Radical Addition of Arylboronic Acids to Various Olefins under Oxidative Conditions

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Supporting Information

1. General Methods

^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a *Bruker* DPX 300, a *Bruker* AV 400, a *Varian* INOVA 500 or a *Varian* 600 unity plus spectrometer at room temperature. Chemical shifts δ in ppm are referenced to the residual solvent signal ($CHCl_3$: $\delta(^{1}H) = 7.26$ ppm, $\delta(^{13}C) = 77.16$ ppm), $CFCl_3$: $\delta(^{19}F) = 0$ ppm ±1 ppm and H_3PO_4 as external standard (H_3PO_4 (85 %): $\delta(^{31}P) = 0$ ppm ±1 ppm) respectively. ^{1}H and ^{13}C assignments were confirmed by 2D COSY and HMQC, as well as DEPT, NOE, NOESY and HMBC when necessary. High resolution mass spectra (ESI) were recorded on *Bruker* Daltonics MicroTof. Melting points (uncorrected) were measured on a *Stuart* SMP-10 melting point apparatus. Flash chromatography (FC) was carried out on *Merck* or *Fluka* silica gel 60 (40 – 63 μm) with an argon pressure of about 1.4-1.6 bar. TLC was carried out on *Merck* silica gel 60 F254 plates; detection by UV (254 nm) and $KMnO_4$ / Na_2CO_3 solution.

2. Chemicals and Solvents

Benzeneboronic acid (*Alfa Aesar* 98+ %), *o*-tolylboronic acid (*Acros* 95 %), *m*-tolylboronic acid (*Acros* 97 %), *p*-tolylboronic acid (*ABCR*), 4-fluorobenzeneboronic acid (*Alfa Aesar* 98+ %), 4-chlorobenzeneboronic acid (*Alfa Aesar* 97 %), 4-bromobenzeneboronic acid (*Alfa Aesar* 97+ %), 4-iodobenzeneboronic acid (*Acros* 97 %), 3-chlorobenzeneboronic acid (*Alfa Aesar* 97 %), 2-fluorobenzeneboronic acid (*Alfa Aesar* 98 %), biphenyl-4-boronic acid (*Alfa Aesar* 98 %), methylacrylate (*Acros* 99+ %), acrylonitrile (*Acros* 99+ %), phenylvinylsulfone (*Alfa Aesar* 99+ %), dimethyl maleate (*Fluka* 95 %), vinyldimethylphosphonate (*Alfa Aesar* 98 %), $Mn(OAc)_3 \cdot 2H_2O$ (*Merck* 97+ %), dichloroethane (DCE) (*Acros* 99.8+ %) and 1,2-dichlorobenzene (DCB) (*Acros* 99 %) were used as received. The solvents for FC were distilled prior to use.

3. Experimental Section

General Procedure A:

$Mn(OAc)_3$ (3 eq) and the corresponding olefin (10 eq or 6 eq) were added to a solution of benzeneboronic acid (1 eq) in DCE (0.2 M). The reaction mixture was stirred at 80 °C under argon atmosphere for 4 h. The suspension was filtered through a pad of celite® and the volatiles were removed under reduced pressure. The residue was purified via FC.

General Procedure B:

$Mn(OAc)_3$ (660 mg, 2.46 mmol, 3.00 eq.) and the corresponding olefin (8.20 mmol, 10.0 eq) were added to a solution of benzeneboronic acid (100 mg, 0.82 mmol, 1.00 eq.) in 1,2-dichlorobenzene (6 mL). The reaction mixture was stirred at 80 °C under oxygen atmosphere for 4 h. The suspension was filtered through a pad of celite® and the volatiles were removed under reduced pressure. 1,2-Dichlorobenzene was distilled off and the residue was purified via FC (pentane-EtOAc 20:1).

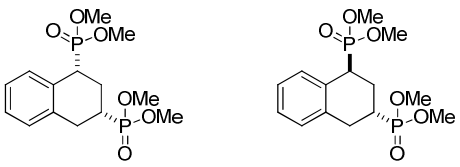
General Procedure C:

$Mn(OAc)_3$ (3 eq) was added to a solution of the corresponding arylboronic acid (100 mg or 125 mg) in dimethyl maleate (0.2 M). The reaction mixture was stirred at 80 °C under oxygen atmosphere for 4 h. The suspension was filtered through a pad of celite® and the volatiles were removed under reduced pressure. The residue was purified via FC (pentane-EtOAc 9:1).

General Procedure D:

$Mn(OAc)_3$ (1.5 mmol) and vinyldimethylphosphonate (3.0 mmol) were added to a solution of the corresponding arylboronic acid (0.50 mmol) in DCE (2.5 mL). The reaction mixture was stirred at 80 °C under argon atmosphere for 6 h. The suspension was filtered through a pad of celite® and the volatiles were removed under reduced pressure. The residue was purified via FC (DCM-MeOH 40:1).

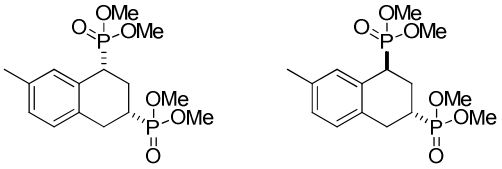
[3-(Dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1a). According to general procedure D, benzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. Purification via FC afforded the bisphosphonate (114 mg, 0.327 mmol, 65 %) as a mixture of both diastereoisomers (*cis* : *trans* = 6.3 : 1.0, determined by ^{31}P NMR) as a colorless oil.



IR (film): 2955*w*, 2853*w*, 1685*m*, 1455*m*, 1238*s*, 1183*s*, 1017*s*, 818*s*, 751*m* cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) *cis*-isomer: δ = 7.70-7.66 (*m*, 1 H, H_{aryl}, *cis*), 7.14-7.06 (2 H, H_{aryl})*, 7.05-7.02 (*m*, 1 H, H_{aryl})*, 3.74 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3, *cis*), 3.74 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3, *cis*), 3.67 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3, *cis*), 3.49 (*d*, $^3J_{P,H}$ = 10.5 Hz, 3 H, OCH_3, *cis*), 3.47-3.38 (*m*, 1 H, C*H*)*, 2.96-2.80 (*m*, 2 H, CH_2)*, 2.52-2.42 (*m*, 1 H, CH_2)*, 2.08-1.86 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 7.29-7.25 (*m*, 1 H, H_{aryl}, *trans*), 7.14-7.06 (2 H, H_{aryl})*, 7.05-7.02 (*m*, 1 H, H_{aryl})*, 3.73 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3, *trans*), 3.72 (*d*, $^3J_{P,H}$ = 10.0 Hz, 3 H, OCH_3, *trans*), 3.58 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3, *trans*), 3.55 (*d*, $^3J_{P,H}$ = 10.5 Hz, 3 H, OCH_3, *trans*), 3.47-3.38 (*m*, 1 H, C*H*)*, 2.96-2.80 (*m*, 2 H, CH_2)*, 2.52-2.42 (*m*, 1 H, CH_2)*, 2.08-1.86 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (126 MHz, $CDCl_3$) *cis*-isomer: δ = 136.3 (*dd*, $^2J_{P,C}$ = 17.0 Hz, $^4J_{P,C}$ = 7.8 Hz, C_q), 129.7 (*d*, $^3J_{P,C}$ = 4.7 Hz, *C*H), 129.4 (*m*, C_q), 129.2 (*m*, *C*H), 126.9 (*d*, $J_{P,C}$ = 2.7 Hz, *C*H), 126.5 (*d*, $J_{P,C}$ = 2.8 Hz, *C*H), 53.4 (*d*, $^2J_{P,C}$ = 6.9, O*C*H_3), 52.8 (*d*, $^2J_{P,C}$ = 7.1 Hz, O*C*H_3), 52.7 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H_3), 52.7 (*d*, $^2J_{P,C}$ = 7.1 Hz, O*C*H_3), 36.4 (*dd*, $^1J_{P,C}$ = 140.7 Hz, $^3J_{P,C}$ = 16.0 Hz, *C*H), 31.7 (*dd*, $^1J_{P,C}$ = 146.4 Hz, $^3J_{P,C}$ = 11.0 Hz, *C*H), 29.9 (*dd*, $^2J_{P,C}$ = 3.5 Hz, $^4J_{P,C}$ = 1.3 Hz, *C*H), 24.4 (*dd*, $^2J_{P,C}$ = 4.3 Hz and 2.8 Hz, *C*H_2); *trans*-isomer: δ = 135.4 (*dd*, $^2J_{P,C}$ = 15.7 Hz, $^4J_{P,C}$ = 7.0 Hz, C_q), 130.4 (*d*, $^3J_{P,C}$ = 4.3 Hz, *C*H), 129.4 (*m*, *C*H), 129.3 (*m*, C_q), 127.3 (*d*, $J_{P,C}$ = 3.6 Hz, *C*H), 125.9 (*d*, $J_{P,C}$ = 3.5 Hz, *C*H), 53.2 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H_3), 53.0 (*d*, $^2J_{P,C}$ = 7.3 Hz, O*C*H_3), 52.7 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H_3), 52.6 (*d*, $^2J_{P,C}$ = 6.7 Hz, O*C*H_3), 36.6 (*dd*, $^1J_{P,C}$ = 136.6 Hz, $^3J_{P,C}$ = 15.7 Hz, *C*H), 28.0 (*dd*, $^2J_{P,C}$ = 3.6 Hz, $^4J_{P,C}$ = 1.6 Hz, *C*H_2), 27.7 (*dd*, $^1J_{P,C}$ = 145.7 Hz, $^3J_{P,C}$ = 1.3 Hz, *C*H), 23.3 (*dd*, $^2J_{P,C}$ = 5.4 Hz and 3.4 Hz, *C*H_2). **^{31}P NMR** (202 MHz, $CDCl_3$) *cis*-isomer: δ = 33.00 (*d*, $^4J_{P,P}$ = 6.9 Hz, *P*C_3), 30.51 (*d*, $^4J_{P,P}$ = 6.9 Hz, *P*C_1); *trans*-isomer: 34.15 (*d*, $^4J_{P,P}$ = 1.9 Hz, *P*C_3), 30.05 (d, $^4J_{P,P}$ = 1.9 Hz, *P*C_1). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{22}O_6P_2$ $[M+Na]^+$:371.0784; found: 371.0790.

* Signals of *cis* and *trans*-isomer could not be assigned.

[3-(Dimethoxy-phosphoryl)-7-methyl-1,2,3,4-tetrahydro-naphthalenyl)]-phosphonic acid dimethyl ester (1b). According to general procedure D, 4-methylbenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. After purification via FC the bisphosphonate was isolated as a mixture of both diastereoisomers (*cis* : *trans* = 7.0 : 1.0, determined by ^{31}P NMR) as a colorless oil (116 mg, 0.32 mmol, 64 %).

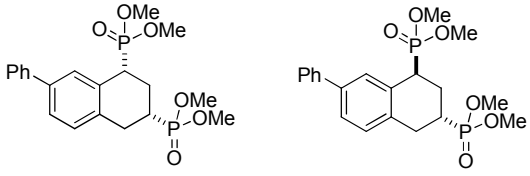


IR (film): 2954*w*, 2853*w*, 1685*m*, 1720*w*, 1505*w*, 1457*m*, 1236*s*, 1183*m*, 1015*s*, 814*s*, 751*m* cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) *cis*-isomer: δ = 7.49 (*s*, 1 H, H_{aryl}), 7.02-6.91 (*m*, 2 H, H_{aryl})*, 3.78 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.78 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.72 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.55 (*d*, $^3J_{P,H}$ = 10.5 Hz, 3 H, OCH_3), 3.50-3.39 (*m*, 1 H, C*H*)*, 2.97-2.75 (*m*, 2 H, CH_2)*, 2.58-2.42 (*m*, 1 H, CH_2)*, 2.26 (*s*, 3 H, CH_3), 2.08-1.91 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 7.12 (*s*,

1 H, H_{aryl}), 7.02-6.91 (*m*, 2 H, H_{aryl})*, 3.77 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.76 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.71 (*d*, $^3J_{P,H}$ = 11.1 Hz, 3 H, OCH_3), 3.63 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.59 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.50-3.39 (*m*, 1 H, C*H*)*, 2.97-2.75 (*m*, 2 H, CH_2)*, 2.58-2.42 (*m*, 1 H, CH_2)*, 2.25 (*s*, 3 H, CH_3), 2.08-1.91 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (126 MHz, $CDCl_3$) *cis*-isomer: δ = 136.2 (*d*, *J* = 2.9 Hz, C_q), 133.4 (*dd*, $^2J_{P,C}$ = 17.2 Hz, $^4J_{P,C}$ = 7.8 Hz, C_q), 130.2 (*d*, *J* = 4.7 Hz, *C*H), 129.1 (*d*, *J* = 2. Hz, *C*H), 129.1 (*dd*, *J* = 8.7 Hz and 1.0 Hz, C_q), 127.8 (*d*, *J* = 2.6 Hz, *C*H), 53.5 (*d*, $^2J_{P,C}$ = 7.0 Hz, OCH_3), 52.9 (*d*, $^2J_{P,C}$ = 6.8 Hz, OCH_3), 52.9 (*d*, $^2J_{P,C}$ = 7.0 Hz, OCH_3), 52.9 (*d*, $^2J_{P,C}$ = 7.0 Hz, OCH_3), 36.2 (*dd*, $^1J_{P,C}$ = 140.8 Hz, $^3J_{P,C}$ = 16.1 Hz, *C*H), 31.7 (*dd*, $^1J_{P,C}$ = 146.3 Hz, $^3J_{P,C}$ = 11.0 Hz, *C*H), 29.5 (*dd*, *J* = 3.6 Hz and 1.4 Hz, *C*H_2), 24.4 (*dd*, $^2J_{P,C}$ = 4.2 Hz and 2.7 Hz, *C*H_2), 21.2 (*C*H_3); *trans*-isomer: δ = 135.5 (*d*, ^4J = 3.6 Hz, C_q), 132.3 (*dd*, $^2J_{P,C}$ = 15.8 Hz, $^4J_{P,C}$ = 7.1 Hz, C_q), 130.9 (*d*, *J* = 4.2 Hz, *C*H), 129.4 (*dd*, *J* = 3.0 Hz and *J* = 0.8 Hz, *C*H), 128.9 (*dd*, *J* = 6.9 Hz and 1.7 Hz, C_q), 128.4 (*d*, *J* = 2.6 Hz, *C*H), 53.3 (*d*, $^2J_{P,C}$ = 7.2 Hz, OCH_3), 53.1 (*d*, $^2J_{P,C}$ = 7.3 Hz, OCH_3), 52.9 (*d*, $^2J_{P,C}$ = 7.1 Hz, OCH_3), 52.8 (*d*, $^2J_{P,C}$ = 6.8 Hz, OCH_3), 36.5 (*dd*, $^1J_{P,C}$ = 136.7 Hz, $^3J_{P,C}$ = 15.7 Hz, *C*H), 27.8 (*dd*, $^1J_{P,C}$ = 145.7 Hz, $^3J_{P,C}$ = 1.5 Hz, *C*H), 27.6 (*dd*, $^2J_{P,C}$ = 3.7 Hz and 1.6 Hz, *C*H_2), 23.4 (*dd*, $^2J_{P,C}$ = 5.4 Hz and 3.5 Hz, *C*H_2), 21.0 (*C*H_3). **^{31}P NMR** (202 MHz, $CDCl_3$) *cis*-isomer: δ = 33.34 (*d*, $^4J_{P,P}$ = 6.9 Hz), 30.78 (*d*, $^4J_{P,P}$ = 6.9 Hz); *trans*-isomer: δ = 34.45 (*d*, $^4J_{P,P}$ = 3.0 Hz, minor), 30.31 (*d*, $^4J_{P,P}$ = 3.0 Hz, minor). **HRMS (ESI)**: m/z = calcd for $C_{15}H_{24}O_6P_2$ $[M+Na]^+$: 385.0940; found: 385.9045.

* Signals of *cis* and *trans*-isomer could not be assigned.

[3-(Dimethoxy-phosphoryl)-7-phenyl-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1c). According to general procedure D, biphenyl-4-boronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. Purification via FC afforded the bisphosphonate (136 mg, 0.320 mmol, 64 %) as a mixture of both diastereoisomers (*cis* : *trans* = 4.5 : 1.0, determined by ^{31}P NMR) as a colorless oil.

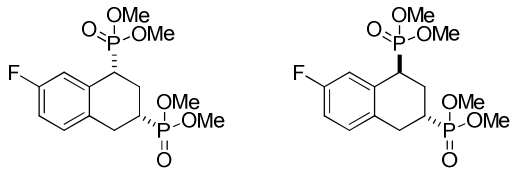


IR (film): 2954*w*, 1238*s*, 1023*s*, 822*s*, 761*m*, 699 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomer: δ = 8.17-7.16 (*m*, 8 H, H_{aryl})*, 3.86 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.80 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.63 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.49 (*d*, $^3J_{P,H}$ = 10.4 Hz, 3 H, OCH_3), 3.60-3.42 (*m*, 1 H, C*H*)*, 3.18-2.92 (*m*, 2 H, CH_2)*, 2.72-2.52 (*m*, 1 H, CH_2)*, 2.27-1.96 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 8.17-7.16 (*m*, 8 H, H_{aryl})*, 3.87 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.83 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.70 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.70 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.60-3.42 (*m*, 1 H, C*H*)*, 3.18-2.90 (*m*, 2 H, CH_2)*, 2.72-2.52 (*m*, 1 H, CH_2)*, 2.27-1.96 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (75 MHz, $CDCl_3$) *cis*-isomer: δ = 140.5(*s*, C_q)*, 139.3 (*d*, *J* = 2.8 Hz, C_q), 135.4 (*dd*, *J* = 17.1 Hz, 4.7 Hz, C_q), 130.0-195.5 (*m*, C_q and *C*H)*, 128.8 (*s*, *C*H)*, 128.4 (*d*, $J_{P,C}$ = 4.7 Hz, *C*H), 127.2 (*s*, *C*H), 126.9 (*s*, *C*H), 125.5 (*d*, $J_{P,C}$ = 2.5 Hz, *C*H), 53.4 (*d*,

$^{2}J_{P,C}$ = 6.9 Hz, OCH_3), 52.8 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, OCH_3), 52.7 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, OCH_3), 52.7 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, OCH_3), 36.6 (*dd*, $^{1}J_{P,C}$ = 140.6 Hz, $^{3}J_{P,C}$ = 16.0 Hz, *C*H), 31.8 (*dd*, $^{1}J_{P,C}$ = 146.4 Hz, $^{3}J_{P,C}$ = 11.0 Hz, *C*H), 29.7 (*dd*, ^{2}J = 2.8 Hz, ^{4}J = 1.0 Hz, *C*H_2), 24.4 (*dd*, $^{2}J_{P,C}$ = 4.2 Hz and 2.8 Hz, *C*H_2); *trans*-isomer: δ = 140.5 (*s*, C_q)*, 138.8 (*d*, *J* = 3.5 Hz, C_q), 134.6 (*dd*, $J_{P,C}$ = 15.8 Hz and 7.0 Hz, C_q), 130.0-195.5 (*m*, C_q and *C*H)*, 129.0 (*d*, $J_{P,C}$ = 4.4 Hz, *C*H), 128.8 (*s*, *C*H)*, 127.4 (*s*, *C*H), 126.9 (*s*, *C*H), 126.1 (*d*, $J_{P,C}$ = 3.6 Hz, *C*H), 53.2 (*d*, $^{2}J_{P,C}$ = 7.0 Hz, OCH_3), 53.0 (*d*, $^{2}J_{P,C}$ = 7.0 Hz, OCH_3), 52.7 (*d*, $^{2}J_{P,C}$ = 7.0 Hz, OCH_3), 52.6 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, OCH_3), 36.7 (*dd*, $^{1}J_{P,C}$ = 138.7 Hz, $^{3}J_{P,C}$ = 16.3 Hz, *C*H), 27.9 (*dd*, $^{1}J_{P,C}$ = 145.7 Hz, ^{3}J = 1.6 Hz, *C*H), 27.8 (*dd*, $^{2}J_{P,C}$ = 3.7 Hz, $^{4}J_{P,C}$ = 1.6 Hz, *C*H_2), 23.4 (*dd*, $^{2}J_{P,C}$ = 5.1 Hz and 3.6 Hz, *C*H_2). **^{31}P NMR** (122 MHz, $CDCl_3$) *cis*-isomer: δ = 32.97 (*d*, $^{4}J_{P,P}$ = 7.0 Hz), 30.53 (*d*, $^{4}J_{P,P}$ = 7.0 Hz); *trans*-isomer: δ = 34.11 (*d*, $^{4}J_{P,P}$ = 2.8 Hz), 30.07 (*d*, $^{4}J_{P,P}$ = 2.8 Hz). **HRMS (ESI)**: m/z = calcd for $C_{20}H_{26}O_6P_2$ $[M+Na]^+$: 447.1097; found: 447.1562.

* Signals of *cis* and *trans*-isomer could not be assigned.

[7-Fluoro-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1d). According to general procedure D, 4-fluorobenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. After purification via FC the bisphosphonate was isolated as a mixture of both diastereoisomers (*cis* : *trans* = 4.8 : 1.0, determined by ^{31}P NMR) as a colorless oil (101 mg, 0.276 mmol, 55 %).



IR (film): 2956*w*, 2854*w*, 1498*m*, 1240*s*, 1185*m*, 1024*s*, 820*s*, 783*m* cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) *cis*-isomer: δ = 7.52-7.43 and 7.09-6.99 and 6.90-6.80 (*m*, 3 H, H_{aryl})*, 3.78 (*d*, *J* = 10.7 Hz, 3 H, OCH_3), 3.78 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.74(*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.60 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.47-3.34 (*m*, 1 H, C*H*)*, 2.98-2.75 (*m*, 2 H, CH_2)*, 2.60-2.40 (*m*, 1 H, CH_2)*, 2.07-1.86 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 7.52-7.43 and 7.09-6.99 and 6.90-6.80 (*m*, 3 H, H_{aryl})*, 3.76 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.76 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.65 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.65 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.47-3.34 (*m*, 1 H, C*H*)*, 2.98-2.75 (*m*, 2 H, CH_2)*, 2.60-2.40 (*m*, 1 H, CH_2)*, 2.07-1.86 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (126 MHz, $CDCl_3$) *cis*-isomer: δ = 161.2 (*dd*, *J* = 244.3 Hz and 3.2 Hz, C_q), 132.1-131.8 (*m*, C_q)*, 131.6-131.3 (*m*, C_q)*, 130.6 (*ddd*, *J* = 8.3 Hz, 1.4 Hz and 1.4 Hz, *C*H), 116.3 (*dd*, *J* = 22.8 Hz and 4.6 Hz, *C*H), 114.2 (*dd*, *J* = 21.4 Hz and 2.4 Hz, *C*H), 53.5 (*d*, *J* = 7.0 Hz, OCH_3), 52.9 (*d*, *J* = 7.1 Hz, OCH_3), 52.9 (*d*, *J* = 6.9 Hz, OCH_3), 52.9 (*d*, *J* = 7.0 Hz, OCH_3), 36.6 (*ddd*, *J* = 141.1 Hz, 16.1 Hz and 1.6 Hz, *C*H), 31.8 (*dd*, *J* = 147.0 Hz and 11.3 Hz, *C*H), 29.3 (*dd*, *J* = 3.5 Hz and 1.5 Hz, *C*H_2), 24.1 (*dd*, $^{2}J_{P,C}$ = 4.2 Hz and 2.8 Hz, *C*H_2); *trans*-isomer: δ = 160.9 (*dd*, *J* = 244.5 Hz and 3.9 Hz, C_q), 132.1-131.8 (*m*, C_q)*, 130.9-130.8 (*m*, *C*H), 116.8 (*dd*, *J* = 22.0 Hz and 4.1 Hz, *C*H), 114.7 (*dd*, *J* = 21.7 Hz and 3.5 Hz, *C*H), 53.4 (*d*, *J* = 7.1 Hz,

O*C*H$_3$), 53.2 (*d*, *J* = 7.3 Hz, O*C*H$_3$), 52.8 (*d*, *J* = 7.3 Hz, O*C*H$_3$), 52.7 (*d*, *J* = 6.7 Hz, O*C*H$_3$), 36.7 (*ddd*, *J* = 137.5 Hz, 15.8 Hz and 1.3 Hz, *C*H), 27.9 (*dd*, *J* = 146.2 Hz and 1.6 Hz, *C*H), 27.6 (*dd*, *J* = 3.4 Hz and 1.5 Hz, *C*H$_2$), 23.1 (*dd*, $^2J_{P,C}$ = 5.1 Hz and 3.4 Hz, *C*H$_2$). **^{31}P NMR** (202 MHz, CDCl$_3$) *cis*-isomer: δ = 32.70 (*d*, $^4J_{P,P}$ = 7.1 Hz), 29.87 (*dd*, $^4J_{P,P}$ = 7.1 Hz, $^5J_{F,P}$ = 1.3 Hz); *trans*-isomer: δ = 33.86 (*d*, $^4J_{P,P}$ = 2.2 Hz), 29.46 (*dd*, $^4J_{P,P}$ = 2.2 Hz, $^5J_{F,P}$ = 2.2 Hz). **^{19}F NMR** (470 MHz, CDCl$_3$) *cis*-isomer: δ = -115.4 (*m*); *trans*-isomer: δ = -116.7 (*m*). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{21}FO_6P_2$ $[M+Na]^+$: 389.0690; found: 389.0686.

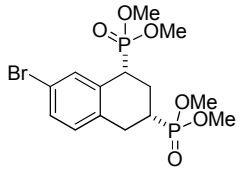
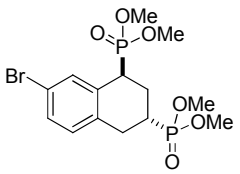
* Signals of *cis* and *trans*-isomer could not be assigned.

[7-Chloro-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1e). According to general procedure D, 4-chlorobenzeneboronic acid was reacted with Mn(OAc)$_3$ and vinyldimethylphosphonate. Purification via FC afforded the bisphosphonate (114 mg, 0.297 mmol, 60 %) as a mixture of both diastereoisomers (*cis* : *trans* = 4.1 : 1.0, determined by ^{31}P NMR) as a colorless oil.

IR (film): 2955*w*, 2855*w*, 1720*w*, 1458*m*, 1238*s*, 1182*m*, 1016*s*, 815*s*, 749*m* cm^{-1}. **^{1}H NMR** (500 MHz, CDCl$_3$) *cis*-isomer: δ = 7.72-7.68 (*m*, 1 H, H_{aryl}), 7.15-7.08 (*m*, 1 H, H_{aryl})*, 7.05-6.96 (*m*, 1 H, H_{aryl})*, 3.77 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.77 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.72 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.60 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.44-3.28 (*m*, 1 H, C*H*)*, 2.95-2.76 (*m*, 2 H, CH_2)*, 2.56-2.45 (*m*, 1 H, CH_2)*, 2.08-1.83 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 7.30-7.26 (*m*, 1 H, H_{aryl}), 7.15-7.08 (*m*, 1 H, H_{aryl})*, 7.05-6.96 (*m*, 1 H, H_{aryl})*, 3.76 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.73 (*d*, $^3J_{P,H}$ = 10.9 Hz, 3 H, OCH_3), 3.66 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.64 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.44-3.28 (*m*, 1 H, C*H*)*, 2.95-2.76 (*m*, 2 H, CH_2)*, 2.56-2.45 (*m*, 1 H, CH_2)*, 2.08-1.83 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (126 MHz, CDCl$_3$) *cis*-isomer: δ = 135.0 (*dd*, $^2J_{P,C}$ = 17.2 Hz, $^4J_{P,C}$ = 7.7 Hz, C_q), 132.3 (*d*, $^4J_{P,C}$ = 3.3 Hz, C_q), 131.6 (*dd*, $^3J_{P,C}$ = 7.0 Hz and 1.0 Hz, C_q), 130.5 (*d*, $^3J_{P,C}$ = 2.2 Hz, *C*H), 129.6 (*d*, $^3J_{P,C}$ = 4.7 Hz, *C*H), 127.2 (*d*, $^5J_{P,C}$ = 2.7 Hz, *C*H), 53.5 (*d*, $^2J_{P,C}$ = 7.0 Hz, O*C*H$_3$), 53.1 (*d*, $^2J_{P,C}$ = 7.0 Hz, O*C*H$_3$), 53.0 (*d*, $^2J_{P,C}$ = 7.1 Hz, O*C*H$_3$), 52.9 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H$_3$), 36.5 (*dd*, $^1J_{P,C}$ = 141.2 Hz, $^3J_{P,}$C = 16.0 Hz, *C*H), 31.7 (*dd*, $^1J_{P,C}$ = 147.1 Hz, $^3J_{P,C}$ = 11.0 Hz, *C*H), 29.6 (*dd*, $^2J_{P,C}$ = 3.4 Hz, $^4J_{P,C}$ = 1.4 Hz, *C*H$_2$), 24.1 (*dd*, $^2J_{P,C}$ = 4.1 Hz and 2.8 Hz, *C*H$_2$); *trans*-isomer: δ = 134.1 (*dd*, $^2J_{P,C}$ = 15.9 Hz, $^4J_{P,C}$ 7.0 Hz, C_q), 131.6 (*d*, $^4J_{P,C}$ = 4.2 Hz, C_q), 131.4 (*dd*, $^3J_{P,C}$ = 6.9 Hz and 1.7 Hz, C_q), 130.8 (*d*, $^3J_{P,C}$ = 2.5 Hz, *C*H), 130.2 (*d*, $^3J_{P,C}$ = 4.3 Hz, *C*H), 127.6 (*d*, $^5J_{P,C}$ = 3.6 Hz, *C*H), 53.4 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H$_3$), 53.3 (*d*, $^2J_{P,C}$ = 7.3 Hz, O*C*H$_3$), 52.9 (*d*, $^2J_{P,C}$ = 8.2 Hz, O*C*H$_3$), 52.8 (*d*, $^2J_{P,C}$ = 6.8 Hz, O*C*H$_3$), 36.6 (*dd*, $^1J_{P,C}$ = 137.4 Hz, $^3J_{P,C}$ 15.8 Hz, *C*H), 27.8 (*dd*, $^1J_{P,C}$ = 146.3 Hz, $^3J_{P,C}$ = 1.5 Hz, *C*H), 27.7 (*dd*, $^2J_{P,C}$ = 3.5 Hz, $^4J_{P,C}$ = 1.6 Hz, *C*H$_2$), 23.2 (*dd*, $^2J_{P,C}$ = 5.2 Hz and 3.4 Hz, *C*H$_2$). **^{31}P NMR** (202 MHz, CDCl$_3$) *cis*-isomer: δ = 32.58 (*d*, $^4J_{P,P}$ = 6.6 Hz), 29.86 (*d*, $^4J_{P,P}$ = 6.6 Hz); *trans*-isomer: δ = 33.78 (*d*, $^4J_{P,P}$ = 2.6 Hz), 29.42 (*d*,

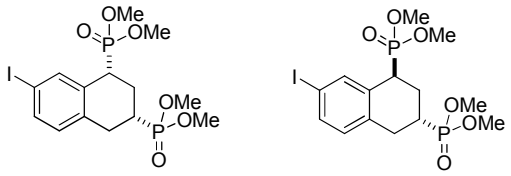
$^4J_{P,P}$ = 2.6 Hz). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{21}ClO_6P_2$ $[M+Na]^+$: 405.0394; found: 405.0399.

* Signals of *cis* and *trans*-isomer could not be assigned.

[7-Bromo-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1f).   According to general procedure D, 4-bromobenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. Purification via FC afforded the bisphosphonate (96 mg, 45 %) as a mixture of both diastereoisomers (*cis* : *trans* = 4.0 : 1.0, determined by ^{31}P NMR) as a colorless oil.

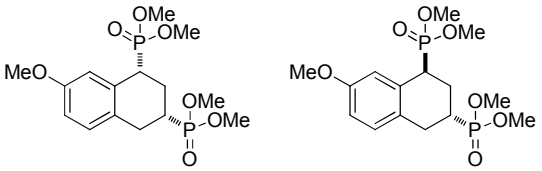
IR (film): 2955*w*, 1652*w*, 1483*w*, 1241*s*, 1184*m*, 1026*s*, 821*s* cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) *cis*-isomer: δ = 7.84-7.81 (*m*, 1 H, H_{aryl}), 7.27-7.20 (*m*, 1 H, H_{aryl})*, 6.98-6.89 (*m*, 1 H, H_{aryl})*, 3.75 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.75 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.71 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.59 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.45-3.24 (*m*, 1 H, C*H*)*, 2.98-2.72 (*m*, 2 H, CH_2)*, 2.55-2.42 (*m*, 1 H, CH_2)*, 2.10-1.82 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: 7.44-7.37 (*m*, 1 H, H_{aryl}), 7.27-7.20 (*m*, 1 H, H_{aryl})*, 6.98-6.89 (*m*, 1 H, H_{aryl})*, 3.74 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.73 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.64 (*d*, $^3J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.62 (*d*, $^3J_{P,H}$ = 10.7 Hz, 3 H, OCH_3),), 3.45-3.24 (*m*, 1 H, C*H*)*, 2.98-2.72 (*m*, 2 H, CH_2)*, 2.55-2.42 (*m*, 1 H, CH_2)*, 2.10-1.82 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (126 MHz, $CDCl_3$) *cis*-isomer: δ = 135.5 (*dd*, $^2J_{P,C}$ = 17.2 Hz, $^4J_{P,C}$ = 7.7 Hz, C_q), 132.5 (*d*, $^3J_{P,C}$ = 4.7 Hz, *C*H), 131.9 (*dd*, $^3J_{P,C}$ = 6.9 Hz and 1.1 Hz, C_q), 130.8 (*dd*, $^4J_{P,C}$ = 2.0 Hz and 1.2 Hz, *C*H), 130.1 (*d*, $^5J_{P,C}$ = 2.7 Hz, *C*H), 120.2 (*d*, $^4J_{P,C}$ = 3.4 Hz, C_q), 53.5 (*d*, $^2J_{P,C}$ = 7.0 Hz, O*C*H$_3$), 53.3 (*d*, $^2J_{P,C}$ = 7.0 Hz, O*C*H$_3$), 52.9 (*d*, $^2J_{P,C}$ = 7.1 Hz, O*C*H$_3$), 52.7 (*d*, $^2J_{P,C}$ = 7.1 Hz, O*C*H$_3$), 36.5 (*dd*, $^1J_{P,C}$ = 137.5 Hz, $^3J_{P,C}$ = 15.7 Hz, *C*H), 31.6 (*dd*, $^1J_{P,C}$ = 147.1 Hz, $^3J_{P,C}$ = 10.9 Hz, *C*H), 29.6 (*dd*, $^2J_{P,C}$ = 3.4, $^4J_{P,C}$ = 1.4 Hz, *C*H$_2$), 24.1 (*dd*, $^2J_{P,C}$ = 4.1 Hz and 2.8 Hz, *C*H$_2$); *trans*-isomer: 134.6 (*dd*, $^2J_{P,C}$ = 15.8 Hz, $^4J_{P,C}$ = 7.0 Hz, C_q), 133.1 (*d*, $^3J_{P,C}$ = 4.3 Hz, *C*H), 131.8 (*dd*, $^3J_{P,C}$ = 6.8 Hz and 1.7 Hz, C_q), 131.1 (*dd*, $^4J_{P,C}$ = 2.6 Hz and 0.8 Hz, *C*H), 130.4 (*d*, $^5J_{P,C}$ = 3.5 Hz, *C*H), 119.5 (*d*, $^4J_{P,C}$ = 4.2 Hz, C_q), 53.3 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H$_3$), 53.1 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H$_3$), 52.9 (*d*, $^2J_{P,C}$ = 7.2 Hz, O*C*H$_3$), 52.8 (*d*, $^2J_{P,C}$ = 6.8 Hz, O*C*H$_3$), 36.3 (*dd*, $^1J_{P,C}$ = 141.2 Hz, $^3J_{P,C}$ = 16.0 Hz, *C*H), 27.7 (*dd*, $^2J_{P,C}$ = 3.5 Hz, $^4J_{P,C}$ = 1.6 Hz, *C*H$_2$), 27.6 (*dd*, $^1J_{P,C}$ = 146.3 Hz, $^3J_{P,C}$ = 1.6 Hz, *C*H), 23.1 (*dd*, $^2J_{P,C}$ = 5.2 Hz and 3.3 Hz, *C*H$_2$). **^{31}P NMR** (202 MHz, $CDCl_3$) *cis*-isomer: δ = 32.53 (*d*, $^4J_{P,P}$ = 5.7 Hz), 29.85 (*d*, $^4J_{P,P}$ = 5.7 Hz); *trans*-isomer: δ = 33.74 (*d*, $^4J_{P,P}$ = 1.3 Hz), 29.40 (*d*, $^4J_{P,P}$ = 1.3 Hz). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{21}BrO_6P_2$ $[M+Na]^+$: 450.9872; found: 450.9872.

* Signals of *cis* and *trans*-isomer could not be assigned.

[7-Iodo-3-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1g).  According to general procedure D, 4-iodobenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. Purification via FC afforded the bisphosphonate (105 mg, 0.221 mmol, 44 %) as a mixture of both diastereoisomers (*cis* : *trans* = 3.5 : 1.0, determined by ^{31}P NMR) as a colorless oil.

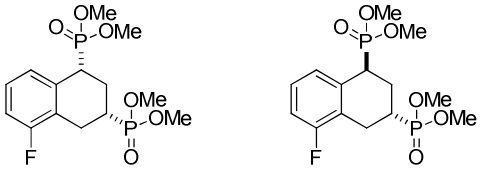
IR (film): 2954*w*, 2852*w*, 1457*w*, 1238*s*, 1182*m*, 1017*s*, 817*s*, 749 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomer: δ = 8.07-7.98 (*m*, 1 H, H_{aryl}), 7.54-7.37 (*m*, 1 H, H_{aryl})*, 6.93-6.73 (*m*, 1 H, H_{aryl})*, 3.77 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.77 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.72 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, 3 H, OCH_3), 3.61 (*d*, $^{3}J_{P,H}$ = 10.7 Hz, 3 H, OCH_3), 3.49-3.23 (*m*, 1 H, CH)*, 2.98-2.73 (*m*, 2 H, CH_2)*, 2.58-2.40 (*m*, 1 H, CH_2)*, 2.18-1.77 (*m*, 2 H, CH_2 and CH)*; *trans*-isomer: δ = 7.65-7.59 (*m*, 1 H, H_{aryl}), 7.54-7.37 (*m*, 1 H, H_{aryl})*, 6.93-6.73 (*m*, 1 H, H_{aryl})*, 3.76 (*d*, $^{3}J_{P,H}$ = 10.5 Hz, OCH_3), 3.75 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, OCH_3), 3.67 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, OCH_3), 3.64 (*d*, $^{3}J_{P,H}$ = 10.6 Hz, OCH_3), .49-3.23 (*m*, 1 H, CH)*, 2.98-2.73 (*m*, 1 H, CH_2)*, 2.58-2.40 (*m*, 1 H, CH_2)*, 2.18-1.77 (*m*, 2 H, CH_2 and CH)*. **^{13}C NMR** (75 MHz, $CDCl_3$) *cis*-isomer: δ = 138.4 (*d*, $J_{P,C}$ = 4.7 Hz, *C*H), 136.3 (*dd*, $J_{P,C}$ = 17.1 Hz and 7.6 Hz, C_q), 135.9 (*d*, $J_{P,C}$ = 2.7 Hz, *C*H), 132.3 (*dd*, $J_{P,C}$ = 7.0 Hz and 1.0 Hz, C_q), 131.0 (*dd*, $J_{P,C}$ = 2.1 Hz and 1.0 Hz, *C*H), 91.5 (*d*, $J_{P,C}$ = 3.5 Hz, C_q), 53.4 (*d*, $^{2}J_{P,C}$ = 7.1 Hz, O*C*H$_3$), 53.1 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, O*C*H$_3$), 52.9 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, O*C*H$_3$), 52.8 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, O*C*H$_3$), 36.2 (*dd*, $^{1}J_{P,C}$ = 141.1 Hz, $^{3}J_{P,C}$ = 15.9 Hz, *C*H), 31.6 (*dd*, $^{1}J_{P,C}$ = 147.0 Hz $^{3}J_{P,C}$ = 10.7 Hz, *C*H), 29.7 (*dd*, $^{2}J_{P,C}$ = 3.4 Hz, $^{4}J_{P,C}$ = 1.3 Hz, *C*H$_2$), 24.0 (*dd*, $^{2}J_{P,C}$ = 4.0 Hz and 2.8 Hz, *C*H$_2$); *trans*-isomer: δ = 139.1 (*d*, $J_{P,C}$ = 4.3 Hz, *C*H), 136.3 (*dd*, $J_{P,C}$ = 3.6 Hz and 0.8 Hz, *C*H), 135.4 (*dd*, $J_{P,C}$ = 15.4 Hz and 7.0 Hz, C_q), 132.1 (*dd*, $J_{P,C}$ = 6.9 Hz and 1.6 Hz, C_q), 131.3 (*dd*, J = 3.0 Hz and 4.6 Hz, *C*H), 90.7 (*d*, J = 4.2 Hz, C_q), 53.3 (*d*, $^{2}J_{P,C}$ = 7.3 Hz, O*C*H$_3$), 53.3 (*d*, $^{2}J_{P,C}$ = 7.3 Hz, O*C*H$_3$), 52.8 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, O*C*H$_3$), 52.7 (*d*, $^{2}J_{P,C}$ = 6.9 Hz, O*C*H$_3$), 36.3 (*dd*, $^{1}J_{P,C}$ = 137.8 Hz, $^{3}J_{P,C}$ = 15.7 Hz, *C*H), 27.8 (*dd*, $^{2}J_{P,C}$ = 3.6 Hz, $^{4}J_{P,C}$ = 1.5 Hz, *C*H$_2$), 27.6 (*dd*, $^{1}J_{P,C}$ = 146.2 Hz, $^{3}J_{P,C}$ = 1.6 Hz, *C*H), 23.1 (*dd*, $^{2}J_{P,C}$ = 5.2 Hz and 3.5 Hz, *C*H$_2$). **^{31}P NMR** (122 MHz, $CDCl_3$) *cis*-isomer: δ = 32.63 (*d*, $^{4}J_{P,P}$ = 6.7 Hz), 29.94 (*d*, $^{4}J_{P,P}$ = 6.7 Hz); *trans*-isomer: δ = 33.81 (*d*, $^{4}J_{P,P}$ = 2.9 Hz), 29.43 (*d*, $^{4}J_{P,P}$ = 2.9 Hz). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{21}IO_6P_2$ $[M+Na]^+$: 496.9750; found: 496.9754.

* Signals of *cis* and *trans*-isomer could not be assigned.

[7-Methoxy-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1h).  According to general procedure D, 4-methoxybenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. After purification via FC the bisphosphonate was isolated as a mixture of both diastereoisomers (*cis* : *trans* = 7.0 : 1.0, determined by ^{31}P NMR) as a colorless oil (65 mg, 0.172 mmol, 34 %).

IR (film): 2955*w*, 2852*w*, 1721*w*, 1503*m*, 1459*w*, 1236*s*, 1183*m*, 1018*s*, 816*s*, 728*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomer: δ = 7.35 (*t*, *J* = 2.3 Hz, 1 H, H_{Aryl}), 6.98 (*d*, *J* = 8.5 Hz, 1 H, H_{Aryl}), 6.71 (*dt*, *J* = 8.5 Hz, 2.3 Hz, 1 H, H_{aryl}), 3.78 (*d*, *J* = 10.7 Hz, 3 H, OCH_3), 3.78 (*d*, *J* = 10.7 Hz, 3 H, OCH_3), 3.73 (*d*, *J* = 10.7 Hz, 3 H, OCH_3), 3.56 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.53-3.31 (*m*, 1 H, C*H*)*, 3.02-2.70 (*m*, 2 H, CH_2)*, 2.63-2.39 (*m*, 1 H, CH_2)*, 2.09-1.85 (*m*, 2 H, CH_2 and C*H*)*; *trans*-isomer: δ = 7.01 (*d*, *J* = 8.0 Hz, 1 H, H_{Aryl}), 6.90 (*t*, *J* = 2.6 Hz, 1 H, H_{Aryl}), 6.76-6.70 (*m*, 1 H, H_{aryl}), 3.77 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.76 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.65 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.61 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.53-3.31 (*m*, 1 H, C*H*)*, 3.02-2.70 (*m*, 2 H, CH_2)*, 2.63-2.39 (*m*, 1 H, CH_2)*, 2.09-1.85 (*m*, 2 H, CH_2 and C*H*)*. **^{13}C NMR** (75 MHz, $CDCl_3$) *cis*-isomer: δ = 158.1 (*d*, *J* = C_q), 130.3 (*dd*, *J* = 7.0 Hz and 0.9 Hz, C_q), 130.1 (*dd*, *J* = 1.5 Hz and 1.2 Hz, *C*H)*, 128.3 (*dd*, *J* = 7.3 Hz and 17.0 Hz, C_q), 114.1 (*d*, *J* = 4.9 Hz, *C*H), 113.7 (*d*, *J* = 2.6 Hz, *C*H), 55.3 (*C*H_3), 53.6 (*d*, *J* = 7.0 Hz, O*C*H_3), 52.9 (*d*, *J* = 6.8 Hz, O*C*H_3), 52.9 (*d*, *J* = 7.0 Hz, O*C*H_3), 52.8 (*d*, *J* = 7.2 Hz, O*C*H_3), 36.7 (*dd*, *J* = 140.5 Hz and 16.3 Hz, *C*H), 31.9 (*dd*, *J* = 146.7 Hz and 11.0 Hz, *C*H), 29.0 (*dd*, *J* = 4.0 Hz and 1.5 Hz, *C*H_2), 24.2 (*dd*, $^2J_{P,C}$ = 4.3 Hz and 2.8 Hz, *C*H_2); *trans*-isomer: δ = 157.6 (*d*, *J* = 3.6 Hz, C_q), 130.4-130.3 (*m*, C_q)*, 130.1-130.0 (*m*, *C*H), 115.4-114.8 (*m*, *C*H) 53.5 (*C*H_3), 53.4 (*d*, *J* = 6.8 Hz, O*C*H_3), 53.1 (*d*, *J* = 7.0 Hz, O*C*H_3), 52.8-52.7 (*m*, O*C*H_3), 52.7 (*d*, *J* = 6.7 Hz, O*C*H_3), 36.8-358 (*m*, *C*H), 29.7-26.0 (*m*, *C*H_2 and *C*H), 23.3 (*dd*, $^2J_{P,C}$ = 5.4 Hz and 3.0 Hz, *C*H_2). **^{31}P NMR** (122 MHz, $CDCl_3$) *cis*-isomer: δ = 33.25 (*d*, $^4J_{P,P}$ = 7.5 Hz), 30.58 (*d*, $^4J_{P,P}$ = 7.5 Hz); *trans*-isomer: δ = 34.37 (*d*, $^4J_{P,P}$ = 2.8 Hz), 30.12 (*d*, $^4J_{P,P}$ = 2.8 Hz). **HRMS (ESI)**: m/z = calcd for $C_{15}H_{24}O_7P_2$ $[M+Na]^+$: 401.0889; found: 401.0889.

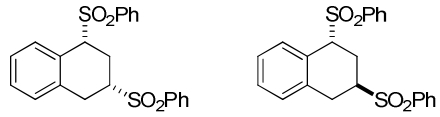
* Signals of *cis* and *trans*-isomer could not be assigned. Not all Signals of the *trans*-isomer were found.

[5-Fluoro-(dimethoxy-phosphoryl)-1,2,3,4-tetrahydro-naphthalenyl]-phosphonic acid dimethyl ester (1i).  According to general procedure D, 4-fluorobenzeneboronic acid was reacted with $Mn(OAc)_3$ and vinyldimethylphosphonate. After purification via FC the bisphosphonate was isolated as a mixture of both diastereoisomers (*cis* : *trans* = 4.8 : 1.0, determined by ^{31}P NMR) as a colorless oil (101 mg, 55 %).

IR (film): 2957*w*, 1693*w*, 1581*w*, 1461*m*, 1241*s*, 1022*s*, 820*s*, 751*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomers: δ = 7.68-6.78 (*m*, 3 H, H_{aryl})*, 3.80 (*d*, $J_{P,C}$ = 10.7 Hz, 3 H, OCH_3), 3.80 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.74 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.57 (*d*, *J* = 10.5 Hz, 3 H, OCH_3), 3.51-3.33 (*m*, 1 H, C*H*)*, 3.26-3.05 (*m*, 1 H, C*H*)*, 2.90-2.45 (*m*, 2 H, CH_2)*, 2.13-1.81 (*m*, 2 H, CH_2)*; *trans*-isomer: δ = 7.68-6.78 (*m*, 3 H, H_{aryl})*, 3.78 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.78 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.64 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.64 (*d*, *J* = 10.6 Hz, 3 H, OCH_3), 3.51-3.33 (*m*, 1 H, C*H*)*, 3.26-3.05 (*m*, 1 H, C*H*)*, 2.90-2.45 (*m*, 2 H, CH_2)*, 2.13-1.81 (*m*, 2 H, CH_2)*. **^{13}C NMR** (75 MHz, $CDCl_3$) *cis*-isomer: δ = 160.4 (*d*, *J* = 244.6 Hz, C_q), 131.9 (*m*, C_q)*, 127.2 (*dd*, *J* = 8.8 Hz and 2.7 Hz, *C*H)*, 125.0 (*dd*, *J* = 4.5 Hz and 2.7 Hz, *C*H), 123.9 (*td*, *J* = 17.6 Hz and 8.3 Hz, C_q), 113.3 (*dd*, *J* = 21.8 Hz and 2.4 Hz, *C*H), 53.4 (*d*, *J* = 6.9 Hz, O*C*H_3), 52.8 (*d*, *J* = 7.0 Hz, O*C*H_3), 52.8 (*d*, *J* = 7.0 Hz, O*C*H_3), 52.7 (*d*, *J* = 7.2 Hz, O*C*H_3), 36.5 (*ddd*, $^{1}J_{P,C}$ = 141.7 Hz, $^{3}J_{P,C}$ = 16.0 Hz, $^{4}J_{F,C}$ = 2.4 Hz, *C*H), 30.9 (*dd*, $^{1}J_{P,C}$ = 147.7 Hz, $^{3}J_{P,C}$ = 11.9 Hz, *C*H), 24.1 (*dd*, $^{2}J_{P,C}$ = 4.3 Hz and $^{4}J_{P,C}$ = 2.7 Hz, *C*H_2), 22.2 (*dd*, $^{2}J_{P,C}$ = 4.2 Hz and 2.8 Hz, *C*H_2); *trans*-isomer: δ = 160.8 (*dd*, *J* = 245.4 Hz and 3.2 Hz, C_q), 128.9-128.0 (*m*, C_q), 126.7 (*qd*, *J* = 7.3 Hz and 2.9 Hz, *CH*),125.8 (*t*, *J* = 3.8 Hz, *C*H), 123.7-123.0 (*m*, C_q), 113.6 (*dd*, *J* = 21.4 Hz and 3.6 Hz, *C*H), 53.3 (*d*, *J* = 7.2 Hz, O*C*H_3), 53.1 (*d*, *J* = 7.4 Hz, O*C*H_3), 52.7 (*d*, *J* = 6.6 Hz, O*C*H_3), 52.3 (*d*, *J* = 7.2 Hz, O*C*H_3), 36.4 (*ddd*, $^{1}J_{P,C}$ = 136.2 Hz, $^{3}J_{P,C}$ = 15.5 Hz, $^{4}J_{F,C}$ = 2.8 Hz, *C*H), 26.9 (*dd*, $^{1}J_{P,C}$ = 147.2 Hz, $^{3}J_{P,C}$ = 1.5 Hz, *C*H), 22.9 (*dd*, $^{2}J_{P,C}$ = 5.2 Hz and 3.2 Hz, *C*H_2), 21.3 (*m*, *C*H_2). **^{31}P NMR** (122 MHz, $CDCl_3$) *cis*-isomer: δ = 32.67 (*d*, $^{4}J_{P,P}$ = 8.0 Hz), 29.87 (*d*, $^{4}J_{P,P}$ = 8.0 Hz); *trans*-isomer: 33.87 (*d*, $^{4}J_{P,P}$ = 2.4 Hz), 29.48 (*dd*, $^{4}J_{P,P}$ = 2.4 Hz, $^{5}J_{F,P}$ = 2.4 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) *cis*-isomer: δ = -117.4 (s); *trans*-isomer: -116.7 (*d*, *J* = 2.4 Hz). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{21}FO_6P_2$ $[M+Na]^+$: 389.0690; found: 389.0694.

* Signals of *cis* and *trans*-isomer could not be assigned.

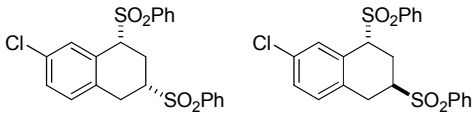
1,3-Bis-benzenesulfonyl-1,2,3,4-tetrahydro-naphthalene (1j). According to general procedure A, $Mn(OAc)_3$ (330 mg, 1.23 mmol) and phenylvinylsulfone (414 mg, 2.46 mmol) were added to a solution of benzeneboronic acid (50 mg, 0.41 mmol) in DCE. Purification via FC (pentane-MTBE 2:1) afforded **1i** as a mixture of both diastereoisomers (*cis* : *trans* = 1.7 : 1.0, determined by ^{1}H NMR) as a pale yellow solid (82 mg, 0.20 mmol, 48 %).



IR (film): 3061*w*, 1446*m*, 1304*s*, 1285*s*, 1138*s*, 1082*s*, 752*m*, 718*m*, 687*m* cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) *cis*-isomer: δ = 7.99-6.95 (*m*, 14 H, H_{aryl})*, 4.57 (*dd*, *J* = 10.0 Hz and 6.8 Hz, 1 H, C*H*), 3.15-3.02 (*m*, 1 H, C*H*), 2.86 (*ddd*, *J* = 14.7 Hz, 2.9 Hz and 2.9 Hz, 1 H, CH_2), 2.66-2.55 (*m*, 1 H, CH_2), 2.37 (*ddd*, *J* = 14.7 Hz, 12.8 Hz and 6.8 Hz, 1 H, CH_2), 2.18-2.05 (*m*, 1 H, CH_2)*; *trans*-isomer: δ = 7.95-6.84 (*m*, 14 H, H_{aryl})*, 4.40-4.34 (*m*, 1 H, C*H*), 4.27-4.16 (*m*, 1 H, C*H*), 3.22 (*dd*, *J* = 16.7 Hz and 5.9 Hz, 1 H, CH_2), 3.20-2.97 (*m*, 1 H, CH_2), 2.44-2.35 (*m*, 1 H, CH_2), 2.18-2.05 (*m*, 1 H, CH_2)*. **^{13}C NMR** (100 MHz, $CDCl_3$) both isomers: δ = 137.1 (C_q)*, 137.1 (C_q)*, 136.9 (C_q)*, 136.5 (C_q)*, 135.6 (C_q)*, 135.4 (C_q)*, 134.4 (*C*H)*, 134.3 (*C*H)*, 134.2 (*C*H)*, 134.2 (*C*H)*, 132.5 (*C*H)*, 131.5 (*C*H)*, 129.8 (*C*H)*, 129.7 (*C*H)*, 129.7 (*C*H)*, 129.6 (*C*H)*, 129.6 (*C*H)*, 129.5 (*C*H)*, 129.3 (*C*H)*, 129.3 (*C*H)*, 129.2 (*C*H)*, 129.1 (*C*H)*, 129.0 (C_q)*, 129.0 (*C*H)*, 127.4 (*C*H)*, 126.6 (C_q)*, 126.6 (*C*H)*, 124.4 (*C*H)*, 64.1 (*C*H, *cis*-isomer), 63.1 (*C*H, *trans*-isomer), 59.9 (*C*H, *cis*-isomer), 54.8 (*C*H, *trans*-isomer), 29.1 (*C*H_2, *cis*-isomer), 27.3 (*C*H_2, *trans*-isomer), 24.1 (*C*H_2, *cis*-isomer), 23.4 (*C*H_2, *trans*-isomer). **HRMS (ESI)**: calcd for $C_{22}H_{20}O_4S_2$ [M+Na]$^+$: 435.0695; found: 435.0692.

* Signals of *cis* and *trans*-isomer could not be assigned.

1,3-Bis-benzenesulfonyl-7-chloro-1,2,3,4-tetrahydro-naphthalene (1k). According to general procedure A, $Mn(OAc)_3$ (402 mg, 1.50 mmol) and phenylvinylsulfone (505 mg, 3.00 mmol) were added to a solution of 4-chlorobenzeneboronic acid (78 mg, 0.50 mmol) in DCE. Purification via FC (pentane-MTBE 2:1) afforded **1j** as a mixture of both diastereoisomers (*cis* : *trans* = 1.0 : 1.2, determined by ^{1}H NMR) as a pale yellow oil (99 mg, 0.22 mmol, 44 %).

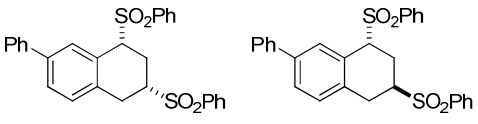


IR (film): 3028*w*, 2050*w*, 1486*m*, 1446*m*, 1307*s*, 1144*s*, 1085*s*, 756*m*, 727*m*, 690*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomer: δ = 7.98-6.90 (*m*, 13 H, H_{aryl})*, 4.48 (*dd*, *J* = 9.8 Hz and 7.0 Hz, 1 H, C*H*), 3.20-2.96 (*m*, 1 H, C*H*), 2.88 (*ddd*, *J* = 14.8 Hz, 2.6 Hz and 2.6 Hz, 1 H, CH_2), 2.63-2.52 (*m*, 1 H, CH_2), 2.36 (*ddd*, *J* = 14.6 Hz, 12.7 Hz and 6.9 Hz, 1 H, CH_2), 2.22-2.00 (*m*, 1 H, CH_2)*; *trans*-isomer: δ = 7.98-6.90 (*m*, 13 H, H_{aryl})*, 4.29 (*dd*, *J* = 5.6 Hz and 1.0 Hz, 1 H,

C*H*), 4.26-4.15 (*m*, 1 H, C*H*), 3.20-2.96 (*m*, 2 H, CH_2), 2.52-2.45 (*m*, 1 H, CH_2), 2.22-2.00 (*m*, 1 H, CH_2)*. **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 137.1*, 136.7*, 136.4*, 135.3*, 135.3*, 134.4*, 134.4*, 134.3*, 134.1*, 133.0*, 132.2*, 132.0*, 131.1*, 130.9*, 130.3*, 129.8*, 129.7*, 129.6*, 129.6*, 129.6*, 129.3*, 129.3*, 129.1*, 129.1*, 129.0*, 128.9*, 128.4*, 126.3*, 63.7 (*C*H_2, *cis*-isomer), 62.8 (*C*H_2, *trans*-isomer), 59.6 (*C*H_2, *trans*-isomer), 54.7 (*C*H_2, *cis*-isomer), 28.6 (*C*H, *cis*-isomer), 27.1 (*C*H, *trans*-isomer), 23.8 (*C*H, *cis*-isomer), 23.1 (*C*H, *trans*-isomer). **HRMS (ESI)**: calcd for $C_{22}H_{19}ClO_4S_2$ $[M+Na]^+$: 469.0305; found: 469.0290.

* Signals of *cis* and *trans*-isomer could not be assigned.

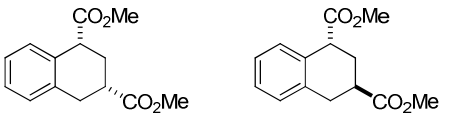
1,3-Bis-benzenesulfonyl-7-phenyl-1,2,3,4-tetrahydro-naphthalene (1l). According to general procedure A, $Mn(OAc)_3$ (402 mg, 1.5 mmol) and phenylvinylsulfone (505 mg, 3 mmol) were added to a solution of biphenylboronic acid (99 mg, 0.5 mmol) in DCE. Purification via FC (pentane-EtOAc 4:1) afforded **1k** as a mixture of both diastereoisomers (*cis* : *trans* = 1.3 : 1.0, determined by ^{1}H NMR) as a pale yellow oil (110 mg, 0.244 mmol, 49 %).



IR (film): 3061*w*, 3030*w*, 1485*m*, 1447*m*, 1307*s*, 1144*s*, 1084*s*, 759*s*, 691*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) *cis*-isomer: δ = 7.98-7.02 (*m*, 18 H, H_{aryl})*, 4.59 (*dd*, *J* = 9.9 Hz and 6.9 Hz, 1 H, C*H*), 3.19-3.04 (*m*, 1 H, C*H*), 2.92 (*ddd*, *J* = 14.7 Hz, 2.7 Hz and 2.7 Hz, 1 H, C*H*), 2.69-2.58 (*m*, 1 H, CH_2), 2.36 (*ddd*, *J* = 14.7 Hz, 12.8 Hz and 6.9 Hz, 1 H, CH_2), 2.25-2.12 (*m*, 1 H, CH_2)*; *trans*-isomer: δ = 7.98-7.02 (*m*, 18 H, H_{aryl})*, 4.44-4.36 (*m*, 1 H, C*H*), 3.25 (*dd*, *J* = 17.1 Hz and 6.0 Hz, 1 H, C*H*), 3.19-3.04 (*m*, 2 H, CH_2), 2.57-2.50 (*m*, 1 H, CH_2), 2.25-2.12 (*m*, 1 H, CH_2)*. **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 140.3*, 140.0*, 139.9*, 139.5*, 137.2*, 137.2*, 136.6*, 135.8*, 135.6*, 134.6*, 134.4*, 134.2*, 134.1*, 131.0*, 130.2*, 130.0*, 129.8*, 129.6*, 129.6*, 129.5*, 129.3*, 129.3*, 129.1*, 129.0*, 129.0*, 128.9*, 128.3*, 127.8*, 127.8*, 127.7*, 127.5*, 127.2*, 127.1*, 127.1*, 127.1*, 124.9*, 64.3 (*C*H$_2$, *cis*-isomer), 63.4 (*C*H$_2$, *trans*-isomer), 59.9 (*C*H$_2$, *cis*-isomer), 55.0 (*C*H$_2$, *trans*-isomer), 28.9 (*C*H, *cis*-isomer), 27.1 (*C*H, *trans*-isomer) 24.0 (*C*H, *cis*-isomer), 23.4 (*C*H, *trans*-isomer). **HRMS (ESI)**: calcd for $C_{28}H_{24}O_4S_2$ $[M+Na]^+$: 511.1008; found: 511.0998.

* Signals of *cis* and *trans*-isomer could not be assigned.

1,2,3,4-Tetrahydro-naphthalene-1,3-dicarboxylic acid dimethyl ester (1m). According to general procedure A, $Mn(OAc)_3$ (925 mg, 4.45 mmol) and methylacrylate (1.04 mL, 11.5 mmol) were added to a solution of benzeneboronic acid (140 mg, 1.15 mmol) in DCE. Purification via FC (pentane-EtOAc 20:1) afforded **1l** as a mixture of both diastereoisomers (*cis* : *trans* = 1.8 : 1.0, determined by ^{1}H NMR) as a pale yellow oil (76 mg, 0.31 mmol, 27 %).

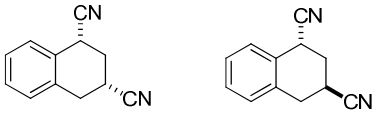


IR (film): 3030*w*, 2953*m*, 1728*s*, 1495*w*, 1434*s*, 1194*s*, 1159*s*, 1026*m*, 746*s* cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) *cis*-isomer: δ = 7.26-7.08 (*m*, 4 H, H_{aryl})*, 3.93 (*dd*, *J* = 11.5 Hz and 6.0 Hz, 1 H, C*H*), 3.73 (*s*, 3 H, CH_3), 3.72 (*s*, 3 H, CH_3), 3.03-3.00 (*m*, 2 H, CH_2), 2.73-2.67 (*m*, 1 H, C*H*), 2.48-2.43 (*m*, 1 H, CH_2), 2.18-2.11 (*m*, 1 H, CH_2); *trans*-isomer: δ = 7.26-7.08 (*m*, 4 H, H_{aryl})*, 3.91 (*dd*, *J* = 6.1 Hz and 2.7 Hz, 1 H, C*H*), 3.71 (*s*, 3 H, CH_3), 3.68 (*s*, 3 H, CH_3), 3.18-3.13 (*m*, 1 H, C*H*), 3.11-3.06 (*m*, 1 H, CH_2), 2.92 (*dd*, ^2J = 16.7 Hz and 11.1 Hz, 1 H, CH_2), 2.52-2.49 (*m*, 1 H, CH_2), 1.99 (*ddd*, *J* = 13.6 Hz, 11.5 Hz and 6.1 Hz, 1 H, CH_2). **^{13}C NMR** (150 MHz,

$CDCl_3$) *cis*-isomer: δ = 174.9 (C_q), 174.7 (C_q), 135.2 (C_q), 132.5 (C_q), 129.5 (*C*H), 128.0 (*C*H), 127.2 (*C*H), 126.6 (*C*H), 52.3 (CH_3)*, 52.0 (CH_3), 45.8 (*C*H), 39.1 (*C*H), 32.0 (CH_2), 29.5 (CH_2); *trans*-isomer: δ = 175.5 (C_q), 174.4 (C_q), 135.3 (C_q), 132.0 (C_q), 129.8 (*C*H), 129.5 (*C*H), 127.4 (*C*H), 126.2 (*C*H), 52.3 (CH_3)*, 51.9 (CH_3), 43.3 (*C*H), 36.6 (*C*H), 31.5 (CH_2), 28.2 (CH_2). **HRMS (ESI)**: m/z = calcd for $C_{14}H_{16}O_4$ $[M+Na]^+$: 271.0941; found: 271.0935.

* Signals of *cis* and *trans*-isomer could not be assigned.

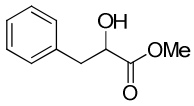
1,3-Biscyano-1,2,3,4-tetrahydronaphthalene (1n). According to general procedure A, acrylonitrile (653 µL, 12.3 mmol) and $Mn(OAc)_3$ (989 mg, 3.69 mmol) were added to a solution of benzeneboronic acid (150 mg, 1.23 mmol) in DCE. Purification via FC (P-EtOAc 20:1) afforded **1m** as a mixture of both diastereoisomers (*cis* : *trans* = 1.0 : 4.0, determined by ^{1}H NMR) as a white solid (43 mg, 0.24 mmol, 19 %).



IR (film): 2912*w*, 2848*w*, 2241*m*, 1490*m*, 1451*s*, 1437*m*, 744*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): *cis*-isomers: δ = 7.54-7.26 (*m*, 3 H, H_{aryl})*, 7.24-7.13 (*m*, 1 H, H_{aryl})*, 4.10 (*dd*, ^3J = 11.5 Hz and 5.9 Hz, 1 H, C*H*), 3.38-3.15 (*m*, 3 H), 2.79-2.70 (*m,* 1 H), 2.54-2.23 (*m*, 1 H); *trans*-isomer: δ = 7.54-7.26 (*m*, 3 H, H_{aryl})*, 7.24-7.13 (*m*, 1 H, H_{aryl})*, 4.24 (*dd*, ^3J = 6.0 Hz and 6.0 Hz, 1 H, C*H*), 3.38-3.15 (*m*, 2 H), 3.00-2.88 (*m*, 1 H), 2.54-2.23 (*m*, 2 H). **^{13}C NMR** (75 MHz, $CDCl_3$) *cis*-isomer: δ = 132.1 (C_q), 129.5 (*C*H), 128.9 (*C*H), 128.4 (*C*H), 128.1 (*C*H), 128.1 (C_q), 120.2 (*C*N), 119.8 (*C*N), 32.0(CH_2), 30.4 (*C*H), 30.2 (CH_2), 24.8 (*C*H); *trans*-isomer: δ = 131.9 (C_q), 129.8 (*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.1 (*C*H), 128.0 (C_q), 120.4 (*C*N), 120.2 (*C*N), 29.7 (CH_2), 29.1 (*C*H), 31.7 (CH_2), 23.8 (*C*H). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{10}N_2$ [M+Na]+: 205.0736; found: 205.0734. **Anal.** calcd for $C_{12}H_{10}N_2$: C 79.10, H 5.53, N 15.37; found: C 78.84, H 5.57, N 15.22.

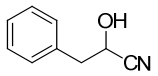
* Signals of *cis* and *trans*-isomer could not be assigned.

2-Hydroxy-3-phenyl-propionic acid methylester (2a). According to general procedure B, benzeneboronic acid was reacted with methylacrylate (736 µL). Purification via FC afforded **2a** (49 mg, 0.27 mmol, 33 %) as a yellow oil.



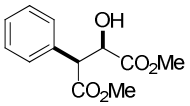
IR (film): 3463*br*, 3030*w*, 2954*w*, 1735*s*, 1497*m*, 1441*m*, 1209*s*, 1095*m*, 748*w*, 702*s*, 632*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.33-7.14 (*m*, 5 H, H_{aryl}), 4.46-4.38 (*m*, 1 H, C*H*), 3.73 (*s*, 3 H, CH_3), 3.09 (*dd*, ^2J = 13.9 Hz, ^3J = 4.6 Hz, 1 H, CH_2), 2.94 (*dd*, ^2J = 13.9 Hz, ^3J = 6.8 Hz, 1 H, CH_2), 2.67 (*d*, ^3J = 4.6 Hz, 1 H, CHO*H*). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 174.8 ($C_{carbonyl}$), 136.5 (C_q), 129.7 (*C*H), 128.7 (*C*H), 127.1 (*C*H), 71.5 (*C*H), 52.6 (OCH_3), 40.8 (CH_2). **HRMS (ESI)**: m/z = calcd for $C_{10}H_{12}O_3$ $[M+Na]^+$: 203.0679; found: 203.0672.

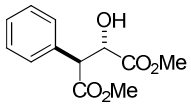
2-Hydroxy-3-phenyl-propionitrile (2b). According to general procedure B, benzeneboronic acid was reacted with acrylonitrile (544 µL) to afford **2b** (47 mg, 0.32 mmol, 39 %) as colorless oil.



IR (film): 3405*br*, 3032*w*, 2935*w*, 1497*m*, 1455*m*, 1064*s*, 745*s*, 649*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.46-7.26 (*m*, 5 H, H_{aryl}), 4.68 (*td*, ^3J = 6.6 Hz and 6.6 Hz, 1 H, C*H*OH), 3.14 (*d*, ^3J = 6.6 Hz, 2 H, CH_2), 2.40 (*d*, ^3J = 6.6 Hz, 1 H, O*H*). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 133.8 (C_q), 129.9 (*C*H), 129.2 (*C*H), 128.1 (*C*H), 119.3 (*C*N), 62.3 (*C*H), 41.6 (CH_2). **HRMS (ESI)**: m/z = calcd for C_9H_9NO $[M+Na]^+$: 170.0576; found: 170.0579.

2-Hydroxy-3-phenyldimethyl succinate (2c). According to general procedure C, benzeneboronic acid (100 mg, 0.820 mmol) was reacted with dimethyl maleate (4.1 mL). The succinate was isolated as a mixture of both diastereoisomers (2.6 : 1.0, determined by ^{1}H NMR) as a colorless viscous oil (93 mg, 0.39 mmol, 48 %). The relative configuration could not be assigned.



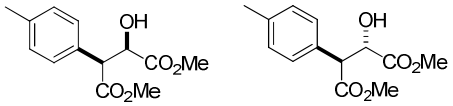


IR (film): 3477*s*, 3032*w*, 2955*w*, 1729*s*, 1437*m*, 1165*s*, 1109*m*, 1007*m*, 727*w*, 700*s* cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) both isomers: δ = 7.31-7.18 (*m*, 5 H, H_{aryl})*, 4.87 (*dd*, ^3J = 5.4 Hz and 5.0 Hz, 1 H, C*H*OH, minor), 4.48 (*dd*, ^3J = 7.7 Hz and 5.4 Hz, 1H, C*H*OH, major), 4.04 (*d*, ^3J = 5.4 Hz, 1 H, PhC*H*, major), 4.02 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, minor), 3.66 (*s,* 3 H, CH_3, minor), 3.64 (*s*, 3 H, CH_3, minor), 3.64 (*s,* 3 H, CH_3, major), 3.61 (*s*, 3 H, CH_3, major), 3.34 (*d*, ^3J = 7.7 Hz, 1 H, O*H*, major), 2.97 (*d*, ^3J = 5.4 Hz, 1 H, O*H*, minor). **^{13}C NMR** (100 MHz, $CDCl_3$) both isomers: δ = 173.1 ($C_{carbonyl}$, major), 172.8 ($C_{carbonyl}$, minor), 172.2 ($C_{carbonyl}$, major), 171.9 ($C_{carbonyl}$, minor), 134.9 (C_q, major), 133.6 (C_q, minor), 129.6 (*C*H, minor), 129.0 (*C*H, major), 128.8 (*C*H, major), 128.7 (*C*H, minor), 128.2 (*C*H, minor), 128.2 (*C*H, major), 73.3 (*C*HOH, major), 71.9 (*C*HOH, minor), 55.3 (*C*HPh, major), 54.7 (*C*HPh, minor), 52.8 (CH_3,

minor), 52.7 (CH_3, major), 52.6 (CH_3, minor), 52.6 (CH_3, major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{14}O_5$ $[M+Na]^+$: 261.0733; found: 261.0716. **Anal.** calcd for $C_{12}H_{14}O_5$: C: 60.50, H: 5.92; found: C: 60.45, H: 6.06.

* Signals of major and minor-isomer could not be assigned.

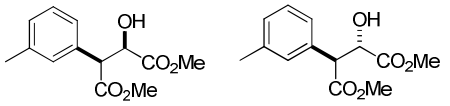
2-Hydroxy-3-(4-methylphenyl)dimethyl succinate (2d). According to general procedure C, 4-methylphenylboronic acid (100 mg, 0.735 mmol) was reacted with dimethyl maleate (3.7 mL). The succinate was isolated as a mixture of both diastereoisomers (1.5 : 1, determined by ^{1}H NMR) as a pale yellow oil (71 mg, 0.28 mmol, 38 %). The relative configuration could not be assigned.



IR (film): 3481*s*, 2955*m*, 1732*s*, 1515*m*, 1437*m*, 1163*s*, 1119*m*, 1017*m*, 819*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: 7.23-7.06 (*m*, 4 H, H_{aryl})*, 4.90 (*dd*, ^3J = 5.5 Hz and 5.0 Hz, 1 H, C*H*OH, minor), 4.51 (*dd*, ^3J = 7.8 Hz and 5.5 Hz, 1 H, C*H*OH, major), 4.06 (*d*, ^3J = 5.5 Hz, 1 H, PhC*H*, major), 4.03 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, minor), 3.71 (*s*, 3 H, OCH_3, minor), 3.70 (*s*, 3 H, OCH_3, minor), 3.68 (*s*, 3 H, OCH_3, major), 3.67 (*s*, 3 H, OCH_3, major), 3.38 (*d*, ^3J = 7.8 Hz, 1 H, O*H*, major), 3.00 (^3J = 5.5 Hz, 1 H, O*H*, minor), 2.31 (*s*, CH_3, major), 2.31 (*s*, CH_3, minor). **^{13}C NMR** (75 MHz, CDCl3) both isomers: δ = 173.2 ($C_{carbonyl}$, major), 172.9 ($C_{carbonyl}$, minor), 172.4 ($C_{carbonyl}$, major), 172.1 ($C_{carbonyl}$, minor), 138.1 (C_q, minor), 138.0 (C_q, major), 131.9 (C_q, major), 130.6 (C_q, minor), 129.6 (*C*H, major), 129.5 (*C*H, minor), 129.5 (*C*H, minor) 128.9 (*C*H, major), 128.8 (*C*H, major), 73.5 (*C*HOH, major), 72.0 (*C*HOH, minor), 54.9 (*C*HPh, major), 54.5 (*C*HPh, minor), 52.9 (O*C*H$_3$, minor), 52.8 (O*C*H$_3$, major), 52.6 (O*C*H$_3$, minor), 52.6 (O*C*H$_3$, major), 21.3 (CH_3)*. **HRMS (ESI)**: m/z = calcd for $C_{13}H_{16}O_5$ $[M+Na]^+$: 275.0890; found: 275.0861. **Anal.** calcd for $C_{13}H_{16}O_5$: C: 61.90, H: 6.39; found: C: 61.89, H: 6.32.

* Signals of major and minor-isomer could not be assigned.

2-Hydroxy-3-(3-methylphenyl)dimethyl succinate (2e). According to general procedure C, 3-methylphenylboronic acid (100 mg, 0.735 mmol) was reacted with dimethyl maleate. The desired succinate was isolated as a mixture of both diastereoisomers (3.0 : 1, determined by ^{1}H NMR) as a pale yellow oil (50 mg, 0.20 mmol, 27 %). The relative configuration could not be assigned.

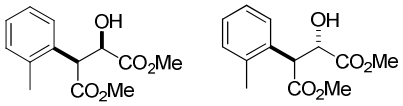


IR (film): 3475*s*, 2954*m*, 1730*s*, 1608*m*, 1437*s*, 1165*s*, 1098*m*, 1017*m*, 791*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: 7.25-7.02 (*m*, 4 H, H_{aryl})*, 4.92 (*dd*, ^3J = 5.4 Hz and 5.1 Hz, 1 H, C*H*OH, minor), 4.53 (*dd*, ^3J = 8.0 Hz and 5.3 Hz, 1 H, C*H*OH, major), 4.07 (*d*, ^3J = 5.3 Hz, 1 H, PhC*H*, major), 4.04 (*d*, ^3J = 5.2 Hz, 1 H, PhC*H*, minor), 3.74 (*s*, 3 H, CH_3, minor), 3.73 (*s*, 3 H, CH_3, minor), 3.71 (*s*, 3 H, CH_3, major), 3.69 (*s*, 3 H, CH_3, major), 3.38 (*d*, ^3J = 8.0 Hz, 1 H,

O*H*, major), 2.96 (*d*, ^3J = 5.4 Hz, 1 H, O*H*, minor), 2.35 (*s*, 3 H, CH_3, major), 2.34 (*s*, 3 H, CH_3, minor). **^{13}C NMR** (75 MHz, CDCl3) both isomers: δ = 173.2 ($C_{carbonyl}$, major), 172.9 ($C_{carbonyl}$, minor), 172.4 ($C_{carbonyl}$, major), 172.1 ($C_{carbonyl}$, minor), 138.6 (C_q, major), 138.4 (C_q, minor), 134.9 (C_q, major), 133.6 (C_q, minor), 130.3 (*C*H, minor), 129.7 (*C*H, major), 129.1 (*C*H, minor) 129.0 (*C*H, major), 128.8 (*C*H, major), 128.7 (*C*H, minor), 126.6 (*C*H, minor), 126.1 (*C*H, major), 73.5 (*C*HOH, major), 72.0 (*C*HOH, minor), 55.2 (*C*HPh, major), 54.8 (*C*HPh, minor), 52.8 (O*C*H3, minor), 52.8 (O*C*H3, major), 52.7 (O*C*H3, minor), 52.6 (O*C*H3, major), 21.6 (*C*H_3, minor), 21.6 (*C*H_3, major). **HRMS (ESI)**: m/z = calcd for $C_{13}H_{16}O_5$ $[M+Na]^+$: 275.0890; found: 275.0853. **Anal.** calcd for $C_{13}H_{16}O_5$: C: 61.90, H: 6.39; found: C: 61.65, H: 6.32.

* Signals of major and minor-isomer could not be assigned.

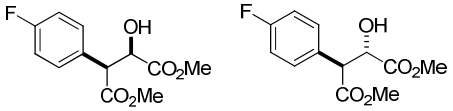
2-Hydroxy-3-(2-methylphenyl)dimethyl succinate (2f). According to general procedure C, 2-methylphenylboronic acid (100 mg, 0.735 mmol) was reacted with dimethyl maleate (3.7 mL). The succinate was isolated as a mixture of both diastereoisomers (3.3 : 1, determined by ^{1}H NMR) as a pale yellow oil (43 mg, 0.17 mmol, 23 %). The relative configuration could not be assigned.



IR (Film): 3477*s*, 2954*m*, 1730*s*, 1436*m*, 1160*s*, 1120*m*, 1001*m*, 736*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.45-7.31 (*m*, 1 H, H_{aryl})*, 7.25-7.15 (*m*, 3 H, H_{aryl})*, 4.90 (*dd*, ^3J = 6.1 Hz and 4.7 Hz, 1 H, C*H*OH, minor), 4.53 (*dd*, ^3J = 7.2 Hz and 5.4 Hz, 1 H, C*H*OH, major), 4.41 (*d*, ^3J = 5.4 Hz, 1 H, PhC*H*, major), 4.39 (*d*, ^3J = 6.1 Hz, 1 H, PhC*H*, minor), 3.73 (*s*, 3 H, OCH_3, minor), 3.71 (*s*, 3 H, OCH_3, minor), 3.70 (*s*, 3 H, OCH_3, major), 3.69 (*s*, 3 H, OCH_3, major), 3.45 (*d*, ^3J = 7.2 Hz, 1 H, O*H*, major), 2.98 (^3J = 4.7 Hz, 1 H, O*H*, minor), 2.37 (*s*, 3 H, CH_3, major), 2.36 (*s*, 3 H, CH_3, minor). **^{13}C NMR** (75 MHz, CDCl3) both isomers: δ = 173.2 ($C_{carbonyl}$, major), 173.1 ($C_{carbonyl}$, minor), 172.8 ($C_{carbonyl}$, major), 172.3 ($C_{carbonyl}$, minor), 137.2 (C_q, minor), 136.4 (C_q, minor), 133.5 (C_q, major), 132.6 (C_q, minor), 130.9 (*C*H, minor), 130.9 (*C*H, major), 128.8 (*C*H, minor) 128.7 (*C*H, major), 128.1 (*C*H, minor), 128.1 (*C*H, major), 126.5 (*C*H, major), 126.4 (*C*H, minor), 72.6 (*C*HOH, major), 71.8 (*C*HOH, minor), 52.9 (O*C*H$_3$)*, 52.6 (O*C*H$_3$)*, 50.8 (*C*HPh, major), 50.2 (*C*HPh, minor), 20.0 (*C*H_3, minor), 19.9 (*C*H_3, major). **HRMS (ESI)**: m/z = calcd for $C_{13}H_{16}O_5$ $[M+Na]^+$:275.0890; found: 275.0864. **Anal.** calcd for $C_{13}H_{16}O_5$: C: 61.90, H: 6.39; found: C: 61.46; H: 6.33.

* Signals of major and minor-isomer could not be assigned.

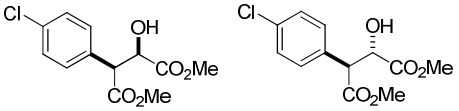
2-Hydroxy-3-(4-fluorophenyl)dimethyl succinate (2g). According to general procedure C, 4-fluorophenylboronic acid (100 mg, 0.715 mmol) was reacted with dimethyl maleate (3.55 mL). The succinate was isolated as a mixture of both



diastereoisomers (2.4 : 1.0, determined by ^{1}H NMR) as a colorless viscous oil (84 mg, 0.33 mmol, 46 %). The relative configuration could not be assigned.

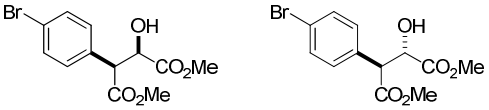
IR (film): 3483*w*, 1732*s*, 1606*w*, 1510*s*, 1437*m*, 1224*s*, 1159*s*, 910*m*, 729*s*, 648*w* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.36-7.24 (*m*, 2 H, H_{aryl})*, 7.05-6.93 (*m*, 2 H, H_{aryl})*, 4.93 (*dd*, ^{3}J = 4.8 Hz and 4.8 Hz, 1 H, C*H*OH, minor), 4.51 (*dd*, ^{3}J = 7.6 Hz and 5.2 Hz, 1H, C*H*OH, major), 4.10 (*d*, ^{3}J = 5.2 Hz, 1 H, PhC*H*, major), 4.08 (*d*, ^{3}J = 4.8 Hz, 1 H, PhC*H*, minor), 3.75 (*s*, 3 H, CH_3, minor), 3.71 (s, 6 H, CH_3)*, 3.71 (*s*, 3 H, OCH_3, major), 3.36 (*d*, ^{3}J = 7.6 Hz, 1 H, O*H*, major), 3.05 (*d*, ^{3}J = 5.4 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 173.0 ($C_{carbonyl}$, major), 172.7 ($C_{carbonyl}$, minor), 171.9 (*d*, $^{6}J_{F,C}$ = 0.6 Hz, $C_{carbonyl}$, major), 171.7 (*d*, $^{6}J_{F,C}$ = 0.6 Hz, $C_{carbonyl}$, minor), 162.7 (*d*, $^{1}J_{F,C}$ = 246.9 Hz, *C*H, minor), 162.1 (*d*, $^{1}J_{F,C}$ = 246.9 Hz, *C*H, major), 131.4 (*d*, $^{3}J_{F,C}$ = 8.1 Hz, *C*H, minor), 130.8 (*d*, $^{3}J_{F,C}$ = 8.1 Hz, *C*H, major), 130.8 (*d*, $^{4}J_{F,C}$ = 3.6 Hz, C_q, major), 129.5 (*d*, $^{4}J_{F,C}$ = 3.4 Hz, C_q, minor), 115.8 (*d*, $^{2}J_{F,C}$ = 21.5 Hz, *C*H, major), 115.6 (*d*, $^{2}J_{F,C}$ = 21.5 Hz, *C*H, minor), 73.3 (*d*, $^{6}J_{F,C}$ = 0.6 Hz, *C*HOH, major), 71.9 (*d*, $^{6}J_{F,C}$ = 0.6 Hz, *C*HOH, minor), 54.5 (*C*HPh, major), 53.9 (*C*HPh, minor), 53.0 (O*C*H$_3$, minor), 52.9 (O*C*H$_3$, major), 52.8 (O*C*H$_3$, minor), 52.7 (O*C*H$_3$, major). **^{19}F NMR** (282 MHz, $CDCl_3$) both isomers: δ = -114.1 (minor), -114.2 (major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{13}FO_5$ $[M+Na]^+$: 279.0639; found: 279.0649. **Anal.** calcd for $C_{12}H_{13}FO_5$: C: 56.25, H: 5.11; found: C: 56.24, H: 5.11.

* Signals of major and minor-isomer could not be assigned.

2-Hydroxy-3-(4-chlorophenyl)dimethyl succinate (2h). According to general procedure C,  4-chlorophenylboronic acid (100 mg, 0.639 mmol) was reacted with dimethyl maleate (3.2 mL). The succinate was isolated as a mixture of both diastereoisomers (1.9 : 1.0, determined by ^{1}H NMR) as a pale yellow viscous oil (92 mg, 0.34 mmol, 53 %). The relative configuration could not be assigned.

IR (film): 3478*w*, 2955*w*, 1732*s*, 1492*m*, 1437*m*, 1217*m*, 1163*s*, 1089*s*, 1014*s*, 827*m*, 763*m*, 702*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.30-7.15 (*m*, 4 H, H_{aryl})*, 4.87 (*dd*, ^3J = 4.8 Hz and 4.8 Hz, 1 H, C*H*OH, minor), 4.44 (*dd*, ^3J = 7.5 Hz and 5.0 Hz, 1 H, C*H*OH, major), 4.04 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, major), 4.00 (*d*, ^3J = 4.8 Hz, 1 H, PhC*H*, minor), 3.68 (*s*, 3 H, CH_3, minor), 3.66 (*s*, 3 H, CH_3, major), 3.66 (*s*, 3 H, CH_3, minor), 3.65 (*s*, 3 H, CH_3, major), 3.33 (*d*, ^3J = 7.5 Hz, 1 H, O*H*, major), 3.01 (*d*, ^3J = 4.8 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 173.0 ($C_{carbonyl}$, major), 172.7 ($C_{carbonyl}$, minor), 171.7 ($C_{carbonyl}$, major), 171.5 ($C_{carbonyl}$, minor), 134.4 (C_q, minor), 134.3 (C_q, major), 133.6 (C_q, major), 133.6 (C_q, minor), 131.1 (*C*H, minor), 130.6 (*C*H, major), 129.0 (*C*H, major), 128.9 (*C*H, minor), 73.1 (*C*HOH, major), 71.9 (*C*HOH, minor), 54.6 (*C*HPh, major), 54.1 (*C*HPh, minor), 53.0 (CH_3, minor), 52.9 (CH_3, major), 52.8 (CH_3, minor), 52.7 (CH_3, major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{13}ClO_5$ $[M+Na]^+$: 295.0344; found: 295.0339. **Anal.** calcd for $C_{12}H_{13}ClO_5$: C: 52.86; H: 4.81; found: C: 52.58, H: 4.63.

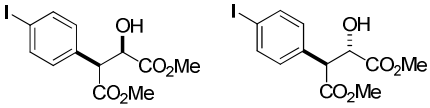
* Signals of *cis* and *trans*-isomer could not be assigned.

2-Hydroxy-3-(4-bromophenyl)dimethyl succinate (2i). According to general procedure C,  4-bromophenylboronic acid (125 mg, 0.625 mmol) was reacted with $Mn(OAc)_3$ (503 mg, 1.88 mmol). The succinate was isolated as a mixture of both diastereoisomers (1.7 : 1.0, determined by ^{1}H NMR) as a pale yellow viscous oil (92 mg, 0.29 mmol, 46 %). The relative configuration could not be assigned.

IR (film): 3481*w*, 1732*s*, 1489*m*, 1437*m*, 1265*m*, 1203*m*, 1165*m*, 1074*s*, 1010*m*, 910*m*, 823*m*, 731*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.50-7.35 (*m*, 2 H, H_{aryl})*, 7.21-7.08 (*m*, 2 H, H_{aryl})*, 4.88 (*dd*, ^3J = 5.1 Hz and 4.7 Hz, 1 H, C*H*OH, minor), 4.44 (*dd*, ^3J = 7.5 Hz and 5.0 Hz, 1 H, C*H*OH, major), 4.03 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, major), 4.00 (*d*, ^3J = 4.7 Hz, 1 H, PhC*H*, minor), 3.68 (*s*, 3 H, CH_3, minor), 3.67 (*s*, 3 H, CH_3, major), 3.66 (*s*, 3 H, CH_3, minor), 3.64 (*s*, 3 H, CH_3, major), 3.33 (*d*, ^3J = 7.5 Hz, 1 H, O*H*, major), 3.01 (^3J = 4.8 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 172.9 ($C_{carbonyl}$, major), 172.6 ($C_{carbonyl}$, minor), 171.5 ($C_{carbonyl}$, major), 171.3 ($C_{carbonyl}$, minor), 134.0 (C_q, major), 132.6 (C_q, minor), 131.9 (*C*H, major), 131.7 (*C*H, minor), 131.4 (*C*H, minor), 130.8 (*C*H, major), 122.5 (C_q, minor), 122.3 (C_q, major), 73.0 (*C*HOH, major), 71.7 (*C*HOH, minor), 54.5 (*C*HPh, major), 54.1 (*C*HPh,

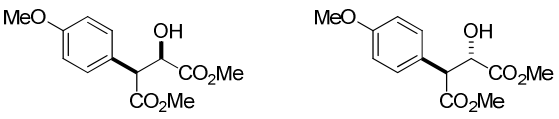
minor), 52.9 (*C*H_3, minor), 52.9 (*C*H_3, major), 52.7 (*C*H_3, minor), 52.7 (*C*H_3, major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{13}BrO_5$ $[M+Na]^+$: 338.9839; found: 338.9845.

* Signals of major and minor-isomer could not be assigned.

2-Hydroxy-3-(4-iodoophenyl)dimethyl succinate (2j).  According to general procedure C, 4-iodophenylboronic acid (100 mg, 0.404 mmol) was reacted with $Mn(OAc)_3$ (325 mg, 1.21 mmol). The succinate was isolated as a mixture of both diastereoisomers (2.0 : 1.0, determined by ^{13}C NMR) as a pale yellow oil (50 mg, 0.14 mmol, 34 %). The relative configuration could not be assigned.

IR (film): 3487*w*, 1732*s*, 1485*m*, 1437*m*, 1404*w*, 1265*m*, 1165*s*, 1006*s*, 908*m*, 729*s* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.70-7.62 (*m*, 2 H, H_{aryl})*, 7.14-7.01 (*m*, 2 H, H_{aryl})*, 4.93 (*dd*, ^3J = 5.0 Hz and 4.7 Hz, 1 H, C*H*OH, minor), 4.49 (*dd*, ^3J = 7.3 Hz and 5.1 Hz, 1 H, C*H*OH, major), 4.07 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, major), 4.03 (*d*, ^3J = 4.7 Hz, 1 H, PhC*H*, minor), 3.74 (*s*, 3 H, CH_3, minor), 3.73 (*s*, 3 H, CH_3, major), 3.72 (*s*, 3 H, CH_3, minor), 3.70 (*s*, 3 H, CH_3, minor), 3.39 (*d*, ^3J = 7.3 Hz, 1 H, O*H*, major), 3.06 (^3J = 5.0 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 172.6 ($C_{carbonyl}$, major), 172.3 ($C_{carbonyl}$, minor), 171.2 ($C_{carbonyl}$, major), 171.1 ($C_{carbonyl}$, minor), 137.6 (*C*H, major), 137.5 (*C*H, minor), 134.5 (C_q, major), 133.1 (C_q, minor), 131.4 (*C*H, minor), 130.8 (*C*H, major), 93.9 (C_q, minor), 93.7 (C_q, major), 72.7 (*C*HOH, major), 71.4 (*C*HOH, minor), 54.4 (*C*HPh, major), 54.0 (*C*HPh, minor), 52.7 (*C*H_3, minor), 52.6 (*C*H_3, major), 52.5 (*C*H_3, minor), 52.4 (*C*H_3, major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{13}IO_5$ $[M+Na]^+$: 386.9700; found: 386.9685. **Anal.** calcd for $C_{12}H_{13}IO_5$: C: 39.58; H: 3.60; found: C: 39.97, H: 3.63.

* Signals of major and minor-isomer could not be assigned.

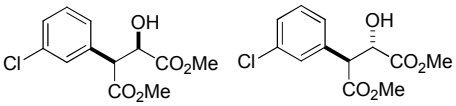
2-Hydroxy-3-(4-methoxyphenyl)dimethyl succinate (2k).  According to general procedure C, 4-methoxyphenylboronic acid (125 mg, 0.82 mmol) was reacted with $Mn(OAc)_3$ in dimethyl maleate (4.1 mL). The succinate was isolated as a mixture of both diastereoisomers (2.8 : 1.0, determined by ^{1}H NMR) as a pale yellow viscous oil (82 mg, 0.31, 37 %). The relative configuration could not be assigned.

IR (film): 3479*s*. 2956*m*, 2840*w*, 1733*s*, 1612*m*, 1514*s*, 1438*m*, 1250*s*, 1031*m*, 832*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.25-7.15 (*m*, 2 H, H_{aryl})*, 6.85-6.74 (*m*, 2 H, H_{aryl})*, 4.86 (*dd*, ^3J = 5.2 Hz and 4.6 Hz, 1 H, C*H*OH, minor), 4.47 (*dd*, ^3J = 7.6 Hz and 5.4 Hz, 1 H, C*H*OH, major), 4.00 (*d*, ^3J = 5.4 Hz, 1 H, PhC*H*, major), 3.99 (*d*, ^3J = 4.6 Hz, 1 H, PhC*H*, minor), 3.75 (*s*, 3 H, C_{aryl}OCH_3, major), 3.74 (*s*, 3 H, C_{aryl}OCH_3, minor), 3.69 (*s*, 3 H, OCH_3, minor) 3.67 (*s*, 3 H, OCH_3, minor), 3.66 (*s*, 3 H, OCH_3, major), 3.64 (*s*, 3 H, OCH_3, major), 3.31 (*d*, ^3J = 7.6 Hz, 1 H,

O*H*, major), 2.97 (^3J = 5.2 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, CDCl3): δ = 173.1 ($C_{carbonyl}$, major), 172.8 ($C_{carbonyl}$, minor), 172.3 ($C_{carbonyl}$, major), 172.1 ($C_{carbonyl}$, minor), 159.5 (C_q, minor), 159.4 (C_q, major), 130.6 (*C*H, minor), 130.1 (*C*H, major), 126.9 (C_q, minor), 125.5 (C_q, major), 114.2 (*C*H, major) 114.1 (*C*H, minor), 73.4 (*C*HOH, major), 72.0 (*C*HOH, minor), 55.3 ($C_{aryl}OCH_3$, major), 55.3 ($C_{aryl}OCH_3$, minor), 54.5 (*C*HPh, major), 53.9 (*C*HPh, minor), 52.7 (OCH_3, minor), 52.6 (OCH_3, major), 52.5 (OCH_3, minor), 52.5 (OCH_3, major). **HRMS (ESI)**: m/z = calcd for $C_{13}H_{16}O_6$ $[M+Na]^+$:291.0839; found: 291.0830. **Anal.** calcd for $C_{13}H_{16}O_6$: C: 58.20, H: 6.01; found: C: 58.16; H: 6.14.

* Signals of major and minor-isomer could not be assigned.

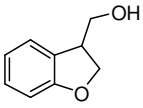
2-Hydroxy-3-(3-chlorophenyl)dimethyl succinate (2l). According to general procedure C, 3-chlorophenylboronic acid (100 mg, 0.639 mmol) was reacted with dimethyl maleate (3.2 mL). The succinate was isolated as a mixture of both diastereoisomers (1.9 : 1.0, determined by ^{1}H NMR) as a pale yellow viscous oil (69 mg, 0.25 mmol, 40 %). The relative configuration could not be assigned.



IR (film): 3483*w*, 2955*w*, 1738*s*, 1437*m*, 1228*m*, 1110*m*, 1010*m*, 779*m*, 711*m* cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers: δ = 7.39-7.15 (*m*, 4 H, H_{aryl})*, 4.93 (*dd*, ^3J = 5.0 Hz and 5.0 Hz, 1 H, C*H*OH, minor), 4.51 (*dd*, ^3J = 7.5 Hz and 4.9 Hz, 1 H, C*H*OH, major), 4.10 (*d*, ^3J = 4.9 Hz, 1 H, PhC*H*, major), 4.05 (*d*, ^3J = 5.0 Hz, 1 H, PhC*H*, minor), 3.75 (*s*, 3 H, CH_3, minor), 3.73 (*s*, 3 H, CH_3)*, 3.72 (*s*, 3 H, CH_3, major), 3.42 (*d*, ^3J = 7.5 Hz, 1 H, O*H*, major), 3.08 (*d*, ^3J = 5.0 Hz, 1 H, O*H*, minor). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers: δ = 172.9 ($C_{carbonyl}$, major), 172.6 ($C_{carbonyl}$, minor), 171.4 ($C_{carbonyl}$, major), 171.2 ($C_{carbonyl}$, minor), 137.0 (C_q, major), 135.6 (C_q, minor), 134.6 (C_q, major), 134.4 (C_q, minor), 130.0 (*C*H, major), 129.8 (*C*H, minor), 129.8 (*C*H, minor), 129.3 (*C*H, major), 128.4 (*C*H, minor), 128.4 (*C*H, major), 127.9 (*C*H, minor), 127.4 (*C*H, major), 73.0 (*C*HOH, major), 71.8 (*C*HOH, minor), 54.7 (*C*HPh, major), 54.3 (*C*HPh, minor), 52.9 (*C*H_3, minor), 52.9 (*C*H_3, major), 52.8 (*C*H_3, minor), 52.7 (*C*H_3, major). **HRMS (ESI)**: m/z = calcd for $C_{12}H_{13}ClO_5$ $[M+Na]^+$: 295.0344; found: 295.0339. **Anal.** calcd for $C_{12}H_{13}ClO_5$: C: 52.86; H: 4.81; found: C: 52.58, H: 4.63.

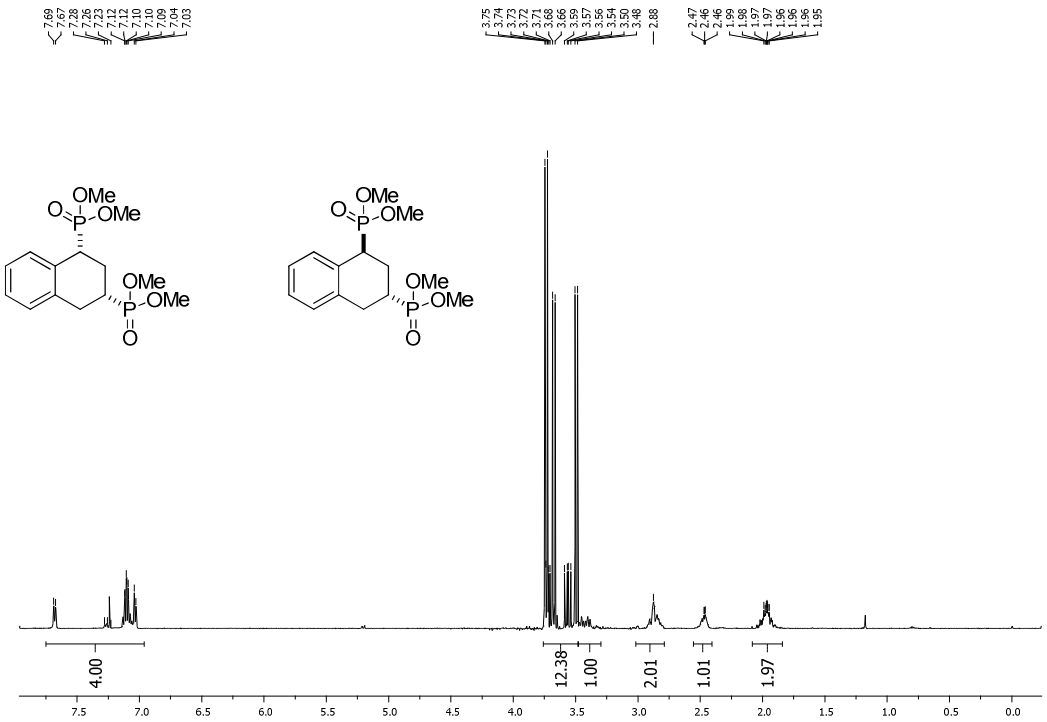
* Signals of major and minor-isomer could not be assigned.

2,3-Dihydro-benzofuran-3-ylmethanol (4). According to general procedure C, 2-Allyloxybenzeneboronic acid **3** (100 mg, 0.562 mmol) was added to a solution of $Mn(OAc)_3$ (452 mg, 1.69 mmol) in DCE (2.8 mL). Purification via FC pentane : EtOAc = 40 : 1) afforded **4** as a colorless oil (24.0 mg, 0.158 mmol, 28 %).

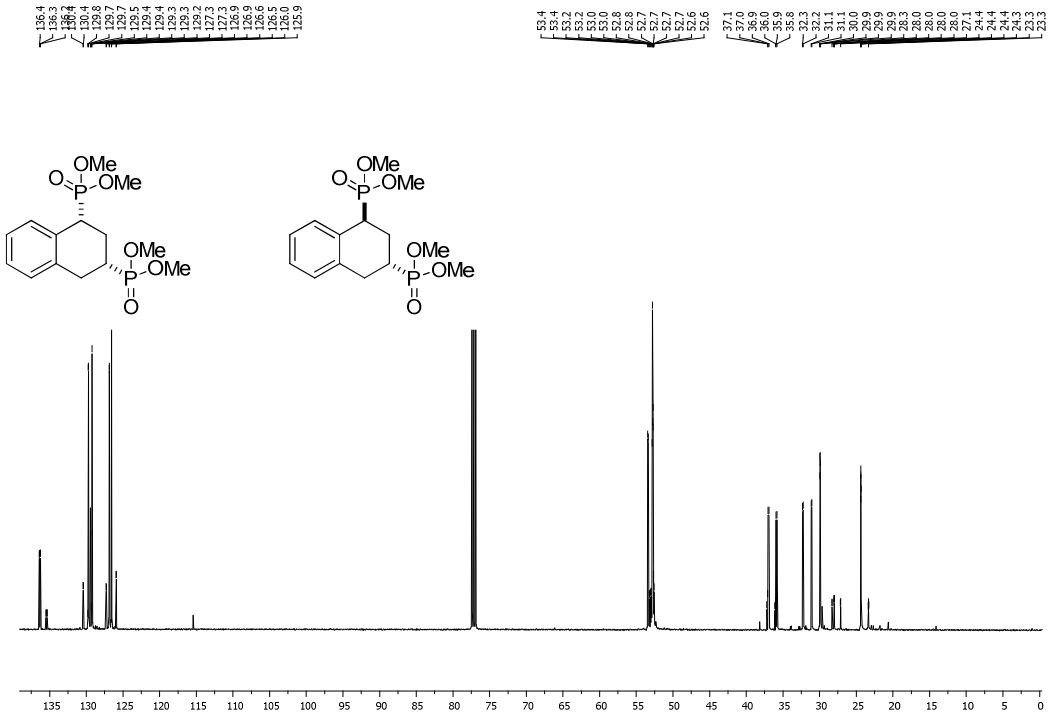


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.20 (*m*, 1 H, H_{aryl}), 7.16 (*dddd*, *J* = 7.8 Hz, 7.4 Hz, 1.4 Hz, 0.6 Hz, 1 H, H_{aryl}) 6.87 (*ddd*, *J* = 7.4 Hz, 7.4 Hz and 1.0 Hz, 1 H, H_{aryl}), 6.82 (*d*, *J* = 7.8 Hz, 1 H, H_{aryl}), 4.64 (*d*, *J* = 9.0 Hz, 1 H, CH_2), 4.48 (*dd*, *J* = 9.0 Hz and 5.3 Hz ,1 H, CH_2), 3.88-3.74 (*m*, 2 H, CH_2), 3.70-3.57 (*m*, 1 H, C*H*), 1.63 (*s*, 1 H, O*H*). **HRMS (ESI)**: m/z = calcd for $C_9H_{10}O_2$ $[M+Na]^+$: 173.0573; found: 173.0577.

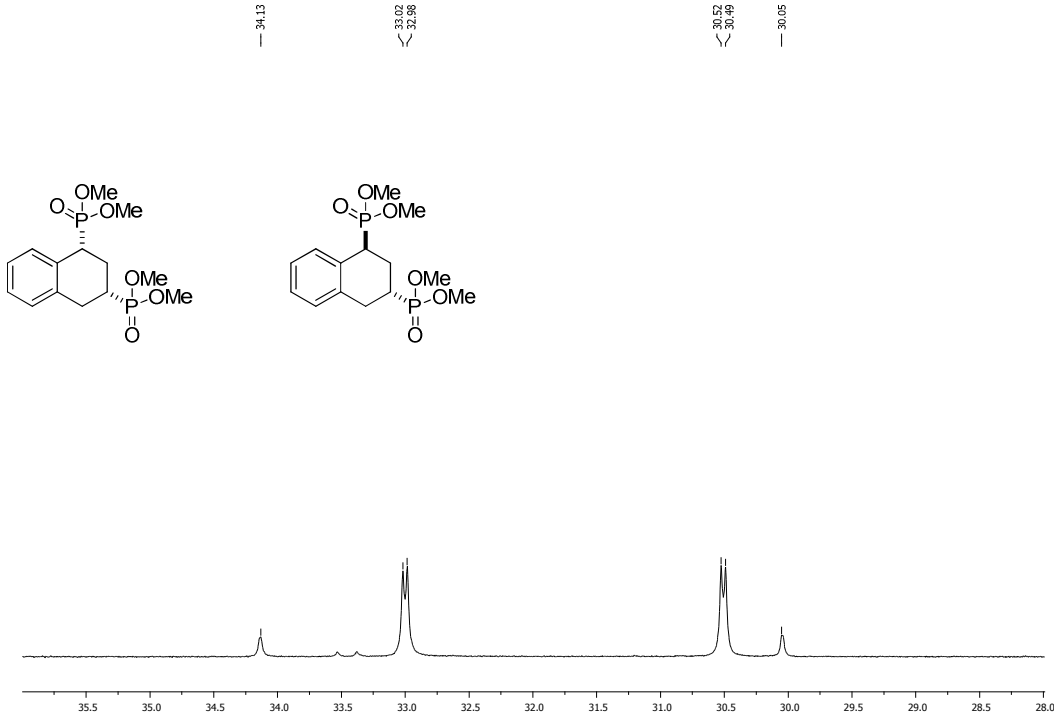
^{1}H NMR (500 MHz, $CDCl_3$) of Compound **1a**.



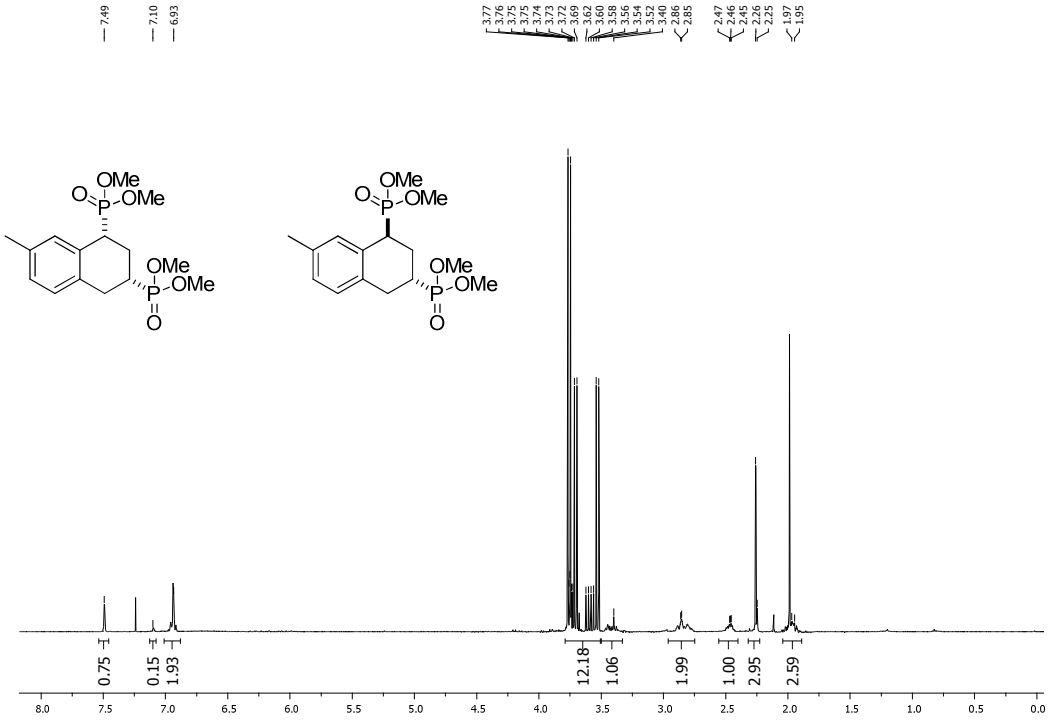
^{13}C NMR (126 MHz, $CDCl_3$) of Compound **1a**.



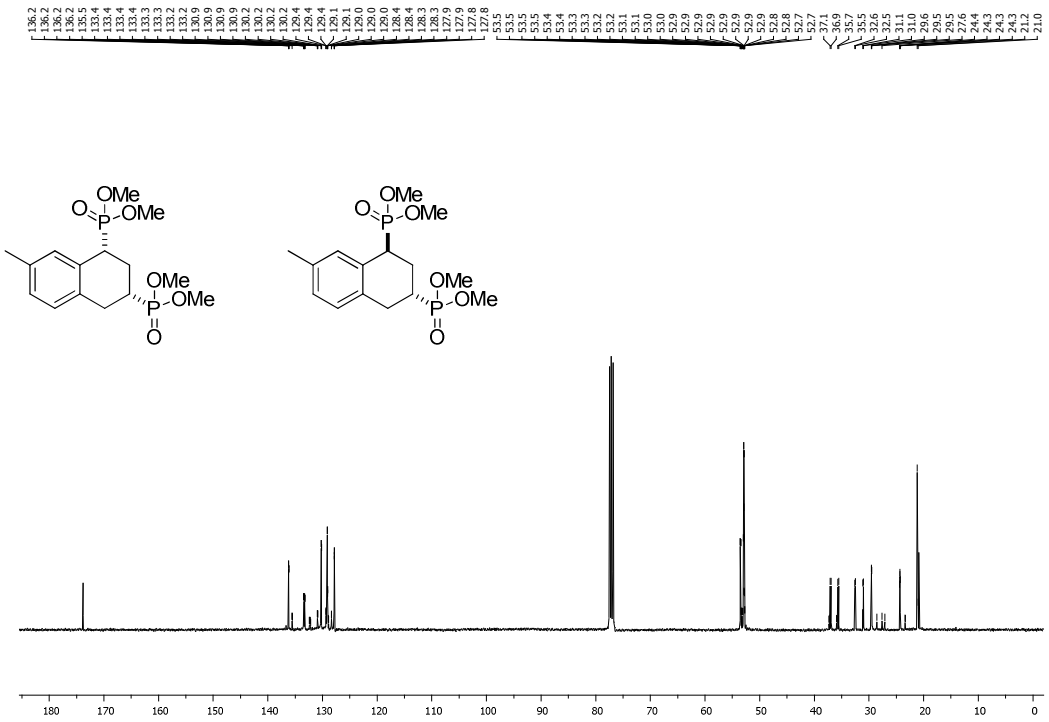
^{31}P NMR (202 MHz, $CDCl_3$) of Compound **1a**.



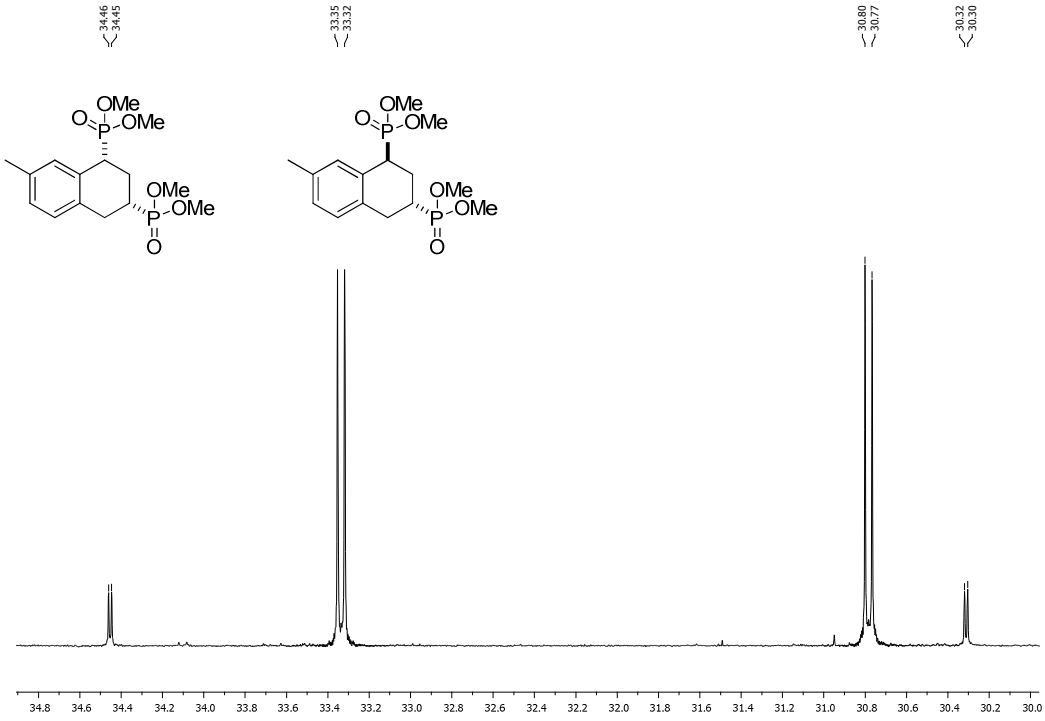
^{1}H NMR (500 MHz, $CDCl_3$) of Compound **1b**.



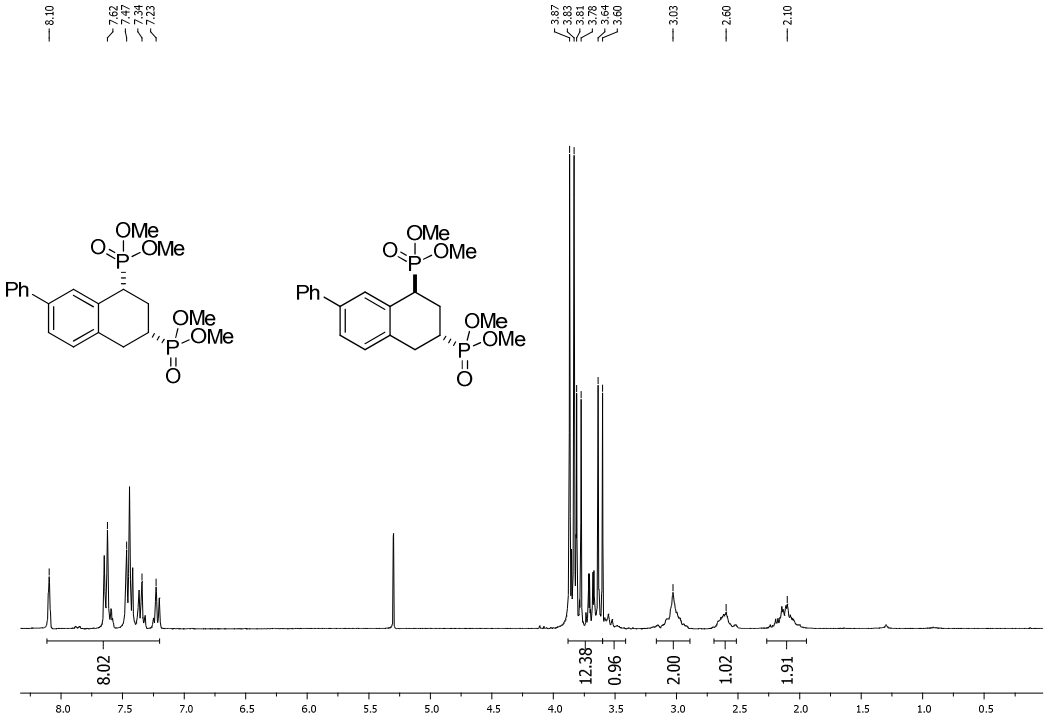
^{13}C NMR (126 MHz, $CDCl_3$) of Compound **1b**.



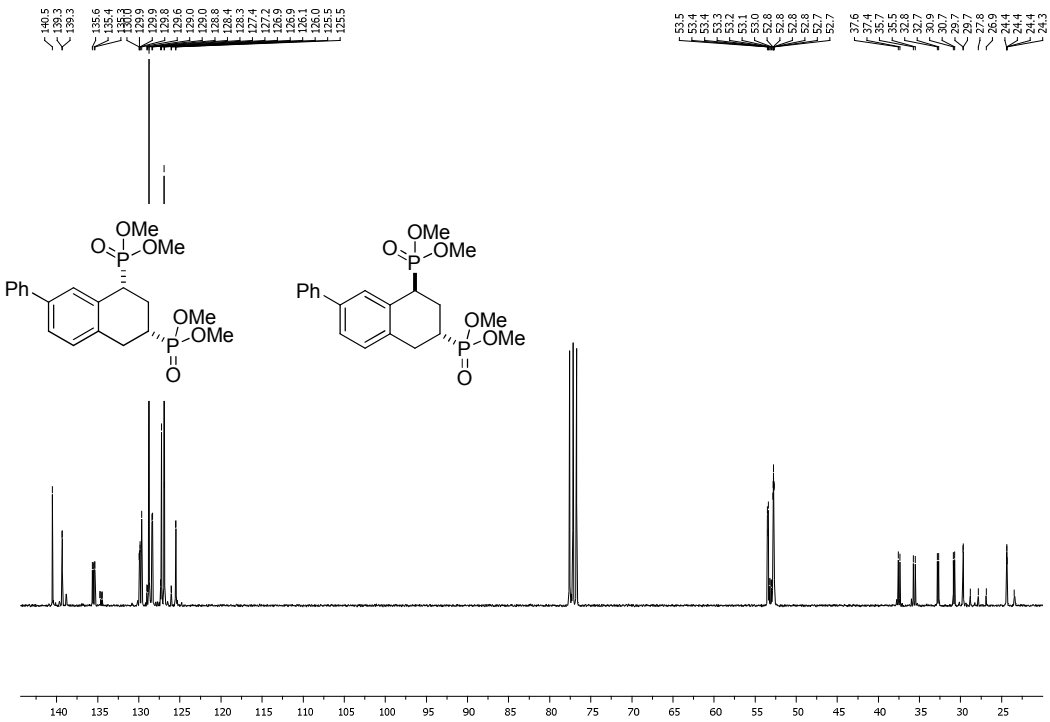
^{31}P NMR (202 MHz, $CDCl_3$) of Compound **1b**.



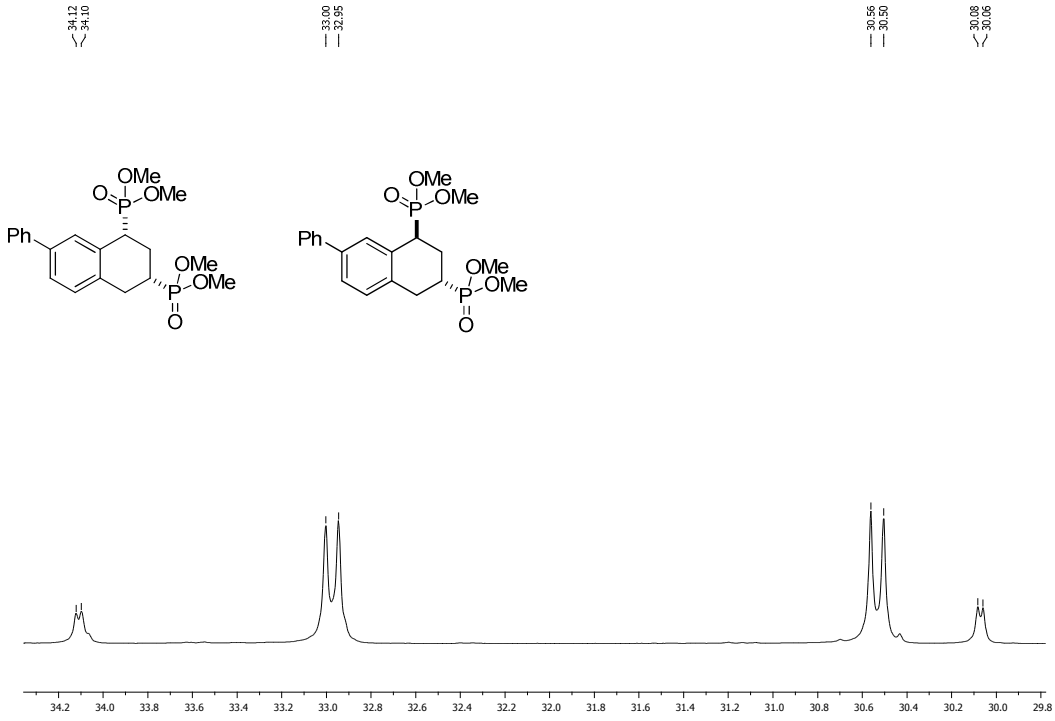
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1c**.



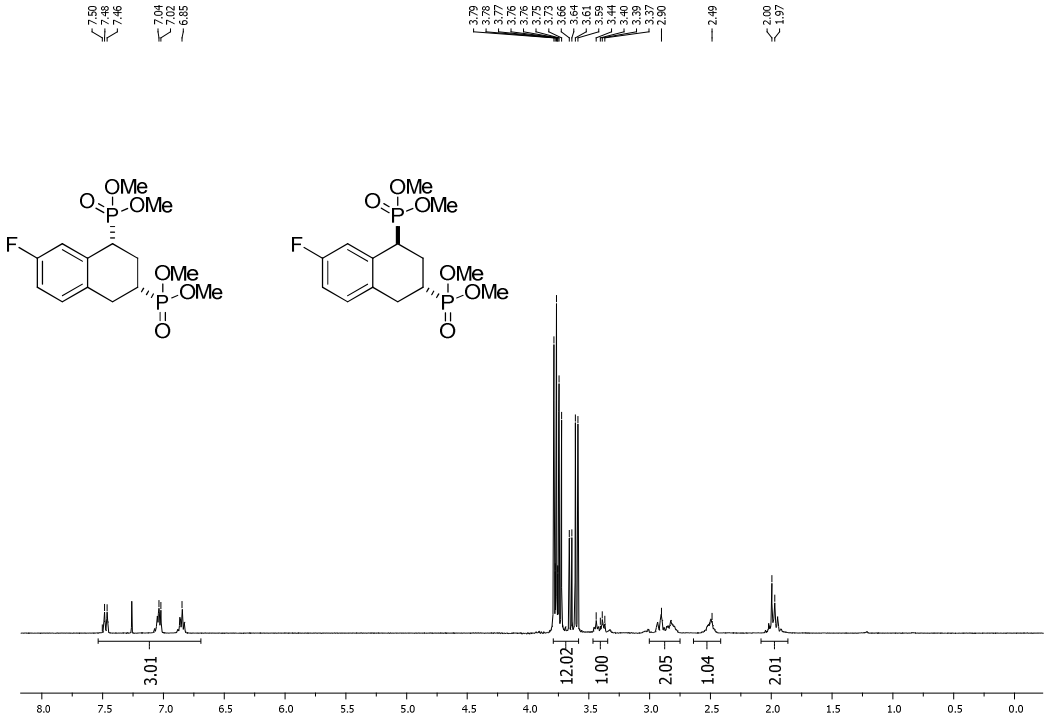
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1c**.



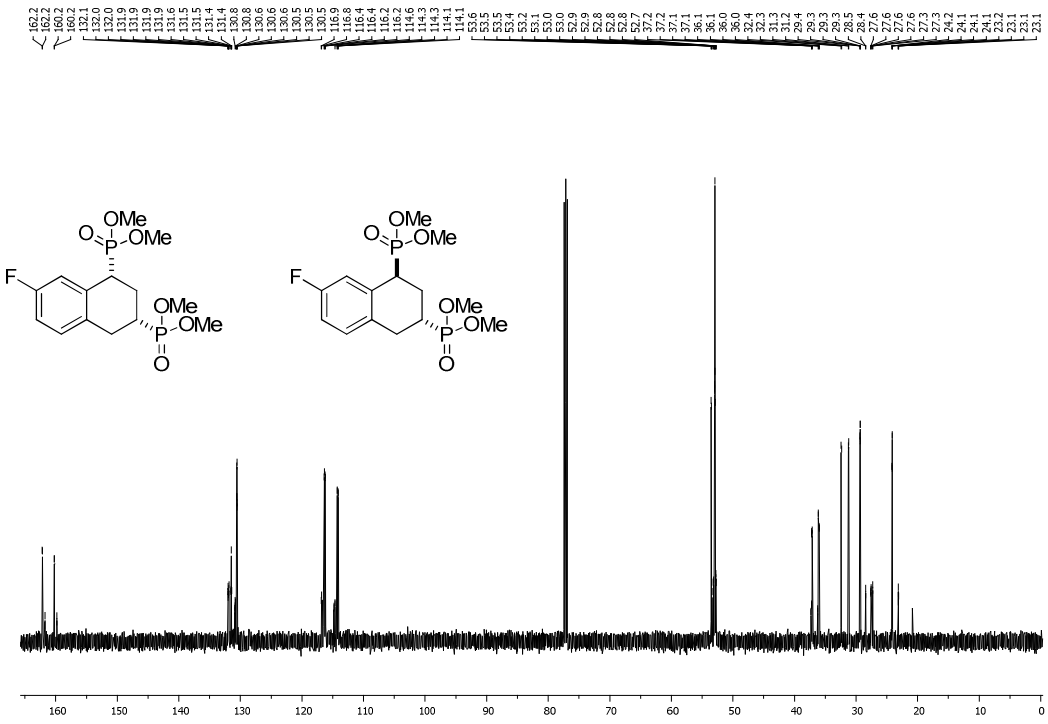
^{31}P NMR (122 MHz, $CDCl_3$) of Compound **1c**.



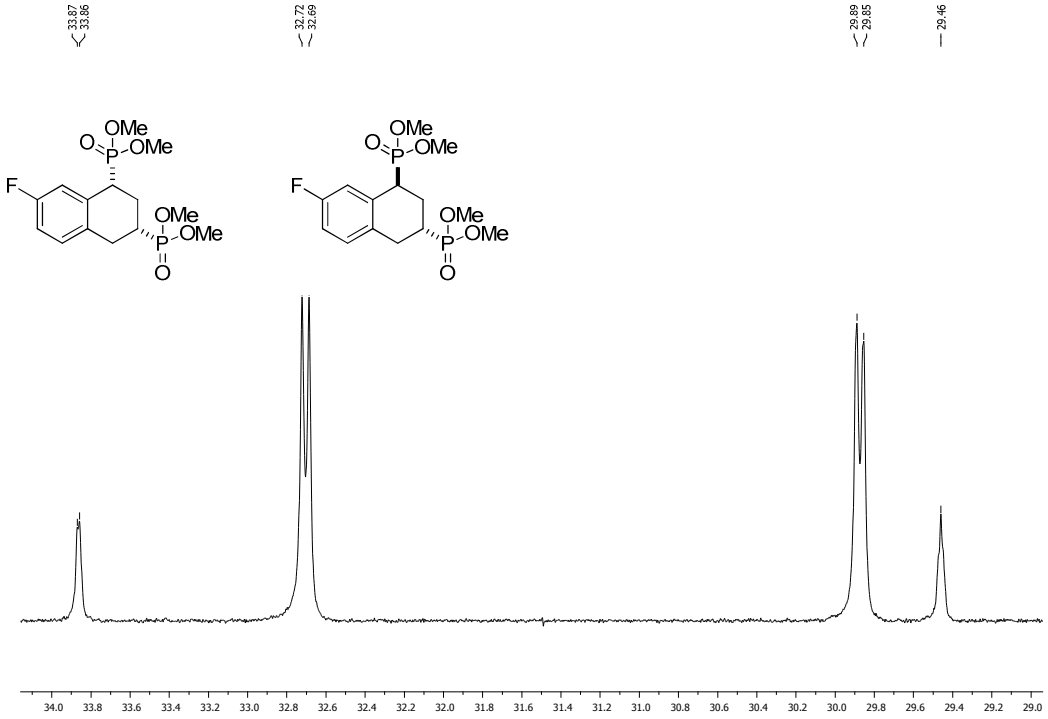
^{1}H NMR (500 MHz, $CDCl_3$) of Compound **1d**.



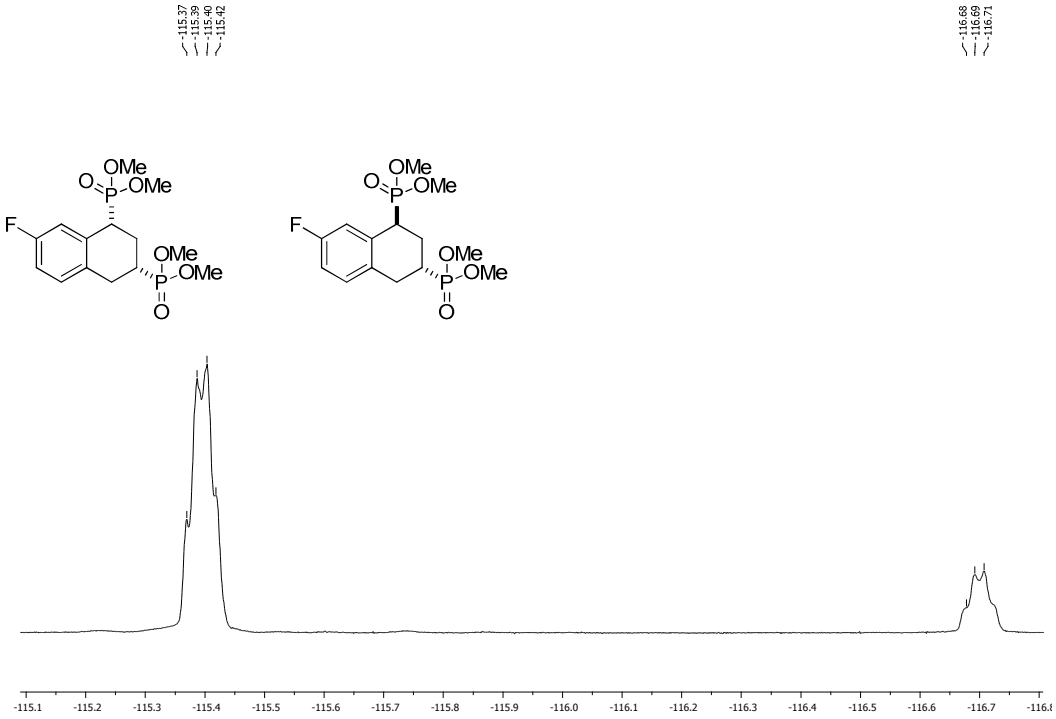
^{13}C NMR (126 MHz, $CDCl_3$) of Compound **1d**.



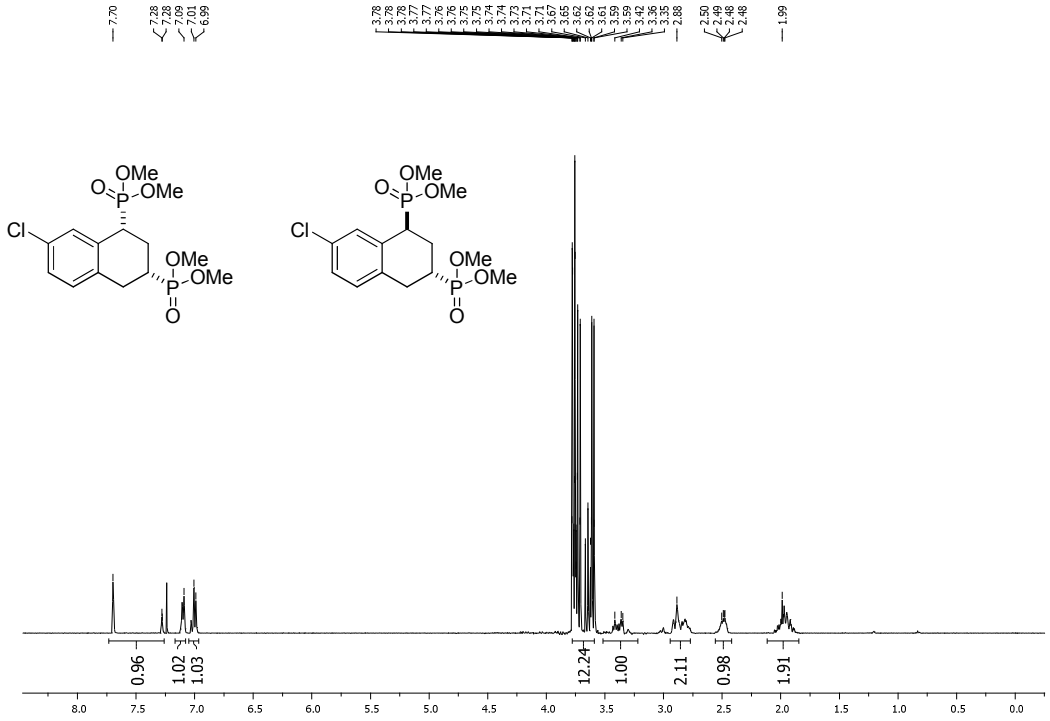
^{31}P NMR (202 MHz, $CDCl_3$) of Compound **1d**.



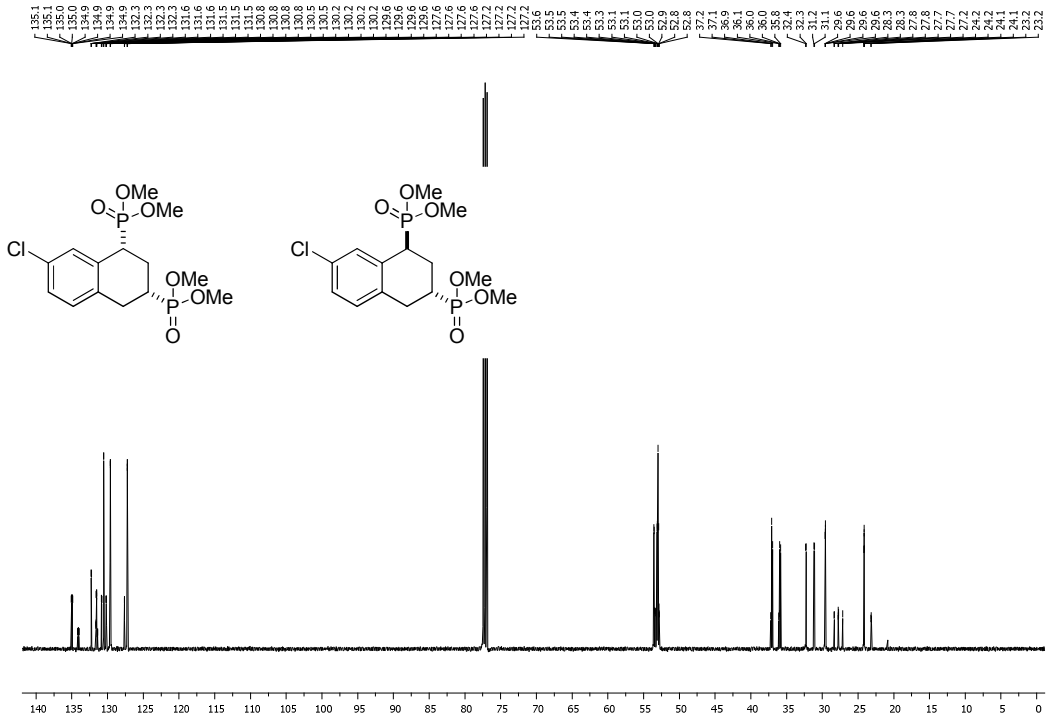
^{19}F NMR (470 MHz, $CDCl_3$) of Compound **1d**.



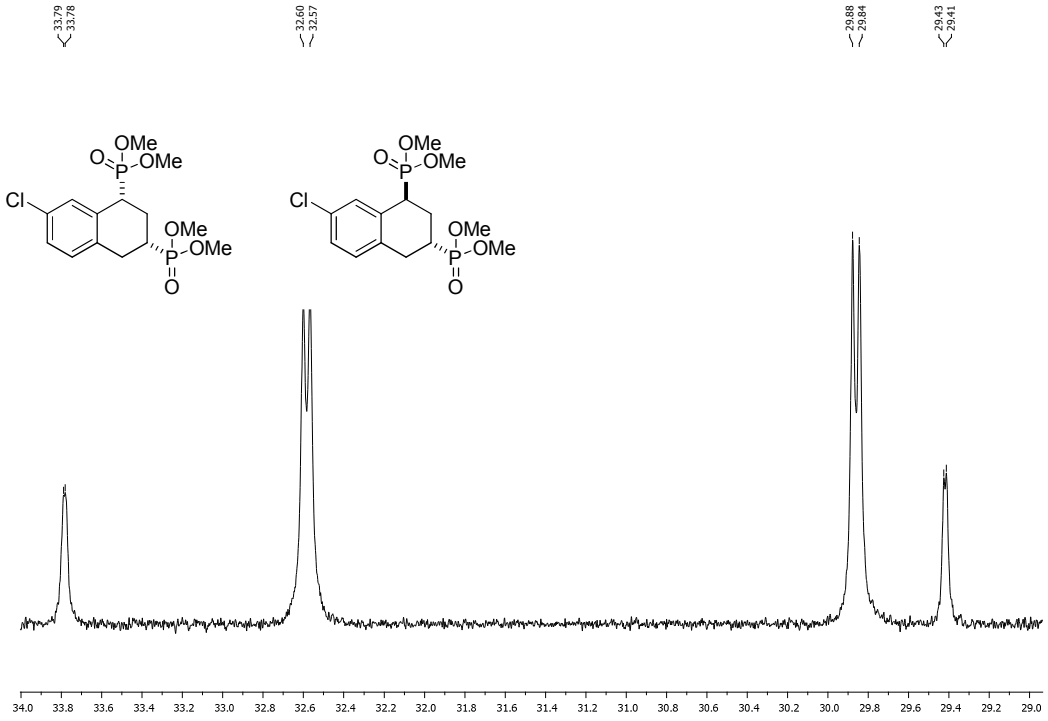
^{1}H NMR (500 MHz, $CDCl_3$) of Compound **1e**.



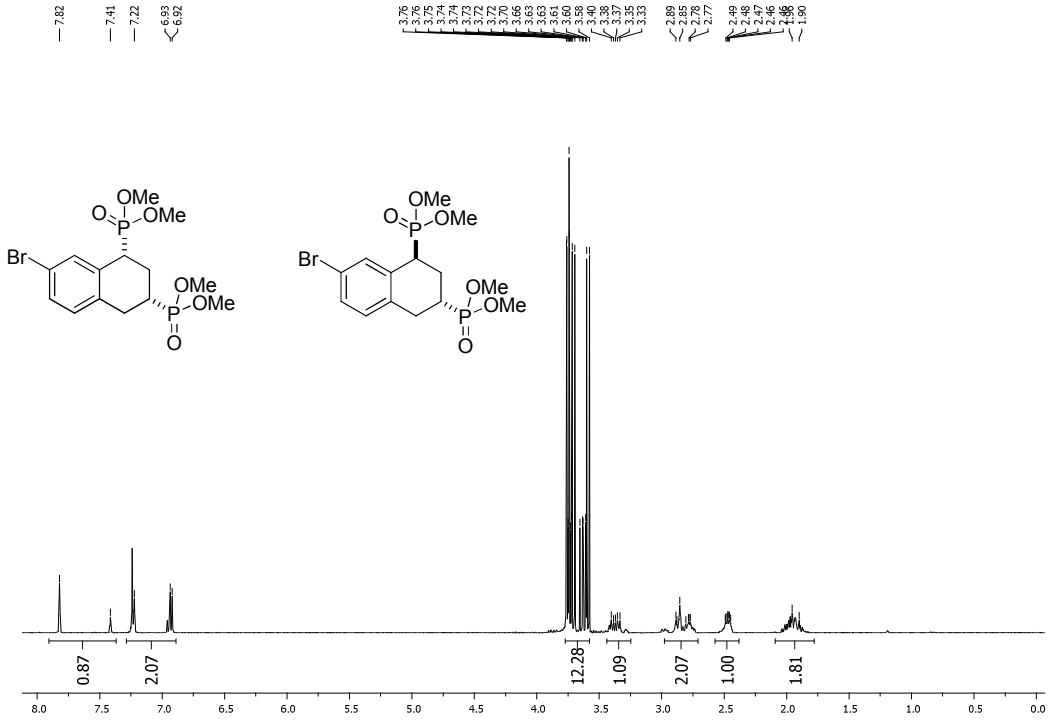
^{13}C NMR (126 MHz, $CDCl_3$) of Compound **1e**.



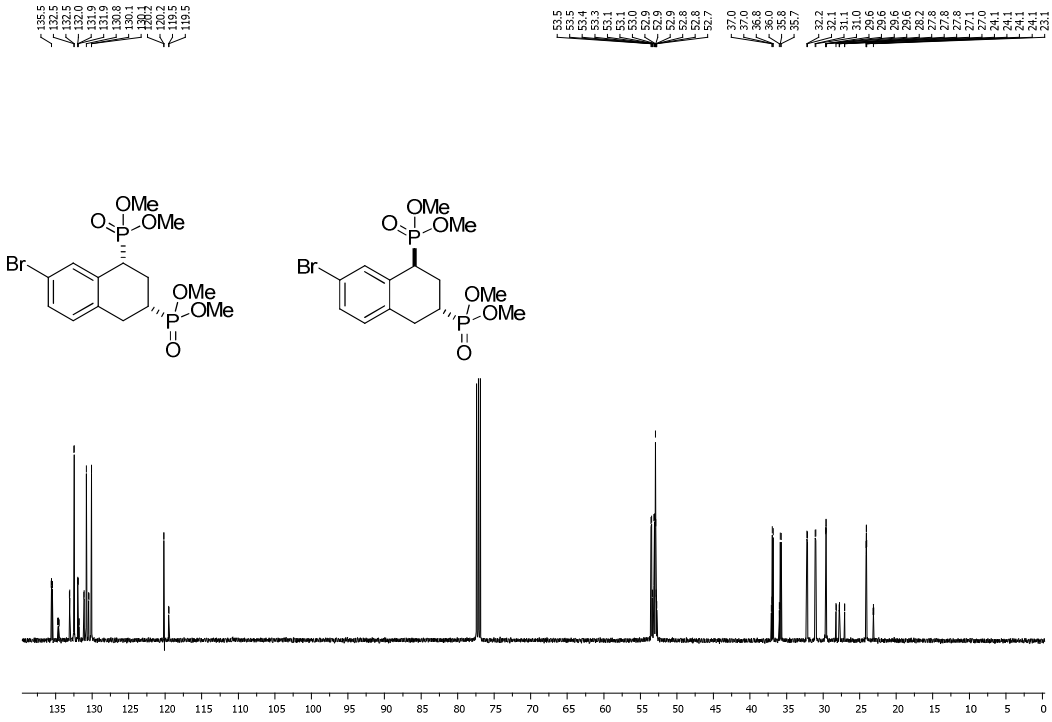
^{31}P NMR (202 MHz, $CDCl_3$) of Compound **1e**.



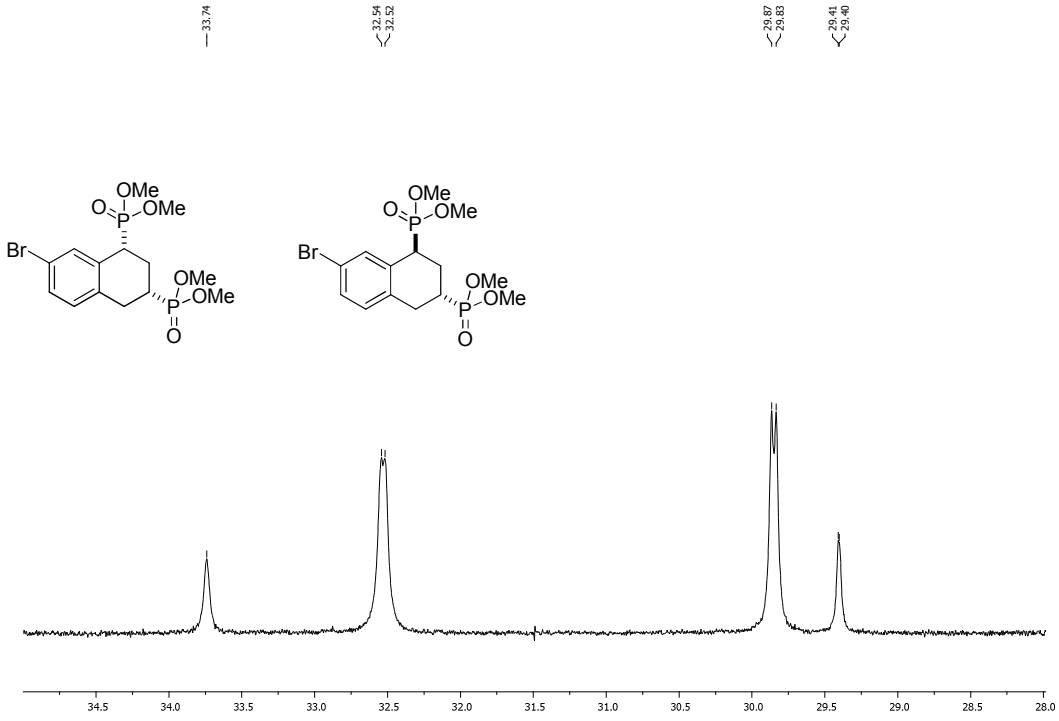
^{1}H NMR (500 MHz, $CDCl_3$) of Compound **1f**.



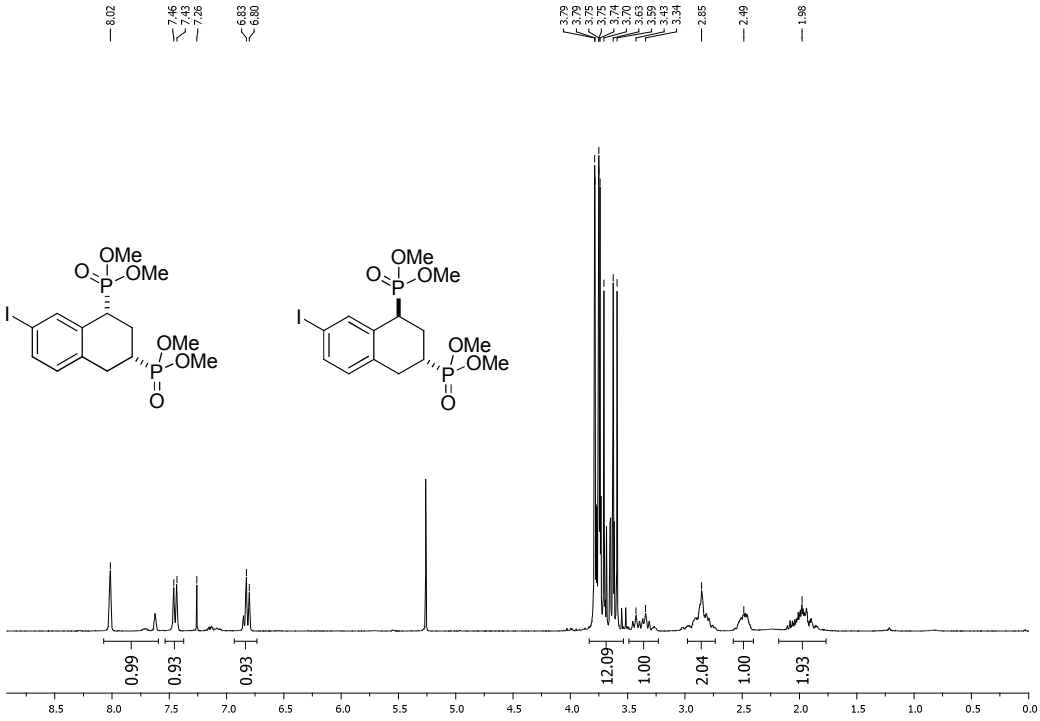
^{13}C NMR (126 MHz, $CDCl_3$) of Compound **1f**.



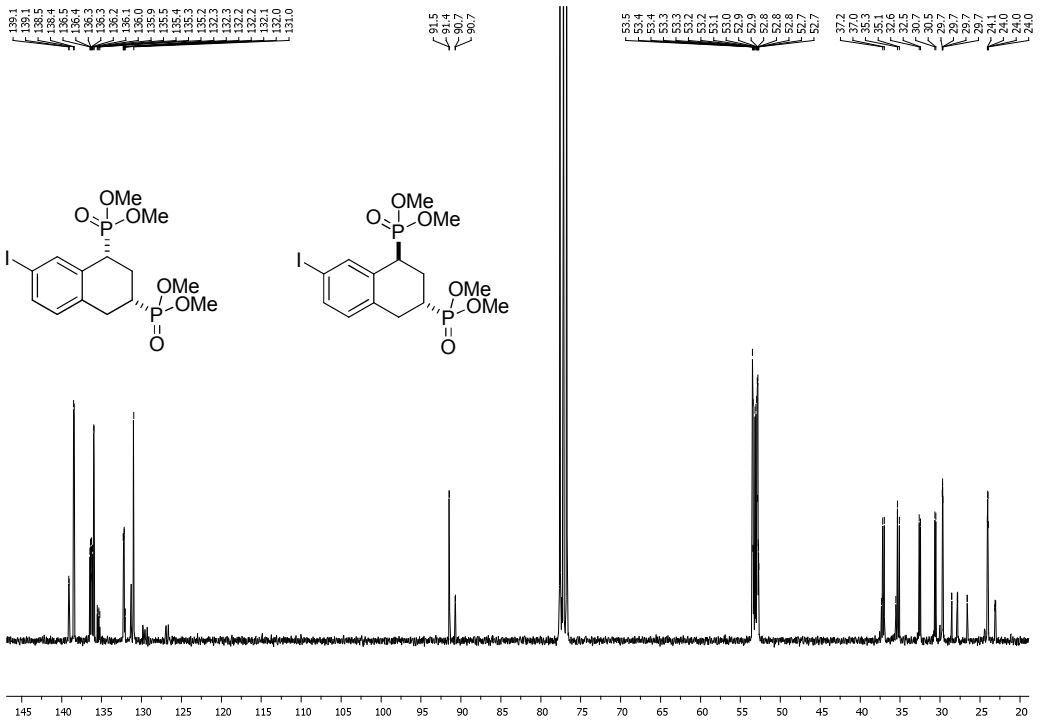
^{31}P NMR (202 MHz, $CDCl_3$) of Compound **1f**.



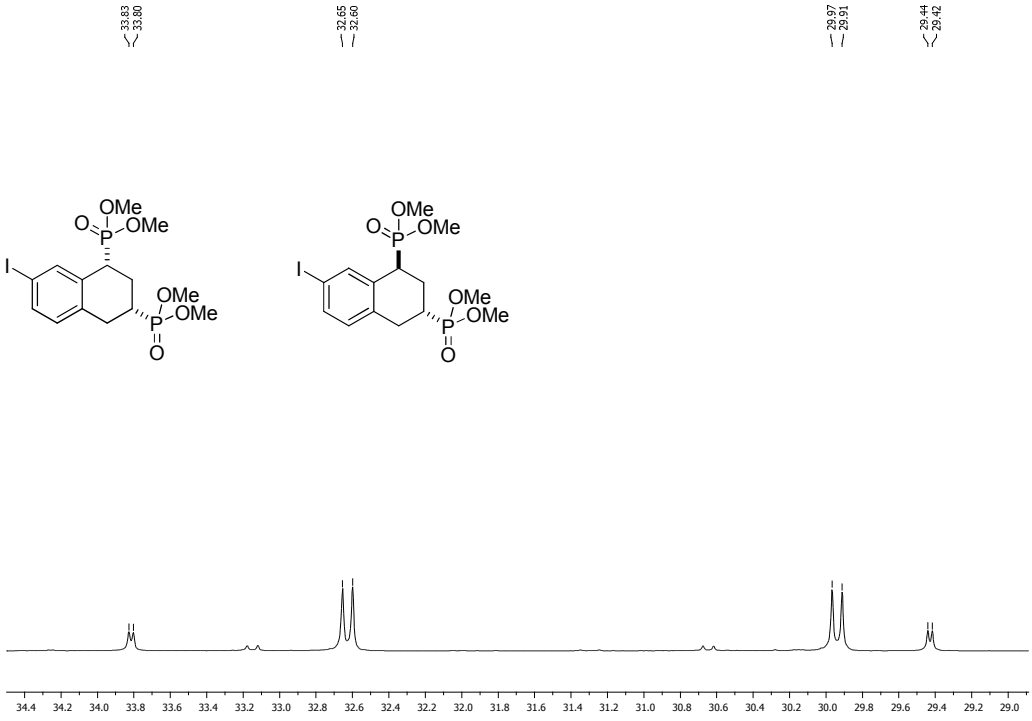
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1g**.



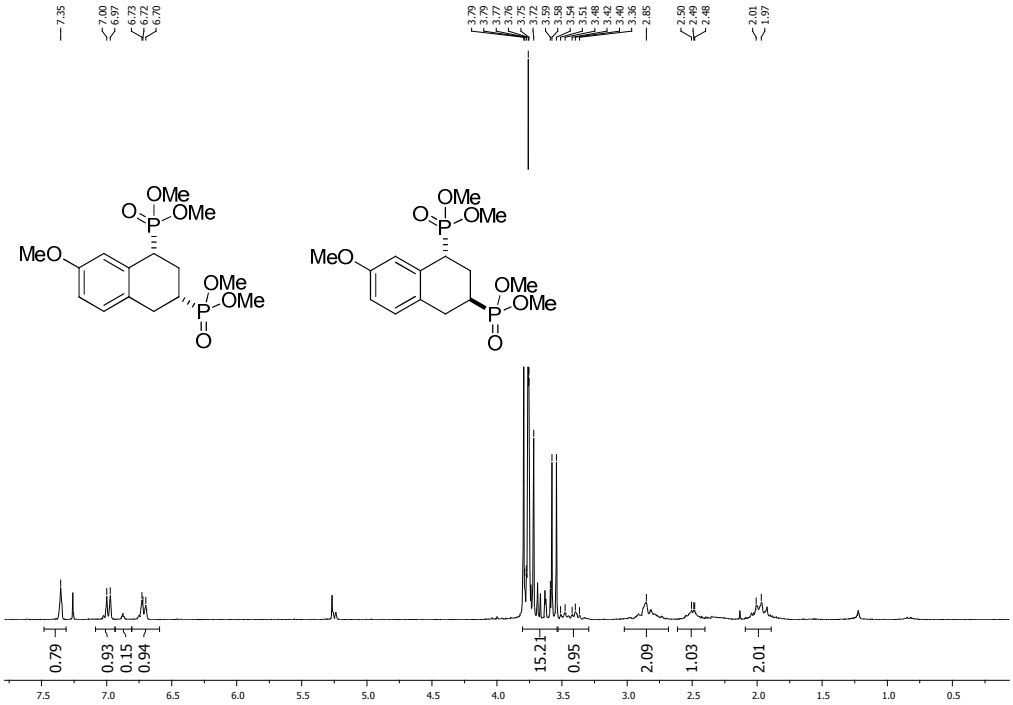
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1g**.



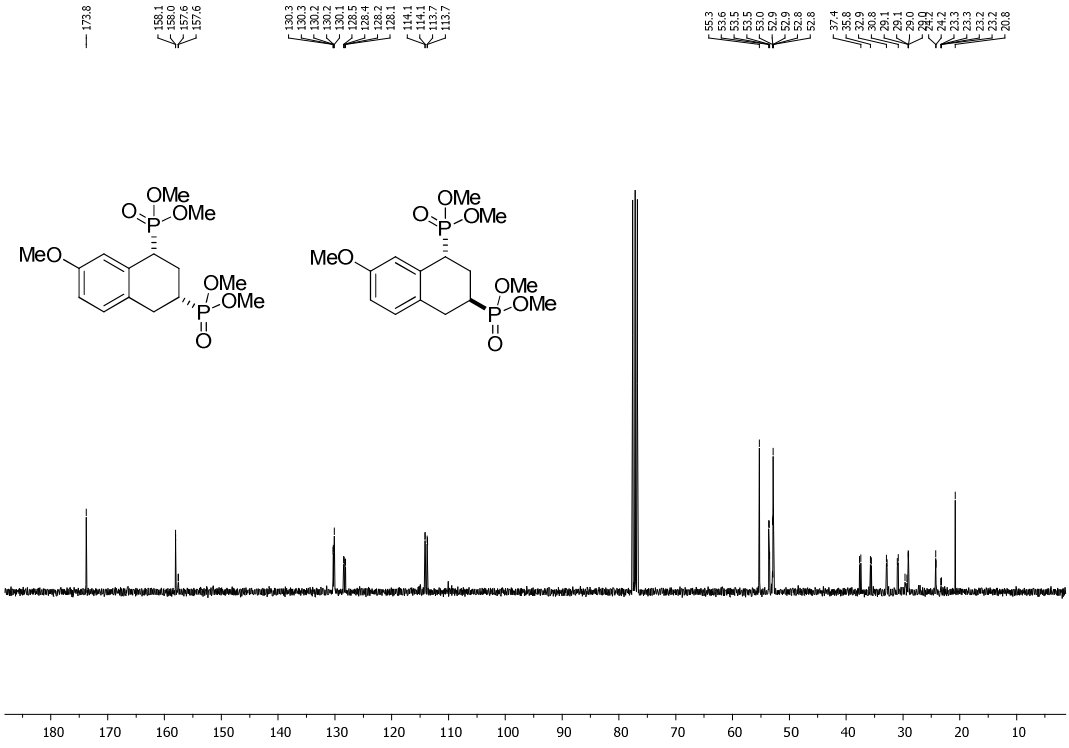
^{31}P NMR (122 MHz, $CDCl_3$) of Compound **1g**.



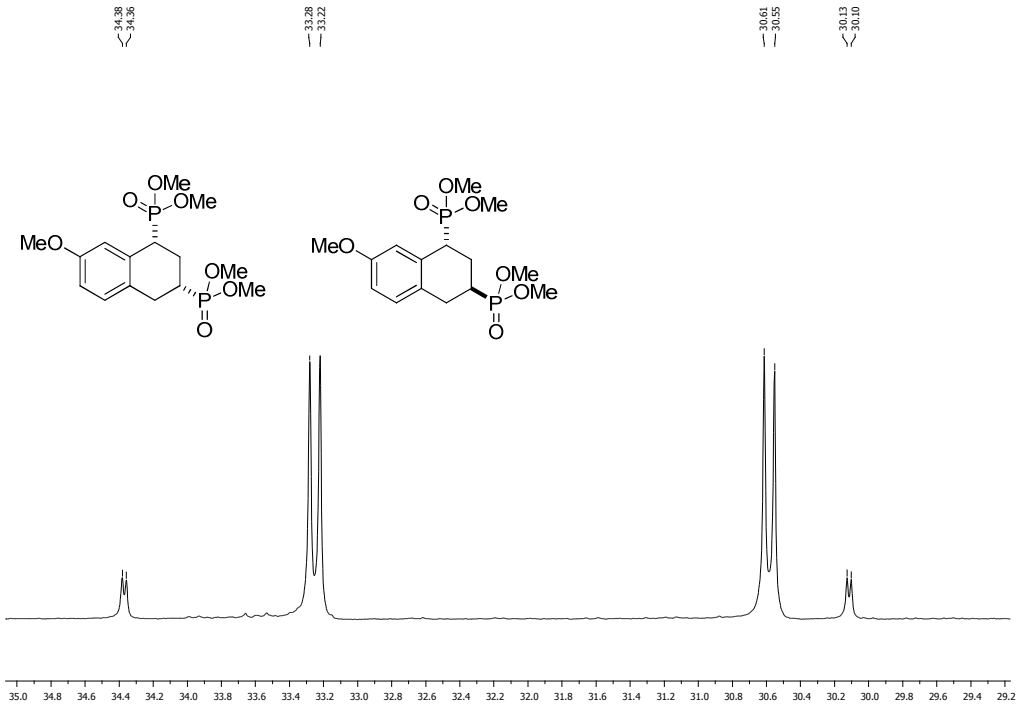
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1h**.



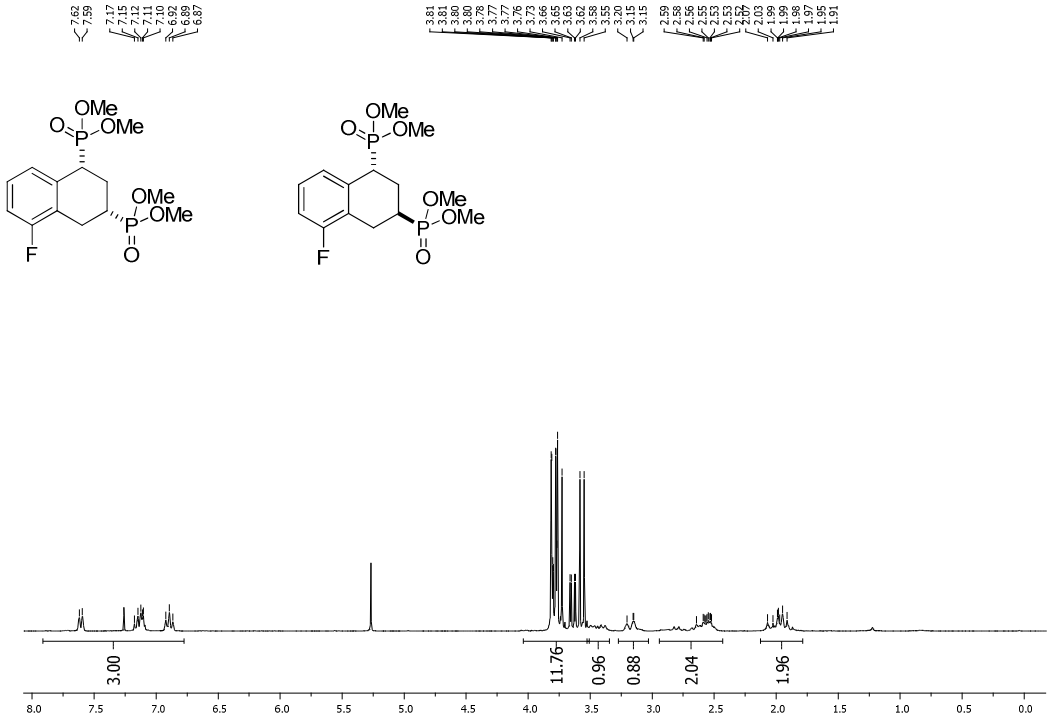
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1h**.



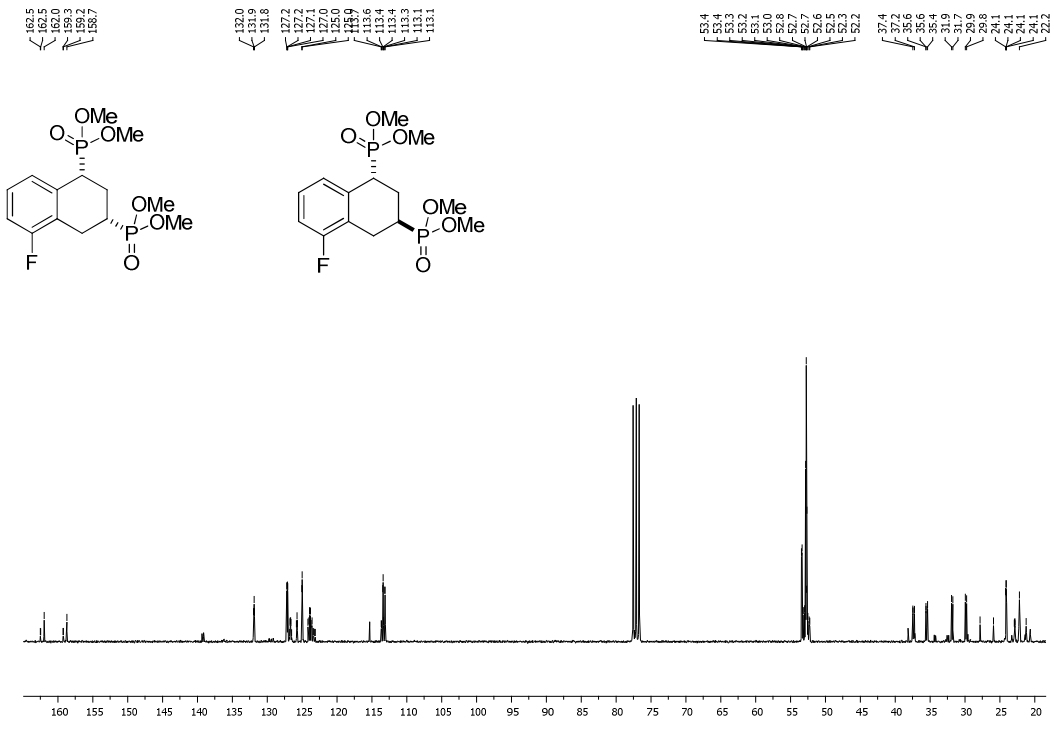
^{31}P NMR (122 MHz, $CDCl_3$) of compound **1h**.



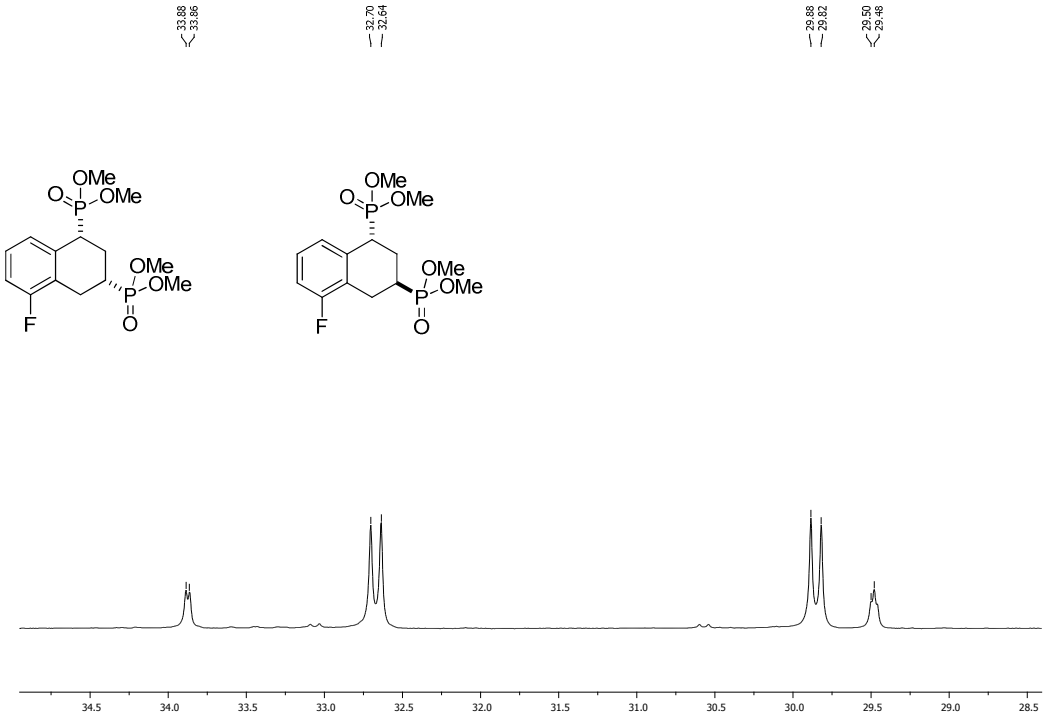
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1i**.



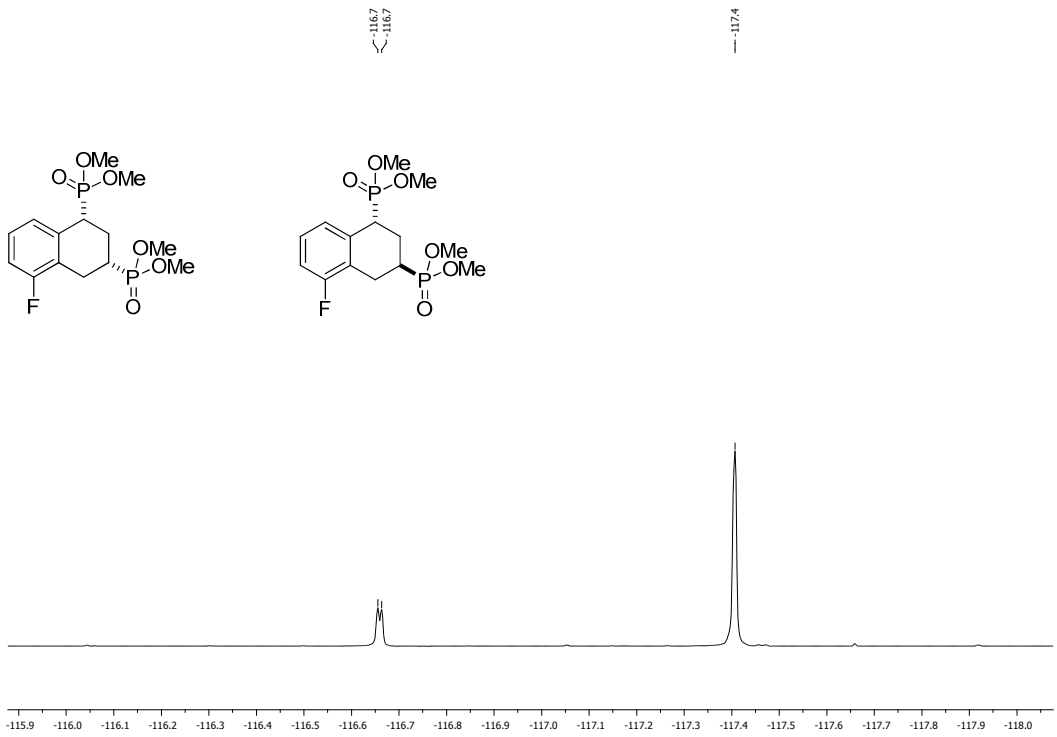
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1i**.



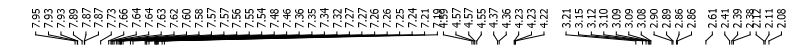
^{31}P NMR (122 MHz, $CDCl_3$) of Compound **1i**.

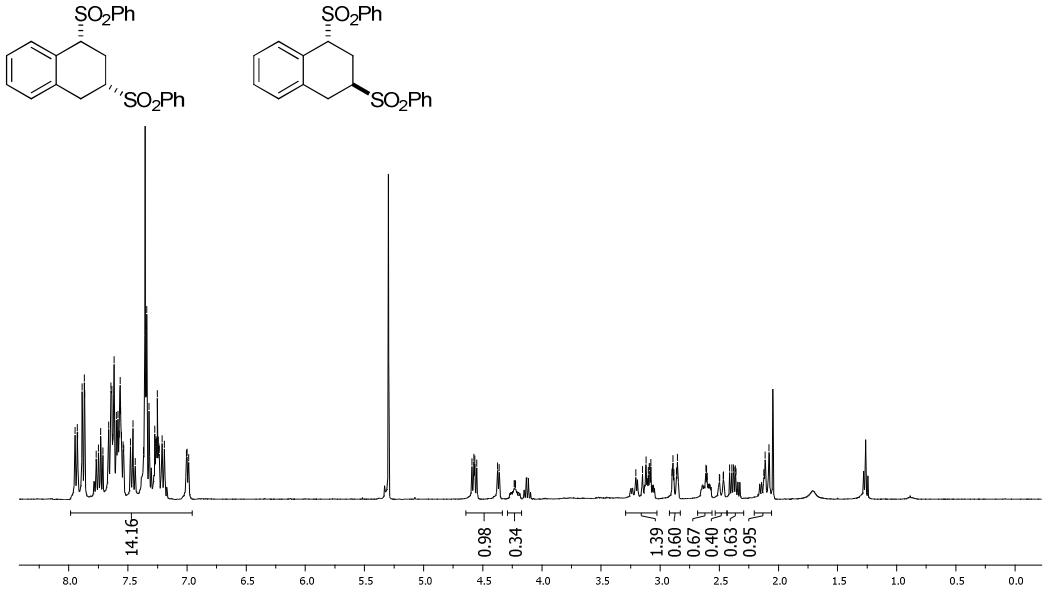


^{19}F NMR (282 MHz, $CDCl_3$) of Compound **1i**.

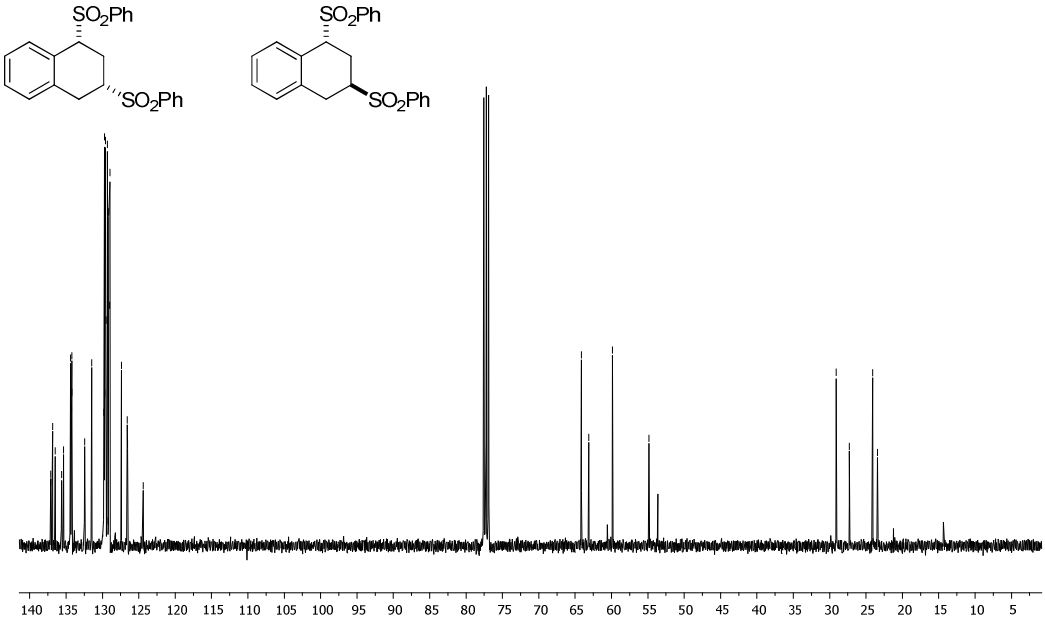


^{1}H NMR (400 MHz, $CDCl_3$) of Compound **1j**.

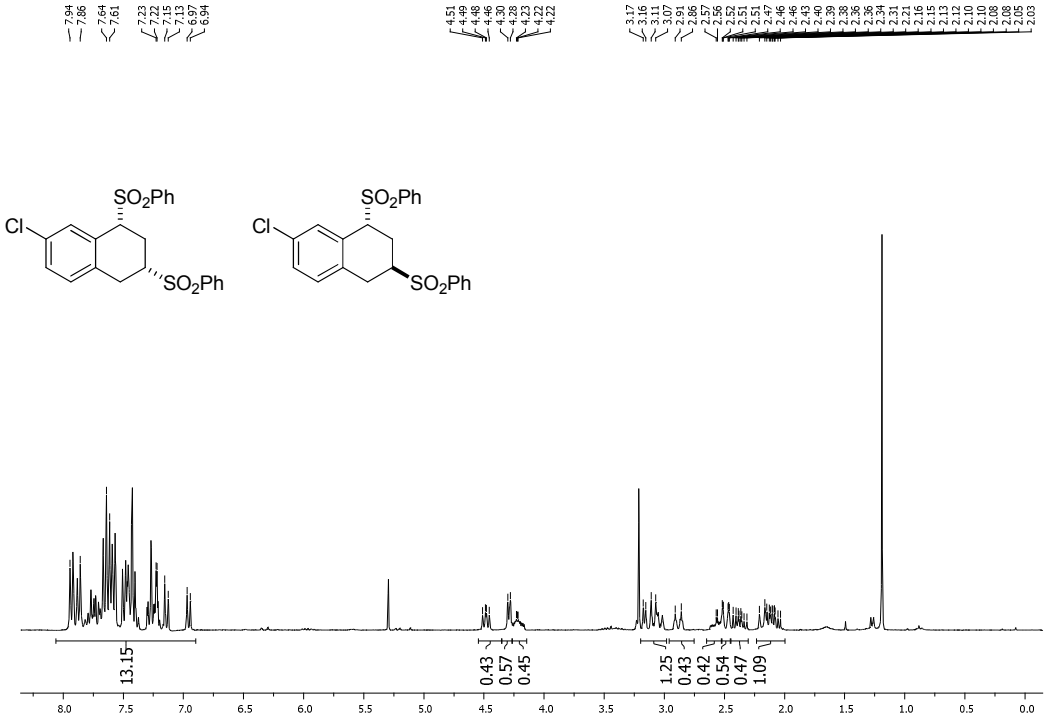




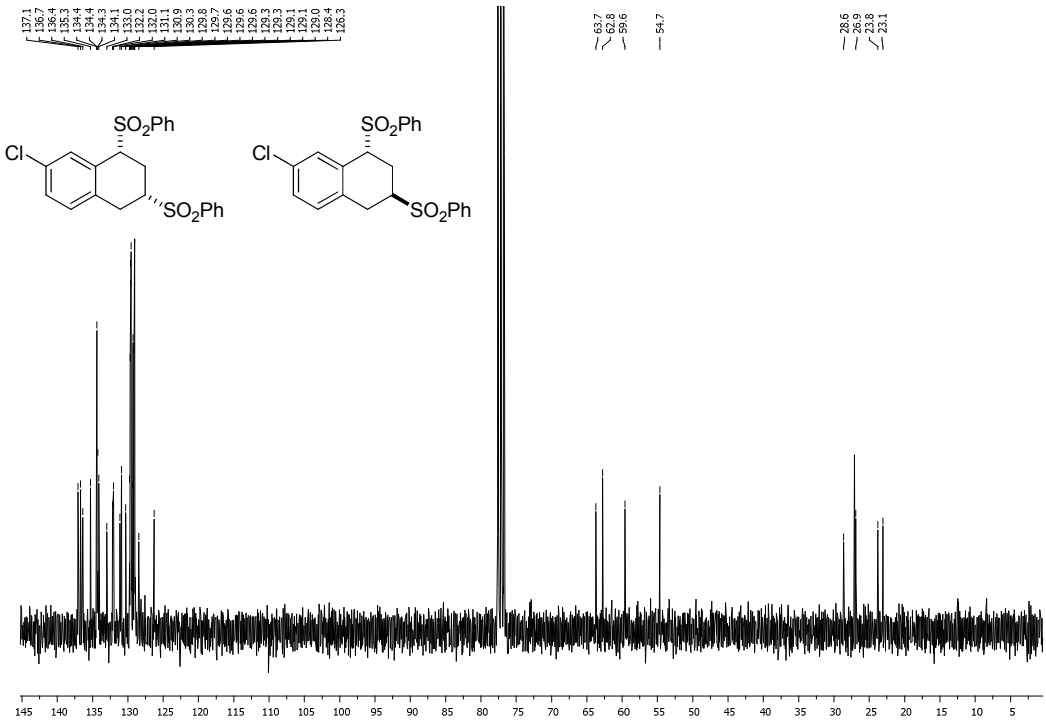
^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1j**.



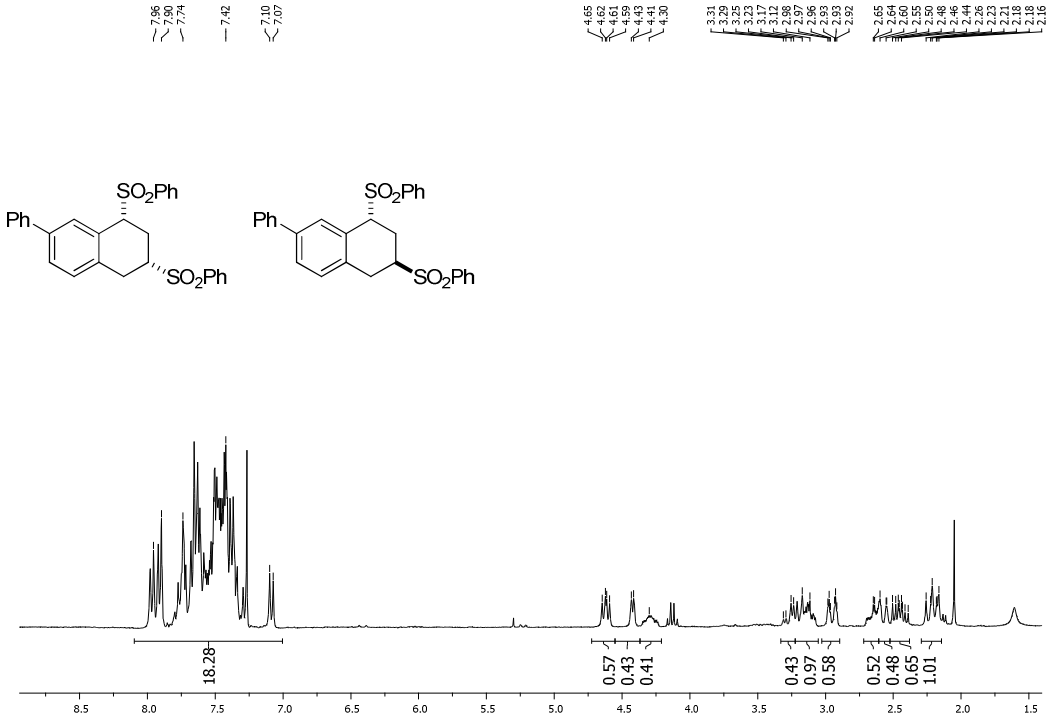
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1k**.



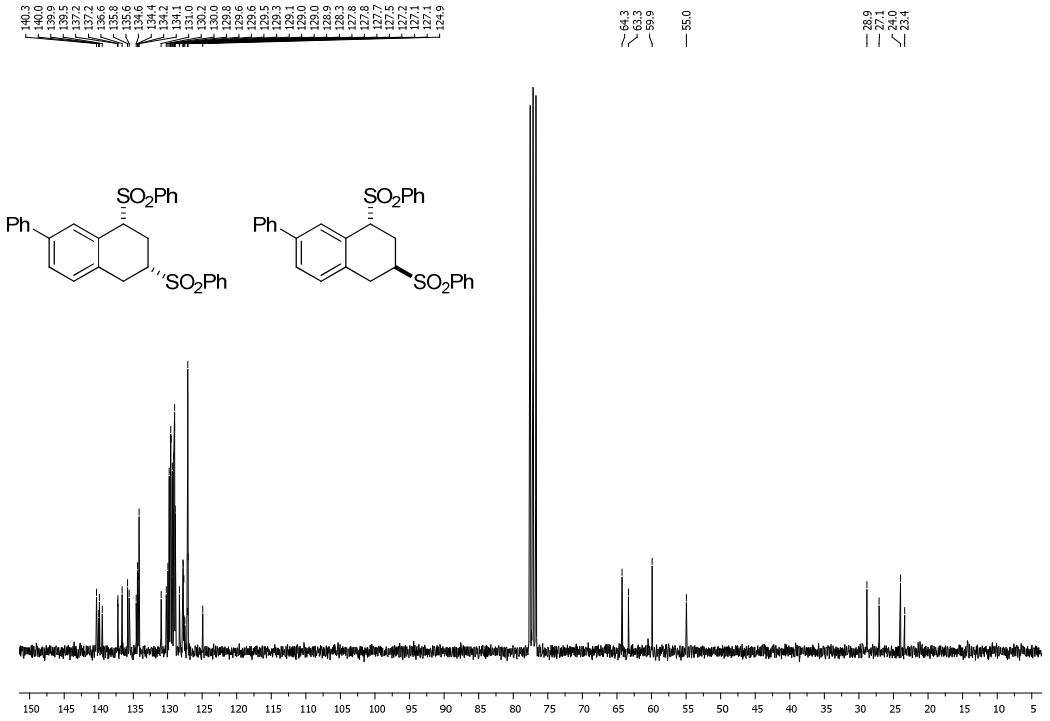
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1k**.



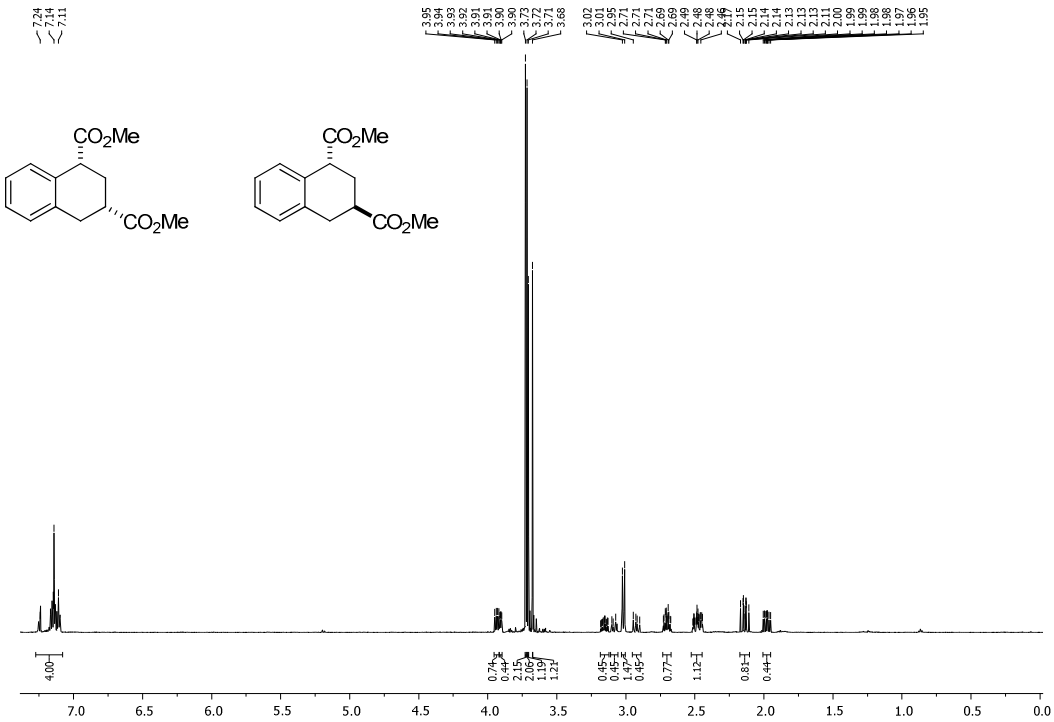
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1l**.



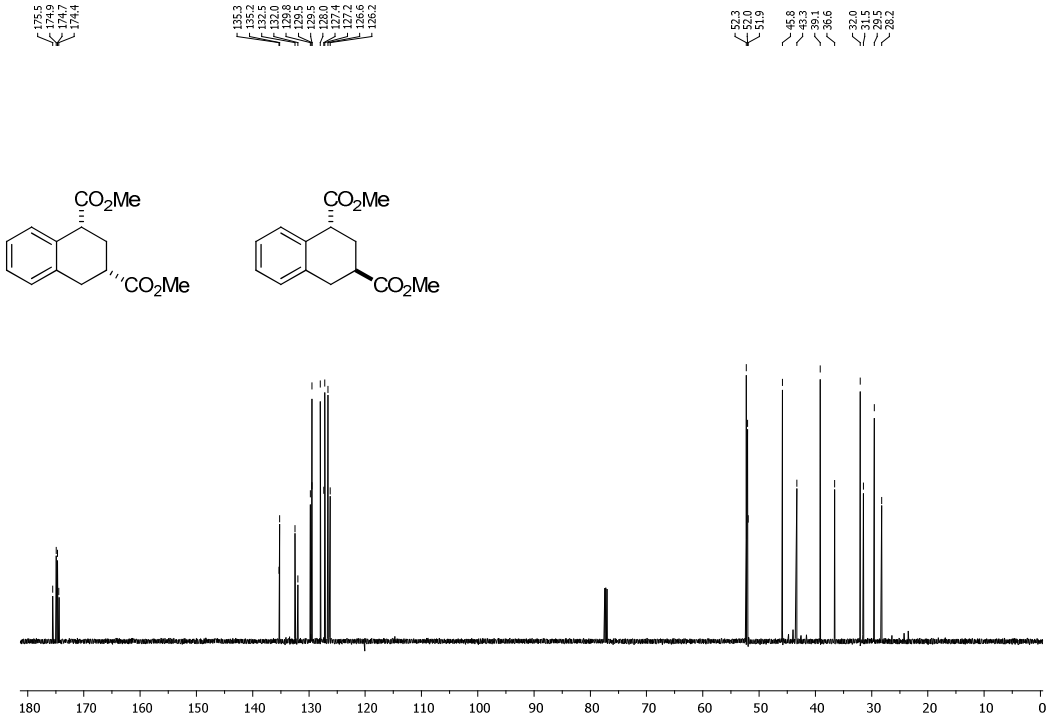
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1l**.



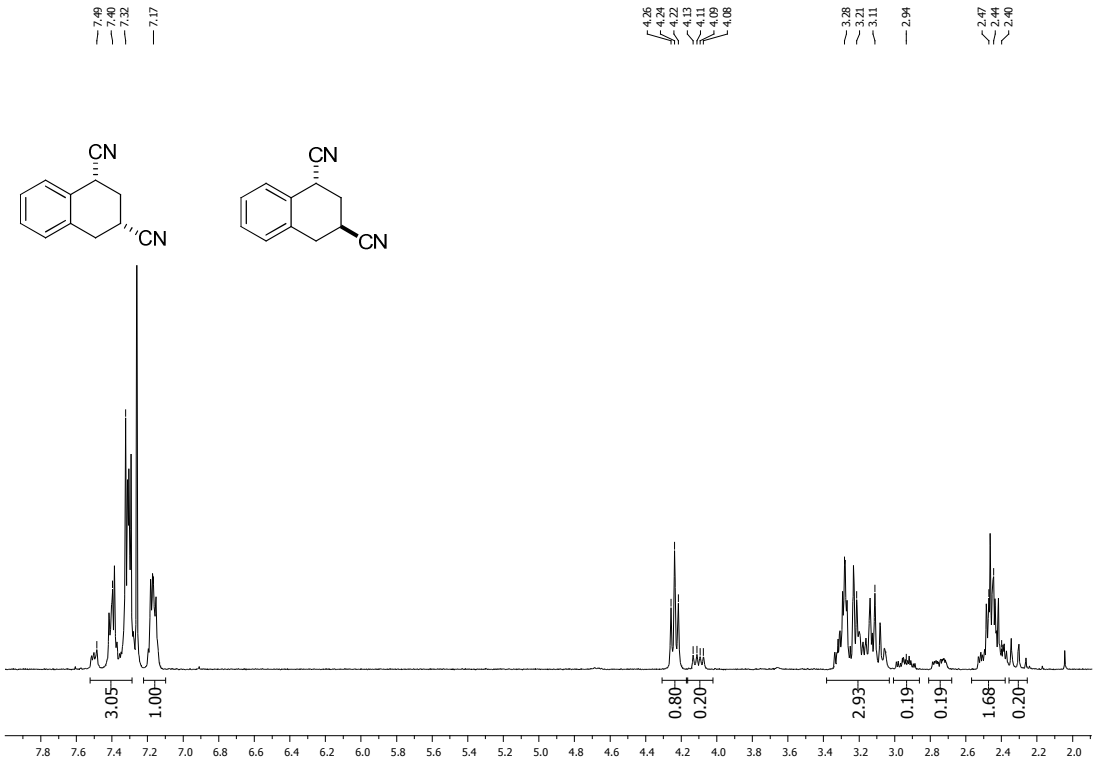
^{1}H NMR (600 MHz, $CDCl_3$) of Compound **1m**.



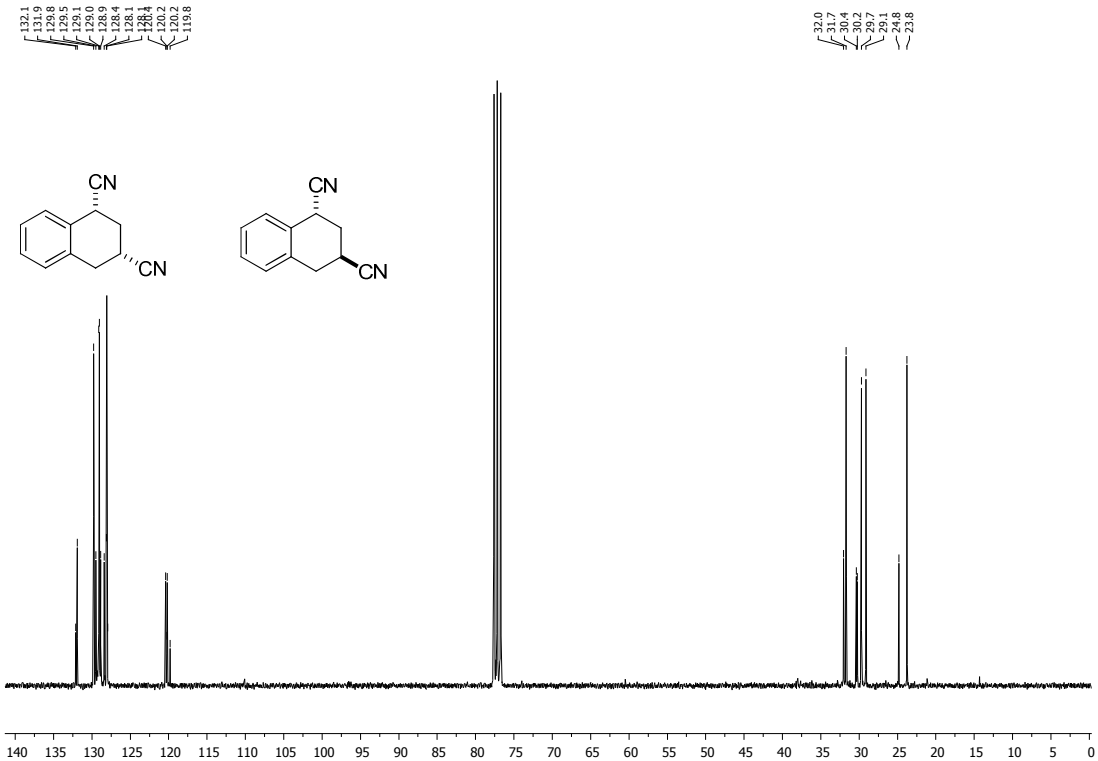
^{13}C NMR (150 MHz, $CDCl_3$) of Compound **1m**.



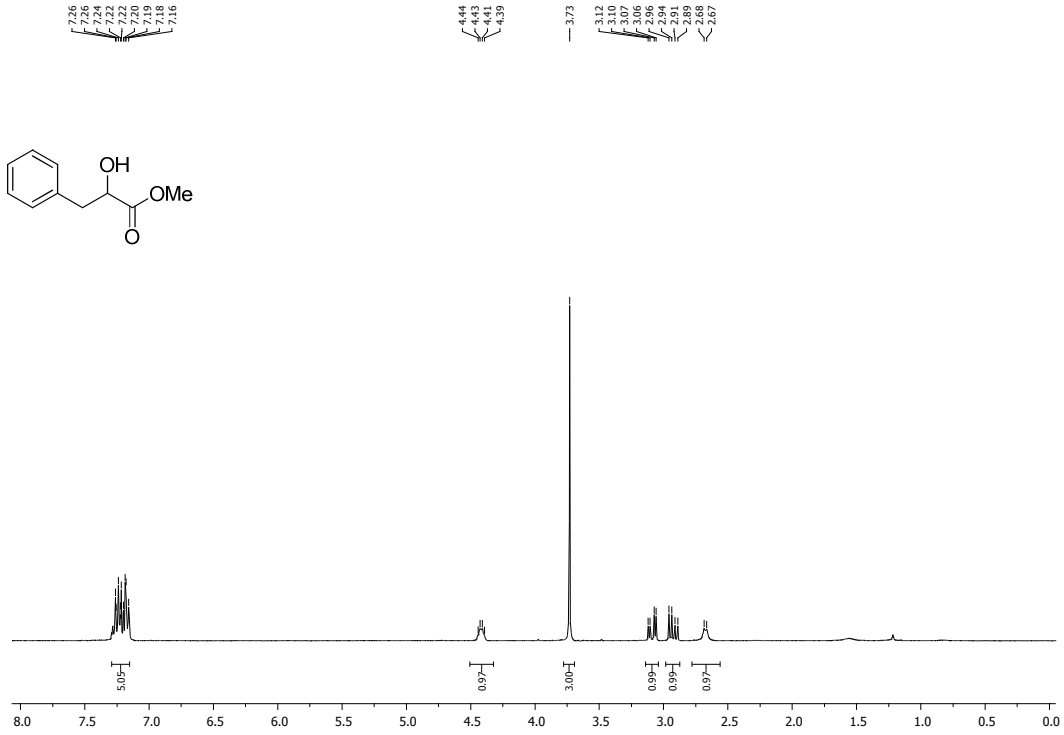
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **1n**.



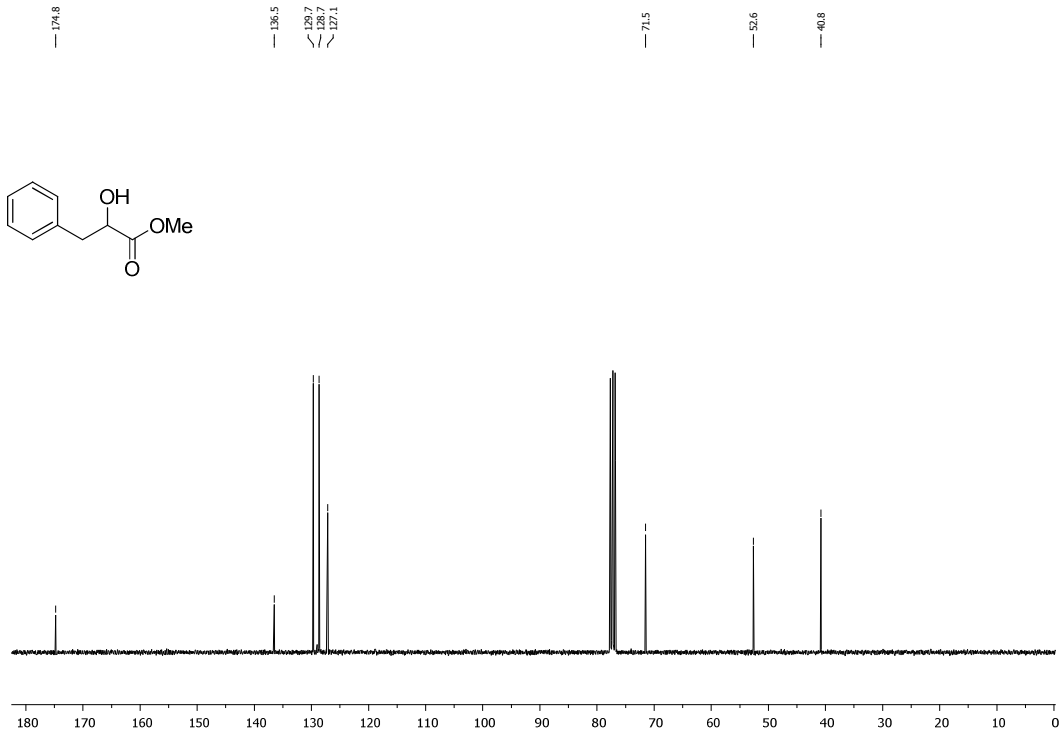
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **1n**.



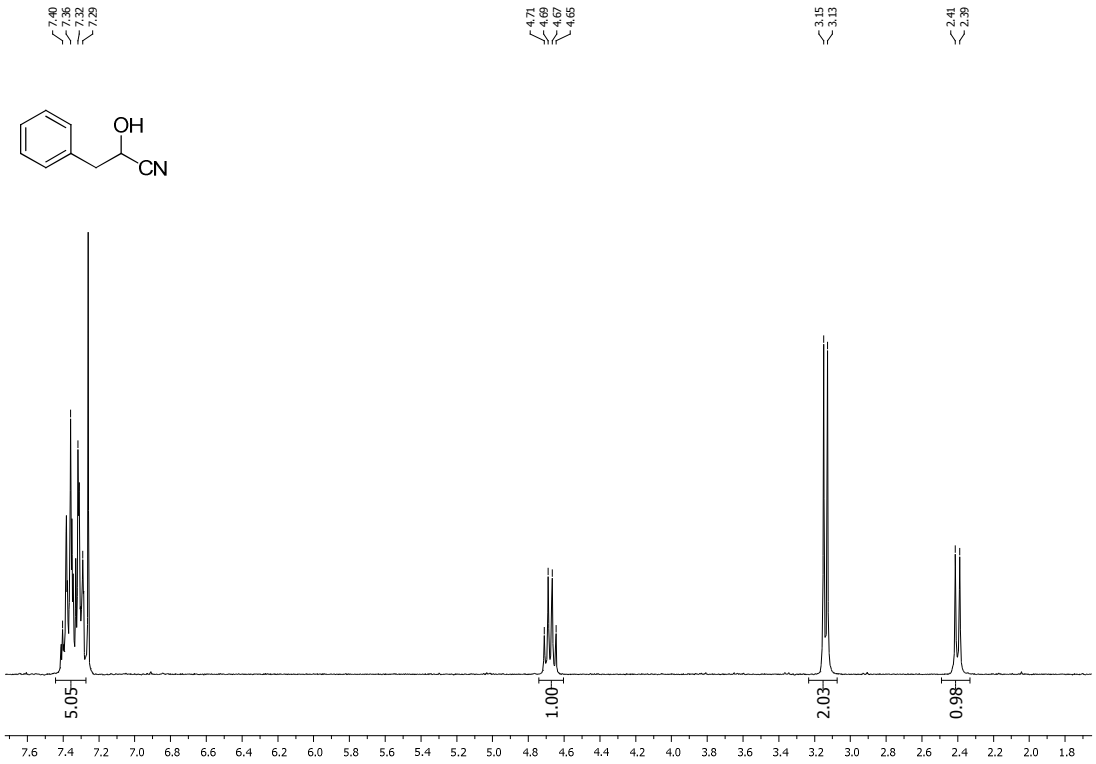
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2a**.



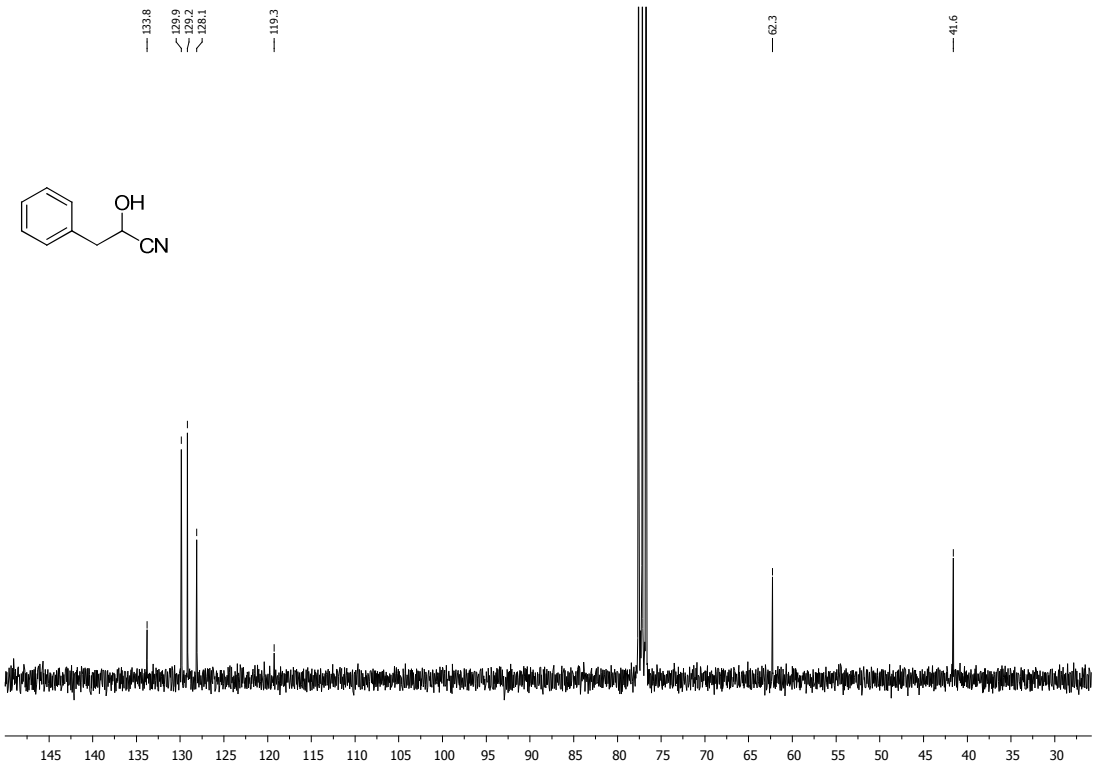
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2a**.



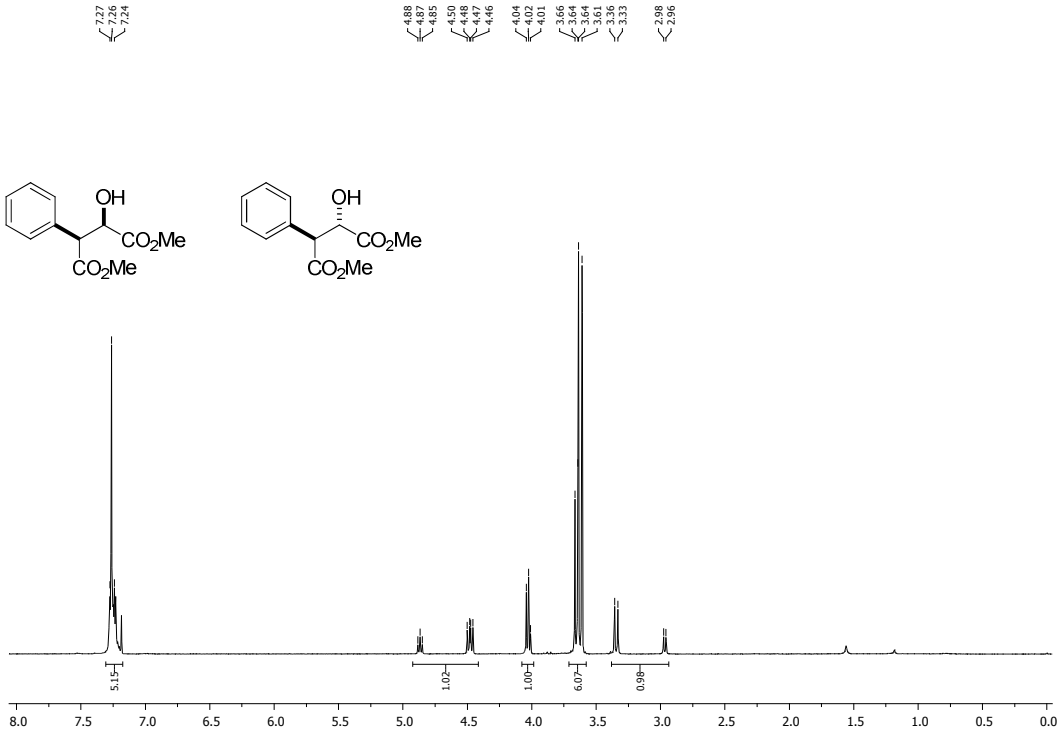
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2b**.



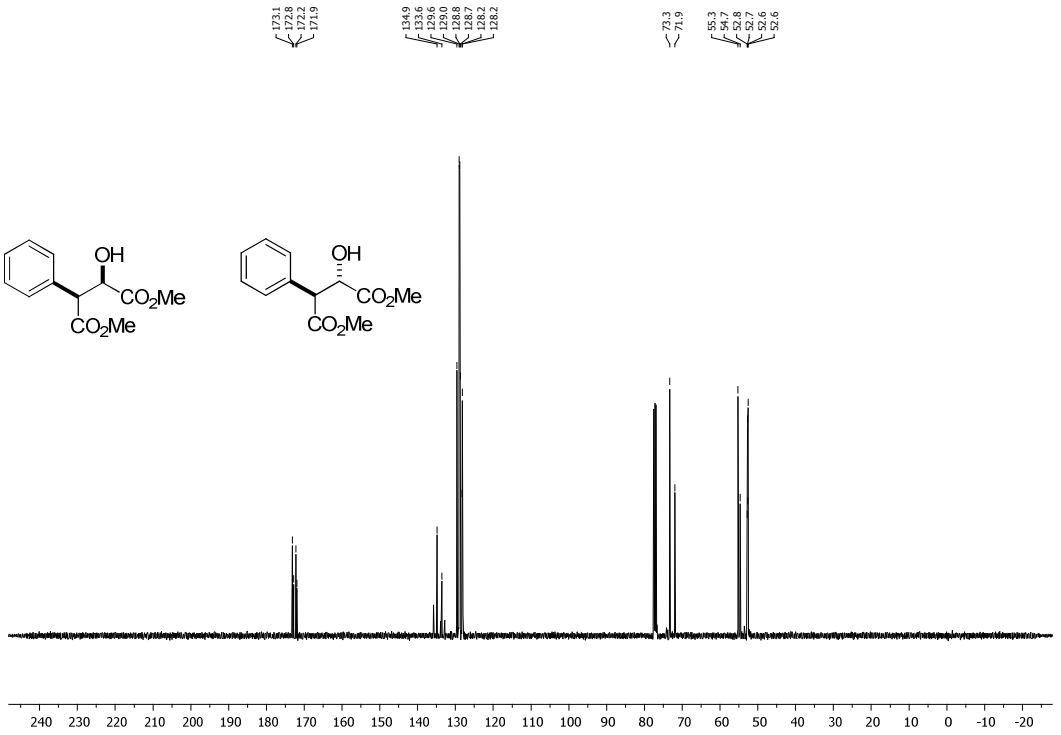
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2b**.



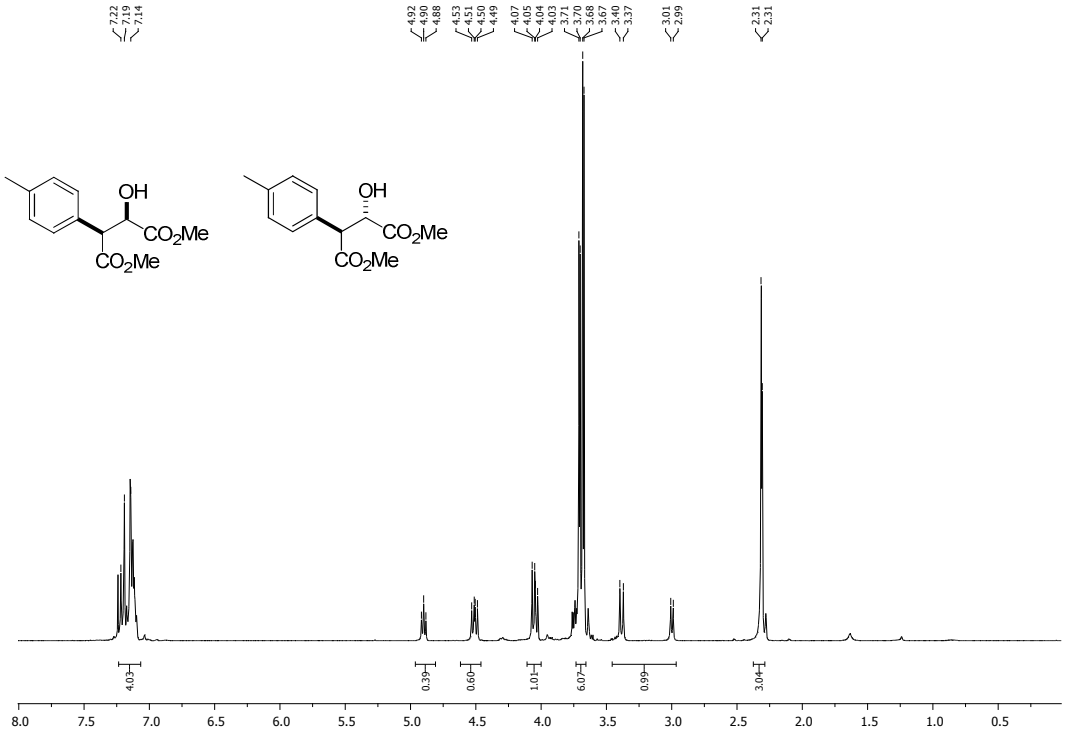
^{1}H NMR (400 MHz, $CDCl_3$) of Compound **2c**.



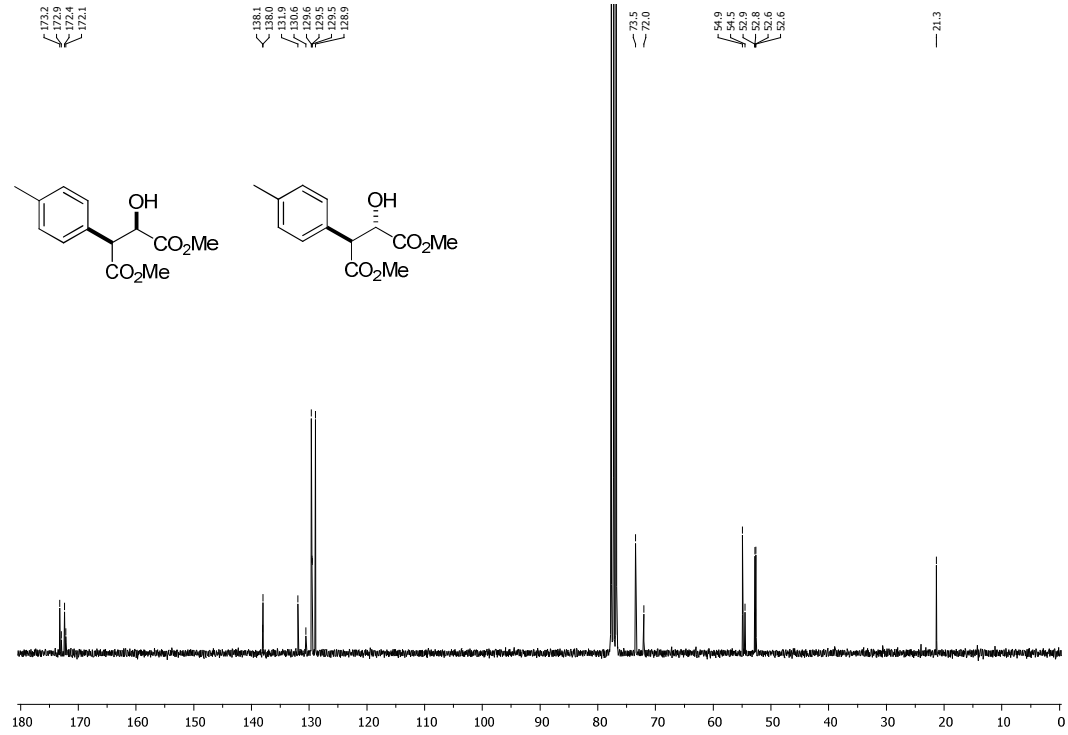
^{13}C NMR (125 MHz, $CDCl_3$) of Compound **1h**.



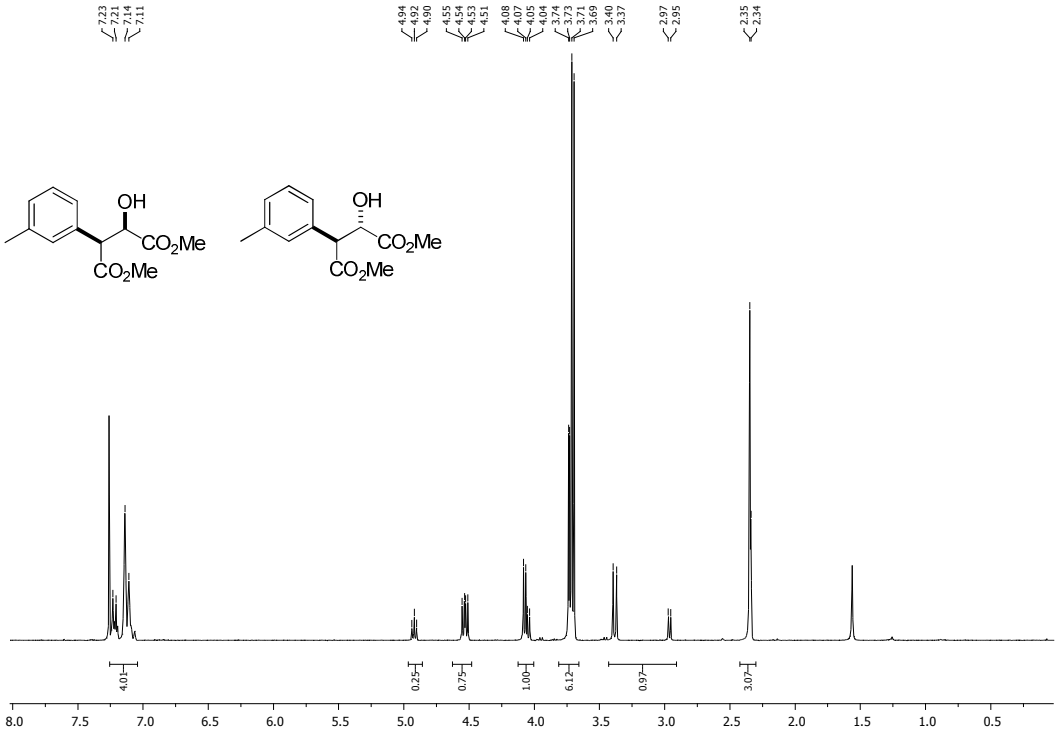
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2d**.



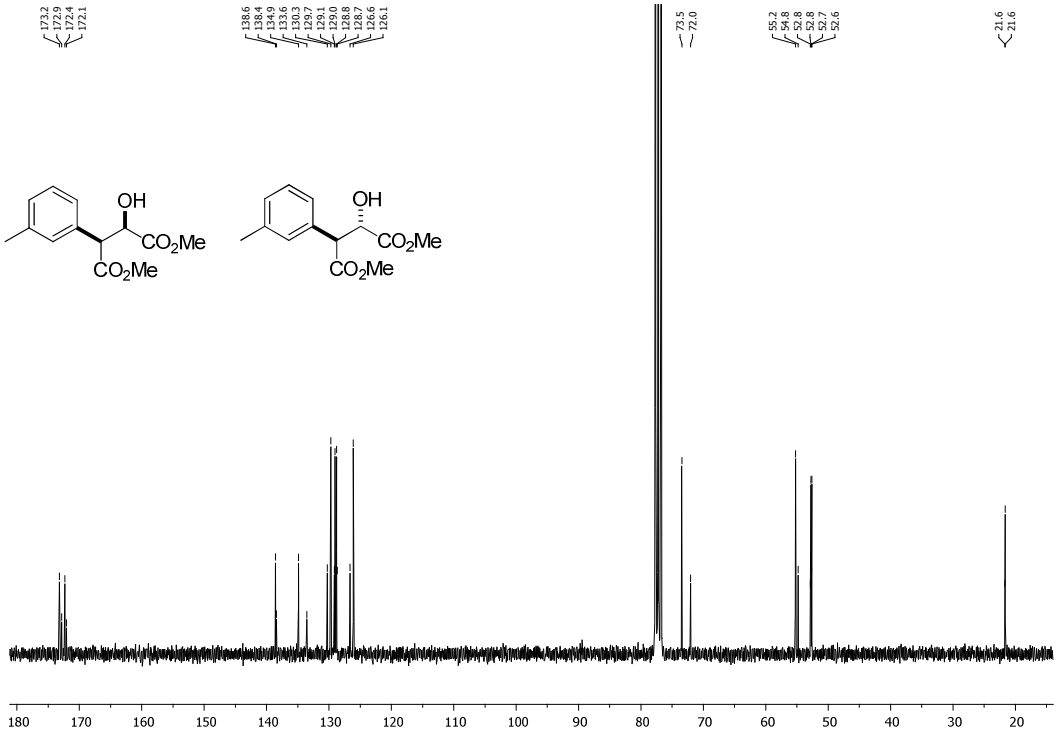
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2d**.



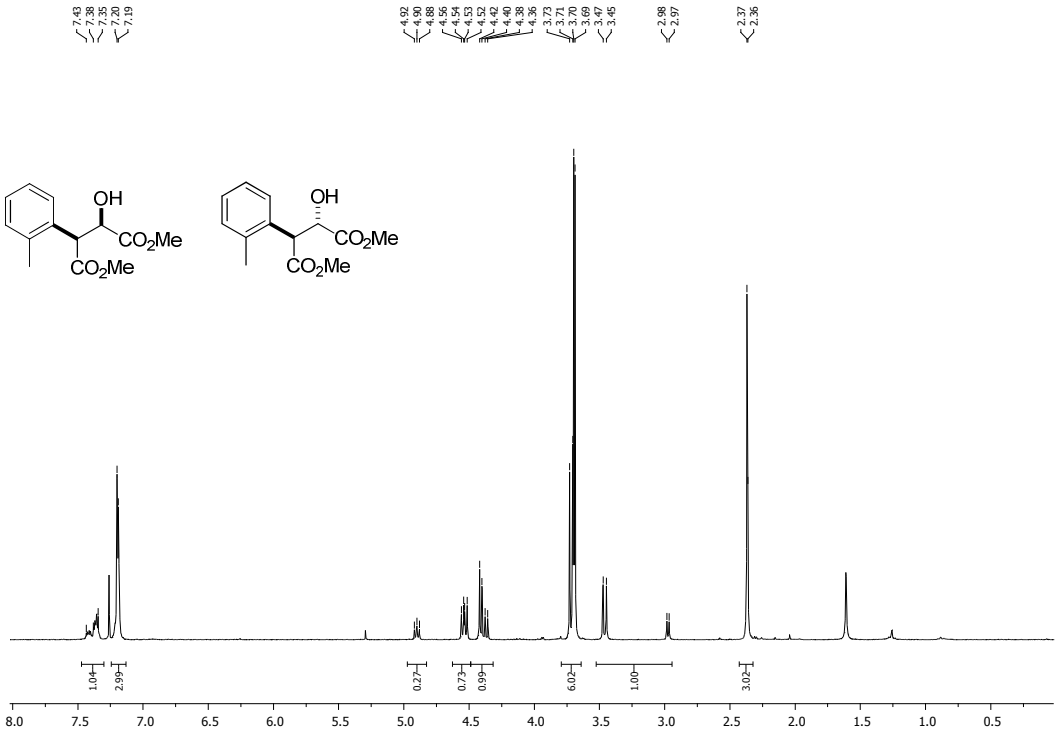
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2e**.



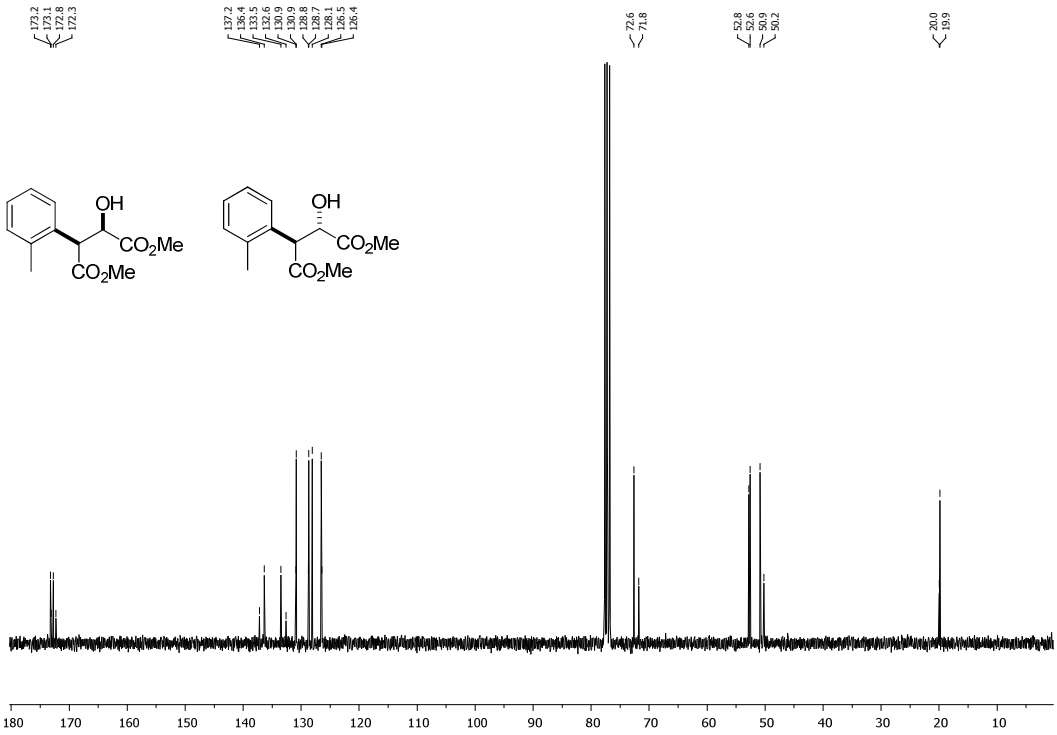
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2e**.



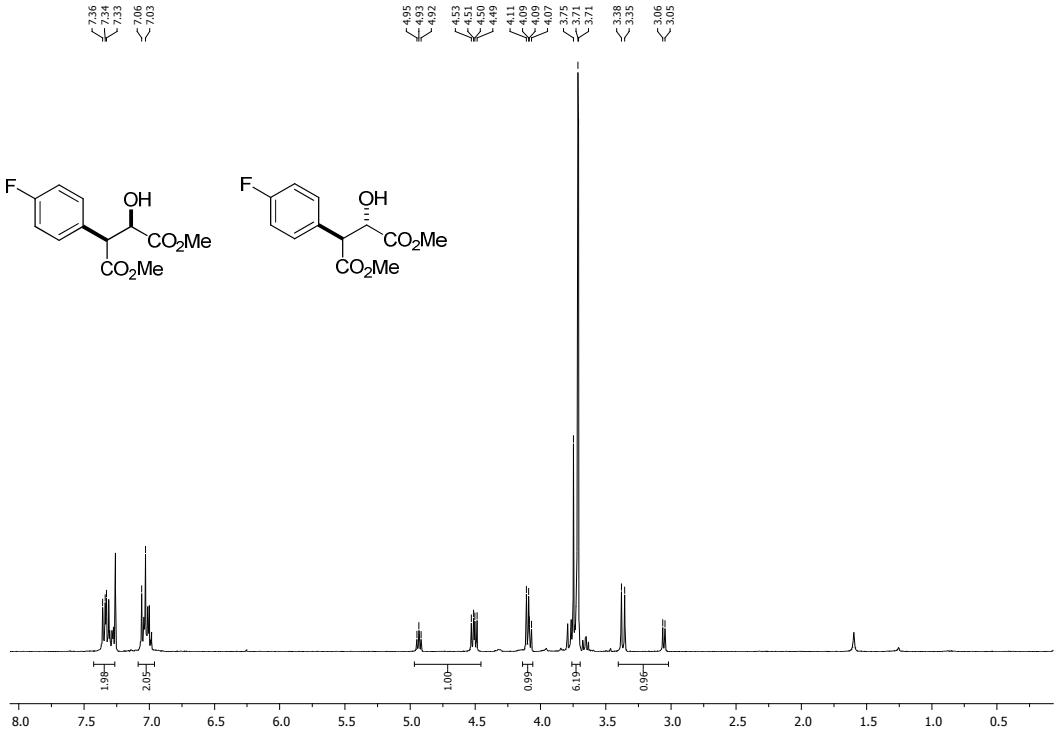
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2f**.



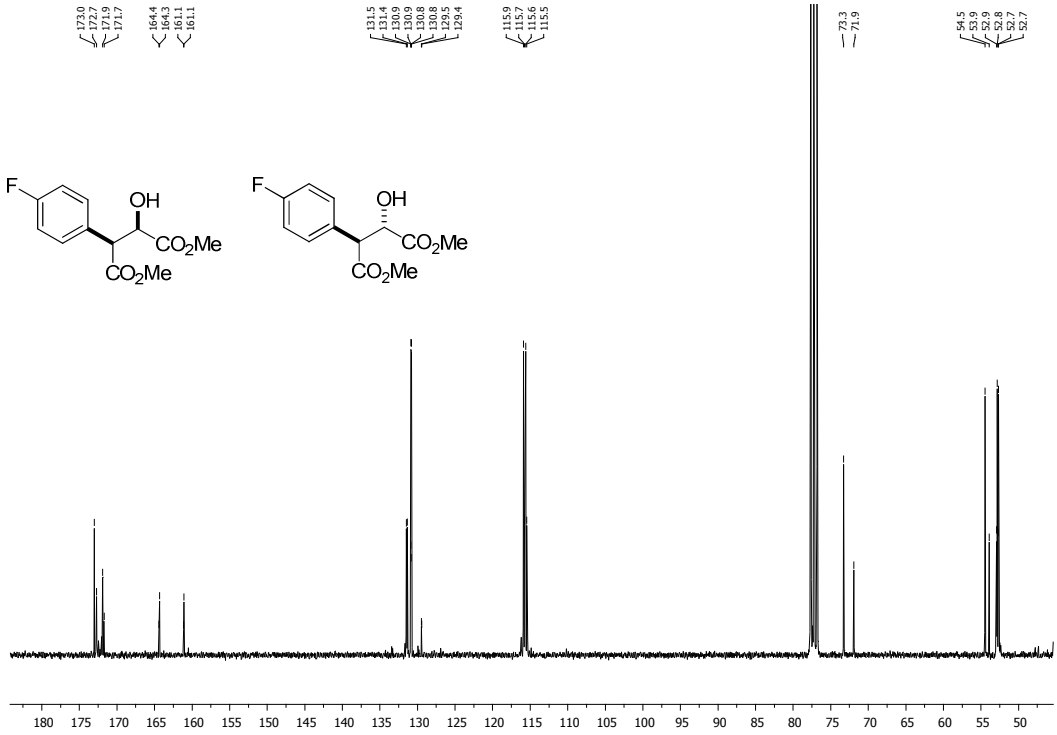
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2f**.



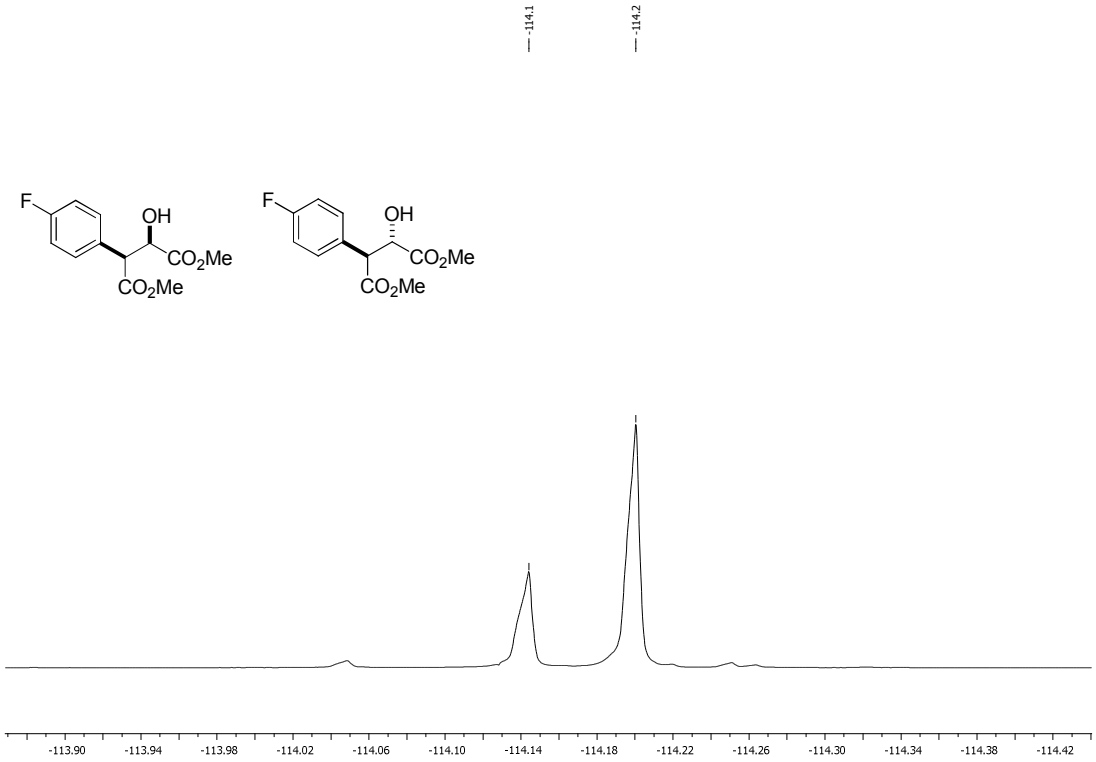
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2g**.



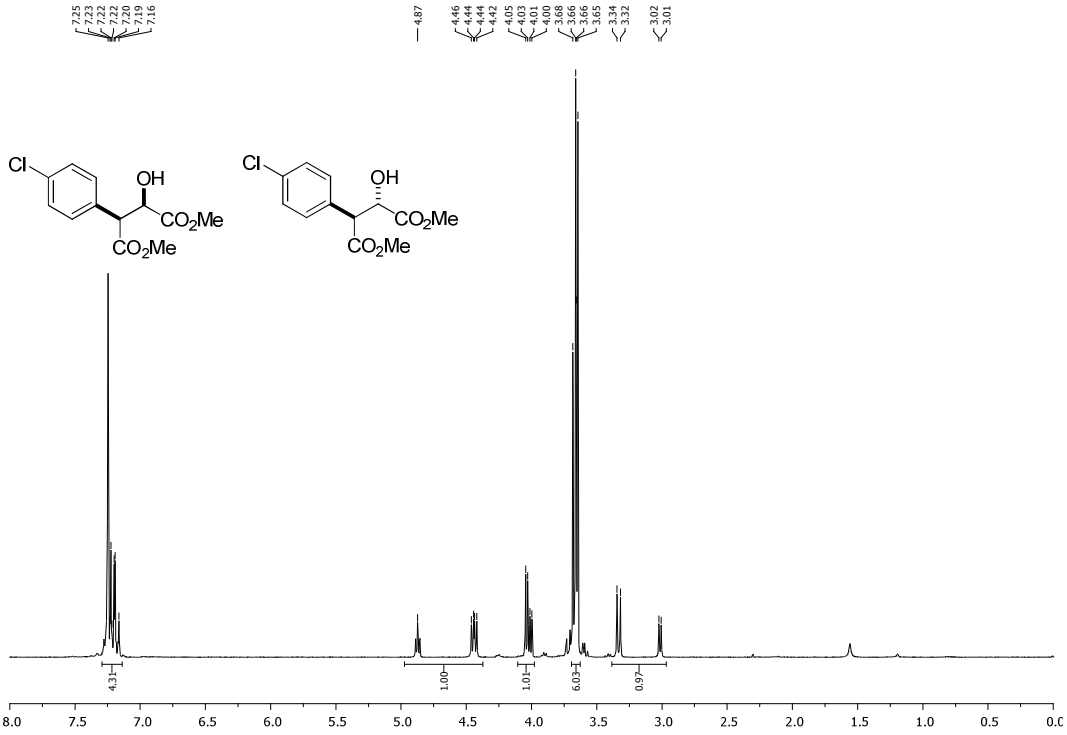
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2g**.



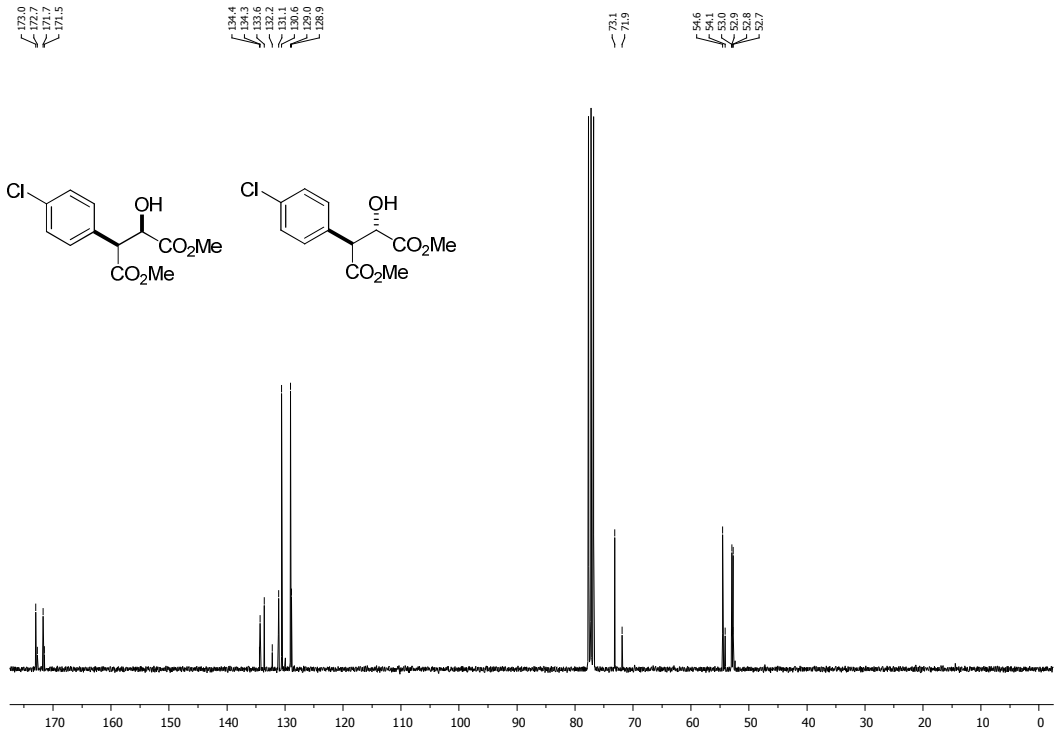
^{19}F NMR (282 MHz, $CDCl_3$) of Compound **2g**.



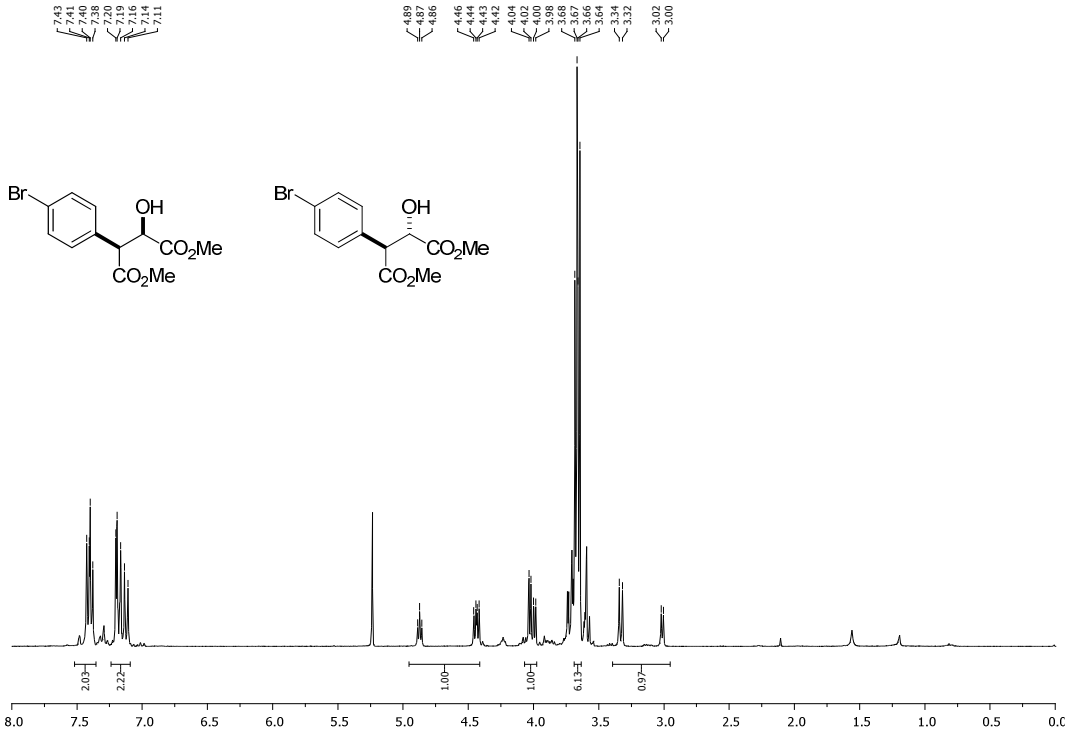
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2h**.



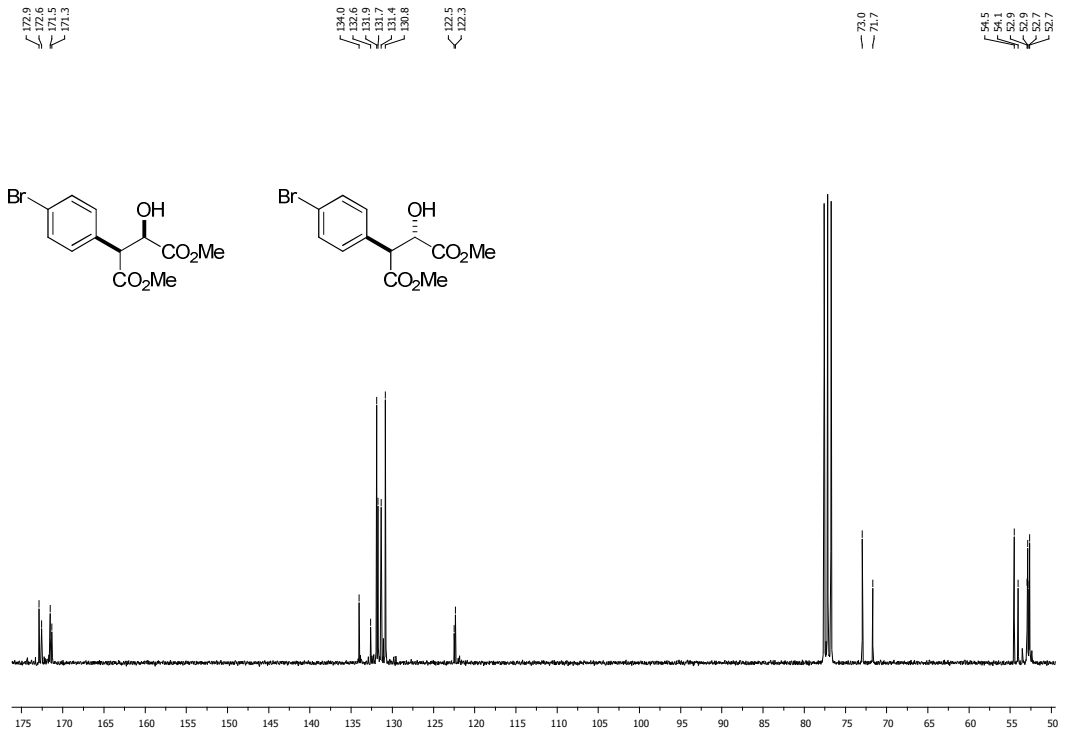
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2h**.



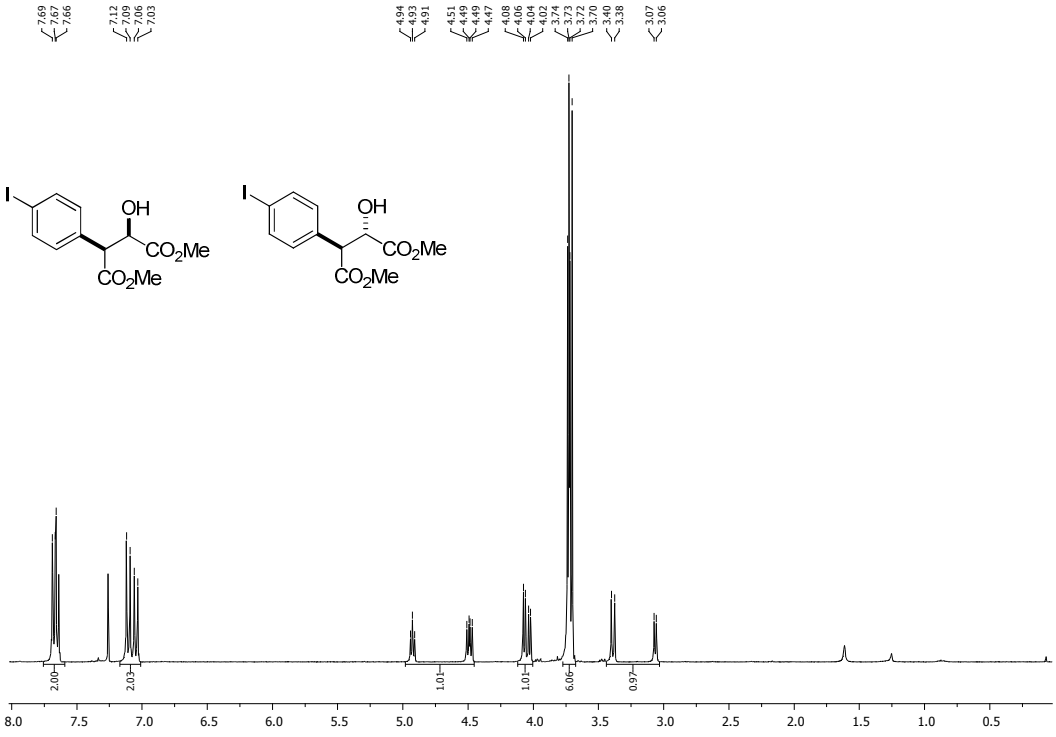
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2i**.



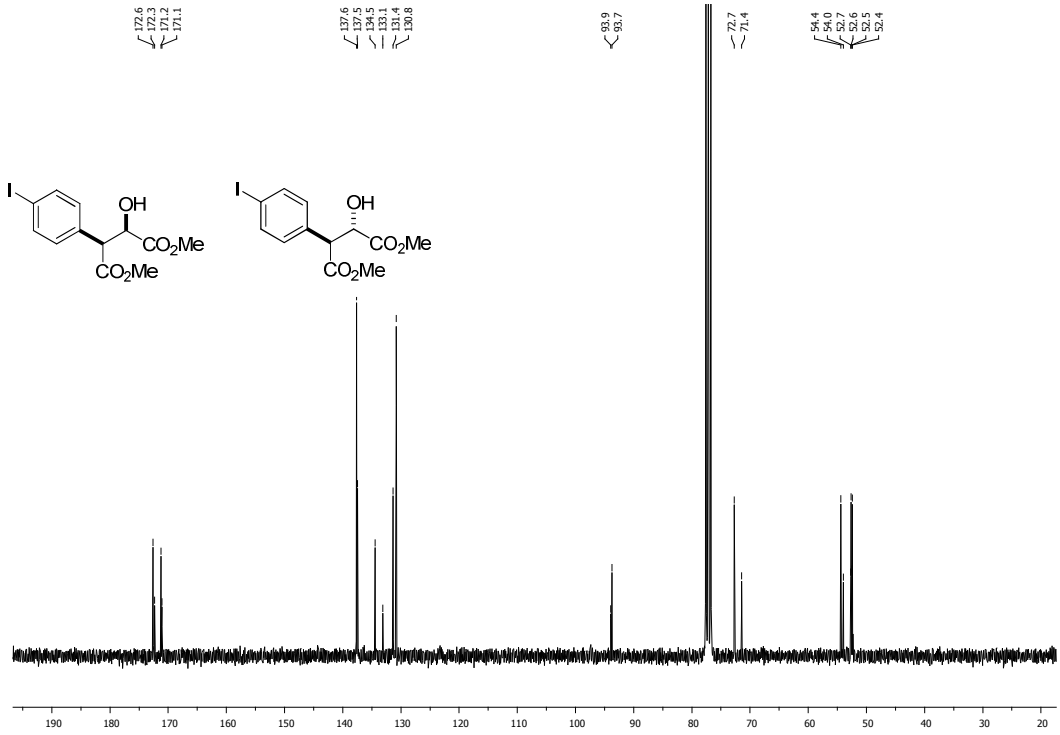
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2i**.



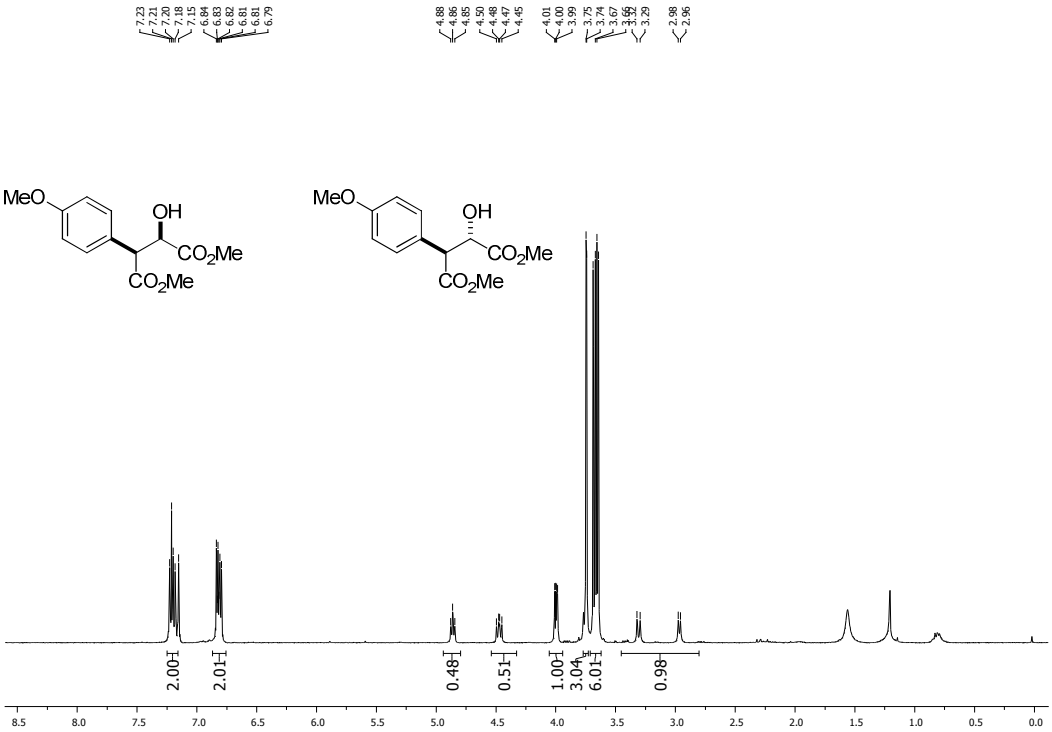
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2j**.



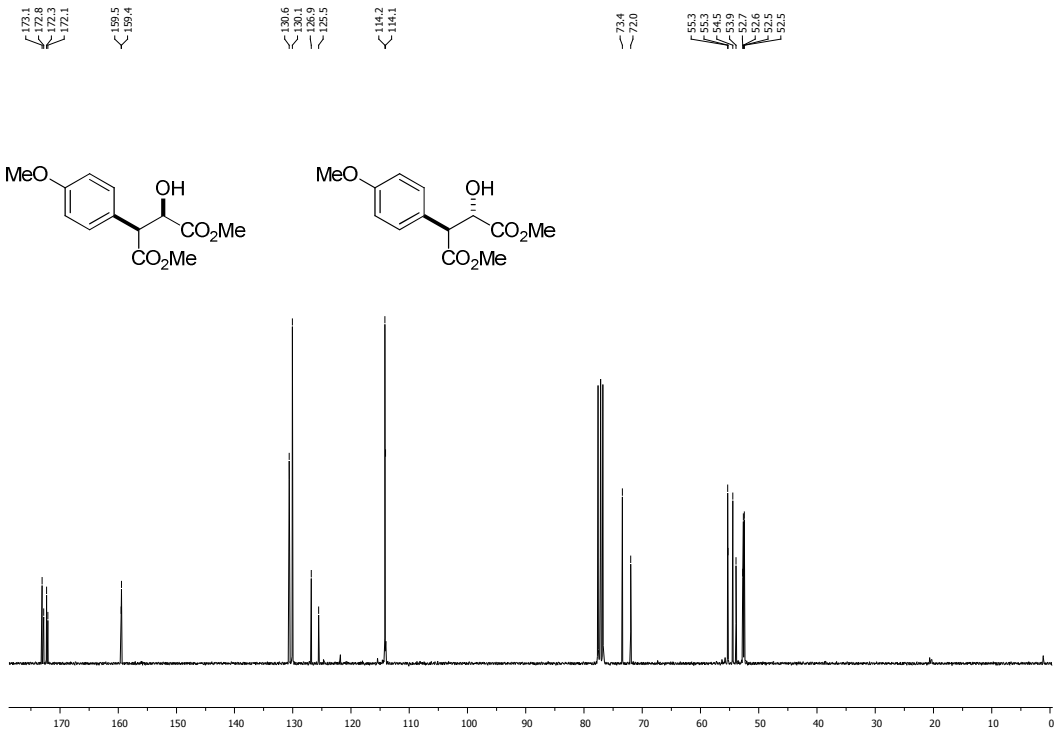
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2j**.



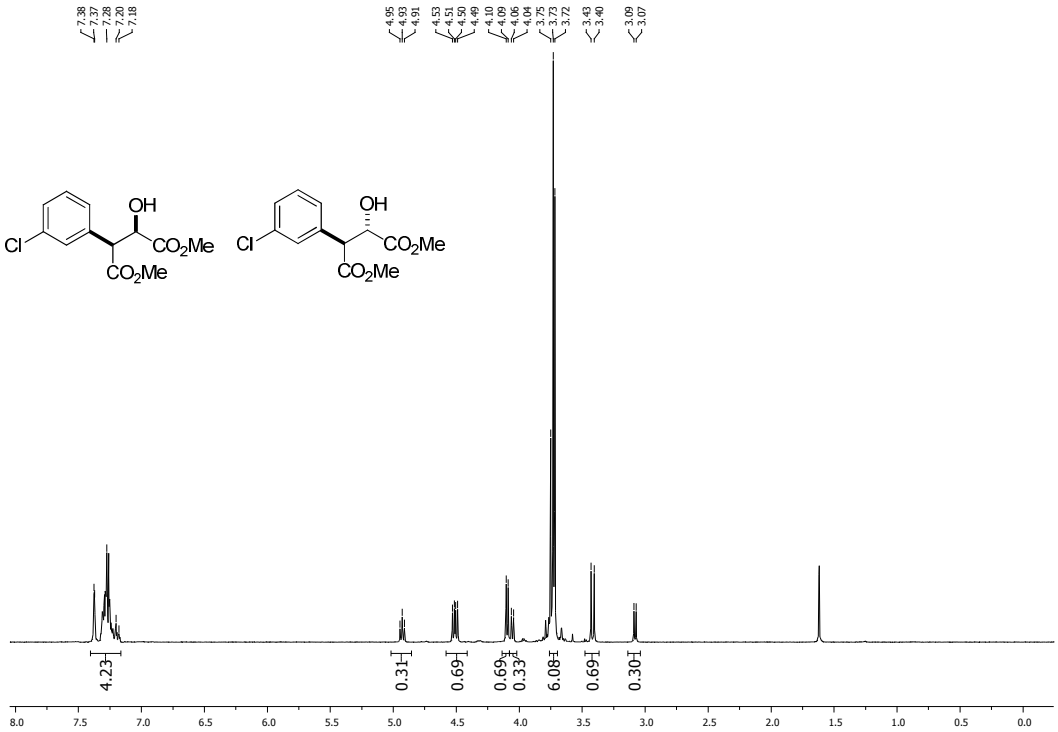
^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2k**.



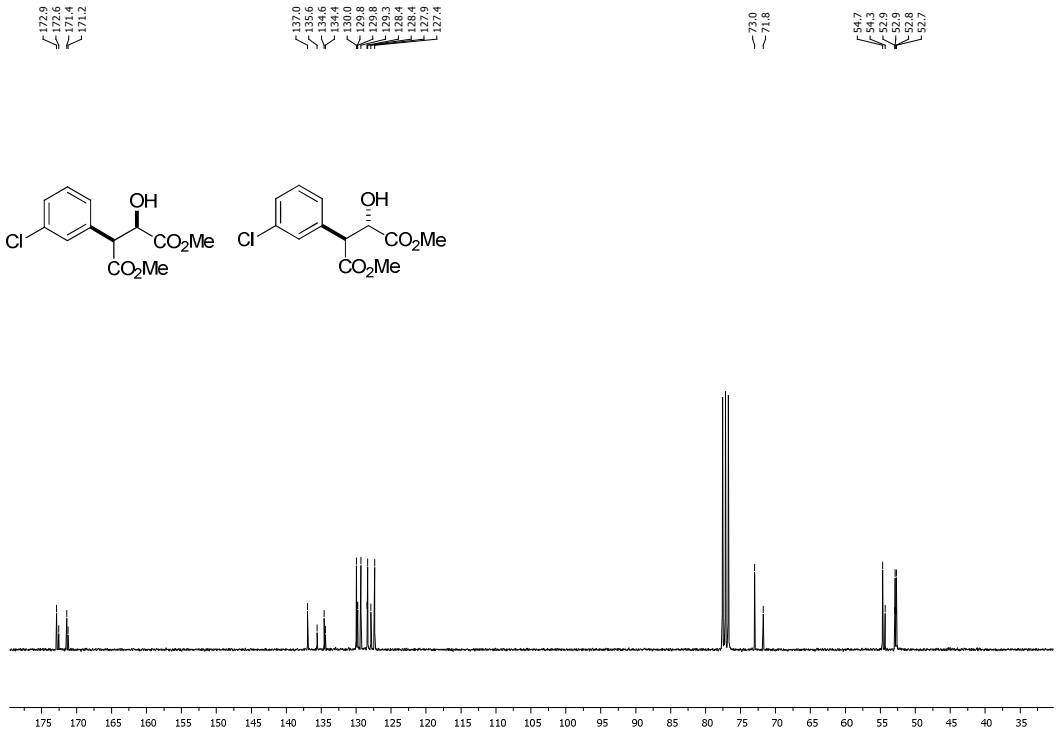
^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2k**.



^{1}H NMR (300 MHz, $CDCl_3$) of Compound **2l**.



^{13}C NMR (75 MHz, $CDCl_3$) of Compound **2l**.



^{1}H NMR (300 MHz, $CDCl_3$) of Compound **4**.