Supporting Information for

Chemistry of Epoxysulfones: Straightforward Synthesis of Versatile Chiral Building Blocks

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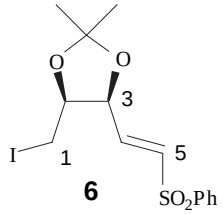
Compound 6. (2*S*, 3*S*,4*E*)-5-benzenesulfonyl-1-iodo-2,3-isopropylidendioxy-pent-4-ene



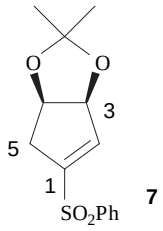
6

To a solution of **5** (80 mg, 0.18 mmol) in dry acetone (2.0 mL) was added NaI (81 mg, 0.54 mmol). The reaction mixture was refluxed overnight. The solvent was evaporated and the residue was dissolved in water (2mL) and extracted with EtOAc. The combined organic layers were washed with aqueous 10 % $Na_2S_2O_3$, 5 % $NaHCO_3$ and brine. The organic extract was dried over Na_2SO_4. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc: 85/15) gave compound **6** (55 mg, 75 %).

Data for compound **6**: $[\alpha]_D^{20}$ = -13.5 (c = 1.10, $CDCl_3$); IR (film) ν (cm^{-1}) 1383, 1148, 1086, 1038, 880, 760; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.94-7.52 (5H, m, -Ar), 6.99 (1H, dd, J = 4.4 and 15.0 Hz, H-4), 6.66 (1H, dd, J = 1.4 and 15.0 Hz, H-5), 4.85 (1H, m, H-3), 4.57 (1H, ddd, J = 6.6, 6.6, and 7.8 Hz, H-2), 3.10 (1H, dd, J = 6.6 and 10.2 Hz, H_A-1), 2.90 (1H, dd, J = 7.8 and

10.2 Hz, H_B-1), 1.47 (3H, s, Me-acetonide), 1.35 (3H, s, Me-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 140.1 (C-*ipso*), 139.6 (CH-4), 133.9 (CH-5), 133.4 (CH-*para*), 129.6 (2CH-*meta*), 128.1 (2CH-*ortho*), 110.2 (C-acetonide), 77.9 (CH-3), 76.1 (CH-2), 76.1 (CH_2-1), 28.1 (Me-acetonide), 25.5 (Me-acetonide); EIMS m/z (%) 408 (M^+, 5), 238 (91), 125 (60), 97 (100), 77 (80); HRMS (EI) calcd for $C_{14}H_{17}O_4SI$ 407.9892 found 407.9921.

Compound 7. (3*S*,4*R*)-1-benzenesulfonyl-3,4-isopropylidendioxy-cyclopentene



7

*General procedure for the synthesis of **7**:*

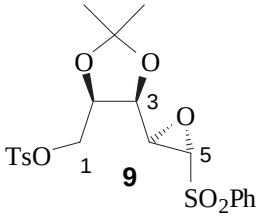
LDA was generated by addition of *n*-BuLi 1.6 M (0.79 mmol, 0.5 mL) to a solution of diisopropylamine (0.1 mL, 0.79 mmol) in THF (1.5 mL) at –78ºC. After 5 minutes the mixture was allowed to warm to room temperature and then recooled to –78ºC. Compound **5** or **6** (0.26 mmol) was then added to the reaction flask via cannula as a solution in THF (1.5 mL). The reaction mixture was left to stir for 1 h at – 78 ºC under argon before the addition of saturated ammonium chloride solution. The reaction mixture was extracted with EtOAc and dried over Na_2SO_4. The residue obtained after concentration was purified by chromatography.

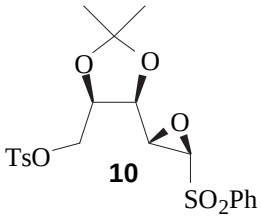
Reaction of **5** with LDA: The residue was purified by flash chromatography using a mixture of *n*-hexane/EtOAc 85:15 as eluent. Compound **7** (8 mg, 10 %) was obtained as a white solid: mp = 66 ºC (lit[23]= 66 ºC); $[\alpha]_D^{20}$ = +16.2 (c= 0.88, $CHCl_3$) along with unreactive starting material (99 mg).

Reaction of **6** with LDA: Purification in the same conditions to those described before afford compound **7** (14 mg, 19 %) recovering the unreactive starting material (79 mg).
Spectroscopic data for compound **7** are identical to those describe in the literature.[23]

Compounds 9 and 10.

9: (2*R*,3*S*,4*R*,5*R*)-5-benzenesulfonyl-4,5-epoxy-2,3-isopropylidenedioxy-pentan-1-yl tosylate
10: (2*R*, 3*S*,4S,5*S*)-5-benzenesulfonyl-4,5-epoxy-2,3-isopropylidenedioxy-pentan-1-yl tosylate





A solution containing *t*-BuOOH (1.0 mL, 5.64 mmol) in dry THF (10.0 mL), was cooled at –78ºC under argon. *n*-BuLi (3.5 mL. 5.64 mmol) was added dropwise and the resulting solution was stirred at –78ºC for 15 min. Then, **5** (1.02 g, 2.25 mmol) dissolved in 12.0 mL in THF was added via cannula. The reaction was warmed to room temperature and stirred overnight. The reaction mixture was quenched with saturated ammonium chloride, the organic layer was extracted with EtOAc and dried over Na_2SO_4. Concentration followed by purification via flash chromatography (*n*-hexane/EtOAc, 85:15) gave **9** (0.95 g, 90 %) as a white solid and **10** (50 mg, 5 %) as a viscous oil.

Identical results are obtained using TBHP and KH instead following the procedure described below:

TBHP (2.5 equiv) was added to a mixture of THF washed KH (2.5 equiv) in dry THF at – 78 ºC under argon. The resulting solution was stirred at –78ºC for 15 min. Then, **5** (1 equiv) dissolved in THF was added via cannula. The reaction was warmed to room temperature and stirred overnight. The reaction mixture was quenched with saturated ammonium chloride, the organic layer was extracted with EtOAc and dried over Na_2SO_4. Concentration followed by flash chromatography gave compounds **9** and **10**.

Data for compound **9**: mp = 125 ºC; $[\alpha]_D^{20}$ = + 32.6 (c= 1.61, $CHCl_3$); IR (film) ν (cm^{-1}) 2934, 1449, 1373, 1329, 1179, 1088, 990; ^{1}H NMR ($CDCl_3$, 400 MHz) 8.01-7.28 (9H, m, Ar), 4.46 (1H, ddd, J = 5.7, 6.2 and 6.2 Hz, H-2), 4.20 (1H, dd, J = 5.7 and 11.4 Hz, H_A-1), 4.18 (1H, dd, J = 6.2 and 11.4 Hz, H_B-1), 4.10 (1H, d, J = 1.6 Hz, H-5), 4.05 (1H, dd, J = 5.6 and 6.2 Hz, H-3), 3.61 (1H, dd, J = 1.6 and 5.6 Hz, H-4), 2.46 (3H, s, Me-Ts), 1.40 (3H, s, Me-acetonide), 1.30 (3H, s, Me-acetonide);

^{13}C NMR ($CDCl_3$, 50.3 MHz) 145.4 (C-*ipso*, -Ts), 136.7 (C-*ipso*, -SO_2Ph), 134.9 (CH-*para*, -SO_2Ph), 132.7 (C-*ipso*, -Ts), 130.2 (2CH-*meta*, -Ts), 129.7 (2CH-*meta*, -SO_2Ph), 129.1 (2CH-*ortho*, -Ts), 128.4 (2CH-*ortho*, -SO_2Ph), 110.9 (C-acetonide), 75.0 (CH-2), 74.2 (CH-3), 67.1 (CH_2-1), 66.6 (CH-5), 54.6 (CH-4), 27.5 (Me-acetonide), 25.1 (Me-acetonide), 21.9 (Me, -Ts); MS (FAB) m/z (%) 469 (M^++1, 12), 327 (11), 289 (10), 221 (10), 154 (90), 125 (100), 91 (68), 69 (28); HRMS (FAB) m/z calcd for $C_{21}H_{25}O_8S_2$ 469.0990, found 469.0984.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 210152

Summary of Data

Authors: D.Diez,M.Templo Beneitez,I.S.Marcos,N.M.Garrido,P.Basabe, F.Sanz, J.G.Urones

Formula: C21 H24 O8 S2

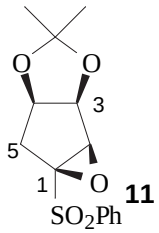
Unit cell parameters: a 5.4080(11) b 8.242(2) c 13.494(3)

alpha 96.40(3) beta 97.35(3) gamma 104.99(3)

space group P1.

Data for compound **10**: $[\alpha]_D^{20}$ = -65.9 (c = 0.57, $CHCl_3$); IR (film) ν (cm^{-1}) 2934, 1449, 1373, 1177, 1088, 988; ^{1}H NMR ($CDCl_3$, 400 MHz) 8.01-7.28 (9H, m, Ar), 4.56 (1H, ddd, J = 5.8, 6.2 and 6.2 Hz, H-2), 4.42 (1H, dd, J = 2.2 and 6.6 Hz, H-3), 4.22 (1H, dd, J = 5.8 and 10.8 Hz, H_A-1), 4.19 (1H, dd, J = 6.6 and 10.8 Hz, H_B-1), 4.14 (1H, d, J = 1.4 Hz, H-5), 3.68 (1H, dd, J = 1.4 and 2.2 Hz, H-4), 2.45 (3H, s, Me-Ts), 1.27 (6H, s, 2Me-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 144.1 (C-*ipso*, -Ts), 136.2 (C-*ipso*, -SO_2Ph), 134.8 (CH-*para*, -SO_2Ph), 132.4 (C-*ipso*, -Ts), 130.3 (2CH-*meta*, -Ts), 129.7 (2CH-*meta*, -SO_2Ph), 129.0 (2CH-*ortho*, -Ts), 128.4 (2CH-*ortho*, -SO_2Ph), 110.9 (C-acetonide), 74.7 (CH-2), 72.9 (CH-3), 67.6 (CH_2-1), 64.9 (CH-5), 54.7 (CH-4), 26.7 (Me-acetonide), 25.3 (Me-acetonide), 21.9 (Me, -Ts); MS (FAB) m/z (%) 469 (M^++1, 12), 353 (10), 307 (11), 258 (15), 154 (100), 125 (55), 91 (51); HRMS (FAB) m/z calcd for $C_{21}H_{25}O_8S_2$ 469.0990, found 469.1000.

Compound 11: (1*R* , 2*R*,3*R*,4*R*)-1-benzenesulfonyl-1,2-epoxy-3,4-isopropylidenedioxy-cyclopentane



11

To a solution of **9** (0.94 g, 2.01 mmol) in dry THF (10.0 mL) was added at –78 ºC a solution 1M of LiHMDS (4.42 mmol, 4.4 mL) in THF under argon atmosphere. The mixture was stirred for 1 h and then quenched with saturated aqueous ammonium chloride and extracted with EtOAc. The organic layer was separated, washed with brine, and dried over Na_2SO_4. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc, 80:20) gave **11** as a white solid (517 mg, 87 %): mp = 178 ºC; $[\alpha]_D^{20}$ = + 31.7 (c = 0.71, $CHCl_3$); IR (film) ν (cm^{-1}) 1373, 1321, 1258, 1161, 1076; ^{1}H NMR ($CDCl_3$, 200 MHz) 8.01-7.40 (5H, m, Ar), 4.78 (1H, dd, J = 6.6 and 7.0 Hz, H-4), 4.73 (1H, d, J = 7.0 Hz, H-3), 4.06 (1H, s, H-2), 2.71 (1H, dd, J = 6.6 and 15.4 Hz, H_A-5), 2.16 (1H, d, J = 15.4, H_B-5), 1.45 (3H, s, Me), 1.25 (3H, s, Me); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 136.1 (C-*ipso*), 134.8 (CH-*para*), 129.6 (2CH-*meta*), 129.4 (2CH-*ortho*), 113.3 (C-acetonide), 79.9 (CH-4), 79.3 (C-1), 78.8 (CH-3), 64.1 (CH-2), 30.8 (CH_2-5), 26.4 (Me-acetonide), 25.3 (Me- acetonide); MS (FAB) m/z (%) 297 (M^++1, 20), 256 (20), 154 (100), 125 (38), 77 (35); HRMS (FAB) m/z calcd for $C_{14}H_{17}O_5S$ 297.0797, found 297.0783.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 210151

Summary of Data

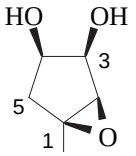
Authors: D.Diez,M.Templo Beneitez,I.S.Marcos,N.M.Garrido,P.Basabe, F.Sanz, J.G.Urones

Journal: Organic Letters (1336)

Formula: C14 H16 O5 S1

Unit cell parameters: a 15.814(3) b 10.550(2) c 10.919(2) beta 128.76(3), space group C2

Compound 12: (1*R*,2*R*,3*R*,4*R*)-1-benzenesulfonyl-1,2-epoxy-3,4-dihydroxy-cyclopentane



12

Compound **11** (250 mg, 0.84 mmol) was dissolved in MeOH (2.5 mL) and a catalitic amount of *p*-TsOH was added. The mixture was stirred for 5 days and then quenched with aqueous 5% $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. Concentration followed by chromatography on silica gel (*n*-hexane/EtOAc, 20:80) gave **12** as a white solid (205 mg, 95 %): mp = 174 ºC; $[\alpha]_D^{20}$ = + 9.9 (c = 0.91, MeOH); IR (film) ν (cm^{-1}) 3500, 1310, 1159, 1111, 1042, 891; ^{1}H NMR (MeOD, 200 MHz) 7.94-762 (5H, m, Ar), 4.28 (1H, d, J = 6.2 Hz, H-3), 4.11 (1H, dd, J = 6.2 and 6.6 Hz, H-4), 4.00 (1H, s, H-2), 2.68 (1H, dd, J = 6.6 and 15.0 Hz, H_A-5), 2.00 (1H, d, J = 15.0, H_B-5); ^{13}C NMR (MeOD, 50.3 MHz) 137.6 (C-*ipso*), 135.8 (CH-*para*), 130.6 (2CH-*meta*), 130.2 (2CH-*ortho*), 79.2 (C-1), 73.3 (CH-3), 69.7 (CH-4), 66.2 (CH-2), 34.6 (CH_2-5); EIMS m/z (%) 256 (M^+, 5), 153 (10), 115 (13), 71 (100); HRMS (EI) m/z calcd for $C_{11}H_{12}O_5S$ 256.0405 found 256.0412.

General procedure for the reaction with $MgBr_2Et_2O$:

To a solution of $MgBr_2Et_2O$ (0.40 mmol, 103 mg) in dry Et_2O or THF (1.0 mL) was added compound **11** or **12** (0.20 mmol) in THF (1.5 mL) via cannula. The mixture was then either stirred at room temperature or heated for the time indicated, then quenched with water and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc, 85:15) gave a mixture of compounds **13** and **14**.

Reaction of **11** with $MgBr_2Et_2O$ (solvent = THF): The mixture was refluxed for 5 h. After flash chromatography compounds **13** (13 mg, 43 %) and **14** (7 mg, 19 %) were obtained.

Reaction of **11** with $MgBr_2Et_2O$ (solvent = THF/Et_2O): The mixture was stirred for 3 h at 60 ºC. After chromatography a mixture of compounds **13** (21 mg, 60 %) and **14** (9 mg, 26 %) were obtained in a ratio 7:3.

Reaction of **12** with $MgBr_2Et_2O$ (solvent = THF/Et_2O): The mixture was stirred for 12 h at room temperature. After chromatography a mixture of compounds **13** (9 mg, 26 %) and **14** (23 mg, 66 %) were obtained in a ratio 3:7.

Compounds 13 and 14

13: (4*R*)-2-Bromo-4-hydroxy-cyclopent-2-enone

Data for compound **13**: $[\alpha]_D^{20}$ = + 17.5 (c = 0.82, $CHCl_3$); IR (film) ν (cm^{-1}) 3500, 1719, 1281, 1042; ^{1}H NMR ($CDCl_3$, 200 MHz) 7.65 (1H, d, J = 2.6 Hz, H-3), 5.00 (1H, m, H-4), 2.99 (1H, dd, J = 6.2 and 18.6 Hz, H_A-5), 2.38 (1H, dd, J = 1.8 and 18.6 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 197.8 (C=O), 160.0 (CH-3), 128.8 (C-2), 69.1 (CH-4), 42.9 (CH_2-5); EIMS m/z (%) 176 (M^+, 10), 153 (15), 108 (100), 79 (92); HRMS (EI) m/z calcd for $C_5H_5O_2Br$ 175.9473 found 175.9461.

14: (4*R*,5*S*)-5-Bromo-4-hydroxy-cyclopent-2-enone

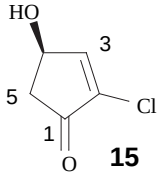
Data for compound **14**: $[\alpha]_D^{20}$ = -15.4 (c = 0.72, $CHCl_3$); IR (film) ν (cm^{-1}) 3500, 2928, 1723, 1339, 1040; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.54 (1H, dd, J = 2.2 and 6.0 Hz, H-3), 6.36 (1H, dd, J = 0.9 and 6.0 Hz, H-2), 5.09 (1H, m, H-4), 4.26 (1H, d, J = 2.4 Hz, H-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 205.5 (C=O), 160.4 (CH-3), 133.9 (C-2), 79.8 (CH-4), 51.5 (CH-5); EIMS m/z (%) 176 (M^+, 10), 97 (100), 69 (25); HRMS (EI) m/z calcd for $C_5H_5O_2Br$ 175.9473 found 175.9495.

General procedure for the reaction with LiCl:

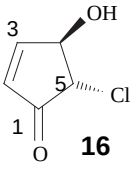
To a solution of compound **11** or **12** (0.21 mmol) in 2 mL of acetone or dry THF was added LiCl (0.63 mmol). The mixture was refluxed for the time indicated, then quenched with water and extracted with EtOAc. The combined organic layers were washed with brine and dried over

Na_2SO_4. Concentration followed by flash chromatography gave a mixture of compounds depending on the case.

Reaction of **11** with LiCl (solvent = acetone): The reaction was refluxed for 1 day. A mixture of compounds **15** and **16** were isolated (17 mg, 62 %) but they could not be isolated by chromatography.



15



16

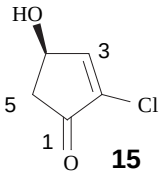
15: (4*R*)-2-Chloro-4-hydroxy-cyclopent-2-enone

16: (4*R*,5*S*)-5-Chloro-4-hydroxy-cyclopent-2-enone

Data for compound **15** $[\alpha]_D^{20}$ = + 17.0 (c = 0.93); IR (film) ν (cm^{-1}) 3500, 2926, 1732, 1310, 1262, 1086; ^{1}H NMR ($CDCl_3$, 200 MHz) 7.46 (1H, d, J = 3.0 Hz, H-3), 5.04 (1H, m, H-4), 3.00 (1H, dd, J = 6.4 and 18.8 Hz, H_A-5), 2.39 (1H, dd, J = 1.8 and 18.8 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 197.5 (C=O), 155.5 (CH-3), 138.3 (C-2), 67.3 (CH-4), 43.4 (CH_2-5); EIMS m/z (%) 132 (M^+, 100), 89 (80), 77 (88); HRMS (EI) m/z calcd for $C_5H_5O_2Cl$ 131.9978 found 175.9973.

Data for compound **16**: ^{1}H NMR ($CDCl_3$, 400 MHz) 7.50 (1H, dd, J = 2.4 and 6.1 Hz, H-3), 6.37 (1H, dd, J = 1,0 and 6.1 Hz, H-2), 5.00 (1H, m, H-4), 4.21 (1H, d, J = 2.5 Hz, H-5).

Reaction of **11** with LiCl (solvent = THF): The reaction mixture was refluxed for 12 h. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc, 85:15) gave a mixture of compounds **15** (22 mg, 80 %) and **17** (3 mg, 6%).



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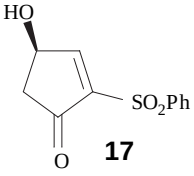


17

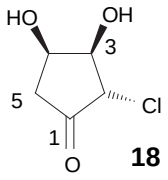
17: (4*R*)-2-Benzenesulfonyl-4-hydroxy-cyclopent-2-enone

Data for compound **17** $[\alpha]_D^{20}$ = + 5.4 (c = 0.83, $CDCl_3$); IR (film) ν (cm^{-1}) 3500, 1734, 1310, 1150, 1084, 974; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.94-7.52 (5H, m, -Ar), 7.43 (1H, d, J = 2.8 Hz, H-3), 4.46 (1H, ddd, J = 2.8, 2.8 and 6.2 Hz, H-4), 2.92 (1H, dd, J = 2.8 and 19.4 Hz, H_A-5), 2.70 (1H, dd, J = 6.2 and 19.4 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 195.2 (C=O), 146.8 (CH-3), 141.8 (C-*ipso*), 135.8 (C-2), 134.8 (CH-*para*), 129.7 (2CH-*meta*), 128.9 (2CH-*ortho*), 63.1 (CH-

4), 34.3 (CH_2-5); MS (FAB) m/z (%) 239 (M^++1, 90), 154 (100), 107 (30) 77 (30); HRMS (FAB) m/z calcd for $C_{11}H_{11}O_4S$ 239.0378 found 239.0376.

Reaction of **12** with LiCl (solvent = THF): The reaction mixture was refluxed for 4 h. After chromatography compounds **17** (4 mg, 8%), **18** (24 mg, 75 %), and a mixture of **15** and **16** (3 mg, 10%) were obtained.

Compound **18: (3*R*,4*R*)-2-Chloro-3,4-dihydroxy-cyclopentanone**



18

Data for compound **18**: $[\alpha]_D^{20}$ = + 22.2 (c = 0.77, MeOH); IR (film) ν (cm^{-1}) 3500, 2928, 1761, 1130, 1096, 1032; ^{1}H NMR ($CDCl_3$, 400 MHz) 4.54 (1H, m, H-4), 4.35 (1H, dd, J = 1.0 and 8.4 Hz, H-2), 4.20 (1H, dd, J = 4.0 and 8.4 Hz, H-3), 2.66 (1H, dd, J = 1.2 and 19.8 Hz, H_A-5), 2.61 (1H, dd, J = 5.2 and 19.8 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 205.3 (C=O), 77.2 (CH-3), 68.2 (CH-4), 62.7 (CH-2), 43.6 (CH_2-5); EIMS m/z (%) 150 (M^+, 1), 132 (20), 115 (60), 71 (100); HRMS (EI) m/z calcd for $C_5H_7O_3Cl$ 150.0084 found 150.0088.

*Treatment of **18** with p-TsOH in acetone*

Compound **18** (20 mg, 0.13 mmol) was dissolved in acetone (1.0 mL) and a catalitic amount of *p*-TsOH was added. The mixture was stirred for 10 h, neutralized with aqueous 5% $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and a mixture of compounds **15** and **16** (15 mg, 90%) were obtained in a ratio 1:1.

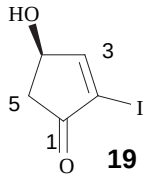
General procedure for the reaction with LiI:

To a solution of compound **11** or **12** (0.34 mmol) in dry THF (3.5 mL) was added LiI (136 mg, 1.01 mmol) in the absent of light. The mixture was heated for the time indicated, then quenched with saturated $Na_2S_2O_3$ and extracted with EtOAc. The combined organic layers were washed with aqueous solution 5% $NaHCO_3$, water and brine. The organic layer was dried over Na_2SO_4.

Concentration followed by flash chromatography gave compounds **R-1** or **19** depending on the case.

Reaction of **11** with LiI: The reaction mixture was heated at 60 ºC for 3h. The residue was purified by flash chromatography using a mixture of *n*-hexane/EtOAc 7:3 as eluent. Compound **R-1** (27 mg, 81 %) was isolated: $[\alpha]_D^{20}$ = +75.2 (c = 0.87, $CHCl_3$), (lit[13] = +78.0); Data are identical to those described in the literature[13].

Reaction of **12** with LiI: The reaction mixture was heated at 53 ºC for 1h. After purification by flash chromatography using a mixture of *n*-hexane/EtOAc 7:3 compound **19** (55 mg, 72 %) was isolated as a viscous oil.



19

19: (4*R*)-4-Hydroxy-2-iodo -cyclopent-2-enone

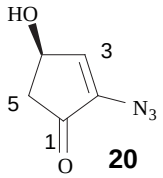
Data for compound **19**: $[\alpha]_D^{20}$ = + 10.0 (c = 0.87, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 200 MHz) 7.91 (1H, d, J = 2.4 Hz, H-3), 5.02 (1H, m, H-4), 2.98 (1H, dd, J = 6.2 and 18.4 Hz, H_A-5), 2.35 (1H, dd, J = 2.2 and 18.4 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 200.1(C=O), 168.1 (CH-3), 106.0 (C-2), 71.7 (CH-4), 41.6 (CH_2-5); EIMS m/z (%) 224 (M^+, 100), 154 (33), 127 (15), 97 (28), 77 (19); HRMS (EI) m/z calcd for $C_5H_5O_2I$ 223.9334 found 223.9338.

General procedure for the reaction with NaN_3:

NH_4Cl (22 mg, 0.42 mmol) and NaN_3 (0.51 mmol, 33 mg) was added to a solution of **11** or **12** (0.17 mmol) in absolute EtOH (2 mL). The mixture was refluxed until TLC showed disappearance of starting material. The reaction was cooled down, quenched with water and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. Concentration followed by chromatography on silica gel (*n*-hexane/EtOAc, 70:30) gave **20** as a brown oil, which decomposes quickly when dry.

Reaction of **11** with NaN_3: The mixture was stirred for 5 h. After chromatography compound **20** (17 mg, 70 %) was isolated.

Reaction of **12** with NaN_3: The mixture was stirred for 3 h to afford compound **20** (23 mg, 95 %).

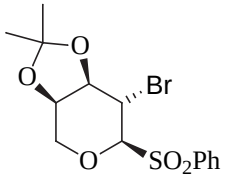


20

20: (4*R*)-2-Azido -4-hydroxy-cyclopent-2-enone

Data for compound **20**: IR (film) ν (cm^{-1}) 3500, 2928, 2122, 1717, 1622, 1344; ^{1}H NMR ($CDCl_3$, 200 MHz) 6.72 (1H, d, J = 3.0 Hz, H-3), 4.97 (1H, m, H-4), 2.86 (1H, dd, J = 5.8 and 19.0 Hz, H_A-5), 2.36 (1H, dd, J = 1.8 and 19.0 Hz, H_B-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 199.0 (C=O), 141.6 (C-2), 140.1 (CH-3), 66.4 (CH-4), 44.2 (CH_2-5).

Compound 21: (2*R*,3*S*,4*R*,5*R*)- 2-benzenesulfonyl-3-bromo-4,5-isopropylidenedioxy-tetrahidropirane

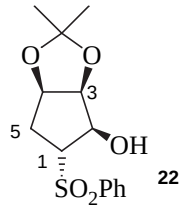


21

To a solution of **9** (35 mg, 0.07 mmol) in 1.0 mL of THF was added $MgBr_2Et_2O$ (54 mg, 0.21 mmol). The mixture was refluxed for 12 h, then quenched with water and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. Concentration followed by flash chomatography on silica gel (*n*-hexane.EtOAc: 85/15) gave compound **21** (18 mg, 70%): $[\alpha]_D^{20}$= -25.7 (c= 1.02, $CHCl_3$); IR (film) ν (cm^{-1}): 2986, 1329, 1155, 1082, 1053; ^{1}H NMR ($CDCl_3$, 200 MHz): 7.93-7.35 (5H, m, -Ar), 4.97 (1H, dd, J= 1.4 and 6.2 Hz, H-4), 4.88 (1H, d, J= 4.8 Hz, H-2), 4.86 (1H, m, H-5), 4.68 (1H, dd, J= 1.4 y 4.8 Hz, H-3), 4.12 (1H, dd, J= 4.4 and 10.6 Hz, H_A-6), 4.00 (1H, dd, J= 1.4 y 10.6 Hz, H_B-6), 1.51 (3H, s, Me), 1.35 (3H, s, Me); ^{13}C NMR ($CDCl_3$, 50.3 MHz): 136.0 (C-*ipso*), 135.0 (CH-*para*), 130.2 (2CH-*meta*), 129.4 (2CH-*ortho*), 113.4 (C-acetonide), 84.1 (CH-4), 83.8 (CH-5), 81.4 (CH-2), 74.5 (CH_2-6), 64.8 (CH-3), 26.8 (Me-acetonide), 25.2 (Me-acetonide); MS(

FAB) m/z (%): 377 (M^++1, 8), 307 (15), 154 (100), 107 (30), 77 (32); HRMS (FAB) m/z cald for $C_{14}H_{18}O_5SBr$ 377.0058 (M^++1), found 377.0037.

Compound 22: (1*R*,2*R*,3*S*,4*R*)-1-benzenesulfonyl-2-hydroxy-3,4-isopropylidenedioxy-cyclopentane

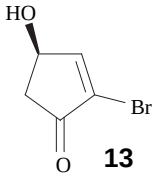


22

A solution of compound **11** (150mg, 0.51 mmol) in anhydrous MeOH (5 mL) was canulated to 2.5 g of 2% Na (Hg) amalgam under argon The mixture was stirred for 2 h and then filtered off to remove the Hg from the reaction mixture. The solvent was evaporated and the residue was dissolved in water (2 mL) and extracted with EtOAc. The combined organic layers were washed with water and brine. The organic extract was dried over Na_2SO_4. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc: 70/30) gave compound **21** (139 mg, 91 %): $[\alpha]_D^{20}$ = -55.3 (c = 0.92, $CHCl_3$); IR (film) ν (cm^{-1}) 3500, 1447, 1304, 1209, 1146, 1084, 1042; ^{1}H NMR ($CDCl_3$, 400 MHz) 7.95-7.54 (5H, m, Ar), 4.65 (1H, dd, J = 5.1 and 5.1 Hz, H-4), 4.57 (1H, dd, J = 5.6 and 5.6 Hz, H-3), 4.25 (1H, m, H-2), 3.46 (1H, ddd, J = 6.6, 9.1, 15.8 Hz, H-1), 2.11 (1H, dd, J = 6.6 and 14.1 Hz, H_A-5), 1.99 (1H, ddd, J = 5.0, 14.1 and 15.8 Hz, H_B-5), 1.44 (3H, s, Me-acetonide), 1.31 (3H, s, Me-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 138.7 (C-*ipso*), 133.8 (CH-*para*), 129.1 (2CH-*meta*), 128.6 (2CH-*ortho*), 110.9 (C-acetonide), 78.4 (CH-3), 76.9 (CH-4), 72.6 (CH-2), 69.9 (CH-1), 29.6 (CH_2-5), 25.8 (Me-acetonide), 23.9 (Me- acetonide); MS (FAB) m/z (%) 299 (M^++1, 10), 154 (100), 107 (28), 91 (30), 77 (27); HRMS (FAB) m/z calcd for $C_{14}H_{19}O_5S$ 299.0953, found 299.0953.

Spectra

Compound 13



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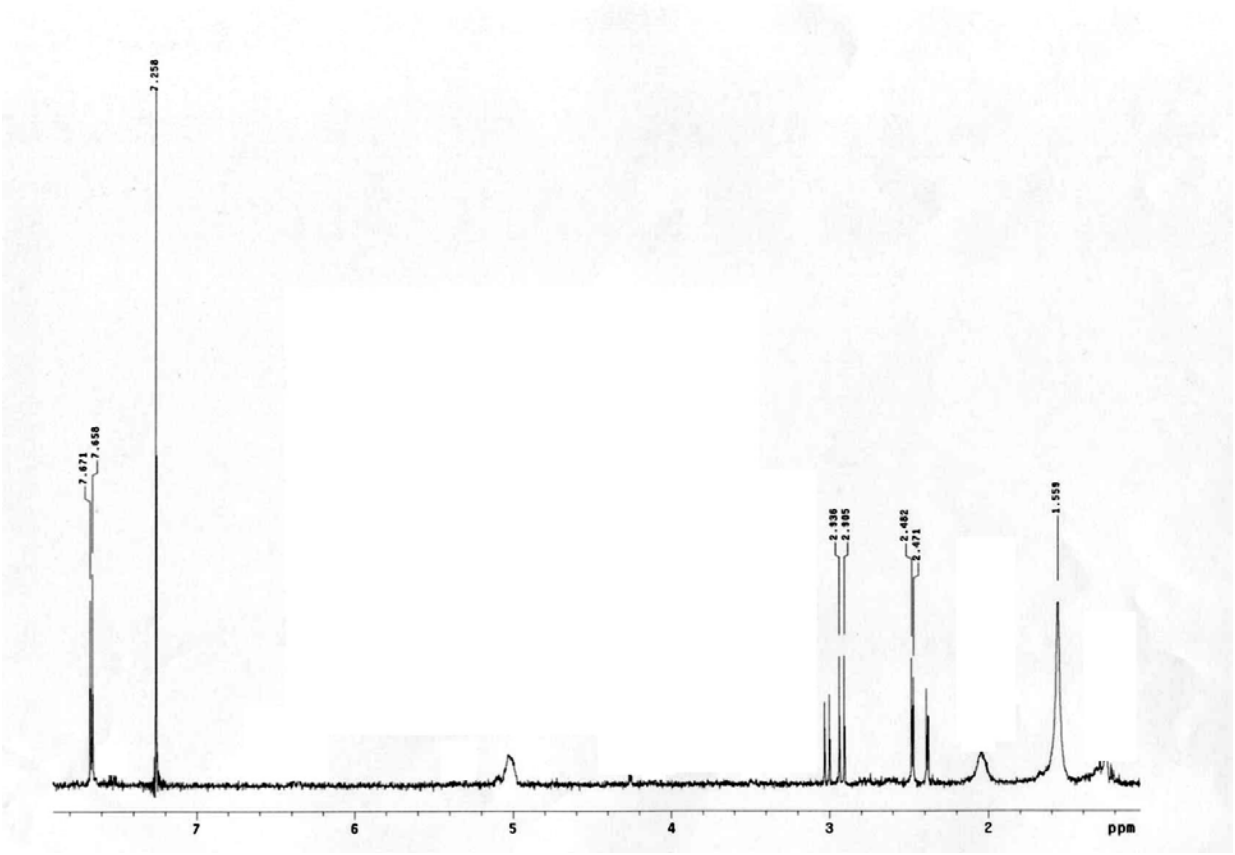

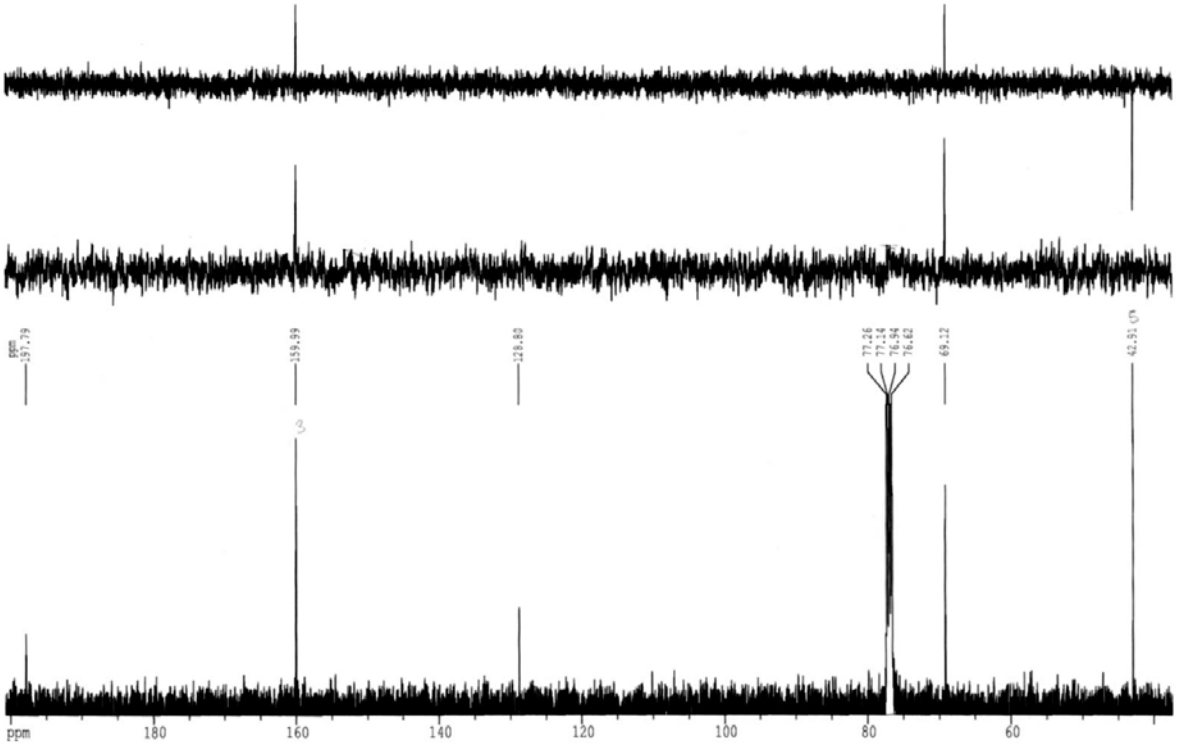
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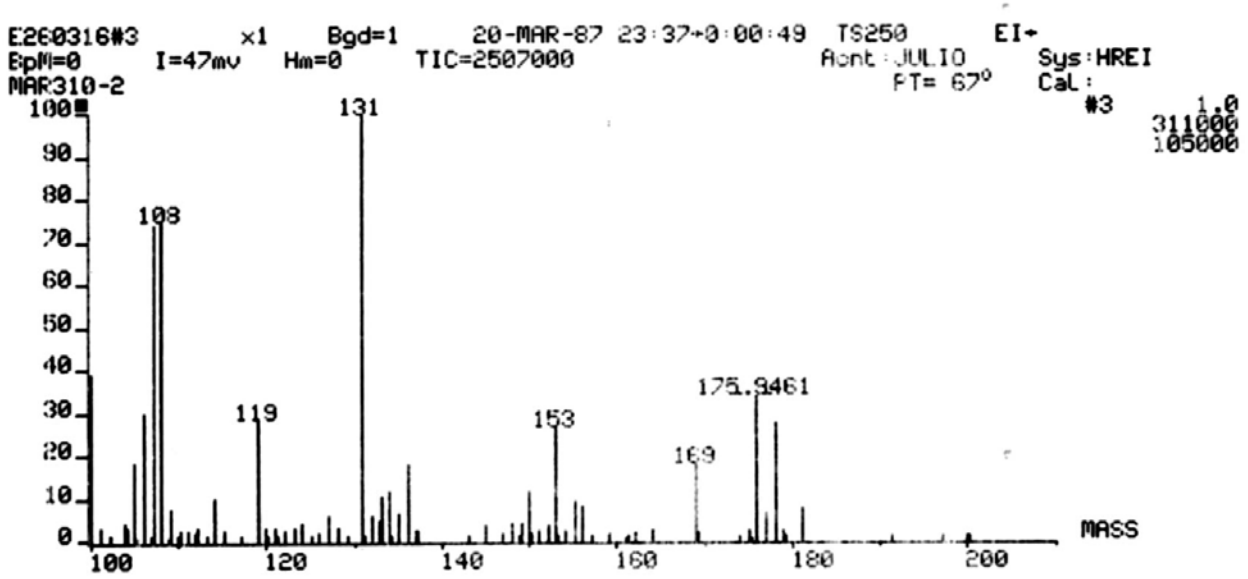

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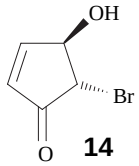

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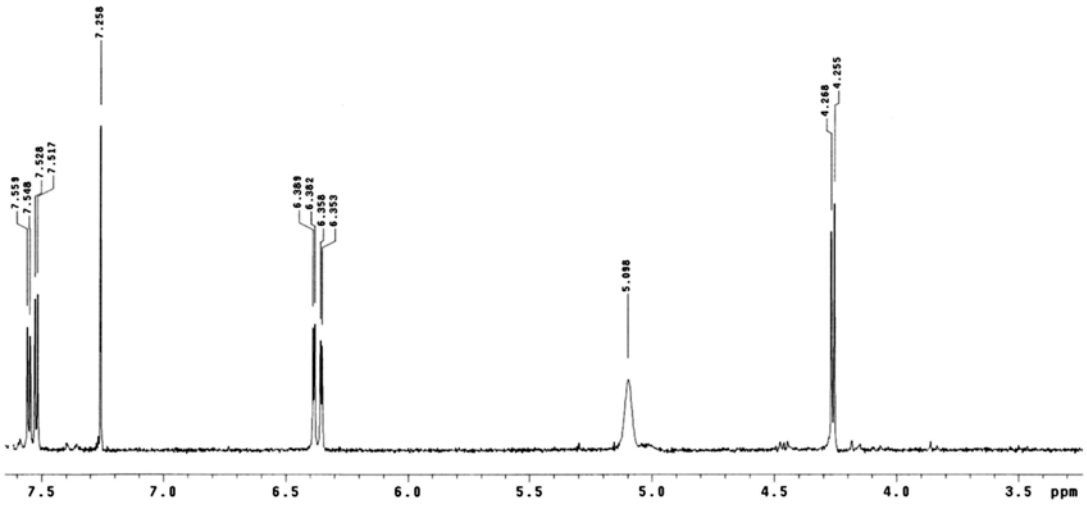

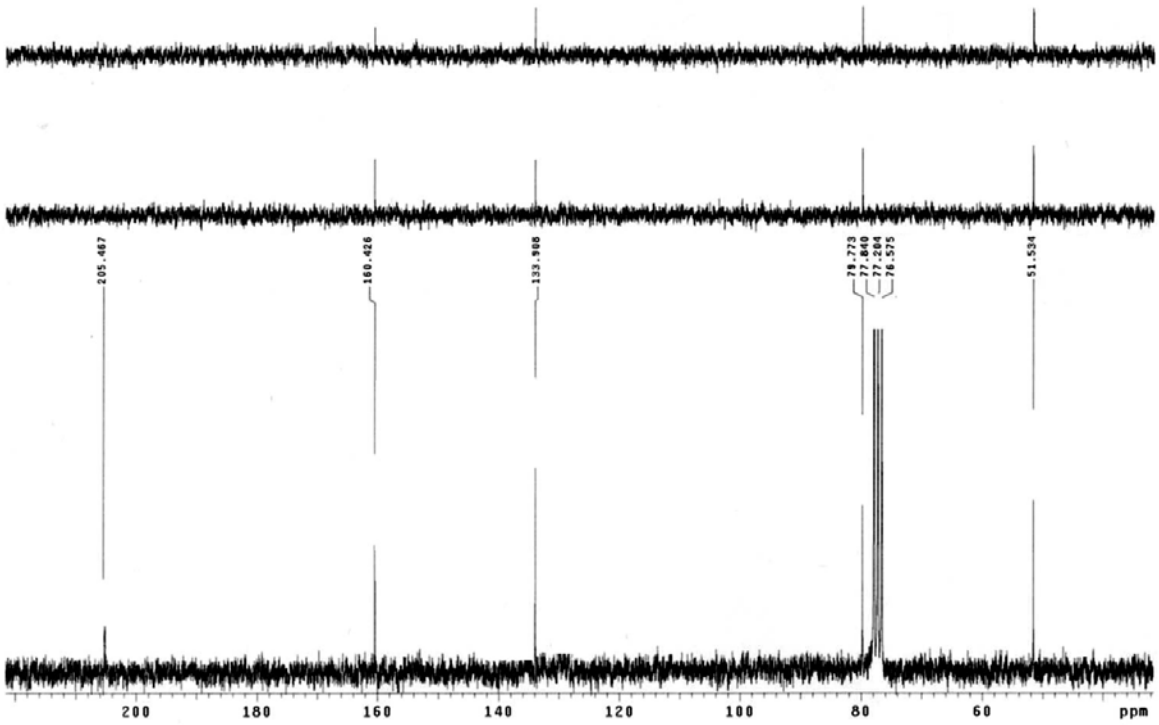
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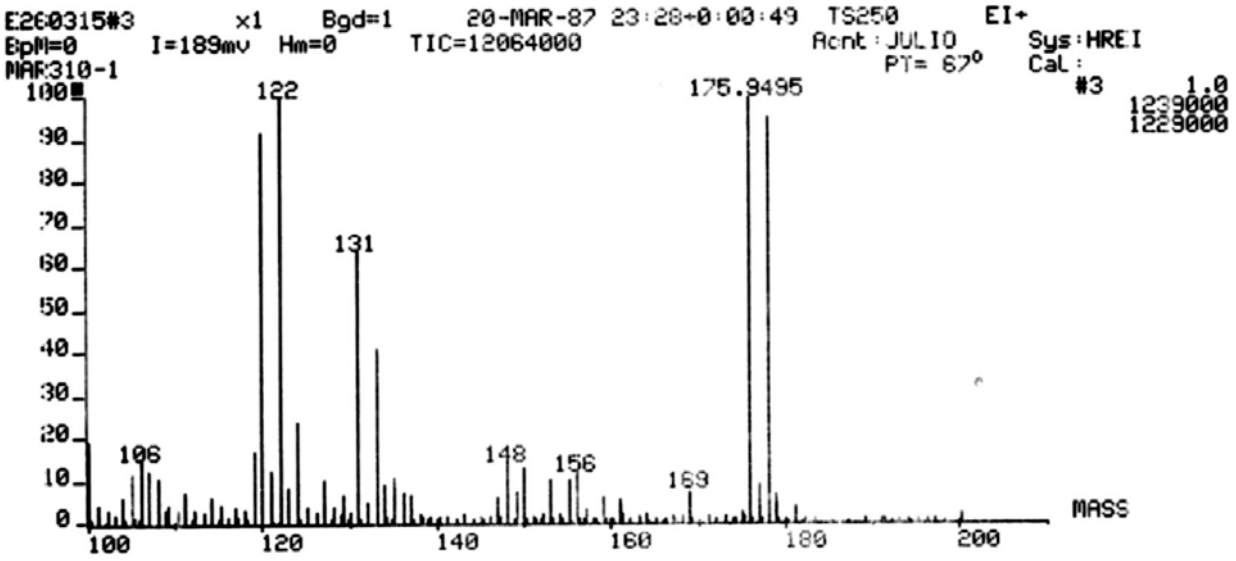

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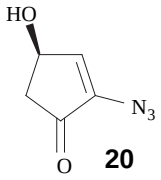

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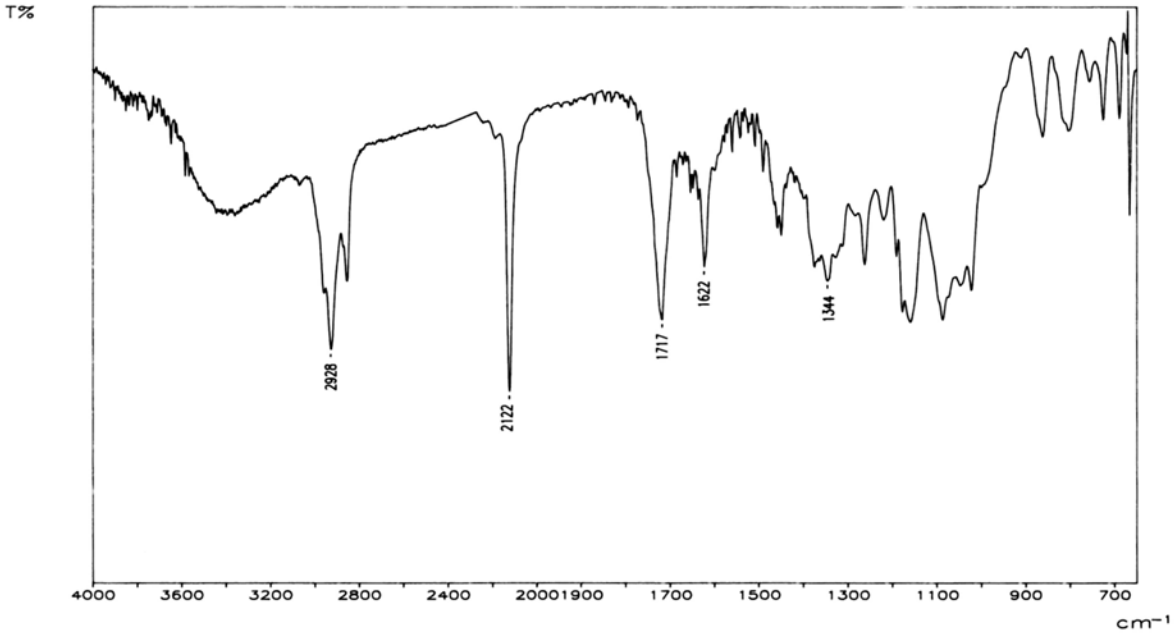

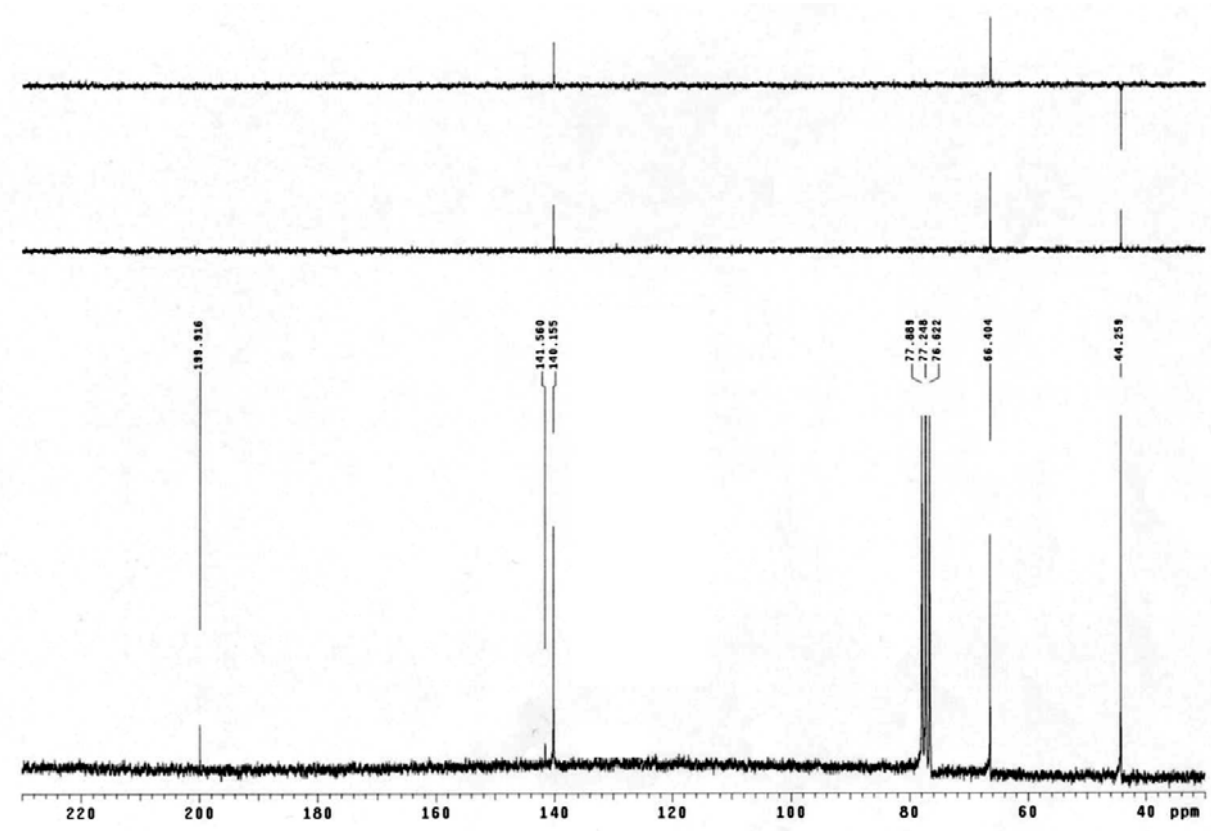
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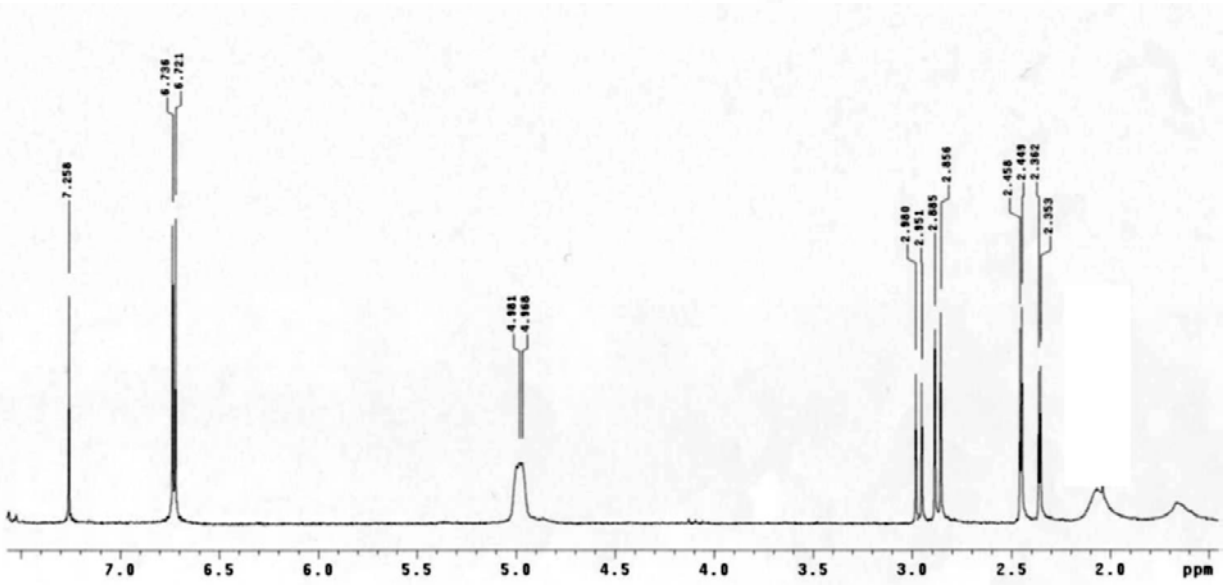
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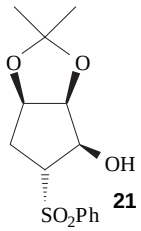
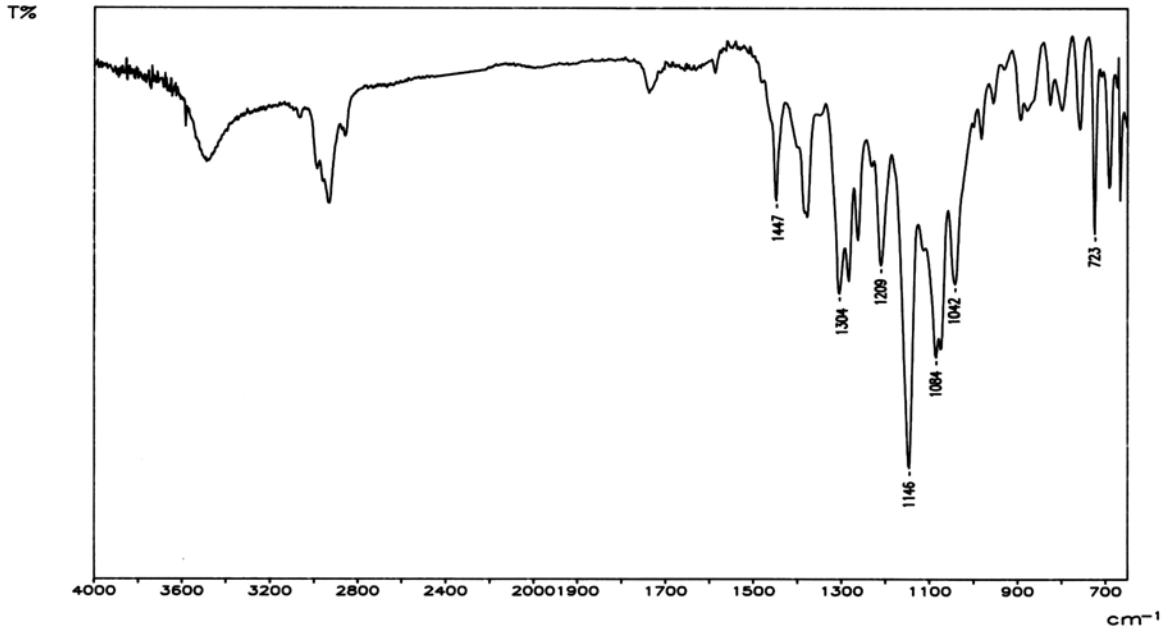
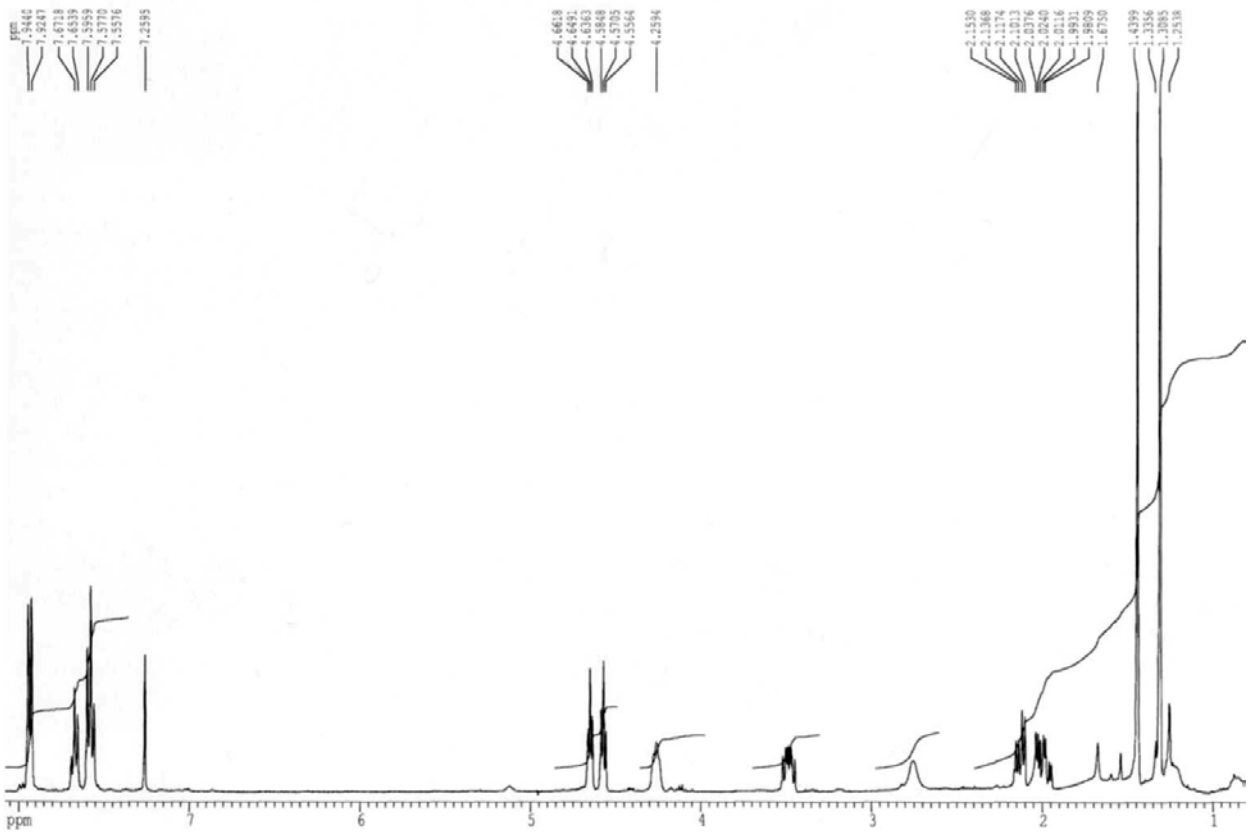
Compound 21



21

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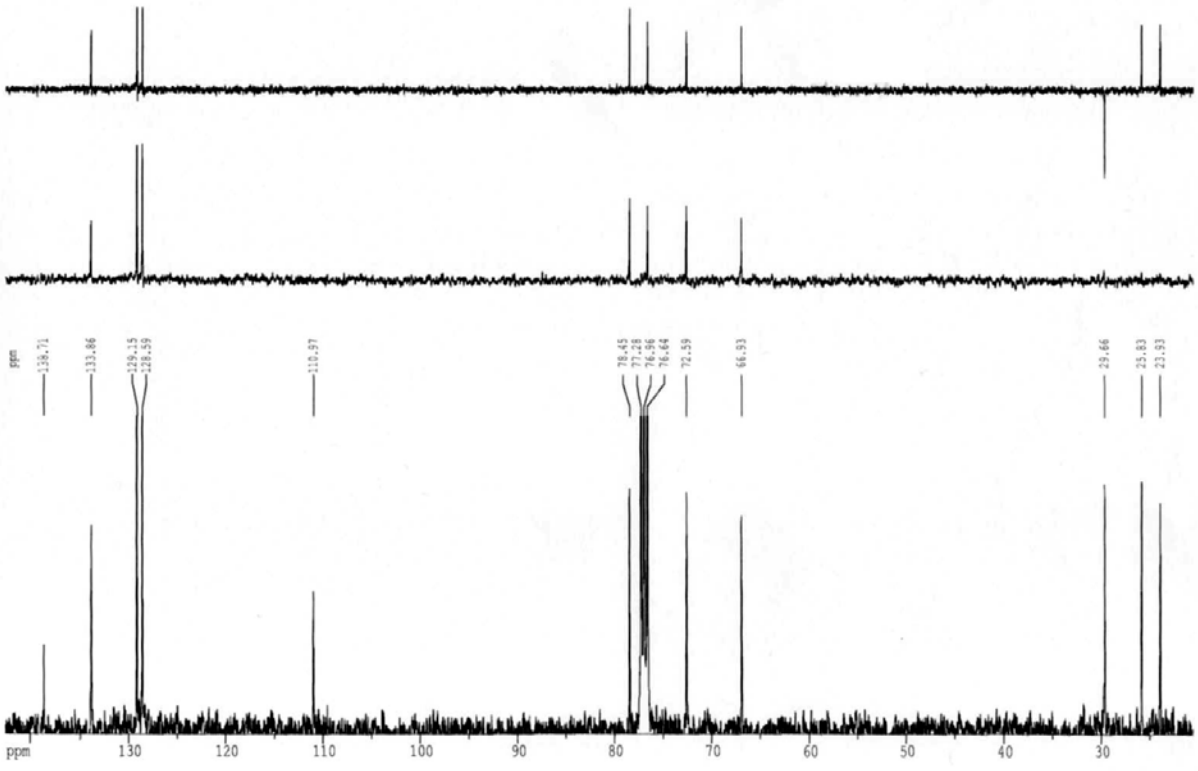
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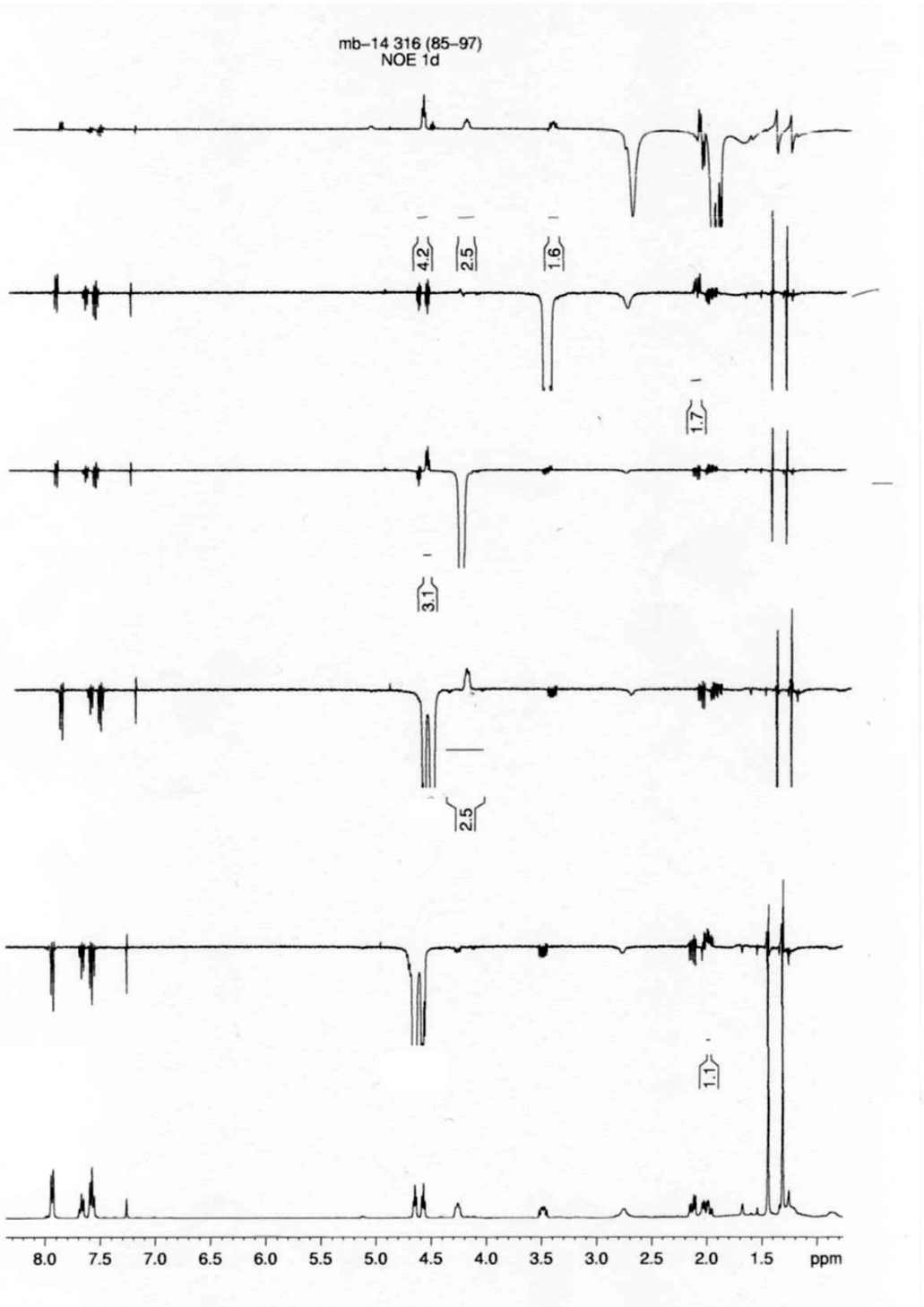
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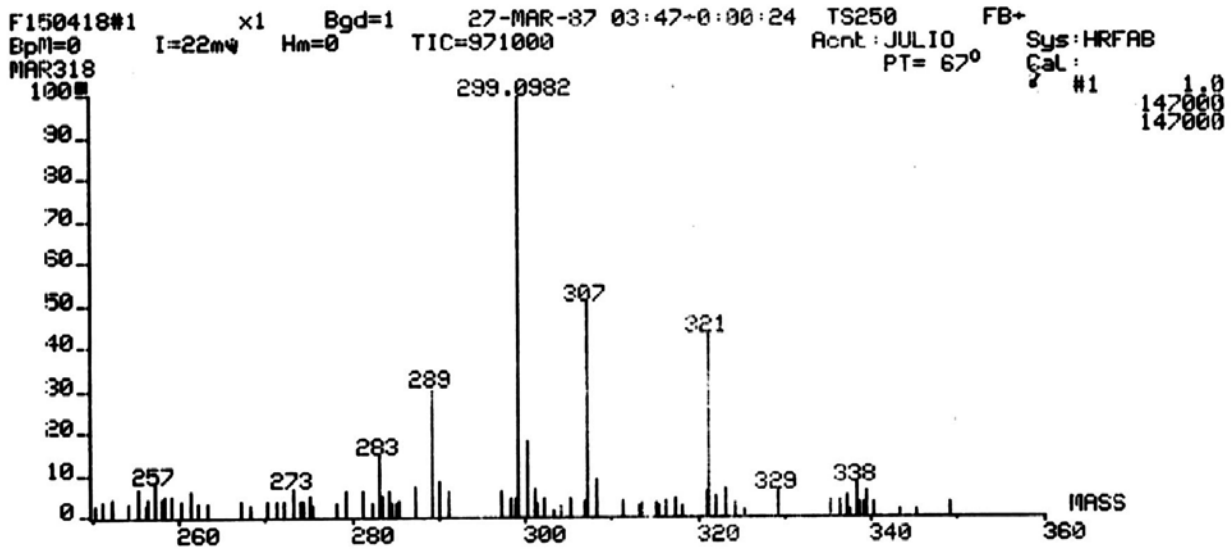

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