SUPPORTING INFORMATION

Palladium-catalyzed Oxidative Domino Carbocyclization-Carbonylation-Alkynylation of Enallenes

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Methods: Unless otherwise noted, all reagents were used as received from the commercial suppliers. $Pd(OAc)_2$ was obtained from Pressure Chemicals and used without further purification. Palladium-catalyzed carbocyclizations were performed without any efforts to exclude moisture. Dry solvents (THF) were obtained from a VAC Solvent Purifier. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain or Vanillin stain. Flash chromatography was carried out with 60Å (particle size 35-70 μm) normal flash silica gel. NMR spectra were recorded at 400 MHz (1H) or 500 MHz (1H) and at 100 MHz (13C) or 125 MHz (13C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δ_H = 7.26 and δ_C = 77.0 ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

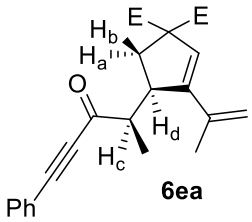
Typical Experimental Procedure: In a sealable microwave tube were placed 1.0 equiv of enallene (0.12 mmol), 5 mol % of $Pd(TFA)_2$, 2.0 equiv of 1,4-benzoquinone. The tube was closed with a septum. The tube was evacuated and filled with carbon monoxide gas using a balloon. 1.0 mL of 1,2-dichloroethane and the terminal alkyne (2.0 equiv) were added and continued stirring at the reported temperature for 12 h. The reaction was monitored by TLC and after complete consumption of starting material; the crude reaction mixture was directly loaded onto column chromatography on silica gel to get the pure product.

Typical Experimental Procedure for Aerobic Oxidative Conditions: In a sealable microwave tube were placed 1.0 equiv of enallene (0.12 mmol), 5 mol % of $Pd(TFA)_2$, 5 mol % of cobalt(salophen) and 20 mol % of 1,4-benzoquinone. The tube was closed with a septum. The tube was evacuated and a balloon consisting of approximately equal amounts of carbon monoxide gas and oxygen gas was attached to the reaction via a needle. 1.0 mL of 1,2-dichloroethane and the terminal alkyne (2.0 equiv) were added and the mixture was stirred at room temperature for 36 h. The reaction was monitored by TLC and after

complete consumption of starting material; the crude reaction mixture was directly loaded onto column chromatography on silica gel to get the pure product.

All bromoallenes were prepared following a procedure reported in the literature.[1] Enallenes **1a-f** were prepared according to previously reported procedures.[2]

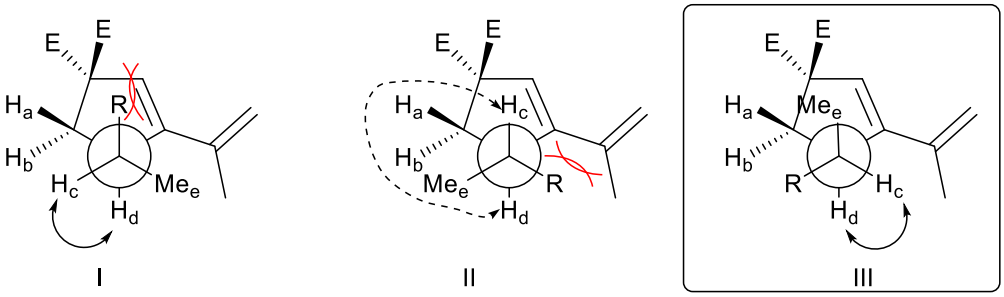
Stereochemical assignment for the compound 6ea: Based on the *syn*-carbopalladation occurring in vinylpalladium(II) intermediate (**10** in Scheme 3) from **1e,** a single diastereomer of the product **6ea** was isolated and the configuration shown in Figure S1 was assigned to **6ea**. Three different conformations (**I** – **III**) are possible as shown in Figure S1. Inspection of these conformations suggests that conformation **III** should be the most stable conformation. The coupling constants between the hydrogens H_c and H_d (J_{cd}) of 3.5 Hz confirms the stereochemical assignment.



6ea

Me 0.93 (d, J = 6.9 Hz, 3H),
H_a 2.27 (dd, J = 14.8 Hz, 4.3 Hz, 1H),
H_b 2.84 (dd, J = 14.8 Hz, 9.5 Hz, 1H),
H_c 3.24 (qd, J = 6.9 Hz, 3.5 Hz, 1H),
H_d 4.00 - 4.08 (m, 1H),

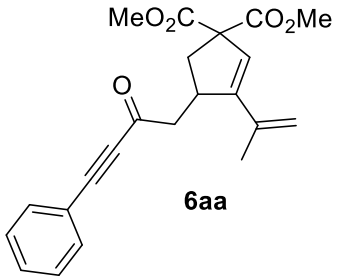
J_{ab} = 14.8 Hz
J_{ad} = 4.3 Hz
J_{bd} = 9.5 Hz
J_{ce} = 6.9 Hz
J_{cd} = 3.5 Hz, indicates a gauche arrangement between the two hydrogens



R= Ynone

J_{cd} = 3.5 Hz
Most stable conformation

Figure S1.



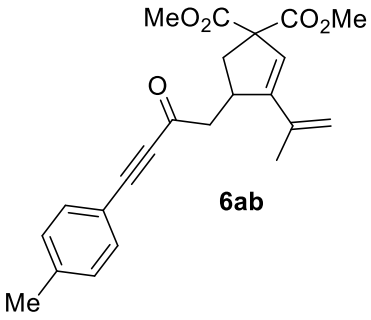
6aa

Dimethyl 4-(2-oxo-4-phenylbut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6aa)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.50 (dd, *J* = 14.2 Hz, 2.2 Hz, 1H), 2.74 (dd, *J* = 14.2 Hz, 8.7 Hz, 1H), 2.78 (dd, *J* = 17.5 Hz, 10.9 Hz, 1H), 3.10 (dd, *J* = 17.5 Hz, 2.5 Hz, 1H), 3.63 – 3.69 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.07 (bs, 1H), 5.14 – 5.15 (m, 1H), 5.84 (s, 1H), 7.38 – 7.42 (m, 2H), 7.45 – 7.49 (m, 1H), 7.57 – 7.63 (m, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.72, 171.61, 171.56, 150.24, 137.49, 133.08, 130.77, 128.65, 125.11, 119.91, 115.78, 91.14, 87.89, 65.70, 52.96, 52.85, 50.42, 39.72, 37.69, 21.11

HRMS (ESI): $C_{22}H_{22}O_5Na$ calculated = 389.1359; found = 389.1379.



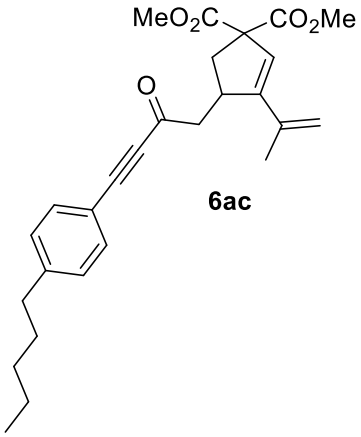
6ab

Dimethyl 4-(2-oxo-4-(p-tolyl)but-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ab)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.40 (s, 3H), 2.49 (dd, *J* = 14.4 Hz, 2.2 Hz, 1H), 2.74 (dd, *J* = 14.4 Hz, 8.7 Hz, 1H), 2.76 (dd, *J* = 17.5 Hz, 11.1 Hz, 1H), 3.10 (dd, *J* = 17.5 Hz, 2.5 Hz, 1H), 3.62 – 3.69 (m, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 5.07 (bs, 1H), 5.13 – 5.15 (m, 1H), 5.84 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.75, 171.62, 171.57, 150.29, 141.51, 137.48, 133.12, 129.44, 125.07, 116.78, 115.78, 91.84, 87.78, 65.70, 52.95, 52.84, 50.38, 39.76, 37.70, 21.74, 21.11

HRMS (ESI): $C_{23}H_{24}O_5Na$ calculated = 403.1516; found = 403.1512.



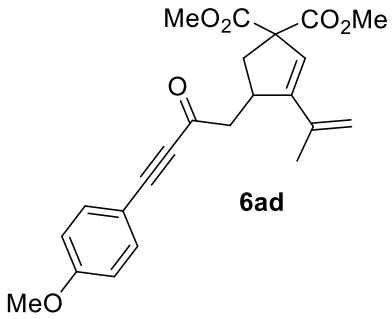
6ac

Dimethyl 4-(2-oxo-4-(4-pentylphenyl)but-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ac)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3H), 1.25 – 1.40 (m, 4H), 1.59 – 1.67 (m, 2H), 1.97 (s, 3H), 2.49 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.74 (dd, *J* = 14.3 Hz, 8.6 Hz, 1H), 2.76 (dd, *J* = 17.5 Hz, 10.8 Hz, 1H), 3.08 (dd, *J* = 17.5 Hz, 2.5 Hz, 1H), 3.63 – 3.69 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.07 (bs, 1H), 5.13 – 5.15 (m, 1H), 5.83 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.76, 171.61, 171.56, 150.29, 146.50, 137.47, 133.16, 128.79, 125.07, 116.95, 115.77, 91.94, 87.78, 65.69, 52.94, 52.83, 50.38, 39.79, 37.69, 36.03, 31.39, 30.74, 22.48, 21.11, 13.98

HRMS (ESI): $C_{27}H_{32}O_5Na$ calculated = 459.2142; found = 459.2154.



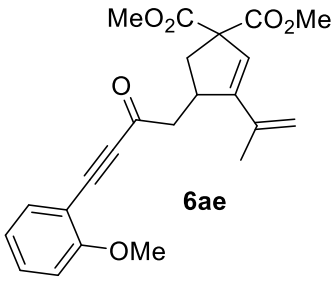
6ad

Dimethyl 4-(4-(4-methoxyphenyl)-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ad)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.50 (dd, *J* = 14.2 Hz, 2.3 Hz, 1H), 2.73 (dd, *J* = 14.2 Hz, 8.7 Hz, 1H), 2.74 (dd, *J* = 17.3 Hz, 11.1 Hz, 1H), 3.07 (dd, *J* = 17.3 Hz, 2.4 Hz, 1H), 3.62 – 3.68 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 3.87 (s, 3H), 5.07 (bs, 1H), 5.12 – 5.15 (m, 1H), 5.83 (bs, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.70, 171.62, 171.58, 161.70, 150.33, 137.48, 135.14, 125.03, 115.77, 114.38, 111.66, 92.35, 87.86, 65.69, 55.42, 52.94, 52.83, 50.29, 39.82, 37.70, 21.11

HRMS (ESI): $C_{23}H_{24}O_6Na$ calculated = 419.1465; found = 419.1541.



6ae

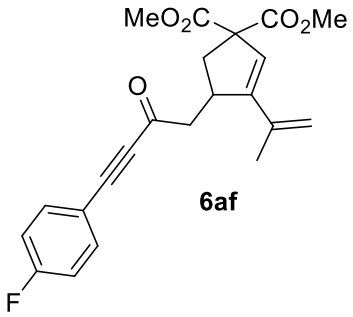
Dimethyl 4-(4-(2-methoxyphenyl)-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ae)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (s, 3H), 2.50 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.71 (dd, *J* = 17.1 Hz, 11.2 Hz, 1H), 2.77 (dd, *J* = 14.3 Hz, 8.7 Hz, 1H), 3.10 (dd, *J* = 17.1 Hz, 2.5 Hz, 1H), 3.71 – 3.75 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 3.91 (s, 3H), 5.14 (bs, 1H), 5.15 – 5.16 (m, 1H), 5.84 (bs, 1H), 6.93 (d, *J* = 8.5

Hz, 1H), 6.97 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.44 (ddd, 8.5 Hz, 7.5 Hz, 1.7 Hz, 1H), 7.53 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.87, 171.63, 171.61, 161.60, 150.36, 137.47, 135.08, 132.57, 124.99, 120.60, 115.81, 110.80, 109.16, 91.92, 88.73, 65.73, 55.76, 52.93, 52.83, 50.49, 40.05, 37.62, 21.12

HRMS (ESI): $C_{23}H_{24}O_6Na$ calculated = 419.1465; found = 419.1468.



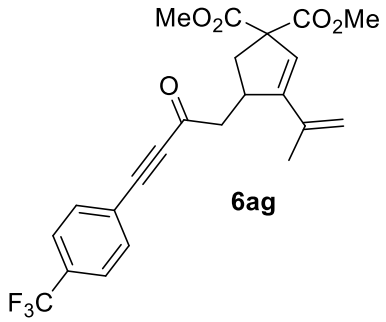
6af

Dimethyl 4-(4-(4-fluorophenyl)-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6af)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 2.49 (dd, *J* = 14.3 Hz, 2.1 Hz, 1H), 2.72 (dd, *J* = 14.3 Hz, 8.7 Hz, 1H), 2.77 (dd, *J* = 17.6 Hz, 11.0 Hz, 1H), 3.10 (dd, *J* = 17.6 Hz, 2.6 Hz, 1H), 3.60 – 3.68 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.05 (bs, 1H), 5.11 – 5.15 (m, 1H), 5.83 (bs, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 7.58 (dd, *J* = 8.7 Hz, 5.3 Hz, 2H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 186.54, 171.59, 171.52, 164.00 (d, *J* = 253 Hz), 150.18, 137.48, 135.36 (d, *J* = 9 Hz), 125.13, 116.30, 116.04 (d, *J* = 4 Hz), 115.90 (d, *J* = 34 Hz), 89.99, 87.83, 65.68, 52.94, 52.83, 50.35, 39.68, 37.68, 21.09

HRMS (ESI): $C_{22}H_{21}FO_5Na$ calculated = 407.1265; found = 407.1286.



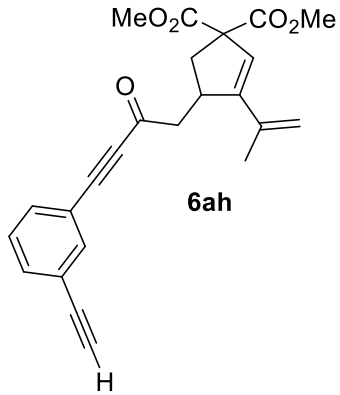
6ag

Dimethyl 4-(2-oxo-4-(4-(trifluoromethyl)phenyl)but-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ag)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.50 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.73 (dd, *J* = 14.3 Hz, 8.8 Hz, 1H), 2.83 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 3.11 (dd, *J* = 17.6 Hz, 2.5 Hz, 1H), 3.61 – 3.68 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 5.05 (bs, 1H), 5.13 – 5.15 (m, 1H), 5.86 (bs, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.36, 171.59, 171.50, 150.07, 137.49, 133.17, 132.22 (q, *J* = 33Hz), 125.58 (q, *J* = 2 Hz), 125.22, 123.75, 123.52 (q, *J* = 272 Hz), 115.75, 89.03, 88.41, 65.69, 52.98, 52.85, 50.43, 39.54, 37.67, 21.09

HRMS (ESI): $C_{23}H_{21}F_3O_5Na$ calculated = 457.1233; found = 457.1241.



6ah

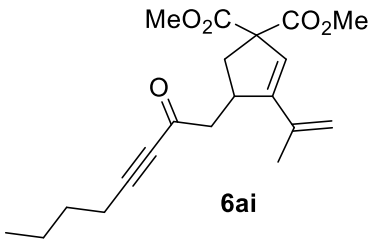
Dimethyl 4-(4-(3-ethynylphenyl)-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ah)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (s, 3H), 2.49 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.73 (dd, *J* = 14.3 Hz, 8.6 Hz, 1H), 2.79 (dd, *J* = 17.6 Hz, 11.0 Hz, 1H), 3.09 (dd, *J* = 17.6 Hz, 2.5 Hz, 1H), 3.14 (s, 1H), 3.61 –

3.69 (m, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 5.06 (bs, 1H), 5.12 – 5.16 (m, 1H), 5.84 (bs, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.56 (tt, *J* = 7.7 Hz, 1.4 Hz, 2H), 7.70 (t, *J* = 1.4 Hz, 1H)

^{13}C NMR (100.6 MHz, $CDCl_3$): 186.50, 171.58, 171.53, 150.17, 137.48, 136.35, 134.15, 133.07, 128.77, 125.16, 122.99, 120.36, 115.78, 89.57, 88.10, 82.02, 78.63, 65.69, 52.97, 52.85, 50.42, 39.65, 37.68, 21.11

HRMS (ESI): $C_{24}H_{22}O_5Na$ calculated = 413.1359; found = 413.1345.



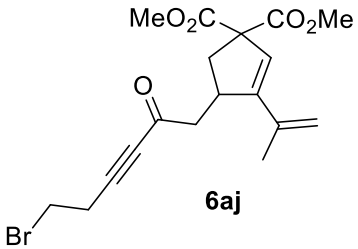
6ai

Dimethyl 4-(2-oxooct-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ai)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.3 Hz, 3H), 1.41 – 1.49 (m, 2H), 1.54 – 1.61 (m, 2H), 1.95 (s, 3H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.41 (dd, *J* = 14.3 Hz, 2.1 Hz, 1H), 2.62 (dd, *J* = 17.5 Hz, 11.0 Hz, 1H), 2.69 (dd, *J* = 14.3 Hz, 8.7 Hz, 1H), 2.95 (dd, *J* = 17.5 Hz, 2.5 Hz, 1H), 3.55 – 3.61 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.02 (bs, 1H), 5.09 – 5.12 (m, 1H), 5.81 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.93, 171.61, 171.58, 150.30, 137.46, 124.95, 115.69, 94.83, 80.92, 65.65, 52.91, 52.82, 50.42, 39.61, 37.67, 29.70, 21.96, 21.09, 18.66, 13.48

HRMS (ESI): $C_{20}H_{26}O_5Na$ calculated = 369.1672; found = 369.1669.



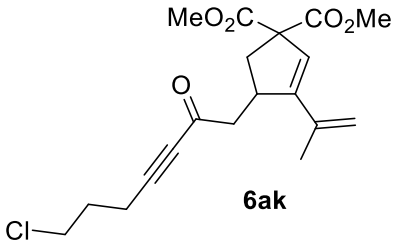
6aj

Dimethyl 4-(6-bromo-2-oxohex-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6aj)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 2.42 (dd, *J* = 14.2 Hz, 2.2 Hz, 1H), 2.66 (dd, *J* = 17.5 Hz, 11.0 Hz, 1H), 2.69 (dd, *J* = 14.2 Hz, 8.8 Hz, 1H), 2.97 (t, *J* = 7.1 Hz, 2H), 2.98 (dd, *J* = 17.5 Hz, 2.4 Hz, 1H), 3.50 (t, *J* = 7.1 Hz, 2H), 3.56 – 3.63 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.02 (bs, 1H), 5.10 – 5.13 (m, 1H), 5.82 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.51, 171.57, 171.53, 150.14, 137.43, 125.07, 115.77, 89.92, 81.88, 65.65, 52.97, 52.85, 50.38, 39.52, 37.62, 27.64, 23.32, 21.09

HRMS (ESI): $C_{18}H_{21}BrO_5Na$ calculated = 419.0465; found = 419.0500.



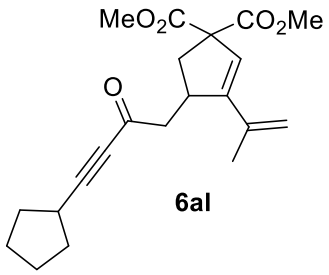
6ak

Dimethyl 4-(7-chloro-2-oxohept-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ak)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 2.03 – 2.09 (m, 2H), 2.42 (dd, *J* = 14.2 Hz, 2.2 Hz, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.65 (dd, *J* = 17.6 Hz, 11.1 Hz, 1H), 2.68 (dd, *J* = 14.2 Hz, 8.8 Hz, 1H), 2.95 (dd, *J* = 17.6 Hz, 2.4 Hz, 1H), 3.53 – 3.61 (m, 1H), 3.67 (t, *J* = 6.9 Hz, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 5.00 (bs, 1H), 5.10 – 5.13 (m, 1H), 5.81 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.65, 171.58, 171.55, 150.20, 137.45, 125.03, 115.72, 92.15, 81.49, 65.64, 52.95, 52.84, 50.39, 43.26, 39.51, 37.66, 30.37, 21.08, 16.40

HRMS (ESI): $C_{19}H_{23}ClO_5Na$ calculated = 389.1126; found = 389.1136.



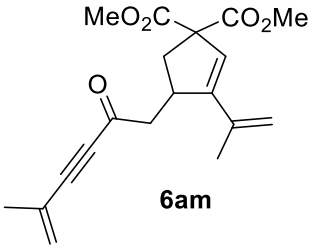
6al

Dimethyl 4-(4-cyclopentyl-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6al)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.57 – 1.64 (m, 2H), 1.65 – 1.80 (m, 4H), 1.95 (s, 3H), 1.96 – 2.02 (m, 2H), 2.41 (dd, *J* = 14.3 Hz, 2.3 Hz, 1H), 2.61 (dd, *J* = 17.4 Hz, 11.1 Hz, 1H), 2.70 (dd, *J* = 14.3 Hz, 8.7 Hz, 1H), 2.75 – 2.82 (m, 1H), 2.94 (dd, *J* = 17.4 Hz, 2.4 Hz, 1H), 3.54 – 3.61 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 5.01 (bs, 1H), 5.09 – 5.12 (m, 1H), 5.80 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 187.05, 171.61, 171.58, 150.31, 137.46, 124.93, 115.69, 98.93, 80.41, 65.65, 52.90, 52.82, 50.44, 39.67, 37.68, 33.19, 30.01, 25.19, 21.08

HRMS (ESI): $C_{21}H_{26}O_5Na$ calculated = 381.1672; found = 381.1683.



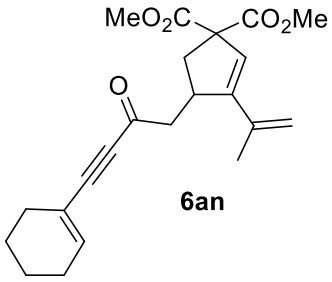
6am

Dimethyl 4-(5-methyl-2-oxohex-5-en-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6am)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 1.96 (t, *J* = 1.3 Hz, 3H), 2.44 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.69 (dd, *J* = 17.6 Hz, 11.0 Hz, 1H), 2.71 (dd, *J* = 14.3 Hz, 8.7 Hz, 1H), 3.01 (dd, *J* = 17.6 Hz, 2.4 Hz, 1H), 3.57 – 3.63 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.02 (bs, 1H), 5.10 – 5.13 (m, 1H), 5.53 – 5.55 (m, 1H), 5.60 – 5.62 (m, 1H), 5.82 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.69, 171.59, 171.55, 150.21, 137.46, 127.78, 125.05, 124.72, 115.72, 91.92, 86.60, 65.57, 52.93, 52.83, 50.39, 39.59, 37.66, 22.45, 21.09

HRMS (ESI): $C_{19}H_{22}O_5Na$ calculated = 353.1365; found = 353.1348.



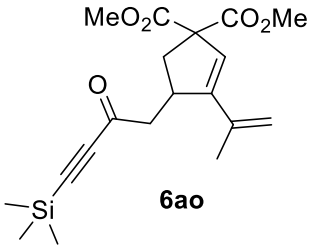
6an

Dimethyl 4-(4-(cyclohex-1-en-1-yl)-2-oxobut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6an)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.57 – 1.64 (m, 2H), 1.64 – 1.71 (m, 2H), 1.95 (s, 3H), 2.14 – 2.20 (m, 4H), 2.43 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.64 (dd, *J* = 17.3 Hz, 11.1 Hz, 1H), 2.70 (dd, *J* = 14.3 Hz, 8.8 Hz, 1H), 2.98 (dd, *J* = 17.3 Hz, 2.4 Hz, 1H), 3.56 – 3.63 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 5.03 (bs, 1H), 5.10 – 5.12 (m, 1H), 5.80 (bs, 1H), 6.45 – 6.48 (m, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.87, 171.60, 171.57, 150.31, 142.67, 137.44, 124.96, 118.92, 115.72, 93.77, 86.22, 65.66, 52.91, 52.81, 50.34, 39.80, 37.66, 28.27, 26.14, 21.92, 21.08, 21.06

HRMS (ESI): $C_{22}H_{26}O_5Na$ calculated = 393.1672; found = 393.1707.



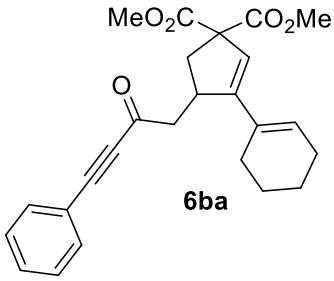
6ao

Dimethyl 4-(2-oxo-4-(trimethylsilyl)but-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ao)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26 (s, 9H), 1.95 (s, 3H), 2.41 (dd, *J* = 14.3 Hz, 2.2 Hz, 1H), 2.66 (dd, *J* = 17.8 Hz, 11.0 Hz, 1H), 2.70 (dd, *J* = 14.3 Hz, 8.8 Hz, 1H), 2.98 (dd, *J* = 17.8 Hz, 2.3 Hz, 1H), 3.55 – 3.61 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.01 (bs, 1H), 5.11 – 5.13 (m, 1H), 5.81 (bs, 1H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.48, 171.59, 171.54, 150.17, 137.43, 125.06, 115.72, 101.95, 98.22, 65.67, 52.93, 52.83, 50.29, 39.46, 37.64, 21.08, 0.79

HRMS (ESI): $C_{19}H_{26}O_5SiNa$ calculated = 385.1447; found = 385.1424.



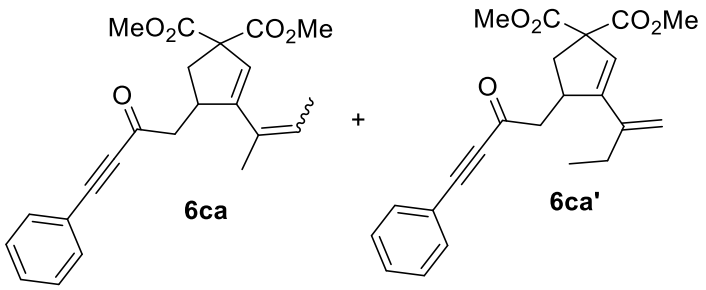
6ba

Dimethyl 3-(cyclohex-1-en-1-yl)-4-(2-oxo-4-phenylbut-3-yn-1-yl)cyclopent-2-ene-1,1-dicarboxylate (6ba)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 – 1.66 (m, 2H), 1.66 – 1.76 (m, 2H), 2.10 – 2.26 (m, 3H), 2.30 – 2.38 (m, 1H), 2.49 (dd, *J* = 14.3 Hz, 2.1 Hz, 1H), 2.70 (dd, *J* = 14.2 Hz, 8.7 Hz, 1H), 2.79 (dd, *J* = 17.6 Hz, 11.0 Hz, 1H), 3.06 (dd, *J* = 17.6 Hz, 2.5 Hz, 1H), 3.62 – 3.69 (m, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 5.72 (bs, 1H), 5.86 – 5.90 (m, 1H), 7.38 – 7.43 (m, 2H), 7.46 – 7.50 (m, 1H), 7.58 – 7.62 (m, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.95, 171.90, 171.88, 150.68, 133.08, 131.24, 130.74, 128.64, 128.24, 121.42, 119.97, 91.05, 88.00, 65.48, 52.87, 52.77, 50.70, 39.31, 37.51, 26.36, 25.81, 22.52, 22.05

HRMS (ESI): $C_{25}H_{26}O_5Na$ calculated = 429.1672; found = 429.1689.



(*Z*/*E*) = 8:1 **6ca**:**6ca'** = 2:1

Dimethyl (*Z*)-3-(but-2-en-2-yl)-4-(2-oxo-4-phenylbut-3-yn-1-yl)cyclopent-2-ene-1,1-dicarboxylate ((*Z*)-6ca) (major isomer)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.69 (dq, *J* = 6.8 Hz, 1.5 Hz, 3H), 1.81 (t, *J* = 1.5 Hz, 3H), 2.23 (dd, *J* = 14.2 Hz, 4.1 Hz, 1H), 2.61 (dd, *J* = 17.0 Hz, 10.8 Hz, 1H), 2.85 (dd, *J* = 17.0 Hz, 3.4 Hz, 1H), 2.93 (dd, *J* = 14.2 Hz, 8.5 Hz, 1H), 3.58 – 3.64 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 5.54 (qq, *J* = 6.8 Hz, 1.5 Hz, 1H), 5.61 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.43 (m, 2H), 7.45 – 7.50 (m, 1H), 7.57 – 7.61 (m, 2H)

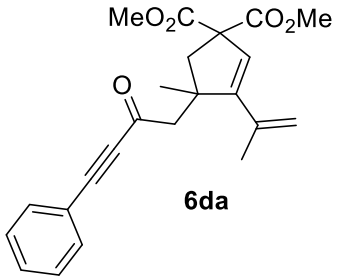
Dimethyl 3-(but-1-en-2-yl)-4-(2-oxo-4-phenylbut-3-yn-1-yl)cyclopent-2-ene-1,1-dicarboxylate (6ca')

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.4 Hz, 3H), 2.26 – 2.39 (m, 2H), 2.46 (dd, *J* = 14.4 Hz, 2.4 Hz, 1H), 2.75 (dd, *J* = 17.4 Hz, 10.9 Hz, 1H), 2.76 (dd, *J* = 14.4 Hz, 8.7 Hz, 1H), 3.07 (dd, *J* = 17.4 Hz, 2.4 Hz, 1H), 3.64 – 3.70 (m, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 5.09 (bs, 1H), 5.15 – 5.16 (m, 1H), 5.86 (bs, 1H), 7.38 – 7.43 (m, 2H), 7.45 – 7.50 (m, 1H), 7.57 – 7.61 (m, 2H)

Combined for (*Z*)-**6ca** and **6ca'**

^{13}C NMR (125.8 MHz, $CDCl_3$): 186.74, 186.43, 172.08, 171.68, 171.56, 171.49, 149.73, 149.62, 143.46, 133.07, 130.79, 130.76, 130.51, 128.65, 125.35, 125.27, 124.42, 119.91, 119.88, 113.60, 91.17, 91.11, 87.90, 87.84, 65.72, 65.58, 52.93, 52.88, 52.84, 52.78, 50.36, 49.76, 41.67, 39.99, 37.60, 37.44, 27.05, 22.94, 14.85, 12.72

HRMS (ESI): $C_{23}H_{24}O_5Na$ calculated = 403.1516; found = 403.1517.



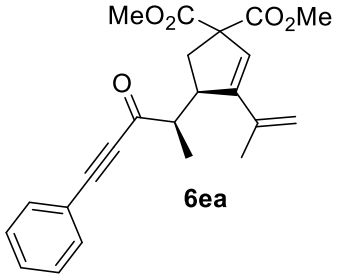
6da

Dimethyl 4-methyl-4-(2-oxo-4-phenylbut-3-yn-1-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6da)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (s, 3H), 1.97 (s, 3H), 2.58 (d, *J* = 14.2 Hz, 1H), 2.99 (d, *J* = 14.2 Hz, 1H), 3.00 (d, *J* = 15.8 Hz, 1H), 3.13 (d, *J* = 15.8 Hz, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 5.14 – 5.16 (m, 1H), 5.20 (bs, 1H), 5.83 (bs, 1H), 7.38 – 7.43 (m, 2H), 7.45 – 7.49 (m, 1H), 7.58 – 7.61 (m, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 185.98, 171.54, 153.27, 137.80, 133.02, 130.71, 128.62, 125.76, 120.02, 115.41, 90.48, 88.98, 63.63, 54.40, 52.90, 48.80, 45.59, 26.95, 23.64

HRMS (ESI): $C_{23}H_{24}O_5Na$ calculated = 403.1516; found = 403.1523.



6ea

Dimethyl-4-(3-oxo-5-phenylpent-4-yn-2-yl)-3-(prop-1-en-2-yl)cyclopent-2-ene-1,1-dicarboxylate (6ea)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 6.9 Hz, 3H), 2.00 (s, 3H), 2.27 (dd, *J* = 14.8 Hz, 4.3 Hz, 1H), 2.84 (dd, *J* = 14.8 Hz, 9.5 Hz, 1H), 3.24 (qd, *J* = 6.9 Hz, 3.5 Hz, 1H), 3.74 (s, 3H), 3.77 (s, 3H), 4.00 – 4.08 (m, 1H), 5.14 – 5.18 (m, 2H), 5.87 (d, *J* = 1.3 Hz, 1H), 7.38 – 7.44 (m, 2H), 7.45 – 7.51 (m, 1H), 7.58 – 7.63 (m, 2H)

^{13}C NMR (125.8 MHz, $CDCl_3$): 190.16, 171.52, 171.39, 148.61, 137.85, 133.08, 130.79, 128.68, 126.03, 119.94, 115.21, 91.96, 87.27, 65.95, 53.02, 52.82, 49.28, 45.26, 31.89, 21.49, 8.73

HRMS (ESI): $C_{23}H_{24}O_5Na$ calculated = 403.1516; found = 403.1494.

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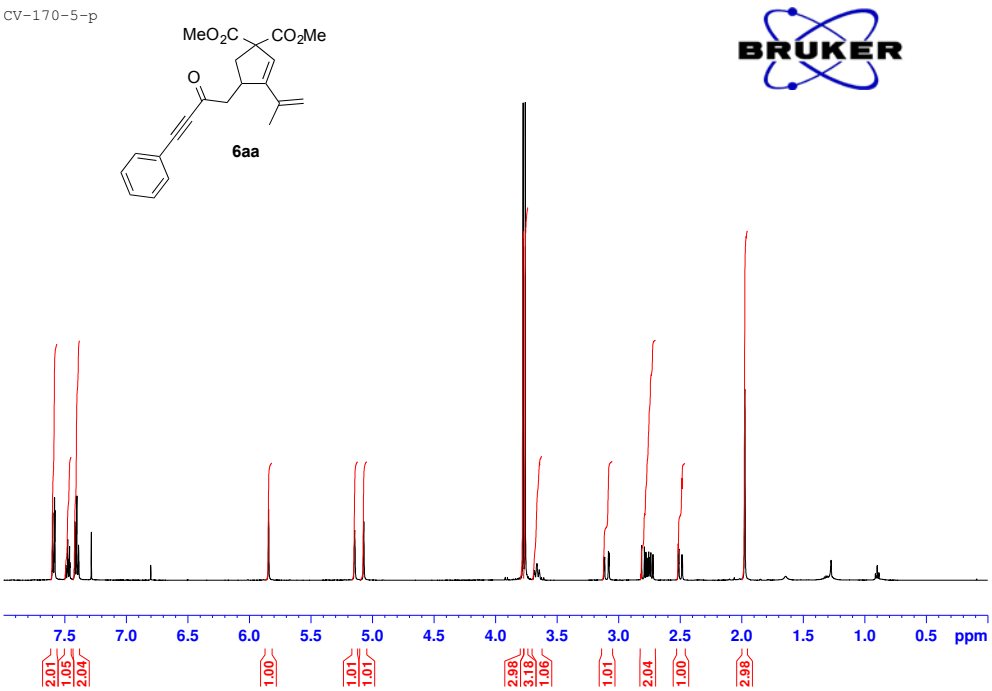
[1] a) Black D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *Tetrahedron Lett*, **1963**, *4*, 483; b) Persson, A. K. Å.; Johnston, E. V.; Bäckvall, J.-E. *Org. Lett.* **2009**, *11*, 3814.

[2] a) Franzén, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2003**, *125*, 6056; b) Persson, A. K. Å.; Jiang, T.; Johnson, M. T.; Bäckvall, J.-E. *Angew. Chem. Int. Ed.* **2011**, *50*, 6155; c) Jiang, T.; Persson, A. K. Å.; Bäckvall, J.-E. *Org. Lett.* **2011**, *13*, 5838.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CO2Me
O
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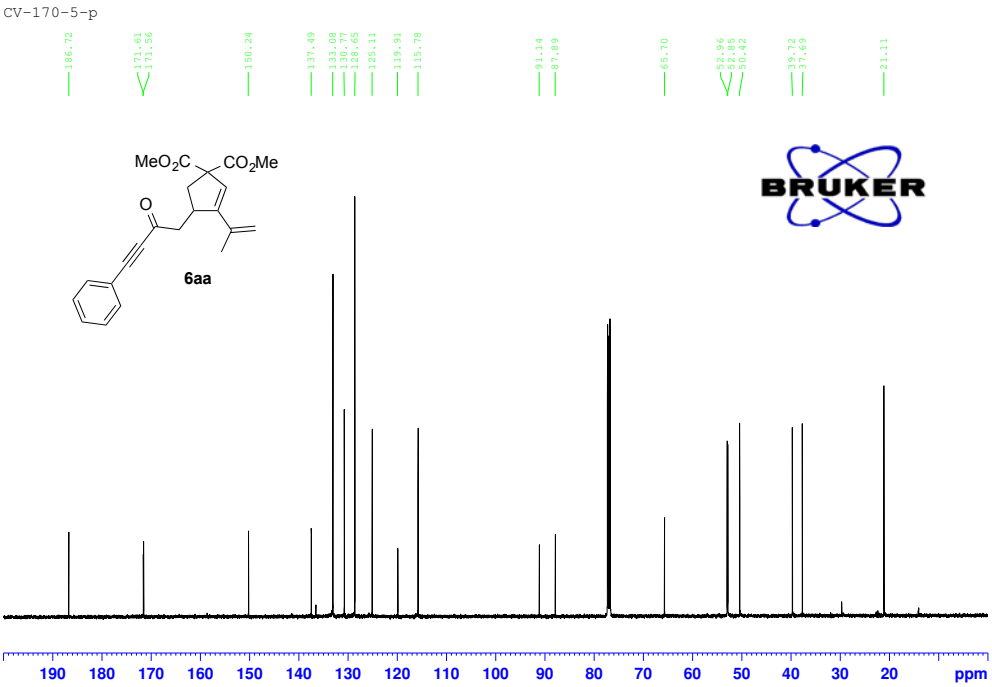
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
1.05
2.04
1.00
1.01
1.01
2.98
3.18
1.06
1.01
2.04
1.00
2.98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171.56
150.24
137.49
133.08
130.77
128.65
125.11
119.91
115.78
91.14
87.89
65.70
52.96
52.85
50.42
39.72
37.69
21.11
MeO2C
CO2Me
O
6aa
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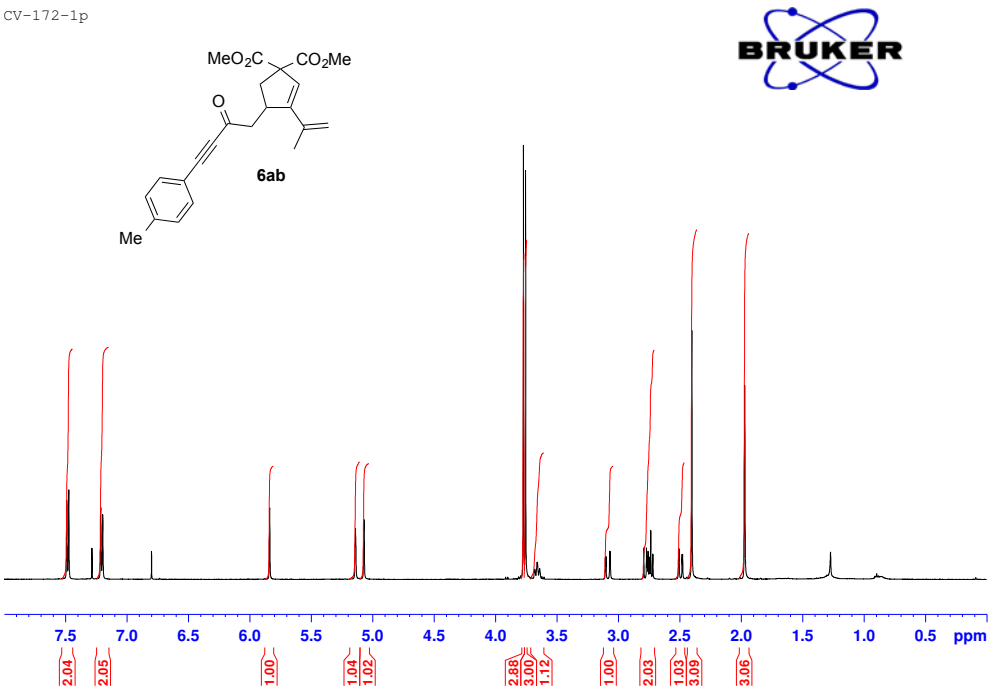
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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CO2Me
O
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Me
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6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.04
2.05
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1.04
1.02
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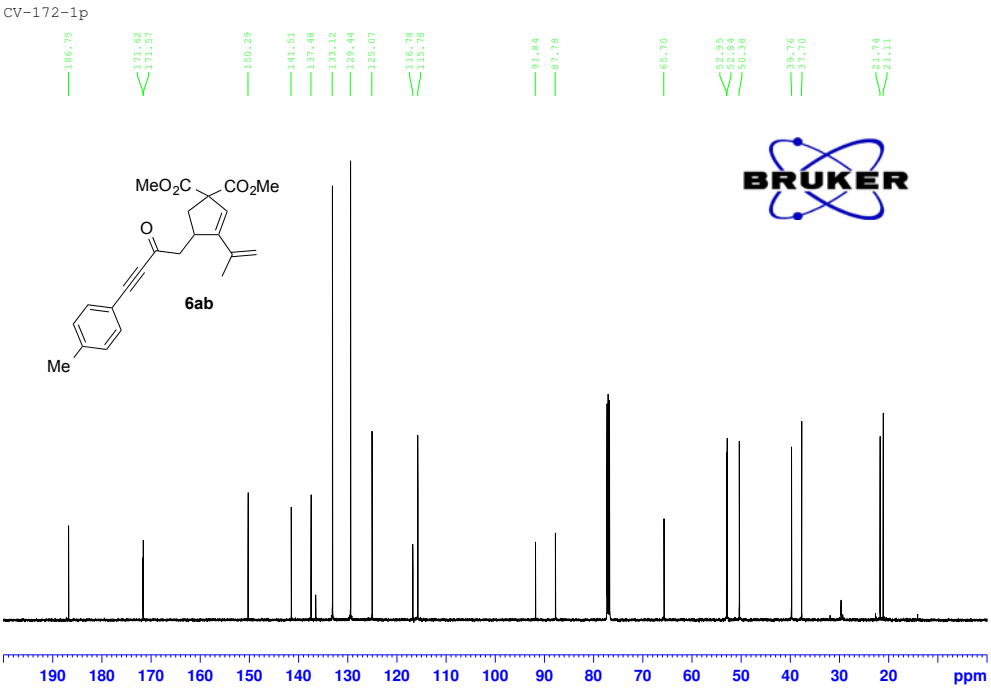
3.00
1.12
1.00
2.03
1.03
3.09
3.06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129.44
125.07
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65.70
52.95
52.84
50.38
39.76
37.70
21.74
21.11
MeO2C
CO2Me
O
6ab
Me
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180
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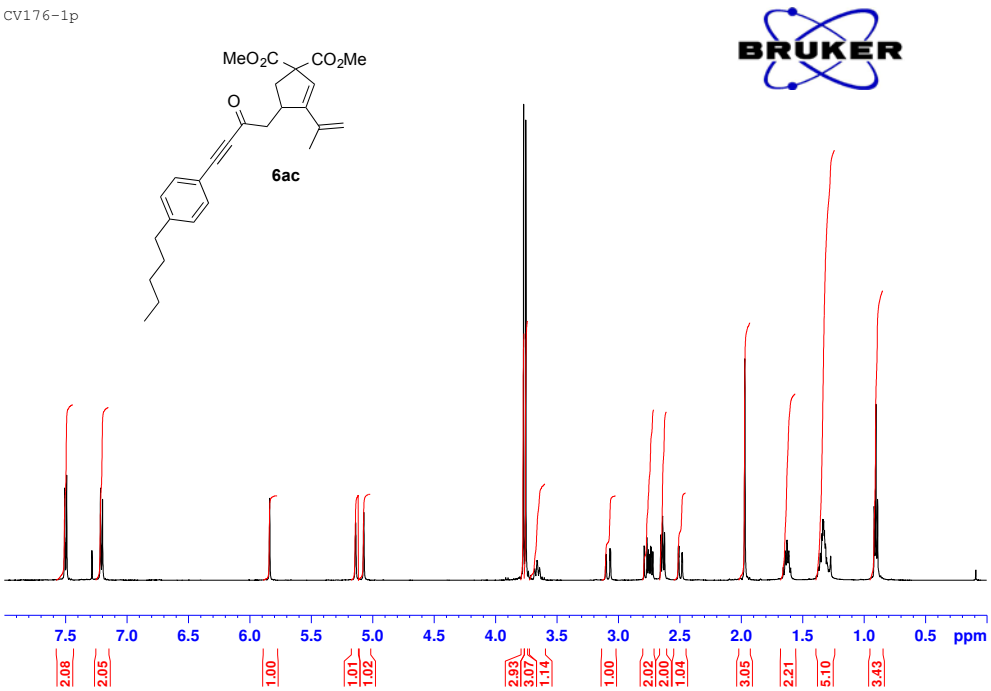
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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CO2Me
O
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4.0
3.5
3.0
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1.5
1.0
0.5
ppm
2.08
2.05
1.00
1.01
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1.04
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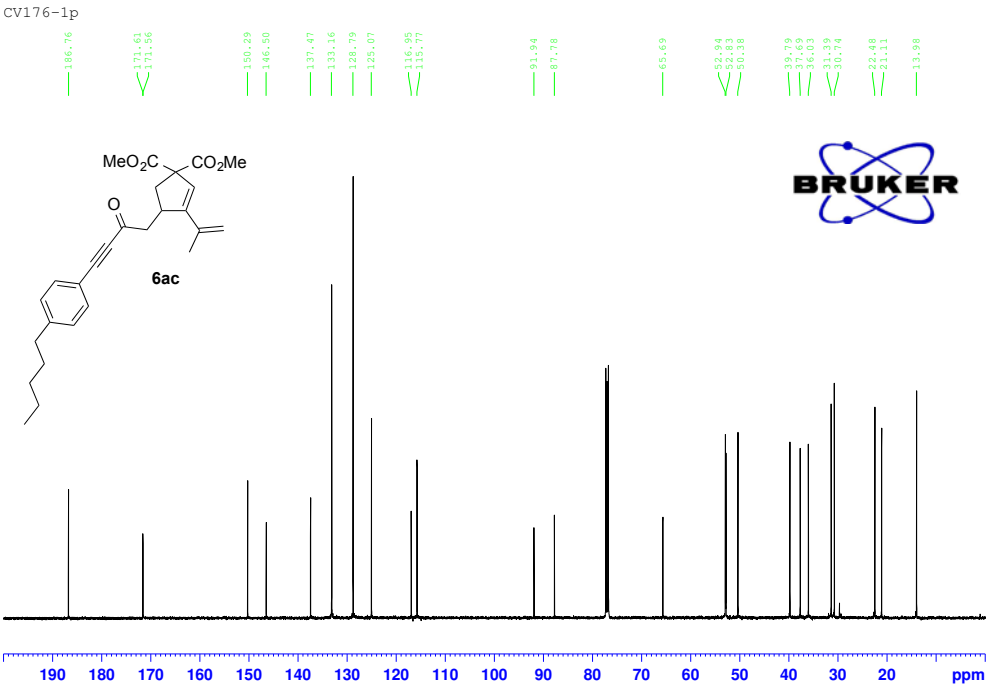
3.43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125.07
116.95
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87.78
65.69
52.94
52.83
50.38
39.79
37.69
36.03
31.39
30.74
22.48
21.11
13.98
MeO2C
CO2Me
O
6ac
BRUKER
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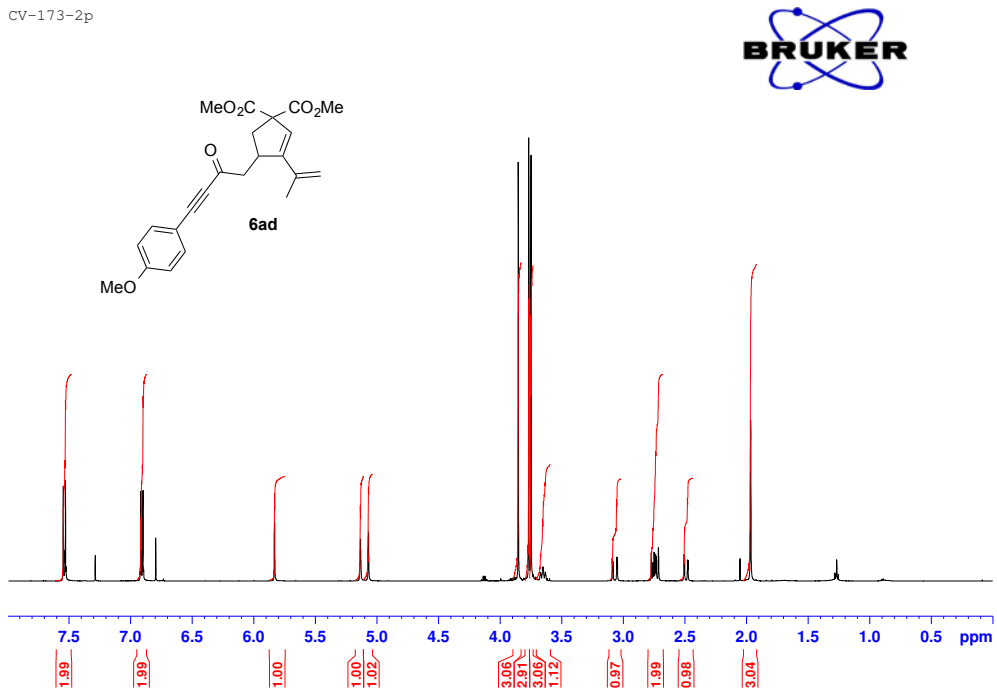
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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CO2Me
O
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5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
1.99
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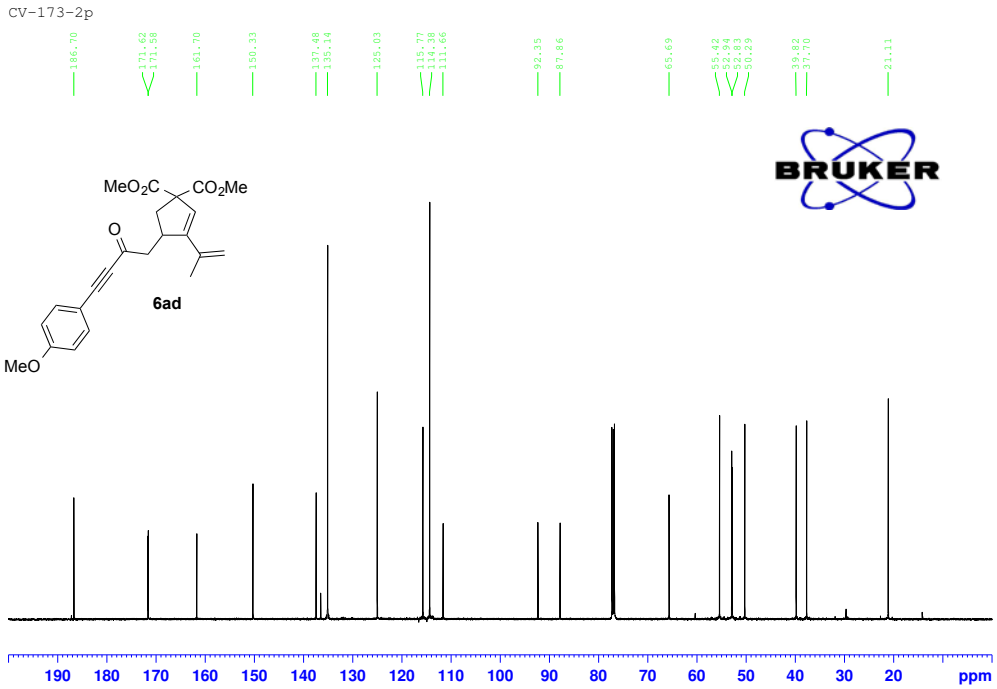
1.00
1.02
3.06
2.91
3.06
1.12
0.97
1.99
0.98
3.04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171.62
171.58
161.70
150.33
137.48
135.14
125.03
115.77
114.38
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37.70
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CO2Me
O
6ad
MeO
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
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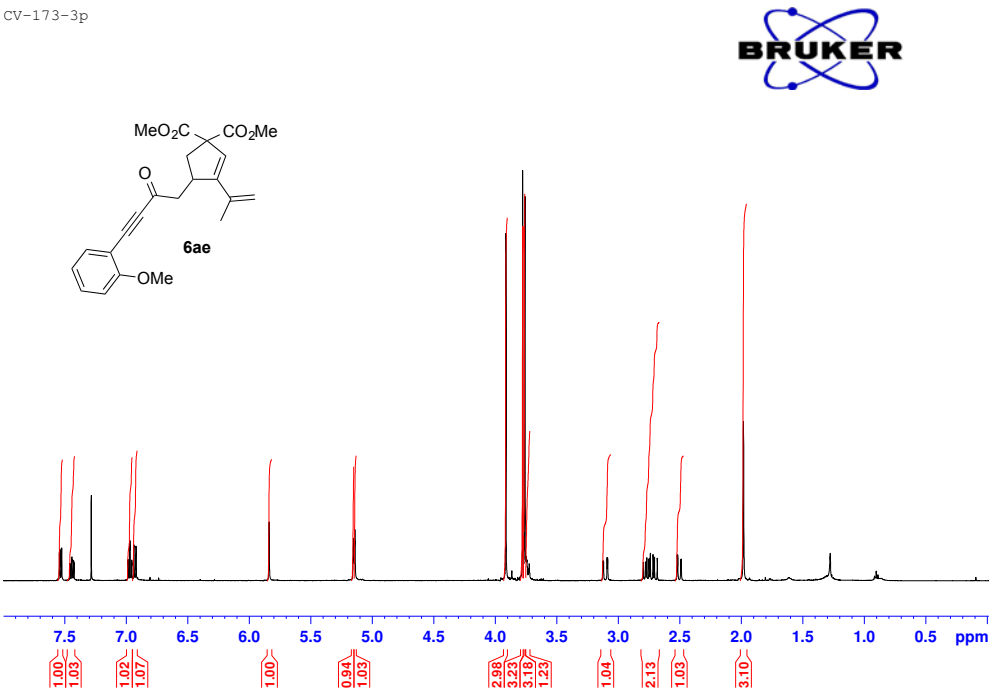
30
20
ppm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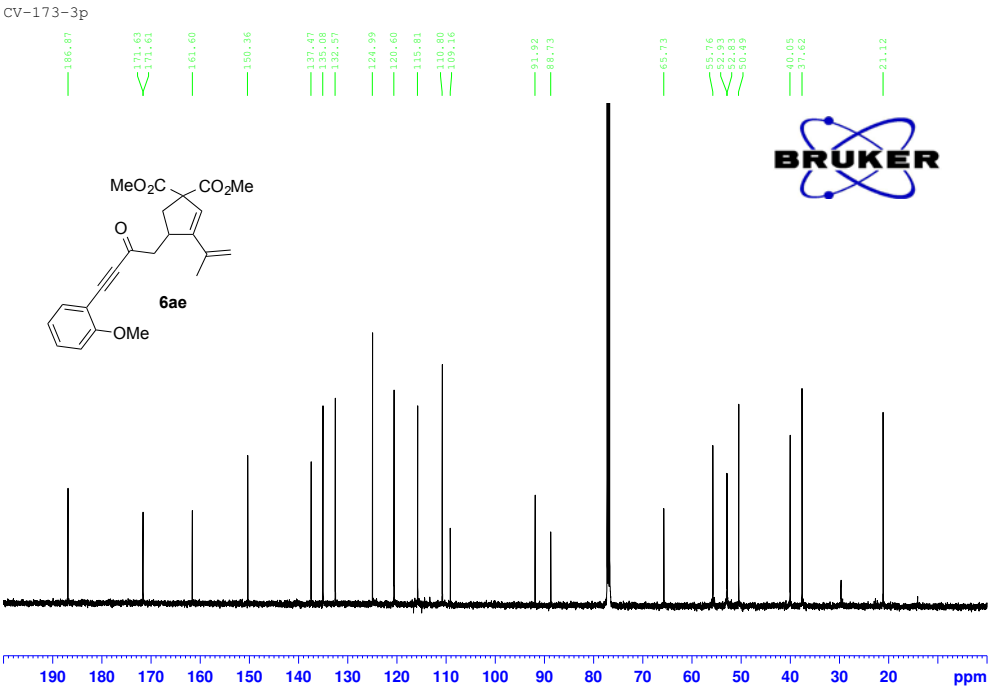
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.02
1.07
1.00
0.94
1.03
2.98
3.23
3.18
1.23
1.04
2.13
1.03
3.10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171.61
161.60
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137.47
135.08
132.57
124.99
120.60
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110.80
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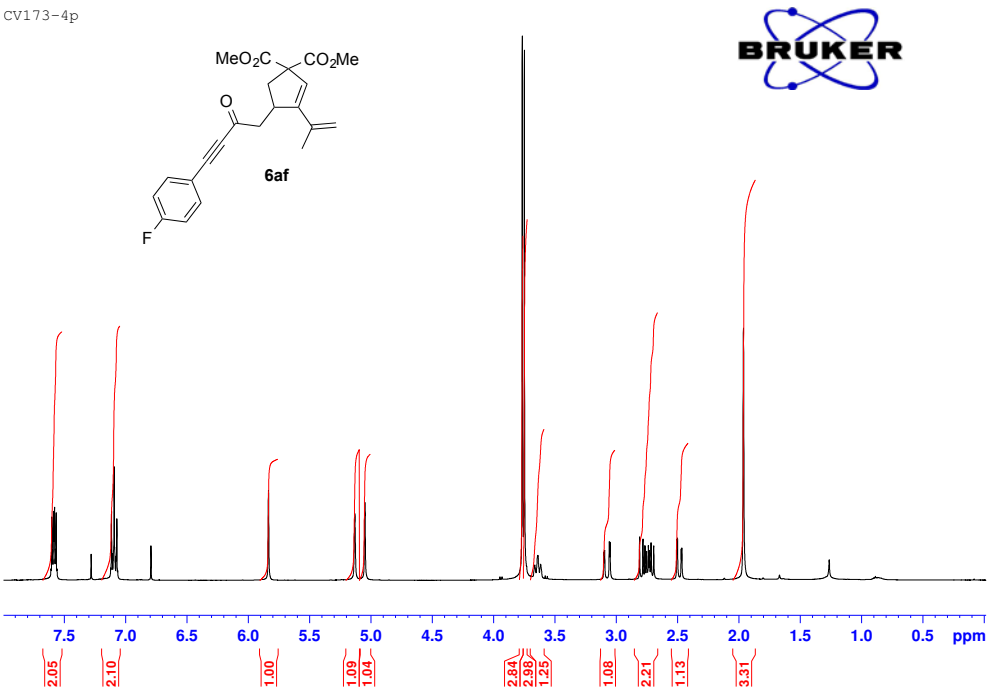
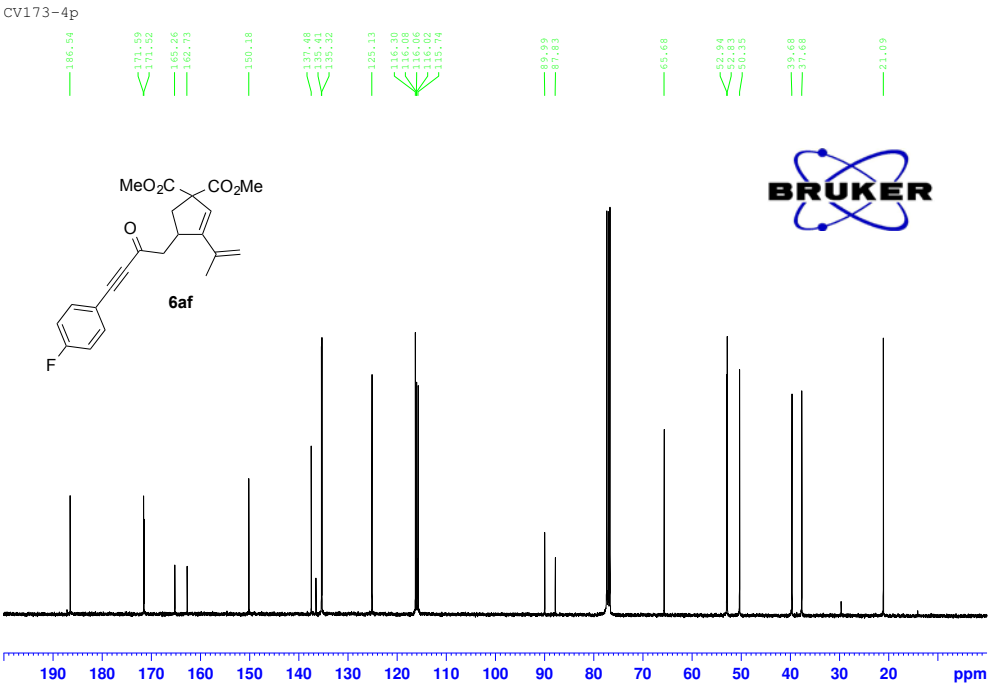
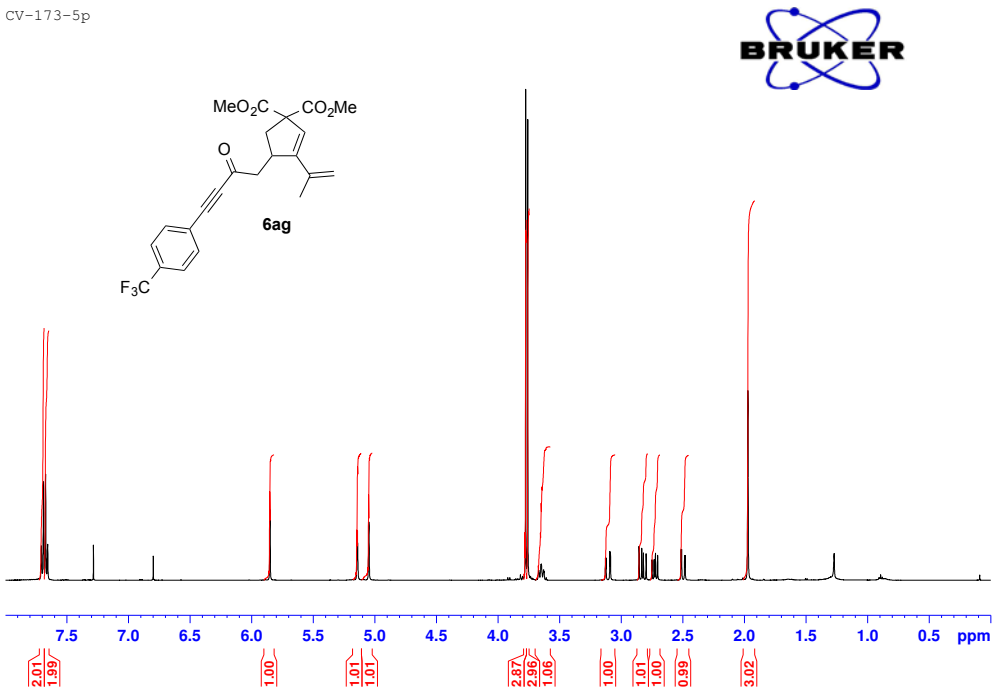
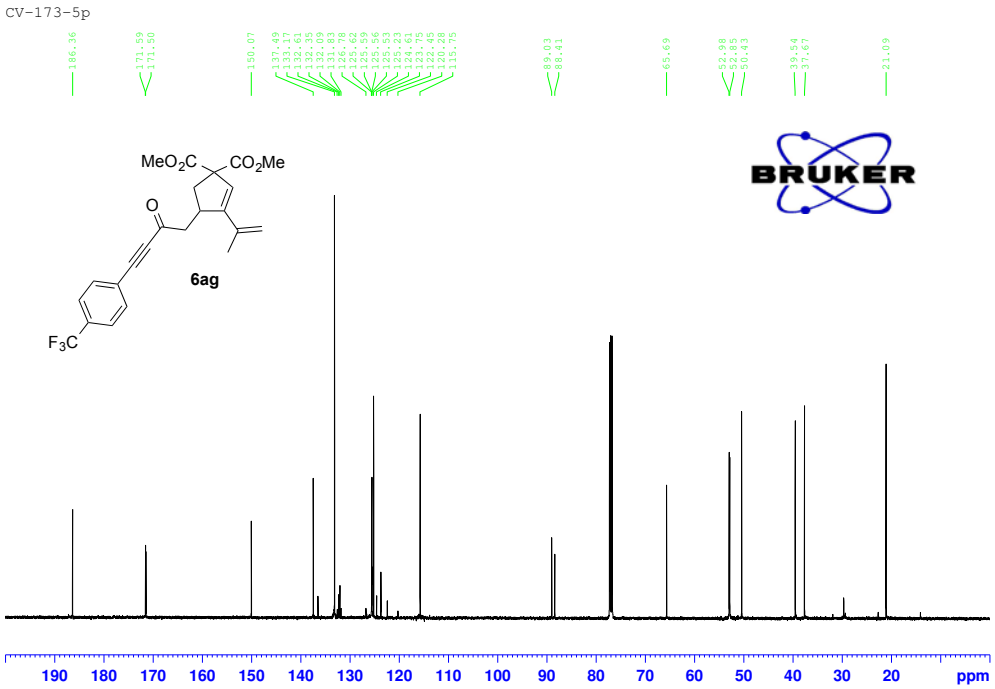
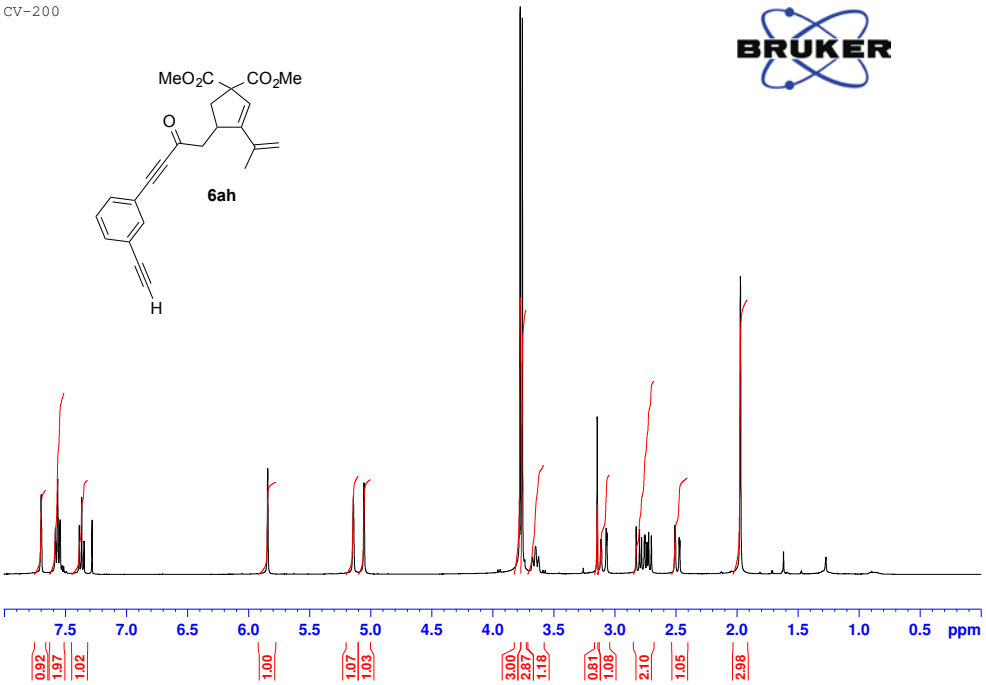
88.73
65.73
55.76
52.93
52.83
50.49
40.05
37.62
21.12
MeO2C
CO2Me
O
6ae
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

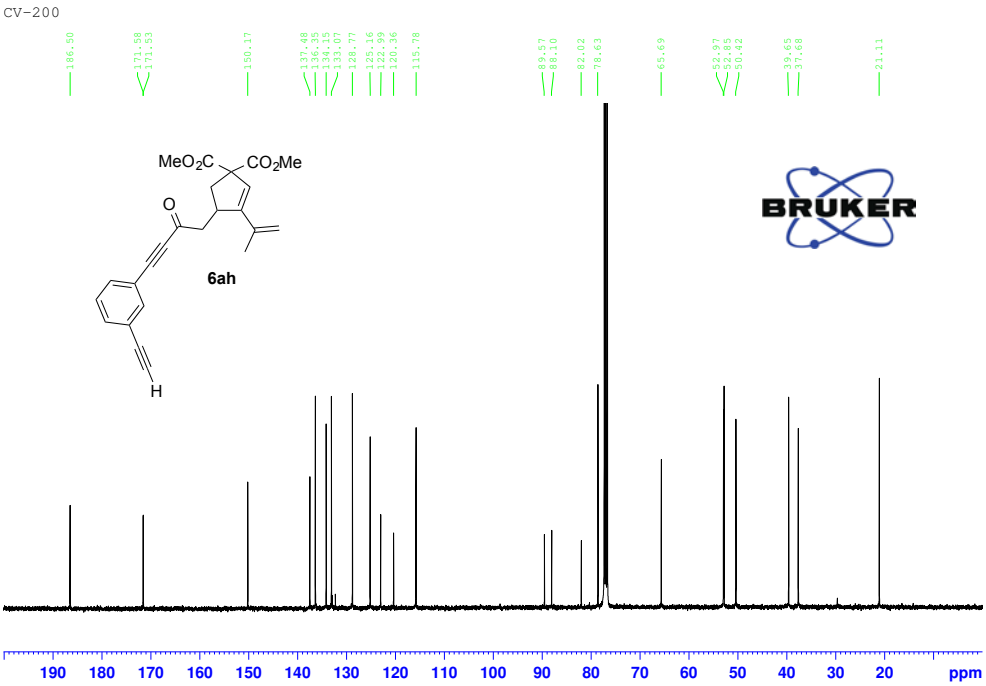

CV173-4p
MeO2C
CO2Me
O
6af
F
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
2.10
1.00
1.09
1.04
2.84
2.98
1.25
1.08
2.21
1.13
3.31


CV173-4p
186.54
171.59
171.52
165.26
162.73
150.18
137.48
135.41
135.32
125.13
116.30
116.08
116.06
116.02
115.74
89.99
87.83
65.68
52.94
52.83
50.35
39.68
37.68
21.09
MeO2C
CO2Me
O
6af
F
BRUKER
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

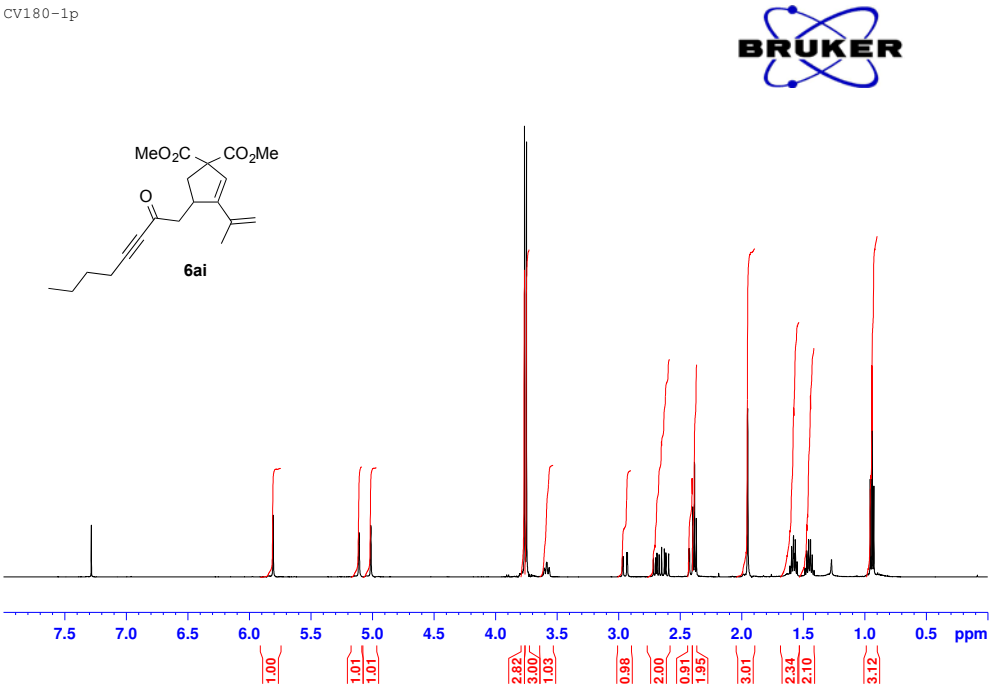

CV-173-5p
MeO2C
CO2Me
O
6ag
F3C
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
1.99
1.00
1.01
1.01
2.87
2.96
1.06
1.00
1.01
1.00
0.99
3.02


CV-173-5p
186.36
171.59
171.50
150.07
137.49
133.17
132.65
132.35
132.09
131.83
126.78
125.60
125.59
125.56
125.53
125.23
124.61
123.75
122.45
120.28
115.75
89.03
88.41
65.69
52.98
52.85
50.48
39.54
37.67
21.09
MeO2C
CO2Me
O
6ag
F3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

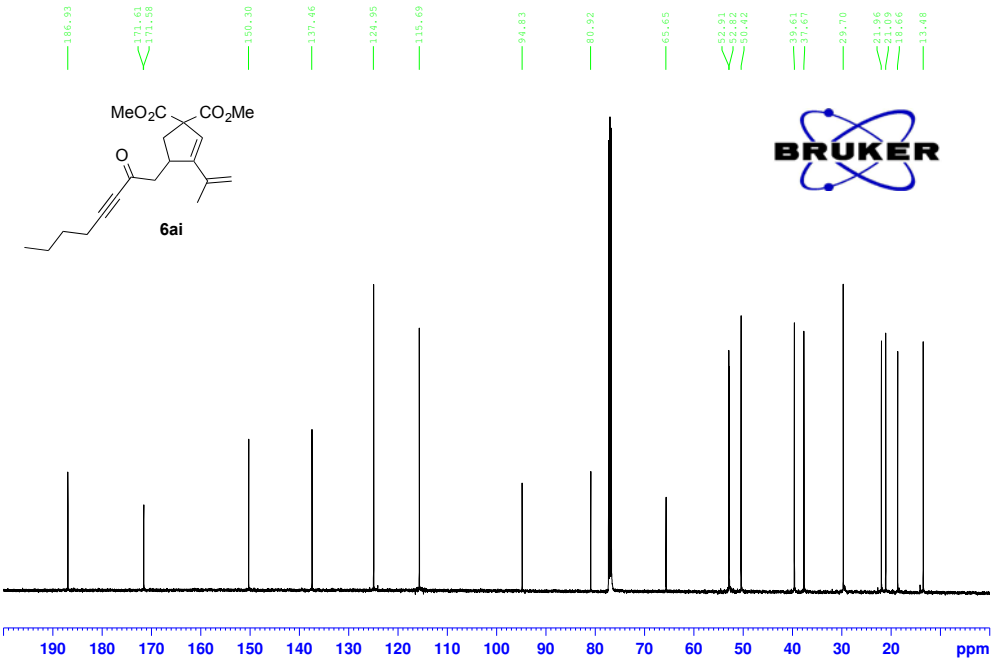

CV-200
MeO2C
CO2Me
O
6ah
H
BRUKER
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.92 1.97 1.02 1.00 1.07 1.03 3.00 2.87 1.18 0.81 1.08 2.10 1.05 2.98

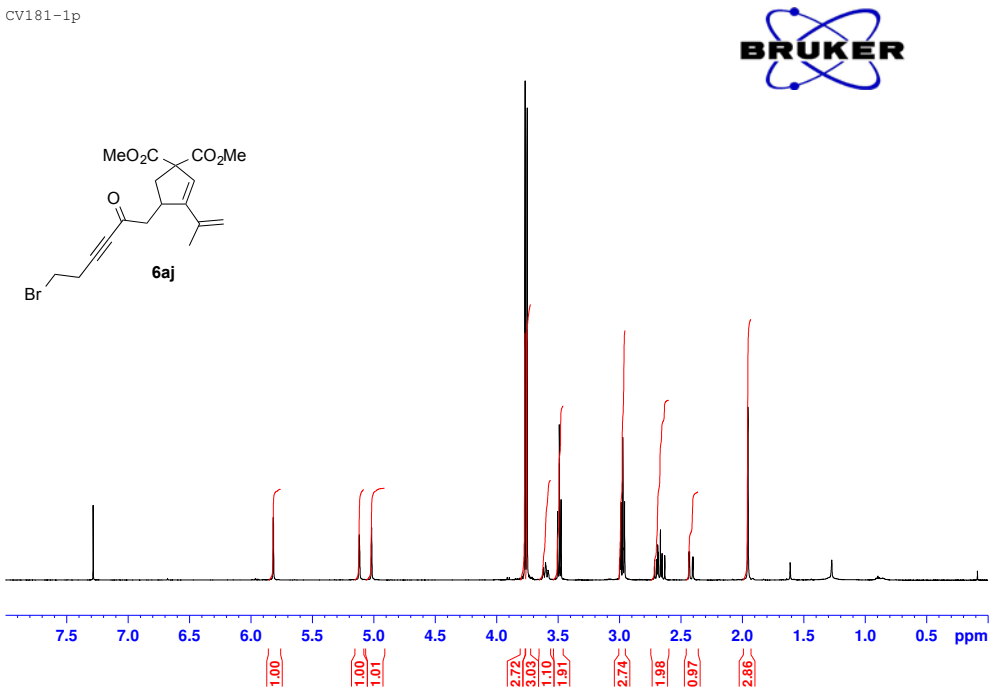

CV-200
186.50
171.58
171.53
150.17
137.48
136.35
134.15
133.07
128.77
125.16
122.99
120.36
115.78
89.57
88.10
82.02
78.63
65.69
52.97
52.85
50.42
39.65
37.68
21.11
MeO2C
CO2Me
O
6ah
H
BRUKER
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

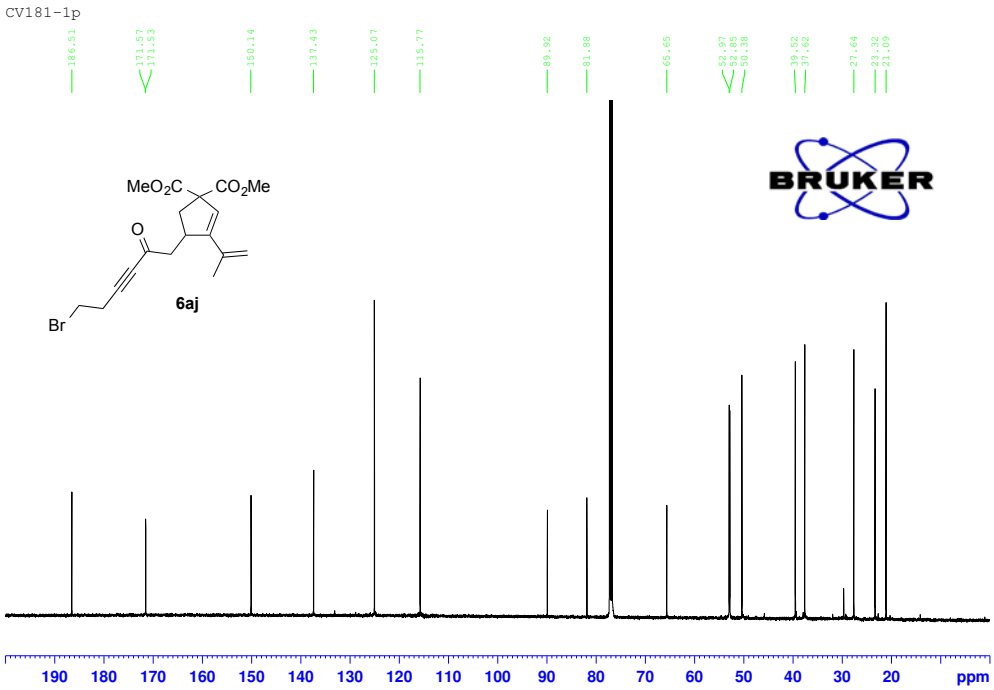
CV180-1p

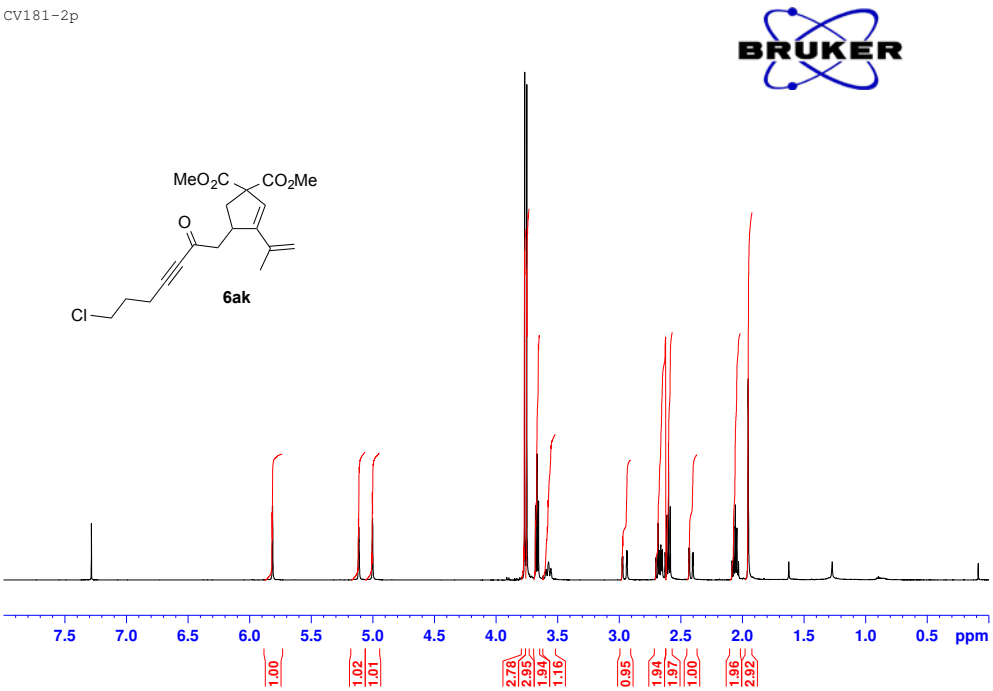


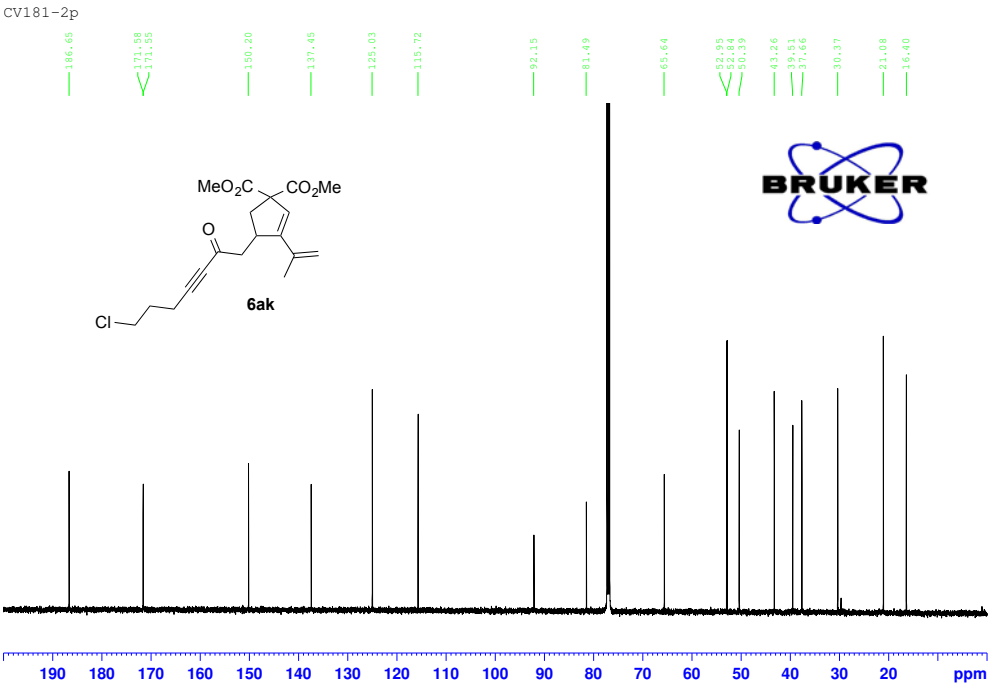
CV180-1p

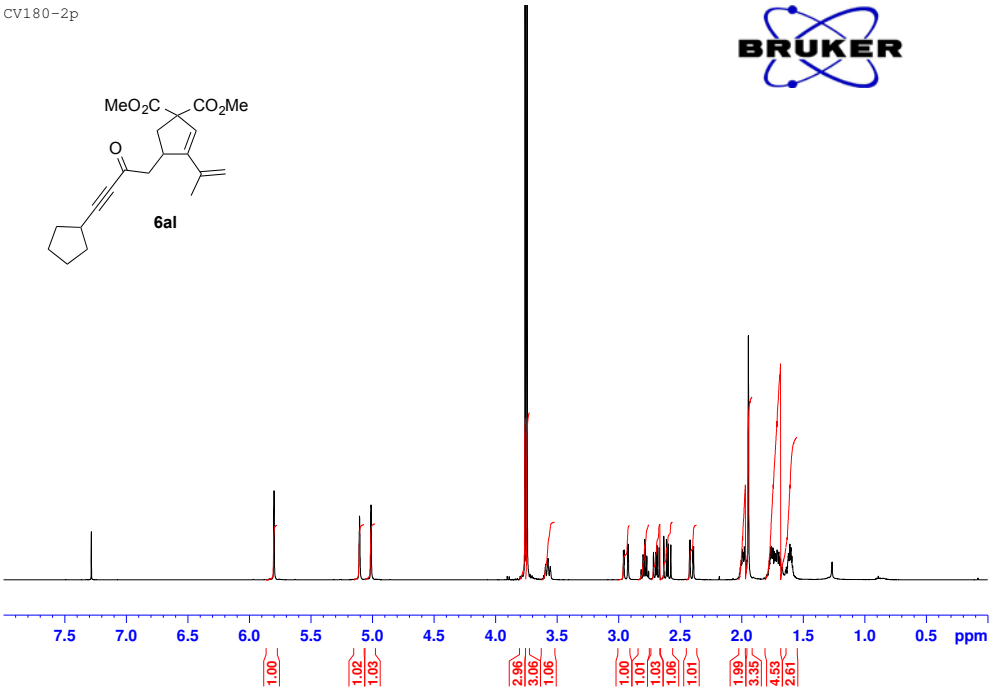


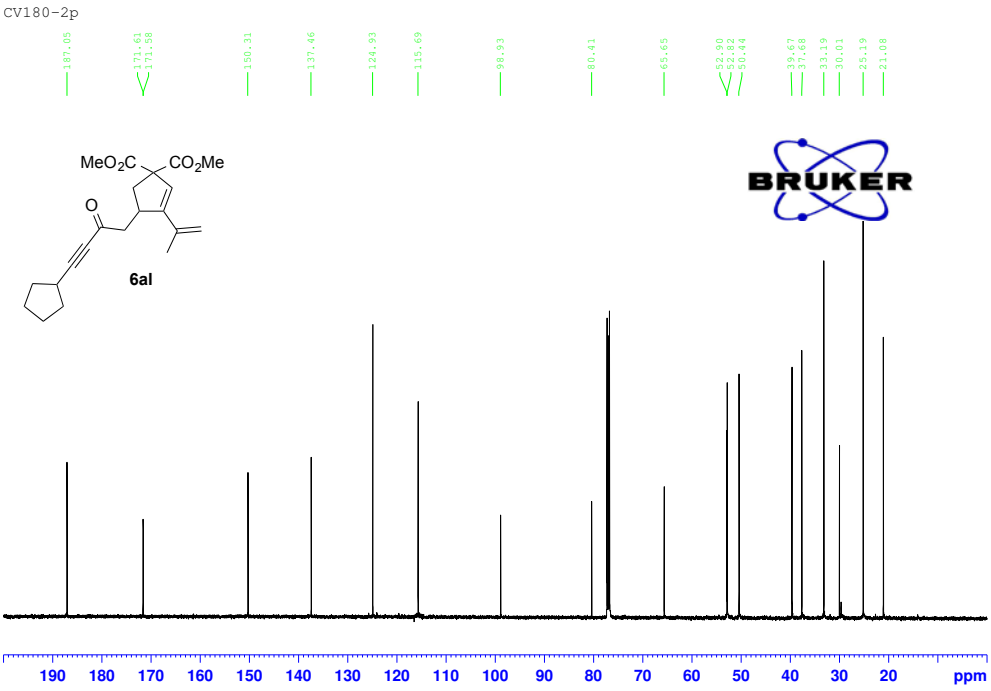

CV181-1p
MeO2C
CO2Me
O
Br
6aj
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.00 1.01 2.72 3.03 1.10 1.91 2.74 1.98 0.97 2.86

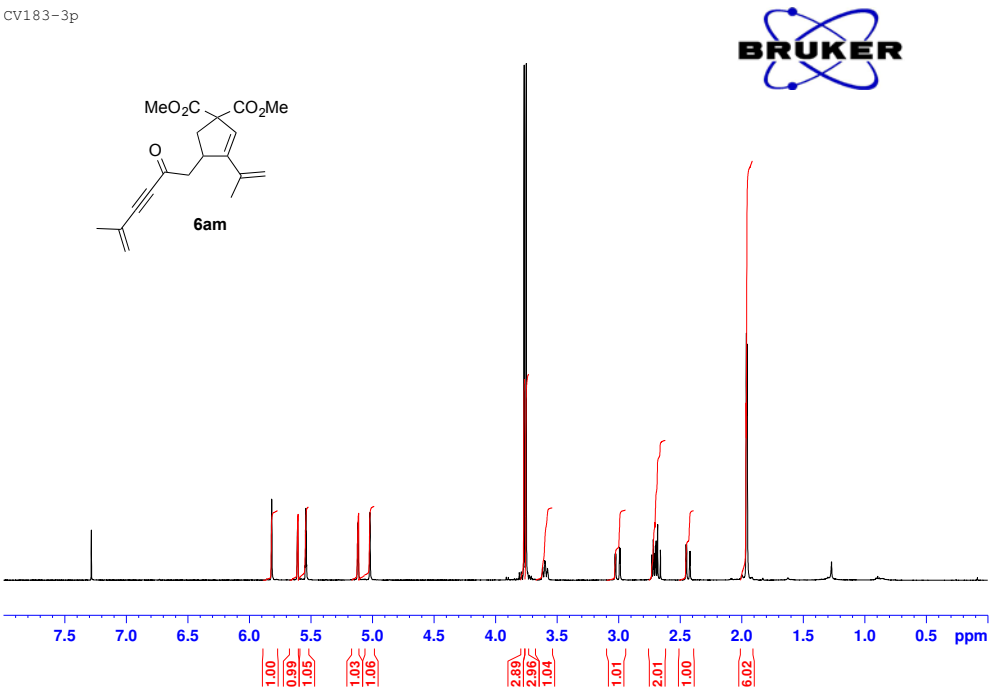

CV181-1p
186.51
171.57
171.53
150.14
137.43
125.07
115.77
89.92
81.88
65.65
52.97
52.85
50.38
39.52
37.62
27.64
23.32
21.09
MeO2C
CO2Me
O
Br
6aj
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

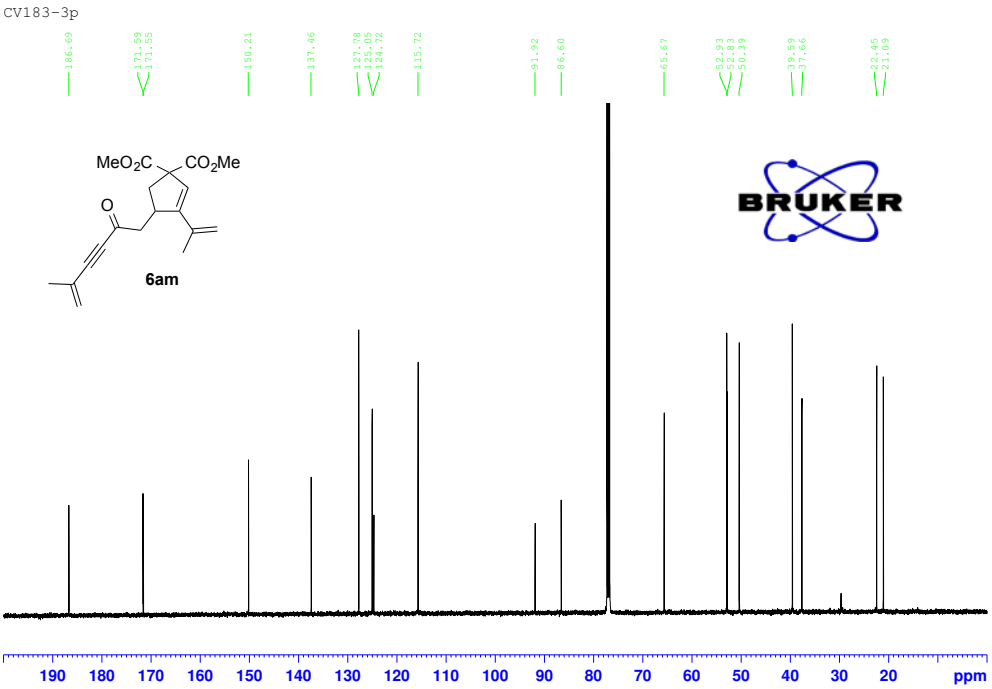

CV181-2p
MeO2C
CO2Me
O
Cl
6ak
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.02 1.01 2.78 2.95 1.94 1.16 0.95 1.94 1.97 1.00 1.96 2.92


CV181-2p
186.65 171.58 171.55 150.20 137.45 125.03 115.72 92.15 81.49 65.64 52.95 52.84 50.39 43.26 39.51 37.66 30.37 21.08 16.40
MeO2C
CO2Me
O
Cl
6ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

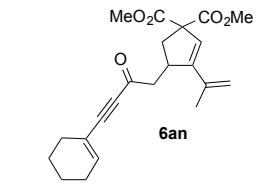

CV180-2p
MeO2C
CO2Me
O
6al
BRUKER
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.02 1.03 2.96 3.06 1.06 1.00 1.01 1.03 1.06 1.01 1.99 3.35 4.53 2.61


CV180-2p
187.05
171.61
171.58
150.31
137.46
124.93
115.69
98.93
80.41
65.65
52.90
52.32
50.44
39.67
37.68
33.19
30.01
25.19
21.08
MeO2C
CO2Me
O
6al
BRUKER
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


CV183-3p
MeO2C
CO2Me
O
6am
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.99
1.05
1.03
1.06
2.89
2.96
1.04
1.01
2.01
1.00
6.02

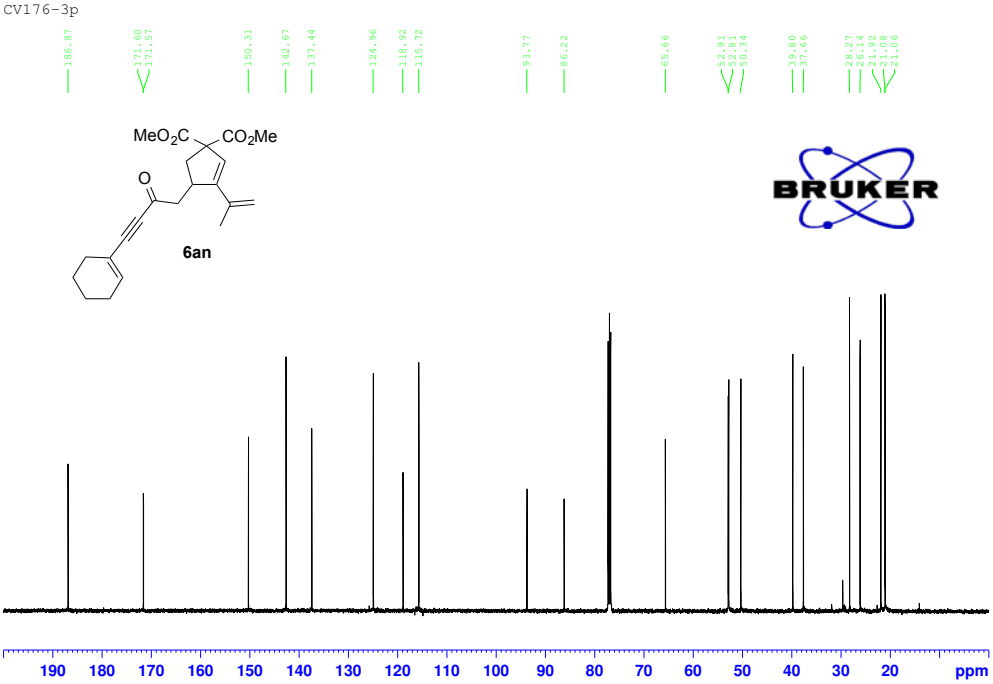

CV183-3p
186.69
171.59
171.55
150.21
137.46
127.78
125.05
124.72
115.72
91.92
86.60
65.67
52.93
52.33
50.39
39.59
37.66
22.45
21.09
MeO2C
CO2Me
O
6am
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

CV176-3p



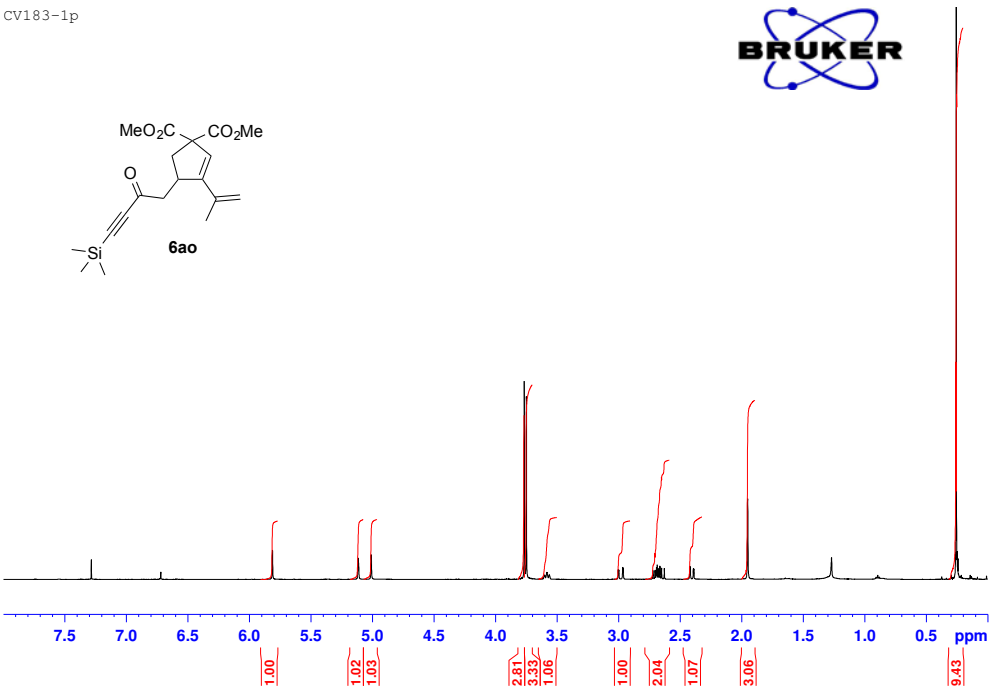
6an

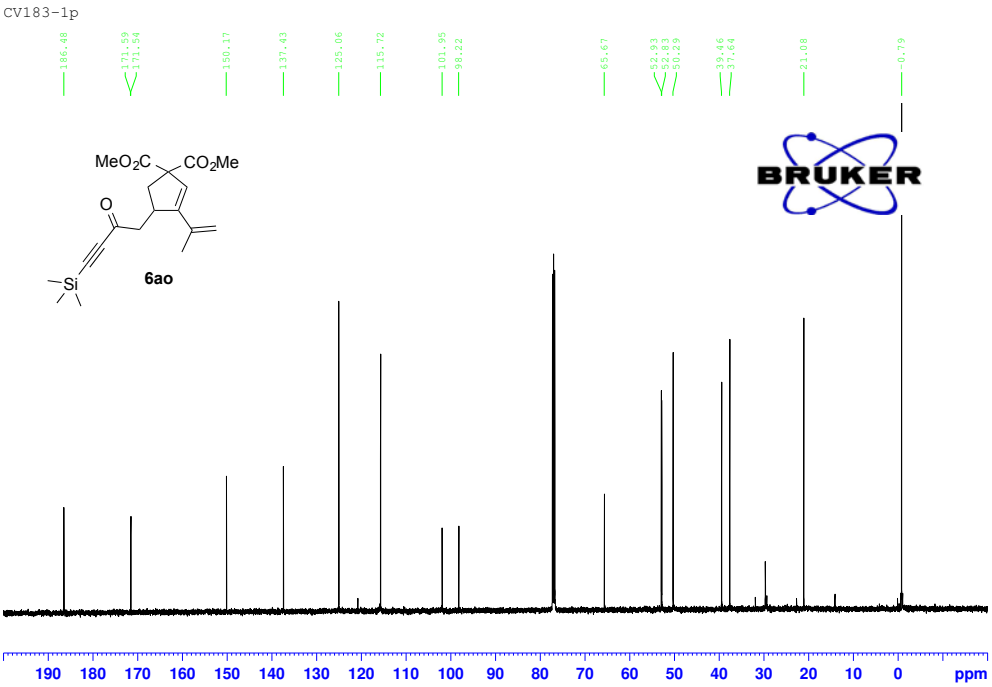
CV176-3p

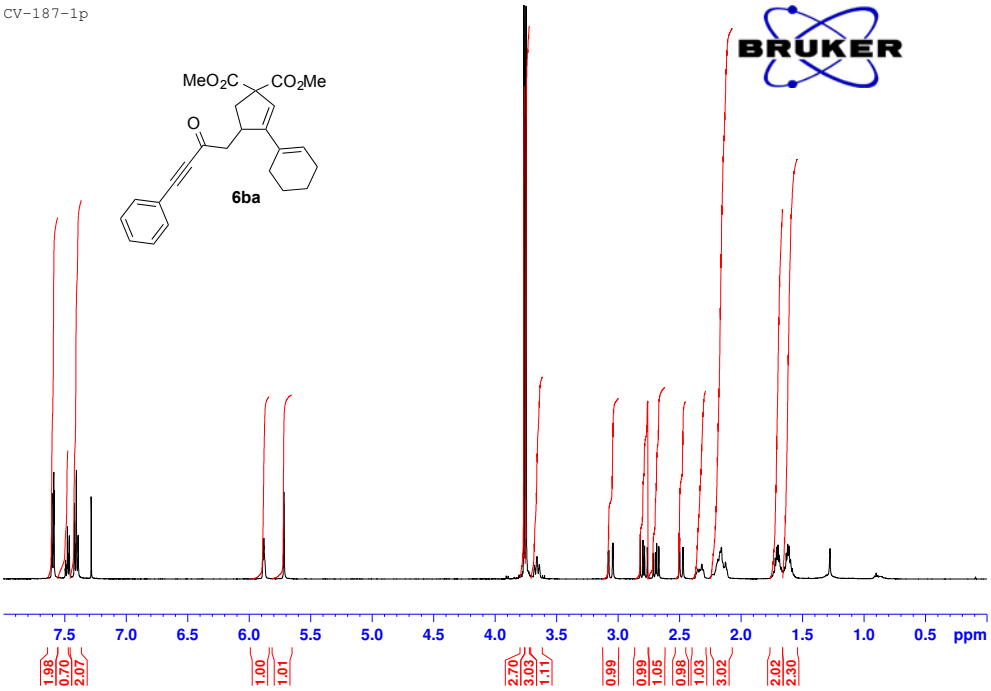


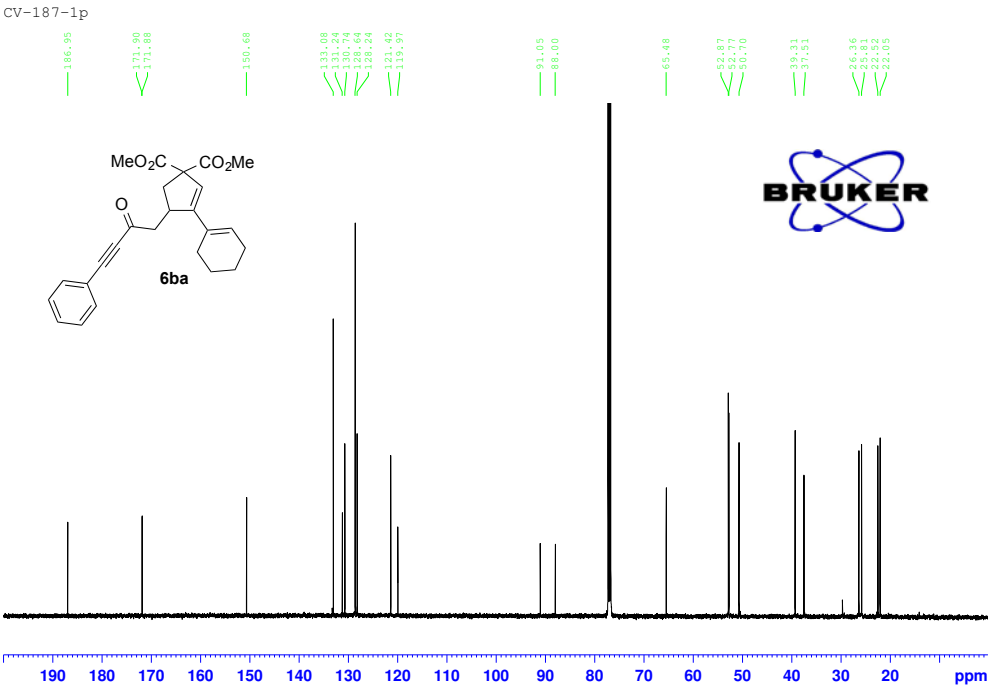
MeO2C
CO2Me
O

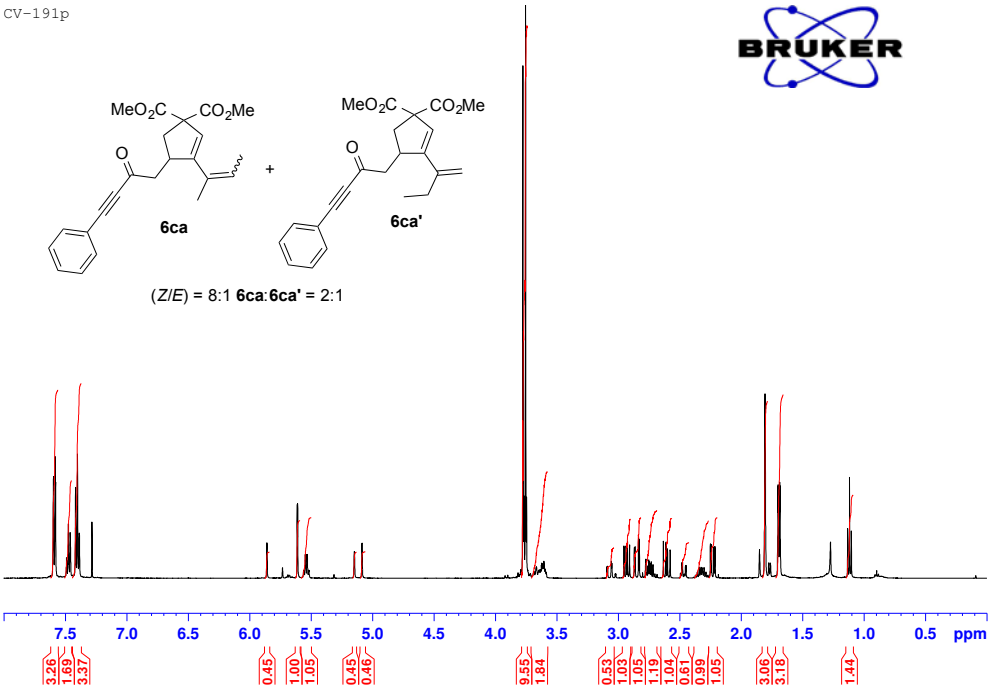
6an

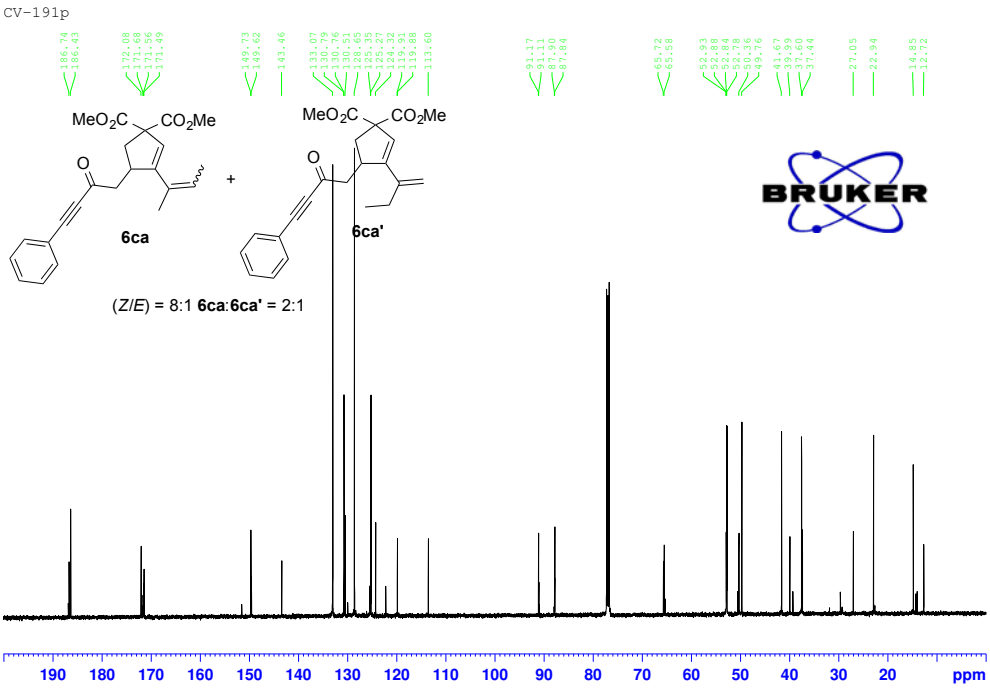

CV183-1p
MeO2C
CO2Me
O
Si
6ao
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.02 1.03 2.81 3.33 1.06 1.00 2.04 1.07 3.06 9.43

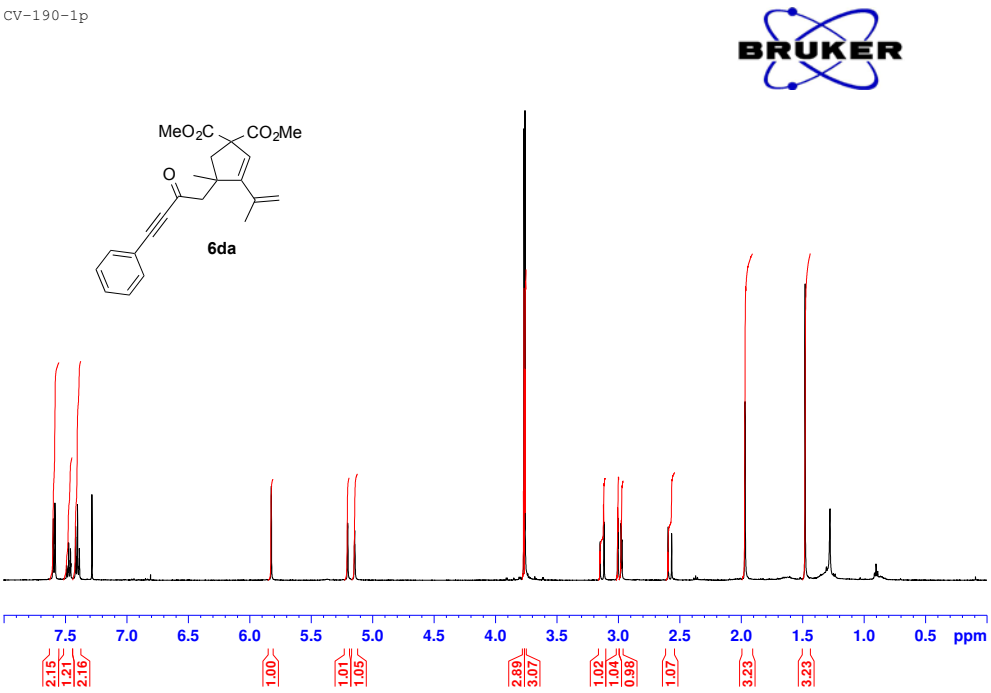

CV183-1p
186.48
171.59
171.54
150.17
137.43
125.06
115.72
101.95
98.22
65.67
52.93
52.83
50.29
39.46
37.64
21.08
-0.79
MeO2C
CO2Me
O
Si
6ao
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

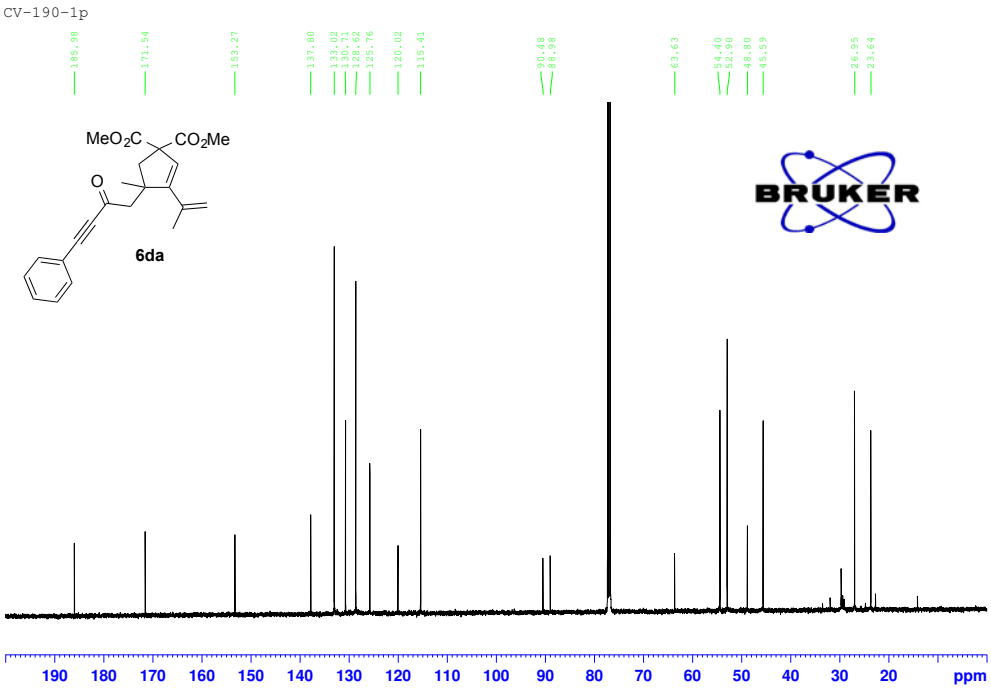

CV-187-1p
MeO2C
CO2Me
O
6ba
BRUKER
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
0.70
2.07
1.00
1.01
2.70
3.03
1.11
0.99
0.99
1.05
0.98
1.03
3.02
2.02
2.30

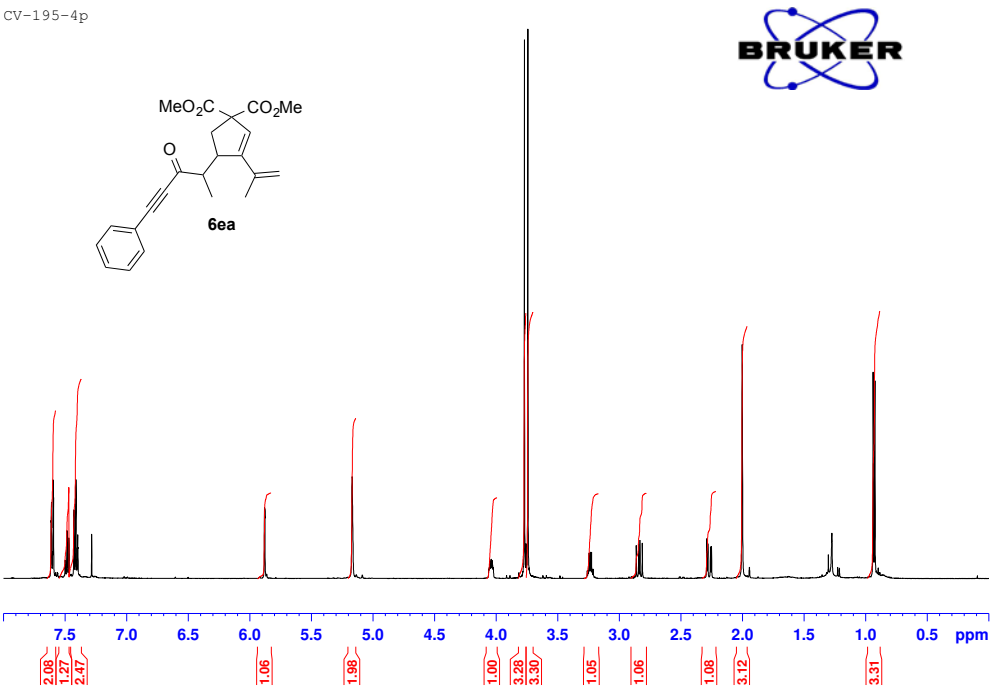

CV-187-1p
186.95
171.90
171.88
150.68
133.08
131.24
130.74
128.64
128.24
121.42
119.97
91.05
88.00
65.48
52.87
52.77
50.70
39.31
37.51
26.36
25.81
22.52
22.05
MeO2C
CO2Me
O
6ba
BRUKER
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

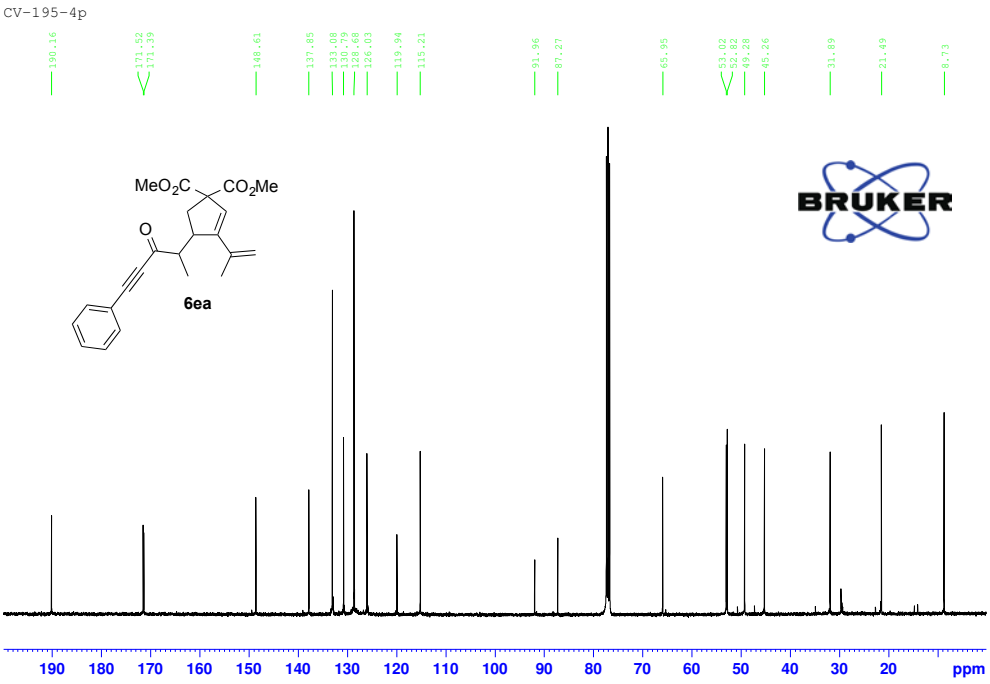

CV-191p
BRUKER
MeO2C
CO2Me
O
6ca
+
6ca'
(Z/E) = 8:1 6ca:6ca' = 2:1
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.26 1.69 3.37 0.45 1.00 1.05 0.45 0.46 9.55 1.84 0.53 1.03 1.05 1.19 1.04 0.61 0.99 1.05 3.06 3.18 1.44


CV-191p
BRUKER
MeO2C
CO2Me
O
6ca
+
6ca'
(Z/E) = 8:1 6ca:6ca' = 2:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


CV-190-1p
MeO2C
CO2Me
O
6da
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.15
1.21
2.16
1.00
1.01
1.05
2.89
3.07
1.02
1.04
0.98
1.07
3.23
3.23


CV-190-1p
185.98
171.54
153.27
137.80
133.02
130.71
128.62
125.76
120.02
115.41
90.48
88.98
63.63
54.40
52.90
48.80
45.59
26.95
23.64
MeO2C
CO2Me
O
6da
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


CV-195-4p
MeO2C
CO2Me
O
6ea
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
1.27
2.47
1.06
1.98
1.00
3.28
3.30
1.05
1.06
1.08
3.12
3.31


CV-195-4p
190.16
171.52
171.39
148.61
137.85
133.08
130.79
128.68
126.03
119.94
115.21
91.96
87.27
65.95
53.02
52.82
49.28
45.26
31.89
21.49
8.73
MeO2C
CO2Me
O
6ea
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm