One-pot synthesis of benzothiazolines and napthathiazolines via cascade ortho-lithiation, cyclisation and elimination of N-arylsulfonyl lactams


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General method for N-alkylsulfonyl protection of lactams.

To a cold (0 °C) solution of lactam (0.34 M, 1.0 eq) in dry THF was added a solution
of n-BuLi (1.6 M, 1.1 eq) via a syringe and the reaction mixture was stirred at 0 °C for
1 h (white precipitate (salt) forms). To this was added a cold (0 °C) solution of
arylsulfonyl chloride (1.0 M, 1.3 eq) in dry THF via cannula. The reaction mixture was
stirred at 0 °C and followed by TLC or LCMS until all the starting material was
consumed. The reaction was warmed to room temperature and concentrated in
vacuo, the crude material was taken into DCM, washed with water (3x), dried over
MgSO4 and concentrated under reduced pressure.

N-[(4'-methylphenyl)sulfonyl]pyrrolidin-2-one 4b

Crude material collected as a pale brown/orange solid. Purification by flash
chromatography ([7:3] pet. ether/ethyl acetate) afforded the title compound as a white
solid (2.33 g, 9.74 mmol, 65%). mp 139-141 °C. νmax (KBr) 3028, 1737 (C=O), 1598,
1359 (NSO2), 1238, 1217, 1169 (NSO2), 1121, 957, 662, 596, 558 cm⁻¹. δH (500MHz,
CDCl3) 2.06 (2H, t, J = 8 Hz, 4-H2), 2.39-2.47 (5H, m, 4'-CH3, 3-H2), 3.88 (2H, t,
J = 7 Hz, 5-H2), 7.33 (2H, d, J = 8 Hz, 3'-H, 5'-H), 7.91 (2H, d, J = 8 Hz, 2'-H, 6'-H).
δC (125MHz, CDCl3) 18.4 (C-4), 21.2 (4'-CH3), 32.5 (C-3), 47.5 (C-5), 128.3 (C-2'),
558 cm⁻¹
129.9 (C-3’), 135.3 (C-1’), 145.5 (C-4’), 173.7 (CO). m/z (ES+) 240 (MH+). HRMS (ES) found MH+ 240.0691, C₁₁H₁₄NO₃S requires M+ 240.0689, found MNa+ 262.0509, C₁₁H₁₃NO₃SNa requires M+ 262.0508.

\[ N-\{[4’-methylphenyl]sulfonyl\}piperidin-2-one 4c \]

Crude material collected as a colourless oil which solidified on standing. Purification by flash chromatography ([7:3] pet. ether/ethyl acetate) afforded the title compound as a white solid (2.02 g, 7.9 mmol, 33%). mp 136-138 °C. Found; C, 56.87; H, 5.97; N, 5.37%; Calc. for C₁₂H₁₅NO₃S; C, 56.90; H, 5.97; N, 5.53%. \( \nu_{\max} \) (KBr) 2958, 1691 (C=O), 1457, 1354 (NSO₂), 1283, 1171 (NSO₂), 1089, 969, 830, 577, 549 cm⁻¹. \( \delta_h \) (400MHz, CDCl₃) 1.74 (2H, quintet, J = 6 Hz, 4-H₂), 1.87 (2H, quintet, J = 6 Hz, 5-H₂), 2.28-2.48 (5H, m, 3-H₂, 4’-CH₃), 3.88 (2H, t, J = 6 Hz, 6-H₂), 7.28 (2H, d, J = 8 Hz, 3’-H, 5’-H), 7.87 (2H, d, J = 8 Hz, 2’-H, 6’-H). \( \delta_c \) (100MHz, CDCl₃) 21.9 (4’-CH₃), 23.5 (C-5), 34.3 (C-3), 47.2 (C-6), 128.9 (C-2’), 129.5 (C-3’), 136.3 (C-1’), 145.0 (C-4’), 170.5 (CO). m/z (ES+) 254.1 (MH+), 276.1 (MNa+), 308.1 (MNaMeOH+), 529 (2MNa+). HRMS (ES) found MH+ 254.0847, C₁₂H₁₆NO₃S requires M+ 254.0845, found MNa+ 276.0666, C₁₂H₁₅NO₃SNa requires M+ 276.0665.

\[ N-\{[4’-methylphenyl]sulfonyl\}2-oxoazocine 4d \]

Crude material collected as a brown solid. Purification by flash chromatography ([7:3] pet. ether/ethyl acetate) afforded the title compound as a white solid (3.46 g, 12.30 mmol, 80%). mp 116-118 °C. Found; C, 59.64; H, 6.82; N, 4.79%; Calc. for C₁₄H₁₉NO₃S; C, 59.76; H, 6.81; N, 4.98%. \( \nu_{\max} \) (KBr) 2938, 1687 (C=O), 1448, 1358 (NSO₂), 1211, 1167 (NSO₂), 1119, 1083, 814, 683, 634, 542 cm⁻¹. \( \delta_h \) (500MHz, CDCl₃) 1.46 (2H, qt, J = 6 Hz, 6-H₂), 1.54 (2H, qt, J = 6 Hz, 5-H₂), 1.75 (2H, qt, J = 6 Hz, 4-H₂), 1.87 (2H, qt, J = 6 Hz, 7-H₂), 2.41 (3H, s, 4’-CH₃), 2.48 (2H, m, 3-H₂), 4.06 (2H, t, J = 6 Hz, 8-H₂), 7.28 (2H, d, J = 9 Hz, 3’-H, 5’-H), 7.90 (2H, d, J = 9 Hz, 2’-H, 6’-H). \( \delta_c \) (125MHz, CDCl₃) 21.9 (4’-CH₃), 23.9 (C-6), 26.3 (C-5), 28.7 (C-4), 31.3
(C-7), 36.6 (C-3), 46.3 (C-8), 129.2, 129.4 (C-2', C-3'), 136.6 (C-1'), 144.8 (C-4'), 175.1 (CO). m/z (ES⁺) 282.1 (MH⁺).

N-(1'-Napthylsulfonyl)-2-oxoazepane 4e

Crude material collected as a brown solid. Purification by flash chromatography ([7:3] pet. ether/ethyl acetate) afforded the title compound as a white solid (1.46 g, 4.81 mmol, 49%). mp 132-134 °C. Found; C, 63.10; H, 5.61; N, 4.42%; Calc. for C₁₆H₁₇NO₃S; C, 63.34; H, 5.65; N, 4.62%.

ν max (KBr) 3028, 2944, 1699 (C=O), 1510, 1354 (NSO 2), 1210, 1165 (NSO 2), 1134, 880, 690, 506 cm⁻¹.

δ H (500MHz, CDCl₃) 1.71 (2H, qt, J = 6 Hz, 4-H₂), 1.77 (2H, qt, J = 6 Hz, 5-H₂), 1.98 (2H, qt, J = 6 Hz, 6-H₂), 2.47 (2H, m, 3-H₂), 4.26 (2H, m, 7-H₂), 7.59 (1H, t, J = 8 Hz, 6'-H), 7.62 (1H, t, J = 8 Hz, 3'-H), 7.66 (1H, t, J = 8 Hz, 7'-H), 7.95 (1H, d, J = 9 Hz, 5'-H), 8.10 (1H, d, J = 9 Hz, 4'-H), 8.35 (1H, d, J = 9 Hz, 8'-H), 8.53 (1H, d, J = 8 Hz, 2'-H). δ C (125MHz, CDCl₃) 23.2 (C-4), 29.5 (C-5), 29.7 (C-6), 39.0 (C-3), 46.3 (C-7), 123.7 (C-8'), 124.5 (C-3'), 126.9 (C-6'), 128.4 (C-8''), 129.6 (C-5'), 133.1 (C-2'), 134.3 (C-4''), 134.8 (C-1'), 135.3 (C-4'), 175.1 (CO). m/z (ES⁺) 304.1 (MH⁺).

N-([4'-Bromophenyl]sulfonyl)-2-oxoazepane 4f

Purification on the Horizon automated chromatography system (1. 15 %, 2. 30 % ethyl acetate/cyclohexane) afforded the desired product as a white solid (1.43 g, 4.30 mmol, 49 %). mp 111-113 °C. ν max (KBr) 2931, 2857, 1691 (NC=O), 1574, 1469, 1389, 1338 (SO₂), 1161 (SO₂), 1117, 1084, 1069, 1010, 960, 881, 820, 769, 743 (C-Br), 703 cm⁻¹. δ H (400MHz, CDCl₃) 1.63-1.76 (4H, m, 4-H₂, 5-H₂), 1.76-1.84 (2H, m, 6-H₂), 2.52 (2H, m, 3-H₂), 3.99 (2H, m, 7-H₂), 7.62 (2H, d, J = 9 Hz, 3'-H, 5'-H), 7.84 (2H, d, J = 9 Hz, 2'-H, 6'-H). δ C (100MHz, CDCl₃) 22.9 (C-4), 28.9 (C-5), 29.6 (C-6), 38.9 (C-3), 46.9 (C-7), 128.6 (C-4'), 130.1 (C-2'), 131.9 (C-3'), 138.7 (C-1'), 175.0 (C-2). m/z (ES⁺) 332.2 (MH[Br79]+), 334.2 (MH[Br81]+). HRMS (ES) found MH⁺ 331.9953, C₁₂H₁₃NO₃SBr⁷⁹ requires M⁺ 331.9951.
Purification on the Horizon automated chromatography system (1. 15 %, 2. 30 % ethyl acetate/cyclohexane) afforded the desired product as a clear oil. (1.16 g, 4.11 mmol, 46 %). \( \nu_{\text{max}} \) (KBr) 2942, 2863, 1698 (NC=O), 1599, 1484, 1465, 1435, 1354 (SO\(_2\)), 1254, 1167 (SO\(_2\)), 1122, 1090, 1078, 1037, 577, 517 cm\(^{-1}\). \( \delta \) (400MHz, CDCl\(_3\)) 1.64-1.79 (4H, m, 4-\( H_2 \)), 1.85 (2H, m, 6-\( H_2 \)), 2.55 (2H, m, 3-\( H_2 \)), 3.86 (3H, s, OCH\(_3\)), 7.12 (1H, ddd, J\(_1\) = 8 Hz, J\(_2\) = 3 Hz, J\(_3\) = 1 Hz, 4'-\( H \)), 7.40 (1H, t, J = 8 Hz, 5'-\( H \)), 7.53 (2H, m, 2'-\( H \), 6'-\( H \)). \( \delta \) (100MHz, CDCl\(_3\)) 23.2 (C-4), 29.4 (C-5), 29.6 (C-6), 39.0 (C-3), 46.8 (C-7), 55.9 (OCH\(_3\)), 113.5 (ArCH), 120.2 (C-4'), 120.4 (ArCH), 129.9 (C-5'), 140.9 (C-1'), 159.6 (C-3'), 175.1 (C-2). m/z (ES\(^+\)) 284.2 (MH\(^+\)), 306.2 (MNa\(^+\)), 589.3 (2MNa\(^+\)). HRMS (ES) found MH\(^+\) 284.0953, C\(_{13}\)H\(_{19}\)NO\(_4\)S requires M\(^+\) 284.0951.

\( \nu_{\text{max}} \) (KBr) 2958, 2872, 1700 (NC=O), 1607, 1537, 1463, 1353 (SO\(_2\)), 1179 (SO\(_2\)), 1123, 1080 cm\(^{-1}\). \( \delta \) (400MHz, CDCl\(_3\)) 1.66-1.81 (4H, m, 4-\( H_2 \), 5-\( H_2 \)), 1.81-1.90 (2H, m, 6-\( H_2 \)), 2.55 (2H, m, 3-\( H_2 \)), 4.06 (2H, m, 7-\( H_2 \)), 7.35 (1H, t, J = 8 Hz, 5'-\( H \)), 8.34 (1H, d, J = 8 Hz, 6'-\( H \)), 8.43 (1H, d, J = 8 Hz, 4'-\( H \)), 8.75 (1H, s, 2'-\( H \)). \( \delta \) (100MHz, CDCl\(_3\)) 23.2 (C-4), 29.5 (C-5), 29.9 (C-6), 39.0 (C-3), 46.2 (C-7), 124.0 (C-2'), 128.3 (C-4'/6'), 130.4 (C-5'), 134.8 (C-4'/6'), 142.0 (C-1'), 148.3 (C-3'), 175.5 (C-2). m/z (ES\(^+\)) 299.2 (MH\(^+\)), 316.2 (M2H\(_2\)O\(^+\)), 614.2 (2M2H\(_2\)O\(^+\)).
To a cold solution (0.08 M, -78 °C) of N-sulfonyl lactam (1 eq) and TMEDA (1.3 eq) in dry THF was added a cold solution of LDA (1.3 eq) via cannula. The resulting reaction mixture was stirred at -78 °C for 2 h after which time a cold (0.2 M, -78 °C) solution of diphenylphosphonic chloride (1.2 eq) in dry THF was added via cannula. The reaction mixture was stirred at -78 °C for 1 h then warmed to room temperature and quenched with NH₄Cl(aq). The mixture was concentrated in vacuo and the aqueous layer extracted with ethyl acetate. The organic phase was washed with NaHCO₃(aq) then brine, dried over MgSO₄ and concentrated in vacuo affording crude material.

1,2,3,4,5-Quintahydro-8-methylazocine[1,2-b][1,2]benzothiazole-11,11-dioxide 5d

Purification on a Horizon® column chromatography system (1. 20% ethyl acetate/pet. ether, 2. 40% ethyl acetate/pet.ether) afforded the title compound as a clear oil (0.09 g, 0.34 mmol, 18%) and phosphonite (0.21 g, 0.44 mmol, 25%). νₘₐₓ (KBr) 2925, 2854, 1651, 1601, 1455, 1289, 1171, 1142, 1050, 1016, 896, 819, 802 cm⁻¹. δₕ (400MHz, CDCl₃) 1.71 (2H, m, 3-H₂), 1.79 (2H, m, 4-H₂), 2.02 (2H, quint, J = 7 Hz, 2-H₂), 2.46 (3H, s, 8-C₃H₃), 2.59 (2H, m, J = 7 Hz, 5-H₂), 4.02 (2H, t, J = 7 Hz, 1-H₂), 5.55 (1H, t, J = 9 Hz, 6-H), 7.30 (1H, d, J = 8 Hz, 8-H), 7.44 (1H, s, 7-H), 7.67 (1H, d, J = 8 Hz, 9-H). δₐ (100MHz, CDCl₃) 22.3 (8-CH₃), 22.5 (C-3), 23.6 (C-5), 28.6 (C-4), 30.5 (C-2), 40.3 (C-1), 100.6 (C-6), 120.9 (C-7), 121.1 (C-10), 128.9 (C-10a), 130.6 (C-9), 132.1 (C-6b), 134.0 (C-6a), 143.9 (C-8). m/z (ES⁺) 264.1 (MH⁺), 286.1 (MNa⁺), 318.1 (MMeOHNa⁺), 549.3 (2MNa⁺). HRMS (ES) found MH⁺ 264.1052, C₁₄H₁₈NO₂S requires M⁺ 264.1053.

1,2,3,4-Tetrahydroazepino[1,2-b][1,2]napthathiazole-12,12-dioxide 5e

1,2,3,4-Tetrahydroazepino[1,2-b][1,2]napthathiazole-12,12-dioxide 5e
Purification on the Horizon column chromatography system (20% ethyl acetate/pet. ether) afforded the title compound as a white solid (0.35 g, 1.23 mmol, 26%), recovered starting material (41%) and phosphonite (0.17 g, 0.34 mmol, 17%).

\[ \text{mp 183-186 °C.} \]

\[ \nu_{\text{max}} (\text{KBr}) 2930, 2868, 1657, 1626, 1592, 1512, 1288, 1154, 1131, 1074, 1005, 936, 826, 807, 761. \]

\[ \delta (\text{H} (500MHz, \text{CDCl}_3) 1.83 (2H, \text{ quint, } J = 6 \text{ Hz, 3-}H_2), 2.05 (2H, m, 2-}H_2), 2.50 (2H, q, J = 6 \text{ Hz, 4-}H_2), 3.67 (2H, m, 1-}H_2), 5.93 (1H, t, J = 6 \text{ Hz, 5-}H), 7.57-7.63 (2H, m, 6-}H, 9-}H), 7.70 (1H, t, J = 8 \text{ Hz, 10-}H), 7.91 (1H, d, J = 8 \text{ Hz, 8-}H), 7.98 (1H, d, J = 9 \text{ Hz, 11-}H). \]

\[ \delta (\text{C} (125MHz, \text{CDCl}_3) 27.0 (\text{C-3}), 27.6 (\text{C-4}), 29.0 (\text{C-2}), 45.5 (\text{C-1}), 108.5 (\text{C-5}), 117.3 (\text{ArCH}), 123.5 (\text{C-11}), 125.5 (\text{C-11a}), 126.2 (\text{C-11b}), 127.9 (\text{ArCH}), 128.9 (\text{C-8}), 129.4 (\text{C-10}), 131.2 (\text{C-5b}), 133.5 (\text{C-7a}), 134.0 (\text{C-7}), 136.5 (\text{C-5a}). \]

\[ m/z (\text{ES}^+) 286.1 (\text{MH}^+), 308.1 (\text{MNa}^+), 340.1 (\text{MMeOHNa}^+), 593.3 (2\text{MNa}^+), 878.4 (3\text{MNa}^+). \]

HRMS (ES) found MH$^+$ 286.0899, C$_{16}$H$_{16}$NO$_2$S requires M$^+$ 286.0896.

\[ 1,2,3,4-\text{Tetrahydro-6/8-methoxyazepino[1,2-b][1,2]benzothiazole-10,10-dioxide 5g} \]

The crude material was collected as a pale brown oil which was purified by flash chromatography (1. 10% EtOAc/Pet. ether, 2. 15% EtOAc/Pet. ether, 3. 50% EtOAc/Pet. ether) affording a mixture of isomers and phosphonite. The initial fraction provided \( 1,2,3,4-\text{Tetrahydro-6-methoxyazepino[1,2-b][1,2]benzothiazole-10,10-dioxide} \) as a colourless oil. (0.067 g, 0.25 mmol, 25%).

\[ \nu_{\text{max}} (\text{KBr}) 2941, 1647, 1595, 1485, 1440, 1304, 1273, 1212, 1171, 1158, 1044. \]

\[ \delta (\text{H} (400MHz, \text{CDCl}_3) 1.81 (2H, \text{ quint, } J = 6 \text{ Hz, 3-}H_2), 1.95 (2H, \text{ quint, } J = 6 \text{ Hz, 2-}H_2), 2.44 (2H, q, J = 6 \text{ Hz, 4-}H_2), 3.59 (2H, m, 1-}H_2), 3.95 (3H, s, O\text{CH}_3), 6.52 (1H, t, J = 6 \text{ Hz, 5-}H), 7.08 (1H, m, \text{ArCH}), 7.34-7.44 (2H, m, 8-}CH, \text{ArCH}). \]

\[ \delta (\text{C} (100MHz, \text{CDCl}_3) 26.2 (\text{C-3}), 27.6 (\text{C-4}), 29.0 (\text{C-2}), 45.5 (\text{C-1}), 56.1 (\text{OCH}_3), 113.2 (\text{ArC}), 114.5 (\text{C-5}), 114.7 (\text{ArC}), 120.0 (\text{C-5b}), 130.5 (\text{C-8}), 133.8 (\text{C-9a}), 135.9 (\text{C-5a}), 155.7 (\text{C-6}). \]

\[ m/z (\text{ES}^+) 266.2 (\text{MH}^+). \]

HRMS (ES) found MH$^+$ 266.08454, C$_{13}$H$_{16}$NO$_3$S requires M$^+$ 266.0843. Further elution then afforded \( 1,2,3,4-\text{Tetrahydro-8-methoxyazepino[1,2-b][1,2]benzothiazole-10,10-dioxide} \) as a colourless oil. (0.017 g, 0.06 mmol, 6%).

\[ \nu_{\text{max}} (\text{KBr}) 2941, 1664, 1611, 1495, 1464, 1441, 1303, 1274, 1168, 1056, 1027. \]

\[ \delta (\text{H} (400MHz, \text{CDCl}_3) 1.80 (2H, \text{ quint, } J = 6 \text{ Hz, 3-}H_2), 1.98 (2H, m, 2-}H_2), 2.42 (2H, q, J = 6 \text{ Hz, 4-}H_2), 3.59 (2H, m, 1-}H_2), 5.65 (1H, t, J = 6 \text{ Hz, 5-}H), 7.13 (1H, m, 7-}H), 7.19 (1H, s, 9-}H), 7.50 \]
(1H, d, J = 9 Hz, 6-H). δC (100MHz, CDCl₃) 27.1, 27.2 (C-4, C-3), 28.9 (C-2), 45.4 (C-1), 56.1 (CH₃), 103.3 (C-9), 104.9 (C-5), 122.0 (C-6), 122.3 (C-7), 124.9 (C-5b), 132.4 (C-9a), 135.7 (C-5a), 160.9 (C-8). m/z (ES⁺) 266.2 (MH⁺). HRMS (ES) found MH⁺ 266.08480, C₁₃H₁₆NO₃S requires M⁺ 266.08454.

1-Tosyl-4,5,6,7,8-quintahydro-1H-azepin-2-yl diphenylphosphinate 8d

mp 199-200 °C. HPLC r.t. = 6.02 min, 98.13%. νmax (KBr) 2928, 2851, 1671, 1593, 1440, 1348, 1235, 1156, 1126, 1076, 1006, 874, 829, 730 cm⁻¹. δH (400MHz, CDCl₃) 1.43-1.60 (6H, m, 5-H₂, 6-H₂, 7-H₂), 2.13 (2H, m, 4-H₂), 2.36 (3H, s, 4''-CH₃), 3.31 (2H, m, 8-H₂), 5.54 (1H, dt, J₁ = 2 Hz, J₂ = 8 Hz, 3-H), 7.09 (2H, d, J = 8 Hz, 3''-H, 5''-H), 7.73 (2H, d, J = 8 Hz, 2''-H, 6''-H). δC (100MHz, CDCl₃) 21.9 (4''-C₃H₃), 26.2 (C-4), 26.9 (C-6), 27.2 (C-7), 28.8 (C-5), 50.3 (C-8), 119.3 (C-3), 128.1 (C-2'b), 128.8 (ArCH), 129.8 (C-3''), 130.5 (ArC), 132.1 (ArCH), 132.8 (C-4''), 137.7 (ArC), 138.4 (ArC), 143.6 (C-2). δP (162MHz, CDCl₃) 32.4. m/z (ES⁺) 482.1 (MH⁺), 980.4 (2MH₂O⁺). HRMS (ES) found MH⁺ 482.1554, C₂₆H₂₉N₁O₄S₁P₁ requires M⁺ 482.1550, found MNa⁺ 504.1367, C₂₆H₂₈N₁O₄S₁P₁Na₁ requires M⁺ 504.1369.

1-(1''-Naphthylsulfonyl-4,5,6,7-tetrahydro-1H-azepin-2-yl diphenylphosphinate 8e

Pure material isolated as a colourless oil. νmax (KBr) 3064, 2943, 1672, 1440, 1338, 1226, 1200, 1160, 1133, 1097, 1062, 803 cm⁻¹. δH (500MHz, CDCl₃) 1.29 (2H, m, 5-H₂), 1.47 (2H, quint, J = 6 Hz, 6-H₂), 1.86 (2H, q, J = 7 Hz, 4-H₂), 3.26 (2H, m, 7-H₂), 5.64 (1H, dt, J₁ = 7 Hz, J₂ = 3 Hz, 3-H), 7.31-7.39 (5H, m, 3''-H, 3'-H, 5''-H), 7.46-7.59 (4H, m, 4''-H, 7''-H, 6''-H), 7.70 (4H, m, 2''-H, 6'-H), 7.90 (1H, d, J = 8 Hz, 5''-H), 7.98 (1H, d, J = 8 Hz, 4''-H). 8.25 (1H, m, 2''-H), 8.70 (1H, d, J = 8.5 Hz, 8''-H). δC (125MHz, CDCl₃) 23.9 (C-5), 24.2 (C-4), 29.9 (C-6), 49.6 (C-7), 114.1 (C-3), 124.4 (C-3''), 125.5 (C-8''), 127.4, 128.4 (C-6'', C-7''), 128.6, 128.7 (C-3''), 129.0 (C-5''), 129.6 (C-2''), 130.1, 131.2 (2 x ArC), 132.1 (ArC), 132.2 (C-2''), 132.6 (C-4''), 134.4 (C-4''), 134.5 (ArC), 136.4 (ArC), 143.6 (C-2), δP (162MHz, CDCl₃) 31.2. m/z (ES⁺) 504.1 (MH⁺), 526.1 (MNa⁺), 1029.4 (2MNa⁺). HRMS (ES) found MH⁺ 504.1401, C₂₈H₂₇NO₄PS requires M⁺ 504.1393.
Pure material collected as a clear oil. $\nu_{\text{max}}$ (KBr) 3065, 2943, 1673, 1599, 1484, 1440, 1360, 1240, 1158, 1131, 1105, 1049 cm$^{-1}$. $\delta_H$ (500MHz, CDCl$_3$) 1.35 (2H, m, 5-H$_2$), 1.66 (2H, quint, J = 6 Hz, 6-H$_2$), 1.87 (2H, q, J = 7 Hz, 4-H$_2$), 3.19 (2H, m, 7-H$_2$), 3.67 (3H, s, 3''-OC$_3$H$_3$), 5.55 (1H, dt, $J_1 = 7$ Hz, $J_2 = 3$ Hz, 3-H), 7.00 (1H, m, Ar-H), 7.21 (1H, t, J = 8 Hz, 5''-H), 7.36 (1H, m, 2''-H), 7.38-7.46 (5H, m, 3'-H, 5'-H, Ar-H), 7.54 (2H, m, 4'-H), 7.81 (4H, m, 2'-H, 6'-H). $\delta_C$ (125MHz, CDCl$_3$) 23.9 (C-5), 24.3 (C-4), 30.0 (C-6), 49.5 (C-7), 55.7 (CH$_3$), 111.9 (C-2''), 113.9 (C-3), 119.5, 119.7 (C-4'', C-6''), 128.7, 128.8 (C-3'), 130.2 (C-5''), 131.2 (C-1'), 132.1, 132.2 (C-2'), 132.7 (C-4''), 142.2 (C-1''), 143.6 (d, C-2), 160.0 (C-3''), $\delta_P$ (162MHz, CDCl$_3$) 31.4. m/z (ES$^+$) 484.2 (MH$^+$), 506.2 (MNa$^+$), 988.8 (2MNa$^+$). HRMS (ES) found MH$^+$ 484.1345, C$_{25}$H$_{27}$NO$_5$PS requires M$^+$ 484.1342, found MNa$^+$ 506.1165, C$_{25}$H$_{26}$NO$_5$PSNa requires M$^+$ 506.1162.