A readily accessible and modular carbohydrate-derived thioether/selenoether-phosphite ligand library for Pd-catalyzed asymmetric allylic substitutions

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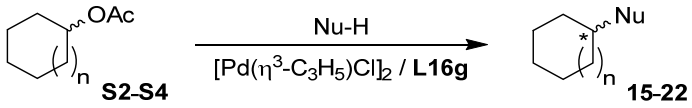
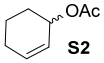
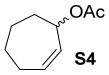
Table of Contents

1. Full set of results for the asymmetric allylic alkylation of cyclic substrates S2-S4 using ligand L16g



Entry	Substrate	Nu-H	Product	% Conv	% ee
1		$MeCH(CO_2Me)_2$	**15**	100	88 (+)
2	**S2**	$(allyl)CH(CO_2Me)_2$	**16**	100	86 (-)
3	**S2**	$(propargyl)CH(CO_2Me)_2$	**17**	100	90 (*S*)
4	**S2**	$CH_2(COMe)_2$	**18**	100	88 (-)
5		$CH_2(CO_2Me)_2$	**19**	100	82 (-)
6	**S3**	$(propargyl)CH(CO_2Me)_2$	**20**	100	80 (*S*)
7		$CH_2(CO_2Me)_2$	**21**	100	91 (*S*)
8	**S4**	$(propargyl)CH(CO_2Me)_2$	**22**	100	91 (*S*)

Reactions were run at 23 °C with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.5 mol %), CH_2Cl_2 as solvent, ligand (1.1 mol %), BSA (3 equiv), and KOAc (3 mol%). Conversions measured by ^{1}H-NMR after 6 h.

2. NMR spectra of [Pd(η^3-1,3-cyclohexenyl)(L10f)]BF_4 (29)

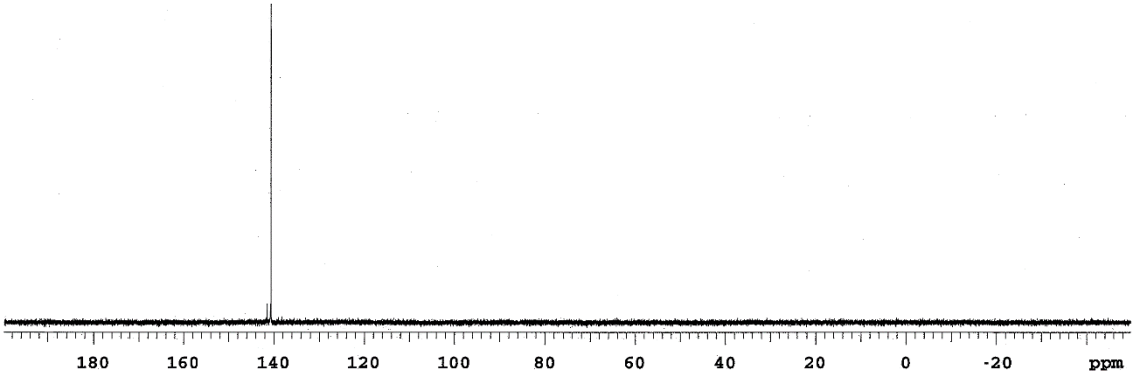


Figure SI.1. ^{31}P NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10f**)]BF_4 (**29**) in CD_2Cl_2 at 218 K.

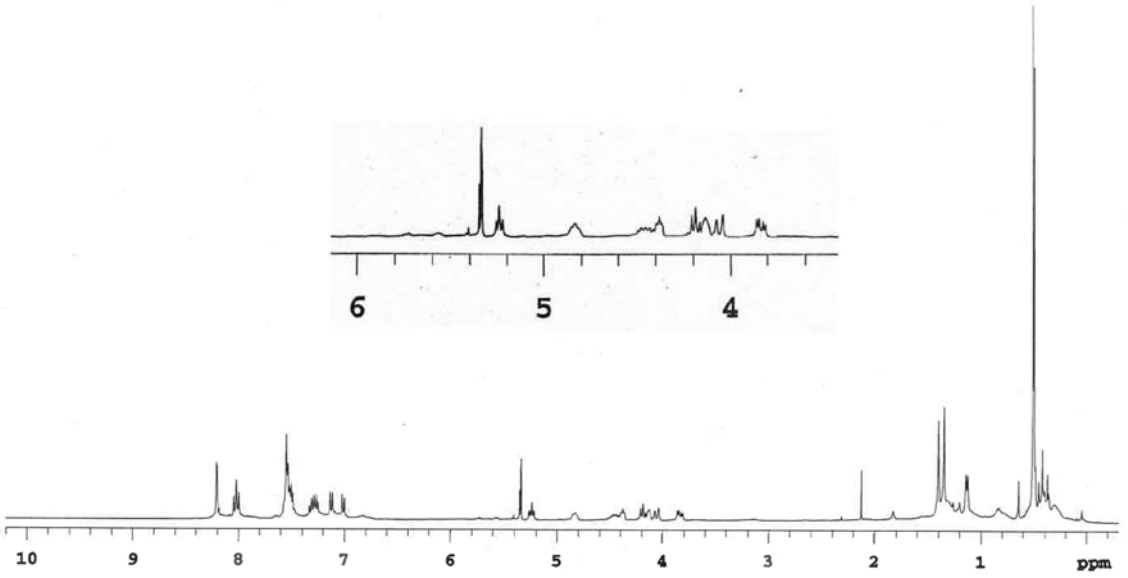


Figure SI.2. ^{1}H NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10f**)]BF_4 (**29**) in CD_2Cl_2 at 218 K.

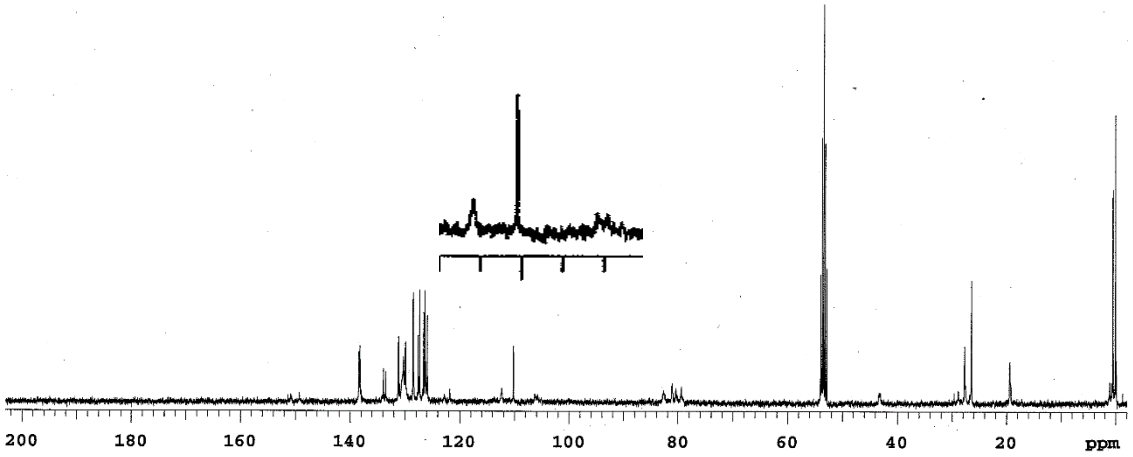


Figure SI.3. ^{13}C NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10f**)]BF_4 (**29**) in CD_2Cl_2 at 218 K.

3. NMR spectra of [Pd(η^3-1,3-cyclohexenyl)(L10g)]BF_4 (30)

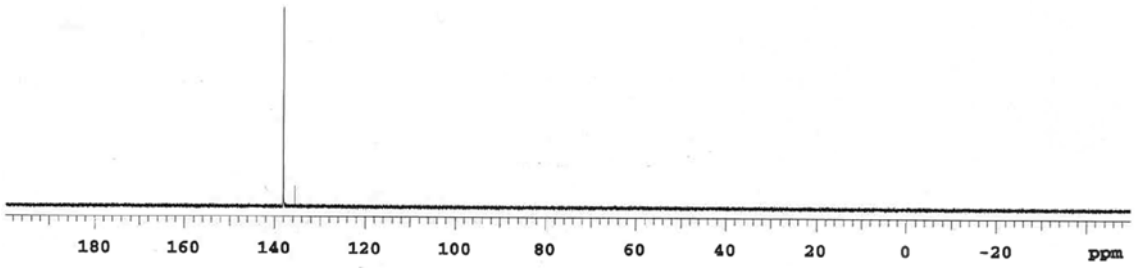


Figure SI.4. ^{31}P NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10g**)]BF_4 (**30**) in CD_2Cl_2 at rt.

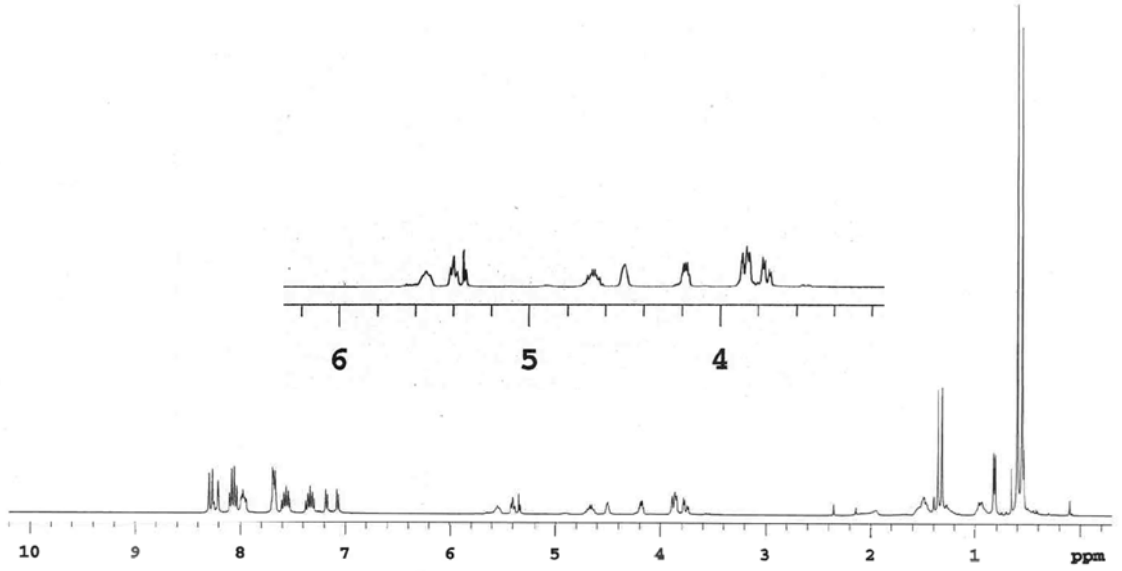


Figure SI.5. ^{1}H NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10g**)]BF_4 (**30**) in CD_2Cl_2 at rt.

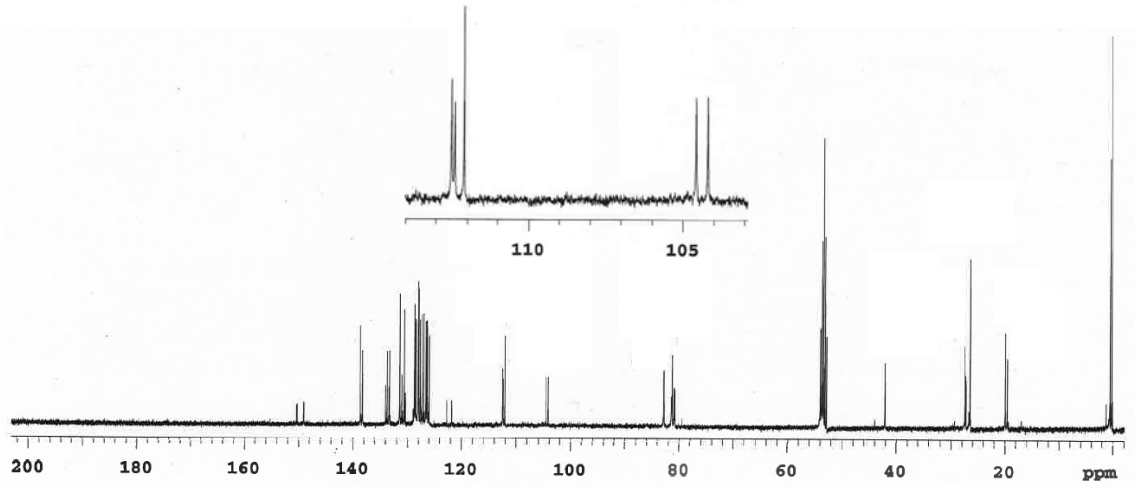


Figure SI.6. ^{13}C NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L10g**)]BF_4 (**30**) in CD_2Cl_2 at rt.

4. NMR spectra of [Pd(η^3-1,3-cyclohexenyl)(L1f)]BF_4 (31)

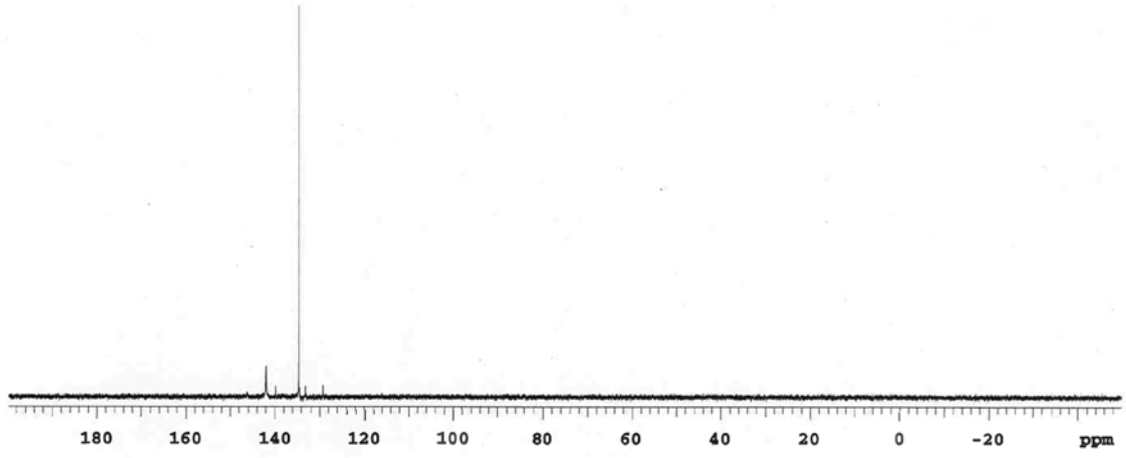


Figure SI.7. ^{31}P NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L1f**)]BF_4 (**31**) in CD_2Cl_2 at rt.

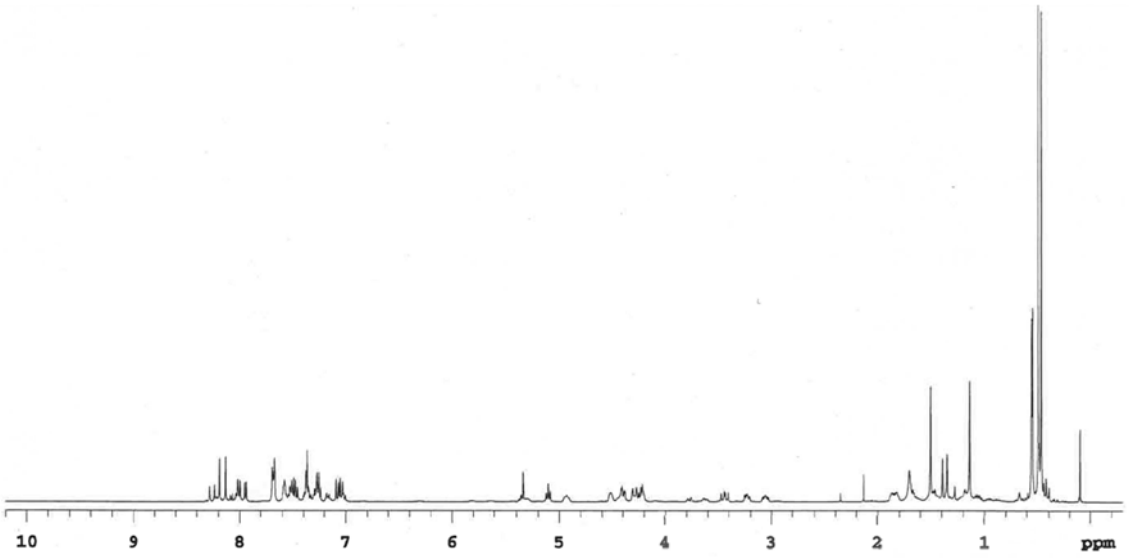


Figure SI.8. ^{1}H NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L1f**)]BF_4 (**31**) in CD_2Cl_2 at rt.

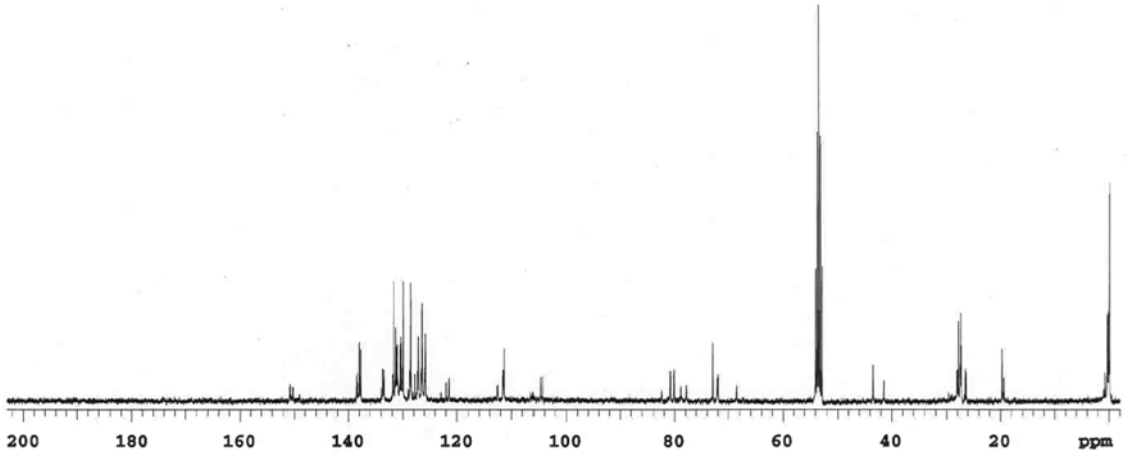


Figure SI.9. ^{13}C NMR spectrum of [Pd(η^3-1,3-cyclohexenyl)(**L1f**)]BF_4 (**31**) in CD_2Cl_2 at rt.

5. NMR spectra of [Pd(η³-1,3-diphenylallyl)(L10f)]BF_4 (32)

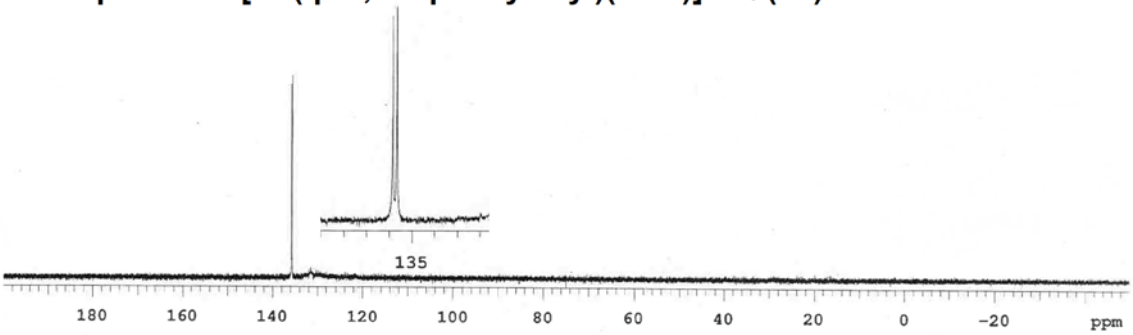


Figure SI.10. ^{31}P NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10f**)]BF_4 (**32**) in CD_2Cl_2 at 233 K.

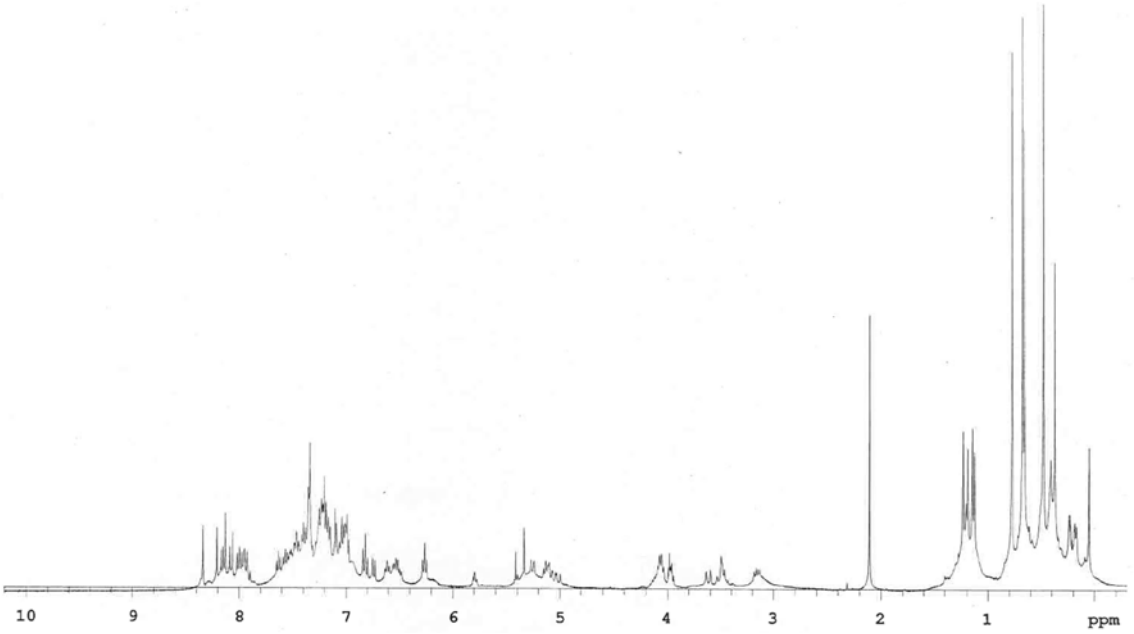


Figure SI.11. ^{1}H NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10f**)]BF_4 (**32**) in CD_2Cl_2 at 233 K.

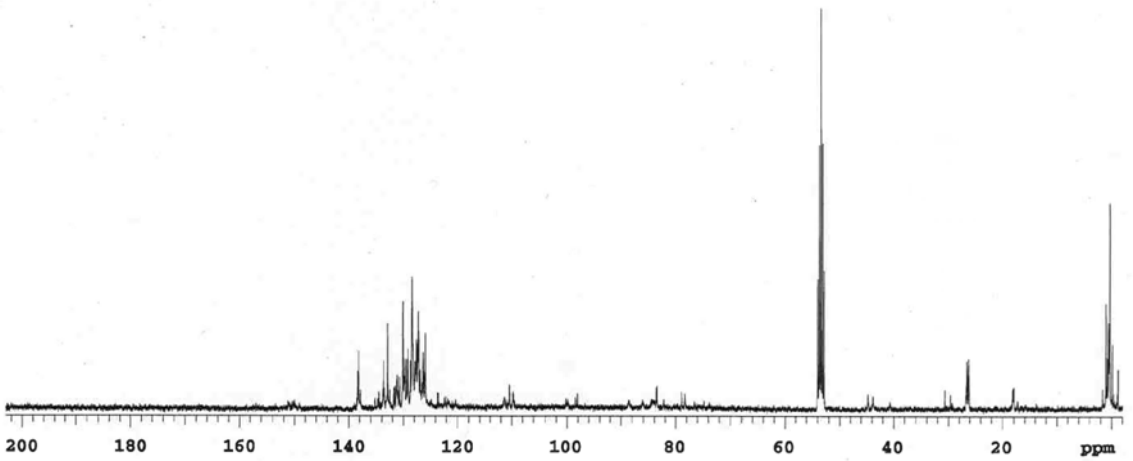


Figure SI.12. ^{13}C NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10f**)]BF_4 (**32**) in CD_2Cl_2 at 233 K.

6. NMR spectra of [Pd(η³-1,3-diphenylallyl)(L10g)]BF_4 (33)

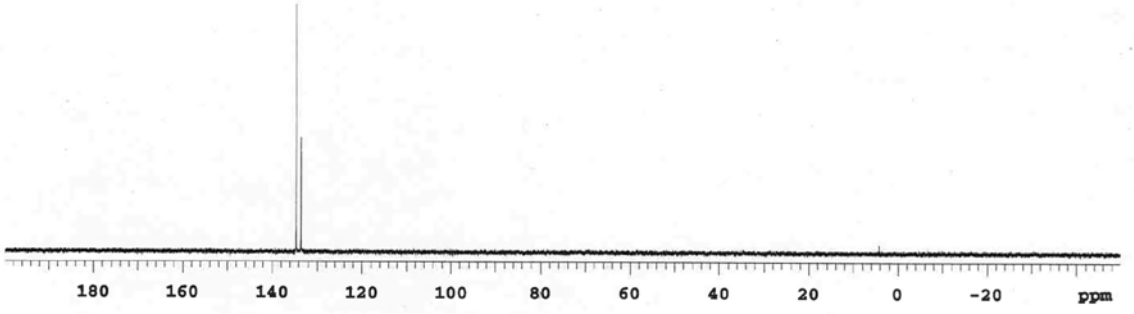


Figure SI.13. ^{31}P NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10g**)]BF_4 (**33**) in CD_2Cl_2 at rt.

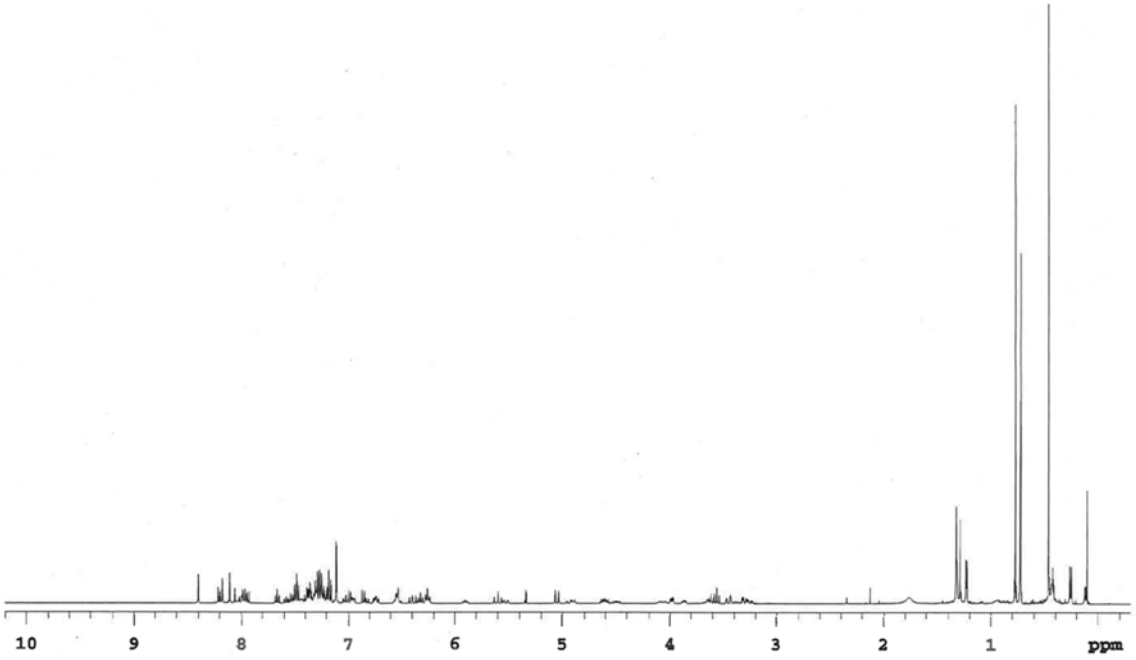


Figure SI.14. ^{1}H NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10g**)]BF_4 (**33**) in CD_2Cl_2 at rt.

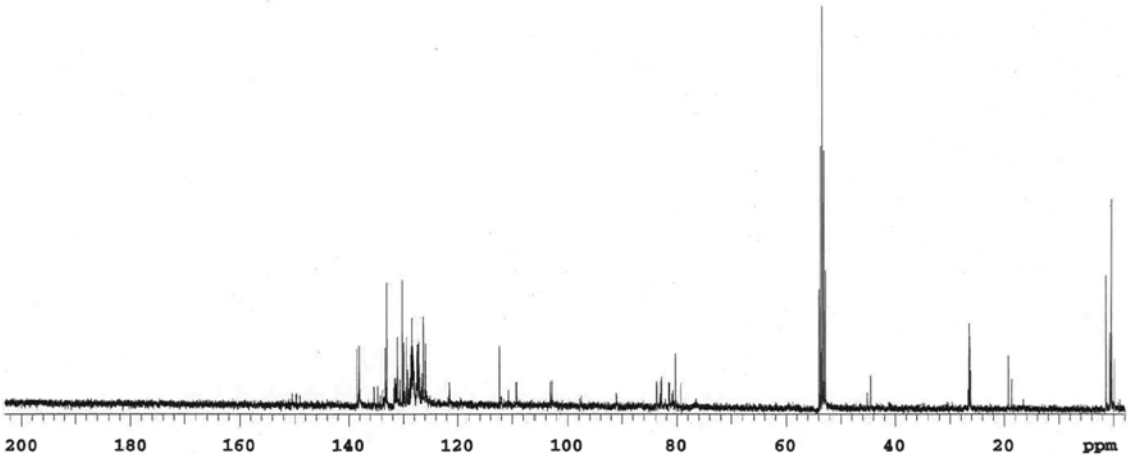


Figure SI.15. ^{31}C NMR spectrum of [Pd(η³-1,3-diphenylallyl)(**L10g**)]BF_4 (**33**) in CD_2Cl_2 at rt.

7. NOE contacts for Pd-η³-allyl intermediate 31

The NOESY spectrum showed interaction between one of the TMS group of the biaryl phosphite moiety and both, the terminal allylic proton *trans* to the sulfur and the central allylic proton. There was also a NOE contact corresponding to the other TMS of the phosphite moiety with the methylenic proton of the carbon next to the thioether group. All these NOE contacts are in agreement with an *exo* disposition.

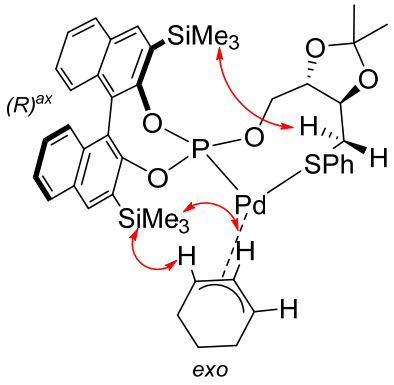
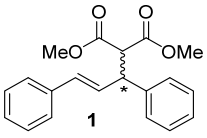


Figure SI.16. Selected NOE contacts from NOESY spectra for the major isomer of Pd-η³-allyl intermediate **31**.

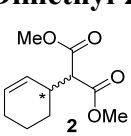
8. Characterization details and methods for enantiomeric excess determination of substitution products

Dimethyl 2-(1,3-diphenylallyl)malonate (1).[1,2] Enantiomeric excess determined by



HPLC using Chiralcel OJ-H column (87% hexane/2-propanol, flow 0.5 mL/min). t_R 32.8 min (*R*); t_R 38.6 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 3.52 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.95 (d, 1H, CH, *J*=10.9 Hz), 4.26 (m, 1H, CH), 6.34 (dd, 1H, CH=, *J*=16.0 Hz, *J*=8.4 Hz), 6.48 (d, 1H, CH=, *J*=16.0 Hz), 7.1-7.4 (m, 10H, CH=).

Dimethyl 2-(1,3-cyclohexanylallyl)malonate (2).[2] Enantiomeric excess determined by



GC using Chiralsil-Dex CB column (77 kPa H_2, Isotherm at 110 ºC). t_R 20.1 min (*S*); t_R 20.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.36 (m, 1H, CH_2), 1.56 (m, 1H, CH_2), 1.70 (m, 1H, CH_2), 1.76 (m, 1H, CH_2), 1.99 (m, 2H, CH_2), 3.29 (d, 1H, CH, *J*=9.6 Hz), 3.73 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 5.22 (m, 1H, CH=), 5.79 (m, 1H, CH=).

Diethyl 2-(1,3-diphenylallyl)malonate (3).[3] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (87% hexane/2-propanol, flow 0.5 mL/min). t_R 17.5 min (*R*); t_R 20.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.01 (t, 6H, CH_3, *J*=6.8 Hz), 3.92 (d, 1H, CH, *J*=11.2 Hz), 4.19 (q, 4H, CH_2, *J*=7.2 Hz), 4.23 (m, 1H, CH), 6.34 (dd, 1H, CH=, *J*=20 Hz, *J*=10 Hz), 6.41 (d, 1H, CH=,*J*=18 Hz), 7.1-7.4 (m, 10H, CH=).

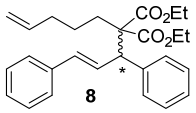
Dibenzyl 2-(1,3-diphenylallyl)malonate (4).[3] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (95% hexane/2-propanol, flow 1 mL/min). t_R 94.0 min (*R*); t_R 107.3 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 4.03 (d, 1H, CH, *J*=9.6 Hz), 4.29 (t, 1H, CH, *J*=10 Hz), 4.92 (s, 2H, CH_2), 5.09 (s, 2H, CH_2), 6.28 (dd, 1H, CH=, *J*=24 Hz, *J*=8.4 Hz), 6.40 (d, 1H, CH=, *J*=17 Hz), 7.0-7.4 (m, 20H, CH=).

Dimethyl 2-(1,3-diphenylallyl)-2-methylmalonate (5).[2] Enantiomeric excess determined by HPLC using Chiralcel OD-H column (90% hexane/2-propanol, flow 1 mL/min, λ = 254 nm). t_R 9.9 min (*S*); t_R 12.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.48 (s, 3H, CH_3), 3.62 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 4.29 (d, 1H, CH, *J*=8.8 Hz), 6.46 (d, 1H, CH=, *J*=16 Hz), 6.68 (dd, 1H, CH=, *J*=16 Hz, *J*=8.8 Hz), 7.1-7.4 (m, 10H, CH=).

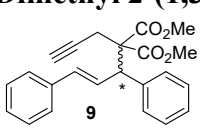
Dimethyl 2-allyl-2-(1,3-diphenylallyl)malonate (6).[4] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (87% hexane/2-propanol, flow 0.5 mL/min, λ = 254 nm). t_R 19.4 min (*S*); t_R 26.1 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 2.48 (dd, 1H, CH_2, *J*=14 Hz, *J*=8.8 Hz), 2.67 (dd, 1H, CH_2, *J*=14 Hz, *J*=8 Hz), 3.66 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 4.20(d, 1H, CH, *J*=8.8 Hz), 5.06 (m, 2H, CH_2=), 5.77 (m, 1H, CH=), 6.40 (d, 1H, CH=, *J*=15.6 Hz), 6.77 (dd, 1H, CH=, *J*=16.4 Hz, *J*=8.4 Hz), 7.2-7.4 (m, 10H, CH=).

Diethyl 2-(but-3-en-1-yl)-2-(1,3-diphenylallyl)malonate (7).[5] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (87% hexane/2-propanol, flow 0.15 mL/min, λ = 254 nm). t_R 29.9 min (*S*); t_R 34.2 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.22 (m, 6H, CH_3), 1.97 (m, 2H, CH_2), 2.08 (m, 2H, CH_2), 3.98 (m, 2H, CH_2), 4.17 (m, 3H, CH_2), 4.89 (m, 2H, CH_2=), 5.68 (m, 1H, CH=), 6.32 (d, 1H, CH=, *J*=16.0 Hz), 6.76 (dd, 1H, CH=, *J*=16.0 Hz, *J*=9.2 Hz), 7.1-7.4 (m, 10H, CH=).

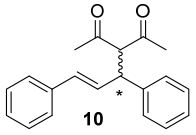
Diethyl 2-(1,3-diphenylallyl)-2-(pent-4-en-1-yl)malonate (8).[5] Enantiomeric excess determined by HPLC using Chiralcel IA column (99% hexane/2-propanol, flow 0.5 mL/min, λ = 254 nm). t_R 12.3 min (*S*); t_R 14.4 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.20 (t, 3H, CH_3, *J*=6.4 Hz), 1.26 (t, 3H, CH_3, *J*=6.4 Hz), 1.31 (m, 1H, CH_2), 1.45 (m, 1H, CH_2), 1.74 (m, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.96 (m, 2H, CH_2), 4.18 (m, 5H, CH_2-O, CH), 4.94 (m, 2H, CH_2=), 5.72 (m, 1H, CH=), 6.36 (d, 1H, CH=, *J*=15.6 Hz), 6.78 (dd, 1H, CH=, *J*=15.6 Hz, *J*=8.8 Hz), 7.1-7.4 (m, 10H, CH=).



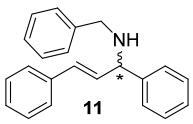
Dimethyl 2-(1,3-diphenylallyl)-2-(prop-2-yn-1-yl)malonate (9).[5] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (90% hexane/2-propanol, flow 0.5 mL/min, λ = 254 nm). t_R 19.5 min (*S*); t_R 41.7 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 2.13 (m, 1H, CH), 2.64 (dd, 1H, CH_2, *J*=17.2 Hz, *J*=2.4 Hz), 2.82 (dd, 1H, CH_2, *J*=14.2 Hz, *J*=2.8 Hz), 3.71 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 4.45 (d, 1H, CH, *J*=8.4 Hz), 6.46 (d, 1H, d, CH=, *J*=15.6 Hz,), 6.79 (dd, 1H, CH=, *J*=8.4 Hz, *J*=8.4 Hz), 7.31 (m, 10H, CH=).



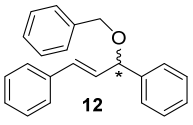
(1,3-Diphenylallyl)pentane-2,4-dienone (10).[4,6] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (98% hexane/2-propanol, flow 1 mL/min). t_R 53.1 min (*R*); t_R 56.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.93 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.34 (m, 2H, CH), 6.20 (dm, 1H, CH=, *J*=15.6 Hz), 6.44 (d, 1H, CH=, *J*=15.6 Hz), 7.1-7.4 (m, 10H, CH=).



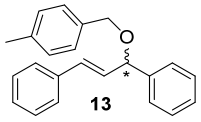
***N*-Benzyl-1,3-diphenylprop-2-en-1-amine (11)**.[7] Enantiomeric excess determined by HPLC using Chiralcel OD-H column (99% hexane/2-propanol, flow 0.5 mL/min). t_R 22.4 min (*R*); t_R 26.2 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 3.77 (d, 1H, NH, *J*= 13.2 Hz), 3.80 (d, 1H, CH, *J*= 13.2 Hz), 4.41 (m, 2H, CH_2), 6.34 (dd, 1H, CH=, *J*= 16 Hz, *J*= 7.2 Hz), 6.57 (d, 1H, CH=, *J*= 16 Hz), 7.12-7.45 (m, 15H, CH=).



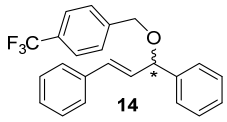
1,3-Diphenyl-3-(benzyloxy)-1-propene (12).[8] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (98% hexane/2-propanol, flow 0.75 mL/min). t_R 18.2 min (*S*); t_R 21.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 4.64 (m, 2H, CH_2), 5.08 (d, 1H, CH, *J*=6.8 Hz), 6.41 (dd, 1H, CH=, *J*=16.0 Hz, *J*=7.2 Hz), 6.68 (d, 1H, CH=, *J*=16.0 Hz), 7.1-7.5 (m, 15H, CH=).



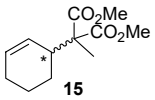
1,3-Diphenyl-3-(4-methylbenzyloxy)-1-propene (13).[8] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (98% hexane/2-propanol, flow 0.75 mL/min). t_R 16.8 min (+); t_R 24.1 min (-). ^{1}H NMR ($CDCl_3$), δ: 2.44 (s, 3H, CH_3), 4.63 (m, 2H, CH_2), 5.08 (d, 1H, CH, *J*=7.2 Hz), 6.43 (dd, 1H, CH=, *J*=16.4 Hz, *J*=7.6 Hz), 6.70 (d, 1H, CH=, *J*=16.0 Hz), 7.1-7.5 (m, 14H, CH=).


13

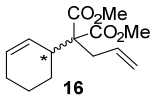
1,3-Diphenyl-3-(4-trifluoromethylbenzyloxy)-1-propene (14).[8] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (96% hexane/2-propanol, flow 0.75 mL/min). t_R 20.8 min (+); t_R 25.2 min (-). ^{1}H NMR ($CDCl_3$), δ: 4.67 (m, 2H, CH_2), 5.06 (d, 1H, CH, *J*=7.6 Hz), 6.39 (dd, 1H, CH=, *J*=16.4 Hz, *J*=7.2 Hz), 6.70 (d, 1H, CH=, *J*=16.0 Hz), 7.1-7.7 (m, 14H, CH=).


14

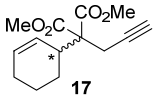
Dimethyl 2-(1,3-cyclohexanylallyl)-2-methylmalonate (15).[9,10] Enantiomeric excess determined by HPLC using Chiralpak IC column (99.5% hexane/2-propanol, flow 0.5 mL/min, λ = 226 nm). t_R 36.4 min (-); t_R 39.8 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 3H, CH_3), 1.51 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 2.99 (m, 1H, CH), 3.68 (s, 6H, CH_3), 5.43 (m, 1H, CH=), 5.74 (m, 1H, CH=).


15

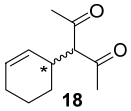
Dimethyl 2-allyl-2-(1,3-cyclohexanylallyl)malonate (16).[9] Enantiomeric excess determined by HPLC using Chiralpak IC column (87% hexane/2-propanol, flow 0.5 mL/min, λ = 226 nm). t_R 15.3 min (-); t_R 17.0 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.49 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 2.86 (m, 1H, CH), 3.65 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 5.06 (m, 2H, CH_2=), 5.71 (m, 3H, CH=).


16

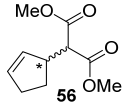
Dimethyl 2-propargyl-2-(1,3-cyclohexanylallyl)malonate (17).[11] Enantiomeric excess determined by GC using Chiraldex β-DM column (90 kPa H_2, 110 ºC, 40 min- 5 ºC/min- 150 ºC). t_R 50.0 min (*S*); t_R 51.2 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.33 (m, 2H, CH_2), 1.52 (m, 1H), 1.77 (m, 2H, CH_2), 1.92 (m, 1H, CH_2), 2.00 (m, 1H, CH), 3.03 (m, 2H, CH_2), 3.09 (m, 1H, CH), 3.68 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 5.67 (m, 1H, CH=), 5.74 (m, 1H, CH=).


17

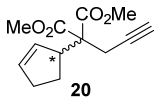
(1,3-cyclohexanylallyl)pentane-2,4-dienone (18).[9] Enantiomeric excess determined by GC using Chiralsil-Dex CB column (77 kPa H_2, Isotherm at 100 ºC). t_R 21.6 min (-); t_R 22.4 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.48 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.91 (m, 2H, CH_2),2.09 (s, 3H, CH_3),2.12 (s, 3H, CH_3), 2.94 (m, 1H, CH), 3.54 (d, 1H, CH, *J*=10.8 Hz), 5.30 (m, 1H, CH=), 5.70 (m, 1H, CH=).


18

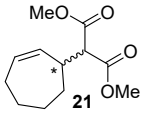
Dimethyl 2-(1,3-cyclopentanylallyl)malonate (56).[2] Enantiomeric excess determined by ^{1}H NMR using [Eu(hfc)$_3$] in C_6D_6. ^{1}H NMR ($CDCl_3$), δ: 1.61 (m, 1H, CH_2), 2.15 (m, 1H, CH_2), 2.35 (m, 2H, CH_2), 3.30 (d, 1H, CH, *J*=9.6 Hz), 3.39 (m, 1H, CH), 3.71 (s, 6H, CH_3), 5.65 (m, 1H, CH=), 5.84 (m, 1H, CH=).



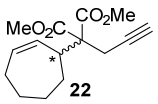
Dimethyl 2-propargyl-2-(1,3-cyclopentanylallyl)malonate (20).[11] Enantiomeric excess determined by GC using Chiraldex β-DM column (90 kPa H_2, Isotherm at 110 ºC). t_R 29.9 min (*R*); t_R 30.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.70 (m, 1H, CH_2), 2.07 (m, 2H, CH_2, CH), 2.24 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 3.61 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 5.74 (m, 1H, CH=), 5.79 (m, 1H, CH=).



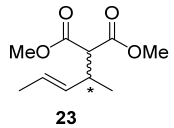
Dimethyl 2-(1,3-cycloheptanylallyl)malonate (54).[2] Enantiomeric excess determined by GC using Chiralsil-Dex CB column (90 kPa H_2, Isotherm at 110 ºC). t_R 28.8 min (*S*); t_R 29.7 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.33 (m, 1H, CH_2), 1.95 (m, 3H, CH_2), 2.17 (m, 1H, CH_2), 3.05 (m, 1H, CH_2), 3.49 (d, 1H, CH, *J*=8.4 Hz), 3.73 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 5.60 (m, 1H, CH=), 5.84 (m, 1H, CH=).



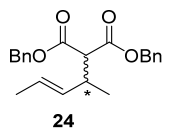
Dimethyl 2-propargyl-2-(1,3-cycloheptanylallyl)malonate (22).[11] Enantiomeric excess determined by HPLC using Chiralpak OJ-H column (98% hexane/2-propanol, flow 0.5 mL/min, λ = 226 nm). t_R 11.3 min (*R*); t_R 12.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.24 (m, 3H), 1.70 (m, 2H, CH_2), 1.83 (m, 1H, CH_2), 2.03 (m, 2H, CH_2, CH), 2.16 (m, 2H, CH_2), 2.84 (m, 2H, CH_2), 3.18 (m, 1H, CH), 3.74 (s, 6H, CH_3), 5.66 (m, 1H, CH=), 5.84 (m, 1H, CH=).



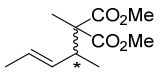
Dimethyl 2-(1,3-dimethylallyl)malonate (23).[2] Enantiomeric excess determined by GC using Chiralsil-Dex CB column (90 kPa H_2, Isotherm at 65 ºC). t_R 38.6 min (*R*); t_R 39.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.03 (d, 3H, CH_3, *J*=6.4 Hz), 1.62 (d, 3H, CH_3, *J*=6.4Hz), 2.88 (m, 1H, CH), 3.25 (d, 1H, CH_3, *J*=9.0 Hz), 3.68 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 5.31 (dd, 1H, CH=,*J*=15.2 Hz, *J*=8 Hz), 5.50 (m, 1H, CH=).



Dibenzyl 2-(1,3-dimethylallyl)malonate (24).[12] Enantiomeric excess determined by HPLC using Chiralcel IA column (98% hexane/2-propanol, flow 0.5 mL/min). t_R 21.9 min (+); t_R 23.4 min (-). ^{1}H NMR ($CDCl_3$), δ: 1.02 (d, 3H, CH_3, *J*=6.4 Hz), 1.53 (d, 3H, CH_3, *J*=6.4 Hz), 2.90 (m, 1H, CH), 3.32 (d, 1H, CH_3, *J*=6.8 Hz), 5.02 (s, 2H, CH_2), 5.13 (s, 2H, CH_2), 5.32 (m, 1H, CH=), 5.44 (m, 1H, CH=), 7.2-7.4 (m, 10H, CH=).

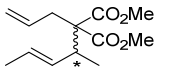


Dimethyl 2-(1,3-dimethylallyl)-2-methylmalonate (25).[13] Enantiomeric excess determined by GC using Chiralsil-Dex CB column (90 kPa H_2, Isotherm at 60 ºC). t_R 69.6 min (-); t_R 71.1 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.01 (d, 3H, CH_3, *J*=8 Hz), 1.32 (s, 3H, CH_3), 1.62 (d, 3H, CH_3, *J*=8 Hz), 2.92 (m, 1H, CH), 3.67 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 5.31 (dd, 1H, CH=,*J*=16 Hz, *J*=8 Hz), 5.47 (m, 1H, CH=).



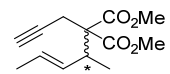
25

Dimethyl 2-allyl-2-(1,3-dimethylallyl)malonate (26).[9] Enantiomeric excess determined by HPLC using Chiralcel OD-H column (99.5% hexane/2-propanol, flow 0.5 mL/min). t_R 10.3 min (+); t_R 10.9 min (-). ^{1}H NMR ($CDCl_3$), δ: 1.06 (d, 3H, CH_3, *J*=6.4 Hz), 1.64 (d, 3H, CH_3, *J*=6.8 Hz), 2.59 (m, 2H, CH_2), 2.77 (m, 1H, CH), 3.68 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 5.03 (m, 2H, CH_2=), 5.33 (dd, 1H, CH=, *J*=16.4 Hz, *J*=8.8 Hz), 5.48 (m, 1H, CH=), 5.76 (m, 1H, CH=).

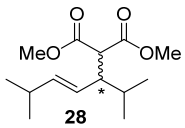


26

Dimethyl 2-(1,3-dimethylallyl)-2-(prop-2-yn-1-yl)malonate (27).[14] Enantiomeric excess determined by HPLC using Chiralcel IC column (98% hexane/2-propanol, flow 0.5 mL/min, λ = 254 nm). t_R 13.5 min (*S*); t_R 15.1 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.09 (d, 3H, CH_3, *J*=6.4 Hz), 1.62 (d, 3H, CH_3, *J*=6.4 Hz), 1.98 (m, 1H, CH), 2.74 (m, 2H, CH_2), 2.98 (m, 1H, CH), 3.70 (m, 3H, CH_3), 3.72 (m, 3H, CH_3), 5.25 (m, 1H, CH=), 5.53 (m, 1H, CH=).



27



28

Dimethyl 2-(1,3-diisopropylallyl)malonate (28).[2] Enantiomeric excess determined by ^{1}H-NMR using [Eu(hfc)$_3$] in C_6D_6. ^{1}H NMR ($CDCl_3$), δ: 0.81 (d, 3H, CH_3, *J*=6.8 Hz), 0.87 (d, 3H, CH_3, *J*=6.8 Hz), 0.93 (d, 3H, CH_3, *J*=6.8 Hz), 0.95 (d, 3H, CH_3, *J*=6.8 Hz), 1.69 (m, 1H, CH), 2.25 (m, 1H, CH), 2.58 (m, 1H, CH), 3.51 (d, 1H, CH, *J*=10.0 Hz), 3.66 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 5.23 (dd, 1H, CH=, *J*=15.2 Hz, *J*=10.0 Hz), 5.44 (dd, 1H, CH=, *J*=15.2 Hz, *J*=6.8 Hz).

9. References

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