Azadiene Diels-Alder Cycloaddition of Fulvenes: A Facile Approach to the [1]Pyrindines System.

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SUPPORTING INFORMATION:

Contents: Experimental procedures and characterization data for the new compounds **3a**-**4i**, **5** and X-ray cif file of **4d** and **5**.

Experimental Section:

General Procedure. All solvents were reagent grade. All chemicals were purchased from Aldrich Chemical Co. Reactions were normally carried out under argon atmosphere in flame-dried glassware. Merck silica gel 60 (partial size 0.04-0.063 mm) was employed for flash chromatography. Focused microwave irradiation was carried out at atmospheric pressure with a Synthewave S402 Prolabo microwave reactor (300 W, monomode system, 10 mL reactors). The apparatus has a quartz reactor, visual control, PC controlled 300W irradiation, infrared temperature measurement with continuous feedback control. HPLC was equipped with the ultraviolet and refractive index detectors. The sample was analyzed and/or separated on a μ-Porasil column (25 cm x 1.0 cm) by elution with gradient of ethyl acetate and hexane. The flow rate of the indicated elution solvent is maintained at 5 mL/min, and the retention time of a compound is recorded. Melting points are uncorrected. ^{1}H NMR and COSY spectra were obtained in $CDCl_3$ unless otherwise noted at 400 or 500 MHz. ^{13}C NMR spectra, HMBC, HMQC and DEPT experiments were obtained at 100 or 125 Hz MHz.

Representative Procedure for the reaction:

Method A, for the synthesis of adduct 3a: A solution of dimethylfulvene (132 mg, 1.24 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (268 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was stirred at 25 $^{\circ}$C for 65 h. The solution was concentrated *in vacuo* to give a brown oil. The crude product was purified by flash column chromatography (silica gel) with 15% EtOAc-hexane to give adduct **3a** (261mg, 70% yield; R_f = 0.25 in 15% EtOAc-hexane) as a yellow oil.

Method B, for the synthesis of adduct 3a: A mixture of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in

chlorobenzene (3mL) were placed in a 10 mL quartz vial and subjected to programmed microwave irradiation at 30W for 120 min. After a period of 2-3 min, the temperature reached a plateau of 125 °C where it remained throughout the reaction. After irradiation for 29 min and cooling, the solution was concentrated and the residue was subjected to flash column chromatography (15% EtOAc-hexane, R_f = 0.25) to give adduct **3a** as a colorless liquid (179 g, 96% yield) as a yellow oil.

Method C, for the synthesis of adduct 3a: A mixture of dimethylfulvene (66mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in toluene (5 mL) were placed in a 25 mL TinyClave® and heated in a 110 °C oil bath for 3.5 h. After cooling, the solution was concentrated and the residue was subjected to flash column chromatography (15% EtOAc-hexane, R_f = 0.25) to give adduct **3a** as a yellow liquid (155 mg, 83% yield).

Method D, for the synthesis of adduct 3a: A solution of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in ethylene dichloride (5 mL) was heated to reflux for 5.5 h. The solution was concentrated *in vacuo* to give a brown oil. The crude product was purified by flash column chromatography (silica gel) with 15% EtOAc-hexane to give adduct **3a** (142 mg, 76% yield) as a yellow oil.

Method E, for the synthesis of adduct 3a: A solution of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in benzene (5 mL) was heated to reflux for 7 h. The solution was concentrated *in vacuo* to give a brown oil. The crude product was purified by flash column chromatography (silica gel) with 15% EtOAc-hexane to give adduct **3a** (120 mg, 64% yield) as a yellow oil..

Method F, for the synthesis of adduct 3a: A solution of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134mg, 0.5 mmol) in toluene (5 mL) was heated to reflux for 3.5 h. The solution was concentrated *in vacuo* to give a brown oil. The crude product was purified by flash column chromatography (silica gel) with 15% EtOAc-hexane to give adduct **3a** (125 mg, 67% yield) as a yellow oil.

Method G, for the synthesis of adduct 3a: A mixture of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in DMF (3 mL) were placed in a 10 mL quartz vial and subjected to programmed microwave irradiation at 30W for 120 min. After a period of 2-3 min, the temperature reached a plateau of 110 °C where it remained throughout the reaction. After irradiation for 30 min, TLC indicated that most of the dimethylfulvene was consumed and that product **3a**

and many other products had formed. The solution was concentrated and the residue was subjected to flash column chromatography to give adduct **3a** as a yellow liquid (54 mg, 29% yield).

Method H, for the synthesis of adduct 3a: A mixture of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in toluene (3 mL) were placed in a 10 mL quartz vial and subjected to programmed microwave irradiation at 30W for 120 min. After a period of 2-3 min, the temperature reached a plateau of 100 °C where it remained throughout the reaction. After irradiation for 50 min and cooling, the solution was concentrated and the residue was subjected to flash column chromatography to give adduct **3a** (127 mg, 68% yield) as a yellow oil..

Method I, for the synthesis of adduct 3a: A mixture of dimethylfulvene (66 mg, 0.62 mmol) and ethyl (*E*)-4-[(phenylsulfonyl)imino]-2-butenoate (134 mg, 0.5 mmol) in 1,4-dioxane (3 mL) were placed in a 10 mL quartz vial and subjected to programmed microwave irradiation at 30W for 120 min. After a period of 2-3 min, the temperature reached a plateau of 90 °C where it remained throughout the reaction. After irradiation for 50 min and cooling, the solution was concentrated and the residue was subjected to flash column chromatography to give adduct **3a** (121 mg, 65% yield) as a yellow oil..

Spectroscopic data for **3a**: IR (neat): 3067, 2980, 2851, 1732, 1358, 1343, 1170, 725, 575 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 2 H), 7.50-7.39 (m, 3 H), 6.85 (d, J = 8.3 Hz, 1 H), 6.19 (dd, J = 5.7, 2.3 Hz, 1 H), 5.90 (d, J = 5.7 Hz, 1 H), 4.88 (dd, J = 8.0, 6.1 Hz, 1 H), 4.57 (d, J = 7.3 Hz, 1 H), 3.85-3.74 (m, 2 H), 3.15 (dd, J = 7.6, 6.3 Hz, 1 H), 2.86 (dd, J = 7.8, 7.8 Hz, 1 H), 1.61 (s, 3 H), 1.60 (s, 3 H), 0.99 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 171.48 (C), 138.51 (C), 136.56 (C), 134.89 (CH), 132.98 (CH), 131.03 (CH), 129.18 (two CH), 127.11 (two CH), 126.61 (CH), 126.05 (C), 102.81 (CH), 60.39 (CH_2), 59.84 (CH), 40.04 (CH), 39.99 (CH), 21.58 (CH_3), 20.63 (CH_3), 13.99 (CH_3); MS (m/z, relative intensity): 373 (M^+, 20), 300 (32), 233 (34), 157 (82), 143 (100), 106 (91), 77 (89); exact mass calculate for $C_{20}H_{23}NO_4S$ (M^+): 373.1348; found 373.1343.

Spectroscopic data for **4a** (yellow oil, R_f = 0.44 in 10% EtOAc-hexane): IR (neat): 3026, 2923, 2854, 1355, 1167, 1093, 755, 691, 564, 547 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.1Hz, 2 H), 7.07-7.04 (m, 3 H), 7.03 (d, J = 8.2 Hz, 1 H), 6.95-6.93 (m, 2 H), 5.88 (d, J = 5.8 Hz, 1 H), 5.72 (dd, J = 5.8, 2.7 Hz, 1 H), 5.22 (dd, J = 8.2, 6.2 Hz, 1 H), 4.65 (d, J = 7.2 Hz, 1 H), 3.38 (dd, J = 6.8, 6.8 Hz, 1 H), 3.03 (dd, J = 7.4, 7.4 Hz, 1 H), 2.44 (s, 3 H), 1.75 (s, 3 H), 1.52 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 143.89 (C), 139.71 (C), 138.03 (C), 135.65 (CH), 135.03 (C), 131.77 (CH), 129.82 (two CH),

129.79 (two CH), 127.32 (two CH), 126.59 (two CH), 126.19 (CH), 125.37 (CH), 124.63 (C), 109.38 (CH), 60.91 (CH), 43.27 (CH), 39.25 (CH), 21.73 (CH_3), 21.54 (CH_3), 20.18 (CH_3); MS (m/z, relative intensity): 391 (M^+, 15), 312 (10), 286 (24), 105 (100), 91 (57); exact mass calculate for $C_{24}H_{25}NO_2S$ (M^+): 391.1606; found 391.1601.

Spectroscopic data for **3b** (yellow oil, R_f = 0.26 in 15% EtOAc-hexane): IR (neat): 3067, 2966, 2873, 1727, 1360, 1343, 1171, 725, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.83 (d, J = 7.5 Hz, 2 H), 7.58-7.49 (m, 3 H), 6.95 (d, J = 8.3 Hz, 1 H), 6.28 (dd, J = 5.9, 2.6 Hz, 1 H), 6.02 (d, J = 5.2 Hz, 1 H), 4.97 (dd, J = 8.2, 6.1 Hz, 1 H), 4.66 (d, J = 7.4 Hz, 1 H), 3.91-3.86 (m, 2 H), 3.20 (dd, J = 7.1, 6.6 Hz, 1 H), 2.94 (t, J = 7.6 Hz, 1 H), 2.08 (q, J = 7.5 Hz, 4 H), 1.09 (t, J = 7.1 Hz, 3 H), 1.00 (t, J = 7.5 Hz, 3 H), 0.93 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 171.01 (C), 138.10 (C), 137.17 (C), 135.41 (C), 135.32 (CH), 132.84 (CH), 130.49 (CH), 129.00 (two CH), 126.83 (two CH), 126.56 (CH), 102.26 (CH), 60.10 (CH_2), 59.56 (CH), 40.27 (CH), 39.24 (CH), 25.60 (CH_2), 23.95 (CH_2), 13.73 (CH_3), 13.31 (CH_3), 12.31 (CH_3); MS (m/z, relative intensity): 401 (M^+, 8), 328 (36), 260 (49), 185 (53), 105 (66), 77 (100), 51 (54); exact mass calculate for $C_{22}H_{27}NO_4S$ (M^+): 401.1661; found 401.1655.

Spectroscopic data for **4b** (yellow oil, R_f = 0.50 in 10% EtOAc-hexane)**:** IR (neat): 3027, 2965, 2873, 1350, 1166, 1094, 755, 707, 680, 547 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.2 Hz, 2 H), 7.09-6.98 (m, 6 H), 5.92 (dd, J = 5.8, 1.3 Hz, 1 H), 5.76 (dd, J = 5.8, 2.7 Hz, 1 H), 5.22 (dd, J = 8.2, 6.3 Hz, 1 H), 4.65 (d, J = 7.2 Hz, 1 H), 3.41 (dd, J = 6.8, 6.8 Hz, 1 H), 3.03 (dd, J = 7.3, 7.3 Hz, 1 H), 2.44 (s, 3 H), 2.28-2.15 (m, 1 H), 2.13-2.05 (m, 1 H), 2.02-1.92 (m, 1 H), 1.90-1.80 (m, 1 H), 1.02 (t, J = 7.5 Hz, 3 H), 0.76 (t, J = 7.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$): 143.82 (C), 139.58 (C), 136.94 (C), 136.11 (C), 135.93 (CH), 134.97 (C), 131.65 (CH), 130.09 (two CH), 129.74 (two CH), 127.21 (two CH), 126.55 (two CH), 126.06 (CH), 125.02 (CH), 109.21 (CH), 60.65 (CH), 42.33 (CH), 39.37 (CH), 25.60 (CH_2), 23.84 (CH_2), 21.44 (CH_3), 12.98 (CH_3), 12.93 (CH_3); MS (m/z, relative intensity): 419 (M^+, 8), 340 (7), 286 (10), 134 (100), 91 (38); exact mass calculate for $C_{26}H_{29}NO_2S$ (M^+): 419.1919; found 419.1926.

Spectroscopic data for **3c** (yellow oil, R_f = 0.25 in 15% EtOAc-hexane)**:** IR (neat): 3068, 2957, 2870, 1726, 1360, 1343, 1170, 725, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.83 (d, J = 7.5 Hz, 2 H), 7.82-7.45 (m, 1 H), 7.50 (d, J = 7.7 Hz, 2 H), 6.93 (d, J = 8.3 Hz, 1 H), 6.27 (dd, J = 5.9, 2.6 Hz, 1H), 6.00(d, J = 5.8 Hz, 1 H), 4.97 (dd, J = 8.0, 6.2 Hz, 1 H), 4.66 (d, J = 7.3 Hz, 1 H), 3.90-3.84 (m, 2 H), 3.19 (dd, J = 6.9, 6.9 Hz, 1 H), 2.95 (dd, J = 7.6, 7.6 Hz,

1 H), 2.01-1.95 (m, 4 H), 1.53-1.44 (m, 1 H), 1.40-1.24 (m, 1 H), 1.08 (t, J = 7.1 Hz, 3 H), 0.86 (t, J = 7.3 Hz, 3 H), 0.85 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$): 171.26 (C), 138.56 (C), 136.76 (C), 135.36 (CH), 134.74 (C), 132.96 (CH), 130.96 (CH), 129.16 (two CH), 127.09 (two CH), 126.76 (CH), 102.66 (CH), 60.39 (CH_2), 59.81 (CH), 40.60 (CH), 39.88 (CH), 35.58 (CH_2), 33.89 (CH_2), 22.18 (CH_2), 21.19 (CH_2), 14.32 (CH_3), 14.16 (CH_3), 13.91 (CH_3); MS (m/z, relative intensity): 429 (M^+, 8), 370 (22), 356 (25), 288 (39), 214 (40), 119 (58), 77 (100), 51 (56); exact mass calculate for $C_{24}H_{31}NO_4S$ (M^+): 429.1974; found 429.1964.

Spectroscopic data for **4c** (yellow oil, R_f = 0.58 in 10% EtOAc-hexane)**:** IR (neat): 3027, 2957, 2869, 1354, 1168, 1093, 1042, 757, 681, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.08-6.96 (m, 6 H), 5.90 (dd, J = 5.8, 1.6 Hz, 1 H), 5.76 (dd, J = 5.9, 2.7 Hz, 1 H), 5.21 (dd, J = 8.2, 6.3 Hz, 1 H), 4.63 (d, J = 7.3 Hz, 1 H), 3.39 (dd, J = 6.8, 6.8 Hz, 1 H), 3.02 (dd, J = 7.4, 7.4 Hz, 1 H), 2.44 (s, 3 H), 2.18-2.00 (m, 2 H), 1.93-1.85 (m, 1 H), 1.84-1.74 (m, 1 H), 1.56-1.47 (m, 1 H), 1.40-1.19 (m, 2 H), 1.06-0.97 (m, 1 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.73 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 143.86 (C), 139.68 (C), 138.11 (C), 135.90 (CH), 134.99 (C), 133.53 (C), 131.94 (CH), 130.10 (two, CH), 129.78 (two CH), 127.27 (two CH), 126.63 (two CH), 126.11 (CH), 125.02 (CH), 109.34 (CH), 60.68 (CH), 42.63 (CH), 39.39 (CH), 35.52 (CH_2), 33.79 (CH_2), 21.85 (CH_2), 21.55 (CH_2), 21.51 (CH_3), 14.41 (CH_3), 14.26 (CH_3); MS (m/z, relative intensity): 447 (M^+, 6), 417 (6), 368 (5), 286 (17), 162 (51), 91 (100); exact mass calculate for $C_{28}H_{33}NO_2S$ (M^+): 447.2232; found 447.2233.

Spectroscopic data for **3d** (yellow oil, R_f = 0.22 in 15% EtOAc-hexane): IR (neat): 3056, 2981, 1723, 1358, 1341, 1170, 1032, 754, 703, 571 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.84 (d, J = 7.5 Hz, 2 H), 7.60-7.50 (m, 3 H), 7.30-7.19 (m, 8 H), 7.12 (d, J = 8.4 Hz, 2 H), 6.92 (d, J = 8.3 Hz, 1 H), 6.39 (dd, J = 5.9, 2.5 Hz, 1 H), 6.29 (dd, J = 5.8, 1.6 Hz, 1 H), 4.85 (dd, J = 8.1, 6.4 Hz, 1 H), 4.78-4.75 (m, 1 H), 3.99 (q, J = 7.1 Hz, 2 H), 3.02 (dd, J = 7.4, 7.3 Hz, 1 H), 2.92 (dd, J = 6.7, 7.0 Hz, 1 H), 1.14 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 171.13(C), 141.86 (C), 141.50 (C), 141.08 (C), 139.17 (CH), 138.35(C), 135.53(C), 133.06 (CH), 132.14 (CH), 129.23 (two CH), 129.21 (two CH), 129.05 (two CH), 128.19 (two CH), 127.96 (two CH), 127.08 (two CH) , 127.02 (CH), 126.91 (CH), 126.89 (CH), 102.07 (CH), 60.62 (CH_2), 59.75 (CH), 40.69 (CH), 40.41 (CH), 13.95 (CH_3); MS (m/z, relative intensity): 497 (M^+, 12), 424 (32), 356 (100), 282 (56), 229 (84), 77 (63); exact mass calculate for $C_{30}H_{27}NO_4S$ (M^+): 497.1661; found 497.1657.

Spectroscopic data for **4d** (colorless solid, mp 183-184 °C, R_f = 0.33 in 15% EtOAc-hexane)**:** IR (neat): 3026, 2924, 2854, 1358, 1167, 1039, 756, 702, 671, 544 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 7.6 Hz, 2 H), 7.27-7.11 (m, 9 H), 7.04 (d, J = 7.0 Hz, 2 H), 6.92 (d, J = 8.3 Hz, 1 H), 6.59-6.52 (m, 2 H), 6.23 (dd, J = 5.8, 1.8 Hz, 1 H), 5.90 (dd, J = 5.9, 2.5 Hz, 1 H), 5.07 (dd, J = 7.9, 6.5 Hz, 1 H), 4.75 (d, J = 7.4 Hz, 1 H), 3.53 (dd, J = 7.5, 7.4 Hz, 1 H), 2.97 (dd, J = 6.9, 6.8 Hz, 1 H), 2,47 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 144.07 (C), 142.99 (C), 142.34 (C), 141.95 (C), 139.93 (C), 139.30 (CH), 134.89 (C), 134.83 (C), 134.07 (CH), 130.20 (two CH), 129.91 (two CH), 129.76 (two CH), 129.58 (two CH), 128.28 (two CH), 127.79 (two CH), 127.41 (two CH), 126.97 (two CH), 126.70 (two CH), 126.53 (CH), 124.75 (CH), 109.49 (CH), 60.41 (CH), 40.97 (CH), 38.90 (CH), 21.57 (CH_3); MS (m/z, relative intensity): 515 (M^+, 1), 357 (3), 229 (100), 130 (8), 91 (11); exact mass calculate for $C_{34}H_{29}NO_2S$ (M^+): 515.1919; found: 515.1921.

Spectroscopic data for **3e** (orange oil, R_f = 0.28 in 15% EtOAc-hexane): IR (neat): 3066, 2981, 1724, 1489, 1360, 1169 1092, 754, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.83 (d, J = 7.3 Hz, 2 H), 7.65-7.50 (m, 3 H), 7.32-7.15 (m, 6 H), 7.02 (dd, J = 6.6, 1.8 Hz, 2 H), 6.91 (d, J = 8.3 Hz, 1 H), 6.34-6.29 (m, 2 H), 4.85 (dd, J = 8.2, 6.3 Hz, 1 H), 4.73 (d, J = 7.0 Hz, 1 H), 3.96 (q, J = 7.2 Hz, 2 H), 2.95 (dd, J = 7.3, 7.2 Hz, 1 H), 2.87 (dd, J = 6.6, 7.2 Hz, 1 H), 1.11 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 170.90 (C), 142.20 (C), 140.42 (CH), 139.78 (C), 139.46 (C), 138.06 (C), 133.16(C), 133.14 (CH), 132.97 (C), 132.86 (C), 131.53 (CH), 130.52 (two CH), 130.43 (two CH), 129.24 (two CH), 128.55 (two CH), 128.27 (two CH), 127.03 (two CH), 126.91(CH), 101.77 (CH), 60.69 (CH_2), 59.52 (CH), 40.61 (CH), 40.30 (CH), 13.93 (CH_3); MS (m/z, relative intensity): 565 (M^+, 11), 492 (9), 424 (20), 350 (30), 298 (40), 263(83), 228 (70), 113 (46), 77 (100); exact mass calculate for $C_{30}H_{25}Cl_2NO_4S$ (M^+): 565.0881; found: 565.0873.

Spectroscopic data for **4e** (orange oil, R_f = 0.36 in 10% EtOAc-hexane)**:** IR (neat): 3028, 2925, 1489, 1356, 1167, 1092, 1014, 758, 669, 546 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 7.25-7.08 (m, 7 H), 6.98 (d, J = 7.3 Hz, 2 H), 6.93 (d, J = 8.3 Hz, 1 H), 6.43 (d, J = 8.4 Hz, 2 H), 6.29 (dd, J = 5.8, 1.8 Hz, 1 H), 5.85 (dd, J = 5.8, 2.5 Hz, 1 H), 5.07 (dd, J = 8.1, 6.5 Hz, 1 H), 4.76-4.72 (m, 1 H), 3.50 (dd, J = 7.5, 7.5 Hz, 1 H), 2.96 (dd, J = 6.9, 6.9 Hz, 1 H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 144.28 (C), 144.18 (C), 140.43 (CH), 140.33 (C), 139.91 (C), 139.89 (C), 134.75 (C), 133.69 (CH), 133.12 (C), 132.85 (C), 132.35 (C), 131.09 (two CH), 130.90 (two CH), 130.08 (two CH), 129.95 (two CH), 128.68 (two CH), 128.17 (two

CH), 127.41 (two CH), 127.07 (two CH), 126.70 (CH), 124.74 (CH), 109.31 (CH), 60.22 (CH), 40.84 (CH), 38.95 (CH), 21.59 (CH_3); MS (m/z, relative intensity): 583 (M^+, 4), 428 (15), 298 (83), 263 (100), 228 (66), 130 (33), 91 (63); exact mass calculate for $C_{34}H_{27}Cl_2NO_2S$ (M^+): 583.1140; found: 583.1149.

Spectroscopic data for **3f** (yellow oil, R_f = 0.19 in 15% EtOAc-hexane)**:** IR (neat): 2952, 1727, 1358, 1342, 1170, 725, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.81 (d, J = 7.5 Hz, 2 H), 7.57-7.40 (m, 3 H), 6.93 (d, J = 8.3 Hz, 1 H), 6.14 (dd, J = 5.8, 2.5 Hz, 1 H), 5.98 (d, J = 5.7 Hz, 1 H), 4.99 (dd, J = 8.2, 6.0 Hz, 1 H), 4.68 (d, J = 7.6 Hz, 1 H), 3.92-3.85 (m, 2 H), 3.29 (dd, J = 7.6, 6.3 Hz, 1 H), 2.86 (dd, J = 7.8, 7.9 Hz, 1 H), 2.32-2.10 (m, 4 H), 1.72-1.50 (m, 4 H), 1.08 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): 171.51(C), 138.52 (C), 137.42 (C), 134.11 (CH), 133.08 (C), 132.97 (CH), 132.05 (CH), 129.17 (two CH), 127.13 (two CH), 126.74 (CH), 102.77 (CH), 60.39 (CH_2), 60.16 (CH), 40.73 (CH), 39.36 (CH), 31.15 (CH_2), 30.98 (CH_2), 26.52 (CH_2), 26.36 (CH_2), 14.05 (CH_3); MS (m/z, relative intensity): 399 (M^+, 6), 326 (17), 258 (35), 183 (42), 131 (92), 77 (100); exact mass calculate for $C_{22}H_{25}NO_4S$ (M^+): 399.1504; found 399.1514.

Spectroscopic data for **4f** (yellow oil, R_f = 0.58 in 10% EtOAc-hexane): IR (neat): 3028, 2951, 2868, 1453, 1354, 1167, 1093, 1043, 756, 692, 547 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.10-6.92 (m, 6 H), 5.84 (d, J = 5.6 Hz, 1 H), 5.61 (dd, J = 5.7, 2.6 Hz, 1 H), 5.24 (dd, J = 8.2, 6,2 Hz, 1 H), 4.67 (d, J = 7.2 Hz, 1 H), 3.43 (dd, J = 6.7, 6.7 Hz, 1 H), 2.92 (dd, J = 7.4, 7.4 Hz, 1 H), 2.43 (s, 3 H), 2.25-2.20 (m, 2 H), 2.12-2.06 (m, 1 H), 2.02-1.90 (m, 1 H), 1.69-1.50 (m, 4 H); ^{13}C NMR ($CDCl_3$): δ 143.87 (C), 139.82 (C), 136.01 (C), 135.11 (C), 134.78 (CH), 134.32 (C), 132.77 (CH), 129.80 (two CH), 129.78 (two CH), 127.32 (two CH), 126.63 (two CH), 126.19 (CH), 125.37 (CH), 109.79 (CH), 61.19 (CH), 44.36 (CH), 38.32 (CH), 31.31 (CH_2), 30.53 (CH_2), 26.51 (CH_2), 26.28(CH_2), 21.52 (CH_3); MS (m/z, relative intensity): 417 (M^+, 3), 338 (8), 286 (32), 132 (66), 91 (100); exact mass calculate for $C_{26}H_{27}NO_2S$ (M^+): 417.1762; found 417.1772.

Spectroscopic data for **3g** (yellow oil, R_f = 0.18 in 15% EtOAc-hexane)**:** IR (neat): 3067, 2930, 2854, 1725, 1360, 1344, 1168, 725, 574 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.82 (d, J = 7.4 Hz, 2 H), 7.58-7.42 (m, 3 H), 6.94 (d, J = 8.3 Hz, 1 H), 6.31 (dd, J = 5.9, 2.6 Hz, 1 H), 6.01 (dd, J = 5.9, 1.2 Hz, 1 H), 4.96 (dd, J = 8.2, 6.0 Hz, 1 H), 4.67 (d, J = 7.5 Hz, 1 H), 3.94-3.86 (m, 2 H), 3.18 (dd, J = 7.4, 6.4 Hz, 1 H), 2.98 (dd, J = 7.7, 7.7 Hz, 1 H), 2.17-2.08 (m, 4 H), 1.70-1.60 (m, 1 H), 1.53-1.40 (m, 5 H), 1.10 (t, J = 7.1 Hz, 3 H); ^{13}C

NMR ($CDCl_3$): δ 171.18 (C), 138.12 (C), 135.08 (CH), 133.93 (C), 133.36 (C), 132.86 (CH), 130.20 (CH), 129.02 (two CH), 126.88 (two CH), 126.64 (CH), 102.32 (CH), 60.17 (CH_2), 59.57 (CH), 40.46 (CH), 39.00 (CH), 32.08 (CH_2), 31.10 (CH_2), 27.45 (CH_2), 27.07 (CH_2), 26.32 (CH_2), 13.86 (CH_3); MS (m/z, relative intensity): 413 (M^+, 33), 340 (30), 272 (64), 268 (60), 198 (46), 146 (98), 141 (100), 117 (72); exact mass calculate for $C_{23}H_{27}NO_4S$ (M^+): 413.1661; found 413.1653.

Spectroscopic data for **4g** (yellow oil, R_f = 0.44 in 10% EtOAc-hexane)**:** IR (neat): 2926, 2854, 1451, 1351, 1167, 1095, 755, 679, 547 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.2 Hz, 2 H), 7.08-6.99 (m, 6 H), 5.89 (dd, J = 5.8, 0.9 Hz, 1 H), 5.78 (dd, J = 5.8, 2.6 Hz, 1 H), 5.23 (dd, J = 8.2, 6.3 Hz, 1 H), 4.65 (d, J = 7.4 Hz, 1 H), 3.33 (dd, J = 6.8, 6.7 Hz, 1 H), 3.07 (dd, J = 7.3, 7.3 Hz, 1 H), 2.44 (s, 3 H), 2.30-2.20 (m, 1 H), 2.18-2.00 (m, 1 H), 1.92-1.82 (m, 1 H), 1.92-1.82 (m, 1 H), 1.70-1.20 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ 143.86 (C), 139.56 (C), 135.85 (CH), 135.12 (C), 135.03 (C), 132.63 (C), 131.24 (CH), 130.09 (two CH), 129.80 (two CH), 127.31 (two CH), 126.50 (two CH), 126.16 (CH), 125.35 (CH), 109.49 (CH), 60.85 (CH), 42.68 (CH), 39.88 (CH), 32.08 (CH_2), 30.83 (CH_2), 27.46 (CH_2), 27.26 (CH_2), 26.52 (CH_2), 21.52 (CH_3); MS (m/z, relative intensity): 431 (M^+, 4), 286 (51), 146 (33), 91 (100); exact mass calculate for $C_{27}H_{29}NO_2S$ (M^+): 431.1919; found 431.1926.

3h. Yellow oil, R_f = 0.31 and 0.22 in 15% EtOAc-hexane. Higher R_f isomer : lower R_f isomer = 4:3. Spectroscopic data for lower R_f isomer of **3h**: IR (neat): 2924, 2854, 1728, 1346, 1169, 756, 725, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.84 (d, J = 7.4 Hz, 2 H), 7.62-7.45 (m, 3 H), 7.35-7.15 (m, 5 H), 6.95 (d, J = 8.2 Hz, 1 H), 6.41 (br.s, 1 H), 6.23 (dd, 5.7, 2.4 Hz, 1 H), 6.19 (dd, 5.7, 1.5 Hz, 1 H), 5.00 (dd, J = 8.2, 6.0 Hz, 1 H), 4.79 (d, J = 7.0 Hz, 1 H), 3.86 (q, J = 7.1 Hz, 2 H), 3.46 (dd, J = 7.3, 7.4 Hz, 1 H), 3.32 (dd, J = 7.6, 6.2 Hz, 1 H), 1.04 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 170.95 (C), 144.30 (C), 138.40 (C), 137.04 (C), 137.00 (CH), 135.94 (CH), 133.17 (CH), 129.33 (two CH), 128.57 (two CH), 128.10 (two CH), 127.20 (two CH), 126.96 (CH), 126.77 (CH), 123.87 (CH), 102.97 (CH), 60.60 (CH_2), 60.50 (CH), 39.81 (CH), 39.44 (CH), 13.90 (CH_3); MS (m/z, relative intensity): 421 (M^+, 12), 348 (18), 280 (22), 205 (32), 153 (100), 77 (43); exact mass calculate for $C_{24}H_{23}NO_4S$ (M^+): 421.1348; found 421.1344.

Spectroscopic data for higher R_f isomer of **3h**: IR (neat): 2924, 2854, 1728, 1348, 1167, 1095, 756, 727, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.86 (d, J = 7.4 Hz, 2 H), 7.60-7.45 (m, 3 H), 7.35-7.10 (m, 5 H), 6.72 (d, J = 5.8 Hz, 1 H), 6.58 (dd, J = 7.2, 2.2 Hz, 1 H), 6.06 (s,

1 H), 6.00 (d, J = 5.7 Hz, 1 H), 5.74 (dd, J = 7.1, 4.0 Hz, 1 H), 5.09 (d, J = 8.0 Hz, 1 H), 4.13 (q, J = 7.1 Hz, 2 H), 3.89 (dd, J = 6.8, 7.1 Hz, 1 H), 3.00-2.96 (m, 1 H), 1.22 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 170.78 (C), 143.75 (C), 139.86 (C), 137.97 (CH), 137.36 (C), 133.72 (CH), 132.95 (CH), 129.27 (two CH), 128.28 (two CH), 128.22 (two CH), 126.81 (CH), 126.76 (CH), 126.68 (two CH), 122.15 (CH), 113.51 (CH), 62.29 (CH), 60.95 (CH_2), 48.38 (CH), 41.52 (CH), 14.06 (CH_3); MS (m/z, relative intensity): 421 (M^+, 12), 348 (18), 280 (18), 206 (21), 153 (100), 76 (20); exact mass calculate for $C_{24}H_{23}NO_4S$ (M^+): 421.1348; found: 421.1351.

Spectroscopic data for **4h** (yellow oil, R_f = 0.42 in 10% EtOAc-hexane), 4:1 isomeric mixtures: IR (neat): 3026, 2924, 2852, 1342, 1165, 758, 700, cm^{-1}; ^{1}H NMR ($CDCl_3$, 4:1 isomeric forms, denotes major isomer): δ 7.84-7.81 (m, 2 H), 7.39-7.35 (m, 4 H), 7.26-7.21 (m, 2 H), 7.18-7.09 (m, 4 H), 6.99 (d, J =7.3 Hz, 2 H), 6.92 (d, J = 7.6 Hz, 1 H), 6.33 (dd, J = 7.6, 5.7 Hz, 1 H), 6.08 (d, J = 5.7 Hz, 1 H), 5.76 (s, 1 H), 5.51 (dd, J = 7.8, 5.3 Hz, 1 H), 4.96 (d, J = 7.4 Hz, 1 H), 3.45-3.41 (m, 1 H), 3.33 (dd, J = 7.4, 7.4 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR ($CDCl_3$, 4:1 isomeric forms, denotes major isomer): δ 144.34 (C), 143.97 (C), 139.93 (CH), 139.34 (C), 137.50 (C), 135.75 (C), 132.48 (CH), 130.01 (two CH), 129.88 (two CH), 128.15 (two CH), 127.98 (two CH), 127.24 (two CH), 127.16 (two CH), 126.45 (CH), 126.38 (CH), 126.12 (CH), 122.66 (CH), 113.36 (CH), 61.05 (CH), 49.28 (CH), 41.65 (CH0, 21.52 (CH_3); MS (m/z, relative intensity): 439 (M^+, 3), 307 (4), 284 (5), 154 (100), 130 (21), 91 (22); exact mass calculate for $C_{28}H_{25}NO_2S$ (M^+): 439.1606; found: 439.1600.

3i. Yellow oil, R_f = 0.33 and 0.25 in 15% EtOAc-hexane. Higher R_f isomer : lower R_f isomer = 4:3. Spectroscopic data for lower R_f isomer of **3i:** IR (neat): 2924, 2852, 1730, 1342, 1169, 1034, 756, 725, 575 cm^{-1}; NMR ($CDCl_3$): δ 7.83 (d, J = 7.3 Hz, 2 H), 7.58 (d, J = 7.3 Hz, 1 H), 7.52 (d, J = 7.8 Hz, 2 H), 6.91 (dd, J = 8.3, 0.7 Hz, 1 H), 6.05 (dd, J = 5.7, 2.3 Hz, 1 H), 5.98 (dd, J = 6.1, 1.0 Hz, 1 H), 5.45 (dd, J = 14.2, 7.3 Hz, 1 H), 5.04 (dd, J = 8.3, 5.9 Hz, 1 H), 4.71 (d, J = 7.6 Hz, 1 H), 3.96-3.88 (m, 2 H), 3.26 (dd, J = 7.0, 6.0 Hz, 1 H), 3.08 (dd, J = 8.1, 7.8 Hz, 1 H), 1.68 (d, J = 7.1 Hz, 3 H), 1.10 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 171.35 (C), 143.84 (C), 135.12 (CH), 134.53 (CH), 133.06 (CH), 129.28 (C), 129.22 (two CH), 127.11 (two CH), 126.75 (CH), 118.80 (CH), 103.34 (CH), 60.53 (CH_2), 60.10 (CH), 40.15 (CH), 38.91 (CH), 14.95 (CH_3), 13.93 (CH_3); MS (m/z, relative intensity): 359 (M^+, 6), 286 (19), 218 (20), 144 (70), 129 (43), 92 (100), 77 (57); exact mass calculate for $C_{19}H_{21}NO_4S$ (M^+): 359.1191; found 359.1196.

Spectroscopic data for higher R_f isomer of **3i:** IR (neat): 2981, 2927, 1724, 1342, 1169, 1095, 756, 725, 573 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 2 H), 7.60-7.41 (m, 3 H), 6.53-6.49 (m, 1 H), 6.44 (d, J = 5.8 Hz, 1 H), 5.82 (dd, J = 3.7, 2.1 Hz, 1 H), 5,74 (dd, J = 7.1, 3.8 Hz, 1 H), 5.05-4.95 (m, 2 H), 4.20-4.06 (m, 2 H), 3.80-3.76 (m, 1 H), 2.84-2.81 (m, 1 H), 1.63 (d, J = 7.0 Hz, 3 H), 1.23 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 171.01 (C), 142.45 (C), 140.19 (C), 134.45 (CH), 133.04 (CH), 129.36 (CH), 129.24 (two CH), 126.80 (CH), 126.67 (two CH), 117.08 (CH), 114.46 (CH), 63.12 (CH), 60.83 (CH_2), 47.62 (CH), 41.24 (CH), 14.51 (CH_3), 14.08 (CH_3); MS (m/z, relative intensity): 359 (M^+, 14), 286 (30), 218 (43), 144 (91), 130 (44), 91 (76), 77 (100); exact mass calculate for $C_{19}H_{21}NO_4S$ (M^+): 359.1191; found 359.1196.

Spectroscopic data for **4i** (yellow oil, R_f = 0.42 in 10% EtOAc-hexane), 1:1 isomeric mixture: IR (neat): 3028, 2925, 2854, 1346, 1167, 758, 675 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.80-7.70 (m, 4 H), 7.38-7.25 (m, 5 H), 7.20-6.95 (m, 10 H), 6.82 (d, J = 7.6 Hz, 1 H), 6.04 (d, J = 5.6 Hz, 1 H), 5.92 (d, J = 5.2 Hz, 1 H), 5.85 (d, J = 5.4 Hz, 1 H), 5.59 (dd, J = 3.8, 1.6 Hz, 1 H), 5.46 (dd, J = 7.4, 5.4 Hz, 1 H), 5.28-5.15 (m, 2 H), 4.88 (d, J = 7.4 Hz, 1 H), 4.69 (d, J = 7.2 Hz, 1 H), 4.64 (q, J = 7.0 Hz, 1 H), 3.40 (dd, J = 6.7, 6.8 Hz, 1 H), 3.25 (dd, J = 6.0, 5.7 Hz, 1 H), 3.14-3.05 (m, 2 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.66 (d, J = 7.0 Hz, 3 H), 1.47 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ 144.75 (C), 143.86 (C), 143.71 (C), 142.56 (C), 139.57 (C), 139.52 (C), 135.90 (CH), 135.55 (CH), 135.19 (CH), 131.64 (CH), 129.81 (CH), 129.73 (CH), 129.69 (two CH), 129.67 (two CH), 128.93 (C), 128.32 (C), 127.16 (CH), 126.94 (two CH), 126.91 (two CH), 126.71 (CH), 126.16 (CH), 126.13 (CH), 125.96 (CH), 125.14 (CH), 117.68 (CH), 117.63 (CH), 113.95 (CH), 110.19 (CH), 61.56 (CH), 61.00 (CH), 48.20 (CH), 42.25 (CH), 41.20 (CH), 39.23 (CH), 21.39 (CH_3), 21.37 (CH_3), 14.90 (CH_3), 13.86 (CH_3); MS (m/z, relative intensity): 377 (M^+, 14), 286 (21), 222 (8), 92 (100); exact mass calculate for $C_{23}H_{23}NO_2S$ (M^+): 377.1449; found: 377.1457.

Spectroscopic data for **5** (colorless solid, R_f = 0.39 in 15% EtOAc-hexane): IR (neat): 3028, 1656, 1487, 1358, 1167, 756, 671, 544 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.60 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H), 7.19-7.11 (m, 3H), 7.06 (d, J = 8.4 Hz, 2 H), 6.97 (d, J = 7.1 Hz, 2 H), 6.92 (d, J = 8.4 Hz, 1 H), 6.36 (d, J = 8.4 Hz, 2 H), 6.29 (dd, J = 5.8, 1.9 Hz, 1 H), 5.84 (dd, J = 5.8, 2.3 Hz, 1 H), 5.07 (dd, J= 8.2 6.3 Hz, 1 H), 4.73 (d, J = 7.4 Hz, 1 H), 3.49 (dd, J = 7.5, 7.5 Hz, 1 H), 2.96 (dd, J = 6.9, 6.9 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 144.31 (C), 144.21 (C), 140.72 (C), 140.58 (CH), 140.29 (C), 139.85 (C), 134.65 (C), 133.68 (CH), 132.38 (C),

131.66 (two CH), 131.45 (two CH), 131.25 (two CH), 131.15 (two CH), 130.08 (two CH), 129.97 (two CH), 127.42 (two CH), 127.08 (two CH), 126.72 (CH), 124.74 (CH), 121.31 (C), 121.07 (C), 109.29 (CH), 60.19 (CH), 40.77 (CH), 38.90 (CH), 21.63 (CH_3); MS (m/z, relative intensity): 675 (M^++4, 7), 673 (M^++2, 11), 671 (M^+, 6), 614 (3), 517 (11), 460 (38), 391 (97), 389 (100), 388 (89); exact mass calculate for $C_{34}H_{28}Br_2NO_2S$ (M^++1): 672.0207; found: 672.0214.