SUPPORTING INFORMATION

Kinetic resolution of 2-aryl-2,3-dihydroquinolin-4(1H)-one derivatives by rhodium-catalysed asymmetric transfer hydrogenation

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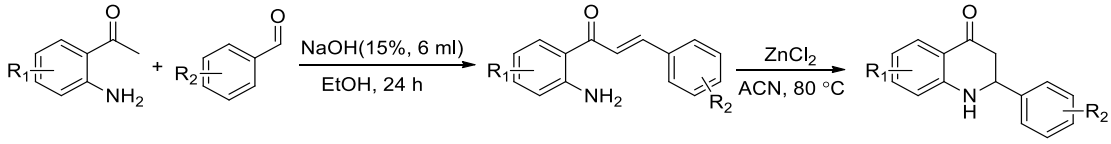
I. General information

All manipulations were carried out under an argon atmosphere. Dichloromethane was distilled from calcium hydride. Reactions were monitored by thin layer chromatography carried out on precoated silica gel plates (E. Merck ref. 5554 60 F254) and revealed with either a ultra-violet lamp (λ = 254 nm) or a potassium permanganate solution. The nuclear magnetic resonance spectra were recorded on Bruker AV300 or AV400 instruments. The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) and residual acetone (2.05 ppm for ^{1}H and 29.84 ppm for ^{13}C). Coupling constants (*J*) are given in Hz and refer to apparent peak multiplicities. The following abbreviations are used: s = singlet, br = broad signal, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points were determined with a Kofler Heizbank 7841 apparatus and are uncorrected. Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris (ENSCP). High resolution mass spectra were performed at the University Pierre and Marie Curie (Paris). Sigma-Aldrich Silica gel (high-purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size) was employed for flash column chromatography. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates (Merck 60 F254), spots were detected with UV light (254 nm) and revealed with a $KMnO_4$ or ninhydrin stain solution. All reagents were used as received from commercial sources.

II. General procedure for the preparation of substrates 1a–1r[1]



2'-Aminoacetophenone (20 rmmol) and benzaldehyde (21 mmol) were dissolved in ethanol and a solution of sodium hydroxide (15%, 6 mL) was added under stirring. After 24 h the reaction mixture was neutralized with 10% HC1 and diluted with water, then extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude

[1] (a) Wang, J. F.; Liao, Y. X.; Kuo, P. Y.; Gau, Y. H.; Yang, D.Y. *Synlett.* **2006**, *17*, 2791; (b) Lee, J. I.; Jung, H. J. *J. Korean. Chem. Soc.* **2007**, *51*, 106.

product was used in the next step without further purification The crude *trans*-2'-amino-chalcone and anhydrous zinc chloride (20 mmol) were dissolved in acetonitrile (60 mL), and the mixture was heated at 80℃ for 24 h. After evaporation of the solvent, the mixture was poured into sat. NH_4Cl (60 mL) and the aqueous phase was extracted with dichloromethane (3x70 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified first by flash column chromatography on silica gel (petroleum ether/EtOAc, 4:1) then crystallized from *n*-hexane/EtOAc (9:1) to give the target product.

III. General procedure for the preparation of substrates 3a-3r[2]

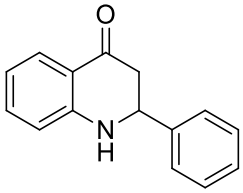
A solution of 2-aryl-1,2,3,4-tetrahydro-4-quinolones (5 mmol) in an acetic acid–acetic anhydride (1:1, 20 mL) mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure to dryness, and the residue was purified by column chromatography over silica gel using petroleum ether/EtOAc (2:1) to afford *N*-acetyl-2-aryl-1,2,3,4-tetrahydro-4-quinolones (**3a–3r**).

IV. General procedure for the synthesis of (*S*)-3a–3r and 4a–4r by ATH

In a round-bottom tube charged with ketone **3** (0.4 mmol, 1.0 equiv) was added a solution of the Rh complex (*R*,*R*)-**A** (80–160 μL, $5.0.10^{-3}$ $mol.L^{-1}$, 0.1–0.2 mol%). A solution of HCO_2H/DABCO (2:1) mixture (31 μL HCO_2H and 45 mg DABCO, 2.0 equiv) in CH_3CN (0.5 mL) was added and an additional volume of CH_3CN (0.5 mL) was introduced. The reaction mixture was stirred at room temperature for 7–48 h, then concentrated under vacuum. Purification of the residue by flash column chromatography on silica gel (petroleum ether/ethyl acetate) afforded compounds **3'** and **4** and the enantiomeric excesses were determined by SFC analysis.

V. Analytical data for compounds 1a–1r

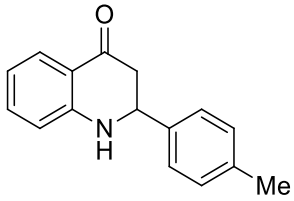
2-Phenyl-2,3-dihydroquinolin-4(1H)-one (1a)



[2] Singh, O.; Muthukrishnan, M.; Sundaravedivelu, M. *Synth. Commun*. **2006**, *36*, 943-950.

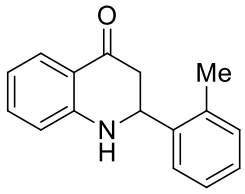
White solid, 17 g, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.31 (m, 2H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 4.75 (dd, *J* = 13.7, 3.9 Hz, 1H), 4.54 (br, 1H), 2.88 (dd, *J* = 16.3, 13.7 Hz, 1H), 2.77 (ddd, *J* = 16.3, 3.9, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 151.7, 141.1, 135.5, 129.1, 128.6, 127.7, 126.7, 119.1, 118.6, 116.1, 58.6, 46.5.

2-(*p*-Tolyl)-2,3-dihydroquinolin-4(1H)-one (1b)



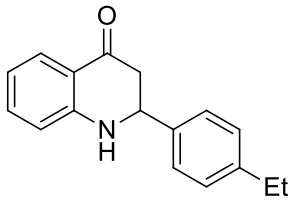
White solid, 3.0 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.24 – 7.10 (m, 2H), 6.78 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 4.71 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.50 (s, 1H), 2.87 (dd, *J* = 16.2, 13.8 Hz, 1H), 2.75 (ddd, *J* = 16.3, 3.8, 1.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 156.8, 149.9, 138.1, 132.9, 128.0, 122.4, 121.8, 111.0, 106.0, 86.4 , 55.7, 28.0.

2-(*o*-Tolyl)-2,3-dihydroquinolin-4(1H)-one (1c)



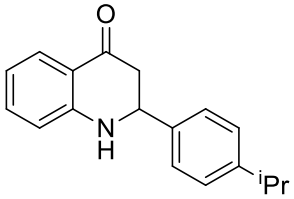
White solid, 2.0 g, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.19 (m, 4H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 5.09 (dd, *J* = 12.7, 4.9 Hz, 1H), 4.53 (br, 1H), 2.96 – 2.73 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 152.1, 139.2, 135.5, 135.2, 131.0, 128.1, 127.8, 126.9, 126.0, 119.1, 118.5, 116.1, 54.6, 45.3, 19.2.

2-(4-Ethylphenyl)-2,3-dihydroquinolin-4(1H)-one (1d)



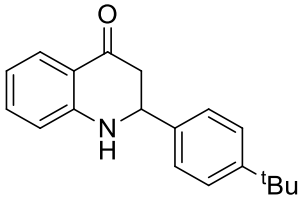
Colourless solid, 2.5 g, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.78 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 4.72 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.51 (br, 1H), 2.88 (dd, *J* = 16.2, 13.7 Hz, 1H), 2.76 (ddd, *J* = 16.2, 3.8, 1.8 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 151.7, 144.8, 138.4, 135.5, 128.6, 127.7, 126.8, 119.1, 118.5, 116.0, 58.4, 46.6, 28.7, 15.7.

2-(4-*iso*-Propylphenyl)-2,3-dihydroquinolin-4(1H)-one (1e)



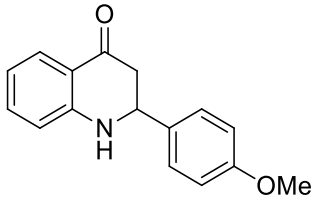
White solid, 2.5 g, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.33 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.78 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 4.71 (dd, *J* = 13.8, 3.8 Hz, 1H), 4.59 (br, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.87 (dd, *J* = 16.2, 13.7 Hz, 1H), 2.75 (ddd, *J* = 16.2, 3.8, 1.7 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 151.8, 149.3, 138.4, 135.4, 127.6, 127.1, 126.7, 119.0, 118.4, 116.0, 58.2, 46.5, 33.9, 24.1.

2-(4-(*tert*-Butyl)phenyl)-2,3-dihydroquinolin-4(1H)-one (1f)



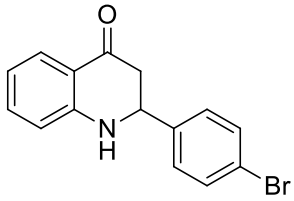
White solid, 4.5 g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 – 7.35 (m, 4H), 7.33 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 4.72 (dd, *J* = 13.7, 3.8 Hz, 1H), 4.53 (br, 1H), 2.89 (dd, *J* = 16.1, 13.8 Hz, 1H), 2.76 (dd, *J* = 16.2, 3.8 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 151.7, 151.6, 138.0, 135.5, 127.7, 126.5, 126.0, 119.1, 118.4, 116.0, 58.2, 46.4, 34.7, 31.4.

2-(4-Methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (1g)



White solid, 2.5 g, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.41 – 7.32 (m, 3H), 6.99 – 6.91 (m, 2H), 6.79 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.69 (dd, *J* = 13.8, 3.7 Hz, 1H), 4.57 (br, 1H), 3.84 (s, 3H), 2.86 (dd, *J* = 16.2, 13.8 Hz, 1H), 2.73 (ddd, *J* = 16.3, 3.8, 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 159.7, 151.8, 135.5, 133.2, 127.9, 127.7, 119.0, 118.4, 116.0, 114.4, 58.0, 55.4, 46.6 .

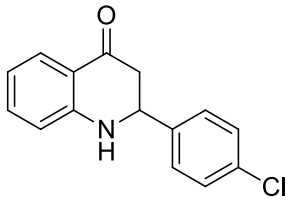
2-(4-Bromophenyl)-2,3-dihydroquinolin-4(1H)-one (1h)



White solid, 4.5 g, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 – 7.46

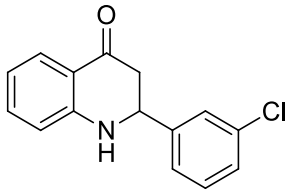
(m, 2H), 7.39 – 7.29 (m, 3H), 6.79 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.69 (dd, *J* = 12.6, 4.8 Hz, 1H), 4.61 (s, 1H), 2.92 – 2.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 151.5, 140.2, 135.6, 132.2, 128.4, 127.7, 122.3, 119.1, 118.8, 116.1, 58.0, 46.4.

2-(4-Cchlorophenyl)-2,3-dihydroquinolin-4(1H)-one (1i)



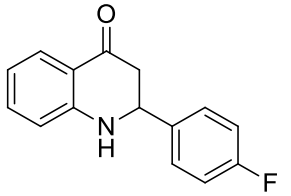
White solid, 1.9 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.45 – 7.32 (m, 5H), 6.80 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 4.72 (dd, *J* = 13.2, 4.3 Hz, 1H), 4.57 (br, 1H), 2.81 (dd, *J* = 16.2, 13.1 Hz, 1H), 2.73 (dd, *J* = 16.2, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 151.5, 139.6, 135.6, 134.3, 129.3, 128.1, 127.7, 119.1, 118.8, 116.1, 58.0, 46.5.

2-(3-Chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (1j)



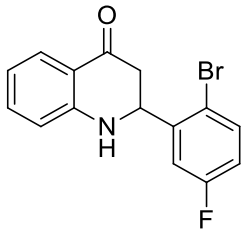
White solid, 2.5 g, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.47 (s, 1H), 7.39 – 7.29 (m, 4H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.72 (dd, *J* = 13.1, 4.3 Hz, 1H), 4.55 (br, 1H), 2.88 – 2.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 151.4, 143.2, 135.6, 135.0, 130.4, 128.7, 127.7, 126.9, 125.0, 119.2, 118.9, 116.1, 58.1, 46.4.

2-(4-Fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (1k)



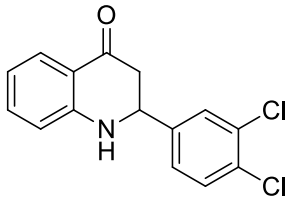
White solid, 3.0 g, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.35 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.14 – 7.02 (m, 2H), 6.80 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 4.73 (dd, *J* = 13.5, 4.0 Hz, 1H), 4.53 (br, 1H), 2.83 (dd, *J* = 16.2, 13.4 Hz, 1H), 2.73 (ddd, *J* = 16.3, 4.0, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 162.7 (d, *J* = 247.0 Hz), 151.6, 137.0 (d, *J* = 3.1 Hz), 135.6, 128.4 (d, *J* = 8.2 Hz), 127.7, 119.2, 118.7, 116.1 (d, *J* = 3.3 Hz), 115.9, 58.0, 46.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.36 (tt, *J* = 9.0, 5.4 Hz).

2-(2-Bromo-5-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (1l)



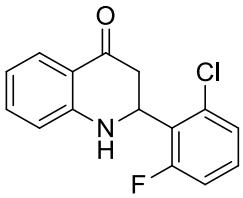
White solid, 1.5 g, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.8, 5.3 Hz, 1H), 7.44 (dd, *J* = 9.5, 3.0 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.93 (ddd, *J* = 8.8, 7.6, 3.1 Hz, 1H), 6.82 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.16 (ddd, *J* = 12.7, 3.9, 1.3 Hz, 1H), 4.57 (br, 1H), 2.95 (dd, *J* = 16.3, 4.0 Hz, 1H), 2.68 (dd, *J* = 16.3, 12.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 162.4 (d, *J* = 248.2 Hz), 151.4, 142.3 (d, *J* = 6.8 Hz), 135.7, 134.7 (d, *J* = 7.8 Hz), 127.7, 119.3, 119.1, 117.0 (d, *J* = 22.6 Hz), 116.7 (d, *J* = 3.3 Hz), 116.3, 115.2 (d, *J* = 24.3 Hz), 57.0, 44.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.33 (q, *J* = 7.6 Hz).

2-(3,4-Dichlorophenyl)-2,3-dihydroquinolin-4(1H)-one (1m)



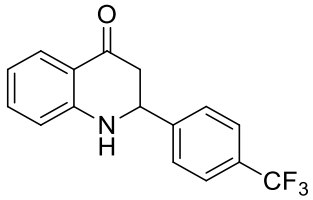
White solid, 2.0 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.1, 1.6 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.81 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.70 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.58 (br, 1H), 2.84 – 2.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 151.3, 141.4, 135.7, 133.2, 132.5, 131.1, 128.8, 127.7, 126.1, 119.2, 119.0, 116.2, 57.6, 46.4.

2-(2-Chloro-6-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (1n)



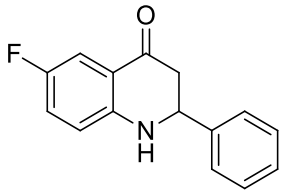
Yellow solid, 2.0 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.03 (ddd, *J* = 10.8, 7.9, 1.7 Hz, 1H), 6.77 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 5.41 (ddd, *J* = 14.2, 3.9, 1.3 Hz, 1H), 4.35 (br, 1H), 3.37 (dd, *J* = 16.1, 14.2 Hz, 1H), 2.71 (dd, *J* = 16.3, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 162.4 (d, *J* = 253.5 Hz), 151.5, 135.4, 134.9 (d, *J* = 6.4 Hz), 130.4 (d, *J* = 10.2 Hz), 127.8, 126.3 (d, *J* = 3.4 Hz), 125.1 (d, *J* = 13.8 Hz), 119.0, 118.5, 116.1, 115.8 (d, *J* = 23.0 Hz), 52.3, 41.7 (d, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.59 (dd, *J* = 10.0, 4.5 Hz).

2-(4-(Trifluoromethyl)phenyl)-2,3-dihydroquinolin-4(1H)-one (1o)



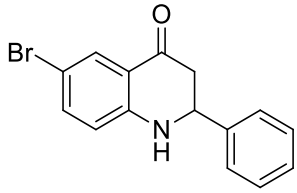
White solid, 3.3 g, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.36 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.81 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.81 (dd, *J* = 12.6, 4.7 Hz, 1H), 4.64 (br, 1H), 2.83 (dd, *J* = 16.2, 12.6 Hz, 1H), 2.76 (ddd, *J* = 16.2, 4.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 151.4, 145.2, 135.7, 130.8 (q, *J* = 32.5 Hz), 127.7, 127.1, 126.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.4 Hz), 119.2, 119.0, 116.2, 58.2, 46.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.58.

6-Fluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one (1p)



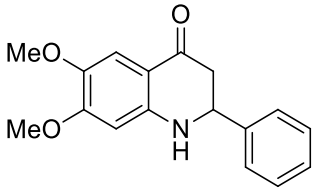
White solid, 1.0 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.45 – 7.31 (m, 3H), 7.10 (ddd, *J* = 8.9, 7.8, 3.1 Hz, 1H), 6.70 (dd, *J* = 8.9, 4.1 Hz, 1H), 4.72 (dd, *J* = 13.6, 4.0 Hz, 1H), 4.47 (br, 1H), 2.86 (dd, *J* = 16.4, 13.6 Hz, 1H), 2.77 (dd, *J* = 16.4, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 156.1 (d, *J* = 238.9 Hz), 148.3, 140.9, 129.2, 128.7, 126.8, 123.5 (d, *J* = 24.4 Hz), 119.4 (d, *J* = 5.9 Hz), 117.6 (d, *J* = 7.0 Hz), 112.5 (d, *J* = 22.1 Hz), 58.9, 46.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.59 (td, *J* = 8.5, 4.1 Hz).

6-Bromo-2-phenyl-2,3-dihydroquinolin-4(1H)-one (1q)



White solid, 900 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.50 – 7.30 (m, 6H), 6.63 (d, *J* = 8.7 Hz, 1H), 4.72 (dd, *J* = 13.4, 4.1 Hz, 1H), 4.60 (br, 1H), 2.86 (dd, *J* = 16.3, 13.4 Hz, 1H), 2.76 (dd, *J* = 16.3, 3.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 150.4, 140.6, 138.1, 130.1, 129.2, 128.8, 126.7, 120.3, 117.9, 110.8, 58.4, 46.1.

6,7-Dimethoxy-2-phenyl-2,3-dihydroquinolin-4(1H)-one (1r)

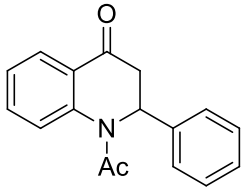


White solid, 1.5 g, 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.28 (m, 1H), 6.18 (s, 1H), 4.71

(dd, *J* = 13.5, 4.2 Hz, 1H), 2.82 (dd, *J* = 16.3, 13.5 Hz, 1H), 2.71 (dd, *J* = 16.3, 4.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 156.2, 148.4, 143.2, 141.3, 129.1, 128.5, 126.8, 111.8, 108.0, 98.1, 59.4, 56.3, 56.2, 46.1.

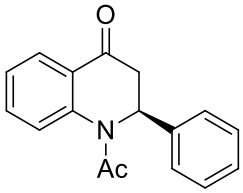
VI. Analytical data for compounds 3a–3r and (*S*)-3a-3r[3]

1-Acetyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one (3a)



White solid, 3.2 g, 76% yield, m.p.174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.26 (br, 1H), 7.23 – 7.11 (m, 6H), 6.47 (br, 1H), 3.37 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.24 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.2, 141.9, 138.1, 134.5, 128.7, 127.7, 127.4, 126.9, 126.2, 125.6, 125.2, 54.8, 42.7, 23.5.

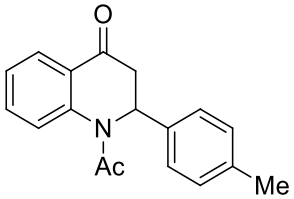
(*S*)-1-Acetyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one ((*S*)-3a)



White solid, 51 mg, 48% yield, m.p.174 °C, *ee* = 98%, $[\alpha]_D^{25}$ = –271.3 (c 1.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.26 (br, 1H), 7.23 – 7.11 (m, 6H), 6.47 (br, 1H), 3.37 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.24 (dd, *J* = 18.0, 5.9 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.2, 141.9, 138.1, 134.5, 128.7, 127.7, 127.4, 126.9, 126.2, 125.6, 125.2, 54.8, 42.7, 23.5.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 70/30, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 6.13 min, t_R (*R*) =11.51 min.

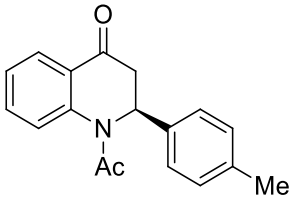
1-Acetyl-2-(p-tolyl)-2,3-dihydroquinolin-4(1H)-one (3b)



Colourless solid, 1.0 g, 71% yield, m.p.196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.29 (br, 1H), 7.16 (td, *J* = 7.8, 1.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.41 (br, 1H), 3.34 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.42 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 170.2, 142.0, 137.4, 135.0, 134.5, 129.4, 127.4, 126.8, 126.2, 125.5, 125.2, 54.7, 42.8, 23.6, 21.1.

[3] Lei, B.-L.; Ding, C.-H.; Yang, X.-F.; Wan, X.-L.; Hou, X.-L. *J. Am. Chem. Soc.* **2009**, *131*, 18250–18251

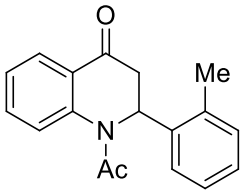
(*S*)-1-Acetyl-2-(p-tolyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3b)



Colourless solid, 55 mg, 49% yield, m.p.196 °C, *ee* = 99%, $[\alpha]_D^{25}$ = –255.0 (c 1.59, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.29 (br, 1H), 7.16 (td, *J* = 7.8, 1.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.41 (br, 1H), 3.34 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.42 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 170.2, 142.0, 137.4, 135.0, 134.5, 129.4, 127.4, 126.8, 126.2, 125.5, 125.2, 54.7, 42.8, 23.6, 21.1.

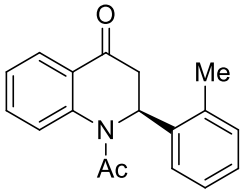
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 5.27 min, t_R (*R*) =7.35 min.

1-Acetyl-2-(o-tolyl)-2,3-dihydroquinolin-4(1H)-one (3c)



Colourless solid, 1.0 g, 71% yield, m.p.138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.05 (td, *J* = 7.3, 1.3 Hz, 1H), 6.90 (td, *J* = 7.7, 1.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 4.7 Hz, 1H), 3.26 (dd, *J* = 18.2, 5.6 Hz, 1H), 3.19 (dd, *J* = 18.2, 2.0 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 169.4, 142.2, 137.4, 136.0, 134.5, 131.2, 128.0, 127.5, 127.2, 126.9, 126.4, 125.8, 125.6, 52.9, 43.2, 23.1, 19.8.

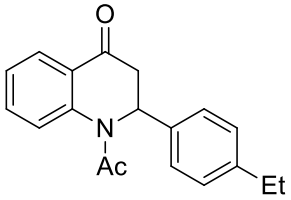
(*S*)-1-Acetyl-2-(o-tolyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3c)



Colourless solid, 55 mg, 49% yield, m.p.138 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –179.2 (c 1.07, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.05 (td, *J* = 7.3, 1.3 Hz, 1H), 6.90 (td, *J* = 7.7, 1.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 4.7 Hz, 1H), 3.26 (dd, *J* = 18.2, 5.6 Hz, 1H), 3.19 (dd, *J* = 18.2, 2.0 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 169.4, 142.2, 137.4, 136.0, 134.5, 131.2, 128.0, 127.5, 127.2, 126.9, 126.4, 125.8, 125.6, 52.9, 43.2, 23.1, 19.8.

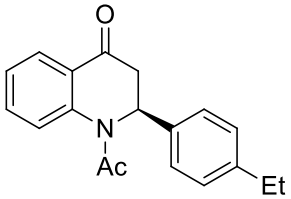
SFC: Chiralpak ID, *sc*CO_2/ ^{i}PrOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 6.34 min, t_R (*R*) =7.11 min.

1-Acetyl-2-(4-ethylphenyl)-2,3-dihydroquinolin-4(1H)-one (3d)



Light yellow solid, 1.1 g, 76% yield, m.p.196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.31 (br, 1H), 7.12 (td, *J* = 7.7, 1.1 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.39 (br, 1H), 3.33 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.49 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.11 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.1, 143.5, 141.9, 135.1, 134.4, 128.1, 127.2, 126.8, 126.0, 125.4, 125.2, 54.7, 42.7, 28.3, 23.5, 15.3.

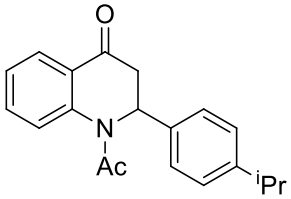
(*S*)-1-Acetyl-2-(4-ethylphenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3d)



Light yellow solid, 55 mg, 47% yield, m.p.196 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –239.7 (c 1.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.31 (br, 1H), 7.12 (td, *J* = 7.7, 1.1 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.39 (br, 1H), 3.33 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.49 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.11 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.1, 143.5, 141.9, 135.1, 134.4, 128.1, 127.2, 126.8, 126.0, 125.4, 125.2, 54.7, 42.7, 28.3, 23.5, 15.3.

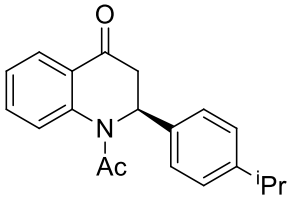
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 5.62 min, t_R (*R*) =9.69 min.

1-Acetyl-2-(4-isopropylphenyl)-2,3-dihydroquinolin-4(1H)-one (3e)



White solid, 1.2 g, 78% yield, m.p.70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.43 (td, *J* = 7.8, 1.7 Hz, 1H), 7.32 (br, 1H), 7.16 – 7.03 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.38 (br, 1H), 3.33 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.75 (hept, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.1, 148.1, 141.9, 135.2, 134.4, 127.2, 126.7, 126.0, 125.3, 125.1, 54.8, 42.7, 33.5, 23.8, 23.8, 23.5.

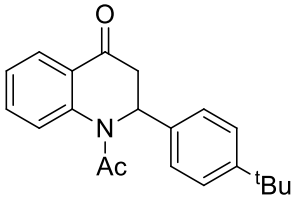
(*S*)-1-Acetyl-2-(4-isopropylphenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3e)



White solid, 60 mg, 49% yield, m.p.70 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –227.9 (c 1.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.43 (td, *J* = 7.8, 1.7 Hz, 1H), 7.32 (br, 1H), 7.16 – 7.03 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.38 (br, 1H), 3.33 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.22 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.75 (hept, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.1, 148.1, 141.9, 135.2, 134.4, 127.2, 126.7, 126.0, 125.3, 125.1, 54.8, 42.7, 33.5, 23.8, 23.8, 23.5.

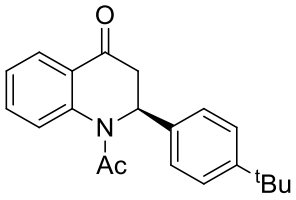
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R(*S*) = 5.19 min, t_R(*R*) =11.38 min.

1-Acetyl-2-(4-(*tert*-butyl)phenyl)-2,3-dihydroquinolin-4(1H)-one (3f)



Colorless solid, 2.1 g, 66% yield, m.p.146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.35 (br, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.38 (br, 1H), 3.34 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.23 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.42 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.2, 150.4, 142.0, 134.9, 134.4, 127.3, 126.5, 126.0, 125.6, 125.4, 125.2, 54.8, 42.8, 34.4, 31.2, 23.6.

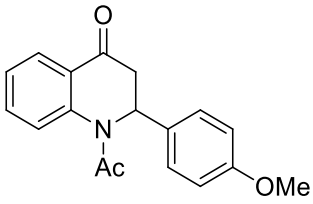
(*S*)-1-Acetyl-2-(4-(*tert*-butyl)phenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3f)



Colorless solid, 63 mg, 49% yield, m.p.146 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –171.9 (c 1.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.35 (br, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.38 (br, 1H), 3.34 (dd, *J* = 17.9, 2.0 Hz, 1H), 3.23 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.42 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 170.2, 150.4, 142.0, 134.9, 134.4, 127.3, 126.5, 126.0, 125.6, 125.4, 125.2, 54.8, 42.8, 34.4, 31.2, 23.6.

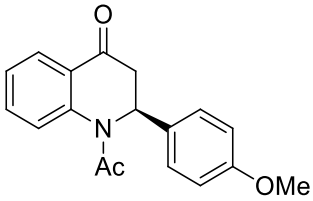
SFC: Chiralpak ID, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R(*S*) = 3.51 min, t_R(*R*) =5.61 min.

1-Acetyl-2-(4-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (3g)



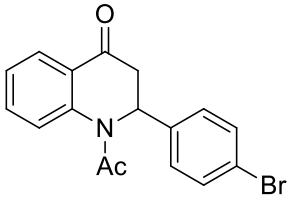
Light yellow solid, 1.3 g, 88% yield, m.p.122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.25 (br, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.40 (br, 1H), 3.68 (s, 3H), 3.31 (dd, *J* = 18.0, 1.9 Hz, 1H), 3.21 (dd, *J* = 17.9, 5.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 170.1, 158.9, 141.8, 134.5, 130.0, 128.1, 127.3, 126.1, 125.5, 125.2, 114.0, 55.2, 42.8, 23.5.

(*S*)-1-Acetyl-2-(4-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3g)



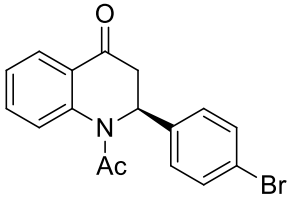
Light yellow solid, 58 mg, 49% yield, m.p.122 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –233.1 (c 1.86, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.25 (br, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.40 (br, 1H), 3.68 (s, 3H), 3.31 (dd, *J* = 18.0, 1.9 Hz, 1H), 3.21 (dd, *J* = 17.9, 5.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 170.1, 158.9, 141.8, 134.5, 130.0, 128.1, 127.3, 126.1, 125.5, 125.2, 114.0, 55.2, 42.8, 23.5.
SFC: Chiralpak IF, *sc*CO_2/ MeOH 70/30, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 8.60 min, t_R (*R*) =12.81 min.

1-Acetyl-2-(4-bromophenyl)-2,3-dihydroquinolin-4(1H)-one (3h)



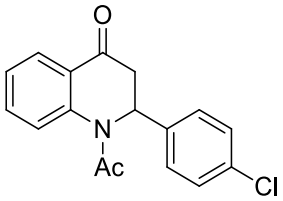
Yellow solid, 1.3 g, 76% yield, m.p.174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.12 (m, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.43 (br, 1H), 3.30 (dd, *J* = 18.1, 2.2 Hz, 1H), 3.22 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 170.2, 141.6, 137.2, 134.7, 131.8, 128.6, 127.5, 126.0, 125.8, 125.1, 121.8, 54.2, 42.5, 23.4.

(*S*)-1-Acetyl-2-(4-bromophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3h)



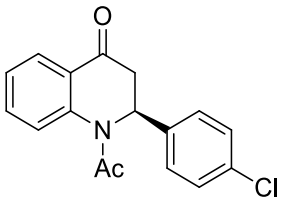
Yellow solid, 69 mg, 50% yield, m.p.174 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –209.1 (c 1.94, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.12 (m, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.43 (br, 1H), 3.30 (dd, *J* = 18.1, 2.2 Hz, 1H), 3.22 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 170.2, 141.6, 137.2, 134.7, 131.8, 128.6, 127.5, 126.0, 125.8, 125.1, 121.8, 54.2, 42.5, 23.4.
SFC: Chiralpak AS-H, *sc*CO_2/ MeOH 90/10, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*R*) = 8.30 min, t_R (*S*) =9.23 min.

1-Acetyl-2-(4-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (3i)



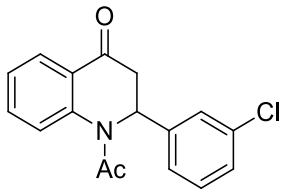
Colorless solid, 1.1 g, 73% yield, m.p.194 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.24 – 7.11 (m, 4H), 7.14 – 7.06 (m, 2H), 6.46 (br, 1H), 3.31 (dd, *J* = 18.0, 2.2 Hz, 1H), 3.23 (dd, *J* = 18.1, 5.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 170.2, 141. 7, 136.7, 134.7, 133.6, 128.9, 128.3, 127.5, 126.0, 125.8, 125.1, 54.2, 42.6, 23.4.

(*S*)-1-Acetyl-2-(4-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3i)



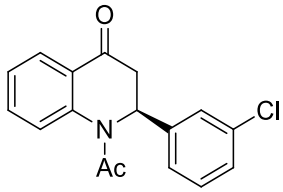
Colorless solid, 57 mg, 48% yield, m.p.194 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –251.5 (c 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.24 – 7.11 (m, 4H), 7.14 – 7.06 (m, 2H), 6.46 (br, 1H), 3.31 (dd, *J* = 18.0, 2.2 Hz, 1H), 3.23 (dd, *J* = 18.1, 5.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 170.2, 141. 7, 136.7, 134.7, 133.6, 128.9, 128.3, 127.5, 126.0, 125.8, 125.1, 54.2, 42.6, 23.4.
SFC: Chiralpak AS-H, *sc*CO_2/ MeOH 90/10, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*R*) = 6.89 min, t_R (*S*) =7.73 min.

1-Acetyl-2-(3-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (3j)



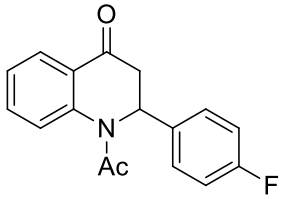
Light yellow solid, 583 mg, 78% yield, m.p.152 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.25 (br, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 2H), 7.07 – 7.01 (m, 1H), 6.47 (br, 1H), 3.32 (dd, *J* = 18.1, 2.1 Hz, 1H), 3.23 (dd, *J* = 18.1, 5.7 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 170.2, 141.7, 140.3, 134.9, 134.7, 130.0, 128.0, 127.6, 127.3, 126.0, 125.8, 125.2, 124.9, 54.2, 42.4, 23.4.

(*S*)-1-Acetyl-2-(3-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3j)



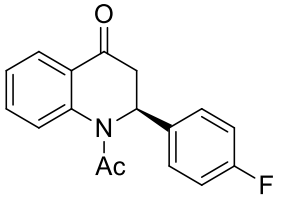
Light yellow solid, 57 mg, 48% yield, m.p.152 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –196.8 (c 1.50, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.25 (br, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 2H), 7.07 – 7.01 (m, 1H), 6.47 (br, 1H), 3.32 (dd, *J* = 18.1, 2.1 Hz, 1H), 3.23 (dd, *J* = 18.1, 5.7 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 170.2, 141.7, 140.3, 134.9, 134.7, 130.0, 128.0, 127.6, 127.3, 126.0, 125.8, 125.2, 124.9, 54.2, 42.4, 23.4.
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 5.21 min, t_R (*R*) =7.35 min.

1-Acetyl-2-(4-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (3k)



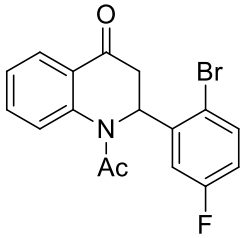
White solid, 1.0 g, 71% yield, m.p.166 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.22 (br, 1H), 7.20 – 7.09 (m, 3H), 6.91 – 6.83 (m, 2H), 6.46 (br, 1H), 3.31 (dd, *J* = 18.0, 2.2 Hz, 1H), 3.23 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.50. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 170.2, 162.1 (d, *J* = 246.9 Hz), 141.70, 134.6, 133.9 (d, *J* = 2.9 Hz), 128.6 (d, *J* = 8.2 Hz), 127.4, 126.0, 125.7, 125.1, 115.6 (d, *J* = 21.5 Hz), 54.2, 42.7, 23.4.

(*S*)-1-Acetyl-2-(4-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3k)



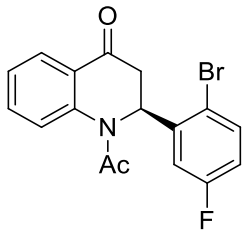
White solid, 55 mg, 49% yield, m.p.166 °C, *ee* = 98%, $[\alpha]_D^{25}$ = –246.0 (c 1.21, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.22 (br, 1H), 7.20 – 7.09 (m, 3H), 6.91 – 6.83 (m, 2H), 6.46 (br, 1H), 3.31 (dd, *J* = 18.0, 2.2 Hz, 1H), 3.23 (dd, *J* = 18.0, 5.6 Hz, 1H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.50. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 170.2, 162.1 (d, *J* = 246.9 Hz), 141.70, 134.6, 133.9 (d, *J* = 2.9 Hz), 128.6 (d, *J* = 8.2 Hz), 127.4, 126.0, 125.7, 125.1, 115.6 (d, *J* = 21.5 Hz), 54.2, 42.7, 23.4.
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 4.46 min, t_R (*R*) =5.27 min.

1-Acetyl-2-(2-bromo-5-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (3l)



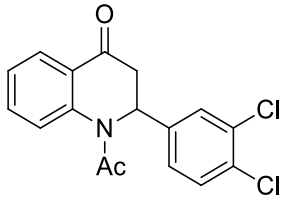
White solid, 660 mg, 35% yield, m.p.137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.46 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.75 (ddd, *J* = 8.7, 7.6, 2.9 Hz, 1H), 6.59 (ddd, *J* = 9.8, 2.9, 0.7 Hz, 1H), 6.38 (d, *J* = 6.4 Hz, 1H), 3.30 (dd, *J* = 18.1, 6.5 Hz, 1H), 3.20 (dd, *J* = 18.1, 1.9 Hz, 1H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 170.0, 161.6 (d, *J* = 247.8 Hz), 142.4, 139.8 (d, *J* = 6.8 Hz), 135.1 (d, *J* = 8.2 Hz), 135.0, 127.5, 126.0, 125.9, 124.8, 117.2 (d, *J* = 3.4 Hz), 116.5 (d, *J* = 22.2 Hz), 115.8 (d, *J* = 24.8 Hz), 55.6, 42.6, 23.4.

(*S*)-1-Acetyl-2-(2-bromo-5-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3l)



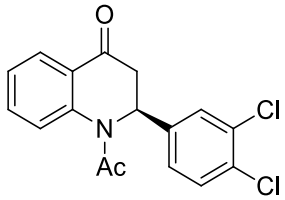
White solid, 66 mg, 46% yield, m.p.137 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –125.8 (c 1.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.46 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.75 (ddd, *J* = 8.7, 7.6, 2.9 Hz, 1H), 6.59 (ddd, *J* = 9.8, 2.9, 0.7 Hz, 1H), 6.38 (d, *J* = 6.4 Hz, 1H), 3.30 (dd, *J* = 18.1, 6.5 Hz, 1H), 3.20 (dd, *J* = 18.1, 1.9 Hz, 1H), 2.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 170.0, 161.6 (d, *J* = 247.8 Hz), 142.4, 139.8 (d, *J* = 6.8 Hz), 135.1 (d, *J* = 8.2 Hz), 135.0, 127.5, 126.0, 125.9, 124.8, 117.2 (d, *J* = 3.4 Hz), 116.5 (d, *J* = 22.2 Hz), 115.8 (d, *J* = 24.8 Hz), 55.6, 42.6, 23.4.
SFC: Chiralpak AD-H, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*R*) = 4.39 min, t_R (*S*)=12.76 min.

1-Aacetyl-2-(3,4-dichlorophenyl)-2,3-dihydroquinolin-4(1H)-one (3m)



White solid, 1.0 g, 75% yield, m.p.149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.51 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 7.33 – 7.17 (m, 4H), 7.00 (ddd, *J* = 8.4, 2.3, 0.9 Hz, 1H), 6.48 (br, 1H), 3.58 – 3.12 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 170.2, 141.5, 138.6, 134.8, 133.1, 131.9, 130.6, 129.1, 127.6, 126.2, 126.0, 125.9, 125.1, 53.7, 42.3, 23.4.

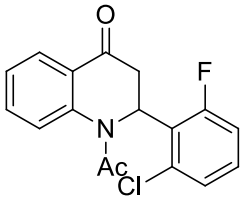
(*S*)-1-Acetyl-2-(3,4-dichlorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3m)



White solid, 65 mg, 49% yield, m.p.149 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –210.8 (c 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.51 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 7.33 – 7.17 (m, 4H), 7.00 (ddd, *J* = 8.4, 2.3, 0.9 Hz, 1H), 6.48 (br, 1H), 3.58 – 3.12 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 170.2, 141.5, 138.6, 134.8, 133.1, 131.9, 130.6, 129.1, 127.6, 126.2, 126.0, 125.9, 125.1, 53.7, 42.3, 23.4.

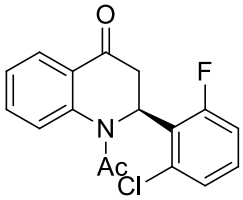
SFC: Chiralpak AS-H, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*R*) = 4.30 min, t_R (*S*)=4.75 min.

1-Acetyl-2-(2-chloro-6-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (3n)



White solid, 400 mg, 44% yield, m.p.183 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.44 (td, *J* = 7.7, 1.6 Hz, 1H), 7.29 (ddd, *J* = 8.6, 7.2, 1.0 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.80 – 6.67 (m, 2H), 3.30 (dddd, *J* = 18.4, 6.5, 5.4, 0.8 Hz, 1H), 3.22 (dddd, *J* = 18.3, 5.5, 2.3, 0.7 Hz, 1H), 2.20 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.91 (dd, *J* = 11.8, 5.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4 (d, *J* = 5.7 Hz), 169.0, 161.8 (d, *J* = 249.9 Hz), 142.2, 136.2 (d, *J* = 6.9 Hz), 133.8, 129.9 (d, *J* = 10.5 Hz), 128.6, 127.2, 126.8, 126.5 (d, *J* = 3.2 Hz), 126.1, 123.6 (d, *J* = 14.8 Hz), 115.2 (d, *J* = 25.6 Hz), 52.0 (d, *J* = 2.0 Hz), 42.82 (d, *J* = 6.2 Hz), 22.7.

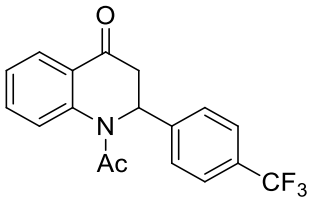
(*S*)-1-Acetyl-2-(2-chloro-6-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3n)



White solid, 56 mg, 44% yield, m.p.183 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –43.4 (c 1.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.44 (td, *J* = 7.7, 1.6 Hz, 1H), 7.29 (ddd, *J* = 8.6, 7.2, 1.0 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.80 – 6.67 (m, 2H), 3.30 (dddd, *J* = 18.4, 6.5, 5.4, 0.8 Hz, 1H), 3.22 (dddd, *J* = 18.3, 5.5, 2.3, 0.7 Hz, 1H), 2.20 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.91 (dd, *J* = 11.8, 5.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4 (d, *J* = 5.7 Hz), 169.0, 161.8 (d, *J* = 249.9 Hz), 142.2, 136.2 (d, *J* = 6.9 Hz), 133.8, 129.9 (d, *J* = 10.5 Hz), 128.6, 127.2, 126.8, 126.5 (d, *J* = 3.2 Hz), 126.1, 123.6 (d, *J* = 14.8 Hz), 115.2 (d, *J* = 25.6 Hz), 52.0 (d, *J* = 2.0 Hz), 42.82 (d, *J* = 6.2 Hz), 22.7.

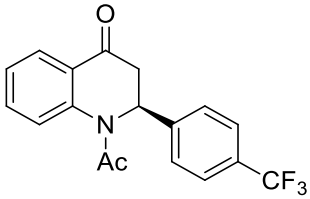
SFC: Chiralpak IE, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*R*) = 11.80 min, t_R (*S*)=12.82 min.

1-Aacetyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydroquinolin-4(1H)-one (3o)



Light yellow solid, 900 mg, 54% yield, m.p.128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.30 (dd, *J* = 8.1, 0.8 Hz, 2H), 7.24 (br, 1H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 6.55 (br, 1H), 3.37 (dd, *J* = 18.1, 2.1 Hz, 1H), 3.28 (dd, *J* = 18.1, 5.7 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 170.3, 142.3, 141.7, 134.8, 130.0 (q, *J* = 32.6 Hz), 127.6, 127.3, 126.0, 125.7 (q, *J* = 3.8 Hz), 125.1, 123.9 (q, *J* = 272.1 Hz) 131.8, 128.6, 127.5, 126.0, 125.8, 125.1, 121.8, 54.4, 42.5, 23.4.

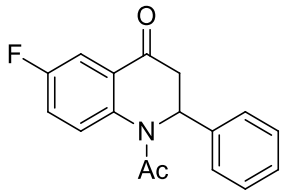
(*S*)-1-Acetyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydroquinolin-4(1H)-one ((*S*)-3o)



Light yellow solid, 65 mg, 49% yield, m.p.128 °C, *ee* > 99%, $[\alpha]_D^{25}$ = –176.6 (c 1.17, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.30 (dd, *J* = 8.1, 0.8 Hz, 2H), 7.24 (br, 1H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 6.55 (br, 1H), 3.37 (dd, *J* = 18.1, 2.1 Hz, 1H), 3.28 (dd, *J* = 18.1, 5.7 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 170.3, 142.3, 141.7, 134.8, 130.0 (q, *J* = 32.6 Hz), 127.6, 127.3, 126.0, 125.7 (q, *J* = 3.8 Hz), 125.1, 123.9 (q, *J* = 272.1 Hz) 131.8, 128.6, 127.5, 126.0, 125.8, 125.1, 121.8, 54.4, 42.5, 23.4.

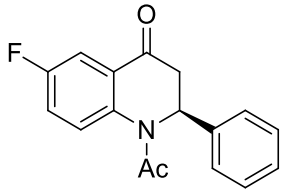
SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 4.95 min, t_R (*R*)=5.51 min.

1-Acetyl-6-fluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one (3p)



White solid, 700 mg, 88% yield, m.p.153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.3, 3.1 Hz, 1H), 7.36 (br, 1H), 7.21 – 7.06 (m, 6H), 6.36 (br, 1H), 3.35 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.21 (dd, *J* = 18.0, 5.8 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 169.9, 159.6 (d, *J* = 248.0 Hz), 137.9, 137.7 (d, *J* = 40.9 Hz), 128.7, 127.7, 127.4 (d, *J* = 6.5 Hz), 127.2 (d, *J* = 7.3 Hz), 126.6, 121.6 (d, *J* = 23.4 Hz), 113.0 (d, *J* = 23.2 Hz), 55.0, 42.2, 23.2.

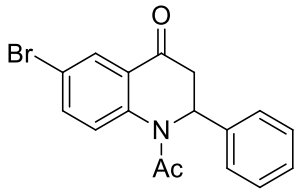
(*S*)-1-Acetyl-6-fluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one ((*S*)-3p)



White solid, 54 mg, 48% yield, m.p.153 °C, *ee* = 99%, $[\alpha]_D^{25}$ = –212.2 (c 1.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.3, 3.1 Hz, 1H), 7.36 (br, 1H), 7.21 – 7.06 (m, 6H), 6.36 (br, 1H), 3.35 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.21 (dd, *J* = 18.0, 5.8 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 169.9, 159.6 (d, *J* = 248.0 Hz), 137.9, 137.7 (d, *J* = 40.9 Hz), 128.7, 127.7, 127.4 (d, *J* = 6.5 Hz), 127.2 (d, *J* = 7.3 Hz), 126.6, 121.6 (d, *J* = 23.4 Hz), 113.0 (d, *J* = 23.2 Hz), 55.0, 42.2, 23.2.

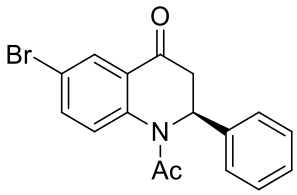
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 4.50 min, t_R (*R*) =8.82 min.

1-Acetyl-6-bromo-2-phenyl-2,3-dihydroquinolin-4(1H)-one (3q)



Light yellow solid, 2.0 g, 65% yield, m.p.119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.30 (s, 1H), 7.22 – 7.05 (m, 5H), 6.31 (br, 1H), 3.34 (dd, *J* = 17.9, 2.1 Hz, 1H), 3.20 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 169.8, 140.6, 137.3, 137.0, 129.8, 128.7, 127.7, 126.9, 126.7, 126.5, 118.6, 55.0, 42.2, 23.3.

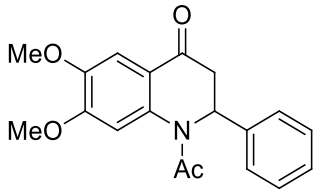
(*S*)-1-Acetyl-6-bromo-2-phenyl-2,3-dihydroquinolin-4(1H)-one ((*S*)-3q)



Light yellow solid, 79 mg, 58% yield, m.p.119 °C, *ee* = 71%, $[\alpha]_D^{25}$ = –127.3 (c 1.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.30 (s, 1H), 7.22 – 7.05 (m, 5H), 6.31 (br, 1H), 3.34 (dd, *J* = 17.9, 2.1 Hz, 1H), 3.20 (dd, *J* = 17.9, 5.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 169.8, 140.6, 137.3, 137.0, 129.8, 128.7, 127.7, 126.9, 126.7, 126.5, 118.6, 55.0, 42.2, 23.3.

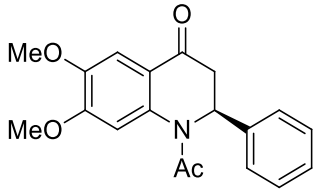
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 7.27 min, t_R (*R*) =13.16 min.

1-Acetyl-6,7-dimethoxy-2-phenyl-2,3-dihydroquinolin-4(1H)-one (3r)



Colorless solid, 800 mg, 71% yield, m.p.182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.22 – 7.07 (m, 5H), 6.87 (br, 1H), 6.24 (br, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.35 – 3.09 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 169.9, 153.9, 146.7, 138.0, 137.0, 128.6, 127.6, 126.6, 119.2, 107.6, 56.3, 56.0, 42.1, 23.7.

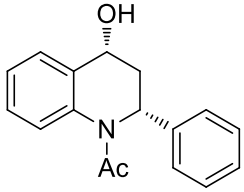
(*S*)-1-acetyl-6,7-dimethoxy-2-phenyl-2,3-dihydroquinolin-4(1H)-one ((*S*)-3r)



Colorless solid, 62 mg, 48% yield, m.p.182 °C, *ee* = 93%, $[\alpha]_D^{25}$ = –269.4 (c 0.87, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.22 – 7.07 (m, 5H), 6.87 (br, 1H), 6.24 (br, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.35 – 3.09 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 169.9, 153.9, 146.7, 138.0, 137.0, 128.6, 127.6, 126.6, 119.2, 107.6, 56.3, 56.0, 42.1, 23.7.
SFC: Chiralpak IF, *sc*CO_2/ MeOH 60/40, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R (*S*) = 5.15 min, t_R (*R*)=5.74 min.

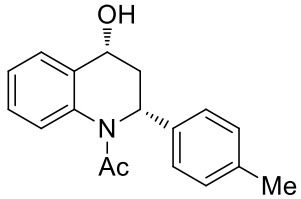
VII. Analytical data for compounds 4a–4r

1-((2*R*,4*R*)-4-Hydroxy-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (4a)



Colorless solid, 53 mg, 50% yield, m.p.72 °C, *ee* > 99%, $[\alpha]_D^{25}$ = +242.1 (c 1.49, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.26 (m, 2H), 7.29 – 7.19 (m, 3H), 7.23 – 7.11 (m, 3H), 5.69 (br, 1H), 4.71 (dd, *J* = 11.3, 4.3 Hz, 1H), 2.83 (ddd, *J* = 12.8, 8.5, 4.4 Hz, 1H), 2.27 (br, 1H), 2.14 (s, 3H), 1.79 (q, *J* = 11.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 143.0, 138.9, 136.3, 128.7, 127.5, 127.2, 126.4, 126.2, 125.6, 123.0, 66.1, 54.6, 43.9, 23.1.
HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{18}NO_2$ 268.1338, found 268.1333.
SFC: Chiralpak AS-H, *sc*CO_2/ EtOH 90/10, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 8.90 min (major), t_R = 9.99 min, t_R = 11.86 min, t_R =14.52 min.

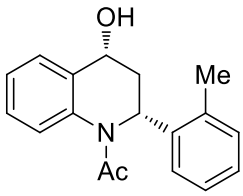
1-((2*R*,4*R*)-4-Hydroxy-2-(p-tolyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (4b)



Colorless oil, 56 mg, 50% yield, *ee* = 99%, $[\alpha]_D^{25}$ = +225.2 (c 1.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.21 (br, 1H), 7.08 – 7.02 (m, 4H), 5.65 (br, 1H), 4.69 (dd, *J* = 11.3, 4.3 Hz, 1H), 2.80 (ddd, *J* = 12.8, 8.5, 4.5 Hz, 1H), 2.62 (br, 1H), 2.27 (s, 3H), 2.13 (s, 3H), 1.78 (q, *J* = 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 139.9, 138.7, 136.7, 136.2, 129.2, 127.3, 126.3, 126.0, 125.4, 122.9, 65.9, 54.3, 43.8, 23.0, 21.0. HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_2$ 282.1494, found 282.1490.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 6.76 min, t_R = 8.87 min (major).

1-((2*R*,4*R*)-4-Hydroxy-2-(o-tolyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (4c)

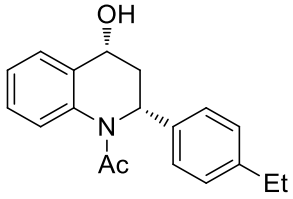


White solid, 57 mg, 50% yield, m.p.143 °C, *ee* = 95%, $[\alpha]_D^{25}$ = +216.6 (c 1.63, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.27 (m, 3H), 7.11 – 7.00 (m, 3H), 6.89 (br, 1H), 5.71 (br, 1H), 4.68 (dd, *J* = 11.9, 3.9 Hz, 1H), 2.76 (ddd, *J* = 12.2, 8.1, 4.0 Hz, 1H), 2.50 (s, 4H), 2.12 (s, 3H), 1.54 (td, *J* = 12.1, 11.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 142.5, 139.0, 136.9, 134.8, 130.4, 127.4, 126.9, 126.6, 125.9, 125.3, 124.9, 122.6, 66.2, 52.3, 43.3, 23.2, 19.2.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_2$ 282.1494, found 282.1488.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 5.25 min, t_R = 5.64 min (major), t_R = 6.14 min, t_R = 6.53 min.

1-((2*R*,4*R*)-2-(4-Ethylphenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4d)

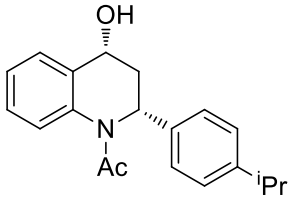


Light yellow solid, 60 mg, 50% yield, m.p.124 °C, *ee* = 96%, $[\alpha]_D^{25}$ = +204.2 (c 1.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.20 (br, 1H), 7.09 – 7.04 (m, 4H), 5.66 (br, 1H), 4.68 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.83 – 2.77 (m, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.13 (s, 3H), 1.78 (q, *J* = 11.5 Hz, 1H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 143.1, 140.2, 139.0, 136.3, 128.1, 127.4, 126.5, 126.1, 125.6, 123.0, 66.0, 54.4, 43.9, 28.5, 23.1, 15.5.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{19}H_{22}NO_2$ 296.1646, found 296.1651.

SFC: Chiralpak ID, *sc*CO_2/ EtOH 85/15, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 6.26 min, t_R = 6.75 min (major), t_R = 7.83 min, t_R = 8.62 min.

1-((2*R*,4*R*)-4-Hydroxy-2-(4-isopropylphenyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (4e)

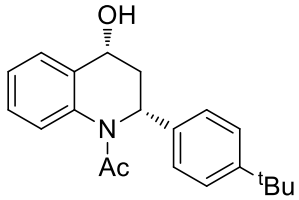


Colorless oil, 62 mg, 50% yield, *ee* = 96%, $[\alpha]_D^{25}$ = +161.8 (c 1.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.31 (tt, *J* = 6.9, 3.5 Hz, 2H), 7.21 (br, 1H), 7.08 (q, *J* = 8.4 Hz, 4H), 5.68 (br, 1H), 4.69 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.62 (br, 1H), 2.13 (s, 3H), 1.79 (q, *J* = 11.6 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 147.7, 140.2, 139.0, 136.3, 127.4, 126.7, 126.4, 126.1, 125.6, 123.0, 66.1, 54.3, 43.9, 33.8, 24.0, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{20}H_{24}NO_2$ 310.1807, found 310.1802.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 6.23 min, t_R = 8.45 min (major).

1-((2*R*,4*R*)-2-(4-(*tert*-Butyl)phenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4f)

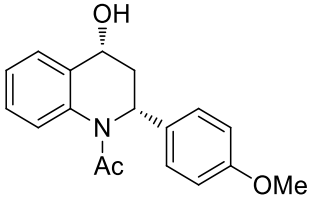


White oil, 62 mg, 48% yield, *ee* = 99%, $[\alpha]_D^{25}$ = +198.9 (c 0.97, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.18 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.69 (br, 1H), 4.70 (dd, *J* = 11.3, 4.2 Hz, 1H), 2.83 (ddd, *J* = 12.7, 8.6, 4.4 Hz, 1H), 2.47 (br, 1H), 2.13 (s, 3H), 1.79 (q, *J* = 11.3 Hz, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 149.9, 139.8, 138.9, 136.3, 127.4, 126.1, 125.6, 125.6, 123.0, 66.1, 54.2, 43.8, 34.5, 31.4, 23.2.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{21}H_{26}NO_2$ 324.1964, found 324.1959.

SFC: Chiralpak AD-H, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 4.31 min, t_R = 5.27 min (major).

1-((2*R*,4*R*)-4-Hydroxy-2-(4-methoxyphenyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (4g)

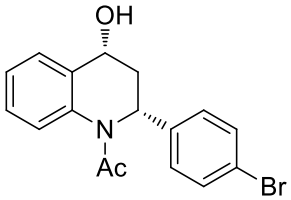


Colorless oil, 60 mg, 50% yield, *ee* = 97%, $[\alpha]_D^{25}$ = +191.2 (c 1.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 1H), 7.37 – 7.25 (m, 2H), 7.18 (br, 1H), 7.11 – 7.02 (m, 2H), 6.81 – 6.72 (m, 2H), 5.65 (br, 1H), 4.69 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.74 (s, 3H), 2.80 (ddd, *J* = 12.8, 8.6, 4.5 Hz, 1H), 2.47 (br, 1H), 2.12 (s, 3H), 1.78 (dd, *J* = 22.2, 11.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 158.7, 138.8, 136.2, 135.1, 127.8, 127.4, 126.2, 125.6, 123.0, 114.0, 66.1, 55.4, 54.0, 43.9, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_3$ 298.1443, found 298.1437.

SFC: Chiralpak IE, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 11.04min, t_R = 12.39 min (major).

1-((2*R*,4*R*)-2-(4-Bromophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4h)

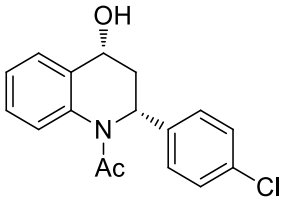


White solid, 69 mg, 50% yield, m.p.78 °C, *ee* = 98%, $[\alpha]_D^{25}$ = +163.8 (c 1.32, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 1H), 7.38 – 7.28 (m, 4H), 7.18 (br, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 5.64 (br, 1H), 4.71 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.81 (ddd, *J* = 12.8, 8.6, 4.4 Hz, 1H), 2.45 (br, 1H), 2.13 (s, 3H) 1.71 (q, *J* = 11.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 142.1, 138.7, 136.0, 131.8, 128.3, 127.6, 126.3, 125.4, 123.0, 121.0, 66.0, 54.2, 43.7, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{17}BrNO_2$ 346.0443, found 346.0437.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 10.81min, t_R = 15.08 min (major).

1-((2*R*,4*R*)-2-(4-Chlorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4i)

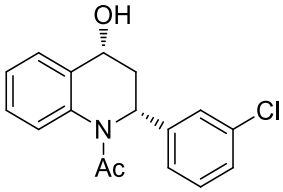


Colorless oil, 60 mg, 50% yield, *ee* = 97%, $[\alpha]_D^{25}$ = +153.2 (c 0.95, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 1H), 7.33 (ddd, *J* = 6.8, 4.6, 1.7 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 3H), 7.07 (d, *J* = 8.5 Hz, 2H), 5.65 (br, 1H), 4.71 (dd, *J* = 11.7, 4.0 Hz, 1H), 2.81 (ddd, *J* = 12.3, 8.2, 3.8 Hz, 1H), 2.58 (br, 1H), 2.13 (s, 3H), 1.72 (q, *J* = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 141.6, 138.8, 136.0, 132.9, 128.8, 127.9, 127.6, 126.3, 125.4, 123.0, 66.0, 54.1, 43.8, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{17}ClNO_2$ 302.0948, found 302.0944.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 6.01 min, t_R = 7.69 min, t_R = 8.28 min, t_R = 11.30 min (major).

1-((2*R*,4*R*)-2-(3-Chlorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4j)

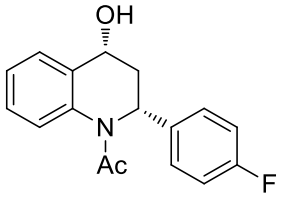


Colorless oil, 61 mg, 50% yield, *ee* = 96%, $[\alpha]_D^{25}$ = +199.9 (c 1.80, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.22 (br, 1H), 7.18 – 7.10 (m, 3H), 7.07 – 6.98 (m, 1H), 5.63 (br, 1H), 4.69 (dt, *J* = 11.0, 5.1 Hz, 1H), 2.85 (d, *J* = 6.2 Hz, 1H), 2.80 (ddd, *J* = 12.7, 8.6, 4.4 Hz, 1H), 2.14 (s, 3H), 1.69 (q, *J* = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 145.2, 138.8, 136.0, 134.4, 130.0, 127.6, 127.4, 126.6, 126.4, 125.4, 124.6, 123.0, 65.9, 54.3, 43.8, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{17}ClNO_2$ 302.0948, found 302.0944.

SFC: Chiralpak ID, *sc*CO_2/ ^{i}PrOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 7.03 min, t_R = 8.02 min (major), t_R = 9.67 min, t_R = 11.64 min.

1-((2*R*,4*R*)-2-(4-Fluorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4k)

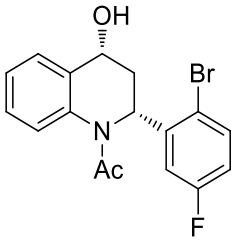


White solid, 58 mg, 50% yield, m.p.158 °C, *ee* = 97%, $[\alpha]_D^{25}$ = +203.2 (c 2.12, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.32 – 7.21 (m, 2H), 7.11 (br, 1H), 7.07 – 6.99 (m, 2H), 6.92 – 6.78 (m, 2H), 5.60 (br, 1H), 4.63 (dd, *J* = 11.4, 4.3 Hz, 1H), 2.74 (ddd, *J* = 12.8, 8.6, 4.4 Hz, 1H), 2.45 (br, 1H), 2.05 (s, 3H), 1.66 (ddd, *J* = 12.6, 11.5, 10.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 162.9 (d, *J* = 245.4 Hz), 138.8 (2C), 136.1, 128.2 (d, *J* = 8.0 Hz), 127.5, 126.3, 125.5, 123.0, 115.5 (d, *J* = 21.4 Hz), 66.0, 54.0, 44.0, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}FNO_2$ 286.1243, found 286.1238.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 5.02 min, t_R = 6.25 min (major).

1-((2*R*,4*R*)-2-(2-Bromo-5-fluorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4l)

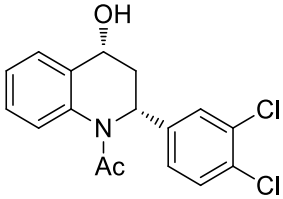


Yellow solid, 70 mg, 48% yield, m.p.174 °C, *ee* = 93%, $[\alpha]_D^{25}$ = +198.5 (c 1.85, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.41 – 7.28 (m, 3H), 6.89 – 6.63 (m, 2H), 5.73 (br, 1H), 4.71 (dt, *J* = 10.7, 4.7 Hz, 1H), 3.00 (ddd, *J* = 12.1, 8.0, 3.9 Hz, 1H), 2.75 (br, 1H), 2.18 (s, 3H), 1.39 (q, *J* = 11.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.39. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 162.4 (d, *J* = 247.1 Hz), 145.6 (d, *J* = 6.6 Hz), 138.9, 136.2, 134.3 (d, *J* = 7.9 Hz), 127.6, 126.2, 124.9, 123.0, 116.1, 115.7 (d, *J* = 22.7 Hz), 113.2 (d, *J* = 23.9 Hz), 65.8, 55.7, 41.8, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}BrFNO_2$ 364.0348, found 364.0343.

SFC: Chiralpak ID, *sc*CO_2/ ^{i}PrOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 7.52 min (major), t_R = 8.85 min.

1-((2*R*,4*R*)-2-(3,4-Dichlorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4m)



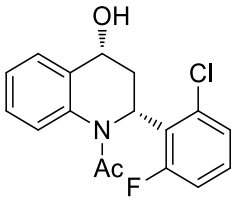
White solid, 68 mg, 50% yield, m.p.94 °C, *ee* = 96%, $[\alpha]_D^{25}$ = +114.8 (c 1.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 1H), 7.40 – 7.31 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.19 (br, 1H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.62 (t, *J* = 9.4 Hz, 1H), 4.71 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.81 (ddd, *J* = 12.7, 8.6, 4.3 Hz, 1H), 2.48 (br, 1H), 2.14 (s, 3H), 1.68 (dd, *J* = 22.7, 11.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.4, 138.7, 135.8, 132.6, 131.2, 130.6, 128.6, 127.7, 126.5, 125.9, 125.3, 123.0, 65.8, 53.8, 43.6, 23.0.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}Cl_2NO_2$ 336.0558, found 336.0554.

SFC: Chiralpak AS-H, *sc*CO_2/ EtOH 90/10, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 9.65 min (major), t_R = 13.72 min.

1-((2*R*,4*R*)-2-(2-Chloro-6-fluorophenyl)-4-hydroxy-3,4-dihydroquinolin-1(2H)-yl)ethanone (4n)

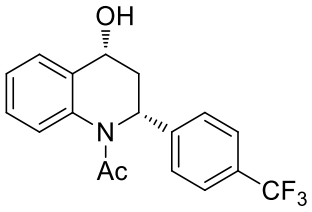


Colorless oil, 65 mg, 50% yield, *ee* = 86%, $[\alpha]_D^{25}$ = +121.4 (c 1.09, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.26 (m, 2H), 7.21 – 7.06 (m, 3H), 6.84 (ddd, *J* = 10.6, 8.0, 1.6 Hz, 1H), 5.90 (dd, *J* = 12.5, 7.4 Hz, 1H), 4.75 (dt, *J* = 10.9, 6.0 Hz, 1H), 2.66 (ddd, *J* = 11.6, 7.4, 3.7 Hz, 1H), 2.44 (d, *J* = 6.6 Hz, 1H), 2.16 (s, 3H), 1.74 (q, *J* = 12.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.87. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 161.0 (d, *J* = 250.8 Hz), 137.8, 136.7, 134.2 (d, *J* = 5.8 Hz), 128.7 (d, *J* = 9.7 Hz), 127.8 (d, *J* = 15.3 Hz), 127.0, 125.7 (d, *J* = 3.4 Hz), 125.6, 122.4, 114.9 (d, *J* = 22.6 Hz), 66.5, 52.3, 39.7, 23.4.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}ClFNO_2$ 320.0854, found 320.0849.

SFC: Chiralpak AD-H, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 4.26 min, t_R = 4.67 min, t_R = 5.06 min, t_R = 5.59 min (major).

1-((2*R*,4*R*)-4-Hydroxy-2-(4-(trifluoromethyl)phenyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (4o)

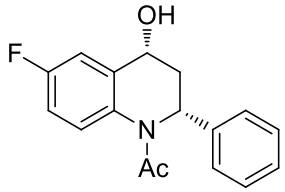


Colorless oil, 65 mg, 49% yield, *ee* = 96%, $[\alpha]_D^{25}$ = +160.8 (c 1.57, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.30 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.21 (br, 1H), 5.72 (t, *J* = 8.7 Hz, 1H), 4.74 (dd, *J* = 11.5, 4.2 Hz, 1H), 2.85 (ddd, *J* = 12.8, 8.6, 4.3 Hz, 1H), 2.56 (br, 1H), 2.15 (s, 3H), 1.72 (q, *J* = 11.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 147.1, 138.7, 136.0, 129.4 (q, *J* = 32.4 Hz), 127.7, 126.8, 126.4, 125.7 (q, *J* = 3.9 Hz), 125.3, 124.2 (q, *J* = 272.0 Hz), 123.0, 66.0, 54.4, 43.8, 23.0.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{18}H_{17}F_3NO_2$ 336.1211, found 336.1207.

SFC: Chiralpak AS-H, *sc*CO_2/ EtOH 92/8, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 5.08 min (major), t_R = 5.80 min.

1-((2*R*,4*R*)-6-Fluoro-4-hydroxy-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (4p)

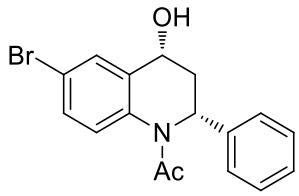


Colorless oil, 58 mg, 50% yield, *ee* = 97%, $[\alpha]_D^{25}$ = +158.1 (c 1.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.15 (m, 4H), 7.16 – 7.09 (m, 2H), 7.02 (td, *J* = 8.4, 3.1 Hz, 1H), 5.67 (br, 1H), 4.65 (dt, *J* = 10.6, 4.6 Hz, 1H), 2.89 – 2.68 (m, 2H), 2.11 (s, 3H), 1.81 – 1.68 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.62. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 161.0 (d, *J* = 244.2 Hz), 142.8, 141.8, 132.0, 128.7, 127.3, 127.0, 126.3, 114.0 (d, *J* = 23.3 Hz), 110.6 (d, *J* = 24.2 Hz), 65.7, 54.5, 43.6, 23.0.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}FNO_2$ 286.1243, found 286.1239.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 4.85 min, t_R = 6.25 min (major).

1-((2*R*,4*R*)-6-Bromo-4-hydroxy-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (4q)

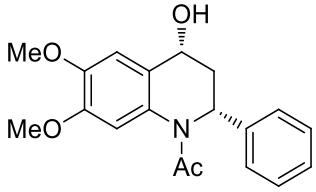


Light yellow solid, 57 mg, 41% yield, m.p.112 °C, *ee* > 99%, $[\alpha]_D^{25}$ = +154.4 (c 2.02, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.45 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.30 – 7.17 (m, 3H), 7.13 – 7.08 (m, 3H), 5.60 (br, 1H), 4.65 (dd, *J* = 11.5, 4.3 Hz, 1H), 2.79 (ddd, *J* = 12.8, 8.5, 4.4 Hz, 2H), 2.12 (s, 3H), 1.75 (td, *J* = 12.0, 10.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 142.7, 140.9, 135.2, 130.5, 128.8, 127.4, 127.0, 126.6, 126.3, 119.8, 65.6, 54.8, 43.8, 23.1.

HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{17}H_{17}BrNO_2$ 346.0443, found 346.0437.

SFC: Chiralpak IF, *sc*CO_2/ MeOH 80/20, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 7.75 min, t_R = 10.02 min. (major).

1-((2*R*,4*R*)-4-Hydroxy-6,7-dimethoxy-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (4r)



Light yellow solid, 63 mg, 48% yield, m.p.129 °C, *ee* > 99%, $[\alpha]_D^{25}$ = +176.0 (c 1.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.20 – 7.09 (m, 4H), 6.70 (br, 1H), 5.70 (br, 1H), 4.63 (dt, *J* = 10.7, 5.3 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 2.76 (ddd, *J* = 12.7, 8.3, 4.5 Hz, 2H), 2.14 (s, 3H), 1.84 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 147.9, 147.5, 142.8, 128.7, 127.2, 126.5, 109.7, 106.5, 65.7, 56.5, 56.2, 54.5, 43.7, 23.3.

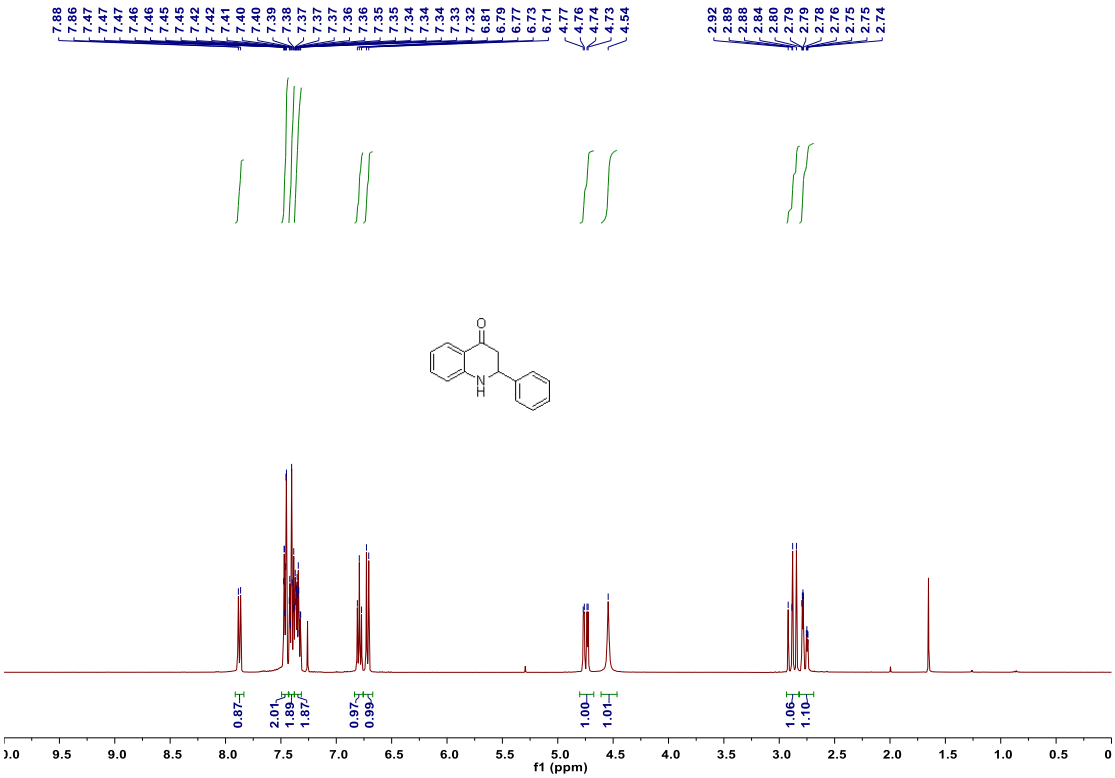
HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{19}H_{22}NO_4$ 328.1549, found 328.1543.

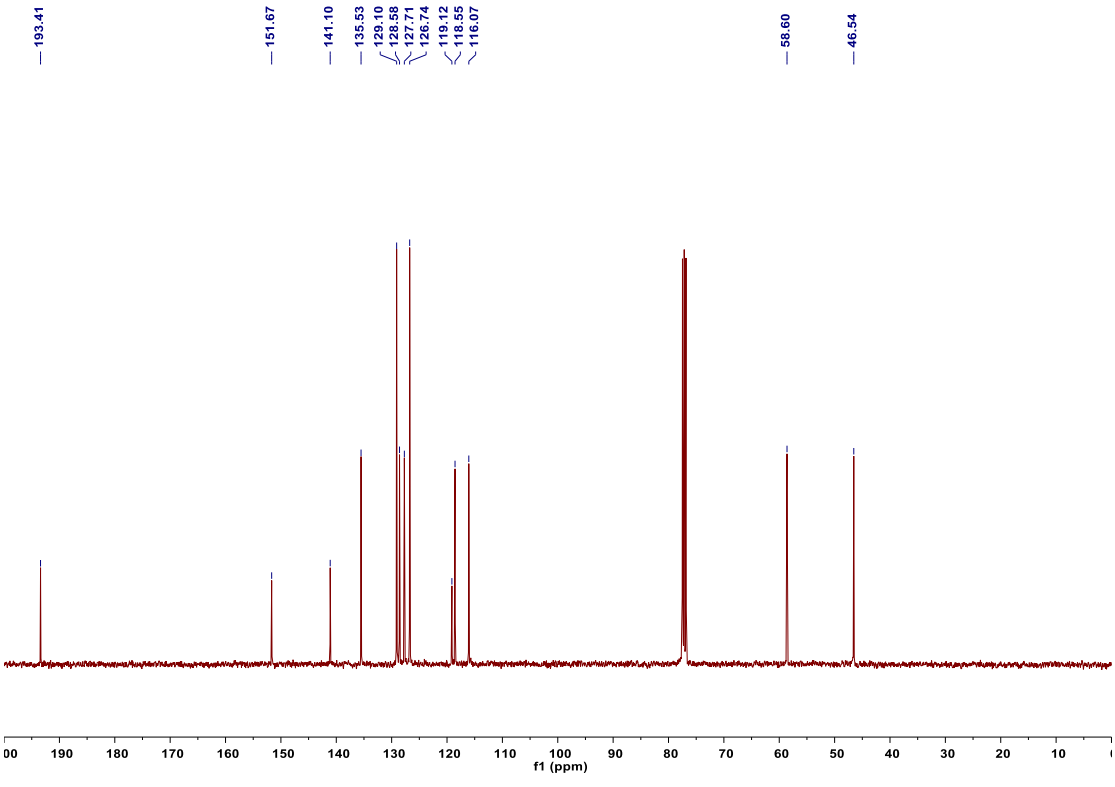
SFC: Chiralpak AD-H, *sc*CO_2/ EtOH 85/15, 2.0 mL/min, P = 100 bar, λ = 254 nm, t_R = 5.97 min

(major), t_R = 9.70 min.

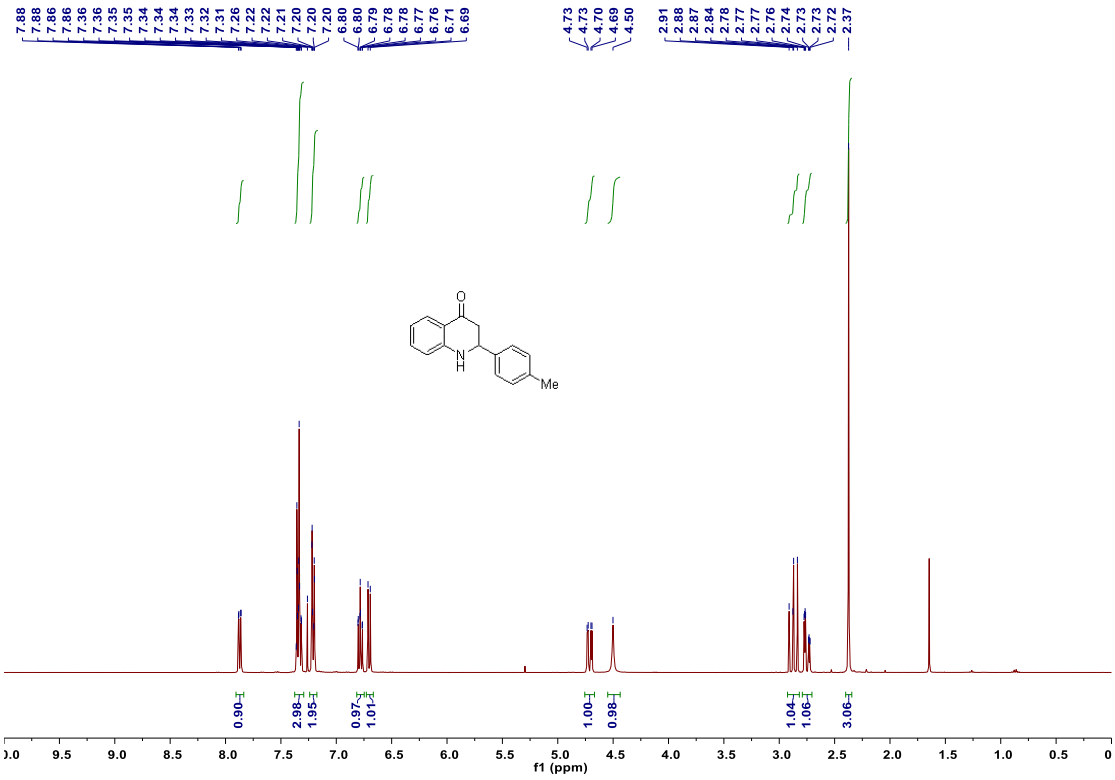
VIII. NMR spectra of compounds 1a-1r

Compound **1a**





Compound **1b**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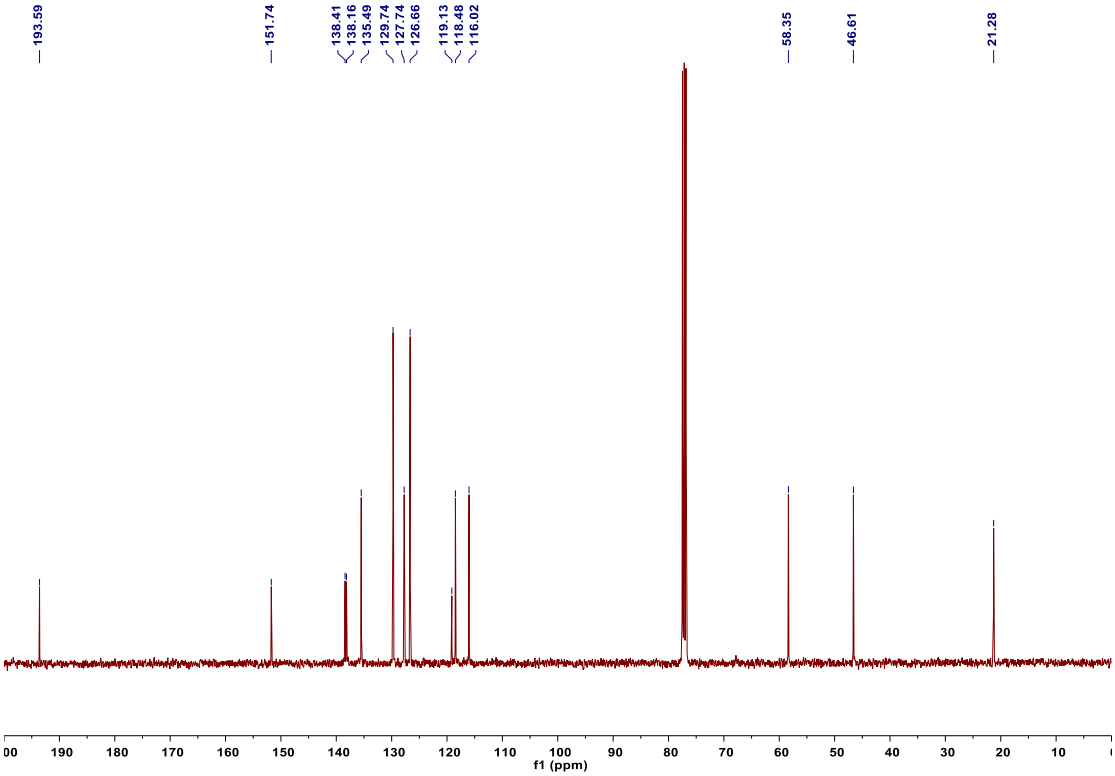
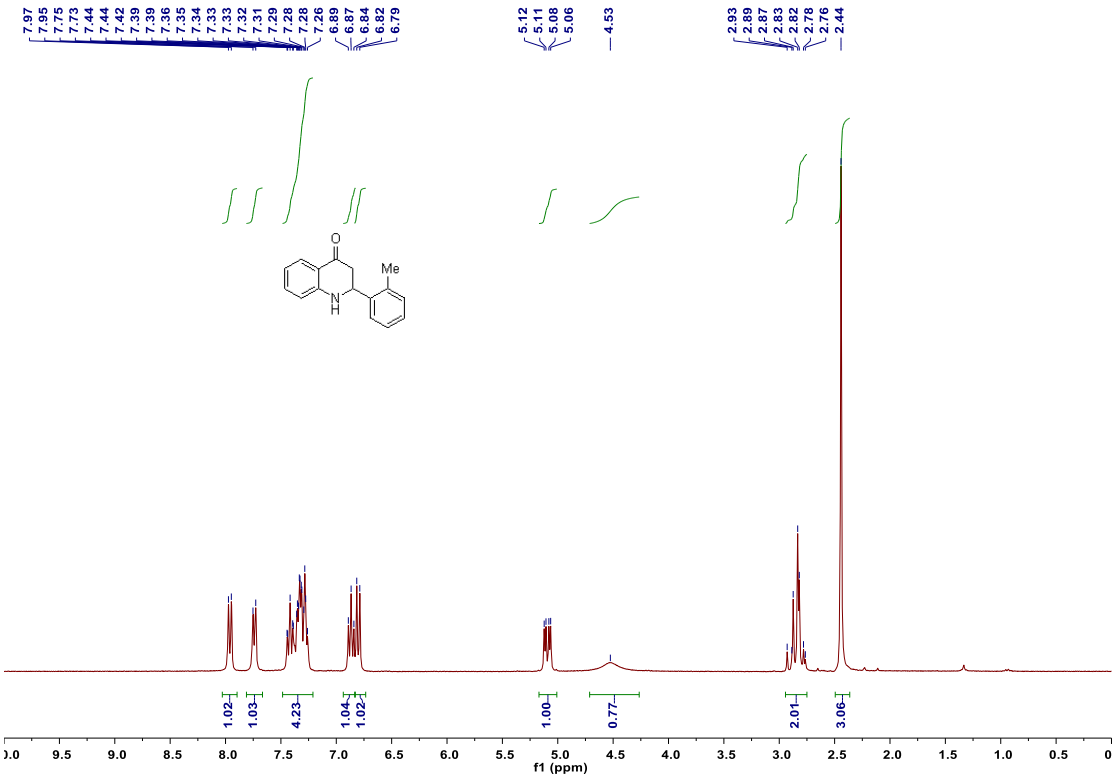
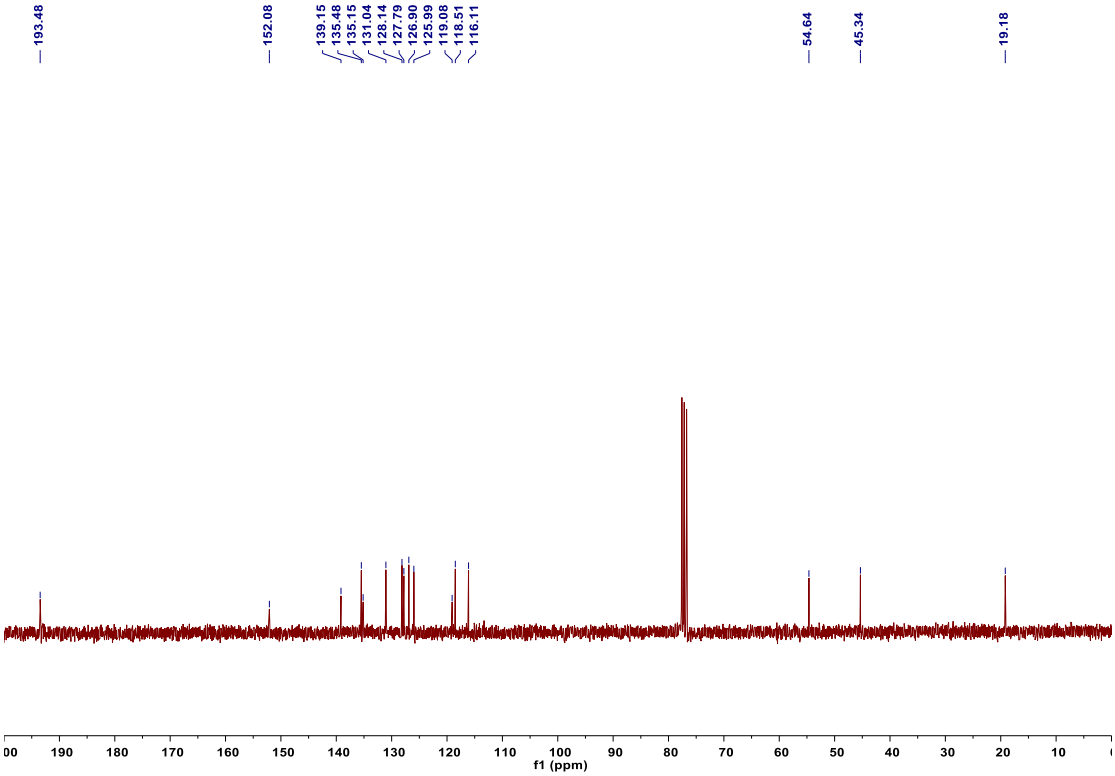
7.88
7.86
7.86
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.31
7.26
7.22
7.22
7.21
7.20
7.20
7.20
6.80
6.80
6.79
6.78
6.78
6.77
6.76
6.71
6.69
4.73
4.73
4.70
4.69
4.50
2.91
2.88
2.87
2.84
2.78
2.77
2.77
2.76
2.74
2.73
2.73
2.72
2.37
O
N
H
Me
0.90
2.98
1.95
0.97
1.01
1.00
0.98
1.04
1.06
3.06
f1 (ppm)

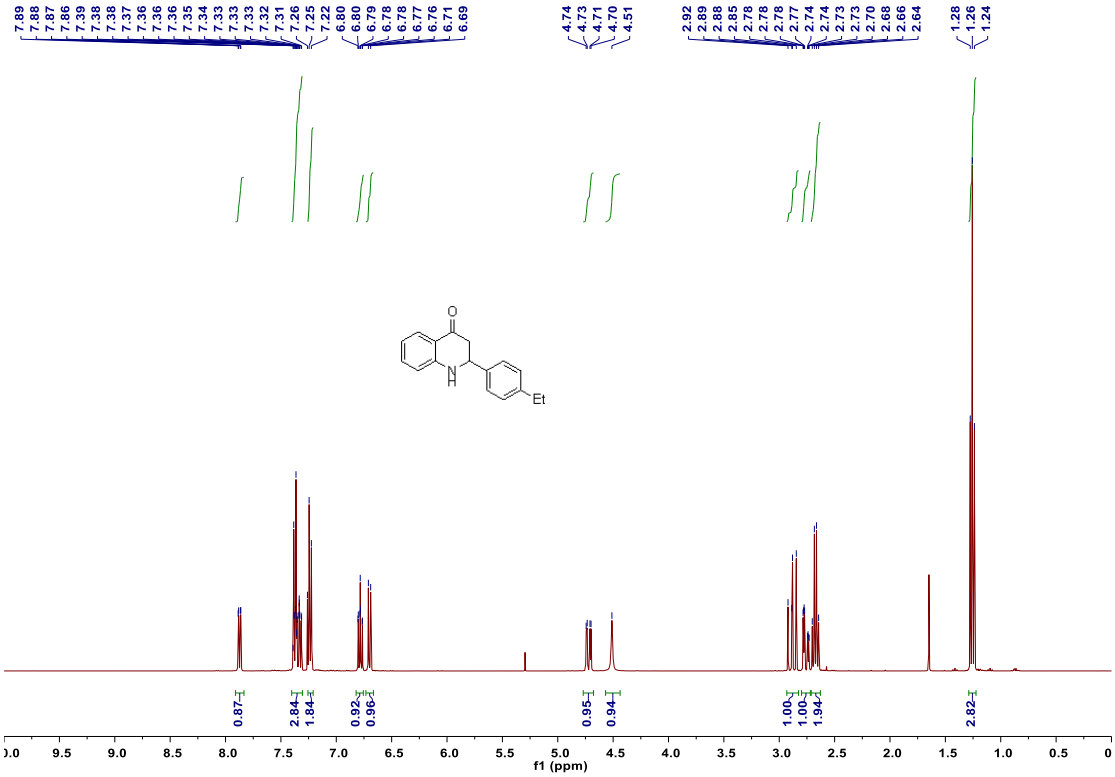

193.59
151.74
138.41
138.16
135.49
129.74
127.74
126.66
119.13
118.48
116.02
58.35
46.61
21.28
f1 (ppm)

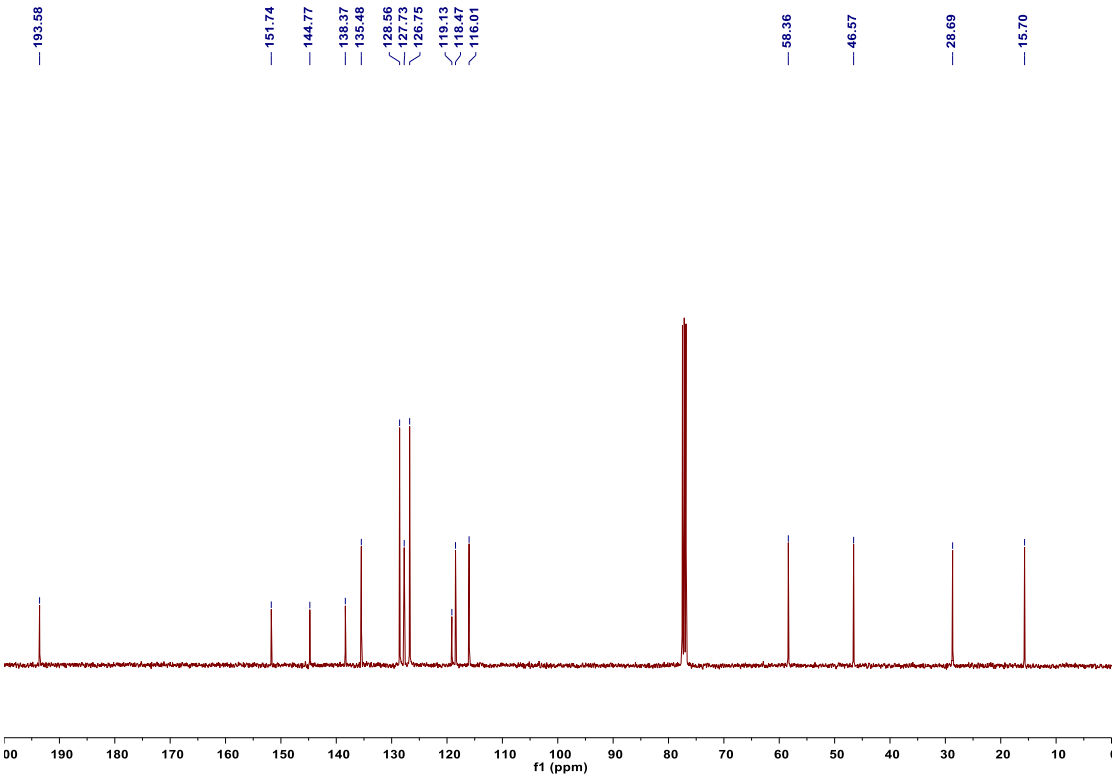
Compound **1c**


7.97
7.95
7.75
7.73
7.44
7.42
7.39
7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.28
7.26
6.89
6.87
6.84
6.82
6.79
5.12
5.11
5.08
5.06
4.53
2.93
2.89
2.87
2.83
2.82
2.78
2.76
2.44
O
Me
N
H
1.02
1.03
4.23
1.04
1.02
1.00
0.77
2.01
3.06
f1 (ppm)


193.48
152.08
139.15
135.48
135.15
131.04
128.14
127.79
126.90
125.99
119.08
118.51
116.11
54.64
45.34
19.18
f1 (ppm)

Compound **1d**


7.89 7.88 7.87 7.86 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.31 7.26 7.25 7.22 6.80 6.80 6.79 6.78 6.78 6.77 6.76 6.71 6.69
4.74 4.73 4.71 4.70 4.51
2.92 2.89 2.88 2.85 2.78 2.78 2.78 2.77 2.74 2.74 2.73 2.73 2.70 2.68 2.66 2.64
1.28 1.26 1.24
O
N
H
Et
0.87 2.84 1.84 0.92 0.96 0.95 0.94 1.00 1.00 1.94 2.82
f1 (ppm)


193.58
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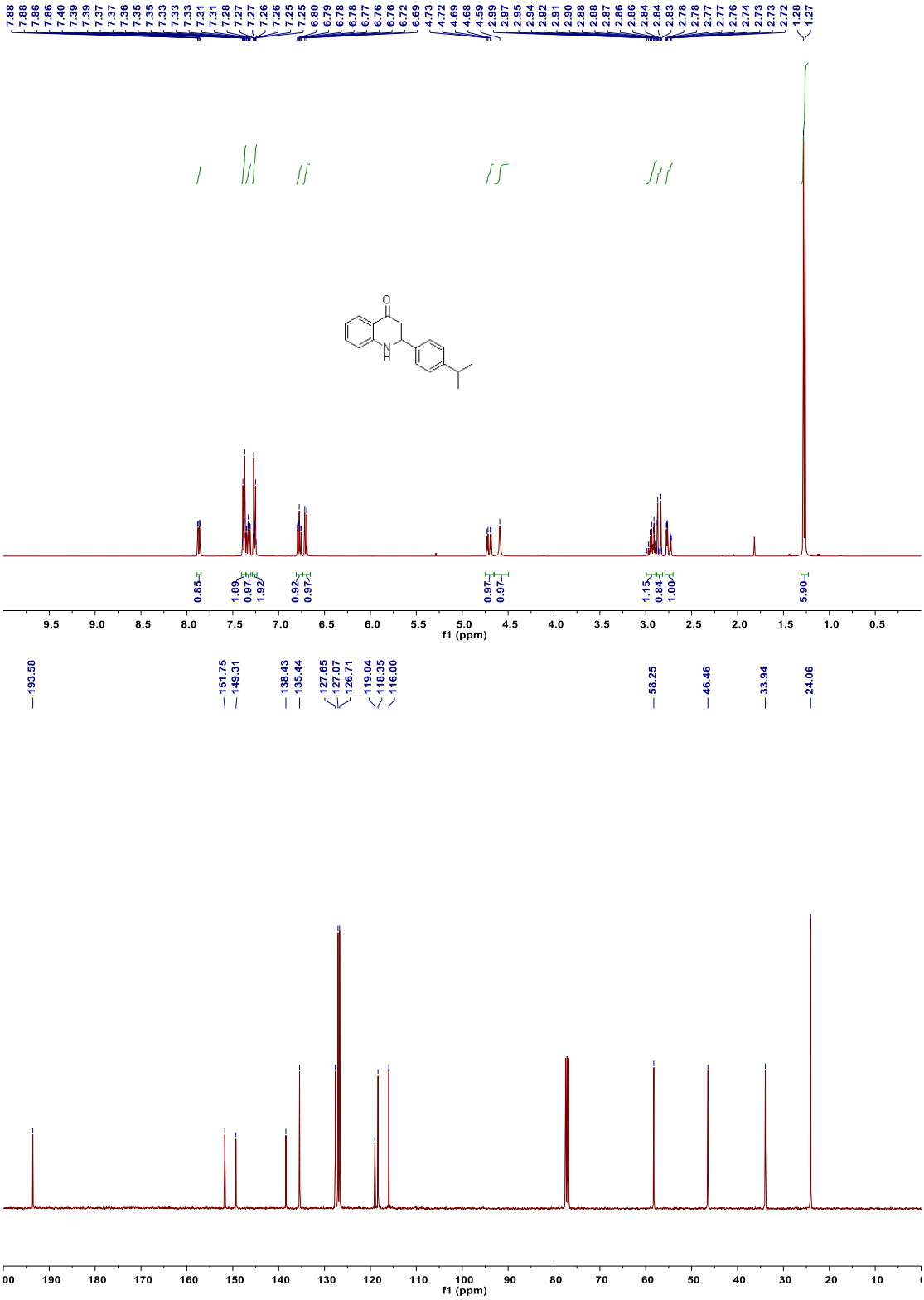
144.77
138.37
135.48
128.56
127.73
126.75
119.13
118.47
116.01
58.36
46.57
28.69
15.70
f1 (ppm)

Compound **1e**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7.88
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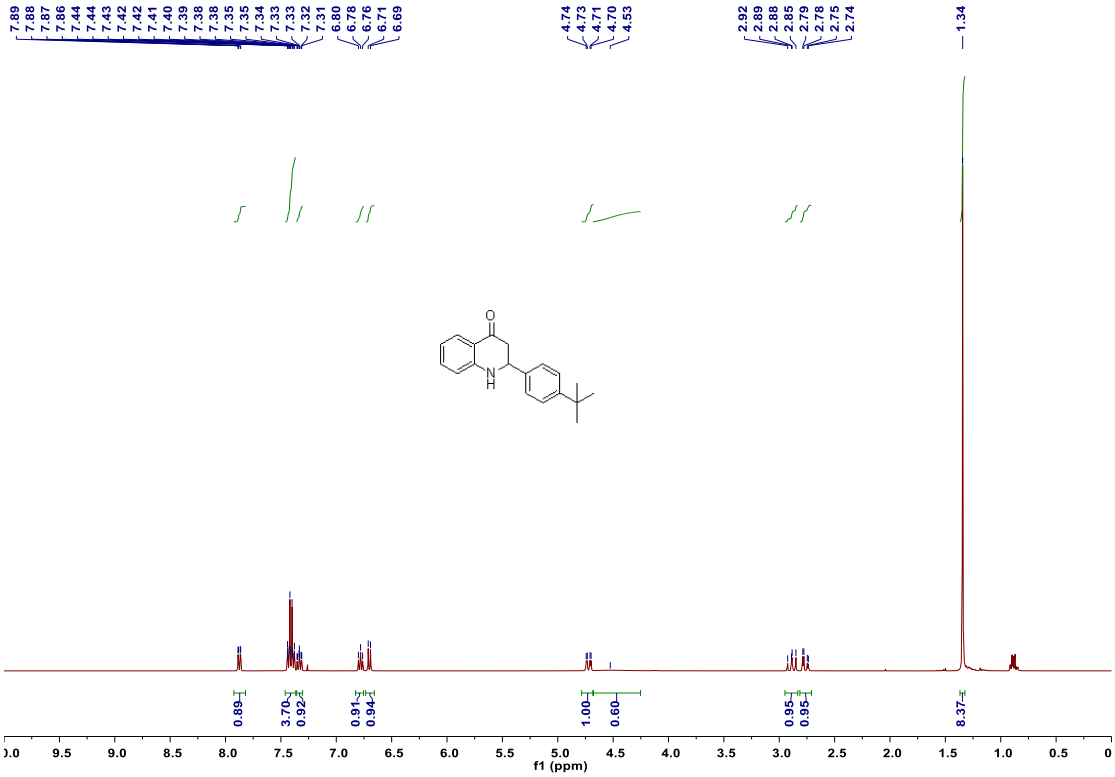
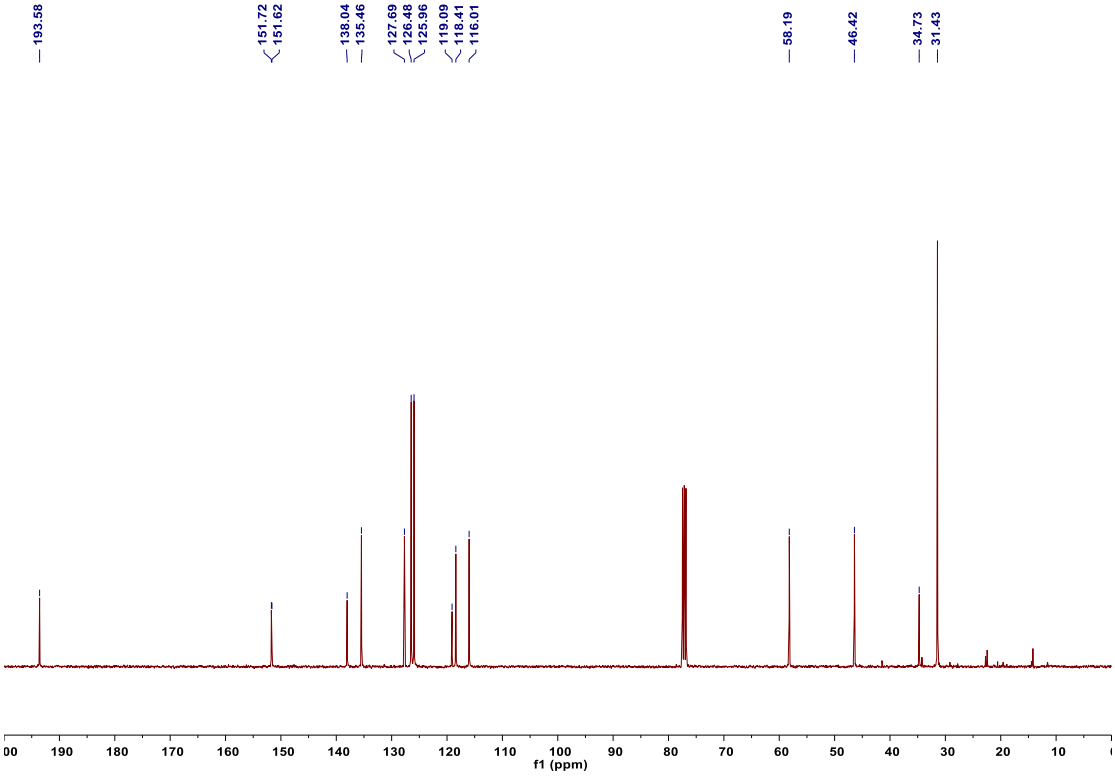
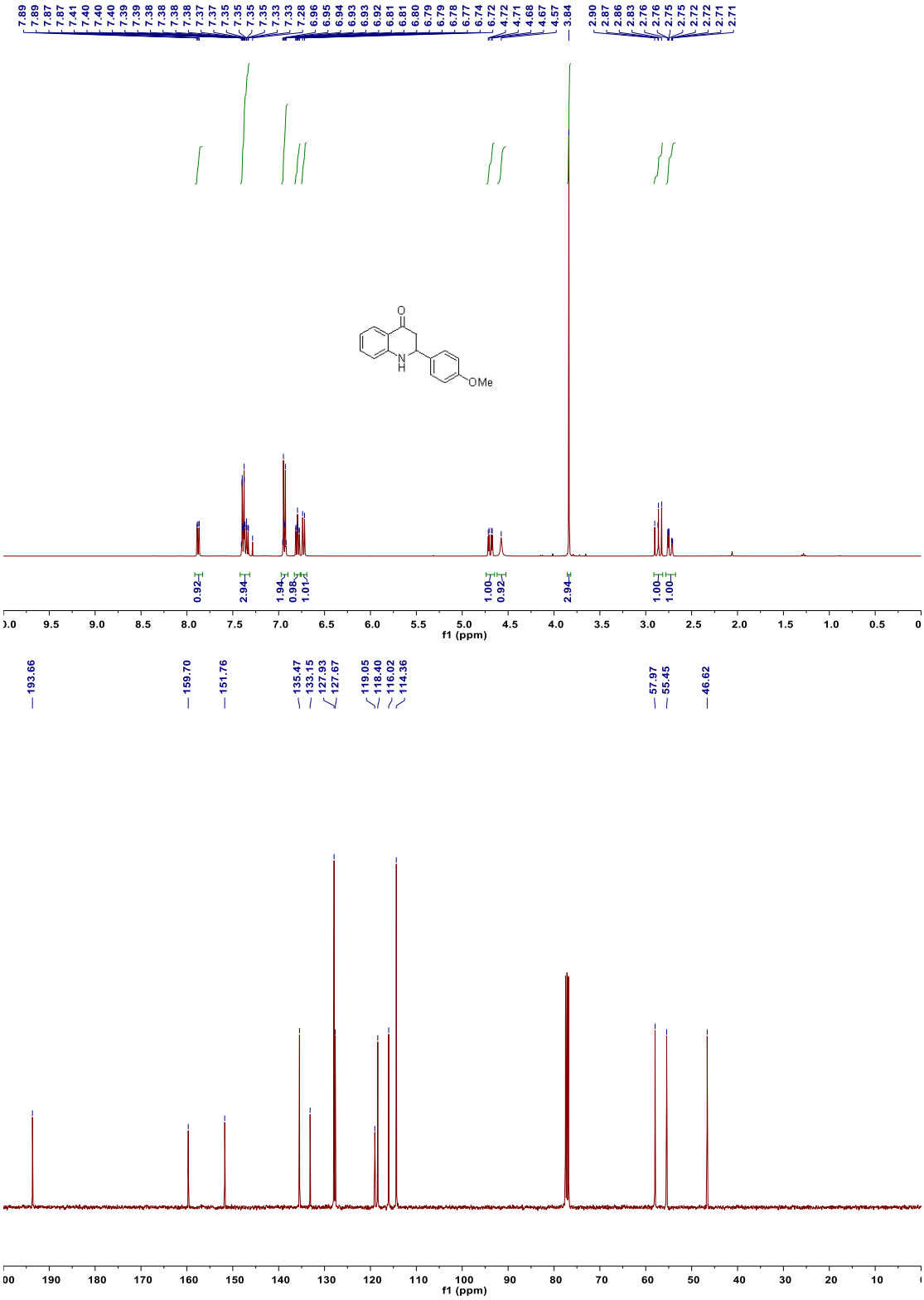
7.86
7.40
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.33
7.31
7.31
7.28
7.27
7.27
7.26
7.26
7.25
7.25
6.80
6.79
6.78
6.78
6.77
6.76
6.76
6.72
6.69
4.73
4.72
4.69
4.68
4.59
2.99
2.97
2.95
2.94
2.92
2.91
2.90
2.88
2.88
2.87
2.86
2.86
2.84
2.84
2.83
2.78
2.78
2.77
2.77
2.76
2.74
2.73
2.73
2.72
1.28
1.27
O
N
H
0.85
1.89
0.97
1.92
0.92
0.97
0.97
0.97
1.15
0.84
1.00
5.90
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
193.58
151.75
149.31
138.43
135.44
127.65
127.07
126.71
119.04
118.35
116.00
58.25
46.46
33.94
24.06
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Compound **1f**

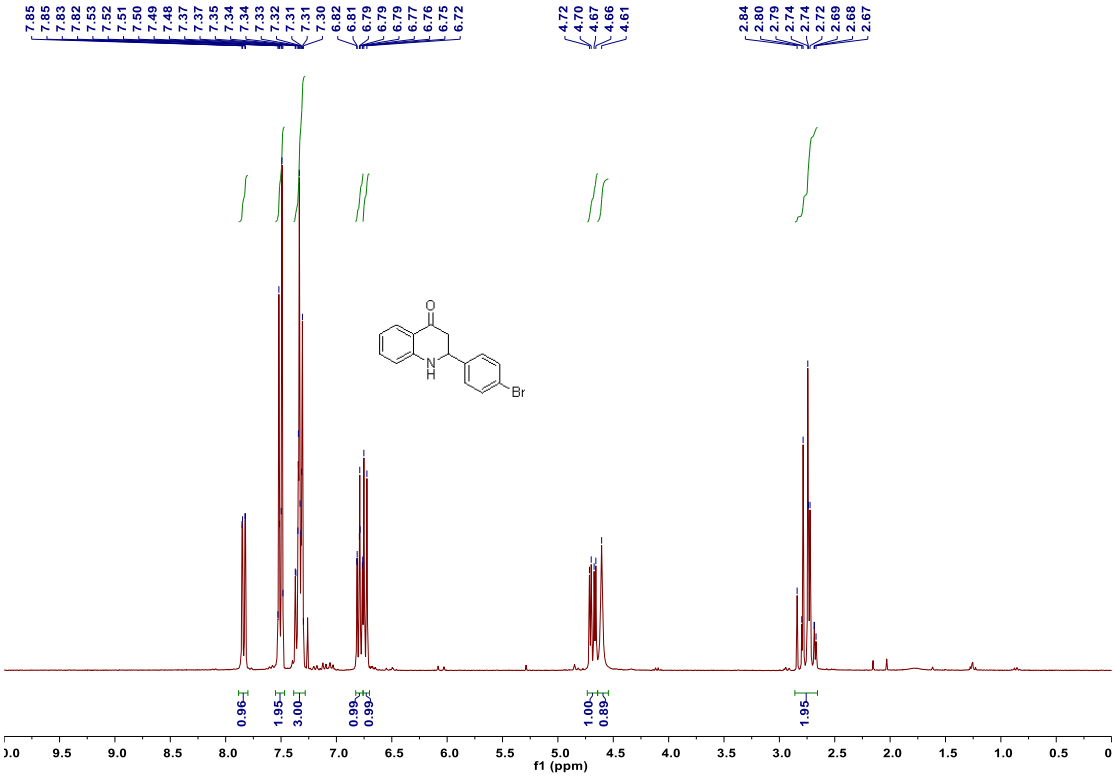

7.89
7.88
7.87
7.86
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.38
7.35
7.35
7.34
7.33
7.33
7.32
7.31
6.80
6.78
6.76
6.71
6.69
4.74
4.73
4.71
4.70
4.53
2.92
2.89
2.88
2.85
2.79
2.78
2.75
2.74
1.34
O
N
H
0.89
3.70
0.92
0.91
0.94
1.00
0.60
0.95
0.95
8.37
f1 (ppm)

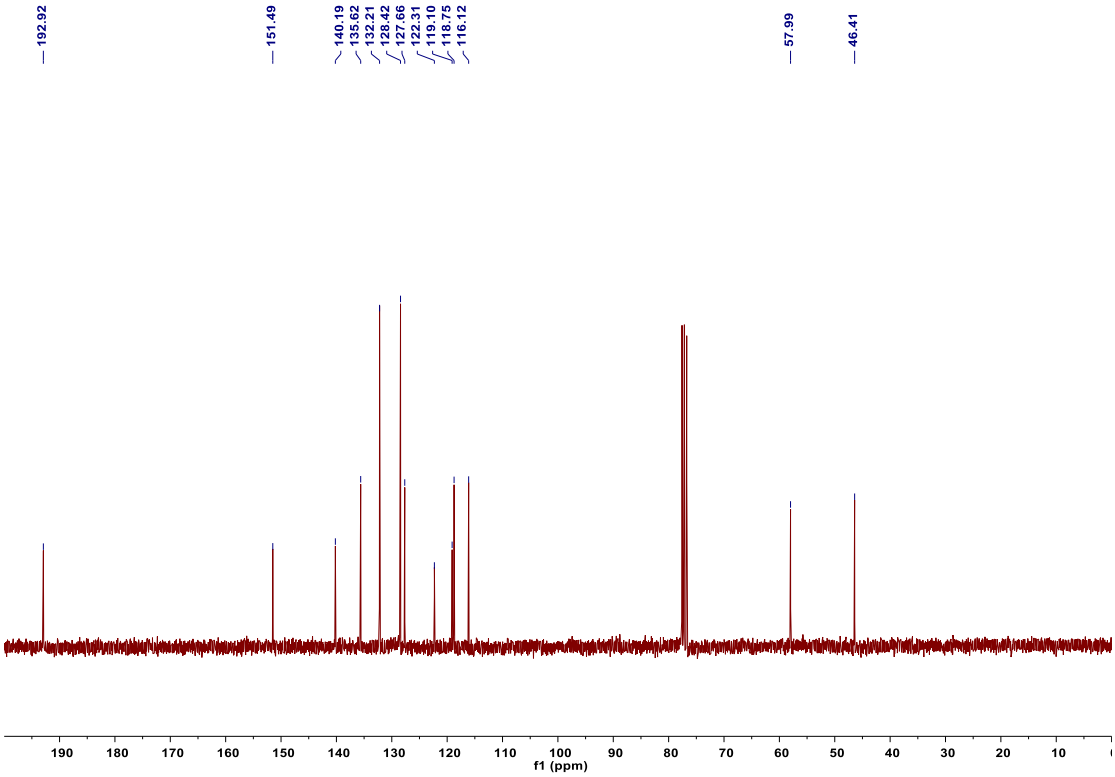

193.58
151.72
151.62
138.04
135.46
127.69
126.48
125.96
119.09
118.41
116.01
58.19
46.42
34.73
31.43
f1 (ppm)

Compound **1g**

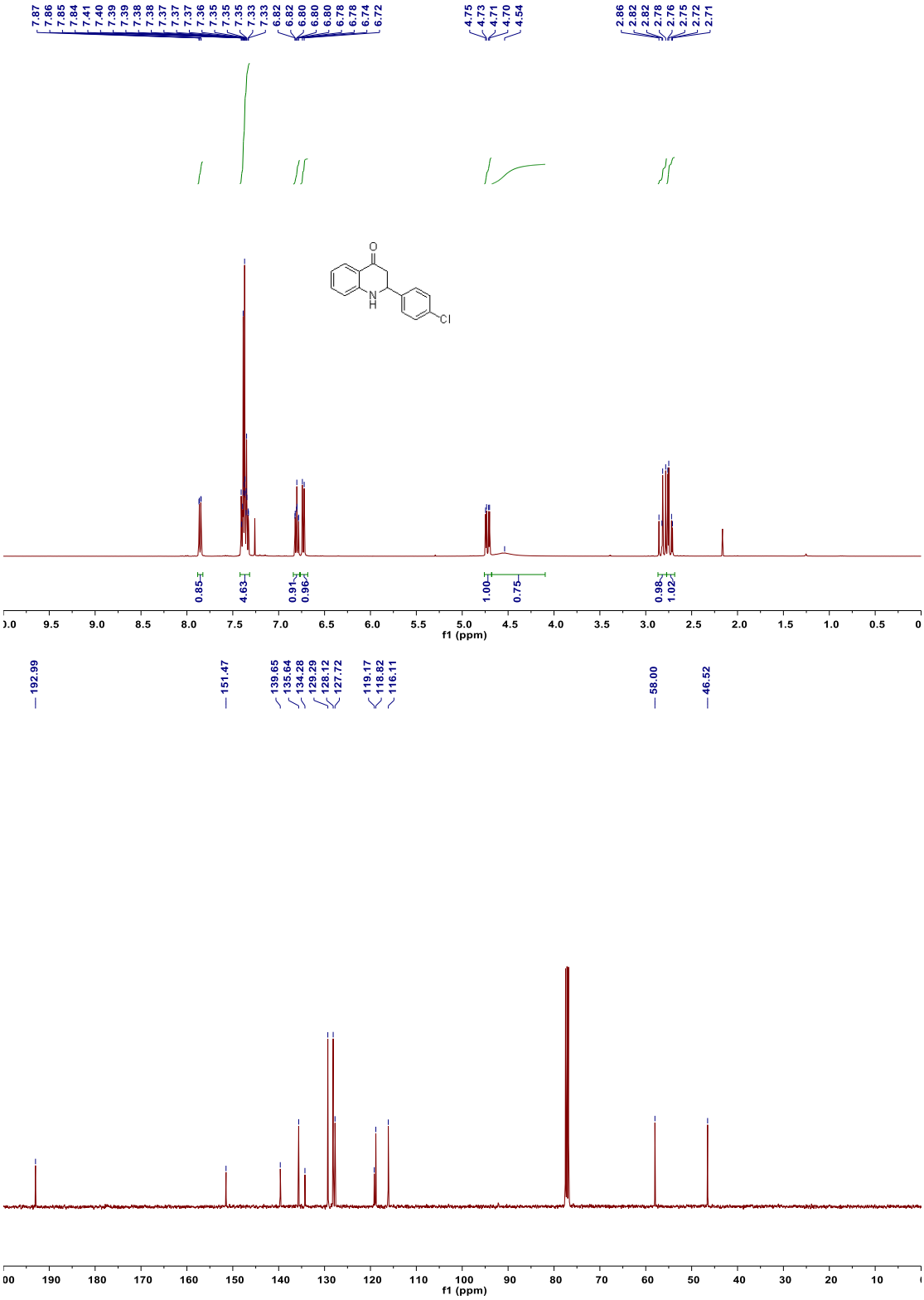

7.89 7.89 7.87 7.87 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.35 7.35 7.35 7.33 7.33 7.28 6.96 6.95 6.94 6.93 6.92 6.81 6.81 6.80 6.79 6.79 6.78 6.77 6.74 6.72 4.72 4.71 4.68 4.67 4.57 3.84 2.90 2.87 2.86 2.83 2.76 2.76 2.75 2.75 2.72 2.72 2.71 2.71
O
N
H
OMe
0.92 2.94 1.94 0.98 1.01 1.00 0.92 2.94 1.00 1.00
f1 (ppm)
193.66 159.70 151.76 135.47 133.15 127.93 127.67 119.05 118.40 116.02 114.36 57.97 55.45 46.62
f1 (ppm)

Compound **1h**


7.85
7.85
7.83
7.82
7.53
7.52
7.51
7.50
7.49
7.48
7.37
7.37
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
6.82
6.81
6.79
6.79
6.79
6.77
6.76
6.75
6.72
4.72
4.70
4.67
4.66
4.61
2.84
2.80
2.79
2.74
2.74
2.72
2.69
2.68
2.67
O
N
H
Br
0.96
1.95
3.00
0.99
0.99
1.00
0.89
1.95
f1 (ppm)


192.92
151.49
140.19
135.62
132.21
128.42
127.66
122.31
119.10
118.75
116.12
57.99
46.41
f1 (ppm)

Compound **1i**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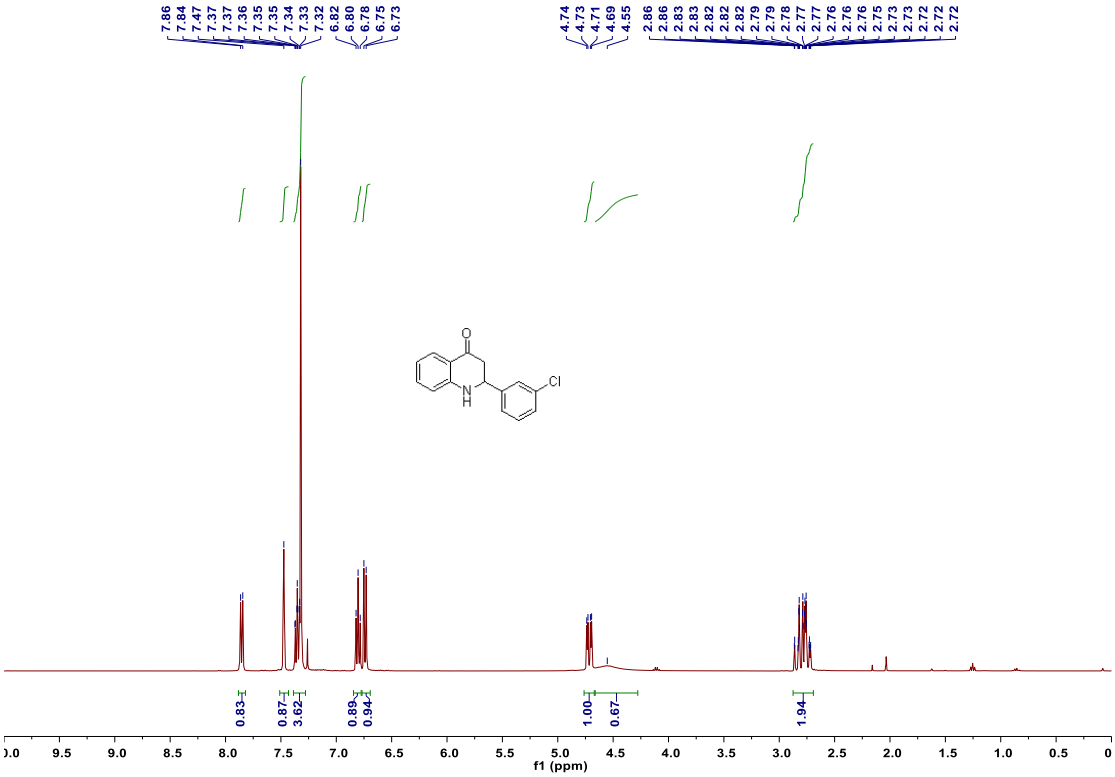
7.86
7.85
7.84
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.33
6.82
6.82
6.80
6.80
6.80
6.78
6.78
6.74
6.72
4.75
4.73
4.71
4.70
4.54
2.86
2.82
2.82
2.78
2.76
2.75
2.72
2.71
O
N
H
Cl
0.85
4.63
0.91
0.96
1.00
0.75
0.98
1.02
f1 (ppm)
192.99
151.47
139.65
135.64
134.28
129.29
128.12
127.72
119.17
118.82
116.11
58.00
46.52
f1 (ppm)

Compound **1j**


7.86
7.84
7.47
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
6.82
6.80
6.78
6.75
6.73
4.74
4.73
4.71
4.69
4.55
2.86
2.86
2.83
2.83
2.82
2.82
2.82
2.79
2.79
2.78
2.77
2.77
2.76
2.76
2.76
2.75
2.73
2.73
2.72
2.72
2.72
O
N
H
Cl
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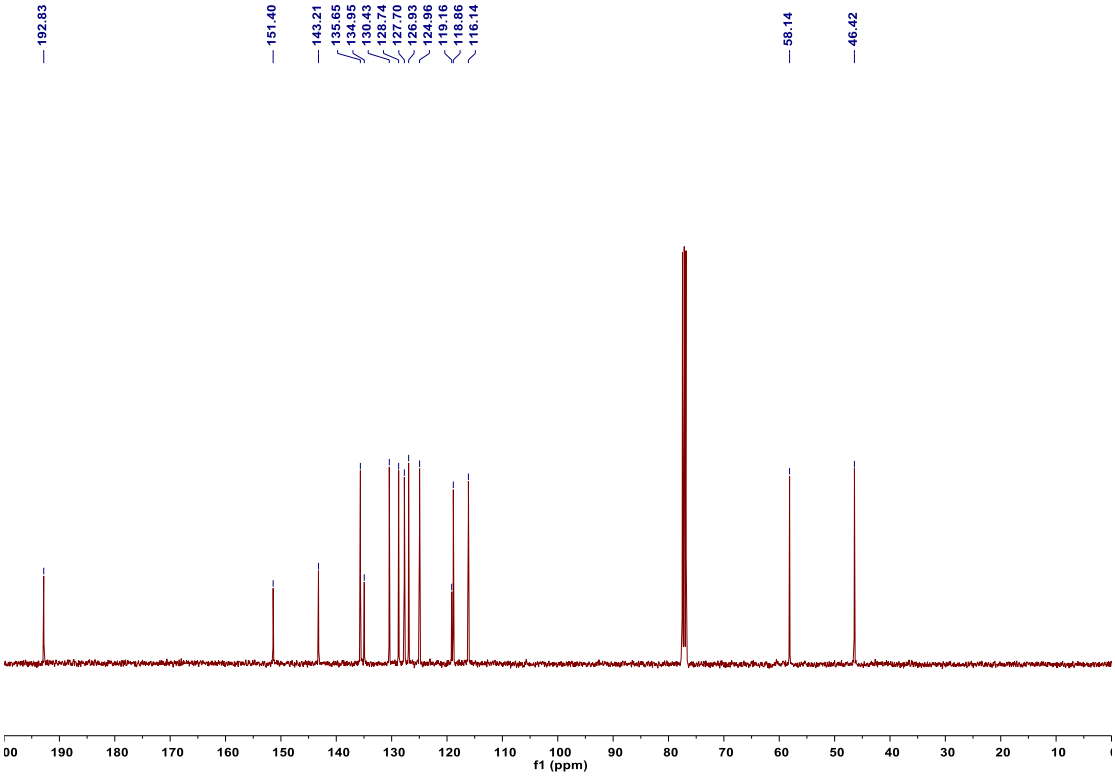
0.87
3.62
0.89
0.94
1.00
0.67
1.94
f1 (ppm)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143.21
135.65
134.95
130.43
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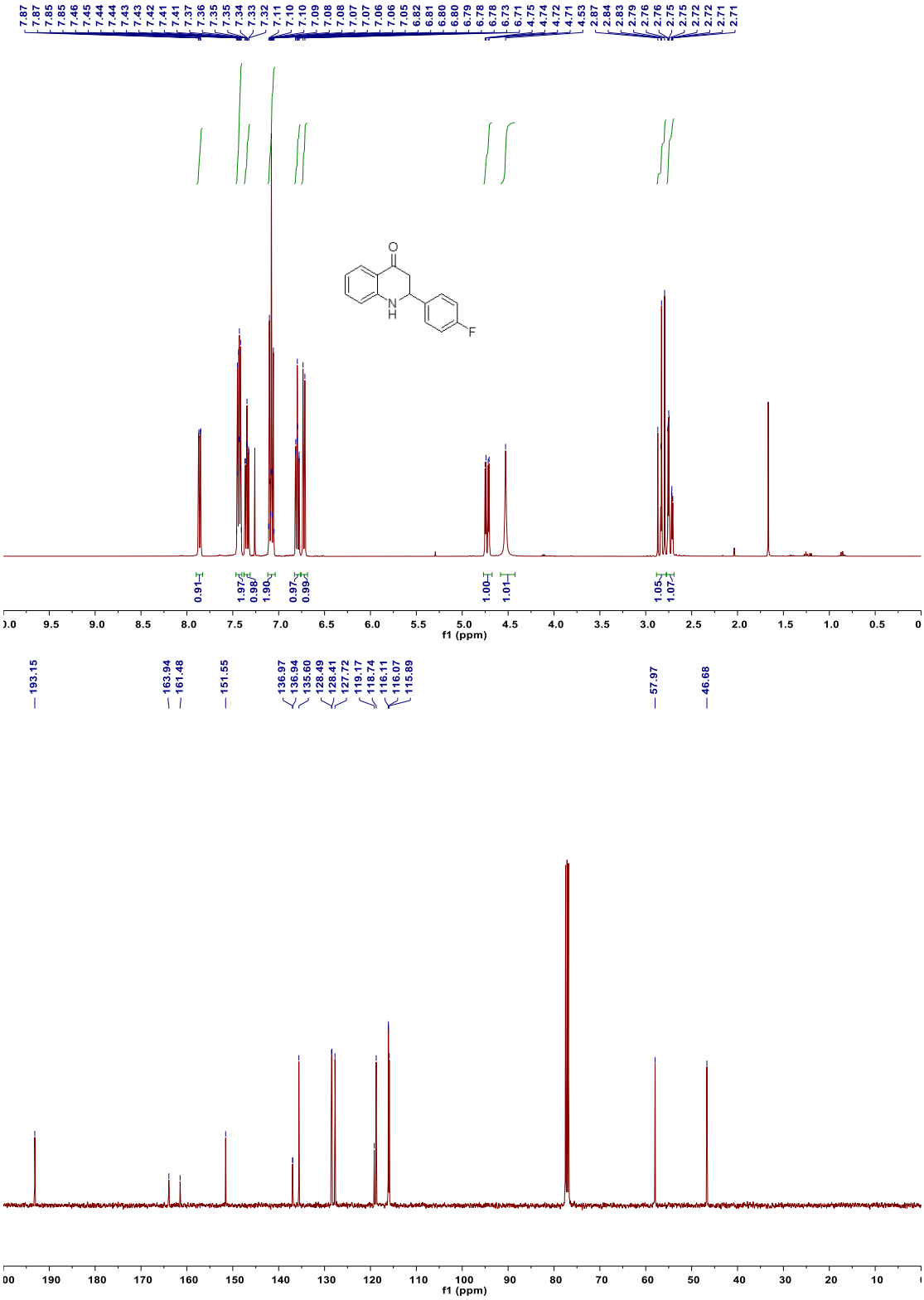
127.70
126.93
124.96
119.16
118.86
116.14
58.14
46.42
f1 (ppm)

Compound **1k**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7.87
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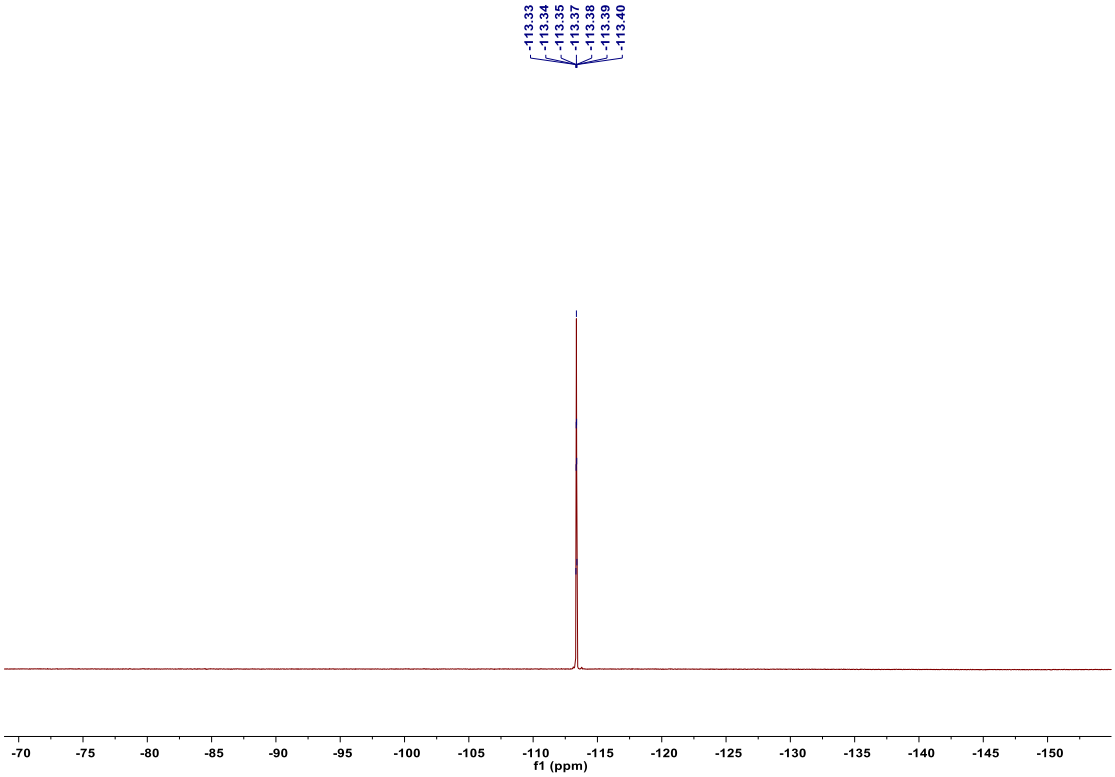
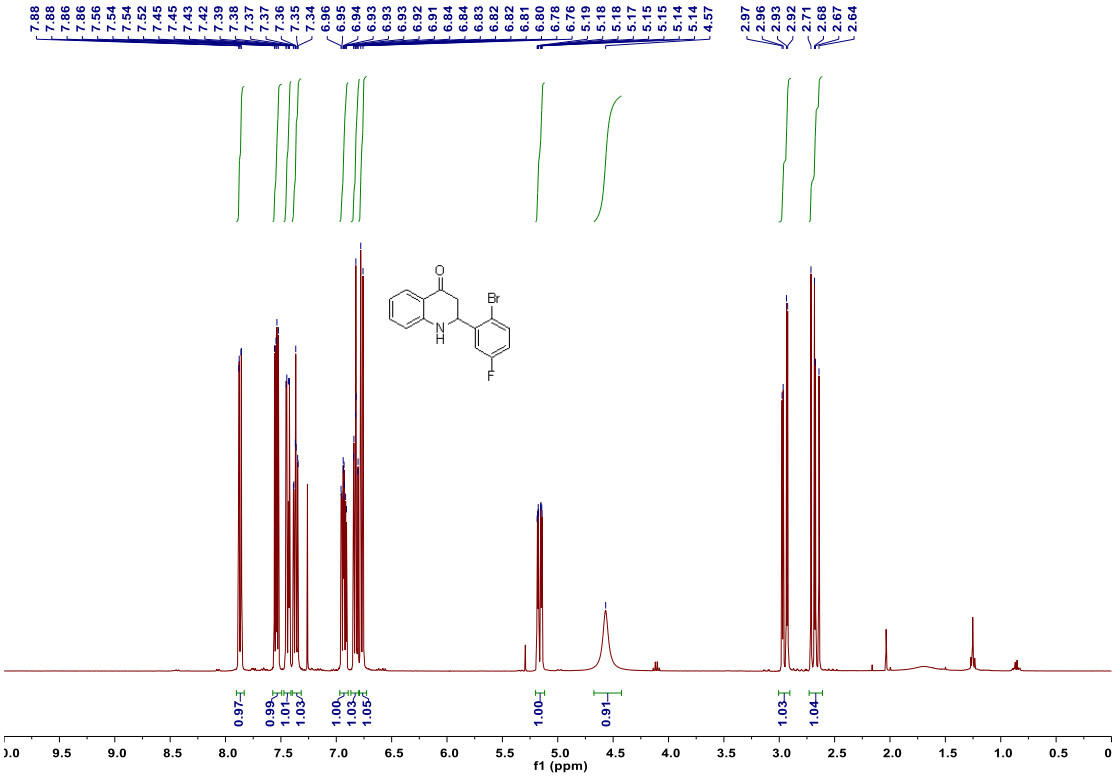
7.85
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.11
7.10
7.10
7.09
7.08
7.08
7.07
7.07
7.06
7.06
7.05
6.82
6.81
6.80
6.79
6.78
6.78
6.73
6.71
4.75
4.74
4.72
4.71
4.53
2.87
2.84
2.83
2.79
2.76
2.76
2.75
2.75
2.72
2.72
2.71
2.71
O
N
H
F
0.91
1.97
0.98
1.90
0.97
0.99
1.00
1.01
1.05
1.07
f1 (ppm)
193.15
163.94
161.48
151.55
136.97
136.94
135.60
128.49
128.41
127.72
119.17
118.74
116.11
116.07
115.89
57.97
46.68
f1 (ppm)


-113.33
-113.34
-113.35
-113.37
-113.38
-113.39
-113.40
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

Compound **1l**


7.88
7.88
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7.86
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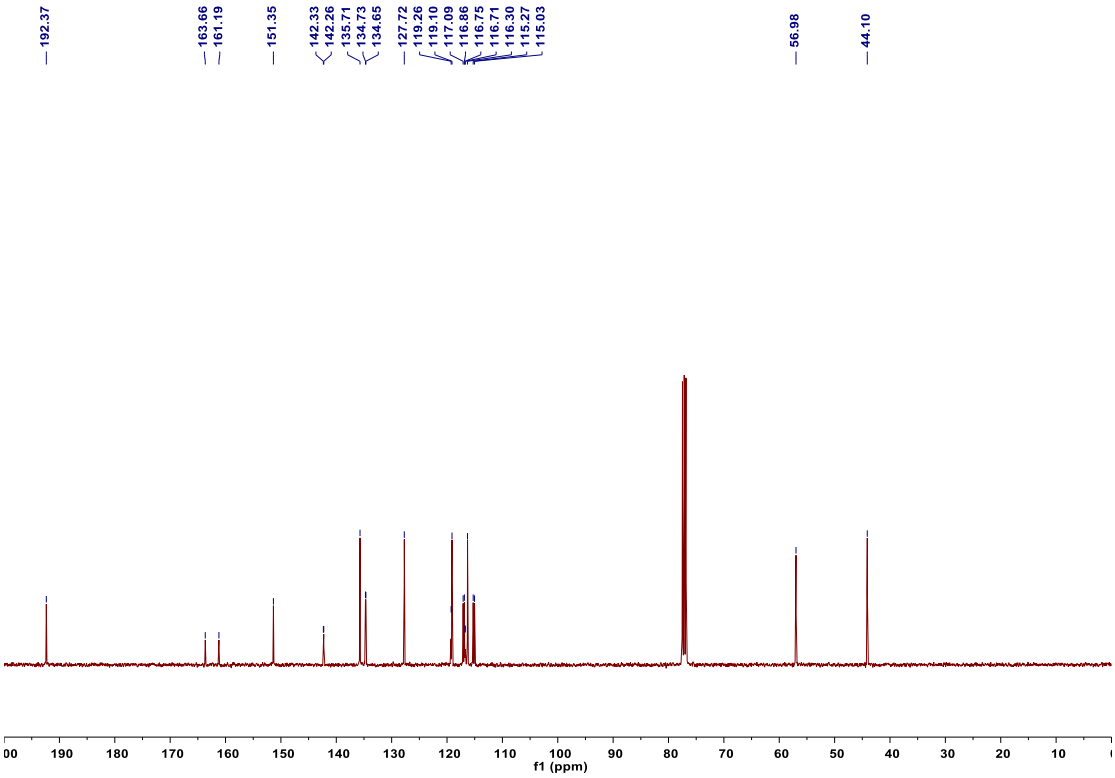
7.54
7.52
7.45
7.45
7.43
7.42
7.39
7.38
7.37
7.37
7.36
7.35
7.34
6.96
6.95
6.94
6.93
6.93
6.93
6.92
6.91
6.84
6.84
6.83
6.82
6.82
6.81
6.80
6.78
6.76
5.19
5.18
5.18
5.17
5.15
5.15
5.14
5.14
4.57
2.97
2.96
2.93
2.92
2.71
2.68
2.67
2.64
O
Br
N
H
F
0.97
0.99
1.01
1.03
1.00
1.03
1.05
1.00
0.91
1.03
1.04
f1 (ppm)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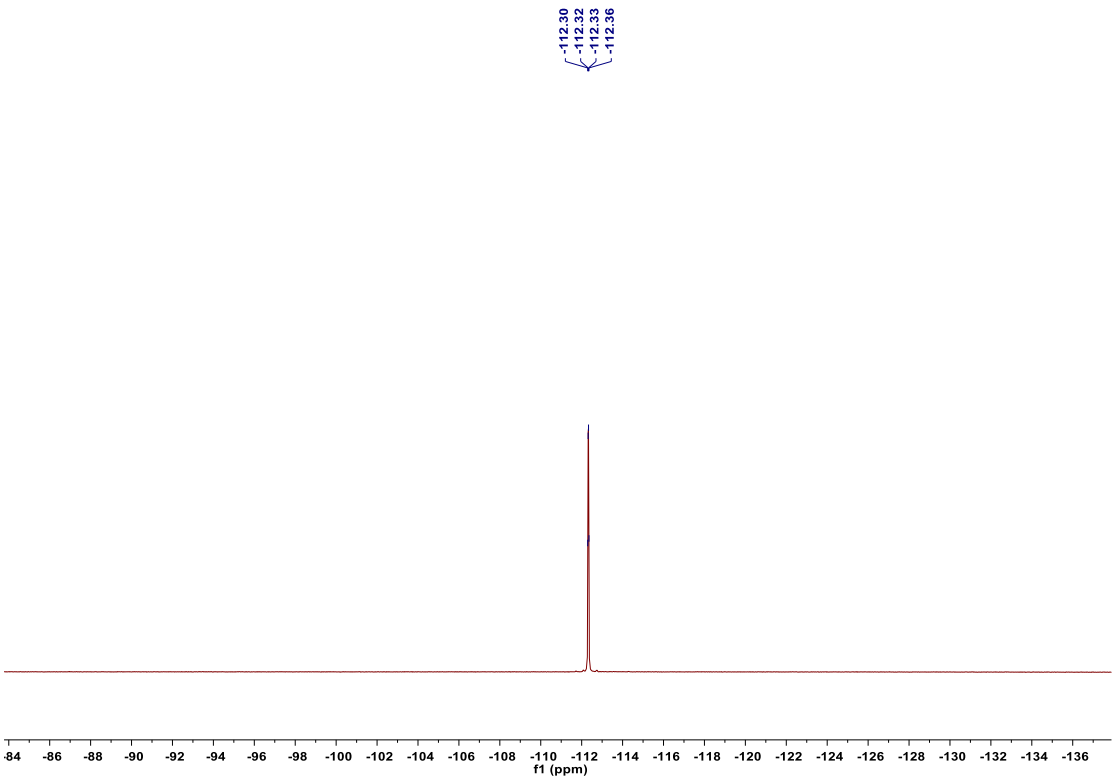
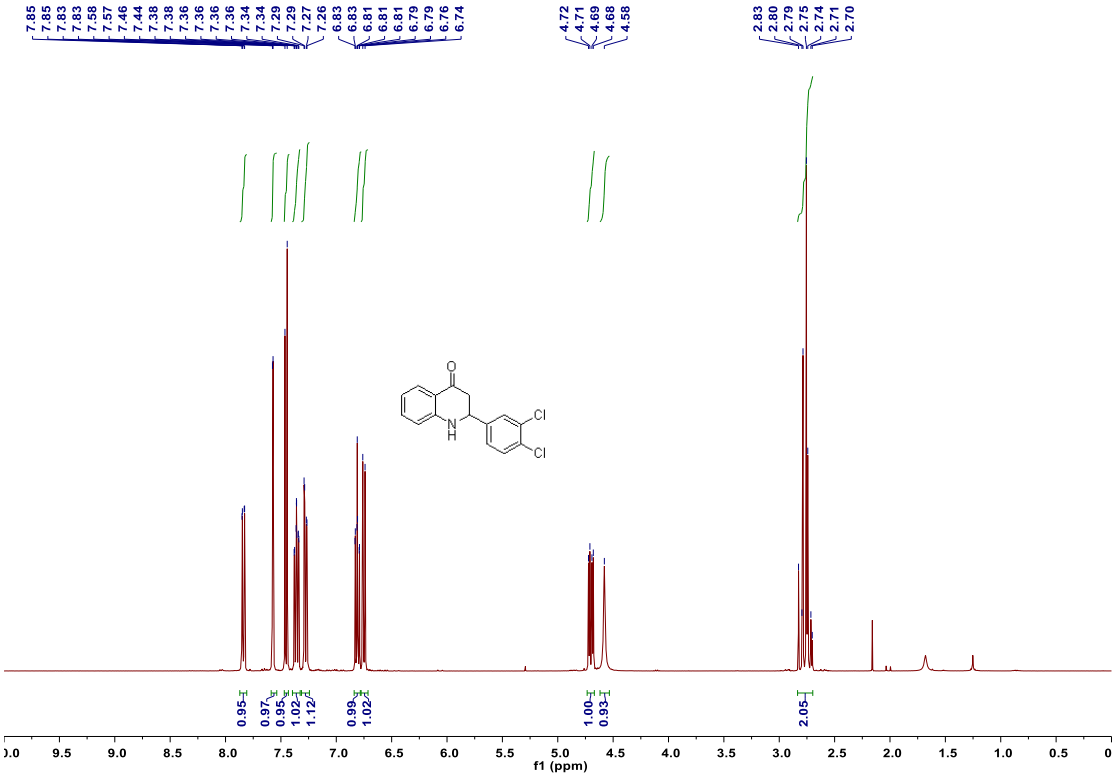
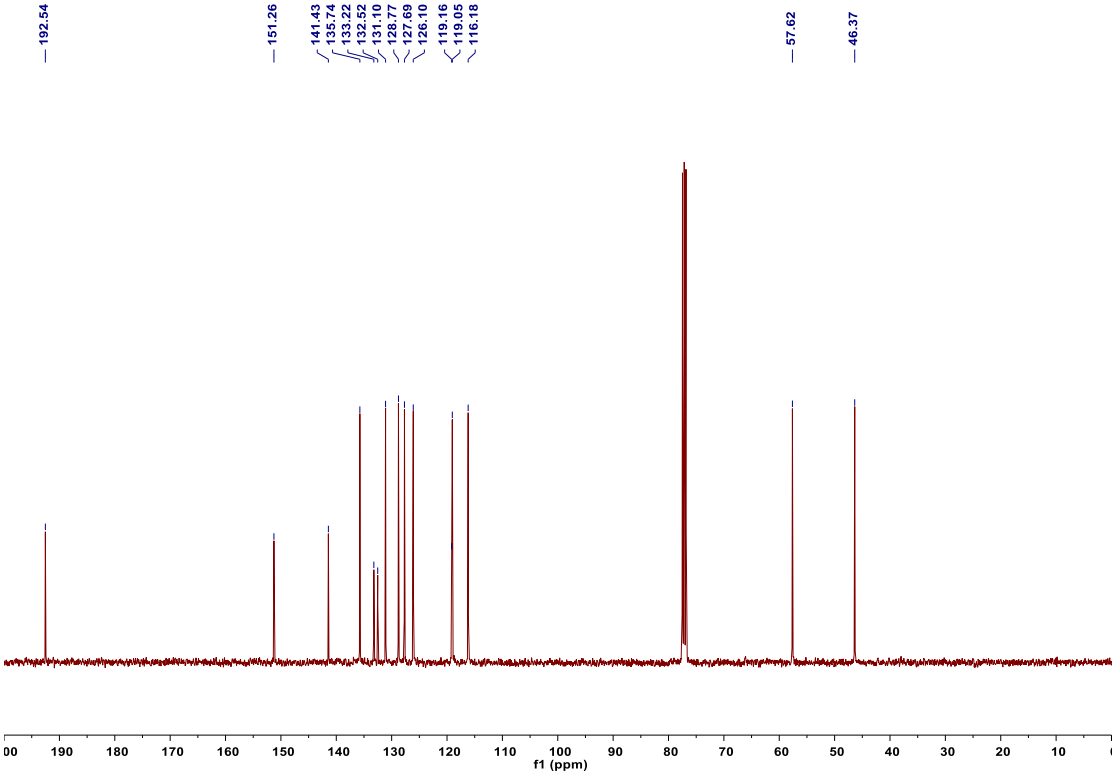
163.66
161.19
151.35
142.33
142.26
135.71
134.73
134.65
127.72
119.26
119.10
117.09
116.86
116.75
116.71
116.30
115.27
115.03
56.98
44.10
f1 (ppm)

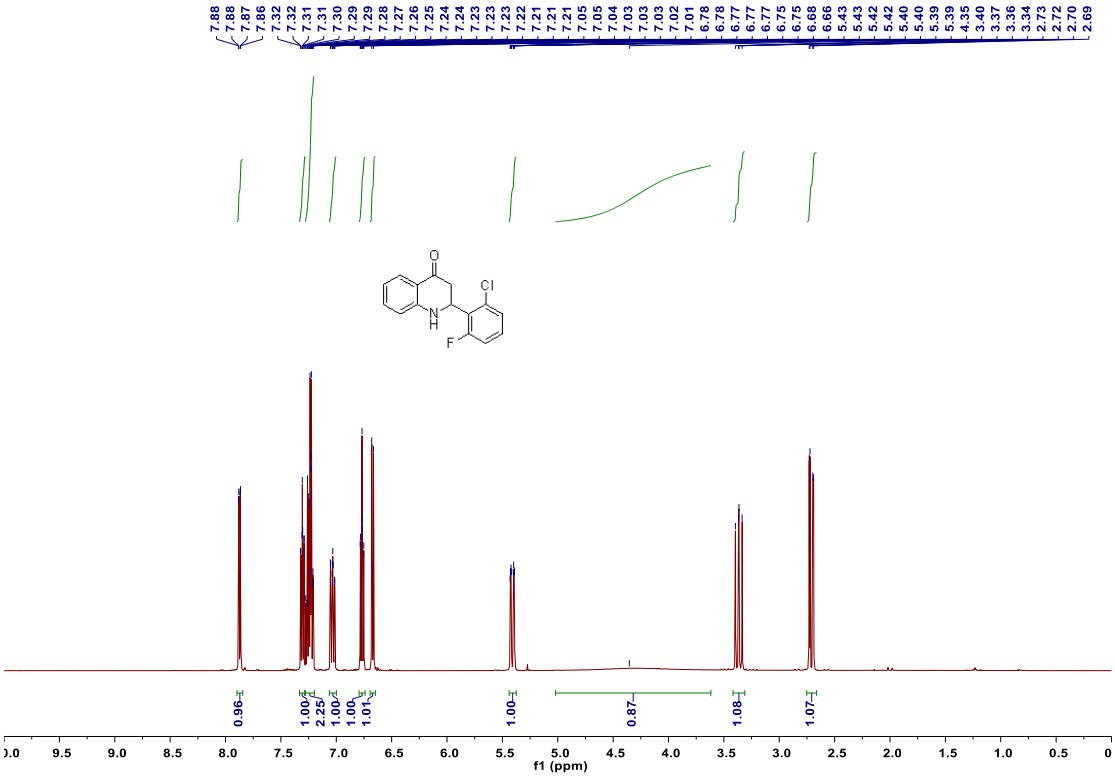

-112.30
-112.32
-112.33
-112.36
-84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136
f1 (ppm)

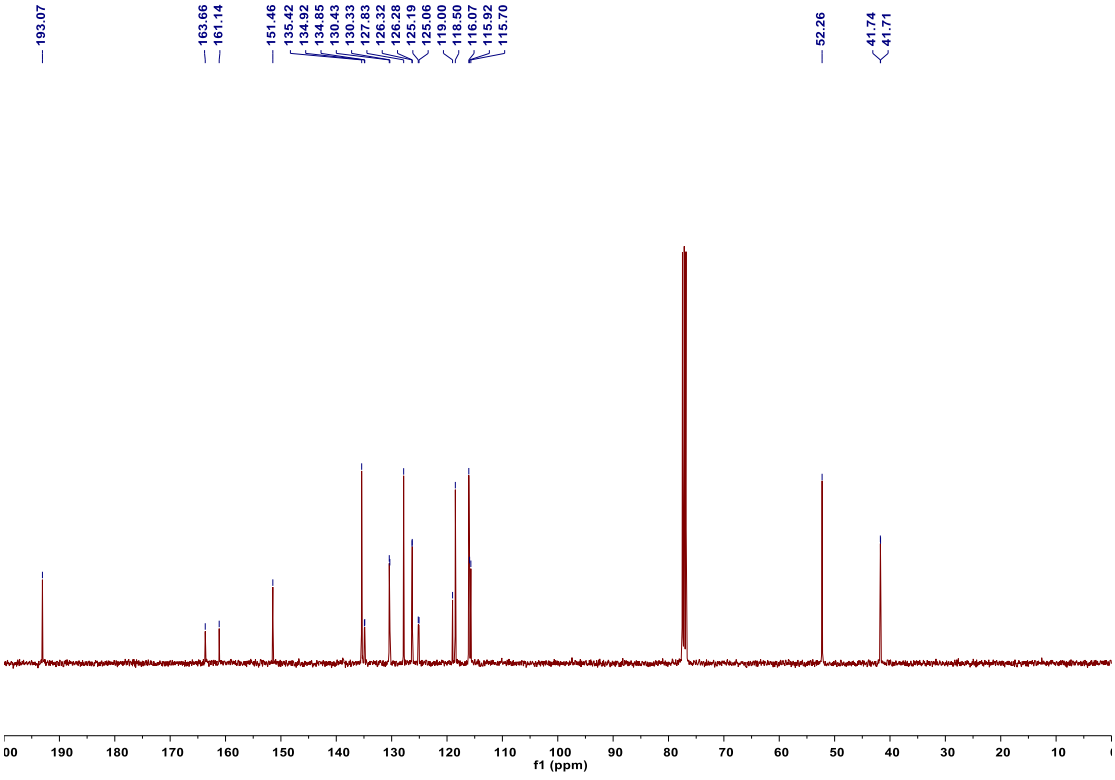
Compound **1m**

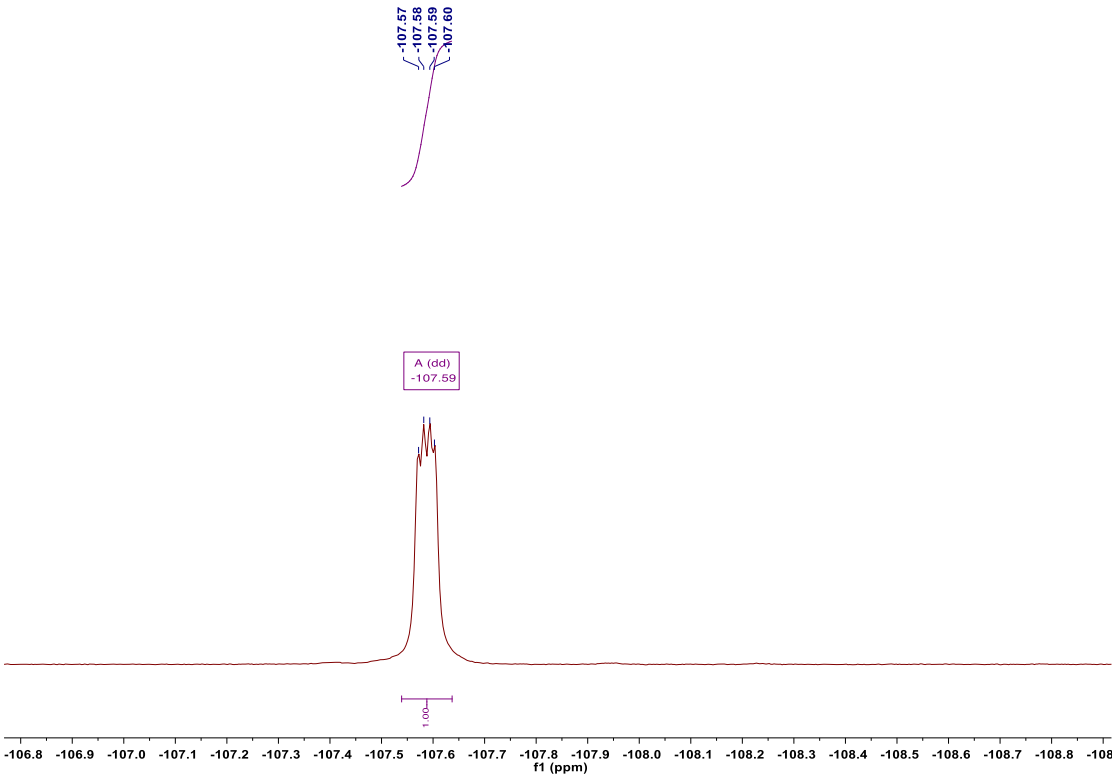

7.85
7.85
7.83
7.83
7.58
7.57
7.46
7.44
7.38
7.38
7.36
7.36
7.36
7.36
7.34
7.34
7.29
7.29
7.27
7.26
6.83
6.83
6.81
6.81
6.81
6.79
6.79
6.76
6.74
4.72
4.71
4.69
4.68
4.58
2.83
2.80
2.79
2.75
2.74
2.71
2.70
O
N
H
Cl
Cl
0.95
0.97
0.95
1.02
1.12
0.99
1.02
1.00
0.93
2.05
f1 (ppm)


192.54
151.26
141.43
135.74
133.22
132.52
131.10
128.77
127.69
126.10
119.16
119.05
116.18
57.62
46.37
f1 (ppm)

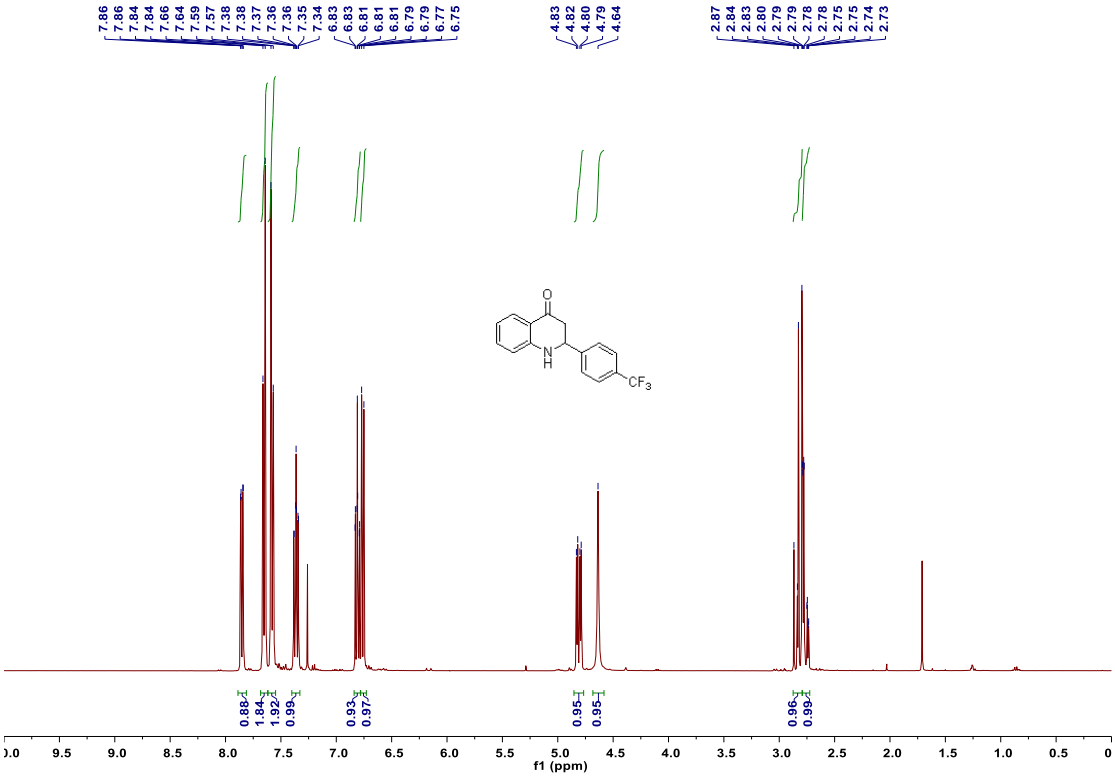
Compound **1n**

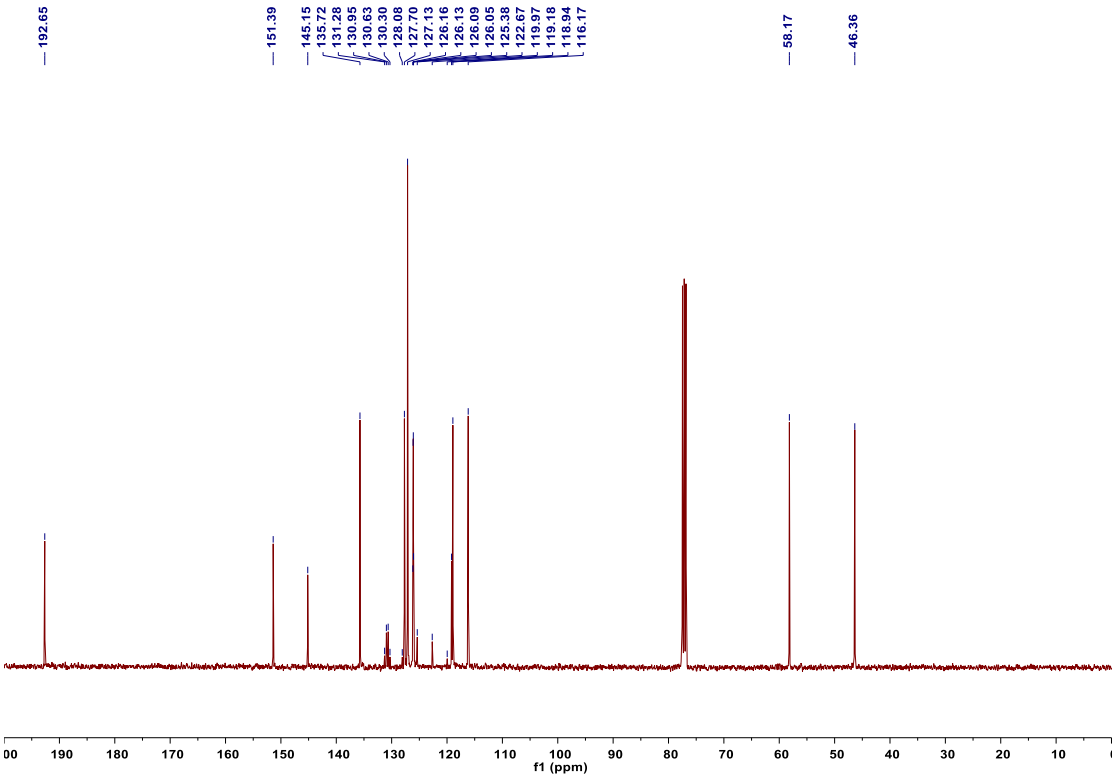

7.88 7.88 7.87 7.86 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.21 7.21 7.21 7.05 7.04 7.03 7.03 7.03 7.02 7.01 6.78 6.78 6.77 6.77 6.75 6.75 6.68 6.66 5.43 5.43 5.42 5.42 5.40 5.40 5.39 5.39 4.35 3.40 3.37 3.36 3.34 2.73 2.72 2.70 2.69
O
Cl
N
H
F
0.96 1.00 2.25 1.00 1.00 1.01 1.00 0.87 1.08 1.07
f1 (ppm)

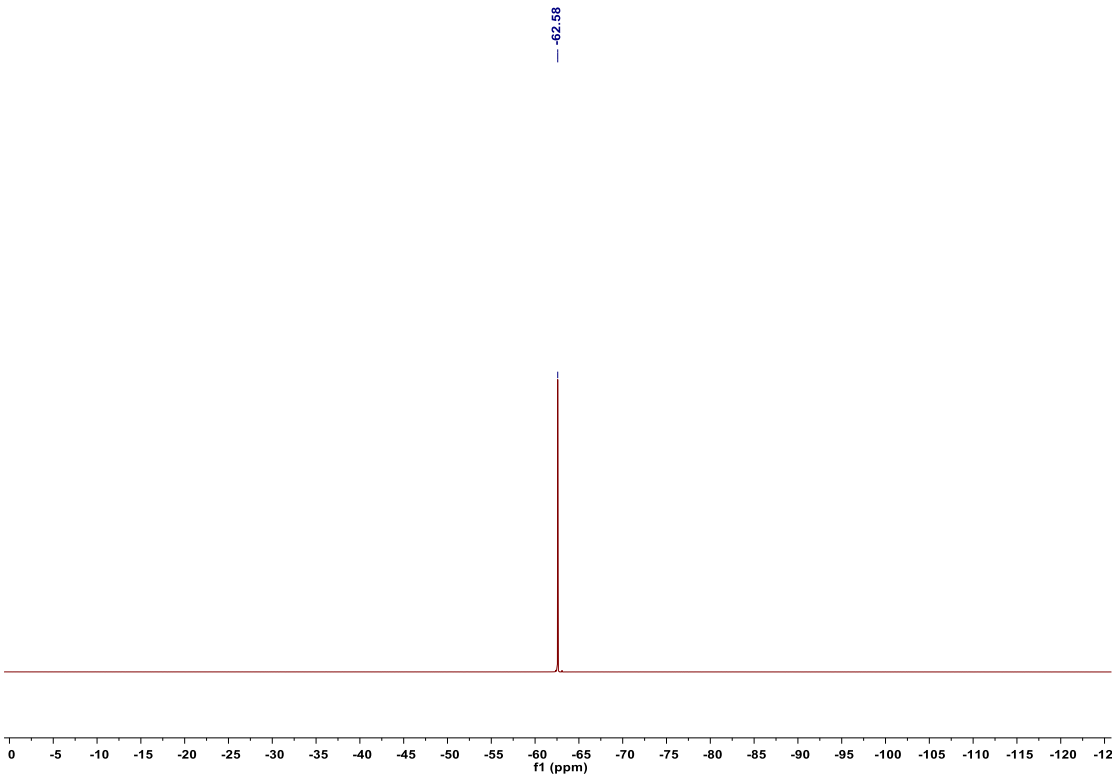

193.07
163.66 161.14
151.46 135.42 134.92 134.85 130.43 130.33 127.83 126.32 126.28 125.19 125.06 119.00 118.50 116.07 115.92 115.70
52.26
41.74 41.71
f1 (ppm)


-107.57
-107.58
-107.59
-107.60
A (dd)
-107.59
1.00
-106.8 -106.9 -107.0 -107.1 -107.2 -107.3 -107.4 -107.5 -107.6 -107.7 -107.8 -107.9 -108.0 -108.1 -108.2 -108.3 -108.4 -108.5 -108.6 -108.7 -108.8 -108
f1 (ppm)

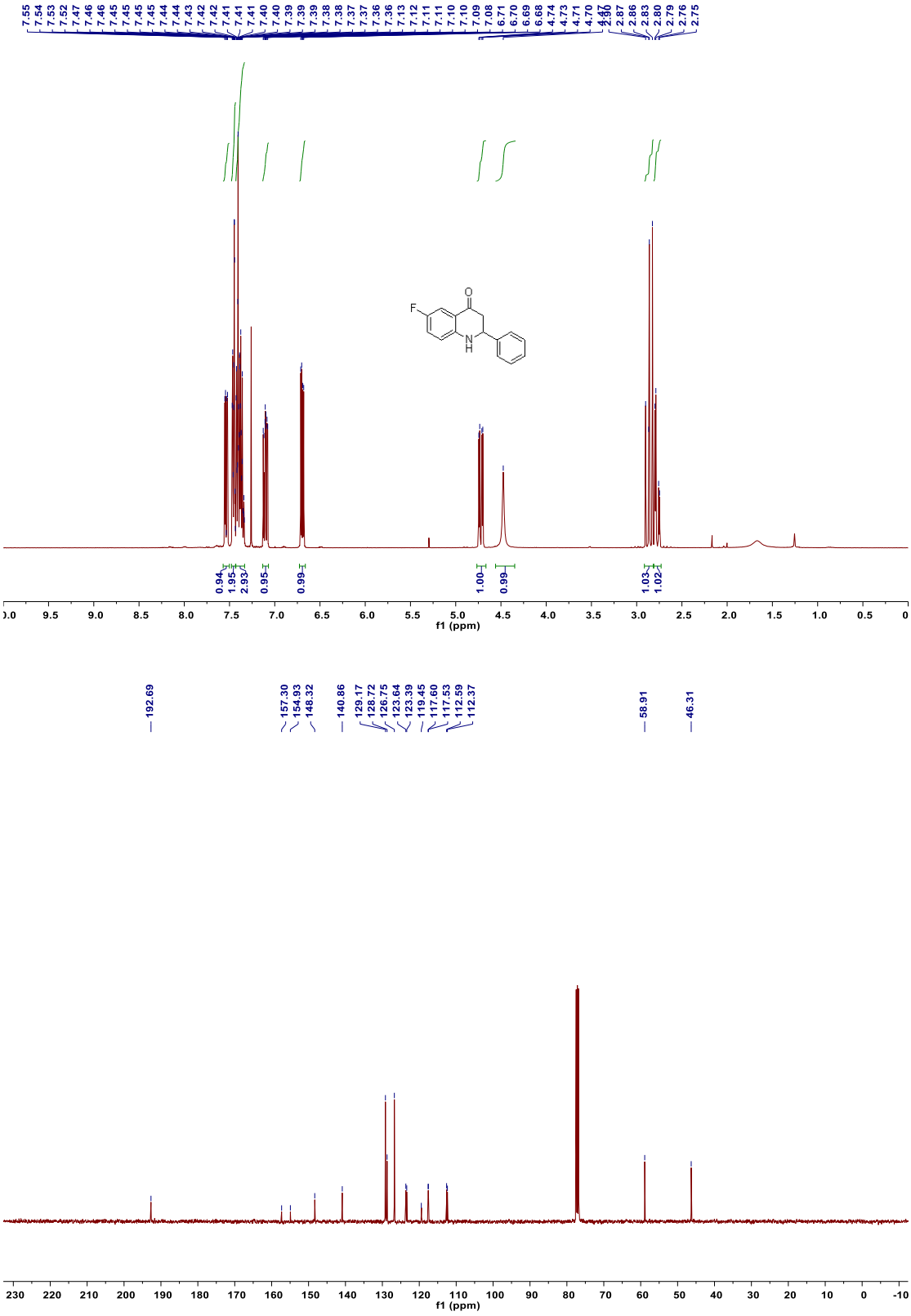
Compound **1o**

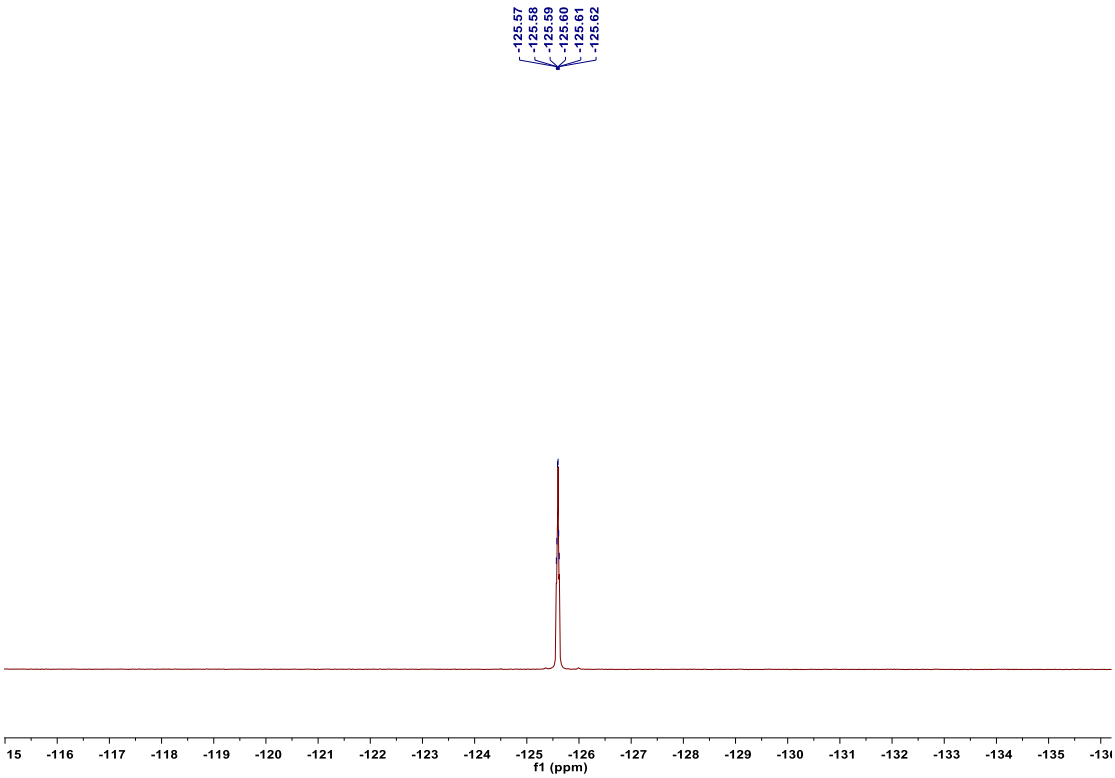

7.86
7.86
7.84
7.84
7.66
7.64
7.59
7.57
7.38
7.37
7.36
7.36
7.35
7.34
6.83
6.83
6.81
6.81
6.81
6.79
6.79
6.77
6.75
4.83
4.82
4.80
4.79
4.64
2.87
2.84
2.83
2.80
2.79
2.79
2.78
2.78
2.75
2.75
2.74
2.73
O
N
H
CF3
0.88
1.84
1.92
0.99
0.93
0.97
0.95
0.95
0.96
0.99
f1 (ppm)


192.65
151.39
145.15
135.72
131.28
130.95
130.63
130.30
128.08
127.70
127.13
126.16
126.13
126.09
126.05
125.38
122.67
119.97
119.18
118.94
116.17
58.17
46.36
f1 (ppm)

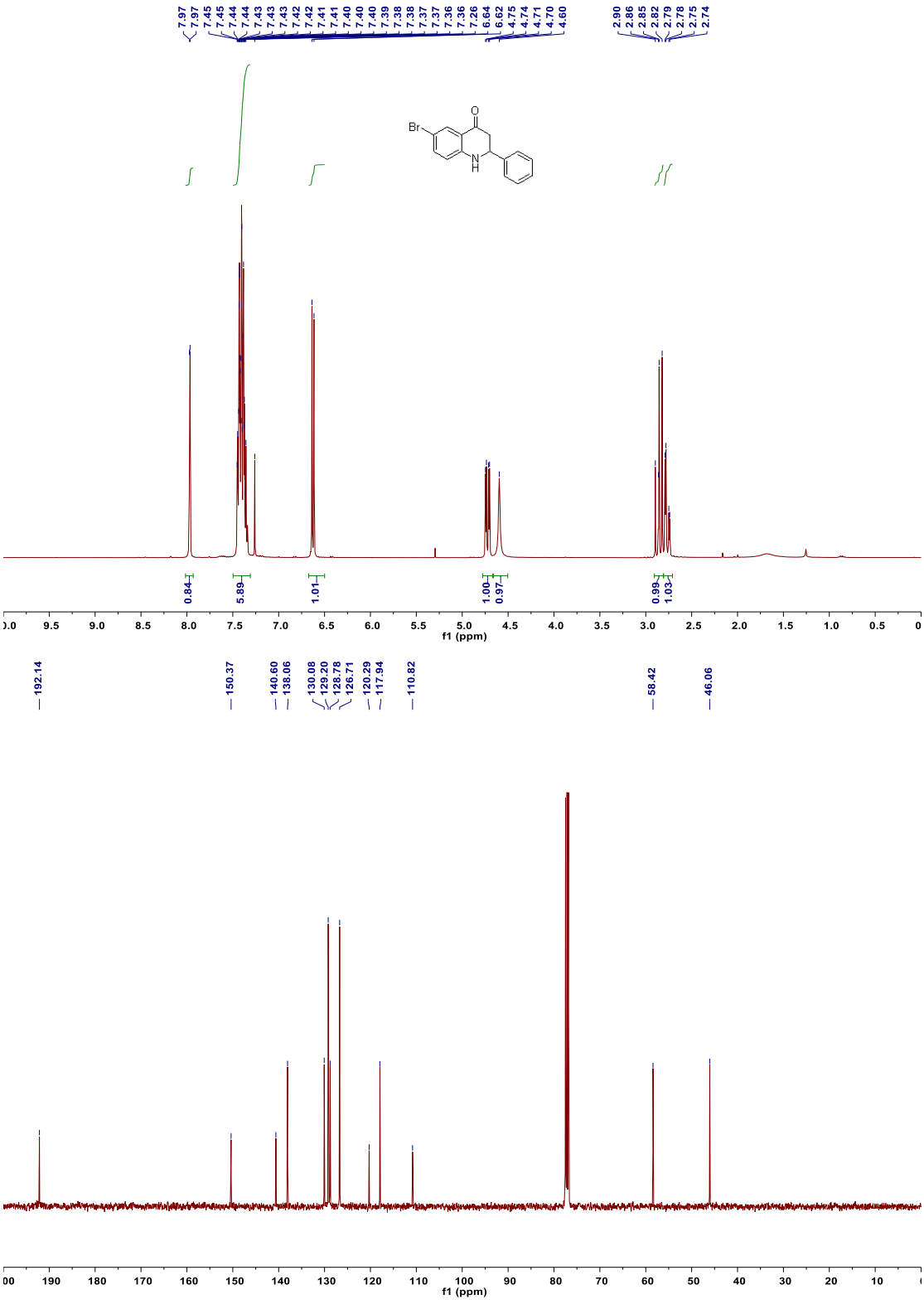

-62.58
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-12
f1 (ppm)

Compound **1p**

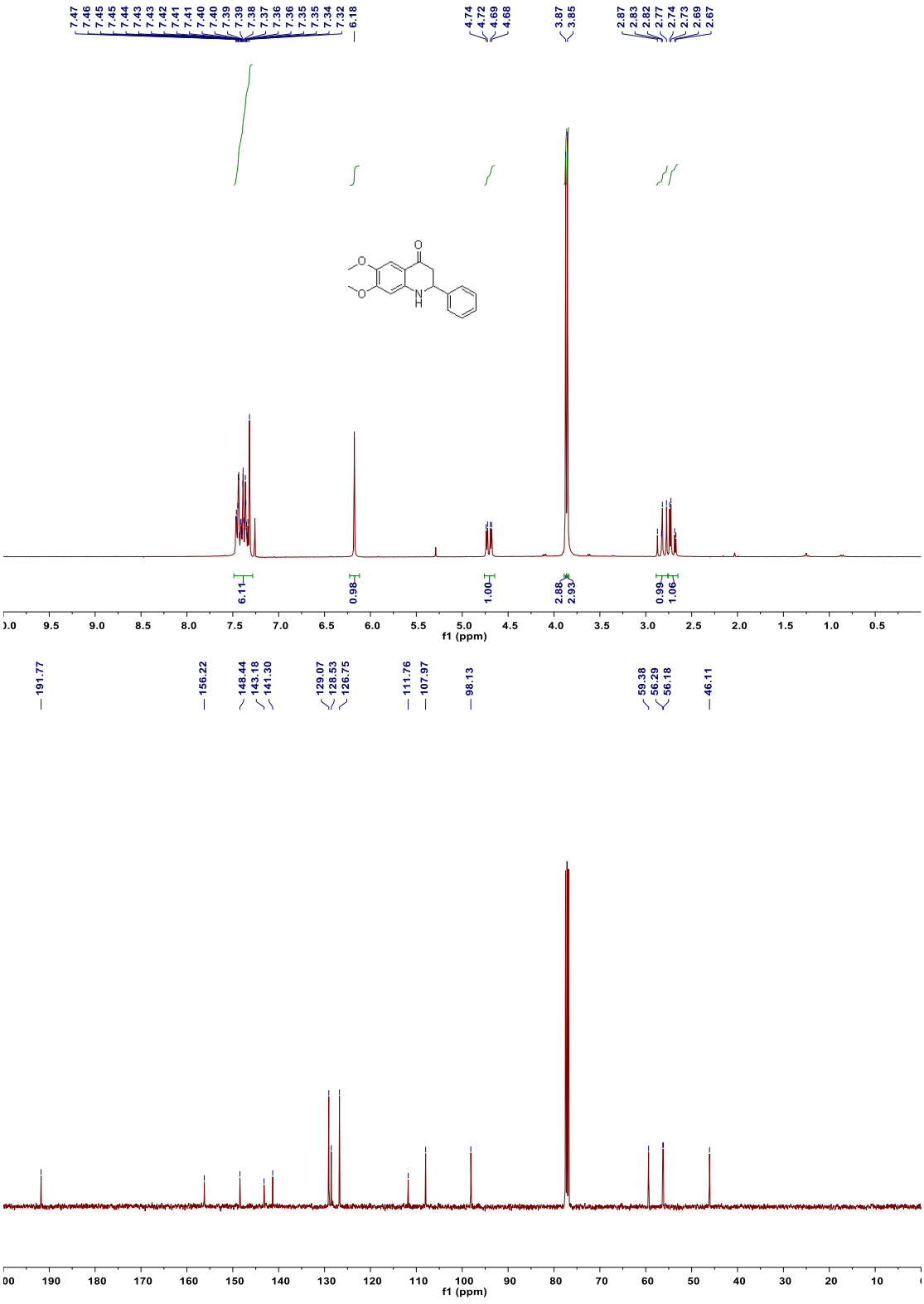

7.55 7.54 7.53 7.52 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.13 7.12 7.11 7.11 7.10 7.10 7.09 7.08 6.71 6.70 6.69 6.68 4.74 4.73 4.71 4.70 2.87 2.86 2.83 2.80 2.79 2.76 2.75
F
O
N
H
0.94 1.95 2.93 0.95 0.99 1.00 0.99 1.03 1.02
f1 (ppm)
192.69 157.30 154.93 148.32 140.86 129.17 128.72 126.75 123.64 123.39 119.45 117.60 117.53 112.59 112.37 58.91 46.31
f1 (ppm)


-125.57
-125.58
-125.59
-125.60
-125.61
-125.62
15
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
f1 (ppm)

Compound **1q**

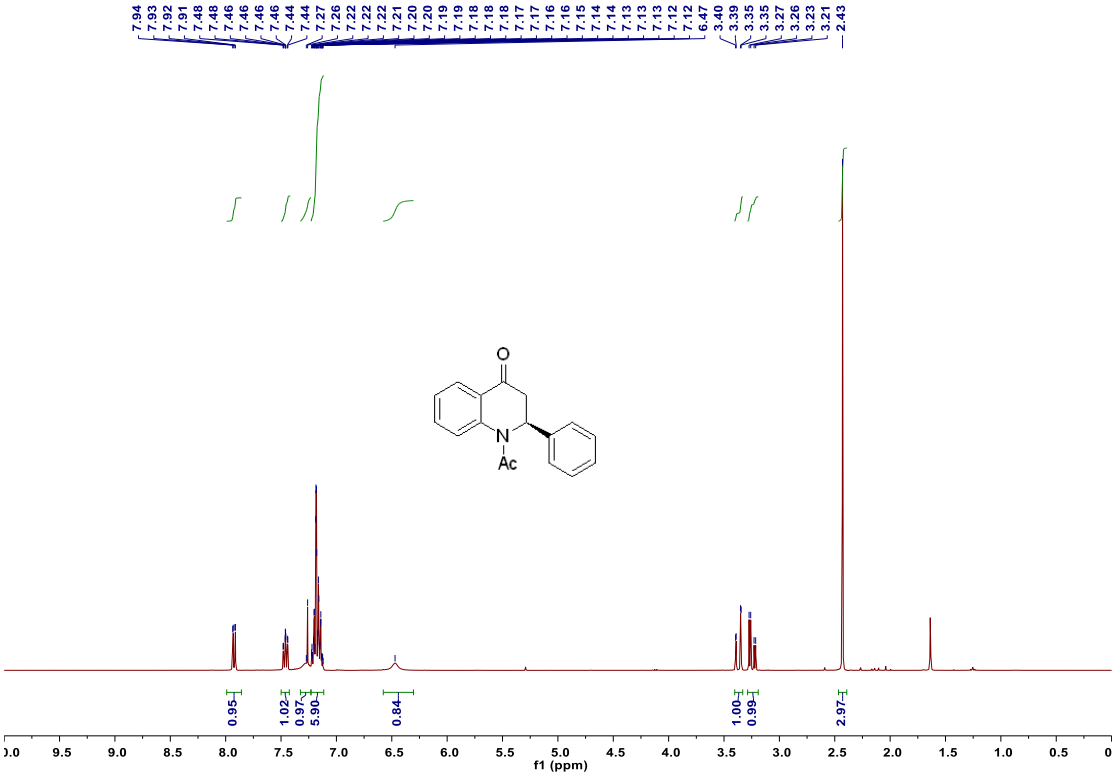

7.97
7.97
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.26
6.64
6.62
4.75
4.74
4.71
4.70
4.60
2.90
2.86
2.85
2.82
2.79
2.78
2.75
2.74
Br
O
N
H
0.84
5.89
1.01
1.00
0.97
0.99
1.03
f1 (ppm)
192.14
150.37
140.60
138.06
130.08
129.20
128.78
126.71
120.29
117.94
110.82
58.42
46.06
f1 (ppm)

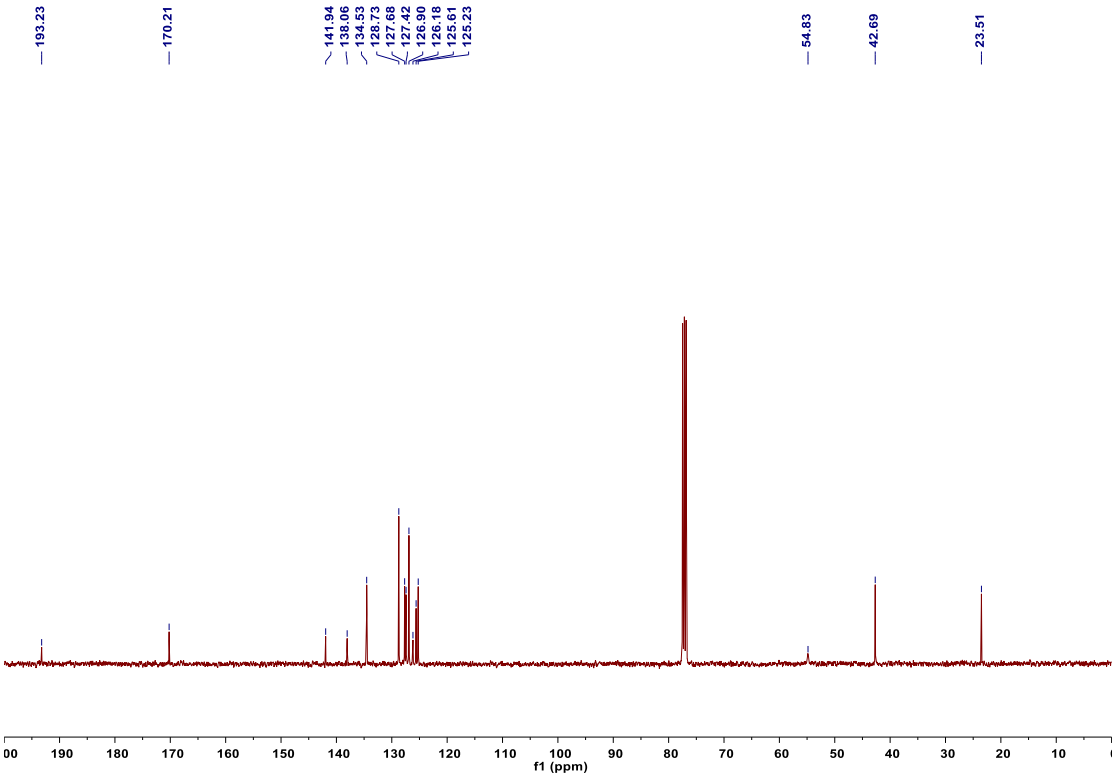
Compound **1r**


7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.32
6.18
4.74
4.72
4.69
4.68
3.87
3.85
2.87
2.83
2.82
2.77
2.74
2.73
2.69
2.67
O
O
O
N
H
6.11
0.98
1.00
2.88
2.93
0.99
1.06
f1 (ppm)
191.77
156.22
148.44
143.18
141.30
129.07
128.53
126.75
111.76
107.97
98.13
59.38
56.29
56.18
46.11
f1 (ppm)

IX. NMR spectra and SFC chromatograms of compounds (*S*)-3a-3r

Compound **(*S*)-3a**

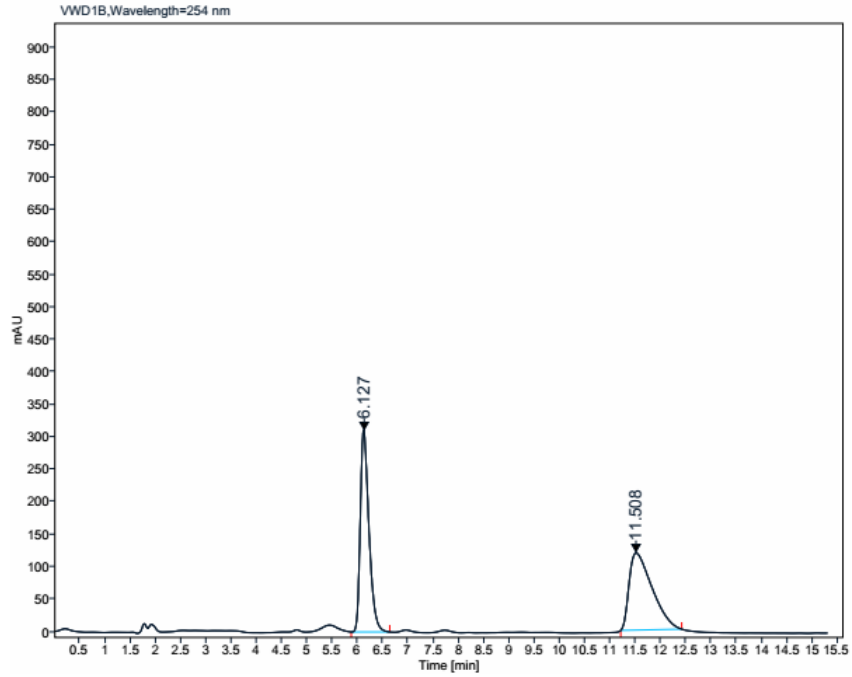




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 30% MeOH.amx

Injection Acquired Date 2020-03-09 13:50:37+01:00

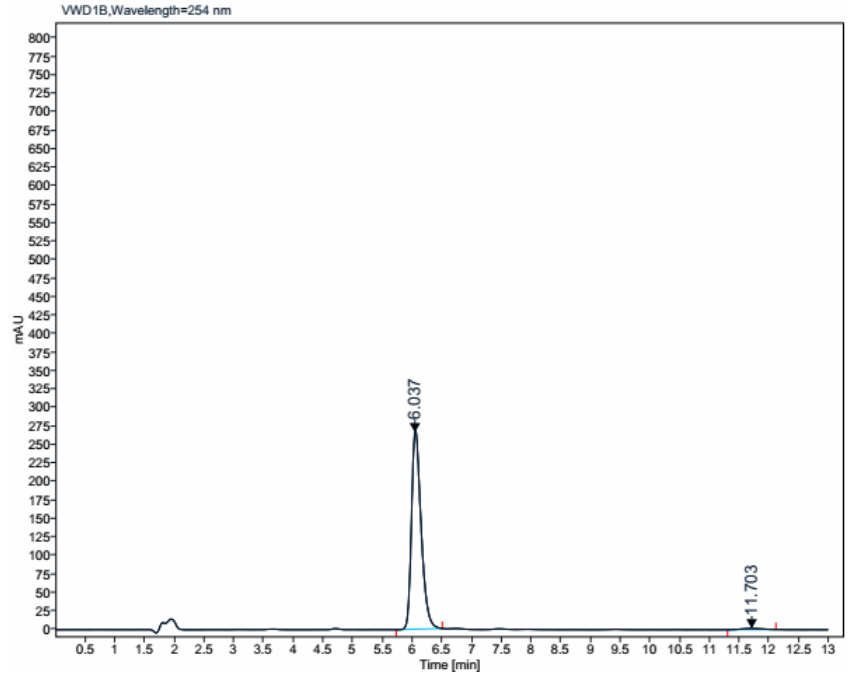
RT	*Peak Area %*
6.127	49.71
11.508	50.29



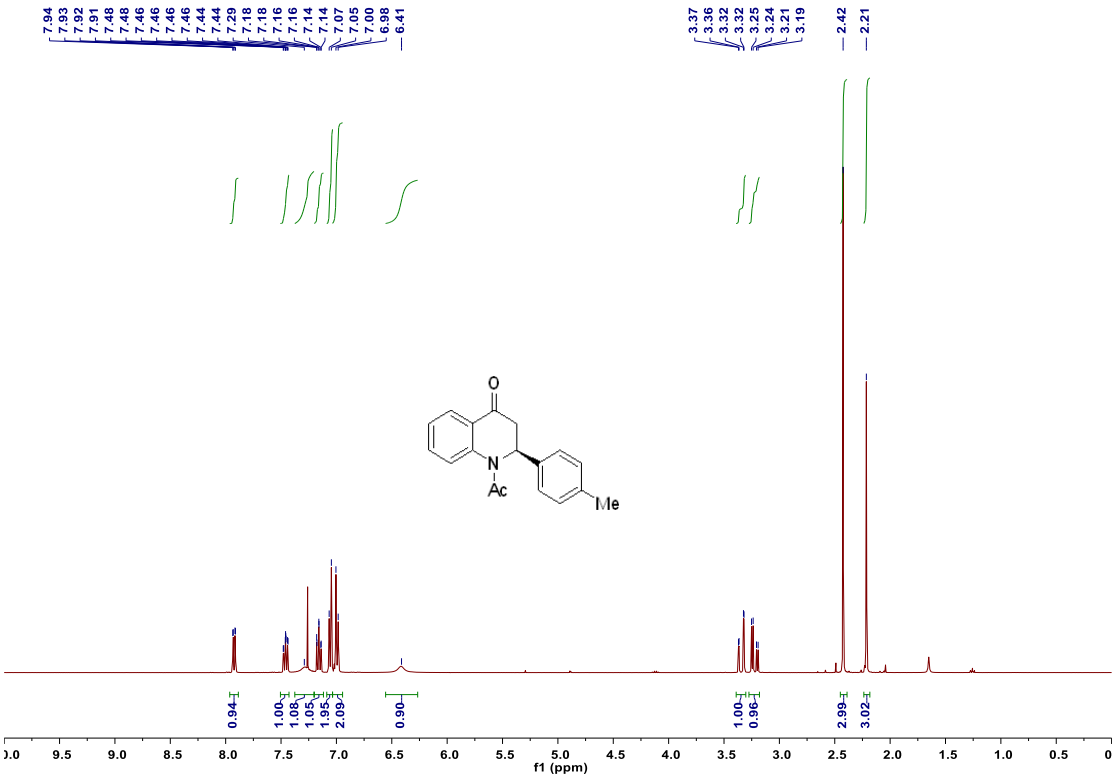
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 30% MeOH.amx

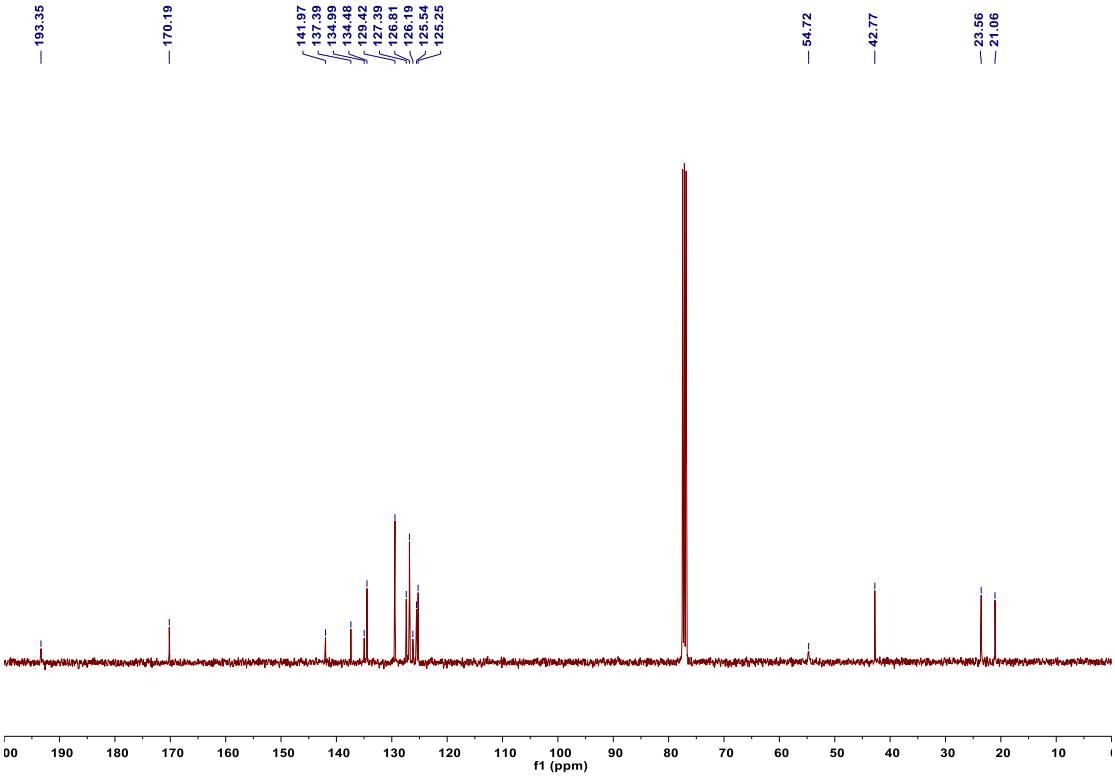
Injection Acquired Date 2020-08-05 10:34:02+02:00

RT	*Peak Area %*
6.037	98.87
11.703	1.13



Compound **(*S*)-3b**

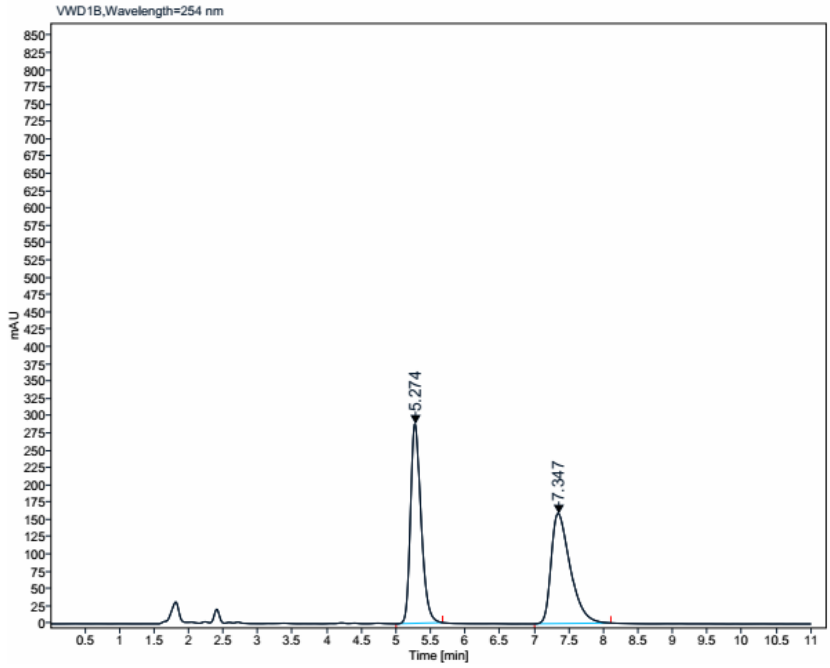




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-08-26 09:55:14+02:00

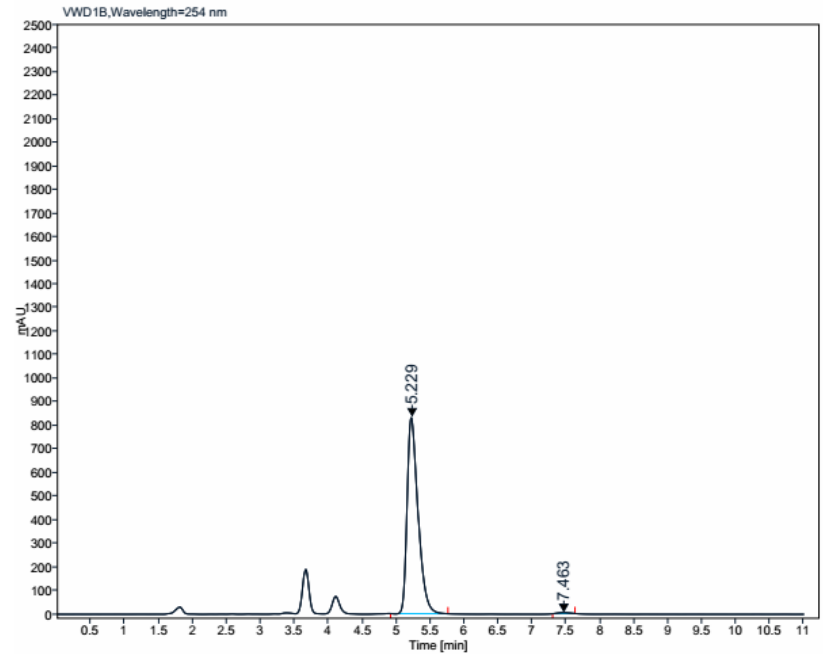
RT	Peak Area %
5.274	49.86
7.347	50.14



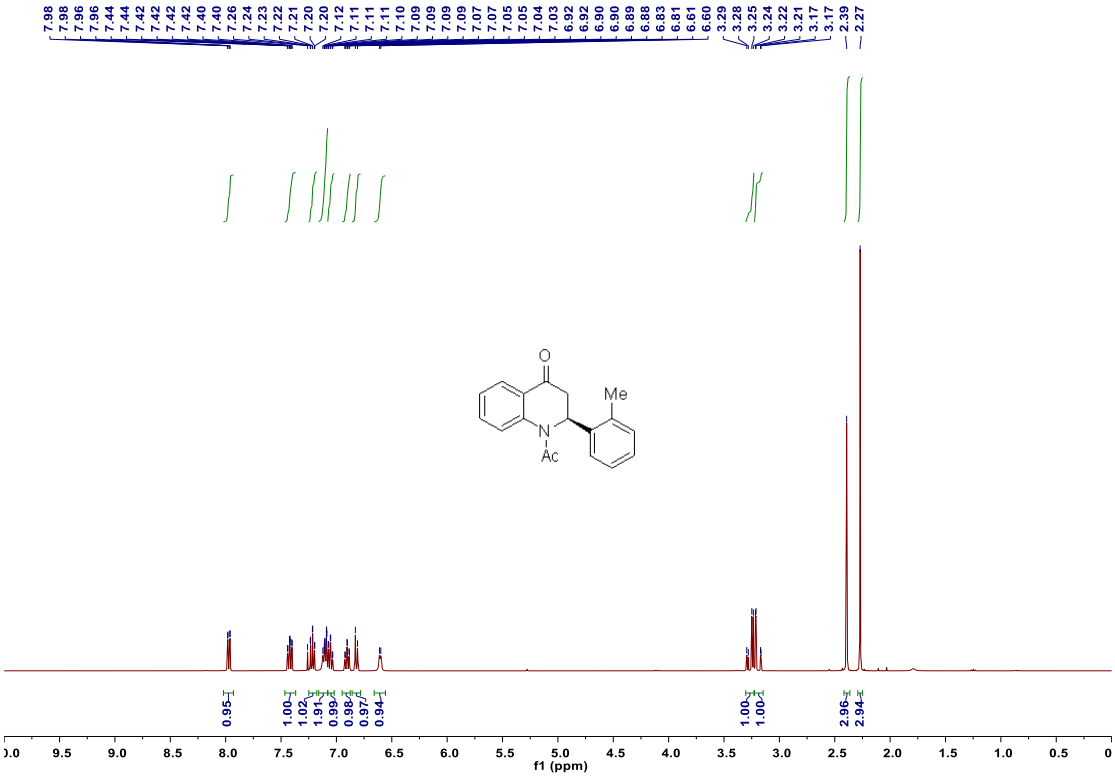
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

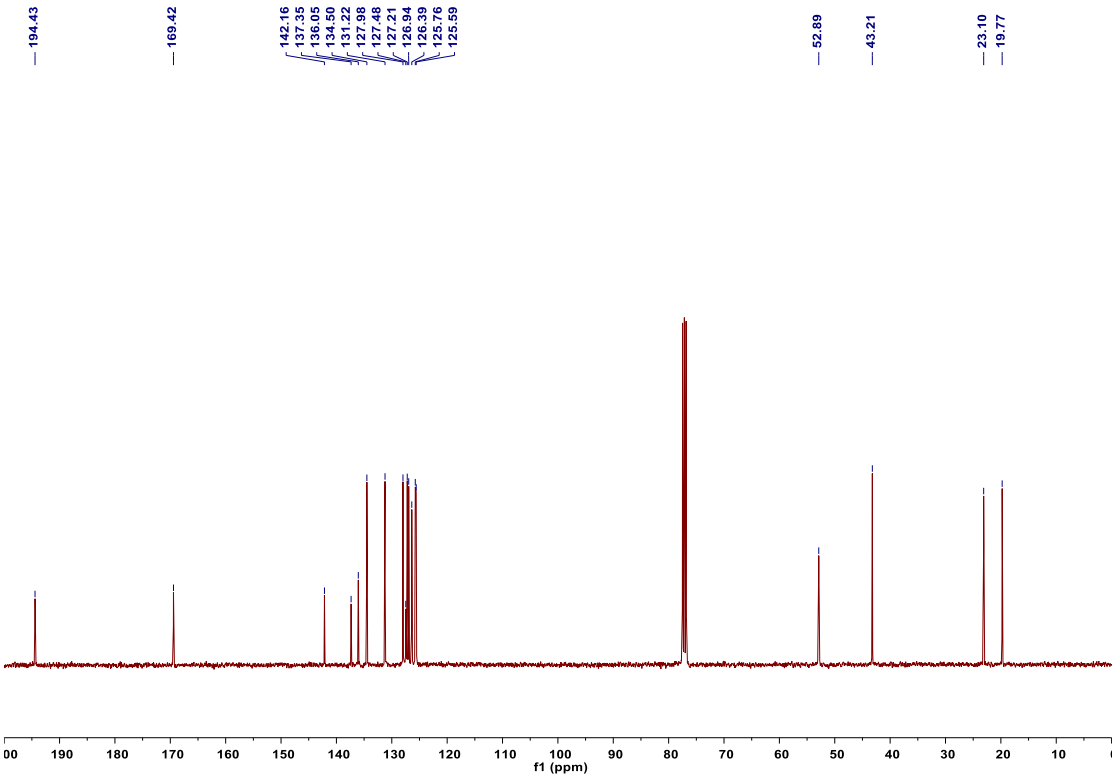
Injection Acquired Date 2020-08-26 10:06:57+02:00

RT	Peak Area %
5.229	99.46
7.463	0.54



Compound **(*S*)-3c**

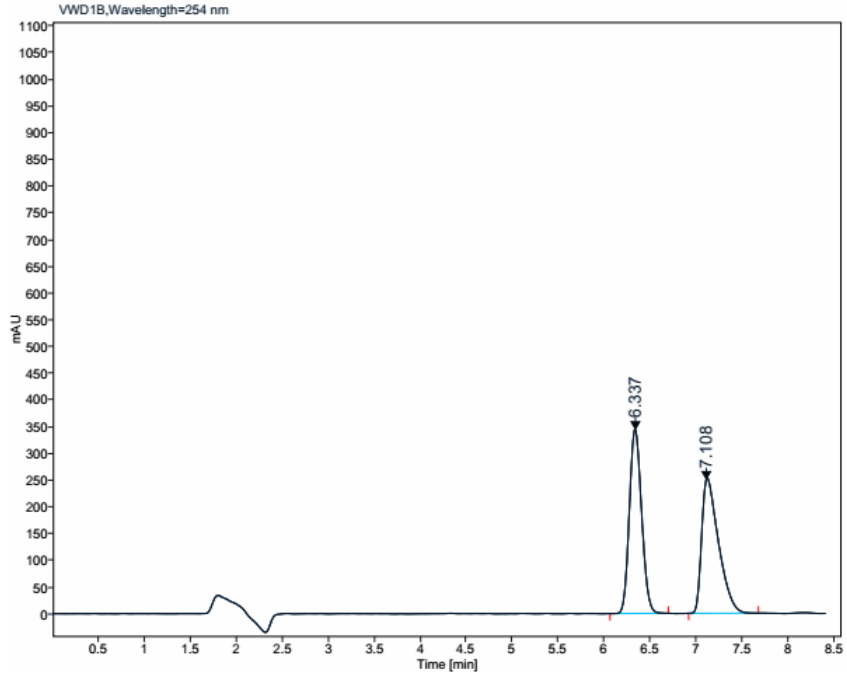




Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

Injection Acquired Date 2020-07-10 17:26:05+02:00

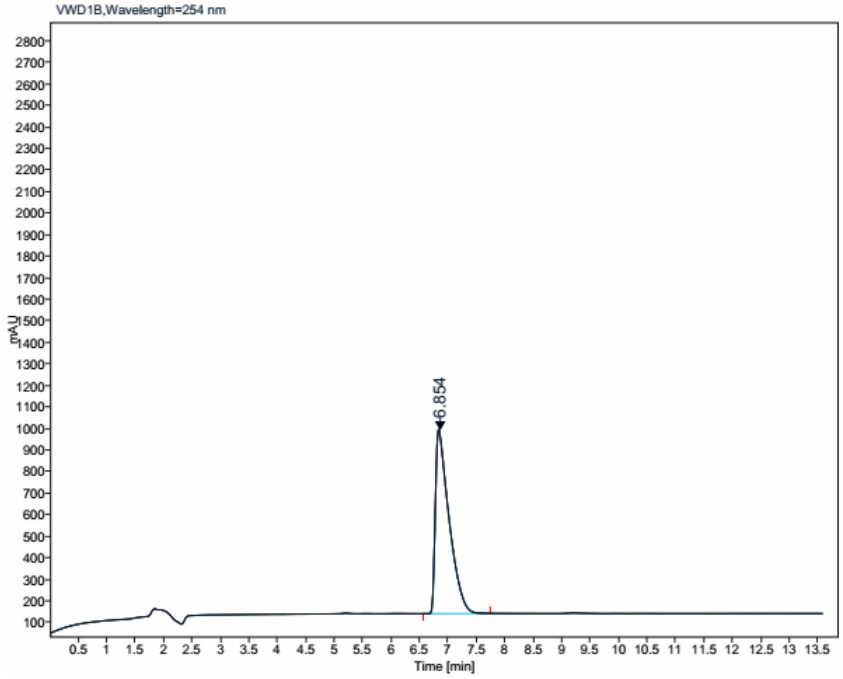
RT	*Peak Area %*
6.337	49.84
7.108	50.16



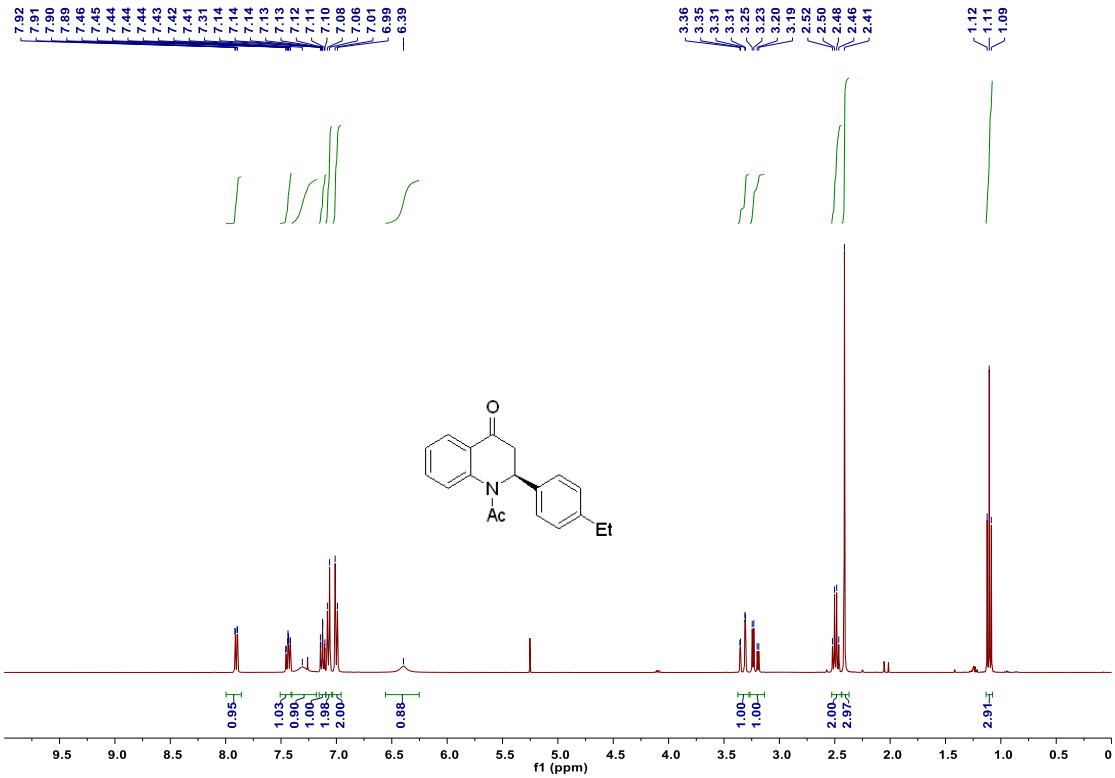
Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

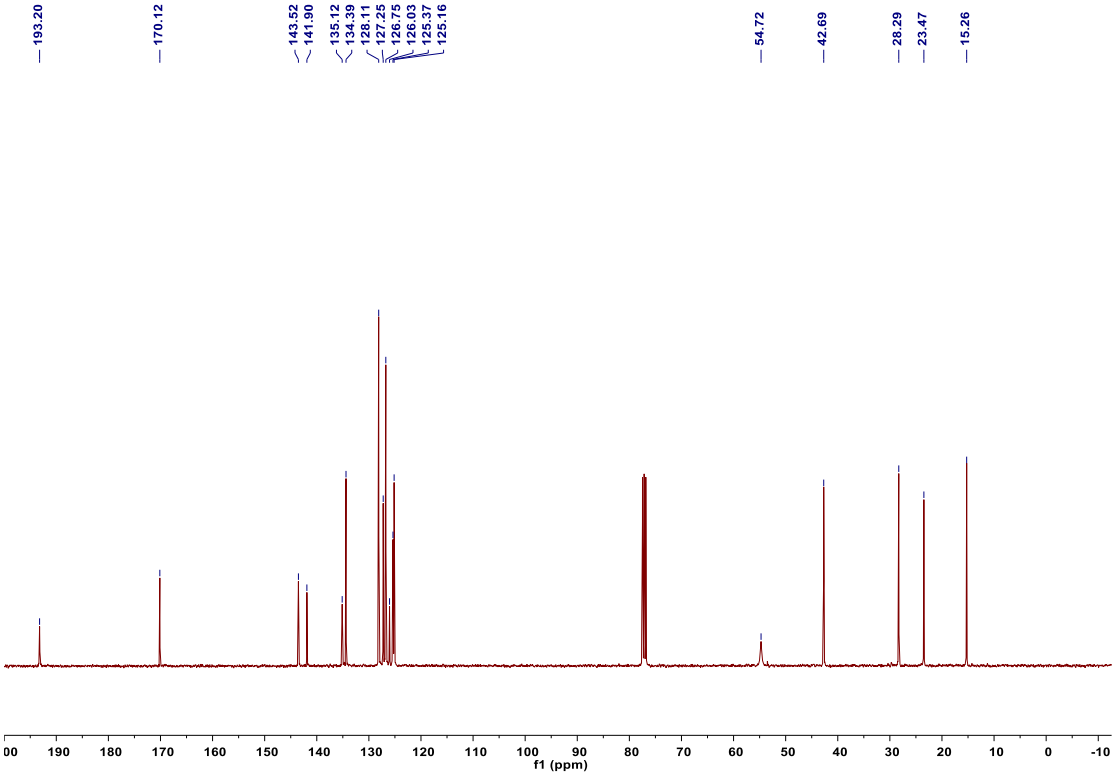
Injection Acquired Date 2020-07-23 16:34:41+02:00

RT	*Peak Area %*
6.854	100.00



Compound **(*S*)-3d**

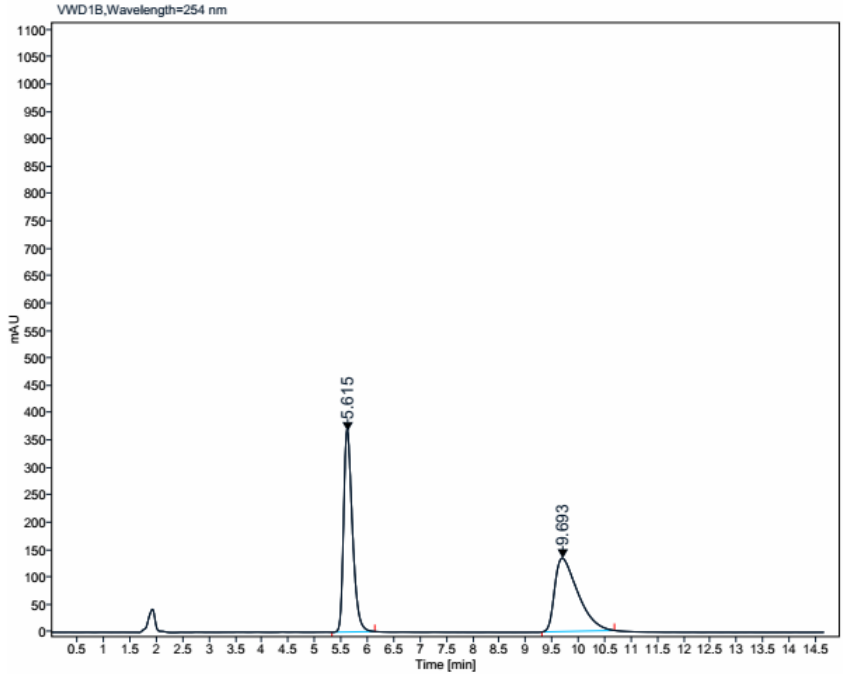




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-02 15:23:36+02:00

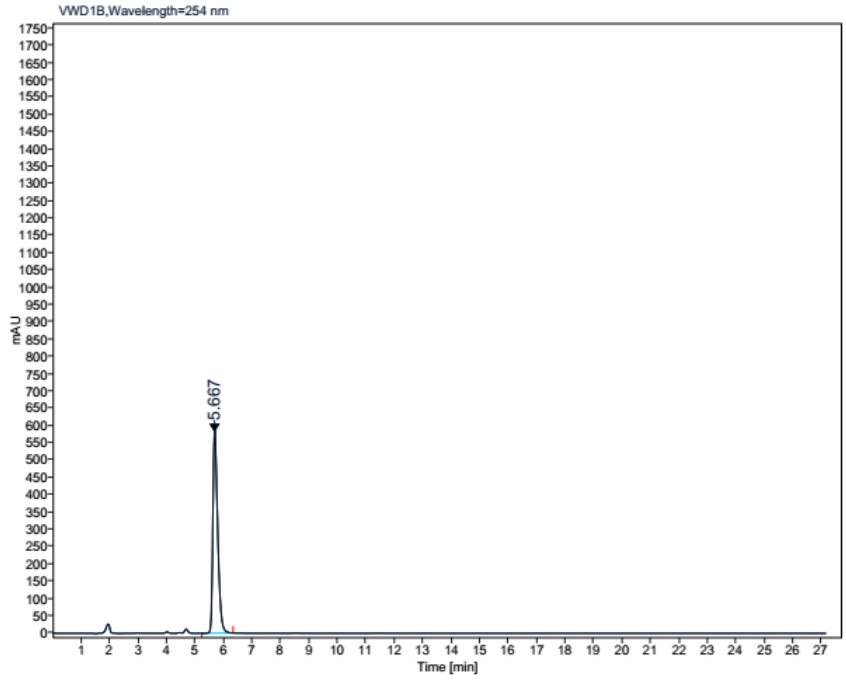
RT	Peak Area %
5.615	51.12
9.693	48.88



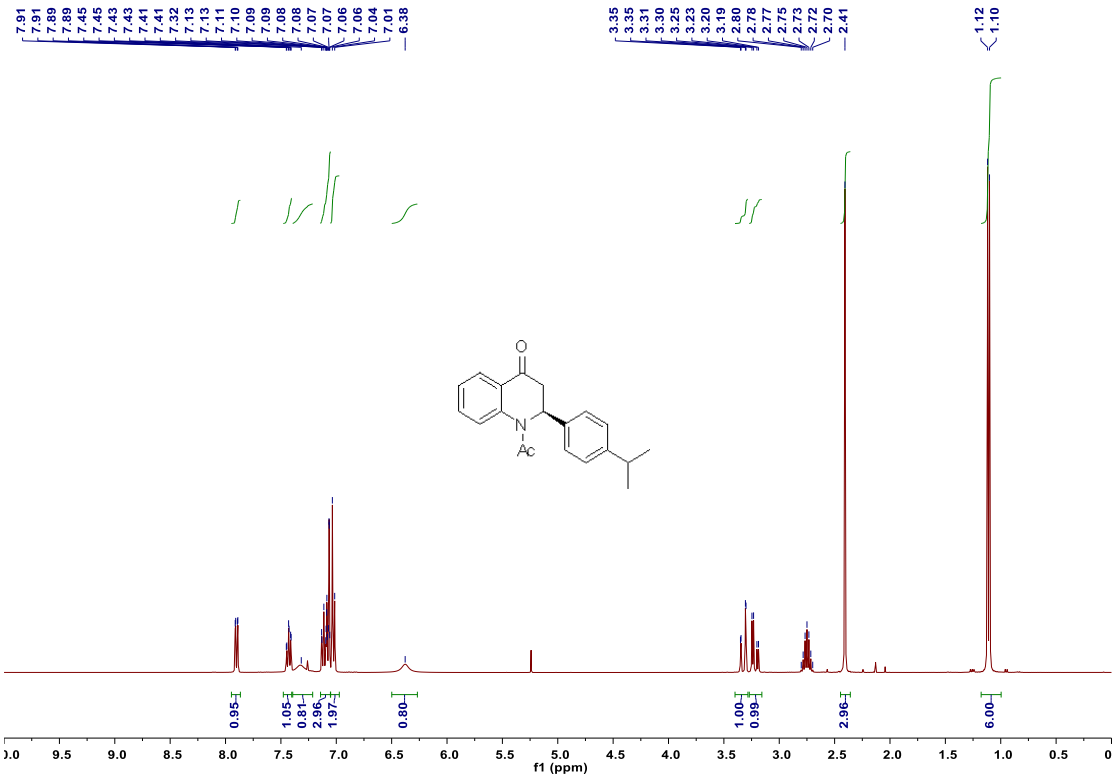
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

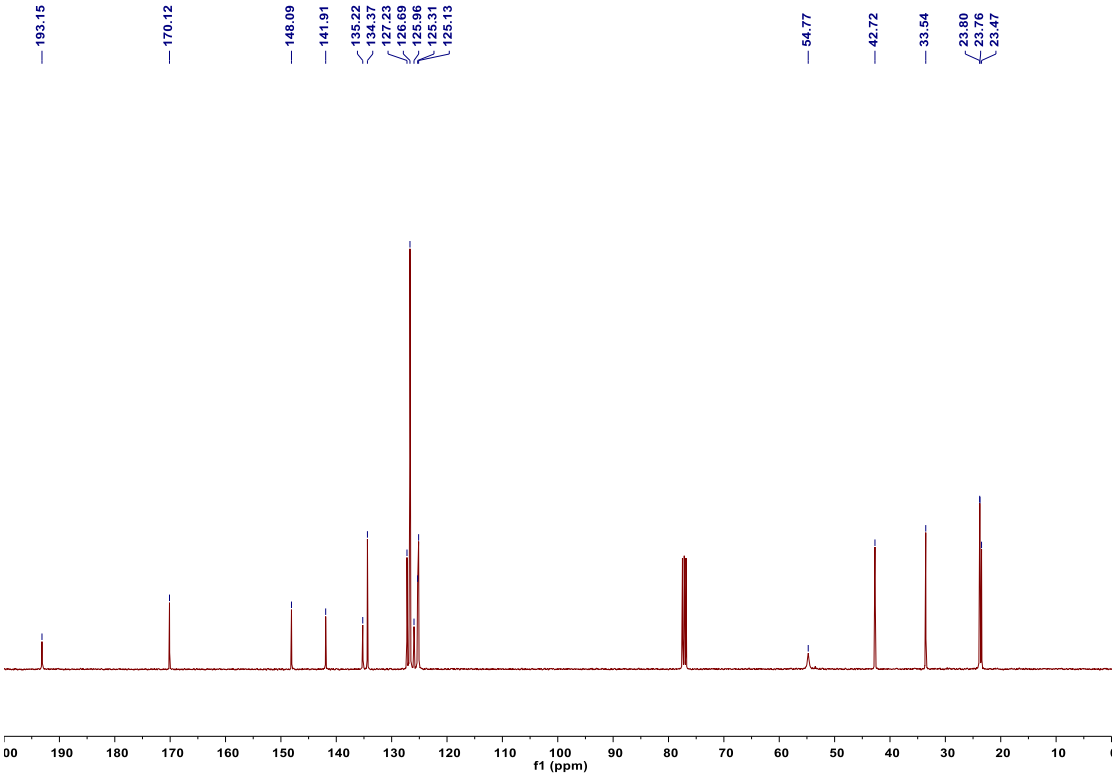
Injection Acquired Date 2020-07-22 14:48:01+02:00

RT	Peak Area %
5.667	100.00



Compound **(*S*)-3e**

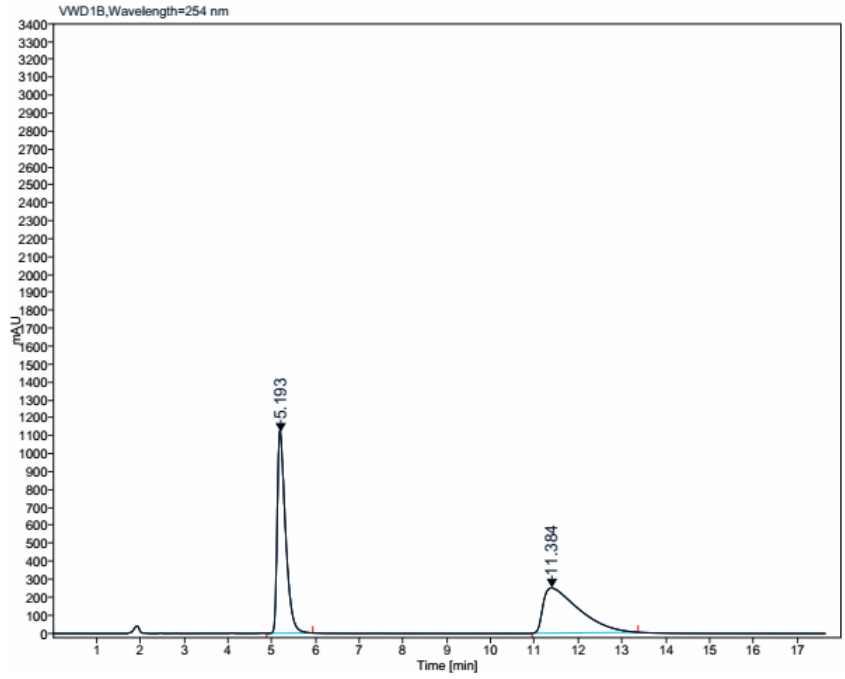




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-02 15:39:16+02:00

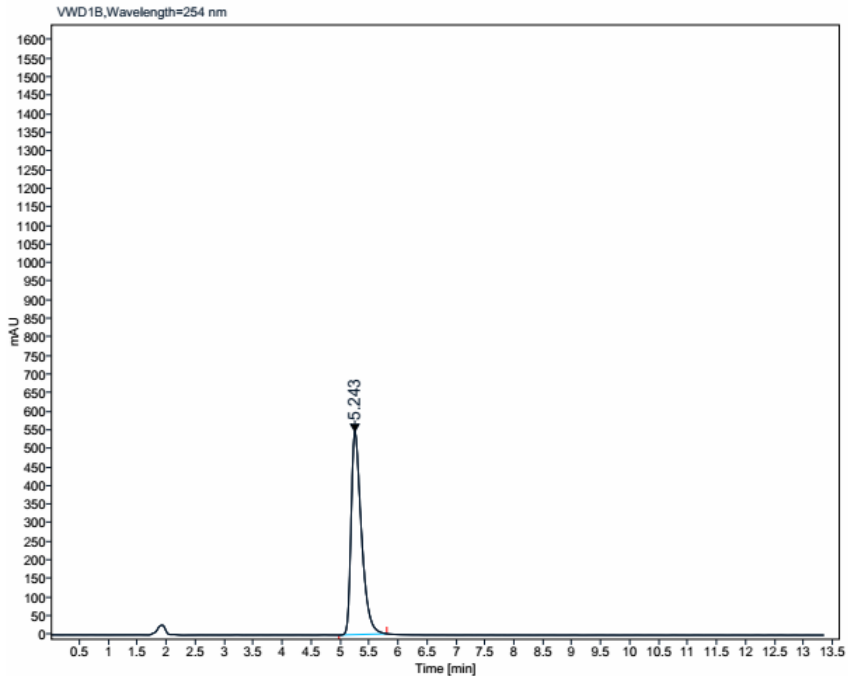
RT	*Peak Area %*
5.193	51.02
11.384	48.98



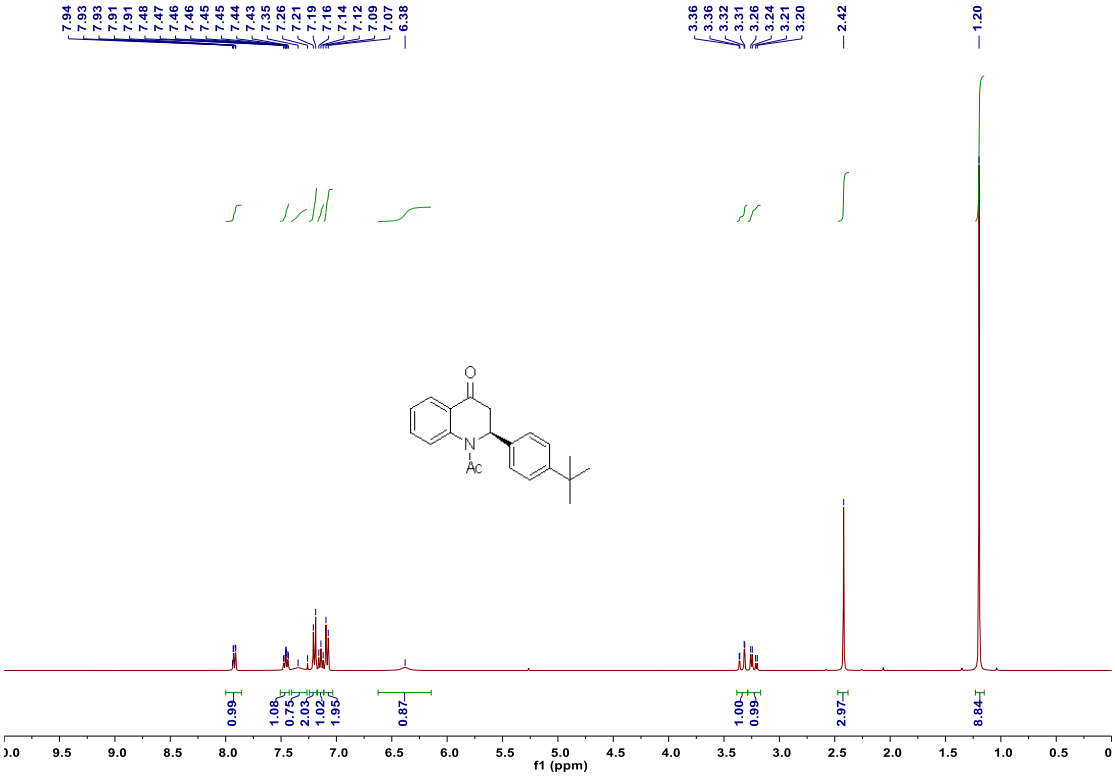
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

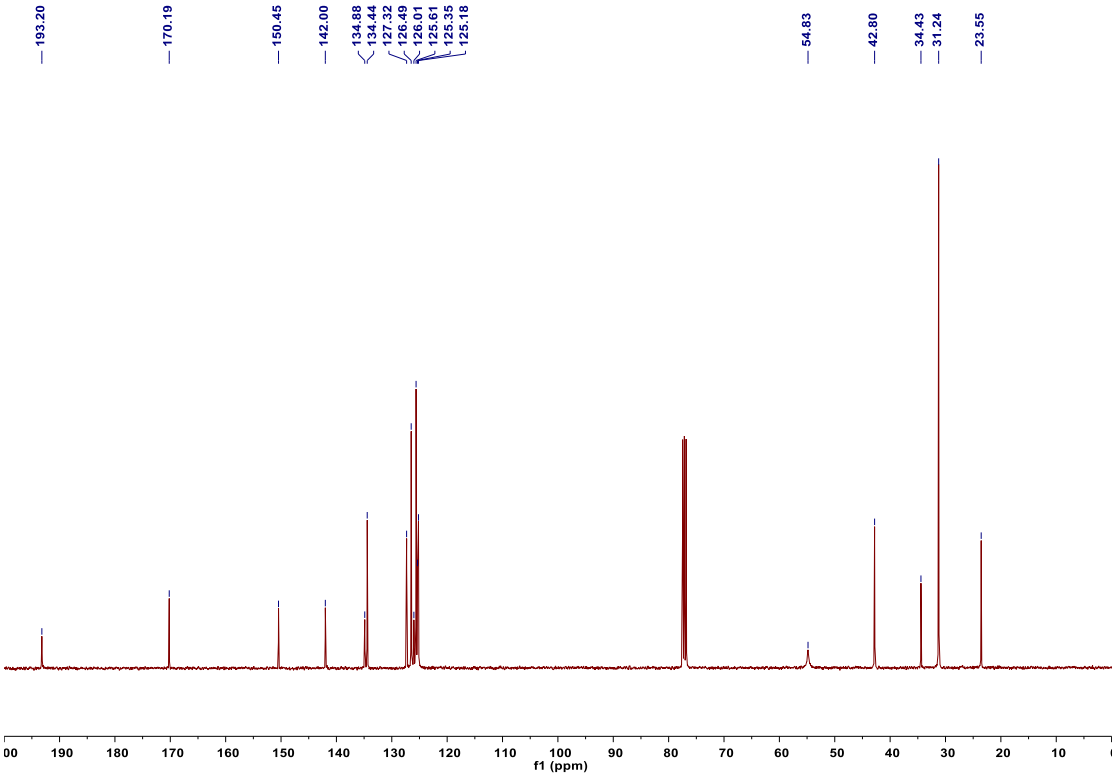
Injection Acquired Date 2020-07-21 18:30:00+02:00

RT	*Peak Area %*
5.243	100.00



Compound ***(S)*-3f**

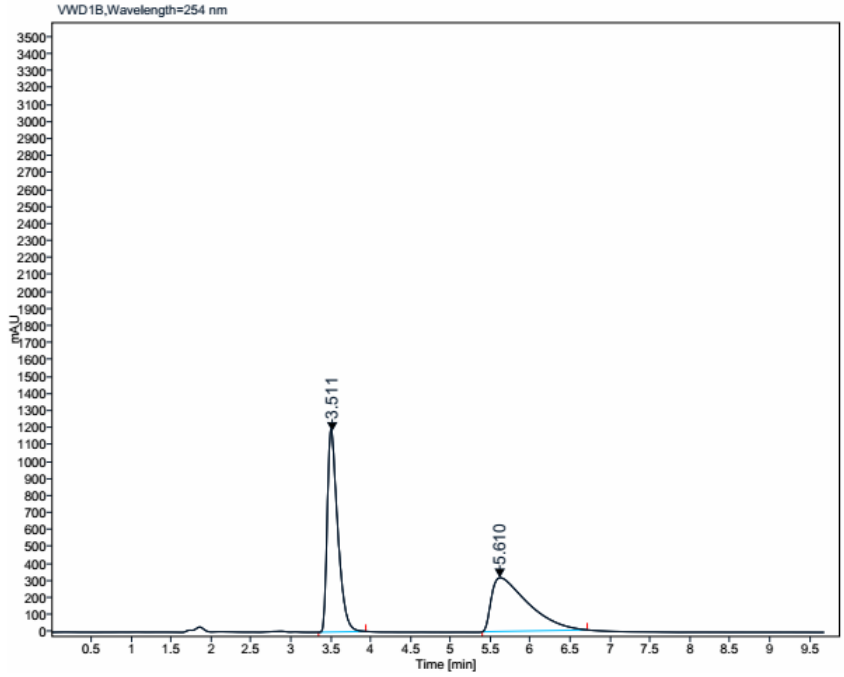




Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-06-12 14:52:29+02:00

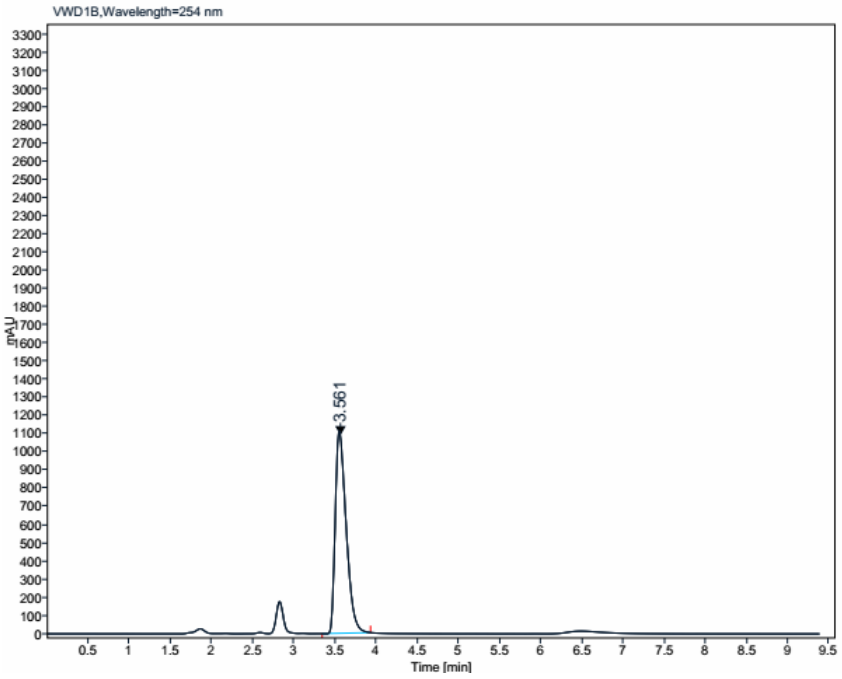
RT	*Peak Area %*
3.511	52.10
5.610	47.90



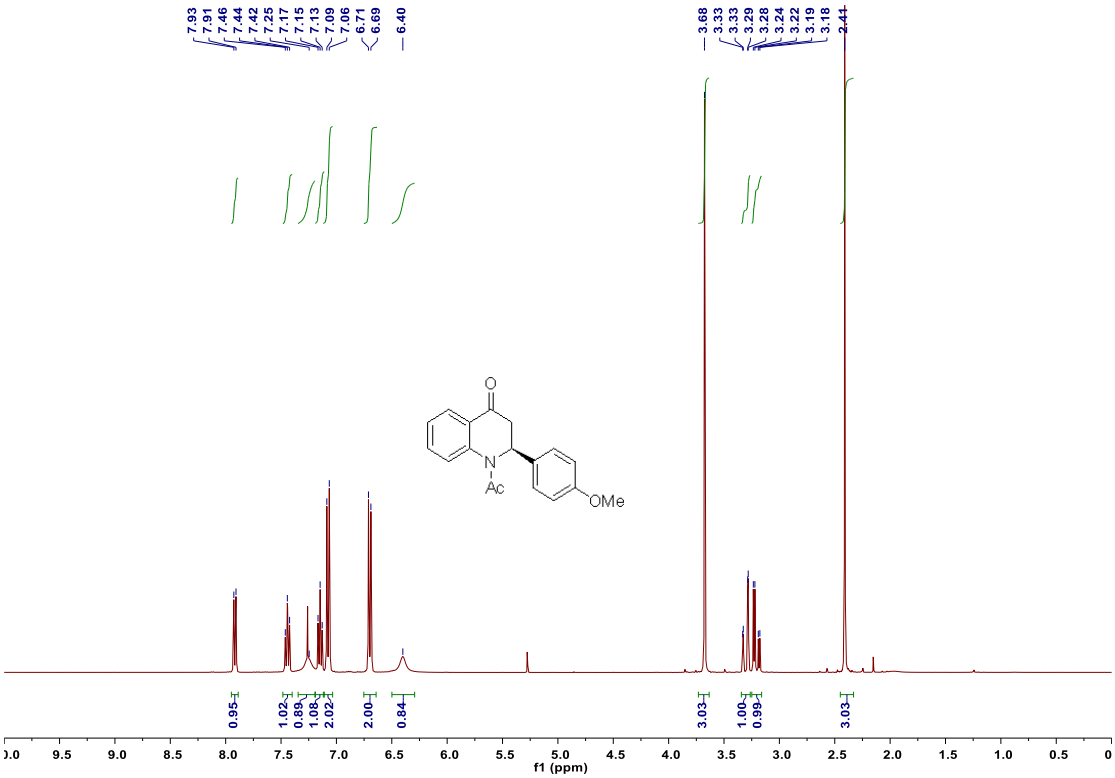
Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 40% MeOH.amx

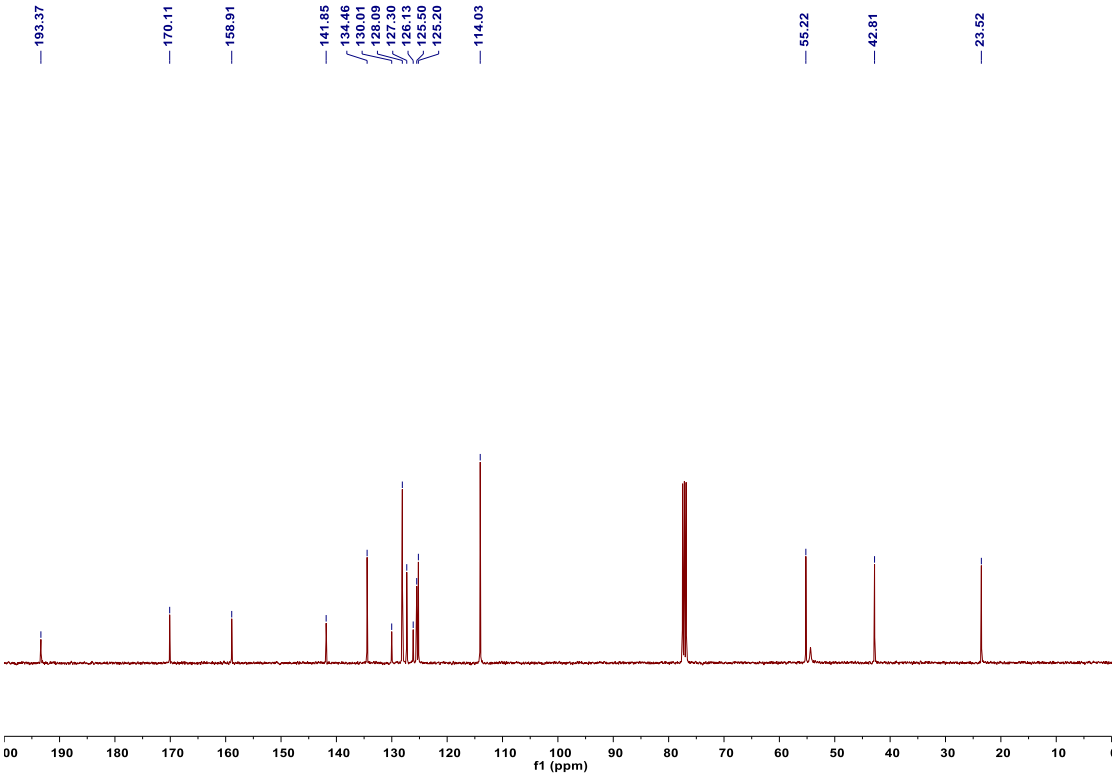
Injection Acquired Date 2020-07-28 12:08:07+02:00

RT	*Peak Area %*
3.561	100.00



Compound **(*S*)-3g**

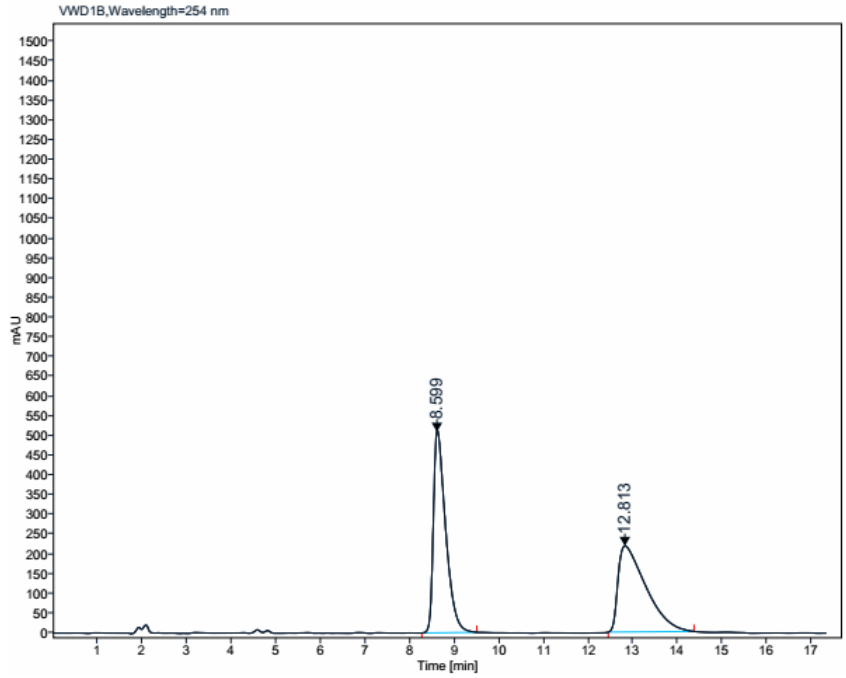




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 30% MeOH.amx

Injection Acquired Date 2020-06-12 16:43:34+02:00

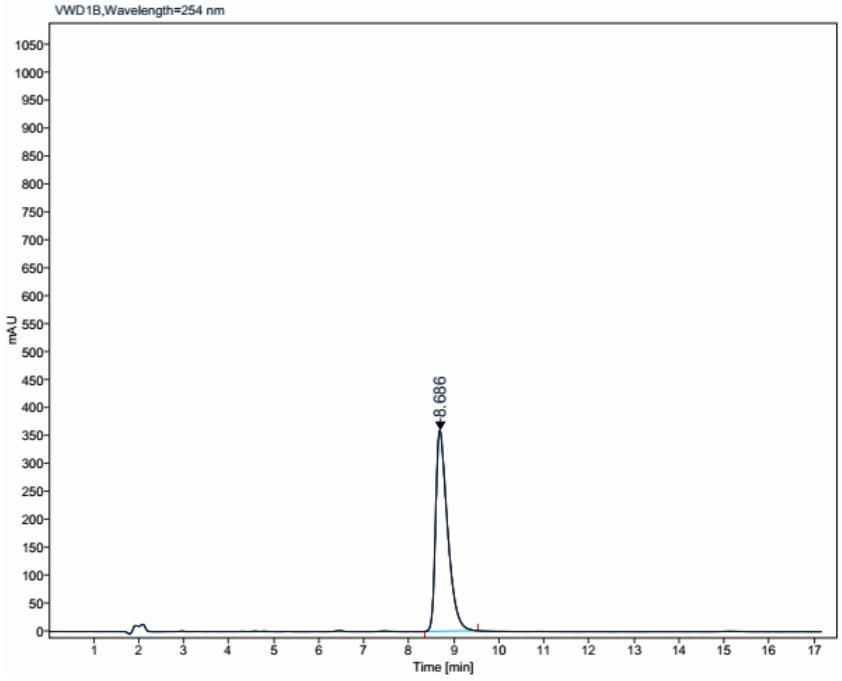
RT	*Peak Area %*
8.599	50.96
12.813	49.04



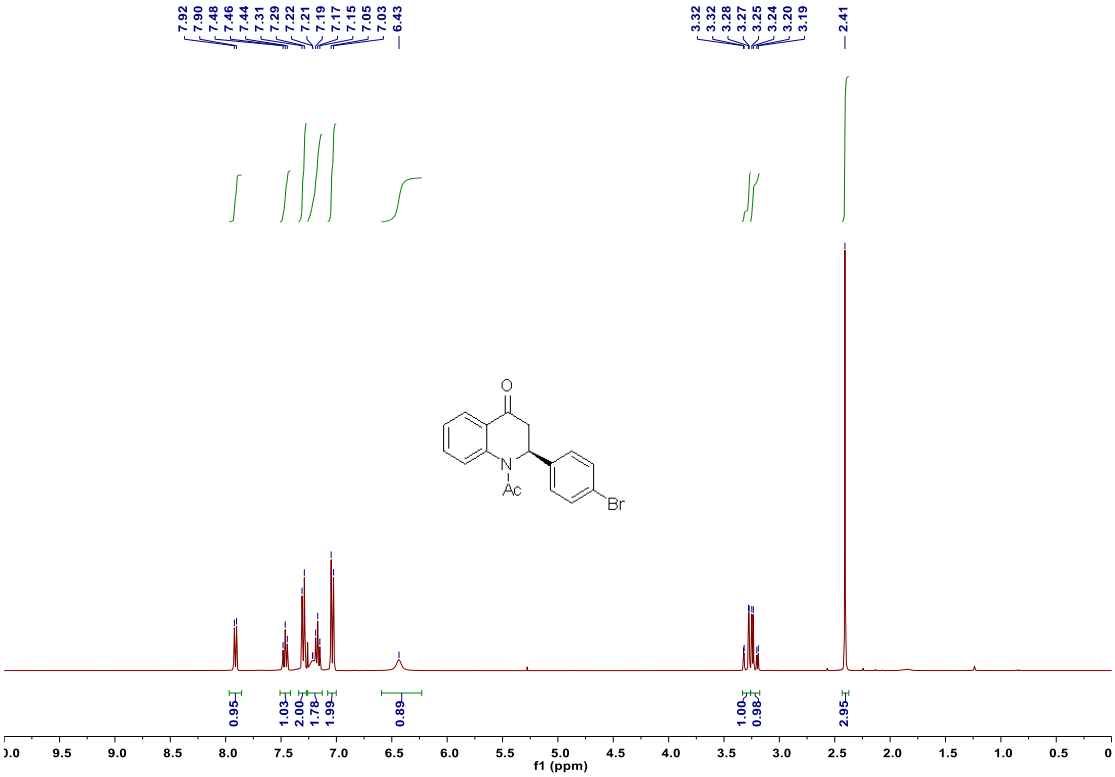
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 30% MeOH.amx

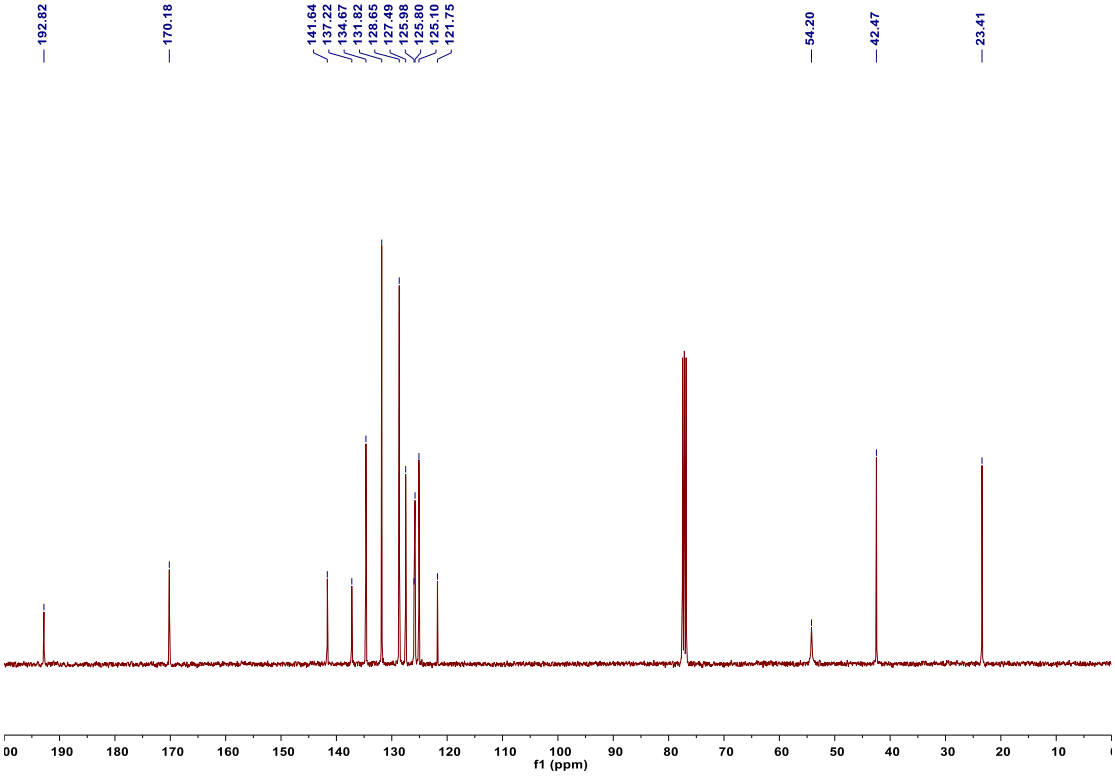
Injection Acquired Date 2020-07-24 15:19:00+02:00

RT	*Peak Area %*
8.686	100.00



Compound ***(S)*-3h**

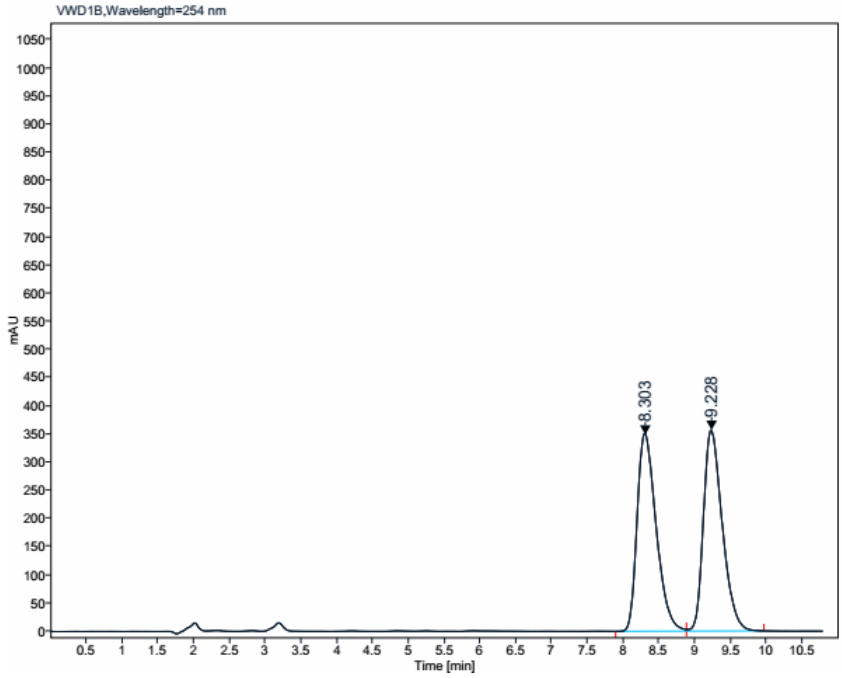




Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 10% MeOH.amx

Injection Acquired Date 2020-07-08 13:13:37+02:00

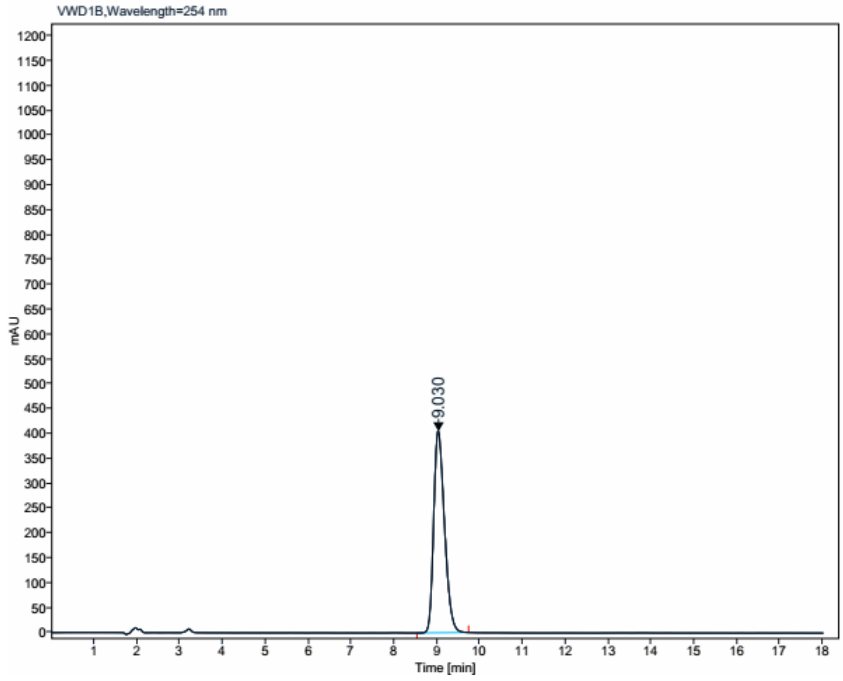
RT	*Peak Area %*
8.303	49.83
9.228	50.17



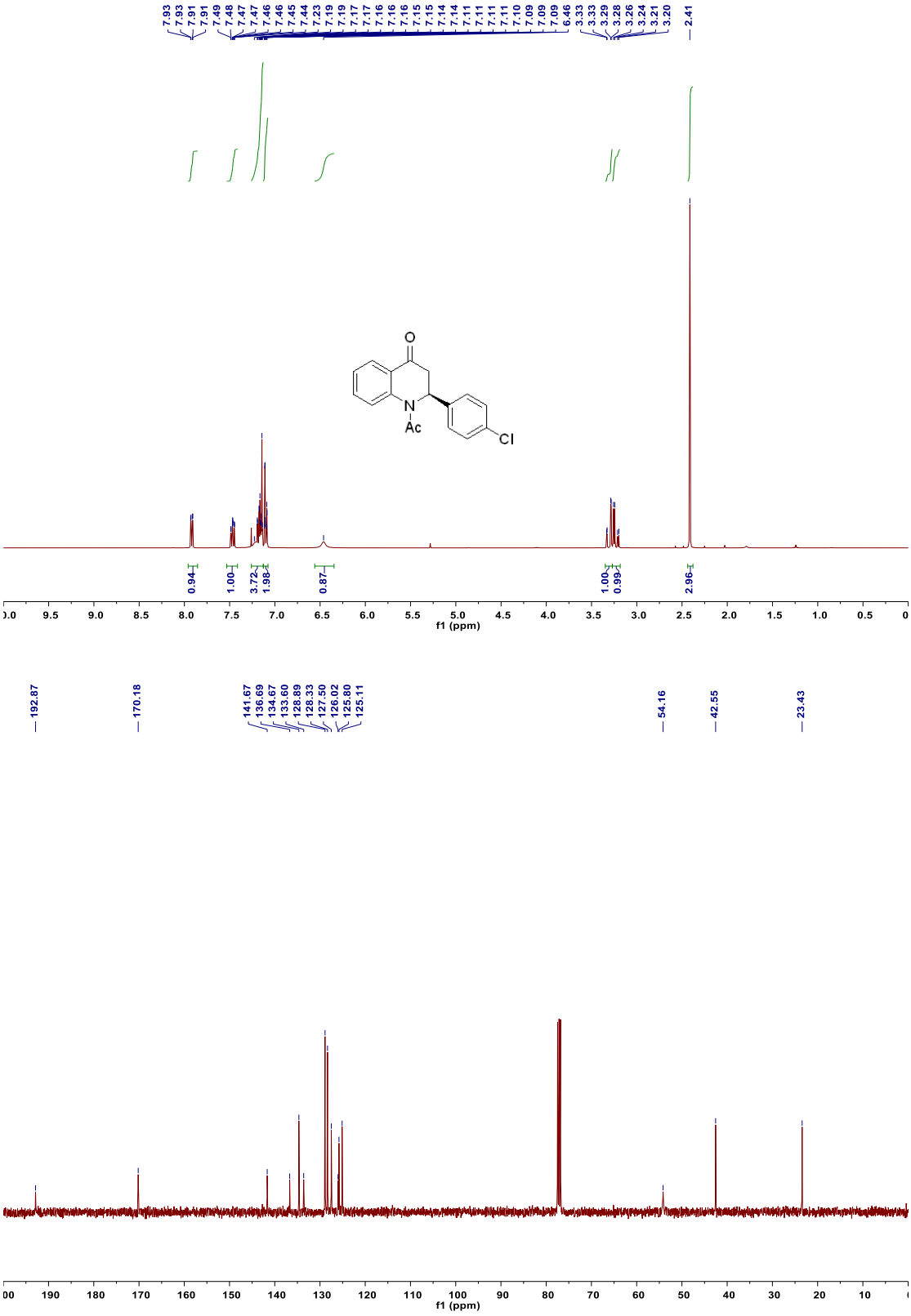
Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 10% MeOH.amx

Injection Acquired Date 2020-07-28 10:04:39+02:00

RT	*Peak Area %*
9.030	100.00



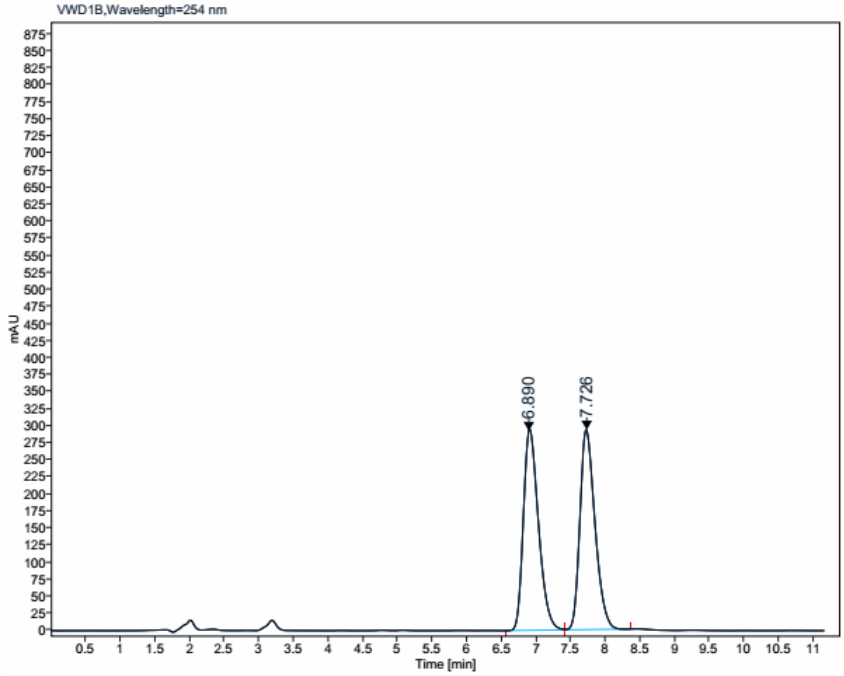
Compound ***(S)*-3l**



Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 10% MeOH.amx

Injection Acquired Date 2020-07-08 13:25:14+02:00

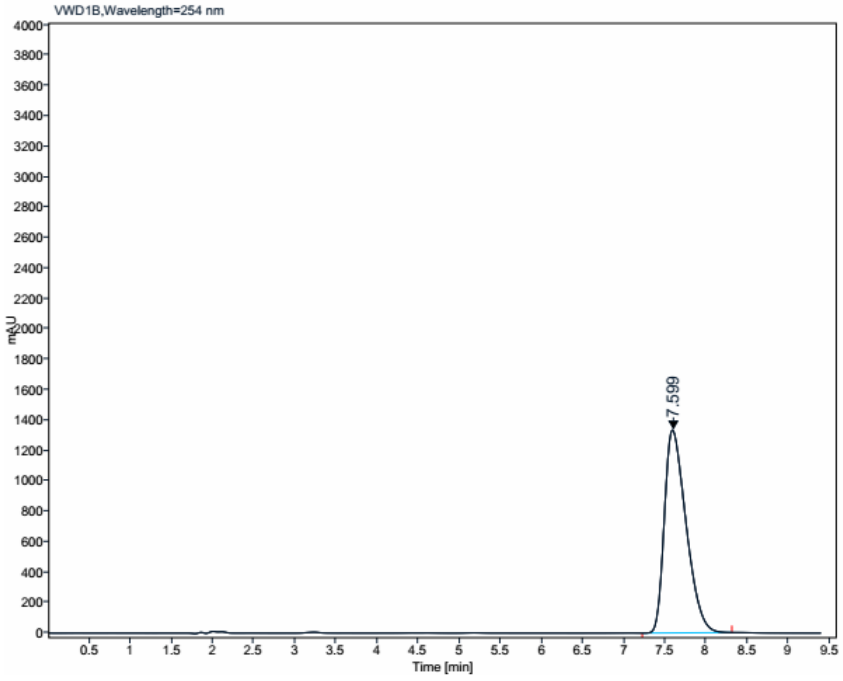
RT	*Peak Area %*
6.890	50.23
7.726	49.77



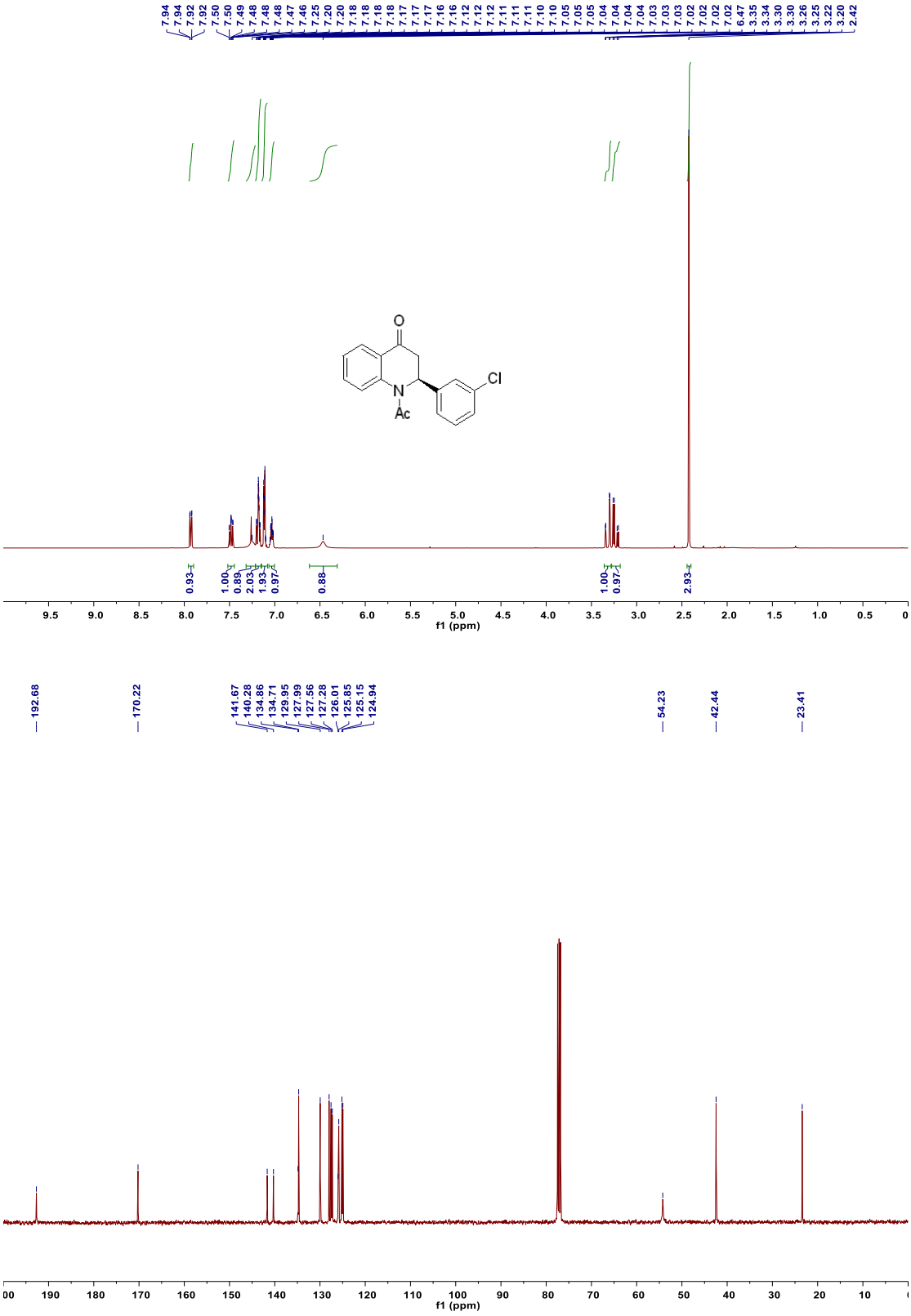
Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 10% MeOH.amx

Injection Acquired Date 2020-07-23 14:49:36+02:00

RT	*Peak Area %*
7.599	100.00



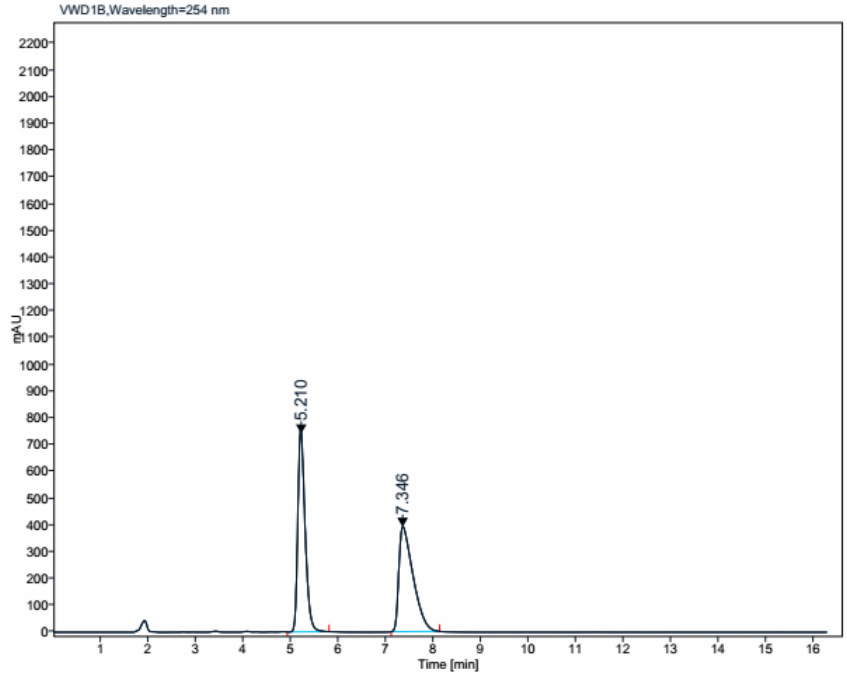
Compound ***(S)*-3j**



Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-02 15:57:47+02:00

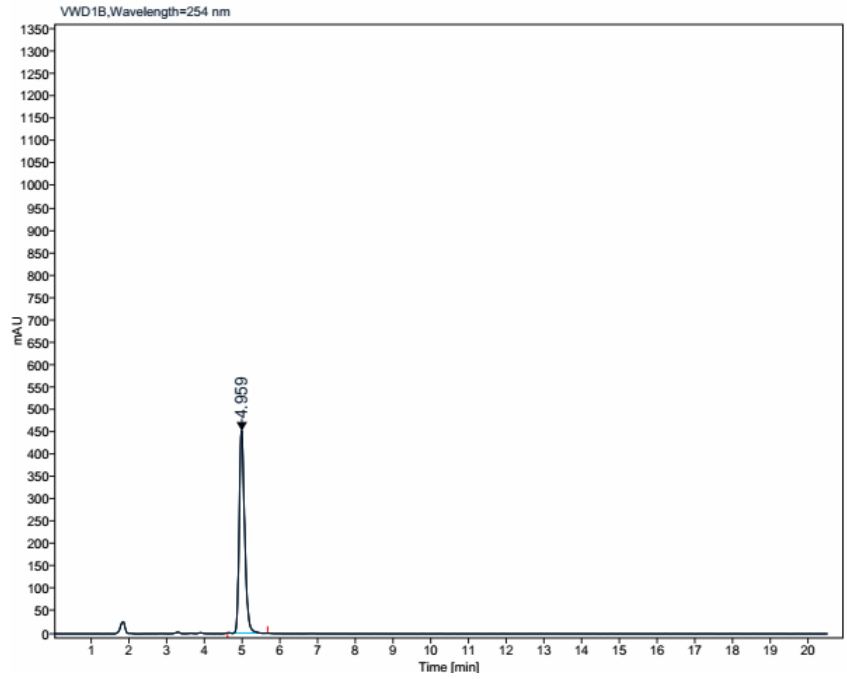
RT	Peak Area %
5.210	49.69
7.346	50.31



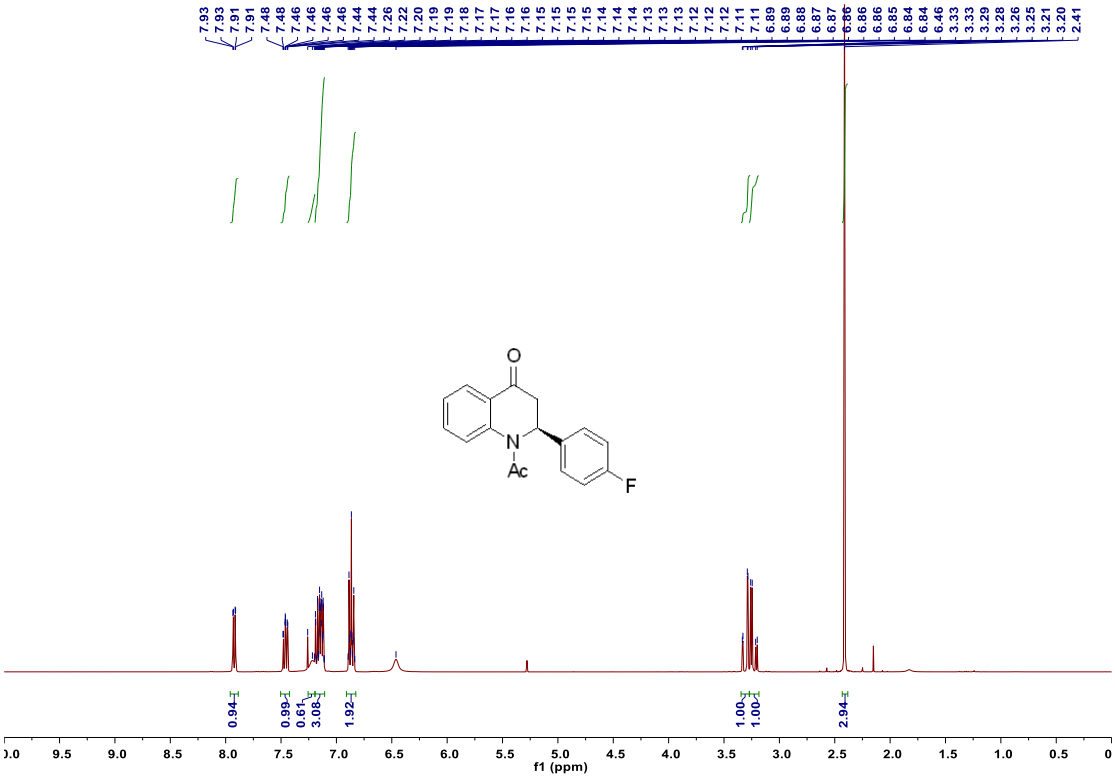
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

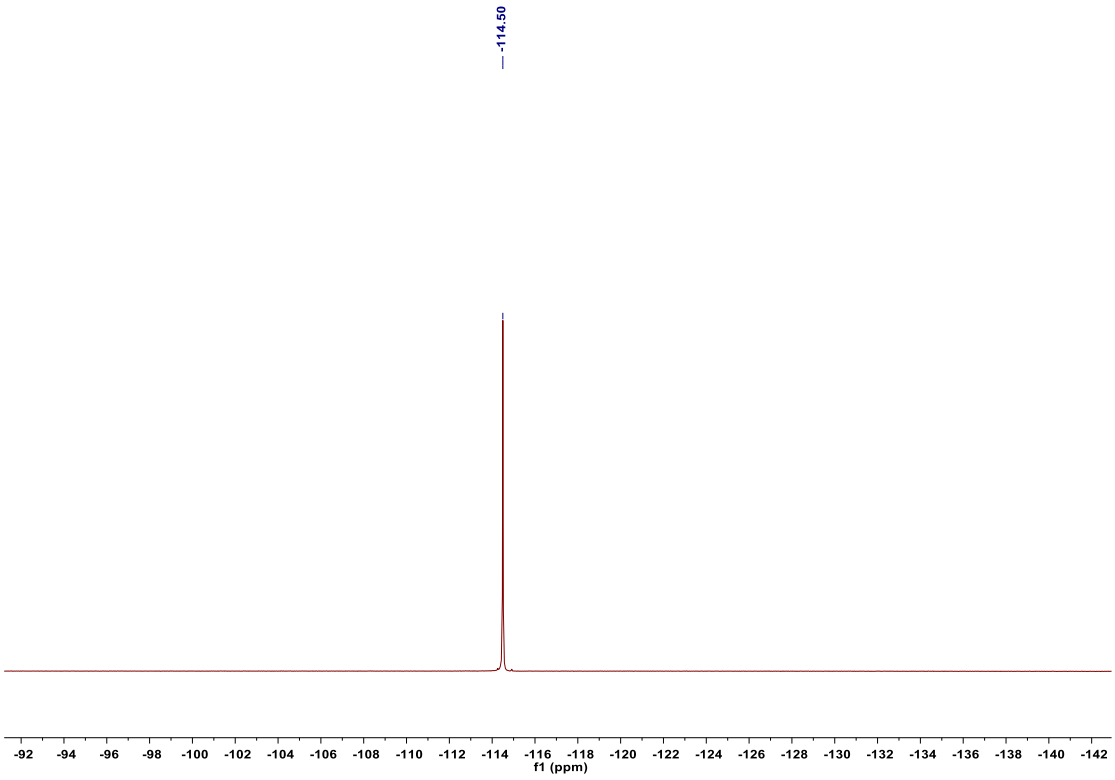
Injection Acquired Date 2020-07-30 09:49:23+02:00

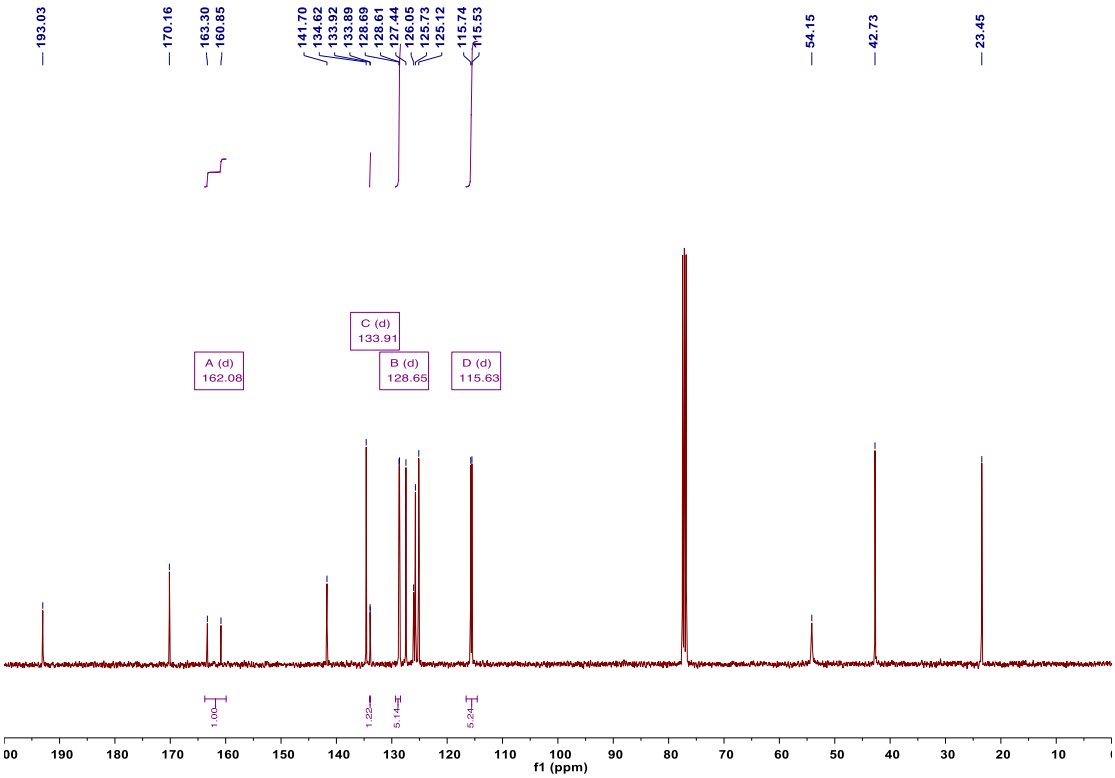
RT	Peak Area %
4.959	100.00



Compound ***(S)*-3k**



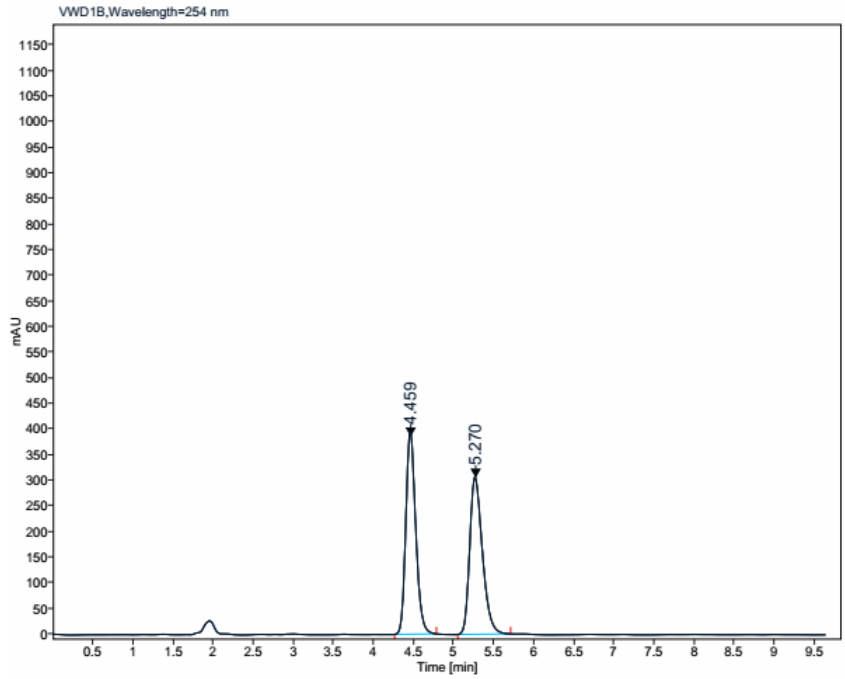




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-06-12 12:20:47+02:00

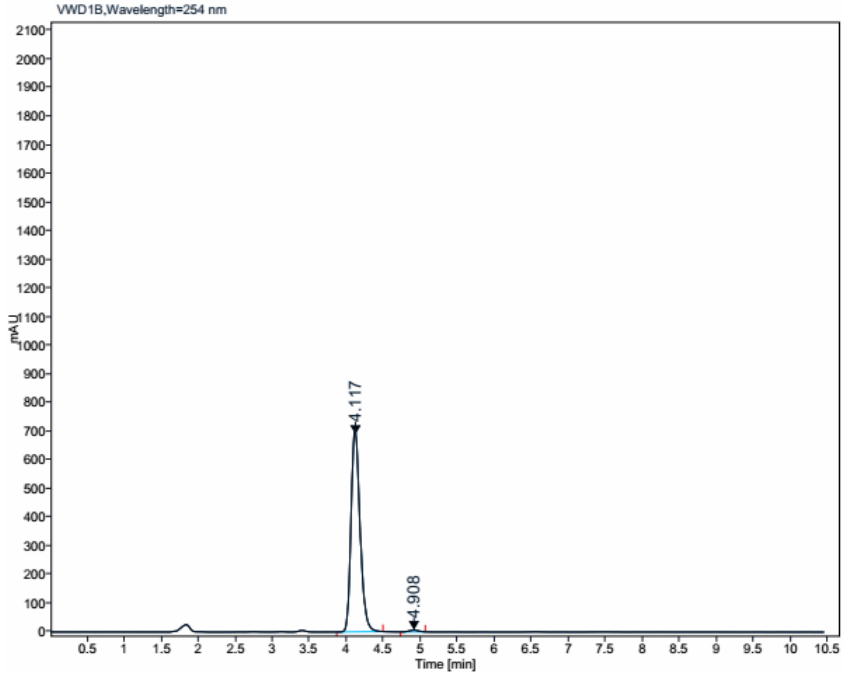
RT	*Peak Area %*
4.459	50.17
5.270	49.83



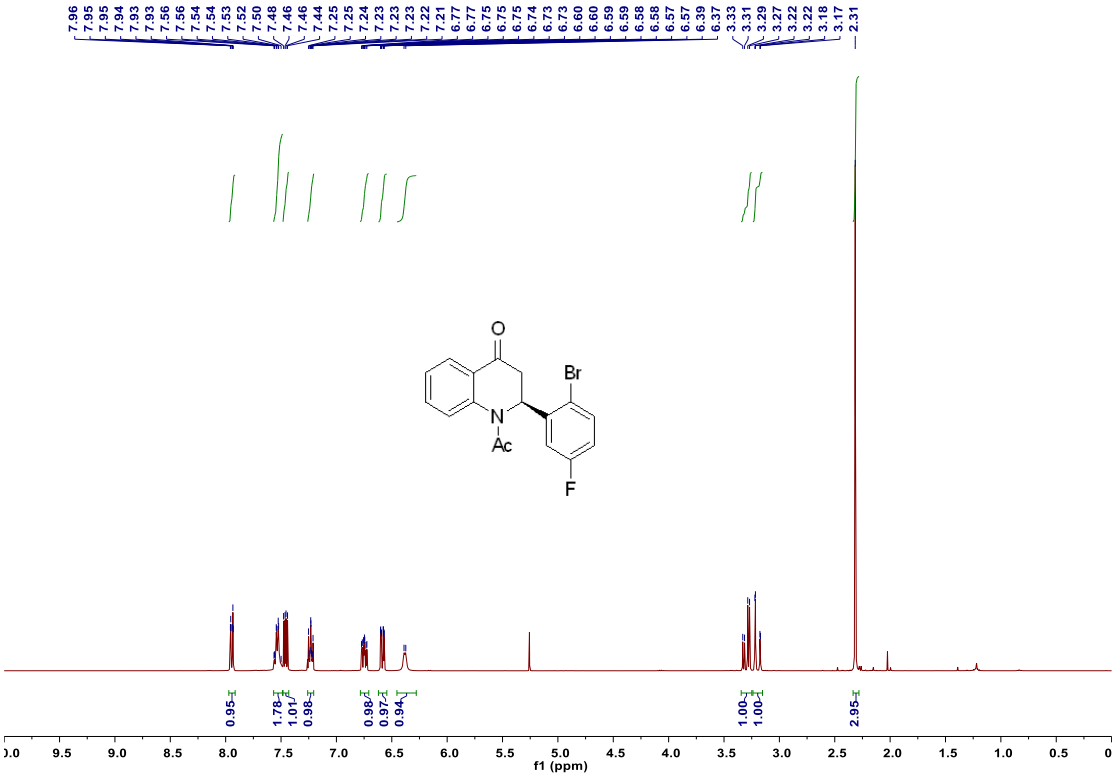
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

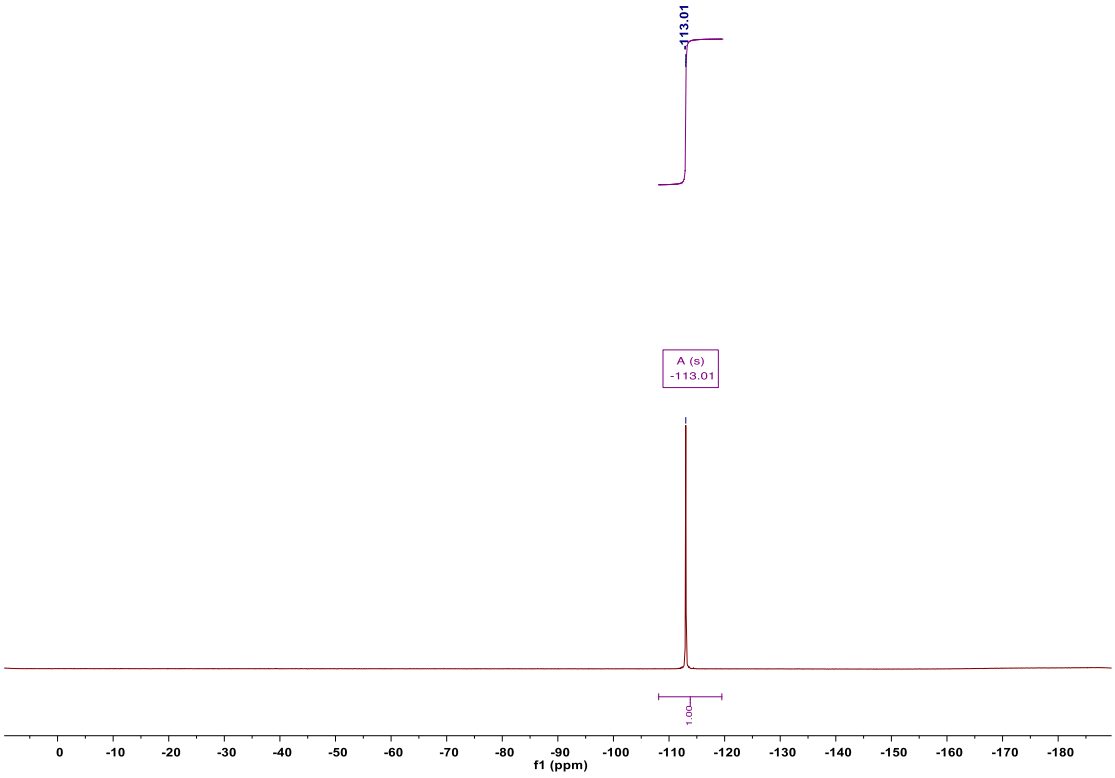
Injection Acquired Date 2020-08-05 10:11:58+02:00

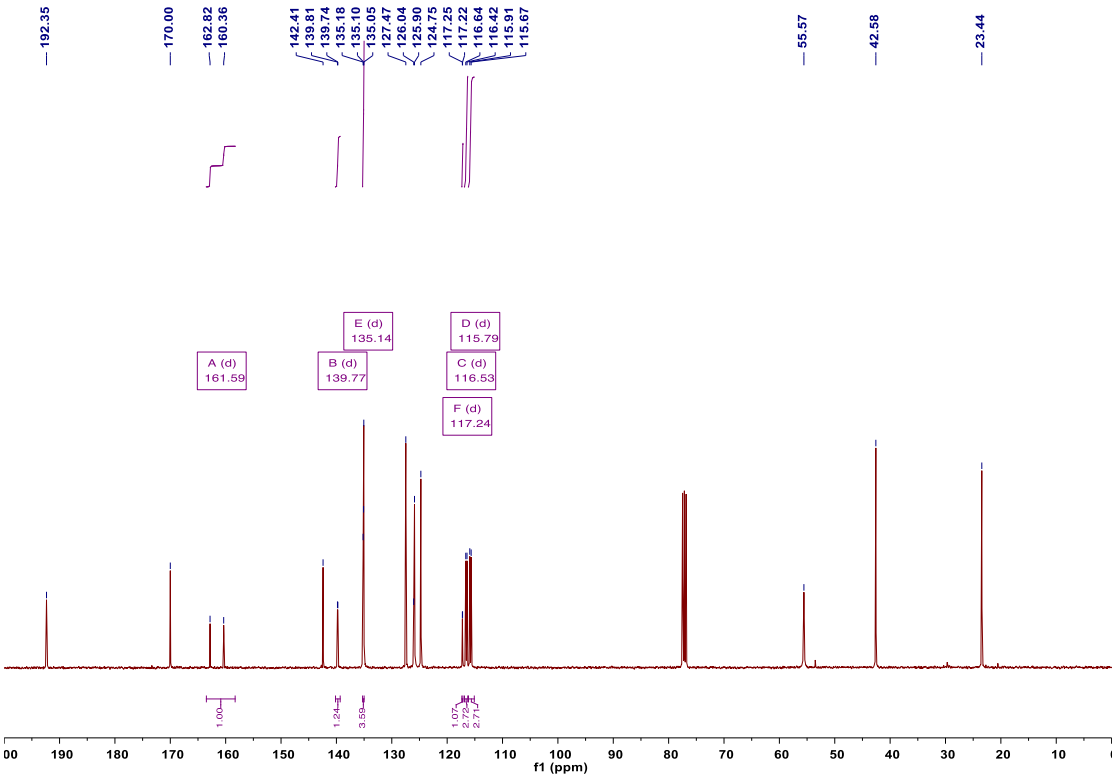
RT	*Peak Area %*
4.117	99.13
4.908	0.87



Compound ***(S)*-3l**



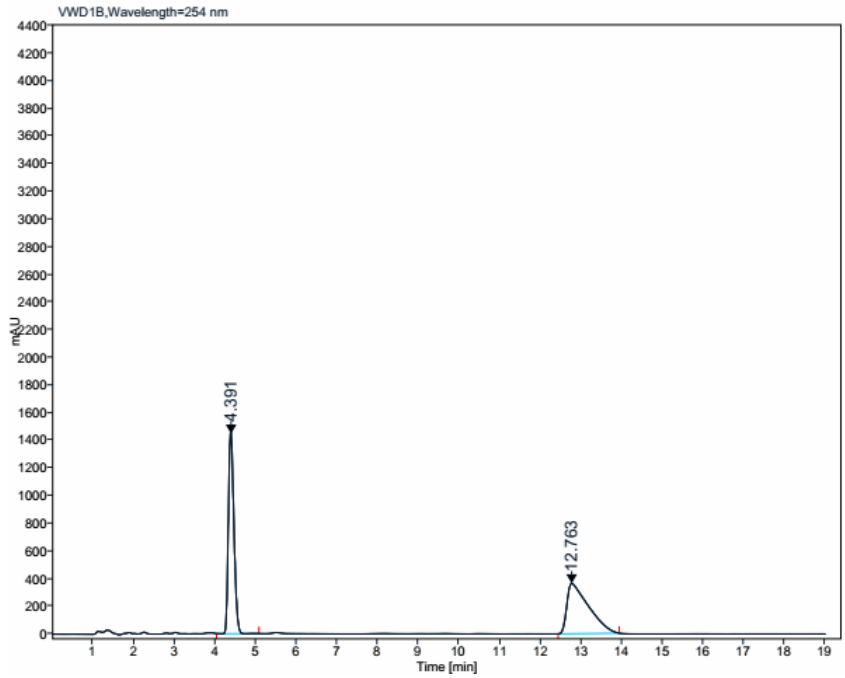




Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-10 09:42:08+02:00

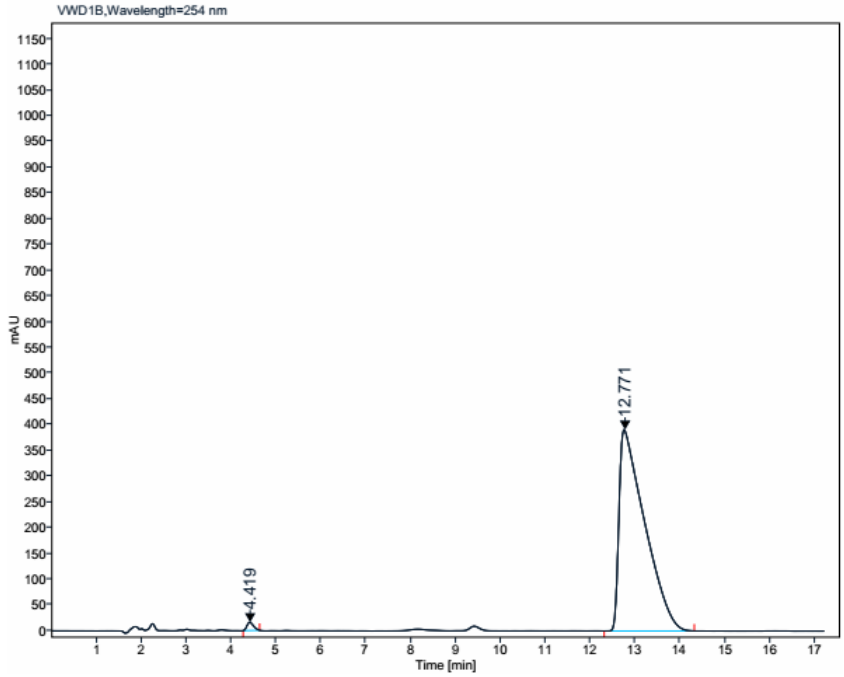
RT	*Peak Area %*
4.391	50.46
12.763	49.54



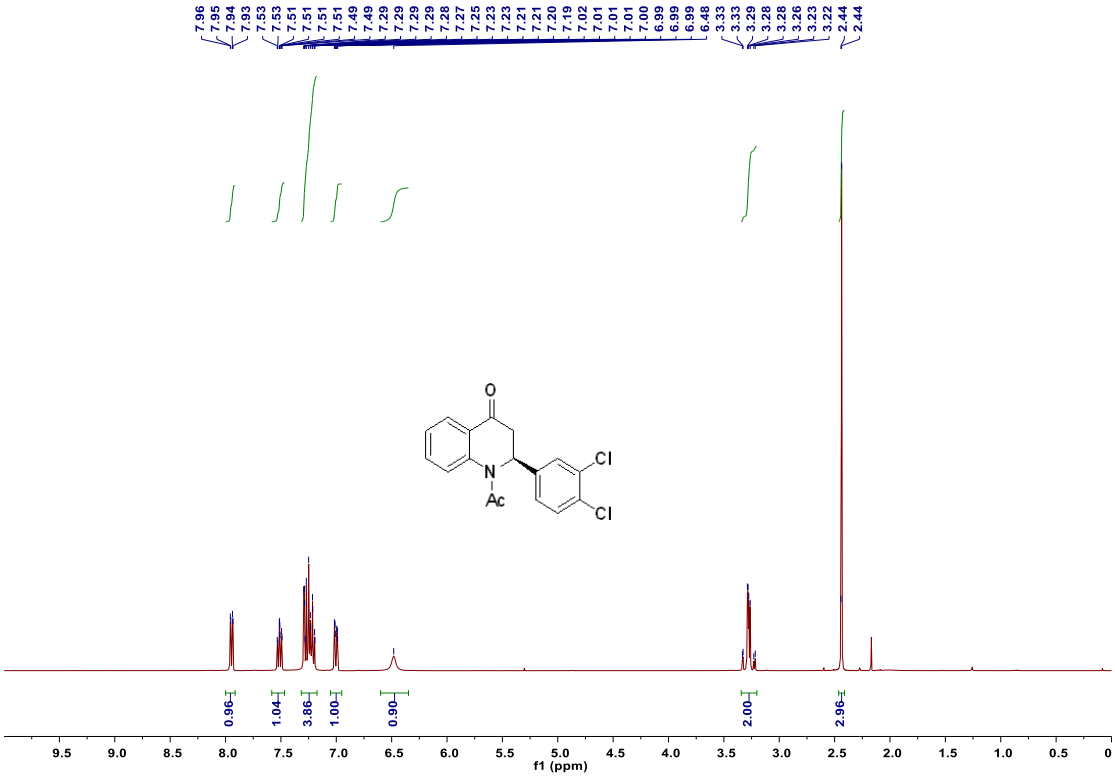
Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

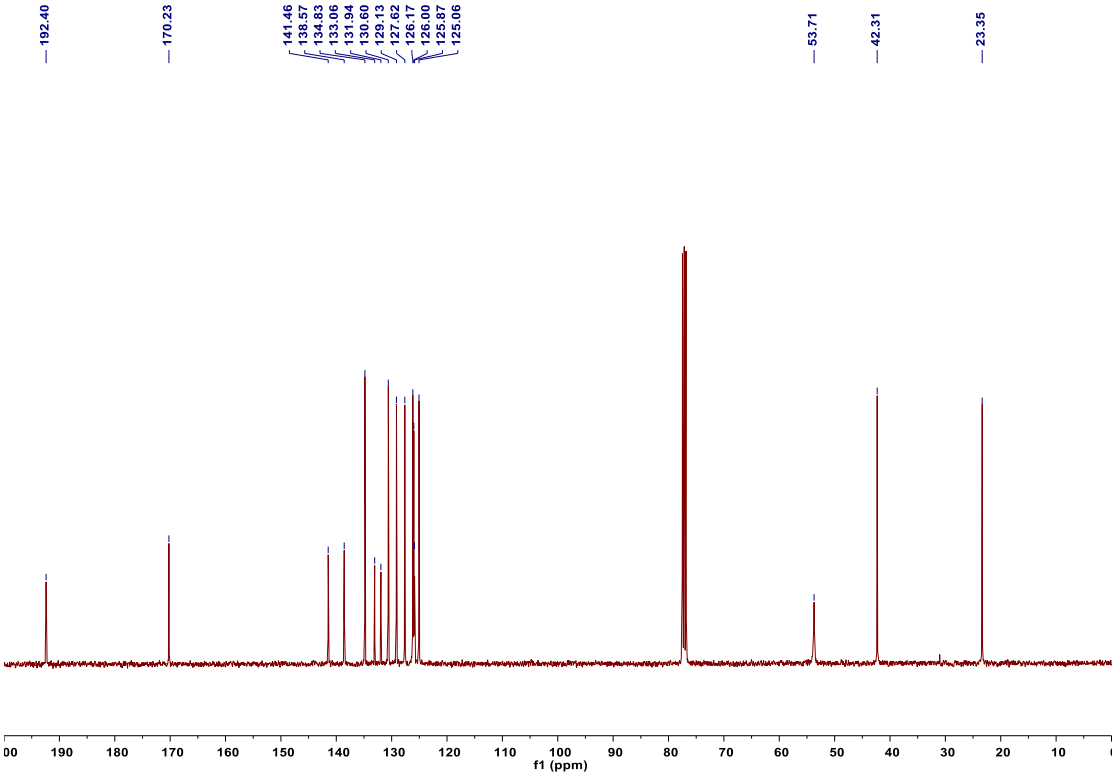
Injection Acquired Date 2020-08-04 10:35:16+02:00

RT	*Peak Area %*
4.419	1.04
12.771	98.96



Compound **(*S*)-3m**

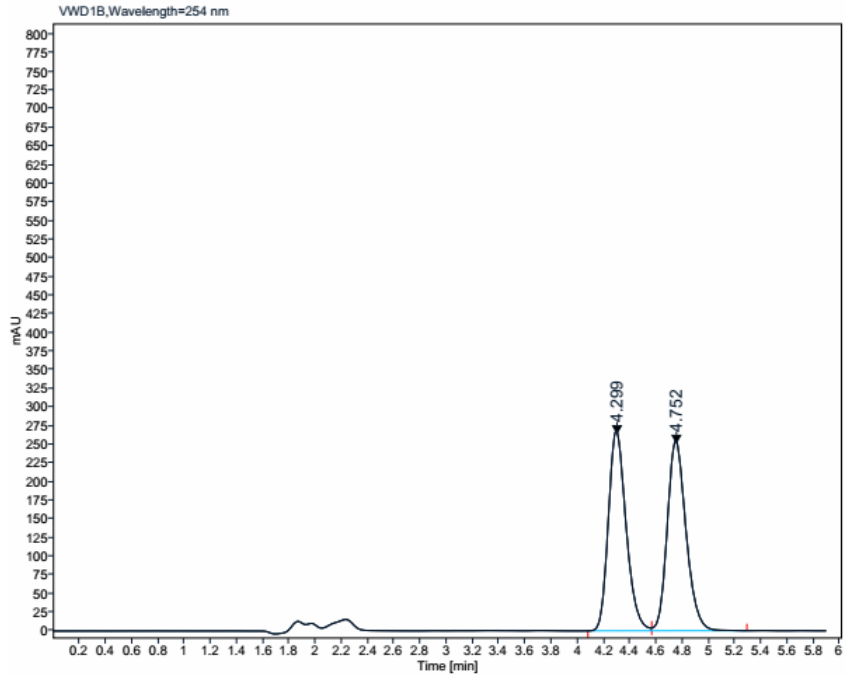




Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-08 12:14:24+02:00

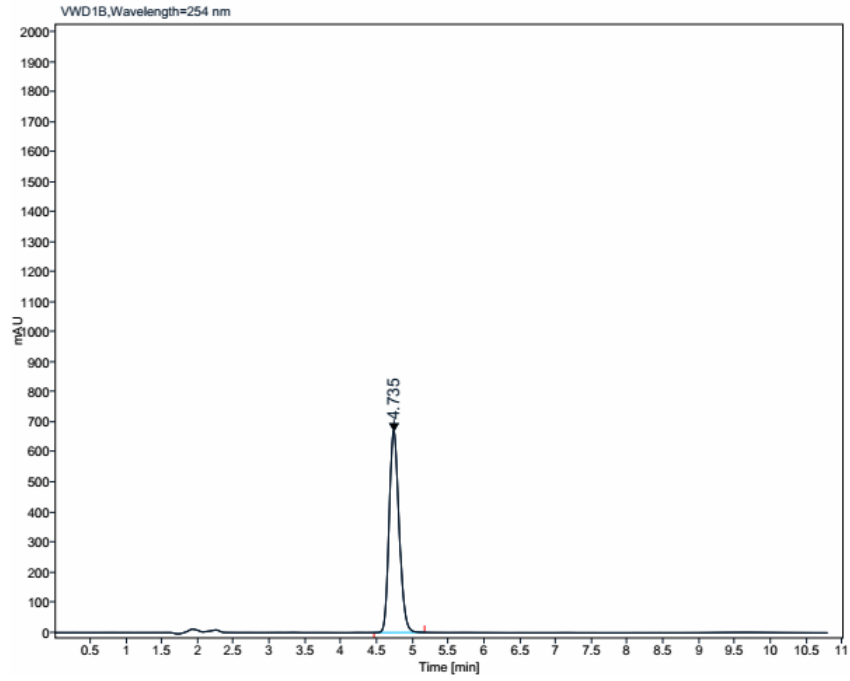
RT	Peak Area %
4.299	49.85
4.752	50.15



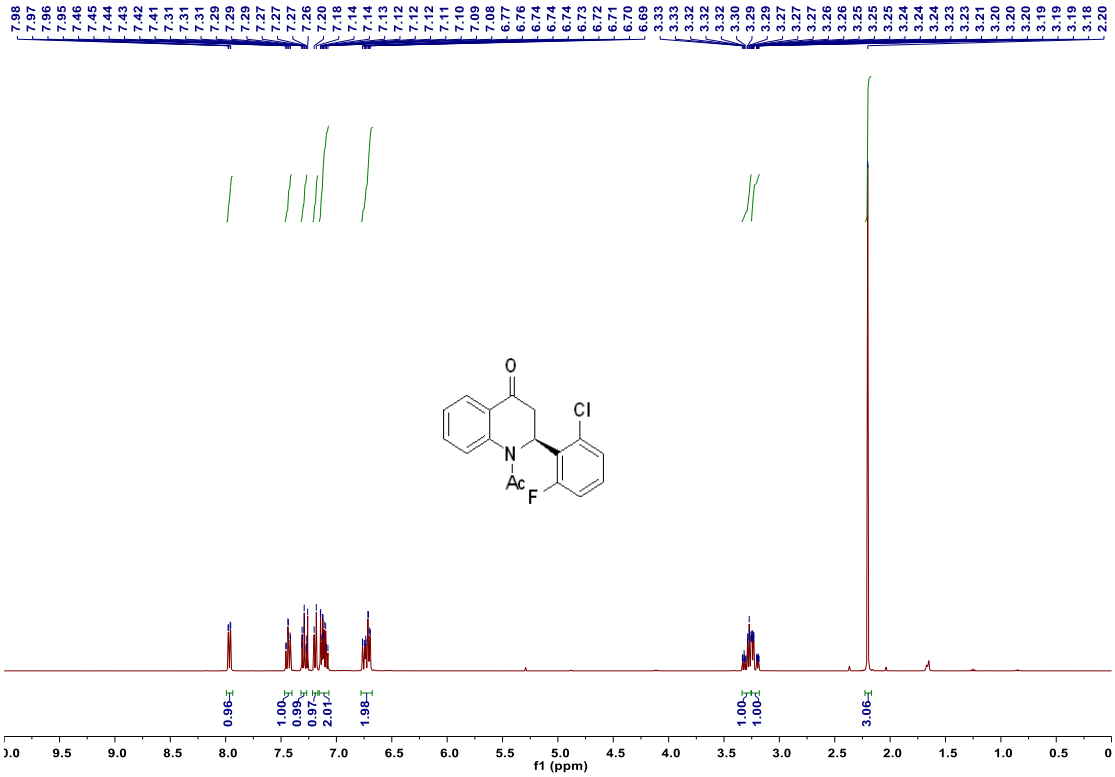
Injection Acq Method Name ASH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

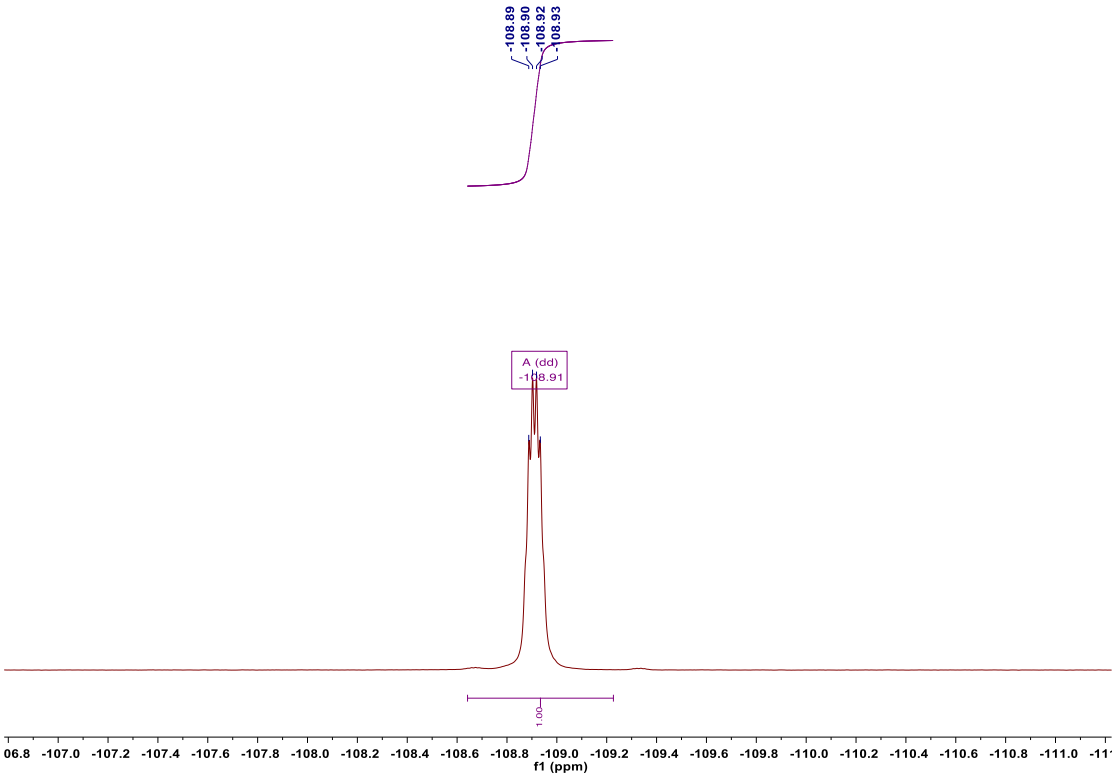
Injection Acquired Date 2020-07-29 17:06:30+02:00

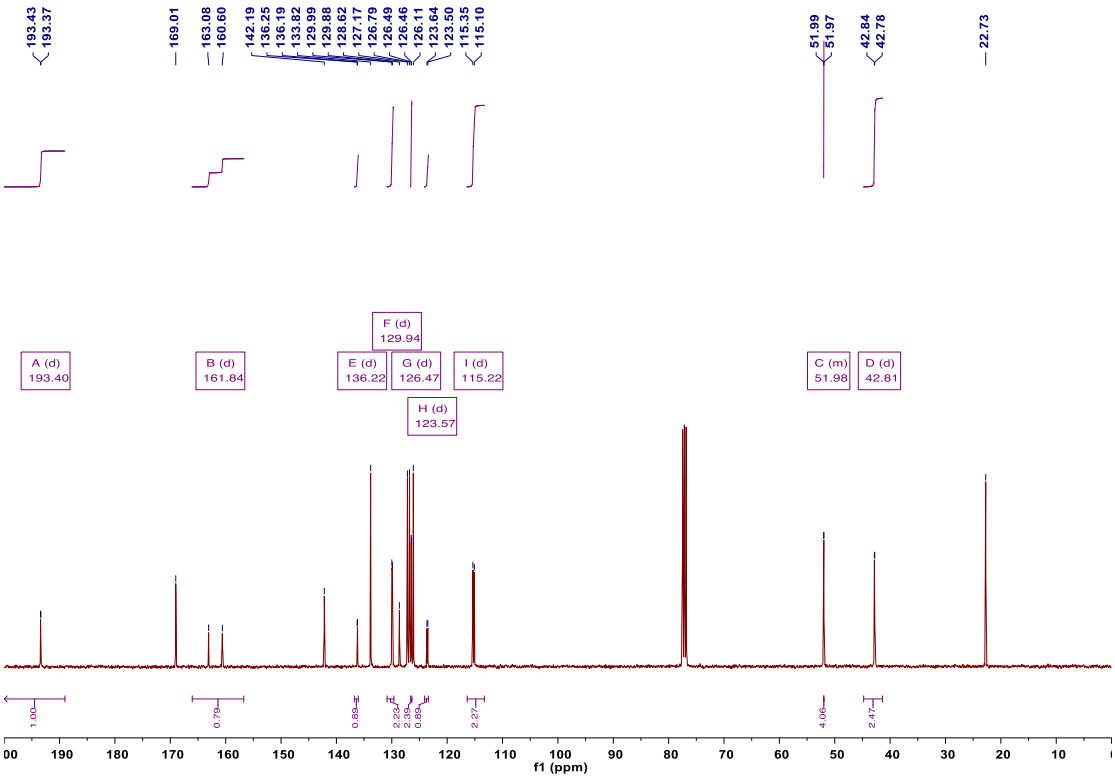
RT	Peak Area %
4.735	100.00



Compound **(*S*)-3n**



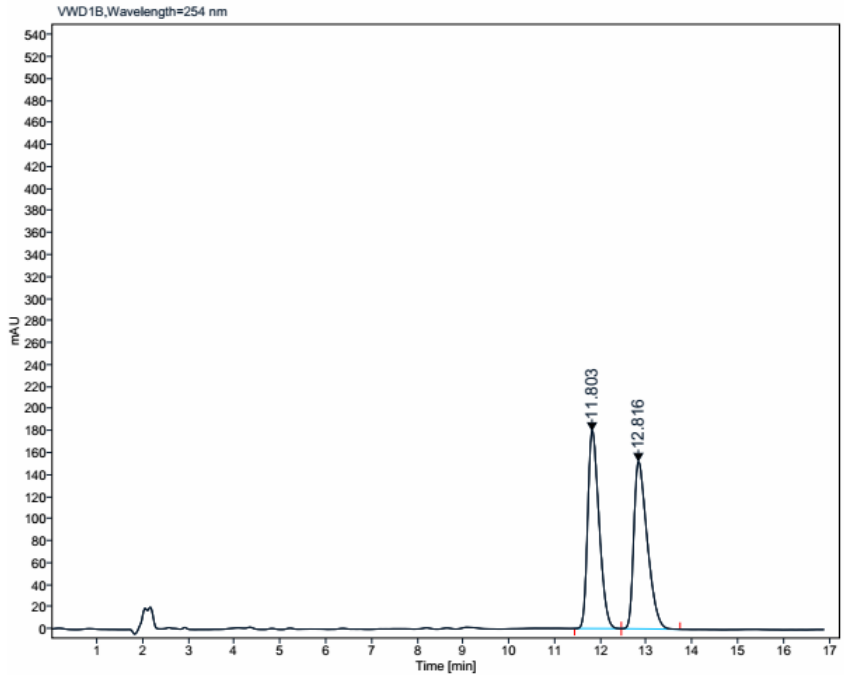




Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-08 14:52:22+02:00

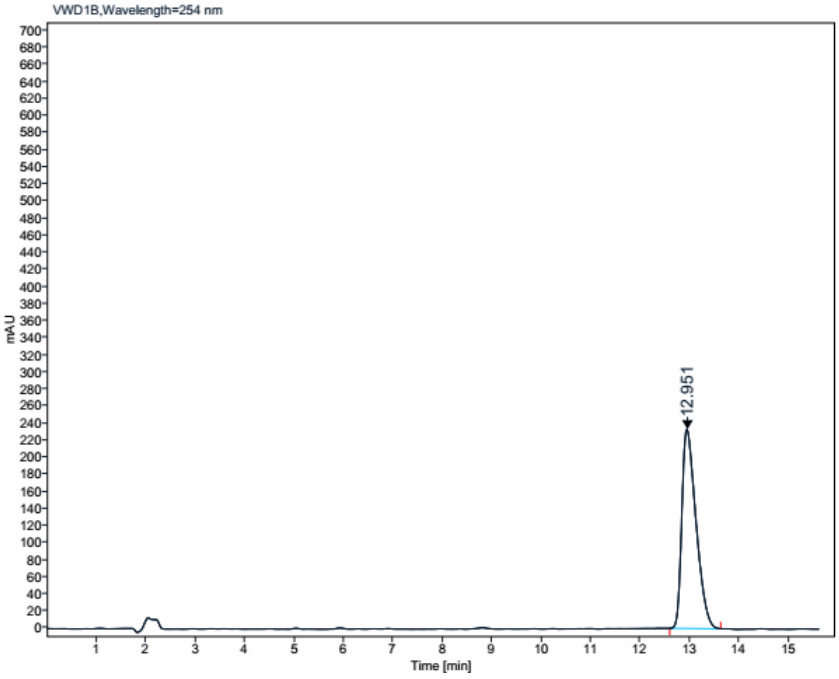
RT	*Peak Area %*
11.803	50.06
12.816	49.94



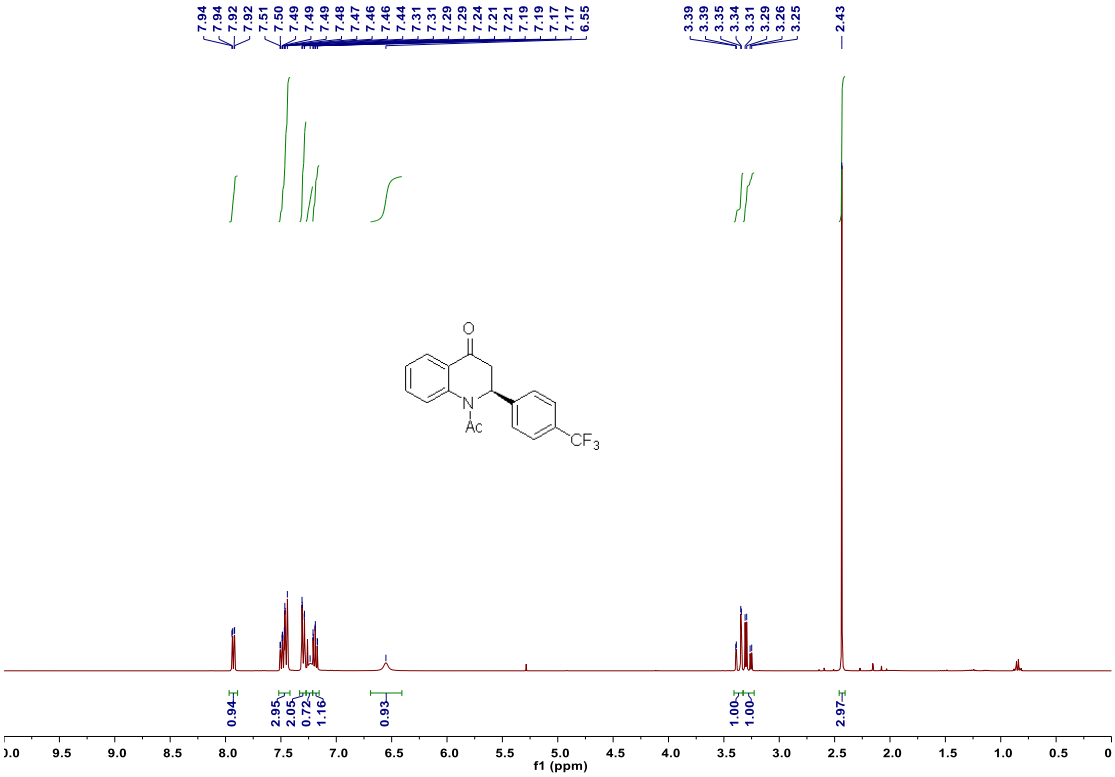
Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 20% MeOH.amx

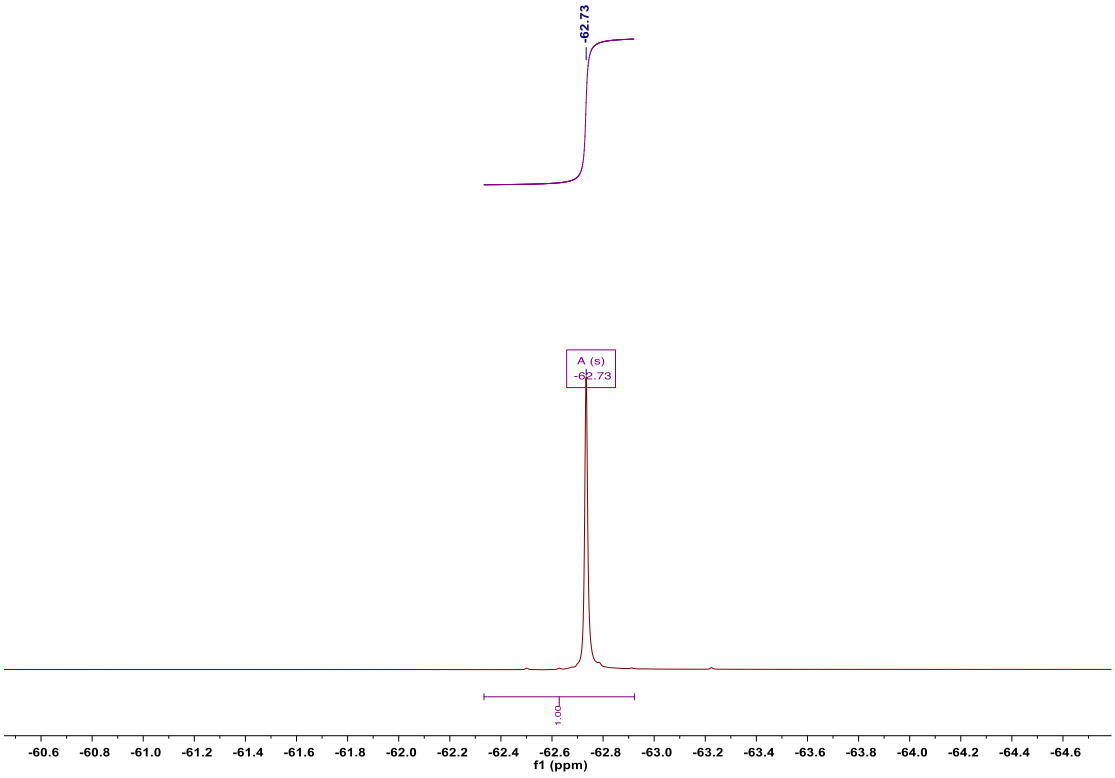
Injection Acquired Date 2020-08-04 16:07:22+02:00

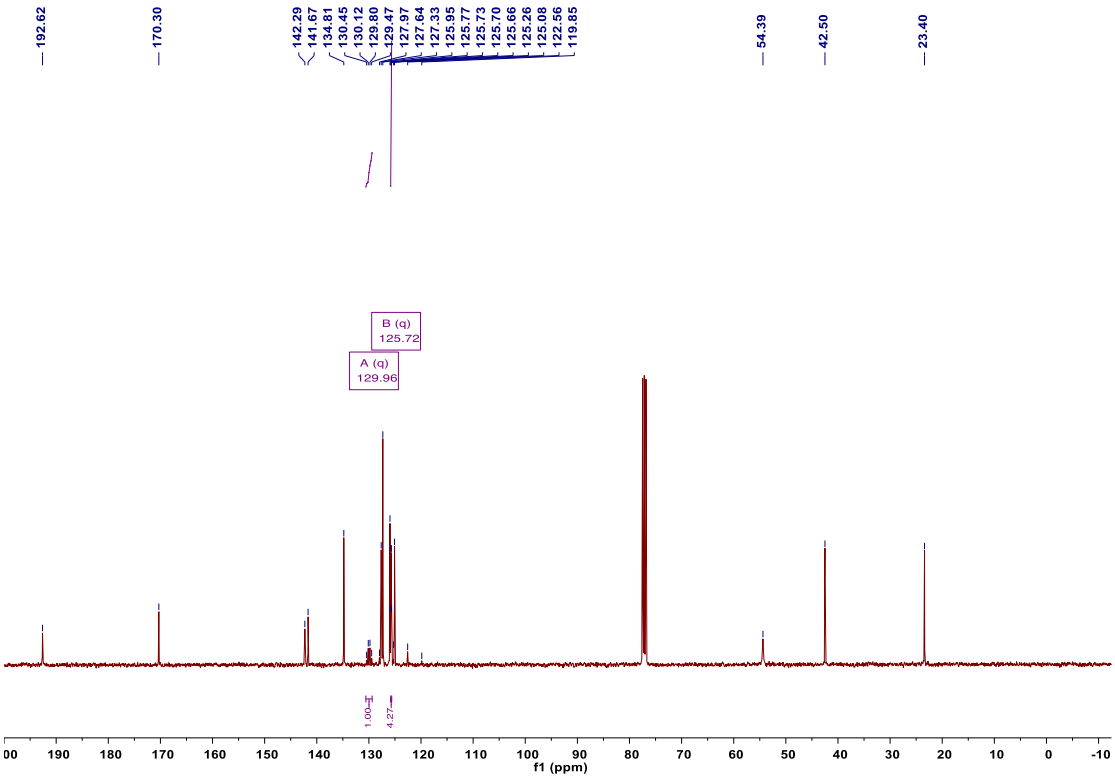
RT	*Peak Area %*
12.951	100.00



Compound ***(S)*-3o**



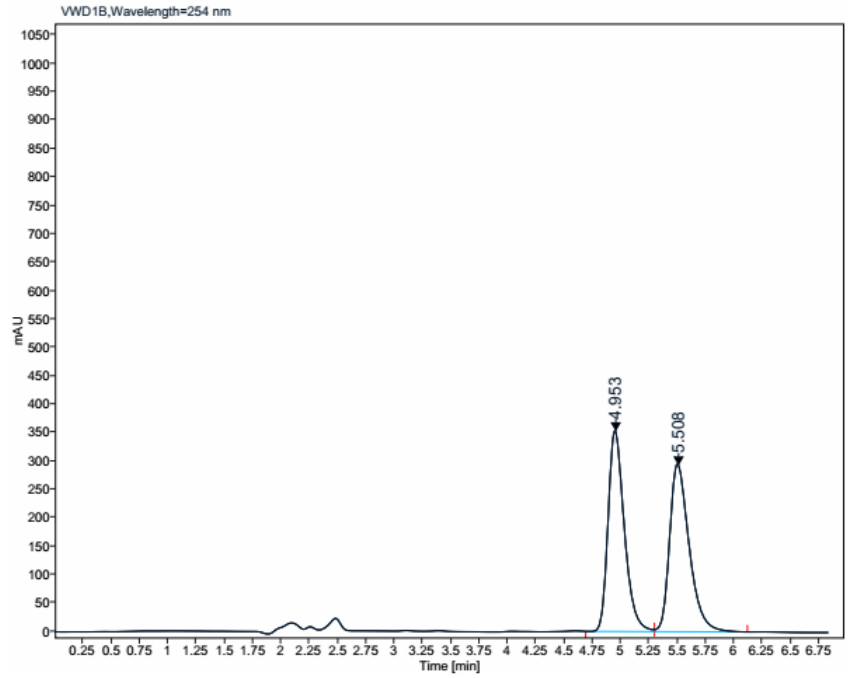




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-08 14:06:18+02:00

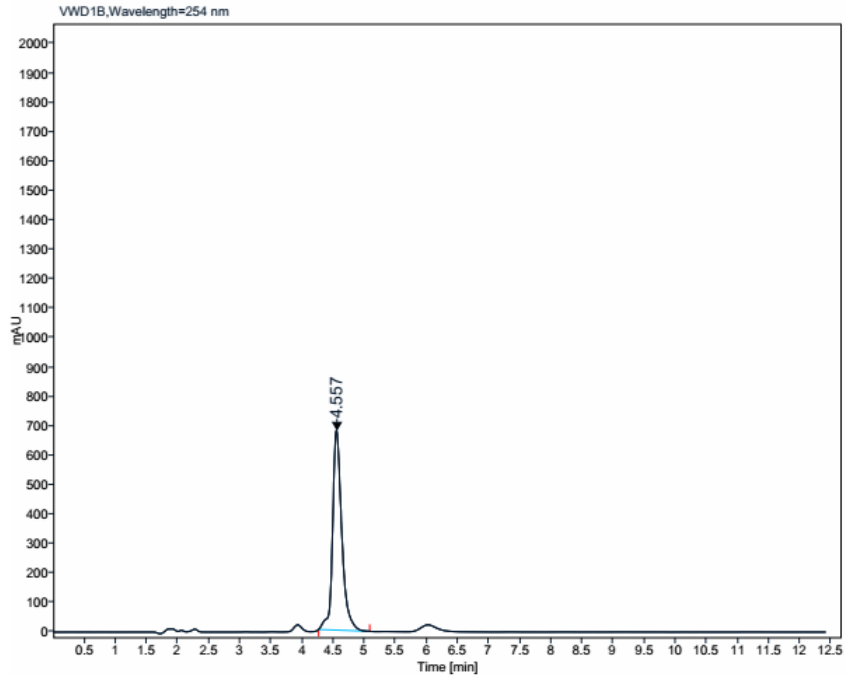
RT	*Peak Area %*
4.953	49.88
5.508	50.12



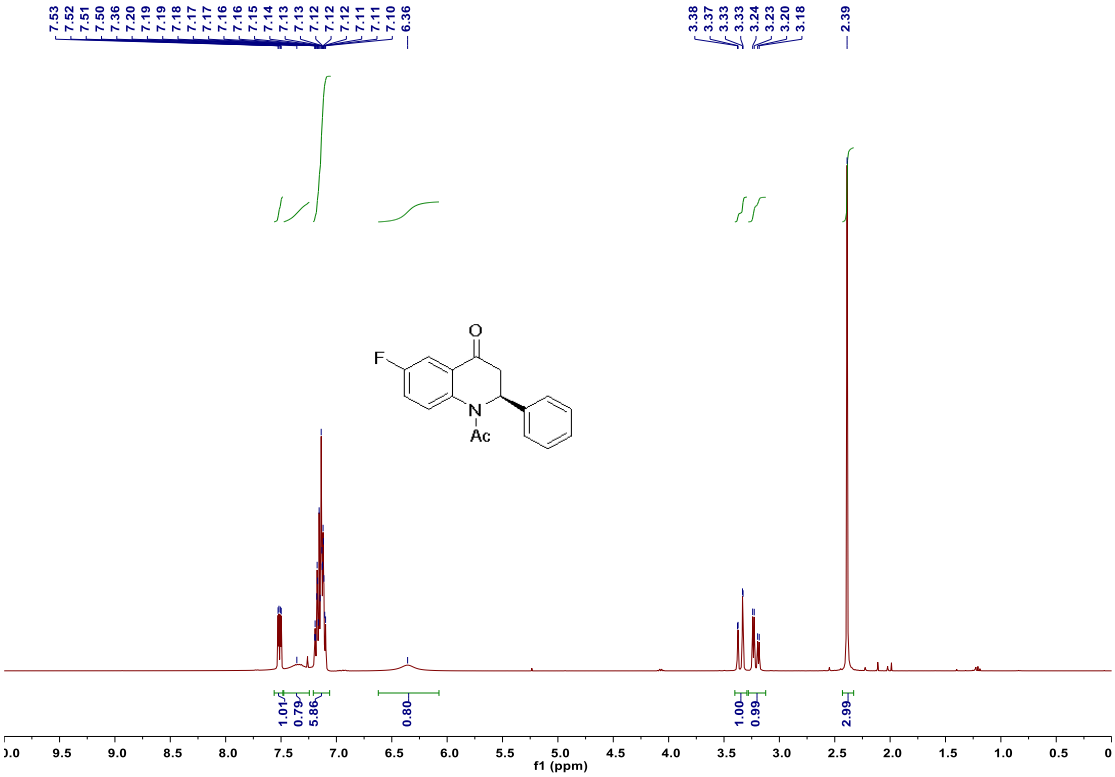
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

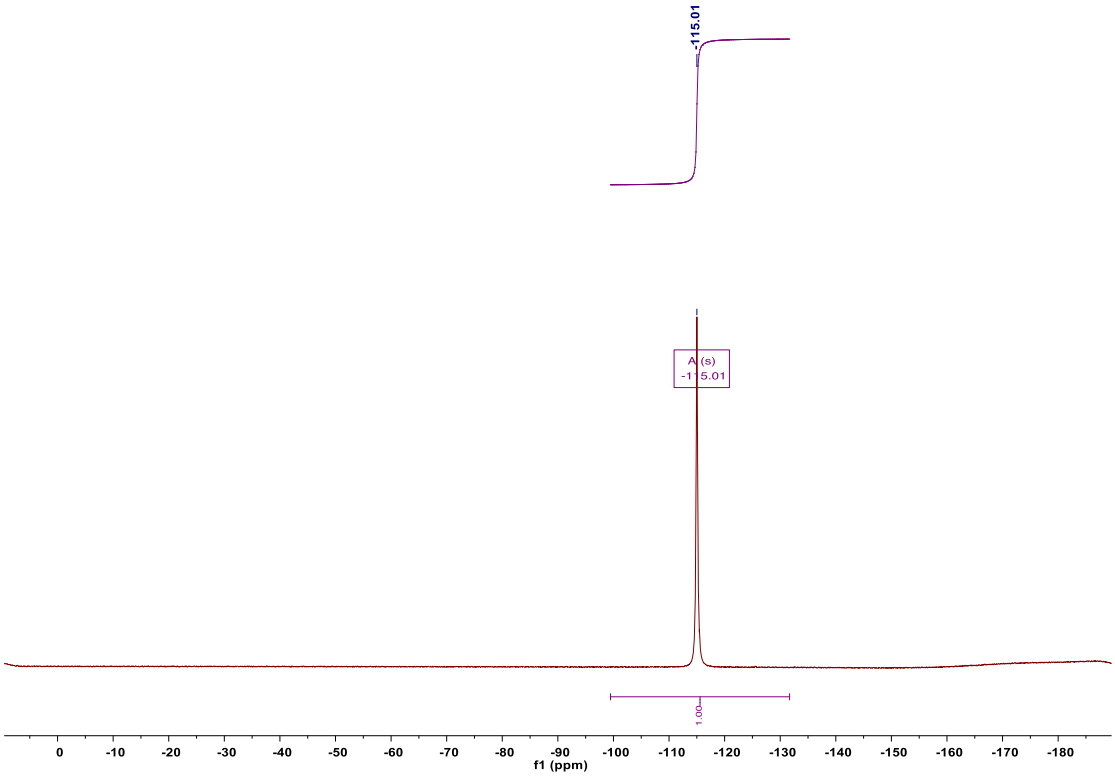
Injection Acquired Date 2020-07-30 10:18:11+02:00

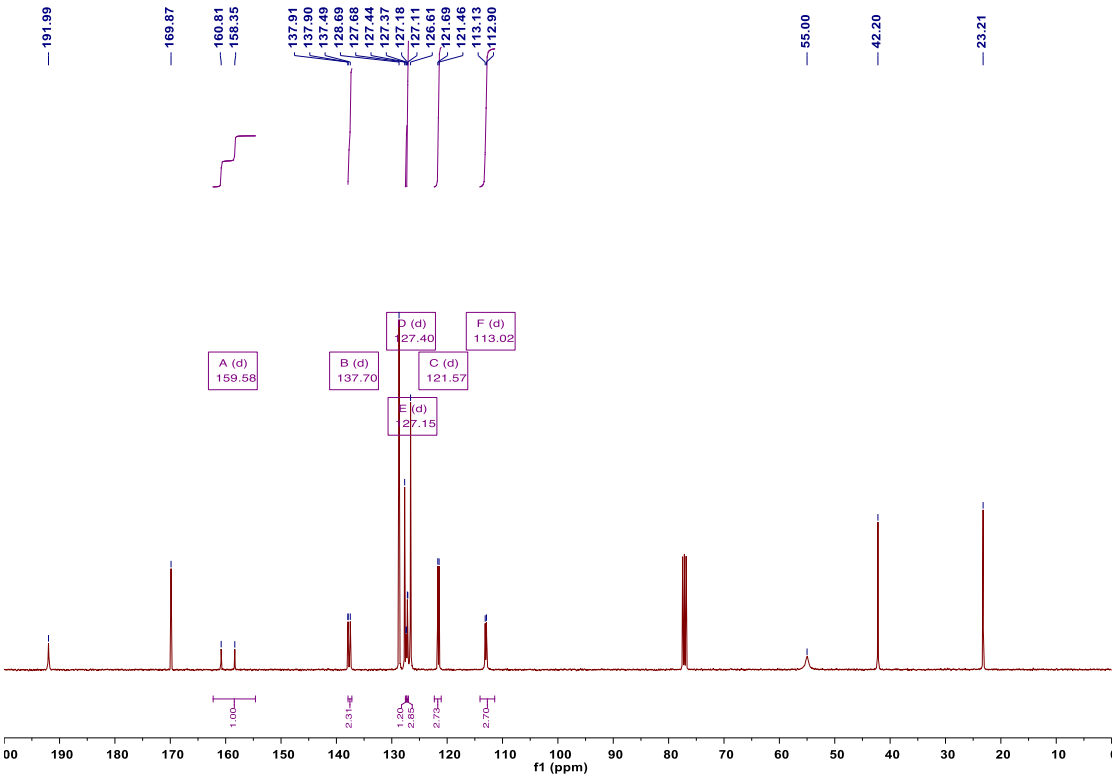
RT	*Peak Area %*
4.557	100.00



Compound ***(S)*-3p**



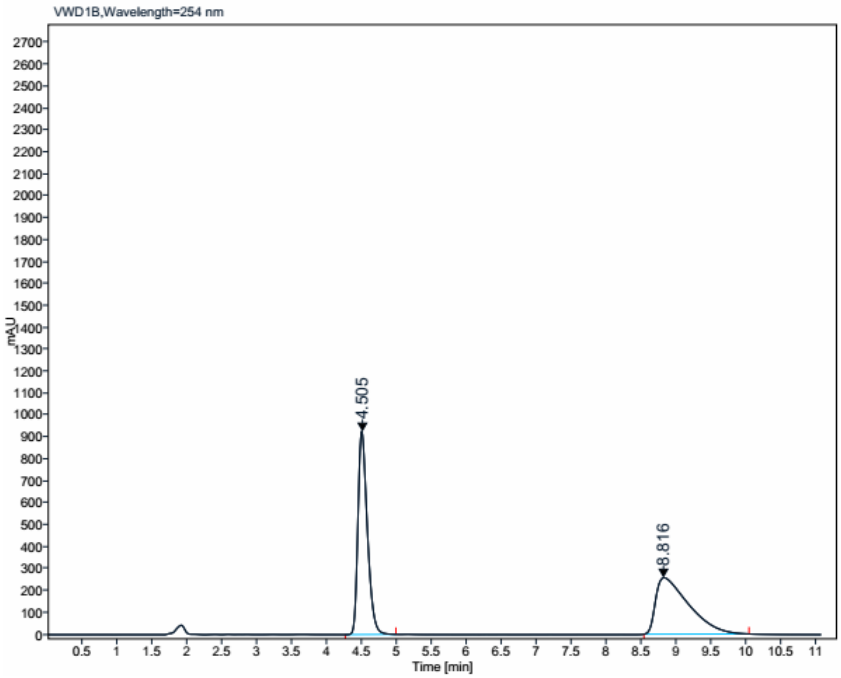




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-02 16:25:55+02:00

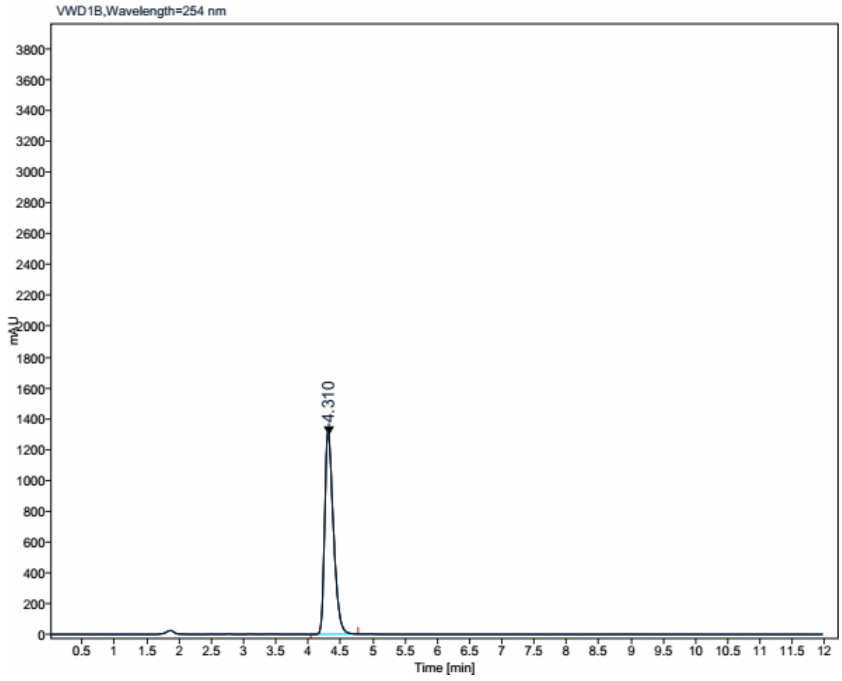
RT	*Peak Area %*
4.505	50.69
8.816	49.31



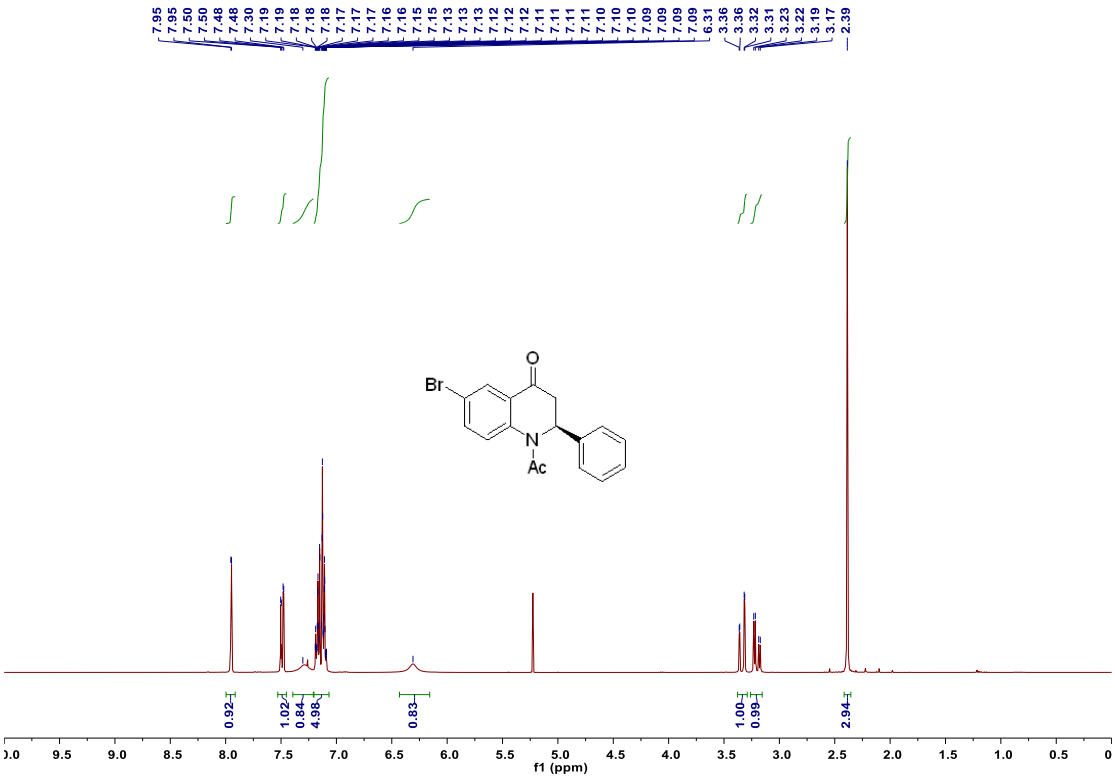
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

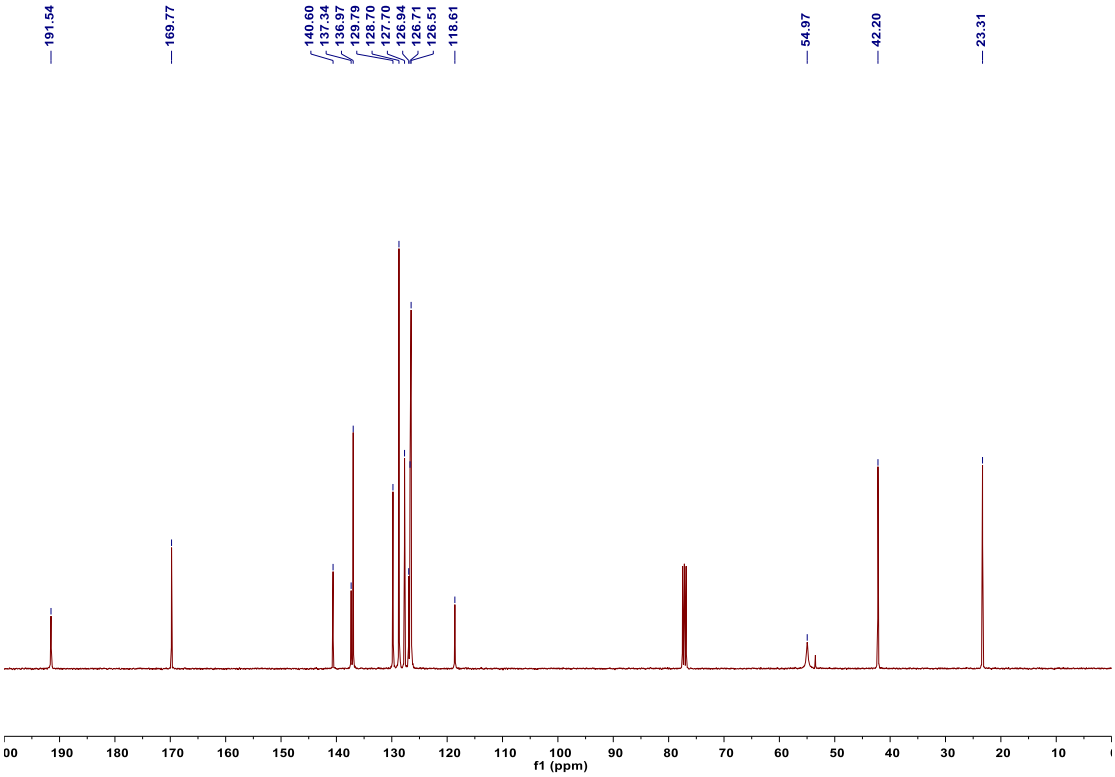
Injection Acquired Date 2020-08-05 15:29:00+02:00

RT	*Peak Area %*
4.310	100.00



Compound ***(S)*-3q**

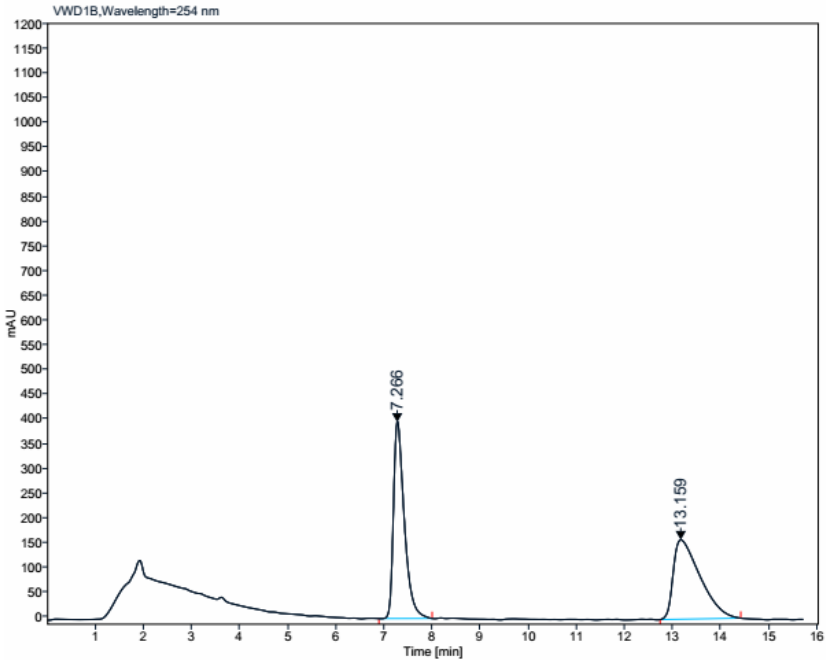




Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-06-12 13:47:00+02:00

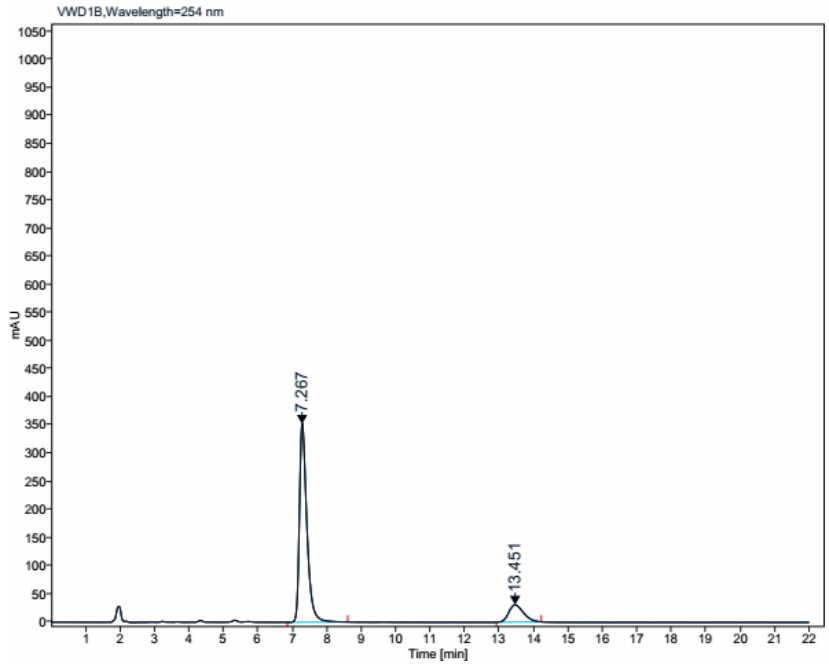
RT	Peak Area %
7.266	50.12
13.159	49.88



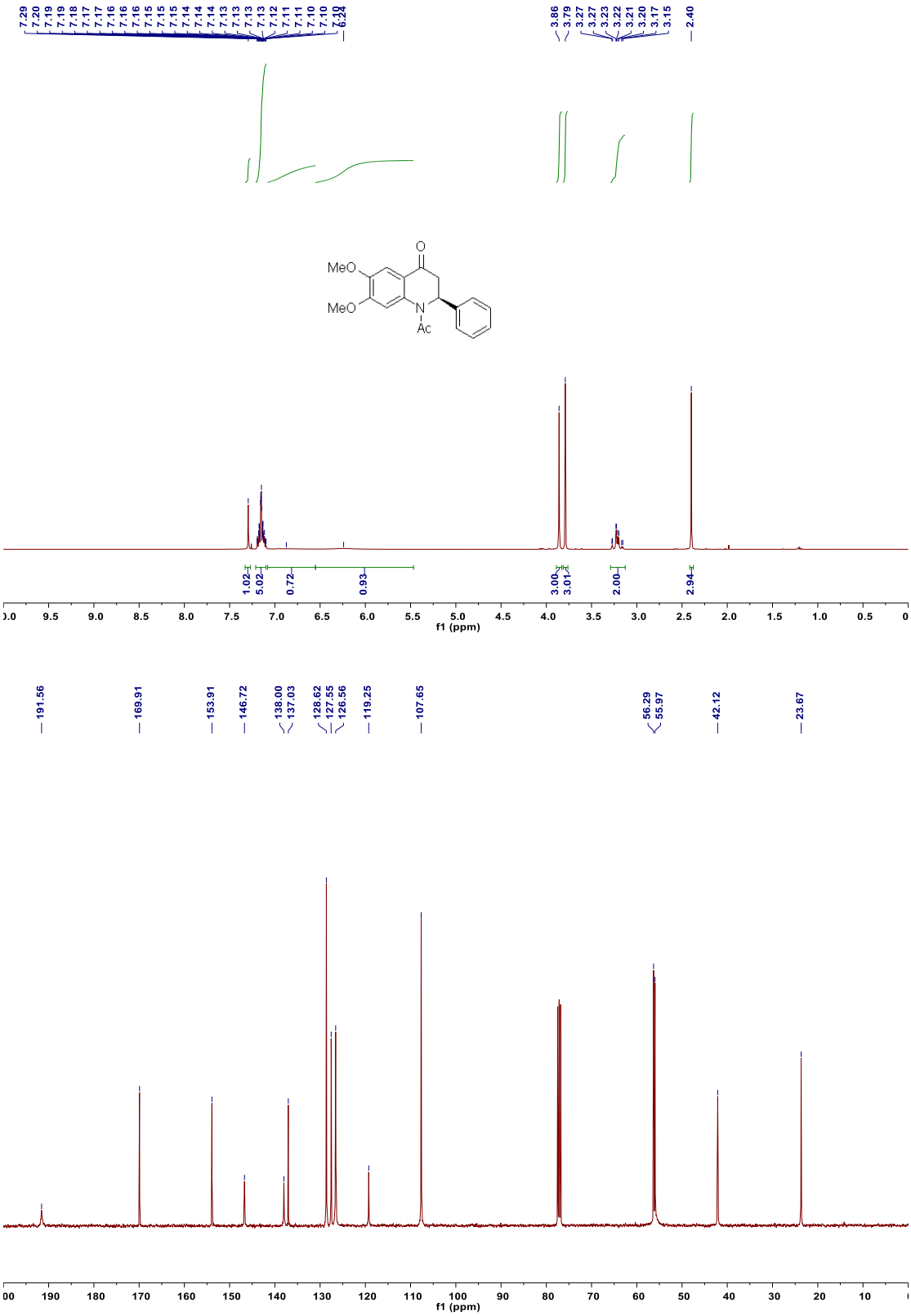
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-23 17:26:20+02:00

RT	Peak Area %
7.267	85.56
13.451	14.44



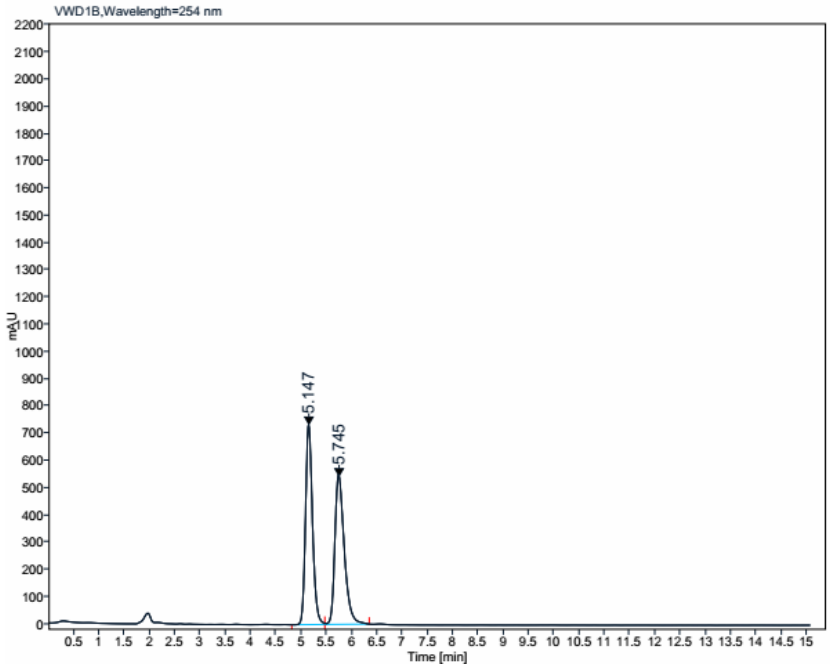
Compound **(*S*)-3r**



Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

Injection Acquired Date 2020-07-10 10:40:54+02:00

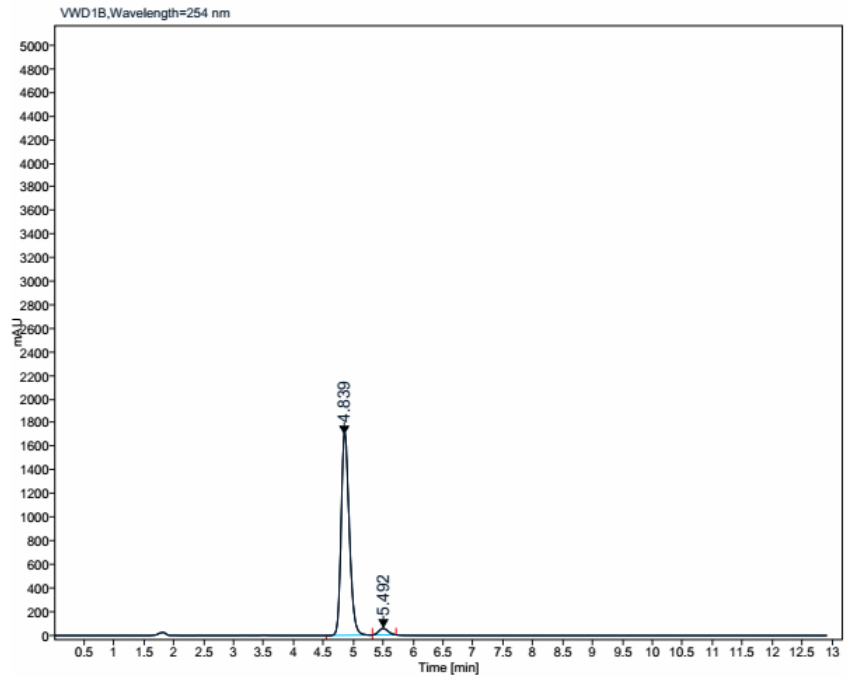
RT	*Peak Area %*
5.147	49.82
5.745	50.18



Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 40% MeOH.amx

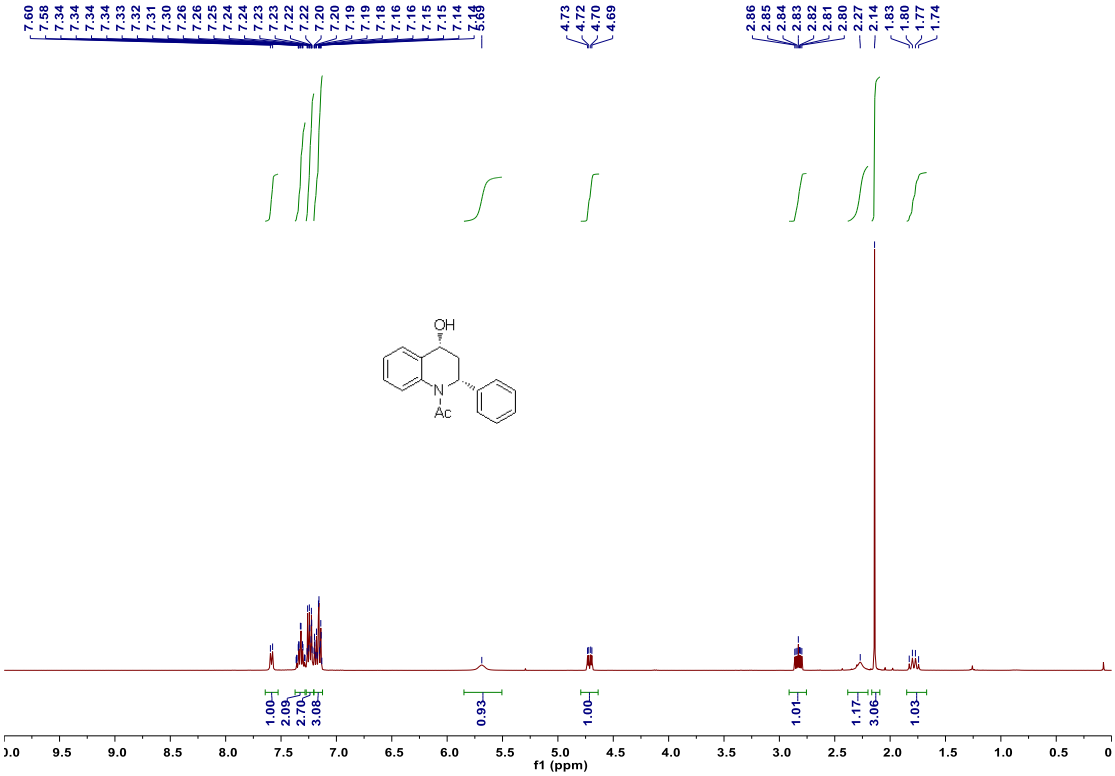
Injection Acquired Date 2020-07-30 09:35:35+02:00

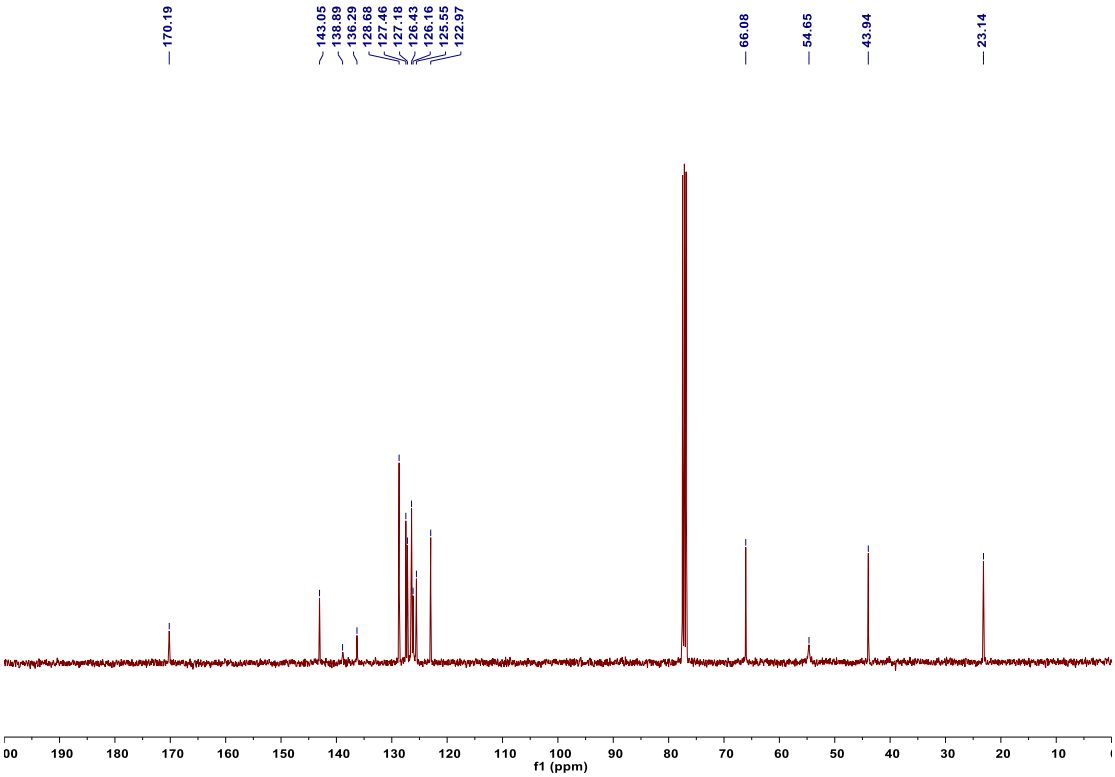
RT	*Peak Area %*
4.839	96.52
5.492	3.48



X. NMR spectra and SFC of compounds 4a-4r

Compound **4a**

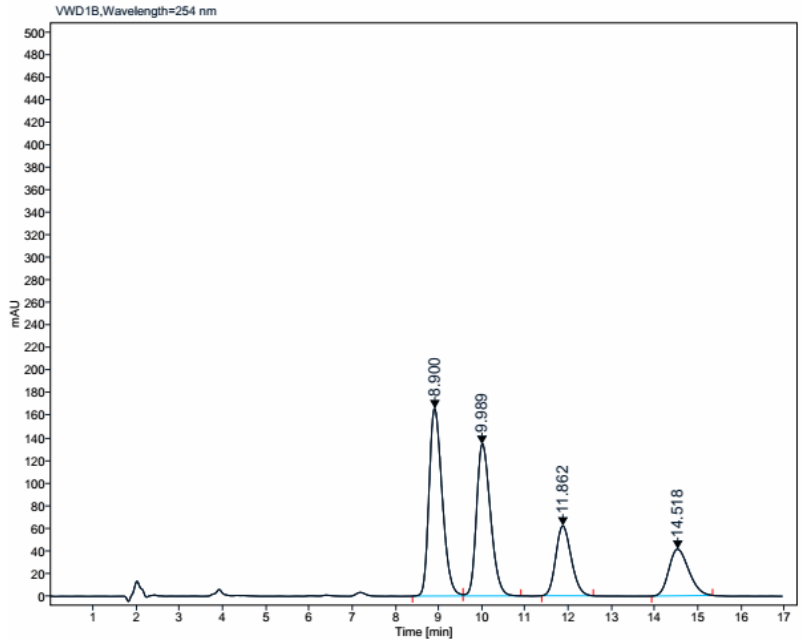




Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 10% EtOH.amx

Injection Acquired Date 2020-08-05 11:54:02+02:00

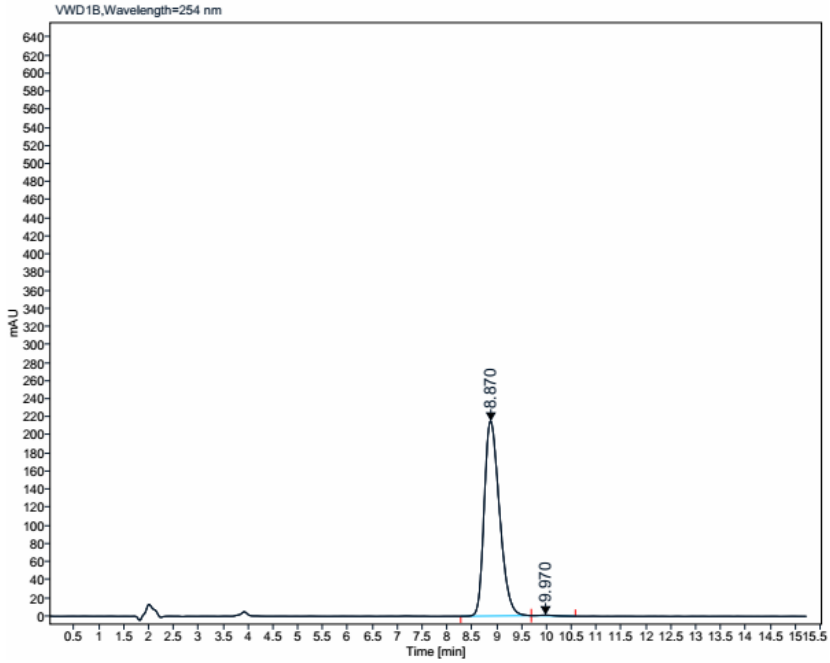
RT	*Peak Area %*
8.900	37.36
9.989	32.23
11.862	16.37
14.518	14.03



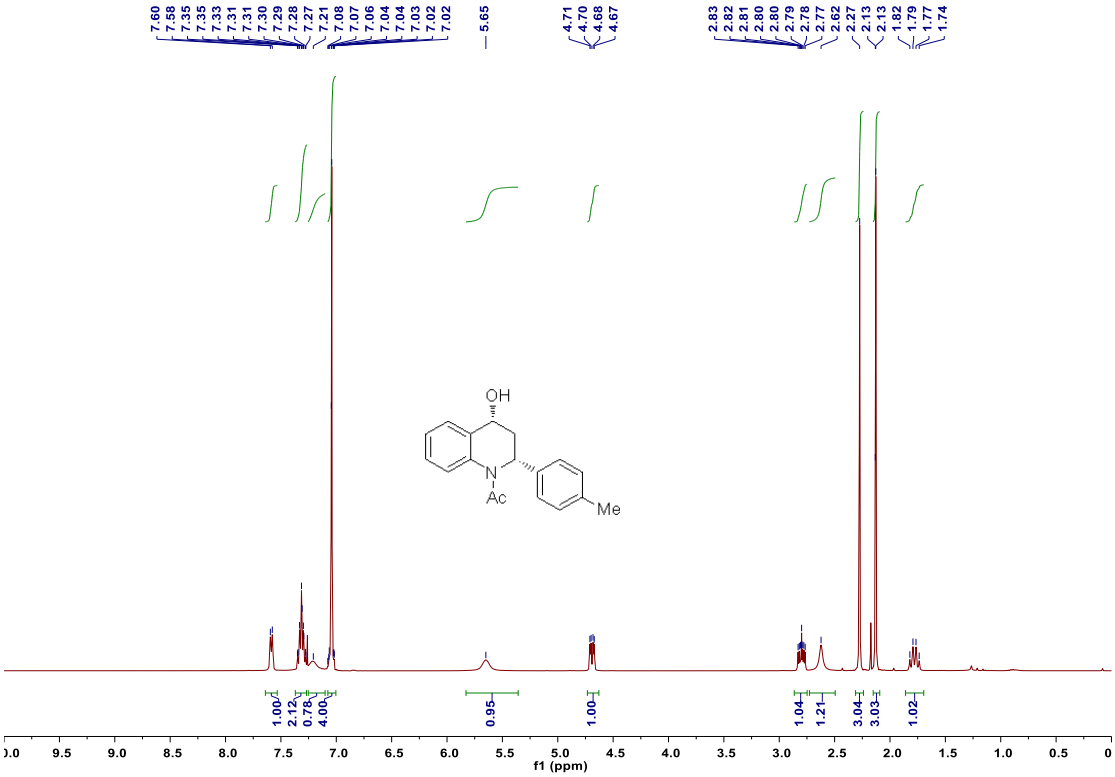
Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 10% EtOH.amx

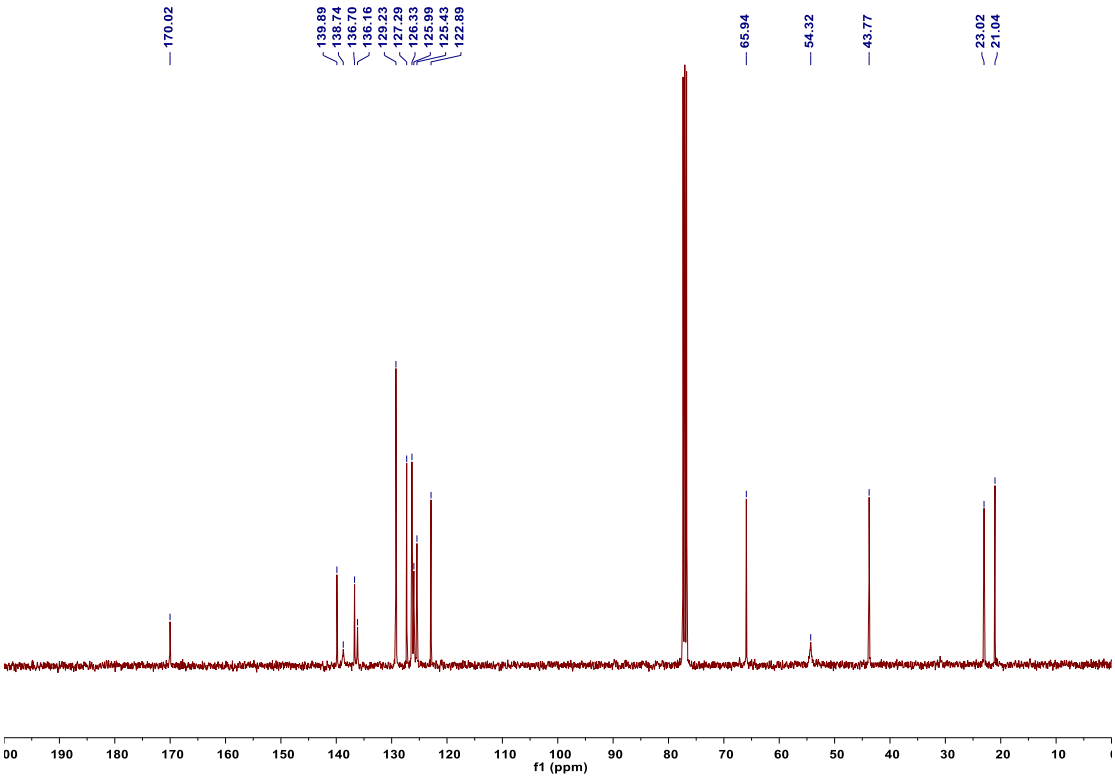
Injection Acquired Date 2020-08-05 11:37:56+02:00

RT	*Peak Area %*
8.870	99.72
9.970	0.28



Compound **4b**

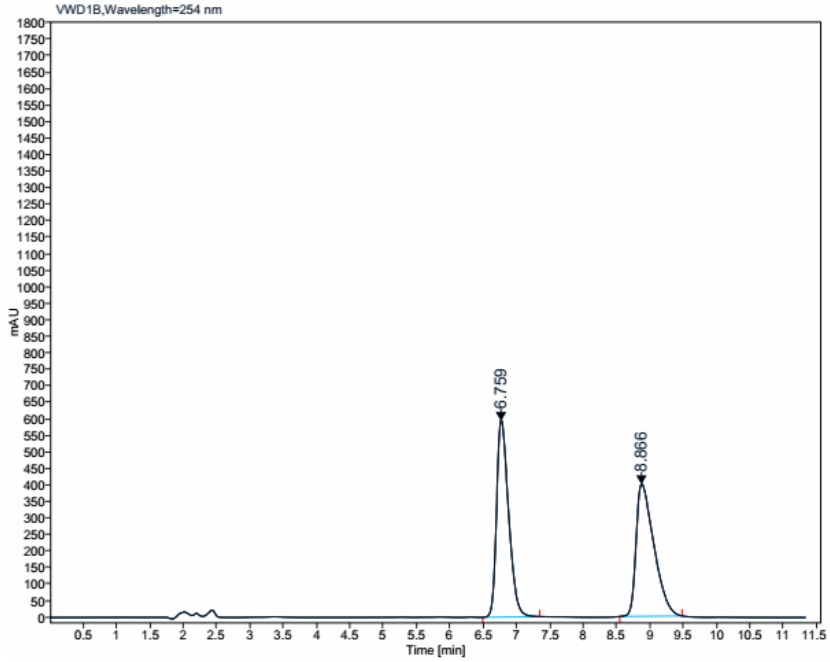

7.60
7.58
7.35
7.35
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.21
7.08
7.07
7.06
7.04
7.04
7.03
7.02
7.02
5.65
4.71
4.70
4.68
4.67
2.83
2.82
2.81
2.80
2.80
2.79
2.78
2.77
2.62
2.27
2.13
2.13
1.82
1.79
1.77
1.74
OH
N
Ac
Me
1.00
2.12
0.78
4.00
0.95
1.00
1.04
1.21
3.04
3.03
1.02
f1 (ppm)


170.02
139.89
138.74
136.70
136.16
129.23
127.29
126.33
125.99
125.43
122.89
65.94
54.32
43.77
23.02
21.04
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-07 18:35:12+02:00

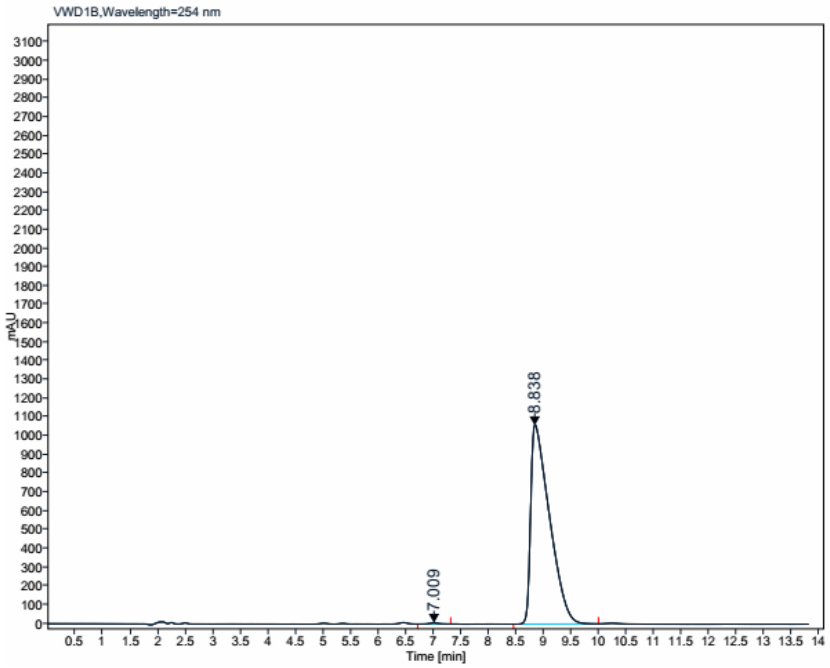
RT	*Peak Area %*
6.759	50.14
8.866	49.86



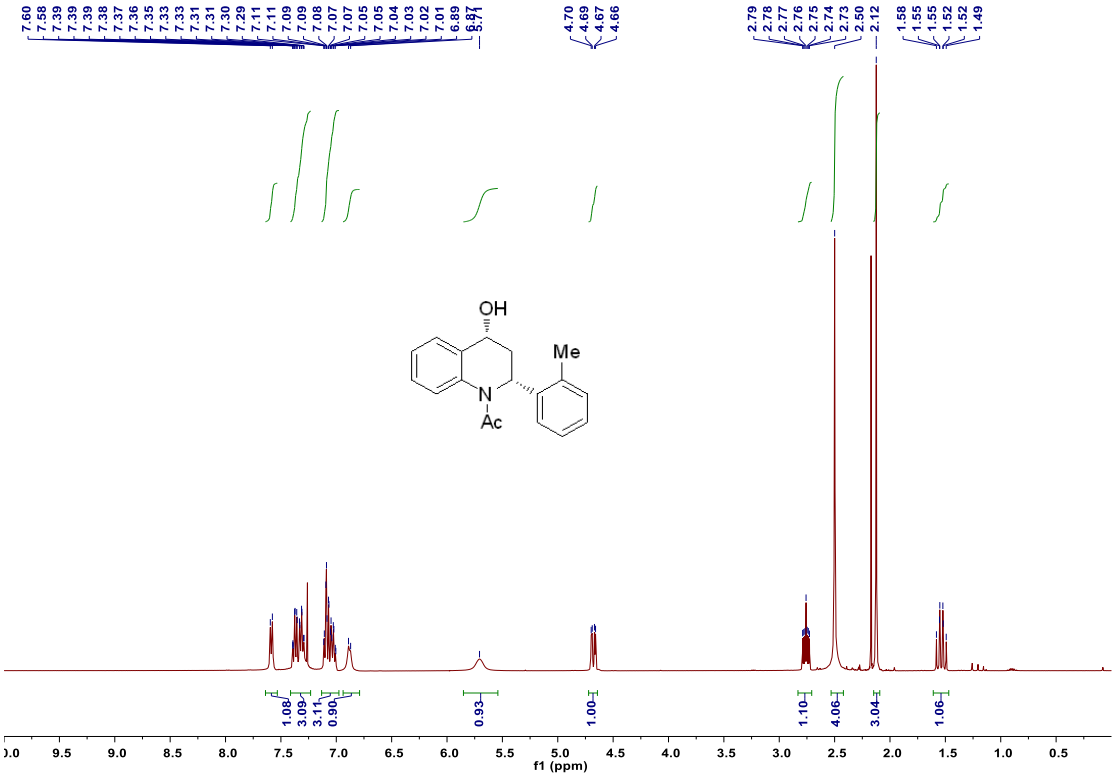
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

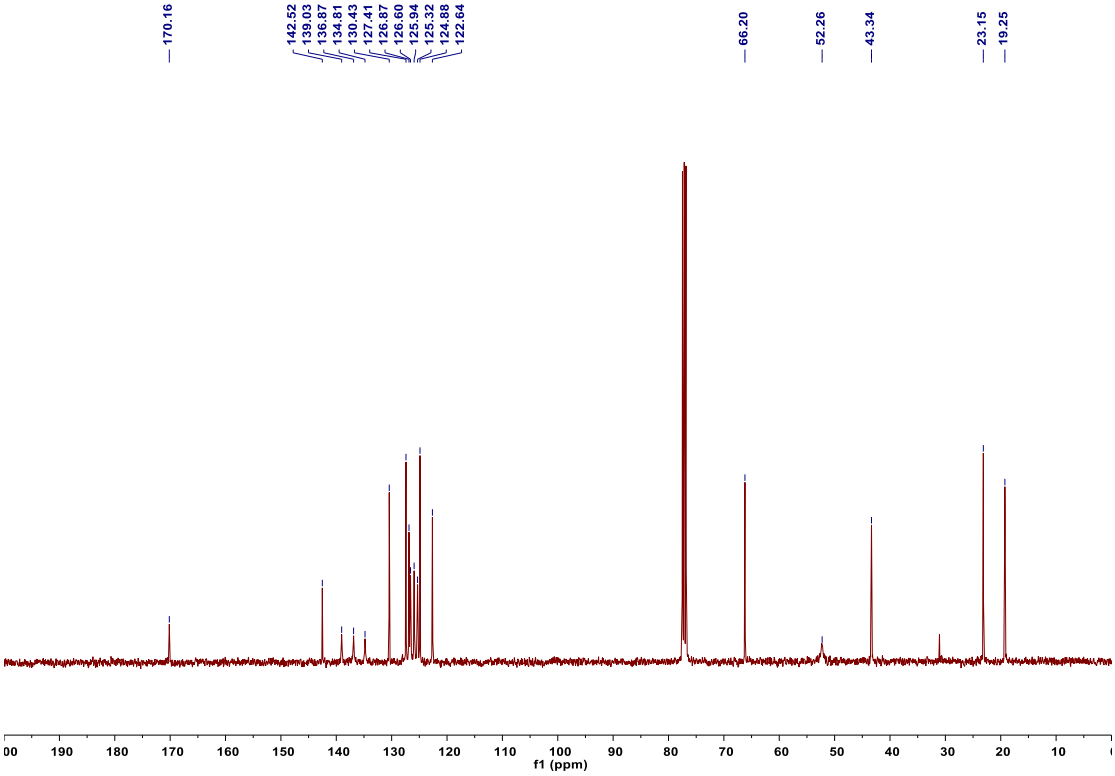
Injection Acquired Date 2020-07-27 14:25:32+02:00

RT	*Peak Area %*
7.009	0.26
8.838	99.74



Compound **4c**

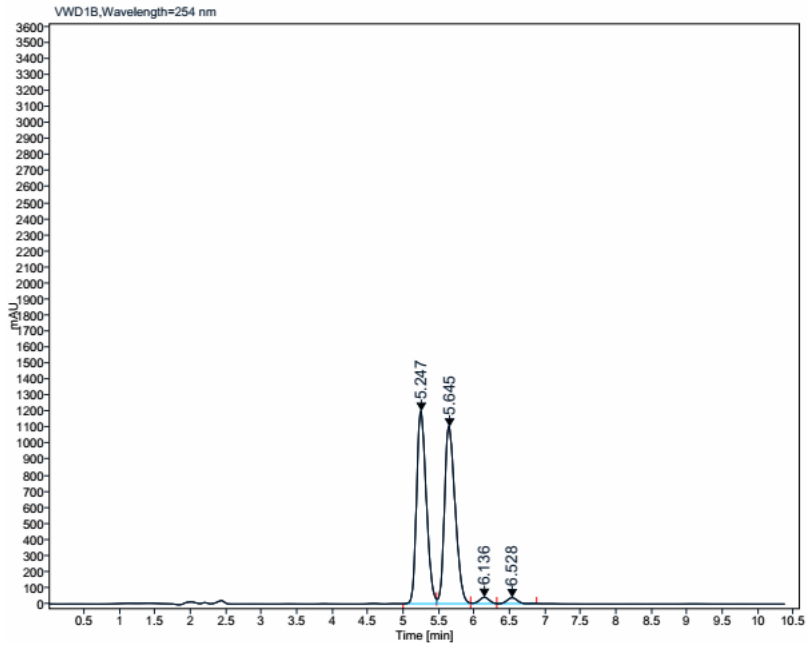

7.60 7.58 7.39 7.39 7.39 7.38 7.37 7.36 7.35 7.33 7.33 7.31 7.31 7.30 7.29 7.11 7.11 7.09 7.09 7.08 7.07 7.07 7.05 7.05 7.04 7.03 7.02 7.01 6.89 6.87 5.71
4.70 4.69 4.67 4.66
2.79 2.78 2.77 2.76 2.75 2.74 2.73 2.50 2.12
1.58 1.55 1.55 1.52 1.52 1.49
OH
Me
N
Ac
1.08 3.09 3.11 0.90 0.93 1.00 1.10 4.06 3.04 1.06
f1 (ppm)


170.16
142.52 139.03 136.87 134.81 130.43 127.41 126.87 126.60 125.94 125.32 124.88 122.64
66.20 52.26 43.34 23.15 19.25
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-07 18:14:02+02:00

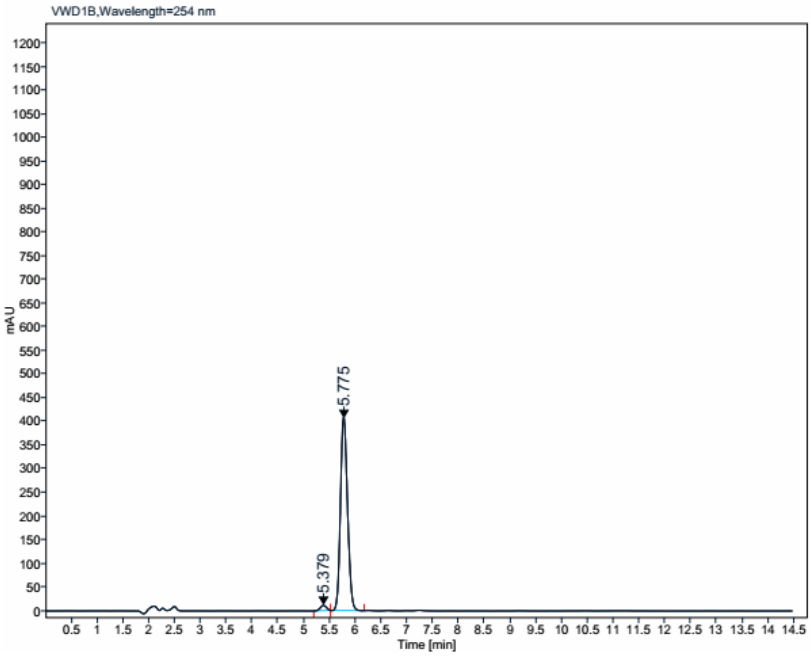
RT	*Peak Area %*
5.247	48.11
5.645	48.84
6.136	1.58
6.528	1.46



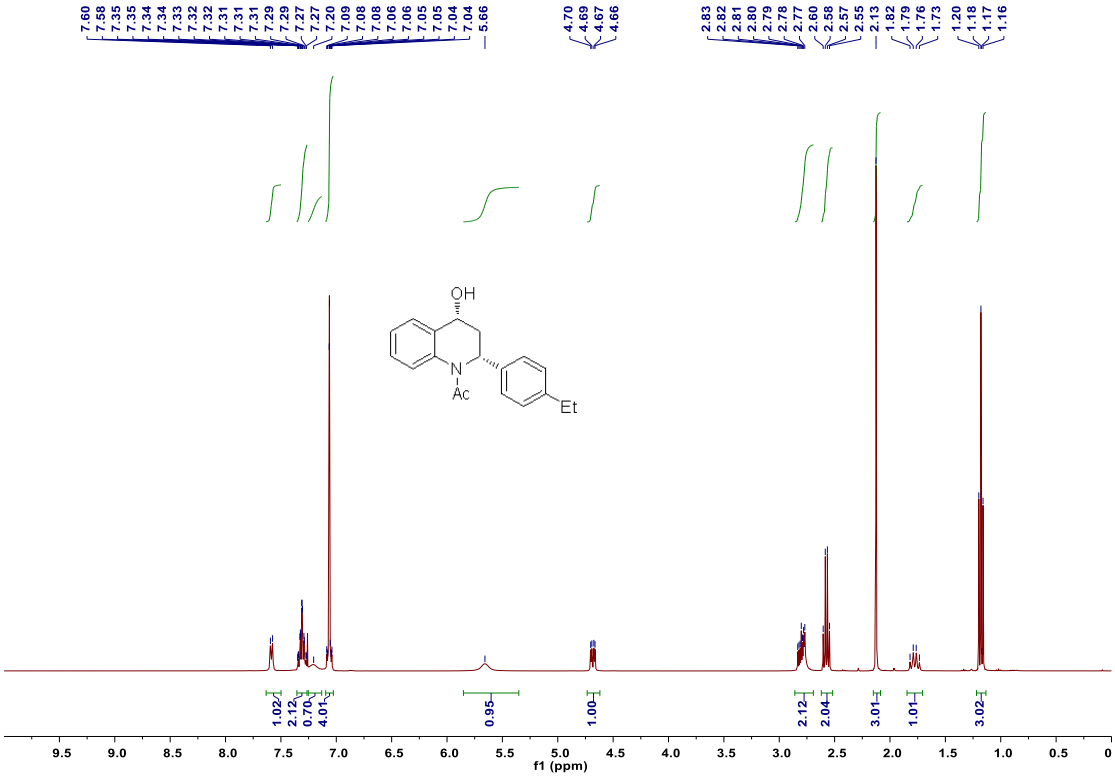
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

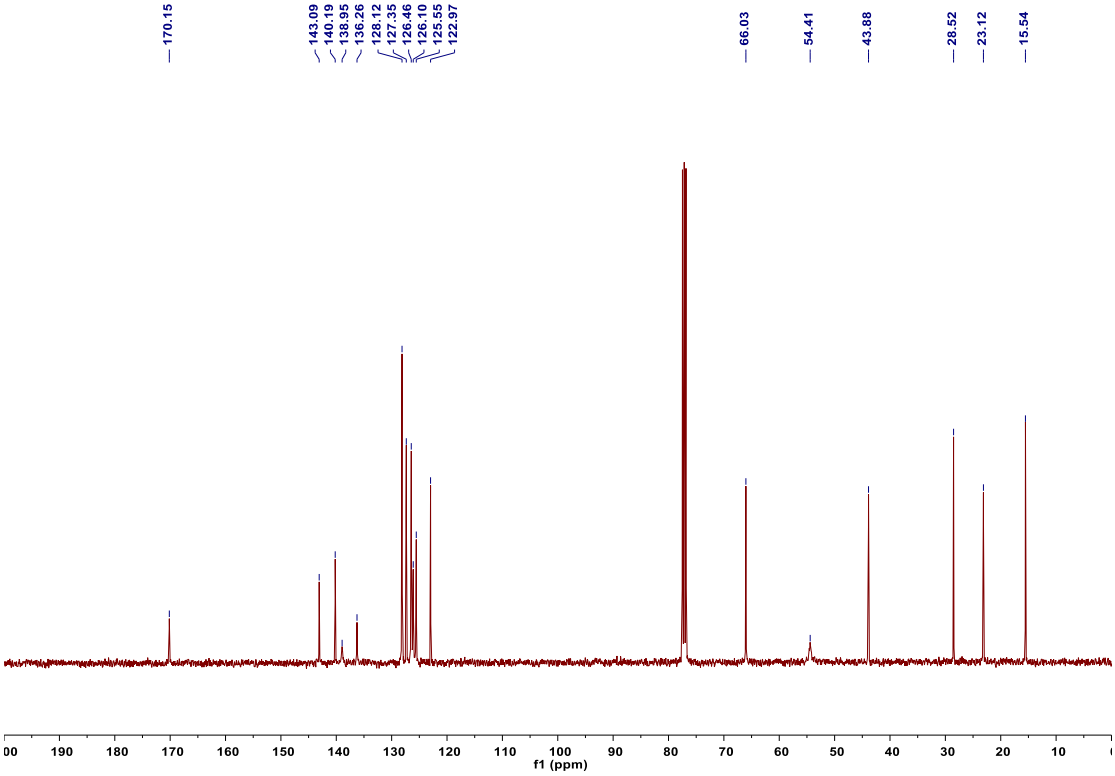
Injection Acquired Date 2020-07-24 09:37:10+02:00

RT	*Peak Area %*
5.379	2.27
5.775	97.73



Compound **4d**

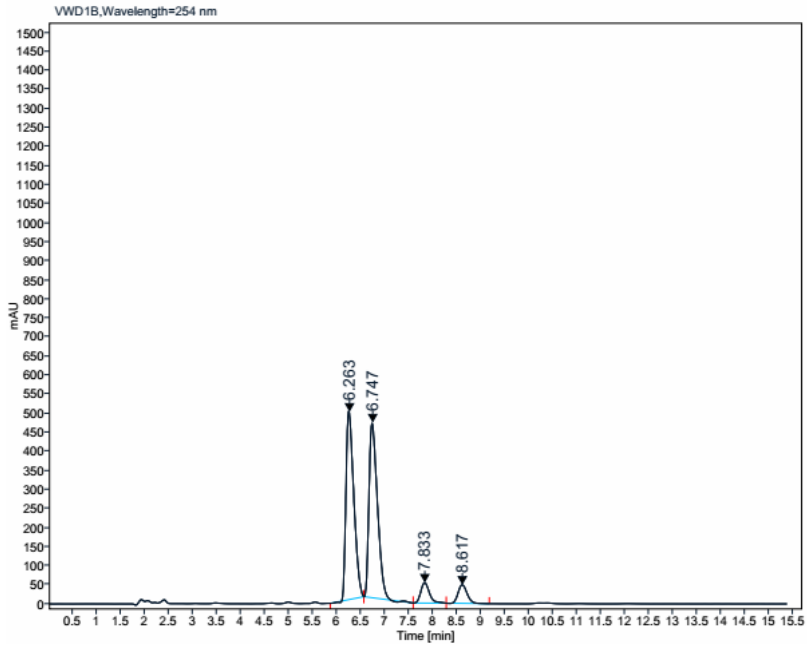

7.60 7.58 7.35 7.35 7.34 7.33 7.32 7.31 7.31 7.31 7.29 7.29 7.27 7.27 7.20 7.09 7.08 7.08 7.06 7.06 7.05 7.05 7.04 7.04 5.66
4.70 4.69 4.67 4.66
2.83 2.82 2.81 2.80 2.79 2.78 2.77 2.60 2.58 2.57 2.55 2.13 1.82 1.79 1.76 1.73 1.20 1.18 1.17 1.16
OH
N
Ac
Et
1.02 2.12 0.70 4.01 0.95 1.00 2.12 2.04 3.01 1.01 3.02
f1 (ppm)


170.15
143.09 140.19 138.95 136.26 128.12 127.35 126.46 126.10 125.55 122.97
66.03 54.41 43.88 28.52 23.12 15.54
f1 (ppm)

Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 15% EtOH.amx

Injection Acquired Date 2020-07-10 14:41:35+02:00

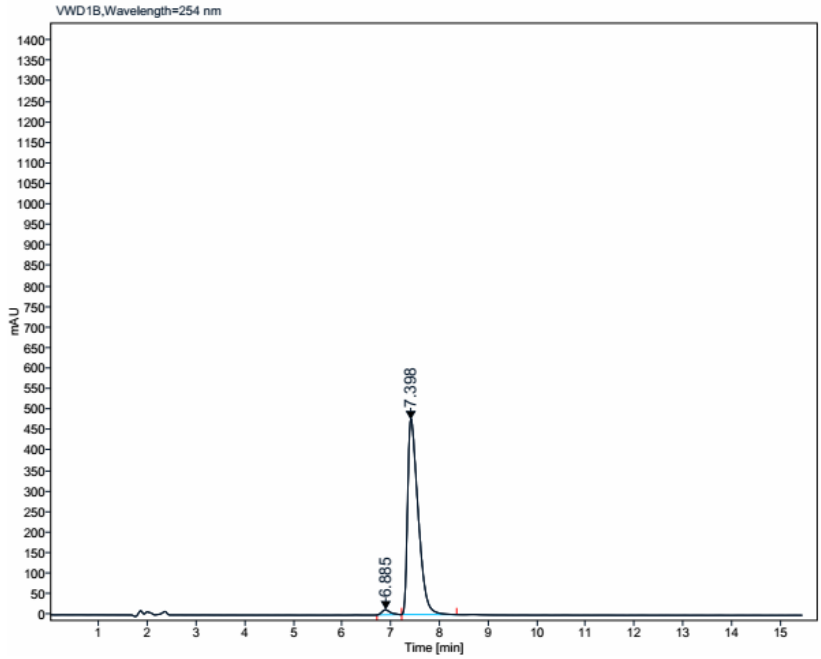
RT	*Peak Area %*
6.263	44.75
6.747	44.87
7.833	5.34
8.617	5.04



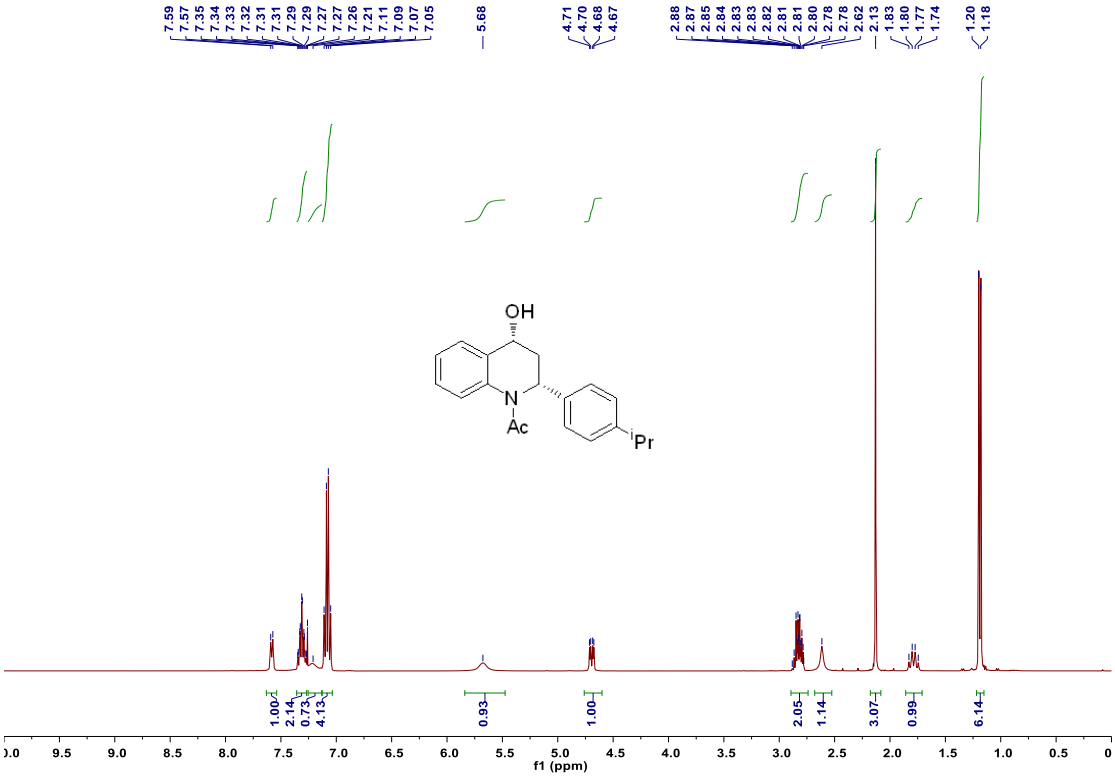
Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 15% EtOH.amx

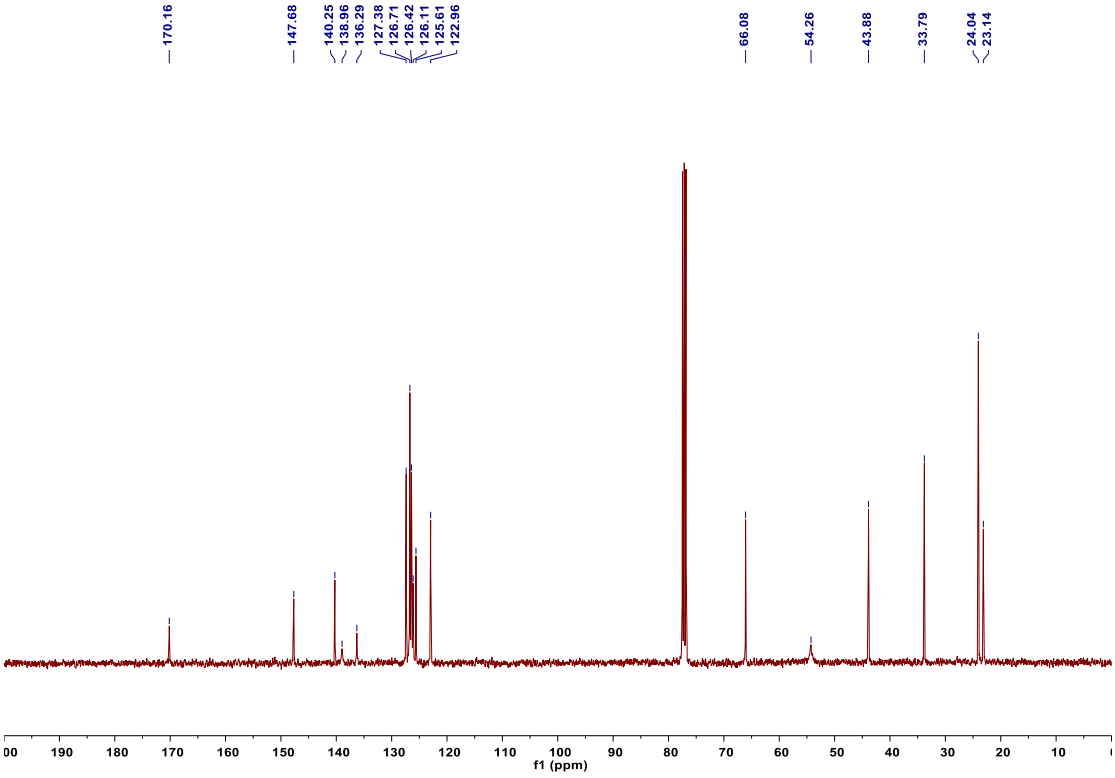
Injection Acquired Date 2020-07-22 14:04:39+02:00

RT	*Peak Area %*
6.885	1.98
7.398	98.02



Compound **4e**

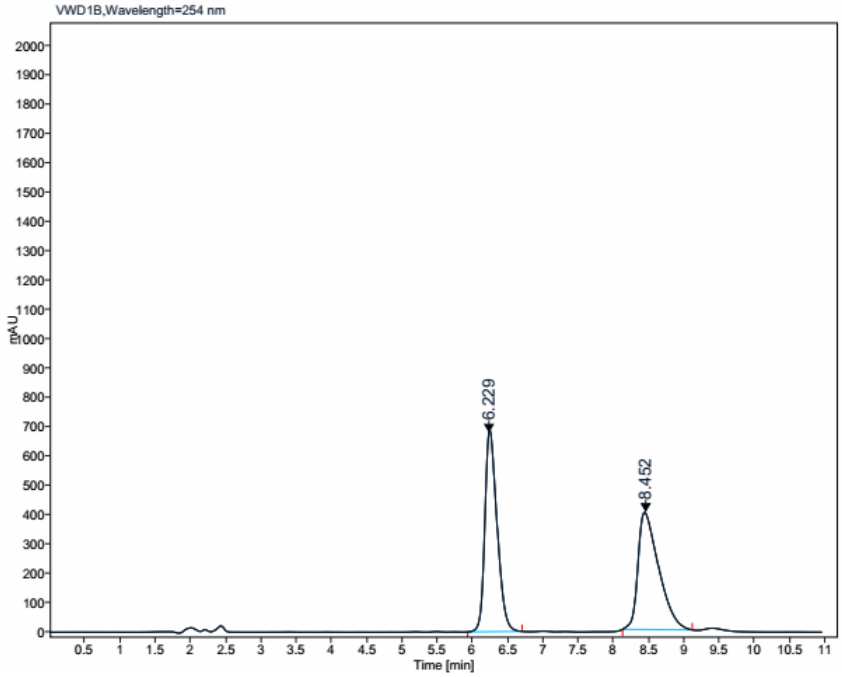

7.59
7.57
7.35
7.34
7.33
7.32
7.31
7.31
7.29
7.29
7.27
7.27
7.26
7.21
7.11
7.09
7.07
7.05
5.68
4.71
4.70
4.68
4.67
2.88
2.87
2.85
2.84
2.83
2.83
2.82
2.81
2.81
2.80
2.78
2.78
2.62
2.13
1.83
1.80
1.77
1.74
1.20
1.18
OH
N
Ac
iPr
1.00
2.14
0.73
4.13
0.93
1.00
2.05
1.14
3.07
0.99
6.14
f1 (ppm)


170.16
147.68
140.25
138.96
136.29
127.38
126.71
126.42
126.11
125.61
122.96
66.08
54.26
43.88
33.79
24.04
23.14
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-07 18:02:05+02:00

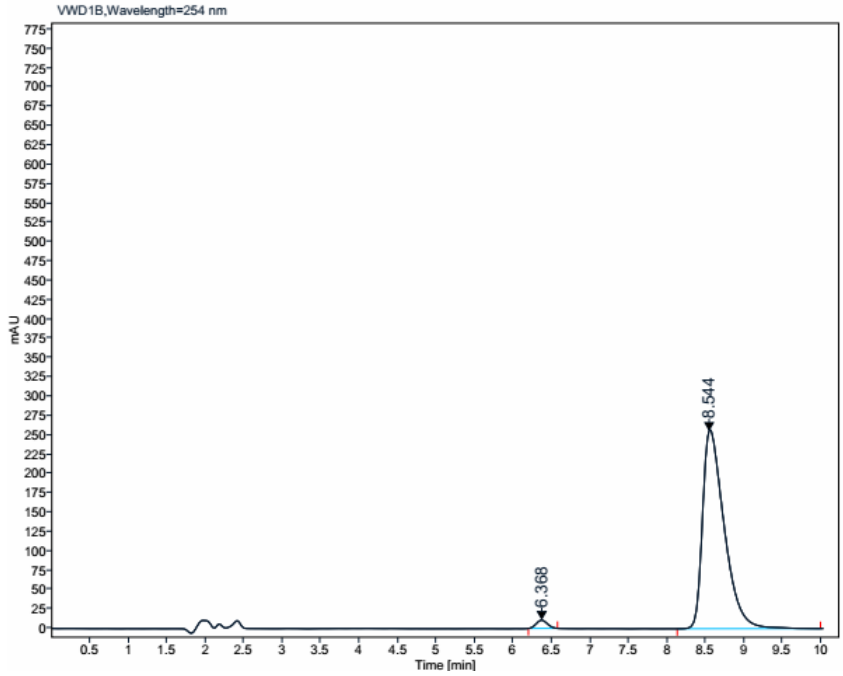
RT	Peak Area %
6.229	50.33
8.452	49.67



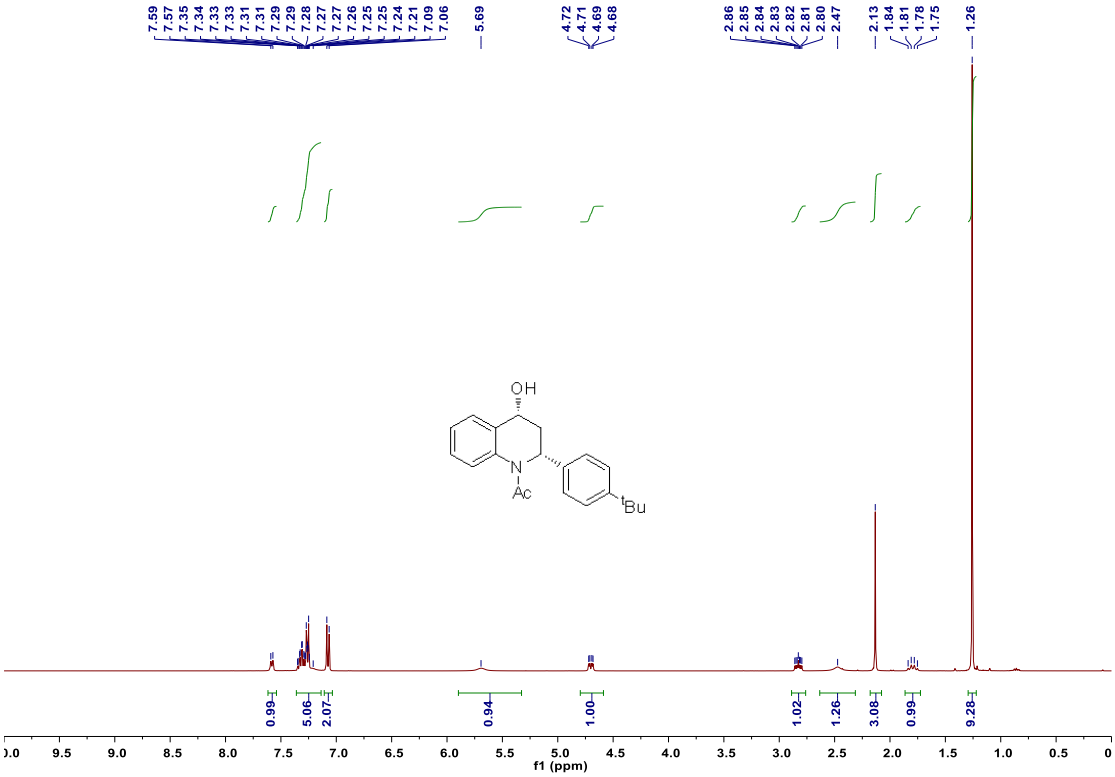
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

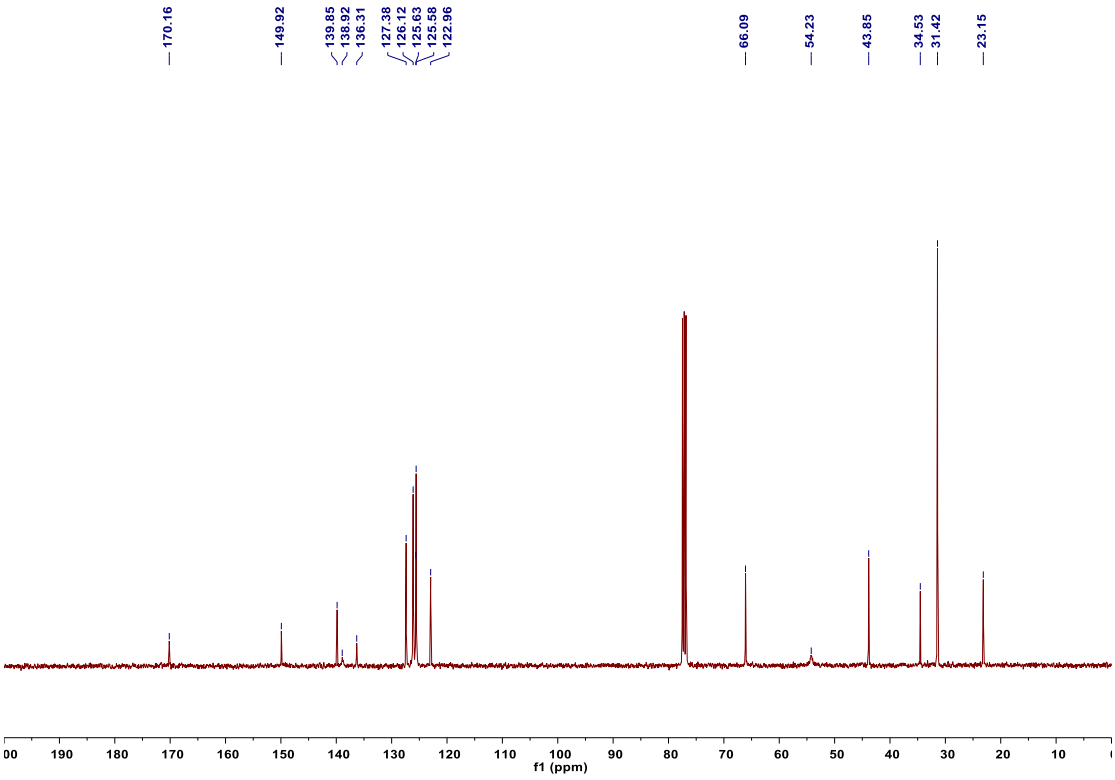
Injection Acquired Date 2020-07-21 18:13:34+02:00

RT	Peak Area %
6.368	2.06
8.544	97.94



Compound **4f**

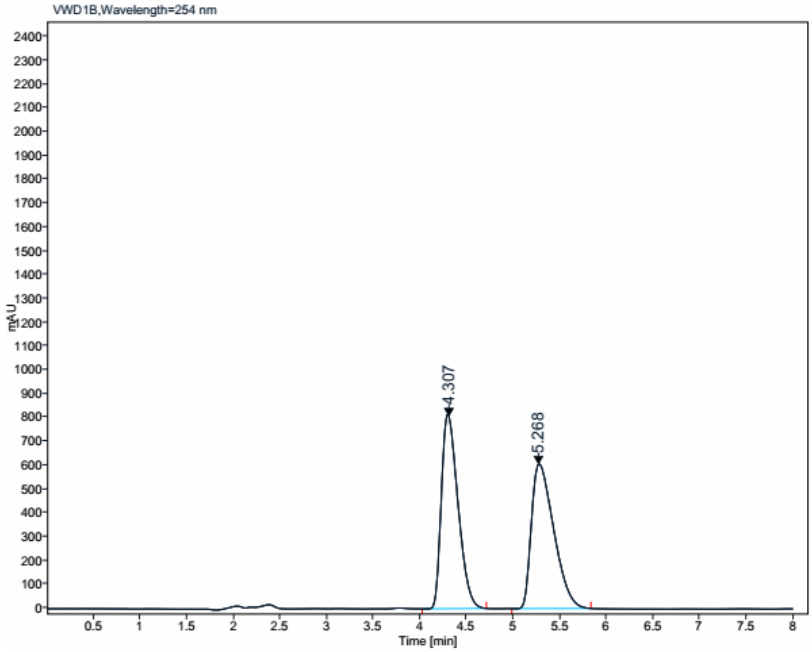

7.59
7.57
7.35
7.34
7.33
7.33
7.31
7.31
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.21
7.09
7.06
5.69
4.72
4.71
4.69
4.68
2.86
2.85
2.84
2.83
2.82
2.81
2.80
2.47
2.13
1.84
1.81
1.78
1.75
1.26
OH
N
Ac
tBu
0.99
5.06
2.07
0.94
1.00
1.02
1.26
3.08
0.99
9.28
f1 (ppm)


170.16
149.92
139.85
138.92
136.31
127.38
126.12
125.63
125.58
122.96
66.09
54.23
43.85
34.53
31.42
23.15
f1 (ppm)

Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-09 17:26:31+02:00

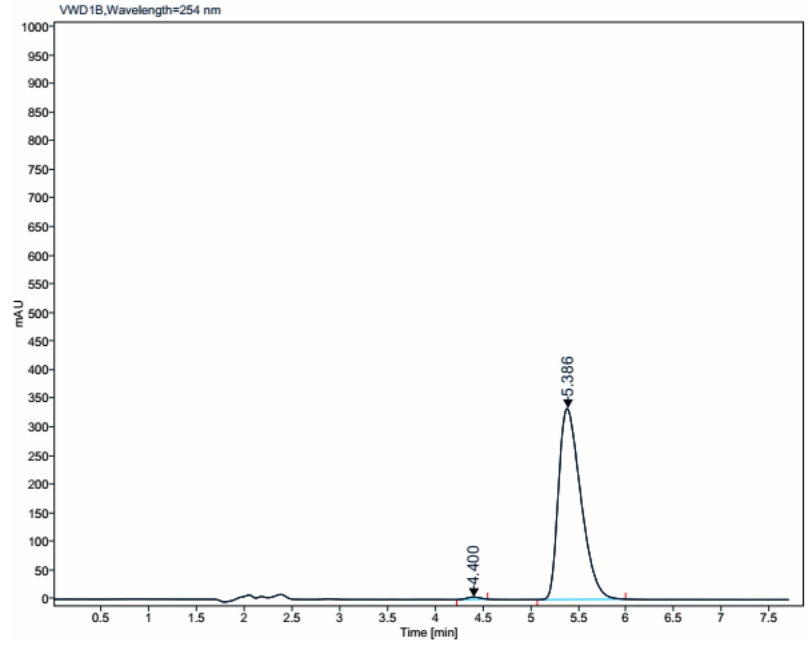
RT	*Peak Area %*
4.307	49.98
5.268	50.02



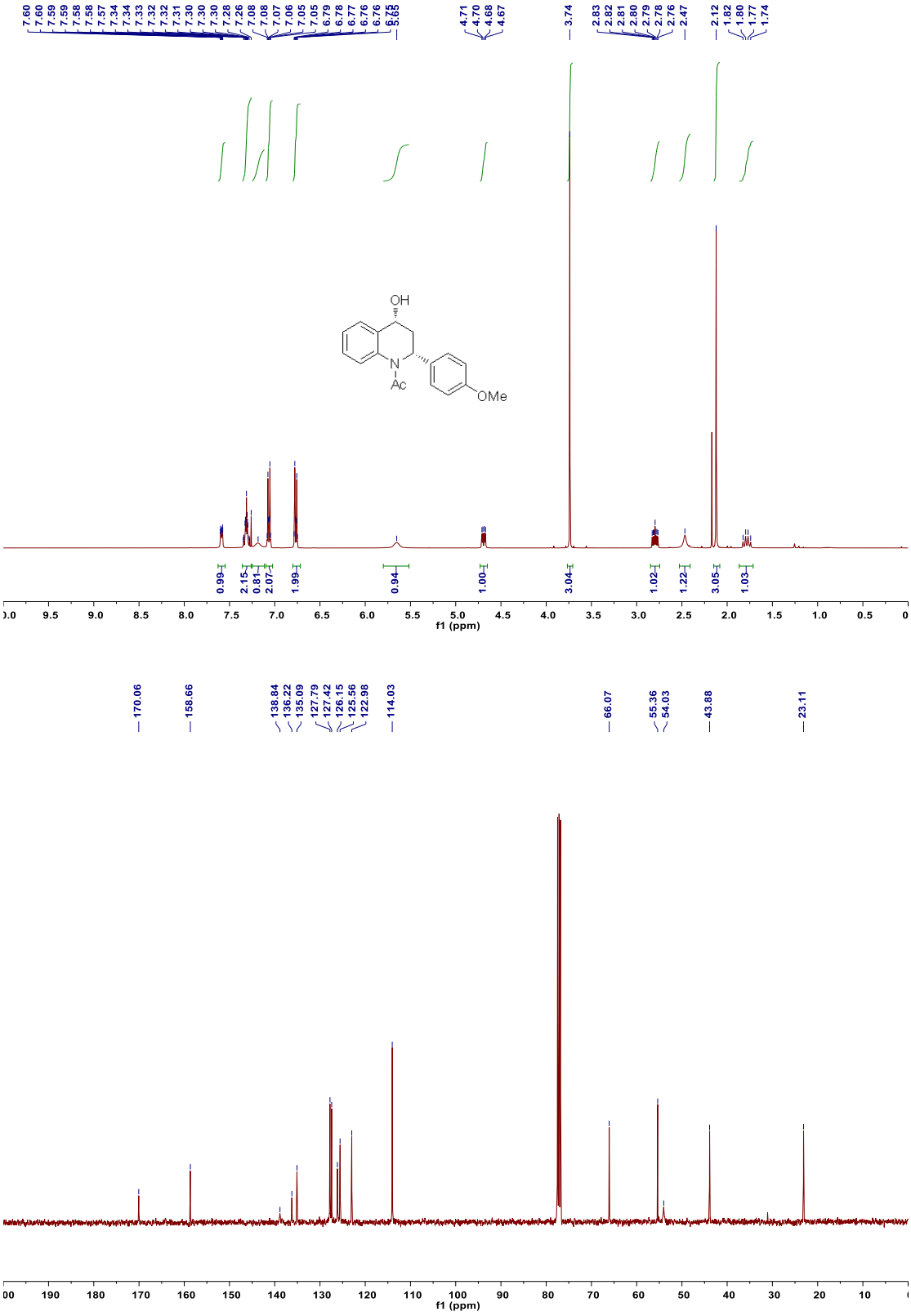
Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-27 18:28:45+02:00

RT	*Peak Area %*
4.400	0.70
5.386	99.30



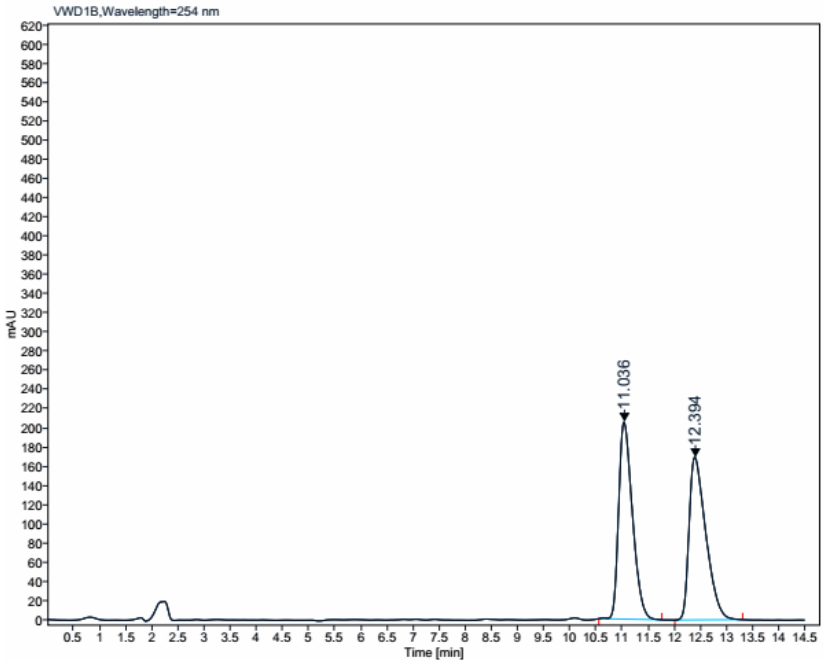
Compound **4g**


7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.28
7.26
7.08
7.08
7.07
7.06
7.05
7.05
6.79
6.78
6.77
6.76
6.76
6.75
5.65
4.71
4.70
4.68
4.67
3.74
2.83
2.82
2.81
2.80
2.79
2.78
2.76
2.47
2.12
1.82
1.80
1.77
1.74
OH
N
Ac
OMe
0.99
2.15
0.81
2.07
1.99
0.94
1.00
3.04
1.02
1.22
3.05
1.03
f1 (ppm)
170.06
158.66
138.84
136.22
135.09
127.79
127.42
126.15
125.56
122.98
114.03
66.07
55.36
54.03
43.88
23.11
f1 (ppm)

Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-09 16:06:00+02:00

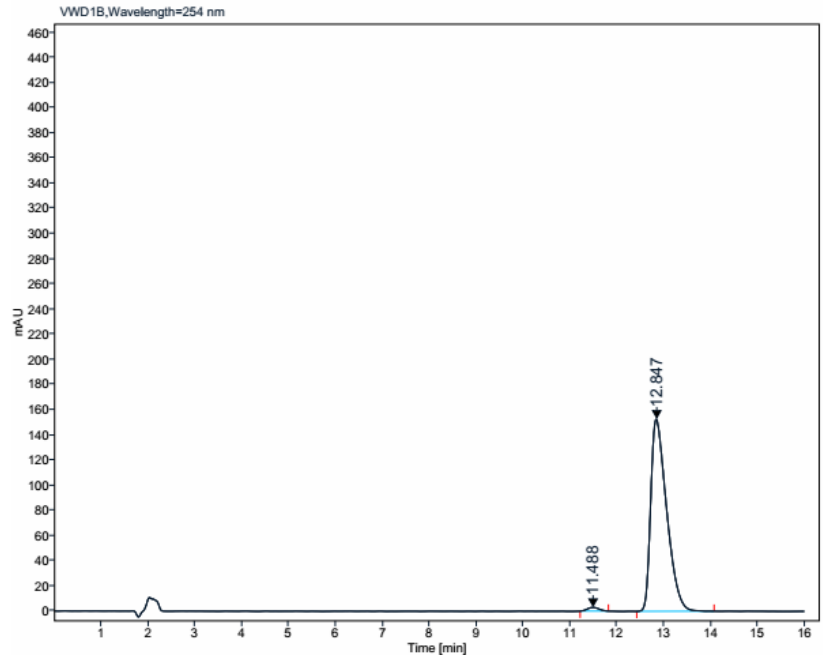
RT	*Peak Area %*
11.036	49.83
12.394	50.17



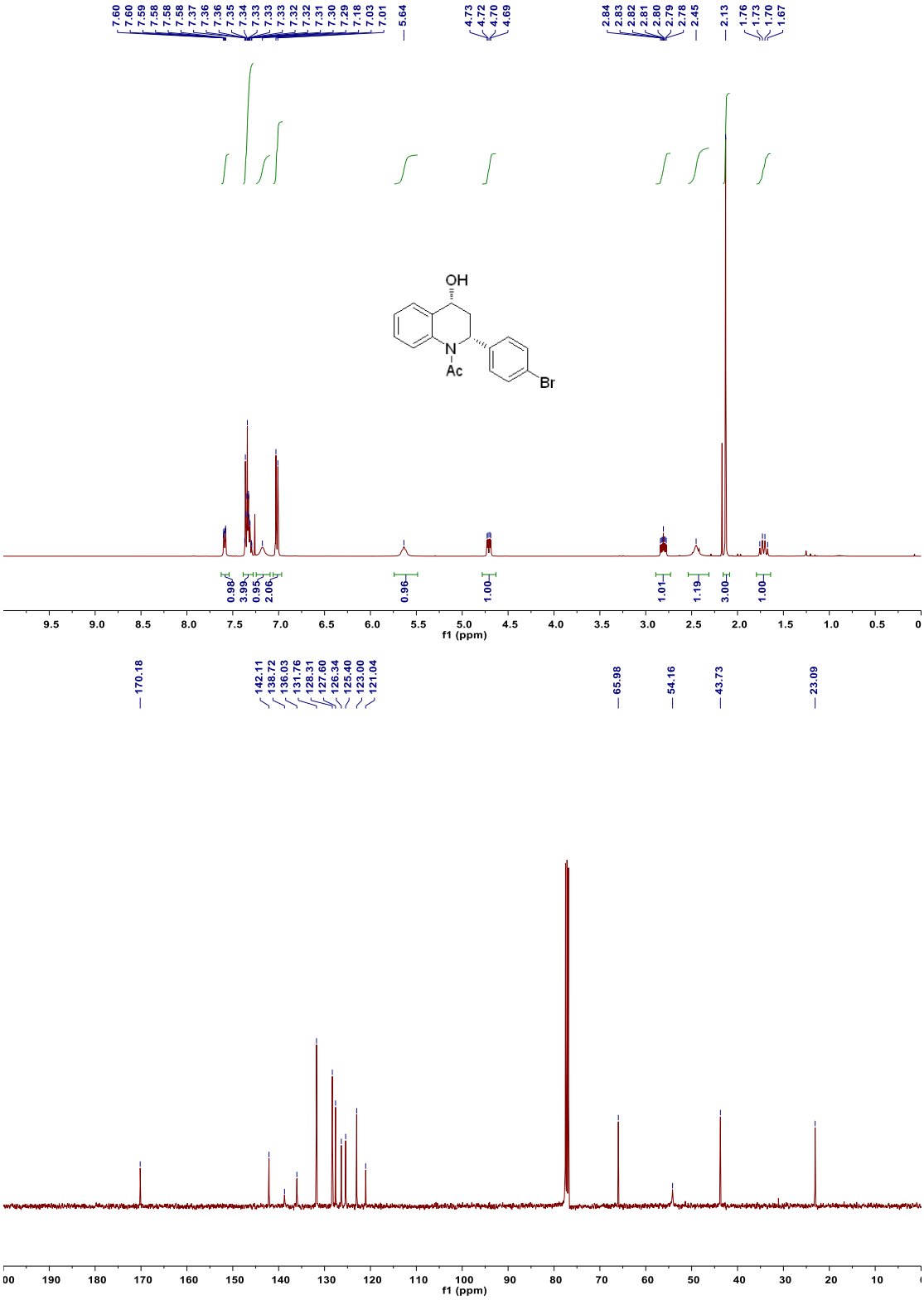
Injection Acq Method Name IE - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-24 16:00:25+02:00

RT	*Peak Area %*
11.488	1.37
12.847	98.63



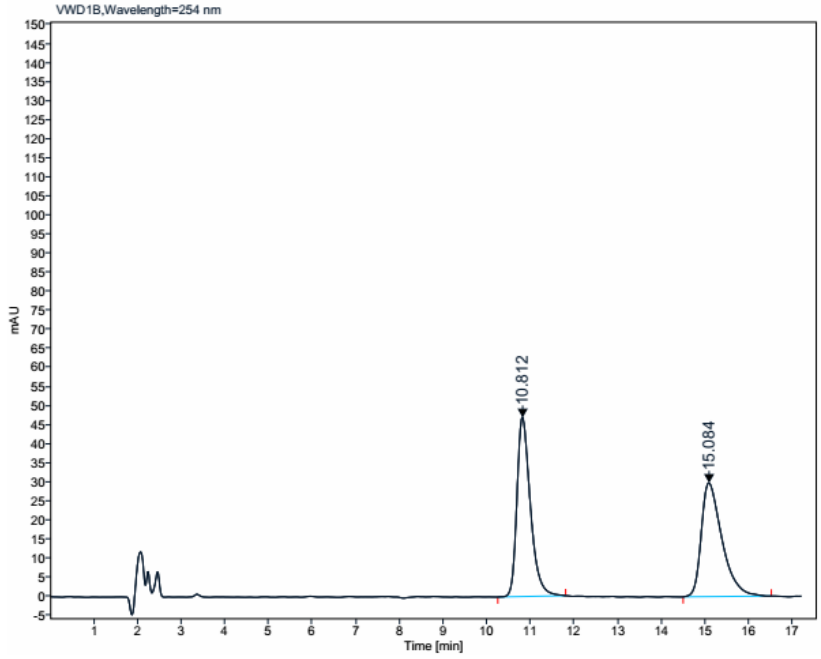
Compound **4h**


7.60
7.60
7.59
7.58
7.58
7.58
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.18
7.03
7.01
5.64
4.73
4.72
4.70
4.69
2.84
2.83
2.82
2.81
2.80
2.79
2.78
2.45
2.13
1.76
1.73
1.70
1.67
OH
N
Ac
Br
0.98
3.99
0.95
2.06
0.96
1.00
1.01
1.19
3.00
1.00
f1 (ppm)
170.18
142.11
138.72
136.03
131.76
128.31
127.60
126.34
125.40
123.00
121.04
65.98
54.16
43.73
23.09
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-15 10:54:33+02:00

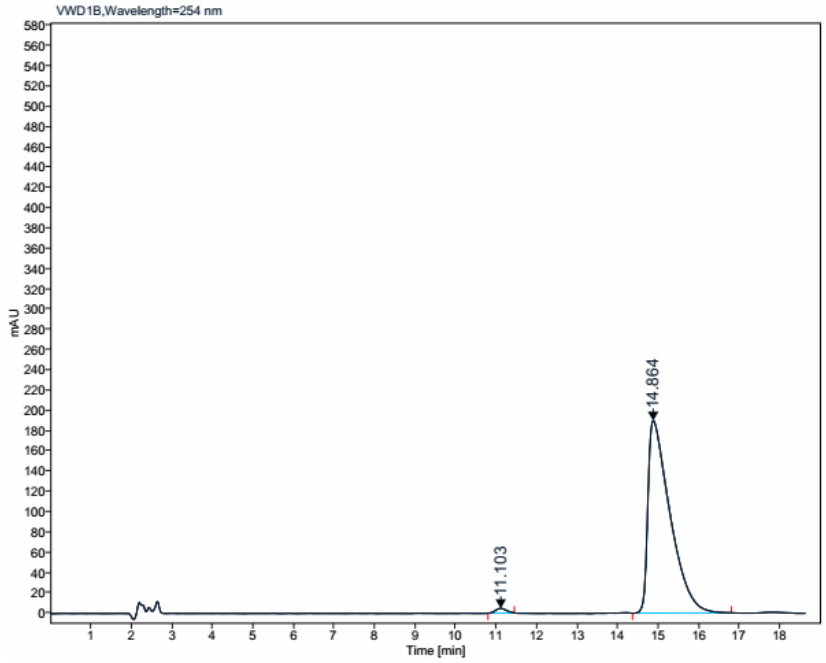
RT	Peak Area %
10.812	50.66
15.084	49.34



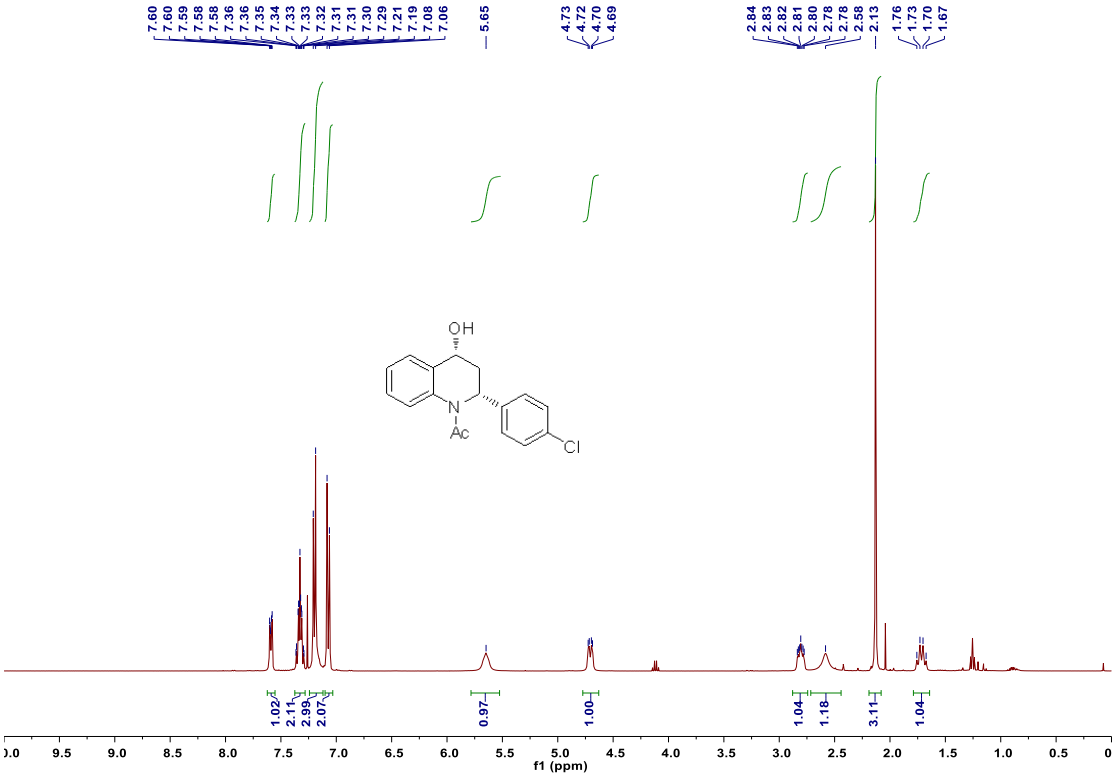
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

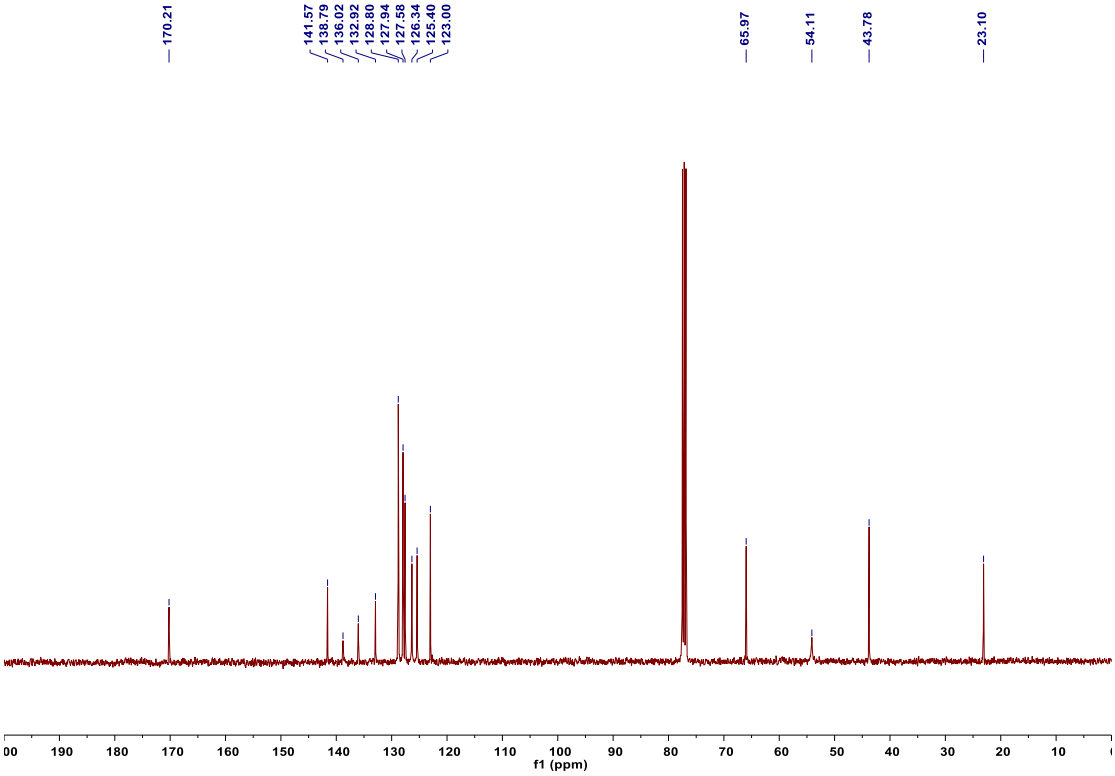
Injection Acquired Date 2020-07-27 17:07:38+02:00

RT	Peak Area %
11.103	1.16
14.864	98.84



Compound **4i**

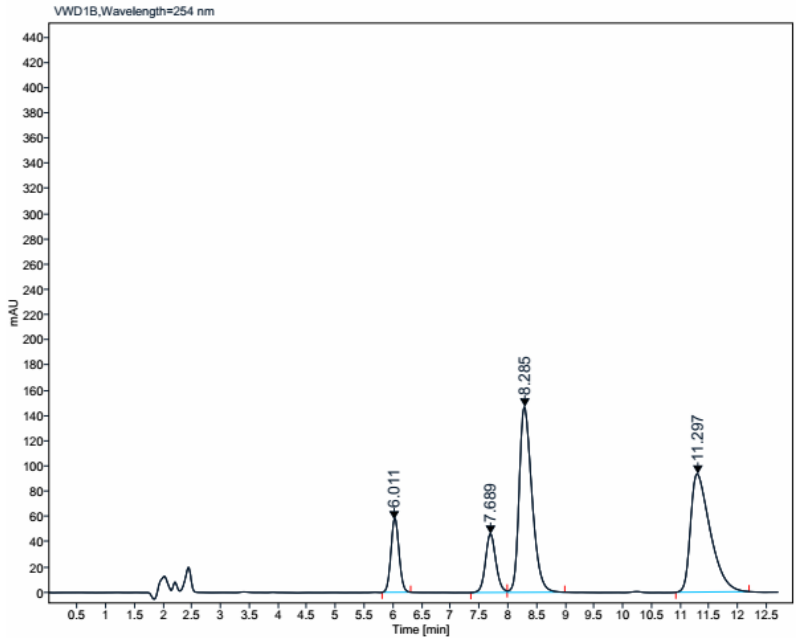

7.60
7.60
7.59
7.58
7.58
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.21
7.19
7.08
7.06
5.65
4.73
4.72
4.70
4.69
2.84
2.83
2.82
2.81
2.80
2.78
2.78
2.58
2.13
1.76
1.73
1.70
1.67
OH
N
Ac
Cl
1.02
2.11
2.99
2.07
0.97
1.00
1.04
1.18
3.11
1.04
f1 (ppm)


170.21
141.57
138.79
136.02
132.92
128.80
127.94
127.58
126.34
125.40
123.00
65.97
54.11
43.78
23.10
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-07 17:20:39+02:00

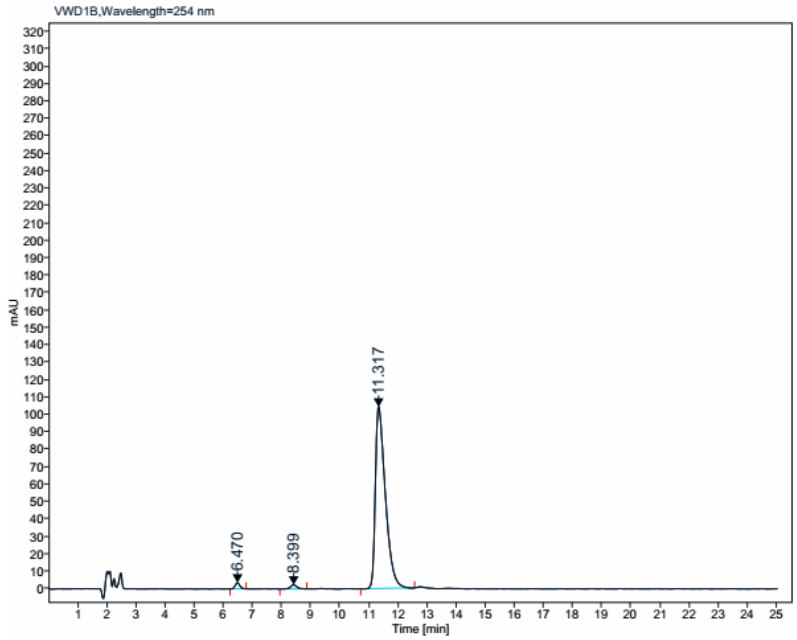
RT	*Peak Area %*
6.011	10.15
7.689	10.33
8.285	40.14
11.297	39.38



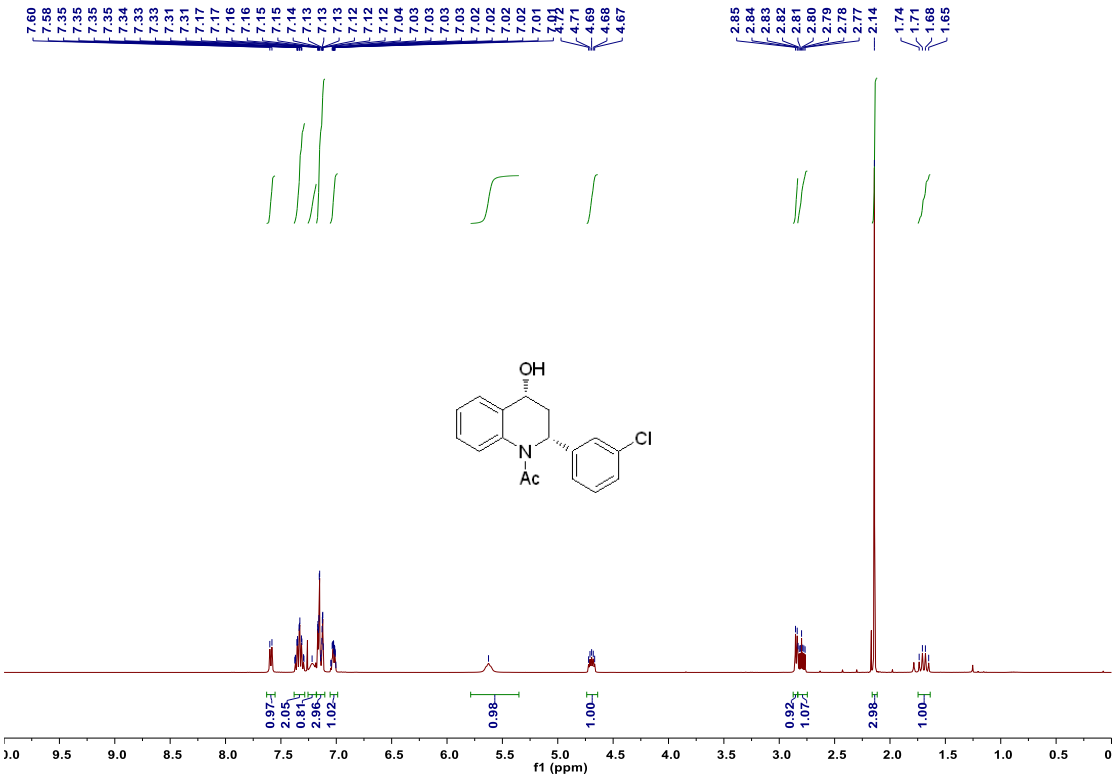
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

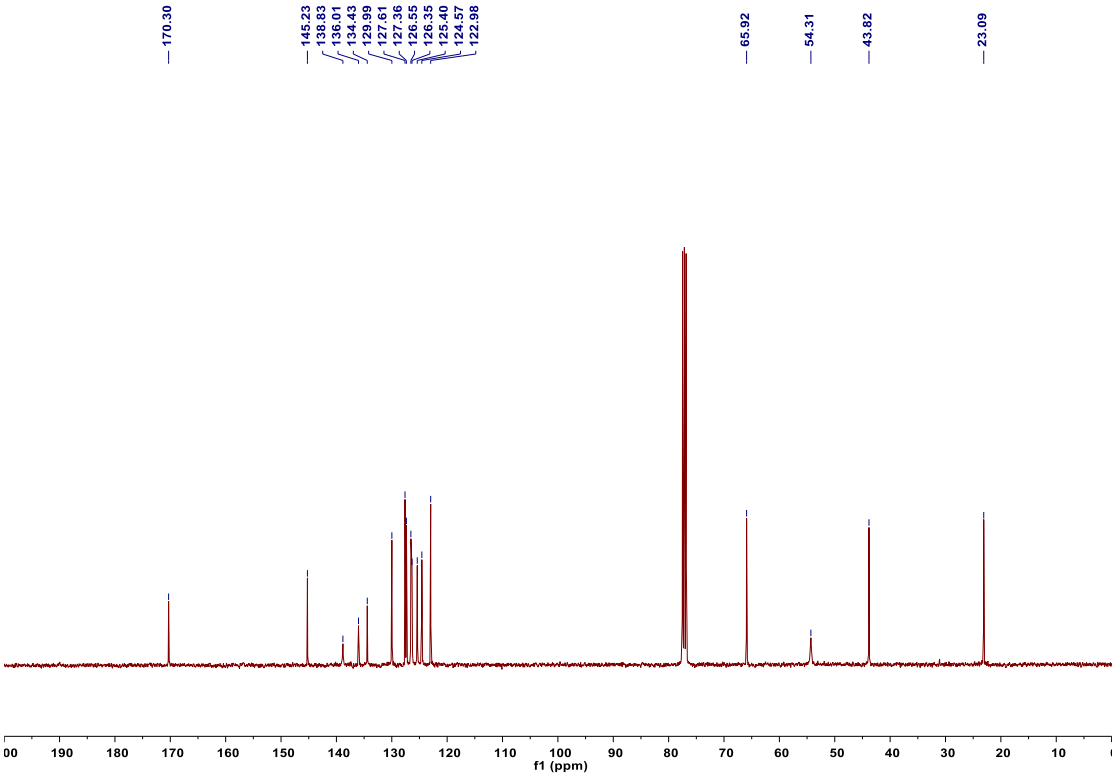
Injection Acquired Date 2020-07-23 13:43:45+02:00

RT	*Peak Area %*
6.470	1.53
8.399	1.39
11.317	97.08



Compound **4j**

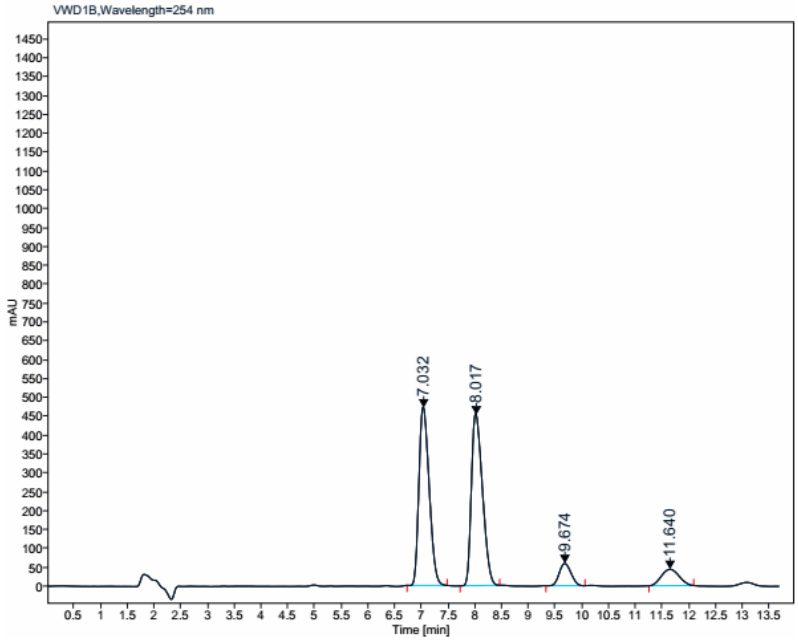

7.60 7.58 7.35 7.35 7.35 7.35 7.34 7.33 7.33 7.31 7.31 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.13 7.12 7.12 7.12 7.04 7.03 7.03 7.03 7.02 7.02 7.02 7.01 4.71 4.69 4.68 4.67
2.85 2.84 2.83 2.82 2.81 2.80 2.79 2.78 2.77 2.14 1.74 1.71 1.68 1.65
OH
N
Ac
Cl
0.97 2.05 0.81 2.96 1.02 0.98 1.00 0.92 1.07 2.98 1.00
f1 (ppm)


170.30
145.23 138.83 136.01 134.43 129.99 127.61 127.36 126.55 126.35 125.40 124.57 122.98
65.92 54.31 43.82 23.09
f1 (ppm)

Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

Injection Acquired Date 2020-07-10 17:05:23+02:00

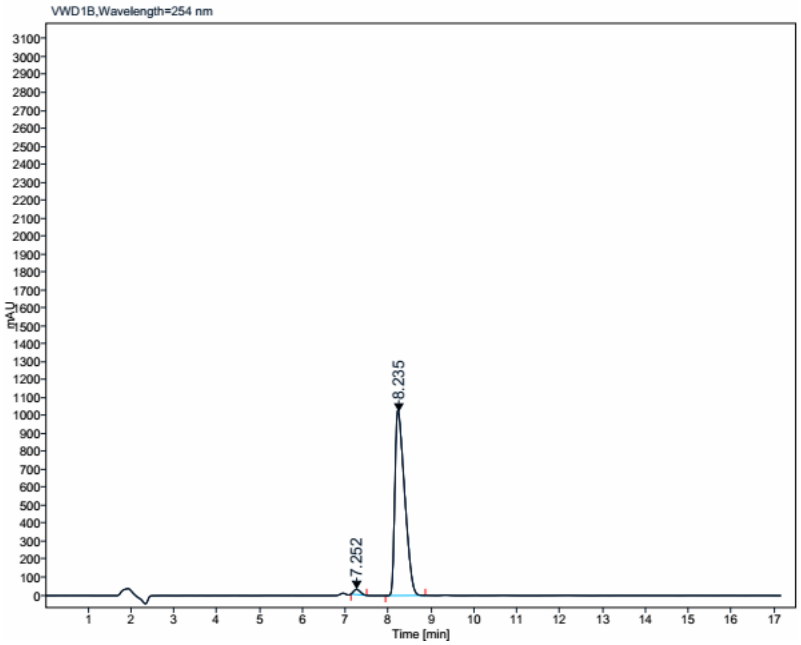
RT	*Peak Area %*
7.032	42.76
8.017	44.41
9.674	6.07
11.640	6.77



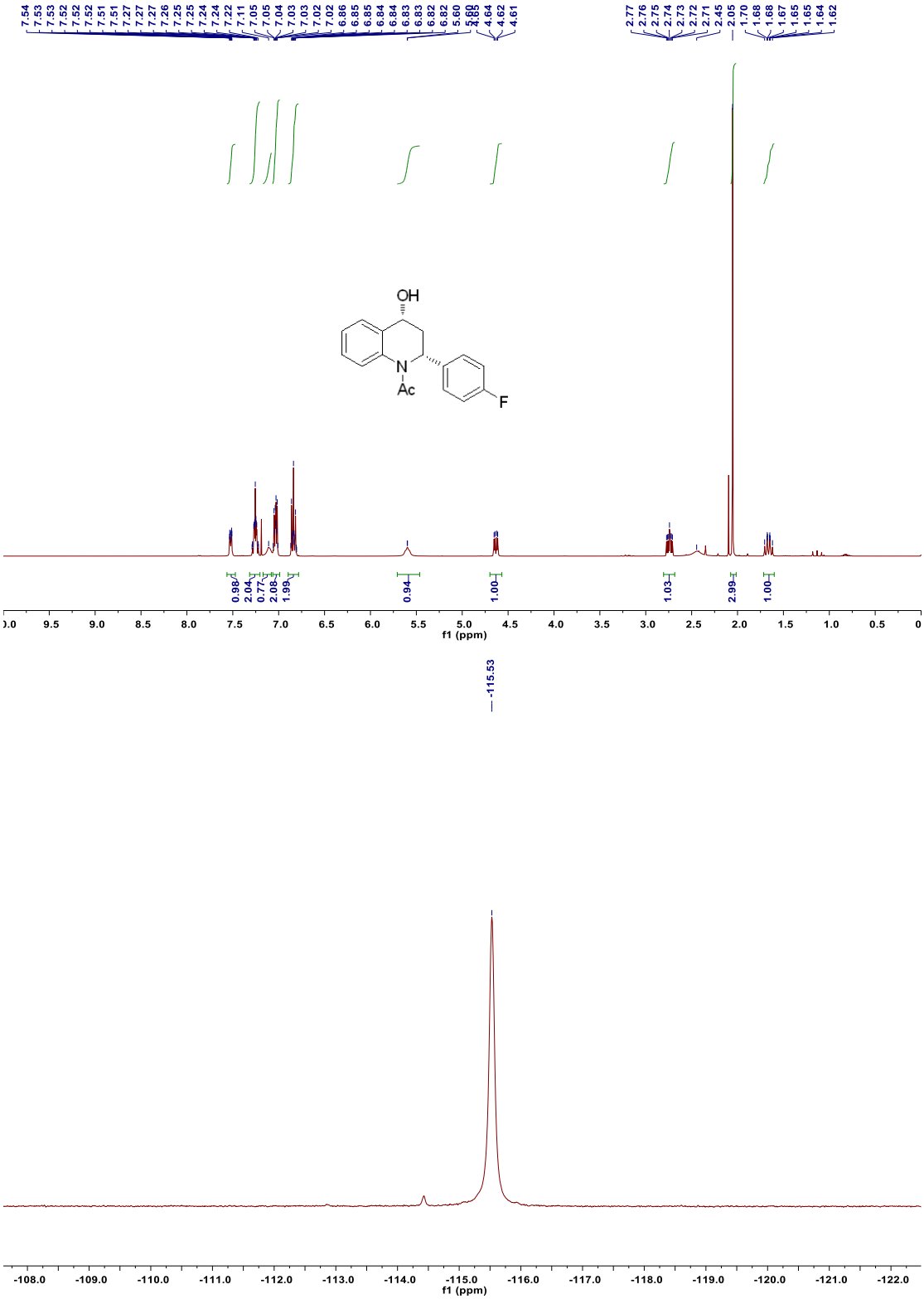
Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

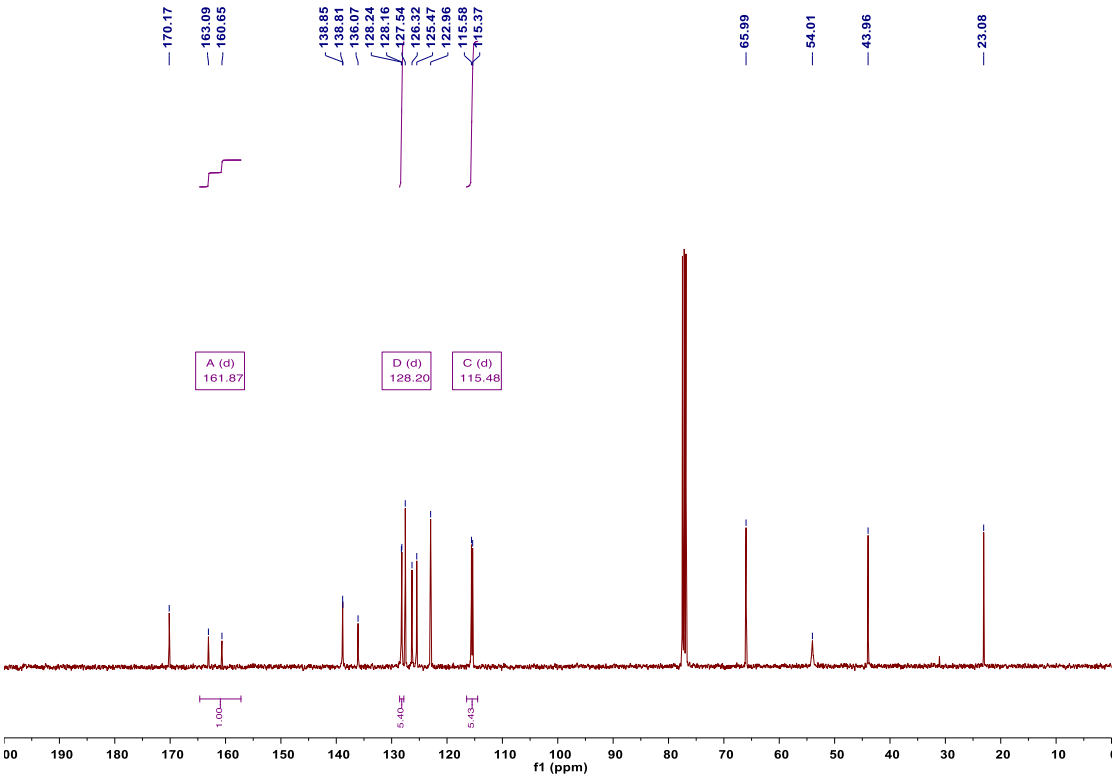
Injection Acquired Date 2020-07-30 12:29:36+02:00

RT	*Peak Area %*
7.252	1.83
8.235	98.17



Compound **4k**

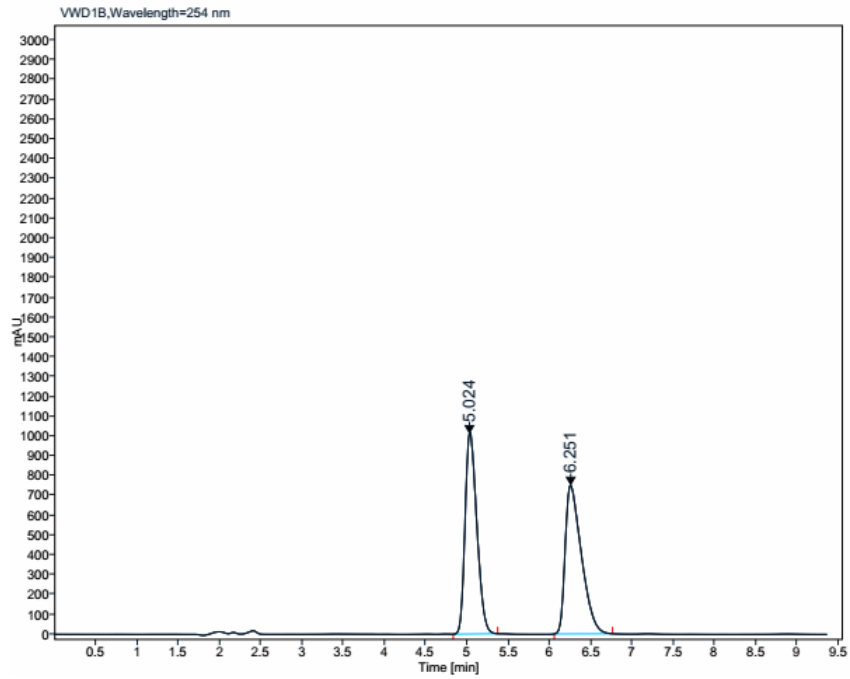

7.54 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.27 7.27 7.27 7.26 7.25 7.24 7.24 7.22 7.11 7.05 7.05 7.04 7.03 7.03 7.02 7.02 6.86 6.85 6.85 6.84 6.84 6.83 6.83 6.82 6.82 5.60 4.64 4.62 4.61
2.77 2.76 2.75 2.74 2.73 2.72 2.71 2.45 2.05 1.70 1.68 1.68 1.67 1.65 1.65 1.64 1.62
OH
N
Ac
F
0.98 2.04 0.77 2.08 1.99 0.94 1.00 1.03 2.99 1.00
f1 (ppm)
-115.53
f1 (ppm)



Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-08 09:20:51+02:00

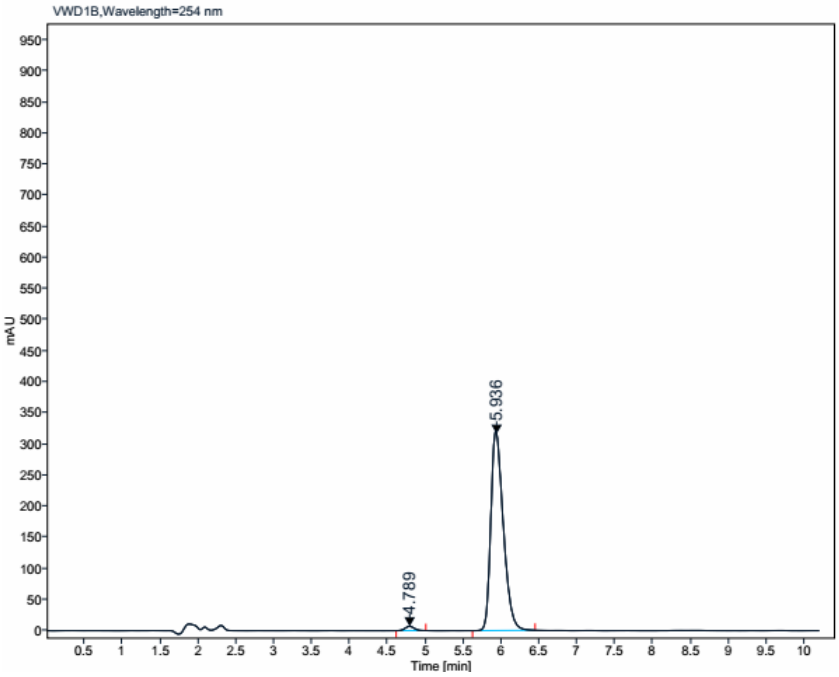
RT	*Peak Area %*
5.024	49.49
6.251	50.51



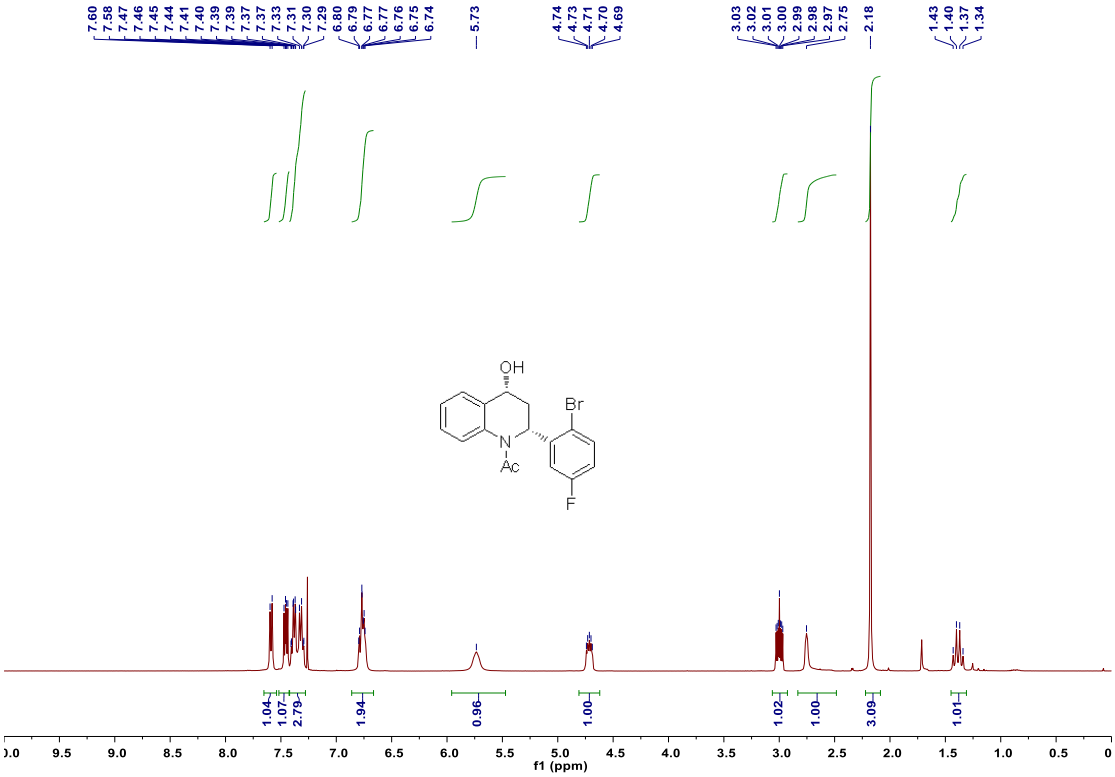
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

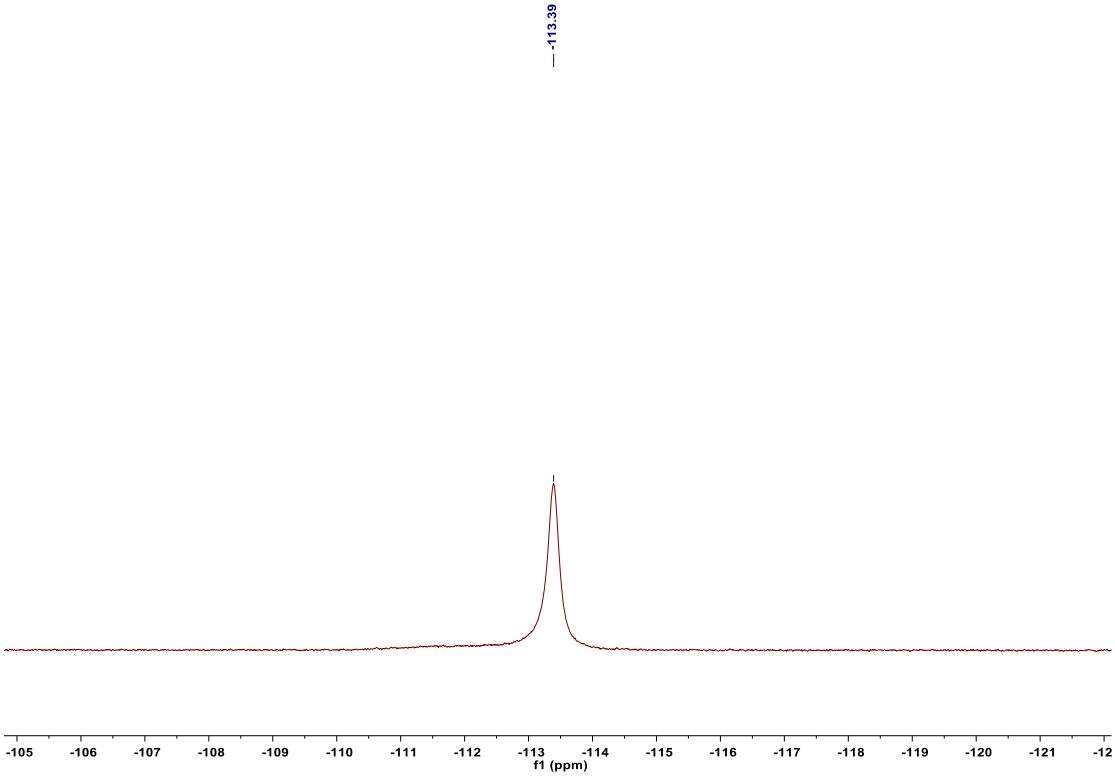
Injection Acquired Date 2020-08-05 11:00:49+02:00

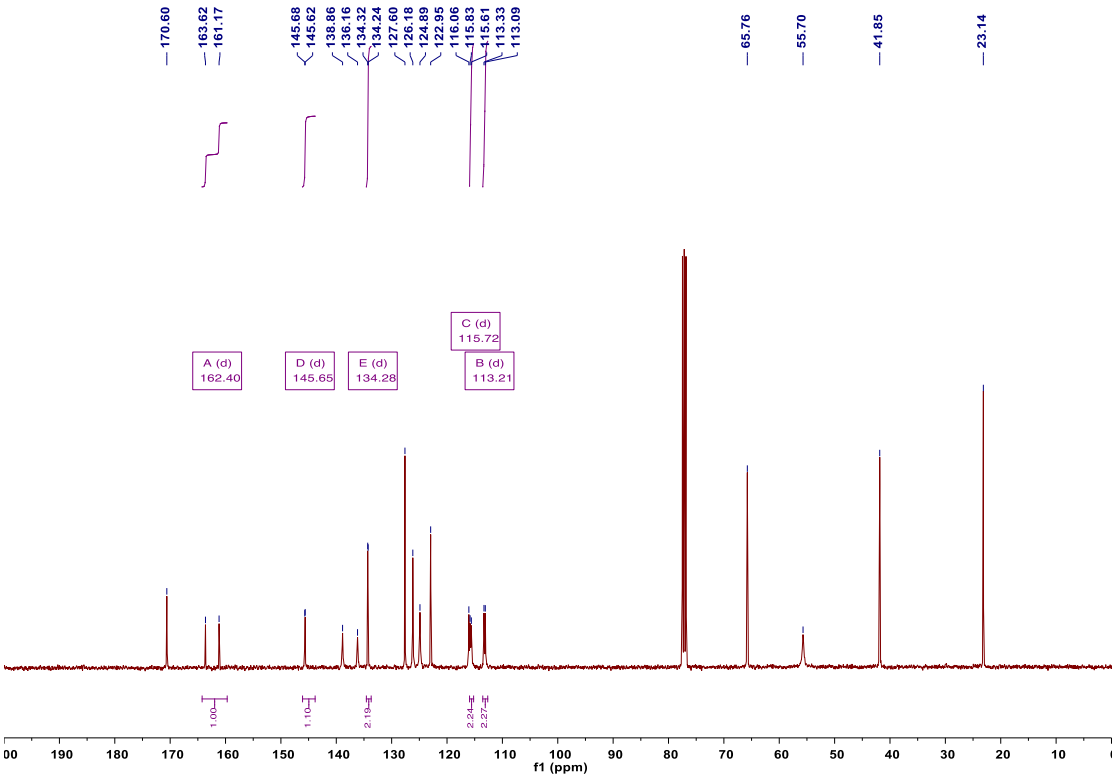
RT	*Peak Area %*
4.789	1.55
5.936	98.45



Compound **4l**


7.60
7.58
7.47
7.46
7.45
7.44
7.41
7.40
7.39
7.39
7.37
7.37
7.33
7.31
7.30
7.29
6.80
6.79
6.77
6.77
6.76
6.75
6.74
5.73
4.74
4.73
4.71
4.70
4.69
3.03
3.02
3.01
3.00
2.99
2.98
2.97
2.75
2.18
1.43
1.40
1.37
1.34
OH
Br
N
Ac
F
1.04
1.07
2.79
1.94
0.96
1.00
1.02
1.00
3.09
1.01
f1 (ppm)

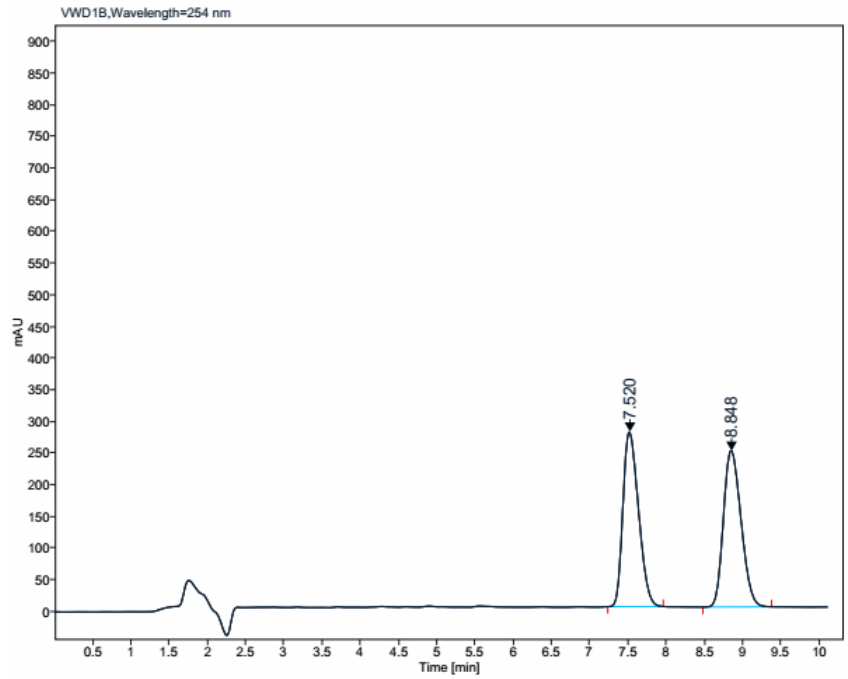

-113.39
f1 (ppm)



Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

Injection Acquired Date 2020-07-21 09:41:50+02:00

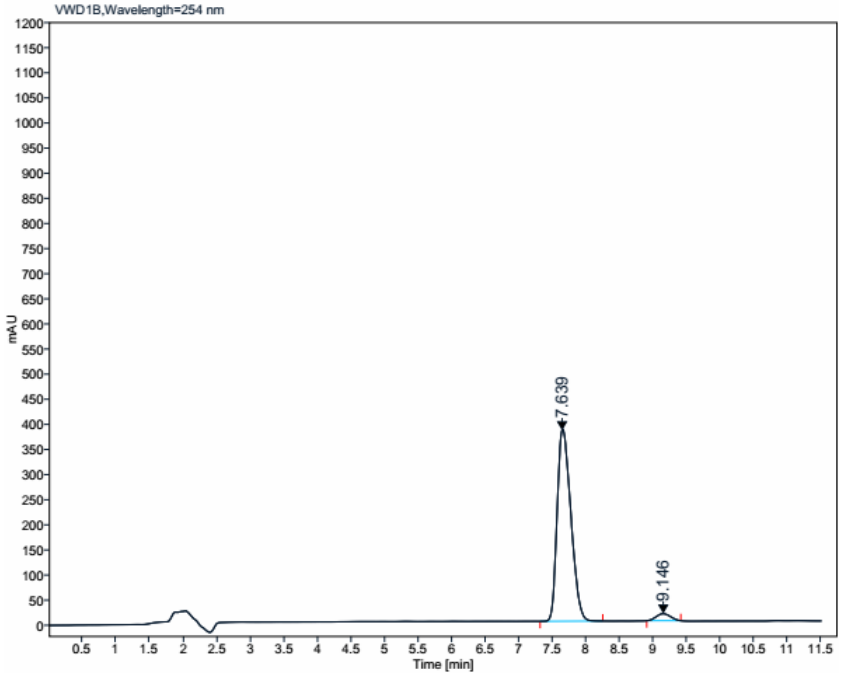
RT	*Peak Area %*
7.520	49.69
8.848	50.31



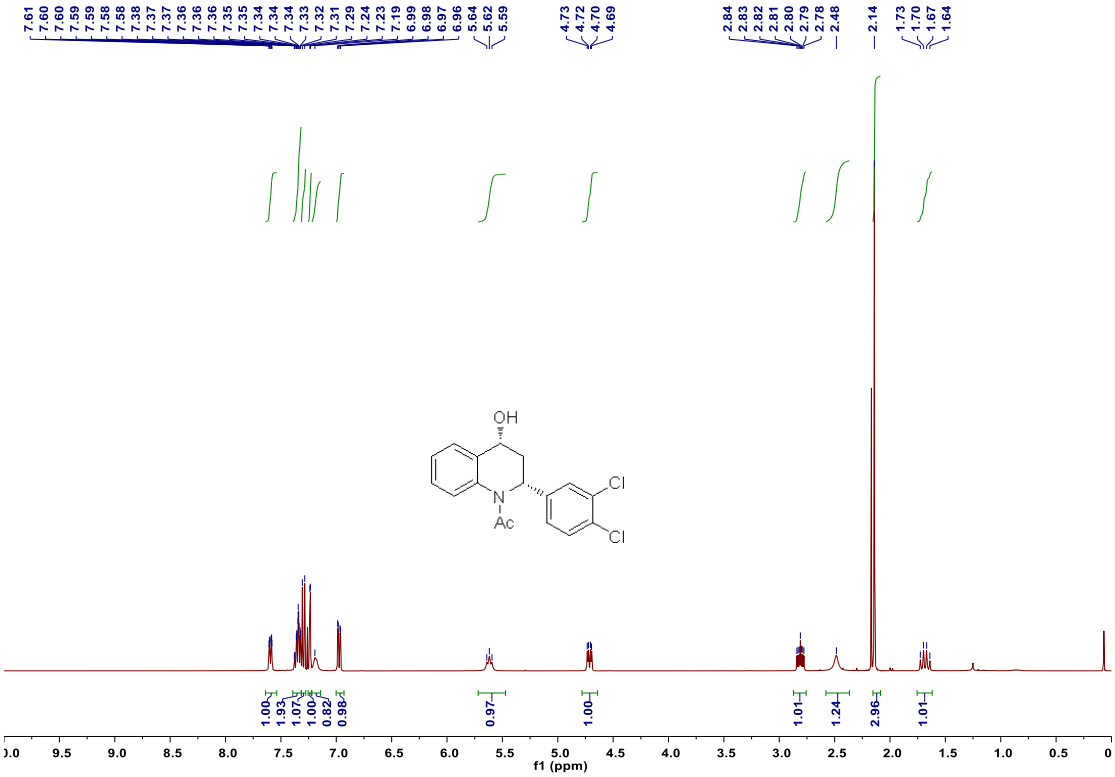
Injection Acq Method Name ID - 100 bars - 2 mL.min-1 - 20% iPrOH.amx

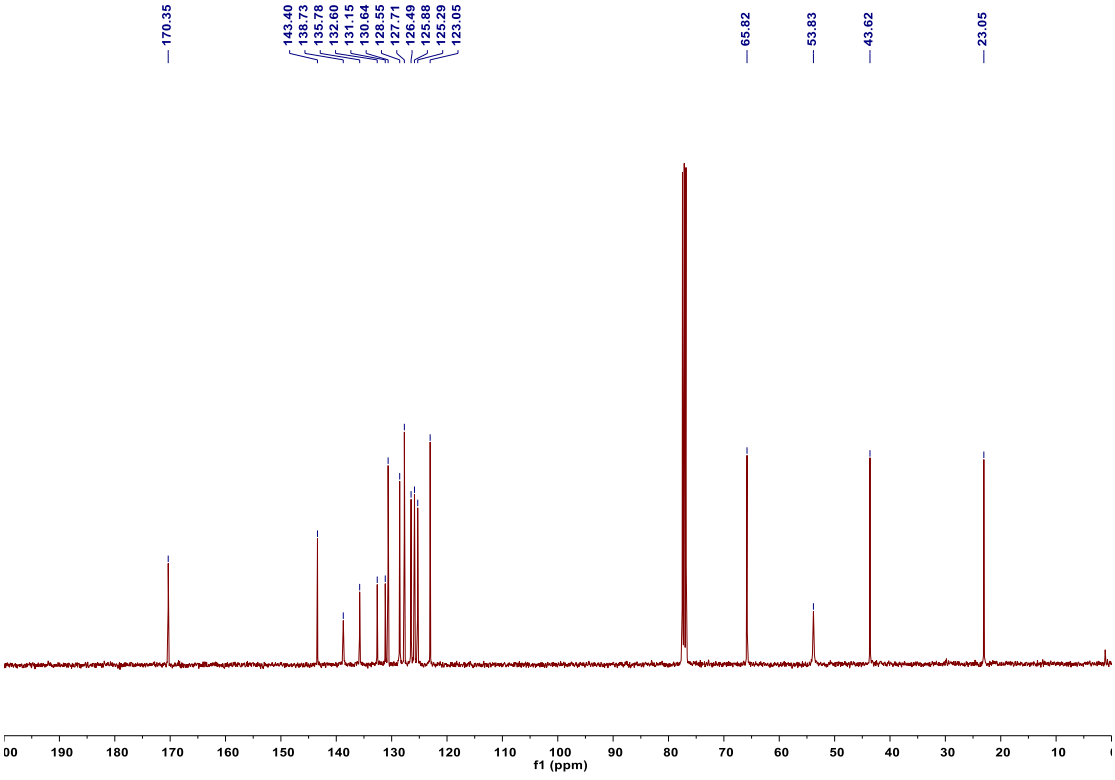
Injection Acquired Date 2020-07-31 12:20:21+02:00

RT	*Peak Area %*
7.639	96.38
9.146	3.62



Compound **4m**

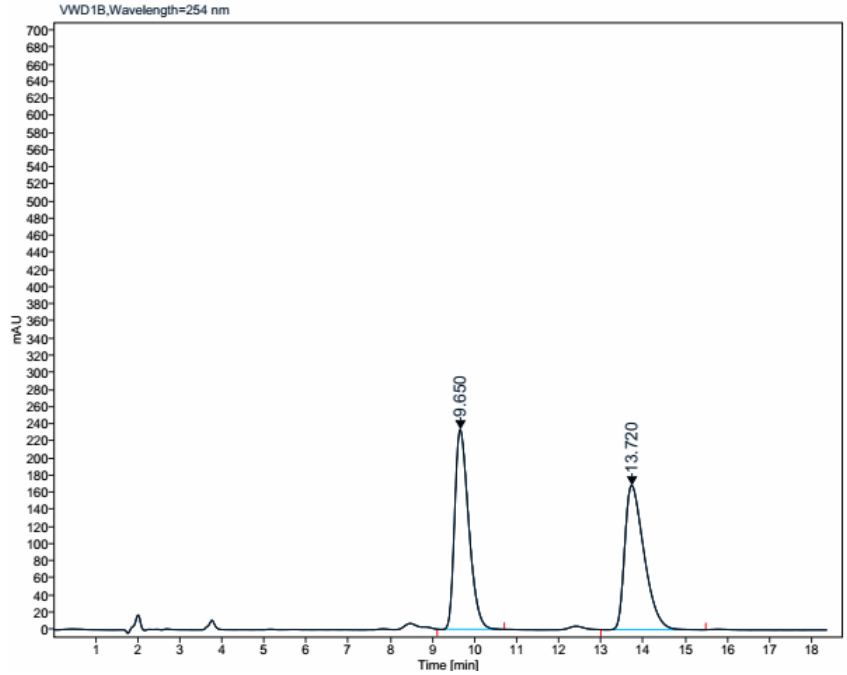

7.61 7.60 7.60 7.59 7.59 7.58 7.58 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.31 7.29 7.24 7.23 7.19 6.99 6.98 6.97 6.96 5.64 5.62 5.59
4.73 4.72 4.70 4.69
2.84 2.83 2.82 2.81 2.80 2.79 2.78 2.48 2.14 1.73 1.70 1.67 1.64
OH
N
Ac
Cl
Cl
1.00 1.93 1.07 1.00 0.82 0.98 0.97 1.00 1.01 1.24 2.96 1.01
f1 (ppm)


170.35
143.40 138.73 135.78 132.60 131.15 130.64 128.55 127.71 126.49 125.88 125.29 123.05
65.82 53.83 43.62 23.05
f1 (ppm)

Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 10% EtOH.amx

Injection Acquired Date 2020-07-07 10:33:25+02:00

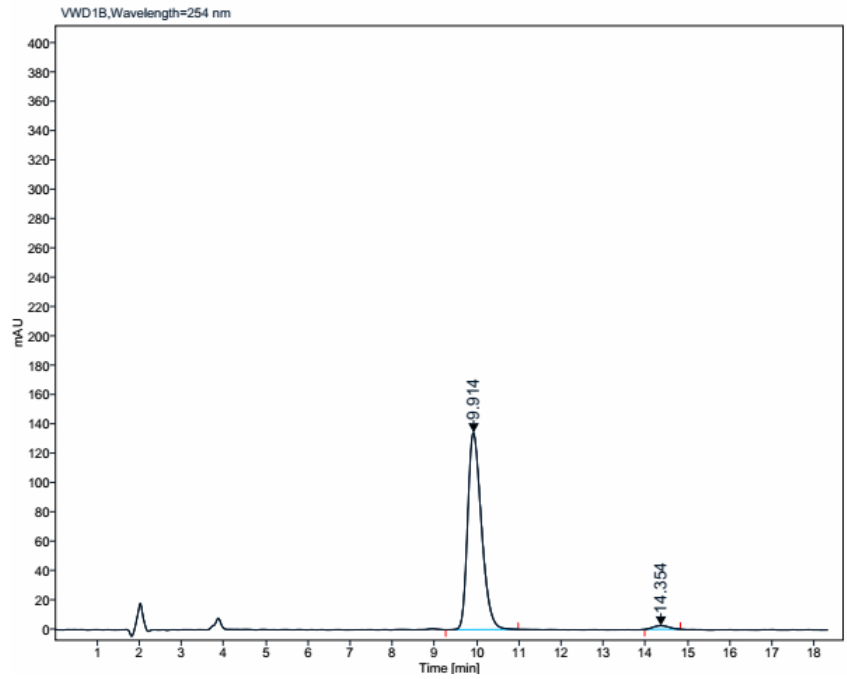
RT	Peak Area %
9.650	50.24
13.720	49.76



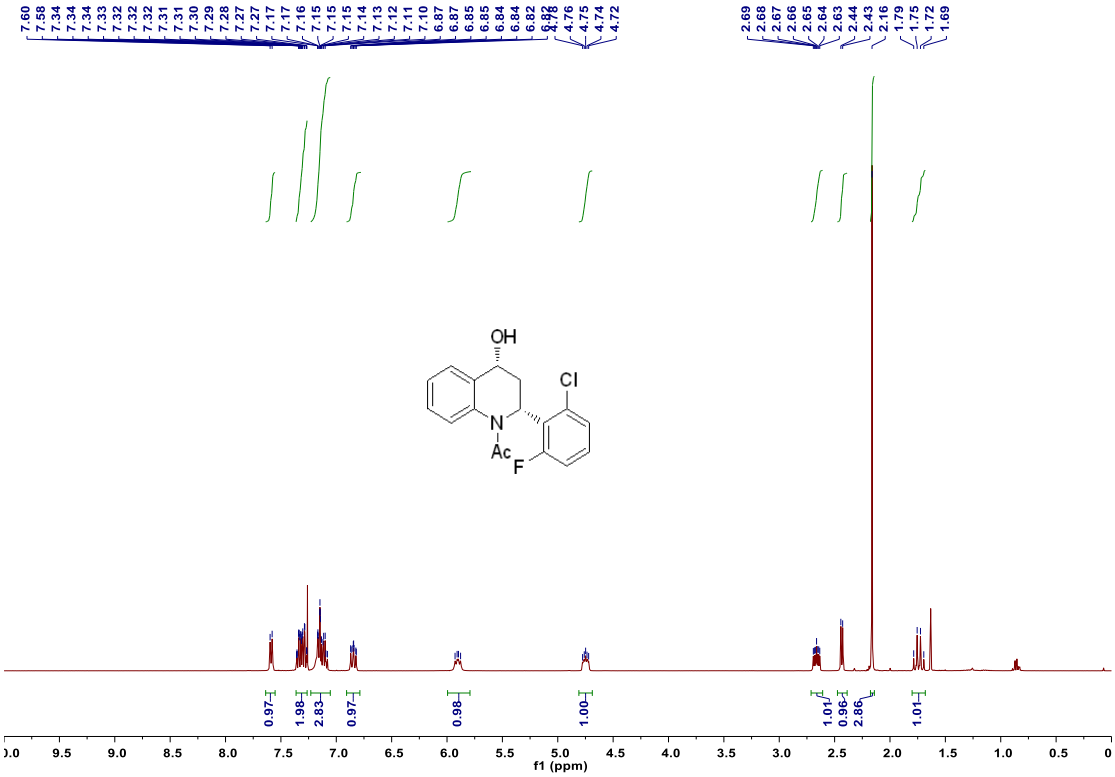
Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 10% EtOH.amx

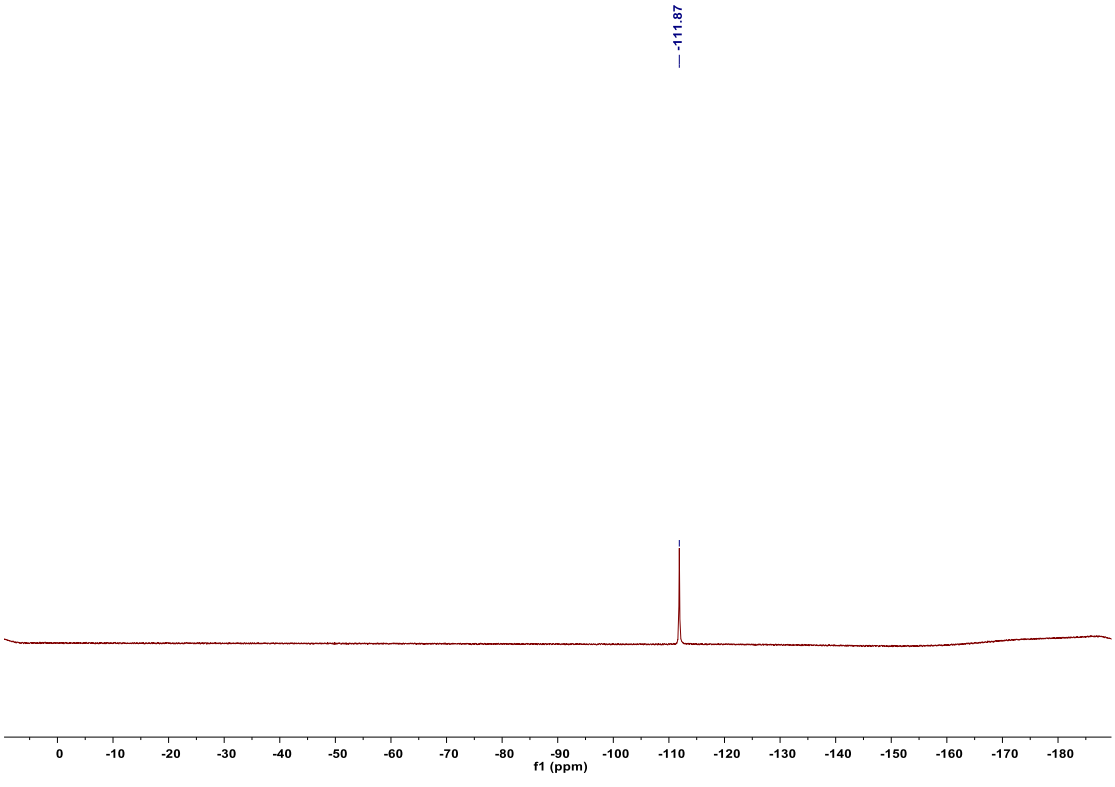
Injection Acquired Date 2020-07-29 16:39:36+02:00

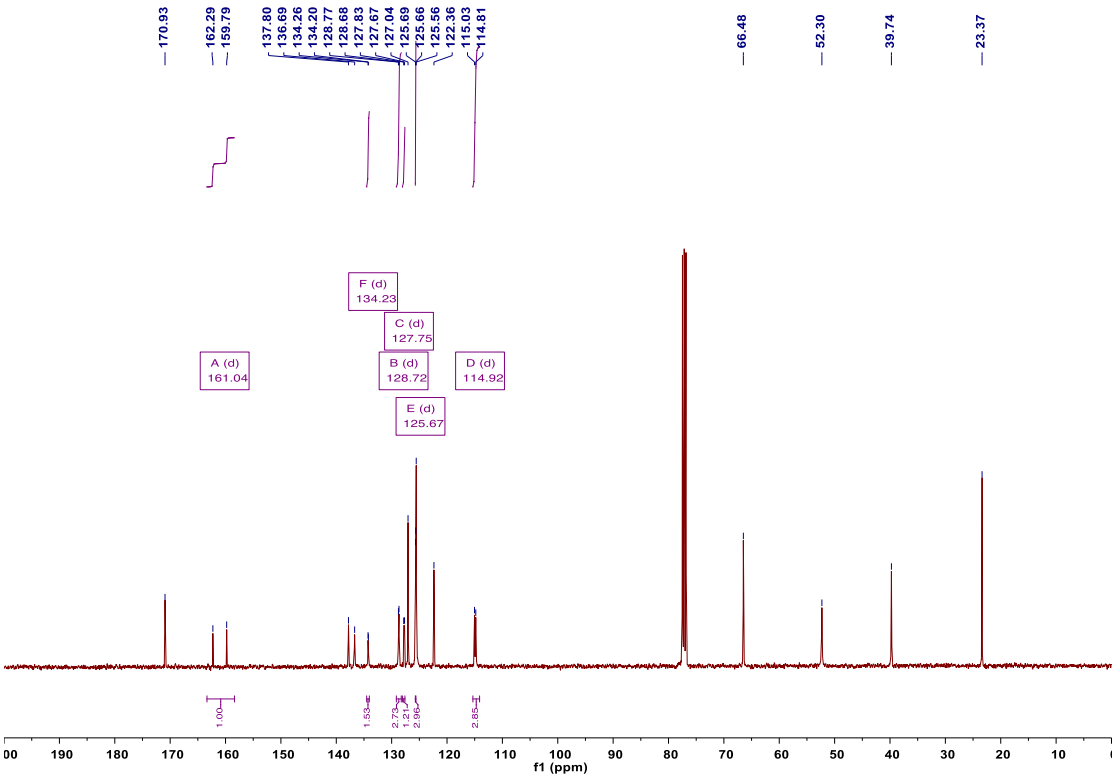
RT	Peak Area %
9.914	97.94
14.354	2.06



Compound **4n**


7.60 7.58 7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.27 7.17 7.17 7.16 7.15 7.15 7.15 7.14 7.13 7.12 7.11 7.10 6.87 6.87 6.85 6.85 6.84 6.84 6.82 6.82 4.76 4.75 4.74 4.72
2.69 2.68 2.67 2.66 2.65 2.64 2.63 2.44 2.43 2.16 1.79 1.75 1.72 1.69
OH
Cl
N
Ac
F
0.97 1.98 2.83 0.97 0.98 1.00 1.01 0.96 2.86 1.01
f1 (ppm)

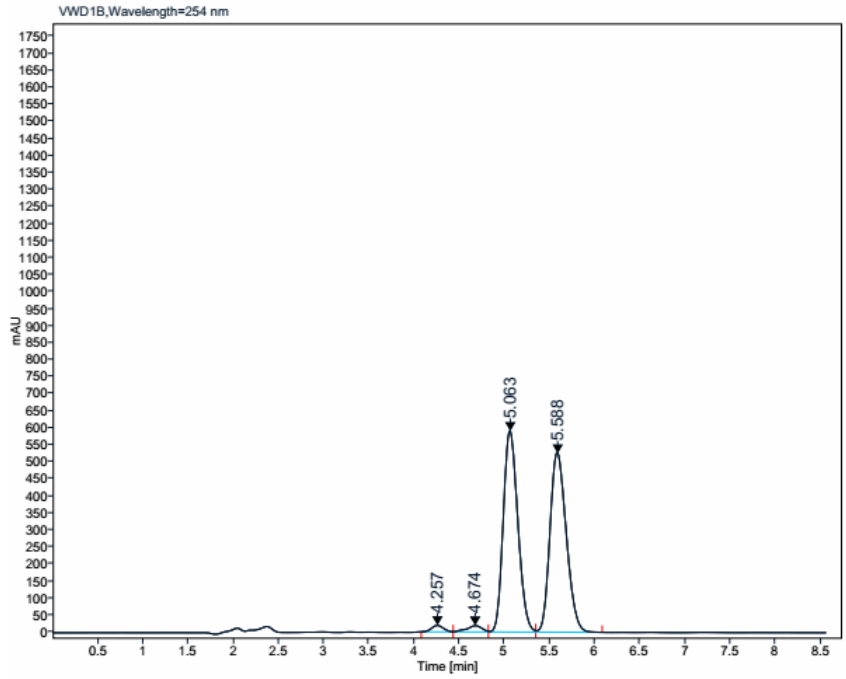

-111.87
f1 (ppm)



Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-09 17:48:19+02:00

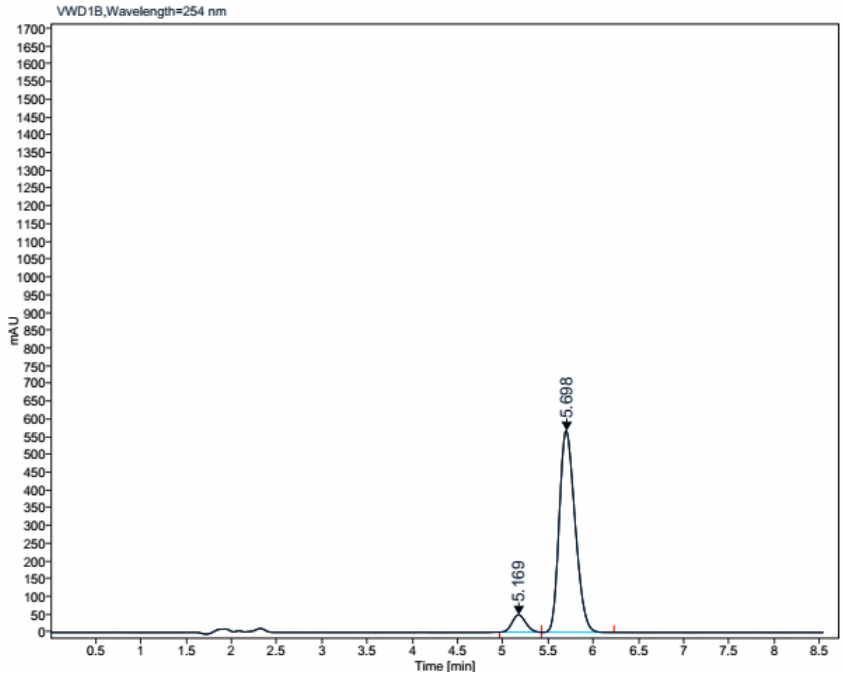
RT	*Peak Area %*
4.257	1.24
4.674	1.56
5.063	48.60
5.588	48.60



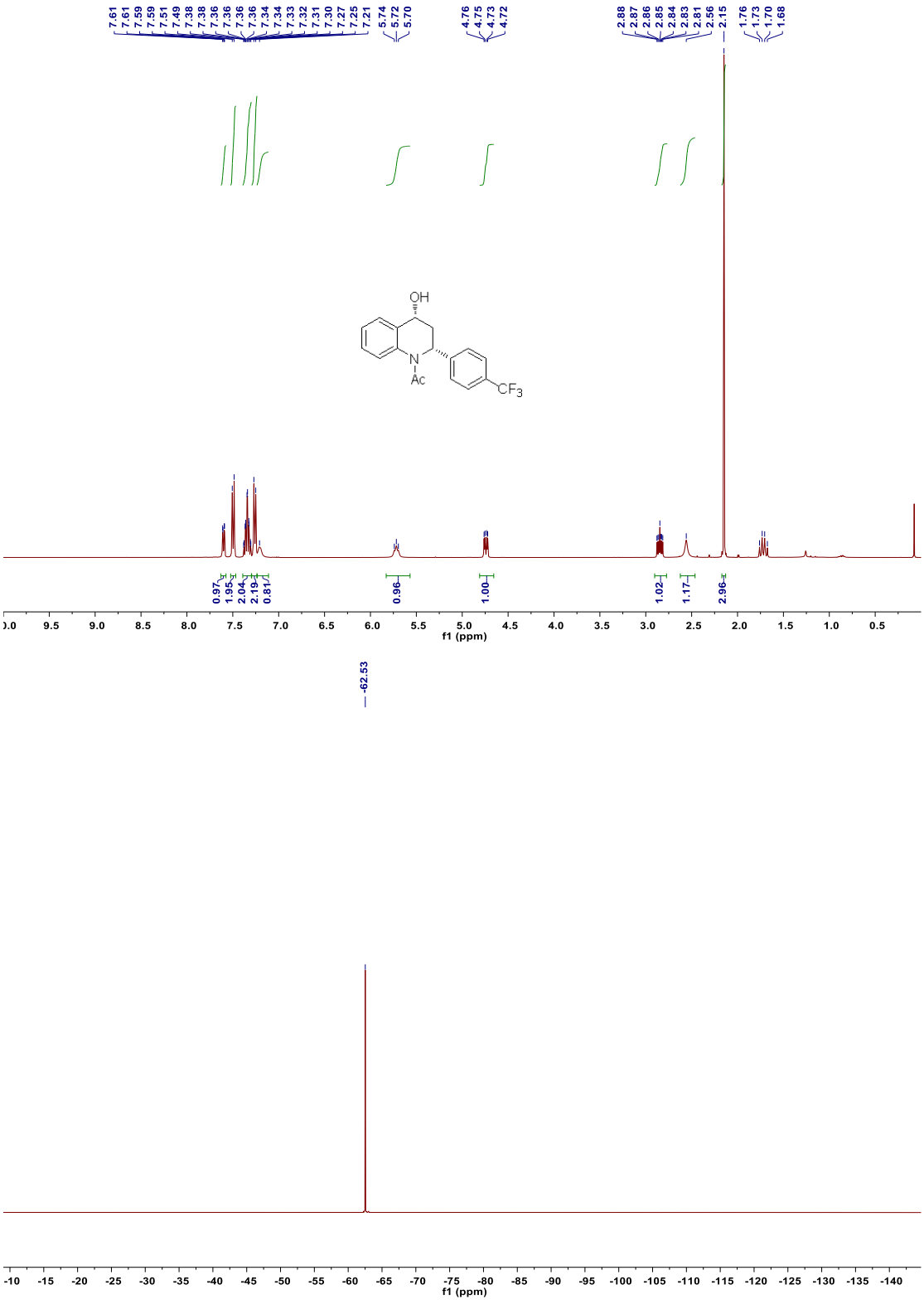
Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 20% MeOH.amx

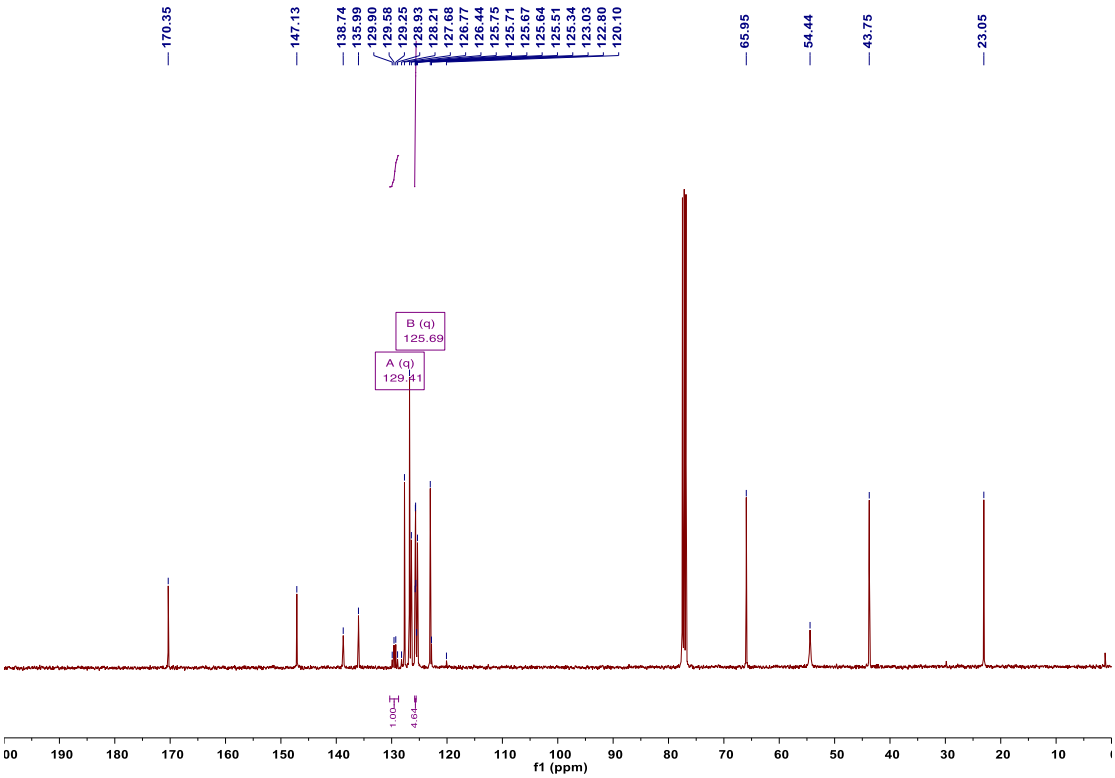
Injection Acquired Date 2020-08-04 15:39:52+02:00

RT	*Peak Area %*
5.169	6.83
5.698	93.17



Compound **4o**

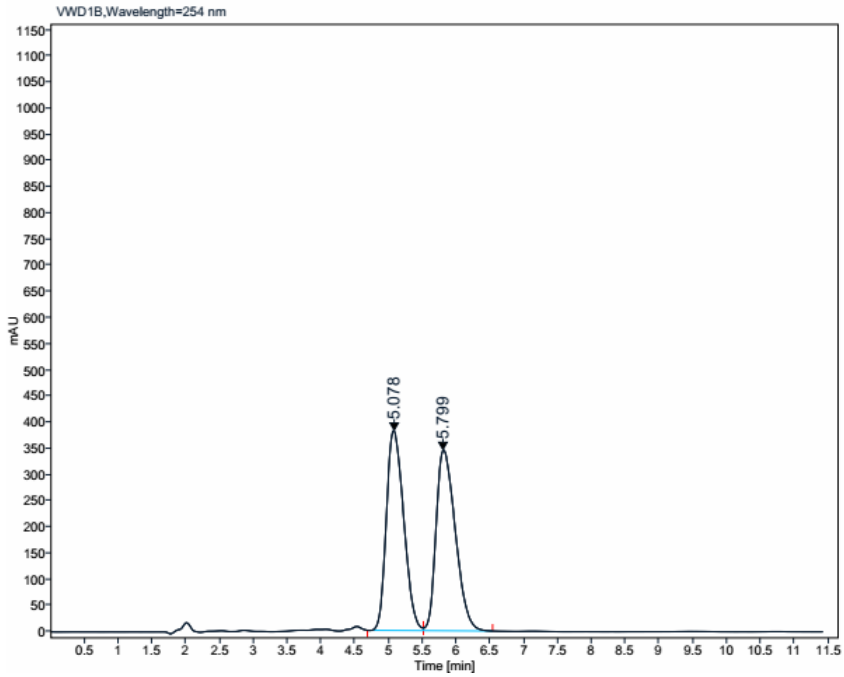

7.61
7.61
7.59
7.59
7.51
7.49
7.38
7.38
7.36
7.36
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.27
7.25
7.21
5.74
5.72
5.70
4.76
4.75
4.73
4.72
2.88
2.87
2.86
2.85
2.84
2.83
2.81
2.56
2.15
1.76
1.73
1.70
1.68
OH
N
Ac
CF3
0.97
1.95
2.04
2.19
0.81
0.96
1.00
1.02
1.17
2.96
f1 (ppm)
-62.53
f1 (ppm)



Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 8% EtOH.amx

Injection Acquired Date 2020-07-07 09:54:54+02:00

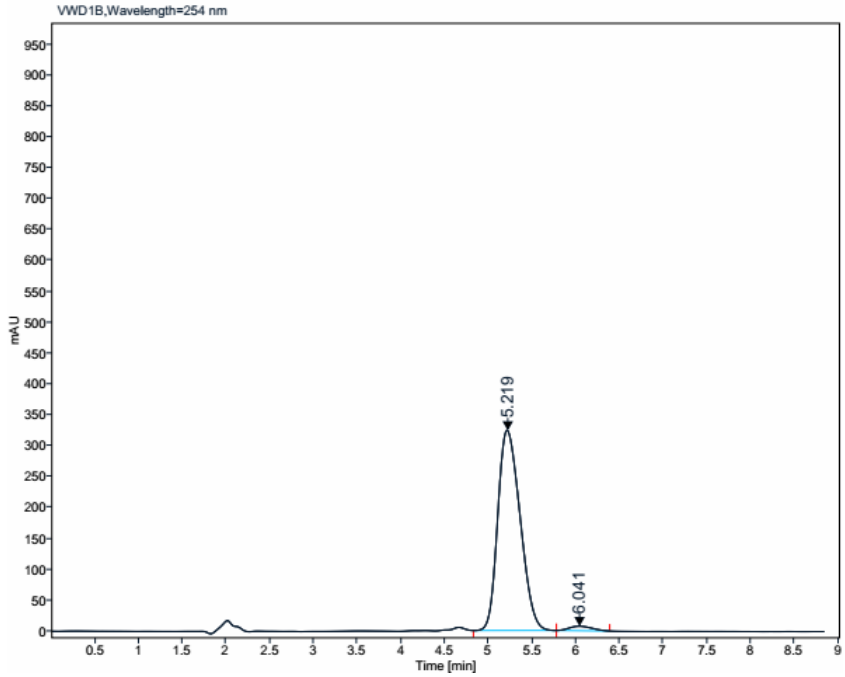
RT	*Peak Area %*
5.078	49.84
5.799	50.16



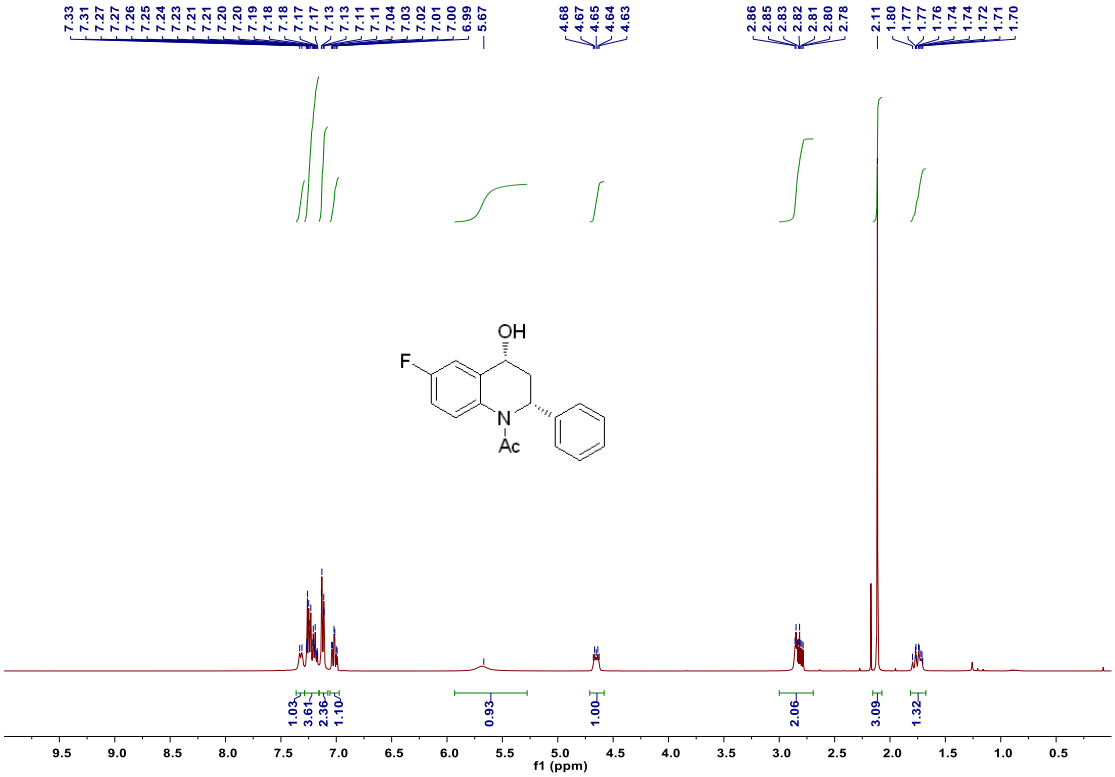
Injection Acq Method Name AS-H - 100 bars - 2 mL.min-1 - 8% EtOH.amx

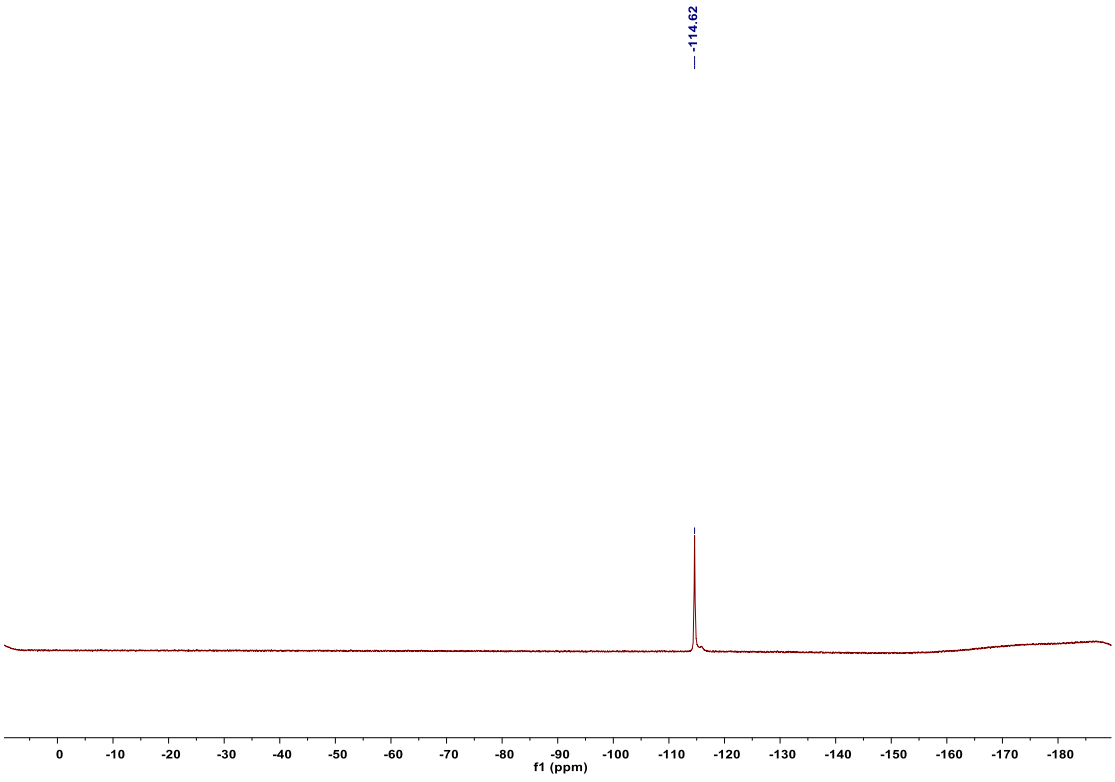
Injection Acquired Date 2020-07-29 16:22:16+02:00

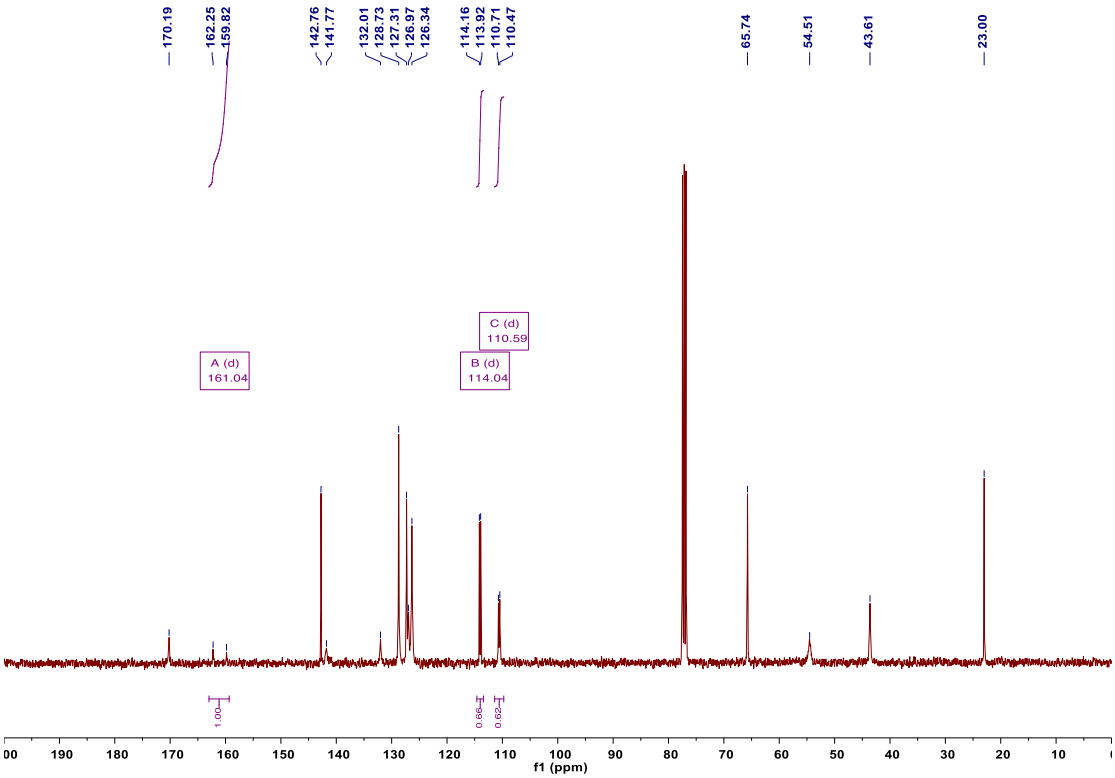
RT	*Peak Area %*
5.219	97.81
6.041	2.19



Compound **4p**


7.33
7.31
7.27
7.27
7.26
7.25
7.24
7.23
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.13
7.13
7.11
7.11
7.04
7.03
7.02
7.01
7.00
6.99
5.67
4.68
4.67
4.65
4.64
4.63
2.86
2.85
2.83
2.82
2.81
2.80
2.78
2.11
1.80
1.77
1.77
1.76
1.74
1.74
1.72
1.71
1.70
OH
F
N
Ac
1.03
3.61
2.36
1.10
0.93
1.00
2.06
3.09
1.32
f1 (ppm)

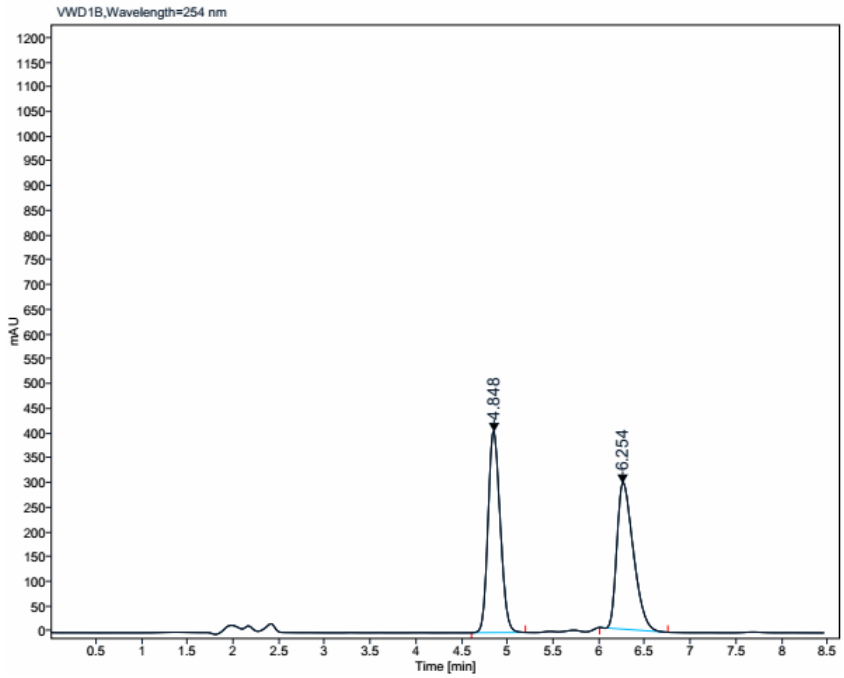

-114.62
f1 (ppm)



Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-08 09:31:59+02:00

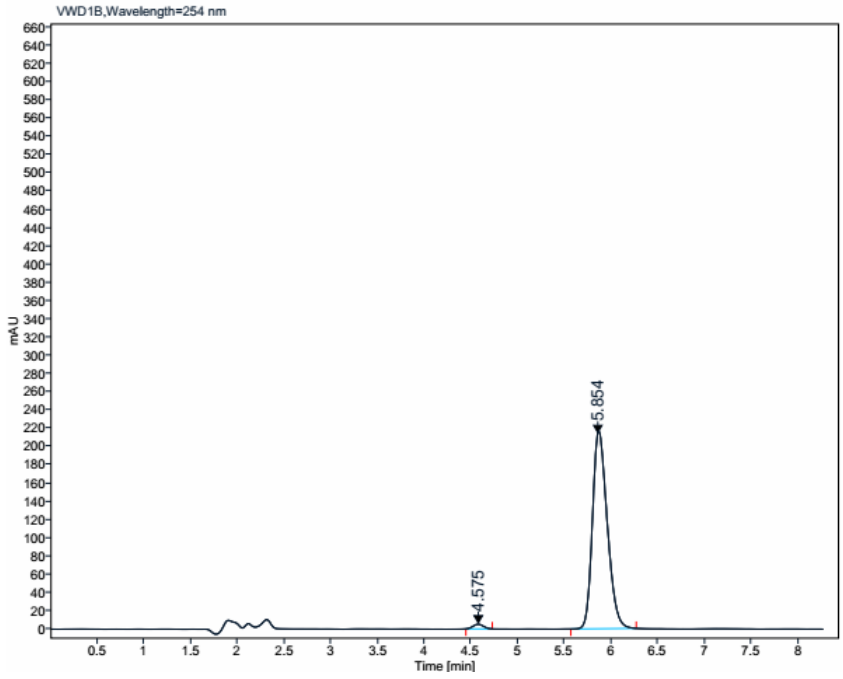
RT	*Peak Area %*
4.848	50.43
6.254	49.57



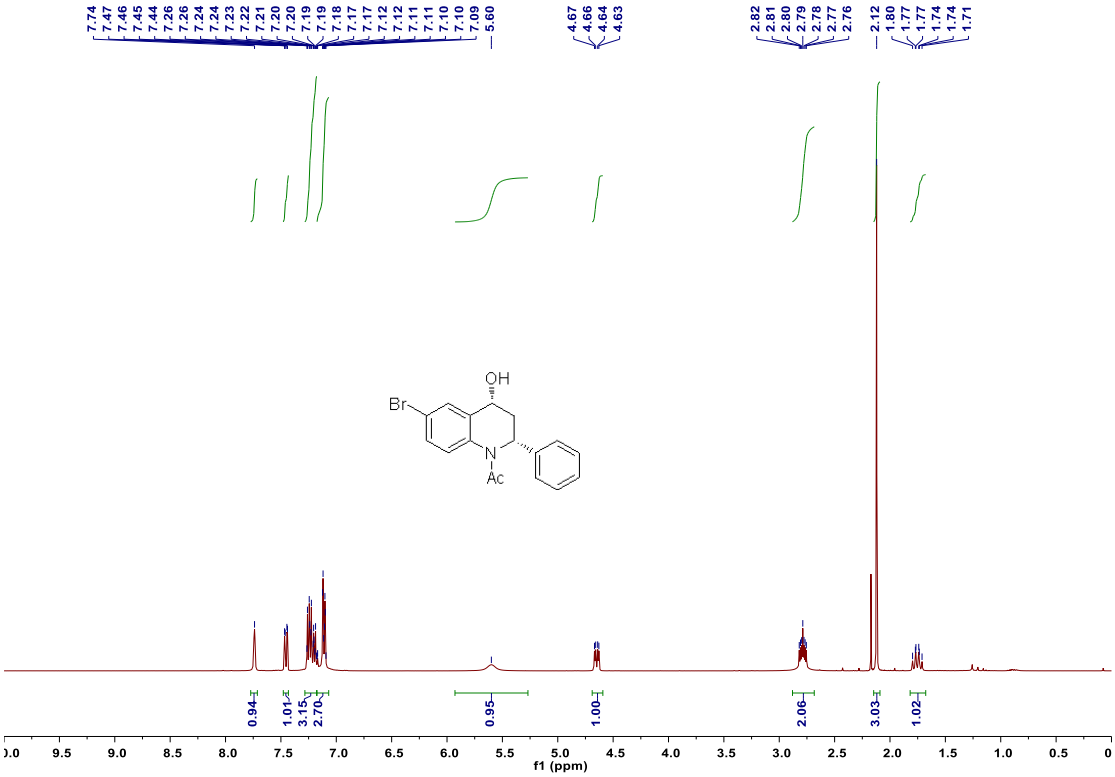
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

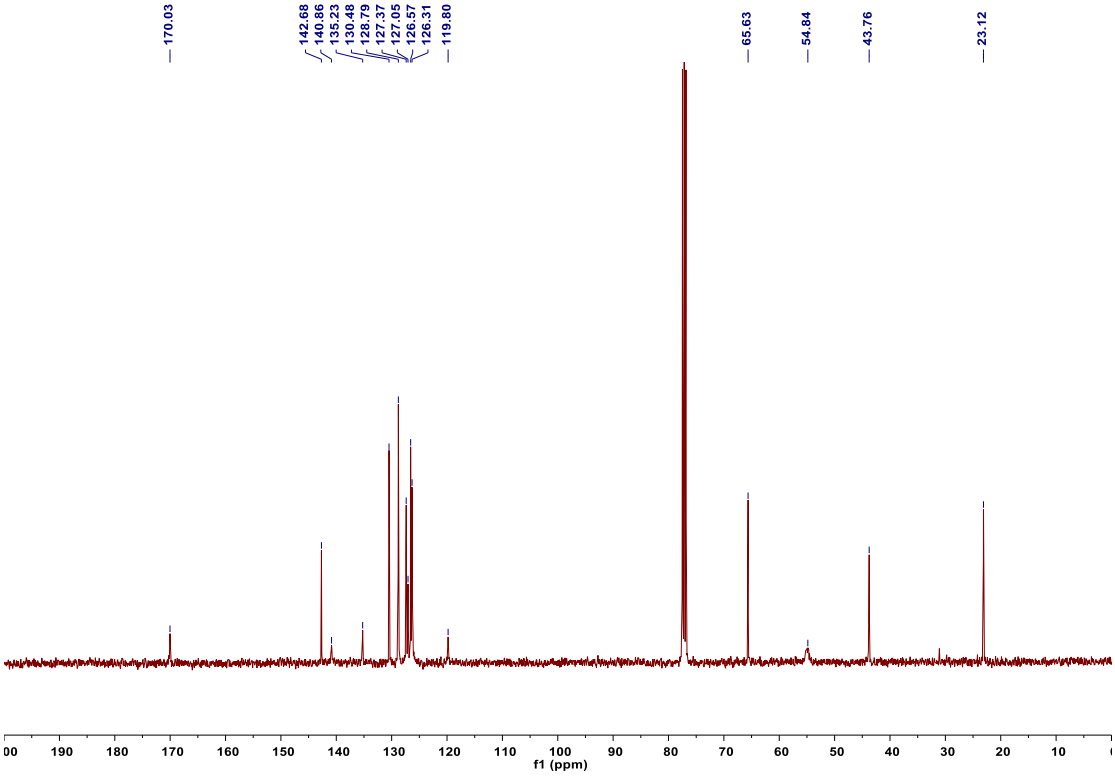
Injection Acquired Date 2020-08-05 15:04:16+02:00

RT	*Peak Area %*
4.575	1.61
5.854	98.39



Compound **4q**

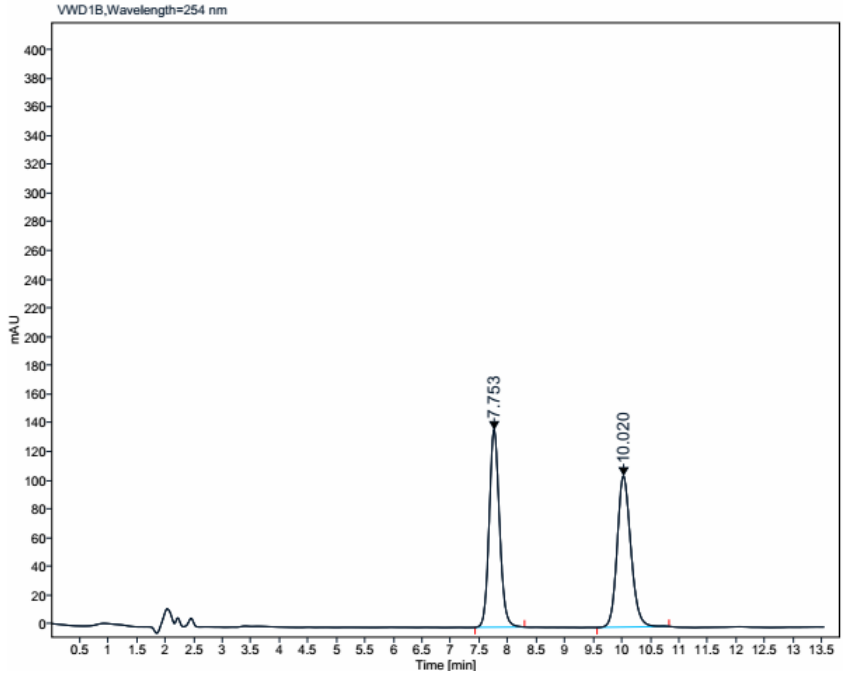

7.74
7.47
7.46
7.45
7.44
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.12
7.12
7.11
7.11
7.10
7.10
7.09
5.60
4.67
4.66
4.64
4.63
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.12
1.80
1.77
1.77
1.74
1.74
1.71
OH
Br
N
Ac
0.94
1.01
3.15
2.70
0.95
1.00
2.06
3.03
1.02
f1 (ppm)


170.03
142.68
140.86
135.23
130.48
128.79
127.37
127.05
126.57
126.31
119.80
65.63
54.84
43.76
23.12
f1 (ppm)

Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

Injection Acquired Date 2020-07-15 10:06:52+02:00

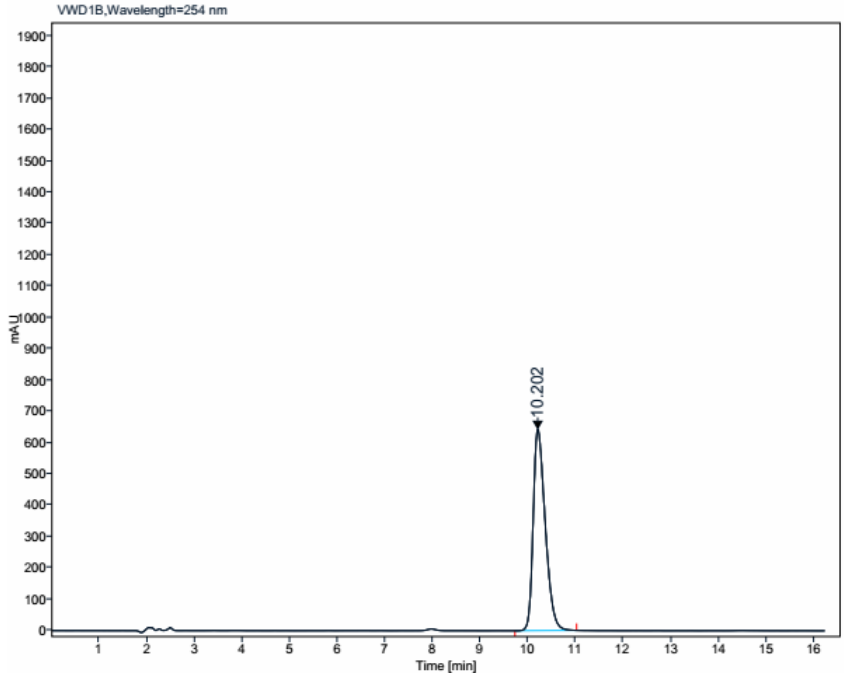
RT	Peak Area %
7.753	49.74
10.020	50.26



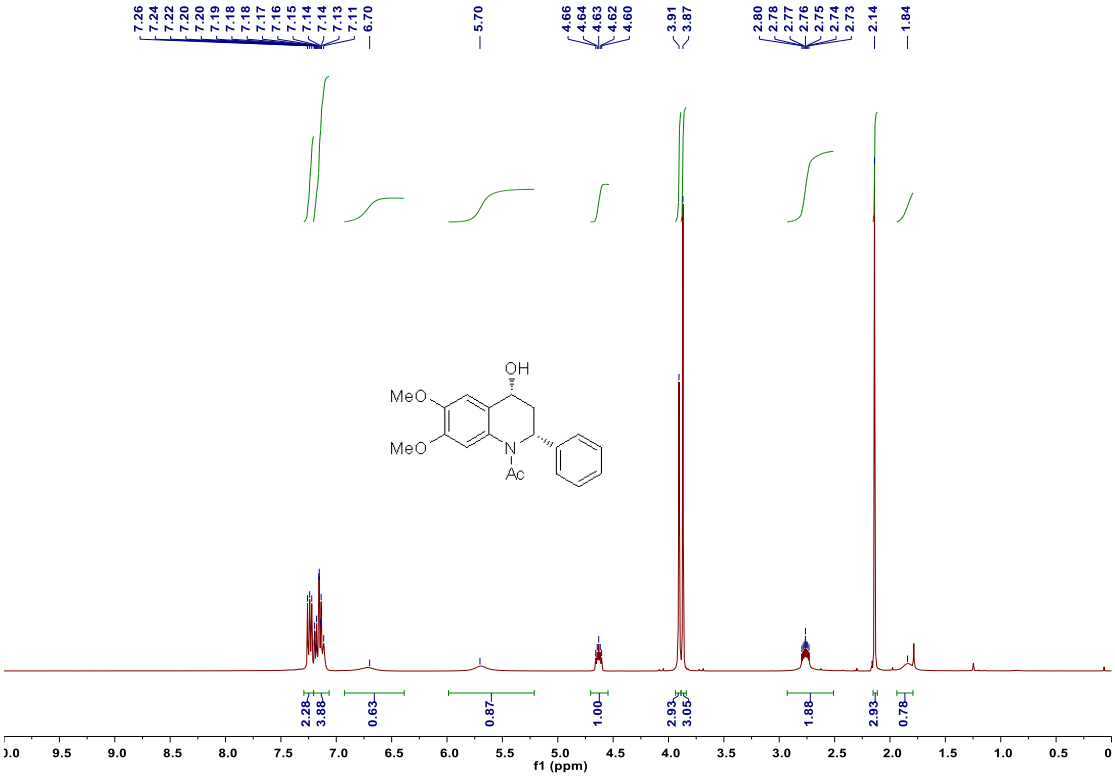
Injection Acq Method Name IF- 100 bars - 2 mL.min-1 - 20% MeOH.amx

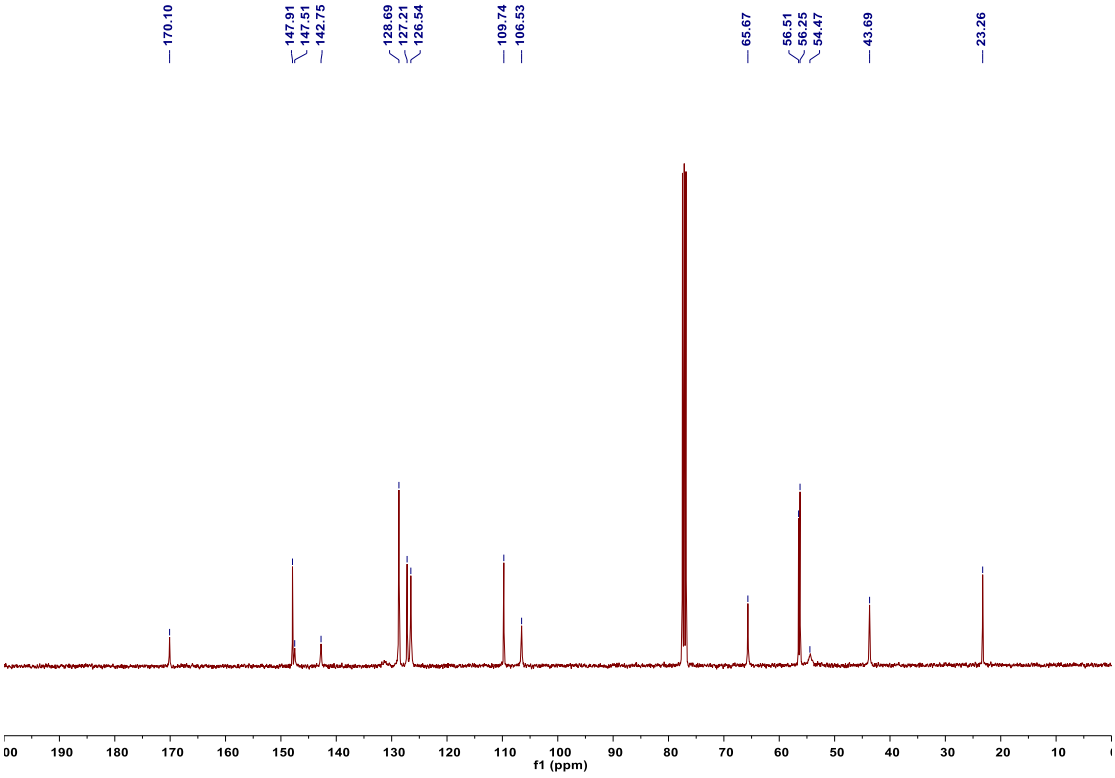
Injection Acquired Date 2020-07-24 09:19:54+02:00

RT	Peak Area %
10.202	100.00



Compound **4r**

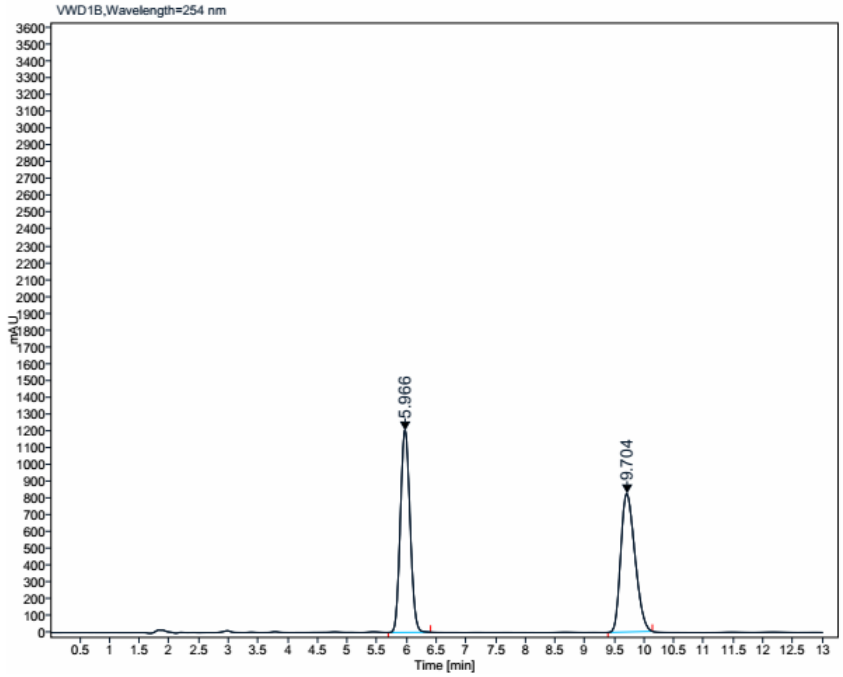

7.26
7.24
7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.11
6.70
5.70
4.66
4.64
4.63
4.62
4.60
3.91
3.87
2.80
2.78
2.77
2.76
2.75
2.74
2.73
2.14
1.84
OH
MeO
MeO
N
Ac
2.28
3.88
0.63
0.87
1.00
2.93
3.05
1.88
2.93
0.78
f1 (ppm)


170.10
147.91
147.51
142.75
128.69
127.21
126.54
109.74
106.53
65.67
56.51
56.25
54.47
43.69
23.26
f1 (ppm)

Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 15% EtOH.amx

Injection Acquired Date 2020-08-25 17:53:14+02:00

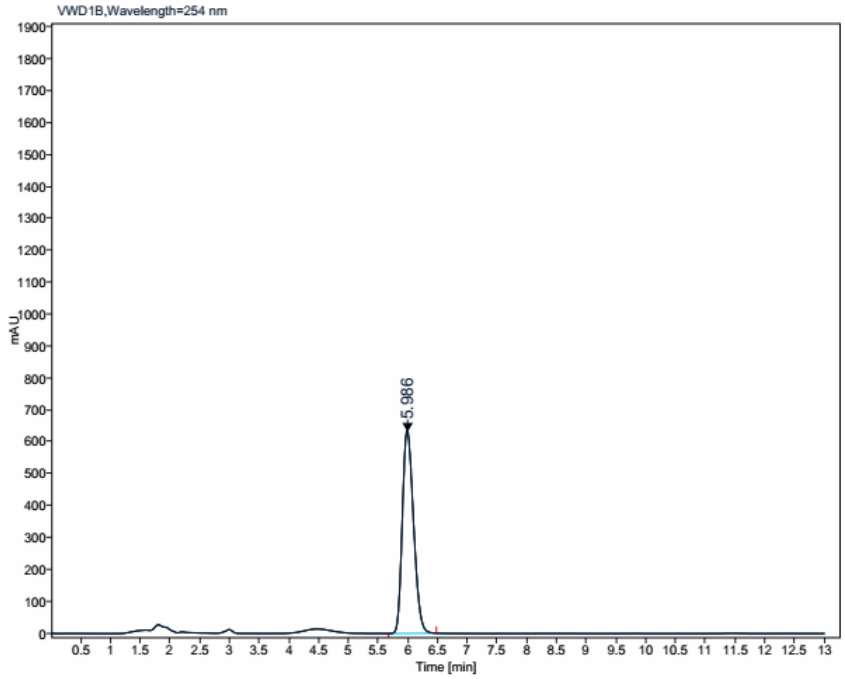
RT	*Peak Area %*
5.966	49.97
9.704	50.03



Injection Acq Method Name ADH - 100 bars - 2 mL.min-1 - 15% EtOH.amx

Injection Acquired Date 2020-08-25 18:06:57+02:00

RT	*Peak Area %*
5.986	100.00

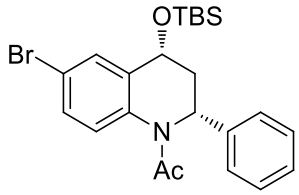


XI. Analytical data and procedures for compounds 5-7

1-((2*R*,4*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-2,6-diphenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (5)

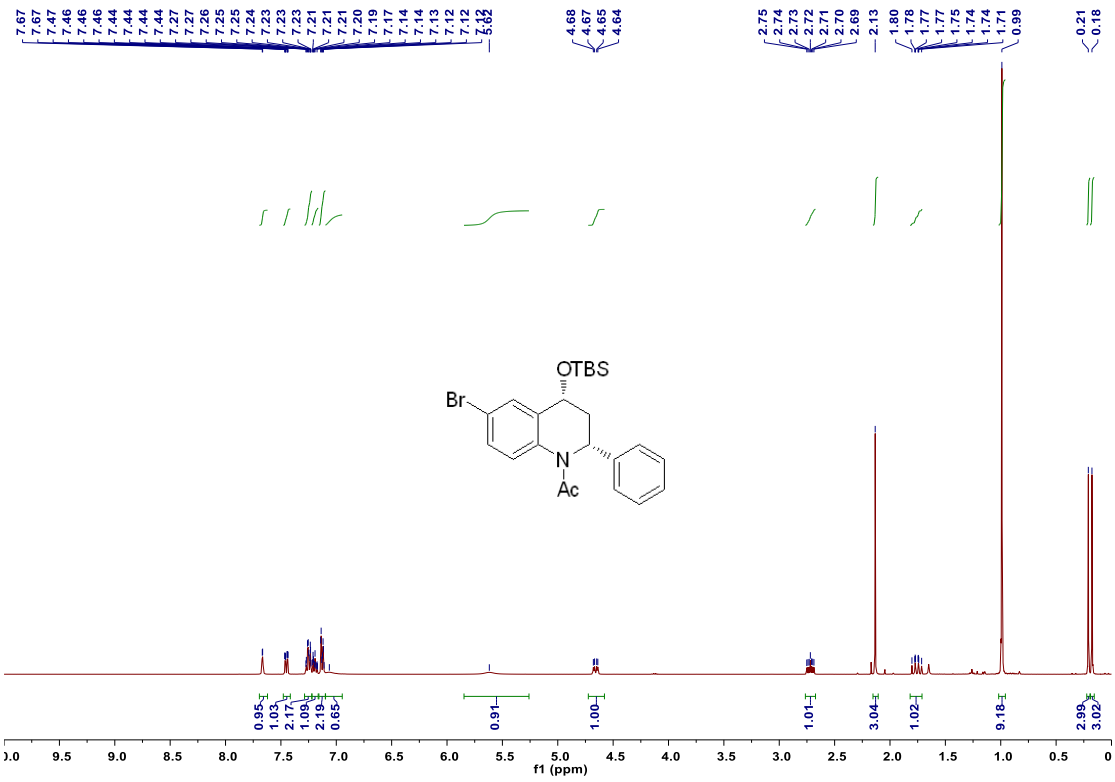
A solution of 1-((2*R*,4*R*)-6-bromo-4-hydroxy-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone **4q** (150 mg, 0.43 mmol) and imidazole (35 mg, 0.52 mmol) in DMF (0.3 mL) was added dropwise to a cooled (0 °C) solution of TBSCl (78 mg, 0.52 mmol) in DMF (0.2 mL) and the mixture was stirred at room temperature for 24 h. Water (10 ml) was added and the mixture was extracted with Et_2O (3 x 20 mL). The organic extracts were combined, dried with $MgSO_4$ and concentrated. The reside was purified by flash column chromatography to give pure 1-((2*R*,4*R*)-6-bromo-4-((*tert*-butyldimethylsilyl)oxy)-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (**5'**) (133 mg, 67% yield). The latter compound (130 mg, 0.28 mmol) was placed in a round-bottom tube, and phenylboronic acid (73 mg, 0.6 mmol), K_2CO_3 (124 mg, 0.9 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol) and cataCXium A (10.7 mg, 0.03 mmol) were added. The tube was purged with argon three times and DMF (1.5 ml) was added. The reaction was heated at 100 °C overnight, quenched with water and extracted by CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (Petroleum ether/EtOAc 10:1) to give pure **5** (125 mg, 98% yield) as a white solid.[4]

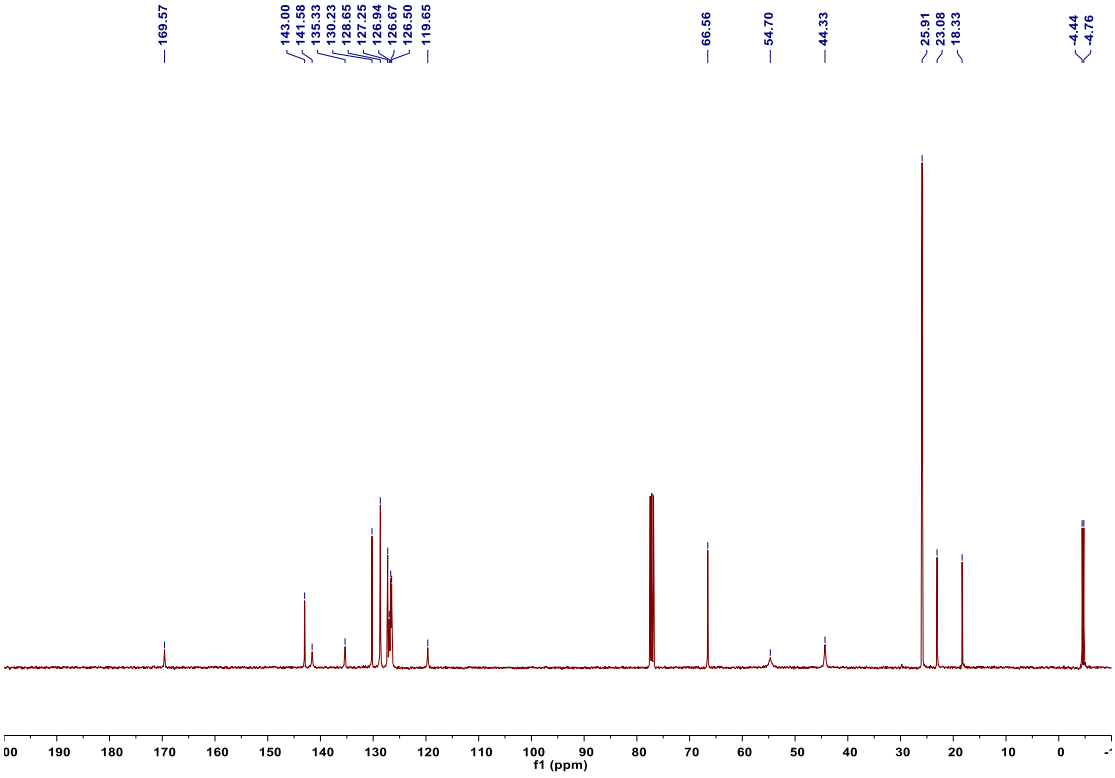
Compound 5'



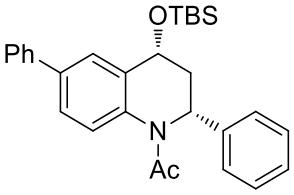
White solid, 133 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (br, 1H), 7.45 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.10 (m, 2H), 7.06 (br, 1H), 5.62 (br, 1H), 4.66 (dd, *J* = 11.9, 4.2 Hz, 1H), 2.72 (ddd, *J* = 13.0, 8.7, 4.4 Hz, 1H), 2.13 (s, 3H), 1.76 (ddd, *J* = 12.7, 11.8, 10.4 Hz, 1H), 0.99 (s, 9H), 0.21 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 143.0, 141.6, 135.3, 130.2, 128.6, 127.2, 126.9, 126.7, 126.5, 119.6, 66.6, 54.7, 44.3, 25.9, 23.1, 18.3, -4.4, -4.8.

[4] (a) S. G. Davies and C. L. Goodfellow, *J. Organomet. Chem*, **1988**, *340*, 195-201.
(b) B. He, P. Phansavath and V. Ratovelomanana-Vidal, *Org. Lett,* **2019**, *21,* 3276-3280.


OTBS
Br
N
Ac
f1 (ppm)

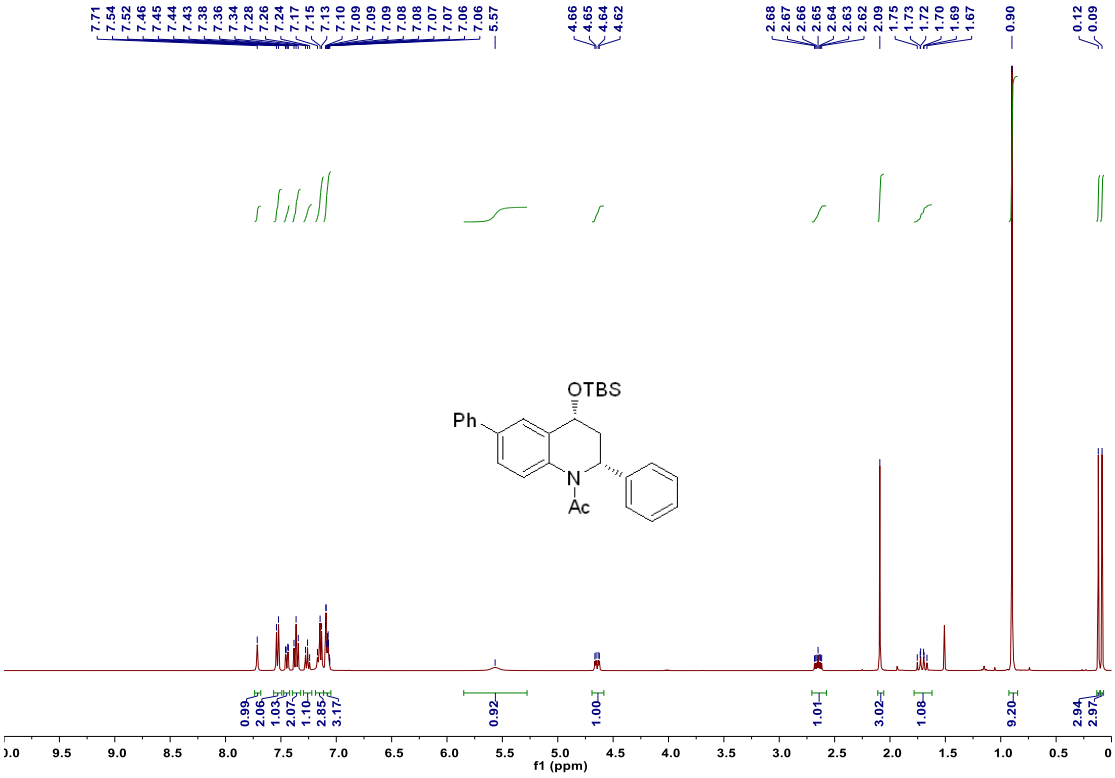

f1 (ppm)

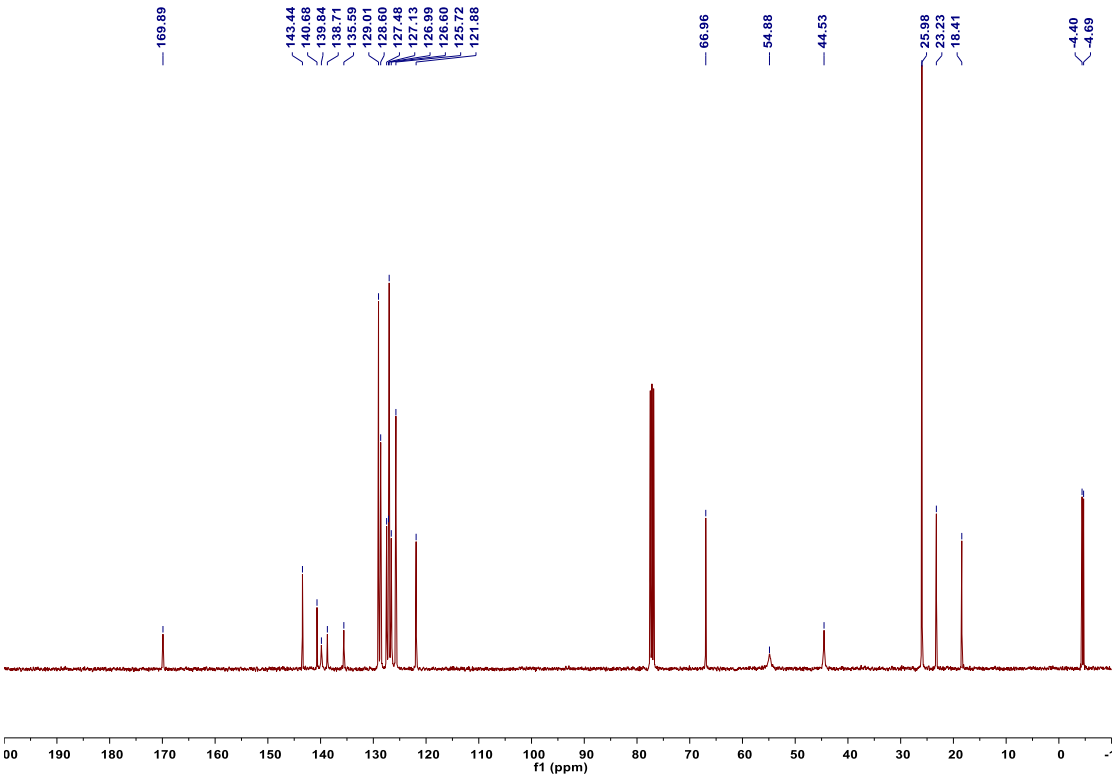
Compound 5



Light yellow solid, 133 mg, 67% yield, m.p.175 °C, $[\alpha]_D^{25}$ = +93.0 (c 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (br, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.45 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.11 – 7.04 (m, 3H), 5.57 (s, 1H), 4.64 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.65 (ddd, *J* = 12.9, 8.7, 4.4 Hz, 1H), 2.09 (s, 3H), 1.71 (td, *J* = 12.1, 10.6 Hz, 1H), 0.90 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 143.4, 140.7, 139.8, 138.7, 135.6, 129.0, 128.6, 127.5, 127.1, 127.0, 126.6, 125.7, 121.9, 67.0, 54.9, 44.5, 26.0, 23.2, 18.4, -4.4, -4.7.

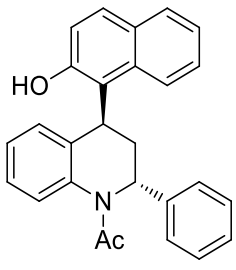
HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{29}H_{36}NO_2Si$ 458.2515, found 458.2510.





1-((2*R*,4*S*)-4-(2-Hydroxynaphthalen-1-yl)-2-phenyl-3,4-dihydroquinolin-1(2H)-yl)ethanone (6)

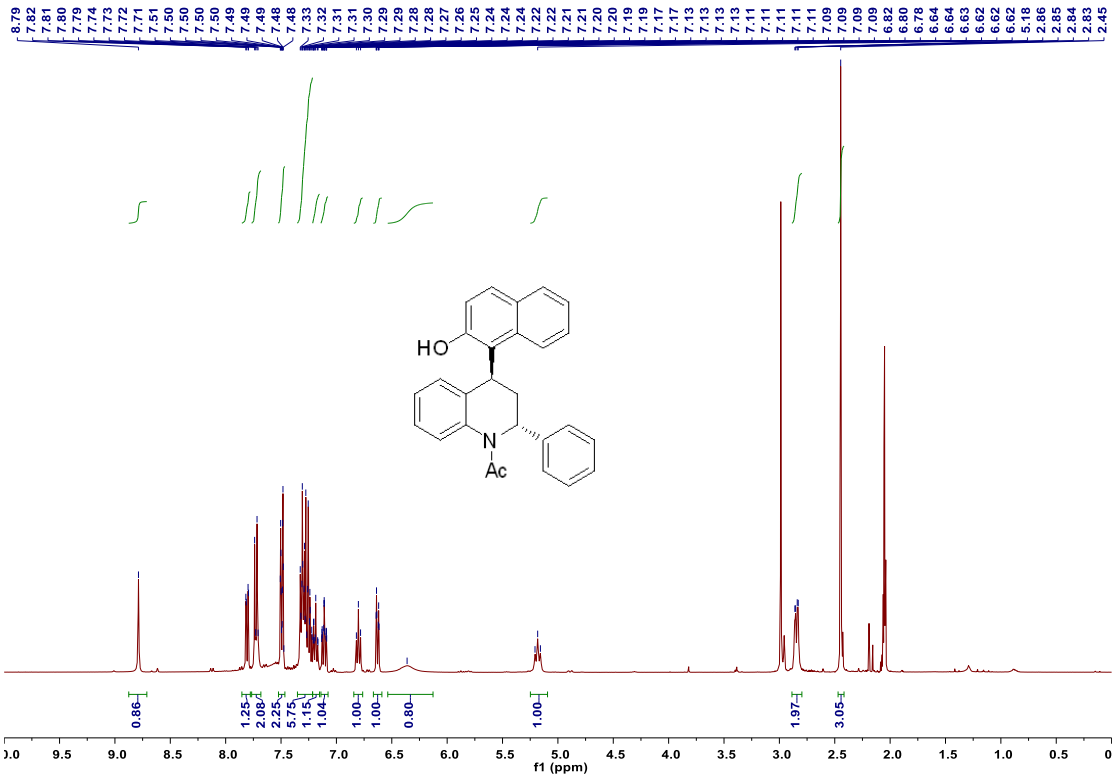
To a stirred solution of azaflavanol **4a** (107 mg, 0.4 mmol) and 2-naphthol (72 mg,0.5 mmol) in CH_2Cl_2 (4 mL) was added BF_3OEt_2 (493 ul, 4.0 mmol). The mixture was stirred at r.t. for 12 h and then quenched by the addition of $NaHCO_3$ solution (5 mL, 25%). The mixture was stirred for 10 min and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under vacuum. Flash chromatography over silica gel using petroleum ether/ EtOAc (1:1) gave compound **6**, as a white solid (140 mg, 89%).[5]

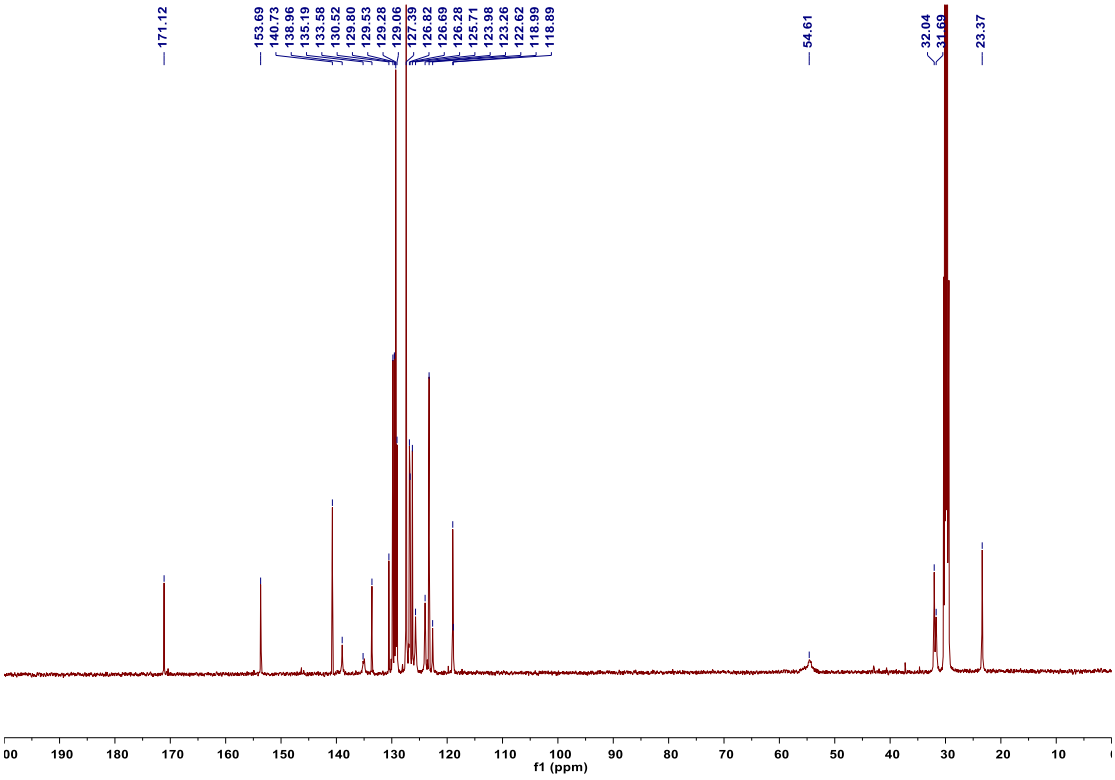


White solid, 140 mg, 89% yield, m.p.240 °C, $[\alpha]_D^{25}$ = -48.6 (c 1.16, $CHCl_3$). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.79 (s, 1H), 7.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72 (m, 2H), 7.49 (dq, *J* = 7.7, 1.2 Hz, 2H), 7.34 – 7.22 (m, 6H), 7.21 – 7.16 (m, 1H), 7.11 (dddd, *J* = 8.1, 7.2, 1.6, 0.9 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.63 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.36 (br, 1H), 5.18 (t, *J* = 9.8 Hz, 1H), 2.85 (dd, *J* = 9.0, 3.2 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 171.1, 153.7, 140.7, 139.0, 135.2, 133.6, 130.5, 129.8, 129.5, 129.3, 129.1, 127.4, 126.8, 126.7, 126.3, 125.7, 124.0, 123.3, 122.6, 119.0, 119.0, 54.6, 32.0, 31.7, 23.4.

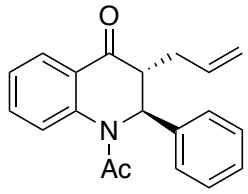
HRMS (ESI/ion trap): *m/z* $[M + H]^+$ calcd for $C_{27}H_{24}NO_2$ 394.1807, found 394.1802.

[5] R. Devakaram, D. StC. Black and N. Kumar, *Tetrahedron Lett*. **2012**, *53*, 2269–2272


HO
N
Ac
f1 (ppm)

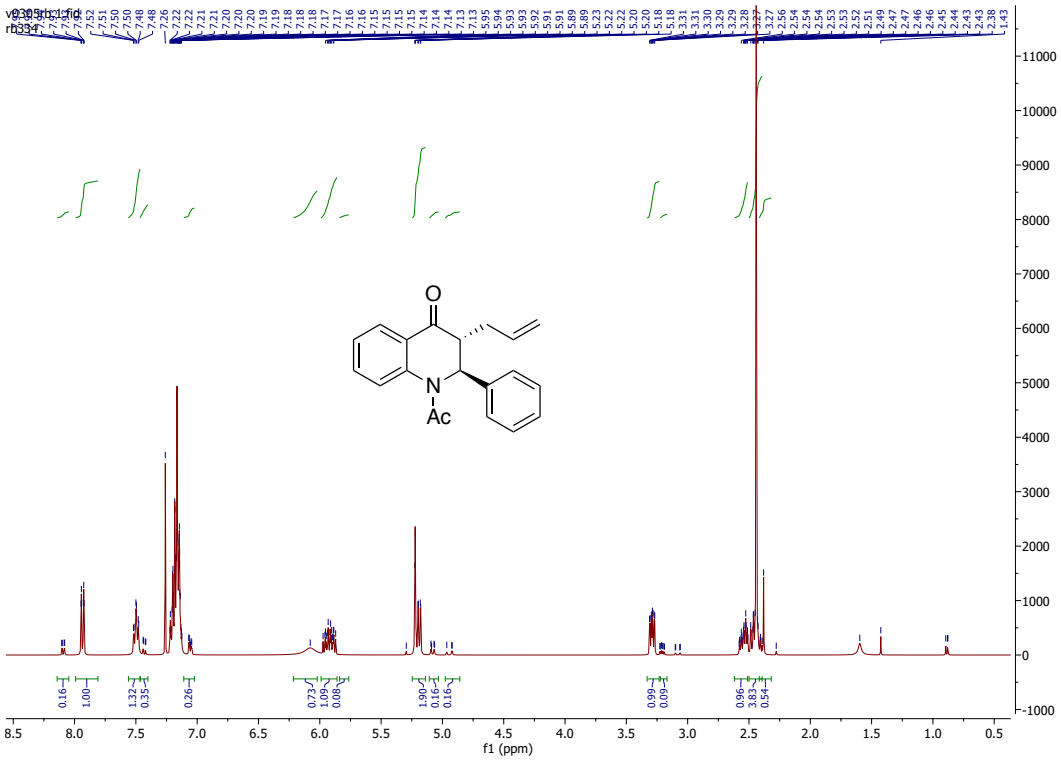

f1 (ppm)

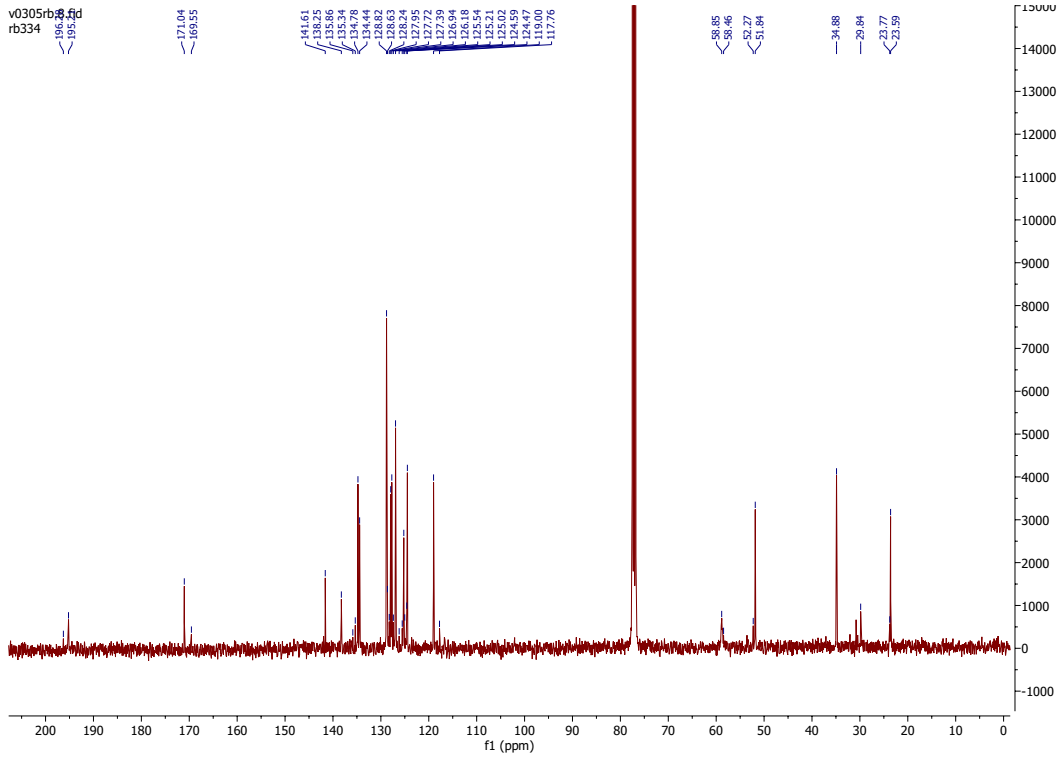
1-acetyl-3-allyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-one (7)



NaH (16.5 mg, 0.42 mmol, 1.1 eq, 60% suspension in oil) was introduced in a dry tube set under argon atmosphere. THF (0.5 mL) was added and the resulting mixture was stirred at 0 °C for one min before introducing with a syringe a solution of (*S*)-**3a** (80 mg, 0.30 mmol, 1.0 eq) in THF (2.5 mL). The slightly yellow-coloured solution was stirred at 0 °C for 40 min then for 10 min at room temperature (23 °C) resulting in a slightly red-coloured solution. Freshly distilled allyl bromide (29 µL, 0.33 mmol, 1.1 eq) was added and the mixture was stirred at 0 °C for 2 h then left to gently warm-up to room temperature for 12 h. After this time period, the mixture was quenched with NH_4Cl saturated aqueous solution (5 mL) and extracted with ethyl acetate (3 x 8 mL). The organic layer was combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford a yellow oil. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate, 95:5 to 80:20) yielded the allylated product as a mixture of diastereomers (39 mg, 0.13 mmol, 43% yield) and as a yellow oil.

Major diastereoisomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 1.7 Hz, 1H), 7.23 – 7.09 (m, 7H), 6.08 (br, 1H), 5.99 – 5.86 (m, 1H), 5.27 – 5.15 (m, 2H), 3.29 (ddd, *J* = 9.5, 5.5, 1.8 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.44 (m + s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.2, 171.0, 141.6, 138.3, 134.8, 134.4, 128.8, 128.0, 127.7, 126.9, 125.2, 124.6, 124.5, 119.0, 58.8, 51.8, 34.9, 23.6.
Minor diastereoisomer : ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.33 – 7.10 (m, 5H), 7.10 – 7.01 (m, 2H), 6.00 – 5.84 (br, 1H), 5.85 – 5.65 (m, 2H), 5.08 – 5.01 (m, 1H), 4.83 (dd, *J* = 17.0, 1.5 Hz, 1H), 2.58 – 2.48 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3, 169.6, 142.0, 138.1, 135.9, 135.3, 128.6, 128.2, 127.4, 126.2, 125.5, 125.0, 124.6, 117.8, 58.5, 52.3, 29.8, 23.8.


v0305rb1.1.fid
rb334
O
N
Ac
f1 (ppm)


v0305rb8.fid
rb334
f1 (ppm)