Supporting Information

InCl$_3$-catalyzed Prins bicyclization for the synthesis of spirotetrahydropyran derivatives

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Experimental section:

**General.** All solvents were dried according to standard literature procedures. Reactions were performed in oven-dried round bottom flasks, and the flasks were fitted with rubber septa and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of \( p \)-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. IR spectra were recorded on FT-IR spectrometer. \(^1\)H and \(^{13}\)C NMR (proton-decoupled) spectra were recorded in CDCl\(_3\) solvent on 200, 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (\( \delta \)) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (\( J \)) are quoted in hertz (Hz). Mass spectra were recorded on mass spectrometer by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

**Preparation of the starting material for Table 1:**

![Chemical Structures](image-url)
To a stirred mixture of **A** (3.0 g, 9.2 mmol), **B** (1.01 g, 9.2 mmol) in 30 mL of dry acetonitrile was added potassium carbonate (2.50 g, 18.4 mmol). The resulting mixture was stirred under reflux for 8 h. After completion of the reaction, as indicated by TLC, the mixture was filtered and the filtrate was evaporated on rotary evaporator. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/n-hexane gradient mixture to afford the pure product **C** in 75% yield as colorless liquid; Yield 2.12 g, 75%; ¹H NMR (300 MHz, CDCl₃): δ 6.98-675 (m, 4H), 5.17 (s, 1H), 5.06 (s, 1H), 5.81 (s, 1H), 4.57 (s, 2H), 3.79 (t, J = 6.6 Hz, 2H), 2.37 (t, J = 6.2Hz, 2H), 0.9 (s, 9H), 0.06 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ145.9, 145.7, 142.1, 121.6, 119.9, 114.6, 114.0, 112.4, 72.0, 62.3, 36.6, 25.8, 18.2, -5.3; IR (KBr): ν 3446, 2950, 2904, 2840, 1735, 1656, 1516, 1282, 1037, 793, 745, 548; MS-ESI: m/z 309.1 [M+H]+.

To a solution of **C** (2.0 g, 6.4 mmol) in THF at 0 °C was added TBAF (9.7 mmol) dropwise and the resulting mixture was allowed to stir at rt for 1 h. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with a sat. solution of NaHCO₃ and the aqueous layer was extracted with ethyl acetate. Removal of the solvent followed by purification on silica gel column chromatography (silica gel, 60-120 mesh) using ethyl acetate/n-hexane gradient mixture afforded the pure product **1** in 95% yield as a white solid; Yield 1.18 g, 95%; m.p. 90-92°C; ¹H NMR (300 MHz, CDCl₃): ¹H NMR (300 MHz, CDCl₃): δ 6.91-6.70 (m, 4H), 6.23 (b s, 1H), 5.23 (s, 1H), 5.12 (s, 1H), 4.53 (s, 2H), 3.82 (t, J = 6.0Hz, 2H), 2.44 (t, J = 6.0Hz, 2H), 1.91 (b s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 146.1, 145.7, 141.6, 121.9, 119.9, 115.7, 115.0, 112.7, 72.3, 61.2, 36.3; IR (neat): ν 3480, 3115, 2925, 1743, 1595, 1394, 1245, 1109, 1006, 901, 741,557; MS-ESI: m/z 195.1 [M+H]+; HRMS ( ESI) calcd for C₁₁H₁₅O₃ [M+H]+: 195.1015 Found: 195.1020.
General experimental procedure for the Prins Cyclisation Table 1:

To a mixture of 2-(4-hydroxy-2-methylenebutoxy)phenol (0.5 mmol) and benzaldehyde (0.6 mmol) in anhydrous 1,2-DCE (5 mL) was added InCl₃ (10 mol%) at 0 °C. The resulting mixture was allowed to stir at room temperature under nitrogen atmosphere for the specified time (Table 1). After completion of the reaction, the reaction mixture was quenched with NaHCO₃ solution and then extracted with dichloromethane (2x5 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated on rotary evaporator. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product 3a (Table 1, entry a).

![Table 1, 3a](image)

3a: 2'-{(4-Bromophenyl)}-2',3',5',6'-tetrahydro-3H-spiro[benzo[b][1,4]dioxide-2,4'-pyran]:

Solid; Yield 81%; m.p. 160-162°C; ¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9Hz, 2H), 6.91-6.80 (m, 4H), 4.41 (dd, J = 11.9, 2.0 Hz, 1H), 4.31 (d, J = 10.9 Hz, 1H), 4.24-4.16 (m, 2H), 3.68 (td, J = 12.9, 2.9Hz, 1H), 2.17-2.12 (m, 1H), 2.05-1.97 (m, 1H), 1.84-1.76 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 142.2, 142.0, 140.3, 131.5, 127.5, 122.0, 121.6, 121.2, 117.6, 116.8, 76.0, 72.1, 67.1, 64.8, 39.8, 32.6; IR (KBr): ν 3446, 2923, 2853, 1591, 1491, 1247, 1088, 927, 758; MS-ESI: m/z 383.3 [M+Na]⁺; HRMS ( ESI) calcd for C₁₈H₁₈BrO₃ [M+H]⁺: 361.0432 Found: 361.0427.
3b: 2'-Phenyl-2',3',5',6'-tetrahydro-3H-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Viscous liquid; Yield 75%; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.43-7.25 (m, 5H), 6.93-6.81 (m, 4H), 4.46 (d, $J = 11.0$ Hz, 1H), 4.34 (d, $J = 11.0$ Hz, 1H), 4.28-4.19 (m, 2H), 3.71 (td, $J = 12.2$, 2.2 Hz, 1H), 2.21-2.15 (m, 1H), 2.09-1.99 (m, 1H), 1.98-1.85 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 142.3, 142.1, 141.2, 128.4, 127.8, 125.8, 121.9, 121.3, 117.6, 116.7, 76.8, 72.3, 67.2, 64.8, 39.9, 32.6; IR (KBr): $\nu$ 3442, 2924, 2854, 1743, 1594, 1492, 1263, 1091, 1042, 802, 755; MS-ESI: $m/z$ 305.3 [M+Na$^+$]; HRMS ( ESI) calcd for C$_{18}$H$_{19}$O$_3$ [M+H$^+$]: 283.1072  Found: 283.1077.

3c: 2'-(4-Nitrophenyl)-2',3',5',6'-tetrahydro-3H-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Solid; Yield 70%; m.p. 120-122°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.02-6.96 (m, 3H), 6.91-6.86 (m, 1H), 4.58 (dd, $J = 11.7$, 2.1 Hz, 1H), 4.53 (d, $J = 10.6$ Hz, 1H), 4.43 (d, $J = 10.6$ Hz, 1H), 4.17 (ddd, $J = 12.5$, 4.8, 1.9 Hz, 1H), 3.77 (td, $J = 12.0$, 3.3 Hz, 1H), 2.60 (dt, $J = 13.8$, 4.1Hz, 1H), 2.45-2.34 (m, 2H), 2.19-2.12 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 148.0, 147.4, 146.4, 145.4, 126.3, 123.7, 123.3, 120.3, 115.6, 114.0, 75.6, 72.8, 67.4, 65.0, 44.8, 37.3; IR (KBr): $\nu$ 3445, 2956, 2856, 1596, 1491, 1355, 1249,
1166, 1091, 946, 752, 664, 575, 541; MS-ESI: \( m/z \) 327.1 [M+H]^+; HRMS (ESI) calcd for \( \text{C}_{18}\text{H}_{18}\text{O}_5\text{N} \) [M+H]^+: 328.1174 Found: 328.1162.

![Table 1, 3d](image)

**3d: 2'-Isopropyl-2',3',5',6'-tetrahydro-3\text{H}-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:**

Liquid; Yield 72%; ¹H NMR (300 MHz, CDCl₃): \( \delta \) 6.92-6.80 (m, 4H), 4.22-4.09 (m, 2H), 4.08-3.99 (m, 1H), 3.54-3.43 (m, 1H) 3.11 (ddd, \( J = 12.0, 6.0, 2.2 \) Hz,1H), 1.94-1.81(m, 2H), 1.79-1.67 (m, 1H), 1.63-1.52 (m, 2H), 0.93 (dd, \( J = 12.0, 6.7 \) Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): \( \delta \) 142.4, 142.3, 121.9, 120.9, 117.6, 116.7, 79.4, 72.5, 67.4, 64.3, 35.1, 32.9, 32.7, 18.3, 18.2; IR (KBr): \( \nu \) 3446, 2958, 2924, 2852, 1594, 1493, 1465, 1262, 1107, 1044, 747, 619; MS-ESI: \( m/z \) 249.1 [M+H]^+; HRMS (Orbitrap ESI) calcd for \( \text{C}_{15}\text{H}_{21}\text{O}_3 \) [M+H]^+: 249.1495 Found: 249.1437.

![Table 1, 3e](image)

**3e: 2'-(Naphthalen-2-yl)-2',3',5',6'-tetrahydro-3\text{H}-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:**

Solid; Yield 70%; m.p. 159-161°C; ¹H NMR (500 MHz, CDCl₃): \( \delta \) 7.84-7.78 (m, 4H), 7.50-7.43 (m, 3H), 6.93-6.81 (m, 4H), 4.62 (dd, \( J = 12.1, 1.73 \) Hz, 1H), 4.37 (d, \( J = 12.1 \) Hz, 1H), 4.31-4.22 (m, 2H) 3.76 (td, \( J = 12.9, 2.5 \) Hz, 1H), 2.29-2.23 (m, 1H), 2.12-2.02 (m, 1H), 2.01-1.93 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): \( \delta \) 142.6, 141.7, 139.4, 133.2, 132.9, 128.1, 127.9,
127.6, 126.0, 125.7, 124.4, 124.0, 121.9, 121.3, 117.7, 117.0, 74.2, 71.8, 71.4, 63.3, 39.2, 31.1;
IR (KBr): ν 3443, 3051, 2962, 2853, 1592, 1504, 1338, 1164, 1092, 975, 890, 766, 652, 542;
MS-ESI: m/z 333.1 [M+H]+; HRMS (ESI) calcd for C_{22}H_{21}O_{3} [M+H]+: 333.1480 Found: 333.1462.

**Preparation of the starting material for Table 3:**

![Diagram](attachment:reaction.png)

To a solution of **D** (2.5 g, 11.5 mmol), **E** (8.2 g, 13.8 mmol) and triphenylphosphine (3.6 g, 13.8 mmol) in dry THF at 0 °C was added diethyl azodicarboxylate (2.4 g, 13.8 mmol) dropwise over 10 min. The resulting mixture was stirred at rt for 6h. After completion of the reaction, as indicated by TLC, the solvent was evaporated on rotary evaporator and the resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product **F** in 64% yield as a colourless liquid.
Yield 4.21 g, 64%; **1**H NMR (500 MHz, CDCl3): δ 7.56 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.17-7.12 (m, 1H), 6.99-6.96 (m, 1H), 6.84-6.80 (m, 2H), 4.84 (s, 1H), 4.77 (s, 1H), 4.17 (s, 2H), 3.68 (t, J = 6.4 Hz, 2H), 2.40 (s, 3H), 2.26 (t, J = 6.1 Hz, 2H), 0.95 (s, 9H), 0.86 (s, 9H), 0.22 (s, 6H), 0.02 (s, 6H); **13**C NMR (125 MHz, CDCl3): δ 153.5, 142.7, 141.7, 137.4, 131.4, 129.2, 129.0, 128.9, 127.6, 120.4, 119.1, 115.1, 61.5, 54.9, 36.4, 25.9, 25.8, 21.4, 18.3, 18.2,
5.3,-4.2; IR (KBr): ν 3447, 3070, 2931, 2858, 1492, 1339, 1159, 1108, 818, 704, 581, 505; MS-ESI: m/z 576.29 [M+H⁺].

To a solution of F (4.0 g, 6.9 mmol) in dry THF at 0 °C was added TBAF (20.8 mmol) dropwise and the mixture was allowed to stir at rt for 1h. After completion of the reaction indicated by TLC, the reaction mixture was quenched with a sat. solution of NaHCO₃ and the aqueous layer was extracted with ethyl acetate. Removal of the solvent followed by purification on silica gel column chromatography (silica gel, 60-120 mesh) using ethyl acetate/hexane gradient mixture afforded the pure product 4 in 90% yield as pale yellow solid; Yield 2.17 g, 90%; m.p. 103-105°C; ¹H NMR (500 MHz, CDCl₃): δ 7.52 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.20-7.15 (m, 1H), 7.02 (dd, J = 8.0, 1.3 Hz, 1H), 6.72-6.67 (m, 1H), 6.37 (dd, J = 8.0, 1.5, Hz, 1H), 4.89 (s, 1H), 4.79 (s, 1H), 3.91-3.81 (m, 2H), 2.47-2.37 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 155.1, 144.2, 140.1, 133.5, 129.7, 129.5, 128.0, 127.3, 125.9, 120.2, 117.9, 117.5, 60.8, 56.8, 36.6, 21.5; IR (neat): ν 3575, 3267, 2958, 2925, 1592, 1492, 1339, 1215, 1156, 1040, 891, 757, 699, 579; MS-ESI: m/z 348.07 [M+H⁺]; HRMS (ESI) calcd for C₁₈H₂₂NO₄S [M+H⁺]: 348.1269 Found: 348.1249.

**General procedure for the Prins cyclisation for Table 3:**

To a mixture of N-(4-hydroxy-2-methylenebutyl)-N-(2-hydroxyphenyl)-4-methylbenzenesulfonamide (0.5 mmol) and benzaldehyde (0.6 mmol) in anhydrous 1,2-DCE (5 ml) was added at InCl₃ (10 mol%) at -20 °C. The resulting mixture was allowed to stir at the same temperature under nitrogen atmosphere for the specified time (Table 3). After completion, the reaction mixture was quenched with NaHCO₃ solution and then extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄ and concentrated on
rotary evaporator. The crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product 5a (Table 2, entry a).

![Table 3, 5a](image)

**5a:** 2’-(4-Chlorophenyl)-4-tosyl-2,3,3’,4,5’,6’-hexahydropyrano[benzo[b][1,4]oxazine-2,4’-pyran] (major diastereomer):

Solid; Yield 85%; m.p. 107-109°C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.40 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.35-7.28 (m, 6H), 6.96-6.92 (m, 1H), 6.85-6.78 (m, 2H), 4.61 (dd, $J = 11.8$, 1.9 Hz, 1H), 4.32 (d, $J = 12.9$ Hz, 1H), 4.20 (ddd, $J = 12.3$, 5.3, 1.3 Hz, 1H), 3.87-3.74 (m, 2H), 2.43 (s, 3H), 2.17 (dt, $J = 13.5$, 4.42 Hz, 1H), 2.11-2.03 (m, 1H), 1.90-1.77 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 144.1, 144.0, 139.9, 137.5, 133.3, 130.0, 128.5, 127.2, 126.6, 124.6, 124.1, 120.6, 119.0, 118.1, 75.7, 73.5, 64.6, 48.6, 41.0, 33.9, 21.5; IR (KBr): ν 3453, 2925, 2855, 1593, 1491, 1350, 1253, 1164, 1090, 947, 751, 661, 573, 543; MS-ESI: m/z 470.06 [M+H]$^+$; HRMS (ESI) calcd for C$_{25}$H$_{25}$O$_4$NCIS [M+H]$^+$: 470.0987 Found: 470.0999.

![Table 3, 5b](image)
5b: 2'-(p-Tolyl)-4-tosyl-2',3',3',4',5',6'-hexahydrospiro[benzo[b][1,4]oxazine-2,4'-pyran] (major diastereomer):

Solid; Yield 82%; m.p. 146-148°C; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, J = 8.3 Hz, 2H), 7.46 (dd, J = 8.3, 1.5 Hz, 1H), 7.32-7.25 (m, 4H), 7.15 (d, J = 7.7 Hz, 2H), 6.95-6.91 (m, 1H), 6.85-6.78 (m, 2H), 4.56 (dd, J = 12.0, 1.9 Hz, 1H) 4.21-4.15 (m, 2H), 3.96 (d, J = 12.8 Hz, 1H), 3.80 (td, J = 12.8, 2.2 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.11 (dt, J = 13.7, 4.4 Hz, 1H), 2.07-2.00 (m, 1H), 1.93-1.84 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 144.1, 138.2, 137.4, 137.3, 129.9, 129.0, 126.7, 125.8, 124.5, 124.2, 120.6, 118.9, 118.1, 76.4, 73.6, 64.7, 48.7, 41.1, 33.8, 21.5, 21.1; IR (KBr): ν 3456, 2924, 2855, 1589, 1492, 1350, 1253, 1164, 1094, 812, 751, 662, 572, 540; MS-ESI: m/z 450.07 [M+H]+; HRMS (ESI) calcd for C₂₆H₂₈O₄NS [M+H]+: 450.1734 Found: 450.1740.

Table 3, 5c

5c: 2'-(4-Nitrophenyl)-4-tosyl-2',3',3',4',5',6'-hexahydrospiro[benzo[b][1,4]oxazine-2,4'-pyran] (major diastereomer):

Solid; Yield 78%; m.p. 185-187°C; ¹H NMR (300 MHz, CDCl₃): δ 8.19 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.32 (dd, J = 11.8, 1.3Hz, 1H), 6.97-6.93 (m, 1H), 6.84-6.78 (m, 2H), 4.79 (dd, J = 11.8, 1.8 Hz, 1H), 4.52 (d, J = 13.1 Hz, 1H), 4.26 (ddd, J = 12.3, 5.3 ,1.3 Hz,1H), 3.83 (td, J = 12.8, 2.2 Hz, 1H), 3.69 (dd, J = 13.1, 0.7 Hz, 1H), 2.45 (s, 3H), 2.31 (dt, J = 13.5, 4.2 Hz 1H), 2.18-2.10 (m, 1H), 1.91-1.86 (m,
1H), 1.77-1.70 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.8, 147.2, 144.3, 144.0, 137.7, 130.1, 126.6, 126.4, 124.7, 124.0, 123.6, 120.7, 119.2, 118.1, 75.3, 73.3, 64.6, 48.5, 40.8, 39.1, 21.5; IR (KBr): v 3448, 2997, 2859, 1521, 1493, 1346, 1160, 1091, 809, 658, 578, 543; MS-ESI: m/z 481.21 [M+H]$^+$; HRMS (ESI) calcd for C$_{25}$H$_{24}$N$_2$O$_6$NaS [M +Na]$^+$: 503.1252 Found: 503.1270.

Table 3, 5d

5d: 2'-Isobutyl-4-tosyl-2',3',3',4,5',6'-hexahydrospiro[benzo[b][1,4]oxazine-2,4'-pyran]
(major diastereomer):

Solid; Yield 75%; m.p. 121-123°C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J =$ 8.3 Hz, 2H), 7.47 (dd, $J =$ 8.3, 1.5 Hz, 1H), 7.32 (d, $J =$ 7.9 Hz, 2H), 6.96-6.92 (m, 1H), 6.86-6.78 (m, 2H), 4.04-3.95 (m, 3H), 3.64-3.54 (m, 2H), 2.42 (s, 3H), 2.48-1.77 (m, 3H), 1.58-1.50 (m, 2H), 1.26-1.17 (m, 2H), 0.95-0.96 (d, $J =$6.5 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.1, 144.0, 137.3, 129.9, 126.7, 124.4, 124.2, 120.5, 118.8, 118.1, 73.4, 72.5, 64.1, 48.9, 45.2, 39.9, 33.9, 24.3, 23.2, 22.2, 21.5; IR (KBr): v 3450, 2955, 2925, 2867, 1599, 1492, 1353, 1261, 1166, 1093, 947, 813, 750, 665, 574, 541; MS-ESI: m/z 416.1 [M+H]$^+$; HRMS (ESI) calcd for C$_{23}$H$_{30}$O$_4$NS [M+H]$^+$: 416.1881 Found: 416.1890.

Table 3, 5e
5e: 2’-(3,4-Dimethoxyphenyl)-4-tosyl-2’3,3′4,5′6′-hexahydrospiro[benzo[b][1,4]oxazine-2,4’-pyran] (major diastereomer):

Semisolid; Yield 65%; 1H NMR (300 MHz, CDCl₃): δ 7.81 (d, J = 8.2 Hz, 2H), 7.42 (dd, J = 8.3, 1.3 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 6.99-6.90 (m, 3H), 6.87-6.78 (m, 3H), 4.57 (dd, J = 11.9, 1.8 Hz, 1H), 4.25 (d, J = 12.9 Hz, 1H), 4.22-4.17 (m, 1H), 4.04-3.99 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.85-3.80 (m, 1H), 2.42 (s, 3H), 2.17-2.12 (m, 1H), 2.10-2.00 (m, 1H), 1.91-1.79 (m, 2H); 13C NMR (125 MHz, CDCl₃): δ 148.9, 148.4, 144.1, 143.6, 136.9, 134.4, 129.8, 126.8, 124.5, 120.9, 124.4, 119.4, 118.2, 110.9, 109.2, 74.2, 72.3, 63.2, 55.9, 53.1, 55.8, 40.5, 32.4, 21.4; IR (KBr): v 3450, 2925, 2859, 1594, 1491, 1350, 1256, 1164, 1088, 1032, 810, 753, 665, 572, 542; MS-ESI: m/z 496.1 [M+H]+; HRMS (ESI) calcd for C₂₇H₂₉NO₆NaS [M+Na]+: 518.1613 Found: 518.1632.
2D Double Quantum Coherence Spectrum (DQFCOSY) of compound 3a
2D Nuclear Overhauser effect spectrum (NOESY) of compound 3a
2D Double Quantum Coherence Spectrum (DQFCOSY) of compound 5e
2D Nuclear Overhauser effect spectrum (NOESY) of compound 5e
Table 1, 3c

$^1$H NMR

Table 1, 3c

$^{13}$C NMR
Table 1, 3d
$^1$H NMR

Table 1, 3d
$^{13}$C NMR
Table 3, 5a

$^1$H NMR

Table 3, 5a

$^{13}$C NMR
Table 3, 5b

$^{1}$H NMR

Table 3, 5b

$^{13}$C NMR
Table 3, 5d

$^1$H NMR

Table 3, 5d

$^{13}$C NMR
Table 3, 5e

$^1$H NMR

Table 3, 5e

$^{13}$C NMR