

# Experimental Section

## General Information:

The solvents were purified by standard procedures before use, petroleum ether of boiling range 60°-80°C was used. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on an ATI MATTSON RS-1 FT-IR spectrometer.  $^1\text{H}$ NMR spectra were recorded on Bruker AC-200 NMR spectrometer. The chemical shifts are reported in parts per million ( $\delta$ ) with tetramethyl silane as an internal standard. Mass spectra were obtained with a Finnigan MAT-1020B-70ev mass spectrometer.

## Experimental procedures for **2**, **3**, **7b** and **8**

### Procedure for *O*-Acyl(aroyl)salicylic acid **2**:

⇒ Dry salicylic acid or its substituted derivative **1** (50mmol) and acid anhydride (100mmol) were placed in a small conical flask; 5 drops of conc. sulfuric acid was added and the flask was rotated in order to secure thorough mixing. The mixture was warmed on a water bath to about 50-60°C, and then stirred for about 15 minutes. The mixture was allowed to cool and stirred occasionally. Water was added to the reaction mixture and solid thus obtained was filtered. The solid was then dissolved in about 30ml of hot ethanol and the solution was poured into 75ml of warm water. Solid separated out at this point; the mixture was warmed until it is clear solution and then the solution was cooled slowly. Beautiful needle like crystals separated out. The air dried crude product **2** was recrystallised from pet-ether / ethyl acetate, or hexane.

⇒ 10g of ice followed by freshly distilled acid chloride (10mmol) were added to an ice-cold solution of salicylic acid or its substituted derivative **1** (7mmol) and potassium hydroxide (18mmol) in water (12ml). The mixture was stirred for 0.5 h at room temperature, acidified with dil.HCl; and the material which precipitated out was filtered and washed with water. The air dried crude product **2** was recrystallised from pet-ether / ethyl acetate, or hexane.

Yield:- 75-80%

### Procedure for *tert*-butyldimethylsilyl ester of *O*-Acyl(aroyl)salicylic acid **3**:

A solution of compound **2** (10mmol) and imidazole (15mmol) in dichloromethane (5ml) was cooled to 0°C, and mixture was stirred under nitrogen atmosphere. To the above solution, was added *tert*-butyldimethylsilyl chloride (13mmol) at 0°C and the reaction mixture was stirred at room temperature under nitrogen atmosphere for 7-8 hours. After the reaction was complete, the reaction mixture was quenched with saturated solution of ammonium chloride and extracted with dichloromethane. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure to give the product **3**.  
yield . 65-70%

## Experimental procedure for **7b**

Compound **3b** was prepared in 68% yield from **2b** following the general experimental procedure as described for **3**.

The (trimethylsilyl)methylenetriphenylphosphorane **4** was prepared following the literature procedure<sup>3</sup> from methylenetriphenylphosphorane and trimethylsilyl chloride.

### Preparation of **7b**:

To a solution of **3b** (1 g, 3.2 mmol) dissolved in absolute THF (5 ml) was added the equimolar amount of silylated ylide **4** (1.13 g, 3.2 mmol) in THF (5 ml). The reaction mixture was heated at 50°C for 8 hours. The reaction was monitored by TLC. After completion of reaction, the solvent was evaporated under reduced pressure and residue thus obtained was washed several times with petroleum ether to afford 1.25 g (85%) of sufficiently pure acylphosphorane **7b** which was fully characterized by spectroscopic data.

**7b**: oil; IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1730, 1625, 1580, 1525, 1243, 1215;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 1.25(t,  $J=8\text{Hz}$ , 3H), 2.10(q,  $J=8\text{Hz}$ , 2H), 2.6(d,  $J=4\text{Hz}$ , 1H), 6.8-7.25(m, 2H), 7.3-8.1(m, 15H), 8.3-8.75(m, 2H). Mass (EI), m/z(%):  $\text{M}^+$  452(5), 215(85), 201(70), 138(60), 120(100).

### Procedure for Chromones **8**:

To a solution of compound **3** (50mmol) in absolute THF (5ml) was added under stirring the equimolar amount of silylated ylide **4** (50mmol) in THF (5ml), Then the reaction mixture was refluxed for the indicated length of time (Table 1). The reaction was monitored by TLC. After completion of reaction, the solvent was evaporated and the residue was purified by column chromatography (pet.ether:ethyl acetate, 98:2), to afford the product **3**.

Yield:- 55-80%

### Spectroscopic data for compounds **8a-8l** :

**8a**: M.P. 72°-73°C (Lit.<sup>7j</sup> 70°-71°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1661;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 2.36(s,3H), 6.92-7.02(m, 1H), 7.46-7.74(m, 3H), 7.75-7.95(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  160(100), 145(10), 138(55), 120(87).

**8b**: Oil; IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1676;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 1.29(t,  $J=8\text{Hz}$ , 3H), 2.66(q,  $J=8\text{Hz}$ , 2H), 6.9-7.0(m, 1H), 7.3-7.6(m, 3H), 7.9-8.2(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  174(100), 138(57), 120(85).

**8c:** M.P. 96°C (Lit. <sup>7j</sup> 94°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1673;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 6.98(s, 1H), 7.46-8.13(m, 9H). Mass (EI), m/z(%):  $\text{M}^+$  222(15), 194(90), 138(40), 120(100), 77(36).

**8d:** M.P. 242°-244°C(Lit. <sup>7j</sup> 240°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1664;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 6.92-7.05(m, 3H), 7.50-7.59(m, 2H), 7.91-7.98(m, 2H), 8.32-8.36(m, 2H). Mass (EI), m/z(%):  $\text{M}^+$  267(20), 163(100), 138(45), 120(50).

**8e:** M.P. 186°-188°C(Lit. <sup>7j</sup> 189°-190°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1687;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 6.90(m, 1H), 7.43-8.05(m, 8H). Mass (EI), m/z(%):  $\text{M}^+$  256(20), 228(40), 138(60), 120(100).

**8f:** M.P. 156°-157°C (Lit. <sup>7j</sup> 157°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1663;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 3.90(s, 3H), 6.92-7.02(m, 3H), 7.50-7.56(m, 2H), 7.94(m, 2H), 8.06(m, 2H). Mass (EI), m/z(%):  $\text{M}^+$  252(25), 224(100), 209(22), 120(87).

**8g:** M.P. 98°-100°C(Lit. <sup>9</sup> 100°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1661;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 2.35(s, 3H), 2.43(s, 3H), 6.73-6.82(m, 1H), 6.96-7.18(m, 2H), 7.78-8.04(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  174(100), 154(80), 105(36).

**8h:** M.P. 128°-130°C (Lit. <sup>7j</sup> 130°-132°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1660;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 2.38(s, 3H), 6.74-7.83(m, 3H), 7.46-7.65(m, 5H), 8.13(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  236(100), 134(86), 105(30), 77(24).

**8i:** M.P. 114°-115°C (Lit. <sup>7d</sup> 115°-116°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1661;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 2.35(s, 3H), 6.88-7.02(m, 1H), 7.46-7.55(m, 2H), 7.68-7.91(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  194(100), 173(40), 155(80).

**8j:** M.P. 181°-183°C (Lit. <sup>7d</sup> 183°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1685;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 6.95(s, 1H), 7.44-7.65(m, 5H), 7.89-8.0(m, 2H), 8.11-8.15(m, 1H). Mass (EI), m/z(%):  $\text{M}^+$  256(100), 155(70), 77(40).

**8k:** M.P. 192°-193°C(Lit. <sup>7c</sup> 194°-195°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1677;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 6.90(m, 2H), 7.43-8.10(m, 8H). Mass (EI), m/z(%):  $\text{M}^+$  256(20), 228(40), 138(60), 120(100).

**8l:** M.P. 226°-228°C (Lit. <sup>7c</sup> 229°C); IR.  $\nu_{\text{max}}/\text{cm}^{-1}(\text{CHCl}_3)$ : 1667;  $^1\text{H}$  NMR( $\text{CDCl}_3$ )  $\delta$ : 3.90(s, 6H), 6.92-7.02(m, 2H), 7.50-7.56(m, 2H), 7.94(m, 2H), 8.06(m, 2H). Mass (EI), m/z(%):  $\text{M}^+$  282(25), 264(100), 240(22), 120(87).

