Supporting Information

An Allenic Pauson−Khand Approach to 6,12-Guaianolides

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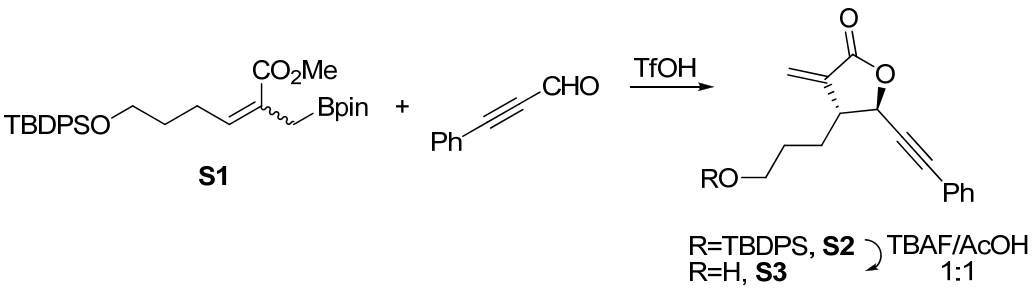
General Methods

Unless otherwise noted, all reactions were performed under N_2 in flame-dried glassware using standard syringe, cannula, and septum techniques. All commercially available compounds were used as received unless otherwise noted. The reaction solvents tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purified by passing through alumina using the Sol-Tek ST-002 solvent purification system. Lithium chloride and cerium (III) trichloride were stored in a glovebox. Toluene and triethylamine (NEt_3) were freshly distilled from CaH_2 prior to use. Flash chromatography was performed using silica gel (32-63 μm particle size, 60 Å pore size). Thin layer chromatography (TLC) analysis was performed using silica gel 60 F_{254} plates (250 μm thickness). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 MHz, 400 MHz, 500 MHz or 700 MHz spectrometers. Spectra were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.0 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) and m (multiplet). Coupling constants, *J*, are reported in hertz. All NMR spectra were obtained at room temperature. IR spectra were obtained using a Nicolet Avatar E.S.P. 360 FT-IR. EI mass spectroscopy was performed on a Micromass Autospec high resolution mass spectrometer.

Experimental Section



4-(3-hydroxypropyl)-3-methylidene-5-(phenylethynyl)dihydrofuran-2(3*H*)-one (S3): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S1** (5.30 g, 10 mmol, *E*:*Z* = 1:2), 3-phenylprop-2-ynal (2.6 g, 20 mmol) and toluene (250 mL) at 0 °C. The resulting solution was treated with trifluoromethanesulfonic acid (150 mg, 1.0 mmol) and stirred at 0 °C under a nitrogen atmosphere for 16 h. The mixture was then diluted with NH_4Cl (aq) : NH_4OH (9:1, v/v, 100 mL) and extracted with Et_2O (3×50 mL). The combined extracts were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded *trans*-lactone **S2** (283 mg, 37%) and c*is*-lactone **S2** (124 mg, 16%) as yellow oils. The two isomers were obtained in a *trans*:*cis* 4.74:1 ratio. Along with the two TBDPS-protected isomers was also obtained a mixture of *cis* and *trans* desilylated lactones **S3** (37.6 mg, 9%) in a *trans*:*cis* 3:1 ratio.

Data for *trans*-lactone **S2** :

^{1}H NMR ($CDCl_3$, 300 MHz)

7.72 − 7.69 (m, 4H), 7.47 − 7.34 (m, 11H), 6.36 (d, *J* = 2.7 Hz, 1H), 5.66 (d, *J* = 2.4Hz, 1H), 4.98 (d, *J* = 5.7 Hz, 1H), 3.81 − 3.76 (m, 2H), 3.24 − 3.20 (m, 1H), 1.91 − 1.90 (m, 1H), 1.80 − 1.70 (m, 3H), 1.10 (s, 9H).

TLC R_f = 0.47 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]

Data for *cis*-lactone **S2** :

^{1}H NMR ($CDCl_3$, 300 MHz)

7.72 − 7.68 (m, 4H), 7.45 − 7.31 (m, 11H), 6.34 (d, *J* = 3.0 Hz, 1H), 5.62 (d, *J* = 2.7 Hz, 1H), 5.46 (d, *J* = 8.4 Hz, 1H), 3.80 − 3.75 (m, 2H), 3.25 − 3.15 (m, 1H), 1.99 − 1.92 (m, 2H), 1.82 − 1.72 (m, 2H), 1.08 (s, 9H).

TLC R_f = 0.37 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]

Trans-lactone **S2** (1.20 g, 2.43 mmol) was charged into a round bottom flask equipped with a Teflon-coated stir-bar, and THF (25 mL) was added. The resulting mixture was then treated with a TBAF/AcOH (1:1, 1.0M, 2.7 mL, 2.7 mmol) solution.[1] The progress of the reaction was monitored by TLC and upon completion (2 h), the mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded the title compound **S3** (400 mg, 63%) as a light yellow oil.

Data for desilylated *trans*-lactone **S3** :

^{1}H NMR (300 MHz, $CDCl_3$)

7.46 − 7.42 (m, 2H), 7.37 − 7.30 (m, 3H), 6.34 (d, J = 2.7 Hz, 1H), 5.69 (d, J = 2.4 Hz, 1H), 4.99 (d, J = 5.4 Hz, 1H), 3.73 (t, J = 6.0 Hz, 2H), 3.24 − 3.20 (m, 1H), 1.91 − 1.88 (m, 2H), 1.79 − 1.73 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz)

169.4, 137.6, 131.8 (2C), 129.2, 128.4 (2C), 123.2, 121.5, 87.9, 85.0, 72.5, 62.1, 46.7, 29.5, 29.2.

IR Thin film

3423, 2937, 2868, 2231, 1769, 1495, 1270, 1127, 984, 760.

MS *m/z* (%) 256 (30), 198 (100), 131 (75), 98 (70), 83 (75).

HRMS EI+: $C_{16}H_{16}O_3$ $[M]^+$

Calculated: 256.1099. Found: 256.1006.

TLC R_f = 0.1 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]

Cis-lactone **S2** (370 mg, 0.75 mmol) was charged into a round bottom flask equipped with a Teflon-coated stir-bar, followed by THF (15 mL). The resulting mixture was then treated with a TBAF/AcOH (1:1, 1.0 M in THF, 0.8 mL, 0.8 mmol) solution.[1] The progress of the reaction was monitored by TLC and upon completion (3 h), the mixture was concentrated under reduced

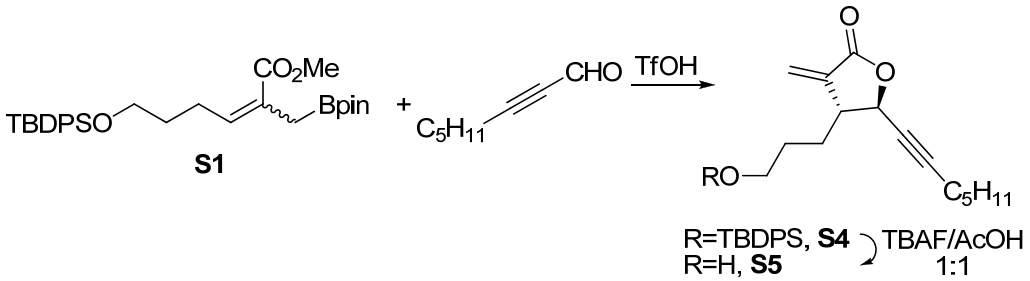
[1] The TBAF/AcOH solution was prepared from a modified procedure reported by Hall : A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with tetra-*n*-butylammonium fluoride (10 mL, 1.0 M solution in THF, 10 mmol), and glacial acetic acid (572 µL, 10 mmol) was added to this solution at rt. The solution was stirred under argon for 30 min.

T. G. Elford, D. G. Hall, *J. Am. Chem. Soc.* **2010**, *132*, 1488-1489.

pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded the title compound **S3** (153 mg, 80%) as a light yellow oil.

Data for desilylated *cis*-lactone **S3** :

^{1}H NMR	($CDCl_3$, 300 MHz)
	7.42 − 7.39 (m, 2H), 7.32 − 7.28 (m, 3H), 6.28 (d, *J* = 3.0 Hz, 1H), 5.63 (d, *J* = 2.7 Hz, 1H), 5.46 (br s, 1H), 3.68 (dt, *J* = 1.5, 6.0 Hz, 2H), 3.23 − 3.14 (m, 1H), 2.91 (s, 1H), 1.91 − 1.86 (m, 2H), 1.74 − 1.69 (m, 2H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	170.0, 137.4, 131.8 (2C), 129.2, 128.5 (2C), 122.7, 121.4, 89.8, 82.2, 71.7, 62.3, 43.0, 29.5, 26.3.
IR	Thin film
	3420, 2938, 2868, 2235, 1769, 1659, 1487, 1266, 968, 760.
HRMS	EI+: $C_{16}H_{16}O_3Na_1$ $[M+Na]^+$
	Calculated: 279.0997. Found: 279.1016.
TLC	R_f = 0.15 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]

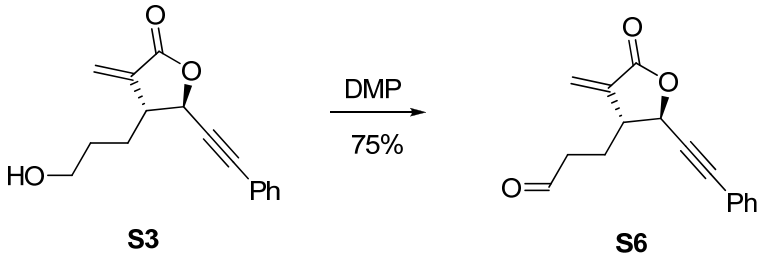


5-(hept-1-yn-1-yl)-4-(3-hydroxypropyl)-3-methylidenedihydrofuran-2(3*H*)-one (S5): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S1** (1.0 g, 1.9 mmol, *E*:*Z* = 1:1.5), oct-2-ynal (473 mg, 3.8 mmol) and toluene (50 mL) at 0 °C. The resulting solution was treated with trifluoromethanesulfonic acid (25 mg, 0.16 mmol) and stirred at 0 °C, using a large Dewar filled with ice, under a nitrogen atmosphere for 14 h. The mixture was then diluted with NH_4Cl (aq) : NH_4OH (9:1, v/v, 50 mL) and extracted with Et_2O (3×25 mL). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The two isomers were obtained in a *trans*:*cis* 1.65:1 ratio, as judged by crude ^{1}H NMR. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded *trans*-

lactone **S4** (320 mg, 34%) and c*is*-lactone **S4** (160 mg, 17%) as yellow oils. Along with the two TBDPS-protected isomers was also obtained a mixture of *cis* and *trans* desilylated lactones **S5** (100 mg, 21%) in a *trans*:*cis* 2.5:1 ratio. *Trans*-TBDPS-protected lactone **S4** (300 mg, 0.62 mmol) was charged into a round bottom flask equipped with a Teflon-coated stir-bar and THF (5 mL) was added. The resulting mixture was then treated with a TBAF/AcOH (1:1, 1.0 M in THF, 0.68 mL, 0.68 mmol) solution.[1] The progress of the reaction was monitored by TLC and upon completion (3 h), the mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded the title compound **S5** (60 mg, 65%) as a brown oil.

Data for desilylated *trans*-lactone **S5** :

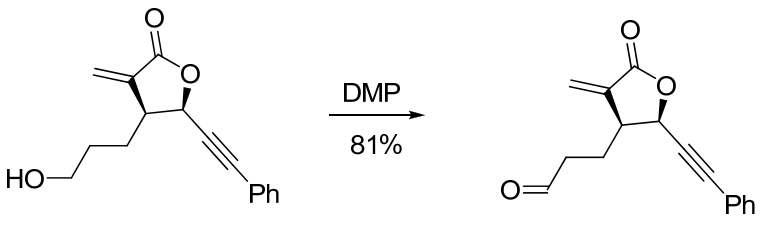
^{1}H NMR	($CDCl_3$, 300 MHz)
	6.29 (d, J = 3.0 Hz, 1H), 5.66 (d, J = 2.4 Hz, 1H), 4.76 (dt, J = 2.1, 5.7 Hz, 1H), 3.70 (t, J = 6.0 Hz, 2H), 3.10 − 3.00 (m, 1H), 2.75 (br s, 1H), 2.2 (dt, J = 1.8, 6.9 Hz, 2H), 1.86 − 1.83 (m, 1H), 1.73 − 1.64 (m, 3H), 1.54 − 1.49 (m, 2H), 1.36 − 1.30 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	169.6, 137.9, 122.7, 89.5, 76.5, 72.6, 62.0, 46.9, 30.9, 29.4, 29.1, 27.9, 22.1, 18.6, 13.9.
IR	Thin film
	3420, 2929, 2864, 2235, 1773, 1401, 1266, 1127, 972, 813.
MS	*m/z* (%) 250 (15), 126 (100), 98 (55), 69 (56).
HRMS	EI+: $C_{15}H_{22}O_3$ $[M]^+$
	Calculated: 250.1569. Found: 250.1564.
TLC	R_f = 0.1 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]



S3 **S6**

3-[4-methylidene-5-oxo-2-(phenylethynyl)tetrahydrofuran-3-yl]propanal (S6): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S5** (400 mg, 1.56 mmol) and CH_2Cl_2 (30 mL). The resulting solution was treated with Dess-Martin periodinane (728 mg, 1.72 mmol). The progress of the reaction was monitored by TLC and upon completion (3 h), the mixture was concentrated under reduced pressure and purified by flash chromatography (80% Et_2O/hexanes) to afford the title compound **S6** (300 mg, 75%) as a slightly yellow oil.

^{1}H NMR	($CDCl_3$, 300 MHz)
	9.82 (br s, 1H), 7.43 − 7.40 (m, 2H), 7.34 − 7.30 (m, 3H), 6.35 (d, J = 2.7 Hz, 1H), 5.67 (d, J = 2.7 Hz, 1H), 4.93 (d, J = 6.0 Hz, 1H), 3.24 − 3.20 (m, 1H), 2.69 (t, J = 7.5 Hz, 2H), 2.17 − 2.12 (m, 1H), 2.10 − 2.07 (m, 1H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	200.6, 168.9, 137.0, 131.8 (2C), 129.3, 128.4 (2C), 123.4, 121.2, 88.2, 84.7, 72.2, 46.0, 40.2, 24.5.
IR	Thin film
	3524, 2933, 2827, 2729, 2230, 1773, 1716, 1442, 1270, 1131, 972.
HRMS	EI+: $C_{16}H_{14}O_3Na_1$ $[M+Na]^+$
	Calculated: 277.0841. Found: 277.0823.
TLC	R_f = 0.35 (33:33:33, Et_2O/CH_2Cl_2/hexanes) [silica gel, UV, $KMnO_4$ stain]



S3 **S6**

3-[4-methylidene-5-oxo-2-(phenylethynyl)tetrahydrofuran-3-yl]propanal (S6): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S3** (150 mg, 0.59 mmol) and CH_2Cl_2 (5 mL). The resulting solution was treated with Dess-Martin periodinane (300 mg, 0.7 mmol). The progress of the reaction was monitored by TLC and upon completion (2 h), the mixture was concentrated under reduced pressure and purified by flash

chromatography (80% Et_2O/hexanes) to afford the title compound **S6** (120 mg, 81%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

9.83 (t, *J* = 0.9 Hz, 1H), 7.43 − 7.40 (m, 2H), 7.37 − 7.31 (m, 3H), 6.35 (d, *J* = 2.7 Hz, 1H), 5.69 (d, *J* = 2.7 Hz, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 3.31 − 3.23 (m, 1H), 2.69 (t, *J* = 8.4 Hz, 2H), 2.17 (q, *J* = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz)

200.9, 169.2, 137.0, 131.8 (2C), 129.4, 128.5 (2C), 123.2, 121.2, 90.3, 81.8, 71.1, 42.0, 40.6, 22.3.

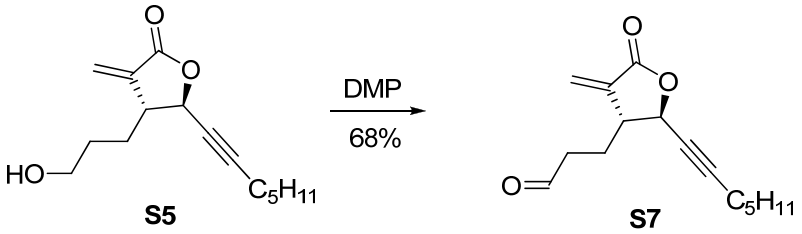
IR Thin film

2921, 2827, 2725, 2238, 1761, 1708.

HRMS EI+: $C_{16}H_{14}O_3Na_1$ $[M+Na]^+$

Calculated: 277.0841. Found: 277.0817.

TLC R_f = 0.3 (33:33:33, Et_2O/CH_2Cl_2/hexanes) [silica gel, UV, $KMnO_4$ stain]

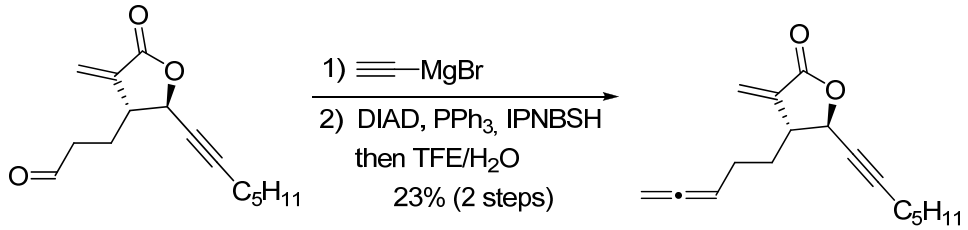


3-[2-(hept-1-yn-1-yl)-4-methylidene-5-oxotetrahydrofuran-3-yl]propanal (S7): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S5** (90 mg, 0.36 mmol) and CH_2Cl_2 (5 mL). The resulting solution was treated with Dess-Martin periodinane (183 mg, 0.43 mmol). The progress of the reaction was monitored by TLC and upon completion (2 h), the mixture was concentrated under reduced pressure and purified by flash chromatography (80% Et_2O/hexanes) to afford the title compound **S7** (60 mg, 68%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

9.83 (br s, 1H), 6.32 (d, *J* = 2.7 Hz, 1H), 5.66 (d, *J* = 2.1 Hz, 1H), 4.72 (dt, *J* = 2.1, 6.0 Hz, 1H), 3.10 − 3.07 (m, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.23

	(dt, J = 2.1, 7.2 Hz, 2H), 2.14 − 2.06 (m, 1H), 1.92 − 1.85 (m, 1H), 1.54 − 1.49 (m, 2H), 1.38 − 1.30 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	200.4, 168.9, 137.4, 122.9, 89.9, 76.2, 72.2, 46.2, 40.2, 31.0, 27.8, 24.5, 22.1, 18.6, 13.9.
IR	Thin film
	2925, 2859, 2717, 2247, 1765, 1728, 1266, 1135, 968, 812.
MS	*m/z* (%) 248 (55), 192 (35), 124 (100), 96 (70), 66 (91).
HRMS	EI+: $C_{15}H_{20}O_3$ $[M]^+$
	Calculated: 248.1412. Found: 248.1412.
TLC	R_f = 0.5 (33:33:33, Et_2O/CH_2Cl_2/hexanes) [silica gel, UV, $KMnO_4$ stain]



S7 **16**

5-(hept-1-yn-1-yl)-3-methylidene-4-(penta-3,4-dien-1-yl)dihydrofuran-2(3*H*)-one (16): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S7** (50 mg, 0.20 mmol) and THF (3 mL) at 0 °C. The resulting solution was treated with ethynyl magnesium bromide (0.5 M in THF, 0.48 mL, 0.24 mmol) and stirred at 0 °C under nitrogen atmosphere for 1 h. The mixture was then diluted with saturated NH_4Cl (aq.) (10 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The propargyl alcohol was not stable to column chromatography, so it was taken on immediately to the next step. The crude product was then charged into a flame-dried 10 mL round bottom flask equipped with a Teflon-coated stir-bar, followed by PPh_3 (63 mg, 0.24 mmol), *N*-isopropylidene-*N*'-2-nitrobenzenesulfonyl hydrazine[2] (62 mg, 0.24 mmol) and THF (3 mL). The resulting solution

[2] This procedure was performed according to the following described procedure :
M. Movassaghi, O. K. Ahmad, *J. Org. Chem.* **2007**, *72*, 1838-1841.

was cooled to 0 °C, stirred under nitrogen and diisopropylazodicarboxylate (50 mg, 0.24 mmol) was added dropwise. After 5 min, the ice/water bath was removed and the reaction was stirred at rt. The progress of the reaction was monitored by TLC and upon completion (19 h), TFE/H_2O (1:1, 3.0 mL) was added. After 4 h, the mixture was diluted with pentane/H_2O (1:1, 10 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded the title compound **16** (12 mg, 23%, 2 steps) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.29 (d, *J* = 2.7 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 5.13 (p, *J* = 6.6 Hz, 1H), 4.76 – 4.71 (m, 3H), 3.11 – 3.08 (m, 1H), 2.22 (dt , *J* = 1.8, 6.9 Hz, 2H), 2.19 – 2.13 (m, 2H), 1.83 – 1.79 (m, 1H), 1.79 – 1.72 (m, 1H), 1.54 – 1.49 (m, 2H), 1.37 – 1.30 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz)

208.7, 169.4, 137.9, 122.6, 89.5, 88.7, 76.6, 75.8, 72.6, 46.4, 32.3, 30.1, 27.9, 24.7, 22.1, 18.7, 14.0.

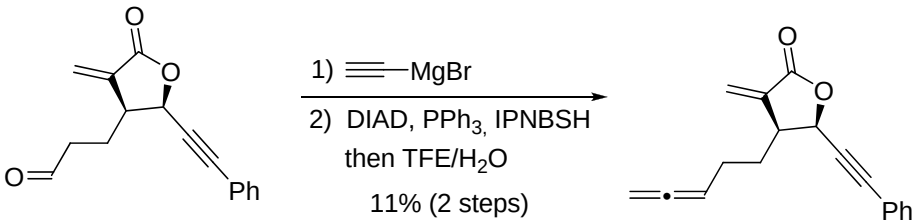
IR Thin film

2925, 2852, 2238, 1956, 1769, 1270, 1127, 976.

HRMS EI+: $C_{17}H_{22}O_2Na_1$ $[M+Na]^+$

Calculated: 281.1517. Found: 281.1528.

TLC R_f = 0.77 (20% Et_2O/hexanes) [silica gel, $KMnO_4$ stain]

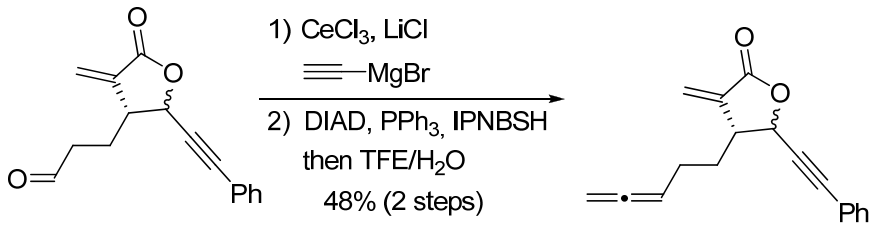


S6 **14**

3-methylidene-4-(penta-3,4-dien-1-yl)-5-(phenylethynyl)dihydrofuran-2(3*H*)-one (14): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S6** (100 mg, 0.39 mmol) and THF (3 mL) at 0 °C. The resulting solution was treated with ethynyl

magnesium bromide (0.5 M in THF, 1.01 mL, 0.51 mmol) and stirred at 0 °C under nitrogen atmosphere for 1 h. The mixture was then diluted with saturated NH_4Cl (aq.) (10 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The propargyl alcohol was not stable to column chromatography, so it was taken on immediately to the next step. The crude product was then charged into a flame-dried 10 mL round bottom flask equipped with a Teflon-coated stir-bar, followed by PPh_3 (98 mg, 0.37 mmol), *N*-isopropylidene-*N*'-2-nitrobenzenesulfonyl hydrazine (96 mg, 0.37 mmol) and THF (5 mL). The resulting solution was cooled to 0 °C, stirred under nitrogen and diisopropylazodicarboxylate (75 mg, 0.37 mmol) was added dropwise. After 5 min, the ice/water bath was removed and the reaction was stirred at rt. The progress of the reaction was monitored by TLC and upon completion (19 h), TFE/H_2O (1:1, 3.0 mL) was added. After 4 h, the mixture was diluted with pentane/H_2O (1:1, 10 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (20% Et_2O/hexanes) afforded the title compound **14** (11 mg, 11%, 2 steps) as a slightly yellow oil.

^{1}H NMR	($CDCl_3$, 300 MHz)
	7.45 – 7.42 (m, 2H), 7.35 – 7.26 (m, 3H), 6.33 (d, *J* = 2.7 Hz, 1H), 5.65 (d, *J* = 2.7 Hz, 1H), 5.48 (d, *J* = 2.7 Hz, 1H), 5.16 (p, *J* = 6.6 Hz, 1H), 4.74 (dt, *J* = 3.0, 6.3 Hz, 2H), 3.29 – 3.26 (m, 1H), 2.25 – 2.17 (m, 2H), 2.06 – 1.94 (m, 2H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	208.7, 169.6, 137.4, 131.9 (2C), 129.2, 128.4 (2C), 122.6, 121.5, 89.9, 88.8, 82.2, 75.7, 71.4, 42.3, 29.0, 25.1.
IR	Thin film
	2925, 2848, 2231, 1957, 1773, 1433, 1258, 1102, 976.
MS	*m/z* (%) 264 (50), 235 (70), 207 (85), 179 (75), 155 (100), 115 (95), 91 (55).
HRMS	EI+: $C_{18}H_{16}O_2$ $[M]^+$
	Calculated: 264.1150. Found: 264.1146.
TLC	R_f = 0.75 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]



S6 **12**

3-methylidene-4-(penta-3,4-dien-1-yl)-5-(phenylethynyl)dihydrofuran-2(3*H*)-one (12): Lithium chloride (51 mg, 1.2 mmol) and cerium (III) trichloride (anhydrous beads, 149 mg, 0.60 mmol) were added to a flame-dried 25 mL Schlenk tube equipped with a Teflon-coated stir-bar in a glove box.[3] The Schlenk tube was removed from the glove box, THF (3.6 mL) was added, and the suspension was stirred vigorously at rt under nitrogen atmosphere for 13 h. The resulting solution was cooled to 0 °C, treated with ethynyl magnesium bromide (0.5 M in THF, 1.2 mL, 0.60 mmol) and stirred at 0 °C for 1.5 h. A solution of aldehyde **S6** (102 mg, 0.40 mmol, *E*:*Z* = 4:1) in THF (1.7 mL with a 0.3 mL rinse) was added and the mixture was stirred at 0 °C for 1 h. The solution was then diluted with saturated ammonium chloride (2 mL) and Et_2O (6 mL). After stirring for 1 h, the mixture was filtered through a Celite plug and the filter cake was rinsed with Et_2O (40 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (10 mL, 2×). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The propargyl alcohol was not stable to column chromatography, so it was taken on immediately to the next step.

Half of the crude product was then charged into a flame-dried 25 mL round bottom flask equipped with a Teflon-coated stir-bar, followed by PPh_3 (56 mg, 0.21 mmol), *N*-isopropylidene-*N*'-2-nitrobenzenesulfonyl hydrazine (55 mg, 0.21 mmol) and THF (1.5 mL). The resulting solution was cooled to 0 °C, stirred under nitrogen and diisopropylazodicarboxylate (43 mg, 0.21 mmol) was added dropwise. After 5 min, the ice/water bath was removed and the reaction was stirred at rt. The progress of the reaction was monitored by TLC and upon completion (13 h), TFE/H_2O (1:1, 1.4 mL) was added. After 3 h, the mixture was diluted with pentane/H_2O (1:1, 6.7 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was loaded onto a 25 g SNAP column and purified using a Biotage normal phase automated

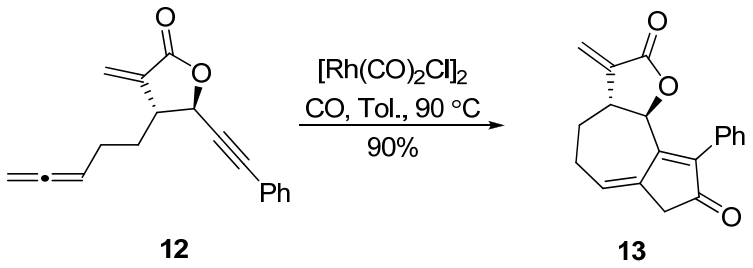
[3] This procedure was adapted from a literature procedure :
B. M. Trost, J. Waser, A. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 16424-16434.

purification system with a gradient of 6 − 14% Et_2O/pentane to afford *trans*-allene **12** (18.2 mg, 39%, 2 steps) along with a second fraction of a *cis*:*trans* 6:4 mixture of allenes (4.2 mg, 9%, 2 steps) as slightly yellow oils.

Data for the *trans*-isomer **12** :

^{1}H NMR	($CDCl_3$, 300 MHz)
	7.46 – 7.43 (m, 2H), 7.36 –7.32 (m, 3H), 6.35 (d, *J* = 2.4 Hz, 1H), 5.69 (d, *J* = 2.1 Hz, 1H), 5.17 (p, *J* = 6.6 Hz, 1H), 5.00 (d, *J* = 5.4 Hz, 1H), 4.74 (dt, *J* = 3.3, 6.6 Hz, 2H), 3.29 – 3.25 (m, 1H), 2.23 – 2.17 (m, 2H), 1.90 – 1.77 (m, 2H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	208.7, 169.3, 137.5, 131.8 (2C), 129.2, 128.4 (2C), 123.1, 121.5, 88.6, 87.8, 85.1, 76.0, 72.4, 46.2, 32.4, 24.7.
IR	Thin film
	2925, 2847, 2230, 1961, 1769, 1433, 1270, 1127, 976.
MS	*m/z* (%) 264 (50), 165 (50), 129 (85), 115 (70), 91 (100), 77 (62).
HRMS	EI+: $C_{18}H_{16}O_2$ $[M]^+$
	Calculated: 264.1150. Found: 264.1148.
TLC	R_f = 0.8 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]

General Procedure for the $[Rh(CO)_2Cl]_2$-Catalyzed Cyclocarbonylation Reaction. A flame-dried vial (15 x 45 mm) equipped with a Teflon-coated stir-bar and a septa cap was charged with allene-yne and toluene (0.1 M, toluene degassed by bubbling with nitrogen for ~ 5 min). The tube was evacuated for 3-5 sec. and refilled with CO (g) (3 x). To the allene-yne solution was added $[Rh(CO)_2Cl]_2$ (0.10 equiv) in one portion, and the vial was evacuated and refilled with CO (g) (3 x). The vial was placed in a preheated 90 °C oil bath and stirred under CO (g). After the reaction was complete by TLC, the mixture was cooled to rt, passed through a short plug of Celite using Et_2O, and concentrated in vacuo. The crude material was purified by flash chromatography.



12 **13**

3-methylene-9-phenyl-3,3a,4,5-tetrahydroazuleno[4,5-*b*]furan-2,8(7*H*,9*bH*)-dione (13):

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **12** (10 mg, 0.038 mmol) and $[Rh(CO)_2Cl]_2$ (1 mg, 2.5 x 10^{-3} mmol) were reacted in toluene (1 mL) for 30 min. Purification of the residue by flash chromatography (80% Et_2O/hexanes) afforded the title compound **13** (10 mg, 90%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

7.42 – 7.36 (m, 3H), 7.29 – 7.26 (m, 2H), 6.77 (d, *J* = 3.3 Hz, 1H), 6.02 (t, *J* = 6.3 Hz, 1H), 5.60 (d, *J* = 3.0 Hz, 1H), 5.36 (d, *J* = 9.9 Hz, 1H), 3.24 (s, 2H), 3.21 – 3.14 (m, 1H), 2.59 – 2.58 (m, 2H), 2.49 – 2.40 (m, 1H), 1.95 – 1.86 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$)

202.9, 168.3, 159.7, 143.1, 138.5, 134.2, 130.8, 129.7 (2C), 128.5, 128.3, 127.6 (2C), 126.4, 80.0, 44.3, 41.9, 26.7, 25.9.

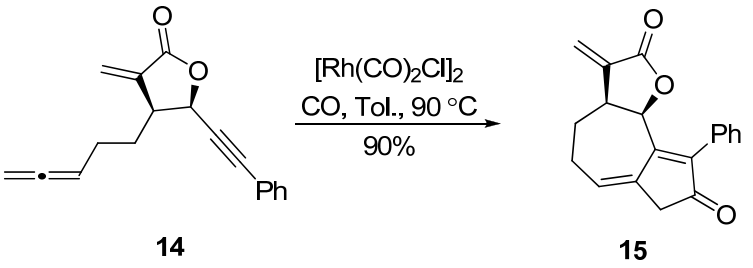
IR Thin film

2925, 2859, 2079, 2006, 1777, 1703, 1266, 1139, 1008.

HRMS EI+: $C_{19}H_{16}O_3$ $[M+H]^+$

Calculated: 293.1178. Found: 293.1156.

TLC R_f = 0.5 (80% Et_2O/pentane) [silica gel, UV, $KMnO_4$ stain]



14 **15**

3-methylene-9-phenyl-3,3a,4,5-tetrahydroazuleno[4,5-*b*]furan-2,8(7*H*,9*bH*)-dione (15):
Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **14** (10 mg, 0.038 mmol) and $[Rh(CO)_2Cl]_2$ (1 mg, 2.5 x 10^{-3} mmol) were reacted in toluene (1 mL) for 30 min. Purification of the residue by flash chromatography (80% Et_2O/hexanes) afforded the title compound **15** (10 mg, 90%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)
7.45 – 7.43 (m, 3H), 7.32 – 7.29 (m, 2H), 6.43 (d, *J* = 1.8 Hz, 1H), 6.11 (t, *J* = 5.1 Hz, 1H), 5.75 (d, *J* = 1.8 Hz, 1H), 5.60 (d, *J* = 7.5 Hz, 1H), 3.57 – 3.55 (m, 1H), 3.36 (d, *J* = 21 Hz, 1H), 3.16 (d, *J* = 21 Hz, 1H), 2.36 – 2.34 (m, 2H), 2.21 – 2.17 (m, 1H), 2.04 – 1.98 (m, 1H).

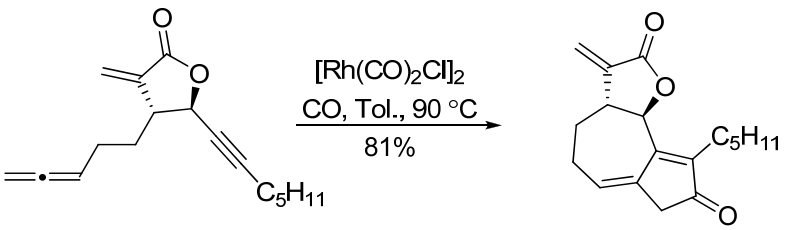
^{13}C NMR ($CDCl_3$, 75 MHz)
202.9, 169.7, 157.2, 148.1, 139.0, 134.0, 130.2, 129.5 (2C), 129.8, 129.1, 128.6 (2C), 124.2, 76.5, 42.5, 42.2, 35.0, 24.4.

IR Thin film
2917, 2852, 1765, 1711, 1274, 1143, 1082, 976.

MS *m/z* (%) 292 (70), 165 (21), 84 (100).

HRMS EI+: $C_{19}H_{16}O_3$ $[M]^+$
Calculated: 292.1099. Found: 292.1089.

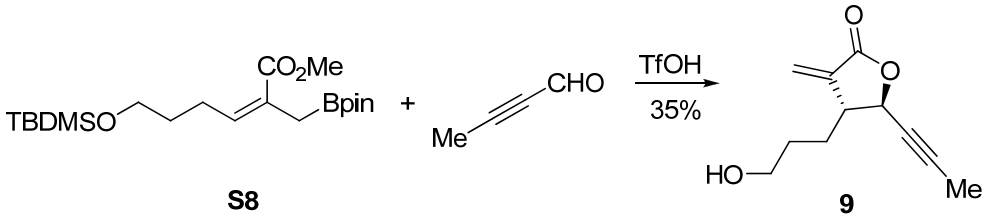
TLC R_f = 0.2 (20% Et_2O/hexanes) [silica gel, UV, $KMnO_4$ stain]



16 **17**

3-methylidene-9-pentyl-3a,5,7,9b-tetrahydroazuleno[4,5-*b*]furan-2,8(3*H*,4*H*)-dione (17):
Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **16** (10 mg, 0.038 mmol) and $[Rh(CO)_2Cl]_2$ (1 mg, 2.5 x 10^{-3} mmol) were reacted in toluene (1 mL) for 30 min. Purification of the residue by flash chromatography (67% Et_2O/hexanes) afforded the title compound **17** (9 mg, 81%) as a slightly yellow oil.

^{1}H NMR	($CDCl_3$, 300 MHz)
	6.35 (d, *J* = 2.7 Hz, 1H), 5.83 (t, *J* = 4.5 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 5.20 (d, *J* = 9.9 Hz, 1H), 3.10 – 3.08 (m, 1H), 3.03 (s, 2H), 2.58 – 2.51 (m, 3H), 2.40 – 2.37 (m, 1H), 1.86 – 1.80 (m, 1H), 1.45 – 1.38 (m, 2H), 1.36 – 1.25 (m, 5H), 0.87 (t, *J* = 5.4 Hz, 3H).
^{13}C NMR	($CDCl_3$, 75 MHz)
	204.8, 169.0, 158.6, 145.8, 138.4, 134.0, 124.4, 121.3, 81.1, 44.3, 41.5, 31.9, 29.3, 27.0, 25.9, 23.6, 22.5, 14.0.
IR	Thin film
	2933, 2856, 2006, 1772, 1703, 1254, 1131, 1082, 1004.
HRMS	EI+: $C_{18}H_{23}O_3$ $[M+H]^+$
	Calculated: 287.1647. Found: 287.1663.
TLC	R_f = 0.2 (33% Et_2O/hexanes) [silica gel, $KMnO_4$ stain]



S8 **9**

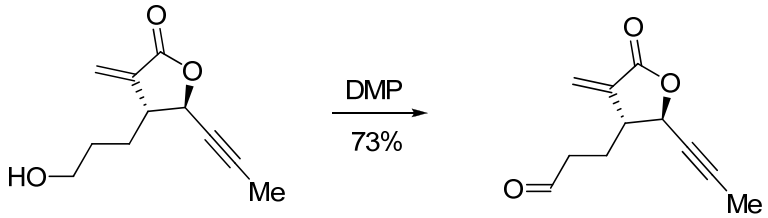
4-(3-hydroxypropyl)-3-methylene-5-(prop-1-ynyl)dihydrofuran-2(3*H*)-one (9): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S8** (1.2 g, 3 mmol, *E*:*Z* = 1:4), but-2-ynal[4] (0.41 g, 6 mmol) and toluene (9.5 mL) at 0 °C. The resulting solution was treated with trifluoromethanesulfonic acid (45 mg, 0.3 mmol) and stirred at 0 °C under a nitrogen atmosphere for 12 h. The mixture was then diluted with NH_4Cl (aq) : NH_4OH (9:1, v/v, 61 mL) and extracted with Et_2O (3×50 mL). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was loaded onto a 50 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 45− 95% Et_2O/pentane to afford the title compound **9** (0.207 g, 35%) as a yellow oil. The product was obtained as a mixture of lactone

[4] This compound was synthesized according to the following procedure :
J. Einhorn, C. Einhorn, F. Ratajczak, J.-L. Pierre, *J. Org. Chem.* **1996**, *61*, 7452-7454.

isomers in a *trans*:*cis* 4:1 ratio. A pure fraction of the *trans*-lactone was collected for characterization purposes.

Data for *trans*-lactone **9** :

^{1}H NMR	($CDCl_3$, 400 MHz)
	6.23 (d, J = 2.4 Hz, 1H), 5.61 (d, J = 2.4 Hz, 1H), 4.69 – 4.68 (m, 1H), 3.65 – 3.62 (t, J = 4 Hz, 2H), 3.01 (br. s, 1H), 2.26 – 2.24 (m, 1H), 1.82 (d, J = 4 Hz, 3H), 1.77 – 1.75 (m, 1H), 1.64 – 1.61 (m, 3H).
^{13}C NMR	($CDCl_3$, 100 MHz)
	169.5, 137.7, 122.7, 84.9, 75.6, 72.4, 61.9, 46.6, 29.3, 29.0, 3.5.
IR	Thin film
	3440, 2929, 2859, 2247, 1761, 1659, 1270.
HRMS	ES+: $C_{11}H_{15}O_3$ $[M+H]^+$
	Calculated: 195.1031. Found: 195.1021.
TLC	R_f = 0.2 (75% Et_2O/pentane) [silica gel, $KMnO_4$ stain]

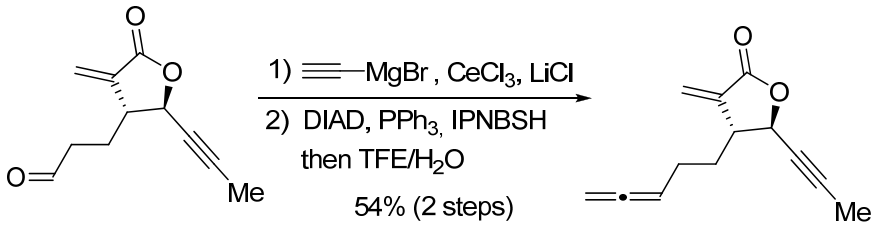


9 **S9**

3-[4-methylene-5-oxo-2-(prop-1-ynyl)tetrahydrofuran-3-yl)]propanal (S9): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **9** (130 mg, 0.67 mmol, *trans*:*cis* 6.5:3.5) and CH_2Cl_2 (9 mL). The resulting solution was treated with Dess-Martin periodinane (343 mg, 0.8 mmol). The progress of the reaction was monitored by TLC and upon completion (3 h), the mixture was concentrated under reduced pressure. The crude residue was loaded onto a 25 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 40−85% Et_2O/pentane to afford the title compound **S9** (94 mg, 73%) as a slightly yellow oil. The product was obtained as a mixture of isomers in a *trans*:*cis* 7:3 ratio. A pure fraction of the *trans*-lactone was collected for characterization purposes.

Data for *trans*-lactone **S9** :

^{1}H NMR	($CDCl_3$, 400 MHz)
	9.80 (s, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 5.64 (d, *J* = 2.4 Hz, 1H), 4.67 – 4.66 (m, 1H), 3.06 – 3.04 (m, 1H), 2.64 (t, *J* = 4.0 Hz, 2H), 2.08 – 2.03 (m, 1H), 1.90 – 1.86 (m, 1H), 1.85(d, *J* = 2.0 Hz, 3H).
^{13}C NMR	($CDCl_3$, 100 MHz)
	200.3, 168.8, 137.2, 122.9, 85.4, 75.4, 72.1, 45.9, 40.1, 24.5, 3.6.
IR	Thin film
	2923, 2850, 2730, 2245, 1769, 1723, 1662, 1447.
HRMS	ES+: $C_{11}H_{13}O_3$ $[M+H]^+$
	Calculated: 193.0885. Found: 193.0865.
TLC	R_f = 0.6 (85% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



S9 **11**

3-methylene-4-(penta-3,4-dienyl)-5-(prop-1-ynyl)dihydrofuran-2(3*H*)-one (11) : Lithium chloride (30 mg, 0.71 mmol) and cerium (III) trichloride (anhydrous beads, 88 mg, 0.36 mmol) were added to a flame-dried 25 mL Schlenk tube equipped with a Teflon-coated stir-bar in a glove box. The Schlenk tube was removed from the glove box, THF (2.3 mL) was added, and the suspension was stirred vigorously at rt under nitrogen atmosphere for 13 h. The resulting solution was cooled to 0 °C, treated with ethynyl magnesium bromide (0.5 M in THF, 0.71 mL, 0.36 mmol) and stirred at 0 °C for 1.5 h. A solution of *trans* aldehyde **S9** (46 mg, 0.24 mmol) in THF (1.0 mL with a 0.2 mL rinse) was added and the mixture was stirred at 0 °C for 1 h. The solution was then diluted with saturated ammonium chloride (2 mL) and Et_2O (6 mL). After stirring for 1 h, the mixture was filtered through a Celite plug and the filter cake was rinsed with Et_2O (40 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (10 mL, 2×). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The propargyl alcohol was not stable to column chromatography, so it was taken on immediately to the next step.

The crude product was then charged into a flame-dried 25 mL round bottom flask equipped with a Teflon-coated stir-bar, followed by PPh_3 (63 mg, 0.24 mmol), *N*-isopropylidene-*N*'-2-nitrobenzenesulfonyl hydrazine (61 mg, 0.24 mmol) and THF (1.4 mL). The resulting solution was cooled to 0 °C, stirred under nitrogen and diisopropylazodicarboxylate (48 mg, 0.24 mmol) was added dropwise. After 5 min, the ice/water bath was removed and the reaction was stirred at rt. The progress of the reaction was monitored by TLC and upon completion (13 h), TFE/H_2O (1:1, 1.6 mL) was added. After 3 h, the mixture was diluted with pentane/H_2O (1:1, 8 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was loaded onto a 10 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 6−10% Et_2O/pentane to afford the title compound **11** (22 mg, 54%, 2 steps) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.30 (d, *J* = 2.1 Hz, 1H), 5.63 (d, *J* = 2.1 Hz, 1H), 5.16 – 5.11 (m, 1H), 4.76 – 4.71 (m, 3H), 3.13 – 3.06 (m, 1H), 2.17 – 2.11 (m, 2H), 1.87 (d, *J* = 2.1 Hz, 3H), 1.82 – 1.72 (m, 2H).

^{13}C NMR ($CDCl_3$, 175 MHz)

208.6, 169.3, 137.7, 122.7, 88.7, 84.9, 75.8, 75.7, 72.4, 46.1, 32.3, 24.7, 3.7.

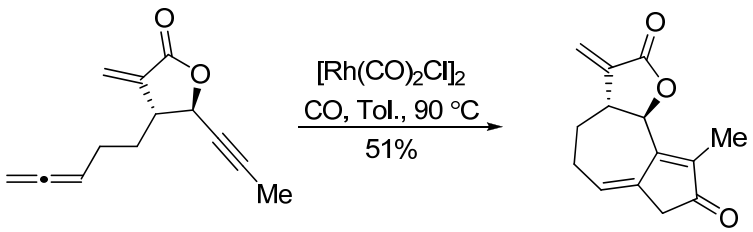
IR Thin film

2917, 2849, 2250, 1957, 1762, 1665, 1444.

HRMS APCI+: $C_{13}H_{15}O_2$ $[M+H]^+$

Calculated: 203.1072. Found: 203.1097.

TLC R_f = 0.4 (10% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



11 **22**

9-methyl-3-methylene-3,3a,4,5-tetrahydroazuleno[4,5-*b*]furan-2,8(7*H*,9*bH*)-dione (22):

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **11** (16 mg, 0.08 mmol) and $[Rh(CO)_2Cl]_2$ (3.2 mg, 8 x 10^{-3} mmol) were reacted in toluene (0.7 mL) for 30 min. Purification of the residue by flash chromatography (75% Et_2O/pentane) afforded the title compound **22** (9.5 mg, 51%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.34 (d, *J* = 3.0 Hz, 1H), 5.83(t, *J* = 6 Hz, 1H), 5.63 (d, *J* = 3.0 Hz, 1H), 5.18 (d, *J* = 9.0 Hz, 1H), 3.10 – 3.08 (m, 1H), 3.04 (s, 2H), 2.57 – 2.51 (m, 2H), 2.43 – 2.36 (m, 1H), 1.86 (s, 3H), 1.84 – 1.78 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz)

204.7, 168.9, 158.6, 140.9, 138.2, 133.5, 124.4, 121.2, 81.1, 44.1, 41.1, 26.6, 25.9, 9.5.

IR Thin film

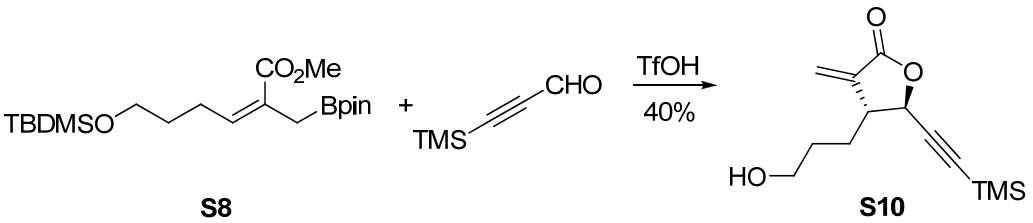
2917, 2847, 1777, 1699, 1658, 1629, 1492, 1258.

MS *m/z* (%) 229 (2), 269 (38), 254 (23), 232 (1).

HRMS ESI+: $C_{14}H_{15}O_3$ $[M+H]^+$

Calculated: 231.1021. Found: 231.1020.

TLC R_f = 0.4 (80% Et_2O/pentane) [silica gel, UV, $KMnO_4$ stain]



S8 **S10**

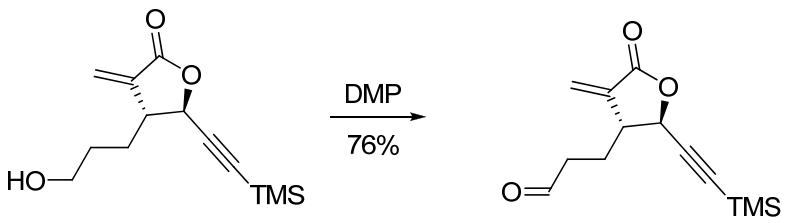
4-(3-hydroxypropyl)-3-methylene-5-((trimethylsilyl)ethynyl)dihydrofuran-2(3*H*)-one (S10):

A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S8** (6.13 g, 15.8 mmol, *E*:*Z* = 2.5:6.5), 3-(trimethylsilyl)propiolaldehyde (4 g, 31.5 mmol) and toluene (42 mL) at 0 °C. The resulting solution was treated with trifluoromethanesulfonic acid (237 mg, 1.57 mmol) and stirred at 0 °C under a nitrogen atmosphere for 12 h. The mixture was then diluted with NH_4Cl (aq) : NH_4OH (9:1, v/v, 314 mL) and extracted with Et_2O (3×150 mL). The combined extracts were washed with brine (70 mL), dried over Na_2SO_4, filtered and

concentrated under reduced pressure. The crude residue was loaded onto a 100 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 5 − 90% Et_2O/pentane to afford the title compound **XX** (1.47 g, 40%) as a yellow oil. The product was obtained as a mixture of lactone isomers in a *trans*:*cis* 4:1 ratio. A pure fraction of the *trans*-lactone was collected for characterization purposes.

Data for *trans*-lactone **S10** :

^{1}H NMR	($CDCl_3$, 300 MHz)
	6.30 (d, *J* = 3.0 Hz, 1H), 5.65(d, *J* = 3 Hz, 1H), 4.73 (d, *J* = 6 Hz, 1H), 3.72 – 3.71 (m, 2H), 3.14 – 3.10 (m, 1H), 1.87 – 1.83 (m, 1H), 1.71 – 1.68 (m, 3H), 1.46 – 1.44 (m, 1H), 0.17 (s, 9H).
^{13}C NMR	($CDCl_3$, 175 MHz)
	169.2, 137.2, 122.8, 93.38, 74.7, 72.0, 61.4, 49.2, 29.2, 28.7, -0.7 (3C).
IR	Thin film
	3452, 2953, 1777, 1659, 1405, 1250, 1131, 1066, 988.
HRMS	ES+: $C_{13}H_{21}O_3Si$ $[M+H]^+$
	Calculated: 253.1285. Found: 253.1260.
TLC	R_f = 0.20 (50% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



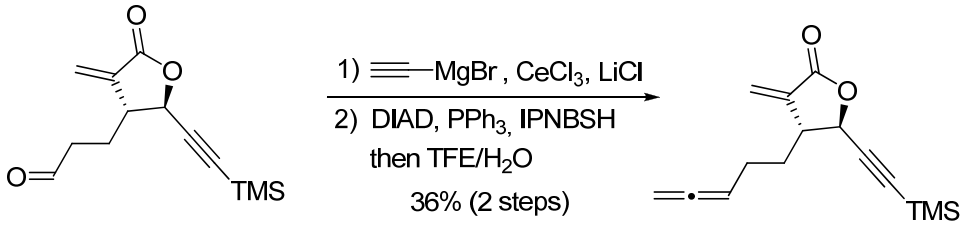
S10 **S11**

3-[4-methylene-5-oxo-2-((trimethylsilyl)ethynyl)tetrahydrofuran-3-yl)]propanal (S11): A flame-dried round bottom flask equipped with a Teflon-coated stir-bar was charged with **S10** (571 mg, 2.40 mmol, *trans*:*cis* 7.5:2.5) and CH_2Cl_2 (34 mL). The resulting solution was treated with Dess-Martin periodinane (1.22 g, 2.87 mmol). The progress of the reaction was monitored by TLC and upon completion (3 h), the mixture was concentrated under reduced pressure. The crude residue was loaded onto a 25 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 40 − 60% Et_2O/pentane to afford the *trans*-

lactone isomer **S11** (40 mg, 7%) and a mixture of isomers (393 mg, 69%) in a *trans*:*cis* 7:3 ratio as a slightly yellow oils.

Data for *trans*-lactone **S11** :

^{1}H NMR	($CDCl_3$, 400 MHz)
	9.82 (br s, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 5.64 (d, *J* = 2.4 Hz, 1H), 4.69 – 4.68 (m, 1H), 3.15 – 3.10 (m, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.13 – 2.08 (m, 1H), 1.90 – 1.85 (m, 1H), 0.17 (s, 9H).
^{13}C NMR	($CDCl_3$, 175 MHz)
	200.1, 168.4, 136.7, 122.8, 100.5, 93.8, 71.5, 45.6, 39.9, 24.2, -0.7 (3C).
IR	Thin film
	2966, 2897, 2190, 1764, 1712, 1667, 1417, 1332, 1275, 1131.
HRMS	ES+: $C_{13}H_{19}O_3Si$ $[M+H]^+$
	Calculated: 251.1125. Found: 251.1103.
TLC	R_f = 0.9 (85% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



S11 **18**

3-methylene-4-(penta-3,4-dienyl)-5-((trimethylsilyl)ethynyl)dihydrofuran-2(3*H*)-one (18): Lithium chloride (90 mg, 2.12 mmol) and cerium (III) trichloride (anhydrous beads, 261 mg, 1.06 mmol) were added to a flame-dried 50 mL Schlenk tube equipped with a Teflon-coated stir-bar in a glove box. The Schlenk tube was removed from the glove box, THF (6.5 mL) was added, and the suspension was stirred vigorously at rt under nitrogen atmosphere for 12 h. The resulting solution was cooled to 0 °C, treated with ethynyl magnesium bromide (0.5 M in THF, 2.12 mL, 1.06 mmol) and stirred at 0 °C for 1.5 h. A solution of aldehyde **S11** (167 mg, 0.71 mmol, *trans*:*cis* 3:7) in THF (6.5 mL with a 1.5 mL rinse) was added and the mixture was stirred at 0 °C for 1 h. The solution was then diluted with saturated ammonium chloride (10 mL) and Et_2O (40 mL). After stirring for 1 h, the mixture was filtered through a Celite plug and the filter

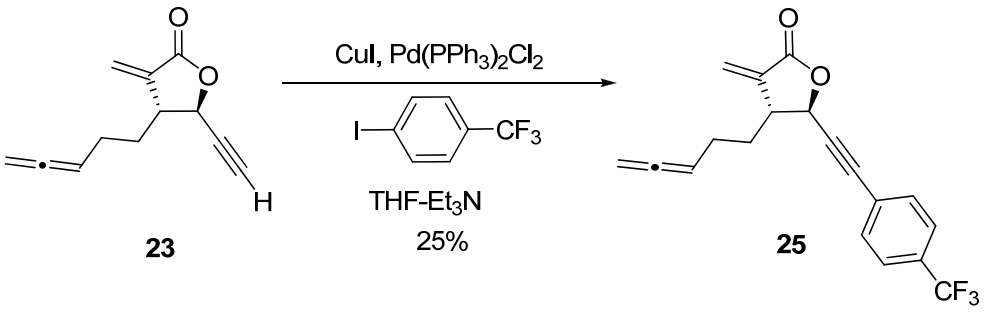
cake was rinsed with Et_2O (40 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (10 mL, 2×). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The propargyl alcohol was not stable to column chromatography, so it was taken on immediately to the next step.

The crude product was then charged into a flame-dried 50 mL round bottom flask equipped with a Teflon-coated stir-bar, followed by PPh_3 (229 mg, 0.87 mmol), *N*-isopropylidene-*N*'-2-nitrobenzenesulfonyl hydrazine (220 mg, 0.87 mmol) and THF (12.3 mL). The resulting solution was cooled to 0 °C, stirred under nitrogen and diisopropylazodicarboxylate (17.6 mg, 0.87 mmol) was added dropwise. After 5 min, the ice/water bath was removed and the reaction was stirred at rt. The progress of the reaction was monitored by TLC and upon completion (13 h), TFE/H_2O (1:1, 5.5 mL) was added. After 3 h, the mixture was diluted with pentane/H_2O (1:1, 50 mL) and extracted with Et_2O (3×40 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was loaded onto a 25 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 4 − 8% Et_2O/pentane to afford the title compound **18** (65.2 mg, 36%, 2 steps) as a slightly yellow oil. The product was obtained as a mixture of isomers in a *trans*:*cis* 3:7 ratio. A pure fraction of the *trans*-lactone was collected for characterization purposes.

Data for *trans*-lactone **18** :

^{1}H NMR	($CDCl_3$, 400 MHz)
	6.28 (d, *J* = 2.4 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 5.13 (m, 1H), 4.73 – 4.71 (m, 3H), 3.15 – 3.12 (m, 1H), 2.15 – 2.11 (m, 2H), 1.84 – 1.70 (m, 2H), 0.16 (s, 9H).
^{13}C NMR	($CDCl_3$, 175 MHz)
	208.6, 169.0, 137.3, 122.9, 101.0, 93.5, 88.6, 75.9, 72.0, 45.9, 32.3, 24.5, -0.5 (3C).
IR	Thin film
	2958, 2925, 2852, 1957, 1773, 1667, 1446, 1409, 1303, 1250, 1140, 1250, 841.
HRMS	ES+: $C_{15}H_{21}O_2Si$ $[M+H]^+$
	Calculated: 261.1325. Found: 261.1311.

TLC R_f = 0.7(10% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



3-methylene-4-(penta-3,4-dienyl)-5-((4-(trifluoromethyl)phenyl)ethynyl)dihydrofuran-2(3*H*)-one (25) : For the preparation of compound **25**, slight modifications were made to a literature procedure.[5] THF (1.9 mL) and triethylamine (1.3 mL) were placed in a 4 mL vial fitted with a septa cap under an argon atmosphere. The vial was degassed by placing a needle into the solution and bubbling N_2 through for 15 min. The resulting solution was added to a 10 mL round bottom flask containing allene **23** (44 mg, 0.253 mmol) and 1-iodo-4-(trifluoromethyl)benzene (103 mg, 0.379 mmol). The resulting solution was transferred to a 4 mL vial fitted with a septa cap containing [$PdCl_2(PPh_3)_2$] (7 mg, 0.010 mmol, 4 mol %) and CuI (3.9 mg, 0.020 mmol, 8 mol %). The mixture was degassed for 5 min, stirred at room temperature for 8 h and concentrated under reduced pressure. The crude residue was loaded onto a 10 g SNAP column and purified using a Biotage normal phase automated purification system with a gradient of 5 − 12% Et_2O/pentane to afford the title compound **25** (20.6 mg, 25%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

7.61 – 7.53 (m, 4H), 6.36 (d, J = 2.4 Hz, 1H), 5.71 (d, J = 2.4 Hz, 1H), 5.19 – 5.14 (m, 1H), 5.01 (d, J = 5.1 Hz, 1H), 4.76 – 4.72 (m, 2H), 3.30 – 3.26 (m, 1H), 2.22 – 2.19 (m, 2H), 1.88 – 1.81 (m, 2H).

^{13}C NMR ($CDCl_3$, 175 MHz)

208.6, 168.9, 137.1, 132.0 (4C), 130.7 (q, $^2J_{C\text{-}F}$ = 33.3 Hz), 125.22 (q, $^1J_{C\text{-}F}$ = 3.5 Hz), 124.4, 123.2, 88.5, 87.4, 86.2, 75.8, 72.0, 45.9, 32.3, 24.6.

IR Thin film

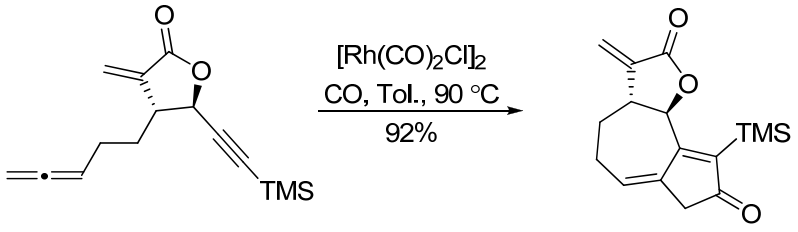
2921, 2852, 1952, 1777, 1670, 1614, 1442, 1409, 1323, 1262, 1127.

[2] M. Gruit, D. Michalik, K. Krüger, A. Spannenberg, A. Tillack, A. Pews-Davtyan, M. Beller, *Tetrahedron* **2010**, *66*, 3341-3352.

HRMS ES+: $C_{19}H_{16}O_2F_3$ $[M+H]^+$

Calculated: 333.1102. Found: 333.1100.

TLC R_f = 0.4 (25% Et_2O/pentane) [silica gel, UV]



18 **19**

3-methylene-9-(trimethylsilyl)-3,3a,4,5-tetrahydroazuleno[4,5-b]furan-2,8(7*H*,9*bH*)-dione (19) : Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **18** (16 mg, 0.06 mmol) and $[Rh(CO)_2Cl]_2$ (2.4 mg, 6 x 10^{-3} mmol) were reacted in toluene (1.7 mL) for 20 min. Purification of the residue by flash chromatography (80% Et_2O/pentane) afforded the title compound **19** (16.5 mg, 92%) as a slightly yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.32 (d, *J* = 3.0 Hz, 1H), 5.90 (t, *J* = 6 Hz, 1H), 5.60 (d, *J* = 3.0 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 3.03 (m, 3H), 2.53 (m, 2H), 2.39 (m, 1H), 1.85 (m, 1H), 0.32 (s, 9H).

^{13}C NMR ($CDCl_3$, 175 MHz)

207.7, 173.2, 168.3, 144.7, 138.7, 136.5, 124.8, 120.9, 80.1, 43.9, 42.6, 26.2, 25.4, 0.5 (3C).

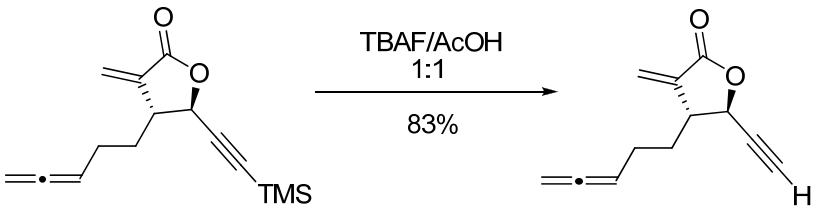
IR Thin film

2950, 2247, 1769, 1695, 1540, 1458, 1397, 1303, 1258, 1140, 1095, 1017.

HRMS ES+: $C_{16}H_{21}O_3Si$ $[M+H]^+$

Calculated: 289.1260. Found: 289.1231.

TLC R_f = 0.6 (80% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



18 **23**

5-ethynyl-3-methylene-4-(penta-3,4-dienyl)dihydrofuran-2(3*H*)-one (23) : A solution of tetrabutylammonium fluoride (52 mg, 0.197 mmol) and glacial acetic acid (11 μL, 0.197 mmol) in THF (1 mL) was stirred for 30 min under argon. The mixture was then added to a solution of allene-yne **18** (34 mg, 0.132 mmol) in THF (1 mL). After stirring 1 h at room temperature, the solution was concentrated under reduced pressure. Purification of the residue by flash chromatography (10% Et_2O/pentane) afforded the title compound **23** (20 mg, 83%) as a slightly yellowish oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.32 (d, J = 2.7 Hz, 1H), 5.66 (d, J = 2.7 Hz, 1H), 5.12 (m, 1H), 4.75 (m, 3H), 3.21 – 3.14 (m, 1H), 2.65 (s, 1H), 2.18 – 2.14 (m, 2H), 1.84 – 1.72 (m, 2H).

^{13}C NMR ($CDCl_3$, 175 MHz)

208.6, 169.0, 137.2, 123.0, 89.1, 80.0, 76.2, 75.3, 71.4, 46.5, 32.5, 25.4.

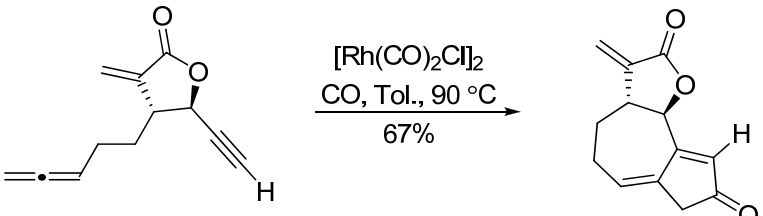
IR Thin film

3285, 2921, 2856, 2124, 1961, 1777, 1667, 1262, 1107, 968.

HRMS ES+: $C_{12}H_{13}O_2$ $[M+H]^+$

Calculated: 189.0909. Found: 189.0916.

TLC R_f=0.8 (20% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



23 **24**

3-methylene-3,3a,4,5-tetrahydroazuleno[4,5-b]furan-2,8(7*H*,9*bH*)-dione (24): Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **23** (18.8 mg, 0.11 mmol) and $[Rh(CO)_2Cl]_2$ (4.2 mg, 0.011 mmol) were reacted in toluene (2.9 mL) for 30 min. Purification of the residue by flash chromatography (70% Et_2O/ pentane) afforded the title compound **24** (15.5 mg, 67%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz)

6.24 (s, 1H), 6.34 (d, *J* = 3.0 Hz, 1H), 5.95 (t, *J* = 6 Hz, 1H), 5.62 (d, *J* = 3.0 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 3.09 – 2.99 (m, 3H), 2.61 – 2.56 (m, 2H), 2.43 – 2.37 (m, 1H), 1.90 – 1.82 (m, 1H).

^{13}C NMR ($CDCl_3$, 175 MHz)

203.8, 168.7, 167.5, 138.4, 134.1, 129.5, 127.4, 121.4, 79.7, 43.6, 41.8, 26.3, 26.1.

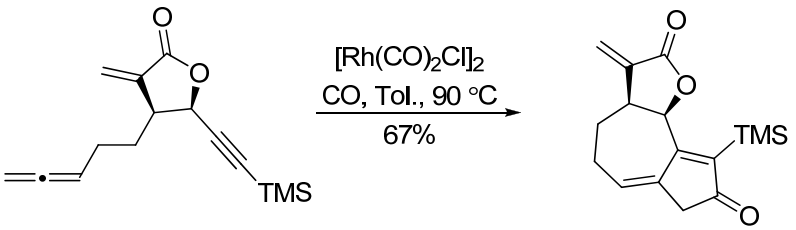
IR Thin film

2950, 2917, 2860, 1769, 1708, 1585, 1405, 1381, 1258, 1242, 1136, 1087.

HRMS ES+: $C_{13}H_{13}O_3$ $[M+H]^+$

Calculated: 217.0865. Found: 217.0858.

TLC R_f = 0.2 (70% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



20 **21**

3-methylene-9-(trimethylsilyl)-3,3a,4,5-tetrahydroazuleno[4,5-b]furan-2,8(7*H*,9*bH*)-dione (21) : Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **20** (13.3 mg, 0.055 mmol) and $[Rh(CO)_2Cl]_2$ (2.2 mg, 0.056 mmol) were reacted in toluene (1.5 mL) for 150 min. Purification of the residue by flash chromatography (50% Et_2O/pentane) afforded the title compound **21** (9.9 mg, 67%) as a slightly yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz)

6.43 (d, *J* = 1.7 Hz, 1H), 5.98 (t, *J* = 6 Hz, 1H), 5.75 (d, *J* = 1.7 Hz, 1H), 5.65 (d, *J* = 7.2 Hz, 1H), 3.52 – 3.49 (m, 1H), 3.18 (d, *J* = 20.8 Hz, 1H),

2.97 (d, J = 20.8 Hz, 1H), 2.30 – 2.29 (m, 2H), 2.10 – 2.06 (m, 1H), 1.99 – 1.95 (m, 1H), 0.87 (s, 9H).

^{13}C NMR ($CDCl_3$, 175 MHz)

208.4, 169.6, 169.5, 150.4, 138.9, 136.2, 128.6, 123.7, 77.9, 43.9, 42.1, 33.9, 24.8, -0.3 (3C).

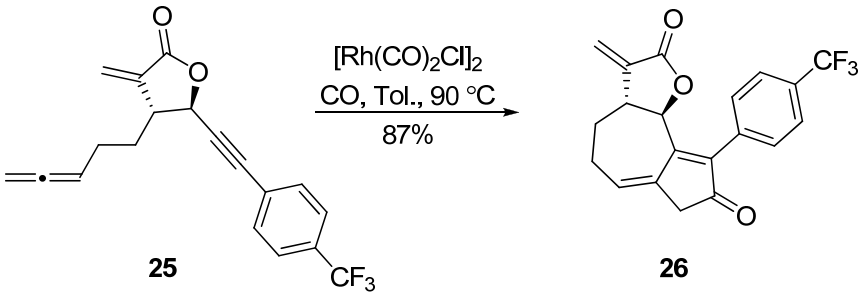
IR Thin film

2950, 2247, 1769, 1695, 1540, 1458, 1397, 1303, 1258, 1140, 1095, 1017.

HRMS ES+: $C_{16}H_{21}O_3Si$ $[M+H]^+$

Calculated: 289.1260. Found: 289.1241.

TLC R_f = 0.7 (80% Et_2O/pentane) [silica gel, $KMnO_4$ stain]



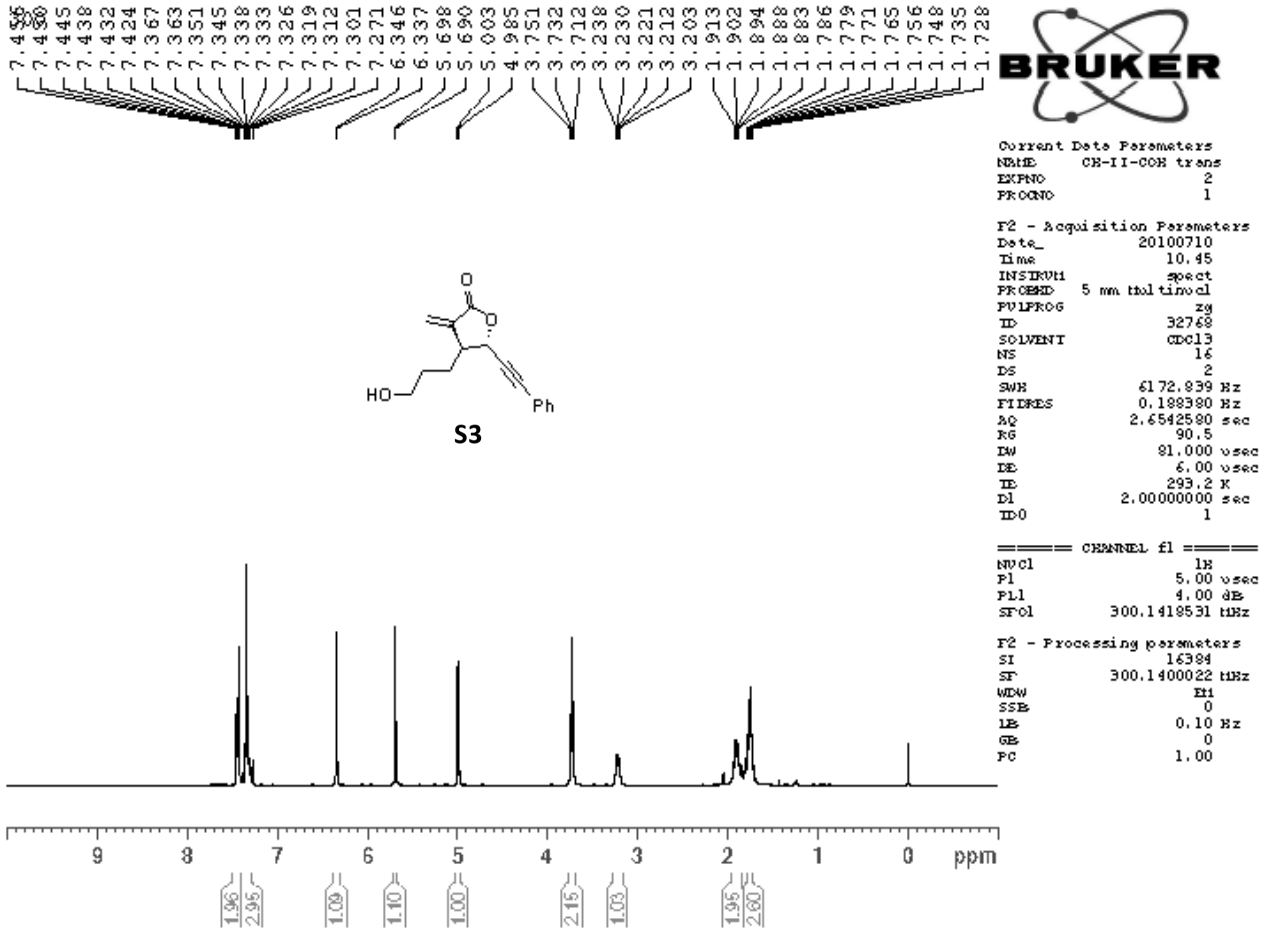
3-methylene-9-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydroazuleno[4,5-*b*]furan-2,8 (7*H*,9*bH*)-dione (25) : Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **25** (15 mg, 0.045 mmol) and $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.045 mmol) were reacted in toluene (1.3 mL) for 30 min. Purification of the residue by flash chromatography (80% Et_2O/pentane) afforded the title compound **26** (14 mg, 87%) as a slightly yellowish oil.

^{1}H NMR ($CDCl_3$, 500 MHz)

7.64 (d, J = 8 Hz, 2H), 7.38 (d, J = 8 Hz, 2H), 6.29 (d, J = 3.0 Hz, 1H), 6.07(t, J = 6 Hz, 1H), 5.60 (d, J = 3.0 Hz, 1H), 5.34 (d, J = 10.0 Hz, 1H), 3.25 (s, 2H), 3.17 – 3.14 (m, 1H), 2.64 – 2.61 (m, 2H), 2.45 – 2.40 (m, 1H), 1.93 – 1.86 (m, 1H).

^{13}C NMR ($CDCl_3$, 175 MHz)

	202.2, 168.0, 160.8, 141.4, 138.1, 134.6, 133.8, 130.2 (4C), 130.1 (q, $^{2}J_{C\text{-}F}$ = 15 Hz), 127.7, 124.4 (q, $^{1}J_{C\text{-}F}$ = 3.5 Hz), 121.4, 79.7, 44.1, 41.7, 26.5, 25.8.
IR	Thin film
	2967, 2921, 2079, 2009, 1777, 1703, 1523, 1319, 1262, 1172, 1123.
HRMS	ES+: $C_{20}H_{16}O_3F_3$ $[M+H]^+$
	Calculated: 361.1052. Found: 361.1042.
TLC	R_f = 0.4 (80% Et_2O/pentane) [silica gel, UV]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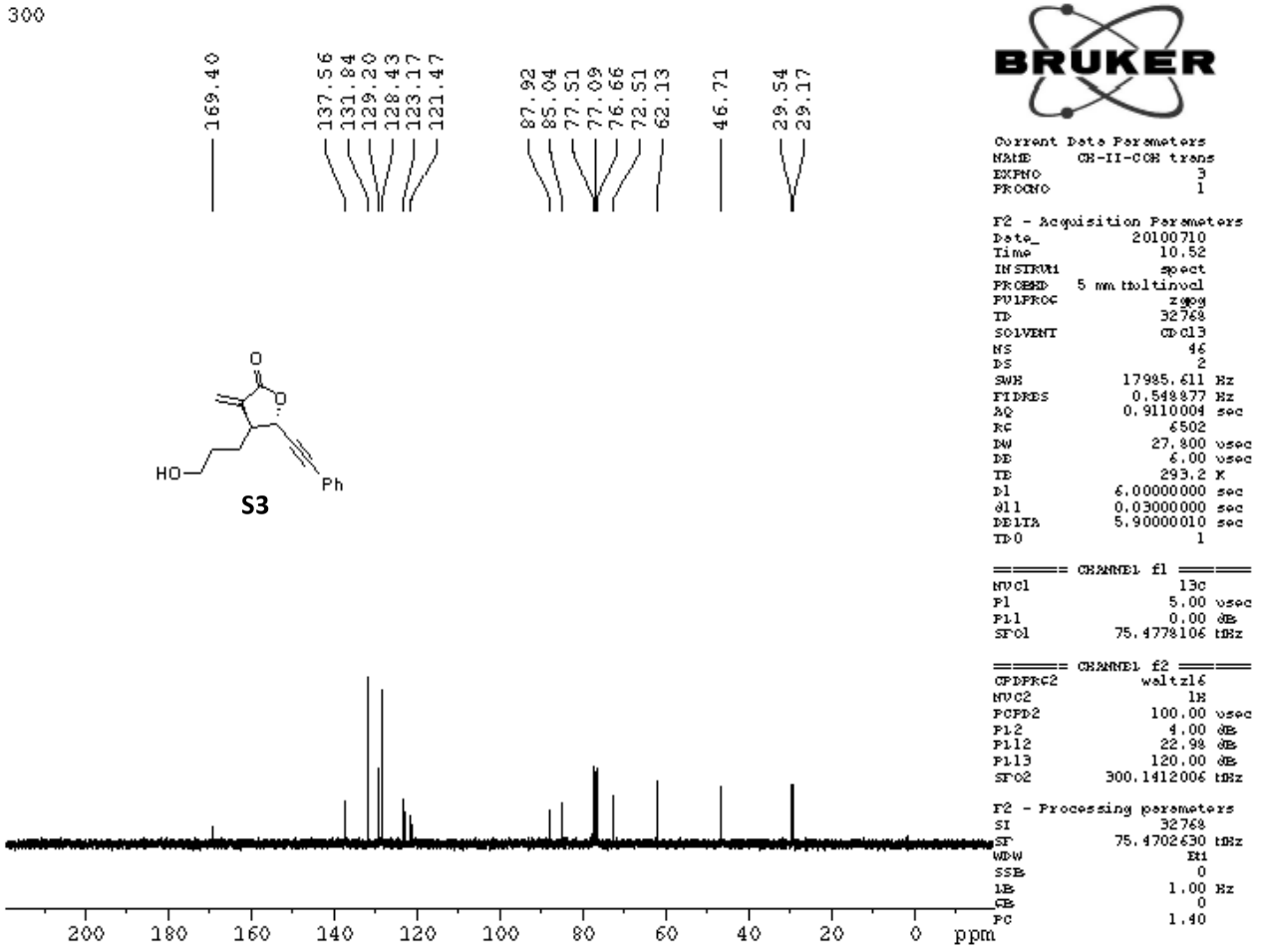

S3

BRUKER

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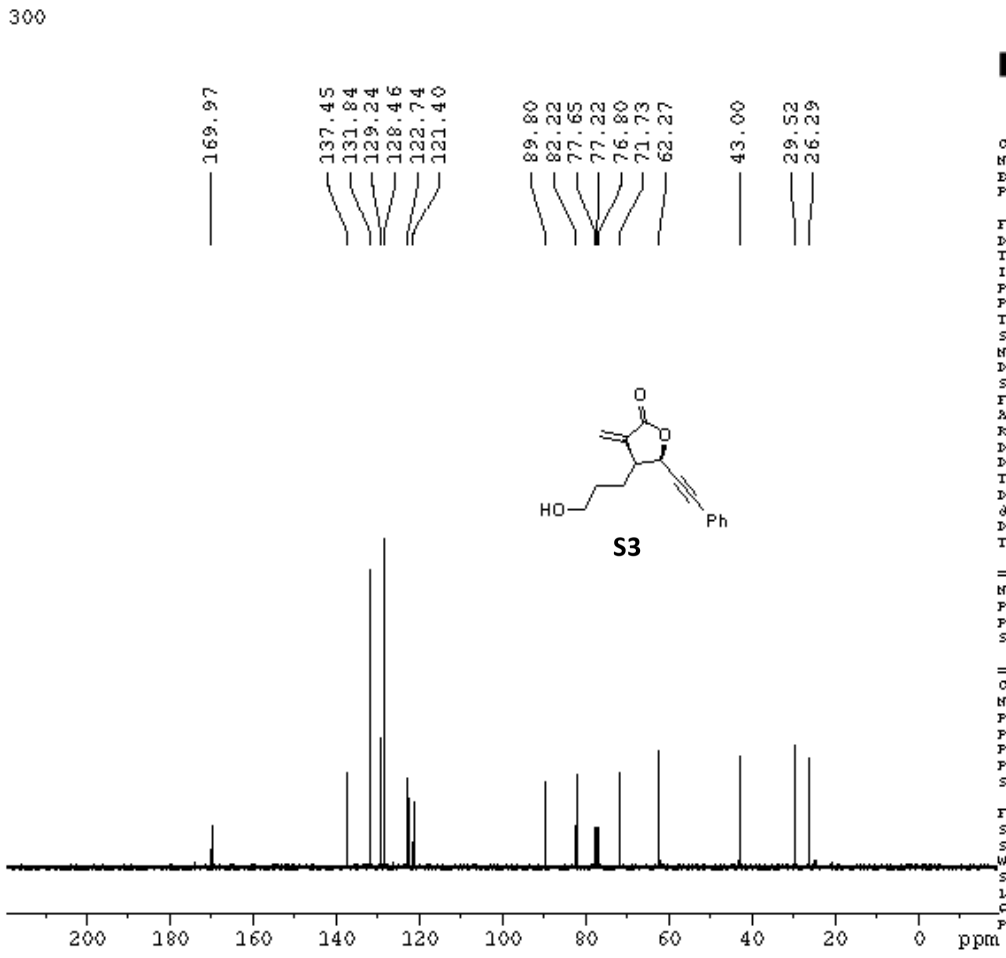

S3

BRUKER

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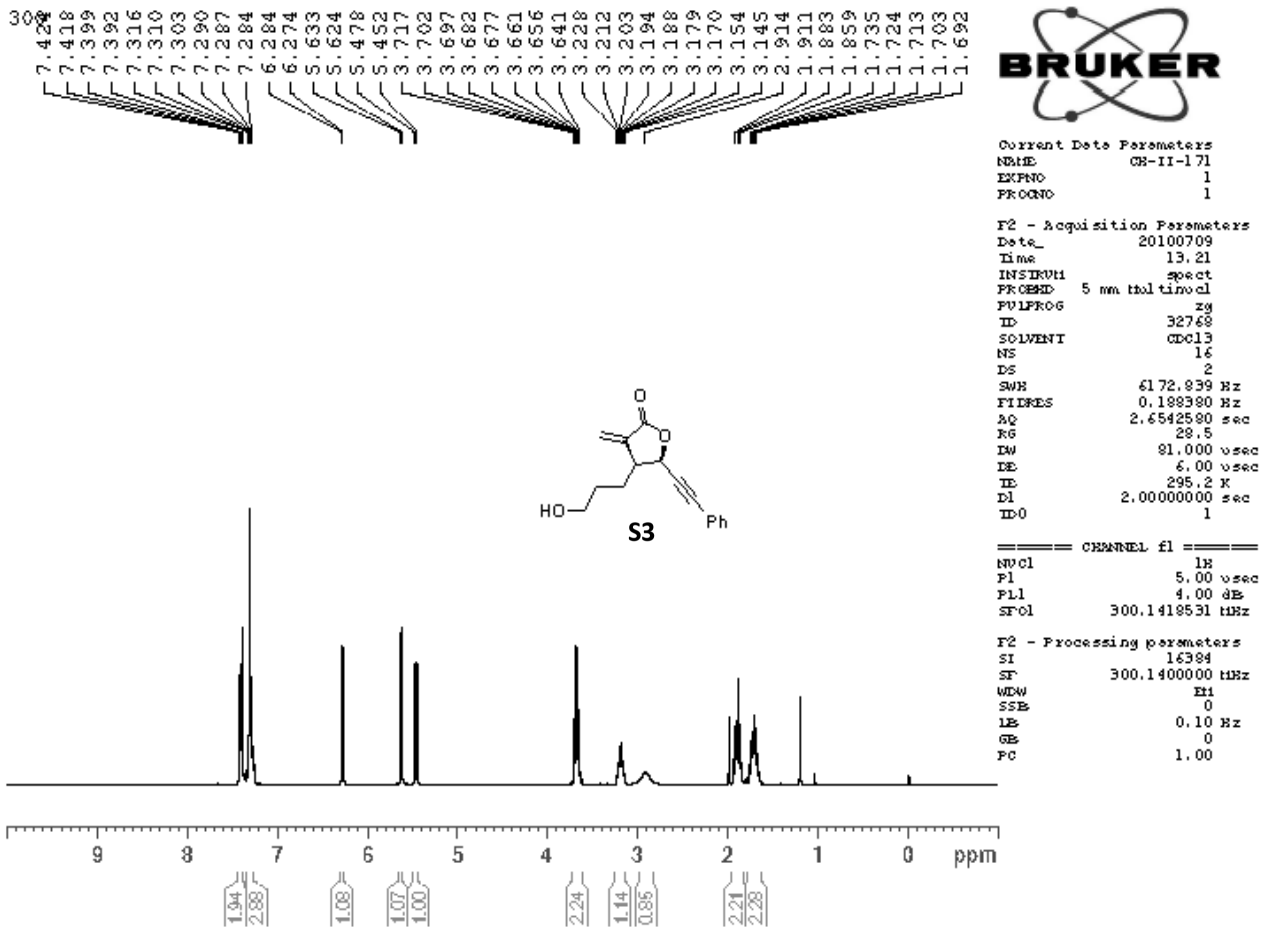

BRUKER

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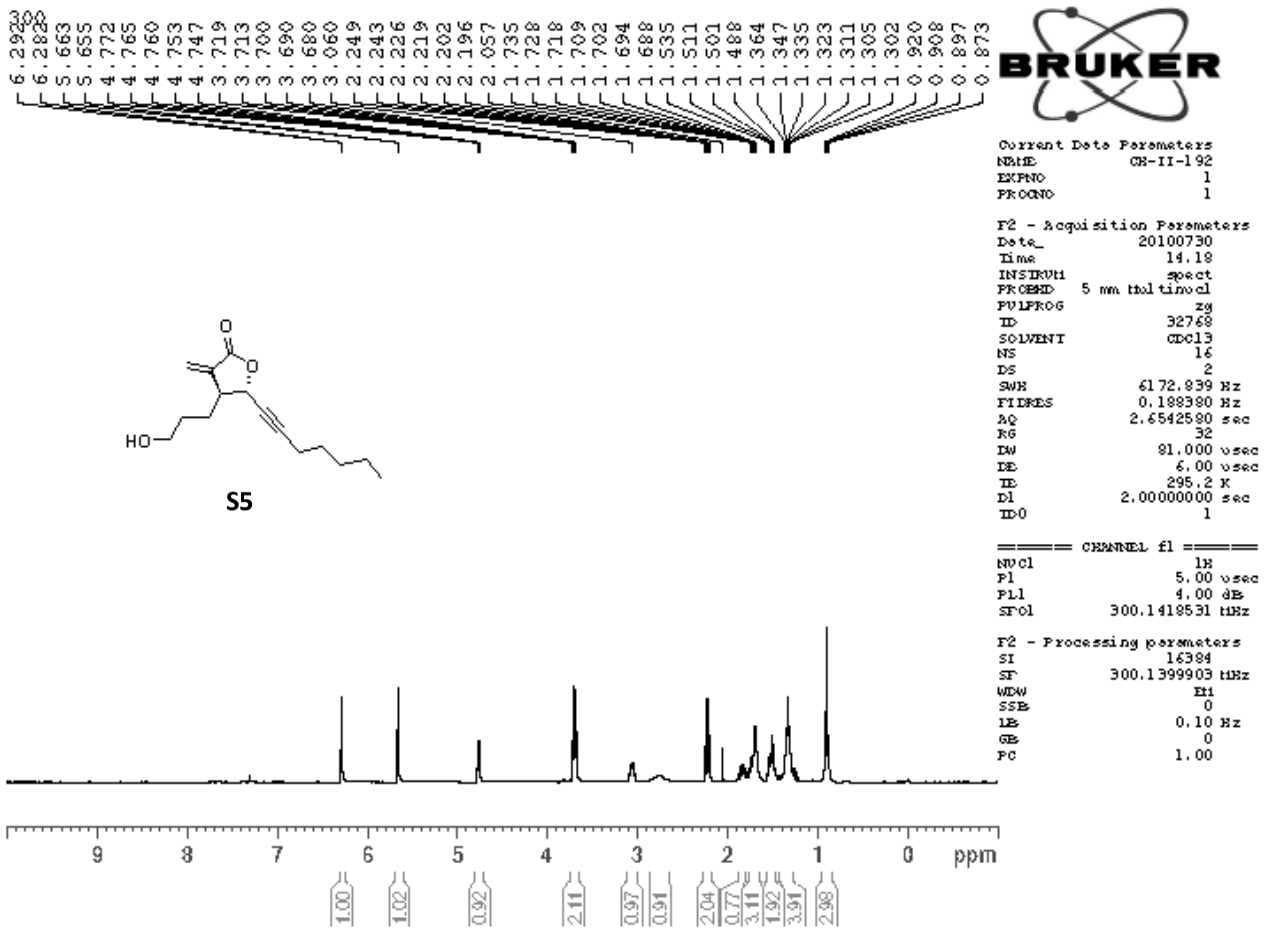
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 28.5
DW 81.000 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
TD0 1

====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz

F2 - Processing parameters
SI 16384
SF 300.1400000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



S5

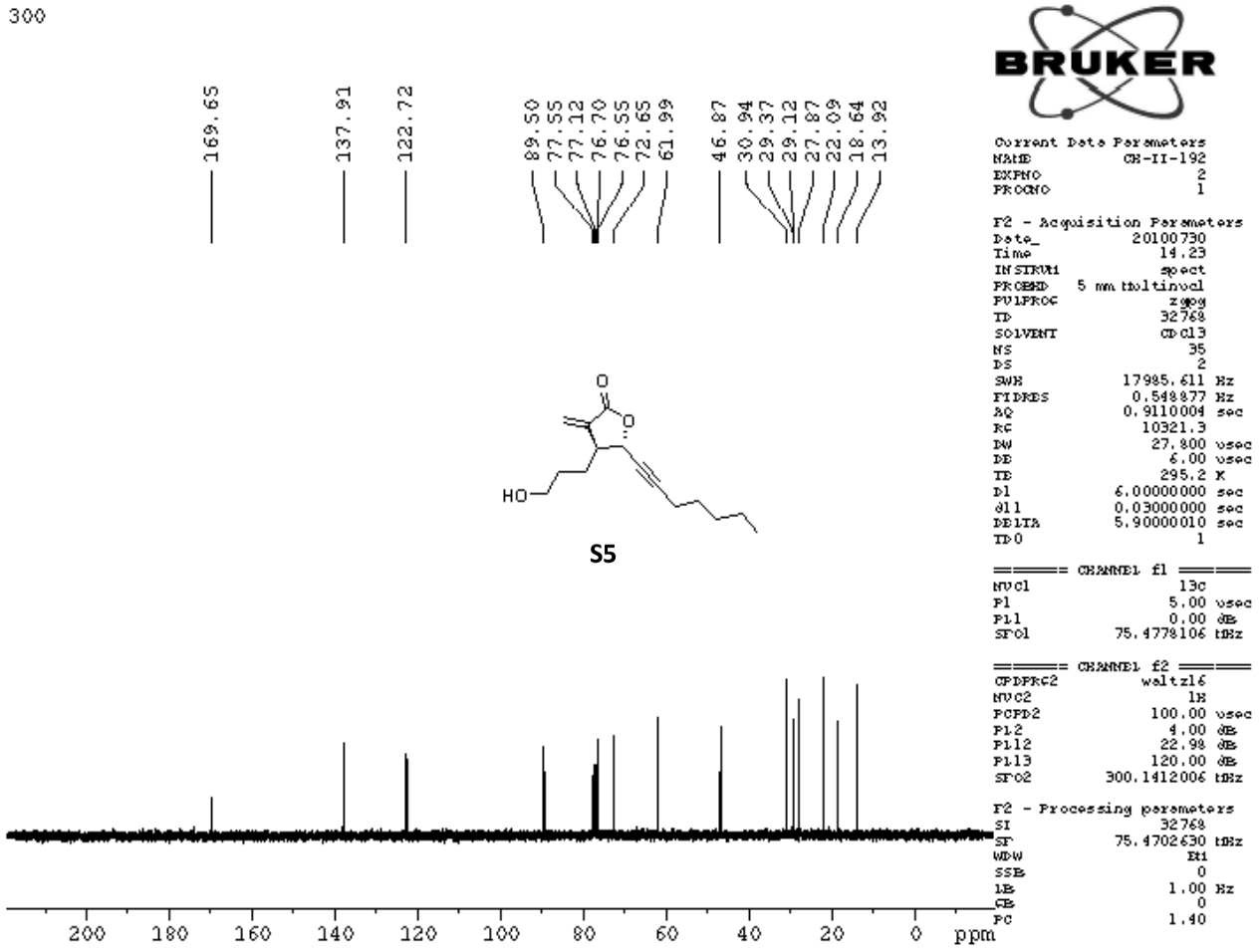
BRUKER

Current Data Parameters
NAME CH-II-192
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100730
Time 14.18
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 32
DW 81.000 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
TD0 1

====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz

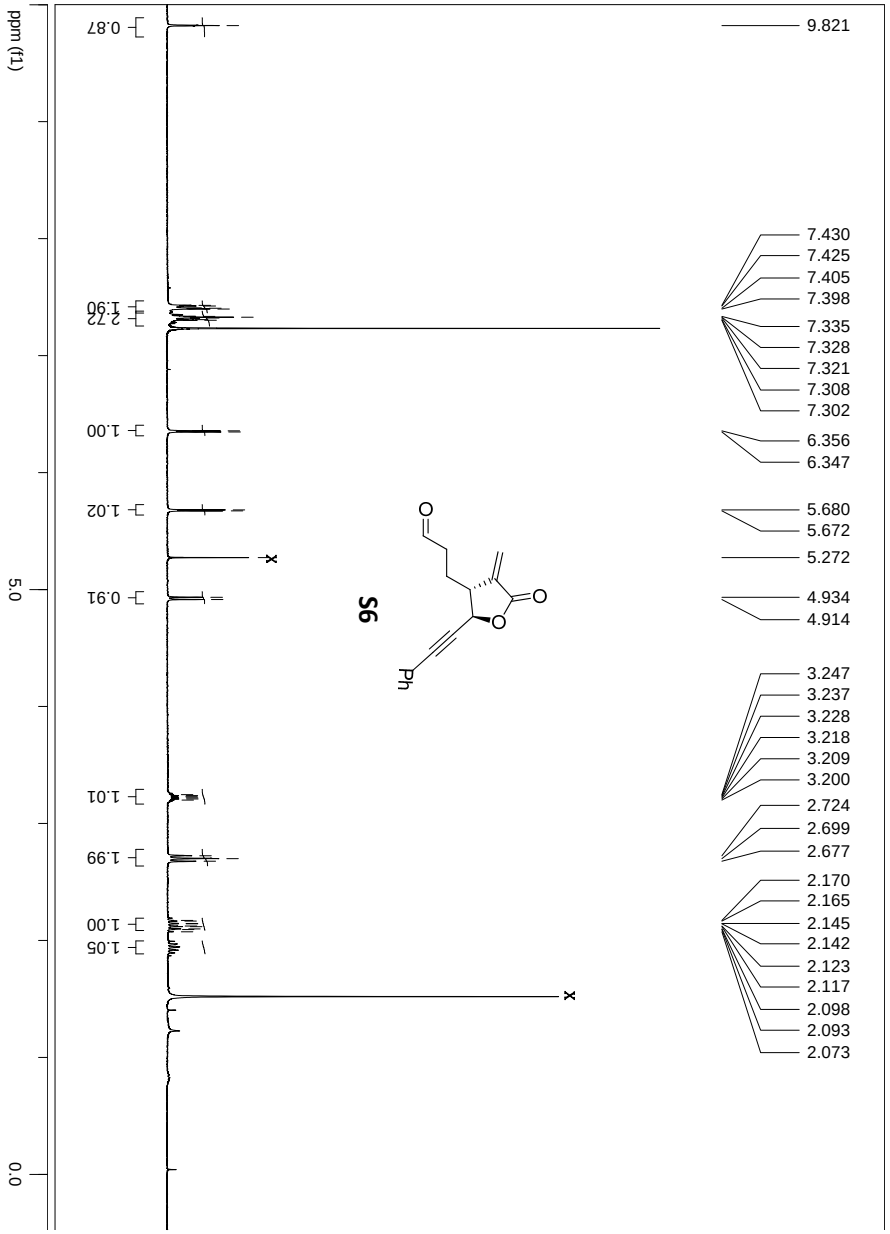
F2 - Processing parameters
SI 16384
SF 300.1399903 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

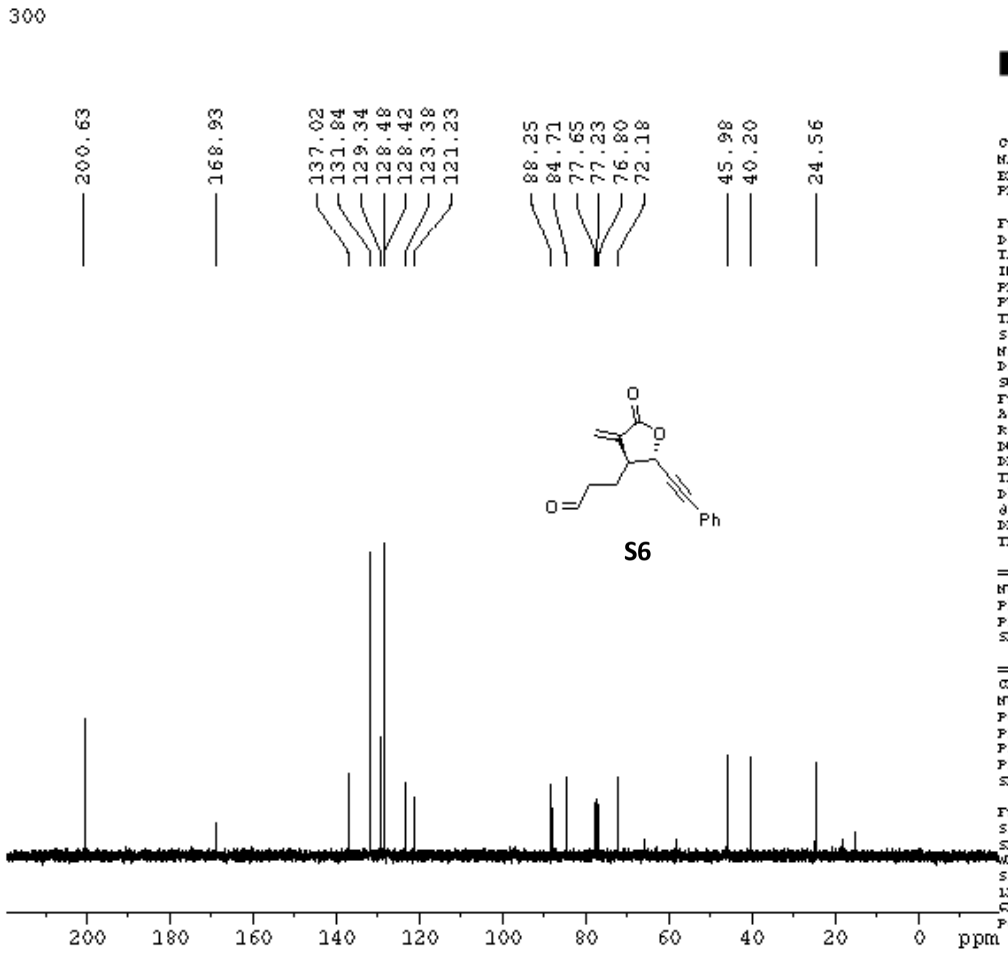


S5

BRUKER

```
Current Data Parameters
NAME            CH-II-192
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20100730
Time               14.23
INSTRUM              spect
PROBHD    5 mm tholtinvcl
PULPROG              zgpg
TD                  32768
SOLVENT             CDCl3
NS                     35
DS                      2
SWH           17985.611 Hz
FIDRES         0.548877 Hz
AQ             0.9110004 sec
RG                10321.3
DW                27.800 usec
DE                 6.00 usec
TE                295.2 K
D1             6.00000000 sec
D11            0.03000000 sec
DELTA          5.90000010 sec
TD0                     1

====== CHANNEL f1 ======
NUC1                  13C
P1                   5.00 usec
PL1                  0.00 dB
SFO1          75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  4.00 dB
PL12                22.9% dB
PL13                120.00 dB
SFO2         300.1412006 MHz

F2 - Processing parameters
SI                  32768
SF            75.4702630 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

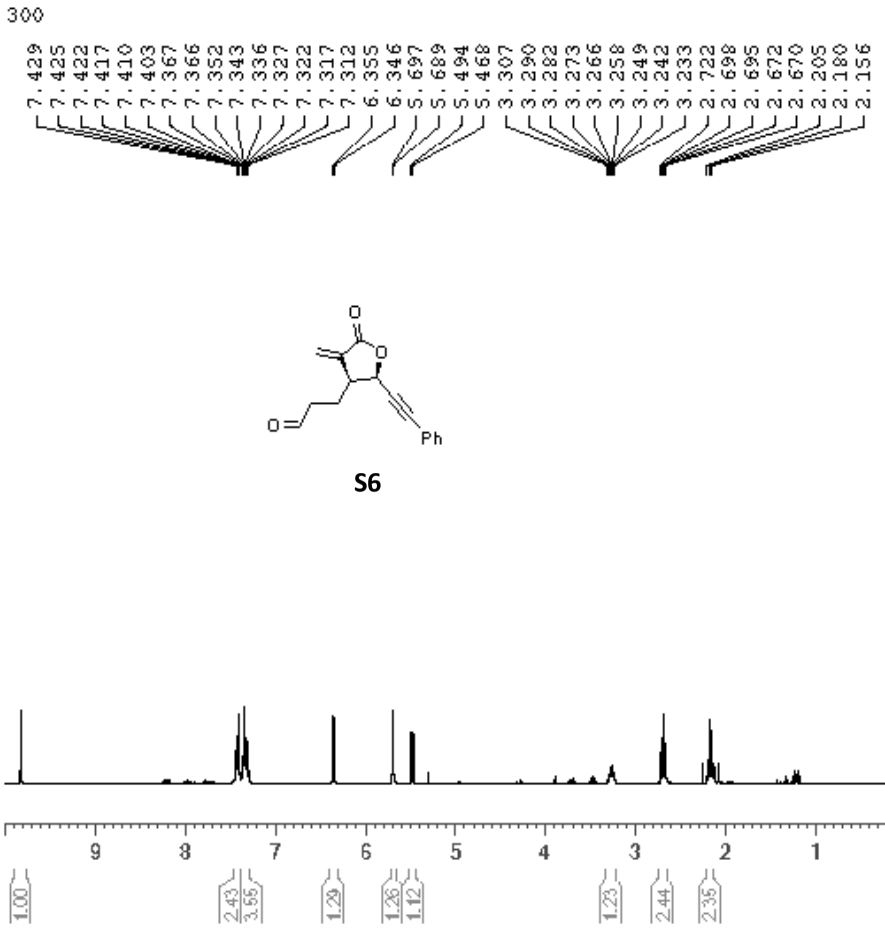

ppm (f1)
5.0
0.0
0.87
2.22
1.90
1.00
1.02
0.91
1.01
1.99
1.00
1.05
9.821
7.430
7.425
7.405
7.398
7.335
7.328
7.321
7.308
7.302
6.356
6.347
5.680
5.672
5.272
4.934
4.914
3.247
3.237
3.228
3.218
3.209
3.200
2.724
2.699
2.677
2.170
2.165
2.145
2.142
2.123
2.117
2.098
2.093
2.073
S6
O
O
O
Ph



S6

BRUKER

```
Current Data Parameters
NAME      CH-II-CHO trans
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20100710
Time             10.39
INSTRUM          spect
PROBHD   5 mm tboltinvcl
PULPROG          zgpg
TD               32768
SOLVENT          CDCl3
NS                  15
DS                   2
SWH          17985.611 Hz
FIDRES        0.548877 Hz
AQ            0.9110004 sec
RG               9195.2
DW              27.800 usec
DE               6.00 usec
TE              293.2 K
D1           6.00000000 sec
d11          0.03000000 sec
DELTA        5.90000010 sec
TD0                  1

====== CHANNEL f1 ======
NUC1               13c
P1                5.00 usec
PL1               0.00 dB
SFO1         75.4779106 MHz

====== CHANNEL f2 ======
CPDPRG2        waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               4.00 dB
PL12             22.99 dB
PL13            120.00 dB
SFO2        300.1412006 MHz

F2 - Processing parameters
SI               32768
SF          75.4702630 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```



S6

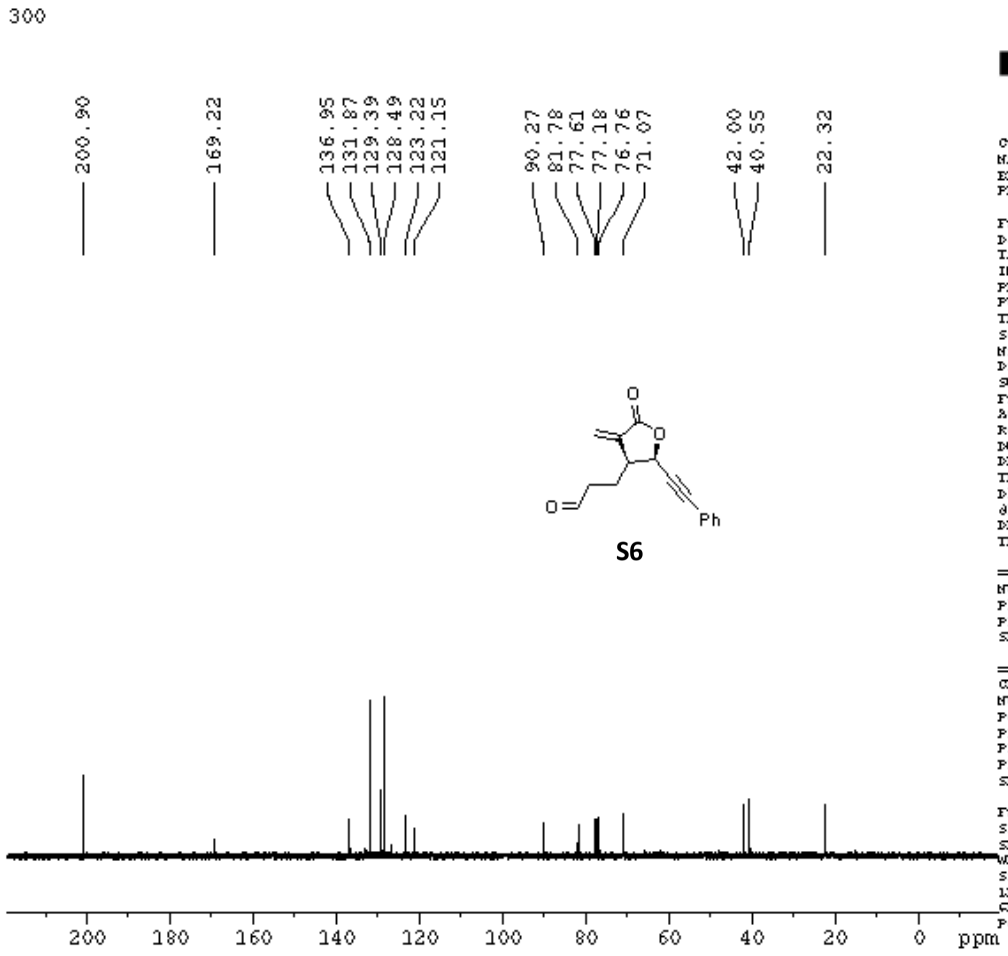
BRUKER

Current Data Parameters
NAME CH-II-154
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100709
Time 16.45
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 40.3
DW 81.000 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
TD0 1

====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz

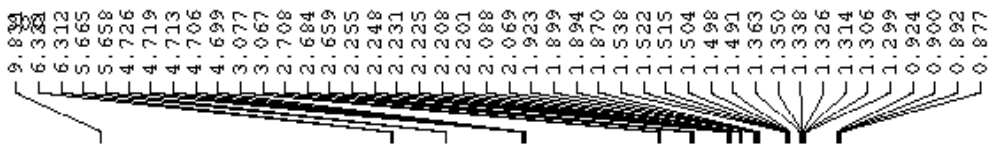
F2 - Processing parameters
SI 16384
SF 300.1399954 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

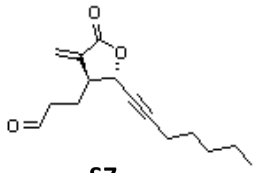


S6

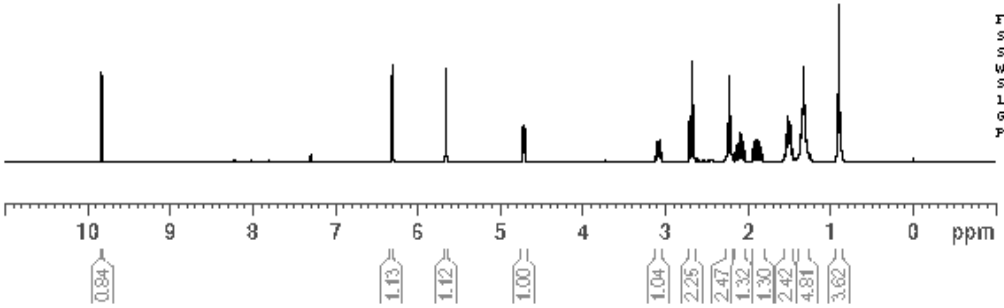
BRUKER

```
Current Data Parameters
NAME                  CH-II-154
EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
Date_              20100709
Time                   16.49
INSTRUM                spect
PROBHD    5 mm multinucl
PULPROG                zgpg
TD                        32768
SOLVENT                CDCl3
NS                           29
DS                            2
SWH                17985.611 Hz
FIDRES              0.548877 Hz
AQ                  0.9110004 sec
RG                       16384
DW                     27.800 usec
DE                      6.00 usec
TE                     295.2 K
D1                 6.00000000 sec
d11                0.03000000 sec
DELTA              5.90000010 sec
TD0                           1

====== CHANNEL f1 ======
NUC1                        13C
P1                        5.00 usec
PL1                       0.00 dB
SFO1               75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       4.00 dB
PL12                     22.99 dB
PL13                    120.00 dB
SFO2              300.1412006 MHz

F2 - Processing parameters
SI                        32768
SF                 75.4702630 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

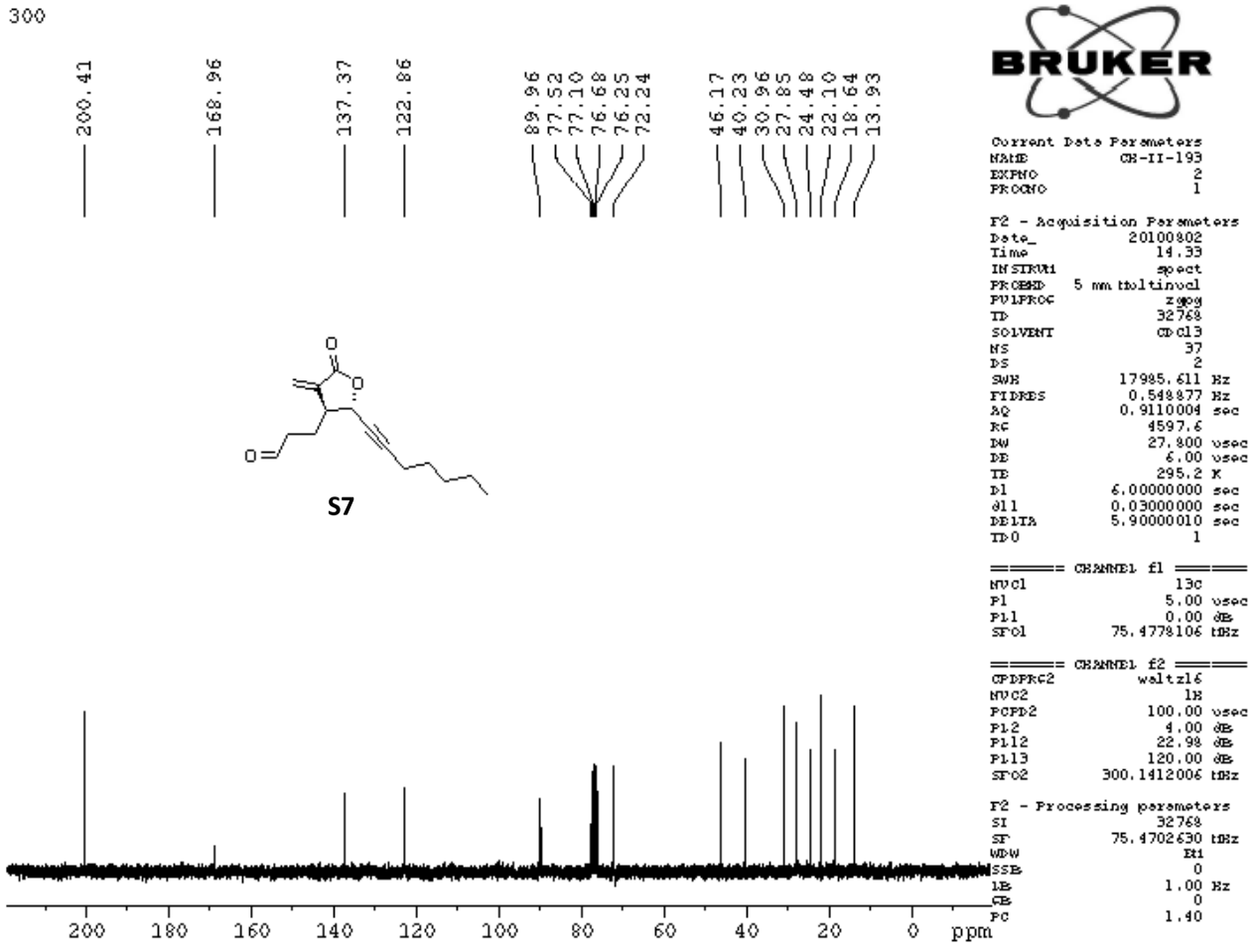




S7



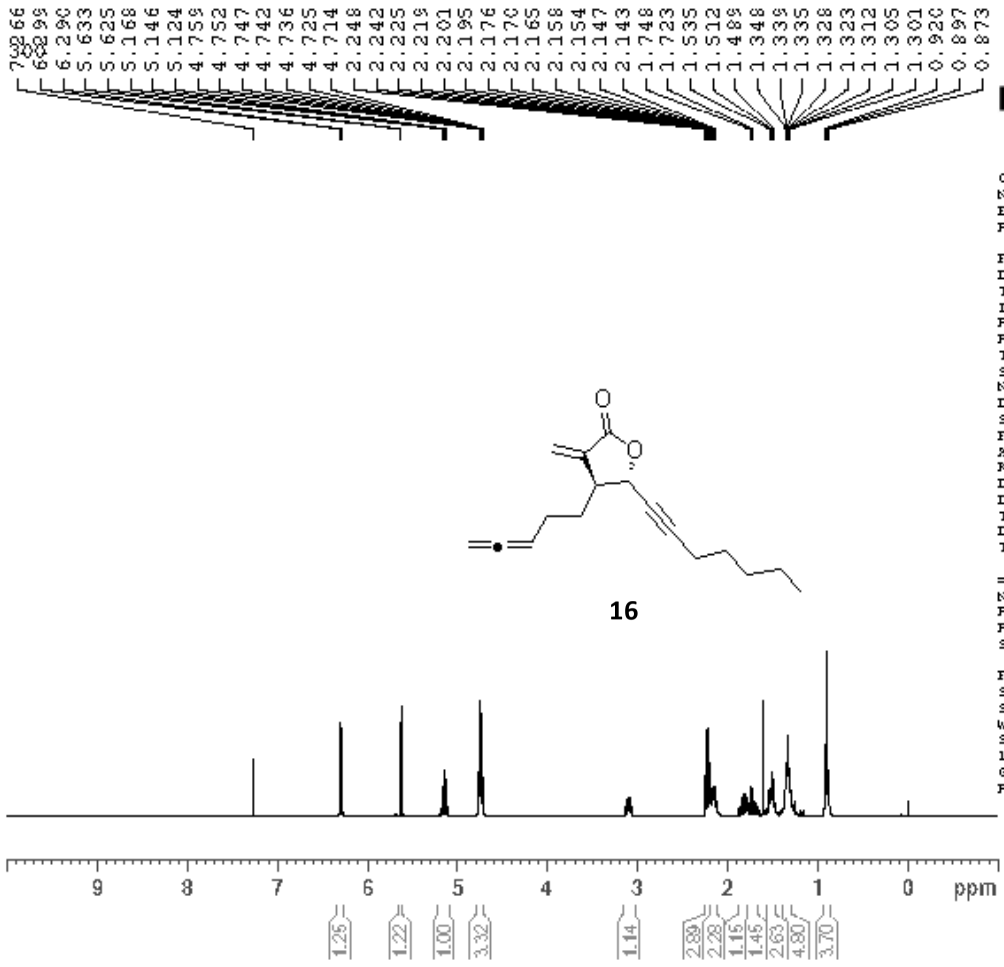

```
Current Data Parameters
NAME              CH-II-193
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_          20100802
Time               14.27
INSTRUM              spect
PROBHD   5 mm multinucl
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542580 sec
RG                   40.3
DW                 81.000 usec
DE                  6.00 usec
TE                 295.2 K
D1              2.00000000 sec
TD0                     1

====== CHANNEL f1 ======
NUC1                   1H
P1                  5.00 usec
PL1                 4.00 dB
SFO1          300.1418531 MHz

F2 - Processing parameters
SI                  16384
SF          300.1399939 MHz
WDW                    EM
SSB                     0
LB                 0.10 Hz
GB                      0
PC                   1.00
```

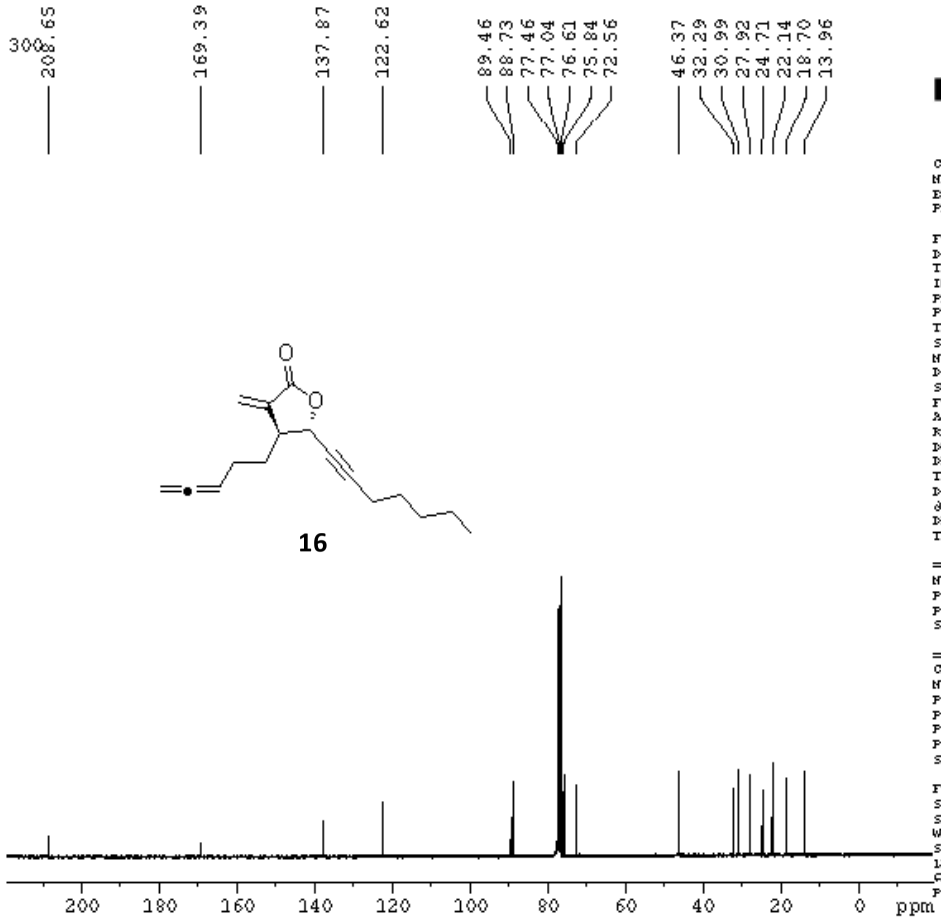


S7

BRUKER

```
Current Data Parameters
NAME              CH-II-193
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_           20100802
Time                14.33
INSTRUM              spect
PROBHD    5 mm multinucl
PULPROG              zgpg
TD                  32768
SOLVENT              CDCl3
NS                      37
DS                       2
SWH             17985.611 Hz
FIDRES           0.548877 Hz
AQ               0.9110004 sec
RG                  4597.6
DW                 27.800 usec
DE                  6.00 usec
TE                 295.2 K
D1              6.00000000 sec
d11             0.03000000 sec
DELTA           5.90000010 sec
TD0                      1

====== CHANNEL f1 ======
NUC1                   13C
P1                    5.00 usec
PL1                   0.00 dB
SFO1          75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                   1H
PCPD2               100.00 usec
PL2                   4.00 dB
PL12                 22.9% dB
PL13                120.00 dB
SFO2          300.1412006 MHz

F2 - Processing parameters
SI                  32768
SF             75.4702630 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```


7.32 7.30 6.29 5.63 5.62 5.16 5.14 5.12 4.75 4.75 4.74 4.74 4.73 4.72 2.24 2.24 2.22 2.21 2.20 2.19 2.17 2.17 2.16 2.15 2.15 2.14 2.14 1.74 1.72 1.53 1.51 1.48 1.34 1.33 1.33 1.32 1.32 1.30 1.30 0.92 0.89 0.87
BRUKER
Current Data Parameters
NAME CH-II-195
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100804
Time 15.08
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 297.2 K
D1 2.00000000 sec
TD0 1
====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz
F2 - Processing parameters
SI 16384
SF 300.1400039 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
16
9 8 7 6 5 4 3 2 1 0 ppm
1.25 1.22 1.00 3.32 1.14 2.89 2.28 1.15 1.45 2.63 4.80 3.70



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BRUKER

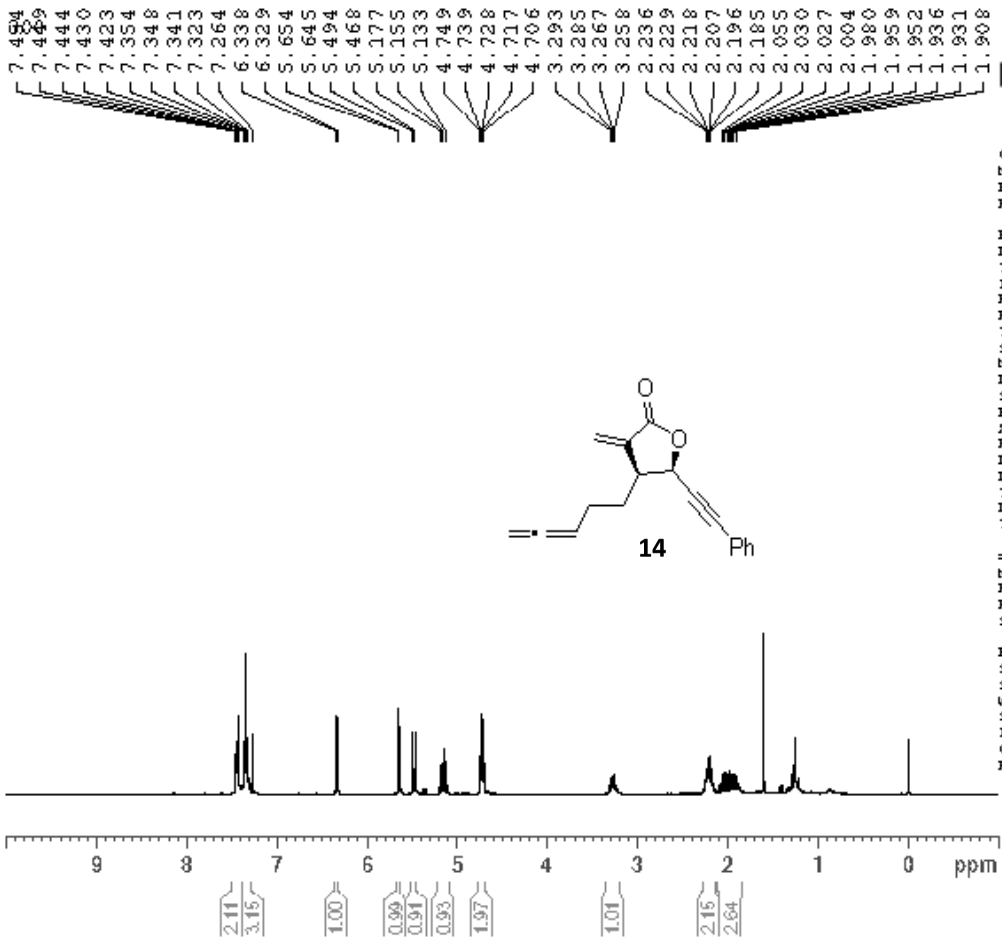
Current Data Parameters
NAME CH-II-195
EXPNO 2
PROCNO 1

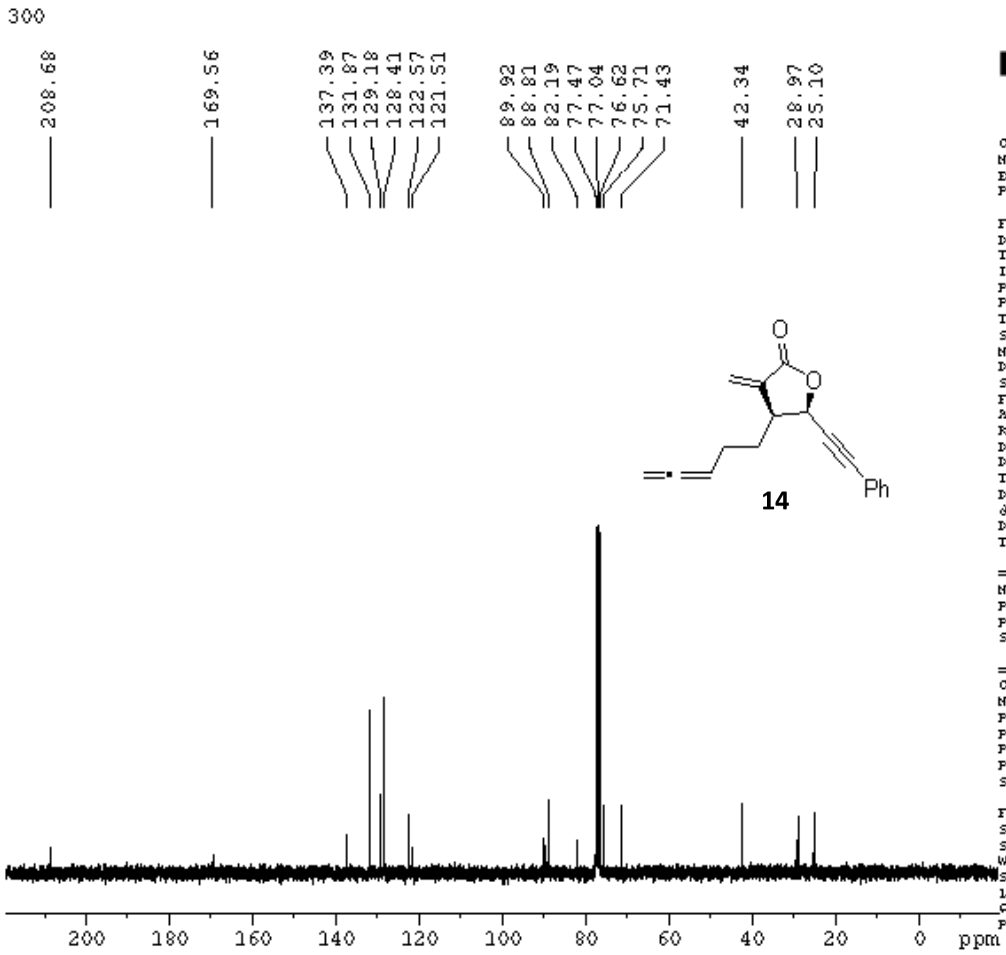
F2 - Acquisition Parameters
Date_ 20100804
Time 19.47
INSTRUM spect
PROBHD 5 mm ttoltinvcl
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 627
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 18390.4
DW 27.800 usec
DE 6.00 usec
TE 296.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1

====== CHANNEL f1 ======
NUC1 13c
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 22.98 dB
PL13 120.00 dB
SFO2 300.1412006 MHz

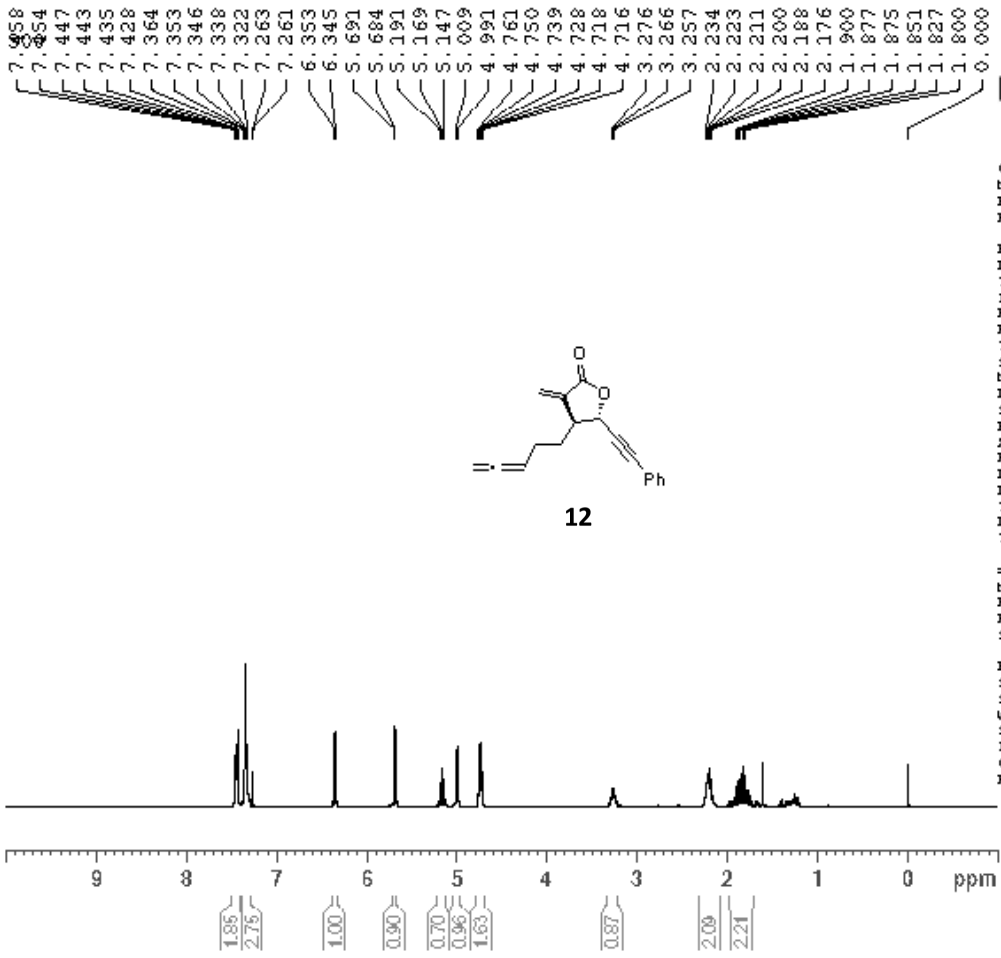
F2 - Processing parameters
SI 32768
SF 75.4702630 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.464
7.449
7.444
7.430
7.423
7.354
7.348
7.341
7.323
7.264
6.338
6.329
5.654
5.645
5.494
5.468
5.177
5.155
5.133
4.749
4.739
4.728
4.717
4.706
3.293
3.285
3.267
3.258
2.236
2.229
2.218
2.207
2.196
2.185
2.055
2.030
2.027
2.004
1.980
1.959
1.952
1.936
1.931
1.908
BRUKER
Current Data Parameters
NAME CH-II-187
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100727
Time 20.15
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 256
DW 81.000 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
TD0 1
====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz
F2 - Processing parameters
SI 16384
SF 300.1400045 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
O
14
Ph
9
8
7
6
5
4
3
2
1
0
ppm
2.11
3.15
1.00
0.99
0.91
0.93
1.97
1.01
2.15
2.64

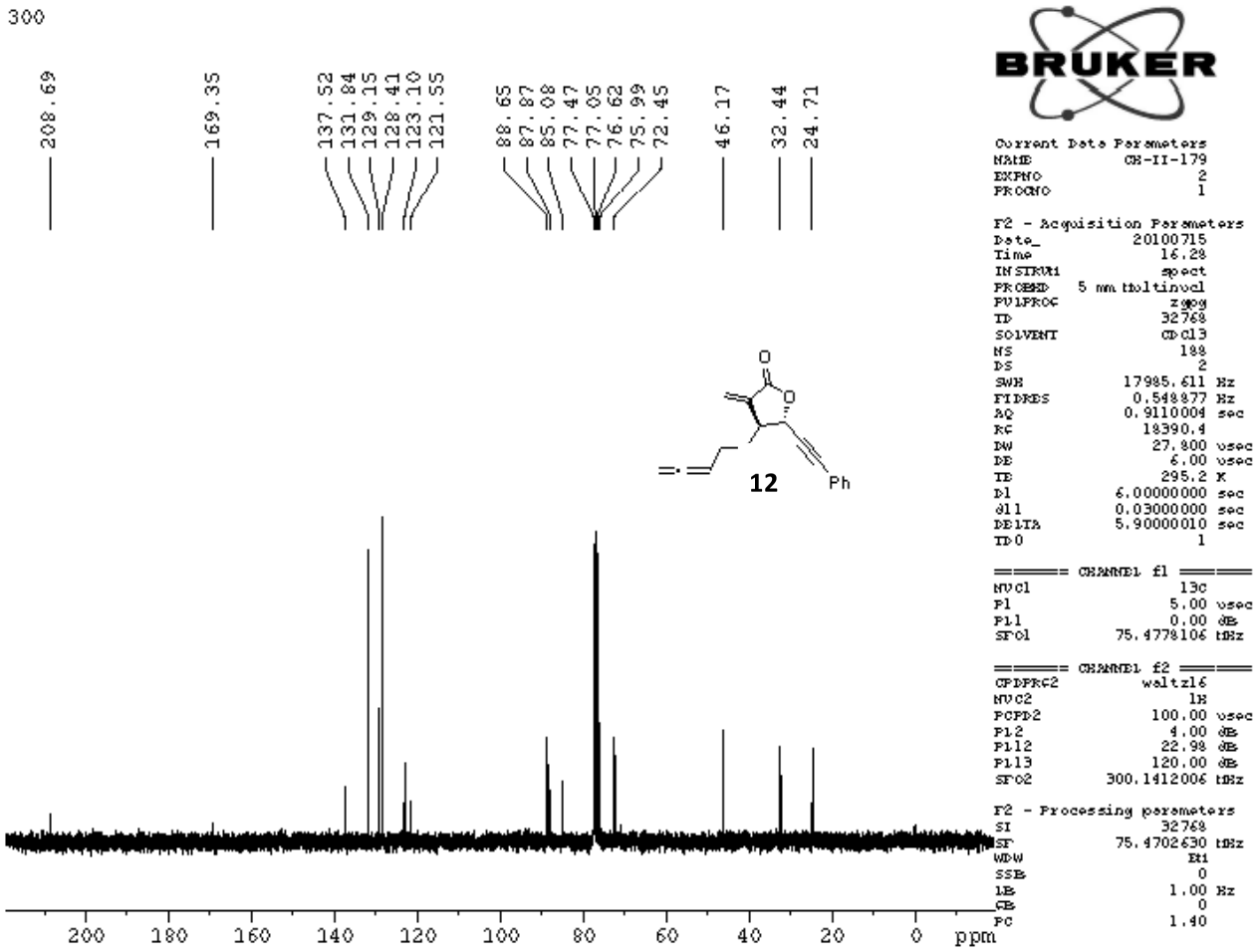


BRUKER

```
Current Data Parameters
NAME                  CH-II-187
EXPNO                         6
PROCNO                        1

F2 - Acquisition Parameters
Date_               20100728
Time                      9.12
INSTRUM                   spect
PROBHD     5 mm tholtinvcl
PULPROG                   zgpg
TD                       32768
SOLVENT                  CDCl3
NS                         246
DS                           2
SWH                 17985.611 Hz
FIDRES              0.548877 Hz
AQ                  0.9110004 sec
RG                     11585.2
DW                     27.800 usec
DE                      6.00 usec
TE                     294.2 K
D1                  6.00000000 sec
d11                 0.03000000 sec
DELTA               5.90000010 sec
TD0                           1

====== CHANNEL f1 ======
NUC1                        13C
P1                         5.00 usec
PL1                        0.00 dB
SFO1                75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    100.00 usec
PL2                        4.00 dB
PL12                      22.98 dB
PL13                     120.00 dB
SFO2                300.1412006 MHz

F2 - Processing parameters
SI                       32768
SF                  75.4702630 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

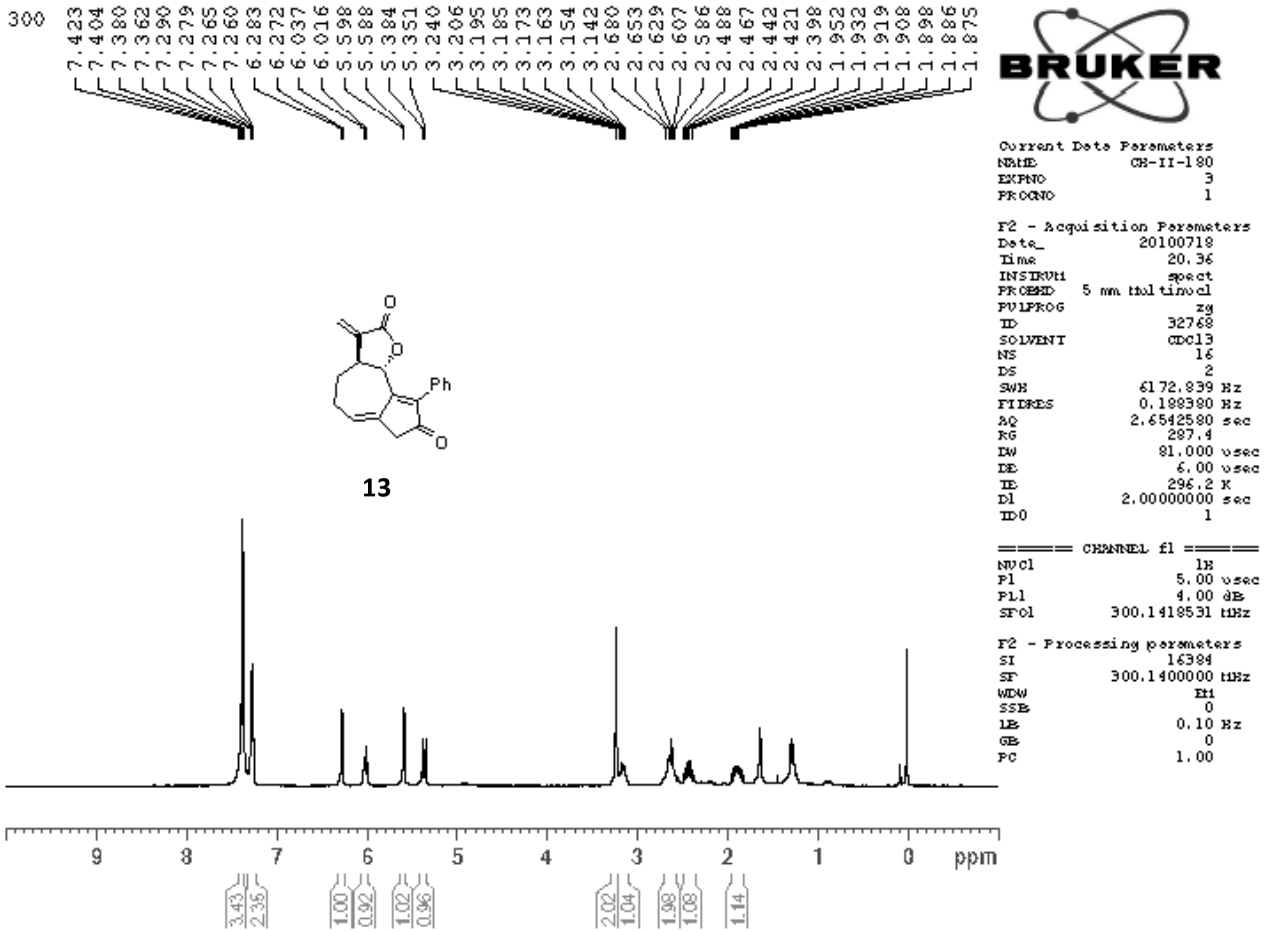

7.458
7.454
7.447
7.443
7.435
7.428
7.364
7.353
7.346
7.338
7.322
7.263
7.261
6.353
6.345
5.691
5.684
5.191
5.169
5.147
5.009
4.991
4.761
4.750
4.739
4.728
4.718
4.716
3.276
3.266
3.257
2.234
2.223
2.211
2.200
2.188
2.176
1.900
1.877
1.875
1.851
1.827
1.800
0.000
BRUKER
Current Data Parameters
NAME CR-II-179
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100715
Time 16.20
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
TD0 1
====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz
F2 - Processing parameters
SI 16384
SF 300.1400049 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
O
Ph
9
8
7
6
5
4
3
2
1
0
ppm
1.85
2.76
1.00
0.90
0.70
0.96
1.63
0.87
2.09
2.21

12



BRUKER

```
Current Data Parameters
NAME                  CH-II-179
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_               20100715
Time                    16.28
INSTRUM                 spect
PROBHD     5 mm Multinucl
PULPROG                 zgpg
TD                         32768
SOLVENT                 CDCl3
NS                           188
DS                             2
SWH                 17985.611 Hz
FIDRES               0.548877 Hz
AQ                   0.9110004 sec
RG                     18390.4
DW                      27.800 usec
DE                        6.00 usec
TE                       295.2 K
D1                   6.00000000 sec
D11                  0.03000000 sec
DELTA                5.90000010 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         5.00 usec
PL1                        0.00 dB
SFO1                75.4778106 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     100.00 usec
PL2                         4.00 dB
PL12                       22.98 dB
PL13                      120.00 dB
SFO2                300.1412006 MHz

F2 - Processing parameters
SI                         32768
SF                  75.4702630 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



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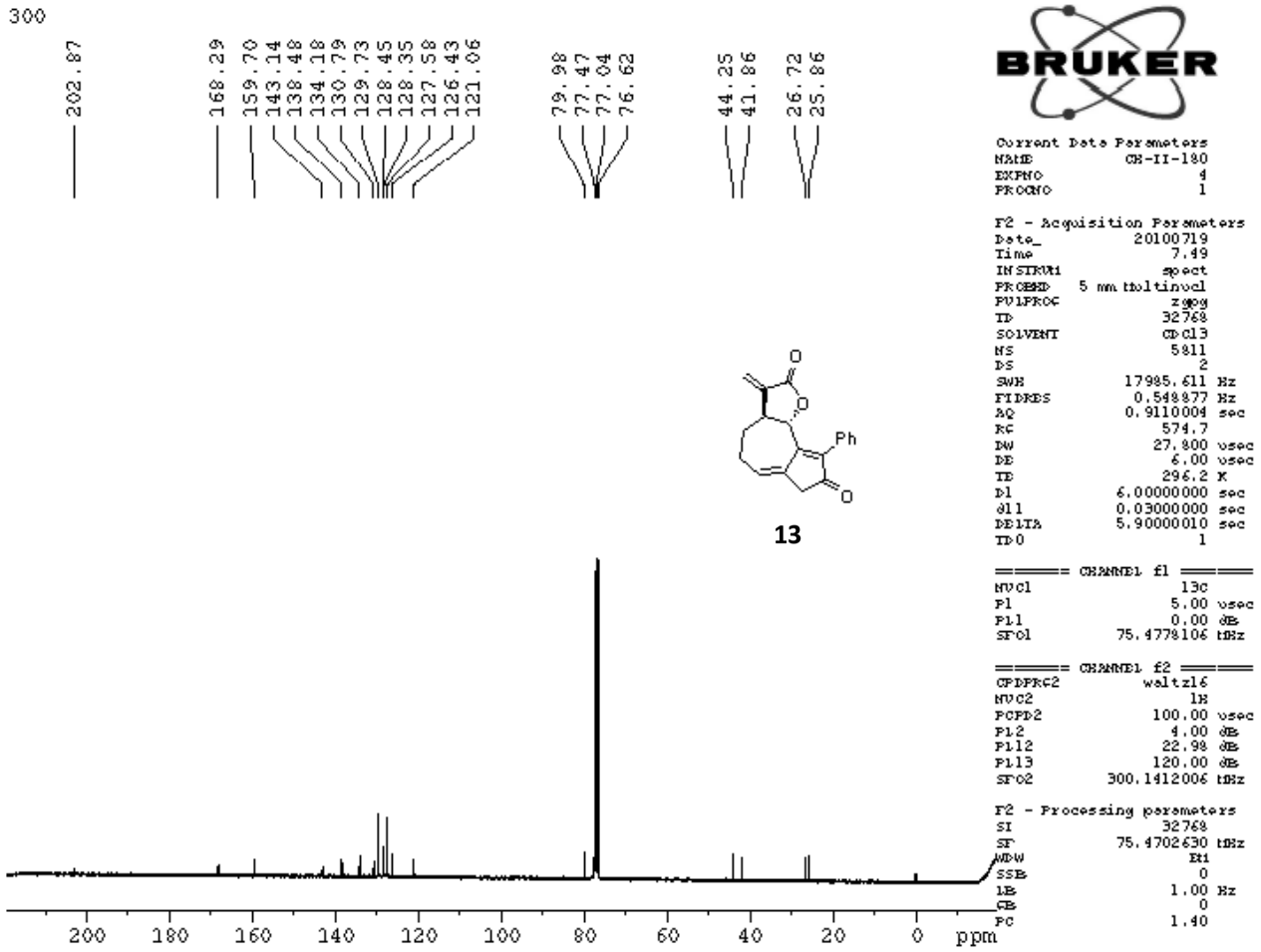
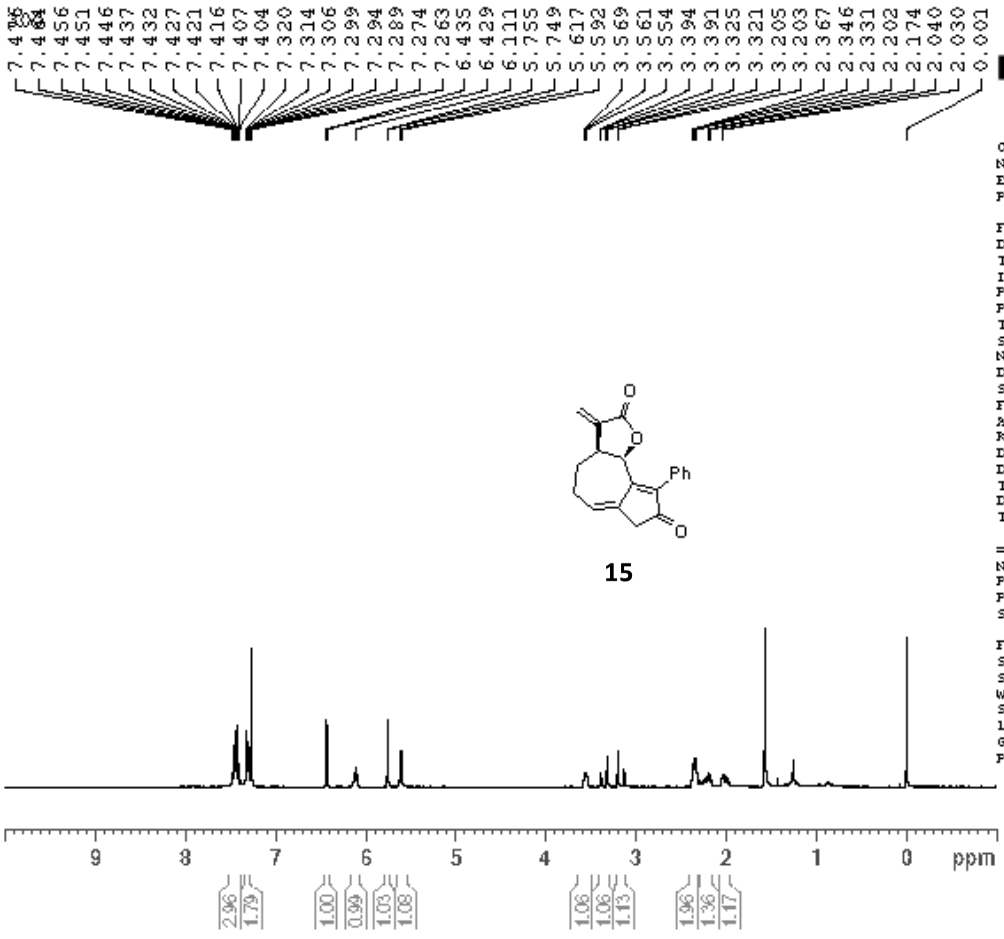
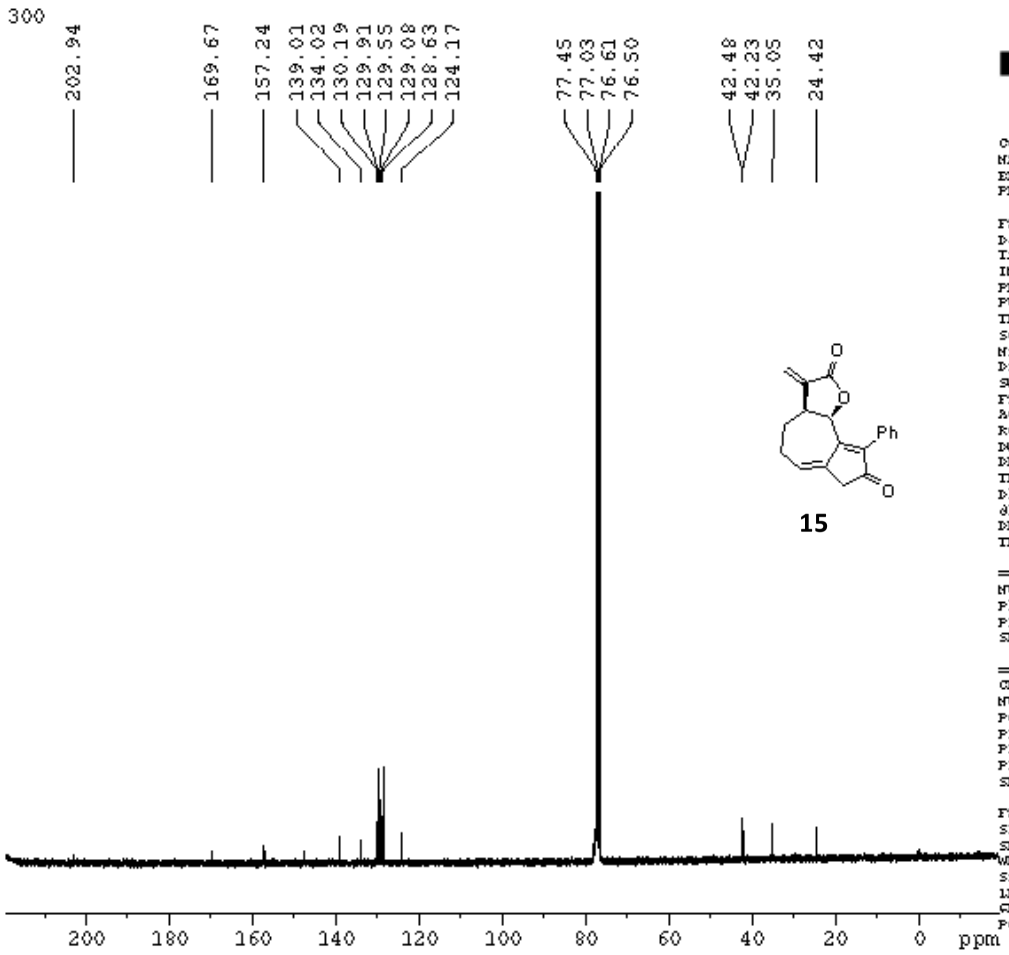
BRUKER

```
Current Data Parameters
NAME                  CH-II-180
EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20100719
Time                      20.36
INSTRUM                   spect
PROBHD    5 mm multinucl
PULPROG                      zg
TD                        32768
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                  6172.839 Hz
FIDRES               0.188380 Hz
AQ                   2.6542580 sec
RG                       287.4
DW                      81.000 usec
DE                        6.00 usec
TE                       296.2 K
D1                   2.00000000 sec
TD0                           1

====== CHANNEL f1 ======
NUC1                         1H
P1                        5.00 usec
PL1                       4.00 dB
SFO1              300.1418531 MHz

F2 - Processing parameters
SI                        16384
SF                300.1400000 MHz
WDW                         EM
SSB                          0
LB                        0.10 Hz
GB                           0
PC                        1.00
```


300
202.87
168.29
159.70
143.14
138.48
134.18
130.79
129.73
128.45
128.35
127.58
126.43
121.06
79.98
77.47
77.04
76.62
44.25
41.86
26.72
25.86
BRUKER
Current Data Parameters
NAME CH-II-180
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100719
Time 7.49
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 5811
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 574.7
DW 27.800 usec
DE 6.00 usec
TE 296.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4778106 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 22.98 dB
PL13 120.00 dB
SFO2 300.1412006 MHz
F2 - Processing parameters
SI 32768
SF 75.4702630 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
Ph
O
13
200
180
160
140
120
100
80
60
40
20
0
ppm


7.456
7.451
7.446
7.437
7.432
7.427
7.421
7.416
7.407
7.404
7.320
7.314
7.306
7.299
7.294
7.289
7.274
7.263
6.435
6.429
6.111
5.755
5.749
5.617
5.592
3.569
3.561
3.554
3.394
3.391
3.325
3.321
3.205
3.203
2.367
2.346
2.331
2.202
2.174
2.040
2.030
0.001
BRUKER
Current Data Parameters
NAME GH-II-190
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100729
Time 17.36
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 296.2 K
D1 2.00000000 sec
TD0 1
====== CHANNEL f1 ======
NUC1 1H
P1 5.00 usec
PL1 4.00 dB
SFO1 300.1418531 MHz
F2 - Processing parameters
SI 16384
SF 300.1400045 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
O
O
Ph
O
15
9
8
7
6
5
4
3
2
1
0
ppm
2.96
1.79
1.00
0.99
1.03
1.08
1.06
1.06
1.13
1.96
1.36
1.17



15

BRUKER

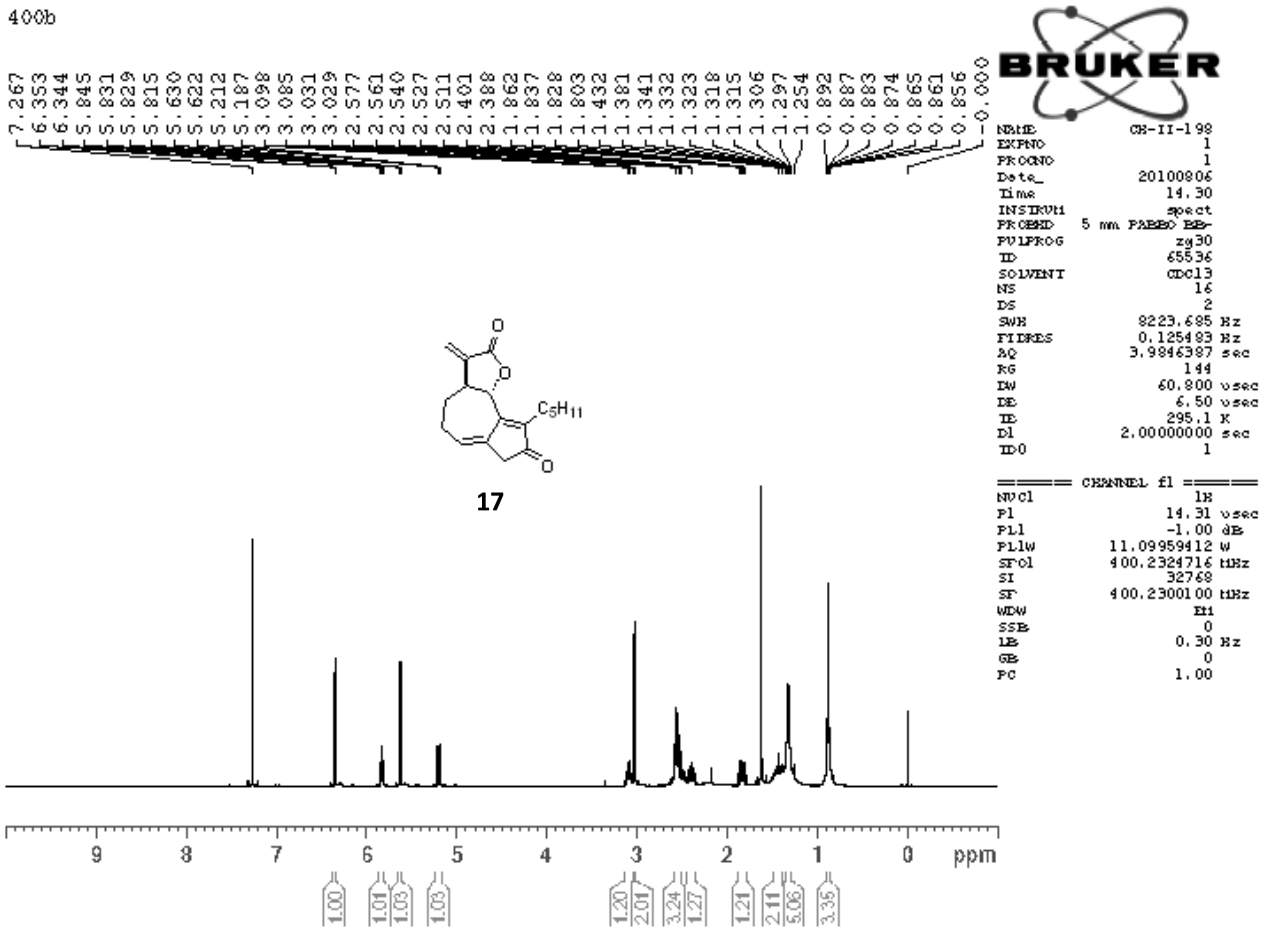
Current Data Parameters
NAME CH-II-190
EXPNO 7
PROCNO 1

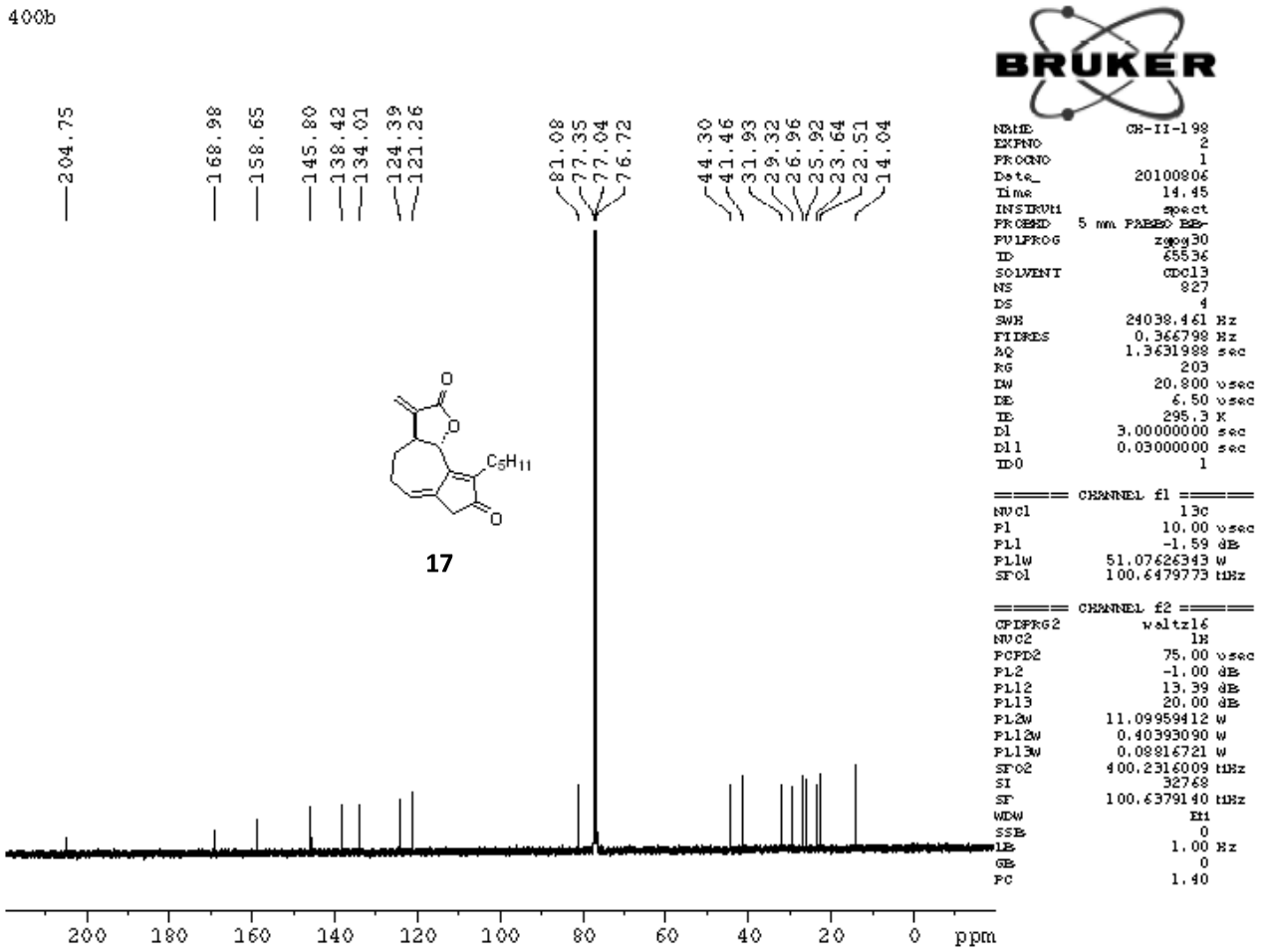
F2 - Acquisition Parameters
Date_ 20100729
Time 20.30
INSTRUM spect
PROBHD 5 mm multinucl
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 6185
DS 2
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 6.00000000 sec
d11 0.03000000 sec
DELTA 5.90000010 sec
TD0 1

====== CHANNEL f1 ======
NUC1 13C
P1 5.00 usec
PL1 0.00 dB
SFO1 75.4778106 MHz

====== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 4.00 dB
PL12 22.98 dB
PL13 120.00 dB
SFO2 300.1412006 MHz

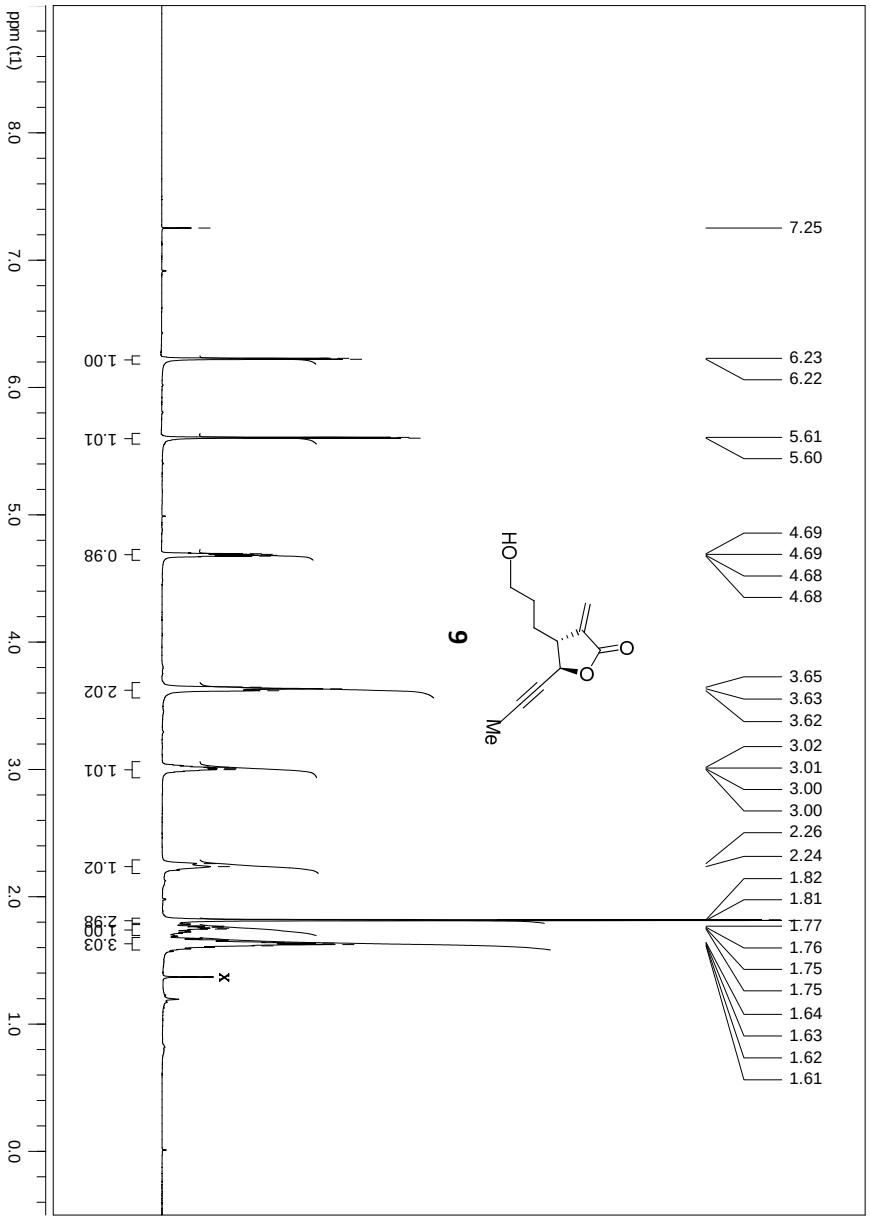
F2 - Processing parameters
SI 32768
SF 75.4702630 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

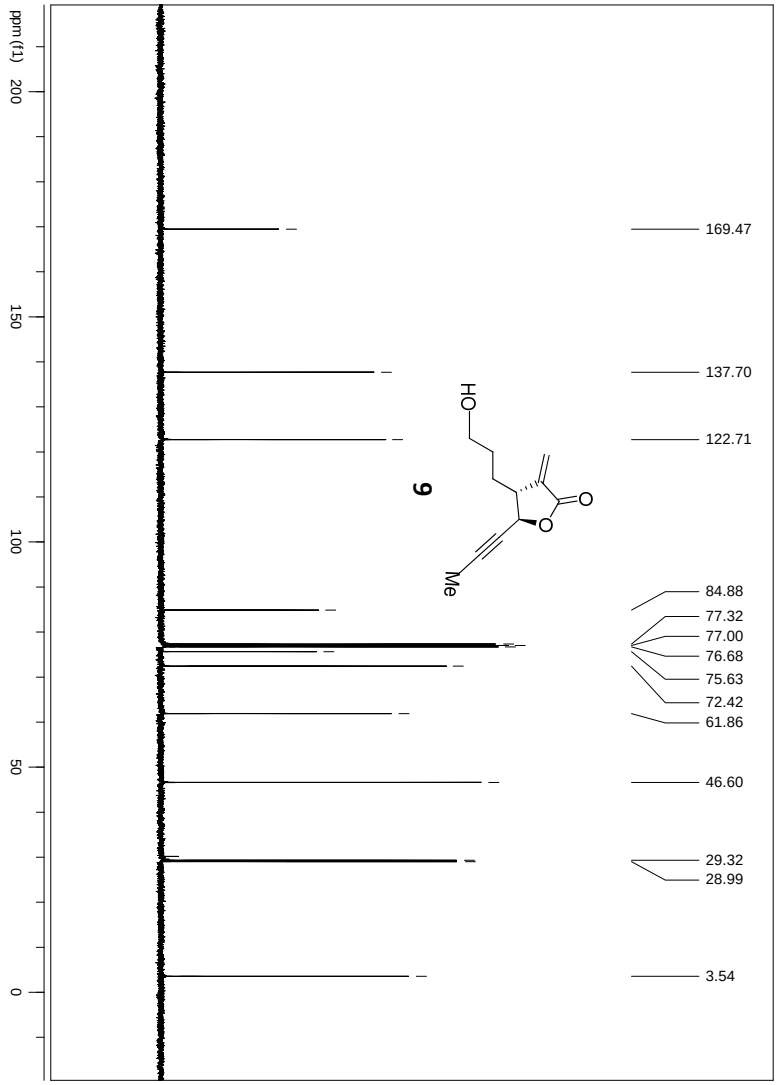

400b
7.267
6.353
6.344
5.845
5.831
5.829
5.815
5.630
5.622
5.212
5.187
3.098
3.085
3.031
3.029
2.577
2.561
2.540
2.527
2.511
2.401
2.388
1.862
1.837
1.828
1.803
1.432
1.381
1.341
1.332
1.323
1.318
1.315
1.306
1.297
1.254
0.892
0.887
0.883
0.874
0.865
0.861
0.856
0.000
BRUKER
NAME CH-II-198
EXPNO 1
PROCNO 1
Date_ 20100806
Time 14.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125493 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.31 usec
PL1 -1.00 dB
PL1W 11.09959412 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
O
C5H11
17
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.03
1.03
1.20
2.01
3.24
1.27
1.21
2.11
5.06
3.35

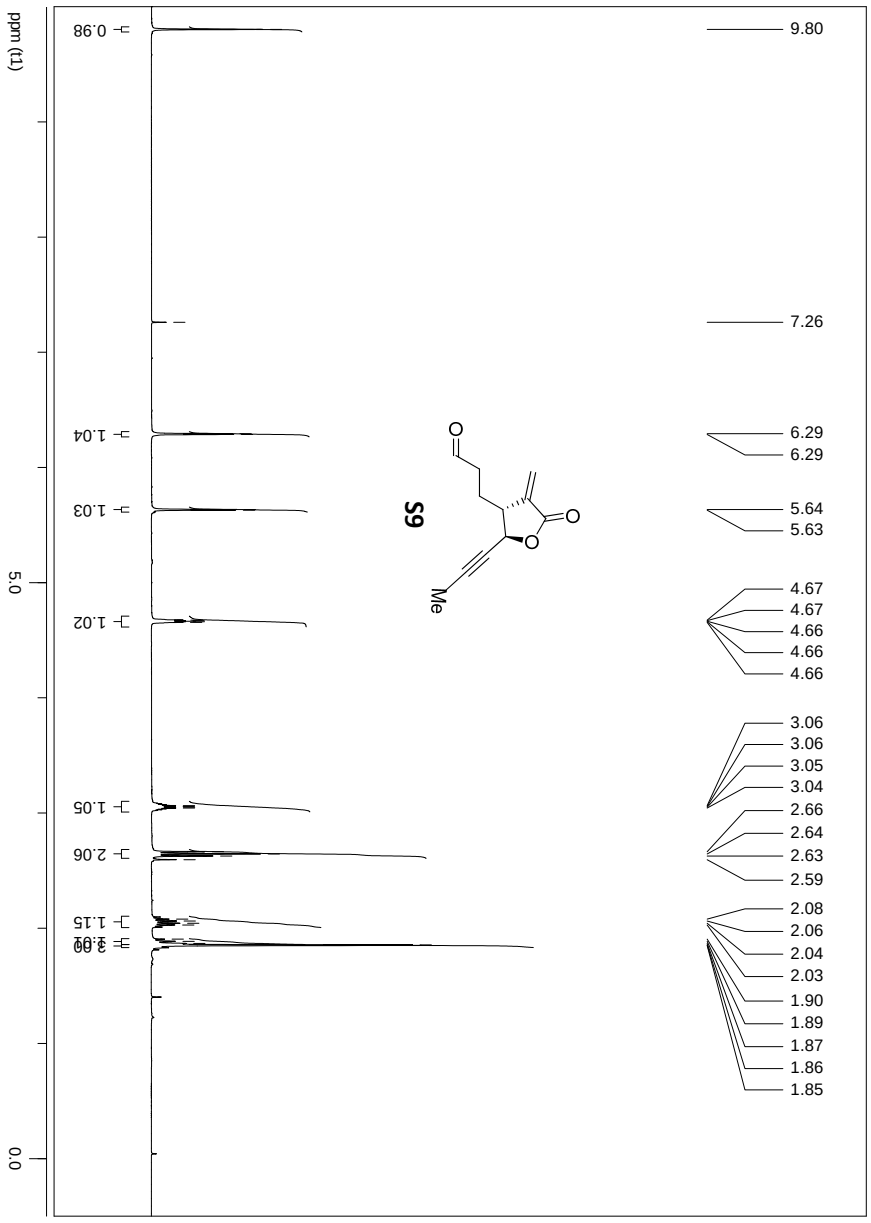


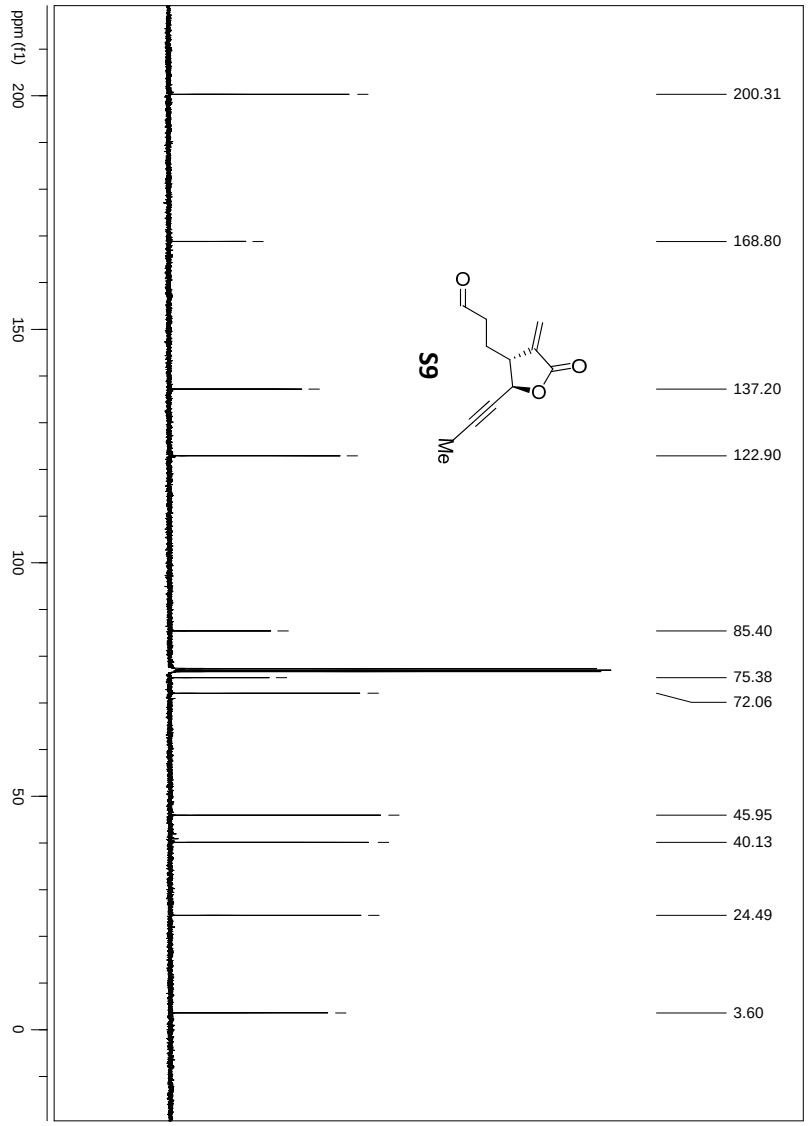
BRUKER

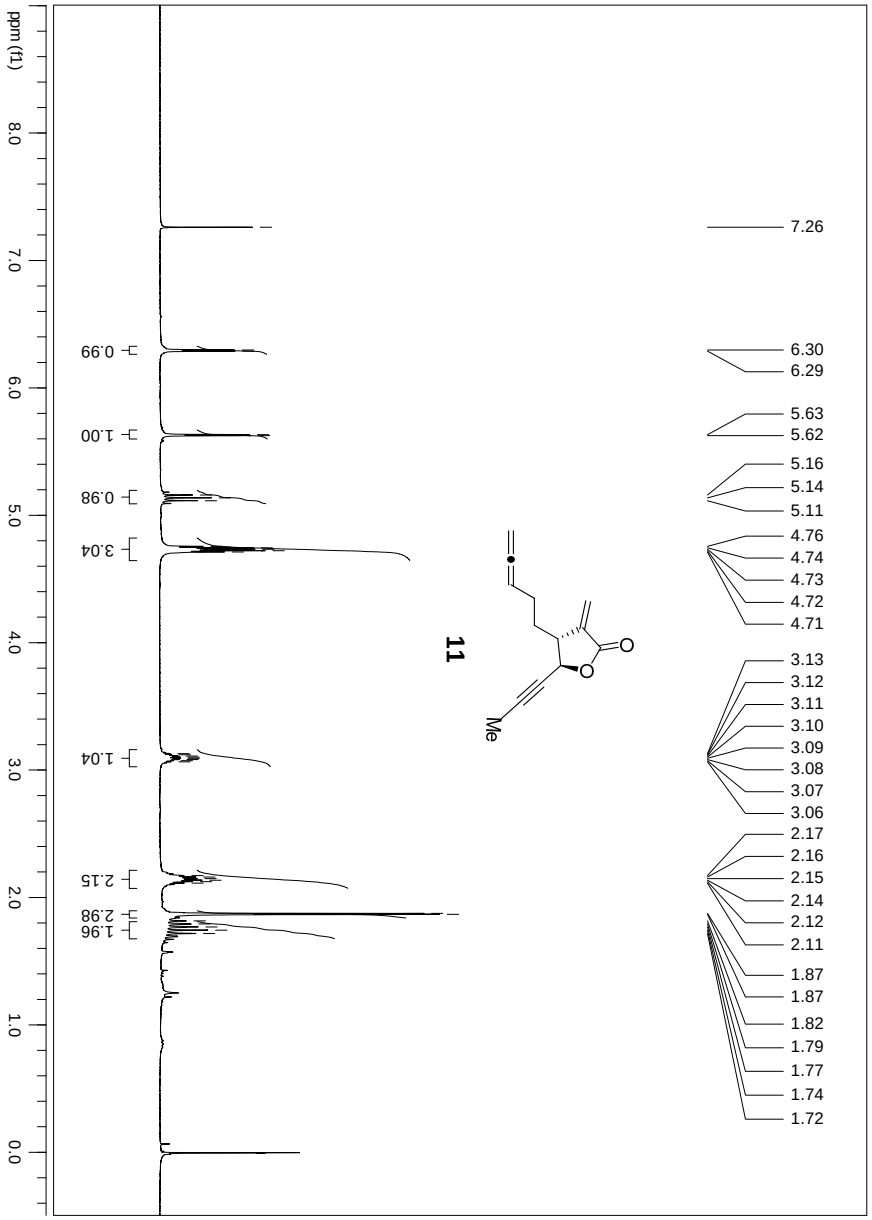
NAME	CH-II-198
EXPNO	2
PROCNO	1
Date_	20100806
Time	14.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	827
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.3 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
====== CHANNEL f1 ======	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
====== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

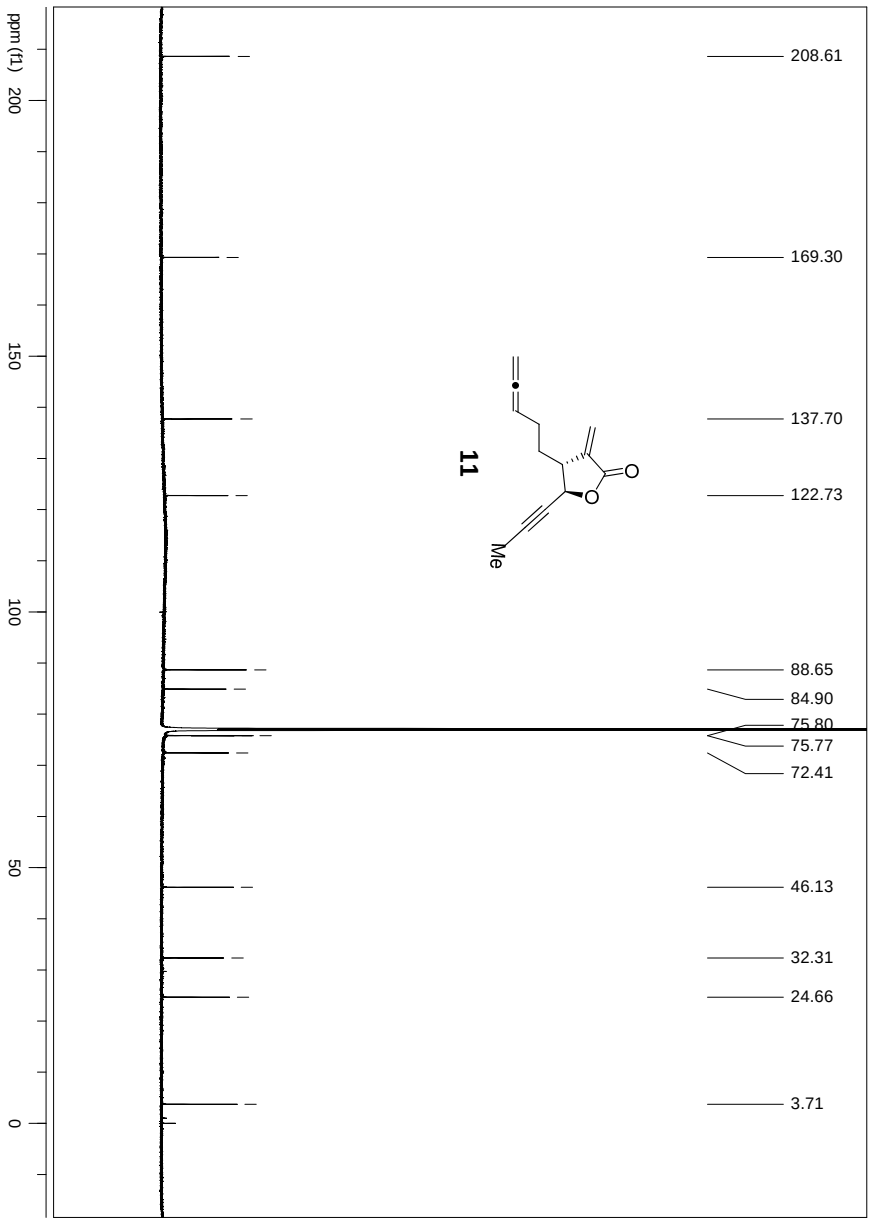

ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.01
0.98
2.02
1.01
1.02
2.98
1.00
3.03
x
HO
O
O
Me
9
7.25
6.23
6.22
5.61
5.60
4.69
4.69
4.68
4.68
3.65
3.63
3.62
3.02
3.01
3.00
3.00
2.26
2.24
1.82
1.81
1.77
1.76
1.75
1.75
1.64
1.63
1.62
1.61

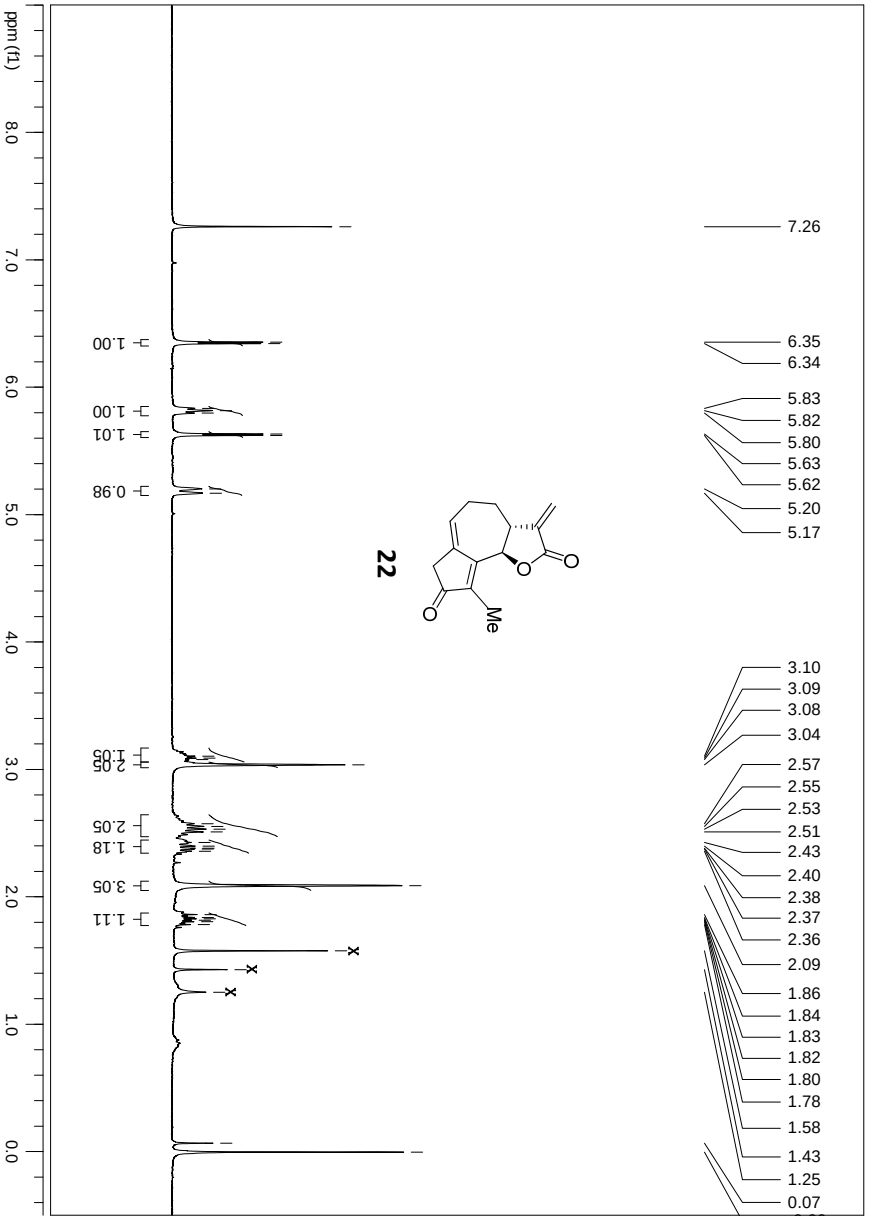

ppm (f1)
200
150
100
50
0
169.47
137.70
122.71
84.88
77.32
77.00
76.68
75.63
72.42
61.86
46.60
29.32
28.99
3.54
HO
O
O
Me
9

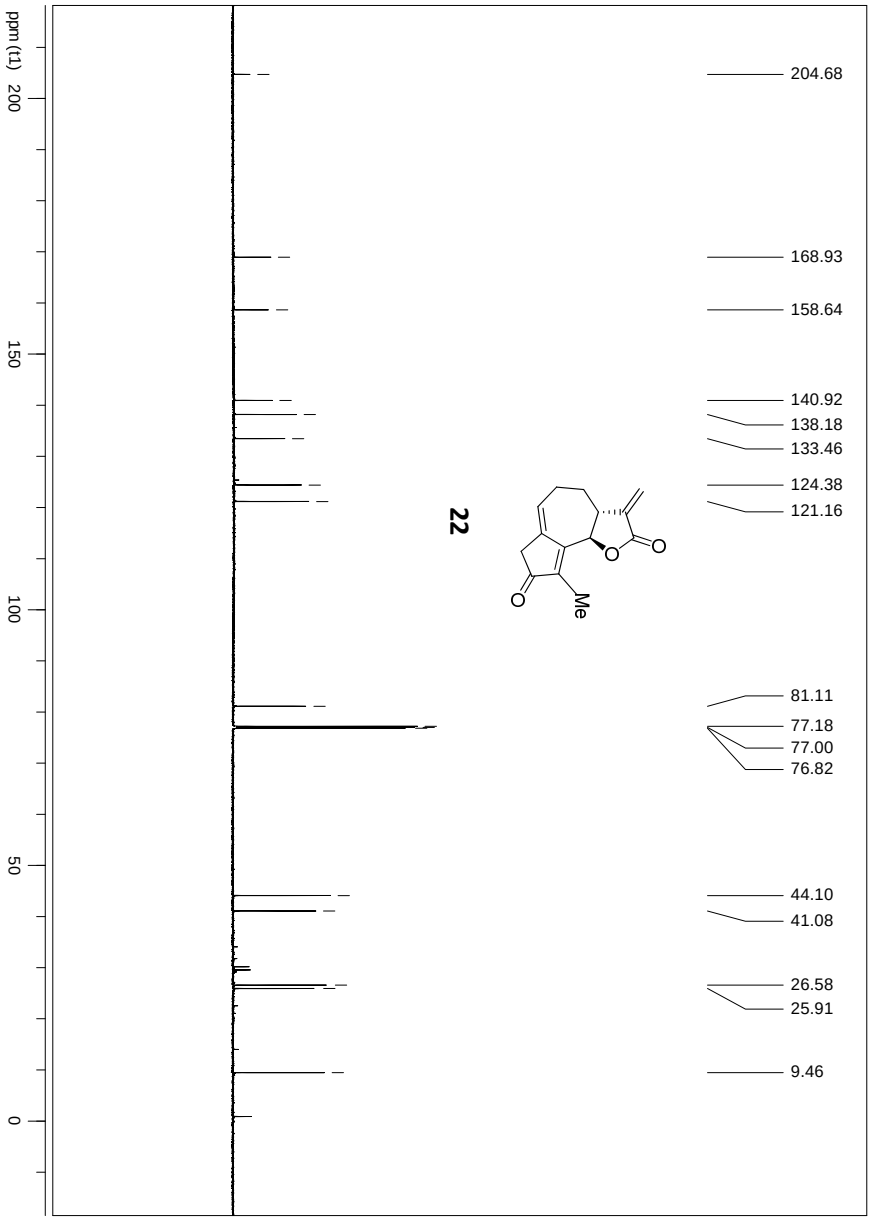

ppm (t1)
5.0
0.0
0.98
1.04
1.03
1.02
1.05
2.06
1.15
3.00
9.80
7.26
6.29
6.29
5.64
5.63
4.67
4.67
4.66
4.66
4.66
3.06
3.06
3.05
3.04
2.66
2.64
2.63
2.59
2.08
2.06
2.04
2.03
1.90
1.89
1.87
1.86
1.85
S9
Me

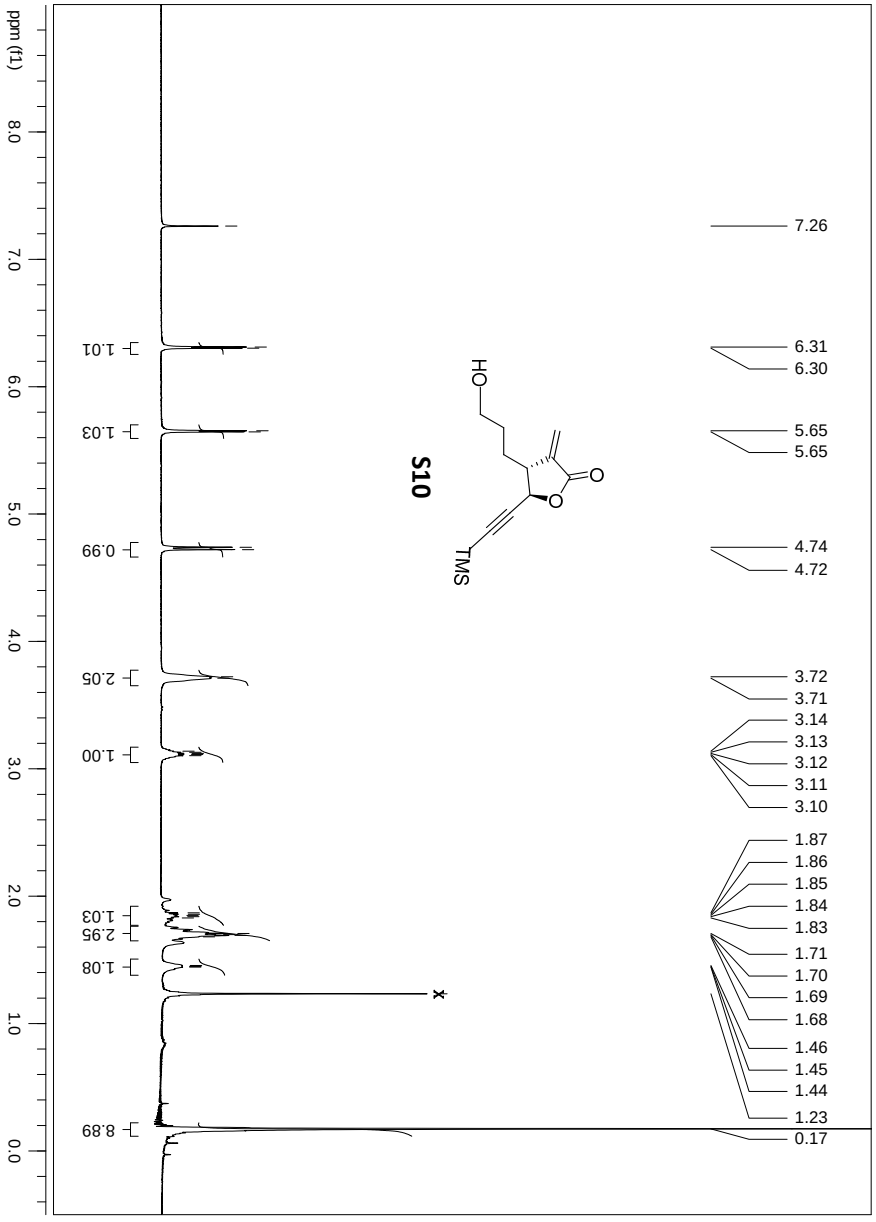

ppm (f1)
200
150
100
50
0
200.31
168.80
137.20
122.90
85.40
75.38
72.06
45.95
40.13
24.49
3.60
S9
O
O
O
Me

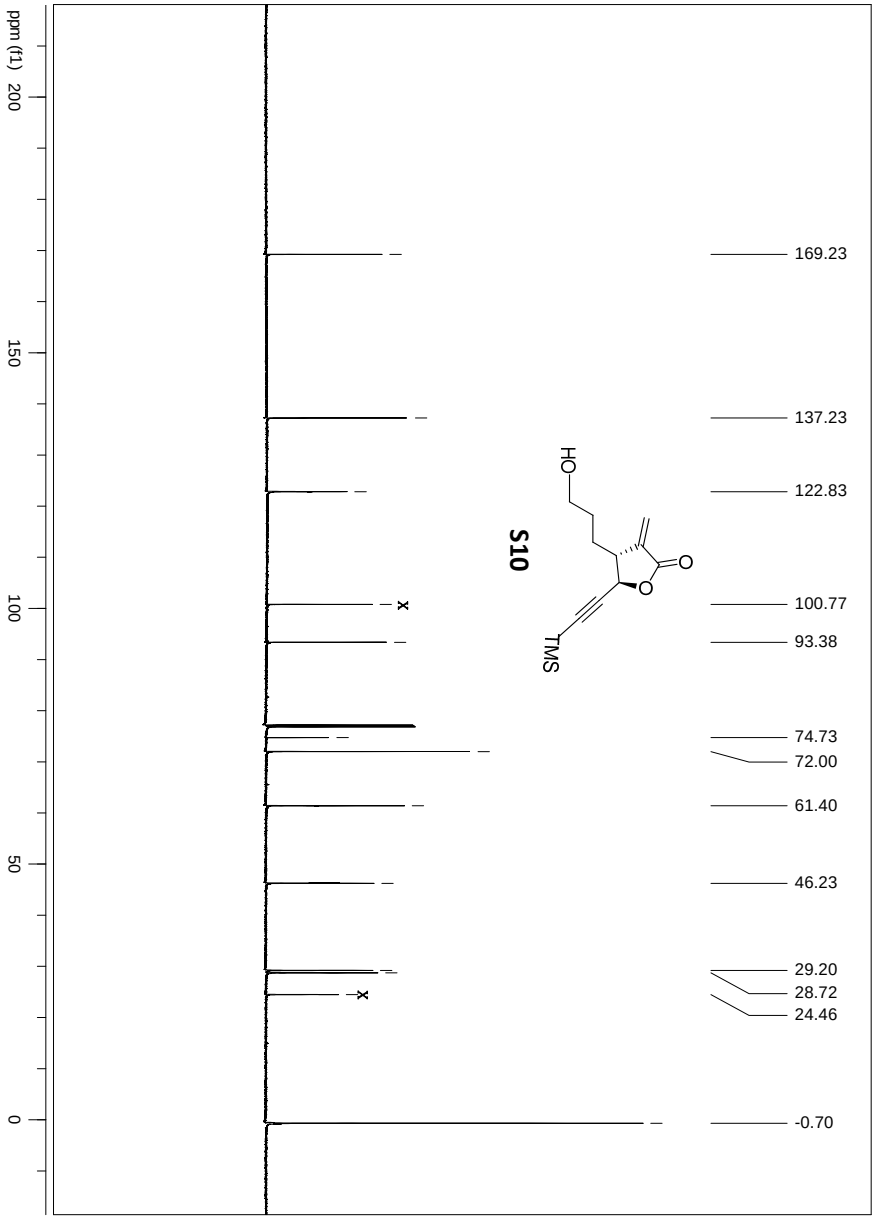

ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.99
1.00
0.98
3.04
1.04
2.15
2.98
1.96
7.26
6.30
6.29
5.63
5.62
5.16
5.14
5.11
4.76
4.74
4.73
4.72
4.71
3.13
3.12
3.11
3.10
3.09
3.08
3.07
3.06
2.17
2.16
2.15
2.14
2.12
2.11
1.87
1.87
1.82
1.79
1.77
1.74
1.72
11
Me
O
O

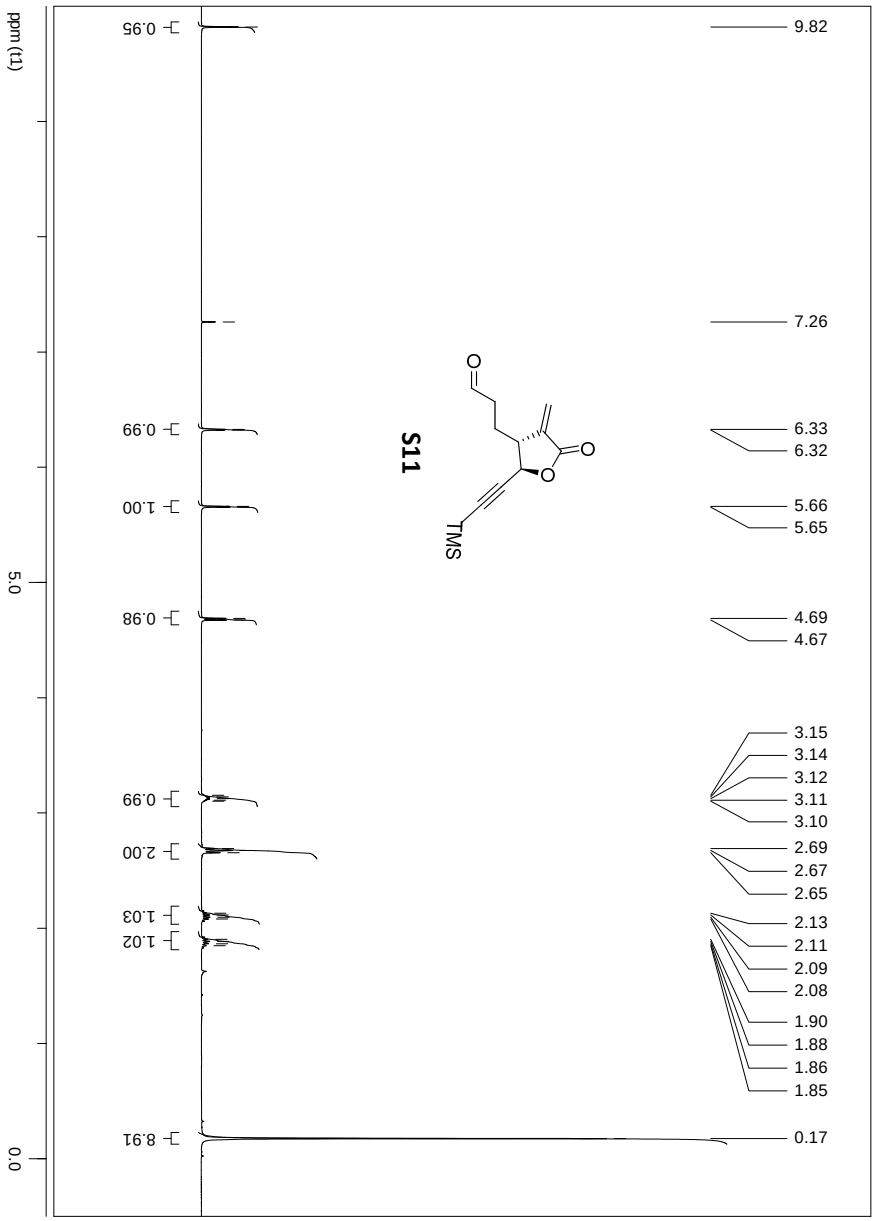

ppm (f1)
200
150
100
50
0
208.61
169.30
137.70
122.73
88.65
84.90
75.80
75.77
72.41
46.13
32.31
24.66
3.71
11
O
O
Me

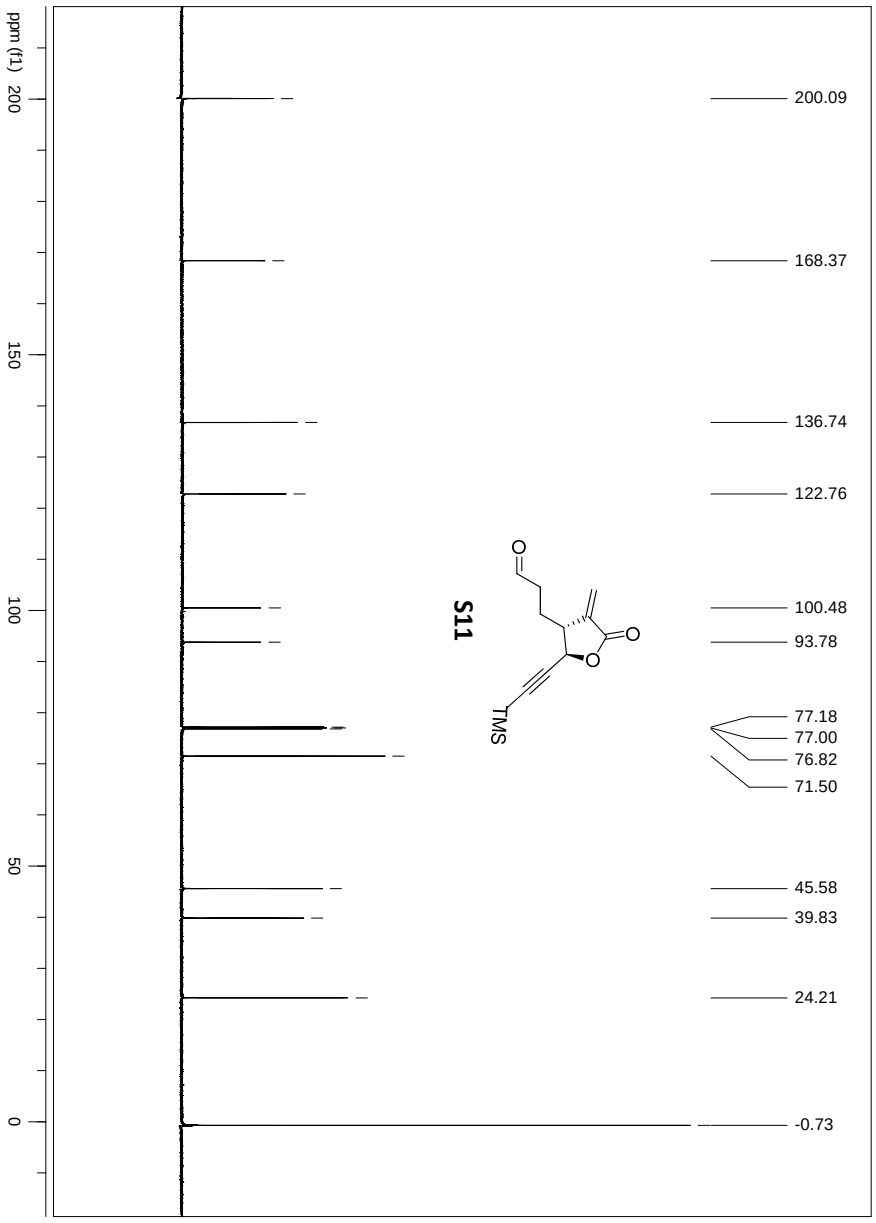

ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.00
1.01
0.98
1.05
2.05
2.05
1.18
3.05
1.11
22
Me
O
O
O
7.26
6.35
6.34
5.83
5.82
5.80
5.63
5.62
5.20
5.17
3.10
3.09
3.08
3.04
2.57
2.55
2.53
2.51
2.43
2.40
2.38
2.37
2.36
2.09
1.86
1.84
1.83
1.82
1.80
1.78
1.58
1.43
1.25
0.07

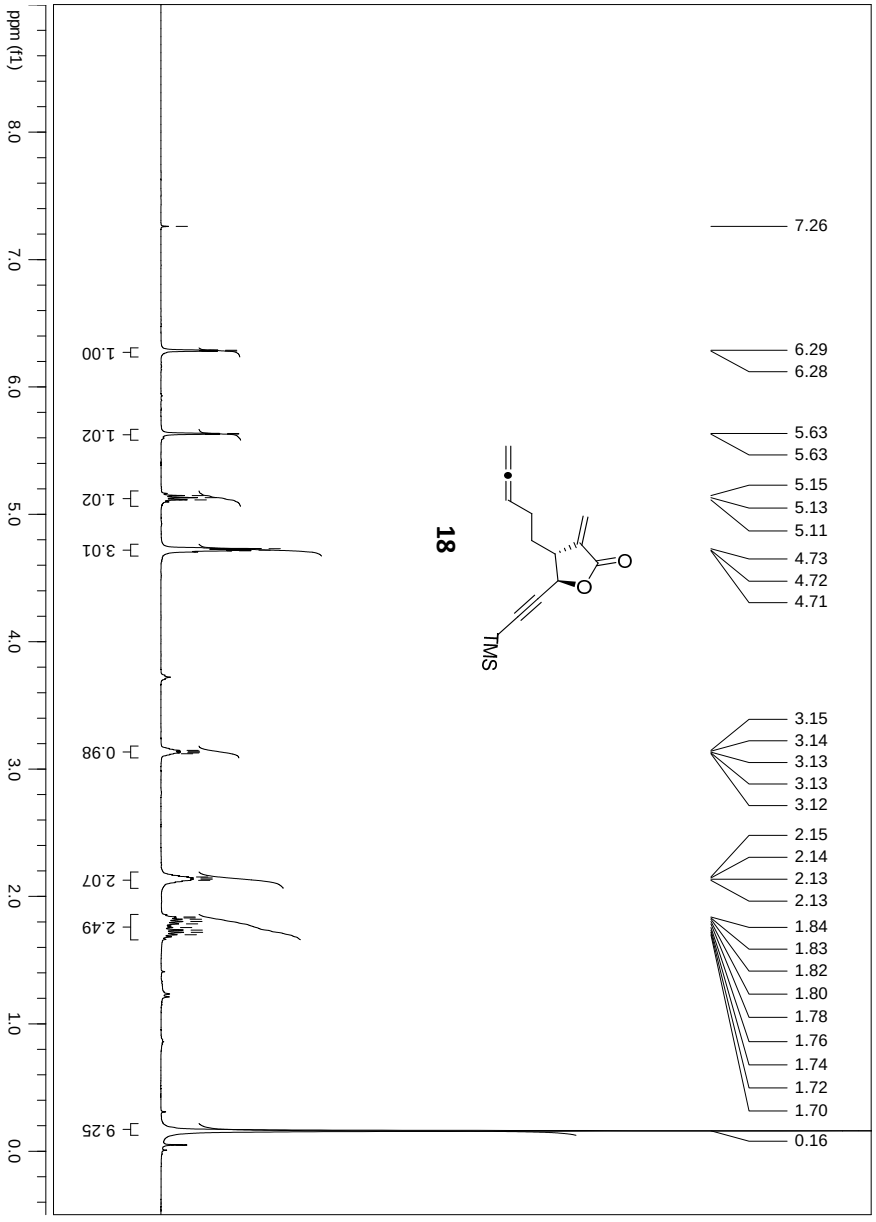

ppm (t1)
200
150
100
50
0
204.68
168.93
158.64
140.92
138.18
133.46
124.38
121.16
81.11
77.18
77.00
76.82
44.10
41.08
26.58
25.91
9.46
22
O
O
O
Me

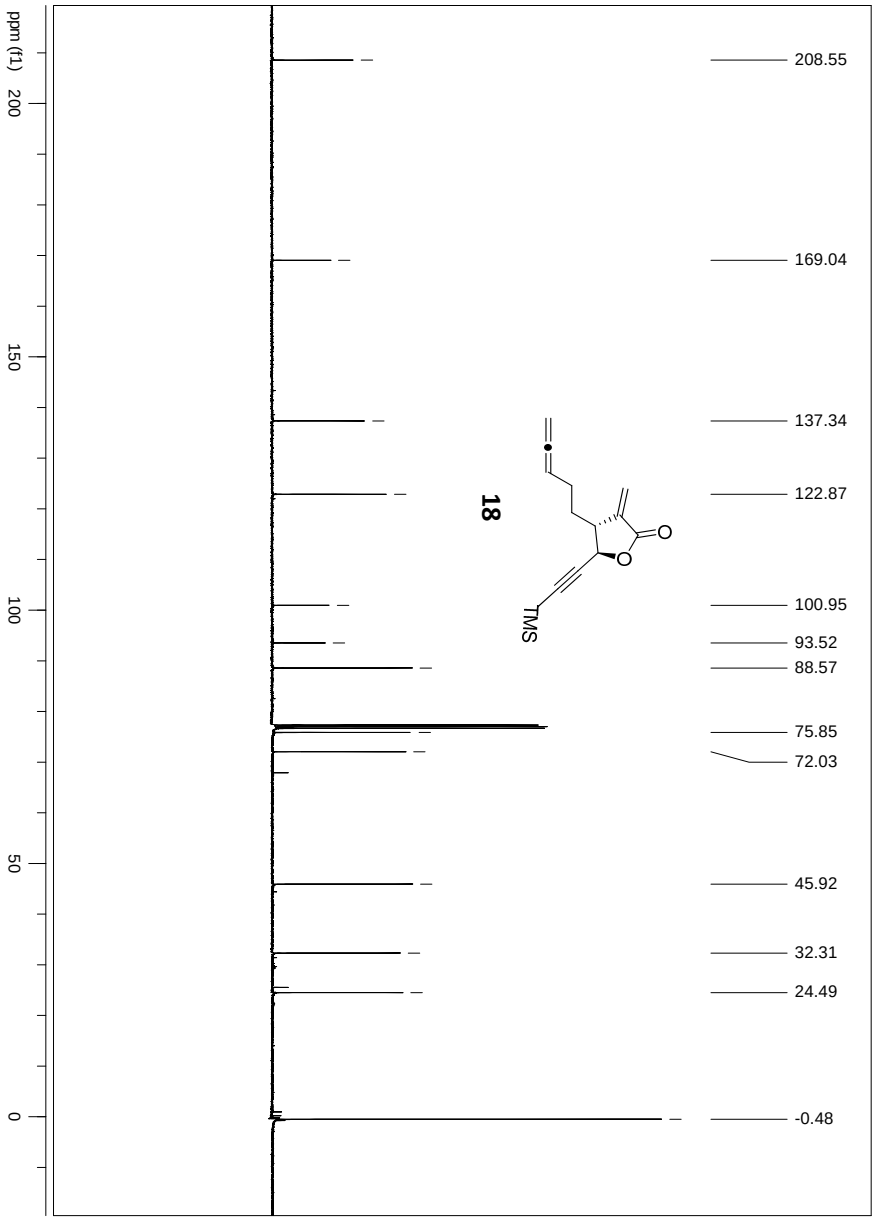

S10
HO
O
O
TMS
7.26
6.31
6.30
5.65
5.65
4.74
4.72
3.72
3.71
3.14
3.13
3.12
3.11
3.10
1.87
1.86
1.85
1.84
1.83
1.71
1.70
1.69
1.68
1.46
1.45
1.44
1.23
0.17
1.01
1.03
0.99
2.05
1.00
1.03
2.95
1.08
8.89
x
ppm (f1)

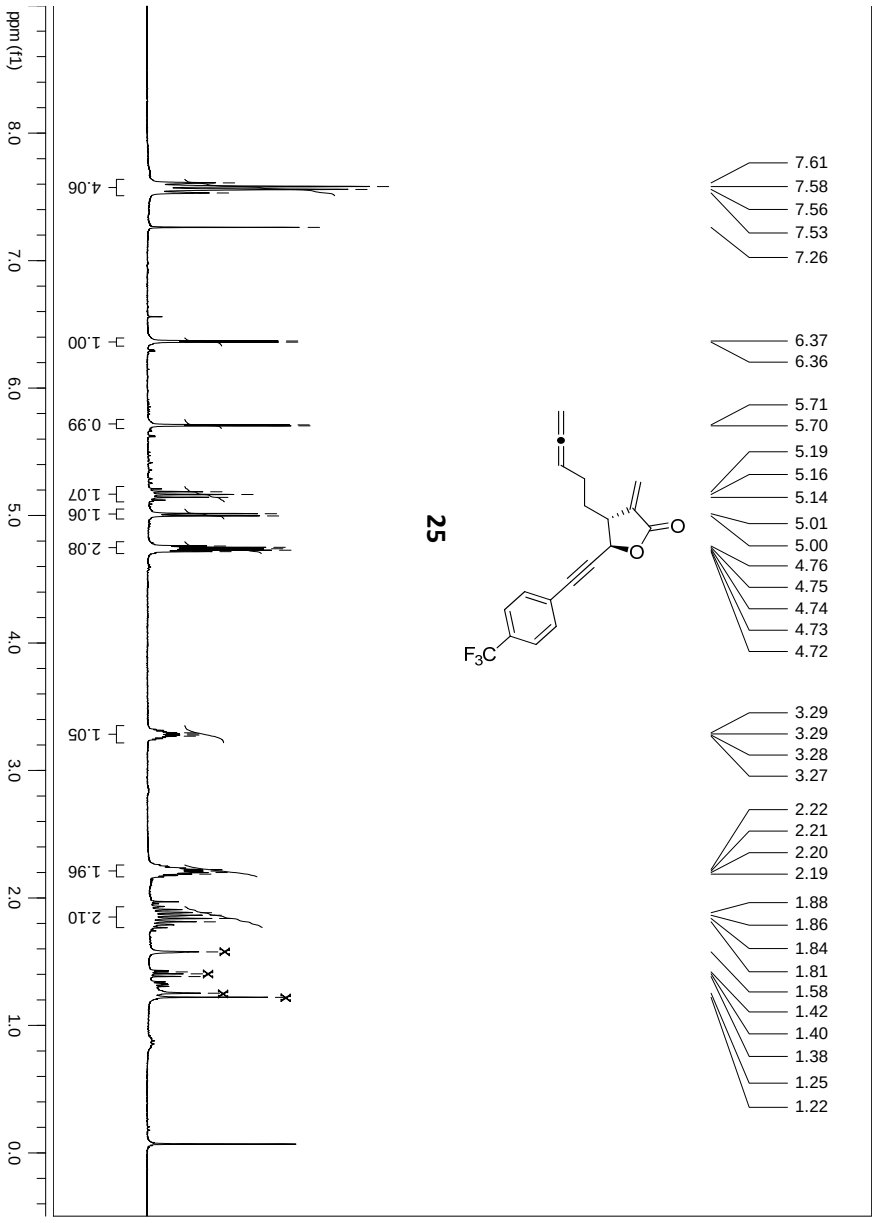

ppm (f1)
200
150
100
50
0
169.23
137.23
122.83
100.77
93.38
74.73
72.00
61.40
46.23
29.20
28.72
24.46
-0.70
x
x
S10
HO
O
O
TMS

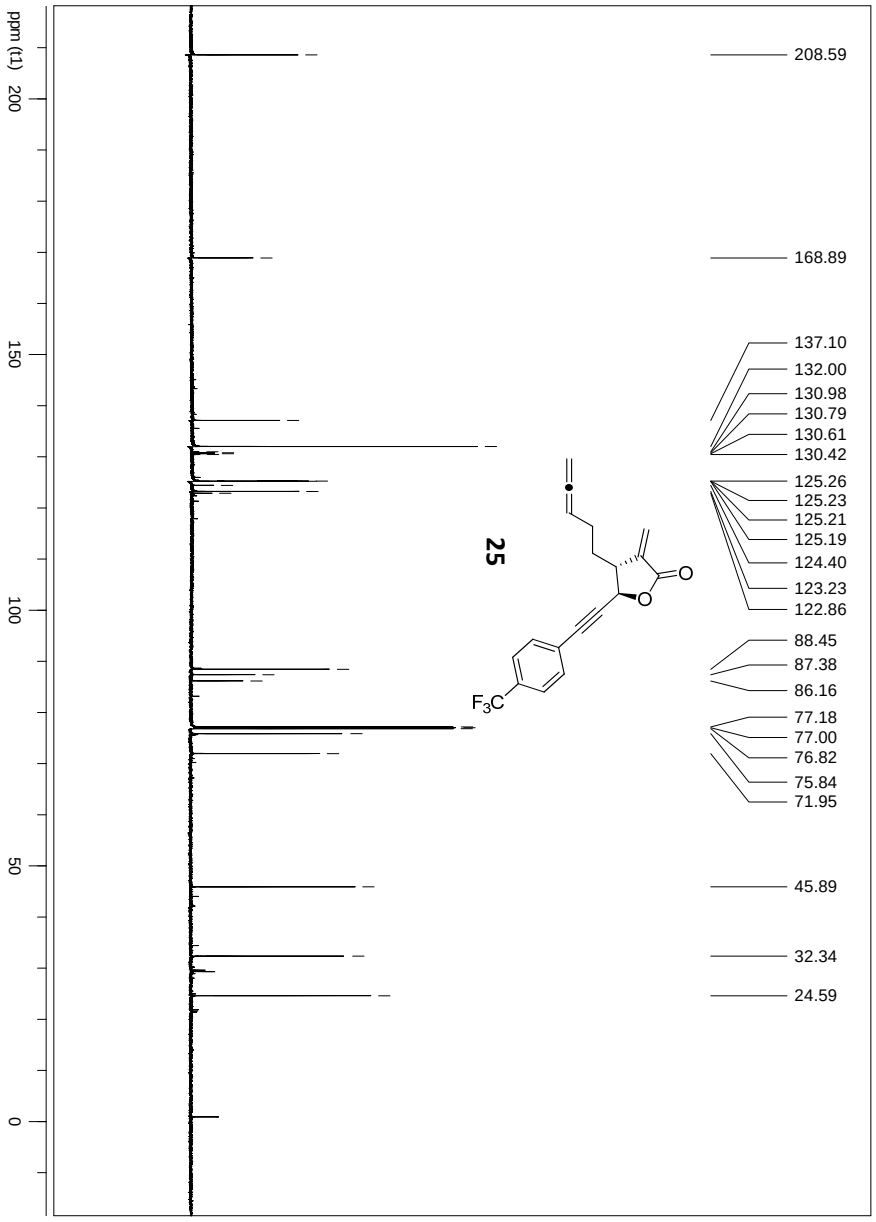

ppm (t1)
5.0
0.0
0.95
8.91
0.99
1.00
0.98
0.99
2.00
1.03
1.02
9.82
7.26
6.33
6.32
5.66
5.65
4.69
4.67
3.15
3.14
3.12
3.11
3.10
2.69
2.67
2.65
2.13
2.11
2.09
2.08
1.90
1.88
1.86
1.85
0.17
S11
O
O
O
TMS

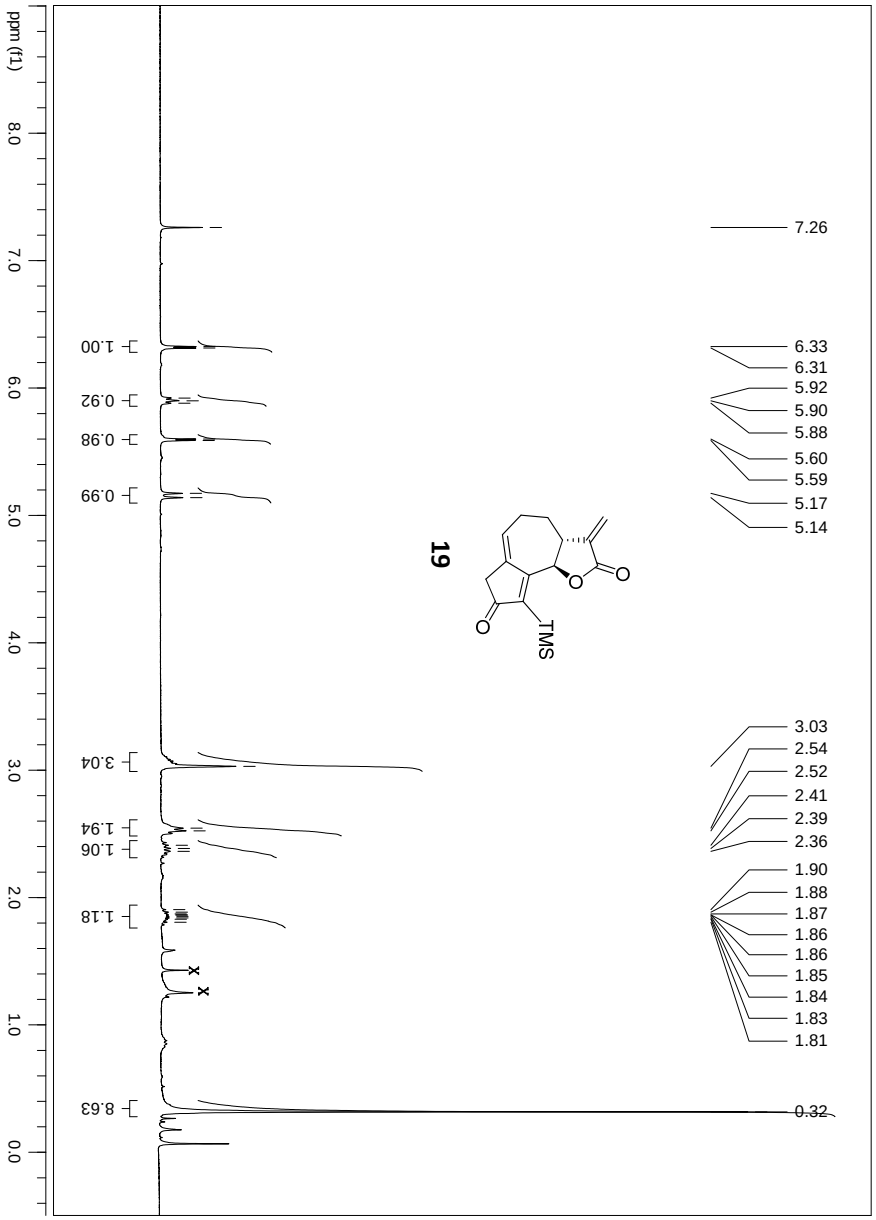

ppm (f1)
200
150
100
50
0
200.09
168.37
136.74
122.76
100.48
93.78
77.18
77.00
76.82
71.50
45.58
39.83
24.21
-0.73
S11
O
O
O
TMS

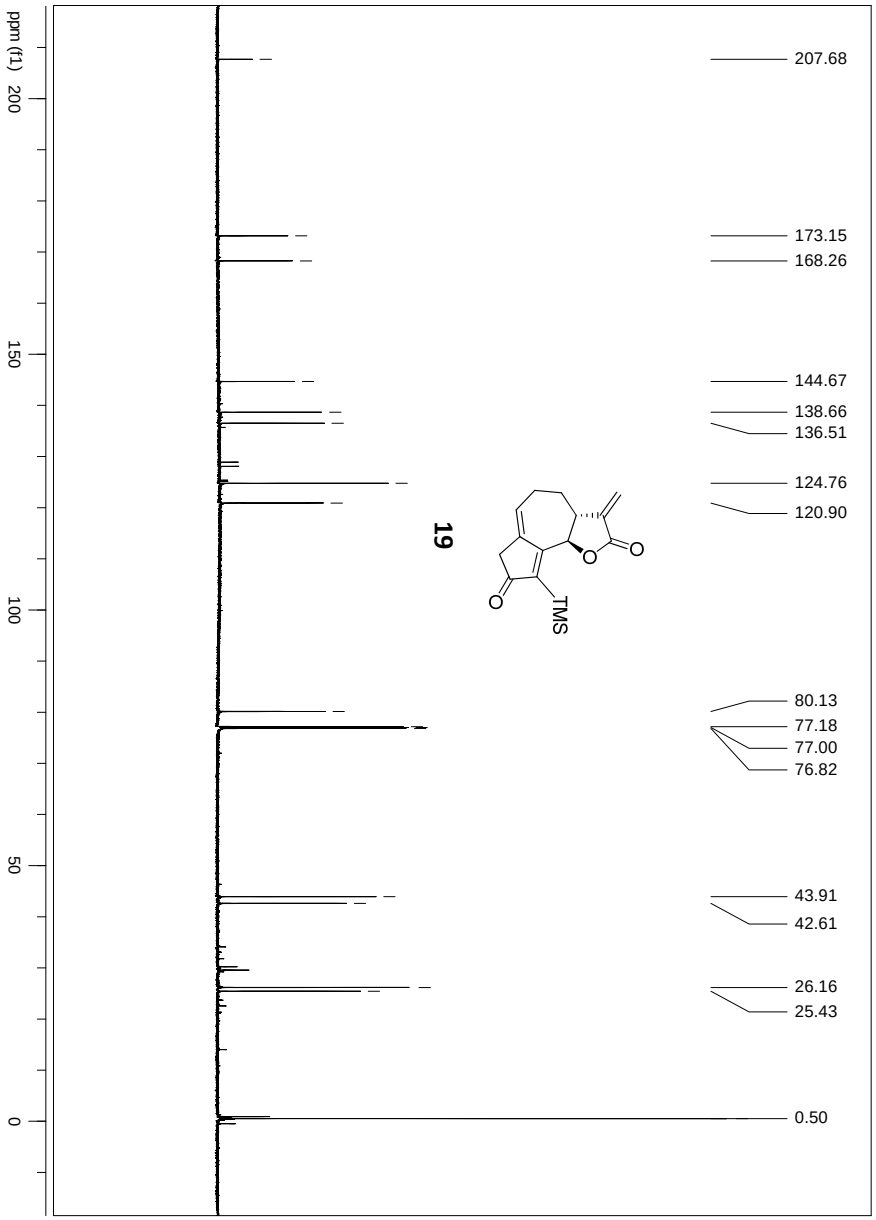

ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.02
1.02
3.01
0.98
2.07
2.49
9.25
18
TMS
O
O
7.26
6.29
6.28
5.63
5.63
5.15
5.13
5.11
4.73
4.72
4.71
3.15
3.14
3.13
3.13
3.12
2.15
2.14
2.13
2.13
1.84
1.83
1.82
1.80
1.78
1.76
1.74
1.72
1.70
0.16

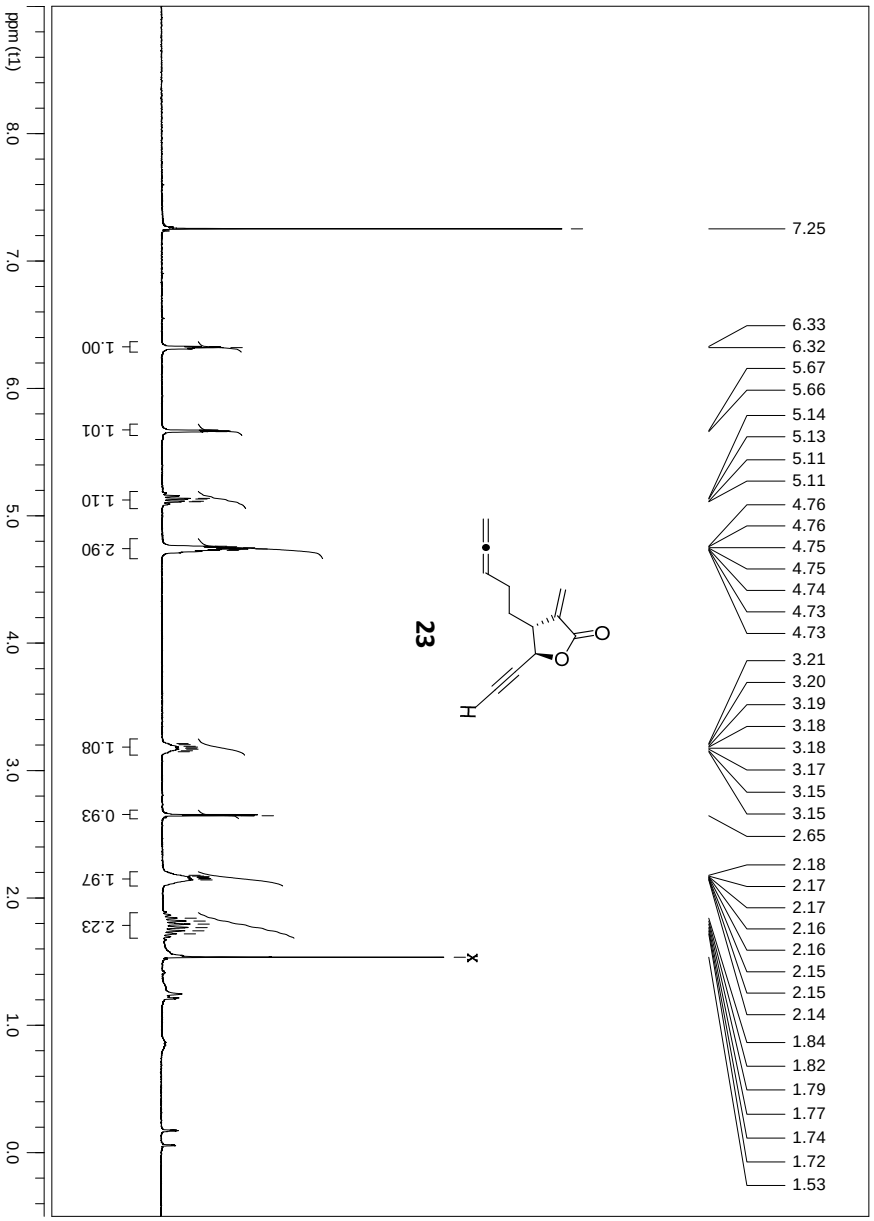

ppm (f1)
200
150
100
50
0
208.55
169.04
137.34
122.87
100.95
93.52
88.57
75.85
72.03
45.92
32.31
24.49
-0.48
18
O
O
TMS


ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
4.06
1.00
0.99
1.07
1.06
2.08
1.05
1.96
2.10
25
O
O
F3C
7.61
7.58
7.56
7.53
7.26
6.37
6.36
5.71
5.70
5.19
5.16
5.14
5.01
5.00
4.76
4.75
4.74
4.73
4.72
3.29
3.29
3.28
3.27
2.22
2.21
2.20
2.19
1.88
1.86
1.84
1.81
1.58
1.42
1.40
1.38
1.25
1.22


ppm (t1)
200
150
100
50
0
208.59
168.89
137.10
132.00
130.98
130.79
130.61
130.42
125.26
125.23
125.21
125.19
124.40
123.23
122.86
88.45
87.38
86.16
77.18
77.00
76.82
75.84
71.95
45.89
32.34
24.59
25
O
O
F3C


ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
0.92
0.98
0.99
3.04
1.94
1.06
1.18
8.63
x
x
7.26
6.33
6.31
5.92
5.90
5.88
5.60
5.59
5.17
5.14
3.03
2.54
2.52
2.41
2.39
2.36
1.90
1.88
1.87
1.86
1.86
1.85
1.84
1.83
1.81
0.32
19
O
O
O
TMS


ppm (f1)
200
150
100
50
0
207.68
173.15
168.26
144.67
138.66
136.51
124.76
120.90
80.13
77.18
77.00
76.82
43.91
42.61
26.16
25.43
0.50
19
O
O
O
TMS


ppm (t1)
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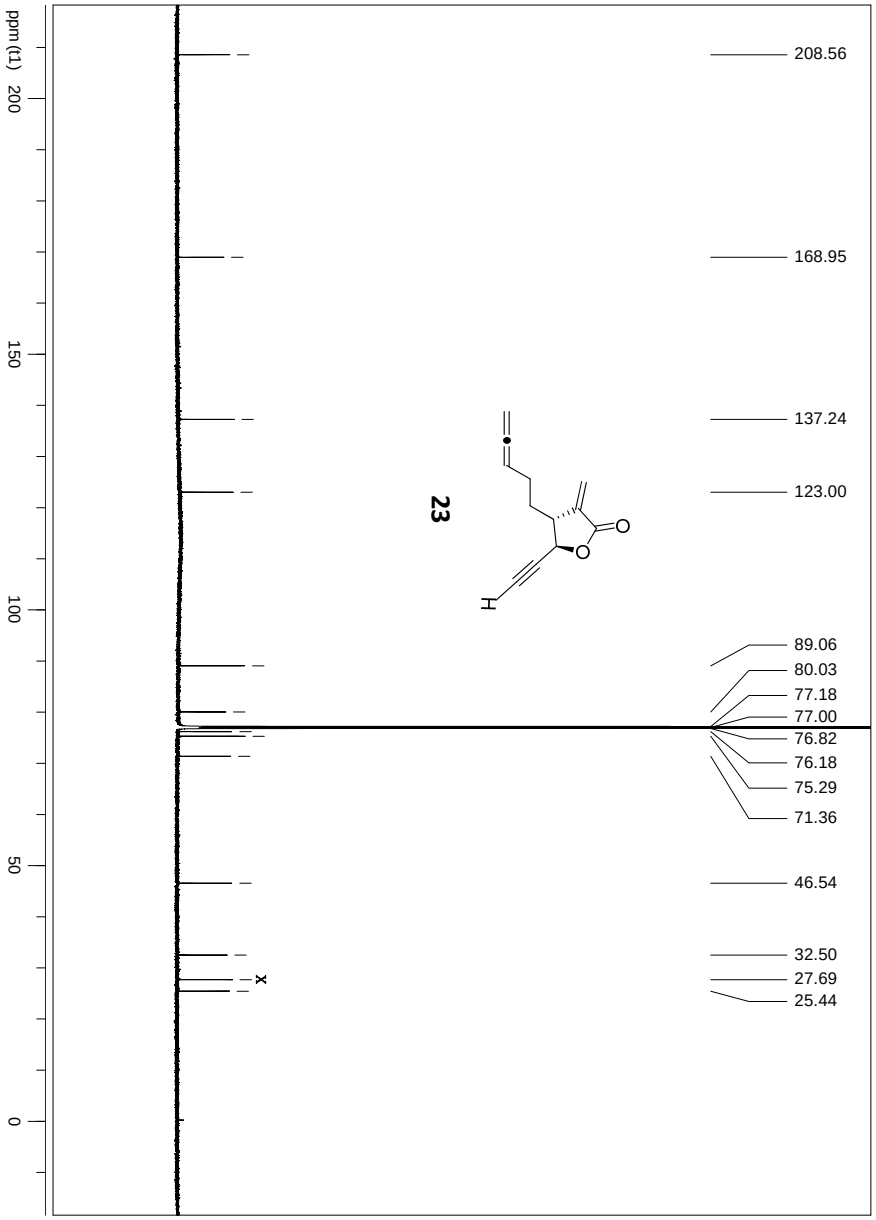
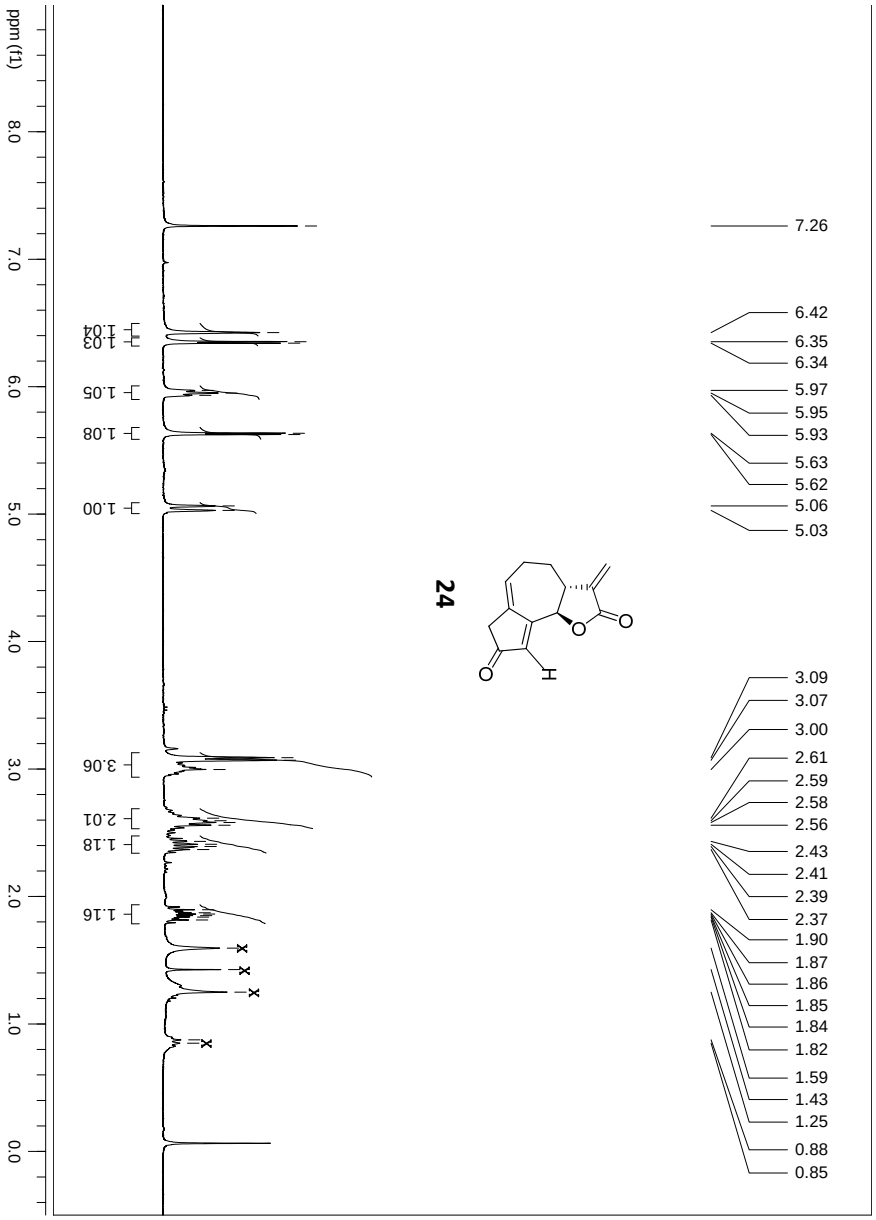
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
1.01
1.10
2.90
1.08
0.93
1.97
2.23
x
23
O
O
H
7.25
6.33
6.32
5.67
5.66
5.14
5.13
5.11
5.11
4.76
4.76
4.75
4.75
4.74
4.73
4.73
3.21
3.20
3.19
3.18
3.18
3.17
3.15
3.15
2.65
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.14
1.84
1.82
1.79
1.77
1.74
1.72
1.53


ppm (t1)
200
150
100
50
0
208.56
168.95
137.24
123.00
89.06
80.03
77.18
77.00
76.82
76.18
75.29
71.36
46.54
32.50
27.69
25.44
x
23
O
O
H


ppm (f1)
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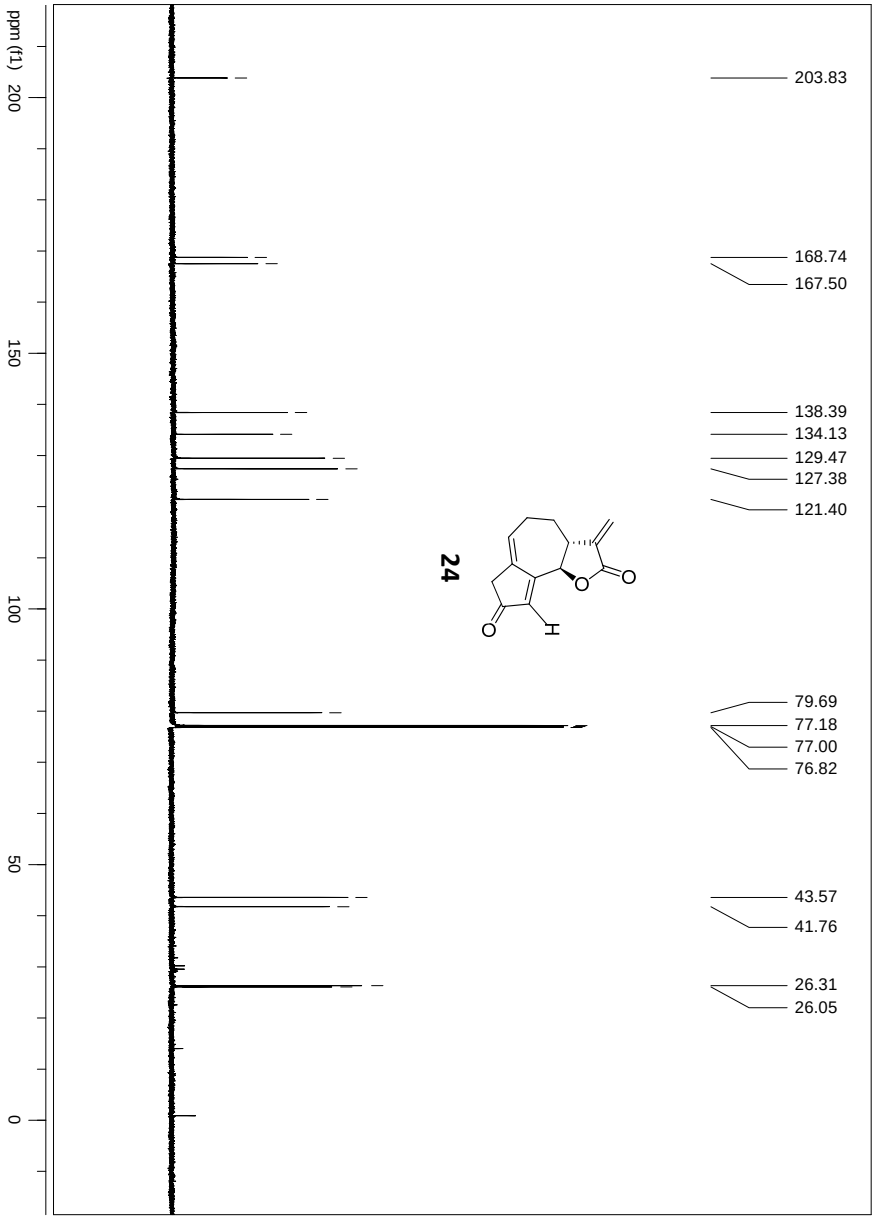
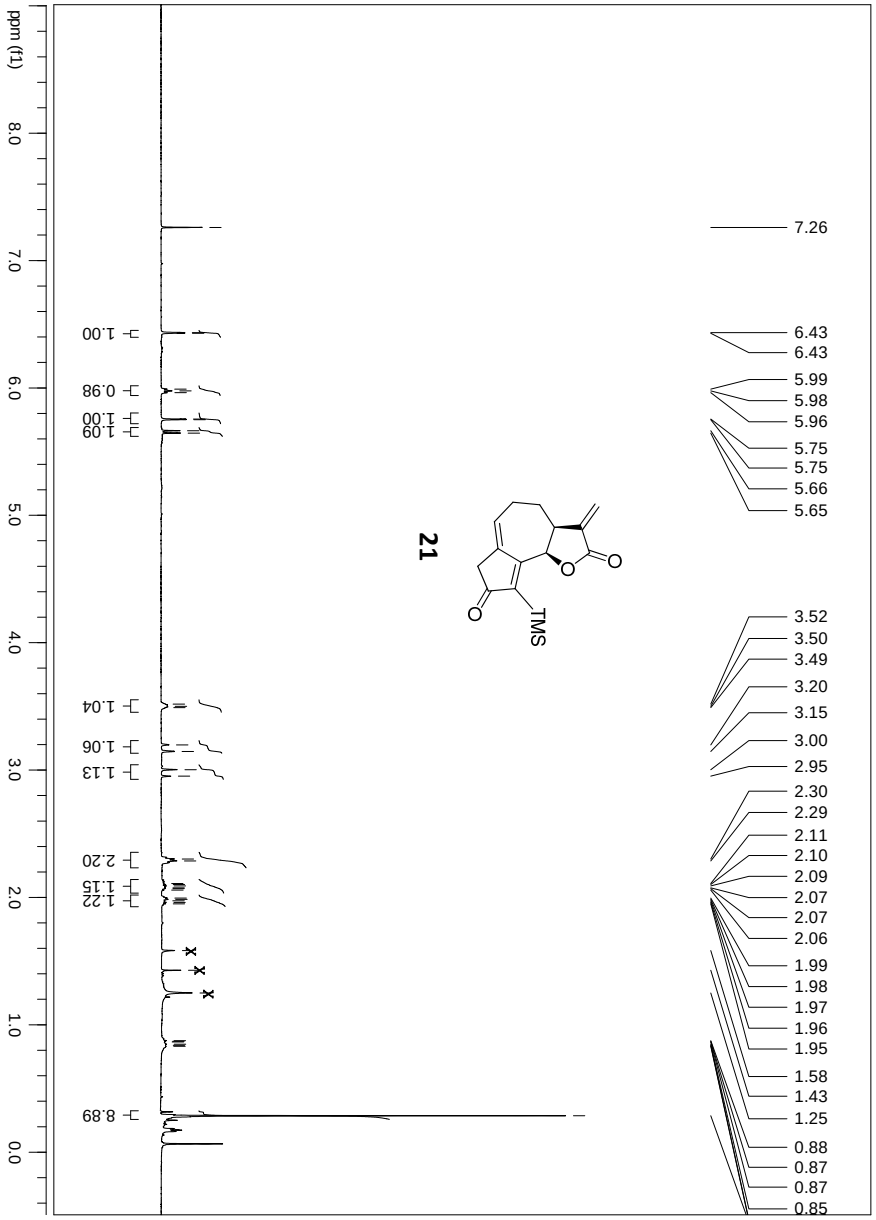
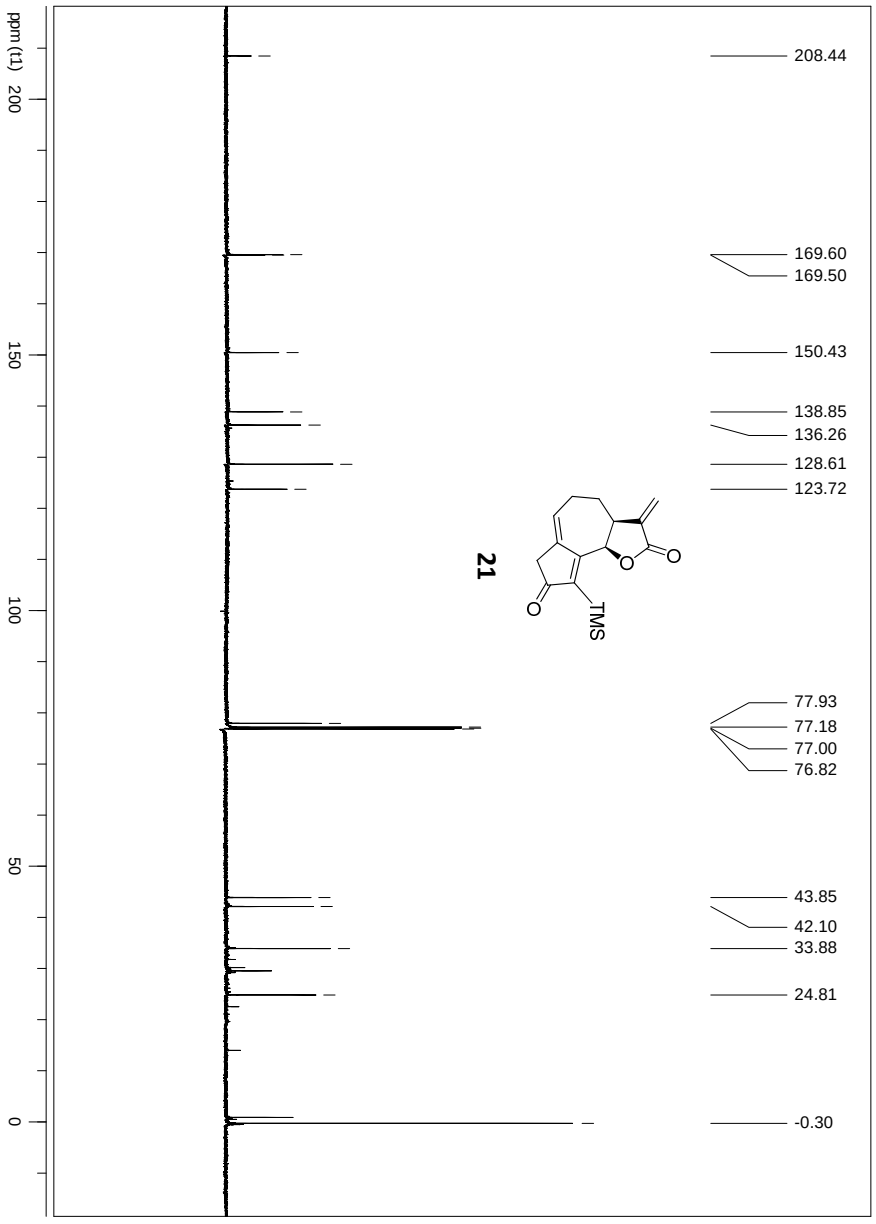
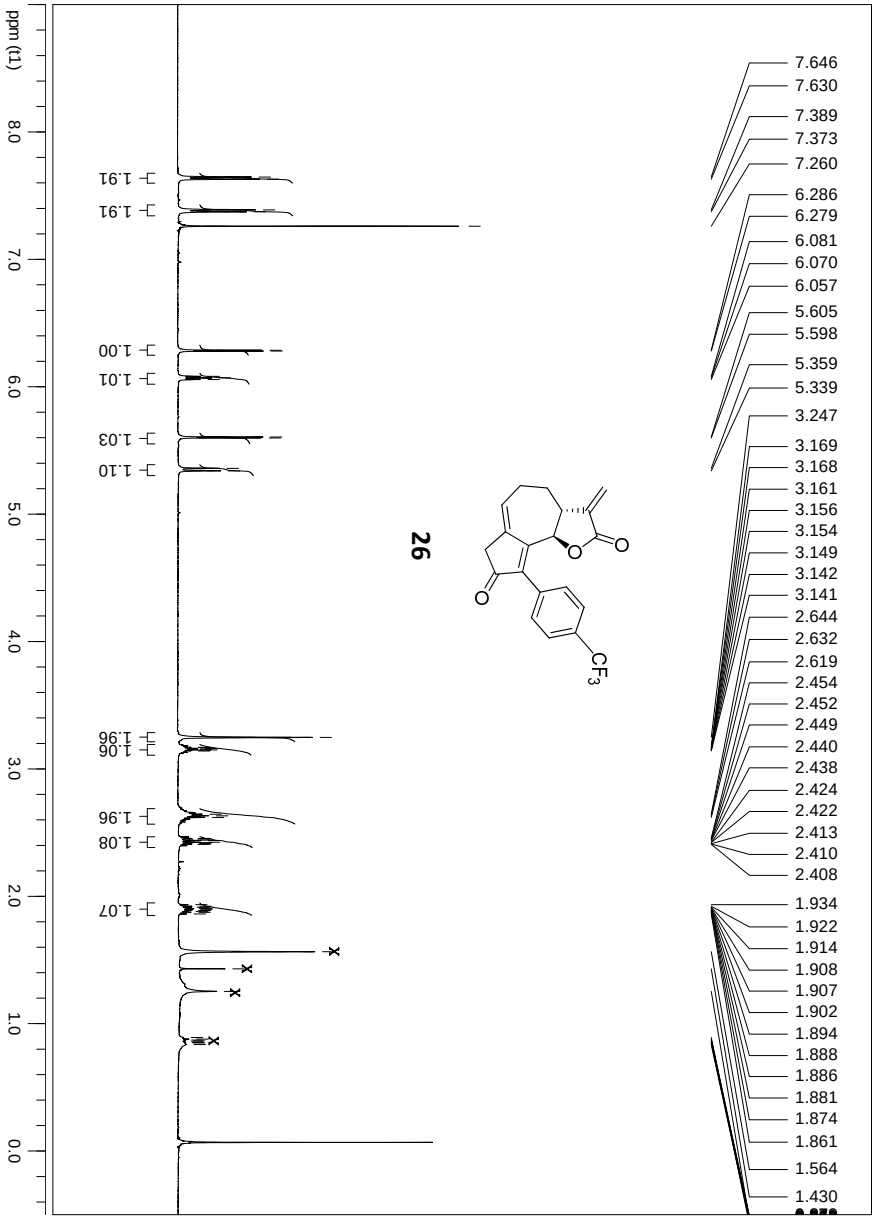
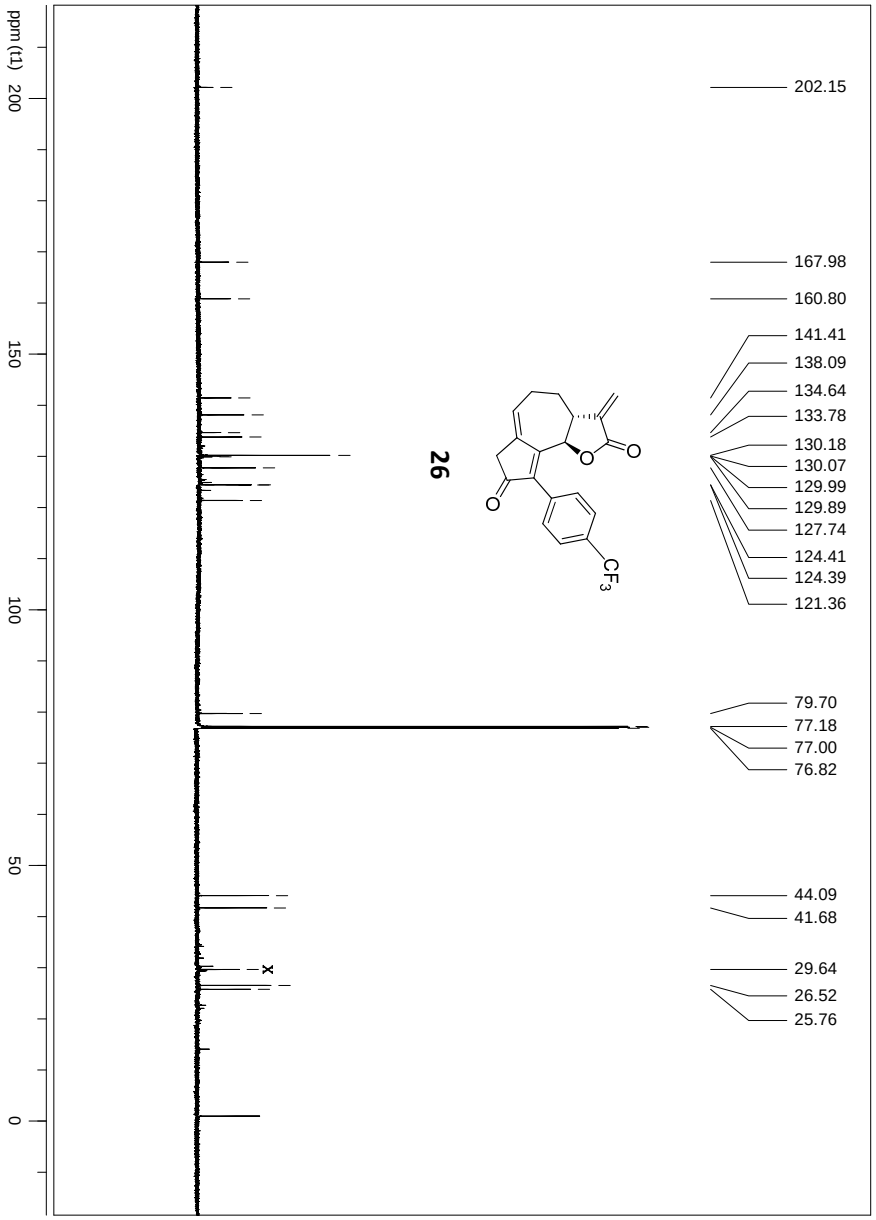
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.04
1.03
1.05
1.08
1.00
3.06
2.01
1.18
1.16
7.26
6.42
6.35
6.34
5.97
5.95
5.93
5.63
5.62
5.06
5.03
3.09
3.07
3.00
2.61
2.59
2.58
2.56
2.43
2.41
2.39
2.37
1.90
1.87
1.86
1.85
1.84
1.82
1.59
1.43
1.25
0.88
0.85
24
O
O
O
H


ppm (f1)
200
150
100
50
0
203.83
168.74
167.50
138.39
134.13
129.47
127.38
121.40
79.69
77.18
77.00
76.82
43.57
41.76
26.31
26.05
24
O
O
O
H


ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.00
0.98
1.00
1.09
1.04
1.06
1.13
2.20
1.15
1.22
8.89
21
TMS
7.26
6.43
6.43
5.99
5.98
5.96
5.75
5.75
5.66
5.65
3.52
3.50
3.49
3.20
3.15
3.00
2.95
2.30
2.29
2.11
2.10
2.09
2.07
2.07
2.06
1.99
1.98
1.97
1.96
1.95
1.58
1.43
1.25
0.88
0.87
0.87
0.85


ppm (t1)
200
150
100
50
0
208.44
169.60
169.50
150.43
138.85
136.26
128.61
123.72
77.93
77.18
77.00
76.82
43.85
42.10
33.88
24.81
-0.30
21
O
O
O
TMS


ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.91
1.91
1.00
1.01
1.03
1.10
1.96
1.06
1.96
1.08
1.07
7.646
7.630
7.389
7.373
7.260
6.286
6.279
6.081
6.070
6.057
5.605
5.598
5.359
5.339
3.247
3.169
3.168
3.161
3.156
3.154
3.149
3.142
3.141
2.644
2.632
2.619
2.454
2.452
2.449
2.440
2.438
2.424
2.422
2.413
2.410
2.408
1.934
1.922
1.914
1.908
1.907
1.902
1.894
1.888
1.886
1.881
1.874
1.861
1.564
1.430
26
O
O
O
CF3


ppm (t1)
200
150
100
50
0
202.15
167.98
160.80
141.41
138.09
134.64
133.78
130.18
130.07
129.99
129.89
127.74
124.41
124.39
121.36
79.70
77.18
77.00
76.82
44.09
41.68
29.64
26.52
25.76
x
26
O
O
O
CF3