# Supporting Information:

**Electrosynthesis of α-arylated β-substituted cyclopropylphosphonates. Synthesis of a phosphonic analogue of Minalcipran.**

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## Experimental

$^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on Bruker DPX-300 spectrometer. The chemical shifts are expressed in ppm relative to tetramethylsilane for $^{1}H$ and $^{13}C$ and to $H_3PO_4$ for $^{31}P$ nucleus, the coupling constants (J) are given in Hz and conventional abbreviations are used. Reagents and solvents were purchased from commercial suppliers. DMF was purified by distillation on BaO under reduced pressure and distilled just before use. Tetraethylammonium bromide was purified by recristalisation (ethanol-ether) and dried at 120 °C under vaccum during 5h. Cathodes, purchased from Le Carbone Lorraine, are carbon felt plates (45 mm x 35 mm, depth: 5 mm, specific area: 0.3 $m^2.g^{-1}$). Magnesium anodes, purchased from Prolabo, are rods (diameter: 20 mm). TLC was performed on Merck 60 F-254 silica gel plates and flash chromatography over silica gel (230-400 mesh). Mass spectra under electronic impact at 70 eV (m/z and relative abundance in % are given) were obtained with a GC-MS Hewlett Packard 5970 mass selective detector. HRMS measurements under chemical ionisation were performed on a Jeol AX 500 spectrometer.

**Typical Procedure for the Electrosynthesis of 2e**: In a one-compartment cell, equipped with a carbon felt cathode (S = 16 $cm^2$) and a magnesium anode, a solution of diethyl α,α-dichlorobenzylphosphonate **1** (1.8 g, 6 mmol.) and methacrylonitrile (2g, 30 mmol, 5 eq.) in DMF (35 mL) containing $Et_4NBr$ (0.02 $mol.L^{-1}$) was introduced. A 100 mA constant current was applied. The electrolysis was continued until **1** was completely consumed (monitored by $^{31}P$ NMR spectroscopy). The reaction mixture was poured into THF (80 mL), then acidified with 1N HCl (100 mL) and extracted with diethyl ether (3x50 mL). The combined organic layers were washed with 1N HCl (2x50 mL) and dried. The solvents were evaporated in vacuo to give **2e**. Further purification on silica gel ($CH_2Cl_2$/$CH_3OH$: 98/2) gave pure **2 e** ( 1.28g, yield: 73 %).

**Diethyl α,α-dichlorobenzylphosphonate (1)**: oil, TLC (EtOAc/cyclohexane (1:9) $R_f$ = 0.2); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 11.8 (s); $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.2 (m, 6H, $O=P(OCH_2C\boldsymbol{H_3})_2$); 4.1 (m, 4H, $O=P(OC\boldsymbol{H_2}CH_3)_2$); 7.3 (m, 5H, ***H***arom.); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.5 MHz): 16.7 (d, $^{3}J_{CP}$= 5.5; $O=P(OCH_2\underline{\boldsymbol{C}}H_3)_2$); 66.2 (d, $^{2}J_{CP}$= 7.2; $O=P(O\underline{\boldsymbol{C}}H_2CH_3)_2$); 82.7 (d, $^{1}J_{CP}$= 177.8; $\underline{\boldsymbol{C}}Cl_2$); 128.3; 128.7; 130.0 (3s, $\underline{\boldsymbol{C}}_{o,m,p}$arom.); 136.9 (s, $\underline{\boldsymbol{C}}_{ipso}$).

**Diethyl 1-phenyl-2-methoxycarbonylcyclopropyl-1-phosphonate (2a)**: oil, TLC (MeOH/$CH_2Cl_2$ (2/98) $R_f$= 0.25) and distillation (Teb : 125°C/ 0.05 mmHg); FAB-MS *m/z* (rel. Intensity) 312 ($M^+$, 4), 256 (7), 224 (21), 196 (24), 174 (100), 159 (16), 115 (52).

**Diethyl 1-phenyl-*c*-2-methoxycarbonylcyclopropyl-*r*-1-phosphonate (2a *cis*)**: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): 24.2 (s); $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.2 (m, 6H, O=P($OCH_2C\boldsymbol{H_3}$)$_2$); 1.8 (m, 2H, C$\boldsymbol{H_2}$cycle); 2.6 (m, 1H, C$\boldsymbol{H}CO_2CH_3$); 3.4 (s, 3H, $CO_2C\boldsymbol{H_3}$); 4.0 (m, 4H, O=P($OC\boldsymbol{H_2}CH_3$)$_2$); 7.2 (m, 5H, ***H***arom.); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.5 MHz):16.7 (m, ***C3*** + O=P($OCH_2\boldsymbol{C}H_3$)$_2$); 28.9 (d, $^{2}J_{CP}$ =2.6; ***C2***,); 30.4 (d, $^{1}J_{CP}$ =189.0; ***C1***); 52.7 (s, O=$CO\boldsymbol{C}H_3$); 62.7; 63.1 (2d, $^{2}J_{CP}$= 6.6; O=P($O\boldsymbol{C}H_2CH_3$)$_2$); 128.0 (d, $^{5}J_{CP}$= 2.3; $\boldsymbol{C}_p$-arom); 128.7 (d, $^{4}J_{CP}$= 2.0, $\boldsymbol{C}_m$-arom); 130.9 (d, $^{3}J_{CP}$= 3.4; $\boldsymbol{C}_o$-arom); 139.1 (d, $^{2}J_{CP}$= 1.7; $\boldsymbol{C}_{ipso}$); 170.1 (d, $^{3}J_{CP}$= 7.3; O=$\boldsymbol{C}OCH_3$)

**Diethyl 1-phenyl-*t*-2-methoxycarbonylcyclopropyl-*r*-1-phosphonate (2a *trans*)**: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 25.5 (s); $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.2 (m, 6H, O=P($OCH_2C\boldsymbol{H_3}$)$_2$); 1.95 (m, 2H, C$\boldsymbol{H_2}$cycle); 2.6 (m, 1H, C$\boldsymbol{H}CO_2CH_3$); 3.45 (s, 3H, $CO_2C\boldsymbol{H_3}$); 4.0 (m, 4H, O=P($OC\boldsymbol{H_2}CH_3$)$_2$); 7.2 (m, 5H, ***H***arom.); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.5 MHz): 16.4 (d, $^{2}J_{CP}$= 2.5; ***C3***); 16.7 (m, O=P($OCH_2\boldsymbol{C}H_3$)$_2$); 24.9 (s, ***C2***); 30.3 (d, $^{1}J_{CP}$ =187; ***C1***); 52.3 (s, O=$CO\boldsymbol{C}H_3$); 63.2; 63.3 (2d, $^{2}J_{CP}$= 6.6; O=P($O\boldsymbol{C}H_2CH_3$)$_2$); 128.1 (d, $^{5}J_{CP}$= 2.6, $\boldsymbol{C}_p$-arom); 128.5 (d, $^{4}J_{CP}$ =2.2; $\boldsymbol{C}_m$-arom); 131.2 (d, $^{3}J_{CP}$= 3.9; $\boldsymbol{C}_o$-arom); 134.2 (s, $\boldsymbol{C}_{ipso}$); 170,0 (d, $^{3}J_{CP}$= 4.4; O=$\boldsymbol{C}OCH_3$);

**Diethyl 1-phenyl-2-*tert*-butoxycarbonylcyclopropyl-1-phosphonate (2b)**: oil, TLC (MeOH/$CH_2Cl_2$ (2/98) $R_f$= 0.2) and distillation (Teb: 125°C/ 0.05 mmHg); FAB-MS *m/z* (rel. Intensity) 354 ($M^+$, 5), 298 (81), 281 (46), 253 (20), 225 (24), 196 (24), 165 (45), 139 (30), 115 (100), 57 (62), 41 (44).

**Diethyl 1-phenyl-*c*-2-*tert*-butoxycarbonylcyclopropyl-*r*-1-phosphonate (2b *cis*)**: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): 24.5; $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.14 (td, $^{4}J_{HP}$= $^{3}J_{HH}$= 7.2; 6H, O=P($OCH_2C\boldsymbol{H_3}$)$_2$); 1.35 (m, 1H, C$\boldsymbol{H_2}$cycle); 1.45 (s, 9H, O=$COC(C\boldsymbol{H_3})_3$); 1.94 (m, 1H, C$\boldsymbol{H_2}$cycle); 2.1 (m, 1H, C$\boldsymbol{H}$-$CO_2C(CH_3)_2$); 3.94 (m, 4H, O=P($OC\boldsymbol{H_2}CH_3$)$_2$); 7.2 (m, 3H, ***H***arom.); 7.4 (d, $^{3}J_{HH}$= 6.6; 2H, ***H***arom.); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.5 MHz): 16.6 (m, ***C3***); 28.4 (s, O=$COC(\boldsymbol{C}H_3)_3$); 30.3 (d, $^{2}J_{CP}$= 2.4; ***C2***); 30.4 (d, $^{1}J_{CP}$= 189.2; ***C1***); 62.5; 62.9 (2d, $^{2}J_{CP}$= 6.5; O=P($O\boldsymbol{C}H_2CH_3$)$_2$); 81.4 (s, O=$CO\boldsymbol{C}(CH_3)_3$); 127.87 (d, $^{5}J_{CP}$= 2.3; $\boldsymbol{C}_{.p}$-arom); 128.6 (d, $^{4}J_{CP}$= 2.0; $\boldsymbol{C}_{.m}$-arom); 131.0 (d, $^{3}J_{CP}$= 3.4; $\boldsymbol{C}_{.o}$-arom); 139.5 (d, $^{2}J_{CP}$= 1.8; $\boldsymbol{C}_{.ipso}$); 168.54 (d, $^{3}J_{CP}$= 7.4; O=$\boldsymbol{C}OC(CH_3)_3$).

**Diethyl 1-phenyl-*t*-2-*tert*-butoxycarbonylcyclopropyl-*r*-1-phosphonate (2b *trans*)**: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): 25.5; $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.16 (td, $^{4}J_{HP}$= $^{3}J_{HH}$= 7.1; 6H, O=P($OCH_2C\boldsymbol{H_3}$)$_2$); 1.5 (s, 9H, O=$COC(C\boldsymbol{H_3})_3$); 1.7 (m, 1H, C$\boldsymbol{H_2}$cycle); 1.96 (m, 1H, C$\boldsymbol{H_2}$cycle); 2.4 (m, 1H, C$\boldsymbol{H}$-$CO_2C(CH_3)_2$); 3.94 (m, 4H, O=P($OC\boldsymbol{H_2}CH_3$)$_2$); 7.2 (m, 3H, ***H***arom.); 7.34 (m, 2H, ***H***arom.); $^{13}C\{^{1}H\}$ ($CDCl_3$, 75.5 MHz): 16.15 (d, $^{2}J_{CP}$= 2.6; ***C3***); 26.0 (d, $^{2}J_{CP}$= 1.4 (***C2***); 28.1 (s, O=$COC(\boldsymbol{C}H_3)_3$); 30.1 (d, $^{1}J_{CP}$= 186.7; ***C1***); 63.0; 63.2 (2d, $^{2}J_{CP}$= 6.5; O=P($O\boldsymbol{C}H_2CH_3$)$_2$); 81.3 (s, O=$CO\boldsymbol{C}(CH_3)_3$); 128.0 (d, $^{5}J_{CP}$= 2.5; $\boldsymbol{C}_{.(para)}$arom); 128.4 (d, $^{4}J_{CP}$= 2.1; $\boldsymbol{C}_{.(méta)}$arom); 131.5 (d, $^{3}J_{CP}$= 4.0; $\boldsymbol{C}_{.(ortho)}$arom); 134.3 (s, $\boldsymbol{C}_{.ipso}$); 168.5 (d, $^{3}J_{CP}$= 3.2; O=$\boldsymbol{C}OC(CH_3)_3$).

**Diethyl 1-phenyl-2-cyanocyclopropyl-1-phosphonate (2c)**: yellow oil, non-purified product. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):21 (s); 23 (s). $^{1}H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.18 (m, 6H, O=P($OCH_2C\boldsymbol{H_3}$)$_2$); 1.6 (m, 1H, C$\boldsymbol{H_2}$cycle); 2.0 (m, 1H, C$\boldsymbol{H_2}$cycle); 2.34 (m, 1H, C$\boldsymbol{H}$-CN); 4 (m, 4H, O=P($OC\boldsymbol{H_2}CH_3$)$_2$); 7.3 (m, 5H, ***H***arom.). FAB-MS *m/z* (rel. Intensity): 279 ($M^+$, 70), 252(5), 251 (29), 223 (70), 196 (100), 178 (7), 158 (19), 143 (35), 115 (64), 91 (18), 81 (28), 51 (13), 39 (7).

**Diethyl 1-phenyl-*c*-2-methoxycarbonyl-*t*-2-methylcyclopropyl-*r*-1-phosphonate (2d)**: oil, TLC (MeOH/$CH_2Cl_2$ (2/98) $R_f$= 0.2) and distillation (Teb : 125°C/ 0.1 mmHg); FAB-MS *m/z* (rel. Intensity): 326 ($M^+$, 61), 295 (15), 266 (21), 238 (72), 220 (15), 209 (29), 188 (100), 157 (24), 130 (18), 129 (96), 103 (19), 77 (25), 65 (16). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz): 25.2 (s). $^{1}H$ NMR

($CDCl_3$/TMS, 300 MHz):1.0 (s, 3H, C-C***H₃***); 1.2 (m, 6H, O=P($OCH_2C$***H₃***)$_2$ + 1H, C***H***$_2$ cycle); 2.2 (dd, 1H, $^2J_{HH}$= 5.1, $^3J_{HP}$= 18.0, C***H***$_2$ cycle); 3.7 (s, 3H, O=COC***H₃***); 4.0 (m, 4H, O=P(OC***H₂***$CH_3$)$_2$); 7,2 (m, 5H, ***H***arom.). $^{13}C\{^1H\}$ ($CDCl_3$, 75.5 MHz): 15.3 (d, $^3J_{CP}$= 5.6; O=P($OCH_2$***C***$H_3$)$_2$); 18.8 (s, ***C***$H_3$); 20.9 (s, ***C3***); 30.7 (s, ***C2***); 31.6 (d, $^1J_{CP}$= 186.2; ***C1***); 51.3 (s, O=CO***C***$H_3$); 61.2 (d, $^2J_{CP}$= 5.9; O=P(O***C***$H_2CH_3$)$_2$); 61.7 (d, $^2J_{CP}$= 6.0; O=P(O***C***$H_2CH_3$)$_2$); 126.5, 127.1, 133.7 (s, ***C***arom.); 171.6 (d, $^3J_{CP}$= 6.7; O=***C***$OCH_3$).

**Diethyl 1-phenyl-2-cyano-2-methylcyclopropyl-1-phosphonate (2e)**: oil, TLC ($MeOH/CH_2Cl_2$ (2/98) $R_f$= 0.3); FAB-MS *m/z* (rel. Intensity): 293 ($M^+$, 100), 265 (30), 237 (40), 219 (43), 210 (46), 185 (54), 156 (87), 154 (23), 128 (79), 103 (35), 91 (18), 77 (43), 51 (20), 39 (8)
**Diethyl 1-phenyl-2-*c*-cyano-2-*t*-methylcyclopropyl-*r*-1-phosphonate (2e *cis*)**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): 21.8 (s). $^1H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.0 (s, 3H, C-C***H₃***); 1.2 (m, 6H, O=P($OCH_2C$***H₃***)$_2$); 1.4 (dd, 1H, $^2J_{HH}$= 5.2; $^3J_{HP}$= 12.1; C***H***$_2$ cycle); 2.2 (dd, 1H, $^2J_{HH}$= 5.2; $^3J_{HP}$= 17.7; C***H***$_2$ cycle); 4.0 (m, 4H, O=P(OC***H₂***$CH_3$)$_2$); 7.3 (m, 5H, ***H***arom.). $^{13}C\{^1H\}$ ($CDCl_3$, 75.5 MHz): 14.6 (d, $^2J_{CP}$= 4.1; ***C2***); 16.4 (m, $^2J_{CP}$= 4.7; O=P($OCH_2$***C***$H_3$)$_2$); 20.2 (s, C-***C***$H_3$); 24.4 (s, ***C3***); 34.3 (d, $^1J_{CP}$= 185.0; ***C1***); 63.0; 63.5 (2d, $^2J_{CP}$= 6.5; $^2J_{CP}$= 6.8; O=P(O***C***$H_2CH_3$)$_2$); 121.3 (d, $^3J_{CP}$= 8.4; ***C***N); 128.5; 128.7; 132.8 (s, ***C***$_{o, m, p}$-arom.); 135,4 (s, ***C***$_{ipso}$).
**Diethyl 1-phenyl-2-*t*-cyano-2-*c*-methylcyclopropyl-*r*-1-phosphonate (2e *trans*)**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): 22.8 (s). $^1H$ NMR ($CDCl_3$/TMS, 300 MHz): 1.0 (m, 6H, O=P($OCH_2C$***H₃***)$_2$ + 1H, C***H***$_2$ cycle); 1.8 (s, 3H, C-C***H₃***); 1.9 (m, 1H, C***H***$_2$ cycle); 4,0 (m, 4H, O=P(OC***H₂***$CH_3$)$_2$); 7.3 (m, 5H, ***H***arom.). **RMN $^{13}C\{^1H\}$ ($CDCl_3$/TMS, 75,5 MHz)**: 16.4 (m, $^2J_{CP}$= 4.7; O=P($OCH_2$***C***$H_3$)$_2$); 17.9 (d, $^3J_{CP}$= 3.5; C-***C***$H_3$); 18.5 (s, ***C2***); 24.7 (s, ***C3***); 33.5 (d, $^1J_{CP}$= 185.0; ***C1***); 62.8; 63.0 (2d, $^2J_{CP}$= 7.0; $^2J_{CP}$= 6.5; O=P(O***C***$H_2CH_3$)$_2$); 121.0 (d, $^3J_{CP}$= 4.5; ***C***N); 128.5; 128.7; 132.8 (s, ***C***$_{o, m, p}$-arom.); 135.4 (s, ***C***$_{ipso}$).

**Diethyl 1-phenyl-2-ethoxycarbonyl-3-methylcyclopropyl-1-phosphonate (2f)**: oil, non-purified product. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz):24.5 (s); 24.0 (s). $^1H$ NMR ($CDCl_3$/TMS, 300 MHz): 0.95 (d, $^3J_{HH}$= 6.5, 3H, C-C***H₃***); 1.2 (m, 6H, O=P($OCH_2C$***H₃***)$_2$ + 3H, O=$COCH_2C$***H***$_3$); 1.52 (d, $^3J_{HH}$= 6.5, 3H, C-C***H₃***); 1.98 (dd, $^3J_{HH}$= 6.9, $^3J_{HP}$= 10.7, 1H, C***H***-cycle); 2.17 (m, 2H, CH-cycle), 2.47 (dd, dd, $^3J_{HH}$= 6.3, $^3J_{HP}$= 17, 1H, C***H***-cycle); 3.94 (m, 4H, O=P(OC***H₂***$CH_3$)$_2$ + 2H, O=$COC$***H***$_2CH_3$); 7.3 (m, 5H, ***H***arom.). FAB-MS *m/z* (rel. Intensity) 340 ($M^+$, 9), 298 (12), 266 (30), 188 (100), 129 (75), 159 (16).

**Diethyl 1-phenyl-2-*c*-methylamino-2-*t*-methylcyclopropyl-*r*-1-phosphonate (4)**: yellow oil. HRMS required for $C_{15}H_{24}O_3PN$ ($MH^+$): 297.1494; found: 297.1497. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): 28.7 (s). $^1H$ NMR ($CDCl_3$/TMS, 300 MHz): 0.8 (s, 3H, C-C***H₃***); 1.1 (m, 6H, O=P($OCH_2C$***H₃***)$_2$); 1.3 (dd, 1H, $^2J_{HH}$= 4.7; $^3J_{HP}$= 10; C***H***$_2$ cycle); 1.45 (b, N***H***$_2$), 1.65 (dd, 1H, $^2J_{HH}$= 4.7; $^3J_{HP}$= 17.8; C***H***$_2$ cycle); 2.9 (dd, 2H, $^2J_{HH}$= 13.8, C***H***$_2NH_2$); 4.0 (m, 4H, O=P(OC***H₂***$CH_3$)$_2$); 7.3 (m, 5H, ***H***arom.). $^{13}C\{^1H\}$ ($CDCl_3$, 75.5 MHz): 15. 3 (m, O=P($OCH_2$***C***$H_3$)$_2$); 16.2 (s, C-***C***$H_3$); 21.4 (s, ***C3***); 31.1 (d, $^1J_{CP}$= 179.8, ***C1***); 45.6 (s, ***C***$H_2NH_2$); 61.1 (m, O=P(O***C***$H_2CH_3$)$_2$); 126.1; 129. 0; 131.2 (3s, ***C***arom., 1dia); 136 (s, ***C***$_{ipso}$); ***C2*** not clearly identified.