Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Intermolecular Reactions of Gold(I)-Carbenes with Furans by Related Mechanisms

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General Information

Unless otherwise stated, reactions were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck GF_{234}) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatograpy purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 mm) or automated flash chromatographer CombiFlash Companion. Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

NMR spectra was recorded at 298 K on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra was recorded on a Waters Micromass LCT Premier (ESI), Waters Micromass GCT (EI, CI) and Bruker Daltonics Autoflex (MALDI) spectrometers. Melting points were determined using a Büchi melting point apparatus.

Crystal structure determinations were carried out using a Bruker-Nonius diffractomer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK_a radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = □173 ºC). Full-sphere data collection was used with w and j scans. *Programs used*: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implement in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non hydrogen atoms were refined including anisotropic displacement parameters.

Experimental Part

Intermolecular Cyclizations of Propargyl Esters with Furans

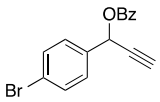
The physical and spectral data (^{1}H NMR and ^{13}C NMR) for the following compounds are in agreement with the data previously reported: Propargyl esters **1a**,[2] **1b**,[1] **1c**,[2] **1e**,[3] **1g**,[4] **1h**,[2] and furans **2c**,[5] **2d**[6].

General procedure for the preparation of propargylic acetates and benzoates

A solution of ethynylmagnesium bromide (3.60 mmol, 0.5 M in THF) was added slowly to a solution of aldehyde (3 mmol) in THF (3 mL) at –20 ºC. The cold bath was then removed and the reaction mixture was stirred at room temperature until completion of the reaction. The reaction was then quenched with saturated NH_4Cl aqueous solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation to furnish the corresponding propargylic alcohol, which was used in the next step without further purification.

To a solution of the propargylic alcohol (0.50 mmol) in CH_2Cl_2 (0.7 M) at 0 ºC were added DMAP (0.025 mmol), triethylamine (1.00 mmol), Ac_2O (0.55 mmol) or BzCl (0.55 mmol), and the reaction mixture was stirred for 2 h at room temperature. After addition of water, the reaction was extracted with EtOAc. The combined organic layers were washed twice with saturated NaCl aqueous solution, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography over silica gel (cyclohexane/EtOAc, 10:1) to give the desired propargylic carboxylate.

1-(4-Bromophenyl)prop-2-yn-1-yl benzoate (1d)



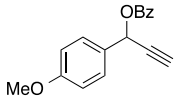
Transparent oil, yield 85% (over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.62-7.52 (m, 5H), 7.49-7.45 (m, 2H), 6.68 (d, J = 2.3 Hz, 1H), 2.73 (d, J = 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 135.8, 133.6, 132.1, 130.1, 129.5, 128.6, 123.5, 79.9, 76.1, 65.3, 29.9.

HRMS-APCI: *m/z* calcd for $C_{16}H_{12}BrO_2$ $[M+H]^+$: 315.0015, found: 315.0017.

1-(4-Methoxyphenyl)prop-2-yn-1-yl benzoate (1f)



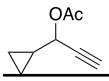
Yellow oil, yield 81% (over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.61-7.57 (m, 3H), 7.47-7.44 (m, 2H), 6.97-6.95 (m, 2H), 6.69 (d, J = 2.3 Hz, 1H), 3.85 (s, 3H), 2.71 (d, J = 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.2, 134.5, 133.3, 129.9, 129.3, 128.9, 128.4, 114.1, 80.5, 75.4, 65.6, 55.4.

HRMS-ESI: *m/z* calcd for $C_{17}H_{14}NaO_3$ $[M+Na]^+$: 289.0835, found: 289.0837.

1-Cyclopropylprop-2-yn-1-yl acetate (1i)



Transparent oil, yield 53% (over two steps, volatile).

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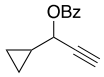
[1] T. Okada, K. Shishido, M. Yoshida, *Tetrahedron* **2007**, *63*, 6996-7002.
[2] N. Ghosh, S. Nayak, A. K. Sahoo, *J. Org. Chem.* **2011**, *76*, 500-511.
[3] R. J. Detz, M. M. E. Delville, H. Hiemstra, J. H. van Maarseveen, *Angew. Chem. Int. Ed.* **2008**, *47*, 3777-3780.
[4] A. Bartels, R. Mahrwald, K. Mueller, *Adv. Synth. Catal* **2004**, *346*, 483-485.
[5] M. Tofi, K. Koltsida, G. Vassilikogiannakis, *Org. Lett.* **2009**, *11*, 313-316.
[6] S. J. Pridmore, P. A. Slatford, J. E. Taylor, M. K. Whittlesey, J. M. J. Williams, *Tetrahedron* **2009**, *65*, 8981-8986.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (dd, J = 7.1, 2.2 Hz, 1H), 2.44 (d, J = 2.2 Hz, 1H), 2.13 (s, 3H), 1.36-1.27 (m, 1H), 0.69-0.48 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 79.3, 73.5, 67.2, 21.1, 14.3, 3.5, 2.2.

HRMS-ESI: *m/z* calcd for $C_8H_{10}NaO_2$ [*M*+Na]$^+$: 161.0573, found: 161.0565.

1-Cyclopropylprop-2-yn-1-yl benzoate (1j)



Transparent oil, 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.62-7.59 (m, 1H), 7.50-7.47 (m, 2H), 5.47 (dd, J = 7.1, 2.2 Hz, 1H), 2.49 (d, J = 2.2 Hz, 1H), 1.49-1.43 (m, 1H), 0.72-0.60 (m, 4H).

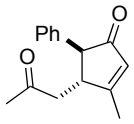
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 133.2, 129.9, 129.8, 128.4, 79.4, 73.7, 67.7, 14.5, 3.6, 2.3.

HRMS-ESI: *m/z* calcd for $C_{13}H_{12}NaO_2$ [*M*+Na]$^+$: 223.0730, found: 223.0723.

General procedure for the gold(I) catalyzed intermolecular cyclizations of propargyl esters with furans

A solution of alkyne (1.00 mmol) and furan (2.00 mmol) in dry CH_2Cl_2 (2.5 mL) was added to a solution of gold(I) catalyst **A** (3 mol%) in dry CH_2Cl_2 (2.5 mL). The reaction mixture was stirred at 23°C until TLC showed full conversion. Then, a drop of Et_3N was added, the solvent was evaporated under vacuum, and the crude product was purified by flash column chromatography using different gradients of cyclohexane and ethyl acetate to obtain the pure desired products.

3-Methyl-4-(2-oxopropyl)-5-phenylcyclopent-2-en-1-one (3a)



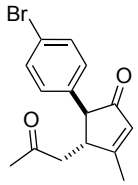
Orange oil, yield 57%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.26-7.21 (m, 1H), 7.11-7.08 (m, 2H), 6.05–6.02 (m, 1H), 3.33-3.29 (m, 1H), 3.22 (d, J = 3.0 Hz, 1H), 2.91 (dd, J = 17.2, 5.5 Hz, 1H), 2.62 (dd, J = 17.2, 7.6 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 206.0, 178.9, 138.8, 130.4, 128.8, 127.8, 127.1, 59.7, 49.1, 46.0, 30.2, 17.6.

HRMS-ESI: *m/z* calcd for $C_{15}H_{15}O_2$ [*M*-H]$^-$: 227.1077, found: 227.1080.

5-(4-Bromophenyl)-3-methyl-4-(2-oxopropyl)cyclopent-2-en-1-one (3b)



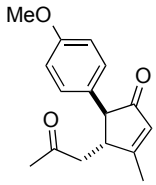
Orange oil, yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.00-6.97 (m, 2H), 6.05-6.02 (m, 1H), 3.27-3.23 (m, 1H), 3.17 (d, J = 3.0 Hz, 1H), 2.92 (dd, J = 17.2, 5.5 Hz, 1H), 2.60 (dd, J = 17.2, 7.6 Hz, 1H), 2.15 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 205.8, 179.0, 137.9, 131.9, 130.4, 129.6, 121.1, 59.1, 48.9, 46.0, 30.2, 17.6.

HRMS-ESI: *m/z* calcd for $C_{15}H_{15}O_2BrNa$ [*M*+Na]$^+$: 329.0148, found: 329.0145.

5-(4-Methoxyphenyl)-3-methyl-4-(2-oxopropyl)cyclopent-2-en-1-one (3c)



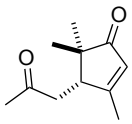
Orange oil, yield 36%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-7.00 (m, 2H), 6.85-6.83 (m, 2H), 6.03-6.01 (m, 1H), 3.77 (s, 3H), 3.28-3.25 (m, 1H), 3.16 (d, J = 3.0 Hz, 1H), 2.89 (dd, J = 17.2, 5.6 Hz, 1H), 2.60 (dd, J = 17.2, 7.7 Hz, 1H), 2.13 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 206.3, 178.8, 158.8, 131.0, 130.5, 129.0, 114.4, 59.1, 55.4, 49.3, 46.2, 30.3, 17.8.

HRMS-ESI: *m/z* calcd for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found: 259.1331.

3,5,5-Trimethyl-4-(2-oxopropyl)cyclopent-2-en-1-one (3d)



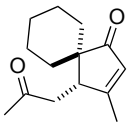
Orange oil, yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87-5.85 (m, 1H), 3.14-3.10 (m, 1H), 2.66-2.51 (m, 2H), 2.22 (s, 3H), 2.01 (s, 3H), 1.14 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 206.7, 177.1, 128.5, 50.7, 47.4, 42.8, 30.2, 26.2, 20.4, 17.6.

HRMS-ESI: *m/z* calcd for $C_{11}H_{16}O_2Na$ $[M+Na]^+$: 203.1043, found: 203.1041.

3-Methyl-4-(2-oxopropyl)spiro[4.5]dec-2-en-1-one (3e)



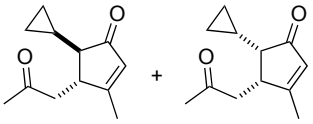
Orange oil, yield 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.78 (m, 1H), 3.25-3.22 (m, 1H), 2.75 (dd, J = 17.2, 5.5 Hz, 1H), 2.45 (dd, J = 17.2, 7.6 Hz, 1H), 2.25 (s, 3H), 1.99 (t, J = 1.1 Hz, 3H), 1.88-1.83 (m, 1H), 1.82-1.76 (m, 1H), 1.74-1.68 (m, 1H), 1.55-1.41 (m, 5H), 1.32-1.22 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 206.8, 177.4, 128.1, 51.3, 49.4, 43.4, 37.1, 30.5, 28.0, 25.3, 22.7, 22.1, 18.1.

HRMS-ESI: *m/z* calcd for $C_{14}H_{20}O_2Na$ $[M+Na]^+$: 243.1356, found: 243.1361.

5-Cyclopropyl-3-methyl-4-(2-oxopropyl)cyclopent-2-en-1-one (3f)



Yellow oil, yield 61%; an inseparable mixture of diastereoisomers in a 2.5:1 ratio was obtained starting from the propargyl ester **1i**, while 60% yield in a 5:1 ratio was obtained starting from the propargyl ester **1j**. All signals corresponding to the major and minor diasteroisomer could be identified separately.

Major isomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88-5.87 (m, 1H), 3.00-2.97 (m, 1H), 2.78 (dd, J = 17.2, 5.0 Hz, 1H), 2.44 (dd, J = 17.3, 8.3 Hz, 1H), 2.19 (s, 3H), 2.04 (s, 3H), 1.64 (dd, J = 7.9, 2.1 Hz, 1H), 0.91-0.86 (m, 1H), 0.55-0.49 (m, 2H), 0.46-0.41 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 206.4, 178.3, 130.5, 55.9, 46.6, 46.3, 30.4, 17.5, 13.0, 2.5, 1.8.

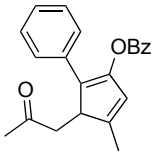
Minor isomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93-5.92 (m, 1H), 3.56-3.51 (m, 1H), 2.93 (dd, J = 18.1, 9.1 Hz, 1H), 2.62 (dd, J = 18.0, 4.5 Hz, 1H), 2.25 (s, 3H), 2.04 (s, 3H), 1.83 (dd, J = 9.7, 6.6 Hz, 1H), 0.66-0.61 (m, 1H), 0.40-0.37 (m, 1H), 0.29-0.24 (m, 2H), 0.14-0.09 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 206.6, 178.2, 130.4, 53.9, 43.1, 42.5, 30.4, 17.6, 10.1, 4.0, 3.4.

HRMS-ESI: *m/z* calcd for $C_{12}H_{16}NaO_2$ $[M+Na]^+$: 215.1043, found: 215.1042.

4-Methyl-3-(2-oxopropyl)-2-phenylcyclopenta-1,4-dien-1-yl benzoate (4a)



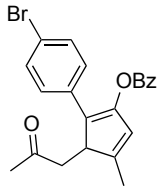
Yellow oil, yield 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.65-7.61 (m, 1H), 7.52-7.48 (m, 2H), 7.39-7.30 (m, 4H), 7.21-7.16 (m, 1H), 6.30-6.27 (m, 1H), 4.06 (ddd, J = 8.5, 3.5, 1.0 Hz, 1H), 2.74 (dd, J = 17.3, 3.5 Hz, 1H), 2.56 (dd, J = 17.3, 8.4 Hz, 1H), 2.09 (s, 3H), 2.00 (d, J = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 164.3, 147.9, 146.5, 133.7, 132.9, 130.2, 129.2, 128.7, 128.6, 127.4, 126.4, 125.2, 46.6, 43.3, 30.5, 15.6.

HRMS-ESI: *m/z* calcd for $C_{22}H_{20}O_3Na$ $[M+Na]^+$: 355.1305, found: 355.1303.

2-(4-Bromophenyl)-4-methyl-3-(2-oxopropyl)cyclopenta-1,4-dien-1-yl benzoate (4b)



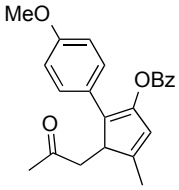
Yellow oil, yield 44%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.13 (m, 2H), 7.66-7.63 (m, 1H), 7.53-7.49 (m, 2H), 7.45-7.43 (m, 2H), 7.24-7.22 (m, 2H), 6.29-6.27 (m, 1H), 4.02 (ddd, *J* = 8.5, 3.6, 1.0 Hz, 1H), 2.69 (dd, *J* = 17.5, 3.4 Hz, 1H), 2.55 (dd, *J* = 17.5, 8.3 Hz, 1H), 2.11 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 164.2, 148.5, 147.2, 134.0, 132.0, 131.7, 130.8, 130.3, 129.0, 128.9, 127.6, 125.3, 120.4, 46.6, 43.2, 30.7, 15.7.

HRMS-ESI: *m/z* calcd for $C_{22}H_{19}O_3BrNa$ $[M+Na]^+$: 433.0410, found: 433.0415.

2-(4-Methoxyphenyl)-4-methyl-3-(2-oxopropyl)cyclopenta-1,4-dien-1-yl benzoate (4c)



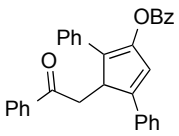
Yellow oil, yield 48%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 2H), 7.65-7.61 (m, 1H), 7.52-7.48 (m, 2H), 7.31-7.29 (m, 2H), 6.88-6.86 (m, 2H), 6.25 (m, 1H), 3.99 (ddd, *J* = 8.4, 3.6, 1.0 Hz, 1H), 3.79 (s, 3H), 2.71 (dd, *J* = 17.3, 3.6 Hz, 1H), 2.55 (dd, *J* = 17.3, 8.4 Hz, 1H), 2.08 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 164.4, 158.2, 146.8, 145.2, 133.6, 130.2, 129.3, 128.6, 128.4, 125.7, 125.1, 114.2, 55.2, 46.7, 43.5, 30.5, 15.6.

HRMS-ESI: *m/z* calcd for $C_{23}H_{22}O_4Na$ $[M+Na]^+$: 385.1410, found: 385.1422.

3-(2-Oxo-2-phenylethyl)-2,4-diphenylcyclopenta-1,4-dien-1-yl benzoate (4d)



Yellow solid, yield 75%.

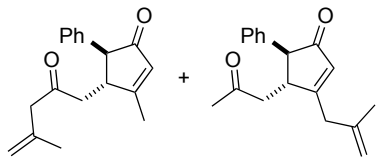
mp 149-153 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.22 (m, 2H), 7.72-7.70 (m, 2H), 7.69-7.65 (m, 1H), 7.56-7.50 (m, 6H), 7.47-7.44 (m, 1H), 7.34-7.28 (m, 6H), 7.24-7.22 (m, 1H), 7.17-7.13 (m, 1H), 6.98 (s, 1H), 5.15 (t, *J* = 4.9 Hz, 1H), 3.25 (d, *J* = 4.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 164.3, 150.3, 146.7, 137.1, 134.4, 133.8, 132.9, 132.8, 132.4, 130.3, 129.2, 128.8, 128.7, 128.6, 128.3, 128.0, 127.9, 127.5, 126.8, 126.5, 125.1, 43.6, 39.0.

HRMS-ESI: *m/z* calcd for $C_{32}H_{24}O_3Na$ $[M+Na]^+$: 479.1618, found: 479.1627.

3-Methyl-4-(4-methyl-2-oxopent-4-en-1-yl)-5-phenylcyclopent-2-en-1-one (3i/3i'')



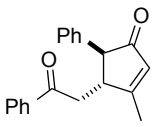
Orange oil, 56%; an inseparable mixture of diastereoisomers in a 1.6:1 ratio was obtained. The following characterization data is reported for the mixture of isomers with the relative integration for each signal.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 3.2H), 7.25-7.22 (m, 1.6H), 7.11-7.06 (m, 3.2H), 6.09-6.06 (m, 0.6H), 6.05-6.02 (m, 1H), 4.98-4.95 (m, 1.6H), 4.86 (s, 0.6H), 4.81 (s, 1H), 3.35-3.29 (m, 1.6H), 3.25 (d, *J* = 3.0 Hz, 0.6H), 3.21 (d, *J* = 3.0 Hz, 1H), 3.14-3.05 (m, 3.2H), 2.96-2.91 (m, 1.6H), 2.67-2.57 (m, 1.6H), 2.12 (s, 3H), 2.11 (s, 1.8H), 1.78 (s, 1.8H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 207.0, 206.0, 205.9, 180.1, 179.0, 140.6, 138.9, 138.8, 138.5, 130.7, 130.4, 128.9, 128.8, 127.8, 127.7, 127.1, 127.0, 115.6, 114.7, 59.8, 59.7, 52.4, 49.1, 48.1, 46.1, 44.0, 40.0, 30.1, 22.6, 22.3, 17.6.

HRMS-ESI: *m/z* calcd for $C_{18}H_{20}O_2Na$ $[M+Na]^+$: 291.1356, found: 291.1356.

3-Methyl-4-(2-oxo-2-phenylethyl)-5-phenylcyclopent-2-en-1-one (3j)



Orange oil, yield 35%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.61-7.56 (m, 1H), 7.51-7.44 (m, 2H), 7.35-7.20 (m, 3H), 7.12-7.09 (m, 2H), 6.10-6.07 (m, 1H), 3.55-3.42 (m, 2H), 3.34 (d, J = 2.7 Hz, 1H), 2.60 (dd, J = 16.5, 6.5 Hz, 1H), 2.18 (s, 3H).

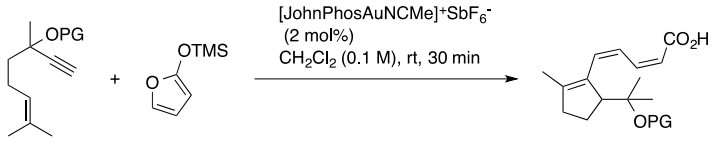
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 197.8, 179.4, 139.0, 136.7, 133.7, 130.6, 128.9, 128.2, 128.0, 127.2, 60.1, 49.6, 40.9, 18.0.

HRMS-ESI: *m/z* calcd for $C_{30}H_{18}O_2Na$ [*M*+Na]$^+$: 313.1199, found: 313.1187.

1,5-Migration and trapping of Au(I)-carbene with furans

1,6-Enynes bearing -OMe,[7] -OAc,[8] -OPNB[7] were identified by comparison of their ^{1}H NMR spectra with the previously reported data.

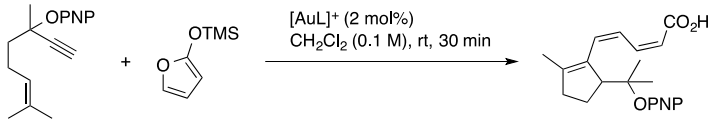
Screening of Migrating groups



Entry	OPG	Yield (%)[a]
1	OMe	**12a** (36)
2	OAc	**12a'** (19)
3	OPNB	**12a''** (35)
4	OPNP	**12d** (60)

[a] Isolated yield.

Screening of Au(I) catalysts

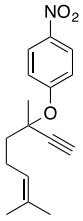


Entry	[AuL]$^+$	Yield 12d (%)
1	**A**	33[a]
2	**B**	64[a]
3	**C**	25[a]
3	**D**	28[a]
1	**E**	60
2	**F**	82

[a] Determined by ^{1}H NMR (diphenylmethane as internal standard).

[7] E. Jiménez-Núñez, M. Raducan, T. Lauterbach, K. Molawi, C. R. Solorio and A. M. Echavarren, *Angew. Chem. Int. Ed.* **2009**, *48*, 6152-6155.
[8] M. J. Ardolino, J. P. Morken, *J. Am. Chem. Soc.* **2012**, 134, 8770-8773.

1-((3,7-Dimethyloct-6-en-1-yn-3-yl)oxy)-4-nitrobenzene



To a solution of propargylic alcohol (1.0 g, 6.57 mmol) in dry acetonitrile (7 mL) were added DBU (1.47 mL, 9.85 mmol) and trifluoroacetic anhydride (1.42 mL, 10.18 mmol) at −15ºC. After stirring at this temperature for 2h, a solution of DBU (1.47 mL, 9.85 mmol), $CuCl_2.2H_2O$ (11.0 mg, 0.066 mmol) and *p*-nitrophenol (1.01 g, 7.23 mmol) was added dropwise. After stirring for 30 min at room temperature, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The crude product was purified by flash chromatography over silica gel (cyclohexane/EtOAc, 33:1 to 20:1) to give the protected alcohol as a yellowish oil (0.99 g, 3.62 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.15 (m, 2H), 7.32-7.28 (m, 2H), 5.14 (ddq, *J* = 8.6, 5.8, 1.5 Hz, 1H), 2.71 (s, 1H), 2.26 (m, 2H), 2.00 (ddd, *J* = 13.6, 11.3, 5.2 Hz, 1H), 1.90 (ddd, *J* = 13.5, 11.5, 5.2 Hz, 1H), 1.70 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H).

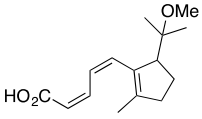
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 142.2, 132.8, 125.4, 123.1, 119.2, 83.7, 76.8, 76.1, 42.6, 26.8, 25.8, 23.1, 17.8.

HRMS-ESI calcd for $C_{16}H_{20}NO_3$ [*M*+H]$^+$: 274.1443; found: 274.1432.

General procedure

A solution of the enyne (0.10 mmol) in anhydrous CH_2Cl_2 (0.33 mL) was added dropwise over 30 min to a solution of gold catalyst (0.002 mmol) and furan (0.20 mmol) in anhydrous CH_2Cl_2 (0.66 mL) at room temperature. Then, a drop of Et_3N was added, the solvent was evaporated under vacuum, and the crude product was purified by flash column chromatography using different gradients of cyclohexane and ethyl acetate to obtain the pure desired products.

(2*Z*,4*Z*)-5-(5-(2-Methoxypropan-2-yl)-2-methylcyclopent-1-en-1-yl)penta-2,4-dienoic acid (12a)



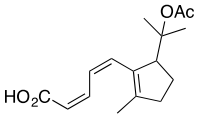
Yellow oil, yield 36% (gold catalyst **E**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 11.8 Hz, 1H), 6.71 (td, *J* = 11.6, 1.0 Hz, 1H), 6.35 (d, *J* = 11.8 Hz, 1H), 5.66 (dt, *J* = 11.5, 1.3 Hz, 1H), 3.17 (s, 3H), 3.04-3.00 (m, 1H), 2.49-2.41 (m, 1H), 2.33-2.24 (m, 1H), 2.02-1.93 (m, 1H), 1.74-1.67 (m, 1H), 1.58 (s, 3H), 1.05 (s, 3H), 1.04 (s, 3H). The proton of the carboxylic acid was not observed.

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 144.7, 143.1, 139.0, 134.1, 124.0, 115.6, 77.87, 57.8, 48.9, 38.1, 25.2, 23.0, 22.0, 16.5.

HRMS-ESI: *m*/*z*: calcd for $C_{15}H_{21}O_3$ [*M*-H]$^-$: 249.1489, found: 249.1496.

(2*Z*,4*Z*)-5-(5-(2-Acetoxypropan-2-yl)-2-methylcyclopent-1-en-1-yl)penta-2,4-dienoic acid (12a')



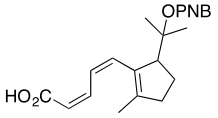
Yellow oil, yield 19% (gold catalyst **E**). (Contaminated by some impurities that could not be separated).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 11.3 Hz, 1H), 6.73 (td, *J* = 11.6, 1.0 Hz, 1H), 6.32-6.29 (m, 1H), 5.71 (dt, *J* = 11.5, 1.3 Hz, 1H), 3.51-3.48 (m, 1H), 2.52-2.46 (m, 1H), 2.37-2.29 (m, 1H), 2.06-2.00 (m, 2H), 1.96 (s, 3H), 1.62 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H). The proton of the carboxylic acid was not observed.

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (2C), 144.3, 143.8, 138.2, 133.3, 124.2, 115.8, 85.4, 58.0, 37.9, 25.1, 24.4, 22.8, 22.8, 16.4.

HRMS-ESI: *m*/*z*: calcd for $C_{16}H_{21}O_4$ [*M*-H]$^-$: 277.1442, found: 277.1445.

(2*Z*,4*Z*)-5-(2-Methyl-5-(2-((4-nitrobenzyl)oxy)propan-2-yl)cyclopent-1-en-1-yl)penta-2,4-dienoic acid (12a'')



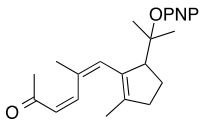
Yellow oil, yield 35% (gold catalyst **E**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.17 (m, 2H), 7.50-7.48 (m, 2H), 7.26 (t, J = 11.5 Hz, 1H), 6.73 (td, J = 11.6, 1.1 Hz, 1H), 6.37-6.31 (m, 1H), 5.67 (dt, J = 11.5, 1.3 Hz, 1H), 4.55-4.49 (m, 2H), 3.13-3.10 (m, 1H), 2.53-2.46 (m, 1H), 2.35-2.28 (m, 1H), 2.06-2.01 (m, 1H), 1.78-1.72 (m, 1H), 1.60 (s, 3H), 1.18 (s, 3H), 1.16 (s, 3H). The proton of the carboxylic acid was not observed.

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 147.6, 147.2, 144.5, 143.5, 139.1, 133.8, 127.7, 124.0, 123.6, 115.9, 79.0, 62.7, 58.7, 38.0, 25.4, 23.6, 22.2, 16.5.

HRMS-ESI: *m*/*z*: calcd for $C_{21}H_{24}NO_5$ [*M*-H]$^-$: 370.1655, found: 370.1660.

(3*Z*,5*Z*)-5-Methyl-6-(2-methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)hexa-3,5-dien-2-one (12b)



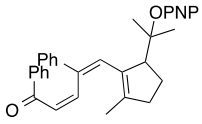
Yellow oil, yield 32% (gold catalyst **B**).

^{1}H NMR (500 MHz, $CDCl_3$ δ 8.15-8.13 (m, 2H), 7.01-6.99 (m, 2H), 6.25 (dd, J = 12.5, 1.3 Hz, 1H), 6.07 (brs, 1H), 5.99 (dd, J = 12.5, 1.1 Hz, 1H), 3.27-3.24 (m, 1H), 2.48-2.44 (m, 1H), 2.33-2.28 (m, 1H), 2.25 (s, 3H), 2.09-2.01 (m, 1H), 1.91 (s, 3H), 1.79-1.74 (m, 1H), 1.53 (s, 3H), 1.36 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 162.0, 145.3, 142.4, 140.6, 134.3, 133.9, 133.2, 126.7, 125.4, 121.6, 85.9, 59.4, 37.9, 31.1, 25.7, 25.1, 23.5, 22.0, 16.9.

HRMS-ESI: *m*/*z*: calcd for $C_{22}H_{27}NNaO_4$ [*M*+Na]$^+$: 392.1837, found: 392.1832.

(2*Z*,4*E*)-5-(2-Methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)-1,4-diphenylpenta-2,4-dien-1-one (12c)



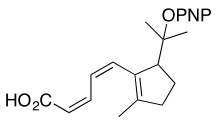
Yellow oil, yield 42% (gold catalyst **E**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.99 (m, 2H), 7.59-7.57 (m, 2H), 7.43-7.42 (m, 1H), 7.30-7.27 (m, 2H), 7.09-7.05 (m, 5H), 6.85-6.83 (m, 2H), 6.73 (dd, J = 12.3, 1.3 Hz, 1H), 6.61 (dd, J = 12.3, 1.1 Hz, 1H), 6.26 (brs, 1H), 3.36-3.33 (m, 1H), 2.58-2.52 (m, 1H), 2.39-2.32 (m, 1H) 2.13-2.07 (m, 1H), 1.84-1.79 (m, 1H), 1,74 (s, 3H), 1.41 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 161.8, 145.3, 142.4, 141.9, 139.8, 138.4, 138.1, 134.3, 132.5, 128.3, 128.3, 128.1, 127.6, 127.0, 126.8, 125.2, 121.7, 121.1, 85.9, 59.6, 38.0, 25.8, 25.5, 23.2, 17.1.

HRMS-ESI: *m*/*z*: calcd for $C_{32}H_{31}NNaO_4$ [*M*+Na]$^+$: 516.2153, found: 516.2145.

(2*Z*,4*Z*)-5-(2-methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)penta-2,4-dienoic acid (12d)



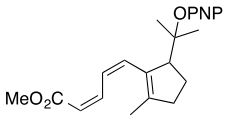
Yellow oil, yield 82% (gold catalyst **F**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.16 (m, 2H), 7.33 (td, J = 11.4, 1.1 Hz, 1H), 7.04-7.02 (m, 2H), 6.76 (td, J = 11.6, 1.1 Hz, 1H), 6.42-6.40 (m, 1H), 5.72 (dt, J = 11.5, 1.3 Hz, 1H), 3.35-3.32 (m, 1H), 2.57-2.51 (m, 1H), 2.41-2.34 (m, 1H), 2.16-2.10 (m, 1H), 1.83-1.77 (m, 1H), 1.66 (s, 3H), 1.38 (s, 3H), 1.28 (s, 3H). The proton of the carboxylic acid was not observed.

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 161.6, 144.1, 142.4, 138.3, 133.1, 125.2, 124.1, 121.6, 115.9, 85.5, 59.7, 37.7, 26.9, 25.4, 24.9, 23.0, 16.4.

HRMS-ESI: *m*/*z*: calcd for $C_{20}H_{22}NO_5$ [*M*-H]$^-$: 356.1516, found: 356.1503.

Methyl (2*Z*,4*Z*)-5-(2-methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)penta-2,4-dienoate (12e)



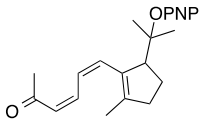
Yellow oil, yield 57% (gold catalyst **E**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.32 (t, J = 11.1 Hz, 1H), 7.01-6.99 (m, 2H), 6.62 (t, J = 12.0 Hz, 1H), 6.34-6.31 (m, 1H), 5.67 (dt, J = 11.4, 1.4 Hz, 1H), 3.73 (s, 3H), 3.31-3.28 (m, 1H), 2.54-2.47 (m, 1H), 2.39-2.29 (m, 1H), 2.13-2.04 (m, 1H), 1.81-1.72 (m, 1H), 1.61 (s, 3H), 1.35 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.8, 143.9, 142.5, 142.1, 137.5, 133.2, 125.3, 124.3, 121.7, 116.8, 85.7, 59.8, 51.3, 37.8, 25.5, 25.0, 23.2, 16.5.

HRMS-ESI: *m*/*z*: calcd for $C_{21}H_{25}NNaO_5$ [*M*+Na]$^+$: 394.1644, found: 394.1625.

(3*Z*,5*Z*)-6-(2-Methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)hexa-3,5-dien-2-one (12f)



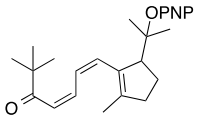
Yellow oil, yield 56% (gold catalyst **F**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.32 (t, J = 11.8 Hz, 1H), 7.01-6.99 (m, 2H), 6.46 (t, J = 11.5 Hz, 1H), 6.36-6.34 (m, 1H), 6.01 (dt, J = 11.4, 1.4 Hz, 1H), 3.31-3.28 (m, 1H), 2.55-2.48 (m, 1H), 2.38-2.31 (m, 1H), 2.24 (s, 3H), 2.12-2.05 (m, 1H), 1.81-1.76 (m, 1H), 1.62 (s, 3H), 1.35 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 161.8, 144.2, 139.7, 138.5, 133.3, 125.4, 125.3, 125.1, 124.2, 121.7, 85.7, 59.8, 37.9, 31.9, 25.5, 25.0, 23.3, 16.5.

HRMS-ESI: *m*/*z*: calcd for $C_{21}H_{25}NNaO_4$ [*M*+Na]$^+$: 378.1688, found: 378.1676.

(4*Z*,6*Z*)-2,2-Dimethyl-7-(2-methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)hepta 4,6-dien-3-one (12g)



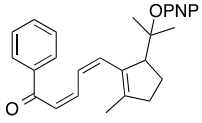
Yellow oil, yield 62% (gold catalyst **E**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.30 (t, J = 11.6 Hz, 1H), 7.01-6.99 (m, 2H), 6.52 (t, J = 11.5 Hz, 1H), 6.31-6.27 (m, 2H), 3.30-3.27 (m, 1H), 2.51-2.47 (m, 1H), 2.36-2.31 (m, 1H), 2.11-2.04 (m, 1H), 1.82-1.76 (m, 1H), 1.61 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.5, 161.7, 143.7, 142.3, 140.3, 137.5, 133.2, 125.3, 125.2, 121.5, 120.0, 85.6, 59.6, 43.8, 37.7, 26.5, 25.4, 24.8, 23.3, 16.4.

HRMS-ESI: *m*/*z*: calcd for $C_{24}H_{31}NNaO_4$ [*M*+Na]$^+$: 420.2151, found: 420.2145.

(2*Z*,4*Z*)-5-(2-Methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)-1-phenylpenta-2,4-dien-1-one (12h)



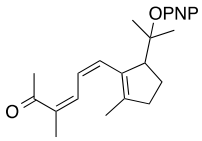
Yellow oil, yield 59% (gold catalyst **E**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.32 (m, 2H), 7.98-7.95 (m, 2H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.42-7.35 (m, 1H), 7.05-7.02 (m, 2H), 6.76-6.74 (m, 2H), 6.43-6.39 (m, 1H), 3.37-3.31 (m, 1H), 2.60-2.50 (m, 1H), 2.44-2.31 (m, 1H), 2.17-2.06 (m, 1H), 1.86-1.76 (m, 1H), 1.69 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 161.8, 144.2, 141.6, 139.1, 138.5, 133.5, 132.7, 128.7, 128.4, 125.5, 125.4, 121.7, 121.3, 85.7, 59.9, 37.9, 27.1, 25.6, 25.0, 23.3, 16.6.

HRMS-ESI: *m*/*z*: calcd for $C_{26}H_{27}NNaO_4$ [*M*+Na]$^+$: 440.1843, found: 440.1832.

(3*Z*,5*Z*)-3-methyl-6-(2-methyl-5-(2-(4-nitrophenoxy)propan-2-yl)cyclopent-1-en-1-yl)hexa-3,5-dien-2-one (12i)



Yellow oil, 88% (Gold(I) catalyst **E**).

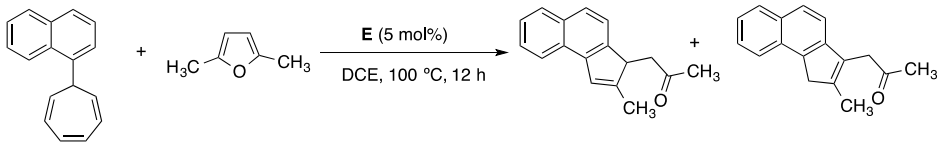
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.04-7.03 (m, 2H), 6.78 (t, J = 11.4 Hz, 1H), 6.29 (dt, J = 11.6, 1.4 Hz, 1H), 6.14 (d, J = 11.2 Hz, 1H), 3.32-3.29 (m, 1H), 2.57-2.51 (m, 1H), 2.41-2.36 (m, 1H), 2.33 (s, 3H), 2.13-2.07 (m, 1H), 2.04 (s, 3H), 1.86-1.81 (m, 1H), 1.65 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.0, 161.8, 143.0, 142.3, 134.5, 134.3, 134.0, 133.2, 125.2, 125.1, 121.5, 85.7, 59.6, 37.6, 30.2, 25.4, 24.8, 23.5, 21.6, 16.3.

HRMS-ESI: *m*/*z*: calcd for $C_{22}H_{27}NNaO_4$ [*M*+Na]$^+$: 392.1832, found: 392.1832.

Reaction of Cycloheptatrienes with Furans

1-(2-Methyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)propan-2-one (19a)



A solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene[9] **17a** (0.1 mmol, 22 mg), 2,5-dimethylfuran **2a** (0.5 mmol, 48 mg) and gold catalyst **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 100 ºC in a sealed tube overnight (12 h). The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compound **19a** together with a regioisomer (13 mg, 59%, ratio 3:1) as a yellow oil. The two isomers can be separated partially by careful preparative TLC.

Major isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 7.56 - 7.42 (m, 3H), 7.08 (d, J = 0.7 Hz, 1H), 4.05 - 3.93 (m, 1H), 2.95 (dd, J = 17.2, 5.4 Hz, 1H), 2.68 (dd, J = 17.2, 7.9 Hz, 1H), 2.19 (s, 3H), 2.17 (d, J = 1.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 149.1, 144.1, 140.5, 132.9, 128.3, 127.1, 125.4, 125.0, 124.6, 124.1, 123.9, 121.6, 48.5, 44.2, 30.7, 15.5.

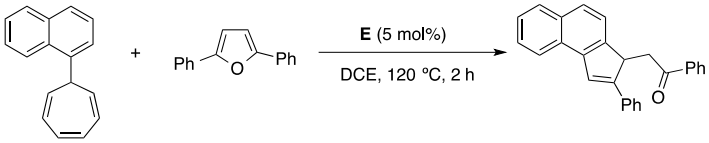
Minor isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.0 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.49 (ddd, J = 8.3, 6.8, 1.2 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.39 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 3.71 (s, 2H), 3.70 (s, 2H), 2.24 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 143.1, 141.4, 138.3, 131.3, 130.8, 129.8, 128.9, 127.2, 126.2, 124.3, 123.3, 118.1, 41.7, 41.6, 29.0, 14.3.

HRMS-ESI: calculated for $C_{17}H_{16}NaO$ [*M*+Na]$^+$: 259.1093; found: 259.1096.

1-Phenyl-2-(2-phenyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)ethan-1-one (19b)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene **17a** (0.1 mmol, 22 mg), 2,5-diphenylfuran **2b** (0.2 mmol, 44 mg) and gold complex **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in

[9] Arylcycloheptatrienes were prepared according to the procedure reported in the following references: (a) Solorio-Alvarado, C. R.; Wang, Y.; Echavarren, A. M. *J. Am. Chem. Soc.* **2011**, *133*, 11952–11955. (b) Wang, Y.; McGonigal, P. R.; Herlé, B.; Besora, M.; Echavarren, A. E. *J. Am. Chem. Soc.* **2014**, *136*, 801–809.

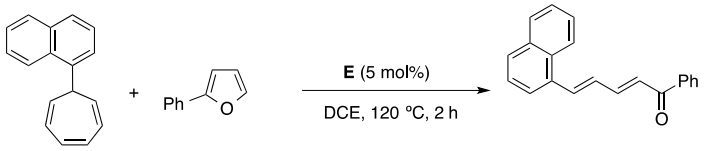
a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compound **19b** (31 mg, 88%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.90 (dd, *J* = 8.3 Hz, 1H), 7.80 (s, 1H), 7.69-7.64 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.58-7.55 (m, 2H), 7.51-7.42 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.09-4.95 (m, 1H), 3.50 (dd, *J* = 18.1, 2.5 Hz, 1H), 3.10 (dd, *J* = 18.1, 10.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 151.1, 145.9, 139.8, 136.9, 134.9, 133.3, 133.0, 129.0, 128.6, 128.5, 128.2, 127.7, 127.6, 126.9, 125.8, 125.4, 125.3, 124.4, 123.8, 122.4, 45.2, 40.9.

HRMS-ESI: calculated for $C_{27}H_{20}NaO$ $[M+Na]^+$: 383.1406; found: 383.1412.

(2*E*,4*E*)-5-(Naphthalen-1-yl)-1-phenylpenta-2,4-dien-1-one (20a)



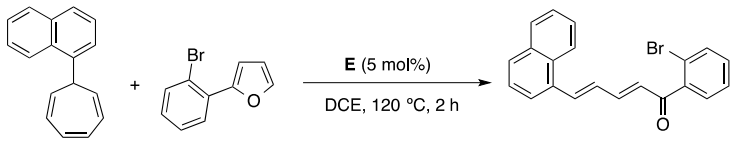
The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene **17a** (0.1 mmol, 22 mg), 2-phenylfuran **2i** (0.2 mmol, 29 mg) and gold catalyst **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compounds **20a** (20 mg, 51%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.07-8.02 (m, 2H), 7.92-7.74 (m, 5H), 7.64-7.50 (m, 6H), 7.21-7.09 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 145.0, 138.6, 138.2, 133.8, 133.3, 132.7, 131.2, 129.6, 129.5, 128.8, 128.6, 128.4, 126.7, 126.1, 125.7, 125.5, 124.2, 123.3.

HRMS-APCI: calculated for $C_{21}H_{17}O$ $[M+H]^+$: 285.1274; found: 285.1272.

(2*E*,4*E*)-1-(2-Bromophenyl)-5-(naphthalen-1-yl)penta-2,4-dien-1-one (20b)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene **17a** (0.1 mmol, 22 mg), 2-(2-bromophenyl)furan[10] **2j** (0.2 mmol, 45 mg) and gold catalyst **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compounds **20b** (27 mg, 75%) as a yellow oil.

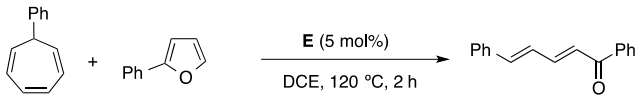
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.92-7.86 (m, 2H), 7.83-7.74 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60-7.48 (m, 3H), 7.47-7.44 (m, 2H), 7.40-7.32 (m, 2H), 7.10 (ddd, *J* = 15.2, 11.1, 0.7 Hz, 1H), 6.71 (d, *J* = 15.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 146.9, 141.2, 139.1, 133.8, 133.4, 133.0, 131.3, 131.1, 129.9, 129.7, 129.2, 129.1, 128.8, 127.4, 126.7, 126.2, 125.6, 124.4, 123.2, 119.5.

HRMS-APCI: calculated for $C_{21}H_{16}OBr$ $[M+H]^+$: 363.0379; found: 363.0373.

[10] Compound prepared according to the procedure reported in the following reference: Becht, J. A.; Ngouela, S.; Wagner, A.; Mioskowski, C. *Tetrahedron* **2004**, *60*, 6853–6857.

(2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-one (20c)



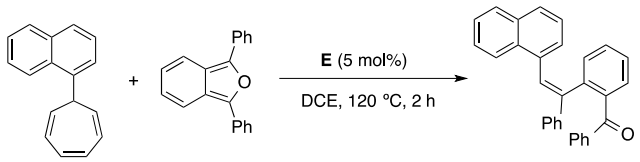
The solution of 7-phenylcyclohepta-1,3,5-triene **17b** (0.15 mmol, 25 mg), 2-phenylfuran[11] **2i** (0.3 mmol, 43 mg) and gold catalyst **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compounds **20c** (18 mg, 51%) as a yellow oil.

The spectroscopic data are in agreement with those reported in the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.69-7.58 (m, 2H), 7.55-7.48 (m, 4H), 7.43-7.34 (m, 3H), 7.12 (d, *J* = 15.0 Hz, 1H), 7.08-6.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 144.9, 141.9, 138.2, 136.1, 132.7, 129.2, 128.9, 128.6, 128.4, 127.3, 127.0, 125.5.

(*Z*)-(2-(2-(Naphthalen-1-yl)-1-phenylvinyl)phenyl)(phenyl)methanone (21)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene **17a** (0.3 mmol, 65 mg), 1,3-diphenylisobenzofuran **2k** (0.1 mmol, 27 mg) and gold catalyst **E** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, and the solvent removed in *vacuo*. The crude product was purified by preparative TLC to give compound **21** (23 mg, 56%) as a yellow solid.

m.p.: 141-144 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 1H), 7.67-7.62 (m, 1H), 7.59-7.56 (m, 1H), 7.47-7.44 (m, 3H), 7.39-7.15 (m, 14H), 7.04 (dd, *J* = 8.2, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.4, 142.9, 141.1, 139.5, 136.1, 134.9, 133.3, 132.5, 132.4, 132.1, 130.1, 129.7, 129.1, 128.1, 128.1, 128.1, 127.8, 127.5, 127.4, 127.3, 126.8, 126.2, 125.8, 125.5, 125.1, 124.4.

HRMS-APCI: calculated for $C_{31}H_{23}O$ [*M*+H]$^+$: 411.1743; found: 411.1741.

X Ray structures

3-(2-Oxo-2-phenylethyl)-2,4-diphenylcyclopenta-1,4-dien-1-yl benzoate (4d)

[11] Prepared according to the reference: Kuhl, N.; Hopkinson, M. N.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 8230–8234.
[12] Pinto, D. C. G. A.; Silva, A. M. S.; Lévai, A.; Cavaleiro, J. A. S.; Patonay, T. and Elguero, J. *Eur. J. Org. Chem.,* **2000**, 2593–2599.

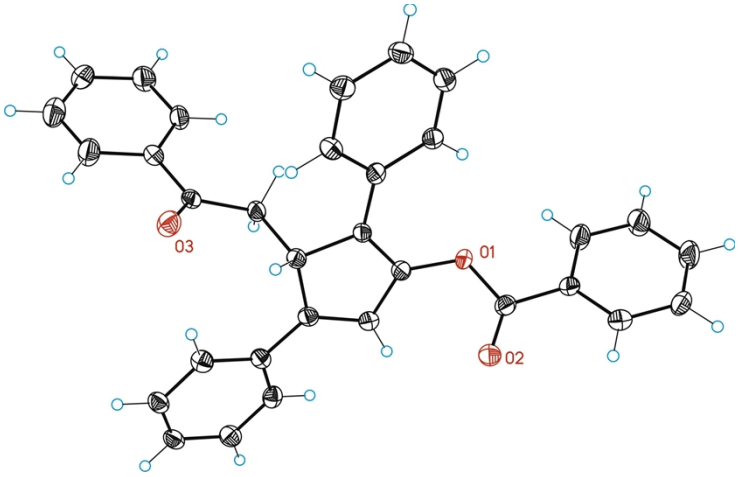


Table 1. Crystal data and structure refinement for **4d** (CCDC 1000511)

Empirical formula	C32 H24 O3
Formula weight	456.51
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 5.5702(14) Åa= 90.00 °.
	b = 24.243(6) Å b = 93.744(10) °.
	c = 17.573(5) Å g = 90.00 °.
Volume	2368.1(11) Å3
Z	4
Density (calculated)	1.280 Mg/m3
Absorption coefficient	0.081 mm-1
F(000)	960
Crystal size	0.40 x 0.04 x 0.02 mm3
Theta range for data collection	2.04 to 28.11 °.
Index ranges	-6 <=h<=7 ,-31 <=k<=31 ,-23 <=l<=23
Reflections collected	15211
Independent reflections	5364 [R(int) = 0.0633]
Completeness to theta =28.11 °	99.6%
Absorption correction	Empirical
Max. and min. transmission	0.9984 and 0.9683
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	5364 / 2 / 318
Goodness-of-fit on F2	0.986

Final R indices [I>2sigma(I)] R1 = 0.0547 , wR2 = 0.1105

R indices (all data) R1 = 0.1013 , wR2 = 0.1281

Flack parameter x =0.8(14)

Largest diff. peak and hole 0.203 and -0.262 e.Å-3

(*Z*)-(2-(2-(naphthalen-1-yl)-1-phenylvinyl)phenyl)(phenyl)methanone (21)

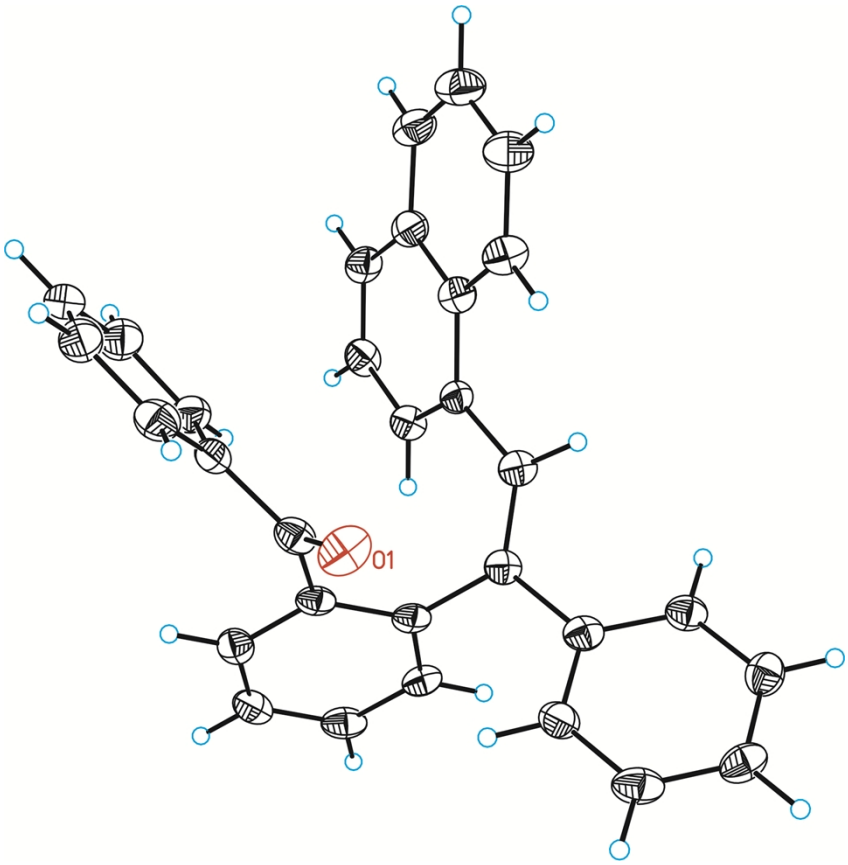
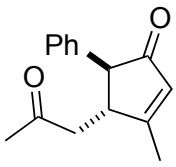


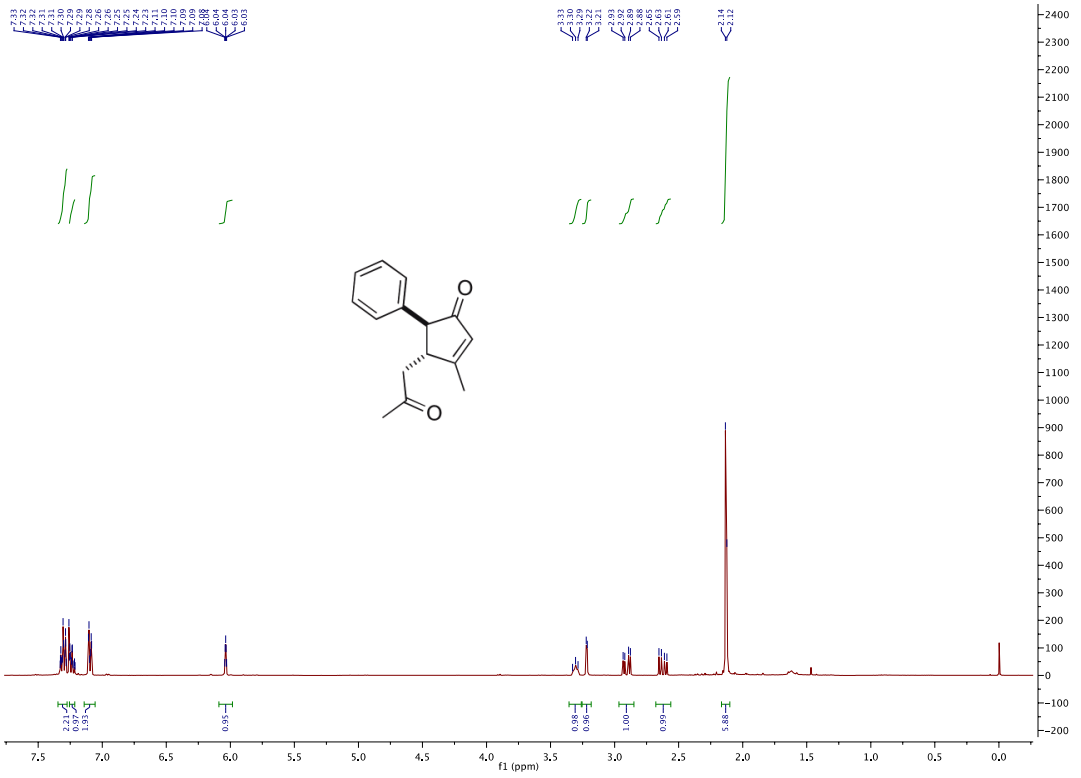
Table 1. Crystal data and structure refinement for **21** (CCDC 1000512)

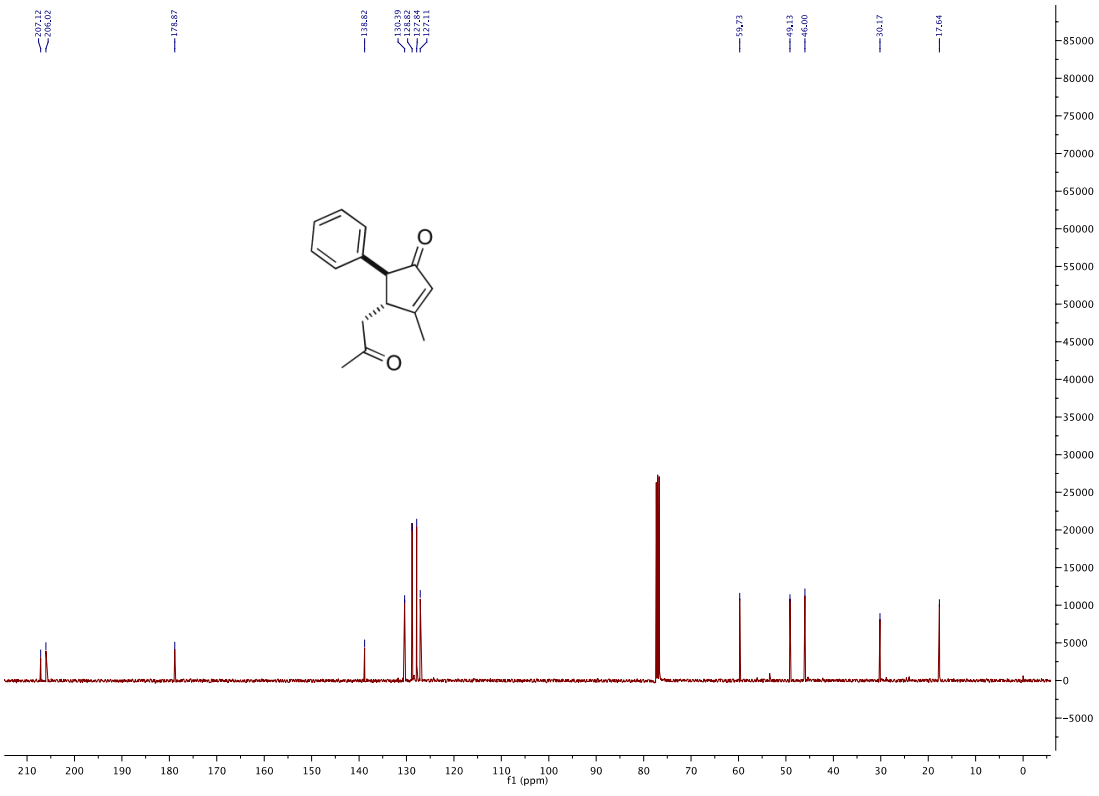
Empirical formula	C31 H22 O	
Formula weight	410.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.2685(19) Å	a= 90.00 °.
	b = 9.1961(15) Å	b = 92.368(6) °.
	c = 20.509(4) Å	g = 90.00 °.
Volume	2123.5(6) Å^3	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	

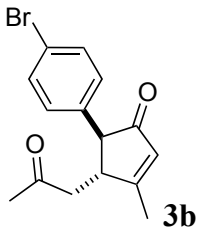
F(000)	864
Crystal size	0.51 x 0.15 x 0.10 mm^3
Theta range for data collection	1.81 to 25.09 °.
Index ranges	-13 <=h<=13 ,-10 <=k<=10 ,-24 <=l<=24
Reflections collected	17032
Independent reflections	3760 [R(int) = 0.0843]
Completeness to theta =25.09 °	99.7%
Absorption correction	Empirical
Max. and min. transmission	0.9925 and 0.9623
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3760 / 0 / 289
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0614 , wR2 = 0.1395
R indices (all data)	R1 = 0.1103 , wR2 = 0.1581
Largest diff. peak and hole	0.330 and -0.234 e.$Å^{-3}$



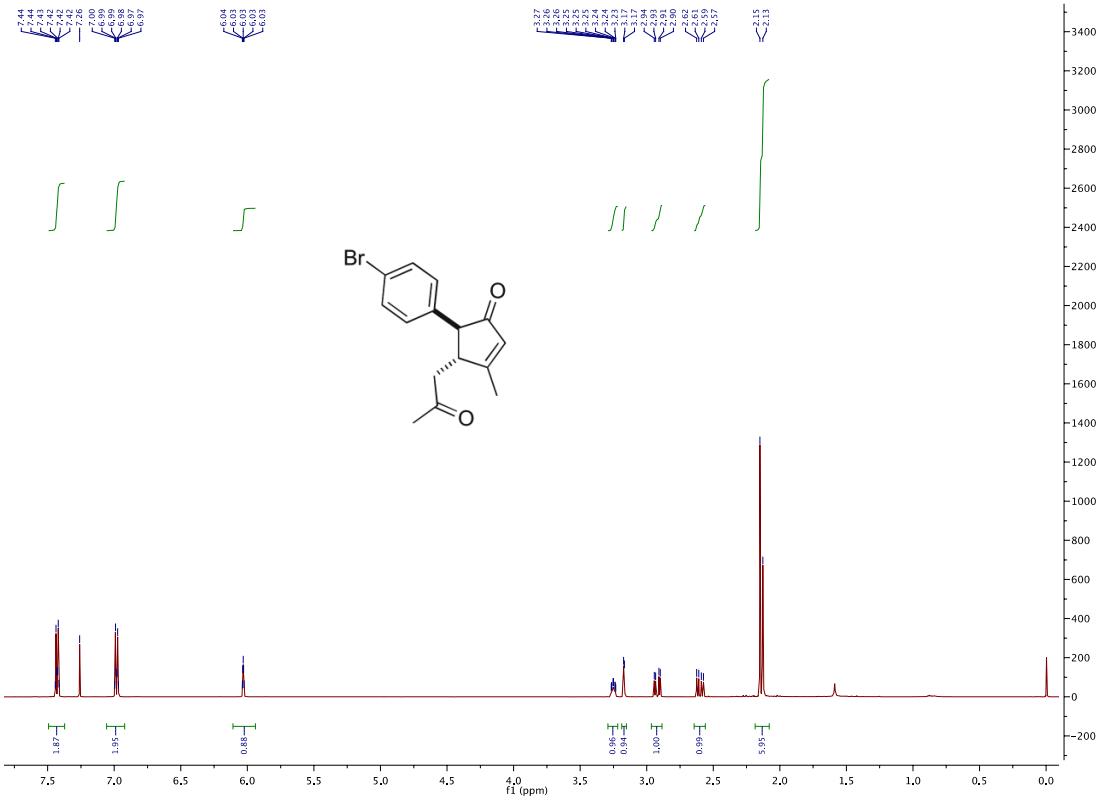
3a

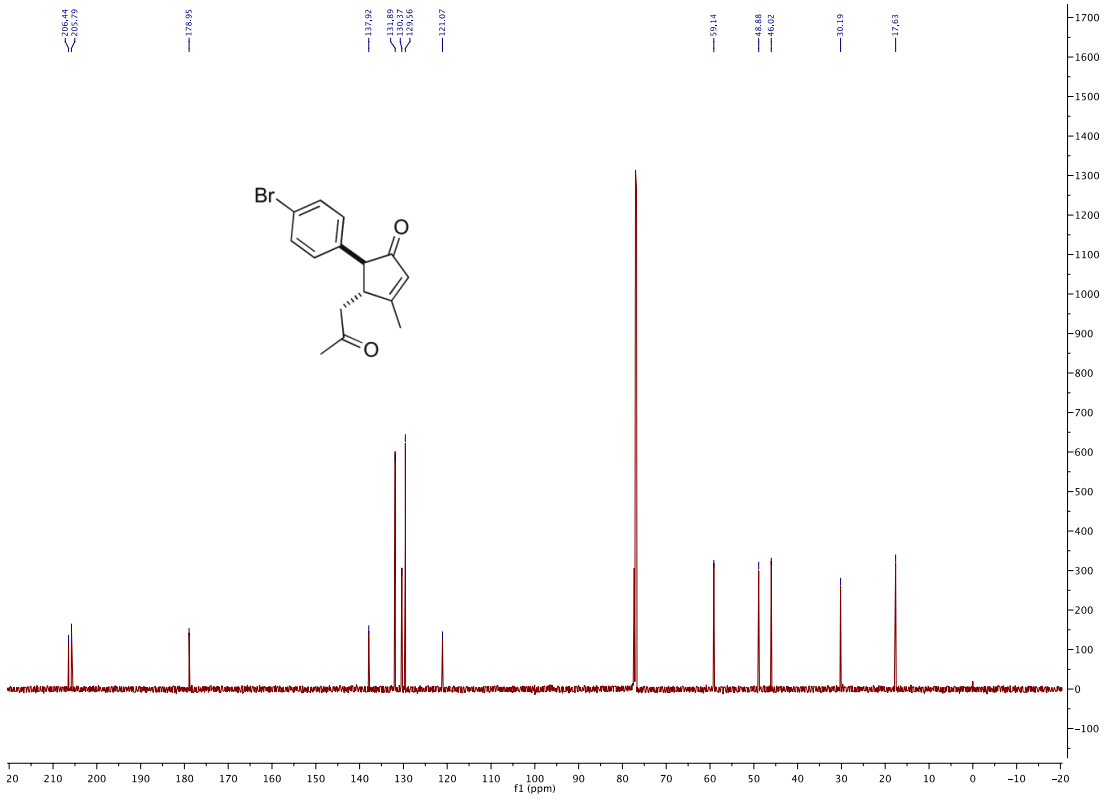


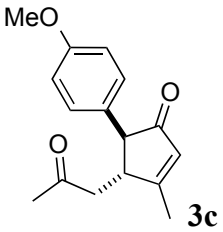




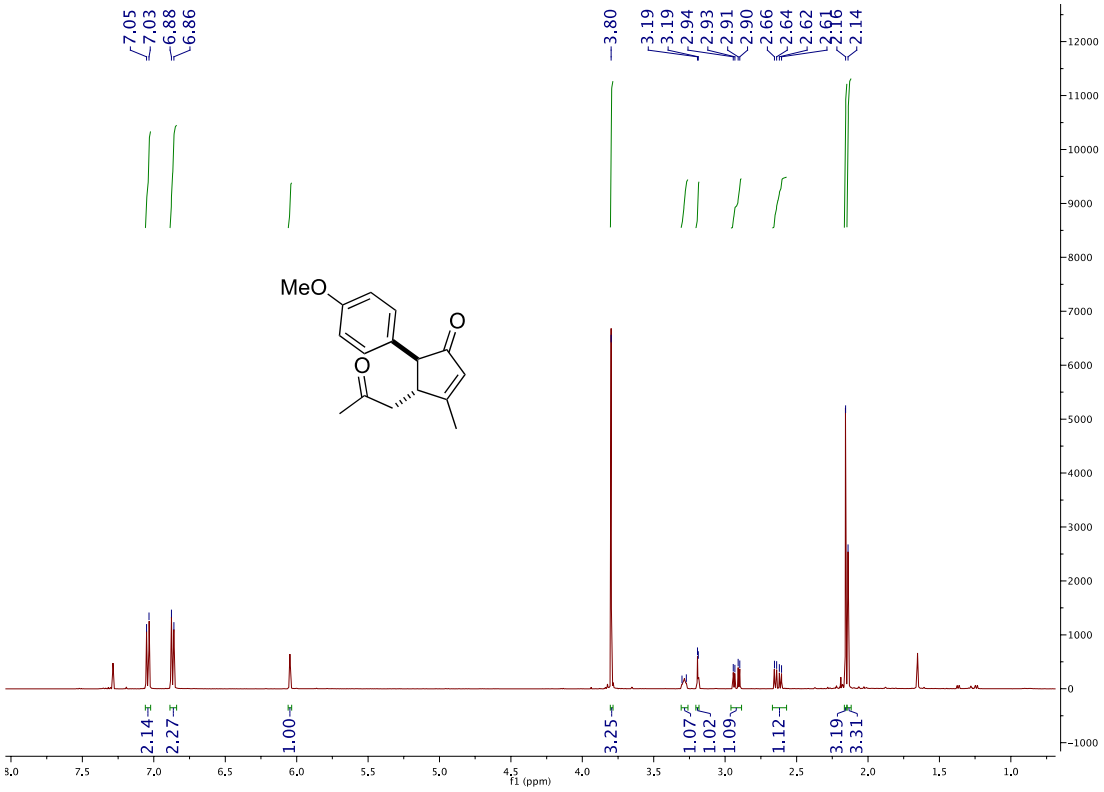
3b

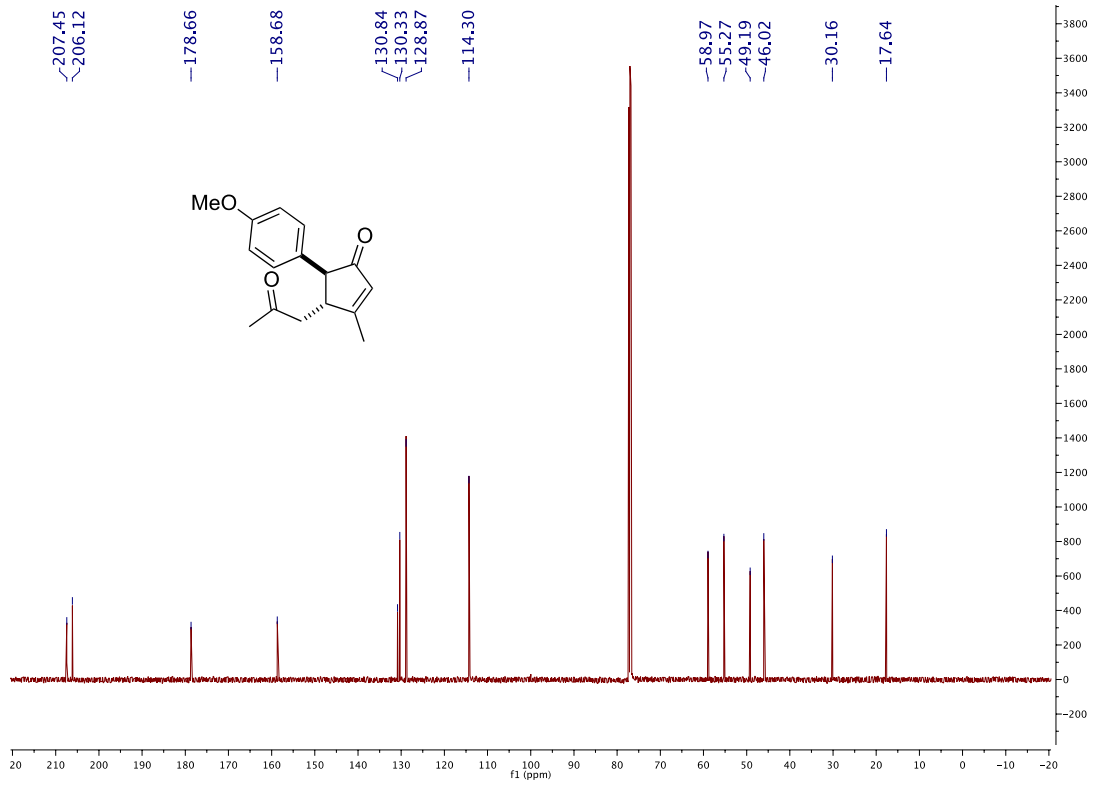


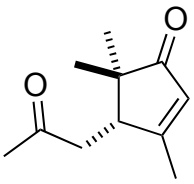



MeO
O
O

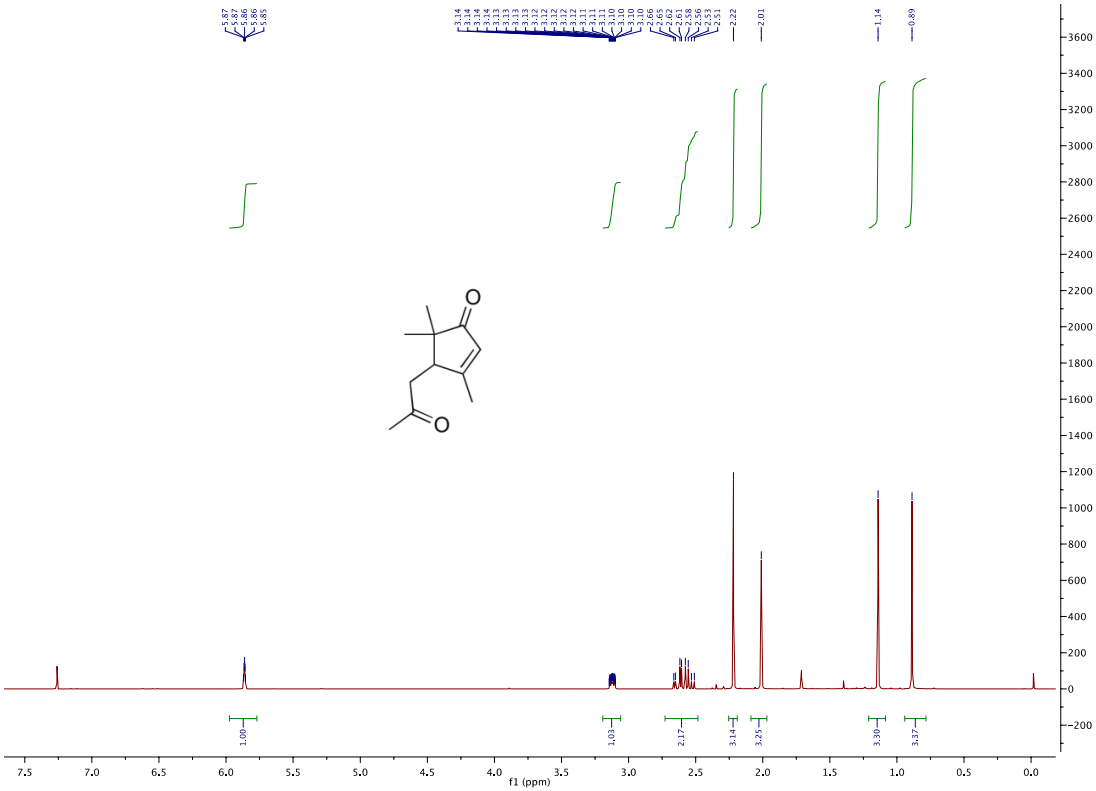
3c

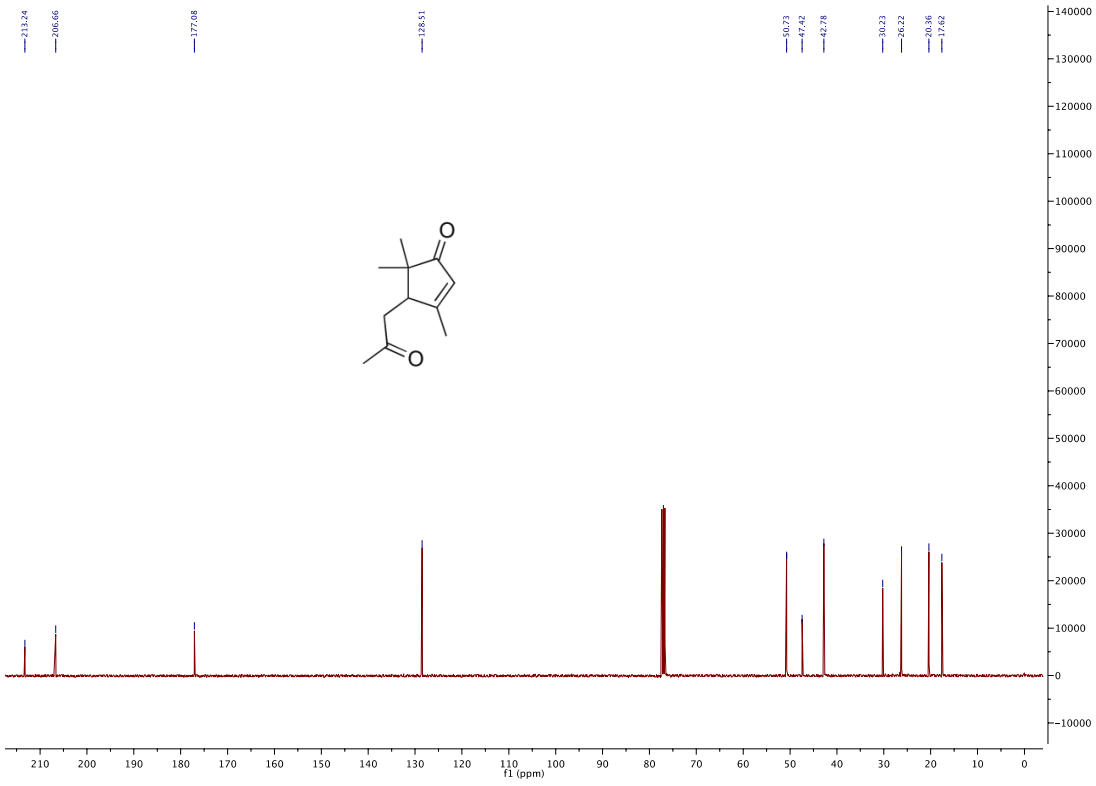

7.05
7.03
6.88
6.86
3.80
3.19
3.19
2.94
2.93
2.91
2.90
2.66
2.64
2.62
2.16
2.14
MeO
O
O
2.14
2.27
1.00
3.25
1.07
1.02
1.09
1.12
3.19
3.31
f1 (ppm)

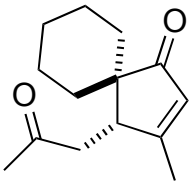

207.45
206.12
178.66
158.68
130.84
130.33
128.87
114.30
58.97
55.27
49.19
46.02
30.16
17.64
MeO
O
O
f1 (ppm)



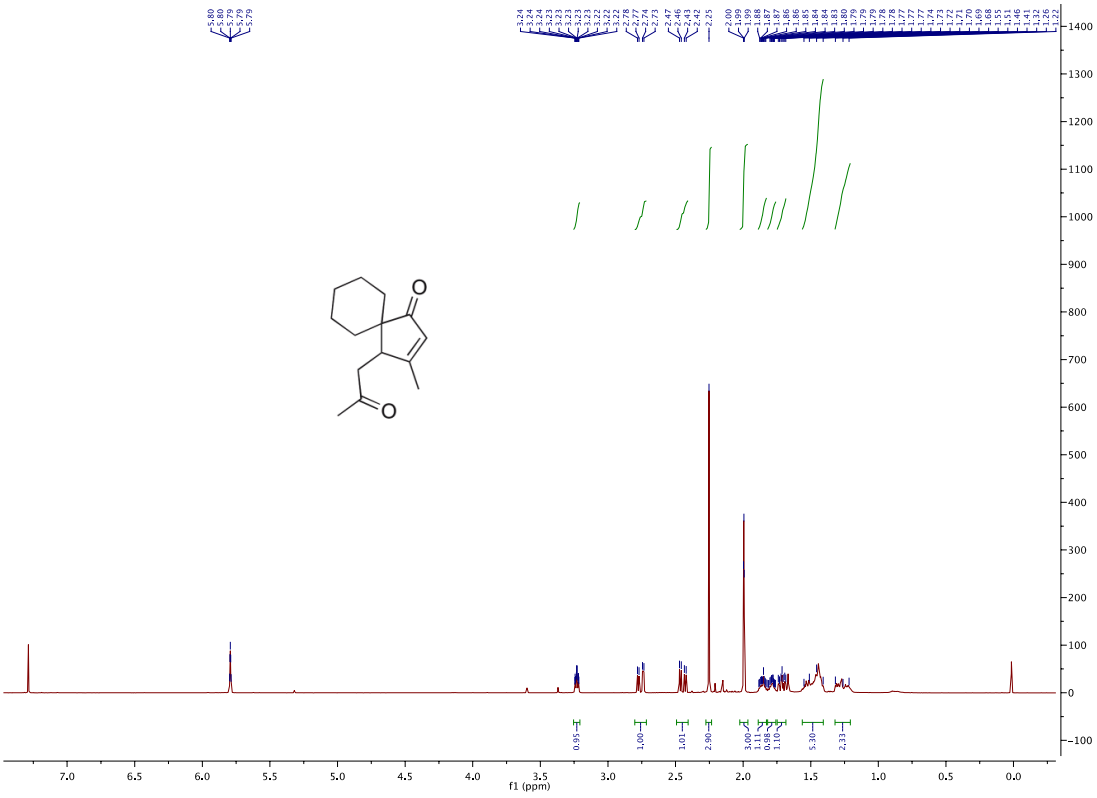
3d

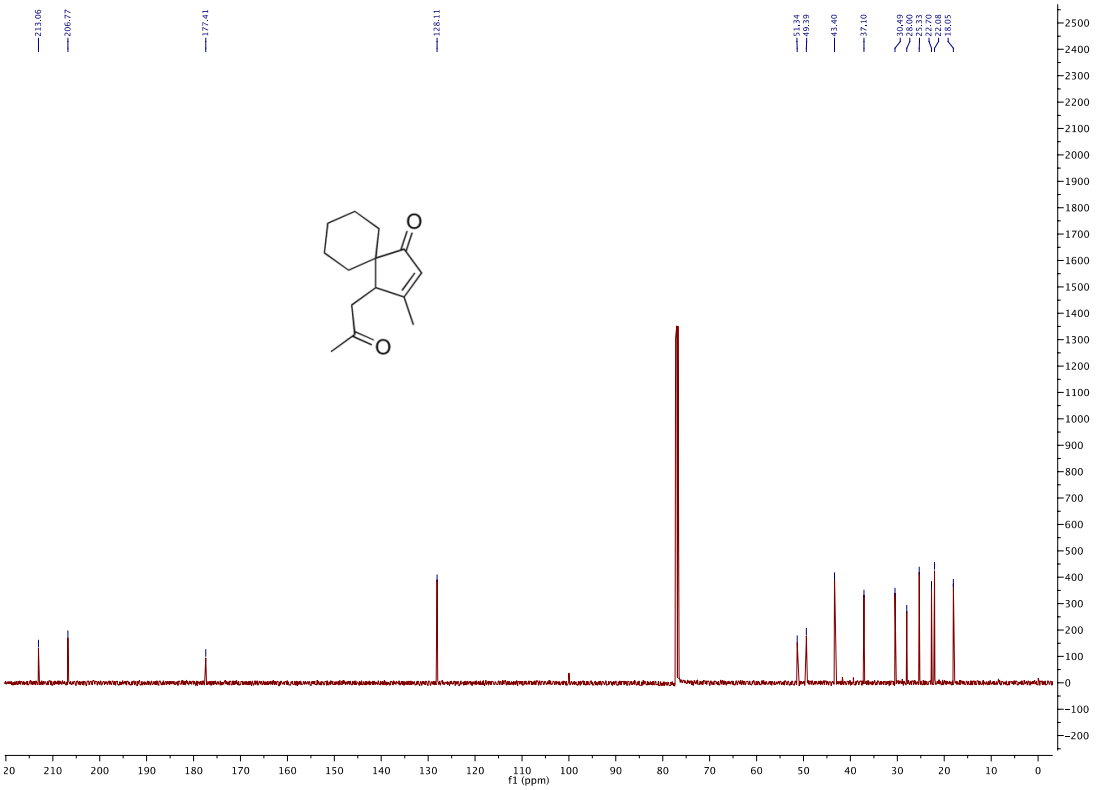


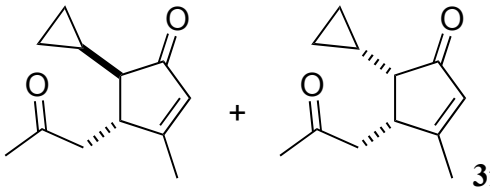




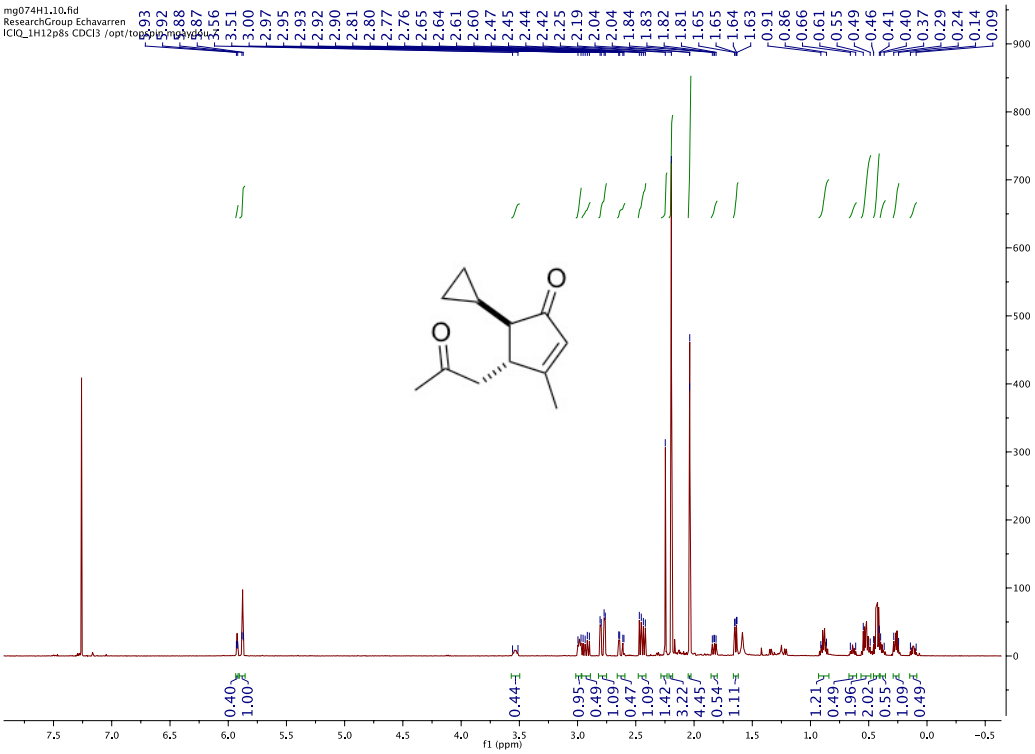
3e

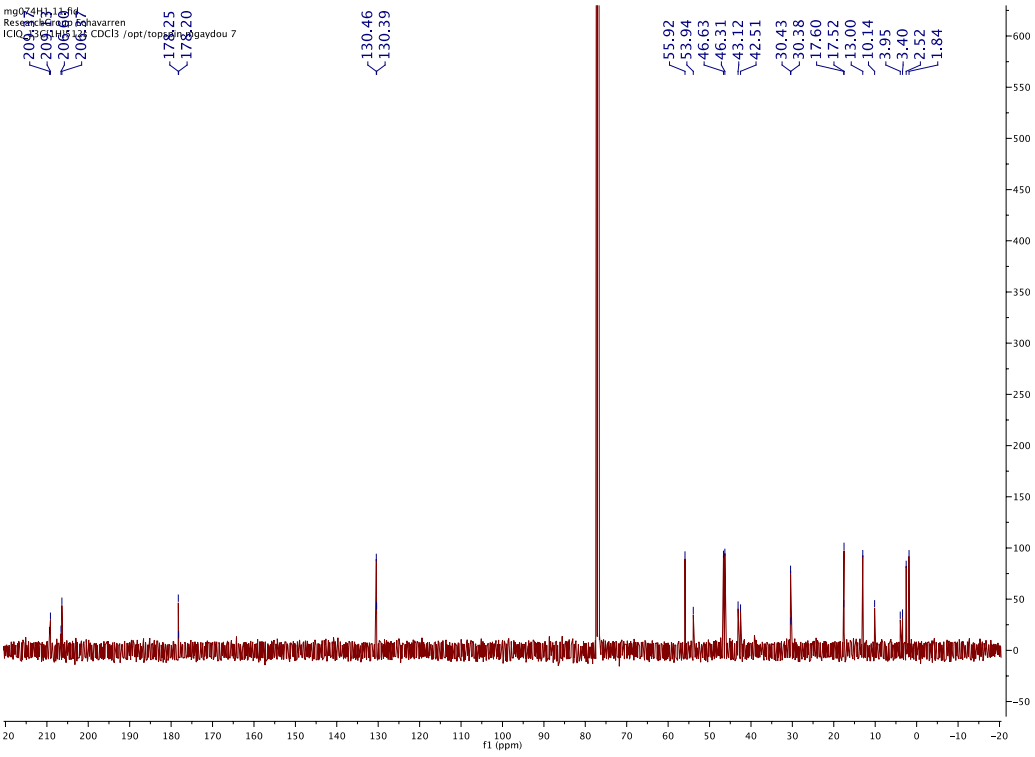

f1 (ppm)

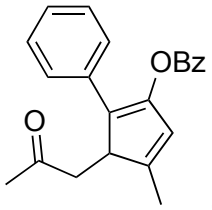

213.06
206.77
177.41
128.11
51.34
49.39
43.40
37.10
30.49
28.00
25.73
22.70
22.08
18.05
f1 (ppm)



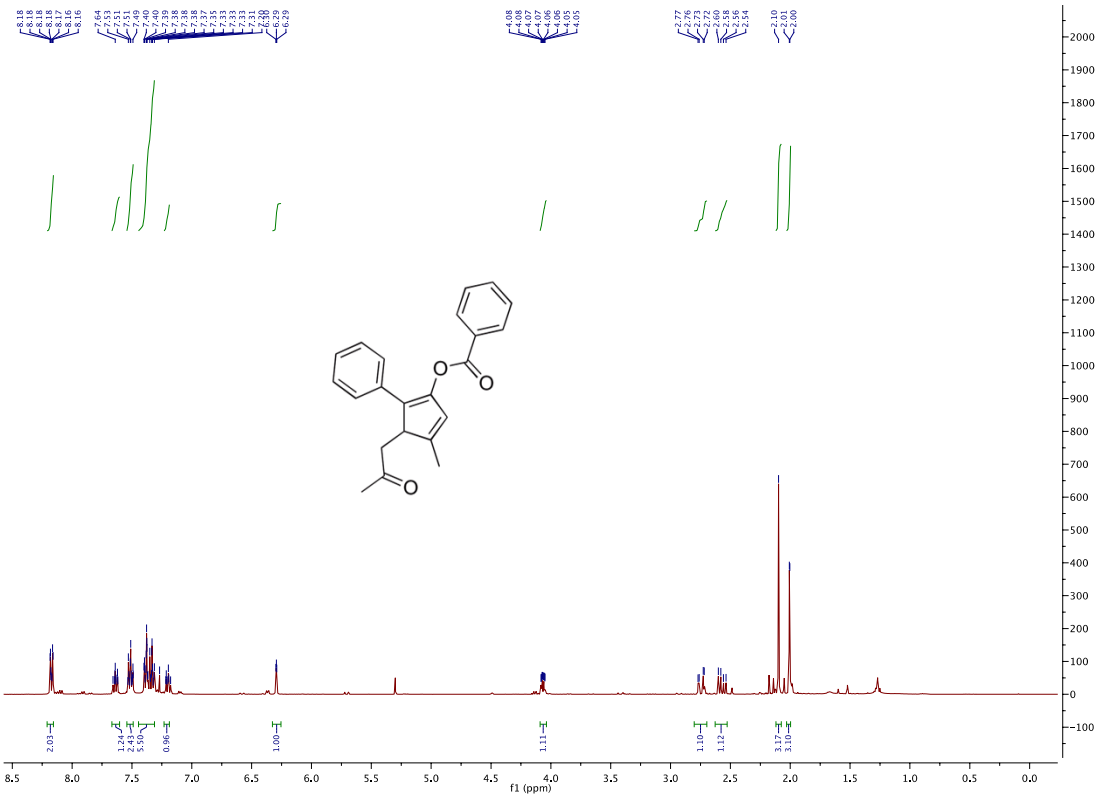
3f

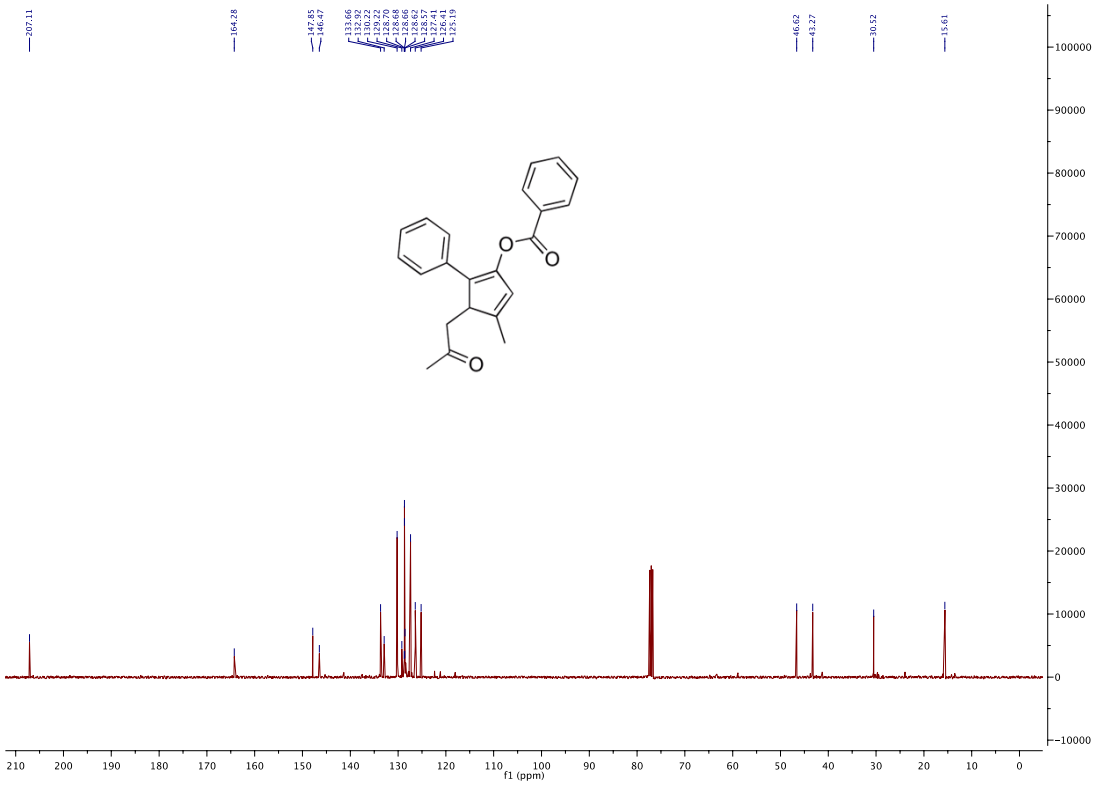


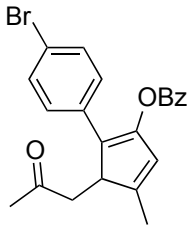




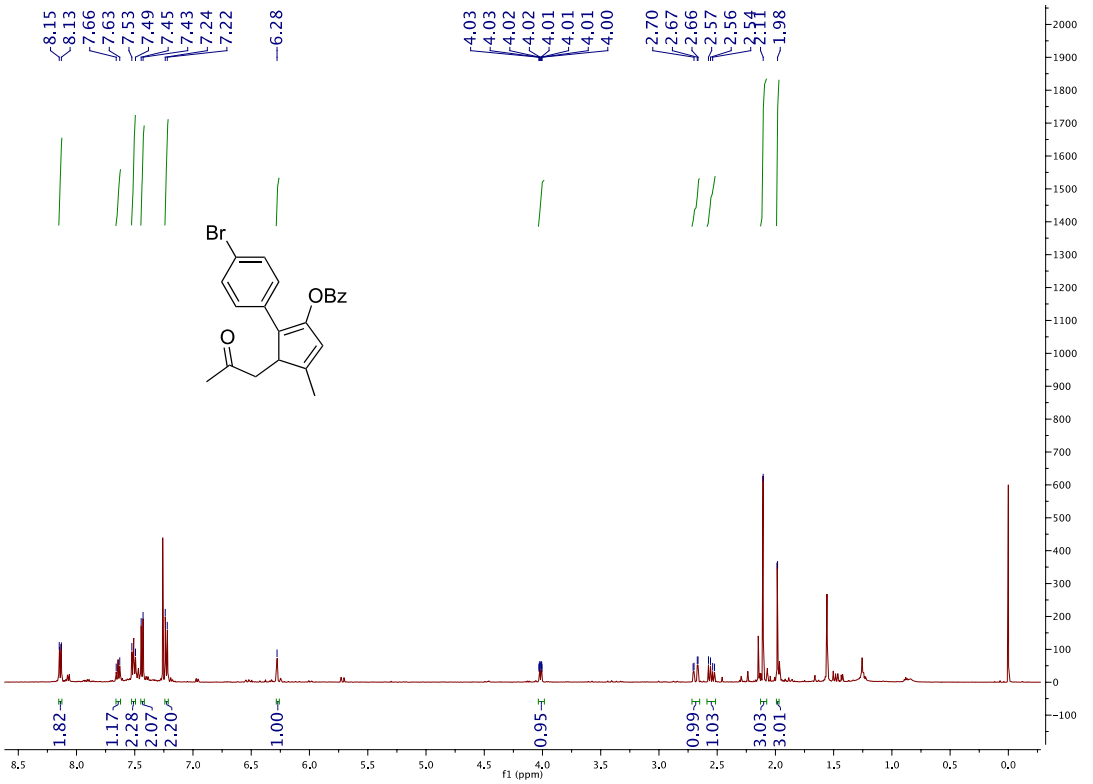
4a

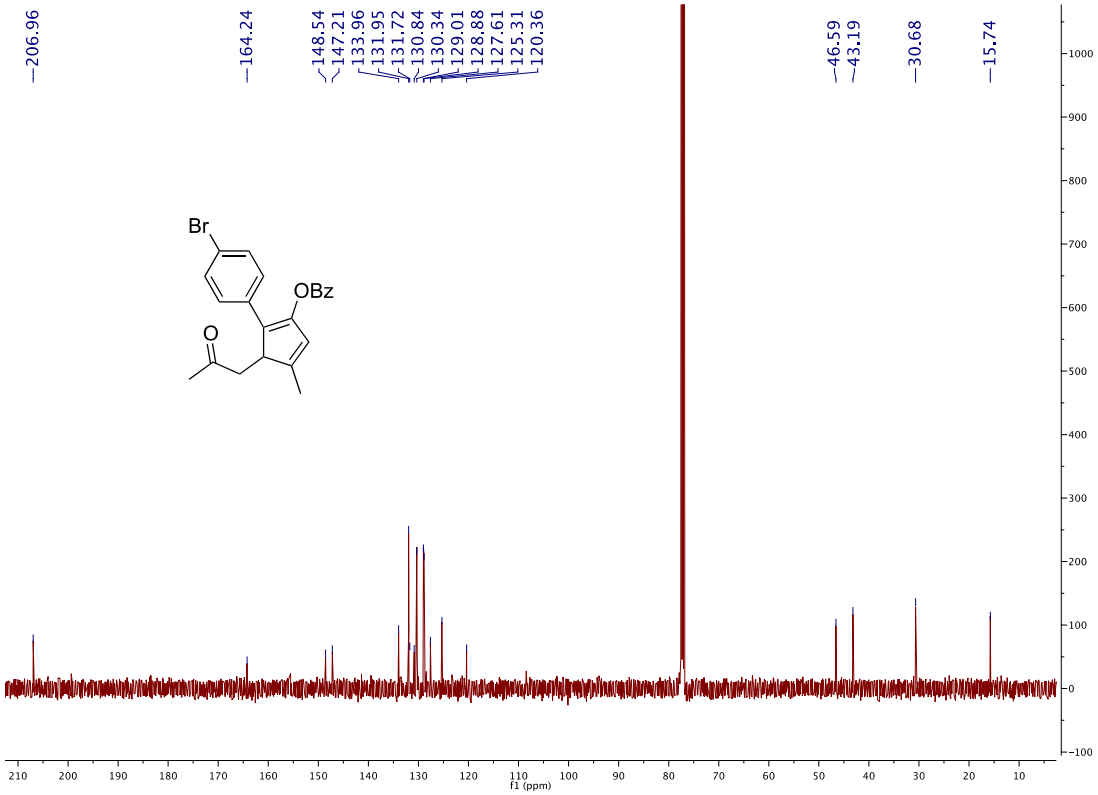


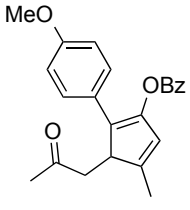



Br
OBz
O

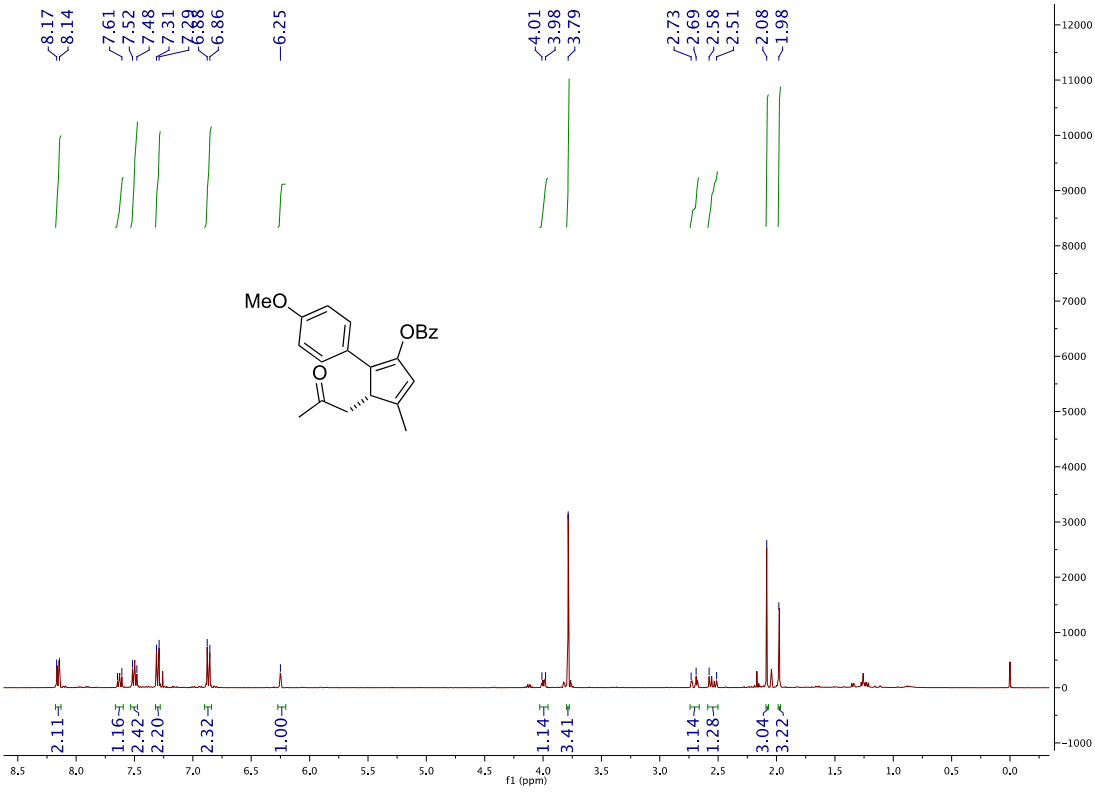
4b

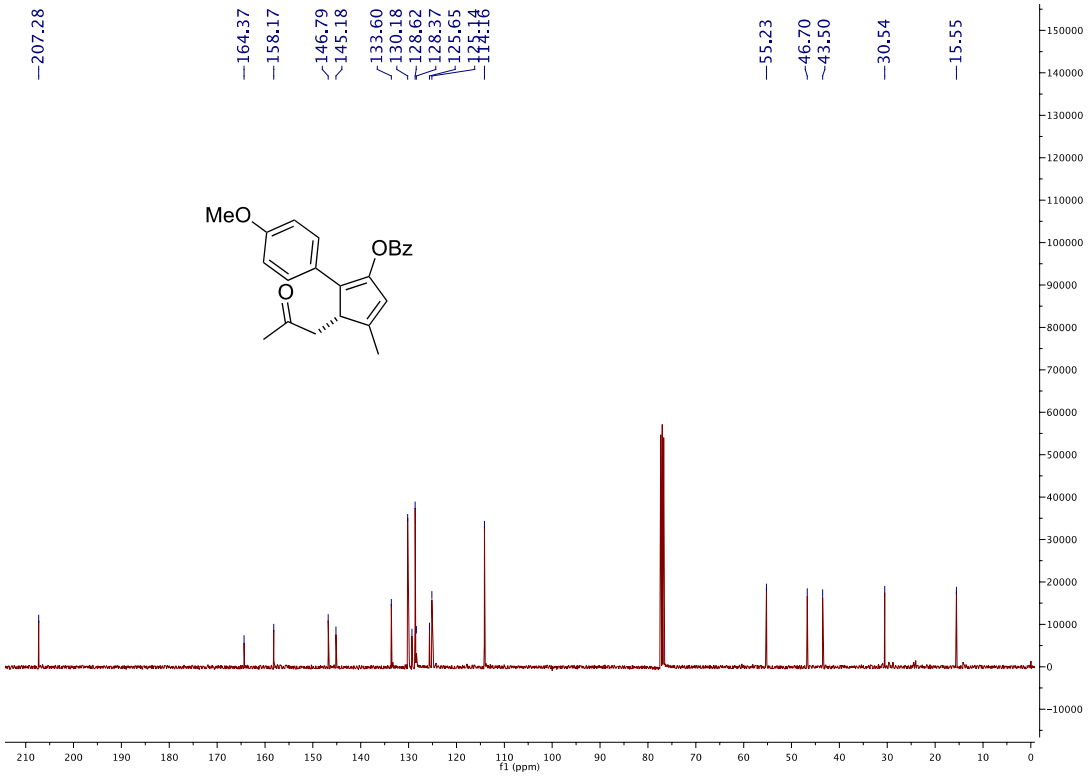

8.15
8.13
7.66
7.63
7.53
7.49
7.45
7.43
7.24
7.22
6.28
4.03
4.03
4.02
4.02
4.01
4.01
4.01
4.00
2.70
2.67
2.66
2.57
2.56
2.54
2.11
1.98
Br
OBz
O
1.82
1.17
2.28
2.07
2.20
1.00
0.95
0.99
1.03
3.03
3.01
f1 (ppm)

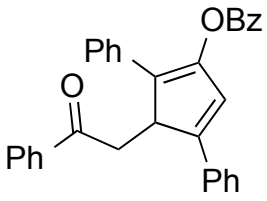

206.96
164.24
148.54
147.21
133.96
131.95
131.72
130.84
130.34
129.01
128.88
127.61
125.31
120.36
46.59
43.19
30.68
15.74
Br
OBz
O
f1 (ppm)


MeO
OBz
O

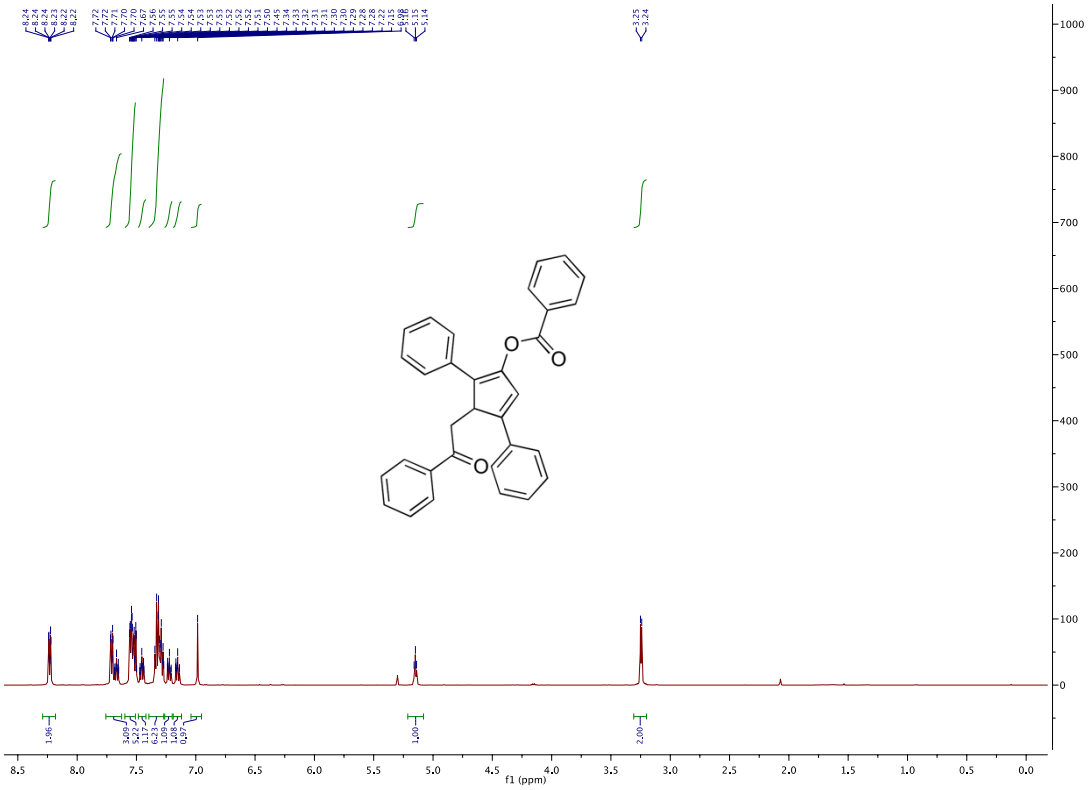
4c

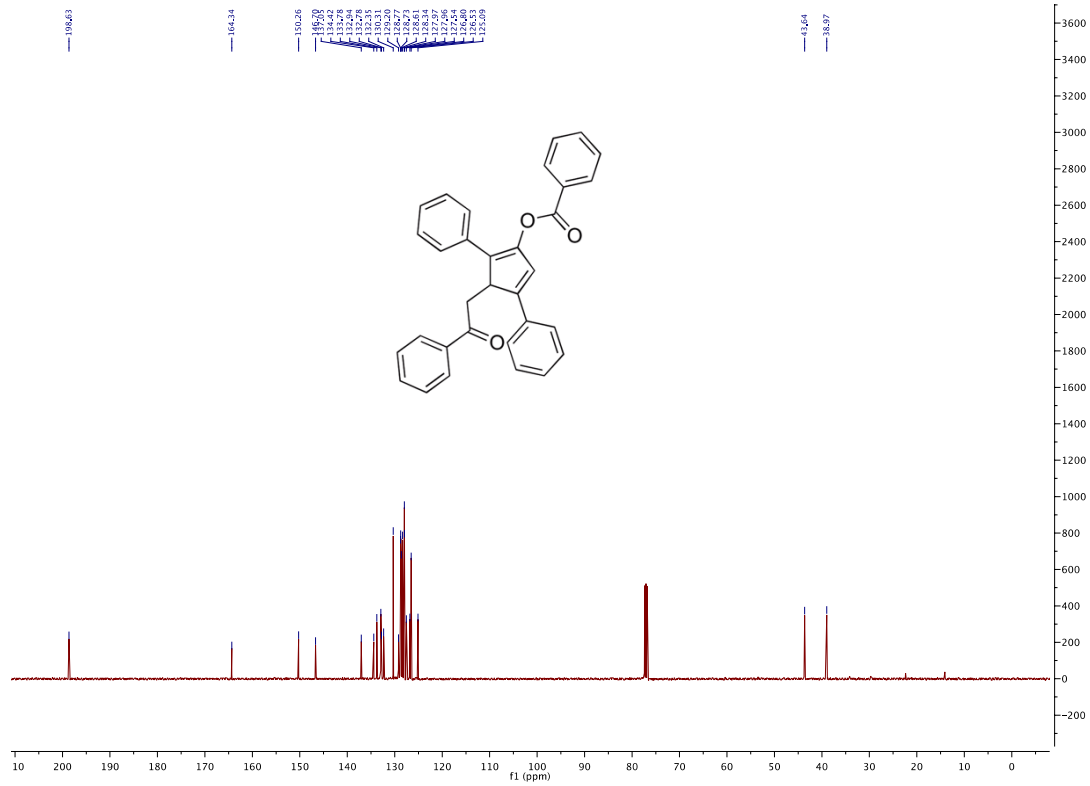

8.17
8.14
7.61
7.52
7.48
7.31
7.29
6.88
6.86
6.25
4.01
3.98
3.79
2.73
2.69
2.58
2.51
2.08
1.98
MeO
OBz
O
2.11
1.16
2.42
2.20
2.32
1.00
1.14
3.41
1.14
1.28
3.04
3.22
f1 (ppm)

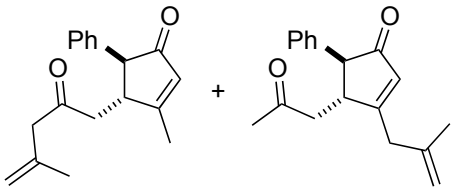

207.28
164.37
158.17
146.79
145.18
133.60
130.18
128.62
128.37
125.65
125.14
114.16
55.23
46.70
43.50
30.54
15.55
MeO
OBz
O
f1 (ppm)



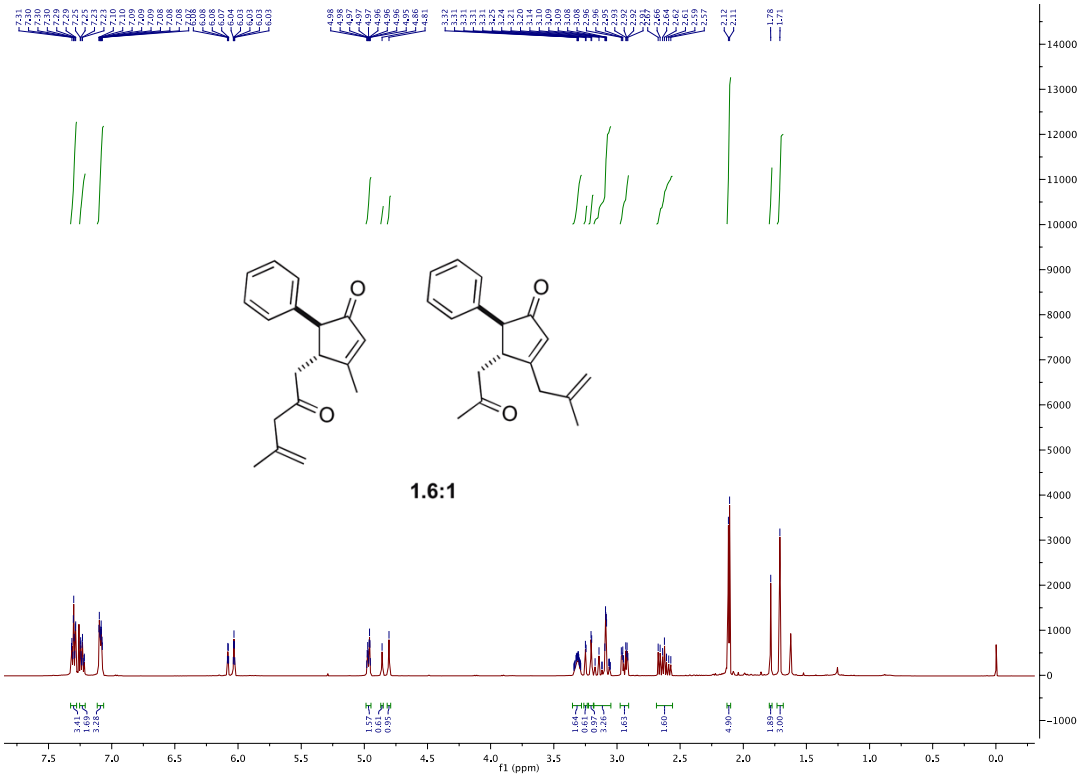
4d

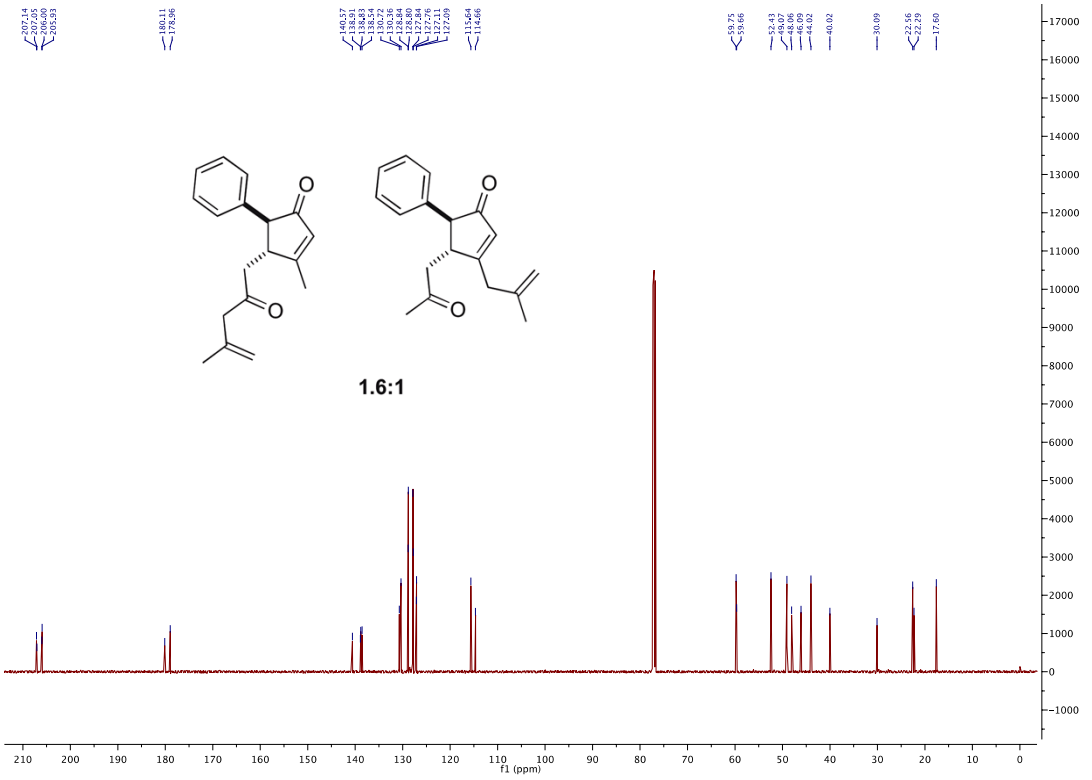


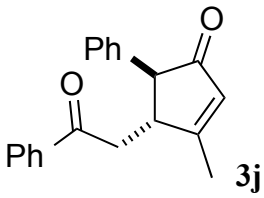




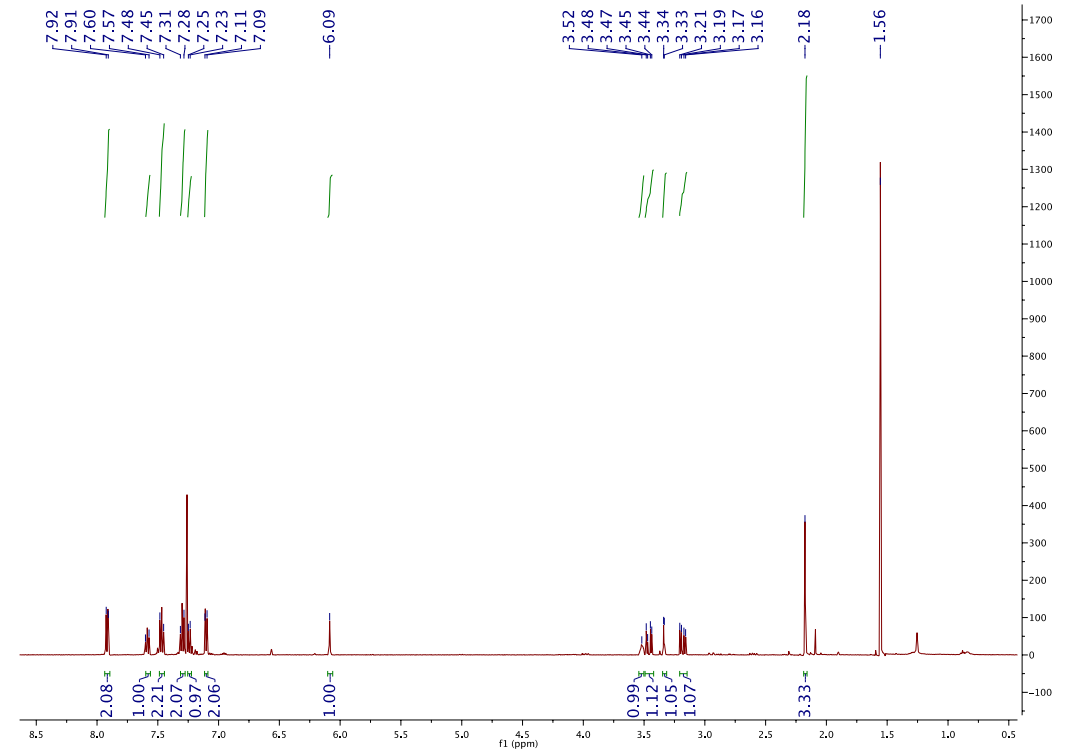
3i/3i''

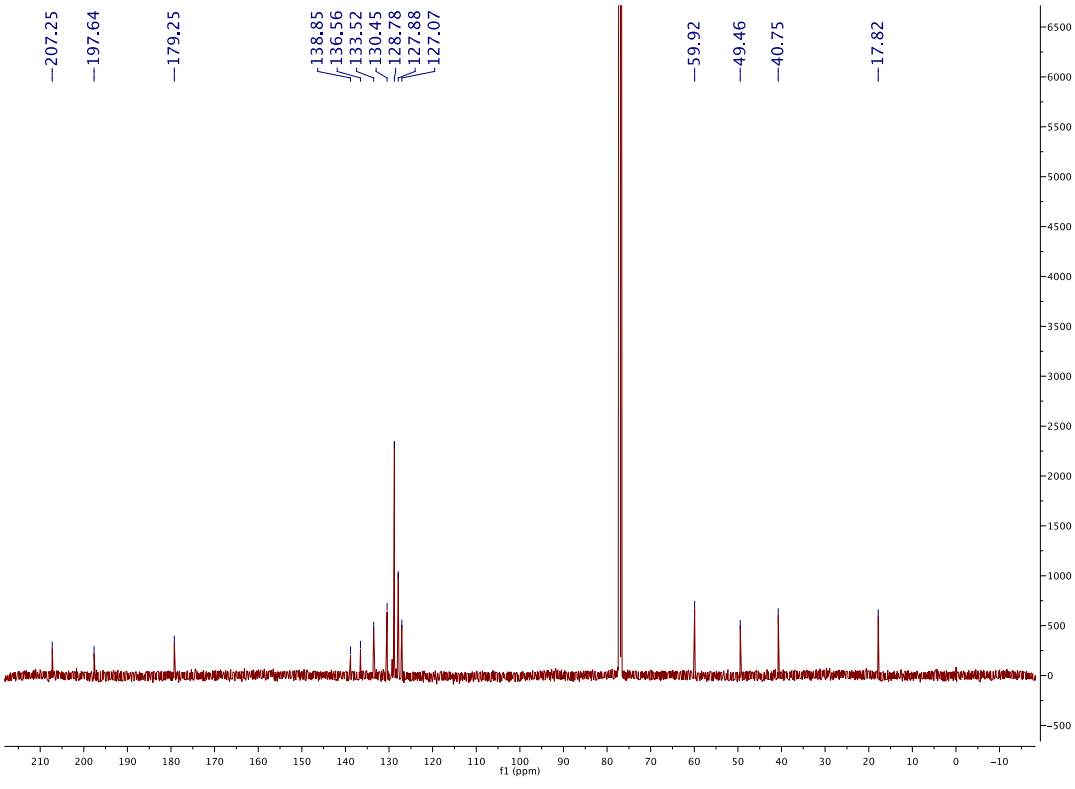


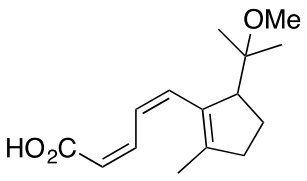



Ph
O
O
Ph

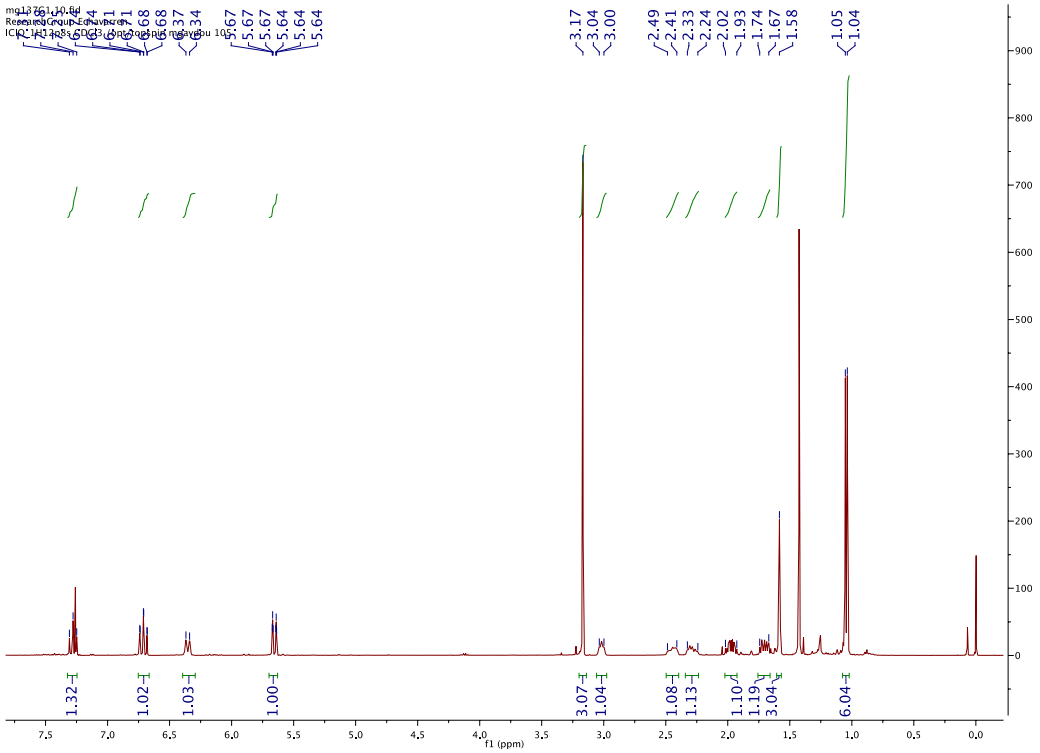
3j

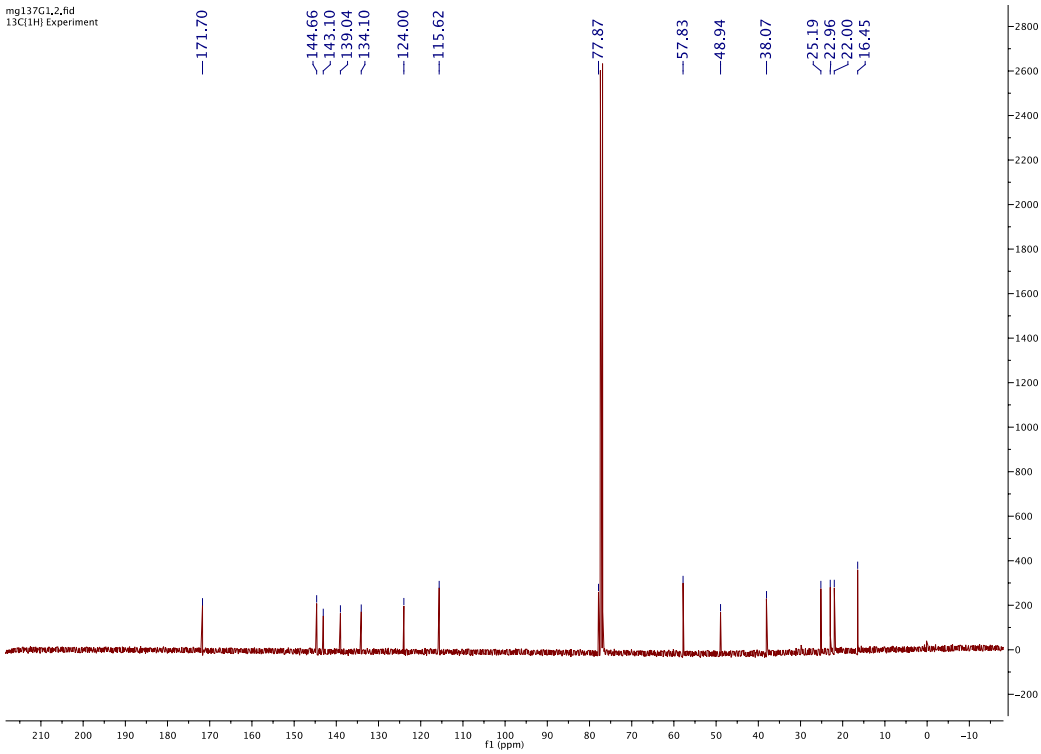

7.92
7.91
7.60
7.57
7.48
7.45
7.31
7.28
7.25
7.23
7.11
7.09
6.09
3.52
3.48
3.47
3.45
3.44
3.34
3.33
3.21
3.19
3.17
3.16
2.18
1.56
2.08
1.00
2.21
2.07
0.97
2.06
1.00
0.99
1.12
1.05
1.07
3.33
f1 (ppm)

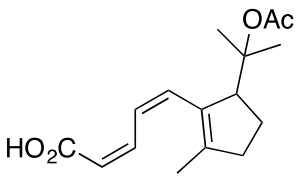

207.25
197.64
179.25
138.85
136.56
133.52
130.45
128.78
127.88
127.07
59.92
49.46
40.75
17.82
f1 (ppm)


OMe
HO2C

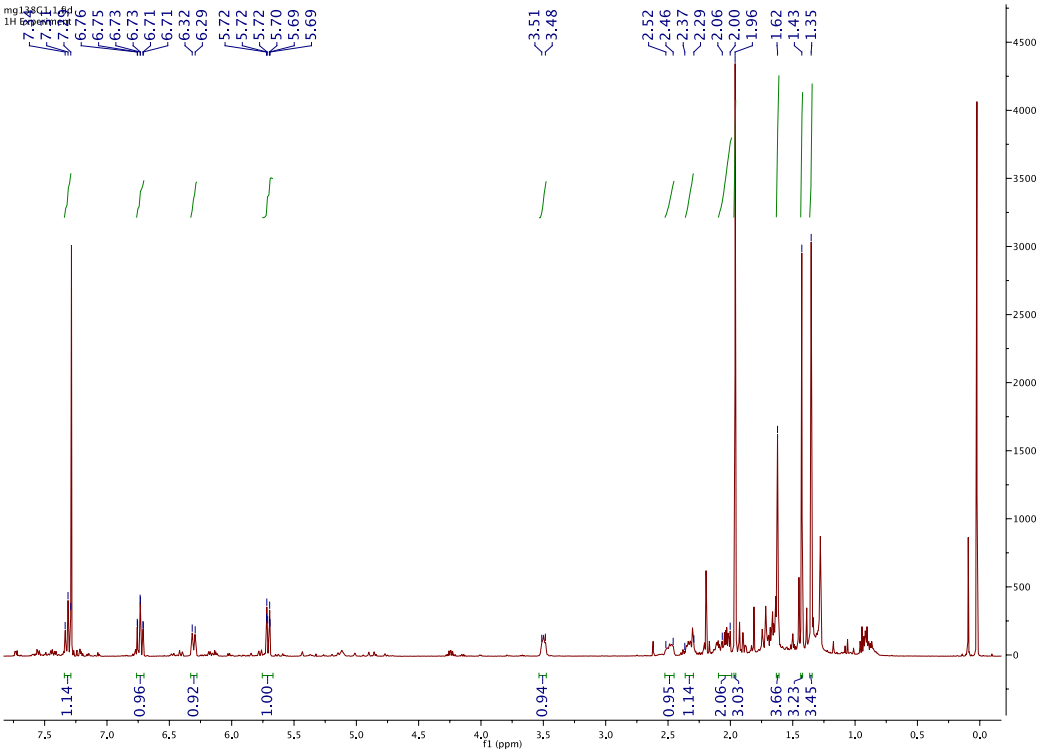
12a

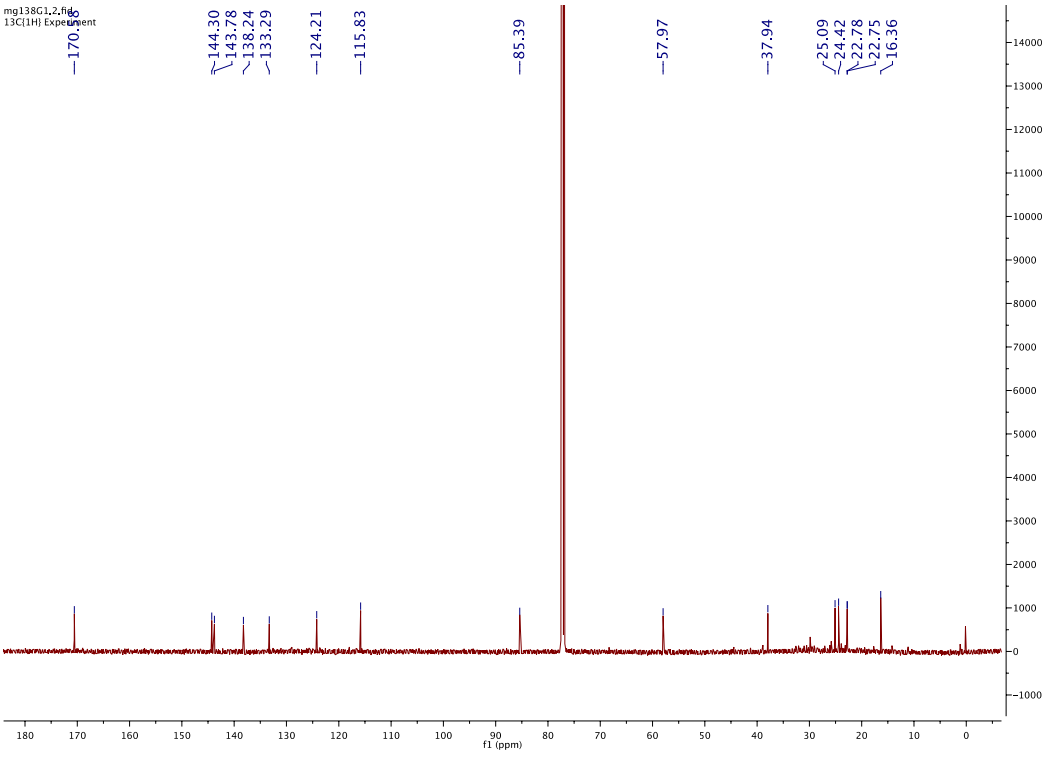

3.17
3.04
3.00
2.49
2.41
2.33
2.24
2.02
1.93
1.74
1.67
1.58
1.05
1.04
5.67
5.67
5.64
5.64
5.64
1.32
1.02
1.03
1.00
3.07
1.04
1.08
1.13
1.10
1.19
3.04
6.04
f1 (ppm)

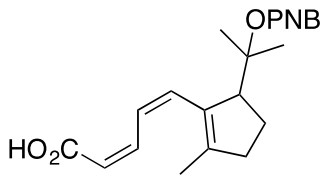

mg137G1,2,fid
13C{1H} Experiment
171.70
144.66
143.10
139.04
134.10
124.00
115.62
77.87
57.83
48.94
38.07
25.19
22.96
22.00
16.45
f1 (ppm)



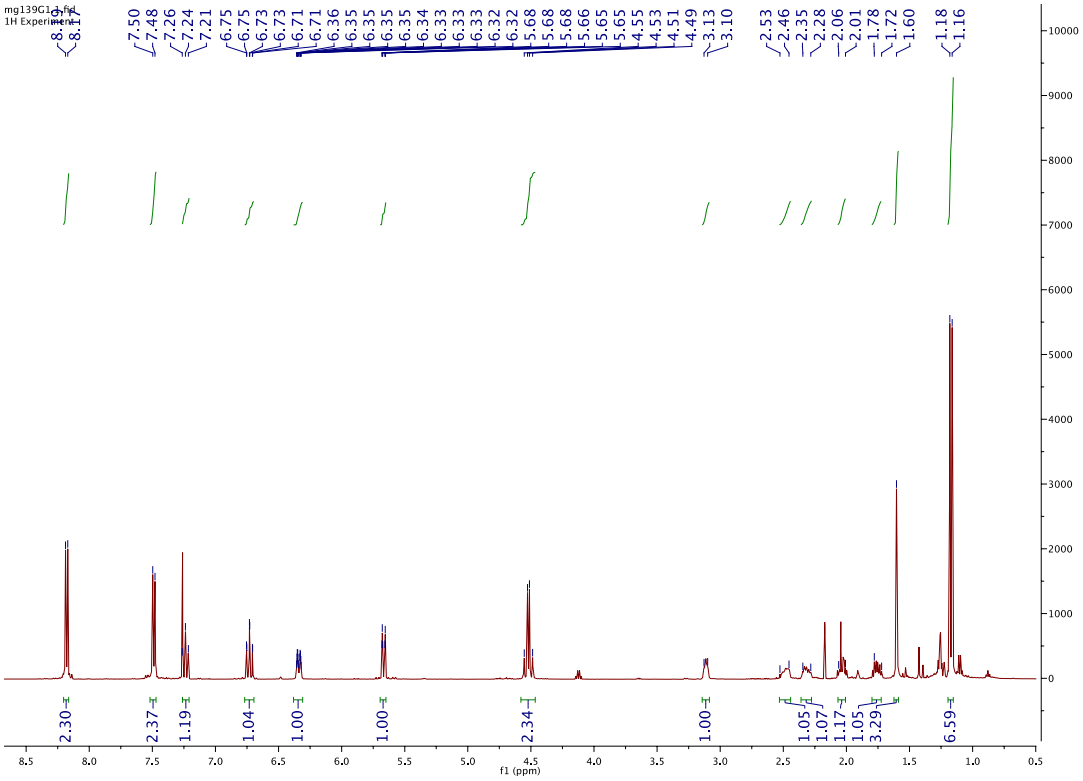
12a' (Contaminated by some impurities that could not be separated)

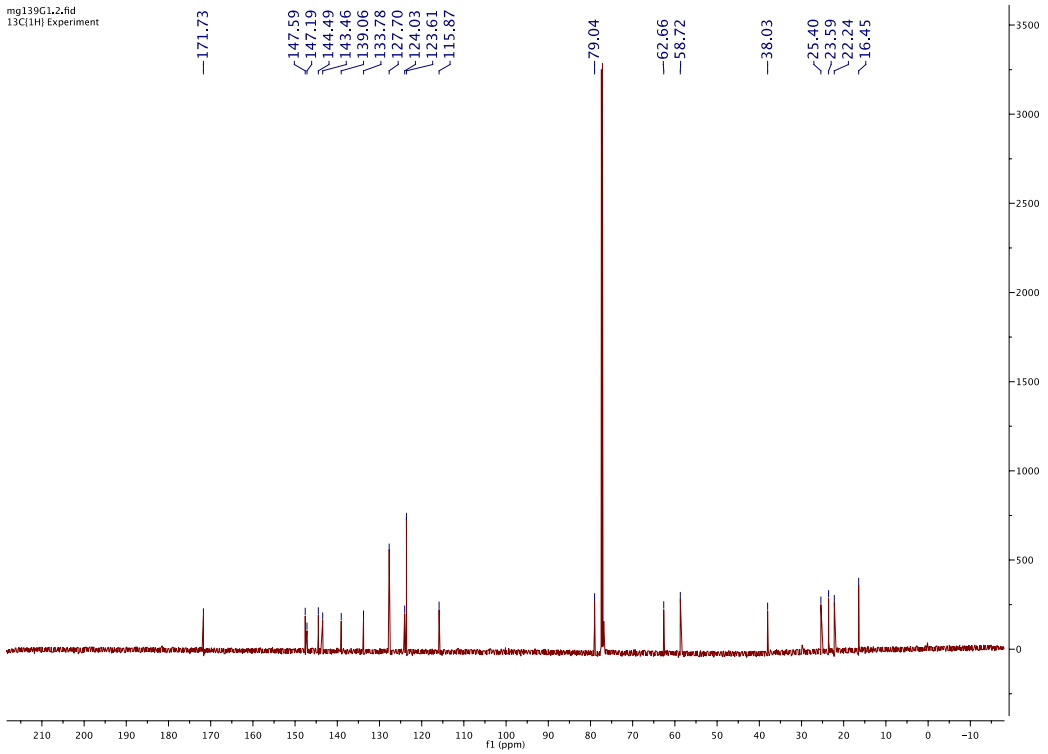


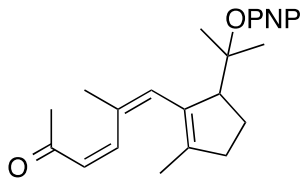



OPNB
HO2C

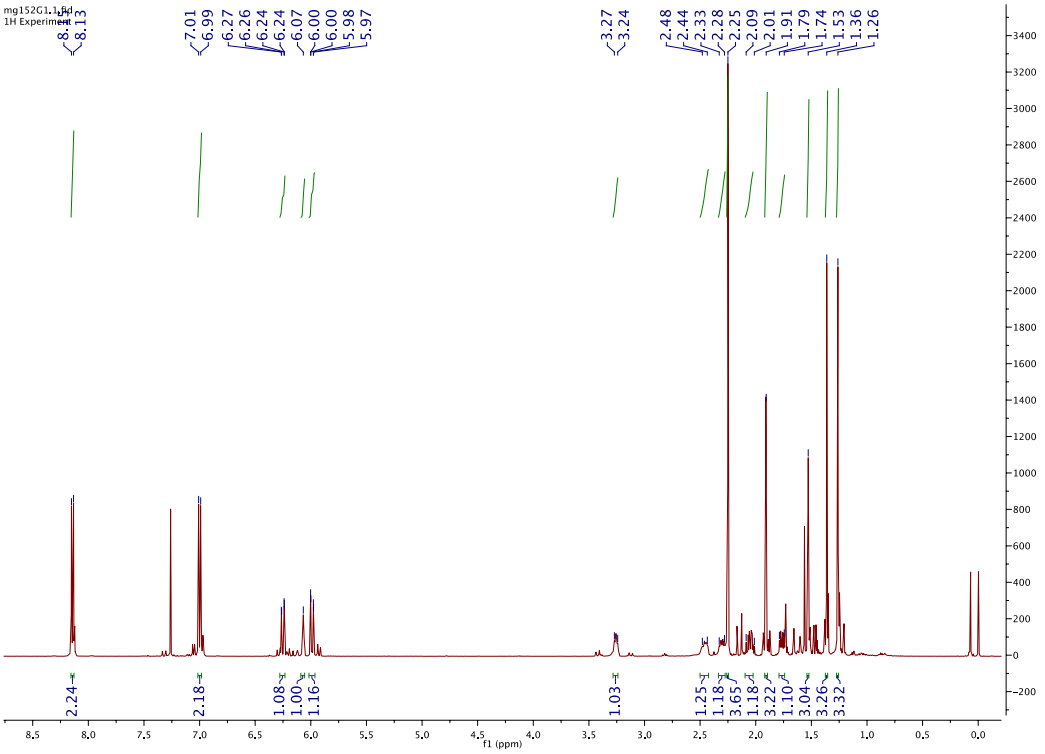
12a''

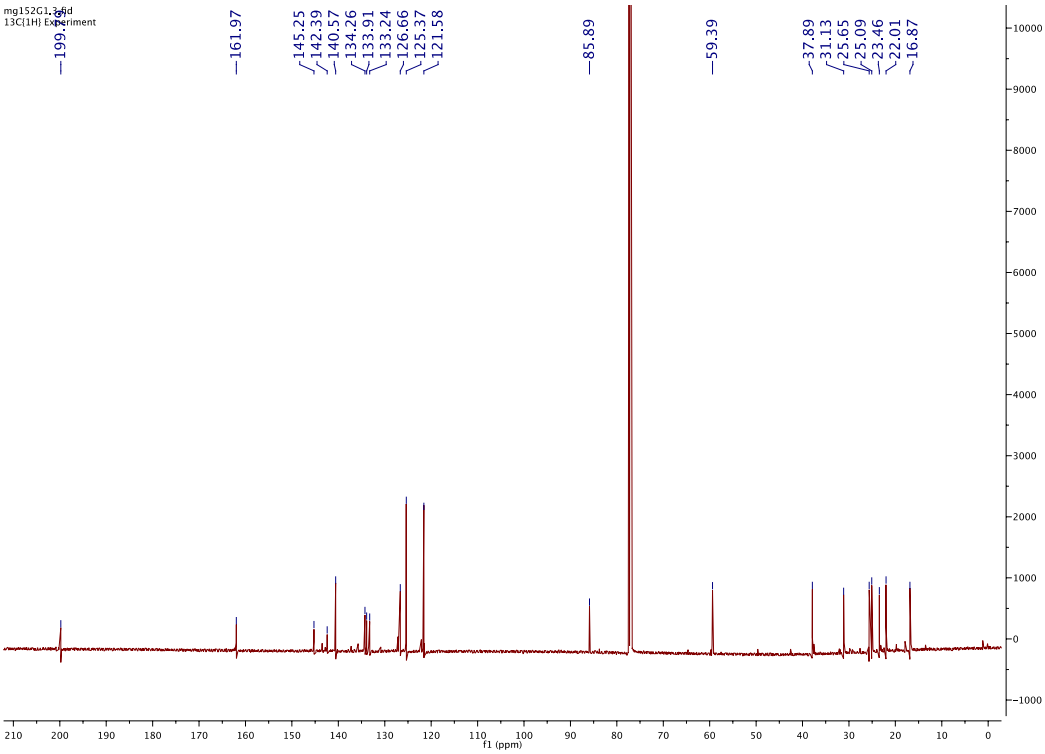

mg139G1.1.fid
1H Experiment
f1 (ppm)

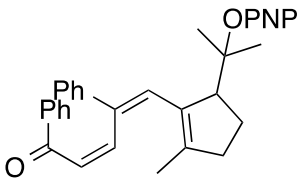

mg139G1.2.fid
13C{1H} Experiment
f1 (ppm)


OPNP
O

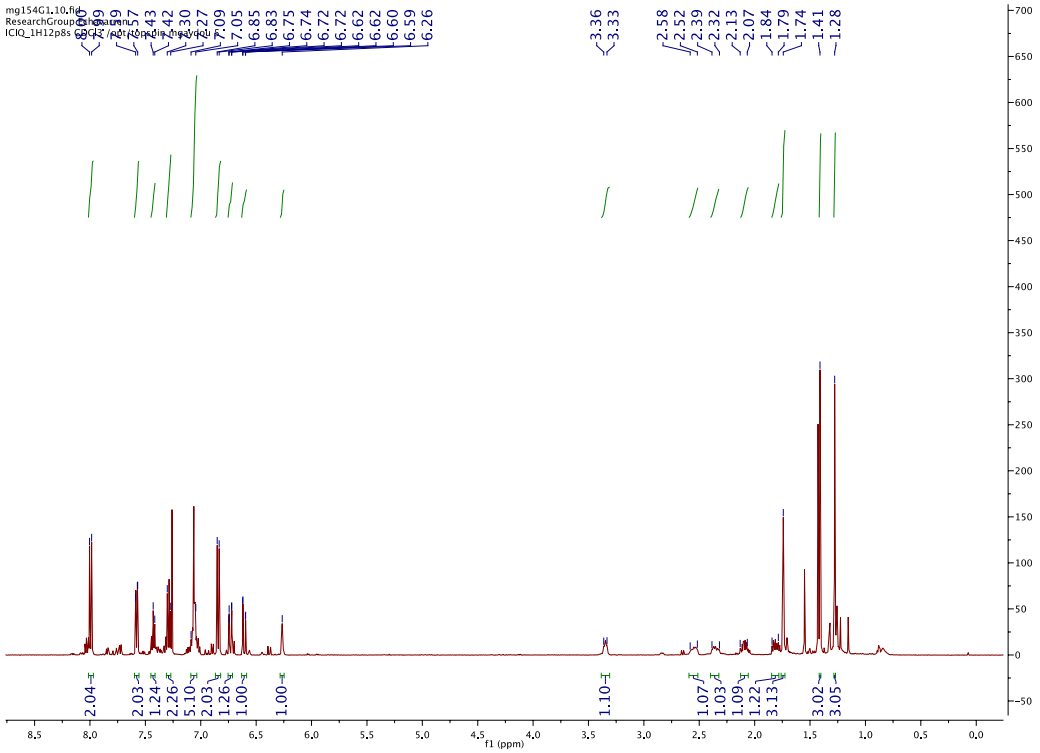
12b

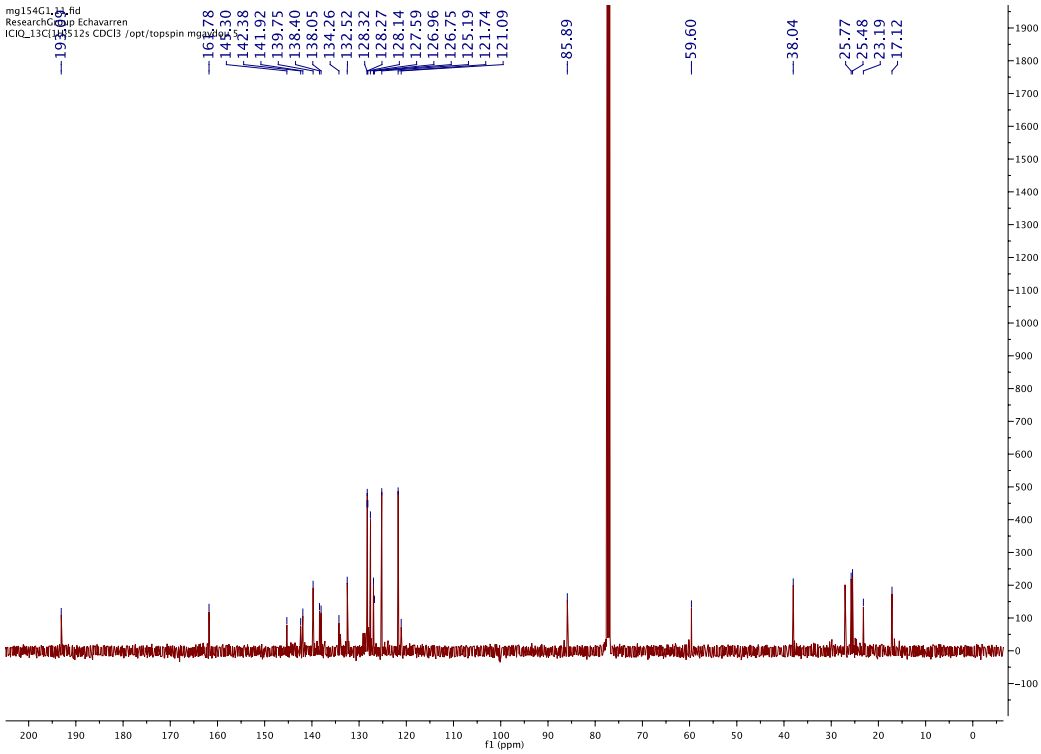

8.15
8.13
7.01
6.99
6.27
6.26
6.24
6.24
6.07
6.00
6.00
5.98
5.97
3.27
3.24
2.48
2.44
2.33
2.28
2.25
2.09
2.01
1.91
1.79
1.74
1.53
1.36
1.26
2.24
2.18
1.08
1.00
1.16
1.03
1.25
1.18
3.65
1.18
3.22
1.10
3.04
3.26
3.32
f1 (ppm)

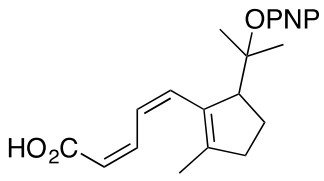

199.58
161.97
145.25
142.39
140.57
134.26
133.91
133.24
126.66
125.37
121.58
85.89
59.39
37.89
31.13
25.65
25.09
23.46
22.01
16.87
f1 (ppm)


OPNP
Ph
Ph
O

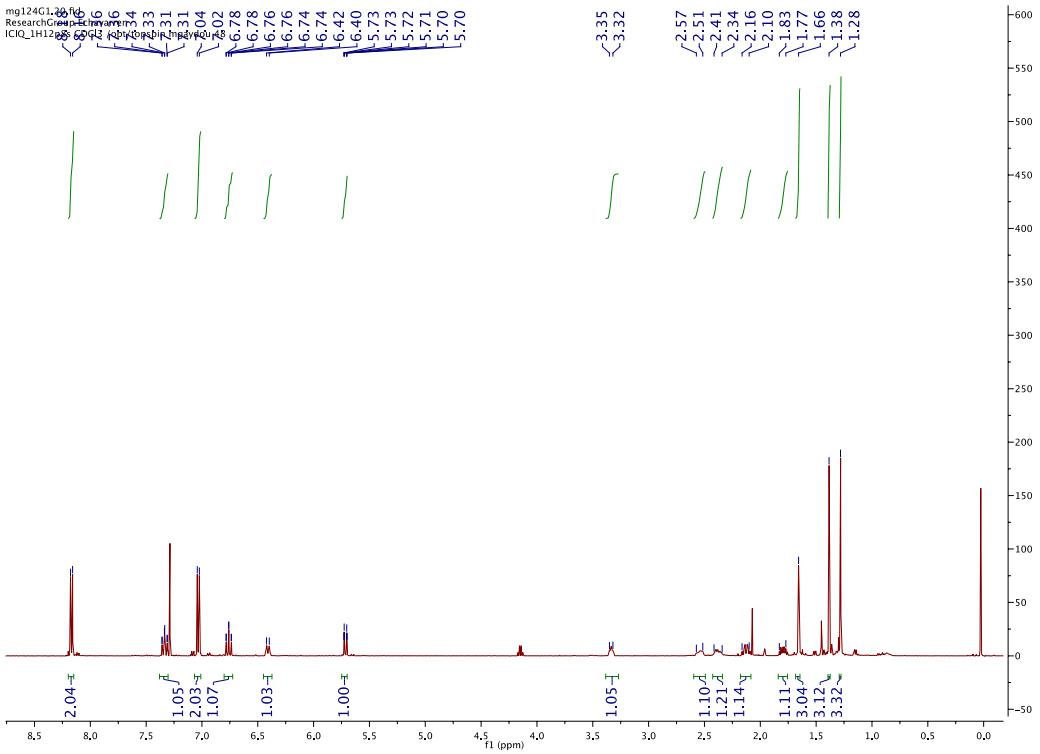
12c

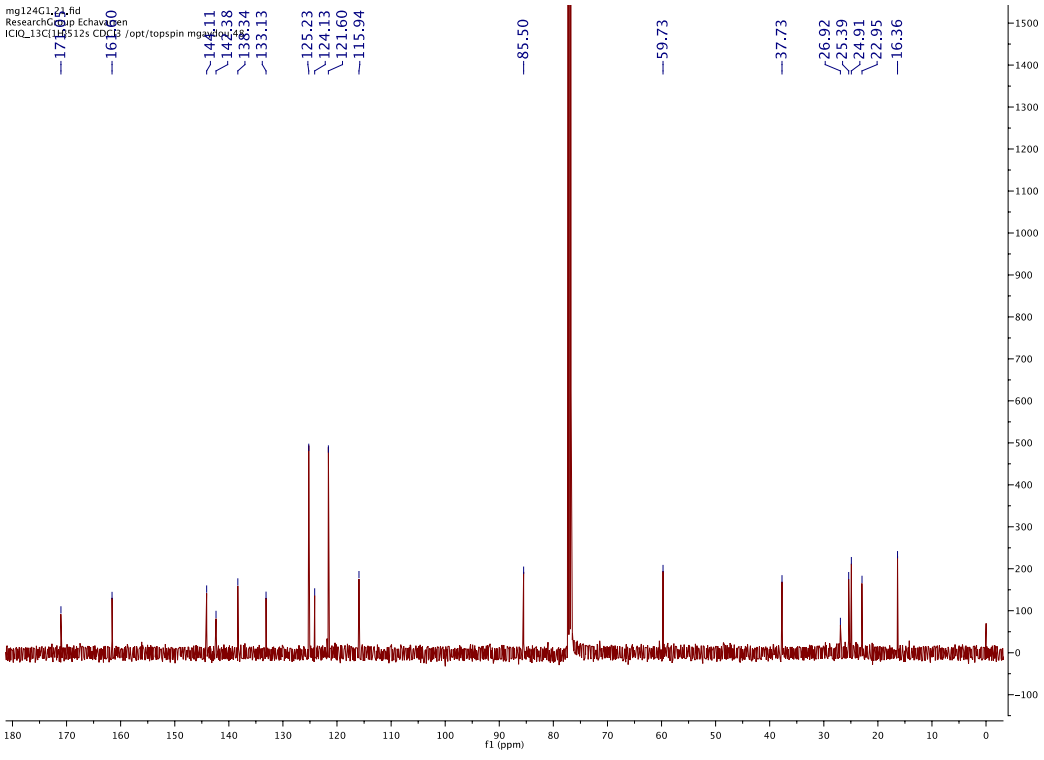

mg154G1.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin mgavilo 1
7.69
7.57
7.43
7.42
7.30
7.27
7.09
7.05
6.85
6.83
6.75
6.74
6.72
6.72
6.62
6.62
6.60
6.59
6.26
3.36
3.33
2.58
2.52
2.39
2.32
2.13
2.07
1.84
1.79
1.74
1.41
1.28
2.04
2.03
1.24
2.26
5.10
2.03
1.26
1.00
1.00
1.10
1.07
1.03
1.09
1.22
3.13
3.02
3.05
f1 (ppm)


mg154G1.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin mgavilo 1
193.62
163.78
143.30
142.38
141.92
139.75
138.40
138.05
134.26
132.52
128.32
128.27
128.14
127.59
126.96
126.75
125.19
121.74
121.09
85.89
59.60
38.04
25.77
25.48
23.19
17.12
f1 (ppm)


OPNP
HO2C

12d


mg124G1.20.fid
ResearchGroup Echavarren
ICIQ_1H12gs CDCl3 /opt/topspin mgavido 48
8.16
8.15
7.36
7.34
7.33
7.31
7.31
7.04
7.02
6.78
6.78
6.76
6.76
6.74
6.74
6.42
6.40
5.73
5.73
5.72
5.71
5.70
5.70
3.35
3.32
2.57
2.51
2.41
2.34
2.16
2.10
1.83
1.77
1.66
1.38
1.28
2.04
1.05
2.03
1.07
1.03
1.00
1.05
1.10
1.21
1.14
1.11
3.04
3.12
3.32
f1 (ppm)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ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin mgavido 48
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161.00
144.11
142.38
133.34
133.13
125.23
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85.50
59.73
37.73
26.92
25.39
24.91
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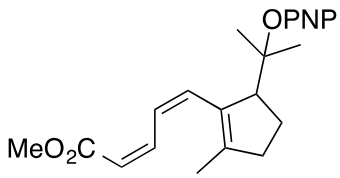
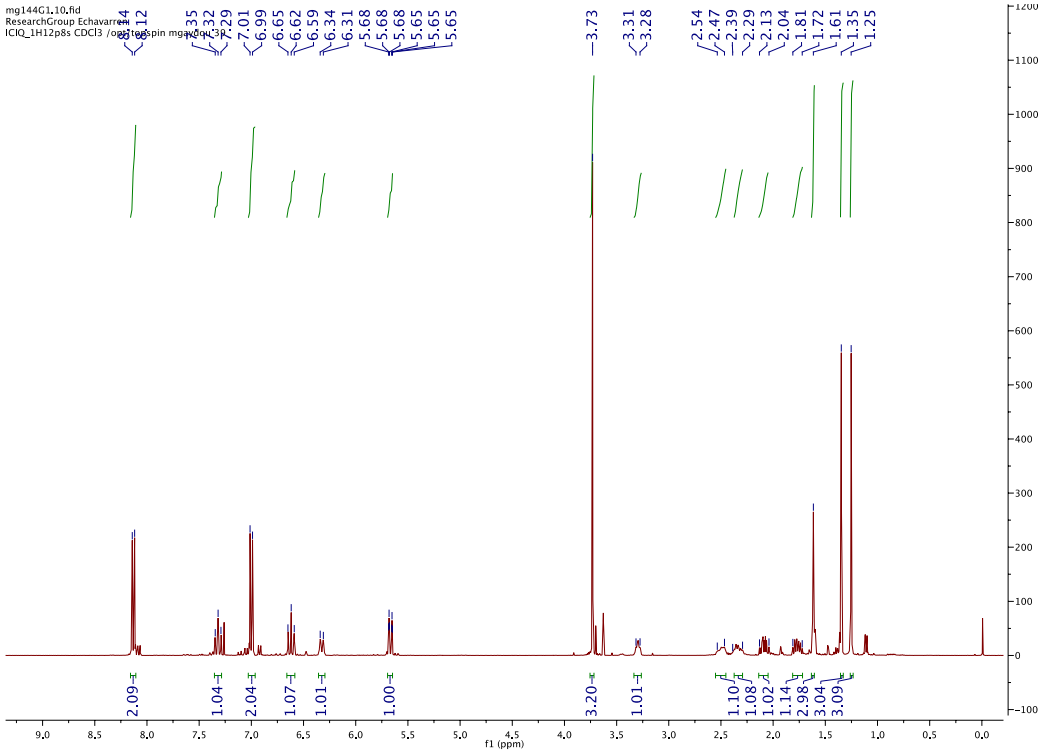
16.36
f1 (ppm)


OPNP
MeO2C

12e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ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin mgavdu_3p
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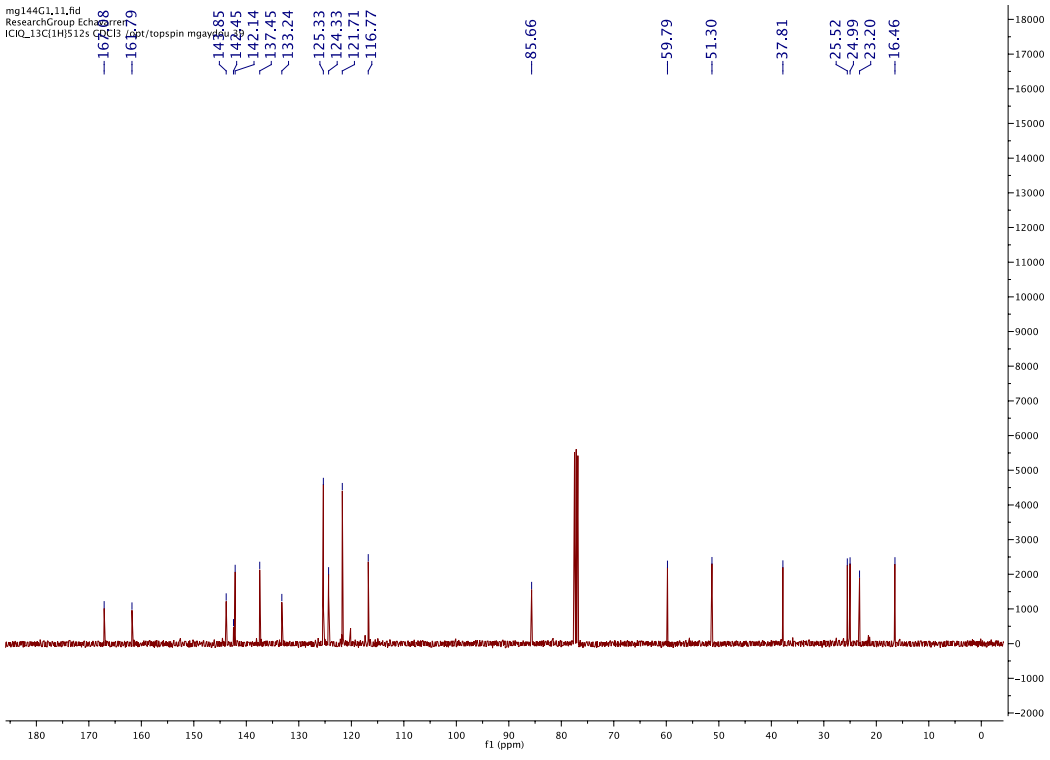
7.32
7.29
7.01
6.99
6.65
6.62
6.59
6.34
6.31
5.68
5.68
5.68
5.65
5.65
5.65
3.73
3.31
3.28
2.54
2.47
2.39
2.29
2.13
2.04
1.81
1.72
1.61
1.35
1.25
2.09
1.04
2.04
1.07
1.01
1.00
3.20
1.01
1.10
1.08
1.02
1.14
2.98
3.04
3.09
f1 (ppm)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ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin mgavdu_2p
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145.85
142.45
142.14
137.45
133.24
125.33
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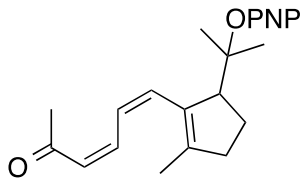
16.46
f1 (ppm)


OPNP
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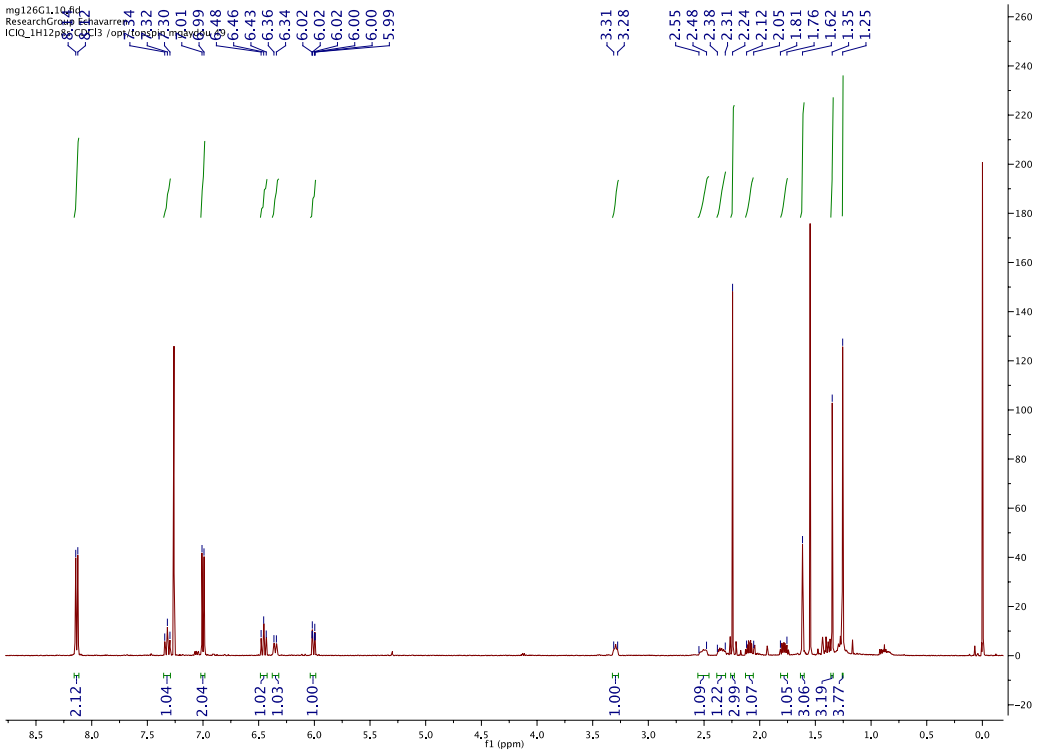
12f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6.43
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6.34
6.02
6.02
6.02
6.00
6.00
5.99
3.31
3.28
2.55
2.48
2.38
2.31
2.24
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1.76
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1.25
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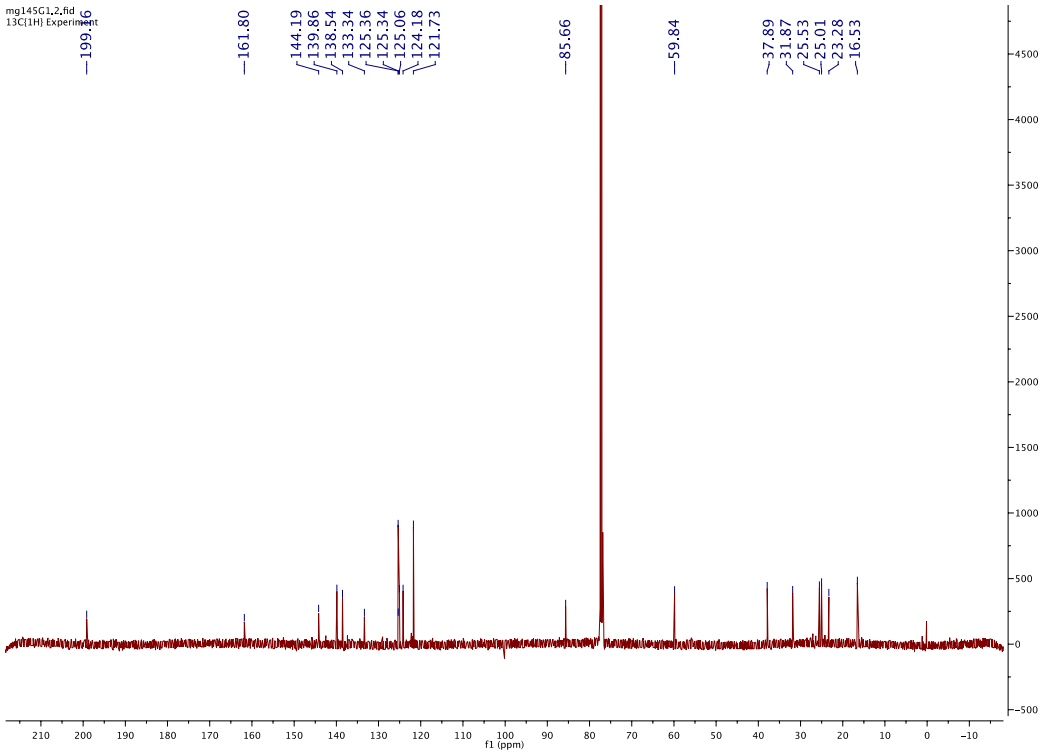
f1 (ppm)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13C{1H} Experiment
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139.86
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125.36
125.34
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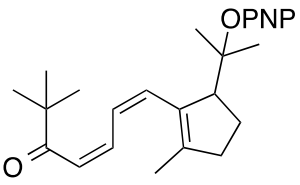
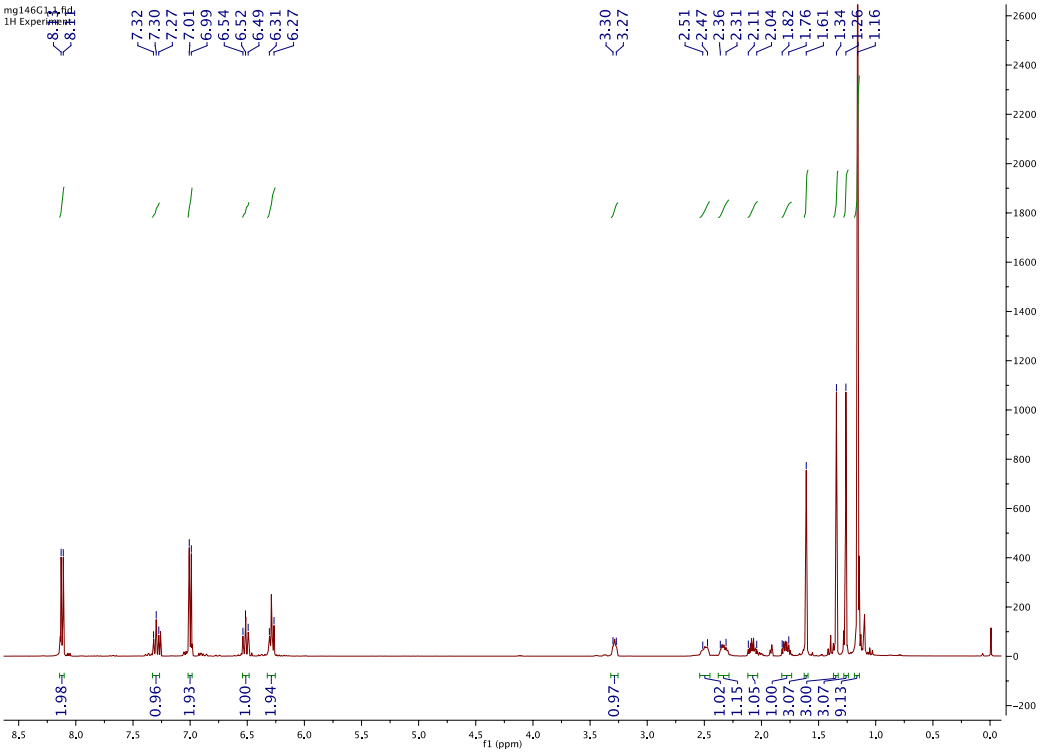
25.01
23.28
16.53
f1 (ppm)


OPNP
O

12g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1H Experiment
8.41
8.41
7.32
7.30
7.27
7.01
6.99
6.54
6.52
6.49
6.31
6.27
3.30
3.27
2.51
2.47
2.36
2.31
2.11
2.04
1.82
1.76
1.61
1.34
1.26
1.16
1.98
0.96
1.93
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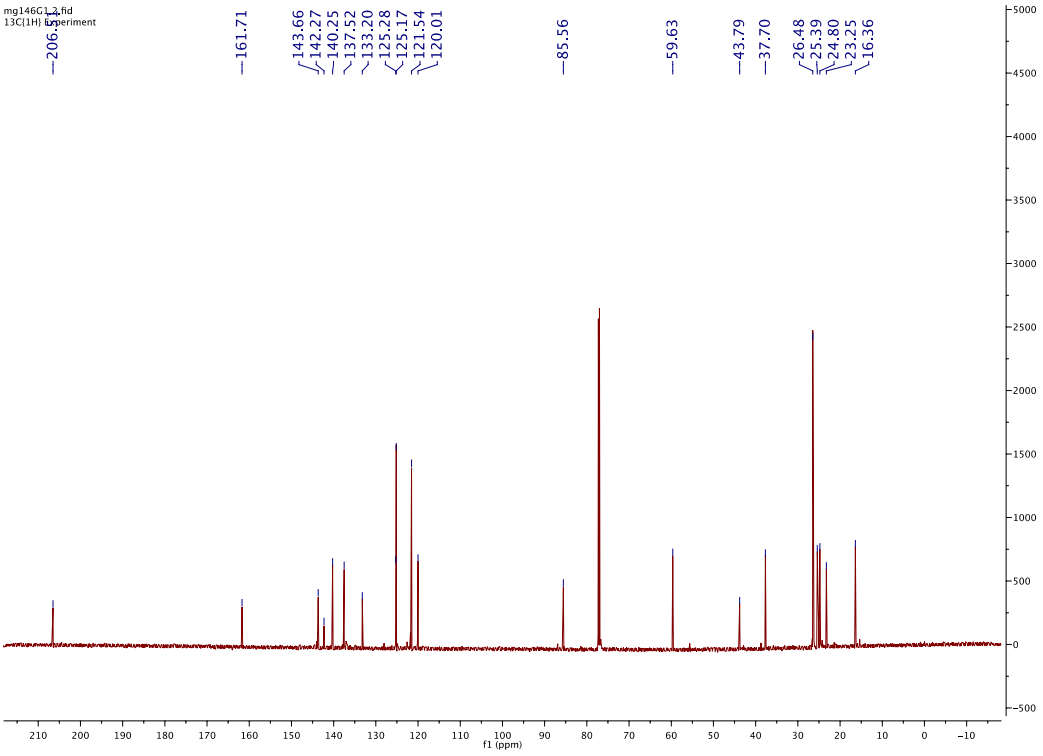
1.94
0.97
1.02
1.15
1.05
1.00
3.07
3.00
3.07
9.13
f1 (ppm)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13C{1H} Experiment
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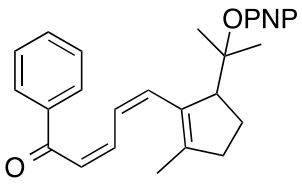
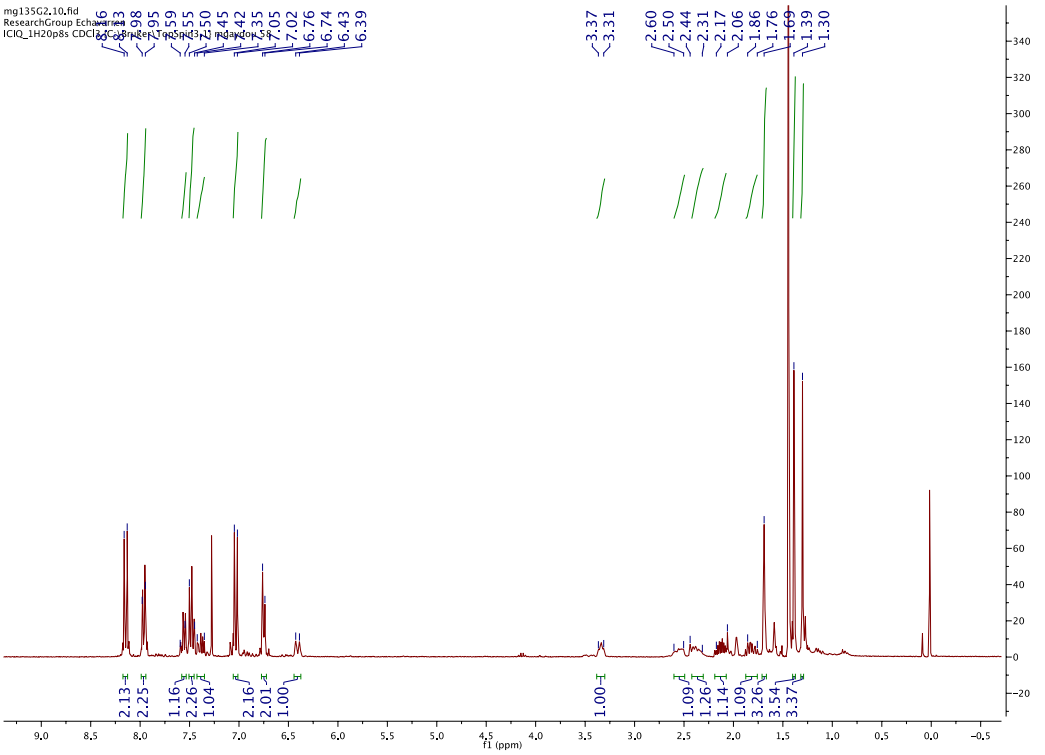
161.71
143.66
142.27
140.25
137.52
133.20
125.28
125.17
121.54
120.01
85.56
59.63
43.79
37.70
26.48
25.39
24.80
23.25
16.36
f1 (ppm)


OPNP
O

12h


mg135G2.10.fid
ResearchGroup Echavarren
ICIQ_1H20p8s CDCl3 /Co Bruker Top5nid3+1 mdavdon 58
7.46
7.43
7.98
7.95
7.59
7.55
7.50
7.45
7.42
7.35
7.05
7.02
6.76
6.74
6.43
6.39
3.37
3.31
2.60
2.50
2.44
2.31
2.17
2.06
1.86
1.76
1.69
1.39
1.30
2.13
2.25
1.16
2.26
1.04
2.16
2.01
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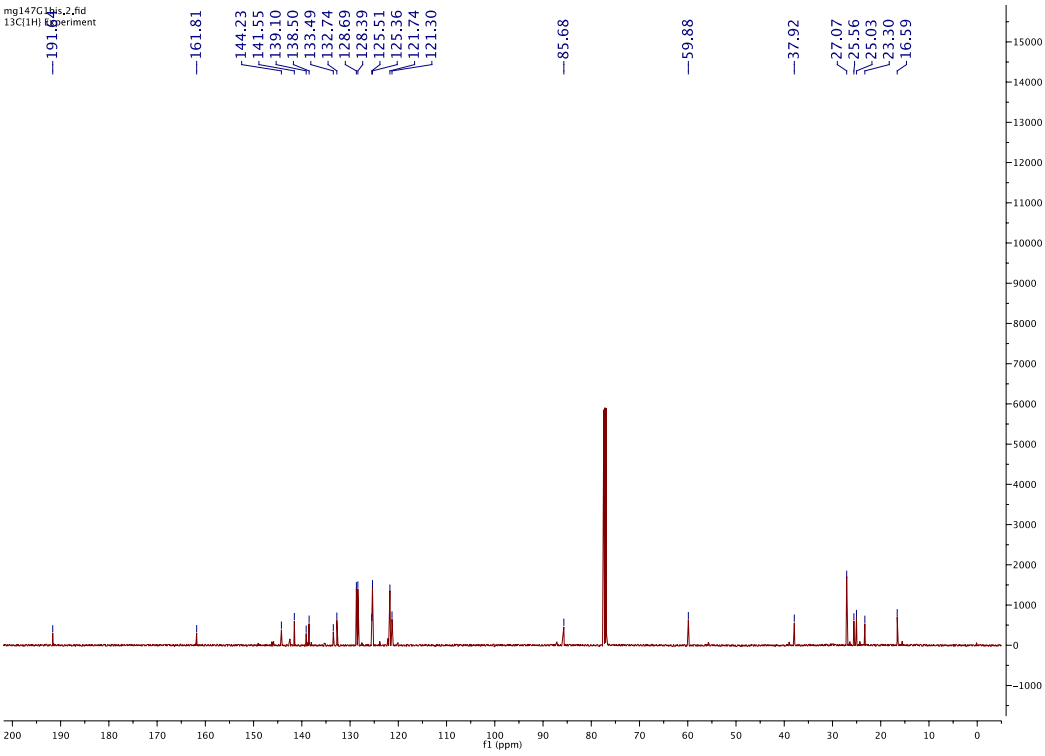
1.00
1.09
1.26
1.14
1.09
3.26
3.54
3.37
f1 (ppm)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13C{1H} Experiment
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144.23
141.55
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133.49
132.74
128.69
128.39
125.51
125.36
121.74
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85.68
59.88
37.92
27.07
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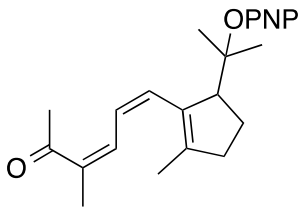
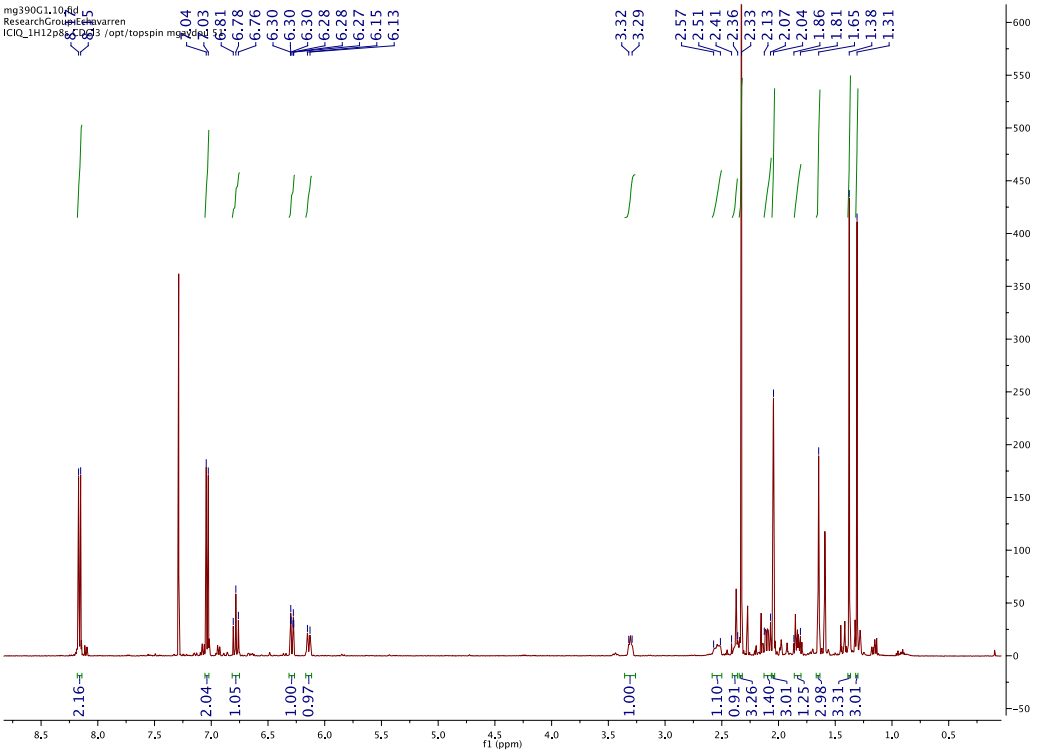
25.03
23.30
16.59
f1 (ppm)


OPNP
O

12i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6.15
6.13
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1.86
1.81
1.65
1.38
1.31
2.16
2.04
1.05
1.00
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0.91
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1.25
2.98
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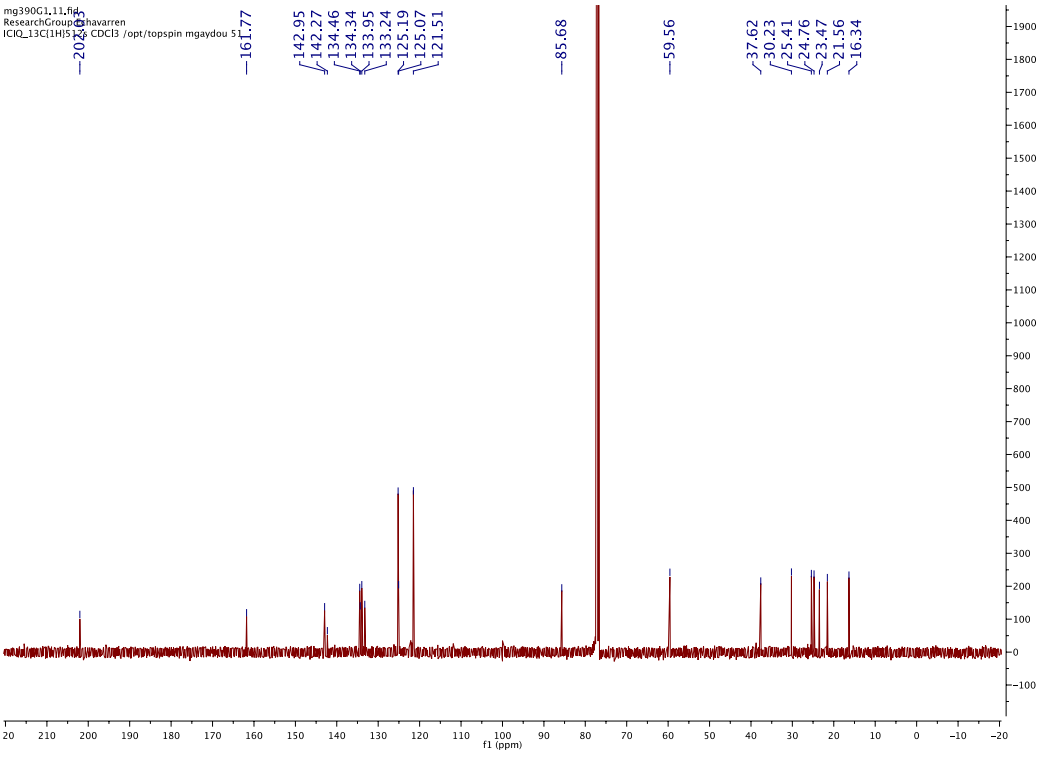
3.01
f1 (ppm)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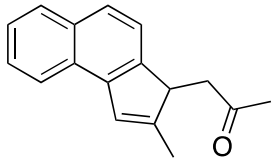
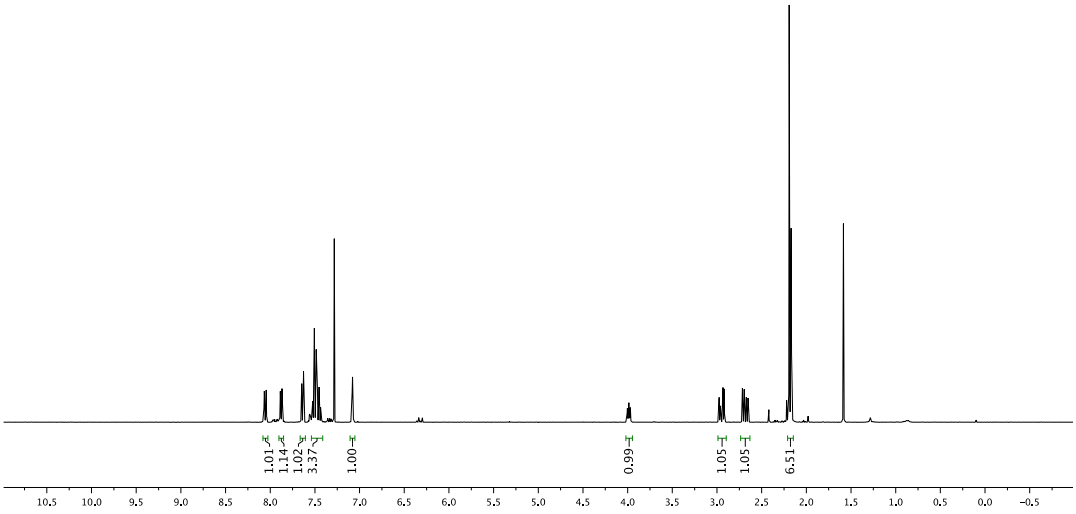
23.47
21.56
16.34
f1 (ppm)

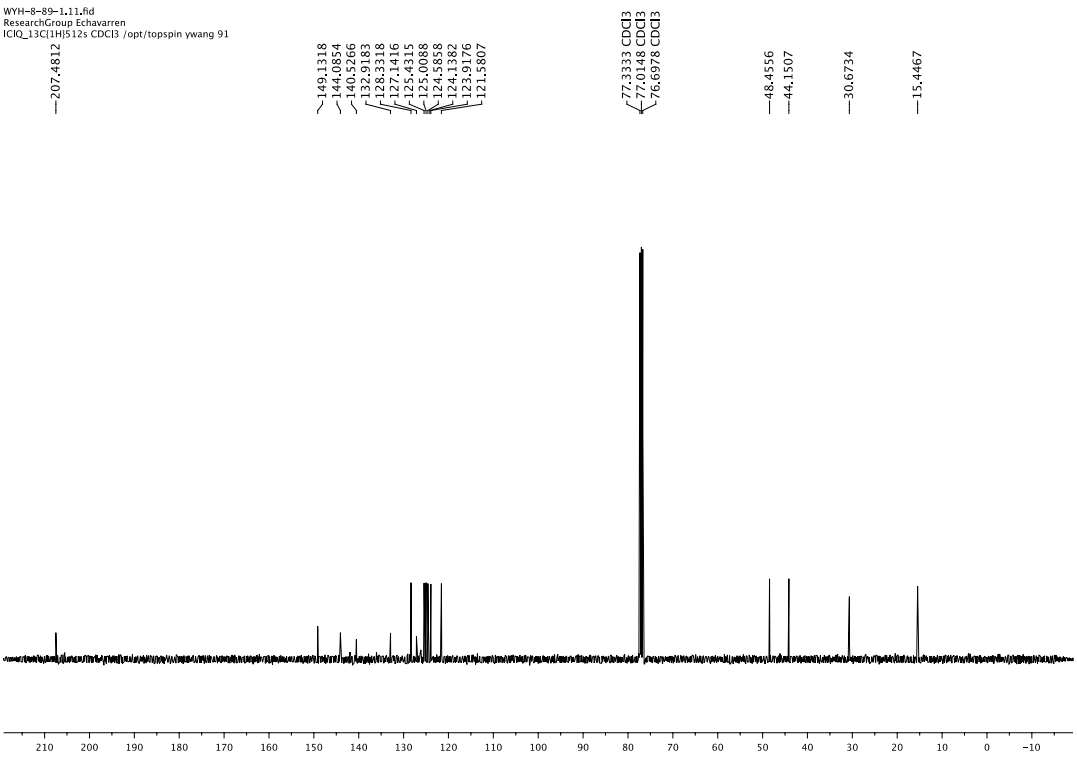


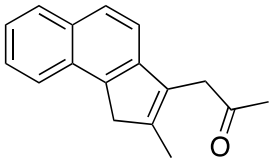
19a

WYH-8-89-1.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 91



WYH-8-89-1.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywang 91





19a’

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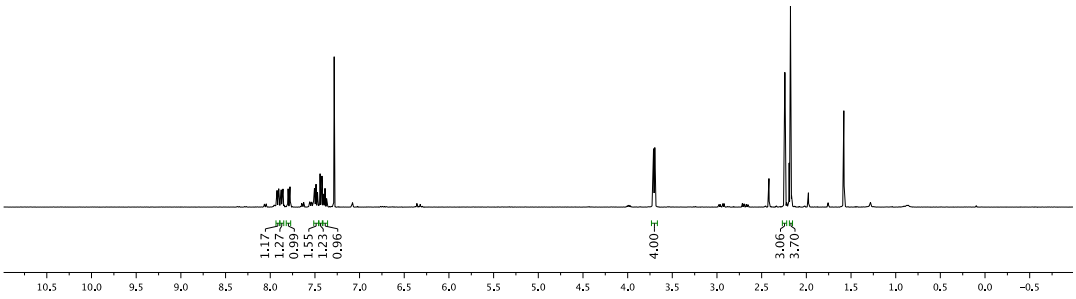
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 92



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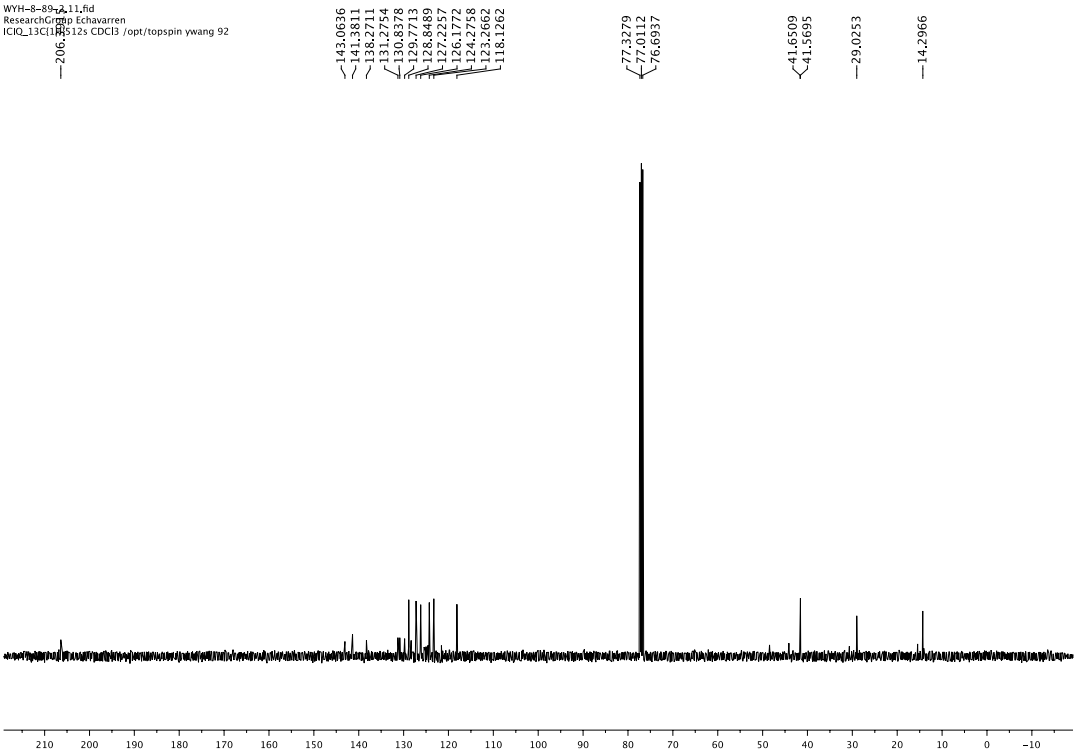
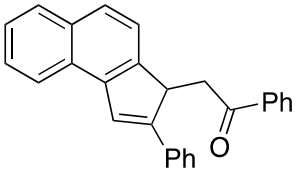
ResearchGroup Echavarren
ICIQ_13C(1H)512s CDCl3 /opt/topspin ywang 92





19b

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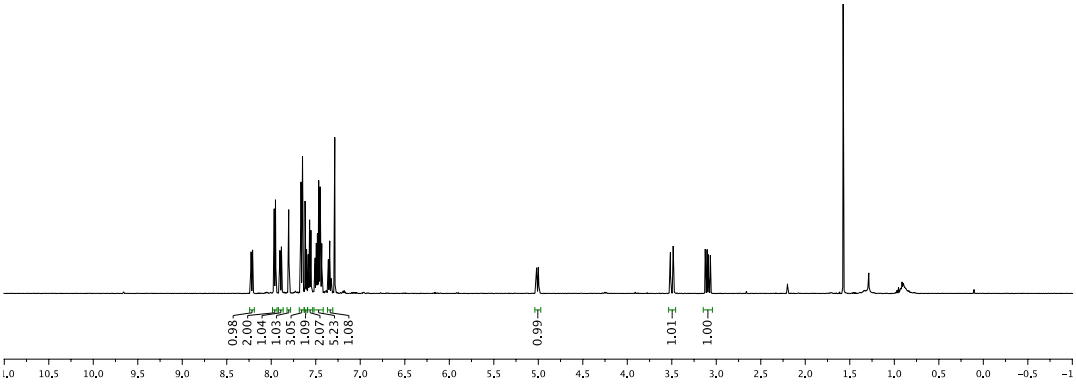
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 21



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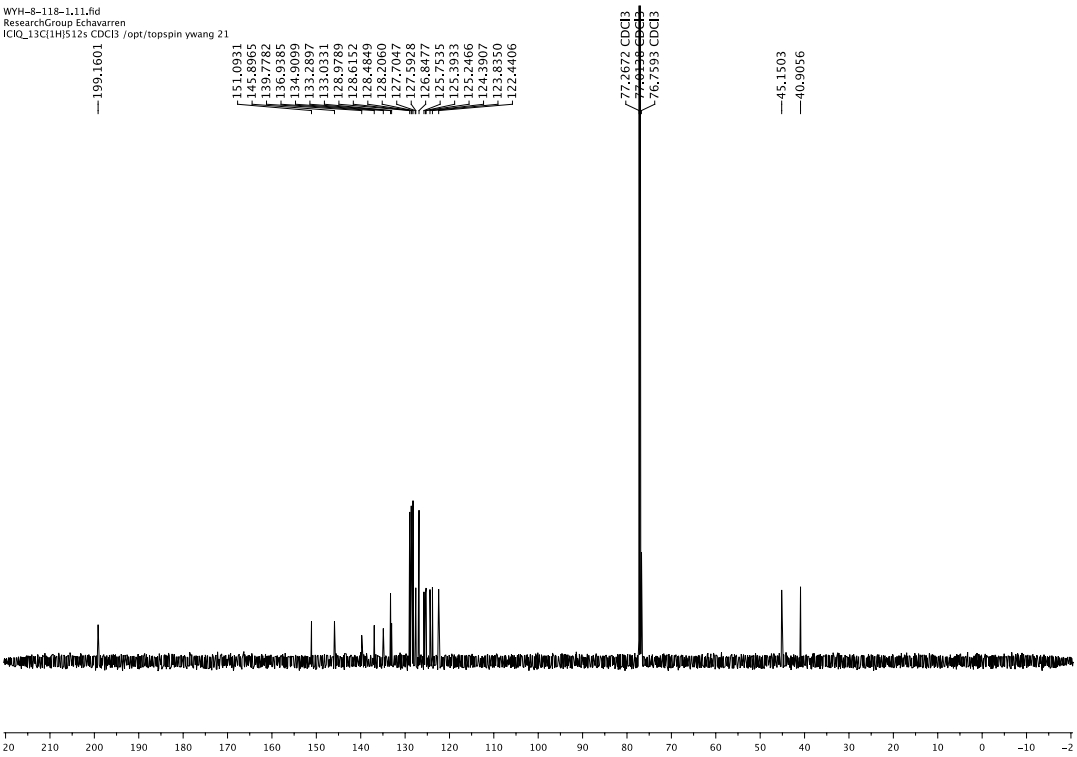
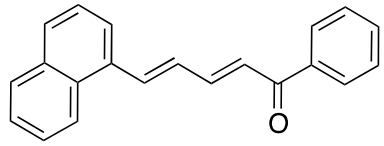
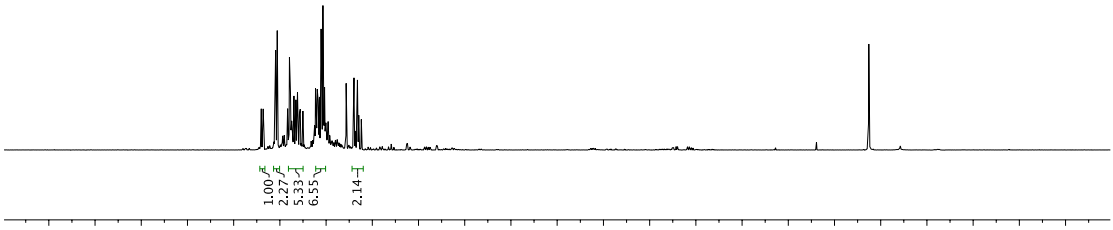
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywang 21





20a

WYH-8-156.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 103



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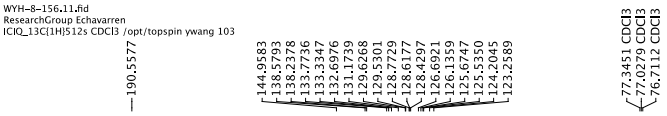
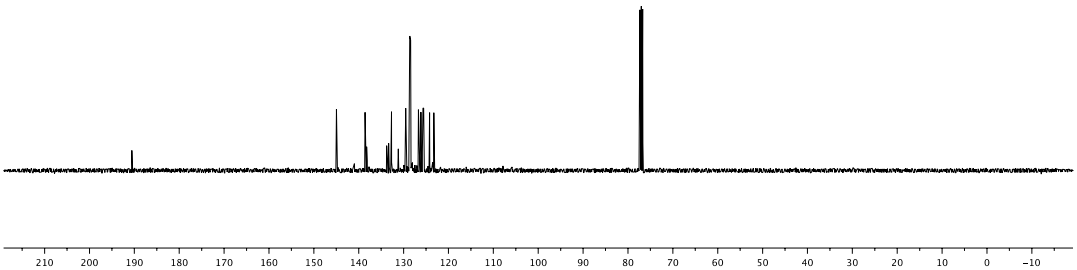
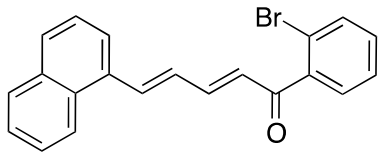
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywang 103

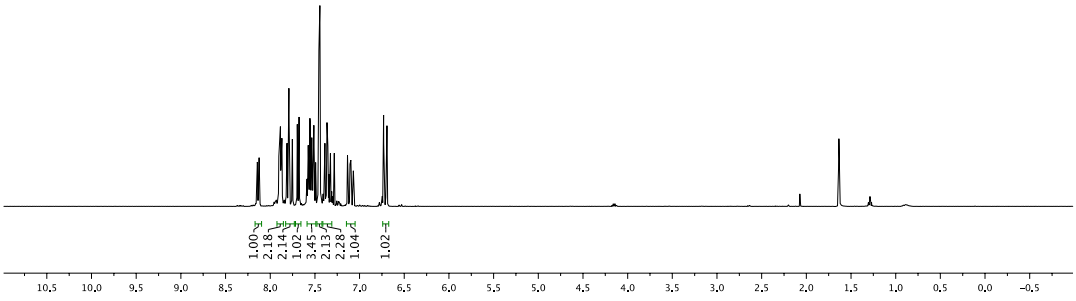






20b

WYH-8-135.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 118



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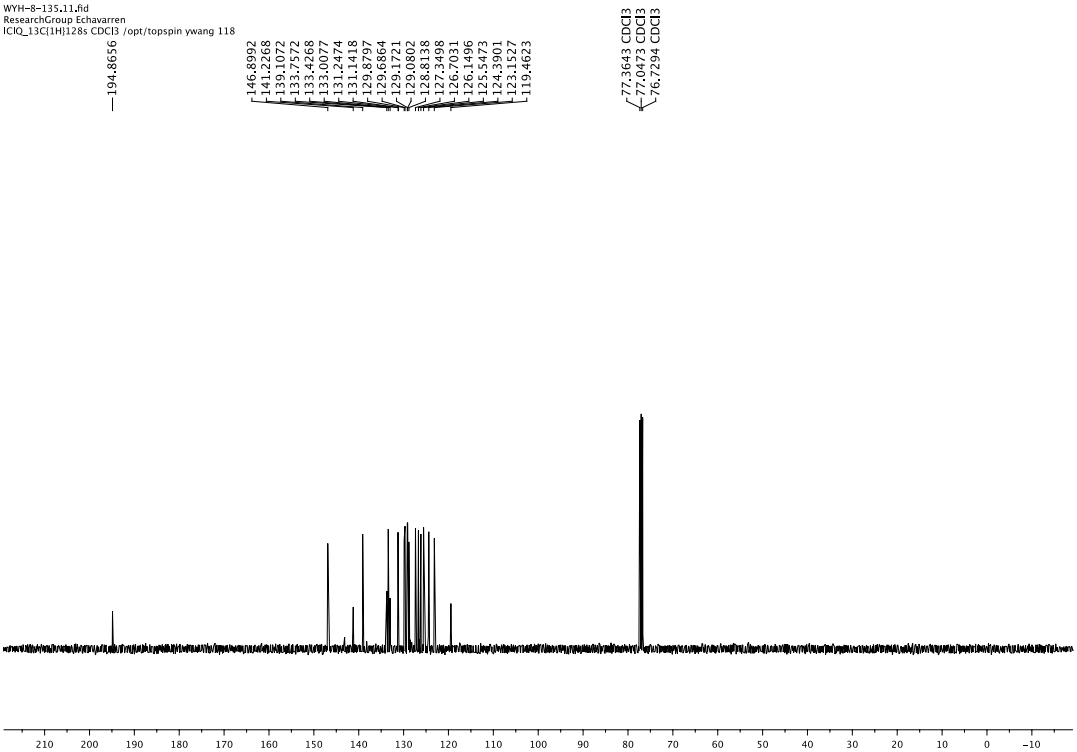
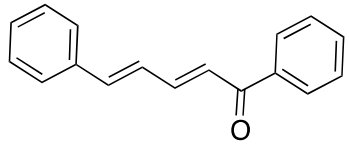
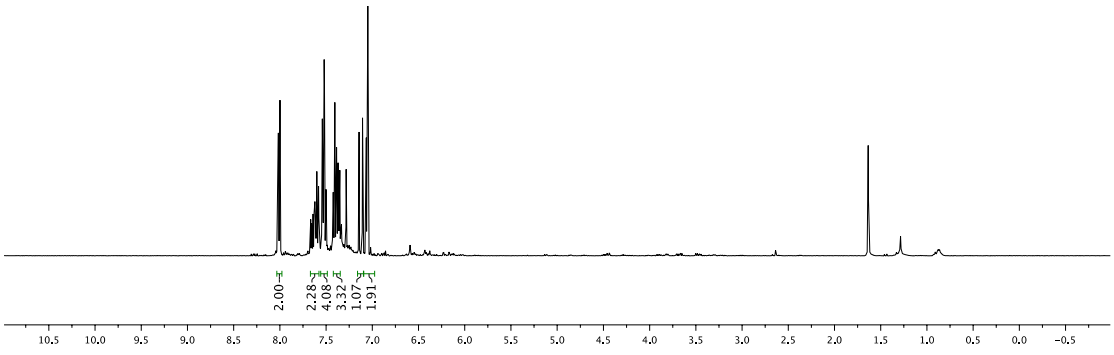
ICIQ_13C{1H}128s CDCl3 /opt/topspin ywang 118



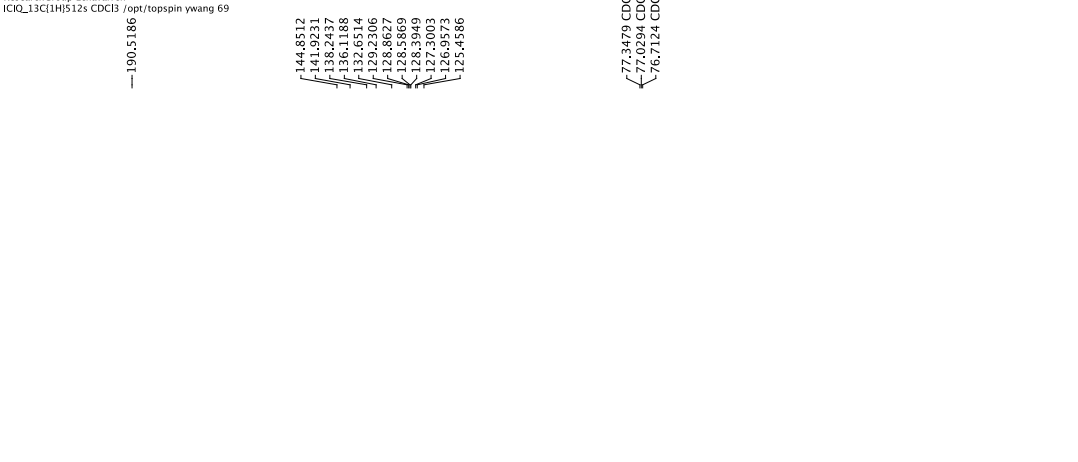


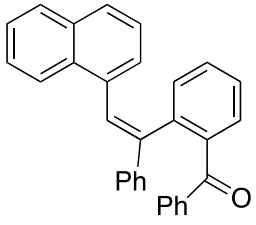
20c

WYH-8-159-2.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 69



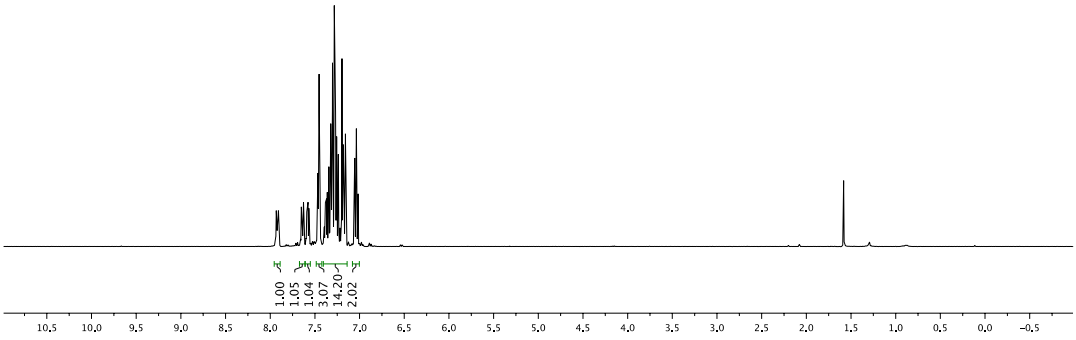
WYH-8-159-2.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywang 69





21

WYH-8-98-1.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin ywang 67



WYH-8-98-1.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywang 67

196.2154
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136.1230
134.8914
133.2850
132.5318
132.3893
132.0615
130.1352
129.6900
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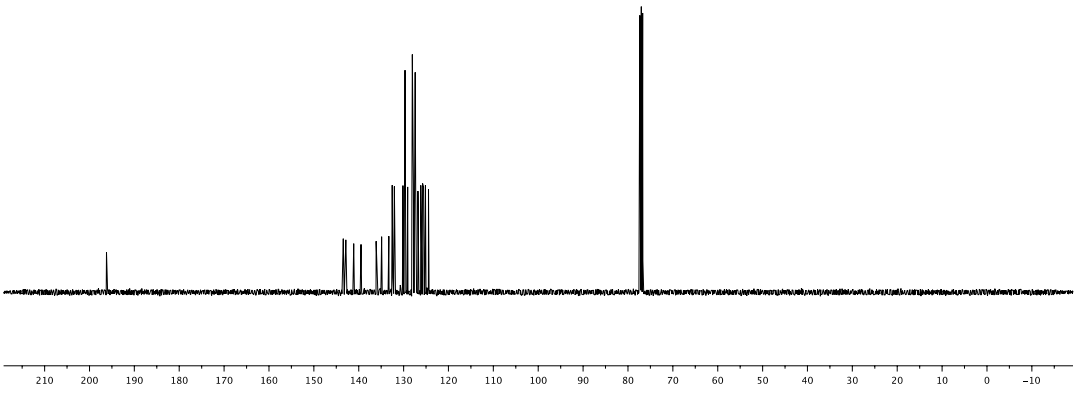
77.0357 CDCl3
76.7184 CDCl3



Computational details

All reported calculations were performed by the means of the Gaussian 09 suite of programs.[13] Density Functional Theory (DFT) was applied using the Meta-Hybrid Generalised Gradient Approximation (MH-GGA) M06 functional.[14] The SDD basis set and ECP was used to describe Au[15] while 6-31+G(d) was used for all remaining atoms.[16] Full geometry optimizations were performed in 1,2-dichloroethane, through an implicit solvent PCM model.[17] The nature of the stationary points as minima or transition states was confirmed by inspection of frequencies. All reported energies are free energies in solution, computed at 298 K and 1 atm.

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Cartesian coordinates

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22b + **2a**, Energy: -737432.2450085

C	-0.74314	-0.18408	-1.11178
C	-1.84125	-0.95712	-0.66797
C	-3.03279	-1.02603	-1.43782
C	-1.77473	-1.70138	0.53820
C	-4.08504	-1.83090	-1.04425
H	-3.09814	-0.44234	-2.35652
C	-2.83809	-2.49052	0.94168
H	-0.86220	-1.64753	1.13310
C	-3.98737	-2.55816	0.14827
H	-4.98717	-1.89260	-1.64889
H	-2.78083	-3.06085	1.86623
H	-4.81914	-3.18766	0.46090
C	-3.15028	1.27579	1.22283
C	-1.91005	1.39273	1.78481
C	-1.07306	1.97906	0.79951
C	-1.85448	2.19097	-0.31361
O	-3.12478	1.77702	-0.04948
H	-1.63766	1.07677	2.78546
H	-0.02844	2.25674	0.89345
C	-1.63585	2.91987	-1.58218
H	-2.02612	3.94532	-1.52091
H	-0.56381	2.97794	-1.80395
H	-2.14340	2.42773	-2.42221
C	-4.44266	0.76293	1.71475
H	-4.35707	0.48745	2.77110
H	-5.23422	1.51667	1.61252
H	-4.76334	-0.12863	1.15437
H	-0.94503	0.34194	-2.05384
Au	1.18423	-0.15347	-0.39254
P	3.41717	-0.13120	0.40441
C	3.59200	0.56956	2.08028
H	3.00649	-0.02243	2.79292
H	4.64671	0.56132	2.38560
H	3.22136	1.60105	2.09490
C	4.59331	0.82816	-0.60649
H	5.59899	0.76448	-0.17031
H	4.61819	0.43020	-1.62711
H	4.28444	1.87873	-0.64732
C	4.18754	-1.77982	0.53001
H	5.20170	-1.68879	0.94107
H	3.58930	-2.42349	1.18471
H	4.24144	-2.24255	-0.46187

42
TS1, Energy: -737431.2092665

C	0.81752	-0.02397	-0.87077
C	1.83846	0.91988	-0.51733
C	3.02382	1.01406	-1.27926
C	1.68808	1.78660	0.59000
C	3.99505	1.96087	-0.97855
H	3.16207	0.33707	-2.12314
C	2.66224	2.71980	0.90030

H	0.78311	1.70827	1.19465
C	3.81546	2.81021	0.11208
H	4.89577	2.03087	-1.58569
H	2.53147	3.38574	1.75095
H	4.57762	3.54955	0.35280
C	3.56097	-1.32853	0.71548
C	2.66324	-1.13958	1.74480
C	1.42578	-1.60709	1.28049
C	1.60314	-2.02222	-0.03597
O	2.94088	-1.89801	-0.33949
H	2.88961	-0.69277	2.70586
H	0.47950	-1.62349	1.81145
C	0.83027	-2.96507	-0.88191
H	1.09581	-4.00386	-0.64405
H	-0.24346	-2.83566	-0.70356
H	1.02930	-2.80280	-1.94798
C	5.01295	-1.08482	0.60190
H	5.58176	-1.96687	0.92738
H	5.29295	-0.86674	-0.43441
H	5.30833	-0.24103	1.23551
H	1.04249	-0.53991	-1.81194
Au	-1.17457	0.05164	-0.29441
P	-3.46751	0.18842	0.28128
C	-3.89546	-0.47585	1.92606
H	-3.33789	0.05947	2.70291
H	-4.97180	-0.35846	2.10988
H	-3.63632	-1.53935	1.97826
C	-4.58866	-0.69352	-0.85571
H	-5.62893	-0.57466	-0.52502
H	-4.48466	-0.28862	-1.86878
H	-4.33772	-1.76003	-0.87769
C	-4.11968	1.89182	0.30939
H	-5.18519	1.88337	0.57451
H	-3.56946	2.48994	1.04448
H	-3.99711	2.35232	-0.67747

42

23b, Energy: -737427.3493428

C	0.99286	-0.15736	-0.77572
C	1.67199	1.11521	-0.37029
C	2.43735	1.81098	-1.31494
C	1.58142	1.64870	0.92297
C	3.09251	2.99503	-0.98238
H	2.52301	1.40991	-2.32631
C	2.24446	2.82477	1.26355
H	0.96576	1.14545	1.67104
C	3.00237	3.50529	0.31110
H	3.67824	3.51763	-1.73763
H	2.15539	3.22014	2.27472
H	3.51372	4.42998	0.57419
C	3.91788	-1.57514	0.30960
C	3.12502	-1.60343	1.52843
C	1.82353	-1.49446	1.22687
C	1.48348	-1.40016	-0.21420
O	2.95599	-1.48093	-0.65782
H	3.55377	-1.69695	2.52113

H	1.01737	-1.49938	1.95902
C	0.99788	-2.69705	-0.81307
H	1.71697	-3.50425	-0.63475
H	0.04927	-2.98415	-0.34282
H	0.83295	-2.58486	-1.89032
C	5.39371	-1.63632	0.29520
H	5.73176	-2.52651	0.84136
H	5.78223	-1.64907	-0.72545
H	5.79472	-0.76817	0.83609
H	0.95320	-0.25590	-1.87012
Au	-1.11651	-0.11186	-0.24432
P	-3.40781	0.06358	0.25263
C	-3.88582	-0.57268	1.89405
H	-3.34133	-0.03371	2.67751
H	-4.96493	-0.43799	2.04729
H	-3.64284	-1.63865	1.96691
C	-4.49803	-0.82786	-0.90568
H	-5.54689	-0.69885	-0.60709
H	-4.36191	-0.43621	-1.92009
H	-4.25190	-1.89567	-0.90629
C	-4.04267	1.77257	0.23608
H	-5.11447	1.77557	0.47479
H	-3.50600	2.37696	0.97589
H	-3.89195	2.21662	-0.75424

42

TS2, Energy: -737444.9971744

C	0.98486	-0.15590	-0.76929
C	1.65828	1.12051	-0.36643
C	2.42371	1.81577	-1.31140
C	1.56226	1.65814	0.92472
C	3.07368	3.00333	-0.98117
H	2.51357	1.41152	-2.32114
C	2.22013	2.83777	1.26302
H	0.94639	1.15526	1.67286
C	2.97818	3.51773	0.31028
H	3.65959	3.52543	-1.73664
H	2.12688	3.23631	2.27257
H	3.48548	4.44516	0.57155
C	3.91200	-1.55933	0.32888
C	3.11592	-1.58627	1.54564
C	1.81487	-1.48305	1.24017
C	1.47842	-1.39496	-0.20213
O	3.24738	-1.48735	-0.72938
H	3.54230	-1.67482	2.53982
H	1.00675	-1.48835	1.97015
C	0.99913	-2.69566	-0.79781
H	1.72064	-3.49963	-0.61475
H	0.05029	-2.98457	-0.32916
H	0.83674	-2.58780	-1.87590
C	5.38807	-1.61523	0.31870
H	5.72783	-2.50230	0.86886
H	5.77941	-1.63010	-0.70084
H	5.78448	-0.74377	0.85766
H	0.94853	-0.25836	-1.86344
Au	-1.12611	-0.11618	-0.24378

P	-3.41937	0.05270	0.24633
C	-3.89956	-0.57961	1.88865
H	-3.35916	-0.03597	2.67171
H	-4.97956	-0.44829	2.03849
H	-3.65294	-1.64443	1.96587
C	-4.50321	-0.84668	-0.91183
H	-5.55333	-0.72043	-0.61653
H	-4.36574	-0.45805	-1.92722
H	-4.25323	-1.91359	-0.90807
C	-4.06034	1.75931	0.22214
H	-5.13279	1.75927	0.45792
H	-3.52787	2.36819	0.96130
H	-3.90852	2.20048	-0.76931

42

24b-AuL, Energy: -737303.5951507

C	1.05073	-0.30471	-1.00904
C	1.75097	0.91674	-0.55623
C	2.57060	1.57015	-1.48554
C	1.64946	1.44347	0.73884
C	3.29610	2.70133	-1.12290
H	2.65220	1.17215	-2.49752
C	2.36376	2.58195	1.09702
H	0.99621	0.96923	1.47245
C	3.19506	3.21042	0.17009
H	3.93798	3.18802	-1.85519
H	2.26590	2.98402	2.10417
H	3.75525	4.10010	0.45280
C	3.84855	-1.39768	0.50625
C	2.72168	-1.71541	1.42121
C	1.43801	-1.73916	1.03957
C	0.94994	-1.50980	-0.34044
O	3.78663	-1.64173	-0.69044
H	2.96563	-1.89336	2.46962
H	0.67638	-2.00101	1.77896
C	0.51315	-2.76121	-1.04595
H	1.40536	-3.38101	-1.21995
H	-0.17696	-3.35329	-0.43107
H	0.04049	-2.54782	-2.01151
C	5.04854	-0.76629	1.14171
H	5.49952	-1.46323	1.86238
H	5.78819	-0.49467	0.38333
H	4.75270	0.12491	1.71337
H	0.84991	-0.34843	-2.08514
Au	-1.12657	-0.22854	-0.23078
P	-3.32123	0.36243	0.31851
C	-3.62315	0.45137	2.11109
H	-2.94488	1.18022	2.56799
H	-4.66130	0.75777	2.29564
H	-3.44974	-0.52855	2.56905
C	-4.57942	-0.78553	-0.32111
H	-5.57959	-0.42837	-0.04209
H	-4.50975	-0.84672	-1.41257
H	-4.42217	-1.78498	0.09913
C	-3.79847	1.99686	-0.32360
H	-4.82959	2.22236	-0.02093

H	-3.12776	2.76576	0.07511
H	-3.73273	2.00367	-1.41697

42

25, Energy: -737437.1632709

C	1.65086	0.11776	0.33183
Au	-0.73651	-0.29554	-0.07705
P	-3.03231	-0.30633	0.04280
C	-3.81559	-1.56029	-1.01455
H	-3.47935	-2.56000	-0.71860
H	-4.90646	-1.49775	-0.90846
H	-3.54471	-1.39076	-2.06216
C	-3.65076	-0.63161	1.72145
H	-3.28622	0.13998	2.40847
H	-4.74877	-0.62351	1.71666
H	-3.29708	-1.60854	2.06840
C	-3.77393	1.27978	-0.44415
H	-3.50904	1.51628	-1.48049
H	-4.86641	1.21707	-0.35359
H	-3.40115	2.07831	0.20676
H	1.44279	-0.31773	1.31626
C	1.46101	1.59488	0.23094
C	1.24751	2.27210	-0.97614
C	1.50496	2.33530	1.41879
C	1.09076	3.65551	-0.99229
H	1.19450	1.72299	-1.91704
C	1.34457	3.71787	1.40081
H	1.66254	1.81825	2.36589
C	1.13935	4.38467	0.19434
H	0.92650	4.16370	-1.94117
H	1.38110	4.27567	2.33522
H	1.01571	5.46596	0.17850
C	2.48917	-2.69435	0.21737
C	1.45182	-2.35826	-0.56838
C	1.58944	-0.92905	-0.92721
C	2.87354	-0.52688	-0.28702
O	3.36406	-1.65747	0.41207
H	0.64953	-3.01763	-0.88132
H	1.32584	-0.53767	-1.91007
C	3.97424	0.27125	-0.90689
H	4.57550	-0.37450	-1.55716
H	3.58697	1.10088	-1.50555
H	4.62500	0.68716	-0.12740
C	2.84978	-3.96015	0.88776
H	2.11883	-4.74017	0.65356
H	3.84337	-4.29705	0.56472
H	2.88688	-3.82975	1.97693