Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

The Role of Cyclobutenes in Gold(I)-Catalysed Skeletal Rearrangement of 1,6-Enynes

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Contents

General methods

All reactions were carried out under Ar on N_2 in dry freshly distilled solvents under anhydrous conditions. Solvents were used from a Solvent Purification System (SPS-400-6). Thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merk GF234). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm) with distilled solvents. NMR spectra were recorded at 23 ºC on the following spectrometers: Bruker Avance 400 Ultrashield (400 MHz in ^{1}H, 100 MHz in ^{13}C, and 161.32 MHz in ^{31}P) and Bruker Avance 500 Ultrashield (500 MHz in ^{1}H, 100 MHz in ^{13}C, and 202.5 MHz in ^{31}P). Melting points were determined using a Büchi-B450 apparatus. Elemental analyses were carried out in Universidad Complutense de Madrid. Mass Spectrometry was performed on a Waters LCT Premier (ESI) or Waters GCT (EI, CI) spectrometers.

The following known starting compounds were prepared following the reported procedures: 1-(4-(3-bromoprop-1-ynyl)phenyl)ethanone,[1] 1-(3-bromoprop-1-ynyl)-4-chlorobenzene,[2] dimethyl 2-(3-phenylprop-2-ynyl)malonate,[3] dimethyl 2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate,[4] dimethyl 2-(3-(3-methoxyphenyl)prop-2-ynyl)malonate,[3] dimethyl 2-(3-(4-(trifluoromethyl)phenyl)prop-2-ynyl)malonate,[5] dimethyl 2-(3-(4-cyanophenyl)prop-2-ynyl)malonate,[3] dimethyl 2-(3-(4-nitrophenyl)prop-2-ynyl)malonate,[3] dimethyl 2-allyl-2-(3-phenylprop-2-ynyl)malonate (**14a**),[3,6] dimethyl 2-allyl-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (**14b**),[7] dimethyl 2-allyl-2-(3-(4-chlorophenyl)prop-2-ynyl)malonate (**14f**),[8] dimethyl 2-(3-(4-acetylphenyl)prop-2-yn-1-yl)-2-allylmalonate (**14g**),[8] dimethyl 2-Allyl-2-(3-(4-(trifluoromethyl)phenyl)prop-2-ynyl)malonate (**14h**),[8] dimethyl 2-allyl-2-(3-(4-nitrophenyl)prop-2-ynyl)malonate (**14j**),[7] dimethyl 2-(but-2-ynyl)-2-(but-3-enyl)malonate (**29**),[9] and dimethyl 2-(2-ethynylbenzyl)-2-(2-methylallyl)malonate (**38**).[10]

The following cycloisomerised products are known: (1*R**,5*S**)-dimethyl 7-phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (**17a**),[3,6] (*E*)-dimethyl 3-(4-nitrostyryl)cyclopent-3-ene-1,1-dicarboxylate (**15j**),[11] dimethyl 2a-methyl-2a,3-dihydro-2*H*-benzo[*a*]cyclobuta[*c*][7]annulene-4,4(5*H*)-dicarboxylate (**39**).[10]

Gold(I) complexes **A**,[12] **B**, **C**, and **E**,[13] and platinum complex **D**[14] were prepared according to previously described methods.

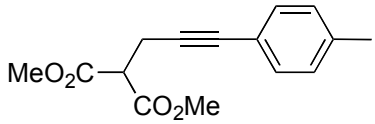
Activation parameters for the [2+2] cycloaddition of 1,8-enyne **38** and for the skeletal rearrangement of 1,6-enyne **40** were determined as previously described.[15]

General Procedures for the Preparation of 1,6-Enynes 14, 27, 29, and 31a-b

General procedure for Sonogashira cross-couplings:[16] CuI (0.1 mmol) and $[Pd(PPh_3)_2Cl_2]$ (0.05 mmol) were suspended in *i*-Pr_2NH, and stirred for 5 min. Then the corresponding aryl halide (1.3 mmol) and a solution of the alkyne (1 mmol) in *i*-Pr_2NH were added sequentially. The reaction was stirred at 23 ºC (unless other temperature was specified) until T.L.C. showed total conversion. The crude mixture was dissolved in Et_2O, filtered through Celite, and purified by chromatography to give the substituted alkynes.

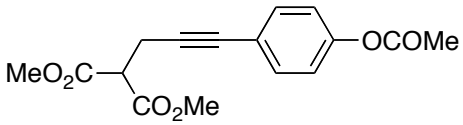
General procedure for the alkylation of malonate derivatives: To a suspension of NaH (60% in mineral oil, 10 mmol) in DMF (15 mL) at 0 ºC, was added the dimethyl malonate (10 mmol) and the mixture was stirred at 23 ºC for 30 min. Then, the corresponding electrophile was added dropwise. After extractive work-up (Et_2O/HCl (3.5%)) and chromatography (EtOAc:hexane mixtures), the corresponding enyne was obtained.

Dimethyl 2-(3-*p*-tolylprop-2-ynyl)malonate



Starting from dimethyl propargyl malonate and 4-iodotoluene, the title compound was obtained in 84% yield as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.80 (s, 6H), 3.71 (t, J = 7.8 Hz, 1H), 3.02 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 138.1, 131.5, 129.0, 120.0, 84.4, 82.6, 52.8, 51.3, 21.4, 19.5; HMRS-ESI calcd. for $C_{15}H_{16}O_4Na$ $[M+Na]^+$: 283.0946. Found: 283.0959.

Dimethyl 2-(3-(4-Acetoxyphenyl)prop-2-ynyl)malonate

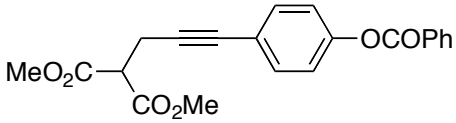


To a suspension of the 4-iodophenol (1.0 g, 4.54 mmol) in pyridine was added at room temperature acetic anhydride (4.3 mL, 45 mmol) and the mixture was stirred for 3 h. The reaction was quenched adding a solution of HCl (10%) and the organic layer was

extracted with CH_2Cl_2 (50 mL x 3). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography to give 4-iodophenyl acetate as a brown oil (1.18 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 9.2 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 150.52, 138.5, 123.8, 89.9, 21.1.

Starting from dimethyl propargyl malonate and 4-iodophenyl acetate, the title compound was obtained in 60% yield as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 3.77 (s, 6H), 3.67 (t, J = 7.9 Hz, 1H), 2.98 (d, J = 7.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.3, 132.7, 121.7, 120.9, 85.3, 81.7, 52.9, 51.2, 21.1, 19.5. HRMS-ESI calcd. for $C_{16}H_{16}O_6Na$ $[M+Na]^+$: 327.0845. Found: 327.0847.

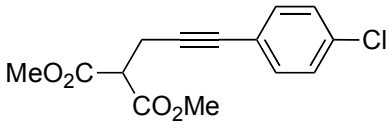
Dimethyl 2-(3-(4-(Benzoyloxy)phenyl)prop-2-ynyl)malonate



To a suspension of 4-iodophenol (1.075 g, 4.90 mmol) in CH_2Cl_2 (20 mL) were added at 0 ºC benzoyl chloride (0.57 mL, 4.90 mmol) and Et_3N (0.68 mL, 4.90 mmol) and the mixture was stirred for 3 h at 0º C. The reaction was diluted with more CH_2Cl_2 and washed with a solution of $NaHCO_3$ (1 M). The combined organic layers were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography to give 4-iodophenyl benzoate as brown oil (1.50 g, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 1.4, 8.2 Hz, 2H), 7.74 (dd, J = 2.0, 6.9 Hz, 2H), 7.52 (t, J = 7.6 Hz, 3H), 7.00 (dd, J = 2.6, 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 138.6, 133.6, 130.2, 128.7, 124.0, 89.9. HRMS-ESI calcd. for $C_{13}H_9IO_2Na$ $[M+Na]^+$: 346.9545. Found: 346.9551.

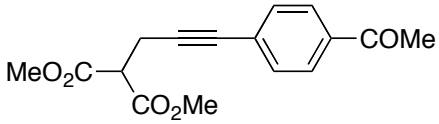
Starting from dimethyl propargyl malonate and 4-iodophenyl benzoate, the title compound was obtained in 87% as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 1.7, 8.3 Hz, 2H), 7.64 (td, J = 7.3, 2.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.43 (dd, J = 2.1, 6.9 Hz, 2H), 7.15 (dd, J = 2.1, 6.9 Hz, 2H), 3.78 (s, 6H), 3.70 (t, J = 7.8 Hz, 1H), 3.02 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.3, 132.9, 130.2, 128.6, 125.5, 121.7, 85.4, 81.8, 52.9, 51.2, 20.7, 19.4. HRMS-ESI calcd. for $C_{21}H_{18}O_6Na$ $[M+Na]^+$: 389.1001. Found: 389.1009.

Dimethyl 2-(3-(4-chlorophenyl)prop-2-ynyl)malonate



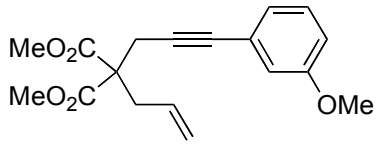
Starting from dimethyl propargyl malonate and 1-chloro-4-iodobenzene, the title compound was obtained in 99% yield as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 4H), 3.80 (s, 6H), 3.70 (t, J = 7.7 Hz, 1H), 3.01 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 134.0, 132.9, 128.5, 121.6, 86.3, 81.5, 52.8, 51.0, 19.5. HRMS-ESI calcd. for $C_{14}H_{13}O_4NaCl$ $[M+Na]^+$: 303.0400. Found: 303.0402.

Dimethyl 2-(3-(4-acetylphenyl)prop-2-ynyl)malonate



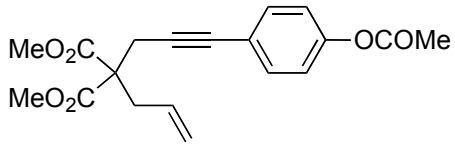
Starting from dimethyl propargyl malonate and the *p*-iodoacetophenone, the title compound was obtained in 90% yield as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.80 (s, 6H), 3.71 (t, J = 7.9 Hz, 1H), 3.04 (d, J = 7.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 168.3, 136.1, 131.8, 128.0, 88.9, 81.9, 53.4, 51.0, 26.6, 19.6. HRMS-ESI calcd. for $C_{16}H_{16}O_5Na$ $[M+Na]^+$: 311.0895. Found: 311.0884.

Dimethyl 2-Allyl-2-(3-(3-methoxyphenyl)prop-2-ynyl)malonate (14c)



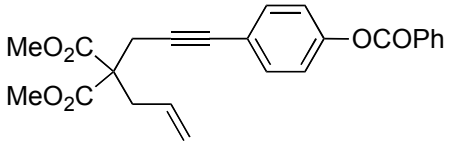
Starting from the corresponding substituted alkyne and allyl bromide, **14c** was obtained in 99% as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18(d, J = 16.4 Hz, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, J = 9.0, 2.8 Hz, 1H), 5.74-5.62 (m, 1H), 5.19 (dd, J = 17.1, 2.3 Hz, 1H), 5.16 (dd, J = 2.3, 19.7 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.01 (s, 2H), 2.87 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.3, 131.8, 129.3, 124.3, 119.9, 116.6, 114.5, 84.1, 83.6, 57.3, 55.3, 52.8, 36.8, 23.7. HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1205. Found: 339.1208.

Dimethyl 2-(3-(4-Acetoxyphenyl)prop-2-ynyl)-2-allylmalonate (14d)



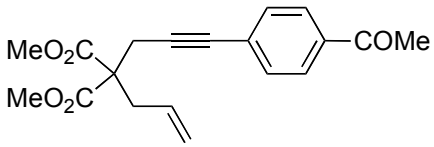
Starting from the corresponding substituted alkyne and allyl bromide, **14d** was obtained in 80% as a pale brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 5.67 (ddt, J = 17.5, 10.1, 7.5 Hz, 1H), 5.19 (dd, J = 17.0, 1.9 Hz, 1H), 5.14 (dd, J = 10.1, 2.0 Hz, 1H), 3.75 (s, 6H), 3.00 (s, 2H), 2.85 (d, J = 7.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.3, 150.4, 132.9, 132.0, 121.7, 121.0, 120.0, 84.5, 83.0, 57.4, 52.9, 37.0, 23.8, 21.3. HRMS-ESI calcd. for $C_{19}H_{20}O_6Na$ $[M+Na]^+$: 367.1158. Found 367.1147.

Dimethyl 2-Allyl-2-(3-(4-(benzoyloxy)phenyl)prop-2-ynyl)malonate (14e)



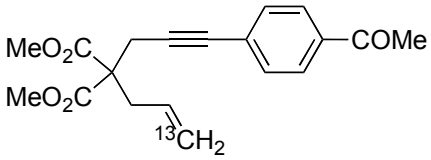
Starting from the corresponding substituted alkyne and allyl bromide, **14e** was obtained in 82% as a pale brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.1 Hz, 2H), 7.68 (t, J = 7.6, 2.8 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 5.80-5.66 (m, 1H), 5.25 (dd, J = 17.0, 1.9 Hz, 1H), 5.20 (dd, J = 10.1, 1.9 Hz, 1H), 3.81 (s, 6H), 3.07 (s, 2H), 2.92 (d, J = 7.4 Hz, 2H), 2.08 (s, 1H), 1.30 (t, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 164.9, 150.6, 133.7, 132.9, 131.75, 130.2, 129.3, 128.6, 128.4, 127.6, 125.6, 121.8, 120.9, 119.9, 84.4, 82.9, 57.3, 52.8, 36.8, 23.7, 20.70, 19.8. HRMS-ESI calcd. for $C_{24}H_{22}O_6Na$ $[M+Na]^+$: 429.1314. Found 429.1316.

Dimethyl 2-(3-(4-Acetylphenyl)prop-2-ynyl)-2-allylmalonate (14g)



Starting from the corresponding substituted alkyne and the corresponding allyl bromide, **14g** was obtained in 89% as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.75-5.04 (m, 1H), 5.20 (dd, J = 23.0, 1.9 Hz, 1H), 5.17 (dd, J = 16.0, 1.9 Hz, 1H), 3.77 (s, 6H), 3.05 (s, 2H), 2.86 (d, J = 7.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.1, 132.7, 130.2, 128.7, 123.9, 122.9, 115.1, 113.1, 82.9, 82.4, 57.3, 57.1, 55.0, 53.2, 52.4, 35.3, 29.4, 23.3, 17.8, 12.7. HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1220.

^{13}C-Dimethyl 2-(3-(4-Acetylphenyl)prop-2-ynyl)-2-allylmalonate (14g-^{13}C)

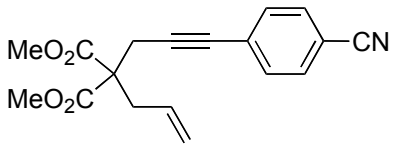


An ozone stream was bubbled during 30 minutes through a solution of dimethyl allyl malonate (2 mL, 12.4 mmol) in MeOH at -78 ºC. Then PPh_3 (4.9 g, 18.6 mmol) was added and the mixture was stirred 18 h at -78 ºC and then allowed to warm up to room temperature. The crude mixture was purified by flash chromatography (4:1 hexane/ethyl acetate) to give 1.87 g (87%) of the dimethyl 2-(2-oxoethyl)malonate as an colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 3.89 (d, J = 13.8 Hz, 1H), 3.74 (s, 6H), 3.09 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 168.8, 52.9, 45.2, 42.4.

To a mixture of $^{13}CH_3PPh_3I$ (0.61 g, 1.52 mmol) and dimethyl 2-(2-oxoehtyl)malonate (0.20 g, 1.17 mmol) in THF (30 mL) was added 0.7 M NaHMDS in THF (3.9 mL, 2.73 mmol) at -78 ºC, and the mixture was warmed slowly to room temperature. After the mixture was stirred for 20 h, the reaction was quenched by adding saturated aqueous NH_4Cl (150 mL) and the mixture was extracted with Et_2O (50 mL x 3). The organic layer was washed with water (50 mL x 3) and dried over $MgSO_4$. After the solvent was removed, the residue was used for the next step.

Starting from ^{13}C-dimethyl allyl malonate and 1-(4-(3-bromoprop-1-ynyl)phenyl)ethanone, **14g-^{13}C** was obtained in 22% overall yield as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.75-5.04 (m, 1H), 5.20 (dd, J = 23.0, 1.9 Hz, 1H), 5.17 (dd, J = 16.0, 1.9 Hz, 1H), 3.77 (s, 6H), 3.05 (s, 2H), 2.86 (d, J = 7.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 131.8, 128.2, 120.0, 119.8, 87.8, 82.9, 52.8, 36.9, 26.4, 23.8. HRMS-ESI calcd. for $^{12}C_{18}{}^{13}CH_{20}O_5Na$ $[M+Na]^+$: 352.1242. Found: 352.1231.

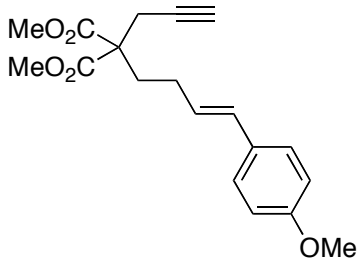
Dimethyl 2-Allyl-2-(3-(4-cyanophenyl)prop-2-ynyl)malonate (14i)



Starting from the corresponding substituted alkyne and allyl bromide, **14i** was obtained in 75% yield as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 5.74-5.62 (m, 1H), 5.25-5.16 (m, 2H), 3.79 (s, 6H), 3.07 (s, 2H), 2.88 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 132.2, 132.0,

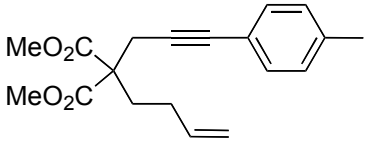
131.6, 128.1, 120.1, 118.5, 111.5, 89.3, 82.3, 57.1, 52.9, 36.9, 23.7. HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1067. Found: 334.1055.

(*E/Z*)-Dimethyl 2-(4-(4-Methoxyphenyl)but-3-en-1-yl)-2-(prop-2-yn-1-yl)malonate (27)



To a mixture of 4-methoxybenzyl)triphenylphosphonium chloride (1.6 mmol) in dry THF (20 mL) was added *t*-BuOK (1.8 mmol) at 0 ºC. The mixture was stirred over 40 min at this temperature and the reaction was warmed to room temperature and stirred 10 more min at this temperature. Then dimethyl 2-(3-oxopropyl)-2-(prop-2-yn-1-yl)malonate (1.3 mmol)[17] was added to the mixture. The mixture was stirred 1 h and was quenched adding a saturated solution of NH_4Cl. The organic layer was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (10:1 hexane: ethyl acetate) to give **27** as a pail yellow oil in 74% yield as a 2.5/1 *E/Z* mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ (*E*) 7.26 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 6.35 (d, J = 15.7 Hz, 1H), 6.07-5.98 (m, 1H), 3.79 (s, 3H), 3.73 (s, 6H), 2.88 (bs, 2H), 2.27-2.22 (m, 2H), 2.17-2.11 (m, 2H), 2.0 (bs, 1H); (Z) 7.19 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.39 (d, J = 10.0 Hz, 1H), 5.58-5.50 (m, 1H), 3.80 (s, 3H), 3.71 (s, 6H), 2.84 (bs, 2H), 2.27-2.22 (m, 2H), 2.17-2.11 (m, 2H), 2.0 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 159.0, 158.5, 130.5, 130.2, 130.0, 129.6, 129.4, 127.3, 126.9, 114.1, 113.8, 78.9, 71.7, 56.8, 55.4, 53.0, 32.3, 32.0, 27.8, 23.6, 23.2, 23.1. HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1365. Found: 353.1375.

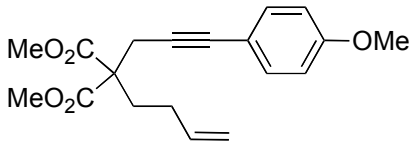
Dimethyl 2-(But-3-enyl)-2-(3-p-tolylprop-2-ynyl)malonate (31a)



Starting from the corresponding substituted alkyne and 4-bromo-1-butene, **31a** was obtained in 70% yield as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.88-5.77 (m, 1H), 5.12-4.98 (m, 2H), 3.77 (s, 6H),

3.03 (s, 2H), 2.34 (s, 3H), 2.28-2.21 (m, 2H), 2.09-2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.0, 137.3, 131.5, 128.9, 120.1, 115.3, 83.6, 83.3, 57.1, 52.7, 31.5, 28.4, 23.9, 21.4. HRMS-ESI calcd. for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1420. Found: 337.1416.

Dimethyl 2-(But-3-enyl)-2-(3-(4-methoxyphenyl)prop-2-ynyl)malonate (31b)

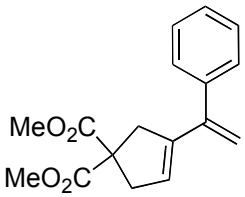


Starting from the corresponding substituted alkyne and 4-bromo-1-butene, **31b** was obtained in 80% as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 5.87-5.73 (m, 1H), 5.10-4.98 (m, 2H), 3.77 (s, 6H), 3.11 (s, 2H), 2.25-2.18 (m, 2H), 2.08-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.4, 137.4, 133.0, 115.3, 113.8, 83.3, 82.5, 57.1, 55.3, 52.7, 31.5, 28.4, 23.9. HRMS-ESI calcd. for $C_{19}H_{22}O_6Na$ $[M+Na]^+$: 353.1365. Found: 353.1371.

General method for the gold(I)-catalyzed reactions of Table 1.

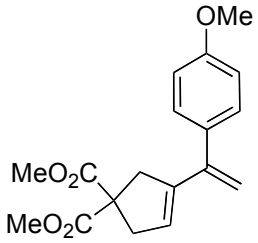
The corresponding substituted 1,6-enynes (50 mg), the gold catalyst (5 mol%) were heated for 10-60 min in CH_2Cl_2 (1 mL) at 80 °C in a microwave oven (Biotage Initiator). When the reactions were finished, Et_3N was added

Dimethyl 3-(1-Phenylvinyl)cyclopent-3-ene-1,1-dicarboxylate (15a)



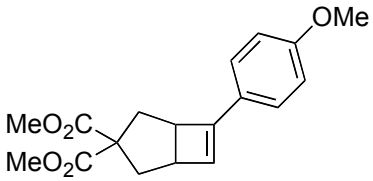
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 5.44 (t, J = 2.6 Hz, 1H), 5.19 (s, 1H), 5.13 (s, 1H), 3.77 (s, 6H), 3.30 (d, J = 1.9 Hz, 2H), 3.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 145.3, 141.3, 140.5, 128.5, 128.0, 127.4, 114.8, 58.9, 53.0, 41.3, 41.1. HRMS-ESI calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1283. Found: 287.1271.

Dimethyl 3-(1-(4-Methoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15b)



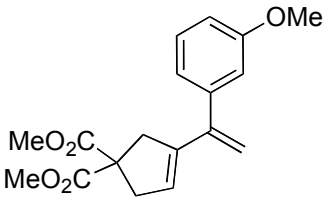
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.89-6.85 (m, 2H), 5.49-5.45 (m, 1H), 5.13 (s, 1H), 5.11 (s, 1H), 3.83 (s, 3H), 3.79 (s, 6H), 3.30 (d, J = 1.4 Hz, 2H), 3.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.0, 144.8, 140.8, 133.7, 129.51, 127.2, 114.1, 113.3, 58.9, 55.3, 52.9, 41.3, 41.2. HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1198.

Dimethyl 6-(4-Methoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (17b)



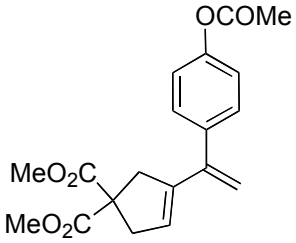
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.92 (s, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.61-3.57 (m, 1H), 3.33-3.28 (m, 1H), 3.26 (s, 3H), 2.78 (d, J = 13.2 Hz, 1H), 2.67 (d, J = 13.2 Hz, 1H), 2.00-1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.0, 146.0, 126.9, 126.0, 125.7, 60.6, 55.0, 52.5, 51.6, 45.5, 43.1, 35.3, 33.8. HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208. Found: 339.1198.

Dimethyl 3-(1-(3-Methoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15c)



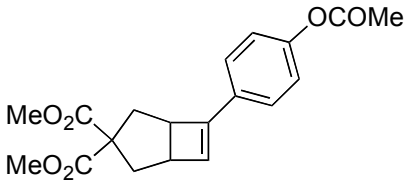
Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 1H), 6.92-6.83 (m,, 3H), 5.49 (s, 1H), 5.18 (d, J = 14.6 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 3.31 (s, 2H), 3.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.0, 145.2, 142.5, 140.2, 128.7, 127.3, 121.0, 114.7, 114.0, 113.0, 58.9, 55.5, 55.3, 53.0, 41.3, 41.1. HRMS-ESI calcd. for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1214. Found: 339.1208.

Dimethyl 3-(1-(4-Acetoxyphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15d)



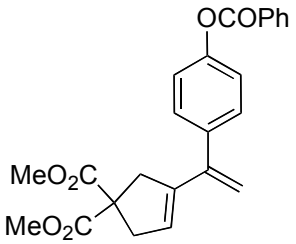
Light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 2.2, 6.3 Hz, 2H), 7.03 (dd, J = 2.1, 6.5 Hz, 2H), 5.45 (t, J= 2.8 Hz, 1H), 5.18 (s, 1H), 5.13 (s, 1H), 3.77 (s, 6H), 3.29 (d, J = 1.7 Hz, 2H), 3.12 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.0, 144.3, 140.3, 138.7, 129.5, 127.5, 120.8, 115.0, 58.9, 53.0, 41.3, 41.1, 21.2. This compound undergoes partial decomposition at room temperature and a HRMS could not be obtained.

Dimethyl 6-(4-Acetoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (17d)



Light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 2.0, 6.8 Hz, 2H), 7.05 (dd, J = 2.0, 6.6 Hz, 2H), 6.07 (s, 1H), 3.70 (s, 3H), 3.63 (dd, J = 3.4, 7.3, 1H), 3.35 (dd, J = 3.4, 7.6 Hz, 1H), 3.26 (s, 3H), 2.80 (d, J = 12.7 Hz, 1H), 2.69 (d, J = 12.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.9, 150.2, 145.8, 131.2, 129.9, 125.7, 121.5, 60.9, 52.9, 51.9, 45.8, 43.5, 35.3, 34.0, 21.2. HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

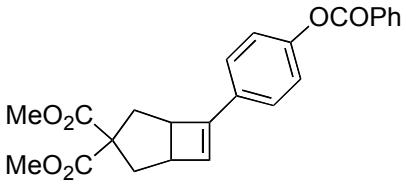
Dimethyl 3-(1-(4-(Benzoyloxy)phenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15e)



White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.1 Hz, 2H), 7.64 (t, J = 8.2 Hz, 1H), 7.52 (t, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 5.49 (bs, 1H), 5.19 (d, J = 16.1Hz, 2H), 3.78 (s, 6H), 3.31 (s, 2H), 3.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 140.1, 133.3, 129.9, 129.2, 128.3, 127.3, 125.7, 120.9, 114.8, 114.3, 58.6, 52.7, 41.1, 40.1. This compound undergoes partial

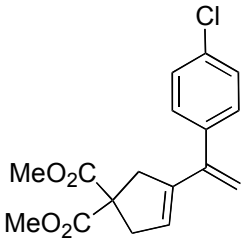
decomposition at room temperature and a satisfactory mp and HRMS could not be obtained.

Dimethyl 6-(4-(Benzoyloxy)phenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (17e)



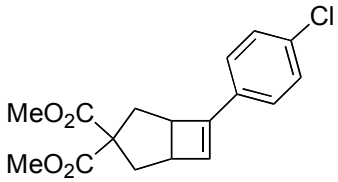
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.09 (s, 1H), 3.70 (s, 3H), 3.64 (dd, J = 7.4, 3.6 Hz, 1H), 3.35 (dd, J = 7.6, 3.4 Hz, 1H), 3.29 (s, 3H), 2.81 (d, J = 13.4 Hz, 1H), 2.70 (d, J = 13.4 Hz, 1H), 2.06-1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 164.8, 150.2, 145.5, 133.4, 130.9, 129.9, 129.7, 128.3, 125.5, 121.4, 60.6, 51.6, 45.5, 43.2, 35.1, 33.7, 22.4, 13.9. This compound undergoes partial decomposition at room temperature and a HRMS could not be obtained.

Dimethyl 3-(1-(4-Chlorophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15f)



Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 5.43 (s, 1H), 5.21 (s, 1H), 5.14 (s, 1H), 3.75 (s, 6H), 3.30 (s, 2H), 3.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 143.7, 139.7, 139.1, 132.6, 129.6, 127.7, 127.1, 115.1, 58.8, 53.0, 41.3, 41.1. HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

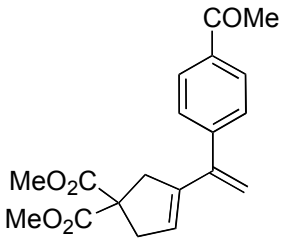
Dimethyl 6-(4-Chlorophenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (17f)



Brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 4H), 6.08 (s, 1H), 3.77 (s, 3H), 3.63-3.58 (m, 1H), 3.35-3.30 (m, 1H), 3.27 (s, 3H), 2.76 (d, J = 13.6 Hz, 1H), 2.67

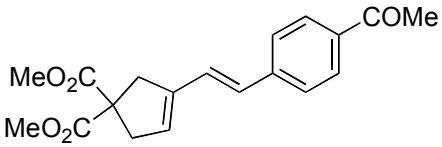
(d, J = 13.6 Hz, 1H), 2.06-1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 145.5, 130.3, 128.5, 128.0, 125.7, 60.8, 52.9, 51.9, 45.7, 43.6, 35.2, 33.9. HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

Dimethyl 3-(1-(4-Acetylphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15g)



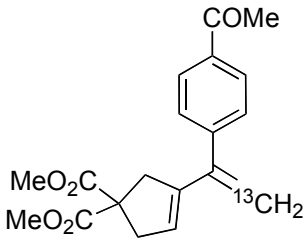
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 3.76 (s, 6H), 3.35 (s, 2H), 3.18 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 144.7, 140.2, 128.9, 128.4, 127.9, 115.9, 59.0, 53.2, 41.6, 41.3, 29.9, 26.9. HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1208.

(*E*)-dimethyl 3-(4-Acetylstyryl)cyclopent-3-ene-1,1-dicarboxylate (16g)



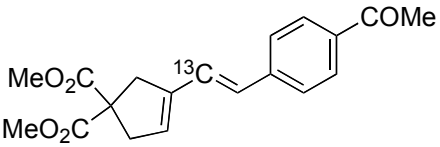
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 5.82 (s, 1H), 3.82 (s, 6H), 3.29 (s, 2H), 3.20 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 142.1, 139.7, 136.1, 129.7, 129.0, 128.9, 127.1, 126.6, 59.0, 53.2, 41.3, 39.8, 26.8. HRMS-ESI calcd. for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208. Found: 351.1208.

^{13}C-Dimethyl 3-(1-(4-Acetylphenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15g-^{13}C)



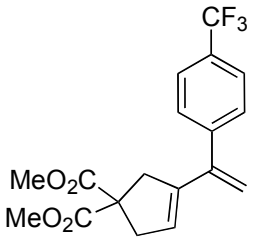
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 3.76 (s, 6H), 3.35 (s, 2H), 3.18 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.9.

^{13}C-(*E*)-dimethyl 3-(4-Acetylstyryl)cyclopent-3-ene-1,1-dicarboxylate (16g-^{13}C)



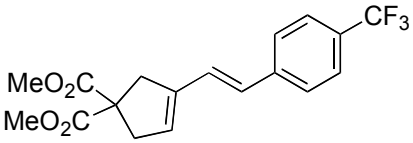
Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 5.82 (s, 1H), 3.82 (s, 6H), 3.29 (s, 2H), 3.20 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.1.

Dimethyl 3-(1-(4-(Trifluoromethyl)phenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15h)



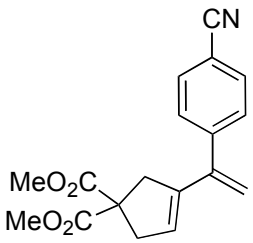
Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 5.37 (s, 1H), 5.25 (s, 1H), 5.16 (s, 1H), 3.77 (s, 6H), 3.30 (d, J = 1.8 Hz, 2H), 3.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 144.9, 144.3, 140.0, 128.8, 128.4, 127.8, 126.4, 125.5, 124.9, 115.8, 58.8, 53.0, 41.4, 41.1. This compound undergoes partial decomposition at room temperature and a HRMS could not be obtained.

(*E*)-dimethyl 3-(4-(Trifluoromethyl)styryl)cyclopent-3-ene-1,1-dicarboxylate (16h)



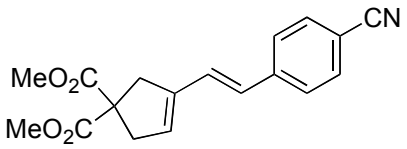
Brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 16.1 Hz, 1H), 6.45 (d, J = 16.1 Hz, 1H), 5.77 (s, 1H), 3.77 (s, 6H), 3.26 (s, 2H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 140.7, 139.4, 129.3, 128.5, 126.6, 126.4, 125.6, 125.5, 58.8, 53.0, 41.1, 39.6.

Dimethyl 3-(1-(4-Cyanophenyl)vinyl)cyclopent-3-ene-1,1-dicarboxylate (15i)



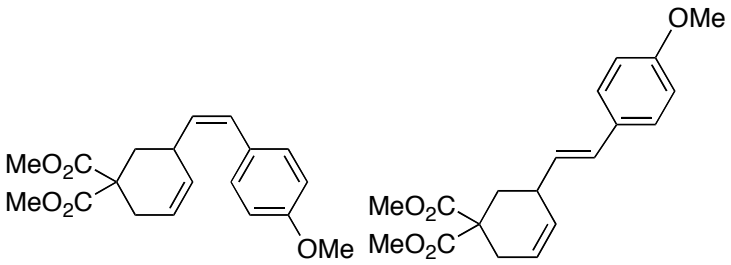
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 5.37 (s, 1H), 5.28 (s, 1H), 5.17 (s, 1H), 3.77 (s, 6H), 3.29 (s, 2H), 3.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 139.7, 131.9, 131.7, 129.2, 128.0, 116.3, 58.7, 53.0, 41.4, 41.0. HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1055. Found: 334.1042.

(*E*)-Dimethyl 3-(4-Cyanostyryl)cyclopent-3-ene-1,1-dicarboxylate (16i)



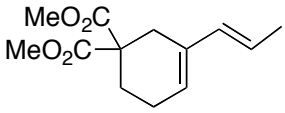
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 15.8 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 5.83 (s, 1H), 3.77 (s, 6H), 3.26 (s, 2H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 141.7, 139.3, 132.4, 130.4, 128.1, 127.8, 126.7, 125.1, 119.0, 110.5, 58.8, 53.1, 41.2, 39.5. HRMS-ESI calcd. for $C_{18}H_{17}NO_4Na$ $[M+Na]^+$: 334.1055. Found: 334.1048.

(*Z*/*E*)-Dimethyl 5-(4-methoxystyryl)cyclohex-3-ene-1,1-dicarboxylate (28)



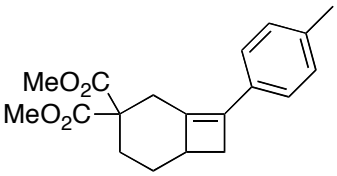
Colorless oil. (*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.30 (d, J = 12.1 Hz, 1H), 5.92 (d, J = 12.1 Hz, 1H), 5.68 (bs, 1H), 3.79 (s, 3H), 3.70 (s, 6H), 2.54 (bs, 2H), 2.19 (bs, 1H), 2.14-2.10 (m, 2H); (*E*): 7.34 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 16.4 Hz, 1H), 6.47 (d, J = 16.4 Hz, 1H), 5.79 (t, J = 4.1 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 6H), 2.82 (bs, 2H), 2.27 (bs, 2H), 2.17 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.14, 172.08, 159.14, 158.63, 133.30, 132.58, 130.78, 130.59, 130.53, 130.22, 129.33, 128.44, 127.61, 127.46, 126.25, 125.44, 114.24, 113.54, 77.55, 77.23, 76.91, 55.48, 55.42, 53.66, 53.54, 52.93, 52.79, 33.52, 30.52, 30.32, 27.76, 27.37, 23.33, 22.97. HRMS-ESI calcd. for $C_{19}H_{22}O_5Na$ $[M+Na]^+$: 353.1365. Found: 353.1371.

(*E*)-Dimethyl 3-(Prop-1-enyl)cyclohex-3-ene-1,1-dicarboxylate (30)



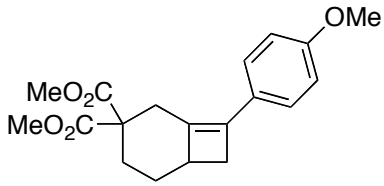
Colorless oil, 95 %: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, J = 16.0 Hz, 1H), 5.70-5.58 (m, 1H), 5.55 (bs, 1H), 3.72 (s, 6H), 2.67 (s, 2H), 2.18 (bs, 2H), 2.14 (d, J = 5.6 Hz, 2H), 1.76 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 133.6, 133.1, 124.7, 122.6, 53.5, 52.8, 30.4, 27.8, 22.9, 18.4. HRMS-ESI calcd. for $C_{13}H_{18}O_4Na$ $[M+Na]^+$: 261.1103. Found: 261.1113.

Dimethyl 8-*p*-tolylbicyclo[4.2.0]oct-1(8)-ene-3,3-dicarboxylate (32a)



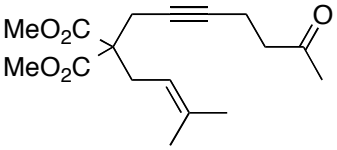
Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 3.74 (s, 3H), 3.57 (s, 3H), 2.82 (dt, J = 12.5, 3.8 Hz, 1H), 2.54-2.39 (m, 2H), 2.33 (s, 3H), 2.22 (ddd, J = 12.8, 2.7, 1.4 Hz, 1H), 2.13-2.03 (m, 2H), 1.85 (td, J = 14.0, 3.3 Hz, 1H), 1.25-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 170.9, 138.9, 136.6, 135.4, 133.0, 125.6, 56.6, 52.8, 52.4, 36.0, 34.3, 32.7, 29.7, 29.2, 21.3. HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

Dimethyl 8-(4-Methoxyphenyl)bicyclo[4.2.0]oct-1(8)-ene-3,3-dicarboxylate (32b)



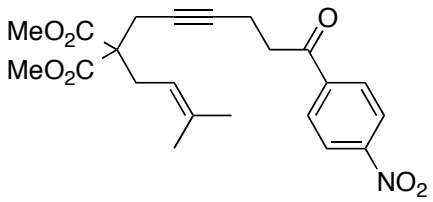
White sticky solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.57 (s, 3H), 2.81 (dt, J = 12.7, 3.8 Hz, 1H), 2.48-2.38 (m, 2H), 2.20 (d, J = 12.7 Hz, 1H), 2.12-2.04 (m, 2H), 1.85 (td, J = 13.8, 3.8 Hz, 1H), 1.29-1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.9, 158.6, 137.4, 134.9, 134.8, 128.8, 127.0, 113.7, 56.5, 52.8, 52.4, 35.9, 34.4, 32.6, 31.6, 29.2, 22.7, 14.2. HRMS-ESI calcd. for $C_{17}H_{170}O_4NaCl$ $[M+Na]^+$: 343.0713. Found: 343.0712.

Dimethyl 2-(3-Methylbut-2-en-1-yl)-2-(6-oxohept-2-yn-1-yl)malonate (42a).



To a solution of [$RuCl_2$(*p*-cymene)$_2$] (0.13 g, 0.21 mmol, 5 mol%) in toluene (8 mL), pyrrolidine (0.07 mL, 0.84 mmol, 0.2 equiv) was added. The mixture was stirred 10 min at rt followed by the addition of a solution of enyne (1.00 g, 4.21 mmol, 1 equiv.) and methyl vinyl ketone (1.8 mL, 21.03 mmol, 5 equiv.) in toluene (8 mL). The mixture was stirred during 13 h at 60 ºC then it was filtered over Celite and concentrated under low pressure. The purification was done by silica gel column chromatography (8:1, c-Hex/EtOAc) to give **42a** (1.02 g, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (apparent t septuplet, J = 7.8 Hz, 1H), 3.70 (s, 6H), 2.71-2.68 (overlapping signals (2.71,d, J = 7.8 Hz, 2H), (2.69, t, J = 2.5 Hz, 2H), 4H), 2.59 (apparent t, J = 7.0 Hz, 2H), 2.39-2.34 (m, 2H), 2.15 (s, 3H), 1.68 (d, J = 0.7 Hz, 3H), 1.63 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 206.8 (C), 170.9 (2C), 136.8 (C), 117.4 (CH), 82.0 (C), 75.6 (C), 57.6 (C), 52.8 ($2CH_3$), 42.9 (CH_2), 20.9 (CH_2), 30.0 (CH_3), 26.2 (CH_3), 23.0 (CH_2), 18.1 (CH_3), 13.5 (CH_2). HRMS-ESI Caldc for $C_{17}H_{24}O_5$ [M+Na]$^+$ 331.1521, found 331.1528.

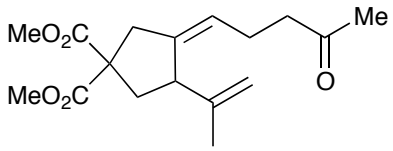
Dimethyl 2-(3-Methylbut-2-en-1-yl)-2-(6-(4-nitrophenyl)-6-oxohex-2-yn-1-yl)malonate (42b).



To the solution of [$RuCl_2$(*p*-cymene)$_2$] (0.15 g, 0.24 mmol, 5 mol%) in THF (20 mL) was added pyrrolidine (0.08 mL, 0.94 mmol) at rt and stirred for 10 min. To this mixture were added malonate (1.1 g, 4.7 mmol, 1 equiv.) and 1-(4-nitrophenyl)prop-2-en-1-one (1.0 g, 5.6 mmol, 5 equiv.) and stirred for 13 h at 60 ºC. The resulting mixture was cooled to room temperature and quenched by sat. NH_4Cl. The organic layer was extracted by Et_2O, washed by water and brine, and dried over $MgSO_4$. After the filtration the solvent was evaporated under reduced pressure to give crude mixture (2.1 g). Purification was done by silica column chromatography (6:1, *c*-Hex/EtOAc) to give **42b** (880 mg, 45%) as a yellow sticky liquid. After several weeks, the product became a crystalline yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$,) δ 8.33 (m, 2H), 8.11 (m, 1H), 4.88 (br t, J = 7.8 Hz, 1H), 3.69 (apparent t, J = 1.1 Hz, 6H), 3.20 (t, J = 7.3 Hz, 2H), 2.70-2.69 (m, 4H), 2.58 (apparent td, J = 6.5, 1.1 Hz, 2H), 1.67 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.6 (C), 170.8 (2C), 150.6 (C), 141.2 (C), 136.9 (C),

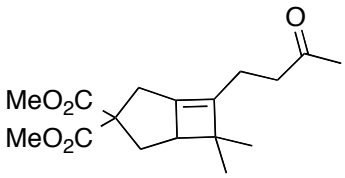
129.2 (2CH), 124.1 (2CH), 117.3 (CH), 81.6 (C), 76.2 (C), 57.6 (C), 52.8 ($2CH_3$), 38.8 (CH_2), 31.0 (CH_2), 29.2 (CH_3), 23.0 (CH_2), 18.1 (CH_3), 13.7 (CH_2). HRMS-ESI Caldc for $C_{14}H_{24}O_5$ $[M+Na]^+$ 331.1521, found 331.1528.

(*Z*)-Dimethyl 3-(3-Oxobutylidene)-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (44).



To dimethyl 2-(3-methylbut-2-en-1-yl)-2-(6-oxohept-2-yn-1-yl)malonate (118.6 mg, 0.39 mmol) in a vessel filled with argon was added a solution of complex **D** (15.7 mg, 0.02 mmol, 5 mol%) in CH_2Cl_2 (4 mL) and stirred at 23 °C. The reaction was quenched by Et_3N/*c*-Hex, and the resulting mixture was passed through a pad of Celite. The solvent was removed under reduced pressure to obtain crude mixture as yellow oil. Purification was done by silica column chromatography (10:1, *c*-Hex/EtOAc) to give **44** (49.2 mg, 41%) as a colourless oil (41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (tquin, J = 7.4, 2.9 Hz, 1H), 4.82 (hex, J = 1.3 Hz, 1H), 4.79-4.78 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.22 (br t, J = 1.5 Hz, 1H), 3.08 (dhex, J = 17.0, 0.8 Hz, 1H), 2.78 (dhep, J = 17.0, 1.4 Hz, 1H), 2.49-2.42 (m, 3H), 2.26 (br q, J = 7.2 Hz, 2H), 2.12-2.09 (overlapping signals (2.12, s, 3H), (2.09, dd J = 12.8, 11.6 Hz, 1H), 3H), 1.59-1.58 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.5 (C), 172.3 (2C), 145.0 (C), 140.8 (C), 121.8 (CH), 113.9 (CH), 58.9 (C), 53.0 (CH_3), 53.0 (CH_3), 51.3 (CH), 43.0 (CH_2), 38.5 (CH_2), 37.5 (CH_2), 30.9 (CH_3), 24.0 (CH_2), 18.0 (CH_3). HRMS-ESI Caldc for $C_{17}H_{24}O_5$ $[M+Na]^+$ 331.1521, found 331.1526.

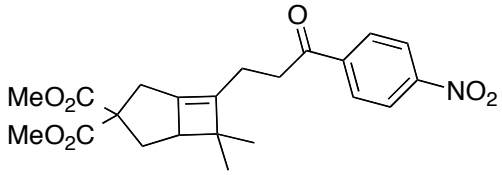
Dimethyl 7,7-Dimethyl-6-(3-oxobutyl)bicyclo[3.2.0]hept-5-ene-3,3-dicarboxylate (43a).



To **42a** (0.15 g, 0.50 mmol) in a flask filled with argon was added a solution of complex **E** (0.02 g, 0.03 mmol, 5 mol%) in CH_2Cl_2 (5 mL) and the mixture stirred at 23 °C for 90 min. The reaction was quenched by adding a solution of Et_3N in cyclohexane (0.1 M), and the resulting mixture was passed through a membrane filter. The solvent was

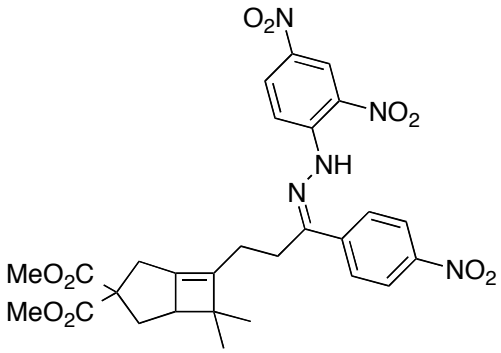
removed under reduced pressure to obtain crude mixture as yellow oil. Purification was done by flash column chromatography (10:1, *c*-Hex/EtOAc) to give **43a** (80%). Variable yields were obtained in this preparation because of the instability of **43a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.71 (s, 3H), 2.77 (br d, J = 1.5 Hz, 2H), 2.60 (dt, J = 7.2, 6.5 Hz, 2H), 2.39 (dt, J = 12.9, 7.2 Hz, 1H), 2.29 (br t, J = 7.6 Hz, 1H), 2.20-2.16 (overlapping signals (m, 2H), (2.16, s, 3H), 5H), 1.72 (dd, J = 12.9, 9.4 Hz, 3H), 1.14 (s, 3H), 0.95 (s, 3H). ^{13}C (400 MHz, $CDCl_3$) δ 208.2 (C), 172.9 (C), 172.5 (C), 141.1 (C), 140.1 (C), 65.3 (C), 53.0 (CH_3), 52.9 (CH_3), 51.6 (CH), 41.6 (C), 40.8 (CH_2), 35.1 (CH_2), 33.8 (CH_2), 30.0 (CH_3), 26.2 (CH_3), 20.8 (CH_2), 20.3 (CH_3). HRMS-ESI Caldc for $C_{17}H_{24}O_5$ $[M+Na]^+$ 331.1521, found 331.1537.

Dimethyl 7,7-Dimethyl-6-(3-(4-nitrophenyl)-3-oxopropyl)bicyclo[3.2.0]hept-5-ene-3,3-dicarboxylate (43b).



To a solution of **42b** (208 mg, 0.50 mmol) in CH_2Cl_2 (3 mL) was added a solution of complex **E** (23.11 mg, 0.03 mmol, 5 mol%) in CH_2Cl_2 (2 mL) at 23 °C. After stirring at this temeparture for 12 h, the reaction was quenched by addition of a solution of Et_3N in cyclohexane (0.1 M) and the resulting mixture was filtered through membrane filter. The filtrate was concentrated under reduced pressure to obtain crude mixture (280 mg, brown gum). The target product was isolated by silica gel column chromatography (10:1 to 4:1, *c*-Hex/EtOAc) to give **43b** (182 mg, 88 %) as a yellow sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (br d, J = 7.0 Hz, 2H), 8.14 (dt, J = 7.1, 1.7 Hz, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3-24-3.20 (m, 2H), 2.81 (br d, J = 12.4 Hz, 1H), 2.77 (br dd, J = 12.4, 1.4 Hz, 1H), 2.43 (dd, J = 10.5, 5.9 Hz, 1H), 2.40-2.32 (m, 3H), 1.76 (dd, J = 10.5, 6.1 Hz, 3H), 1.18 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.9 (C), 172.7 (C), 172.3 (C), 150.4 (C), 145.8 (C), 141.4 (C), 140.4 (C), 129.1 (2CH), 1240 (2CH), 65.2 (C), 52.9 (CH_3), 52.8 (CH_3), 51.5 (CH), 41.7 (C), 36.3 (CH_2), 34.9 (CH_2), 33.8 (CH_2), 26.1 (CH_3), 20.8 (CH_2), 20.3 (CH_3). HRMS-ESI Caldc for $C_{22}H_{25}NO_7$ $[M+Na]^+$ 438.1529, found 438.1518.

(*Z*)-Dimethyl 6-(3-(2-(2,4-Dinitrophenyl)hydrazono)-3-(4-nitrophenyl)propyl)-7,7-dimethylbicyclo[3.2.0]hept-5-ene-3,3-dicarboxylate.



To a mixture of H_2O (4.7 mL) and EtOH (16.8 mL) was added a solution of 2,4-2,dinitrophenylhydrazine (1.0 g, 3.38 mmol, 0.97 equiv.) in sulfuric acid (3.31 ml, 60.9 mmol, 18 equiv.) thoroughly and stirred for 10 min at RT. This solution was ready for the immediate use. To a solution of dimethyl 7,7-dimethyl-6-(3-(4-nitrophenyl)-3-oxopropyl)bicyclo[3.2.0]hept-5-ene-3,3-dicarboxylate (147 mg, 0.35 mmol, 1 equiv.) in a mixture of EtOH (1.2 mL) and CH_2Cl_2 (0.5 mL) was added an activated hydrazine solution (2,4-dinitrophenyl)hydrazine at 23 °C and stirred for 15 min to form a precipitate. The mixture was diluted with CH_2Cl_2 then water was added, the organic layer was extracted by CH_2Cl_2, washed with sat $NaHCO_3$, brine and dried over MgSO4, finally it was filtrated and evaporated to give crude mixture (147 mg, orange gum). The target product was isolated by silica gel column chromatography (10:1 to 6:1, *c*-Hex/EtOAc) to give the title compound (100 mg, 48 %) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, J = 2.5 Hz, 1H), 8.41 (dd, J = 9.5, 2.6 Hz, 1H), 8.31 (dt, J = 9.0, 2.4 Hz, 2H), 8.12 (d, J = 9.5 Hz, 1H), 8.02 (dt, J = 9.0, 2.4 Hz, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.09 (td, J = 15.4, 6.5 Hz, 2H), 2.94 (d, J = 15.5 hz, 1H), 2.80 (dd, J = 15.6, 1.6 Hz, 1H), 2.49 (dd, J = 13.2, 7.6 Hz, 1H), 2.40 (br t, J = 9.0 Hz, 1H), 2.28 (t, J = 8.6 Hz, 1H), 1.80 (dd, J = 13.2, 8.9 Hz, 1H), 1.62 (d, J = 1.4 Hz, 1H), 1.20 (s, 3H), 1.00 (s, 3H). ^{13}C (400 MHz, $CDCl_3$) δ 172.6 (C), 172.4 (C), 152.9 (C), 148.6 (C), 144.8 (C), 144.3 (C), 142.7 (C), 142.3 (C), 139.1 (C), 130.6 (C), 130.4 (C), 127.4 (2CH), 124.2 (2CH), 123.5 (CH), 116.9 (CH), 65.1 (CH_2), 53.1 (CH_3), 53.0 (CH_3), 51.7 (CH), 42.2 (C), 34.7 (CH_2), 34.0 (CH_2), 23.6 (CH_3), 25.3 (CH_2), 22.6 (CH_2), 20.4 (CH_3). HRMS-ESI Caldc for $C_{17}H_{24}O_5$ [M+Na]$^+$ 331.1521, found 331.1537.

Crystallographic data for 43b-2,4-dinitrophenylhydrazone

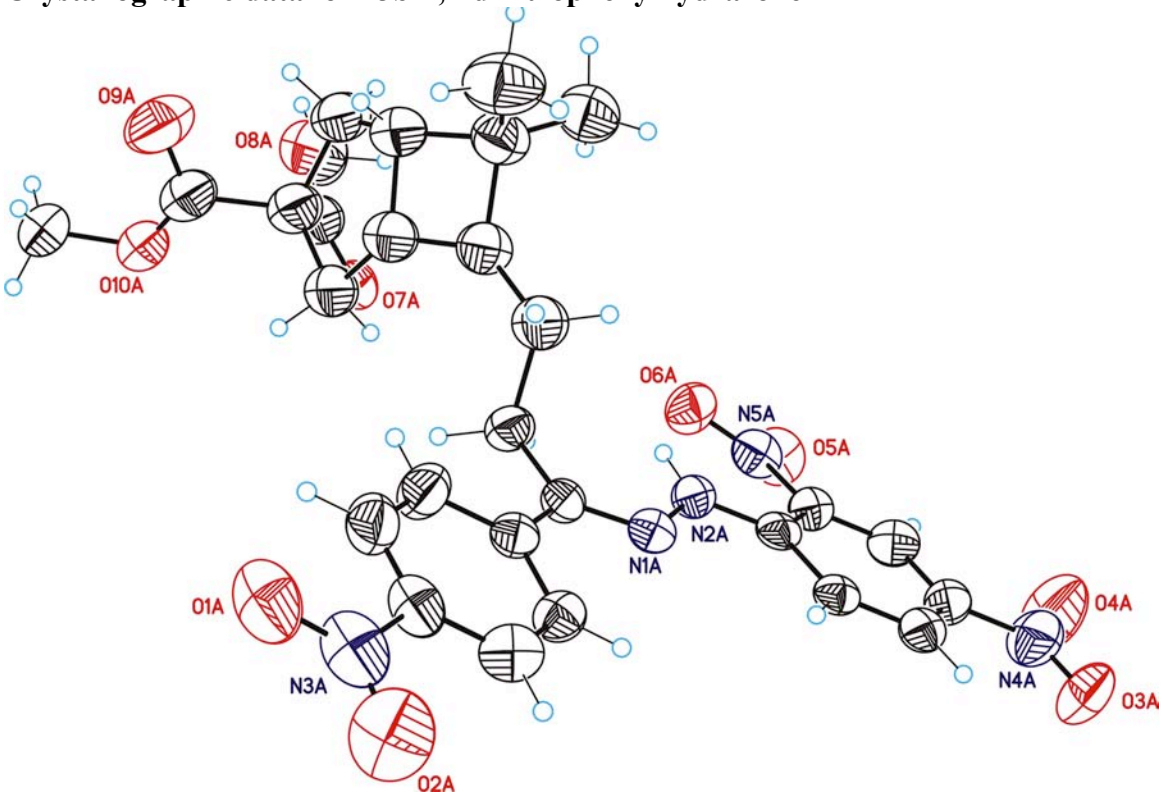


Table 1. **Crystal data and structure refinement**

Empirical formula	C28 H29 N5 O10	
Formula weight	595.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1962(10) Å	α= 87.116(7) °.
	b = 13.6978(16) Å	β = 76.553(7) °.
	c = 20.614(2) Å	γ = 68.060(7) °.
Volume	2849.8(5) $Å^3$	
Z	4	
Density (calculated)	1.388 Mg/m^3	
Absorption coefficient	0.904 mm^{-1}	
F(000)	1248	
Crystal size	0.20 x 0.20 x 0.04 mm^3	
Theta range for data collection	3.48 to 67.04 °.	
Index ranges	-12 <=h<=13 ,-13 <=k<=13 ,0 <=l<=23	
Reflections collected	7193	

Independent reflections	7193 [R(int) = 0.0556]
Completeness to theta =67.04 °	0.693 %
Absorption correction	Empirical
Max. and min. transmission	0.9647 and 0.8399
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7193 / 462 / 1054
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.1066 , wR2 = 0.2549
R indices (all data)	R1 = 0.1353 , wR2 = 0.2805
Largest diff. peak and hole	0.577 and -0.524 e.Å^{-3}

Table 2. **Bond lengths [Å] and angles [°] for XX**

Bond lengths	
C1A-N1A	1.292(6)
C1A-C2A	1.485(8)
C1A-C14A	1.501(6)
C2A-C7A	1.388(7)
C2A-C3A	1.394(7)
C3A-C4A	1.388(8)
C4A-C5A	1.377(8)
C5A-C6A	1.366(8)
C5A-N3A	1.484(8)
C6A-C7A	1.379(9)
C8A-N2A	1.350(6)
C8A-C9A	1.412(6)
C8A-C13A	1.421(7)
C9A-C10A	1.364(7)
C10A-C11A	1.400(8)
C11A-C12A	1.366(7)
C11A-N4A	1.456(7)
C12A-C13A	1.387(7)
C13A-N5A	1.454(6)
C14A-C15A	1.546(8)
C15A-C16A	1.427(7)
C16A-C17'	1.327(9)
C16A-C17A	1.366(8)
C16A-C22A	1.536(8)

C16A-C21'	2.040(5)
C17A-C21A	1.509(12)
C17A-C18A	1.534(5)
C18A-C19A	1.538(5)
C19A-C25A	1.537(4)
C19A-C20A	1.537(5)
C19A-C27A	1.539(3)
C20A-C21A	1.524(5)
C21A-C22A	1.549(7)
C22A-C23A	1.482(9)
C22A-C24A	1.520(9)
C22A-C21'	1.533(4)
C25A-O7A	1.182(6)
C25A-O8A	1.376(6)
C26A-O8A	1.452(5)
C27A-O9A	1.252(9)
C27A-O10A	1.287(10)
C28A-O10A	1.454(5)
C17'-C21'	1.505(11)
C17'-C18'	1.534(5)
C18'-C19'	1.527(11)
C19'-C25'	1.534(5)
C19'-C27'	1.538(5)
C19'-C20'	1.540(5)
C20'-C21'	1.508(5)
C25'-O7A'	1.178(6)
C25'-O8A'	1.369(6)
C26'-O8A'	1.454(6)
C27'-O9A'	1.250(9)
C27'-O10'	1.288(9)
C28'-O10'	1.456(6)
C25"-O7A"	1.210(10)
C25"-O8A"	1.423(11)
C26"-O8A"	1.431(11)
C27"-O9A"	1.04(3)
C27"-O10"	1.45(3)
C28"-O10"	1.44(3)

N1A-N2A	1.377(6)
N3A-O1A	1.216(6)
N3A-O2A	1.218(7)
N4A-O3A	1.224(6)
N4A-O4A	1.238(7)
N5A-O5A	1.220(6)
N5A-O6A	1.244(5)
C1B-N1B	1.283(5)
C1B-C2B	1.490(6)
C1B-C14B	1.541(5)
C1B-C14"	1.545(5)
C2B-C3B	1.388(6)
C2B-C7B	1.412(7)
C3B-C4B	1.400(6)
C4B-C5B	1.376(7)
C5B-C6B	1.377(7)
C5B-N3B	1.477(5)
C6B-C7B	1.379(6)
C8B-N2B	1.362(6)
C8B-C9B	1.400(8)
C8B-C13B	1.407(6)
C9B-C10B	1.356(8)
C10B-C11B	1.375(8)
C11B-C12B	1.338(9)
C11B-N4B	1.476(8)
C12B-C13B	1.423(8)
C13B-N5B	1.461(8)
C14B-C15B	1.543(4)
C15B-C16B	1.542(5)
C14"-C15"	1.539(5)
C15"-C16B	1.542(5)
C16B-C17"	1.294(13)
C16B-C17B	1.302(7)
C16B-C22B	1.522(6)
C16B-C22"	1.556(8)
C17B-C21B	1.494(8)
C17B-C18B	1.515(8)

C18B-C19B	1.547(4)
C17"-C21"	1.498(16)
C17"-C18"	1.516(16)
C18"-C19B	1.575(16)
C19B-C25B	1.527(4)
C19B-C27B	1.533(4)
C19B-C20"	1.540(3)
C19B-C20B	1.549(4)
C20B-C21B	1.541(4)
C21B-C22B	1.550(3)
C22B-C24B	1.529(6)
C22B-C23B	1.530(6)
C20"-C21"	1.542(5)
C21"-C22"	1.553(4)
C22"-C24"	1.529(6)
C22"-C23"	1.532(6)
C25B-O7B	1.215(8)
C25B-O7B"	1.228(8)
C25B-O8B	1.315(5)
C26B-O8B	1.436(6)
C27B-O9B"	1.207(8)
C27B-O9B	1.227(7)
C27B-O10B	1.354(5)
C28B-O10B	1.435(5)
N1B-N2B	1.363(5)
N3B-O2B	1.229(6)
N3B-O1B	1.230(5)
N4B-O4B	1.206(7)
N4B-O3B	1.232(9)
N5B-O5B	1.228(5)
N5B-O6B	1.232(6)

Angles

N1A-C1A-C2A	115.8(4)
N1A-C1A-C14A	124.6(5)
C2A-C1A-C14A	119.2(4)
C7A-C2A-C3A	118.6(5)

C7A-C2A-C1A	120.8(4)
C3A-C2A-C1A	120.6(4)
C4A-C3A-C2A	120.0(5)
C5A-C4A-C3A	119.4(5)
C6A-C5A-C4A	121.8(6)
C6A-C5A-N3A	118.0(5)
C4A-C5A-N3A	120.2(5)
C5A-C6A-C7A	118.6(6)
C6A-C7A-C2A	121.6(5)
N2A-C8A-C9A	121.2(5)
N2A-C8A-C13A	122.2(4)
C9A-C8A-C13A	116.6(4)
C10A-C9A-C8A	121.2(5)
C9A-C10A-C11A	120.0(4)
C12A-C11A-C10A	121.4(5)
C12A-C11A-N4A	119.3(5)
C10A-C11A-N4A	119.3(5)
C11A-C12A-C13A	118.5(5)
C12A-C13A-C8A	122.2(4)
C12A-C13A-N5A	116.0(5)
C8A-C13A-N5A	121.7(4)
C1A-C14A-C15A	108.7(4)
C16A-C15A-C14A	115.1(5)
C17'-C16A-C17A	35.9(7)
C17'-C16A-C15A	135.8(7)
C17A-C16A-C15A	136.3(6)
C17'-C16A-C22A	95.5(5)
C17A-C16A-C22A	90.1(5)
C15A-C16A-C22A	127.4(5)
C17'-C16A-C21'	47.5(4)
C17A-C16A-C21'	49.7(5)
C15A-C16A-C21'	173.9(5)
C22A-C16A-C21'	48.3(2)
C16A-C17A-C21A	96.9(6)
C16A-C17A-C18A	132.9(8)
C21A-C17A-C18A	119.2(5)
C17A-C18A-C19A	103.7(5)

C25A-C19A-C20A	118.5(6)
C25A-C19A-C18A	114.3(6)
C20A-C19A-C18A	101.8(5)
C25A-C19A-C27A	110.4(4)
C20A-C19A-C27A	98.7(5)
C18A-C19A-C27A	111.9(6)
C21A-C20A-C19A	120.2(6)
C17A-C21A-C20A	94.3(6)
C17A-C21A-C22A	84.5(5)
C20A-C21A-C22A	139.4(8)
C23A-C22A-C24A	111.2(5)
C23A-C22A-C21'	124.4(6)
C24A-C22A-C21'	104.7(6)
C23A-C22A-C16A	118.1(5)
C24A-C22A-C16A	112.1(5)
C21'-C22A-C16A	83.3(4)
C23A-C22A-C21A	94.4(6)
C24A-C22A-C21A	131.3(6)
C21'-C22A-C21A	31.8(6)
C16A-C22A-C21A	88.5(5)
O7A-C25A-O8A	124.2(7)
O7A-C25A-C19A	125.3(7)
O8A-C25A-C19A	106.0(5)
O9A-C27A-O10A	126.2(7)
O9A-C27A-C19A	124.6(8)
O10A-C27A-C19A	108.5(6)
C25A-O8A-C26A	114.2(7)
C27A-O10A-C28A	117.0(8)
C16A-C17'-C21'	91.9(6)
C16A-C17'-C18'	150.8(10)
C21'-C17'-C18'	111.7(6)
C19'-C18'-C17'	95.9(6)
C18'-C19'-C25'	102.1(7)
C18'-C19'-C27'	117.9(7)
C25'-C19'-C27'	110.2(5)
C18'-C19'-C20'	116.2(5)
C25'-C19'-C20'	94.6(6)

C27'-C19'-C20'	112.4(6)
C21'-C20'-C19'	96.2(5)
C17'-C21'-C20'	105.3(7)
C17'-C21'-C22A	88.7(4)
C20'-C21'-C22A	154.6(7)
C17'-C21'-C16A	40.5(4)
C20'-C21'-C16A	143.5(7)
C22A-C21'-C16A	48.4(3)
O7A'-C25'-O8A'	124.7(7)
O7A'-C25'-C19'	126.7(7)
O8A'-C25'-C19'	107.1(5)
O9A'-C27'-O10'	126.3(6)
O9A'-C27'-C19'	121.3(8)
O10'-C27'-C19'	112.3(6)
C25'-O8A'-C26'	114.5(6)
C27'-O10'-C28'	116.7(7)
O7A"-C25"-O8A"	114(2)
O9A"-C27"-O10"	128(3)
C25"-O8A"-C26"	99(2)
C28"-O10"-C27"	112(2)
C1A-N1A-N2A	116.3(4)
C8A-N2A-N1A	121.1(4)
O1A-N3A-O2A	124.9(6)
O1A-N3A-C5A	118.4(5)
O2A-N3A-C5A	116.6(5)
O3A-N4A-O4A	123.0(5)
O3A-N4A-C11A	118.5(5)
O4A-N4A-C11A	118.6(5)
O5A-N5A-O6A	122.5(4)
O5A-N5A-C13A	118.4(4)
O6A-N5A-C13A	119.1(5)
N1B-C1B-C2B	115.5(4)
N1B-C1B-C14B	123.0(4)
C2B-C1B-C14B	120.1(4)
N1B-C1B-C14"	118.2(4)
C2B-C1B-C14"	119.0(4)
C14B-C1B-C14"	37.7(4)

C3B-C2B-C7B	119.2(4)
C3B-C2B-C1B	122.4(4)
C7B-C2B-C1B	118.5(4)
C2B-C3B-C4B	120.6(5)
C5B-C4B-C3B	118.2(4)
C4B-C5B-C6B	122.8(4)
C4B-C5B-N3B	118.3(4)
C6B-C5B-N3B	118.9(4)
C5B-C6B-C7B	118.9(5)
C6B-C7B-C2B	120.3(4)
N2B-C8B-C9B	120.5(4)
N2B-C8B-C13B	122.2(5)
C9B-C8B-C13B	117.2(5)
C10B-C9B-C8B	121.8(5)
C9B-C10B-C11B	119.7(6)
C12B-C11B-C10B	122.2(6)
C12B-C11B-N4B	119.4(6)
C10B-C11B-N4B	118.4(6)
C11B-C12B-C13B	118.9(5)
C8B-C13B-C12B	120.1(5)
C8B-C13B-N5B	121.4(5)
C12B-C13B-N5B	118.5(5)
C1B-C14B-C15B	108.3(4)
C16B-C15B-C14B	107.3(4)
C15"-C14"-C1B	113.7(6)
C14"-C15"-C16B	103.1(5)
C17"-C16B-C17B	20.3(11)
C17"-C16B-C22B	96.5(7)
C17B-C16B-C22B	95.1(4)
C17"-C16B-C15"	131.4(9)
C17B-C16B-C15"	120.4(6)
C22B-C16B-C15"	125.1(6)
C17"-C16B-C15B	123.1(10)
C17B-C16B-C15B	133.7(5)
C22B-C16B-C15B	128.3(4)
C15"-C16B-C15B	50.5(4)
C17"-C16B-C22"	93.3(8)

C17B-C16B-C22"	88.7(4)
C22B-C16B-C22"	10.5(3)
C15"-C16B-C22"	122.8(6)
C15B-C16B-C22"	136.6(4)
C16B-C17B-C21B	93.8(4)
C16B-C17B-C18B	145.5(7)
C21B-C17B-C18B	115.3(5)
C17B-C18B-C19B	100.5(4)
C16B-C17"-C21"	94.6(9)
C16B-C17"-C18"	150.1(15)
C21"-C17"-C18"	111.4(11)
C17"-C18"-C19B	97.1(11)
C25B-C19B-C27B	109.6(4)
C25B-C19B-C20"	88.0(4)
C27B-C19B-C20"	130.2(6)
C25B-C19B-C18B	108.8(5)
C27B-C19B-C18B	110.1(4)
C20"-C19B-C18B	107.1(5)
C25B-C19B-C20B	111.7(4)
C27B-C19B-C20B	108.7(3)
C20"-C19B-C20B	26.3(5)
C18B-C19B-C20B	108.0(4)
C25B-C19B-C18"	106.5(11)
C27B-C19B-C18"	111.1(11)
C20"-C19B-C18"	107.3(9)
C18B-C19B-C18"	2.3(12)
C20B-C19B-C18"	109.3(7)
C21B-C20B-C19B	105.1(3)
C17B-C21B-C20B	100.0(4)
C17B-C21B-C22B	86.7(4)
C20B-C21B-C22B	126.7(3)
C16B-C22B-C24B	115.1(5)
C16B-C22B-C23B	114.7(4)
C24B-C22B-C23B	109.2(4)
C16B-C22B-C21B	83.5(3)
C24B-C22B-C21B	117.4(3)
C23B-C22B-C21B	115.1(4)

C19B-C20"-C21"	94.8(4)
C17"-C21"-C20"	104.3(9)
C17"-C21"-C22"	86.0(7)
C20"-C21"-C22"	126.0(5)
C24"-C22"-C23"	109.0(5)
C24"-C22"-C21"	117.2(5)
C23"-C22"-C21"	114.3(5)
C24"-C22"-C16B	106.6(8)
C23"-C22"-C16B	125.3(7)
C21"-C22"-C16B	82.9(4)
O7B-C25B-O7B"	48.5(7)
O7B-C25B-O8B	115.9(6)
O7B"-C25B-O8B	115.8(7)
O7B-C25B-C19B	125.0(6)
O7B"-C25B-C19B	119.5(7)
O8B-C25B-C19B	115.3(4)
O9B"-C27B-O9B	39.9(5)
O9B"-C27B-O10B	118.4(6)
O9B-C27B-O10B	120.1(5)
O9B"-C27B-C19B	124.8(6)
O9B-C27B-C19B	127.2(5)
O10B-C27B-C19B	109.7(4)
C1B-N1B-N2B	118.6(4)
C8B-N2B-N1B	118.0(4)
O2B-N3B-O1B	124.4(4)
O2B-N3B-C5B	117.4(4)
O1B-N3B-C5B	118.2(4)
O4B-N4B-O3B	124.6(6)
O4B-N4B-C11B	117.3(7)
O3B-N4B-C11B	118.0(6)
O5B-N5B-O6B	123.0(5)
O5B-N5B-C13B	116.9(5)
O6B-N5B-C13B	120.1(4)
C25B-O8B-C26B	118.4(5)
C27B-O10B-C28B	115.9(4)

Table 3. **Torsion angles [°] for XX**

N1A-C1A-C2A-C7A	167.1(5)
C14A-C1A-C2A-C7A	-6.7(7)
N1A-C1A-C2A-C3A	-13.3(7)
C14A-C1A-C2A-C3A	172.9(5)
C7A-C2A-C3A-C4A	-0.2(8)
C1A-C2A-C3A-C4A	-179.8(5)
C2A-C3A-C4A-C5A	0.5(8)
C3A-C4A-C5A-C6A	-0.6(9)
C3A-C4A-C5A-N3A	177.4(5)
C4A-C5A-C6A-C7A	0.3(10)
N3A-C5A-C6A-C7A	-177.7(5)
C5A-C6A-C7A-C2A	0.0(10)
C3A-C2A-C7A-C6A	0.0(9)
C1A-C2A-C7A-C6A	179.5(5)
N2A-C8A-C9A-C10A	179.1(4)
C13A-C8A-C9A-C10A	1.9(7)
C8A-C9A-C10A-C11A	-1.0(7)
C9A-C10A-C11A-C12A	-0.1(8)
C9A-C10A-C11A-N4A	179.8(5)
C10A-C11A-C12A-C13A	0.1(8)
N4A-C11A-C12A-C13A	-179.9(5)
C11A-C12A-C13A-C8A	1.0(8)
C11A-C12A-C13A-N5A	-176.6(5)
N2A-C8A-C13A-C12A	-179.1(5)
C9A-C8A-C13A-C12A	-2.0(7)
N2A-C8A-C13A-N5A	-1.6(7)
C9A-C8A-C13A-N5A	175.5(4)
N1A-C1A-C14A-C15A	-82.6(7)
C2A-C1A-C14A-C15A	90.7(6)
C1A-C14A-C15A-C16A	-170.3(6)
C14A-C15A-C16A-C17'	-10.4(14)
C14A-C15A-C16A-C17A	42.3(13)
C14A-C15A-C16A-C22A	-174.2(6)
C14A-C15A-C16A-C21'	-131(6)
C17'-C16A-C17A-C21A	-100.9(11)
C15A-C16A-C17A-C21A	150.2(9)

C22A-C16A-C17A-C21A	-1.6(7)
C21'-C16A-C17A-C21A	-30.8(6)
C17'-C16A-C17A-C18A	40.6(11)
C15A-C16A-C17A-C18A	-68.3(17)
C22A-C16A-C17A-C18A	139.9(11)
C21'-C16A-C17A-C18A	110.7(14)
C16A-C17A-C18A-C19A	-125.1(11)
C21A-C17A-C18A-C19A	9.8(13)
C17A-C18A-C19A-C25A	122.6(8)
C17A-C18A-C19A-C20A	-6.4(9)
C17A-C18A-C19A-C27A	-110.9(8)
C25A-C19A-C20A-C21A	-123.8(8)
C18A-C19A-C20A-C21A	2.5(10)
C27A-C19A-C20A-C21A	117.2(8)
C16A-C17A-C21A-C20A	140.8(8)
C18A-C17A-C21A-C20A	-7.6(12)
C16A-C17A-C21A-C22A	1.5(7)
C18A-C17A-C21A-C22A	-146.9(10)
C19A-C20A-C21A-C17A	2.7(10)
C19A-C20A-C21A-C22A	89.3(14)
C17'-C16A-C22A-C23A	131.3(8)
C17A-C16A-C22A-C23A	95.7(7)
C15A-C16A-C22A-C23A	-60.0(9)
C21'-C16A-C22A-C23A	125.6(7)
C17'-C16A-C22A-C24A	-97.5(8)
C17A-C16A-C22A-C24A	-133.1(7)
C15A-C16A-C22A-C24A	71.2(9)
C21'-C16A-C22A-C24A	-103.1(7)
C17'-C16A-C22A-C21'	5.6(9)
C17A-C16A-C22A-C21'	-29.9(7)
C15A-C16A-C22A-C21'	174.4(8)
C17'-C16A-C22A-C21A	37.1(8)
C17A-C16A-C22A-C21A	1.5(7)
C15A-C16A-C22A-C21A	-154.2(8)
C21'-C16A-C22A-C21A	31.4(6)
C17A-C21A-C22A-C23A	-119.4(7)
C20A-C21A-C22A-C23A	150.4(12)

C17A-C21A-C22A-C24A	117.3(9)
C20A-C21A-C22A-C24A	27.1(17)
C17A-C21A-C22A-C21'	78.3(9)
C20A-C21A-C22A-C21'	-11.9(8)
C17A-C21A-C22A-C16A	-1.4(7)
C20A-C21A-C22A-C16A	-91.5(12)
C20A-C19A-C25A-O7A	112.6(10)
C18A-C19A-C25A-O7A	-7.5(12)
C27A-C19A-C25A-O7A	-134.7(10)
C20A-C19A-C25A-O8A	-44.2(7)
C18A-C19A-C25A-O8A	-164.3(7)
C27A-C19A-C25A-O8A	68.5(8)
C25A-C19A-C27A-O9A	-125.5(11)
C20A-C19A-C27A-O9A	-0.5(12)
C18A-C19A-C27A-O9A	106.0(12)
C25A-C19A-C27A-O10A	44.8(10)
C20A-C19A-C27A-O10A	169.8(8)
C18A-C19A-C27A-O10A	-83.7(9)
O7A-C25A-O8A-C26A	23.1(15)
C19A-C25A-O8A-C26A	-179.8(7)
O9A-C27A-O10A-C28A	-1.5(19)
C19A-C27A-O10A-C28A	-171.6(10)
C17A-C16A-C17'-C21'	76.7(10)
C15A-C16A-C17'-C21'	-172.9(9)
C22A-C16A-C17'-C21'	-5.7(9)
C17A-C16A-C17'-C18'	-68(3)
C15A-C16A-C17'-C18'	42(3)
C22A-C16A-C17'-C18'	-150(2)
C21'-C16A-C17'-C18'	-145(3)
C16A-C17'-C18'-C19'	153(2)
C21'-C17'-C18'-C19'	11.8(14)
C17'-C18'-C19'-C25'	115.3(9)
C17'-C18'-C19'-C27'	-123.9(9)
C17'-C18'-C19'-C20'	13.9(12)
C18'-C19'-C20'-C21'	-32.7(10)
C25'-C19'-C20'-C21'	-138.7(6)
C27'-C19'-C20'-C21'	107.3(7)

C16A-C17'-C21'-C20'	164.2(8)
C18'-C17'-C21'-C20'	-33.5(14)
C16A-C17'-C21'-C22A	5.7(9)
C18'-C17'-C21'-C22A	168.0(11)
C18'-C17'-C21'-C16A	162.3(17)
C19'-C20'-C21'-C17'	36.5(9)
C19'-C20'-C21'-C22A	157.8(16)
C19'-C20'-C21'-C16A	53.8(12)
C23A-C22A-C21'-C17'	-124.5(9)
C24A-C22A-C21'-C17'	106.3(8)
C16A-C22A-C21'-C17'	-4.9(8)
C21A-C22A-C21'-C17'	-103.0(12)
C23A-C22A-C21'-C20'	111.0(18)
C24A-C22A-C21'-C20'	-18.2(19)
C16A-C22A-C21'-C20'	-129.4(18)
C21A-C22A-C21'-C20'	133(2)
C23A-C22A-C21'-C16A	-119.6(8)
C24A-C22A-C21'-C16A	111.2(6)
C21A-C22A-C21'-C16A	-98.1(9)
C17A-C16A-C21'-C17'	-48.4(10)
C15A-C16A-C21'-C17'	125(6)
C22A-C16A-C21'-C17'	172.4(11)
C17'-C16A-C21'-C20'	-26.2(13)
C17A-C16A-C21'-C20'	-74.7(12)
C15A-C16A-C21'-C20'	99(6)
C22A-C16A-C21'-C20'	146.2(13)
C17'-C16A-C21'-C22A	-172.4(11)
C17A-C16A-C21'-C22A	139.2(9)
C15A-C16A-C21'-C22A	-47(6)
C18'-C19'-C25'-O7A'	-3.6(11)
C27'-C19'-C25'-O7A'	-129.6(10)
C20'-C19'-C25'-O7A'	114.5(10)
C18'-C19'-C25'-O8A'	162.9(7)
C27'-C19'-C25'-O8A'	36.8(9)
C20'-C19'-C25'-O8A'	-79.1(7)
C18'-C19'-C27'-O9A'	123.4(10)
C25'-C19'-C27'-O9A'	-120.1(9)

C20'-C19'-C27'-O9A'	-15.9(11)
C18'-C19'-C27'-O10'	-60.6(10)
C25'-C19'-C27'-O10'	56.0(10)
C20'-C19'-C27'-O10'	160.1(8)
O7A'-C25'-O8A'-C26'	-12.1(14)
C19'-C25'-O8A'-C26'	-178.8(7)
O9A'-C27'-O10'-C28'	-2.8(16)
C19'-C27'-O10'-C28'	-178.6(8)
O7A"-C25"-O8A"-C26"	4(3)
O9A"-C27"-O10"-C28"	-8(5)
C2A-C1A-N1A-N2A	-177.6(4)
C14A-C1A-N1A-N2A	-4.1(7)
C9A-C8A-N2A-N1A	-6.9(7)
C13A-C8A-N2A-N1A	170.1(4)
C1A-N1A-N2A-C8A	-173.0(4)
C6A-C5A-N3A-O1A	-4.0(9)
C4A-C5A-N3A-O1A	177.9(6)
C6A-C5A-N3A-O2A	174.1(6)
C4A-C5A-N3A-O2A	-4.0(9)
C12A-C11A-N4A-O3A	-179.3(6)
C10A-C11A-N4A-O3A	0.8(8)
C12A-C11A-N4A-O4A	-0.2(9)
C10A-C11A-N4A-O4A	179.9(6)
C12A-C13A-N5A-O5A	13.8(7)
C8A-C13A-N5A-O5A	-163.9(5)
C12A-C13A-N5A-O6A	-167.9(5)
C8A-C13A-N5A-O6A	14.5(7)
N1B-C1B-C2B-C3B	-173.9(4)
C14B-C1B-C2B-C3B	-7.0(6)
C14"-C1B-C2B-C3B	36.6(7)
N1B-C1B-C2B-C7B	5.0(6)
C14B-C1B-C2B-C7B	171.8(4)
C14"-C1B-C2B-C7B	-144.5(6)
C7B-C2B-C3B-C4B	-1.6(7)
C1B-C2B-C3B-C4B	177.2(4)
C2B-C3B-C4B-C5B	1.3(7)
C3B-C4B-C5B-C6B	-1.0(7)

C3B-C4B-C5B-N3B	179.7(4)
C4B-C5B-C6B-C7B	1.1(7)
N3B-C5B-C6B-C7B	-179.6(4)
C5B-C6B-C7B-C2B	-1.4(7)
C3B-C2B-C7B-C6B	1.7(7)
C1B-C2B-C7B-C6B	-177.2(4)
N2B-C8B-C9B-C10B	-179.7(5)
C13B-C8B-C9B-C10B	-2.1(8)
C8B-C9B-C10B-C11B	2.3(10)
C9B-C10B-C11B-C12B	-0.5(10)
C9B-C10B-C11B-N4B	-179.4(6)
C10B-C11B-C12B-C13B	-1.6(9)
N4B-C11B-C12B-C13B	177.3(5)
N2B-C8B-C13B-C12B	177.6(5)
C9B-C8B-C13B-C12B	0.0(7)
N2B-C8B-C13B-N5B	-2.6(7)
C9B-C8B-C13B-N5B	179.7(5)
C11B-C12B-C13B-C8B	1.8(8)
C11B-C12B-C13B-N5B	-178.0(5)
N1B-C1B-C14B-C15B	-84.6(6)
C2B-C1B-C14B-C15B	109.6(5)
C14"-C1B-C14B-C15B	10.1(5)
C1B-C14B-C15B-C16B	175.9(4)
N1B-C1B-C14"-C15"	95.9(8)
C2B-C1B-C14"-C15"	-115.4(7)
C14B-C1B-C14"-C15"	-12.6(6)
C1B-C14"-C15"-C16B	-175.7(6)
C14"-C15"-C16B-C17"	110.6(15)
C14"-C15"-C16B-C17B	131.8(7)
C14"-C15"-C16B-C22B	-105.6(7)
C14"-C15"-C16B-C15B	8.1(4)
C14"-C15"-C16B-C22"	-117.9(7)
C14B-C15B-C16B-C17"	-128.7(11)
C14B-C15B-C16B-C17B	-106.5(7)
C14B-C15B-C16B-C22B	97.9(6)
C14B-C15B-C16B-C15"	-9.6(6)
C14B-C15B-C16B-C22"	89.1(7)

C17"-C16B-C17B-C21B	-103(2)
C22B-C16B-C17B-C21B	-7.8(4)
C15"-C16B-C17B-C21B	128.4(6)
C15B-C16B-C17B-C21B	-168.9(5)
C22"-C16B-C17B-C21B	0.4(5)
C17"-C16B-C17B-C18B	46(2)
C22B-C16B-C17B-C18B	140.7(10)
C15"-C16B-C17B-C18B	-83.0(12)
C15B-C16B-C17B-C18B	-20.3(14)
C22"-C16B-C17B-C18B	149.0(10)
C16B-C17B-C18B-C19B	-135.7(9)
C21B-C17B-C18B-C19B	9.1(8)
C17B-C16B-C17"-C21"	91(2)
C22B-C16B-C17"-C21"	4.1(12)
C15"-C16B-C17"-C21"	155.0(8)
C15B-C16B-C17"-C21"	-140.9(7)
C22"-C16B-C17"-C21"	14.1(11)
C17B-C16B-C17"-C18"	-60(4)
C22B-C16B-C17"-C18"	-147(4)
C15"-C16B-C17"-C18"	4(5)
C15B-C16B-C17"-C18"	68(4)
C22"-C16B-C17"-C18"	-137(4)
C16B-C17"-C18"-C19B	155(3)
C21"-C17"-C18"-C19B	6(2)
C17B-C18B-C19B-C25B	-108.7(5)
C17B-C18B-C19B-C27B	131.3(5)
C17B-C18B-C19B-C20"	-14.9(8)
C17B-C18B-C19B-C20B	12.7(7)
C17B-C18B-C19B-C18"	-112(24)
C17"-C18"-C19B-C25B	-128.6(14)
C17"-C18"-C19B-C27B	112.2(15)
C17"-C18"-C19B-C20"	-35.5(19)
C17"-C18"-C19B-C18B	48(23)
C17"-C18"-C19B-C20B	-7.8(19)
C25B-C19B-C20B-C21B	90.2(5)
C27B-C19B-C20B-C21B	-148.8(4)
C20"-C19B-C20B-C21B	62.8(9)

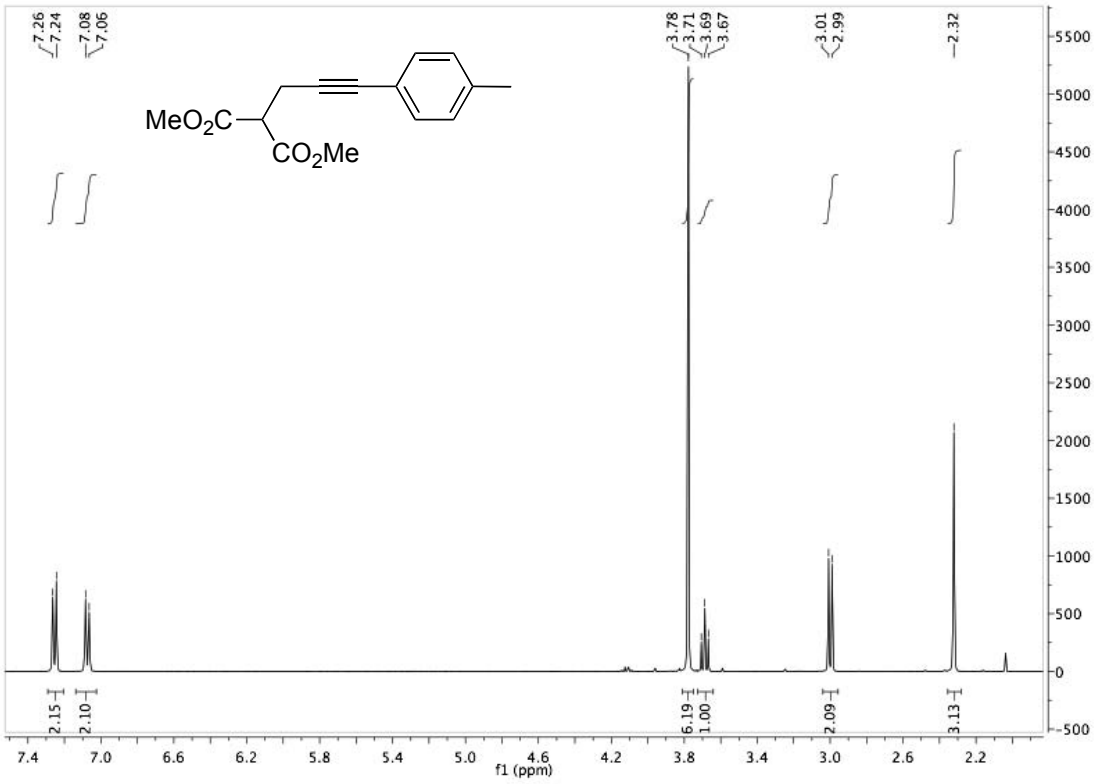
C18B-C19B-C20B-C21B	-29.4(6)
C18"-C19B-C20B-C21B	-27.4(13)
C16B-C17B-C21B-C20B	134.4(4)
C18B-C17B-C21B-C20B	-26.5(7)
C16B-C17B-C21B-C22B	7.7(4)
C18B-C17B-C21B-C22B	-153.3(6)
C19B-C20B-C21B-C17B	32.2(5)
C19B-C20B-C21B-C22B	125.6(5)
C17"-C16B-C22B-C24B	-89.4(11)
C17B-C16B-C22B-C24B	-109.7(5)
C15"-C16B-C22B-C24B	117.1(6)
C15B-C16B-C22B-C24B	52.9(6)
C22"-C16B-C22B-C24B	-162.0(13)
C17"-C16B-C22B-C23B	142.6(11)
C17B-C16B-C22B-C23B	122.3(5)
C15"-C16B-C22B-C23B	-10.9(8)
C15B-C16B-C22B-C23B	-75.1(6)
C22"-C16B-C22B-C23B	69.9(14)
C17"-C16B-C22B-C21B	28.0(11)
C17B-C16B-C22B-C21B	7.6(4)
C15"-C16B-C22B-C21B	-125.5(6)
C15B-C16B-C22B-C21B	170.2(5)
C22"-C16B-C22B-C21B	-44.7(12)
C17B-C21B-C22B-C16B	-6.6(4)
C20B-C21B-C22B-C16B	-106.6(6)
C17B-C21B-C22B-C24B	108.4(5)
C20B-C21B-C22B-C24B	8.4(8)
C17B-C21B-C22B-C23B	-120.9(4)
C20B-C21B-C22B-C23B	139.0(5)
C25B-C19B-C20"-C21"	156.2(7)
C27B-C19B-C20"-C21"	-89.6(7)
C18B-C19B-C20"-C21"	47.2(8)
C20B-C19B-C20"-C21"	-49.1(6)
C18"-C19B-C20"-C21"	49.5(13)
C16B-C17"-C21"-C20"	-140.4(11)
C18"-C17"-C21"-C20"	25(2)
C16B-C17"-C21"-C22"	-14.2(11)

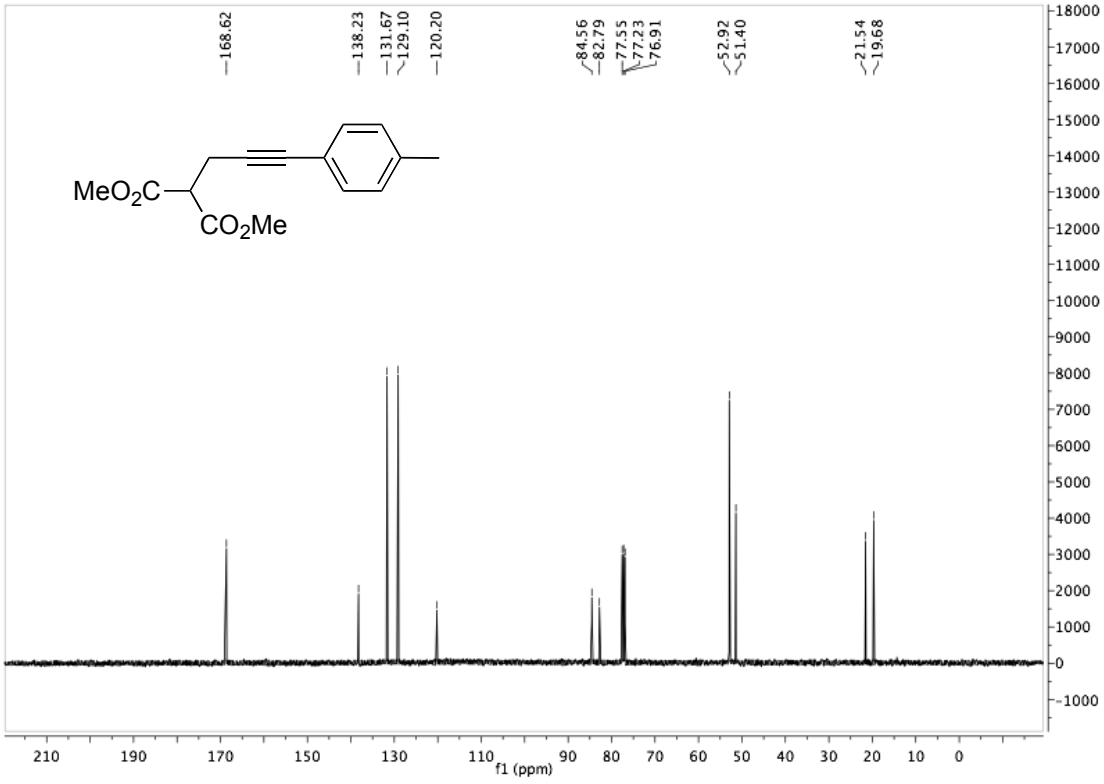
C18"-C17"-C21"-C22"	150.8(18)
C19B-C20"-C21"-C17"	-43.1(11)
C19B-C20"-C21"-C22"	-138.6(7)
C17"-C21"-C22"-C24"	116.8(12)
C20"-C21"-C22"-C24"	-138.4(11)
C17"-C21"-C22"-C23"	-113.8(11)
C20"-C21"-C22"-C23"	-9.1(11)
C17"-C21"-C22"-C16B	11.8(9)
C20"-C21"-C22"-C16B	116.5(9)
C17"-C16B-C22"-C24"	-130.0(11)
C17B-C16B-C22"-C24"	-149.8(6)
C22B-C16B-C22"-C24"	-21.8(13)
C15"-C16B-C22"-C24"	84.3(8)
C15B-C16B-C22"-C24"	19.0(9)
C17"-C16B-C22"-C23"	101.1(12)
C17B-C16B-C22"-C23"	81.4(7)
C22B-C16B-C22"-C23"	-150.7(16)
C15"-C16B-C22"-C23"	-44.6(9)
C15B-C16B-C22"-C23"	-109.9(8)
C17"-C16B-C22"-C21"	-13.7(11)
C17B-C16B-C22"-C21"	-33.4(5)
C22B-C16B-C22"-C21"	94.5(13)
C15"-C16B-C22"-C21"	-159.4(6)
C15B-C16B-C22"-C21"	135.4(6)
C27B-C19B-C25B-O7B	172.4(8)
C20"-C19B-C25B-O7B	-55.4(10)
C18B-C19B-C25B-O7B	52.0(9)
C20B-C19B-C25B-O7B	-67.1(9)
C18"-C19B-C25B-O7B	52.1(12)
C27B-C19B-C25B-O7B"	-129.8(9)
C20"-C19B-C25B-O7B"	2.5(10)
C18B-C19B-C25B-O7B"	109.8(9)
C20B-C19B-C25B-O7B"	-9.3(10)
C18"-C19B-C25B-O7B"	110.0(12)
C27B-C19B-C25B-O8B	15.3(6)
C20"-C19B-C25B-O8B	147.6(7)
C18B-C19B-C25B-O8B	-105.0(6)

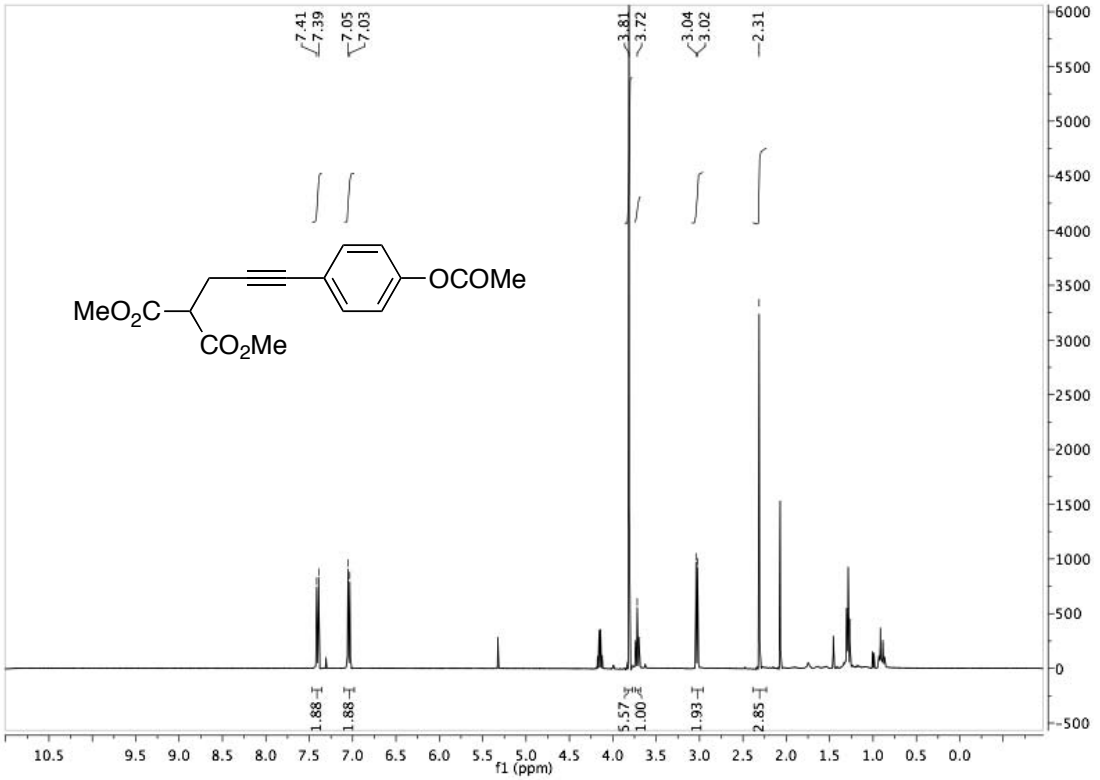
C20B-C19B-C25B-O8B	135.8(5)
C18"-C19B-C25B-O8B	-104.9(10)
C25B-C19B-C27B-O9B"	-139.3(8)
C20"-C19B-C27B-O9B"	116.2(8)
C18B-C19B-C27B-O9B"	-19.7(9)
C20B-C19B-C27B-O9B"	98.5(8)
C18"-C19B-C27B-O9B"	-21.9(12)
C25B-C19B-C27B-O9B	-89.5(8)
C20"-C19B-C27B-O9B	166.0(7)
C18B-C19B-C27B-O9B	30.1(9)
C20B-C19B-C27B-O9B	148.3(7)
C18"-C19B-C27B-O9B	27.9(12)
C25B-C19B-C27B-O10B	70.9(5)
C20"-C19B-C27B-O10B	-33.6(7)
C18B-C19B-C27B-O10B	-169.5(5)
C20B-C19B-C27B-O10B	-51.3(5)
C18"-C19B-C27B-O10B	-171.7(9)
C2B-C1B-N1B-N2B	178.4(4)
C14B-C1B-N1B-N2B	12.0(6)
C14"-C1B-N1B-N2B	-31.8(7)
C9B-C8B-N2B-N1B	2.0(7)
C13B-C8B-N2B-N1B	-175.5(4)
C1B-N1B-N2B-C8B	-178.8(4)
C4B-C5B-N3B-O2B	179.1(4)
C6B-C5B-N3B-O2B	-0.3(6)
C4B-C5B-N3B-O1B	-2.9(6)
C6B-C5B-N3B-O1B	177.8(4)
C12B-C11B-N4B-O4B	8.5(10)
C10B-C11B-N4B-O4B	-172.6(6)
C12B-C11B-N4B-O3B	-167.0(7)
C10B-C11B-N4B-O3B	12.0(10)
C8B-C13B-N5B-O5B	168.3(5)
C12B-C13B-N5B-O5B	-12.0(7)
C8B-C13B-N5B-O6B	-11.5(7)
C12B-C13B-N5B-O6B	168.2(5)
O7B-C25B-O8B-C26B	18.4(10)
O7B"-C25B-O8B-C26B	-36.0(11)

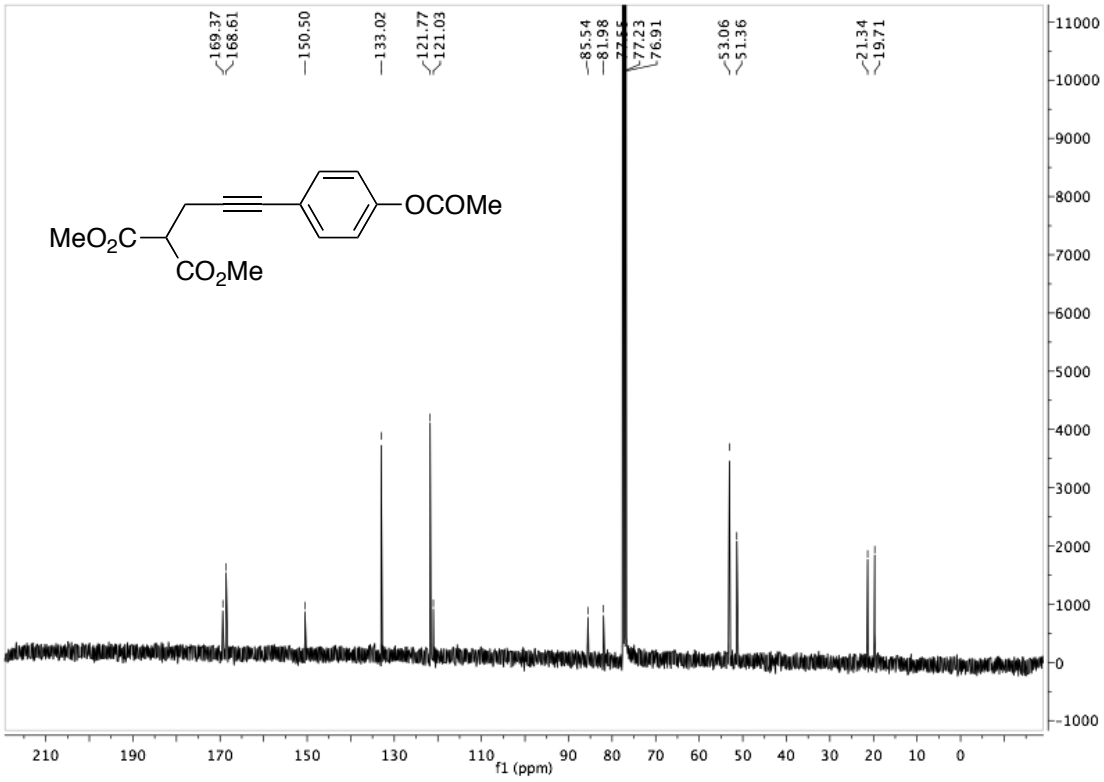
C19B-C25B-O8B-C26B	177.6(5)
O9B"-C27B-O10B-C28B	27.1(9)
O9B-C27B-O10B-C28B	-18.9(9)
C19B-C27B-O10B-C28B	179.1(4)

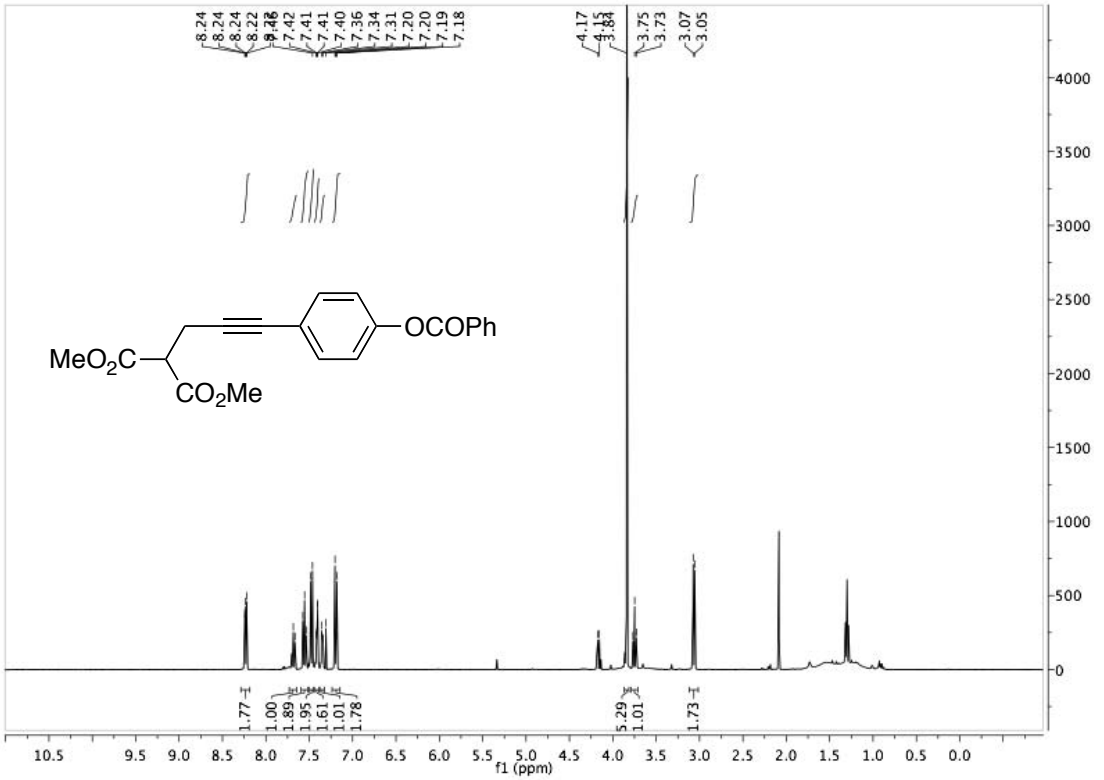
NMR spectra of propargyl malonates

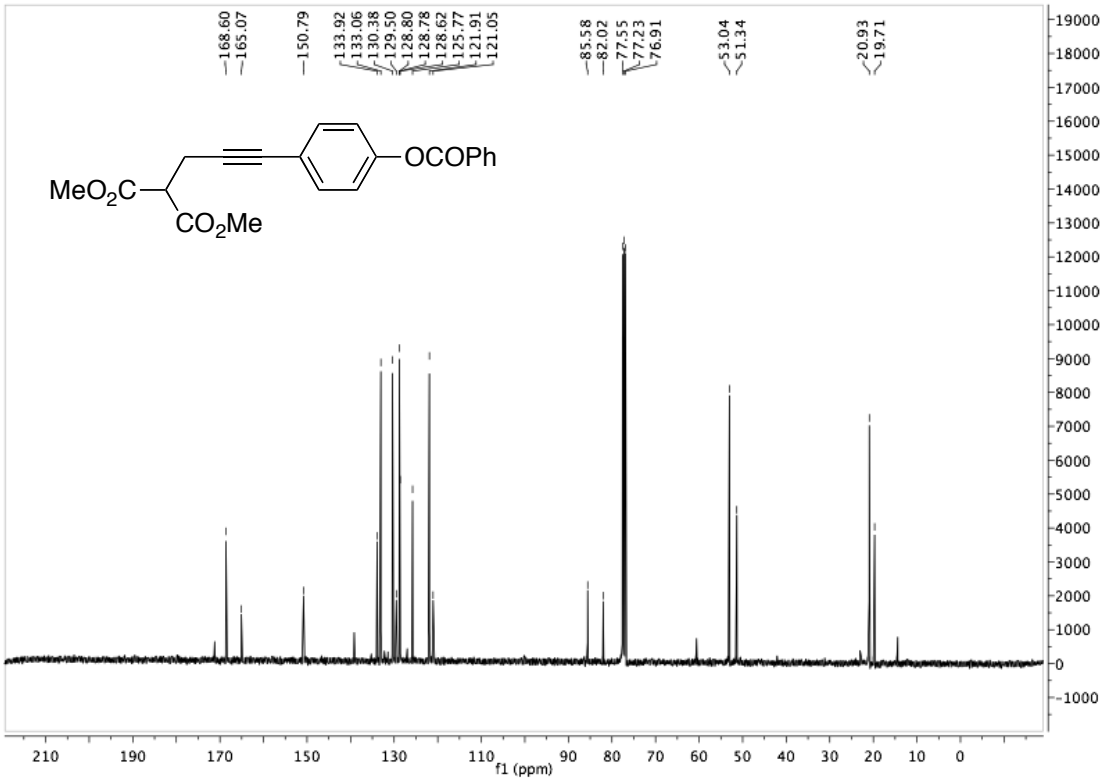


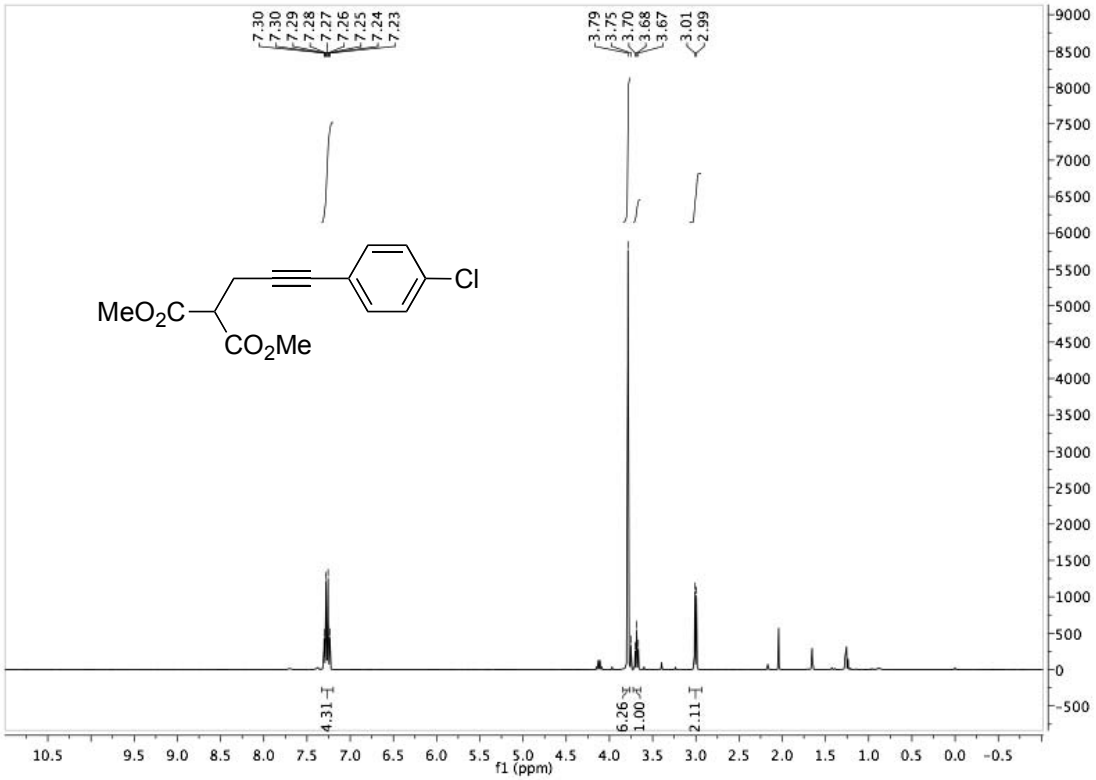


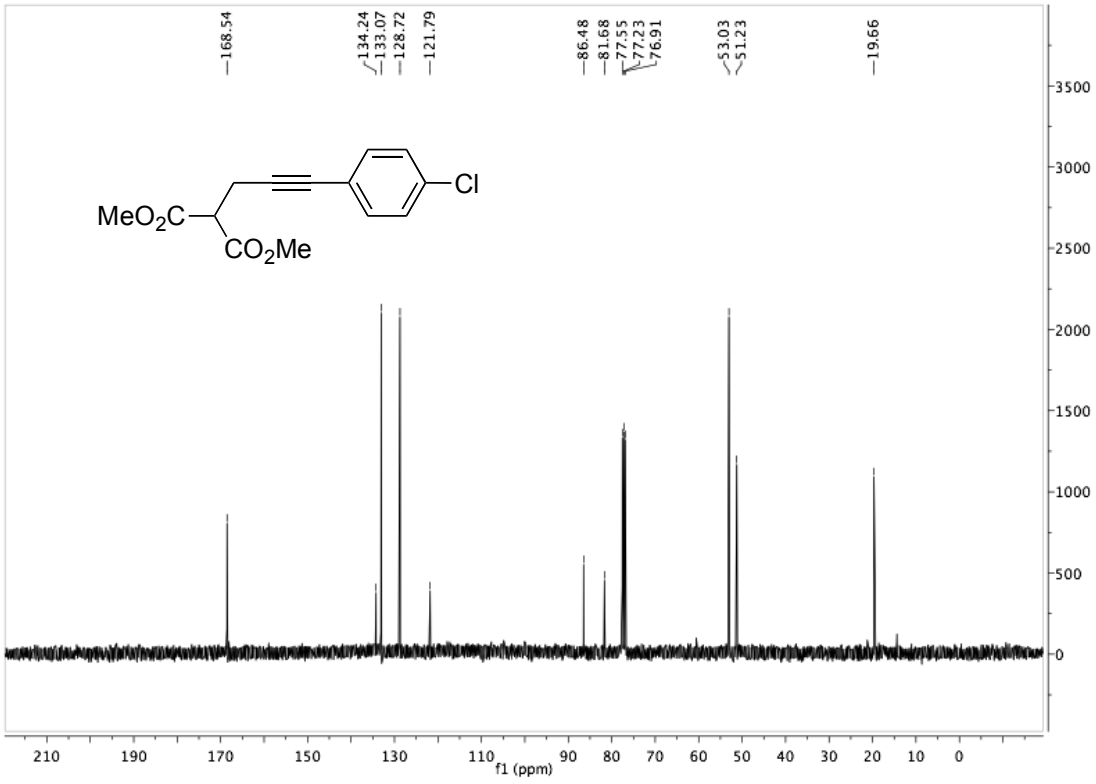


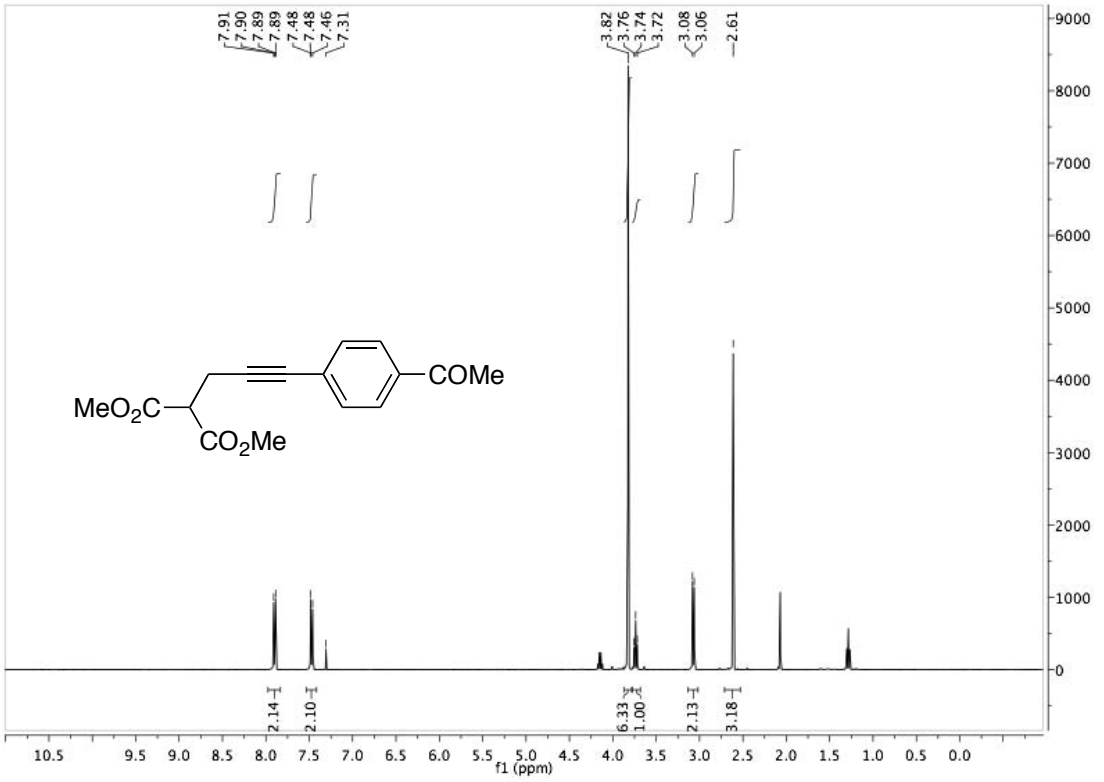


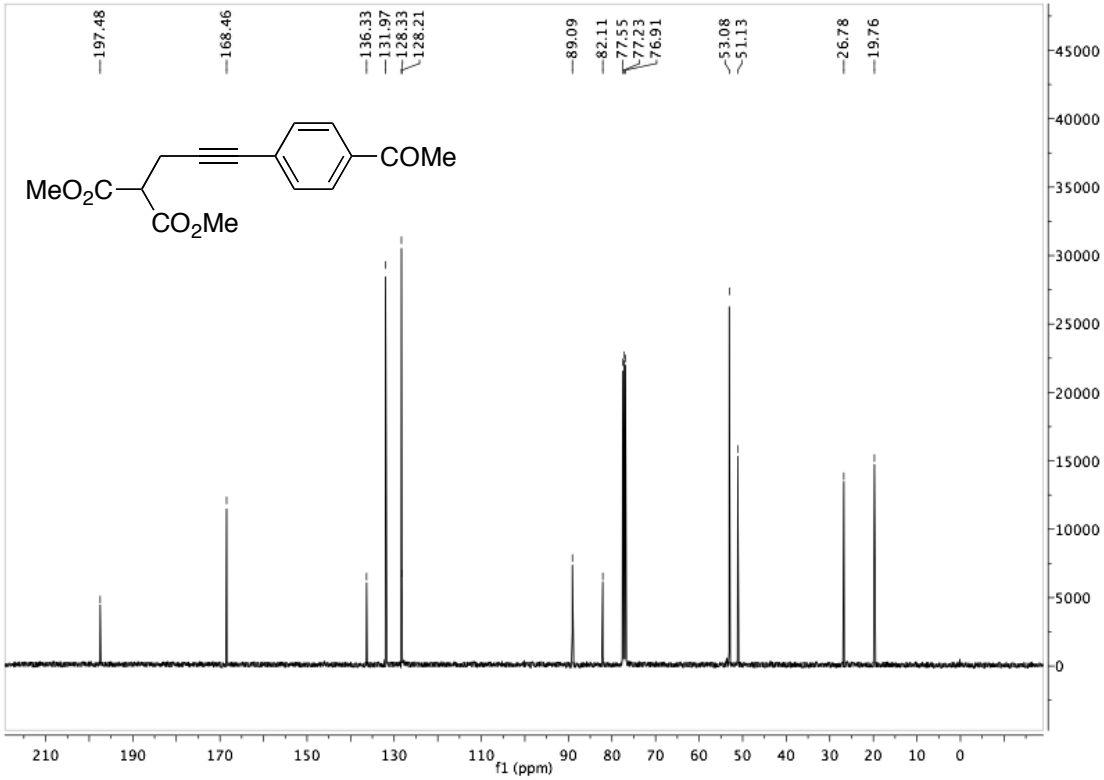


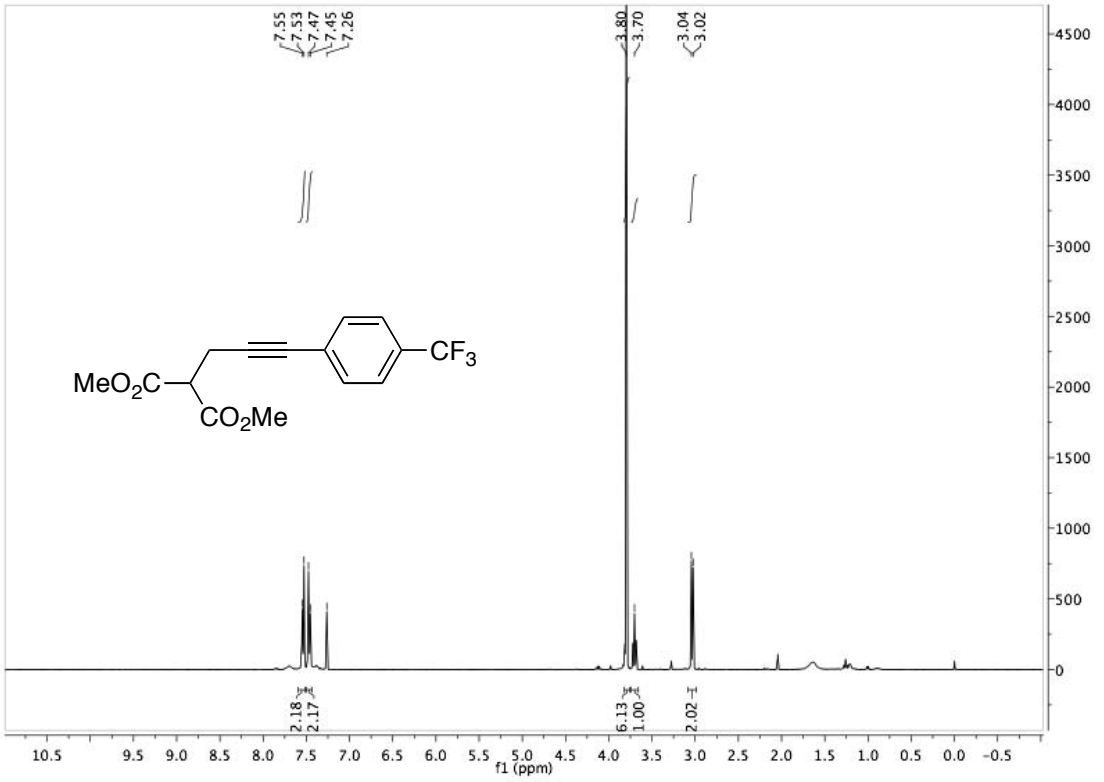


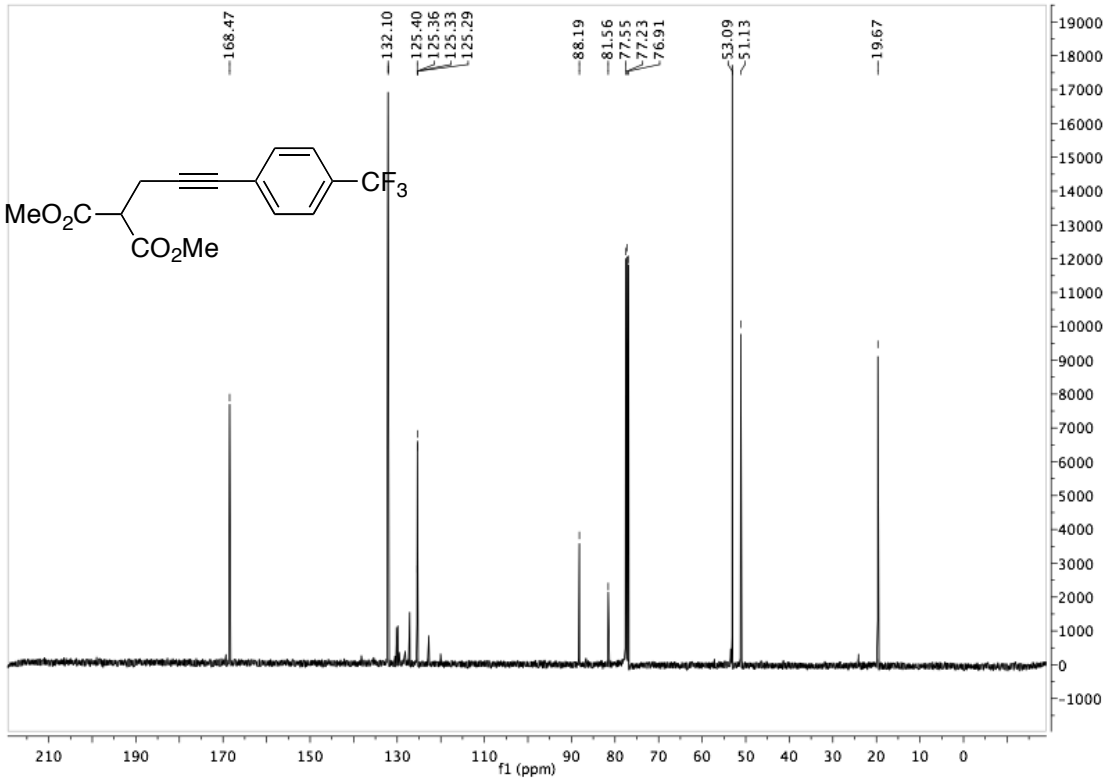






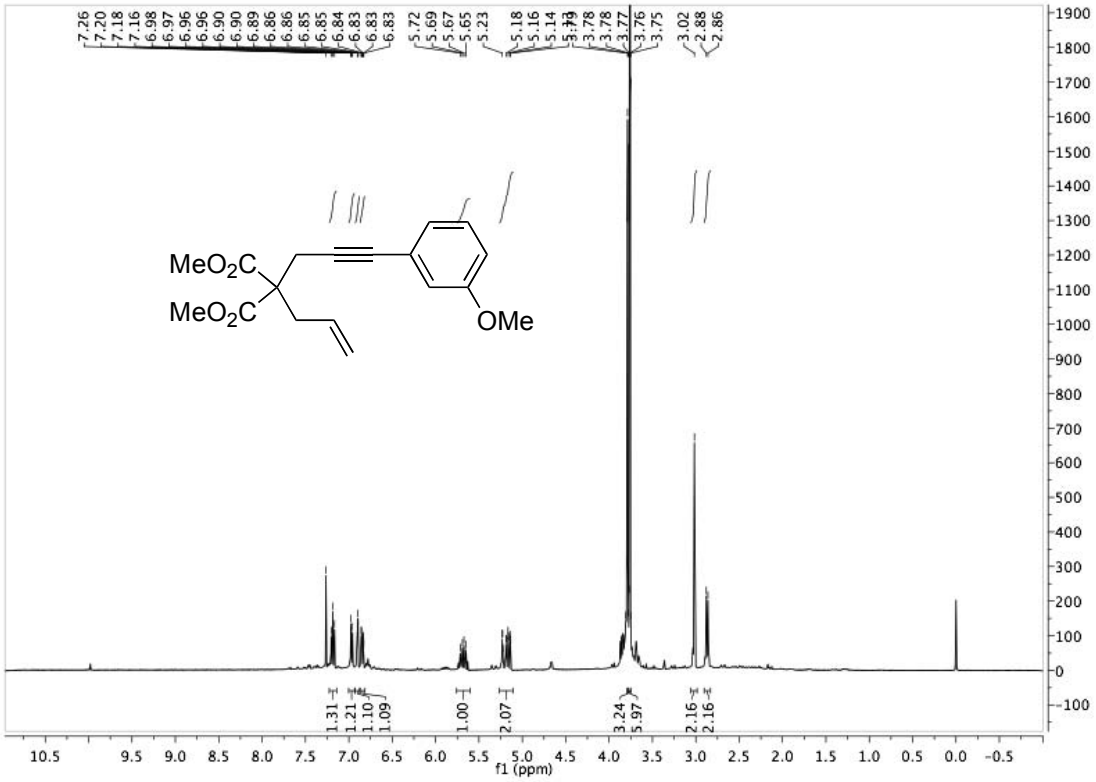


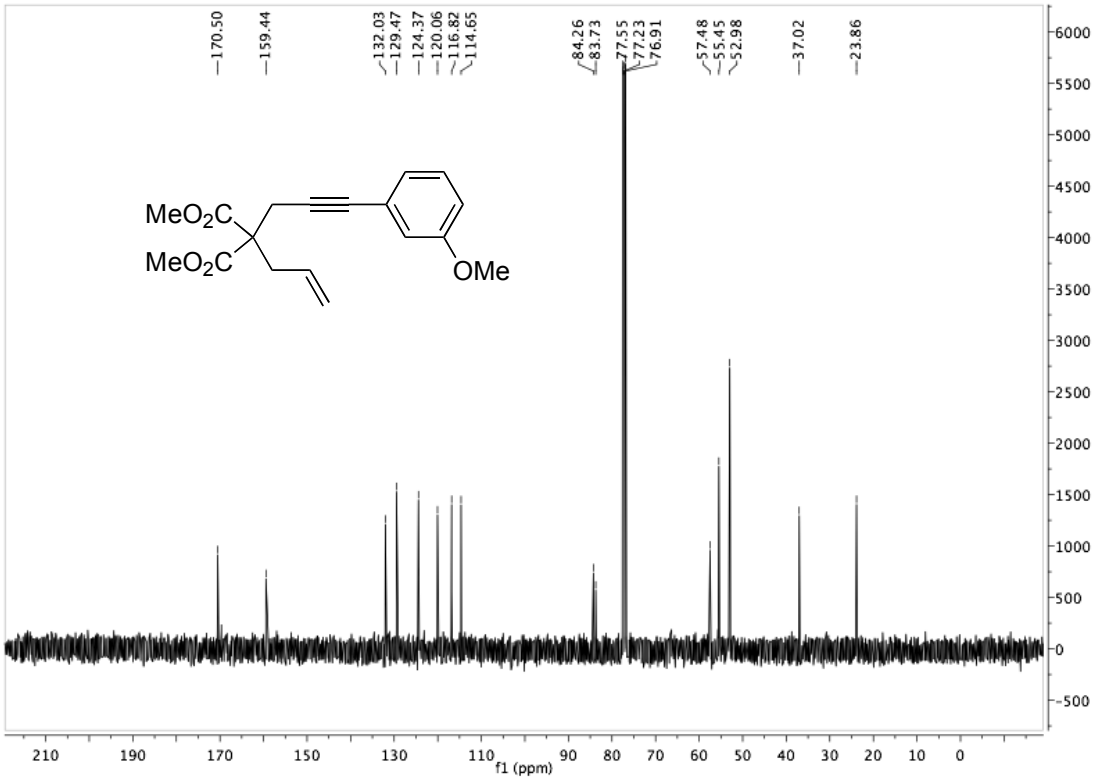




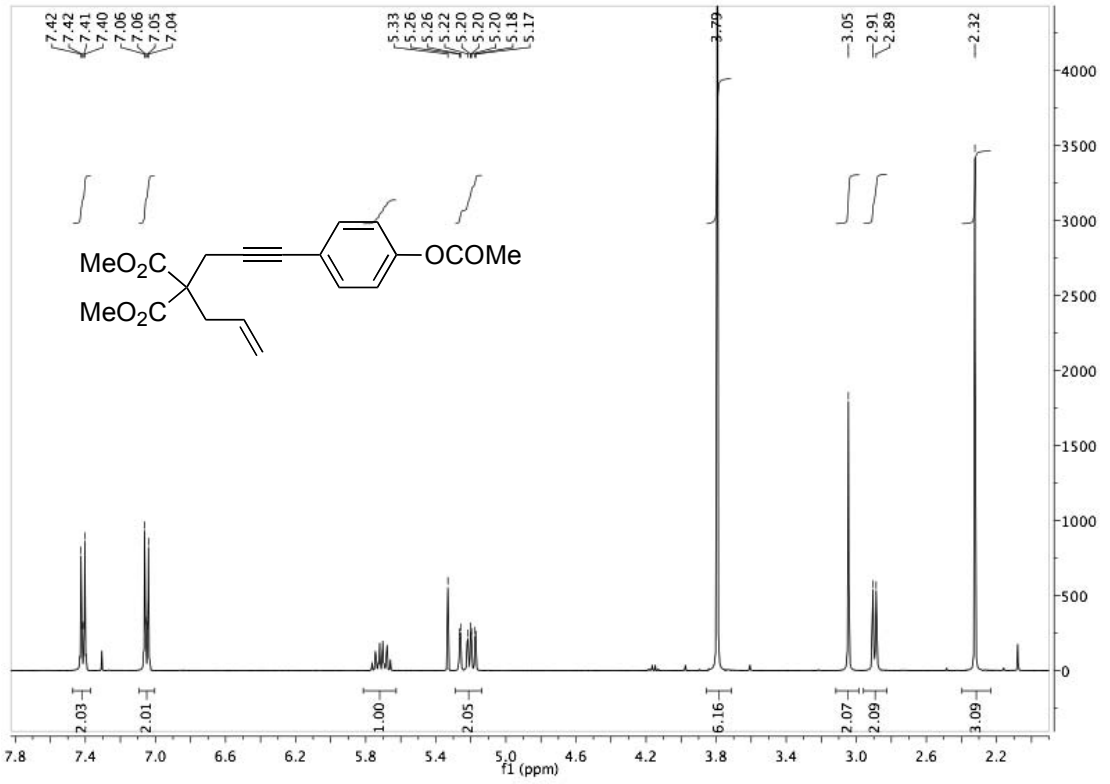
NMR spectra of 1,6-enynes

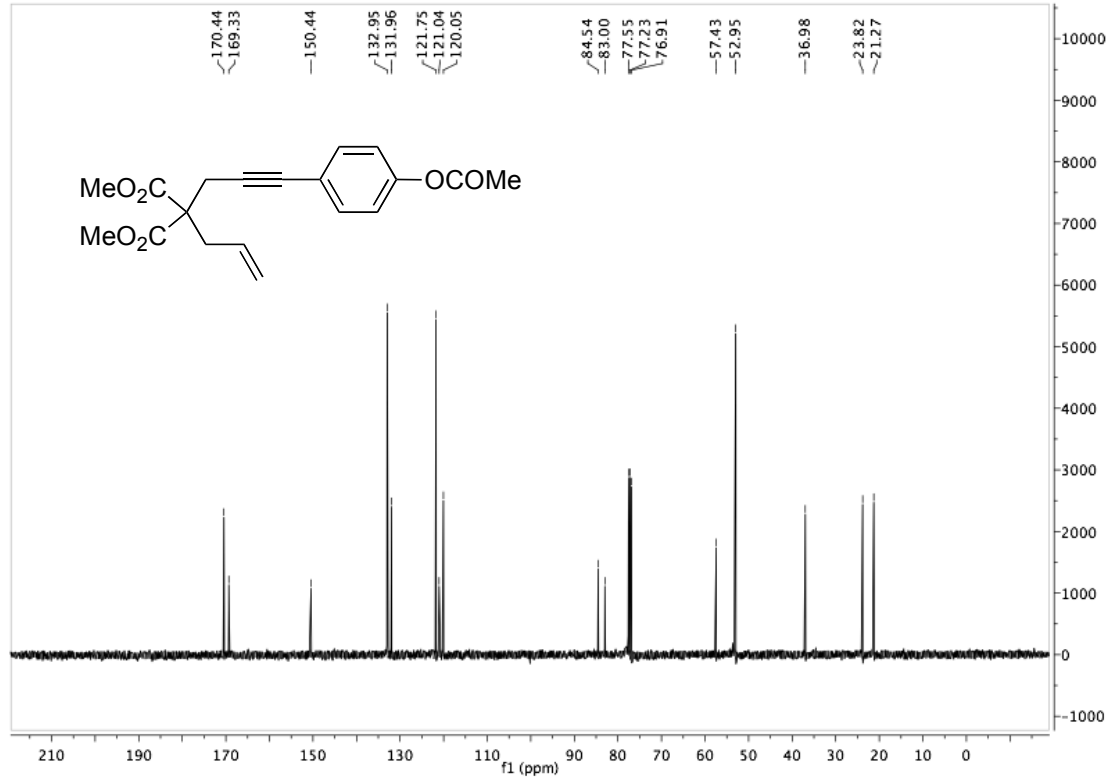
Enyne 14c



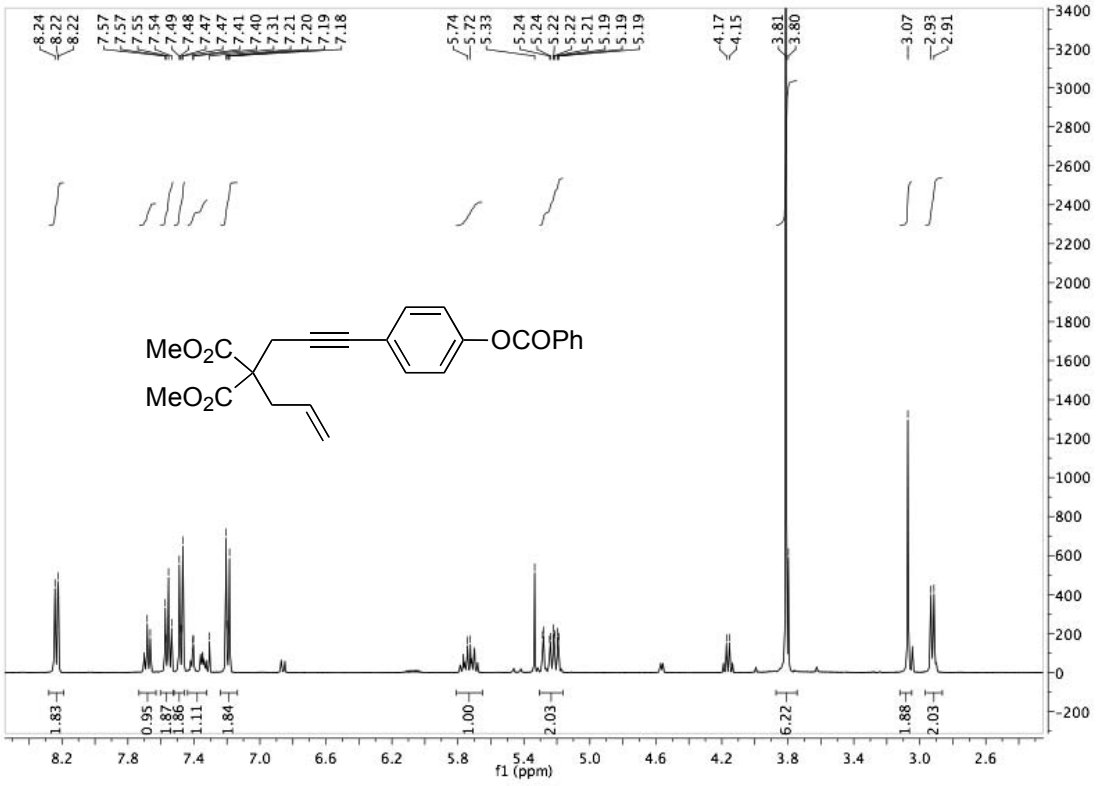


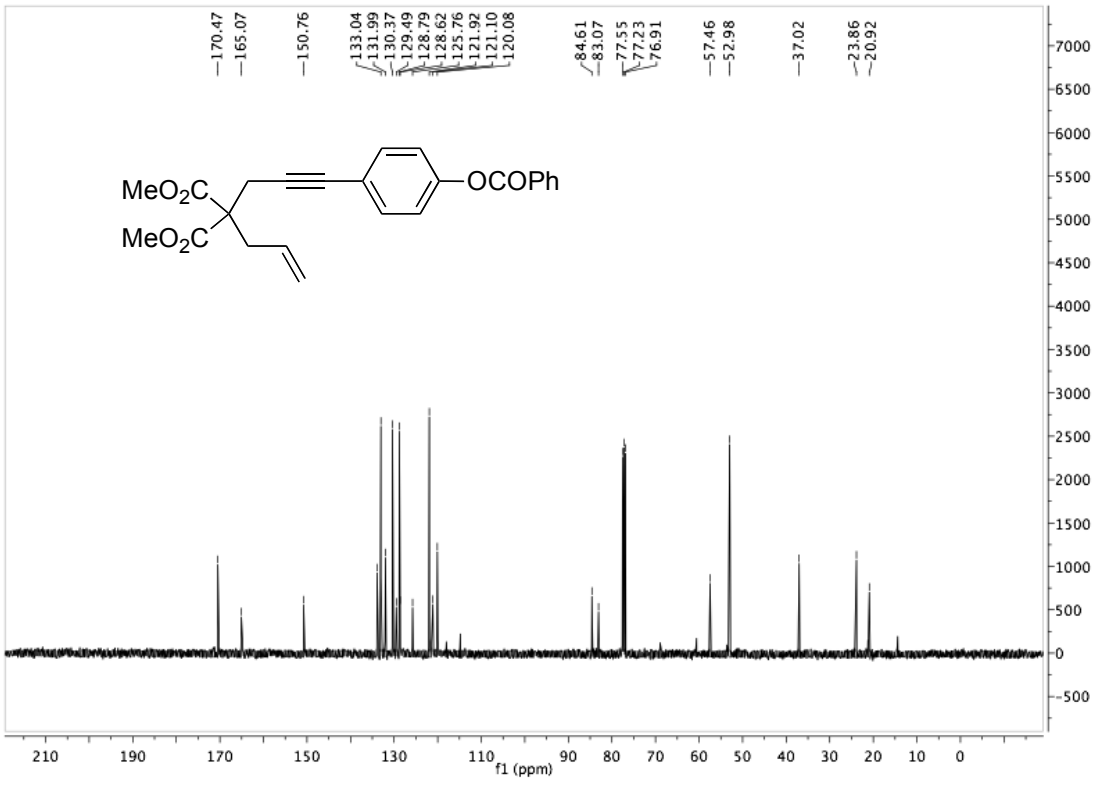
Enyne 14d


7.42
7.42
7.41
7.40
7.06
7.06
7.05
7.04
5.33
5.26
5.26
5.22
5.20
5.20
5.20
5.18
5.17
3.79
3.05
2.91
2.89
2.32
MeO2C
MeO2C
OCOMe
2.03
2.01
1.00
2.05
6.16
2.07
2.09
3.09
f1 (ppm)

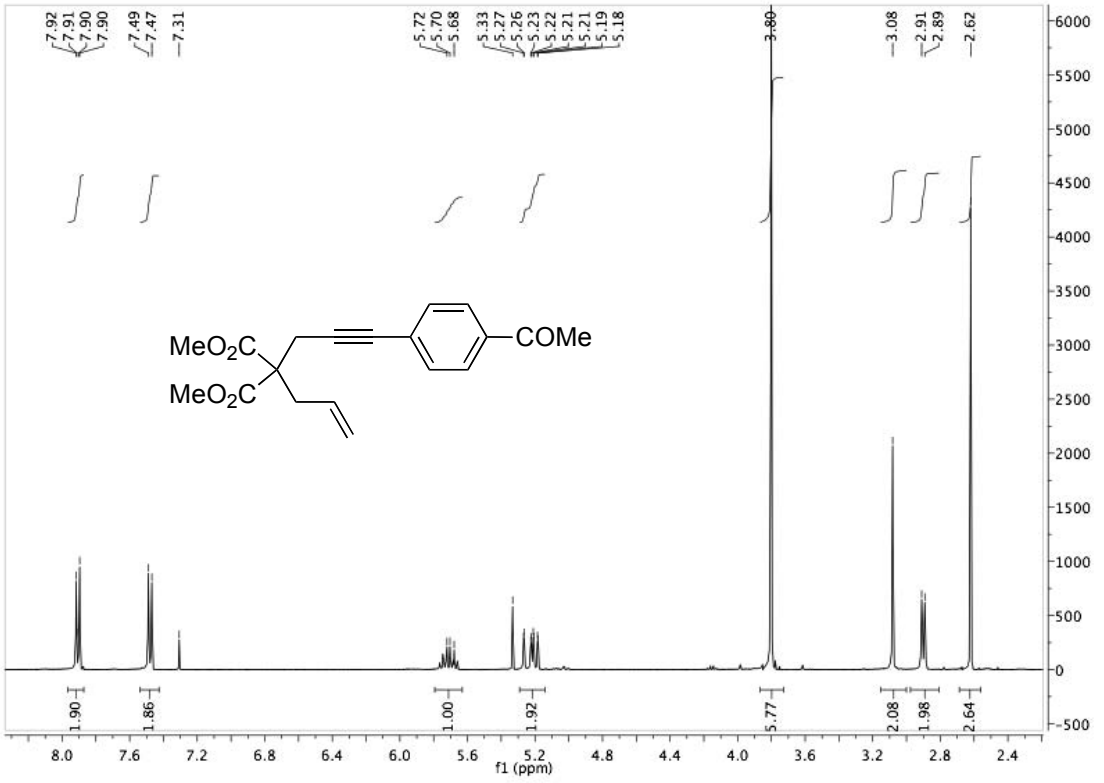

170.44
169.33
150.44
132.95
131.96
121.75
121.04
120.05
84.54
83.00
77.55
77.23
76.91
57.43
52.95
36.98
23.82
21.27
MeO2C
MeO2C
OCOMe
f1 (ppm)

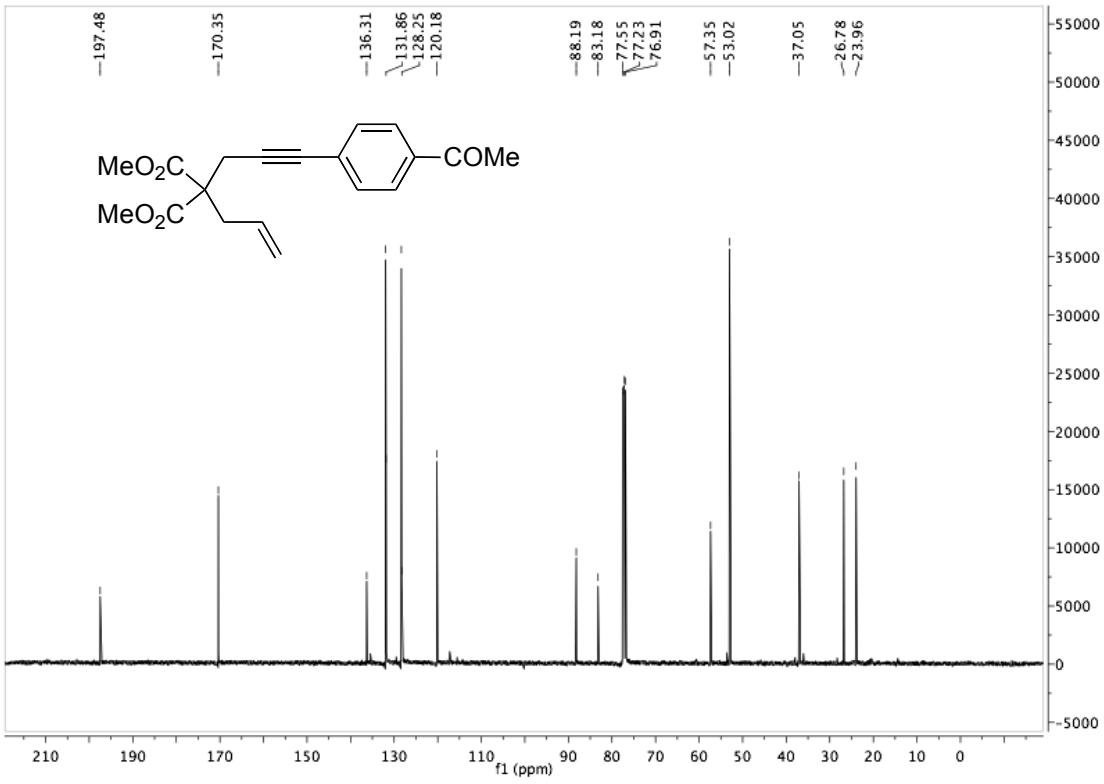
Enyne 14e


8.24
8.22
8.22
7.57
7.57
7.55
7.54
7.49
7.48
7.47
7.47
7.41
7.40
7.31
7.21
7.20
7.19
7.18
5.74
5.72
5.33
5.24
5.24
5.22
5.22
5.21
5.19
5.19
5.19
4.17
4.15
3.81
3.80
3.07
2.93
2.91
MeO2C
MeO2C
OCOPh
1.83
0.95
1.87
1.86
1.11
1.84
1.00
2.03
6.22
1.88
2.03
f1 (ppm)

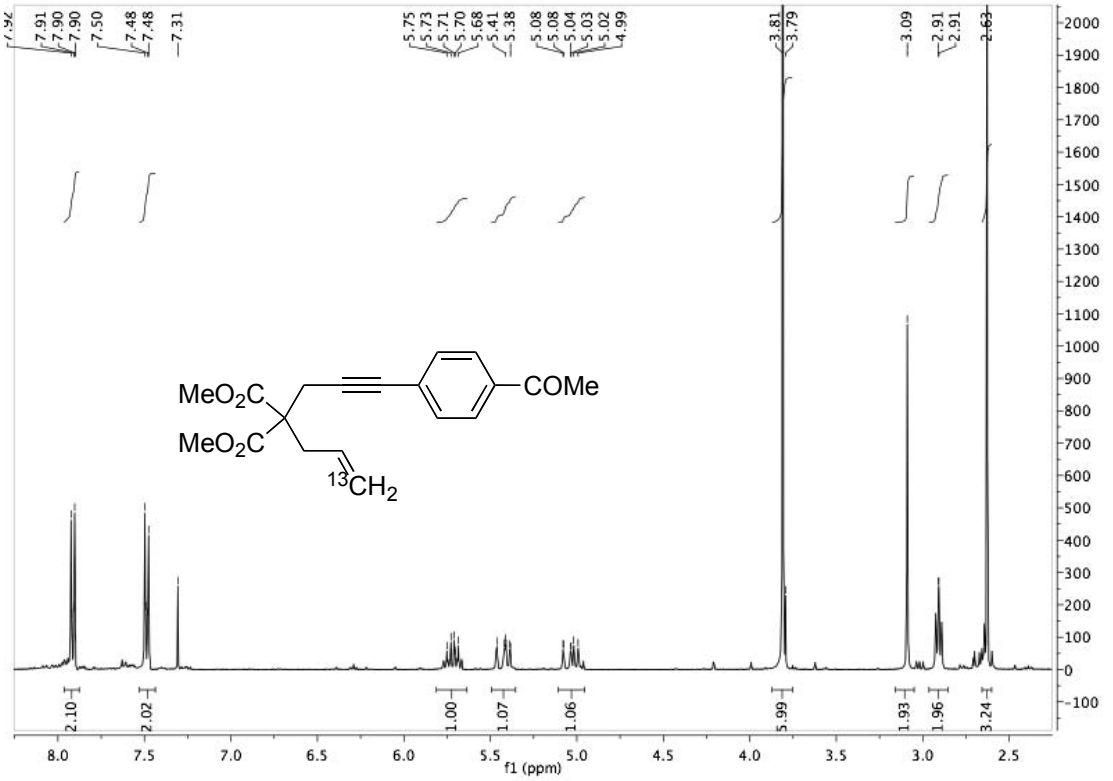

170.47
165.07
150.76
133.04
131.99
130.37
129.49
128.79
128.62
125.76
121.92
121.10
120.08
84.61
83.07
77.55
77.23
76.91
57.46
52.98
37.02
23.86
20.92
MeO2C
MeO2C
OCOPh
f1 (ppm)

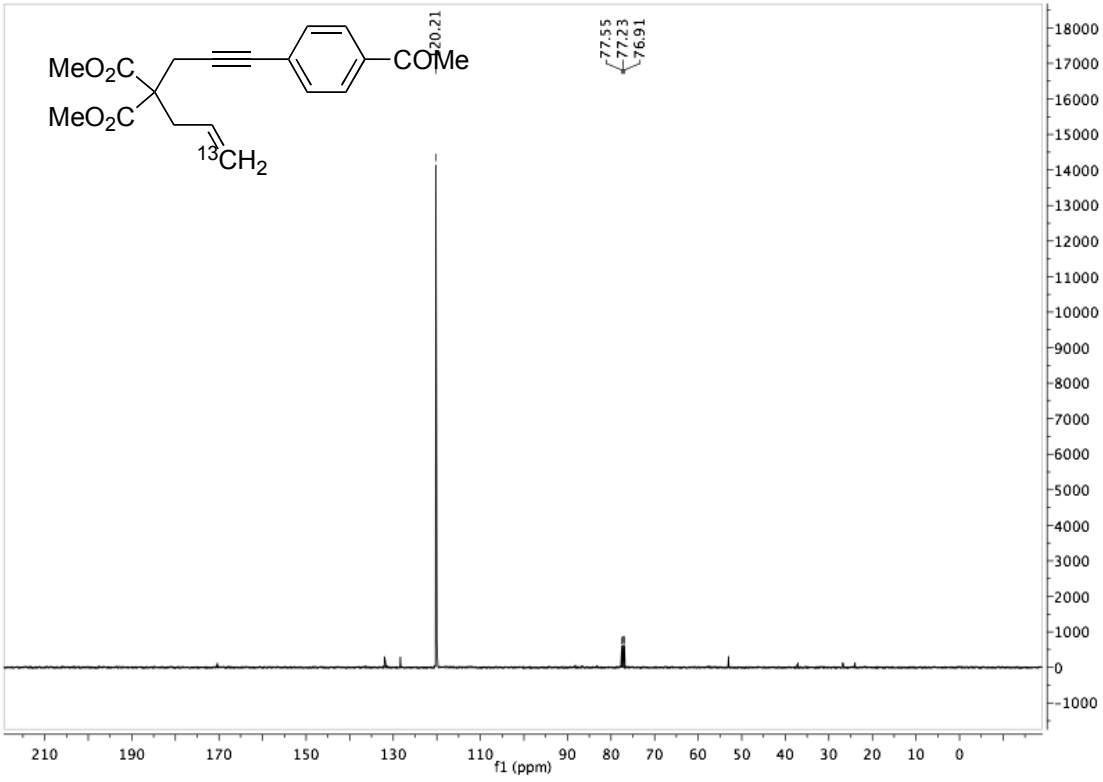
Enyne 14g


7.92
7.91
7.90
7.90
7.49
7.47
7.31
5.72
5.70
5.68
5.33
5.27
5.26
5.23
5.22
5.21
5.21
5.19
5.18
3.80
3.08
2.91
2.89
2.62
MeO2C
MeO2C
COMe
1.90
1.86
1.00
1.92
5.77
2.08
1.98
2.64
f1 (ppm)

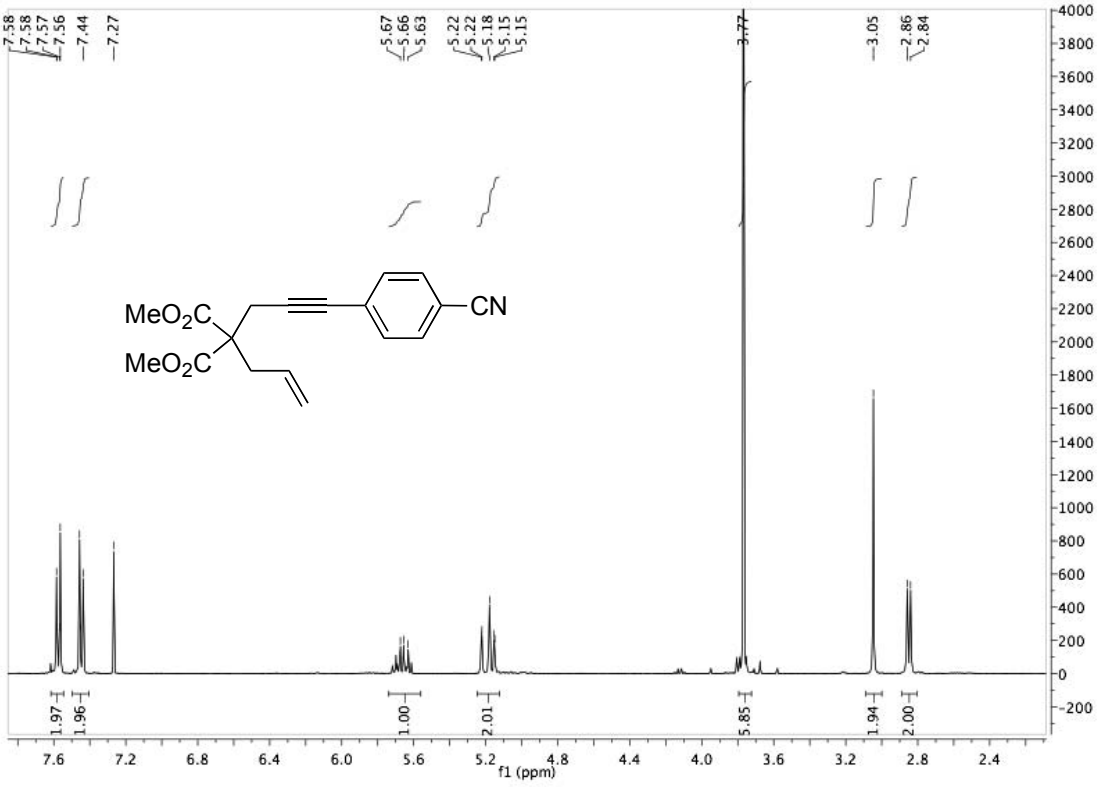

197.48
170.35
136.31
131.86
128.25
120.18
88.19
83.18
77.55
77.23
76.91
57.35
53.02
37.05
26.78
23.96
MeO2C
MeO2C
COMe
f1 (ppm)

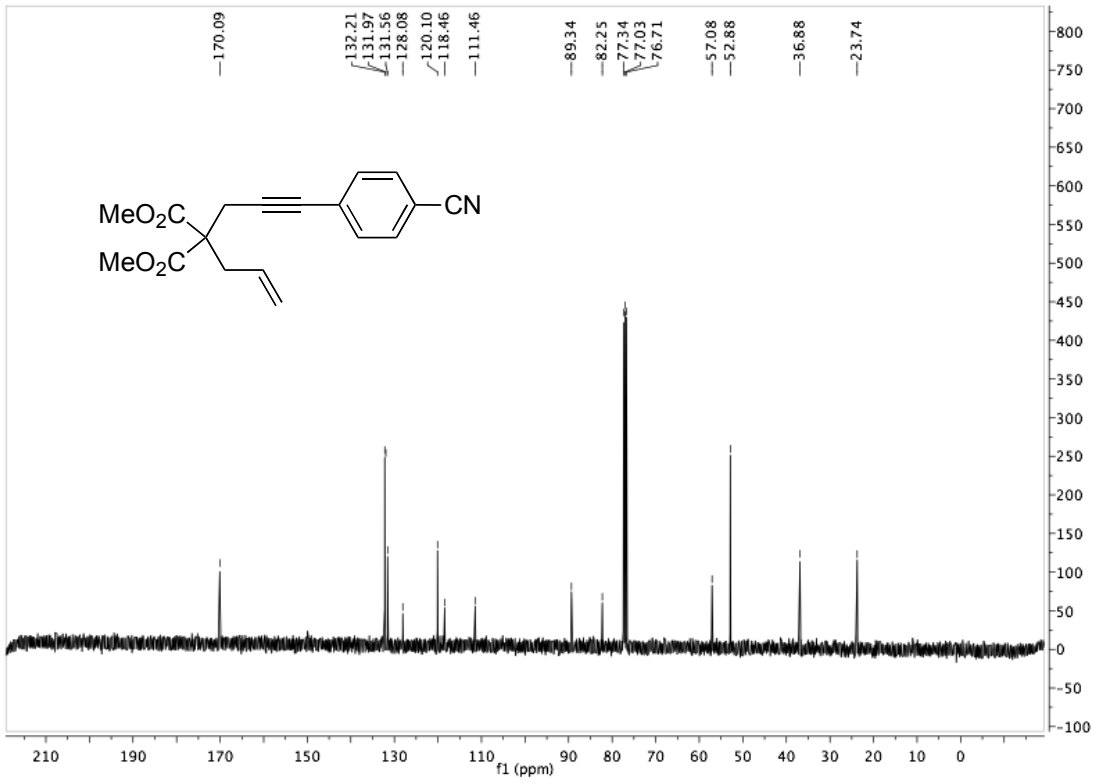
Enyne 14g-^{13}C





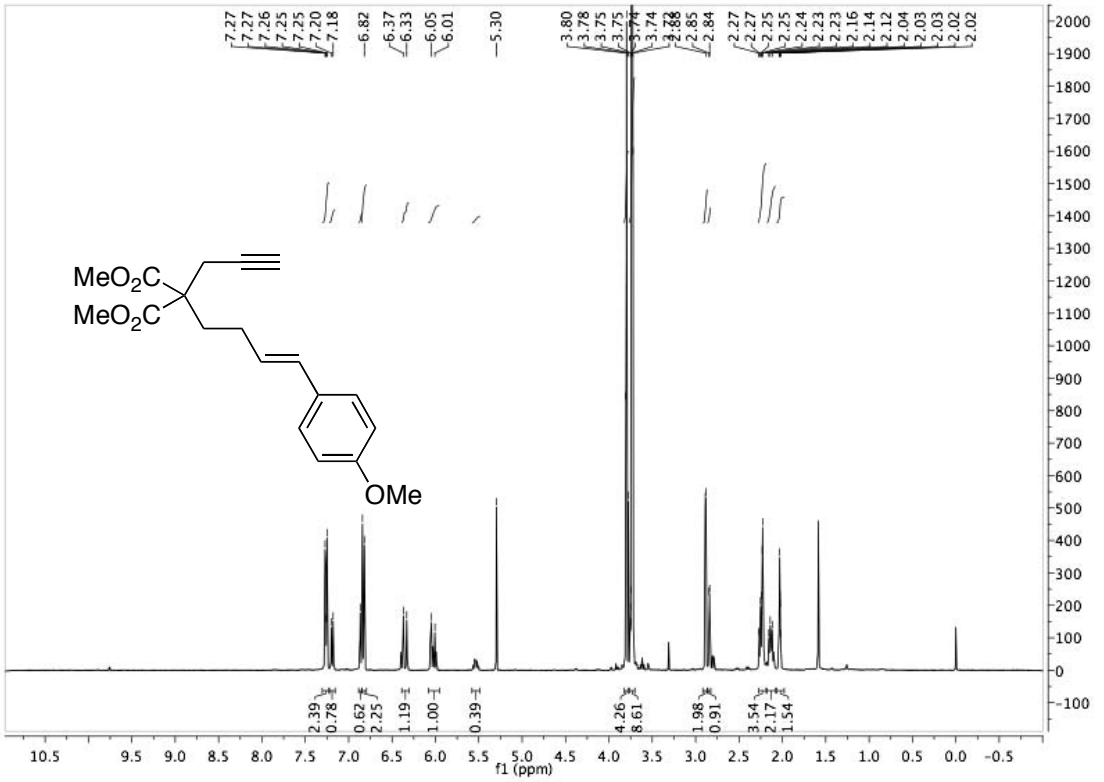
Enyne 14i

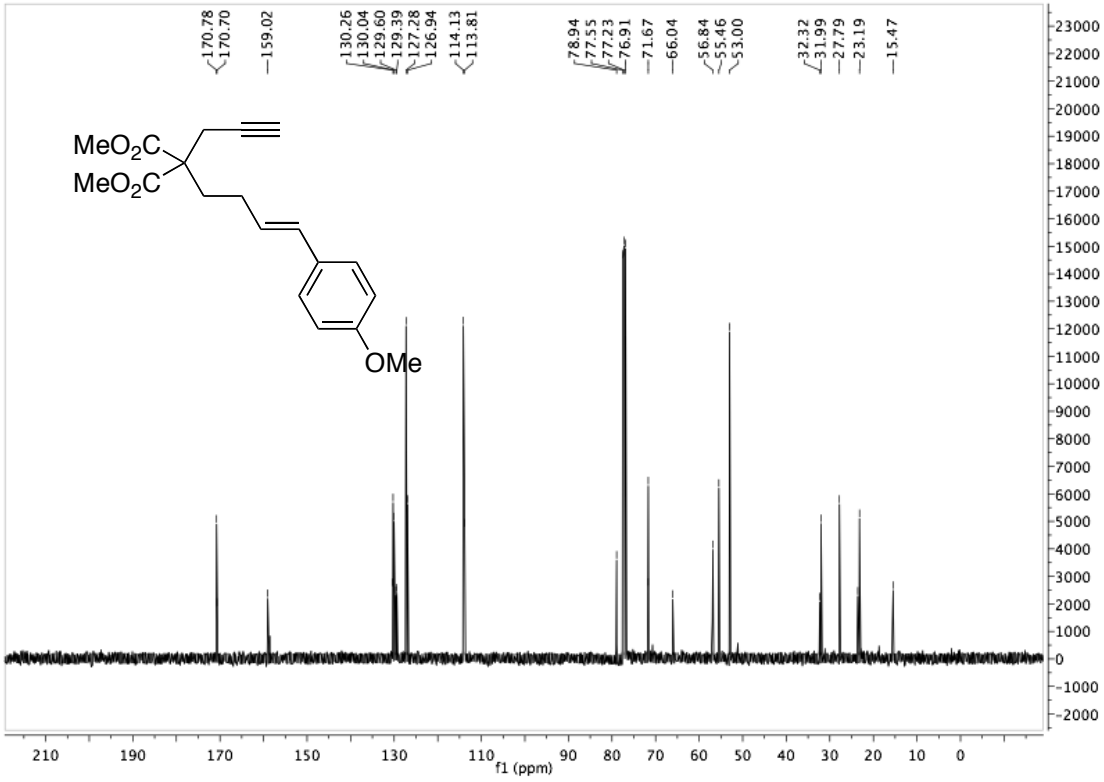




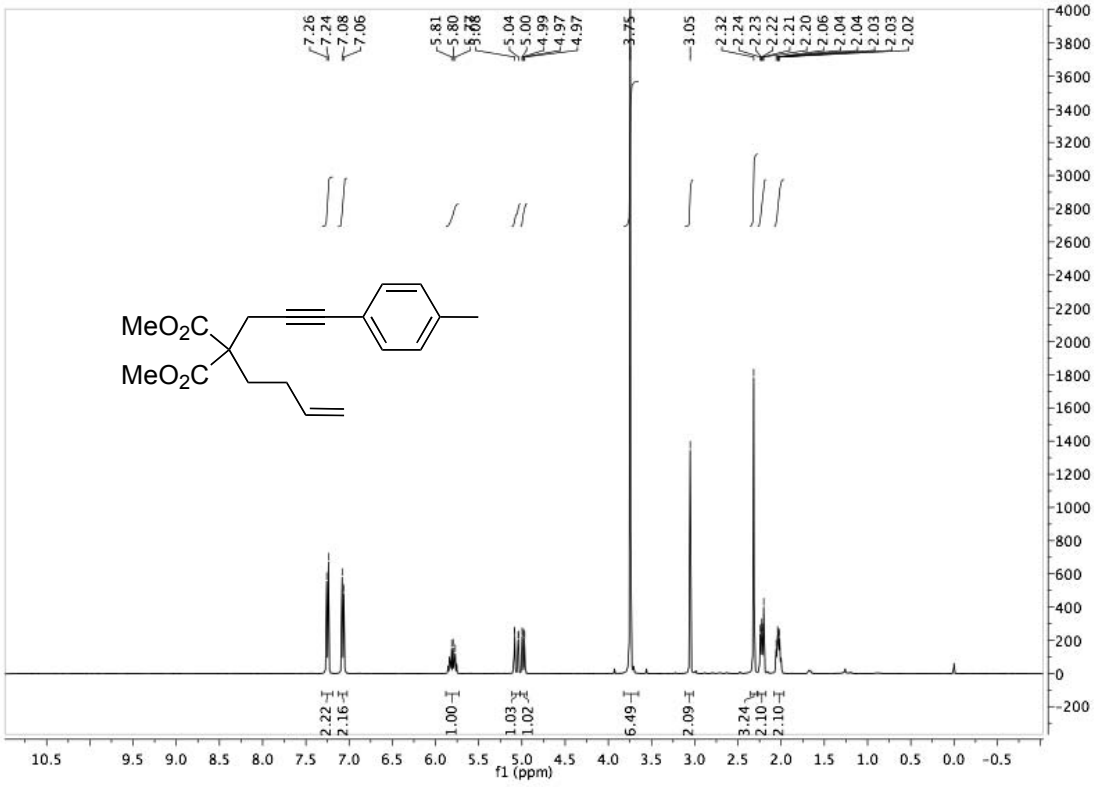
NMR spectra of 1,7-enynes

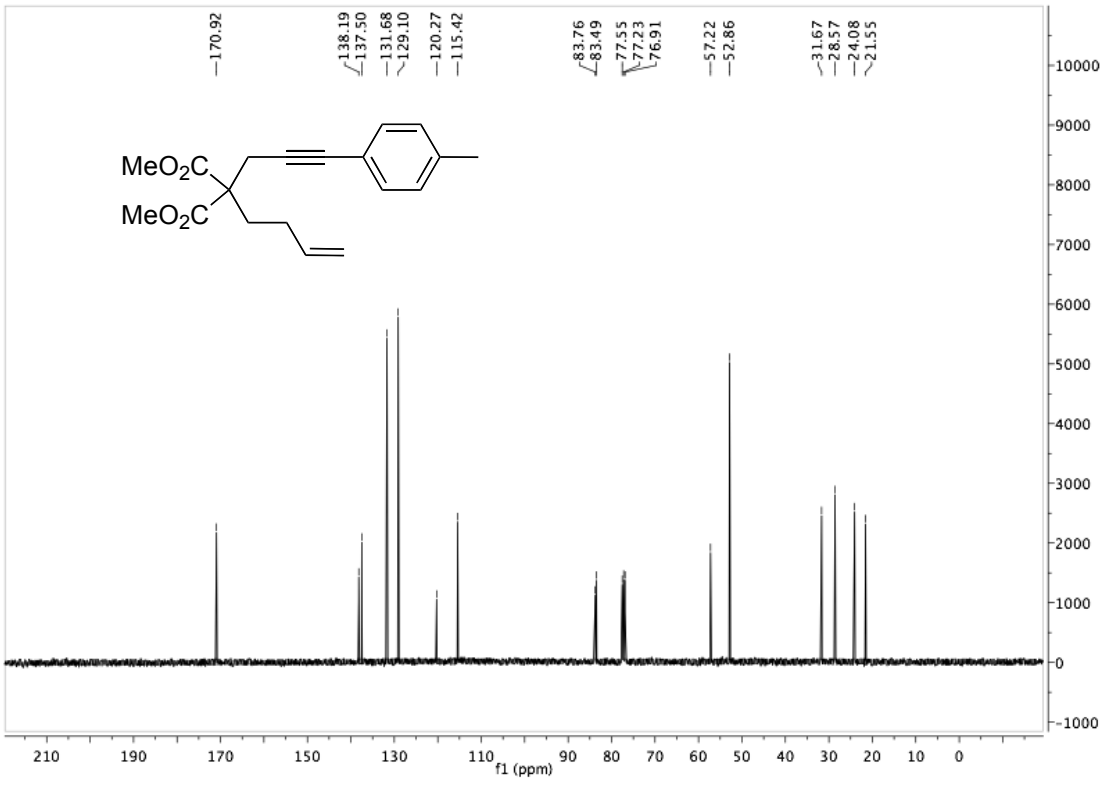
Enyne 27



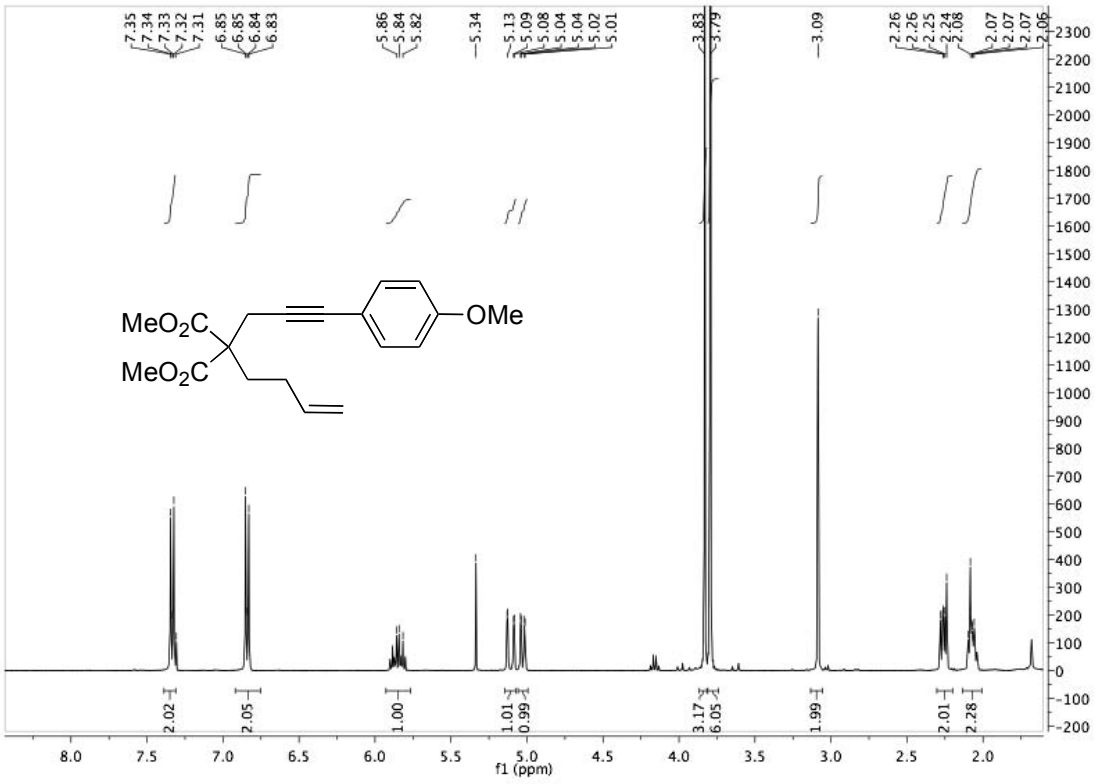


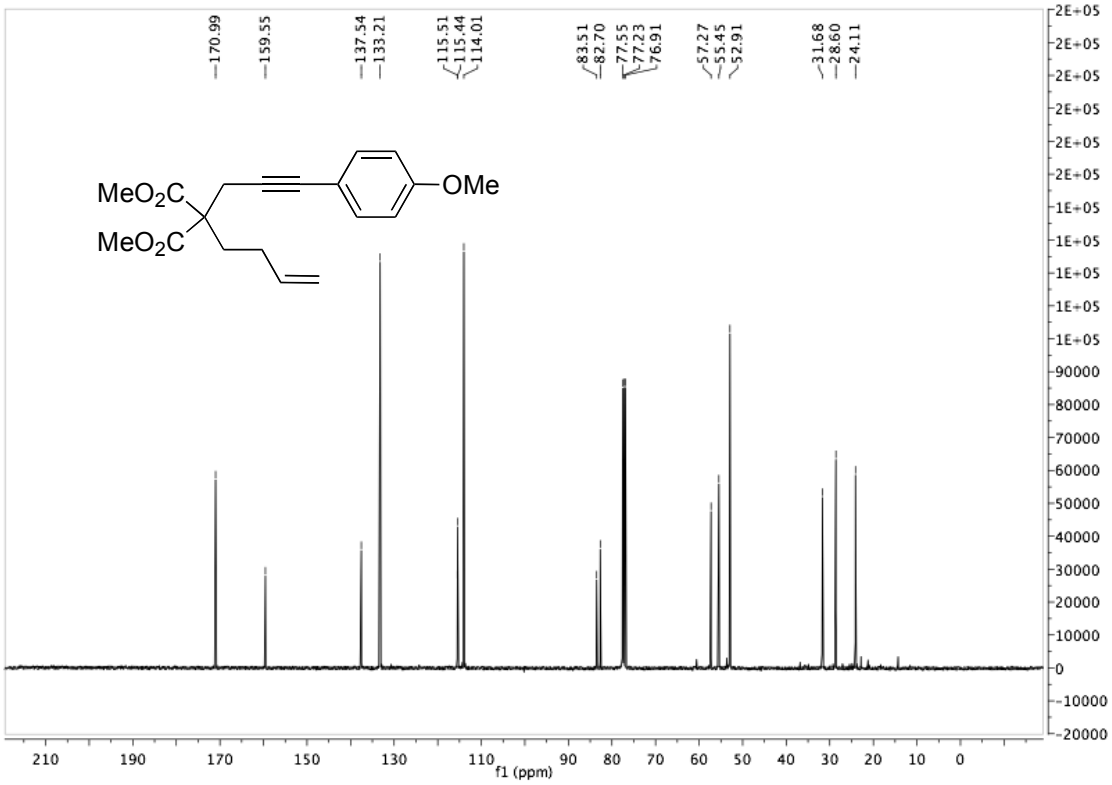
Enyne 31a





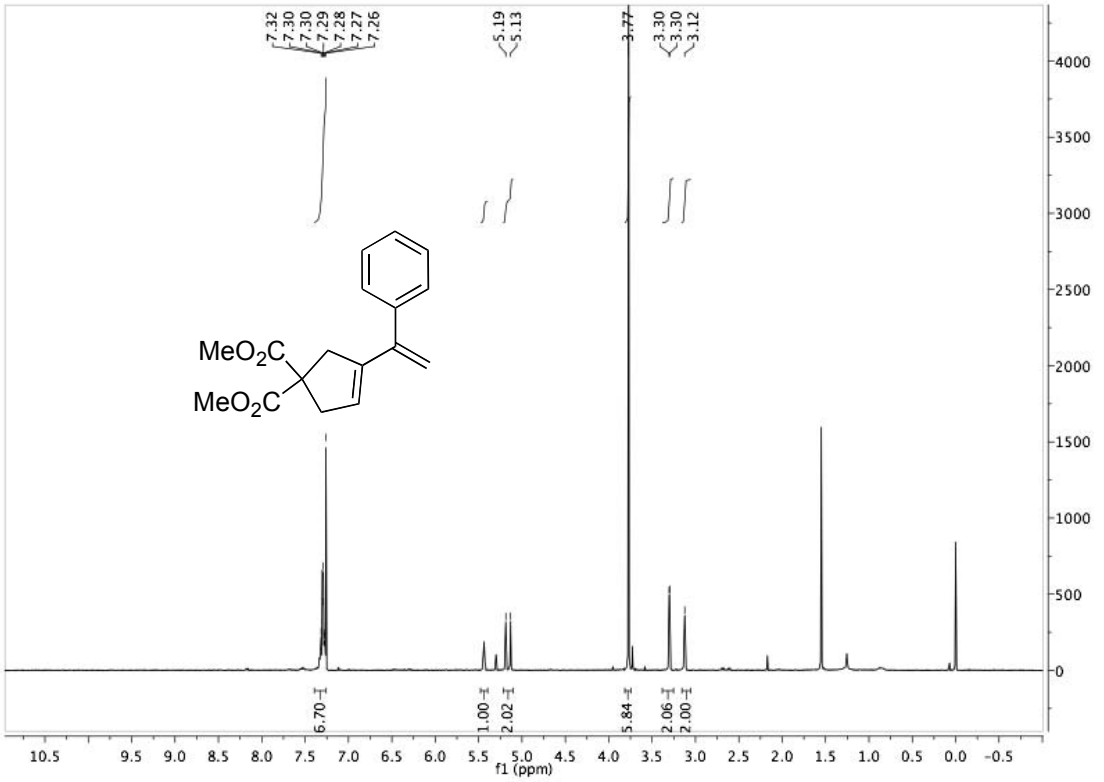
Enyne 31b

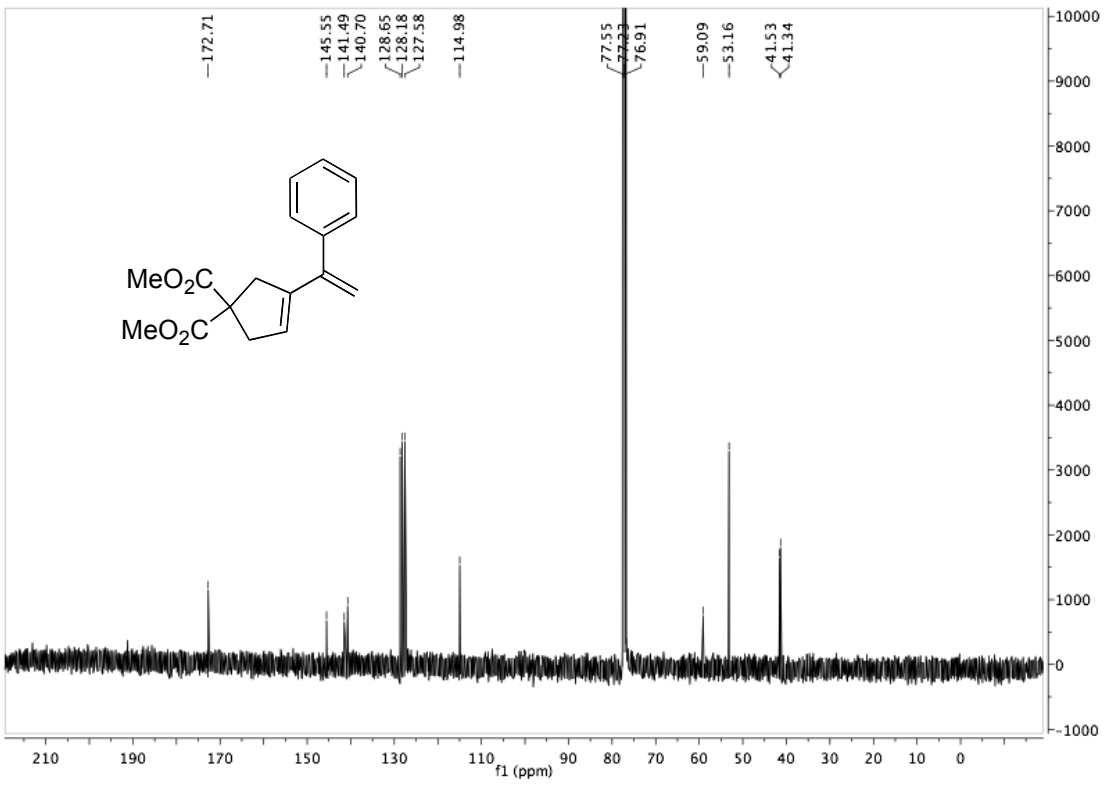




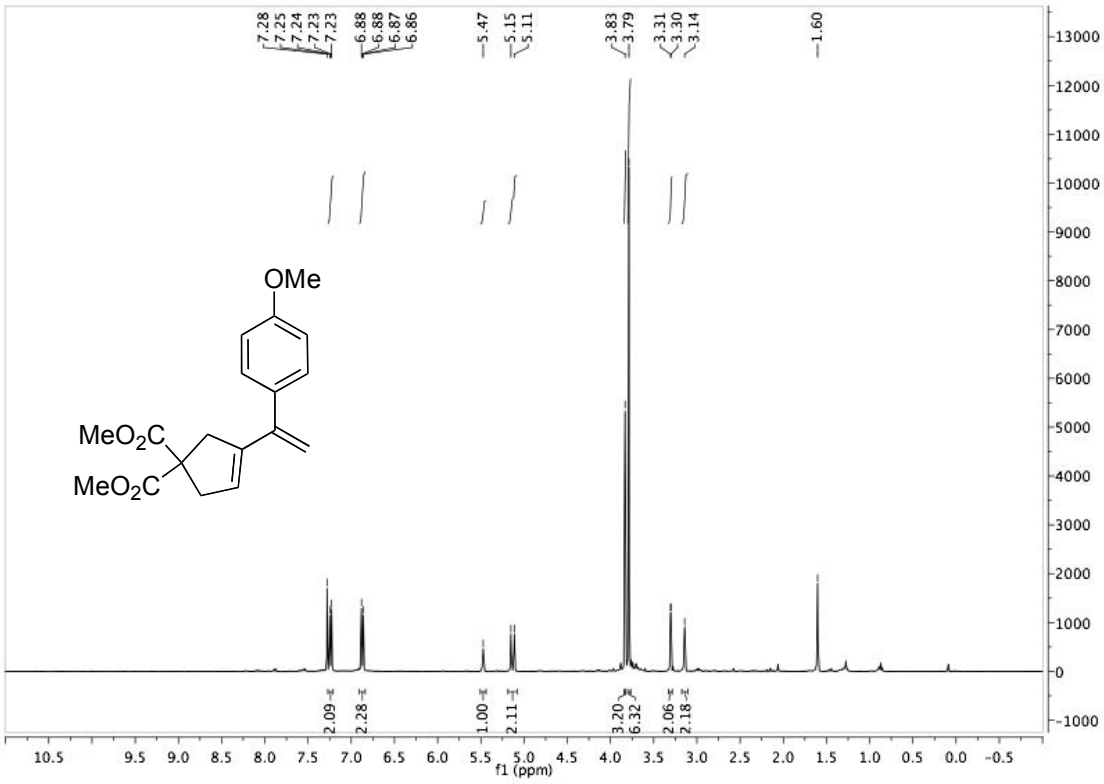
NMR spectra of cycloisomerisation products

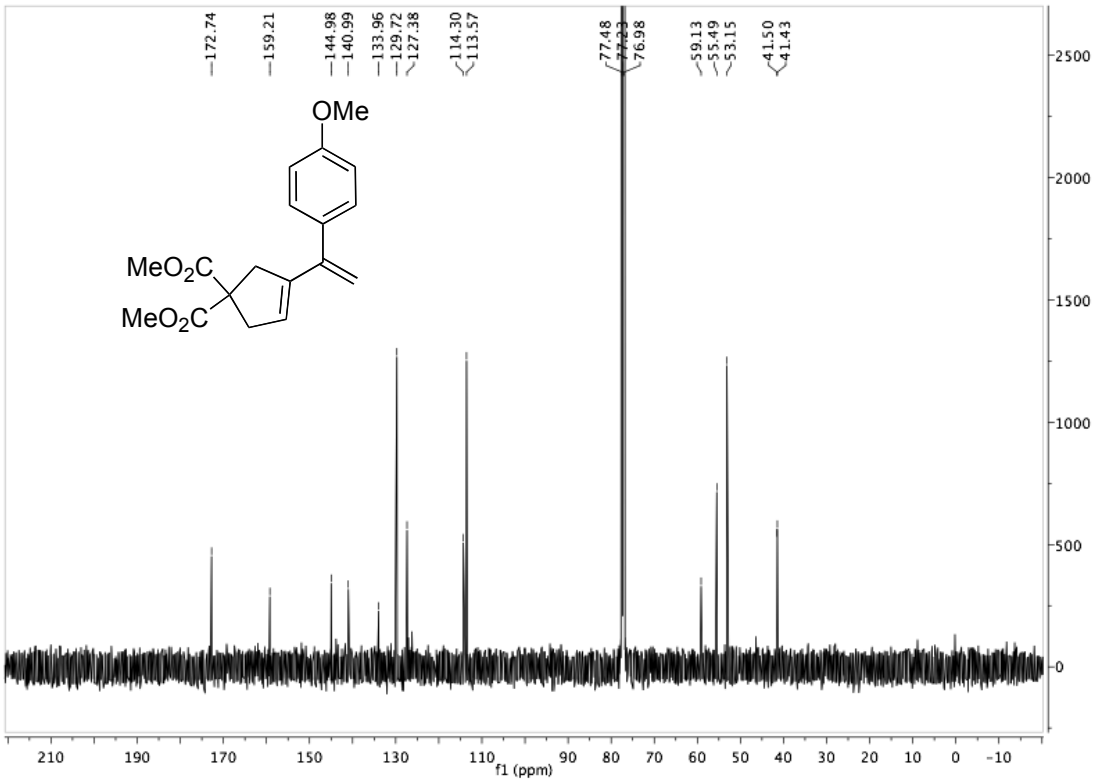
15a



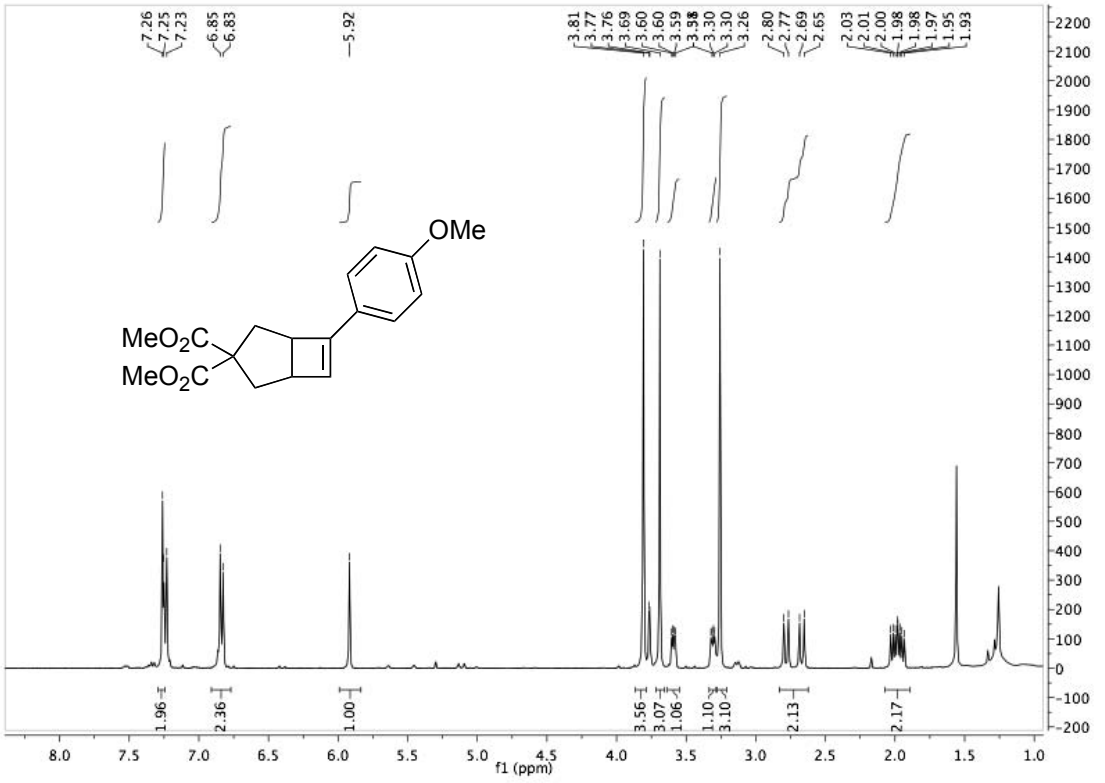


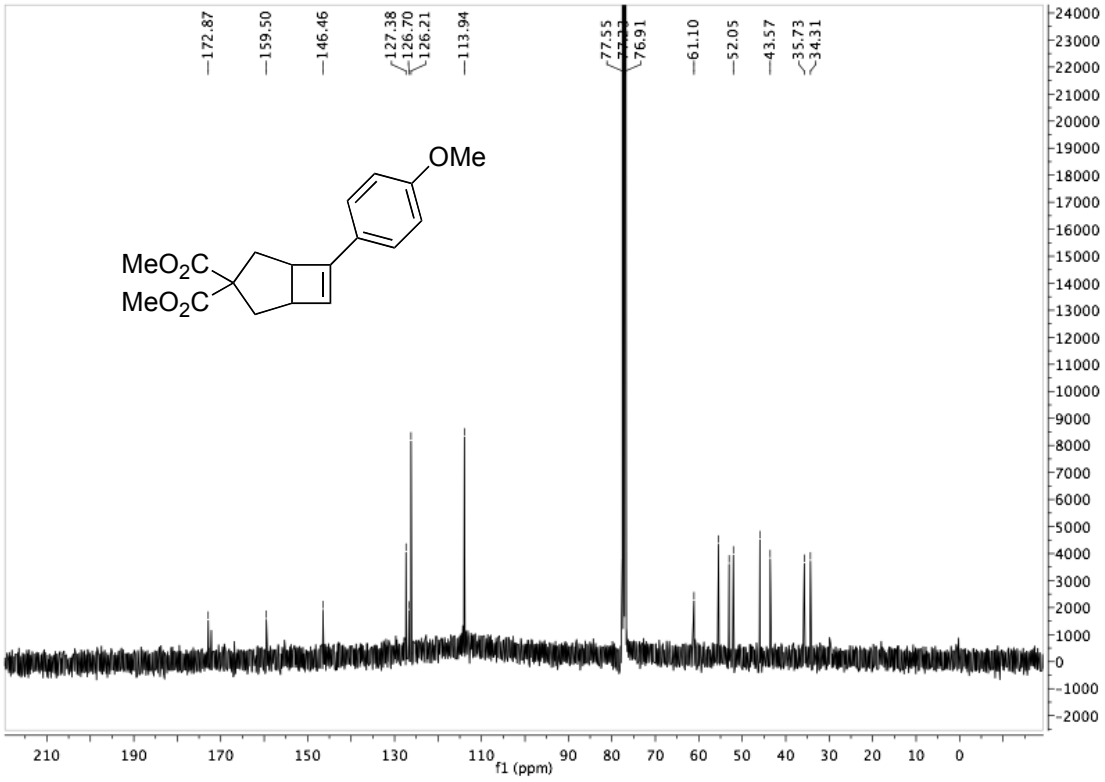
15b


7.28
7.25
7.24
7.23
7.23
6.88
6.88
6.87
6.86
5.47
5.15
5.11
3.83
3.79
3.31
3.30
3.14
1.60
OMe
MeO2C
MeO2C
2.09
2.28
1.00
2.11
3.20
6.32
2.06
2.18
f1 (ppm)

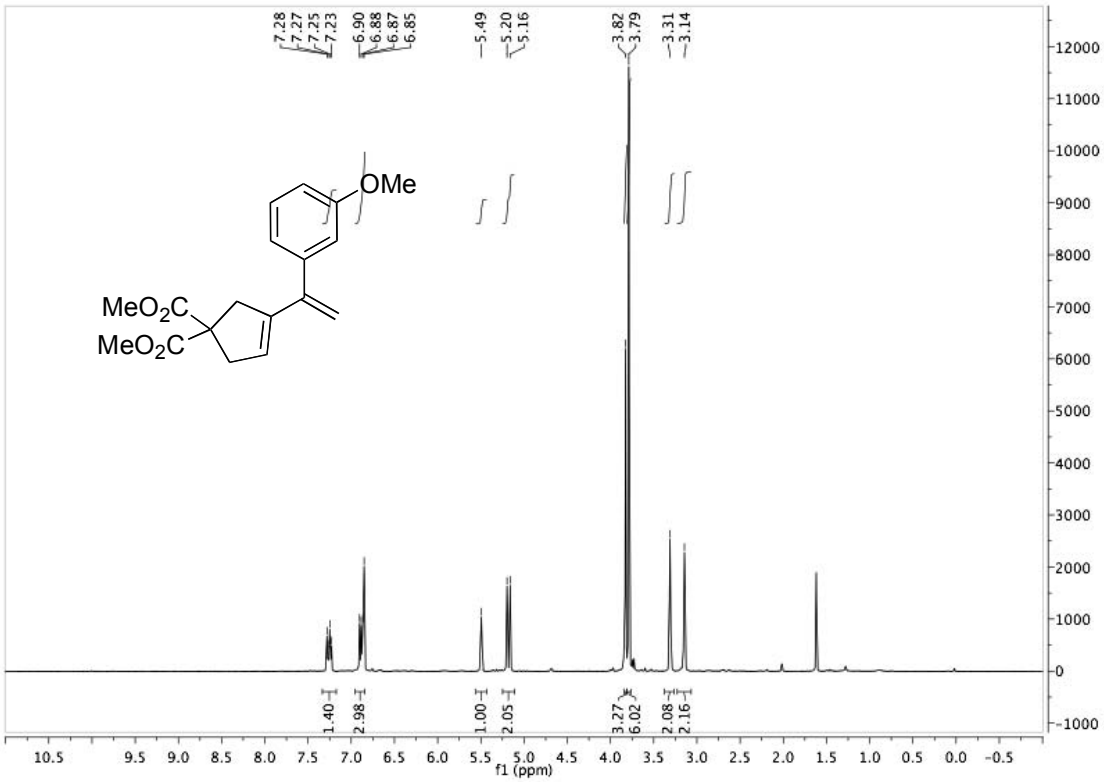

172.74
159.21
144.98
140.99
133.96
129.72
127.38
114.30
113.57
77.48
77.23
76.98
59.13
55.49
53.15
41.50
41.43
OMe
MeO2C
MeO2C
f1 (ppm)

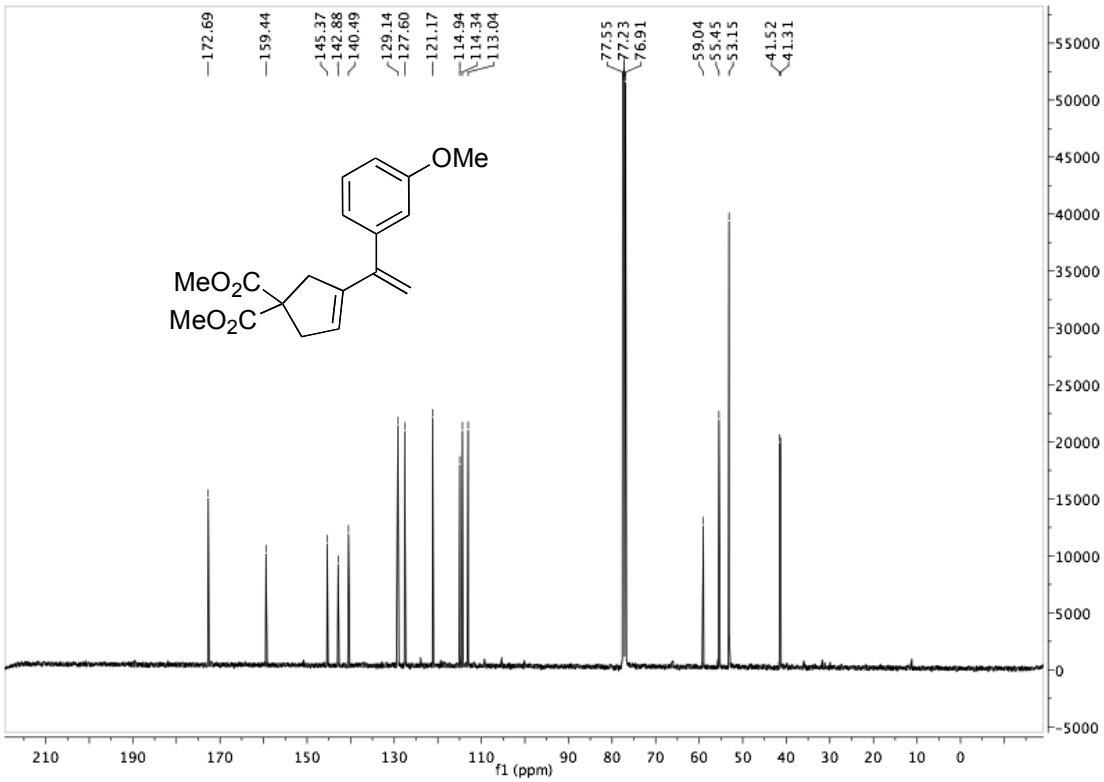
17b


7.26
7.25
7.23
6.85
6.83
5.92
3.81
3.77
3.76
3.69
3.60
3.60
3.59
3.30
3.30
3.26
2.80
2.77
2.69
2.65
2.03
2.01
2.00
1.98
1.98
1.97
1.95
1.93
OMe
MeO2C
MeO2C
1.96
2.36
1.00
3.56
3.07
1.06
1.10
3.10
2.13
2.17
f1 (ppm)

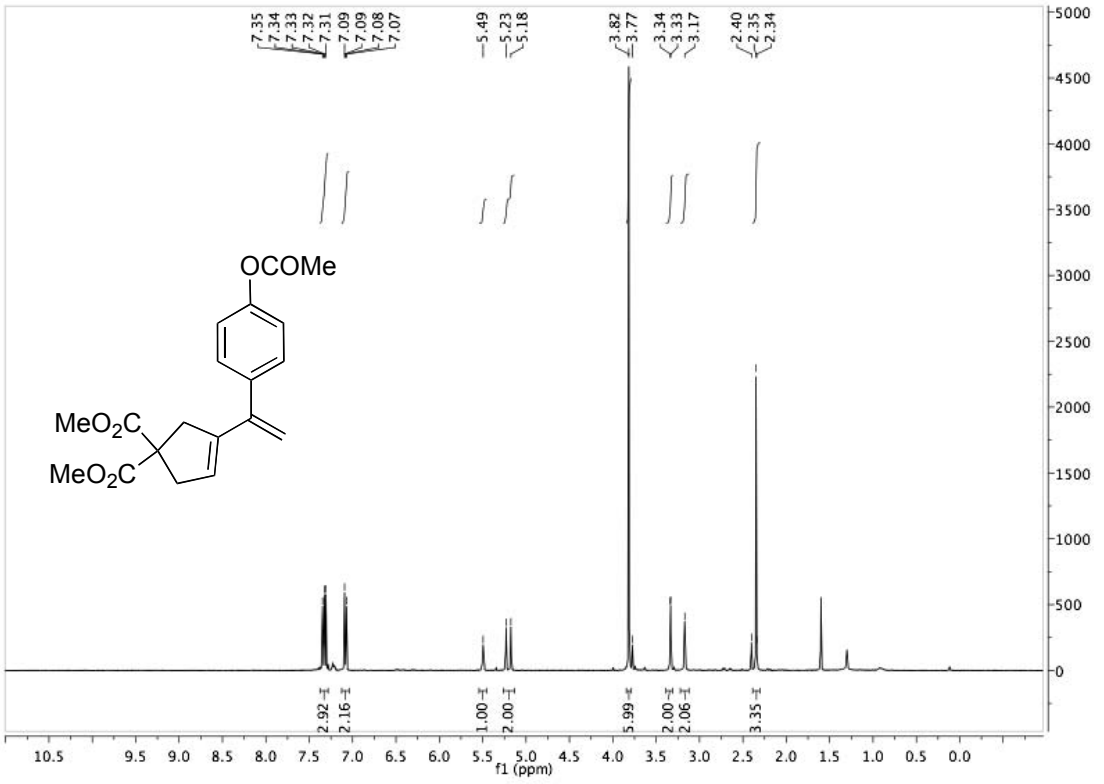

172.87
159.50
146.46
127.38
126.70
126.21
113.94
77.55
76.91
61.10
52.05
43.57
35.73
34.31
OMe
MeO2C
MeO2C
f1 (ppm)

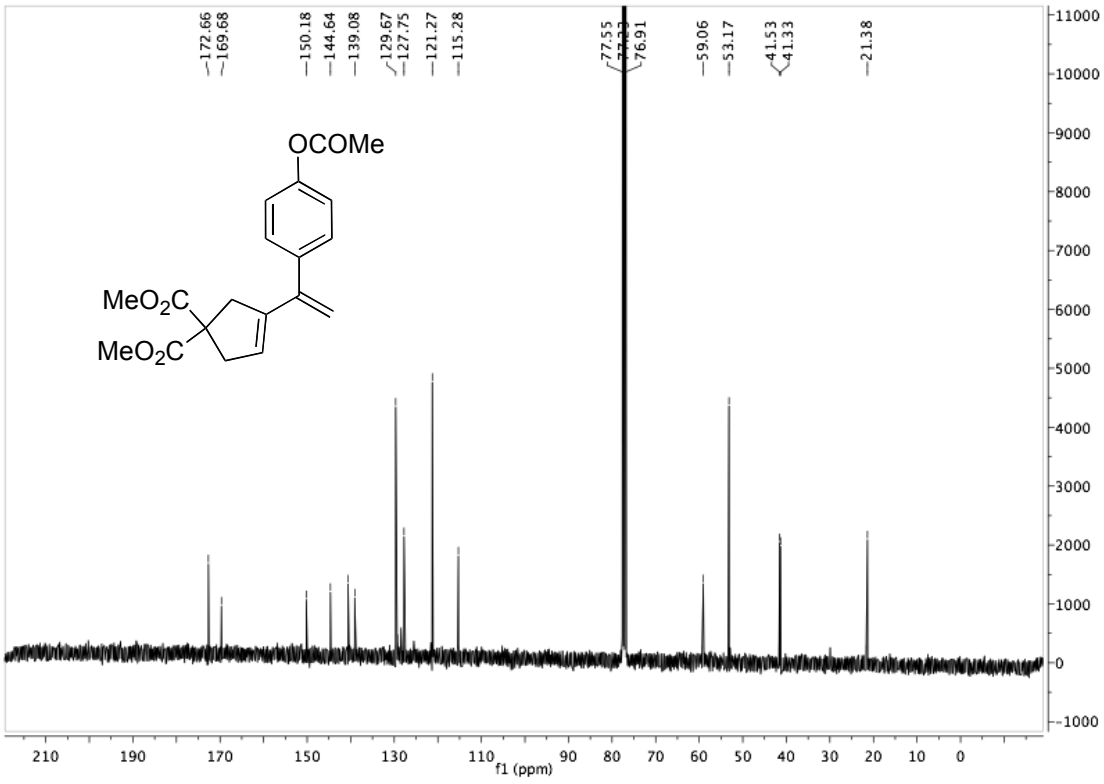
15c



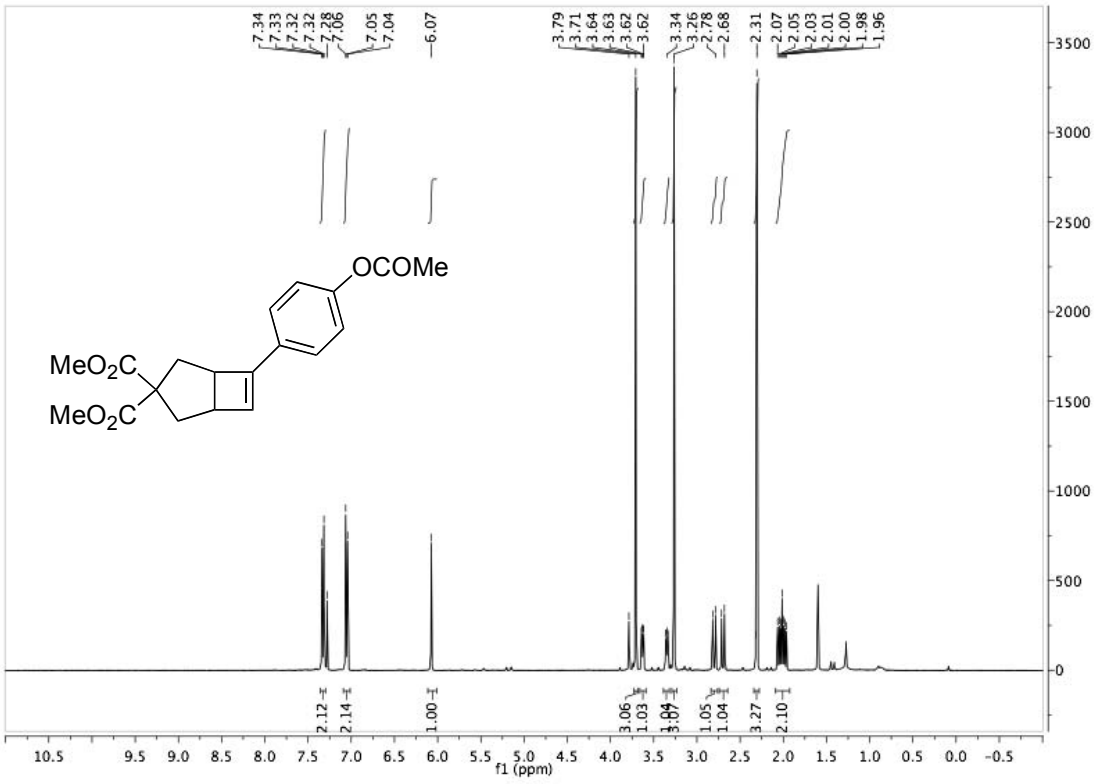


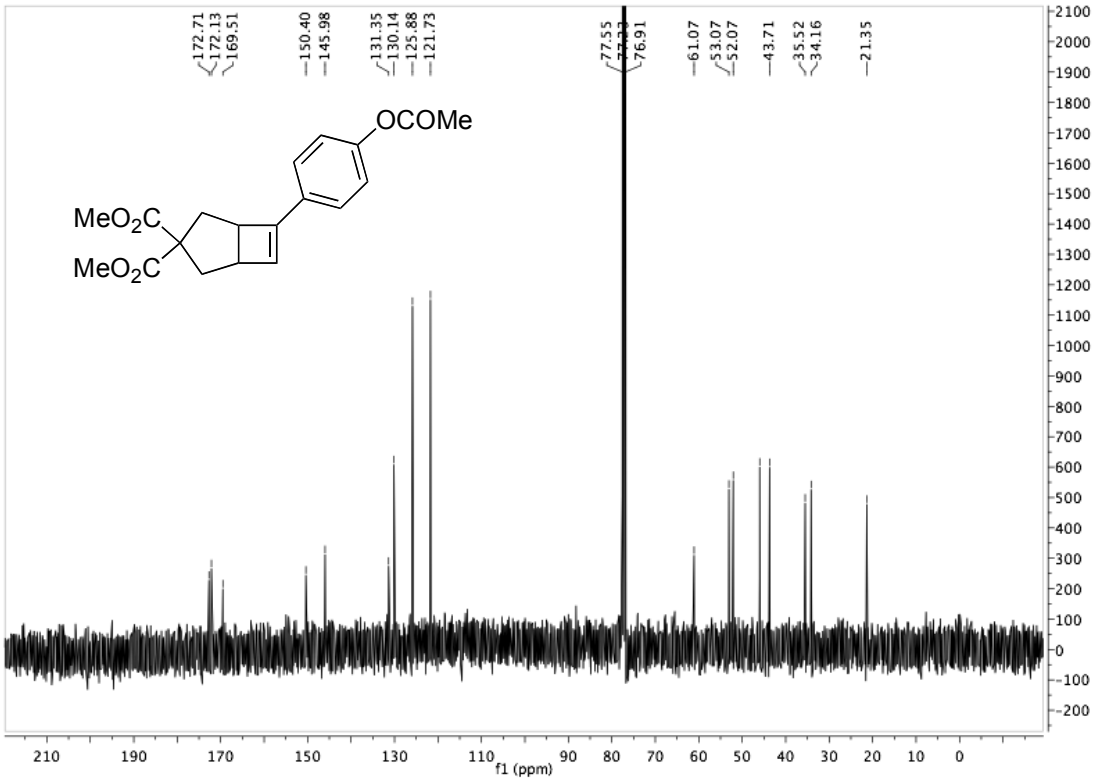
15d



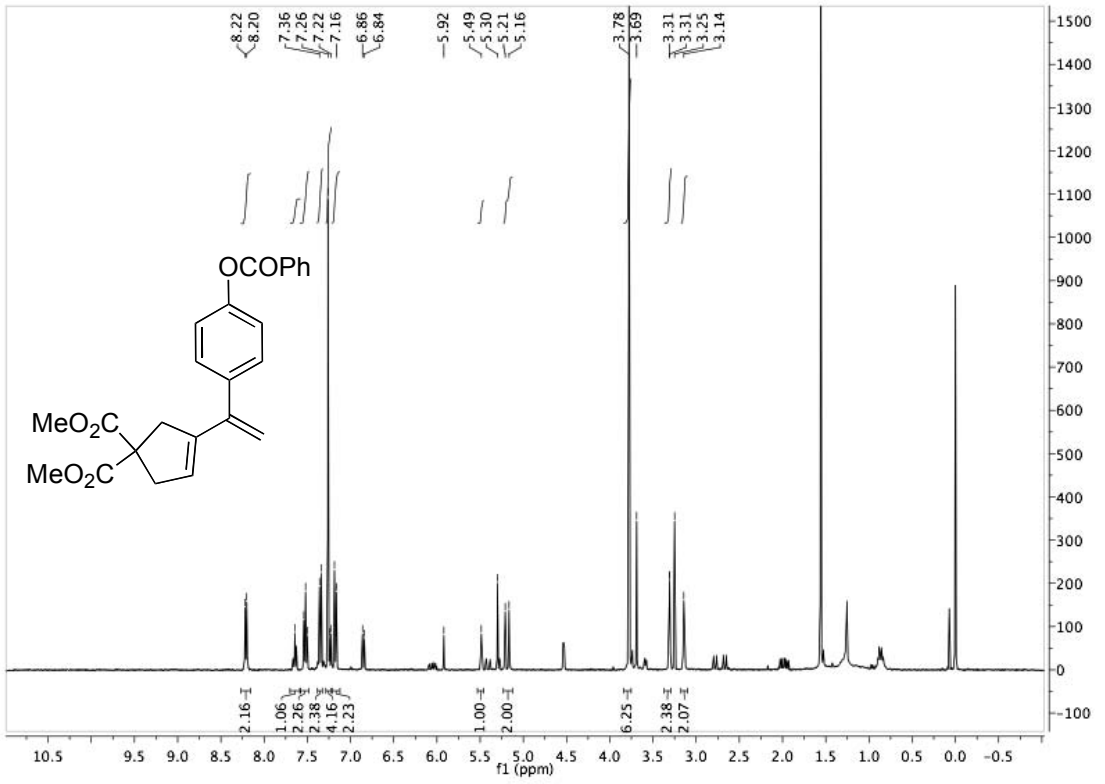


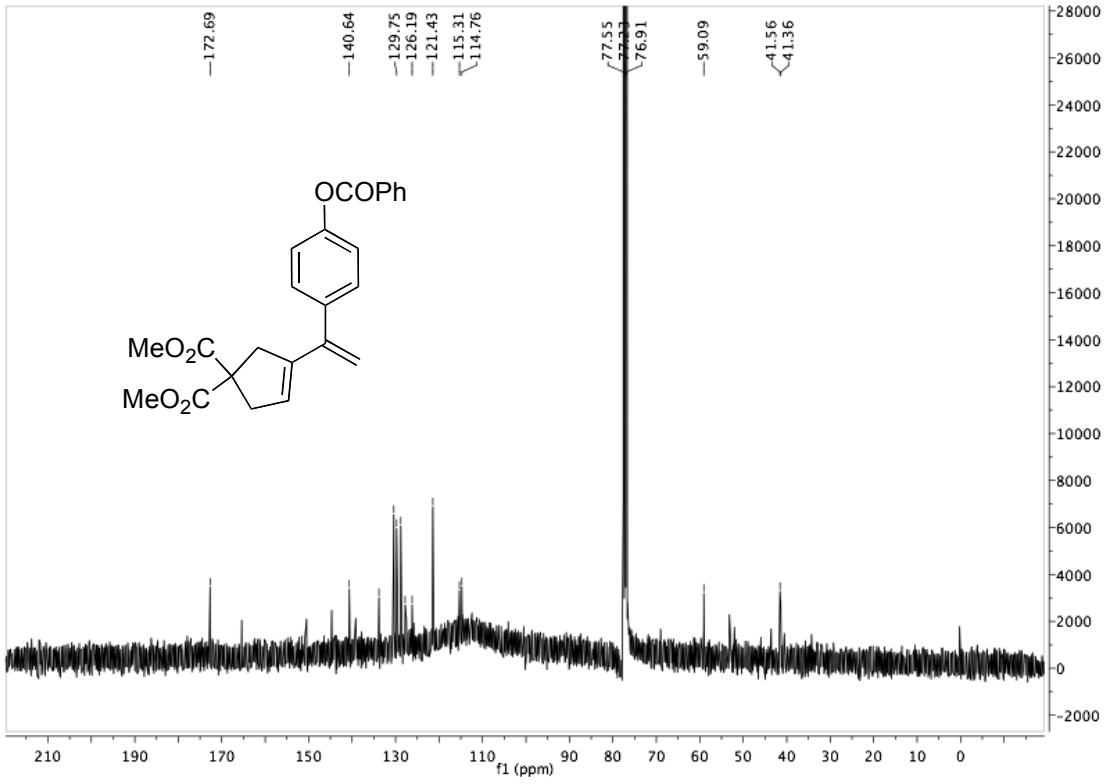
17d



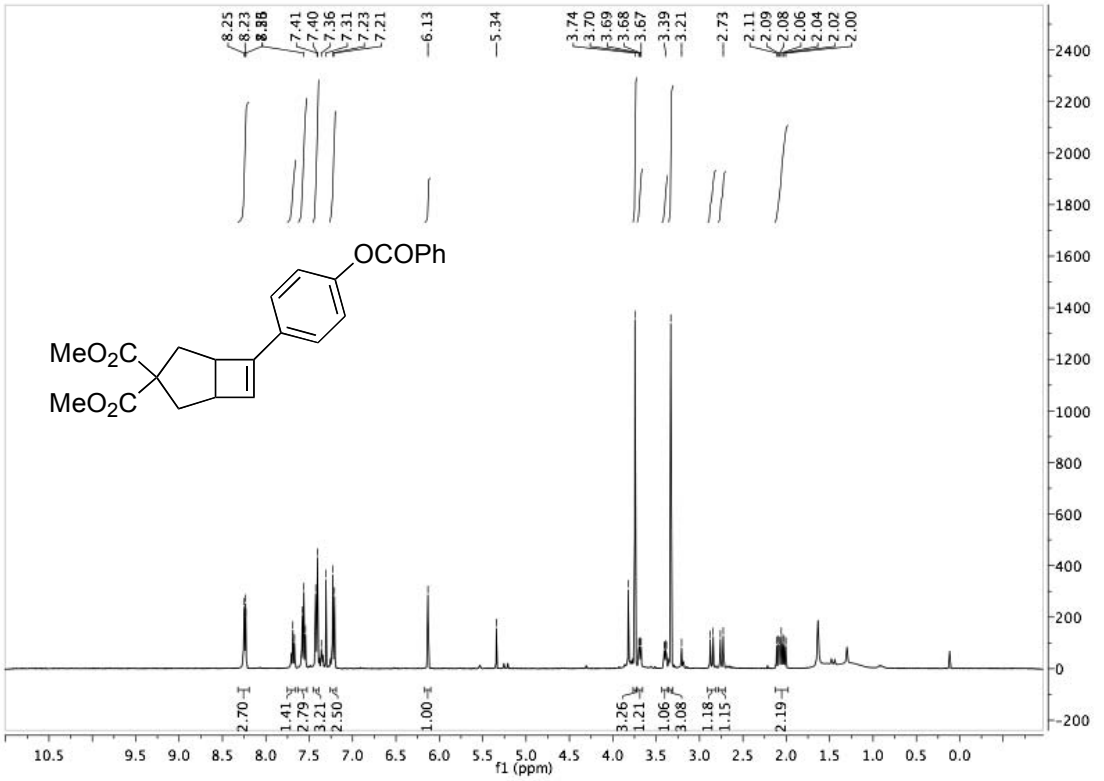


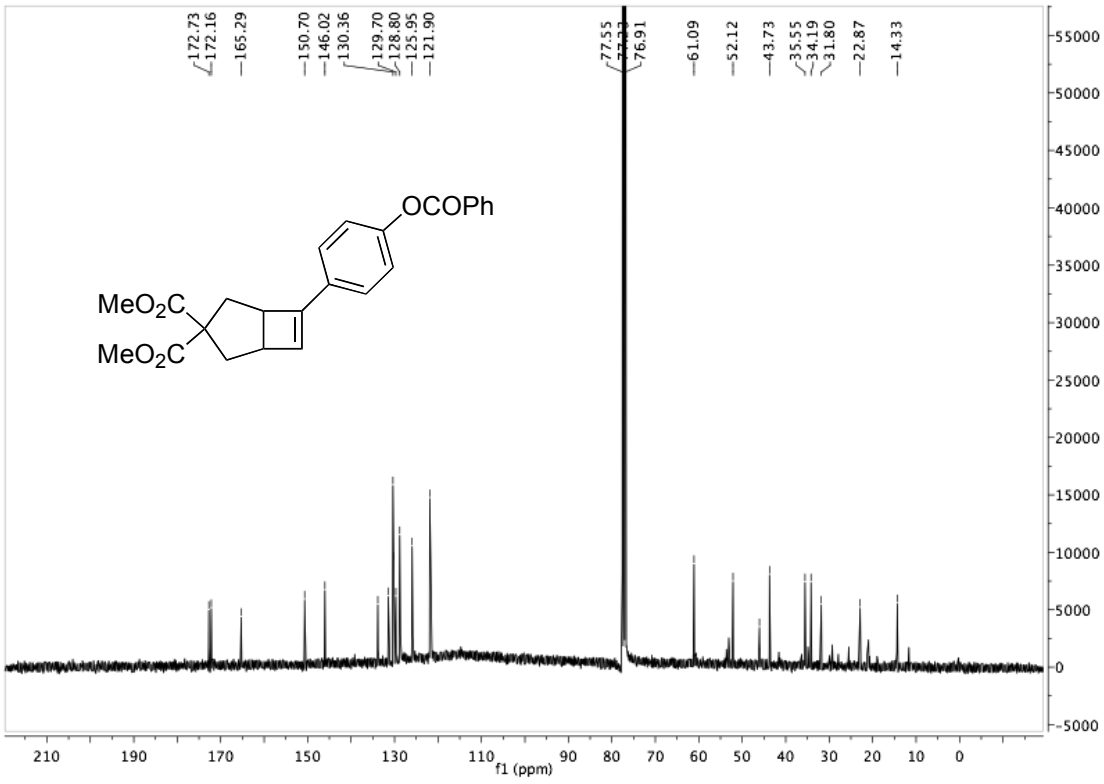
15e


8.22
8.20
7.36
7.26
7.22
7.16
6.86
6.84
5.92
5.49
5.30
5.21
5.16
3.78
3.69
3.31
3.31
3.25
3.14
OCOPh
MeO2C
MeO2C
2.16
1.06
2.26
2.38
4.16
2.23
1.00
2.00
6.25
2.38
2.07
f1 (ppm)

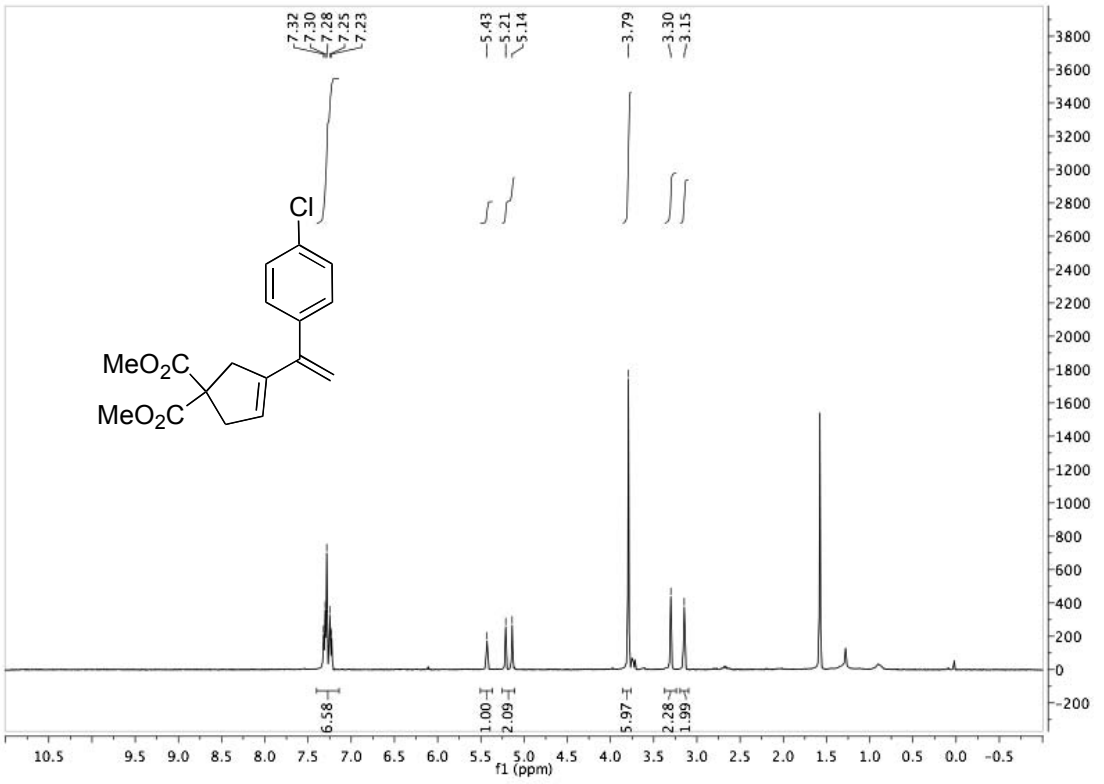

172.69
140.64
129.75
126.19
121.43
115.31
114.76
77.55
77.33
76.91
59.09
41.56
41.36
OCOPh
MeO2C
MeO2C
f1 (ppm)

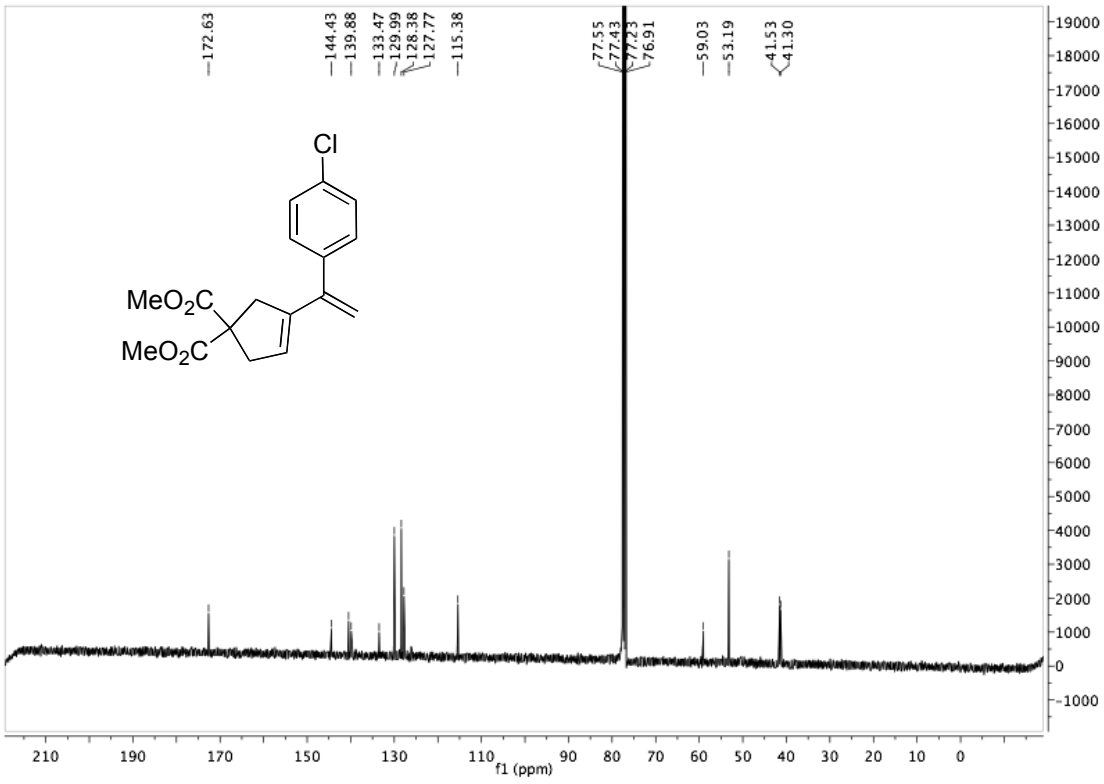
17e



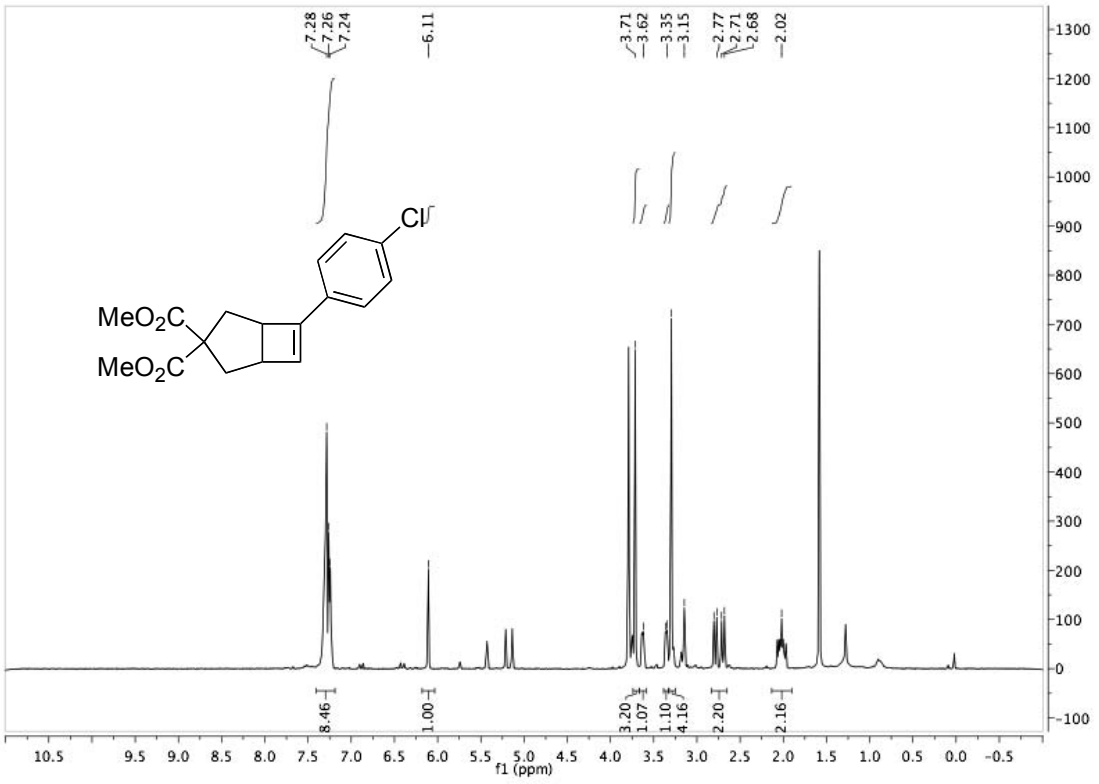


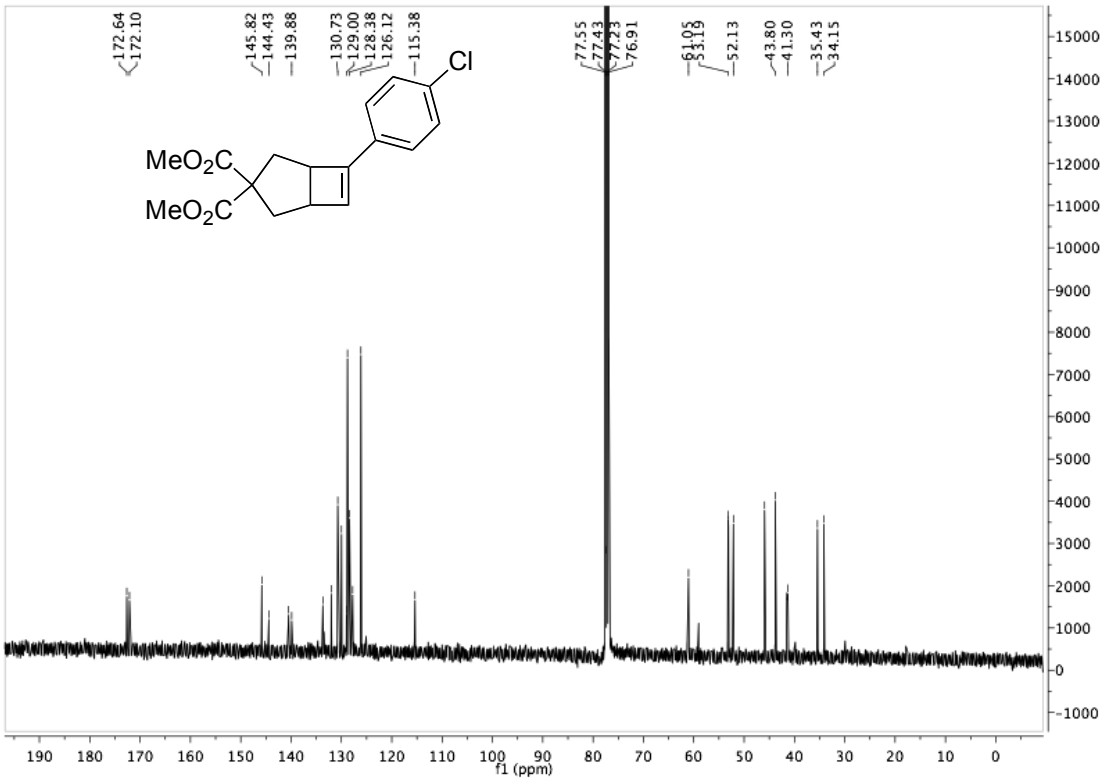
15f



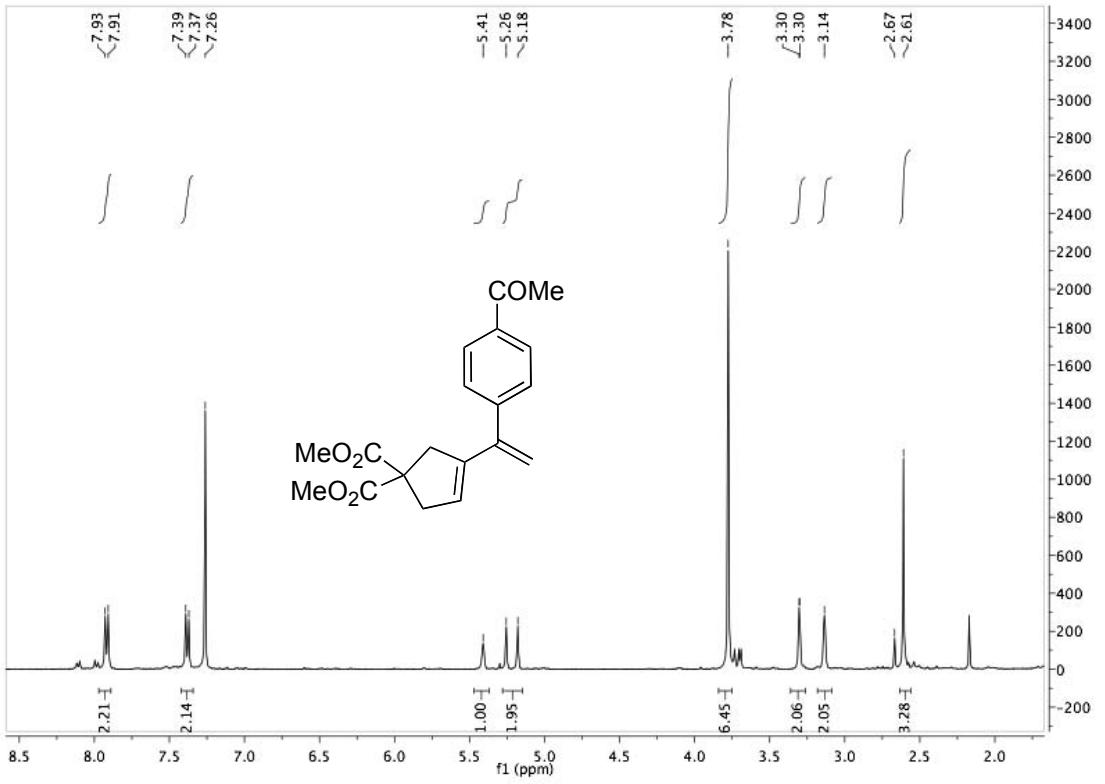


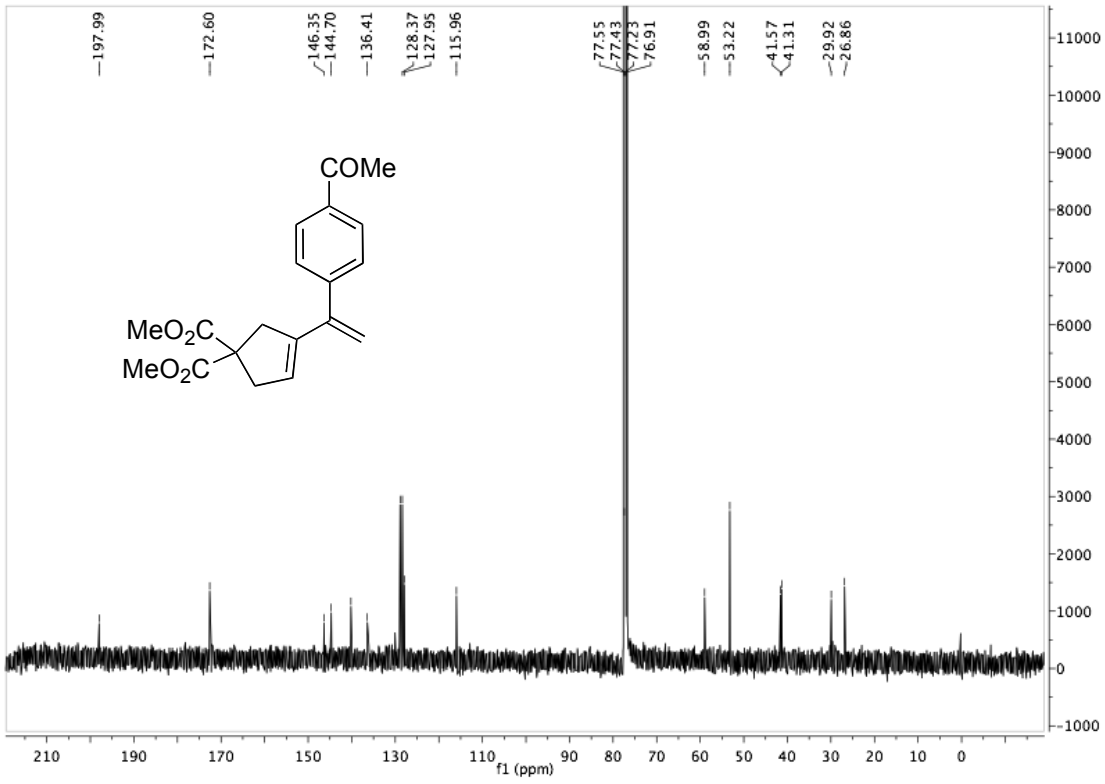
17f



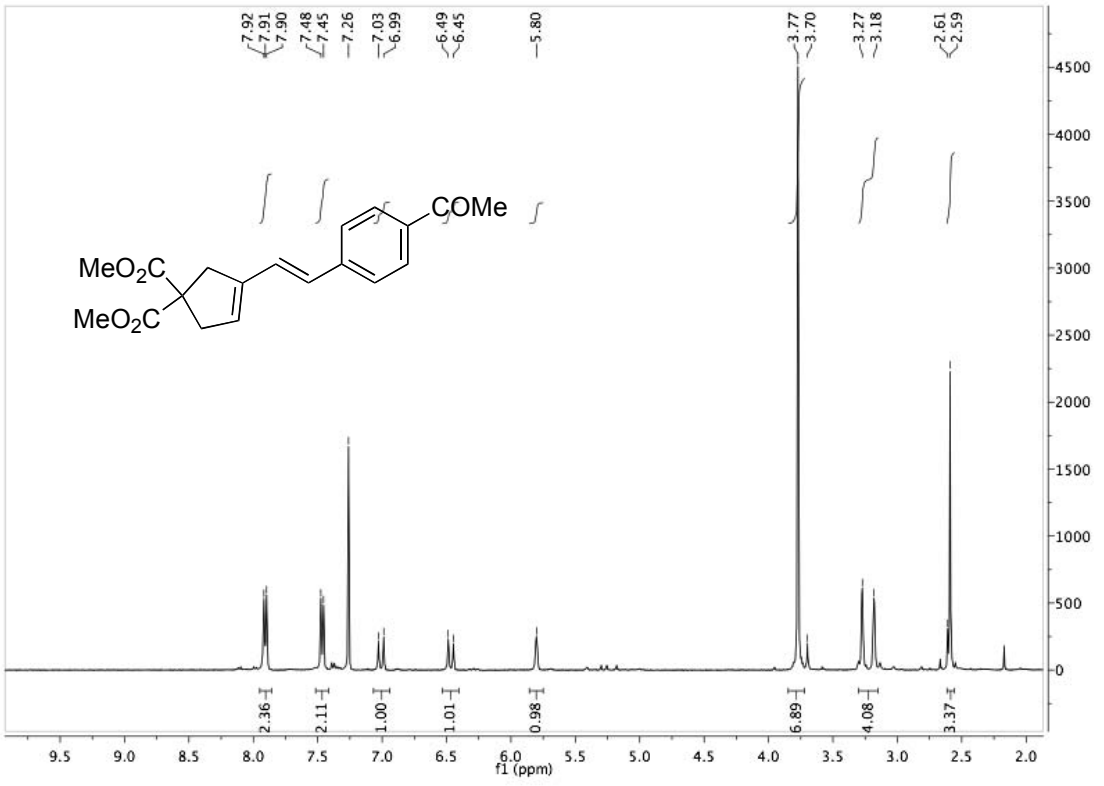


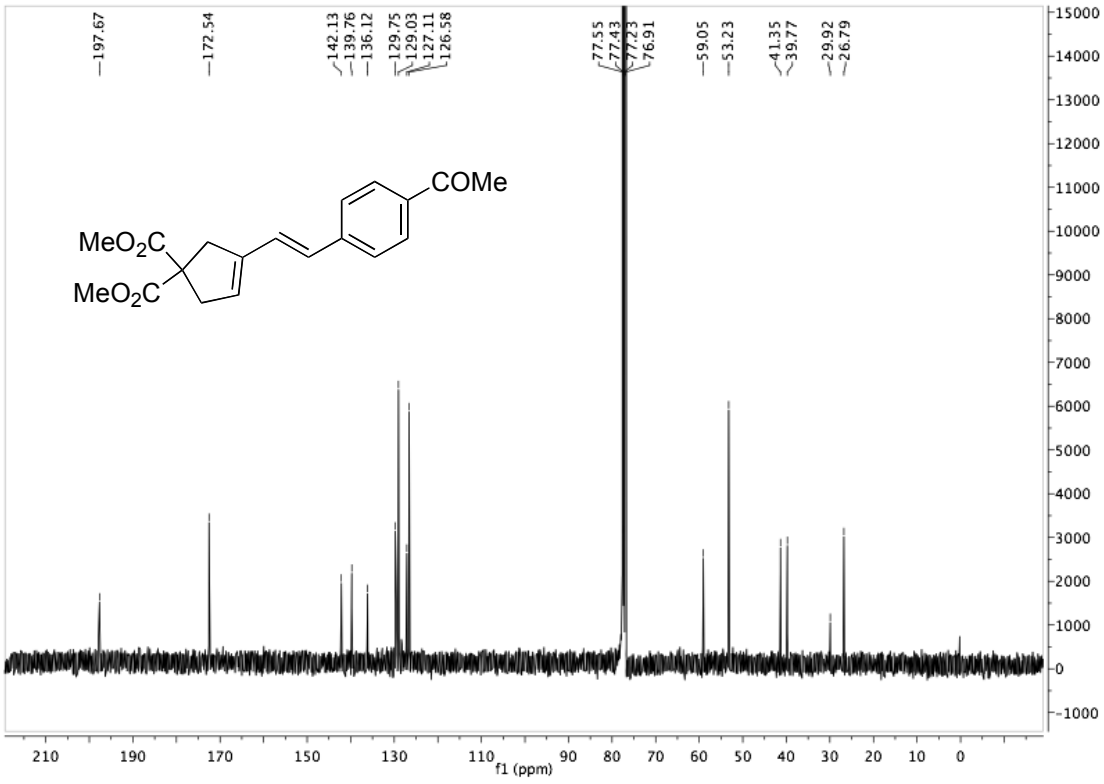
15g



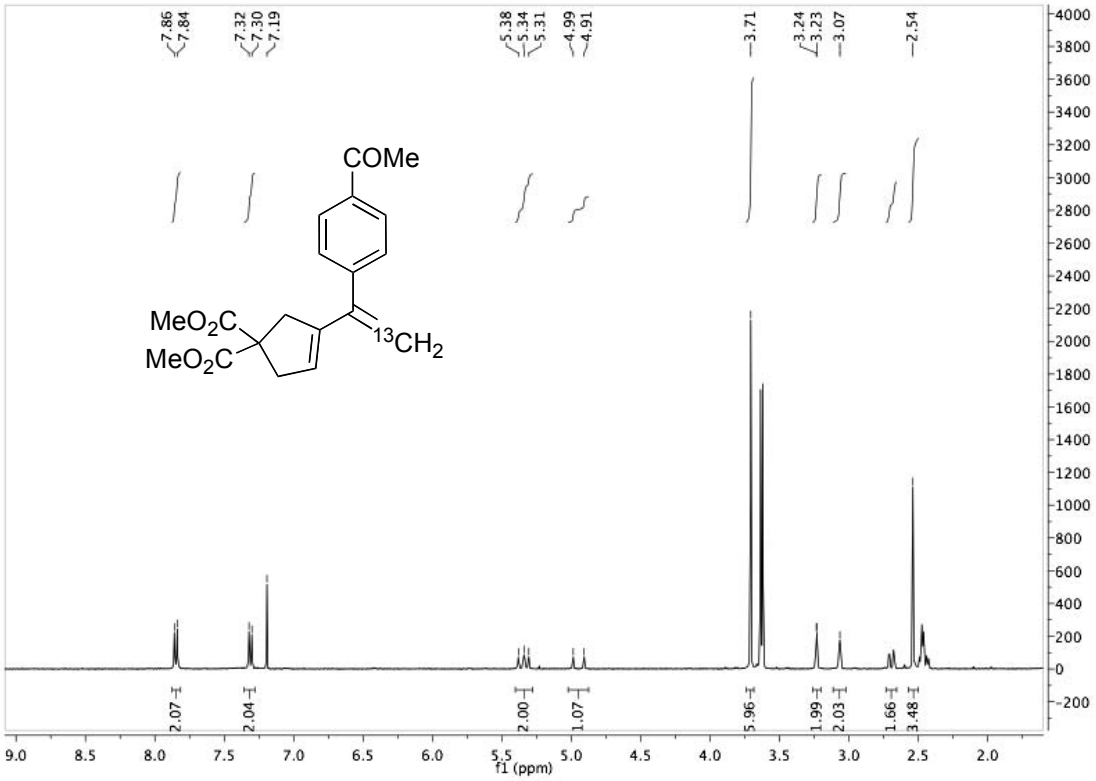


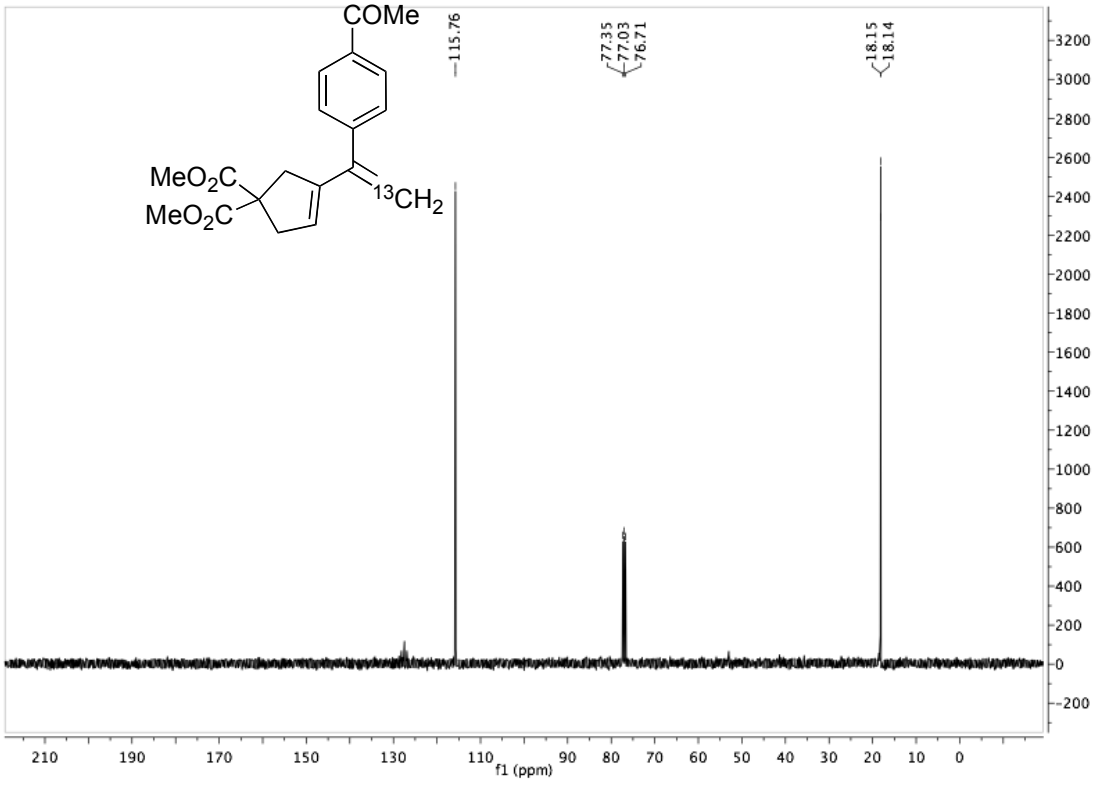
16g



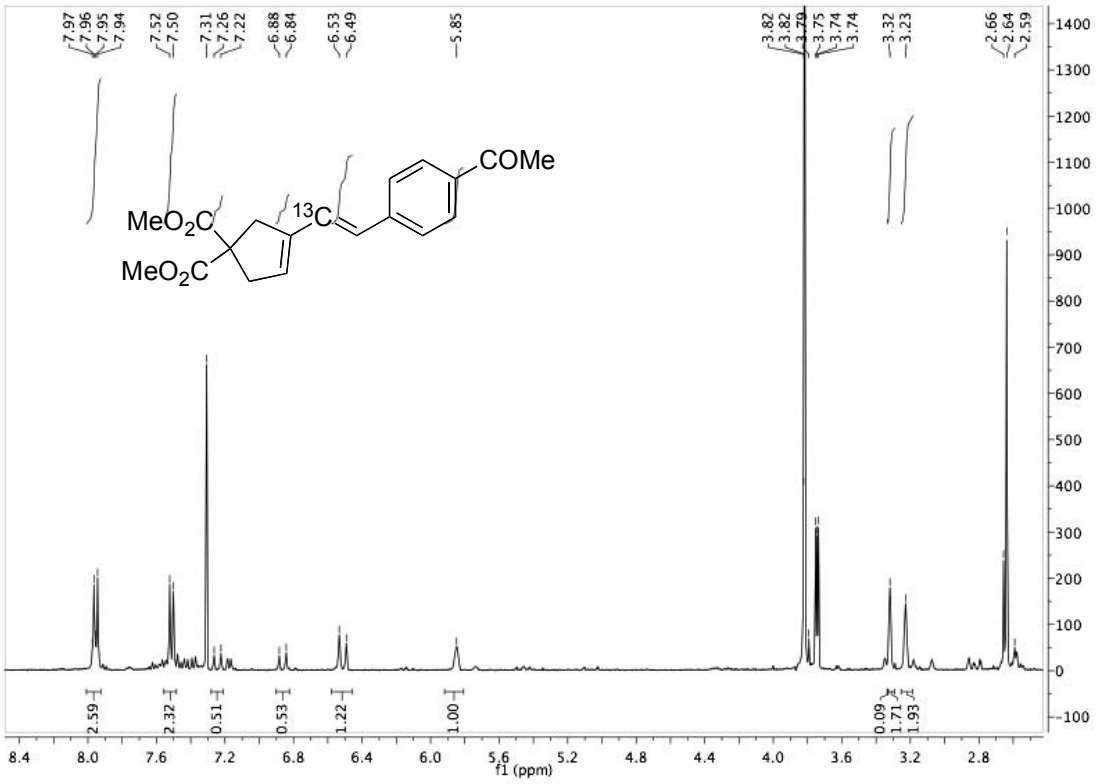


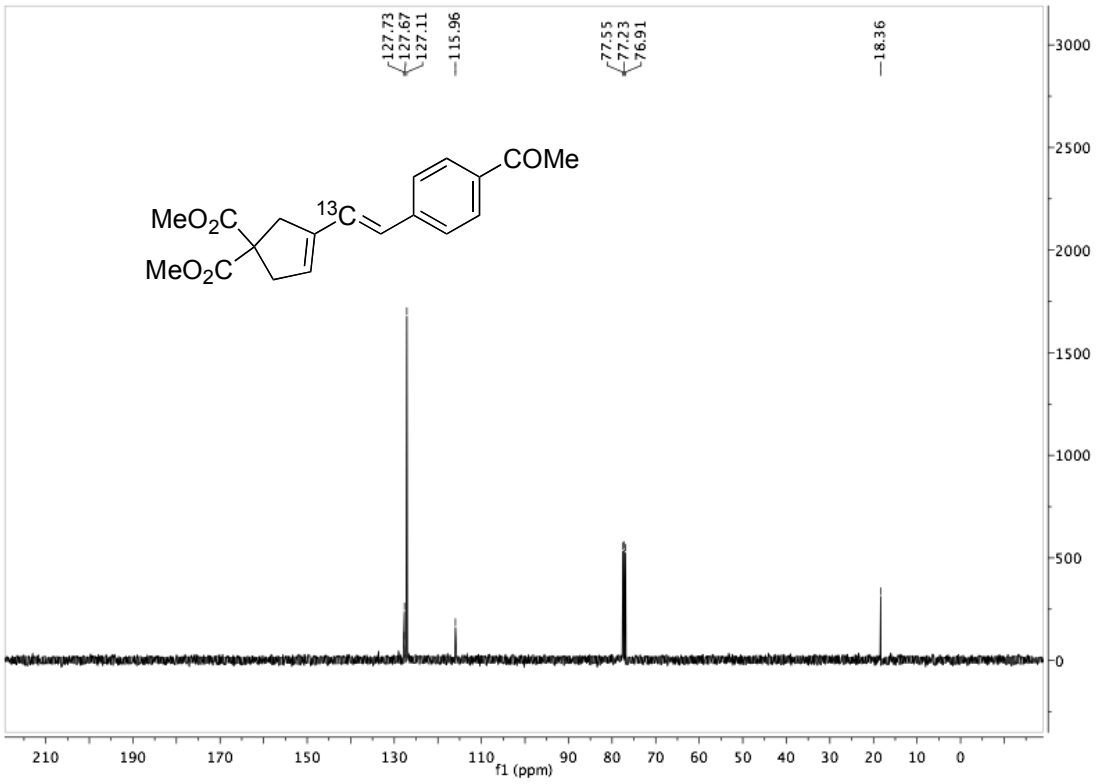
15g-^{13}C



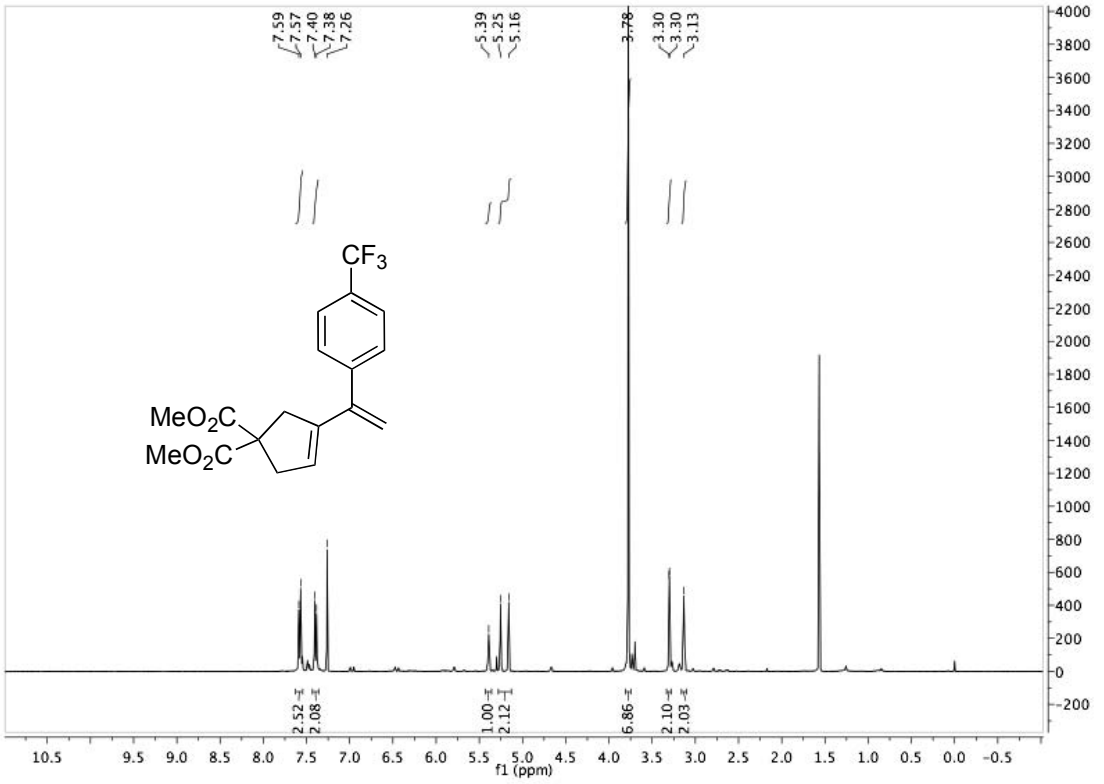


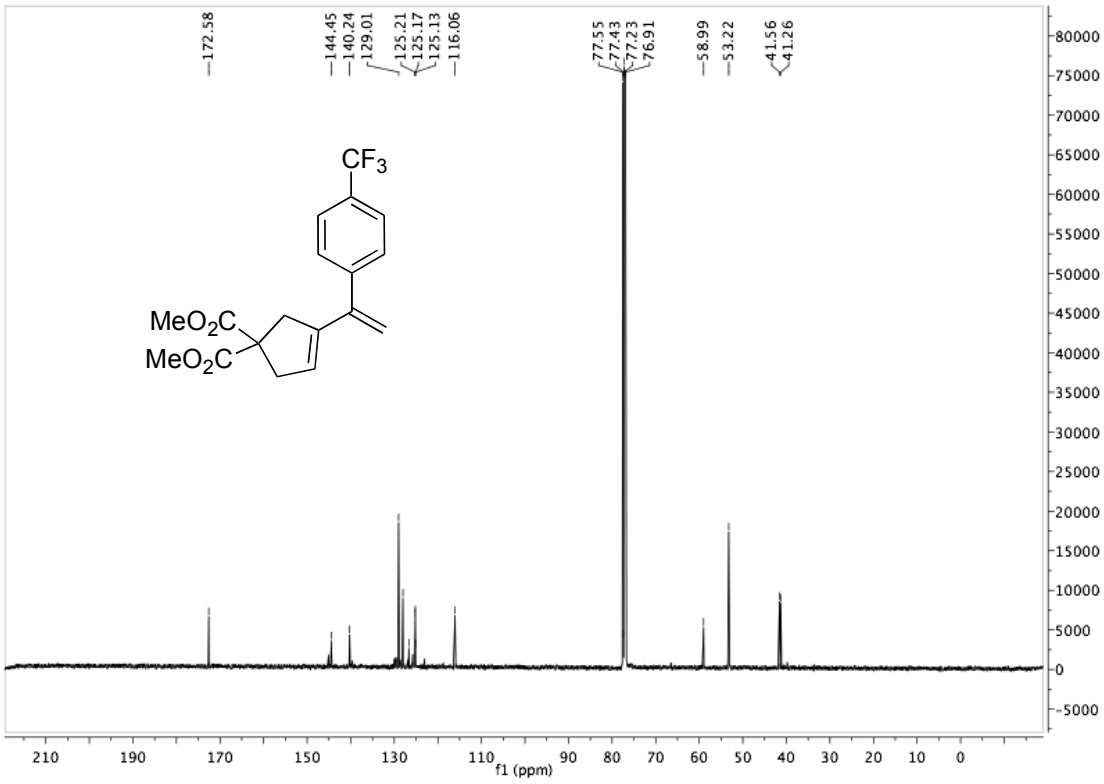
16g-^{13}C



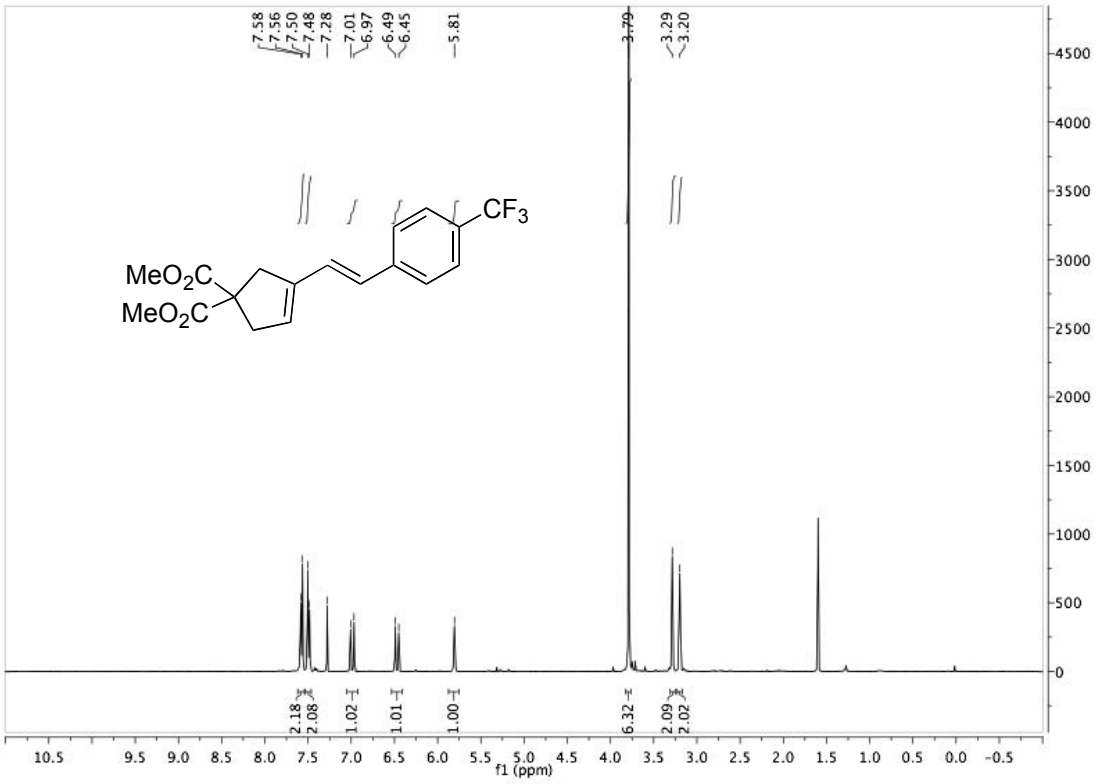


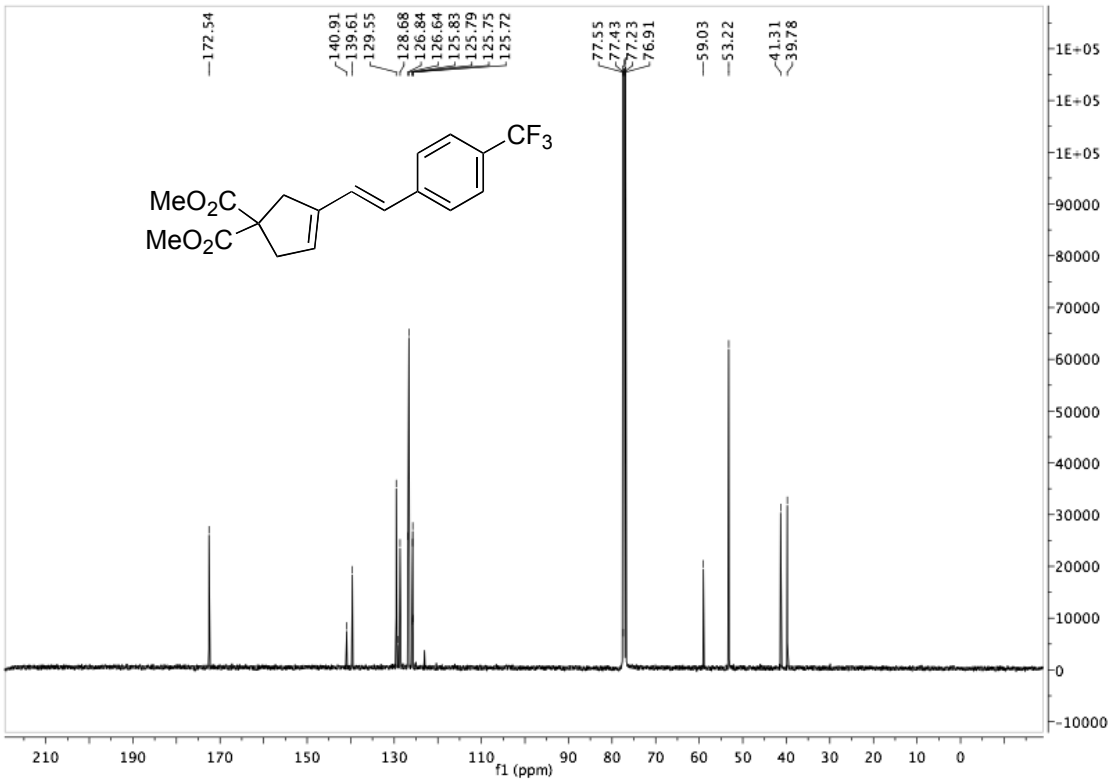
15h



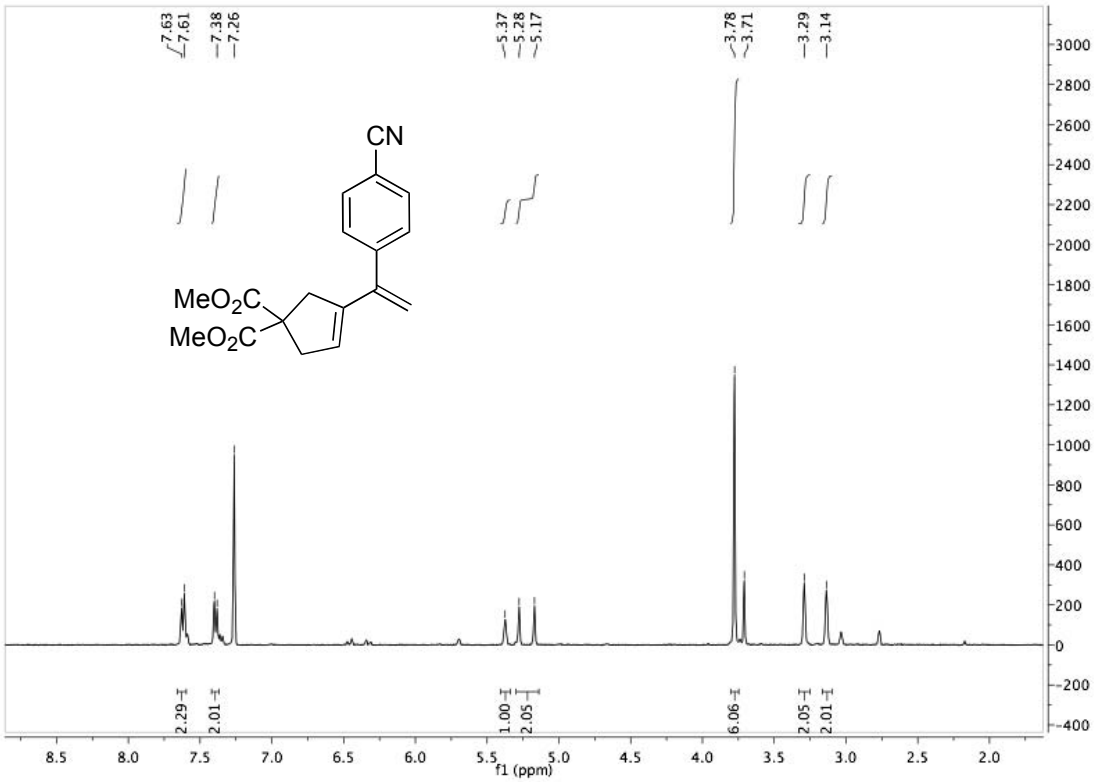


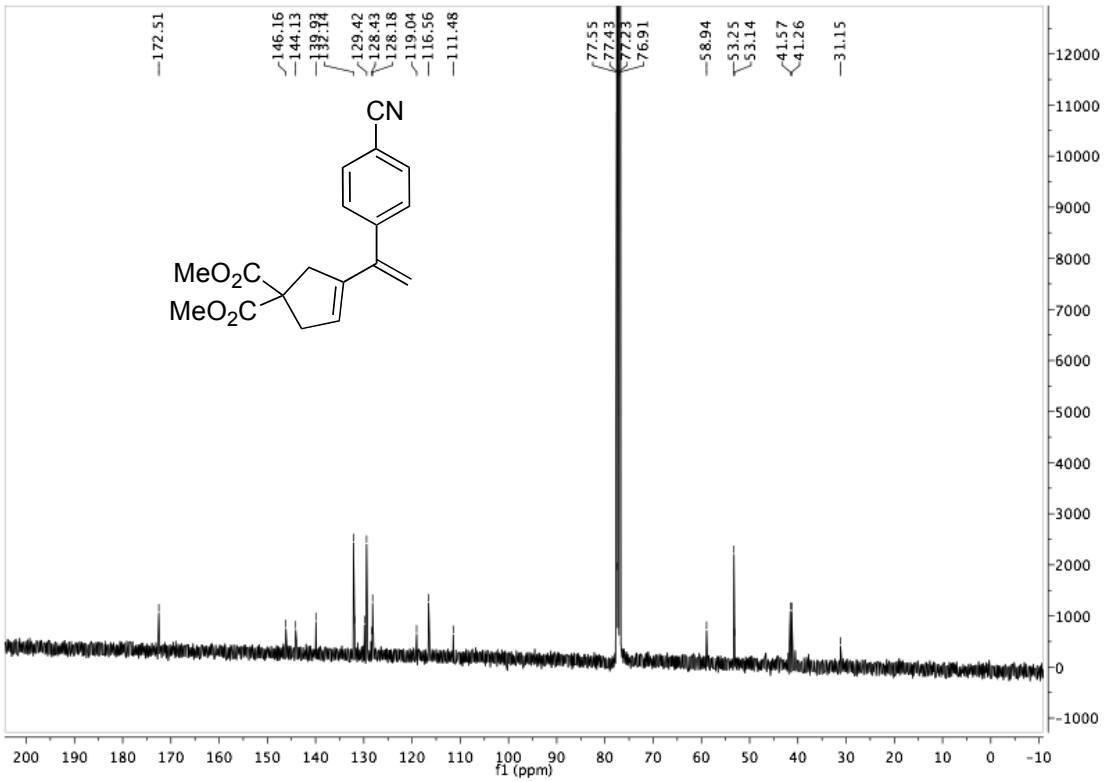
16h


7.58
7.56
7.50
7.48
7.28
7.01
6.97
6.49
6.45
5.81
3.79
3.29
3.20
CF3
MeO2C
MeO2C
2.18
2.08
1.02
1.01
1.00
6.32
2.09
2.02
f1 (ppm)

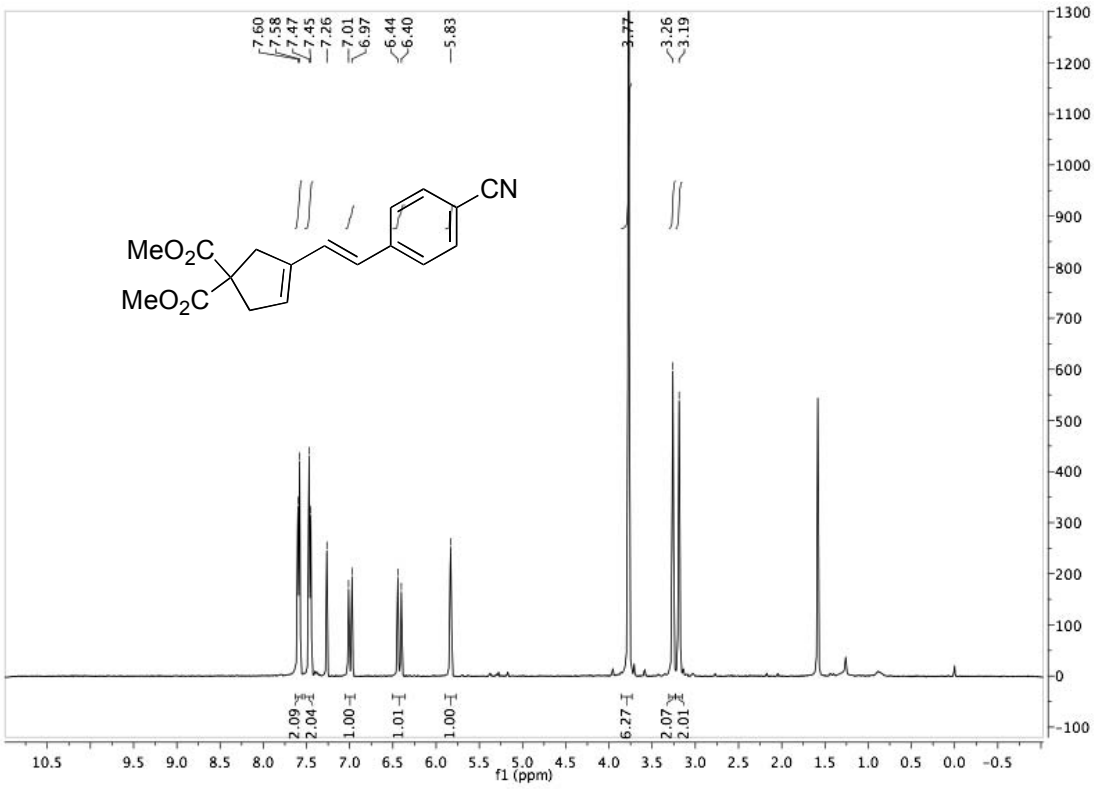

172.54
140.91
139.61
129.55
128.68
126.84
126.64
125.83
125.79
125.75
125.72
77.55
77.43
77.23
76.91
59.03
53.22
41.31
39.78
CF3
MeO2C
MeO2C
f1 (ppm)

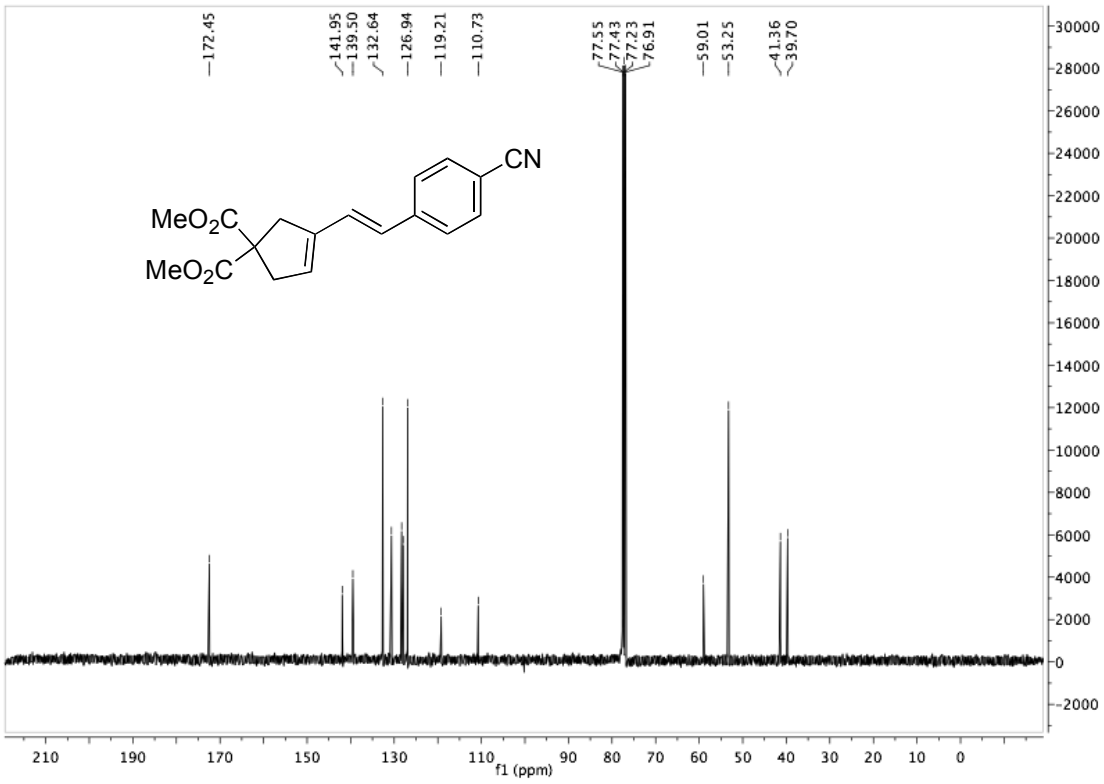
15i



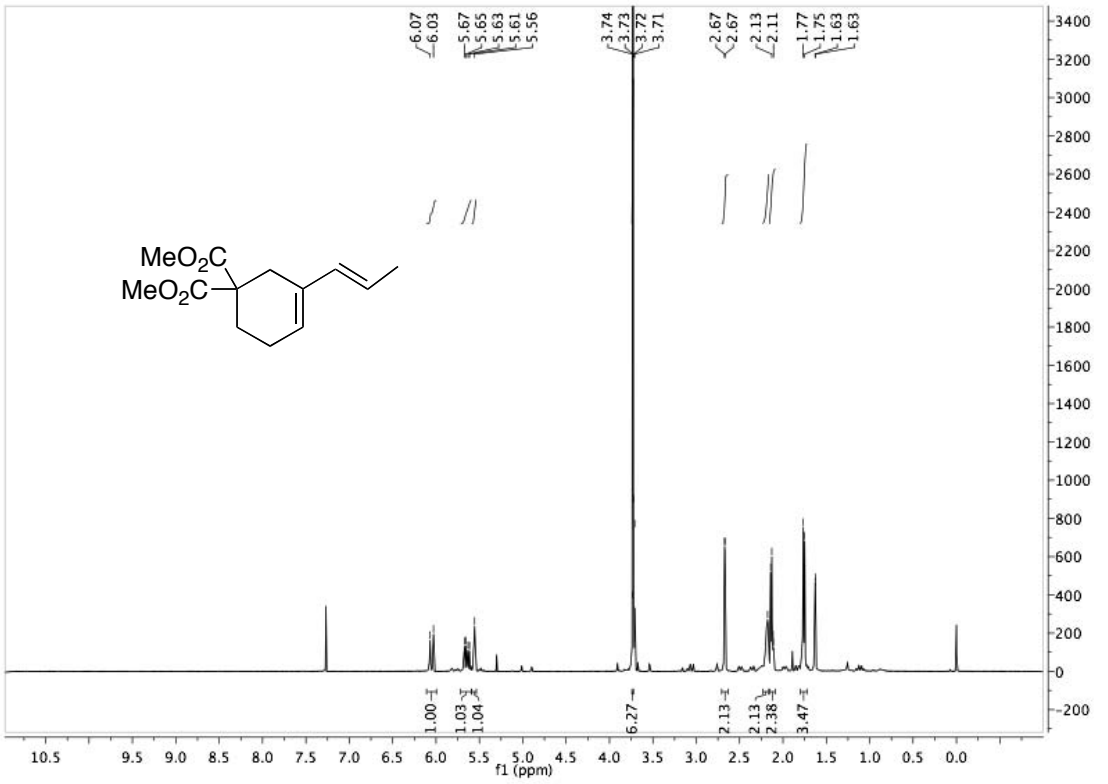


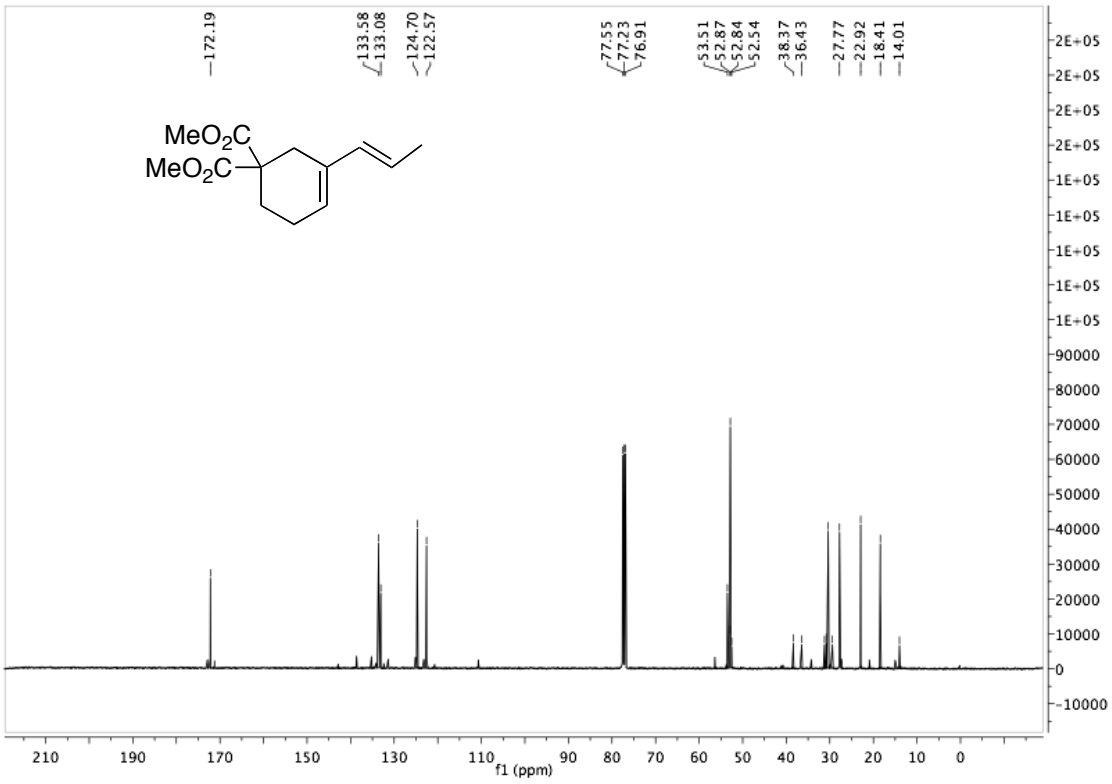
16i



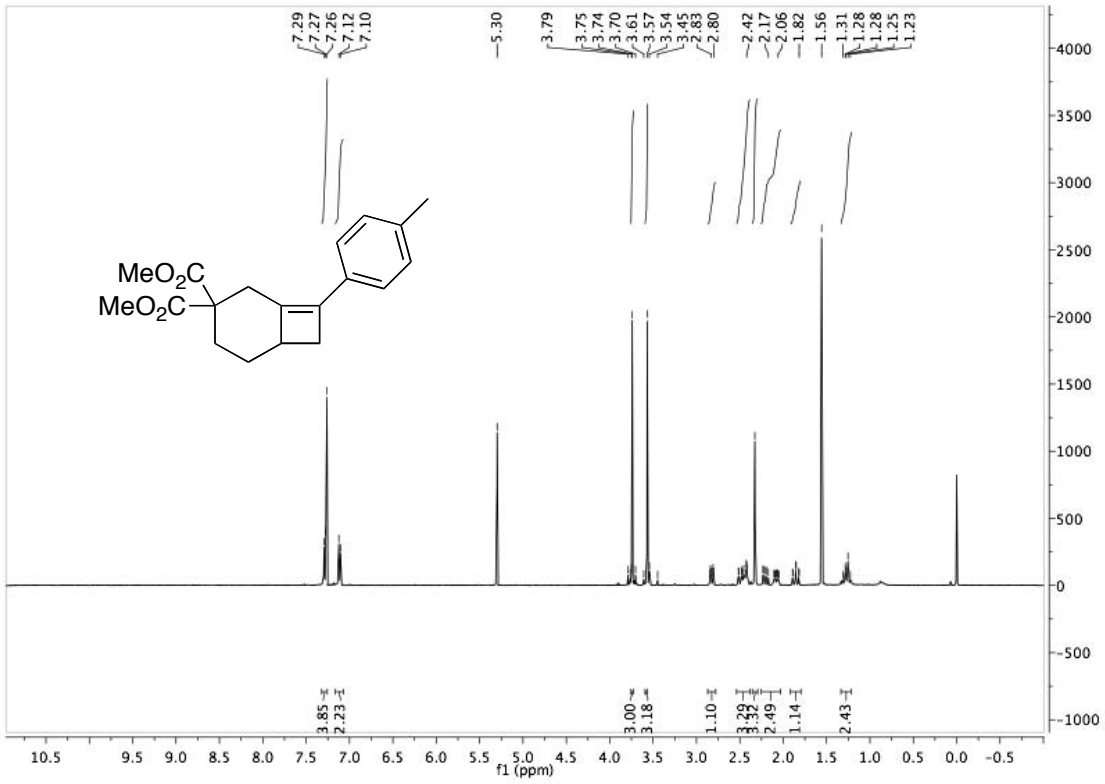


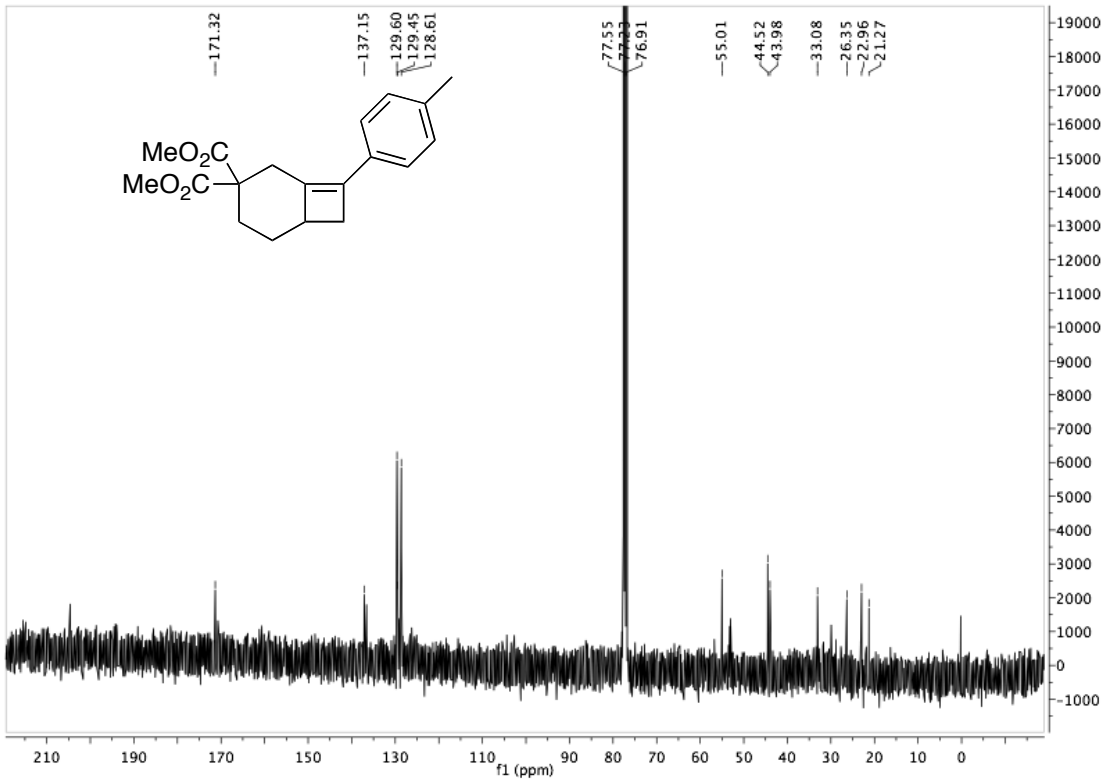
30


6.07
6.03
5.67
5.65
5.63
5.61
5.56
3.74
3.73
3.72
3.71
2.67
2.67
2.13
2.11
1.77
1.75
1.63
1.63
MeO2C
MeO2C
1.00
1.03
1.04
6.27
2.13
2.13
2.38
3.47
f1 (ppm)

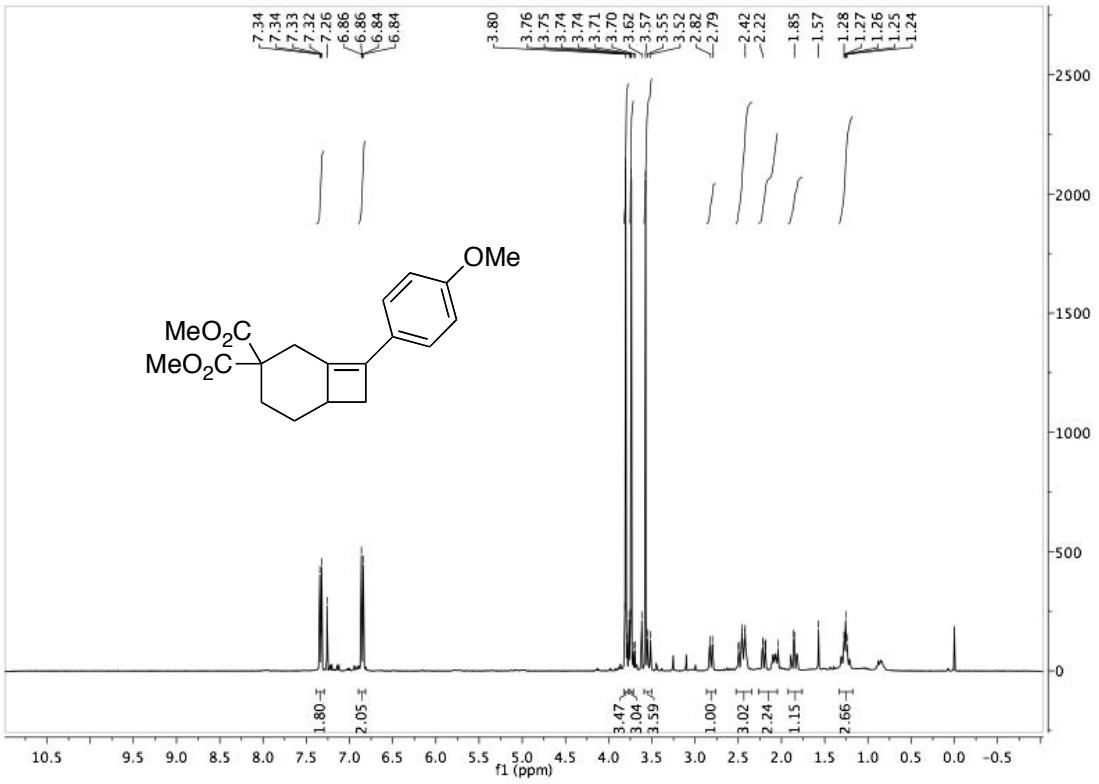

172.19
133.58
133.08
124.70
122.57
77.55
77.23
76.91
53.51
52.87
52.84
52.54
38.37
36.43
27.77
22.92
18.41
14.01
MeO2C
MeO2C
f1 (ppm)

32a


7.29
7.27
7.26
7.12
7.10
5.30
3.79
3.75
3.74
3.70
3.61
3.57
3.54
3.45
2.83
2.80
2.42
2.17
2.06
1.82
1.56
1.31
1.28
1.28
1.25
1.23
MeO2C
MeO2C
3.85
2.23
3.00
3.18
1.10
3.29
3.32
2.49
1.14
2.43
f1 (ppm)


171.32
137.15
129.60
129.45
128.61
77.55
77.23
76.91
55.01
44.52
43.98
33.08
26.35
22.96
21.27
MeO2C
MeO2C
f1 (ppm)

32b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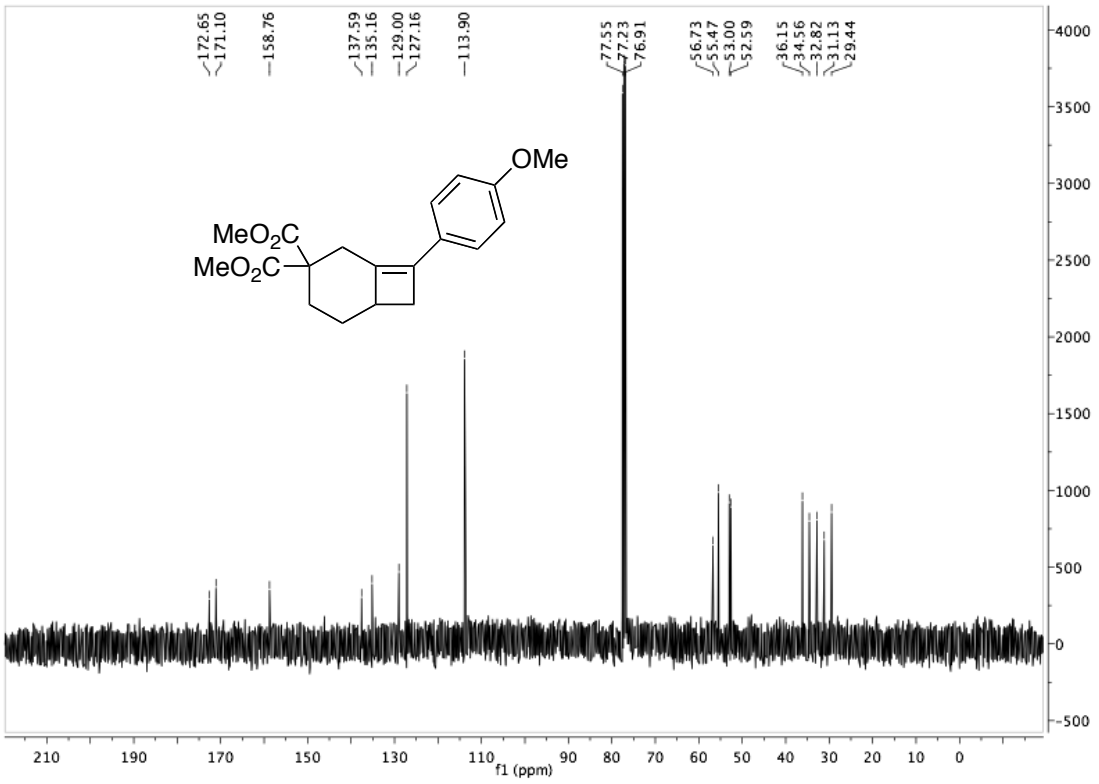
7.34
7.33
7.32
7.26
6.86
6.86
6.84
6.84
3.80
3.76
3.75
3.74
3.74
3.71
3.70
3.62
3.57
3.55
3.52
2.82
2.79
2.42
2.22
1.85
1.57
1.28
1.27
1.26
1.25
1.24
OMe
MeO2C
MeO2C
1.80
2.05
3.47
3.04
3.59
1.00
3.02
2.24
1.15
2.66
f1 (ppm)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171.10
158.76
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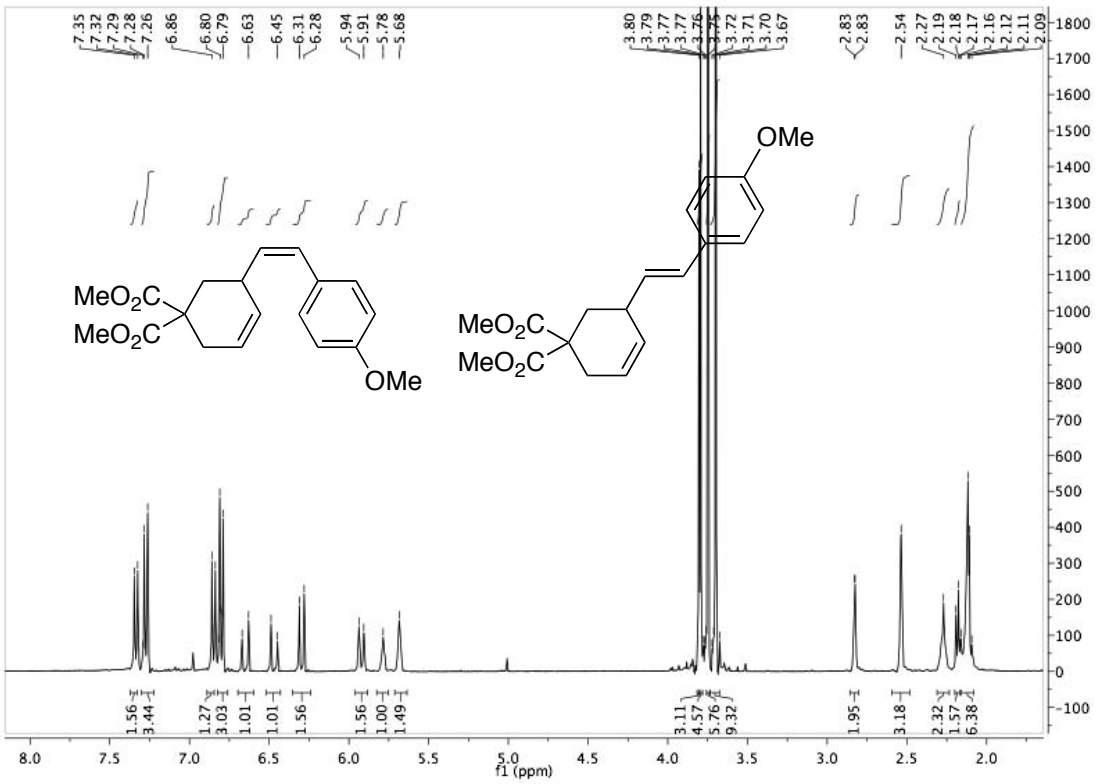
135.16
129.00
127.16
113.90
77.55
77.23
76.91
56.73
55.47
53.00
52.59
36.15
34.56
32.82
31.13
29.44
OMe
MeO2C
MeO2C
f1 (ppm)

***E* / *Z*-28**


7.35
7.32
7.29
7.28
7.26
6.86
6.80
6.79
6.63
6.45
6.31
6.28
5.94
5.91
5.78
5.68
3.80
3.79
3.77
3.77
3.76
3.75
3.72
3.71
3.70
3.67
2.83
2.83
2.54
2.27
2.19
2.18
2.17
2.16
2.12
2.11
2.09
OMe
MeO2C
MeO2C
OMe
MeO2C
MeO2C
1.56
3.44
1.27
3.03
1.01
1.01
1.56
1.56
1.00
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4.57
5.76
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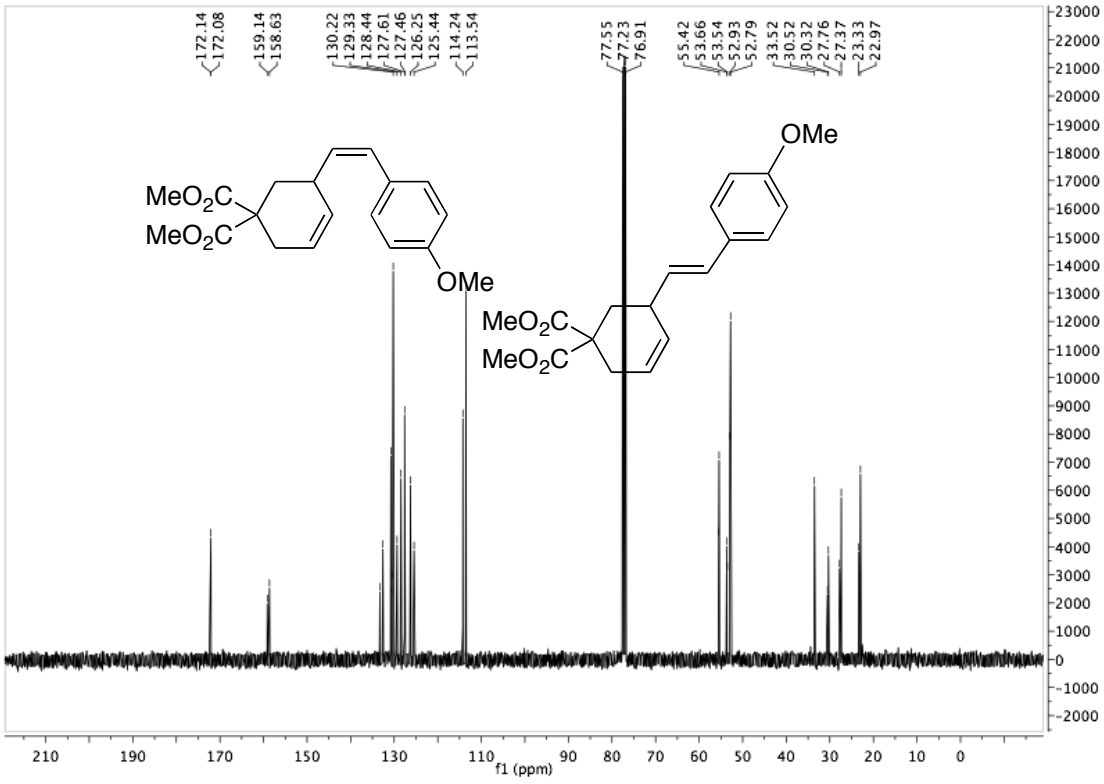
3.18
2.32
1.57
6.38
f1 (ppm)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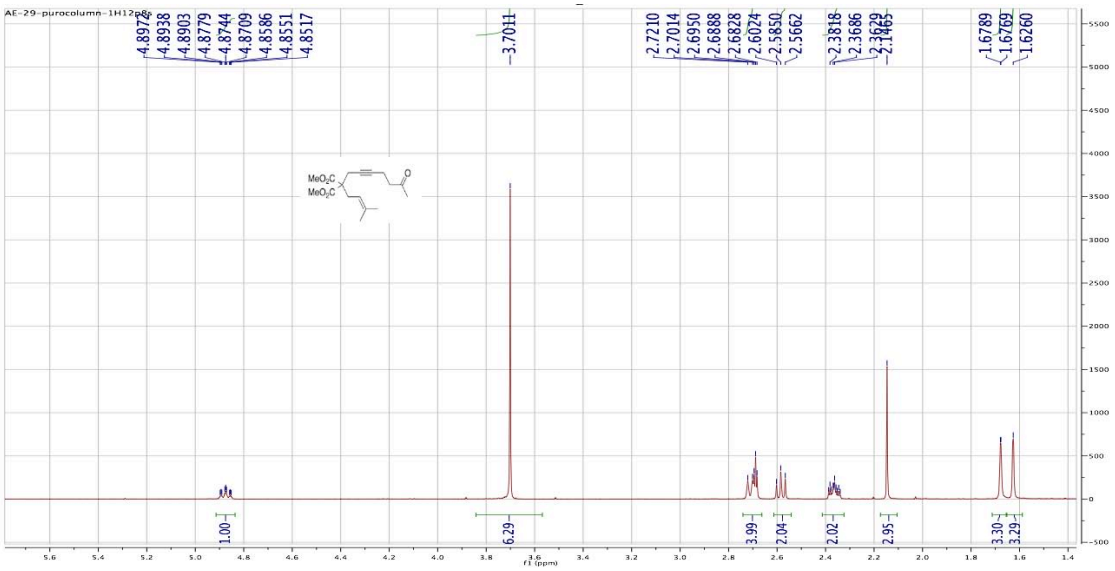
172.08
159.14
158.63
130.22
129.33
128.44
127.61
127.46
126.25
125.44
114.24
113.54
77.55
77.23
76.91
55.42
53.66
53.54
52.93
52.79
33.52
30.52
30.32
27.76
27.37
23.33
22.97
OMe
MeO2C
MeO2C
OMe
MeO2C
MeO2C
f1 (ppm)

42a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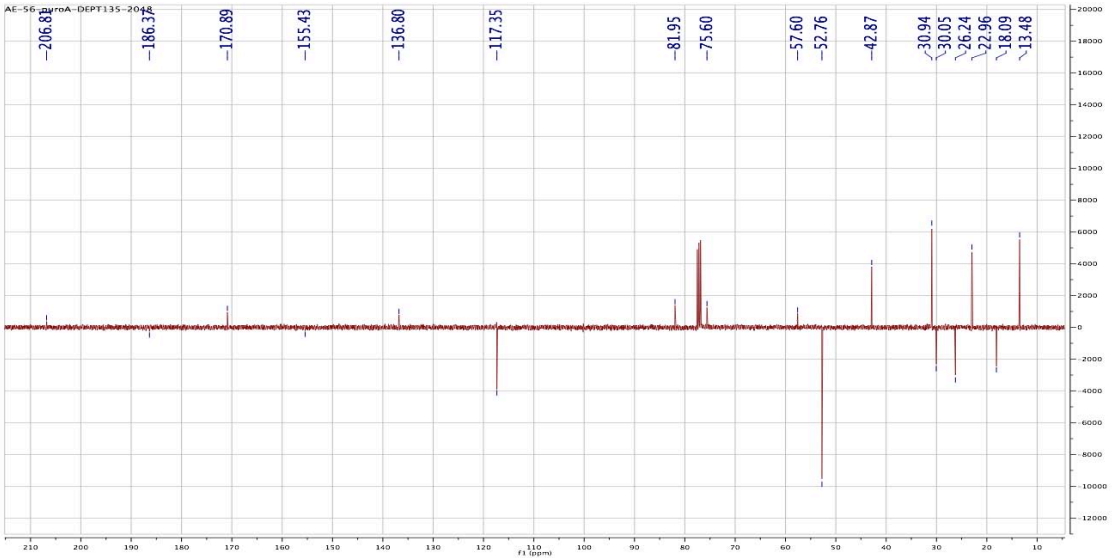
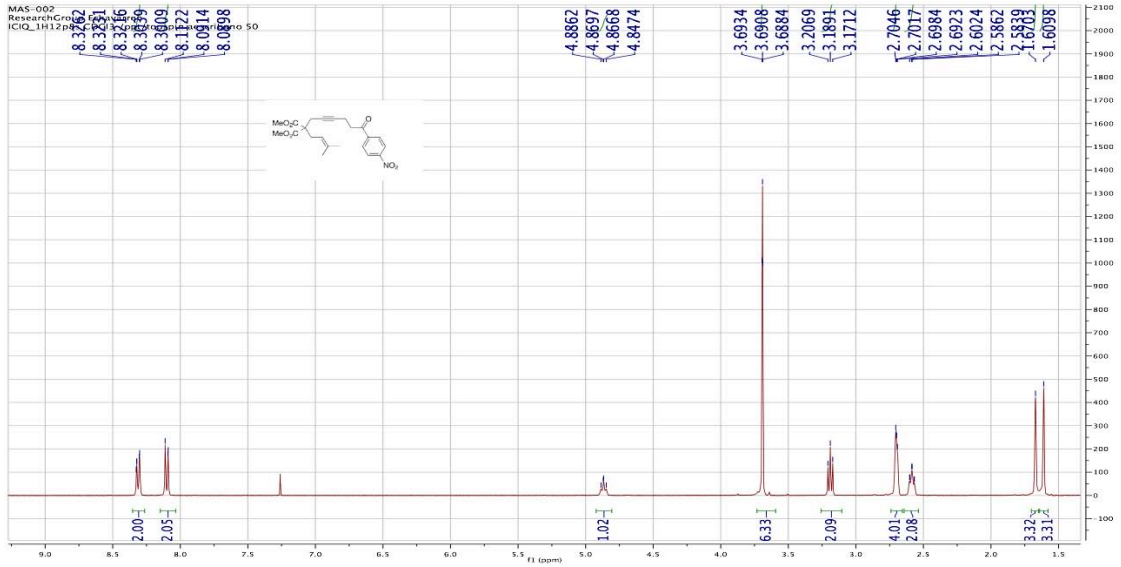
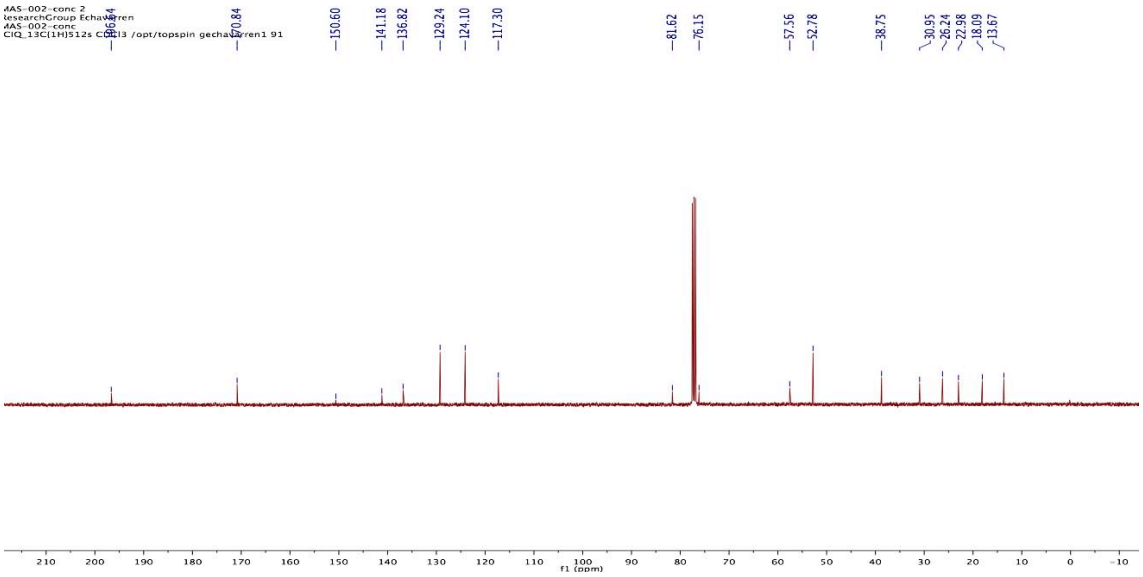
4.8903
4.8779
4.8744
4.8709
4.8586
4.8551
4.8517
3.7011
2.7210
2.7014
2.6950
2.6888
2.6828
2.6074
2.5850
2.5662
2.3818
2.3686
2.3629
2.1465
1.6789
1.6769
1.6260
MeO2C
MeO2C
O
1.00
6.29
3.99
2.04
2.02
2.95
3.30
3.29

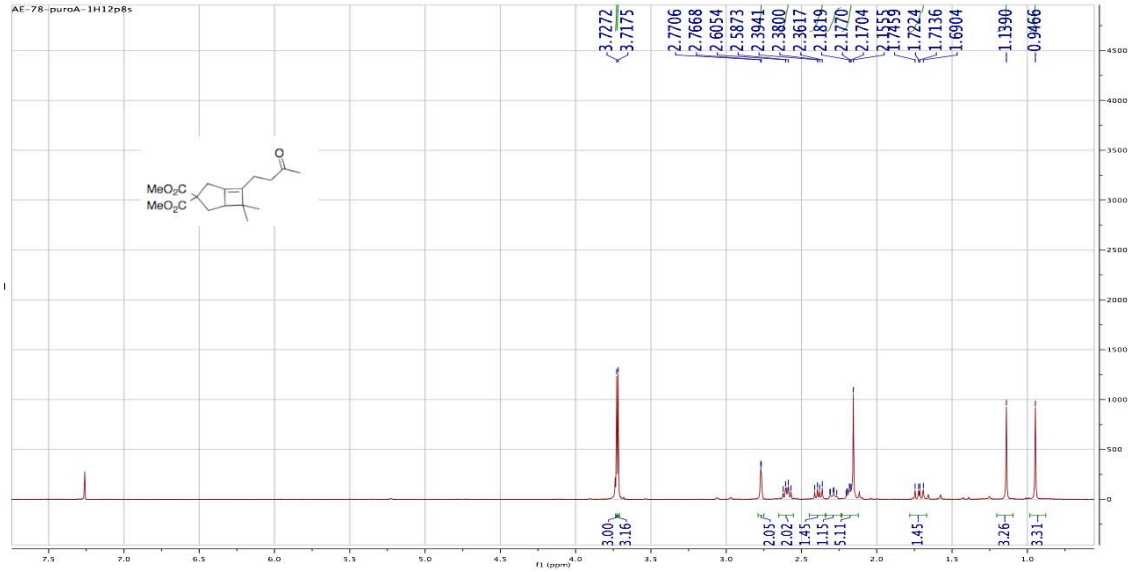

206.81
186.37
170.89
155.43
136.80
117.35
81.95
75.60
57.60
52.76
42.87
30.94
30.05
26.24
22.96
18.09
13.48

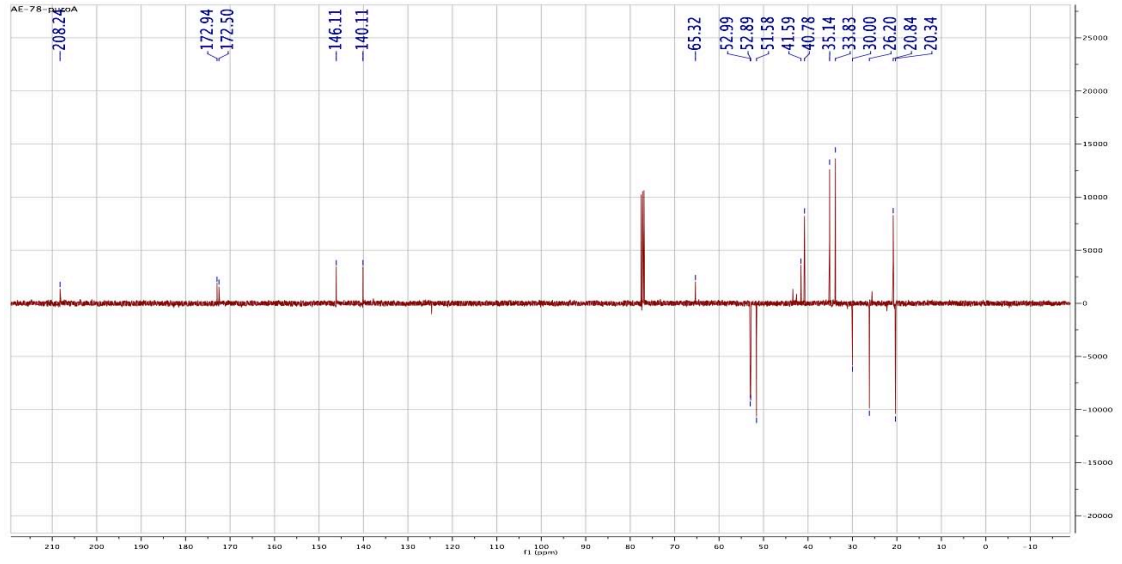
42b


8.3262
8.3221
8.3216
8.3199
8.3189
8.3122
8.0914
8.0898
4.8862
4.8697
4.8668
4.8474
3.6934
3.6908
3.6884
3.2069
3.1891
3.1712
2.7046
2.7017
2.6984
2.6923
2.6024
2.5862
2.5839
1.6703
1.6098
2.00
2.05
1.02
6.33
2.09
4.01
2.08
3.32
3.31
F1 (ppm)

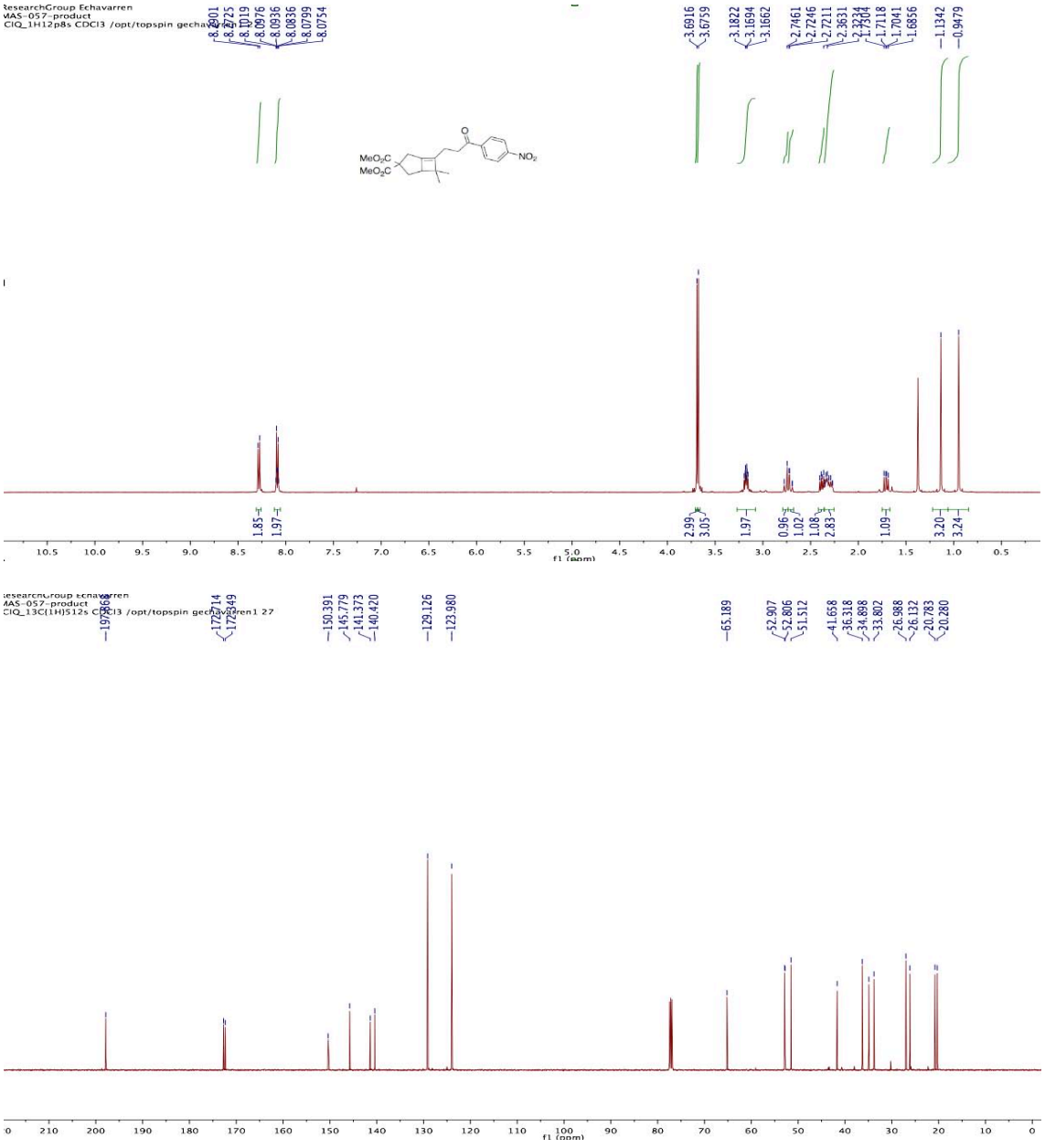

150.60
141.18
136.82
129.24
124.10
117.30
61.62
76.15
57.56
52.78
38.75
30.95
26.24
22.98
18.09
13.67
F1 (ppm)

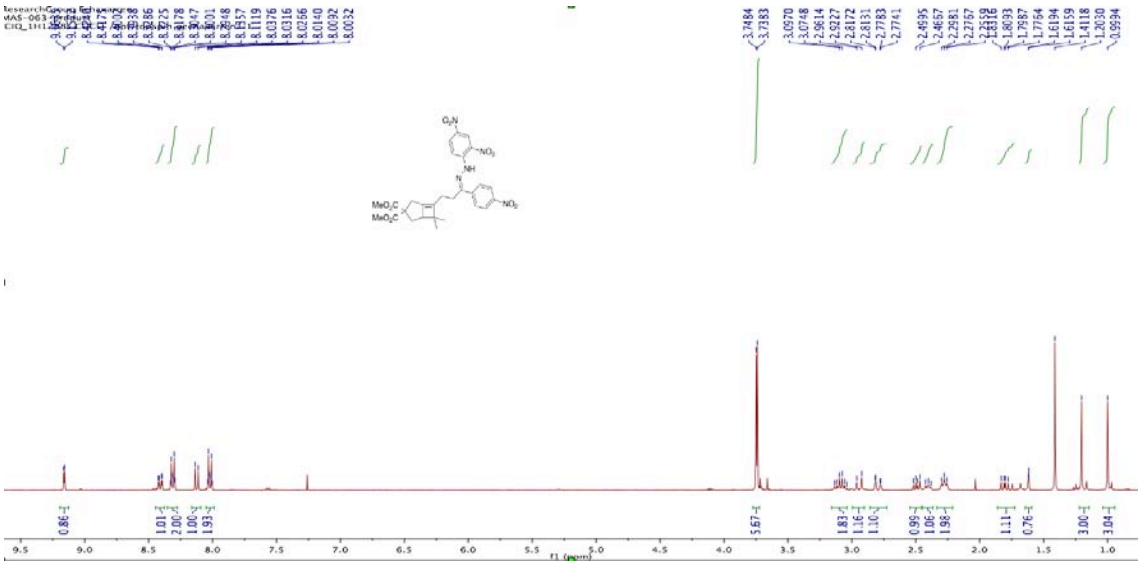
43a

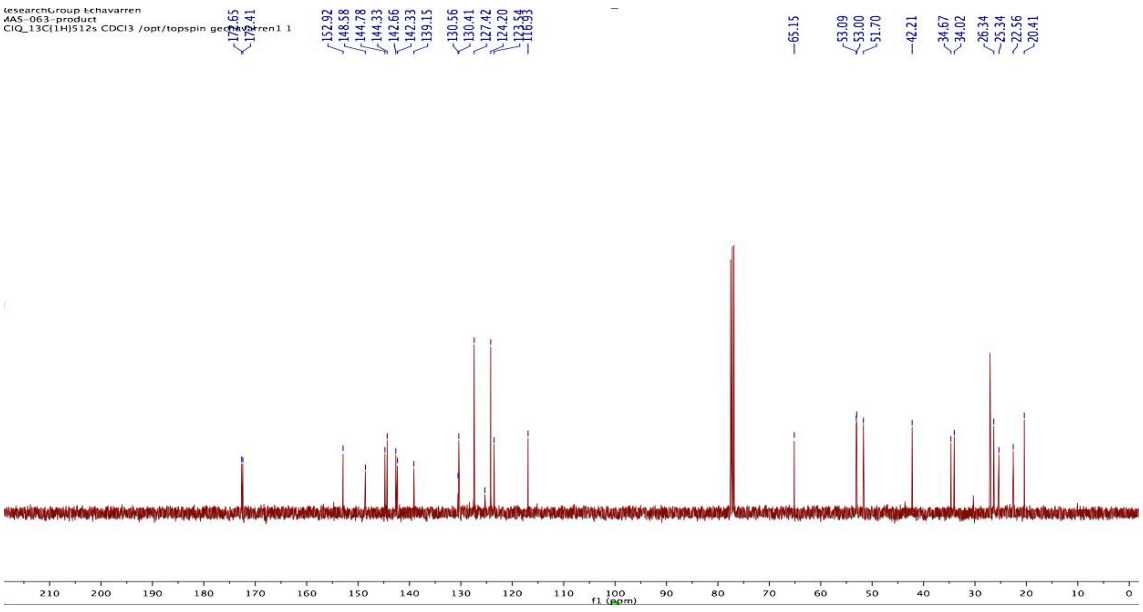

AE-78-puroA-1H12p8s
3.7272
3.7175
2.7706
2.7668
2.6054
2.5873
2.3941
2.3800
2.3617
2.1819
2.1770
2.1704
2.1555
2.1459
1.7224
1.7136
1.6904
1.1390
0.9466
MeO2C
MeO2C
O
3.00
3.16
2.05
2.02
1.45
1.15
5.11
1.45
3.26
3.31
f1 (ppm)


AE-78-PuroA
208.23
172.94
172.50
146.11
140.11
65.32
52.99
52.89
51.58
41.59
40.78
35.14
33.83
30.00
26.20
20.84
20.34
f1 (ppm)

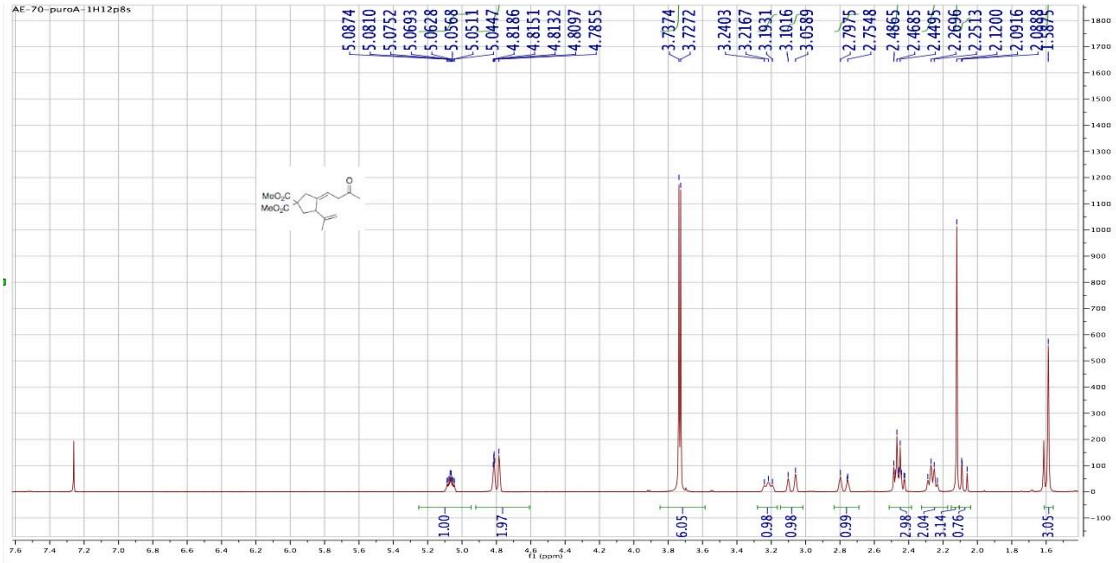
43b

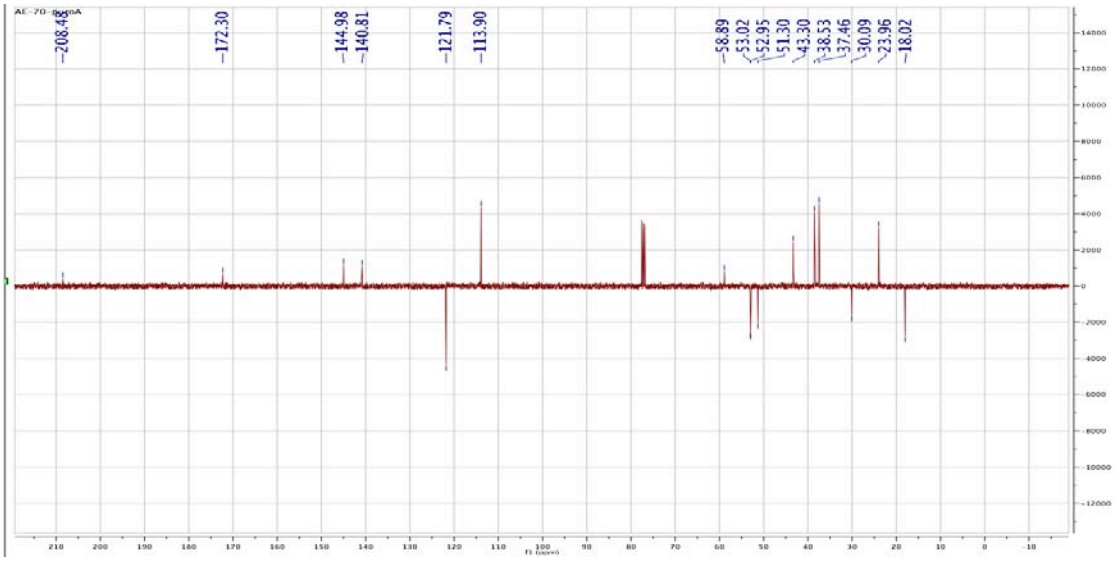






44


AE-70-puroA-1H12p8s
5.0874
5.0810
5.0752
5.0693
5.0628
5.0568
5.0511
5.0447
4.8186
4.8151
4.8132
4.8097
4.7855
3.7374
3.7272
3.2403
3.2167
3.1931
3.1016
3.0589
2.7975
2.7548
2.4865
2.4685
2.4495
2.2696
2.2513
2.1200
2.0916
2.0888
1.9875
MeO2C
MeO2C
O
1.00
1.97
6.05
0.98
0.98
0.99
2.98
2.04
3.14
0.76
3.05


208.48
172.30
144.98
140.81
121.79
113.90
58.89
53.02
52.95
51.30
43.30
38.53
37.46
30.09
23.96
18.02

Calculations: General Methods.

Calculations were carried out with DFT using the B3LYP functional[18] as implemented in Gaussian 03[19] or 09.[20] The 6-31G(d) basis set[21] was used for all atoms except gold, which was treated with SDD and the associated effective core potential.[22] Frequency calculations were performed to characterize the stationary points as minima.

The solvent effect was taken into account by single-point calculations using the polarizable continuum model (PCM),[23,24,25,26] in particular IEF-PCM as implemented in Gaussian 03 or 09. Default options were used, except that individual spheres were placed on all hydrogen atoms to get a more accurate cavity. The calculations were performed using CH_2Cl_2 (ε = 8.93) as solvent. The standard Gibbs energies in dichloromethane (ΔG_{DCM}) were obtained by adding the solvation energies to the gas-phase Gibbs energies computed at 298 K. The same procedure was employed to calculate zero-point corrected energies in CH_2Cl_2.

Conformers for the study of the skeletal rearrangement of 1,7-enynes were obtained using Maestro. Selected conformers were then recalculted using DFT methods.

The following abbreviations are used: ΔV (potential energy), ΔG (free energy in gas phase), ΔV_{ZPE} (zero-point corrected potential energy in gas phase), ΔV_{DCM} (potential energy including solvation effects in dichloromethane), ΔG_{DCM} (free energy including solvation effects in dichloromethane), $\Delta V_{ZPE+DCM}$ (zero-point corrected potential energy including solvation effects in dichloromethane).

Calculations: Skeletal Rearrangement of 1,6-Enynes (Scheme 4 and Table 2)

1. Ar = Ph. Relative energies referred to 1,6-enyne-Au(I) complex **18a**.

(a) *anti*-5-*exo* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}19a}$	13.24	13.51	16.2	13.08	13.35	16.04
19a	-7.23	-4.71	-0.71	-7.36	-4.84	-0.84
$TS_{19\text{-}20a}$	8.14	9.64	13.85	6.21	7.7	11.92
20a	-9.09	-7.16	-4.96	-8.5	-6.57	-4.37

(a) *syn*-5-*exo* pathway:

Relative energies (in kcal·mol^{-1}) referred to enyne **1**.

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}21a}$	24.32	23.87	26.08	24.34	23.9	26.11
21a	-5.57	-3.15	0.72	-5.79	-3.36	0.51
$TS_{21\text{-}23a}$	4.56	6.13	10.31	3.25	4.83	9
23a	-17.3	-14.58	-10.99	-17.13	-14.41	-10.82
$TS_{23\text{-}24a}$	13.94	14.61	18.10	13.84	14.52	18.01
24a	-27.35	-25.48	-21.88	-28.26	-26.4	-22.8

(c) *6-endo-dig* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}22a}$	12.73	13.4	16.52	13.62	14.29	17.41
22a	-4.51	-2.15	1.23	-4.89	-2.53	0.85
$TS_{22\text{-}23a}$	8.21	10.56	15.25	7.38	9.73	14.41

2. Ar = *p*-$MeOC_6H_4$. Relative energies referred to 1,6-enyne-Au(I) complex **18b**.

(a) *anti*-5-*exo* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}19b}$	16.16	16.19	17.71	16.16	16.19	17.71
19b	-8.48	-6.00	-2.72	-8.07	-5.58	-2.30
$TS_{19\text{-}20b}$	11.26	12.31	15.55	8.81	9.86	13.10
20b	-13.47	-11.50	-9.63	-12.70	-10.73	-8.86

(b) *syn*-5-*exo* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}21b}$	26.77	26.24	28.65	25.89	25.36	27.77
21b	-10.74	-8.08	-4.33	-10.97	-8.31	-4.57
$TS_{21\text{-}23b}$	7.34	8.67	12.85	5.57	6.89	11.08
23b	-18.23	-15.66	-12.15	-17.40	-14.83	-11.31
$TS_{23\text{-}24b}$	14.53	15.06	18.46	14.28	14.80	18.21
24b	-25.25	-23.58	-20.69	-26.48	-24.82	-21.92

(c) *6-endo-dig* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}22b}$	13.47	14.00	16.89	14.31	14.84	17.73
22b	-1.85	0.34	3.79	-2.37	-0.18	3.27
$TS_{22\text{-}23b}$	8.15	10.27	14.27	7.35	9.47	13.47

3. Ar = *p*-$O_2NC_6H_4$. Relative energies referred to 1,6-enyne-Au(I) complex **18c**.

(a) *anti*-5-*exo* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}19c}$	10.84	11.19	13.39	11.07	11.42	13.61
19c	-7.72	-5.2	-1.24	-7.87	-5.35	-1.39
$TS_{19\text{-}20c}$	5.11	6.79	11.16	2.73	4.42	8.79
20c	-7.3	-5.41	-2.73	-5.43	-3.54	-0.86

(b) *syn*-5-*exo* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
$TS_{18\text{-}21c}$	21.55	21.34	23.05	21.66	21.45	23.16
21c	-6.45	-4.07	-0.3	-6.64	-4.26	-0.49
$TS_{21\text{-}23c}$	1.94	3.73	8.24	0.47	2.27	6.77
23c	-17.9	-15.04	-10.92	-17.73	-14.87	-10.75
$TS_{23\text{-}24c}$	12.17	13.02	16.98	11.96	12.81	16.77
24c	-30.03	-28.01	-25.22	-30.73	-28.71	-25.92

(c) *6-endo-dig* pathway:

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}

$TS_{18\text{-}22c}$	12.12	12.79	15.43	13.62	14.29	16.93
22c	-6.72	-4.1	-0.14	-6.4	-3.77	0.18
$TS_{22\text{-}23c}$	8.35	10.6	15.67	8.69	10.94	16.01

Cartesian Coordinates and Absolute Energies

18a Energy= -1100.15004172 a.u.

C	3.199499	-2.146682	-0.852701
C	1.667932	-2.085258	-0.657287
C	1.168531	-0.705172	-0.410992
C	1.285582	0.524331	-0.266742
C	4.009122	-1.778883	0.403263
C	5.494614	-1.850797	0.163756
C	6.328354	-2.679006	0.793315
P	-3.352029	-0.510077	0.208392
Au	-1.033913	-0.392172	-0.084456
C	1.676898	2.487171	1.158195
C	1.442251	1.932023	-0.118803
C	1.406141	2.769961	-1.254739
C	1.603971	4.138576	-1.108884
C	1.836084	4.681873	0.159445
C	1.872904	3.857523	1.289364
H	3.446002	-3.171713	-1.154260
H	3.481035	-1.495641	-1.689760
H	1.368706	-2.725738	0.181928
H	1.162335	-2.484819	-1.544449
H	3.738423	-0.760543	0.720781
H	3.734165	-2.451358	1.226734
H	5.888354	-1.169935	-0.592559
H	7.392824	-2.691150	0.577265
H	5.979831	-3.374223	1.554639
H	1.710303	1.836832	2.026705
H	1.231126	2.336124	-2.234276
H	1.581339	4.783436	-1.981832
H	2.058555	4.285121	2.269712
C	-4.171345	-1.542056	-1.068933
H	-3.771811	-2.559663	-1.035284
H	-5.252170	-1.574292	-0.894831

H	-3.978417	-1.125307	-2.061551
C	-3.826592	-1.238069	1.824807
H	-4.917014	-1.284644	1.916028
H	-3.415317	-2.247996	1.909605
H	-3.422410	-0.629082	2.638417
C	-4.169367	1.131891	0.130851
H	-5.250138	1.024032	0.272425
H	-3.767119	1.783480	0.911662
H	-3.978220	1.594016	-0.841761
H	1.991686	5.751261	0.267330

$TS_{18\text{-}19a}$ Energy = -1100.12894280 a.u.

C	-2.782667	-3.513417	0.249910
C	-1.491097	-2.673815	0.143394
C	-1.693506	-1.195888	0.199459
C	-1.187030	-0.018244	0.105524
C	-3.892685	-2.896116	-0.614286
C	-4.034658	-1.433343	-0.299782
C	-3.834105	-0.915480	0.939863
P	3.301389	-0.060012	-0.092050
Au	0.946839	-0.140649	0.026145
C	-2.450956	1.755058	-1.108599
C	-1.726393	1.349454	0.025690
C	-1.512142	2.266477	1.069237
C	-2.044344	3.552996	0.991331
C	-2.772180	3.947955	-0.134133
C	-2.969602	3.048042	-1.183730
H	-2.568740	-4.537871	-0.067965
H	-3.101659	-3.573316	1.295305
H	-0.997425	-2.899613	-0.810486
H	-0.798498	-2.960224	0.943636
H	-3.668574	-3.021460	-1.679997
H	-4.844627	-3.415845	-0.437358

H	-4.277741	-0.752423	-1.112765
H	-3.927217	0.149585	1.120712
H	-3.694854	-1.542491	1.815300
H	-2.590502	1.061651	-1.932779
H	-0.942408	1.962385	1.942867
H	-1.886079	4.249225	1.809773
H	-3.177707	4.953365	-0.195286
H	-3.526628	3.352007	-2.065271
C	4.136250	-0.515960	1.480469
H	3.865944	-1.538188	1.760273
H	5.223958	-0.448649	1.370856
H	3.812699	0.158285	2.278641
C	4.015426	-1.178050	-1.363972
H	5.107545	-1.095674	-1.377058
H	3.736114	-2.213031	-1.146837
H	3.622954	-0.912532	-2.349831
C	3.931575	1.614353	-0.510225
H	5.025783	1.612038	-0.557668
H	3.529551	1.928157	-1.477823
H	3.605686	2.331967	0.248190

19a Energy = -1100.16155895 a.u.

C	-1.659167	3.841377	-0.044678
C	-1.113731	2.649079	-0.867756
C	-1.895487	1.403898	-0.440159
C	-1.266899	0.152899	-0.196695
C	-2.145646	3.229666	1.283005
C	-2.685377	1.857722	0.942416
C	-3.413655	1.630130	-0.316078
P	3.169796	-0.299913	0.013597
Au	0.793337	-0.021417	-0.077997
C	-1.692606	-2.024287	0.941075
C	-2.029367	-1.083434	-0.061040

C	-3.050397	-1.420389	-0.982523
C	-3.705587	-2.645058	-0.896346
C	-3.396893	-3.535542	0.136242
C	-2.395244	-3.217623	1.060486
H	-0.898104	4.610171	0.113467
H	-2.488369	4.328292	-0.568181
H	-0.050452	2.491001	-0.656703
H	-1.207650	2.814778	-1.947107
H	-1.324954	3.129251	2.002261
H	-2.925511	3.834470	1.764124
H	-2.780249	1.111129	1.725278
H	-4.066583	0.768351	-0.352212
H	-3.784267	2.489939	-0.868228
H	-0.893929	-1.790892	1.639481
H	-3.280215	-0.744593	-1.799683
H	-4.461220	-2.904469	-1.631638
H	-3.924015	-4.481984	0.211801
H	-2.149174	-3.912852	1.857295
C	4.102877	1.015615	-0.870767
H	3.872069	1.990873	-0.432167
H	5.181172	0.837303	-0.800803
H	3.810150	1.032407	-1.924698
C	3.855431	-0.297451	1.720700
H	4.942171	-0.431098	1.698679
H	3.620600	0.650943	2.212593
H	3.406376	-1.108293	2.301668
C	3.754855	-1.877088	-0.730516
H	4.846013	-1.950730	-0.671114
H	3.308573	-2.723927	-0.201036
H	3.448378	-1.926510	-1.779479

$TS_{19\text{-}20a}$ Energy = -1100.13706532 a.u.

C	2.496552	-3.693210	0.181334

C	1.492492	-2.658798	0.747406
C	2.025464	-1.307729	0.309753
C	1.266044	-0.150654	-0.190551
C	3.802858	-2.895656	-0.062547
C	3.346467	-1.465086	-0.166435
C	1.958361	-0.981908	-1.328678
P	-3.201831	0.075307	0.080780
Au	-0.834662	-0.108548	-0.068411
C	1.905229	2.123358	-1.110573
C	1.883272	1.219204	-0.037278
C	2.388407	1.634881	1.204490
C	2.912750	2.918174	1.364598
C	2.938953	3.807076	0.288102
C	2.432702	3.404948	-0.950007
H	2.646456	-4.540851	0.853177
H	2.123792	-4.096392	-0.765971
H	1.499165	-2.640990	1.846360
H	0.456855	-2.819497	0.437381
H	4.488917	-2.957085	0.794797
H	4.369440	-3.228246	-0.937666
H	4.034855	-0.636763	-0.295958
H	2.611022	-0.369128	-1.941790
H	1.450337	-1.791947	-1.841071
H	1.496276	1.828110	-2.074803
H	2.367482	0.952010	2.050742
H	3.302747	3.221677	2.331993
H	3.348027	4.805083	0.413124
H	2.444807	4.090409	-1.792606
C	-4.117186	-0.771575	-1.272204
H	-3.883840	-1.840319	-1.266146
H	-5.197460	-0.640035	-1.148758
H	-3.814512	-0.357502	-2.238491
C	-3.908742	-0.621029	1.630255

H	-4.996688	-0.496088	1.648468
H	-3.668929	-1.685939	1.701872
H	-3.475311	-0.110661	2.495334
C	-3.803561	1.813140	0.034189
H	-3.501771	2.283190	-0.906389
H	-4.895038	1.846534	0.118964
H	-3.361238	2.379326	0.859082

20a Energy = -1100.16452276 a.u.

C	-1.316093	4.307443	0.579294
C	-0.708931	3.331484	-0.462556
C	-1.677371	2.164821	-0.452790
C	-1.235991	-0.118033	-0.685320
C	-2.267567	3.444094	1.451714
C	-2.502756	2.218042	0.609862
C	-1.638353	1.059489	-1.507103
P	3.122828	-0.408011	0.208392
Au	0.770810	-0.261840	-0.224100
C	-3.569941	-1.057905	-0.688615
C	-2.211613	-1.080310	-0.256343
C	-1.819173	-2.133332	0.618571
C	-2.719397	-3.102411	1.033656
C	-4.045498	-3.051977	0.587200
C	-4.467366	-2.029425	-0.273694
H	-0.552752	4.819945	1.170414
H	-1.895447	5.076938	0.059409
H	0.299521	2.994942	-0.176892
H	-0.616046	3.778283	-1.460269
H	-1.805648	3.156518	2.408484
H	-3.198141	3.963837	1.708584
H	-3.248762	1.469637	0.861625
H	-2.595921	0.968458	-2.028010
H	-0.873338	1.298637	-2.250861

H	-3.918337	-0.279369	-1.356689
H	-0.790265	-2.164769	0.963477
H	-2.398947	-3.896146	1.700927
H	-4.752960	-3.811212	0.908407
H	-5.496459	-2.000179	-0.617659
C	3.707602	-2.114628	0.566386
H	4.789187	-2.124262	0.737951
H	3.201295	-2.501227	1.455740
H	3.473123	-2.769843	-0.277692
C	3.675922	0.596415	1.646949
H	4.756339	0.496539	1.795394
H	3.433826	1.649620	1.477326
H	3.157218	0.264600	2.551074
C	4.161788	0.162193	-1.198248
H	5.225658	0.070909	-0.954675
H	3.944195	-0.439713	-2.085435
H	3.934651	1.207630	-1.426417

$TS_{18\text{-}21a}$ Energy= -1100.11129285 a.u.

C	-3.855005	-2.807331	-0.097412
C	-3.505587	-1.380926	0.354540
C	-2.158547	-0.870148	0.044163
C	-1.294240	0.077223	0.010653
C	-2.879265	-3.807038	0.549939
C	-1.456102	-3.389591	0.306230
C	-1.025357	-2.889126	-0.872089
P	3.166791	0.006292	-0.027533
Au	0.806727	-0.032492	-0.008782
C	-2.635181	1.939478	-1.052158
C	-1.818874	1.496550	-0.002171
C	-1.492918	2.373282	1.043611
C	-1.994248	3.675078	1.039954
C	-2.805754	4.117453	-0.007867

C	-3.119968	3.248845	-1.054128
H	-4.882412	-3.029807	0.205044
H	-3.822534	-2.874996	-1.189487
H	-3.665253	-1.296480	1.438438
H	-4.182962	-0.660012	-0.129052
H	-3.067926	-3.872407	1.627315
H	-3.055637	-4.812008	0.142672
H	-0.751977	-3.462555	1.133229
H	0.003593	-2.571984	-1.005219
H	-1.650662	-2.856811	-1.759825
H	-2.872046	1.268460	-1.873020
H	-0.859709	2.033009	1.857978
H	-1.744451	4.346047	1.856844
H	-3.186477	5.134289	-0.010134
H	-3.745127	3.586576	-1.875647
C	3.946352	-1.592938	-0.489899
H	3.617692	-1.889496	-1.490159
H	5.037848	-1.502686	-0.484371
H	3.647745	-2.369666	0.220072
C	3.849278	1.236057	-1.210163
H	4.944194	1.230220	-1.180809
H	3.514661	0.999353	-2.224269
H	3.486850	2.235272	-0.951993
C	3.894153	0.445056	1.602044
H	4.987536	0.465571	1.541641
H	3.532906	1.429609	1.912600
H	3.588448	-0.288594	2.353484

21a Energy= -1100.15891848 a.u.

C	-4.030339	-2.594686	-0.160762
C	-3.487327	-1.295911	-0.815561
C	-1.990212	-1.226405	-0.480065
C	-1.212004	-0.061667	-0.261334

C	-3.095543	-2.899170	1.027163
C	-1.713269	-2.432130	0.618145
C	-1.261502	-2.569833	-0.761317
P	3.240093	-0.013978	0.156110
Au	0.858122	-0.086672	-0.083633
C	-1.251591	2.376683	-0.734231
C	-1.827583	1.252488	-0.097204
C	-2.944960	1.462510	0.746167
C	-3.460232	2.740158	0.935170
C	-2.914464	3.828653	0.246967
C	-1.815890	3.640626	-0.596748
H	-5.070271	-2.486024	0.158532
H	-4.010968	-3.422159	-0.876958
H	-4.016389	-0.419705	-0.444134
H	-3.622928	-1.307935	-1.903232
H	-3.404493	-2.359013	1.929687
H	-3.077685	-3.966580	1.282948
H	-0.975908	-2.224005	1.386520
H	-0.196962	-2.495898	-0.960643
H	-1.806545	-3.223244	-1.437899
H	-0.382250	2.238277	-1.370543
H	-3.366089	0.632162	1.303115
H	-4.293818	2.888370	1.614994
H	-3.334992	4.820977	0.379617
H	-1.385082	4.484204	-1.127368
C	4.064622	-1.654877	0.056344
H	3.853242	-2.116546	-0.912612
H	5.148335	-1.549449	0.173736
H	3.682025	-2.310866	0.843712
C	4.067268	1.011360	-1.127564
H	5.151782	1.018677	-0.975388
H	3.847083	0.610340	-2.121213
H	3.692387	2.037872	-1.078072

C	3.788830	0.699991	1.760291
H	4.882186	0.729328	1.816898
H	3.396412	1.715783	1.864442
H	3.403102	0.095469	2.586412

$TS_{21\text{-}23a}$ Energy= -1100.14278084 a.u.

C	-4.059448	-2.546397	0.250598
C	-3.423740	-1.305284	0.925076
C	-2.004007	-1.257280	0.409913
C	-1.245843	-0.174393	-0.092239
C	-2.872029	-3.469469	-0.117728
C	-1.689996	-2.522393	-0.288918
C	-1.775673	-1.354850	-1.325337
P	3.229526	0.026763	0.121432
Au	0.870747	-0.153446	-0.035417
C	-1.871446	1.979949	-1.230332
C	-1.824945	1.203436	-0.060930
C	-2.274234	1.766470	1.145332
C	-2.771747	3.069863	1.175830
C	-2.836710	3.825365	0.003533
C	-2.386749	3.275457	-1.199137
H	-4.783927	-3.041265	0.901307
H	-4.600815	-2.238506	-0.649880
H	-3.327977	-1.455798	2.011255
H	-3.972459	-0.372407	0.777653
H	-2.642029	-4.161848	0.700400
H	-3.064853	-4.073653	-1.009006
H	-0.683077	-2.929322	-0.242390
H	-0.953463	-1.331223	-2.029281
H	-2.744563	-1.141962	-1.770198
H	-1.507018	1.566497	-2.167435
H	-2.216735	1.191932	2.066720
H	-3.110990	3.492753	2.117025

H	-2.430167	3.857938	-2.114877
C	4.139098	-1.507183	-0.328048
H	3.906288	-1.787599	-1.359417
H	5.219492	-1.354322	-0.233441
H	3.834673	-2.325447	0.331033
C	3.932890	1.333373	-0.964332
H	5.021317	1.382349	-0.852881
H	3.688586	1.118678	-2.008743
H	3.500631	2.303139	-0.701046
C	3.812620	0.447246	1.813492
H	4.904574	0.528840	1.834865
H	3.375073	1.399044	2.128508
H	3.496902	-0.327771	2.517963
H	-3.229643	4.837281	0.027686

23a Energy = -1100.17761104 a.u.

C	-2.516455	-2.978777	1.150824
C	-1.409478	-1.974471	1.591155
C	-1.075804	-1.362065	0.244146
C	-1.744680	-0.357813	-0.499254
C	-2.092080	-3.510313	-0.247792
C	-1.231140	-2.396223	-0.896089
C	-1.912395	-1.254548	-1.719792
P	3.010087	0.652883	-0.033829
Au	0.830979	-0.255428	-0.001862
C	-3.100658	1.583784	-1.183543
C	-2.328059	0.933410	-0.199062
C	-2.173658	1.547019	1.064771
C	-2.787252	2.763423	1.333903
C	-3.558591	3.393319	0.348103
C	-3.712849	2.803435	-0.909374
H	-2.653290	-3.785015	1.877605
H	-3.467611	-2.437622	1.080775

H	-0.547483	-2.506875	2.008333
H	-1.762211	-1.258637	2.338184
H	-1.475446	-4.408044	-0.132498
H	-2.955431	-3.795122	-0.857965
H	-0.320418	-2.791541	-1.352003
H	-1.442914	-0.946832	-2.659354
H	-2.976482	-1.444100	-1.912835
H	-3.227077	1.121757	-2.158266
H	-1.562088	1.068969	1.824436
H	-2.667879	3.227190	2.308400
H	-4.310523	3.293267	-1.671832
C	3.926648	0.351674	1.529018
H	4.008214	-0.723910	1.710373
H	4.931687	0.782945	1.470416
H	3.389933	0.805241	2.367241
C	4.067536	-0.039195	-1.366684
H	5.067033	0.407203	-1.328697
H	4.153445	-1.123100	-1.247868
H	3.618797	0.168938	-2.342248
C	3.036570	2.473268	-0.279989
H	4.067844	2.842377	-0.279710
H	2.565310	2.724247	-1.234553
H	2.478144	2.963664	0.522416
H	-4.036100	4.344973	0.562172

$TS_{23\text{-}24a}$ Energy = -1100.12783269 a.u.

C	1.569449	3.552714	1.151352
C	1.226559	2.087423	1.556121
C	1.112040	1.375965	0.190742
C	2.147499	0.563765	-0.446073
C	0.931001	3.770591	-0.243196
C	0.878560	2.386669	-0.840676
C	2.651623	1.387116	-1.474322

P	-2.857267	-0.888748	-0.117930
Au	-0.802628	0.252740	-0.006613
C	3.658649	-1.371713	-0.848113
C	2.555955	-0.814119	-0.168833
C	1.930866	-1.585858	0.831781
C	2.387390	-2.863347	1.139512
C	3.466116	-3.410088	0.437019
C	4.098188	-2.660438	-0.558153
H	1.213599	4.274948	1.890872
H	2.656561	3.672385	1.080261
H	0.285795	2.062754	2.115003
H	1.995946	1.639488	2.191141
H	-0.099325	4.153330	-0.171881
H	1.471611	4.486761	-0.871867
H	0.376394	2.182028	-1.779524
H	3.085989	1.015688	-2.403874
H	2.992101	2.383396	-1.199702
H	4.191219	-0.783612	-1.588766
H	1.082651	-1.177341	1.375559
H	1.900590	-3.437814	1.922243
H	4.945705	-3.073770	-1.096465
C	-4.146882	0.022895	-1.056782
H	-3.808997	0.190021	-2.083566
H	-5.080922	-0.548984	-1.074632
H	-4.329460	0.994269	-0.588376
C	-2.725518	-2.528677	-0.935102
H	-3.703495	-3.020885	-0.965361
H	-2.354345	-2.403503	-1.956325
H	-2.021165	-3.160493	-0.386540
C	-3.595452	-1.217373	1.531840
H	-4.548312	-1.746732	1.425145
H	-2.911333	-1.826364	2.129707
H	-3.766524	-0.272564	2.055689

H	3.816078	-4.411383	0.669914

24a Energy = -1100.19362056 a.u.

C	0.370453	2.751850	1.829586
C	1.572138	1.916073	1.339371
C	1.236019	1.563008	-0.100340
C	2.134085	0.744460	-0.952370
C	-0.235622	3.345648	0.537587
C	0.150092	2.325430	-0.520438
C	2.314247	1.091375	-2.243731
P	-2.604124	-1.355721	-0.009456
Au	-1.012412	0.371271	-0.151154
C	4.245375	-0.584682	-0.668682
C	2.895230	-0.380892	-0.336602
C	2.291156	-1.270044	0.569070
C	3.005818	-2.337850	1.110615
C	4.344128	-2.533111	0.762553
C	4.961035	-1.651856	-0.127368
H	-0.363300	2.094165	2.314328
H	0.656386	3.515215	2.556962
H	1.808663	1.052487	1.964872
H	2.489943	2.523768	1.295906
H	-1.310842	3.535242	0.601839
H	0.241961	4.303042	0.280352
H	-0.111654	2.450928	-1.570667
H	2.974550	0.522479	-2.890382
H	1.833677	1.959183	-2.683815
H	4.743006	0.112305	-1.336587
H	1.246922	-1.133586	0.844372
H	2.520128	-3.016994	1.805849
H	6.005485	-1.787131	-0.392395
C	-4.211626	-0.898300	-0.769254
H	-4.068657	-0.662638	-1.827772

H	-4.921667	-1.727314	-0.678663
H	-4.622675	-0.017148	-0.268403
C	-2.070784	-2.894822	-0.857017
H	-2.842453	-3.666134	-0.760222
H	-1.895648	-2.692832	-1.917622
H	-1.139342	-3.259156	-0.414762
C	-2.987749	-1.840999	1.719272
H	-3.731959	-2.644574	1.731087
H	-2.078073	-2.187011	2.218233
H	-3.379779	-0.980161	2.268370
H	4.903793	-3.360439	1.188600

$TS_{18\text{-}22a}$ Energy = -1100.12974875 a.u.

C	2.216731	-3.097616	0.827308
C	1.275155	-2.647254	-0.308279
C	1.041195	-1.152320	-0.276104
C	1.915274	-0.188857	-0.317151
C	3.941919	-1.302490	0.192630
C	3.695818	-2.741021	0.554991
H	1.698461	-2.931423	-1.283457
H	0.322743	-3.174356	-0.224967
H	1.882003	-2.655627	1.773058
H	2.153682	-4.185459	0.940509
H	4.047052	-3.369858	-0.273188
H	4.295081	-2.996792	1.435644
Au	-0.931405	-0.424160	-0.106643
P	-3.190302	0.260270	0.079702
C	-4.264858	-0.989334	0.894301
H	-3.892648	-1.195789	1.901960
H	-5.296706	-0.627896	0.958929
H	-4.246108	-1.921231	0.321763
C	-3.419809	1.800167	1.058241
H	-2.864037	2.618737	0.591876

H	-4.480223	2.069094	1.111188
H	-3.035010	1.654295	2.071696
C	-3.995032	0.600185	-1.538274
H	-3.969536	-0.299493	-2.159855
H	-5.036077	0.907799	-1.392866
H	-3.454421	1.395433	-2.059657
C	3.833169	-0.818587	-1.080265
H	4.179676	0.174766	-1.338349
H	3.607019	-1.483034	-1.910388
C	2.115849	1.233535	-0.094316
C	2.235937	2.122178	-1.180946
C	2.169861	1.738104	1.219628
C	2.391262	3.486926	-0.954733
H	2.195430	1.735568	-2.195269
C	2.332200	3.104385	1.438752
H	2.074745	1.053964	2.057575
C	2.444221	3.978682	0.353845
H	2.474508	4.167792	-1.796413
H	2.371599	3.487316	2.454077
H	2.574454	5.042881	0.527094
H	4.260499	-0.622198	0.980530

22a Energy = -1100.15722419 a.u.

C	2.491089	-2.805906	0.866797
C	1.648732	-2.516387	-0.409857
C	1.252842	-1.075428	-0.350819
C	2.259815	-0.086581	-0.351136
C	3.700028	-0.616401	0.261175
C	3.814307	-2.030177	0.818889
H	2.262982	-2.737774	-1.295671
H	0.773863	-3.167601	-0.446733
H	1.912035	-2.516918	1.752359
H	2.674103	-3.882424	0.940979

H	4.530034	-2.580029	0.194191
H	4.244109	-1.975108	1.823894
Au	-0.720553	-0.564041	-0.124467
P	-3.038424	0.005514	0.087168
C	-4.072699	-1.312611	0.845276
H	-3.697927	-1.547452	1.845817
H	-5.116429	-0.989503	0.919903
H	-4.021041	-2.219530	0.235689
C	-3.334911	1.499240	1.118368
H	-2.791799	2.350076	0.696984
H	-4.403473	1.736004	1.157567
H	-2.968661	1.325635	2.134425
C	-3.844779	0.374957	-1.524448
H	-3.780938	-0.498617	-2.179697
H	-4.897829	0.636427	-1.375950
H	-3.332632	1.210187	-2.011039
C	3.595735	-0.350287	-1.158975
H	4.006998	0.571548	-1.558881
H	3.571826	-1.182444	-1.856397
C	1.919084	1.358870	-0.099519
C	1.786925	2.254892	-1.169058
C	1.713258	1.822055	1.208103
C	1.450487	3.589638	-0.935854
H	1.943488	1.908364	-2.187711
C	1.382032	3.158030	1.441562
H	1.819294	1.136693	2.045617
C	1.250287	4.044022	0.369778
H	1.352177	4.274609	-1.773011
H	1.234921	3.507035	2.459614
H	1.000600	5.085280	0.551522
H	4.110917	0.184476	0.870209

$TS_{22\text{-}23a}$ Energy = -1100.13695468 a.u.

C	-0.360814	3.569196	-0.025930
C	-0.756260	2.557136	-1.105688
C	-0.977696	1.208391	-0.384890
C	-2.292185	0.662790	-0.301582
C	-1.976484	1.929355	1.007713
C	-1.356069	3.338423	1.129141
H	-1.657270	2.891459	-1.634908
H	0.023114	2.436768	-1.863386
H	0.659206	3.362731	0.318155
H	-0.380481	4.598786	-0.395650
H	-2.175380	4.065776	1.104019
H	-0.873801	3.423060	2.107332
Au	0.830611	0.183669	-0.138091
P	2.980960	-0.833513	0.078124
C	3.639777	-0.830705	1.796245
H	2.964560	-1.386975	2.453063
H	4.633680	-1.289228	1.832625
H	3.706445	0.197805	2.162849
C	3.045430	-2.595581	-0.448248
H	2.731259	-2.680081	-1.492740
H	4.060720	-2.993043	-0.345344
H	2.364575	-3.192043	0.166071
C	4.281594	-0.002228	-0.923139
H	4.371640	1.043923	-0.616318
H	5.248629	-0.499294	-0.791866
H	4.005908	-0.028581	-1.981494
C	-3.223239	1.749615	0.131482
H	-4.143056	1.426831	0.613319
H	-3.387025	2.591597	-0.538623
C	-2.699569	-0.731425	-0.073004
C	-4.014172	-1.069556	-0.461973
C	-1.865661	-1.745162	0.435277
C	-4.463062	-2.384686	-0.385991

H	-4.673100	-0.304015	-0.860716
C	-2.331162	-3.051525	0.545603
H	-0.864921	-1.502290	0.776266
C	-3.624592	-3.377635	0.125333
H	-5.467949	-2.631567	-0.713928
H	-1.686567	-3.819513	0.962516
H	-3.979406	-4.400981	0.204138
H	-1.968471	1.323259	1.909871

18b Energy = -1214.63461989 a.u.

C	0.573491	4.711033	0.101689
C	1.237226	3.472374	-0.565495
C	0.636268	2.156689	-0.314587
C	0.662874	0.890924	-0.109890
C	-0.449676	4.302767	1.167237
C	-1.396228	3.259738	0.642858
C	-1.739390	3.103086	-0.654400
P	-2.943305	-1.755191	-0.043172
Au	-1.090561	-0.298914	-0.066498
C	2.080843	-0.900696	0.957901
C	1.941042	0.123739	0.000128
C	3.034727	0.409289	-0.830562
C	4.233202	-0.295508	-0.719713
C	4.364211	-1.300219	0.250161
C	3.273913	-1.592600	1.089777
H	1.343386	5.351554	0.540712
H	0.087698	5.306707	-0.677269
H	2.255027	3.327686	-0.162018
H	1.354496	3.634357	-1.643687
H	0.054748	3.908057	2.057344
H	-1.008068	5.187735	1.502897
H	-1.815797	2.568794	1.371891
H	-2.423464	2.317714	-0.960343

H	-1.403020	3.773337	-1.440089
H	1.249860	-1.137377	1.616133
H	2.945541	1.169151	-1.601833
H	5.049920	-0.057825	-1.391094
H	3.389727	-2.374620	1.833150
C	-4.385456	-1.155200	-1.012584
H	-4.089462	-0.995363	-2.053400
H	-5.200209	-1.886422	-0.979100
H	-4.740509	-0.205731	-0.601466
C	-2.549935	-3.409605	-0.739364
H	-3.429900	-4.060723	-0.703498
H	-2.221368	-3.304388	-1.777334
H	-1.739020	-3.867383	-0.165527
C	-3.596378	-2.081035	1.643577
H	-4.446801	-2.769888	1.600722
H	-2.809877	-2.519259	2.264713
H	-3.916877	-1.142143	2.104099
O	5.475772	-2.042667	0.450752
C	6.619815	-1.804752	-0.365423
H	6.991866	-0.780534	-0.240215
H	7.377678	-2.510339	-0.023989
H	6.398852	-1.989845	-1.423766

$TS_{18\text{-}21b}$ Energy = -1214.63461989 a.u.

C	0.573491	4.711033	0.101689
C	1.237226	3.472374	-0.565495
C	0.636268	2.156689	-0.314587
C	0.662874	0.890924	-0.109890
C	-0.449676	4.302767	1.167237
C	-1.396228	3.259738	0.642858
C	-1.739390	3.103086	-0.654400
P	-2.943305	-1.755191	-0.043172
Au	-1.090561	-0.298914	-0.066498

C	2.080843	-0.900696	0.957901
C	1.941042	0.123739	0.000128
C	3.034727	0.409289	-0.830562
C	4.233202	-0.295508	-0.719713
C	4.364211	-1.300219	0.250161
C	3.273913	-1.592600	1.089777
H	1.343386	5.351554	0.540712
H	0.087698	5.306707	-0.677269
H	2.255027	3.327686	-0.162018
H	1.354496	3.634357	-1.643687
H	0.054748	3.908057	2.057344
H	-1.008068	5.187735	1.502897
H	-1.815797	2.568794	1.371891
H	-2.423464	2.317714	-0.960343
H	-1.403020	3.773337	-1.440089
H	1.249860	-1.137377	1.616133
H	2.945541	1.169151	-1.601833
H	5.049920	-0.057825	-1.391094
H	3.389727	-2.374620	1.833150
C	-4.385456	-1.155200	-1.012584
H	-4.089462	-0.995363	-2.053400
H	-5.200209	-1.886422	-0.979100
H	-4.740509	-0.205731	-0.601466
C	-2.549935	-3.409605	-0.739364
H	-3.429900	-4.060723	-0.703498
H	-2.221368	-3.304388	-1.777334
H	-1.739020	-3.867383	-0.165527
C	-3.596378	-2.081035	1.643577
H	-4.446801	-2.769888	1.600722
H	-2.809877	-2.519259	2.264713
H	-3.916877	-1.142143	2.104099
O	5.475772	-2.042667	0.450752
C	6.619815	-1.804752	-0.365423

H	6.991866	-0.780534	-0.240215
H	7.377678	-2.510339	-0.023989
H	6.398852	-1.989845	-1.423766

21b Energy = -1214.69440225 a.u.

C	-1.525756	4.499287	-0.255540
C	-1.992098	3.096762	0.200124
C	-0.733865	2.216771	0.298822
C	-0.669515	0.792991	0.122660
C	-0.238253	4.266170	-1.067881
C	0.430043	3.061324	-0.434909
C	0.462276	2.918947	1.019227
P	3.282212	-1.322855	0.016227
Au	1.181925	-0.176837	0.044618
C	-1.766713	-1.294952	-0.640655
C	-1.840890	-0.032961	0.027702
C	-3.097316	0.294563	0.613231
C	-4.188680	-0.552889	0.542026
C	-4.088866	-1.764778	-0.172298
C	-2.857975	-2.121678	-0.768566
H	-2.294760	5.011852	-0.839917
H	-1.319044	5.134301	0.612322
H	-2.671956	2.662615	-0.541499
H	-2.537668	3.159778	1.148235
H	-0.467032	4.039851	-2.115706
H	0.423911	5.140324	-1.059031
H	1.138450	2.486769	-1.022846
H	1.201486	2.261593	1.464365
H	0.164075	3.749111	1.654202
H	-0.826245	-1.589910	-1.095891
H	-3.199284	1.201518	1.192682
H	-5.111539	-0.276336	1.037638
H	-2.800458	-3.061536	-1.307178

C	4.629391	-0.402404	-0.834256
H	4.788466	0.560220	-0.339474
H	5.562631	-0.975139	-0.812490
H	4.348862	-0.213684	-1.874661
C	3.947194	-1.686505	1.692871
H	4.902433	-2.217701	1.623810
H	4.095894	-0.752131	2.241974
H	3.233085	-2.301846	2.247866
C	3.221572	-2.954741	-0.831183
H	4.204692	-3.437164	-0.817030
H	2.497490	-3.604120	-0.330287
H	2.904915	-2.819522	-1.869585
O	-5.083949	-2.642042	-0.329006
C	-6.370325	-2.373933	0.244040
H	-6.797323	-1.454460	-0.170105
H	-6.992362	-3.225066	-0.030921
H	-6.303735	-2.301863	1.334866

$TS_{21\text{-}23b}$ Energy = -1214.66558477 a.u.

C	-1.862193	4.453382	-0.183578
C	-1.890375	3.094053	-0.926491
C	-0.710722	2.323116	-0.385334
C	-0.615708	0.993731	0.090139
C	-0.394466	4.646410	0.271335
C	0.156647	3.230770	0.401286
C	-0.530154	2.215023	1.370384
P	3.197726	-1.362939	-0.121521
Au	1.224850	-0.059499	0.039918
C	-2.469082	-0.100147	-1.243779
C	-1.785522	0.073829	-0.024015
C	-2.192315	-0.699541	1.072328
C	-3.267464	-1.584051	0.983181
C	-3.943118	-1.738750	-0.236462

C	-3.524635	-0.993749	-1.352551
H	-2.212878	5.273471	-0.814266
H	-2.530866	4.411194	0.682425
H	-1.680297	3.228711	-1.998746
H	-2.835733	2.552110	-0.850021
H	0.187993	5.174746	-0.492393
H	-0.310436	5.221755	1.197968
H	1.234490	3.090458	0.386148
H	0.137137	1.770578	2.098879
H	-1.497176	2.496604	1.780885
H	-2.154069	0.450759	-2.126512
H	-1.669218	-0.605251	2.020973
H	-3.563467	-2.148098	1.859851
H	-4.046502	-1.134491	-2.293526
C	3.784585	-2.028994	1.489152
H	3.003124	-2.648294	1.938959
H	4.686563	-2.634455	1.349446
H	4.008225	-1.204426	2.172261
C	3.000182	-2.839215	-1.200119
H	3.931960	-3.413388	-1.241244
H	2.201708	-3.476870	-0.809727
H	2.726884	-2.525112	-2.211673
C	4.640314	-0.457244	-0.814267
H	5.514688	-1.114080	-0.873006
H	4.400214	-0.089765	-1.816230
H	4.878426	0.400720	-0.178825
O	-4.989201	-2.572091	-0.443735
C	-5.465437	-3.361606	0.641934
H	-5.821702	-2.732162	1.466812
H	-6.298400	-3.941085	0.242730
H	-4.689320	-4.044526	1.009176

23b Energy = -1214.70634587 a.u.

C	0.553255	3.822077	1.212177
C	-0.001048	2.421202	1.592723
C	-0.056696	1.755315	0.217202
C	1.066382	1.256946	-0.520119
C	-0.089869	4.173509	-0.155226
C	-0.338473	2.827724	-0.878480
C	0.822466	2.182879	-1.699479
P	-2.968512	-1.716975	-0.067407
Au	-1.372343	0.028633	0.015130
C	3.198688	0.234349	-1.189888
C	2.158979	0.382132	-0.242481
C	2.262918	-0.339008	0.978971
C	3.350071	-1.141788	1.237257
C	4.387837	-1.263474	0.281514
C	4.300821	-0.567850	-0.940738
H	0.341615	4.575436	1.977192
H	1.644369	3.753985	1.116383
H	-1.003263	2.508360	2.026376
H	0.632297	1.897888	2.314533
H	-1.054312	4.667603	0.007285
H	0.526587	4.865722	-0.738775
H	-1.308561	2.802081	-1.379460
H	0.565164	1.719424	-2.657896
H	1.672804	2.857362	-1.865895
H	3.141564	0.772671	-2.131413
H	1.464769	-0.267333	1.711363
H	3.440987	-1.697530	2.164526
H	5.084210	-0.650273	-1.684268
C	-3.793814	-2.018610	1.547106
H	-4.305521	-1.109937	1.877374
H	-4.524245	-2.829899	1.458337
H	-3.047777	-2.288246	2.300248

C	-4.334896	-1.396771	-1.253912
H	-5.047439	-2.228666	-1.252645
H	-4.856983	-0.476718	-0.975648
H	-3.929209	-1.272874	-2.262129
C	-2.268904	-3.343629	-0.562086
H	-3.052467	-4.108917	-0.577310
H	-1.822332	-3.266573	-1.557548
H	-1.489496	-3.641254	0.145255
O	5.400198	-2.065776	0.632324
C	6.500968	-2.254543	-0.264492
H	7.010048	-1.305192	-0.462931
H	7.179783	-2.934892	0.248828
H	6.166516	-2.706175	-1.204824

$TS_{23\text{-}24b}$ Energy = -1214.65413114 a.u.

C	-1.012625	3.941647	1.196222
C	-0.491614	2.522483	1.573362
C	-0.220615	1.866922	0.196624
C	1.106381	1.780540	-0.434745
C	-1.668302	3.797010	-0.199492
C	-0.952570	2.624314	-0.818069
C	1.113369	2.811014	-1.396056
P	-2.439447	-2.115807	-0.130954
Au	-1.278610	-0.067336	-0.001151
C	3.414994	0.964632	-0.864662
C	2.170087	0.811956	-0.219397
C	2.044310	-0.259131	0.696651
C	3.091350	-1.124596	0.946446
C	4.319163	-0.967038	0.271255
C	4.471895	0.090813	-0.641145
H	-1.706135	4.334948	1.944352
H	-0.172834	4.643156	1.136182
H	-1.253563	1.984066	2.145189

H 0.409763 2.562232 2.191636
H -2.739033 3.547451 -0.129676
H -1.612987 4.702378 -0.813932
H -1.235114 2.215551 -1.781287
H 1.722586 2.800633 -2.300965
H 0.828616 3.809415 -1.071987
H 3.573955 1.801588 -1.537168
H 1.104797 -0.408949 1.222294
H 2.995112 -1.941448 1.654289
H 5.410664 0.248374 -1.158511
C -2.746736 -2.885921 1.508837
H -3.348336 -2.213313 2.126967
H -3.276236 -3.837545 1.392328
H -1.794919 -3.065019 2.017195
C -4.093269 -1.975982 -0.920020
H -4.580603 -2.955825 -0.965834
H -4.720968 -1.289487 -0.344564
H -3.986516 -1.580686 -1.934278
C -1.542314 -3.389497 -1.105596
H -2.110801 -4.325433 -1.128647
H -1.392993 -3.034276 -2.129296
H -0.561753 -3.574390 -0.657610
O 5.271254 -1.869833 0.572125
C 6.541636 -1.785836 -0.075941
H 7.041839 -0.838989 0.157873
H 7.127835 -2.615159 0.319953
H 6.438650 -1.893963 -1.161890

24b Energy = -1214.71751937 a.u.

C -0.893469 2.754661 1.996540
C 0.479206 2.388242 1.392613
C 0.183383 2.030328 -0.054313
C 1.238630 1.603744 -1.007090

C	-1.744860	3.187426	0.780959
C	-1.116903	2.415705	-0.367609
C	1.215566	2.098253	-2.263809
P	-2.461384	-1.998980	-0.052170
Au	-1.551234	0.169634	-0.112024
C	3.661161	0.943022	-0.960708
C	2.343579	0.731586	-0.526777
C	2.117741	-0.345357	0.354067
C	3.147977	-1.179108	0.760378
C	4.459360	-0.959284	0.303106
C	4.710033	0.116127	-0.561300
H	-1.340125	1.866989	2.463530
H	-0.823460	3.528087	2.765023
H	1.022592	1.614570	1.939409
H	1.146731	3.263758	1.356428
H	-2.815843	3.004564	0.906736
H	-1.627317	4.262409	0.577239
H	-1.470723	2.510929	-1.393892
H	1.971374	1.819572	-2.990924
H	0.467797	2.813024	-2.591441
H	3.881331	1.787282	-1.607637
H	1.112266	-0.544278	0.719697
H	2.970937	-2.010655	1.435133
H	5.712870	0.325431	-0.914426
C	-2.382285	-2.770284	1.612186
H	-2.940513	-2.162546	2.330003
H	-2.810952	-3.777829	1.584009
H	-1.341824	-2.832981	1.943311
C	-4.231814	-2.039234	-0.536848
H	-4.612694	-3.065217	-0.493207
H	-4.816609	-1.409649	0.139880
H	-4.347042	-1.656732	-1.555081
C	-1.605133	-3.162081	-1.185825

H	-2.054199	-4.158704	-1.115940
H	-1.686385	-2.802394	-2.215603
H	-0.545354	-3.224539	-0.922871
O	5.393604	-1.824658	0.758709
C	6.746713	-1.658461	0.341368
H	7.146751	-0.690057	0.665351
H	7.304946	-2.461270	0.823879
H	6.841550	-1.750614	-0.747425

$TS_{18\text{-}19b}$ Energy = -1214.65153953 a.u.

C	0.326560	4.656218	0.164496
C	-0.385261	3.296888	0.354104
C	0.522457	2.116732	0.228460
C	0.636127	0.843541	0.072637
C	1.453584	4.509391	-0.867183
C	2.312176	3.325168	-0.509708
C	2.618516	2.973496	0.767989
P	-3.306296	-1.304997	-0.003949
Au	-1.288016	-0.081887	0.040357
C	2.049961	-0.713658	-1.283338
C	1.755473	-0.103585	-0.047007
C	2.527844	-0.451945	1.070784
C	3.585586	-1.356944	0.964433
C	3.885507	-1.936687	-0.276936
C	3.105743	-1.603918	-1.399924
H	-0.398886	5.411105	-0.151518
H	0.732015	4.998873	1.121820
H	-1.154159	3.181083	-0.419938
H	-0.895844	3.266091	1.323436
H	1.043014	4.369905	-1.873516
H	2.064080	5.421644	-0.903530
H	2.725911	2.727554	-1.319510
H	3.256218	2.120990	0.970685

H	2.310367	3.565900	1.624367
H	1.451066	-0.473531	-2.157398
H	2.292608	-0.022331	2.040518
H	4.160814	-1.603708	1.849048
H	3.349171	-2.064017	-2.352096
C	-3.989601	-1.646329	1.667886
H	-4.190589	-0.703591	2.184800
H	-4.918823	-2.221385	1.593759
H	-3.261371	-2.213703	2.254564
C	-4.666413	-0.476020	-0.921422
H	-5.569964	-1.094999	-0.909233
H	-4.887792	0.491093	-0.460831
H	-4.361908	-0.304871	-1.957954
C	-3.123397	-2.952636	-0.797100
H	-4.077182	-3.490979	-0.791426
H	-2.786192	-2.829279	-1.830279
H	-2.374906	-3.540098	-0.257597
O	4.885265	-2.820895	-0.498074
C	5.711183	-3.213157	0.594660
H	5.124988	-3.706429	1.379771
H	6.431755	-3.919610	0.181645
H	6.244933	-2.353880	1.019086

19b Energy = -1214.69080797 a.u.

C	0.881450	4.241880	-0.312767
C	0.561180	2.923583	-1.055827
C	-0.608600	2.261225	-0.313184
C	-0.659927	0.827339	-0.132591
C	0.504529	3.966654	1.154625
C	-0.684168	3.027074	1.096317
C	-1.739787	3.218369	0.068263
P	3.135113	-1.535390	-0.016030
Au	1.114102	-0.248206	-0.066363

C	-1.965171	-1.101980	0.743689
C	-1.896719	0.115839	0.001028
C	-3.079465	0.516567	-0.682836
C	-4.244375	-0.228039	-0.631156
C	-4.292810	-1.393130	0.163410
C	-3.134306	-1.816969	0.856250
H	1.929950	4.531135	-0.426242
H	0.284728	5.067666	-0.714014
H	1.426198	2.250521	-1.026746
H	0.316195	3.085376	-2.111999
H	1.327369	3.476090	1.688553
H	0.257481	4.881491	1.708033
H	-0.945691	2.449961	1.979047
H	-2.714291	2.811099	0.305393
H	-1.780576	4.157100	-0.478889
H	-1.075867	-1.448139	1.261922
H	-3.051213	1.391360	-1.321883
H	-5.107116	0.087341	-1.205650
H	-3.194043	-2.722991	1.449815
C	4.450953	-0.896041	-1.131869
H	4.715795	0.125399	-0.843277
H	5.344864	-1.526572	-1.078809
H	4.084566	-0.879159	-2.162495
C	3.928908	-1.625621	1.641846
H	4.839450	-2.232836	1.601643
H	4.184222	-0.618819	1.985109
H	3.234082	-2.068578	2.361355
C	2.901479	-3.288915	-0.521255
H	3.851186	-3.833383	-0.487606
H	2.186657	-3.774175	0.149822
H	2.500648	-3.328943	-1.538355
O	-5.368242	-2.171376	0.309040
C	-6.589776	-1.838829	-0.363746

H	-6.451330	-1.849377	-1.450132
H	-7.298378	-2.614693	-0.075979
H	-6.960044	-0.860746	-0.039015

$TS_{19\text{-}20b}$ Energy = -1214.65934715 a.u.

C	-0.034269	4.632574	-0.369891
C	-0.370729	3.208862	-0.877949
C	0.723765	2.319921	-0.316695
C	0.593710	0.964614	0.246242
C	1.478440	4.593009	-0.035381
C	1.770948	3.131703	0.170502
C	0.707491	2.085871	1.335484
P	-3.163090	-1.449739	-0.130582
Au	-1.206172	-0.108408	0.062669
C	2.186539	-0.666357	1.362811
C	1.813457	0.075566	0.226685
C	2.566073	-0.092490	-0.941416
C	3.663605	-0.955661	-0.986929
C	4.028495	-1.678526	0.157051
C	3.276047	-1.524357	1.334867
H	-0.278658	5.406272	-1.100720
H	-0.610115	4.852373	0.535244
H	-0.287180	3.134877	-1.971229
H	-1.371020	2.859181	-0.609939
H	2.095444	4.932844	-0.880347
H	1.760883	5.211274	0.822318
H	2.762637	2.753063	0.392946
H	1.537579	1.918767	2.013785
H	-0.163370	2.572888	1.761292
H	1.608501	-0.576785	2.280441
H	2.293643	0.454013	-1.841646
H	4.221426	-1.054885	-1.910837
H	3.566849	-2.093201	2.212145

C	-4.293448	-1.338959	1.317011
H	-4.627444	-0.305387	1.447120
H	-5.167885	-1.983487	1.177168
H	-3.763122	-1.646042	2.223190
C	-4.221120	-1.042112	-1.579994
H	-5.095640	-1.700289	-1.619151
H	-4.558125	-0.003561	-1.512130
H	-3.644204	-1.158134	-2.502208
C	-2.803611	-3.245719	-0.306325
H	-2.239174	-3.595421	0.563030
H	-3.731900	-3.821238	-0.387698
H	-2.196422	-3.414969	-1.200423
O	5.072177	-2.539197	0.233459
C	5.875050	-2.746999	-0.923653
H	6.639299	-3.466746	-0.628575
H	5.284565	-3.161029	-1.750559
H	6.357278	-1.816141	-1.247562

20b Energy = 1214.69875506 a.u.

C	-0.145718	5.057468	0.491853
C	0.185484	4.142161	-0.713681
C	-0.482937	2.829296	-0.347411
C	-0.673664	0.378832	-0.728520
C	-0.500325	4.093470	1.655677
C	-0.844394	2.806450	0.945560
C	-0.647234	1.729675	-1.383864
P	3.348575	-1.247440	0.279394
Au	1.165745	-0.408541	-0.246430
C	-3.169712	0.386949	-0.654086
C	-1.903067	-0.244191	-0.428908
C	-1.935586	-1.560410	0.143643
C	-3.113389	-2.193658	0.443429
C	-4.347489	-1.536102	0.205460

C	-4.360885	-0.229047	-0.341276
H	0.672626	5.738487	0.740611
H	-1.019086	5.672566	0.250687
H	1.269449	3.993758	-0.835170
H	-0.178207	4.547152	-1.666873
H	0.351885	3.937799	2.334124
H	-1.321817	4.468011	2.277938
H	-1.305890	1.964771	1.453682
H	-1.527537	1.932021	-2.009900
H	0.216199	1.774466	-2.059286
H	-3.202551	1.392025	-1.058070
H	-0.991511	-2.063351	0.329525
H	-3.138438	-3.192599	0.865218
H	-5.297729	0.286284	-0.515189
C	3.412516	-3.063090	0.570200
H	4.433718	-3.380454	0.806318
H	2.753910	-3.328646	1.402363
H	3.071323	-3.592704	-0.324221
C	4.070258	-0.501407	1.798636
H	5.068022	-0.908268	1.994645
H	4.142186	0.583373	1.677221
H	3.422847	-0.709443	2.655529
C	4.599066	-0.941793	-1.035153
H	5.575954	-1.338684	-0.738882
H	4.283247	-1.423795	-1.965069
H	4.688674	0.133172	-1.217012
O	-5.433869	-2.226073	0.531041
C	-6.742915	-1.663698	0.335484
H	-7.436954	-2.429874	0.678014
H	-6.865633	-0.755786	0.934077
H	-6.916277	-1.450776	-0.723828

$TS_{18\text{-}22b}$ Energy= -1214.65581644 a.u.

C	0.092209	3.959380	-1.091599
C	-0.598266	3.191597	0.053928
C	-0.057529	1.783470	0.192920
C	1.182391	1.410898	0.383817
C	2.404904	3.345342	-0.166859
C	1.518882	4.424881	-0.721705
H	-0.466541	3.734397	1.002507
H	-1.674334	3.157316	-0.127676
H	0.114443	3.329360	-1.988632
H	-0.494663	4.850922	-1.339116
H	1.428865	5.218402	0.031485
H	1.995371	4.864968	-1.604379
Au	-1.392022	0.163787	0.072669
P	-2.993725	-1.578471	-0.062654
C	-4.352987	-1.233629	-1.251936
H	-3.937938	-1.078530	-2.252002
H	-5.062655	-2.067351	-1.281656
H	-4.880871	-0.323368	-0.953000
C	-2.294898	-3.194316	-0.595778
H	-1.518488	-3.509234	0.107426
H	-3.077050	-3.960031	-0.635725
H	-1.842486	-3.090623	-1.586277
C	-3.838325	-1.931565	1.532561
H	-4.355177	-1.033420	1.883031
H	-4.565460	-2.741927	1.413727
H	-3.099160	-2.219281	2.285833
C	2.393644	2.961939	1.146549
H	3.166507	2.319693	1.550772
H	1.774418	3.484025	1.871393
C	2.071925	0.272424	0.316108
C	2.578567	-0.337126	1.487846
C	2.447256	-0.262694	-0.930553
C	3.406673	-1.440378	1.411289

H	2.300580	0.059601	2.460215
C	3.286139	-1.369005	-1.019975
H	2.068612	0.194868	-1.839868
C	3.775212	-1.966387	0.155106
H	3.792058	-1.921383	2.304152
H	3.553856	-1.757575	-1.995312
H	3.111675	2.864030	-0.840330
O	4.593413	-3.034079	0.191007
C	5.036653	-3.618288	-1.034644
H	5.686434	-4.444687	-0.746839
H	4.191372	-4.002260	-1.617791
H	5.604214	-2.896650	-1.633462

22b Energy= -1214.68023376 a.u.

C	-0.028413	3.957214	-1.137246
C	-0.648176	3.297169	0.127761
C	-0.049644	1.931430	0.249564
C	1.347998	1.801663	0.397600
C	2.201679	3.079496	-0.204230
C	1.471046	4.204730	-0.928401
H	-0.417324	3.923979	1.002857
H	-1.734894	3.247396	0.041420
H	-0.189148	3.299516	-2.000216
H	-0.551001	4.895610	-1.347867
H	1.604581	5.124089	-0.343693
H	1.954946	4.368850	-1.896295
Au	-1.236142	0.268901	0.073294
P	-2.643414	-1.665047	-0.063345
C	-4.129547	-1.457020	-1.127049
H	-3.823838	-1.210115	-2.147929
H	-4.723708	-2.376852	-1.142907
H	-4.745999	-0.638652	-0.743677
C	-1.779280	-3.144030	-0.733322

H	-0.901229	-3.363982	-0.119132
H	-2.445099	-4.013486	-0.738745
H	-1.443425	-2.942781	-1.754836
C	-3.302118	-2.198394	1.569143
H	-3.893322	-1.390937	2.010887
H	-3.933471	-3.086403	1.457880
H	-2.473431	-2.428955	2.244935
C	2.124668	2.907853	1.231138
H	2.967757	2.478541	1.763835
H	1.505865	3.581784	1.816067
C	2.015458	0.456297	0.316835
C	2.331468	-0.262724	1.482683
C	2.322903	-0.119817	-0.920493
C	2.930238	-1.512586	1.411299
H	2.104569	0.160914	2.458109
C	2.932359	-1.373620	-1.009821
H	2.091314	0.417295	-1.837369
C	3.241614	-2.079231	0.162080
H	3.179552	-2.069956	2.308430
H	3.166115	-1.782427	-1.985875
H	3.089569	2.681423	-0.687851
O	3.834728	-3.295600	0.200418
C	4.224754	-3.909397	-1.024433
H	4.692022	-4.854461	-0.746099
H	3.357096	-4.107133	-1.666527
H	4.949097	-3.290129	-1.567436

$TS_{22\text{-}23b}$ Energy= -1214.66430684 a.u.

C	1.657790	3.547543	0.080330
C	0.928193	2.819930	-1.053589
C	0.115487	1.684187	-0.412317
C	-1.300105	1.772809	-0.339533
C	-0.594291	2.843163	1.000766

C	0.586864	3.812317	1.159384
H	0.294164	3.519782	-1.611884
H	1.630767	2.391882	-1.774682
H	2.439407	2.897805	0.490816
H	2.140833	4.467846	-0.261905
H	0.188454	4.830405	1.073468
H	0.995786	3.705907	2.168403
Au	1.281848	-0.025847	-0.140429
P	2.746137	-1.901328	0.072201
C	4.381513	-1.488537	0.808386
H	4.243032	-1.083746	1.815218
H	5.017136	-2.378720	0.863952
H	4.879989	-0.730259	0.197430
C	2.099726	-3.271394	1.117720
H	1.158889	-3.642234	0.700324
H	2.819658	-4.095454	1.163160
H	1.909875	-2.906778	2.131590
C	3.147298	-2.696062	-1.538298
H	3.618536	-1.965724	-2.202597
H	3.827991	-3.541916	-1.394232
H	2.228906	-3.051469	-2.014754
C	-1.711083	3.172441	0.023179
H	-2.713974	3.280796	0.427659
H	-1.458394	3.979367	-0.662065
C	-2.267504	0.697328	-0.097830
C	-3.597705	0.923867	-0.507906
C	-1.962888	-0.566259	0.456534
C	-4.573085	-0.061963	-0.420019
H	-3.870889	1.879917	-0.944815
C	-2.930313	-1.543760	0.583960
H	-0.963076	-0.767871	0.826148
C	-4.246832	-1.310689	0.134967
H	-5.575106	0.147592	-0.774183

H	-2.705076	-2.504763	1.034645
H	-0.905976	2.302026	1.889923
O	-5.105448	-2.332610	0.290774
C	-6.463865	-2.175175	-0.126328
H	-6.524890	-1.979129	-1.202894
H	-6.950955	-3.123322	0.100736
H	-6.954725	-1.367707	0.428789

18c Energy = -1304.63547998 a.u.

C	-0.359353	4.152859	-0.811543
C	0.707392	3.060933	-0.555107
C	0.112807	1.716013	-0.375282
C	-0.728124	0.810077	-0.299719
C	-1.297065	4.409316	0.381224
C	-2.309607	5.484580	0.083880
C	-2.397306	6.646090	0.732367
P	3.345478	-1.520763	0.215742
Au	1.539572	-0.063459	-0.057186
C	-2.413038	-0.379779	1.040834
C	-1.769805	-0.168877	-0.196416
C	-2.172267	-0.895254	-1.336062
C	-3.203015	-1.822870	-1.240090
C	-3.818395	-2.012170	-0.004237
C	-3.445511	-1.305684	1.137482
H	0.181383	5.075317	-1.053313
H	-0.940715	3.884905	-1.702303
H	1.296755	3.312439	0.335519
H	1.410856	3.024695	-1.395318
H	-1.819589	3.474969	0.637221
H	-0.703659	4.692616	1.260667
H	-3.002440	5.273715	-0.732030
H	-3.145814	7.389305	0.473369
H	-1.727570	6.896881	1.552686

H	-2.104270	0.186999	1.912941
H	-1.680051	-0.722309	-2.287432
H	-3.537322	-2.394725	-2.096977
H	-3.961923	-1.487857	2.071961
C	4.853474	-0.935663	-0.649669
H	5.153181	0.039392	-0.255272
H	5.670937	-1.649663	-0.503093
H	4.652537	-0.833489	-1.719841
C	3.822208	-1.754264	1.971628
H	4.668707	-2.445645	2.042805
H	4.104548	-0.793382	2.411090
H	2.977360	-2.160614	2.534814
C	2.992879	-3.195475	-0.446431
H	3.863569	-3.845676	-0.309110
H	2.134961	-3.628081	0.075952
H	2.757044	-3.130085	-1.512334
N	-4.910907	-3.007480	0.100294
O	-5.208580	-3.618307	-0.921276
O	-5.432935	-3.149394	1.201319

$TS_{18\text{-}21c}$ Energy = -1304.60113405 a.u.

C	-0.012421	4.893415	-0.047233
C	0.769300	3.656659	0.423831
C	0.236645	2.327196	0.080708
C	0.341937	1.051128	0.022078
C	-1.427876	4.871307	0.558408
C	-2.098362	3.553553	0.293131
C	-1.992209	2.893835	-0.881111
P	-2.776516	-2.150160	-0.042215
Au	-1.192951	-0.401159	-0.019461
C	2.593383	0.682275	-1.056100
C	1.717870	0.435916	0.012852
C	2.125764	-0.388532	1.074663

C	3.398872	-0.950595	1.074430
C	4.248674	-0.693387	0.000519
C	3.864852	0.112957	-1.067071
H	0.523973	5.790216	0.275798
H	-0.049964	4.921304	-1.140703
H	0.901511	3.704972	1.513472
H	1.776204	3.660941	-0.023745
H	-1.378502	5.053289	1.637707
H	-2.022963	5.691161	0.133155
H	-2.666677	3.096498	1.101382
H	-2.471500	1.931772	-1.029940
H	-1.508575	3.322957	-1.754128
H	2.274021	1.304552	-1.886280
H	1.449845	-0.582257	1.901725
H	3.739241	-1.583728	1.884819
H	4.556223	0.285187	-1.883065
C	-2.382783	-3.445312	-1.283810
H	-1.398319	-3.872516	-1.072242
H	-3.134649	-4.241275	-1.256461
H	-2.361111	-3.004752	-2.284674
C	-2.887133	-3.029788	1.566740
H	-3.618767	-3.842769	1.508600
H	-1.909257	-3.444635	1.827424
H	-3.187986	-2.330820	2.352410
C	-4.491444	-1.611939	-0.423975
H	-5.170969	-2.470870	-0.415703
H	-4.826396	-0.883687	0.320278
H	-4.521778	-1.142316	-1.411426
N	5.594025	-1.298937	-0.007424
O	5.893281	-2.016196	0.943897
O	6.320304	-1.043662	-0.964418

21c Energy = -1304.64576593 a.u.

C	1.331187	4.653146	-0.130074
C	1.642768	3.261563	-0.738315
C	0.410281	2.384300	-0.491204
C	0.381204	0.995946	-0.283966
C	0.317053	4.406331	1.005451
C	-0.566462	3.260643	0.560084
C	-0.936619	3.111242	-0.832225
P	-3.237415	-1.581341	0.193820
Au	-1.332730	-0.153967	-0.066230
C	1.830594	-0.890875	-1.023547
C	1.631859	0.226217	-0.184792
C	2.612375	0.535485	0.782617
C	3.756080	-0.245796	0.907386
C	3.939135	-1.312391	0.030696
C	2.998067	-1.641705	-0.941892
H	2.234234	5.148424	0.235616
H	0.898080	5.315645	-0.886141
H	2.524914	2.823373	-0.270698
H	1.852219	3.326690	-1.812185
H	0.817996	4.133944	1.941297
H	-0.297118	5.291697	1.216288
H	-1.092266	2.672366	1.304832
H	-1.763642	2.453792	-1.079834
H	-0.793167	3.943938	-1.516095
H	1.076022	-1.151072	-1.759599
H	2.458512	1.362713	1.467932
H	4.506749	-0.037456	1.660134
H	3.180320	-2.483657	-1.598544
C	-4.727970	-0.733759	0.858164
H	-5.023053	0.077830	0.186695
H	-5.560022	-1.439458	0.953271
H	-4.506248	-0.308455	1.841332
C	-3.785181	-2.348222	-1.385027

H	-4.647782	-3.001386	-1.215746
H	-4.061019	-1.568396	-2.100828
H	-2.968631	-2.937026	-1.812998
C	-2.934814	-2.989559	1.336007
H	-3.828137	-3.617762	1.418144
H	-2.103451	-3.595290	0.963859
H	-2.669844	-2.611701	2.327793
N	5.164665	-2.130118	0.145606
O	5.973818	-1.807943	1.010662
O	5.283958	-3.072040	-0.632545

$TS_{21\text{-}23c}$ Energy = -1304.63239554 a.u.

C	1.341572	4.650094	0.251198
C	1.542777	3.254281	0.890149
C	0.385937	2.415862	0.390284
C	0.359760	1.086597	-0.083680
C	-0.169160	4.739847	-0.076342
C	-0.606937	3.292442	-0.268010
C	0.119153	2.406500	-1.324026
P	-3.216860	-1.611307	0.124000
Au	-1.369841	-0.130994	-0.039271
C	2.125857	-0.276029	-1.252761
C	1.620710	0.286747	-0.067865
C	2.281945	0.030292	1.146740
C	3.428236	-0.759321	1.178872
C	3.913557	-1.285165	-0.015517
C	3.279934	-1.053685	-1.234022
H	1.670807	5.454757	0.912307
H	1.939045	4.727826	-0.662927
H	1.409256	3.300195	1.981431
H	2.522034	2.806786	0.705921
H	-0.731753	5.159043	0.765775
H	-0.378259	5.364991	-0.949133

H	-1.665299	3.050578	-0.210522
H	-0.548785	1.889712	-2.000492
H	1.027754	2.782264	-1.786987
H	1.614381	-0.105263	-2.195712
H	1.890001	0.435560	2.075562
H	3.949061	-0.968207	2.105479
H	3.689483	-1.485328	-2.139223
C	-4.825853	-0.868694	-0.364875
H	-4.778797	-0.530913	-1.404184
H	-5.632263	-1.602708	-0.263285
H	-5.044899	-0.006347	0.271513
C	-3.041051	-3.112909	-0.921822
H	-3.910785	-3.767313	-0.800427
H	-2.952350	-2.825289	-1.973433
H	-2.137846	-3.659200	-0.634980
C	-3.476970	-2.241350	1.830992
H	-4.332145	-2.924829	1.861515
H	-2.582290	-2.771698	2.169932
H	-3.662109	-1.404984	2.511304
N	5.131332	-2.118156	0.011418
O	5.661181	-2.303708	1.103813
O	5.528817	-2.567221	-1.060416

23c Energy = -1304.66399997 a.u.

C	-0.112026	4.043141	1.268786
C	-0.437314	2.573833	1.685422
C	-0.447277	1.938815	0.316020
C	0.572099	1.448111	-0.524377
C	-0.827548	4.288602	-0.092863
C	-0.981424	2.898852	-0.763673
C	0.141446	2.329598	-1.695166
P	-2.730841	-2.023006	-0.029170
Au	-1.384728	-0.084988	-0.011321

C	2.727495	0.588180	-1.375093
C	1.793961	0.676178	-0.324099
C	2.079608	0.039037	0.903149
C	3.267552	-0.656831	1.079151
C	4.170247	-0.718157	0.016576
C	3.921837	-0.106473	-1.208935
H	-0.420372	4.760102	2.035039
H	0.973782	4.136989	1.152248
H	-1.424225	2.514596	2.157906
H	0.300122	2.157730	2.376391
H	-1.823621	4.709129	0.078657
H	-0.283189	5.005451	-0.715606
H	-1.994553	2.730116	-1.136485
H	-0.157350	1.848148	-2.631100
H	0.917122	3.073622	-1.917551
H	2.520752	1.074061	-2.323477
H	1.361175	0.081752	1.715981
H	3.509088	-1.151057	2.012168
H	4.654282	-0.182081	-2.003257
C	-3.663772	-2.244840	1.536170
H	-4.313057	-1.381524	1.707742
H	-4.276832	-3.151003	1.484935
H	-2.967700	-2.329665	2.375608
C	-3.990169	-2.004993	-1.364717
H	-4.591762	-2.919534	-1.328415
H	-4.646461	-1.138345	-1.244324
H	-3.498656	-1.937411	-2.339474
C	-1.770262	-3.570186	-0.264389
H	-2.442479	-4.435047	-0.266111
H	-1.231325	-3.532325	-1.215321
H	-1.043002	-3.682409	0.544697
N	5.432554	-1.468288	0.198211
O	5.607318	-2.012954	1.284545

O	6.210157	-1.493463	-0.750493

$TS_{23\text{-}24c}$ Energy = -1304.61608647 a.u.

C	-1.529957	3.849224	1.354630
C	-0.858142	2.474835	1.656529
C	-0.572918	1.927254	0.244887
C	0.691549	1.946064	-0.475780
C	-2.233742	3.691945	-0.017491
C	-1.448470	2.605895	-0.709568
C	0.498568	2.927385	-1.472679
P	-2.270958	-2.322327	-0.151365
Au	-1.367928	-0.156013	-0.014950
C	3.033335	1.352437	-1.083730
C	1.885891	1.113004	-0.300478
C	1.948063	0.114248	0.693348
C	3.104591	-0.627567	0.894681
C	4.206767	-0.382097	0.076795
C	4.189733	0.599320	-0.910687
H	-2.222547	4.145859	2.146508
H	-0.762526	4.628650	1.287937
H	-1.547601	1.834064	2.215429
H	0.051652	2.577821	2.254328
H	-3.275165	3.349808	0.087313
H	-2.282872	4.619747	-0.598135
H	-1.778455	2.160599	-1.642012
H	0.977168	2.915357	-2.453451
H	0.192667	3.919218	-1.145853
H	3.031964	2.147441	-1.821876
H	1.080598	-0.083108	1.317115
H	3.168494	-1.391793	1.659538
H	5.074068	0.767483	-1.513053
C	-2.588887	-3.076895	1.492430
H	-3.286541	-2.453669	2.059108

H	-3.016759	-4.078001	1.372889
H	-1.653810	-3.152019	2.054830
C	-3.879156	-2.367367	-1.036978
H	-4.259585	-3.393512	-1.082326
H	-4.606802	-1.737331	-0.517480
H	-3.752311	-1.986953	-2.054588
C	-1.184042	-3.506153	-1.039631
H	-1.656383	-4.493430	-1.083789
H	-1.000679	-3.149925	-2.057341
H	-0.223966	-3.590555	-0.522610
N	5.429999	-1.187734	0.267187
O	5.394961	-2.064498	1.127194
O	6.391412	-0.926867	-0.449559

24c Energy = -1304.68333109 a.u.

C	1.093154	-2.659825	2.112616
C	-0.276835	-2.405866	1.448049
C	0.051396	-2.090841	-0.003243
C	-0.993197	-1.777012	-1.011316
C	2.009709	-3.096550	0.947378
C	1.378875	-2.417993	-0.256236
C	-0.900532	-2.300689	-2.250622
P	2.534919	2.060518	-0.124766
Au	1.681337	-0.132924	-0.077041
C	-3.461669	-1.304997	-1.061728
C	-2.175758	-0.961288	-0.607257
C	-2.037783	0.170336	0.216788
C	-3.137106	0.949959	0.561534
C	-4.391278	0.585185	0.079560
C	-4.572003	-0.534889	-0.726781
H	1.470026	-1.725589	2.549644
H	1.041397	-3.398952	2.915270
H	-0.882840	-1.644612	1.944509

H	-0.887911	-3.322233	1.430139
H	3.063643	-2.845674	1.097410
H	1.961829	-4.184611	0.789912
H	1.779681	-2.530962	-1.263120
H	-1.652583	-2.098328	-3.006456
H	-0.086653	-2.956544	-2.541906
H	-3.598435	-2.196692	-1.665069
H	-1.055653	0.455982	0.585060
H	-3.044082	1.827005	1.190325
H	-5.566805	-0.793440	-1.068718
C	2.945467	2.721071	1.538033
H	3.684161	2.076230	2.022569
H	3.354669	3.733253	1.450229
H	2.046738	2.750892	2.160679
C	4.081634	2.168846	-1.107180
H	4.449314	3.200486	-1.119215
H	4.846559	1.520165	-0.670810
H	3.892817	1.843810	-2.134356
C	1.376760	3.269905	-0.877311
H	1.834325	4.264919	-0.897707
H	1.132502	2.965434	-1.898976
H	0.451637	3.313365	-0.295702
N	-5.561588	1.408846	0.442043
O	-5.358014	2.392326	1.150628
O	-6.654192	1.055834	0.008876

$TS_{18\text{-}19c}$ Energy = -1304.61820223 a.u.

C	0.204959	4.741307	-0.229921
C	0.815605	3.325641	-0.135492
C	-0.168009	2.206880	-0.194608
C	-0.405322	0.948435	-0.113434
C	-1.062138	4.834454	0.632357
C	-1.997484	3.706251	0.298977

C	-2.123844	3.185860	-0.948929
P	3.334418	-1.543864	0.098163
Au	1.432863	-0.153327	-0.014179
C	-2.389767	0.060004	1.103736
C	-1.615610	0.113075	-0.069485
C	-1.998859	-0.648503	-1.188429
C	-3.150676	-1.428458	-1.147577
C	-3.902704	-1.454959	0.025024
C	-3.539036	-0.724490	1.153552
H	0.950428	5.471816	0.096692
H	-0.024138	4.977582	-1.273788
H	1.352865	3.231791	0.817010
H	1.548592	3.185116	-0.938709
H	-0.809676	4.798636	1.698393
H	-1.562468	5.798915	0.467724
H	-2.584964	3.270119	1.104717
H	-2.802916	2.363390	-1.144992
H	-1.650108	3.633984	-1.817236
H	-2.083243	0.626174	1.977648
H	-1.397758	-0.619716	-2.091999
H	-3.471468	-2.013562	-2.000888
H	-4.151409	-0.779582	2.045461
C	4.790749	-0.875654	-0.800570
H	5.079636	0.088427	-0.372214
H	5.635625	-1.568803	-0.727286
H	4.538746	-0.726616	-1.854399
C	3.913468	-1.850648	1.814225
H	4.786642	-2.511804	1.809688
H	4.182538	-0.903356	2.290211
H	3.113031	-2.316263	2.396320
C	3.032494	-3.206547	-0.621970
H	3.936019	-3.821827	-0.553924
H	2.219483	-3.700729	-0.082389

H	2.742728	-3.107983	-1.672024
N	-5.120324	-2.288170	0.074377
O	-5.404888	-2.927310	-0.935026
O	-5.762779	-2.283143	1.121066

19c Energy = -1304.64778190 a.u.

C	1.141272	4.403322	0.097319
C	1.101711	3.093689	-0.727380
C	-0.234428	2.410505	-0.436667
C	-0.356929	1.025995	-0.209632
C	0.278575	4.131253	1.345665
C	-0.847981	3.226599	0.902102
C	-1.446716	3.373961	-0.424697
P	3.110529	-1.775255	0.017165
Au	1.275928	-0.240263	-0.091918
C	-1.956875	-0.483579	0.982596
C	-1.667639	0.369719	-0.104758
C	-2.619846	0.499483	-1.140503
C	-3.822624	-0.198645	-1.090521
C	-4.089539	-0.993708	0.020573
C	-3.178641	-1.140459	1.065674
H	2.162755	4.686795	0.363440
H	0.726529	5.236909	-0.478436
H	1.914415	2.423446	-0.428187
H	1.214826	3.280932	-1.801281
H	0.854688	3.636021	2.135052
H	-0.135525	5.052229	1.777598
H	-1.373506	2.624051	1.636944
H	-2.429145	2.944293	-0.573892
H	-1.274288	4.293006	-0.979067
H	-1.222132	-0.614226	1.771458
H	-2.395462	1.111141	-2.008448
H	-4.553335	-0.130095	-1.887423

H	-3.428048	-1.776922	1.905934
C	4.622733	-1.187239	-0.847885
H	4.964239	-0.249279	-0.400467
H	5.421962	-1.932178	-0.772807
H	4.399927	-1.006952	-1.903574
C	3.655076	-2.144503	1.734541
H	4.494062	-2.848358	1.728652
H	3.965858	-1.220831	2.231404
H	2.826301	-2.579986	2.300271
C	2.736601	-3.412804	-0.730990
H	3.604727	-4.076200	-0.656025
H	1.888724	-3.871279	-0.213907
H	2.471599	-3.286728	-1.784819
N	-5.376468	-1.719345	0.087592
O	-6.155625	-1.563769	-0.847614
O	-5.570459	-2.422770	1.074598

$TS_{19\text{-}20c}$ Energy = -1304.62734350 a.u.

C	0.831155	4.655244	0.271175
C	0.965476	3.217170	0.829689
C	-0.258896	2.479205	0.325720
C	-0.332898	1.117141	-0.218617
C	-0.677690	4.828348	-0.036781
C	-1.185758	3.418239	-0.189595
C	-0.348460	2.238477	-1.329568
P	3.070401	-1.787259	0.107382
Au	1.310006	-0.198588	-0.070647
C	-2.170474	-0.285308	-1.256629
C	-1.646492	0.382927	-0.136767
C	-2.332627	0.295558	1.086764
C	-3.516232	-0.429794	1.191611
C	-4.011851	-1.072454	0.059816
C	-3.354318	-1.011402	-1.166755

H	1.202108	5.409454	0.968054
H	1.415026	4.754058	-0.649740
H	0.891552	3.196974	1.926510
H	1.897675	2.712768	0.562978
H	-1.219715	5.280447	0.806099
H	-0.883330	5.453499	-0.910879
H	-2.233860	3.191831	-0.355396
H	-1.209779	2.140075	-1.982247
H	0.564640	2.581678	-1.803755
H	-1.640877	-0.251317	-2.205547
H	-1.934654	0.794436	1.966293
H	-4.057755	-0.502574	2.127034
H	-3.771368	-1.529166	-2.021979
C	4.484278	-1.489230	-1.030573
H	4.921858	-0.507026	-0.829548
H	5.253383	-2.257544	-0.897847
H	4.136227	-1.507359	-2.067497
C	3.822331	-1.871736	1.783749
H	4.618010	-2.623817	1.811075
H	4.240871	-0.897509	2.052676
H	3.056354	-2.133867	2.519415
C	2.525472	-3.506161	-0.253883
H	2.134911	-3.563554	-1.274110
H	3.361163	-4.206337	-0.149609
H	1.727933	-3.793746	0.437408
N	-5.265881	-1.841172	0.162588
O	-5.817148	-1.875027	1.259920
O	-5.672072	-2.394128	-0.856581

20c Energy = -1304.64710719 a.u.

C	1.107758	4.505637	0.970381
C	1.385674	3.436435	-0.119891
C	0.013145	2.849030	-0.386769

C	-0.449640	0.681747	-0.807942
C	-0.256956	4.113288	1.598038
C	-0.869029	3.198947	0.574010
C	-0.276946	1.936968	-1.579884
P	3.236788	-1.593109	0.246265
Au	1.253902	-0.351408	-0.262187
C	-2.945294	0.658027	-1.165226
C	-1.779516	0.188912	-0.501622
C	-1.936194	-0.840949	0.463384
C	-3.182504	-1.370065	0.765264
C	-4.291709	-0.877588	0.079962
C	-4.195300	0.123302	-0.885854
H	1.908539	4.566932	1.711382
H	1.023330	5.489846	0.499473
H	2.078245	2.657660	0.231811
H	1.828401	3.861034	-1.029018
H	-0.136132	3.572442	2.549324
H	-0.892051	4.978516	1.821404
H	-1.901109	2.864854	0.627456
H	-1.141537	2.283026	-2.151704
H	0.594286	1.906807	-2.237973
H	-2.875740	1.428892	-1.923133
H	-1.057846	-1.209795	0.983105
H	-3.313160	-2.149238	1.506062
H	-5.089137	0.462542	-1.395050
C	2.947706	-3.404659	0.372639
H	3.884232	-3.929172	0.589581
H	2.229499	-3.611530	1.171456
H	2.536371	-3.780679	-0.568691
C	4.026728	-1.122536	1.839289
H	4.920608	-1.729770	2.016752
H	4.310587	-0.066449	1.814930
H	3.322013	-1.272834	2.662252

C	4.559527	-1.405968	-1.017200
H	5.440531	-1.995502	-0.742177
H	4.192046	-1.743657	-1.990659
H	4.845191	-0.353384	-1.101451
N	-5.628921	-1.444041	0.388125
O	-5.673959	-2.331427	1.233204
O	-6.583480	-0.979518	-0.225043

$TS_{18\text{-}22c}$ Energy = -1304.61616044 a.u.

C	0.762754	4.059189	0.942881
C	1.277659	3.127811	-0.173794
C	0.493799	1.835283	-0.225684
C	-0.783571	1.647169	-0.342959
C	-1.675750	3.814471	0.168532
C	-0.573768	4.748219	0.586023
H	1.207357	3.633141	-1.148559
H	2.336569	2.914819	-0.015305
H	0.667579	3.490978	1.875536
H	1.502173	4.847477	1.120868
H	-0.383329	5.448802	-0.237033
H	-0.911884	5.338042	1.445095
Au	1.525546	-0.009428	-0.080036
P	2.811083	-1.991673	0.069383
C	4.616938	-1.672364	0.187768
H	4.829315	-1.071509	1.076769
H	5.169803	-2.615694	0.251105
H	4.952899	-1.118213	-0.693437
C	2.406133	-3.027208	1.533135
H	1.356013	-3.330651	1.492680
H	3.037428	-3.921954	1.556719
H	2.565415	-2.451122	2.449192
C	2.611924	-3.105322	-1.379324
H	2.904621	-2.579678	-2.292791

H	3.233808	-3.999441	-1.263328
H	1.564529	-3.406198	-1.473449
C	-1.855533	3.389925	-1.116279
H	-2.748499	2.853305	-1.414674
H	-1.221711	3.758492	-1.919028
C	-1.859802	0.674771	-0.212355
C	-2.438272	0.087690	-1.354906
C	-2.308535	0.294692	1.067422
C	-3.433849	-0.874490	-1.223827
H	-2.094262	0.380170	-2.342093
C	-3.308494	-0.663159	1.206882
H	-1.861124	0.744902	1.947703
C	-3.851943	-1.231146	0.057149
H	-3.887683	-1.347771	-2.085980
H	-3.668450	-0.975734	2.179509
H	-2.387746	3.492608	0.927092
N	-4.910915	-2.256164	0.201953
O	-5.367967	-2.737057	-0.830193
O	-5.250653	-2.551054	1.343678

22c Energy = -1304.64619278 a.u.

C	1.968811	3.552943	1.019237
C	2.115010	2.732552	-0.296936
C	0.973501	1.768325	-0.324759
C	-0.344270	2.276063	-0.373001
C	-0.495262	3.772854	0.308770
C	0.714188	4.434672	0.958496
H	2.092208	3.427743	-1.149274
H	3.075197	2.214787	-0.319885
H	1.909186	2.863104	1.869829
H	2.866392	4.162156	1.163354
H	0.942379	5.344759	0.389010
H	0.437875	4.750588	1.969150

Au	1.339598	-0.242911	-0.128779
P	1.811269	-2.585869	0.073021
C	3.156549	-2.966141	1.267573
H	2.888909	-2.589502	2.259092
H	3.322230	-4.046964	1.327873
H	4.083009	-2.478519	0.950420
C	0.370336	-3.576044	0.642390
H	-0.458451	-3.461203	-0.062124
H	0.635507	-4.636107	0.714935
H	0.041714	-3.221262	1.623548
C	2.337366	-3.366912	-1.506361
H	3.246226	-2.882082	-1.874409
H	2.534209	-4.434034	-1.358675
H	1.552621	-3.248604	-2.259171
C	-0.627478	3.634850	-1.128605
H	-1.617999	3.651949	-1.573475
H	0.169634	3.991624	-1.774215
C	-1.521440	1.348526	-0.218025
C	-2.233732	0.910708	-1.343944
C	-1.900748	0.893268	1.054171
C	-3.299581	0.022844	-1.209994
H	-1.950465	1.256379	-2.334225
C	-2.966211	0.008531	1.204766
H	-1.359886	1.232851	1.933180
C	-3.646540	-0.414534	0.065592
H	-3.859073	-0.330375	-2.067695
H	-3.276669	-0.351789	2.177983
H	-1.422952	3.787444	0.875385
N	-4.768456	-1.364903	0.215922
O	-5.350853	-1.713131	-0.807139
O	-5.033255	-1.745072	1.353378

$TS_{22\text{-}23c}$ Energy = -1304.62217456 a.u.

C	-2.196124	3.412997	0.054536
C	-1.290227	2.763340	1.105214
C	-0.399841	1.746841	0.337428
C	1.013761	1.975658	0.273035
C	-0.008638	2.827238	-1.029024
C	-1.269223	3.723345	-1.136654
H	-0.685552	3.522948	1.615927
H	-1.855656	2.240761	1.881274
H	-2.972785	2.704152	-0.254347
H	-2.699507	4.305515	0.437853
H	-0.941953	4.768777	-1.136995
H	-1.753197	3.530301	-2.098408
Au	-1.399773	-0.085859	0.122557
P	-2.688030	-2.090090	-0.058742
C	-4.168783	-1.923995	-1.138368
H	-3.861059	-1.656744	-2.153523
H	-4.729324	-2.864345	-1.169573
H	-4.818885	-1.132465	-0.754363
C	-1.772829	-3.533509	-0.740524
H	-0.915138	-3.763919	-0.101612
H	-2.424321	-4.412269	-0.792281
H	-1.407138	-3.301722	-1.745245
C	-3.347847	-2.674765	1.555791
H	-3.979675	-1.899681	1.999348
H	-3.939174	-3.587097	1.423313
H	-2.520896	-2.879644	2.242049
C	1.192219	3.370161	-0.220132
H	2.118473	3.585687	-0.749077
H	0.899934	4.188906	0.435585
C	2.107945	1.010353	0.095322
C	3.404709	1.465905	0.422955
C	1.938775	-0.330258	-0.301438

C	4.494363	0.602714	0.393853
H	3.556299	2.493413	0.737364
C	3.026840	-1.191749	-0.368326
H	0.956690	-0.691286	-0.585243
C	4.284848	-0.712712	-0.009117
H	5.490490	0.930876	0.664215
H	2.921530	-2.220510	-0.690174
H	0.275564	2.297108	-1.934753
N	5.442644	-1.636952	-0.065475
O	6.536172	-1.179633	0.247641
O	5.217530	-2.789778	-0.420292

Skeletal Rearrangement of 1,7-Enynes (Scheme 6)

1,7-Enyne-Au(I) complex 33a

	ΔV	ΔZPE	ΔG	ΔV_{DCM}	ΔZPE_{DCM}	ΔG_{DCM}
$TS_{33a-34a}$	5.66	5.95	7.79	6.26	6.54	8.38
34a	-11.00	-7.74	-4.94	-11.03	-7.77	-4.97
TS_{34a-35}	-5.32	-2.17	1.53	-5.05	-1.91	1.79
35	-5.56	-2.42	1.03	-5.26	-2.12	1.33
TS_{35-36a}	-4.9	-2.11	1.6	-4.48	-1.69	2.02
36	-44.02	-40.91	-38.37	-42.82	-39.72	-37.17

1,7-Enyne-Au(I) complex 33b

	ΔV	ΔZPE	ΔG	ΔV_{DCM}	ΔZPE_{DCM}	ΔG_{DCM}
$TS_{33b-34b}$	11.62	12.63	14.72	13.43	14.44	16.53
34b	-7.86	-4.78	-2.34	-6.86	-3.78	-1.33
TS_{34b-37}	3.18	5.59	8.92	3.95	6.36	9.69
37	-9.37	-6.89	-4.38	-7.1	-4.62	-2.11

Cartesian Coordinates and Absolute Energies

33a Energy= -947.717032293 a.u.

C -1.722082 -2.528741 0.541674
C -3.952796 -1.292867 0.516202
C -0.391588 -2.693485 -0.034863
C 0.719048 -2.855249 -0.544722
C -2.553451 -1.393997 -0.101253
C -4.223145 1.236639 0.288825
C -3.839058 2.163651 -0.595177
C -3.340621 3.538472 -0.248968
P 2.072039 1.444072 0.159876
Au 1.181010 -0.702385 -0.095329
C -4.777440 -0.120679 -0.057001
H -1.632232 -2.379807 1.625362
H -2.233002 -3.493843 0.404930

H	-4.496087	-2.231617	0.345920
H	-3.865425	-1.176868	1.606030
H	1.524959	-3.370818	-1.032207
H	-2.023261	-0.441423	0.025563
H	-2.629560	-1.572713	-1.180812
H	-4.163059	1.468301	1.355362
H	-3.919295	1.936825	-1.660235
H	-3.275126	3.685202	0.834566
H	-4.007203	4.311877	-0.652591
H	-2.350074	3.732296	-0.685464
H	-5.798830	-0.205366	0.339605
H	-4.858696	-0.225594	-1.146923
C	3.811127	1.534128	-0.416283
H	3.866583	1.257070	-1.472876
H	4.197368	2.551168	-0.289941
H	4.429780	0.840429	0.160144
C	2.077756	2.013449	1.903639
H	2.668762	1.326088	2.515481
H	2.508415	3.018246	1.971012
H	1.054900	2.033754	2.290114
C	1.149161	2.710341	-0.794013
H	0.108053	2.741286	-0.460083
H	1.604326	3.696258	-0.650699
H	1.166897	2.456600	-1.857749

$TS_{33a-34a}$ Energy= -947.708005854 a.u.

P	3.258183	-0.208954	0.035377
Au	0.944658	0.223317	-0.098470
C	-2.355233	-1.149905	1.086799
C	-1.938546	-0.008272	0.262308
C	-1.097597	0.757927	-0.306237
C	-4.655830	-0.765671	-1.133408
C	-4.131962	0.608714	-0.786813

C	-4.219305	1.245875	0.405924
C	-3.870962	2.685484	0.634768
H	-1.262777	1.656453	-0.885712
H	-3.751407	1.184509	-1.631261
H	-4.637118	0.716274	1.261508
H	-3.404973	3.140081	-0.245341
H	-3.202976	2.809513	1.495371
H	-4.781738	3.256207	0.860932
C	-4.622345	-1.810658	-0.008843
C	-3.206151	-2.240043	0.396314
H	-5.174579	-1.454248	0.870798
H	-5.158989	-2.700609	-0.356383
H	-3.273024	-3.076268	1.101287
H	-2.664556	-2.610553	-0.483258
H	-2.856485	-0.788324	1.992683
H	-1.408384	-1.597919	1.425522
H	-4.091362	-1.148213	-1.993662
H	-5.688088	-0.645669	-1.494024
C	3.773991	-0.995665	1.613452
H	3.261245	-1.954314	1.733324
H	4.856276	-1.163652	1.620648
H	3.504809	-0.349565	2.453916
C	3.870281	-1.322265	-1.291507
H	4.950621	-1.474111	-1.194213
H	3.363471	-2.289314	-1.226651
H	3.655350	-0.883469	-2.270071
C	4.265124	1.320949	-0.104026
H	4.004621	2.009394	0.705009
H	5.332809	1.083873	-0.045899
H	4.057718	1.813356	-1.058417

34a Energy= -947.734561787 a.u.

P	-3.096503	0.274093	-0.006931

Au	-0.775017	-0.325929	-0.059865
C	2.237832	0.962498	1.253981
C	2.296895	-0.307586	0.409200
C	1.176950	-0.909694	-0.133960
C	4.008586	1.018209	-1.258724
C	3.474103	-0.340788	-0.877041
C	3.701154	-1.044743	0.365696
C	3.795181	-2.557661	0.423453
H	1.372675	-1.832074	-0.683742
H	3.141752	-0.948216	-1.715598
H	4.355304	-0.538509	1.074240
H	3.171150	-3.047718	-0.329198
H	3.507627	-2.930022	1.411238
H	4.832049	-2.858259	0.236368
C	4.085033	2.052781	-0.126707
C	2.718733	2.239262	0.539189
H	4.835810	1.758185	0.618679
H	4.432075	2.999700	-0.552815
H	2.760321	3.054799	1.268972
H	1.981617	2.531932	-0.221623
H	2.839306	0.808064	2.158687
H	1.202643	1.092429	1.585456
H	3.395443	1.413406	-2.077327
H	5.006643	0.833610	-1.685930
C	-3.636540	1.027346	1.581590
H	-3.064252	1.940056	1.771298
H	-4.703328	1.272757	1.549135
H	-3.454338	0.328245	2.403006
C	-3.569074	1.495099	-1.298983
H	-4.636458	1.731286	-1.233901
H	-2.989973	2.414066	-1.169292
H	-3.352118	1.086802	-2.290361
C	-4.224384	-1.155039	-0.265568

H	-4.060807	-1.901329	0.517373
H	-5.270169	-0.830979	-0.240225
H	-4.015910	-1.619320	-1.233884

TS_{34a-35} Energy= -947.725503388 a.u.

P	-3.057970	0.305130	0.230769
Au	-0.769414	-0.199424	-0.229862
C	2.263602	1.554085	-0.135176
C	2.321381	0.124516	-0.622496
C	1.184592	-0.699999	-0.682478
C	4.854944	0.013020	-0.004804
C	3.569399	-0.674679	-0.457152
C	2.518398	-1.188926	0.546544
C	2.327239	-2.694064	0.717125
H	1.308695	-1.604220	-1.277504
H	3.728406	-1.438221	-1.221204
H	2.454466	-0.643524	1.485267
H	2.425408	-3.236180	-0.225592
H	1.358198	-2.925938	1.165600
H	3.114627	-3.043217	1.396473
C	4.609565	1.300166	0.795683
C	3.637828	2.218273	0.044106
H	4.211296	1.066549	1.793253
H	5.564917	1.808981	0.958990
H	3.508116	3.168052	0.572674
H	4.059517	2.463080	-0.939524
H	1.682013	1.586996	0.796465
H	1.654154	2.092916	-0.873178
H	5.435900	0.252473	-0.904254
H	5.455990	-0.702052	0.569304
C	-3.928199	-1.010367	1.177702
H	-4.972187	-0.731479	1.355864
H	-3.899149	-1.949457	0.617339

H	-3.429914	-1.166209	2.138976
C	-4.069647	0.543267	-1.286475
H	-4.033518	-0.361391	-1.900439
H	-5.111191	0.759376	-1.026179
H	-3.666749	1.374106	-1.873063
C	-3.310516	1.839226	1.214407
H	-4.376877	2.013315	1.392897
H	-2.796931	1.750343	2.176190
H	-2.893451	2.696139	0.677292

35 Energy= -947.725833691 a.u.

P	-3.043555	0.312615	0.226229
Au	-0.756382	-0.213477	-0.212663
C	2.270476	1.590496	-0.246961
C	2.336788	0.158102	-0.684073
C	1.210137	-0.734809	-0.643442
C	4.805996	0.008644	0.092774
C	3.543224	-0.638370	-0.458823
C	2.360104	-1.194853	0.483433
C	2.375826	-2.718948	0.664704
H	1.288518	-1.568467	-1.344303
H	3.726751	-1.434163	-1.182195
H	2.275658	-0.669301	1.432912
H	2.480240	-3.241276	-0.288801
H	1.446071	-3.039252	1.143257
H	3.217451	-2.991684	1.310383
C	4.532475	1.314742	0.853810
C	3.636280	2.241299	0.021267
H	4.054569	1.102746	1.820462
H	5.483204	1.806803	1.081327
H	3.483496	3.199007	0.528498
H	4.131370	2.467266	-0.931932
H	1.606118	1.655279	0.626415

H	1.719101	2.104412	-1.049640
H	5.474885	0.210610	-0.753724
H	5.328294	-0.718297	0.726751
C	-4.200294	-0.374271	-1.029643
H	-4.115131	-1.464989	-1.051565
H	-5.234014	-0.098571	-0.794446
H	-3.941350	0.012393	-2.019976
C	-3.403153	2.117252	0.255330
H	-4.465800	2.296440	0.450755
H	-2.808072	2.601856	1.035171
H	-3.136352	2.559542	-0.709136
C	-3.672082	-0.315542	1.837632
H	-4.725610	-0.047357	1.971003
H	-3.571128	-1.404333	1.874522
H	-3.085447	0.114325	2.655114

$TS_{35\text{-}36}$ Energy= -947.724842893 a.u.

P	-3.051078	0.323438	0.202080
Au	-0.766216	-0.220224	-0.199438
C	2.262425	1.566285	-0.151834
C	2.357154	0.142708	-0.624788
C	1.207608	-0.790904	-0.587696
C	4.844092	0.052405	0.001615
C	3.574383	-0.566957	-0.529665
C	2.198237	-1.240495	0.508609
C	2.508311	-2.725429	0.674564
H	1.251899	-1.544742	-1.378738
H	3.696966	-1.455343	-1.144164
H	2.132718	-0.711741	1.457696
H	2.581982	-3.243243	-0.284270
H	1.674774	-3.163963	1.236125
H	3.427601	-2.885411	1.245510
C	4.600991	1.350526	0.786260

C	3.622352	2.258701	0.029782
H	4.199349	1.118225	1.782063
H	5.554778	1.861824	0.948557
H	3.478777	3.205265	0.560059
H	4.041912	2.510801	-0.952838
H	1.670062	1.588821	0.773708
H	1.635868	2.078668	-0.896655
H	5.494017	0.247538	-0.863865
H	5.377522	-0.691564	0.607102
C	-4.221325	-0.655674	-0.825717
H	-5.257590	-0.380049	-0.603156
H	-4.021911	-0.474887	-1.886078
H	-4.083544	-1.722524	-0.626603
C	-3.592132	0.029346	1.936104
H	-4.651817	0.276233	2.061020
H	-3.436812	-1.021778	2.196393
H	-2.998152	0.644640	2.618256
C	-3.488333	2.078632	-0.135128
H	-4.551685	2.256979	0.057007
H	-2.893865	2.738078	0.503916
H	-3.268217	2.319406	-1.179295

36 Energy= -947.738248075 a.u.

P	-2.878854	0.409420	0.042406
Au	-0.636225	-0.377740	-0.145859
C	2.339453	0.828104	1.339876
C	2.612948	-0.263507	0.320187
C	1.240703	-1.209907	-0.359119
C	3.879002	1.346865	-1.164385
C	3.356194	-0.003295	-0.803122
C	2.162891	-1.718725	0.647309
C	3.088468	-2.894499	0.374650
H	1.485363	-1.545332	-1.368733

H	3.579178	-0.810359	-1.496775
H	1.777447	-1.706942	1.668242
H	3.454799	-2.909344	-0.656296
H	2.540827	-3.828324	0.541469
H	3.949424	-2.882229	1.050569
C	3.760381	2.390765	-0.042253
C	2.442407	2.232310	0.728449
H	4.602107	2.272876	0.651949
H	3.844609	3.395622	-0.467670
H	2.372714	2.985107	1.520464
H	1.592140	2.399779	0.052324
H	3.077343	0.717204	2.147492
H	1.357043	0.667360	1.796621
H	3.323655	1.667401	-2.062851
H	4.916118	1.238061	-1.511727
C	-3.932432	-0.060852	-1.389048
H	-3.955759	-1.150070	-1.488214
H	-4.954385	0.308809	-1.253631
H	-3.517439	0.360728	-2.309213
C	-3.031184	2.238223	0.167855
H	-2.590361	2.707703	-0.716360
H	-4.083453	2.532461	0.242977
H	-2.496027	2.594737	1.052759
C	-3.757974	-0.246145	1.518150
H	-4.783257	0.136581	1.558324
H	-3.784789	-1.338965	1.476228
H	-3.227818	0.051302	2.427547

33b Energy = -908.397486758 a.u.

C	-2.588700	-1.445366	-0.402426
C	-4.305060	0.061060	0.771794
C	-1.309919	-2.144854	-0.318173
C	-0.247366	-2.762179	-0.226057

C	-2.953321	-0.660202	0.880517
C	-3.374980	2.317625	0.023565
C	-2.473099	2.793711	-0.839412
P	2.216288	1.071558	0.129318
Au	0.781298	-0.762630	-0.060711
C	-4.353763	1.209531	-0.259946
H	-2.579051	-0.788342	-1.279785
H	-3.348587	-2.215919	-0.601739
H	-5.093356	-0.666144	0.537240
H	-4.549247	0.464022	1.762832
H	0.425851	-3.597461	-0.185734
H	-2.972889	-1.358736	1.724386
H	-2.159486	0.069540	1.084254
H	-3.447606	2.769975	1.014601
H	-2.382872	2.400581	-1.850745
H	-5.371839	1.623412	-0.243086
H	-4.201636	0.831002	-1.279322
C	2.315506	1.726543	1.839896
H	2.676601	0.946217	2.515790
H	3.000124	2.580722	1.876334
H	1.323762	2.045229	2.173029
C	1.684354	2.471644	-0.929381
H	0.661460	2.759581	-0.670288
H	2.351885	3.328532	-0.788581
H	1.705205	2.167427	-1.979787
C	3.935567	0.669613	-0.367062
H	3.950739	0.323471	-1.404430
H	4.571579	1.556352	-0.273595
H	4.331321	-0.124651	0.272373
H	-1.834160	3.636817	-0.587265

$TS_{33b\text{-}34b}$ Energy = -908.387119311 a.u.

P	3.075183	0.309295	0.063883

Au	0.799180	-0.307569	0.005486
C	-2.571174	1.089636	-0.916630
C	-2.096777	-0.205575	-0.404129
C	-1.195241	-1.014360	-0.003514
C	-4.960876	0.031106	1.043761
C	-4.266407	-1.175157	0.467912
C	-4.130345	-1.484211	-0.842538
H	-1.305473	-2.038416	0.327798
H	-3.885536	-1.889377	1.197238
C	-4.937827	1.296198	0.173155
C	-3.537382	1.897068	-0.017882
H	-5.405244	1.106986	-0.802118
H	-5.564909	2.050540	0.661191
H	-3.636681	2.883676	-0.484142
H	-3.065603	2.057665	0.959929
H	-2.998399	0.959902	-1.917953
H	-1.649058	1.674082	-1.056063
H	-4.518674	0.256254	2.022700
H	-6.001577	-0.257409	1.255443
H	-4.544274	-0.863747	-1.631481
H	-3.690448	-2.425961	-1.154959
C	4.198717	-1.127066	-0.157766
H	3.995151	-1.610678	-1.117448
H	5.244475	-0.802549	-0.132461
H	4.028729	-1.855416	0.640368
C	3.580775	1.088500	1.648693
H	4.646050	1.342114	1.627771
H	2.997307	1.998301	1.816153
H	3.391227	0.398532	2.475957
C	3.547267	1.507352	-1.246695
H	4.613234	1.749278	-1.177550
H	3.339269	1.078262	-2.231043
H	2.963084	2.425564	-1.137166

34b Energy = -908.417425643 a.u.

P	-2.900266	0.393482	-0.086908
Au	-0.638214	-0.396487	0.015719
C	2.473214	0.821401	1.218218
C	2.418965	-0.558437	0.570142
C	1.255638	-1.143229	0.095620
C	4.210220	0.361074	-1.284176
C	3.547101	-0.875385	-0.732023
C	3.722654	-1.410438	0.604445
H	1.388170	-2.158558	-0.287942
H	3.146064	-1.551708	-1.480864
C	4.410735	1.515257	-0.291877
C	3.079289	1.932157	0.339199
H	5.132978	1.236924	0.487523
H	4.853917	2.357256	-0.833259
H	3.213983	2.828603	0.953464
H	2.369142	2.197220	-0.456428
H	3.050654	0.740671	2.147534
H	1.452856	1.093551	1.506205
H	3.629853	0.710591	-2.146176
H	5.177486	0.019442	-1.685411
H	4.484442	-0.966082	1.239722
H	3.584874	-2.478549	0.749438
C	-4.109378	-0.911590	-0.550146
H	-4.074192	-1.723809	0.181829
H	-5.124669	-0.502474	-0.583663
H	-3.854821	-1.320798	-1.532171
C	-3.155776	1.741315	-1.312220
H	-4.203518	2.059916	-1.321238
H	-2.522931	2.596688	-1.058506
H	-2.879528	1.390676	-2.310878
C	-3.517364	1.071981	1.507292

H	-4.552657	1.414261	1.405346
H	-3.470091	0.299435	2.280369
H	-2.890883	1.912358	1.820060

TS_{34b-37} Energy = -908.408577576 a.u.

P	-2.932580	0.388711	0.104271
Au	-0.677721	-0.345368	-0.094339
C	2.447420	1.251143	-0.294752
C	2.471618	-0.250294	-0.479503
C	1.264078	-1.087859	-0.301083
C	4.975677	-0.321925	0.078082
C	3.671574	-0.971840	-0.299359
C	2.236244	-1.273790	0.880779
H	1.293463	-2.007694	-0.888895
H	3.726867	-1.985153	-0.691965
H	2.198873	-0.624043	1.748906
C	4.807306	1.105647	0.617617
C	3.841355	1.899307	-0.270573
H	4.430264	1.074416	1.648785
H	5.785126	1.594908	0.659400
H	3.752367	2.933215	0.077011
H	4.241977	1.946487	-1.291613
H	1.875911	1.489863	0.611691
H	1.841422	1.636665	-1.125391
H	5.592926	-0.315438	-0.833368
H	5.508118	-0.967379	0.787226
H	2.531812	-2.297232	1.090585
C	-3.315236	1.916254	-0.847297
H	-4.368353	2.192308	-0.728048
H	-2.687373	2.739692	-0.494482
H	-3.105754	1.752280	-1.908385
C	-4.153241	-0.852093	-0.490969
H	-5.175049	-0.473667	-0.380546

H	-3.966320	-1.078529	-1.544769
H	-4.049575	-1.777190	0.083719
C	-3.453144	0.767408	1.827704
H	-4.499580	1.089637	1.853843
H	-3.336846	-0.123285	2.452099
H	-2.823546	1.561801	2.239026

37 Energy = -908.421105526 a.u.

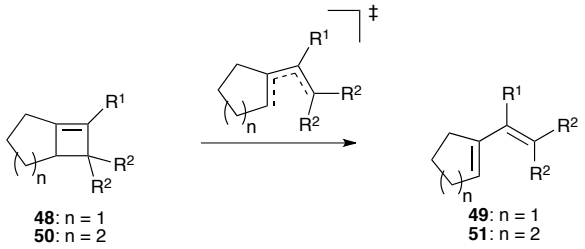
P	-2.696206	0.541044	-0.015343
Au	-0.538396	-0.469766	-0.092197
C	2.521029	0.575673	1.343870
C	2.704677	-0.630689	0.443107
C	1.250336	-1.490549	-0.210236
C	4.113646	0.696086	-1.185275
C	3.472440	-0.557883	-0.693104
C	2.111907	-1.987429	0.858512
H	1.472610	-1.926817	-1.183921
H	3.627099	-1.457205	-1.286900
H	1.729045	-1.946283	1.876652
C	4.086925	1.852159	-0.171256
C	2.757853	1.895091	0.595702
H	4.912009	1.726139	0.541154
H	4.265455	2.797926	-0.692163
H	2.758465	2.726880	1.307557
H	1.928584	2.073018	-0.103320
H	3.240005	0.479077	2.170237
H	1.524671	0.549332	1.797825
H	3.590916	0.973609	-2.116786
H	5.137512	0.460758	-1.507932
H	2.741316	-2.856024	0.665052
C	-2.910629	1.930752	-1.200711
H	-3.922786	2.343405	-1.131962
H	-2.186431	2.720579	-0.981113

H	-2.736920	1.575891	-2.220758
C	-4.046902	-0.640820	-0.413231
H	-5.019847	-0.139658	-0.373872
H	-3.895660	-1.053234	-1.415031
H	-4.039055	-1.465940	0.304931
C	-3.140197	1.237731	1.627482
H	-4.146819	1.668352	1.603710
H	-3.105877	0.448982	2.384665
H	-2.424379	2.016383	1.906542

Calculations: Opening of Cyclobutenes

1. Opening of Bicyclo[3.2.0]hept-5-enes and Bicyclo[4.2.0]oct-6-enes Complexes

We computed (B3LYP, 6-31G(d) C, H) the energies for the opening of bicyclo[3.2.0]hept-5-enes **48** and bicyclo[4.2.0]oct-6-enes **50** to give dienes **49** and **51**, respectively.



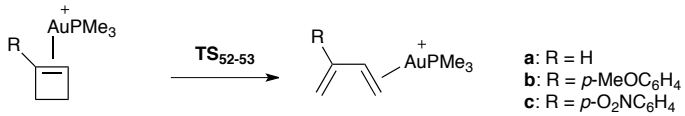
48: n = 1
50: n = 2

49: n = 1
51: n = 2

n	R^1	R^2	$\Delta G^{‡}$	$\Delta H^{‡}$	ΔG
1	H	H	33.38	33.44	-14.67
1	H	Me	23.90	23.61	-26.89
1	Me	Me	39.88	39.23	-5.35
1	Ph	H	25.20	25.12	-16.40
1	Ph	Me	41.06	41.13	-1.74
2	H	H	30.52	30.71	-13.60
2	H	Me	29.51	30.19	-16.79
2	Me	Me	31.64	31.96	-9.84
2	Ph	H	31.06	30.90	-7.46
2	Ph	Me	30.18	30.12	-9.29

2. Opening of Cyclobutene-Gold(I) Complexes

The ring opening of simple cyclobutenes catalyzed by group 11 metals was computed (B3LYP, 6-31G(d) C, H, P, N, O, LAN2DZ for Au). For comparison, this transformation was also calculated in the absence of metal



52a-d **53a-d**

a: R = H
b: R = *p*-$MeOC_6H_4$
c: R = *p*-$O_2NC_6H_4$

Parent cyclobutene

	V	ZPE	G	V_{DCM}	ZPE_{DCM}	G_{DCM}
TS	35.70	33.99	33.54	35.64	33.92	33.48

***trans*-diene**	-11.64	-12.56	-13.49	-11.90	-12.82	-13.75

52a

	V	**ZPE**	**G**	**V_{DCM}**	**ZPE_{DCM}**	**G_{DCM}**
$TS_{52\text{-}53a}$	35.12	33.34	33.73	35.73	33.95	34.34
***s-cis*-53a**	-9.62	-10.31	-10.58	-9.27	-9.96	-10.24
***s-trans*-53a**	-13.17	-13.82	-14.17	-12.46	-13.11	-13.46

52b

	V	**ZPE**	**G**	**V_{DCM}**	**ZPE_{DCM}**	**G_{DCM}**
$TS_{52\text{-}53b}$	40.88	38.84	39.03	40.06	38.03	38.21
***s-trans*-53b**	-1.46	-2.18	-3.03	-5.21	-5.92	-6.77

54c

	V	**ZPE**	**G**	**V_{DCM}**	**ZPE_{DCM}**	**G_{DCM}**
$TS_{52\text{-}53c}$	39.53	37.66	38.28	38.83	36.97	37.59
***s-trans*-53c**	-6.22	-6.72	-6.97	-7.34	-7.83	-8.08

Cartesian Coordinates and Absolute Energies

52a Energy = -752.384080227 a.u.

C	-3.165816	0.912153	0.690987
C	-3.177133	0.714825	-0.866643
C	-2.524210	-0.638413	-0.604605
C	-2.514567	-0.465238	0.765053
H	-2.596867	1.760721	1.080535
H	-4.164954	0.924575	1.139490
H	-2.614496	1.437876	-1.463287
H	-4.182365	0.617769	-1.290396
H	-2.392445	-1.517388	-1.232628
H	-2.367086	-1.158694	1.590553
Au	-0.255748	-0.186551	0.011794
P	2.067773	0.158561	-0.014420
C	2.725778	0.523117	1.658779
H	3.809867	0.672112	1.611755
H	2.255361	1.426520	2.057032
H	2.506532	-0.310855	2.331487
C	2.986938	-1.307623	-0.622127
H	2.670324	-1.548373	-1.640989
H	4.063399	-1.105138	-0.619181
H	2.781490	-2.168549	0.020453
C	2.570209	1.560043	-1.085919
H	3.657130	1.690088	-1.046488
H	2.268867	1.364929	-2.119069
H	2.085577	2.480300	-0.747847

TS$_{52\text{-}53a}$ Energy = -752.328114536 a.u.

C	2.850536	1.049179	0.602461
C	3.938468	-0.753920	0.641121
C	2.938278	-0.959931	-0.322896
C	2.408999	0.338599	-0.587459
H	2.432442	0.788734	1.567628

H	3.323755	2.033007	0.561411
H	4.217976	-1.475849	1.409883
H	4.716780	-0.029952	0.401851
H	2.565947	-1.925175	-0.658477
H	2.331259	0.795464	-1.575636
Au	0.208468	0.090620	-0.151370
P	-2.111356	-0.091483	0.138806
C	-2.958608	1.535022	0.070144
H	-4.038016	1.405333	0.203431
H	-2.574734	2.187895	0.859149
H	-2.770805	2.009683	-0.897143
C	-2.904569	-1.129722	-1.149713
H	-2.485927	-2.139743	-1.122317
H	-3.985204	-1.183515	-0.979317
H	-2.717552	-0.701635	-2.138654
C	-2.575554	-0.840788	1.748679
H	-3.665446	-0.908271	1.834024
H	-2.146357	-1.843639	1.827532
H	-2.188051	-0.229691	2.568747

***s-cis*-53a** Energy = -752.399406609 a.u.

C	2.293782	-1.208331	-0.376463
C	3.894397	1.431863	-0.543771
C	3.192363	1.002448	0.516919
C	2.626072	-0.342757	0.646575
H	2.484146	-0.950615	-1.416722
H	2.104779	-2.256948	-0.158705
H	4.326045	2.427655	-0.561674
H	4.091891	0.802184	-1.407388
H	3.081473	1.648817	1.384526
H	2.517461	-0.711714	1.667103
Au	0.200724	-0.303361	-0.004103
P	-2.069058	0.301303	-0.013348

C	-3.168911	-1.149612	-0.238981
H	-4.216852	-0.831096	-0.242517
H	-2.940975	-1.645068	-1.187022
H	-3.012644	-1.863643	0.574640
C	-2.595473	1.104376	1.550423
H	-2.013306	2.015433	1.714778
H	-3.659244	1.360728	1.500870
H	-2.428223	0.425383	2.391337
C	-2.484857	1.475625	-1.359802
H	-3.550670	1.725682	-1.325702
H	-1.897012	2.391259	-1.249132
H	-2.252400	1.026240	-2.329460

***s-trans*-53a** Energy = -752.464429462 a.u.

C	2.196992	-1.464228	0.129885
H	2.275462	-1.696687	1.190792
C	2.707294	-0.279609	-0.367632
H	2.767426	-0.158358	-1.449695
C	3.264267	0.795663	0.434181
H	3.241629	0.680082	1.516189
C	3.836397	1.875718	-0.125636
H	3.879181	2.006312	-1.204487
H	4.291784	2.653964	0.478545
H	2.007427	-2.299604	-0.540203
Au	0.189481	-0.350861	-0.012190
P	-2.049374	0.358381	0.009578
C	-3.214967	-1.039102	-0.224785
H	-4.247780	-0.674728	-0.210547
H	-3.019746	-1.528474	-1.183247
H	-3.081754	-1.772837	0.575316
C	-2.426979	1.566642	-1.318745
H	-3.481797	1.858216	-1.272526
H	-1.802447	2.456605	-1.200248

H	-2.219951	1.121318	-2.295962
C	-2.525970	1.163995	1.587309
H	-1.906620	2.049903	1.753688
H	-3.579514	1.461739	1.555098
H	-2.373858	0.470378	2.419143

52b Energy = -1097.97868485 a.u.

C	-0.430013	3.261058	-0.256975
C	0.591903	2.907086	0.870836
C	1.036275	1.735845	0.005852
C	-0.000369	1.943036	-0.938126
H	-1.475728	3.370603	0.037991
H	-0.131073	4.147546	-0.825835
H	0.166978	2.650204	1.846229
H	1.382056	3.650650	1.024183
H	0.039726	1.736615	-2.009327
Au	-1.335162	0.316122	-0.243524
P	-2.911243	-1.349926	0.292043
C	-4.576858	-0.668174	0.659143
H	-5.279261	-1.477678	0.884721
H	-4.519759	0.007155	1.517667
H	-4.944107	-0.103300	-0.202514
C	-3.164311	-2.555301	-1.070738
H	-2.220028	-3.056559	-1.301749
H	-3.909509	-3.305279	-0.784705
H	-3.507917	-2.032041	-1.967764
C	-2.459185	-2.355509	1.762057
H	-3.227988	-3.110288	1.960047
H	-1.501439	-2.854481	1.589200
H	-2.359733	-1.706671	2.636948
C	2.193809	0.902054	0.089779
C	3.050732	0.981549	1.217113
C	2.536810	0.004458	-0.947924
C	4.187834	0.206423	1.301199

H	2.810373	1.666092	2.025325
C	3.676339	-0.777408	-0.877631
H	1.896926	-0.071929	-1.822744
C	4.516756	-0.681548	0.253550
H	4.852749	0.261587	2.156419
H	3.917744	-1.450606	-1.691327
O	5.642149	-1.386563	0.426020
C	6.075578	-2.297321	-0.589838
H	7.003575	-2.728722	-0.215692
H	5.336872	-3.091355	-0.745808
H	6.266975	-1.771257	-1.531455

$TS_{52\text{-}53b}$ Energy = -1097.91354288 a.u.

C	-0.762554	1.923406	1.627371
C	0.141624	3.100404	-0.095034
C	-0.193221	1.777969	-0.569669
C	-1.163844	1.333093	0.401093
H	0.269228	1.884328	1.950371
H	-1.486082	2.182087	2.399551
H	1.126621	3.547925	-0.228610
H	-0.646575	3.795950	0.167896
H	-0.178521	1.531759	-1.638186
Au	1.482564	0.327399	-0.174722
P	3.271569	-1.161866	0.098008
C	3.469935	-1.745757	1.827890
H	4.314572	-2.439141	1.902251
H	3.647075	-0.892075	2.488350
H	2.557616	-2.253705	2.153281
C	3.098156	-2.679697	-0.920900
H	3.038847	-2.410166	-1.979238
H	3.956514	-3.342028	-0.765131
H	2.180822	-3.207376	-0.644792
C	4.891753	-0.433658	-0.366915

H	5.692720	-1.167786	-0.228501
H	4.869555	-0.118734	-1.414072
H	5.095764	0.442499	0.255168
C	-2.428456	0.669992	0.159789
C	-3.159458	0.096240	1.220902
C	-2.968683	0.571857	-1.145786
C	-4.373310	-0.541598	1.006696
H	-2.754900	0.128349	2.228574
C	-4.171958	-0.064532	-1.374336
H	-2.446967	1.029863	-1.980819
C	-4.891593	-0.627605	-0.299443
H	-4.904105	-0.976728	1.844903
H	-4.597509	-0.131944	-2.369936
O	-6.052618	-1.220335	-0.625388
C	-6.864503	-1.789869	0.403829
H	-7.743463	-2.186744	-0.103866
H	-6.338204	-2.603365	0.916310
H	-7.171523	-1.028289	1.129575

***s-trans*-53b** Energy = -1097.98100765 a.u.

C	-0.076747	-1.835496	-1.459364
H	-0.824770	-1.144711	-1.839137
C	-0.197640	-2.389178	-0.197786
H	0.484172	-3.199412	0.060817
C	-1.188809	-2.052541	0.828778
C	-1.103136	-2.711515	2.006664
H	-0.321194	-3.441757	2.199436
H	-1.822351	-2.541691	2.801605
H	0.579144	-2.305306	-2.188681
Au	1.370320	-0.410492	-0.392871
P	2.889815	1.257170	0.252257
C	4.130265	1.612585	-1.052370
H	4.816569	2.398235	-0.718657

H	4.701858	0.707339	-1.276361
H	3.625494	1.940608	-1.965544
C	3.849118	0.820544	1.755383
H	4.541856	1.630134	2.009452
H	3.168434	0.653000	2.594788
H	4.418010	-0.096698	1.578796
C	2.067894	2.855905	0.621454
H	1.352263	2.724194	1.437848
H	2.811797	3.606158	0.910356
H	1.526244	3.206945	-0.261502
C	-2.220131	-1.007744	0.581564
C	-2.352755	0.077073	1.469816
C	-3.112504	-1.088388	-0.497271
C	-3.328588	1.044646	1.280379
H	-1.679562	0.157106	2.319801
C	-4.103395	-0.126441	-0.696026
H	-3.065808	-1.934451	-1.178210
C	-4.215694	0.953000	0.193460
H	-3.433856	1.880987	1.963883
H	-4.785586	-0.234157	-1.531004
O	-5.131611	1.943325	0.096278
C	-6.085698	1.897867	-0.961748
H	-6.716215	2.777348	-0.828321
H	-5.595994	1.945389	-1.942277
H	-6.703231	0.993569	-0.901965

52c Energy = -1187.93638507 a.u.

C	-0.961318	3.386480	-0.068801
C	0.089666	2.955249	1.008392
C	0.572400	1.910306	0.004964
C	-0.415918	2.240232	-0.925748
H	-2.013784	3.348813	0.222178
H	-0.752054	4.371033	-0.500067

H	-0.303146	2.584767	1.959713
H	0.850574	3.715707	1.216484
H	-0.460800	2.083615	-2.002881
Au	-1.420465	0.309191	-0.181779
P	-2.773376	-1.562694	0.235649
C	-4.137391	-1.201575	1.408177
H	-4.747312	-2.097822	1.564421
H	-3.726329	-0.875062	2.367627
H	-4.768770	-0.402831	1.008651
C	-3.568112	-2.199975	-1.290432
H	-2.802438	-2.491559	-2.015021
H	-4.189566	-3.070590	-1.054954
H	-4.193937	-1.422521	-1.737851
C	-1.843735	-2.974484	0.950495
H	-2.518744	-3.819610	1.123765
H	-1.051483	-3.282974	0.262562
H	-1.387352	-2.678014	1.899068
C	1.775036	1.084303	-0.007723
C	2.567068	1.001315	1.152679
C	2.172226	0.389117	-1.168992
C	3.729147	0.235393	1.162665
H	2.273821	1.540219	2.048414
C	3.329422	-0.377536	-1.169616
H	1.576231	0.457522	-2.074451
C	4.086477	-0.443568	0.001115
H	4.355415	0.156497	2.042840
H	3.659206	-0.916779	-2.049125
N	5.315526	-1.269522	0.007013
O	5.591180	-1.866777	-1.029092
O	5.963741	-1.299596	1.048130

$TS_{52c\text{-}53c}$ Energy = -1187.87339664 a.u.

C	-0.411413	2.231361	1.529147

C	0.490264	3.235140	-0.244319
C	0.055346	1.926479	-0.662108
C	-0.863302	1.549525	0.365602
H	0.621115	2.168724	1.845913
H	-1.108936	2.587180	2.287279
H	1.495415	3.616894	-0.424172
H	-0.250548	3.990425	-0.008181
H	0.077381	1.592228	-1.705352
Au	1.621479	0.315829	-0.195044
P	3.292160	-1.289641	0.104509
C	2.705602	-2.761278	1.030737
H	3.519436	-3.486086	1.140915
H	2.354980	-2.460504	2.021960
H	1.876156	-3.230534	0.494206
C	3.950036	-1.920965	-1.487596
H	4.377349	-1.096671	-2.065697
H	4.725928	-2.672049	-1.304060
H	3.142317	-2.373623	-2.069736
C	4.739337	-0.648327	1.032400
H	5.494620	-1.434107	1.140780
H	5.176993	0.199452	0.497756
H	4.426006	-0.311929	2.024711
C	-2.146047	0.856226	0.233888
C	-2.775499	0.308756	1.369703
C	-2.764355	0.722250	-1.025371
C	-3.991700	-0.354710	1.256103
H	-2.296929	0.383576	2.341441
C	-3.976085	0.052759	-1.152373
H	-2.308452	1.167879	-1.903906
C	-4.568428	-0.474557	-0.006712
H	-4.491866	-0.784837	2.115056
H	-4.471365	-0.057405	-2.109243
N	-5.857608	-1.190935	-0.136079

O	-6.351639	-1.642707	0.892428
O	-6.335630	-1.282785	-1.262539

***s-trans*-53c** Energy = -1187.94630386 a.u.

C	0.207013	-1.958466	-1.392497
H	-0.571188	-1.332310	-1.821052
C	0.085773	-2.481203	-0.119578
H	0.815072	-3.230799	0.186991
C	-0.964783	-2.199693	0.863319
C	-0.906333	-2.840706	2.050440
H	-0.101183	-3.531342	2.287686
H	-1.673006	-2.704096	2.806667
H	0.919607	-2.400361	-2.085304
Au	1.546895	-0.405955	-0.348194
P	2.969643	1.375903	0.212522
C	4.399812	1.498535	-0.929602
H	5.038571	2.341498	-0.644733
H	4.984967	0.575277	-0.891513
H	4.046715	1.646124	-1.954209
C	3.676514	1.234875	1.900440
H	4.331055	2.089111	2.104804
H	2.871944	1.213348	2.640842
H	4.255407	0.310861	1.985151
C	2.119682	3.000433	0.147526
H	1.288590	3.013450	0.858184
H	2.821328	3.802954	0.399293
H	1.722376	3.172553	-0.856830
C	-2.056822	-1.229025	0.554737
C	-2.245090	-0.110002	1.382675
C	-2.921765	-1.427723	-0.535519
C	-3.266282	0.802428	1.126384
H	-1.587018	0.044347	2.232987
C	-3.948531	-0.524663	-0.800482

H	-2.813378	-2.307439	-1.163215
C	-4.098019	0.581229	0.032736
H	-3.428056	1.670836	1.753263
H	-4.631867	-0.666639	-1.628905
N	-5.174754	1.552889	-0.252980
O	-5.268702	2.521958	0.495606
O	-5.894182	1.325319	-1.221008

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