SUPPORTING INFORMATION

Title: Cerium(IV) Ammonium Nitrate Mediated 5-endo-dig Cyclization of α-Amino Allenylphosphonates to Spirodienones
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EXPERIMENTAL SECTION .................................................................1

GENERAL PROCEDURE FOR THE PREPARATION OF THE α-AAPs FROM THE YNAMIDES. ....................1

PROCEDURE A FOR THE CYCLIZATION OF THE α-AAPs INTO THE SPIRODIENONE LACTAMS 3, 12-24. ............8

PROCEDURE B FOR THE CYCLIZATION OF THE α-AAPs INTO THE SPIRODIENONE PHOSPHONATES 35............12

PROCEDURE C FOR THE CYCLIZATION OF THE α-AAPs INTO THE SPIRODIENONE CYCLIC PHOSPHONATES 28. ......14

1H AND 13C NMR SPECTRA ................................................................16
EXPERIMENTAL SECTION

All reactions were carried out under argon with magnetic stirring. All solvents and chemicals were purified based on standard procedures. Reagent grade solvents were used without purification for all extractions and work-up procedures. Rf values refer to values obtained by TLC on 0.25 mm silica gel plates (60F254). Flash chromatography was carried out on silica gel 60 (70–200 μm) with various mixtures of ethyl acetate (EtOAc) and petroleum ether (PE), yields refer to chromatographically and spectroscopically pure compounds. NMR spectra were recorded at 250, 300 and 360 MHz. HRMS spectra were recorded with a MicroTOFq spectrometer.

GENERAL PROCEDURE FOR THE PREPARATION OF THE α-AAPs FROM THE YNAMIDES.

To a solution of ynamide (1.77 mmol) in 10 mL of anhydrous tetrahydrofuran cooled at 0 °C were added triethylamine (1.94 mmol) and chlorophosphite (1.94 mmol). After 1–18 h of stirring at room temperature, the mixture was filtered through a pad of Celite®, the solvent was removed in vacuo, and crude product was purified by flash chromatography on silica gel to yield the amino allenylphosphonates.[1]

Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)propa-1,2-dien-1-yl)phosphonate (S1).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 100/0; yellow solid, 1.17 g, 55% yield; Rf = 0.23 (EtOAc/PE = 50/50); mp = 100-102 °C; 1H NMR (250 MHz, CDCl3) δ 7.82 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.05 (d, J = 10.5 Hz, 2H), 4.48 (s, 2H), 4.11 – 3.84 (m, 4H), 3.78 (s, 3H), 2.44 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H); 13C NMR (62.9 MHz, CDCl3) δ 215.8 (d, J = 26.0 Hz), 159.4, 143.8, 136.3, 130.7, 129.5, 128.3, 127.7, 113.7, 99.4 (d, J = 233.3 Hz), 82.4 (d, J = 11.9 Hz), 63.0 (d, J = 6.0 Hz), 55.3, 53.1, 21.6, 16.2 (d, J = 6.6 Hz); 31P NMR (101.25 MHz, CDCl3) δ 11.1; HRMS (ESI) m/z [MH+] calcd for C22H29NO6PS: 466.1448, found: 466.1429.

Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)buta-1,2-dien-1-yl)phosphonate (S2).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 50/50 to 100/0; yellow solid, 1.03 g, 71% yield; Rf = 0.23 (EtOAc/PE = 90/10); mp = 100-102 °C; 1H NMR (250 MHz, CDCl3) δ 7.78 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 5.43 (dq, J = 9.9, 7.4 Hz, 1H), 4.46 (s, 2H), 4.00 – 3.80 (m, 4H), 3.72 (s, 3H), 2.38 (s, 3H), 1.47 (dd, J = 7.4, 4.9 Hz, 3H), 1.19 (t, J = 7.1 Hz, 6H); 13C NMR (91 MHz, CDCl3) δ 212.7 (d, J = 25.6 Hz), 159.1, 143.4, 136.3, 130.3, 129.3, 128.0, 127.7, 113.5, 97.9 (d, J = 235.1 Hz), 94.1 (d, J = 12.1 Hz), 62.6 (d, J = 6.1 Hz), 55.2, 52.7, 21.4, 16.1 (d, J = 4.8 Hz), 12.7 (d, J = 5.1 Hz); 31P NMR (101.25 MHz, CDCl3) δ 11.5; HRMS (ESI) m/z [MH+] calcd for C23H30NO6PS: 480.1644, found: 480.1629.
Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-methylpenta-1,2-dien-1-yl)phosphonate (S3).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 50/50; yellow oil, 269 mg, 33% yield; Rf = 0.34 (EtOAc/PE = 60/40); 1H NMR (250 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 4.60 – 4.42 (m, 2H), 4.05 – 3.77 (m, 4H), 3.73 (s, 3H), 2.39 (s, 3H), 1.96 – 1.80 (m, 2H), 1.53 (d, J = 4.5 Hz, 3H), 1.25 – 1.14 (m, 6H), 0.83 (t, J = 7.4 Hz, 3H); 13C NMR (91 MHz, CDCl₃) δ 210.3 (d, J = 25.5 Hz), 159.2, 143.3, 137.2, 130.3, 129.4, 128.3, 128.1, 113.7, 110.6 (d, J = 12.0 Hz), 96.7 (d, J = 236.6 Hz), 63.0, 55.3, 52.5, 26.9 (d, J = 4.5 Hz), 21.6, 17.4 (d, J = 4.9 Hz), 16.3 (d, J = 6.6 Hz), 11.6. 31P NMR (101.25 MHz, CDCl₃) δ 12.3; HRMS (ESI) m/z [MNa⁺] calef for C_{33}H_{43}NNaO₈PS: 530.1737, found: 530.1727.

Diethyl (2-cyclohexylidene-1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)vinyl)phosphonate (S4).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 70/30; white solid, 352 mg, 30% yield; Rf = 0.24 (EtOAc/PE = 50/50); mp = 69-73 °C; 1H NMR (250 MHz, CDCl₃) δ 7.83 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 4.53 (s, 2H), 4.03 – 3.79 (m, 4H), 3.76 (s, 3H), 2.42 (s, 3H), 1.96 – 1.87 (m, 4H), 1.62 – 1.49 (m, 2H), 1.46 – 1.32 (m, 4H), 1.22 (dt, J = 7.2, 3.6 Hz, 6H); 13C NMR (91 MHz, CDCl₃) δ 207.6 (d, J = 25.9 Hz), 159.3, 143.4, 137.0, 130.5, 129.5, 128.3, 128.2, 113.7, 111.1 (d, J = 11.9 Hz), 95.0 (d, J = 237.2 Hz), 62.6 (d, J = 6.0 Hz), 55.4, 52.7, 30.1 (d, J = 4.3 Hz), 26.7, 25.6, 21.7, 16.4 (d, J = 6.7 Hz); 31P NMR (101.25 MHz, CDCl₃) δ 12.0; HRMS (ESI) m/z [MH⁺] calef for C_{35}H_{37}NO_{10}PS: 534.2074, found: 534.2061.

Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-phenylpropa-1,2-dien-1-yl)phosphonate (S5).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60; orange oil, 160 mg, 35% yield; Rf = 0.65 (EtOAc/PE = 50/50); 1H NMR (250 MHz, CDCl₃) δ 7.86 (d, J = 8.1 Hz, 2H), 7.34 – 7.19 (m, 7H), 7.01 – 6.88 (m, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 10.1 Hz, 1H), 4.63 (s, 2H), 4.02 (dddd, J = 14.2, 10.1, 7.0, 3.3 Hz, 4H), 3.77 (s, 3H), 2.41 (s, 3H), 1.22 (dt, J = 14.3, 7.1 Hz, 6H); 13C NMR (63 MHz, CDCl₃) δ 214.0 (d, J = 24.0 Hz), 159.4, 143.6, 136.7, 130.4, 129.5, 128.7, 128.2, 128.1, 127.9, 113.8, 101.8 (d, J = 231.4 Hz), 101.5 (d, J = 12.1 Hz), 63.1 (t, J = 5.3 Hz), 55.3, 52.6, 21.6, 16.2 (d, J = 6.5 Hz); 31P NMR (101.25 MHz, CDCl₃) δ 10.3; HRMS (ESI) m/z [MH⁺] calef for C_{35}H_{37}NO_{10}PS: 542.1761, found: 542.1734.

Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-phenylbuta-1,2-dien-1-yl)phosphonate (S6).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 90/10; yellow oil, 663 mg, 79% yield; Rf = 0.64 (EtOAc/PE = 90/10); 1H NMR (250 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.25 – 7.17 (m, 7H), 7.07 – 7.01 (m, 2H), 6.75 (d, J = 8.7 Hz, 2H), 4.61 (q, J = 14.7 Hz, 2H), 4.06 – 3.84 (m, 4H), 3.73 (s, 3H), 2.37 (s, 3H), 1.95 (d, J = 4.6 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); 13C NMR (62.9 MHz, CDCl₃) δ 213.3 (d, J = 23.8 Hz), 159.3, 143.4, 137.0, 133.4 (d, J = 5.6 Hz), 130.4, 129.4, 128.4, 128.3, 128.1, 128.0, 126.7, 113.8, 109.1
(d, J = 12.2 Hz), 99.2 (d, J = 233.1 Hz), 62.8 (t, J = 5.9 Hz), 55.2, 52.4, 21.5, 16.3, 16.2, 16.1; 31P NMR (121.5 MHz, CDCl3) δ 11.0; HRMS (ESI) m/z [MH+] calcd for C29H35NO6PS: 556.1917, found: 556.1932.

**Diethyl (3-cyclopropyl-1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-phenylpropa-1,2-dien-1-yl)phosphonate (S7).**

![Diagram of S7]

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 50/50; yellow oil, 173 mg, 45% yield; Rf = 0.35 (EtOAc/PE = 50/50); 1H NMR (250 MHz, CDCl3) δ 7.84 (d, J = 8.3 Hz, 2H), 7.26 – 7.16 (m, 9H), 6.74 (d, J = 8.8 Hz, 2H), 4.62 (d, J = 2.1 Hz, 2H), 4.11 – 3.81 (m, 4H), 3.76 (s, 3H), 1.55 – 1.45 (m, 1H), 1.29 – 1.19 (m, 3H), 1.11 (td, J = 7.1, 0.5 Hz, 3H), 0.87 – 0.72 (m, 2H), 0.57 (dt, J = 10.2, 5.2 Hz, 2H); 13C NMR (62.9 MHz, CDCl3) δ 212.2 (d, J = 22.7 Hz), 159.3, 144.6, 143.4, 137.2, 134.1 (d, J = 5.6 Hz), 130.5, 130.3, 129.7, 129.4, 128.6, 128.1, 127.8, 127.2, 126.9, 117.9 (d, J = 12.1 Hz), 113.8, 101.6 (d, J = 233.0 Hz), 62.7 (d, J = 5.3 Hz), 55.2, 52.5, 21.5, 16.2 (t, J = 7.0 Hz), 11.3 (d, J = 5.2 Hz), 7.5, 6.9; 31P NMR (101.25 MHz, CDCl3) δ 11.1; HRMS (ESI) m/z [MH+] calcd for C31H37NO6PS: 582.2074, found: 582.2063.

**Diethyl (4-(3,4-dimethoxyphenyl)-1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S8).**

![Diagram of S8]

Prepared according to general procedure. Flash Chromatography: EtOAc/heptane 40/60 to 80/20; yellow oil, 636 mg, 64% yield; Rf = 0.35 (EtOAc/PE = 50/50); 1H NMR (250 MHz, CDCl3) δ 7.80 (d, J = 8.2 Hz, 2H), 7.23 (t, J = 8.8 Hz, 4H), 6.73 (dd, J = 9.6, 4.9 Hz, 4H), 6.63 – 6.53 (m, 1H), 4.52 (s, 2H), 4.02 – 3.85 (m, 4H), 3.84 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.15 (s, 2H), 2.36 (s, 3H), 1.38 (d, J = 4.4 Hz, 3H), 1.17 (dd, J = 15.5, 7.2 Hz, 6H); 13C NMR (63 MHz, CDCl3) δ 211.0 (d, J = 25.9 Hz), 159.1, 149.0, 147.8, 143.2, 137.0, 130.2, 129.6, 129.3, 128.0, 127.9, 120.9, 113.5, 112.1, 110.9, 107.3 (d, J = 12.1 Hz), 95.7 (d, J = 235.6 Hz), 62.4 (d, J = 5.0 Hz), 55.9, 55.8, 55.1, 52.4, 39.2 (d, J = 4.0 Hz), 21.4, 16.5 (d, J = 4.5 Hz), 16.1 (d, J = 6.3 Hz); 31P NMR (101.25 MHz, CDCl3) δ 12.1; HRMS (ESI) m/z [MH+] calcd for C32H41NO8PS: 630.2285, found: 630.2282.

**Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-(4-methoxyphenyl)buta-1,2-dien-1-yl)phosphonate (S9).**

![Diagram of S9]

Prepared according to general procedure. Flash Chromatography: EtOAc/EP 40/60 to 50/50; yellow oil, 25 mg, 9% yield; Rf = 0.37 (EtOAc/PE = 40/60); 1H NMR (250 MHz, CDCl3) δ 7.86 (d, J = 8.3 Hz, 2H), 7.32 – 7.21 (m, 4H), 7.00 (d, J = 8.8 Hz, 2H), 6.83 – 6.72 (m, 4H), 6.40 (q, J = 14.7 Hz, 2H), 4.12 – 3.89 (m, 4H), 3.82 (s, 3H), 3.78 (s, 3H), 2.42 (s, 3H), 1.96 (d, J = 4.6 Hz, 3H), 1.22 (dt, J = 13.8, 7.0 Hz, 6H); 13C NMR (63 MHz, CDCl3) δ 213.5 (d, J = 24.0 Hz), 159.8, 159.4, 143.4, 137.3, 130.6, 129.5, 128.3, 128.1, 125.7, 125.6, 113.9 (br. s.), 108.8 (d, J = 12.1 Hz), 98.9 (d, J = 234.4 Hz), 62.8 (t, J = 5.7 Hz), 55.4 (br. s.), 52.4, 21.6, 16.3 (br. s.); 31P NMR (101.25 MHz, CDCl3) δ 11.1; HRMS (ESI) m/z [MH+] calcd for C30H37NO7PS: 586.2023, found: 586.205.
Diethyl (2-(chroman-4-ylidene)-1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)vinyl)phosphonate (S10).

Prepared according to general procedure. Flash Chromatography: EtOAc/heptane 50/50; yellow oil, 396 mg, 62% yield; \( R_f = 0.50 \) (EtOAc/PE = 70/30); \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 7.87 – 7.79 (m, 2H), 7.24 (dd, \( J = 8.5, 2.2 \) Hz, 4H), 7.10 (dd, \( J = 6.4, 2.6 \) Hz, 1H), 6.80 – 6.74 (m, 3H), 6.71 (d, \( J = 4.3 \) Hz, 2H), 4.66 (s, 2H), 4.18 – 4.07 (m, 2H), 4.07 – 3.88 (m, 4H), 3.74 (s, 3H), 2.52 (dd, \( J = 15.1, 7.7, 4.3 \) Hz, 1H), 2.44 (dt, \( J = 8.5, 4.0 \) Hz, 1H), 2.38 (s, 3H), 1.20 (dt, \( J = 11.8, 7.1 \) Hz, 6H); \(^{13}\)C NMR (91 MHz, CDCl\(_3\)) \( \delta \) 209.8 (d, \( J = 24.3 \) Hz), 159.3, 154.5, 143.5, 137.1, 130.3, 130.2, 129.4, 128.7, 128.0, 127.9, 121.1, 117.4, 115.1 (d, \( J = 5.7 \) Hz), 113.8, 104.4 (d, \( J = 12.3 \) Hz), 101.0 (d, \( J = 232.6 \) Hz), 65.2, 62.8 (dd, \( J = 14.8, 6.3 \) Hz), 55.2, 52.2, 26.8, 21.5, 16.2 (d, \( J = 4.0 \) Hz); \(^{31}\)P NMR (101.25 MHz, CDCl\(_3\)) \( \delta \) 10.4; HRMS (ESI) m/z \([\text{MNa}^+]\) calcd for C\(_{30}\)H\(_{34}\)NNaO\(_7\)PS: 606.1686, found: 606.1686.

Diethyl (1-((N-(3,4-dimethoxybenzyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S11).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 50/50; yellow oil, 489 mg, 78% yield; \( R_f = 0.24 \) (EtOAc/PE = 70/30); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 7.77 (d, \( J = 8.2 \) Hz, 2H), 7.24 (d, \( J = 8.2 \) Hz, 2H), 6.86 (s, 1H), 6.68 (d, \( J = 2.3 \) Hz, 2H), 4.43 (s, 2H), 3.95 – 3.77 (m, 4H), 3.76 (s, 3H), 3.74 (s, 3H), 2.34 (s, 3H), 1.47 (d, \( J = 4.5 \) Hz, 6H), 1.14 (t, \( J = 7.1 \) Hz, 6H); \(^{13}\)C NMR (62.9 MHz, CDCl\(_3\)) \( \delta \) 209.9 (d, \( J = 25.0 \) Hz), 148.9, 148.5, 143.3, 136.7, 129.3, 128.5, 128.0, 121.2, 111.8, 110.6, 104.9 (d, \( J = 12.1 \) Hz), 95.9 (d, \( J = 237.4 \) Hz), 62.4 (d, \( J = 6.1 \) Hz), 55.9, 55.7, 52.9, 21.4, 19.2 (d, \( J = 4.9 \) Hz, 16.2 (d, \( J = 6.6 \) Hz); \(^{31}\)P NMR (101.25 MHz, CDCl\(_3\)) \( \delta \) 12.2; HRMS (ESI) m/z \([\text{MH}^+]\) calcd for C\(_{25}\)H\(_{35}\)NO\(_7\)PS: 524.1866, found: 524.1853.

Diethyl (1-((N-(3-chloro-4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S12).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 50/50 to 70/30; yellow oil, 146 mg, 50% yield; \( R_f = 0.24 \) (EtOAc/PE = 70/30); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.75 (d, \( J = 8.3 \) Hz, 2H), 7.26 (d, \( J = 8.1 \) Hz, 2H), 7.15 (dd, \( J = 10.5, 2.0 \) Hz, 2H), 6.79 (d, \( J = 8.3 \) Hz, 1H), 4.49 (s, 2H), 3.98 – 3.82 (m, 4H), 3.81 (s, 3H), 2.38 (s, 3H), 1.55 (d, \( J = 4.5 \) Hz, 6H), 1.19 (t, \( J = 7.0 \) Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 210.5 (d, \( J = 25.6 \) Hz), 154.4, 143.5, 136.8, 130.6, 129.4, 129.2, 128.4, 127.9, 122.0, 111.7, 104.9 (d, \( J = 12.1 \) Hz), 95.4 (d, \( J = 236.7 \) Hz), 62.6 (d, \( J = 6.1 \) Hz), 56.2, 51.9, 21.5, 19.2 (d, \( J = 4.6 \) Hz), 16.2 (d, \( J = 6.5 \) Hz); \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\)) \( \delta \) 11.7; HRMS (ESI) m/z \([\text{MH}^+]\) calcd for C\(_{24}\)H\(_{32}\)ClNO\(_6\)PS: 528.1371, found: 528.1368.

Diethyl (1-((N-(3-chloro-4-methoxybenzyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S13).
Diethyl (1-((N-(2-methoxybenzyl))-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S14).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 20/80 to 100/0; yellow solid, 2.89 g, 73% yield; R<sub>f</sub> = 0.13 (EtOAc (5% NH<sub>3</sub>)/PE = 50/50); mp = 60-64 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.29 (d, J = 8.5 Hz, 2H), 7.19 (dd, J = 7.7, 6.3 Hz, 1H), 6.89 (dd, J = 10.8, 4.1 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 4.65 (s, 2H), 4.06 – 3.77 (m, 4H), 3.71 (s, 3H), 2.41 (s, J = 26.9 Hz), 159.3, 130.3, 128.2, 110.0, 105.1 (d, J = 12.1 Hz), 96.9 (d, J = 235.8 Hz), 62.4 (d, J = 5.9 Hz), 55.1, 47.7, 21.5, 19.3 (d, J = 4.8 Hz), 16.2 (d, J = 6.7 Hz); <sup>31</sup>P NMR (101.25 MHz, CDCl<sub>3</sub>) δ 12.0; HRMS (ESI) m/z [MH<sup>+</sup>] calcd for C<sub>23</sub>H<sub>35</sub>NO<sub>6</sub>PS: 494.1761, found: 494.1759.

Diethyl (1-((N-(4-methoxybenzyl))methylsulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (S15).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 20/80 to 80/20; yellow solid, 4.76 g, 73% yield; R<sub>f</sub> = 0.13 (EtOAc(5% NH<sub>3</sub>)/PE = 50/50); mp = 60-64 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.29 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 4.63 (s, 2H), 4.13 – 3.91 (m, 4H), 3.75 (s, 3H), 2.98 (s, 3H), 1.57 (d, J = 4.4 Hz, 6H), 1.28 (t, J = 7.1 Hz, 6H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>) δ 211.3 (d, J = 26.9 Hz), 159.3, 130.3, 128.2, 113.7, 103.9 (d, J = 12.1 Hz), 94.7 (d, J = 232.0 Hz), 62.8 (d, J = 6.1 Hz), 55.3, 52.3, 40.4, 19.1 (d, J = 4.6 Hz), 16.2 (d, J = 6.6 Hz); <sup>31</sup>P NMR (101.25 MHz, CDCl<sub>3</sub>) δ 12.3; HRMS (ESI) m/z [MH<sup>+</sup>] calcd for C<sub>18</sub>H<sub>25</sub>NO<sub>6</sub>PS: 418.1448, found: 418.1440.

Diethyl (2-cyclohexylidene-1-((N-(4-methoxybenzyl))methylsulfonamido)vinyl)phosphonate (S16).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 40/60 to 50/50; colorless oil, 471 mg, 55% yield; R<sub>f</sub> = 0.55 (EtOAc/PE = 90/10); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.32 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.66 (s, 2H), 4.14 – 3.91 (m, 4H), 3.78 (s, 3H), 3.02 (s, 3H), 1.97 (br. s, 4H), 1.62 – 1.34 (m, 6H), 1.30 (t, J = 7.3 Hz, 6H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>) δ 208.1 (d, J = 27.0 Hz), 159.2, 130.3, 128.3, 113.6, 110.1 (d, J = 11.7 Hz), 94.0 (d, J = 233.0 Hz), 62.8 (d, J = 6.2 Hz), 55.2, 52.3, 40.4, 29.7 (d, J = 4.2 Hz), 26.4, 25.3, 16.2 (d, J = 6.6 Hz); <sup>31</sup>P NMR (101.25 MHz, CDCl<sub>3</sub>) δ 12.3; HRMS (ESI) m/z [MNa<sup>+</sup>] calcd for C<sub>23</sub>H<sub>35</sub>NaO<sub>6</sub>PS: 480.1580, found: 480.1583.
Diethyl  \((S)-(1-(N-(1-(4-methoxyphenyl)ethyl)methylsulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate\) (S17).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 50/50 to 100/0; yellow oil, 131 mg, 12% yield on two steps; \(R_f = 0.17\) (EtOAc/PE = 50/50); \([\alpha]_D^{20} = -8.3\) (c 1.0; CHCl₃); \(^1\)H NMR (250 MHz, CDCl₃) \(\delta\) 7.41 (d, \(J = 8.8\) Hz, 2H), 6.84 (d, \(J = 8.8\) Hz, 2H), 5.16 (q, \(J = 7.1\) Hz, 1H), 4.22 – 3.90 (m, 4H), 3.77 (s, 3H), 2.95 (s, 3H), 1.76 – 1.66 (m, 6H), 1.45 (d, \(J = 4.5\) Hz, 3H), 1.38 – 1.22 (m, 6H); \(^1^3\)C NMR (75 MHz, CDCl₃) \(\delta\) 212.2 (d, \(J = 27.9\) Hz), 159.0, 131.8, 129.5, 113.4, 103.2 (d, \(J = 238.4\) Hz), 62.5, 58.5, 55.2, 41.3, 19.2 (d, \(J = 4.4\) Hz), 18.7, 16.2; \(^3^1\)P NMR (101.25 MHz, CDCl₃) \(\delta\) 13.8; HRMS (ESI) m/z [MNa⁺] calcd for C₁₉H₃₀NNaO₆PS: 454.1424, found: 454.1425.

\(N-(4\text{-}\text{Methoxybenzyl})-4\text{-}methyl-\text{N}-(3\text{-}methyl-3-(\text{tetrahydro}-2\text{H}-\text{pyran}-2\text{-}yloxy)\text{buta-1,2-dien-1-yl})\text{benzenesulfonamide (S18).}\)

The \(N\)-\text{para}-methoxybenzyl \(N\)-tosylsulfonyl amine (1.6 mmol), CuSO₄·5H₂O (0.16 mmol), and K₃PO₄ (3.2 mmol) were heated to 70 °C in 3.3 mL of dry toluene under inert atmosphere. Bromoalkyne (2.4 mmol) in 3.3 mL of dry toluene was then slowly added. After 3 h at 70 °C and 22 h at 90 °C, the mixture was cooled to room temperature, filtered through a pad of Celite®, and concentrated in vacuo. The residue was purified flash chromatography (Et₂O/PE 10/90 to 50/50) on neutral silica gel to yield the ynamide S18 as a colorless oil (728 mg, quantitative yield). \(R_f = 0.21\) (Et₂O/PE = 30/70); \(^1\)H NMR (250 MHz, CDCl₃) \(\delta\) 7.75 (d, \(J = 8.3\) Hz, 2H), 7.32 (d, \(J = 8.1\) Hz, 2H), 7.20 (d, \(J = 8.7\) Hz, 2H), 6.82 (d, \(J = 8.7\) Hz, 2H), 4.66 (dd, \(J = 5.6, 2.9\) Hz, 1H), 4.41 (s, 2H), 3.91 – 3.80 (m, 1H), 3.78 (s, 3H), 3.39 – 3.26 (m, 1H), 2.44 (s, 3H), 1.84 – 1.70 (m, 1H), 1.54 – 1.40 (m, 5H), 1.41 (s, 3H), 1.39 (s, 3H); \(^1^3\)C NMR (63 MHz, CDCl₃) \(\delta\) 159.7, 144.5, 134.7, 130.5, 129.6, 127.8, 126.5, 113.8, 96.3, 77.9, 73.8, 71.4, 63.5, 55.3, 55.0, 31.9, 30.6, 29.9, 25.4, 21.6, 20.7; HRMS (ESI) m/z [MNa⁺] calcd for C₂₅H₃₁NNaO₅S: 480.1815, found: 480.1814.

\(N-(4\text{-}\text{Methoxybenzyl})-4\text{-}methyl-\text{N}-(3\text{-}methylbuta-1,2-dien-1-yl)benzenesulfonamide (6).\)

Prepared according to the procedure reported by Murakami et al. [2]. To a suspension of LiAlH₄ (0.55 mmol) in 1 mL of freshly distilled diethyl ether is added at room temperature over 5 minutes a solution of the ynamide S18 (0.22 mmol) in freshly distilled diethyl ether (0.5 mL). After 1h30 of stirring at room temperature, the reaction was quenched by addition of a mixture of Celite® and a saturated solution of sodium sulfate. The aqueous layer was extracted with ether. The organic layer was dried over Na₂SO₄ and filtered over neutral silica (eluent Et₂O). The solvent was removed in vacuo to yield the allenylamide 6 as a colorless oil (41 mg, 53%). Due to its high sensitivity the allenylamide 6 was subjected to the cyclization without further purification. \(R_f = 0.41\) (Et₂O/PE = 30/70); \(^1\)H NMR (360 MHz, CDCl₃) \(\delta\) 7.71 (d, \(J = 8.4\) Hz, 2H), 7.31 (d, \(J = 8.1\) Hz, 2H), 7.17 (d, \(J = 8.7\) Hz, 2H), 6.81 (d, \(J = 8.7\) Hz, 2H), 6.54 (dt, \(J = 4.8, 2.4\) Hz, 1H), 4.16 (s, 2H), 3.77 (s, 3H), 2.43 (s, 3H), 1.44 (d, \(J = 2.5\) Hz, 6H); \(^1^3\)C NMR (91 MHz, CDCl₃) \(\delta\) 193.7, 158.9, 143.6, 135.6, 129.7, 129.1, 128.7, 127.4, 113.7, 108.8, 97.1, 55.4, 49.7, 21.8, 21.6; HRMS (ESI) m/z [MH⁺] calcd for C₂₀H₂₄NO₅S: 358.1471, found: 358.1465.
Diethyl (1-((N-(4-methoxybenzyl)-4-methylphenyl)sulfonamido)-4-methylpenta-2,3-dien-2-yl)phosphonate (7).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 50/50 to 100/0; yellow oil, 302 mg, 75% yield; RF = 0.15 (EtOAc/PE = 50/50); 1H NMR (250 MHz, CDCl3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 4.33 (s, 2H), 4.12 – 3.93 (m, 4H), 3.88 (d, J = 5.5 Hz, 2H), 3.78 (s, 3H), 2.44 (s, 3H), 1.75 (d, J = 6.7 Hz, 6H), 1.28 (t, J = 7.1 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 207.6 (d, J = 3.3 Hz), 159.4, 143.2, 138.0, 130.2, 129.7, 127.7 (s, J = 22.6 Hz), 127.3, 114.0, 101.2 (d, J = 15.6 Hz), 89.4 (d, J = 188.6 Hz), 62.3 (d, J = 5.9 Hz), 55.4, 50.4, 45.0 (d, J = 17.4 Hz), 21.6, 19.5 (d, J = 6.5 Hz), 16.4 (d, J = 6.5 Hz); 31P NMR (101.25 MHz, CDCl3) δ 16.3; HRMS (ESI) m/z [MH+] calcd for C25H35NO6PS: 508.1917, found: 508.1913.

N-(1-(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-3-methylbuta-1,2-dien-1-yl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (29).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 40/60 to 50/50; white solid, 1.27 g, 62% yield; RF = 0.50 (EtOAc/PE = 80/20); mp = 105-108 °C; 1H NMR (360 MHz, CDCl3) δ 7.80 (d, J = 8.3 Hz, 2H), 7.29 (dd, J = 8.6, 2.3 Hz, 4H), 6.81 (d, J = 8.7 Hz, 2H), 4.58 (s, 2H), 3.91 (ddd, J = 29.2, 14.5, 8.0 Hz, 4H), 3.78 (s, 3H), 2.43 (s, 3H), 1.59 (d, J = 4.6 Hz, 6H), 1.22 (s, 3H), 0.81 (s, 3H); 13C NMR (91 MHz, CDCl3) δ 210.3 (d, J = 26.2 Hz), 159.1, 143.4, 136.9, 130.7, 129.3, 127.8, 113.5, 105.0 (d, J = 12.3 Hz), 94.0 (d, J = 231.9 Hz), 77.0 (d, J = 6.7 Hz), 55.2, 52.3, 32.2 (d, J = 6.9 Hz), 21.8, 21.4, 20.6, 19.2 (d, J = 5.0 Hz); 31P NMR (101.25 MHz, CDCl3) δ 3.9; HRMS (ESI) m/z [MNa+] calcd for C25H32NNaO6PS: 528.1580, found: 528.1565.

Diethyl (1-((N-(4-methoxyphenethyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (30).

Prepared according to the general procedure. Flash Chromatography: EtOAc/PE 40/60 to 100/0; yellow oil, 1.96 g, quantitative yield; RF = 0.50 (EtOAc/PE = 80/20); mp = 105-108 °C; 1H NMR (250 MHz, CDCl3) δ 7.66 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 4.14 – 3.98 (m, 4H), 3.69 (s, 3H), 3.53 – 3.42 (m, 2H), 2.77 (d, J = 9.6, 6.6 Hz, 2H), 2.33 (s, 3H), 1.73 (d, J = 4.7 Hz, 6H), 1.25 (t, J = 7.0 Hz, 6H); 13C NMR (62.9 MHz, CDCl3) δ 209.0 (d, J = 25.4 Hz), 158.1, 143.2, 136.6, 130.3, 129.6, 129.2, 127.7, 113.8, 105.2 (d, J = 12.3 Hz), 96.8 (d, J = 238.4 Hz), 62.6 (d, J = 6.2 Hz), 55.1, 51.5, 33.8, 21.3, 19.4 (d, J = 4.9 Hz), 16.2 (d, J = 6.4 Hz); 31P NMR (101.25 MHz, CDCl3) δ 11.9; HRMS (ESI) m/z [MH+] calcd for C25H35NO6PS: 508.1917, found: 508.1903.

Diethyl (1-((N-(4-methoxyphenyl)-4-methylphenyl)sulfonamido)-3-methylbuta-1,2-dien-1-yl)phosphonate (33).

Prepared according to general procedure. Flash Chromatography: EtOAc/PE 40/60 to 100/0; pink oil, 294 mg, 22% yield on two steps; RF = 0.28 (EtOAc/PE = 90/10); 1H NMR (250 MHz, CDCl3) δ 7.41 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 4.14 – 3.98 (m, 4H), 3.69 (s, 3H), 3.53 – 3.42 (m, 2H), 2.77 (d, J = 9.6, 6.6 Hz, 2H), 2.33 (s, 3H), 1.73 (d, J = 4.7 Hz, 6H), 1.25 (t, J = 7.0 Hz, 6H); 13C NMR (62.9 MHz, CDCl3) δ 209.0 (d, J = 25.4 Hz), 158.1, 143.2, 136.6, 130.3, 129.6, 129.2, 127.7, 113.8, 105.2 (d, J = 12.3 Hz), 96.8 (d, J = 238.4 Hz), 62.6 (d, J = 6.2 Hz), 55.1, 51.5, 33.8, 21.3, 19.4 (d, J = 4.9 Hz), 16.2 (d, J = 6.4 Hz); 31P NMR (101.25 MHz, CDCl3) δ 11.9; HRMS (ESI) m/z [MH+] calcd for C25H35NO6PS: 508.1917, found: 508.1903.
\[ \delta = 8.9 \text{ Hz, } 2 \text{H}, \ 6.77 \text{ (d, } J = 9.0 \text{ Hz, } 2 \text{H}), \ 4.10 - 3.80 \text{ (m, } 4 \text{H}), \ 3.77 \text{ (s, } 3 \text{H}), \ 2.37 \text{ (s, } 3 \text{H}), \ 1.81 \text{ (d, } J = 4.8 \text{ Hz, } 6 \text{H}), \ 1.17 \text{ (t, } J = 7.1 \text{ Hz, } 6 \text{H}) \]; \[ ^{13} \text{C NMR (62.9 MHz, CDCl}_3 \] \[ \delta \ 207.7 \text{ (d, } J = 24.7 \text{ Hz), } 159.2, \ 143.4, \ 136.4, \ 132.6, \ 130.5, \ 128.9, \ 128.2, \ 113.9, \ 106.0 \text{ (d, } J = 12.4 \text{ Hz), } 99.4 \text{ (d, } J = 237.1 \text{ Hz), } 62.5 \text{ (d, } J = 5.2 \text{ Hz), } 55.4, \ 21.5, \ 19.8 \text{ (d, } J = 5.0 \text{ Hz), } 16.1 \text{ (d, } J = 6.8 \text{ Hz)}; \[ ^{31} \text{P NMR (101.25 MHz, CDCl}_3 \] \[ \delta \ 11.8; \text{ HRMS (ESI) m/z } [\text{MNa}^+] \text{ calcd for } C_{23}H_{30}NNaO_6P: \ 502.1424, \text{ found: } 502.1418. \]

**Procedure A for the Cyclization of the α-AAPs into the Spirodienone Lactams 3,12-24.**

To a solution of allenylphosphonate (0.20 mmol) in 3 mL of acetonitrile was added the solution of CAN (0.60 mmol) in distilled water (1.5 mL). The mixture was stirred at room temperature. After 30 minutes to 18 hours, the solution was diluted with water and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel to yield the spirodienones lactams 3,12-24.

**4-(Propan-2-ylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (3).**

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 20/80; white solid, 61 mg, 84% yield; \( R_f = 0.70 \) (EtOAc/PE = 60/40); mp = 202-205 °C; \( ^1H \) NMR (360 MHz, CDCl\(_3\)) \[ \delta \ 7.93 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{H), } 7.35 \text{ (d, } J = 8.2 \text{ Hz, } 2 \text{H), } 6.83 \text{ (d, } J = 10.0 \text{ Hz, } 2 \text{H), } 6.35 \text{ (d, } J = 10.0 \text{ Hz, } 2 \text{H), } 3.74 \text{ (s, } 2 \text{H), } 2.44 \text{ (s, } 3 \text{H), } 2.22 \text{ (s, } 3 \text{H), } 1.67 \text{ (s, } 3 \text{H); } ^{13} \text{C NMR (91 MHz, CDCl}_3 \] \[ \delta \ 184.5, \ 164.7, \ 158.4, \ 149.0, \ 145.6, \ 134.9, \ 129.9, \ 129.4, \ 128.4, \ 122.5, \ 51.2, \ 45.0, \ 23.0, \ 22.4, \ 21.8; \text{ HRMS (ESI) m/z } [\text{MH}^+] \text{ calcd for } C_{19}H_{20}NO_4S: \ 358.1108, \text{ found: } 358.1099. \]

**4-Ethylidene-2-tosyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (12).**

Prepared according to general procedure A (\( Z/E = 80:20 \)). Flash Chromatography: EtOAc/PE 30/70; white solid, 40 mg, 84% yield; \( R_f = 0.75 \) (\( Z \) stereoisomer), 0.69 (\( E \) isomer) (EtOAc/PE = 90/10); \( Z \) stereoisomer: \( ^1H \) NMR (250 MHz, CDCl\(_3\)) \[ \delta \ 7.96 \text{ (dd, } J = 8.7, \ 2.1 \text{ Hz, } 2 \text{H), } 7.37 \text{ (dd, } J = 8.0, \ 4.3 \text{ Hz, } 2 \text{H), } 6.79 - 6.70 \text{ (m, } 2 \text{H), } 6.34 - 6.24 \text{ (m, } 2 \text{H), } 6.04 \text{ (q, } J = 7.4 \text{ Hz, } 1 \text{H), } 2.45 \text{ (s, } 3 \text{H), } 2.11 \text{ (d, } J = 7.4 \text{ Hz, } 3 \text{H); } ^{13} \text{C NMR (63 MHz, CDCl}_3 \] \[ \delta \ 184.8, \ 147.4, \ 141.3, \ 129.6, \ 127.0, \ 51.6, \ 29.8, \ 21.6, \ 13.3; \text{ HRMS (ESI) m/z } [\text{MNa}^+] \text{ calcd for } C_{18}H_{17}NNaO_4S: \ 366.0770, \text{ found: } 366.0764. \]

**4-(Butan-2-ylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (13).**

Prepared according to general procedure A (\( Z/E = 64:36 \)). Flash Chromatography: EtOAc/PE 20/80; white solid, 33 mg, 54% yield; \( R_f = 0.81 \) (EtOAc/PE = 70/30); \( Z \) stereoisomer: \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \[ \delta \ 7.94 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{H), } 7.36 \text{ (d, } J = 8.2 \text{ Hz, } 2 \text{H), } 6.86 \text{ (t, } J = \)
10.2 Hz, 2H), 6.41 – 6.29 (m, 2H), 3.74 (s, 2H), 2.68 (q, \( J = 7.5 \) Hz, 2H), 2.44 (s, 3H), 1.66 (s, 3H), 0.98 (t, \( J = 7.5 \) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 184.6, 164.5, 164.2, 149.1, 145.6, 134.9, 129.9, 129.4, 128.4, 122.0, 51.2, 45.0, 28.2, 21.8, 20.5, 12.6; characteristic signals for the \( E \) stereoisomer: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 2.44 (s, 3H), 2.19 (s, 3H), 1.94 (q, \( J = 7.5 \) Hz, 2H), 0.90 (t, \( J = 7.6 \) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 149.7, 128.9, 29.2, 19.4, 12.3; HRMS (ESI) m/z [MNa\(^{+}\)] calcld for C\(_{20}\)H\(_{19}\)NNaO\(_3\): 394.1083, found: 394.1089.


Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 20/80 to 50/50; white solid, 47 mg, 64% yield; \( R_f \) = 0.89 (EtOAc/PE = 90/10); mp = 196-201 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 7.93 (d, \( J = 8.3 \) Hz, 2H), 7.35 (d, \( J = 8.2 \) Hz, 2H), 6.89 (d, \( J = 10.0 \) Hz, 2H), 6.33 (d, \( J = 10.0 \) Hz, 2H), 3.74 (s, 2H), 3.00 – 2.82 (m, 2H), 2.44 (s, 3H), 1.97 (m, 2H), 1.65 – 1.40 (m, 6H); \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \( \delta \) 184.6, 167.1, 164.9, 149.9, 145.6, 134.9, 129.9, 128.9, 128.5, 119.7, 51.1, 45.0, 32.6, 30.3, 28.7, 28.6, 25.9, 21.8; HRMS (ESI) m/z [MH\(^{+}\)] calcld for C\(_{24}\)H\(_{22}\)NO\(_3\): 398.1421, found: 398.1409.


Prepared according to general procedure A. (\( Z/E = 27:73 \)). Flash Chromatography: EtOAc/PE 20/80 to 60/40; white solid, 40 mg, 60% yield; \( R_f \) = 0.69 (EtOAc/PE = 50/50); \( E \) stereoisomer: \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 8.00 (d, \( J = 8.3 \) Hz, 2H), 7.71 (s, 1H), 7.40 (d, \( J = 8.2 \) Hz, 2H), 7.36 – 7.22 (m, 3H), 7.09 (d, \( J = 7.3 \) Hz, 2H), 6.80 – 6.72 (m, 2H), 6.34 – 6.29 (m, 2H), 3.83 (s, 2H), 2.47 (s, 3H); \(^{13}\)C NMR (91 MHz, CDCl\(_3\)) \( \delta \) 184.4, 165.4, 147.6, 146.0, 141.6, 134.6, 132.4, 130.4, 130.1, 128.5, 128.4, 119.1, 53.0, 45.1, 21.9; characteristic signals for the \( Z \) stereoisomer: \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 6.85 (d, \( J = 10.1 \) Hz, 2H), 6.57 (s, 1H), 6.38 (d, \( J = 10.1 \) Hz, 2H), 4.00 (s, 2H), 2.44 (s, 3H); \(^{13}\)C NMR (91 MHz, CDCl\(_3\)) \( \delta \) 148.0, 143.5, 131.7, 131.0, 129.4, 128.2, 127.0, 51.4; HRMS (ESI) m/z [MNa\(^{+}\)] calcld for C\(_{23}\)H\(_{19}\)NNaO\(_3\): 428.0927, found: 428.0915.

\( (E) \)-4-(1-Phenylethylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (16).

Prepared according to general procedure A. (\( Z/E < 5:95 \)). Flash Chromatography: EtOAc/PE 30/70 to 50/50; yellow solid, 29 mg, 43% yield; \( R_f \) = 0.69 (EtOAc/PE = 60/40); mp = 240-245 °C; \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 7.99 (d, \( J = 8.4 \) Hz, 2H), 7.40 (d, \( J = 8.2 \) Hz, 2H), 7.21 (d, \( J = 7.4 \) Hz, 1H), 7.14 (dd, \( J = 8.1, 6.7 \) Hz, 2H), 6.86 (dd, \( J = 7.0, 1.4 \) Hz, 2H), 6.59 – 6.51 (m, 2H), 5.87 – 5.80 (m, 2H), 3.69 (s, 2H), 2.48 (s, 6H); \(^{13}\)C NMR (91 MHz, CDCl\(_3\)) \( \delta \) 184.6, 165.0, 158.5, 147.9, 145.8, 141.0, 135.0, 135.0, 129.1, 128.5, 128.3, 128.1, 126.1, 125.8, 52.2, 46.1, 22.9, 21.9; HRMS (ESI) m/z [MH\(^{+}\)] calcld for C\(_{24}\)H\(_{22}\)NO\(_3\): 420.1264, found: 420.1253.

\( (S) \)-1-Methyl-2-(methylsulfonyl)-4-(propan-2-ylidene)-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (17).

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 40/60; yellow oil, 43 mg, 73% yield; \( R_f \) = 0.60 (EtOAc/PE = 70/30); \( [\alpha]_D^{20} = 52.9 \) (c 2.2, CHCl\(_3\)); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 6.96 (dd, \( J = 10.1, 2.8 \) Hz, 1H), 6.89 (dd, \( J = 10.1, 2.8 \) Hz, 1H), 6.47 (dd,
$J = 10.1$, $1.8$ Hz, $1H$), $6.33$ (dd, $J = 9.9$, $1.8$ Hz, $1H$), $4.09$ (q, $J = 6.4$ Hz, $1H$), $3.34$ (s, $3H$), $2.31$ (s, $3H$), $1.75$ (s, $3H$), $1.41$ (d, $J = 6.5$ Hz, $3H$); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 184.5, 165.9, 159.2, 148.8, 148.2, 131.2, 128.4, 122.2, 59.9, 49.1, 42.3, 23.4, 22.7, 19.8; HRMS (ESI) m/z [MNa$^+$] calcd for C$_{14}$H$_{15}$NNaO$_4$: 318.0770, found: 318.0774.


Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 20/80 to 30/70; white solid, 610 mg, 91% yield; $R_f = 0.62$ (EtOAc/PE = 90/10); mp = 182-185 °C; $^1$H NMR (250 MHz, CDCl$_3$) δ 6.92 (d, $J = 10.0$ Hz, 2H), 6.38 (d, $J = 9.9$ Hz, 2H), 3.72 (s, 2H), 3.33 (s, 3H), 2.31 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (91 MHz, CDCl$_3$) δ 184.5, 166.0, 159.4, 148.8, 129.4, 122.3, 50.4, 44.9, 40.7, 23.1, 22.4; HRMS (ESI) m/z [MH$^+$] calcd for C$_{13}$H$_{15}$NO$_4$: 304.0614, found: 304.0610.

4-Cyclohexylidene-2-(methylsulfonyl)-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (19).

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 30/70 to 70/30; white solid, 49 mg, 69% yield; $R_f = 0.68$ (EtOAc/PE = 70/30); mp = 208-212 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 6.97 (d, $J = 10.1$ Hz, 2H), 6.36 (d, $J = 10.0$ Hz, 2H), 3.71 (s, 2H), 3.34 (s, 3H), 3.04 – 2.94 (m, 2H), 2.09 – 2.03 (m, 2H), 1.69 – 1.61 (m, 2H), 1.60 – 1.50 (m, 4H); $^{13}$C NMR (91 MHz, CDCl$_3$) δ 184.5, 168.1, 166.2, 149.7, 129.0, 119.6, 50.3, 45.0, 40.8, 32.8, 30.5, 28.9, 28.7, 25.9; HRMS (ESI) m/z [MH$^+$] calcd for C$_{16}$H$_{20}$NO$_4$: 322.1108, found: 322.1103.

4’-(Propan-2-ylidene)-1’-tosyl-4H-spiro[naphthalene-1,3’-pyrrolidine]-4,5’-dione (22).

Prepared according to general procedure A. Flash Chromatography: EtOAc/EP 40/60; colorless oil, 20 mg, 43% yield; $R_f = 0.78$ (EtOAc/PE = 60/40); $^1$H NMR (300 MHz, CDCl$_3$) δ 8.18 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.49 (dtd, $J = 20.6$, 7.4, 1.1 Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.16 (d, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 10.1$ Hz, 1H), 6.53 (d, $J = 10.1$ Hz, 1H), 3.95 (dd, $J = 21.6$, 10.4 Hz, 2H), 2.49 (s, 3H), 2.26 (s, 3H), 1.30 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 183.8, 165.3, 157.8, 149.2, 146.2, 145.6, 135.1, 134.0, 131.0, 129.9, 128.5, 128.2, 128.0, 127.2, 126.5, 56.0, 45.1, 23.5, 22.1, 21.9; HRMS (ESI) m/z [MH$^+$] calcd for C$_{23}$H$_{22}$NO$_5$: 408.1264, found: 408.1253.


Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 40/60; orange solid, 37 mg, 50% yield; $R_f = 0.39$ (EtOAc/PE = 50/50); mp = 190-193 °C; $^1$H NMR (250 MHz, CDCl$_3$) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 6.83 (dd, $J = 9.8$, 2.6 Hz, 1H), 6.37 (d, $J = 9.8$ Hz, 1H), 5.77 (d, $J = 2.6$ Hz, 1H), 3.76 (s, 2H), 3.65 (s, 3H), 2.44 (s, 3H), 2.22 (s, 3H), 1.66 (s, 3H); $^{13}$C NMR (63 MHz, CDCl$_3$) δ 179.9, 164.9, 157.9, 151.7, 149.3, 145.6, 134.9, 129.9, 128.7, 128.4, 123.2, 116.9, 55.3, 52.6, 45.8, 23.0, 22.4, 21.8; HRMS (ESI) m/z [MH$^+$] calcd for C$_{20}$H$_{22}$NO$_5$: 388.1213, found: 388.1197.

Prepared according to general procedure A. Flash Chromatography: EtOAc/heptane 10/90 to 25/75; white solid, 47 mg, 47% yield; \( R_f = 0.72 \) (EtOAc/PE = 50/50); mp = 179-183 °C; \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 7.9 \) Hz, 2H), 7.37 (d, \( J = 8.0 \) Hz, 2H), 7.04 – 7.00 (m, 1H), 6.89 (dd, \( J = 9.8, 2.0 \) Hz, 1H), 6.46 (d, \( J = 9.9 \) Hz, 1H), 3.80 (s, 2H), 2.45 (s, 3H), 2.24 (s, 3H), 1.68 (s, 3H); \(^1^3\)C NMR (63 MHz, CDCl\(_3\)) \( \delta \) 177.7, 164.3, 159.1, 149.1, 145.7, 145.0, 134.7, 133.8, 130.0, 128.4, 128.2, 121.7, 50.8, 47.1, 23.1, 22.4, 21.8; HRMS (ESI) m/z [MH\(^+\)] calcd for C\(_{19}\)H\(_{19}\)ClNO\(_4\)S: 392.0718, found: 392.0709.

**4-(4-Methoxyphenyl)-3-(propan-2-ylidene)-1-tosylpyrrolidin-2-one (32).**

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 30/70 to 100/0; white oil, 15 mg, 20% yield; \( R_f = 0.88 \) (EtOAc/PE = 60/40); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 7.88 (d, \( J = 8.4 \) Hz, 2H), 7.30 (dd, \( J = 8.5, 0.5 \) Hz, 2H), 6.98 – 6.92 (m, 2H), 6.81 – 6.74 (m, 2H), 4.10 (dd, \( J = 14.6, 6.2 \) Hz, 2H), 3.78 (s, 3H), 3.81 – 3.70 (m, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 1.62 (s, 3H); \(^1^3\)C NMR (63 MHz, CDCl\(_3\)) \( \delta \) 166.9, 158.8, 153.1, 144.9, 144.9, 144.9, 135.7, 135.4, 129.7, 128.1, 126.6, 125.7, 126.6, 114.5, 55.4, 52.7, 40.8, 24.3, 21.8, 20.5; HRMS (ESI) m/z [MH\(^+\)] calcd for C\(_{21}\)H\(_{23}\)NO\(_4\)S: 386.1421, found: 386.1404.

**1′-Ethoxy-6′-tosyl-5′,6′-dihydrodispirocyclohexane-1,3′-[1,2]oxaphospholo[3,4-b]pyrrole-4′,1″-cyclohexane]-2″,5″-dien-4″-one 1′-oxide (28b).**

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 20/80 to 50/50; white solid, 12 mg, 16% yield; \( R_f = 0.47 \) (EtOAc/PE = 60/40); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 8.02 (d, \( J = 8.3 \) Hz, 2H), 7.40 (d, \( J = 8.4 \) Hz, 2H), 6.74 (dd, \( J = 9.9, 2.8 \) Hz, 1H), 6.37 – 6.19 (m, 3H), 4.53-4.35 (m, 2H), 4.01 (d, \( J = 10.8 \) Hz, 1H), 3.66 (d, \( J = 10.8 \) Hz, 1H), 2.46 (s, 3H), 1.70 – 1.20 (m, 10H), 1.43 (t, \( J = 7.1 \) Hz, 3H); \(^3^1\)P NMR (101.25 MHz, CDCl\(_3\)) \( \delta \) 9.8; HRMS (ESI) m/z [MH\(^+\)] calcd for C\(_{24}\)H\(_{29}\)NO\(_6\)PS: 490.1448, found: 490.1424.

**1′-Ethoxy-6′-tosyl-5′,6′-dihydrodispiro[chromane-4,3′-[1,2]oxaphospholo[3,4-b]pyrrole-4′,1″-cyclohexane]-2″,5″-dien-4″-one 1′-oxide (28c).**

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 30/70 to 50/50; white solid, 77 mg, 30% yield; \( R_f = 0.44 \) and 0.33 (EtOAc/PE = 50/50); \( R_f = 0.44 \). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 8.18 (d, \( J = 8.3 \) Hz, 2H), 7.50 (d, \( J = 8.2 \) Hz, 2H), 7.24 – 7.13 (m, 1H), 7.00 (d, \( J = 7.8 \) Hz, 1H), 6.88 (dd, \( J = 10.0, 2.8 \) Hz, 1H), 6.85-6.74 (m, 2H), 6.28 (d, \( J = 15.0 \) Hz, 2H), 37.1 (d, \( J = 14.1 \) Hz), 24.2, 21.8, 21.5, 16.7 (d, \( J = 6.1 \) Hz); \(^3^1\)P NMR (101.25 MHz, CDCl\(_3\)) \( \delta \) 9.8; HRMS (ESI) m/z [MH\(^+\)] calcd for C\(_{24}\)H\(_{29}\)NO\(_5\)PS: 490.1448, found: 490.1424.

**1'-Ethoxy-6'-tosyl-5',6'-dihydrodispiro[cyclohexane-4,3'-[1,2]oxaphospholo[3,4-b]pyrrole-4',1''-cyclohexane]-2'',5''-dien-4''-one 1'-oxide (28b).**

Prepared according to general procedure A. Flash Chromatography: EtOAc/PE 20/80 to 50/50; white solid, 12 mg, 16% yield; \( R_f = 0.47 \) (EtOAc/PE = 60/40); \( R_f = 0.47 \). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 8.02 (d, \( J = 8.3 \) Hz, 2H), 7.40 (d, \( J = 8.4 \) Hz, 2H), 6.74 (dd, \( J = 9.9, 2.8 \) Hz, 1H), 6.37 – 6.19 (m, 3H), 4.53-4.35 (m, 2H), 4.01 (d, \( J = 10.8 \) Hz, 1H), 3.66 (d, \( J = 10.8 \) Hz, 1H), 2.46 (s, 3H), 1.70 – 1.20 (m, 10H), 1.43 (t, \( J = 7.1 \) Hz, 3H); \(^3^1\)P NMR (101.25 MHz, CDCl\(_3\)) \( \delta \) 9.8; HRMS (ESI) m/z [MH\(^+\)] calcd for C\(_{24}\)H\(_{29}\)NO\(_5\)PS: 490.1448, found: 490.1424.
78.6, 66.3, 63.3, 62.2, 49.8 (d, $J = 14.9$ Hz); 35.3, 21.9, 16.7; $^{31}$P NMR (101.25 MHz, CDCl$_3$) $\delta$ 10.9; HRMS (ESI) m/z [MNa$^+$] calcd for C$_{27}$H$_{26}$NNaO$_7$PS: 562.1060, found: 562.1051.

**PROCEDURE B FOR THE CYCLIZATION OF THE $\alpha$-AAPs INTO THE SPIRODIENONE PHOSPHONATES 35.**

To a solution of allenylphosphonate (0.20 mmol) in 3 mL of alcohol (methanol or ethanol) was added the solution of CAN (0.60 mmol) in the alcohol (1.5 mL). The mixture was stirred at room temperature. After 30 minutes to 18 hours, the solvent is removed in vacuo. The residue was diluted with water and ethyl acetate and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel to yield the spirodienones 35.

**Diethyl (3-methoxy-8-oxo-4-(propan-2-ylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-dien-3-yl)phosphonate (35a).**

Prepared according to general procedure B. Flash Chromatography: EtOAc/PE 30/70 to 70/30; white solid, 47 mg, 83% yield; $R_f = 0.46$ (EtOAc/PE = 90/10); mp = 120-125 °C; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 6.84 (d, $J = 9.9$ Hz, 2H), 6.32-6.20 (m, 2H), 4.32 – 4.16 (m, 2H), 4.16-3.92 (m, 2H), 3.51 – 3.32 (m, 5H), 2.40 (s, 3H), 1.95 (d, $J = 3.4$ Hz, 3H), 1.55 (d, $J = 3.3$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.17 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 185.2, 151.3, 150.5, 144.0, 143.8 (d, $J = 4.9$ Hz), 136.1, 129.6, 129.3, 128.4, 127.6, 124.5 (d, $J = 5.6$ Hz), 99.0 (d, $J = 196.4$ Hz), 64.3 (d, $J = 6.6$ Hz), 63.2 (d, $J = 7.7$ Hz), 53.6, 50.5 (d, $J = 13.7$ Hz), 46.3, 22.5, 21.6, 21.5, 16.6 (d, $J = 5.1$ Hz), 16.3 (d, $J = 6.0$ Hz); $^{31}$P NMR (121.5 MHz, CDCl$_3$) $\delta$ 15.1; HRMS (ESI) m/z [MH$^+$] calcd for C$_{24}$H$_{33}$NO$_7$PS: 510.1710, found: 510.1703.

**Diethyl (3-ethoxy-8-oxo-4-(propan-2-ylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-dien-3-yl)phosphonate (35b).**

Prepared according to general procedure B. Flash Chromatography: EtOAc/PE 20/80 to 100/0; white solid, 57 mg, 83% yield; $R_f = 0.35$ (EtOAc/PE = 80/20); mp = 105-112 °C; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 6.86 (dd, $J = 10.0$, 2.6 Hz, 1H), 6.86 (dd, $J = 10.0$, 2.6 Hz, 1H), 6.29 (dd, $J = 6.2$, 1.9 Hz, 1H), 6.29 (dd, $J = 4.9$, 1.7 Hz, 1H), 4.33 (p, $J = 7.2$ Hz, 2H), 4.18 – 4.02 (m, 2H), 4.02 – 3.87 (m, 2H), 3.43 (s, 2H), 2.42 (s, 3H), 2.00 (d, $J = 3.4$ Hz, 3H), 1.57 (d, $J = 3.3$ Hz, 3H), 1.39 (t, $J = 5.5$ Hz, 3H), 1.34 (t, $J = 5.3$ Hz, 3H), 1.12 (t, $J = 6.2$ Hz, 3H); $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 185.2, 151.4, 150.6, 143.8, 143.6 (d, $J = 5.0$ Hz), 136.1, 129.6, 129.2, 128.4, 127.5, 124.6 (d, $J = 6.3$ Hz), 98.6 (d, $J = 203.6$ Hz), 64.7 (d, $J = 6.3$ Hz), 62.9 (d, $J = 7.6$ Hz), 58.4 (d, $J = 12.5$ Hz), 53.6, 46.4, 24.0, 22.6, 21.5 (d, $J = 12.0$ Hz), 16.6 (d, $J = 5.0$ Hz), 16.1 (d, $J = 6.2$ Hz), 14.4; $^{31}$P NMR (101.25 MHz, CDCl$_3$) $\delta$ 15.1; HRMS (ESI) m/z [MH$^+$] calcd for C$_{25}$H$_{34}$NNaO$_7$PS: 546.1686, found: 546.1684.

**3-(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-3-methoxy-4-(propan-2-ylidene)-2-tosyl-2-azaspiro[4.5]deca-6,9-dien-8-one (35c).**
Prepared according to general procedure B. Flash Chromatography: EtOAc/heptane 50/50; white solid, 89 mg, 86% yield; Rf = 0.16 (EtOAc/PE = 50/50); mp = 230-235 °C; 1H NMR (250 MHz, CDCl3) δ 7.74 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 10.1, 2.8 Hz, 1H), 6.77 (dd, J = 10.1, 2.8 Hz, 1H), 6.23 (dd, J = 6.3, 1.9 Hz, 1H), 6.19 (dd, J = 6.3, 2.0 Hz, 1H), 4.77 (d, J = 10.7 Hz, 1H), 4.46 (d, J = 10.2 Hz, 1H), 4.10 – 3.79 (m, 2H), 3.59 (d, J = 9.8 Hz, 1H), 3.48 (d, J = 0.7 Hz, 3H), 3.21 (d, J = 9.8 Hz, 1H), 2.36 (s, 3H), 1.86 (d, J = 3.1 Hz, 3H), 1.51 (d, J = 3.3 Hz, 3H), 1.29 (s, 3H), 0.86 (s, 3H); 13C NMR (63 MHz, CDCl3) δ 185.2, 152.2, 150.2, 144.2, 141.1 (d, J = 5.0 Hz), 136.1, 129.6, 129.1, 127.9, 127.6, 125.4 (d, J = 5.6 Hz), 101.0 (d, J = 197.3 Hz), 79.5 (d, J = 7.1 Hz), 78.9 (d, J = 6.6 Hz), 53.1, 50.8 (d, J = 13.5 Hz, 46.6), 32.4 (d, J = 7.8 Hz), 22.1, 21.5, 21.4, 21.3, 20.4; 31P NMR (101.25 MHz, CDCl3) δ 4.1; HRMS (ESI) m/z [MNa+]+ calcd for C25H32NNaO7PS: 544.1529, found: 544.1521.


Prepared according to general procedure B. Flash Chromatography: EtOAc/PE 40/60; yellow solid, 78 mg, 70% yield; Rf = 0.18 (EtOAc/PE = 70/30); mp = 150 - 155 °C; 1H NMR (250 MHz, CDCl3) δ 7.01 – 6.86 (m, 2H), 6.34 (dd, J = 5.1, 1.7 Hz, 1H), 6.30 (dd, J = 5.1, 1.8 Hz, 1H), 4.41-4.15 (m, 4H), 3.65-3.52 (m, 2H), 3.31 (d, J = 1.1 Hz, 3H), 3.10 (s, 3H), 1.94 (d, J = 3.4 Hz, 3H), 1.57 (d, J = 3.4 Hz, 3H), 1.34 (td, J = 7.1, 1.7 Hz, 6H); 13C NMR (63 MHz, CDCl3) δ 185.0, 151.0, 150.4, 143.7 (d, J = 5.0 Hz), 136.1, 129.6, 127.5, 124.6 (d, J = 6.0 Hz), 98.5 (d, J = 202.6 Hz), 64.4 (d, J = 5.8 Hz), 64.3 (d, J = 6.4 Hz), 53.4, 49.9 (d, J = 13.4 Hz), 46.0, 37.9, 22.2, 21.3, 16.4 (d, J = 5.2 Hz), 16.3 (d, J = 5.9 Hz); 31P NMR (101.25 MHz, CDCl3) δ 14.5; HRMS (ESI) m/z [MNa+]+ calcd for C18H28NNaO7PS: 456.1216, found: 456.1215.

Diethyl (3-ethoxy-2-(methylsulfonyl)-8-oxo-4-(propan-2-ylidene)-2-azaspiro[4.5]deca-6,9-dien-3-yl)phosphonate (35e).

Prepared according to general procedure B. Flash Chromatography: EtOAc/PE 40/60; yellow solid, 85 mg, 70% yield; Rf = 0.20 (EtOAc/PE = 70/30); mp = 191-195 °C; 1H NMR (250 MHz, CDCl3) δ 7.00 – 6.79 (m, 2H), 6.31 (dd, J = 7.7, 1.8 Hz, 1H), 6.27 (dd, J = 7.7, 1.8 Hz, 1H), 4.42 – 4.05 (m, 4H), 3.88 - 3.76 (m, 1H), 3.64 – 3.45 (m, 2H), 3.37 – 3.18 (m, 1H), 3.07 (s, 3H), 1.93 (d, J = 3.4 Hz, 3H), 1.53 (d, J = 3.5 Hz, 3H), 1.32 (t, J = 7.0 Hz, 6H), 1.18 (t, J = 7.0 Hz, 3H); 13C NMR (63 MHz, CDCl3) δ 185.0, 151.0, 150.4, 143.7 (d, J = 5.0 Hz), 129.6, 127.5, 124.6 (d, J = 6.0 Hz), 98.5 (d, J = 202.6 Hz), 64.4 (d, J = 5.8 Hz), 64.3 (d, J = 6.4 Hz), 53.4, 49.9 (d, J = 13.4 Hz), 46.0, 37.9, 22.2, 21.3, 16.4 (d, J = 5.2 Hz), 16.3 (d, J = 5.9 Hz); 31P NMR (101.25 MHz, CDCl3) δ 14.5; HRMS (ESI) m/z [MNa+]+ calcd for C19H30NNaO7PS: 470.1373, found: 470.1376.

Diethyl (7-chloro-3-methoxy-8-oxo-(propan-2-ylidene)-2-tosyl-2-azaspiro[4.5]dec-6,9-dien-3-yl)phosphonate (35g).

Prepared according to general procedure B. Flash Chromatography: EtOAc/PE 20/80 to 50/50; yellow oil, 46 mg, 78% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.85 – 7.75 (m, 2H), 7.31 (d, \(J = 8.4\) Hz, 2H), 7.04 (d, \(J = 2.7\) Hz, 1H), 6.87 (dd, \(J = 9.8, 2.7\) Hz, 1H), 6.35 (d, \(J = 9.8\) Hz, 1H), 4.25 (dd, \(J = 14.2, 7.1\) Hz, 2H), 4.16 – 4.01 (m, 2H), 4.03 – 3.97 (m, 2H), 3.59 – 3.58 (m, 2H), 3.56 – 3.49 (m, 2H), 3.44 (d, \(J = 7.1\) Hz, 2H), 2.42 (s, 3H), 1.98 (d, \(J = 3.4\) Hz, 3H), 1.57 (d, \(J = 3.3\) Hz, 3H), 1.34 (t, \(J = 7.1\) Hz, 3H), 1.20 (t, \(J = 7.1\) Hz, 3H); \(^1^C\)NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.3, 150.5, 147.3, 144.5 (d, \(J = 5.0\) Hz), 144.2, 136.0, 133.5, 129.4, 128.5, 126.6, 123.8 (d, \(J = 6.4\) Hz), 99.0 (d, \(J = 204.8\) Hz), 64.5 (d, \(J = 6.6\) Hz), 63.5 (d, \(J = 7.5\) Hz), 53.3, 50.6 (d, \(J = 13.7\) Hz), 48.5, 22.6, 21.7, 21.5, 16.6 (d, \(J = 5.2\) Hz), 16.3 (d, \(J = 5.8\) Hz); \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\)) \(\delta\) 14.9; 2\textsuperscript{nd} stereoisomer: \(R_\ell = 0.30\) (EtOAc/PE = 60/40); \(^1\)H NMR (360 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 6.99 (d, \(J = 2.7\) Hz, 1H), 6.90 (dd, \(J = 9.9, 2.7\) Hz, 1H), 6.37 (d, \(J = 9.9\) Hz, 1H), 4.34 – 4.17 (m, 2H), 4.16 – 4.03 (m, 2H), 3.59 – 3.38 (m, 2H), 3.45 (d, \(J = 0.8\) Hz, 3H), 2.42 (s, 3H), 1.99 (d, \(J = 3.3\) Hz, 3H), 1.58 (d, \(J = 3.3\) Hz, 3H), 1.34 (t, \(J = 7.1\) Hz, 3H), 1.20 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.2, 151.5, 146.4, 144.7 (d, \(J = 4.9\) Hz), 144.3, 136.0, 132.3, 129.4, 128.5, 123.8 (d, \(J = 6.5\) Hz), 99.0 (d, \(J = 204.5\) Hz), 64.4 (d, \(J = 6.6\) Hz), 63.5 (d, \(J = 7.4\) Hz), 53.2, 50.7 (d, \(J = 13.6\) Hz), 48.7, 22.6, 21.6 (d, \(J = 8.0\) Hz), 16.7 (d, \(J = 5.1\) Hz), 16.3 (d, \(J = 5.8\) Hz); \(^{31}\)P NMR (121.5 MHz, CDCl\(_3\)) \(\delta\) 14.8; HRMS (ESI) m/z [MNa\(^{+}\)] calcd for C\(_{25}\)H\(_{31}\)CINaO\(_3\): 558.1686, found: 558.1678.

\textbf{Procedure C for the cyclization of the \(\alpha\)-AAPs into the spirodienone cyclic phosphonates 28.}

To a solution of allenylphosphonate (0.20 mmol) in 3 mL of acetonitrile was added the solution of CAN (0.60 mmol) in acetonitrile (1.5 mL). The mixture was stirred at room temperature. After 30 minutes to 18 hours, the solution was diluted with water and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel to yield the spirodienones 28.
1'-Ethoxy-3'-methyl-3'-phenyl-6'-tosyl-3',5',6'-trihydrospiro[cyclohexane-1,4'-[1,2]oxaphospholo[3,4-b]pyrrole]-2,5-dien-4-one 1'-oxide (28a).

Prepared according to general procedure A or C. Flash Chromatography: EtOAc/PE 30/70 to 50/50; procedure A: 34 mg, 37% yield; procedure D: 14 mg, 70% yield; 1st stereoisomer: white solid; R\textsubscript{f} = 0.60 (EtOAc/PE = 60/40); mp = 185-190 °C; 1H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.10 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.27 (m, 5H), 6.78 (dd, J = 10.0, 2.9 Hz, 1H), 6.32 (dd, J = 10.0, 1.6 Hz, 1H), 5.60 (d, J = 10.0 Hz, 1H), 5.40 (dd, J = 10.0, 2.9 Hz, 1H), 4.61 – 4.44 (m, 2H), 4.01 (d, J = 11.0 Hz, 1H), 3.61 (d, J = 11.0 Hz, 1H), 2.49 (s, 3H), 1.80 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H); 13C NMR (75 MHz, CDCl\textsubscript{3}) δ 183.9, 149.8 (d, J = 32.4 Hz), 146.3 (d, J = 1.5 Hz), 145.9 (d, J = 1.6 Hz), 145.4, 139.0 (d, J = 3.5 Hz), 136.7 (d, J = 194.1 Hz), 132.2, 130.4, 130.3, 129.0, 128.8, 128.7, 125.9, 83.9 (d, J = 2.2 Hz), 66.1 (d, J = 6.4 Hz), 63.0 (d, J = 6.8 Hz), 50.2 (d, J = 14.9 Hz), 26.1, 21.9, 16.8 (d, J = 6.3 Hz); 31P NMR (101.25 MHz, CDCl\textsubscript{3}) δ 12.7; 2nd stereoisomer: white solid; R\textsubscript{f} = 0.31 (EtOAc/PE = 60/40); mp = 166-170 °C; 1H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.08 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.34 – 7.17 (m, 5H), 6.39 (dd, J = 10.0, 2.7 Hz, 1H), 6.25 (d, J = 10.1 Hz, 1H), 5.93 (dd, J = 10.0, 2.8 Hz, 1H), 5.53 (d, J = 9.9 Hz, 1H), 4.73 – 4.51 (m, 2H), 3.92 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 2.49 (s, 3H), 1.86 (s, 3H), 1.54 (t, J = 7.1 Hz, 3H); 13C NMR (91 MHz, CDCl\textsubscript{3}) δ 183.9, 149.6 (d, J = 32.5 Hz), 145.7, 145.4, 139.1, 136.7 (d, J = 194.5 Hz), 131.9, 131.0, 130.3, 129.1, 128.8, 128.1, 125.6, 84.0, 66.5 (d, J = 5.9 Hz), 62.9 (d, J = 6.7 Hz), 50.1 (d, J = 15.2 Hz), 26.9, 21.9, 16.8 (d, J = 6.0 Hz); 31P NMR (121.5 MHz, CDCl\textsubscript{3}) δ 12.2; HRMS (ESI) m/z [MH\textsuperscript{+}] calcd for C\textsubscript{26}H\textsubscript{27}NO\textsubscript{6}PS: 512.1291, found: 512.1292.

1'-Ethoxy-3',3'-dimethyl-6'-tosyl-3',5',6'-trihydrospiro[cyclohexane-1,4'-[1,2]oxaphospholo[3,4-b]pyrrole]-2,5-dien-4-one 1'-oxide (28d).

Prepared according to general procedure C. Flash Chromatography: EtOAc/PE 20/80 to 50/50; white solid, 27 mg, 30% yield; R\textsubscript{f} = 0.57 (EtOAc/PE = 90/10); mp = 147-151 °C; 1H NMR (250 MHz, CDCl\textsubscript{3}) δ 8.02 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.34 – 7.17 (m, 5H), 6.39 (dd, J = 10.0, 2.7 Hz, 1H), 6.25 (d, J = 10.1 Hz, 1H), 5.93 (dd, J = 10.0, 2.8 Hz, 1H), 5.53 (d, J = 9.9 Hz, 1H), 4.73 – 4.51 (m, 2H), 3.92 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 2.49 (s, 3H), 1.86 (s, 3H), 1.54 (t, J = 7.1 Hz, 3H); 13C NMR (63 MHz, CDCl\textsubscript{3}) δ 183.8, 149.6 (d, J = 32.5 Hz), 145.7, 145.4, 139.1, 136.7 (d, J = 194.5 Hz), 131.9, 131.0, 130.3, 129.1, 128.8, 128.1, 125.6, 84.0, 66.5 (d, J = 5.9 Hz), 62.9 (d, J = 6.7 Hz), 50.1 (d, J = 15.2 Hz), 26.9, 21.9, 16.8 (d, J = 6.0 Hz); 31P NMR (121.5 MHz, CDCl\textsubscript{3}) δ 12.2; HRMS (ESI) m/z [MH\textsuperscript{+}] calcd for C\textsubscript{20}H\textsubscript{27}NO\textsubscript{6}PS: 512.1291, found: 512.1292.

References
$^{1}\text{H}$ AND $^{13}\text{C}$ NMR SPECTRA
**$^1$H NMR – 250 MHz – CDCl$_3$**

```
H NMR – 250 MHz – CDCl$_3$

$^1$H NMR spectrum with peaks at various ppm values.
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**$^{13}$C NMR – 63 MHz – CDCl$_3$**

```
$^{13}$C NMR – 63 MHz – CDCl$_3$

$^{13}$C NMR spectrum with peaks at various ppm values.
```
$^{1}H$ NMR – 250 MHz – CDCl$_3$

$^{13}C$ NMR – 91 MHz – CDCl$_3$
**$^1$H NMR – 250 MHz – CDCl$_3$**

![Chemical Structure](image)

**$^{13}$C NMR – 91 MHz – CDCl$_3$**

![Chemical Structure](image)
\[ ^1\text{H NMR} \text{ -250 MHz - CDCl}_3 \]

\[ ^{13}\text{C NMR} \text{ -91 MHz - CDCl}_3 \]
$^1$H NMR – 250 MHz – CDCl$_3$

$^{13}$C NMR – 63 MHz – CDCl$_3$
**1H NMR – 250 MHz – CDCl₃**

**13C NMR – 63 MHz – CDCl₃**
» **$^1$H NMR – 250 MHz – CDCl$_3$**

![1H NMR spectrum](image)

» **$^{13}$C NMR – 63 MHz – CDCl$_3$**

![13C NMR spectrum](image)
**1H NMR – 250 MHz – CDCl₃**

**13C NMR – 63 MHz – CDCl₃**
**$^1$H NMR – 360 MHz – CDCl$_3$**

![NMR spectrum](image)

**$^{13}$C NMR – 91 MHz – CDCl$_3$**

![NMR spectrum](image)
\[ ^1H \text{ NMR} - 250 \text{ MHz} - \text{CDCl}_3 \]

\[ ^13C \text{ NMR} - 63 \text{ MHz} - \text{CDCl}_3 \]
» **$^1$H NMR – 300 MHz – CDCl$_3$**

MeO

Cl

N

Me

\(\text{O} (\text{OEt})_2\)

\(\text{H}_3\text{C} - \text{CH}_3\)

S12

» **$^{13}$C NMR – 75 MHz – CDCl$_3$**
\[ ^1H \text{ NMR} \quad 250 \text{ MHz} \quad \text{CDCl}_3 \]

\[ ^13C \text{ NMR} \quad 63 \text{ MHz} \quad \text{CDCl}_3 \]
1H NMR – 250 MHz – CDCl₃

![](image)

13C NMR – 63 MHz – CDCl₃
$^{1}H$ NMR – 250 MHz – CDCl$_3$

![H NMR spectrum](image)

$^{13}C$ NMR – 63 MHz – CDCl$_3$

![C NMR spectrum](image)
**$^{1}$H NMR – 250 MHz – CDCl$_3$**

![NMR spectrum of a compound](image)

**$^{13}$C NMR – 63 MHz – CDCl$_3$**

![C NMR spectrum of a compound](image)
\[ \text{\textbf{\textit{1}H NMR – 250 MHz – CDCl}_3} \]

![NMR spectrum graph]  

\[ \text{\textbf{\textit{1}C NMR – 75 MHz – CDCl}_3} \]

![C NMR spectrum graph]
\[ \text{H NMR – 250 MHz – CDCl}_3 \]

\[ \text{C NMR – 63 MHz – CDCl}_3 \]
**$^1$H NMR – 360 MHz – CDCl$_3$**

![NMR spectrum](image)

**$^{13}$C NMR – 91 MHz – CDCl$_3$**

![NMR spectrum](image)
» **$^1$H NMR – 360 MHz – CDCl$_3$**

» **$^{13}$C NMR – 91 MHz – CDCl$_3$**
**1H NMR – 250 MHz – CDCl₃**

![1H NMR spectrum](image)

**13C NMR – 75 MHz – CDCl₃**

![13C NMR spectrum](image)
1H NMR – 250 MHz – CDCl₃

Ts

N

O

O

C

H

CH₃

Z/E = 80:20

13C NMR – 63 MHz – CDCl₃
**$^1$H NMR – 300 MHz – CDCl$_3$**

![NMR Spectrogram](image)

**$^{13}$C NMR – 75 MHz – CDCl$_3$**

![C NMR Spectrogram](image)
$$\text{H NMR – 360 MHz – CDCl}_3$$

$$\text{C NMR – 91 MHz – CDCl}_3$$

$$Z/E = 27:73$$
$^{1}$H NMR – 360 MHz – CDCl$_3$

$^{13}$C NMR – 91 MHz – CDCl$_3$
**$^1$H NMR – 250 MHz – CDCl$_3$**

![NMR spectrum](image)

**13C NMR – 91 MHz – CDCl$_3$**

![NMR spectrum](image)
$^{1}H$ NMR – 360 MHz – CDCl$_3$

$^{13}C$ NMR – 91 MHz – CDCl$_3$
**$^1$H NMR – 300 MHz – CDCl$_3$**

![H NMR spectrum](image)

**$^{13}$C NMR – 75 MHz – CDCl$_3$**

![C NMR spectrum](image)
» **$^1$H NMR – 250 MHz – CDCl$_3$**

![NMR Spectrogram](image)

23

» **$^{13}$C NMR – 63 MHz – CDCl$_3$**

![C NMR Spectrogram](image)
NMR $^1$H – 250 MHz – CDCl$_3$

$^{13}$C NMR – 63 MHz – CDCl$_3$
NMR $^1$H – 300 MHz – CDCl$_3$
**1H NMR – 300 MHz – CDCl₃**

![1H NMR spectrum](image)

**13C NMR – 91 MHz – CDCl₃**

![13C NMR spectrum](image)
**$^1$H NMR – 250 MHz – CDCl$_3$**

**$^{13}$C NMR – 63 MHz – CDCl$_3$**
\( ^1H \) NMR – 250 MHz – CDCl\(_3\)

![NMR spectrum](image)

\( ^{13}C \) NMR – 63 MHz – CDCl\(_3\)

![NMR spectrum](image)
$$^{1}H\text{ NMR – 250 MHz – CDCl}_3$$

$$^{13}C\text{ NMR – 63 MHz – CDCl}_3$$
1H NMR – 360 MHz – CDCl₃

13C NMR – 91 MHz – CDCl₃
H NMR – 250 MHz – CDCl$_3$

1H NMR spectrum of compound 30.

13C NMR – 63 MHz – CDCl$_3$

13C NMR spectrum of compound 30.
**1H NMR – 250 MHz – CDCl\textsubscript{3}**

![1H NMR spectrum]

**13C NMR – 63 MHz – CDCl\textsubscript{3}**

![13C NMR spectrum]
**$^1$H NMR – 250 MHz – CDCl$_3$**

![H NMR spectrum](image)

**$^{13}$C NMR – 63 MHz – CDCl$_3$**

![C NMR spectrum](image)
$^{1}H$ NMR – 300 MHz – CDCl$_3$

$^{13}C$ NMR – 63 MHz – CDCl$_3$
**$^1$H NMR – 250 MHz – CDCl$_3$**

![1H NMR spectrum](image)

**$^{13}$C NMR – 63 MHz – CDCl$_3$**

![13C NMR spectrum](image)
$^1$H NMR – 250 MHz – CDCl$_3$

$^{13}$C NMR – 63 MHz – CDCl$_3$
1H NMR – 250 MHz – CDCl₃

13C NMR – 63 MHz – CDCl₃
» **$^1$H NMR – 250 MHz – CDCl$_3$**

![H NMR spectrum](image)

» **$^{13}$C NMR – 63 MHz – CDCl$_3$**

![C NMR spectrum](image)
**$^1$H NMR – 250 MHz – CDCl$_3$**

![NMR spectrum](image)

**$^{13}$C NMR – 63 MHz – CDCl$_3$**

![NMR spectrum](image)
**$^1$H NMR – 300 MHz – CDCl$_3$**

Cl

$^1$H NMR spectrum showing chemical shifts for various protons.

**$^{13}$C NMR – 75 MHz – CDCl$_3$**

$^{13}$C NMR spectrum showing chemical shifts for various carbon atoms.

**Ts**

**OMe**

**P(OEt)$_2$**

**35g**

**Cl**

**H$_3$C**

**Me**

**P(OEt)$_2$**

**NCl$_3$**

**35g**
» $^1$H NMR – 360 MHz – CDCl$_3$

» $^{13}$C NMR – 75 MHz – CDCl$_3$