An Expeditious, Nano-BF₃.SiO₂ Catalyzed Michaelis-Arbuzov reaction in an Ionic Liquid: Synthesis of Privileged Aryl/Heterocyclic Phosphonates

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S.No.	Content	Page No.
1.	Spectral data of compounds 8a-c, 9a-c, 10a-c, 11a-c & 12a-c	1-5
2.	Fig. S-1: IR spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)	6
3.	Fig. S-2: ¹ H-NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)	7
4.	Fig. S-3: ¹³ C-NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)	8
5.	Fig. S-4: ³¹ P-NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)	9
6.	Fig. S-5: Mass spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)	10
7.	Fig. S-6: Elemental analysis of Dimethyl phenanthren-9-ylphosphonate (12a)	11

Preparation of aryl/heterocyclic phosphonates: General procedure

Preparation of aryl/heterocyclic phosphonates: General procedure

The same optimized procedure for the synthesis diethyl 4-methyl-2-nitrophenylphosphonate (**9b**) was adopted for the synthesis of rest of compounds **8-12(a-c)**.

SPECTRAL DATA

Dimethyl thiophen-2-ylphosphonate (8a)^[1]

IR (cm⁻¹) $\nu_{\max}$: 3084, 2982, 1415, 1248; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.53-7.32 (m, 2H, thiophene), 7.16-7.13 (m, 1H, thiophene), 3.74 (d, *J* = 11.6 Hz, 6H, -P(O)-(OCH₃)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 130.2, 128.6, 126.9, 126.2, 53.8 (d, *J* = 8.9 Hz, -P(O)-C); MS (ESI) (+ mode) *m/z*: 193; Anal. calcd. for C₆H₉O₃PS: C: 37.50, H: 4.72, Found: C: 37.41, H: 4.68.

Diethyl thiophen-2-ylphosphonate (8b)^[2]

IR (cm⁻¹) $\nu_{\max}$: 3076, 2982, 1415, 1245; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.51-7.29 (m, 2H, thiophene), 7.18-7.15 (m, 1H, thiophene), 4.23-4.13 (m, 4H, -P(O)-(O-CH₂-CH₃)₂), 1.24 (t, *J* = 7.6 Hz, 6H, P(O)-(O-C-CH₃)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 130.1, 128.0, 126.5, 125.3, 64.1 (d, *J* = 6.8 Hz, -P(O)-C), 17.6; MS (ESI) (+ mode) *m/z*: 221. ; Anal. calcd. for C₈H₁₃O₃PS: C: 43.63, H: 5.95. Found: C: 43.58, H: 5.89.

Diisopropyl thiophen-2-ylphosphonate (8c)

IR (cm⁻¹) $\nu_{\max}$: 3078, 2982, 1412, 1240; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 7.52-7.33 (m, 2H, thiophene), 7.18-7.16 (m, 1H, thiophene), 4.63-4.48 (m, 4H, -P(O)-(O-CH₂-CH₃)₂), 1.28 (d, *J* = 7.2 Hz, 12H, P(O)-(O-CH₂-C(CH₃)₂)); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 129.3, 127.5, 126.2, 125.3, 72.3 (d, *J* = 8.3 Hz, -P(O)-C), 23.8; ³¹P NMR (161.9 MHz, DMSO-*d*₆) δ : 18.2; MS

(ESI) (+ mode) m/z : 190.; Anal. cald. for $C_7H_{10}O_2PS$: C: 44.44, H: 5.33. Found: C: 44.39, H: 5.28.

Dimethyl 4-methyl-2-nitrophenylphosphonate (9a)

IR (cm^{-1}) ν_{max} : 3092, 2986, 1532, 1255; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.28 (d, J = 6.8 Hz, 1H, Ar-H), 8.17 (s, 1H, Ar-H), 7.31 (d, J = 6.4 Hz, 1H, Ar-H), 3.78 (d, J = 9.2 Hz, 6H, -P(O)-(OCH₃)₂), 2.39 (s, 3H, Ar-CH₃); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 143.6, 139.8, 135.1, 132.8, 126.4, 124.7, 54.6 (d, J = 5.8 Hz, -P(O)-C), 21.2; ^{31}P NMR (161.9 MHz, $\text{DMSO-}d_6$) δ : 19.4; MS (ESI) (+ mode) m/z : 246; Anal. cald. for $C_9H_{12}NO_5P$: C: 44.09, H: 4.93, N: 5.71. Found: C: 44.01, H: 4.89, N: 5.66.

Diethyl 4-methyl-2-nitrophenylphosphonate (9b)

IR (cm^{-1}) ν_{max} : 3080, 2982, 1542, 1245; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.23 (d, J = 6.8 Hz, 1H, Ar-H), 8.16 (s, 1H, Ar-H), 7.28 (d, J = 6.4 Hz, 1H, Ar-H), 4.53-4.41 (m, 4H, -P(O)-(O-CH₂-C)₂), 2.32 (s, 3H, Ar-CH₃), 1.19 (t, J = 7.2 Hz, 6H, P(O)-(O-C-CH₃)₂); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 143.3, 139.7, 135.1, 132.2, 126.5, 124.9, 68.5 (d, J = 6.2 Hz, -P(O)-C), 23.4, 19.1; ^{31}P NMR (161.9 MHz, $\text{DMSO-}d_6$) δ : 18.7; MS (ESI) (+ mode) m/z : 274; Anal. cald. for $C_{11}H_{16}NO_5P$: C: 48.36, H: 5.90, N: 5.13. Found: C: 48.29, H: 5.84, N: 5.06.

Diisopropyl 4-methyl-2-nitrophenylphosphonate (9c)

IR (cm^{-1}) ν_{max} : 3092, 2986, 1540, 1248; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.26 (d, J = 6.8 Hz, 1H, Ar-H), 8.12 (s, 1H, Ar-H), 7.24 (d, J = 6.8 Hz, 1H, Ar-H), 4.57-4.52 (m, 2H, -P(O)-(O-CH-(C)₂)₂), 2.27 (s, 3H, Ar-CH₃), 1.18 (t, J = 6.4 Hz, 6H, P(O)-(O-C-(CH₃)₂)), 1.22 (t, J = 6.4 Hz, 6H, P(O)-(O-C-(CH₃)₂)); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 141.8, 139.6, 135.3, 131.5, 126.2, 125.1, 71.2 (d, J = 5.9 Hz, -P(O)-C), 24.2, 23.4, 23.7; ^{31}P NMR (161.9 MHz, $\text{DMSO-}d_6$)

δ : 19.2; MS (ESI) (+ mode) m/z : 302; Anal. calcd. for $C_{13}H_{20}NO_5P$: C: 51.83, H: 6.69, N: 4.65. Found: C: 51.78, H: 6.61, N: 4.60.

Dimethyl biphenyl-2-ylphosphonate (10a)

IR (cm^{-1}) ν_{max} : 3098, 2980, 1510, 1260; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.23-8.10 (m, 2H, Ar-H), 7.66-7.52 (m, 2H, Ar-H), 7.50-7.42 (m, 5H, Ar-H), 3.62 (d, $J = 6.8$ Hz, 6H, -P(O)-(OCH₃)₂); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 137.2, 135.4, 133.1, 132.8, 129.6, 128.2, 127.9, 127.6, 127.3, 123.4, 121.8, 53.2 (d, $J = 6.5$ Hz, -P(O)-C); ^{31}P NMR (161.9 MHz, $\text{DMSO-}d_6$) δ : 18.2; MS (ESI) (+ mode) m/z : 263; Anal. calcd. for $C_{14}H_{15}O_3P$: C: 64.12, H: 5.77. Found: C: 64.03, H: 5.69.

Diethyl biphenyl-2-ylphosphonate (10b)

IR (cm^{-1}) ν_{max} : 3094, 2980, 1510, 1252; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.23-8.12 (m, 2H, Ar-H), 7.68-7.55 (m, 2H, Ar-H), 7.51-7.42 (m, 5H, Ar-H), 4.48-4.40 (m, 4H, -P(O)-(O-CH₂-CH₃)₂), 1.20 (t, $J = 7.6$ Hz, 6H, P(O)-(O-CH₂-CH₃)₂); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 139.8, 136.5, 133.4, 132.6, 129.3, 129.0, 128.5, 127.8, 127.1, 126.7, 122.4, 121.8, 69.1 (d, $J = 5.8$ Hz, -P(O)-C), 18.4; ^{31}P NMR (161.9 MHz, $\text{DMSO-}d_6$) δ : 18.9; MS (ESI) (+ mode) m/z : 291; Anal. calcd. for $C_{16}H_{19}O_3P$: C: 66.20, H: 6.60. Found: C: 66.12, H: 6.52.

Diisopropyl biphenyl-2-ylphosphonate (10c)

IR (cm^{-1}) ν_{max} : 3088, 2984, 1520, 1252; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 8.20-8.08 (m, 2H, Ar-H), 7.73-7.65 (m, 2H, Ar-H), 7.62-7.43 (m, 5H, Ar-H), 4.50-4.42 (m, 2H, -P(O)-(O-CH(CH₃)₂)₂), 1.23 (t, $J = 6.4$ Hz, 6H, P(O)-(O-C-(CH₃)₂)₂), 1.20 (t, $J = 6.4$ Hz, 6H, P(O)-(O-C-(CH₃)₂)); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 137.2, 135.4, 133.1, 132.8, 129.6, 128.2, 127.9, 127.6, 127.3, 123.4, 121.8, 70.8 (d, $J = 6.2$ Hz, -P(O)-C), 24.1, 23.9; ^{31}P NMR (161.9 MHz,

DMSO-*d*₆) δ : 16.9; MS (ESI) (+ mode) m/z : 319; Anal. cald. for : C₁₈H₂₃O₃P: C: 67.91, H: 7.28. Found: C: 67.85, H: 7.21.

Dimethyl 1H-indol-5-ylphosphonate (11a)

IR (cm⁻¹) $\nu_{\max}$: 3320, 3088, 2985, 1508, 1249; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 11.18 (s, 1H, -NH), 8.09 (s, 1H, Ar-H), 7.72 (d, J = 8.0 Hz, 1H, Ar-H), 7.48 (d, J = 8.4 Hz, 1H, Ar-H), 7.21 (d, J = 8.8 Hz, 1H, Ar-H), 6.69 (d, J = 8.8 Hz, 1H, Ar-H), 3.68 (d, J = 7.2 Hz, 6H, -P(O)-(OCH₃)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 141.5, 130.1, 129.7, 125.3, 121.3, 120.6, 113.7, 104.0, 54.8 (d, J = 6.2 Hz, -P(O)-C); ³¹P NMR (161.9 MHz, DMSO-*d*₆) δ : 21.8; MS (ESI) (+ mode) m/z : 226; Anal. cald. for C₁₀H₁₂NO₃P: C: 53.34, H: 5.37, N: 6.22. Found: C: 53.31, H: 5.28, N: 6.19.

Diethyl 1H-indol-5-ylphosphonate (11b)

IR (cm⁻¹) $\nu_{\max}$: 3334, 3092, 2980, 1518, 1254; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 11.23 (s, 1H, -NH), 8.09 (s, 1H, Ar-H), 7.76 (d, J = 8.0 Hz, 1H, Ar-H), 7.54 (d, J = 8.0 Hz, 1H, Ar-H), 7.28 (d, J = 8.4 Hz, 1H, Ar-H), 6.73 (d, J = 8.8 Hz, 1H, Ar-H), 4.62-4.55 (m, 4H, -P(O)-(O-CH₂-CH₃)₂), 1.18 (t, J = 7.2 Hz, 6H, P(O)-(O-CH₂-CH₃)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 139.2, 130.3, 128.9, 125.3, 121.1, 121.4, 113.6, 103.8, 65.4 (d, J = 6.6 Hz, -P(O)-C), 18.2; ³¹P NMR (161.9 MHz, DMSO-*d*₆) δ : 21.2; MS (ESI) (+ mode) m/z : 254; Anal. cald. for C₁₂H₁₆NO₃P: C: 56.92, H: 6.37, N: 5.53. Found: C: 56.88, H: 6.31, N: 5.47.

Diisopropyl 1H-indol-5-ylphosphonate (11c)

IR (cm⁻¹) $\nu_{\max}$: 3328, 3090, 2980, 1520, 1245; ¹H NMR (400 MHz, DMSO-*d*₆) δ : 11.16 (s, 1H, -NH), 8.14 (s, 1H, Ar-H), 7.75 (d, J = 7.2 Hz, 1H, Ar-H), 7.48 (d, J = 7.6 Hz, 1H, Ar-H), 7.35 (d, J = 7.6 Hz, 1H, Ar-H), 6.72 (d, J = 7.6 Hz, 1H, Ar-H), 4.78-4.60 (m, 2H, -P(O)-(O-CH(CH₃)₂)₂), 1.24-1.17 (m, 12H, P(O)-(O-CH(CH₃)₂)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 142.0, 130.1,

128.9, 125.7, 122.6, 121.9, 113.5, 103.7, 71.1 (d, $J = 6.8$ Hz, -P(O)-C), 23.3, 22.7; ^{31}P NMR (161.9 MHz, DMSO- d_6) δ : 19.5; MS (ESI) (+ mode) m/z : 282; Anal. calcd. for $\text{C}_{11}\text{H}_{13}\text{BrNO}_4\text{P}$: C: 59.78, H: 7.17, N: 4.98. Found: C: 59.71, H: 7.13, N: 4.91.

Dimethyl phenanthren-9-ylphosphonate (12a)

IR (cm^{-1}) ν_{max} : 3075, 2981, 1512, 1240; ^1H NMR (400 MHz, DMSO- d_6) δ : 8.78 (d, $J = 6.8$ Hz, 1H, Ar-H), 8.66 (d, $J = 7.2$ Hz, 1H, Ar-H), 8.40 (d, $J = 12.4$ Hz, 1H, Ar-H), 8.12-8.01 (m, 2H, Ar-H), 7.85-7.60 (m, 4H, Ar-H), 3.75 (d, $J = 7.2$ Hz, 6H, -P(O)-(OCH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$); ^{13}C NMR (100 MHz, DMSO- d_6) δ : 138.4, 132.1, 130.7, 130.0, 129.8, 129.4, 129.1, 127.8, 126.4, 125.8, 125.7, 123.7, 123.5, 58.1 (d, $J = 9.7$ Hz, -P(O)-C); ^{31}P NMR (161.9 MHz, DMSO- d_6) δ : 18.4; MS (ESI) (+ mode) m/z : 287; Anal. calcd. for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{P}$: C: 67.13, H: 5.28. Found: C: 67.08, H: 5.28.

Diethyl phenanthren-9-ylphosphonate (12b)^[3]

IR (cm^{-1}) ν_{max} : 3094, 2980, 1513, 1257; ^1H NMR (400 MHz, DMSO- d_6) δ : 8.71 (d, $J = 7.2$ Hz, 1H, Ar-H), 8.66 (d, $J = 7.2$ Hz, 1H, Ar-H), 8.59 (d, $J = 12.2$ Hz, 1H, Ar-H), 8.20-8.07 (m, 2H, Ar-H), 7.73-7.56 (m, 4H, Ar-H), 4.58-4.42 (m, 4H, -P(O)-(O-CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$ -CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$), 1.16 (t, $J = 6.8$ Hz, 6H, P(O)-(O-CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$ -CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$); ^{13}C NMR (100 MHz, DMSO- d_6) δ : 139.2, 132.7, 130.5, 130.2, 129.9, 129.7, 129.4, 127.7, 126.3, 125.6, 123.6, 123.2, 68.7 (d, $J = 8.9$ Hz, -P(O)-C), 19.3; ^{31}P NMR (161.9 MHz, DMSO- d_6) δ : 19.6; MS (ESI) (+ mode) m/z : 315; Anal. calcd. for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{P}$: C: 68.78, H: 6.09. Found: C: 68.71, H: 6.00.

Diisopropyl phenanthren-9-ylphosphonate (12c)

IR (cm^{-1}) ν_{max} : 3090, 2978, 1524, 1255; ^1H NMR (400 MHz, DMSO- d_6) δ : 8.67 (d, $J = 6.4$ Hz, 1H, Ar-H), 8.62 (d, $J = 7.2$ Hz, 1H, Ar-H), 8.55 (d, $J = 9.6$ Hz, 1H, Ar-H), 8.15-8.01 (m, 2H, Ar-H), 7.81-7.63 (m, 4H, Ar-H), 4.72-4.53 (m, 2H, -P(O)-(O-CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$ -(CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$), 1.21 (d, $J = 7.2$ Hz, 6H, P(O)-(O-CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$ -(CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$), 1.18 (d, $J = 7.2$ Hz, 6H, P(O)-(O-CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$ -(CH $\underline{\text{H}}$ $\underline{\text{H}}$ $\underline{\text{H}}$) $_2$); ^{13}C NMR (100 MHz, DMSO- d_6) δ :

139.2, 132.6, 130.7, 130.0, 129.9, 129.4, 129.1, 127.7, 127.5, 126.5, 123.3, 123.1, 70.5 (d, $J = 5.6$ Hz, -P(O)-C), 21.9, 20.3; ^{31}P NMR (161.9 MHz, DMSO- d_6) δ : 19.0; MS (ESI) (+ mode) m/z : 343; Anal. calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{P}$: C: 70.16, H: 6.77. Found: C: 70.13, H: 6.71.

References

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Fig. S-1: IR spectrum of Dimethyl phenanthren-9-ylphosphonate (**12a**)

Fig. S-2: ^1H -NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (**12a**)

Fig. S-3: ^{13}C -NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (12a)

Fig. S-4: ^{31}P -NMR spectrum of Dimethyl phenanthren-9-ylphosphonate (**12a**)

Fig. S-5: Mass spectrum of Dimethyl phenanthren-9-ylphosphonate (**12a**)

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THERMO FINNIGAN

Company name:
 Method filename: \Program Files\Thermo Finnigan\Eager 300 for EA1112\data
 Sample ID: SRD
 Analysis type: Unknown
 Chromatogram filename: UNK
 Sample weight in mg: 1.978

Peak Number(#)	Component Name	Element %	Retention time
1.	Carbon	67.08	1.14
2.	Hydrogen	5.28	3.65

Fig. S-6: Elemental analysis of Dimethyl phenanthren-9-ylphosphonate (*12a*)