

Gold-Catalyzed Intermolecular Formal (3+2) Cycloaddition of Stabilized Vinyldiazo Derivatives and Electronically Unbiased Allenes

Enol López,^{a,b} Giacomo Lonzi,^{a,b} Javier González,^a and Luis A. López^{a,b*}

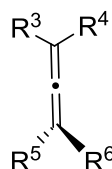
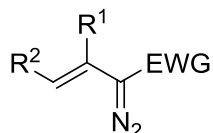
^a Departamento de Química Orgánica e Inorgánica and ^b Instituto Universitario de Química Organometálica "Enrique Moles"
Universidad de Oviedo, c/ Julián Clavería 8, 33006-Oviedo, Spain

TABLE OF CONTENTS

1.	General Considerations	S-2
2.	Summary of Catalyst Screening	S-3
3.	General Procedure for the Synthesis of Compounds 3	S-4
4.	Characterization Data of Compounds 3	S-5
5.	Reaction with phenyl-1,2-propadiene (2i)	S-14
6.	General Procedure for the Synthesis of Compounds 4	S-15
7.	Characterization Data of Compounds 4	S-16
8.	Reaction with cyclohexyl-1,2-propadiene (2k)	S-18
9.	Computational study	S-19
10.	References	S-29
11.	¹ H- and ¹³ C-NMR spectra for new compounds	S-30

1. General Considerations

All reactions were carried out under nitrogen using standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were distilled from CaH₂. The solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial suppliers and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F₂₅₄ indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ¹H NMR (300, 400 MHz) and ¹³C NMR (75.5 and 100 MHz) spectra were recorded at room temperature in CDCl₃ on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 77.0 ppm). 2D NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were determined on a VG Autospec M mass spectrometer. This study was carried out using vinyl diazoacetates **1a-g**¹ and allenes **2a-k**² (Figure S1), which were prepared according to well-known procedures previously described in the literature. Allene [D]-**2k** was prepared following the procedure developed by Moreau and Gaudemar.³ [Au(IPr)(CH₃CN)]SbF₆ was prepared according to a literature procedure.⁴ All other reagents used in this work were of the best commercial grade available and used without further purification.



1a (R¹ = H; R² = H; EWG = COOEt)

1b (R¹ = H; R² = H; EWG = COOBn)

1c (R¹ = H; R² = H; EWG = COOtBu)

1d (R¹ = Me; R² = H; EWG = COOEt)

1e (R¹ = OTBS; R² = H; EWG = COOEt)

1f (R¹ = H; R² = EWG = COOEt)

1g (R¹ = Me; R² = H; EWG = COMe)

2a (R³ = R⁴ = Me; R⁵ = R⁶ = H)

2b (R³, R⁴ = (CH₂)₅; R⁵ = R⁶ = H)

2c (R³, R⁴ = (CH₂)₂CH^tBu(CH₂)₂; R⁵ = R⁶ = H)

2d (R³ = R⁴ = Bn; R⁵ = R⁶ = H)

2e (R³ = R⁴ = Ph; R⁵ = R⁶ = H)

2f (R³ = R⁴ = PMP; R⁵ = R⁶ = H)

2g (R³ = Ph; R⁴ = Me; R⁵ = R⁶ = H)

2h (R³ = TMS; R⁴ = Me; R⁵ = R⁶ = H)

2i (R³ = Ph; R⁴ = R⁵ = R⁶ = H)

2j (R³ = R⁴ = R⁵ = R⁶ = Me)

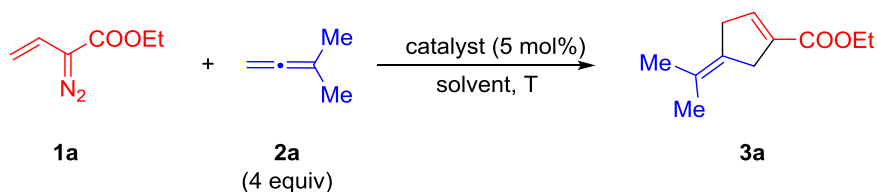
2k (R³ = Cy; R⁴ = R⁵ = R⁶ = H)

[D]-**2k** (R³ = Cy; R⁴ = D; R⁵ = R⁶ = H)

Figure S1. Starting materials used in this work

2. Summary of the Catalyst Screening

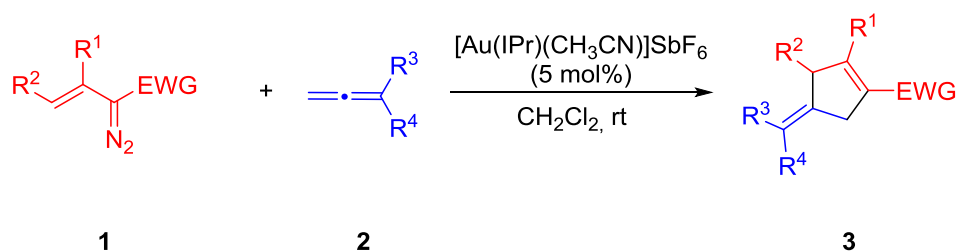
Table S1. Summary of the Catalyst Screening for the Reaction of Diazo Compound **1a** and 3-methylpropa-1,2-diene (**2a**)



entry	catalyst	solvent	T (°C)	3a (%) ^a
1	CuBr	CH ₂ Cl ₂	RT	-
2	CuBr	THF	RT	-
3	[Cu(MeCN) ₄][BF ₄]	CH ₂ Cl ₂	RT	-
4	Cu(OTf) ₂	CH ₂ Cl ₂	RT	-
5	Rh ₂ (OAc) ₄	CH ₂ Cl ₂	RT	-
6	AgSbF ₆	CH ₂ Cl ₂	RT	17
7	AuCl ₃	CH ₂ Cl ₂	RT	-
8	AuCl	CH ₂ Cl ₂	RT	-
9	(Ph ₃ P)AuNTf ₂	CH ₂ Cl ₂	RT	-
10	(JohnPhos)AuNTf ₂	CH ₂ Cl ₂	RT	49
11	(IPr)AuNTf ₂	CH ₂ Cl ₂	RT	36
12	[IPrAu(MeCN)][SbF₆]	CH₂Cl₂	RT	75
13	[IPrAu(MeCN)][SbF ₆]	DCE	50	23
14	[IPrAu(MeCN)][SbF ₆]	DMF	RT	5

^a Yield of isolated product after column chromatography.

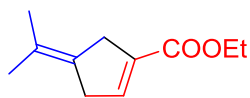
3. General Procedure for the Synthesis of Compounds 3



[Au(IPr)(CH₃CN)]SbF₆ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyl diazo compound **1** (0.5 mmol) and the corresponding allene **2** (2 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate mixtures) to afford the (3+2) cycloadducts as colorless oils.

The reaction of diethyl (*E*)-4-diazopent-2-enedioate (**1f**) and 3-methylbuta-1,2-diene (**2a**) was performed at 50°C in dichloroethane.

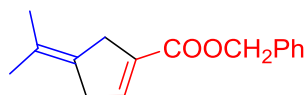
4. Characterization Data of Compounds 3



3a

Ethyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3a). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (**2a**, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound **3a** (68 mg, 75%) as a colorless oil.

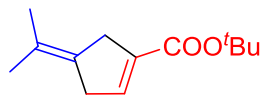
¹H-NMR: 1.30 (t, *J* = 7.2 Hz, 3H), 1.63 (s, 3H), 1.66 (s, 3H), 3.16 (s, 2H), 3.22 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.79-6.81 (m, 1H); ¹³C-NMR: 14.3, 20.7, 20.9, 36.2, 38.0, 60.1, 124.4, 129.8, 135.7, 142.2, 165.1; HRMS (EI) calculated for [C₁₁H₁₆O₂]⁺ (M⁺): 180.1150, found 180.1153.



3b

Benzyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3b). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (**2a**, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound **3b** (102 mg, 84%) as a colorless oil.

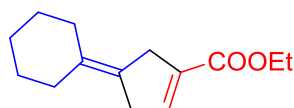
¹H-NMR: 1.66 (s, 3H), 1.68 (s, 3H), 3.19 (s, 2H), 3.28 (s, 2H), 5.24 (s, 2H), 6.88-6.91 (m, 1H), 7.37-7.41 (m, 5H); ¹³C-NMR: 20.8, 21.0, 36.2, 38.1, 65.9, 124.5, 128.1, 128.5, 129.6, 135.4, 136.3, 143.0, 164.8; HRMS (EI) calculated for [C₁₆H₁₈O₂]⁺ (M⁺): 242.1307, found 242.1303.



3c

tert-butyl 4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3c). The general procedure was followed using *tert*-butyl 2-diazobut-3-enoate (**1c**, 84 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (**2a**, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound **3c** (68 mg, 65%) as a colorless oil.

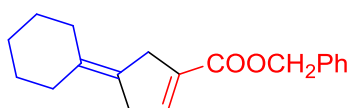
$^1\text{H-NMR}$: 1.51 (s, 9H), 1.64 (s, 3H), 1.66 (s, 3H), 3.15 (s, 2H), 3.19 (s, 2H), 6.71-6.72 (m, 1H); $^{13}\text{C-NMR}$: 20.7, 20.9, 28.2, 36.2, 37.9, 80.1, 124.1, 130.1, 137.3, 141.1, 164.6; **HRMS** (EI) calculated for $[\text{C}_{13}\text{H}_{20}\text{O}_2]^+$ (M^+): 208.1463, found 208.1467.



3d

Ethyl 4-cyclohexylidenecyclopent-1-ene-1-carboxylate (3d). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and vinylidene-cyclohexane (**2b**, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3d** (78 mg, 71%) as a colorless oil.

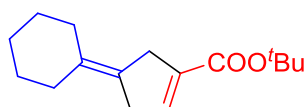
$^1\text{H-NMR}$: 1.32 (t, $J = 7.2$ Hz, 3H), 1.51-1.57 (m, 6H), 2.07-2.11 (m, 4H), 3.20 (s, 2H), 3.26 (s, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 6.83 (m, 1H); $^{13}\text{C-NMR}$: 14.3, 26.5, 27.4, 31.3, 31.5, 35.5, 37.3, 60.1, 126.3, 132.5, 135.6, 142.2, 165.2; **HRMS** (EI) calculated for $[\text{C}_{14}\text{H}_{20}\text{O}_2]^+$ (M^+): 220.1463, found 220.1459.



3e

Benzyl 4-cyclohexylidenecyclopent-1-ene-1-carboxylate (3e). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol) and vinylidene-cyclohexane (**2b**, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3e** (97 mg, 69%) as a colorless oil.

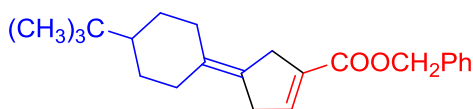
$^1\text{H-NMR}$: 1.50-1.55 (m, 6H), 2.06-2.11 (m, 4H), 3.22 (s, 2H), 3.30 (s, 2H), 5.23 (s, 2H), 6.89-6.90 (m, 1H), 7.34-7.41 (m, 5H); $^{13}\text{C-NMR}$: 26.6, 27.39, 27.42, 31.3, 31.5, 35.5, 37.4, 65.9, 126.1, 128.0, 128.1, 128.5, 132.6, 135.3, 136.3, 143.0, 164.9; **HRMS** (EI) calculated for $[\text{C}_{19}\text{H}_{22}\text{O}_2]^+$ (M^+): 282.1620, found 282.1616.



3f

tert-Butyl 4-cyclohexylidenecyclopent-1-ene-1-carboxylate (3f). The general procedure was followed using *tert*-butyl 2-diazobut-3-enoate (**1c**, 84 mg, 0.5 mmol) and vinylidene-cyclohexane (**2b**, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3f** (79 mg, 64%) as a colorless oil.

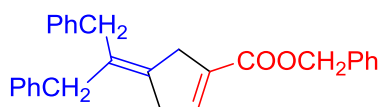
¹H-NMR: 1.50-1.54 (m + s, 15H), 2.06-2.11 (m, 4H), 3.18 (s, 2H), 3.21 (s, 2H), 6.71-6.73 (m, 1H); ¹³C-NMR: 26.6, 27.4, 28.2, 31.3, 31.5, 35.5, 37.2, 80.0, 126.6, 132.3, 137.2, 141.1, 164.6; HRMS (EI) calculated for [C₁₆H₂₄O₂]⁺ (M⁺): 248.1776, found 248.1779.



3g

Benzyl 4-(4-(tert-butyl)cyclohexylidene)cyclopent-1-ene-1-carboxylate (3g). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol) and 1-(*tert*-butyl)-4-vinylidene-cyclohexane (**2c**, 329 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3g** (115 mg, 68%) as a colorless oil.

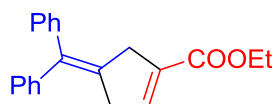
¹H-NMR: 0.87 (s, 9H), 0.94-1.19 (m, 3H), 1.77-1.86 (m, 4H), 2.38-2.49 (m, 2H), 3.12-3.38 (m, 4H), 5.22 (s, 2H), 6.88-6.91 (m, 1H), 7.34-7.41 (m, 5H); ¹³C-NMR: 27.6, 28.0, 31.2, 31.4, 32.5, 35.6, 37.4, 48.1, 65.9, 125.8, 128.0, 128.5, 132.5, 135.3, 136.3, 143.0, 164.9; HRMS (EI) calculated for [C₂₃H₃₀O₂]⁺ (M⁺): 338.2246, found 338.2244.



3h

Benzyl 4-(1,3-diphenylpropan-2-ylidene)cyclopent-1-ene-1-carboxylate (3h). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol) and 1,1-dibenzylpropa-1,2-diene (**2d**, 440 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3h** (118 mg, 60%) as a colorless oil.

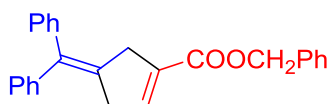
¹H-NMR: 3.32 (s, 2H), 3.36 (s, 2H), 3.45 (br s, 2H), 3.57 (br s, 2H), 5.27 (s, 2H), 6.96-6.97 (m, 1H), 7.13-7.37 (m, 15H); ¹³C-NMR: 36.6, 37.9, 38.3, 38.4, 66.1, 126.1, 128.2, 128.5, 128.6, 128.7, 131.1, 134.3, 135.2, 136.2, 139.5, 139.6, 142.6, 164.7; HRMS (EI) calculated for [C₂₈H₂₆O₂]⁺ (M⁺): 394.1933, found 394.1938.



3i

Ethyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3i). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3i** (134 mg, 88%) as a colorless oil.

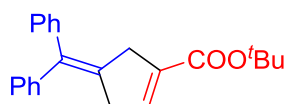
¹H-NMR: 1.30 (t, *J* = 7.2 Hz, 3H), 3.37 (d, *J* = 2.7 Hz, 2H), 3.46 (d, *J* = 1.8 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 6.81-6.83 (m, 1H), 7.22-7.37 (m, 10H); ¹³C-NMR: 14.7, 38.2, 40.2, 60.7, 127.0, 128.8, 129.1, 135.8, 136.7, 137.4, 141.7, 142.7, 142.8, 165.2; HRMS (EI) calculated for [C₂₁H₂₀O₂]⁺ (M⁺): 304.1463, found 304.1466.



3j

Benzyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3j). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3j** (128 mg, 70%) as a colorless oil.

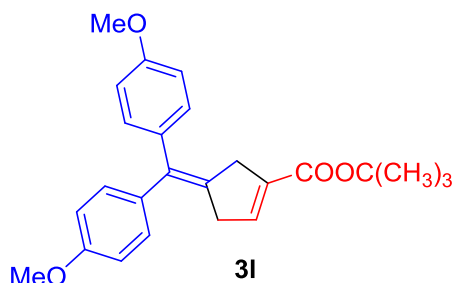
¹H-NMR: 3.38 (d, *J* = 2.4 Hz, 2H), 3.50 (d, *J* = 2.1 Hz, 2H), 5.23 (s, 2H), 6.87-6.89 (m, 1H), 7.23-7.40 (m, 15H); ¹³C-NMR: 37.8, 39.8, 66.0, 126.6, 128.2, 128.4, 128.5, 128.6, 128.7, 135.0, 136.2, 136.5, 136.8, 142.1, 142.4, 164.5; HRMS (EI) calculated for [C₂₆H₂₂O₂]⁺ (M⁺): 366.1620, found 366.1620.



3k

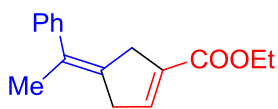
tert-Butyl 4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3k). The general procedure was followed using *tert*-butyl 2-diazobut-3-enoate (**1c**, 84 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3k** (115 mg, 69%) as a colorless oil.

¹H-NMR: 1.51 (s, 9H), 3.35 (d, *J* = 2.7 Hz, 2H), 3.44 (d, *J* = 2.1 Hz, 2H), 6.71-6.72 (m, 1H), 7.22-7.28 (m, 6H), 7.32-7.36 (m, 4H); ¹³C-NMR: 28.2, 37.9, 39.7, 80.3, 126.5, 128.3, 128.4, 128.7, 128.8, 136.2, 136.9, 137.3, 140.2, 142.3, 142.5, 164.3; HRMS (EI) calculated for [C₂₃H₂₄O₂]⁺ (M⁺): 332.1776, found 332.1779.



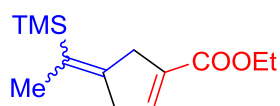
tert-Butyl 4-(bis(4-methoxyphenyl)methylene)cyclopent-1-ene-1-carboxylate (3l). The general procedure was followed using *tert*-butyl 2-diazobut-3-enoate (**1c**, 84 mg, 0.5 mmol) and 1,1-di(4-methoxyphenyl)propa-1,2-diene (**2f**, 504 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3l** (98 mg, 50%) as a colorless oil.

¹H-NMR: 1.49 (s, 9H), 3.32 (d, *J* = 2.4 Hz, 2H), 3.40 (d, *J* = 1.8 Hz, 2H), 3.82 (s, 6H), 6.70 (t, *J* = 2.1 Hz, 1H), 6.84-6.88 (m, 4H), 7.11-7.17 (m, 4H); ¹³C-NMR: 28.6, 38.3, 40.2, 55.6, 80.7, 114.0, 114.05, 130.2, 130.3, 135.5, 135.7, 136.4, 137.3, 140.7, 158.4, 164.8; HRMS (EI) calculated for [C₂₅H₂₈O₄]⁺ (M⁺): 392.1988, found 392.1985.



Ethyl (Z)-4-(1-phenylethylidene)cyclopent-1-ene-1-carboxylate (3m). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and 3-phenylbuta-1,2-diene (**2g**, 260 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3m** (84 mg, 69%) as a 15:1 *Z/E* mixture as a colorless oil.

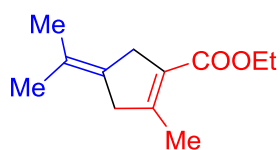
¹H-NMR: 1.28 (t, *J* = 7.2 Hz, 3H), 2.01 (s, 3H), 3.27 (s, 2H), 3.36 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 6.85-6.88 (m, 1H), 7.24-7.27 (m, 3H), 7.33-7.38 (m, 2H); ¹³C-NMR: 14.7, 21.4, 37.4, 39.4, 60.6, 126.7, 127.8, 128.6, 130.2, 134.1, 136.5, 141.5, 144.2, 165.3; HRMS (EI) calculated for [C₁₆H₁₈O₂]⁺ (M⁺): 242.1307, found 242.1305.



3n

Ethyl 4-(1-(trimethylsilyl)ethylidene)cyclopent-1-ene-1-carboxylate (3n). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and 3-trimethylsilylbuta-1,2-diene (**2h**, 252 mg, 2.0 mmol). $^1\text{H-NMR}$ analysis of the crude reaction mixture revealed that two isomers were formed in about 4:1 ratio. Chromatographic work-up (silica gel; hexanes) allowed the isolation of the major isomer in pure form (**3n**, 55 mg, 46%) as a colorless oil. The configuration of this isomer could not be unambiguously assigned due to overlapping of key signals in the $^1\text{H-NMR}$ spectrum.

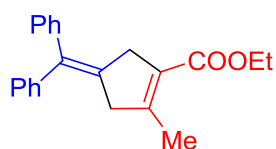
$^1\text{H-NMR}$ (CD_2Cl_2): 0.23 (s, 9H), 1.32 (t, $J = 7.2$ Hz, 3H), 2.01 (s, 2H), 2.07 (s, 5H, accidental equivalence of methyl and methylene groups), 4.21 (q, $J = 7.2$ Hz, 2H), 6.89 (br s, 1H); $^{13}\text{C-NMR}$ (CD_2Cl_2): -0.2, 14.0, 20.2, 22.8, 25.7, 60.2, 134.1, 134.3, 137.6, 138.0, 167.3; **HRMS** (EI) calculated for $[\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}]^+$ (M^+): 238.1389, found 238.1386.



3o

Ethyl 2-methyl-4-(propan-2-ylidene)cyclopent-1-ene-1-carboxylate (3o). The general procedure was followed using ethyl 2-diazo-3-methylbut-3-enoate (**1d**, 77 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (**2a**, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded compound **3o** (54 mg, 56%) as a colorless oil. An unknown byproduct with identical mass (GC-MS analysis) was observed in the ^1H NMR spectrum. On the basis of similar results with other allene derivatives, this byproduct is supposed to be ethyl 3,6-dimethyl-5-methylenehepta-2,6-dienoate.

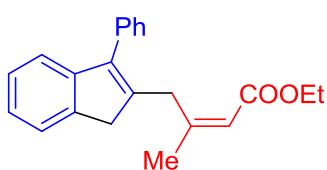
$^1\text{H-NMR}$: 1.32 (t, $J = 7.2$ Hz, 3H), 1.64 (s, 3H), 1.66 (s, 3H), 2.17 (s, 3H), 3.16 (br s, 2H), 3.27 (br s, 2H), 4.24 (q, $J = 7.2$ Hz, 2H); $^{13}\text{C-NMR}$: 14.4, 16.3, 20.6, 20.7, 38.3, 45.1, 59.7, 123.4, 126.5, 128.4, 154.1, 166.1; **HRMS** (EI) calculated for $[\text{C}_{12}\text{H}_{18}\text{O}_2]^+$ (M^+): 194.1307, found 194.1305.



3p

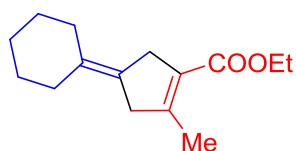
Ethyl 4-(diphenylmethylene)-2-methylcyclopent-1-ene-1-carboxylate (3p). The general procedure was followed using ethyl 2-diazo-3-methylbut-3-enoate (**1d**, 77 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3p** (48 mg, 30%) and **3p'** (24 mg, 15%) as colorless oils.

¹H-NMR: 1.30 (t, *J* = 7.2 Hz, 3H), 2.14 (s, 3H), 3.36 (s, 2H), 3.51 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 7.23-7.38 (m, 10H); ¹³C-NMR: 14.4, 16.1, 39.8, 46.7, 59.8, 126.2, 126.5, 128.4, 128.8, 135.4, 135.7, 142.2, 142.6, 153.4, 165.8; HRMS (EI) calculated for [C₂₂H₂₂O₂]⁺ (M⁺): 318.1620, found 318.1620.



3p'

Ethyl (Z)-3-methyl-4-(3-phenyl-1H-inden-2-yl)but-2-enoate (3p'). ¹H-NMR: 1.33 (t, *J* = 7.2 Hz, 3H), 1.71 (s, 3H), 3.46 (s, 2H), 3.97 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 5.76 (s, 1H), 7.19-7.45 (m, 9H); ¹³C-NMR: 14.3, 24.6, 32.3, 40.4, 59.7, 117.2, 119.7, 123.5, 124.4, 126.2, 127.3, 128.4, 128.5, 129.2, 135.2, 140.8, 141.3, 142.7, 157.5, 166.4; HRMS (EI) calculated for [C₂₂H₂₂O₂]⁺ (M⁺): 318.1620, found 318.1621. The Z configuration of **3p'** was determined by NOE experiments.

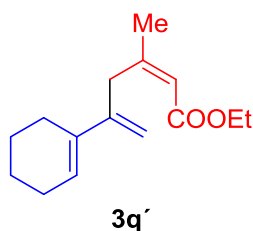


3q

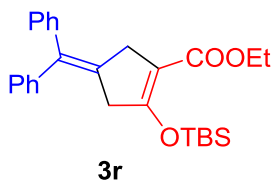
Ethyl 4-cyclohexylidene-2-methylcyclopent-1-ene-1-carboxylate (3q). The general procedure was followed using ethyl 2-diazo-3-methylbut-3-enoate (**1d**, 77 mg, 0.5 mmol) and

vinylidenecyclohexane (**2b**, 216 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded compound **3q** (33 mg, 28%) and **3q'** (27 mg, 23%) as colorless oils.

¹H-NMR: 1.32 (t, *J* = 7.2 Hz, 3H), 1.46-1.55 (m, 6H), 2.01-2.15 (m + s, 7H), 3.20 (br s, 2H), 3.30 (br s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H); ¹³C-NMR: 14.4, 16.3, 26.6, 27.4, 31.1, 31.3, 37.6, 44.4, 59.6, 124.8, 126.4, 131.6, 154.1, 166.1; HRMS (EI) calculated for [C₁₅H₂₂O₂]⁺ (M⁺): 234.1620, found 234.1622.

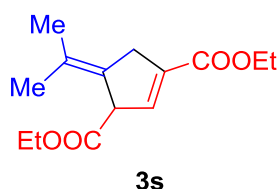


Ethyl (Z)-5-(cyclohex-1-en-1-yl)-3-methylhexa-2,5-dienoate (3q'). ¹H-NMR: 1.29 (t, *J* = 7.2 Hz, 3H), 1.54-1.72 (m, 2H), 1.82 (s, 3H), 2.10-2.26 (m, 4H), 3.39 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.79 (s, 1H), 5.08 (s, 1H), 5.80 (br s, 1H), 5.93 (t, *J* = 3.9 Hz, 3H); ¹³C-NMR: 14.3, 22.1, 22.9, 24.6, 25.9, 26.0, 37.4, 59.5, 110.3, 117.1, 125.0, 135.8, 145.0, 158.8, 166.4; HRMS (EI) calculated for [C₁₅H₂₂O₂]⁺ (M⁺): 234.1620, found 234.1620. The Z configuration of **3q'** was determined by NOE experiments.



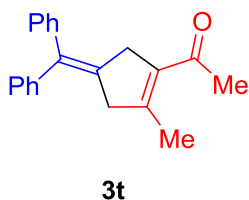
Ethyl 2-(tert-butyldimethylsilyloxy)-4-(diphenylmethylene)cyclopent-1-ene-1-carboxylate (3r). The general procedure was followed using ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**1e**, 135 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound **3r** (55 mg, 25%) as a colorless oil.

¹H-NMR: 0.19 (s, 6H), 0.97 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 3.32 (s, 2H), 3.40 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.19-7.33 (m, 10H); ¹³C-NMR: -3.7, 14.8, 18.4, 25.7, 36.5, 42.3, 59.6, 107.7, 126.8, 128.5, 128.6, 128.8, 129.0, 132.4, 136.6, 141.8, 142.5, 162.1, 165.0; HRMS (EI) calculated for [C₂₇H₃₄O₃Si]⁺ (M⁺): 434.2277, found 434.2271.



Diethyl 4-(propan-2-ylidene)cyclopent-1-ene-1,3-dicarboxylate (3s). The general procedure was followed using diethyl (*E*)-4-diazopent-2-enedioate (**1f**, 106 mg, 0.5 mmol) and 3-methylbuta-1,2-diene (**2a**, 136 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 40:1) afforded compound **3s** (53 mg, 42%) as a colorless oil.

¹H-NMR: 1.29 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.68 (s, 3H), 1.72 (s, 3H), 3.22-3.40 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 4.27-4.30 (m, 1H), 6.68-6.71 (m, 1H); **¹³C-NMR:** 14.2, 14.3, 20.9, 21.4, 36.4, 55.1, 60.5, 61.1, 128.5, 128.9, 138.6, 138.9, 164.6, 171.4; **HRMS (EI)** calculated for [C₁₄H₂₀O₄]⁺ (M⁺): 252.1362, found 252.1361.

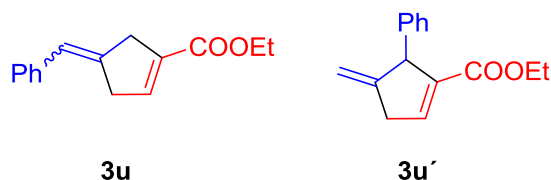


1-[4-(diphenylmethylene)-2-methylcyclopent-1-en-1-yl]ethan-1-one (3t). The general procedure was followed using 3-diazo-4-methylpent-4-en-2-one (**1g**, 62 mg, 0.5 mmol) and 1,1-diphenylpropa-1,2-diene (**2e**, 384 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 20:1) afforded compound **3t** (58 mg, 40%) as a colorless oil.

¹H-NMR: 2.12 (s, 3H), 2.26 (s, 3H), 3.39 (s, 2H), 3.54 (s, 2H), 7.21-7.37 (m, 10H); **¹³C-NMR:** 16.7, 30.4, 40.4, 47.2, 126.6, 128.4, 128.7, 134.6, 135.4, 135.6, 142.2, 142.4, 151.8, 197.6; **HRMS (EI)** calculated for [C₂₁H₂₀O]⁺ (M⁺): 288.1514, found 288.1512.

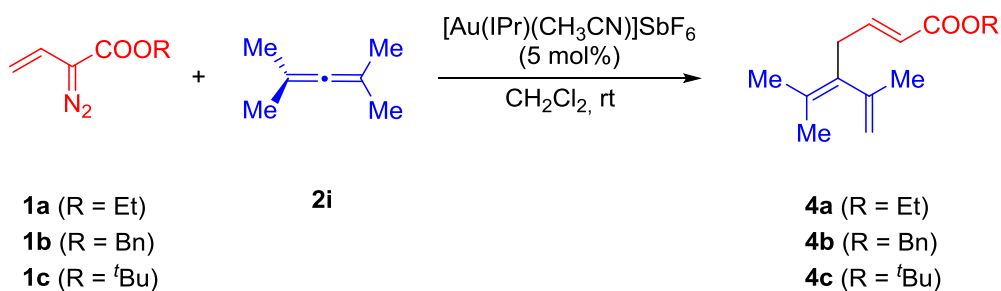
5. Reaction with phenyl-1,2-propadiene (2i)

Ethyl 4-benzylidenecyclopent-1-ene-1-carboxylate (**3u**) and ethyl 4-methylene-5-phenylcyclopent-1-ene-1-carboxylate (**3u'**). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol) and phenylallene (**2i**, 232 mg, 2.0 mmol). Final chromatographic purification (silica gel; hexanes/ethyl acetate 100:1) afforded an inseparable 4: 1 mixture of **3u** and **3u'** (69 mg, 60%).



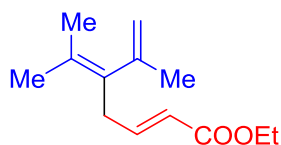
¹H-NMR (*major isomer 3u*): 1.33 (t, *J* = 7.2 Hz, 3H), 3.50-3.61 (m, 4H), 4.25 (t, *J* = 7.2 Hz, 2H), 6.44-6.46 (m, 1H), 6.87-6.89 (m, 1H), 7.17-7.38 (m, 5H); (*minor isomer 3u'*, only clearly assignable signals are listed): 1.14 (t, *J* = 7.2 Hz, 3H), 3.36-3.41 (m, 2H), 4.00-4.13 (m, 2H), 4.62 (br s, 1H), 4.89 (br s, 1H), 5.08-5.10 (m, 1H), 7.02 (br s, 1H); ¹³C-NMR (*major isomer 3u*): 14.3, 37.1, 42.2, 60.4, 123.9, 126.4, 127.5, 128.0, 128.4, 135.7, 137.5, 139.9, 141.2, 141.5, 142.3, 164.7; (*minor isomer 3u'*, only clearly assignable signals are listed): 14.0, 39.1, 55.2, 60.1, 110.5, 142.3, 143.8, 152.0, 164.2; HRMS (EI) calculated for [C₁₅H₁₆O₂]⁺ (M⁺): 228.1150, found 228.1148.

6. General procedure for the synthesis of triene derivatives 4a-c from vinyldiazo compounds 1a-c and tetramethylallene (2j)



$[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of vinyldiazo compound **1** (0.5 mmol) and 2,4-dimethylpenta-2,3-diene (**2j**, 192 mg, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 20:1) to afford triene derivatives **4a-c**.

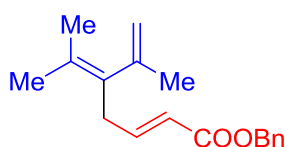
7. Characterization Data of Compounds 4



4a

Ethyl (*E*)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4a). The general procedure was followed using ethyl 2-diazobut-3-enoate (**1a**, 70 mg, 0.5 mmol). Final chromatographic purification afforded compound **4a** (86 mg, 83%) as a colorless oil.

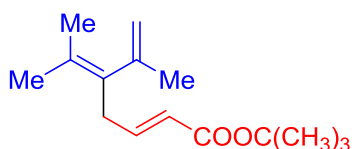
¹H-NMR: 1.29 (t, *J* = 7.2 Hz, 3H), 1.68 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.99 (d, *J* = 6.6 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.61 (br s, 1H), 4.94 (br s, 1H), 5.79 (dt, *J* = 15.6 and 1.5 Hz, 1H), 6.90 (dt, *J* = 15.6 and 6.6 Hz, 1H); **¹³C-NMR:** 14.6, 20.2, 22.1, 22.9, 35.0, 60.5, 114.3, 121.6, 128.9, 132.3, 146.3, 147.2, 167.2; **HRMS** (EI) calculated for [C₁₃H₂₀O₂]⁺ (M⁺): 208.1463, found 208.1467.



4b

Benzyl (*E*)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4b). The general procedure was followed using benzyl 2-diazobut-3-enoate (**1b**, 101 mg, 0.5 mmol). Final chromatographic purification afforded compound **4b** (78 mg, 58%) as a colorless oil.

¹H-NMR: 1.69 (s, 3H), 1.73 (s, 3H), 1.78 (s, 3H), 3.01 (d, *J* = 6.6 Hz, 2H), 4.63 (br s, 1H), 4.96 (br s, 1H), 5.20 (s, 2H), 5.87 (dt, *J* = 15.6 and 1.6 Hz, 1H), 6.98 (dt, *J* = 15.6 and 6.6 Hz, 1H), 7.36-7.41 (m, 5H); **¹³C-NMR:** 19.9, 21.8, 22.6, 34.6, 66.0, 114.0, 120.9, 128.2, 128.6, 131.8, 136.2, 145.8, 147.6, 166.6; **HRMS** (EI) calculated for [C₁₈H₂₂O₂]⁺ (M⁺): 270.1620, found 270.1617.



4c

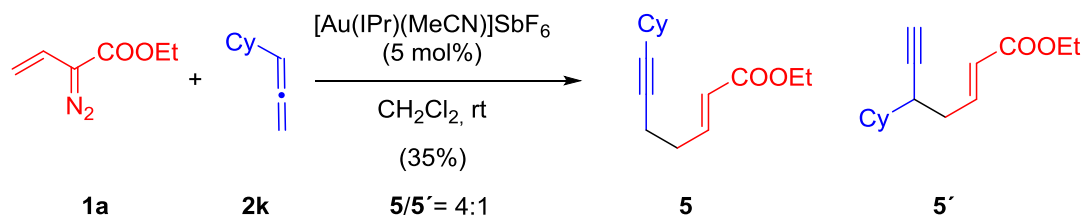
***tert*-Butyl (*E*)-6-methyl-5-(prop-1-en-2-yl)hepta-2,5-dienoate (4c).** The general procedure was followed using *tert*-butyl 2-diazobut-3-enoate (**1c**, 84 mg, 0.5 mmol). Final chromatographic purification afforded compound **4c** (71 mg, 60%) as a colorless oil.

¹H-NMR: 1.49 (s, 9H), 1.68 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.96 (d, *J* = 6.6 Hz, 2H), 4.61-4.62 (m, 1H), 4.94-4.95 (m, 1H), 5.71 (dt, *J* = 15.6 and 1.6 Hz, 1H), 6.80 (dt, *J* = 15.6 and 6.6 Hz, 1H);

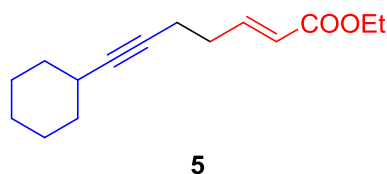
¹³C-NMR: 19.8, 21.8, 22.6, 28.2, 34.4, 80.0, 113.8, 122.9, 128.3, 132.1, 145.6, 145.9, 166.3;

HRMS (EI) calculated for [C₁₅H₂₄O₂]⁺ (M⁺): 236.1776, found 236.1778.

8. Reaction with cyclohexyl-1,2-propadiene (2k)

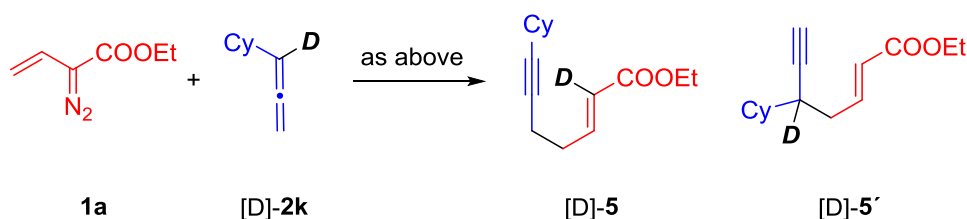


$[\text{Au}(\text{IPr})(\text{CH}_3\text{CN})]\text{SbF}_6$ (21.6 mg, 0.025 mmol, 5 mol%) was added to a solution of ethyl diazoacetate (**1a**, 70 mg, 0.5 mmol) and cyclohexylpropa-1,2-diene (**2k**, 244 mg, 2 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 8 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 40:1) to afford a 4:1 mixture (GC/MS) of **5** and **5'** (41 mg, 35%).



Ethyl (E)-7-cyclohexylhept-2-en-6-ynoate (5). $^1\text{H-NMR}$: 1.22-1.50 (m + t, 9H), 1.60-1.79 (m, 4H), 2.31-2.44 (m, 5H), 4.21 (q, $J = 7.2$ Hz, 2H), 5.89 (d, $J = 15.0$ Hz, 1H), 7.00 (dt, $J = 15.0$ and 2.0 Hz, 1H); $^{13}\text{C-NMR}$: 14.3, 17.8, 24.8, 25.9, 29.0, 31.9, 33.0, 60.2, 78.3, 86.0, 122.2, 147.2, 166.5; **HRMS** (EI) calculated for $[\text{C}_{15}\text{H}_{22}\text{O}_2]^+$ (M^+): 234.1620, found 234.1624. NMR spectroscopic data of compound **5** match those reported in the literature (G. A. Molander, W. H. Retsch, *J. Org. Chem.* **1998**, *63*, 5507).

An experiment performed with the deuteriated allene [**D**]-**2k** afforded the following result:



9. Computational study

Preliminary Density-functional theory calculations on the reaction mechanism of the gold-catalyzed reaction of unbiased allenes and vinyl diazo derivatives, using the hybrid B3LYP functional, have been carried out. The 6-31G(d) basis set was employed for all elements, with the exception of gold which has been described with the LANL2DZ basis set and pseudopotential. The stationary points located were fully optimized and characterized to be a minimum or a first-order saddle point (transition structure) by computing the harmonic vibrational frequencies. The connection of either, the reactants or products, with the corresponding transition structure was established by computation of the intrinsic reaction coordinate (IRC).⁵ All the calculations described in this work were carried out with Gaussian09 package.⁶

The geometries of ethyl 2-diazo-3-butenoate (**1a**) and dimethyl (**2a**)- or cyclohexylallene (**2k**) as reactants and the gold (I)-NHC-carbene complex (**A**), as catalyst are shown in Figure S2.

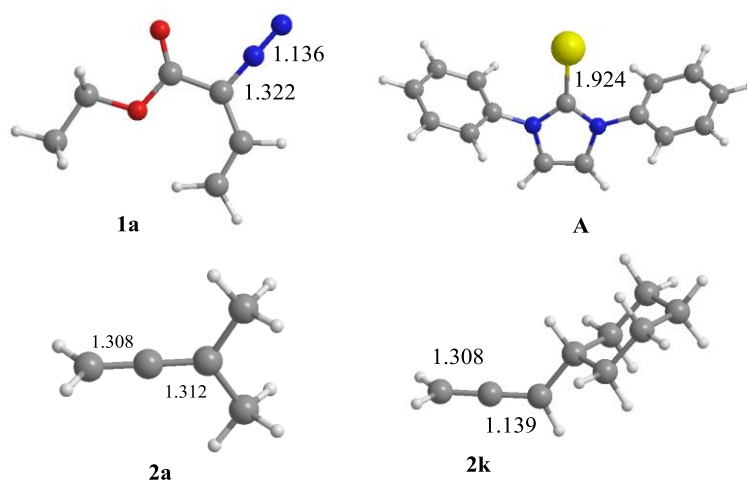


Figure S2. Selected bond lengths (Å) for reactants and gold (I) catalyst.

First, the coordination of allenes and the gold catalyst was studied. The complexes between the catalyst **A** and the allenes **2a** and **2k** were characterized, and in both cases, the complexation to the external or the internal double bond was considered (Figure S3).

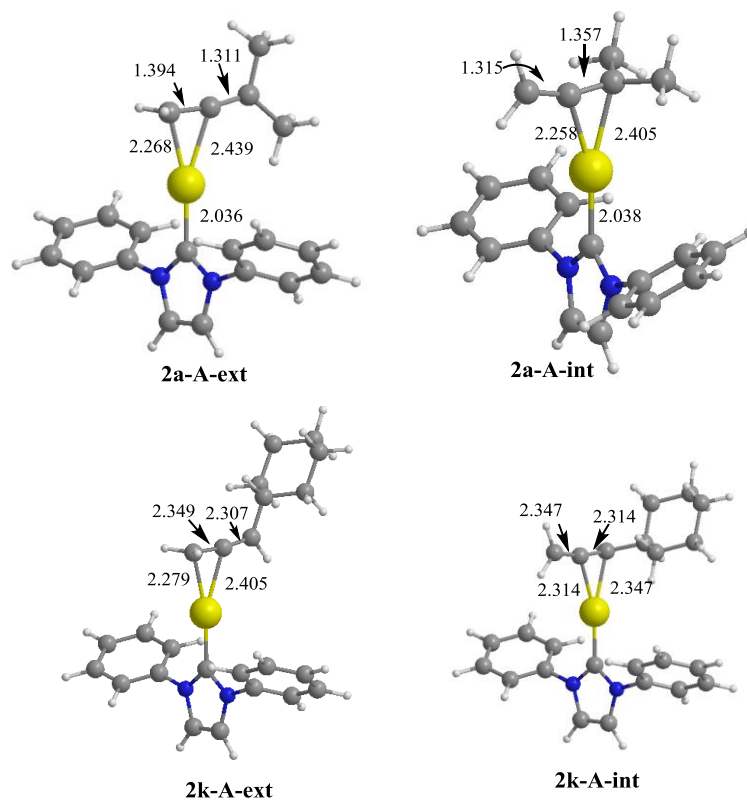


Figure S3. Selected bond lengths (Å) for the complexes formed between the NHC-gold carbene (**A**) and allenes **2a** and **2k**.

The coordination of the allenes to the catalyst is predicted to happen without activation barrier, and the complexation free-energies, ΔG are collected in Table S2.

Table S2.

Complex	ΔG (kcal mol ⁻¹)*
2a-A-ext	-23.5
2a-A-int	-21.3
2k-A-ext	-22.4
2k-A-int	-20.1

* Relative to the free reactants.

The data shown in Table S2 indicates that the coordination of gold catalyst to the external double bond of the allene is favoured, which can be understood on steric grounds, the internal position being more sterically crowded than the external one. The most salient geometrical features of these complexes are the increase (relative to the free cumulene) of the length of the double bond complexed to gold, and the slight bending of the C-C-C moiety in the case of the complexes involving the internal double bond.

On the other hand, the reaction of diazoester derivative **1a** with the gold (I)-NHC-carbene complex, **A**, involves a barrierless coordination of gold to the diazo-carbon atom leading to the intermediate **I** (Figure S4). The diazo-carbon atom in **I** is slightly pyramidalized and its distance to the nitrogen of the diazo group has increased, as compared with the diazoester **1a**.

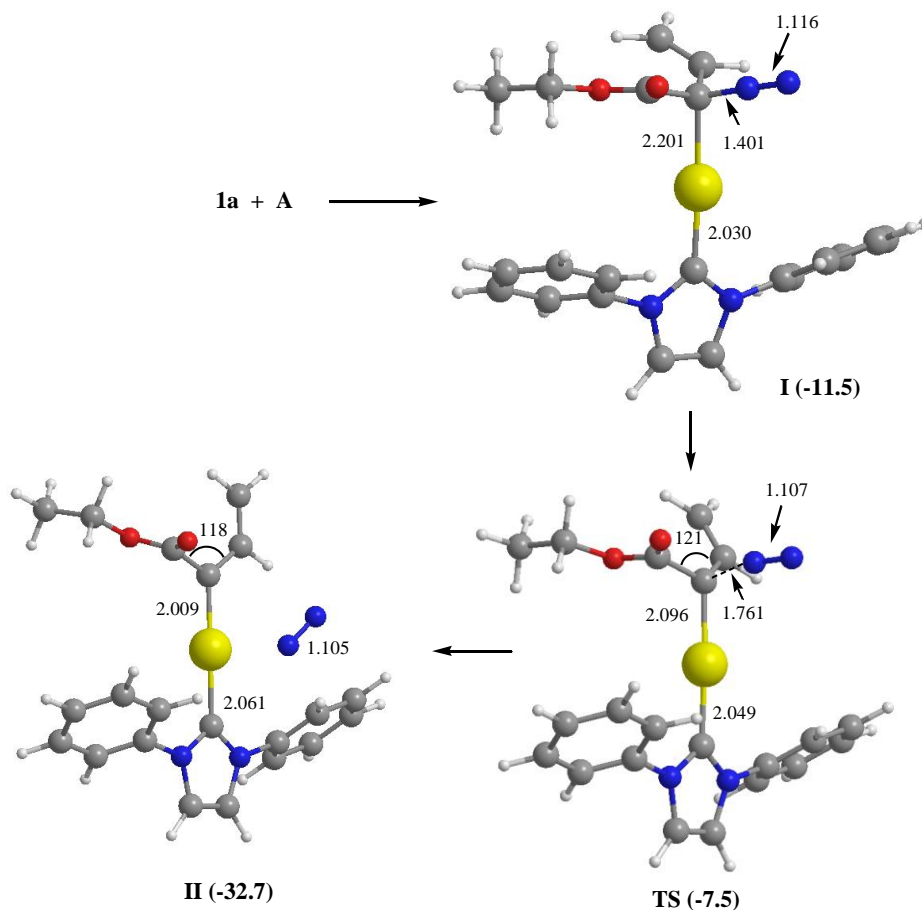


Figure S4. Stationary points located for the reaction of diazoester **1a** with NHC-gold carbene **A**. Selected bond lengths (Å), bond angles (degrees) and relative Gibbs free-energies (kcal mol⁻¹) are shown.

A transition state (**TS**), corresponding to the loss of dinitrogen from intermediate **I** was found, and leads to the NHC-gold(I) carbene intermediate **II**. As could be expected, the normal mode associated with the imaginary frequency of **TS**, corresponds to the stretching of the bond between the diazo carbon atom and one of the nitrogen atoms. The gold-carbene intermediate **II** shows a length of 2.009 Å between the gold atom and the carbon atom coming from the reactant **1a**. In addition, the C-C-C angle in intermediate **II** is very close to the value corresponding to the sp² hybridization.

The dinitrogen molecule is almost fully formed in the transition structure, and the loss of the very stable N₂ molecule can be seen as the driving force of the reaction, with a predicted value for the reaction free-energy of 32.7 kcal mol⁻¹.

According to these data, the key step in the catalytic cycle is the activation of the diazocompound derivative **1a** by the NHC-gold complex **A**: this process is very favoured thermodynamically, and leads to the formation of the gold carbene derivative **II**, an electrophilic intermediate which could easily react with the allene component.

Cartesian Coordinates and Gibbs free-Energies (au) of the Stationary Points.

1a				2a				2a-A-ext			
C	-0.9457	1.7103	0.0001	C	0.8729	-0.0000	0.0001	C	-1.7550	2.9043	0.4808
C	-1.9176	0.7875	0.0002	C	-0.4388	-0.0001	0.0001	C	-1.1020	2.4238	-0.5497
C	-1.7844	-0.6696	0.0002	C	-1.7469	-0.0001	0.0001	C	-0.0690	-3.9759	0.3932
N	-2.9096	-1.3638	0.0003	C	1.6688	-1.2889	0.0000	C	-0.4643	2.1363	-1.7031
C	-0.5980	-1.5461	0.0002	C	1.6685	1.2891	0.0001	C	-2.0996	2.1269	1.7281
H	-2.9531	1.1252	0.0001	H	-2.3213	0.0001	-0.9257	H	0.5813	2.4146	-1.8446
H	-1.2108	2.7626	0.0001	H	1.0177	-2.1669	-0.0006	C	1.2529	-3.6681	0.4411
H	0.1057	1.4557	0.0001	H	2.3206	-1.3417	0.8829	C	-2.2061	4.3545	0.4318
N	-3.8760	-1.9617	0.0001	H	2.3215	-1.3411	-0.8822	H	-1.7601	1.0894	1.6832
O	-0.6551	-2.7626	0.0000	H	2.3207	1.3418	-0.8824	H	-3.1856	2.1328	1.8800
O	0.5517	-0.8406	0.0003	H	2.3207	1.3419	0.8826	N	-0.7404	-2.8121	0.0434
C	1.7643	-1.6332	0.0003	H	1.0171	2.1669	0.0000	H	-1.6467	2.6081	2.6035
C	2.9364	-0.6707	0.0001	H	-2.3215	-0.0002	0.9257	H	-1.7697	4.9053	1.2736
H	1.7602	-2.2792	-0.8830					H	-3.2968	4.4051	0.5328
H	1.7604	-2.2790	0.8837	G=-195.210490				N	1.3637	-2.3207	0.1262
H	2.9193	-0.0309	0.8884					H	-1.9177	4.8508	-0.4973
H	2.9192	-0.0312	-0.8884					H	-1.0292	1.8902	-2.6035
H	3.8760	-1.2337	0.0001					Au	-0.2742	0.1319	-0.6585
G=-493.240241								C	0.1380	-1.7882	-0.1205
								C	-2.1699	-2.7296	-0.1215
								C	2.6165	-1.6094	0.0711
								H	-0.5907	-4.9053	0.5584
2j				A				H	2.1162	-4.2690	0.6797
C	-1.2267	-0.0001	0.5161	C	0.6796	1.6371	0.2480	C	-2.9935	-3.0115	0.9702
C	-2.3951	-0.0001	-0.0733	C	-0.6796	1.6371	0.2480	C	-4.3784	-2.9561	0.8076
C	-3.5580	0.0000	-0.6726	N	1.0882	0.3185	0.0952	C	-4.9272	-2.6183	-0.4318
H	-4.0674	0.9264	-0.9334	N	-1.0882	0.3185	0.0952	C	-4.0919	-2.3413	-1.5166
H	-4.0674	-0.9263	-0.9335	C	-0.0000	-0.4791	-0.0070	C	-2.7053	-2.4023	-1.3692
C	0.1120	-0.0001	-0.1964	C	2.4670	-0.1080	0.0381				

H	-1.1897	-0.0002	1.6084	C	-2.4670	-0.1080	0.0381	H	-2.5558	-3.2599	1.9326
C	0.9230	1.2683	0.1502	Au	-0.0000	-2.4377	-0.3227	H	-5.0262	-3.1735	1.6513
C	2.3076	1.2669	-0.5169	H	1.3927	2.4377	0.3666	H	-6.0053	-2.5775	-0.5539
C	3.1022	0.0000	-0.1680	H	-1.3926	2.4377	0.3666	H	-4.5174	-2.0929	-2.4841
C	2.3077	-1.2669	-0.5170	C	2.9729	-0.9361	1.0427	H	-2.0462	-2.2201	-2.2123
C	0.9231	-1.2684	0.1502	C	4.3108	-1.3296	0.9808	C	3.5829	-2.0150	-0.8514
H	-0.0768	-0.0001	-1.2790	C	5.1255	-0.8874	-0.0642	C	4.8059	-1.3442	-0.8915
H	1.0453	1.3241	1.2429	C	4.6064	-0.0504	-1.0553	C	5.0521	-0.2797	-0.0210
H	0.3552	2.1593	-0.1452	C	3.2688	0.3441	-1.0113	C	4.0771	0.1146	0.8984
H	2.8672	2.1631	-0.2195	H	2.3387	-1.2454	1.8678	C	2.8530	-0.5538	0.9542
H	2.1827	1.3261	-1.6083	H	4.7172	-1.9695	1.7578	H	3.3750	-2.8342	-1.5333
H	3.3292	-0.0000	0.9086	H	6.1669	-1.1915	-0.1040	H	5.5625	-1.6516	-1.6067
H	4.0674	0.0000	-0.6905	H	5.2392	0.2926	-1.8678	H	6.0053	0.2389	-0.0558
H	2.8673	-2.1631	-0.2196	H	2.8505	0.9816	-1.7845	H	4.2725	0.9333	1.5842
H	2.1828	-1.3261	-1.6084	C	-3.2687	0.3440	-1.0113	H	2.0982	-0.2763	1.6832
H	0.3553	-2.1594	-0.1452	C	-4.6064	-0.0505	-1.0554				
H	1.0454	-1.3242	1.2428	C	-5.1255	-0.8874	-0.0642	G=-1018.617312			
				C	-4.3108	-1.3295	0.9808				
G=-351.167050				C	-2.9730	-0.9360	1.0428				
				H	-2.8504	0.9815	-1.7846				
				H	-5.2392	0.2924	-1.8679				
				H	-6.1669	-1.1915	-0.1041				
				H	-4.7173	-1.9693	1.7579				
				H	-2.3387	-1.2453	1.8679				
				G=-823.369308							

2a-A-int				2k-A-ext				2k-A-int			
C	-0.0002	2.9689	-0.7781	C	-1.3231	-0.5395	0.7978	C	-0.6678	-2.3506	-0.4458
C	-0.0001	2.6452	0.5397	C	-0.5109	-0.6037	1.8203	C	-0.2739	-2.3030	0.8452
C	-0.6791	-3.5773	-0.7673	C	0.1634	-0.6827	2.9861	C	-0.0854	-2.4949	2.1289
C	-0.0002	2.7619	1.8493	C	5.6013	-0.8892	-0.4837	C	4.1044	2.0466	-1.0351
C	-1.2918	3.2955	-1.5055	H	0.2836	0.1979	3.6176	H	0.5635	-1.8693	2.7331
C	1.2915	3.2956	-1.5055	H	0.3580	-1.6500	3.4504	H	-0.5886	-3.3220	2.6279
C	0.6792	-3.5772	-0.7673	C	-2.8354	-0.6180	0.9245	C	-1.9856	-1.8248	-1.0009
H	-0.0003	3.7532	2.3013	H	-0.9206	-0.4277	-0.2084	H	-0.1082	-3.0157	-1.1089
H	-2.1725	2.9789	-0.9435	C	5.5040	0.4655	-0.4741	C	3.0860	2.9414	-0.9500
H	-1.3140	2.8422	-2.5018	C	-3.4888	0.6674	0.3674	C	-2.9034	-3.0418	-1.2939
N	-1.0814	-2.2505	-0.7042	C	-5.0229	0.5842	0.4305	C	-4.2391	-2.5878	-1.9058
H	-1.3381	4.3846	-1.6415	C	-5.5530	-0.6634	-0.2912	C	-4.9492	-1.5571	-1.0165
H	1.3378	4.3847	-1.6414	N	4.4559	-1.3791	0.1284	N	3.5549	0.7904	-0.8200
H	1.3136	2.8423	-2.5018	C	-4.9018	-1.9428	0.2544	C	-4.0364	-0.3600	-0.7116
N	1.0815	-2.2505	-0.7042	C	-3.3675	-1.8700	0.1896	C	-2.7000	-0.8069	-0.0973
H	2.1722	2.9789	-0.9435	H	-3.0918	-0.7055	1.9888	H	-1.7635	-1.3455	-1.9657
H	-0.0003	1.9102	2.5213	H	-3.1718	0.8043	-0.6773	H	-3.0899	-3.5788	-0.3532
Au	-0.0001	0.5936	-0.4034	H	-3.1278	1.5403	0.9249	H	-2.3965	-3.7451	-1.9668
C	0.0000	-1.4285	-0.6554	N	4.3032	0.7778	0.1481	N	1.9344	2.2152	-0.6792
C	-2.4592	-1.8296	-0.6752	H	-5.4557	1.4928	-0.0045	H	-4.8796	-3.4627	-2.0668
C	2.4592	-1.8295	-0.6752	H	-5.3399	0.5604	1.4830	H	-4.0510	-2.1503	-2.8968
H	-1.3911	-4.3847	-0.8338	Au	1.8680	-0.4935	1.4850	Au	0.9204	-0.6361	-0.2263
H	1.3913	-4.3846	-0.8338	H	-5.3425	-0.5786	-1.3673	H	-5.2490	-2.0355	-0.0730
C	-3.2778	-2.2635	0.3693	C	3.6525	-0.3555	0.5201	C	2.2178	0.8884	-0.5990
C	-4.6185	-1.8770	0.3861	H	-6.6430	-0.7227	-0.1905	H	-5.8718	-1.2152	-1.4997
C	-5.1281	-1.0638	-0.6291	C	4.1801	-2.7822	0.3108	C	4.3165	-0.4339	-0.8374
C	-4.2988	-0.6387	-1.6696	H	-5.2494	-2.8193	-0.3052	H	-4.5373	0.3385	-0.0310
C	-2.9580	-1.0253	-1.7021	C	3.8392	2.1251	0.3680	C	0.6326	2.8091	-0.5062
H	-2.8680	-2.8830	1.1616	H	-5.2123	-2.0955	1.2979	H	-3.8400	0.1956	-1.6402
H	-5.2614	-2.2082	1.1956	H	6.3615	-1.5462	-0.8759	H	5.1551	2.1801	-1.2391
H	-6.1722	-0.7665	-0.6122	H	-2.9209	-2.7735	0.6226	H	-2.0536	0.0642	0.0751
								H	3.0722	4.0160	-1.0407

H	-4.6976	-0.0193	-2.4672	H	6.1733	1.2307	-0.8345	H	-2.8829	-1.2639	0.8851
H	-2.3107	-0.7277	-2.5212	H	-3.0471	-1.8290	-0.8623	C	5.3205	-0.6191	0.1147
C	2.9580	-1.0253	-1.7022	C	5.0500	-3.5460	1.0911	C	6.0726	-1.7943	0.0872
C	4.2988	-0.6386	-1.6697	C	4.7988	-4.9095	1.2498	C	5.8173	-2.7691	-0.8804
C	5.1281	-1.0636	-0.6291	C	3.6883	-5.4953	0.6372	C	4.8117	-2.5695	-1.8292
C	4.6185	-1.8767	0.3862	C	2.8271	-4.7198	-0.1426	C	4.0577	-1.3950	-1.8169
C	3.2778	-2.2632	0.3694	C	3.0723	-3.3567	-0.3161	H	5.5013	0.1395	0.8705
H	2.3108	-0.7278	-2.5213	H	5.9017	-3.0773	1.5750	H	6.8539	-1.9481	0.8250
H	4.6976	-0.0193	-2.4673	H	5.4688	-5.5107	1.8566	H	6.4053	-3.6816	-0.8980
H	6.1722	-0.7662	-0.6121	H	3.4972	-6.5565	0.7635	H	4.6213	-3.3208	-2.5895
H	5.2614	-2.2078	1.1958	H	1.9713	-5.1767	-0.6300	H	3.2918	-1.2148	-2.5648
H	2.8680	-2.8826	1.1617	H	2.4278	-2.7488	-0.9431	C	0.0602	3.5067	-1.5716
				C	3.5668	2.9353	-0.7357	C	-1.1891	4.1040	-1.3984
G=-1018.613782				C	3.1422	4.2478	-0.5252	C	-1.8546	3.9987	-0.1747
				C	2.9903	4.7369	0.7745	C	-1.2694	3.3002	0.8842
				C	3.2684	3.9161	1.8700	C	-0.0163	2.7054	0.7260
				C	3.7016	2.6040	1.6726	H	0.5804	3.5706	-2.5227
				H	3.6763	2.5402	-1.7414	H	-1.6420	4.6475	-2.2219
				H	2.9268	4.8848	-1.3775	H	-2.8255	4.4667	-0.0442
				H	2.6605	5.7591	0.9334	H	-1.7787	3.2303	1.8405
				H	3.1633	4.2995	2.8804	H	0.4618	2.1843	1.5493
				H	3.9494	1.9654	2.5148				
								G=-1174.568440			
				G=-1174.572117							

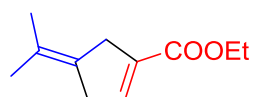
I				TS				II + N ₂			
C	-1.0604	-3.2012	2.3523	C	-1.3808	-4.1047	0.8473	C	1.3663	-4.6234	-0.5340
C	1.2964	3.6450	0.0731	C	1.4308	3.6692	0.1999	C	-2.0171	3.2622	-0.7206
C	-0.3469	-3.0709	1.2323	C	-0.7317	-3.1978	0.1011	C	0.5534	-3.5326	-0.5505
C	2.5293	3.0854	0.1659	C	2.5601	2.9287	0.3358	C	-3.1148	2.4686	-0.8322
C	-0.7945	-2.4044	-0.0470	C	-1.3531	-1.9783	-0.4560	C	1.0489	-2.1919	-0.5041
N	0.3911	2.6012	-0.0769	N	0.4010	2.7824	-0.0877	N	-0.9280	2.4199	-0.5570
N	-0.2748	-3.1032	-1.1446	N	-1.3756	-2.3103	-2.1856	N	-0.0658	-1.2903	3.5780
N	2.3555	1.7100	0.0712	N	2.1981	1.6040	0.1283	N	-2.6728	1.1582	-0.7334
C	1.0389	1.4064	-0.0680	C	0.8651	1.5042	-0.1228	C	-1.3207	1.1162	-0.5749
C	-2.2576	-2.1166	-0.4001	C	-2.8439	-1.7187	-0.3020	C	2.5102	-1.9834	-0.3313
H	0.6789	-3.4323	1.1998	H	0.3400	-3.2949	-0.0536	H	-0.5219	-3.6757	-0.6070
C	-1.0315	2.7827	-0.2064	C	-0.9651	3.1853	-0.2965	C	0.4261	2.8835	-0.4034
H	-0.6076	-3.6744	3.2177	H	-0.8380	-4.9230	1.3113	H	0.9601	-5.6307	-0.5765
C	3.4346	0.7577	0.1298	C	3.1238	0.5029	0.1861	C	-3.5408	0.0125	-0.8015
Au	0.1911	-0.4375	-0.1216	Au	-0.2261	-0.2139	-0.3587	Au	-0.1186	-0.5565	-0.5106
H	-2.0743	-2.8364	2.4534	H	-2.4419	-4.0372	1.0620	H	2.4478	-4.5379	-0.4711
N	0.1691	-3.6418	-2.0156	N	-1.1234	-2.4945	-3.2474	N	0.0896	-0.2350	3.2892
H	0.9807	4.6762	0.0696	H	1.2678	4.7341	0.2488	H	-1.9154	4.3359	-0.7092
O	-2.7064	-2.3039	-1.5083	O	-3.6063	-1.5686	-1.2320	O	2.9255	-1.8397	0.8033
H	3.5077	3.5291	0.2606	H	3.5815	3.2165	0.5284	H	-4.1600	2.7123	-0.9385
O	-2.9066	-1.6017	0.6398	O	-3.1483	-1.6063	0.9904	O	3.2081	-1.9400	-1.4555
C	-1.6855	2.3281	-1.3538	C	-1.6126	2.8519	-1.4884	C	1.1662	2.5021	0.7182
C	-4.3001	-1.2174	0.3951	C	-4.5234	-1.2009	1.2967	C	4.6315	-1.5944	-1.3374
C	-3.0621	2.5269	-1.4742	C	-2.9332	3.2606	-1.6812	C	2.4723	2.9743	0.8594
C	-4.8377	-0.6199	1.6785	C	-4.6569	-1.1577	2.8046	C	5.1960	-1.5224	-2.7404
C	-3.7688	3.1836	-0.4635	C	-3.5892	4.0063	-0.6991	C	3.0212	3.8273	-0.1007
H	-4.8461	-2.1120	0.0849	H	-5.2001	-1.9240	0.8341	H	5.1156	-2.3630	-0.7291
C	-3.1008	3.6405	0.6757	C	-2.9264	4.3432	0.4836	C	2.2659	4.2083	-1.2127
H	-4.3060	-0.5036	-0.4327	H	-4.6935	-0.2257	0.8321	H	4.6989	-0.6411	-0.8062
C	-1.7265	3.4395	0.8113	C	-1.6101	3.9306	0.6928	C	0.9633	3.7350	-1.3715
H	-4.2686	0.2693	1.9671	H	-3.9568	-0.4397	3.2427	H	4.6869	-0.7549	-3.3311

H	-1.1215	1.8461	-2.1459	H	-1.0826	2.2994	-2.2574	H	0.7213	1.8657	1.4762
H	-4.8039	-1.3428	2.4994	H	-4.4722	-2.1413	3.2474	H	5.0987	-2.4829	-3.2555
H	-3.5753	2.1860	-2.3684	H	-3.4419	3.0079	-2.6064	H	3.0521	2.6863	1.7310
H	-5.8820	-0.3266	1.5282	H	-5.6745	-0.8508	3.0679	H	6.2598	-1.2680	-2.6884
H	-4.8370	3.3486	-0.5677	H	-4.6133	4.3300	-0.8579	H	4.0339	4.2000	0.0199
H	-3.6473	4.1529	1.4615	H	-3.4338	4.9230	1.2486	H	2.6903	4.8699	-1.9616
H	-1.2003	3.7773	1.6991	H	-1.0932	4.1709	1.6172	H	0.3758	4.0091	-2.2428
C	4.2316	0.7061	1.2749	C	3.8226	0.2644	1.3711	C	-4.3546	-0.1575	-1.9234
C	5.2940	-0.1975	1.3223	C	4.7427	-0.7836	1.4185	C	-5.2147	-1.2548	-1.9793
C	5.5495	-1.0393	0.2371	C	4.9554	-1.5836	0.2931	C	-5.2542	-2.1715	-0.9259
C	4.7454	-0.9764	-0.9036	C	4.2507	-1.3342	-0.8870	C	-4.4360	-1.9897	0.1916
C	3.6847	-0.0712	-0.9662	C	3.3336	-0.2837	-0.9489	C	-3.5777	-0.8913	0.2630
H	4.0149	1.3546	2.1186	H	3.6388	0.8829	2.2446	H	-4.3034	0.5503	-2.7454
H	5.9179	-0.2450	2.2095	H	5.2891	-0.9758	2.3367	H	-5.8490	-1.3943	-2.8492
H	6.3788	-1.7390	0.2777	H	5.6745	-2.3961	0.3340	H	-5.9270	-3.0225	-0.9731
H	4.9527	-1.6190	-1.7539	H	4.4265	-1.9449	-1.7674	H	-4.4773	-2.6917	1.0190
H	3.0707	0.0095	-1.8577	H	2.8027	-0.0585	-1.8685	H	-2.9608	-0.7215	1.1396
G=-1316.628004				G=-1316.621563				G=-1316.661061			
				$\nu_i=-340.48i \text{ cm}^{-1}$							

10. References

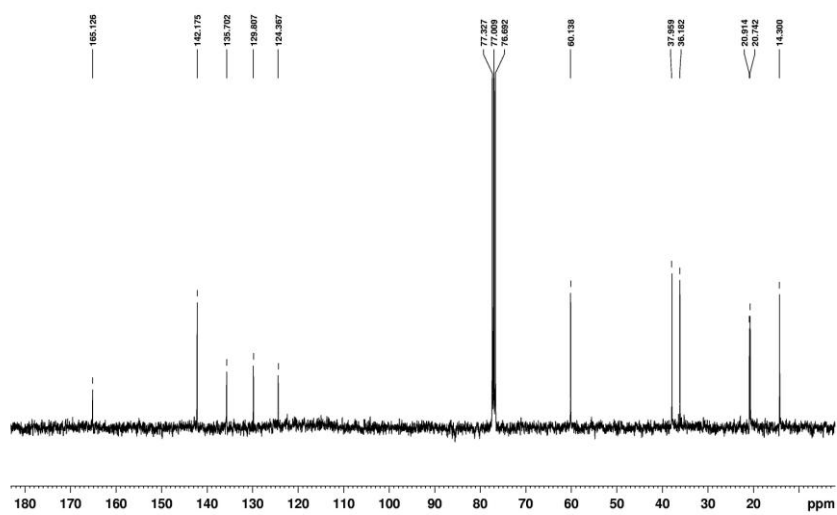
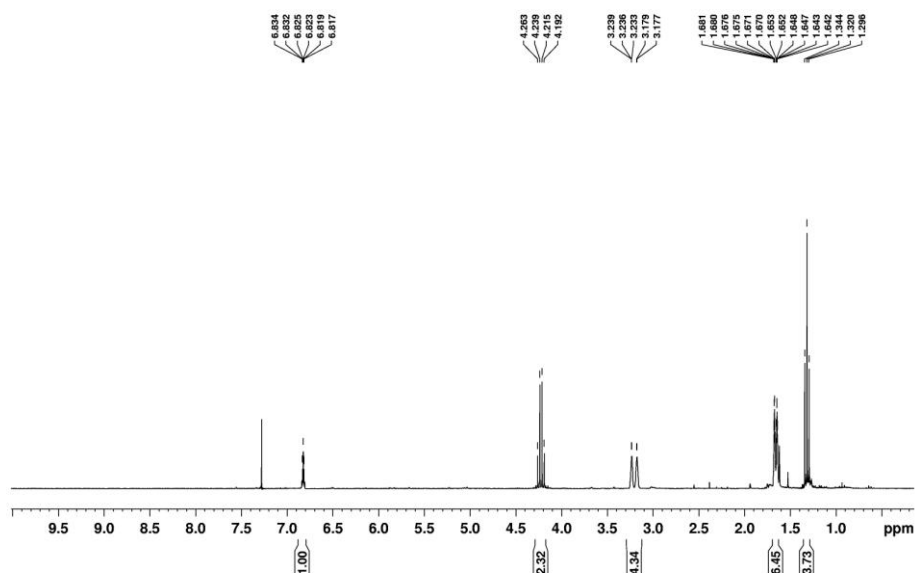
1. a) A. Padwa, Y. S. Kulkarni and Z. Zhang, *J. Org. Chem.* 1990, **55**, 4144; b) H. M. L. Davies, P. W. Hougland and W. R. Cantrell Jr., *Synth. Commun.* 1992, **22**, 971; c) M. P. Doyle, M. Yan, W. Hu and L. Gronenberg, *L. J. Am. Chem. Soc.* 2003, **125**, 4692; d) C. Peng, J. Cheng, and J. Wang, *J. Am. Chem. Soc.* 2007, **129**, 8708.
2. a) M. S. Baird, A. V. Nizoutsev and I. G. Bolesov, *Tetrahedron*, 2002, **58**, 1581; b) T. Jiro, S. Teuro and M. Ichiro, *Synthesis*, 1987, 603.
3. J.-L. Moreau and M. Gaudemar, *J. Organomet. Chem.* 1976, **108**, 159.
4. P. de Frémont, N. Marion and S. P. Nolan, *J. Organomet. Chem.* 2009, **694**, 551.
5. For a detailed presentation of the theoretical methods, see: F. Jensen, *Introduction to Computational Chemistry*, 2nd edition, Wiley **2007**.
6. *Gaussian 09*, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. J.; Burant, C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

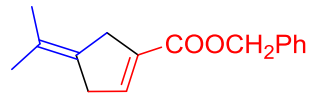
11. ¹H- and ¹³C-NMR spectra for new compounds



3a

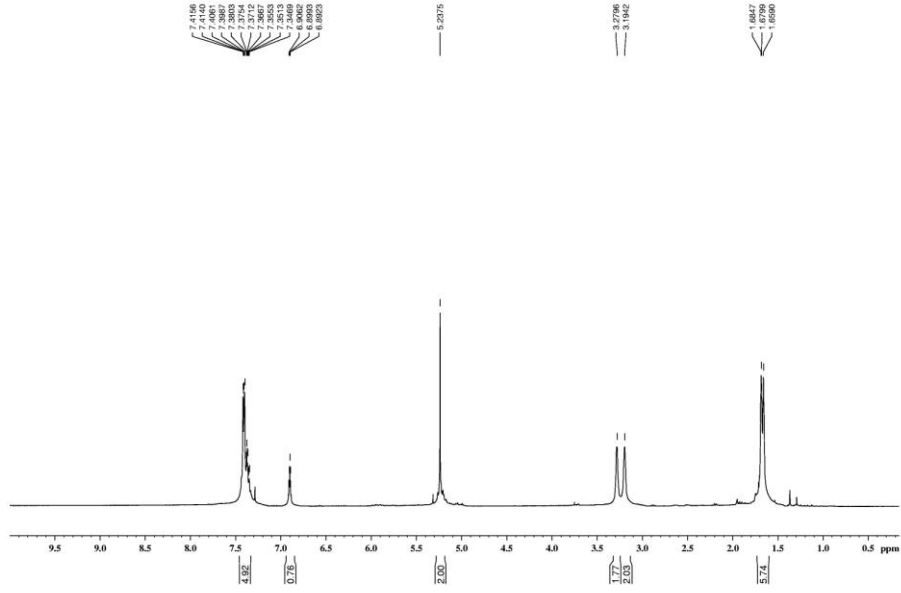
EL-155car



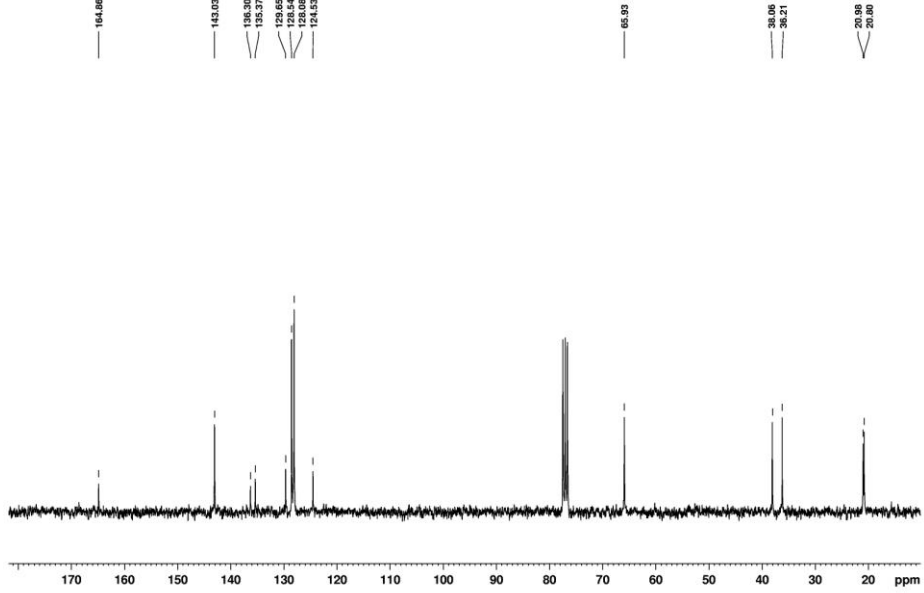


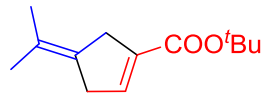
3b

EL-262



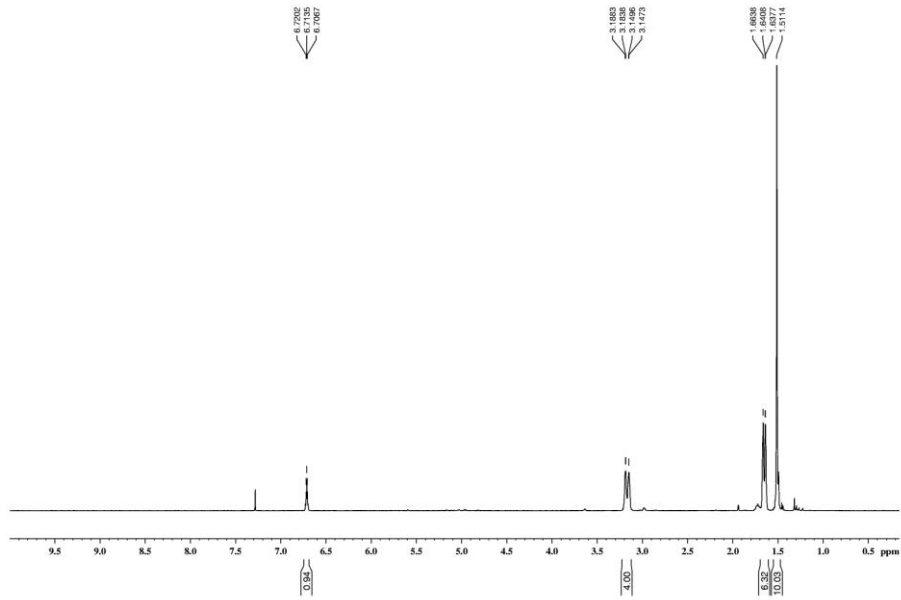
EL-262



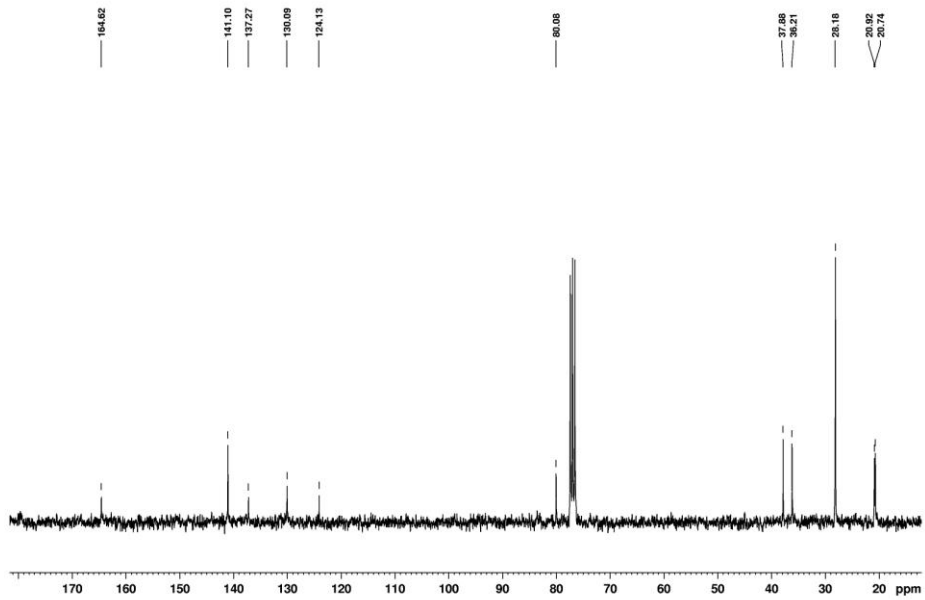


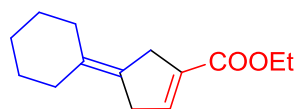
3c

EL-260f1



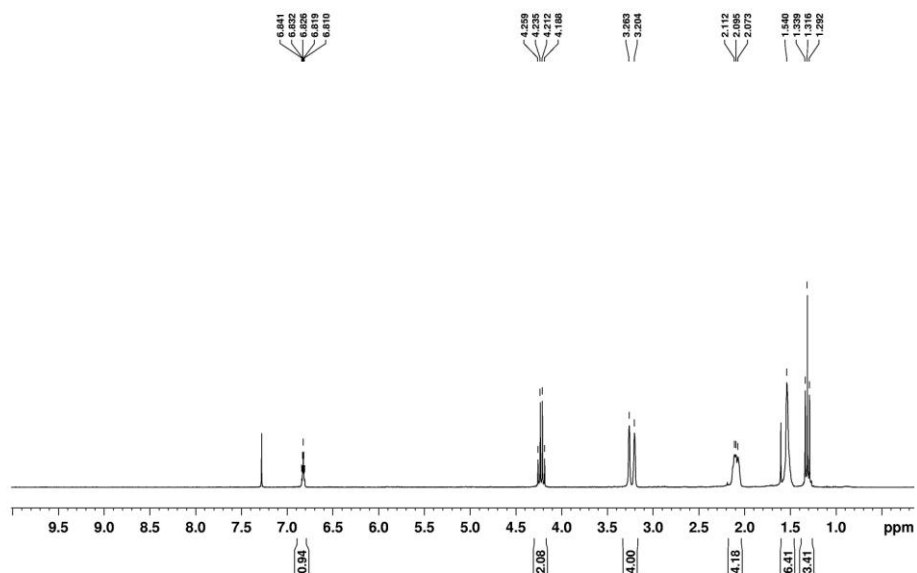
EL-260f1



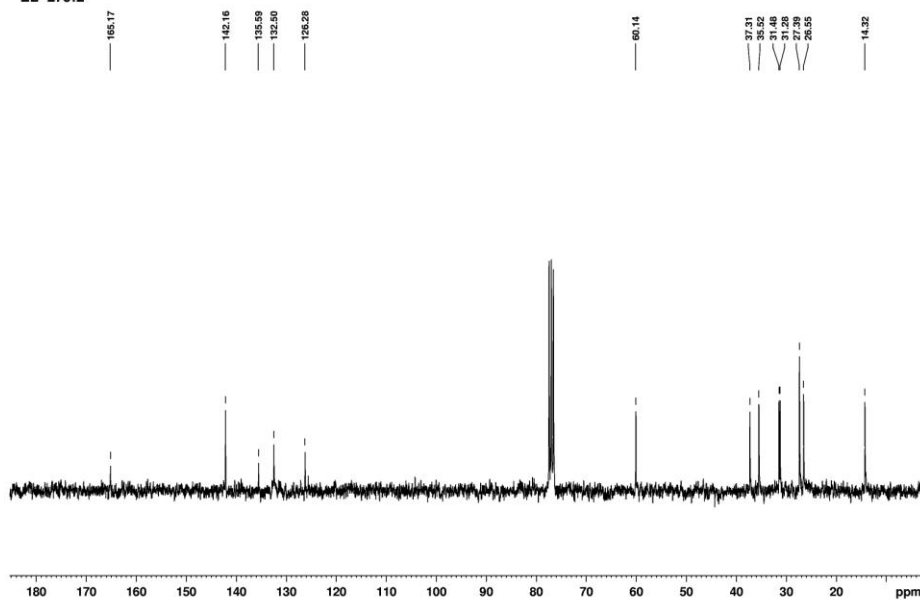


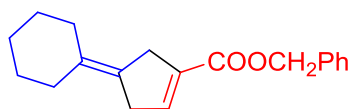
3d

EL-279f2p



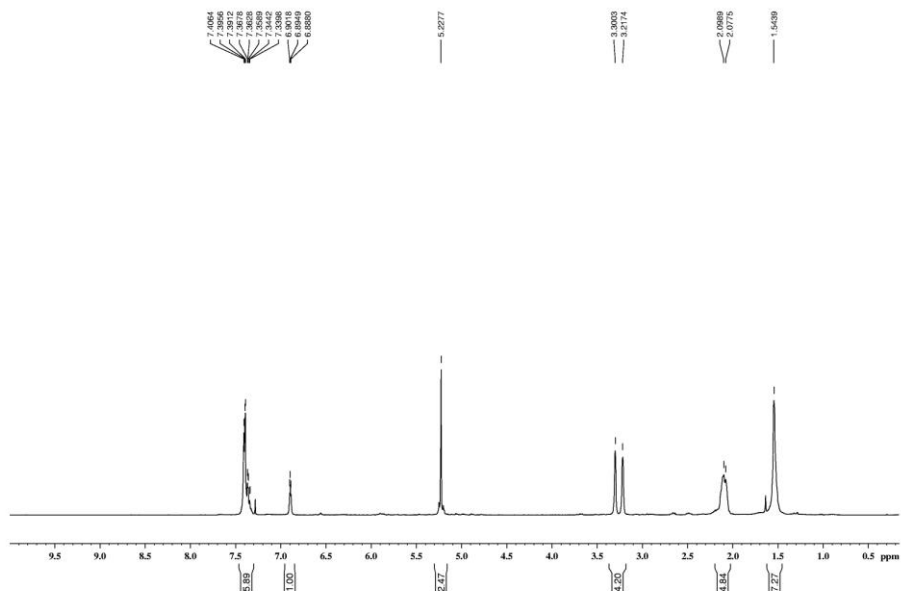
EL-279f2



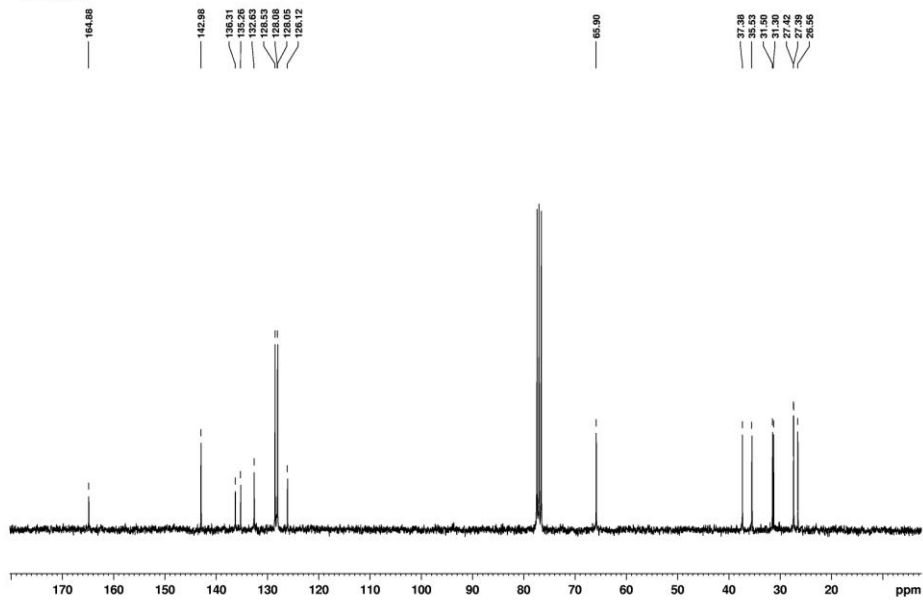


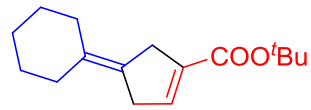
3e

EL-25112



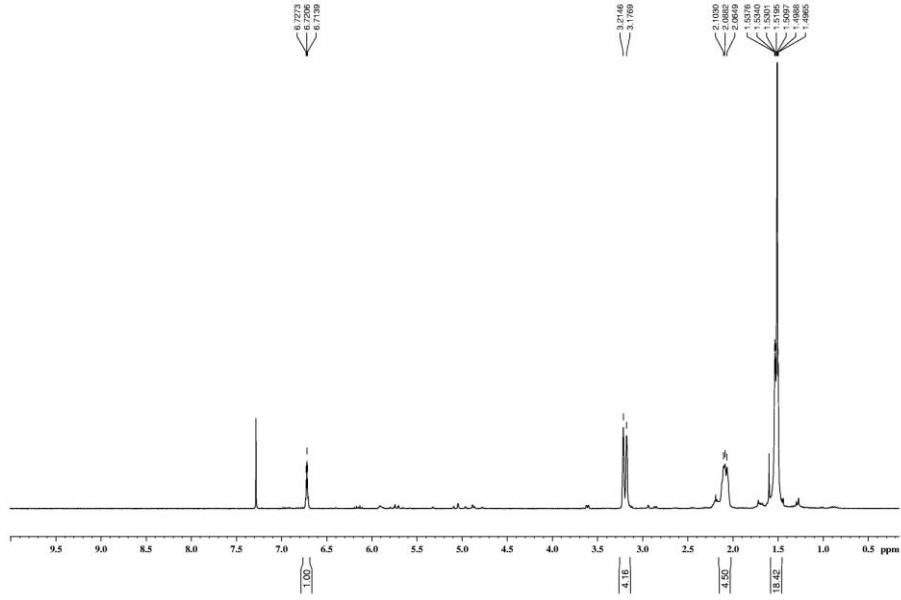
EL-25112



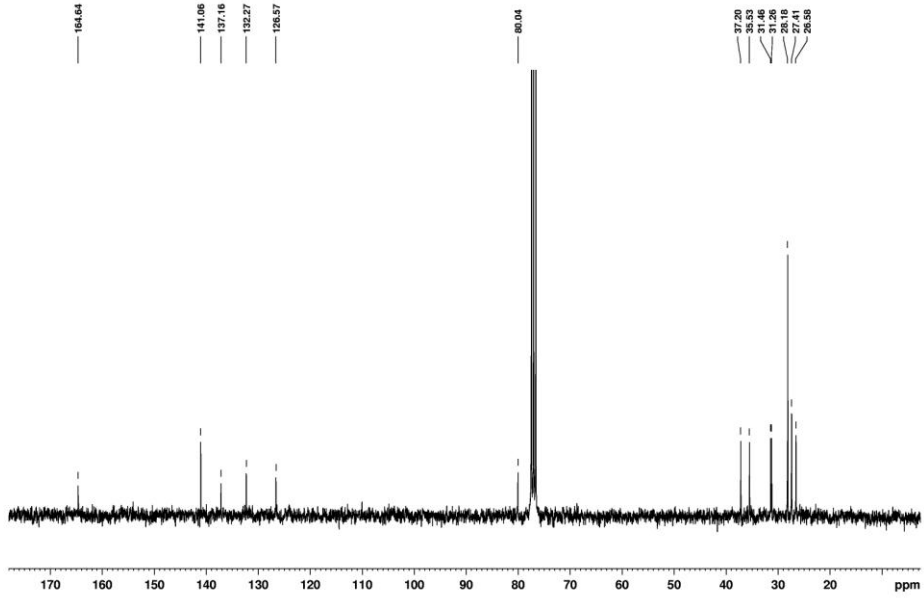


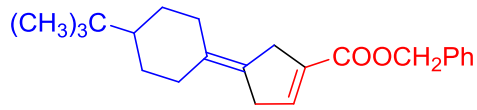
3f

EL-250f2



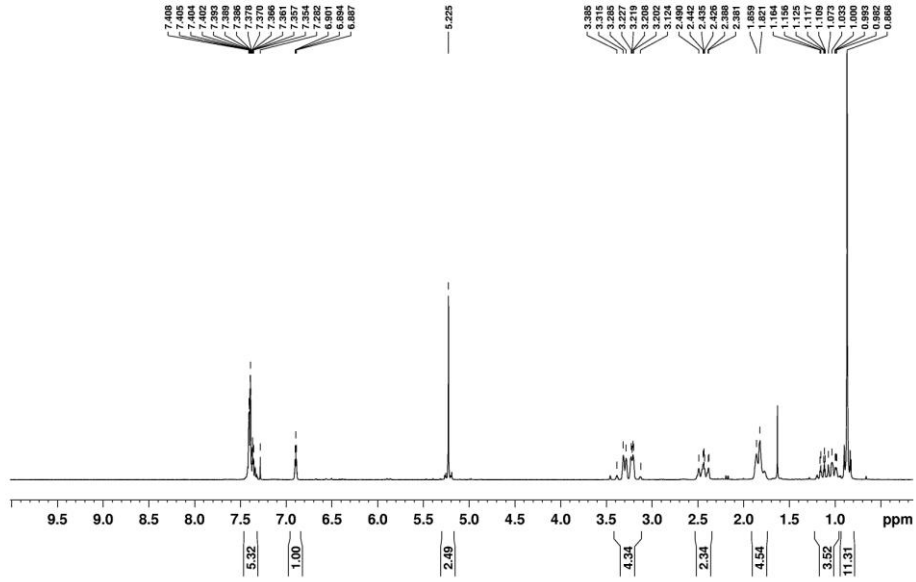
EL-250f2car



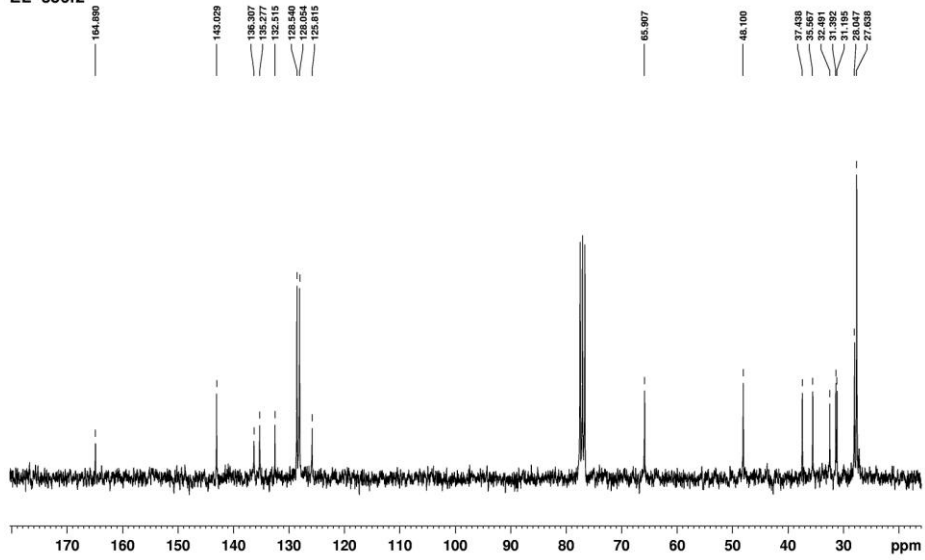


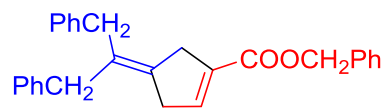
3g

EL-356f3_1h



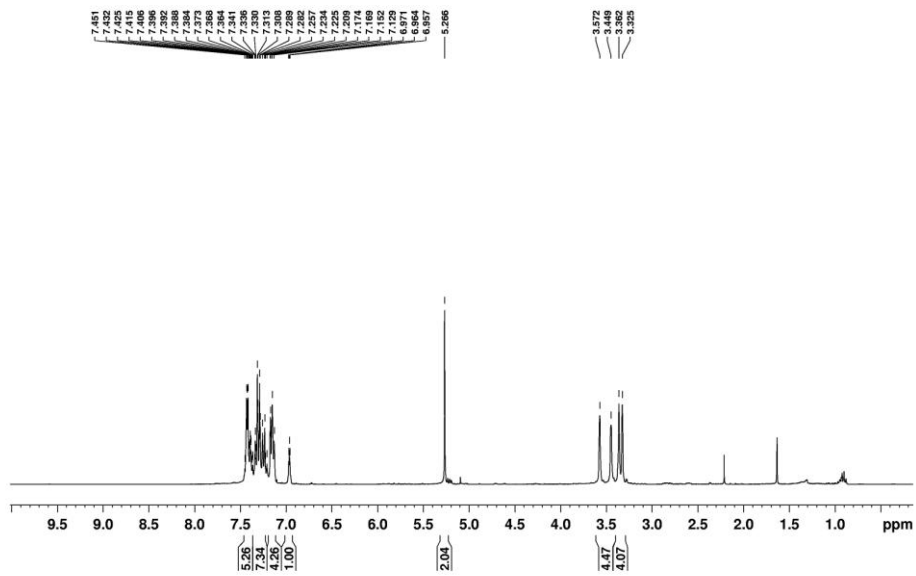
EL-356f2



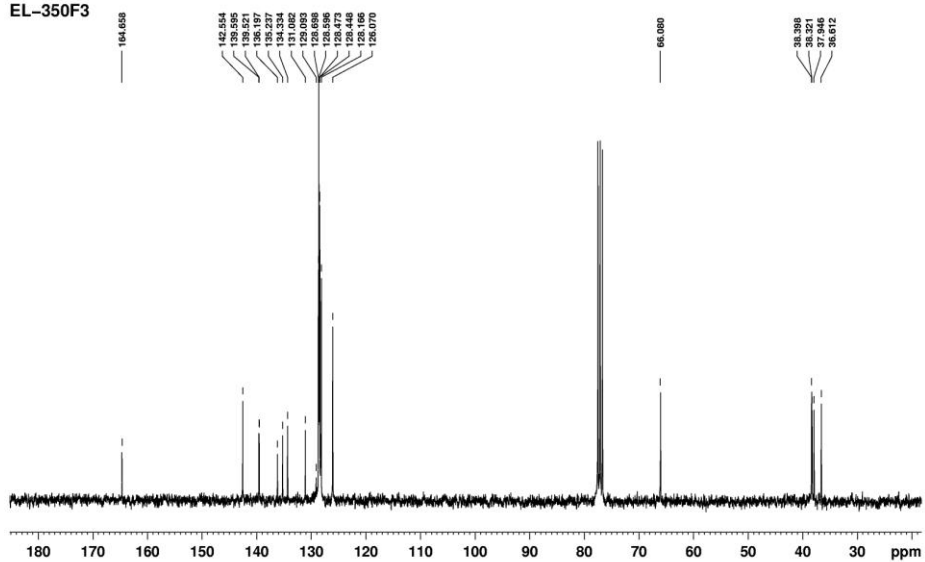


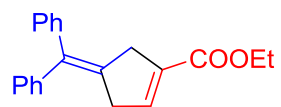
3h

EL-350f3



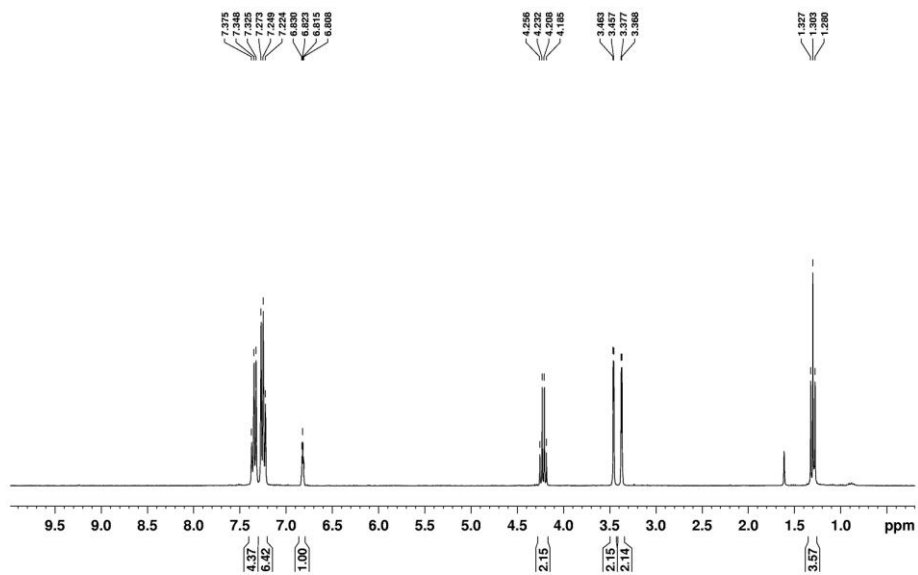
EL-350F3



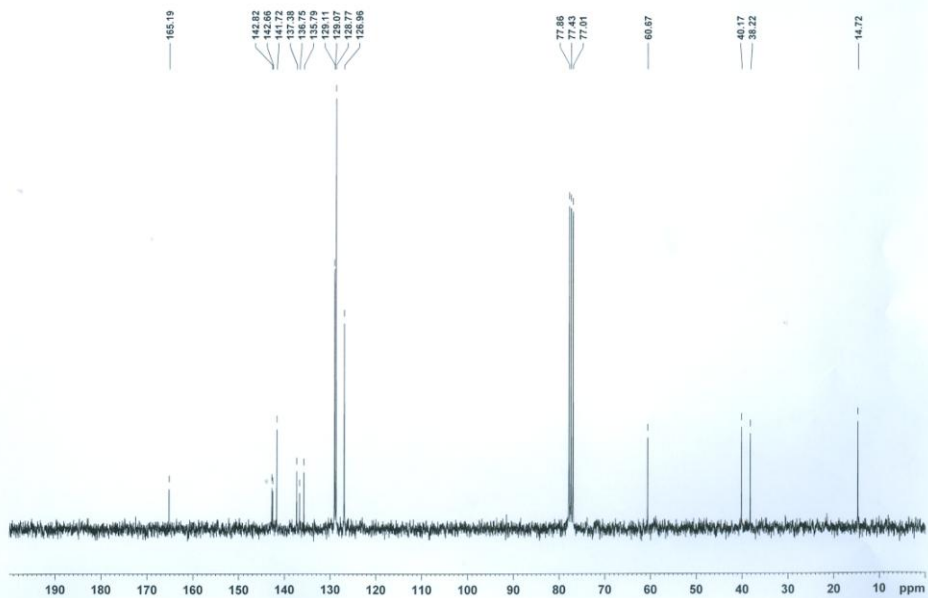


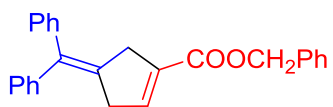
3i

GL-1083f3



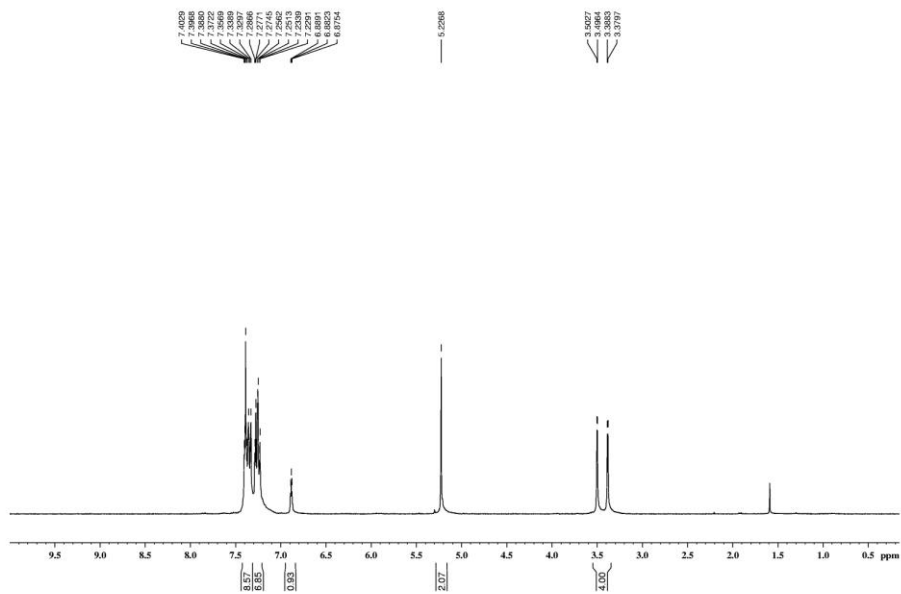
gl1083f3 C13 CPD DPX300



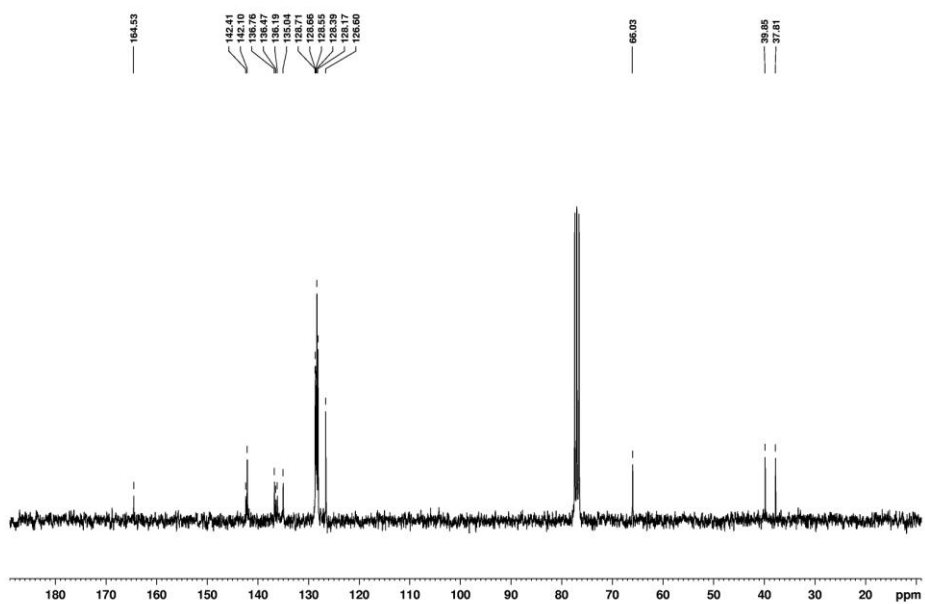


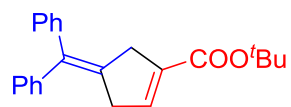
3j

EL-27012



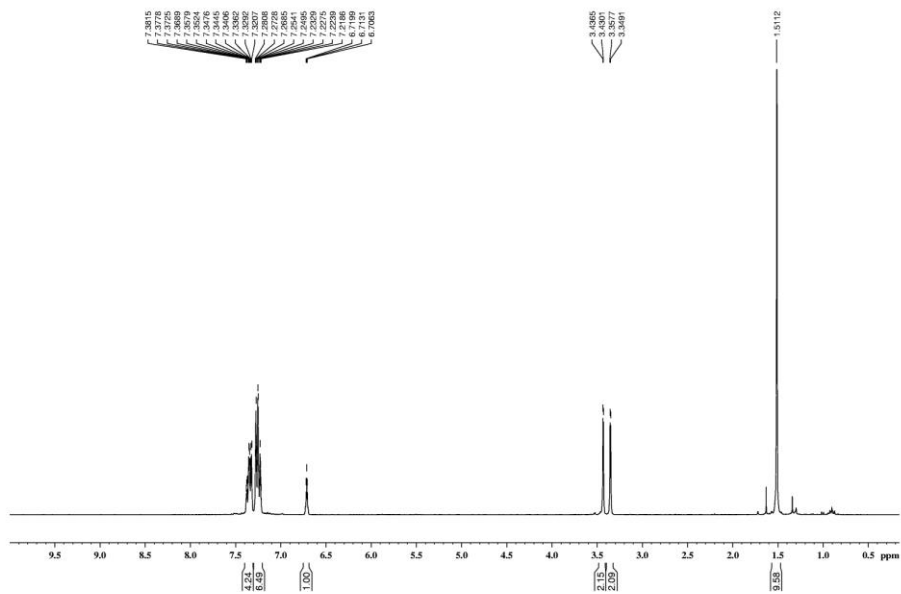
EL-27012



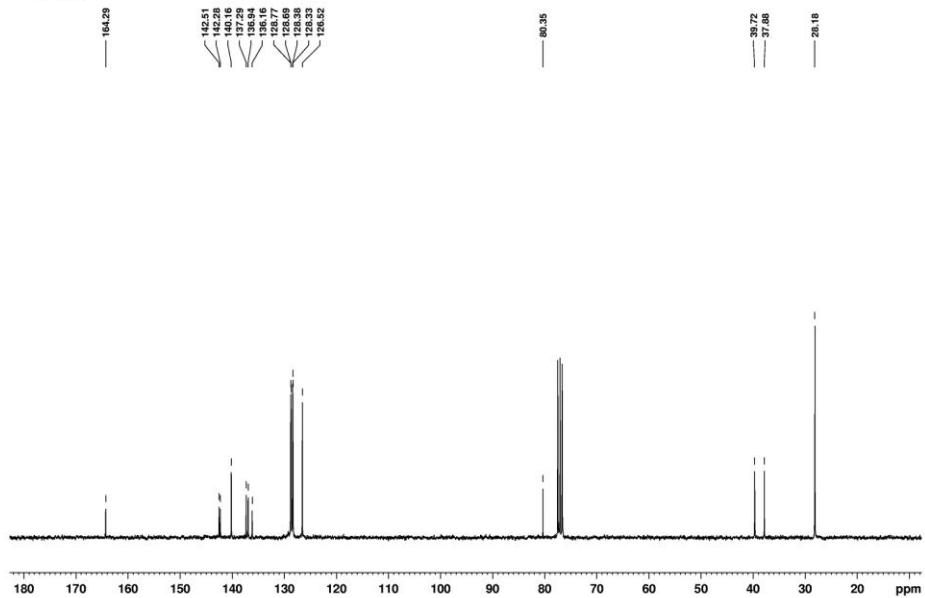


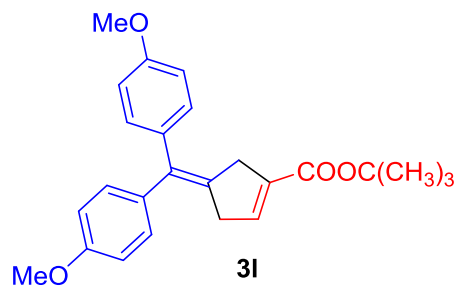
3k

EL-271f2

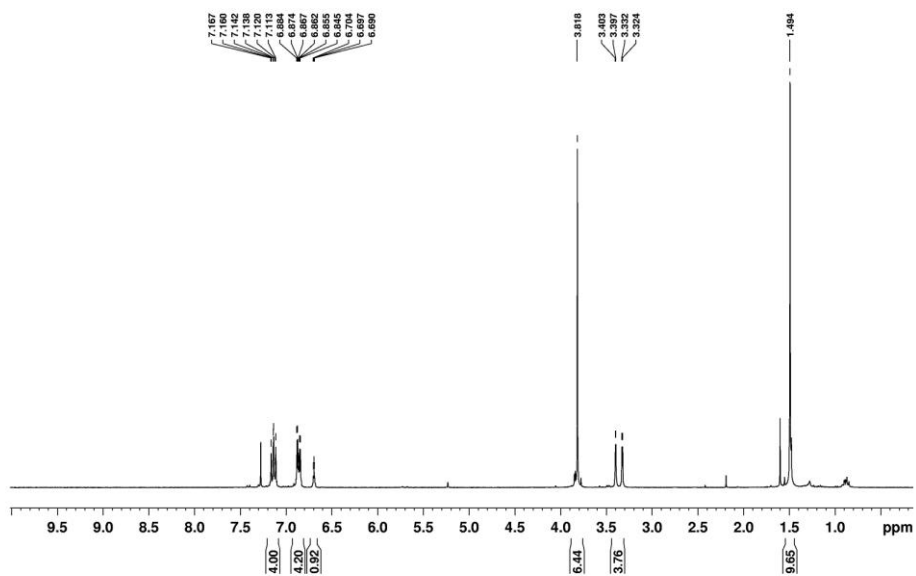


EL-271f2

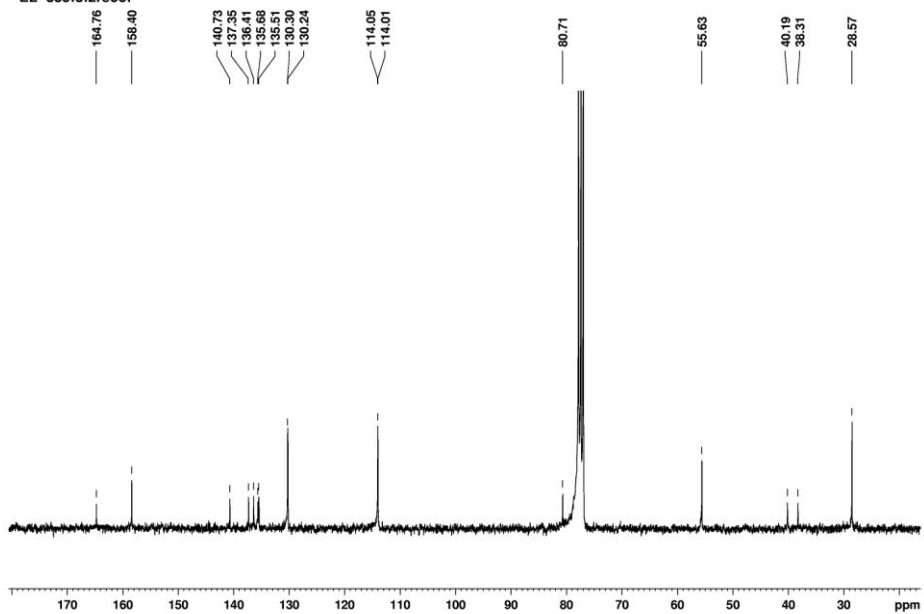


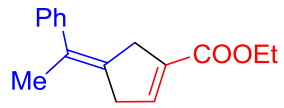


EL-335f3f2



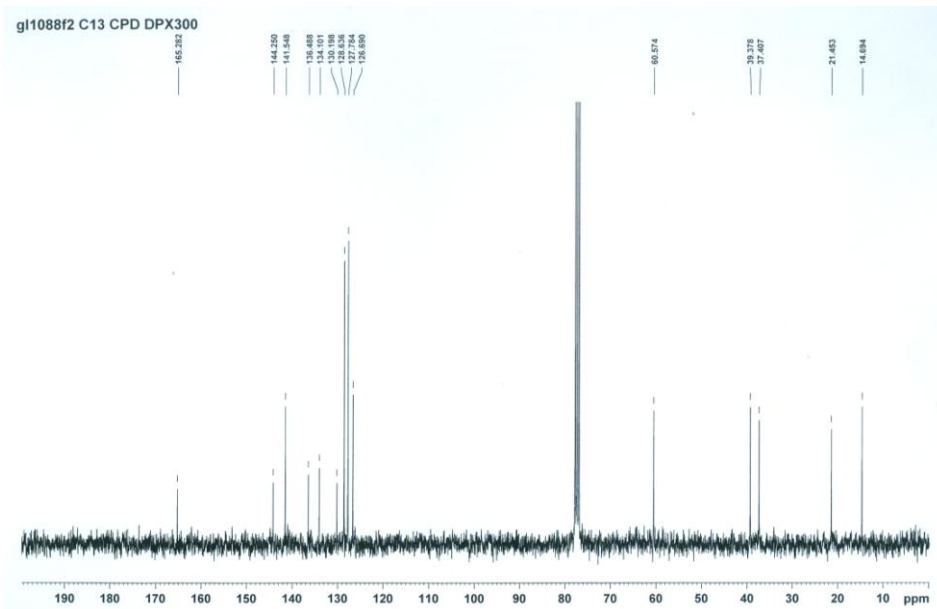
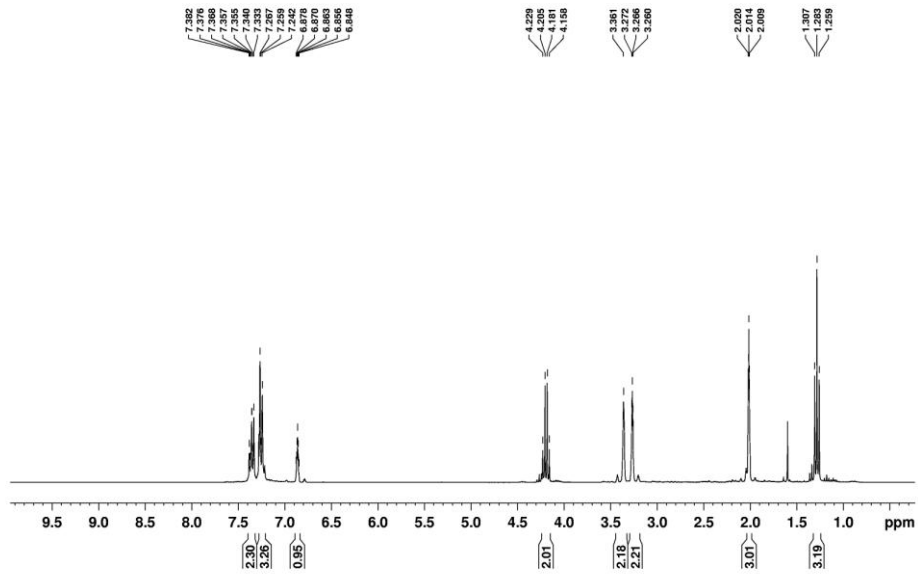
EL-335f3f2recol



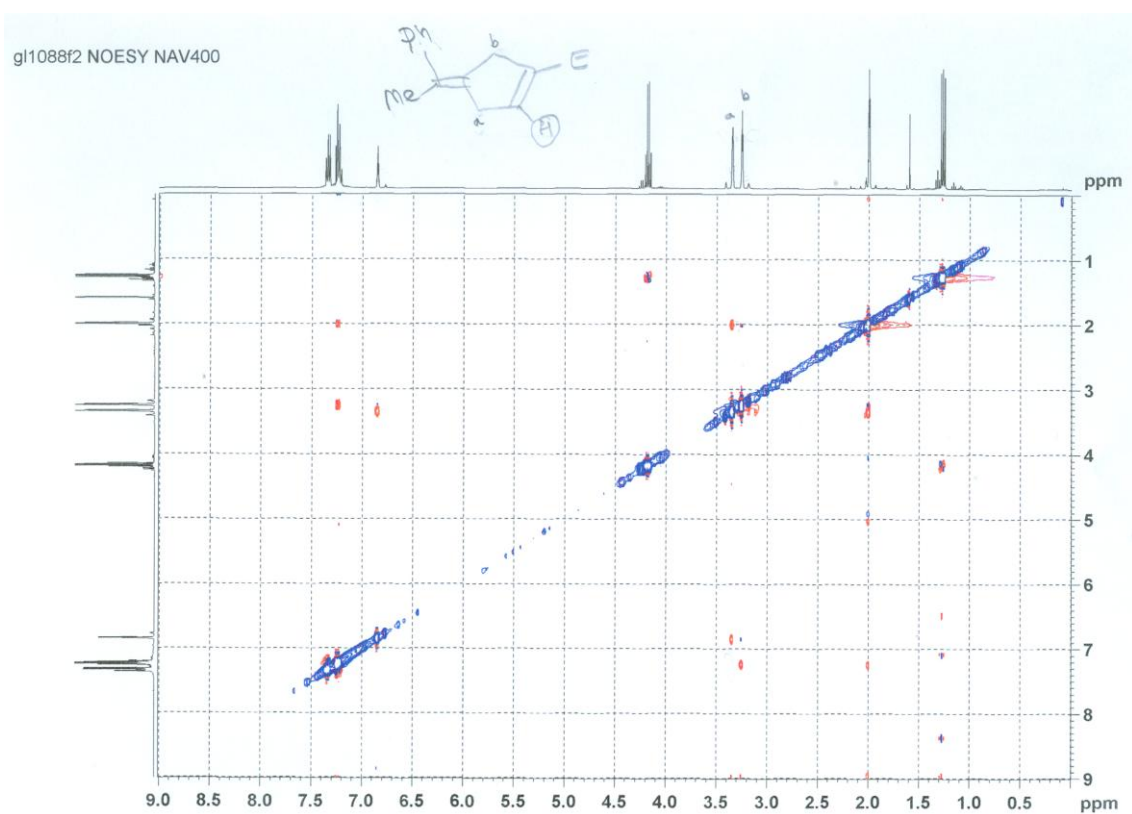


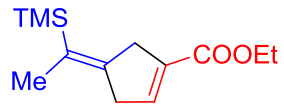
3m

GL-1088F2



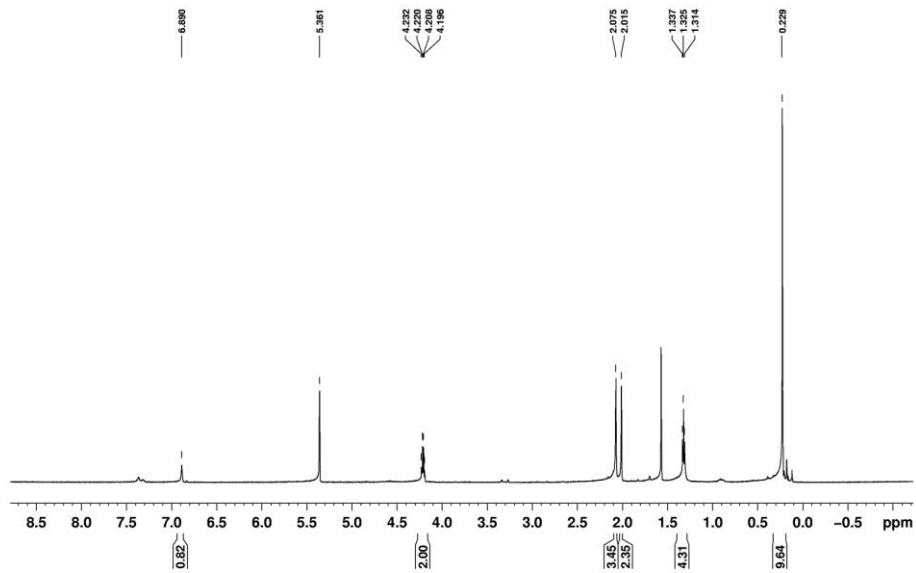
NOESY experiment (400 MHz, CDCl₃) for compound **3m**



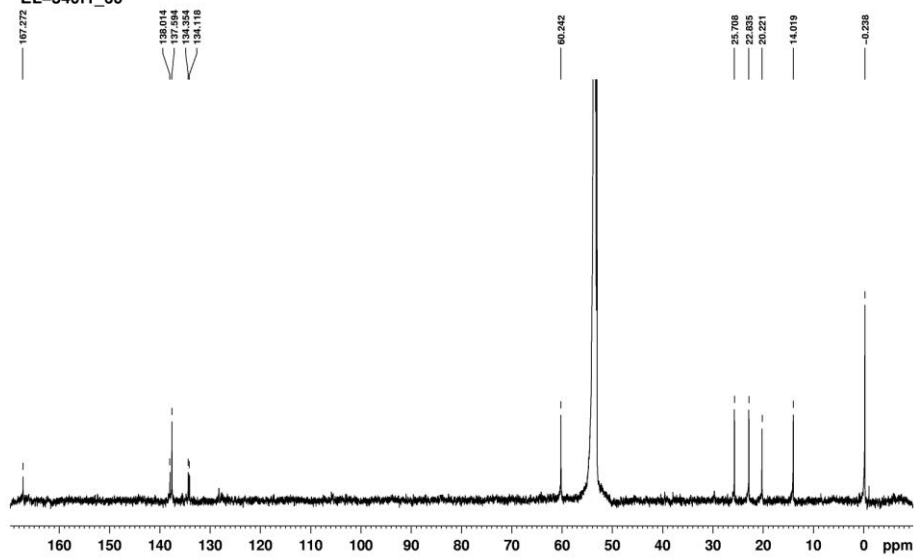


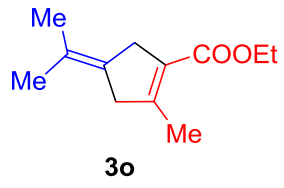
3n

EL-340f1_600

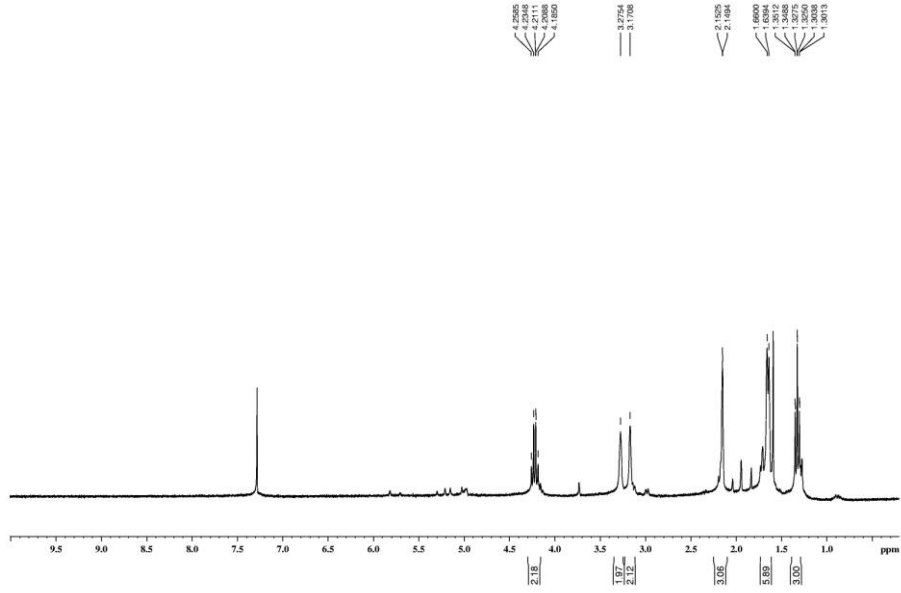


EL-340f1_60

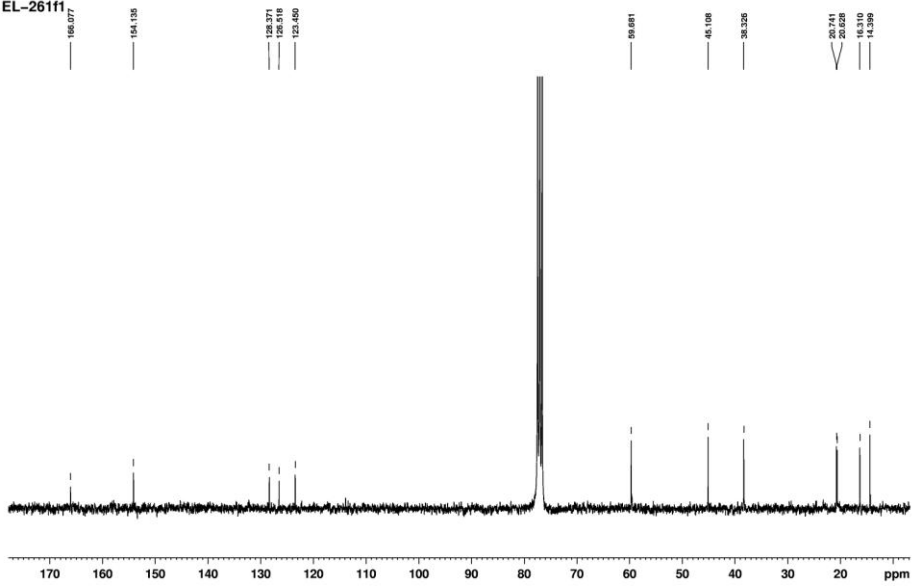


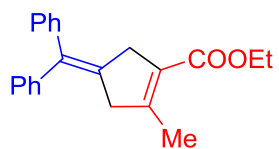


EL-2611f



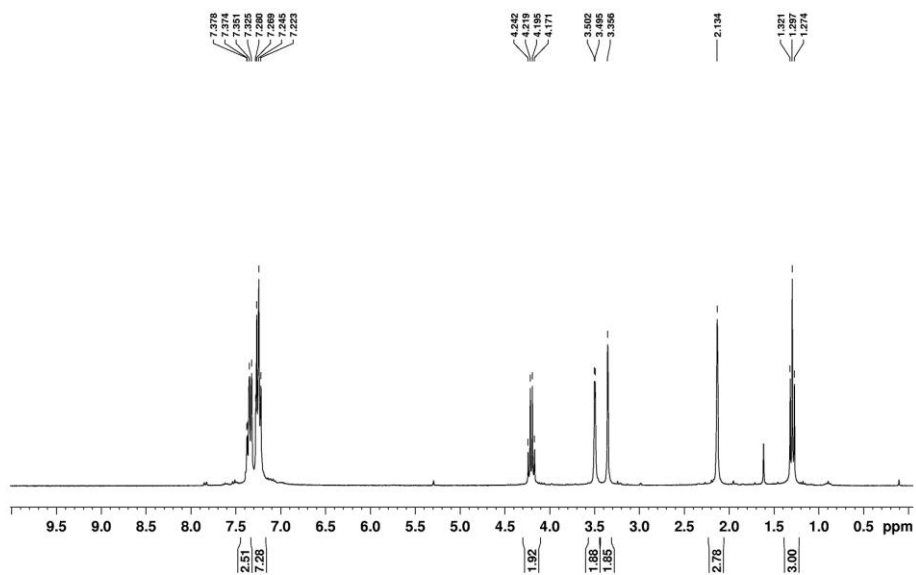
EL-2611f



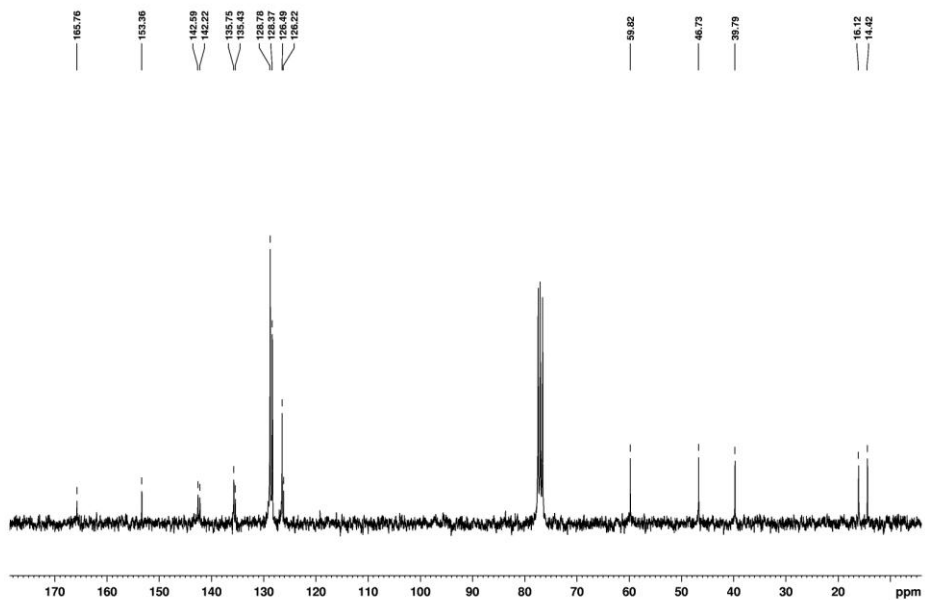


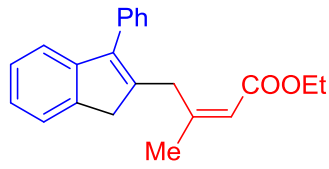
3p

EL-284f2_1



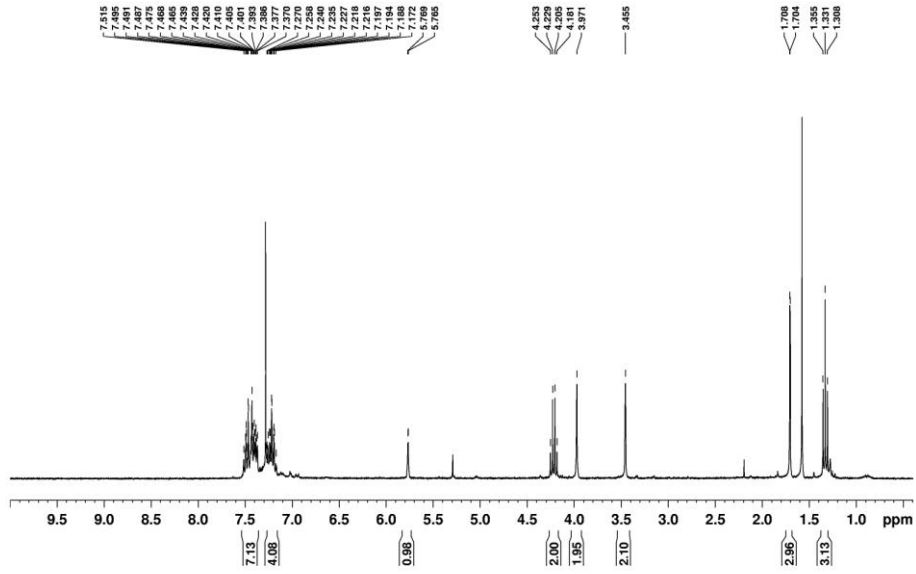
EL-284f2



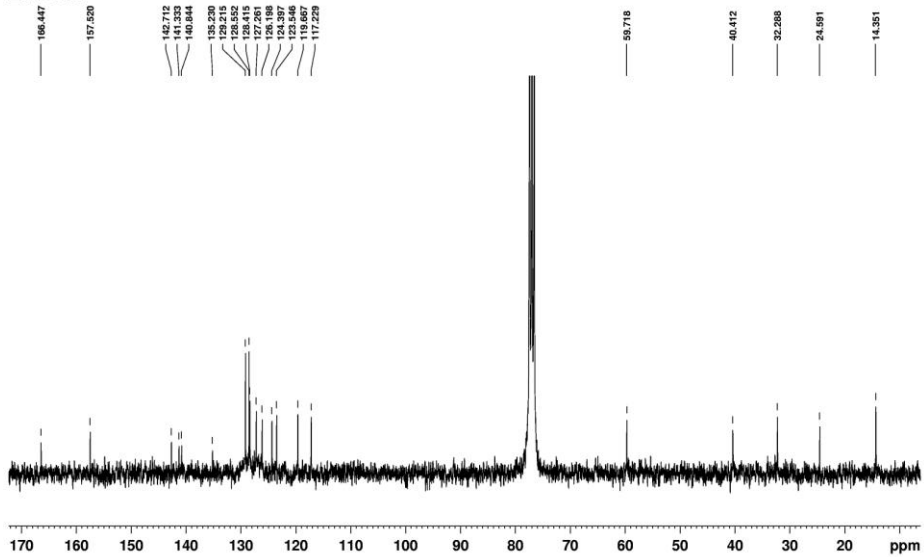


3p'

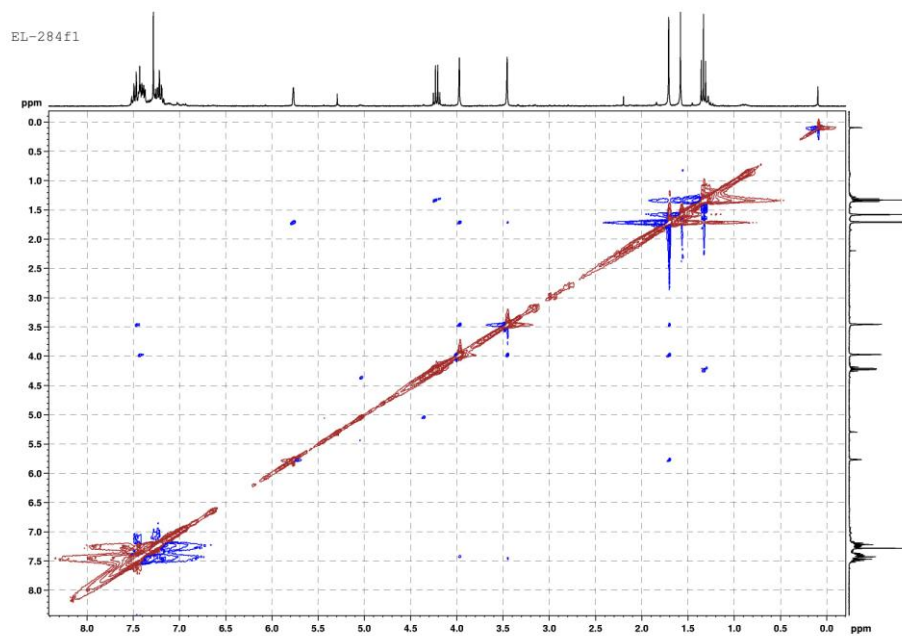
EL-284f1

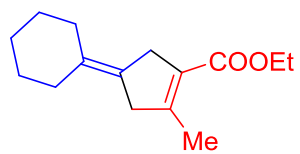


EL-284f1



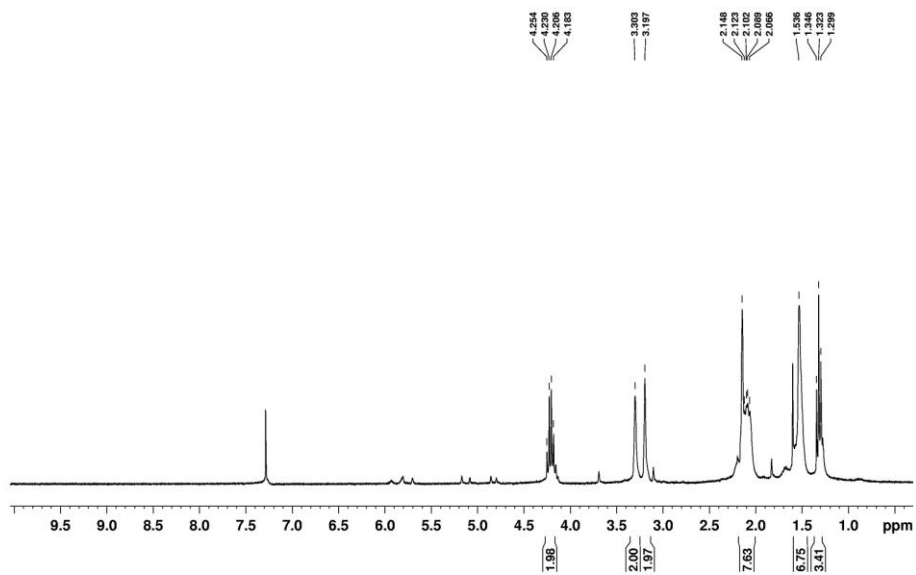
NOESY experiment (400 MHz, CDCl₃) for compound **3p'**



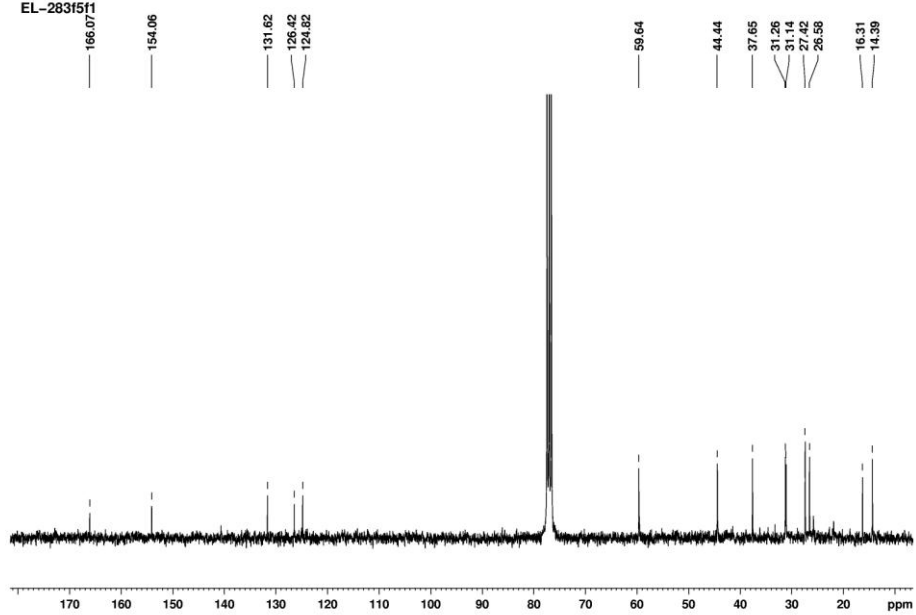


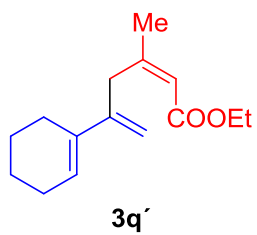
3q

EL-283f5f1

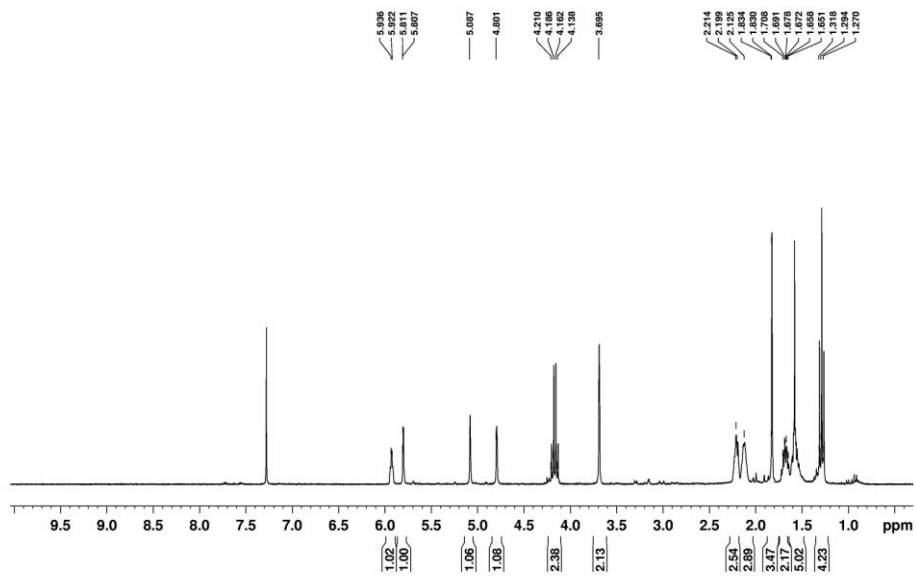


EL-283f5f1

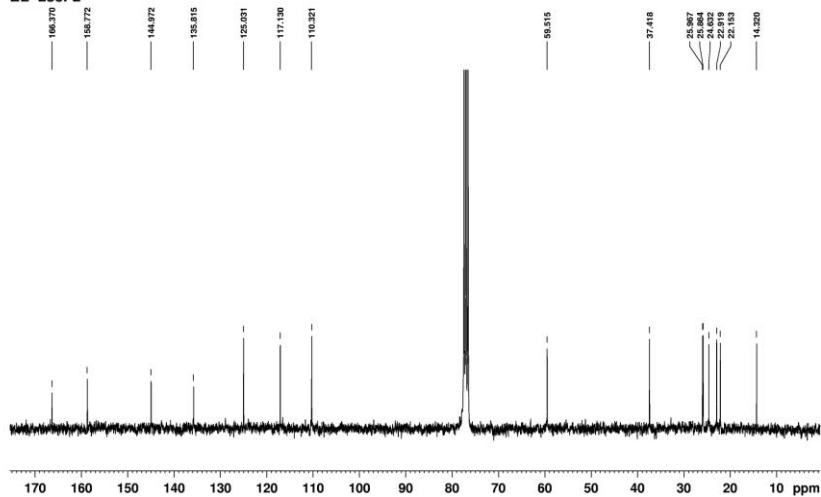


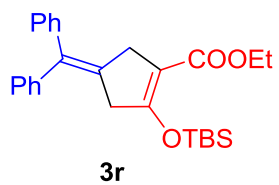


EL-283F2

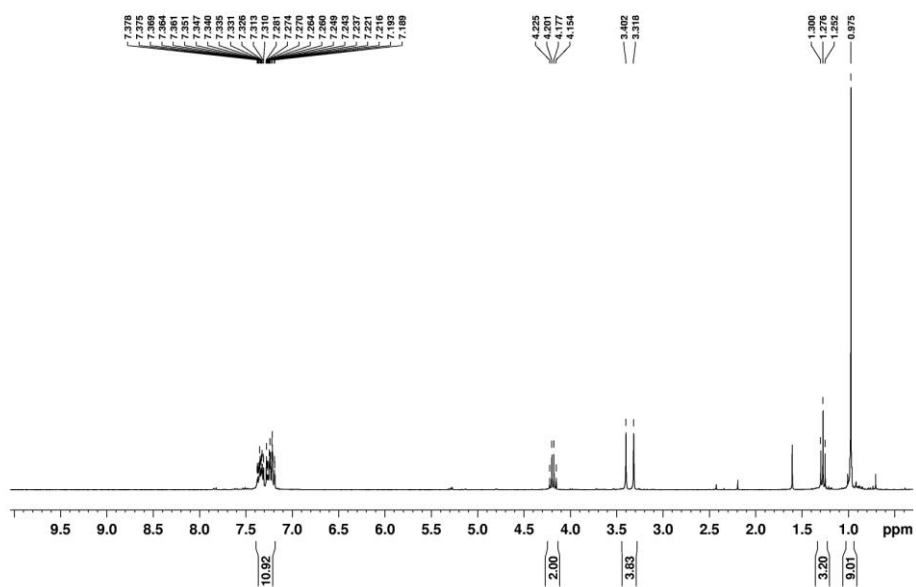


EL-283F2

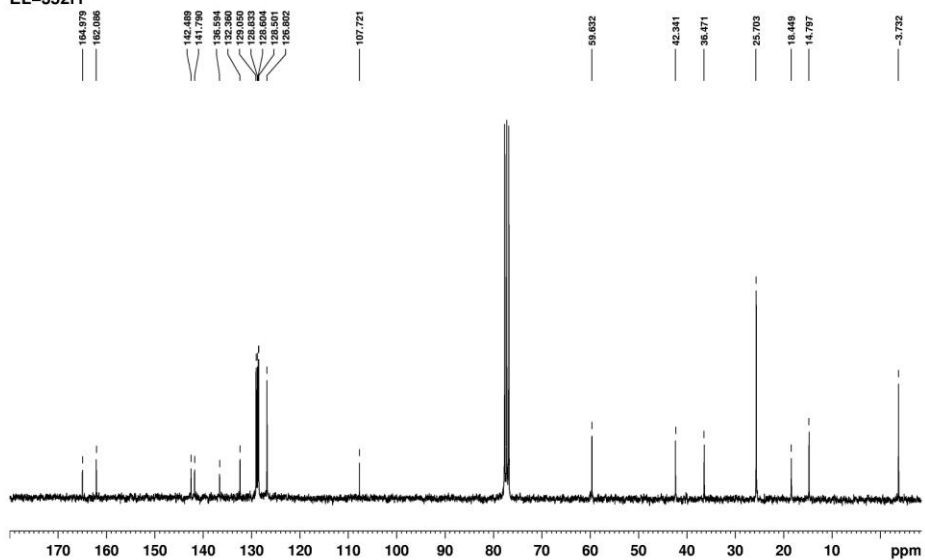


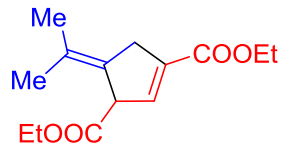


EL-352F1



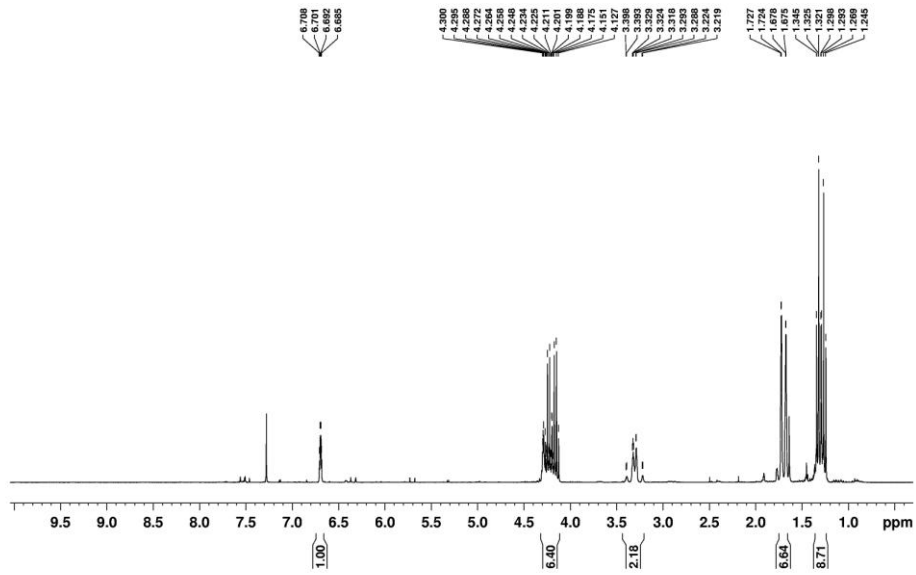
EL-352f1



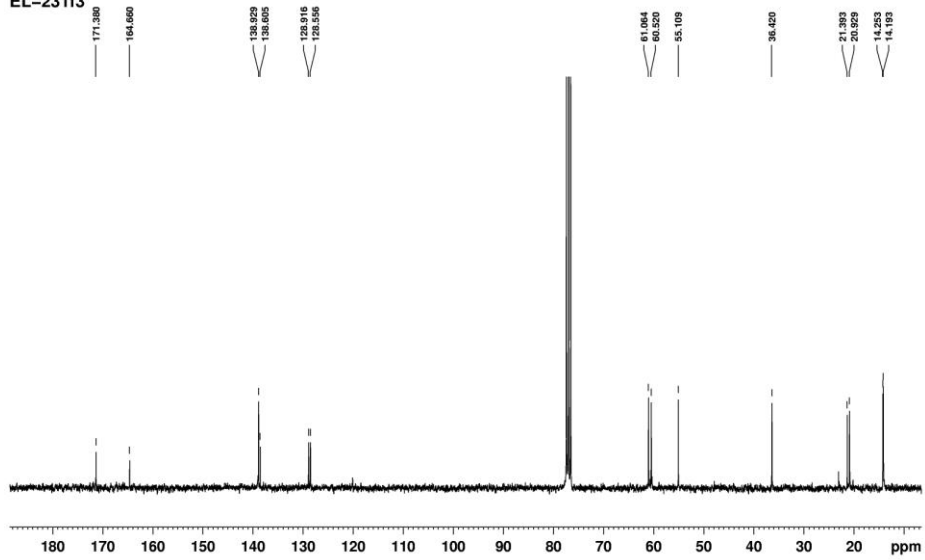


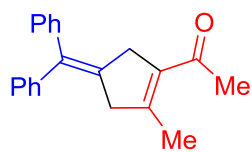
3s

EL-231F3



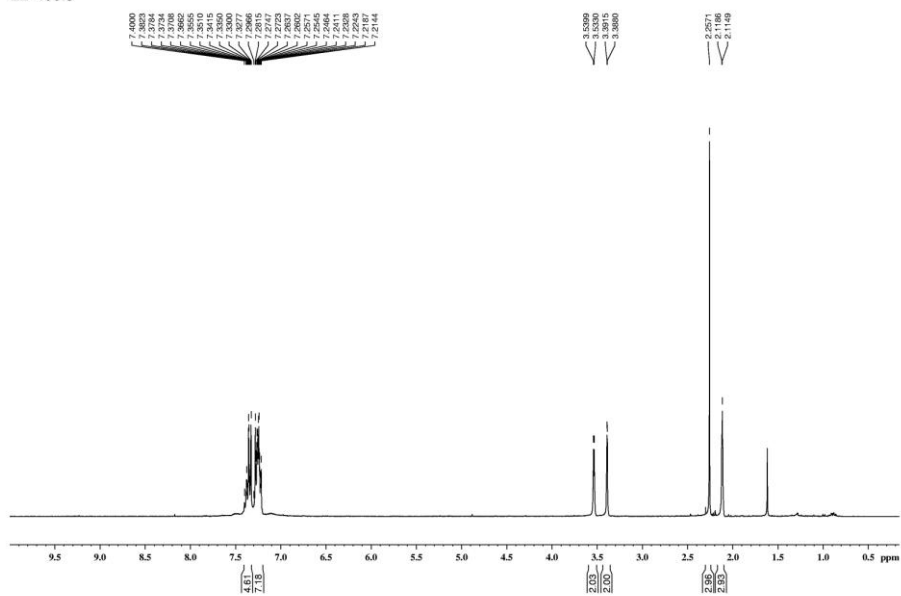
EL-231f3



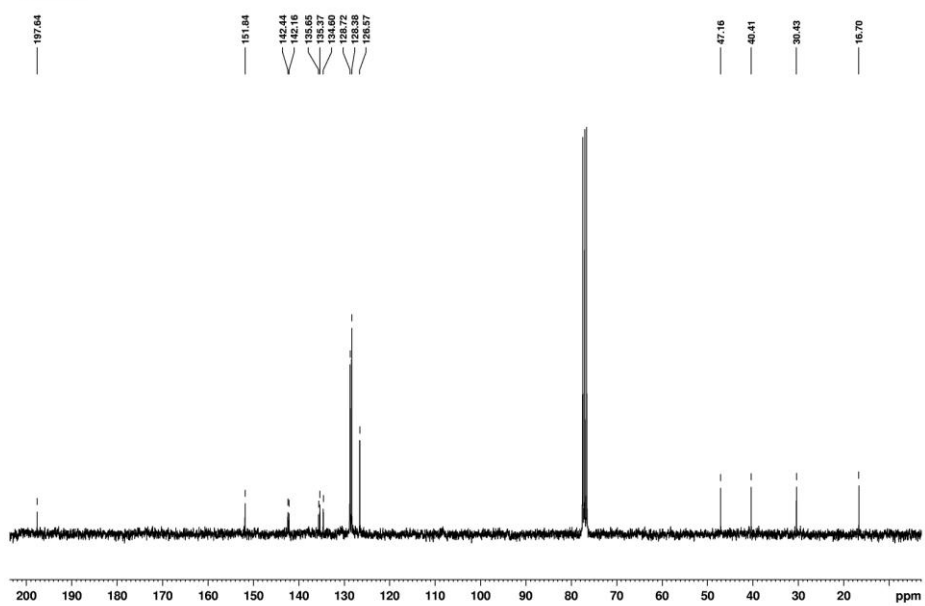


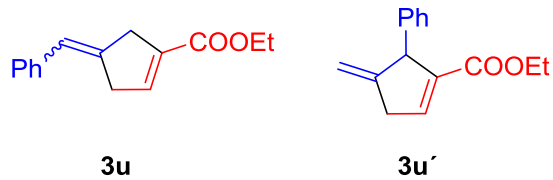
3t

EL-196f3

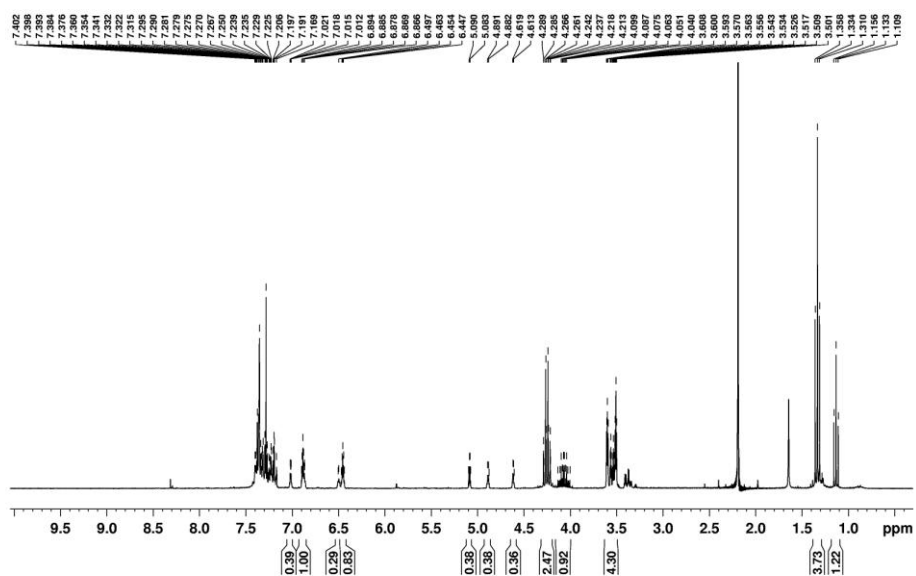


EL-196f3

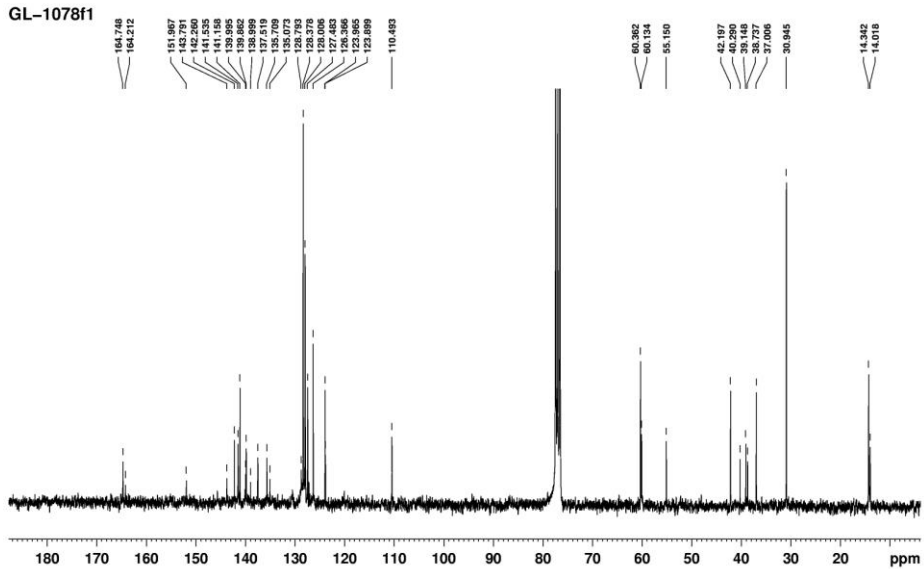


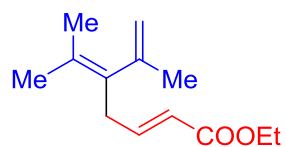


EL-1078f1



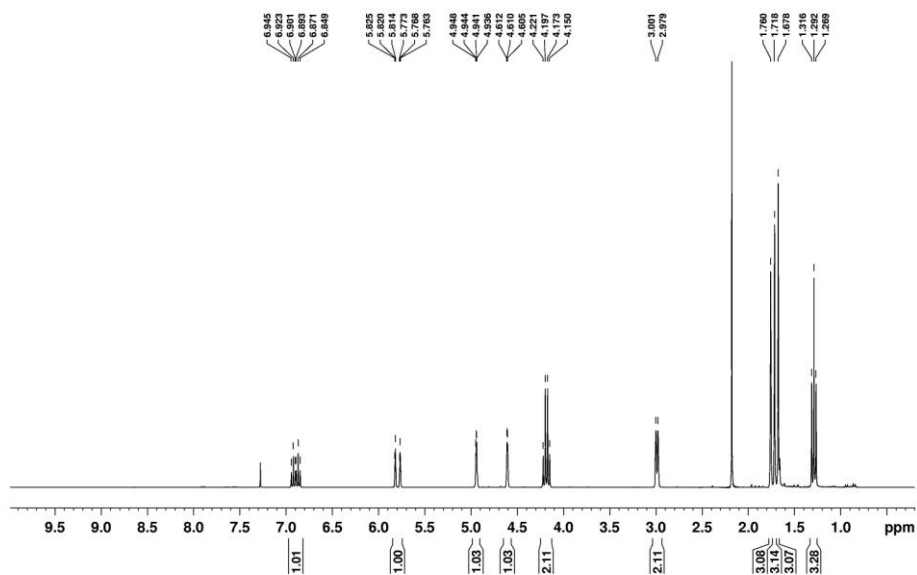
GL-1078f1



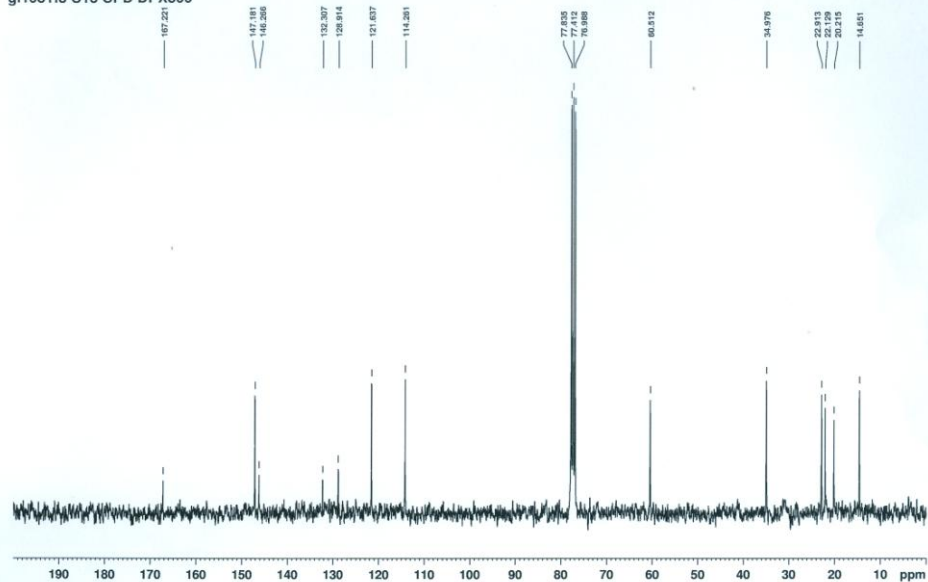


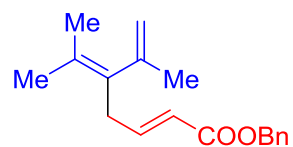
4a

GL-1081f3



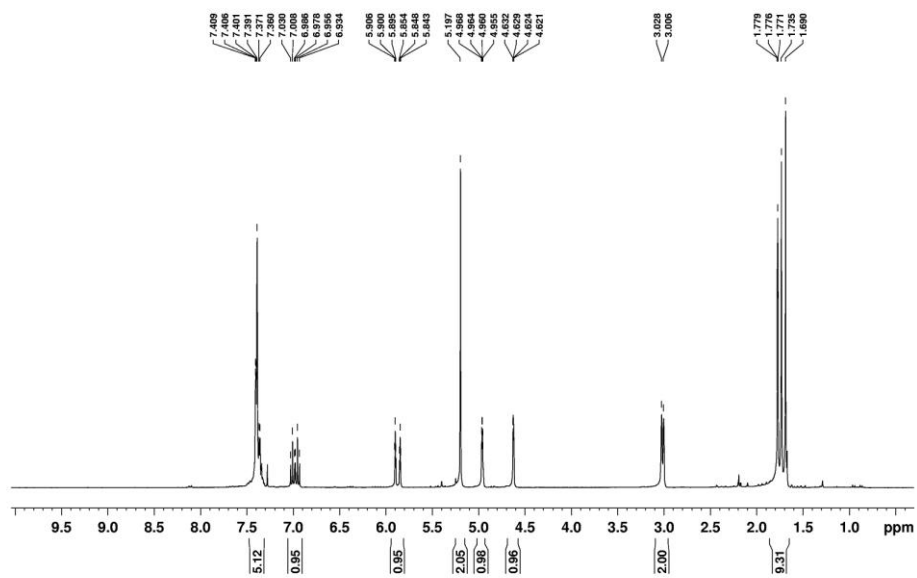
gl1081f3 C13 CPD DPX300



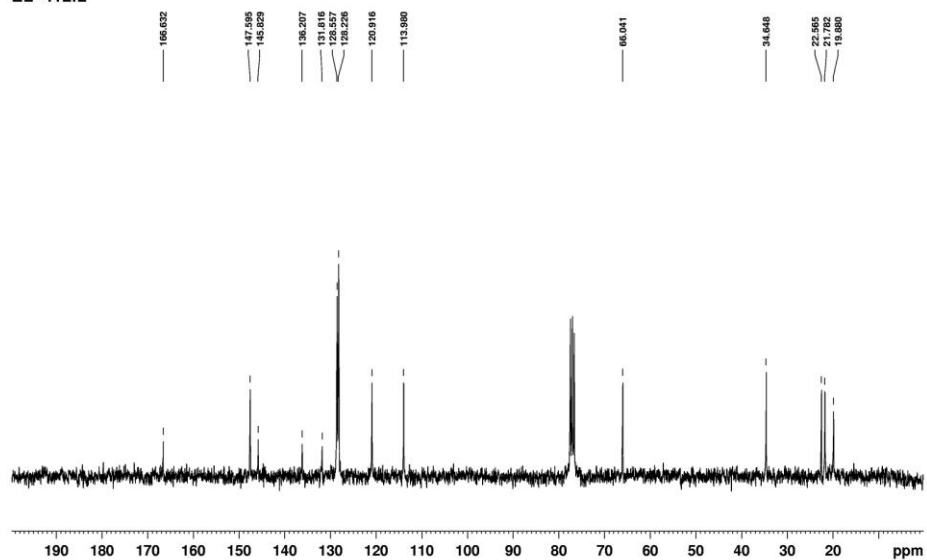


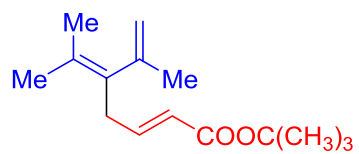
4b

EL-412F2_1H



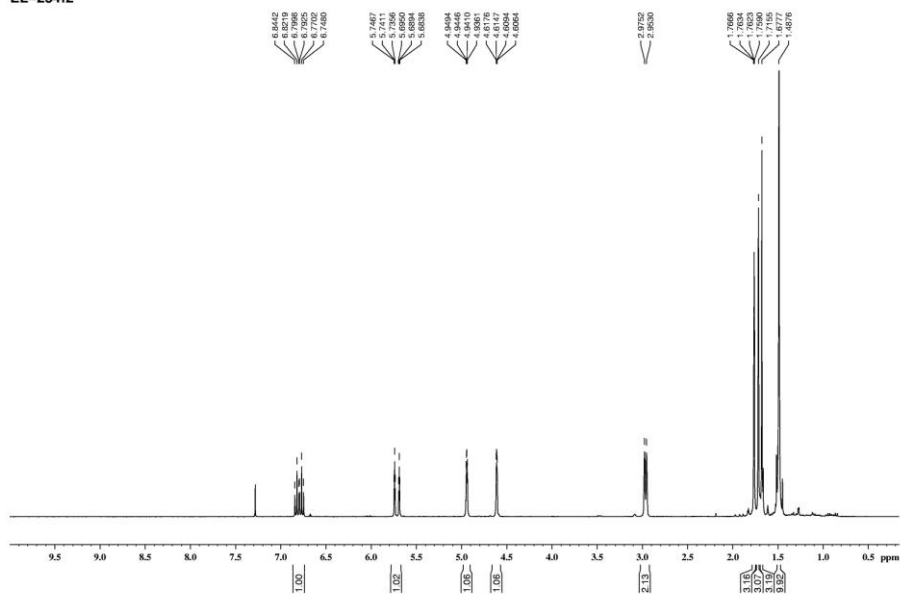
EL-412f2



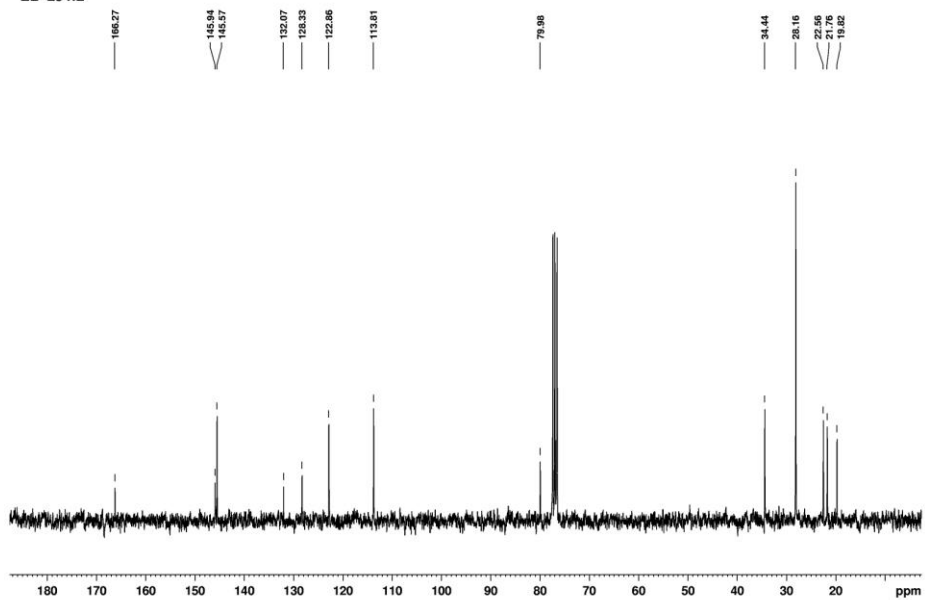


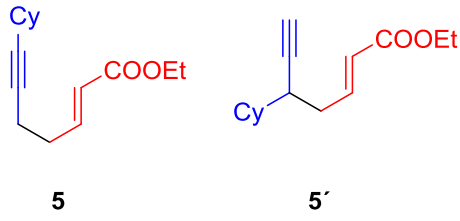
4c

EL-254f2

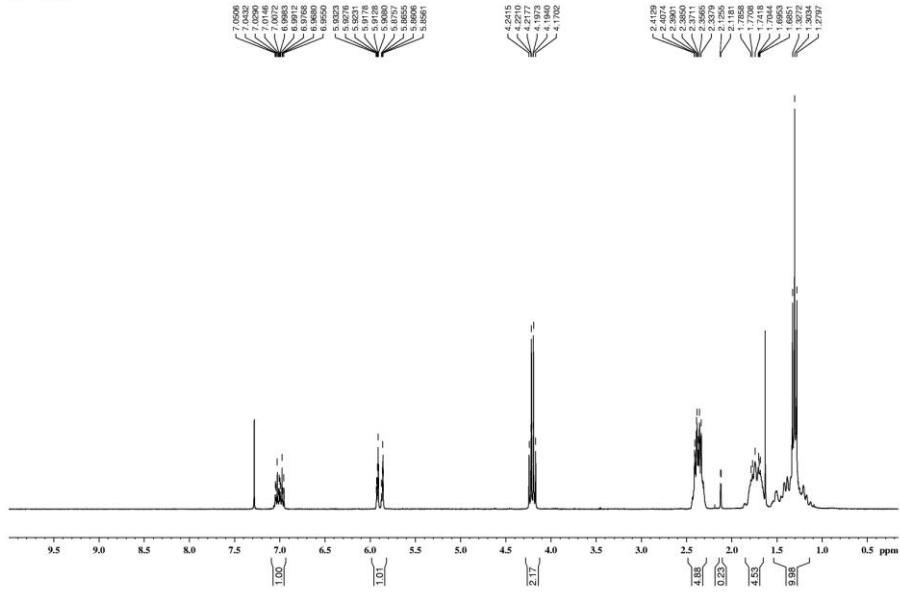


EL-254f2

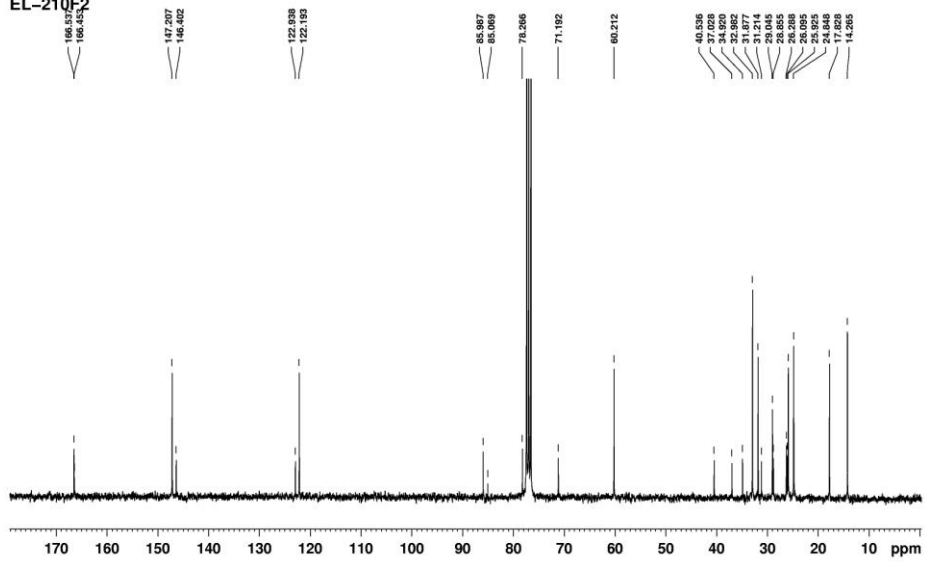


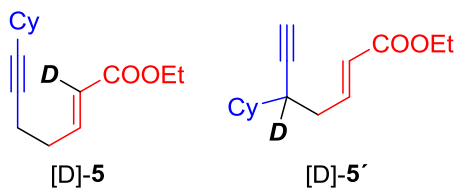


EL-210f2

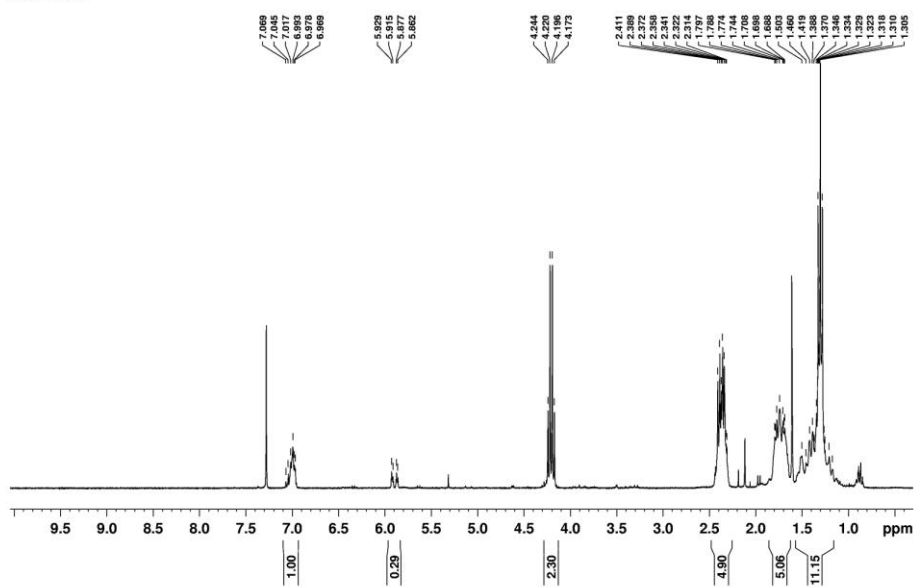


EL-210f2





EL-443f2



EL-443F2

