Supporting Information

α -Arylsulfanyl- α -fluoro Carbenoids: Their Novel Chemistry and Synthetic Applications

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General Methods

The ^1H NMR spectra were recorded on either Bruker DPX-300 (300 MHz) or Bruker DPX-400 (400 MHz) spectrometer in CDCl_3 using tetramethylsilane as an internal standard. The ^{13}C NMR spectra were recorded either on Bruker DPX-300 (75 MHz) and Bruker DPX-400 (100 MHz) spectrometer in CDCl_3 using tetramethylsilane as an internal standard. The ^{19}F NMR spectra were recorded on a Bruker DPX-400 (376 MHz) spectrometer and chemical shifts (δ) were measured with fluorotrichloromethane ($\delta = 0$) as an internal standard. The IR spectra were recorded on either a Jasco A-302 or a Perkin Elmer 683 infrared spectrometer. The mass spectra were recorded by using a Thermo Finnigan Polaris Q mass spectrometer. The high resolution mass spectra were recorded on either HR-TOF-MS Micromass model VQ-TOF2 or Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by a Perkin Elmer Elemental Analyzer 2400 CHN. Melting points were recorded on a Buchi 501 Melting Point Apparatus and were uncorrected. The x-ray crystallography was performed by Kappa CCD.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Dry *N,N*-dimethylformamide (DMF) were distilled over calcium hydride and stored over molecular sieves (4 Å). Other common solvents (dichloromethane, hexanes, ethyl acetate and acetone) were distilled before use.

The reactions regarding anions were run under an argon atmosphere. All glasswares and syringes were oven-dried and kept in a dessicator before use. Preparative plates were prepared by using Merck silica gel 60 PF₂₅₄ (Art. 7747). Radial chromatography on a Chromatotron was performed using Merck silica gel 60 F254 (Art. 7749). Column chromatography was performed by using Merck silica gel 60H (Art. 7736).

1. Preparation of compounds 1 and 2

1.1 Preparation of (α -bromo- α,α -difluoromethylsulfanyl)benzene (1).

General procedure A: To a suspension of sodium hydride (3.6 g, 150.0 mmol) in DMF (200 mL) at room temperature was slowly added thiophenol (10.2 mL, 100.0 mmol) over a period of 30 min. The reaction mixture was brought to -60°C for 15 min before dibromodifluoromethane (28 mL, 300.0 mmol) was bubbled into the reaction mixture over a period of 30 min. The reaction mixture was maintained at -60°C for 3 h. After the reaction was quenched by addition of water (200 mL), the aqueous phase was extracted with hexane (3 $\times$ 100 mL). The combined hexane extracts were washed with water (300 mL), brine (100 mL) and dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2 , hexanes) to give a colorless liquid of **1** (16.38 g, 69% yield).

^1H NMR (300 MHz, CDCl_3): δ 7.68-7.62 (m, 2H, ArH), 7.54-7.747 (m, 1H, ArH), 7.45-7.37 (m, 2H, ArH). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 136.38 (CH), 131.03 (CH), 129.43 (CH), 127.16 (C), 119.24 (t, $J = 336.3$ Hz, CF_2Br). ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -22.49 (s, 2F, CF_2). IR (neat): ν_{max} 3065 m , 2926 w , 1670 w , 1579 w , 1476 m , 1442 m , 1309 w , 1092 s , 1063 s , 920 w , 840 s , 749 s , 702 m , 689 s cm^{-1} . MS: m/z (% relative intensity): 240 (M^+ , 12), 238 (M^+ , 12), 159 (100), 110 (1), 109 (15), 97 (4), 86 (30), 84 (46), 77 (25), 71 (11), 65 (7), 57 (11). HRMS (EI) Calcd. for $\text{C}_7\text{H}_5\text{BrF}_2\text{S}$ (M^+): 237.9262. Found: 237.9283.

1.2 Preparation of 1-(α -bromo- α,α -difluoromethylsulfanyl)-4-methylbenzene (2).

According to the general procedure A, starting from *p*-thiocresol (12.4 g, 100.0 mmol), the crude product obtained was purified by column chromatography (SiO_2 , hexanes) to give a colourless liquid of **2** (13.0 g, 51% yield).

^1H NMR (300 MHz, CDCl_3): δ 7.57 (d, J = 8.0 Hz, 2H, ArH), 7.27 (d, J = 8.0 Hz, 2H, ArH), 2.40 (s, 3H, ArCH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 141.65 (C), 136.40 (CH), 130.20 (CH), 123.73 (C), 119.52 (t, J = 338.3 Hz, CF_2Br), 21.41 (CH₃). ^{19}F NMR (376 MHz, $\text{CDCl}_3/\text{CFCl}_3$): δ -22.80 (s, 2F, CF_2). IR (neat): ν_{max} 3028m, 2925m, 2869w, 1643w, 1598m, 1494s, 1453m, 1401m, 1305w, 1211w, 1183m, 1064s, 1018s, 841s, 809s, 706m cm^{-1} . MS: m/z (% relative intensity): 254 (M^+ , 19), 252 (M^+ , 18), 173 (100), 165 (14), 153 (44), 123 (13), 111 (14), 110 (12), 97 (16), 95 (23), 91 (20), 81 (17), 69 (19), 57 (26). HRMS (EI) Calcd for $\text{C}_8\text{H}_7\text{BrF}_2\text{S}$ (M^+): 251.9420. Found: 251.9381.

2. Reactions of 1 and 2 with various Grignard reagents.

2.1 Reaction of (α -bromo- α,α -difluoromethylsulfanyl)benzene (1) with *i*-PrMgCl.

General procedure B: A solution of *i*-PrMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) was added dropwise to a stirred solution of **1** (0.4789 g, 2.0 mmol) in dry THF (4.0 mL) at -78°C under an argon atmosphere. The resulting yellow solution was then stirred at -78°C for 10 min and then quenched with 1 M HCl (5 mL). The mixture was poured into water (20 mL) and extracted with hexanes (3x50 mL). The combined organic layers were washed with sat. NaHCO_3 (50 mL), water (2x50 mL), brine (50 mL) and dried over anhyd. Na_2SO_4 . After removal of solvent under reduced pressure, the crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **4a** (0.1989 g, 48% yield) and a white solid of **6a** [0.1010 g, 31% yield, mp $73-75^\circ\text{C}$ (EtOH)].

4a

4a: ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.29 (m, 2H, ArH), 7.24-7.11 (m, 2H, ArH), 7.10-7.02 (m, 1H, ArH), 2.67 (t, J = 6.0 Hz, 1H, $\text{SCH}(i\text{-Pr})_2$), 1.99 (sept, J = 6.6 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.96 (sept, J = 6.6 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 0.96 (d, J = 6.7 Hz, 6H, $2\times\text{CH}_3\text{CH}$), 0.95 (d, J = 6.7 Hz, 6H, $2\times\text{CH}_3\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3): δ 139.41 (C), 130.35 (CH), 128.67 (CH), 125.58 (CH), 65.70 (CH), 31.35 (CH), 21.68 (CH₃), 19.56 (CH₃). IR (neat): ν_{max} 3074w, 2961s, 2929s, 2871m, 1584m, 1479s, 1439m, 1383m, 1318w, 1089m, 1067m, 1025m, 842m, 748s, 690s cm^{-1} . MS: m/z (% relative intensity): 208 (M^+ , 100), 207 (13), 205 (26), 204 (12). **4a** was characterised as its corresponding sulfone **21a**.

21a

21a: ^1H NMR (300 MHz, CDCl_3): δ 7.85-7.76 (m, 2H, ArH), 7.59-7.40 (m, 3H, ArH), 2.80 (t, J = 2.0 Hz, 1H, $\text{SO}_2\text{CH}(i\text{-Pr})_2$), 2.21-2.05 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.13 (d, J = 7.0 Hz, 6H, $2\times\text{CH}_3$), 1.06 (d, J = 6.7 Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 140.66 (C), 133.09 (CH), 128.96 (CH), 128.12 (CH), 73.75 (CH), 26.93 (CH), 21.13 (CH₃), 20.93 (CH₃). IR (KBr-disc.): ν_{max} 3075w, 3006m, 2970s, 2935m, 2910m, 2881m, 1583w, 1467s, 1448s, 1393m, 1373m, 1337m, 1298s, 1287s, 1259m, 1242m, 1137s, 1082s, 1070m, 1025w, 997w, 815w, 769s, 740m, 720s, 694s, 624s, 564s, 547s cm^{-1} . MS: m/z (% relative intensity): 241 ($\text{M}^+ + 1$, 100), 240 (M^+ , 13), 143 (13), 125 (97), 99 (17), 97 (38), 83 (17), 78 (36), 77 (17), 57 (72). Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{S}$: C, 64.96; H, 8.39. Found: C, 64.75; H, 8.74.

6a

6a: ^1H NMR (300 MHz, CDCl_3): δ 7.37-7.13 (m, 10H, ArH), 3.47 (br.s, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.32 (d, $J = 7.0$ Hz, 12H, $4\times\text{CH}_3\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3): δ 170.82 (C), 136.39 (C), 128.86 (CH), 128.65 (CH), 125.78 (CH), 120.00 (C), 33.10 (CH), 21.12 (CH_3). IR (nujol): ν_{max} 1580s, 1465s, 1439s, 1379s, 1365s, 1299w, 1207m, 1165m, 1104m, 1086m, 1070m, 1023s, 1010m, 913m, 893m, 829m, 737s, 706m, 689s cm^{-1} . MS: m/z (% relative intensity): 328 (M^+ , 23), 219 (100), 175 (12), 143 (11), 141 (15), 121 (19), 109 (54), 95 (13), 91 (10), 81 (11), 67 (33). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{S}_2$: C, 73.12; H, 7.36. Found: C, 73.41; H, 7.52.

2.2 Reaction of (α -bromo- α,α -difluoromethylsulfanyl)benzene (**1**) with *i*-BuMgCl.

According to the general procedure B, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **1** (0.4898 g, 2.0 mmol) were employed and the reaction mixture was stirred at -78°C for 30 min. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **4b** (0.4014 g, 83% yield) and a white solid of **6b** [0.0206 g, 6% yield, mp $62\text{--}64^\circ\text{C}$ (EtOH)].

4b

4b: ^1H NMR (300 MHz, CDCl_3): δ 7.43-7.37 (m, 2H, ArH), 7.33-7.19 (m, 3H, ArH), 3.15 (quint, $J = 7.4$ Hz, 1H, $\text{SCH}(\text{i-Bu})_2$), 2.04-1.84 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.51-1.33 (m, 4H, $2\times\text{CH}_2(\text{i-Pr})$), 0.90 (d, $J = 6.7$ Hz, 12H, $4\times\text{CH}_3\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3): δ 135.25 (C), 132.25 (CH), 128.66 (CH), 126.58 (CH), 44.92 (CH), 44.72 (CH_2), 25.37 (CH), 22.67 (CH_3), 22.33 (CH_3). IR (neat): ν_{max} 3075w, 2957s, 2929s, 2869s, 1584m, 1467s, 1438m, 1385m, 1367m, 1169w, 1148w, 1090w, 1067w, 1026w, 747s, 692s cm^{-1} . MS: m/z (% relative intensity): 236 (M^+ , 95), 126 (44), 123 (15), 110 (100), 109 (18), 78 (16), 57 (12), 55 (12). **4b** was characterised as its corresponding sulfone **21b**.

21b

21b: ^1H NMR (400 MHz, CDCl_3): δ 7.93-7.88 (m, 2H, ArH), 7.70-7.65 (m, 1H, ArH), 7.62-7.50 (m, 2H, ArH), 3.09-3.01 (m, 1H, $\text{SO}_2\text{CH}(\text{i-Bu})_2$), 1.80-1.65 (m 4H, $2\times\text{CH}_2(\text{i-Pr})$), 1.38-1.26 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 0.92 (d, $J = 6.4$ Hz, 6H, $2\times\text{CH}_3$), 0.83 (d, $J = 6.2$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 138.53 (C), 134.11 (CH), 129.64 (CH), 129.57 (CH), 61.54 (CH), 39.22 (CH_2), 26.22 (CH), 23.49 (CH_3), 22.55 (CH_3). IR (neat): ν_{max} 3067w, 2959s, 2871m, 1586w, 1468m, 1447m, 1388m, 1370m, 1302s, 1213w, 1143s, 1086s, 999w, 765m, 735s, 692s cm^{-1} . MS: m/z (% relative intensity): 269 ($\text{M}^+ + 1$, 32), 169 (14), 143 (84), 125 (62), 97 (20), 85 (64), 79 (28), 78 (56), 77 (75), 71 (100), 69 (32), 57 (73), 55 (33), 51 (60). Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{S}$: C, 67.12; H, 9.01. Found: C, 67.15; H, 8.93.

6b

6b: ^1H NMR (300 MHz, CDCl_3): δ 7.28-7.08 (m, 10H, ArH), 2.55 (d, J = 7.4 Hz, 4H, $2\times\text{CH}_2(i\text{-Pr})$), 2.09-1.88 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 0.99 (d, J = 6.7 Hz, 12H, $4\times\text{CH}_3\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3): δ 159.07 (C), 136.07 (C), 129.47 (CH), 128.54 (CH), 126.05 (CH), 123.80 (C), 43.98 (CH_2), 28.42 (CH), 22.67 (CH_3). IR (neat): ν_{max} 3063w, 3060w, 2956s, 2926s, 2868s, 1583s, 1478s, 1464s, 1439s, 1384m, 1366m, 1166w, 1128w, 1090m, 1068m, 1025s, 903m, 738s, 700s, 688s cm^{-1} . MS: m/z (% relative intensity): 356 (M^+ , 72), 247 (100), 203 (15), 147 (11), 137 (14), 123 (17), 109 (6), 95 (21), 81(42), 79 (8), 77 (5). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{S}_2$: C, 74.10; H, 7.91. Found: C, 74.45; H, 8.18.

2.3 Reaction of (α -bromo- α,α -difluoromethylsulfanyl)benzene (**1**) with EtMgCl.

According to the general procedure B, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **1** (0.4854 g, 2.0 mmol) were employed and the reaction mixture was stirred at -78°C for 30 min. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **4c** (0.1585 g, 43% yield) and a white solid of **6c** [0.0625 g, 21% yield, mp $37\text{-}38^\circ\text{C}$ (EtOH)].

4c

4c: ^1H NMR (300 MHz, CDCl_3): δ 7.47-7.40 (m, 2H, ArH), 7.37-7.27 (m, 2H, ArH), 7.26-7.20 (m, 1H, ArH), 3.03 (quint, J = 6.3 Hz, 1H, SCH_2Et_2), 1.76-1.54 (m, 4H, $2\times\text{CH}_2\text{CH}_3$), 1.05 (t, J = 7.3 Hz, 6H, $2\times\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 135.89 (C), 131.71 (CH), 128.70 (CH), 126.37 (CH), 52.18 (CH), 26.66 (CH_2), 11.17 (CH_3). IR (neat): ν_{max} 3074w, 2966s, 2933s, 2875m, 1585m, 1480s, 1460s, 1439s, 1379m, 1303w, 1213w, 1143w, 1092m, 1066w, 1025m, 740s, 692s cm^{-1} . MS: m/z (% relative intensity): 180 (M^+ , 29), 179 (8), 175 (17), 161 (27), 154 (70), 149 (30), 147 (10), 135 (25), 126 (22), 109 (100), 105 (51), 91 (38), 81 (28), 77 (25), 71 (21). **4c** was characterised as its corresponding sulfone **21c**.

21c

21c: ^1H NMR (300 MHz, CDCl_3): δ 7.95-7.83 (m, 2H, ArH), 7.70-7.50 (m, 3H, ArH), 2.87-2.75 (m, 1H, $\text{SO}_2\text{CH}_2\text{Et}_2$), 1.96-1.79 (m, 2H, CH_2CH_3), 1.78-1.59 (m, 2H, CH_2CH_3), 1.01 (t, J = 7.5 Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 138.29 (C), 133.43 (CH), 129.03 (CH), 128.69 (CH), 66.94 (CH), 20.18 (CH_2), 11.09 (CH_3). IR (neat): ν_{max} 3066w, 2972s, 2940m, 2881m, 1586w, 1462m, 1447s, 1385w, 1340w, 1302s, 1228w, 1143s, 1086s, 1074s, 1024w, 999w, 761m, 727s, 693s cm^{-1} . MS: m/z (% relative intensity): 213 ($\text{M}^+ + 1$, 59), 212 (M^+ , 9), 185 (12), 178 (14), 149 (13), 143 (90), 125 (100), 123 (6), 109 (10), 97 (11), 91 (14), 79 (51), 78 (29), 77 (17), 55 (10). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$: C, 62.23; H, 7.60. Found: C, 62.18; H, 7.98.

6c: ^1H NMR (300 MHz, CDCl_3): δ 7.27-7.20 (m, 4H, ArH), 7.20-7.10 (m, 6H, ArH), 2.63 (q, $J = 7.5$ Hz, 4H, $2\times\text{CH}_2\text{CH}_3$), 1.15 (t, $J = 7.5$ Hz, 6H, $2\times\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 164.57 (C), 136.02 (C), 128.95 (CH), 128.61 (CH), 125.96 (CH), 120.34 (C), 28.44 (CH_2), 13.57 (CH_3). IR (neat): ν_{max} 3073m, 3059m, 2967s, 2932s, 2871m, 1583s, 1478s, 1460s, 1439s, 1374m, 1299w, 1201w, 1156w, 1086m, 1069m, 1025s, 1000w, 947w, 875m, 835m, 738s, 689s cm^{-1} . MS: m/z (% relative intensity): 300 (M^+ , 98), 191 (100), 157 (24), 149 (12), 135 (10), 129 (8), 109 (5). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{S}_2$: C, 71.95; H, 6.71. Found: C, 71.87; H, 6.82.

2.4 Reaction of (α -bromo- α,α -difluoromethylsulfanyl)benzene (**1**) with *t*-BuMgCl.

According to the general procedure B, *t*-BuMgCl (10.0 mL, 1.0 M in THF, 10.0 mmol) and **1** (0.4825 g, 2.0 mmol) were employed and the reaction mixture was stirred at -78°C followed by slowly warming up to room temperature overnight. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **4d** (0.2989 g, 63% yield).

4d: ^1H NMR (300 MHz, CDCl_3): δ 7.46-7.39 (m, 2H, ArH), 7.31-7.23 (m, 2H, ArH), 7.18-7.10 (m, 1H, ArH), 2.96 (s, 1H, CHS), 1.23 (s, 18H, $6\times\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 141.32 (C), 128.80 (CH), 128.71 (CH), 125.01 (CH), 71.93 (CH), 39.17 (C), 31.21 (CH_3). IR (neat): ν_{max} 3060w, 3075w, 2958s, 2909s, 2871m, 1584m, 1479s, 1438m, 1392m, 1367m, 1252w, 1220w, 1087m, 1026m, 751m, 730s, 690s cm^{-1} . MS: m/z (% relative intensity): 236 (M^+ , 100), 179 (70), 177 (15), 127 (15), 123 (15), 110 (4), 109 (4), 69 (45), 57 (7). **4d** was characterised as its corresponding sulfone **21d**.

21d: ^1H NMR (300 MHz, CDCl_3): δ 7.85-7.75 (m, 2H, ArH), 7.55-7.43 (m, 3H, ArH), 3.37 (s, 1H, $\text{SO}_2\text{CH}(t\text{-Bu})_2$), 1.38 (s, 18H, $6\times\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 147.09 (C), 131.96 (CH), 128.83 (CH), 126.25 (CH), 81.90 (CH), 37.75 (C), 32.00 (CH_3). IR (KBr-disc.): ν_{max} 3029m, 3011m, 2972s, 1919m, 1491m, 1476m, 1444s, 1398m, 1370s, 1227w, 1289s, 1260s, 1209m, 1133s, 1084s, 1069m, 1031w, 773m, 756s, 729w, 710m, 690s cm^{-1} . MS: m/z (% relative intensity): 268 (M^+ , 1), 267 (4), 199 (13), 197 (100), 143 (48), 125 (40), 119 (7), 111 (13), 97 (15), 91 (8), 77 (29), 71 (32), 69 (24), 57 (91), 55 (31). Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{S}$: C, 67.12; H, 9.01. Found: C, 67.43; H, 8.55.

2.5 Reaction of 1-(α -bromo- α,α -difluoromethylsulfanyl)-4-methylbenzene (**2**) with *i*-PrMgCl.

According to the general procedure B, *i*-PrMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5074 g, 2.0 mmol) were employed and the reaction mixture was stirred at -78°C for 1 h.

The crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **5a** (0.2243 g, 51% yield) and a white solid of **7a** [0.0941 g, 26% yield, mp 40-43 °C (EtOH)].

5a

5a: ¹H NMR (300 MHz, CDCl₃): δ 7.31 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.05 (d, *J* = 7.8 Hz, 2H, Ar*H*), 2.66 (t, *J* = 6.0 Hz, 1H, SCH(*i*-Pr)₂), 2.50 (s, 3H, ArCH₃), 2.11-1.95 (m, 2H, 2xCH(CH₃)₂), 1.04 (d, *J* = 6.6 Hz, 6H, 2xCH₃CH), 1.02 (d, *J* = 6.6 Hz, 6H, 2xCH₃CH). ¹³C NMR (75 MHz, CDCl₃): δ 135.67 (C), 135.59 (C), 130.91 (CH), 129.46 (CH), 66.32 (CH), 31.34 (CH), 21.70 (CH₃), 20.96 (CH₃), 19.59 (CH₃). IR (neat): ν_{max} 3073w, 3020m, 2960s, 2926s, 2871s, 1599w, 1492s, 1471s, 1383s, 1366m, 1318m, 1209w, 1181w, 1091m, 1018m, 981w, 917w, 806s, 728w, 701w cm⁻¹. MS: *m/z* (% relative intensity): 222 (M⁺, 100), 179 (3), 123 (2), 91 (8). **5a** was characterised as its corresponding sulfone **21h**.

21h

21h: ¹H NMR (300 MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.32 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.84 (t, *J* = 2.0 Hz, 1H, SO₂CH(*i*-Pr)₂), 2.44 (s, 3H, ArCH₃), 2.21 (sept, *J* = 7.0 Hz, 1H, CH(CH₃)₂), 2.20 (sept, *J* = 7.0 Hz, 1H, CH(CH₃)₂), 1.20 (d, *J* = 7.0 Hz, 6H, 2xCH₃), 1.13 (d, *J* = 7.0 Hz, 6H, 2xCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 143.94 (C), 137.82 (C), 129.59 (CH), 128.20 (CH), 73.84 (CH), 26.95 (CH), 21.52 (CH₃), 21.19 (CH₃), 20.98 (CH₃). IR (KBr-disc.): ν_{max} 3068w, 2996m, 2969s, 2893m, 2880m, 1596m, 1475m, 1467m, 1459m, 1459m, 1390m, 1373m, 1297s, 1259m, 1241m, 1136s, 1082s, 1016m, 816s, 748m, 708m, 676s, 598s cm⁻¹. MS: *m/z* (% relative intensity): 255 (M⁺+1, 16), 254 (M⁺, 1), 197 (6), 157 (51), 139 (31), 99 (8), 91 (37), 83 (12), 77 (8), 65 (16), 57 (100), 55(14). Anal. Calcd for C₁₄H₂₂O₂S: C, 66.10; H, 8.72. Found: C, 66.02; H, 8.46.

7a

7a: ¹H NMR (300 MHz, CDCl₃): δ 7.09-6.98 (m, 8H, Ar*H*), 3.15 (br.s, 2H, 2xCH(CH₃)₂), 2.32 (s, 6H, 2xArCH₃), 1.32 (d, *J* = 7.0 Hz, 12H, 4xCH₃CH). ¹³C NMR (75 MHz, CDCl₃): δ 169.36 (C), 135.78 (C), 132.87(C), 129.40 (CH), 129.29 (CH), 121.22 (C), 33.01 (CH), 21.17 (CH₃), 21.06 (CH₃). IR (KBr-disc): ν_{max} 3072w, 3019w, 2959s, 2922s, 2866s, 1597w, 1492s, 1459m, 1398m, 1380m, 1361m, 1303w, 1207m, 1181m, 1102m, 1089m, 1037w, 1018m, 915m, 895m, 833m, 804s, 773m, 701w cm⁻¹. MS: *m/z* (% relative intensity): 356 (M⁺, 63), 233 (100), 159 (10), 149 (10), 135 (23), 109 (29), 67 (25). Anal. Calcd for C₂₂H₂₈S₂: C, 74.10; H, 7.91. Found: C, 73.88; H, 7.80.

2.6 Reaction of 1-(*α*-bromo-*α,α*-difluoromethylsulfanyl)-4-methylbenzene (**2**) with *i*-BuMgCl.

According to the general procedure B, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5045 g, 2.0 mmol) were employed and the reaction mixture was stirred at -78 °C for 1 h.

The crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **5b** (0.4200 g, 84% yield) and a white solid of **7b** [0.0097 g, 2% yield, mp 70-72 °C (EtOH)].

5b

5b: ¹H NMR (300 MHz, CDCl₃): δ 7.33 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.13 (d, *J* = 8.0 Hz, 2H, Ar*H*), 3.07 (app. quint, 1H, SCH(*i*-Bu)₂), 2.36 (s, 3H, ArCH₃), 2.07-1.88 (m, 2H, 2xCH(CH₃)₂), 1.50-1.31 (m, 4H, 2xCH₂(*i*-Pr)), 0.91 (d, *J* = 6.6 Hz, 6H, 2xCH₃CH), 0.90 (d, *J* = 6.6 Hz, 6H, 2xCH₃CH). ¹³C NMR (75 MHz, CDCl₃): δ 136.80 (C), 133.14 (CH), 131.02 (C), 129.43 (CH), 45.21 (CH), 44.66 (CH₂), 25.33 (CH), 22.70 (CH₃), 22.30 (CH₃), 21.07 (CH₃). IR (neat): ν_{max} 3072w, 3021w, 2956s, 2927s, 2868s, 1599w, 1492s, 1467s, 1385s, 1367s, 1300w, 1279w, 1210w 1169m, 1149w, 1093m, 1019m, 891w, 809s cm⁻¹. MS: *m/z* (% relative intensity): 250 (M⁺, 100), 215 (3), 193 (2), 149 (3), 137 (7), 124 (86), 92 (39), 79 (3), 77 (3), 57 (3), 55 (3). **5b** was characterised as its corresponding sulfone **21i**.

21i

21i: ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.37 (d, *J* = 7.9 Hz, 2H, Ar*H*), 3.06-2.98 (m, 1H, SO₂CH(*i*-Bu)₂), 2.47 (s, 3H, ArCH₃), 1.79-1.66 (m, 4H, 2xCH₂(*i*-Pr)), 1.36-1.25 (m, 2H, 2xCH(CH₃)₂), 0.91 (d, *J* = 6.3 Hz, 6H, 2xCH₃), 0.83 (d, *J* = 6.2 Hz, 6H, 2xCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 144.99 (C), 135.55 (C), 130.25 (CH), 129.59 (CH), 61.55 (CH), 39.29 (CH₂), 26.22 (CH), 23.50 (CH₃), 22.57 (CH₃), 22.23 (CH₃). IR (KBr-disc.): ν_{max} 2959s, 2920s, 2869m, 1595m, 1493w, 1467m, 1387m, 1370m, 1315s, 1301s, 1288s, 1221w, 1141s, 1120m, 1084s, 1020w, 821s, 759m, 727s, 664s cm⁻¹. MS: *m/z* (% relative intensity): 283 (M⁺+1, 45), 282 (M⁺, 2), 261 (5), 233 (8), 183 (7), 157 (100), 139 (91), 119 (5), 111 (7), 93 (27), 91 (57), 85 (19), 77 (12), 71 (29), 57 (27). Anal. Calcd for C₁₆H₂₆O₂S: C, 68.04; H, 9.28. Found: C, 67.86; H, 9.14.

7b

7b: ¹H NMR (300 MHz, CDCl₃): δ 7.08-6.99 (m, 8H, Ar*H*), 2.55 (d, *J* = 7.5 Hz, 4H, 2xCH₂(*i*-Pr)), 2.31 (s, 6H, 2xArCH₃), 2.03-1.87 (m, 2H, 2xCH(CH₃)₂), 0.97 (d, *J* = 6.6 Hz, 12H, 4xCH₃CH). ¹³C NMR (75 MHz, CDCl₃): δ 157.56 (C), 136.07 (C), 132.56 (C), 129.97 (CH), 129.35 (CH), 43.98 (CH₂), 28.42 (CH), 22.65 (CH₃), 21.08 (CH₃). IR (KBr-disc): ν_{max} 3022w, 2956s, 2924s, 1595w, 1560w, 1489s, 1459s, 1384m, 1367m, 1334w, 1303w, 1210w, 1181m, 1161m, 1123m, 1085s, 1017m, 942w, 903s, 850w, 826w, 799s cm⁻¹. MS: *m/z* (% relative intensity): 384 (M⁺, 70), 341 (7), 261 (100), 217 (15), 161 (11), 149 (8), 137 (17), 109 (3), 96 (24), 91 (9), 81 (49), 79 (13), 77 (7), 67 (7). Anal. Calcd for C₂₄H₃₂S₂: C, 74.94; H, 8.39. Found: C, 75.00; H, 8.31.

2.7 Reaction of 1-(α -bromo- α,α -difluoromethylsulfanyl)-4-methylbenzene (**2**) with EtMgCl.

According to the general procedure B, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5014 g, 2.0 mmol) were employed and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **5c** (0.1610 g, 42% yield) and a colorless liquid of **7c** (0.0422 g, 13% yield).

5c

5c: ^1H NMR (300 MHz, CDCl_3): δ 7.35 (d, $J = 8.0$ Hz, 2H, ArH), 7.13 (d, $J = 8.0$ Hz, 2H, ArH), 2.94 (quint, $J = 6.3$ Hz, 1H, $\text{SCH}(\text{Et})_2$), 2.36 (s, 3H, ArCH₃), 1.76-1.51 (m, 4H, 2xCH₂CH₃), 1.04 (t, $J = 7.4$ Hz, 6H, 2xCH₂CH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 136.61 (C), 132.62 (CH), 131.82 (C), 129.47 (CH), 52.71 (CH), 26.60 (CH₂), 21.03 (CH₃), 11.17 (CH₃). IR (neat): ν_{max} 3072w, 3020w, 2966s, 2932s, 2874m, 1599w, 1492s, 1458m, 1398w, 1378m, 1301w, 1209w, 1093m, 1018m, 808s cm^{-1} . MS: m/z (% relative intensity): 194 (M^+ , 4), 182 (58), 167 (58), 123 (100), 121 (22), 111 (16), 109 (15), 91 (36), 81 (29), 79 (38), 77 (29), 71 (22), 69 (24), 67 (22), 57 (29), 55 (27). **5c** was characterised as its corresponding sulfone **21j**.

21j

21j: ^1H NMR (300 MHz, CDCl_3): δ 7.75 (d, $J = 8.2$ Hz, 2H, ArH), 7.35 (d, $J = 8.0$ Hz, 2H, ArH), 2.85 (m, 1H, $\text{SO}_2\text{CH}(\text{Et})_2$), 2.45 (s, 3H, ArCH₃), 1.97-1.78 (m, 2H, CH₂CH₃), 1.67 (sept., $J = 7.3$ Hz, 2H, CH₂CH₃), 1.00 (t, $J = 7.5$ Hz, 6H, 2xCH₂CH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 144.28 (C), 135.26 (C), 129.60 (CH), 128.64 (CH), 66.93 (CH), 21.50 (CH₃), 20.19 (CH₂), 11.05 (CH₃). IR (KBr-disc): ν_{max} 3063w, 2974s, 2941m, 2880m, 1937w, 1596m, 1498w, 1459s, 1386m, 1300s, 1285s, 1246m, 1231m, 1142s, 1085s, 1045m, 1020w, 859w, 818s, 800m, 772m, 718s, 694s, 656s cm^{-1} . MS: m/z (% relative intensity): 227 (M^+ , 14), 226 (M^+ , 1), 157 (100), 139 (73), 93 (35), 92 (34), 91 (35), 77 (7), 65 (9). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$: C, 63.68; H, 8.02. Found: C, 63.59; H, 7.85.

7c

7c: ^1H NMR (300 MHz, CDCl_3): δ 7.10-6.98 (m, 8H, ArH), 2.60 (q, $J = 7.5$ Hz, 4H, 2xCH₂CH₃), 2.31 (s, 6H, 2xArCH₃), 1.12 (t, $J = 7.5$ Hz, 6H, 2xCH₂CH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 162.90 (C), 135.97 (C), 132.42 (C), 129.49 (CH), 129.41 (CH), 121.62 (C), 28.38 (CH₂), 21.06 (CH₃), 13.58 (CH₃). IR (neat): ν_{max} 3073w, 3020w, 2967s, 2931s, 2871m, 1598w, 1568w, 1492s, 1460m, 1399w, 1374w, 1302w, 1180w, 1116w, 1103w, 1087m, 1041m, 1017m, 947w, 875m, 832w, 802s cm^{-1} . MS: m/z (% relative intensity): 328 (M^+ , 71), 205 (71), 171 (100), 156 (33), 143 (26), 129 (8), 115 (5), 91 (10), 77 (6). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{S}_2$: C, 73.12; H, 7.36. Found: C, 73.21; H, 7.26.

2.8 Reaction of 1-(α -bromo- α,α -difluoromethylsulfanyl)-4-methylbenzene (**2**) with *t*-BuMgCl.

According to the general procedure B, *t*-BuMgCl (10.0 mL, 1.0 M in THF, 10.0 mmol) and **2** (0.5010 g, 2.0 mmol) were employed and the reaction mixture was stirred and slowly warmed up to room temperature overnight. The crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a white solid of **5d** [0.2275 g, 46% yield, mp 38-40 °C (EtOH)].

5d

5d: ¹H NMR (300 MHz, CDCl₃): δ 7.28 (d, J = 8.2 Hz, 2H, ArH), 7.05 (d, J = 8.1 Hz, 2H, ArH), 2.86 (s, 1H, SCH(*t*-Bu)₂), 2.30 (s, 3H, ArCH₃), 1.20 (s, 18H, 6xCH₃C). ¹³C NMR (75 MHz, CDCl₃): δ 137.76 (C), 134.87 (C), 129.49 (CH), 129.17 (CH), 72.53 (CH), 39.17 (C), 31.25 (CH₃), 20.91 (CH₃). IR (CHCl₃): $\nu_{\max}$ 3075w, 2961s, 2871m, 1599w, 1492s, 1478s, 1393s, 1367s, 1252w, 1117w, 1089m, 943w, 915w, 862w, 808s cm⁻¹. MS: m/z (% relative intensity): 250 (M⁺, 25), 234 (44), 193 (100), 191 (13), 140 (3). **5d** was characterised as its corresponding sulfone **21k**.

21k

21k: ¹H NMR (300 MHz, CDCl₃): δ 7.68 (d, J = 8.3 Hz, 2H, ArH), 7.29 (d, J = 7.9 Hz, 2H, ArH), 3.30 (s, 1H, SO₂CH(*t*-Bu)₂), 2.40 (s, 3H, ArCH₃), 1.32 (s, 18H, 6xCH₃C). ¹³C NMR (75 MHz, CDCl₃): δ 144.21 (C), 142.61 (C), 129.35 (CH), 126.30 (CH), 81.88 (CH), 37.68 (C), 32.00 (CH₃), 21.41 (CH₃). IR (KBr-disc.): $\nu_{\max}$ 3060w, 3039m, 3008s, 2957s, 1597m, 1492s, 1458m, 1399s, 1372s, 1282s, 1259s, 1226m, 1208m, 1172m, 1131s, 1083s, 1035w, 1017m, 822s, 800m, 760m, 733w cm⁻¹. MS: m/z (% relative intensity): 282 (M⁺, 0.5), 211 (67), 157 (100), 139 (35), 119 (7), 111 (12), 105 (7), 91 (36), 77 (9), 71 (21), 65 (15), 57 (58), 55 (21). Anal. Calcd for C₁₆H₂₆O₂S: C, 68.04; H, 9.28. Found: C, 67.77; H, 9.01.

3. Reaction of the anions **13** and **14** with electrophiles.

3.1 Reaction of the anion **13a** with methyl iodide.

General procedure C: A solution of *i*-PrMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) was added dropwise to a stirred solution of (α -bromo- α,α -difluoromethylsulfanyl)benzene (**1**) (0.4828 g, 2.0 mmol) in dry THF (4.0 mL) at -78 °C under an argon atmosphere, and the resulting solution was stirred at -78 °C for 30 min. The solution of the anion **13a** was treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Methyl iodide (0.50 mL, 8.0 mmol) was then added at the same temperature and the reaction mixture was slowly warmed up to room temperature overnight. The resulting solution was quenched with 1 M HCl (5 mL) and 10% NH₄OH (25 mL) was then added. The mixture was stirred until the solution became blue. It was poured into water (30 mL) and extracted with hexanes (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **18a** (0.1635 g, 36% yield) and a white solid **6a** (0.0867 g, 26% yield).

18a

18a: ^1H NMR (300 MHz, CDCl_3): δ 7.60-7.53 (m, 2H, ArH), 7.30-7.21 (m, 3H, ArH), 2.01 (sept, $J = 6.7$ Hz, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.07 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3\text{CH}$), 1.02 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3\text{CH}$), 0.50 (s, 3H, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 137.71 (CH), 133.83 (C), 128.21 (CH), 128.00 (CH), 62.03 (C), 35.59 (CH), 18.60 (CH_3), 18.56 (CH_3), 18.37 (CH_3). IR (neat): ν_{max} 3060w, 3074w, 2963s, 2940s, 2876s, 1583m, 1473s, 1438m, 1382m, 1372s, 1306m, 1148w, 1121w, 1096w, 1067m, 1044m, 1025m, 748s, 705s, 693s cm^{-1} . MS: m/z (% relative intensity): 222 (M^+ , 67), 218 (53), 181 (40), 112 (100), 109 (24), 97 (45), 69 (11), 57 (38). **18a** was characterised as its corresponding sulfone **21e**.

21e

21e: ^1H NMR (300 MHz, CDCl_3): δ 7.93-7.80 (m, 2H, ArH), 7.66-7.48 (m, 3H, ArH), 2.29 (sept, $J = 7.0$ Hz, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.37 (s, 3H, CH_3), 1.12 (d, $J = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $J = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 139.26 (C), 133.10 (CH), 129.76 (CH), 128.73 (CH), 74.21 (C), 31.21 (CH), 19.83 (CH_3), 19.03 (CH_3), 15.57 (CH_3). IR (KBr-disc.): ν_{max} 3009m, 2964s, 2883m, 1401m, 1459m, 1475m, 1447s, 1389m, 1378m, 1284s, 1199m, 1151s, 1119s, 1080s, 1060s, 997m, 935w, 901w, 835w, 769s, 733s, 695s cm^{-1} . MS: m/z (% relative intensity): 254 (M^+ , 0.2), 197 (32), 143 (38), 125 (11), 97 (18), 78(12), 77 (12), 57 (100), 55 (14). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{S}$: C, 66.10; H, 8.72. Found: C, 65.73; H, 8.57.

3.2 Reaction of the anion **13b** with methyl iodide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4802 g, 2.0 mmol), CuCN $\cdot$ 2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) and methyl iodide (0.5 mL, 8.0 mmol) were employed. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **18b** (0.3048 g, 61% yield) and a white solid of **6b** (0.0206 g, 6% yield).

18b

18b: ^1H NMR (300 MHz, CDCl_3): δ 7.47-7.37 (m, 2H, ArH), 7.27-7.16 (m, 3H, ArH), 1.96-1.81 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.39 (app. d, $J \cong 5.0$ Hz, 4H, $2\times\text{CH}_2(i\text{-Pr})$), 1.16 (s, 3H, CH_3), 0.90 (d, $J = 7.1$ Hz, 6H, $2\times\text{CH}_3\text{CH}$), 0.87 (d, $J = 7.1$ Hz, 6H, $2\times\text{CH}_3\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3): δ 137.49 (CH), 132.54 (C), 128.35 (CH), 128.30 (CH), 54.63 (C), 49.83 (CH_2), 26.90 (CH_3), 25.28 (CH_3), 25.26 (CH_3), 24.55 (CH). IR (neat): ν_{max} 3075w, 3060w, 2956s, 2927s, 2869s, 1584w, 1469s, 1438m, 1385m, 1374m, 1366m, 1141m, 1090w, 1067w, 1025m, 749s, 705m, 694s cm^{-1} . MS: m/z (% relative intensity): 250 (M^+ , 100), 141 (57), 140 (42), 137 (23), 110 (98), 109 (32), 83 (43), 57 (43). **18b** was characterised as its corresponding sulfone **21f**.

21f

21f: ^1H NMR (300 MHz, CDCl_3): δ 7.90-7.80 (m, 2H, ArH), 7.69-7.49 (m, 3H, ArH), 1.93 (sept, $J = 6.5$ Hz, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.63 (d, $J = 5.4$ Hz, 4H, $2\times\text{CH}_2(i\text{-Pr})$), 1.39 (s, 3H, CH_3), 0.97 (d, $J = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.93 (d, $J = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 136.46 (C), 133.35 (CH), 130.51 (CH), 128.60 (CH), 67.63 (C), 43.00 (CH_2), 25.25 (CH_3), 25.04 (CH_3), 24.12 (CH), 19.33 (CH_3). IR (neat): ν_{max} 3067w, 2960s, 2871s, 1585w, 1468s, 1447s, 1388m, 1368m, 1298s, 1156s, 1132s, 1084s, 1037w, 1024w, 761m, 726s, 693s, 655s cm^{-1} . MS: m/z (% relative intensity): 282 (M^+ , 10), 281 (17), 267 (15), 253 (15), 215 (14), 202 (21), 178 (50), 165 (29), 164 (41), 151 (18), 149 (26), 115 (25), 109 (18), 105 (35), 95 (29), 91 (100), 81 (42), 79 (50), 77 (52), 67 (42), 65 (36), 57 (26), 55 (52). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{S}$: C, 68.04; H, 9.28. Found: C, 67.94; H, 9.08.

3.3 Reaction of the anion 13b with allyl bromide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4837 g, 2.0 mmol), CuCN $\cdot$ 2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) and allyl bromide (0.7 mL, 8.3 mmol) were employed. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **18c** (0.4254 g, 76% yield) and a white solid of **6b** (0.0165 g, 5% yield).

18c

18c: ^1H NMR (300 MHz, CDCl_3): δ 7.61-7.51 (m, 2H, ArH), 7.47-7.27 (m, 3H, ArH), 6.15-5.99 (m, 1H, $\text{CH}=\text{CH}_2$), 5.17-5.03 (m, 2H, $\text{CH}=\text{CH}_2$), 2.39 (ddd, $J = 1.3, 1.3, 6.8$ Hz, 2H, $\text{CH}_\text{A}\text{H}_\text{B}\text{CH}=\text{CH}_2$), 2.14-1.92 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.53 (d, $J = 5.3$ Hz, 4H, $2\times\text{CH}_2(i\text{-Pr})$), 1.03 (d, $J = 6.6$ Hz, 6H, $2\times\text{CH}_3$), 1.01 (d, $J = 6.6$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 137.31 (CH), 135.02 (CH), 132.28 (C), 128.36 (CH), 128.34 (CH), 117.47 (CH_2), 57.52 (C), 46.45 (CH_2), 42.96 (CH_2), 25.29 (CH_3), 25.23 (CH_3), 24.30 (CH). IR (neat): ν_{max} 3076m, 2956s, 2928s, 2869s, 1638m, 1539w, 1573w, 1469s, 1438s, 1386m, 1366m, 1166w, 1135w, 1068w, 1026m, 996w, 915s, 749s, 705s, 694s cm^{-1} . MS: m/z (% relative intensity): 276 (M^+ , 11), 219 (10), 167 (100), 157 (93), 109 (56), 95 (18), 69 (28), 55 (14). HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{28}\text{S}$: 276.1912. Found: 276.1948.

3.4 Reaction of the anion 13b with crotyl bromide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4803 g, 2.0 mmol), CuCN $\cdot$ 2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) and crotyl bromide (*E/Z* = 80/20, 0.5 mL, 8.0 mmol) were employed. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **18d** (*E/Z* = 80/20), (0.4552 g, 78% yield) and a white solid **6b** (0.0163 g, 5% yield).

18d

18d: ^1H NMR (300 MHz, CDCl_3): δ 7.54-7.45 (m, 2H, ArH of *cis*- and *trans*-isomers), 7.35-7.23 (m, 3H, ArH of *cis*- and *trans*-isomers), 5.47-5.35 (m, 2H, $\text{CH}=\text{CH}$ of *cis*- and *trans*-isomers), 2.26 (d, $J = 6.6$ Hz, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$ of *cis*- and *trans*-isomers), 2.06-1.92 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$ of *cis*- and *trans*-isomers), [1.69 (dd, $J = 1.3$ Hz, 6.3 Hz) and 1.55 (dd, $J = 1.2$ Hz, 6.7 Hz), 3H, $\text{CH}=\text{CH}-\text{CH}_3$ of *cis*- and *trans*-isomers], 1.48 (d, $J = 5.4$ Hz, 2H, $\text{CH}_2(i\text{-Pr})$ of *cis*- and *trans*-isomers), 1.46 (d, $J = 5.1$ Hz, 2H, $\text{CH}_2(i\text{-Pr})$ of *cis*- and *trans*-isomers), 0.98 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3\text{CH}$ of *cis*- and *trans*-isomers), 0.95 (d, $J = 6.7$ Hz, 6H, $2\times\text{CH}_3\text{CH}$ of *cis*- and *trans*-isomers). ^{13}C NMR (75 MHz, CDCl_3): δ 137.36 (CH), 137.27 (CH), 132.50 (C), 132.31 (C), 128.31 (CH), 128.23 (CH), 128.02 (CH), 127.23 (CH), 126.72 (CH), 125.30 (CH), 58.03 (C), 46.52 (CH_2), 46.25 (CH_2), 41.78 (CH_2), 35.44 (CH_2), 25.32 (CH_3), 25.27 (CH_3), 25.10 (CH_3), 24.34 (CH), 24.28 (CH), 18.16 (CH_3), 13.34 (CH_3). IR (neat): ν_{max} 3060w, 3023w, 2955s, 2931s, 1668w, 1584w, 1471s, 1456m, 1438s, 1386m, 1366m, 1303w, 1166w, 1134w, 1067w, 1026m, 969m, 916w, 749s, 705s, 694s cm^{-1} . MS: m/z (% relative intensity): 290 (M^+ , 13), 235 (23), 181 (25), 180 (28), 179 (25), 171 (97), 165 (22), 151 (21), 126 (23), 125 (87), 124 (28), 123 (80), 112 (38), 109 (40), 95 (34), 84 (37), 82 (38), 70 (100), 67 (28), 57 (33), 56 (36). HRMS (EI): Calcd for $\text{C}_{19}\text{H}_{30}\text{S}$: 290.2068. Found: 290.2073.

3.5 Reaction of the anion 13b with benzoyl cyanide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4856 g, 2.0 mmol), $\text{CuCN}\cdot 2\text{LiCl}$ (4.0 mL, 0.5 M in THF, 2.0 mmol) and benzoyl cyanide (1.0 mL, 8.4 mmol) were employed. After quenching with 1 M HCl (5 mL) and the addition of 10% NH_4OH (25 mL), the mixture was poured into water (30 mL) and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the residue was filtered to remove benzoic acid and washed with hexanes (50 mL). After removal of solvent under reduced pressure, the crude product was purified by radial chromatography (SiO_2 , 0-3% EtOAc in hexanes) to give a white solid of **6b** (0.0134 g, 4% yield) and a pale yellow liquid of **18e** (0.3807 g, 56% yield).

18e

18e: ^1H NMR (300 MHz, CDCl_3): δ 8.22-8.15 (m, 2H, ArH), 7.54-7.36 (m, 3H, ArH), 7.34-7.19 (m, 5H, ArH), 2.02-1.85 (m, 2H, $2\times\text{CH}(\text{CH}_3)_2$), 1.96 (m, 4H, $2\times\text{CH}_2(i\text{-Pr})$), 0.99 (d, $J = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.78 (d, $J = 6.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 199.62 (C=O), 138.62 (C), 136.13 (CH), 131.15 (CH), 131.03 (C), 129.90 (CH), 129.05 (CH), 128.64 (CH), 127.94 (CH), 64.19 (C), 42.05 (CH_2), 25.10 (CH), 24.86 (CH_3), 23.81 (CH_3). IR (neat): ν_{max} 3061w, 2957s, 2870m, 1666s, 1596w, 1576w, 1470s, 1439m, 1388m, 1368m, 1271w, 1218s, 1183w, 1070w, 1018m, 749s, 719m, 692s cm^{-1} . MS: m/z (% relative

intensity): 341 ($M^+ + H$, 100), 235 (28), 232 (53), 180 (45), 178 (15), 105 (11). HRMS (ESI-TOF): Calcd for $C_{22}H_{28}OSNa$: 363.1759. Found: 363.1758.

3.6 Reaction of the anion **13b** with benzaldehyde.

General procedure D: A solution of *i*-BuMgCl (4.3 mL, 2.0 M in THF, 8.6 mmol) was added dropwise to a stirred solution of **1** (0.7147 g, 3.0 mmol) in dry THF (4.0 mL) at -78°C under an argon atmosphere. The reaction mixture was stirred for 30 min to produce **13b** at the same temperature followed by the addition of benzaldehyde (0.20 mL, 2.0 mmol). The resulting solution was slowly warmed up to room temperature overnight. The mixture was quenched with 1 M HCl (5 mL), poured into water and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified by radial chromatography (SiO_2 , 0-2% EtOAc in hexanes) to give a pale yellow liquid of **18f** (0.3038 g, 45% yield based on benzaldehyde).

18f

18f: 1H NMR (300 MHz, $CDCl_3$): δ 7.61-7.50 (m, 2H, ArH), 7.44-7.21 (m, 8H, ArH), 4.50 (s, 1H, CHOH), 3.75 (br.s, 1H, OH), 2.44-2.25 (m, 1H, $CH(CH_3)_2$), 2.13-1.92 (m, 1H, $CH(CH_3)_2$), [1.55 (dd, $J = 4.8, 15.0$ Hz) and 1.48 (dd, $J = 5.9, 15.0$ Hz), 2H each $CH_AH_B(i\text{-Pr})$], [1.32 (dd, $J = 3.8, 14.7$ Hz) and 1.25 (dd, $J = 6.2, 14.7$ Hz), 2H each $CH_CH_D(i\text{-Pr})$], 1.05 (d, $J = 6.6$ Hz, 3H, $CHCH_3$), 1.00 (d, $J = 6.6$ Hz, 3H, $CHCH_3$), 0.86 (d, $J = 6.6$ Hz, 6H, $2 \times CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.33 (C), 137.11 (CH), 130.32 (C), 128.88 (CH), 128.68 (CH), 127.56 (CH), 78.35 (CH), 65.38 (C), 44.63 (CH_2), 43.20 (CH_2), 25.84 (CH_3), 25.48 (CH_3), 25.45 (CH_3), 25.05 (CH_3), 24.58 (CH), 24.22 (CH). IR (neat): ν_{max} 3456m, 3061m, 3031m, 2956s, 2927s, 2869s, 1885w, 1810w, 1705w, 1603w, 1583w, 1492m, 1468s, 1453s, 1438s, 1387s, 1366m, 1326m, 1238m, 1187m, 1131m, 1086w, 1054s, 1026s, 941w, 919w, 878w, 841w, 749s, 703s cm^{-1} . MS: m/z (% relative intensity): 342 (M^+ , 2), 318 (12), 305 (17), 235 (96), 178 (100), 135 (27), 123 (92), 109 (24), 105 (44), 91 (49), 77 (46), 55(9). HRMS (ESI-TOF): Calcd for $C_{22}H_{30}OSNa$: 365.1915. Found: 365.1909.

3.7 Reaction of the anion **13b** with *p*-tolualdehyde.

According to the general procedure D, *i*-BuMgCl (4.3 mL, 2.0 M in THF, 8.6 mmol), **1** (0.7170 g, 3.0 mmol) and *p*-tolualdehyde (0.26 mL, 2.2 mmol) were employed. After removal of solvent, the crude product was purified by radial chromatography (SiO_2 , 0-2% EtOAc in hexanes) to give a pale yellow liquid of **18g** (0.3502 g, 45% yield based on *p*-tolualdehyde).

18g

18g: 1H NMR (300 MHz, $CDCl_3$): δ 7.67-7.54 (m, 2H, ArH), 7.45-7.23 (m, 5H, ArH), 7.14 (d, $J = 7.9$ Hz, 2H, ArH), 4.50 (s, 1H, CHOH), 3.73 (br.s, 1H, OH), 2.49-2.30 (m, 1H, $CH(CH_3)_2$), 2.37 (s, 3H, ArCH₃), 2.17-2.00 (m, 1H, $CH(CH_3)_2$), 1.59 (dd, $J = 4.7, 15.0$ Hz) and 1.51 (dd, $J = 5.9, 15.0$ Hz), 2H, each $CH_AH_B(i\text{-Pr})$, 1.32 (dd, $J = 4.0, 14.5$ Hz) and 1.27

(dd, $J = 5.9, 14.5$ Hz), 2H, each $\text{CHCHD}(i\text{-Pr})$, 1.09 (d, $J = 6.5$ Hz, 3H, CHCH_3), 1.04 (d, $J = 6.6$ Hz, 3H, CHCH_3), 0.90 (d, $J = 6.4$ Hz, 3H, CHCH_3), 0.89 (d, $J = 6.8$ Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 137.22 (C), 137.16 (CH), 136.32 (C), 130.50 (C), 128.84 (CH), 128.79 (CH), 128.69 (CH), 128.31 (CH), 78.25 (CH), 65.46 (C), 44.69 (CH_2), 43.27 (CH_2), 25.89 (CH_3), 25.53 (CH_3), 25.49 (CH_3), 25.10 (CH_3), 24.63 (CH), 24.27 (CH), 21.10 (CH_3). IR (neat): ν_{max} 3457m, 3058m, 3022m, 2957s, 2925s, 2869s, 1667w, 1607w, 1582w, 1515m, 1468s, 1438s, 1386s, 1366s, 1320m, 1234m, 1190m, 1178m, 1130m, 1066s, 1026s, 941m, 919m, 808m, 749s, 704s, 693s cm^{-1} . MS: m/z (% relative intensity): 356 (M^+ , 8), 355 (14), 316 (18), 299 (12), 297 (35), 282 (72), 269 (24), 263 (66), 247 (3), 206 (29), 181 (26), 153 (37), 143 (15), 135 (23), 129 (19), 121 (11), 115 (26), 109 (41), 107 (49), 105 (28), 97 (11), 91 (100), 87 (24), 77 (35), 67 (16), 65 (19), 55 (24). HRMS (ESI-TOF): Calcd for $\text{C}_{23}\text{H}_{32}\text{OSNa}$: 379.2072. Found: 379.2078.

3.8 Reaction of the anion 13c with methyl iodide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4813 g, 2.0 mmol), $\text{CuCN}\cdot 2\text{LiCl}$ (4.0 mL, 0.5 M in THF, 2.0 mmol) and methyl iodide (0.5 mL, 8.0 mmol) were employed. The crude product was purified by preparative thin-layer chromatography (SiO_2 , hexanes) to give a colorless liquid of **18h** (0.1381 g, 35% yield) and a white solid of **6c** (0.0776 g, 13% yield).

18h

18h: ^1H NMR (300 MHz, CDCl_3): δ 7.52-7.46 (m, 2H, ArH), 7.35-7.25 (m, 3H, ArH), 1.52-1.42 (m, 4H, $2\times\text{CH}_2\text{CH}_3$), 1.13 (s, 3H, CH_3), 0.98 (t, $J = 7.4$ Hz, 6H, $2\times\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 137.47 (CH), 132.24 (C), 128.43 (CH), 128.35 (CH), 53.74 (C), 31.60 (CH_2), 25.31 (CH_3), 8.71 (CH_3). IR (neat): ν_{max} 3060w, 3074w, 2969s, 2934s, 2878m, 1584w, 1474m, 1457m, 1438m, 1379m, 1154w, 1131m, 1091w, 1067m, 1026m, 1002m, 749s, 705s, 694s cm^{-1} . MS: m/z (% relative intensity): 194 (M^+ , 100), 180 (8), 179 (4), 165 (2), 110 (46), 109 (9), 85 (6), 69 (7), 65 (6). **18h** was characterised as its corresponding sulfones **21g**.

21g

21g: ^1H NMR (300 MHz, CDCl_3): δ 7.93-7.81 (m, 2H, ArH), 7.69-7.48 (m, 3H, ArH), 1.96-1.80 (m, 2H, CH_2CH_3), 1.79-1.57 (m, 2H, CH_2CH_3), 1.21 (s, 3H, CH_3), 1.00 (t, $J = 7.5$ Hz, 6H, $2\times\text{CH}_2\text{CH}_3$). ^{13}C NMR (75 MHz, CDCl_3): δ 136.36 (C), 133.33 (CH), 130.24 (CH), 128.62 (CH), 66.07 (C), 25.52 (CH_2), 19.37 (CH_3), 8.42 (CH_3). IR (neat): ν_{max} 3067w, 2975s, 2944s, 2885m, 1585w, 1463s, 1447s, 1386m, 1286s, 1163s, 1127s, 1079s, 1012m, 999m, 762s, 741s, 720s, 693s, 642s cm^{-1} . MS: m/z (% relative intensity): 227 (M^++1 , 6), 226 (M^+ , 2), 205 (19), 203 (15), 191 (17), 178 (45), 171 (27), 164 (100), 150 (16), 149 (13), 129 (13), 105 (26), 95 (17), 91 (20), 81 (13), 77 (28), 57 (8), 55 (12). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$: C, 63.68; H, 8.02. Found: C, 63.52; H, 8.30.

3.9 Reaction of the anion 13c with allyl bromide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4794 g, 2.0 mmol), $\text{CuCN}\cdot 2\text{LiCl}$ (4.0 mL, 0.5 M in THF, 2.0 mmol) and allyl bromide (0.7 mL, 8.3 mmol) were employed. The crude product was purified by preparative thin-layer

chromatography (SiO₂, hexanes) to give a colorless liquid of **18i** (0.1709 g, 39% yield) and a white solid of **6c** (0.0846 g, 26% yield).

18i

18i: ¹H NMR (300 MHz, CDCl₃): δ 7.52-7.43 (m, 2H, ArH), 7.37-7.24 (m, 3H, ArH), 6.09-5.94 (m, 1H, CH=CH₂), 5.15-5.04 (m, 2H, CH=CH₂), 2.16 (ddd, *J* = 1.3, 1.3, 7.0 Hz, 2H, CH₂CH=CH₂), 1.41 (q, *J* = 7.3 Hz, 4H, 2xCH₂CH₃), 0.99 (t, *J* = 7.3 Hz, 6H, 2xCH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 137.38 (CH), 134.32 (CH), 131.84 (C), 128.54 (CH), 128.46 (CH), 117.31 (CH₂), 56.88 (C), 40.16 (CH₂), 28.40 (CH₂), 8.10 (CH₃). IR (neat): ν_{max} 3075*m*, 2969*s*, 2936*s*, 2879*s*, 1638*w*, 1584*w*, 1474*s*, 1452*s*, 1438*s*, 1376*m*, 1318*w*, 1286*w*, 1148*w*, 1120*w*, 1089*w*, 1068*m*, 1030*m*, 997*m*, 915*s*, 843*w*, 749*s*, 705*s*, 694*s* cm⁻¹. MS: *m/z* (% relative intensity): 220 (M⁺, 100), 191 (20), 179 (30), 129 (14), 112 (44), 110 (38), 109 (83), 96 (15), 82 (37), 69 (19), 65 (6), 55(4). HRMS (EI): Calcd for C₁₄H₂₀S: 220.1286. Found: 220.1287.

3.10 Reaction of the anion 13c with crotyl bromide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4801 g, 2.0 mmol), CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) and crotyl bromide (*E/Z* = 80/20, 0.5 mL, 8.0 mmol) were employed. The crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **18j** (*E/Z* = 80/20), (0.1864 g, 40% yield) and a white solid of **6c** (0.0602 g, 20% yield).

18j

18j: ¹H NMR (300 MHz, CDCl₃): δ 7.63-7.45 (m, 2H, ArH of *cis*- and *trans*-isomers), 7.45-7.19 (m, 3H, ArH of *cis*- and *trans*-isomers), 5.77-5.45 (m, 2H, CH=CH of *cis*- and *trans*-isomers), 2.20-2.07 (m, 2H, CH₂CH=CH of *cis*- and *trans*-isomers), [1.73 (dd, *J* = 1.2, 6.1 Hz) and 1.63 (dd, *J* = 1.2, 6.3 Hz), 3H, CH=CHCH₃ of *cis*- and *trans*-isomer], 1.46 (q, *J* = 7.2 Hz, 2H, CH₂CH₃ of *cis*- and *trans*-isomers), 1.42 (q, *J* = 7.2 Hz, 2H, CH₂CH₃ of *cis*- and *trans*-isomers), 1.02 (t, *J* = 7.3 Hz, 6H, 2xCH₂CH₃ of *cis*- and *trans*-isomers). ¹³C NMR (75 MHz, CDCl₃): δ 137.39 (CH), 137.36 (CH), 132.03 (C), 131.91 (C), 128.48 (CH), 128.41 (CH), 127.80 (CH), 126.51 (CH), 125.85 (CH), 125.54 (CH), 57.32 (C), 38.79 (CH₂), 32.95 (CH₂), 28.43 (CH₂), 18.14 (CH₃), 13.30 (CH₃), 8.24 (CH₃), 8.14 (CH₃). IR (neat): ν_{max} 3075*w*, 3060*w*, 3022*m*, 2968*s*, 2936*s*, 2878*m*, 1584*w*, 1474*s*, 1456*s*, 1438*s*, 1405*w*, 1376*m*, 1331*w*, 1306*w*, 1175*w*, 1120*w*, 1089*w*, 1068*m*, 1026*m*, 968*m*, 942*w*, 838*w*, 775*w*, 749*s*, 705*s*, 694*s* cm⁻¹. MS: *m/z* (% relative intensity): 234 (M⁺, 5), 233 (8), 189 (28), 179 (100), 175 (22), 163 (20), 161 (37), 157 (5), 147 (17), 137 (32), 135 (38), 124 (42), 123 (43), 110 (57), 109 (51), 95 (70), 91 (19), 81 (23), 77 (23), 69 (45), 67 (55), 65 (32), 57 (13), 55 (41). HRMS (EI): Calcd for C₁₅H₂₂S: 234.1442. Found: 234.1400.

3.11 Reaction of the anion 13c with benzoyl cyanide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol), **1** (0.4806 g, 2.0 mmol), CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) and benzoyl cyanide

(1.0 mL, 8.4 mmol) were employed. After quenching with 1 M HCl (5 mL) and the addition of 10% NH₄OH (25 mL), the mixture was poured into water (30 mL) and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the residue was filtered to remove benzoic acid and washed with hexanes (50 mL). After removal of solvent under reduced pressure, the crude product was purified by radial chromatography (SiO₂, 0-3% EtOAc in hexanes) to give a pale yellow liquid of **18k** (0.2048 g, 36% yield) and a white solid of **6c** (0.0836 g, 28% yield).

18k

18k: ¹H NMR (300 MHz, CDCl₃): δ 8.26-8.19 (m, 2H, ArH), 7.56-7.48 (m, 1H, ArH), 7.47-7.39 (m, 2H, ArH), 7.36-7.29 (m, 3H, ArH), 7.28-7.21 (m, 2H, ArH), 1.92 (sext, *J* = 7.3 Hz, 2H, CH₂CH₃), 1.79 (sext, *J* = 7.3 Hz, 2H, CH₂CH₃), 0.87 (t, *J* = 7.3 Hz, 6H, 2xCH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 201.03 (C=O), 138.69 (C), 136.39 (CH), 131.35 (CH), 130.44 (C), 129.28 (CH), 128.80 (CH), 128.05 (CH), 64.00 (C), 24.86 (CH₂), 8.01 (CH₃). IR (neat): ν_{max} 3061m, 3021w, 2971s, 2939s, 2878s, 1668s, 1597m, 1575m, 1474s, 1440s, 1379s, 1290s, 1230s, 1183m, 1145m, 1108m, 1069w, 1026m, 1014m, 990m, 862m, 829m, 768m, 750s, 730m, 703s, 692s, 654m cm⁻¹. MS: *m/z* (% relative intensity): 285 (M⁺+1, 100), 181 (10), 179 (25), 178 (14), 137 (6), 106 (7). HRMS (ESI-TOF): Calcd for C₁₈H₂₀OSNa: 307.1133. Found: 307.1135.

3.12 Reaction of the anion **14a** with methyl iodide.

According to the general procedure C, *i*-PrMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5012 g, 2.0 mmol) were employed. The solution of the anion **14a** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Methyl iodide (0.50 mL, 8.0 mmol) was then added at the same temperature and the resulting solution was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19a** (0.1419 g, 30% yield) and a white solid of **7a** (0.0962 g, 26% yield).

19a

19a: ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.0 Hz, 2H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 2.37 (s, 3H, ArCH₃), 2.03 (sept, *J* = 6.7 Hz, 2H, 2xCH(CH₃)₂), 1.11 (d, *J* = 6.7 Hz, 6H, 2xCH₃), 1.05 (d, *J* = 6.7 Hz, 6H, 2xCH₃), 0.92 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 138.68 (C), 138.29 (CH), 130.86 (C), 129.67 (CH), 62.31 (C), 36.17 (CH), 21.78 (CH₃), 19.26 (CH₃), 19.19 (CH₃), 19.03 (CH₃). IR (neat): ν_{max} 3072w, 3019m, 2976s, 2877s, 1599w, 1491s, 1466s, 1381s, 1306m, 1180w, 1148w, 1121m, 1096m, 1069m, 1044m, 1019m, 998w, 811s, 758w, 710w cm⁻¹. MS: *m/z* (% relative intensity): 236 (M⁺, 20), 193 (7), 124 (100), 123 (11), 113 (12), 112(25), 97 (45), 91 (76), 69 (12), 57 (15). **19a** was characterised as its corresponding sulfones **21l**.

21l

21l: ^1H NMR (300 MHz, CDCl_3): δ 7.73 (d, J = 8.3 Hz, 2H, ArH), 7.31 (d, J = 8.2 Hz, 2H, ArH), 2.44 (s, 3H, ArCH₃), 2.29 (sept, J = 7.0 Hz, 2H, 2xCH(CH₃)₂), 1.34 (s, 3H, CH₃), 1.10 (d, J = 7.0 Hz, 6H, 2xCH₃), 1.08 (d, J = 7.0 Hz, 6H, 2xCH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 143.94 (C), 136.14 (C), 129.68 (CH), 129.33 (CH), 73.90 (C), 31.12 (CH), 21.46 (CH₃), 19.80 (CH₃), 18.99 (CH₃), 15.45 (CH₃). IR (KBr-disc.): ν_{max} 3013m, 2998m, 2968s, 2882m, 1596m, 1492m, 1478m, 1450m, 1399m, 1389m, 1282s, 1183m, 1150s, 1117s, 1081s, 1060s, 1016w, 824w, 733m, 666s, 637s cm^{-1} . MS: m/z (% relative intensity): 268 (M^+ , 0.5), 211 (38), 157 (32), 139 (22), 112 (12), 97 (22), 91 (32), 77 (8), 65 (17), 57 (100), 55 (18). Anal. Calcd for C₁₅H₂₄O₂S: C, 67.12; H, 9.01. Found: C, 67.04; H, 8.79.

3.13 Reaction of anion **14b** with methyl iodide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5053 g, 2.0 mmol) were employed. The solution of the anion **14b** was stirred at -78°C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78°C for 1 h. Methyl iodide (0.5 mL, 8.0 mmol) was then added at the same temperature and the resulting solution was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19b** (0.3269 g, 62% yield) and a white solid of **7b** (0.0060 g, 2% yield).

19b

19b: ^1H NMR (300 MHz, CDCl_3): δ 7.38 (d, J = 8.0 Hz, 2H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 2.34 (s, 3H, ArCH₃), 2.02-1.87 (m, 2H, 2xCH(CH₃)₂), 1.51-1.37 (m, 4H, 2xCH₂(*i*-Pr)), 1.21 (s, 3H, CH₃), 0.96 (d, J = 6.7 Hz, 6H, CH(CH₃)₂), 0.94 (d, J = 6.7 Hz, 6H, CH(CH₃)₂). ^{13}C NMR (75 MHz, CDCl_3): δ 138.45 (C), 137.53 (CH), 129.14 (CH), 128.86 (C), 54.37 (C), 49.71 (CH₂), 26.81 (CH₃), 25.29 (CH₃), 25.28 (CH₃), 24.54 (CH), 21.20 (CH₃). IR (neat): ν_{max} 3073w, 3021m, 2956s, 2925s, 2869s, 1598w, 1491s, 1466s, 1385m, 1374m, 1366m, 1265w, 1179w, 1141m, 1104w, 1019m, 812s, 711w cm^{-1} . MS: m/z (% relative intensity): 264 (M^+ , 5), 246 (5), 215 (6), 124 (100), 91 (32), 83 (4), 79 (4), 77 (2), 57 (6), 55 (4). **19b** was characterised as its corresponding sulfone **21m**.

21m

21m: ^1H NMR (300 MHz, CDCl_3): δ 7.74 (d, J = 8.2 Hz, 2H, ArH), 7.35 (d, J = 8.2 Hz, 2H, ArH), 2.46 (s, 3H, ArCH₃), 1.94 (sept, J = 6.5 Hz, 2H, 2xCH(CH₃)₂), 1.63 (d, J = 5.3 Hz, 4H, 2xCH₂(*i*-Pr)), 1.40 (s, 3H, CH₃), 0.98 (d, J = 6.6 Hz, 6H, CH(CH₃)₂), 0.94 (d, J = 6.6 Hz, 6H, CH(CH₃)₂). ^{13}C NMR (75 MHz, CDCl_3): δ 144.23 (C), 133.42 (C), 130.49 (CH),

129.26 (CH), 67.46 (C), 42.97 (CH₂), 25.26 (CH₃), 25.05 (CH₃), 24.11 (CH), 21.57 (CH₃), 19.27 (CH₃). IR (neat): $\nu_{\max}$ 2960s, 2871m, 1598m, 1494w, 1467m, 1387m, 1368m, 1309s, 1297s, 1286s, 1155m, 1131s, 1085s, 1038w, 1019w, 817m, 734w, 713s, 685s cm⁻¹. MS: m/z (% relative intensity): 297 (M⁺+1, 14), 296 (M⁺, 5), 281 (32), 267 (36), 252 (16), 203 (20), 178 (100), 164 (90), 149 (29), 129 (20), 109 (15), 105 (38), 98 (17), 91 (34), 77 (31), 67 (14), 55 (15). Anal. Calcd for C₁₇H₂₈O₂S: C, 68.87; H, 9.52. Found: C, 68.56; H, 9.28.

3.14 Reaction of the anion **14b** with allyl bromide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5036 g, 2.0 mmol) were employed. The solution of the anion **14b** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Allyl bromide (0.7 mL, 8.3 mmol) was then added at the same temperature and the resulting solution was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19c** (0.3685 g, 64% yield) and a white solid of **7b** (0.0059 g, 2% yield).

19c: ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.12-6.00 (m, 1H, CH=CH₂), 5.17-5.03 (m, 2H, CH=CH₂), 2.38 (s, 3H, ArCH₃), 2.35 (ddd, J = 1.3, 1.3, 6.8 Hz, 2H, CH₂CH=CH₂), 2.09-1.98 (m, 2H, 2xCH(CH₃)₂), 1.50 (d, J = 5.2 Hz, 4H, 2xCH₂(*i*-Pr)), 1.02 (d, J = 6.9 Hz, 6H, 2xCH₃), 1.01 (d, J = 6.9 Hz, 6H, 2xCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 139.10 (C), 138.03 (CH), 135.82 (CH), 129.84 (CH), 129.22 (C), 117.99 (CH₂), 57.92 (C), 47.04 (CH₂), 43.57 (CH₂), 25.94 (CH₃), 25.88 (CH₃), 24.94 (CH), 21.83 (CH₃). IR (neat): $\nu_{\max}$ 3075w, 3020w, 2956s, 2927s, 2869s, 1905w, 1638w, 1492s, 1468s, 1386m, 1366m, 1180w, 1166w, 1135w, 1105w, 1019m, 914w, 812s, 711w cm⁻¹. MS: m/z (% relative intensity): 290 (M⁺, 8), 167 (100), 157 (100), 151 (12), 148 (8), 124 (6), 111 (16), 110 (32), 95 (8), 91 (25), 81 (9), 79 (6), 70 (27), 67 (16), 57 (4), 56 (13). HRMS (ED): Calcd for C₁₉H₃₀S: 290.2068. Found: 290.2020.

3.15 Reaction of the anion **14b** with crotyl bromide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5037 g, 2.0 mmol) were employed. The solution of the anion **14b** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Crotyl bromide (*E/Z* = 80:20, 0.5 mL, 8.0 mmol) was then added at the same temperature and the resulting solution was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19d** (*E/Z* = 80/20) (0.4790 g, 79% yield) and a white solid of **7b** (0.0108 g, 3% yield).

19d: ¹H NMR (300 MHz, CDCl₃): δ 7.39 (d, J = 8.0 Hz, 2H, ArH of *cis*- and *trans*-isomers), 7.10 (d, J = 8.0 Hz, 2H, ArH of *cis*- and *trans*-isomers), 5.75-5.36 (m, 2H, CH=CH)

of *cis*- and *trans*-isomers), 2.34 (s, 3H, ArCH₃ of *cis*- and *trans*-isomers), 2.28-2.20 (m, 2H, CH₂CH=CH₂ of *cis*- and *trans*-isomers), 2.06-1.90 (m, 2H, 2xCH(CH₃)₂ of *cis*- and *trans*-isomers), [1.69 (dd, *J* = 1.3 Hz, 6.4 Hz,) and 1.55 (dd, *J* = 1.6 Hz, 6.6 Hz), 3H, CH=CHCH₃ of *cis*- and *trans*-isomer)], 1.46 (d, *J* = 6.9 Hz, 2H, CH₂(*i*-Pr) of *cis*- and *trans*-isomers), 1.44 (d, *J* = 6.8 Hz, 2H, CH₂(*i*-Pr) of *cis*- and *trans*-isomers), 0.96 (d, *J* = 6.7 Hz, 6H, 2xCH₃ of *cis*- and *trans*-isomers), 0.95 (d, *J* = 6.6 Hz, 6H, 2xCH₃ of *cis*- and *trans*-isomers). ¹³C NMR (75 MHz, CDCl₃): δ 138.39 (C), 138.32 (C), 137.42 (CH), 137.36 (CH), 129.14 (CH), 128.74 (C), 128.58 (C), 127.89 (CH), 127.35 (CH), 126.85 (CH), 125.18 (CH), 57.74 (C), 46.42 (CH₂), 46.14 (CH₂), 41.72 (CH₂), 35.39 (CH₂), 25.33 (CH₃), 25.28 (CH₃), 25.19 (CH₃), 24.32 (CH), 24.26 (CH), 21.19 (CH₃), 18.16 (CH₃), 13.36 (CH₃). IR (neat): ν_{max} 3073w, 3023m, 2955s, 2927s, 2869s, 1598w, 1492s, 1468s, 1456s, 1356m, 1366m, 1300w, 1262w, 1180w, 1166m, 1134m, 1104w, 1039w, 1020m, 969m, 812s cm⁻¹. MS: *m/z* (% relative intensity): 304 (M⁺, 12), 249 (10), 193 (12), 180 (88), 171 (66), 165 (17), 151 (27), 137 (28), 125 (49), 124 (87), 123 (57), 109 (25), 95 (39), 91 (32), 81 (41), 77 (19), 70 (100), 67 (31), 56 (44). HRMS (EI): Calcd for C₂₀H₃₂S: 304.2225. Found: 304.2224.

3.16 Reaction of the anion **14b** with benzoyl cyanide.

According to the general procedure C, *i*-BuMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5040 g, 2.0 mmol) were employed. The solution of the anion **14b** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Benzoyl cyanide (1.0 mL, 8.4 mmol) was then added at the same temperature and the resulting solution was slowly warmed up to room temperature overnight. After quenching with 1 M HCl (5 mL) and addition of 10% NH₄OH (25 mL), the mixture was poured into water (30 mL) and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the residue was filtered to remove benzoic acid and washed with hexanes (50 mL). After removal of solvent under reduced pressure, the crude product was purified by radial chromatography (SiO₂, 0-3% EtOAc in hexanes) to give a white solid of **7b** (0.0074 g, 2% yield) and a pale yellow liquid of **19e** (0.3568 g, 50% yield).

19e

19e: ¹H NMR (300 MHz, CDCl₃): δ 8.21-8.15 (m, 2H, ArH), 7.51-7.38 (m, 3H, ArH), 7.21 (d, *J* = 8.1 Hz, 2H, ArH), 7.05 (d, *J* = 7.9 Hz, 2H, ArH), 2.30 (s, 3H, ArCH₃), 2.03-1.87 (m, 2H, 2xCH(CH₃)₂), 1.95 (d, *J* = 2.0 Hz, 4H, 2xCH₂(*i*-Pr)), 1.01 (d, *J* = 6.2 Hz, 6H, CH(CH₃)₂), 0.78 (d, *J* = 6.3 Hz, 6H, CH(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃): δ 199.54 (C=O), 139.37 (C), 138.79 (C), 136.37 (CH), 131.03 (CH), 129.90 (CH), 129.50 (CH), 127.92 (CH), 127.29 (C), 64.09 (C), 41.93 (CH₂), 25.12 (CH), 24.89 (CH₃), 23.80 (CH₃), 21.26 (CH₃). IR (nujol): ν_{max} 1668s, 1594w, 1576w, 1257m, 1239s, 1179w, 1156w, 1077w, 1018s, 816s, 779w, 724w, 701m cm⁻¹. MS: *m/z* (% relative intensity): 354 (M⁺, 35), 249 (61), 231 (58), 193 (31), 137 (100), 105 (18), 91 (15), 77 (23), 69 (9). HRMS (ESI-TOF): Calcd for C₂₃H₃₀OSNa: 377.1915. Found: 377.1914.

3.17 Reaction of the anion **14b** with benzaldehyde.

According to the general procedure D, *i*-BuMgCl (4.3 mL, 2.0 M in THF, 8.6 mmol) and **2** (0.7611 g, 3.0 mmol) were employed. The solution of the anion **14b** was stirred at -78 °C

for 1 h and benzaldehyde (0.20 mL, 2.0 mmol) was added at -78°C . The mixture was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by radial chromatography (SiO_2 , 0-2% EtOAc in hexanes) to give a pale yellow liquid of **19f** (0.3038 g, 45% yield based on benzaldehyde).

19f

19f: ^1H NMR (300 MHz, CDCl_3): δ 7.46 (d, $J = 8.1$ Hz, 2H, ArH), 7.40-7.21 (m, 5H, ArH), 7.14 (d, $J = 8.0$ Hz, 2H, ArH), 4.45 (s, 1H, CHOH), 2.46-2.29 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.36 (s, 3H, ArCH₃), 2.12-1.98 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.55 (dd, $J = 4.6, 14.9$ Hz) and 1.45 (dd, $J = 6.1, 14.9$ Hz), 2H, each $\text{CH}_A\text{H}_B(i\text{-Pr})$, 1.28 (dd, $J = 3.5, 14.6$ Hz) and 1.19 (dd, $J = 6.6, 14.6$ Hz), 2H, each $\text{CH}_C\text{H}_D(i\text{-Pr})$, 1.05 (d, $J = 6.6$ Hz, 3H, CHCH₃), 1.00 (d, $J = 6.6$ Hz, 3H, CHCH₃), 0.88 (d, $J = 6.8$ Hz, 3H, CHCH₃), 0.85 (d, $J = 6.6$ Hz, 3H, CHCH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 139.35 (C), 139.17 (C), 137.15 (CH), 129.58 (CH), 128.93 (CH), 127.57 (two peaks merged, 2xCH), 126.48 (C), 78.36 (CH), 65.28 (C), 44.70 (CH₂), 43.08 (CH₂), 26.01 (CH₃), 25.65 (CH₃), 25.58 (CH₃), 25.17 (CH₃), 24.69 (CH), 24.31 (CH), 21.28 (CH₃). IR (neat): ν_{max} 3565m, 3456s, 3062m, 3030s, 2956s, 2869s, 1705m, 1602m, 1493s, 1468s, 1455s, 1386s, 1366s, 1326s, 1303m, 1252m, 1238m, 1185s, 1131s, 1054s, 1019s, 941m, 919m, 879w, 838w, 812s, 750s, 702s cm^{-1} . MS: m/z (% relative intensity): 356 (M^+ , 1), 249 (100), 193 (56), 137 (85), 124 (13), 123 (9), 117 (19), 115 (13), 105 (28), 97 (7), 91 (55), 81 (10), 79 (21), 77 (30), 65 (15), 57 (9), 55 (12). HRMS (ESI-TOF): Calcd for $\text{C}_{23}\text{H}_{32}\text{OSNa}$: 379.2072. Found: 379.2063.

3.18 Reaction of the anion **14b** with *p*-tolualdehyde.

According to the general procedure D, *i*-BuMgCl (4.3 mL, 2.0 M in THF, 8.6 mmol) and **2** (0.7590 g, 3.0 mmol) were employed. The solution of the anion **14b** was stirred at -78°C for 1 h and *p*-tolualdehyde (0.26 mL, 2.2 mmol) was added at -78°C . The reaction mixture was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by radial chromatography (SiO_2 , 0-2% EtOAc in hexanes) to give a pale yellow liquid of **19g** (0.3531 g, 43% yield based on *p*-tolualdehyde).

19g

19g: ^1H NMR (300 MHz, CDCl_3): δ 7.37 (d, $J = 8.0$ Hz, 2H, ArH), 7.16 (d, $J = 8.1$ Hz, 2H, ArH), 7.03 (d, $J = 8.3$ Hz, 2H, ArH), 7.00 (d, $J = 8.3$ Hz, 2H, ArH), 4.33 (s, 1H, CHOH), 3.70 (br.s, 1H, OH), 2.36-2.14 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.26 (s, 3H, ArCH₃), 2.23 (s, 3H, ArCH₃), 2.06-1.88 (m, 1H, $\text{CH}(\text{CH}_3)_2$), [1.46 (dd, $J = 4.8, 14.9$ Hz) and 1.36 (dd, $J = 6.1, 14.9$ Hz), 2H each $\text{CH}_A\text{H}_B(i\text{-Pr})$], [1.18 (dd, $J = 3.6, 14.6$ Hz) and 1.11 (dd, $J = 6.2, 14.6$ Hz), 2H each, $\text{CH}_C\text{H}_D(i\text{-Pr})$], 0.96 (d, $J = 6.5$ Hz, 3H, CHCH₃), 0.91 (d, $J = 6.6$ Hz, 3H, CHCH₃), 0.79 (d, $J = 6.3$ Hz, 3H, CHCH₃), 0.77 (d, $J = 6.1$ Hz, 3H, CHCH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 138.98 (C), 137.10 (CH), 137.05 (C), 136.27 (C), 129.48 (CH), 128.75 (CH), 128.22 (CH), 126.60 (C), 78.14 (CH), 65.20 (C), 44.62 (CH₂), 43.08 (CH₂), 25.91 (CH₃), 25.55 (CH₃), 25.47 (CH₃),

25.07 (CH₃), 24.59 (CH), 24.21 (CH), 21.17 (CH₃), 21.06 (CH₃). IR (neat): $\nu_{\max}$ 3565w, 3460s, 3022s, 2956s, 2869w, 1614w, 1598w, 1515s, 1494s, 1471s, 1456s, 1386s, 1366s, 1321s, 1299m, 1252m, 1234m, 1190s, 1179s, 1131s, 1056s, 1020s, 942m, 919m, 880w, 811s, 772m, 721w, 710w cm⁻¹. MS: m/z (% relative intensity): 370 (M⁺, 0.01), 353 (6), 249 (57), 229 (55), 193 (49), 173 (15), 137 (100), 131 (16), 123 (6), 119 (11), 105 (21), 91 (23), 77 (8), 69 (10), 55 (7). HRMS (ESI-TOF): Calcd for C₂₄H₃₄OSNa: 393.2228. Found: 393.2231.

3.19 Reaction of the anion **14c** with methyl iodide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5004 g, 2.0 mmol) were employed. The solution of the anion **14c** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Methyl iodide (0.5 mL, 8.0 mmol) was then added at the same temperature and the resulting mixture was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19h** (0.1563 g, 38% yield) and a colorless liquid of **7c** (0.0522 g, 16% yield).

19h

19h: ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 7.8 Hz, 2H, ArH), 2.39 (s, 3H, ArCH₃), 1.49 (q, J = 7.4 Hz, 2H, CH₂CH₃), 1.48 (q, J = 7.4 Hz, 2H, CH₂CH₃), 1.16 (s, 3H, CH₃), 1.01 (t, J = 7.4 Hz, 6H, 2xCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 139.15 (C), 138.05 (CH), 129.83 (CH), 129.35 (C), 54.11 (C), 32.20 (CH₂), 25.91 (CH₃), 21.83 (CH₃), 9.37 (CH₃). IR (neat): $\nu_{\max}$ 3072w, 3020w, 2969s, 2924s, 2878w, 1598w, 1492s, 1457s, 1329m, 1330w, 1300w, 1179w, 1154m, 1131m, 1104w, 1019w, 811w, 710w cm⁻¹. MS: m/z (% relative intensity): 208 (M⁺, 100), 194 (13), 124 (6), 91 (20). **19h** was characterized as its corresponding sulfone **21n**.

21n

21n: ¹H NMR (300 MHz, CDCl₃): δ 7.75 (d, J = 8.2 Hz, 2H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH), 2.45 (s, 3H, ArCH₃), 1.96-1.78 (m, 2H, CH₂CH₃), 1.75-1.55 (m, 2H, CH₂CH₃), 1.20 (s, 3H, CH₃), 1.00 (t, J = 7.5 Hz, 6H, 2xCH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 144.22 (C), 133.37 (C), 130.23 (CH), 129.25 (CH), 65.91 (C), 25.52 (CH₂), 21.51 (CH₃), 19.33 (CH₃), 8.41 (CH₃). IR (neat): $\nu_{\max}$ 2974s, 2943s, 2884m, 1598m, 1494w, 1463s, 1386m, 1309s, 1299s, 1284s, 1163s, 1128s, 1080s, 1041w, 1018w, 817m, 801w, 740m, 711s, 678s cm⁻¹. MS: m/z (% relative intensity): 241 (M⁺+1, 3), 240 (M⁺, 1), 157 (100), 139 (40), 93 (17), 91 (34), 85 (40), 77 (8), 69 (13), 65 (19), 57 (37). Anal. Calcd for C₁₃H₂₀O₂S: C, 64.96; H, 8.39. Found: C, 64.75; H, 8.26.

3.20 Reaction of the anion **14c** with allyl bromide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5015 g, 2.0 mmol) were employed. The solution of the anion **14c** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Allyl bromide (0.7 mL, 8.3 mmol) was then added at the same temperature and the mixture was slowly warmed up to room temperature overnight. After usual work-up, the crude product was

purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19i** (0.1972 g, 64% yield) and a colorless liquid of **7c** (0.0562 g, 17% yield).

19i

19i: ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 7.1 Hz, 2H, Ar*H*), 7.15 (d, *J* = 7.8 Hz, 2H, Ar*H*), 6.12-6.00 (m, 1H, CH=CH₂), 5.17-5.09 (m, 2H, CH=CH₂), 2.39 (s, 3H, ArCH₃), 2.19 (ddd, *J* = 1.3, 1.3, 7.0 Hz, 2H, CH₂CH=CH₂), 1.43 (q, *J* = 7.3 Hz, 4H, 2xCH₂CH₃), 1.03 (t, *J* = 7.3 Hz, 6H, 2xCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 139.28 (C), 137.95 (CH), 135.09 (CH), 129.94 (CH), 128.93 (C), 117.85 (CH₂), 57.23 (C), 40.79 (CH₂), 29.00 (CH₂), 21.84 (CH₃), 8.75 (CH₃). IR (neat): ν_{max} 3074m, 3020w, 2969s, 2936s, 2878m, 1639m, 1599w, 1492s, 1452s, 1376m, 1318w, 1300w, 1286w, 1180w, 1105w, 1019m, 997m, 955w, 914s, 841w, 812s, 710w cm⁻¹. MS: *m/z* (% relative intensity): 234 (M⁺, 100), 215 (17), 124 (63), 123 (7), 111 (34), 91 (100), 81 (17), 79 (14), 69 (8). HRMS (EI): Calcd for C₁₅H₂₂S: 234.1442. Found: 234.1407.

3.21 Reaction of the anion **14c** with crotyl bromide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5077 g, 2.0 mmol) were employed. The solution of the anion **14c** was stirred at -78 °C for 1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at -78 °C for 1 h. Crotyl bromide (*E/Z* = 80/20, 0.5 mL, 8.0 mmol) was then added at the same temperature and the resulting mixture was slowly warmed up to room temperature overnight. After usual work-up, the crude product was purified by preparative thin-layer chromatography (SiO₂, hexanes) to give a colorless liquid of **19j** (0.2299 g, 46% yield) and a colorless liquid **7c** (0.1031 g, 31% yield).

19j

19j: ¹H NMR (300 MHz, CDCl₃): δ 7.47-7.33 (m, 2H, Ar*H* of *cis*- and *trans*-isomers), 7.15 (d, *J* = 7.8 Hz, 2H, Ar*H* of *cis*- and *trans*-isomers), 5.50-5.46 (m, 2H, CH=CH of *cis*- and *trans*-isomers), 2.38 (s, 3H, ArCH₃ of *cis*- and *trans*-isomers), 2.20-2.08 (m, 2H, CH₂CH=CH of *cis*- and *trans*-isomers), [1.75 (dd, *J* = 1.1, 6.1 Hz) and 1.65 (dd, *J* = 1.2, 6.4 Hz), 3H, CH=CHCH₃ of *cis*- and *trans*-isomer], 1.51-1.36 (m, 4H, 2xCH₂CH₃ of *cis*- and *trans*-isomers), 1.02 (t, *J* = 7.4 Hz, 3H, CH₂CH₃ of *cis*- and *trans*-isomers), 1.01 (t, *J* = 7.4 Hz, 3H, CH₂CH₃ of *cis*- and *trans*-isomers). ¹³C NMR (75 MHz, CDCl₃): δ 138.49 (C), 138.46 (C), 137.28 (CH), 137.25 (CH), 129.20 (CH), 128.41 (C), 128.30 (C), 127.64 (CH), 126.59 (CH), 125.93 (CH), 125.39 (CH), 56.95 (C), 56.92 (C), 38.70 (CH₂), 32.85 (CH₂), 28.32 (CH₂), 21.16 (CH₃), 18.11 (CH₃), 13.28 (CH₃), 8.21 (CH₃), 8.11 (CH₃). IR (neat): ν_{max} 3072w, 3021m, 2968s, 2936s, 2878m, 1651w, 1599w, 1492s, 1546s, 1403w, 1376m, 1332w, 1301w, 1180w, 1105w, 2091w, 1019m, 968m, 838w, 812s, 775w cm⁻¹. MS: *m/z* (% relative intensity): 248 (M⁺, 69), 193 (100), 151 (11), 126 (39), 125 (23), 124 (47), 109 (5), 96 (40), 92 (12), 83 (7), 69 (16), 67 (15) 56 (14). HRMS (EI): Calcd for C₁₆H₂₄S: 248.1599. Found: 248.1585.

3.22 Reaction of the anion **14c** with benzoyl cyanide.

According to the general procedure C, EtMgCl (4.0 mL, 2.0 M in THF, 8.0 mmol) and **2** (0.5031 g, 2.0 mmol) were employed. The solution of the anion **14c** was stirred at -78 °C for

1 h and treated with CuCN·2LiCl (4.0 mL, 0.5 M in THF, 2.0 mmol) at $-78\text{ }^{\circ}\text{C}$ for 1 h. Benzoyl cyanide (1.0 mL, 8.4 mmol) was then added at the same temperature and the mixture was slowly warmed up to room temperature overnight. After quenching with 1 M HCl (5 mL) and addition of 10% NH_4OH (25 mL), the mixture was poured into water (30 mL) and extracted with EtOAc (3x50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the residue was filtered to remove benzoic acid and washed with hexanes (50 mL). After removal of solvent under reduced pressure, the crude product was purified by radial chromatography (SiO_2 , 0-3% EtOAc in hexanes) to give a colorless liquid of **7c** (0.0811 g, 25% yield) and a pale yellow liquid of **19k** (0.2873 g, 48% yield).

19k

19k: ^1H NMR (300 MHz, CDCl_3): δ 8.26-8.19 (m, 2H, ArH), 7.34-7.47 (m, 1H, ArH), 7.46-7.38 (m, 2H, ArH), 7.20 (d, $J = 8.1$ Hz, 2H, ArH), 7.05 (d, $J = 8.1$ Hz, 2H, ArH), 2.30 (s, 3H, ArCH₃), 1.98-1.68 (m, 4H, 2xCH₂CH₃), 0.87 (t, $J = 7.4$ Hz, 6H, 2xCH₂CH₃). ^{13}C NMR (75 MHz, CDCl_3): δ 201.04 (C=O), 139.55 (C), 138.80 (C), 136.44 (CH), 131.27 (CH), 129.63 (CH), 129.29 (CH), 128.02 (CH), 126.81 (C), 63.92 (C), 24.76 (CH₂), 21.26 (CH₃), 8.03 (CH₃). IR (neat): ν_{max} 3064m, 3022m, 2971s, 2940s, 2878s, 1906w, 1668s, 1597s, 1575m, 1492s, 1455s, 1399m, 1379s, 1326w, 1290s, 1230s, 1182s, 1145s, 1107s, 1017s, 991s, 940m, 862s, 829s, 811s, 768s, 730m, 702s cm^{-1} . MS: m/z (% relative intensity): 299 ($\text{M}^+ + 1$, 36), 298 (M^+ , 14), 285 (76), 193 (81), 179 (91), 175 (41), 151 (52), 137 (100), 135 (26), 123 (45), 116 (14), 105 (34), 91 (16), 77 (45), 69 (30), 59 (16), 51 (17). HRMS (ESI-TOF): Calcd for $\text{C}_{19}\text{H}_{22}\text{OSNa}$: 321.1289. Found: 321.1291.

4. Preparation to sulfone derivatives 21a-n of compounds 4a-d, 5a-d, 18a-b, 18h, 19a-b, and 19h.

4.1 Preparation of 2,4-dimethyl-3-phenylsulfonylpentane (21a).

General procedure E: A solution of 30% H_2O_2 (2 mL, 35 mmol) was added dropwise to a stirred solution of **4a** (0.0748 g, 0.36 mmol) in glacial acetic acid (4 mL, 70 mmol) at $0\text{ }^{\circ}\text{C}$. The resulting solution was then stirred and slowly warmed up to room temperature overnight and neutralized with 10% NaOH. The mixture was poured into water (20 mL) and extracted with EtOAc (3x30 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the crude product was purified by radial chromatography (SiO_2 , 5% EtOAc in hexanes) to give a white solid of **21a** [0.0535 g, 62% yield, mp $88\text{--}89\text{ }^{\circ}\text{C}$ (hexanes)].

4.2 Preparation of 2,6-dimethyl-4-phenylsulfonylheptane (21b).

According to the general procedure E, H_2O_2 (4 mL, 70 mmol), **4b** (0.2362 g, 1.00 mmol) and glacial acetic acid (8 mL, 140 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO_2 , 5% EtOAc in hexanes) to give a colorless liquid of **21b** (0.1929 g, 72% yield).

4.3 Preparation of 3-phenylsulfonylpentane (21c).

According to the general procedure E, H₂O₂ (2 mL, 35 mmol), **4c** (0.0459 g, 0.26 mmol) and glacial acetic acid (4 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21c** [0.0351 g, 65% yield, mp 49-50 °C (hexanes)].

4.4 Preparation of (2,2,4,4-tetramethyl-3-phenylsulfonyl)pentane (21d).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **4d** (0.2900 g, 1.23 mmol) and glacial acetic acid (8 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21d** [0.2289 g, 70% yield, mp 137-138 °C (hexanes)].

4.5 Preparation of 2,3,4-trimethyl-3-phenylsulfonylpentane (21e).

According to the general procedure E, H₂O₂ (2 mL, 35 mmol), **18a** (0.0417 g, 0.19 mmol) and glacial acetic acid (4 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21e** [0.0339 g, 70% yield, mp 59-61 °C (hexanes)].

4.6 Preparation of 2,4,6-trimethyl-4-phenylsulfonylheptane (21f).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **18b** (0.1080 g, 0.43 mmol) and glacial acetic acid (8 mL, 140 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a colorless liquid of **21f** (0.1151 g, 94% yield).

4.7 Preparation of 3-methyl-3-phenylsulfonylpentane (21g).

According to the general procedure E, H₂O₂ (2 mL, 35 mmol), **18h** (0.0413 g, 0.21 mmol) and glacial acetic acid (4 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a colorless liquid of **21g** (0.0378 g, 79% yield).

4.8 Preparation of 2,4-dimethyl-3-(*p*-tolylsulfonyl)pentane (21h).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **5a** (0.1616 g, 0.73 mmol) and glacial acetic acid (8 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21h** [0.1584 g, 85% yield, mp 82-83 °C (hexanes)].

4.9 Preparation of 2,6-dimethyl-4-(*p*-tolylsulfonyl)heptane (21i).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **5b** (0.2258 g, 0.90 mmol) and glacial acetic acid (8 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21i** [0.2354 g, 92% yield, mp 75-76 °C (hexanes)].

4.10 Preparation of 3-(*p*-tolylsulfonyl)pentane (21j).

According to the general procedure E, H₂O₂ (2 mL, 35 mmol), **5c** (0.0606 g, 0.31 mmol) and glacial acetic acid (4 mL, 140 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21j** [0.0594 g, 84% yield, mp 65-66 °C (hexanes)].

4.11 Preparation of 2,2,4,4-tetramethyl-3-(*p*-tolylsulfonyl)pentane (**21k**).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **5d** (0.1809 g, 0.72 mmol) and glacial acetic acid (8 mL, 140 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21k** [0.1457 g, 70% yield, mp 144-145 °C (hexanes)].

4.12 Preparation of 2,3,4-trimethyl-3-(*p*-tolylsulfonyl)pentane (**21l**).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **19a** (0.1339 g, 0.56 mmol) and glacial acetic acid (8 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a white solid of **21l** [0.1204 g, 80% yield, mp 60-62 °C (hexanes)].

4.13 Preparation of 2,4,6-trimethyl-4-(*p*-tolylsulfonyl)heptane (**21m**).

According to the general procedure E, H₂O₂ (4 mL, 70 mmol), **19b** (0.1235 g, 0.47 mmol) and glacial acetic acid (8 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a colorless liquid of **21m** (0.1360 g, 98% yield).

4.14 Preparation of 3-methyl-3-(*p*-tolylsulfonyl)pentane (**21n**).

According to the general procedure E, H₂O₂ (2 mL, 35 mmol), **19h** (0.0788 g, 0.38 mmol) and glacial acetic acid (4 mL, 70 mmol) were employed. The crude product obtained was purified by radial chromatography (SiO₂, 5% EtOAc in hexanes) to give a colorless liquid of **21n** (0.0808 g, 89% yield).