Supporting Information

Gold(I)-catalyzed intermolecular (4+2) cycloaddition of allenamides and acyclic dienes

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Contents

1. General experimental procedures

Reactions were conducted in dry solvents under Argon atmosphere unless otherwise stated. Dry solvents were freshly distilled under Argon from an appropriate drying agent before use. Toluene was distilled from Na, THF from Na / benzophenone. CH_2Cl_2 was purchased from Aldrich. $[PtCl_2(C_2H_4)]_2$ and $PtCl_2$ were purchased from Strem Chemicals. $AuCl_3$, AuCl, Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold (IPrAuCl), chloro(triphenylphos phine)gold(I) (Ph_3PAuCl), Chloro[tris(2,4-di-*tert*-butylphenyl)phosphite]gold (I), (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (I), Dichloro(2-pyridinecarboxylato)gold and $AgSbF_6$ were purchased from Aldrich. All other chemicals were purchased from Aldrich and used without further purification.

The abbreviation "*rt*" refers to reactions carried out at a temperature between 21-25 ºC. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. High reaction temperatures were maintained using Thermowatch-controlled silicone oil baths. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and / or by treating the plates with *p*-anisaldehyde or cerium nitrate solutions, followed by heating. Flash chromatography was carried out on silica gel. Dryings were performed with anhydrous Na_2SO_4. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by high vacuum. NMR spectra were recorded in $CDCl_3$, at 250 MHz (Bruker), 300 MHz (Varian), 400 MHz (Varian) or 500 MHz (Bruker). Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReNova© NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; dt, double triplet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) and were recorded at the CACTUS facility of the University of Santiago de Compostela.

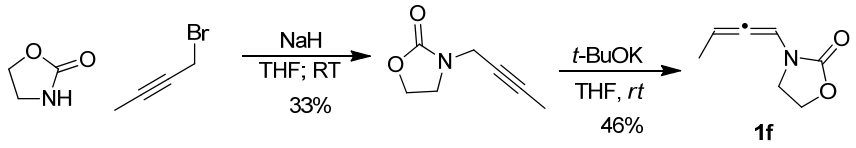
3-(Propa-1,2-dien-1-yl)oxazolidin-2-one (**1d**)[1], tert-butyldiphenyl(propa-1,2-dien-1-yloxy)silane (**1c**),[2] dimethyl 3,4-dimethylenecyclohexane-1,1-dicarboxylate **2g**,[3] (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene **2i**,[4] (R)-4-benzyl-3-(propa-1,2-dien-1-yl)oxazolidin-2-one (**1g**),[1,5] and (4R,5S)-4-methyl-5-phenyl-3-(propa-1,2-dien-1-yl)oxazolidin-2-one (**1h**)[6] are known compounds and were synthesized according to those previously reported procedures.

[1] L. Wei, J. A. Mulder, C. A. Zificsak, C. J. Douglas and R. P. Hsung, *Tetrahedron*. **2001**, *57*, 459-466.
[2] I. A Stergiades and M. A. Tius, *J. Org. Chem.* **1999**, *64*, 7547-7551.
[3] B. M. Trost, L. Zhi, K. Imi, *Tetrahedron Letters*. **1994**, *35*, 1361-1364.
[4] Y. Nakao, H. Idei, K. S. Kanyiva and T. Hiyama, *J. Am. Chem. Soc.* **2009**, *131*, 5070-5071.
[5] A. W. Hill, M. R. J. Elsegood and M. C. Kimber, *J. Org. Chem.* **2010**, *75*, 5406-5409.
[6] J. E. Antoline, R. P. Hsung, J. Huang, Z. Song and G. Li, *Org. Lett.* 2007, **9**, 1275.

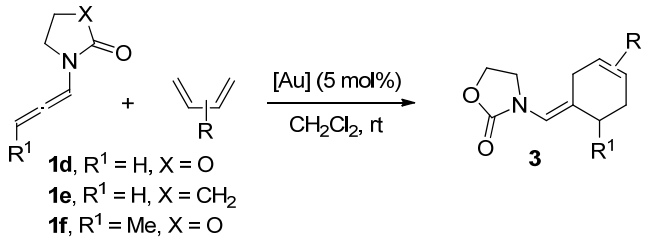
2. Experimental data

3-(Buta-1,2-dien-1-yl)oxazolidin-2-one (1f)

Prepared according to a previously described procedure:[7] Alkylation of 2-oxazolidinone with 1-bromobut-2-yne (1.3 equiv) affords the 3-(but-2-ynyl)oxazolidin-2-one intermediate (33% yield, non optimized), which provides the corresponding allenamide upon isomerization with *t*-BuOK.[8]



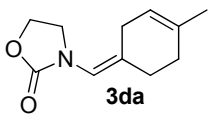
General procedure for the (4+2) cycloaddition of allenamides and acyclic dienes (Exemplified for 3da)



1d, R^1 = H, X = O
1e, R^1 = H, X = CH_2
1f, R^1 = Me, X = O

AuCl (4.65 mg, 0.020 mmol) was added to a dried Schlenk tube containing a solution of isoprene (0.06 mL, 1.20 mmol) and allenamide **1d** (50.1 mg, 0.4 mmol) in CH_2Cl_2 (4 mL), under Argon atmosphere. The resulting mixture was stirred at *rt* for 6 h (the progress of the reaction was easily monitored by *tlc*) and filtered through a short pad of florisil eluting with Et_2O. The filtrate was concentrated affording 78.6 mg of the crude reaction mixture which was purified by flash chromatography (hexane/EtOAc 10-20%) to give (*Z*)-3-((2-methyl-2-vinylcyclobutylidene)methyl)oxazolidin-2-one **4da** (aprox. 1.8 mg, 9.31 µmol, 2 % yield) and 3-((4-methylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one **3da** (51 mg, 0.264 mmol, 66 % yield, ratio *Z* : *E* = 93 : 7). The stereochemistry of the resulting cycloadducts could be determined by –ray crystallographic analysis or by 2D-NMR.In case of 3da, the 2D-NMR data showed the Z-stereochemistry of the major adduct.

3-((4-Methylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3da)



3da
Z : *E* = 93 : 7

66 % yield, colourless oil; corresponding to a 93 : 7 mixture of *Z* : *E* isomers. (*Z*)-**3da**:[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 5.29 – 5.23 (m, 1H), 4.33 (dd, *J* = 8.7, 7.3 Hz, 2H), 3.76 (dd, *J* = 8.7, 7.2 Hz, 2H), 2.77 (tt, *J* = 3.9, 2.0 Hz, 2H), 2.26 (td, *J* = 6.4, 0.8 Hz, 2H), 2.01 (t, *J* = 6.4 Hz,

[7] M. R. Tracey, T. Grebe, J. A. Mulder, R. P. Hsung, *Organic Syntheses*. **2005**, *81*, 147-151.
[8] L. Shen, R. P. Hsung, Y. Zhang, J. E. Antoline and X. Zhang, *Org. Lett.* **2005**, *7*, 3081-3084.
[9] NMR data corresponds to the *Z*-isomer of **3**. The minor *E* isomer could not be separated by standard flash chromatography but it can be detected in the NMR spectra of the mixture. The ratio of isomers was calculated by integrating the NMR signals corresponding to the C-H enamide group.

2H), 1.65 – 1.60 (m, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 157.1 (C), 134.3 (C), 130.3 (C), 118.2 (CH), 116.6 (CH), 62.1 (CH_2), 46.3 (CH_2), 31.1 (CH_2), 29.7 (CH_2), 27.5 (CH_2), 23.3 (CH_3). **LRMS** (*m/z, CI*): 194 [M^+ +1, 100], 166 (25), 126 (49), 107 (94); 88 (93). **HRMS** [M^+ +1], Calculated for $C_{11}H_{16}NO_2$: 194.1181, found 194.1187.

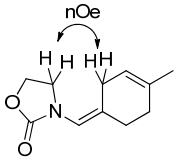
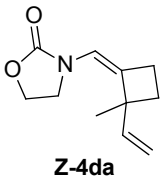


Figure S1. Key noesy signal in **Z-3da**

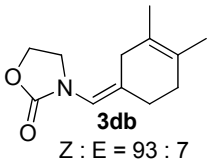
(*Z*)-3-((2-Methyl-2-vinylcyclobutylidene)methyl)oxazolidin-2-one (Z-4da)



Z-4da

2% yield, colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 2.1 Hz, 1H), 6.08 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.04 (dd, *J* = 17.4, 1.4 Hz, 1H), 4.98 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.34 – 4.18 (m, 2H), 3.80 (td, *J* = 8.9, 6.5 Hz, 1H), 3.61 (td, *J* = 9.1, 7.5 Hz, 1H), 2.72 – 2.62 (m, 1H), 2.59-2.52 (m, 1H), 2.01 – 1.95 (m, 1H), 1.87 – 1.78 (m, 1H), 1.40 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.7 (C), 145.3 (CH), 130.1 (C), 116.7 (CH), 111.1 (CH_2), 62.0 (CH_2), 48.4 (C), 46.3 (CH_2), 32.8 (CH_2), 24.7 (CH_3), 24.6 (CH_2). **LRMS** (*m/z, CI*): 194 [M^+ +1, 18], 193 (28), 126 (78), 107 (100); 88 (89). **HRMS** [M^+ +1], Calculated for $C_{11}H_{16}NO_2$: 194.1181, found 194.1183.

(*Z*)-3-((3,4-Dimethylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3db)



3db
Z : E = 93 : 7

76% yield, corresponding to a 93 : 7 mixture of *Z* : *E* isomers, white solids, Mp = 77-79 ºC; (*Z*)-**3db**:[10] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.81 - 5.76 (m, 1H), 4.33 – 4.24 (m, 2H), 3.76 – 3.69 (m, 2H), 2.64 (s, 2H), 2.20 – 2.14 (m, 2H), 1.96 (s, 2H), 1.57 – 1.54 (m, 3H), 1.54 – 1.49 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9 (C), 131.6 (C), 125.8 (C), 122.9 (C), 115.7 (CH), 62.0 (CH_2), 46.3 (CH_2), 33.4 (CH_2), 32.5 (CH_2), 29.9 (CH_2), 18.7 (CH_3), 18.6 (CH_3). **LRMS** (*m/z, CI*): 208 [M^+ +1, 97], 180 (22), 149 (32), 121 (100), 86 (94). **HRMS** [M^+ +1], Calculated for $C_{12}H_{18}NO_2$: 208.1388, found 208.1341. The structure of *Z*-**3db** was further confirmed by X-ray analysis (Figure S2).

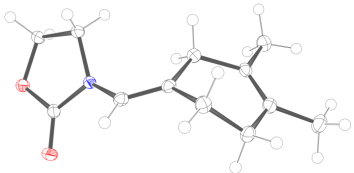
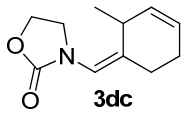


Figure S2: X-Ray structure of *Z*-**3db** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804843)

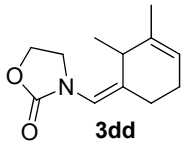
[10] A sample of isomerically pure **Z-3db** could be obtained after crystallization of the isolated *Z : E*, 93 : 7, mixture.

3-((2-Methylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3dc)


3dc
Z : *E* = 93 : 7

60% yield, corresponding to a 93 : 7 mixture of *Z* : *E* isomers; colourless oils; (*Z*)-**3dc**:[9] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.95 (s, 1H), 5.70 – 5.59 (m, 1H), 5.56 – 5.45 (m, 1H), 4.34 (t, *J* = 8.0 Hz, 2H), 3.86 (dd, *J* = 16.1, 8.3 Hz, 1H), 3.78 (dd, *J* = 16.1, 8.6 Hz, 1H), 3.14 – 3.03 (m, 1H), 2.33 – 2.22 (m, 1H), 2.20 – 2.10 (m, 2H), 2.10 – 1.97 (m, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4 (C), 134.4 (C), 131.0 (CH), 126.1 (CH), 116.3 (CH), 62.0 (CH_2), 46.4 (CH_2), 31.4 (CH), 27.3 (CH_2), 26.7 (CH_2), 21.5 (CH_3). **LRMS** (*m/z, CI*): 194 [M^+ +1, 78], 135 (23), 126 (43), 107 (100); 88 (91). **HRMS** [M^+ +1], Calculated for $C_{11}H_{16}NO_2$: 194.1181, found 194.1178.

(*Z*)-3-((2,3-Dimethylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3dd)


3dd
Z : *E* = 9 :1

62% yield, corresponding to a 90 : 10 mixture of *Z* : *E* isomers; white solids, Mp = 98-99 ºC; (*Z*)-**3dd**:[11] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.90 (d, *J* = 1.8 Hz, 1H), 5.38 (brs, 1H), 4.37 (t, *J* = 8.0 Hz, 2H), 3.88 (dd, *J* = 16.1, 8.2 Hz, 1H), 3.77 (dt, *J* = 16.1, 8.1 Hz, 1H), 2.88 (q, *J* = 6.9 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.18 – 1.99 (m, 3H), 1.68 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.5 (C), 136.3 (C), 136.2 (C), 121.4 (CH), 115.5 (CH), 62.0 (CH_2), 46.7 (CH_2), 35.7 (CH), 27.2 (CH_2), 26.2 (CH_2), 21.7 (CH_3), 19.9 (CH_3). **LRMS** (*m/z, CI*): 208 [M^+ +1, 100], 121 (96), 100 (33), 88 (38). **HRMS** [M^+ +1], Calculated for $C_{12}H_{18}NO_2$: 208.1338, found 208.1339. The structure of **3dd** was confirmed by X-ray analysis (Figure S3).

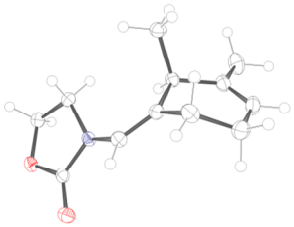
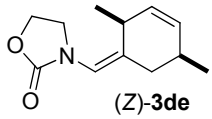


Figure S3: X-Ray structure of *Z*-**3dd** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804844)

3-((*Z*)-((2S*,5S*)-2,5-Dimethylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3de)


(*Z*)-**3de**

67% yield (catalyst **B**), white solid, Mp = 89-90 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.44 (s, 2H), 4.34 – 4.24 (m, 2H), 3.91 – 3.69 (m, 2H), 3.09 – 2.98 (m, 1H), 2.27 – 2.16 (m, 1H), 2.13 (dd, *J* = 13.1, 4.3 Hz, 1H), 1.94 – 1.79 (m, 1H), 1.13 – 1.03 (m, 3H), 0.95 (dd, *J* = 6.8, 3.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (C), 133.9 (C), 132.6 (CH), 130.1 (CH), 116.3 (CH), 62.0 (CH_2), 46.3 (CH_2), 35.8 (CH_2), 33.2 (CH), 31.1 (CH), 21.6 (CH_3), 21.3 (CH_3). **LRMS** (*m/z, CI*): 208 [M^++1, 97], 192 (93), 121 (89), 105 (91), 88 (90). **HRMS** [M^+ +1], Calculated for $C_{12}H_{18}NO_2$: 208.1338, found 208.1337. The structure of **3de** was confirmed by X-ray analysis (Figure S4).

[11] A sample of isomerically pure **Z-3dd** could be obtained after crystallization of the isolated *Z* : *E*, 9 : 1, mixture.

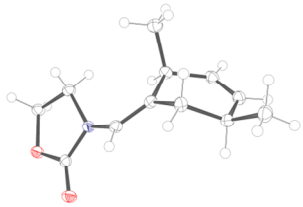
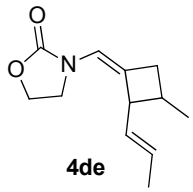


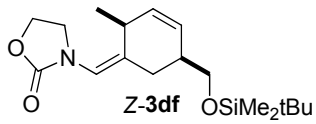
Figure S4: X-Ray structure of *Z*-**3de** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804845)

3-((3-Methyl-2-((*E*)-prop-1-en-1-yl)cyclobutylidene)methyl)oxazolidin-2-one (4de)



17% yield (with catalyst **B**), corresponding to a 5 : 1 mixture of *Z* : *E* isomers, colourless oil; *Z*-**4de**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 5.74 – 5.67 (m, 1H), 5.58 – 5.51 (m, 1H), 4.42 – 4.32 (m, 2H), 4.01 – 3.94 (m, 1H), 3.78 – 3.70 (m, 1H), 3.19 – 3.11 (m, 1H), 2.98 – 2.85 (m, 1H), 2.25 – 2.15 (m, 2H), 1.76 (d, *J* = 6.1 Hz, 3H), 1.23 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3 (C), 133.4 (CH), 124.7 (CH), 124.0 (C), 117.3 (CH), 62.2 (CH_2), 52.3 (CH), 44.9 (CH_2), 34.2 (CH), 33.6 (CH_2), 20.5 (CH_3), 17.8 (CH_3). **LRMS** (*m/z, CI*): 208 [M^++1, 4], 207 (7) 192 (6), 121 (100), 105 (28), 88 (49). **HRMS** (EI) Calculated for $C_{12}H_{17}NO_2$ 207.1259, found 207.1261.

3-((Z)-((2S*,5S*)-5-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-methylcyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3df)



52% yield (with catalyst **B**), white solid, Mp = 68-70 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.98 (d, *J* = 1.5 Hz, 1H), 5.53-5.58 (m, 2H), 4.34 (t, *J* = 8.0 Hz, 2H), 3.86 (dd, *J* = 16.1, 8.3 Hz, 1H), 3.79 (dt, *J* = 16.0, 7.9 Hz, 1H), 3.53 – 3.41 (m, 2H), 3.14 – 3.05 (m, 1H), 2.38 – 2.27 (m, 1H), 2.21 (dd, *J* = 13.0, 5.2 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4 (C), 133.6 (C), 131.7 (CH), 127.9 (CH), 116.6 (CH), 67.0 (CH_2), 62.00 (CH_2), 46.4 (CH_2), 41.3 (CH), 31.7 (CH), 30.6 (CH_2), 25.8 (CH_3), 21.6 (CH_3), 18.2 (C), -5.5 (CH_3). **LRMS** (*m/z, CI*): 338 [M^++1, 65], 322 (33), 280 (37), 205 (100). **HRMS** [M^+ +1], Calculated for $C_{18}H_{32}NO_3Si$: 338.2151, found 338.2158. The structure of **3df** was confirmed by X-ray analysis (Figure S5).

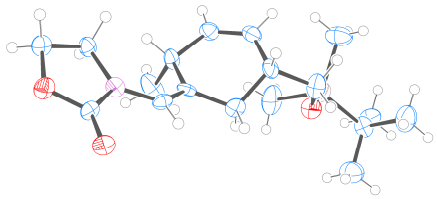
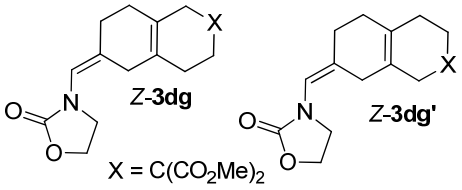


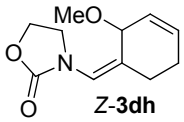
Figure S5: X-Ray structure of *Z*-**3df** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804846)

(*Z*)-Ethyl 7-((2-oxooxazolidin-3-yl)methylene)-1,2,3,4,5,6,7,8-octahydronaphthalene-2-carboxylate (3dg) and (*Z*)-ethyl 6-((2-oxooxazolidin-3-yl)methylene)-1,2,3,4,5,6,7,8-octahydronaphthalene-2-carboxylate (3dg').[12]



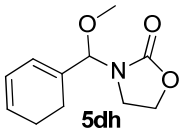
80% global yield (ratio **3dg** : **3dg'** = 1.8 : 1); Colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.84 (s, $1H_{3dg'}$), 5.81 (d, *J* = 1.2 Hz, $1H_{3dg}$), 4.34 - 4.27 (m, $2H_{3dg}$+ $2H_{3dg'}$), 3.76 – 3.69 (m, $2H_{3dg}$ + $2H_{3dg'}$), 3.64 (s, $6H_{3dg'}$), 3.63 (s, $6H_{3dg}$), 2.65 (s, $2H_{3dg'}$), 2.58 (s, $2H_{3dg}$), 2.36 (s, $2H_{3dg}$ + $2H_{3dg'}$), 2.19 (q, *J* = 6.4 Hz, $2H_{3dg}$ + $2H_{3dg'}$), 2.10 – 2.01 (m, $2H_{3dg}$ + $2H_{3dg'}$), 1.94-1.96 (m, $2H_{3dg}$ + $2H_{3dg'}$), 1.87-1.90 (m, $2H_{3dg}$ + $2H_{3dg'}$). **^{13}C NMR** (126 MHz, C_6D_6) δ 171.7 (C_{3dg}), 171.6 ($C_{3dg'}$), 157.0 ($C_{3dg'}$), 156.9 (C_{3dg}), 130.5 (C_{3dg}), 130.3 ($C_{3dg'}$), 127.3 ($C_{3dg'}$), 125.5 (C_{3dg}), 124.4 (C_{3dg}), 122.7 ($C_{3dg'}$), 116.5 ($CH_{3dg'}$), 116.4 (CH_{3dg}), 62.0 ($CH_{2\ 3dg'\ +\ 3dg}$), 53.3 ($C_{3dg'\ +\ 3dg}$), 52.4 ($CH_{3\ 3dg'\ +\ 3dg}$), 46.3 ($CH_{2\ 3dg'\ +\ 3dg}$), 34.9 ($CH_{2\ 3dg}$), 34.8 ($CH_{2\ 3dg'}$), 31.9 ($CH_{2\ 3dg'}$), 31.8 ($CH_{2\ 3dg}$), 30.8 ($CH_{2\ 3dg}$), 30.7 ($CH_{2\ 3dg'}$), 29.5 ($CH_{2\ 3dg}$), 29.4 ($CH_{2\ 3dg'}$), 27.5 ($CH_{2\ 3dg'}$), 27.5 ($CH_{2\ 3dg}$), 26.9 ($CH_{2\ 3dg'}$), 26.8 ($CH_{2\ 3dg}$). **LRMS** (*m/z, CI*): 350 [M^+ +1, 80], 318 (70), 290 (59), 263 (79), 231 (43), 203 (71), 88 (100). **HRMS** [M^+ +1], Calculated for $C_{18}H_{24}NO_6$: 350.1604, found 350.1609.

(*Z*)-3-((2-Methoxycyclohex-3-en-1-ylidene)methyl)oxazolidin-2-one (3dh)



76% yield, colourless oil;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.37 (d, *J* = 1.2 Hz, 1H), 6.03 (dd, *J* = 9.2, 5.5 Hz, 1H), 5.82 – 5.76 (m, 1H), 4.48 (d, *J* = 4.3 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 2H), 4.04 (dd, *J* = 16.3, 8.4 Hz, 1H), 3.89 (dd, *J* = 16.6, 8.2 Hz, 1H), 3.25 (s, 3H), 2.39 – 2.31 (m, 1H), 2.26 – 2.14 (m, 2H), 2.10 – 2.02 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.1 (C), 133.1 (CH), 125.2 (CH), 124.0 (C), 121.1 (CH), 68.8 (CH), 62.2 (CH_2), 54.1 (CH_3), 46.2 (CH_2), 27.4 (CH_2), 27.2 (CH_2). **LRMS** (*m/z, CI*): 210 [M^+ +1, 73], 194 (19), 192 (8), 178 (100), 176 (45), 139 (40), 130 (28), 123 (94), 121 (32), 88 (86). **HRMS** [M^+ +1], Calculated for $C_{11}H_{16}NO_3$: 210.1130, found 210.1129.

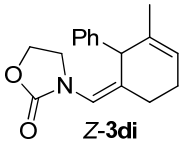
3-(Cyclohexa-1,3-dien-1-yl(methoxy)methyl)oxazolidin-2-one (5dh)



13% yield, colourless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.09 (d, *J* = 5.2 Hz, 1H), 5.97 – 5.90 (m, 1H), 5.85 – 5.74 (m, 1H), 5.35 (s, 1H), 4.43 – 4.22 (m, 2H), 3.49 (td, *J* = 9.2, 7.5 Hz, 1H), 3.37 (s, 3H), 3.36 – 3.32 (m, 1H), 2.25 – 2.13 (m, 2H), 2.13 – 2.03 (m, 1H), 2.03 – 1.91 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.6 (C), 132.4 (C), 126.9 (CH), 123.7 (CH), 121.5 (CH), 85.3 (CH), 62.4 (CH_2), 55.9 (CH_3), 39.2 (CH_2), 22.6 (CH_2), 22.5 (CH_2). **LRMS** (*m/z, CI*): 210 [M^+ +1, 38], 194 (34), 192 (20), 178 (78), 176 (90), 139 (40), 130 (55), 123 (87), 121 (72), 88 (100).

[12] Cycloadducts **3dg** and **3dg'** could not be separated under standard column chromatography. However, their corresponding NMR data could be easily assigned using 1D and 2D-NMR experiments (1H, 13C, dept, HMQC, HMBC, NOESY and COSY).

(*Z*)-3-((6-Methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)oxazolidin-2-one (3di)



Z-**3di**

96% yield, white solid, Mp = 106 -108 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.16 (d, J = 7.3 Hz, 2H), 7.11 (td, J = 7.2, 1.3 Hz, 1H), 5.66 (s, 1H), 5.62 (s, 1H), 4.27 – 4.20 (m, 1H), 4.18 – 4.13 (m, 1H), 4.10 (s, 1H), 3.67 (dt, *J* = 16.7, 8.3 Hz, 1H), 3.39 – 3.34 (m, 1H), 2.27 – 2.17 (m, 2H), 2.16 – 2.10 (m, 1H), 2.10 – 2.02 (m, 1H), 1.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9 (C), 142.5 (C), 138.2 (C), 133.7 (C), 128.2 (CH), 128.0 (CH), 126.3 (CH), 123.5 (CH), 116.1 (CH), 62.0 (CH_2), 46.9 (CH), 46.5 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 22.2 (CH_3). **LRMS** (*m/z, CI*): 270 [M^++1, 62], 254 (1), 192 (6), 183 (100), 167 (84), 105 (20), 101 (76), 88 (77), 77 (12). **HRMS** [M^+ +1], Calculated for $C_{17}H_{20}NO_2$: 270.1494, found 270.1496. The structure of **3di** was confirmed by X-ray analysis (Figure S6).

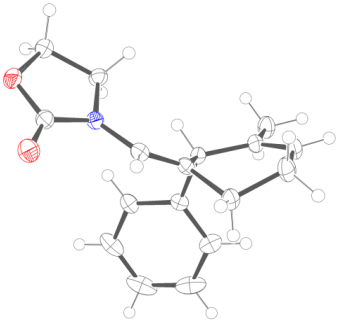
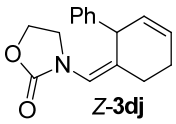


Figure S6: X-Ray structure of *Z*-**3di** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804847)

(*Z*)-3-((3,4-Dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)oxazolidin-2-one (3dj)



Z-**3dj**

78% yield, white solid, Mp = 92-94 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.03 (s, 1H), 5.87 – 5.81 (m, 1H), 5.77 – 5.69 (m, 1H), 4.33 (s, 1H), 4.22 – 4.09 (m, 2H), 3.58 (dd, *J* = 16.3, 8.8 Hz, 1H), 3.47 (td, *J* = 8.9, 6.2 Hz, 1H), 2.37 – 2.26 (m, 2H), 2.22 – 2.15 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.1 (C), 143.3 (C), 133.0 (C), 128.6 (CH), 128.5 (CH), 127.5 (CH), 127.3 (CH), 126.3 (CH), 118.2 (CH), 62.1 (CH_2), 46.1 (CH_2), 41.8 (CH), 28.2 (CH_2), 26.8 (CH_2). **LRMS** (*m/z, CI*): 256 [M^++1, 39], 178 (14), 169 (100), 101 (77), 88 (65), 77 (10). **HRMS** [M^+ +1], Calculated for $C_{16}H_{18}NO_2$: 256.1338, found 256.1338. The structure of **3dj** was confirmed by X-ray analysis (Figure S7).

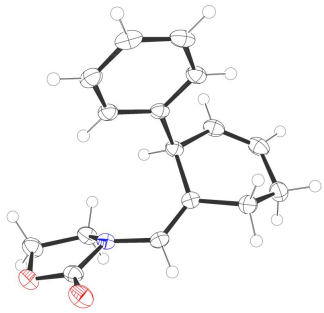
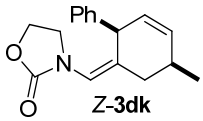


Figure S7: X-Ray structure of *Z*-**3dj**

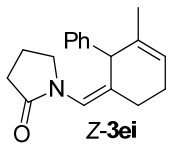
(Z)-3-((4-Methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)oxazolidin-2-one (3dk)



Z-**3dk**

70% yield, white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 6.12 (s, 1H), 5.77 – 5.68 (m, 2H), 4.38 (s, 1H), 4.30 – 4.19 (m, 2H), 3.69 – 3.56 (m, 2H), 2.44 – 2.30 (m, 2H), 2.01 – 1.92 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.2 (C), 143.1 (C), 134.0 (CH), 132.0 (C), 128.5 (CH), 127.5 (CH), 127.2 (CH), 126.3 (CH), 118.3 (CH), 62.1 (CH_2), 46.1 (CH_2), 41.5 (CH), 37.0 (CH_2), 32.8 (CH), 21.2 (CH_3). **LRMS** (*m/z, CI*): 270.9 [M^+ +1, 30], 269.9 (100), 254 (46), 183 (82), 167 (39). **HRMS** [M^+ +1], Calculated for $C_{17}H_{20}NO_2$: 270.1494, found 270.1495.

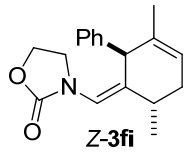
(Z)-1-((6-Methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)pyrrolidin-2-one (3ei)



Z-**3ei**

94% yield, white solid; **^{1}H NMR** (500 MHz, cdcl$_3$) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 5.81 (s, 1H), 5.71 (s, 1H), 4.18 (s, 1H), 3.65 – 3.53 (m, 1H), 3.34 – 3.24 (m, 1H), 2.45 – 2.36 (m, 2H), 2.35 – 2.28 (m, 2H), 2.27 – 2.15 (m, 2H), 2.07 – 2.00 (m, 1H), 1.98 – 1.90 (m, 1H), 1.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.2 (C), 142.7 (C), 137.2 (C), 134.0 (C), 128.0 (CH), 128.0 (CH), 126.1 (CH), 123.4 (CH), 116.7 (CH), 49.2 (CH_2), 47.3 (CH), 30.6 (CH_2), 27.1 (CH_2), 26.7 (CH_2), 22.2 (CH_3), 18.4 (CH_2). **LRMS** (*m/z, CI*): 268 [M^++1, 41], 252 (19), 183 (88), 86 (100). **HRMS** [M^+ +1], Calculated for $C_{18}H_{22}NO$ 268.1701, found 268.1703.

3-((Z)-((1R*,3S*)-((3,6-Dimethyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)oxazolidin-2-one (3fi)



Z-**3fi**

79% yield, white solid, Mp = 85-87 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.17 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 5.61 – 5.58 (m, 1H), 5.57 (s, 1H), 4.34 – 4.22 (m, 2H), 4.21 (s, 1H), 3.73 (td, *J* = 8.9, 7.4 Hz, 1H), 3.45 (td, *J* = 8.8, 6.2 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.32 – 2.22 (m, 1H), 1.83 – 1.74 (m, 1H), 1.54 (d, *J* = 1.5 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3 (C), 143.7 (C), 142.5 (C), 133.5 (C), 128.2 (CH), 128.1 (CH), 126.3 (CH), 123.4 (CH), 114.8 (CH), 62.0 (CH_2), 47.5 (CH), 47.1 (CH_2), 36.0 (CH_2), 29.3 (CH), 22.1 (CH_3), 17.6 (CH_3). **LRMS** (*m/z, CI*): 284 [M^++1, 66], 268 (12), 197 (100). **HRMS** [M^+ +1], Calculated for $C_{18}H_{22}NO_2$: 284.1651, found 284.1652. The structure was confirmed by X-ray analysis (Figure S8).

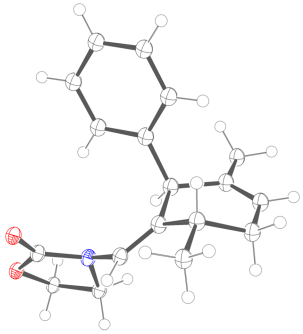


Figure S8: X-Ray structure of *Z*-**3fi** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804848)

(R)-4-Benzyl-3-((Z)-((S)-6-methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)oxazolidin-2-one (**3gi**). 95% yield, white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 8H), 7.10 – 7.06 (m, 2H), 5.82 (s, 1H), 5.65 (s, 1H), 4.28 (t, *J* = 8.1 Hz, 1H), 4.26 – 4.20 (m, 1H), 4.04 (dd, *J* = 8.1, 5.9 Hz, 1H), 2.95 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.42 – 2.20 (m, 6H), 1.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.3 (C), 142.4 (C), 139.9 (C), 135.8 (C), 134.0 (C), 128.8 (CH), 128.4 (CH), 128.3 (CH), 127.1 (CH), 126.5 (CH), 123.8 (CH), 114.9 (CH), 67.2 (CH_2), 59.1 (CH), 47.4 (CH), 38.5 (CH_2), 27.0 (CH_2), 26.9 (CH_2), 22.4 (CH_3). **LRMS** (*m/z, CI*): 360 [M^++1, 98], 282, (10), 268 (5), 183 (100), 178 (98). **HRMS** [M^+ +1], Calculated for $C_{24}H_{26}NO_2$ 360.1964, found 360.1963. The structure of **3gi** was confirmed by X-ray analysis (Figure S9).

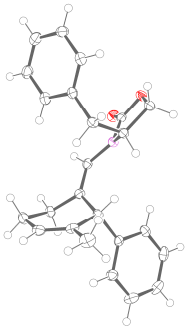


Figure S9: X-Ray structure of *Z*-**3gi** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804849)

(4R,5S)-4-Methyl-3-((Z)-((S)-6-methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)-5-phenyloxazolidin-2-one (**3hi**). 99% yield, white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 3H), 7.35 (m, 2H), 7.28 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 5.75 (br s, 1H), 5.70 (d, *J* = 8.0 Hz, 1H), 5.67 (s, 1H), 4.37 (dq, *J* = 13.3, 6.6 Hz, 1H), 4.27 (s, 1H), 2.37 – 2.18 (m, 3H), 2.15 – 2.08 (m, 1H), 1.67 (d, *J* = 1.1 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 156.6 (C), 141.8 (C), 140.3 (C), 134.9 (C), 133.6 (C), 128.5 (CH), 128.2 (CH), 128.2 (CH), 126.4 (CH), 126.0 (CH), 124.1(CH), 114.3 (CH), 78.6 (CH), 58.2 (CH), 47.3 (CH), 27.4 (CH_2), 26.1 (CH_2), 22.6 (CH_3), 14.7 (CH_3). **LRMS** (*m/z, CI*): 360 [M^++1, 76], 344 (12), 316 (68), 282 (12), 183 (100), 178 (69), 134 (70), 118 (60); **HRMS** [M^+ +1], Calculated for $C_{24}H_{26}NO_2$: 360.1964, found 360.1964. The structure of **3hi** was confirmed by X-ray analysis (Figure S10).

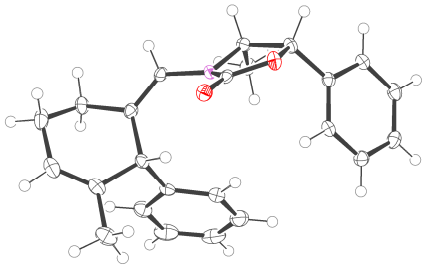
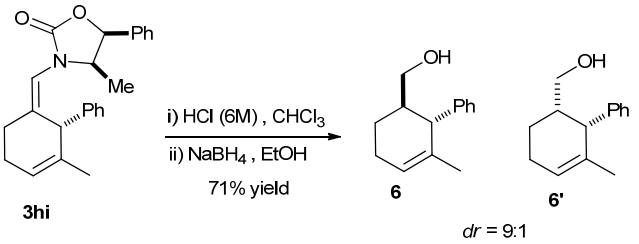


Figure S10: X-Ray structure of *Z*-**3hi** (deposited at the Cambridge Crystallographic Data Centre with the number CCDC 804850)

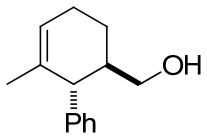
General procedure for the hydrolysis and subsequent reduction of cycloadducts 3, (exemplified for 3hi)



3hi **6** **6'** *dr* = 9:1

A solution of (4R,5S)-4-Methyl-3-((Z)-((S)-6-methyl-3,4-dihydro-[1,1'-biphenyl]-2(1H)-ylidene)methyl)-5-phenyloxazolidin-2-one (**3hi**) (50 mg, 0,14 mmol) and HCl 6 M (3 ml, 18,0 mmol) in $CHCl_3$ (3 ml) was stirred at 60 ºC until *tlc* showed complete consumption of the starting material. The product was extracted with Et_2O, washed with saturated $NaHCO_3$, dried with $NaSO_4$, and concentrated to provide a crude oil which was used as obtained in the next step. To a solution of this oil in ethanol (3 ml), $NaBH_4$ (19 mg, 0,84 mmol) was added. After stirring for 1h, the reaction mixture was quenched by addition of acetone and water. After extraction with Et_2O, the organic phases were dried with $NaSO_4$ concentrated and purified by column chromatography (Hexane/ EtOAc, 9:1) to provide 20 mg (71% yield) of a 9:1 mixture of ((1S,2R)-6-methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)methanol (**6**) and ((1S,2S)-6-methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)methanol (**6'**) (colorless oil).

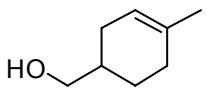
((1S,2R)-6-Methyl-1,2,3,4-tetrahydro-[1,1'-biphenyl]-2-yl)methanol (6).[13] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.17 – 7.08 (m, 2H), 5.58 (d, *J* = 1.3 Hz, 1H), 3.53 (dd, *J* = 10.6, 5.0 Hz, 1H), 3.39 (dd, *J* = 10.6, 6.5 Hz, 1H), 3.01 (d, *J* = 6.4 Hz, 1H), 2.17 – 1.95 (m, 2H), 1.80 – 1.70 (m, 2H), 1.42 – 1.37 (m, 1H), 1.35 (s, 3H), 1.26 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4 (C), 134.3 (C), 128.6 (CH), 128.3 (CH), 126.1 (CH), 123.6 (CH), 65.6 (CH_2), 48.4 (CH), 44.9 (CH), 23.8 (CH_2), 22.8 (CH_2), 22.6 (CH_3). **LRMS** (*m/z, CI*): 203 [M^++ 1, 5], 202 (17), 185 (100), 171 (46), 142 (31). **HRMS** [M^+], Calculated for $C_{14}H_{18}O$: 202.1358, found 202.1353.



6

The same procedure can also be applied to other cycloadducts such as **3da**.

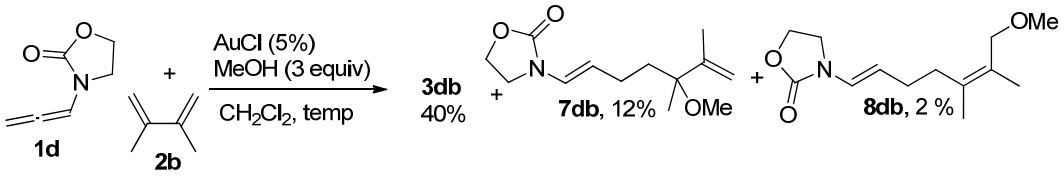
(4-Methylcyclohex-3-en-1-yl)methanol (6da). 61% yield, colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.48 – 5.29 (m, 1H), 3.57 – 3.48 (m, 2H), 2.16 – 1.89 (m, 3H), 1.88 – 1.76 (m, 1H), 1.76 – 1.67 (m, 2H), 1.65 (s, 3H), 1.38 – 1.22 (m, 2H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 134.1 (C), 119.8 (CH), 67.8 (CH_2), 36.1 (CH), 29.4 (CH_2), 28.2 (CH_2), 25.6 (CH_2), 23.6 (CH_3). **LRMS** (*m/z, CI*): 127 [M^+ 1, 8], 126 (2), 125 (19), 109 (100).



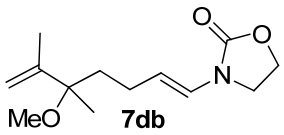
6da

Reaction of 1d and 2b in the presence of MeOH (3 equiv).

[13] The stereochemistry of the major and minor diastereoisomers **6** and **6'** could be established based on several nOe experiments, the values of the NMR coupling constants and the observed shielding of the C*H*$_2$(OH) group by the phenyl ring (significantly higher in the minor **6'** isomer).



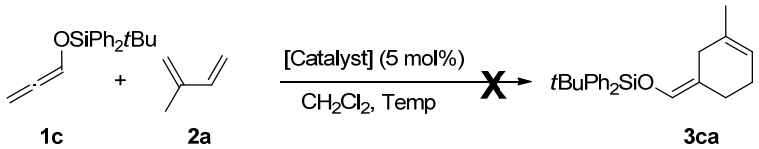
(*E*)-3-(5-Methoxy-5,6-dimethylhepta-1,6-dien-1-yl)oxazolidin-2-one (7db)



^{1}H NMR (250 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.3 Hz, 1H), 5.01 – 4.98 (m, 1H), 4.89 (s, 1H), 4.80 (dt, *J* = 14.2, 7.0 Hz, 1H), 4.42 (dd, *J* = 9.0, 7.2 Hz, 2H), 3.74 – 3.61 (m, 2H), 3.07 (s, 3H), 2.11 – 1.84 (m, 4H), 1.69 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 155.4 (C), 147.0 (C), 123.8 (CH), 113.5 (CH_2), 111.1 (CH), 79.2 (C), 62.1 (CH_2), 49.8 (CH_3), 42.6 (CH_2), 38.6 (CH_2), 24.5 (CH_2), 20.8 (CH_3), 18.5 (CH_3). **LRMS** (*m/z, CI*): 240 [M^++1, 58], 208 (100), 192 (19), 177 (11), 152 (67), 99 (76), 88 (75). **HRMS** [M^+ +1], Calculated for $C_{13}H_{22}NO_3$: 240.1600, found 240.1605. Together with **7db**, we coud also isolate a minor amount of its isomer **8db**, contaminated with **7db** (2% yield).

3. Preliminary results with isoprene and allenes 1c and 1d

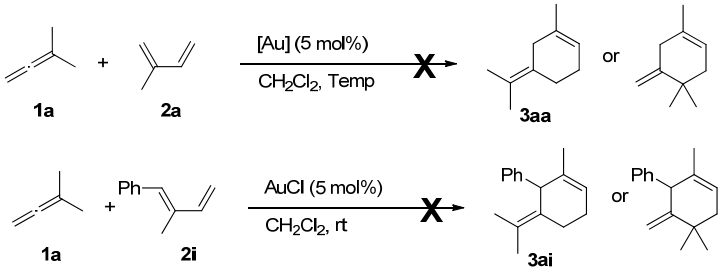
3.1 Table S1. Results of the reactions between allenylsilyl ether **1c** and isoprene (**2a**)

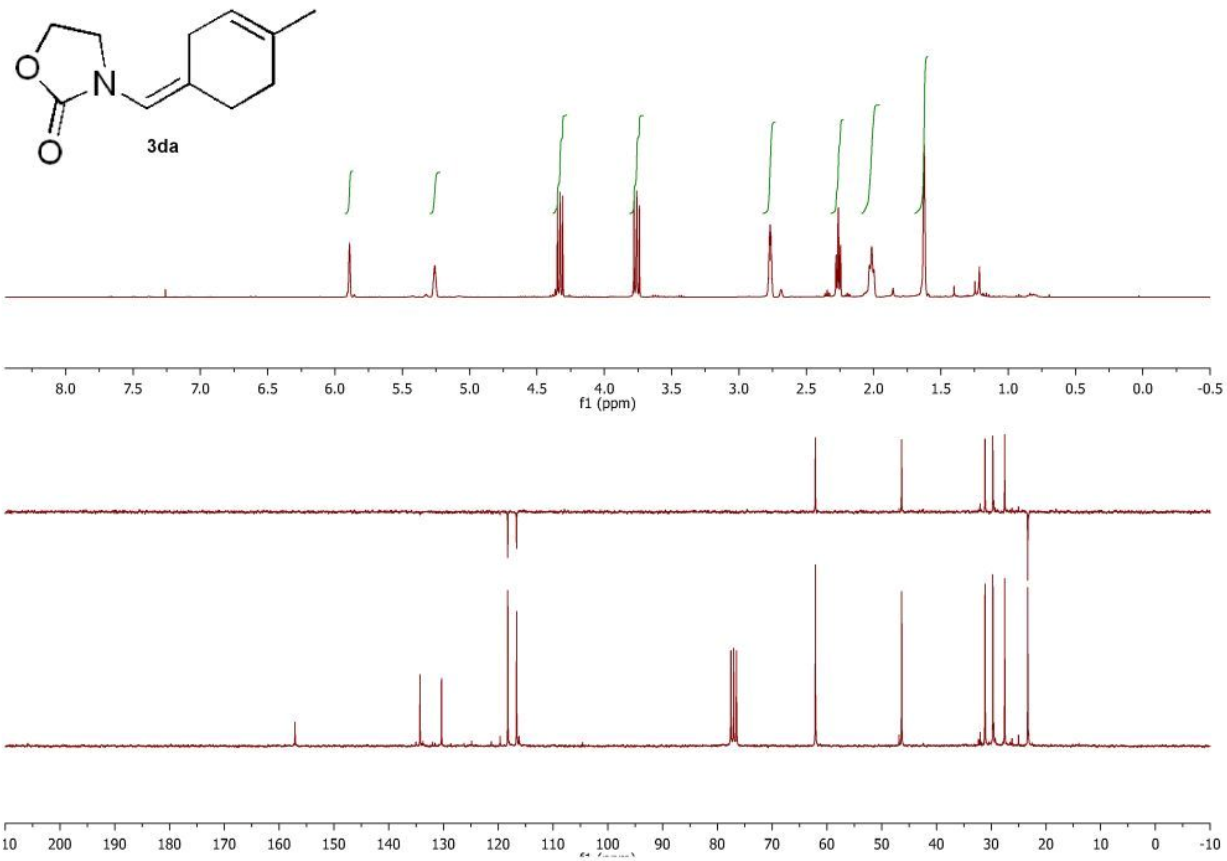


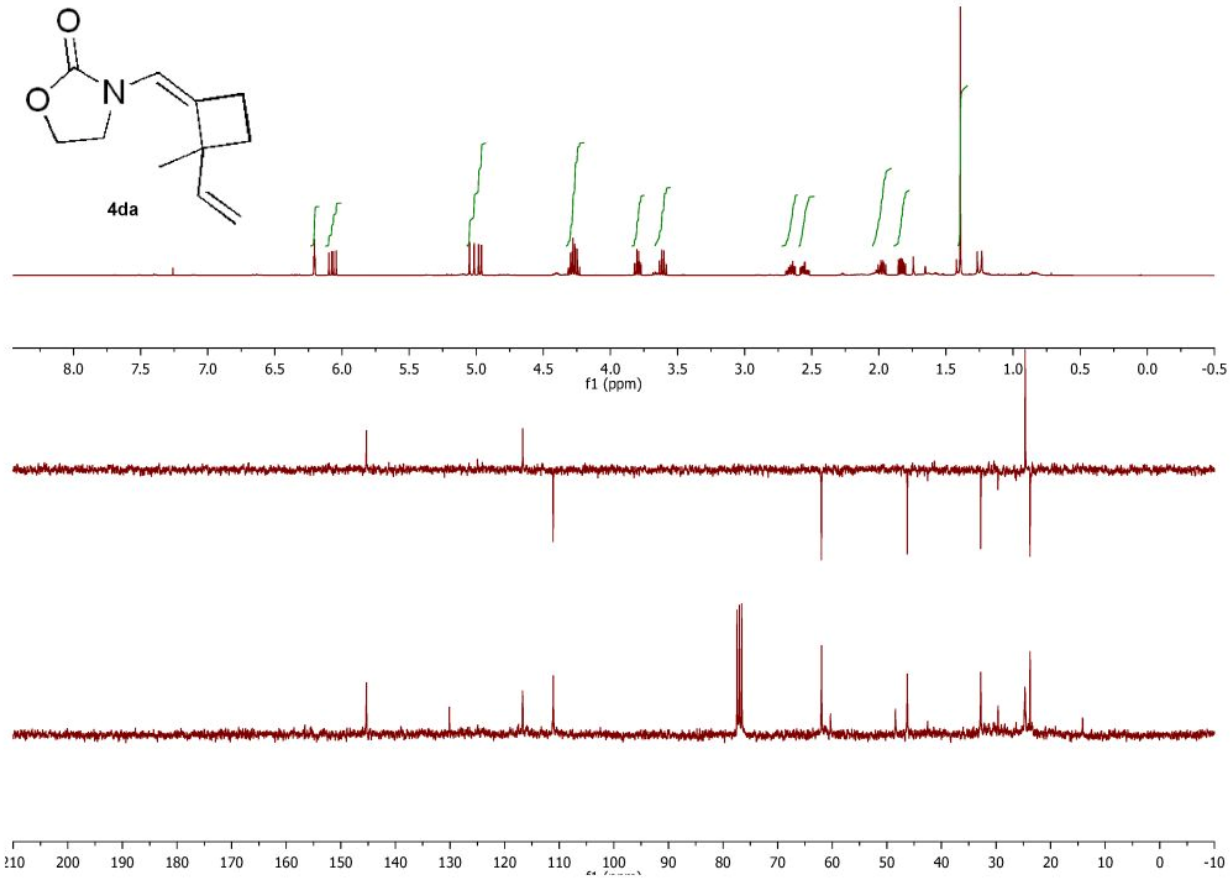
Catalyst	T (ºC) /time	**3**	Observations
$PtCl_2$	3h/ rt, 18h/ 40º C	0%	Allene degradation
$[PtCl_2(C_2H_4)]_2$ (2.5%) / P(*o*-tolyl)$_3$ (5%)	1h/ 0ºC	0%	Full conversion to a complex mixture of products
C	3h/ -15ºC	0%	Full conversion to a complex mixture of products
C	5min/ -50ºC	0%	Full conversion to a complex mixture of products
C	5min/ -75ºC	0%	Full conversion to a complex mixture of products
AuCl	5min/ 0ºC	0%	Full conversion to a complex mixture of products
AuCl	5min/ -50ºC	0%	Full conversion to a complex mixture of products

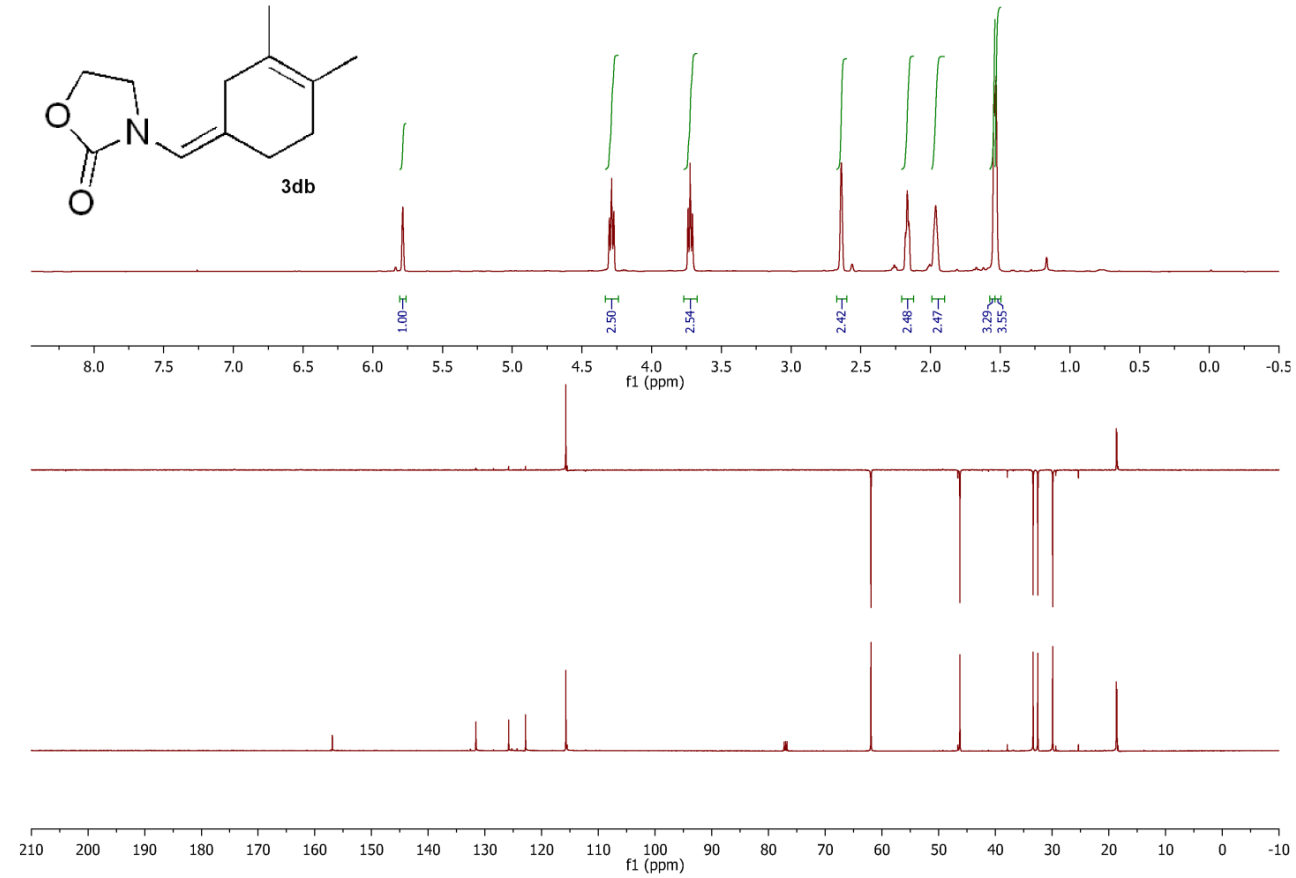
3.2 Reactions between 3-methylbuta-1,2-diene (**1d**) and dienes **2a** and **2j.**

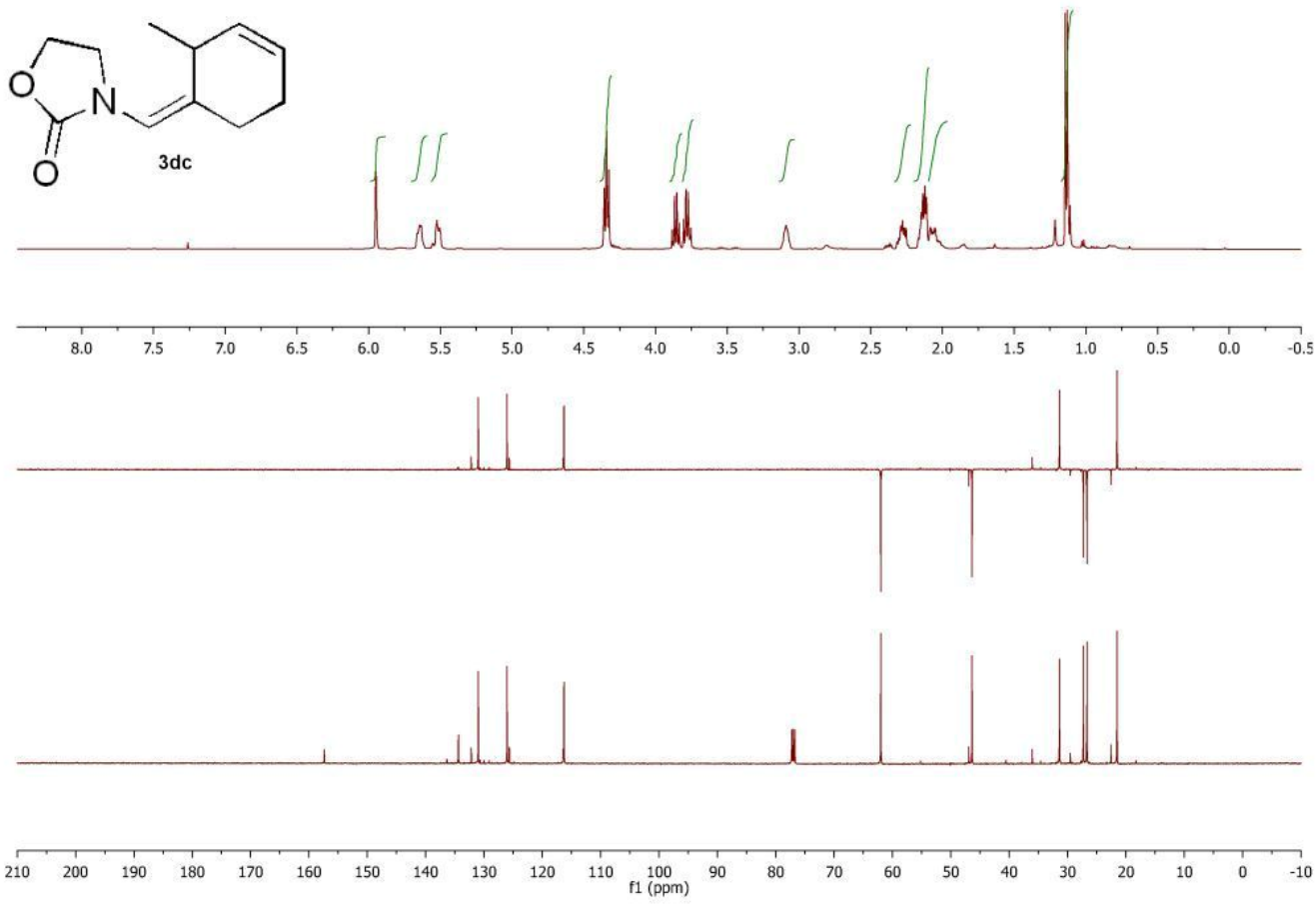
The reaction of 3-methylbuta-1,2-diene (**1a**) and isoprene with several Au catalysts led to complex mixtures of products, from which no [4+2] cycloadduct could be identified. On the other hand, the reaction of **1a** with **2i**, catalyzed by AuCl, led to the recovery of **2i** after 48 hours at *rt*.

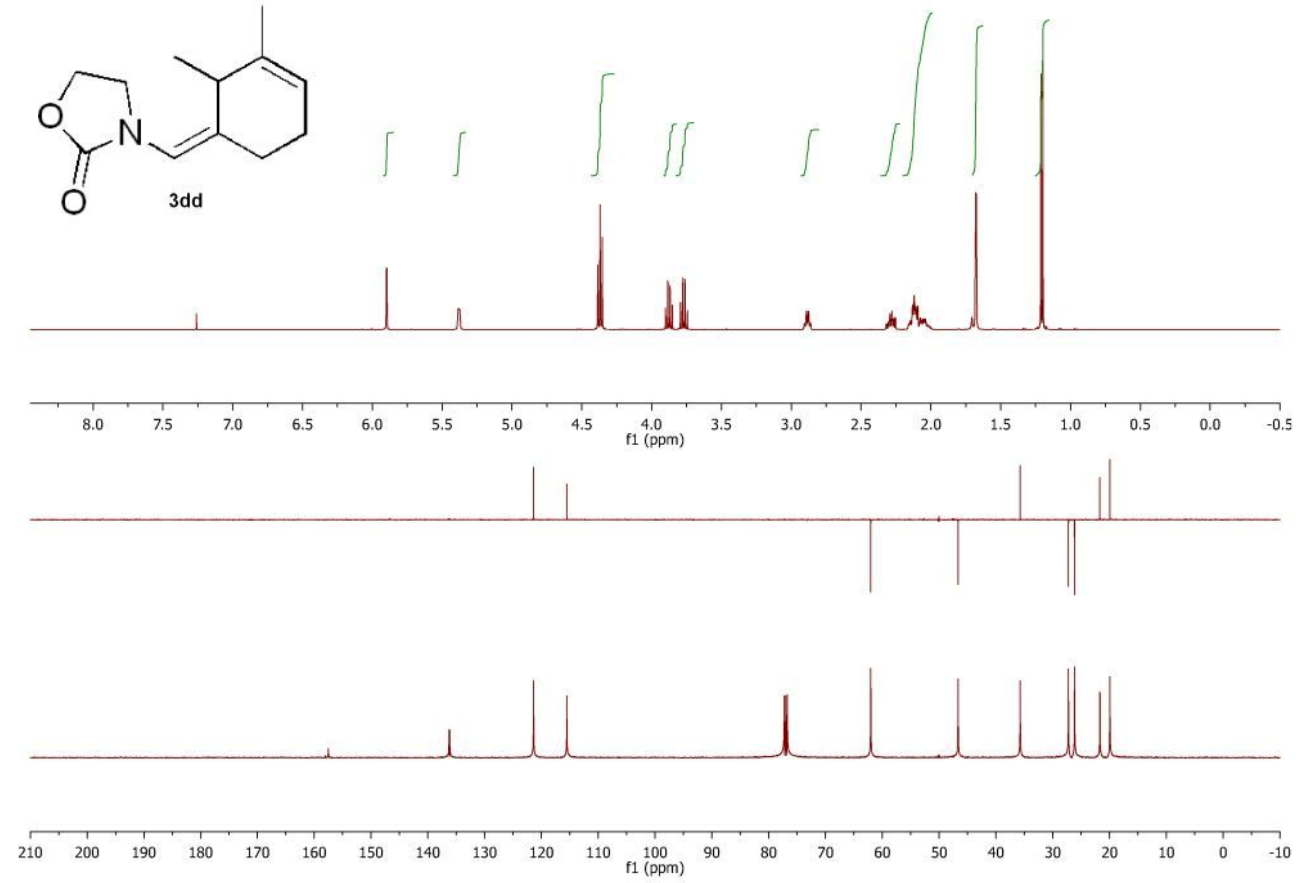


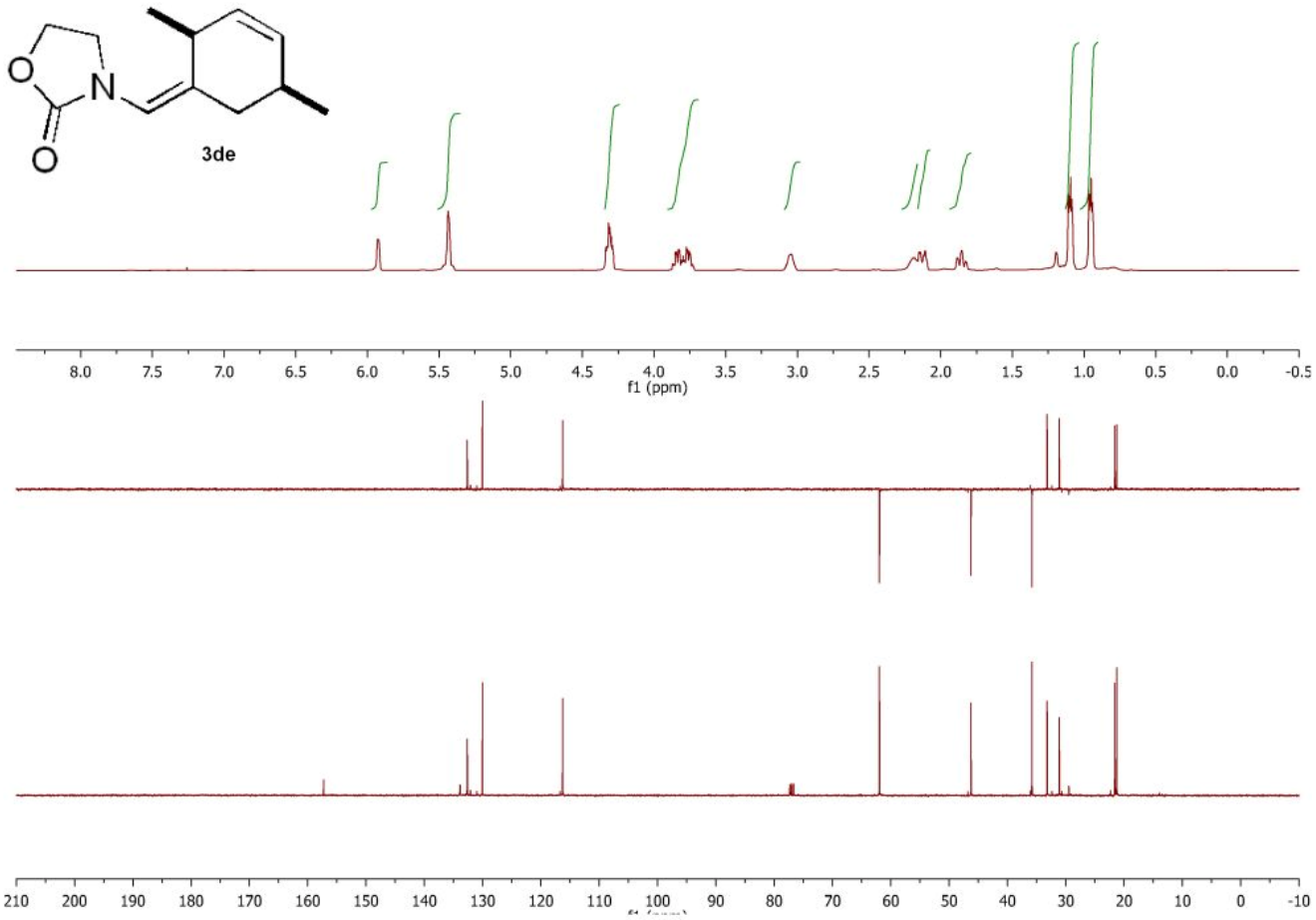

3da
f1 (ppm)

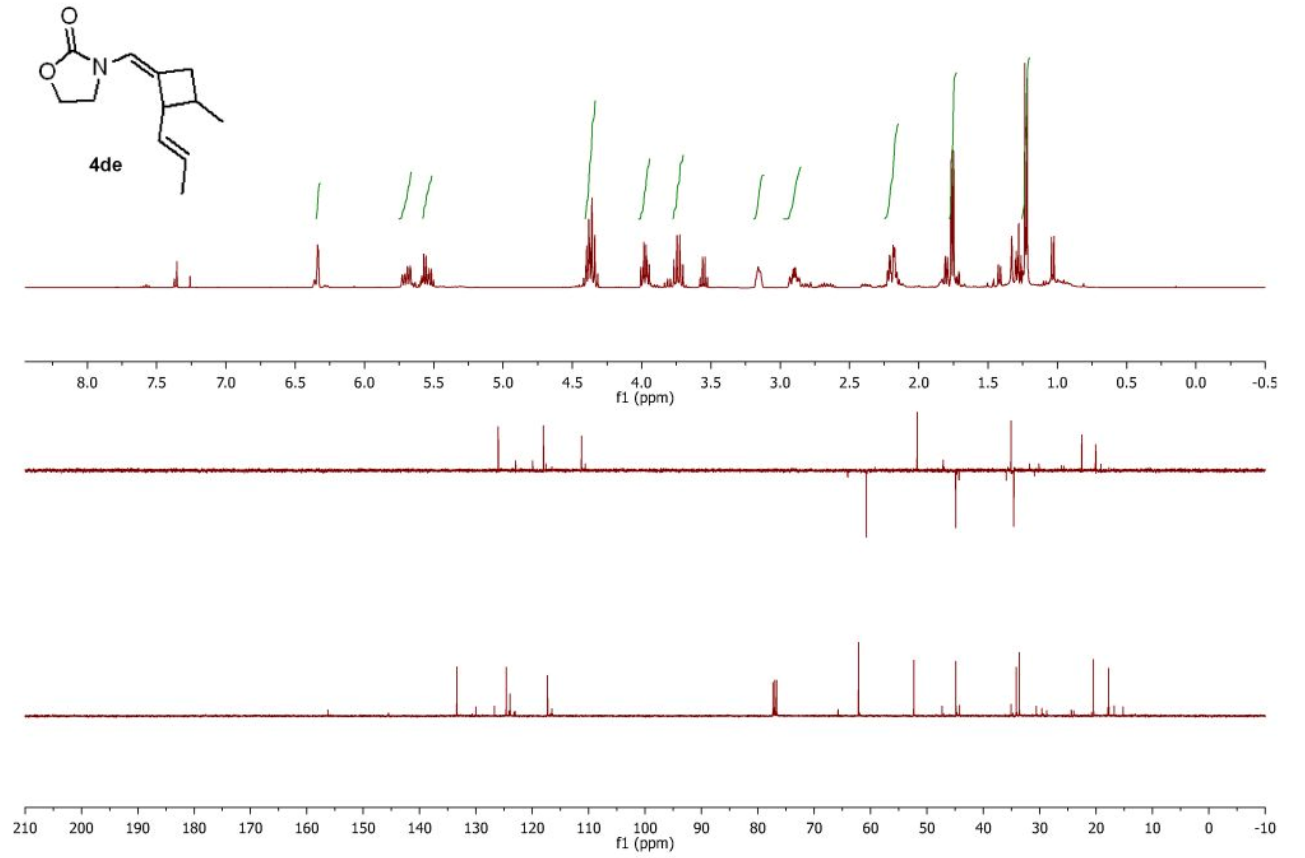

4da
f1 (ppm)

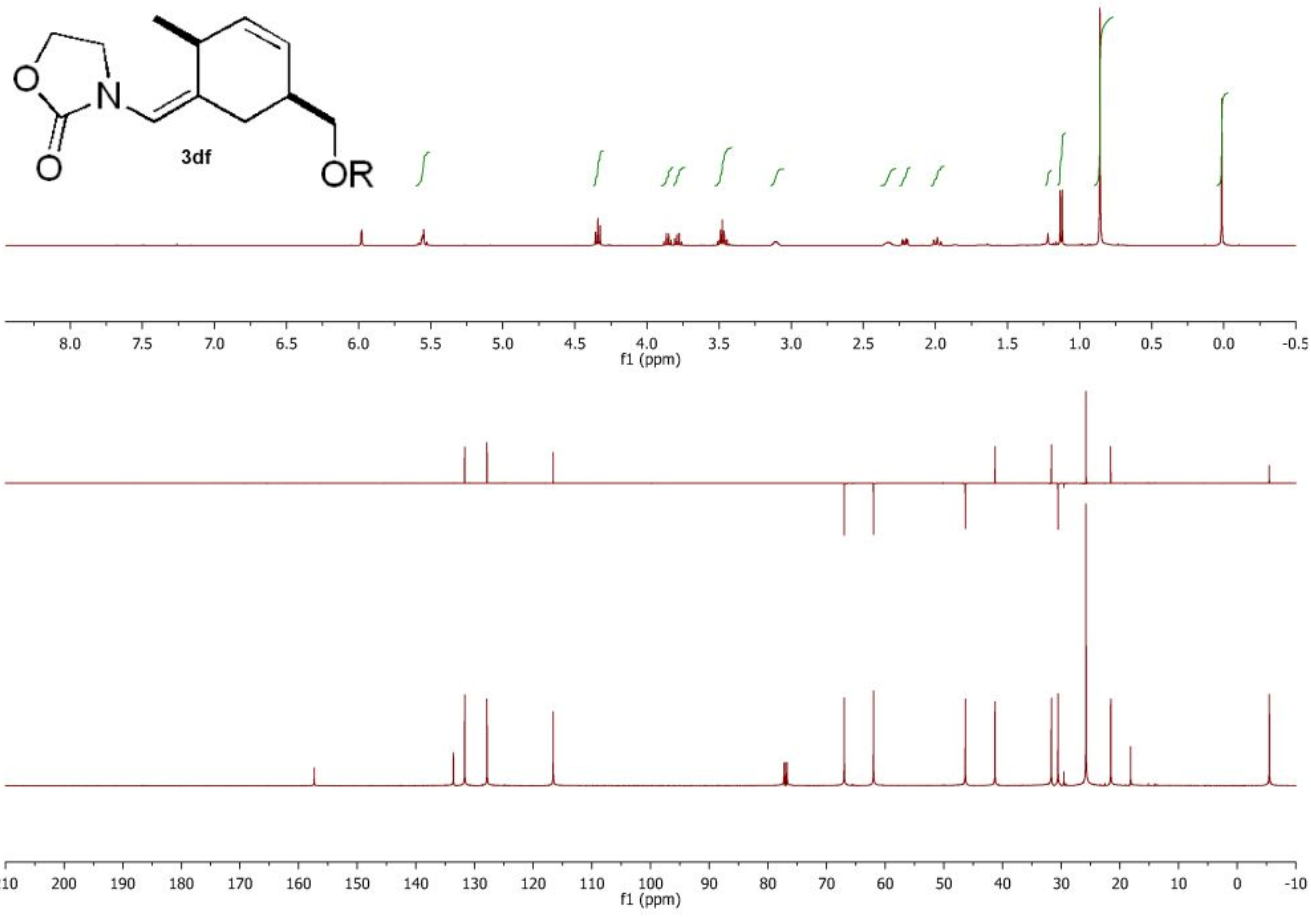

3db
1.00
2.50
2.54
2.42
2.48
2.47
3.29
3.55
f1 (ppm)
f1 (ppm)

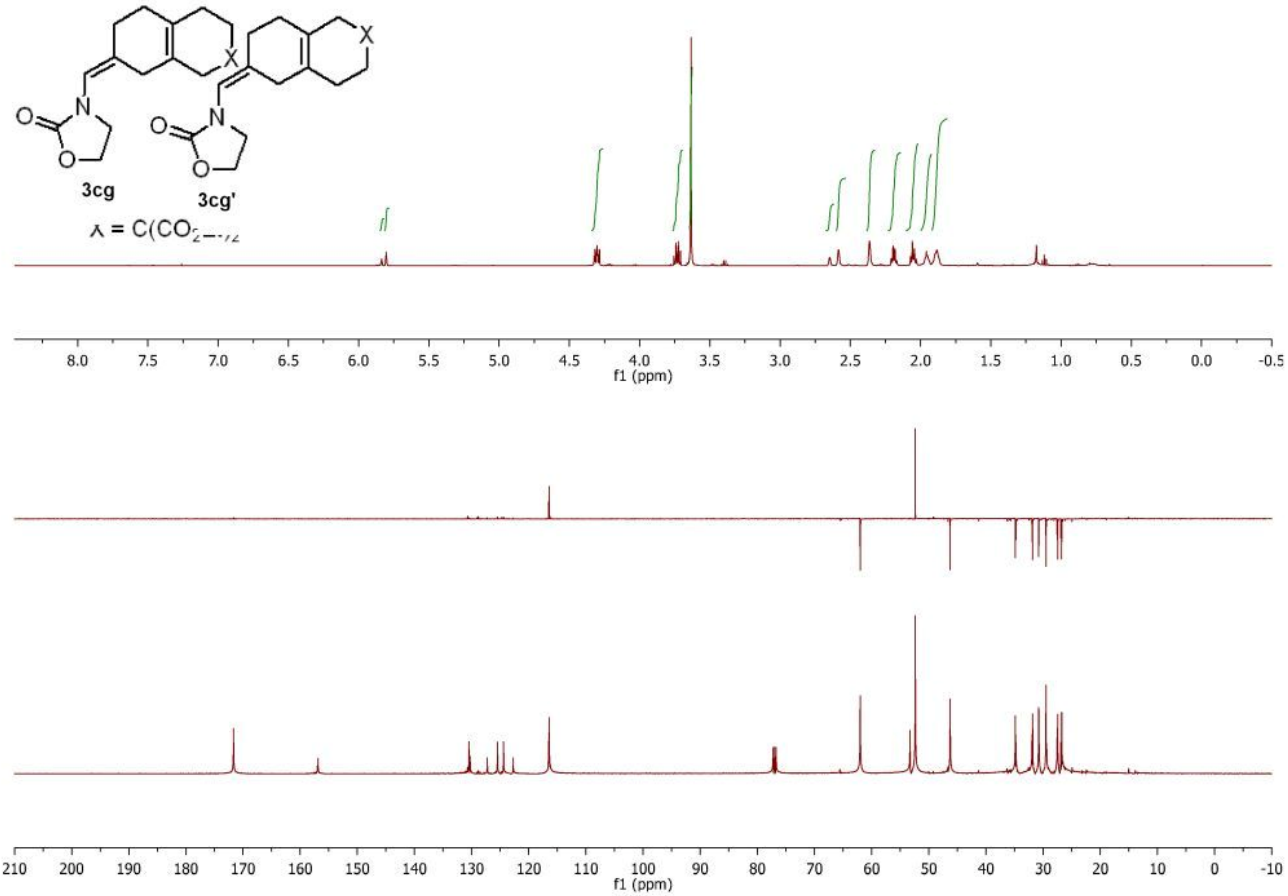

3dc
f1 (ppm)
f1 (ppm)

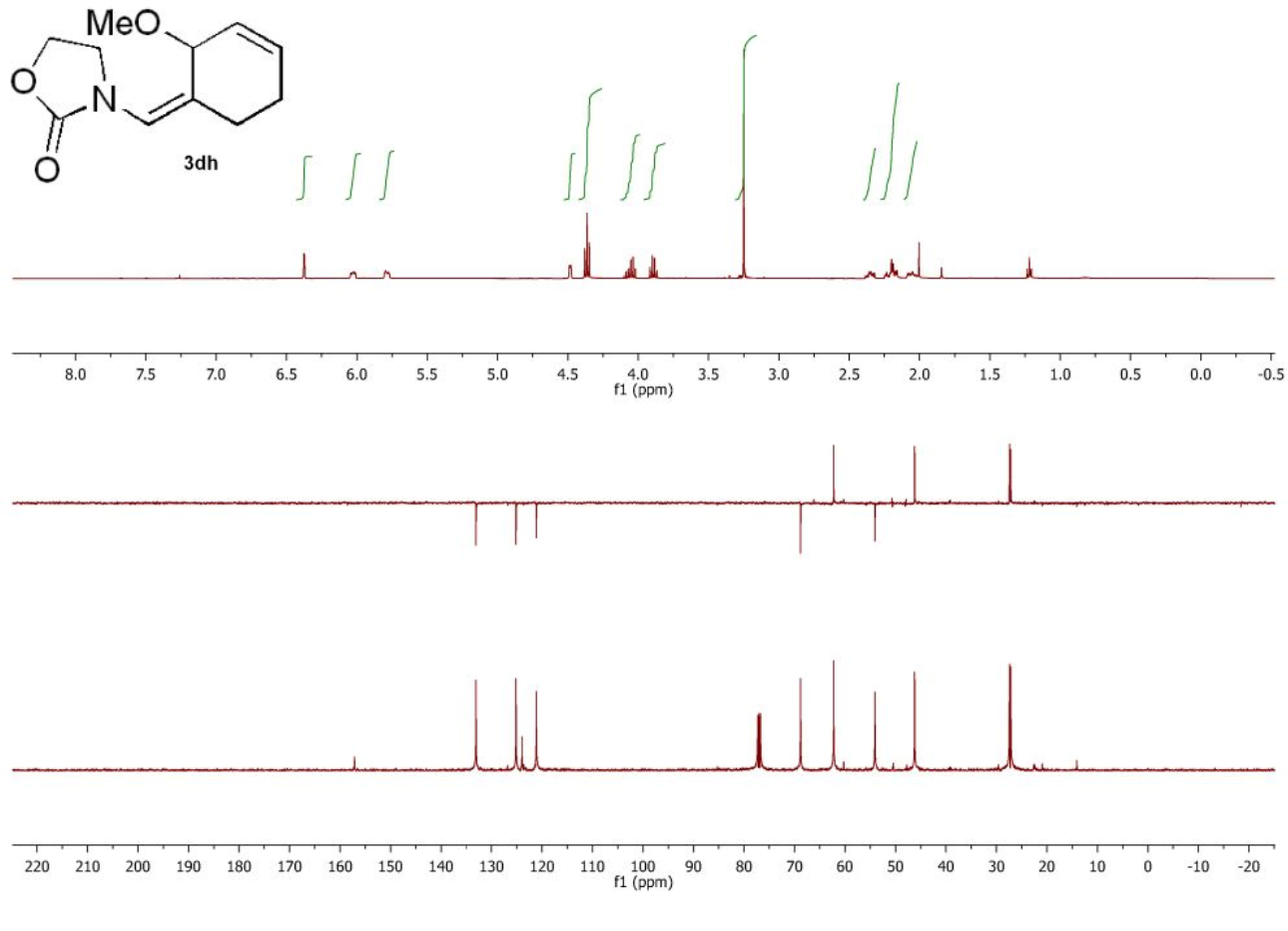

3dd
f1 (ppm)
f1 (ppm)

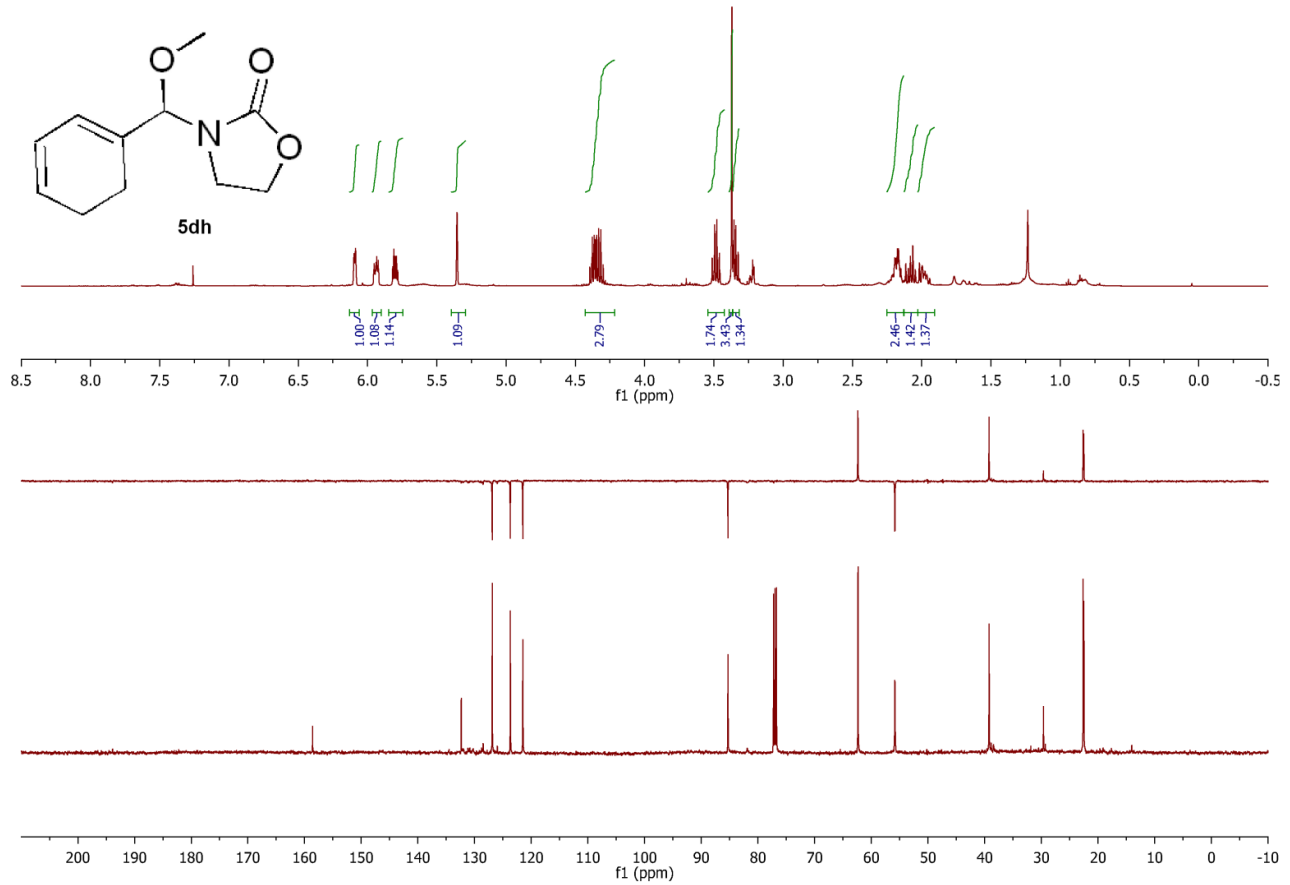

3de
f1 (ppm)

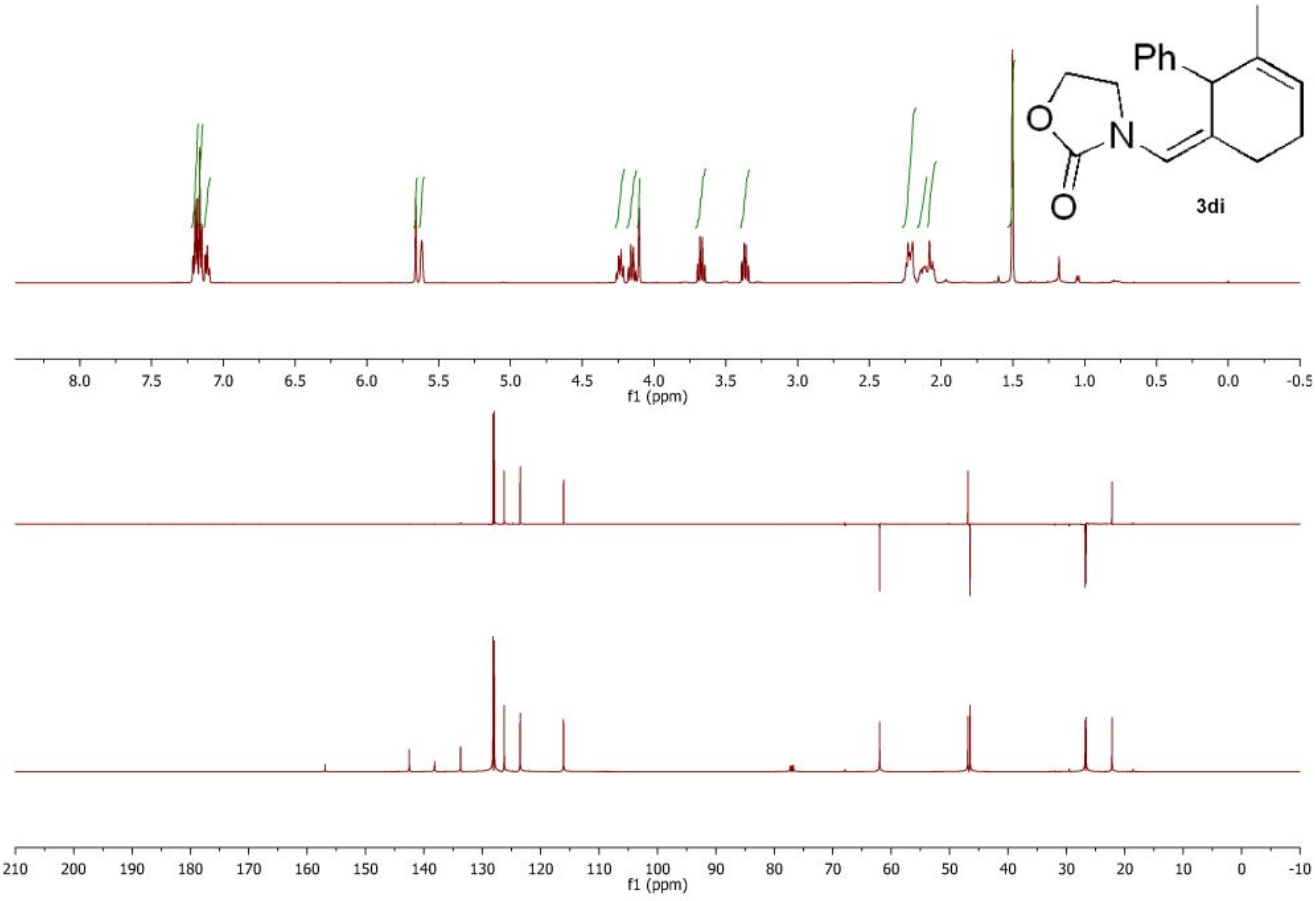

4de
f1 (ppm)
f1 (ppm)

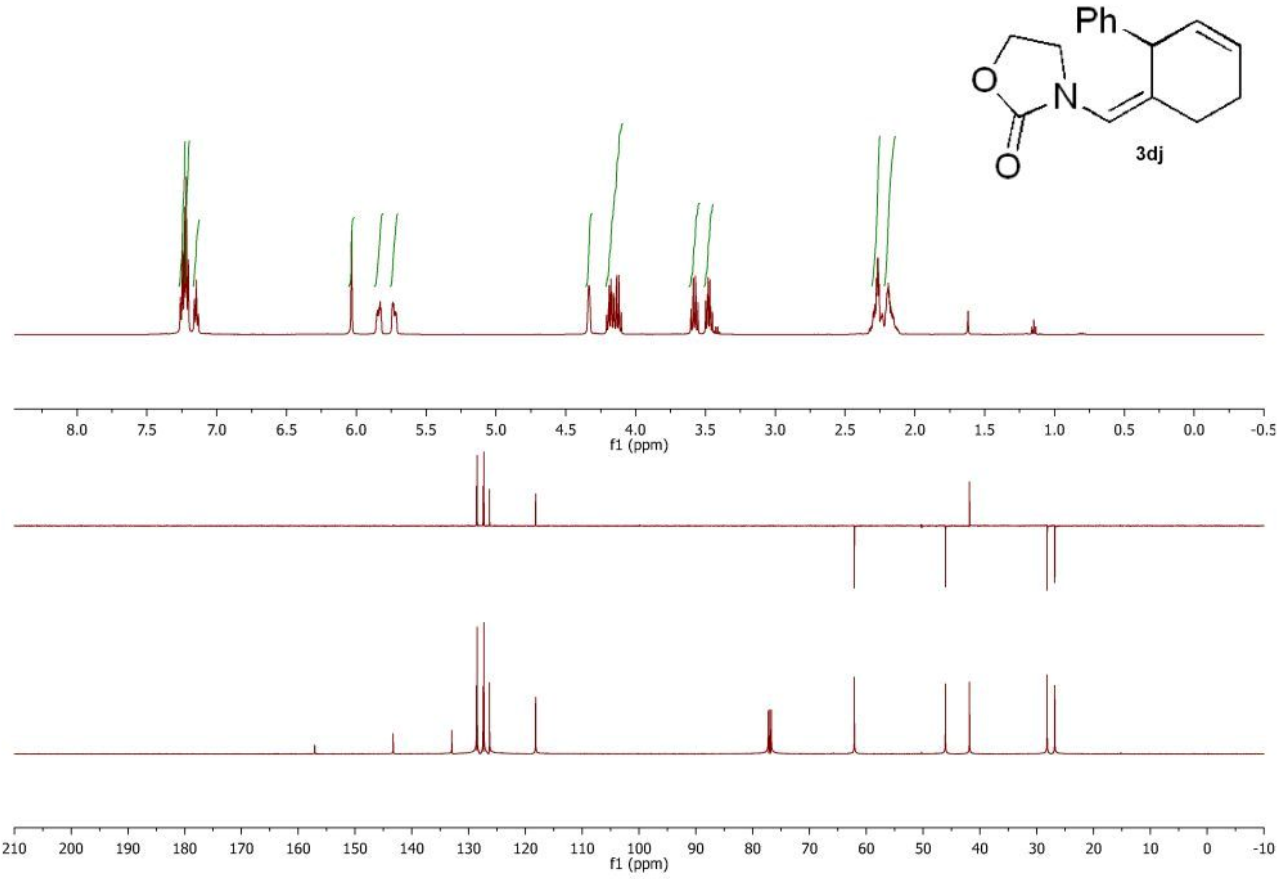

3df
OR
f1 (ppm)
f1 (ppm)

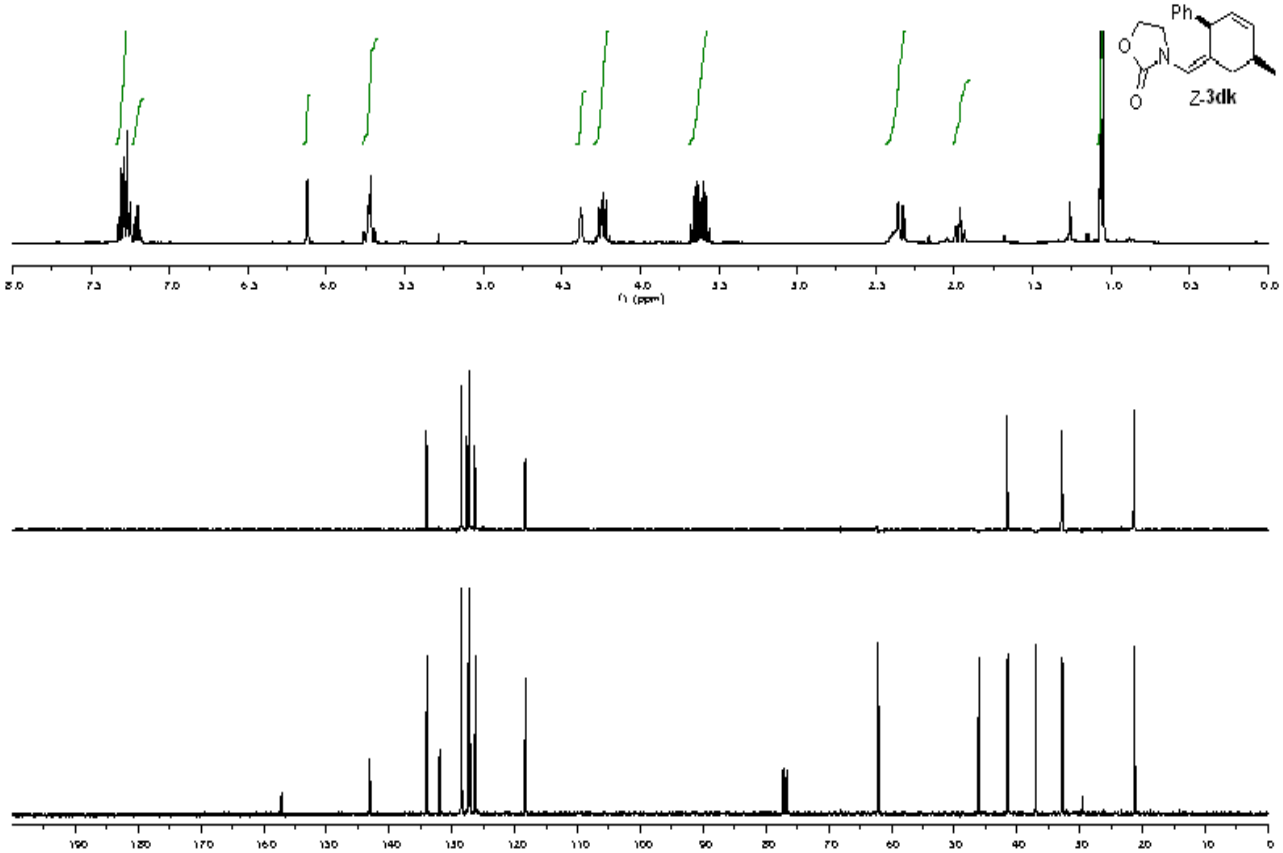

X
X
N
O
O
N
O
3cg
3cg'
X = C(CO2-t-Bu)2
f1 (ppm)

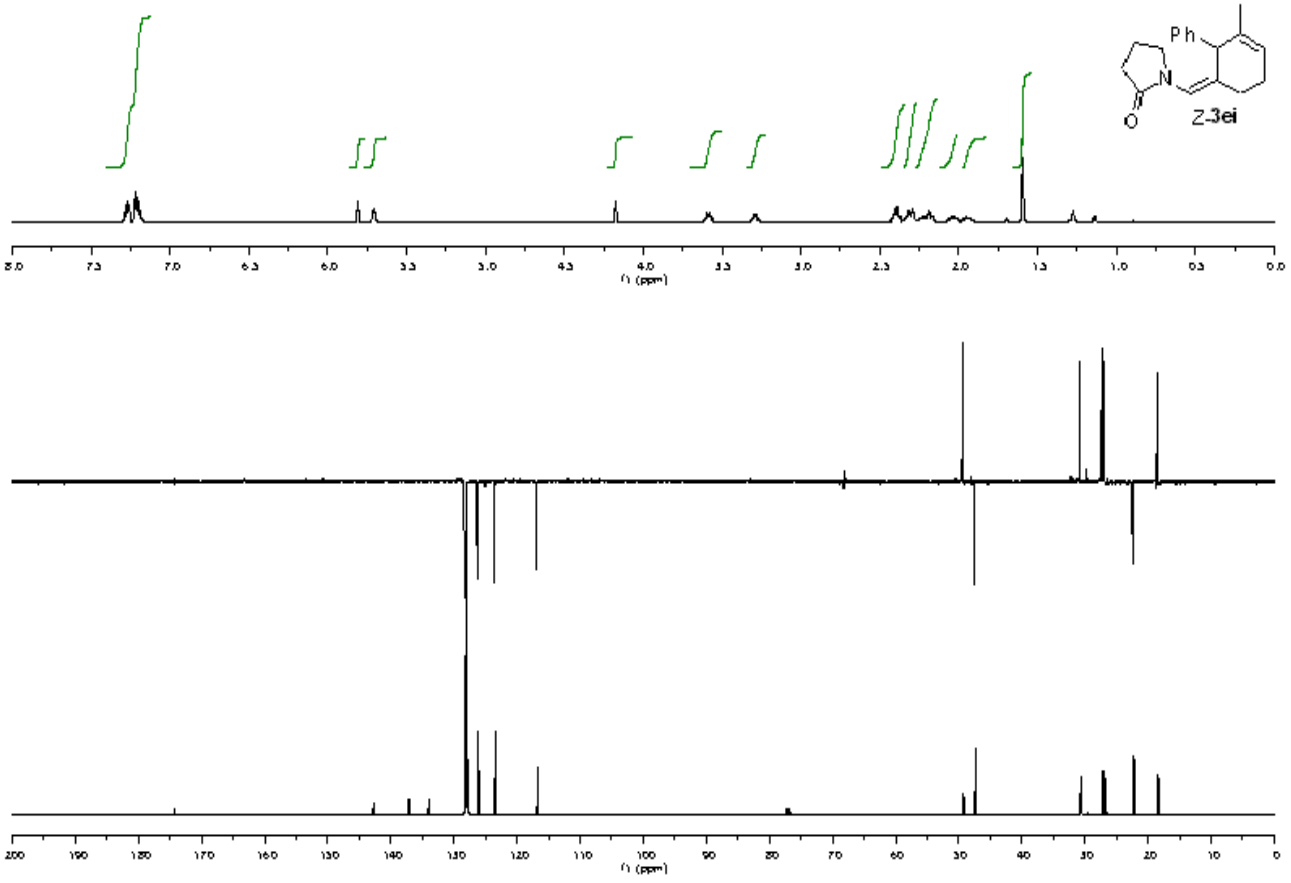

MeO
O
N
O
3dh
f1 (ppm)

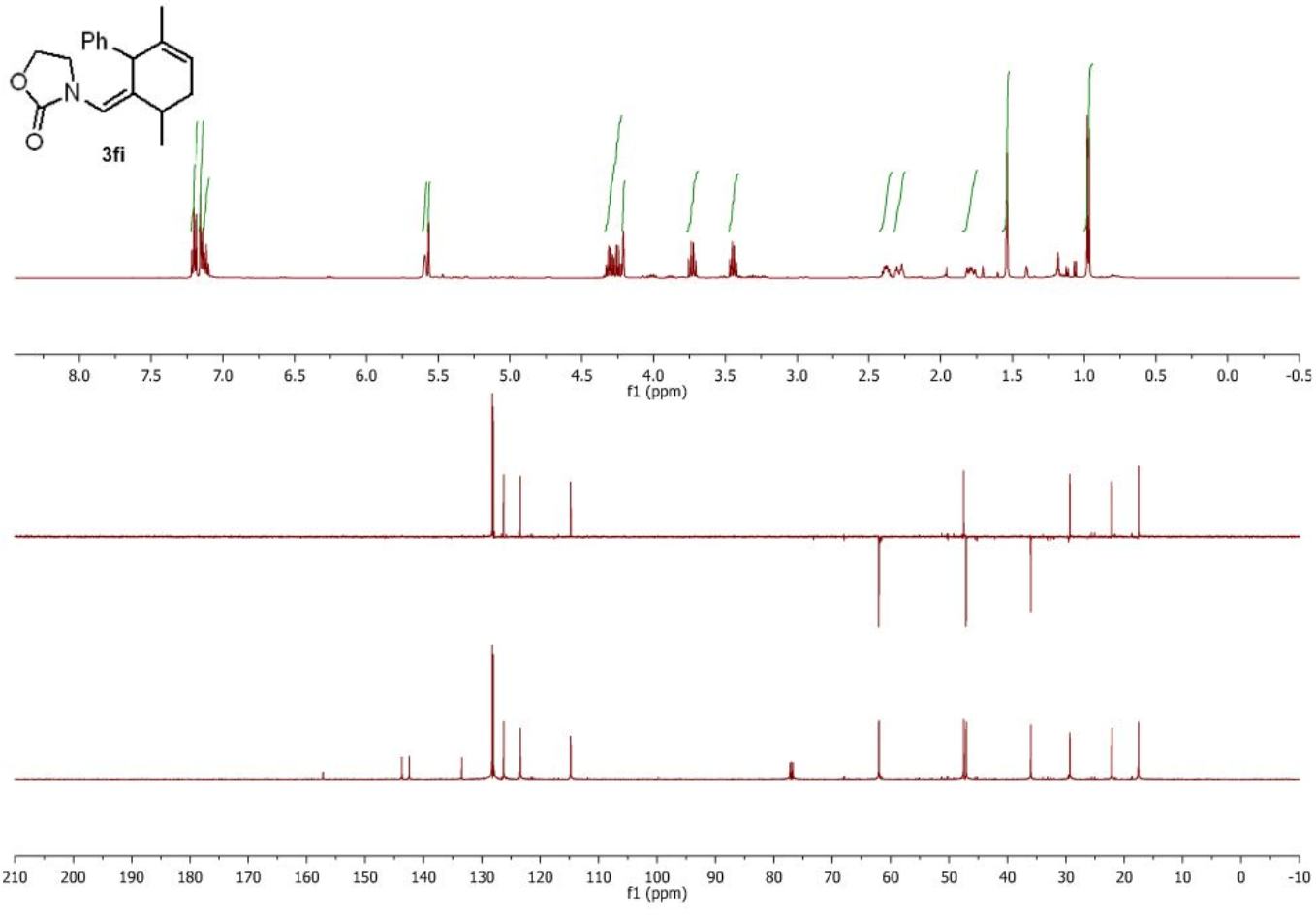

5dh
1.00
1.08
1.14
1.09
2.79
1.74
3.43
1.34
2.46
1.42
1.37
f1 (ppm)
f1 (ppm)

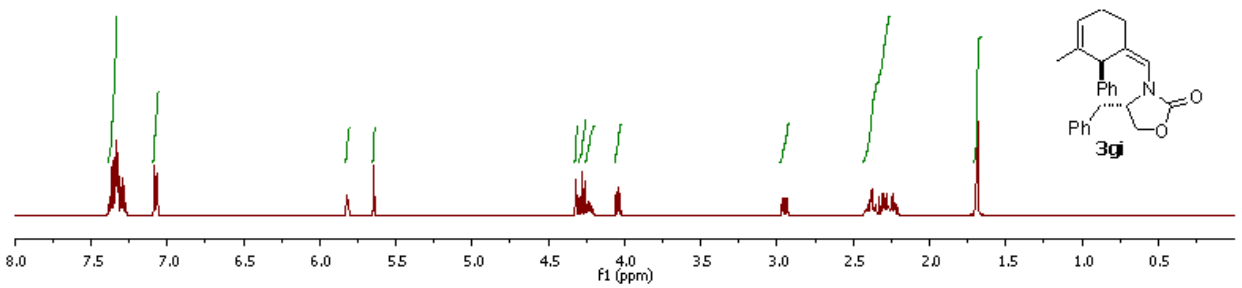

Ph
3di
f1 (ppm)
f1 (ppm)

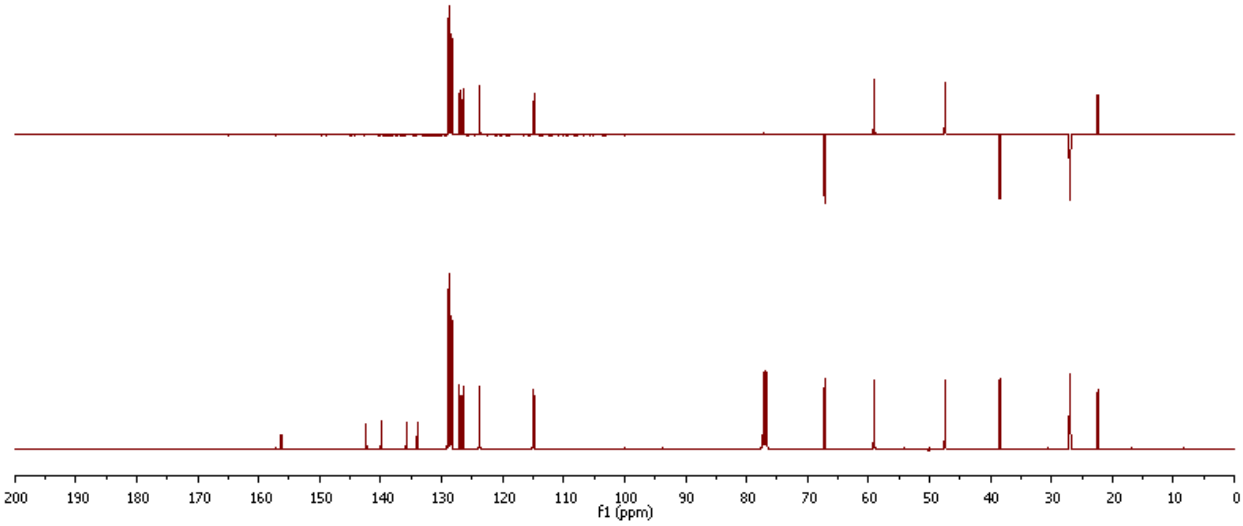

Ph
O
N
O
3dj
f1 (ppm)
f1 (ppm)

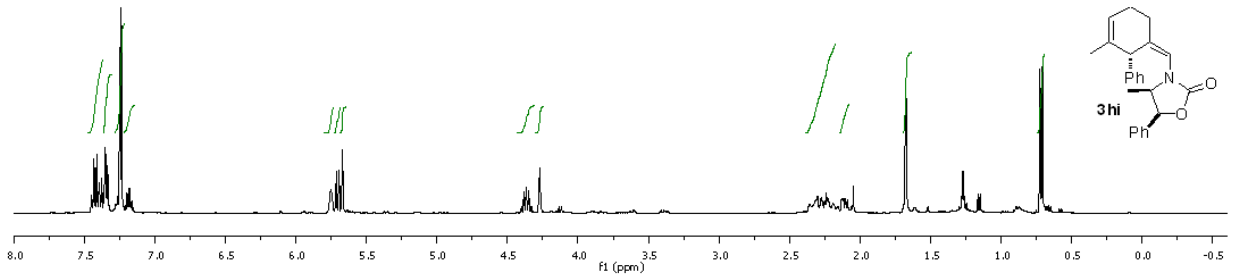

Ph
O
N
O
Z-3dk

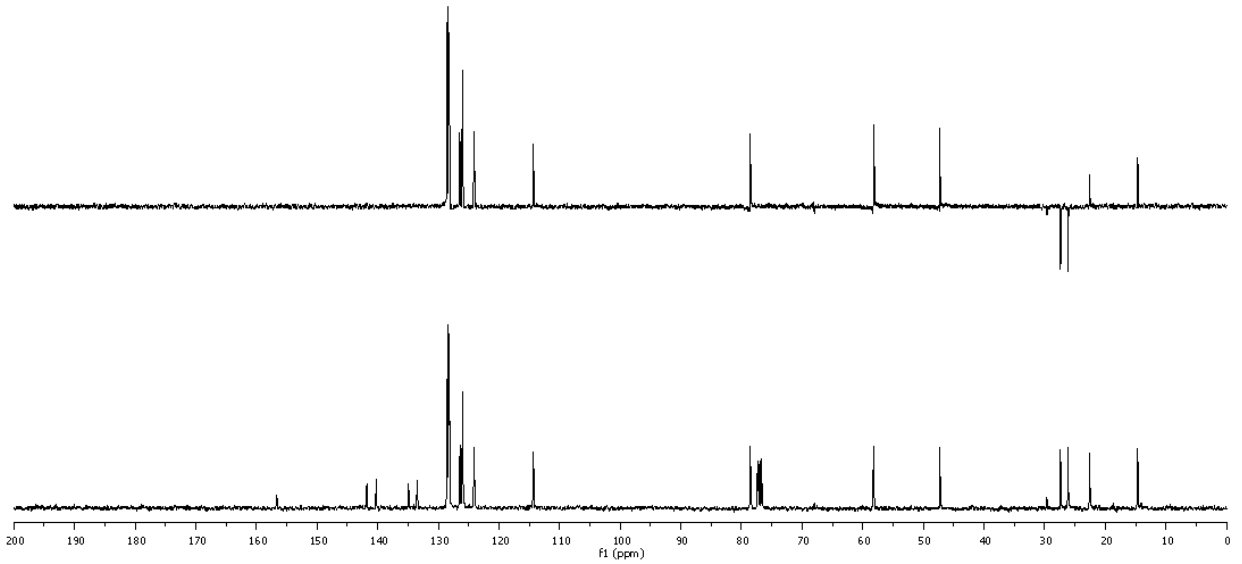

Ph
N
O
Z-3ei


Ph
O
N
O
3fi
f1 (ppm)


Ph
N
O
Ph
O
3gi
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
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
N
O
3hi
O
Ph
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 -0.5
f1 (ppm)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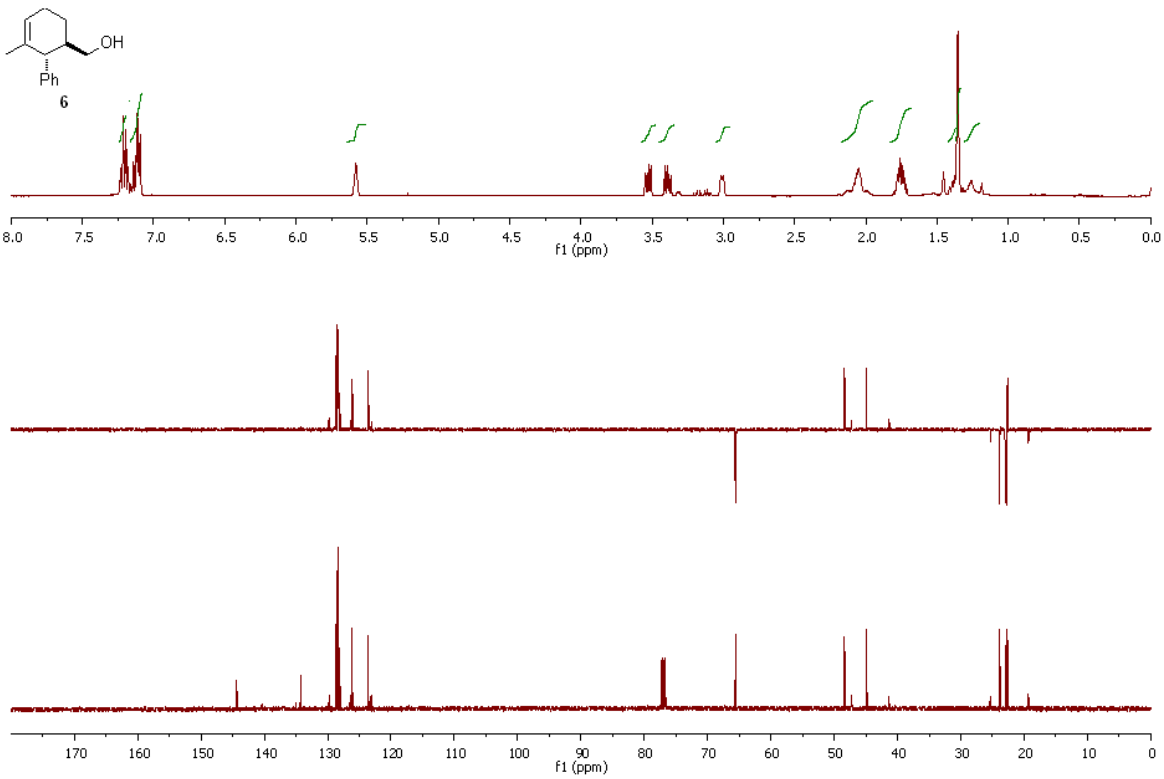
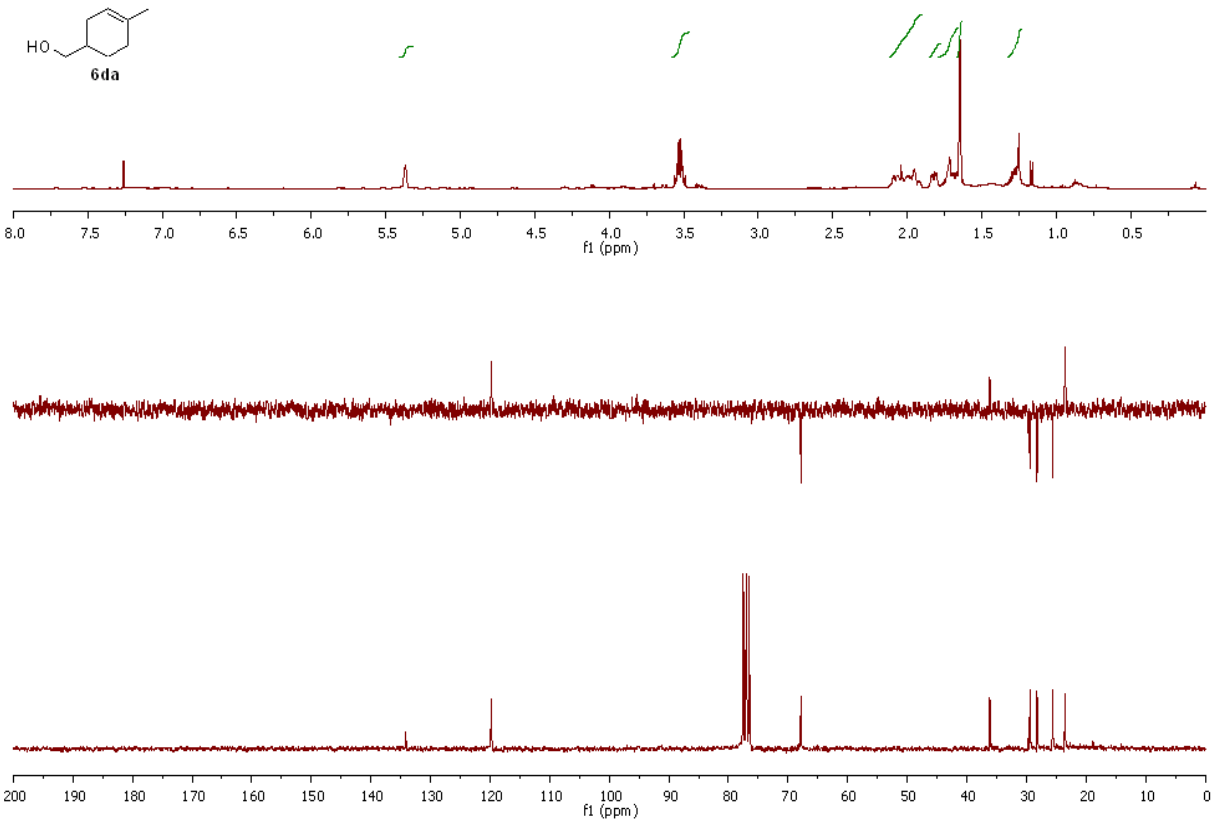
f1 (ppm)


OH
Ph
6
f1 (ppm)


HO
6da
f1 (ppm)