Supporting Information

Stereodivergent Michael addition of diphenylphosphite to α-nitroalkenes in the presence of squaramide-derived tertiary amines: an enantioselective organocatalytic reaction in supercritical carbon dioxide

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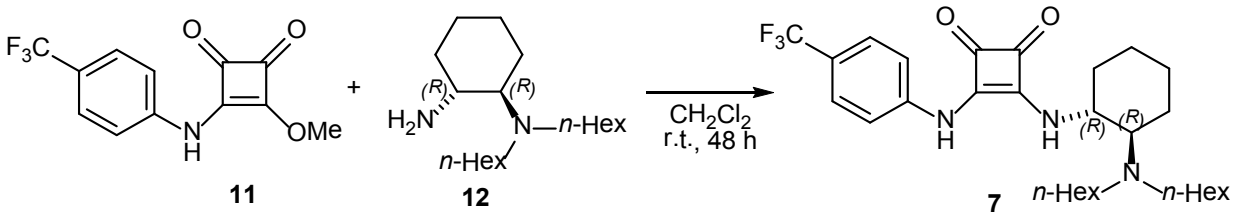
1. General Remarks

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and d_6-DMSO with a Bruker AM 300 spectrometer. Chemical shifts of ^{1}H and ^{13}C were measured relative to Me_4Si or $CDCl_3$, respectively. The high-resolution mass spectra (HRMS) were measured on a Bruker microTOF II spectrometer by using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage 4500 V) or in the negative ion mode (3200 V) in the mass range of m/z = 50–3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. Specific optical rotations $[\alpha]_D^{20}$ were measured with a Jasco DIP-360 instrument at 589 nm. Silica gels 0.060-0.200 and 0.035-0.070 nm (Acros) were used for column chromatography. Solvents were purified by standard methods. Compounds **11**,[1] **12**[2] and **13**[3] were prepared by known procedures. Enantiomeric excess values (*ee*) of products were determined by HPLC on a Stayer chromatograph with the chiral phase Chiralcel OD-H, OJ-H, or Chiralpak AD-H.

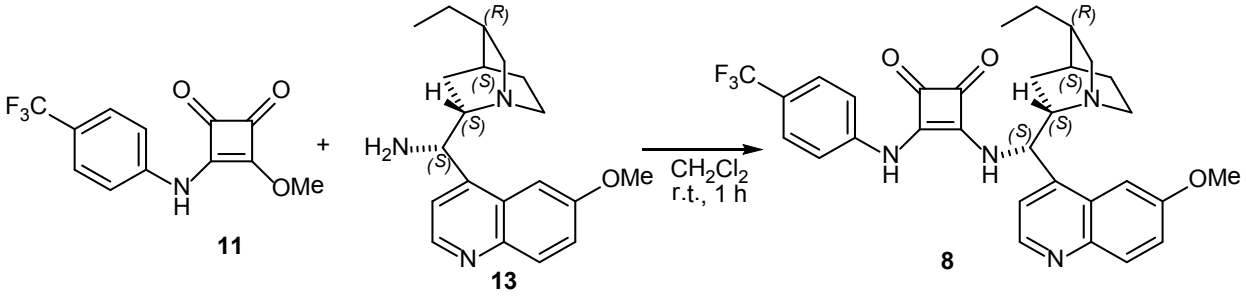
2. Catalysts preparation

3-((1R,2R)-2-(Dihexylamino)cyclohexylamino)-4-(4-(trifluoromethyl)phenylamino) cyclobut-3-ene-1,2-dione (7)



A mixture of **11** (0.27 g, 1.0 mmol), **12** (0.28 g, 1.0 mmol) and CH_2Cl_2 (3 mL) was stirred for 48 h at room temperature. The solid impurities were filtered off and the filtrate was evaporated *in vacuo* (10 torr). A mixture of CCl_4 (8 mL) and n-hexane (2 mL) was added to the residue and a minor amount of unsolved material was filtered off again. The filtrate was evaporated under reduced pressure and the residue was re-dissolved in n-hexane (5 mL). The solution was kept at r.t. for 24 h, during this period compound **7** was gradually precipitated. The precipitate was filtered, washed with n-hexane (2 mL) and dried under reduced pressure (2 torr) to afford catalyst **7** (0.50 g, 96%) as a yellow crystals, m.p. 165−166 °C, $[\alpha]_D^{25}$ = −126 (c = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.5 (br s), 7.48 (br s, 4H), 4.03 (br s, 1H), 2.43−2.39 (m, 1H), 2.21 (s, 6H), 2.11 (d, J = 10.0 Hz, 1H), 1.85 (d, J = 10.0 Hz, 1H), 2.6−2.1 (m, 6H), 1.95−1.65 (m, 3H), 1.45−1.05 (m, 21H), 0.77 (br s, 6H). ^{13}C NMR (75.5 MHz, d_6-DMSO): δ = 183.3, 181.1, 170.9, 161.6, 141.7, 126.5 (q, J ~ 3.8 Hz), 125.4 (q, J = 33.0 Hz), 124.2 (q, J = 275.5 Hz), 64.3, 56.4, 50.1, 34.2, 32.0, 29.4, 27.3, 22.9, 14.1; IR (KBr): ν 3178, 2937, 2855, 2776, 1803, 1662, 1611, 1579, 1551, 1456, 1332, 1161, 1118, 1069, 1015, 876, 835, 765, 740, 728 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{29}H_{42}F_3N_3O_2$ $[M^+H]^+$ 522.3302, found 522.3293.

3-((S)-((2S,4S,8R)-8-ethylquinuclidin-2-yl)(6-methoxyquinolin-4-yl)methylamino)-4-(4-(trifluoromethyl)phenylamino)cyclobut-3-ene-1,2-dione (8)



A mixture of **11** (0.27 g, 1.0 mmol), **13** (0.32 g, 1.0 mmol) and CH_2Cl_2 (3 mL) was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure (10 torr) and Et_2O (5 mL) was added to the residue. The precipitate was filtered off, washed with Et_2O (5 mL) and dried *in vacuo* (2 torr) to afford catalyst **8** (0.54 g, 96%) as a yellow crystals, m.p. 207−208 °C (decomp.), $[\alpha]_D^{25} = -122$ (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (s, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.82 (s, 1H), 7.52 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.02 (br s, 2H), 6.23 (br s, 1H), 3.96 (s, 3H), 3.62 (m, 1H), 3.42 (m, 1H), 3.11 (m, 1H), 2.67 (m, 1H), 2.49 (m, 1H), 1.75−1.15 (m, 9H), 0.79 (br s, 5H). ^{13}C NMR (75.5 MHz, $CDCl_3$ + 2 drops of d_6-DMSO): δ = 184.3, 180.3, 168.5, 163.3, 158.3, 147.0, 144.6, 143.6, 141.7, 131.4, 127.6, 126.24 (q, *J* ~ 3.5 Hz), 124.0 (q, J_{C-F} = 272.0 Hz), 124.0 (q, *J* = 31.7 Hz), 122.1, 117.6, 101.1, 59.7, 57.8, 55.7, 40.6, 39.7, 36.8, 28.1, 25.9, 24.9, 11.7; IR (KBr): ν 3240, 3013, 2947, 2870, 1800, 1672, 1622, 1609, 1570, 1542, 1511, 1464, 1439, 1334, 1322, 1271, 1117, 1071, 837 cm^{-1}; HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{32}F_3N_4O_3$ $[M^+H]^+$ 565.2421, found 565.2411.

3. Asymmetric Michael reaction and working-up procedures

Typical procedure for the asymmetric phospha-Michael reaction in sc-CO_2

α-Nitroalkene **2** (0.20 mmol) and a catalyst **6** or **8** (0.01 mmol) were placed in a stainless steel autoclave (V = 2 mL) equipped with a magnetic stirring bar under argon atmosphere. The autoclave was filled with CO_2 by means of a syringe-press to a total pressure of 70 bar and heated to 35 °C. Then diphenyl phosphite (**1**) (48 μL, 0.25 mmol) was added with a flow of CO_2 to a 100 bar final pressure and the reaction mixture was stirred at 35 °C and 100 bar for a two hours (unless otherwise specified). The autoclave was slowly depressurized, the residue was recovered by rinsing with EtOAc and purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1 as eluent).

Fractional extraction of 3a with sc-CO_2

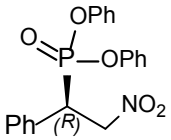
The tertiary amine **6** (8.4 mg, 0.02 mmol)-catalyzed Michael addition of **1** (48 μL, 0.25 mmol) to **2a** (29.8 mg, 0.20 mmol) in sc-CO_2 was carried out as described above. After the reaction completion, a flow (2.0 g/min) of sc-CO_2 (100 bar, 35 ^oC) was gradually passed through the autoclave to receiver (flask) I containing EtOAc (15mL) for 1 h. Then receiver I was replaced by receiver II filled with the same EtOAc amount. The sc-CO_2 pressure was raised up to 150 bar and the supercritical extraction with a flow rate 2.0 g/min at 35^{o}C continued for another 6 h. The solvents in receivers I and II were evaporated under reduced pressure (10 torr) and the residues were analyzed by TLC and ^{1}H NMR. The extract from flask I (21.6 mg) contained starting compounds **1** and **2a** along with the product **3a** (~10 %) whereas the second extract (60.5 mg) represented pure adduct **3a** (isolated yield 79%). Catalyst **6** along with a minor amount of

product **3a** (~ 8% according to ^{1}H NMR) remained in the autoclave after the extraction procedure (the residue total mass 14.4 mg).

After decompression, fresh portions of **1** (48 μL, 0.25 mmol) and **2a** (29.8 mg, 0.20 mmol) were added to the remaining catalyst, the autoclave was charged with a compressed CO_2 and the Michael reaction was re-performed according to the typical procedure. After 2 h, the reaction mixture was extracted with sc-CO_2 as described above and two fractions were collected again. The first fraction (32.5 mg) consisted of compounds **1**, **2a** and **3a** (~14 %) and the second extract (53.7 mg) contained pure adduct **3a** (isolated yield 70%). The residue that left in the autoclave (15.7 mg) consisted of catalyst **6** and the target compound **3a** (~10 %). In addition, minor amount of product **3a** remained inside capillaries and joints of back-pressure regulator.

4. Products characterization

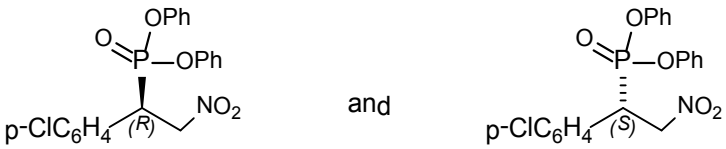
(*R*)-Diphenyl 2-nitro-1-phenylethylphosphonate (3a)



(*R*)-3a

(*R*)-3a : White solid; mp 129 °C (lit.,[4] 131 - 134 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (ddd, *J* = 24.6, 9.9, 4.4 Hz, 1H, CH), 5.08-5.27 (m, 2H, CH_2), 6.77 (d, *J* = 8.1 Hz, 2H, Ar), 7.10-7.23 (m, 6H, Ar), 7.30-7.48 (m, 7H, Ar); HPLC (AD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 18.0 min, t minor = 19.0 min, 94 % *ee*; $[\alpha]_D^{28}$ -2.1 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{26}$ -2.26 (*c* 1.0 in $CHCl_3$)).

Diphenyl 1-(4-chlorophenyl)-2-nitroethylphosphonate (3b) enantiomers

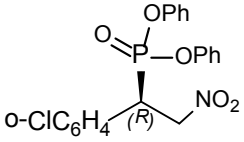


(*R*)-3b **(*S*)-3b**

(*R*)-3b: White solid; mp 130 °C (lit.,[6] 127.8 - 128.2 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (ddd, *J* = 24.9, 11.0, 5.1 Hz, 1H, CH), 5.08-5.27 (m, 2H, CH_2), 6.76 (d, *J* = 7.7 Hz, 2H, Ar), 7.10-7.12 (m, 3H, Ar), 7.20 (t, *J* = 7.7 Hz, 3H, Ar), 7.31-7.40 (m, 4H, Ar), 7.46-7.48 (m, 2H, Ar); HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 17.1 min, t minor = 18.0 min, 92 % *ee*; $[\alpha]_D^{26}$ -3.1 (*c* 1.0 in $CHCl_3$) (lit.,[7] $[\alpha]_D^{22}$ -6.2 (c 1.0 in $CHCl_3$)).

(*S*)-3b: White solid; mp 129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.46 (ddd, *J* = 24.9, 11.1, 5.2 Hz, 1H, CH), 5.08-5.27 (m, 2H, CH_2), 6.77 (d, *J* = 7.7 Hz, 2H, Ar), 7.10-7.12 (m, 3H, Ar), 7.21 (t, *J* = 7.7 Hz, 3H, Ar), 7.31-7.40 (m, 4H, Ar), 7.46-7.48 (m, 2H, Ar); HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 18.0 min, t minor = 17.1 min, 92 % *ee*; $[\alpha]_D^{26}$ 3.0 (*c* 1.0 in $CHCl_3$).

(*R*)-Diphenyl 1-(2-chlorophenyl)-2-nitroethylphosphonate (3c)

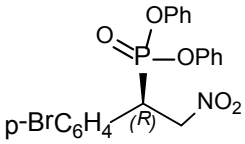


(*R*)-3c

White solid; mp 93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.12-5.33 (m, 3H, CH, CH_2), 6.80 (d, *J* = 7.9 Hz, 2H, Ar), 7.07-7.37 (m, 10H, Ar), 7.45-7.66 (m, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ

38.0, 39.9, 74.6 (d, J = 4.4 Hz), 120.2 (dd, J = 3.9, 37.6 Hz, 4C), 125.7 (d, J = 23.8 Hz, 2C), 127.6 (d, J = 2.8), 129.0-129.17(m, 3C), 129.7 (2C), 130.0 (2C), 130.5 (d, J = 2.8 Hz), 135.6 (d, J = 8.3 Hz), 149.9 (t, J = 9.9 Hz, 2C); IR: ν = 1213 (P-O-C), 1268 (P=O), 1557 (NO_2) cm^{-1}; HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 21.7 min, t minor = 29.0 min, 82 % *ee*; $[\alpha]_D^{28}$ 13.2 (*c* 1.0 in $CHCl_3$); HRMS (ESI): $C_{20}H_{17}ClNO_5P$ $[M^+H]^+$: 418.0601, found: 418.0606.

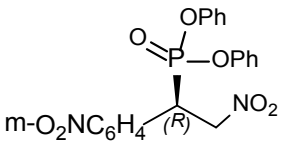
(*R*)-diphenyl 1-(4-bromophenyl)-2-nitroethylphosphonate (3d)



(*R*)-3d

White solid; mp 131 °C (lit.,[4] 131-138 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40 (ddd, J = 24.9, 11.0, 4.8 Hz, 1H, CH), 5.03-5.25 (m, 2H, CH_2), 6.82 (d, J = 8.1 Hz, 2H, Ar), 7.10-7.16 (m, 3H, Ar), 7.19-7.26 (m, 3H, Ar), 7.32-7.36 (m, 4H, Ar), 7.52 (d, J = 8.1 Hz, 2H, Ar); HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 21.6 min, t minor = 24.2 min, 87 % *ee*; $[\alpha]_D^{27}$ -8.0 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{27}$ -11.0 (*c* 1.0 in $CHCl_3$)).

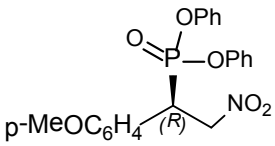
(*R*)-Diphenyl 1-(2-nitrophenyl)-2-nitroethylphosphonate (3e)



(*R*)-3e

White solid; mp 101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.56 (ddd, J = 24.6, 11.0, 4.4 Hz, 1H, CH), 5.12-5.32 (m, 2H, CH_2), 6.91 (d, J = 7.9 Hz, 2H, Ar), 7.10-7.37 (m, 8H, Ar), 7.60 (t, J = 7.9 Hz, 1H, Ar), 7.83 (d, J = 7.9 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.36 (d, J = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.1, 44.1, 74.4 (d, J = 5.0 Hz), 120.1 (dd, J = 19.9, 5.0 Hz, 4C), 123.9 (d, J = 3.3 Hz), 124.3 (d, J = 6.6 Hz), 126.0 (d, J = 16.0 Hz, 2C), 130.1 (d, J = 13.8 Hz, 4C), 130.3 (d, J = 2.8 Hz), 133.3 (d, J = 7.7 Hz), 135.2 (d, J = 6.6 Hz), 148.7, 149.7-149.9 (m, 2C); IR: ν = 1215 (P-O-C), 1268 (P=O), 1556 (NO_2) cm^{-1}; HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 33.7 min, t minor = 21.8 min, 94 % *ee*; $[\alpha]_D^{28}$ -6.4 (*c* 1.0 in $CHCl_3$); HRMS (ESI): $C_{20}H_{17}N_2O_7P$ $[M^+H]^+$: 429.0844, found: 429.0846.

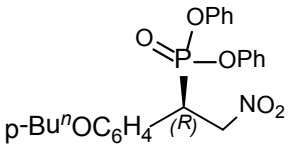
(*R*)-Diphenyl 1-(4-methoxyphenyl)-2-nitroethylphosphonate (3f)



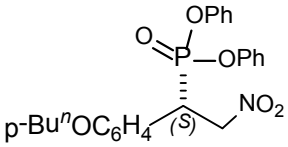
(*R*)-3f

White solid; mp 132 °C (lit.,[4] 133-134 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (c, 3H, CH_3), 4.39 (ddd, J = 24.6, 11.0, 4.8 Hz, 1H, CH), 5.03-5.23 (m, 2H, CH_2), 6.80 (d, J = 8.1 Hz, 2H, Ar), 6.91 (d, J = 8.8 Hz, 2H, Ar), 7.10-7.13 (m, 3H, Ar), 7.19-7.24 (m, 3H, Ar), 7.30-7.40 (m, 4H, Ar); HPLC (OD, 7:3 hexanes: i-PrOH, 0.8 mL/min, 25 °C, 254 nm): t major = 18.7 min, t minor = 16.3 min, 94 % *ee*; $[\alpha]_D^{27}$ -0.3 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{25}$ -0.70 (*c* 1.0 in $CHCl_3$)).

Diphenyl 1-(4-buthoxyphenyl)-2-nitroethylphosphonate (3g) enantiomers



and

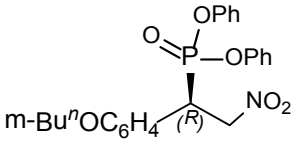


(*R*)-3g **(*S*)-3g**

(*R*)-3g: White solid; mp 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.7 Hz, 3H, CH_3), 1.50 (h, *J* = 7.7 Hz, 2H, CH_2), 1.78 (qui, *J* = 7.0 Hz, 2H, CH_2), 3.96 (t, *J* = 6.6 Hz, 2H, CH_2), 4.38 (ddd, *J* = 24.6, 10.6, 4.8 Hz, 1H, CH), 5.02-5.22 (m, 2H, CH_2), 6.80 (d, *J* = 7.7 Hz, 2H, Ar), 6.90 (d, *J* = 8.8 Hz, 2H, Ar), 7.10-7.37 (m, 10H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.3, 31.3, 41.8, 43.7 (1C), 67.8, 75.3 (d, *J* = 6.1 Hz), 115.3 (d, *J* = 2.8 Hz, 2C), 120.7 (dd, *J* = 16.6, 4.4, Hz, 4C), 122.0 (d, *J* = 7.7 Hz), 125.6 (d, *J* = 18.2 Hz, 2C), 125.8 (d, *J* = 18.8 Hz, 4C), 130.4 (d, *J* = 6.1 Hz, 2C), 150.1 (t, *J* = 8.9, 2C), 159.64 (d, *J* = 3.3); IR: ν = 1215 (P-O-C), 1273 (P=O), 1556 (NO_2) cm^{-1}; HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 18.5 min, t minor = 15.8 min, 92 % *ee*; $[\alpha]_D^{28}$ -0.3 (*c* 1.0 in $CHCl_3$); HRMS (ESI): $C_{24}H_{26}NO_6P$ $[M^+H]^+$: 456.1562, found: 456.1571.

(*S*)-3g: White solid; mp 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, *J* = 7.7 Hz, 3H, CH_3), 1.50 (h, *J* = 7.7 Hz, 2H, CH_2), 1.78 (qui, *J* = 7.0 Hz, 2H, CH_2), 3.97 (t, *J* = 6.7 Hz, 2H, CH_2), 4.38 (ddd, *J* = 24.6, 10.5, 4.6 Hz, 1H, CH), 5.02-5.21 (m, 2H, CH_2), 6.80 (d, *J* = 7.7 Hz, 2H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 7.12-7.36 (m, 10H, Ar); HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 15.8 min, t minor = 18.4 min, 86 % *ee*; $[\alpha]_D^{28}$ 0.4 (*c* 1.0 in $CHCl_3$).

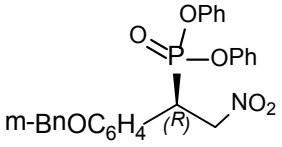
(*R*)-Diphenyl 1-(3-buthoxyphenyl)-2-nitroethylphosphonate (3h)



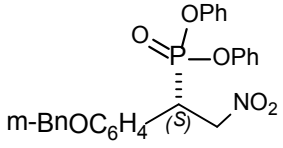
(*R*)-3h

White solid; mp 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.7 Hz, 3H, CH_3), 1.48 (h, *J* = 7.7 Hz, 2H, CH_2), 1.75 (qui, *J* = 6.6 Hz, 2H, CH_2),3.92 (t, *J* = 6.2 Hz, 2H, CH_2), 4.41 (ddd, *J* = 24.6, 10.3, 4.8 Hz, 1H, CH), 5.10-5.20 (m, 2H, CH_2), 6.80 (d, *J* = 8.1 Hz, 2H, Ar), 6.88 (d, *J* = 8.4 Hz, 1H, Ar), 6.96 (d, *J* = 2.2 Hz, 1H, Ar), 7.02 (d, *J* = 7.7 Hz, 1H, Ar),7.09-7.36 (m, 9H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.3, 31.3, 42.5, 44.4 (1C), 67.8, 75.1 (d, *J* = 4.4 Hz), 115.2 (d, *J* = 2.2 Hz), 115.5 (d, *J* = 6.1 Hz), 120.3 (dd, *J* = 18.8, 5.0 Hz, 4C), 121.3 (d, *J* = 6.6 Hz), 125.6 (d, *J* = 18.2 Hz), 125.9 (d, *J* = 19.4 Hz, 4C), 130.3 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 7.2 Hz), 150.1 (dd, *J* = 9.4, 11.6 Hz, 2C), 159.7 (d, *J* = 2.8 Hz); IR: ν = 1216 (P-O-C), 1271 (P=O), 1554 (NO_2) cm^{-1}; HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 11.0 min, t minor = 10.5 min, 92 % *ee*; $[\alpha]_D^{28}$ -2.6 (*c* 1.0 in $CHCl_3$); HRMS (ESI): $C_{24}H_{26}NO_6P$ $[M^+H]^+$: 456.1563, found: 456.1571.

Diphenyl 1-(3-benzeloxyphenyl)-2-nitroethylphosphonate (3i) enantiomers



and



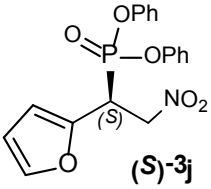
(*R*)-3i **(*S*)-3i**

(*R*)-3i: White solid; mp 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.42 (ddd, *J* = 24.6, 10.6, 4.4 Hz, 1H, CH), 5.02 (c, 2H, O-CH_2-Ar), 5.04-5.24 (m, 2H, CH_2), 6.80 (d, *J* = 7.3 Hz, 2H, Ar), 6.97 (d, *J* = 8.4 Hz, 1H, Ar), 7.05-7.13 (m, 5H, Ar), 7.21 (t, *J* = 7.0 Hz, 3H, Ar), 7.30-7.43 (m,

8H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.5, 44.4, 70.2, 75.1 (d, *J* = 5.0 Hz), 115.5 (d, *J* = 3.3 Hz), 116.0 (d, *J* = 7.2 Hz), 120.3 (dd, *J* = 18.2, 4.4 Hz, 4C), 121.8 (d, *J* = 7.2 Hz), 125.7 (d, *J* = 18.8 Hz), 127.6 (2C), 128.1, 128.7 (2C), 129.9 (d, *J* = 19.9 Hz, 4C), 130.4 (d, *J* = 2.2 Hz), 132.1 (d, *J* = 7.2 Hz), 136.6, 149.9-150.2 (m, 2C), 159.3; IR: ν = 1211 (P-O-C), 1267 (P=O), 1551 (NO_2) cm^{-1}; HPLC (OD, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 254 nm): t major = 21.5 min, t minor = 24.09 min, 89 % *ee*; $[\alpha]_D^{28}$ 3.2 (*c* 1.0 in $CHCl_3$). HRMS (ESI): $C_{27}H_{24}NO_6P$ $[M^+H]^+$: 490.1406, found: 490.1414.

(*S*)-3i: White solid; mp 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.41 (ddd, *J* = 24.6, 10.3, 4.4 Hz, 1H, CH), 5.02 (c, 2H, O-CH_2-Ar), 4.98-5.24 (m, 2H, CH_2), 6.79 (d, *J* = 7.3 Hz, 2H, Ar), 6.96 (d, *J* = 8.8 Hz, 1H, Ar), 7.05-7.13 (m, 5H, Ar), 7.21 (t, *J* = 7.3 Hz, 3H, Ar), 7.30-7.43 (m, 8H, Ar); HPLC (OD, 7:3 hexanes: isopropyl alcohol, 0.7 mL/min, 25 °C, 254nm): t major = 23.9 min, t minor = 21.2 min, 68% *ee*; $[\alpha]_D^{27}$ -2.9 (*c* 1.0 in $CHCl_3$); HRMS (ESI): $C_{27}H_{24}NO_6P$ $[M^+H]^+$: 490.1408, found: 490.1414.

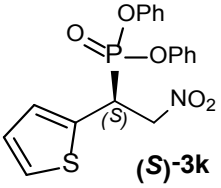
(*S*)-Diphenyl 1-(furan-2-yl)-2-nitroethylphosphonate (3j)



(*S*)-3j

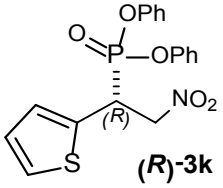
Yellow solid; mp 71 °C (lit.,[4] 71-74 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66 (dt, *J* = 24.9, 7.7 Hz, 1H, CH), 5.13 (t, *J* = 7.7 Hz, 2H, CH_2), 6.40-6.41 (m, 1H, Ar), 6.48 (t, *J* = 3.3 Hz, 1H, Ar), 7.02 (d, *J* = 8.4 Hz, 2H, Ar), 7.11 (d, *J* = 7.7 Hz, 2H, Ar), 7.21 (p, *J* = 15.0, 7.7 Hz, 3H, Ar),7.30-7.36 (m, 3H, Ar), 7.44 (c, 1H, Ar); HPLC (OJ, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 220 nm): t major = 22.7 min, t minor = 18.4 min, 84% *ee*; $[\alpha]_D^{27}$ -10.2 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{25}$ -12.3 (*c* 1.0 in $CHCl_3$)).

Diphenyl 1-(thiophen-2-yl)-2-nitroethylphosphonate (3k) enantiomers



(*S*)-3k

and

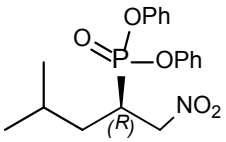


(*R*)-3k

(*S*)-3k: White solid; mp 93 °C (lit.,[4] 95 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 (ddd, *J* = 23.8, 10.6, 4.0 Hz, 1H, CH), 4.99-5.10 (m, 2H, CH_2), 5.17-5.26 (m, 1H, CH_2), 6.90 (d, *J* = 8.4 Hz, 2H, Ar), 7.02 (t, *J* = 4.8 Hz, 1H, Ar), 7.11-7.15 (m, 3H, Ar), 7.18-7.28 (m, 4H, Ar), 7.31-7.36 (m, 3H, Ar); HPLC (OJ, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 220 nm): t major = 25.3 min, t minor = 22.1 min, 94% *ee*; $[\alpha]_D^{25}$ -7.1 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{27}$ -12.1 (*c* 0.8 in $CHCl_3$)).

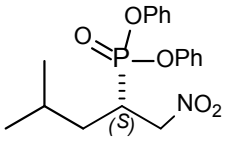
(*R*)-3k: White solid; mp 94 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 (ddd, *J* = 23.8, 10.6, 4.0 Hz, 1H, CH), 4.99-5.10 (m, 2H, CH_2), 5.17-5.26 (m, 1H, CH_2), 6.90 (d, *J* = 8.4 Hz, 2H, Ar), 7.02 (t, *J* = 4.8 Hz, 1H, Ar), 7.11-7.15 (m, 3H, Ar), 7.18-7.28 (m, 4H, Ar), 7.31-7.36 (m, 3H, Ar); HPLC (OJ, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 220 nm): t major = 22.0 min, t minor = 25.2 min, 89% *ee*; $[\alpha]_D^{25}$ 6.1 (*c* 1.0 in $CHCl_3$).

Diphenyl 4-methyl-1-nitropentan-2-ylphosphonate (3l) enantiomers



(*R*)-3l

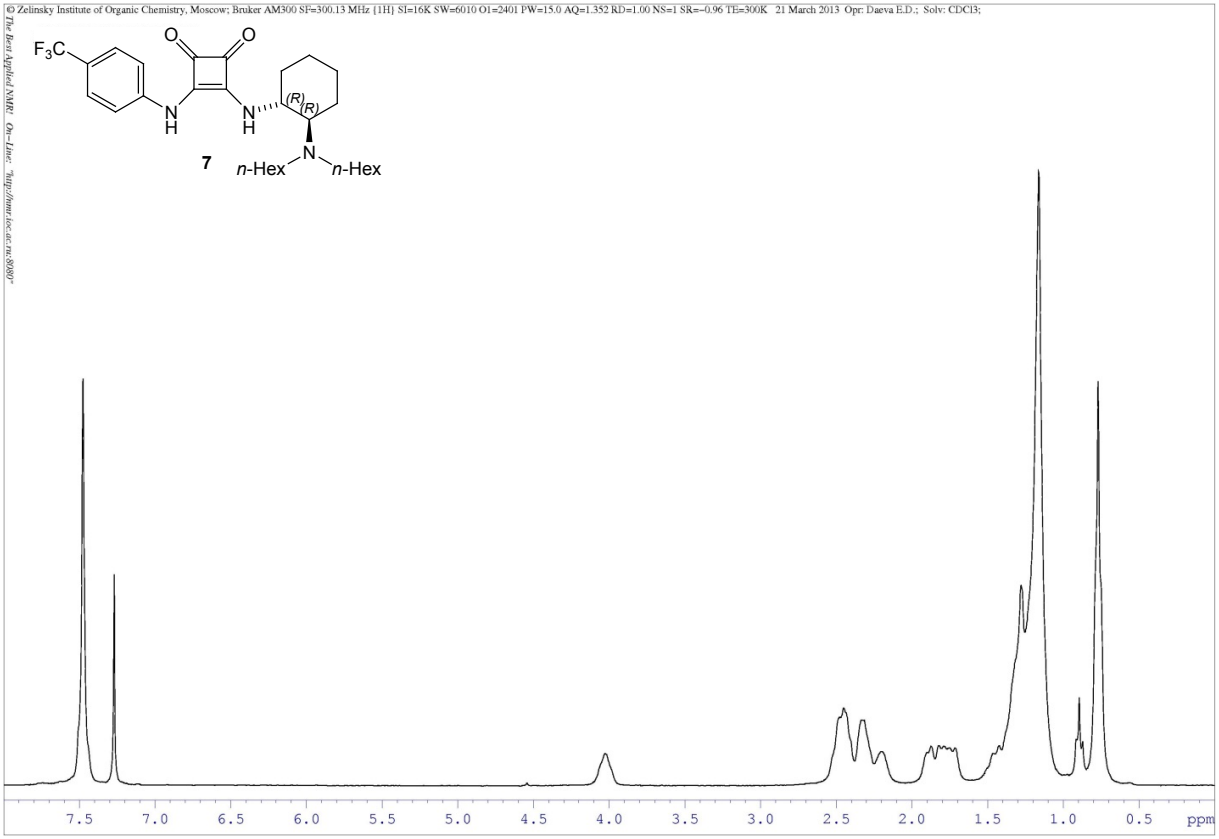
and



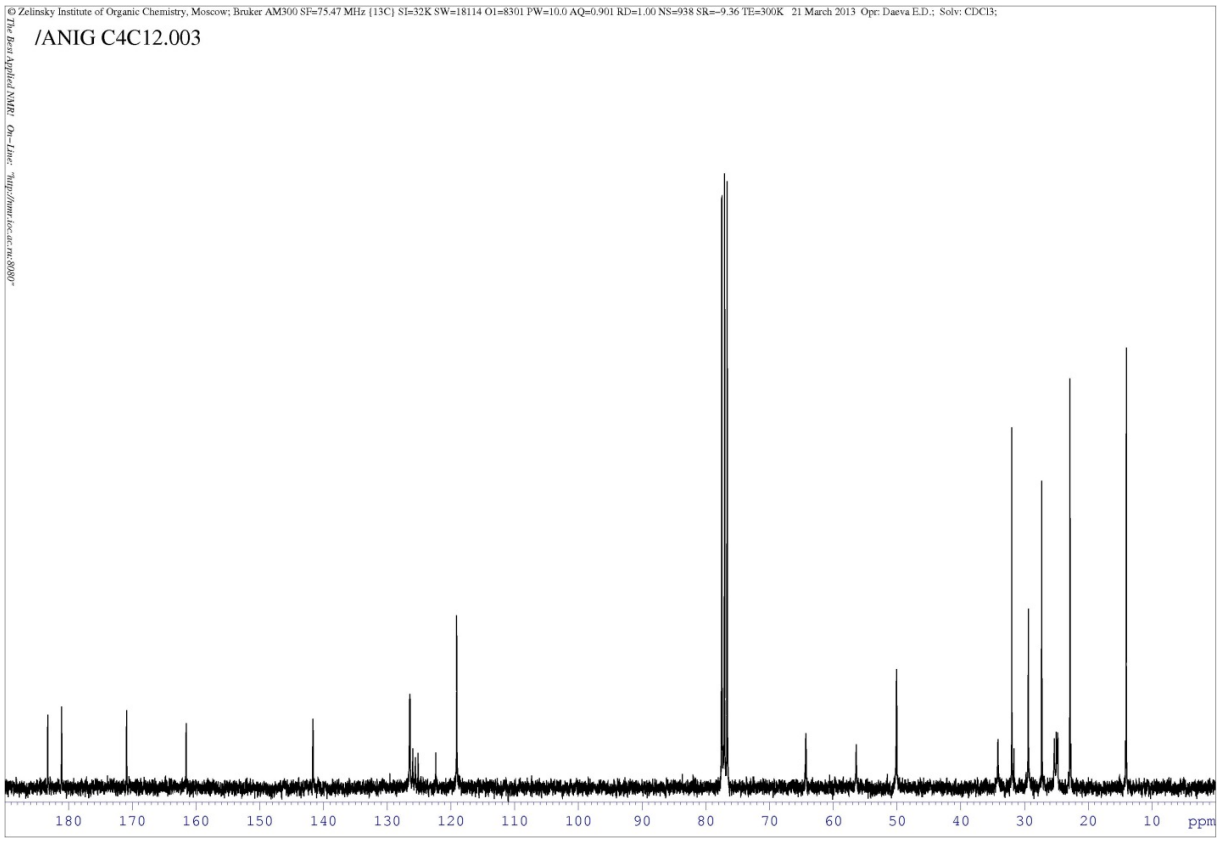
(*S*)-3l

(*R*)-3l: White solid; mp 63 °C (lit.,[5] 55-65 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (3H, d, J = 8.1 Hz, CH_3), 0.99 (3H, d, J = 7.9 Hz, CH_3), 1.45-1.67 (1H, m, CH), 1.81-2.05 (2H, m, CH_2), 3.15-3.34 (1H, m, CH), 4.59-4.92(m, 2H, CH_2), 7.12-7.21 (6H, m, Ar), 7.29-7.35 (4H, m, Ar); HPLC (OJ, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 220 nm): t major = 33.4 min, t minor = 46.2 min, 68% *ee*; $[\alpha]_D^{24}$ -2.3 (*c* 1.0 in $CHCl_3$) (lit.,[5] $[\alpha]_D^{27}$ -3.04 (*c* 1 in $CHCl_3$)).

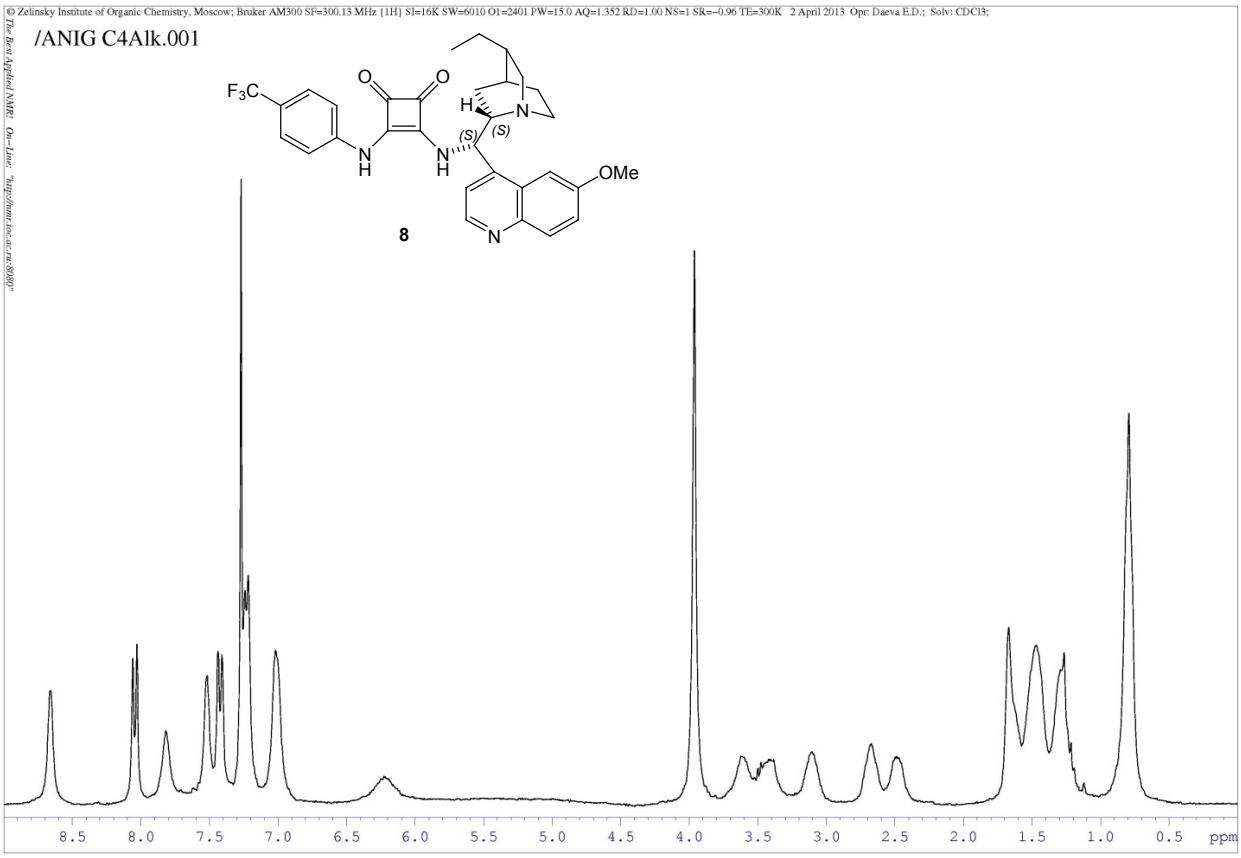
(*S*)-3l: White solid; mp 60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (3H, d, J = 8.1 Hz, CH_3), 1.00 (3H, d, J = 7.7 Hz, CH_3), 1.44-1.67 (1H, m, CH), 1.80-2.07 (2H, m, CH_2), 3.13-3.34 (1H, m, CH), 4.59-4.92 (m, 2H, CH_2), 7.10-7.19 (6H, m, Ar), 7.29-7.35 (4H, m, Ar); HPLC (OJ, 7:3 hexanes: i-PrOH, 0.7 mL/min, 25 °C, 220 nm): t major = 46.2 min, t minor = 33.8 min, 78% *ee*; $[\alpha]_D^{25}$ 3.9 (*c* 1.0 in $CHCl_3$).



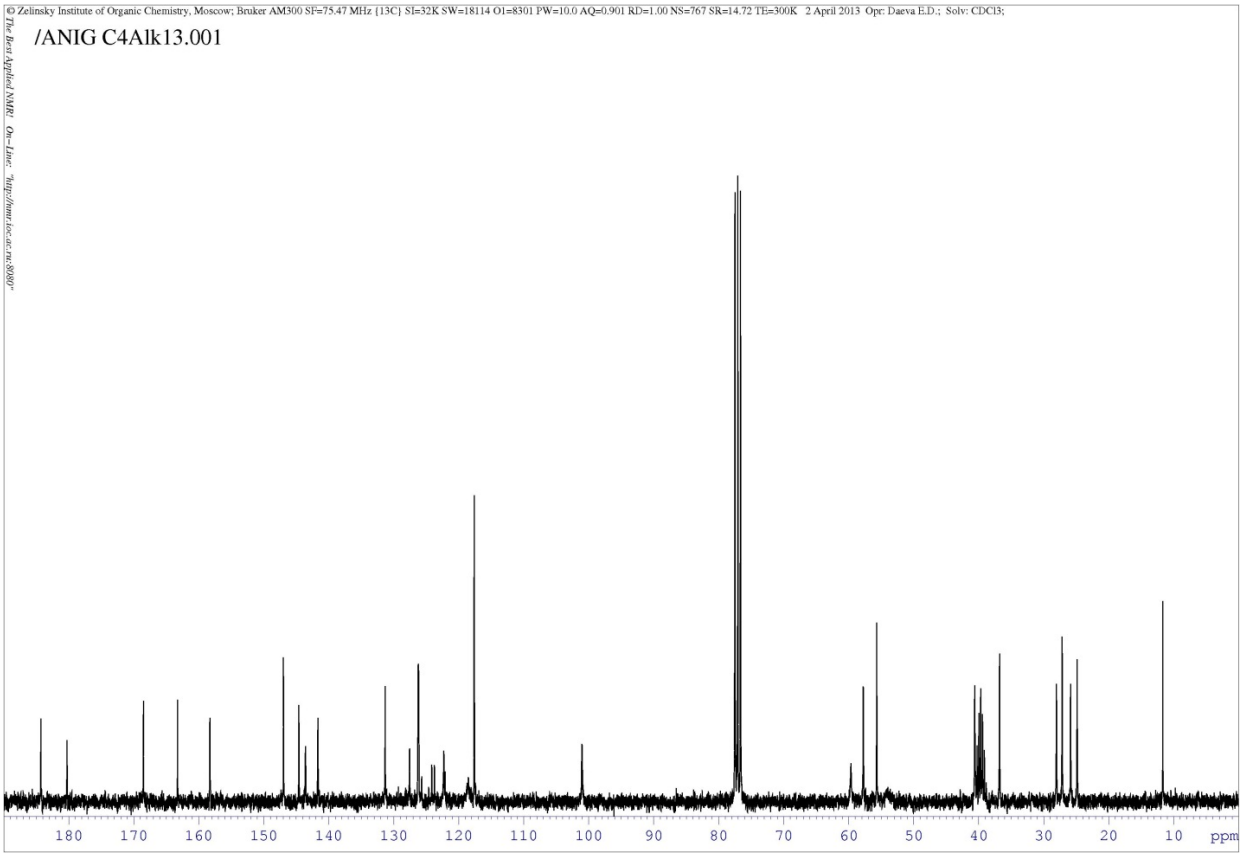
^{1}H NMR



^{13}C NMR



^{1}H NMR



^{13}C NMR

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