Exploitation of Donor-Acceptor Cyclopropanes and N-Sulfonyl 1-Azadienes Towards the Synthesis of Spiro-Cyclopentane Benzofuran Derivatives

Kamal Verma, Irshad Maajid Taily and Prabal Banerjee*

Department of Chemistry, Indian Institute of Technology Ropar,
Nangal Road, Rupnagar, Punjab, India Pin 140001,

E-mail: prabal@iitrpr.ac.in
Experimental Section

All reactions were carried out under inert atmosphere using oven dried glassware. All solvents and reagents were obtained from commercial sources and were purified using standard procedure prior to use. The developed chromatogram was analyzed by UV lamp (254 nm), or p-Anisaldehyde solution. Products were purified by flash chromatography on silica gel (mesh size 230-400). The $^1$H and $^{13}$C-NMR spectra were recorded in CDCl$_3$. Chemical shifts of $^1$H and $^{13}$C-NMR spectra are expressed in parts per million (ppm). All coupling constants are given in absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, q = quartet, pent = pentet, br = broad and m = multiplet. The DACs$^1$ and azadienes$^2c$ were prepared according to the known methods.

(E)-N-((Z)-2-benzylidenebenzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (2a)$^{2c}$: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.78 (d, $J = 8.1$ Hz, 1H), 8.00 (d, $J = 8.2$ Hz, 2H), 7.89 (d, $J = 7.0$ Hz, 2H), 7.69 (ddd, $J = 8.5$, 7.2, 1.4 Hz, 1H), 7.47–7.35 (m, 5H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.12 (s, 1H), 2.48 (s, 3H).

(E)-N-((Z)-2-benzylidenebenzofuran-3(2H)-ylidene)-4-nitrobenzenesulfonamide (2b)$^{2b}$: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.69 (d, $J = 8.0$ Hz, 1H), 8.46-8.37 (m, 2H), 8.34-8.24 (m, 2H), 7.91-7.88 (m, 2H), 7.76-7.70 (m, 1H), 7.49-7.39 (m, 3H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.34-7.29 (m, 1H), 7.12 (s, 1H)

(E)-4-methyl-N-((Z)-2-(4-methylbenzyldiene)benzofuran-3(2H)-ylidene)benzenesulfonamide (2c)$^{2c}$: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.78 (d, $J = 8.1$ Hz, 1H), 8.00 (d, $J = 8.3$ Hz, 2H), 7.79 (d, $J = 7.9$ Hz, 2H), 7.67 (ddd, $J = 8.5$, 7.2, 1.4 Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.12 (s, 1H), 2.47 (s, 3H), 2.40 (s, 3H).
N-((Z)-2-((Z)-4-fluorobenzylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (2d): \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.77 (d, \( J = 8.0 \) Hz, 1H), 7.99 (d, \( J = 8.2 \) Hz, 2H), 7.87 (dd, \( J = 8.7, 5.6 \) Hz, 2H), 7.71-7.63 (m, 1H), 7.37 (d, \( J = 8.1 \) Hz, 2H), 7.33 – 7.27 (m, 2H), 7.11 (t, \( J = 8.7 \) Hz, 2H), 7.05 (s, 1H), 2.47 (s, 3H).

(E)-N-((Z)-2-(4-chlorobenzylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (2e): \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.77 (d, \( J = 8.1 \) Hz, 1H), 7.99 (d, \( J = 8.3 \) Hz, 2H), 7.81 (d, \( J = 8.6 \) Hz, 2H), 7.68 (ddd, \( J = 8.5, 7.3, 1.4 \) Hz, 1H), 7.43-7.35 (m, 4H), 7.32 (d, \( J = 3.9 \) Hz, 1H), 7.29 (d, \( J = 3.7 \) Hz, 1H), 7.03 (s, 1H), 2.47 (s, 3H).

**General procedure of 3**

A two-necked round bottom flask was charged with DACs 1 (1.0 equiv.), N-sulfonyl 1-azadienes 2 (1.0 equiv.) and MgI\(_2\) (0.2 equiv.) under nitrogen atmosphere. DCM was added to the reaction mixture and solution was stirred it at room temperature until the consumption of cyclopropane (as monitored by TLC). Reaction mixture was filtered through thin pad of celite and solvent was concentrated in rotary evaporator. The residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane as eluent.

**Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3aa):** Reaction time: 7 h, 1a (62 mg, 0.21 mmol), 2a (80 mg, 0.21 mmol), yield = 69%, 96 mg, nature = viscous liquid. \( R_f \)-value: 0.30 (Ethyl acetate/hexane) = 2:8. \( ^1 \)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.22 (d, \( J = 8.0 \) Hz, 1H), 8.03 (d, \( J = 8.4 \) Hz, 2H), 7.41 (d, \( J = 8.3 \) Hz, 2H), 7.37-7.33 (m, 1H), 7.19-7.17 (m, 4H), 7.07-7.04 (m, 3H), 6.89 (d, \( J = 8.4 \) Hz, 1H), 6.78 (t, \( J = 8.3 \) Hz, 1H), 6.64 (d, \( J = 8.7 \) Hz, 2H), 4.90 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12 (m, 1H), 3.95-3.87 (m, 1H), 3.83 (t, \( J = 14.1 \) Hz, 1H), 3.66 (s, 3H), 3.64-3.57 (m, 1H), 3.54-3.46 (m, 1H), 2.57 (dd, \( J = 6.9, 6.5 \) Hz, 1H), 2.50 (s, 3H), 1.20 (t, \( J = 6.9 \) Hz, 3H), 0.71 (t, \( J = 7.3 \) Hz, 3H). \( ^{13} \)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 180.2, 171.9, 170.2, 169.9, 158.9, 143.4, 138.9, 134.0, 130.4, 129.6, 128.1, 127.6, 127.0, 126.1, 121.9, 118.4, 113.6, 112.1, 101.2, 62.8, 62.1,
61.5, 60.0, 55.1, 53.9, 38.5, 21.7, 14.0, 13.3. IR (υ, cm⁻¹) 2981, 1720, 1576, 1515, 1464, 1302, 1248, 1181, 1147, 1088, 1018, 905, 877, 828, 747, 704. HRMS (ESI) calcd for C₃₈H₃₈NO₅S⁺ [M+H]⁺; 668.2318 found 668.2334.

**Diethyl(2R,2'R,5'R,E)-5'-(3,4-dimethoxyphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ba):** Reaction time: 8 h, 1b (46 mg, 0.14 mmol), 2a (54 mg, 0.14 mmol), yield = 62%, 61 mg, Nature = yellow solid, Melting Point = 111 °C Rf-value: 0.25 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.37-7.33 (m, 1H), 7.20-7.18 (m, 2H), 7.07-7.06 (m, 3H), 6.87-6.79 (m, 3H), 6.75 (m, 1H), 6.63 (d, J = 8.3 Hz, 1H), 4.93 (s, 1H), 4.32-4.24 (m, 1H), 4.21-4.10 (m, 1H), 3.98-3.87 (m, 1H), 3.81 (d, J = 14.3 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.63 (dd, J = 8.4, 6.7 Hz, 1H), 3.53-3.45 (m, 1H), 2.59 (dd, J = 7.3, 6.5 Hz, 1H), 2.50 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H), 0.71 (t, J = 7.6 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 180.3, 171.9, 170.2, 169.9, 148.3, 143.4, 138.9, 133.9, 130.3, 129.6, 128.0, 127.7, 126.9, 122.0, 120.3, 118.4, 112.0, 111.5, 110.4, 101.2, 62.8, 62.1, 61.5, 59.9, 55.9, 55.7, 54.2, 38.1, 21.7, 14.0, 13.3. IR (υ, cm⁻¹) 2936, 1718, 1601, 1459, 1145, 1087, 1015, 835, 751, 701. HRMS (ESI) calcd for C₃₉H₄₈NO₅S⁺ [M+H]⁺; 698.2424 found 698.2451.

**Dimethyl(2R,2'R,5'R,E)-5'-(benzo[d][1,3]dioxol-5-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ca):** Reaction time: 8 h, 1c (52 mg, 0.18 mmol), 2a (70 mg, 0.18 mmol), yield = 61%, 72 mg, Nature = viscous liquid. Rf-value: 0.25 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.44-7.37 (m, 3H), 7.17-7.14 (m, 2H), 7.09-7.06 (m, 3H), 6.95 (d, J = 8.2 Hz, 1H), 6.84-6.80 (m, 2H), 6.68-6.66 (m, 1H), 6.54 (d, J = 8.7 Hz, 1H), 5.82-5.81 (m, 2H), 4.84 (s, 1H), 3.80-3.73 (m, 1H), 3.75 (s, 3H), 3.58 (dd, J = 7.3, 6.8 Hz, 1H), 326 (s, 3H), 2.57 (dd, J = 6.9, 6.8 Hz, 1H), 2.50 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 179.7, 172.3, 170.2, 170.1, 147.4, 147.0, 143.5, 138.9, 133.6, 130.5, 130.1, 129.6, 128.1, 127.8, 127.0, 122.2, 122.0, 112.2, 108.8, 107.9, 101.0, 100.9, 62.7, 60.3, 54.2, 53.3, 52.4, 38.7, 21.7. IR (υ, cm⁻¹) 2922, 1728, 1595, 1482, 1276, 1144, 1089, 1038, 934, 873, 805, 753, 733, 700. HRMS (ESI) calcd for C₃₆H₃₂NO₅S⁺ [M+H]⁺; 654.1798 found 654.1741.
Diethyl(2R,2'R,5'R,E)-2'-phenyl-3-(tosylimino)-5'-(3,4,5-trimethoxyphenyl)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3da): Reaction time: 6 h, 1d (55 mg, 0.15 mmol), 2a (59 mg, 0.15 mmol), yield = 59%, 64 mg, Nature = viscous liquid. R<sub>f</sub>-value: 0.22 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.42-7.34 (m, 3H), 7.20-7.18 (m, 2H), 7.09-7.06 (m, 3H), 6.86-6.80 (m, 2H), 6.48 (s, 2H), 4.95 (s, 1H), 4.32-4.24 (m, 1H), 4.21-4.13 (m, 1H), 3.95-3.87 (m, 1H), 3.83 (t, J = 13.9 Hz, 1H), 3.78 (s, 6H), 3.68 (s, 3H), 3.64-3.59 (m, 1H), 3.53-3.45 (m, 1H), 2.62 (dd, J = 7.4, 6.0, 1H), 2.49 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 7.2 Hz, 3H). ¹³C-NMR (100 MHz, CDCl<sub>3</sub>) δ 180.3, 171.8, 170.2, 169.9, 152.7, 143.5, 138.9, 137.3, 133.8, 130.3, 129.7, 129.6, 128.0, 127.8, 126.9, 122.1, 118.5, 112.0, 105.4, 101.1, 62.8, 62.2, 61.6, 60.8, 59.7, 56.2, 54.7, 37.9, 21.7, 14.0, 13.3. IR (ʋ, cm⁻¹): 2936, 1725, 1581, 1509, 1458, 1300, 1250, 1146, 1126, 1086, 1018, 905, 827, 734, 702. HRMS (ESI) calcd for C₄₀H₄₂NO₁₀S⁺ [M+H]⁺; 728.2529 found 728.2523.

Diethyl(2S,2'S,R,E)-5'-(furan-2-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ea): Reaction time: 8 h, 1e (39 mg, 0.15 mmol), 2a (57 mg, 0.15 mmol), yield = 66%, 62 mg, Nature = viscous liquid. R<sub>f</sub>-value: 0.28 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.5 Hz, 2H), 7.44-7.37 (m, 3H), 7.19-7.13 (m, 2H), 7.10-7.04 (m, 4H), 6.93 (d, J = 8.3 Hz, 1H), 6.90-6.86 (m, 1H), 6.10-6.07 (m, 2H), 4.84 (s, 1H), 4.30-4.22 (m, 1H), 4.20-4.12 (m, 1H), 3.94-3.86 (m, 1H), 3.81-3.70 (m, 2H), 3.53-3.45 (m, 1H), 2.71-2.61 (m, 1H), 2.48 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H), 0.70 (t, J = 7.0 Hz, 3H). ¹³C-NMR (100 MHz, CDCl<sub>3</sub>) δ 179.7, 171.6, 170.1, 169.5, 149.2, 143.4, 142.0, 138.8, 133.5, 130.6, 130.3, 129.5, 128.0, 127.3, 127.0, 122.0, 118.2, 112.2, 110.0, 107.8, 100.3, 62.9, 62.2, 61.6, 59.7, 48.3, 36.8, 21.7, 14.0, 13.3. IR (ʋ, cm⁻¹): 2980, 1721, 1578, 1515, 1463, 1302, 1249, 1222, 1181, 1147, 1088, 905, 876, 827, 747, 705. HRMS (ESI) calcd for C₃₅H₃₄NO₈S⁺ [M+H]⁺; 628.2005 found 628.2000.

Diethyl(2S,2'S,S,R,E)-5'-(1,3-dioxoisindolin-2-yl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3fa): Reaction time: 6 h, 1f (72 mg, 0.21 mmol), 2a (80 mg, 0.21 mmol), yield = 55%, 81 mg, Nature = white solid. Melting Point = 98 °C, R<sub>f</sub>-value: 0.28 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, J =
8.2 Hz, 1H), 8.15 (d, J = 8.2 Hz, 2H), 7.74-7.72 (m, 2H), 7.63-7.61 (m, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.37-7.33 (m, 1H), 7.25-7.22 (m, 2H), 7.10-7.07 (m, 3H), 7.00 (d, J = 8.4 Hz, 1H), 6.85-6.81 (m, 1H), 5.07-5.01 (m, 1H), 4.97-4.89 (m, 2H), 4.27-4.19 (m, 1H), 4.18-4.10 (m, 1H), 3.94-3.86 (m, 1H), 3.56-3.48 (m, 1H), 2.53 (dd, J = 6.8, 6.5 Hz, 1H), 2.50 (s, 3H), 1.18 (t, J = 6.9 Hz, 3H), 0.72 (t, J = 6.8 Hz, 3H). \(^{13}\text{C-NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 177.6, 171.2, 169.7, 168.7, 167.3, 143.4, 138.9, 134.0, 133.2, 131.2, 130.6, 129.5, 128.0, 127.8, 127.3, 123.5, 122.3, 117.7, 112.3, 99.5, 62.3, 61.8, 61.7, 57.7, 33.2, 21.7, 13.9, 13.3. IR (\(\bar{\nu}\), cm\(^{-1}\)) 2926, 1723, 1600, 1462, 1366, 1266, 1155, 1090, 877, 829, 703. HRMS (ESI) calcd for C\(_{39}\)H\(_{35}\)NO\(_2\)S\(^{+}\) [M+H]\(^{+}\); 707.2063 Found 707.2072.

**Diethyl(2R,2'R,5'R,6)-2'-phenyl-5'-(p-tolyl)-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ga):**

Reaction time: 10 h. \(1\)g (59 mg, 0.21 mmol), \(2\)a (80 mg, 0.21 mmol), yield = 57\%, 78 mg, Nature = viscous liquid, \(R_f\)-value: 0.29 (Ethyl acetate/hexane) = 2:8. \(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.22 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.36-7.32 (m, 1H), 7.20-7.14 (m, 4H), 7.07-7.05 (m, 3H), 6.90 (t, J = 8.6 Hz, 3H), 6.80-6.76 (m, 1H), 4.90 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.11 (m, 1H), 3.96-3.89 (m, 1H), 3.85-3.82 (m, 1H), 3.61 (dd, J = 7.8, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.58 (dd, J = 7.0, 6.1 Hz, 1H), 2.50 (s, 3H), 2.15 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H), 0.71 (t, J = 7.3 Hz, 3H). \(^{13}\text{C-NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 180.1, 171.9, 170.1, 169.9, 143.4, 138.8, 137.3, 133.9, 131.0, 130.4, 130.3, 129.6, 128.8, 128.4, 127.9, 127.7, 127.0, 121.9, 118.4, 112.1, 101.2, 62.8, 62.1, 61.5, 60.2, 54.2, 38.5, 21.7, 21.0, 14.0, 13.3. IR (\(\bar{\nu}\), cm\(^{-1}\)) 2977, 1718, 1577, 1463, 1303, 1273, 1208, 1183, 1147, 1117, 1088, 1017, 905, 877, 827, 705. HRMS (ESI) calcd for C\(_{38}\)H\(_{35}\)NO\(_2\)S\(^{+}\) [M+H]\(^{+}\); 652.2369 found 652.2322.

**Diethyl(2R,2'S,5'S,6'E)-5'-4-isopropylphenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ha):**

Reaction time: 12 h. \(1\)h (65 mg, 0.21 mmol), \(2\)a (80 mg, 0.21 mmol), yield = 56\%, 80 mg, Nature = viscous liquid, \(R_f\)-value: 0.32 (Ethyl acetate/hexane) = 2:8. \(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.21-7.16 (m, 4H), 7.08-7.03 (m, 3H), 6.95 (d, J = 8.2 Hz, 2H), 6.86 (d, J = 8.6 Hz, 1H), 6.76 (t, J = 8.2 Hz, 1H), 4.92 (s, 1H), 4.30-4.22 (m, 1H), 4.20-4.12 (m, 1H), 3.95-3.87 (m, 1H), 3.84 (d, J = 13.9 Hz, 1H), 3.62 (dd, J = 7.5, 6.6 Hz, 1H), 3.54-3.46 (m, 1H), 2.71 (septet, J =
7.5, 6.9, 6.9, 1H), 2.59 (dd, J = 7.1, 6.5 Hz, 1H), 2.50 (s, 3H), 1.19 (t, J = 7.3 Hz, 3H), 1.08 (d, J = 6.9 Hz, 6H), 0.71 (t, J = 6.9 Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 180.2, 171.9, 170.1, 169.9, 148.2, 143.4, 139.0, 138.6, 134.0, 131.3, 130.3, 129.6, 128.5, 127.9, 127.7, 127.0, 126.1, 121.8, 118.4, 112.2, 101.3, 62.9, 62.1, 61.5, 60.0, 54.3, 38.4, 33.6, 23.8, 21.7, 14.0, 13.3. IR (υ, cm$^{-1}$) 2979, 1723, 1574, 1463, 1306, 1258, 1203, 1181, 1147, 1088, 1018, 852, 827, 748, 704. HRMS (ESI) calcd for C$_{40}$H$_{42}$NO$_3$S$^+$ [M+H]$^+$; 680.2682 found 680.2656.

**Diethyl(2S,2'R,5'R,E)-5'-mesityl-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ia):**

Reaction Time: 7 h, 1i (52 mg, 0.17 mmol), 2a (64 mg, 0.17 mmol), yield = 63%, 72 mg, Nature = viscous liquid, R$_f$-value: 0.27 (Ethyl acetate/hexane) = 2:8. $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.42-7.37 (m, 3H), 7.19-7.16 (m, 2H), 7.08-7.04 (m, 3H), 6.96 (d, J = 8.3 Hz, 1H), 6.84-6.80 (m, 1H), 6.65 (d, J = 8.1 Hz, 2H), 4.91 (s, 1H), 4.29-4.12 (m, 4H), 3.99-3.91 (m, 1H), 3.58-3.50 (m, 1H), 2.83 (s, 3H), 2.50 (s, 3H), 2.47 (m, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 1.18 (t, J = 7.3 Hz, 3H), 0.74 (t, J = 7.3 Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 180.1, 172.1, 170.4, 169.5, 143.4, 138.8, 138.6, 136.6, 136.6, 133.7, 131.8, 130.5, 129.8, 129.6, 127.9, 127.7, 127.6, 127.1, 121.9, 117.7, 111.6, 103.5, 63.2, 61.9, 61.5, 60.8, 49.1, 37.5, 23.0, 22.4, 21.7, 20.5, 14.0, 13.3. IR (υ, cm$^{-1}$) 2980, 1726, 1600, 1461, 1264, 1183, 1155, 1089, 908, 830, 732, 702. HRMS (ESI) calcd for C$_{40}$H$_{42}$NO$_3$S$^+$ [M+H]$^+$; 680.2682 found 680.2658.

**Diethyl(2R,2'R,5'R,E)-5'-(4-fluorophenyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ja):**

Reaction time: 9 h, 1j (45 mg, 0.16 mmol), 2a (61 mg, 0.16 mmol), yield = 68%, 71 mg, Nature = viscous liquid, R$_f$-value: 0.30 (Ethyl acetate/hexane) = 2:8. $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.38-7.34 (m, 1H), 7.25-7.21 (m, 2H), 7.19-7.16 (m, 2H), 7.08-7.04 (m, 3H), 6.88 (d, J = 8.7 Hz, 1H), 6.83-6.77 (m, 3H), 4.90 (s, 1H), 4.32-4.24 (m, 1H), 4.20-4.12 (m, 1H), 3.96-3.88 (m, 1H), 3.82 (t, J = 13.6 Hz, 1H), 3.62 (dd, J = 7.7, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.59 (dd, J = 6.9, 6.8 Hz, 1H), 2.50 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 7.0 Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 179.8, 171.8, 170.6, 169.8, 162.2 (d, J = 246.5 Hz), 143.5, 139.0, 133.7, 130.4, 130.3, 130.1 (d, J = 8.3 Hz), 129.8 (d, J = 2.8 Hz) 129.6, 127.9 (d, J = 22.7 Hz),
127.0, 122.1, 115.0 (d, J = 21.1 Hz), 112.1, 101.0, 62.8, 62.1, 61.6, 59.9, 53.9, 38.4, 21.7, 14.0, 13.3. IR (υ, cm⁻¹) 2924, 1727, 1601, 1532, 1462, 1308, 1254, 1158, 1089, 830, 703. HRMS (ESI) calcd for C₃₇H₃₅FNO₇S⁺ [M+H]⁺; 656.2118 found 656.2126.

**Diethyl(2S,2'R,5'R,E)-2',5'-diphenyl-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ka):** Reaction time: 11 h, 1k (56 mg, 0.21 mmol), 2a (80 mg, 0.21 mmol), yield = 52%, 70 mg, Nature = viscous liquid, Rₜ-value: 0.39 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.35-7.31 (m, 1H), 7.28-7.25 (m, 1H), 7.20-7.18 (m, 2H), 7.13-7.04 (m, 7H), 6.87 (d, J = 8.3 Hz, 1H), 6.80-6.76 (m, 1H), 4.92 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.13 (m, 1H), 3.96-3.85 (m, 2H), 3.64 (dd, J = 8.2, 6.2 Hz, 1H), 3.54-3.46 (m, 1H), 2.61 (dd, J = 7.1, 6.5 Hz, 1H), 2.50 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 7.4 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 180.0, 171.9, 170.0, 169.9, 143.4, 138.8, 134.1, 133.9, 130.4, 130.3, 129.6, 128.6, 128.1, 128.0, 127.7, 127.0, 121.9, 118.3, 112.1, 101.2, 62.9, 62.1, 61.6, 60.0, 54.5, 38.2, 21.7, 14.0, 13.3. IR (υ, cm⁻¹) 2964, 1726, 1576, 1461, 1314, 1262, 1149, 1086, 1018, 876, 826, 750, 700. HRMS (ESI) calcd for C₃₇H₃₆N₂O₇S⁺ [M+H]⁺; 638.2212 found 638.2206.

**Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-3-(((4-nitrophenyl)sulfonylimino)-2'-phenyl-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ab):** Reaction time: 10 h, 1a (44 mg, 0.15 mmol), 2b (62 mg, 0.15 mmol), yield = 66%, 69 mg, Nature = viscous liquid, Rₜ-value: 0.26 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.49 (d, J = 9.1 Hz, 2H), 8.38 (d, J = 9.1 Hz, 2H), 8.15 (d, J = 8.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.19-7.15 (m, 4H), 7.10-706 (m, 3H), 6.91 (d, J = 8.4 Hz, 1H), 6.86-6.83 (m, 1H), 6.65 (d, J = 8.7 Hz, 2H), 4.95 (s, 1H), 4.33-4.25 (m, 1H), 4.20-4.12 (m, 1H), 3.94-3.80 (m, 2H), 3.66 (s, 3H), 3.59 (dd, J = 8.0, 6.4 Hz, 1H), 3.52-3.44 (m, 1H), 2.58 (dd, J = 7.2, 6.3 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H), 0.70 (t, J = 7.2 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 182.3, 171.9, 170.7, 169.6, 159.1, 150.1, 147.5, 139.9, 133.7, 130.2, 129.9, 129.4, 128.3, 128.1, 127.9, 125.7, 124.3, 122.3, 118.2, 113.6, 112.4, 101.5, 62.9, 62.3, 61.6, 60.1, 55.1, 54.2, 38.6, 14.0, 13.3. IR (υ, cm⁻¹) 2930, 1724, 1574, 1529, 1460, 1305, 1250, 1156, 1088, 1014, 903, 826, 701. HRMS (ESI) calcd for C₃₇H₃₅N₂O₁₀S⁺ [M+H]⁺; 699.2012 found 699.2010.
Diethyl(2R,2'R,5'R,E)-5'-(4-methoxyphenyl)-2'-((p-tolyl)-3-(tosylimino)-3H-spiro[benzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ac): Reaction time: 9 h, 1a (60 mg, 0.20 mmol), 2c (80 mg, 0.20 mmol), yield = 67%, 91 mg, Nature = viscous liquid. R<sub>t</sub>-value: 0.29 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.89-6.84 (m, 3H), 6.78 (t, J = 7.7 Hz, 1H), 6.63 (d, J = 8.7 Hz, 2H), 4.86 (s, 1H), 4.30-4.22 (m, 1H), 4.19-4.11 (m, 1H), 3.97-3.89 (m, 1H), 3.81 (t, J = 14.0 Hz, 1H), 3.65 (s, 3H), 3.61-3.49 (m, 2H), 2.55 (dd, J = 7.0, 6.5 Hz, 1H), 2.49 (s, 3H), 2.15 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.3 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 180.3, 171.9, 170.2, 170.0, 158.9, 143.4, 138.9, 137.2, 130.8, 130.3, 130.1, 129.6, 128.6, 127.0, 126.2, 121.8, 118.4, 113.4, 112.1, 101.4, 62.8, 62.0, 61.5, 59.7, 55.1, 54.0, 38.5, 21.7, 21.0, 14.0, 13.3. IR (υ, cm⁻¹) 2926, 1726, 1601, 1513, 1461, 1251, 1156, 1089, 1033, 826, 734. HRMS (ESI) calced for C₃₉H₄₅NO₈S⁺ [M+H]⁺; 682.2475 found 682.2463.

Diethyl(2R,2'R,5'R,E)-2'-(4-fluorophenyl)-5'-(4-methoxyphenyl)-3-(tosylimino)-3H-spiro[b enzofuran-2,1'-cyclopentane]-3',3'-dicarboxylate (3ad): Reaction time: 8 h, 1a (52 mg, 0.17 mmol), 2d (70 mg, 0.17 mmol), yield = 68%, 79 mg, Nature = viscous liquid. R<sub>t</sub>-value: 0.31 (Ethyl acetate/hexane) = 2:8. ¹H-NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.39-7.35 (m, 1H), 7.18-7.14 (m, 4H), 6.88 (d, J = 8.3 Hz, 1H), 6.84-6.80 (m, 1H), 6.75 (t, J = 7.7 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.88 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12 (m, 1H), 4.00-3.91 (m, 1H), 3.80 (t, J = 13.8 Hz, 1H), 3.66 (s, 3H), 3.61-3.51 (m, 2H), 2.57 (dd, J = 7.2, 6.5 Hz, 1H), 2.50 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.3 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 179.9, 171.8, 170.0, 169.8, 162.3 (d, J = 246.5 Hz), 159.0, 143.5, 139.0, 131.9 (d, J = 7.4 Hz), 130.4, 129.8 (d, J = 2.7 Hz, 129.6 (d, J = 6.0 Hz), 127.0, 126.2, 126.0, 122.1, 118.3, 114.9 (d, J = 20.8 Hz), 113.5, 112.1, 101.1, 62.7, 62.2, 61.6, 59.2, 55.1, 53.9, 38.4, 21.7, 14.0, 13.4. IR (υ, cm⁻¹) 2981, 1727, 1601, 1582, 1511, 1462, 1303, 1250, 1225, 1182, 1160, 1089, 1017, 880. HRMS (ESI) calced for C₃₉H₄₇NO₈FS⁺ [M+H]⁺; 686.2224 found 686.2209.
Diethyl(2R,2'R,5'R,E)-2′-(4-chlorophenyl)-5′-(4-methoxyphenyl)-3-(tosylimino)-3H-spiro[b enzofuran-2,1'-cyclopentane]-3′,3′-dicarboxylate (3ae): Reaction time: 7 h. 1a (50 mg, 0.17 mmol), 2e (71 mg, 0.17 mmol), yield = 69%, 78 mg, Nature = viscous liquid, Rf-value: 0.30 (Ethyl acetate/hexane) = 2:8. 1H-NMR (400 MHz, CDCl3) δ 8.24 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.42-7.36 (m, 3H), 7.18-7.12 (m, 4H), 7.04 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.5 Hz, 1H), 6.85-6.81 (m, 1H), 6.64 (d, J = 8.9 Hz, 2H), 4.86 (s, 1H), 4.31-4.23 (m, 1H), 4.20-4.12(m, 1H), 4.01-3.92 (m, 1H), 3.80 (t, J = 13.9, 1H), 3.66 (s, 3H), 3.62-3.52 (m, 2H), 2.57 (dd, J = 7.0, 6.7 Hz, 1H), 2.50 (s, 3H), 1.20 (t, J = 7.3 Hz, 3H), 0.79 (t, J = 7.2 Hz, 3H). 13C-NMR (100 MHz, CDCl3) δ 179.8, 171.7, 170.0, 169.7, 159.0, 143.5, 139.1, 133.7, 132.6, 131.6, 130.4, 129.6, 129.5, 128.1, 127.0, 125.8, 122.1, 118.3, 113.5, 112.1, 101.1, 62.7, 62.2, 61.7, 59.1, 55.1, 54.0, 38.4, 21.7, 14.0, 13.4. IR (μ, cm⁻¹) 2922, 1739, 1709, 1549, 1491, 1450, 1289, 1239, 1196, 1166, 1133, 969, 900, 805, 726. HRMS (ESI) calcd for C₃₈H₃₇ClN₂O₈S⁺ [M+Na]⁺; 724.1648 found 724.1681.

5.4.4 Procedure for the synthesis of (1'R,2'S,5'S)-diethyl 5′-(4-methoxyphenyl)-3-oxo-2′-phenyl-3H-spiro[benzofuran-2,1′-cyclopentane]-3′,3′-dicarboxylate (4ab): 3ab (80 mg) was dissolved in toluene (2 mL) and basic alumina (Brockmann activity I, 1.5 g) was added. The reaction mixture was refluxed for overnight. The reaction mixture was purified by silica gel column chromatography.

Reaction time: 14 h, 4ab (80 mg, 0.11 mmol), yield = 80%, 47 mg, Nature = white solid, Melting point = 115 °C, Rf-value: 0.30 (Ethyl acetate/hexane) = 2:8. 1H-NMR (400 MHz, CDCl3) δ 7.35-7.30 (m, 3H), 7.27-7.21 (m, 3H), 7.08-7.04 (m, 3H), 6.94 (d, J = 8.2 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 8.7 Hz, 2H), 4.92 (s, 1H), 4.34-4.19 (m, 2H), 3.95-3.87 (m, 1H), 3.80 (t, J = 14.4, 1H), 3.69-3.62 (m, 1H), 3.66 (s, 3H), 3.53-3.45 (m, 1H), 2.62 (dd, J = 7.0, 6.3 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H), 0.71 (t, J = 6.9 Hz, 3H). 13C-NMR (100 MHz, CDCl3) δ 200.5, 172.0, 171.3, 170.0, 158.8, 138.0, 134.3, 130.4, 129.7, 127.8, 127.5, 126.6, 123.8, 121.6, 121.4, 113.4, 112.8, 99.0, 63.2, 62.1, 61.5, 57.6, 55.1, 51.3, 38.9, 14.1, 13.3. IR (μ, cm⁻¹) 2923, 1724, 1611, 1514, 1461, 1245, 1218, 1178, 1098, 1030, 919, 870, 755, 702. HRMS (ESI) calcd for C₃₁H₃₁O₇⁺ [M+H]⁺; 515.2070 found 515.2065.
$^{1}H$-NMR (CDCl$_3$, 400 MHz)
HRMS Spectra of 3aa:

**Single Mass Analysis**
- Tolerance = 100.0 PPM  /  DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
- 24 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
- Elements Used:
  - C: 30-40  H: 31-40  N: 0-2  O: 0-8  S: 0-1
- Sample Name: 07-04-030  INDIAN INSTITUTE OF TECHNOLOGY
- Test Name: HRMS-1  ROPAR
- 260218-07-04-030 11 (0.122) AM  (Top,4, Ar,10000.0,0.00,0.00): Sm (Mn, 1x3.00); Cm (9:14)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>668.2334</td>
<td>668.2318</td>
<td>1.6</td>
<td>2.4</td>
<td>20.5</td>
<td>405.1</td>
<td>n/a</td>
<td>n/a</td>
<td>C38 H38 N O8 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ba:

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 30-40  H: 31-40  N: 0-2  O: 0-9  S: 0-1

Sample Name : 07-02-320
Test Name : HRMS-1
260218-07-02-320 11 (0.122) AM (Tbp, Ar, 10000.0, 0.00, 0.00); Sm (Mn, 1x3.00); Cm (11:13)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>698.2451</td>
<td>698.2424</td>
<td>2.7</td>
<td>3.9</td>
<td>20.5</td>
<td>345.4</td>
<td>n/a</td>
<td>n/a</td>
<td>C39 H40 N O9 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ca:

**Single Mass Analysis**
- Tolerance = 10.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated within limits (up to 50 closest results for each mass)

Elements Used:
- C: 35-40
- H: 31-42
- N: 0-2
- O: 0-10
- S: 0-1

Sample Name: 07-04-029
Test Name: HRMS-1

XEVO G2-XS QTOF
260218-07-04-029 11 (0.122) AM (Top, Ar, 10000.0.0.0.0.0.00); Sm (Mn, 1x3.00); Cm (4:23)

1: TOF MS ES+
8.29e+007

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>654.1741</td>
<td>654.1798</td>
<td>-5.7</td>
<td>-8.7</td>
<td>21.5</td>
<td>456.0</td>
<td>n/a</td>
<td>n/a</td>
<td>C36 H32 N O9 S</td>
</tr>
</tbody>
</table>
$^1$H-NMR (CDCl$_3$, 400 MHz)

X: parts per Million: 1H
HRMS Spectra of 3da:

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40  H: 31-42  N: 0-2  O: 0-10  S: 0-1
Sample Name : 15-01-026
Test Name : HRMS-1
260218-15-01-026 13 (0.140) AM (Te,4, Ar,10000,0,0.00,0.00); Sm (Mn, 1x3.00); Cm (13:18)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>728.2523</td>
<td>728.2529</td>
<td>-0.6</td>
<td>-0.8</td>
<td>29.5</td>
<td>348.2</td>
<td>n/a</td>
<td>n/a</td>
<td>C40 H42 N O10 S</td>
</tr>
</tbody>
</table>
$^{1}$H-NMR (CDCl$_3$, 400 MHz)

X: parts per Million: 1H
HRMS Spectra of 3ea:

**Single Mass Analysis**
- Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
- 34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
- Elements Used:
  - C: 35-40
  - H: 31-42
  - N: 0-2
  - O: 0-10
  - S: 0-1

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Test Name</th>
<th>INDIAN INSTITUTE OF TECHNOLOGY</th>
<th>XEVO G2-XS QTOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>07-04-033</td>
<td>HRMS-1</td>
<td>ROPAR</td>
<td></td>
</tr>
<tr>
<td>260218-07-04-033</td>
<td>11 (0.122) AM (Top, Ar, 10000.0, 0.00, 0.00); Sm (Mn, 1x3.00); Cm (6:19)</td>
<td>1: TOF MS ES+</td>
<td>1.71e+007</td>
</tr>
</tbody>
</table>

| Minimum: | -1.5 |
| Maximum: | 5.0  | 10.0 | 50.0 |

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>628.2000</td>
<td>628.2005</td>
<td>-0.5</td>
<td>-0.8</td>
<td>19.5</td>
<td>439.6</td>
<td>n/a</td>
<td>n/a</td>
<td>C35 H34 N O8 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3fa:

**Single Mass Analysis**

- **Tolerance** = 50.0 PPM / **DBE**: min = -1.5, max = 50.0
- **Element prediction**: Off
- **Number of isotope peaks used for i-FIT**: 3

**Monoisotopic Mass, Even Electron Ions**

33 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:
- C: 8-40
- H: 30-35
- N: 0-2
- O: 0-9
- S: 0-1

Sample Name: 07-04-120
Test Name: HRMS-1
030119-07-04-120 14 (0.148) AM2 (Ar,19000.0,0.00,0.00); Cm (14:19)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>707.2072</td>
<td>707.2063</td>
<td>0.9</td>
<td>1.3</td>
<td>23.5</td>
<td>364.6</td>
<td>n/a</td>
<td>n/a</td>
<td>C39 H35 N2 O9 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ga:

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-40  H: 31-42  N: 0-2  O: 0-10  S: 0-1
Sample Name: 15-01-027  INDIAN INSTITUTE OF TECHNOLOGY
Test Name: HRMS-1  ROPAR
260218-15-01-027 11 (0.123) AM (Top, 4, Ar, 10000.0, 0.00, 0.00); Sm (Mn, 1x3.00); Cm (6:18)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf (%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>652.2322</td>
<td>652.2369</td>
<td>-4.7</td>
<td>-7.2</td>
<td>20.5</td>
<td>418.2</td>
<td>n/a</td>
<td>n/a</td>
<td>C38 H38 N O7 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ha:

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
49 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

Sample Name: 07-04-136  I.T.ROPAR
Test Name: HRMS-1
190219-07-04-136 16 (0.165) AM (Top,4, Ar,10000.0,0.00,0.00); Cm (16:23)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>680.2656</td>
<td>680.2652</td>
<td>538.2933</td>
<td>569.3096</td>
<td>610.1821</td>
<td>680.1534</td>
<td>739.3342</td>
<td>767.3417</td>
<td>832.2256</td>
</tr>
</tbody>
</table>
$^1$H-NMR (CDCl$_3$, 400 MHz)
$^{13}$C-NMR (CDCl$_3$, 100 MHz)
HRMS Spectra of 3ia:

**Single Mass Analysis**
- Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
67 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:
C: 35-40   H: 35-42   N: 0-2   O: 0-7   Na: 0-1   S: 0-1   Cl: 0-1

Sample Name: 07-04-068
Test Name: HRMS-1
150518-07-04-068 16 (0.165) AM2 (Ar,16000.0,0.00,0.00); Cm (16:19)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>680.2658</td>
<td>680.2682</td>
<td>-2.4</td>
<td>-3.5</td>
<td>20.5</td>
<td>421.6</td>
<td>n/a</td>
<td>n/a</td>
<td>C40 H42 N O7 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ja:

**Single Mass Analysis**

- **Tolerance = 5.0 PPM** / **DBE: min = -1.5, max = 50.0**
- **Element prediction: Off**
- **Number of isotope peaks used for i-FIT = 3**

Monoisotopic Mass, Odd and Even Electron Ions:
26 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
- C: 35-39
- H: 30-35
- N: 0-1
- O: 0-7
- F: 0-1
- S: 0-1

Sample Name: 07-04-040
Test Name: HRMS-1
Lab: INDIAN INSTITUTE OF TECHNOLOGY
Instrument: ROCAR 070318-07-04-040 11 (0.1) AM (Top, Ar, 10000, 0.00, 0.00); Sm (Mn, 1x3.00); Cn (8:19)

**Mass** | **Calc. Mass** | **mDa** | **PPM** | **DBE** | **i-FIT** | **Norm** | **Conf(%)** | **Formula**
--- | --- | --- | --- | --- | --- | --- | --- | ---
656.2126 | 656.2118 | 0.8 | 1.2 | 20.5 | 372.9 | n/a | n/a | C37 H35 N O7 F 5
$^{13}$C-DEPT (CDCl$_3$, 100 MHz)
HRMS Spectra of 3ka:

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
Sample Name : 07-04-137  I.I.T.ROPAR
Test Name : HRMS-1
190219-07-04-137-17 (0.174) AM2 (Ar,21000,0,00,0,00); Cm (17:19)

**Results:**
- **Minimum:** -1.5
- **Maximum:** 5.0 5.0 50.0

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>638.2206</td>
<td>638.2212</td>
<td>-0.6</td>
<td>-0.9</td>
<td>20.5</td>
<td>446.8</td>
<td>n/a</td>
<td>n/a</td>
<td>C37 H36 N O7 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ab:

**Single Mass Analysis**
Tolerance = 15.0 PPM  /  DBE: min = -1.5, max = 50.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
37 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 35-39  H: 30-35  N: 0-2  O: 0-10  S: 0-1

Sample Name : 07-04-079  
Test Name : HRMS-1
210518-07-04-079 19 (0.203) AM2 (Ar,16000.0,0.00,0.00); Cm (19)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>699.2010</td>
<td>699.2012</td>
<td>-0.2</td>
<td>-0.3</td>
<td>21.5</td>
<td>205.2</td>
<td>n/a</td>
<td>n/a</td>
<td>C37 H35 N2 O10 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ac:

**Single Mass Analysis**
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
Sample Name : 07-04-055  I.I.T.ROPAR
Test Name : HRMS-1
010518-07-04-055 17 (0.174) AM (Top,4, Ar,10000.0,0.00,0.000.00): Cm (17:18)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>682.2463</td>
<td>682.2475</td>
<td>-1.2</td>
<td>-1.8</td>
<td>20.5</td>
<td>441.9</td>
<td>n/a</td>
<td>n/a</td>
<td>C39 H40 N O8 S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ad:

**Single Mass Analysis**
- Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron Ions**
58 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:
- C: 32-39
- H: 32-40
- N: 0-2
- O: 0-8
- F: 0-1
- S: 0-1

Sample Name: 07-04-050  
Test Name: HRMS-1
010518-07-04-050 15 (0.157) AM (Top,4, Ar,10000.0.00.00.00.00); Cm (15:18)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>686.2209</td>
<td>686.2224</td>
<td>-1.5</td>
<td>-2.2</td>
<td>20.5</td>
<td>562.0</td>
<td>n/a</td>
<td>n/a</td>
<td>C38 H37 N O8 F S</td>
</tr>
</tbody>
</table>
HRMS Spectra of 3ae:

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
112 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 35-40 H: 35-40 N: 0-2 O: 0-8 S: 0-1 Cl: 0-1 Na: 0-1

Sample Name: 07-04-067
Test Name: HRMS-1
150518-07-04-067 13 (0.140) AM2 (Ar,16000.0,0.00,0.00); Cm (13:18)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>724.1681</td>
<td>724.1748</td>
<td>-6.7</td>
<td>-9.3</td>
<td>20.5</td>
<td>255.6</td>
<td>n/a</td>
<td>n/a</td>
<td>C38 H36 N O8 S Cl Na</td>
</tr>
</tbody>
</table>
HRMS Spectra of 4ab:

**Single Mass Analysis**
- Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
- C: 25-35
- H: 31-35
- O: 0-7

Sample Name: 15-01-129  I.I.T.ROPAR
Test Name: HRMS-1
090818-15-01-129 19 (0.203) AM2 (Ar,19000.0,0.00,0.00); Cm (19)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>Norm</th>
<th>Conf(%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>515.2065</td>
<td>515.2070</td>
<td>-0.5</td>
<td>-1.0</td>
<td>16.5</td>
<td>353.2</td>
<td>n/a</td>
<td>n/a</td>
<td>C31 H31 O7</td>
</tr>
</tbody>
</table>
2. X-Ray diffraction:

For the determination of X-ray crystal structures of 3ba and 4ab a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program³ was used. Absorption correction was done applying SADABS program.⁴ The crystal structure was solved by SIR 92⁵ and refined by full matrix least square method using SHELXL-97⁶ WinGX system, Ver 1.70.01.⁷ All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters.

![ORTEP structure of 3ba]

**Figure 1:** ORTEP structure of 3ba

<table>
<thead>
<tr>
<th>CCDC No.</th>
<th>CCDC 1860991</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C39 H39 N O9 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>697.78</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>17.483(5), 8.483(5), 24.544(5)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>90, 97.103(5), 90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3612(2)</td>
</tr>
</tbody>
</table>
Table 1 Selected bond lengths [Å] of 3ba.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-O1</td>
<td>1.435(3)</td>
<td>C10-C11</td>
<td>1.373(7)</td>
</tr>
<tr>
<td>S1-O2</td>
<td>1.429(3)</td>
<td>C11-C12</td>
<td>1.379(7)</td>
</tr>
<tr>
<td>S1-N1</td>
<td>1.632(3)</td>
<td>C12-C13</td>
<td>1.362(6)</td>
</tr>
<tr>
<td>S1-C5</td>
<td>1.754(4)</td>
<td>C13-C14</td>
<td>1.382(5)</td>
</tr>
<tr>
<td>O3-C34</td>
<td>1.367(4)</td>
<td>C15-C16</td>
<td>1.542(4)</td>
</tr>
<tr>
<td>O3-C38</td>
<td>1.399(5)</td>
<td>C15-C19</td>
<td>1.531(4)</td>
</tr>
<tr>
<td>O4-C35</td>
<td>1.368(4)</td>
<td>C16-C17</td>
<td>1.525(4)</td>
</tr>
<tr>
<td>O4-C39</td>
<td>1.399(5)</td>
<td>C16-C32</td>
<td>1.516(4)</td>
</tr>
<tr>
<td>O5-C14</td>
<td>1.355(4)</td>
<td>C17-C18</td>
<td>1.541(4)</td>
</tr>
<tr>
<td>O5-C15</td>
<td>1.449(3)</td>
<td>C18-C19</td>
<td>1.573(4)</td>
</tr>
<tr>
<td>O6-C29</td>
<td>1.195(4)</td>
<td>C18-C26</td>
<td>1.523(4)</td>
</tr>
<tr>
<td>O7-C29</td>
<td>1.327(4)</td>
<td>C18-C29</td>
<td>1.524(4)</td>
</tr>
<tr>
<td>O7-C30</td>
<td>1.453(4)</td>
<td>C19-C20</td>
<td>1.508(4)</td>
</tr>
<tr>
<td>O8-C26</td>
<td>1.329(4)</td>
<td>C20-C21</td>
<td>1.389(5)</td>
</tr>
<tr>
<td>O8-C27</td>
<td>1.460(4)</td>
<td>C20-C25</td>
<td>1.382(5)</td>
</tr>
<tr>
<td>O9-C26</td>
<td>1.189(4)</td>
<td>C21-C22</td>
<td>1.374(5)</td>
</tr>
<tr>
<td>N1-C8</td>
<td>1.291(4)</td>
<td>C22-C23</td>
<td>1.364(6)</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{C1-C2} & \quad 1.505(6) & \text{C23-C24} & \quad 1.359(7) \\
\text{C2-C3} & \quad 1.364(6) & \text{C24-C25} & \quad 1.381(6) \\
\text{C2-C7} & \quad 1.365(6) & \text{C27-C28} & \quad 1.484(6) \\
\text{C3-C4} & \quad 1.380(6) & \text{C30-C31} & \quad 1.496(6) \\
\text{C4-C5} & \quad 1.378(5) & \text{C32-C33} & \quad 1.402(4) \\
\text{C5-C6} & \quad 1.369(5) & \text{C32-C37} & \quad 1.371(4) \\
\text{C6-C7} & \quad 1.374(6) & \text{C33-C34} & \quad 1.373(4) \\
\text{C8-C9} & \quad 1.439(5) & \text{C34-C35} & \quad 1.395(5) \\
\text{C8-C15} & \quad 1.511(4) & \text{C35-C36} & \quad 1.371(5) \\
\text{C9-C10} & \quad 1.402(5) & \text{C36-C37} & \quad 1.390(5) \\
\text{C9-C14} & \quad 1.386(5) & \text{C1-H1A} & \quad 0.9600 \\
\end{align*}
\]

**Table 2** Selected bond angles [°] of 3ba

\[
\begin{align*}
\text{O1-S1-O2} & \quad 116.93(17) & \text{C9-C10-C11} & \quad 118.3(4) \\
\text{O1-S1-N1} & \quad 108.61(14) & \text{C10-C11-C12} & \quad 120.6(4) \\
\text{O1-S1-C5} & \quad 108.30(16) & \text{C11-C12-C13} & \quad 122.7(4) \\
\text{O2-S1-N1} & \quad 112.23(15) & \text{C12-C13-C14} & \quad 116.7(3) \\
\text{O2-S1-C5} & \quad 108.95(15) & \text{O5-C14-C9} & \quad 114.5(3) \\
\text{N1-S1-C5} & \quad 106.50(14) & \text{O5-C14-C13} & \quad 122.9(3) \\
\text{C34-O3-C38} & \quad 118.4(3) & \text{C9-C14-C13} & \quad 122.6(3) \\
\text{C35-O4-C39} & \quad 117.4(3) & \text{O5-C15-C8} & \quad 105.6(2) \\
\text{C14-O5-C15} & \quad 106.9(2) & \text{O5-C15-C16} & \quad 107.6(2) \\
\text{C29-O7-C30} & \quad 116.0(3) & \text{O5-C15-C19} & \quad 112.9(2) \\
\text{C26-O8-C27} & \quad 117.9(2) & \text{C8-C15-C16} & \quad 113.4(2) \\
\text{S1-N1-C8} & \quad 124.1(2) & \text{C8-C15-C19} & \quad 114.2(2) \\
\text{C1-C2-C3} & \quad 121.5(4) & \text{C16-C15-C19} & \quad 103.2(2) \\
\text{C1-C2-C7} & \quad 121.8(4) & \text{C15-C16-C17} & \quad 101.6(2) \\
\text{C3-C2-C7} & \quad 116.8(4) & \text{C15-C16-C32} & \quad 115.5(2) \\
\text{C2-C3-C4} & \quad 122.1(4) & \text{C17-C16-C32} & \quad 116.2(2) \\
\text{C3-C4-C5} & \quad 119.9(4) & \text{C16-C17-C18} & \quad 105.4(2) \\
\text{S1-C5-C4} & \quad 117.6(3) & \text{C17-C18-C19} & \quad 104.7(2) \\
\text{S1-C5-C6} & \quad 123.6(3) & \text{C17-C18-C26} & \quad 109.3(2) \\
\end{align*}
\]
C4-C5-C6  118.8(3)  C17-C18-C29  111.4(2)  
C5-C6-C7  119.6(4)  C19-C18-C26  110.3(2)  
C2-C7-C6  122.8(4)  C19-C18-C29  111.8(2)  
N1-C8-C9  137.2(3)  C26-C18-C29  109.3(2)  
N1-C8-C15  116.8(3)  C15-C19-C18  105.4(2)  
C9-C8-C15  106.1(3)  C15-C19-C20  118.2(2)  
C8-C9-C10  134.5(3)  C18-C19-C20  117.2(2)  
C8-C9-C14  106.4(3)  C19-C20-C21  123.5(3)  
C10-C9-C14  119.1(3)  C19-C20-C25  118.5(3)  
C2-C20-C25  117.9(3)  C2-C1-H1C  109.00  
C20-C21-C22  120.7(3)  H1A-C1-H1B  109.00  
C21-C22-C23  120.3(4)  H1A-C1-H1C  110.00  
C22-C23-C24  120.2(4)  H1B-C1-H1C  109.00  
C23-C24-C25  120.1(4)  C2-C3-H3  119.00  
C20-C25-C24  120.8(4)  C4-C3-H3  119.00  
O8-C26-O9  123.5(3)  C3-C4-H4  120.00  
O8-C26-C18  110.7(3)  C5-C4-H4  120.00  
O9-C26-C18  125.7(3)  C5-C6-H6  120.00  
O8-C27-C28  106.9(3)  C7-C6-H6  120.00  
O6-C29-O7  124.6(3)  C2-C7-H7  119.00  
O6-C29-C18  124.9(3)  C6-C7-H7  119.00  
O7-C29-C18  110.5(3)  C9-C10-H10  121.00  
O7-C30-C31  106.8(3)  C11-C10-H10  121.00  
C16-C32-C33  120.4(2)  C10-C11-H11  120.00  
C16-C32-C37  122.1(3)  C12-C11-H11  120.00  
C33-C32-C37  117.6(3)  C11-C12-H12  119.00  
C32-C33-C34  121.5(3)  C13-C12-H12  119.00  
O3-C34-C33  125.3(3)  C12-C13-H13  122.00  
O3-C34-C35  114.7(3)  C14-C13-H13  122.00  
C33-C34-C35  120.0(3)  C15-C16-H16  108.00  
O4-C35-C34  116.1(3)  C17-C16-H16  108.00  
O4-C35-C36  125.0(3)  C32-C16-H16  108.00  
C34-C35-C36  118.9(3)  C16-C17-H17A  111.00
Figure 2: ORTEP structure of 4ab

<table>
<thead>
<tr>
<th>CCDC No.</th>
<th>CCDC 1862808</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C31H30O7</td>
</tr>
<tr>
<td>Formula weight</td>
<td>514.55</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>9.539, 9.870, 15.022</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>95.6, 97.2, 99.2</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1374.4(11)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Calculated Density (g/cm³)</td>
<td>1.243</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>0.088</td>
</tr>
<tr>
<td>F(000)</td>
<td>544</td>
</tr>
<tr>
<td>Theta range for data collection:</td>
<td>2.2 to 28.3</td>
</tr>
</tbody>
</table>
### Table 3 Selected bond lengths [Å] of 4ab.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-C4</td>
<td>1.445(4)</td>
<td>C16-C17</td>
<td>1.404(6)</td>
</tr>
<tr>
<td>O1-C31</td>
<td>1.364(4)</td>
<td>C18-C19</td>
<td>1.389(4)</td>
</tr>
<tr>
<td>O2-C25</td>
<td>1.211(4)</td>
<td>C19-C20</td>
<td>1.365(5)</td>
</tr>
<tr>
<td>O3-C15</td>
<td>1.199(4)</td>
<td>C20-C21</td>
<td>1.366(5)</td>
</tr>
<tr>
<td>O4-C15</td>
<td>1.333(4)</td>
<td>C21-C22</td>
<td>1.387(5)</td>
</tr>
<tr>
<td>O4-C16</td>
<td>1.458(5)</td>
<td>C22-C23</td>
<td>1.382(6)</td>
</tr>
<tr>
<td>O5-C12</td>
<td>1.326(4)</td>
<td>C25-C24</td>
<td>1.440(5)</td>
</tr>
<tr>
<td>O5-C13</td>
<td>1.452(7)</td>
<td>C26-C27</td>
<td>1.403(5)</td>
</tr>
<tr>
<td>O6-C12</td>
<td>1.194(4)</td>
<td>C26-C28</td>
<td>1.355(7)</td>
</tr>
<tr>
<td>O7-C21</td>
<td>1.369(4)</td>
<td>C28-C29</td>
<td>1.384(8)</td>
</tr>
<tr>
<td>O7-C24</td>
<td>1.406(5)</td>
<td>C29-C30</td>
<td>1.379(7)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.545(4)</td>
<td>C30-C31</td>
<td>1.377(5)</td>
</tr>
<tr>
<td>C1-C5</td>
<td>1.585(4)</td>
<td>C2-H2A</td>
<td>0.9700</td>
</tr>
<tr>
<td>C1-C15</td>
<td>1.515(4)</td>
<td>C2-H2B</td>
<td>0.9700</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.525(4)</td>
<td>C3-H3</td>
<td>0.9800</td>
</tr>
<tr>
<td>C3-C18</td>
<td>1.503(4)</td>
<td>C5-H5</td>
<td>0.9800</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.526(4)</td>
<td>C7-H7</td>
<td>0.9300</td>
</tr>
<tr>
<td>C4-C25</td>
<td>1.529(4)</td>
<td>C8-H8</td>
<td>0.9300</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.504(4)</td>
<td>C9-H9</td>
<td>0.9300</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.391(5)</td>
<td>C10-H10</td>
<td>0.9300</td>
</tr>
<tr>
<td>Bond Length</td>
<td>Bond Angle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6-C11</td>
<td>1.376(5)</td>
<td>C11-H11</td>
<td>0.9300</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.383(5)</td>
<td>C13-H13A</td>
<td>0.9700</td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.366(7)</td>
<td>C13-H13B</td>
<td>0.9700</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.367(6)</td>
<td>C14-H14A</td>
<td>0.9600</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.390(6)</td>
<td>C14-H14B</td>
<td>0.9600</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.295(9)</td>
<td>C14-H14C</td>
<td>0.9600</td>
</tr>
</tbody>
</table>

**Table 4** Selected bond angles [°] of 4ab.

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-O1-C31</td>
<td>108.2(2)</td>
</tr>
<tr>
<td>C15-O4-C16</td>
<td>119.0(3)</td>
</tr>
<tr>
<td>C12-O5-C13</td>
<td>116.7(3)</td>
</tr>
<tr>
<td>C21-O7-C24</td>
<td>118.9(3)</td>
</tr>
<tr>
<td>C2-C1-C5</td>
<td>104.6(2)</td>
</tr>
<tr>
<td>C2-C1-C12</td>
<td>111.8(2)</td>
</tr>
<tr>
<td>C2-C1-C15</td>
<td>108.3(2)</td>
</tr>
<tr>
<td>C5-C1-C12</td>
<td>111.5(2)</td>
</tr>
<tr>
<td>C5-C1-C15</td>
<td>110.5(2)</td>
</tr>
<tr>
<td>C12-C1-C15</td>
<td>110.0(2)</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>105.4(2)</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>101.1(2)</td>
</tr>
<tr>
<td>C2-C3-C18</td>
<td>117.3(2)</td>
</tr>
<tr>
<td>C4-C3-C18</td>
<td>116.0(2)</td>
</tr>
<tr>
<td>O1-C4-C3</td>
<td>109.2(2)</td>
</tr>
<tr>
<td>O1-C4-C5</td>
<td>112.8(2)</td>
</tr>
<tr>
<td>O1-C4-C25</td>
<td>105.0(2)</td>
</tr>
<tr>
<td>C3-C4-C5</td>
<td>103.0(2)</td>
</tr>
<tr>
<td>C3-C4-C25</td>
<td>112.7(2)</td>
</tr>
<tr>
<td>C5-C4-C25</td>
<td>114.2(2)</td>
</tr>
<tr>
<td>C1-C5-C4</td>
<td>104.7(2)</td>
</tr>
<tr>
<td>C1-C5-C6</td>
<td>118.2(2)</td>
</tr>
<tr>
<td>C4-C5-C6</td>
<td>117.9(2)</td>
</tr>
<tr>
<td>C5-C6-C7</td>
<td>123.8(3)</td>
</tr>
</tbody>
</table>
C5-C6-C11  119.2(3)  C25-C26-C27  133.9(3)
C7-C6-C11  117.1(3)  C25-C26-C31  107.1(3)
C6-C7-C8  121.2(4)  C27-C26-C31  119.0(3)
C7-C8-C9  120.6(4)  C26-C27-C28  118.7(4)
C27-C28-C29  121.0(5)  O5-C13-H13B  108.00
C28-C29-C30  122.0(5)  C14-C13-H13A  108.00
C29-C30-C31  116.4(4)  C14-C13-H13B  108.00
O1-C31-C26  113.6(3)  H13A-C13-H13B  107.00
O1-C31-C30  123.5(3)  C13-C14-H14A  109.00
C26-C31-C30  122.8(3)  C13-C14-H14B  109.00

Reference:


