Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting information

Cis-Selective Single-Cleavage Skeletal Rearrangement of 1,6-Enynes Reveals the Multifaceted Character of the Intermediates in Metal-Catalyzed Cycloisomerizations

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Contents:

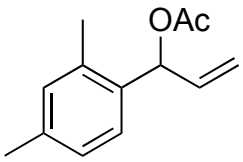
1. General Procedures

All reactions were carried out under N_2 or Ar in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck GF234). Chromatography purifications were carried out using flash grade silica gel. Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 ºC on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier spectrometer. Melting points were determined using a Buchi melting point apparatus.
Complexes **10**,[1] **11a,b**,[2] and **13**[3] were prepared according to the described procedures. Catalyst **12**[4] was prepared from the corresponding NHC-gold complex. The following compounds were previously described: 1-Cyclopropyl-2-propenyl acetate,[5] 1-cyclopentylallyl acetate,[6] ***E*-7a**,[7] **14b**,[2] **14g**,[2] **19d**,[2] and **20a**.[8]

2. General Procedure for the synthesis of allylic acetates

All allylic acetates were prepared by the reaction of the corresponding aldehydes with vinylmagnesium chloride at 0 ºC in THF to generate the allylic alcohol. For the synthesis of the acetates, acetic anhydride (2 equiv) was added to the reaction mixture at 0 °C after complete consumption of aldehyde. The reaction mixtures were stirred for 1 h, at which time conversion of allylic alcohol to allylic acetate was complete. Methanol (2 equiv) was added to quench the excess of acetic anhydride. Then a saturated NH_4Cl solution was added and the aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. Evaporation of the volatiles gave a crude oil that was chromatographed over silica gel with hexanes/EtOAc to give the desired allylic acetates.

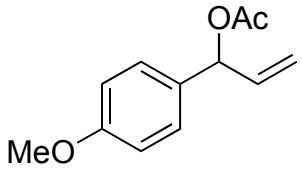
1-(2,4-Dimethylphenyl)allyl acetate (S1).



A solution of vinylmagnesium bromide (1.0 M, 3.94 mL, 3.94 mmol) was added to a cooled solution of 2,4-dimethylbenzaldehyde (0.5 mL, 3.58 mmol) in THF (10 mL) at 0 ºC. After the addition the cooling bath was removed and the mixture was let to warm to room temperature and stirred for 2 h. At that point the mixture was cooled down to 0 ºC with an ice bath and a mixture of pyridine (0.58 mL, 7.17 mmol) and acetic anhydride (0.678 mL, 7.17 mmol) was added. Finally 5 mg of DMAP were added and the mixture was stirred at room temperature for 2 h. Then methanol (0.145 mL, 3.58 mmol) was added to quench the excess of acetic anhydride. Then a saturated NH_4Cl solution was added and the aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$.

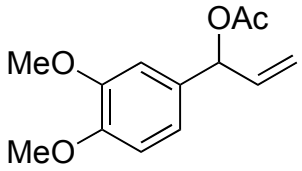
Evaporation of the volatiles gave a yellow oil that was chromatographed with 10:1 hexanes-EtOAc to give **S1** as a yellow oil (720 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.42 (d, J = 5.6 Hz, 1H), 5.99 (dddd, J = 16.9, 10.5, 5.6, 0.8 Hz, 1H), 5.25-5.15 (m, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.97, 137.76, 135.88, 135.64, 134.06, 131.32, 126.97, 126.86, 116.61, 73.36, 21.18, 21.00, 19.11; HRMS-ESI: *m/z* calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048; found 227.1039.

1-(4-Methoxyphenyl)allyl acetate (S2).[9]



A solution of vinylmagnesium bromide (1.0 M, 27.12 mL, 27.12 mmol) was added to a cooled solution of 4-methoxybenzaldexyde (3.0 mL, 24.66 mmol) in THF (75 mL) at 0 ºC. After the addition the cooling bath was removed and the mixture was let to warm to room temperature and stirred for 2 h. At that point the mixture was cooled down to 0 ºC with an ice bath and a mixture of pyridine (3.97 mL, 49.3 mmol) and acetic anhydride (4.70 mL, 49.3 mmol) was added. Finally 5 mg of DMAP were added and the mixture was stirred overnight and let to warm to room temperature slowly. After 15 h stirring, methanol (1 mL, 24.6 mmol) was added to quench the excess of acetic anhydride. Then a saturated NH_4Cl solution was added and the aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. Evaporation of the volatiles gave a yellow oil that was chromatographed with 9:1 to 4:1 hexanes-EtOAc to give **S2** as a yellow oil (4.55 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.26 (m, 2H), 6.92-6.85 (m, 2H), 6.23 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 17.1, 10.5 Hz, J = 5.6 Hz, 1H), 5.31-5.21 (two overlapping dt at 5.27 and 5.23, 2H), 3.80 (s, 3H), 2.09 (s, 3H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 170.01 (C), 159.50 (C), 136.38 (CH), 131.01 (C), 128.69 (CH), 116.46 (CH_2), 113.91 (CH), 75.80 (CH), 55.27 (CH_3), 21.26 (CH_3).

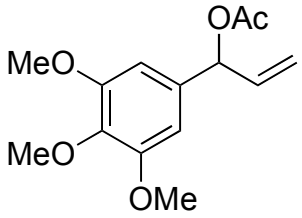
1-(3,4-Dimethoxyphenyl)allyl acetate (S3).



A solution of vinylmagnesium bromide (1.0 M, 14.14 mL, 14.14 mmol) was added to a cooled solution of 3,4-dimethoxybenzaldehyde (2.0 g, 12.04 mmol) in THF (45 mL) at 0 ºC. After the addition the cooling bath was removed and the mixture was let to warm to room temperature and stirred for 2 h. At that point the mixture was cooled down to 0 ºC with an ice bath and a mixture of pyridine (1.94 mL,

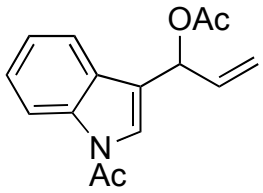
24.07 mmol) and acetic anhydride (2.28 mL, 24.07 mmol) was added. Finally 5 mg of DMAP were added and the mixture was stirred overnight and let to warm to room temperature slowly. After 15 h stirring, methanol (0.5 mL, 12.3 mmol) was added to quench the excess of acetic anhydride. Then a saturated NH_4Cl solution was added and the aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. Evaporation of the volatiles gave a yellow oil that was chromatographed over silica gel with 4:1 hexanes-EtOAc to give **S3** as a light yellow thick oil (2.02 g, 71 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (dd, J = 8.2, 1.9 Hz, 1H), 6.86 (d, J = 1.9 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.22 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 17.2, 10.5, 5.6 Hz, 1H), 5.32-5.21 (two overlapping dt, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.19, 148.52, 135.88, 130.90, 119.37, 115.84, 110.57, 110.09, 75.37, 55.28, 20.59 (several signals overlap); HRMS-ESI: *m/z* calcd for $C_{13}H_{16}O_4Na$ [M+Na]$^+$: 259.0946; found 259.0942.

1-(3,4,5-Trimethoxyphenyl)allyl acetate (S4).[10]



Starting from trimethoxybenzaldehyde and the corresponding vinyl magnesium, and following the general procedure for the synthesis of allylic acetate, **S4** was obtained in 79 % yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (s, 2H), 6.19 (d, J = 5.7 Hz, 1H), 5.99 (ddd, J = 16.9 Hz, J = 10.5 Hz, J = 5.7 Hz, 1H), 5.31 (dt, J = 16.9 Hz, J = 1.2 Hz, 1H), 5.25 (dt, J = 10.5, 1.2 Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 2.12 (s, 3H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 169.94 (C), 153.30 (C), 137.84 (C), 136.01 (CH), 134.40 (C), 116.81 (CH_2), 104.31 (CH), 76.17 (CH), 60.79 (CH_3), 56.11 (CH_3), 21.26 (CH_3).

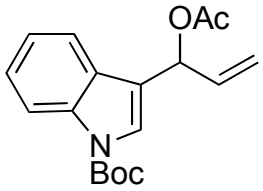
1-(1-Acetyl-1*H*-indol-3-yl)allyl acetate (S5).



A solution of vinylmagnesium bromide (1.0 M, 7.96 mL, 7.96 mmol) was added to a cooled solution of indole-3-carboxaldehyde (525 mg, 3.62 mmol) in THF (10 mL) at 0 ºC. The cooling bath was removed and the mixture was stirred at room temperature for 2 h. Acetic anhydride (1.03 mL, 10.85 mmol) and pyridine (0.874 mL, 10.85 mmol) were sequentially added at room temperature and the mixture was stirred for 2 h at room temperature. Then methanol was added (0.293 mL) and the reaction mixture was

stirred for 20 min, before extractive work-up with a saturated NH_4Cl solution and EtOAc was performed. The crude material was purified by flash chromatography with 4:1 hexanes-EtOAc to give **S5** as a yellow oil that later solidified (220 mg, 24 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.43 (s, 1H), 7.41-7.34 (m, 1H), 7.32-7.26 (m, 1H), 6.57 (d, J = 5.6 Hz, 1H), 6.15 (ddd, J = 17.1, 10.5, 5.7 Hz, 1H), 5.43 (dt, J = 17.1, 1.2 Hz, 1H), 5.34 (dt, J = 10.5 Hz, 1.2 Hz, 1H), 2.64 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.05, 168.50, 136.19, 134.66, 128.32, 125.60, 123.78, 123.73, 120.28, 119.93, 117.80, 116.75, 69.55, 23.95, 21.15; HRMS-ESI: *m/z* calcd for $C_{15}H_{15}NO_3Na$ $[M+Na]^+$: 280.0950; found 280.0951.

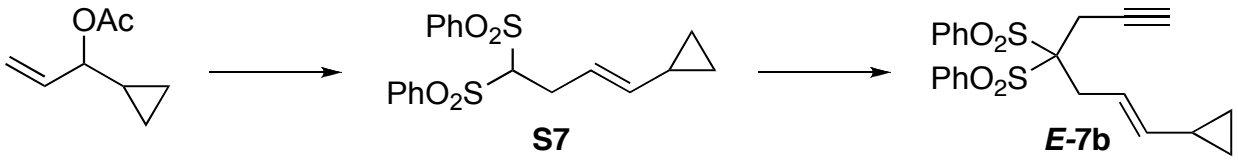
***tert*-Butyl 3-(1-acetoxyallyl)-1*H*-indole-1-carboxylate (S6).**



Starting from *N*-Boc-1*H*-indole-3-carboxaldehyde[11] and the corresponding vinyl magnesium, and following the general procedure for the synthesis of allylic acetate, **S6** was obtained in 79 % yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.57 (s, 1H), 7.31 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H), 7.21 (d, J = 7.3 Hz, 1H), 6.55 (d, J = 5.7 Hz, 1H), 6.14 (ddd, J = 17.2, 10.4, 5.7 Hz, 1H), 5.39 (dt, J = 17.2, 1.5, Hz, 1H), 5.29 (dt, J = 10.4, 1.5 Hz, 1H), 2.09 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.11, 149.52, 135.76, 134.88, 128.38, 124.67, 124.47, 122.70, 119.96, 118.43, 117.49, 115.37, 83.96, 69.72, 28.28, 28.16, 21.18; HRMS-ESI: *m/z* calcd for $C_{18}H_{21}NO_4Na$ $[M+Na]^+$: 338.1368; found 338.1354.

3. Procedure for the cross coupling

(*E*)-4-Cyclopropyl-1-(phenylsulfonyl)-1-(2-propynyl)-3-butenyl phenylsulfone *E*-7b



(*E*)-4-Cyclopropyl-3-butenylbis(phenylsulfonyl)methane (S7).

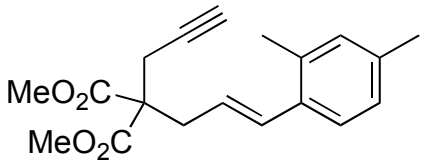
To a stirred solution of $[Pd(PPh_3)_4]$ (346 mg, 0.30 mmol, 5 mol%) in THF (50 mL) was added a solution of 1-cyclopropyl-2-propenyl acetate (840 mg, 5.99 mmol) in THF (50 mL) and the resulting solution was stirred at room temperature for 15 min before adding a solution of bis bis(phenylsulfonyl)methane (1.86 g, 6.29 mmol, 1.05 equiv) in THF (20 mL). After 16 h at room temperature the solvent was evaporated. Purification by flash chromatography (70:30 hexanes-EtOAc) afforded **S7** as a white solid (444 mg, 19 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, J = 7.6 Hz, 4H), 7.69 (t, J = 7.3 Hz, 2H), 7.57 (t, J = 7.6 Hz, 4H), 5.38 (dt, J = 15.2, 7.1 Hz, 1H), 4.90 (dd, J =

8.8, 15.2 Hz, 1H), 4.43 (t, J = 5.9 Hz, 1H), 2.88-2.84 (m, 1H), 1.28-1.20 (m, 1H), 0.68-0.63 (m, 2H), 0.29-0.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, PENDANT): δ = 139.07 (CH), 138.06 (C), 134.51 (CH), 129.66 (CH), 129.03 (CH), 120.98 (C), 84.04 (CH), 28.88 (CH_2), 13.43 (CH), 6.58 (CH_2); HRMS-ESI: *m/z* calcd for $C_{19}H_{20}O_4NaS_2$ [M+Na]$^+$: 399.0701; found: 399.0701.

(*E*)-4-Cyclopropyl-1-(phenylsulfonyl)-1-(2-propynyl)-3-butenyl phenylsulfone (*E*-7b).

To a stirred solution **S7** (423 mg, 1.01 mmol) in dry DMF (5 mL) at 0 ºC was added portion-wise NaH (60 % in mineral oil, 44.9 mg, 1.12 equiv). The flask was then sonicated for *ca.* 2 min after which it was stirred for 30 min at room temperature. Propargyl bromide (125 μL, 1.12 mmol, 1.12 equiv) was added to the reaction, which was further stirred overnight at room temperature. The mixture was partitioned between water and Et_2O. The organic phase was washed (3 x 2 mL of 10 % HCl), dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by flash chromatography (80:20 to 70:30 hexanes/EtOAc) afforded ***E*-7b** as a yellowish oil. The product was precipitated with a mixture hexane/EtOAc to give pure sulfone as a white powder (200 mg, 48 % yield), mp = 141-142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13-8.11 (m, 4H), 7.73-7.69 (m, 2H), 7.60-7.55 (m, 4H), 5.68 (dt, J = 15.1, 7.1 Hz, 1H), 5.17 (dd, J = 8.9, 15.1 Hz, 1H), 3.16 (d, J = 2.6 Hz, 2H), 3.03 (dd, J = 1.0, 7.1 Hz, 2H), 2.07 (t, J = 2.6 Hz, 1H), 1.47-1.39 (m, 1H), 0.75-0.72 (m, 2H), 0.40-0.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.55 (CH), 136.67 (C), 134.69 (CH), 131.61 (CH), 128.52 (CH), 117.60 (CH), 89.12 (C), 76.03 (C), 74.16 (C), 32.27 (CH_2), 20.76 (CH_2), 13.81 (CH), 6.63 (CH_2); HRMS-CI: *m/z* calcd for $C_{22}H_{23}O_4S_2$ [M+H]$^+$: 415.1038; found: 415.1044.

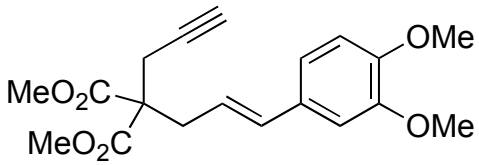
(*E*)-Dimethyl 2-(3-(2,4-dimethylphenyl)allyl)-2-(prop-2-ynyl)malonate (14a).



To a solution of acetate **S1** (300 mg, 1.47 mmol) in THF (4 mL) was added to a solution of $[Pd(PPh_3)]_4$ (127 mg, 0.11 mmol) in THF (5 mL). While the this mixture was stirred at room temperature for 20 min, a second solution was prepared in a different flask by addition of the dimethyl propargylmalonate (0.300 mg, 1.76 mmol) to a NaH (60% dispersion in mineral oil, 70.5 mg, 1.76 mmol) suspension in THF (5 mL) at 0 ºC. The anion was added over the former acetate mixture via cannula and the mixture was stirred for 2 h. The mixture was filtered through Celite and the solvent was evaporated. The crude material was chromatographed with 15:1 hexanes-EtOAc to give the enyne **14a** as a colorless oil (196 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.0 Hz, 1H), 6.97-6.92 (m, 2H), 6.70 (d, J = 15.5 Hz, 1H), 5.81 (dt, J = 15.5, 7.7 Hz, 1H), 3.76 (s, 6H), 2.98 (dd, J = 7.7, 1.2 Hz, 2H), 2.85 (d, J = 2.7 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 2.06 (t, J = 2.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ =

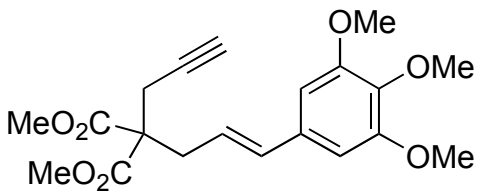
170.20, 137.19, 135.01, 133.42, 132.77, 130.90, 126.74, 125.79, 123.49, 78.84, 71.53, 57.24, 52.81, 36.09, 22.87, 21.02, 19.63; HRMS-ESI: *m/z* calcd for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1416; found 337.1407.

(*E*)-Dimethyl 2-(3-(3,4-dimethoxyphenyl)allyl)-2-(prop-2-ynyl)malonate (14c).



A solution of acetate **S3** (2.03 g, 8.57 mmol) in THF (12 mL) was added to a suspension of $[Pd(PPh_3)_2Cl_2]$ (602 mg, 0.857 mmol) and dppe (341 mg, 0.857 mmol) in THF (12 mL). A solution of the malonate anion was prepared in a different flask by addition of the dimethyl propargylmalonate (1.17 mL, 7.72 mmol) to a NaH (60% dispersion in mineral oil, 343 mg, 8.57 mmol) suspension in THF (26 mL) at 0 ºC. The anion was added over the former acetate mixture via cannula and the mixture was stirred at room temperature for 1 h. Aqueous work-up with saturated NH_4Cl and Et_2O was performed and the organic phase was dried over $MgSO_4$ and solvent evaporated. The crude material was chromatographed 3:1 with hexanes-EtOAc to give crude enyne **14c** as a yellow solid, mixed with starting material. This material was purified by trituration with Et_2O/pentane to afford **14c** as a white solid (1.14 g, 42 % yield). Mp = 93.5-95.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90-6.83 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.45 (d, J = 15.7 Hz, 1H), 5.85 (dt, J = 15.6, 7.7 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.76 (s, 6H), 2.95 (d, J = 7.7 Hz, 2H), 2.85 (d, J = 2.6 Hz, 2H), 2.06 (t, J = 2.6 Hz, 1H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 170.20 (C), 148.97 (C), 148.78 (C), 134.38 (CH), 130.10 (C), 120.93 (CH), 119.32 (CH), 111.08 (CH), 108.93 (CH), 78.88 (C), 71.58 (CH), 57.27 (C), 55.92 (CH_3), 55.88 (CH_3), 52.83 (CH_3), 35.89 (CH_2), 22.92 (CH_2); HRMS-EI: *m/z* calcd for $C_{19}H_{22}O_6$ $[M]^+$: 346.1416; found 346.1416. Anal. Calcd for: $C_{19}H_{22}O_6$ C, 65.88; H, 6.40; Found: C, 65.57; H, 6.25.

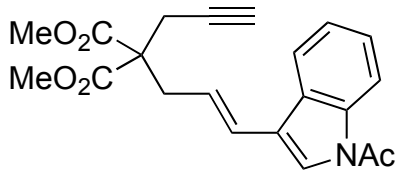
(*E*)-Dimethyl 2-(prop-2-ynyl)-2-(3-(3,4,5-trimethoxyphenyl)allyl)malonate (14d).



A solution of acetate **S4** (2.05 g, 7.70 mmol) in THF (12 mL) was added to a suspension of $PdCl_2$ (136.5 mg, 0.77 mmol) and dppe (307 mg, 0.77 mmol) in THF (12 mL). A solution of the anion of the malonate was prepared in a different flask by addition of the dimethyl propargylmalonate (1.05 mL, 6.93 mmol) to a NaH (60% dispersion in mineral oil, 277 mg, 6.93 mmol) suspension in THF (26 mL) at 0 ºC. The anion was added over the former acetate mixture via cannula and the mixture was stirred at

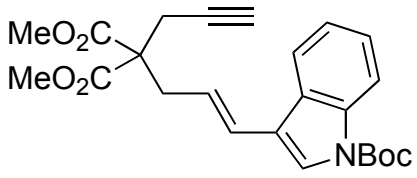
room temperature for 2 h. The mixture was filtered through a short pad of silica gel and the solvent was evaporated. The crude material was chromatographed with 3:1 hexanes-EtOAc to give **14d** as a white solid (3.54 g, 70 % yield). Mp = 123.5-125.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$); δ = 6.54 (s, 2H), 6.43 (d, J = 15.6 Hz, 1H), 5.90 (dt, J = 15.6, 7.6 Hz, 1H), 3.87 (s, 6H), 3.83 (d, 3H), 3.77 (s, 6H), 2.95 (d, J = 7.6 Hz, 2H), 2.85 (d, J = 2.1 Hz, 2H), 2.07 (m_c, 1H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 170.15 (C), 153.28 (C), 137.27 (C), 134.66 (CH), 132.69 (C), 122.43 (CH), 103.46 (CH), 78.82 (C), 71.65 (CH), 60.91 (CH_3), 57.20 (C), 56.14 (CH_3), 52.87 (CH_3), 35.86 (CH_2), 22.97 (CH_2); HRMS-EI: *m/z* calcd for $C_{20}H_{24}O_7$ $[M]^+$: 376.1522; found 376.1525. Anal. Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43; Found: C, 63.76; H, 6.29.

(*E*)-Dimethyl 2-(3-(1-acetyl-1*H*-indol-3-yl)allyl)-2-(prop-2-ynyl)malonate (14e).



A solution of acetate **S5** (200 mg, 0.777 mmol) in THF (3 mL) was added to a solution of $[Pd(PPh_3)]_4$ (67.4 mg, 0.058 mmol) in THF (3 mL). A solution of the malonate anion was prepared in a different flask by addition of the dimethyl propargylmalonate (0.142 mL, 0.933 mmol) to a NaH (60% dispersion in mineral oil, 37.3 mg, 0.933 mmol) suspension in THF (3 mL) at 0 ºC. The anion was added over the former acetate mixture via cannula and the mixture was stirred at room temperature for 24 h. Then filtration through Celite and evaporation of the solvent. The crude material was chromatographed over silica gel with 5:1 hexanes-EtOAc to give the desired enyne **14e** as a yellow solid (114 mg, 40% yield). Mp = 110.5-113.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.41-7.34 (m, 2H), 7.32 (td, J = 7.6, 1.2 Hz, 1H), 6.62 (d, J = 15.8 Hz, 1H), 6.13 (dt, J = 15.8, 7.7 Hz, 1H), 3.78 (s, 6H), 3.02 (dd, J = 7.6, 1.2 Hz, 2H), 2.89 (d, J = 2.7 Hz, 2H), 2.63 (s, 3H), 2.09 (t, J = 2.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.17, 168.39, 136.24, 128.72, 125.56, 125.35, 124.73, 123.92, 122.62, 120.17, 119.65, 116.75, 78.77, 71.73, 57.24, 52.90, 36.55, 24.03, 23.07; HRMS-ESI: *m/z* calcd for $C_{15}H_{15}NO_3Na$ $[M+Na]^+$: 390.1317; found 390.1319.

(*E*)-Dimethyl 2-(3-(1-Boc-1H-indol-3-yl)allyl)-2-(prop-2-ynyl)malonate (14f).



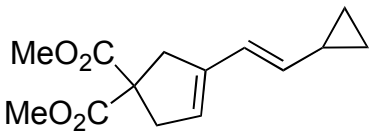
A solution of acetate **S6** (1 g, 3.17 mmol) in THF (2 mL) was added to a solution of $[Pd(PPh_3)]_4$ (183 mg, 0.016 mmol) in THF (5 mL). A solution of the malonate anion was prepared in a different flask by

addition of the dimethyl propargylmalonate (0.593 mL, 3.48 mmol) to a NaH (60% dispersion in mineral oil, 139 mg, 3.48 mmol) suspension in THF (10 mL) at 0 ºC. The anion was added over the former acetate mixture via cannula and the mixture was stirred at 50 ºC for 30 min under microwaves. After filtration through Celite and evaporation of the solvent, the crude material was chromatographed with 6:1 hexanes-EtOAc to give the enyne **14f** as a yellow solid (878 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.56 (s, 1H), 7.33 (dt, J = 7.7, 1.2 Hz, 1H), 7.27 (dt, J = 7.4, 1.2 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.08 (dt, J = 15.9, 7.6 Hz, 1H), 3.77 (s, 6H), 3.0 (dd, J = 7.6, 1.4 Hz, 2H), 2.89 (d, J = 2.7 Hz, 2H), 2.08 (t, J = 2.7 Hz, 1H), 1.67 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.43, 149.80, 128.92, 125.99, 124.84, 123.84, 123.76, 123.13, 119.99, 118.66, 117.64, 115.57, 79.09, 95.21, 71.87, 57.55, 53.08, 36.77, 28.42, 23.23; HRMS-ESI: *m/z* calcd for $C_{24}H_{27}NO_6Na$ $[M+Na]^+$: 448.1736; found 448.1719.

4. General Procedure for the Cyclizations of Table 1

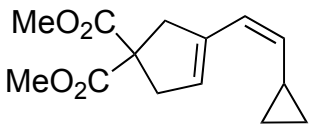
To a stirred solution of gold or metal catalyst (0.04 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was added via syringe a solution of the enyne (0.2 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL). The reaction was stirred for 5 min. The reaction was then treated with Et_3N (*ca.* 2 drops) and either passed directly through a short column (eluted with 95:5 hexanes-EtOAc) or silica was added and the crude product was purified by flash chromatography (95:5 hexanes-EtOAc). In the case of catalyzed cyclization with phosphine gold chloride catalyst, $AgSbF_6$ was employed (0.04 mol, 2 mol%) and was mixed to the gold chloride complex in CH_2Cl_2 (1 mL) before addition of the substrate solution.

(*E*)-3-(2-Cyclopropylethenyl)-3-cyclopentene-1,1-dicarboxylic acid dimethyl ester (*E*-8a)



Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.20 (d, J = 16.0 Hz, 1H), 5.38 (s, 1H), 5.05 (dd, J = 16.0, 8.9 Hz, 1H), 3.70 (s, 6H), 3.05 (s, 4H), 1.43-1.37 (m, 1H), 0.75 (ddd, J = 8.0, 6.3, 4.2 Hz, 2H), 0.42-0.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 172.50 (C), 139.27 (C), 136.26 (CH), 123.38 (CH), 122.97 (CH), 58.70 (C), 52.77 (CH_3), 40.69 (CH_2), 39.72 (CH_2), 14.14 (CH), 7.32 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 273.1103; found: 273.1112. The structure of ***E*-8a** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

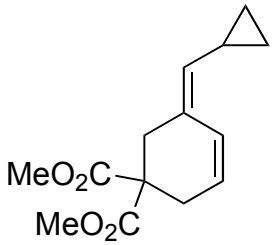
(*Z*)-3-(2-Cyclopropylethenyl)-3-cyclopentene-1,1-dicarboxylic acid dimethyl ester (*Z*-8a)



Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.85 (d, J = 11.8 Hz, 1H), 5.54-5.53 (m, 1H), 4.73 (t, J

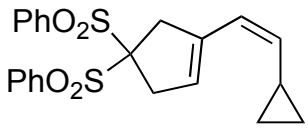
= 11.8 Hz, 1H), 3.74 (s, 6H), 3.32 (d, *J* = 1.6 Hz, 2H), 3.05 (s, 2H), 1.83-1.74 (m, 1H), 0.78 (ddd, *J* = 8.1, 6.4, 4.4, Hz, 2H), 0.40-0.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.50 (C), 138.75 (C), 136.39 (CH), 126.32 (CH), 122.40 (CH), 59.54 (C), 52.81 (CH_3), 42.92 (CH_2), 40.05 (CH_2), 11.35 (CH), 8.09 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 273.1103; found: 273.1112. The structure of ***Z*-8a** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

(*Z*)-Dimethyl 5-(cyclopropylmethylene)cyclohex-3-ene-1,1-dicarboxylate (9a)



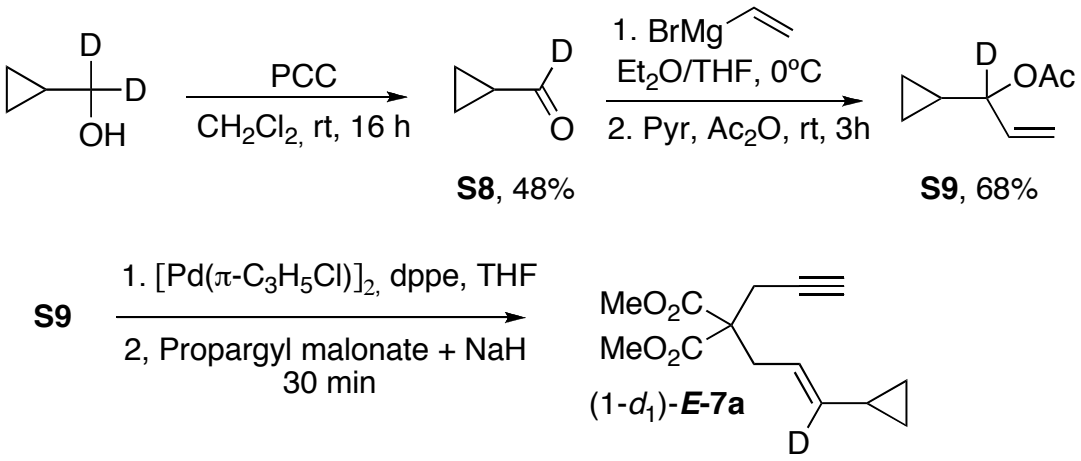
Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.54 (dd, *J* = 10.1, 0.9 Hz, 1H), 5.74 (dtd, *J* = 10.1, 4.1, 1.7 Hz, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 3.69 (s, 6H), 2.76 (d, *J* = 1.4 Hz, 2H), 2.69 (br d, *J* = 1.8 Hz, 2H), 1.64-1.57 (m, 1H), 1.64-1.57 (m, 1H), 0.74 (ddd, *J* = 7.9, 6.3, 4.2 Hz, 2H), 0.35-0.31 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.51 (C), 133.06 (CH), 127.75 (C), 124.98 (CH), 124.37 (CH), 54.01 (C), 52.64 (CH_3), 37.02 (CH_2), 31.66 (CH_2), 9.68 (CH), 7.41 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{17}O_4$ $[M-H]^+$: 249.1127; found: 249.1120.

(*Z*)-1-(3-(2-cyclopropylvinyl)-1-(phenylsulfonyl)cyclopent-3-enylsulfonyl)benzene (*E*-9b)



White solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.01 (d, *J* = 7.9 Hz, 4H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H), 5.59 (d, *J* = 11.4 Hz, 1H), 5.18 (s, 1H), 4.71 (t, *J* = 10.9 Hz, 1H), 3.63 (s, 2H), 3.35 (s, 1H), 1.51-1.41 (m, 1H), 0.79-0.74 (m, 2H), 0.37-0.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 138.35 (C), 137.80 (CH), 136.87 (C), 134.54 (CH), 130.78 (CH), 128.72 (CH), 124.55 (CH), 120.96 (CH), 91.79 (C), 40.70 (CH_2), 38.31 (CH_2), 11.33 (CH), 8.16 (CH_2); HRMS-ESI: *m/z* calcd for $C_{22}H_{22}O_4S_2Na$ $(M+Na)^+$: 437.0857; found: 437.0870.

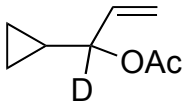
5. Deuterium labeling experiments



Cyclopropanecarbaldehyde-d_1 (S8)

To a stirred cold solution of deuterated cyclopropylmethanol[12] (4.32g, 58.3 mmol) in CH_2Cl_2 (140 mL) was added PCC (18.45g, 87.4 mmol). The reaction was let to warm up to room temperature and was stirred overnight. The mixture was filtered over a pad of neutral alumina and the alumina was rinsed with CH_2Cl_2. The solvent was carefully removed and the crude aldehyde was distilled at atmospheric pressure, T = 48-50 ºC (m = 2.8 g of aldehyde mixed with a bit of CH_2Cl_2 in about 25 % weight, Yield: 48 %) to give aldehyde **S8** as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.86-1.77 (m, 1H), 1.09-1.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 201.25 (t, J = 26.4 Hz, CD), 22.52 (t, J = 4.0 Hz, CH), 7.29 (CH_2); HRMS-EI: *m/z* calcd for C_4H_5DO [M]$^+$: 279.1960; found: 279.1955.

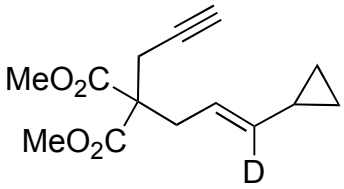
1-Cyclopropylallyl acetate 3-d_1 (S9)



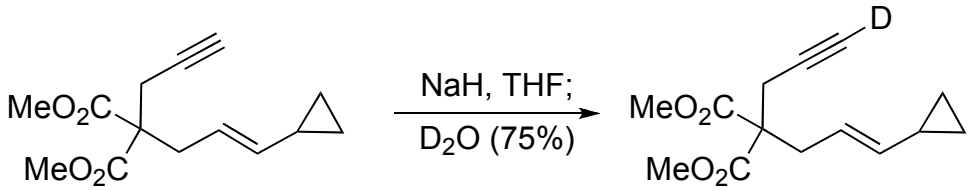
To a solution of vinylmagnesium bromide in THF (1M, 15 mL, 15 mmol) at 0 ºC was added a solution of aldehyde **S8** (1.40g, 14.4 mmol) in ether (15 mL). The reaction was left to stir for 30 min at this temperature. A mixture of Pyr/Ac_2O (2.00 mL, 18.0 mmol/1.45 mL, 18.0 mmol) was then added to the reaction flask and the reaction was warmed up to room temperature and stirred for 3 h. The reaction was quenched with MeOH (0.5 mL) and diluted with Et_2O and water. The aqueous phase was extracted with Et_2O and the combined organic layers were washed with 10% HCl solution, brine, dried ($MgSO_4$) and the solvent removed under reduced pressure carefully. Purification by flash chromatography with 95:5 Pentane-Et_2O gave labeled allylic acetate **S9** as a colorless liquid (1.39 g, 68% yield) ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.83 (dd, J = 17.3, 10.5, Hz, 1H), 5.26 (d, J = 17.3 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 2.07 (s, 6H), 1.08-1.02 (m, 1H), 0.59-0.50 (m, 2H), 0.43-0.78 (m, 1H), 0.33-0.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.39 (C), 135.53 (CH), 116.48 (CH_2), 78.12 (t, J = 22.5 Hz, CD), 21.26

(CH_3), 14.46 (CH_3), 3.38 (CH_2), 2.43 (CH_2); HRMS-ESI: *m/z* calcd for $C_8H_{11}DONa$ [*M*+Na]$^+$: 164.0798; found: 164.0795.

(*E*)-Dimethyl 2-(3-cyclopropylallyl-(3-deuterium))-2-(prop-2-ynyl)malonate-1-d_1 ((1-d_1)-*E*-7a).



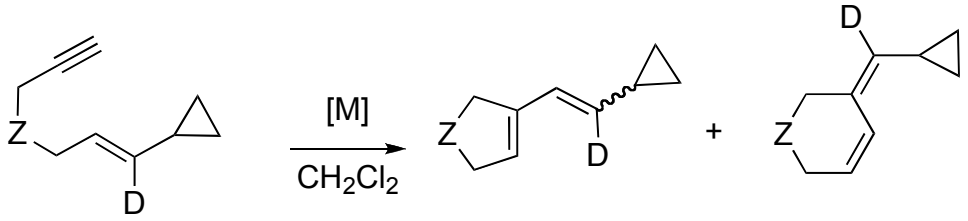
THF (10 mL) was added to a flask containing [Pd(π-C_3H_5)Cl]$_2$ (35.0 mg, 0.096 mmol) and dppe (76.3 mg, 0.192 mmol). The resulting yellow solution was stirred during 30 min. During the meantime dimethylpropargyl malonate (583 μL, 3.83 mmol) was added slowly to a stirred suspension of NaH (60% dispersion in mineral oil, 153.2 mg, 3.83 mmol) in THF (10 mL) cooled at 0 ºC. The resulting solution was left to reach room temperature slowly. A solution of allylic acetate **S9** (540.9 mg, 3.83 mmol) in THF (6 mL) was added to the solution containing the Pd catalyst followed by the addition of the nucleophile. The resulting mixture was stirred at room temperature for 1 h and then it was partitioned between water and EtOAc. The aqueous phase was extracted with EtOAc, the combined organic phases were dried and the solvent evaporated under reduced pressure. Purification by flash chromatography with 95:5 hexanes-EtOAc gave labeled enyne **(1-d_1)-*E*-7a** as a colorless oil (526.7 mg, 55% yield) mixed with 5% in weight of the undesired product coming from the addition of the nucleophile to the π-allyl Pd complex to the other position. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.26 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 6H), 2.78 (d, *J* = 2.7 Hz, 2H), 2.72 (d, *J* = 7.5 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.36-1.29 (m, 1H), 0.68-0.63 (m, 2H), 0.33-0.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.29 (C), 139.36 (t, *J*= 22.5 Hz, CD), 119.95 (CH), 78.96 (C), 71.27 (CH), 57.21 (C), 52.66 (CH_3), 35.17 (CH_2), 22.57 (CH_2), 13.49 (CH), 6.60 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{17}O_4NaD$ [*M*+Na]$^+$: 274.1166; found: 274.1163.



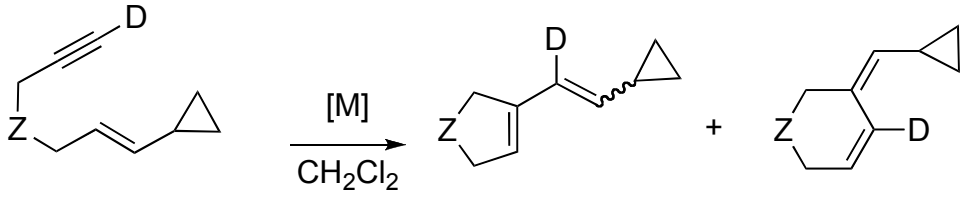
E-**7a** *E*-**7a**-**7d_1**

(*E*)-Dimethyl 2-(3-cyclopropylallyl-2-(prop-2-ynyl)malonate-7-d_1 ((7-d_1)-*E*-7a).

^{1}H NMR ($CDCl_3$, 400 MHz), δ 5.28 (dt, *J* = 15.1, 7.6 Hz, 1H), 5.11 (dd, *J* = 15.1, 8.4 Hz, 1H), 3.73 (s, 6H), 2.78 (s, 2H), 2.72 (d, *J* = 7.6 Hz, 2H), 1.36-1.30 (m, 1H), 0.68-0.68-0.63 (m, 2H), 0.33-0.29 (m, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.29 (C), 139.72 (CH), 120.08 (CH), 71.03 (t, *J* = 38.1 Hz, CD), 57.21 (C), 52.67 (CH_3), 35.2 2 (CH_2), 22.54 (CH_2), 13.60 (CH), 6.62 (CH_2).



(1-d_1)-***E*-7a** (1-d_1)-*E*-**8a** / (1-d_1)-*Z*-**8a** (1-d_1)-**9a**



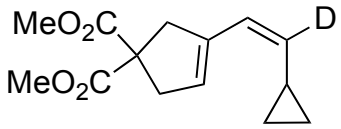
(7-d_1)-***E*-7a** (2-d_1)-*E*-**8a** / (2-d_1)-*Z*-**8a** (3-d_1)-**9a**

***Table S1*:** Deuteration experiments.[a]

entry	enyne	[M]	Yield [%]	*Z*-**8**/*E*-**8**/**9**
1	1-d_1-***E*-7a**	AuCl	85	83: <u>9</u> : 8
2	1-d_1-***E*-7a**	[Au(*o*Tol$_3$P)Cl] / $AgSbF_6$	91	<u>≥95</u> : - : -
3	7-d_1-***E*-7a**	**10a** / $AgSbF_6$	91	78 : 11 : 11

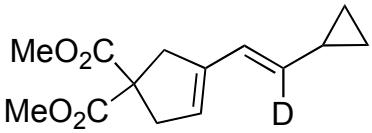
[a] in CH_2Cl_2, at room temperature for 5 min.

(*Z*)-Dimethyl 3-(2-cyclopropylvinyl)cyclopenten-3-1,1-dicarboxylate-1d_1 ((1-d_1)-*Z*-8a)



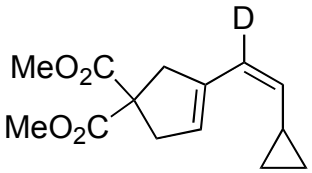
Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.86 (s, 1H), 5.55 (s, 1H), 3.75 (s, 6H), 3.34 (br s, 2H), 3.06 (br s, 2H), δ 1.85-1.75 (m, 1H), 0.81-0.79 (m, 2H), 0.40-0.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 172.53 (C), 138.76 (C), 136.04 (t, J = 23.4 Hz, CD), 126.32 (CH), 122.27 (CH), 59.56 (C), 52.72 (CH_3), 42.94 (CH_2), 40.07 (CH_2), 11.28 (CH), 8.10 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{17}O_4NaD$ [M+Na]$^+$: 274.1166; found: 274.1159.

(*E*)-Dimethyl 3(2-cyclopropylvinyl)cyclopenten-3-1,1-dicarboxylate-1d_1 ((1-d_1)-*E*-8a)



Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.24 (s, 1H), 5.40 (s, 1H), 3.75 (s, 6H), 3.07 (s, 4H), 1.43-1.41 (m, 1H), 0.79-0.74 (m, 2H), 0.43-0.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.53 (C), 139.27 (C), 135.93 (t, J = 23.1 Hz, CD), 123.27 (CH), 122.95 (CH), 58.73 (C), 52.79 (CH_3), 40.71 (CH_2), 39.74 (CH_2), 14.06 (CH), 7.32 (CH_2); HRMS-ESI: *m/z* calcd for $C_{14}H_{17}O_4NaD$ [M+Na]$^+$: 274.1166; found: 274.1167.

(*Z*)-Dimethyl 3-(2-cyclopropylvivnyl)cyclopenten-3-1,1-dicarboxylate-2d_1 ((2-d_1)-*Z*-8a)

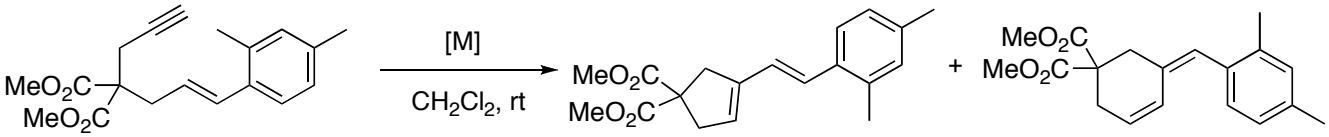


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.56 (m, 1H), 4.75 (m, 1H), 3.75 (s, 6H), 3.34 (s, 2H), 3.05 (m, 2H), 1.84-1.77 (m, 1H), 0.83-0.78 (m, 2H), 0.40-0.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.51 (C), 138.71 (C), 136.26 (CH), 126.31 (CH), 122.10 (t, J = 23.5 Hz, CD), 59.54 (C), 52.83 (CH_3), 42.91 (CH_2), 40.06 (CH_2), 11.32 (CH), 8.11 (CH_2).

6. General Procedure for the Cyclizations of Table 2

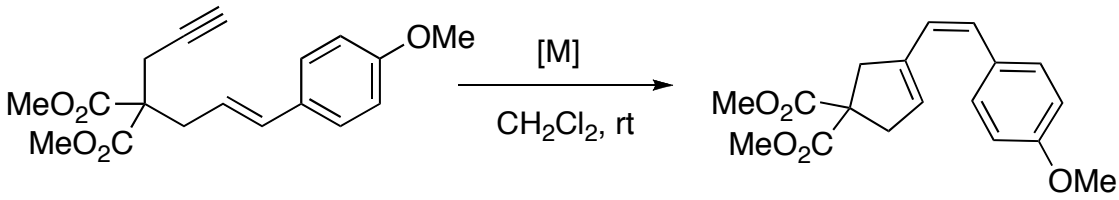
To a solution of gold cationic complex (5-15 % mol) in dry CH_2Cl_2 (0.5 mL) was added a solution of the enyne in dry CH_2Cl_2 (0.5 mL). The reaction was stirred at the stated conditions for 1-48 h. The resulting mixture was filtered through Celite and purified by chromatography (hexanes-EtOAc).

(*E*)-Dimethyl 3-(2,4-dimethylstyryl)cyclopent-3-ene-1,1-dicarboxylate (*E*-15a) and (*Z*)-Dimethyl 5-(2,4-dimethylbenzylidene)cyclohex-3-ene-1,1-dicarboxylate (16a)



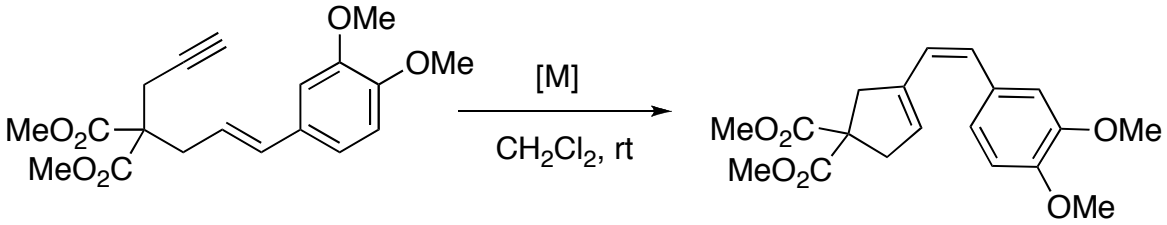
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.7 Hz, 1H), 7.02-6.92 (m, 5H), 6.77 (d, J = 16.1 Hz, 1H), 6.61 (d, J = 16.1 Hz, 1H), 6.36 (overlapping d at 6.34, J = 10.1 Hz, and s at 6.31, 2H), 5.79 (dtd, J = 10.1, 4.1, 1.7 Hz, 1H), 5.67 (m_c, 1H), 3.77 (s, 6H), 3.73 (s, 6H), 3.28 (m_c, 2H), 3.16 (s, 2H), 2.99 (d, J = 1.4 Hz, 2H), 2.76 (ddd, J = 4.0, 2.1, 0.7 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 6H), 2.19 (s, 3H). ^{13}C PENDANT (125 MHz, $CDCl_3$): δ = 172.51 (C), 171.41 (C), 140.07 (C), 137.25 (C), 136.67 (C), 136.27 (C), 135.49 (C), 133.21 (C), 133.10 (C), 131.16 (C), 131.15 (CH), 130.59 (CH), 129.77 (CH), 127.49 (CH), 127.12 (CH), 126.87 (CH), 126.79 (CH), 126.73 (CH), 125.95 (CH), 125.39 (CH), 124.99 (CH), 124.54 (CH), 58.82 (C), 54.33 (C), 52.94 (CH_3), 52.74 (CH_3), 40.97 (CH_2), 39.74 (CH_2), 37.45 (CH_2), 31.88 (CH_2), 21.07 (CH_3), 21.05 (CH_3), 19.83 (CH_3), 19.72 (CH_3); HRMS-ESI: *m/z* calcd for $C_{19}H_{23}O_4$ [M+H]$^+$: 315.1596; found 315.1600.

(*Z*)-Dimethyl 3-(4-methoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (*Z*-15b)



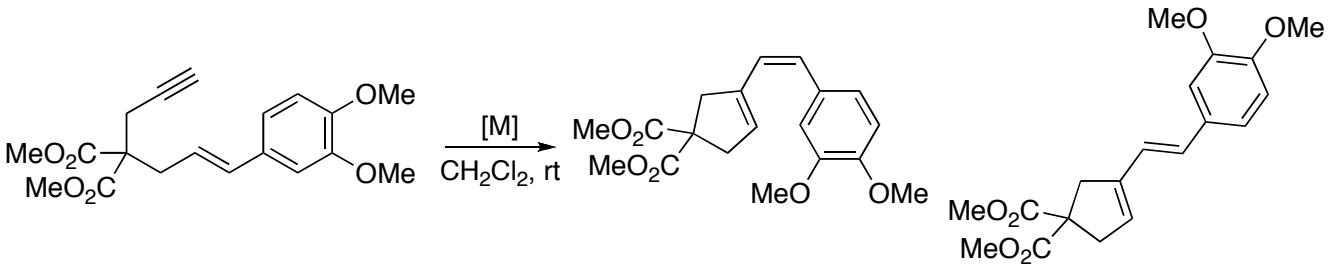
Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 12.0 Hz, 1 H), 6.14 (d, J = 12.0 Hz, 1H), 5.63 (br s, 1H), 3.81 (s, 3H), 3.70 (s, 6H), 3.02 (br s, 2 H), 2.86 (br s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.32, 158.77, 138.42, 130.19, 130.08, 128.41, 124.82, 133.35, 59.34, 55.41, 52.92, 42.13, 40.31; HRMS-ESI: m/z calcd for $C_{18}H_{20}O_5$ $[M]^+$: 339.1208; found 339.1222. The structure of ***Z*-15b** was confirmed by HMQC, HMBC, COSY, and NOESY experiments.

(*Z*)-Dimethyl 3-(3,4-dimethoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (*Z*-15c)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84-6.73 (m, 3H), 6.43 (d, J = 12.1 Hz, 1H), 6.14 (d, J = 12.1 Hz, 1H), 5.65 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.69 (s, 6H), 3.02 (br s, 2H), 2.90 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.46, 148.23, 148.17, 138.54, 130.55, 130.10, 128.81, 124.93, 121.65, 112.04, 110.56, 59.28, 55.84, 55.78, 52.77, 41.95, 40.34; HRMS-ESI: *m/z* calcd for $C_{19}H_{22}O_6Na$ $[M+Na]^+$ 369.1314; found 369.1326.

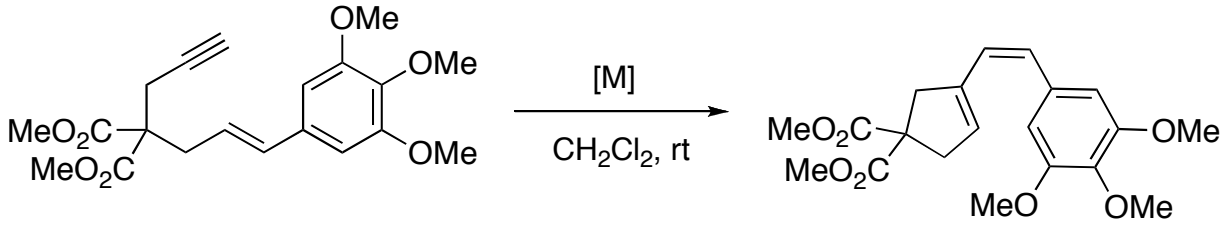
(*E*)- and (*Z*)-Dimethyl 3-(3,4-dimethoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (*E*-15c / *Z*-15c, 1/9)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (s, 1H, *trans*), 6.96 (d, J = 8.1 Hz, 1H, *trans*), 6.84-6.73 (m, 3H, *cis* and *trans*), 6.49 (d, J = 16.5 Hz, 1H, *trans*), 6.43 (d, J = 12.1 Hz, 1H, *cis*), 6.40 (d, J = 16.5 Hz, 1H, *trans*), 6.14 (d, J = 12.1 Hz, 1H, *cis*), 5.84 (br s, 1H, *trans*), 5.65 (br s, 1H, *cis*),), 3.96 (s, 3H, *trans*), 3.90 (s, 3H, *trans*), 3.89 (s, 3H, *cis*), 3.88 (s, 3H, *cis*), 3.69 (s, 6H, *cis* and *trans*), 3.25 (br s, 2H, *trans*),

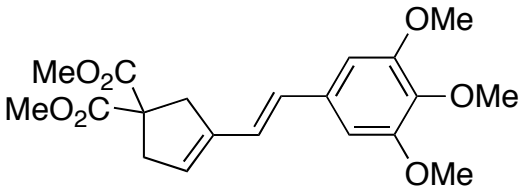
3.15 (br s, 2H, *trans*).3.02 (br s, 2H, *cis*), 2.90 (br s, 2H, *cis*). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.46 (*cis*), 171.64 (*trans*), 149.11 (*trans*), 149.04 (*trans*), 148.23 (*cis*), 148.17 (*cis*), 139.75 (*trans*), 138.54 (*cis*), 131.84 (*trans*), 130.55 (*cis*), 130.10 (*cis*), 129.80 (*trans*), 128.81 (*cis*), 126.40 (*trans*), 126.25 (*trans*), 124.93 (*cis*), 121.65 (*cis*), 119.70 (*trans*), 112.04 (*cis*), 111.13 (*trans*), 110.56 (*cis*), 108.65 (*trans*), 59.28 (*cis*), 58.90 (*trans*), 56.04 (*trans*), 55.92 (*trans*), 55.84 (*cis*), 55.78 (*cis*), 52.93 (*trans*), 52.77 (*cis*), 41.95 (*cis*), 41,00 (*trans*), 40.34 (*cis*), 39,71 (*trans*). HRMS-ESI Calcd for $C_{19}H_{22}O_6Na$ $(M+Na)^+$ 369.1314, Found 369.1302.

(*Z*)-Dimethyl 3-(3,4,5-trimethoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (*Z*-15d)



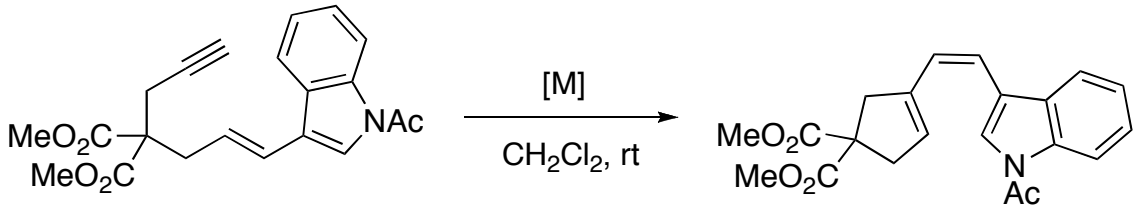
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.48 (s, 2H), 6.41 (d, J = 12.1 Hz, 1H), 6.17 (br d, J = 12.1 Hz, 1H), 5.69-5.65 (m, 1H), 3.85 (s, 3H), 3.84 (s, 6H), 3.68 (s, 6H), 3.02 (s, 2H), 2.93-2.89 (m, 2H); ^{13}C PENDANT (125 MHz, $CDCl_3$): δ = 172.43 (C), 152.68 (C), 138.36 (C), 137.17 (C), 133.36 (C), 130.15 (CH), 129.37 (CH), 125.59 (CH), 106.13 (CH), 60.94 (CH_3), 59.18 (C), 56.04 (CH_3), 52.78 (CH_3), 41.92 (CH_2), 40.38 (CH_2); HRMS-ESI: *m/z* calcd for $C_{20}H_{24}O_7Na$ $[M+Na]^+$: 399.1420; found 399.1418.

(*E*)-Dimethyl 3-(3,4,5-trimethoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (*E*-15d)



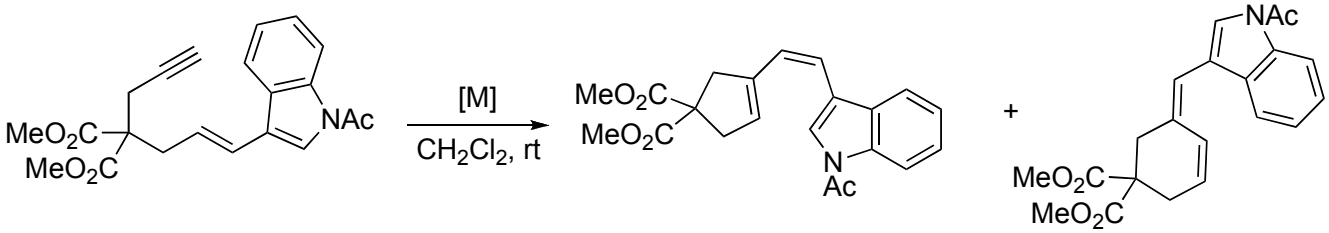
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, J = 16.1 Hz, 1H), 6.62 (s, 2H), 6.38 (d, J = 16.1 Hz, 1H), 5.70 (s, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.77 (s, 6H), 3.25 (s, 2H), 3.16 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.42, 153.34, 139.58, 137.91, 132.94, 130.00, 127.27, 123.84, 103.45, 60.94, 58.84, 56.08, 52.95, 41.03, 39.68; HRMS-ESI: *m/z c*alcd for $C_{20}H_{24}O_7Na$ $[M+Na]^+$: 399.1420; found 399.1418.

(*Z*)-Dimethyl 3-(2-(1-acetyl-1*H*-indol-3-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (*Z*-15e)



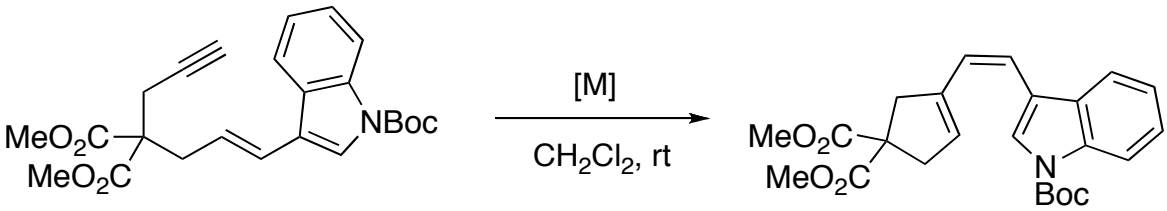
Yellow solid. Mp = 90-95 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.46 (s, 1H), 7.37 (td, J = 7.4, 1.2 Hz, 1H), 7.29 (td, J = 7.3, 1.1 Hz, 1H), 6.42 (part A of an AB system, J = 12.3 Hz, 1H), 6.40 (part B of an AB system, J = 12.2 Hz, 1H), 5.74-5.71 (m, 1H), 3.67 (s, 6H), 3.05 (m_c, 2H), 2.99 (m_c, 2H), 2.69 (s, 3H); ^{13}C PENDANT (125 MHz, $CDCl_3$) δ = 172.37 (C), 168.93 (C), 138.69 (C), 135.36 (C), 130.33 (C), 130.08 (CH), 127.58 (CH), 125.37 (CH), 124.08 (CH), 123.73 (CH), 119.57 (CH), 119.40 (CH), 119.18 (C), 116.62 (CH), 59.19 (C), 52.81 (CH_3), 41.18 (CH_2), 40.20 (CH_2), 23.98 (CH_3); HRMS-ESI: *m/z* calcd for $C_{15}H_{15}NO_3Na$ $[M+Na]^+$: 390.1317; found 390.1305.

(*E*)- and (*Z*)-dimethyl 3-(2-(1-acetyl-1H-indol-3-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate. (*Z*-15e / 16,e 4/1)



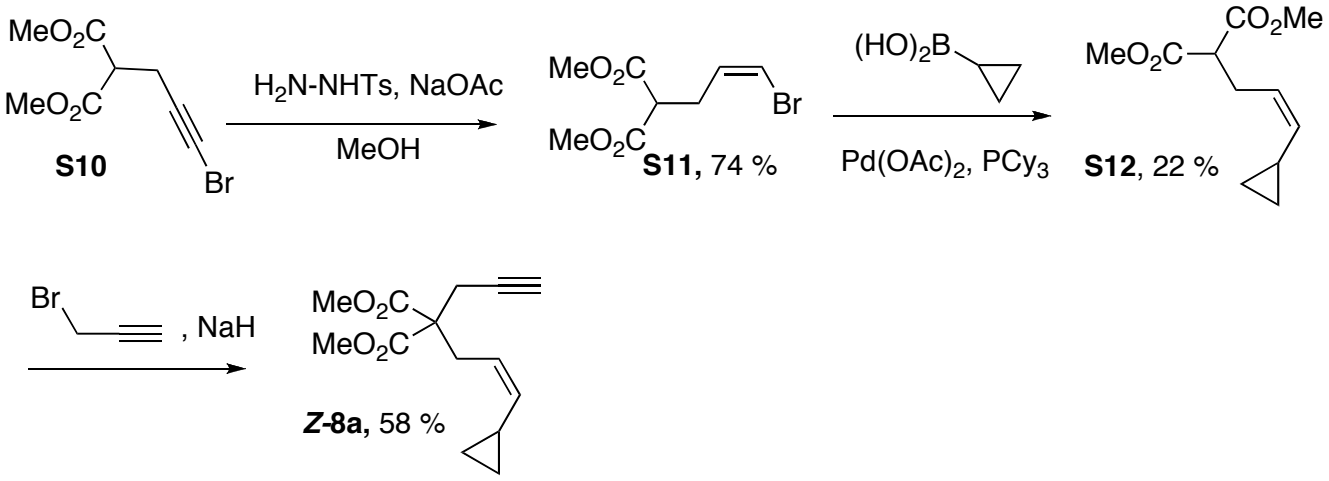
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 8.2 Hz, 1H, *Z-15e*), 8.42 (d, J = 8.2 Hz, 1H, 16e), 7.54-7.46 (m, H_{arom} of both compounds, 2H), 7.39-7.37 (m, H_{arom} of both compounds, 2H), 7.32-7.27 m, H_{arom} of both compounds, 2H), 6.63 (dt, J = 10.1, 2 Hz, 1H, 16e), 6.42 (part A of an AB system, J = 12.3 Hz, 1H, *Z-15e*), 6.40 (part B of an AB system, J = 12.2 Hz, 1H, *Z-15e*), 6.32 (s, 1H, 16e), 5.93 (dtd, J = 10.1, 4.1, 2.0 Hz, 1H, 16e), 5.74-5.71 (m, 1H, *Z-15e*), 3.78 (s, 6H, 16e), 3.67 (s, 6H, *Z-15e*), 3.05 (m_c, 4H, *Z-15e* , 16e), 2.99 (m_c, 2H, *Z-15e*), 2.80 (m_c, 2H, 16e), 2.69 (s, 3H, *Z-15e*), 2.64 (s, 3H, 16e);. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.37(C, 16e), 171.27 (C, 16e), (C, *Z-15e*), 168.93 (C, *Z-15e*), 168.44 (C, 16e), 138.69 (C, *Z-15e*), 135.36 (C, *Z-15e*), 135.36 (C, 16e), 130.33 (C, *Z-15e*), 130.08 (CH, *Z-15e*), 128.43 (CH, 16e), 127.58 (CH, *Z-15e*), 125.37 (CH, *Z-15e*), 125.49 (CH, 16e), 124.08 (CH, *Z-15e*), 123.73 (CH, *Z-15e*), 123.72 (CH, 16e), 123.09 (CH, 16e), 119.57 (CH, *Z-15e*), 119.40 (CH, *Z-15e*), 119.29 (C, 16e), 119.18 (C, *Z-15e*), 119.17 (CH, 16e), 116.62 (CH, *Z-15e*), 116.58 (C, 16e), 65.83 (C, 16e), 54.23 (C, 16e), 52.88 (CH_3, 16e), 52.81 (CH_3, *Z-15e*), 41.18 (CH_2, *Z-15e*), 40.20 (CH_2, *Z-15e*), 37.61 (C, 16e), 31.84 (CH_2, 16e), 29.68 (CH_2, 16e), 24.12 (CH_3, 16e), 23.98 (CH_3, *Z-15e*).

(*Z*)-Dimethyl 3-(2-(1-acetyl-1H-indol-3-yl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (*Z*-15e)

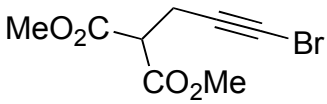


Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.3 Hz, 1H), 7.53 (s, 1H), 7.45 (d, J = 7.9, 1H), 7.32 (td, J = 7.8, 1.2 Hz, 1H), 7.23 (td, J = 7.8, 1.2 Hz, 1H), 6.41 (part A of an AB system, J = 12.5 Hz, 1H), 6.35 (part B of an AB system, J = 12.5 Hz, 1H), 5.71-5.68 (m, 1H), 3.65 (s, 6H), 3.02 (m_c, 2H), 2.96 (m_c, 2H), 1.68 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.33 (C), 138.81 (C), 130.35 (C), 129.73 (CH), 127.46 (CH), 124.58 (C), 124.44 (CH), 123.20 (C), 124.29 (CH), 122.69 (CH), 119.79 (CH), 119.72 (CH), 117.64 (C), 115.11 (CH), 83.70 (C), 59.29 (C), 52.75 (CH_3), 41.47 (CH_2), 40.24 (CH_2), 28.18 (CH_3); HRMS-ESI: *m/z* calcd for $C_{24}H_{27}NO_6Na$ [M+Na]$^{+}$: 448.1701; found 448.1714.

7. Preparation of enyne *Z*-7



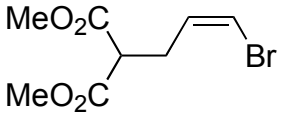
Dimethyl 2-(3-bromo-2-propargyl)malonate (S10)



In a round-bottom flask was dissolved propargyl malonate (2.0 g, 1.30 mL, 11.75 mmol) in acetone (30.0 mL). *N*-bromosuccinimide (2.30 g, 12.93 mmol, 1.1 equiv) and silver nitrate (199.6 mg, 1.17 mmol, 10 mol%) were added to the reaction mixture and it was allowed to stir at room temperature for 30 min. The reaction mixture was diluted with water and ether. The aqueous phase was extracted with Et_2O, the combined organic layers were washed with brine, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude material was purified by flash chromatography with hexanes-EtOAc

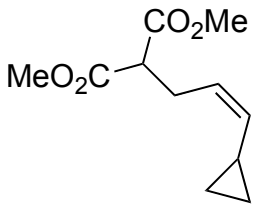
90:10 to give bromoalkyne **S10** as a colorless oil (2.17 g, 74% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.77 (s, 6H), 3.60 (t, J = 7.6 Hz, 1H), 2.81 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 168.14 (C), 75.73 (C), 52.89 (CH_3), 50.62 (CH), 40.92 (C), 19.68 (CH_2); HRMS-CI: *m/z* calcd for $C_8H_{10}O_4Br$ [*M*-H]$^+$: 248.9762; found: 248.9776.

Dimethyl 2 [(*Z*)-3-bromo-2-propenyl]malonate (S11)



A flask equipped with a condenser and a bubbler at the top was charged with alkyne **S10** (1.0 g, 4.01 mmol), tosyl hydrazine (2.24g, 12.04 mmol, 3.0 equiv) and sodium acetate (1.15 g, 14.05 mmol, 3.5 equiv). MeOH (50 mL) was added and the reaction mixture was heated up to reflux. After 9 h, ^{1}H NMR showed complete conversion. The reaction was cooled to room temperature, the solvent was evaporated and the crude product purified by flash chromatography with 9:1 hexanes-EtOAc to give *cis* alkene bromide **S11** as a colorless oil mixed with 10% of over-hydrogenated compound. (534 mg, 48% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.29 (d, J = 7.0 Hz, 1H), 6.14 (dd, J = 14.0, 7.0 Hz, 1H), 3.75 (s, 6H), 3.52 (t, J = 7.5 Hz, 1H), 2.81 (br t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 168.95 (C), 130.20 (CH), 110.79 (CH), 52.69 (CH_3), 50.17 (CH), 28.97 (CH_2); HRMS-CI: *m/z* calcd for $C_8H_{10}O_4Br$ [*M*-H]$^+$: 248.9762; found: 248.9774.

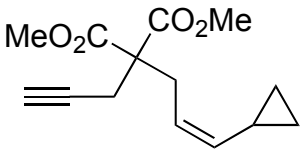
Dimethyl 2 [(*Z*)-3-cyclopropyl-2-propenyl]malonate (S12)



A flask was charged with $[Pd(OAc)_2]_3$ (66.5 mg, 5 mol%), PCy_3 (55.4 mg, 10 mol%), K_3PO_4 (1.47g, 6.91 mmol, 3.5 equiv), cyclopropyl boronic acid (220.6 mg, 2.57 mmol, 1.3 equiv) and bromoalkene **S11** (496.0 mg, 1.97 mmol, 1.0 equiv). Solvents (dry toluene 10 mL and water 0.500 mL) were added and the reaction was heated up to reflux. After 2 h at reflux, more palladium (5 mol% $[Pd(OAc)_2]_3$), more phosphine (10 mol% PCy_3), more base (K_3PO_4, 3.5 equiv) and more cyclopropylboronic acid (1.3 equiv) and water (0.050 mL) were added and the reaction was further heated at reflux for 1 h more. The reaction was partitioned between water and EtOAc. The aqueous phase was extracted with EtOAc. The combined organic layers were dried (Na_2SO_4) and solvent was evaporated. Purification by flash chromatography with 85:15 hexanes-EtOAc afforded vinylcyclopropyl derivative **S12** as a colorless oil (63.5 mg, 22% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.23 (dt, J = 10.6, 7.6 Hz, 1H), 4.83 (t, J = 10.3 Hz, 1H), 3.74 (s, 6H), 3.45 (t, J = 7.7 Hz, 1H), 2.77 (dt, J = 7.6, 1.2 Hz, 2H), 1.31-1.24 (m, 1H), 0.77-

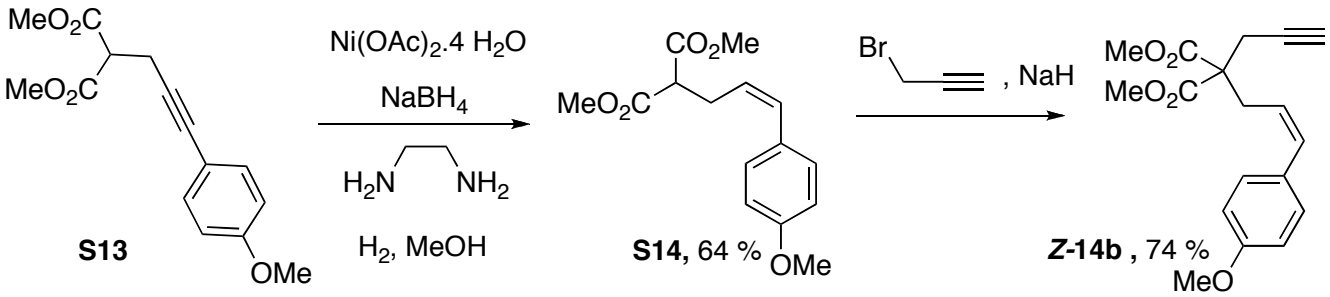
0.72 (m, 2H), 0.34-0.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 169.51 (C), 137.35 (CH), 122.46 (CH), 52.51 (CH_3), 51.89 (CH), 27.14 (CH_2), 9.58 (CH), 6.94 (CH_2).

Dimethyl 2-[(*Z*)-3-cyclopropyl-2-propenyl]-2-(2-propynyl)malonate (*Z*-8a)

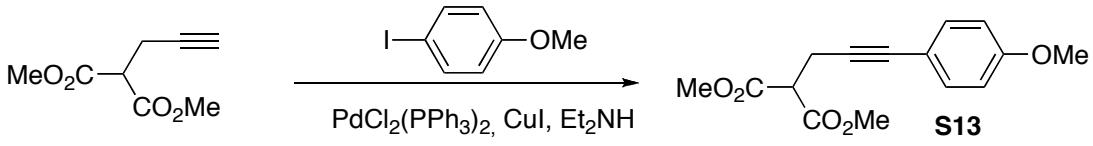


To a stirred solution of monoalkylated malonate **S12** (63.0 mg, 0.30 mmol) in DMF (1 mL) at 0 ºC was added portion wise NaH (60% in mineral oil, 11.9 mg, 1.0 equiv). The reaction was stirred at this temperature for 30 min before adding propargyl bromide (33 mL, 0.30 mmol, 1.0 equiv). The reaction was warmed to room temperature for 2 h. Then extractive work-up with Et_2O and aqueous 10% HCl was performed. The organic phase was dried (Na_2SO_4) and solvent was removed under reduced pressure. Purification by flash chromatography with 95:5 hexanes-EtOAc gave pure enyne ***Z*-8a** as a colorless oil (43mg, 58% yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ = 5.09 (dt, J = 10.4, 8.1 Hz, 1H), 4.91 (t, J = 10.4 Hz, 1H), 3.75 (s, 6H), 2.95 (d, J = 7.8 Hz, 2H), 2.84 (d, J = 2.6 Hz, 2H), 2.00 (t, J = 2.6 Hz, 1H), 1.69-1,61 (m, 1H), 0.76-0.72 (m, 2H), 0.35-0.31 (m, 2H).

8. Synthesis of enyne *Z*-14b



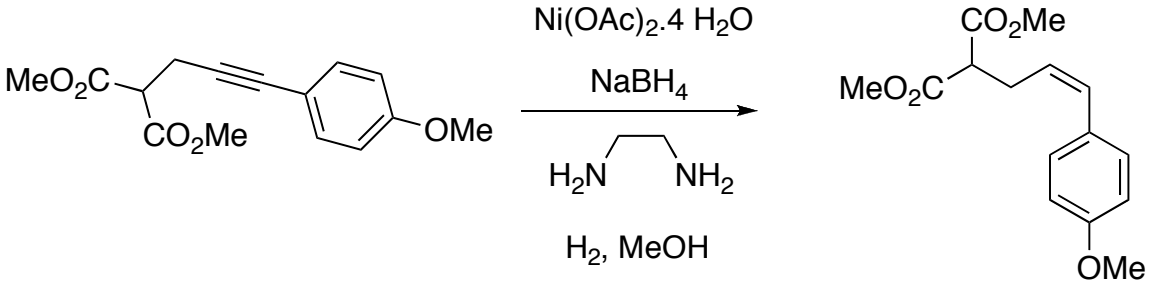
Dimethyl 2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (S13)



A Schlenk flask was charged with [$Pd(PPh_3)_2Cl_2$] (230 mg, 0.327 mmol), CuI (125 mg, 0.654 mmol), and diisopropylamine (30 mL). The mixture was stirred for 5 min at room temperature and then, dimethylpropargyl malonate (1.0 mL, 6.55 mmol) and 4-bromo-anisole (1.07 mL, 8.51 mmol) were sequentially added. The mixture turned black and was stirred at room temperature for 6 h. Then it was warmed up to 50 ºC and was stirred at that temperature overnight. After 18 h, the heating bath was removed and the mixture was let to cool to room temperature before diluting it with Et_2O. Then it was filtered through Celite and the solvents were removed under reduced pressure. The crude residue was

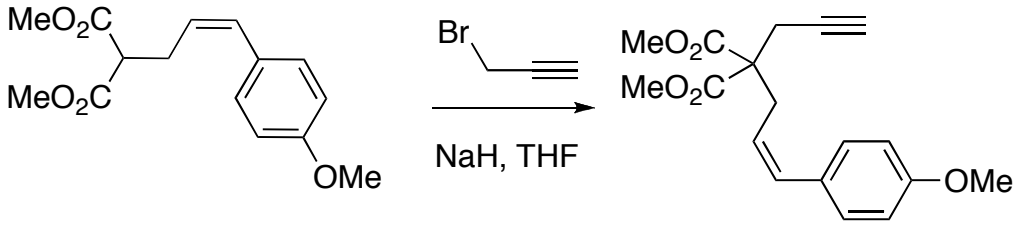
purified by column chromatography with 3:1 hexanes-EtOAc to give compound **S13** as a yellow oil (787 mg, 43% yield) contaminated with palladium. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.27 (m, 2H), 6.83-6.75 (m, 2H), 3.79 (s, 3H), 3.78 (s, 6H), 3.68 (t, J = 7.8 Hz, 1H), 2.99 (d, J = 7.8 Hz, 2H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 168.49 (C), 159.38 (C), 133.02 (CH), 115.25 (C), 113.81 (CH), 83.61 (C), 82.35 (C), 55.25 (CH_3), 52.77 (CH_3), 51.30 (CH), 19.54 (CH_2). HRMS-ESI: *m/z* calcd for $C_{15}H_{16}O_5Na$ [M+Na]$^+$: 299.0895; found 299.0889.

(*Z*)-Dimethyl 2-(3-(4-methoxyphenyl)allyl)malonate (S14)



In a Schlenk flask $Ni(OAc)_2{\cdot}H_2O$ (130 mg, 0.45 mmol) was solubilised in MeOH (4 ml). The blue-green solution was vigorously stirred and cooled to 0 ºC in an ice bath, then $NaBH_4$ powder (17 mg, 0.45 mg) was added in one portion. With the vigorous evolution of gas, the mixture turned black immediately. The ice bath was removed, and the suspension was stirred for 5 min at room temperature, then ethylenediamine (0.06 ml, 0.5 mmol) was added, and the resulting mixture was further stirred for 5 min. A solution of dimethyl 2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate **S13** (0.5 g, 1,8 mmol) in MeOH (1ml) was added to the above reaction mixture under H_2 (1 atm) and it was stirred during 24 h. The crude product is filtered over a pad of Celite, evaporated under vacuum, and purified by flash chromatography with 4:1 hexanes-EtOAc, to give alkene **S14** as a yellow oil (320 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.44 (d, J = 11.8 Hz, 1H), 5.48 (dt, J = 11.8, 7.1 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 6H), 3.48 (t, J = 7.8 Hz, 1H), 2.93 (t, J = 7.8 Hz, 2H); ^{13}C PENDANT (125 MHz, $CDCl_3$): δ = 169.27 (C), 158.57 (C), 131.48 (CH), 129.90 (CH), 129.32 (C), 125.50 (CH), 113.80 (CH), 55.13 (CH_3), 52.45 (CH_3), 51.72 (CH), 27.77 (CH_2); HRMS-ESI: *m/z* calcd for $C_{15}H_{18}O_5Na$ [M+Na]$^+$: 301.1052; found 301.1039.

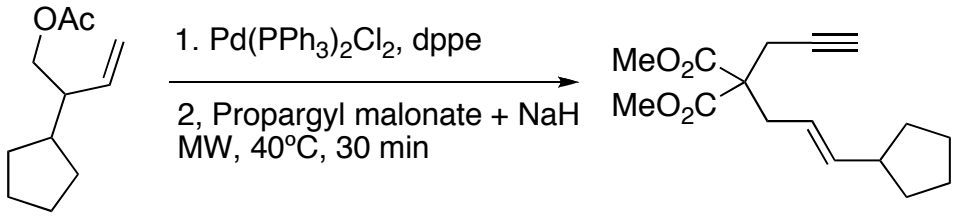
(*Z*)-Dimethyl 2-(3-(4-methoxyphenyl)allyl)-2-(prop-2-ynyl)malonate (*Z*-14b)



To a suspension of NaH (60% dispersion in mineral oil, 50 mg, 1.2 mmol) in THF (4 mL) was added the alkene (320 mg, 1.15 mmol) in THF (1 mL) at 0 ºC and stirred for 30 min. Then propargyl bromide

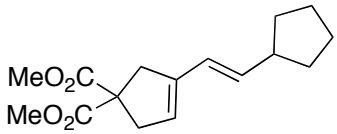
(80 % in Toluene, 0.140 mL, 1.26 mmol) was added and the mixture was stirred for 14 h. After these 14 h, completion was observed and the mixture was quenched with water at 0 ºC. The solution was extracted with EtOAc, and the organic was collected, washed with HCl (10 %), dried over $MgSO_4$, and concentrated under low pressure. The crude material was chromatographed with 8:1 hexanes-EtOAc to give the desired enyne as a yellow oil (270 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 11.7 Hz, 1H), 5.38 (dt, J = 11.7, 7.4 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 6H), 3.12 (dd, J = 7.4, 1.8 Hz, 1H), 2.83 (d, J = 2.7 Hz, 2H), 1.89 (t, J = 2.7 Hz, 1H); ^{13}C RMN (100 MHz, $CDCl_3$): δ = 170.20, 158.46, 132.46, 129.98, 129.40, 123.03, 113.58, 78.57, 71.40, 56.99, 55.20, 52.74, 30.68, 22.80; HRMS-ESI: *m/z* calcd for $C_{16}H_{22}O_5Na$ $[M+Na]^+$: 317.1389; found 317.1378

(*E*)-Dimethyl-2-(3-cyclopentylallyl)-2-(prop-2-ynyl)malonate (17)



THF (20 mL) was added to $[Pd(PPh_3)_2Cl_2]$ (90.1mg, 0.51 mmol) and dppe (202.5 mg, 0.51 mmol) and the mixture was stirred at room temperature for 20 min before adding a solution of cyclopentylallyl acetate (1.71 g, 10.16 mmol, 1.0 equiv) in THF (10 mL). In the meantime dimethylpropargyl malonate (1.62 mL, 10.67 mmol, 1.05 equiv) was added dropwise *via* syringe to a suspension of NaH (60% in mineral oil, 426.9 mg, 10.67 mmol, 1.05 equiv) in THF cooled at 0 ºC. The solution of the nucleophile was added via cannula to the solution containing the catalyst and the allylic acetate and the mixture was stirred overnight at room temperature. After 16 h, $[Pd(PPh_3)_4]$ was added (234.7 mg, 0.21 mmol, 2 mol%) and the reaction was further stirred at room temperature. After 78 h, the reaction mixture was filtered through a pad of Celite and the crude product was purified by flash chromatography 9:1 pentane-Et_2O to give enyne **23** as a colorless oil (1.06 g, 37% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.55 (dd, J = 15.1, 7.5 Hz, 1H), 5.20 (tdd, J = 15.1, 7.5, 1.0 Hz, 1H), 3.73 (s, 6H), 2.77 (d, J = 2.6 Hz, 2H), 2.73 (dd, J = 7.5, 0.5 Hz, 2H), 2.37 (sextuplet, J = 8.0 Hz, 1H), 2.00 (t, J = 2.6 Hz, 1H), 1.77-1.69 (m, 2H), 1.66-1.56 (m, 2H), 1.56-1.49 (m, 2H), 1.28-1.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 170.28 (C), 140.98 (CH), 120.59 (CH), 78.95 (C), 71.27 (CH), 57.23 (C), 52.64 (CH_3), 43.19 (CH), 35.29 (CH_2), 33.04 (CH_2), 25.06 (CH_2), 22.57 (CH_2); HRMS-ESI: *m/z* calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$: 301.1416; found: 301.1410.

(*E*)-Dimethyl 3-(2-cyclopentylvinyl)cyclopent-3-ene-1,1-dicarboxylate (18)

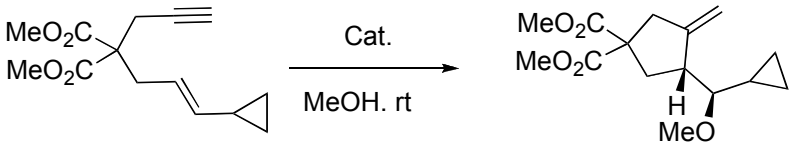


To a solution of complex **10** (2 mol %) in dry CH_2Cl_2 (0.5 mL) was added the enyne dissolved in dry CH_2Cl_2 (0.5 mL). The reaction was stirred at the stated conditions for 5 min. The resulting mixture was filtered through Celite and purified by chromatography (hexane-EtOAc) to give **18** as a colorless oil (92 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.15 (d, J = 15.6 Hz, 1H), 5.56 (dd, J = 15.1, 7.7 Hz, 1H), 5.42-5.41 (m, 1H), 3.74 (s, 6H), 3.12-3.11 (m, 2H), 3.07 (br s, 2H), 2.46 (sextuplet, J = 8.0 Hz, 1H), 1.82-1-74 (m, 2H), 1.69-1.53 (m, 4H), 1.34-1.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 172.63 (C), 139.69 (C), 137.29 (CH), 123.86 (CH), 123.77 (CH), 58.72 (C), 52.85 (CH_3), 43.59 (CH), 40.79 (CH_2), 39.92 (CH_2), 33.21 (CH_2), 25.17 (CH_2); HRMS-ESI: *m/z* calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$: 301.1416; found: 301.1418.

9. General Procedure for the Methoxycyclizations of Table 3

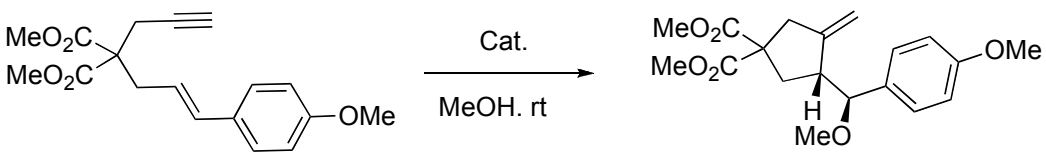
To a solution of complex **10** (2 mol %) in dry MeOH (1 mL) was added the enyne dissolved in dry MeOH (0.5 mL). The reaction was stirred at the stated conditions for 5-120 min. The resulting mixture was filtered through Celite and purified by chromatography (hexane-EtOAc).

Dimethyl 3-cyclopropyl(methoxy)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (19a)



White solid, mp = 56.5-57.5°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.00 (s, 1H), 4.87 (s, 1H), 3.72 (s, 3H), 3.37 (s, 3H), 2.99 (ddd, J = 16.0, 5.0, 2.5 Hz, 1H), 2.91-2.83 (m, 1H), 2.65 (dd, J = 8.7, 3.0 Hz, 1H), 2.55 (ddd, J = 13.3, 8.3, 1.3 Hz, 1H), 2.32 (dd, J = 13.0, 9.8 Hz, 1H), 0.82-0.78 (m, 1H), 0.67-0.64 (m, 1H), 0.48-0.41 (m, 2H), 0.09-0.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 172.34 (C), 171.91 (C), 150.04 (C), 106.89 (CH_2), 86.72 (CH), 58.88 (C), 57.93 (CH_3), 52.69 (CH_3), 52.61 (CH_3), 47.32 (CH), 41.96 (CH_2), 33.98 (CH_2), 13.03 (CH), 5.08 (CH_2), 0.81 (CH_2); HRMS-ESI: *m/z* calcd for $C_{15}H_{22}O_5Na$ $[M+Na]^+$: 305.1365; found: 305.1370.

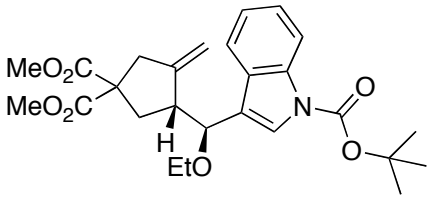
Dimethyl 3-(methoxy(4-methoxyphenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (19b *anti*)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.16 (m, 2H), 6.91-6.83 (m, 2H), 4.90 (s, 1H), 4.46 (s, 1H), 4.08 (d, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 3.17 (s, 3H), 3.01-2.92 (m, 1H), 2.92-2.83 (m, 2H), 2.49 (ddd, *J* = 13.5, 8.1, 1.4 Hz, 1H), 2.31 (dd, *J* = 13.5, 9.0 Hz, 1H); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 172.12 (C), 172.08 (C), 159.07 (C), 148.33 (C), 132.60 (C), 128.47 (CH), 113.58 (CH), 108.71 (CH_2), 85.34 (CH), 58.57 (C), 56.88 (CH_3), 55.22 (CH_3), 52.67 (CH_3), 49.26 (CH_3), 42.05 (CH_2), 35.75 (CH_2); HRMS-ESI: *m/z* calcd for $C_{19}H_{24}O_6Na$ $[M+Na]^+$: 371.1471; found 371.1471.

***anti/syn* 19b (Table 4, entry 3).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.16 (m, 4 H, H_{arom} of both diastereoisomer), 6.91-6.83 (m, 4 H, H_{arom} *of both diastereoisomer*), 5.17 (br s, 1 H, *syn*), 5.02 (br s, 1 H, *syn*), 4.90 (s, 1H, *anti*), 4.46 (s, 1H, *anti*), 4.08 (d, *J* = 6.4 Hz, 1H, *anti*), 4.00 (d, *J* = 7.6 Hz, 1 H, *syn*), 3.81 (s, 6 H, CH_3 *of both diastereoisomer*), 3.73 (s, 3H, *anti*), 3.68 (s, 6 H, CH_3 *of both diastereoisomer*), 3.67 (s, 6 H, *syn*), 3.17 (s, 3H, *anti*), 3.16 (s, 3 H, *syn*), 3.01-3.83 (m, 8 H, CH_2 *of both diastereoisomer*), 2.49 (ddd, *J* = 13.5, 8.1, 1.4 Hz, 1H, *anti*), 2.31 (dd, *J* = 13.5, 9.0 Hz, 1H, *anti*), 2.11 (ddd, *J* = 13.4, 8.2, 1.5 Hz, 1 H, *syn*), 1.74 (dd, *J* = 13.4, 9.8 Hz, 1 H, *syn*); ^{13}C PENDANT (100 MHz, $CDCl_3$): δ = 172.12 (C, *anti*), 172.08 (C, *anti*), 172.02 (C, *syn*), 171, 96 (C, *syn*), 159.17 (C, *syn*), 159.07 (C, *anti*), 148.91 (C, *syn*), 148.33 (C, *anti*), 132.60 (C, *anti*), 132.09 (C, *syn*), 128.70 (CH, *syn*), 128.47 (CH, *anti*), 113.65 (CH, *syn*), 113.58 (CH, *anti*), 109.36 (CH_2, *syn*), 108.71 (CH_2, *anti*), 86.22 (CH, *syn*), 85.34 (CH, *anti*), 58.57 (C, *anti*), 58.20 (C, *syn*), 56.88 (CH_3, *anti*), 56.28 (CH_3, *syn*), 55.22 (CH_3, *anti and syn*), 52.71 (CH_3, *syn*), 52.67 (CH_3, *anti*), 49.26 (CH_3, *anti*), 47.95 (CH_3, *syn*), 42.05 (CH_2, *anti*), 41.94 (CH_2, *syn*), 36.90 (CH_2, *syn*), 35.75 (CH_2, *anti*).

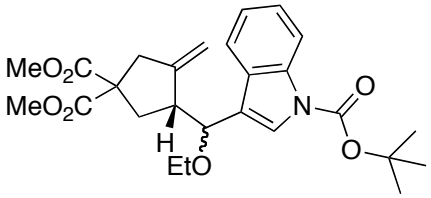
Dimethyl 3-(*N*-*tert*-Butoxycarbonyl)-1*H*-indol-3-yl)(ethoxy)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (19c-*anti*)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.48 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 4.94 (br s, 1H), 4.61 (br s, 1H), 4.53 (d, *J* = 6.2 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.5 (dq, *J* = 9.3, 7.0 Hz, 1H), 3.35 (dq, *J* = 9.3, 7.0 Hz, 1H), 3.16-3.09 (m, 1H), 3.04 (dq, *J* = 16.0, 2.5 Hz, 1H), 2.9 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.53 (part **A** of a **AB** system, ddd, *J* = 13.5, 8.5, 1.6 Hz, 1H), 2.41 (part **B** of a **AB** system, dd, *J* = 13.5, 8.5 Hz, 1H), 1.68 (s, 9H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$): δ = 172.38 (C), 172.36 (C), 149.97 (C), 148.88 (CH), 135.89 (C), 135.89 (C), 124.58 (CH), 124.02 (CH), 122.47 (CH), 121.04 (C), 120.13 (CH), 115.49 (CH), 108.90 (CH), 83.96 (C), 77.78 (CH), 65.04 (C), 58.93 (CH), 52.90 (CH_3), 52.67 (CH_3),

48.06 (CH_2), 42.30 (CH_2), 35.05 (CH_2), 28.44 (CH_3), 15.05 (CH_3). HRMS-ESI: *m/z* calcd for $C_{26}H_{33}NO_7Na$ $[M+Na]^+$ 494.2162; found 494.2155.

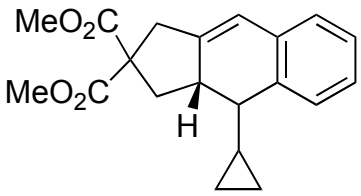
***anti/syn* 19c (Table 4, entry 4).**



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.5 Hz, 1H, *syn*), 7.78 (d, *J* = 7.4 Hz, 1H, *anti*), 7.65 (d, *J* = 7.8 Hz, 1H, *anti*), 7.49 (s, 1H, *syn*), 7.48 (s, 1H, *anti*), 7.31 (t, *J* = 7.7 Hz, 2H, *anti* and *syn*), 7.22 (d, *J* = 7.7 Hz, 2H, *anti* and *syn*), 5.34 (br s, 1H, *syn*), 5.04 (br s, 1H, *syn*), 4.94 (br s, 1H, *anti*), 4.61 (br s, 1H, *anti*), 4.53 (d, *J* = 6.2 Hz, 1H, *anti*), 4.38 (d, *J* = 8.6 Hz, 1H, *syn*), 3.74 (s, 3H, *anti*), 3.67 (s, 3H, *anti*), 3.66 (s, 3H, *syn*), 3.65 (s, 3H, *syn*), 3.55-3.24 (m, 5H, *anti* and *syn*), 3.06-2.94 (m overlapping signal, 5H, *anti* and *syn*), 2.9 (dq, *J* = 15.9, 1.43 Hz, 1H, *anti*), 2.53 (part **A** of a **AB** system, ddd, *J* = 13.5, 8.5, 1.5 Hz, 1H, *anti*), 2.41 (part **B** of a **AB** system, dd, *J* = 13.5, 8.5 Hz, 1H, *anti*), 2.16 (part **A** of a **AB** system, ddd, *J* = 13.4, 8.3, 1.2 Hz, 1H, *syn*), 1.80 (part **B** of a **AB** system, dd, *J* = 13.4, 10.0 Hz, 1H, *syn*), 1.69 (s, 9H, *syn*), 1.68 (s, 9H, *anti*), 1.14 (t, *J* = 7.0 Hz, 3H, *anti* and *syn*); ^{13}C (100 MHz, $CDCl_3$): δ = 172.38 (C *anti*), 172.36 (C *anti*), 172.27 (C *syn*), 172.11 (C *syn*), 149.97 (C, overlapping signal *anti* and *syn*), 149.44 (CH *syn*), 148.88 (CH *anti*), 136.03 (C *syn*), 135.89 (C *anti*), 124.58 (CH *anti*), 129.18 (CH *syn*), 124.69 (CH *syn*), 124.59 (CH *anti*), 124.02 (CH *anti*), 123.12 (CH *syn*), 122.81 (CH *syn*), 122.47 (CH *anti*), 121.04 (C *anti*), 120.83 (C *syn*), 120.24 (CH *syn*), 120.13 (CH *anti*), 115.49 (CH *anti*), 115.33 (CH *syn*), 109.58 (CH *syn*), 108.90 (CH *anti*), 84.01 (C *syn*), 83.96 (C *anti*), 79.12 (CH *syn*), 77.78 (CH *anti*), 65.04 (C *anti*), 64.22 (C *syn*), 58.93 (CH *anti*), 58.37 (CH *syn*), 52.96 (CH_3 *syn*), 52.90 (CH_3 *anti*), 48.06 (CH_2 *anti*), 46.72 (CH_2 *syn*), 42.30 (CH_2 *anti*), 42.11 (CH_2 *syn*), 37.41 (CH_2 *syn*), 35.05 (CH_2 *anti*), 28.44 (CH_3 *anti an syn*), 15.05 (CH_3 *anti*), 15.47 (CH_3 *syn*).

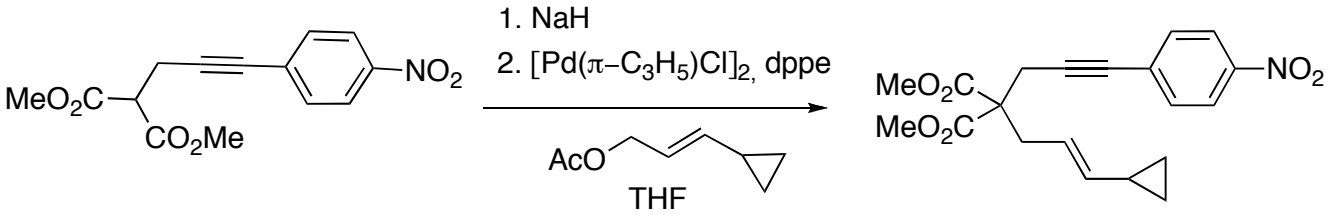
10. Procedure for the cyclizations 4+2 of Table 4

***trans*/*cis* Dimethyl 4-cyclopropyl-3a,4-dihydro-1*H*-cyclopenta[b]naphthalene-2,2(3*H*)-dicarboxylate (21a).**

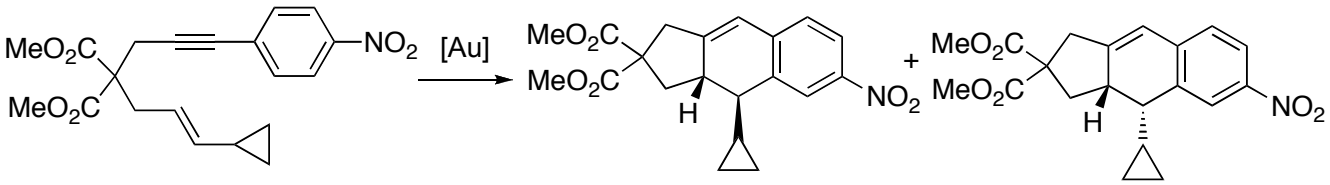


Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81-7.79 (m, 1H), 7.18-7.15 (m, 2H), 7.02-7.00 (m, 1H); 6.32 (br d, J = 2.6 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.31 (dd, J = 1.7, 18.2 Hz, 1H), 3.04 (dt, J = 2.6, 18.2 Hz, 1H), 2.97 (ddd, J = 12.7, 7.1, 1.1 Hz, 1H), 2.72-2.66 (m, 1H), 2.06 (t, J = 12.3 Hz, 1H), 1.75 (dd, J = 14.4, 9.2 Hz, 1H), 0.91-0.84 (m, 2H), 0.66-0.64 (m, 1H), 0.34-0.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 172.20 (C), 172.08 (C), 145.05 (C), 137.79 (C), 135.35 (C), 126.53 (CH), 126.41 (CH), 125.48 (CH), 125.47 (CH), 119.79 (CH), 59.22 (C), 52.83 (CH_3), 49.03 (CH), 45.29 (CH), 40.56 (CH_2), 38.23 (CH_2), 12.92 (CH), 4.74 (CH_2), 3.32 (CH_2); HRMS-ESI: *m/z* calcd for $C_{20}H_{22}O_4Na$ [*M*+Na]$^+$: 349.1416; found: 349.1411.

(*E*)-Dimethyl 2-(3-Cyclopropylallyl)-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (20b)

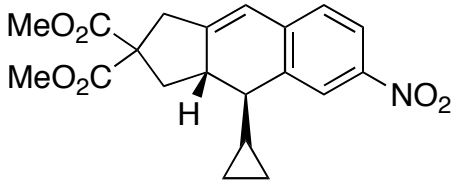


To a flask containing dry THF (18 mL) was added [Pd(π-allyl)Cl)]$_2$ (33 mg, 0,09 mmol) and dppe (71 mg, 0.18 mmol). The mixture was stirred for 30 min before adding a solution of cyclopropylallylic acetate (500 mg, 3,56 mmol) in THF (10 mL). In the meantime a suspension of NaH (60 % dispersion in mineral oil, 142 mg, 3.56 mmol) in THF (9 mL) was cooled down to 0 ºC and a solution of dimethyl-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate[13] (1038 mg, 3.56 mmol) in THF (9 mL) was added slowly via syringe. The solution of the nucleophile was added to the one containing the catalyst and the allylic acetate. The reaction was stirred at room temperature for 2 h and then it was partitioned between ether and water. The aqueous phase was extracted with Et_2O, the combined organic phases were dried and solvent was removed under reduced pressure. The crude material was purified by flash chromatography 95:5 hexanes-EtOAc to give the enyne **20b** as a yellow oil (877 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 5.33 (dt, J = 15.3, 7.6 Hz, 1H), 5.13 (dd, J = 15.3, 8.2 Hz, 1H), 3.76 (s, 6H), 3.05 (s, 2H), 2.77 (d, J = 8.2 Hz, 2H), 1.40-1.31 (m, 1H), 0.68 (ddd, J = 7.9, 6.4, 4.4 Hz, 2H), 0.32 (dt, J = 6.4, 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.46 (C), 147.15 (C), 140.13 (CH), 132.60 (CH), 123.73 (CH), 122.22 (CH), 90.86 (C), 82.12 (C), 57.64 (C), 53.23 (CH_3), 37.12 (CH_2), 23.99 (CH_2), 13.90 (CH), 6.93 (CH_2); HRMS-ESI: *m/z* calcd for $C_{20}H_{21}NO_6Na$ [*M*+Na]$^+$ 394.1267; found 394.1273.



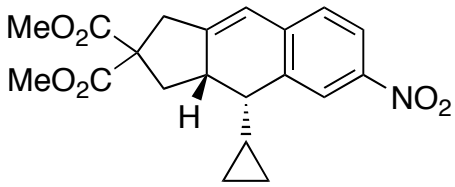
Mixture of two diastereoisomer **21b** (table 3, entry 4) has been separated by combiflash Companion® with C18 column (H_2O/MeOH).

Dimethyl (3a*R,4*R**)-4-cyclopropyl-6-nitro-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (*trans*-21b).**



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 8.05 (dd, J = 8.4, 2.4 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.41 (q, J = 2.4 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.34 (d, J = 18.8 Hz, 1H), 3.09 (dt, J = 18.8, 2.7 Hz, 1H), 3.01 (dd, J = 12.4, 7.1 Hz, 1H), 2.78-2.68 (m, 1H), 2.09 (t, J = 12.4 Hz, 1H), 1.79 (dd, J = 14.7, 9.6 Hz, 1H), 1.04-0.91 (m, 2H), 0.77-0.70 (m, 1H), 0.40-0.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.78 (C), 151.17 (C), 141.68 (C), 139.20 (C), 125.65 (CH), 122.45 (CH), 121.05 (CH), 118.95 (CH), 59.06 (C), 53.04 (CH), 53.02 (CH_3), 48.66 (CH), 45.13 (CH), 40.18 (CH_2), 38.55 (CH_2), 12.60 (CH), 4.56 (CH_2), 3.42 (CH_2); HRMS-ESI: *m/z* calcd for $C_{20}H_{21}NO_6Na$ [M+Na]$^+$: 394.1267; found 394.1267. The structure of ***trans*-21b** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

Dimethyl (3a*R,4*S**)-4-cyclopropyl-6-nitro-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (*cis*-21b).**



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, J = 8.4, 2.3 Hz, 1H), 7.9 (d, J = 2.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.45 (q, J = 2.4 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.34 (d, J = 18.9 Hz, 1H), 3.09 (dt, J = 18.9, 2.8 Hz, 1H), 3.08-3.4 (m, 1H), 2.66 (d, J = 10.6 Hz, 2H), 2.07 (dd, J = 10.1, 6.6 Hz, 1H), 0.88-0.79 (m, 1H), 0.70-0.64 (m, 1H), 0.31-0.21 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.78 (C), 149.44 (C), 140.12 (C), 139.71 (C), 126.06 (CH), 122.98 (CH), 122.58 (CH), 118.15 (CH), 59.08 (C), 52.99 (CH_3), 46.24 (CH), 42.85 (CH), 39.04 (CH_2), 36.90 (CH_2), 11.19 (CH), 7.31 (CH_2), 2.43 (CH_2); HRMS-ESI: *m/z* calcd for $C_{20}H_{21}NO_6Na$ [M+Na]$^+$: 394.1267; found 394.1281. The

structure of ***cis*-21b** was confirmed by COSY, HMQC, HMBC, and NOESY experiments.

11. Influence of solvent in the [4+2] cycloaddition with the enyne 20b

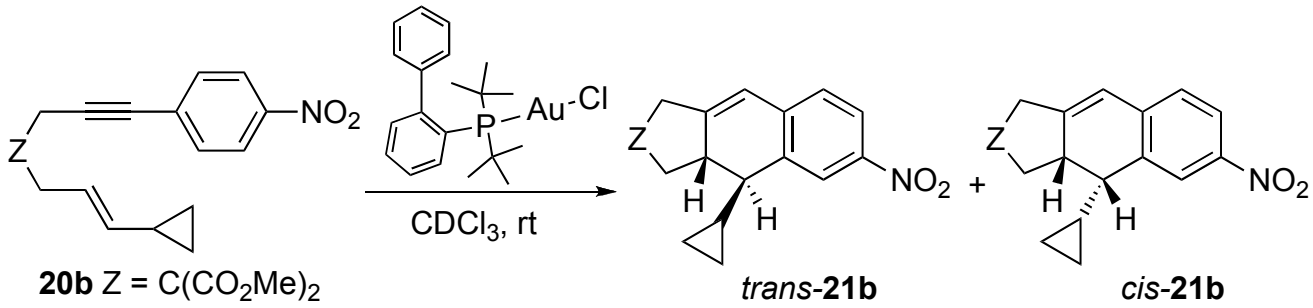


Table S2. Effect of solvent, silver counteranion, and catalyst on *cis/trans* selectivity

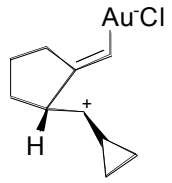
entry	[Salt]	solvent	*t*	Yield [%]	*trans*-**21b**/*cis*-**21b**[a]
1	$AgSbF_6$	CH_2Cl_2	6 h	60	28 : 72
2	$AgSbF_6$	CH_2Cl_2	10 min, MW	95	35 : 65
3	$AgPF_6$	CH_2Cl_2	6 h	88	26 : 74
4	$AgBF_4$	CH_2Cl_2	6 h	80	28 : 72
5	AgOTf	CH_2Cl_2	6 h	100	31 : 69
6	$AgAsF_6$	CH_2Cl_2	6 h	100	26 : 74
7	$AgSbF_6$	$CHCl_3$	10 min, MW	85	33 : 67
8	$AgSbF_6$	acetone	10 min, MW	50	45 : 55
9	$AgSbF_6$	toluene	10 min, MW	100	36 : 64
11	$AgSbF_6$	THF	10 min, MW	-	-

a. *trans*/*cis* ratios determined by GC and confirmed by ^{1}H NMR.

12. Computational methods

Calculations were performed with Gaussian 03 at DFT level.[15] The geometries of all complexes here reported were optimized using the B3LYP hybrid functional.[16] Optimizations were carried out using the standard 6-31G(d) basis set for C, H, O, P, and Cl. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Au.[17] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). The starting approximate geometries for the transition states (TS) were graphically located. Intrinsic reaction coordinate (IRC) studies were performed to confirm the relation of the transition states with the corresponding minima. Solvent effects were considered by performing single point calculations in CH_2Cl_2 using the polarized continuum model (PCM) on the optimized structures.

5c



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.446639	2.767723	0.523440
2	6	0	1.259186	1.834889	0.861424
3	6	0	1.522688	0.506832	0.147028
4	6	0	0.499215	-0.323104	-0.331112
5	6	0	3.006935	2.262158	-0.825300
6	6	0	2.789853	0.758844	-0.837403
7	6	0	3.007141	-0.039247	0.362596
8	17	0	-3.758955	0.083994	0.192898
9	79	0	-1.438424	-0.129027	-0.091133
10	6	0	3.068956	-2.562701	-0.607784
11	6	0	2.598179	-2.643764	0.824576
12	6	0	3.449524	-1.480346	0.374473
13	1	0	2.139470	3.815726	0.465491
14	1	0	3.219085	2.712942	1.298510
15	1	0	0.318572	2.243221	0.479367
16	1	0	1.133372	1.694991	1.940776
17	1	0	0.849388	-1.177033	-0.910886
18	1	0	2.460890	2.704035	-1.666505
19	1	0	4.067690	2.510101	-0.956944
20	1	0	2.765989	0.237418	-1.790316
21	1	0	3.415301	0.500301	1.216558
22	1	0	2.339060	-2.361268	-1.385949
23	1	0	3.859265	-3.235859	-0.928356
24	1	0	3.043974	-3.387760	1.478352
25	1	0	1.547772	-2.450288	1.026567
26	1	0	4.487986	-1.529022	0.701940

Zero-point correction= 0.217035 (Hartree/Particle)
Thermal correction to Energy= 0.229870
Thermal correction to Enthalpy= 0.230814
Thermal correction to Gibbs Free Energy= 0.174876
Sum of electronic and zero-point Energies= -984.873644

```
 Sum of electronic and thermal Energies=              -984.860810
 Sum of electronic and thermal Enthalpies=            -984.859866
 Sum of electronic and thermal Free Energies=         -984.915804

-------------------------------------------------------------------
 Variational PCM results
 =======================
 <psi(f)|   H    |psi(f)>                    (a.u.) =    -985.085005
 <psi(f)|H+V(f)/2|psi(f)>                    (a.u.) =    -985.114143
 Total free energy in solution:
  with all non electrostatic terms           (a.u.) =    -985.104313
 -------------------------------------------------------------------
 (Polarized solute)-Solvent               (kcal/mol) =     -18.28
 -------------------------------------------------------------------
 Cavitation energy                        (kcal/mol) =      20.85
 Dispersion energy                        (kcal/mol) =     -15.79
 Repulsion energy                         (kcal/mol) =       1.10
 Total non electrostatic                  (kcal/mol) =       6.17
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ts_5c

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-------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
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    3          6             0       -1.559855    0.108372    0.105238
    4          6             0       -0.373063    0.067410    0.718007
    5          6             0       -4.024685   -0.003287   -0.136610
    6          6             0       -2.838036   -0.667460    0.590657
    7          6             0       -2.808547   -2.127570    0.490092
    8         17             0        3.466805    1.773829   -0.587589
    9         79             0        1.368507    0.855035    0.081920
   10          6             0       -1.655372   -4.254415   -0.268832
   11          6             0       -1.783251   -4.392858    1.174633
   12          6             0       -1.666077   -2.933961    0.619038
   13          1             0       -4.005048    1.160071   -2.012953
   14          1             0       -3.328882   -0.465945   -2.139422
   15          1             0       -2.028490    1.985821   -0.848064
   16          1             0       -1.275042    0.823364   -1.929655
   17          1             0       -0.321923   -0.484318    1.662917
```

18	1	0	-4.342551	0.883521	0.422160
19	1	0	-4.896245	-0.661002	-0.241839
20	1	0	-2.860236	-0.495266	1.685725
21	1	0	-3.757975	-2.636486	0.302253
22	1	0	-2.520019	-4.414572	-0.904451
23	1	0	-0.691650	-4.398476	-0.747603
24	1	0	-0.918110	-4.680584	1.764591
25	1	0	-2.744010	-4.667896	1.598129
26	1	0	-0.709290	-2.437941	0.735641

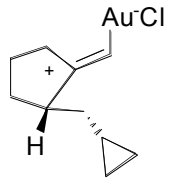
Zero-point correction= 0.212962 (Hartree/Particle)
Thermal correction to Energy= 0.226146
Thermal correction to Enthalpy= 0.227090
Thermal correction to Gibbs Free Energy= 0.169400
Sum of electronic and zero-point Energies= -984.835819
Sum of electronic and thermal Energies= -984.822636
Sum of electronic and thermal Enthalpies= -984.821692
Sum of electronic and thermal Free Energies= -984.879381

Variational PCM results
==========
<psi(f)| H |psi(f)> (a.u.) = -985.035535
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -985.098567
Total free energy in solution:
with all non electrostatic terms (a.u.) = -985.087458

(Polarized solute)-Solvent (kcal/mol) = -39.55

Cavitation energy (kcal/mol) = 21.79
Dispersion energy (kcal/mol) = -15.97
Repulsion energy (kcal/mol) = 1.15
Total non electrostatic (kcal/mol) = 6.97

5c_rot



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4	6	0	0.392828	-0.283631	-0.457727
5	6	0	2.804614	2.456427	-0.708750
6	6	0	2.591342	0.975371	-0.973690
7	6	0	2.924045	-0.022540	0.032099
8	17	0	-3.846768	-0.081987	0.290236
9	79	0	-1.533803	-0.190312	-0.102859
10	6	0	3.246031	-2.514448	0.734692
11	6	0	4.551191	-2.033574	0.159961
12	6	0	3.243026	-1.438951	-0.327071
13	1	0	2.047695	3.740655	0.907795
14	1	0	3.174547	2.505489	1.439276
15	1	0	0.222768	2.169477	0.724609
16	1	0	1.113858	1.395502	2.031191
17	1	0	0.745510	-1.063066	-1.138412
18	1	0	2.191501	3.031123	-1.412199
19	1	0	3.850677	2.742012	-0.875822
20	1	0	2.485812	0.642183	-2.002785
21	1	0	3.428193	0.329719	0.931357
22	1	0	2.995976	-2.220861	1.750922
23	1	0	2.886689	-3.501147	0.457589
24	1	0	5.095101	-2.682174	-0.520569
25	1	0	5.188535	-1.414454	0.786433
26	1	0	2.933106	-1.744123	-1.323926

Zero-point correction= 0.216719 (Hartree/Particle)
Thermal correction to Energy= 0.229714
Thermal correction to Enthalpy= 0.230659
Thermal correction to Gibbs Free Energy= 0.173902
Sum of electronic and zero-point Energies= -984.880612
Sum of electronic and thermal Energies= -984.867617

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 Sum of electronic and thermal Enthalpies=            -984.866673
 Sum of electronic and thermal Free Energies=         -984.923430

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 Variational PCM results
 =======================
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 <psi(f)|H+V(f)/2|psi(f)>                   (a.u.) =    -985.121983
 Total free energy in solution:
  with all non electrostatic terms          (a.u.) =    -985.111551
 -------------------------------------------------------------------
 (Polarized solute)-Solvent               (kcal/mol) =     -19.19
 -------------------------------------------------------------------
 Cavitation energy                        (kcal/mol) =      21.26
 Dispersion energy                        (kcal/mol) =     -15.84
 Repulsion energy                         (kcal/mol) =       1.13
 Total non electrostatic                  (kcal/mol) =       6.55
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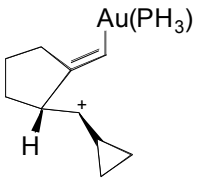
```

5d

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    4          6             0        0.442758   -0.100771   -0.615490
    5          6             0        3.312294    2.300692   -0.487682
    6          6             0        2.830438    0.891551   -0.859250
    7          6             0        3.080876   -0.202852    0.044871
    8         15             0       -3.874065   -0.179195    0.375977
    9         79             0       -1.527299   -0.115510   -0.130306
   10          6             0        2.958226   -2.723377    0.632626
   11          6             0        4.372559   -2.356102    0.408969
   12          6             0        3.249344   -1.582678   -0.345304
   13          1             0        2.533519    3.721133    0.995485
   14          1             0        3.180899    2.248388    1.691963
```

15	1	0	0.488300	2.644042	0.319245
16	1	0	0.841621	1.640727	1.722129
17	1	0	0.779965	-0.888844	-1.289982
18	1	0	2.988456	2.983264	-1.280509
19	1	0	4.403672	2.356667	-0.429470
20	1	0	2.866463	0.629580	-1.916107
21	1	0	3.252344	0.033195	1.093750
22	1	0	-4.667056	0.882995	-0.098151
23	1	0	-4.606864	-1.279974	-0.106325
24	1	0	-4.253737	-0.194240	1.731576
25	1	0	2.493186	-2.455537	1.577014
26	1	0	2.576036	-3.633843	0.180804
27	1	0	4.996251	-2.975882	-0.227480
28	1	0	4.909650	-1.822304	1.186928
29	1	0	3.160969	-1.802846	-1.404995

Zero-point correction= 0.242694
(Hartree/Particle)
Thermal correction to Energy= 0.256928
Thermal correction to Enthalpy= 0.257873
Thermal correction to Gibbs Free Energy= 0.198661
Sum of electronic and zero-point Energies= -867.580110
Sum of electronic and thermal Energies= -867.565875
Sum of electronic and thermal Enthalpies= -867.564931
Sum of electronic and thermal Free Energies= -867.624143

ts_5d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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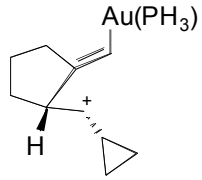
3	6	0	-1.520579	-0.000583	0.165781
4	6	0	-0.310506	0.100607	0.727134
5	6	0	-3.974411	0.067613	0.093603
6	6	0	-2.792741	-0.527336	0.893043
7	6	0	-2.860325	-2.000107	0.997299
8	15	0	3.388363	1.792296	-1.043942
9	79	0	1.378129	0.862757	-0.117409

10	6	0	-1.917462	-4.326287	0.551862
11	6	0	-2.079479	-4.230754	1.981135
12	6	0	-1.795062	-2.863083	1.213514
13	1	0	-4.019133	0.673956	-2.028486
14	1	0	-3.526071	-0.995572	-1.746348
15	1	0	-1.873598	1.533740	-1.297160
16	1	0	-1.339433	0.016955	-2.014555
17	1	0	-0.215450	-0.213017	1.770131
18	1	0	-4.134347	1.101874	0.414982
19	1	0	-4.916226	-0.473551	0.238880
20	1	0	-2.784104	-0.184218	1.945401
21	1	0	-3.851598	-2.454172	0.902513
22	1	0	3.266916	2.901018	-1.905040
23	1	0	4.350583	2.293274	-0.144781
24	1	0	4.211175	0.966835	-1.836402
25	1	0	-2.782413	-4.480396	-0.084615
26	1	0	-0.962443	-4.620502	0.126645
27	1	0	-1.249631	-4.474742	2.638216
28	1	0	-3.066726	-4.326769	2.421088
29	1	0	-0.791135	-2.459614	1.274763

Zero-point correction= 0.241098 (Hartree/Particle)
Thermal correction to Energy= 0.255709
Thermal correction to Enthalpy= 0.256653
Thermal correction to Gibbs Free Energy= 0.195254
Sum of electronic and zero-point Energies= -867.562111
Sum of electronic and thermal Energies= -867.547501
Sum of electronic and thermal Enthalpies= -867.546557
Sum of electronic and thermal Free Energies= -867.607955

5d_rot

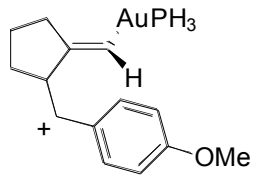


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.371216	1.372425	0.582937

2	6	0	-2.043936	0.925776	-0.079745
3	6	0	-1.071475	0.571533	1.035097
4	6	0	0.255141	0.275204	0.923241
5	6	0	-3.076479	1.563762	2.094211
6	6	0	-1.802602	0.778276	2.413251
7	6	0	-1.757600	-0.668904	2.311443
8	15	0	2.770389	0.174681	-2.721549
9	79	0	1.376059	0.222141	-0.765560
10	6	0	-2.904838	-2.911833	2.617518
11	6	0	-2.396660	-2.927118	1.228906
12	6	0	-2.784986	-1.574026	1.837427
13	1	0	-3.748546	2.298187	0.141213
14	1	0	-4.151875	0.622782	0.427128
15	1	0	-1.591498	1.741660	-0.654344
16	1	0	-2.183422	0.091990	-0.776084
17	1	0	0.778786	0.067005	1.858227
18	1	0	-2.877892	2.616338	2.317972
19	1	0	-3.912829	1.254694	2.729630
20	1	0	-1.161311	1.195986	3.187309
21	1	0	-0.894896	-1.146039	2.769449
22	1	0	2.947293	1.386290	-3.415972
23	1	0	4.110018	-0.220440	-2.547889
24	1	0	2.387626	-0.672189	-3.778910
25	1	0	-2.210237	-3.074969	3.435890
26	1	0	-3.922801	-3.230314	2.819249
27	1	0	-3.046298	-3.284775	0.435870
28	1	0	-1.337557	-3.103155	1.062831
29	1	0	-3.721151	-1.142938	1.505183

Zero-point correction= 0.243306
(Hartree/Particle)
Thermal correction to Energy= 0.258351
Thermal correction to Enthalpy= 0.259295
Thermal correction to Gibbs Free Energy= 0.197150
Sum of electronic and zero-point Energies= -867.577713
Sum of electronic and thermal Energies= -867.562669
Sum of electronic and thermal Enthalpies= -867.561725
Sum of electronic and thermal Free Energies= -867.623870

5e



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.373469	1.678559	-0.118578
2	6	0	-0.873256	4.018804	-0.398653
3	6	0	0.980980	2.405457	-0.477279
4	6	0	0.661209	3.921857	-0.315662
5	6	0	1.851473	1.838117	0.547766
6	6	0	-1.349277	2.751304	0.326576
7	6	0	-0.564159	0.356293	-0.265599
8	79	0	-2.312002	-0.658428	-0.049021
9	15	0	-4.356316	-1.893193	0.185186
10	6	0	4.531245	-0.535313	1.501878
11	6	0	3.522236	0.387748	1.584961
12	6	0	2.855150	0.870480	0.411955
13	6	0	3.273850	0.352084	-0.851401
14	6	0	4.285058	-0.577619	-0.945731
15	6	0	4.928802	-1.033211	0.233112
16	8	0	5.914245	-1.920877	0.254519
17	6	0	6.410767	-2.496372	-0.967170
18	1	0	-1.198774	3.995161	-1.445379
19	1	0	-1.253438	4.942124	0.047607
20	1	0	1.289348	2.161901	-1.495812
21	1	0	1.004011	4.275515	0.664347
22	1	0	1.181467	4.515362	-1.072569
23	1	0	1.651416	2.183448	1.562027
24	1	0	-1.294932	2.894616	1.416045
25	1	0	-2.377929	2.460314	0.093420
26	1	0	0.304155	-0.239643	-0.554550
27	1	0	-4.307525	-3.289504	0.004446
28	1	0	-5.421230	-1.575543	-0.680886
29	1	0	-5.027953	-1.834501	1.422305
30	1	0	5.045869	-0.905268	2.381890
31	1	0	3.217506	0.768134	2.555909
32	1	0	2.794717	0.698852	-1.760460
33	1	0	4.586046	-0.950882	-1.916892

34	1	0	7.203412	-3.176897	-0.659918
35	1	0	6.819260	-1.719035	-1.620119
36	1	0	5.619895	-3.052586	-1.479717

Zero-point correction= 0.294609 (Hartree/Particle)
Thermal correction to Energy= 0.313748
Thermal correction to Enthalpy= 0.314693
Thermal correction to Gibbs Free Energy= 0.242272
Sum of electronic and zero-point Energies= -1096.415864
Sum of electronic and thermal Energies= -1096.396724
Sum of electronic and thermal Enthalpies= -1096.395780
Sum of electronic and thermal Free Energies= -1096.468201

Variational PCM results
=======================
<psi(f)| H |psi(f)> (a.u.) = -1096.709019
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1096.765988
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1096.749886

(Polarized solute)-Solvent (kcal/mol) = -35.75

Cavitation energy (kcal/mol) = 29.31
Dispersion energy (kcal/mol) = -20.25
Repulsion energy (kcal/mol) = 1.04
Total non electrostatic (kcal/mol) = 10.10

ts_5e

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.351247	0.946418	-0.117251
2	6	0	0.290539	3.240976	0.264889
3	6	0	1.144867	1.094093	-0.520967
4	6	0	1.606553	2.466195	0.060488
5	6	0	1.945305	-0.114732	-0.211171
6	6	0	-0.710793	2.163307	0.713250
7	6	0	-1.133585	-0.060289	-0.518695
8	79	0	-3.101977	-0.347455	-0.096641
9	15	0	-5.429522	-0.718643	0.356054

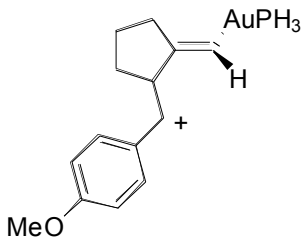
10	6	0	5.130854	-1.889195	0.346533
11	6	0	3.795622	-1.622192	0.228964
12	6	0	3.317073	-0.305763	-0.110209
13	6	0	4.298540	0.718567	-0.334691
14	6	0	5.640805	0.458278	-0.226597
15	6	0	6.077571	-0.851461	0.121892
16	8	0	7.342089	-1.201640	0.256844
17	6	0	8.408030	-0.249053	0.057666
18	1	0	-0.032757	3.678110	-0.687708
19	1	0	0.404126	4.057696	0.983829
20	1	0	1.160975	1.156998	-1.627017
21	1	0	2.106560	2.311089	1.024337
22	1	0	2.299487	3.000485	-0.596784
23	1	0	1.341541	-1.010249	-0.057807
24	1	0	-0.564765	1.946475	1.782735
25	1	0	-1.755293	2.457408	0.581370
26	1	0	-0.676392	-0.823714	-1.157403
27	1	0	-5.846700	-0.820523	1.698857
28	1	0	-6.026991	-1.885918	-0.160991
29	1	0	-6.358201	0.238409	-0.101014
30	1	0	5.502374	-2.874629	0.605177
31	1	0	3.069954	-2.412677	0.397518
32	1	0	3.974617	1.714967	-0.606803
33	1	0	6.361388	1.246413	-0.407592
34	1	0	9.323786	-0.809551	0.237293
35	1	0	8.323498	0.571868	0.775266
36	1	0	8.394328	0.128101	-0.968810

Zero-point correction= 0.293813 (Hartree/Particle)
Thermal correction to Energy= 0.312238
Thermal correction to Enthalpy= 0.313183
Thermal correction to Gibbs Free Energy= 0.243071
Sum of electronic and zero-point Energies= -1096.402902
Sum of electronic and thermal Energies= -1096.384477
Sum of electronic and thermal Enthalpies= -1096.383532
Sum of electronic and thermal Free Energies= -1096.453644

Variational PCM results
==========
<psi(f)| H |psi(f)> (a.u.) = -1096.694668
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1096.754665
Total free energy in solution:

with all non electrostatic terms	(a.u.) =	-1096.739260
(Polarized solute)-Solvent	(kcal/mol) =	-37.65
Cavitation energy	(kcal/mol) =	29.18
Dispersion energy	(kcal/mol) =	-20.58
Repulsion energy	(kcal/mol) =	1.07
Total non electrostatic	(kcal/mol) =	9.67

5e_rot



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.154957	1.400023	0.273385
2	6	0	-0.641688	2.957394	-1.415392
3	6	0	-0.890200	2.331163	0.985725
4	6	0	-1.309135	3.376852	-0.070454
5	6	0	-1.743921	1.195850	1.363225
6	6	0	-0.106286	1.522332	-1.210407
7	6	0	1.103966	0.702476	0.932019
8	79	0	2.646914	-0.351460	0.137916
9	15	0	4.514935	-1.586685	-0.726251
10	6	0	-4.431366	-1.311121	0.903224
11	6	0	-3.354091	-0.607759	1.396881
12	6	0	-2.812251	0.530989	0.725917
13	6	0	-3.425827	0.913677	-0.510340
14	6	0	-4.492484	0.213533	-1.015946
15	6	0	-5.016455	-0.905161	-0.318376
16	8	0	-6.054966	-1.500667	-0.895419
17	6	0	-6.675446	-2.639991	-0.276494
18	1	0	0.191149	3.632938	-1.632966
19	1	0	-1.330907	3.025972	-2.263055
20	1	0	-0.459878	2.779590	1.882159
21	1	0	-2.396297	3.468008	-0.139794

22	1	0	-0.945917	4.356944	0.249696
23	1	0	-1.451187	0.747742	2.311400
24	1	0	-0.848273	0.776748	-1.530607
25	1	0	0.805865	1.314865	-1.777155
26	1	0	1.067198	0.745303	2.022631
27	1	0	5.480220	-2.034471	0.196478
28	1	0	5.350519	-0.946948	-1.662662
29	1	0	4.257864	-2.789437	-1.413154
30	1	0	-4.817197	-2.163578	1.448675
31	1	0	-2.904247	-0.923537	2.334193
32	1	0	-3.055004	1.763722	-1.065344
33	1	0	-4.964642	0.497308	-1.950315
34	1	0	-7.488800	-2.920890	-0.944023
35	1	0	-7.076015	-2.374087	0.706775
36	1	0	-5.963580	-3.466802	-0.188967

Zero-point correction= 0.295247 (Hartree/Particle)
Thermal correction to Energy= 0.314259
Thermal correction to Enthalpy= 0.315204
Thermal correction to Gibbs Free Energy= 0.243237
Sum of electronic and zero-point Energies= -1096.407013
Sum of electronic and thermal Energies= -1096.388000
Sum of electronic and thermal Enthalpies= -1096.387056
Sum of electronic and thermal Free Energies= -1096.459023

Variational PCM results
==========
<psi(f)| H |psi(f)> (a.u.) = -1096.701029
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1096.756737
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1096.741227

(Polarized solute)-Solvent (kcal/mol) = -34.96

Cavitation energy (kcal/mol) = 28.68
Dispersion energy (kcal/mol) = -19.98
Repulsion energy (kcal/mol) = 1.03
Total non electrostatic (kcal/mol) = 9.73

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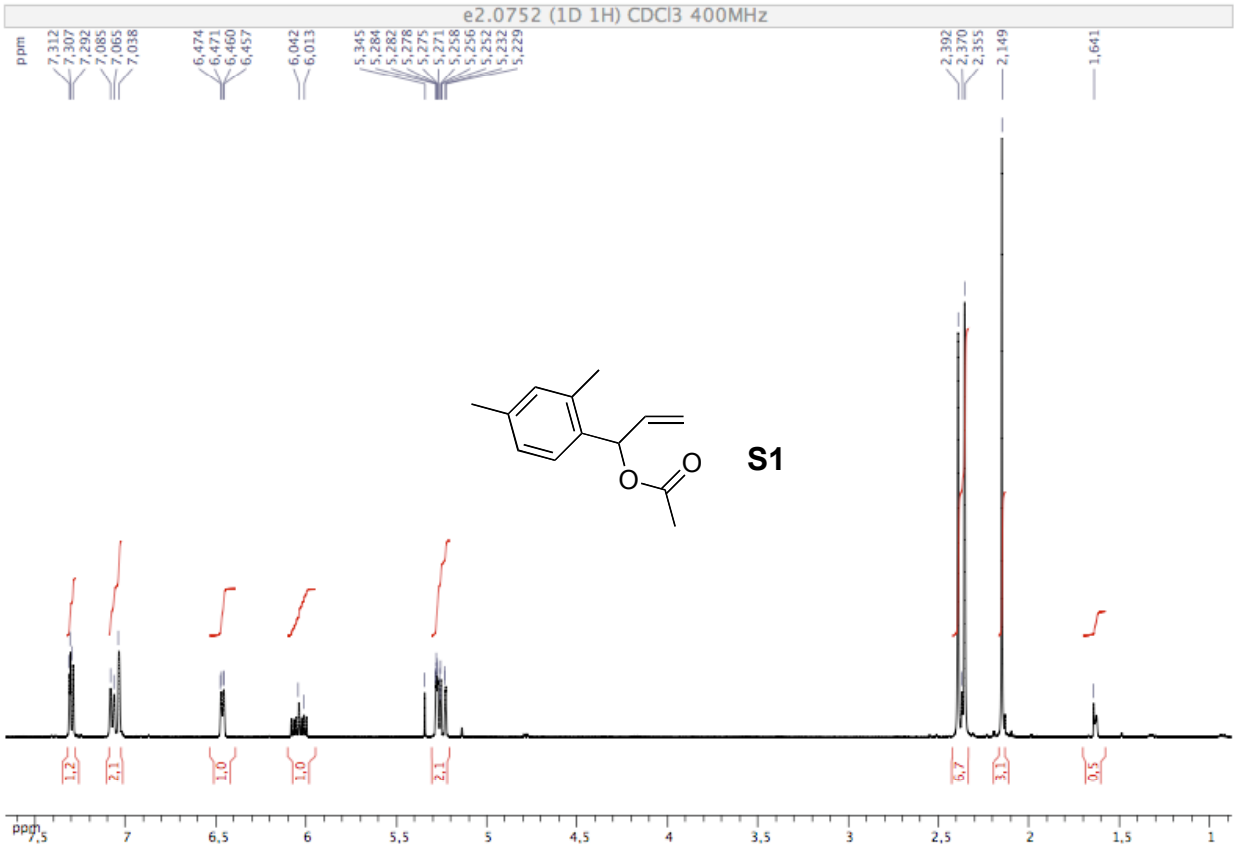
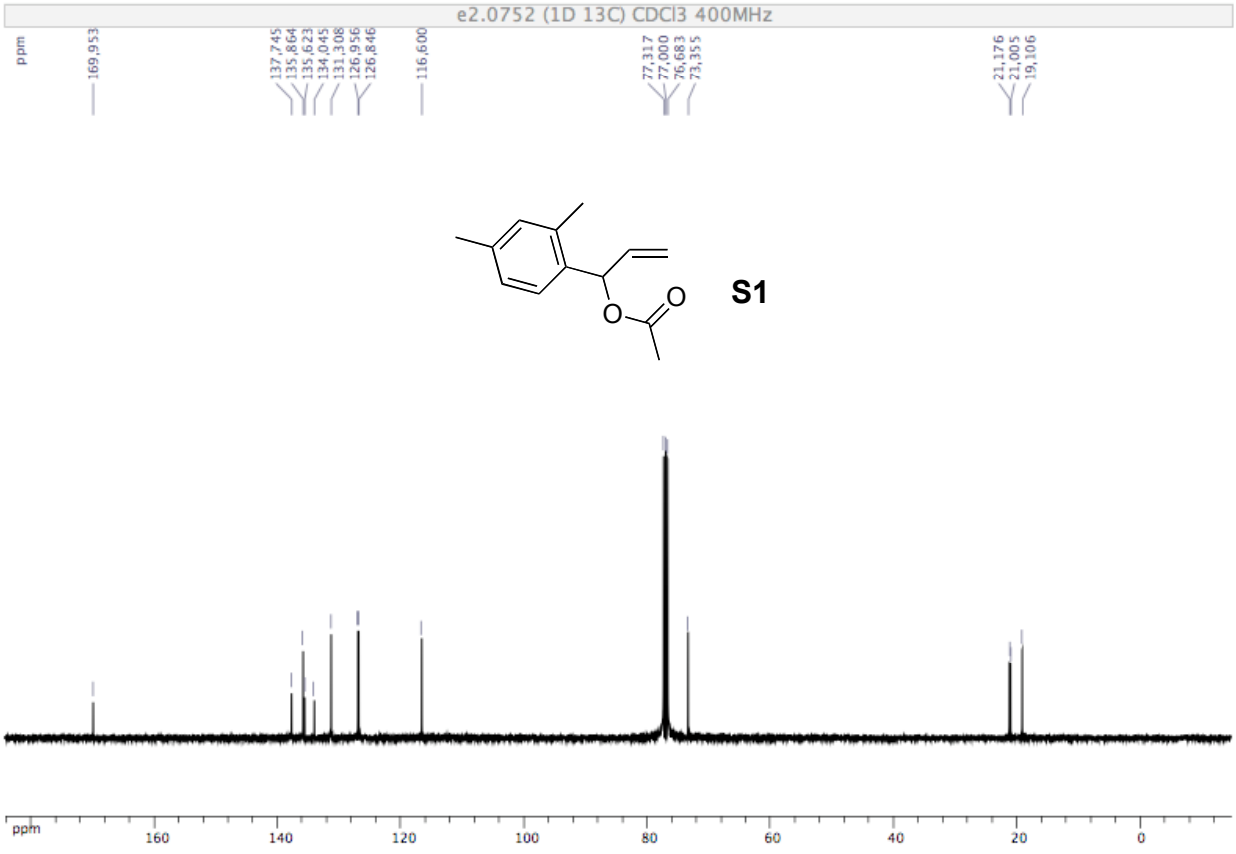
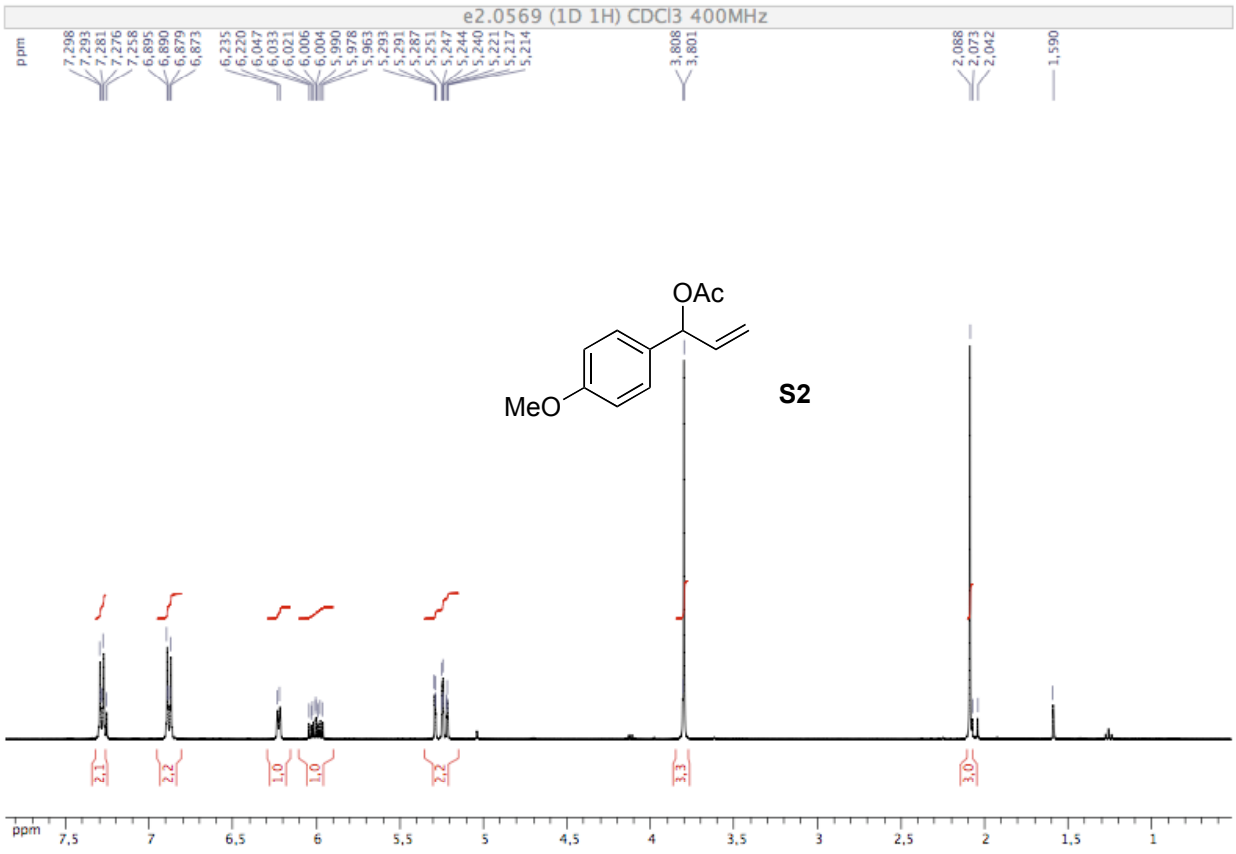
13. NMR Spectra



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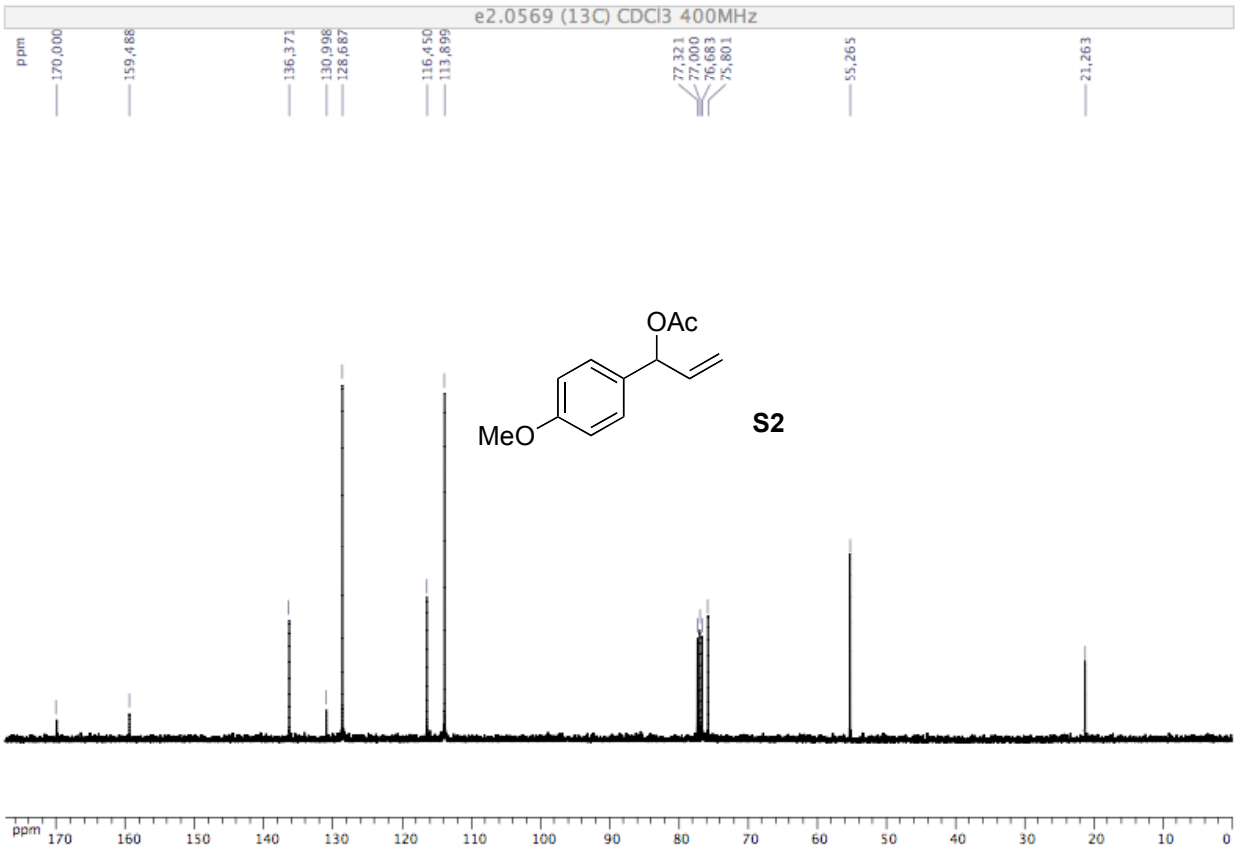
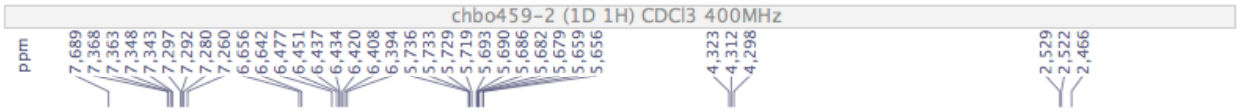
MeO
S2


e2.0569 (13C) CDCl3 400MHz
OAc
MeO
S2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7,292
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6,408
6,394
5,736
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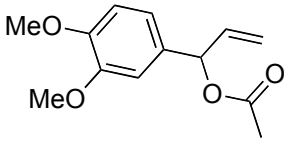
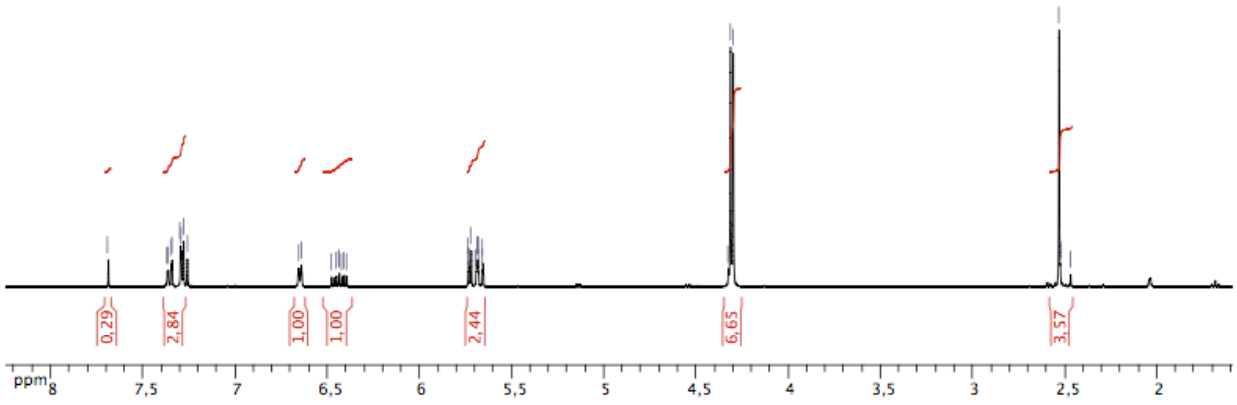
2,522
2,466


MeO
MeO
O
O

S3


0,29
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1,00
2,44
6,65
3,57
ppm
8
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7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2


chbo459 (1D 13C) CDCl3 400MHz
ppm
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148,510
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130,891
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115,831
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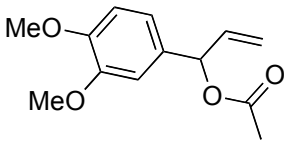
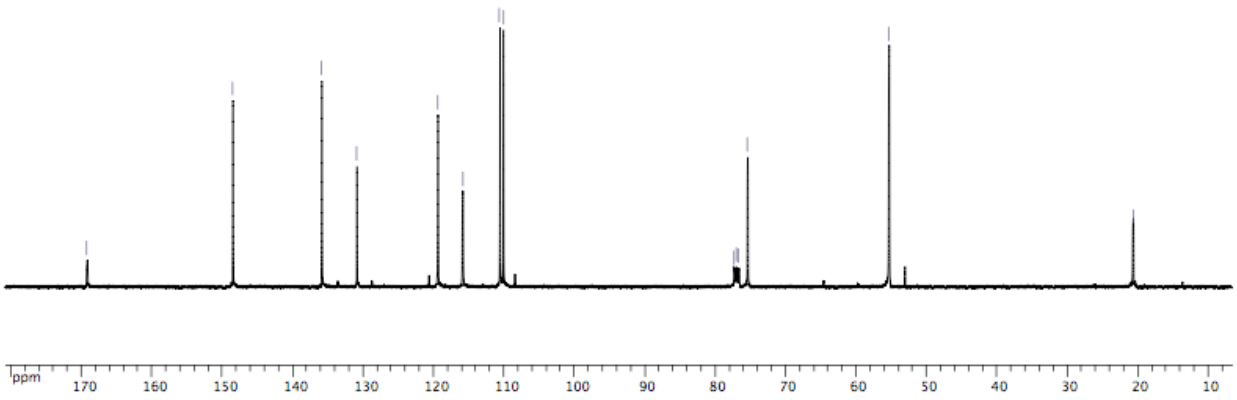
110,086
77,345
77,000
76,651
75,371
55,286
20,666


MeO
MeO
O
O

S3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140
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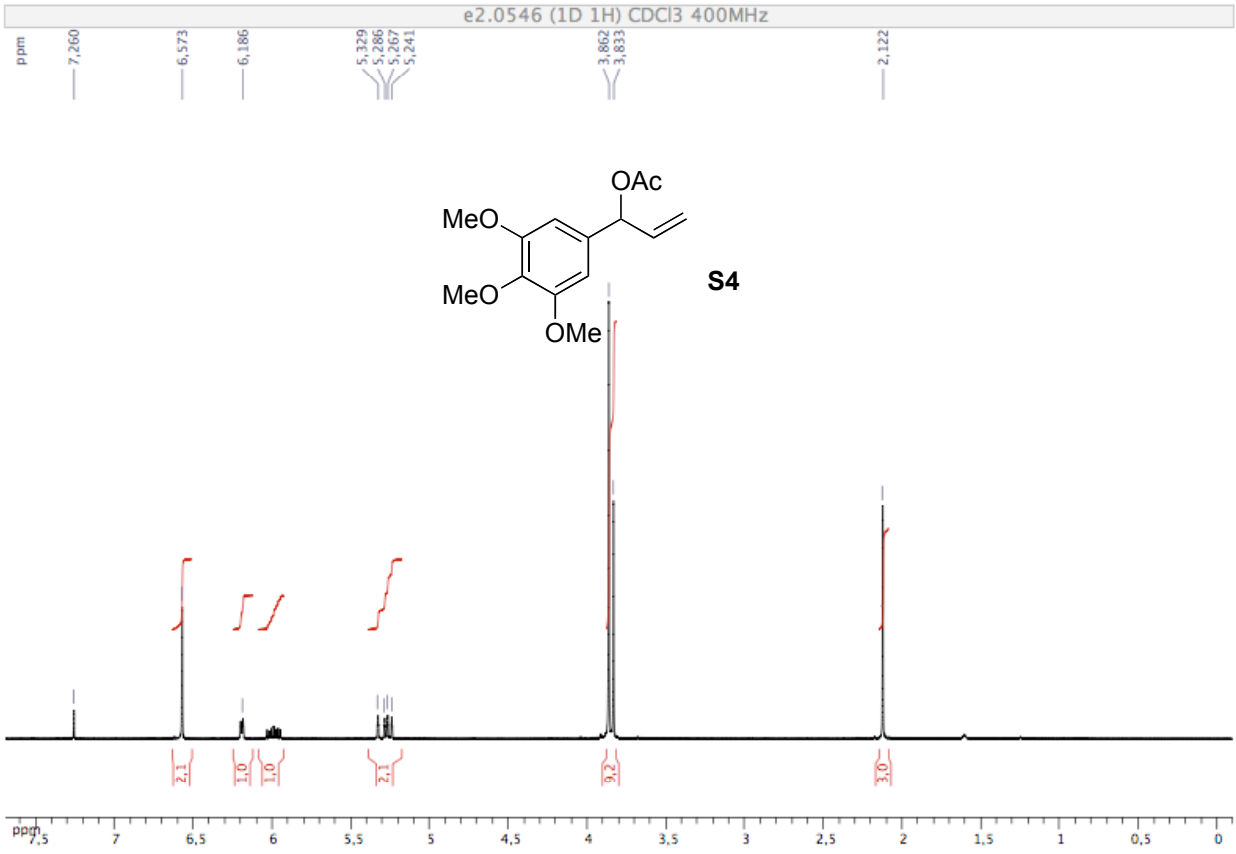
120
110
100
90
80
70
60
50
40
30
20
10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3,833
2,122
OAc
MeO
MeO
OMe
S4
2,1
1,0
1,0
2,1
9,2
3,0
ppm
7,5
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6,5
6
5,5
5
4,5
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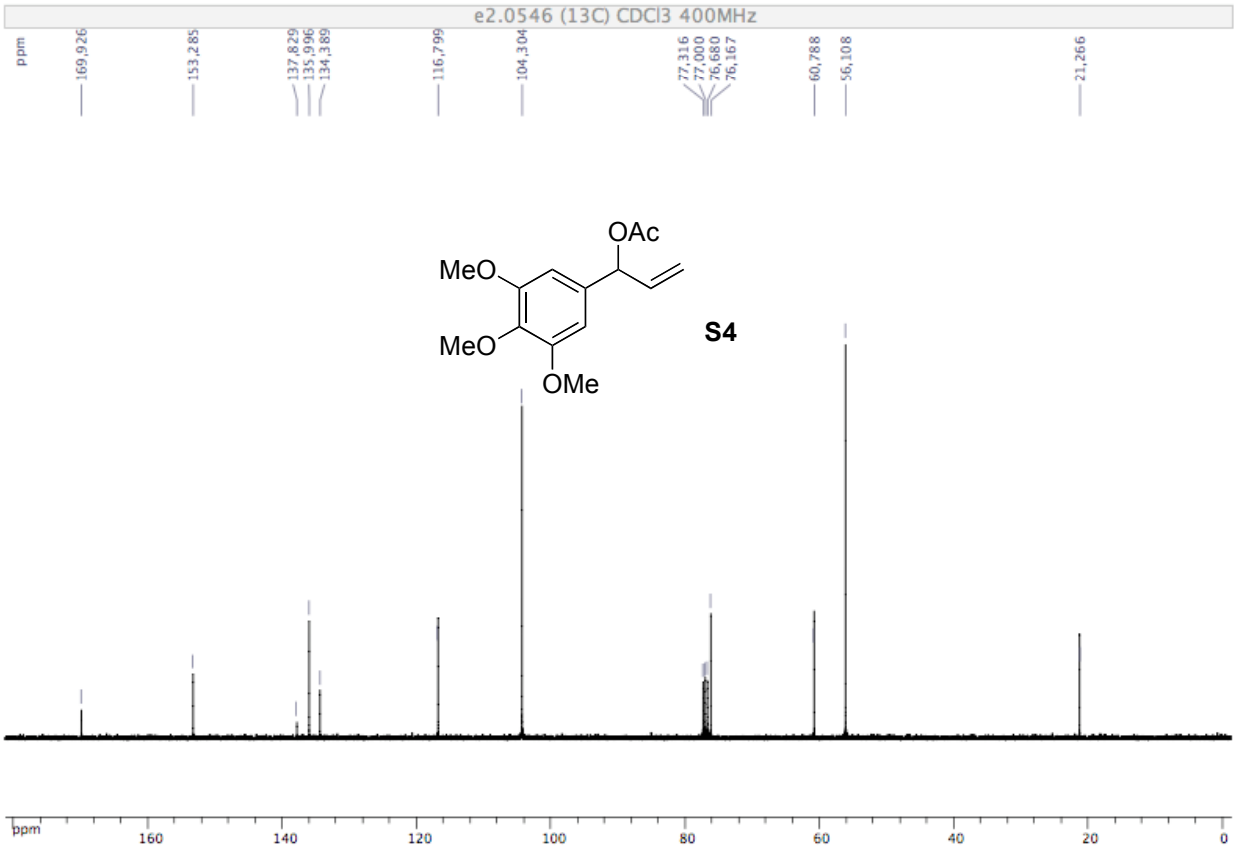
3
2,5
2
1,5
1
0,5
0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116,799
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77,000
76,680
76,167
60,788
56,108
21,266
OAc
MeO
MeO
OMe
S4
ppm
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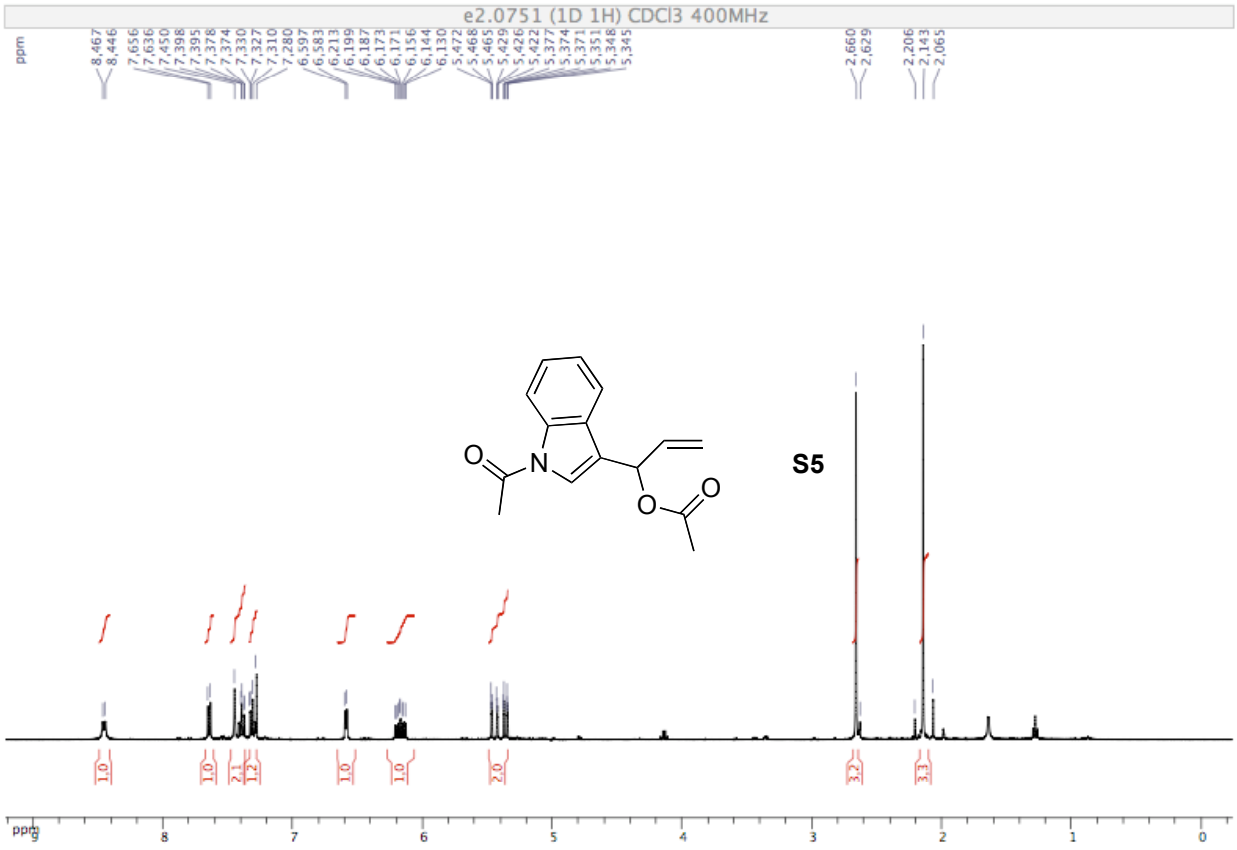
140
120
100
80
60
40
20
0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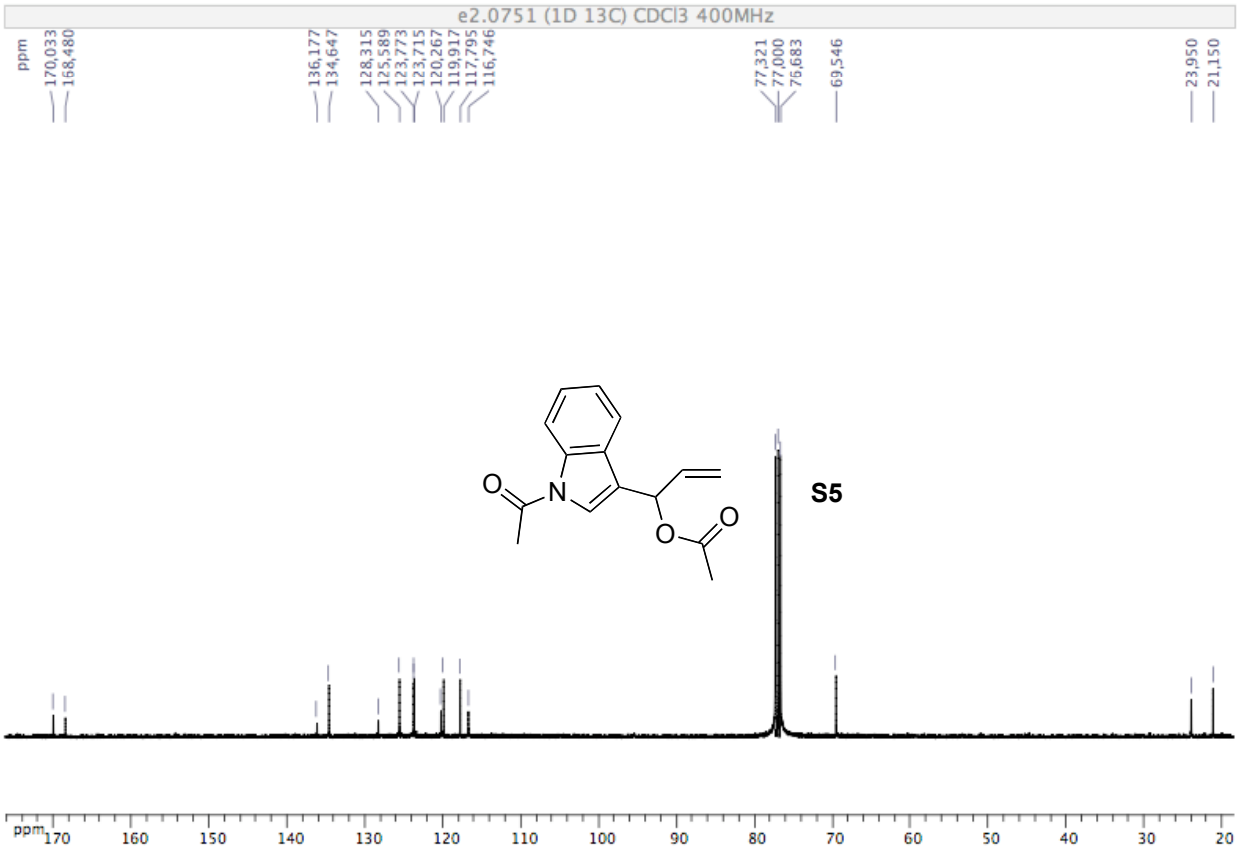
S5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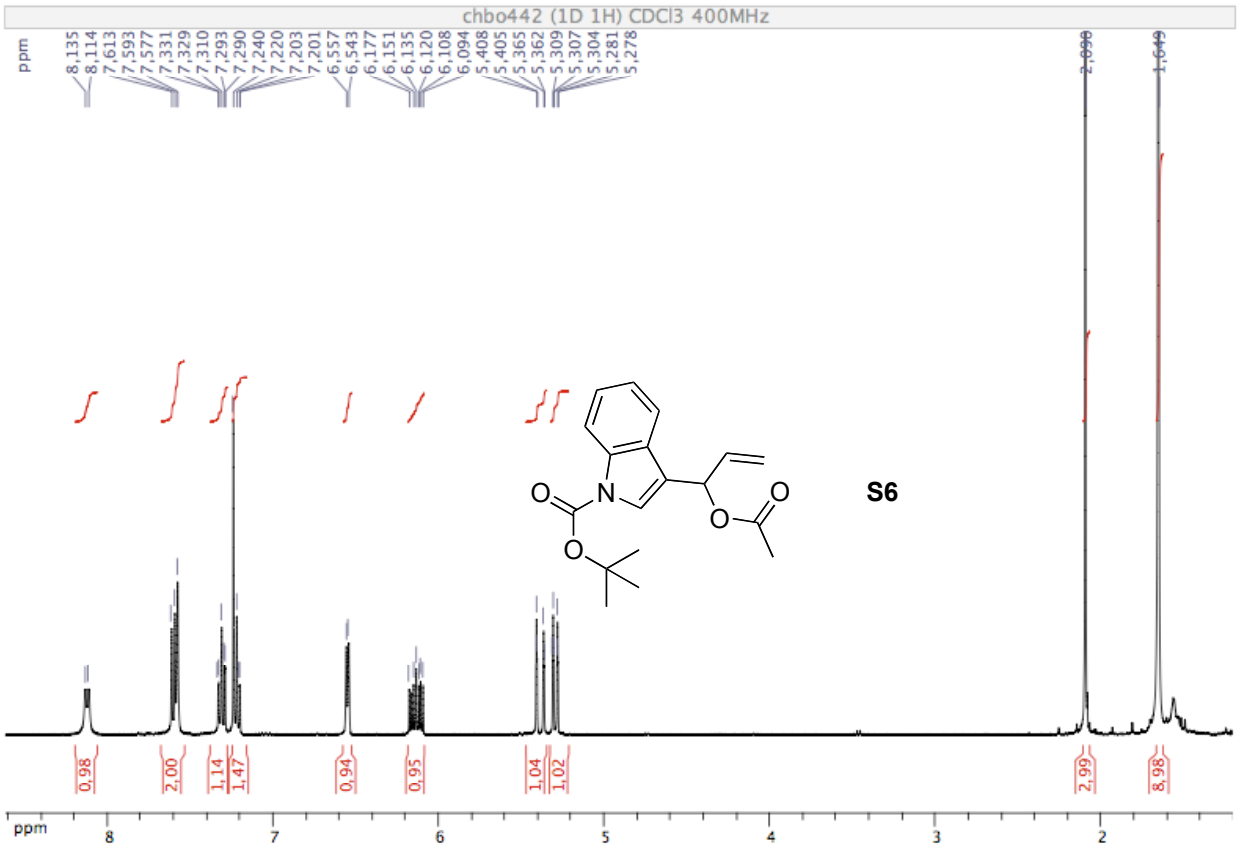
S5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7,593
7,577
7,331
7,329
7,310
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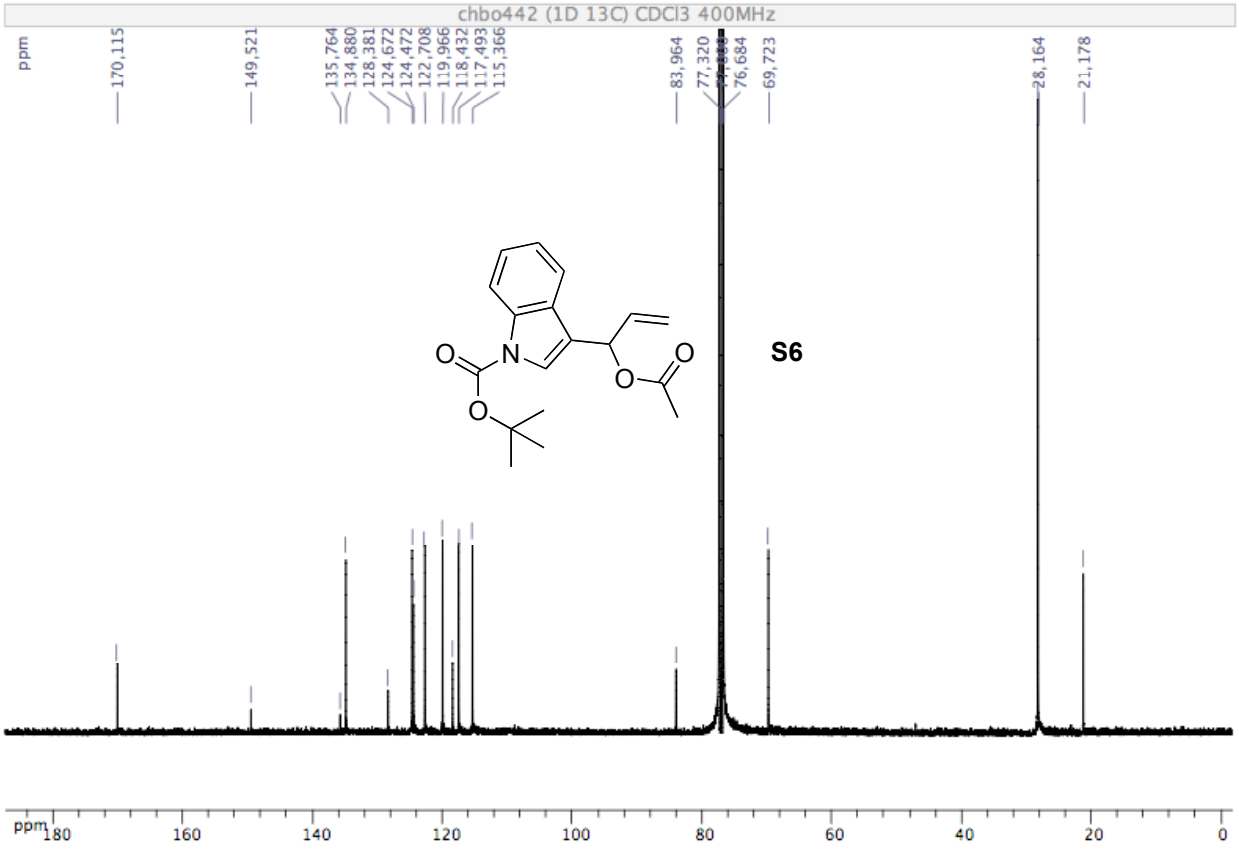
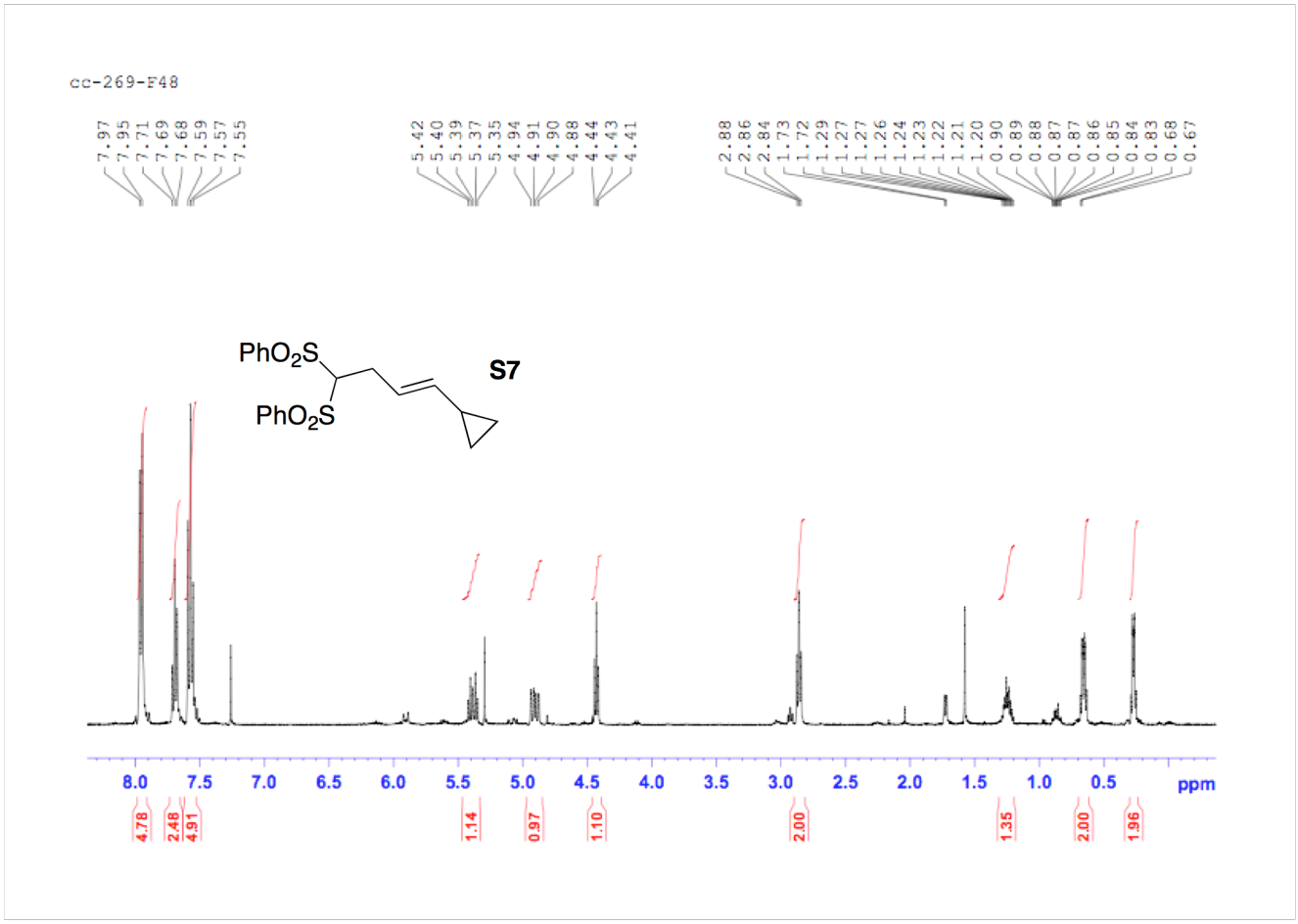
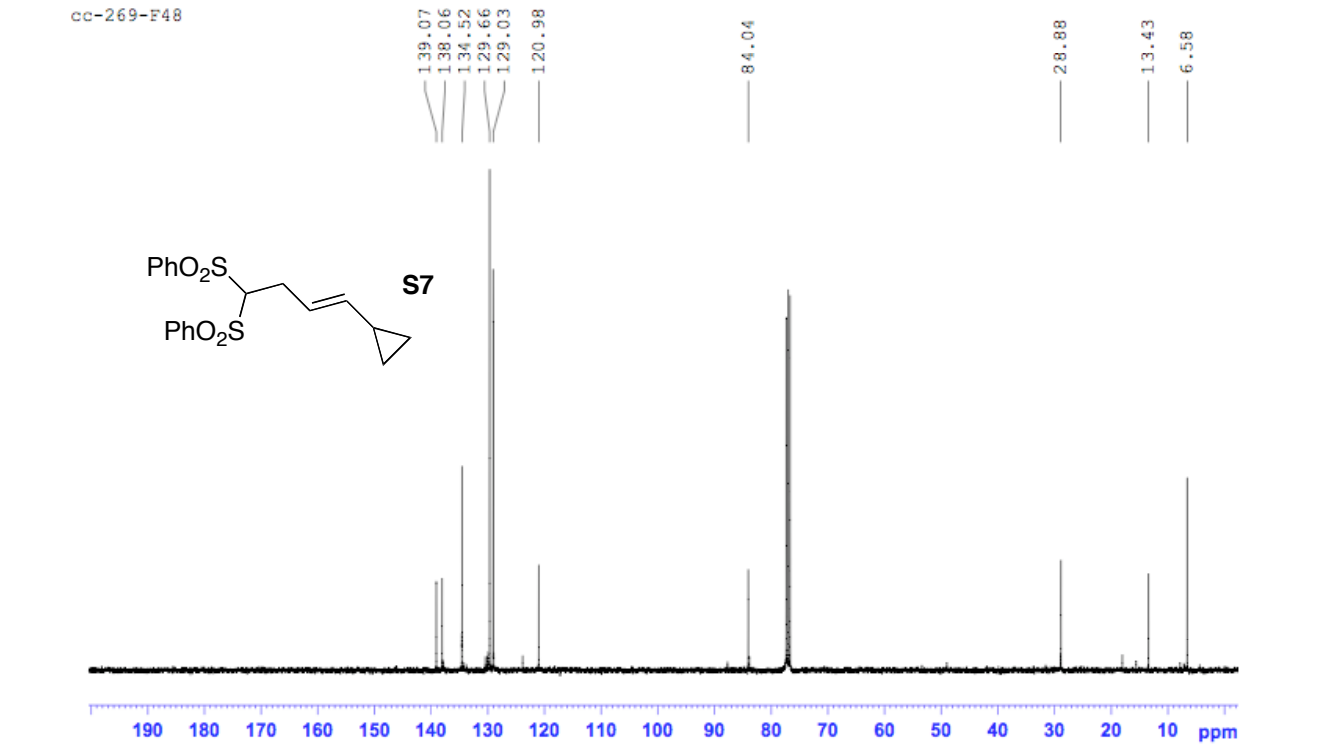
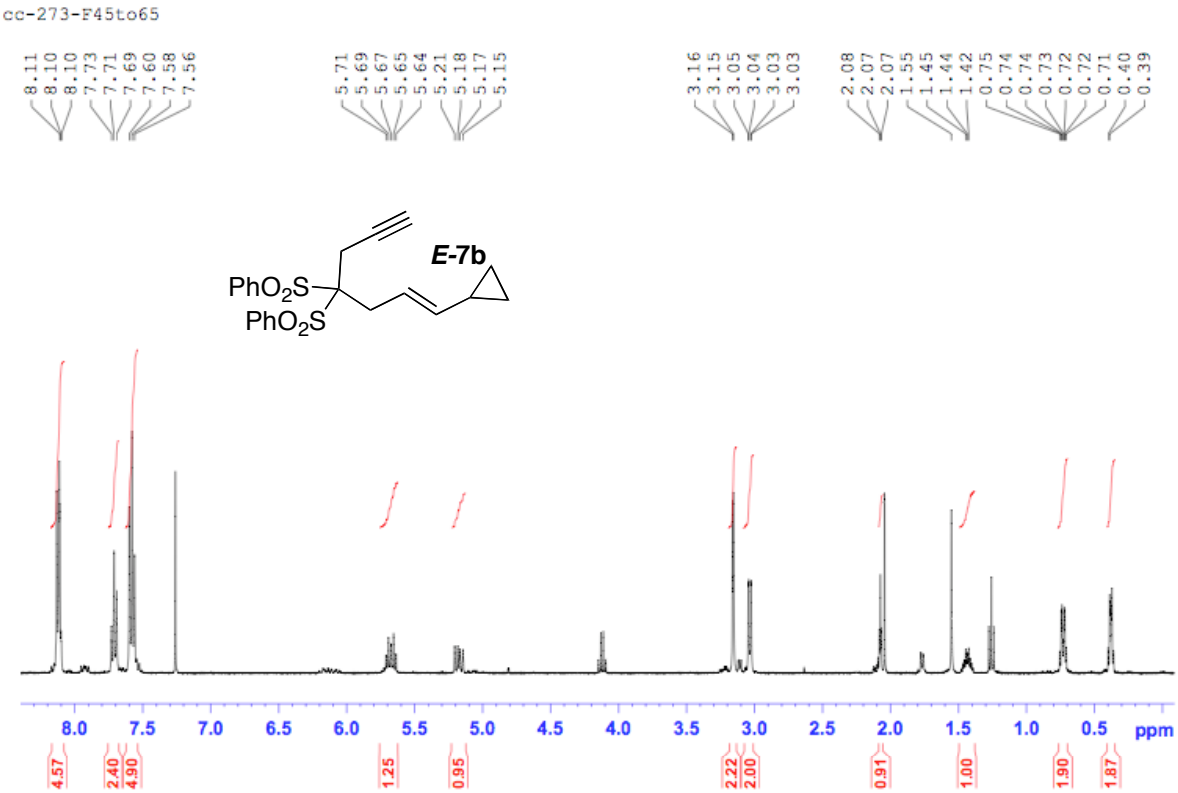
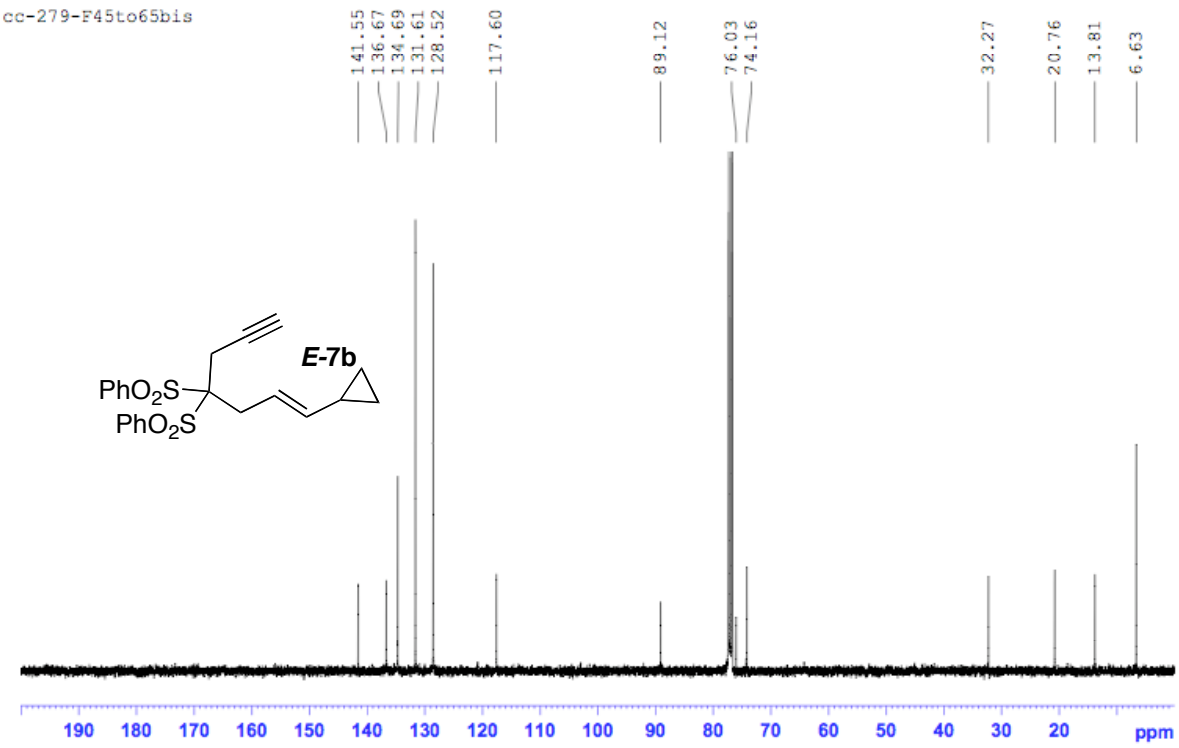
7,201
6,557
6,543
6,177
6,151
6,135
6,120
6,108
6,094
5,408
5,405
5,365
5,362
5,309
5,307
5,304
5,281
5,278
2,096
1,649
0,98
2,00
1,14
1,47
0,94
0,95
1,04
1,02
2,99
8,98
ppm
8
7
6
5
4
3
2
S6

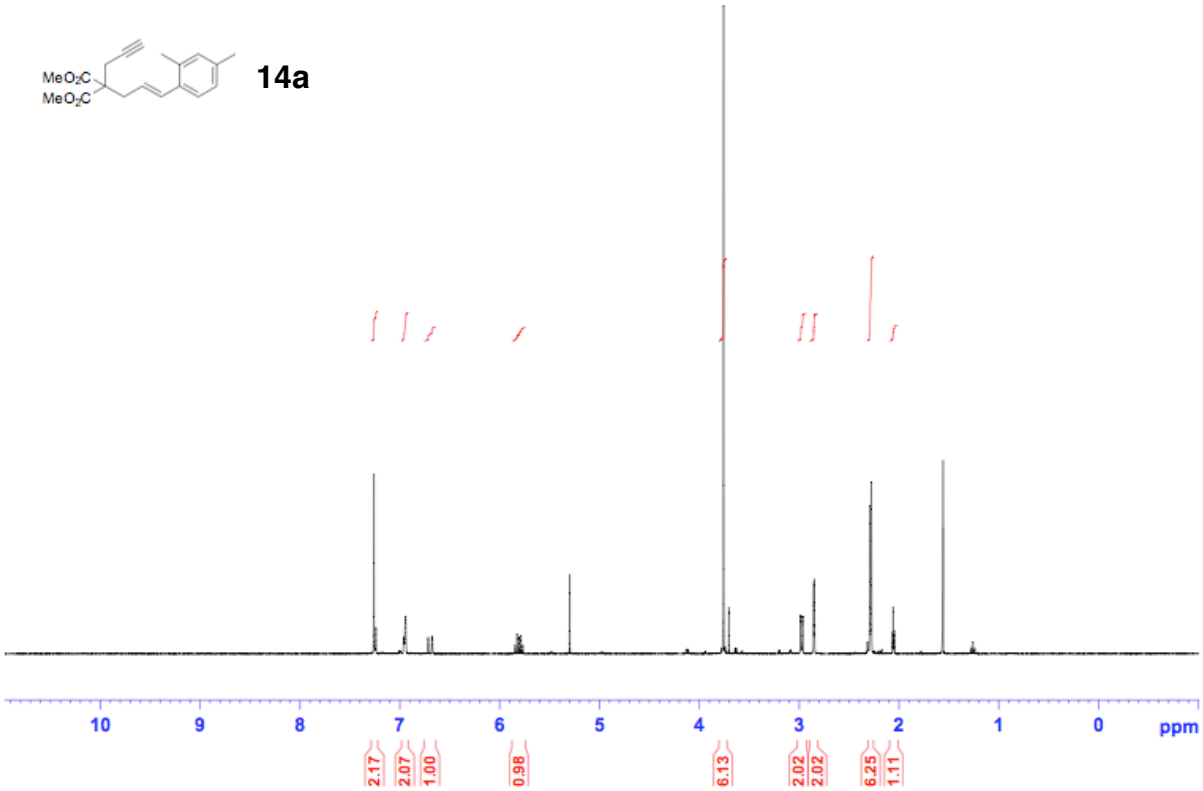

chbo442 (1D 13C) CDCl3 400MHz
ppm
170,115
149,521
135,764
134,880
128,381
124,672
124,472
122,708
119,966
118,432
117,493
115,366
83,964
77,320
76,684
69,723
28,164
21,178
ppm
180
160
140
120
100
80
60
40
20
0
S6

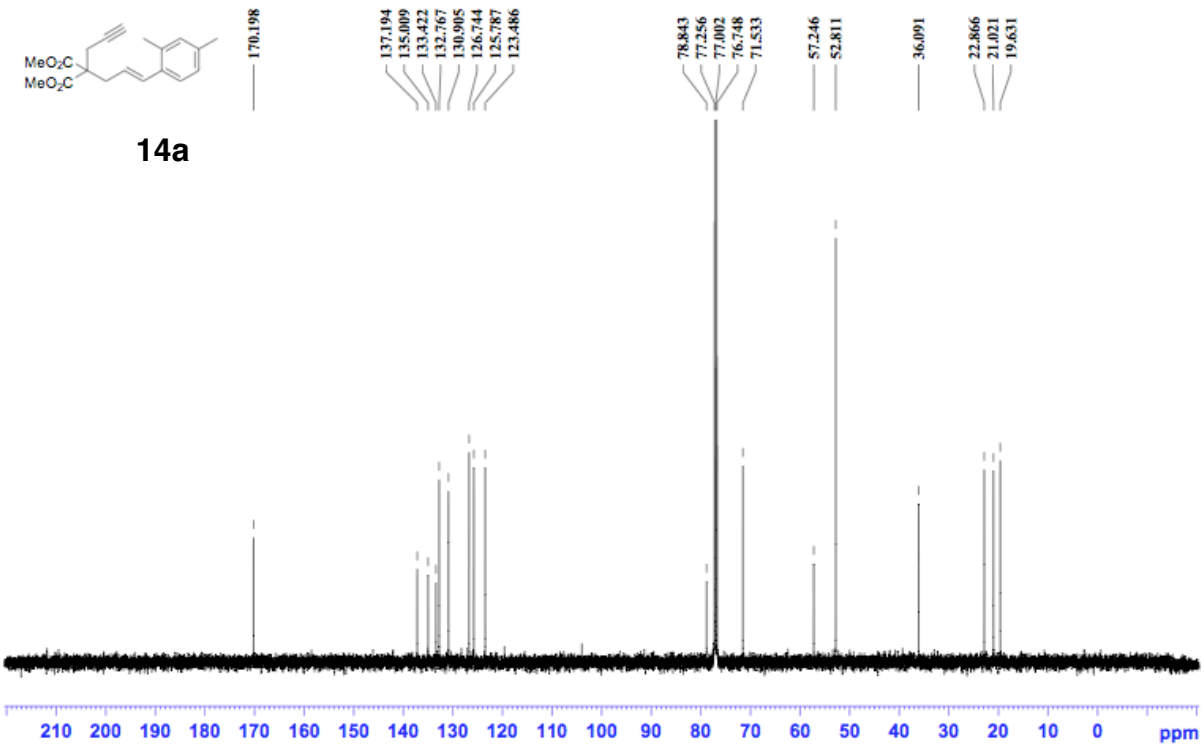

cc-269-F48
7.97 7.95 7.71 7.69 7.68 7.59 7.57 7.55
5.42 5.40 5.39 5.37 5.35 4.94 4.91 4.90 4.88 4.44 4.43 4.41
2.88 2.86 2.84 1.73 1.72 1.29 1.27 1.27 1.26 1.24 1.23 1.22 1.21 1.20 0.90 0.89 0.88 0.87 0.87 0.86 0.85 0.84 0.83 0.68 0.67
PhO2S
PhO2S
S7
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.78 2.48 4.91 1.14 0.97 1.10 2.00 1.35 2.00 1.96

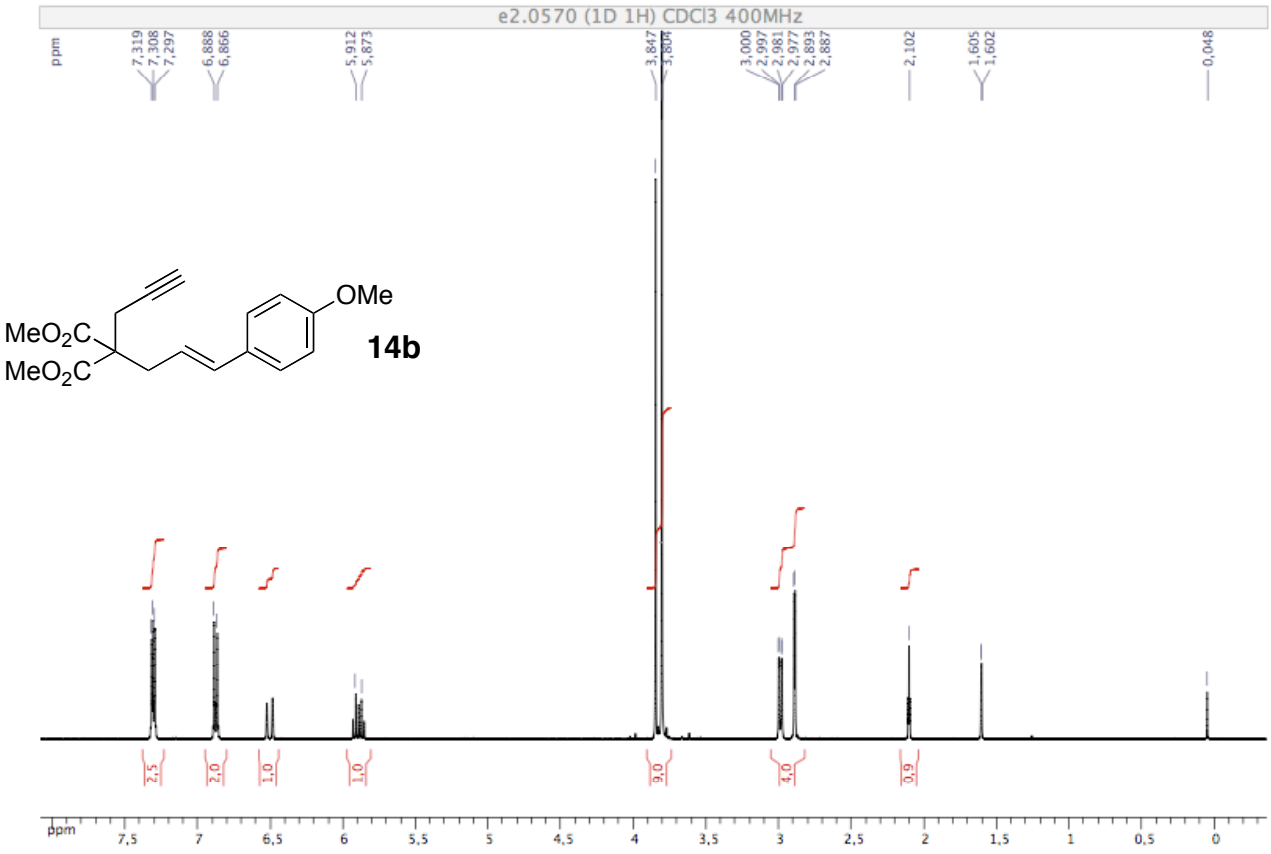

cc-269-F48
139.07 138.06 134.52 129.66 129.03 120.98 84.04 28.88 13.43 6.58
PhO2S
PhO2S
S7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

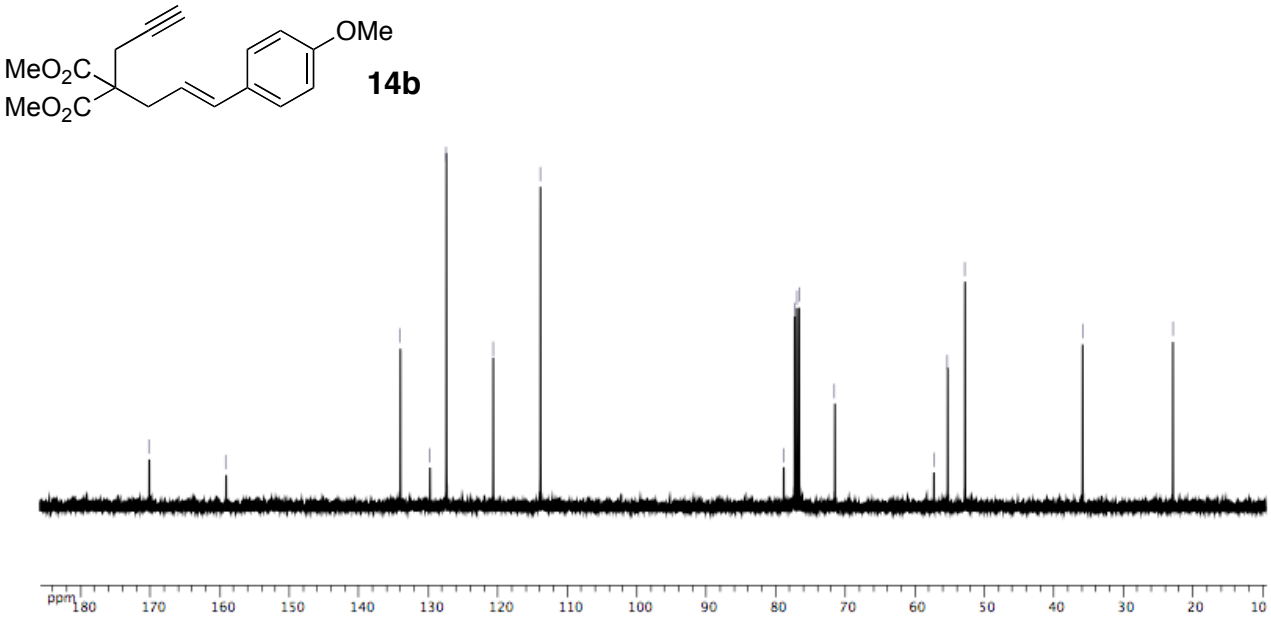

cc-273-F45to65
8.11
8.10
8.10
7.73
7.71
7.69
7.60
7.58
7.56
5.71
5.69
5.67
5.65
5.64
5.21
5.18
5.17
5.15
3.16
3.15
3.05
3.04
3.03
3.03
2.08
2.07
2.07
1.55
1.45
1.44
1.42
0.75
0.74
0.74
0.73
0.72
0.72
0.71
0.40
0.39
E-7b
PhO2S
PhO2S
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.57
2.40
4.90
1.25
0.95
2.22
2.00
0.91
1.00
1.90
1.87


cc-279-F45to65bis
141.55
136.67
134.69
131.61
128.52
117.60
89.12
76.03
74.16
32.27
20.76
13.81
6.63
E-7b
PhO2S
PhO2S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MeO2C
MeO2C
14a
10
9
8
7
6
5
4
3
2
1
0
ppm
2.17
2.07
1.00
0.98
6.13
2.02
2.02
6.25
1.11


MeO2C
MeO2C
14a
170.198
137.194
135.009
133.422
132.767
130.905
126.744
125.787
123.486
78.843
77.256
77.002
76.748
71.533
57.246
52.811
36.091
22.866
21.021
19.631
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


e2.0570 (1D 1H) CDCl3 400MHz
ppm
7,319
7,308
7,297
6,888
6,866
5,912
5,873
3,847
3,809
3,000
2,997
2,981
2,977
2,893
2,887
2,102
1,605
1,602
0,048
2,5
2,0
1,0
1,0
9,0
4,0
0,9
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

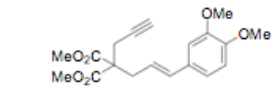

e2.0570 (13C) CDCl3 400MHz
ppm
170,209
159,147
134,069
129,800
127,439
120,697
113,900
78,891
77,320
77,000
76,684
71,527
57,279
55,290
52,806
35,874
22,884
ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

MeO2C
MeO2C
OMe

14b

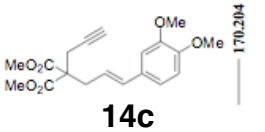
MeO2C
MeO2C
OMe

14b


OMe
OMe
MeO2C
MeO2C

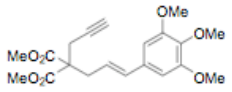
14c

10
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.10
1.00
0.99
6.03
6.00
2.01
1.98
0.89


OMe
OMe
MeO2C
MeO2C

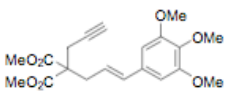
14c

170.204
148.971
148.782
134.385
130.101
120.935
119.316
111.083
108.934
78.880
71.577
57.267
55.925
55.876
52.831
35.888
22.918
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
OMe
OMe
MeO2C
MeO2C

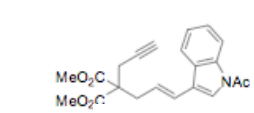
14d

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.02
1.01
6.03
3.10
5.91
2.06
2.01
0.93


OMe
OMe
OMe
MeO2C
MeO2C

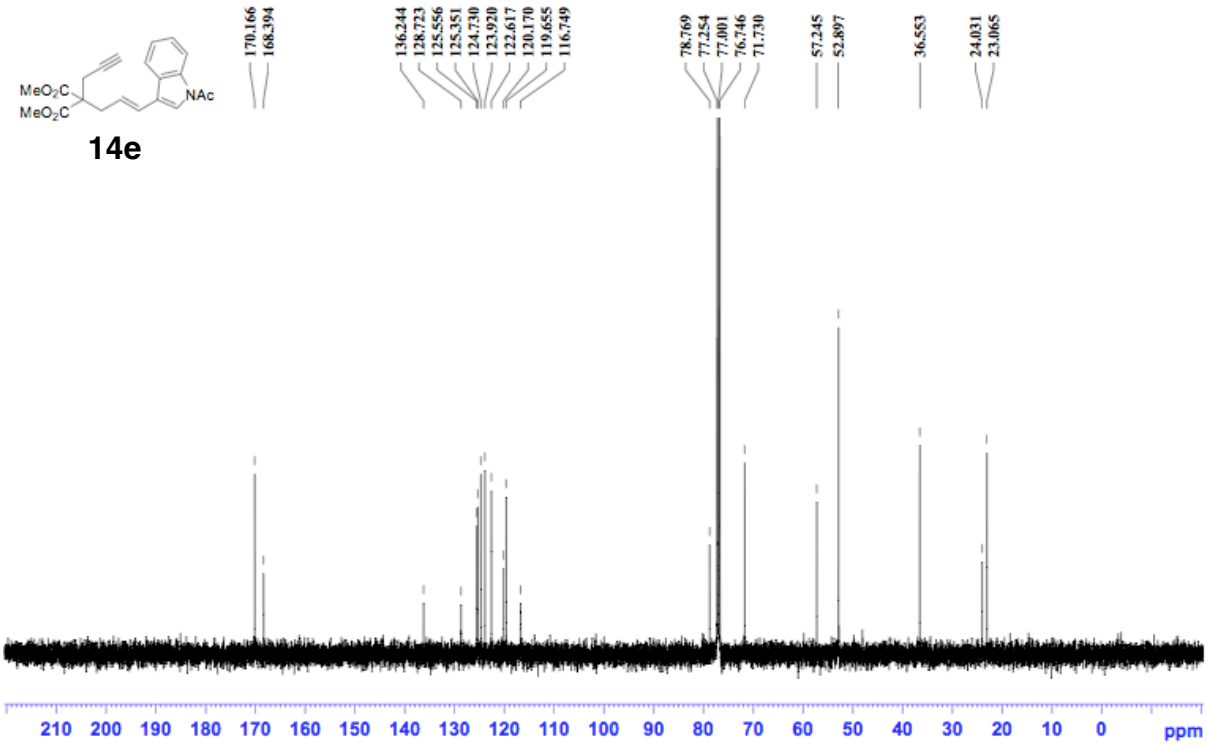
14d

170.151
153.284
137.878
134.665
132.691
122.429
103.457
78.816
77.319
77.002
76.684
71.653
60.908
57.202
56.136
52.870
35.876
22.967
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

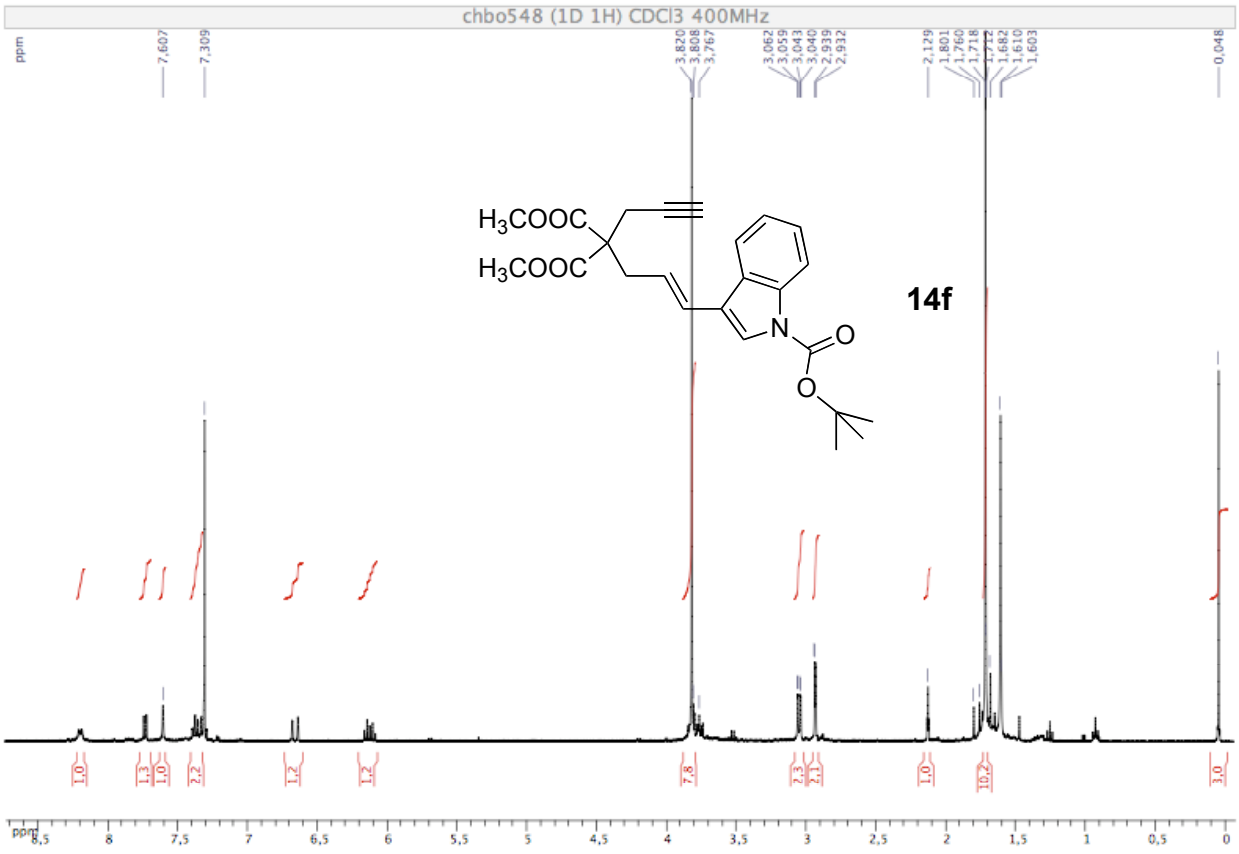

MeO2C
MeO2C
NAc

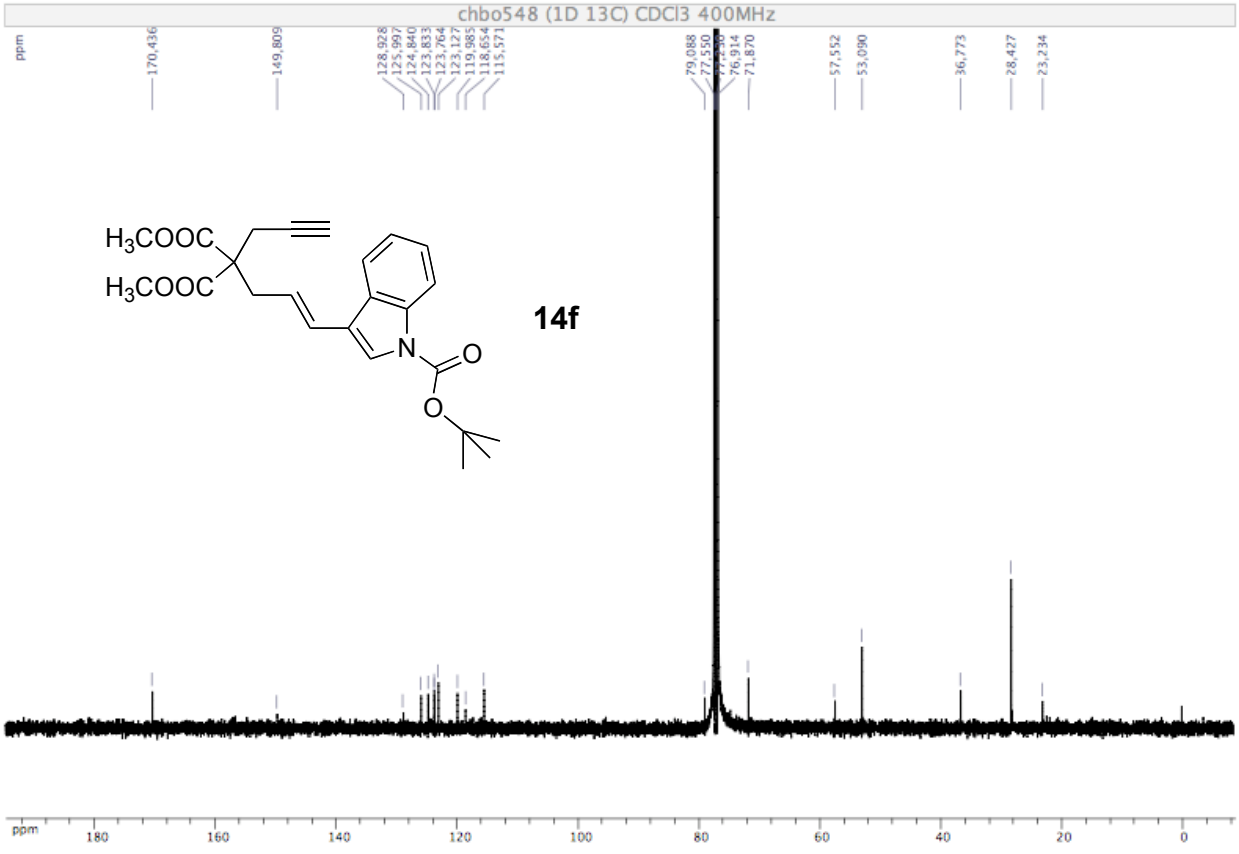
14e

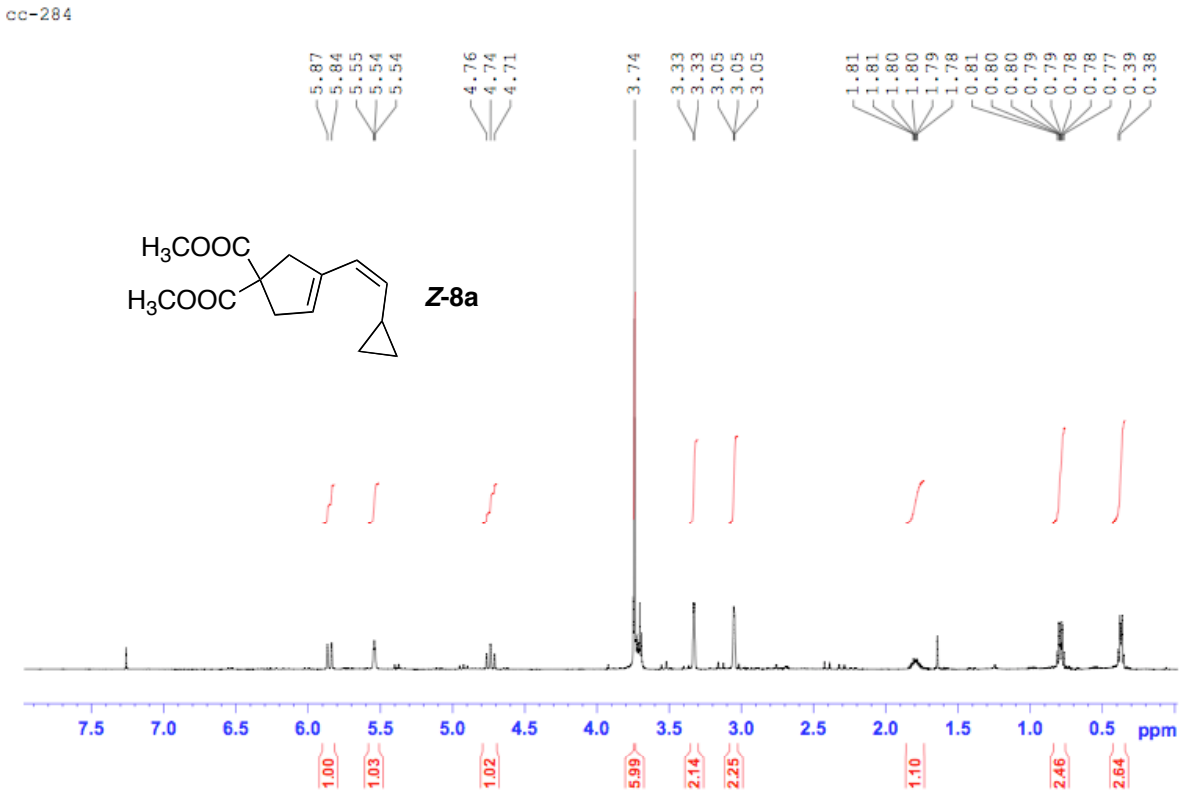
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
2.11
1.11
1.02
1.02
6.87
2.25
2.20
3.17
1.03

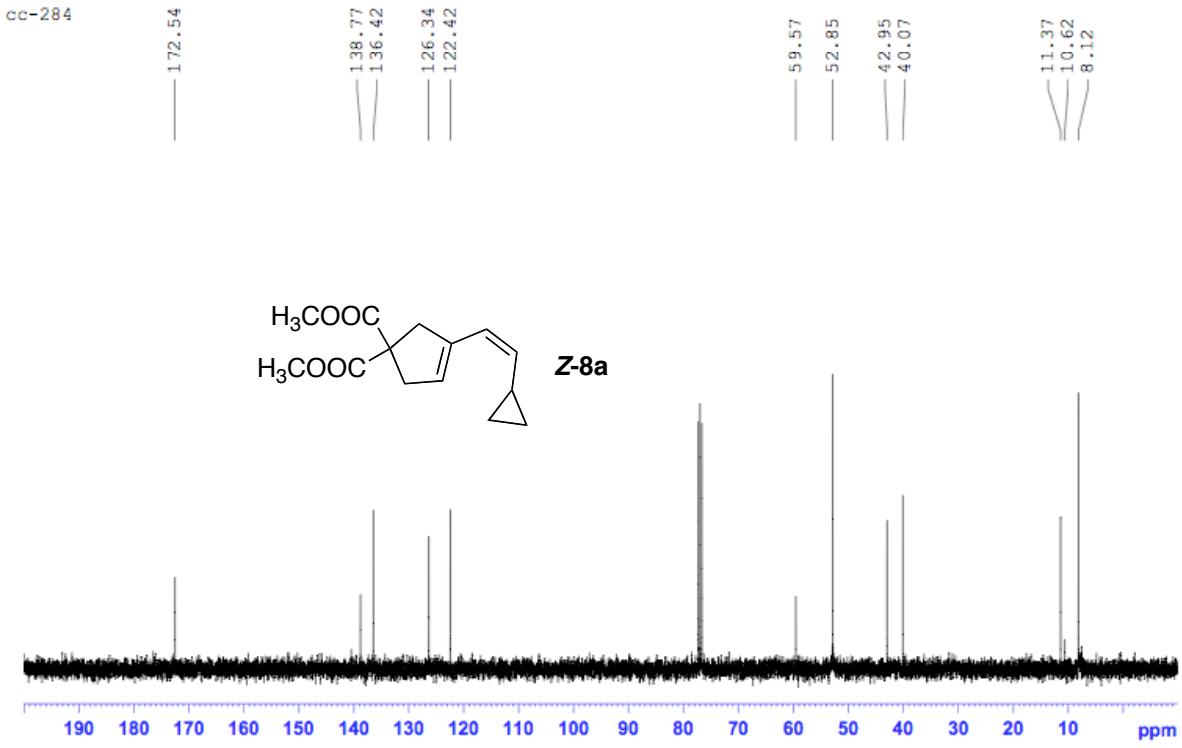

170.166
168.394
136.244
128.723
125.556
125.351
124.730
123.920
122.617
120.170
119.655
116.749
78.769
77.254
77.001
76.746
71.730
57.245
52.897
36.553
24.031
23.065
MeO2C
MeO2C
NAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

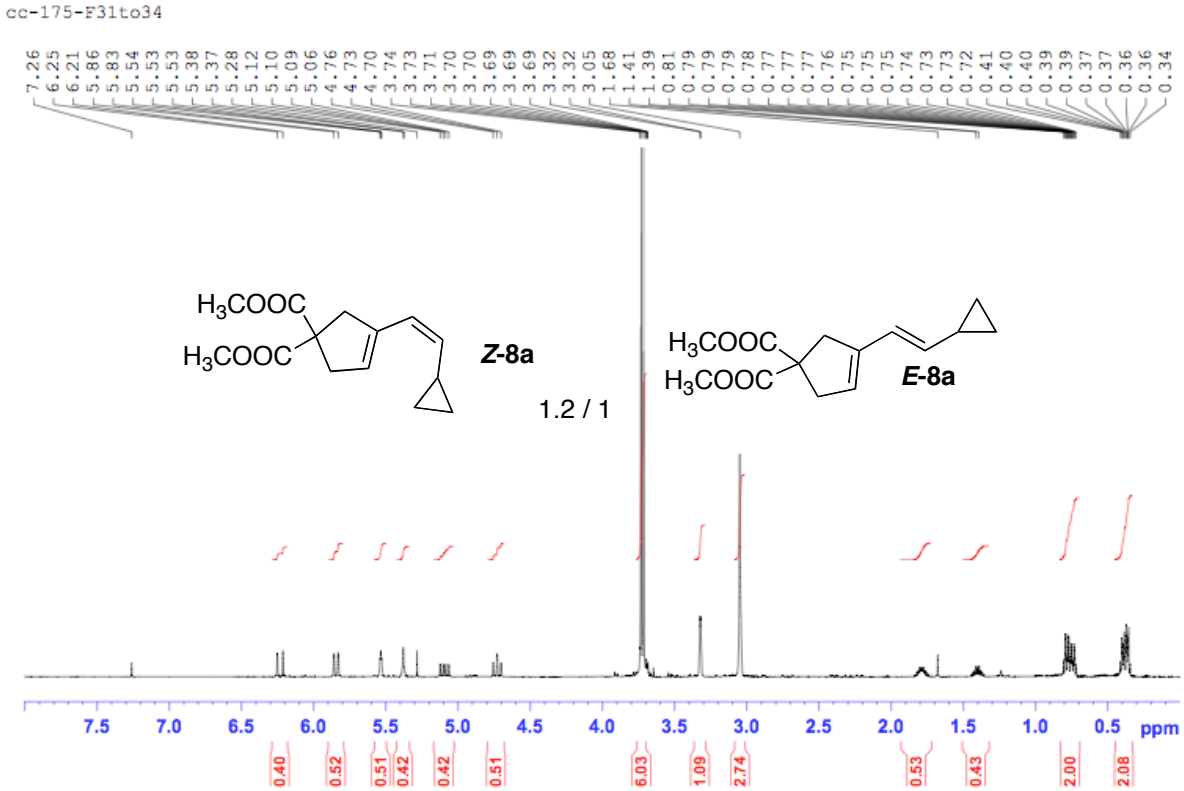
14e

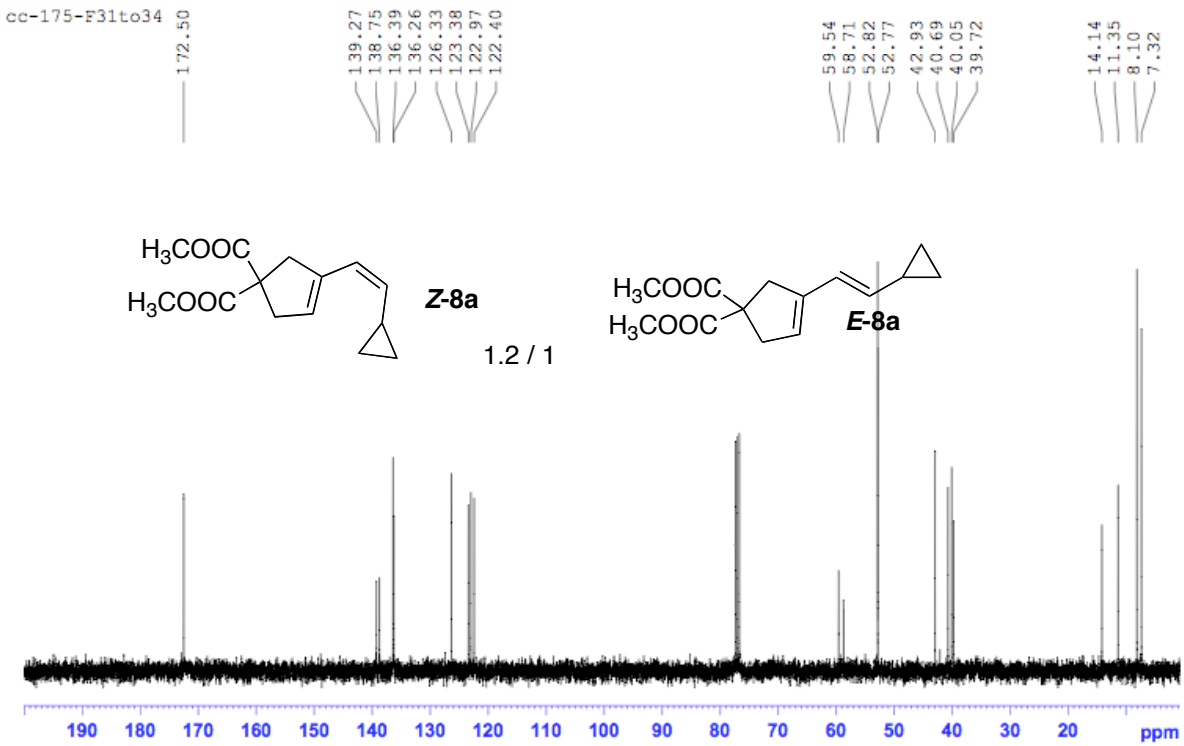

chbo548 (1D 1H) CDCl3 400MHz
ppm
7,607
7,309
3,820
3,808
3,767
3,062
3,059
3,043
3,040
2,939
2,932
2,129
1,801
1,760
1,718
1,712
1,682
1,610
1,603
0,048
H3COOC
H3COOC
N
O
O
14f
1,0
1,3
1,0
2,2
1,2
1,2
7,8
2,3
2,1
1,0
10,2
3,0
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

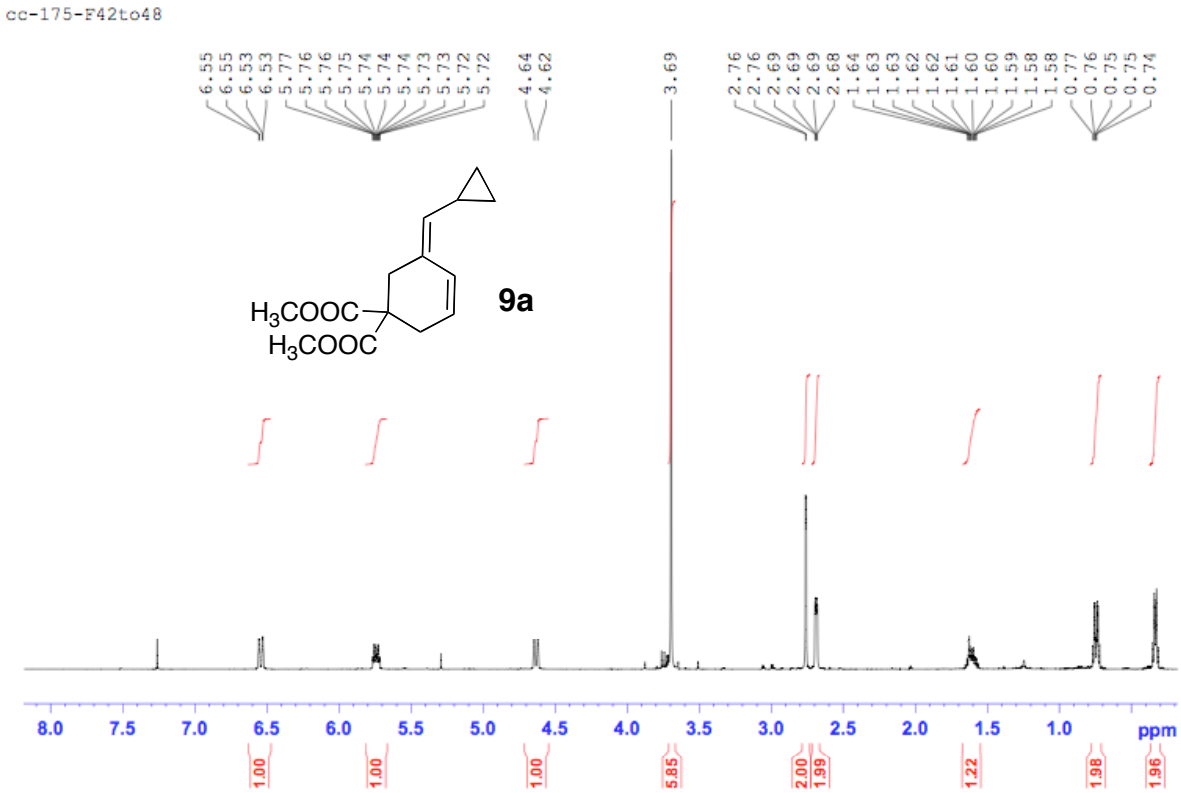

chbo548 (1D 13C) CDCl3 400MHz
ppm
170,436
149,809
128,928
125,997
124,840
123,833
123,764
123,127
119,985
118,654
115,571
79,088
77,550
76,914
71,870
57,552
53,090
36,773
28,427
23,234
H3COOC
H3COOC
N
O
O
14f
ppm
180
160
140
120
100
80
60
40
20
0

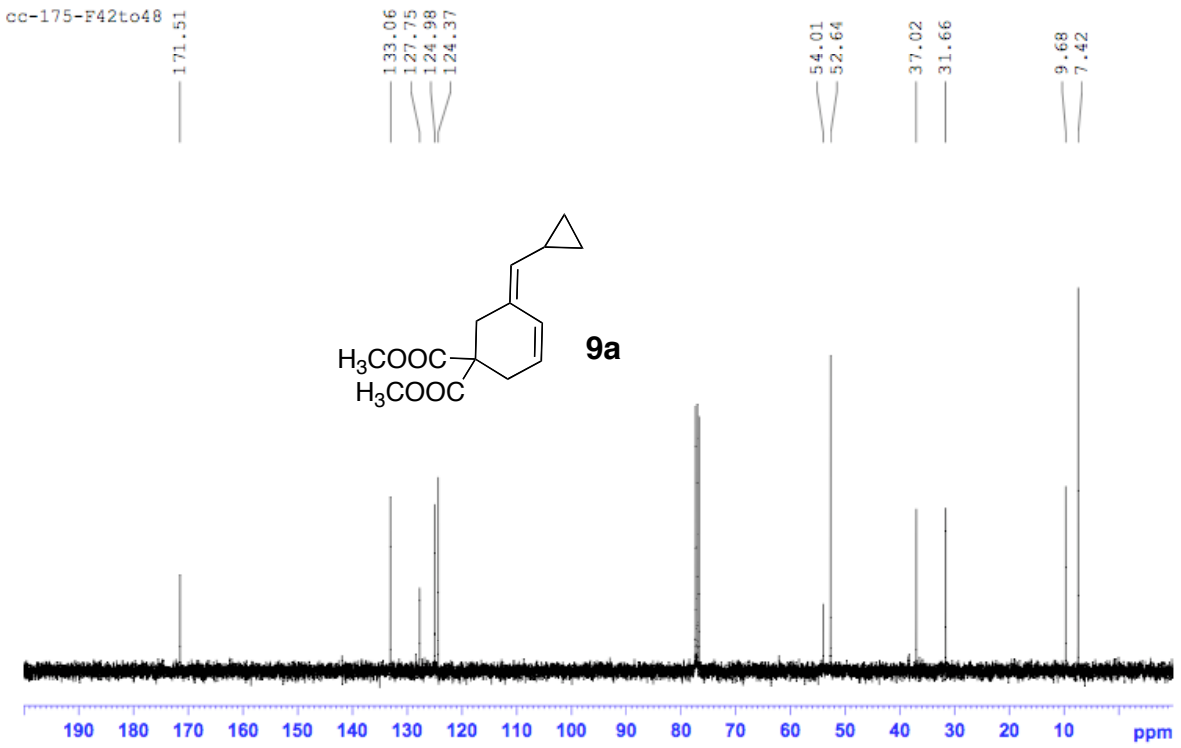

cc-284
5.87
5.84
5.55
5.54
5.54
4.76
4.74
4.71
3.74
3.33
3.33
3.05
3.05
3.05
1.81
1.81
1.80
1.80
1.79
1.78
0.81
0.80
0.80
0.79
0.79
0.78
0.78
0.77
0.39
0.38
H3COOC
H3COOC
Z-8a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.02
5.99
2.14
2.25
1.10
2.46
2.64

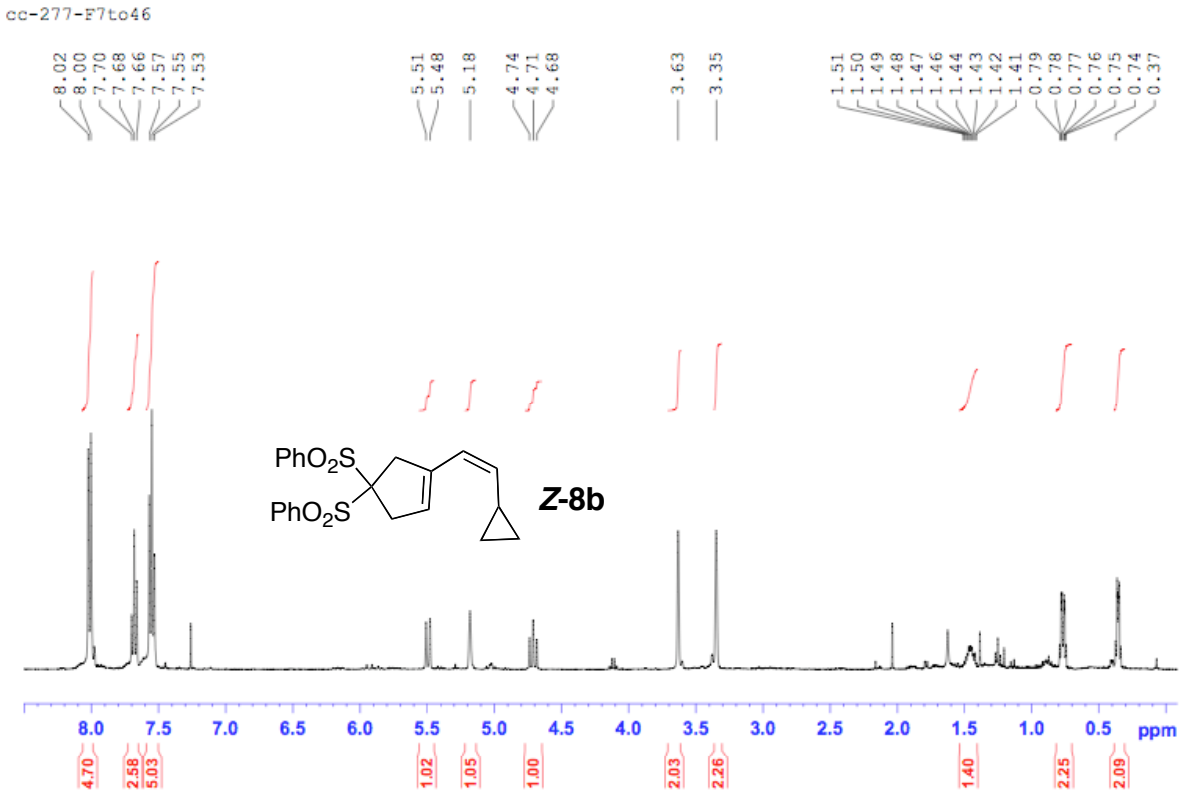

cc-284
172.54
138.77
136.42
126.34
122.42
59.57
52.85
42.95
40.07
11.37
10.62
8.12
H3COOC
H3COOC
Z-8a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

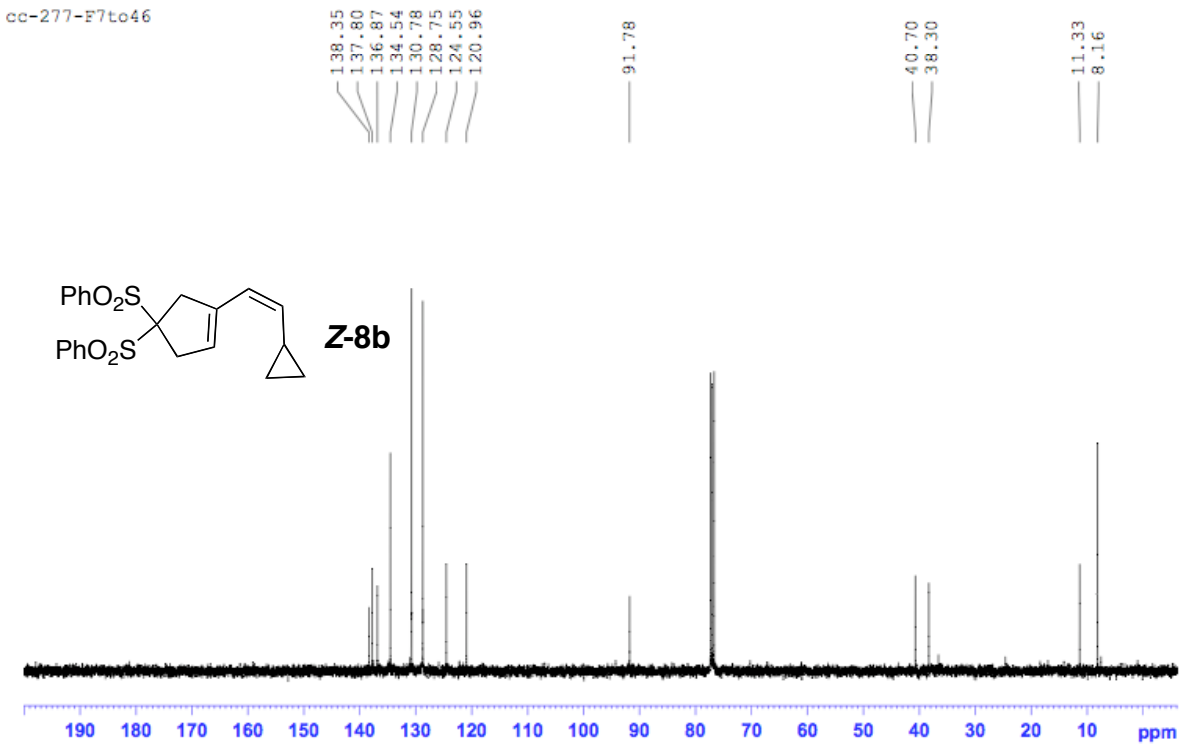

cc-175-F31to34
7.26 6.25 6.21 5.86 5.83 5.54 5.53 5.53 5.38 5.37 5.28 5.12 5.10 5.09 5.06 4.76 4.73 4.70 3.74 3.73 3.71 3.70 3.70 3.69 3.69 3.69 3.32 3.32 3.05 1.68 1.41 1.39 0.81 0.79 0.79 0.79 0.78 0.77 0.77 0.77 0.76 0.75 0.75 0.75 0.75 0.74 0.73 0.73 0.72 0.41 0.40 0.40 0.39 0.39 0.37 0.37 0.36 0.36 0.34
H3COOC
H3COOC
Z-8a
1.2 / 1
H3COOC
H3COOC
E-8a
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
0.40 0.52 0.51 0.42 0.42 0.51 6.03 1.09 2.74 0.53 0.43 2.00 2.08

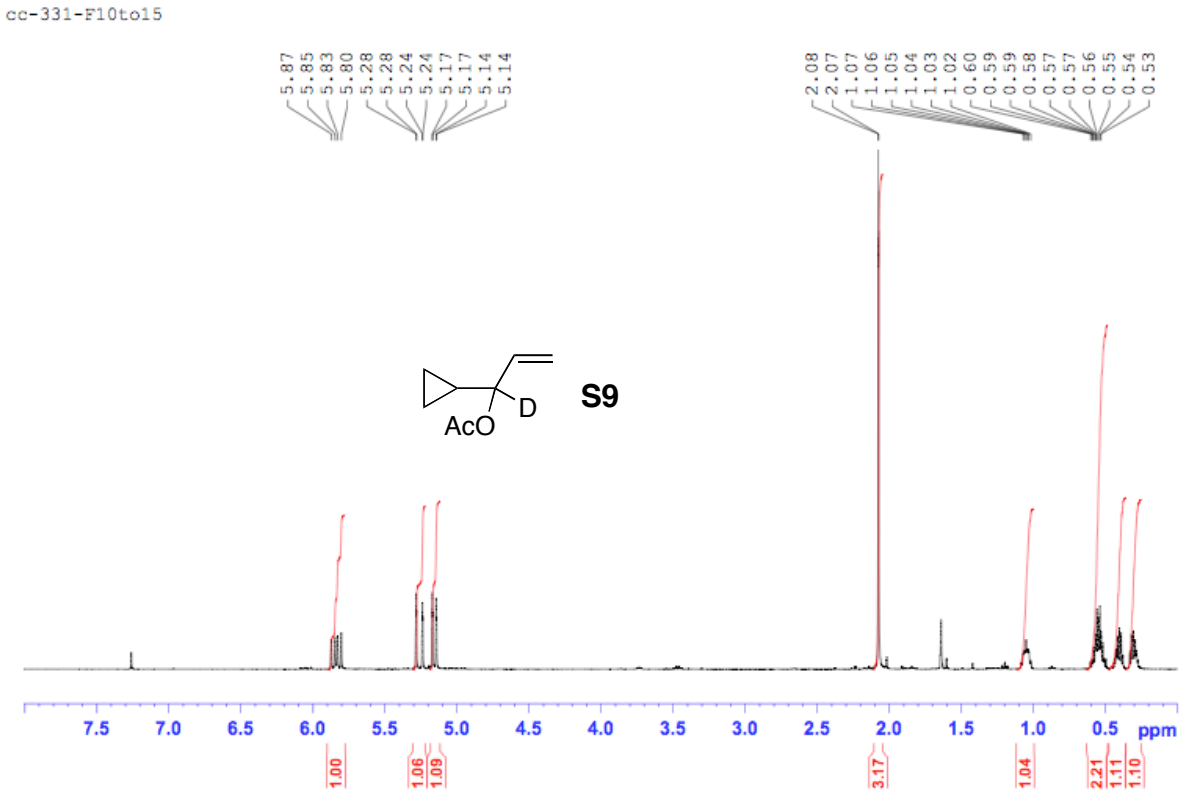

cc-175-F31to34
172.50
139.27 138.75 136.39 136.26 126.33 123.38 122.97 122.40
59.54 58.71 52.82 52.77 42.93 40.69 40.05 39.72
14.14 11.35 8.10 7.32
H3COOC
H3COOC
Z-8a
1.2 / 1
H3COOC
H3COOC
E-8a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

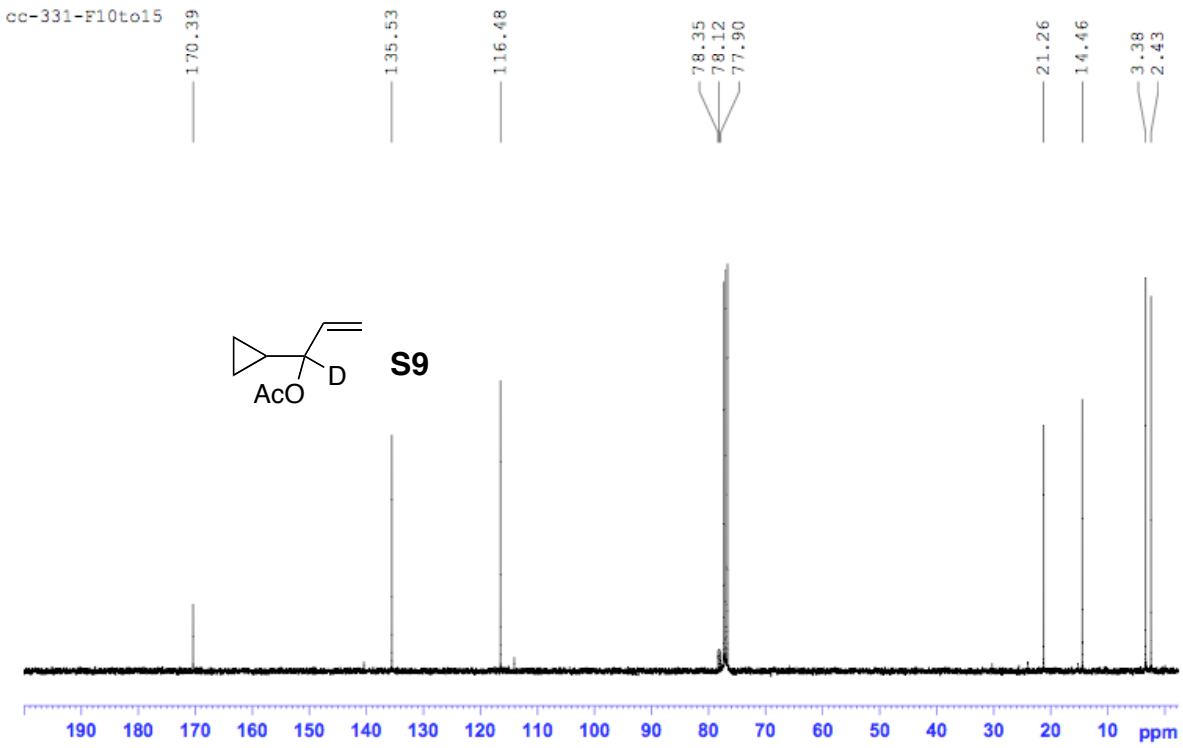

cc-175-F42to48
6.55
6.55
6.53
6.53
5.77
5.76
5.76
5.75
5.74
5.74
5.74
5.73
5.73
5.72
5.72
4.64
4.62
3.69
2.76
2.76
2.69
2.69
2.68
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.60
1.59
1.58
1.58
0.77
0.76
0.75
0.75
0.74
H3COOC
H3COOC
9a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
1.00
5.85
2.00
1.99
1.22
1.98
1.96

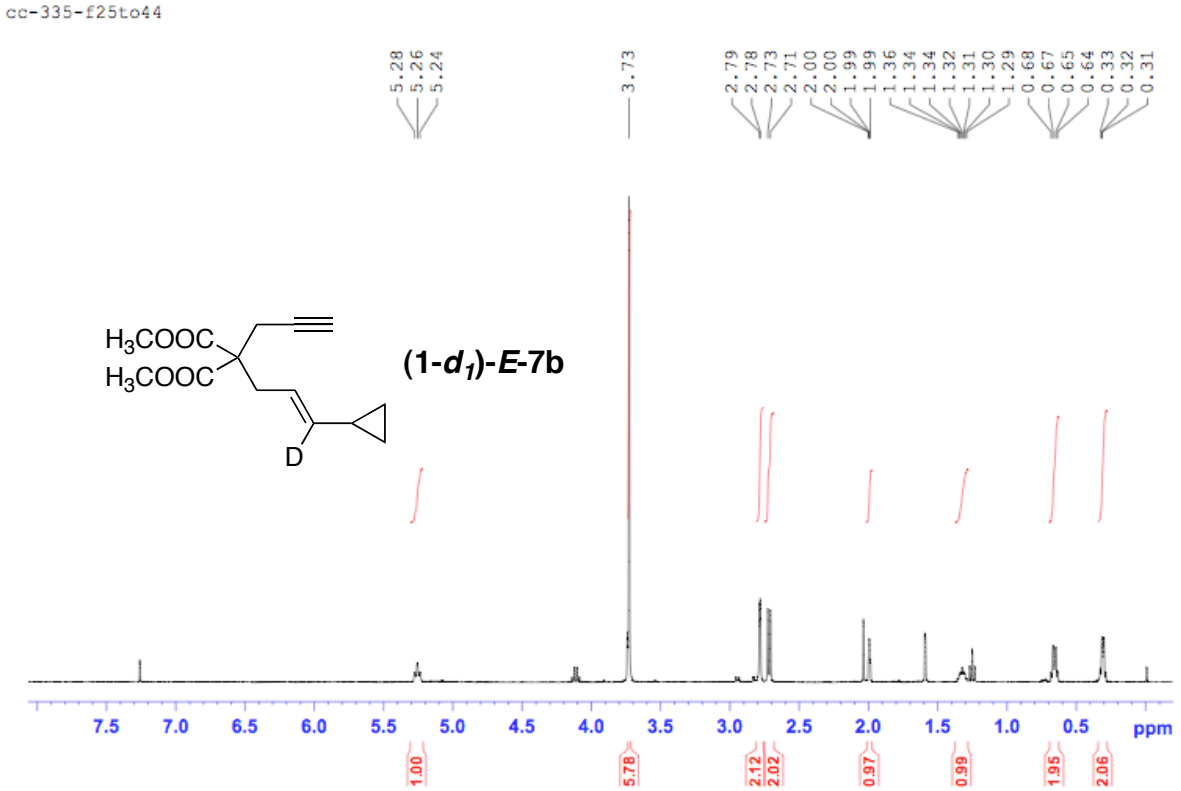

cc-175-F42to48
171.51
133.06
127.75
124.98
124.37
54.01
52.64
37.02
31.66
9.68
7.42
H3COOC
H3COOC
9a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

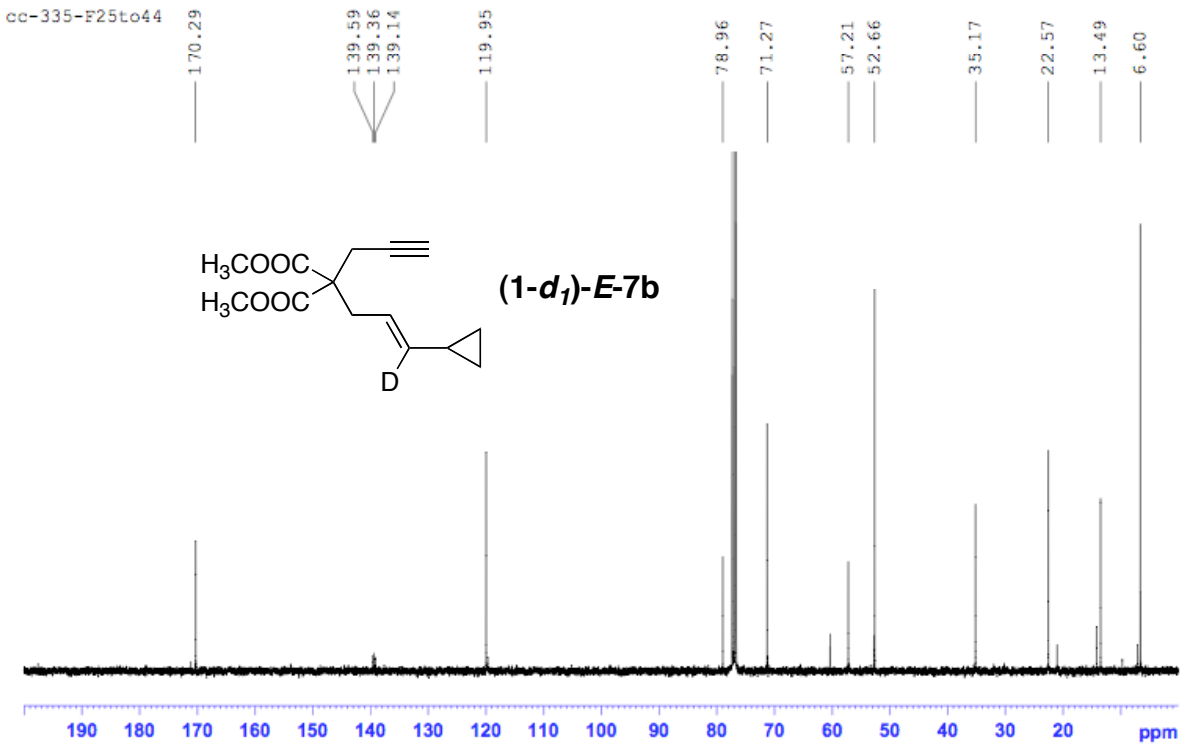

cc-277-F7to46
8.02
8.00
7.70
7.68
7.66
7.57
7.55
7.53
5.51
5.48
5.18
4.74
4.71
4.68
3.63
3.35
1.51
1.50
1.49
1.48
1.47
1.46
1.44
1.43
1.42
1.41
0.79
0.78
0.77
0.76
0.75
0.74
0.37
PhO2S
PhO2S
Z-8b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.70
2.58
5.03
1.02
1.05
1.00
2.03
2.26
1.40
2.25
2.09

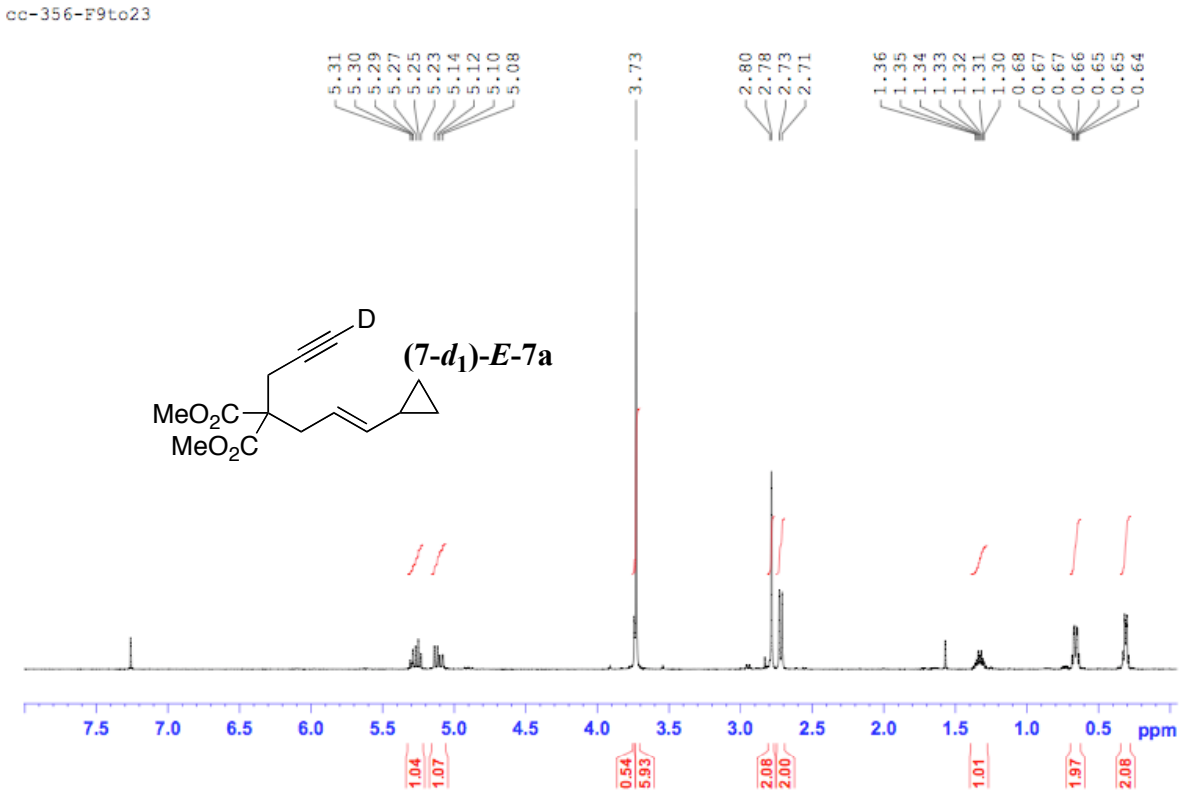

cc-277-F7to46
138.35
137.80
136.87
134.54
130.78
128.75
124.55
120.96
91.78
40.70
38.30
11.33
8.16
PhO2S
PhO2S
Z-8b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

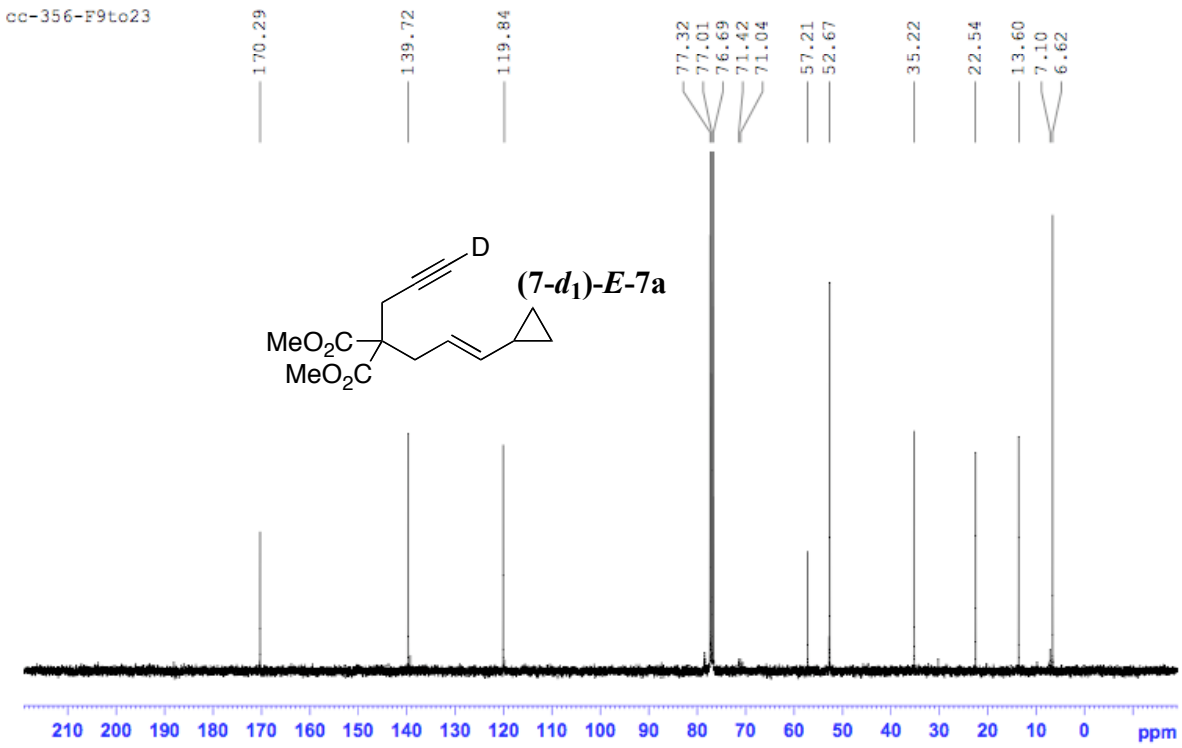

cc-331-F10to15
5.87
5.85
5.83
5.80
5.28
5.28
5.24
5.24
5.17
5.14
5.14
2.08
2.07
1.07
1.06
1.05
1.04
1.03
1.02
0.60
0.59
0.59
0.58
0.57
0.57
0.56
0.55
0.54
0.53
AcO
D
S9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.06
1.09
3.17
1.04
2.21
1.11
1.10

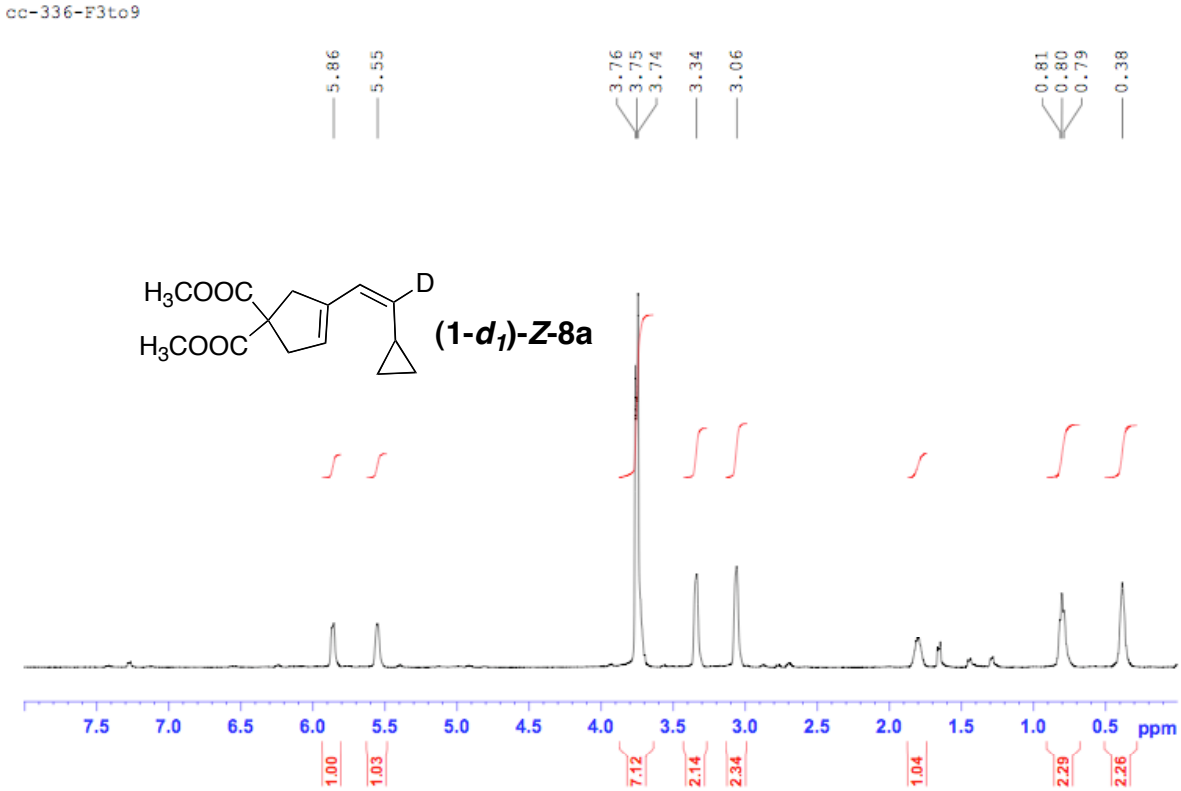

cc-331-F10to15
170.39
135.53
116.48
78.35
78.12
77.90
21.26
14.46
3.38
2.43
AcO
D
S9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

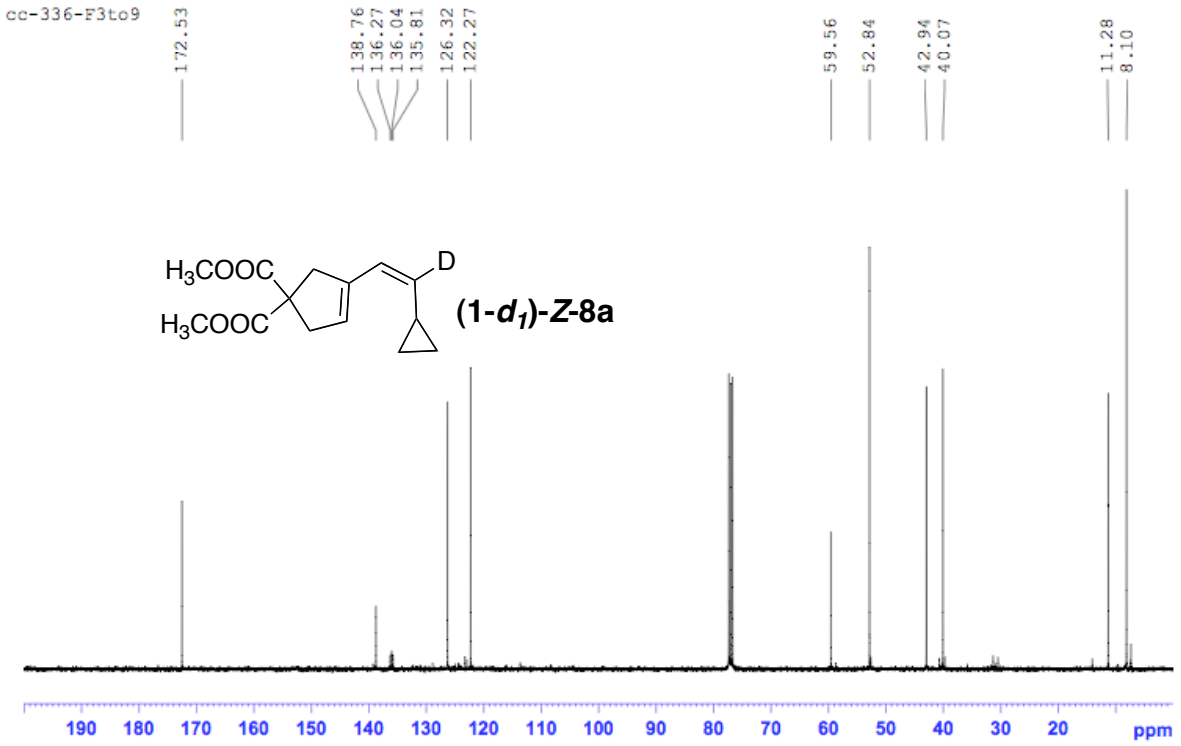

cc-335-f25to44
5.28
5.26
5.24
3.73
2.79
2.78
2.73
2.71
2.00
2.00
1.99
1.99
1.36
1.34
1.34
1.32
1.31
1.30
1.29
0.68
0.67
0.65
0.64
0.33
0.32
0.31
H3COOC
H3COOC
D
(1-d1)-E-7b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
5.78
2.12
2.02
0.97
0.99
1.95
2.06

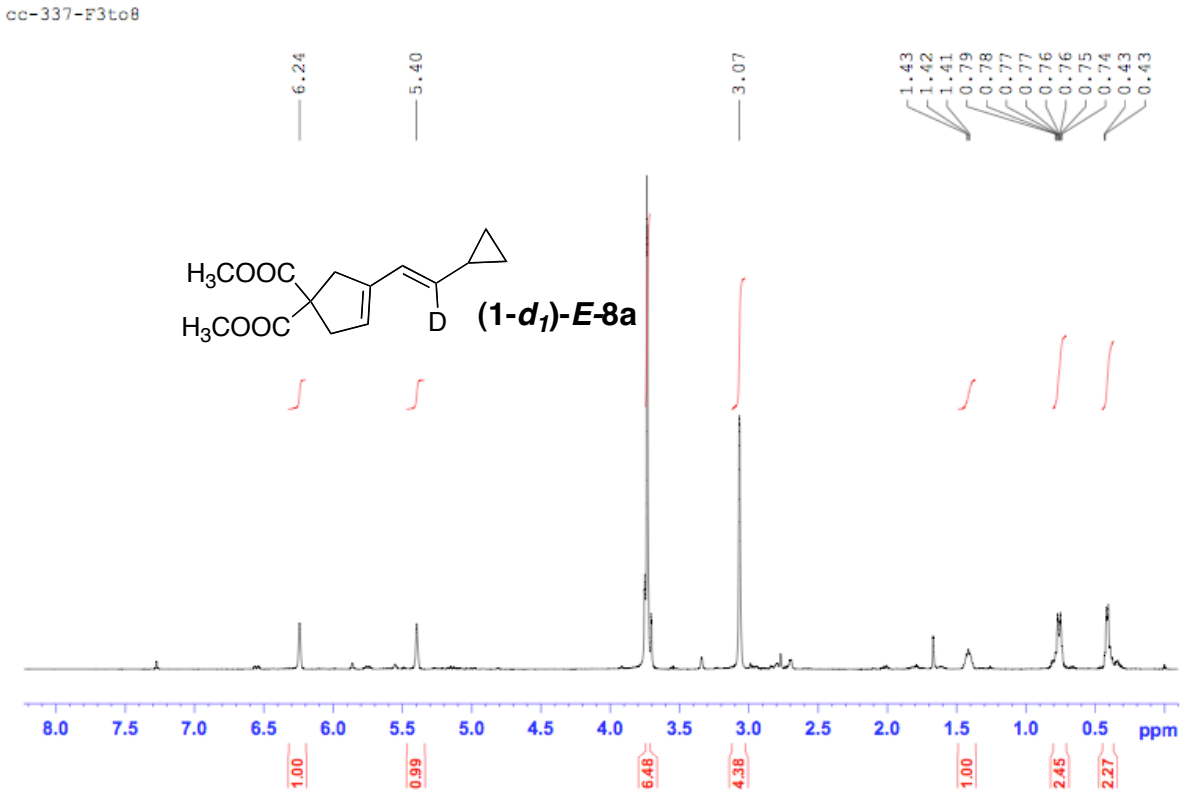

cc-335-F25to44
170.29
139.59
139.36
139.14
119.95
78.96
71.27
57.21
52.66
35.17
22.57
13.49
6.60
H3COOC
H3COOC
D
(1-d1)-E-7b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

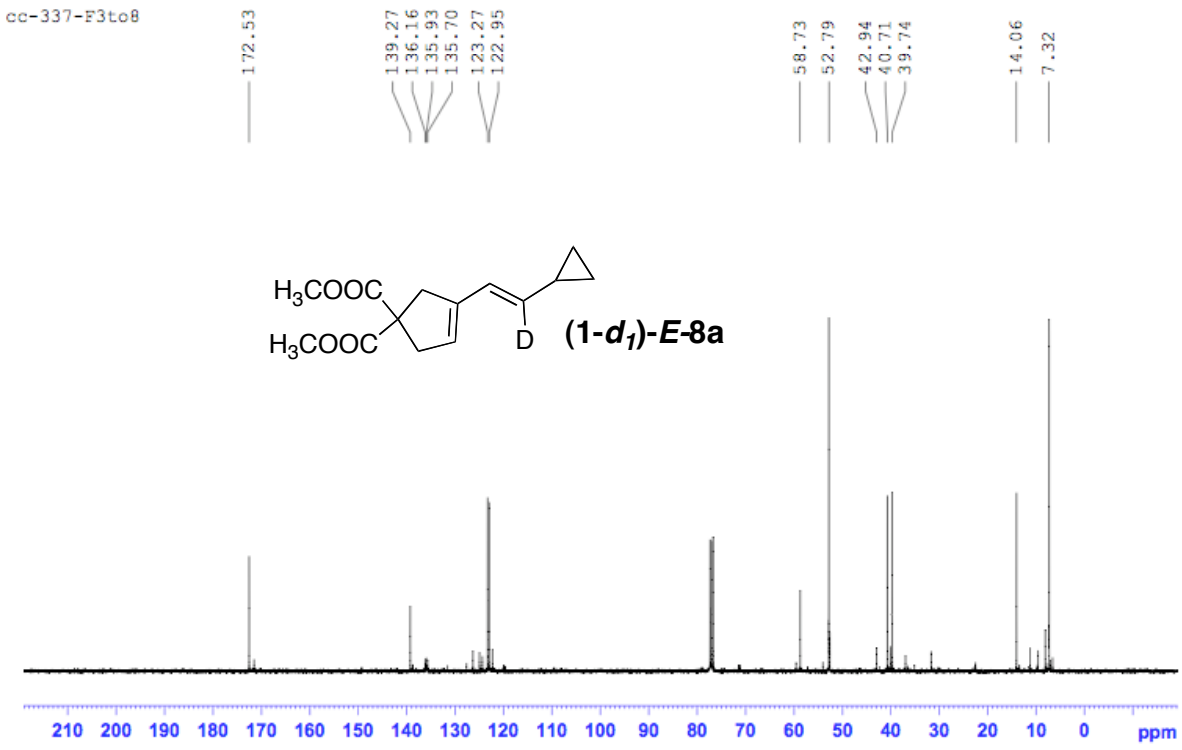

cc-356-F9to23
5.31
5.30
5.29
5.27
5.25
5.23
5.14
5.12
5.10
5.08
3.73
2.80
2.78
2.73
2.71
1.36
1.35
1.34
1.33
1.32
1.31
1.30
0.68
0.67
0.67
0.66
0.65
0.65
0.64
D
(7-d1)-E-7a
MeO2C
MeO2C
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.04
1.07
0.54
5.93
2.08
2.00
1.01
1.97
2.08

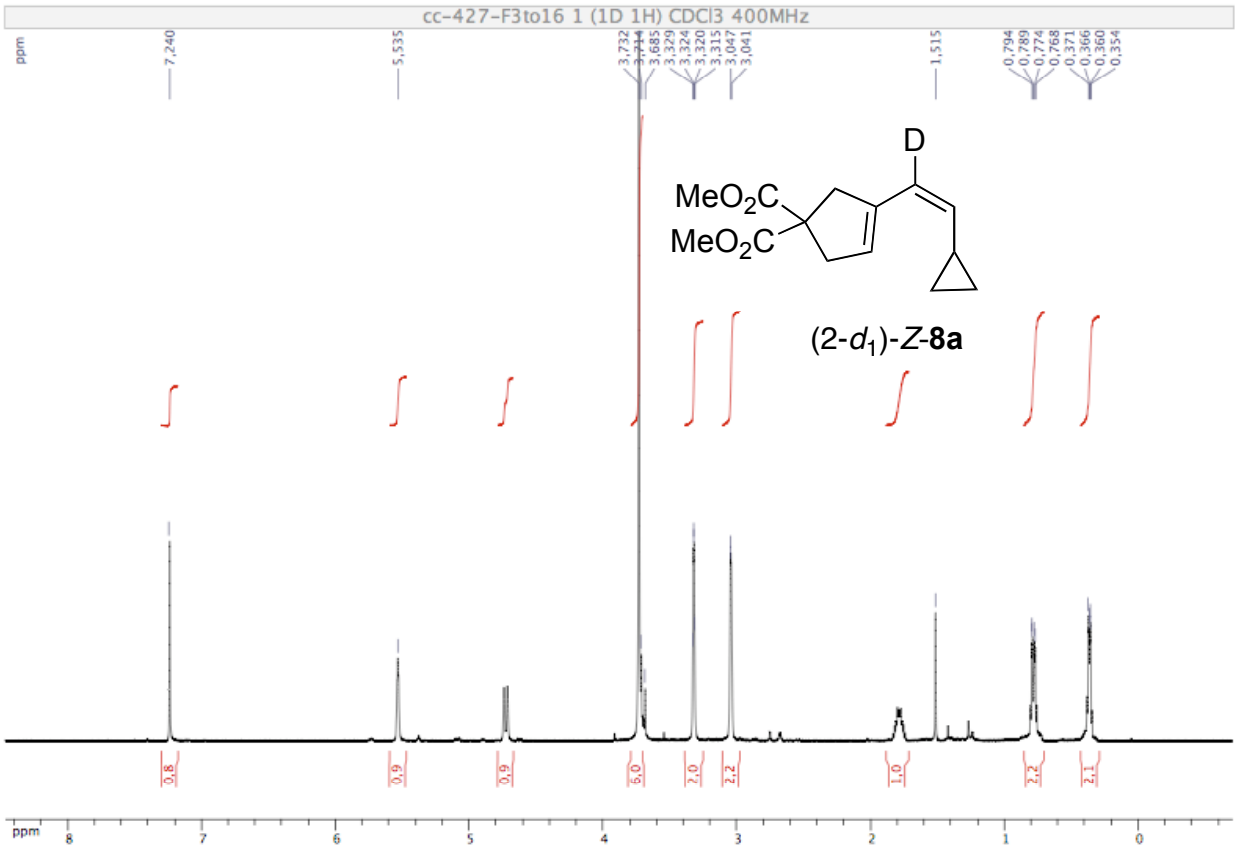

cc-356-F9to23
170.29
139.72
119.84
77.32
77.01
76.69
71.42
71.04
57.21
52.67
35.22
22.54
13.60
7.10
6.62
D
(7-d1)-E-7a
MeO2C
MeO2C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

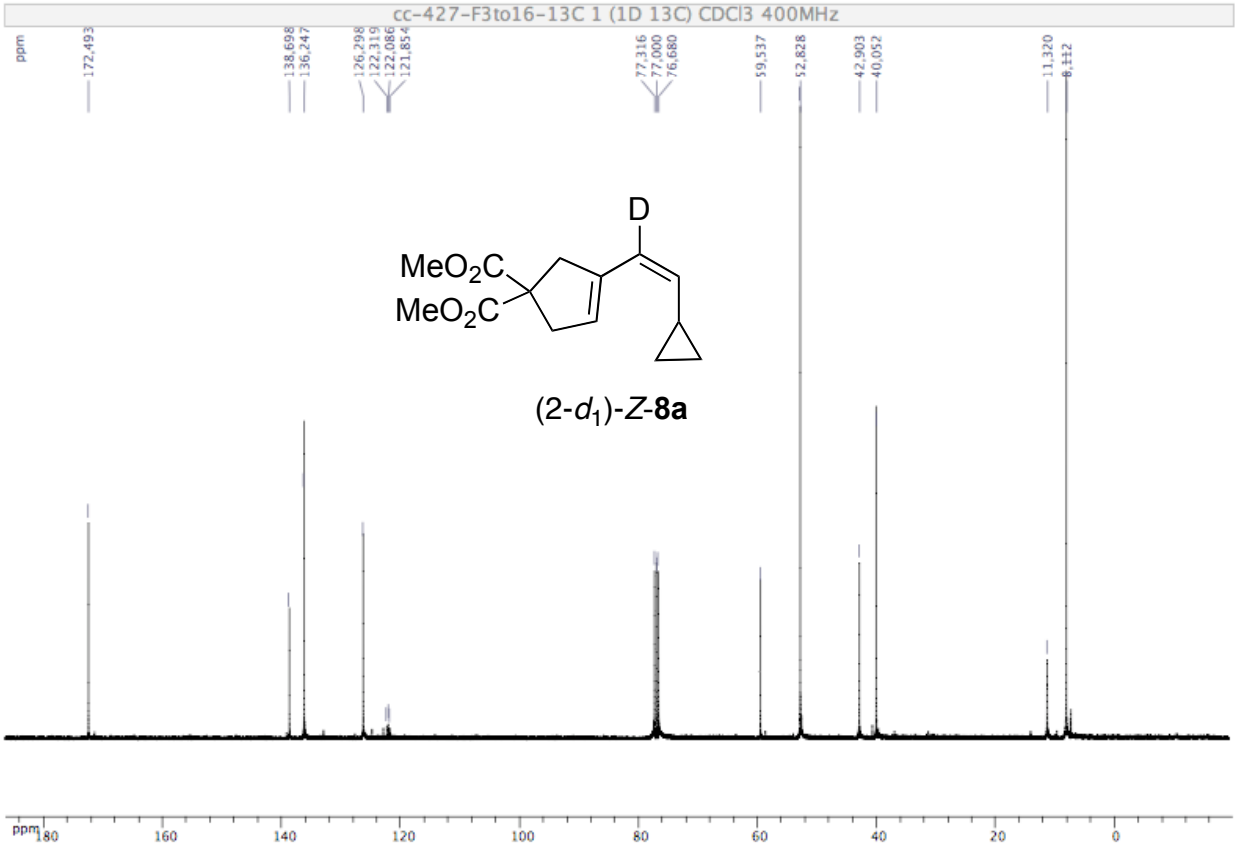

cc-336-F3to9
5.86
5.55
3.76
3.75
3.74
3.34
3.06
0.81
0.80
0.79
0.38
H3COOC
H3COOC
D
(1-d1)-Z-8a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
7.12
2.14
2.34
1.04
2.29
2.26

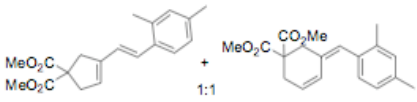

cc-336-F3to9
172.53
138.76
136.27
136.04
135.81
126.32
122.27
59.56
52.84
42.94
40.07
11.28
8.10
H3COOC
H3COOC
D
(1-d1)-Z-8a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


cc-337-F3to8
6.24
5.40
3.07
1.43
1.42
1.41
0.79
0.78
0.77
0.77
0.76
0.76
0.75
0.74
0.43
0.43
H3COOC
H3COOC
D
(1-d1)-E-8a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.99
6.48
4.38
1.00
2.45
2.27

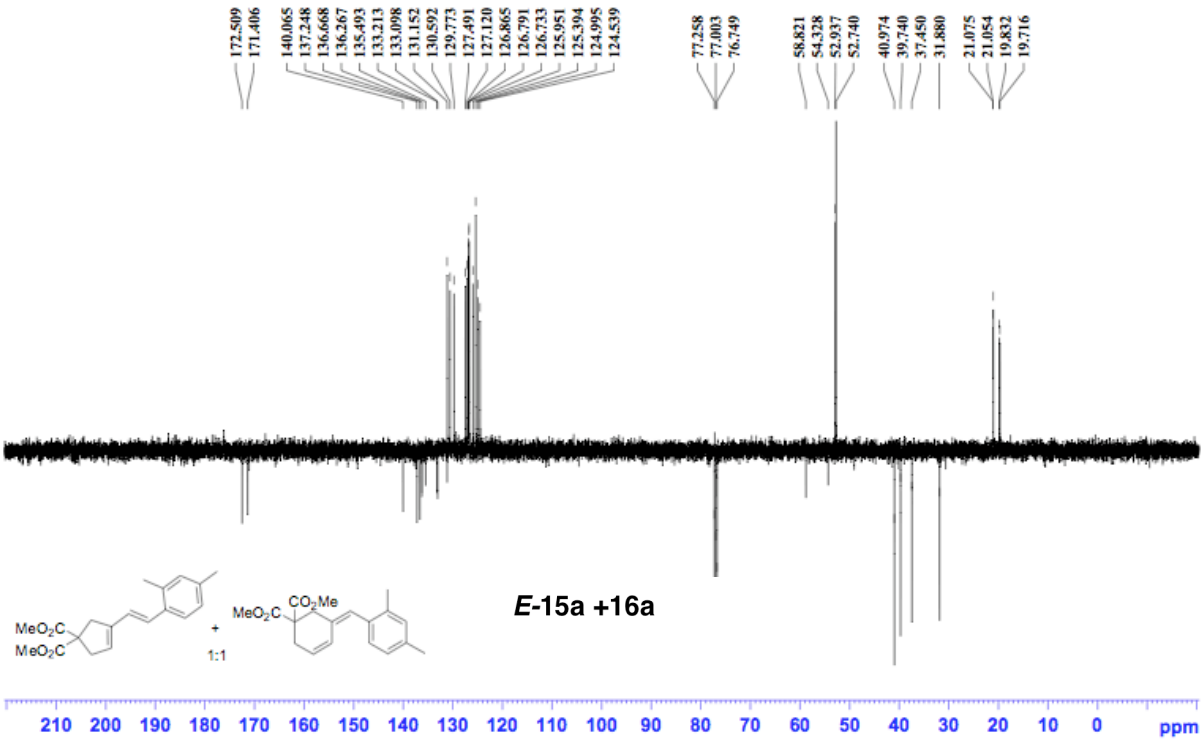

cc-337-F3to8
172.53
139.27
136.16
135.93
135.70
123.27
122.95
58.73
52.79
42.94
40.71
39.74
14.06
7.32
H3COOC
H3COOC
D
(1-d1)-E-8a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


cc-427-F3to16 1 (1D 1H) CDCl3 400MHz
D
MeO2C
MeO2C
(2-d1)-Z-8a

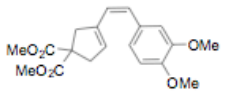

cc-427-F3to16-13C 1 (1D 13C) CDCl3 400MHz
D
MeO2C
MeO2C
(2-d1)-Z-8a



***E*-15a +16a**

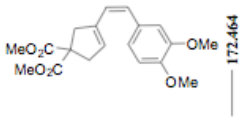


***E*-15a +16a**


MeO2C
MeO2C
OMe
OMe

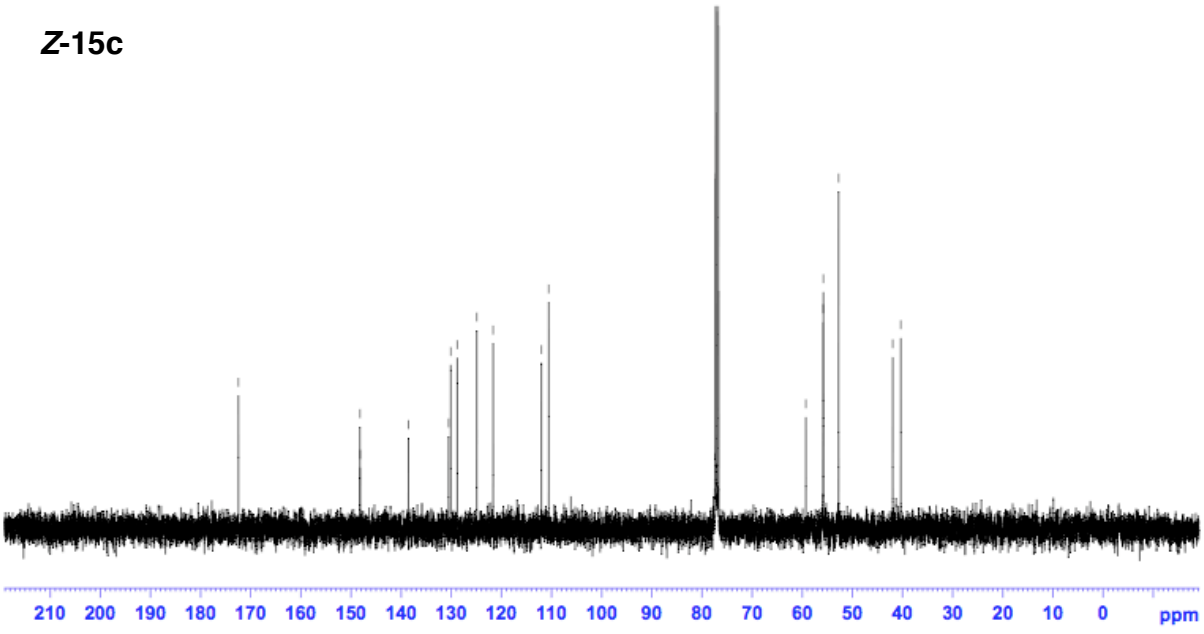
***Z*-15c**

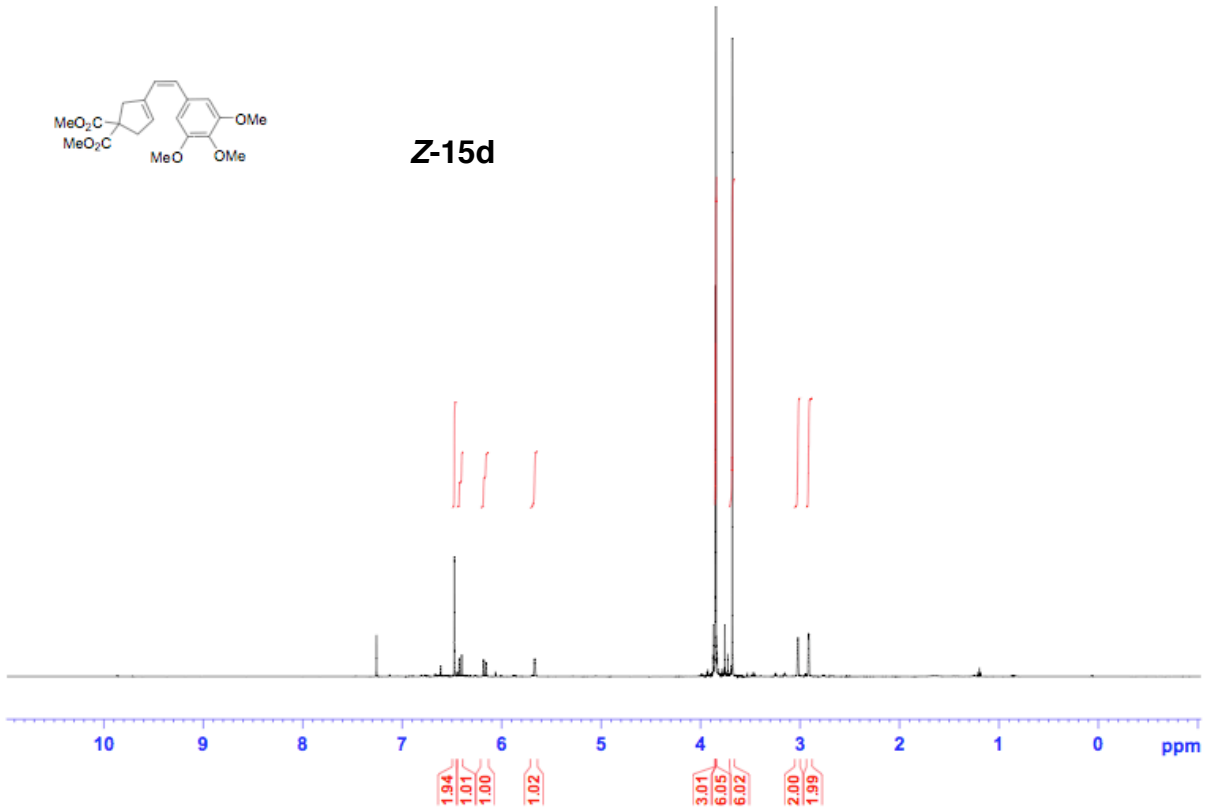
10
9
8
7
6
5
4
3
2
1
0
ppm
3.32
1.04
1.00
1.00
6.98
6.42
2.08
2.03

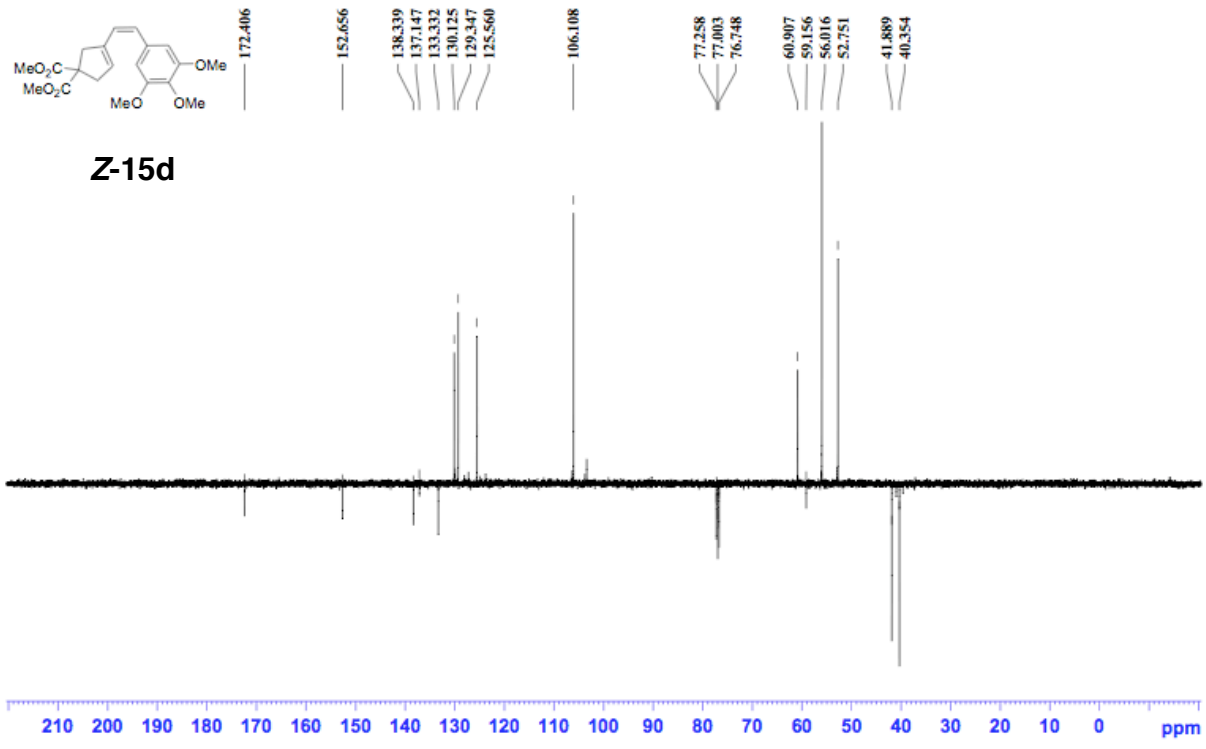

MeO2C
MeO2C
OMe
OMe

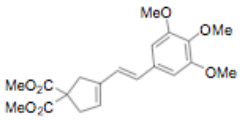

172.464
148.228
148.166
138.542
130.547
130.099
128.806
124.930
121.652
112.038
110.558
77.323
77.005
76.689
59.278
55.836
55.779
52.766
41.949
40.336

***Z*-15c**

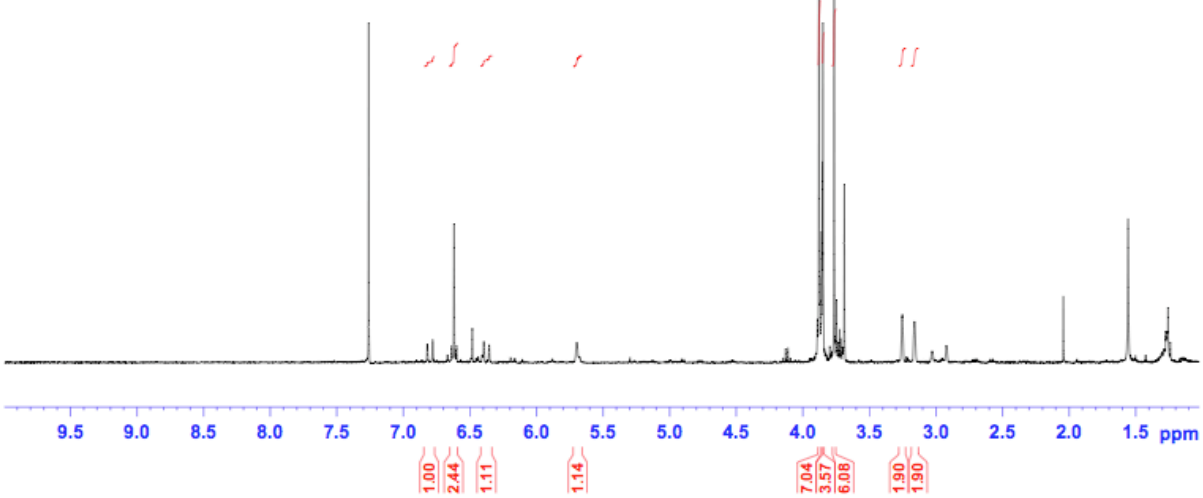

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

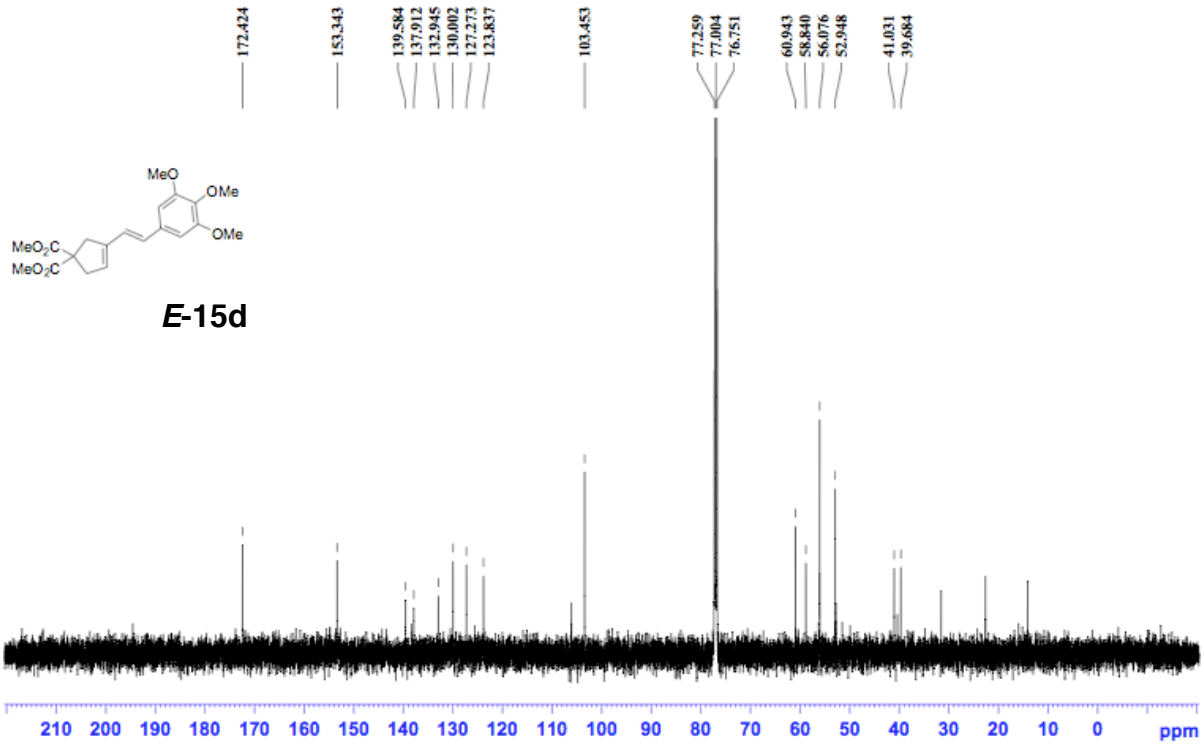

MeO2C
MeO2C
OMe
MeO
OMe
Z-15d
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.01
1.00
1.02
3.01
6.05
6.02
2.00
1.99


MeO2C
MeO2C
OMe
MeO
OMe
Z-15d
172.406
152.656
138.339
137.147
133.332
130.125
129.347
125.560
106.108
77.258
77.003
76.748
60.907
59.156
56.016
52.751
41.889
40.354
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


MeO
OMe
OMe
MeO2C
MeO2C

***E*-15d**


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.00
2.44
1.11
1.14
7.04
3.57
6.08
1.90
1.90


172.424
153.343
139.584
137.912
132.945
130.002
127.273
123.837
103.453
77.259
77.004
76.751
60.943
58.840
56.076
52.948
41.031
39.684
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

MeO
OMe
OMe
MeO2C
MeO2C

***E*-15d**