Supplementary Material

Design and synthesis of novel C_2-symmetric chiral shift reagents derived from squaramide and their recognition of anions and chiral carboxylate anions

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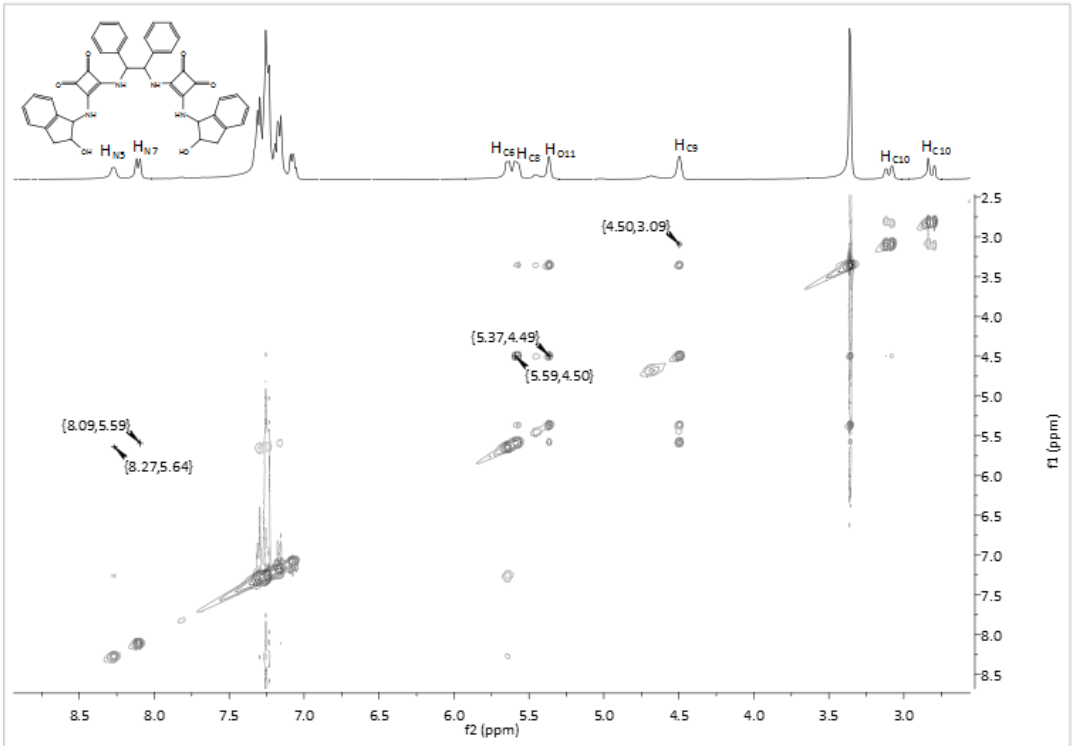
1. General information

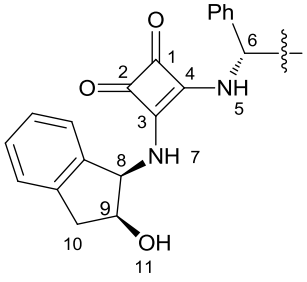
Unless otherwise noted, reagents and materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran and toluene as well as ethanol were dried over Na and distilled prior to use. Dichloromethane was dried over CaH_2 and distilled prior to use. Glassware was oven-dried, assembled while hot, and cooled under an inert atmosphere. Unless otherwise noted, all reactions were conducted in an inert atmosphere. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker Biospin AV400 (400 MHz) instrument. The chemical shifts are reported in ppm and are referenced to either tetramethylsilane or the solvent.

2. Detail studies of C_2-symmertric chiral shift reagent 2 structure from ^{1}H NMR spectra and 2D NOESY spectra.



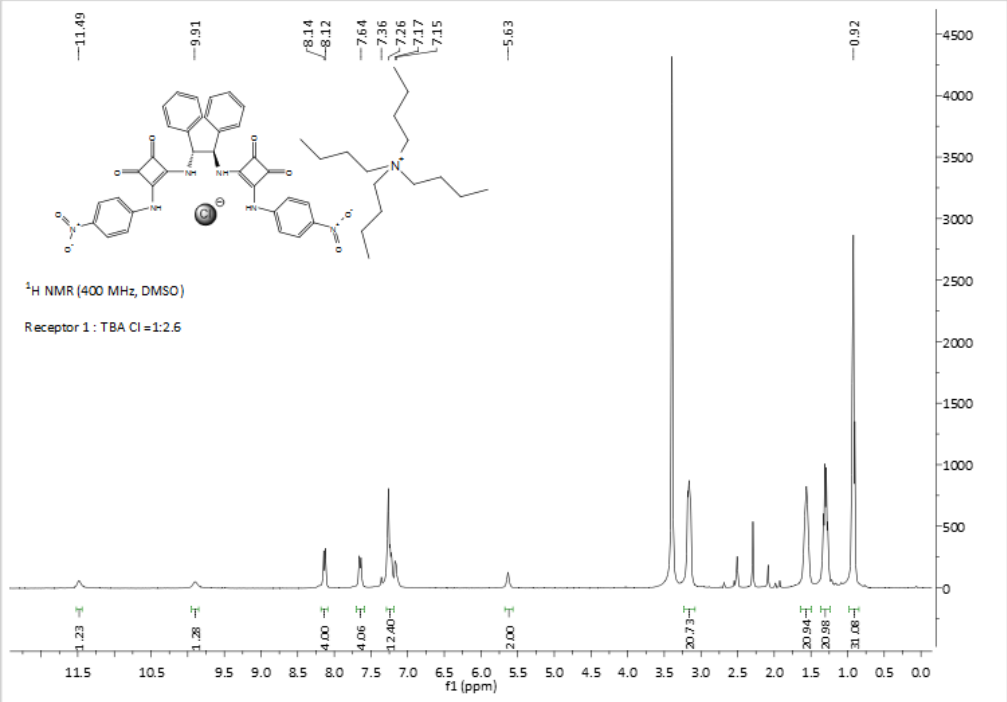
2D NOESY spectra of C_2-symmertric chiral shift reagent **2**

Combined with ^{1}H NMR spectra and 2D NOESY spectra, the chemical shift of each H was assigned: H_{C10} (δ 3.09 ppm and δ 2.85 ppm); H_{C9} (δ 4.50 ppm); H_{O11} (δ 5.37 ppm); H_{C8} (δ 5.59 ppm); H_{C6} (δ 5.64 ppm); H_{N7} (δ 8.09 ppm); H_{N5} (δ 8.27 ppm).

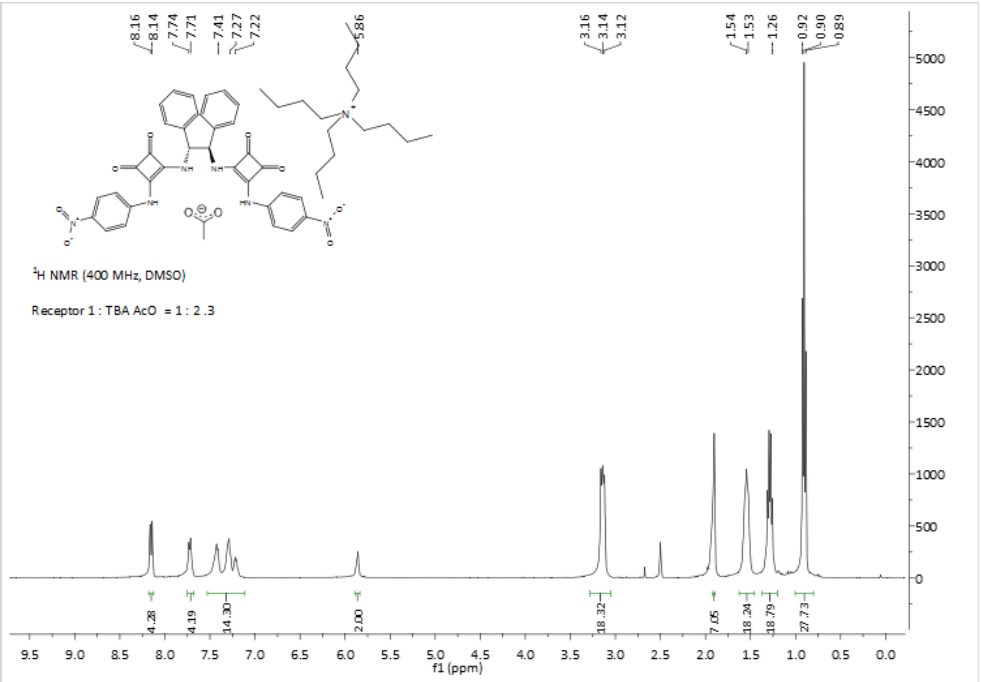


3. The binding properties of C_2-symmertric chiral shift reagent 1 and 2 with different anions.

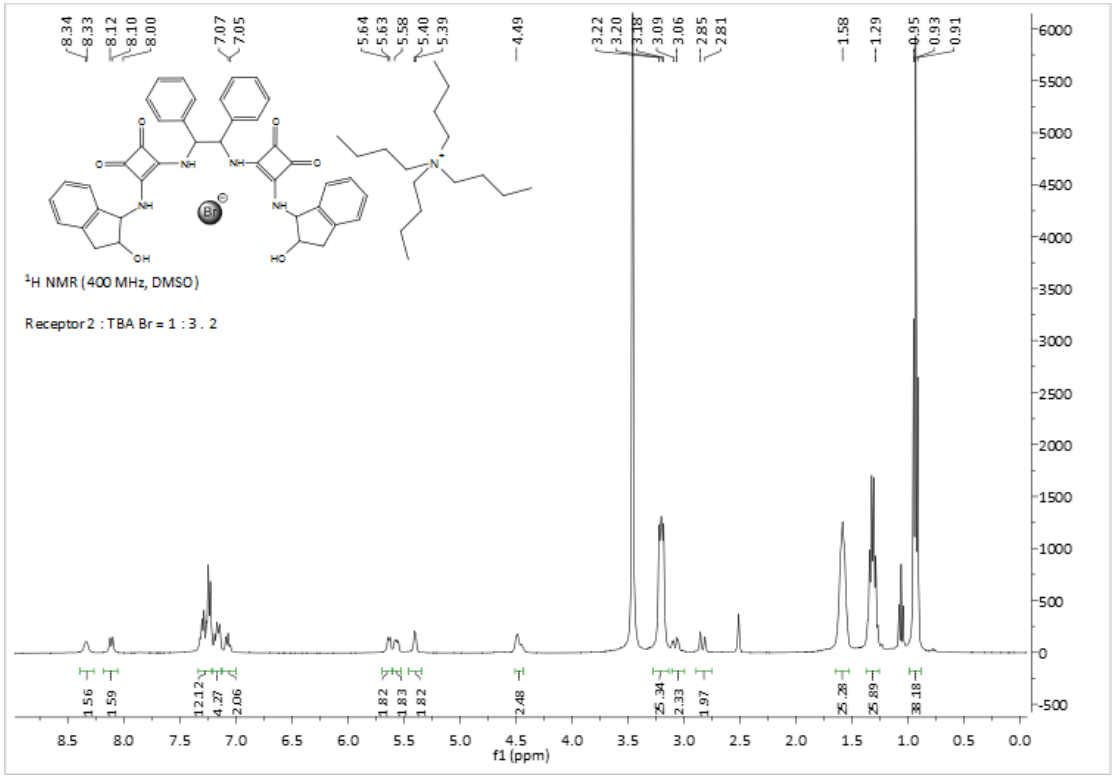
3.1 ^{1}H NMR of Receptor **1** with tetrabutyl ammonium chloride (mole ratio, n/n = 1:2.6) (400MHz, DMSO-d_6)



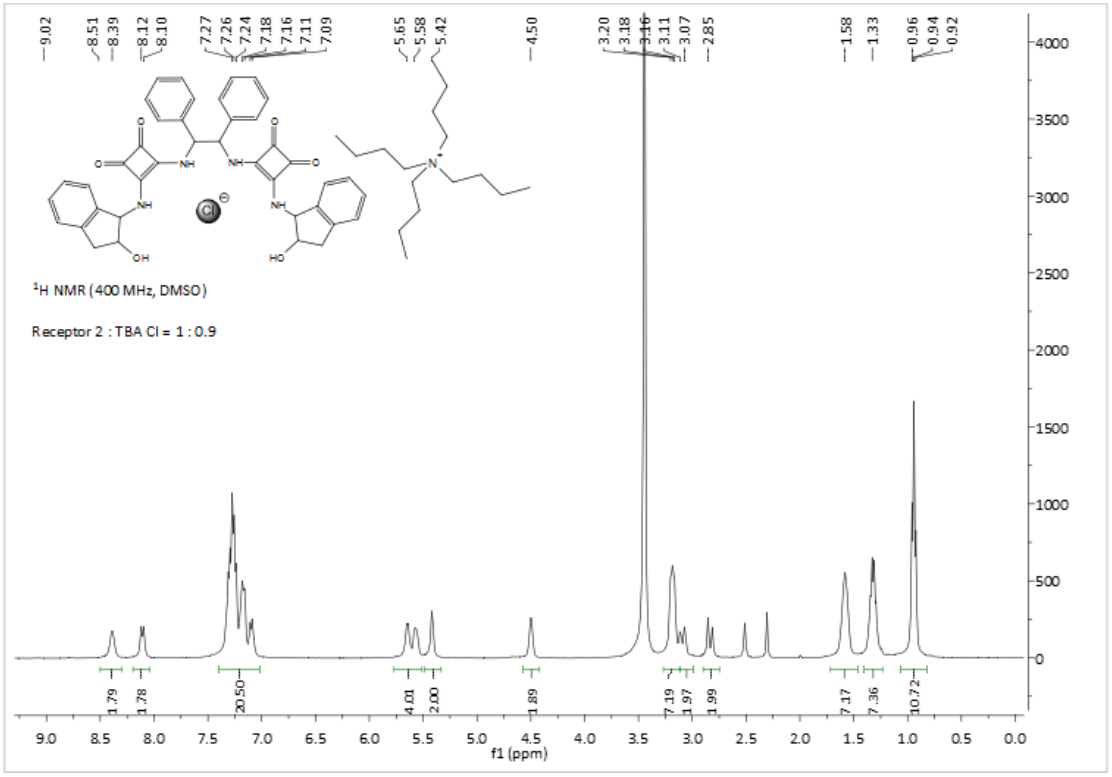
3.2 ^{1}H NMR of Receptor **1** with tetrabutyl ammonium acetate (mole ratio, n:n = 1:2.3) (400MHz, DMSO-d_6)



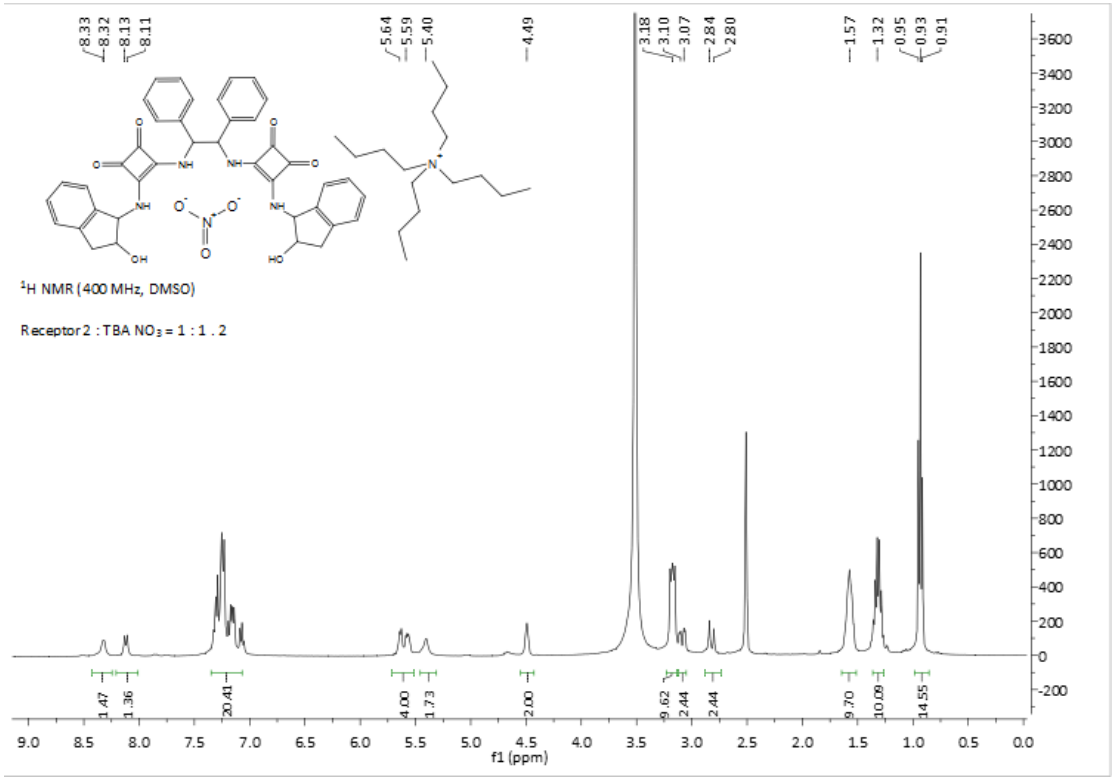
3.3 ^{1}H NMR of Receptor **2** with tetrabutyl ammonium bromide (mole ratio, n/n = 1:3.2) (400MHz, DMSO-d_6)



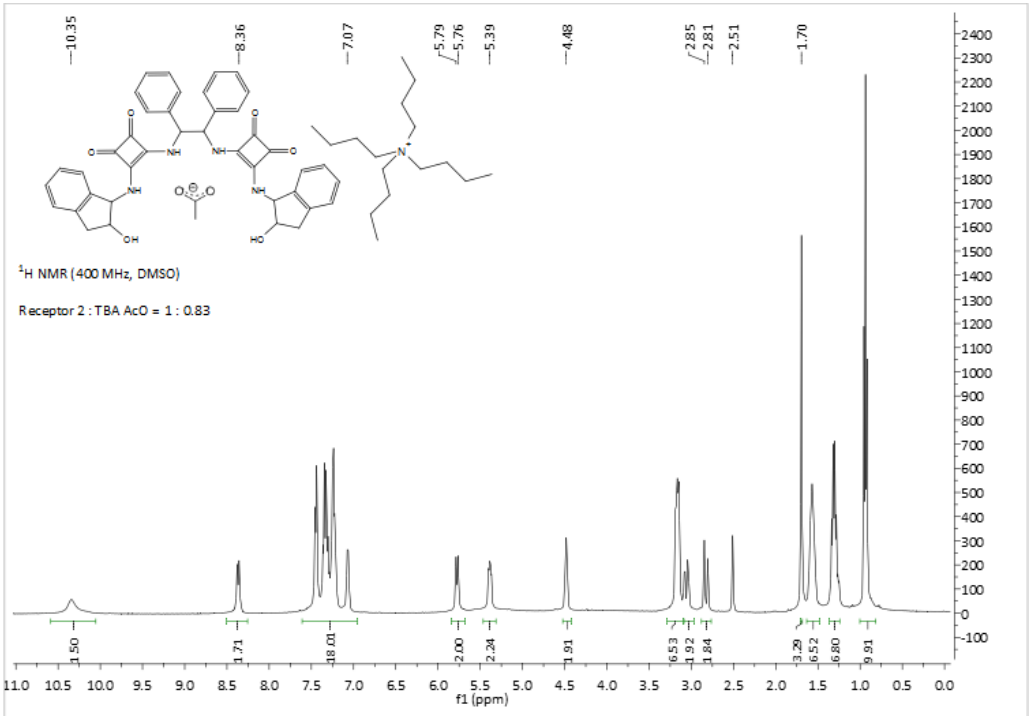
3.4 Receptor **2** with tetrabutyl ammonium chloride (mole ratio, n/n = 1:0.9) (400MHz, DMSO-d_6)



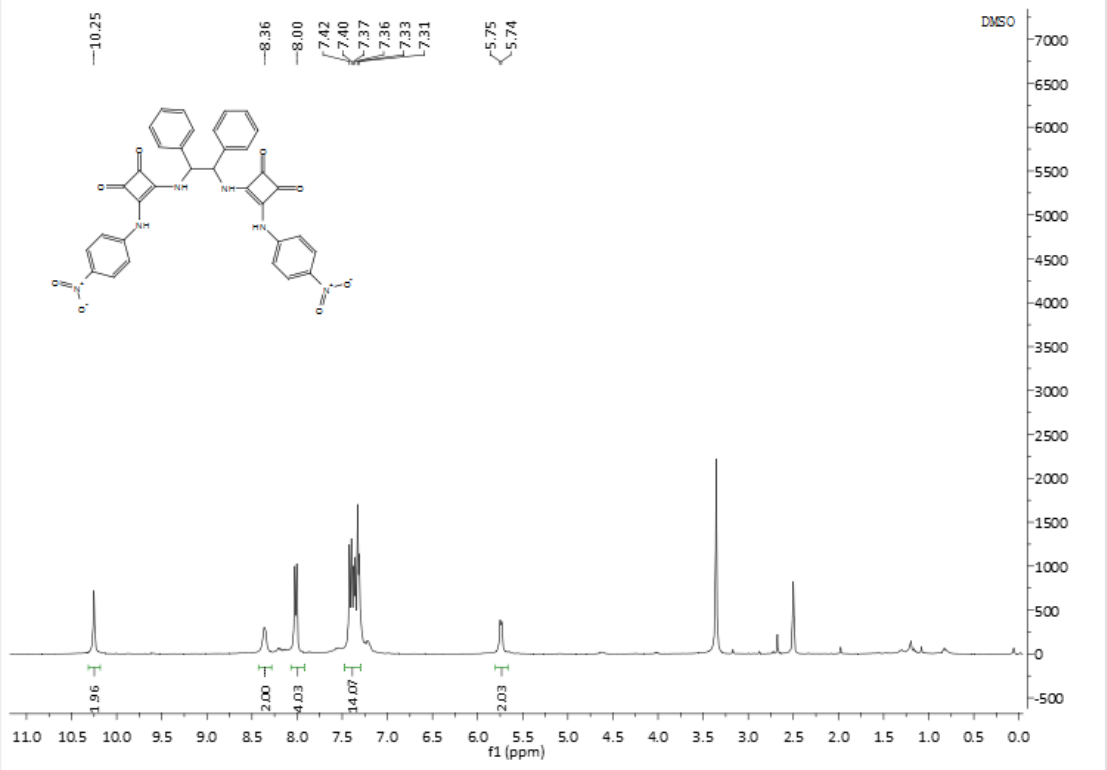
3.5 ^{1}H NMR of Receptor **2** with tetrabutyl ammonium nitrate (mole ratio, n/n = 1:1.2) (400MHz, DMSO-d_6)



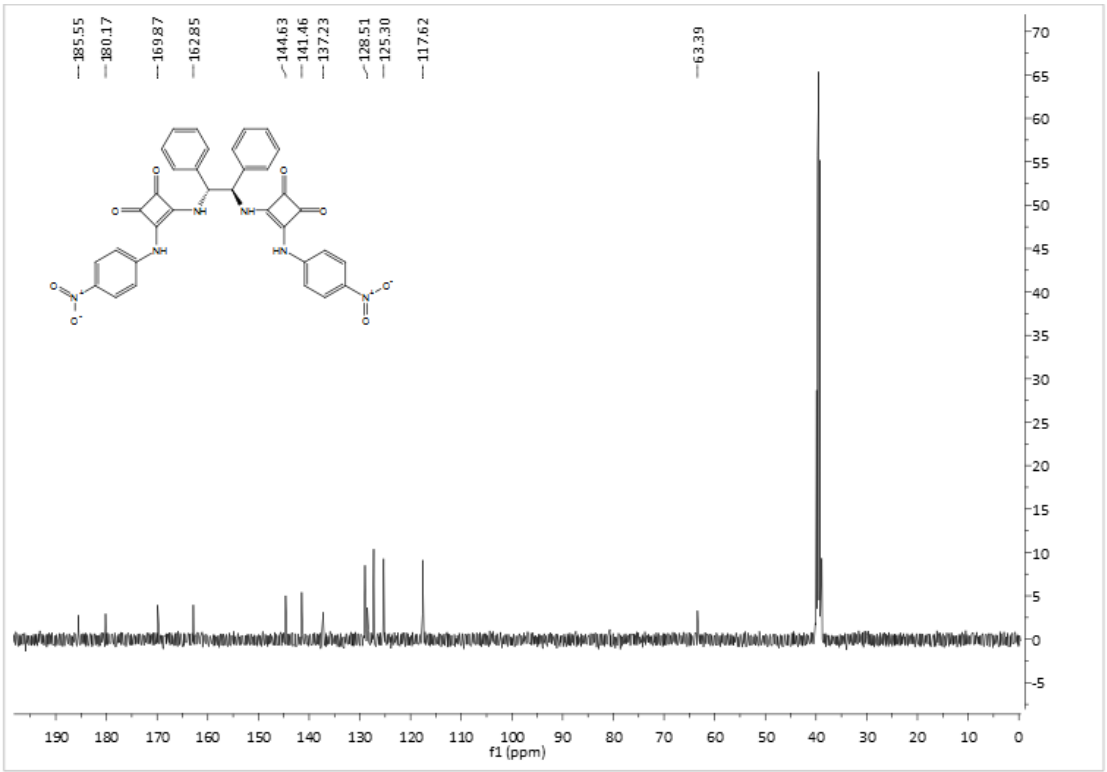
3.6 ^{1}H NMR of Receptor **2** with tetrabutyl ammonium acetate (mole ratio, n/n = 1:0.83) (400MHz, DMSO-d_6)



4. ^{1}H and ^{13}C NMR spectra for 1-3 and 6

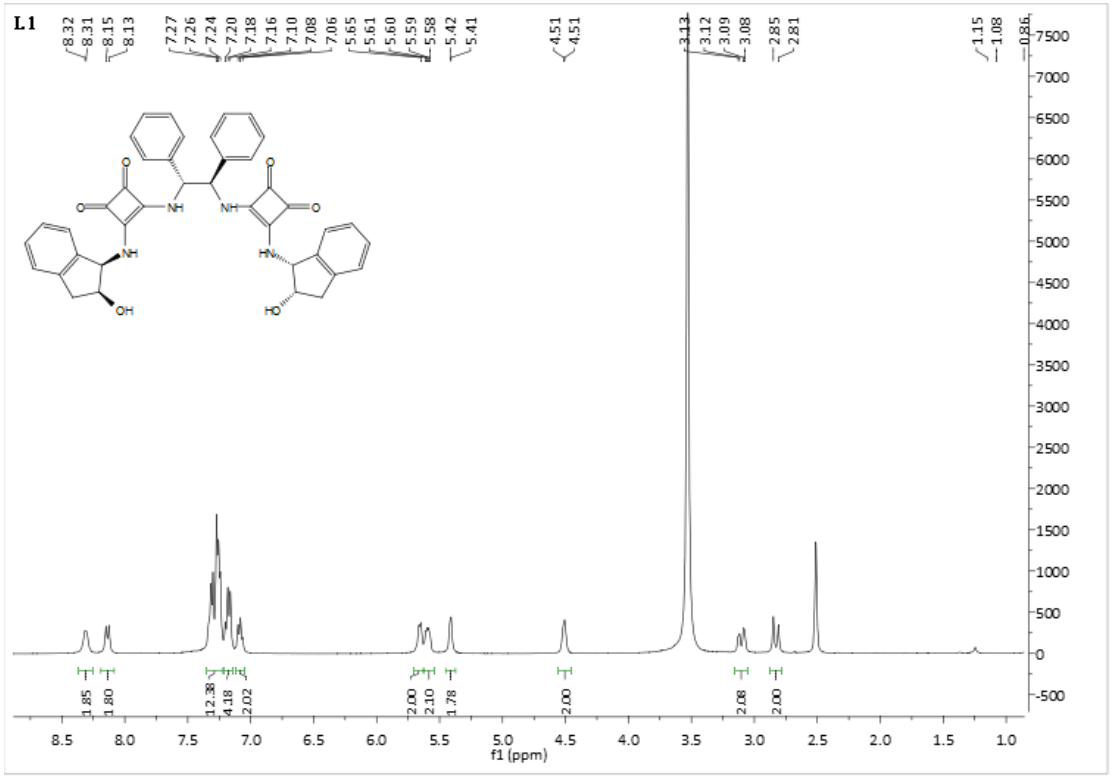


^{13}C NMR (100MHz, DMSO-d_6)

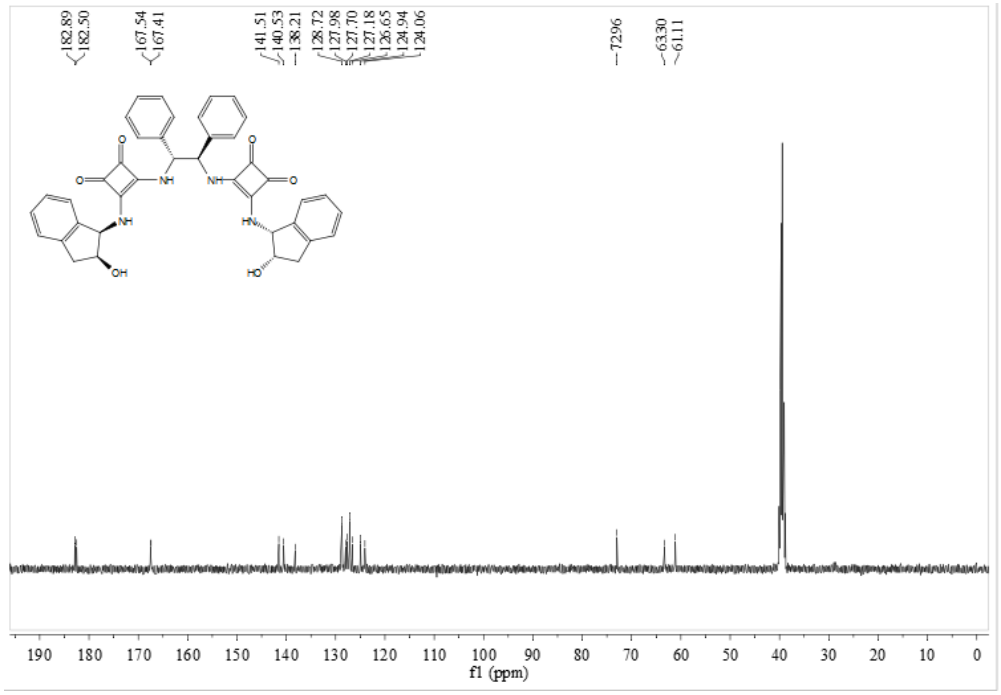


4.2 Receptor 2

^{1}H NMR (400MHz, DMSO-d_6)

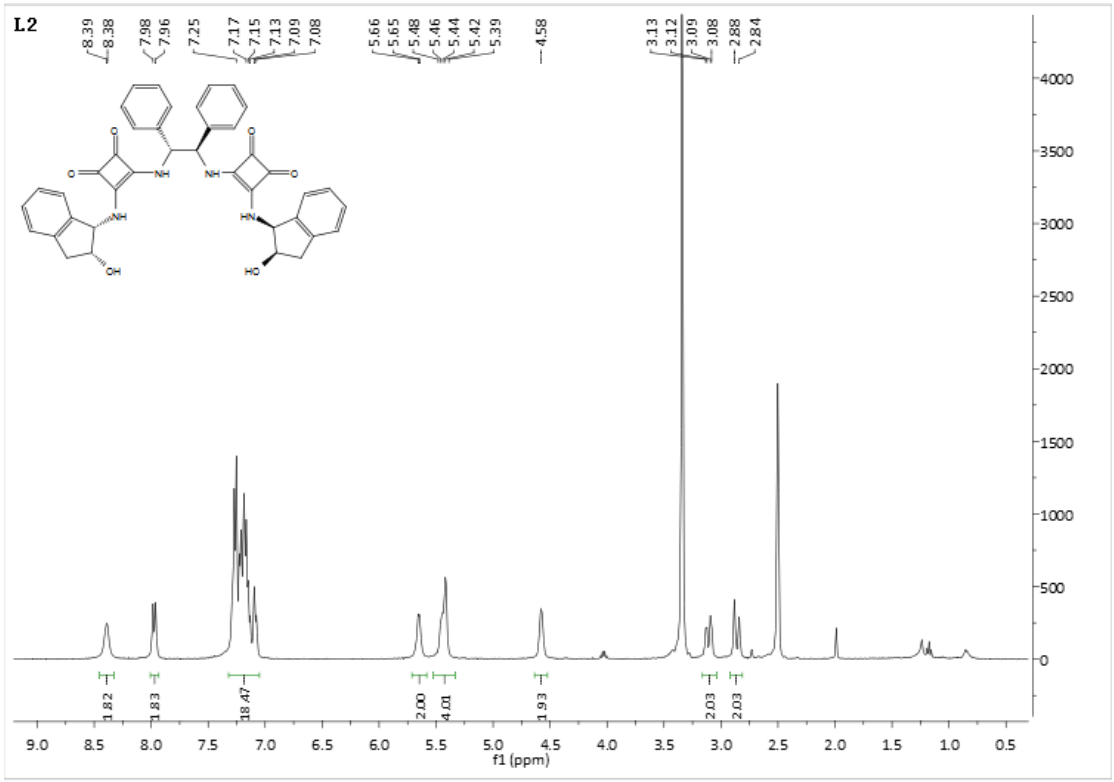


^{13}C NMR (100MHz, DMSO-d_6)

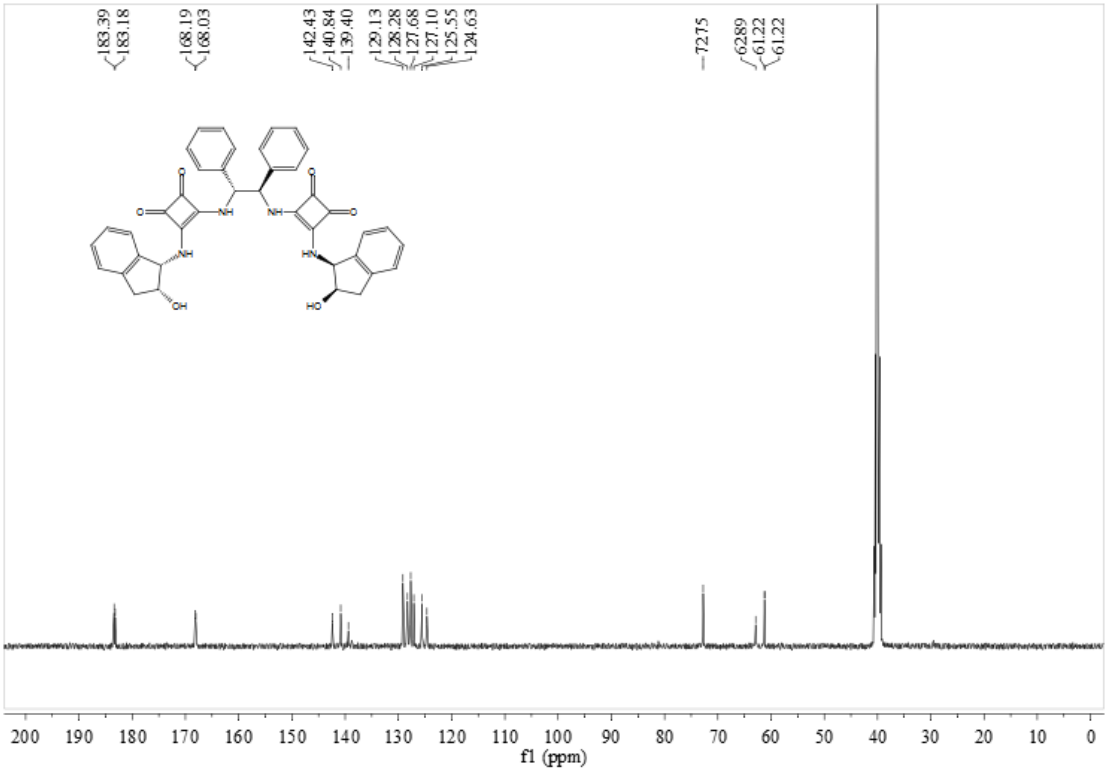


4.3 Receptor 3

^{1}H NMR (400MHz, DMSO-d_6)

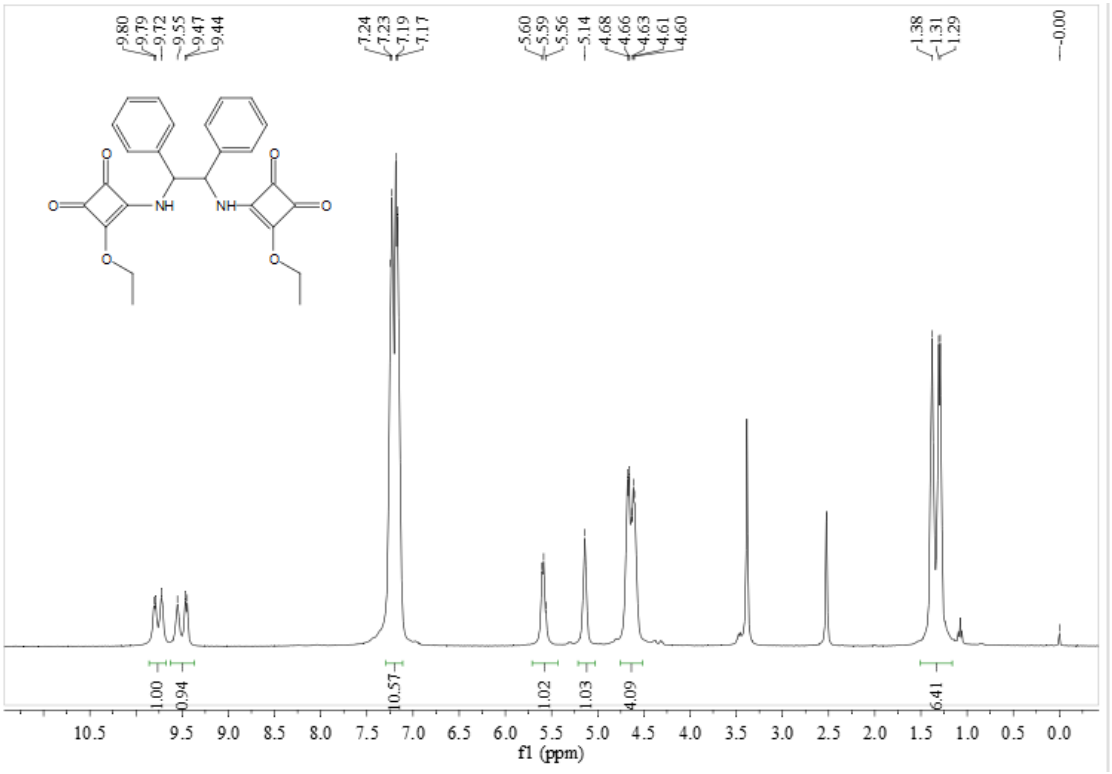


^{13}C NMR (100MHz, DMSO-d_6)

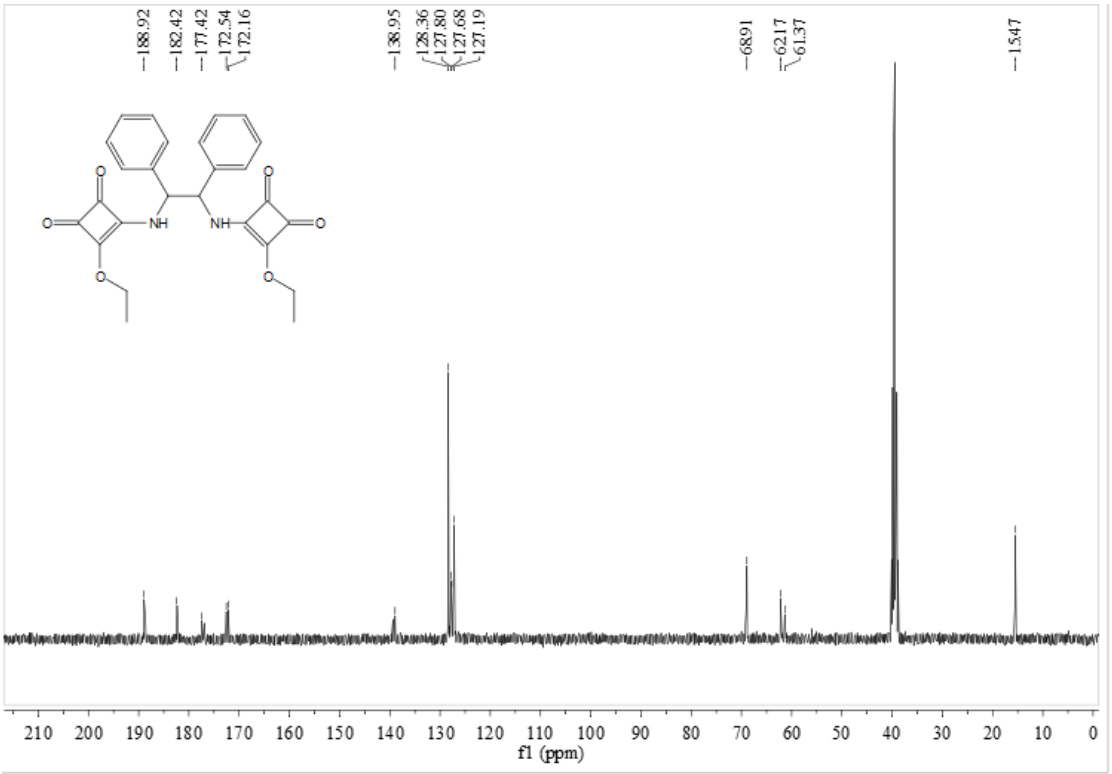


4.4 Compound 6

^{1}H NMR (400MHz, DMSO-d_6)

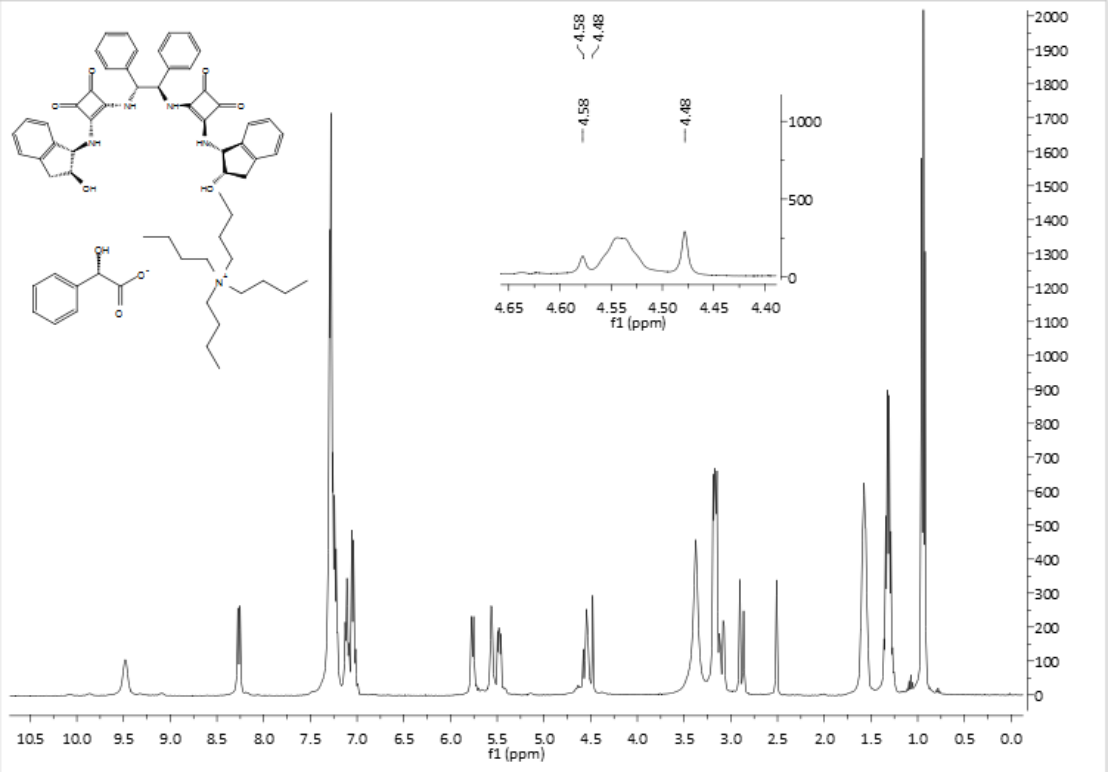


^{13}C NMR (100MHz, DMSO-d_6)

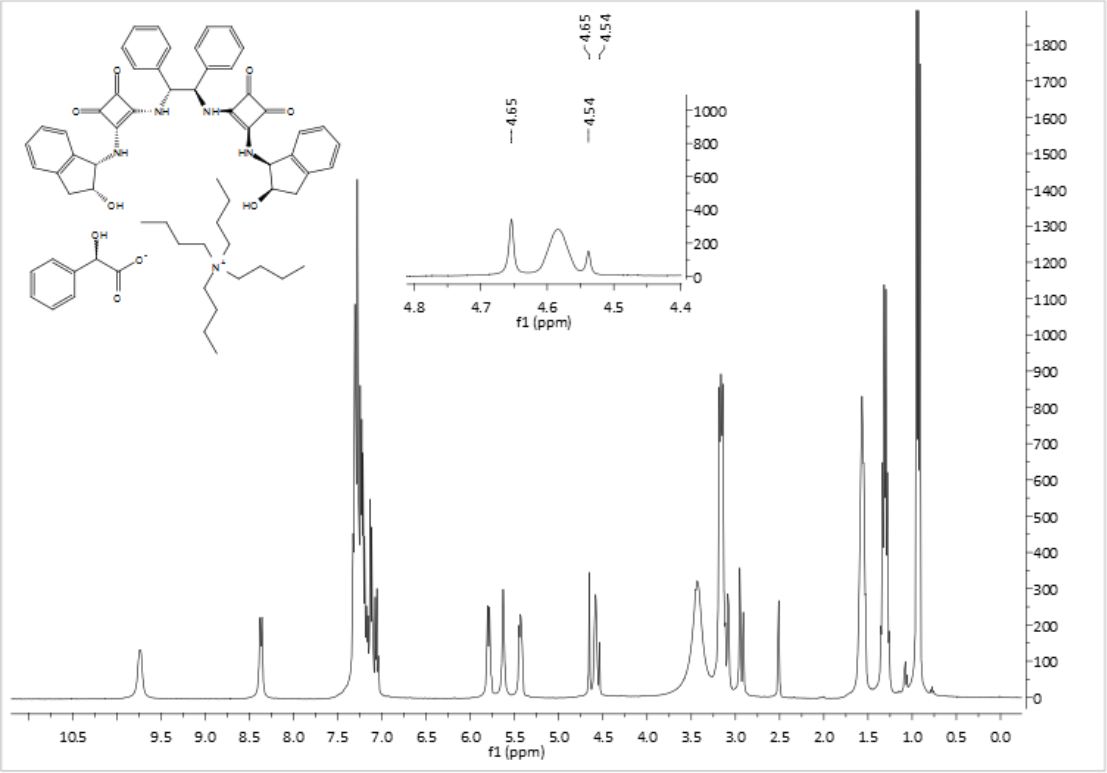


5. ^{1}H NMRof 1 or 2 with carboxylate anions

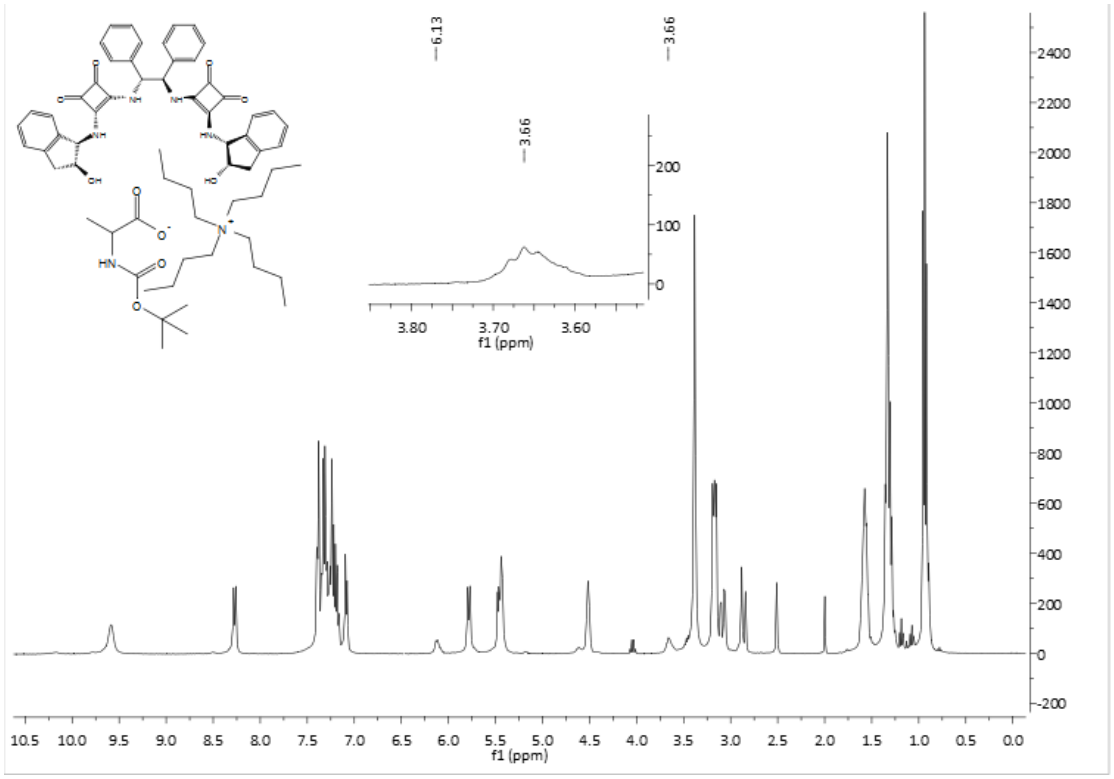
^{1}H NMR of receptor **2** with mandelic tetrabutylammonium salt



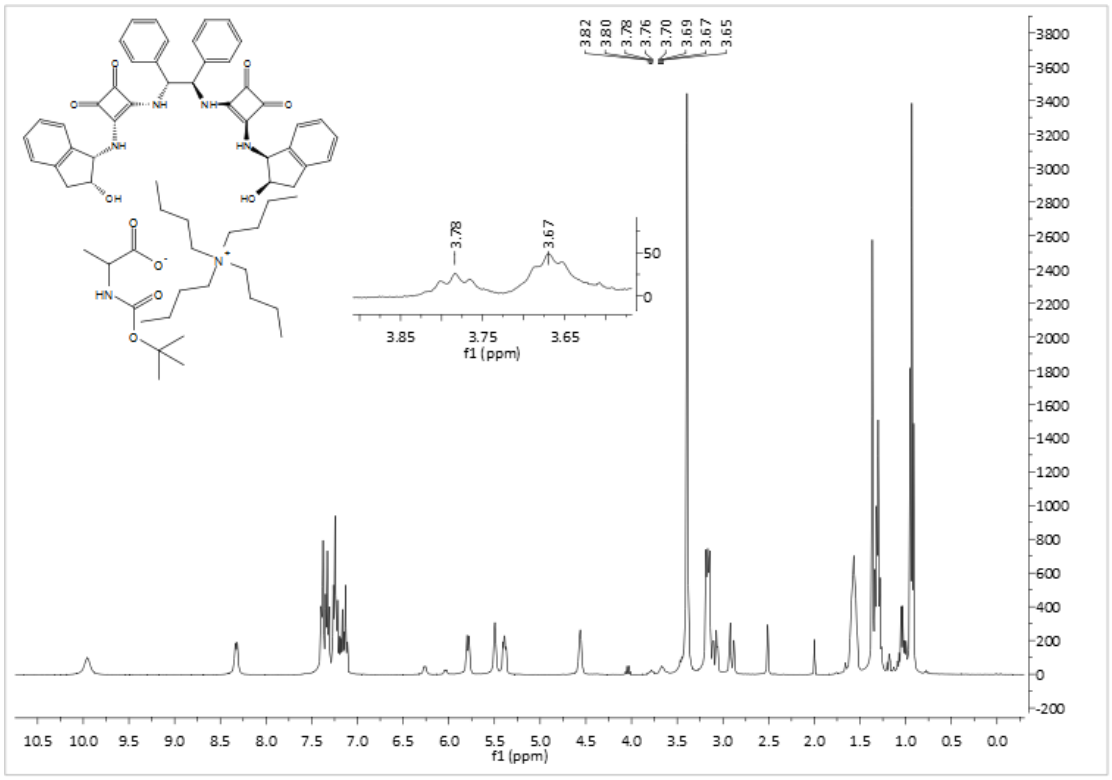
^{1}H NMR of receptor **3** with mandelic tetrabutylammonium salt



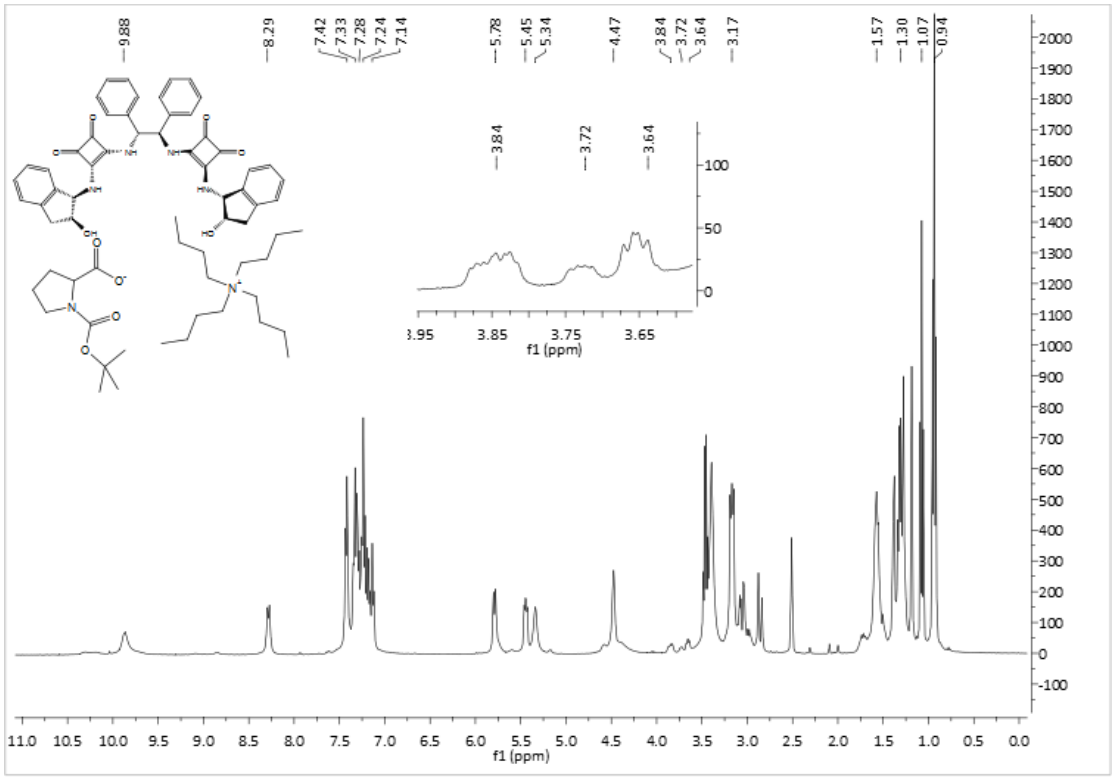
^{1}H NMR of receptor **2** with N-Boc-Ala tetrabutyl ammonium salt



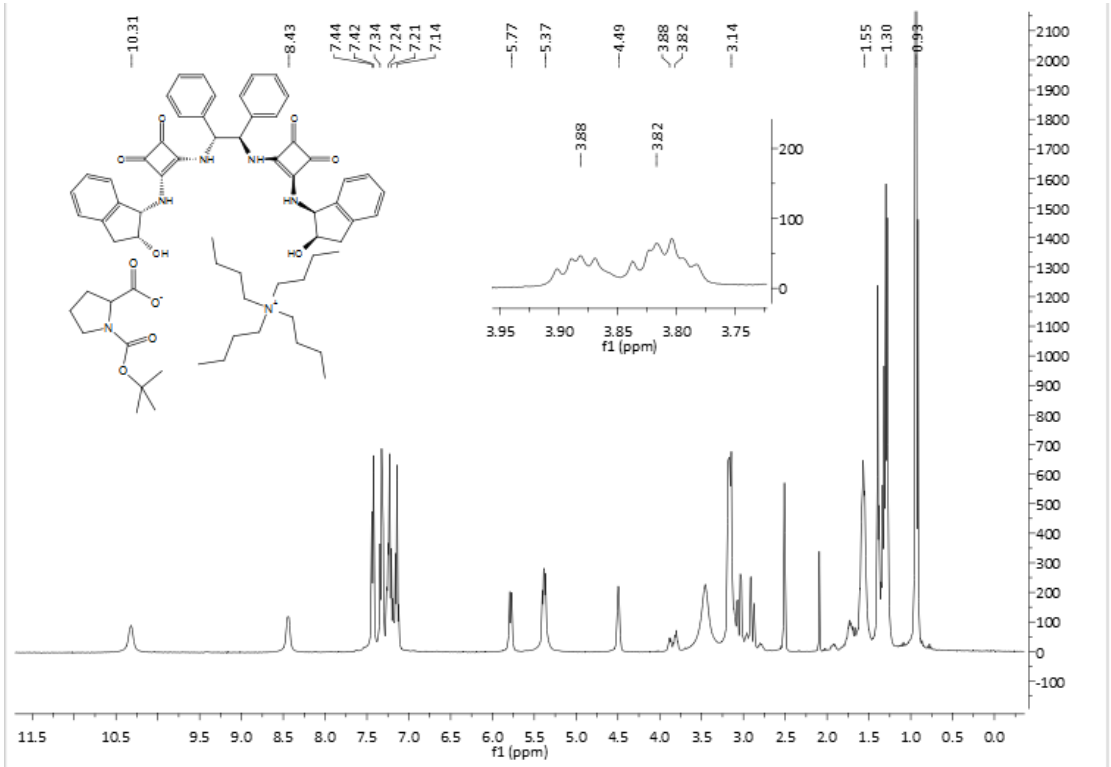
^{1}H NMR of receptor **3** with N-Boc-Ala tetrabutyl ammonium salt



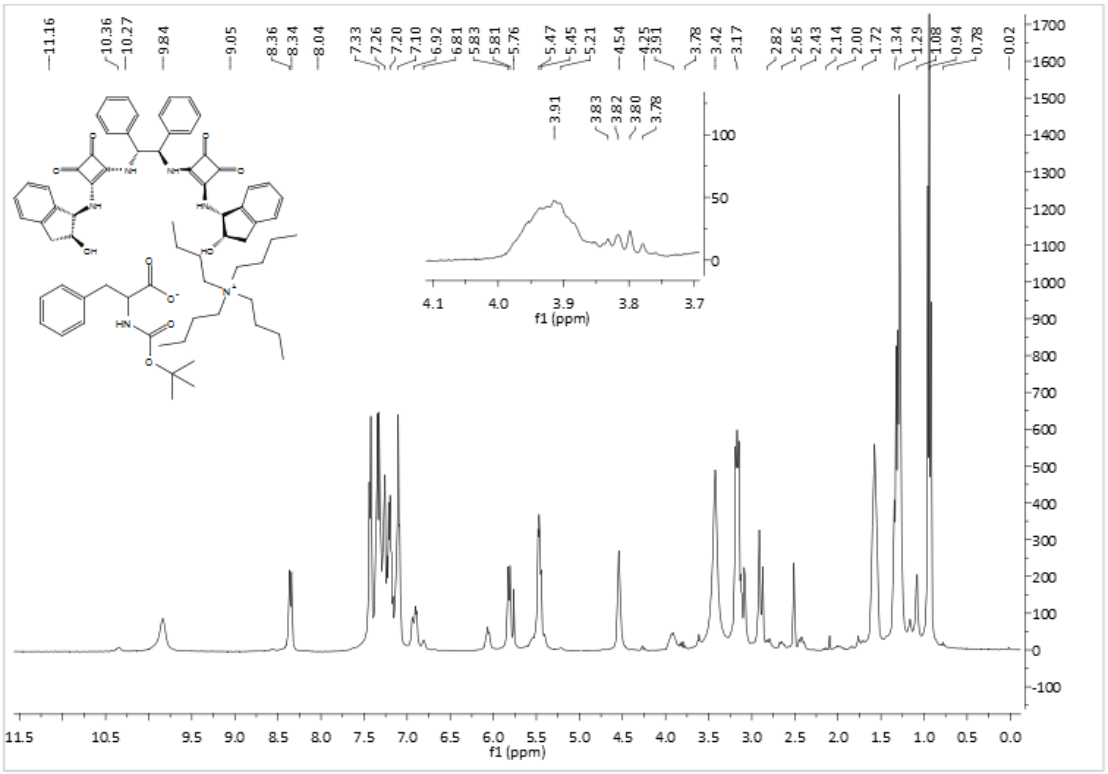
^{1}H NMR of receptor **2** with N-Boc-Pro tetrabutyl ammonium salt



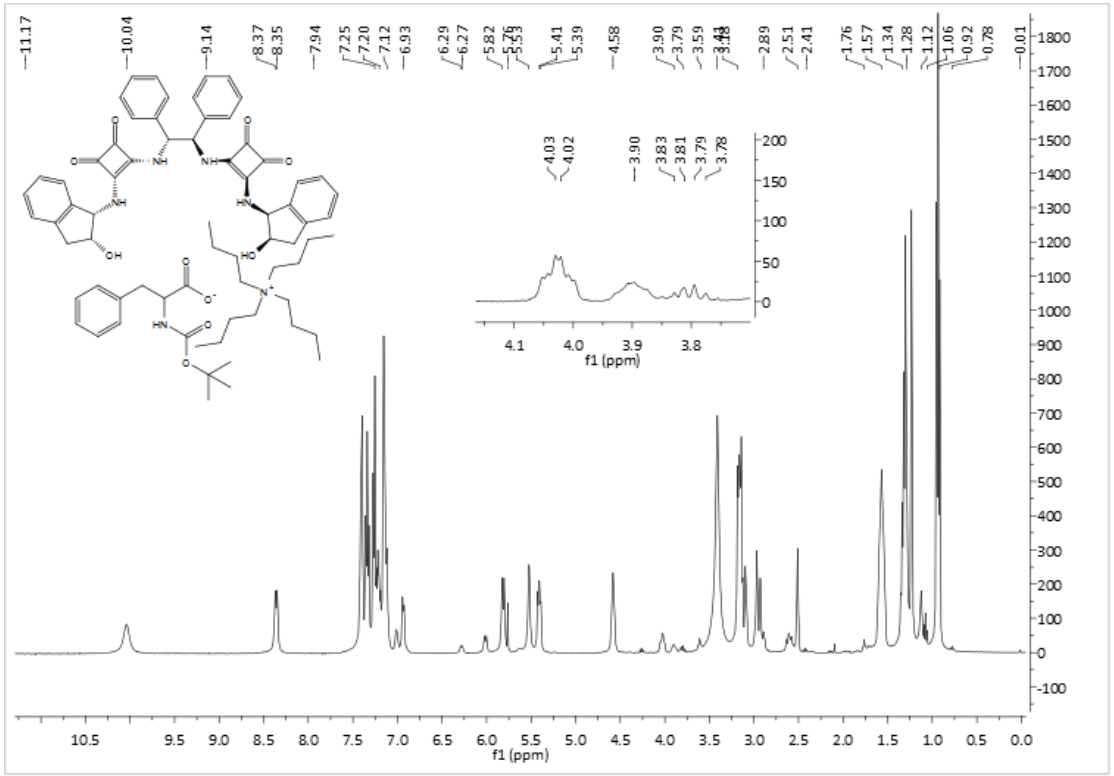
^{1}H NMR of receptor **3** with N-Boc-Pro tetrabutyl ammonium salt



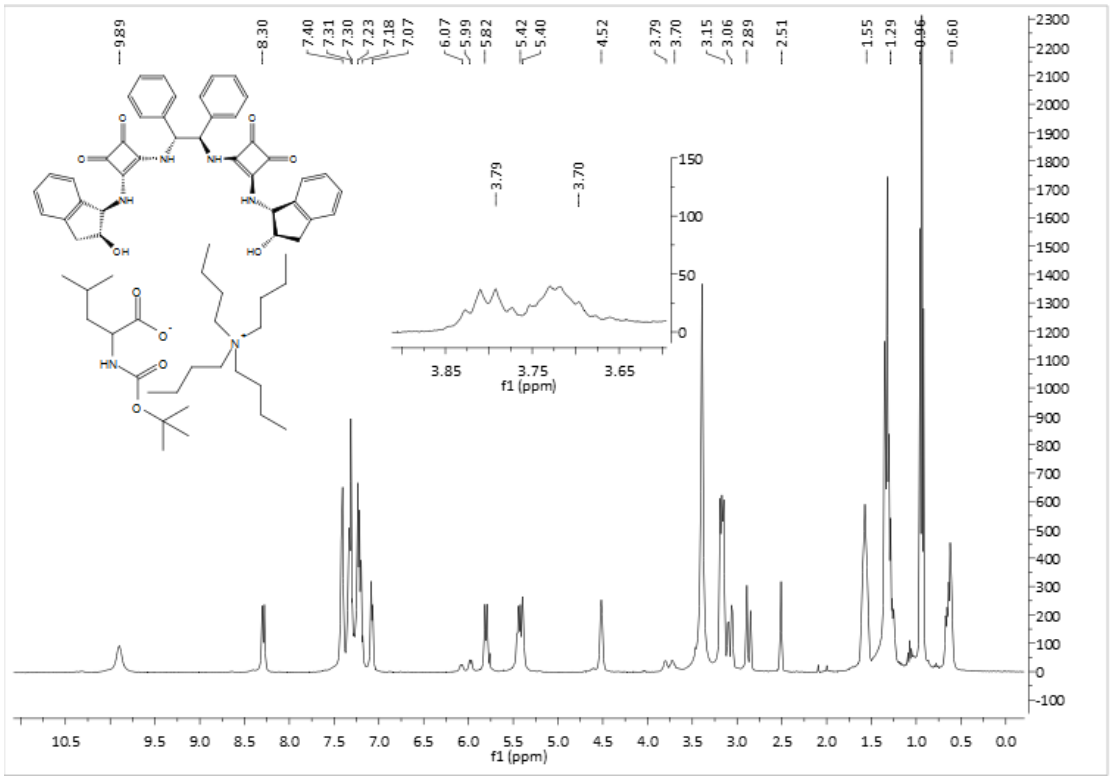
^{1}H NMR of receptor **2** with N-Boc-Phe tetrabutyl ammonium salt



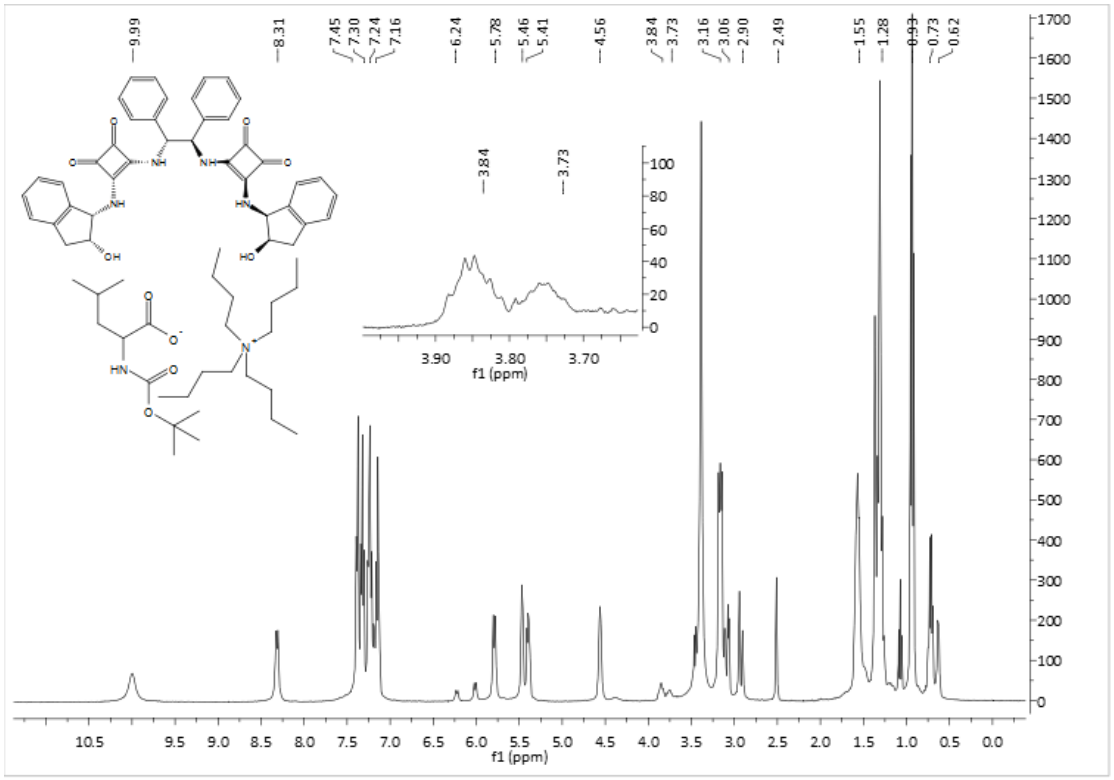
^{1}H NMR of receptor **3** with N-Boc-Phe tetrabutyl ammonium salt



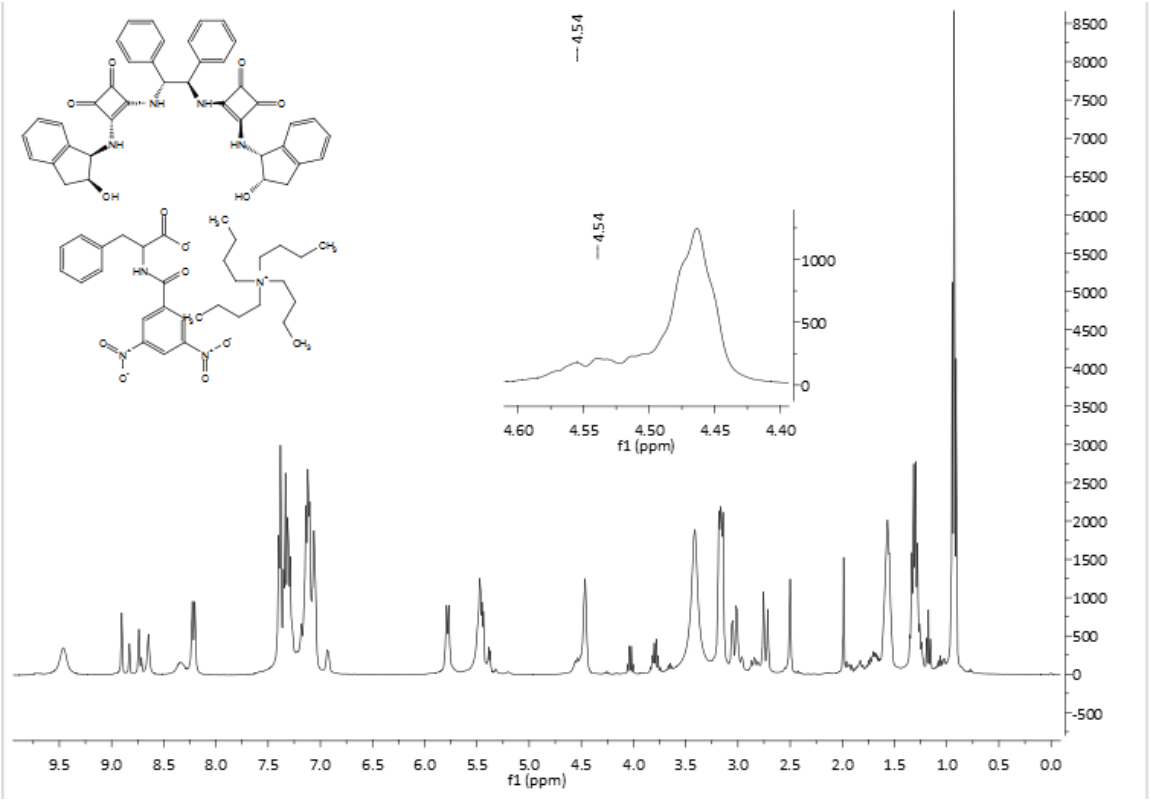
^{1}H NMR of receptor **2** with N-Boc-Leu tetrabutyl ammonium salt



^{1}H NMR of receptor **3** with N-Boc-Leu tetrabutyl ammonium salt



^{1}H NMR of receptor **2** with N-Boc-Phe tetrabutyl ammonium salt



^{1}H NMR of receptor **3** with N-Boc-Phe tetrabutyl ammonium salt