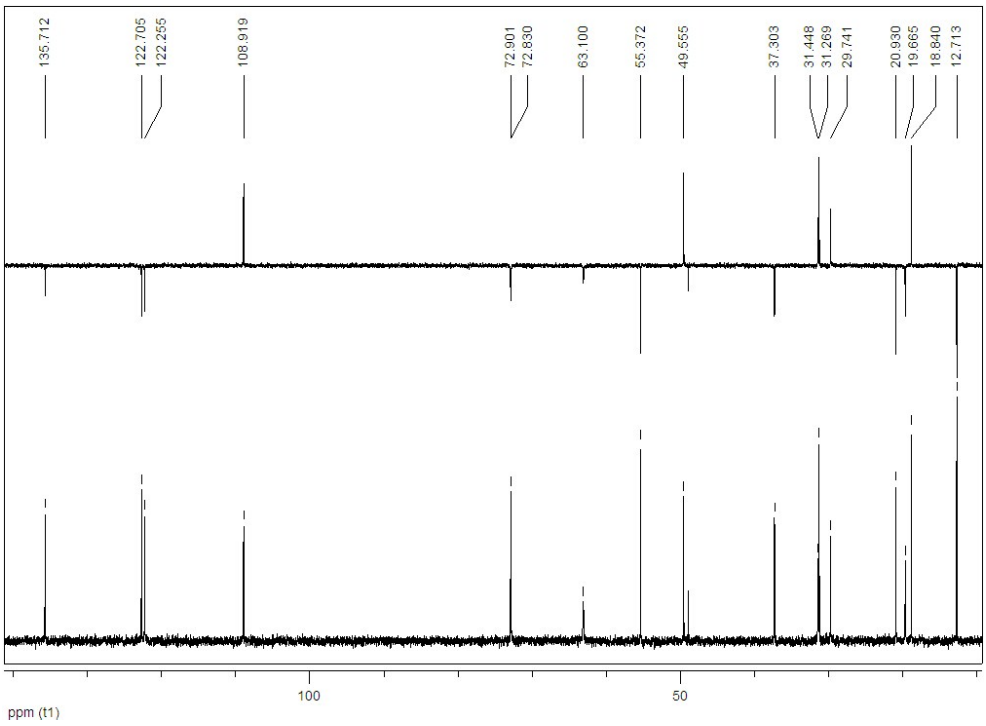
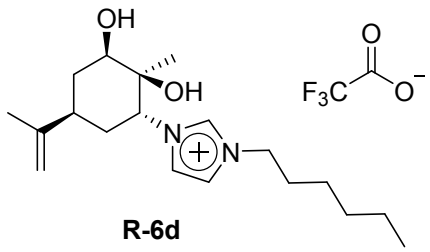


Figure S48- ^{13}C NMR and DEPT spectrum of compound S-6c



R-6d

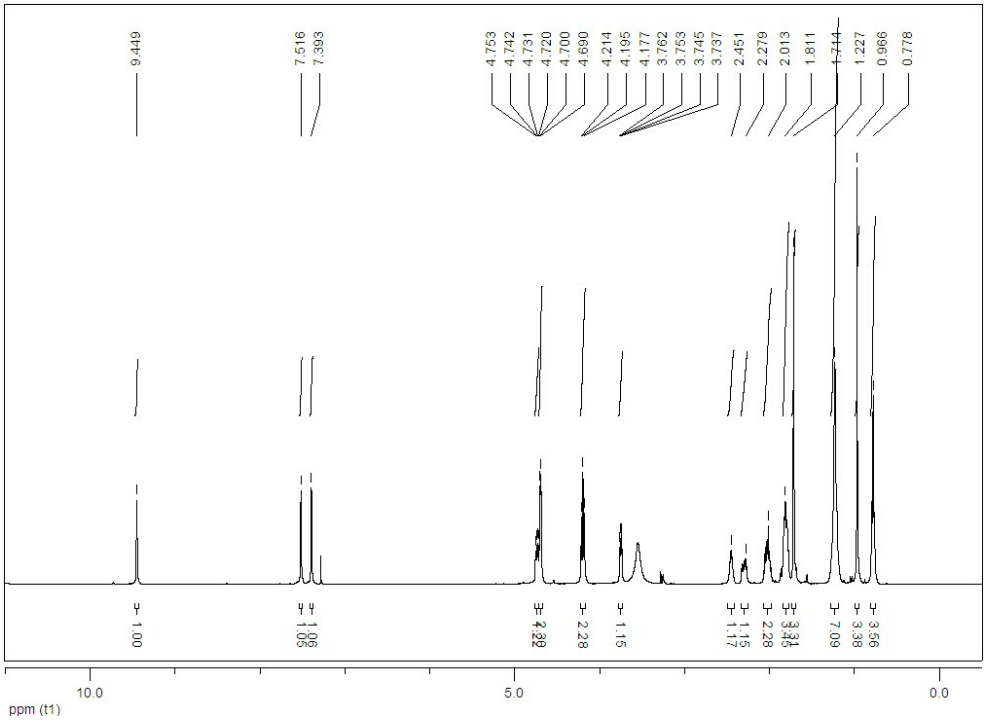


Figure S49- ^{1}H NMR spectrum of compound R-6d

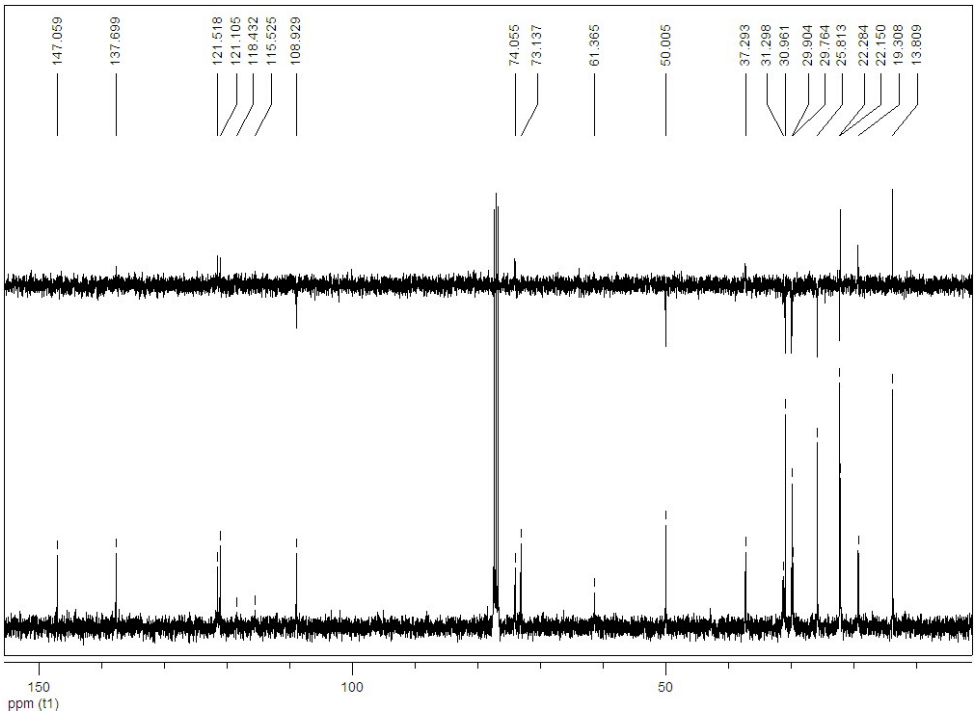
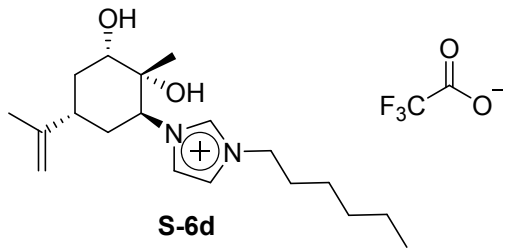


Figure S50- ^{13}C NMR and DEPT spectrum of compound R-6d



S-6d

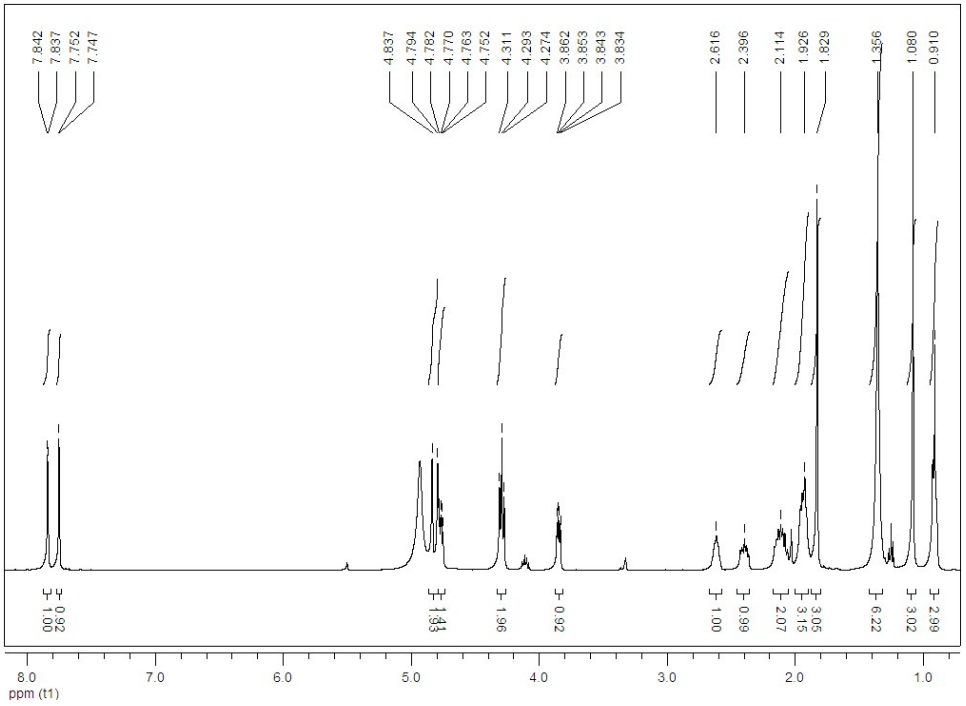


Figure S51- ^{1}H NMR spectrum of compound S-6d

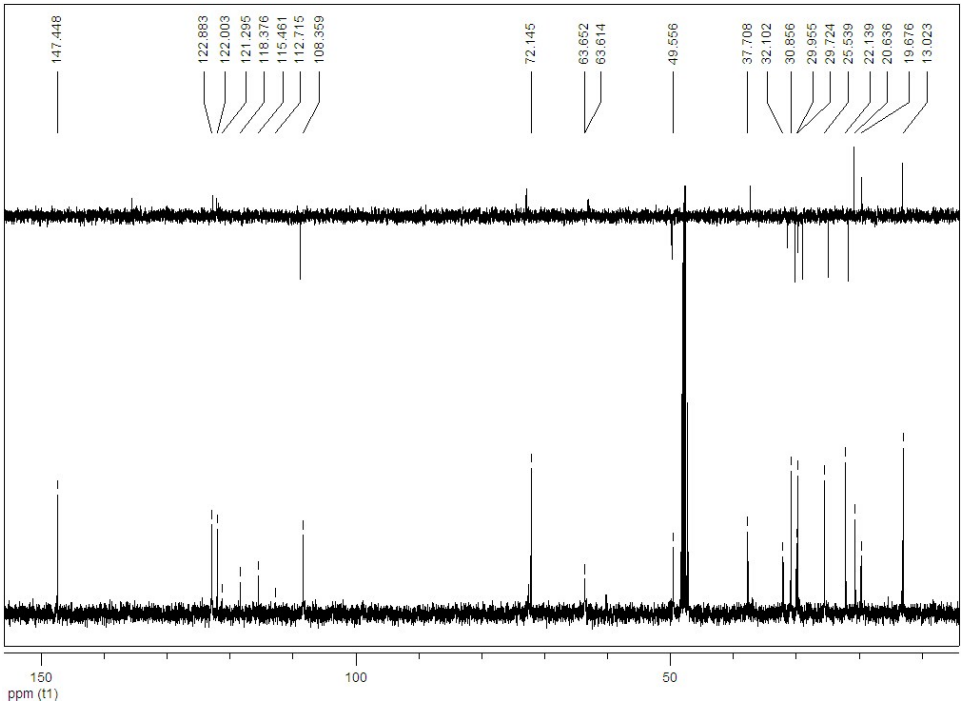
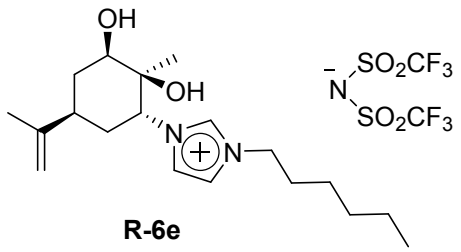


Figure S52- ^{13}C NMR and DEPT spectrum of compound S-6d



R-6e

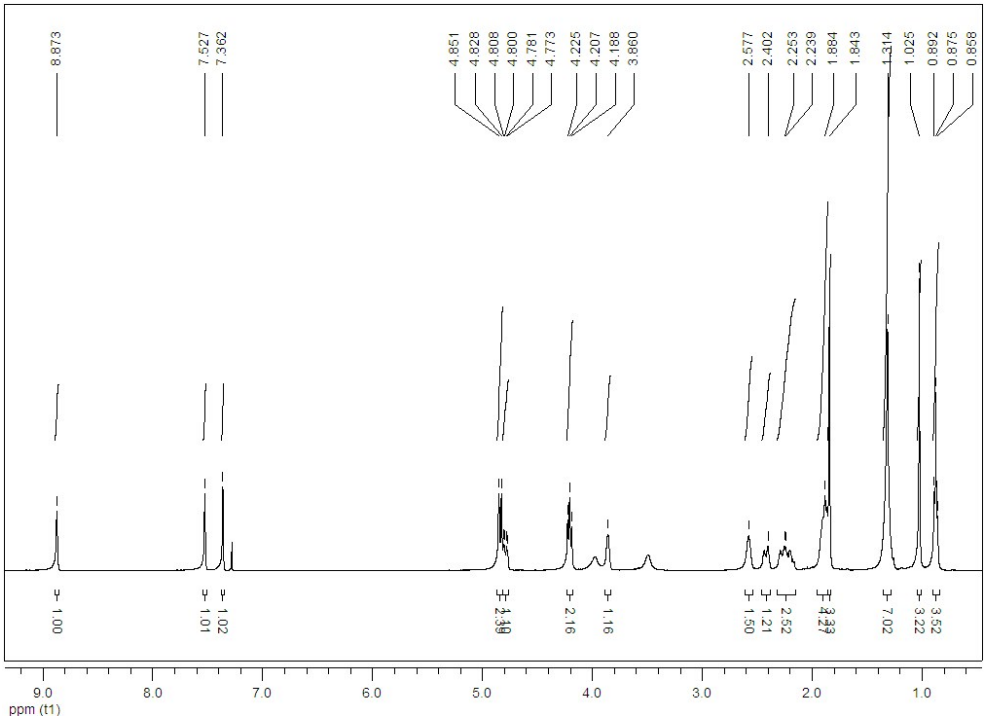


Figure S53- ^{1}H NMR spectrum of compound R-6e

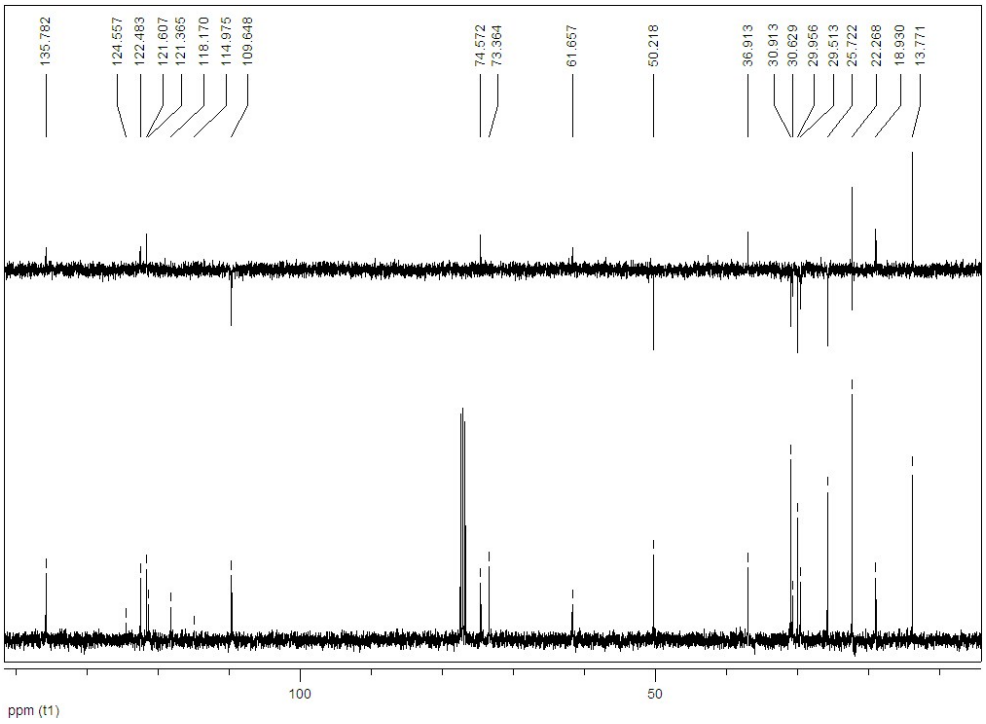
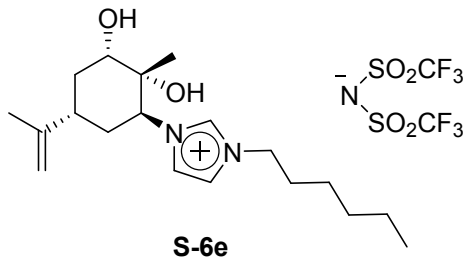


Figure S54- ^{13}C NMR and DEPT spectrum of compound R-6e



S-6e

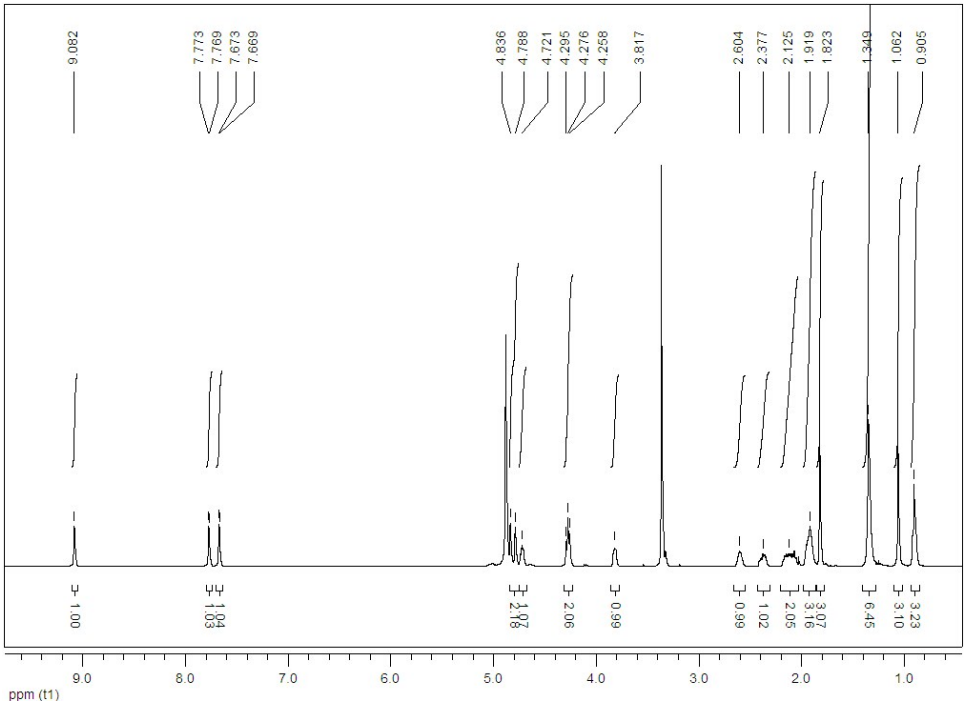


Figure S55- ^{1}H NMR spectrum of compound S-6e

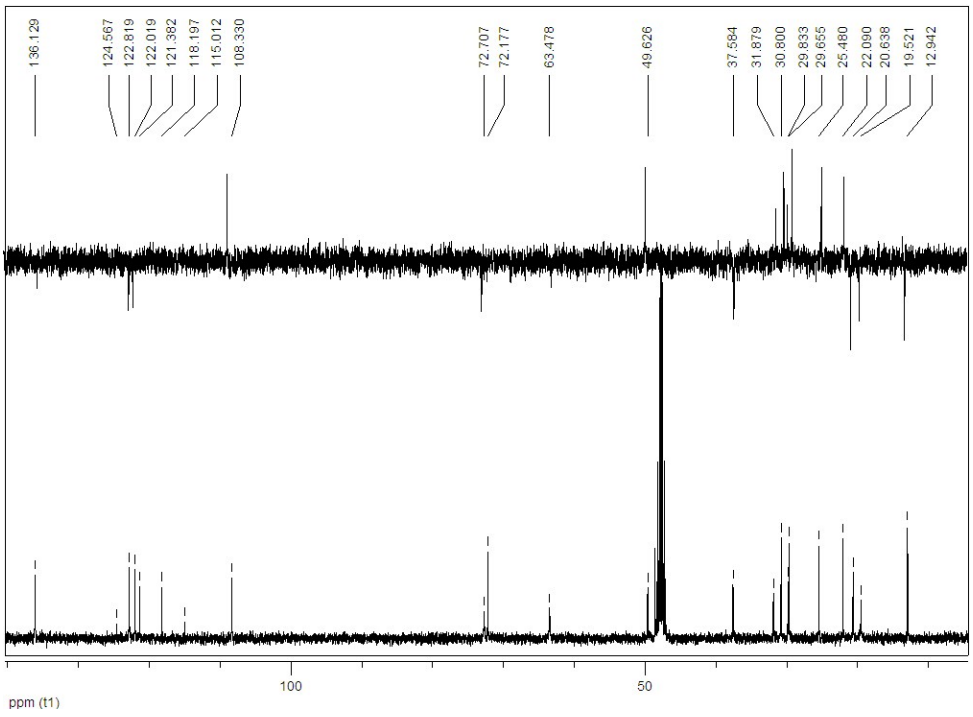
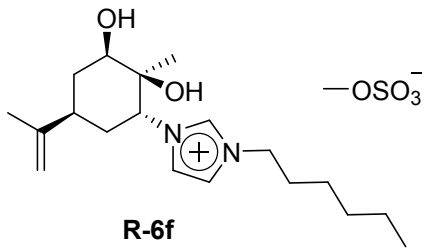


Figure S56- ^{13}C NMR and DEPT spectrum of compound S-6e



R-6f

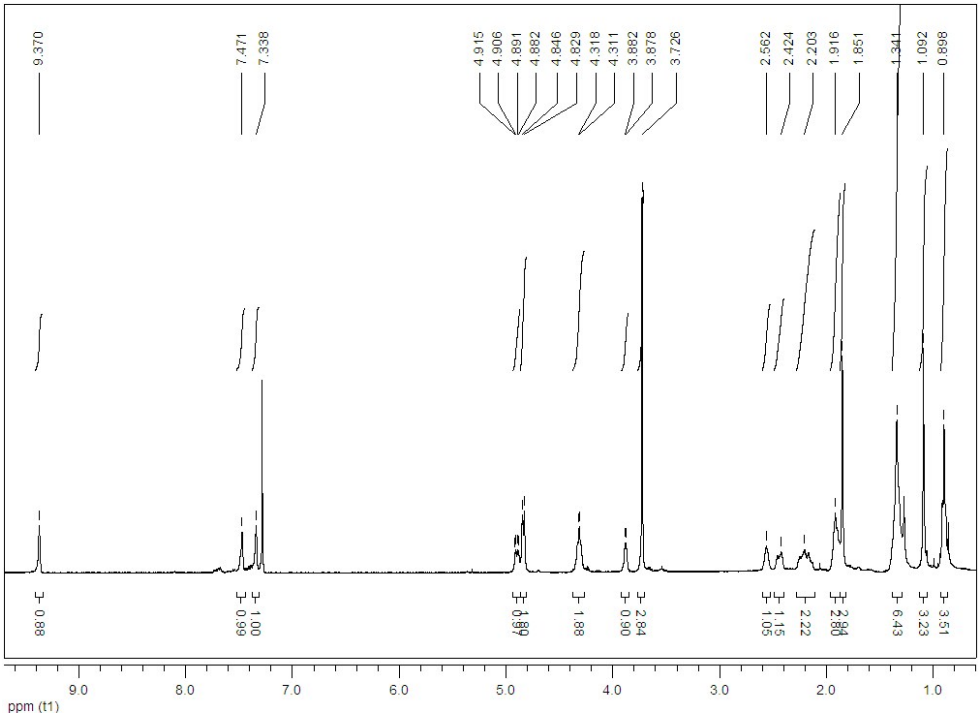


Figure S57- ^{1}H NMR spectrum of compound R-6f

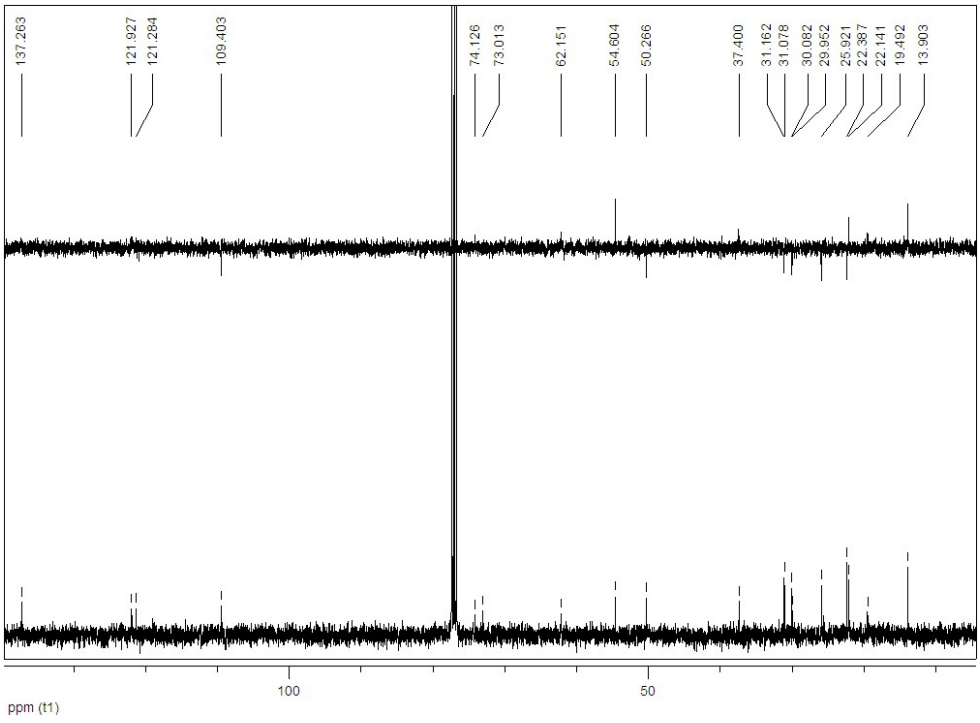
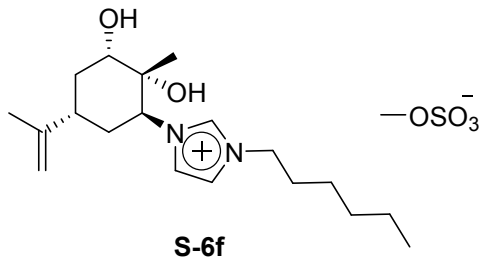


Figure S58- ^{13}C NMR and DEPT spectrum of compound R-6f



S-6f

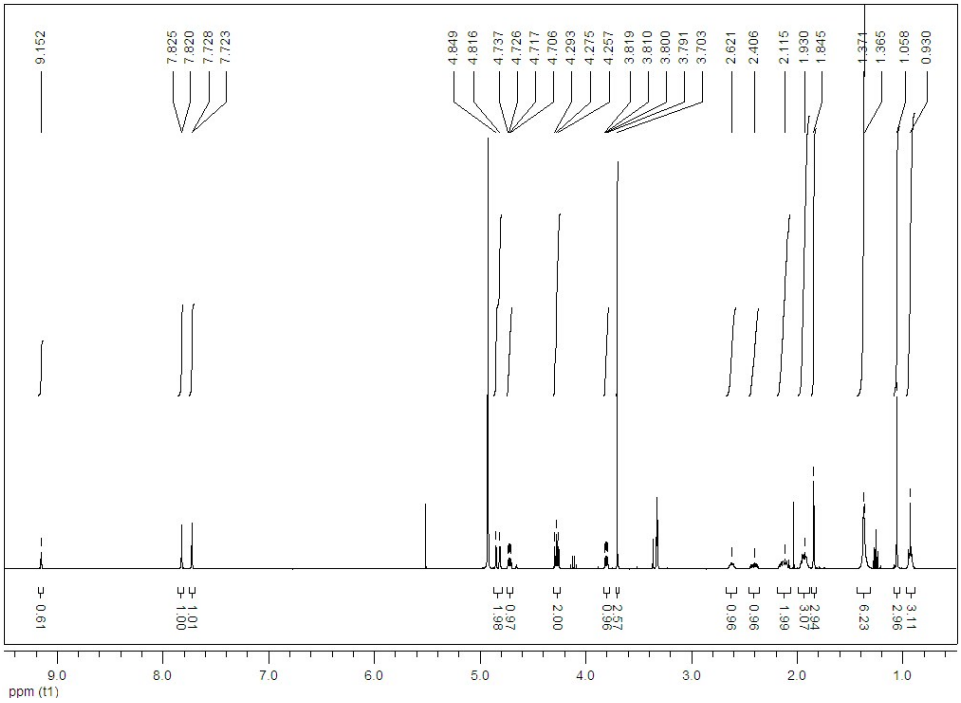


Figure S59- ^{1}H NMR spectrum of compound S-6f

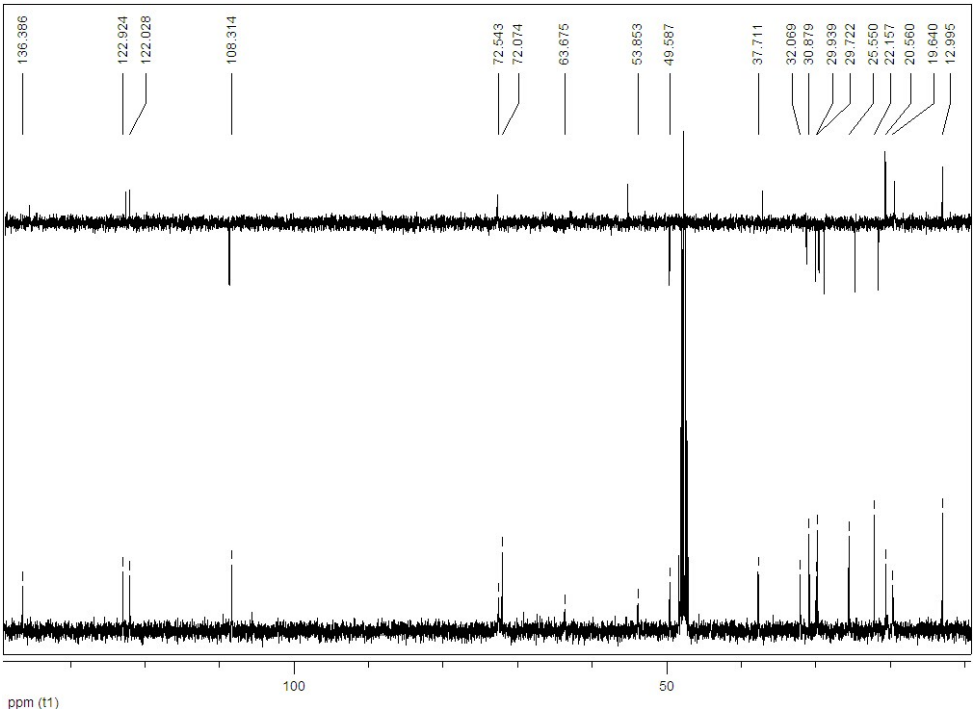
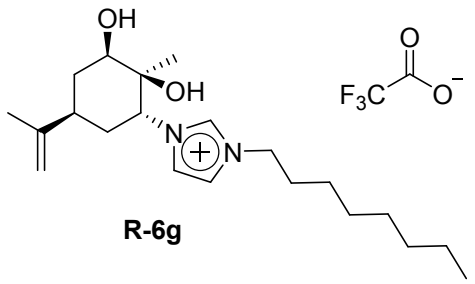


Figure S60- ^{13}C NMR and DEPT spectrum of compound S-6f



R-6g

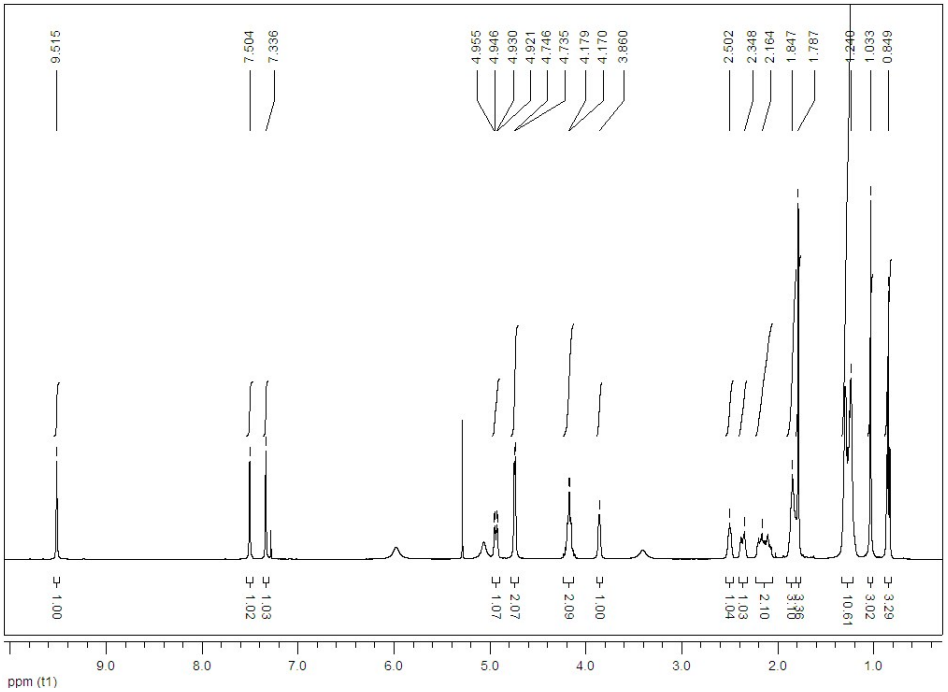


Figure S61- ^{1}H NMR spectrum of compound R-6g

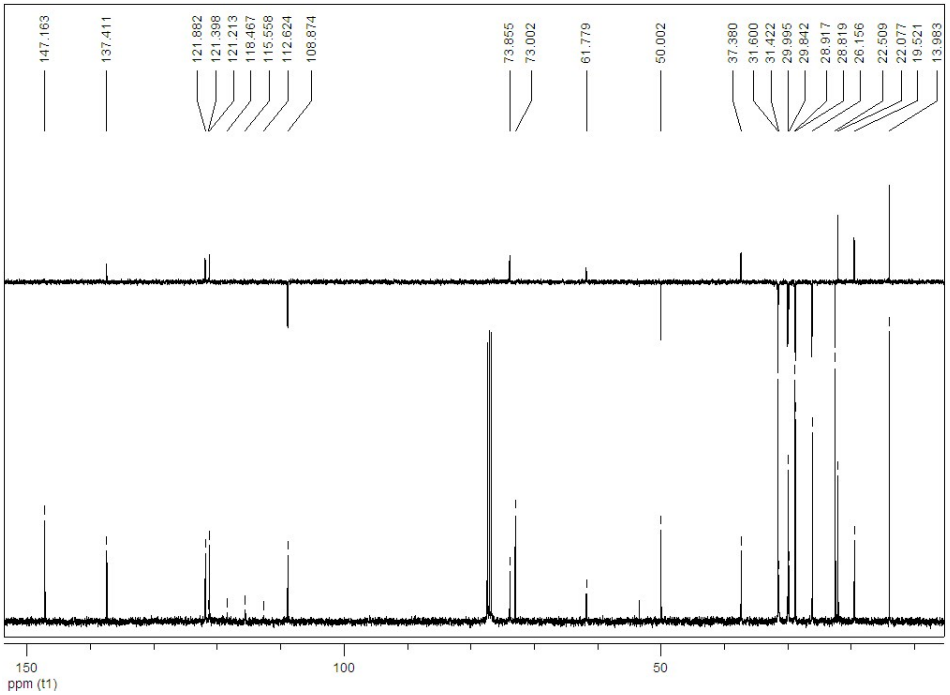
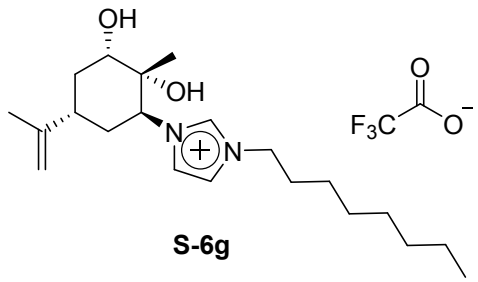


Figure S62- ^{13}C NMR and DEPT spectrum of compound R-6g



S-6g

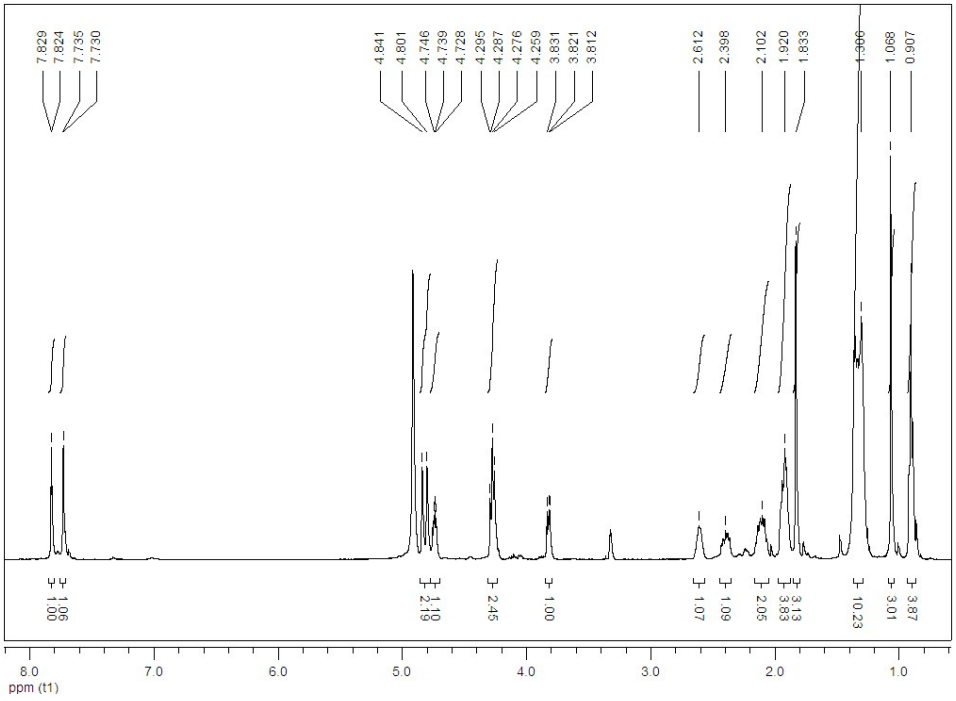


Figure S63- ^{1}H NMR spectrum of compound S-6g

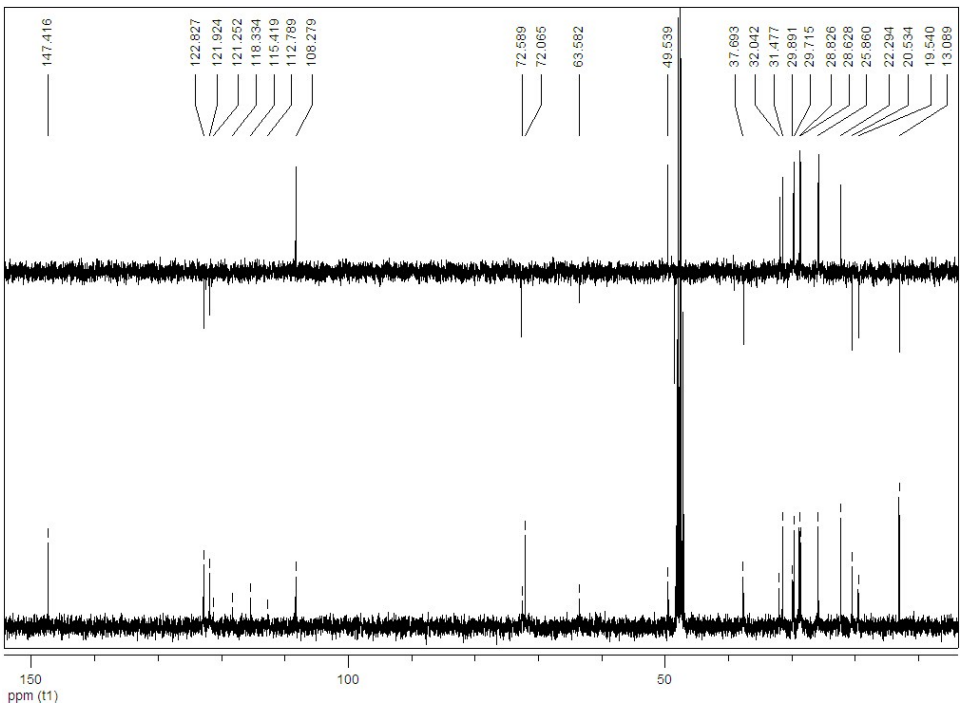
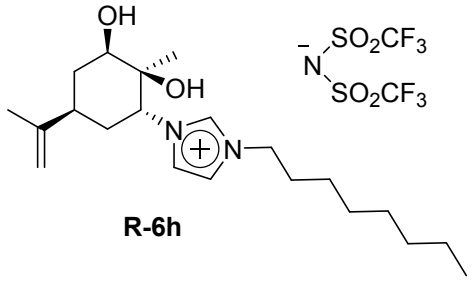


Figure S64- ^{13}C NMR and DEPT spectrum of compound S-6g



R-6h

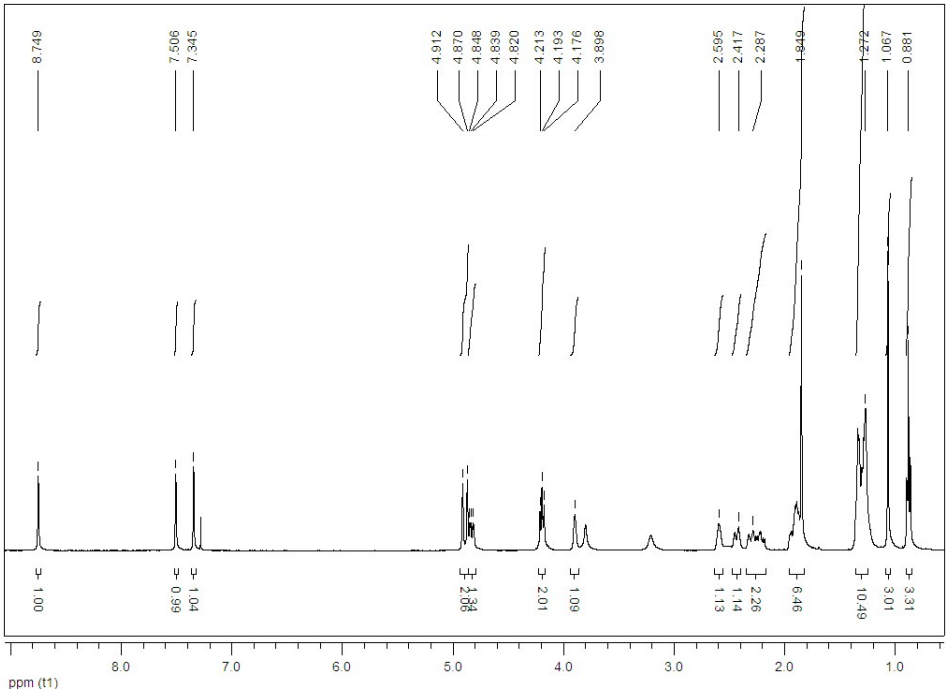


Figure S65- ^{1}H NMR spectrum of compound R-6h

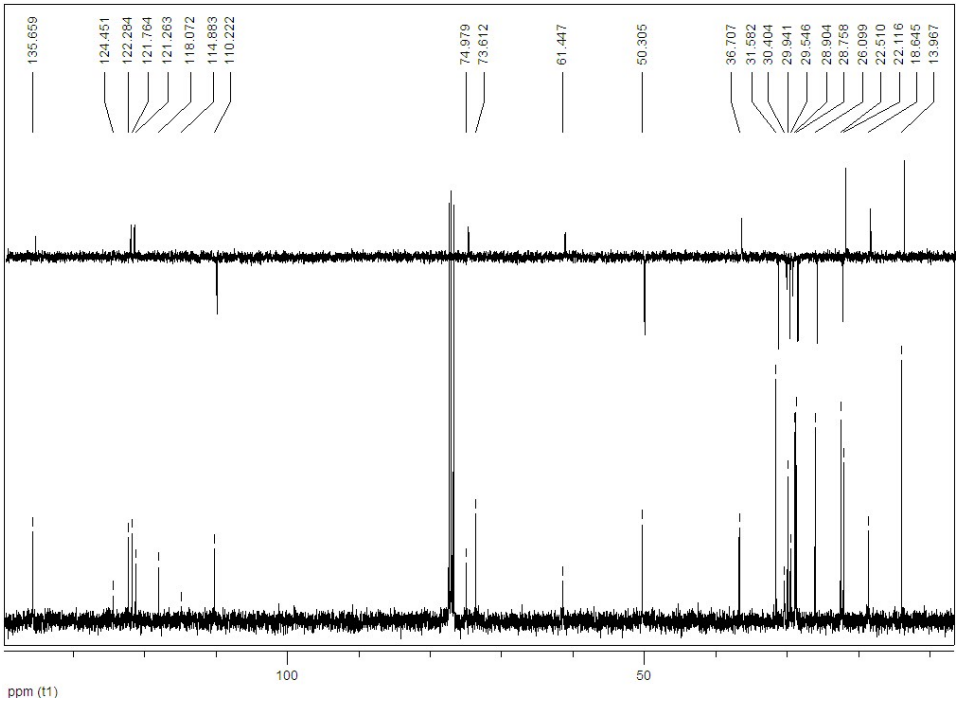
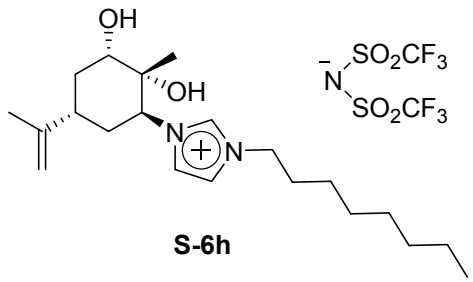


Figure S66- ^{13}C NMR and DEPT spectrum of compound R-6h



S-6h

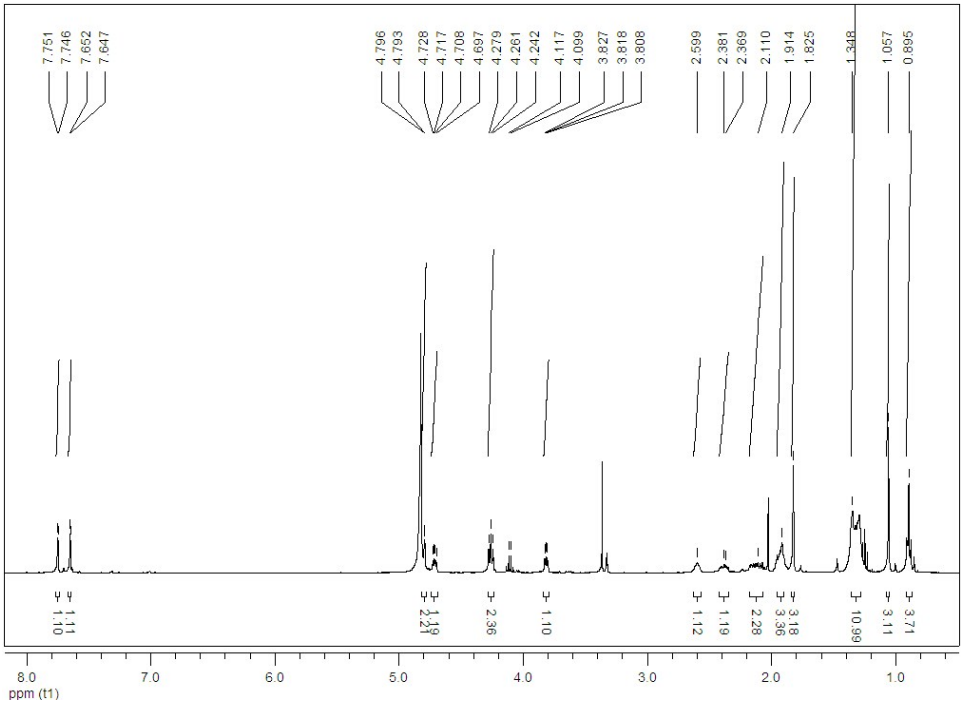


Figure S67- ^{1}H NMR spectrum of compound S-6h

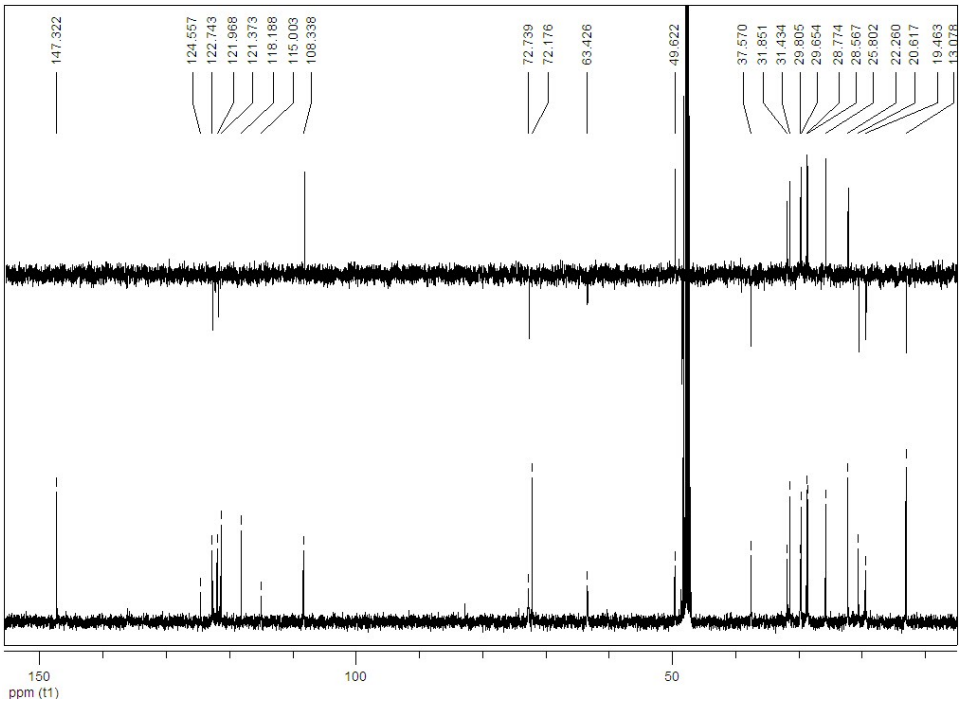
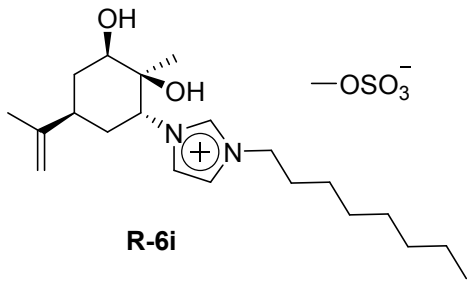


Figure S68- ^{13}C NMR and DEPT spectrum of compound S-6h



R-6i

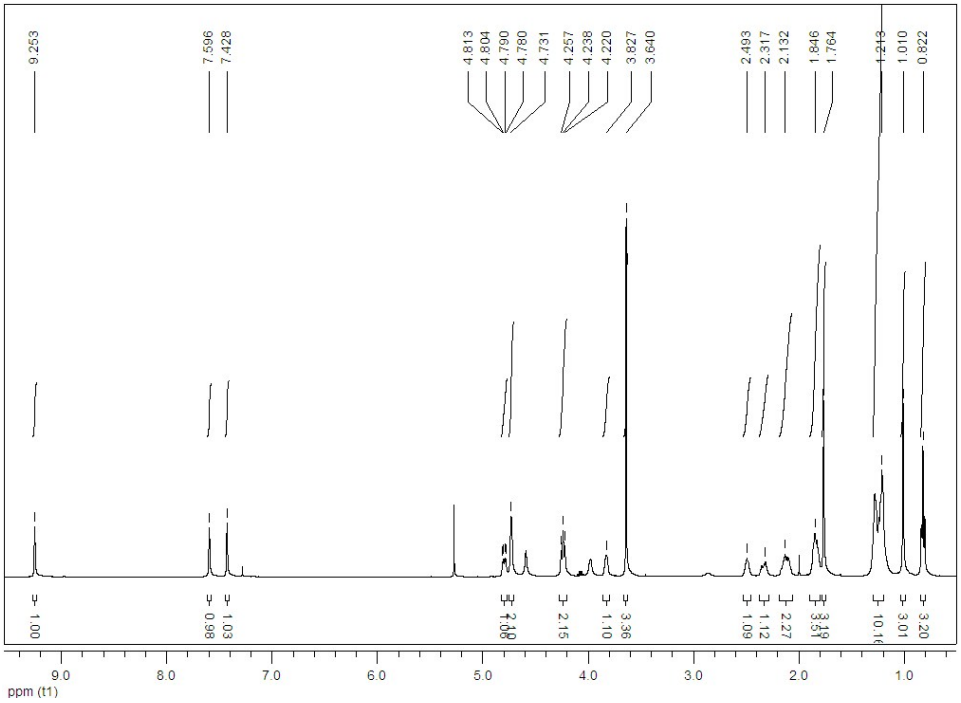


Figure S69- ^{1}H NMR spectrum of compound R-6i

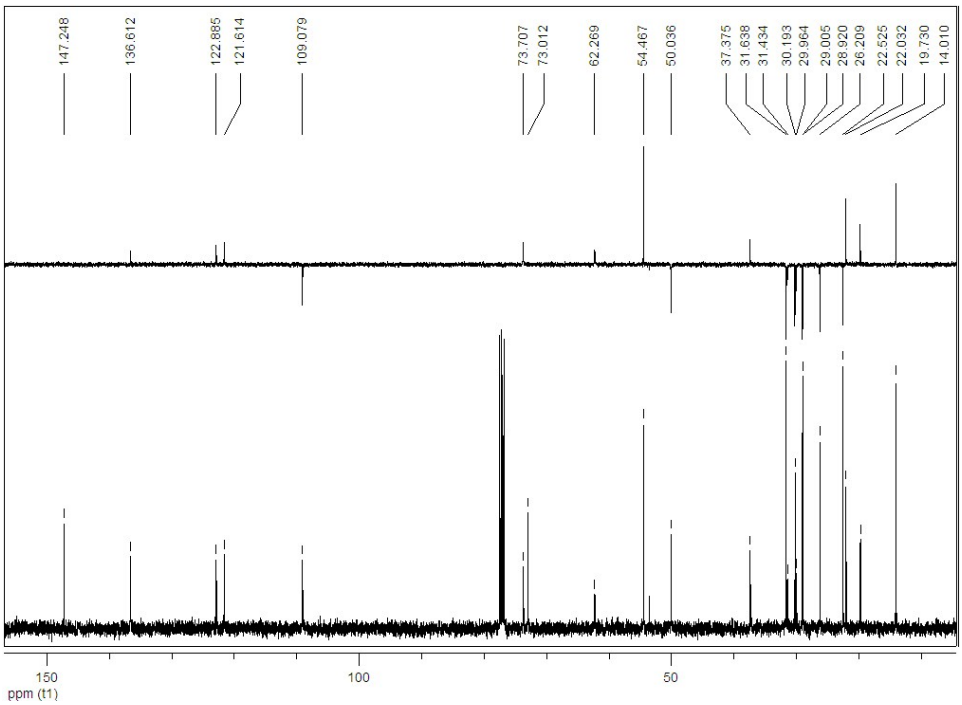
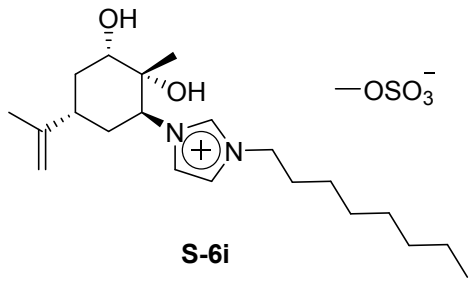


Figure S70- ^{13}C NMR and DEPT spectrum of compound R-6i



S-6i

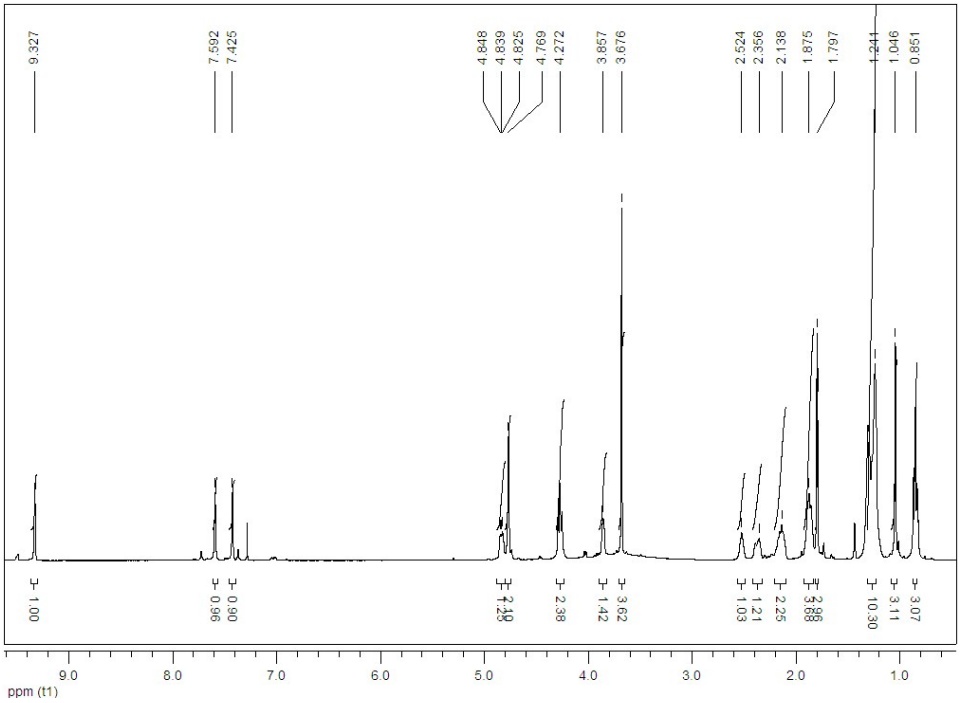


Figure S71- ^{1}H NMR spectrum of compound S-6i

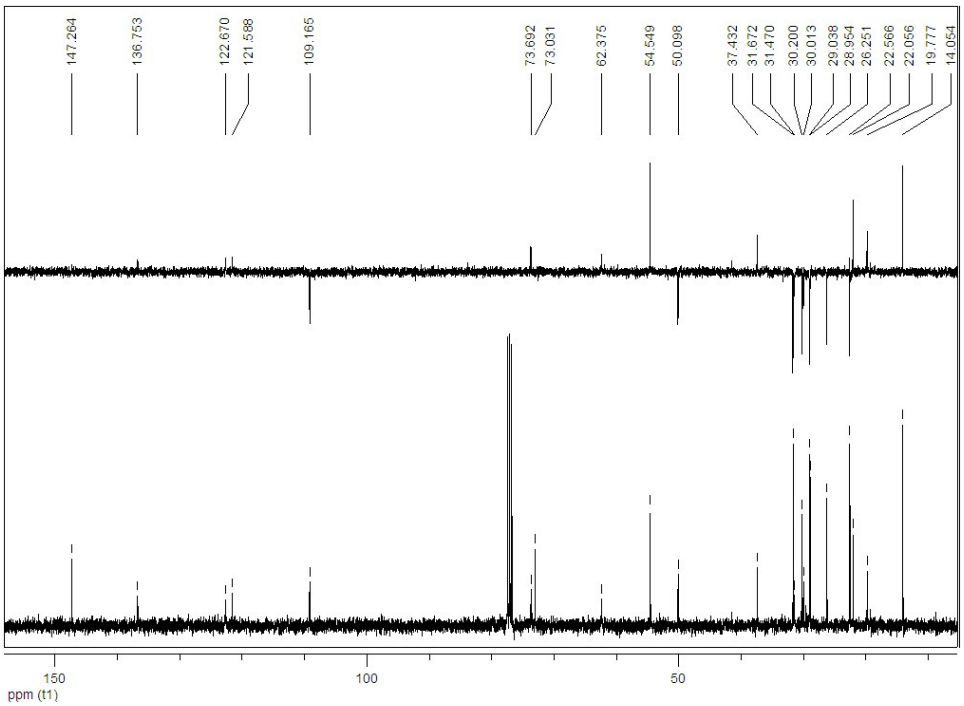
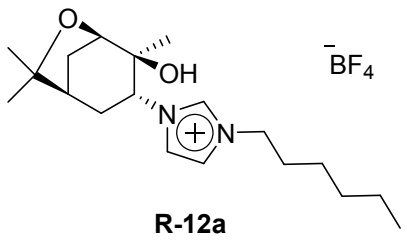


Figure S72- ^{13}C NMR and DEPT spectrum of compound S-6i



R-12a

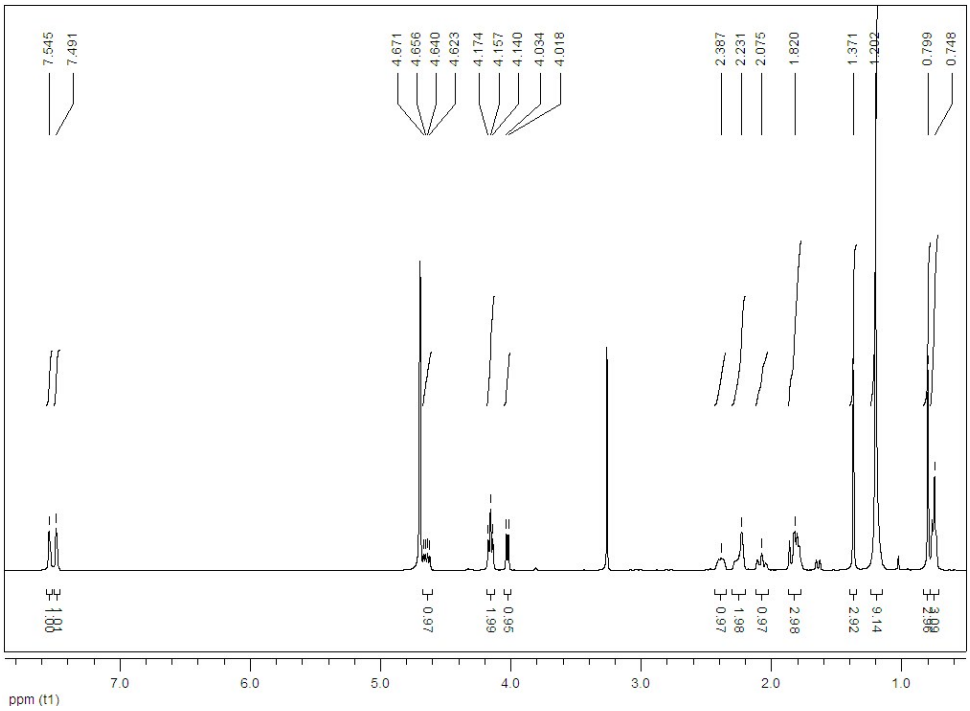


Figure S73- ^{1}H NMR spectrum of compound R-12a

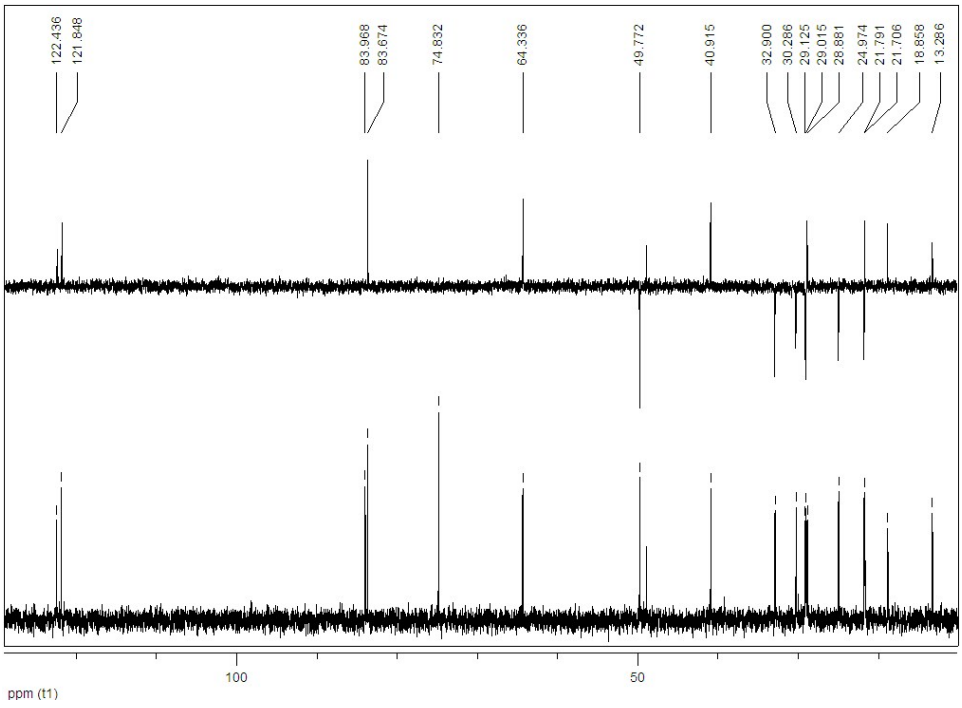
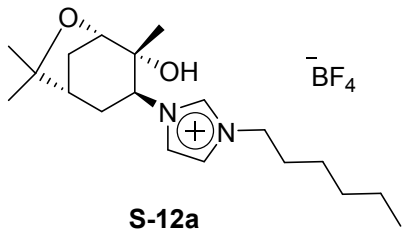


Figure S74- ^{13}C NMR and DEPT spectrum of compound R-12a



S-12a

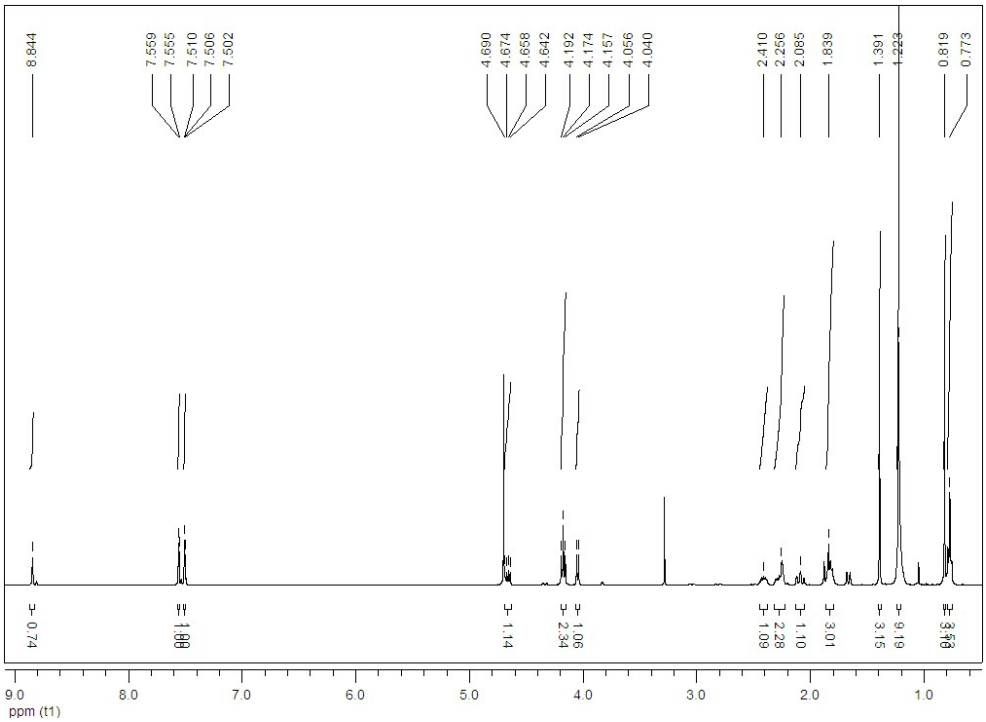


Figure S75- ^{1}H NMR spectrum of compound S-12a

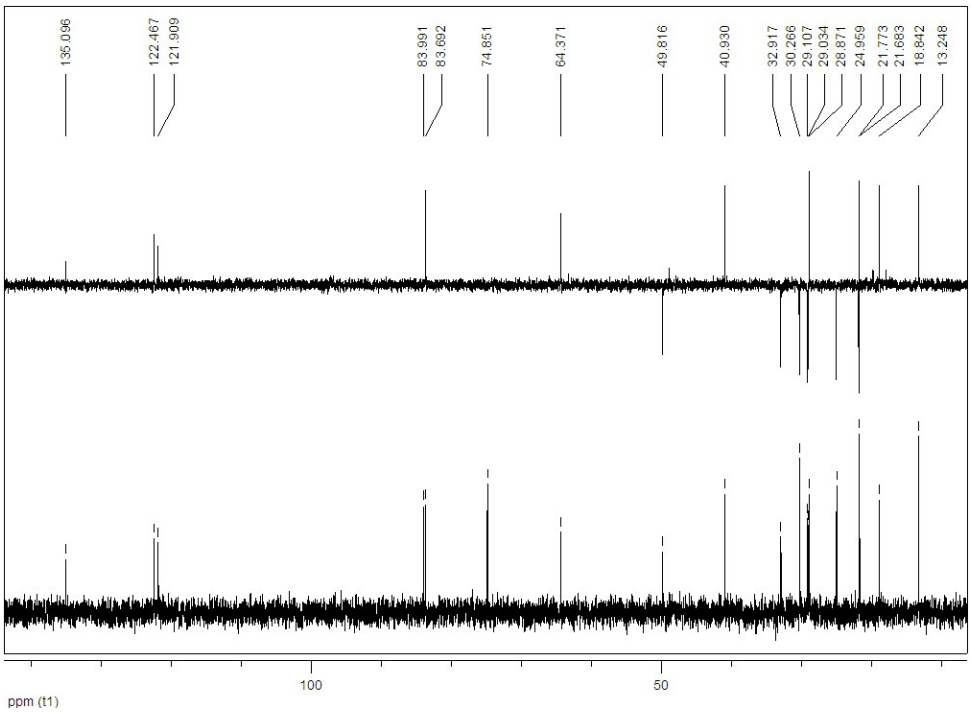
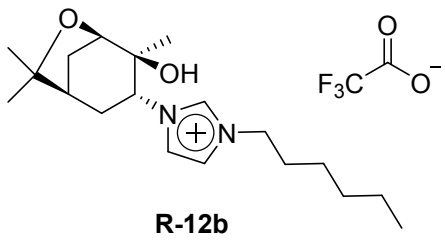


Figure S76- ^{13}C NMR and DEPT spectrum of compound S-12a



R-12b

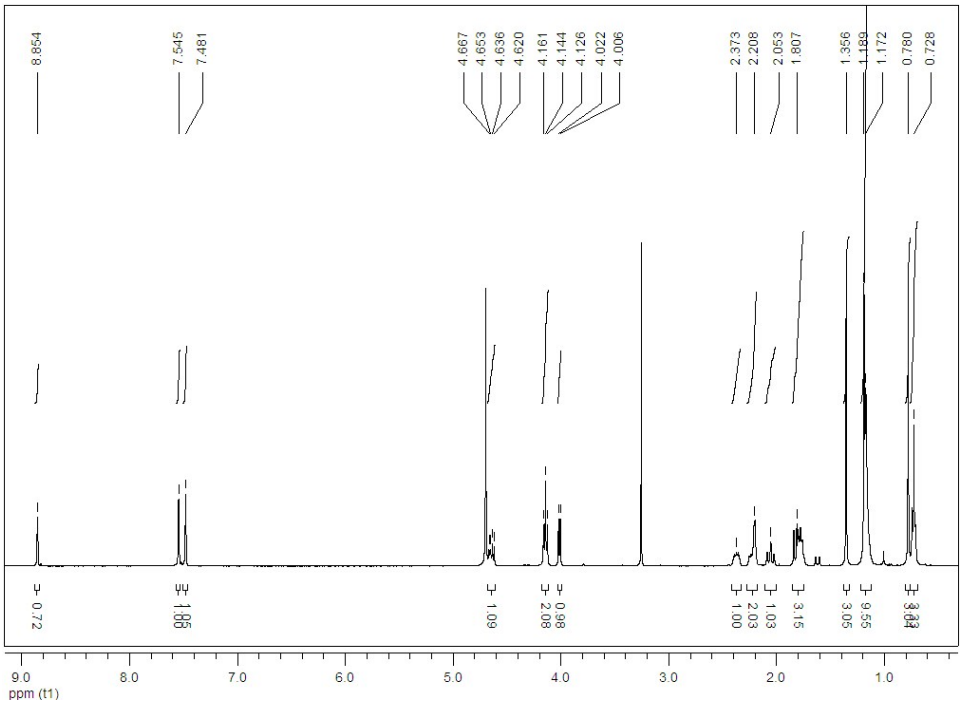


Figure S77- ^{1}H NMR spectrum of compound R-12b

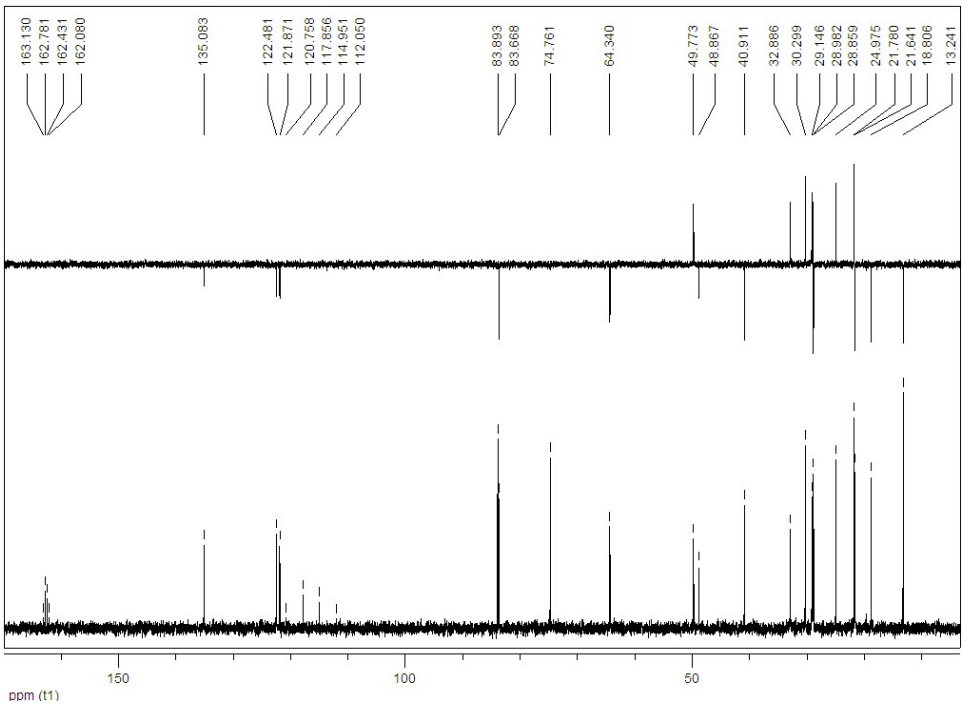
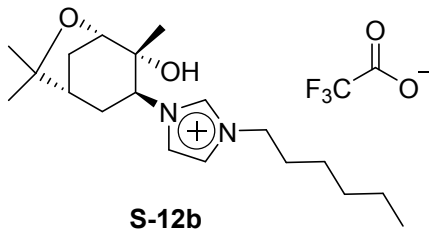


Figure S78- ^{13}C NMR and DEPT spectrum of compound R-12b



S-12b

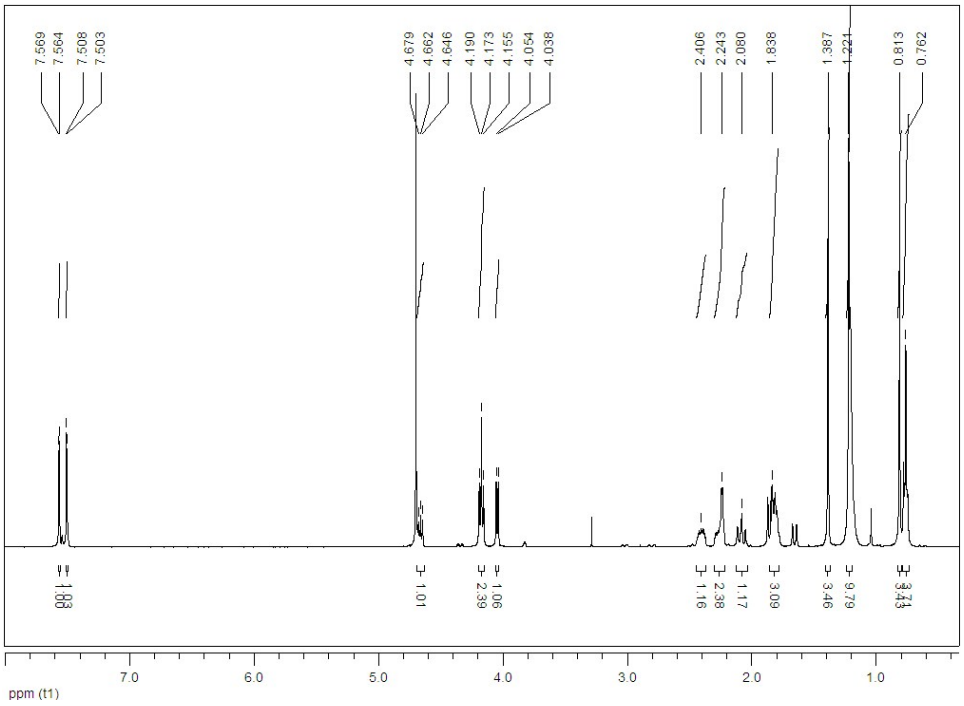


Figure S79- ^{1}H NMR spectrum of compound S-12b

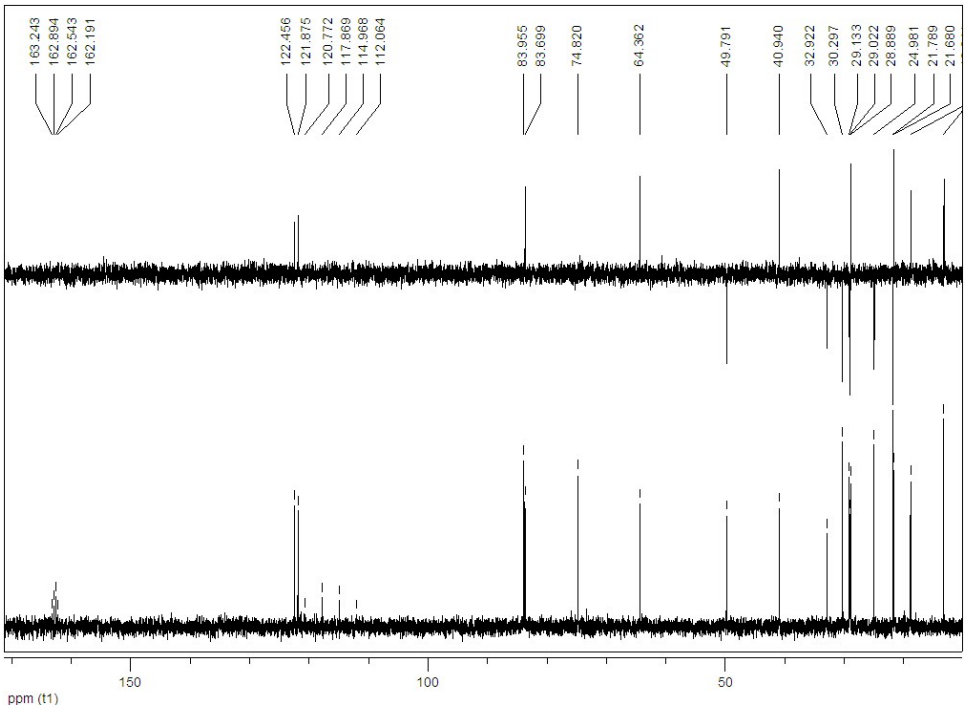
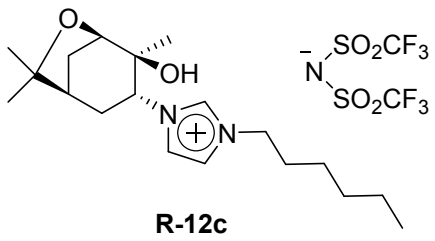


Figure S80- ^{13}C NMR and DEPT spectrum of compound S-12b



R-12c

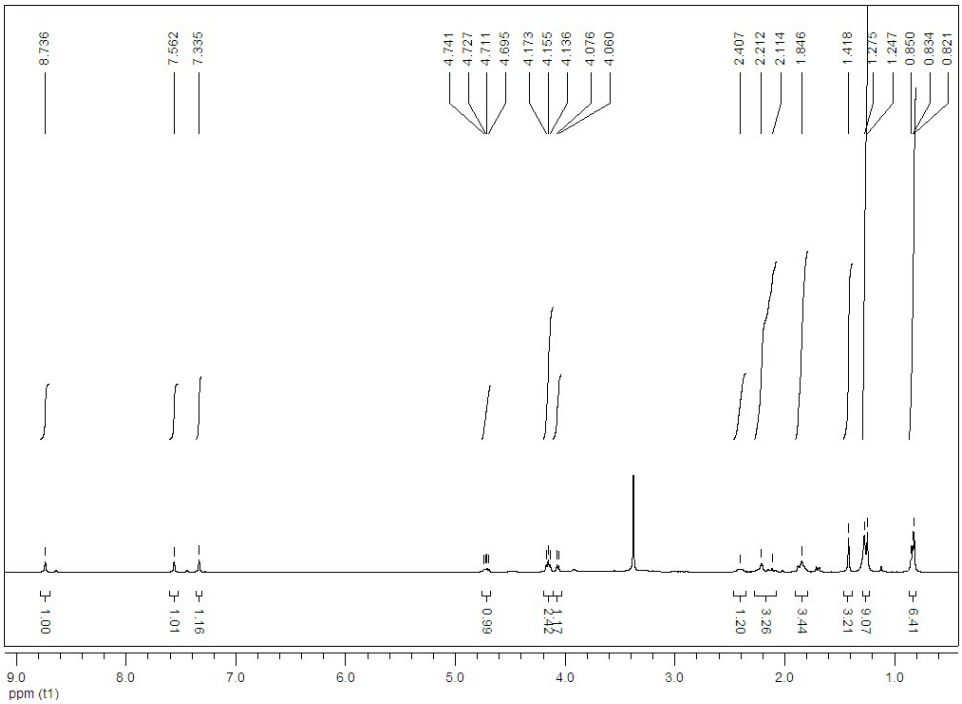


Figure S81- ^{1}H NMR spectrum of compound R-12c

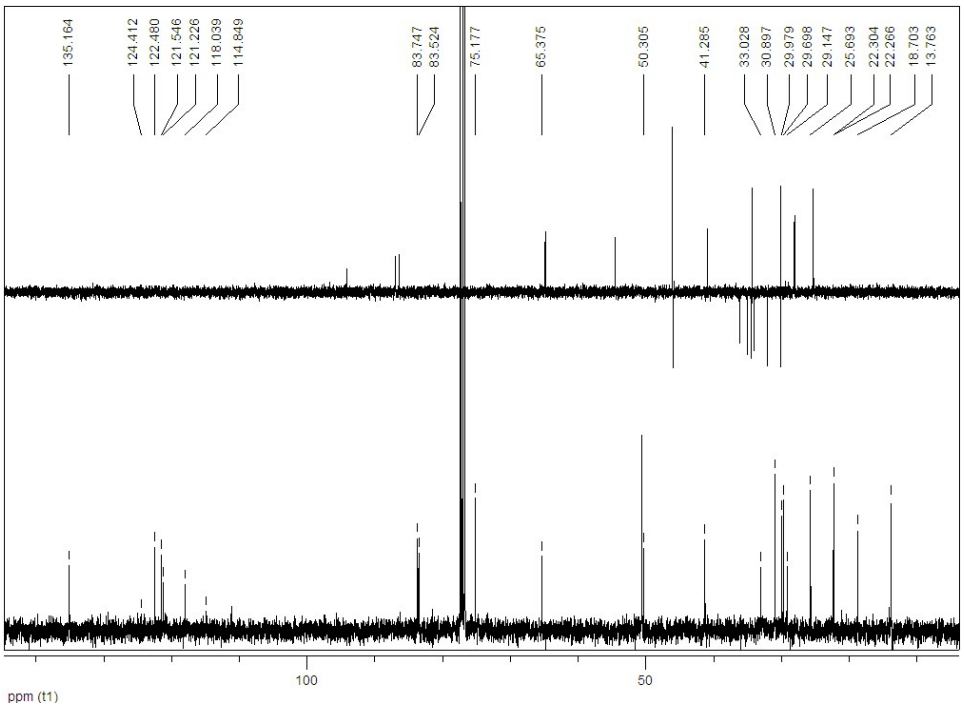
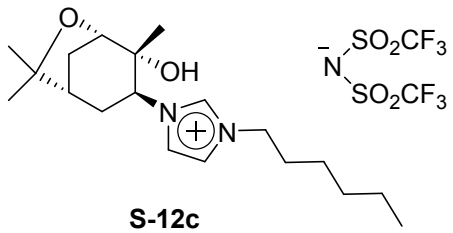


Figure S82- ^{13}C NMR and DEPT spectrum of compound R-12c



S-12c

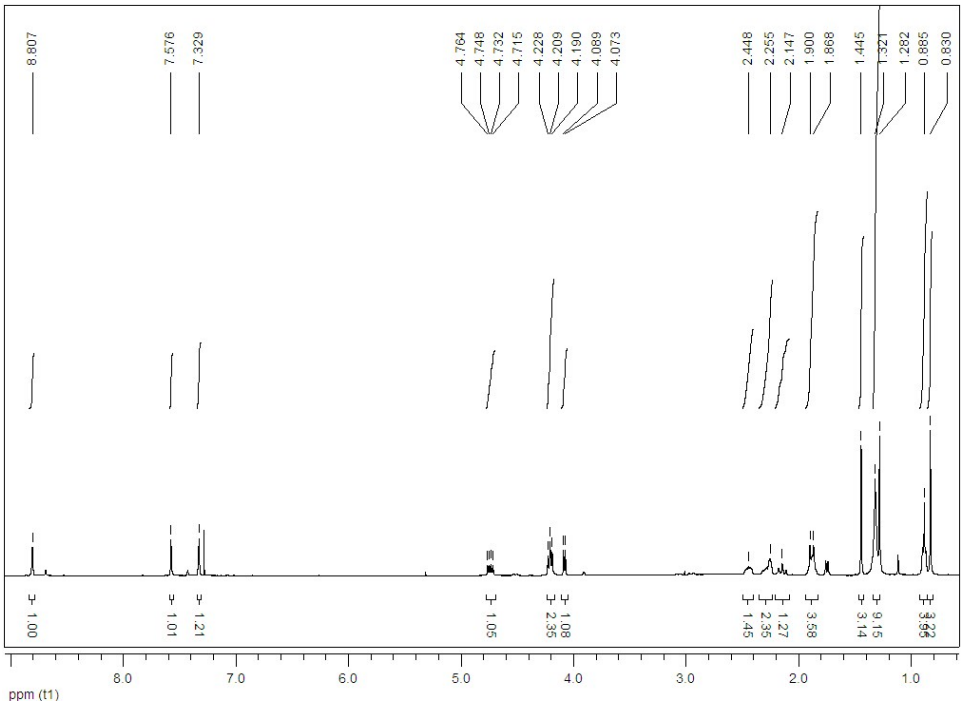


Figure S83- ^{1}H NMR spectrum of compound S-12c

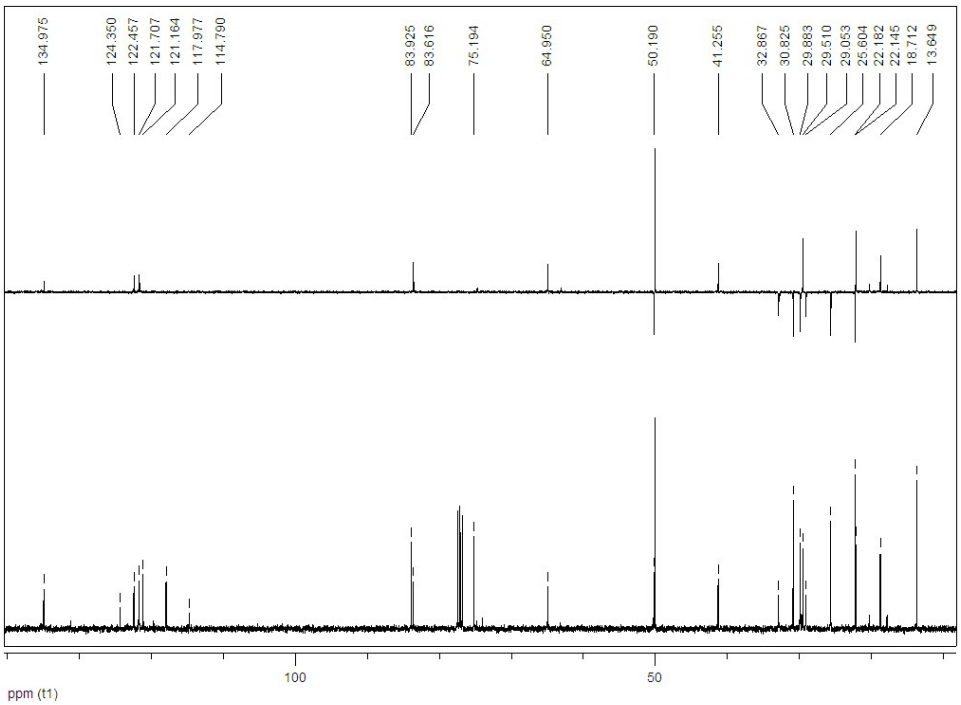
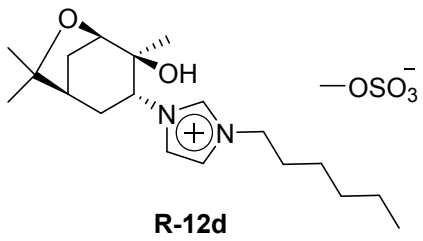


Figure S84- ^{13}C NMR and DEPT spectrum of compound S-12c



R-12d

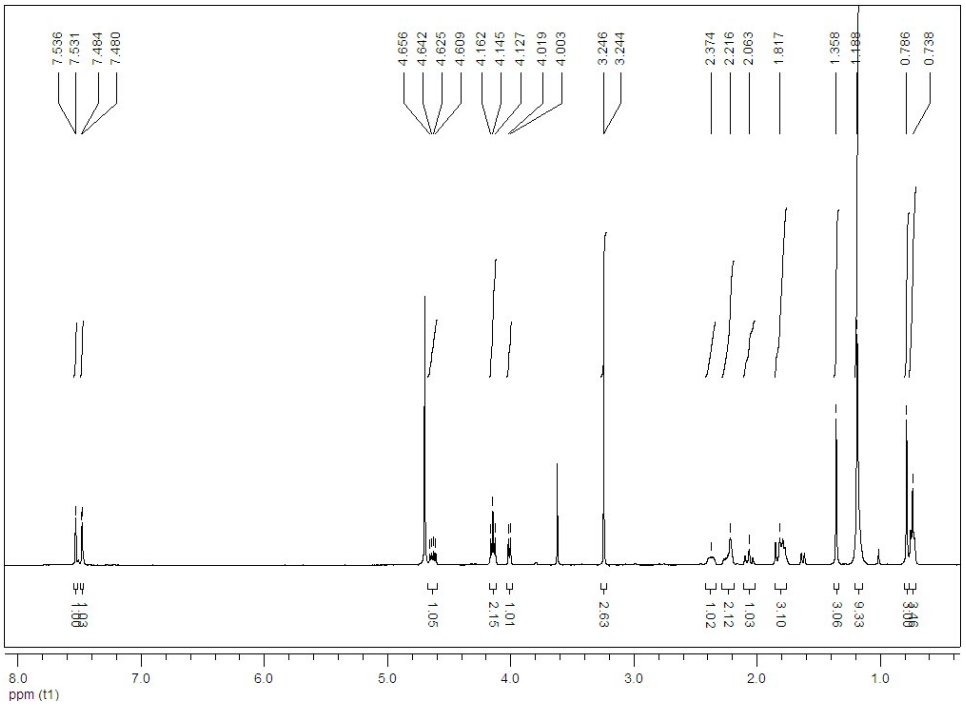


Figure S85- ^{1}H NMR spectrum of compound R-12d

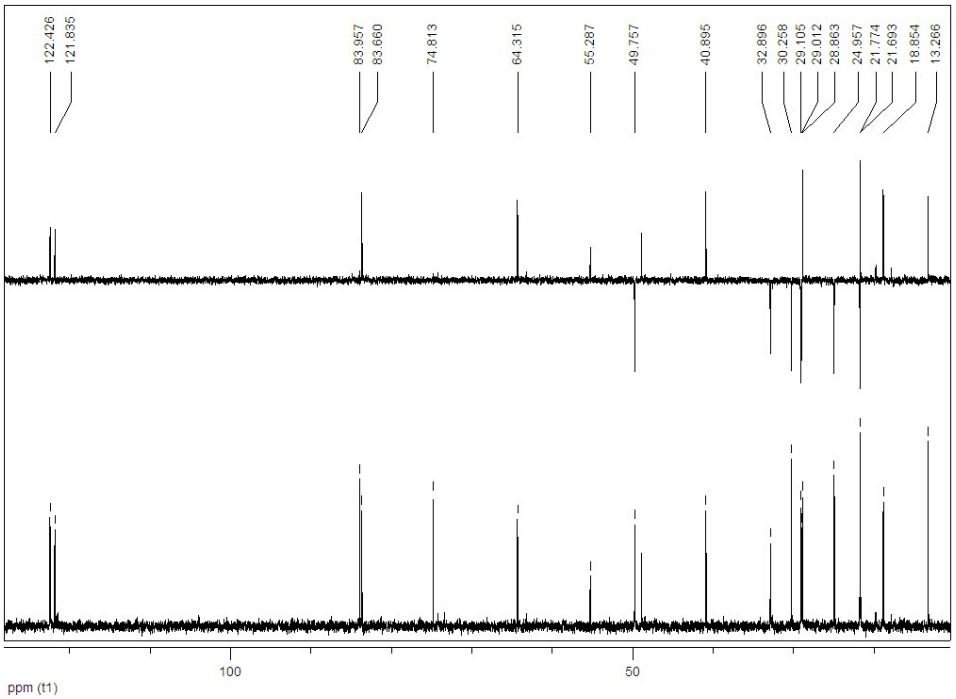
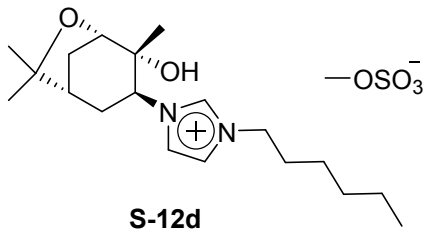


Figure S86- ^{13}C NMR and DEPT spectrum of compound R-12d



S-12d

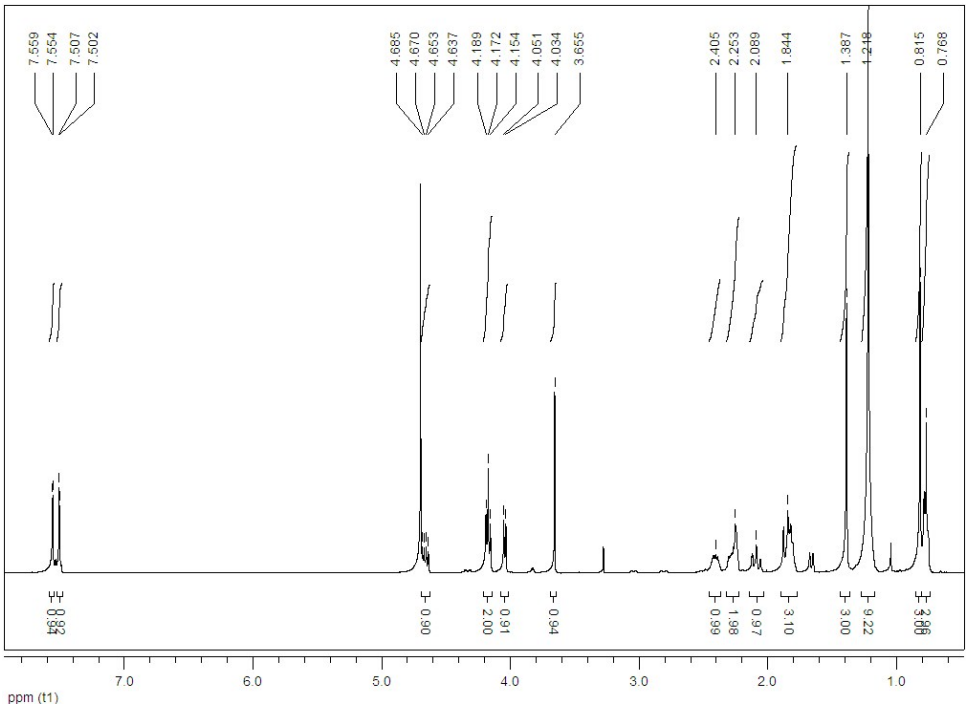


Figure S87- ^{1}H NMR spectrum of compound S-12d

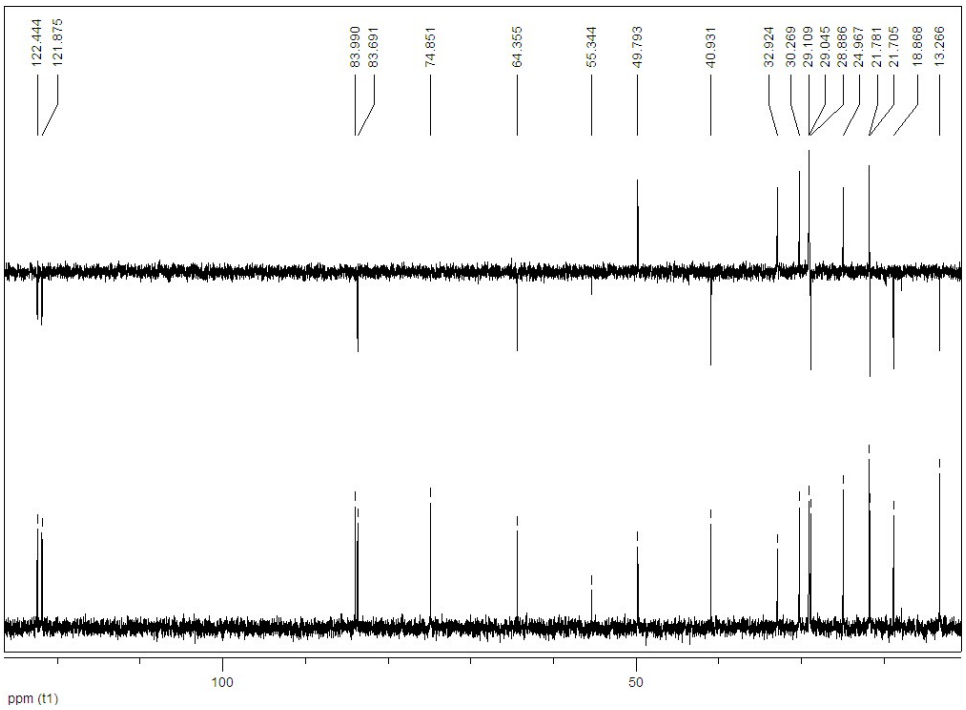
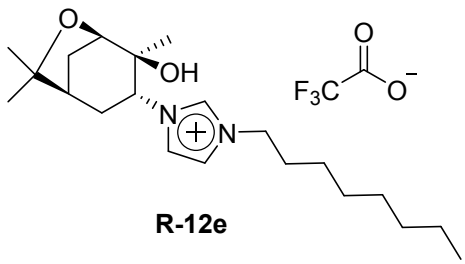


Figure S88- ^{13}C NMR and DEPT spectrum of compound S-12d



R-12e

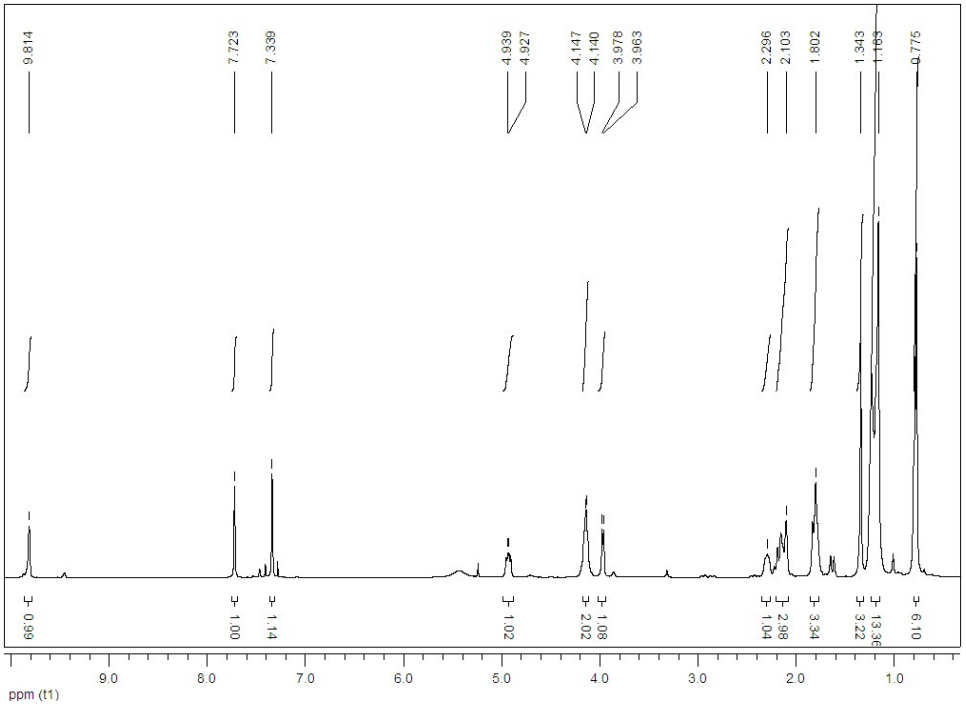


Figure S89- ^{1}H NMR spectrum of compound R-12e

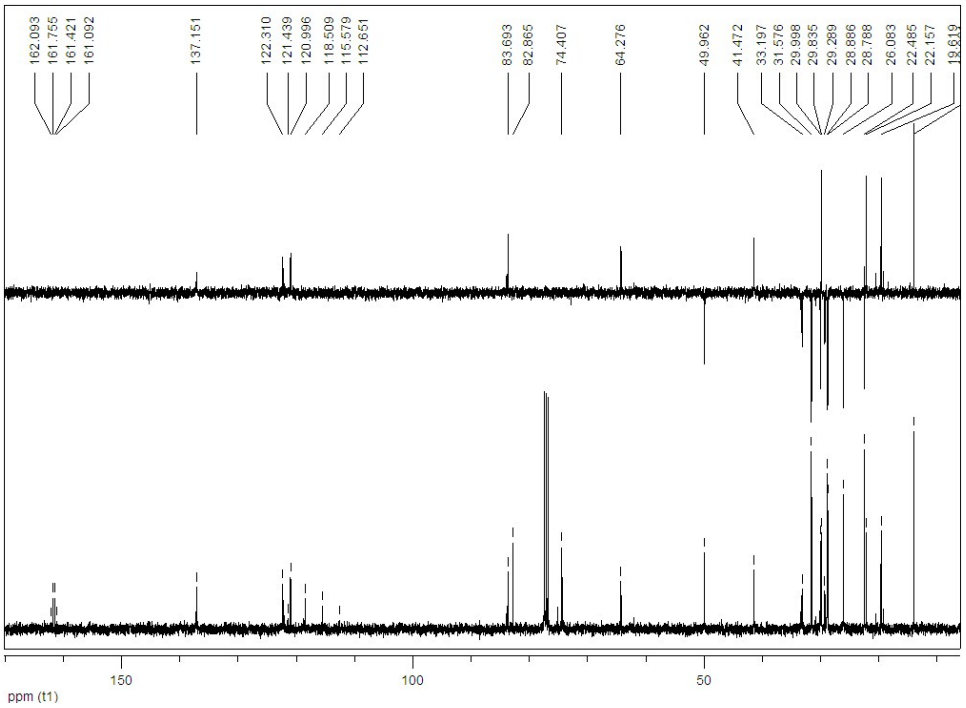
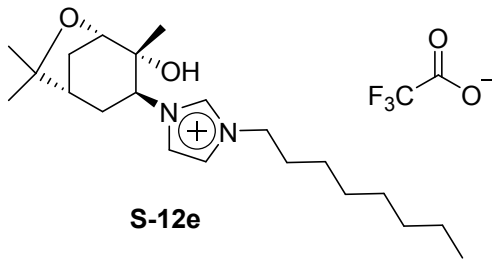


Figure S90- ^{13}C NMR and DEPT spectrum of compound R-12e



S-12e

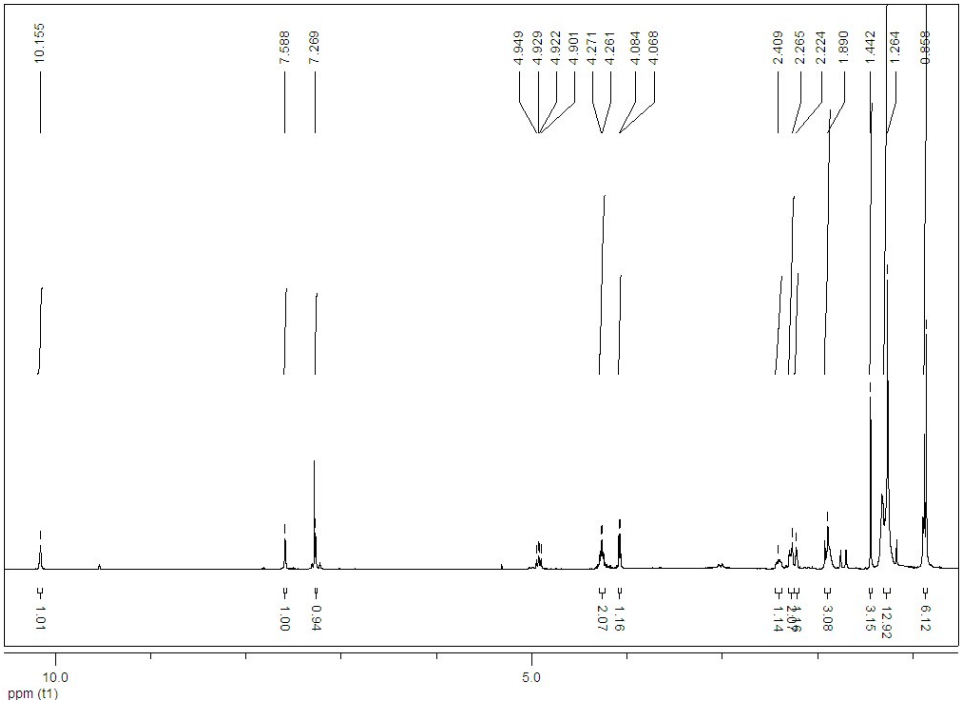


Figure S91- ^{1}H NMR spectrum of compound S-12e

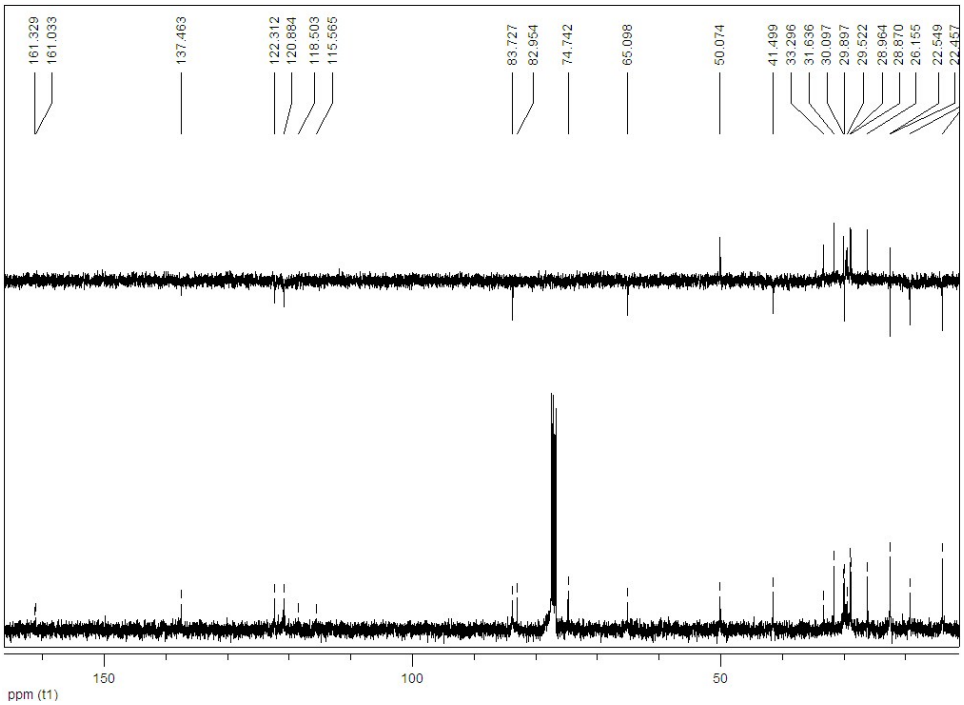
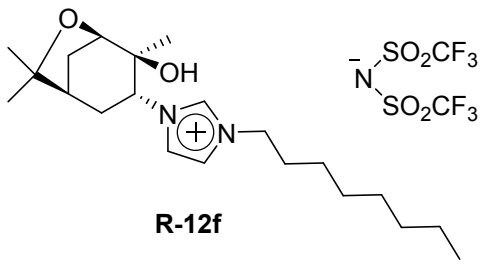


Figure S92- ^{13}C NMR and DEPT spectrum of compound S-12e



R-12f

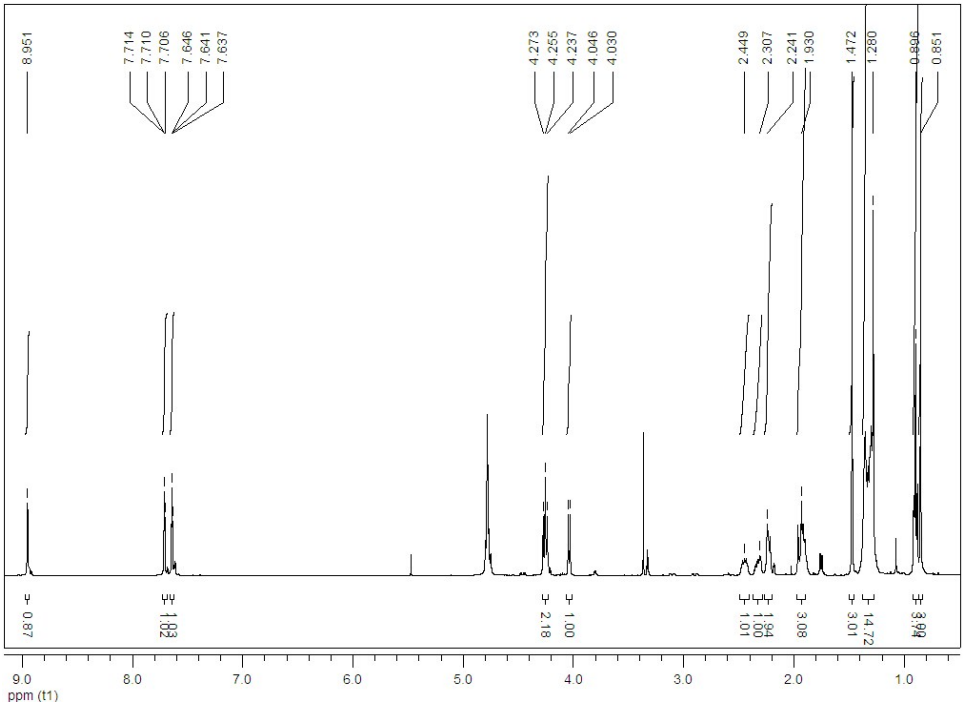


Figure S93- ^{1}H NMR spectrum of compound R-12f

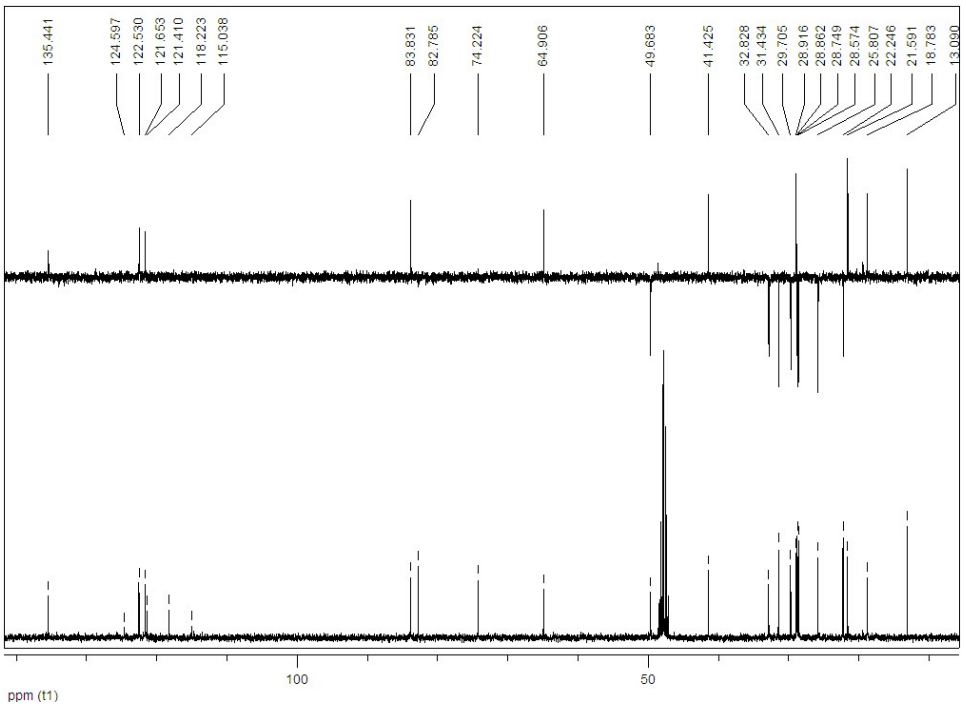
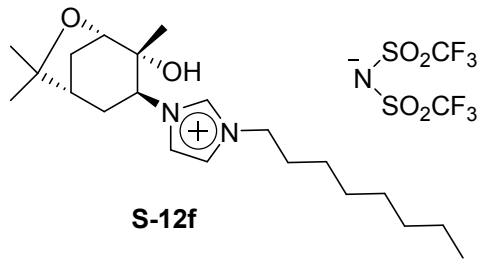


Figure S94- ^{13}C NMR and DEPT spectrum of compound R-12f



S-12f

Figure S95- ^{1}H NMR spectrum of compound S-12f

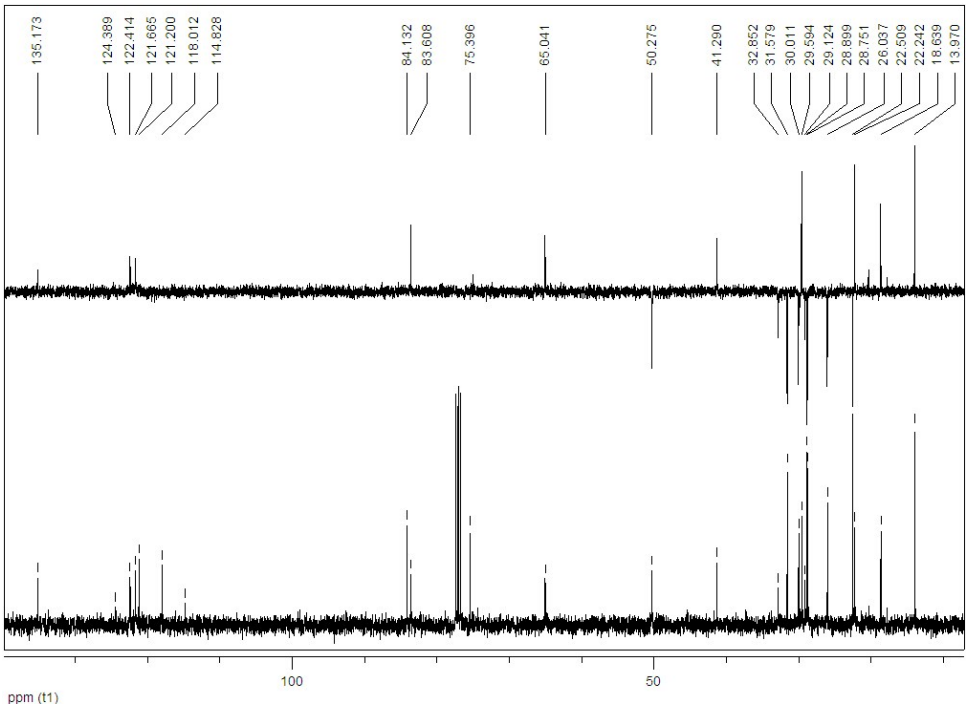
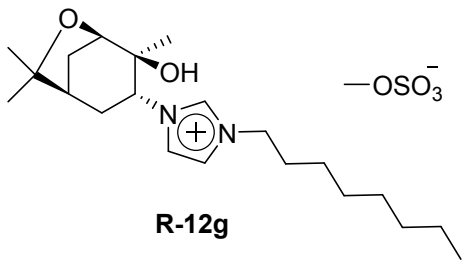


Figure S96- ^{13}C NMR and DEPT spectrum of compound S-12f



R-12g

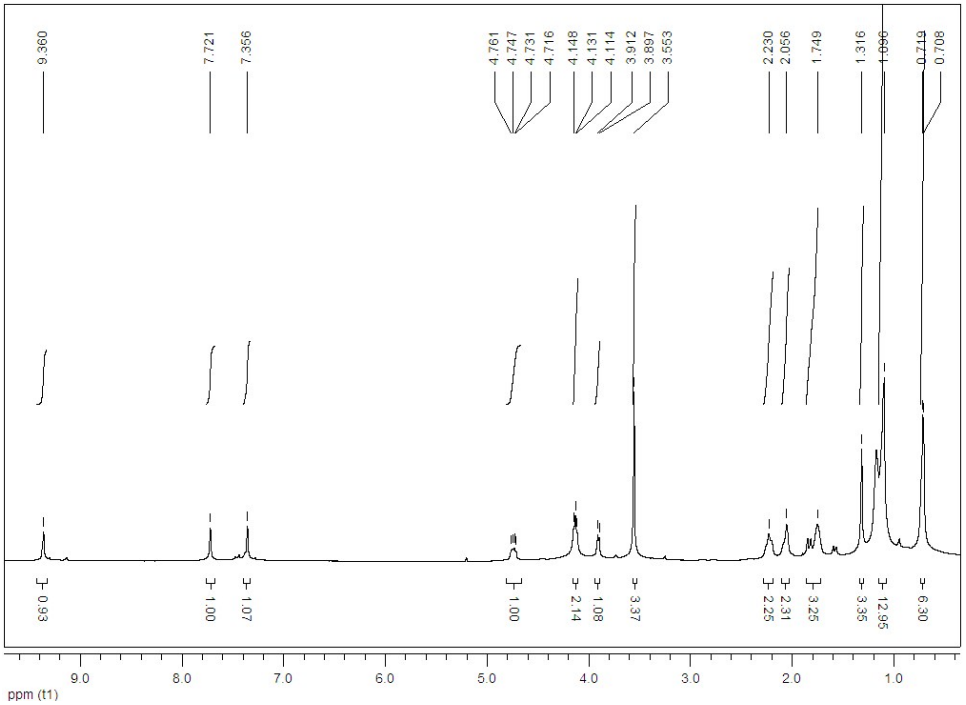


Figure S97- ^{1}H NMR spectrum of compound R-12g

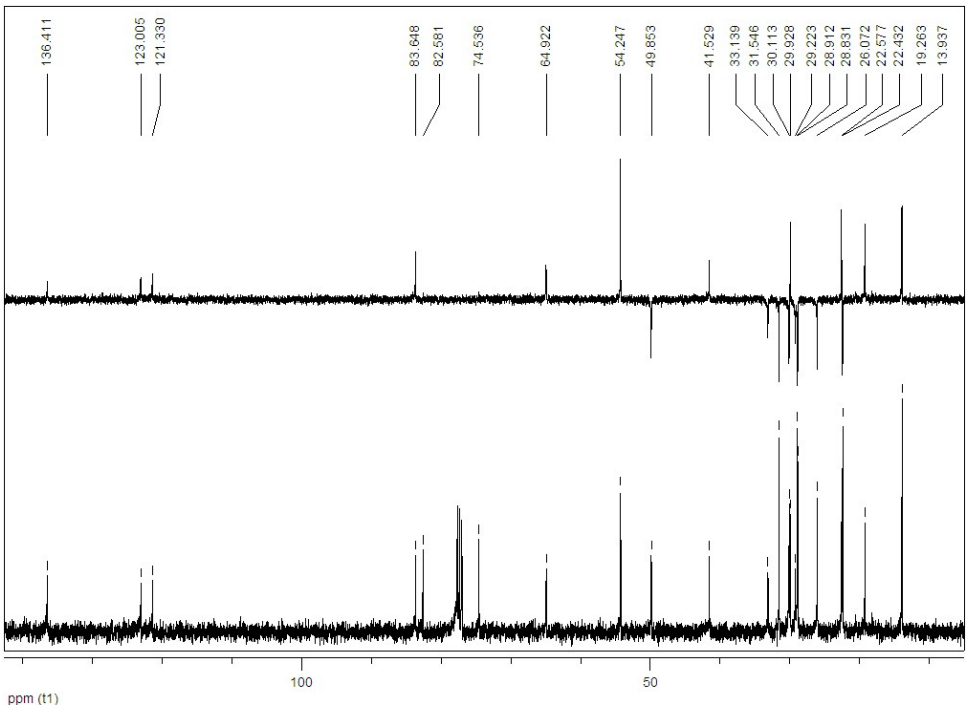
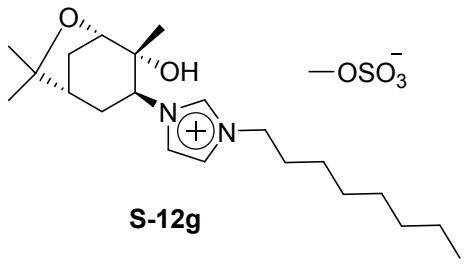


Figure S98- ^{13}C NMR and DEPT spectrum of compound R-12g



S-12g

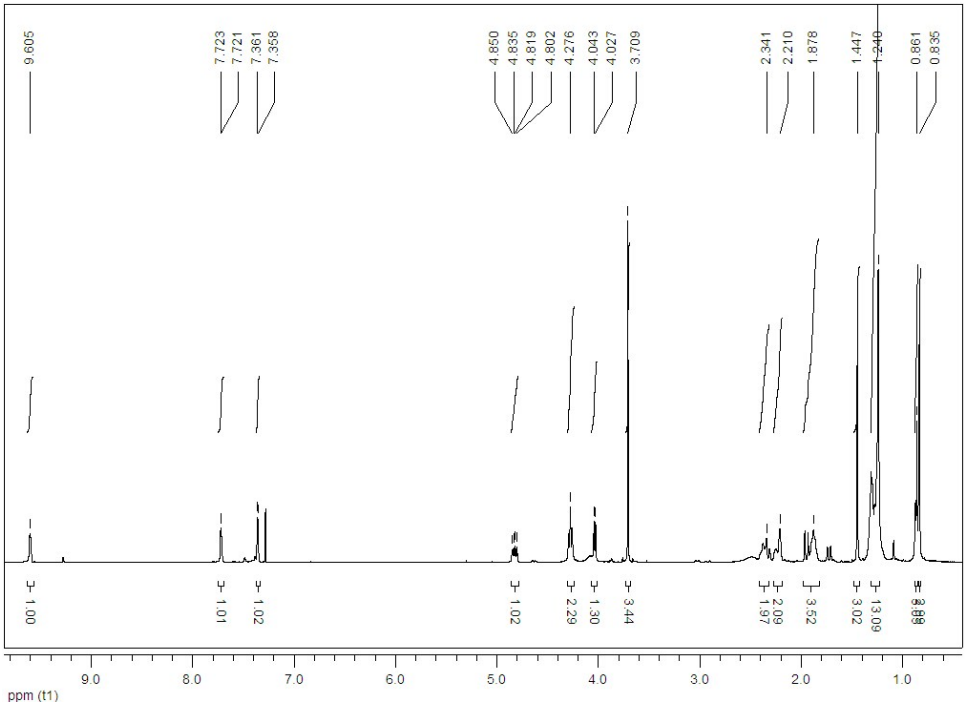


Figure S99- ^{1}H NMR spectrum of compound S-12g

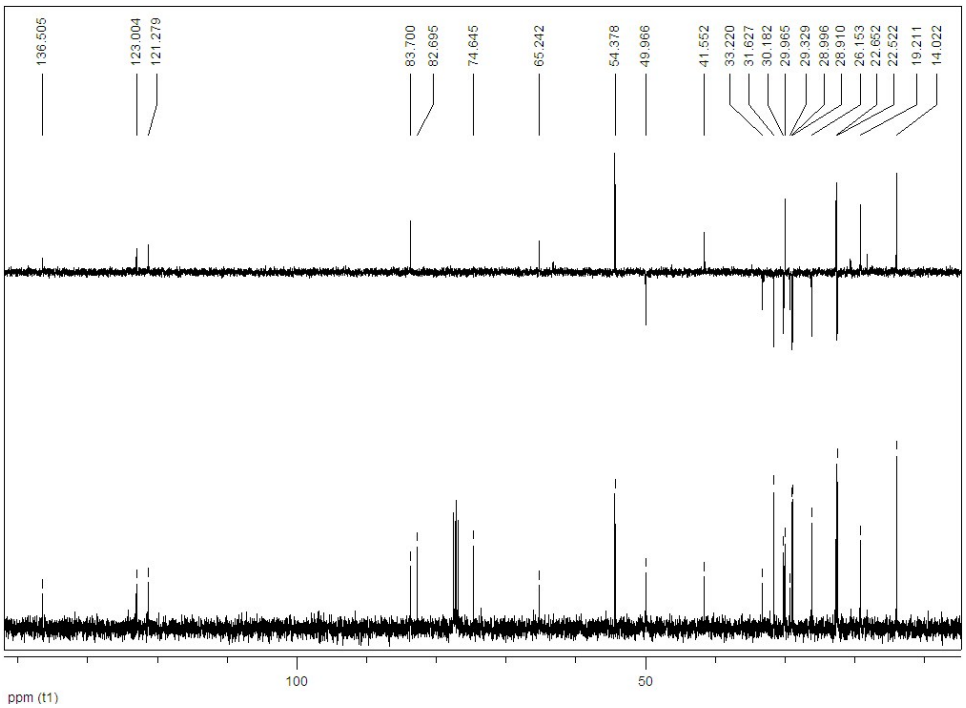
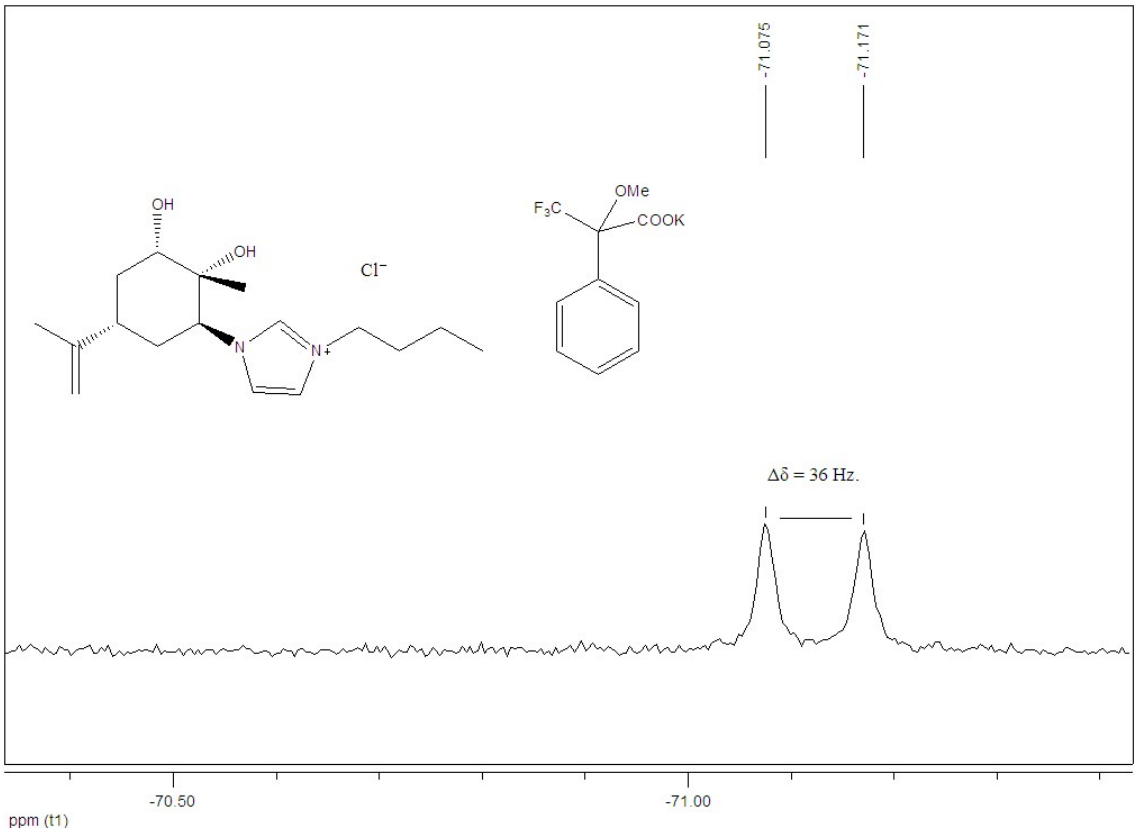
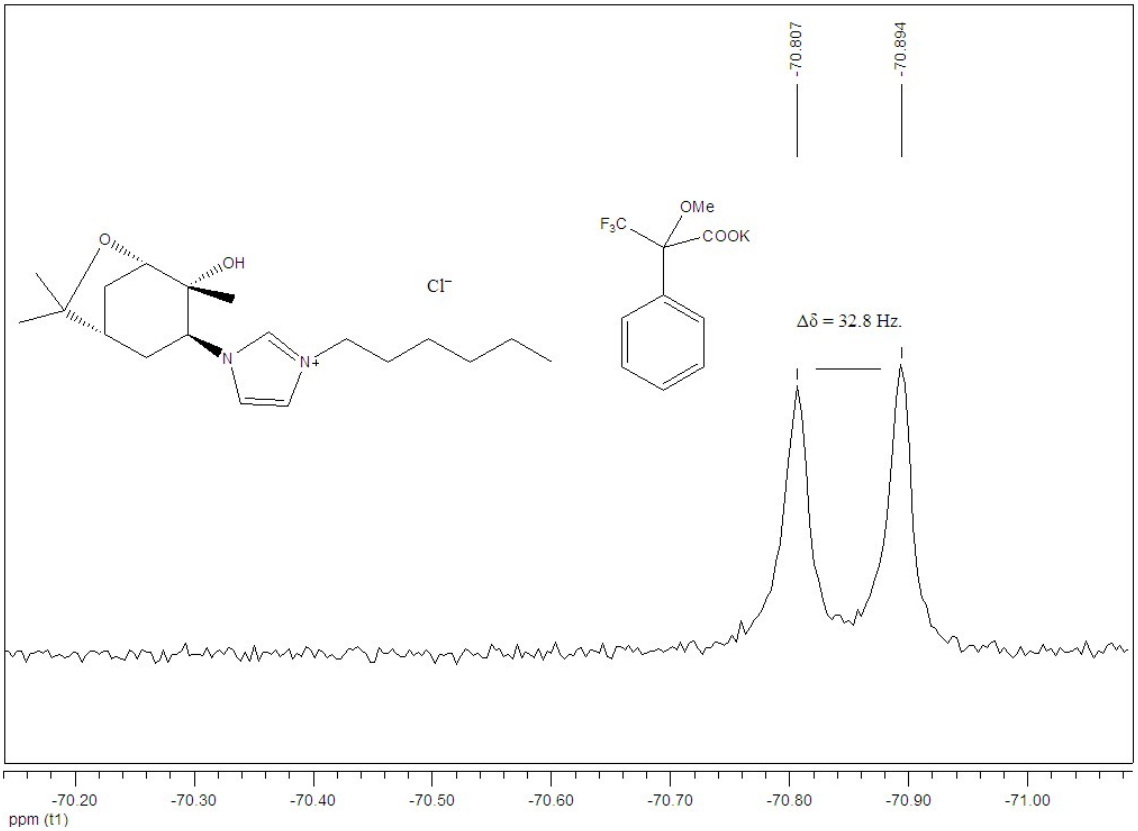
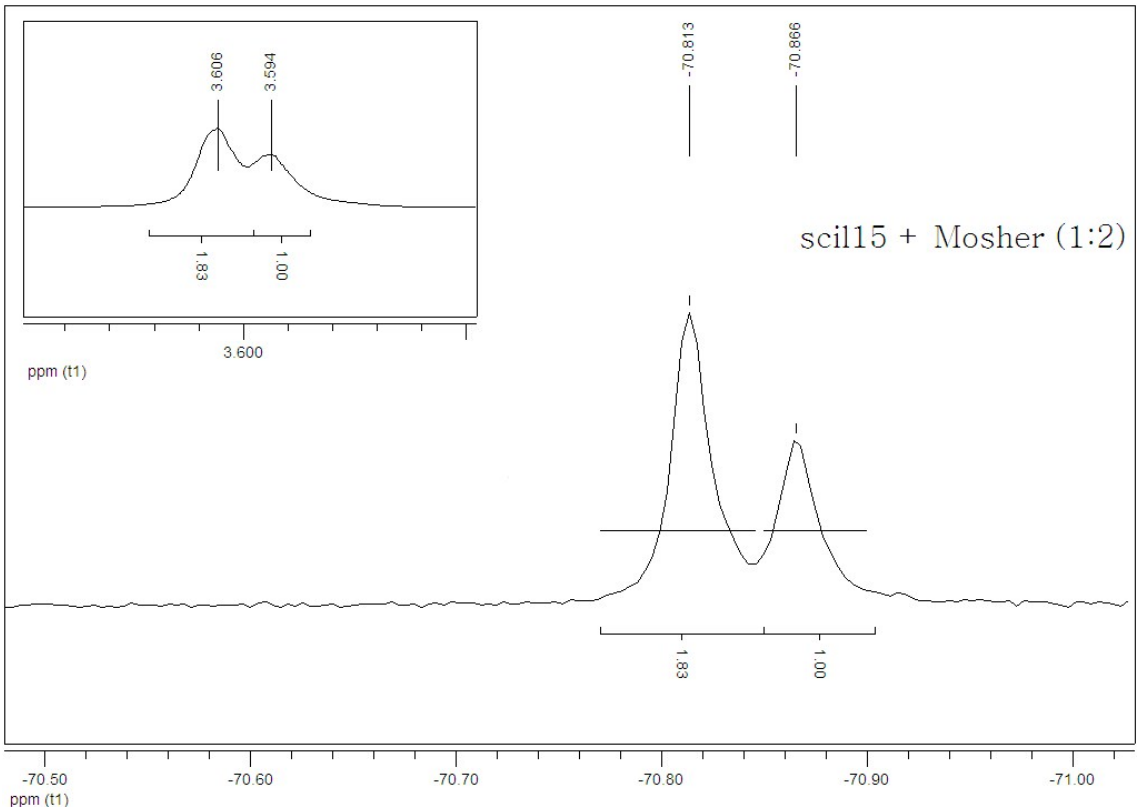
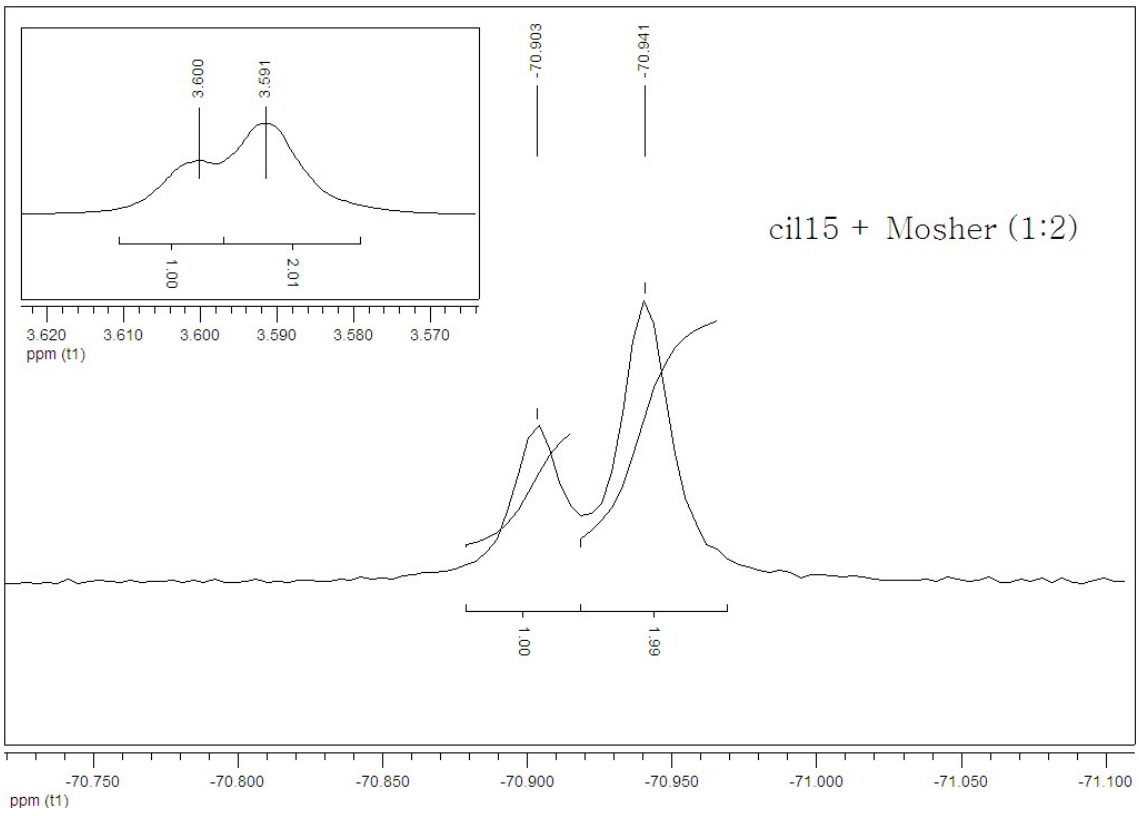


Figure S100- ^{13}C NMR and DEPT spectrum of compound S-12g


-71.075
-71.171
OH
OH
Cl⁻
F3C
OMe
COOK
Δδ = 36 Hz.
-70.50
-71.00
ppm (t1)


-70.807
-70.894
O
OH
Cl⁻
F3C
OMe
COOK
Δδ = 32.8 Hz.
-70.20
-70.30
-70.40
-70.50
-70.60
-70.70
-70.80
-70.90
-71.00
ppm (t1)


3.606
3.594
1.83
1.00
3.600
ppm (t1)
-70.813
-70.866
scil15 + Mosher (1:2)
1.83
1.00
-70.50
-70.60
-70.70
-70.80
-70.90
-71.00
ppm (t1)


3.600
3.591
1.00
2.01
3.620
3.610
3.600
3.590
3.580
3.570
ppm (t1)
-70.903
-70.941
cil15 + Mosher (1:2)
1.00
1.99
-70.750
-70.800
-70.850
-70.900
-70.950
-71.000
-71.050
-71.100
ppm (t1)