Chiral Phosphapalladacycle as Efficient Catalysts for the Asymmetric Hydrophosphination of substituted methylidenemalonate esters – Direct Access to Functionalized Tertiary Chiral Phosphines

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Supporting Information

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General information

All reactions and manipulations were carried out under dry, oxygen-free nitrogen using the standard Schlenk technique. NMR spectra were recorded on a Bruker AV 300 spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{31}P at 121 MHz) or a Bruker AV 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{31}P at 162 MHz) or a Bruker AV 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz, ^{31}P at 202 MHz). Chemical shift are given in ppm and are referenced to residual solvent peak in the respective deutero-solvents. (^{1}H NMR and ^{13}C NMR) or to an 85% H_3PO_4 in D_2O externally (^{31}P NMR). Solvents were degassed prior to use when necessary. DCM, Toluene, THF and acetone were purchased from TEDIA COMPANY (AR) and used as supplied. Low Temp PAIRSTIRRER PSL-1800 machine was used for controlling low temperatures for reactions. Column chromatography was conducted on Silica gel 60 (Merck). Optical rotations of the free phosphine products were measured as soon as possible without inert gas protection on the specified solution in a 0.1 dm cell at 20 ºC with a Perkin-Elmer 341 polarimeter. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

The three palladacycles catalysts (*R*)-**1**, (*S*)-**2,** and (*R*)-**3** were prepared by were prepared by treating the corresponding chloro-bridged dimeric palladium compounds[1] with silver perchlorate in acetonitrile via a procedure reported previously for (*R*)-**1**[2a] and (*R*)-**3**.[2b] All the other reactants and reagents were used as supplied.

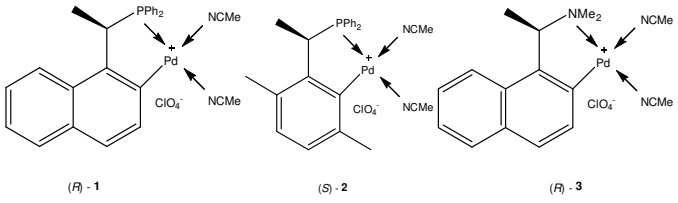
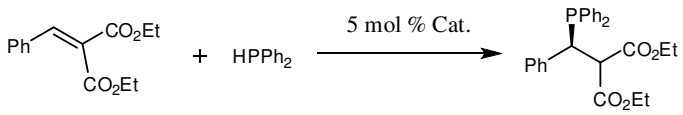


Figure 1.

Experimental Section:

1) Screening of reaction conditions:

Table 1. Screening of reaction conditions.[a]

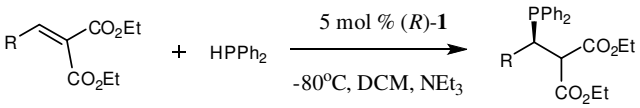


Entry	Cat	Solvent	Base	Temp (°C)	Reactivity (hrs)	Conversion[b] (%)	ee[c] (%)
1	(*R*)-**1**	DCM	NEt_3	RT	1.5	99	63
2	(*R*)-**1**	DCM	NEt_3	-80	3.5	99	96
3	(*S*)-**2**	DCM	NEt_3	-80	24	99	65
4	(*R*)-**3**	DCM	NEt_3	-80	7	99	86
5	(*S*)-**1**	DCM	NEt_3	-80	3.5	99	96
6	(*R*)-**1**	DCM	NEt_3	-40	2.5	99	93
7	(*R*)-**1**	Acetone	NEt_3	-80	> 6	99	95
8	(*R*)-**1**	MeCN	NEt_3	-40	4	99	81
9	(*R*)-**1**	Chloroform	NEt_3	-40	24	99	85
10	(*R*)-**1**	THF	NEt_3	-80	NIL	NIL	NIL
11	(*R*)-**1**	1, 4-dioxane : Water = 10 : 1	NEt_3	RT	10	83	18
12	(*R*)-**1**	Toluene	NEt_3	-80	> 24	NIL	NIL
13	(*R*)-**1**	DCM	DBU	-80	24	35	--
14	(*R*)-**1**	DCM	*t*-BuONa[d]	-40	5.5	99	36

[a] Conditions: $HPPh_2$ (50.0 mg, 2.69 x 10^{-4} mol), 5 mol % Cat, 1.2 equiv diethyl benzylidenemalonate (80.2 mg, 3.23 x 10^{-4} mol), 1 equiv Base (2.69 x 10^{-4} mol), 6 mL of degassed dichloromethane were reacted at indicated temperature. [b] Conversion was calculated from $^{31}P\{^1H\}$ NMR. [c] ee was determined from $^{31}P\{^1H\}$ NMR integration of the respective signals via the use of a chiral derivatizing agent. The detailed procedure is described in S5. [d] Solid ^{t}BuONa was used.

2) Screening of substrates:

Table 2. Substrate scope for the phospalladacycle catalyzed P-H addition of diphenylphosphine to substituted methylidenemalonate esters.[a]



Entry	R	Conversion[b] (%)	ee[c] (%)
1	Ph	99	96
2	OEt	99	74
3	Me	99	ca. 66
4	2 - furan	99	94
5	4-$MeOC_6H_4$	99	ca. 99
6	(*E*)PhCH=CH	99	>99
7	NH_2	NIL	NIL

[a] Conditions: $HPPh_2$ (50.0 mg, 2.69 x 10^{-4} mol), 5 mol % Cat (*R*)-**1** (8.4 mg, 1.34 x 10^{-5} mol, 5 mol% of $HPPh_2$), 1.2 equiv malonate ester (3.23 x 10^{-4} mol), 1 equiv NEt_3 (27.1 mg, 2.69 x 10^{-4} mol), 6 mL of degassed DCM were reacted at -80 °C. [b] Conversion was calculated from $^{31}P\{^1H\}$ NMR. [c] ee was determined from $^{31}P\{^1H\}$ NMR integration of the respective signals via the use of a chiral derivatizing agent. The detailed procedure is described in S5.

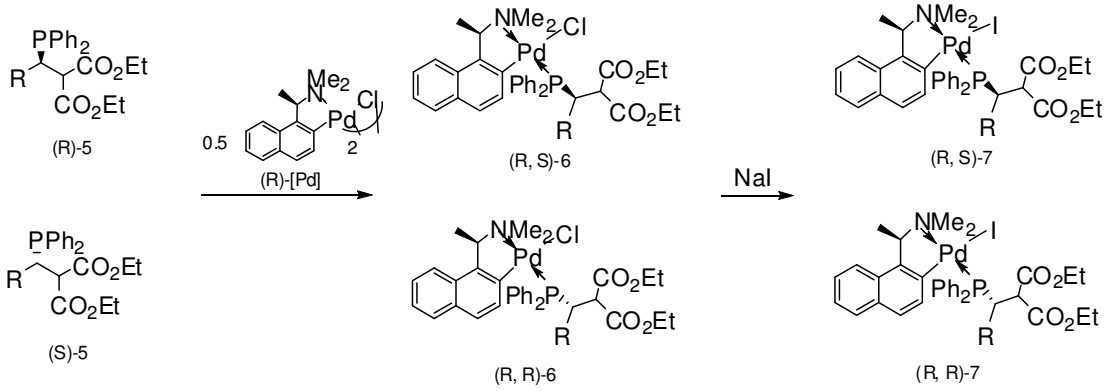
3) General procedure for synthesis of monophosphines via hydrophosphination of substituted methylidenemalonate esters.

Catalyst (*R*)-**1** (8.4 mg, 1.34 x 10^{-5} mol, 5 mol % of $HPPh_2$) was added to a degassed DCM solution (2 mL) of $HPPh_2$ (50.0 mg, 2.69 x 10^{-4} mol). The light yellow mixture was stirred at room temperature for 10 mins and then cooled to -80 ^oC. Subsequently, substrate (3.22 x 10^{-4} mol, 1.2 equivalents of $HPPh_2$) and NEt_3 (27.1 mg, 2.69 x 10^{-4} mol, 1 equivalent of $HPPh_2$) were each dissolved in 2 mL of degassed solvent and added dropwise. The hydrophosphination reaction was monitored by $^{31}P\{^1H\}$ NMR. Upon completion, the reaction mixture was warmed to room temperature and solvent evaporated by vacuum. The yellowish–orange monophosphine product was re-dissolved in degassed DCM (5 mL) and filtered through a short silica gel column (packed with degassed n – Hexane) on a two-neck Schlenk flask protected by N_2. The solvent was removed by vacuum pump to give the enantio-enriched phosphine product (±)**5**.

Determination of ee: enatiomeric excess (ee %) were measured by $^{31}P\{^1H\}$ NMR spectrum of the

corresponding compounds. The obtained phosphine product (±)**5** was dissolved in DCM (3 mL) and added 0.51 equiv (a little excess) of enantio-pure (*R*)-{[Pd[$Me_2NCH(Me)C_{10}H_6$](μ-Cl)}$_2$ solid. After stirring for 30 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR spectrum recorded. ee value was evaluated by integration of the corresponding products. The major diastereomer of **6a** was isolated by column chromatography on a silica column with hexane-dichloromethane.

The isolated **6a** (0.39 g, 0.50 mmol) was mixed with excessive sodium iodide (0.10 g, 0.60 mmol) in acetone (50 ml) and stirred vigorously for 15 min at room temperature. After the solvent were removed, the residue was extracted with dichloromethane. Removal of DCM gave **7a** as a solid, which was then recrystallized from dichloromethane-hexane to give the product as yellow needle crystals (0.40 g, 93%). Its structure was confirmed by X-ray analysis which revealed that the absolute configuration of the major product were *S*. $[\alpha]_D$ = -316.6 (*c* 1.2, DCM). Mp: 167 ^oC dec. ^{31}P NMR ($CDCl_3$, 162 M): δ 50.4; ^1H NMR ($CDCl_3$, 400 M): δ 8.02-7.98 (m, 2H, Ar), 7.67 (d, 1H, *J* = 8.40 Hz, Ar), 7,51-7.48 (m, 4H, Ar), 7.38-7.35 (m, 3H, Ar), 7.28-7.26 (m, 1H, Ar), 7.20-7.15 (m, 2H, Ar), 7.06-7.00 (m, 4H, Ar), 6.90 (d, 1H, *J* = 7.60 Hz, Ar), 6.71 (d, 1H, *J* = 8.40 Hz, Ar), 6.29 (m, 1H, Ar), 5.30-5.28 (m, 1H, C*H*), 5.24-5.19 (m, 1H, C*H*), 4.34-4.28 (m, 1H, C*H*Me), 4.19-4.07 (m, 2H, CH_2), 3.81-3.76 (m, 2H, CH_2), 3.32 (d, 3H, *J* = 8.40 Hz, NMe_2), 2.71 (s, 3H, NMe_2), 2.13 (d, 3H, CH*Me*), 1.19 (t, 3H, *J* = 7.20 Hz, CH_2CH_3), 0.88 (t, 3H, *J* = 7.20 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 M): δ 168.0 (d, 1C, *J* = 67.30 Hz, *C*OOEt), 167.5 (d, 1C, *J* = 88.40 Hz, *C*OOEt), 155.6 (d, 1C, *J* = 5.06 Hz, Ar), 147.8-123.3 (27 C, Ar), 73.3 (1C, *C*HMe), 61.8 (1C, *C*H_2CH_3), 61.2 (1C, *C*H_2CH_3), 56.6 (d, 1C, J_{PC} = 8.66 Hz, *C*H), 52.1 (1C, N*Me*), 51.3 (1C, N*Me*), 49.3 (d, 1C, J_{PC} = 24.81 Hz, *C*H), 22.7 (1C, CH*Me*), 13.9 (1C, CH_2CH_3), 13.5 (1C, CH_2CH_3).



$$ee = \left| \frac{(R)\text{-}5 - (S)\text{-}5}{(R)\text{-}5 + (S)\text{-}5} \right| = \left| \frac{(R,R)\text{-}6 - (R,S)\text{-}6}{(R,R)\text{-}6 + (R,S)\text{-}6} \right| = \left| \frac{(R,R)\text{-}7 - (R,S)\text{-}7}{(R,R)\text{-}7 + (R,S)\text{-}7} \right|$$

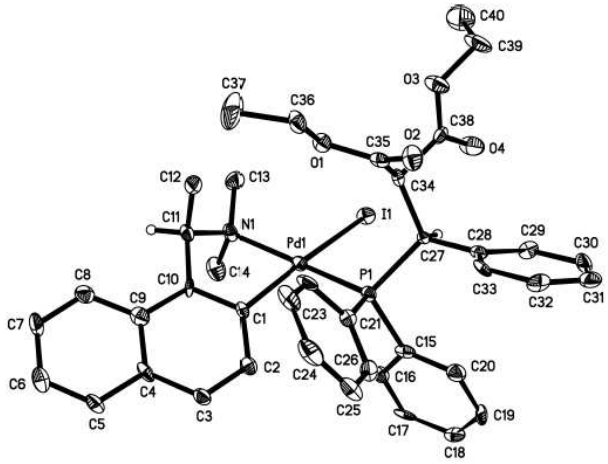


Figure 2.

4) Characterization Data

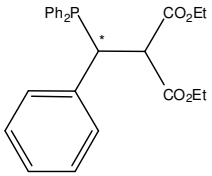


Table 2, **Entry 1**: (±)**5a**

Compound 4a was reacted with $HPPh_2$ at -80 °C for 3.5 h according to the general procedure to provide (±)**5a** (99% conversion, 96% ee) (air sensitive): $[\alpha]_D$ = -82.8 (*c* 1.3, DCM). ^{31}P NMR ($CDCl_3$, 121 M): δ 2.7; ^{1}H NMR ($CDCl_3$, 400 M): δ 7.64-7.59 (m, 2H, Ar), 7.35-7.31 (m, 3H, Ar),

7.23-7.11 (m, 5H, Ar), 7.05-7.03 (m, 3H, Ar), 6.99-6.96 (m, 2H, Ar), 4.40 (dd, 1H, *J* = 10.76, 3.42 Hz, C*H*(COOEt)$_2$), 3.94 (dd, 1H, *J* = 10.76, 7.10 Hz, Ph$_2$PC*H*), 3.91-3.84 (m, 3H, COOC*H*$_2$CH$_3$), 3.78-3.70 (m, 1H, COOC*H*$_2$CH$_3$), 1.15 (t, 3H, *J* = 7.24 Hz, CH$_2$C*H*$_3$), 0.92 (t, 3H, *J* = 7.24 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 75 M): δ 167.9 (1C, *C*OOEt), 167.5 (1C, *C*OOEt), 134.7-126.5 (18 C, Ar), 61.5 (1C, *C*H$_2$CH$_3$), 61.3 (1C, *C*H$_2$CH$_3$), 56.2 (d, 1C, J_{PC} = 27.03 Hz, PPh$_2$*C*H), 44.2 (d, 1C, J_{PC} = 19.57 Hz, *C*H(OEt)$_2$), 13.8 (1C, CH$_2$*C*H$_3$), 13.7 (1C, CH$_2$*C*H$_3$).

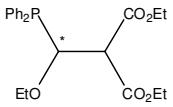


Table 2, **Entry 2**: (±)**5b**

Compound 5b was reacted with HPPh$_2$ at -80 ^{o}C for 8h according to the general procedure to provide (±)**5b** (99% conversion, 74% ee) (airsensitive): [α]$_D$ = -90.7 (*c* 0.4, DCM). ^{31}P NMR (CDCl$_3$, 121 M): δ -2.6; ^{1}H NMR (CDCl$_3$, 300 M): δ 7.83-7.78 (m, 2H, Ar), 7.52-7.48 (m, 2H, Ar), 7.43-7.41 (m, 3H, Ar), 7.34-7.32 (m, 3H, Ar), 4.87 (dd, 1H, *J* = 9.6, 6.9 Hz, PPh$_2$C*H*), 4.19 (q, 2H, *J* = 6.9 Hz, COOC*H*$_2$CH$_3$), 4.10 (qd, 2H, *J* = 7.2, 2.1 Hz, COOC*H*$_2$CH$_3$), 3.66 (dd, 1H, *J* = 9.9, 6.6 Hz, C*H*(COOEt)$_2$), 3.47 (m, 1H, OC*H*$_2$CH$_3$), 3.03 (m, 1H, OC*H*$_2$CH$_3$), 1.30-1.21 (m, 6H, COOCH$_2$C*H*$_3$), 0.90 (t, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, 75 M): δ 167.5 (1C, *C*OOCH$_2$CH$_3$), 167.0 (1C, *C*OOCH$_2$CH$_3$), 135.6-128.2 (12C, Ar), 80.4 (d, 1C, J_{PC} = 20.3 Hz, PPh$_2$*C*H), 69.3 (1C, O*C*H$_2$CH$_3$), 61.5 (2C, COO*C*H$_2$CH$_3$), 56.9 (d, 1C, J_{PC} = 22.5 Hz, *C*H(OEt)$_2$), 15.1 (1C, OCH$_2$*C*H$_3$), 14.0 (1C, COOCH$_2$*C*H$_3$), 13.9 (1C, COOCH$_2$*C*H$_3$).

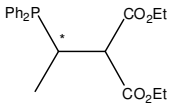
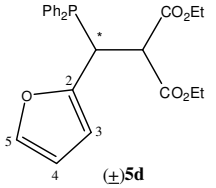


Table 2, **Entry 3**: (±)**5C**

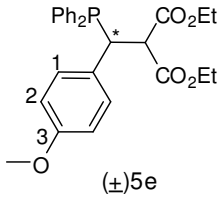
Compound 4c was reacted with HPPh$_2$ at -80 ^{o}C for 4h according to the general procedure to provide (±)**5c** (99% conversion, 66% ee) (airsensitive): [α]$_D$ = -50.2 (*c* 0.3, DCM). ^{31}P NMR (CDCl$_3$, 202 M): δ -3.8; ^{1}H NMR (CDCl$_3$, 500 M): δ 7.55-7.49 (m, 4H, Ar), 7.37-7.32 (m, 6H, Ar), 4.20 (qd, 2H, *J* = 7.4, 1.0 Hz COOC*H*$_2$CH$_3$), 4.14-4.06 (m, 2H, COO*C*H$_2$CH$_3$), 3.32 (t, 1H, *J* = 7.0 Hz, C*H*(OEt)$_2$), 3.20-3.14 (m, 1H, PPh$_2$C*H*), 1.27 (t, 3H, *J* = 7.2 Hz, COOCH$_2$C*H*$_3$), 1.24 (t, 3H, *J* = 7.2 Hz, COOCH$_2$C*H*$_3$), 1.10 (q, 3H, *J* = 7.0 Hz, PPh$_2$CHC*H*$_3$); ^{13}C NMR (CDCl$_3$, 125 M): δ 168.7 (d, 1C, J_{PC} = 7.4 Hz, *C*OOEt), 168.2 (d, 1C, J_{PC} = 9.1 Hz, *C*OOEt), 134.4-128.4 (m, 12C,

Ar), 61.5 (1C, *C*H_2CH_3), 61.3 (1C, *C*H_2CH_3), 54.5 (d, 1C, J_{PC} = 21.1 Hz, *C*H(COOEt)$_2$), 30.5 (d, 1C, J_{PC} = 14.8 Hz, PPh_2*C*H), 14.1 (1C, *C*H_3), 14.0 (1C, *C*H_3), 13.9 (1C, *C*H_3).

Table 2, **Entry 4**: 

(±)**5d**

Compound 4d was reacted with $HPPh_2$ at -80 ^oC for 4h according to the general procedure to provide (±)**5d** (99% conversion, 94% ee) (airsensitive): $[\alpha]_D$ = -120.7 (*c* 0.6, DCM). ^{31}P NMR ($CDCl_3$, 202 M): δ 1.5; ^1H NMR ($CDCl_3$, 500 M): δ 7.57-7.54 (m, 2H, Ar), 7.38-7.32 (m, 3H, Ar), 7.32-7.28 (m, 1H, Ar), 7.23-7.16 (m, 4H, Ar), 7.07 (d, 1H, *J* = 1.0 Hz, C_5*H*), 6.08 (q, 1H, C_4*H*), 5.76 (d, 1H, *J* = 3.2 Hz C_3*H*), 4.51 (d, 1H, *J* = 10.6 Hz, C*H*(OEt)$_2$), 4.09-4.02 (m, 4H, COOC*H*$_2$CH$_3$), 3.80 (dd, 1H, *J* = 10.6, 6.3 Hz, PPh_2C*H*), 1.24 (t, 3H, *J* = 7.3 Hz, COOCH$_2$C*H*$_3$), 1.08 (t, 3H, *J* = 7.5 Hz, COOCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 M): δ 167.7 (1C, *C*OOEt), 167.4 (1C, *C*OOEt), 151.2 (1C, C_2), 140.8 (1C, C_5), 134.6-128.0 (m, 12C, Ar), 110.3 (1C, C_4), 107.4 (d, 1C, *J* = 2.5 Hz, C_3), 61.8 (1C, *C*H_2CH_3), 61.5 (1C, *C*H_2CH_3), 54.5 (d, 1C, J_{PC} = 27.5 Hz, PPh_2*C*H), 38.3 (d, 1C, J_{PC} = 22.0 Hz, *C*H(COOEt)$_2$), 14.0 (1C, COOCH$_2$*C*H$_3$), 13.9 (1C, COOCH$_2$*C*H$_3$).

Table 2, **Entry 5**: 

(±)5e

Compound 4e was reacted with $HPPh_2$ at -80 ^oC for 8h according to the general procedure to provide (±)**5e** (99% conversion, >99% ee) (airsensitive): $[\alpha]_D$ = -92.9 (*c* 0.7, DCM). ^{31}P NMR ($CDCl_3$, 202 M): δ 1.2; ^1H NMR ($CDCl_3$, 500 M): δ 7.61-7.58 (m, 2H, Ar), 7.34-7.31 (m, 3H, Ar), 7.20-7.15 (m, 5H, Ar), 6.92 (d, 2H, *J* = 8.5 Hz, C_1*H*), 6.61 (d, 2H, *J* = 8.5 Hz, C_2*H*), 4.29 (q, 1H, C*H*(OEt)$_2$), 3.89-3.85 (m, 4H, COOC*H*$_2$CH$_3$), 3.76-3.71 (m, 1H, PPh_2C*H*), 1.24 (t, 3H, *J* = 7.3 Hz, COOCH$_2$C*H*$_3$), 1.08 (t, 3H, *J* = 7.5 Hz, COOCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 M): δ 168.0 (1C, *C*OOEt), 167.5 (1C, *C*OOEt), 158.0 (1C, C_3), 134.6-128.0 (m, 15C, Ar), 113.2 (2C, C_2), 61.6 (1C, *C*H_2CH_3), 61.3 (1C, *C*H_2CH_3), 56.3 (d, 1C, J_{PC} = 26.9 Hz, PPh_2*C*H), 55.1 (1C, O*C*H$_3$), 43.3 (d, 1C, J_{PC} = 19.0 Hz, *C*H(COOEt)$_2$), 13.9 (1C, COOCH$_2$*C*H$_3$), 13.8 (1C, COOCH$_2$*C*H$_3$).

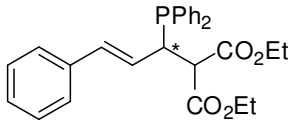


Table 2, **Entry 6**: (±)**5f**

Compound 4f was reacted with $HPPh_2$ at -80 °C for 4h according to the general procedure to provide (±)**5f** (99% conversion, >99% ee) (airsensitive): $[\alpha]_D$ = -160.9 (*c* 1.7, DCM). ^{31}P NMR ($CDCl_3$, 121 M): δ 0.2; ^{1}H NMR ($CDCl_3$, 300 M): δ 7.60-7.51 (m, 4H, Ar), 7.40-7.32 (m, 6H, Ar), 7.28-7.12 (m, 5H, Ar), 6.23 (d, 1H, *J* = 8.5 Hz, PhC*H*), 6.02-5.92 (m, 1H, PhCH=C*H*), 4.24-4.10 (m, 4H, $COOCH_2CH_3$), 3.91 (t, 1H, *J* = 9.7 Hz, $CH(OEt)_2$), 3.61-3.55 (dd, 1H, *J* = 6.7, 2.9 Hz, PPh_2CH), 1.30 (t, 3H, *J* = 7.1 Hz, $COOCH_2CH_3$), 1.18 (t, 3H, *J* = 7.1 Hz, $COOCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 75 M): δ 168.0 (d, 1C, *J* = 4.2 Hz, *C*OOEt), 167.7 (d, 1C, *J* = 13.2 Hz, *C*OOEt), 137.0-1226.1 (m, 20C, Ar, *C*H=*C*H), 61.7 (1C, CH_2CH_3), 61.4 (1C, CH_2CH_3), 54.5 (d, 1C, J_{PC} = 24.9 Hz, PPh_2CH), 42.0 (d, 1C, J_{PC} = 19.3 Hz, $CH(COOEt)_2$), 14.1 (2C, CH_3).

References:

1. (a) Ng, J. K.-P.; Tan, G.-K.; Vittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2003**, *42*, 7674-7682. (b) Ng, J. K.-P.; Li, Y.; Tan, G.-K.; Koh, L.-L.; Vittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2005**, *44*, 9874-9886. (c) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007-1014.

2. (a) Huang, Y.; Chew, R. J.; Li, Y.; Pullarkat, S. A.; Leung, P. H. *Org. Lett.* **2011**, 13, 5862-5865. (b) Chooi, S. Y. M.; Leung, P. H.; Lim, C. C.; Mok, K. F.; Quek,G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529-532.

NMR Spectra

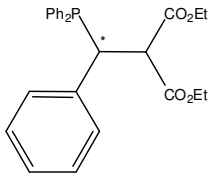
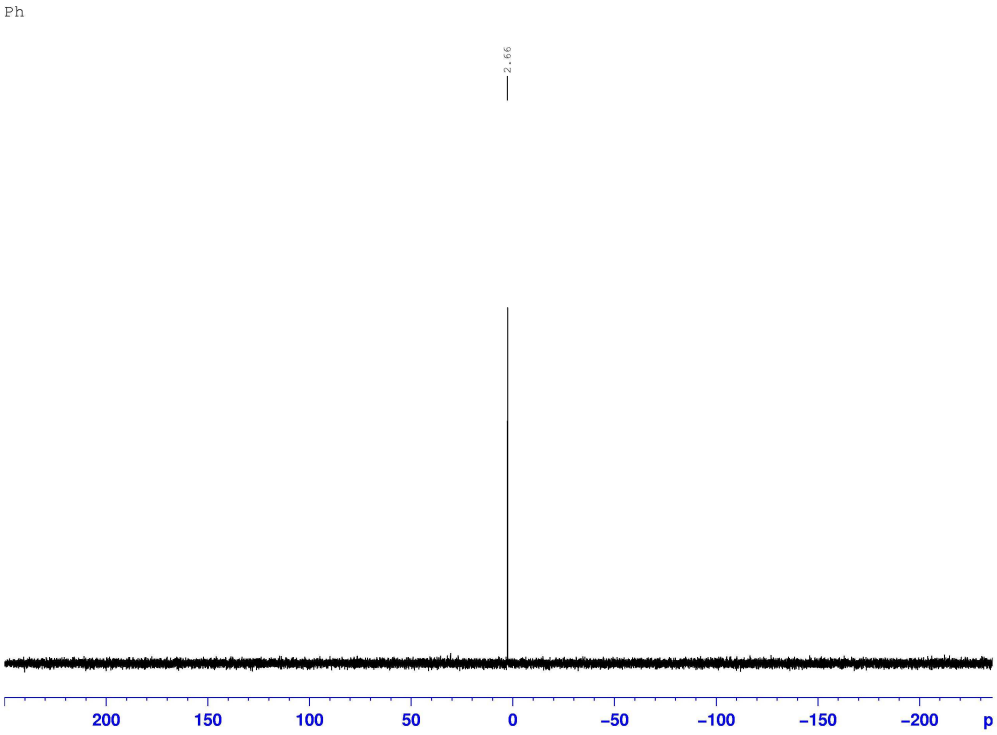
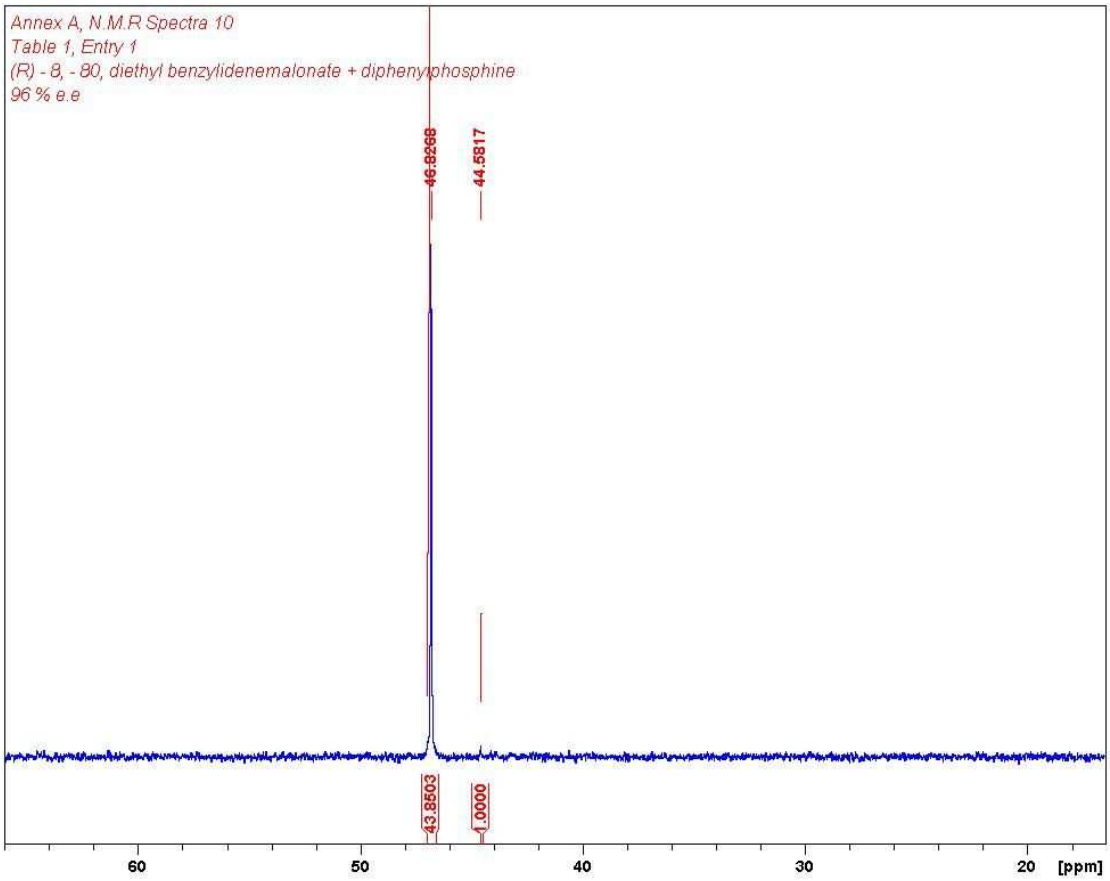
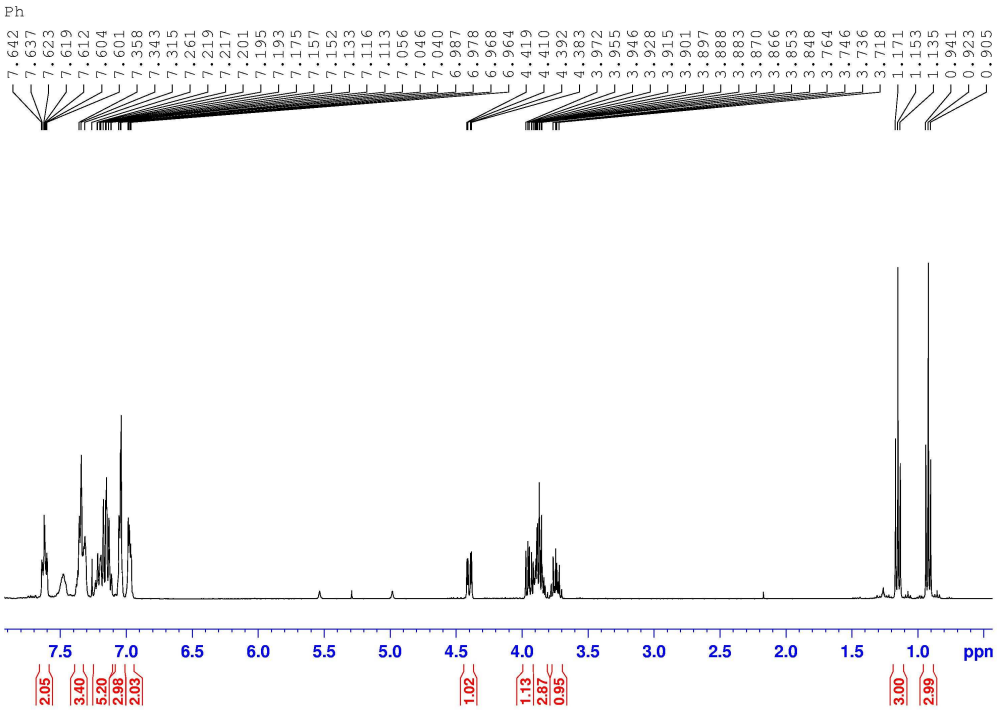
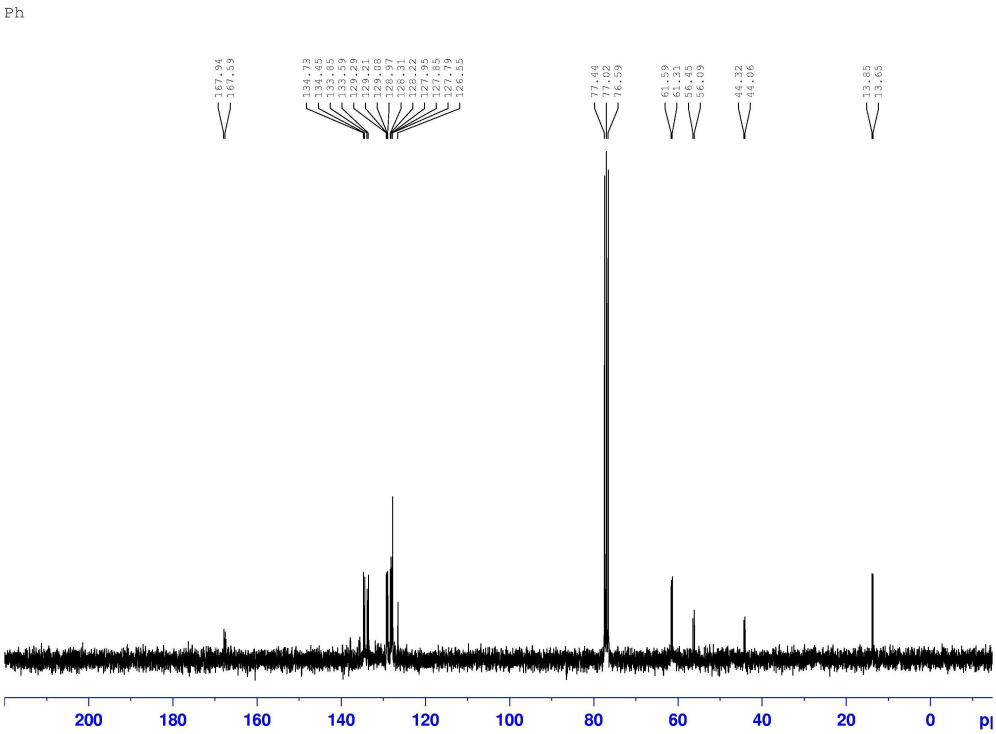


Table 2, **Entry 1**: (±)**5a**




Annex A, N.M.R Spectra 10
Table 1, Entry 1
(R) - 8, - 80, diethyl benzylidenemalonate + diphenylphosphine
96 % e.e
46.8268
44.5817
43.8503
1.0000
60
50
40
30
20
[ppm]


Ph
7.642
7.637
7.623
7.619
7.612
7.604
7.601
7.358
7.343
7.315
7.261
7.219
7.217
7.201
7.195
7.193
7.175
7.157
7.152
7.133
7.116
7.113
7.056
7.046
7.040
6.987
6.978
6.968
6.964
4.419
4.410
4.392
4.383
3.972
3.955
3.946
3.928
3.915
3.901
3.897
3.888
3.883
3.870
3.866
3.853
3.848
3.764
3.746
3.736
3.718
1.171
1.153
1.135
0.941
0.923
0.905
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppn
2.05
3.40
5.20
2.98
2.03
1.02
1.13
2.87
0.95
3.00
2.99



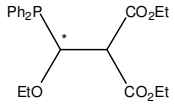
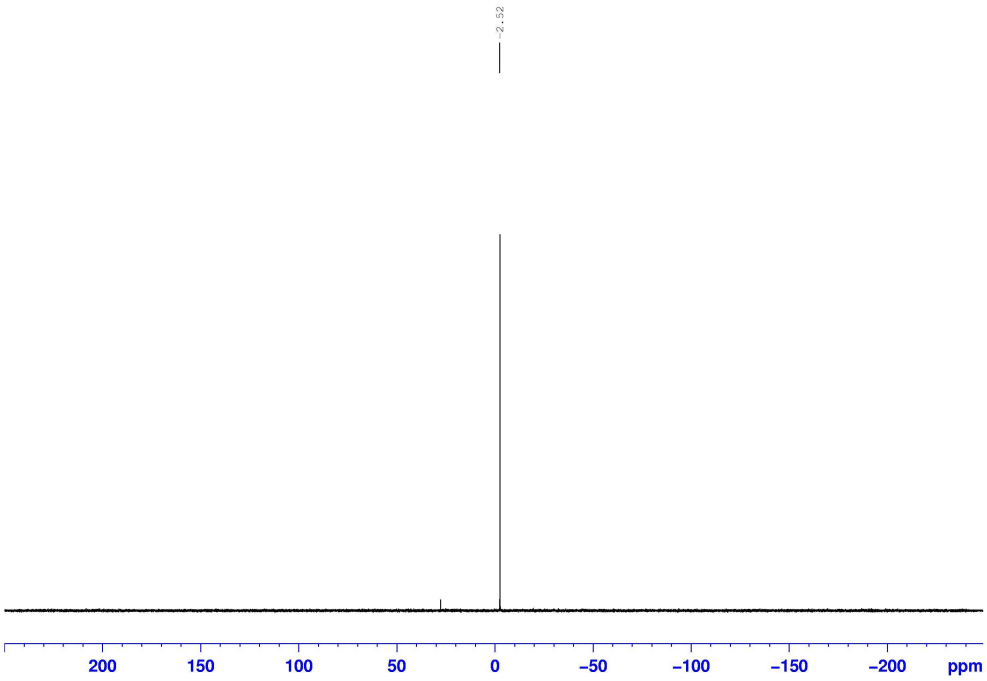
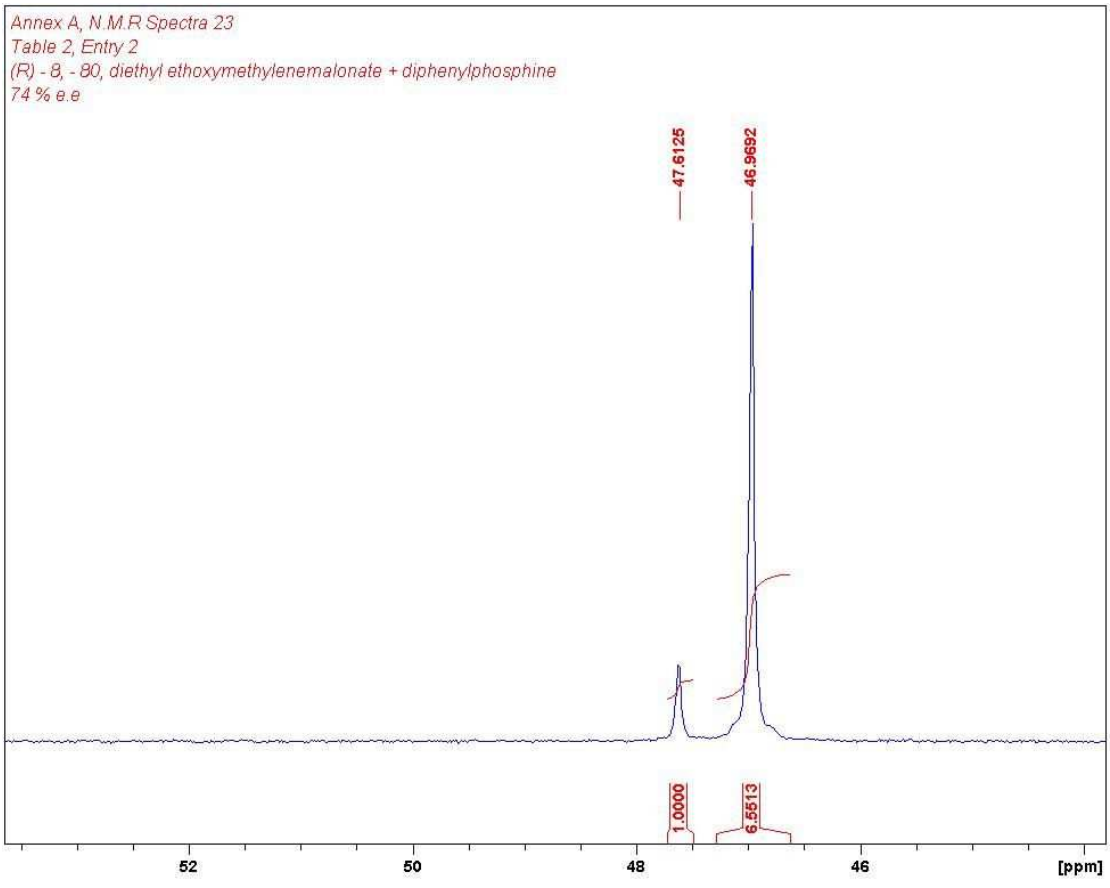
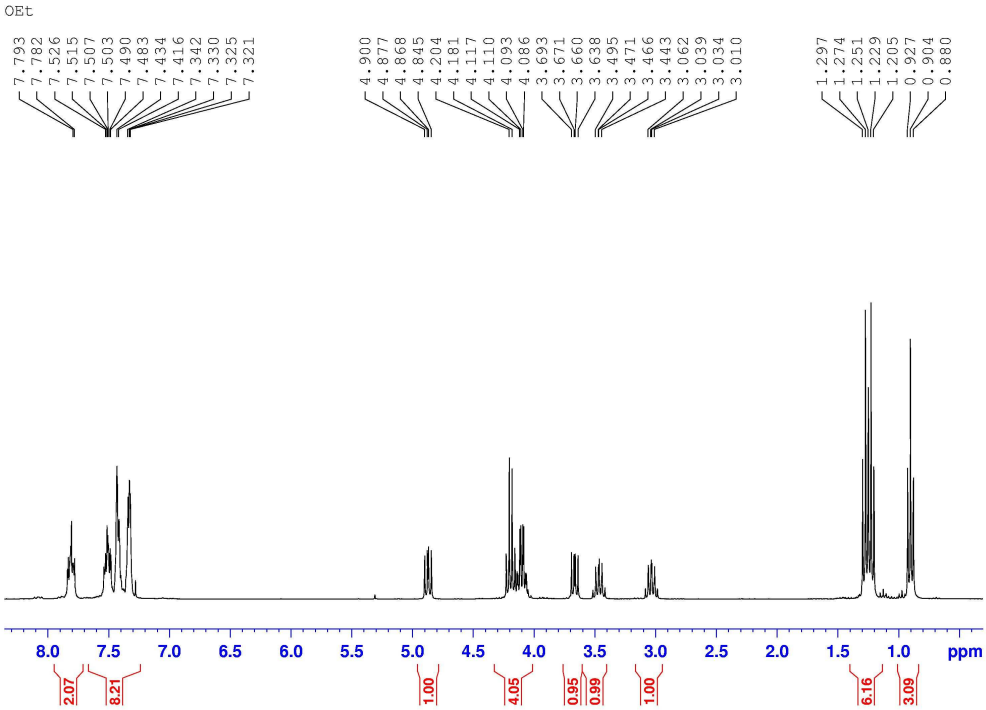


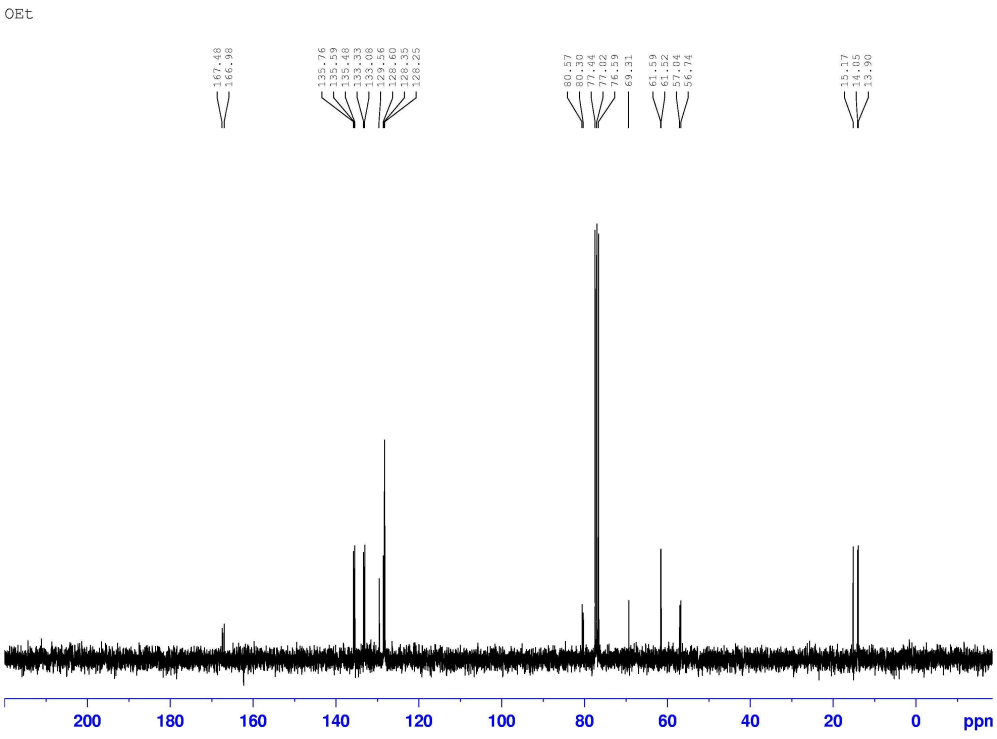
Table 2, **Entry 2**: **(±)5b**

OEt


-2.52
200
150
100
50
0
-50
-100
-150
-200
ppm


Annex A, N.M.R Spectra 23
Table 2, Entry 2
(R) - 8, - 80, diethyl ethoxymethylenemalonate + diphenylphosphine
74 % e.e
47.6125
46.9692
1.0000
6.5513
52
50
48
46
[ppm]


OEt
7.793
7.782
7.526
7.515
7.507
7.503
7.490
7.483
7.434
7.416
7.342
7.330
7.325
7.321
4.900
4.877
4.868
4.845
4.204
4.181
4.117
4.110
4.093
4.086
3.693
3.671
3.660
3.638
3.495
3.471
3.466
3.443
3.062
3.039
3.034
3.010
1.297
1.274
1.251
1.229
1.205
0.927
0.904
0.880
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.07
8.21
1.00
4.05
0.95
0.99
1.00
6.16
3.09


OEt
167.48
166.98
135.76
135.49
135.48
133.33
133.08
129.56
128.60
128.55
128.25
80.57
80.30
77.44
77.02
76.59
69.31
61.59
61.52
57.04
56.74
15.17
14.05
13.90
200
180
160
140
120
100
80
60
40
20
0
ppn

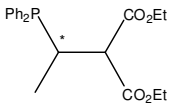
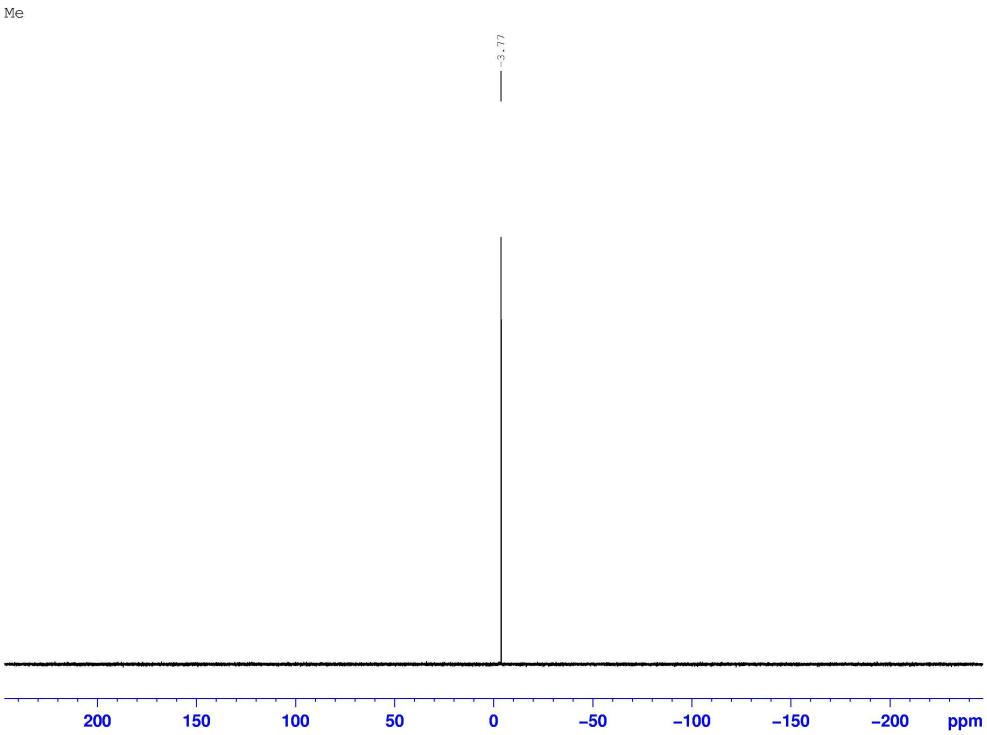
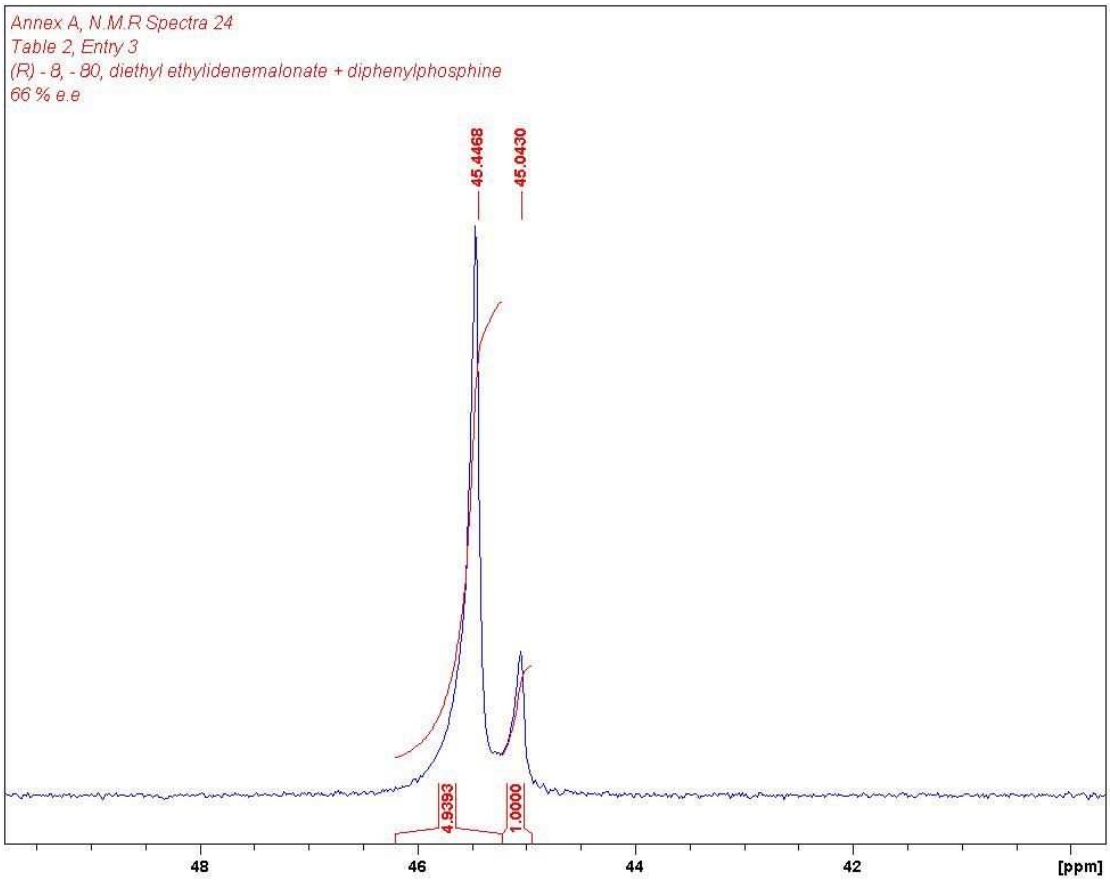
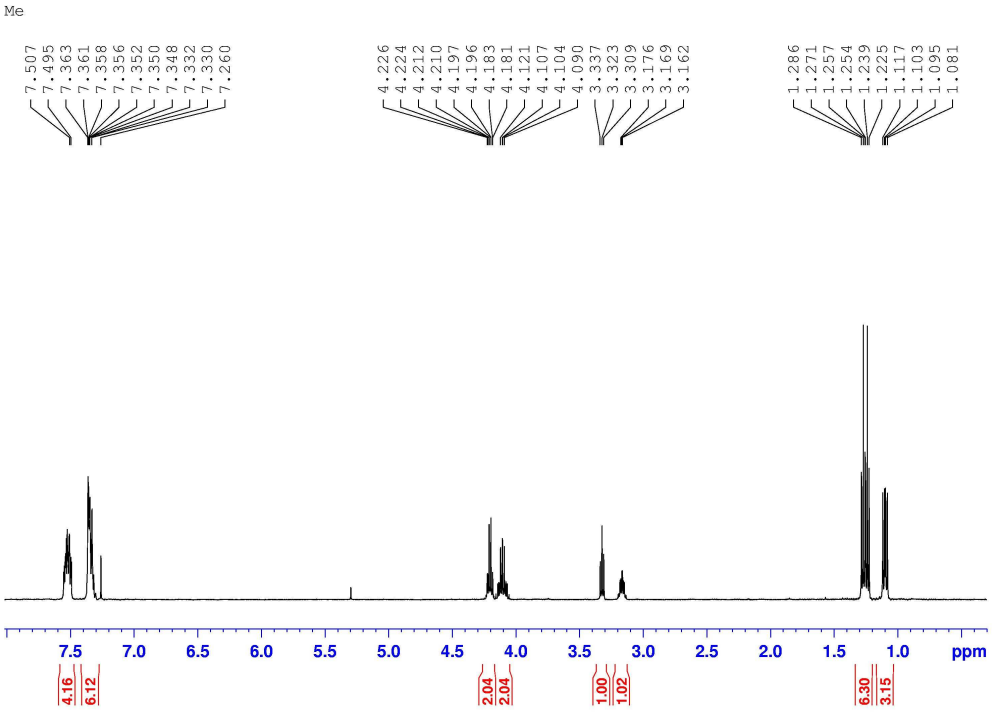


Table 2, **Entry 3**: (±)**5C**




Annex A, N.M.R Spectra 24
Table 2, Entry 3
(R) - 8, - 80, diethyl ethylidenemalonate + diphenylphosphine
66 % e.e
45.4468
45.0430
4.9393
1.0000
48
46
44
42
[ppm]


Me
7.507
7.495
7.363
7.361
7.358
7.356
7.352
7.350
7.348
7.332
7.330
7.260
4.226
4.224
4.212
4.210
4.197
4.196
4.183
4.181
4.121
4.107
4.104
4.090
3.337
3.323
3.309
3.176
3.169
3.162
1.286
1.271
1.257
1.254
1.239
1.225
1.117
1.103
1.095
1.081
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.16
6.12
2.04
2.04
1.00
1.02
6.30
3.15

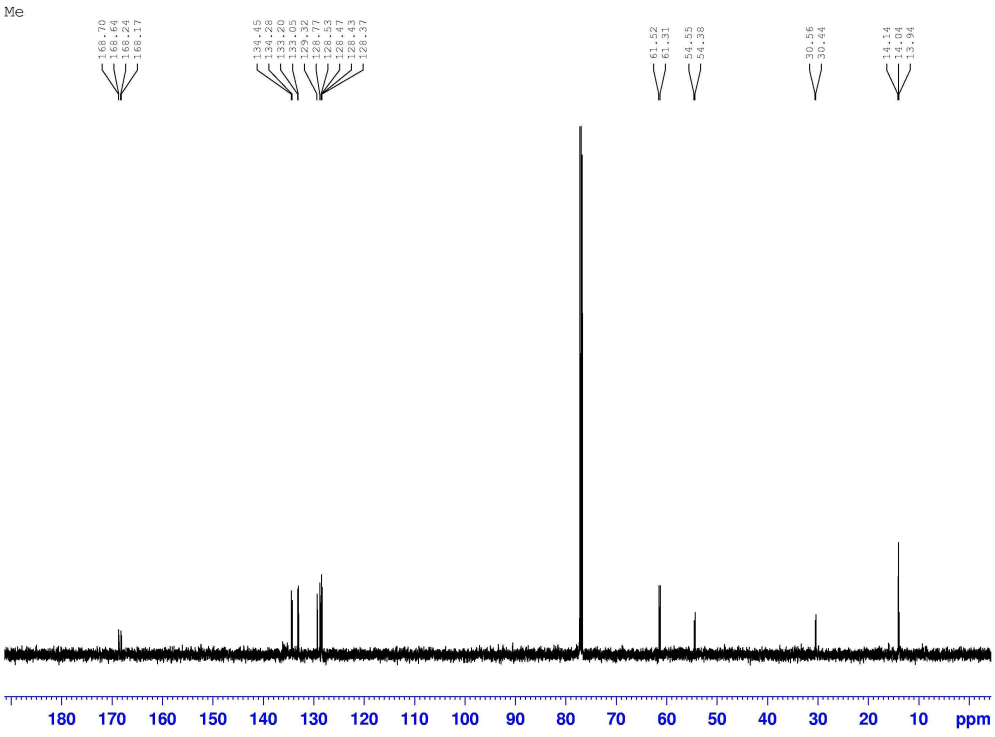
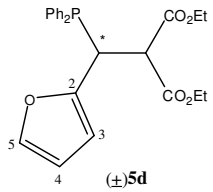
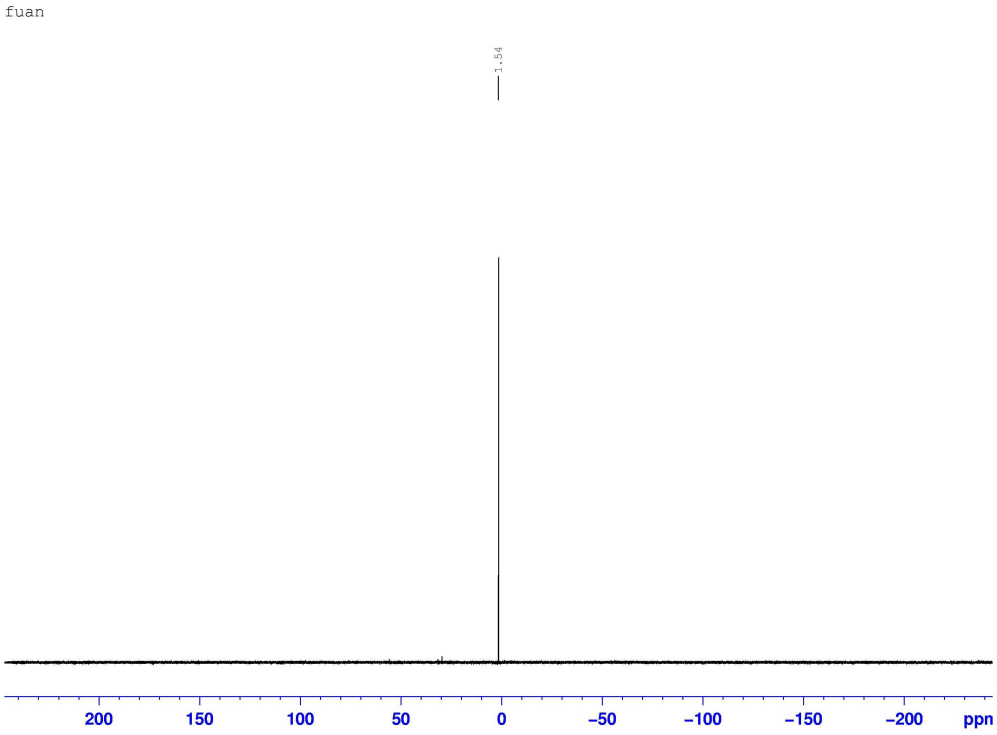
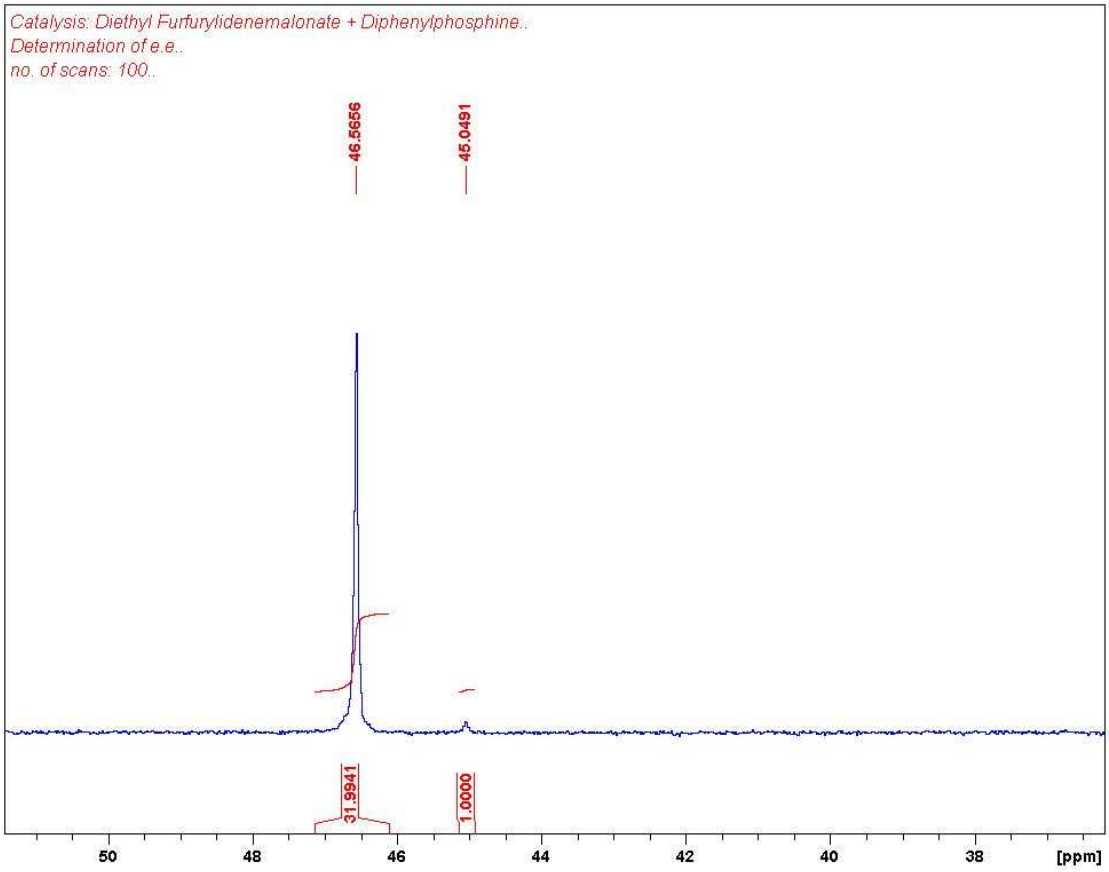

Me
168.70
168.64
168.24
168.17
134.45
134.28
133.20
133.05
129.32
128.77
128.53
128.47
128.43
128.37
61.52
61.31
54.55
54.38
30.56
30.44
14.14
14.04
13.94
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

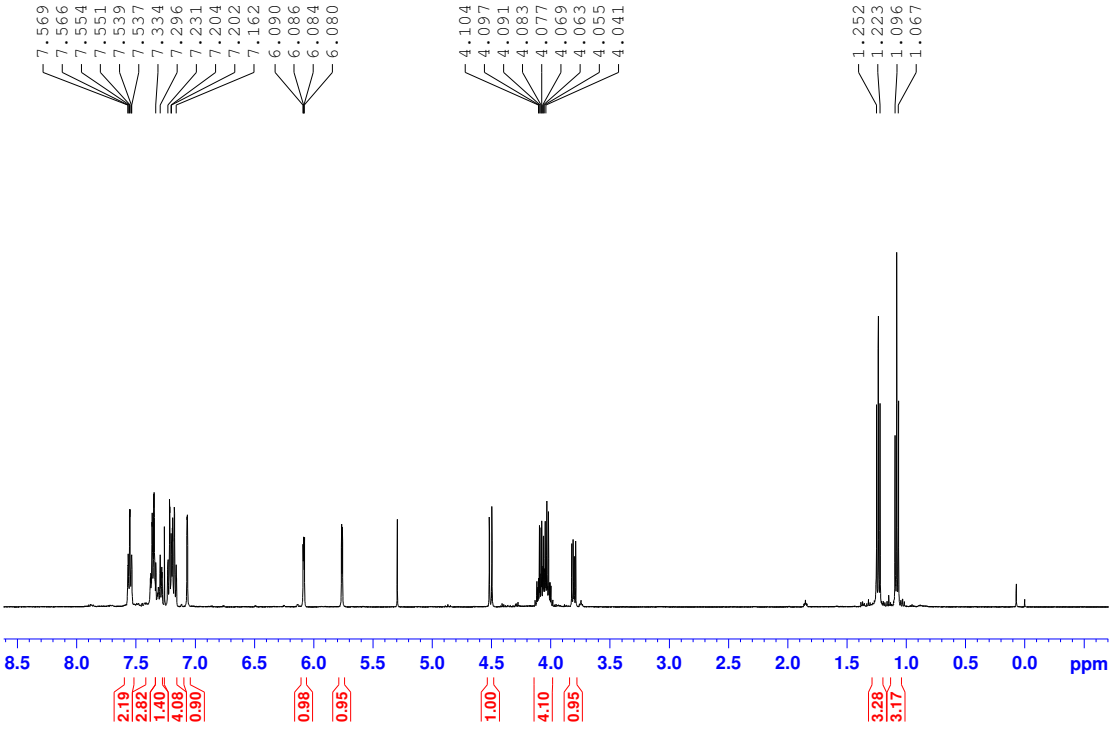
Table 2, **Entry 4**: 

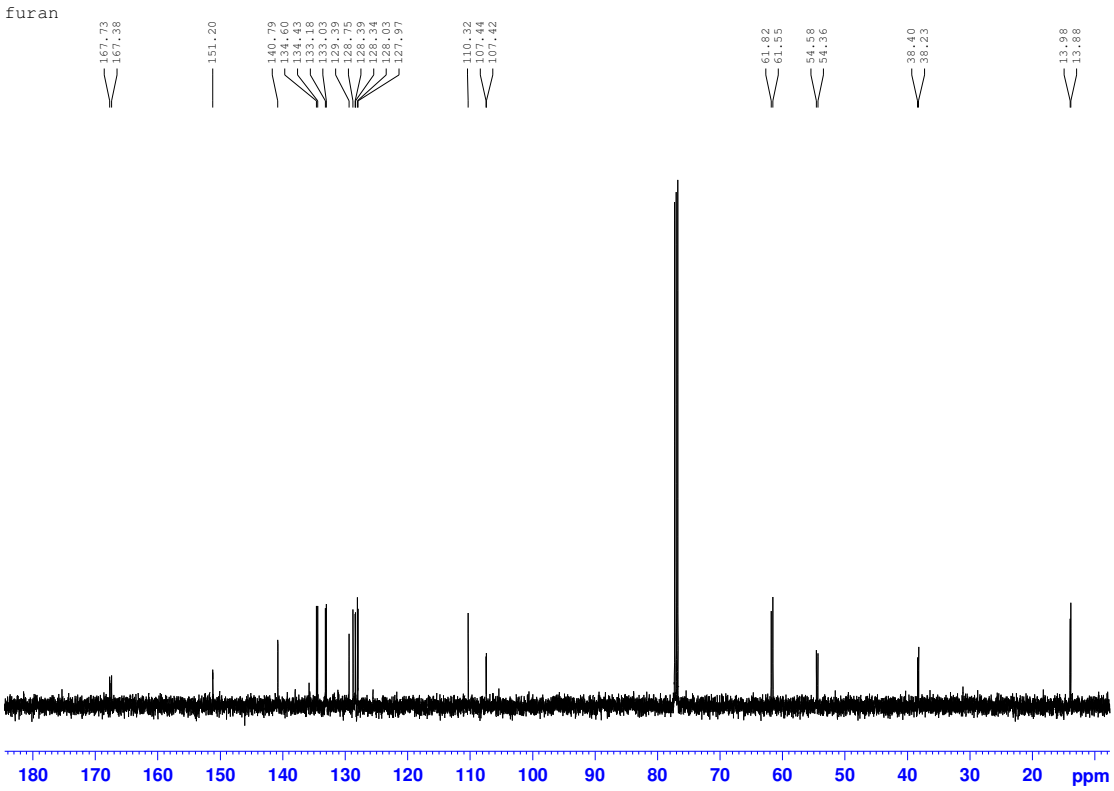
(±)5d




Catalysis: Diethyl Furfurylidenemalonate + Diphenylphosphine..
Determination of e.e..
no. of scans: 100..
46.5656
45.0491
31.9941
1.0000
50
48
46
44
42
40
38
[ppm]

furan


7.569
7.566
7.554
7.551
7.539
7.537
7.334
7.296
7.231
7.204
7.202
7.162
6.090
6.086
6.084
6.080
4.104
4.097
4.091
4.083
4.077
4.069
4.063
4.055
4.041
1.252
1.223
1.096
1.067
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.19
2.82
1.40
4.08
0.90
0.98
0.95
1.00
4.10
0.95
3.28
3.17



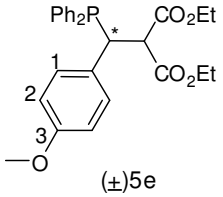
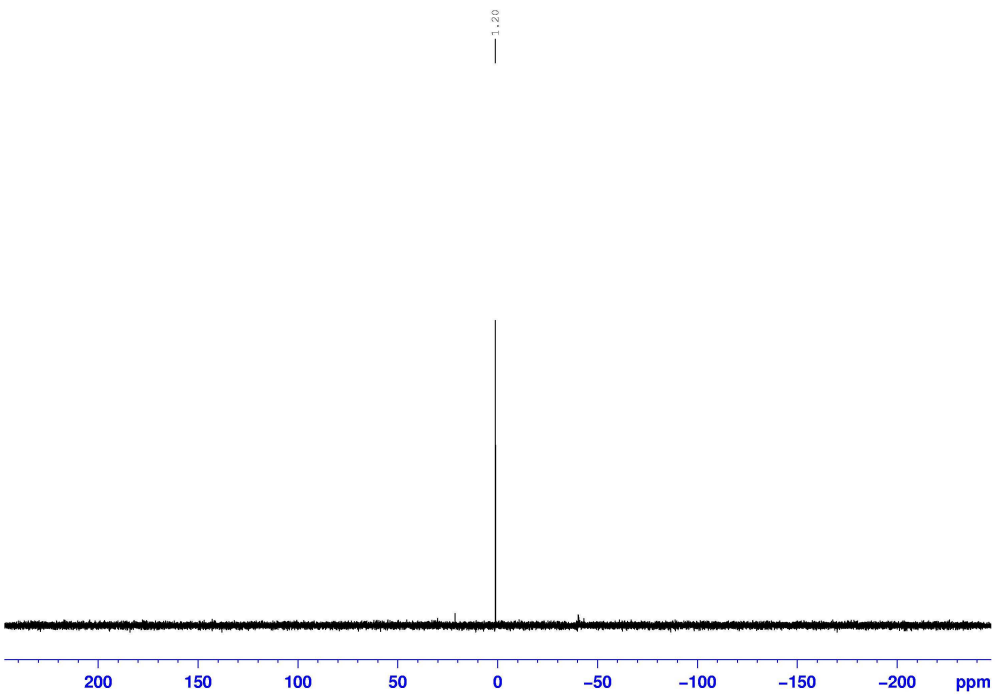
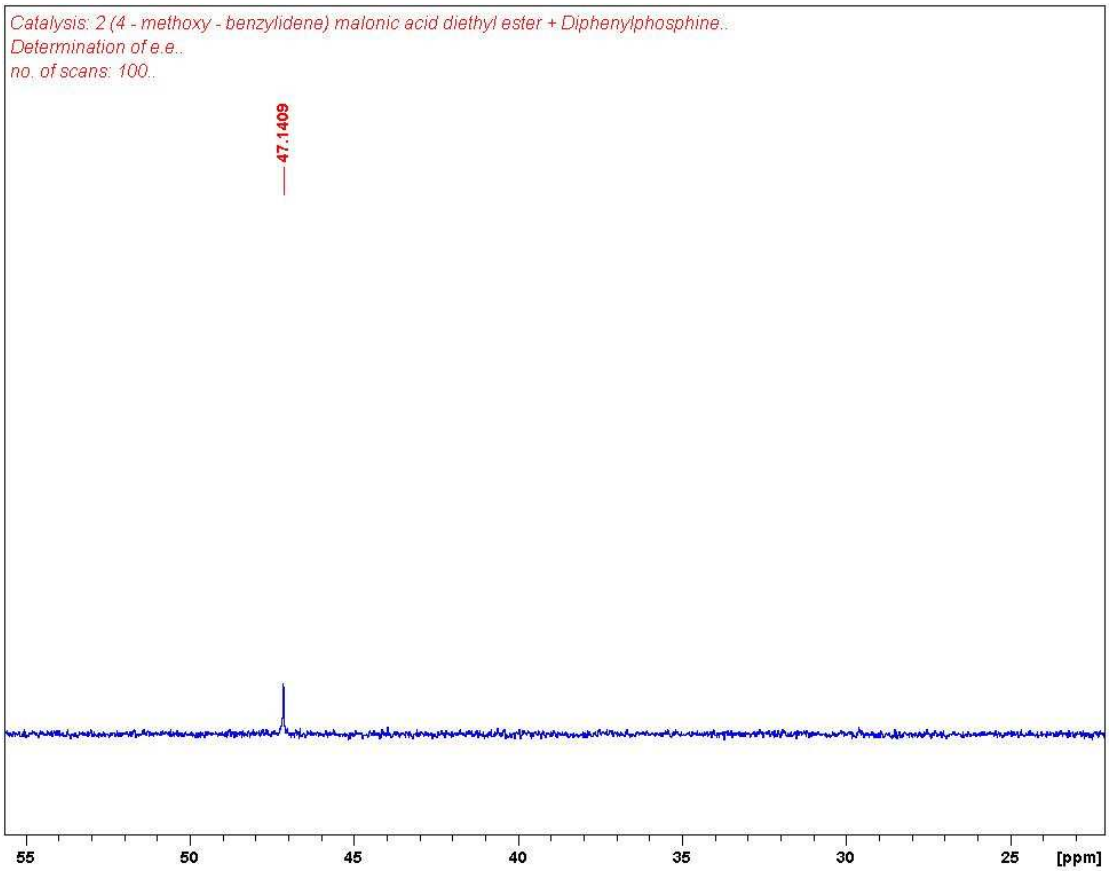


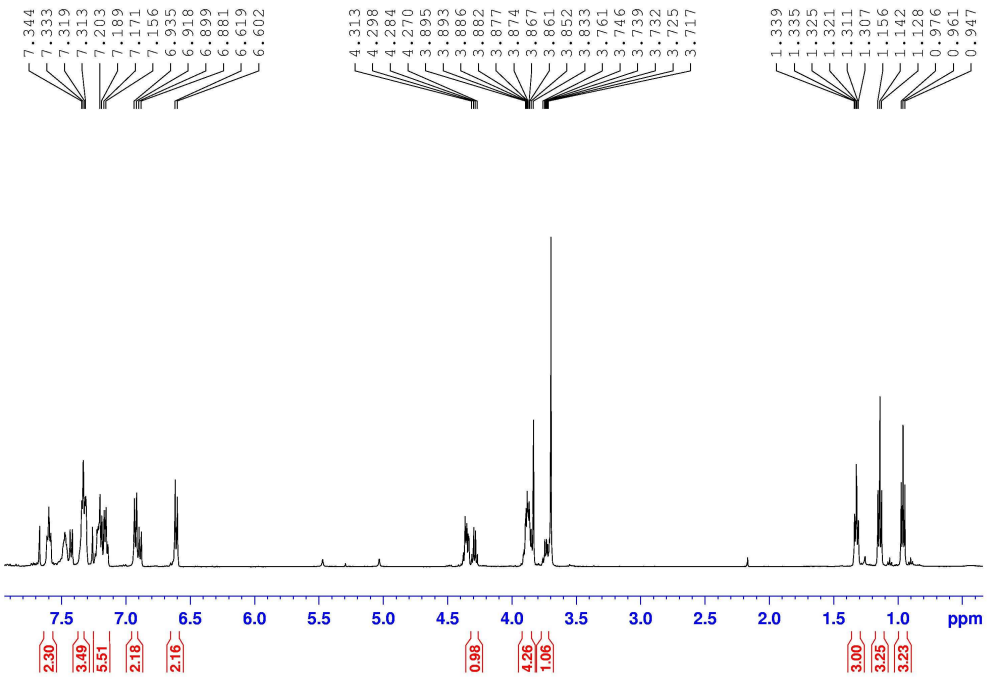
Table 2, **Entry 5**: (±)5e

P-OMe-Ph

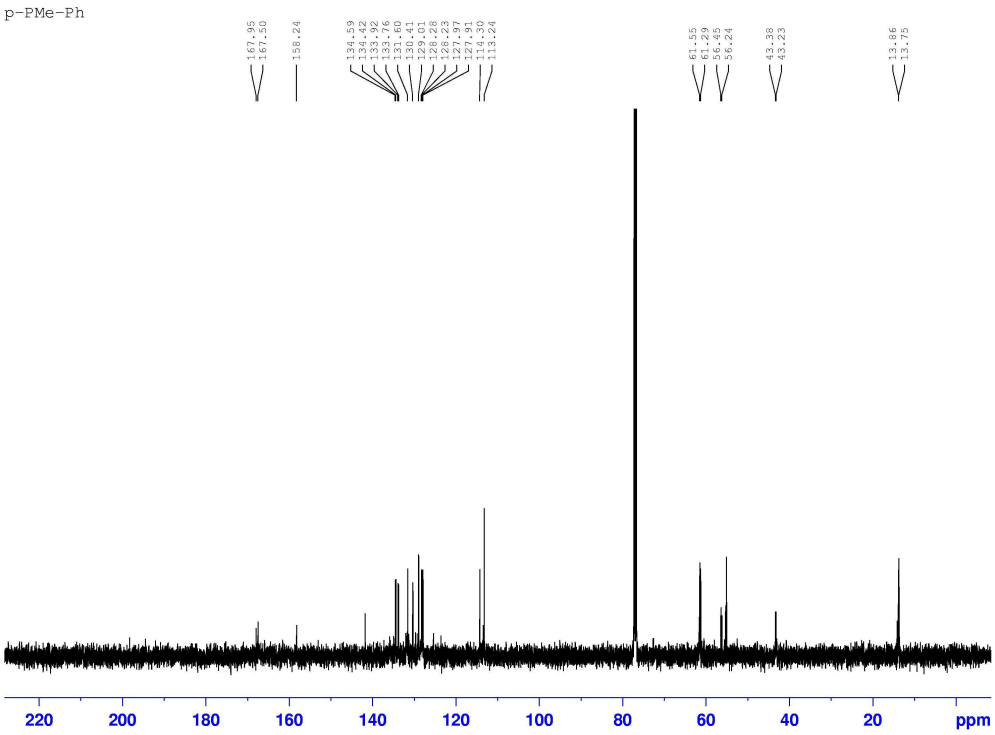

1.20
200
150
100
50
0
-50
-100
-150
-200
ppm


Catalysis: 2 (4 - methoxy - benzylidene) malonic acid diethyl ester + Diphenylphosphine..
Determination of e.e..
no. of scans: 100..
47.1409
55
50
45
40
35
30
25
[ppm]

p-OMe-Ph



p-PMe-Ph



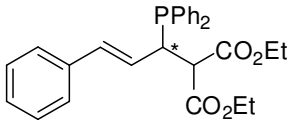
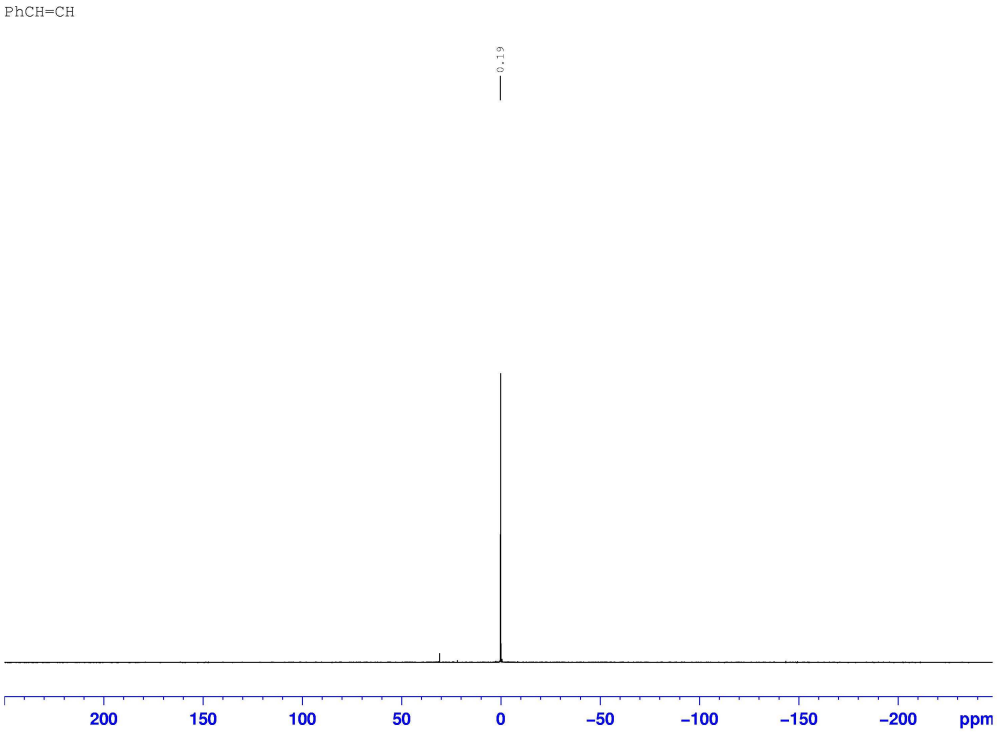
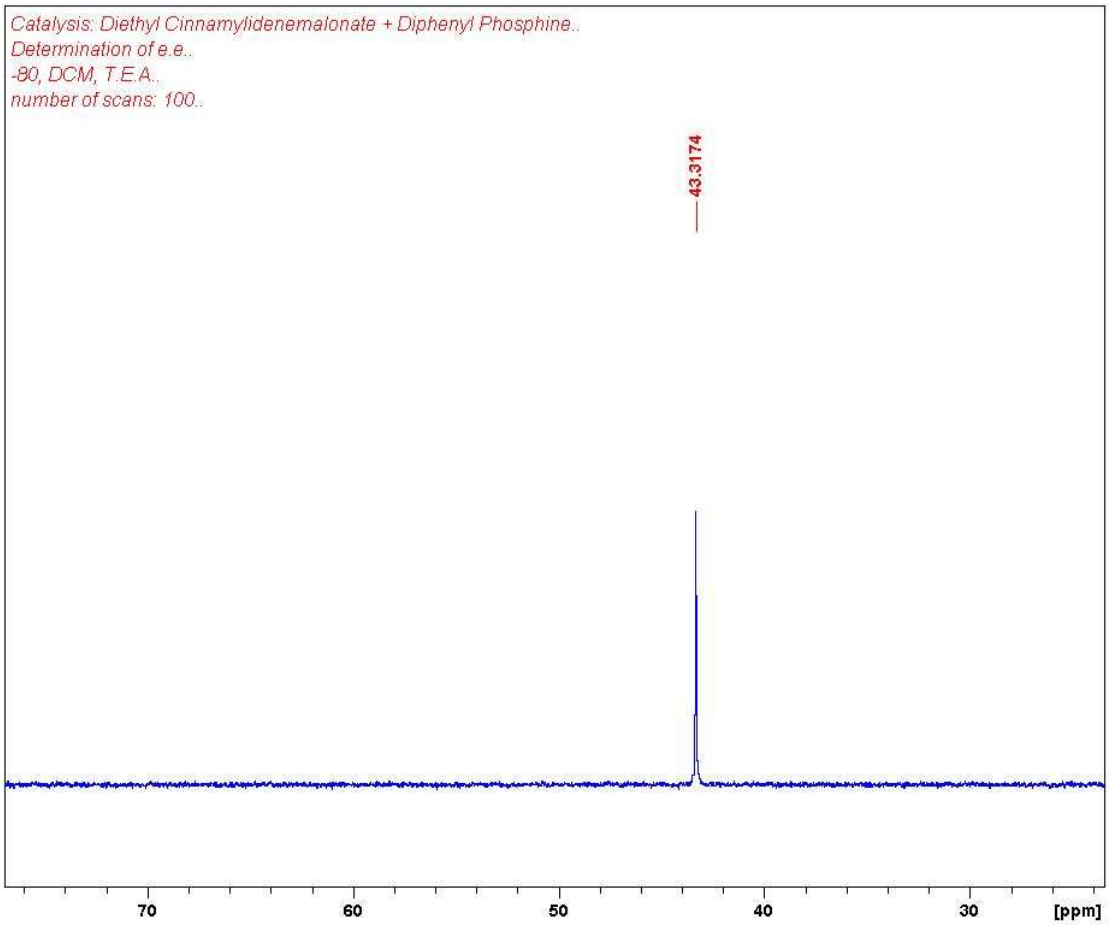
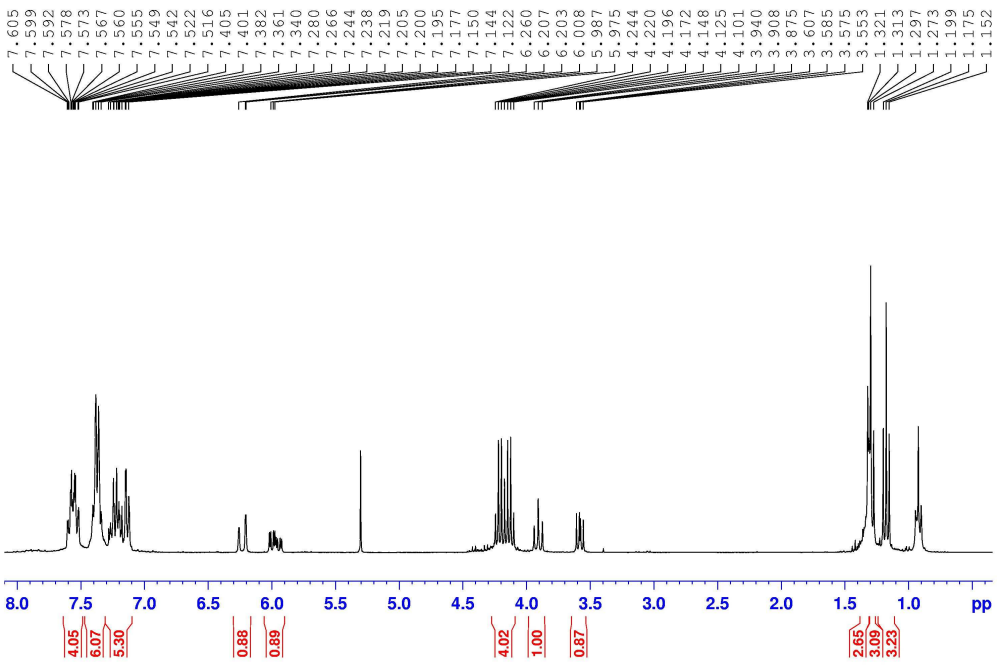


Table 2, **Entry 6**: **(±)5f**

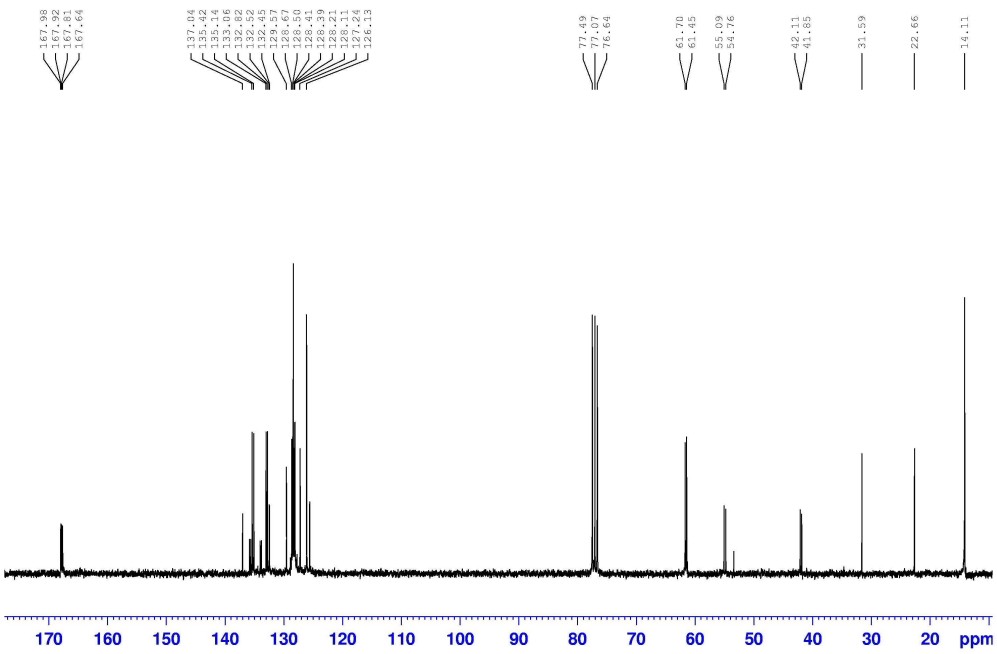




1H: Diethyl Cinnamylidene..



13C: Diethyl Cinnamylidene..



Crystal data and structure refinement for 7a.

Empirical formula	C40 H43 I N O4 P Pd	
Formula weight	866.02	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.6549(7) Å	α= 90°.
	b = 13.8040(10) Å	β= 90°.
	c = 28.1935(19) Å	γ = 90°.
Volume	3757.5(5) $Å^3$	
Z	4	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	1.398 mm^{-1}	
F(000)	1744	
Crystal size	0.40 x 0.04 x 0.04 mm^3	
Theta range for data collection	1.64 to 29.62°.	
Index ranges	-12<=h<=13, -18<=k<=14, -31<=l<=37	
Reflections collected	21296	
Independent reflections	8971 [R(int) = 0.0781]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9462 and 0.6047	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8971 / 0 / 438	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0557, wR2 = 0.1120	
R indices (all data)	R1 = 0.1074, wR2 = 0.1495	
Absolute structure parameter	-0.03(3)	
Largest diff. peak and hole	0.937 and -1.806 $e.Å^{-3}$	