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Supporting Information

Rhodium(I)-Catalyzed Three-Component [4+2+1] Cycloaddition of Two Vinylallenes and CO

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Supporting Information

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1. General information

All the reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using an IKA or Eyela rotary evaporator with a desktop vacuum pump. Super-dried DCM, DCE and synthetic reagents were purchased from J&K, Energy, Acros, Aldrich, and Alfa Aesar, and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

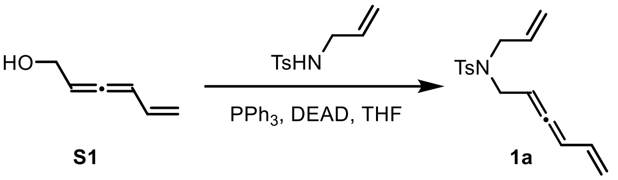
NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz), AVANCE III 500 (^{1}H at 500 MHz, ^{13}C at 126 MHz) and AVENCE NEO 600 (^{1}H at 600 MHz, ^{13}C at 151 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to residual solvent peak (CD_2Cl_2: 5.32 ppm, $CDCl_3$: 7.26 ppm); s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CD_2Cl_2: 53.84 ppm, $CDCl_3$: 77.16 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:
Ac = acetyl
DCE = 1,2-dichloroethane
DIBAL-H = diisobutylaluminum hydride
DMF = N, N-dimethylformamide
Cy = cyclohexyl
EA = ethyl acetate
MsCl = methanesulfonyl chloride
o-Ns = 2-nitrobenzenesulfonyl
PE = petroleum ether
TBS = tertbutyldimethylsilyl
THF = tetrahydrofuran
Ts = tosyl
DEAD = diethyl azodiformate
DIAD = diisopropyl azodiformate

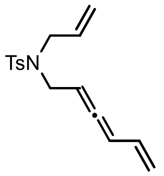
2. Substrate preparation

Vinylallenes **1d**[1-2], **1k**[3], **1o**[4] and **S1**[5] used in this research are known compounds and were synthesized based on procedures in reported literature. Almost all vinylallene substrates and [4+2+1] products are not stable for storage in long time. **S4**[6], **S11**[7], **3**[8] are also known compounds and were synthesized according to the reported literature.

Preparation of substrates 1a-1c:



DEAD (1.57 mL, 10.8 mmol) was added into the mixture of alcohol **S1** (517.7 mg, 5.39 mmol), N-allyl-4-methylbenzenesulfonamide (1.37 g, 6.47 mmol), PPh$_3$ (2.83 g, 10.8 mmol) and THF (50 mL) at 0 °C and then warmed to room temperature and stirred for 12 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1a** (R$_f$: 0.69 (PE : EA = 5 / 1), 376 mg, yield = 24%) as a colorless oil.

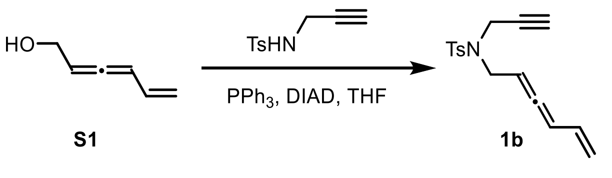


1a

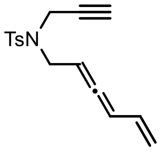
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.07 (ddd, J = 16.9, 10.2, 10.1 Hz, 1H), 5.81 – 5.76 (m, 1H), 5.64 (ddt, J = 16.2, 9.9, 6.4 Hz, 1H), 5.20 – 5.15 (m, 3H), 5.20 – 5.06 (m, 1H), 5.00 (d, J = 9.9 Hz, 1H), 3.89 – 3.82 (m, 4H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 208.5, 143.4, 137.6, 132.7, 132.0, 129.9, 127.3, 119.3, 116.8, 95.9, 88.0, 49.4, 45.8, 21.7.

HRMS (ESI): [M + H]$^+$ calculated for $C_{16}H_{20}NO_2S^+$: 290.1209; found: 290.1202.



DIAD (0.60 mL, 3.0 mmol) was added into the mixture of alcohol **S1** (177 mg, 1.84 mmol), 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (453 mg, 2.17 mmol), PPh$_3$ (786 mg, 3.0 mmol) and THF (20 mL) at 0 °C and then warmed to room temperature and stirred for 16 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1b** (R$_f$: 0.57 (PE : EA = 5 / 1), 432.8 mg, yield = 82%) as a yellow oil.

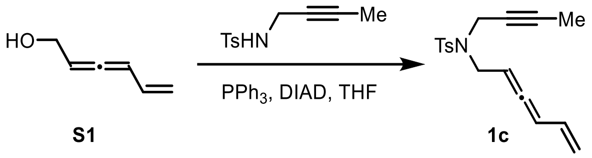


1b

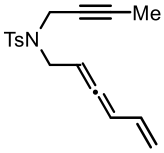
^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.11 (ddd, *J* = 17.0, 10.2, 10.1 Hz, 1H), 5.99 – 5.84 (m, 1H), 5.26 – 5.23 (m, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.15 (d, *J* = 2.4 Hz, 2H), 3.97 – 3.75 (m, 2H), 2.42 (s, 3H), 2.02 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) *δ* 208.9, 143.8, 136.1, 132.0, 129.7, 127.8, 117.0, 96.2, 87.7, 76.5, 73.9, 45.9, 36.1, 21.7.

HRMS (ESI): [M + H]$^+$ calculated for $C_{16}H_{18}NO_2S^+$: 288.1053; found: 288.1046.



DIAD (0.60 mL, 3.0 mmol) was added into the mixture of alcohol **S1** (192 mg, 2.0 mmol), N-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (462 mg, 2.07 mmol), PPh$_3$ (786 mg, 3.0 mmol) and THF (20 mL) at 0 °C and then warmed to room temperature and stirred for 12 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1c** (R*f*: 0.69 (PE : EA = 5 / 1), 403.4 mg, yield = 67%) as a yellow oil.



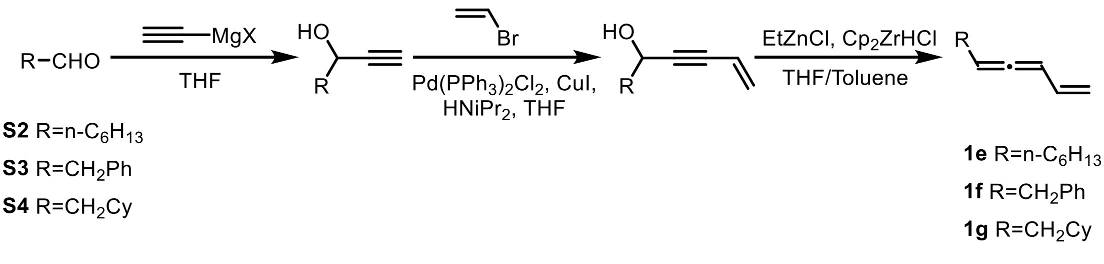
1c

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.11 (ddd, *J* = 17.0, 10.2, 10.2 Hz, 1H), 5.88 – 5.76 (m, 1H), 5.33 – 5.12 (m, 2H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.08 (d, *J* = 2.3 Hz, 2H), 3.97 – 3.64 (m, 2H), 2.41 (s, 3H), 1.54 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) *δ* 208.8, 143.5, 136.3, 132.1, 129.4, 127.9, 116.8, 96.1, 87.9, 81.8, 71.6, 45.8, 36.6, 21.6, 3.4.

HRMS (ESI): [M + H]$^+$ calculated for $C_{17}H_{20}NO_2S^+$: 302.1209; found: 302.1208.

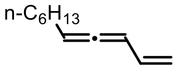
Preparation of substrates 1e-1g:



To aldehyde **S2** (2.28 g, 20 mmol), ethynylmagnesium chloride solution (60 mL, 0.5 M in THF) was added carefully at -78 °C under an inert atmosphere. The reaction was gradually allowed to warm to room temperature, and stirred for 12 h. The solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for the next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol, 2 mol %), CuI (152 mg, 0.8 mmol, 4 mol %), vinyl bromide (30 mL, 1.0 M in THF) and THF (60 mL) at room temperature. Then HN^iPr_2 (10 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (2.45 g, 74% for 2 steps) was used for the next step without purification.

In an oven-dried Schleck flask, $ZnCl_2$ (0.49 g, 3.6 mmol, 0.6 eq.) was added. After changed to an inert atmosphere, $ZnEt_2$ (1.8 mL, 2 M in toluene) and THF (2 mL) were added dropwise. After being stirred for 30 min, toluene (30 mL) was added, and then the aforementioned reddish oil solution (1.00 g in 30 mL toluene, 6 mmol, 1.0 eq.) was added dropwise to the flask at 0 ºC. After being stirred for another 30 min, Schwartz's reagent (2.5 g, 9.68 mmol, 1.6 eq.) was added under an inert atmosphere. After being stirred for 12 h, the solution was quenched by sat. $NaHCO_3$ aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE as the eluent) to yield **1e** (R_f: 0.81 (PE), 248.9 mg, yield = 28%) as a colorless oil [2].



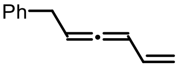
1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dddd, J = 17.0, 10.2, 10.2, 1.0 Hz, 1H), 5.80 (ddt, J = 9.7, 6.1, 2.9 Hz, 1H), 5.35 – 5.26 (m, 1H), 5.15 (dd, J = 17.0, 1.0 Hz, 1H), 4.95 (dd, J = 10.2, 1.0 Hz, 1H), 2.03 (dtd, J = 7.0, 7.0, 2.8 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.36 – 1.17 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 133.8, 114.9, 94.7, 92.5, 31.8, 29.1, 28.9, 28.8, 22.8, 14.2.
HRMS (EI): $[M\cdot]^+$ calculated for $C_{11}H_{18}^+$: 150.1403; found: 150.1403.

To aldehyde **S3** (2.4 g, 20 mmol), ethynylmagnesium chloride solution (60 mL, 0.5 M in THF) was added carefully at -78 °C under an inert atmosphere. The reaction was gradually allowed to warm to room temperature, and stirred for 12 h. The solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol, 2 mol %), CuI (152 mg, 0.8 mmol, 4 mol %), vinyl bromide (30 mL, 1.0 M in THF) and THF (60 mL) at room temperature. Then HN^iPr_2 (10 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (3.10 g, 90% for 2 steps) was used for next step without purification.

In an oven-dried Schleck flask, $ZnCl_2$ (0.49 g, 3.6 mmol, 0.6 eq.) was added. After changed to an inert atmosphere, $ZnEt_2$ (1.8 mL, 2 M in toluene) and THF (2 mL) were added dropwise. After being stirred for 30 min, toluene (30 mL) was added, then the aforementioned reddish oil solution (1.03 g in 30 mL toluene, 6 mmol, 1.0 eq.) was added dropwise to the solution at 0 ºC. After another 30 min, Schwartz's reagent (2.5 g, 9.68 mmol, 1.6 eq.) was added under an inert atmosphere. After being stirred for 12 h, the solution was quenched by sat. $NaHCO_3$ aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE as the eluent) to yield **1f** (R_f: 0.60 (PE), 272.9 mg, yield = 29%) as a colorless oil [2].



1f

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.19 (m, 5H), 6.25 (dddd, J = 17.1, 10.0, 10.0, 0.9 Hz, 1H), 5.96 – 5.86 (m, 1H), 5.60 – 5.49 (m, 1H), 5.23 (dd, J = 17.1, 0.9 Hz, 1H), 5.03 (dd, J = 10.0, 0.9 Hz, 1H), 3.42 (dd, J = 7.3, 2.7 Hz, 2H).

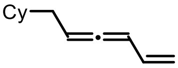
^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.2, 140.6, 133.6, 128.9, 128.8, 126.7, 115.8, 95.3, 92.3, 35.8.

HRMS (EI): $[M\cdot]^+$ calculated for $C_{12}H_{12}^+$: 156.0934; found: 156.0933.

To aldehyde **S4** (2.26 g, 17.9 mmol), ethynylmagnesium chloride solution (60 mL, 0.5 M in THF) was added carefully at -78 °C under an inert atmosphere. The reaction was gradually allowed to warm to room temperature, and stirred for 12 h. The solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol, 2.2 mol %), CuI (152 mg, 0.8 mmol, 4.4 mol %), vinyl bromide (30 mL, 1.0 M in THF) and THF (60 mL) at room temperature. Then HN^iPr_2 (10 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (1.56 g, 49% for 2 steps) was used for next step without purification.

In an oven-dried Schleck flask, $ZnCl_2$ (0.41 g, 3.0 mmol, 0.6 eq.) was added. After changed to an inert atmosphere, $ZnEt_2$ (1.5 mL, 2 M in toluene) and THF (2 mL) were added dropwise. After being stirred for 30 min, toluene (20 mL) was added, then the aforementioned reddish oil solution (0.89 g in 30 mL toluene, 5 mmol, 1.0 eq.) was added dropwise to the solution at 0 ºC. After another 30 min, Schwartz's reagent (2.06 g, 8.0 mmol, 1.6 eq.) was added under an inert atmosphere. After being stirred for 12 h, the solution was quenched by sat. $NaHCO_3$ aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE as the eluent) to yield **1g** (R_f: 0.60 (PE), 0.29 g, yield = 36%) as a colorless oil [2].



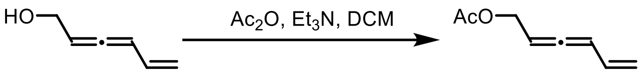
1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dddd, J = 17.1, 10.0, 10.0, 0.9 Hz, 1H), 5.81 – 5.72 (m, 1H), 5.30 – 5.23 (m, 1H), 5.15 (dd, J = 17.1, 0.9 Hz, 1H), 4.94 (dd, J = 10.0, 0.9 Hz, 1H), 1.93 (ddd, J = 9.6, 7.1, 2.6 Hz, 2H), 1.79 – 1.60 (m, 6H), 1.40 – 1.29 (m, 1H), 1.26 – 1.08 (m, 2H), 1.01 – 0.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 133.8, 114.8, 94.1, 90.8, 38.1, 36.8, 33.2, 33.1, 26.7, 26.4.

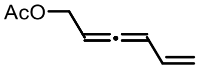
HRMS (EI): $[M\cdot]^+$ calculated for $C_{12}H_{18}^+$: 162.1403; found: 162.1402.

Preparation of substrate 1h:



S1 **1h**

To a stirred of alcohol **S1** (266.8 mg, 2.8 mmol), DCM (30 mL), Et_3N (2.4 mL, 16.9 mmol) and Ac_2O (0.8 mL, 8.4 mmol) was added at 0 °C and stirred for 30 min. The solution was quenched by water and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1h** (R_f: 0.65 (PE : EA = 5 / 1), 324.4 mg, yield = 84%) as a colorless oil.



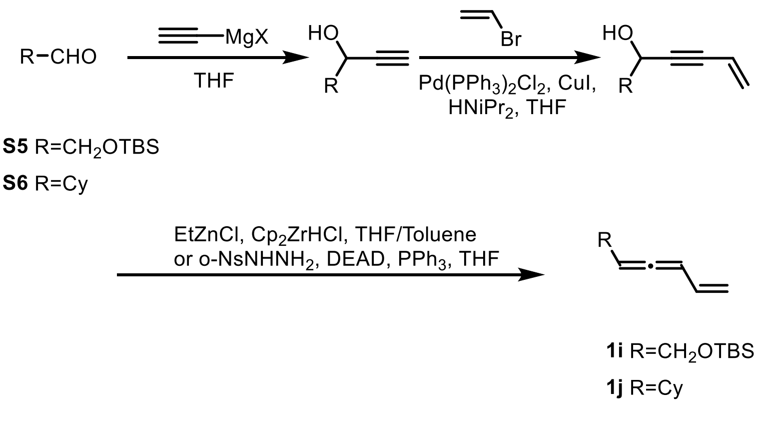
1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (dddd, J = 17.0, 10.2, 10.1, 0.9 Hz, 1H), 5.97 – 5.90 (m, 1H), 5.48 – 5.42 (m, 1H), 5.21 (d, J = 17.0, 0.9 Hz, 1H), 5.02 (d, J = 10.2, 0.9 Hz, 1H), 4.57 (dd, J = 6.7, 2.3 Hz, 2H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 170.8, 131.9, 117.0, 96.5, 88.6, 62.1, 21.0.

HRMS (EI): $[M\cdot]^+$ calculated for $C_8H_{10}O_2^+$: 138.0675; found: 138.0676.

Preparation of substrates 1i-1j:



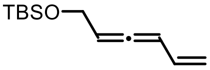
S5 R=CH_2OTBS
S6 R=Cy

1i R=CH_2OTBS
1j R=Cy

To aldehyde **S5** (6.92 g, 40 mmol) in THF (100 mL) solution, ethynylmagnesium chloride solution (120 mL, 0.5 M in THF) was added carefully under an inert atmosphere and warmed to room temperature. After being stirred for 16 h, the solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (393 mg, 0.56 mmol), CuI (213 mg, 1.12 mmol), vinyl bromide (36 mL, 1.0 M in THF) and THF (50 mL) at room temperature. Then HN^iPr_2 (10 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (4.15 g, 46% for 2 steps) was used for next step without purification.

In an oven-dried Schleck flask, PPh_3 (5.24 g, 20.0 mmol, 2.0 eq.) was added. After changed to an inert atmosphere, THF (80 mL) and DEAD (2.9 mL, 20.0 mmol) were added consecutively at -15 °C. After being stirred for 30 min, the aforementioned reddish oil solution (2.26 g in 10 mL THF, 10 mmol, 1.0 eq.) was added dropwise to the solution at -15 °C. After being stirred another 30 min at -15 °C, *o*-$NsNHNH_2$ solution (3.26 g in 10 mL THF, 15.0 mmol, 1.5 eq.) was added under an inert atmosphere and then warmed to room temperature. After being stirred for 18 h, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE as the eluent) to yield **1i** (R_f: 0.29 (PE), 1.27 g, yield = 60%) as a colorless oil [1].



1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (dddd, J =17.1, 10.0, 10.0, 1.0 Hz, 1H), 5.93 – 5.85 (m, 1H), 5.48 – 5.38 (m, 1H), 5.18 (d, J = 17.1, 1.0 Hz, 1H), 4.98 (d, J = 10.0, 1.0 Hz, 1H), 4.22 (dd, J = 6.2, 2.6 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H).

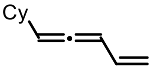
^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 132.7, 116.0, 96.1, 93.4, 61.6, 26.0, 18.5, -4.97, -4.98.

HRMS (ESI): $[M + H]^+$ calculated for $C_{12}H_{23}OSi^+$: 211.1513; found: 211.1509.

To aldehyde **S6** (3.36 g, 30 mmol), ethynylmagnesium bromide solution (72 mL, 0.5 M in THF) was added carefully under an inert atmosphere and warmed to room temperature. After being stirred for 18 h, the solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (420 mg, 0.6 mmol, 2 mol %), CuI (228 mg, 1.2 mmol, 4 mol %), vinyl bromide (33 mL, 1.0 M in THF) and THF (20 mL) at room temperature. Then HN^iPr_2 (15 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (1.22 g, 29% for 2 steps) was used for next step without purification.

In an oven-dried Schleck flask, $ZnCl_2$ (0.34 g, 2.5 mmol, 0.5 eq.) was added. After changed to an inert atmosphere, $ZnEt_2$ (2.5 mL, 1 M in toluene) and THF (2 mL) were added dropwise. After being stirred for 30 min, toluene (25 mL) was added, then the aforementioned reddish oil solution (0.82 g in 25 mL toluene, 5 mmol, 1.0 eq.) was added dropwise to the solution at 0 °C. After another 30 min, Schwartz's reagent (2.06 g, 8 mmol, 1.6 eq.) was added under an inert atmosphere. After being stirred for 16 h, the solution was quenched by sat. $NaHCO_3$ aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE as the eluent) to yield **1j** (R_f: 0.78 (PE), 143.3 mg, yield = 19%) as a colorless oil [2].



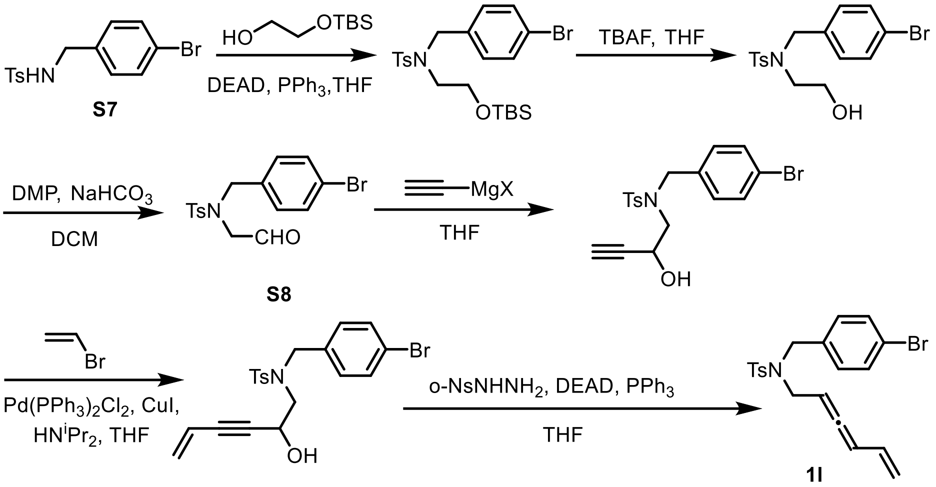
1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dddd, J =17.0, 10.0, 10.0, 1.0 Hz, 1H), 5.87 – 5.80 (m, 1H), 5.34 – 5.27 (m, 1H), 5.15 (d, J = 17.0 Hz, 1H), 4.94 (d, J = 10.0 Hz, 1H), 2.12 – 1.92 (m, 1H), 1.81 – 1.57 (m, 6H), 1.30– 1.18 (m, 2H), 1.14 – 1.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 133.9, 114.8, 98.5, 95.6, 37.4, 33.1, 26.3, 26.11, 26.10.

HRMS (EI): $[M\cdot]^+$ calculated for $C_{11}H_{16}^+$: 148.1247; found: 148.1247.

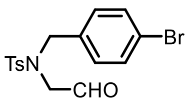
Preparation of substrate 1l:



To a stirred of PPh_3 (5.90 g, 22.5 mmol) in THF (50 mL) solution at 0 °C, DEAD (3.3 mL, 22.5 mmol) was added carefully under an inert atmosphere and warmed to room temperature. After being stirred for 30 min, **S7** (5.1 g, 15 mmol) and 2-((tert-Butyldimethylsilyl)oxy)ethanol (3.17 g, 18 mmol) in THF (15 mL) were added to the above solution and then warmed to room temperature. The reaction was then stirred for 8 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the crude product was used for the next step without further purification.

To a solution of aforementioned product in THF (50 mL), $TBAF\cdot3H_2O$ (9.48 g 30 mmol) was added into at 0 °C. The reaction was then warmed to room temperature and stirred for 12 h. After that, the solution was quenched by water and extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude alcohol was used for the next step without further purification.

To a solution of Dess-Martin periodinane (10.2 g, 24 mmol) and $NaHCO_3$ (4.03 g, 48 mmol) in DCM (30 mL), the alcohol from the previous step in DCM (20 mL) solution was added dropwise. The reaction was then warmed to room temperature and stirred for 2 h. After that, the solution was quenched by water and extracted with DCM. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE : EA = 5 / 1 – 3 / 1 as the eluent) to yield **S8** (R_f: 0.39 (PE : EA = 3 / 1), 4.65 g, yield = 81% for 3 steps) as a white solid.



S8

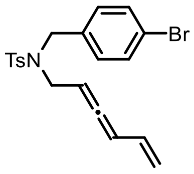
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (t, J = 1.3 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 4.28 (s, 2H), 3.72 (d, J = 1.3 Hz, 2H), 2.45 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 144.4, 135.3, 133.9, 132.2, 130.5, 130.1, 127.5, 122.7, 56.3, 52.5, 21.7.
HRMS (ESI): $[M + H]^+$ calculated for $C_{16}H_{17}BrNO_3S^+$: 382.0107; found: 382.0106.
m.p. = 93 – 95 °C

To aldehyde **S8** (3.82 g, 10 mmol), ethynylmagnesium bromide solution (30 mL, 0.5 M in THF) was added carefully at -78 °C under an inert atmosphere. The reaction was gradually allowed to warm to room temperature, and stirred for 12 h. The solution was quenched by sat. NH_4Cl aq. and extracted with

EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude secondary alcohol was used for the next step without purification.

The aforementioned alcohol was added into the mixture of $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol, 2 mol %), CuI (76 mg, 0.4 mmol, 4 mol %), vinyl bromide (15 mL, 1.0 M in THF) and THF (60 mL) at room temperature. Then HN^iPr_2 (10 mL) was added to the reaction mixture dropwise under an inert atmosphere. The reaction was then stirred for 48 h and the solvent was removed under vacuum. After filtered by a short pad of silica, the reddish oil (1.58 g, 36% for 2 steps) was used for the next step without purification.

In an oven-dried Schleck flask, PPh_3 (1.62 g, 6.2 mmol, 2.0 eq.) was added. After changed to an inert atmosphere, THF (20 mL) and DEAD (0.90 mL, 6.2 mmol) were added consecutively at -15 °C. After being stirred for 30 min, the aforementioned reddish oil solution (1.35 g in 5 mL THF, 3.1 mmol, 1.0 eq.) was added dropwise to the solution at -15 °C. After being stirred another 30 min at -15 °C, *o*-$NsNHNH_2$ solution (1.02 g in 10 mL THF, 4.7 mmol, 1.5 eq.) was added under an inert atmosphere and then warmed to room temperature. After being stirred for 24 h, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 5 / 1 as the eluent) to yield **1l** (R_f: 0.81 (PE : EA = 3 / 1), 385 mg, yield = 30%) as a colorless oil [1].



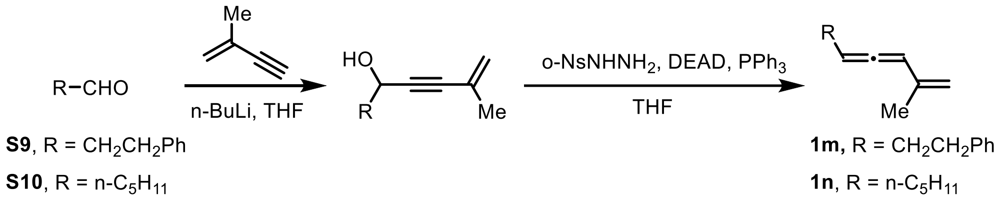
1l

^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 5.98 (ddd, J = 17.0, 10.0, 10.0 Hz, 1H), 5.75 – 5.65 (m, 1H), 5.16 (d, J = 17.0 Hz, 1H), 5.00 (d, J = 10.0 Hz, 1H), 5.00 – 4.91 (m, 1H), 4.32 (s, 2H), 3.85 – 3.70 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 143.7, 137.4, 135.1, 131.8, 131.7, 130.3, 130.0, 127.3, 121.9, 117.1, 95.9, 87.4, 49.8, 46.0, 21.7.

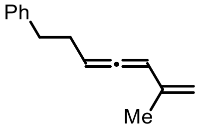
HRMS (ESI): $[M + H]^+$ calculated for $C_{20}H_{21}BrNO_2S^+$: 418.0471; found: 418.0467.

Preparation of substrates 1m-1n:



To a stirred of 2-methylbut-1-en-3-yne (0.86 g, 13 mmol) in THF (20 mL) solution, n-BuLi solution (4.6 mL, 2.4 M in hexanes) was added at -78 °C. After being stirred for 30 min, aldehyde **S9** (1.34 g, 10 mmol) was added carefully under an inert atmosphere and warmed to room temperature. After being stirred for 16 h, the solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was then purified by a short pad of silica, giving a yellow oil (1.72 g, 86%), which was used for the next step without purification.

In an oven-dried Schleck flask, PPh_3 (1.20 g, 4.58 mmol, 1.5 eq.) was added. After changing to an inert atmosphere, THF (29 mL) was added, which was followed by adding DEAD (0.66 mL, 4.56 mmol) dropwise at -15 °C. After being stirred for 15 min, the aforementioned alcohol solution (0.60 g in 1 mL THF, 3 mmol, 1.0 eq.) was added dropwise to the solution at -15 °C. After being stirred another 15 min at -15 °C, *o*-NsNHNH$_2$ (1.0 g, 4.5 mmol, 1.5 eq.) was added under an inert atmosphere and then warmed to room temperature. After being stirred for 16 h, the solvent was removed under vacuum. The residue was purified by flash column chromatograph (PE as the eluent) to yield **1m** (R$_f$: 0.66 (PE), 423.4 mg, yield = 77%) as a colorless oil [1].



1m

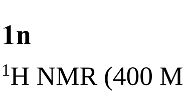
^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 5.91 (dt, J = 6.5, 2.9 Hz, 1H), 5.45 (dt, J = 6.5, 6.5 Hz, 1H), 4.89 (s, 1H), 4.80 (s, 1H), 2.75 (t, J = 7.8 Hz, 2H), 2.43 – 2.28 (m, 2H), 1.70 (s, 3H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ 206.2, 142.2, 140.0, 128.9, 128.7, 126.2, 113.2, 98.3, 93.7, 35.7, 31.1, 19.6.

HRMS (ESI): [M + H]$^+$ calculated for C$_{14}$H$_{17}$$^+$: 185.1325; found: 185.1323.

To a stirred 2-methylbut-1-en-3-yne (0.86 g, 13 mmol) in THF (20 mL) solution at -78 °C, n-BuLi solution (7 mL, 1.6 M in hexanes) was added. After being stirred for 30 min, aldehyde **S10** (1.0 g, 10 mmol) was added carefully under an inert atmosphere and warmed to room temperature. After being stirred for another 16 h, the solution was quenched by sat. NH$_4$Cl aq. and extracted with Et$_2$O. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The residue was purified by a short pad of silica, giving a yellow oil (1.46 g, 88%) which was used for the next step without purification.

In an oven-dried Schleck flask, PPh$_3$ (524 mg, 2 mmol, 2 eq.) was added. After changing to an inert atmosphere, THF (8 mL) and DEAD (0.29 mL, 2 mmol) were added consecutively at -15 °C. After being stirred for 15 min, the aforementioned alcohol solution (166 mg in 1 mL THF, 1 mmol, 1.0 eq.) was added dropwise to the solution at -15 °C. After being stirred another 15 min at -15 °C, *o*-NsNHNH$_2$ (434 mg in THF (1 mL) solution, 2 mmol, 2 eq.) was added under an inert atmosphere and then warmed to room temperature. After being stirred for 16 h, the solvent was removed under vacuum. The residue was purified by flash column chromatograph (PE as the eluent) to yield **1n** (R$_f$: 0.89 (PE), 58.7 mg, yield = 39%) as a colorless oil [1].

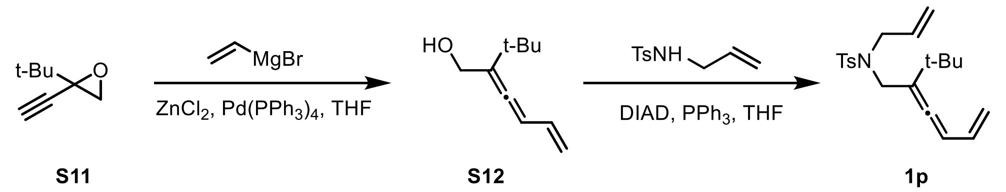


1n

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.89 (dt, J = 7.0, 2.9 Hz, 1H), 5.38 (dt, J = 6.6, 6.6 Hz, 1H), 4.88 (s, 1H), 4.80 (s, 1H), 2.04 (dtd, J = 7.0, 6.6, 2.9 Hz, 2H), 1.78 (s, 3H), 1.46 – 1.38 (m, 2H), 1.37 – 1.20 (m, 4H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 205.9, 139.8, 112.9, 97.7, 94.1, 31.5, 29.01, 28.99, 22.6, 19.8, 14.2.

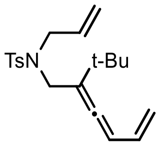
HRMS (EI): $[M\cdot]^+$ calculated for $C_{11}H_{16}^+$: 150.1403; found: 150.1404.



To a stirred solution of $ZnCl_2$ (1.16 g, 8.4 mmol) in THF (3.4 mL), vinyl magnesium bromide solution was added dropwise at 0 °C. **S11** (700 mg, 5.6 mmol) and $Pd(PPh_3)_4$ (129 mg, 2 mol %) in THF (5 mL) were added at -20 °C and then warmed to room temperature. After being stirred for 2 h, the solution was quenched by sat. NH_4Cl aq. and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatograph (PE : EA = 10 / 1 as the eluent) to yield **S12** (339.5 mg, yield = 40%) as a yellow oil [9].

DIAD (0.19 mL, 0.98 mmol) was added into the mixture of alcohol **S12** (98.2 mg, 0.65 mmol), N-allyl-4-methylbenzenesulfonamide (165 mg, 0.78 mmol), PPh_3 (257 mg, 0.98 mmol) and THF (6.5 mL) at 0 °C and then warmed to room temperature and stirred for 4 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1p** (R_f: 0.42 (PE : EA = 10 / 1), 157.3 mg, yield = 71%) as a yellow oil.

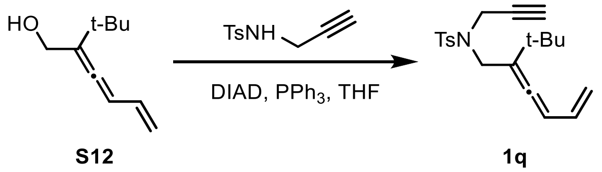
1p



^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.03 (ddd, J = 17.0, 10.3, 10.3 Hz, 1H), 5.68 – 5.45 (m, 2H), 5.22 – 4.98 (m, 3H), 5.01 – 4.85 (m, 1H), 3.96 (dd, J = 16.1, 3.3 Hz, 1H), 3.90 – 3.78 (m, 2H), 3.72 (dd, J = 15.5, 6.8 Hz, 1H), 2.42 (s, 3H), 1.06 (s, 9H).

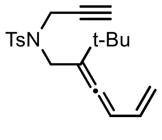
^{13}C NMR (101 MHz, CD_2Cl_2) δ 204.4, 143.6, 138.4, 133.8, 133.3, 130.0, 127.5, 119.1, 115.5, 111.1, 98.7, 49.9, 45.0, 34.0, 29.4, 21.6.

HRMS (ESI): $[M + H]^+$ calculated for $C_{20}H_{28}NO_2S^+$: 346.1835; found: 346.1831.



DIAD (0.24 mL, 1.2 mmol) was added into the mixture of alcohol **S12** (122 mg, 0.8 mmol), 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (201 mg, 0.96 mmol), PPh_3 (314 mg, 1.2 mmol) and THF (8 mL) at 0 °C and then warmed to room temperature and stirred for 16 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1q** (R_f: 0.54 (PE : EA = 10 / 1), 255.6 mg, yield = 93%) as a white powder.

1q

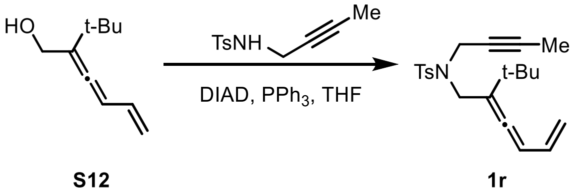


^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.09 (ddd, J = 17.0, 10.1, 10.1 Hz, 1H), 5.84 (dt, J = 10.1, 2.7 Hz, 1H), 5.26 – 5.02 (m, 1H), 4.98 – 4.88 (m, 1H), 4.16 – 4.03 (m, 2H), 3.92 (d, J = 2.7 Hz, 2H), 2.42 (s, 3H), 2.04 (t, J = 2.4 Hz, 1H), 1.11 (s, 9H).

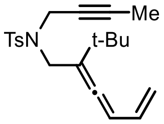
^{13}C NMR (101 MHz, CD_2Cl_2) δ 205.0, 144.1, 136.6, 133.5, 129.9, 128.0, 115.8, 110.1, 98.1, 77.0, 74.0, 45.4, 36.0, 34.1, 29.5, 21.7.

HRMS (ESI): $[M + H]^+$ calculated for $C_{20}H_{26}NO_2S^+$: 344.1679; found: 344.1675.

m.p. = 77 – 80 °C



DIAD (0.24 mL, 1.2 mmol) was added into the mixture of alcohol **S12** (122 mg, 0.8 mmol), N-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (214 mg, 0.96 mmol), PPh_3 (314 mg, 1.2 mmol) and THF (8 mL) at 0 °C and then warmed to room temperature and stirred for 4 h. After that, the solvent was removed under vacuum. The residue was purified by flash column chromatography (PE : EA = 40 / 1 as the eluent) to yield **1r** (R_f: 0.50 (PE : EA = 10 / 1), 257.5 mg, yield = 90%) as a yellow oil.



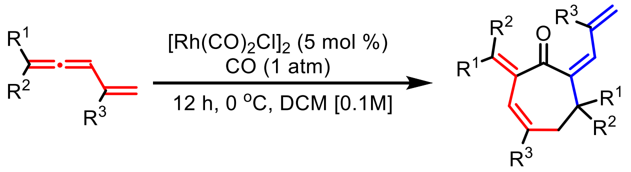
1r

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.11 (ddd, J = 17.0, 10.3, 10.3 Hz, 1H), 5.84 (dt, J = 10.3, 2.6 Hz, 1H), 5.23 – 5.01 (m, 1H), 4.99 – 4.84 (m, 1H), 4.08 – 3.96 (m, 2H), 3.93 – 3.85 (m, 2H), 2.42 (s, 3H), 1.51 (t, J = 2.3 Hz, 3H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 205.2, 143.8, 136.8, 133.6, 129.7, 128.1, 115.6, 110.2, 97.9, 82.1, 71.9, 45.5, 36.6, 34.1, 29.5, 21.6, 3.3.

HRMS (ESI): $[M + H]^+$ calculated for $C_{21}H_{28}NO_2S^+$: 358.1835; found: 358.1829.

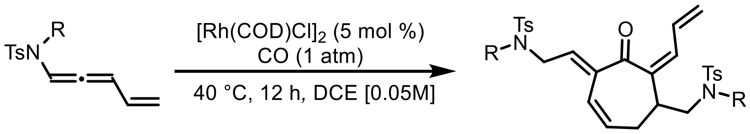
3. General procedure for [4+2+1] cycloaddition



1d-1o **2d-2o**

A solution of substrate (**1d-1o**, 0.3 mmol) in super-dried DCM (1.5 ml) was added to the mixture of $[Rh(CO)_2Cl]_2$ (5.7 mg, 5 mol %) and 1.5 mL DCM. Then CO (1 atm) was bubbled to the solution for 5 minutes and the mixture was stirred at 0 °C (unless specially mentioned). After 12 h, the reaction mixture was concentrated and purified by flash column chromatography on silica gel, affording the cycloaddition product (**2d-2o**). The yield reported for [4+2+1] cycloaddition reaction is the average of two runs.

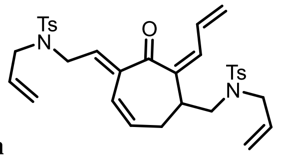
The [4+2+1] reactions for the following substrates were carried out by using the previous optimized reaction conditions of [4+2+1] reaction of ene/yne-ene-allenes (*Angew. Chem. Int. Ed.* **2018**, 57, 15544). Using the general procedure shown above, the reaction yields from both reaction conditions were close to each other. Therefore, we gave the detailed results for the [4+2+1] reaction of **1a-1c** using the conditions indicated in the following reaction scheme.



1a-1c **2a-2c**

A solution of substrate (**1a-1c**, 0.1 mmol) in super-dried DCE (2 ml) was added to the reaction tube with $[Rh(COD)Cl]_2$ (2.5 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes and the mixture was stirred at 40 °C. After 12 h, the mixture was concentrated and purified by flash column chromatography on silica gel to afford the cycloaddition product (**2a-2c**).

4. Products of [4+2+1] cycloaddition



2a

Eluted with PE / EA = 5 / 1 – 3 / 1

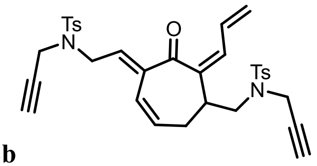
28.6 mg **1a** was converted to 15.0 mg **2a**, yield 50%

2a: yellow oil, TLC R_f : 0.20 (PE / EA = 5 / 1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.67 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.35 – 7.26 (m, 4H), 6.58 (ddd, J = 16.9, 10.6, 10.6 Hz, 1H), 6.32 (t, J = 6.3 Hz, 1H), 6.15 (d, J = 11.6 Hz, 1H), 6.10 (d, J = 11.0 Hz, 1H), 5.93 – 5.83 (m, 1H), 5.71 – 5.60 (m, 1H), 5.57 – 5.43 (m, 1H), 5.25 (d, J = 10.1 Hz, 1H), 5.17 – 5.15 (m, 3H), 5.10 – 5.05 (m, 2H), 4.06 – 3.89 (m, 2H), 3.86 – 3.60 (m, 4H), 3.32 (dd, J = 13.7, 8.7 Hz, 1H), 3.06 (dd, J = 13.7, 6.3 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.60 – 2.52 (m, 1H), 2.42 (s, 3H), 2.42 (s, 3H), 2.23 – 1.93 (m, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 195.3, 144.2, 144.1, 142.8, 139.4, 137.3, 137.2, 135.9, 134.7, 133.5, 133.4, 133.1, 132.1, 130.3, 130.2, 127.62, 127.60, 122.4, 122.3, 119.6, 119.5, 52.1, 51.2, 51.0, 45.1, 41.9, 34.1, 21.68, 21.65.

HRMS (ESI): $[M + H]^+$ calculated for $C_{33}H_{39}N_2O_5S_2^+$: 607.2295; found: 607.2289.



2b

Eluted with PE / EA = 5 / 1

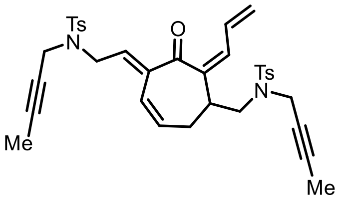
28.6 mg **1b** was converted to 6.4 mg **2b**, yield 21%

2b: yellow oil, TLC R_f : 0.28 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.70 (ddd, J = 16.9, 10.6, 10.6 Hz, 1H), 6.42 (t, J = 6.8 Hz, 1H), 6.25 (d, J = 12.0 Hz, 1H), 6.24 (d, J = 11.0 Hz, 1H), 5.92 (dt, J = 11.0, 5.0 Hz, 1H), 5.40 (d, J = 16.9 Hz, 1H), 5.30 (d, J = 10.6 Hz, 1H), 4.16 – 4.08 (m, 2H), 4.08 – 4.04 (m, 2H), 4.04 – 3.98 (m, 2H), 3.35 (dd, J = 13.8, 8.6 Hz, 1H), 3.22 (dd, J = 13.8, 6.8 Hz, 1H), 3.04 – 2.91 (m, 1H), 2.63 (ddd, J = 17.6, 4.7, 4.7 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 2.32 – 2.17 (m, 1H), 2.14 (t, J = 2.3 Hz, 1H), 2.07 (t, J = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 194.9, 144.6, 144.4, 141.9, 140.5, 136.0, 135.9, 135.6, 134.9, 133.4, 132.1, 130.1, 130.0, 128.1, 128.0, 123.0, 122.0, 76.9, 76.7, 74.5, 74.4, 49.8, 44.7, 40.8, 37.7, 37.3, 34.7, 21.69, 21.67.

HRMS (ESI): $[M + H]^+$ calculated for $C_{33}H_{35}N_2O_5S_2^+$: 603.1982; found: 603.1980.



2c

Eluted with PE / EA = 5 / 1

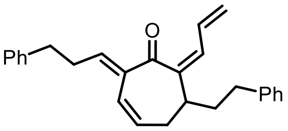
30.2 mg **1c** was converted to 13.4 mg **2c**, yield 42%

2c: colorless oil, TLC R_f : 0.16 (PE / EA = 5 / 1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.71 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.69 (ddd, J = 16.9, 10.3, 10.1 Hz, 1H), 6.43 (t, J = 6.9 Hz, 1H), 6.24 (d, J = 11.0 Hz, 1H), 6.22 (d, J = 11.4 Hz, 1H), 5.93 – 5.88 (m, 1H), 5.38 (d, J = 16.9 Hz, 1H), 5.28 (dd, J = 10.1, 1.4 Hz 1H), 4.07 – 3.99 (m, 5H), 3.94 – 3.87 (m, 1H), 3.32 (dd, J = 13.6, 8.9 Hz, 1H), 3.17 (dd, J = 13.6, 6.4 Hz, 1H), 3.01 – 2.81 (m, 1H), 2.63 (ddd, J = 17.4, 4.7, 4.7 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.29 – 2.18 (m, 1H), 1.55 (t, J = 2.3 Hz, 3H), 1.50 (t, J = 2.3 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 195.0, 144.3, 144.1, 142.4, 140.4, 136.3, 136.2, 135.34, 135.32, 133.6, 132.1, 129.9, 129.8, 128.2, 122.7, 122.2, 82.7, 82.4, 71.91, 71.88, 49.9, 44.8, 40.9, 38.2, 38.0, 34.8, 21.7, 21.6, 3.4, 3.3.

HRMS (ESI): $[M + H]^+$ calculated for $C_{35}H_{39}N_2O_5S_2^+$: 631.2295; found: 631.2294.



2d

Reaction time: 12 h, Eluted with PE / EA = 40 / 1

Run 1: 51.1 mg **1d** was converted to 37.8 mg **2d**, yield 69%. Run 2: 51.1 mg **1d** was converted to 38.8 mg **2d**, yield 70%.

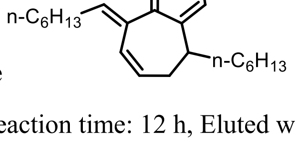
The average yield of two runs was 70%.

2d: colorless oil, TLC R_f : 0.32 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.21 – 7.11 (m, 6H), 6.84 – 6.68 (m, 2H), 6.17 (d, J = 11.0 Hz, 1H), 6.12 (d, J = 12.0 Hz, 1H), 5.72 (ddd, J = 11.0, 4.5, 4.5 Hz, 1H), 5.34 (d, J = 17.0 Hz, 1H), 5.25 (d, J = 10.1 Hz, 1H), 2.87 – 2.69 (m, 2H), 2.69 – 2.44 (m, 6H), 2.24 – 2.09 (m, 1H), 1.98 – 1.82 (m, 1H), 1.82 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 145.4, 141.9, 141.6, 141.1, 137.6, 133.5, 133.1, 130.1, 128.46, 128.45, 128.44, 128.42, 126.1, 125.9, 122.3, 121.2, 40.9, 38.2, 35.5, 34.7, 33.6, 30.5.

HRMS (ESI): $[M + H]^+$ calculated for $C_{27}H_{29}O^+$: 369.2213; found: 369.2218.



2e

Reaction time: 12 h, Eluted with PE - PE / EA = 40 / 1

Run 1: 45.1 mg **1e** was converted to 37.1 mg **2e**, yield 75%. Run 2: 44.8 mg **1e** was converted to 35.4 mg **2e**, yield 72%.

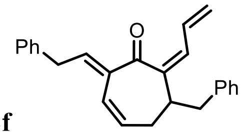
The average yield of two runs was 74%.

2e: yellow oil, TLC *R*$_f$: 0.69 (PE / EA = 20 / 1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.75 – 6.64 (m, 2H), 6.19 (d, *J* = 12.6 Hz, 1H), 6.11 (d, *J* = 11.0 Hz, 1H), 5.81 – 5.71 (m, 1H), 5.30 (dd, *J* = 16.9, 1.9 Hz, 1H), 5.19 (dd, *J* = 10.0, 1.3 Hz, 1H), 2.61 – 2.34 (m, 2H), 2.24 (dt, *J* = 7.5, 7.5 Hz, 2H), 2.18 – 2.08 (m, 1H), 1.59 – 1.51 (m, 1H), 1.52 – 1.40 (m, 3H), 1.35 – 1.14 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.7, 146.7, 143.4, 137.1, 133.7, 132.4, 130.1, 122.7, 120.7, 42.1, 37.9, 34.0, 31.82, 31.77, 29.4, 29.3, 28.67, 28.65, 27.6, 22.74, 22.72, 14.206, 14.202.

HRMS (ESI): [M + H]$^+$ calculated for $C_{23}H_{37}O^+$: 329.2839; found: 329.2839.



2f

Reaction time: 12 h, Eluted with PE - PE / EA = 40 / 1

Run 1: 46.6 mg **1f** was converted to 25.8 mg **2f**, yield 51%. Run 2: 46.8 mg **1f** was converted to 27.2 mg **2f**, yield 53%.

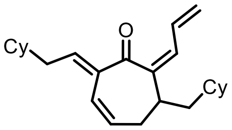
The average yield of two runs was 52%.

2f: yellow oil, TLC *R*$_f$: 0.66 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.36 – 7.12 (m, 10H), 6.80 (t, *J* = 7.8 Hz, 1H), 6.70 (ddd, *J* = 16.9, 11.0, 10.1 Hz, 1H), 6.39 (dd, *J* = 11.9, 1.5 Hz, 1H), 6.17 (d, *J* = 11.1 Hz, 1H), 5.90 – 5.83 (m, 1H), 5.33 (dd, *J* = 16.9, 1.5 Hz, 1H), 5.22 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.60 (d, *J* = 7.8 Hz, 2H), 2.98 – 2.82 (m, 2H), 2.81 – 2.67 (m, 1H), 2.53 – 2.41 (m, 1H), 2.29 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ 196.2, 146.1, 140.7, 140.3, 139.3, 137.9, 133.9, 133.4, 131.3, 129.5, 129.1, 129.0, 128.7, 126.8, 126.6, 122.8, 121.2, 44.2, 40.5, 36.9, 34.9.

HRMS (ESI): [M + H]$^+$ calculated for $C_{25}H_{25}O^+$: 341.1900; found: 341.1901.



2g

Reaction time: 12 h, Eluted with PE / EA = 40 / 1

Run 1: 48.5 mg **1g** was converted to 31.3 mg **2g**, yield 59%. Run 2: 48.3 mg **1g** was converted to 29.6 mg **2g**, yield 56%.

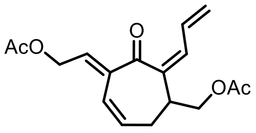
The average yield of two runs was 58%.

2g: colorless oil, TLC *R*$_f$: 0.54 (PE / EA = 20 / 1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.78 – 6.66 (m, 2H), 6.19 (d, *J* = 12.0 Hz, 1H), 6.11 (d, *J* = 11.0 Hz, 1H), 5.78 – 5.68 (m, 1H), 5.30 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.19 (dd, *J* = 10.0, 1.5 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.51 – 2.43 (m, 1H), 2.20 – 1.96 (m, 3H), 1.78 – 1.56 (m, 10H), 1.56 – 1.40 (m, 2H), 1.38 – 1.10 (m, 8H), 1.03 – 0.85 (m, 2H), 0.87 – 0.77 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.5, 146.6, 142.4, 137.6, 133.8, 132.5, 130.0, 122.8, 120.7, 41.6, 38.5, 38.4, 38.1, 36.4, 34.9, 33.6, 33.495, 33.492, 33.47, 26.7, 26.5, 26.4, 26.3.

HRMS (ESI): [M + H]$^+$ calculated for $C_{25}H_{37}O^+$: 353.2839; found: 353.2838.



2h

Reaction time: 12 h, Eluted with PE / EA = 10 / 1

Run 1: 41.2 mg **1h** was converted to 23.7 mg **2h**, yield 52%. Run 2: 41.4 mg **1h** was converted to 26.1 mg **2h**, yield 57%.

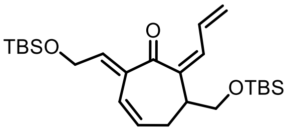
The average yield of two runs was 55%.

2h: colorless oil, TLC R_f : 0.19 (PE / EA = 5 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (ddd, J = 16.9, 10.5, 10.5 Hz, 1H), 6.57 (t, J = 6.2 Hz, 1H), 6.23 (d, J = 11.1 Hz, 1H), 6.17 (d, J = 12.1 Hz, 1H), 5.95 – 5.75 (m, 1H), 5.39 (d, J = 16.9 Hz, 1H), 5.32 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 6.2 Hz, 2H), 4.25 – 3.97 (m, 2H), 3.04 – 2.93 (m, 1H), 2.66 – 2.45 (m, 1H), 2.32 – 2.17 (m, 1H), 2.09 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 171.0, 170.8, 140.8, 138.6, 135.7, 135.1, 133.1, 131.3, 123.4, 121.8, 65.7, 61.0, 40.4, 34.5, 21.0, 20.9.

HRMS (ESI): $[M + H]^+$ calculated for $C_{17}H_{25}O_5^+$: 305.1384; found: 305.1383.



2i

Reaction time: 12 h, Eluted with PE / EA = 40 / 1

Run 1: 62.5 mg **1i** was converted to 33.0 mg **2i**, yield 50%. Run 2: 62.7 mg **1i** was converted to 34.1 mg **2i**, yield 51%.

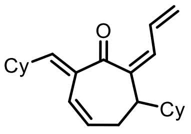
The average yield of two runs was 51%.

2i: colorless oil, TLC R_f : 0.24 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.58 (m, 2H), 6.18 (d, J = 11.0 Hz, 1H), 6.11 (d, J = 11.9 Hz, 1H), 5.87 (ddd, J = 11.0, 5.1, 5.1 Hz, 1H), 5.34 – 5.27 (m, 1H), 5.22 (dd, J = 10.0, 1.3 Hz, 1H), 4.40 (d, J = 5.7 Hz, 2H), 3.70 (dd, J = 10.0, 5.4 Hz, 1H), 3.61 (dd, J = 9.8, 8.3 Hz, 1H), 2.84 – 2.67 (m, 1H), 2.58 (ddd, J = 16.9, 4.8, 4.8 Hz, 1H), 2.29 – 2.11 (m, 1H), 0.90 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 143.5, 141.3, 136.4, 134.0, 133.5, 131.3, 122.6, 121.5, 65.6, 60.7, 45.0, 33.1, 26.1, 26.0, 18.44, 18.40, -5.08, -5.09, -5.25, -5.32.

HRMS (ESI): $[M + H]^+$ calculated for $C_{25}H_{45}O_3Si_2^+$: 449.2902; found: 449.2902.



2j

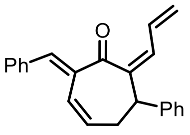
Reaction time: 12 h, Eluted with PE / EA = 10 / 1

Run 1: 44.3 mg **1j** was converted to 24.6 mg **2j**, yield 51%. Run 2: 44.2 mg **1j** was converted to 24.5 mg **2j**, yield 51%.

The average yield of two runs was 51%.

2j: yellow oil, TLC *R*$_f$: 0.50 (PE / EA = 20 / 1)

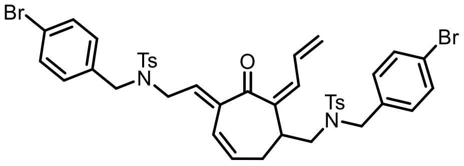
^{1}H NMR (600 MHz, CD_2Cl_2) *δ* 6.55 – 6.46 (m, 2H), 6.27 (d, *J* = 11.7 Hz, 1H), 6.02 (d, *J* = 11.2 Hz, 1H), 5.86 – 5.73 (m, 1H), 5.25 (dd, *J* = 16.9, 1.9 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.9 Hz, 1H), 2.45 – 2.34 (m, 2H), 2.30 – 2.22 (m, 2H), 1.86 – 1.79 (m, 1H), 1.78 – 1.59 (m, 9H), 1.48 – 1.39 (m, 1H), 1.36 – 1.08 (m, 8H), 0.98 – 0.76 (m, 2H).
^{13}C NMR (151 MHz, CD_2Cl_2) *δ* 197.5, 147.43, 147.39, 136.2, 133.9, 132.6, 130.6, 123.6, 119.8, 50.5, 40.9, 37.8, 33.0, 32.4, 32.1, 31.9, 31.2, 26.87, 26.86, 26.82, 26.3, 26.0, 25.9.
HRMS (ESI): [M + H]$^+$ calculated for $C_{23}H_{33}O^+$: 325.2526; found: 325.2525.



2k

Reaction time: 24 h (room temperature), (10 mol % $[Rh(CO)_2Cl]_2$), Eluted with PE / EA = 40 / 1
Run 1: 42.6 mg **1k** was converted to 32.7 mg **2k**, yield 70%. Run 2: 42.6 mg **1k** was converted to 34.5 mg **2k**, yield 74%.
The average yield of two runs was 72%.
2k: yellow oil, TLC *R*$_f$: 0.27 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) *δ* 7.52 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.30 (m, 6H), 7.22 – 7.18 (m, 1H), 6.77 (ddd, *J* = 16.9, 10.9, 10.1 Hz, 1H), 6.56 – 6.36 (m, 1H), 6.21 – 6.02 (m, 2H), 5.27 (d, *J* = 16.9, 1.2 Hz, 1H), 5.23 (dd, *J* = 10.1, 1.9 Hz, 1H), 4.13 (dd, *J* = 9.7, 4.7 Hz, 1H), 2.93 – 2.62 (m, 2H).
^{13}C NMR (101 MHz, CD_2Cl_2) *δ* 197.0, 146.4, 143.0, 137.7, 137.1, 136.1, 136.0, 133.9, 131.6, 131.1, 129.4, 128.9, 128.7, 128.0, 127.0, 125.6, 121.9, 48.4, 36.5.
HRMS (ESI): [M + H]$^+$ calculated for $C_{23}H_{21}O^+$: 313.1587; found: 313.1586.

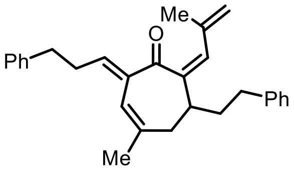


2l

Reaction time: 12 h (0 ºC) then 24 h (room temperature), Eluted with PE / EA = 10 / 1
Run 1: 125.4 mg **2l** was converted to 72.6 mg **2l**, yield 56%. Run 2: 125.4 mg **2l** was converted to 71.8 mg **2l**, yield 55%.
The average yield of two runs was 56%.
2l: yellow oil, TLC *R*$_f$: 0.37 (PE / EA = 3 / 1)

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.71 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.30 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.53 – 6.39 (m, 1H), 6.16 (t, *J* = 6.9 Hz, 1H), 5.82 (d, *J* = 11.1 Hz, 1H), 5.82 (d, *J* = 11.1 Hz, 1H), 5.65 (dt, *J* = 11.0, 5.2 Hz, 1H), 5.26 (d, *J* = 16.0 Hz, 1H), 5.26 (d, *J* = 11.1 Hz, 1H), 4.31 – 4.23 (m, 2H), 4.23

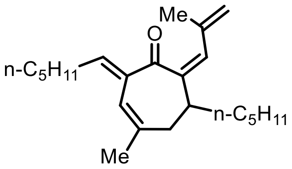
– 4.15 (m, 2H), 3.86 (d, *J* = 6.9 Hz, 2H), 3.33 (dd, *J* = 14.3, 8.3 Hz, 1H), 3.00 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.69 – 2.55 (m, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.34 (ddd, *J* = 16.9, 4.9, 4.9 Hz, 1H), 2.01 – 1.87 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 144.0, 143.9, 141.8, 138.9, 136.8, 136.5, 135.5, 134.78, 134.76, 134.7, 132.9, 132.0, 131.8, 131.6, 130.3, 130.2, 130.1, 130.0, 127.38, 127.36, 122.6, 122.1, 122.0, 121.8, 53.2, 52.3, 51.1, 44.7, 41.8, 33.6, 21.7, 21.6.
HRMS (ESI): $[M + NH_4]^+$ calculated for $C_{41}H_{44}Br_2N_3O_5S_2^+$: 880.1084; found: 880.1082.



2m

Reaction time: 12 h, Eluted with PE / EA = 10 / 1
Run 1: 55.0 mg **1m** was converted to 43.0 mg **2m**, yield 73%. Run 2: 55.0 mg **1m** was converted to 42.2 mg **2m**, yield 71%.
The average yield of two runs was 72%.
2m: yellow oil, TLC R_f : 0.29 (PE / EA = 10 / 1)

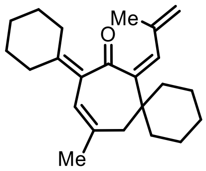
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 – 7.22 (m, 4H), 7.21 – 7.10 (m, 6H), 6.53 (t, *J* = 7.6 Hz, 1H), 6.05 (s, 1H), 5.82 (s, 1H), 4.90 (s, 1H), 4.89 (s, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.72 – 2.60 (m, 1H), 2.62 – 2.44 (m, 4H), 2.20 – 2.01 (m, 2H), 1.86 (s, 3H), 1.81 – 1.67 (m, 2H), 1.64 (s, 3H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.7, 145.6, 142.6, 141.74, 141.71, 141.0, 139.2, 138.4, 130.6, 128.79, 128.78, 128.73, 128.69, 126.4, 126.1, 119.9, 118.5, 46.0, 38.9, 37.3, 35.0, 33.7, 30.6, 25.7, 21.5.
HRMS (ESI): $[M + H]^+$ calculated for $C_{29}H_{31}O^+$: 397.2526; found: 397.2533.



2n

Reaction time: 12 h, Eluted with PE / EA = 40 / 1
Run 1: 45.0 mg **1n** was converted to 32.5 mg **2n**, yield 66%. Run 2: 45.0 mg **1n** was converted to 34.5 mg **2n**, yield 70%.
The average yield of two runs was 68%.
2n: yellow oil, TLC R_f : 0.65 (PE / EA = 20 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (t, *J* = 7.7 Hz, 1H), 6.09 (s, 1H), 5.79 (s, 1H), 4.90 (s, 1H), 4.90 – 4.85 (s, 1H), 2.64 – 2.46 (m, 1H), 2.24 – 2.12 (m, 2H), 2.10 (d, *J* = 8.4 Hz, 2H), 1.89 (s, 3H), 1.68 (s, 3H), 1.53 – 1.41 (m, 4H), 1.34 – 1.23 (m, 10H), 0.92 – 0.75 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 145.8, 141.3, 140.4, 139.9, 138.5, 130.0, 119.8, 118.4, 46.6, 38.4, 35.6, 31.9, 31.7, 28.5, 28.4, 27.1, 25.7, 22.7, 22.6, 21.4, 14.2, 14.1.
HRMS (ESI): $[M + H]^+$ calculated for $C_{23}H_{37}O^+$: 329.2839; found: 329.2838.



2o

Reaction time: 12 h (0 ºC) then 24 h (room temperature), Eluted with PE / EA = 40 / 1

Run 1: 50.2 mg **1o** was converted to 18.3 mg **2o**, yield 34%. Run 2: 50.0 mg **1o** was converted to 17.5 mg **2o**, yield 32%.

The average yield of two runs was 33%.

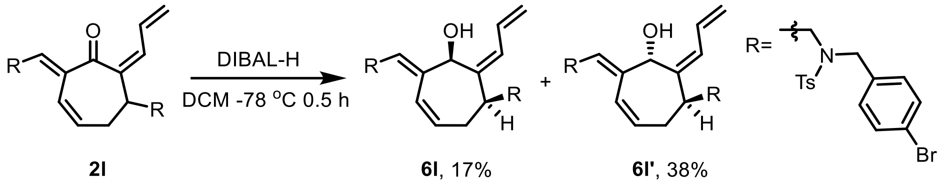
2o: yellow oil, TLC R_f : 0.30 (PE / EA = 20 / 1)

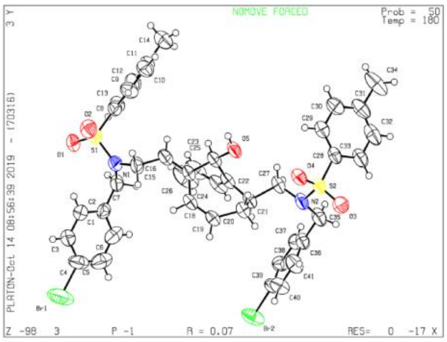
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (s, 1H), 5.76 (s, 1H), 4.84 (s, 1H), 4.81 (s, 1H), 2.67 – 2.51 (m, 2H), 2.29 – 2.23 (m, 2H), 2.19 (s, 2H), 1.87 (s, 3H), 1.71 (s, 3H), 1.69 – 1.43 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 153.1, 151.9, 141.4, 138.5, 133.0, 124.2, 122.9, 116.5, 48.2, 36.7, 35.3, 32.1, 31.5, 28.5, 28.3, 26.9, 26.6, 26.1, 22.3, 22.1.

HRMS (ESI): $[M + H]^+$ calculated for $C_{23}H_{33}O^+$: 325.2526; found: 325.2527.

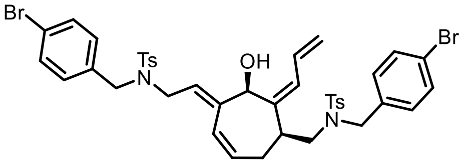
5. Determination of the structure of 2l through further transformation





6l, CCDC: 2031622

To a stirred of **2l** (106.3 mg, 0.123 mmol) in DCM (5 mL) at -78 °C, DIBAL-H solution (0.5 mL, 1 M in hexanes) was added carefully under an inert atmosphere. After being stirred for 0.5 h at -78 °C, the solution was quenched by sat. potassium sodium tartrate solution and extracted with Et$_2$O. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatograph (PE / EA = 5 / 1) to yield **6l** (R$_f$: 0.23 (PE / EA = 3 / 1), 17.2 mg, 17%) and **6l'** (R$_f$: 0.16 (PE / EA = 3 / 1), 40.3 mg, 38%).



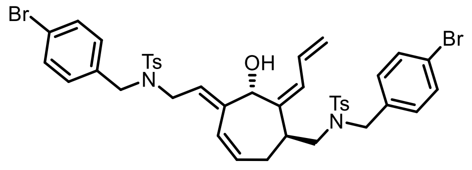
6l

White solid, m.p. = 98 – 100 °C

^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 4H), 7.35 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.26 (ddd, J = 16.9, 10.7, 10.7 Hz, 1H), 5.74 (d, J = 11.7 Hz, 1H), 5.70 – 5.59 (m, 1H), 5.47 (d, J = 11.2 Hz, 1H), 5.18 (t, J = 6.9 Hz, 1H), 5.10 (d, J = 16.9 Hz, 1H), 5.07 (d, J = 10.7 Hz, 1H), 4.96 (s, 1H), 4.30 (d, J = 15.1 Hz, 1H), 4.25 (d, J = 15.1 Hz, 1H), 4.20 (d, J = 15.3 Hz, 1H), 4.09 (d, J = 15.3 Hz, 1H), 3.83 (dd, J = 16.3, 6.8 Hz, 1H), 3.76 (dd, J = 16.3, 7.5 Hz, 1H), 3.29 (dd, J = 14.1, 7.5 Hz, 1H), 3.23 (dd, J = 14.1, 7.4 Hz, 1H), 2.52 – 2.46 (m, 2H), 2.45 (s, 3H), 2.43 (s, 3H), 2.14 – 2.04 (m, 1H), 1.83 (s, 1H).

^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 144.3, 144.1, 142.5, 140.6, 137.4, 137.2, 136.2, 136.0, 132.997, 132.994, 131.9, 131.7, 130.9, 130.6, 130.5, 130.3, 130.2, 127.582, 127.577, 125.9, 124.1, 122.0, 121.9, 118.5, 75.6, 55.2, 53.3, 51.0, 45.4, 45.0, 29.6, 21.72, 21.66.

HRMS (ESI): [M + NH$_4$]$^+$ calculated for C$_{41}$H$_{46}$Br$_2$N$_3$O$_5$S$_2$$^+$: 882.1240; found: 882.1252.



6l’

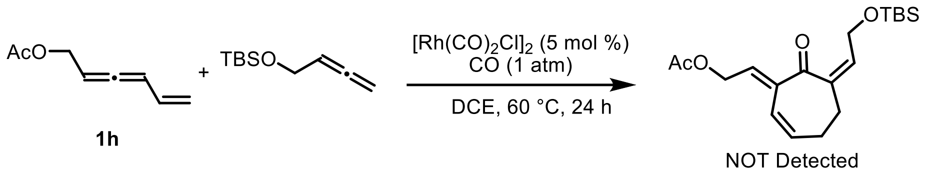
White solid, m.p. = 71 – 73 ºC

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 4H), 7.35 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.74 – 6.63 (m, 1H), 5.74 (d, J = 12.0 Hz, 1H), 5.50 (d, J = 11.2 Hz, 1H), 5.46 – 5.40 (m, 1H), 5.36 – 5.33 (m, 1H), 5.06 (d, J = 17.1 Hz, 1H), 5.05 (d, J = 9.8 Hz, 1H), 4.86 (s, 1H), 4.30 (d, J = 15.2 Hz, 1H), 4.25 (d, J = 15.2 Hz, 1H), 4.15 (d, J = 15.2 Hz, 1H), 4.10 (d, J = 15.2 Hz, 1H), 3.83 (dd, J = 16.1, 6.6 Hz, 1H), 3.76 (dd, J = 16.1, 7.8 Hz, 1H), 3.20 (dd, J = 14.2, 8.5 Hz, 1H), 2.97 (dd, J = 14.2, 6.6 Hz, 1H), 2.59 – 2.48 (m, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.24 (s, 1H), 2.23 – 2.18 (m, 1H), 1.90 – 1.80 (m, 1H).

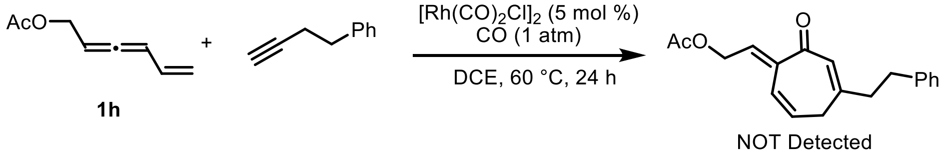
^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.3, 144.1, 142.2, 141.7, 137.5, 136.8, 136.1, 135.9, 132.9, 132.0, 131.9, 130.8, 130.5, 130.30, 130.25, 130.2, 130.1, 127.54, 127.51, 124.3, 122.1, 121.8, 120.5, 118.3, 71.8, 52.9, 52.8, 50.5, 44.5, 42.4, 31.7, 21.69, 21.66.

HRMS (ESI): $[M + NH_4]^+$ calculated for $C_{41}H_{46}Br_2N_3O_5S_2^+$: 882.1240; found: 882.1240.

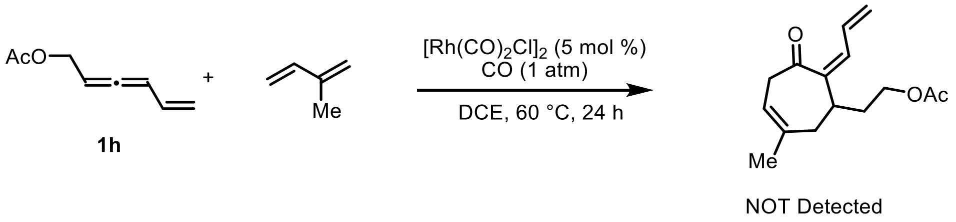
6. Other tests of cross-[4+2+1] and [4+2] cycloadditions



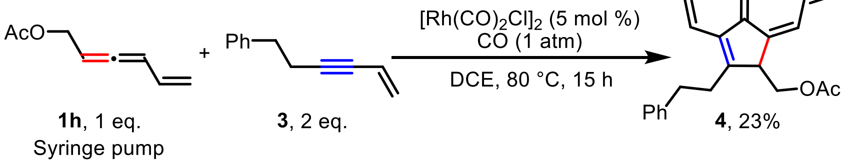
A solution of **1h** (27.6 mg, 0.2 mmol, 1 eq.) and (buta-2,3-dien-1-yloxy)(tert-butyl)dimethylsilane (73.6 mg, 0.4 mmol, 2 eq.) in super-dried DCE (2 ml) was added to the reaction tube with [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes, the mixture was stirred at 60 °C for 24 h. No desired [4+2+1] product was detected.



A solution of **1h** (27.6 mg, 0.2 mmol, 1 eq.) and 4-phenyl-1-butyne (52.0 mg, 0.4 mmol, 2 eq.) in super-dried DCE (2 ml) was added to the reaction tube with [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes, the mixture was stirred at 60 °C for 24 h. No desired [4+2+1] product was detected.

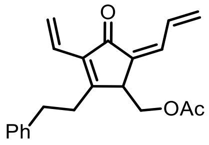


A solution of **1h** (27.6 mg, 0.2 mmol, 1 eq.) and isoprene (0.1 mL, 1.0 mmol, 5 eq.) in super-dried DCE (2 ml) was added to the reaction tube with [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes, the mixture was stirred at 60 °C for 24 h. No desired [4+2+1] product was detected.



A solution of **3** (62.4 mg, 0.4 mmol, 2 eq.) in super-dried DCE (2 ml) was added to the reaction tube with [Rh(CO)$_2$Cl]$_2$ (3.9 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes. After that, **1h** (27.6 mg, 0.2 mmol, 1 eq.) in DCE (8 mL) was added by the syringe pump for 4 h at 80 °C. After being stirred for 15 h at 80 °C, the reaction mixture was cooled down and then concentrated and purified by preparative thin layer chromatography (PE / EA = 20 / 1) to give a yellow oil **4**, (R_f: 0.53 (PE / EA =

20 / 1), 14.9 mg, 23%). The structure was determined by 2D-NMR.



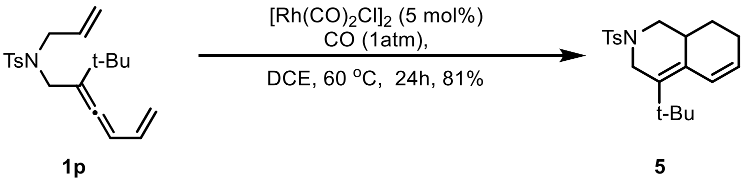
4

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (ddd, *J* = 16.8, 10.7, 10.7 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H). 6.48 (d, *J* = 11.0 Hz, 1H), 6.41 (dd, *J* = 17.7, 11.0 Hz, 1H), 6.34 (dd, *J* = 17.7, 2.9 Hz, 1H), 5.54 (d, *J* = 17.4 Hz, 1H), 5.52 (d, *J* = 9.7 Hz, 1H), 5.45 (dd, *J* = 11.1, 2.8 Hz, 1H), 4.31 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.28 (dd, *J* = 11.4, 5.3 Hz, 1H), 3.37 (t, *J* = 4.9 Hz, 1H), 3.04 – 2.96 (m, 1H) 2.96 – 2.86 (m, 1H), 2.83 – 2.76 (m, 1H), 2.76 – 2.66 (m, 1H), 2.03 (s, 3H).

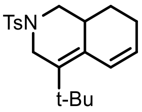
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 170.9, 165.6, 140.5, 139.5, 136.0, 133.6, 132.5, 128.8, 128.3, 126.7, 126.3, 125.6, 121.0, 64.5, 44.8, 34.1, 30.4, 21.0.

HRMS (ESI): $[M + H]^+$ calculated for $C_{21}H_{23}O_3^+$: 323.1642; found: 323.1639.

The following reaction was initially designed for the synthesis of [4+2+1] product, but a [4+2] product was generated unexpectedly.



A solution of substrate **1p** (34.6 mg, 0.1 mmol) in super-dried DCE (2 ml) was added to the reaction tube with $[Rh(CO)_2Cl]_2$ (1.9 mg, 5 mol %). Then CO (1 atm) was bubbled to the solution for 5 minutes and the mixture was stirred at 60 °C. After 24 h, the reaction was complete; the mixture was concentrated and purified by flash column chromatography (PE / EA = 40 / 1) on silica gel to afford the [4+2] cycloaddition product **5** (yellow oil, R*f*: 0.23 (PE / EA = 20 / 1), 28.0 mg, 81%).



5

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 10.3 Hz, 1H), 5.92 – 5.52 (m, 1H), 4.03 (d, *J* = 16.9 Hz, 1H), 3.72 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.13 (d, *J* = 16.9 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.43 (s, 3H), 2.28 – 2.06 (m, 2H), 1.98 – 1.92 (m, 1H), 1.78 – 1.64 (m, 1H), 1.19 – 1.15 (m, 1H), 1.17 (s, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.1, 134.0, 133.3, 130.0, 129.4, 128.2, 128.1, 126.2, 49.0, 47.5, 36.5, 35.3, 30.5, 27.4, 25.5, 21.7.

HRMS (ESI): $[M + H]^+$ calculated for $C_{20}H_{28}NO_2S^+$: 346.1835; found: 346.1834.

7. References

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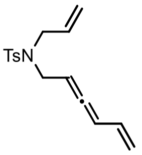
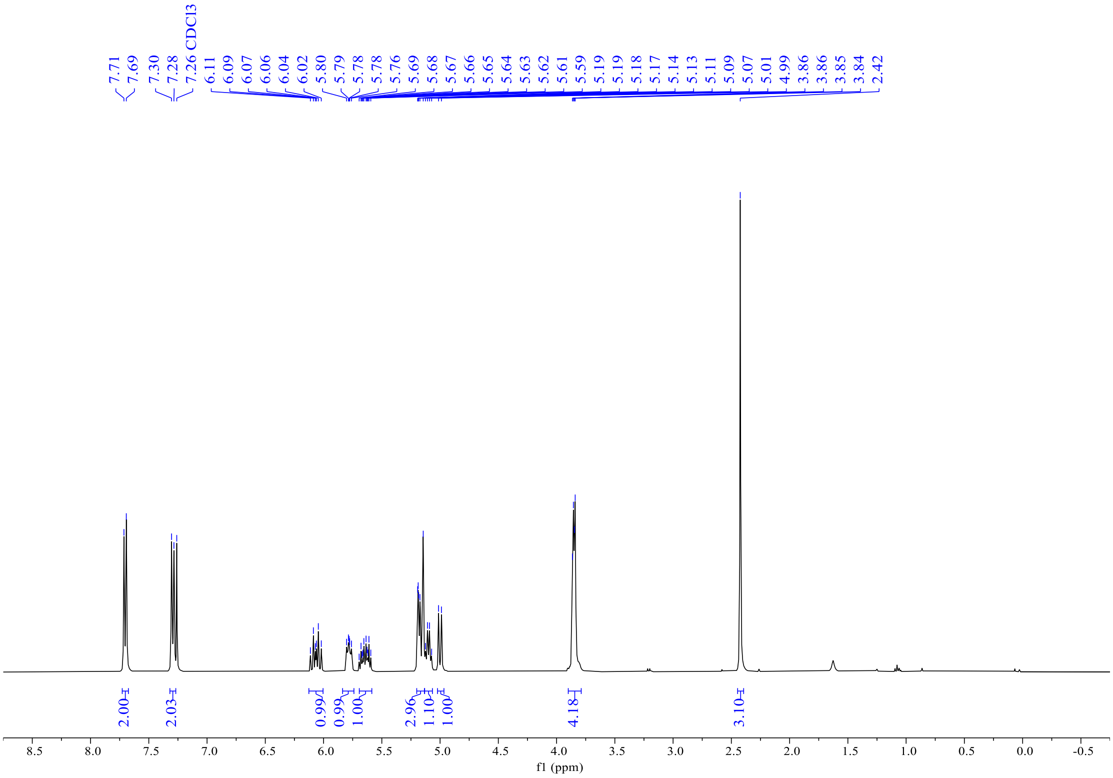
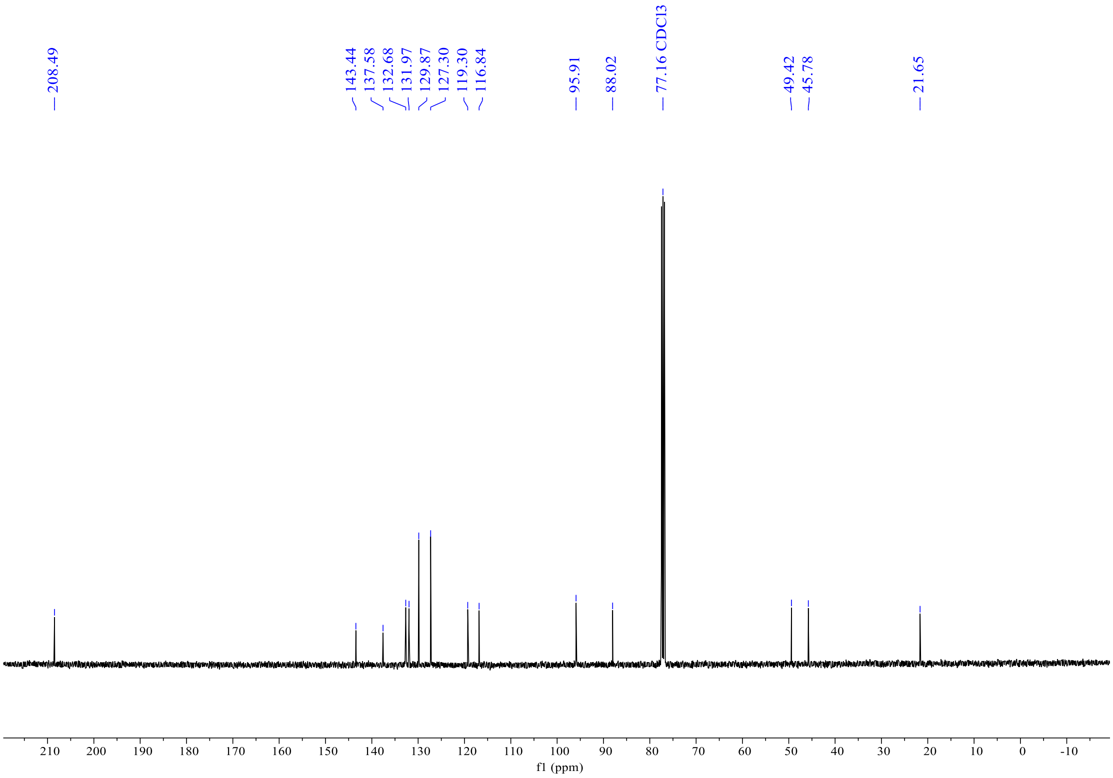
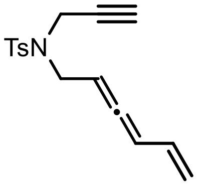
8. NMR spectra of new compounds



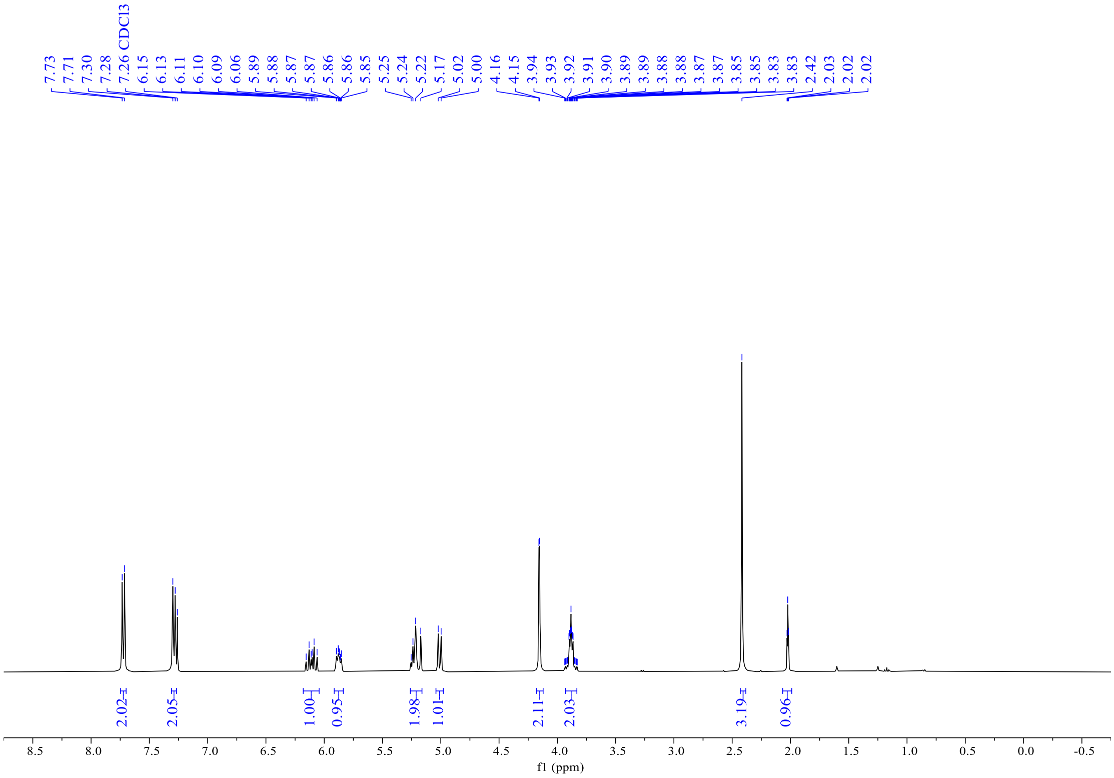
1a






TsN

1b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7.30
7.28
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6.15
6.13
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6.10
6.09
6.06
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5.88
5.87
5.87
5.86
5.86
5.85
5.25
5.24
5.22
5.17
5.02
5.00
4.16
4.15
3.94
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3.92
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3.88
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3.87
3.85
3.85
3.83
3.83
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2.03
2.02
2.02
2.02
2.05
1.00
0.95
1.98
1.01
2.11
2.03
3.19
0.96
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7.0
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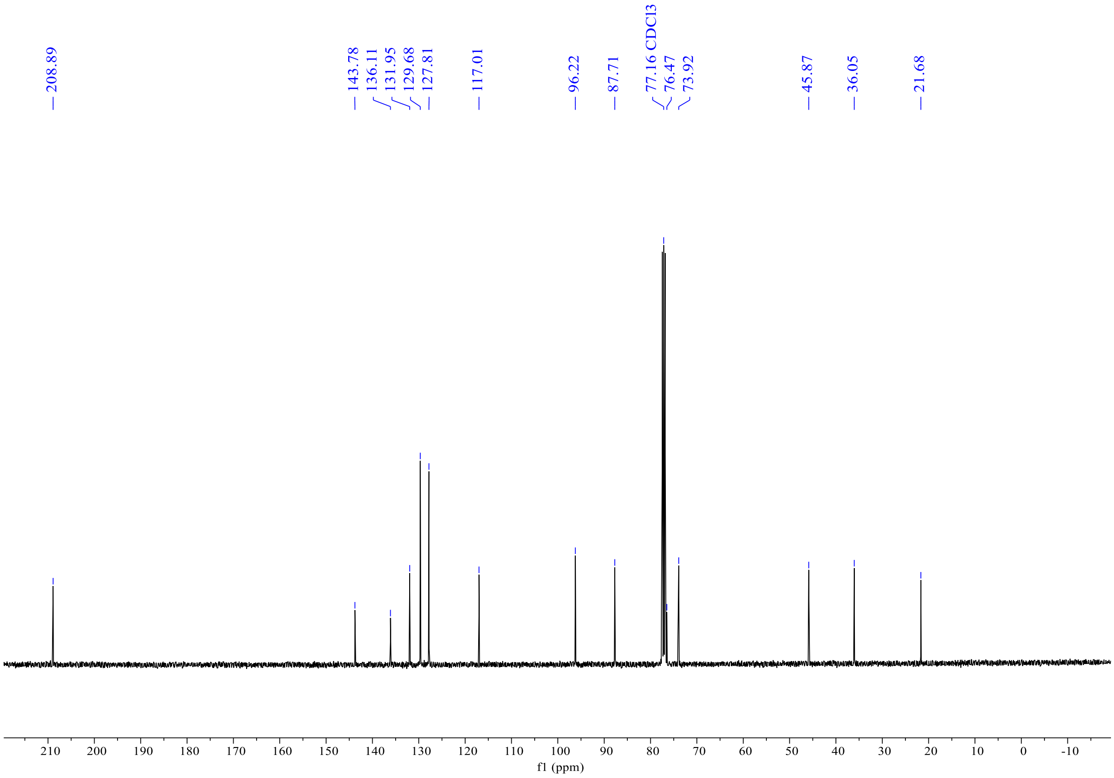
f1 (ppm)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36.05
21.68
210
200
190
180
170
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120
110
100
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80
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50
40
30
20
10
0
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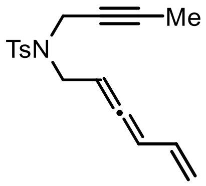
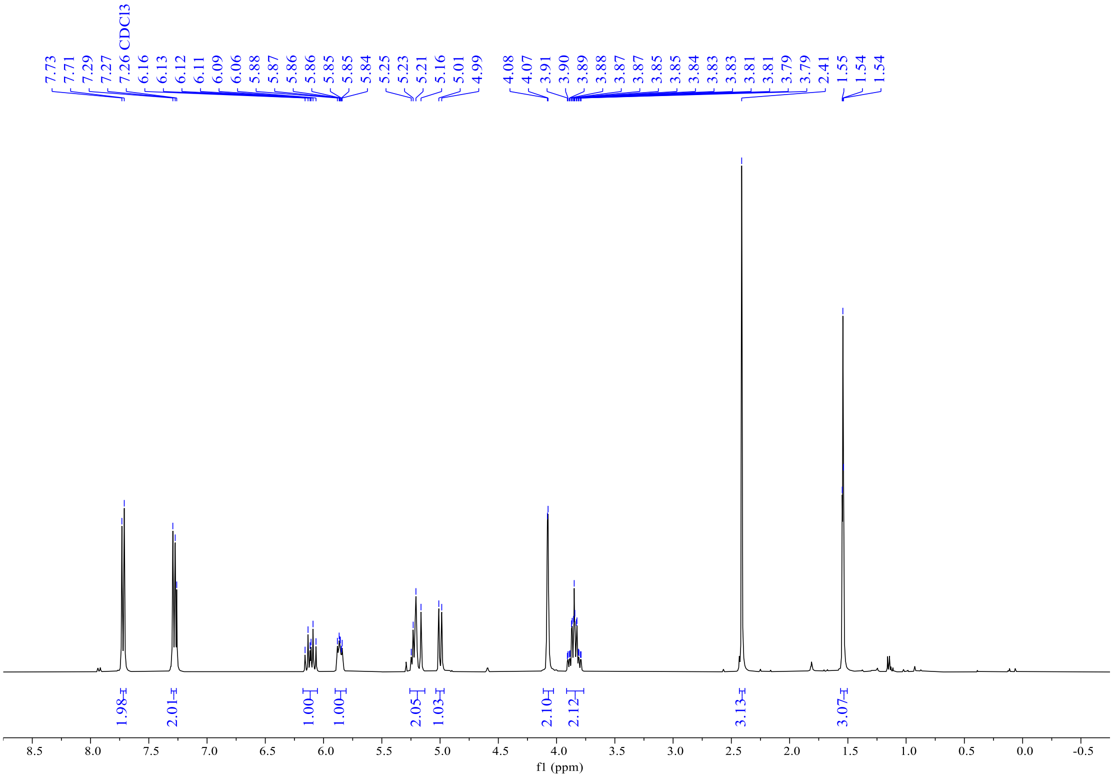
f1 (ppm)


TsN
Me

1c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5.87
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5.86
5.85
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3.87
3.87
3.85
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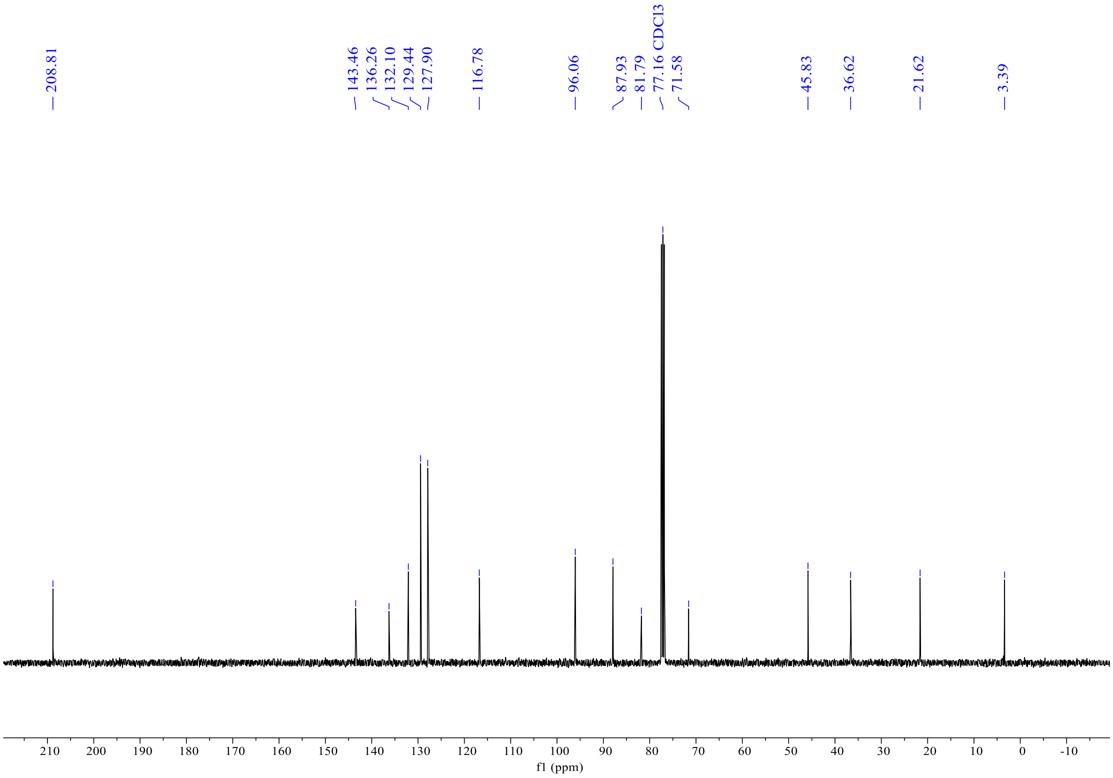
f1 (ppm)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96.06
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81.79
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71.58
45.83
36.62
21.62
3.39
210
200
190
180
170
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150
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110
100
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80
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60
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40
30
20
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0
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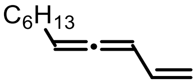
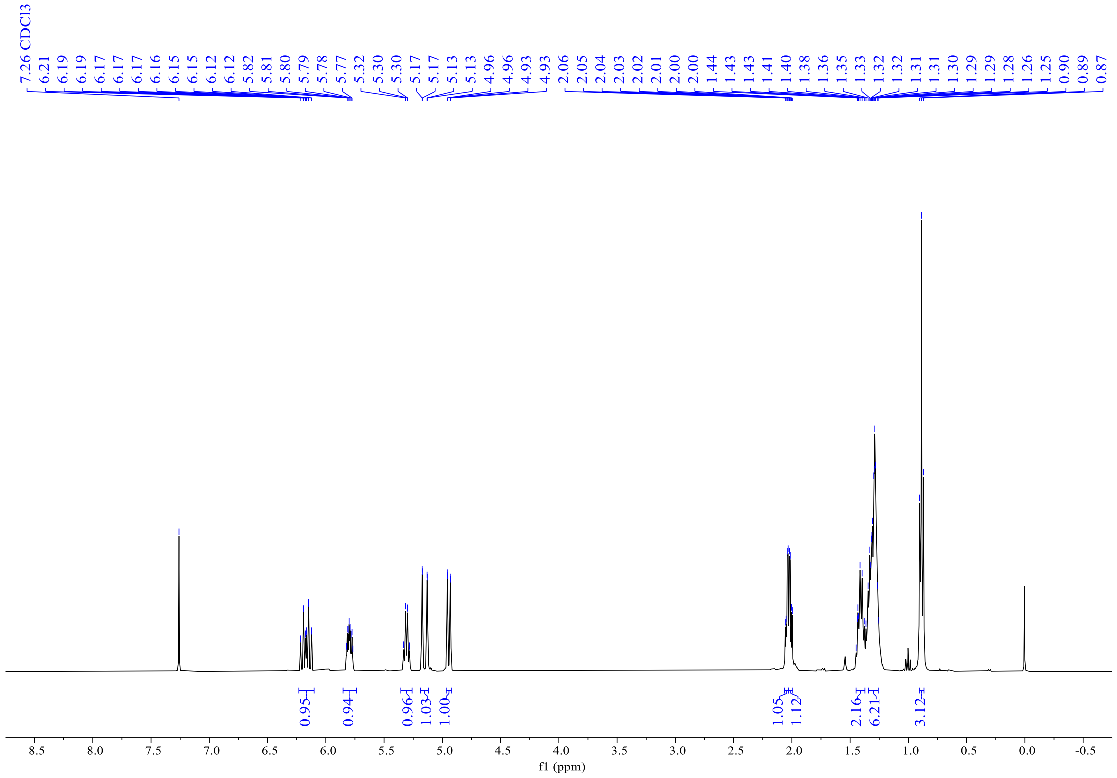
f1 (ppm)


C6H13

1e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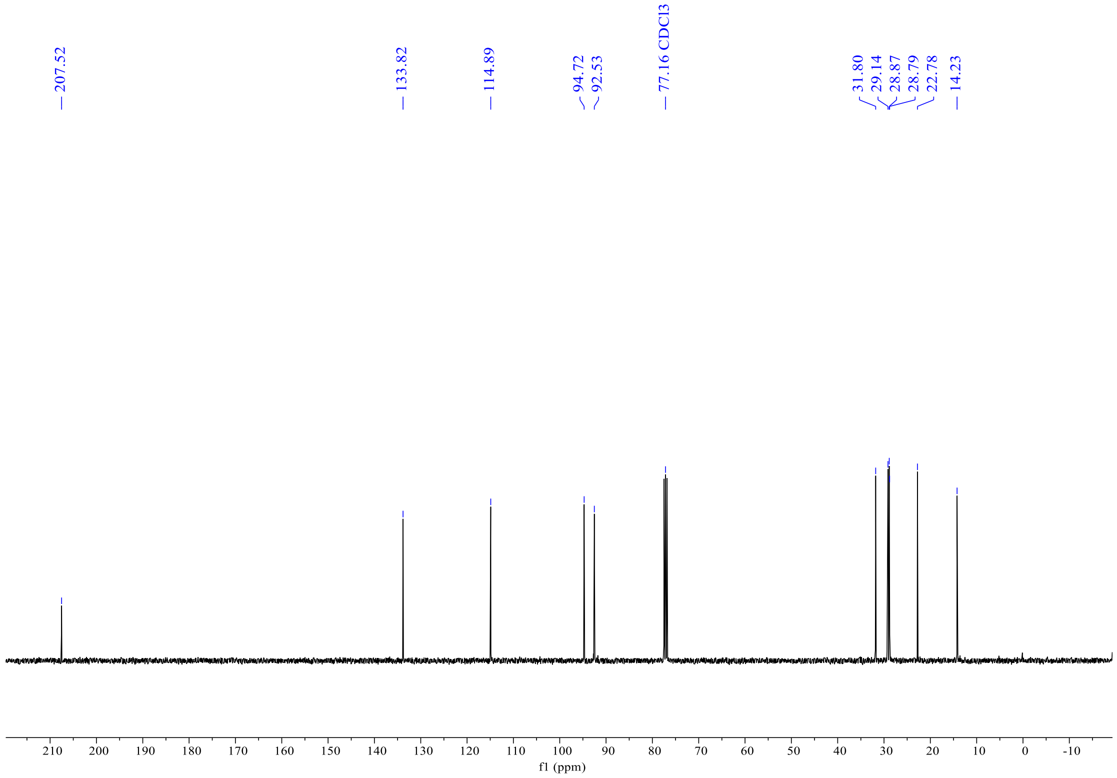
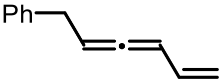
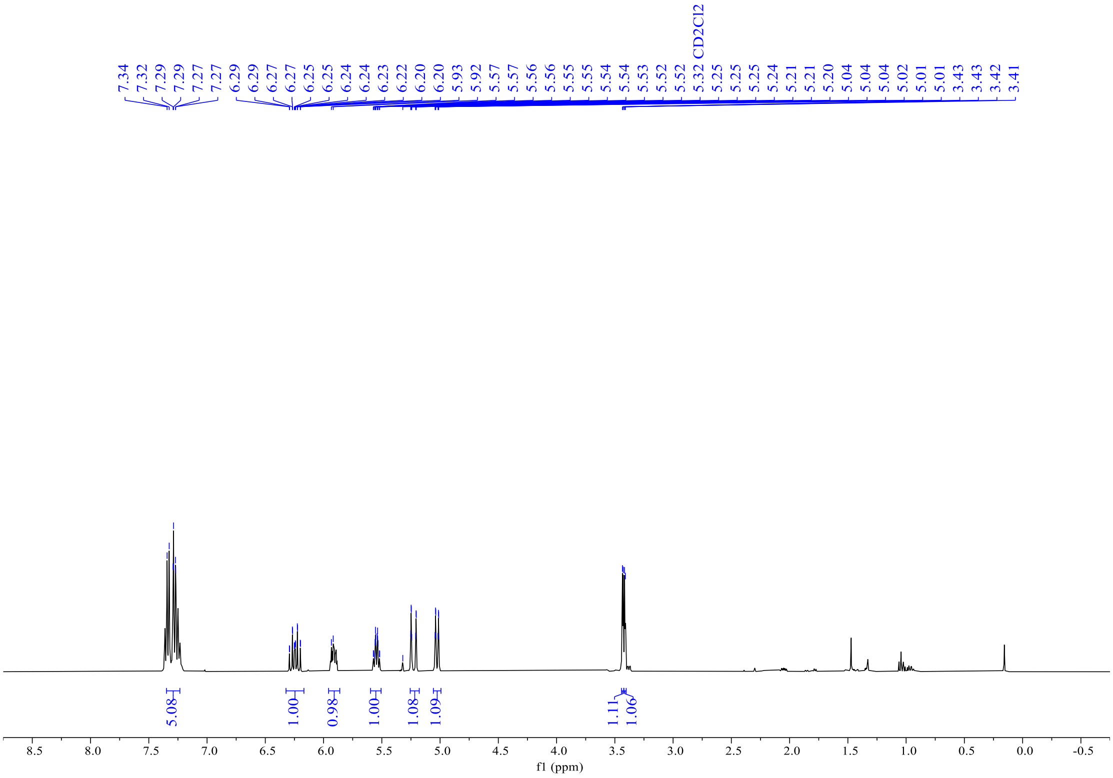
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


207.52
133.82
114.89
94.72
92.53
77.16 CDCl3
31.80
29.14
28.87
28.79
22.78
14.23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph

1f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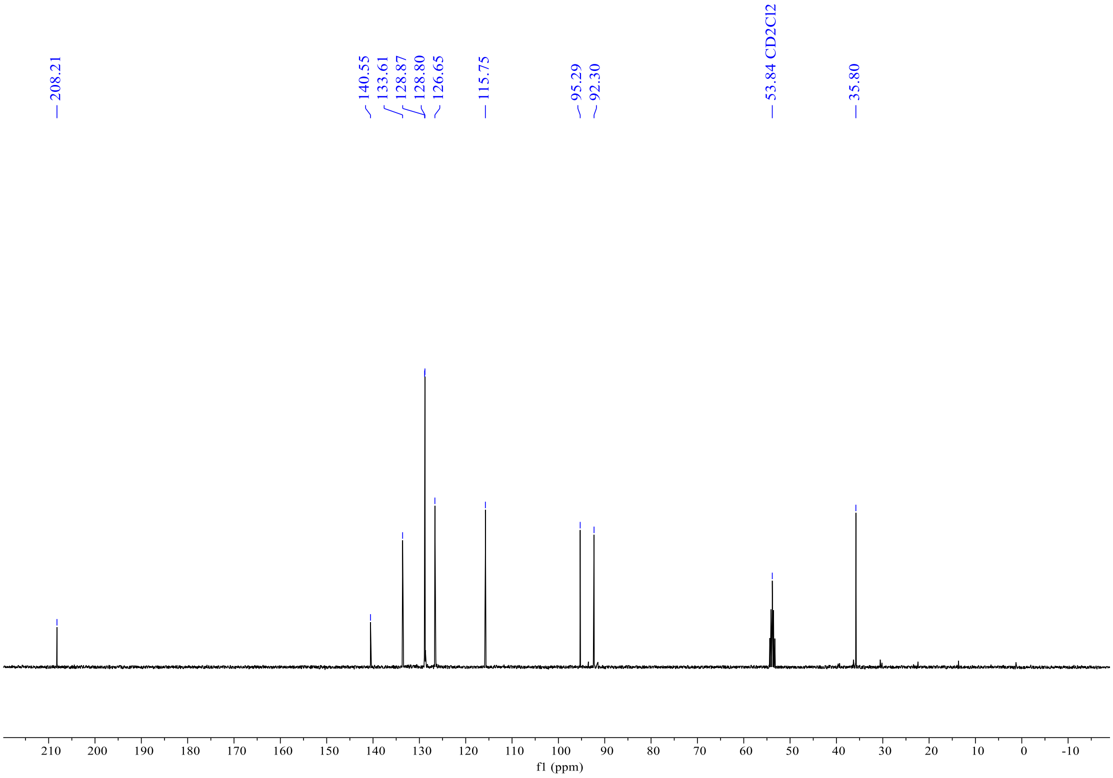
7.32
7.29
7.29
7.27
7.27
6.29
6.29
6.27
6.27
6.25
6.25
6.24
6.24
6.23
6.22
6.20
6.20
5.93
5.92
5.57
5.57
5.56
5.56
5.55
5.55
5.54
5.54
5.53
5.52
5.52
5.32 CD2Cl2
5.25
5.25
5.25
5.24
5.21
5.21
5.20
5.04
5.04
5.04
5.02
5.01
5.01
3.43
3.43
3.42
3.41
5.08
1.00
0.98
1.00
1.08
1.09
1.11
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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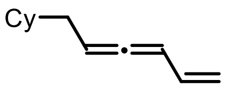
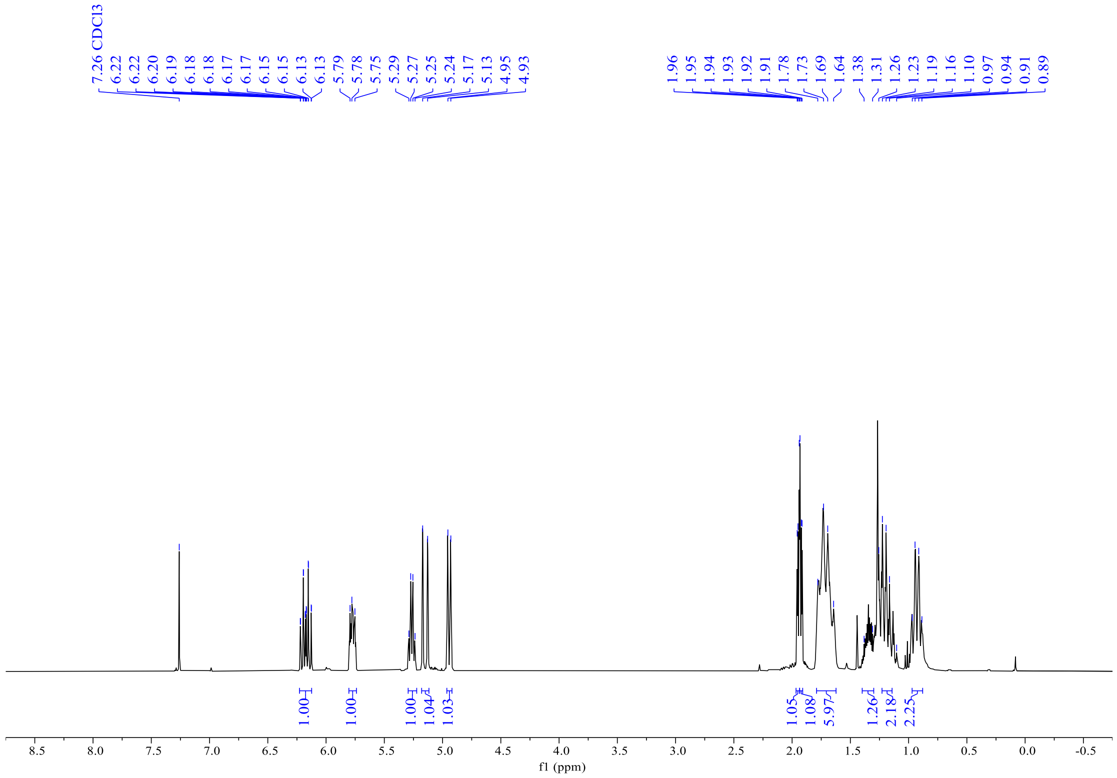
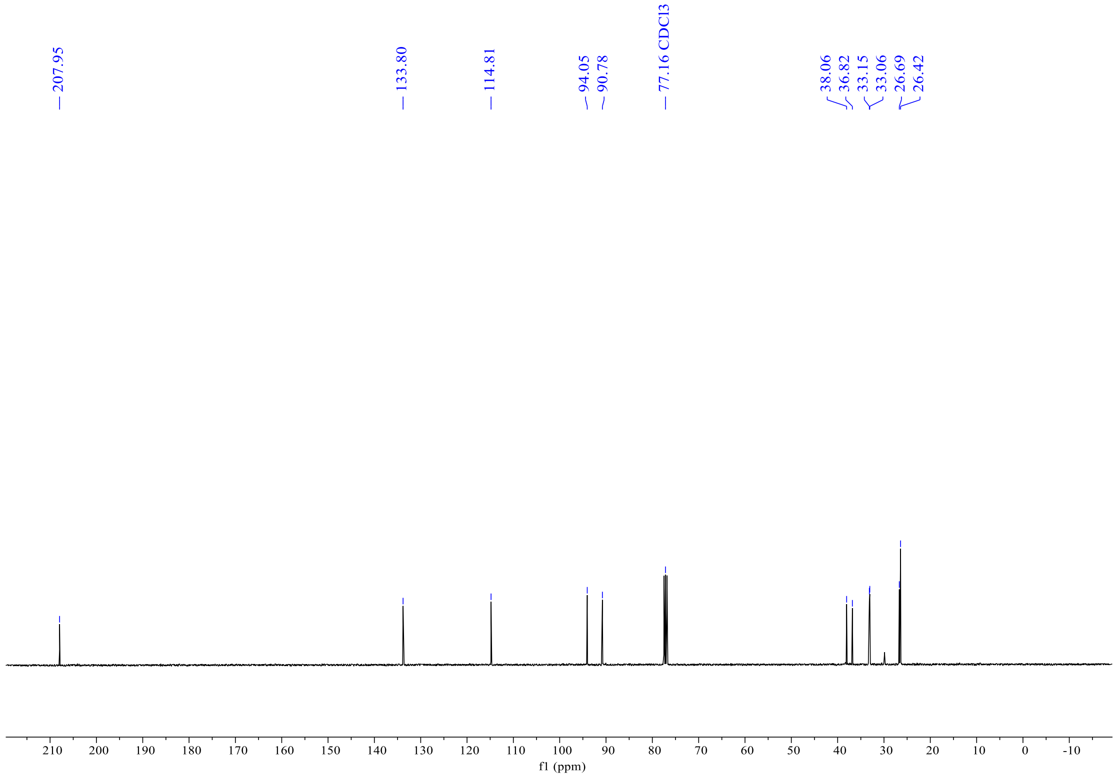
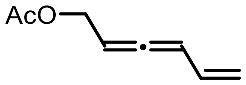
140.55
133.61
128.87
128.80
126.65
115.75
95.29
92.30
53.84 CD2Cl2
35.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cy

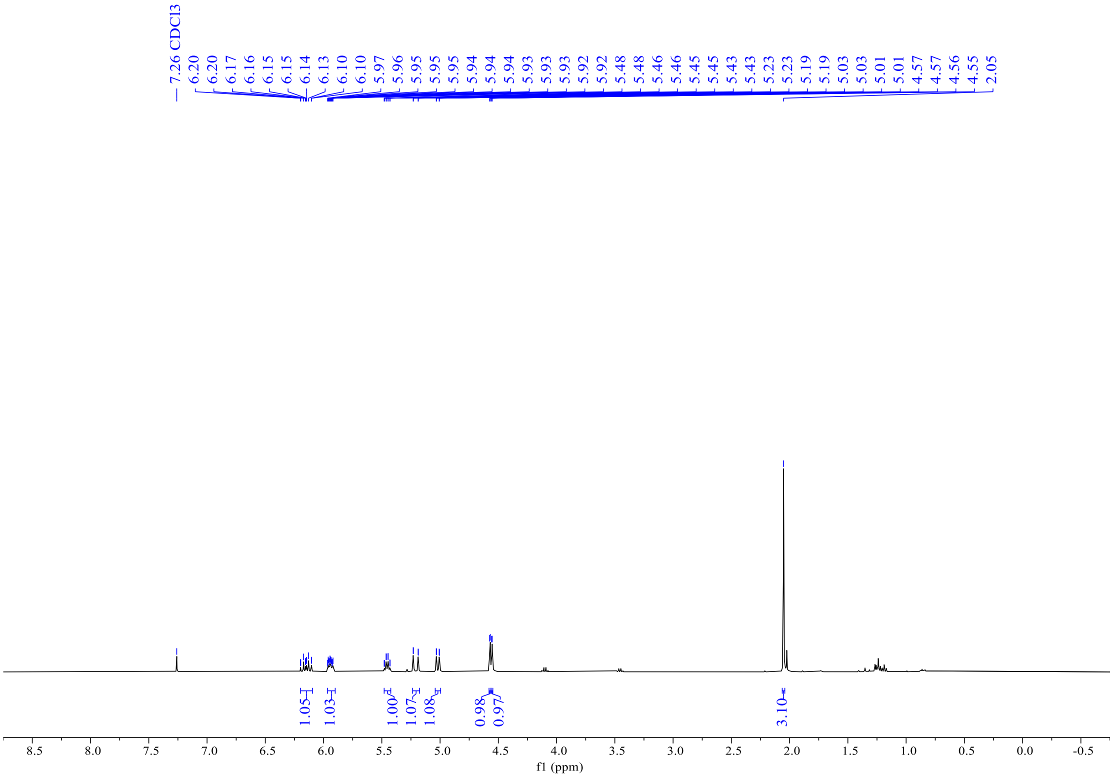
1g

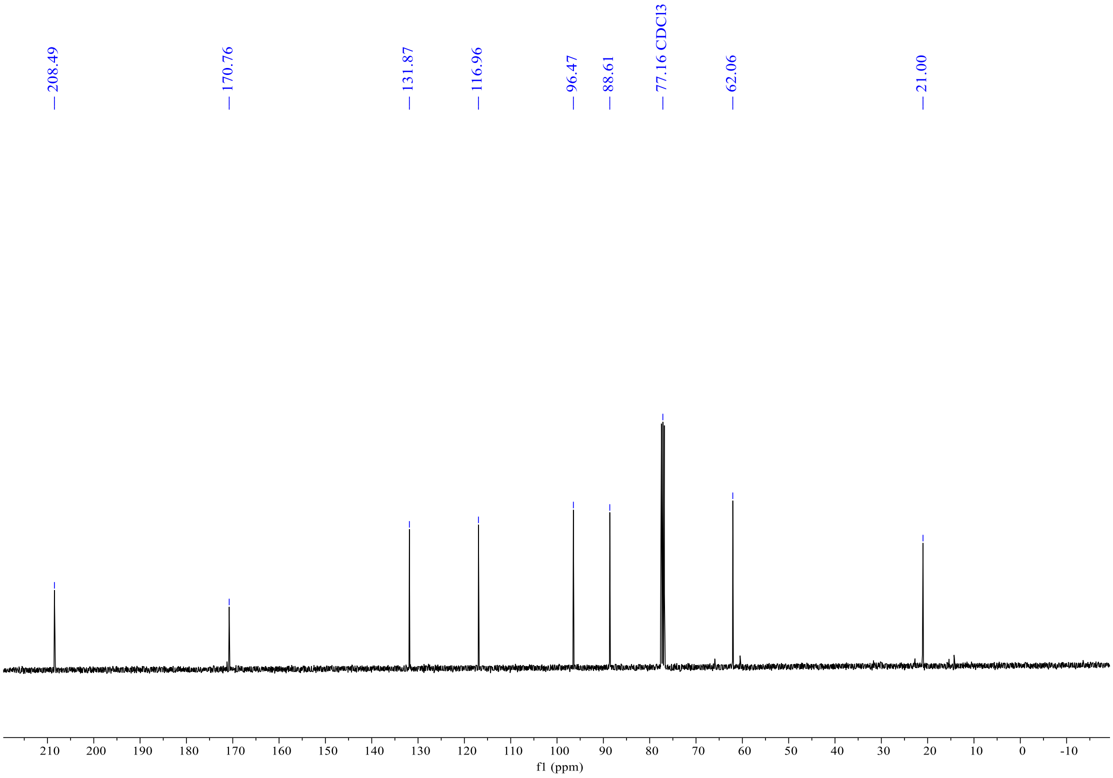

7.26 CDCl3
6.22
6.22
6.20
6.19
6.18
6.18
6.17
6.17
6.15
6.15
6.13
6.13
5.79
5.78
5.75
5.29
5.27
5.25
5.24
5.17
5.13
4.95
4.93
1.96
1.95
1.94
1.93
1.92
1.91
1.78
1.73
1.69
1.64
1.38
1.31
1.26
1.23
1.19
1.16
1.10
0.97
0.94
0.91
0.89
1.00
1.00
1.00
1.04
1.03
1.05
1.08
5.97
1.26
2.18
2.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

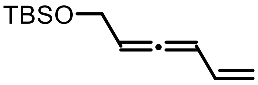

207.95
133.80
114.81
94.05
90.78
77.16 CDCl3
38.06
36.82
33.15
33.06
26.69
26.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO

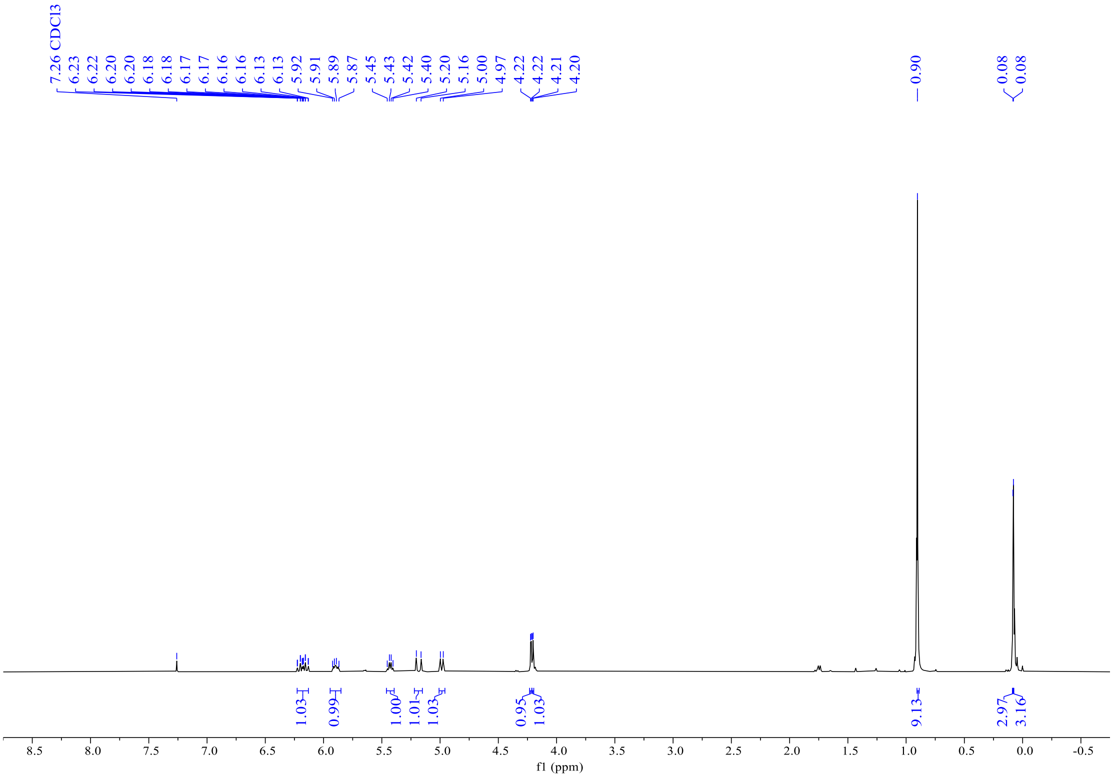
1h

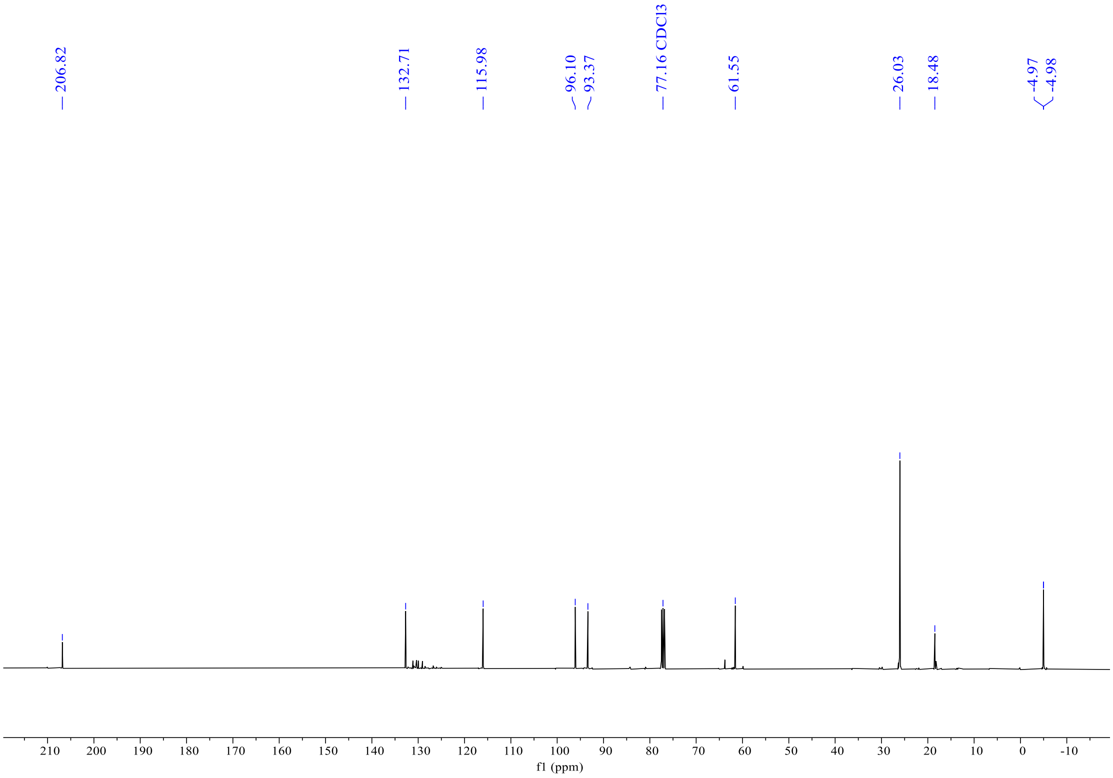

7.26 CDCl3
6.20
6.20
6.17
6.16
6.15
6.15
6.14
6.13
6.10
6.10
5.97
5.96
5.95
5.95
5.95
5.94
5.94
5.94
5.93
5.93
5.93
5.92
5.92
5.48
5.48
5.46
5.46
5.45
5.45
5.43
5.43
5.23
5.23
5.19
5.19
5.03
5.03
5.01
5.01
4.57
4.57
4.56
4.55
2.05
1.05
1.03
1.00
1.07
1.08
0.98
0.97
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

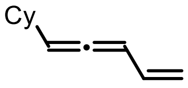

208.49
170.76
131.87
116.96
96.47
88.61
77.16 CDCl3
62.06
21.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO

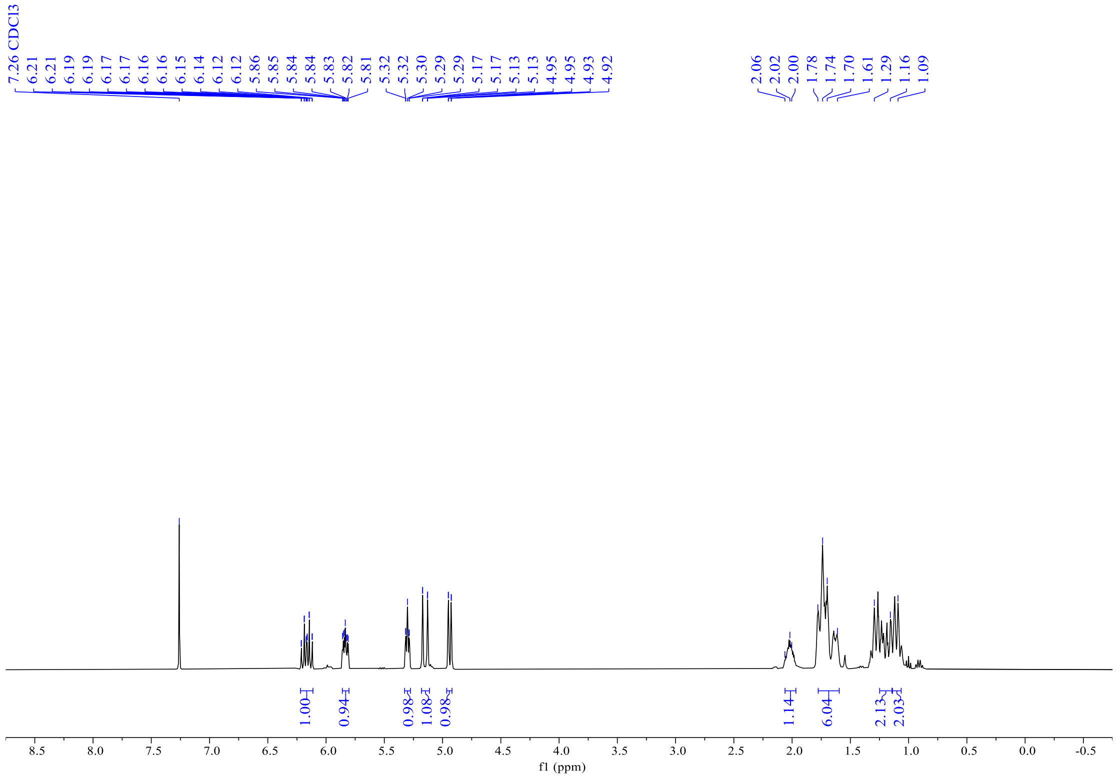
1i

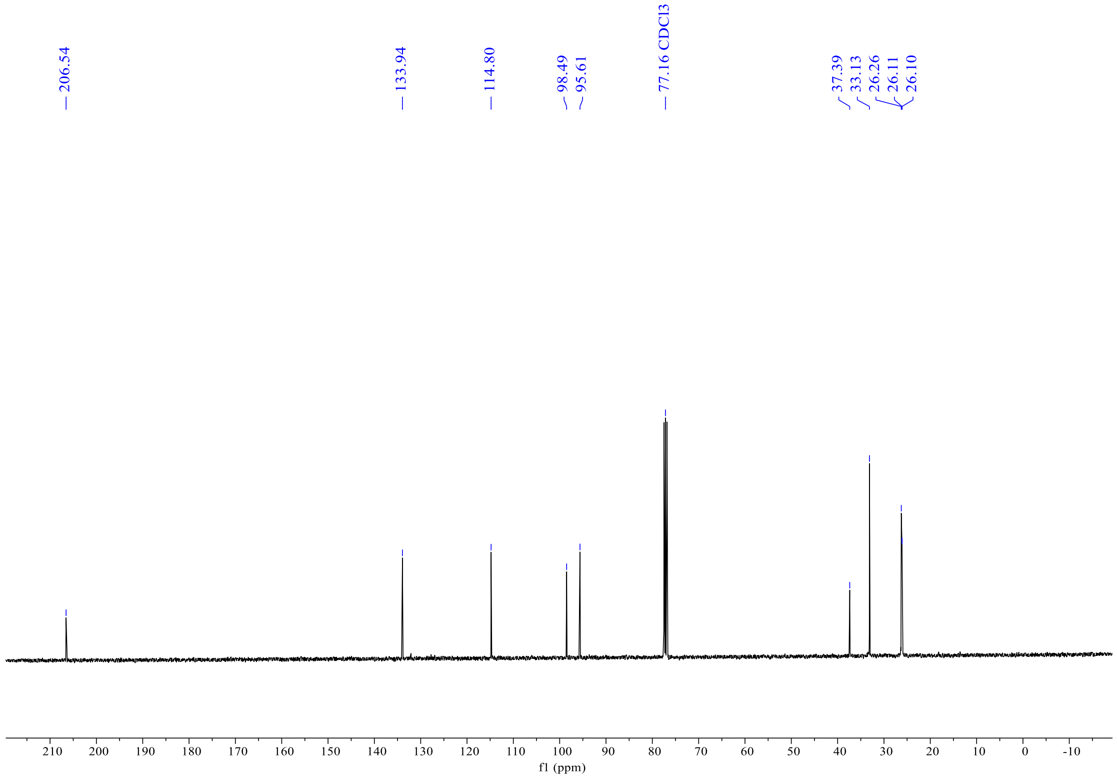

7.26 CDCl3
6.23
6.22
6.20
6.20
6.18
6.18
6.17
6.17
6.16
6.16
6.13
6.13
5.92
5.91
5.89
5.87
5.45
5.43
5.42
5.40
5.20
5.16
5.00
4.97
4.22
4.22
4.21
4.20
0.90
0.08
0.08
1.03
0.99
1.00
1.01
1.03
0.95
1.03
9.13
2.97
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

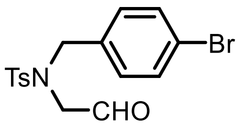

206.82
132.71
115.98
96.10
93.37
77.16 CDCl3
61.55
26.03
18.48
-4.97
-4.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cy

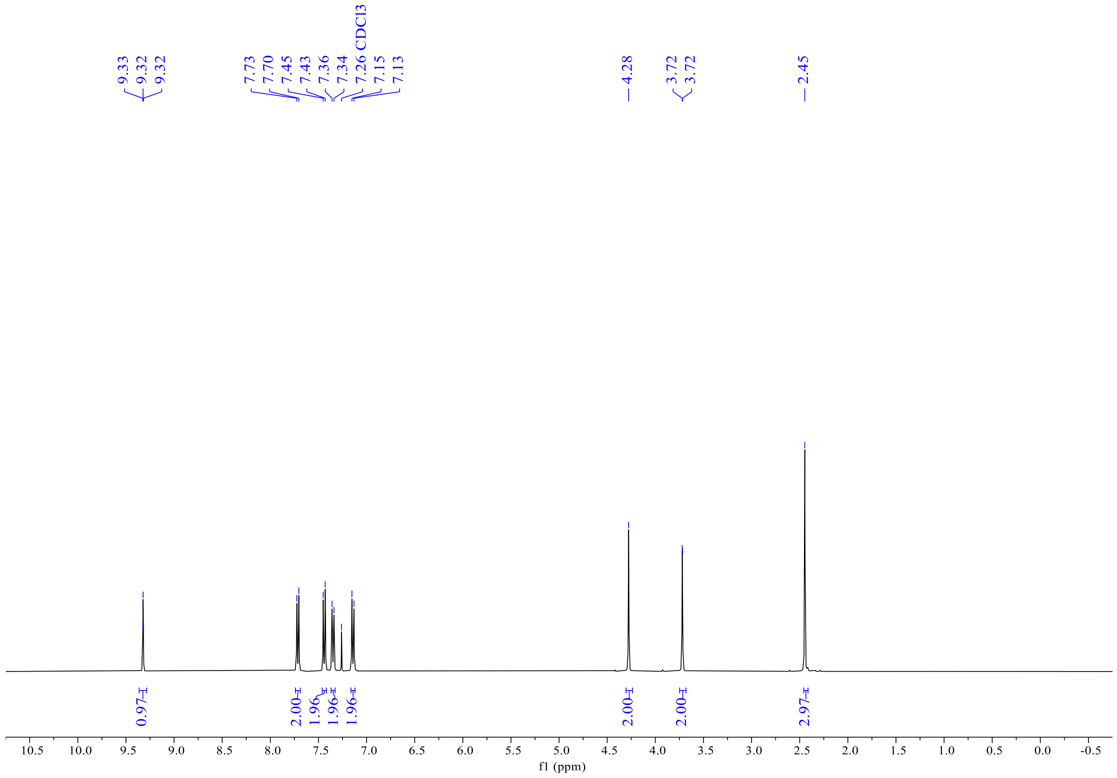
1j

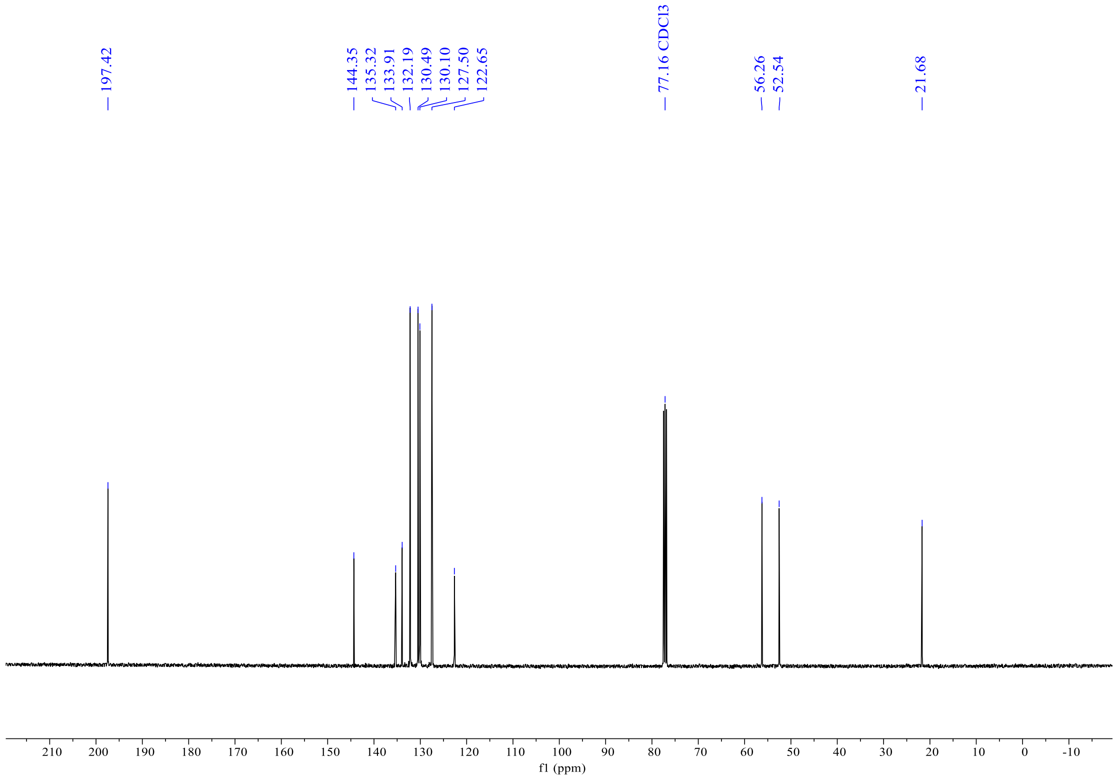

7.26 CDCl3
6.21
6.21
6.19
6.19
6.17
6.17
6.16
6.16
6.15
6.14
6.12
6.12
5.86
5.85
5.84
5.84
5.83
5.82
5.81
5.32
5.32
5.30
5.29
5.29
5.17
5.17
5.13
5.13
4.95
4.95
4.93
4.92
2.06
2.02
2.00
1.78
1.74
1.70
1.61
1.29
1.16
1.09
1.00
0.94
0.98
1.08
0.98
1.14
6.04
2.13
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

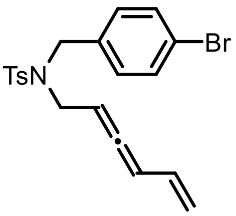

206.54
133.94
114.80
98.49
95.61
77.16 CDCl3
37.39
33.13
26.26
26.11
26.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
CHO
Br

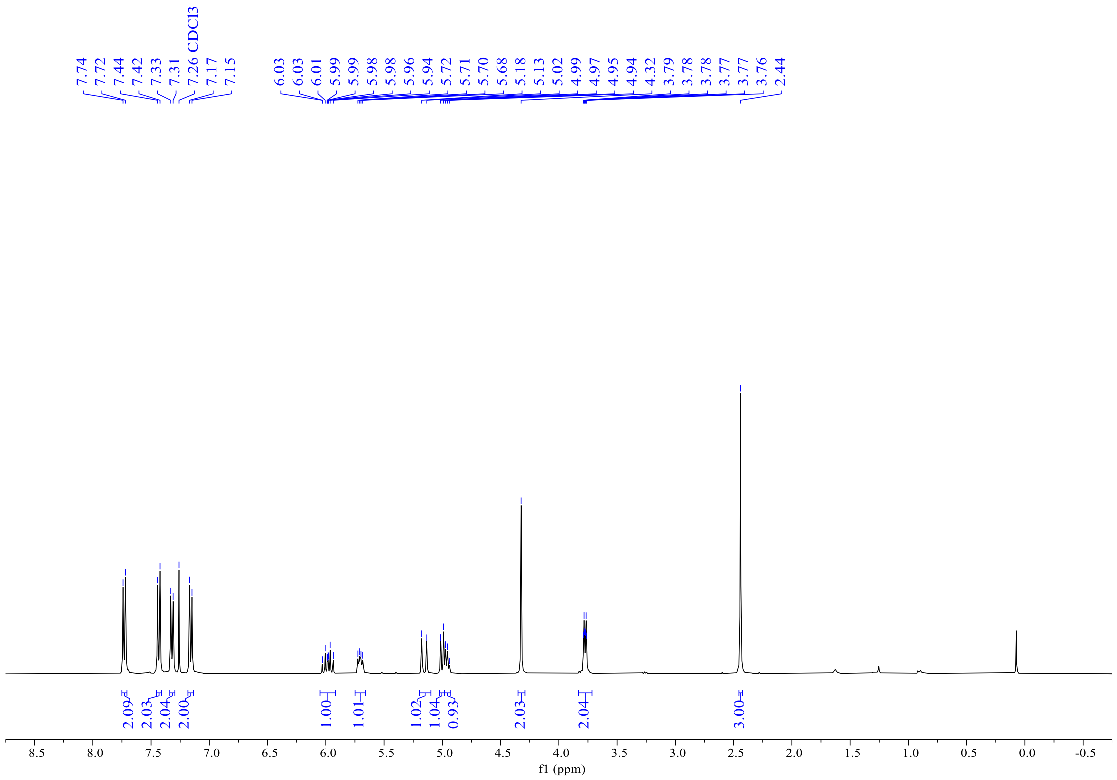
S8


9.33
9.32
9.32
7.73
7.70
7.45
7.43
7.36
7.34
7.26 CDCl3
7.15
7.13
4.28
3.72
3.72
2.45
0.97
2.00
1.96
1.96
1.96
2.00
2.00
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

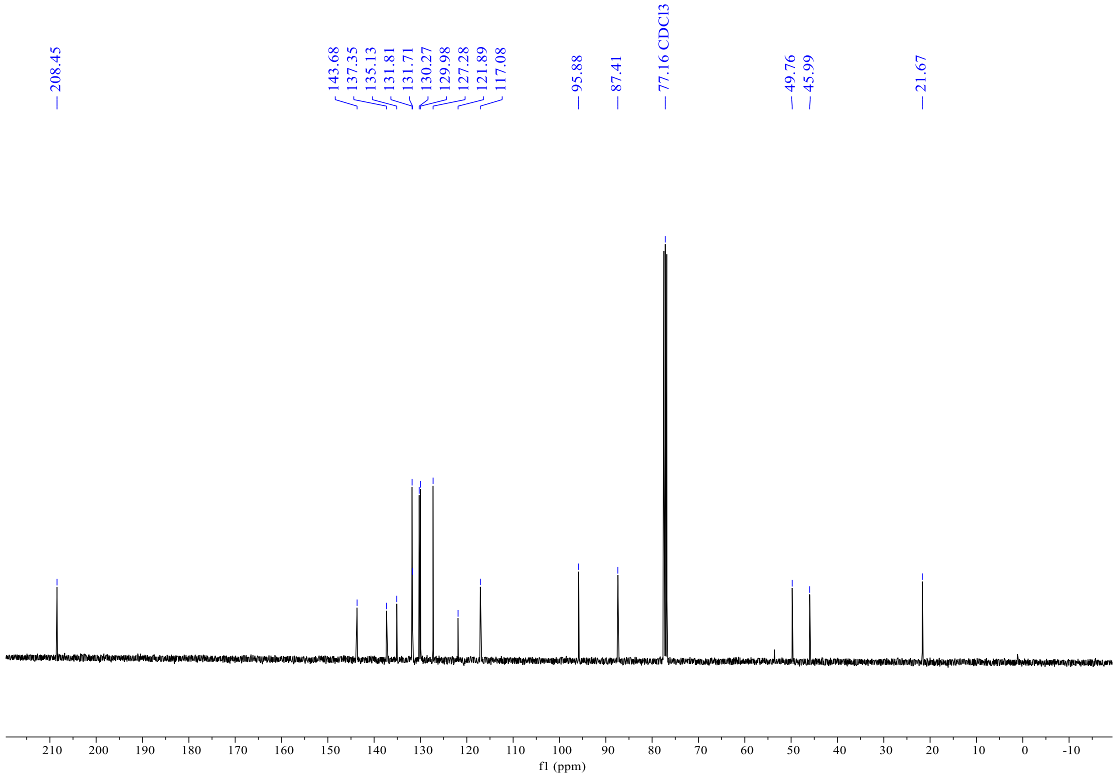

197.42
144.35
135.32
133.91
132.19
130.49
130.10
127.50
122.65
77.16 CDCl3
56.26
52.54
21.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



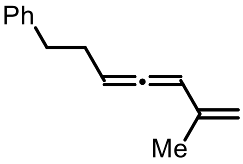
1l



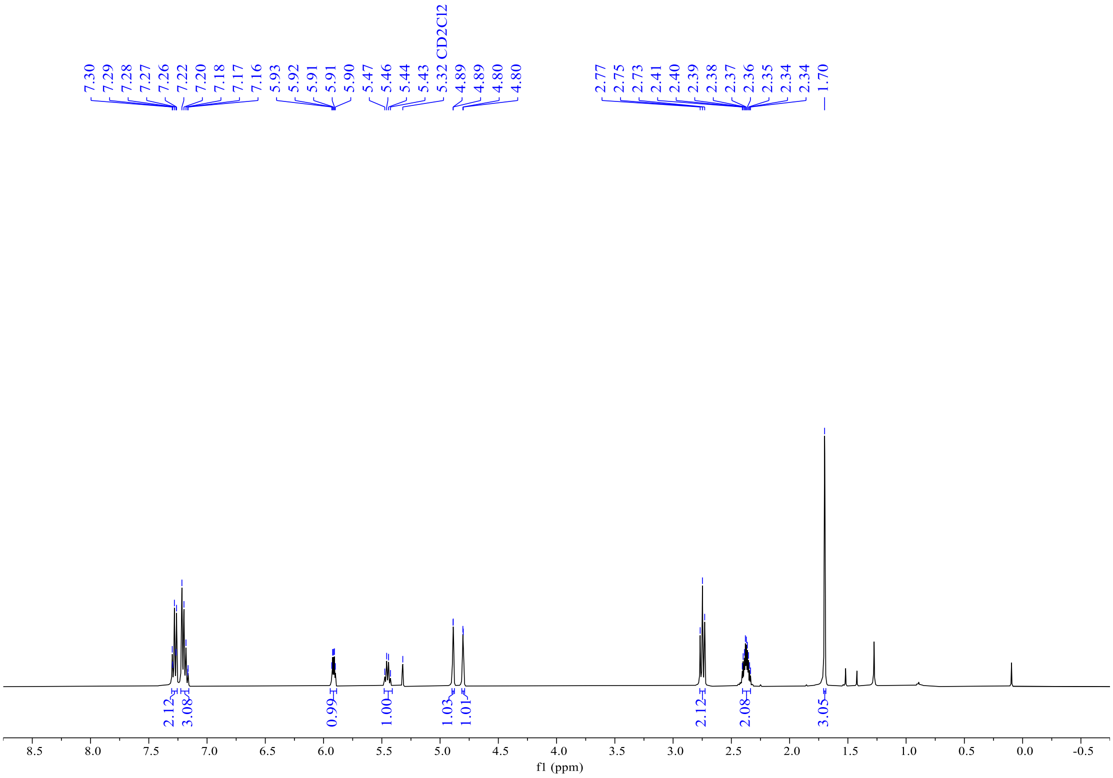
7.74
7.72
7.44
7.42
7.33
7.31
7.26 CDCl3
7.17
7.15
6.03
6.03
6.01
5.99
5.99
5.98
5.98
5.96
5.94
5.72
5.71
5.70
5.68
5.18
5.13
5.02
4.99
4.97
4.95
4.94
4.32
3.79
3.78
3.78
3.77
3.77
3.76
2.44
2.09
2.03
2.04
2.00
1.00
1.01
1.02
1.04
0.93
2.03
2.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

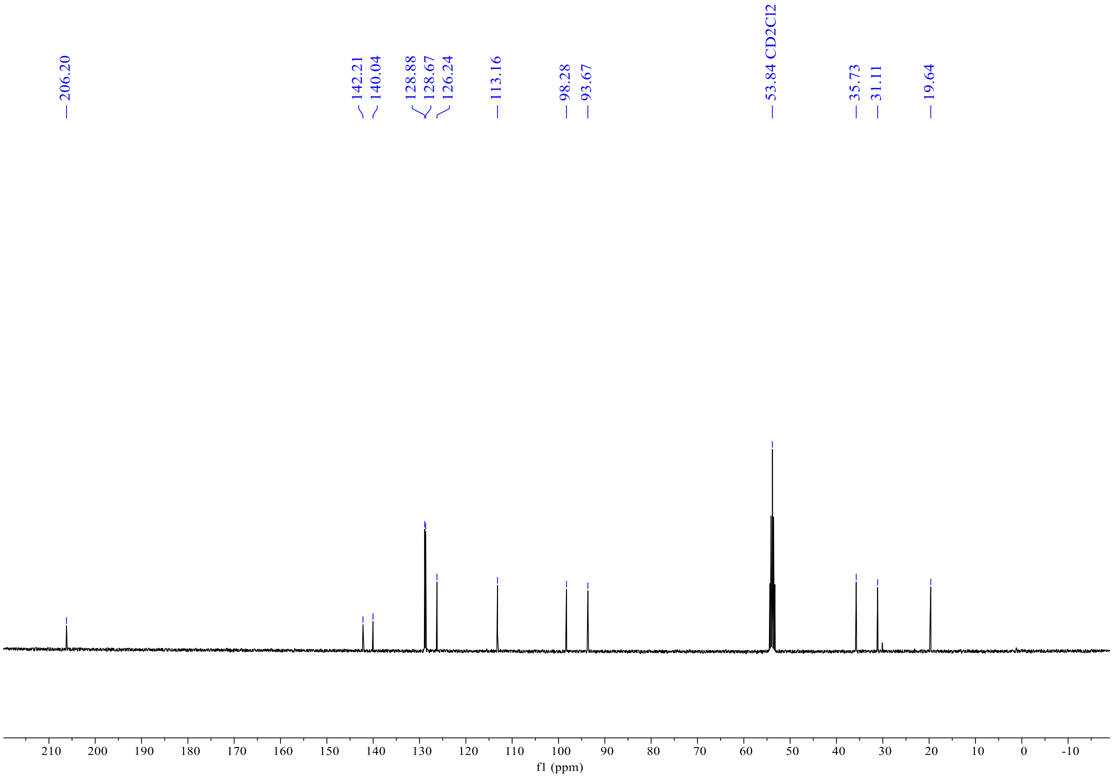


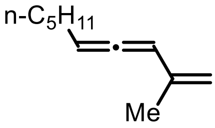
208.45
143.68
137.35
135.13
131.81
131.71
130.27
129.98
127.28
121.89
117.08
95.88
87.41
77.16 CDCl3
49.76
45.99
21.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Me

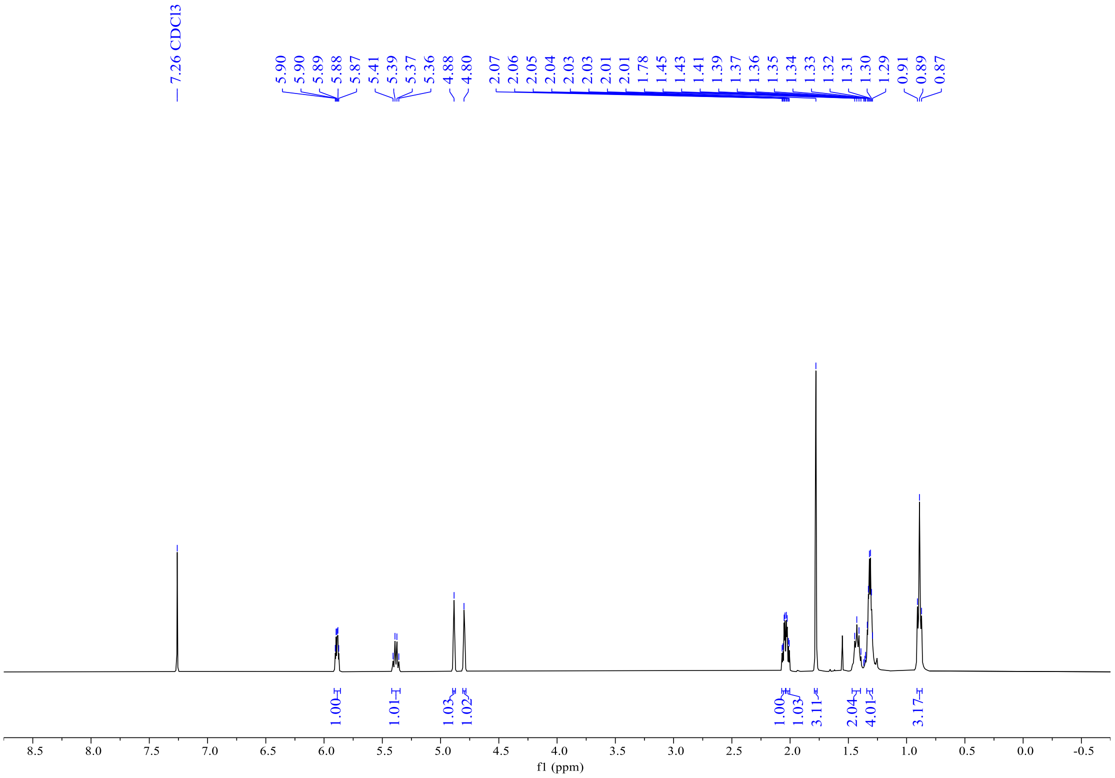
1m

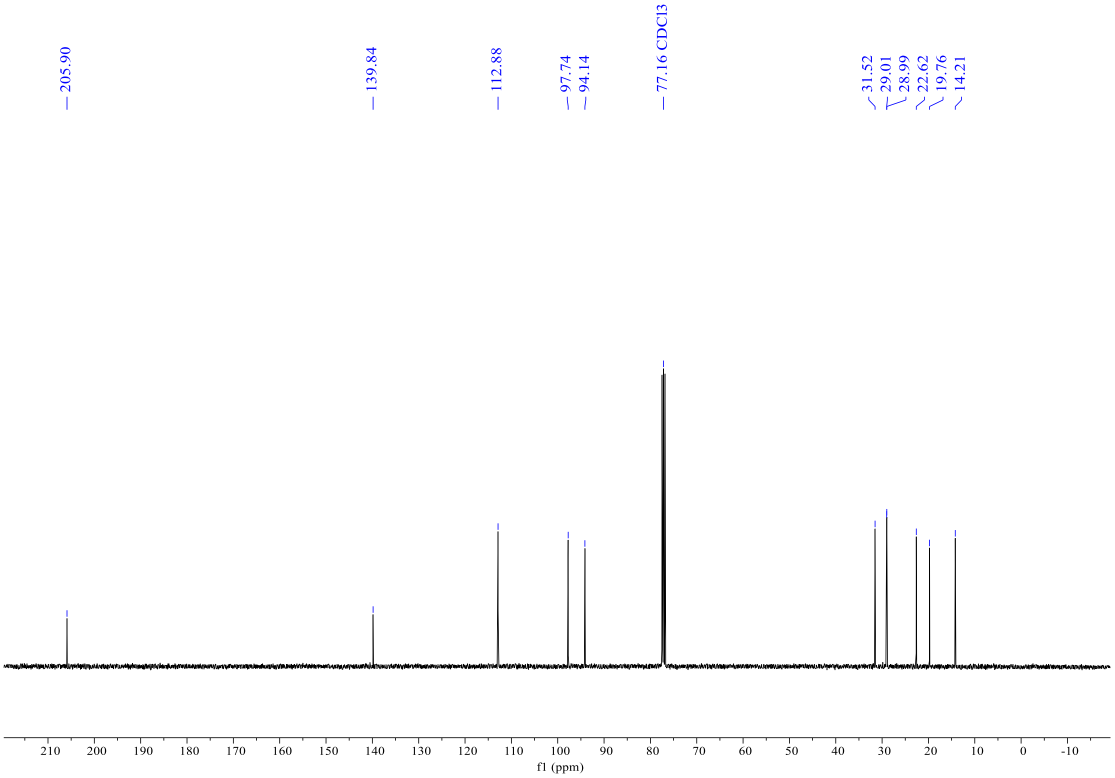

7.30
7.29
7.28
7.27
7.26
7.22
7.20
7.18
7.17
7.16
5.93
5.92
5.91
5.91
5.90
5.47
5.46
5.44
5.43
5.32 CD2Cl2
4.89
4.89
4.80
4.80
2.77
2.75
2.73
2.41
2.40
2.39
2.38
2.37
2.36
2.35
2.34
2.34
1.70
2.12
3.08
0.99
1.00
1.03
1.01
2.12
2.08
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

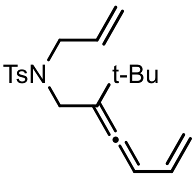

206.20
142.21
140.04
128.88
128.67
126.24
113.16
98.28
93.67
53.84 CD2Cl2
35.73
31.11
19.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


n-C5H11
Me

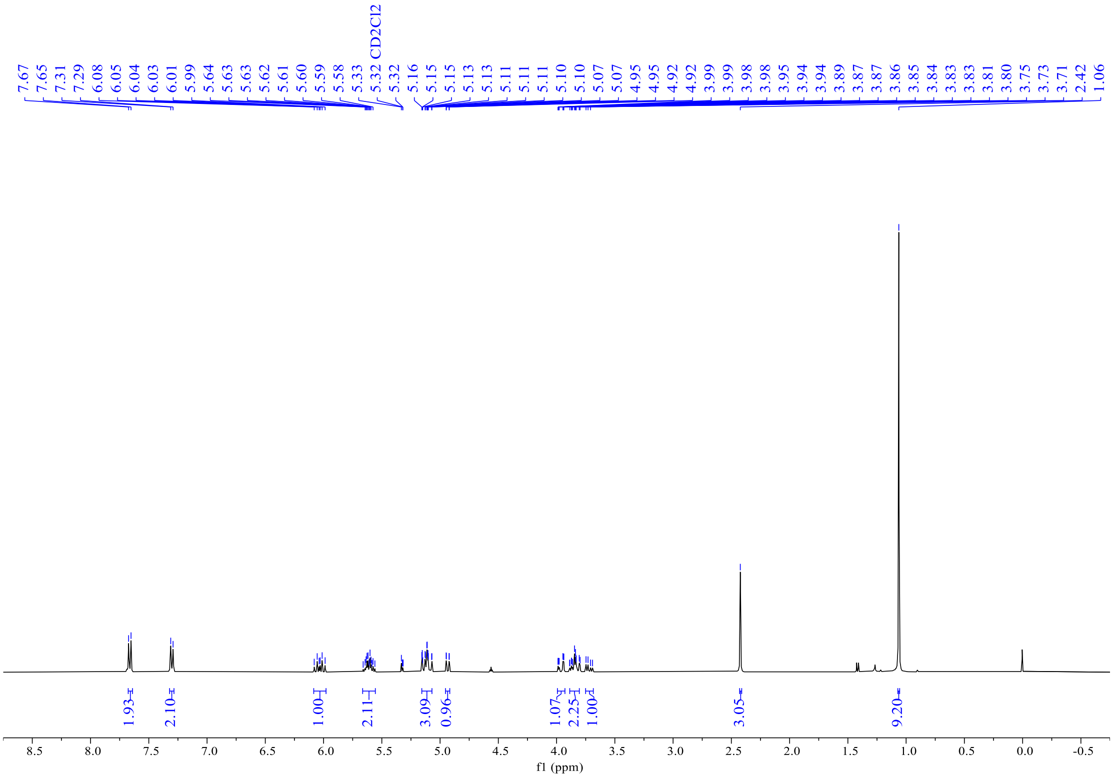
1n


7.26 CDCl3
5.90
5.90
5.89
5.88
5.87
5.41
5.39
5.37
5.36
4.88
4.80
2.07
2.06
2.05
2.04
2.03
2.03
2.01
2.01
1.78
1.45
1.43
1.41
1.39
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
0.91
0.89
0.87
1.00
1.01
1.03
1.02
1.00
1.03
3.11
2.04
4.01
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


205.90
139.84
112.88
97.74
94.14
77.16 CDCl3
31.52
29.01
28.99
22.62
19.76
14.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
t-Bu

1p


7.67
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7.29
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6.04
6.03
6.01
5.99
5.64
5.63
5.63
5.62
5.61
5.60
5.59
5.58
5.33
5.32 CD2Cl2
5.32
5.16
5.15
5.15
5.13
5.13
5.11
5.11
5.11
5.10
5.10
5.07
5.07
4.95
4.95
4.92
4.92
3.99
3.99
3.98
3.98
3.95
3.94
3.94
3.89
3.87
3.87
3.86
3.85
3.84
3.83
3.83
3.81
3.80
3.75
3.73
3.71
2.42
1.06
1.93
2.10
1.00
2.11
3.09
0.96
1.07
2.25
1.00
3.05
9.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
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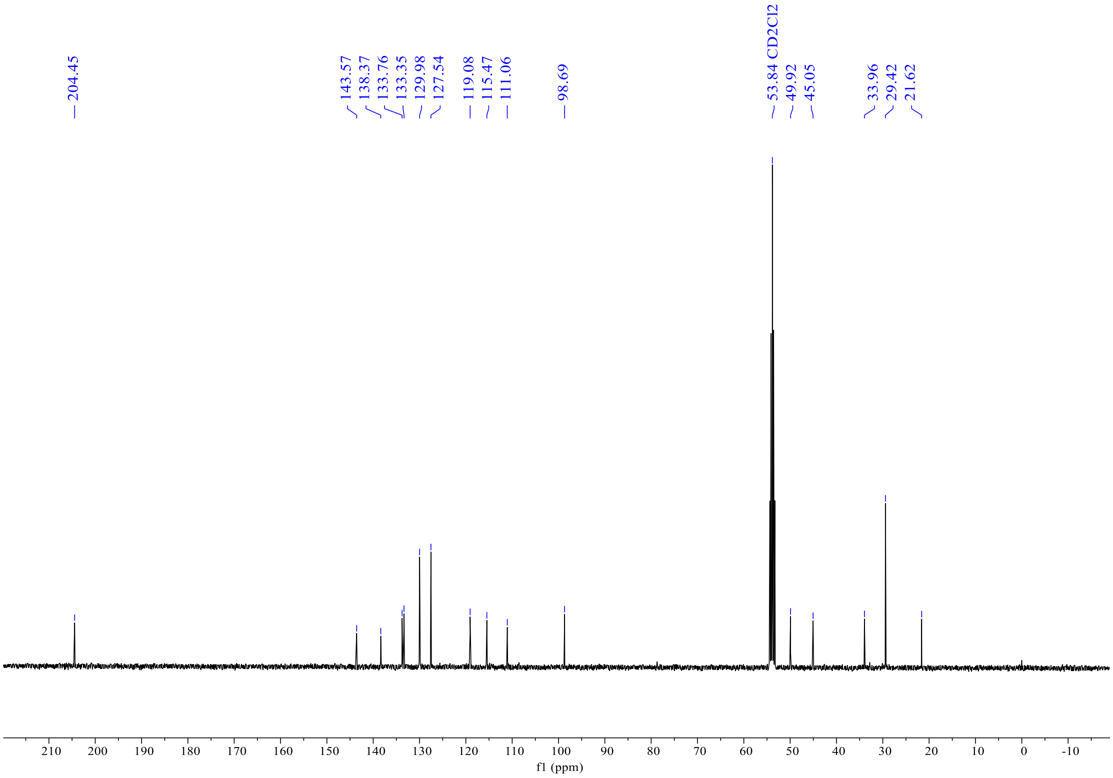
-0.5
f1 (ppm)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133.35
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111.06
98.69
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49.92
45.05
33.96
29.42
21.62
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
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40
30
20
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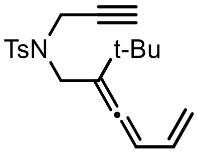
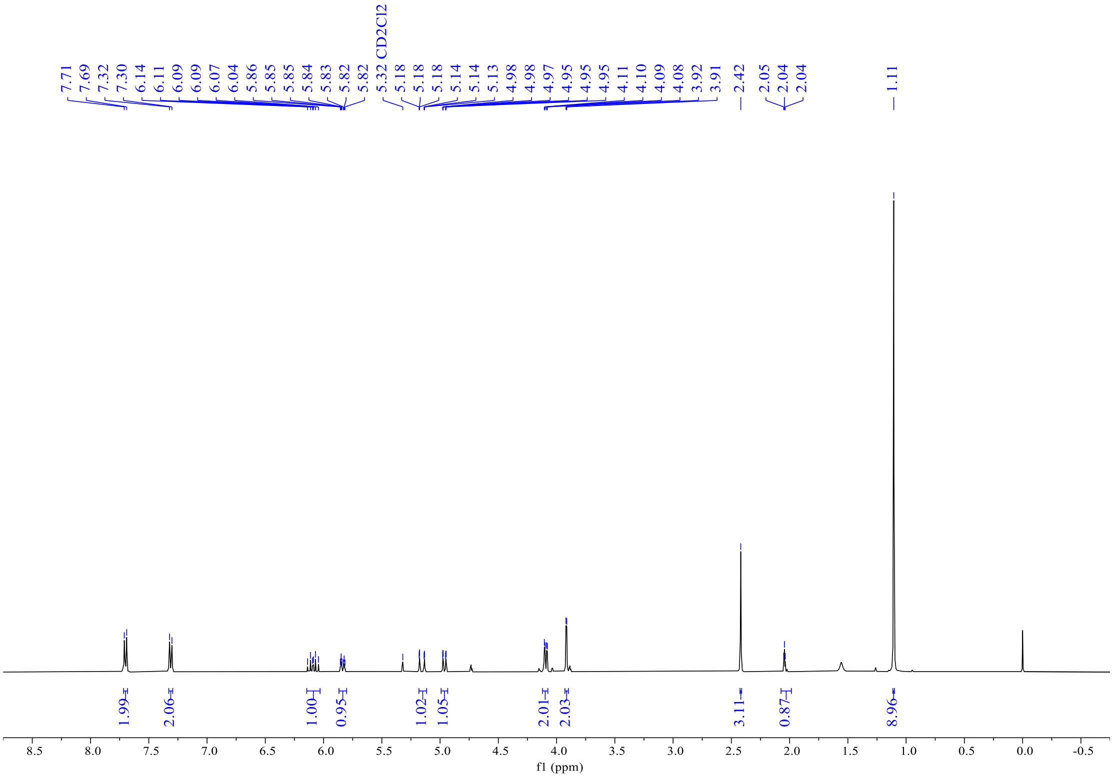
-10
f1 (ppm)


TsN
t-Bu

1q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6.09
6.07
6.04
5.86
5.85
5.85
5.84
5.83
5.82
5.82
5.32 CD2Cl2
5.18
5.18
5.18
5.14
5.14
5.13
4.98
4.98
4.97
4.95
4.95
4.95
4.11
4.10
4.09
4.08
3.92
3.91
2.42
2.05
2.04
2.04
1.11
1.99
2.06
1.00
0.95
1.02
1.05
2.01
2.03
3.11
0.87
8.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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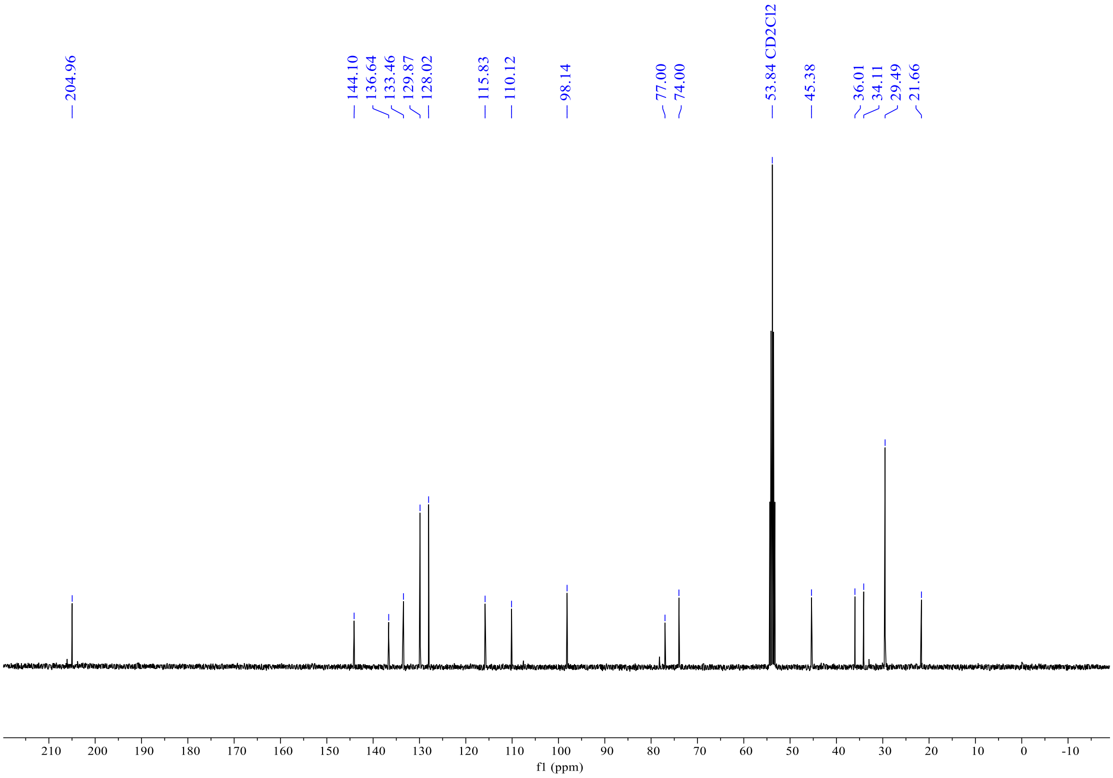
0.5
0.0
-0.5
f1 (ppm)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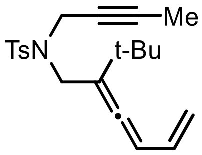
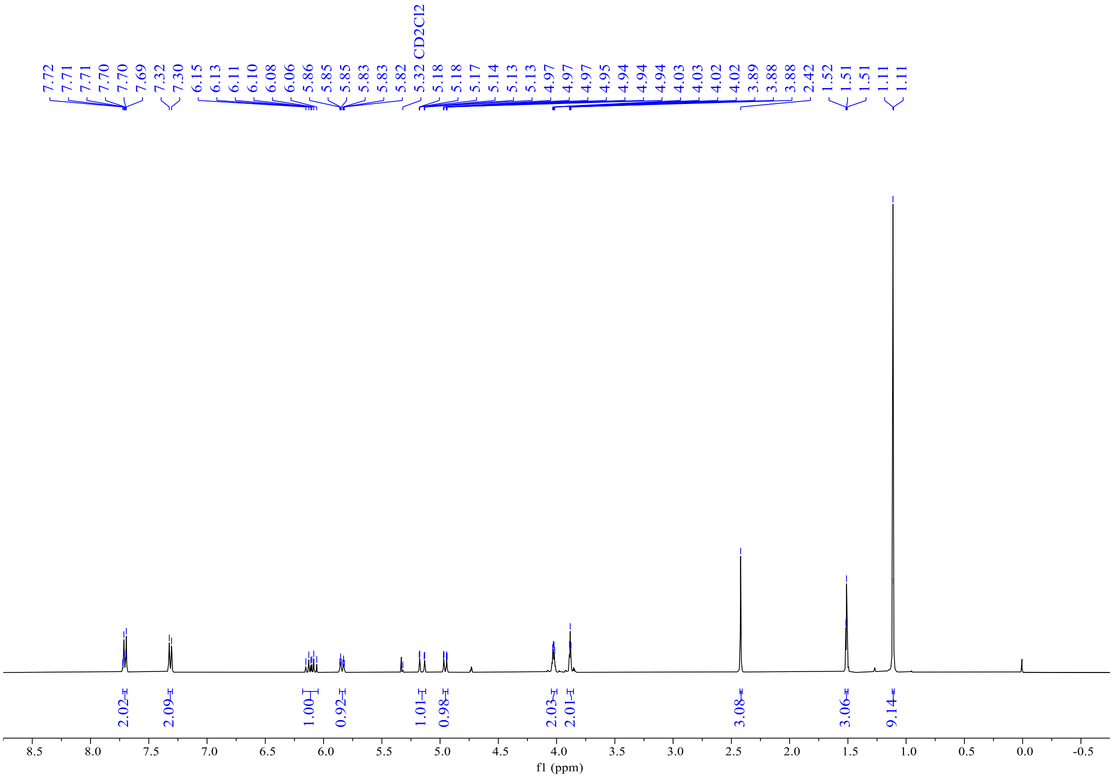
128.02
115.83
110.12
98.14
77.00
74.00
53.84 CD2Cl2
45.38
36.01
34.11
29.49
21.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
TsN
t-Bu

1r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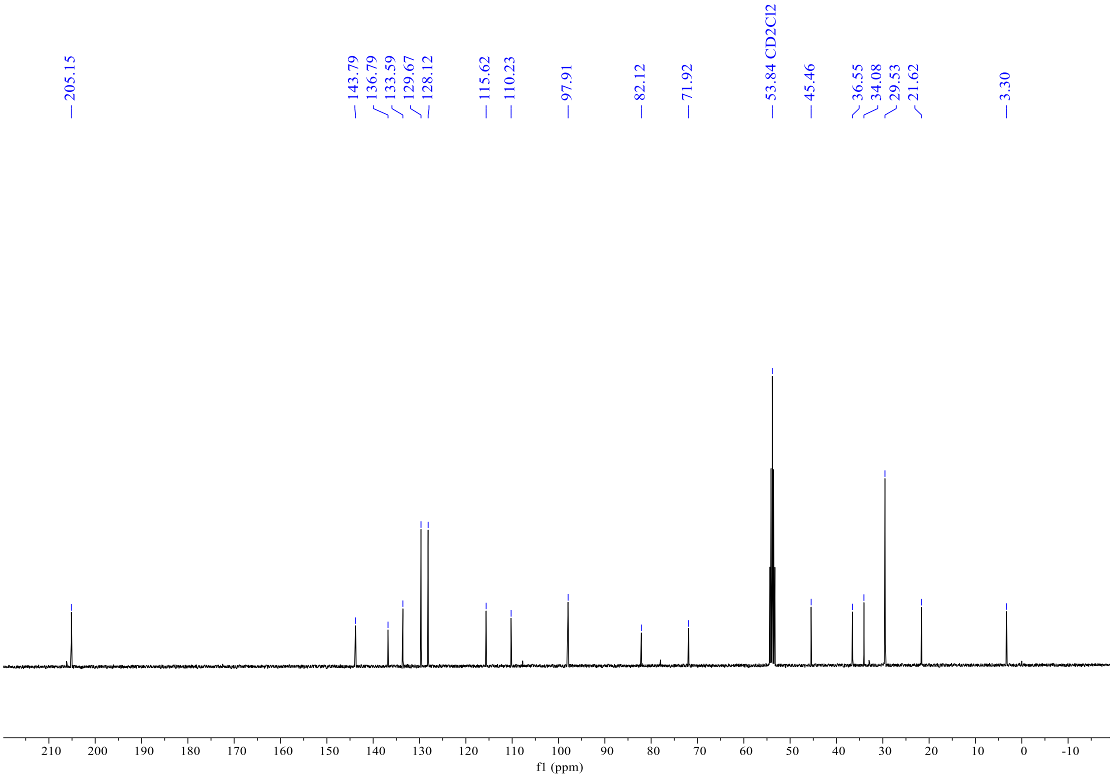
6.13
6.11
6.10
6.08
6.06
5.86
5.85
5.85
5.83
5.83
5.82
5.32 CD2Cl2
5.18
5.18
5.17
5.14
5.13
5.13
4.97
4.97
4.97
4.95
4.94
4.94
4.94
4.03
4.03
4.03
4.02
3.89
3.88
3.88
2.42
1.52
1.51
1.51
1.11
1.11
2.02
2.09
1.00
0.92
1.01
0.98
2.03
2.01
3.08
3.06
9.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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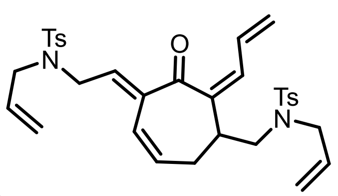
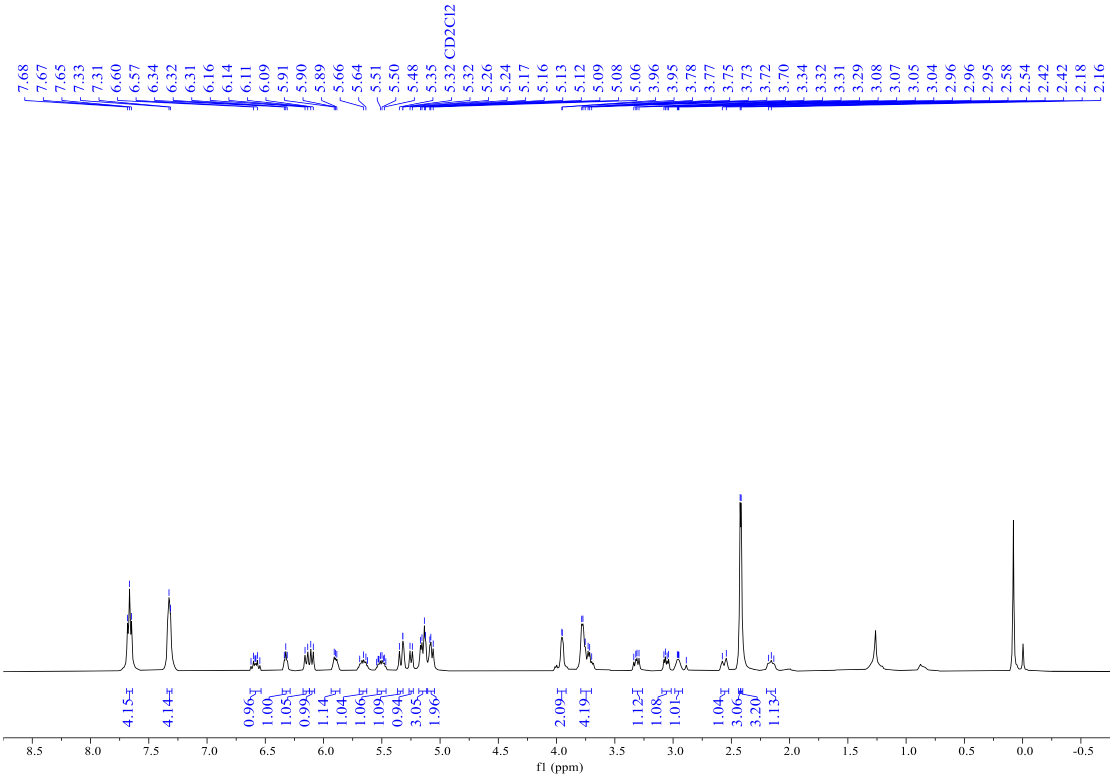
128.12
115.62
110.23
97.91
82.12
71.92
53.84 CD2Cl2
45.46
36.55
34.08
29.53
21.62
3.30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
N
O
Ts
N

2a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7.67
7.65
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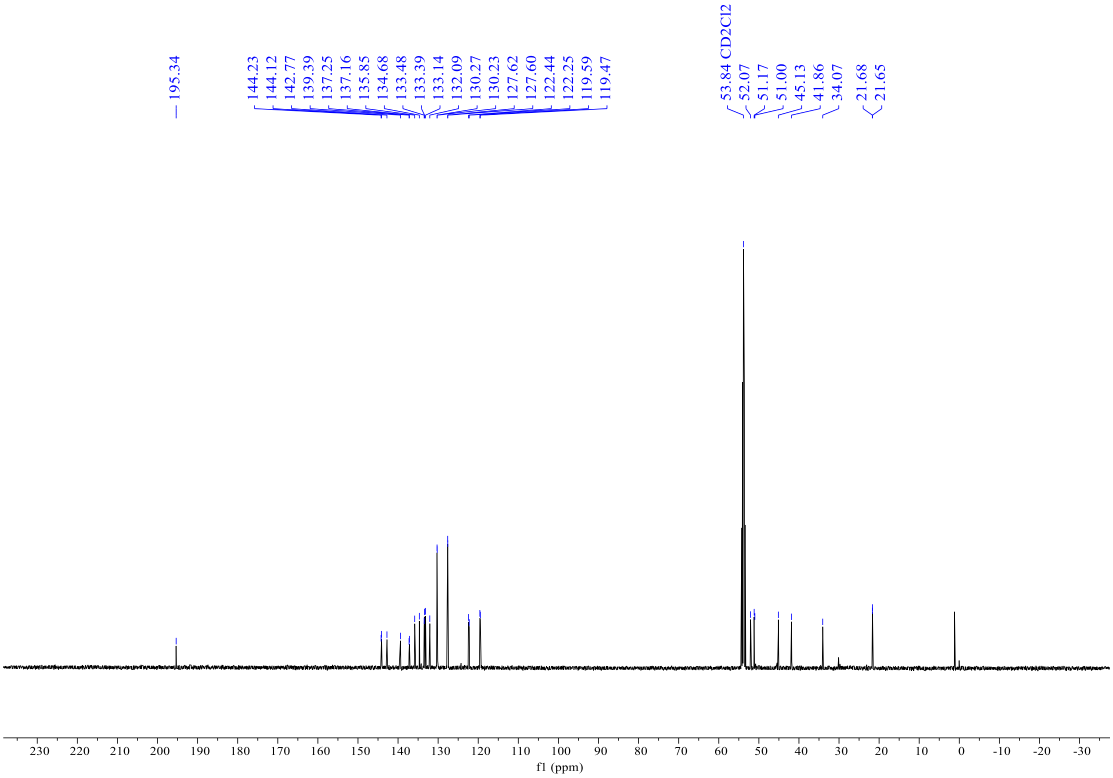
6.60
6.57
6.34
6.32
6.31
6.16
6.14
6.11
6.09
5.91
5.90
5.89
5.66
5.64
5.51
5.50
5.48
5.35
5.32 CD2Cl2
5.32
5.26
5.24
5.17
5.16
5.13
5.12
5.09
5.08
5.06
3.96
3.95
3.78
3.77
3.75
3.73
3.72
3.70
3.34
3.32
3.31
3.29
3.08
3.07
3.05
3.04
2.96
2.96
2.95
2.58
2.54
2.42
2.42
2.18
2.16
4.15
4.14
0.96
1.00
1.05
0.99
1.14
1.04
1.06
1.09
0.94
3.05
1.96
2.09
4.19
1.12
1.08
1.01
1.04
3.06
3.20
1.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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144.12
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139.39
137.25
137.16
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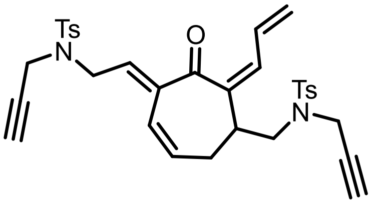
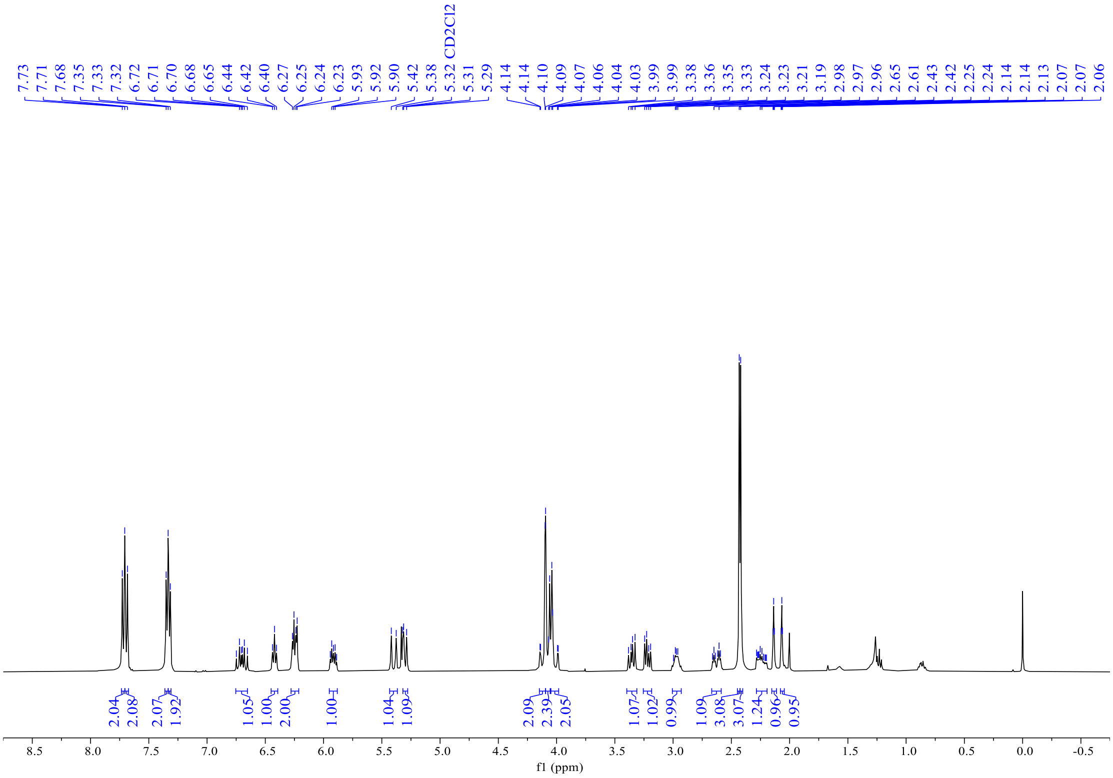
134.68
133.48
133.39
133.14
132.09
130.27
130.23
127.62
127.60
122.44
122.25
119.59
119.47
53.84 CD2Cl2
52.07
51.17
51.00
45.13
41.86
34.07
21.68
21.65
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


Ts
N
O
Ts
N

2b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7.68
7.35
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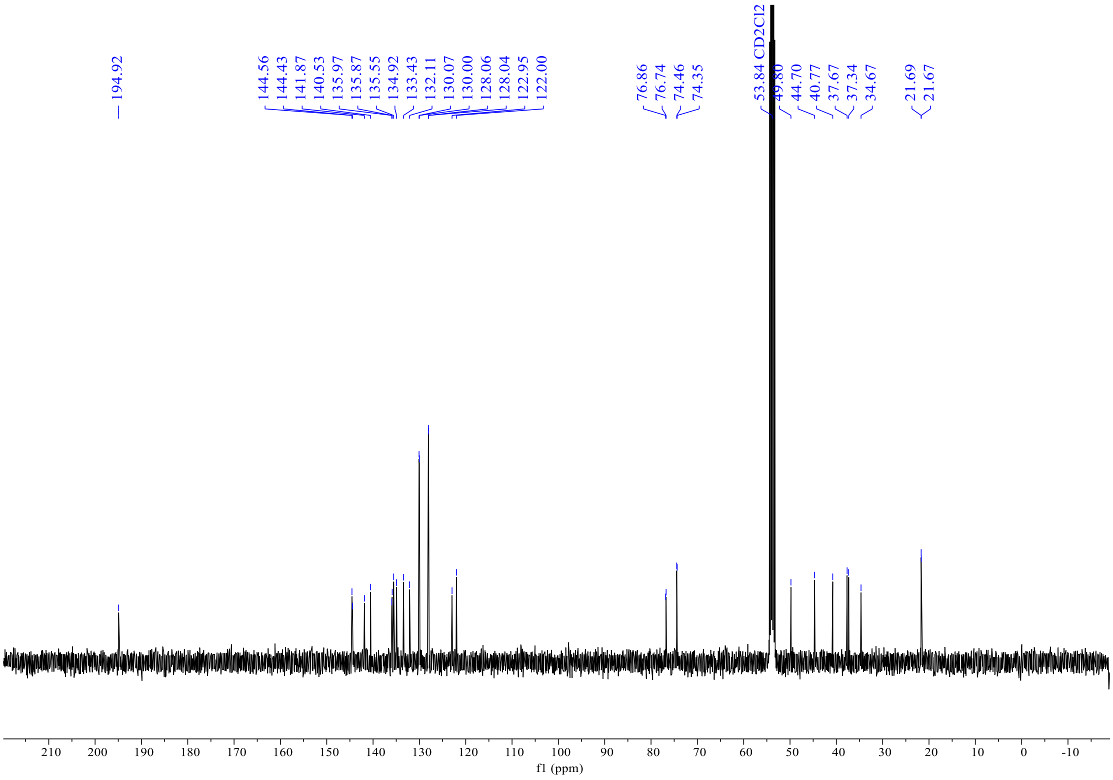
7.32
6.72
6.71
6.70
6.68
6.65
6.44
6.42
6.40
6.27
6.25
6.24
6.23
5.93
5.92
5.90
5.42
5.38
5.32 CD2Cl2
5.31
5.29
4.14
4.14
4.10
4.09
4.07
4.06
4.04
4.03
3.99
3.99
3.38
3.36
3.35
3.33
3.24
3.23
3.21
3.19
2.98
2.97
2.96
2.65
2.61
2.43
2.42
2.25
2.24
2.14
2.14
2.13
2.07
2.07
2.06
2.04
2.08
2.07
1.92
1.05
1.00
2.00
1.00
1.04
1.09
2.09
2.39
2.05
1.07
1.02
0.99
1.09
3.08
3.07
1.24
0.96
0.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


194.92
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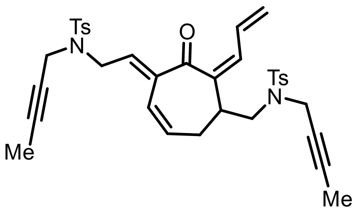
140.53
135.97
135.87
135.55
134.92
133.43
132.11
130.07
130.00
128.06
128.04
122.95
122.00
76.86
76.74
74.46
74.35
53.84 CD2Cl2
49.80
44.70
40.77
37.67
37.34
34.67
21.69
21.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
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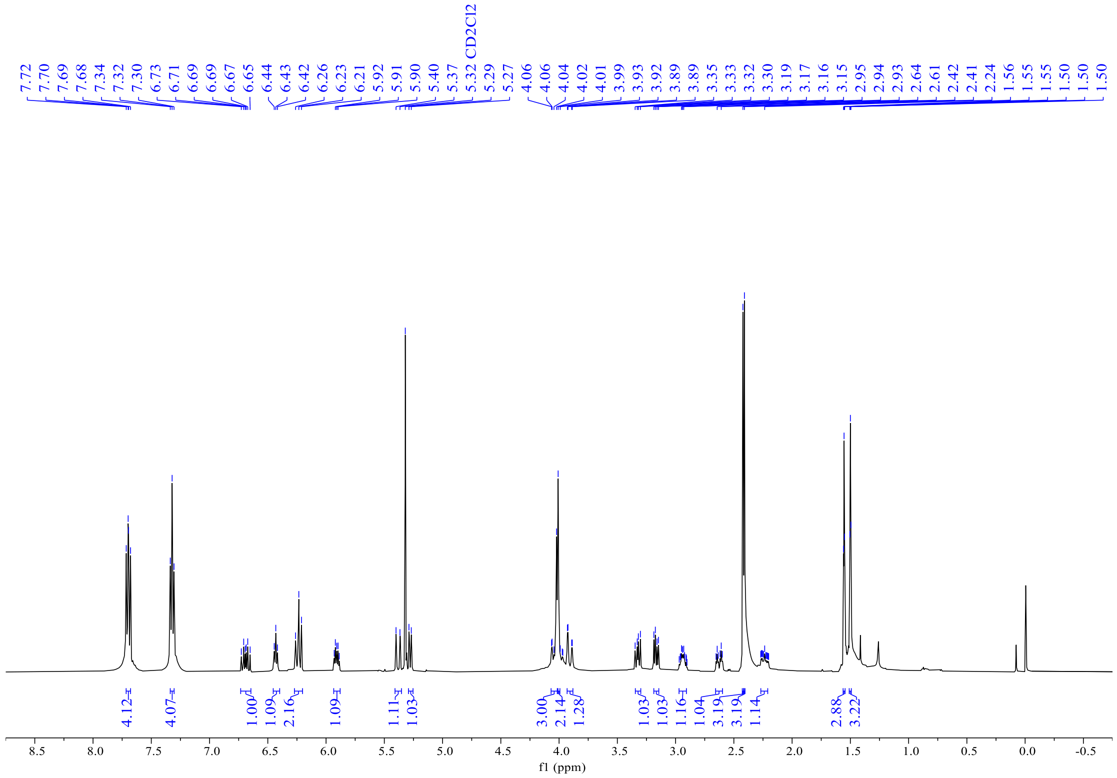
O
Ts
N
Me
Me

2c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7.32
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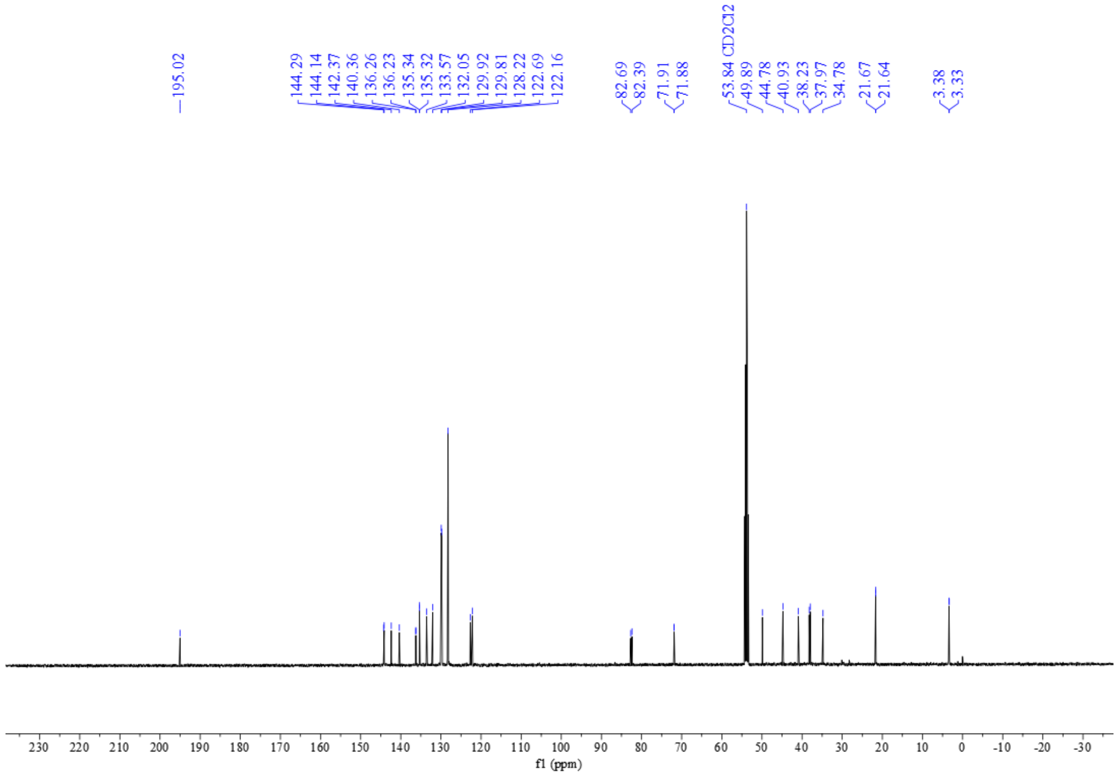
6.71
6.69
6.69
6.67
6.65
6.44
6.43
6.42
6.26
6.23
6.21
5.92
5.91
5.90
5.40
5.37
5.32 CD2Cl2
5.29
5.27
4.06
4.06
4.04
4.02
4.01
3.99
3.93
3.92
3.89
3.89
3.35
3.33
3.32
3.30
3.19
3.17
3.16
3.15
2.95
2.94
2.93
2.64
2.61
2.42
2.41
2.24
1.56
1.55
1.50
1.50
1.50
4.12
4.07
1.00
1.09
2.16
1.09
1.11
1.03
3.00
2.14
1.28
1.03
1.03
1.16
1.04
3.19
3.19
1.14
2.88
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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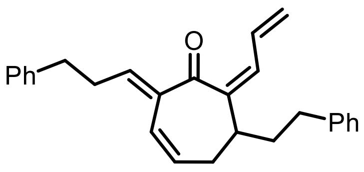
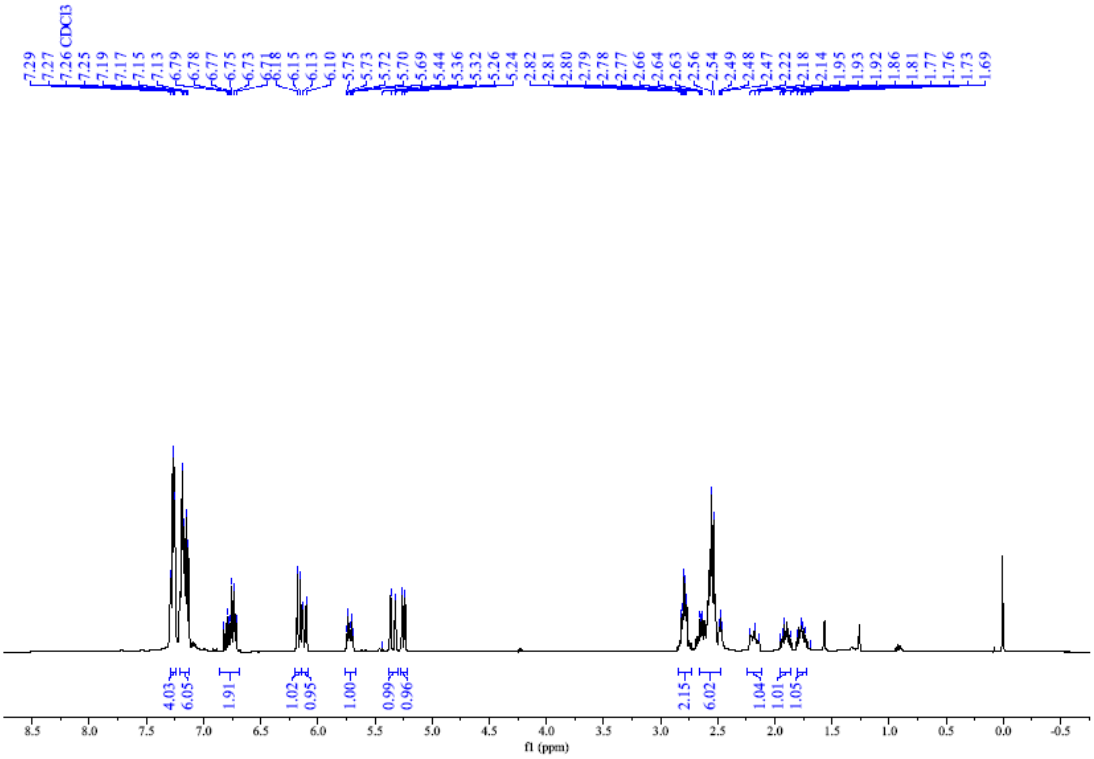
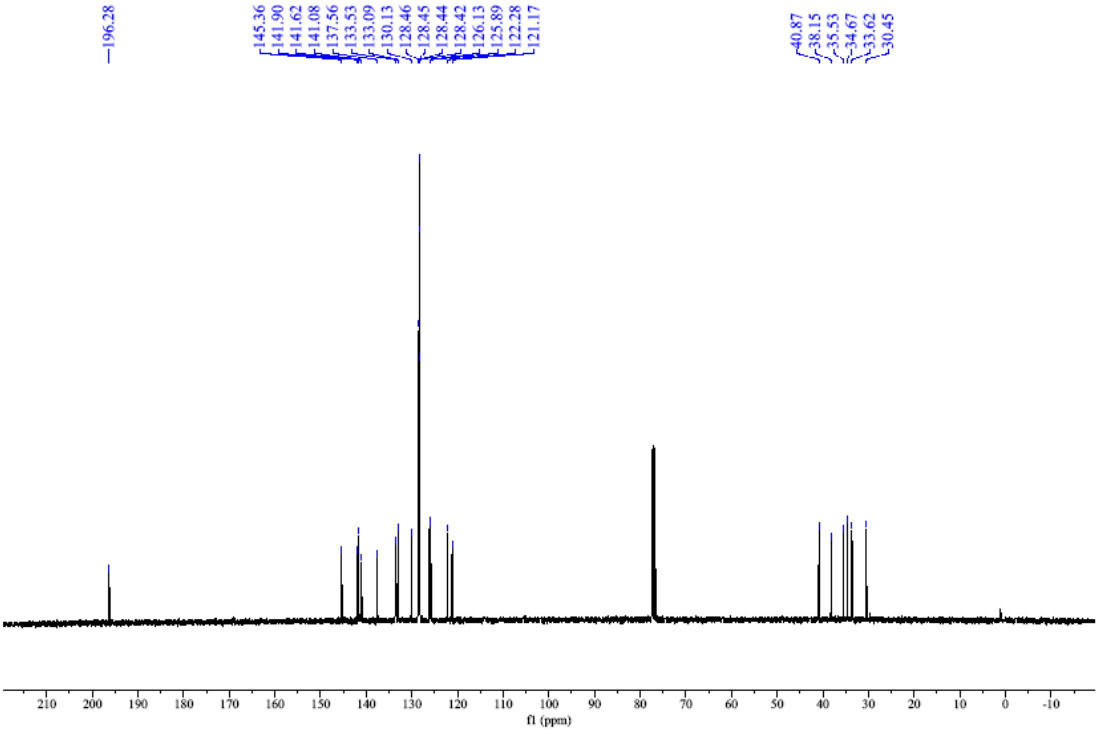
144.29
144.14
142.37
140.36
136.26
136.23
135.34
135.32
133.57
132.05
129.92
129.81
128.22
122.69
122.16
82.69
82.39
71.91
71.88
53.84 CD2Cl2
49.89
44.78
40.93
38.23
37.97
34.78
21.67
21.64
3.38
3.33
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


O
Ph
Ph

2d


7.29
7.27
7.26 CDCl3
7.25
7.19
7.17
7.15
7.13
6.79
6.78
6.77
6.75
6.73
6.71
6.18
6.15
6.13
6.10
5.75
5.73
5.72
5.70
5.69
5.44
5.36
5.32
5.26
5.24
2.82
2.81
2.80
2.79
2.78
2.77
2.66
2.64
2.63
2.56
2.54
2.49
2.48
2.47
2.22
2.18
2.14
1.95
1.93
1.92
1.86
1.81
1.77
1.76
1.73
1.69
4.03
6.05
1.91
1.02
0.95
1.00
0.99
0.96
2.15
6.02
1.04
1.01
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


196.28
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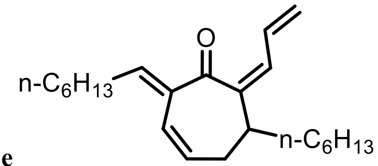
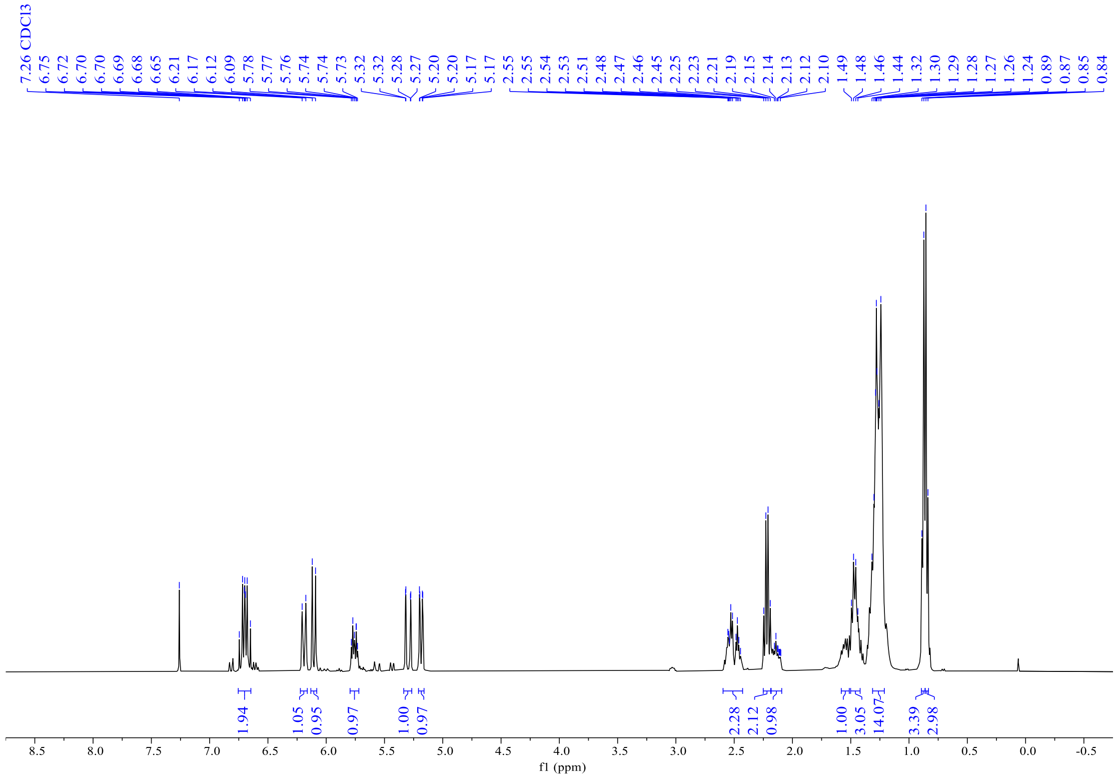
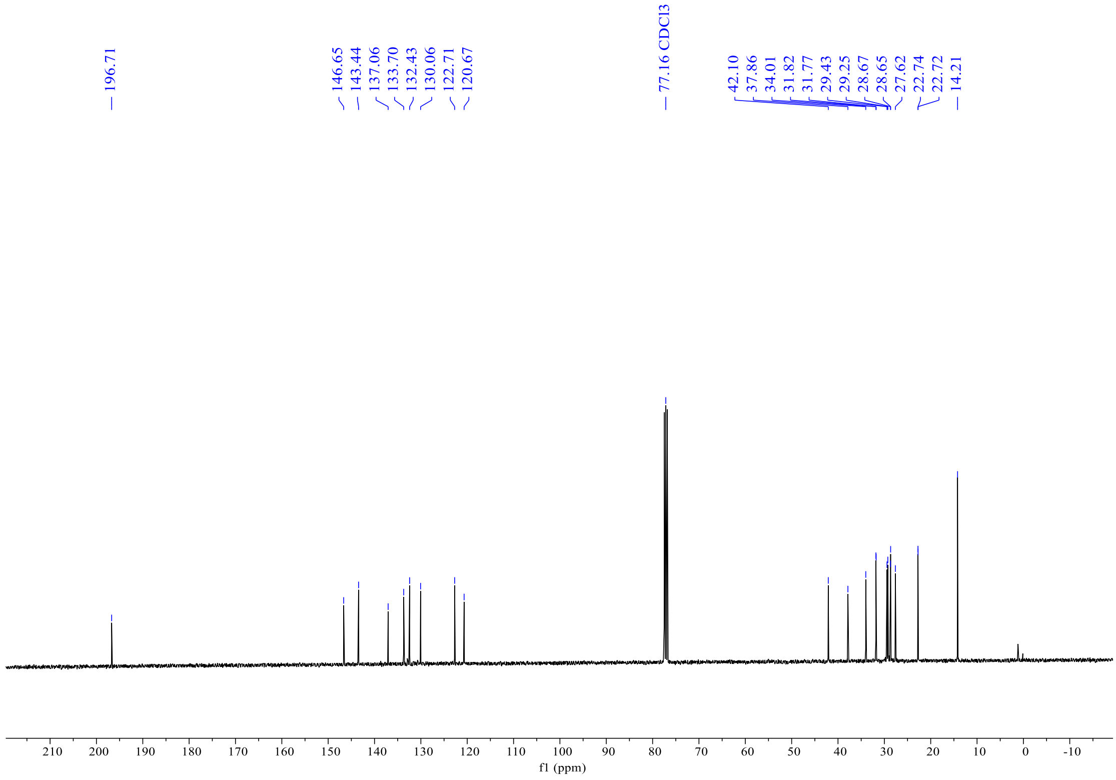
141.62
141.08
137.56
133.53
133.09
130.13
128.46
128.45
128.44
128.42
126.13
125.89
122.28
121.17
40.87
38.15
35.53
34.67
33.62
30.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
n-C6H13
n-C6H13

2e


7.26 CDCl3
6.75
6.72
6.70
6.70
6.69
6.68
6.65
6.21
6.17
6.12
6.09
5.78
5.77
5.76
5.74
5.74
5.73
5.32
5.32
5.28
5.27
5.20
5.20
5.17
5.17
2.55
2.55
2.54
2.53
2.51
2.48
2.47
2.46
2.45
2.25
2.23
2.21
2.19
2.15
2.14
2.13
2.12
2.10
1.49
1.48
1.46
1.44
1.32
1.30
1.29
1.28
1.27
1.26
1.24
0.89
0.87
0.85
0.84
1.94
1.05
0.95
0.97
1.00
0.97
2.28
2.12
0.98
1.00
3.05
14.07
3.39
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


196.71
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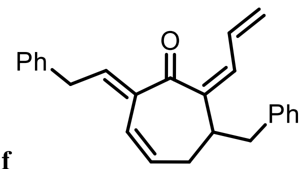
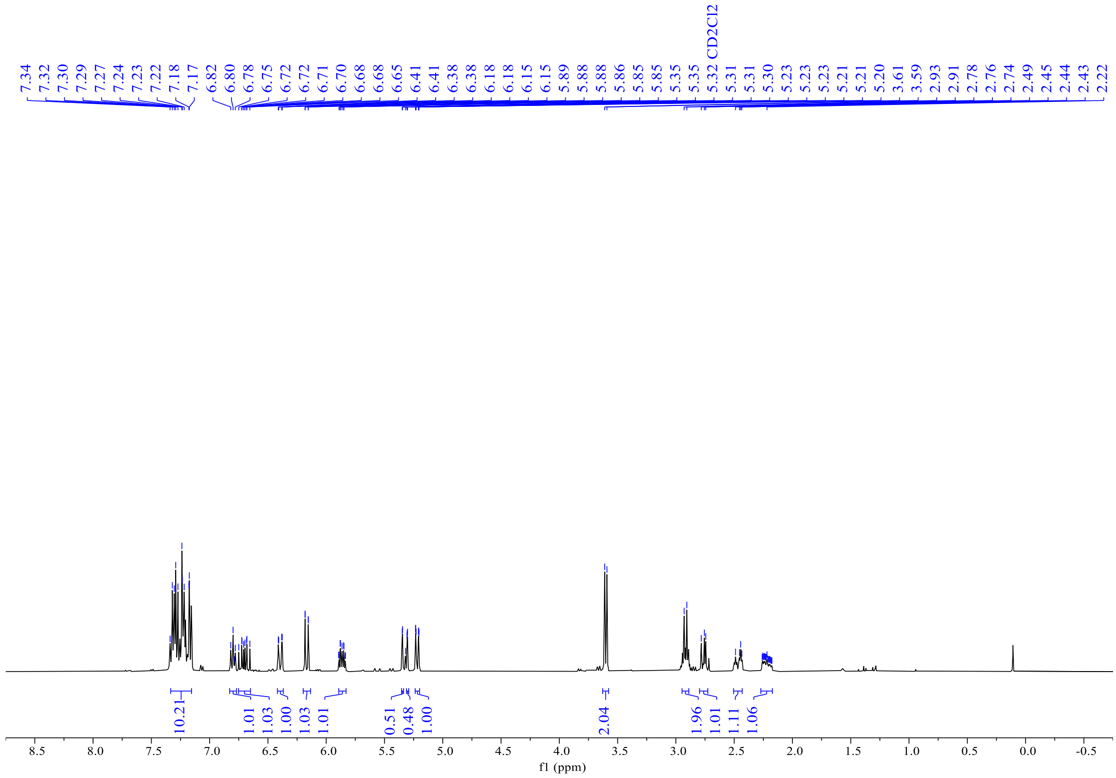
143.44
137.06
133.70
132.43
130.06
122.71
120.67
77.16 CDCl3
42.10
37.86
34.01
31.82
31.77
29.43
29.25
28.67
28.65
27.62
22.74
22.72
14.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Ph
Ph

2f


7.34
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7.30
7.29
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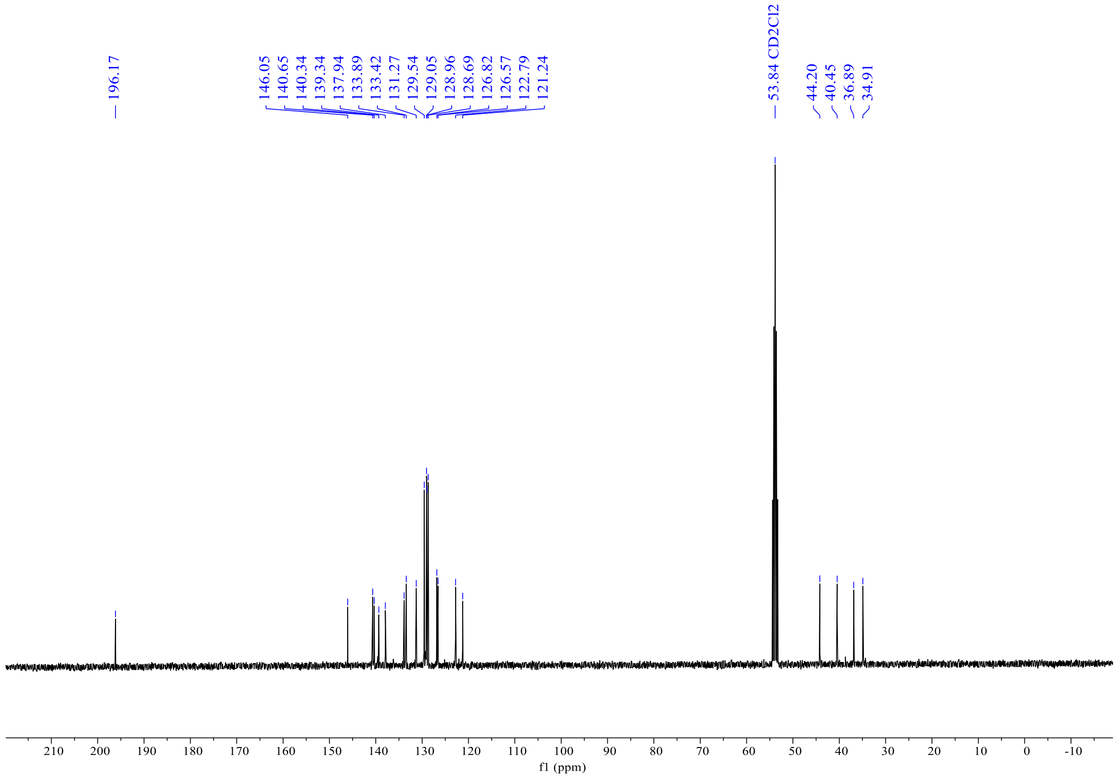
7.24
7.23
7.22
7.18
7.17
6.82
6.80
6.78
6.75
6.72
6.72
6.71
6.70
6.68
6.68
6.65
6.41
6.41
6.38
6.38
6.18
6.18
6.15
6.15
5.89
5.88
5.86
5.85
5.85
5.35
5.35
5.32 CD2Cl2
5.31
5.31
5.30
5.23
5.23
5.23
5.21
5.21
5.20
3.61
3.59
2.93
2.91
2.78
2.76
2.74
2.49
2.45
2.44
2.43
2.22
10.21
1.01
1.03
1.00
1.03
1.01
0.51
0.48
1.00
2.04
1.96
1.01
1.11
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


196.17
146.05
140.65
140.34
139.34
137.94
133.89
133.42
131.27
129.54
129.05
128.96
128.69
126.82
126.57
122.79
121.24
53.84 CD2Cl2
44.20
40.45
36.89
34.91
210
200
190
180
170
160
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100
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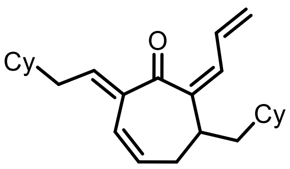
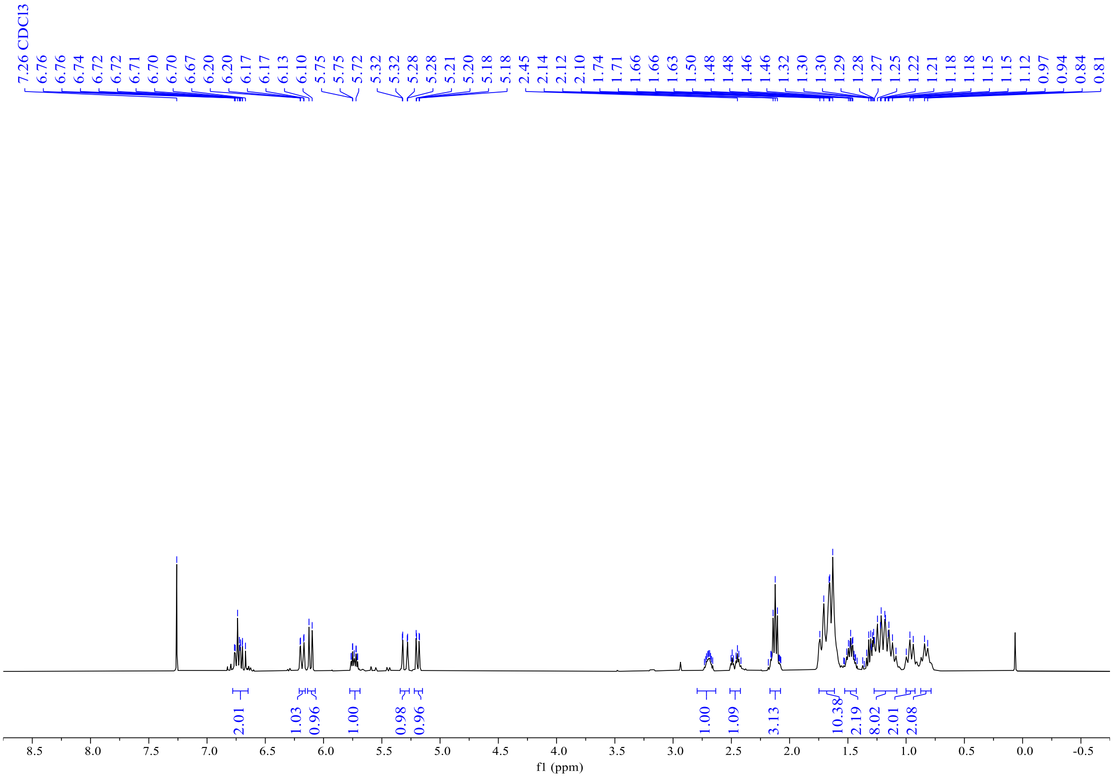
-10
f1 (ppm)


O
Cy
Cy

2g


7.26 CDCl3
6.76
6.76
6.74
6.72
6.72
6.71
6.70
6.70
6.67
6.20
6.20
6.17
6.17
6.13
6.10
5.75
5.75
5.72
5.32
5.32
5.28
5.28
5.21
5.20
5.18
5.18
2.45
2.14
2.12
2.10
1.74
1.71
1.66
1.66
1.63
1.50
1.48
1.48
1.46
1.46
1.32
1.30
1.30
1.29
1.28
1.27
1.25
1.22
1.21
1.18
1.18
1.15
1.15
1.12
0.97
0.94
0.84
0.81
2.01
1.03
0.96
1.00
0.98
0.96
1.00
1.09
3.13
10.38
2.19
8.02
2.01
2.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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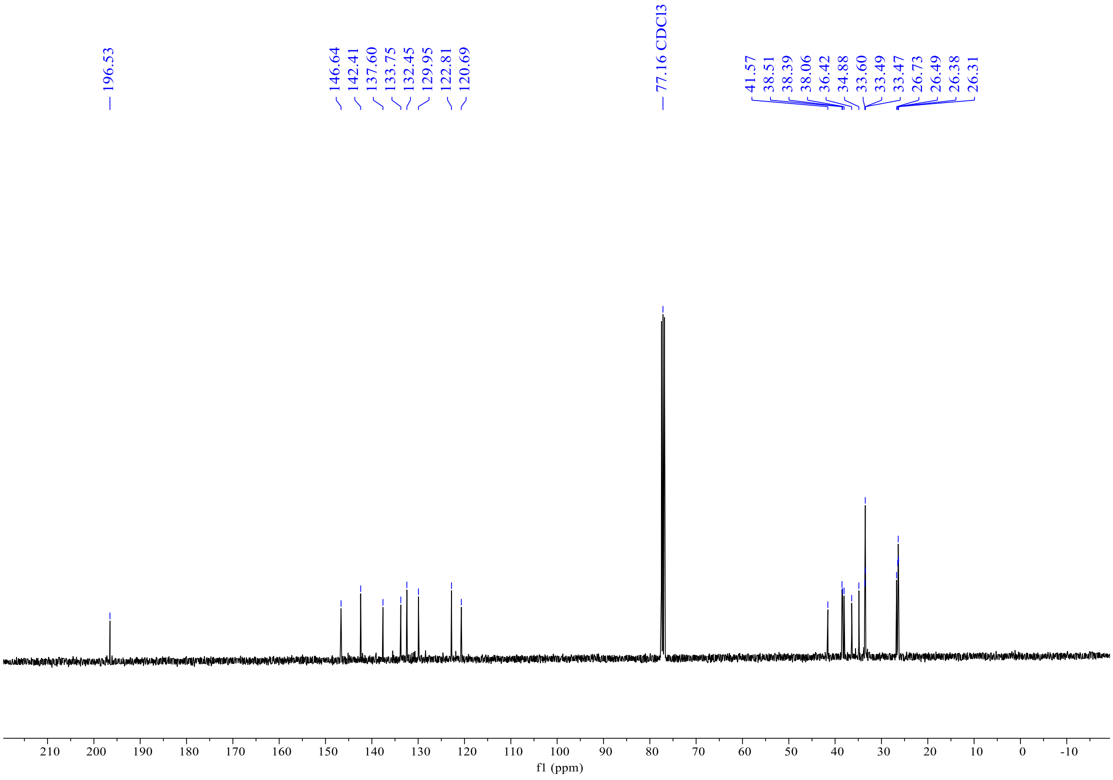
0.0
-0.5
f1 (ppm)


196.53
146.64
142.41
137.60
133.75
132.45
129.95
122.81
120.69
77.16 CDCl3
41.57
38.51
38.39
38.06
36.42
34.88
33.60
33.49
33.47
26.73
26.49
26.38
26.31
210
200
190
180
170
160
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140
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120
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100
90
80
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40
30
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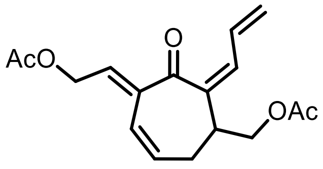
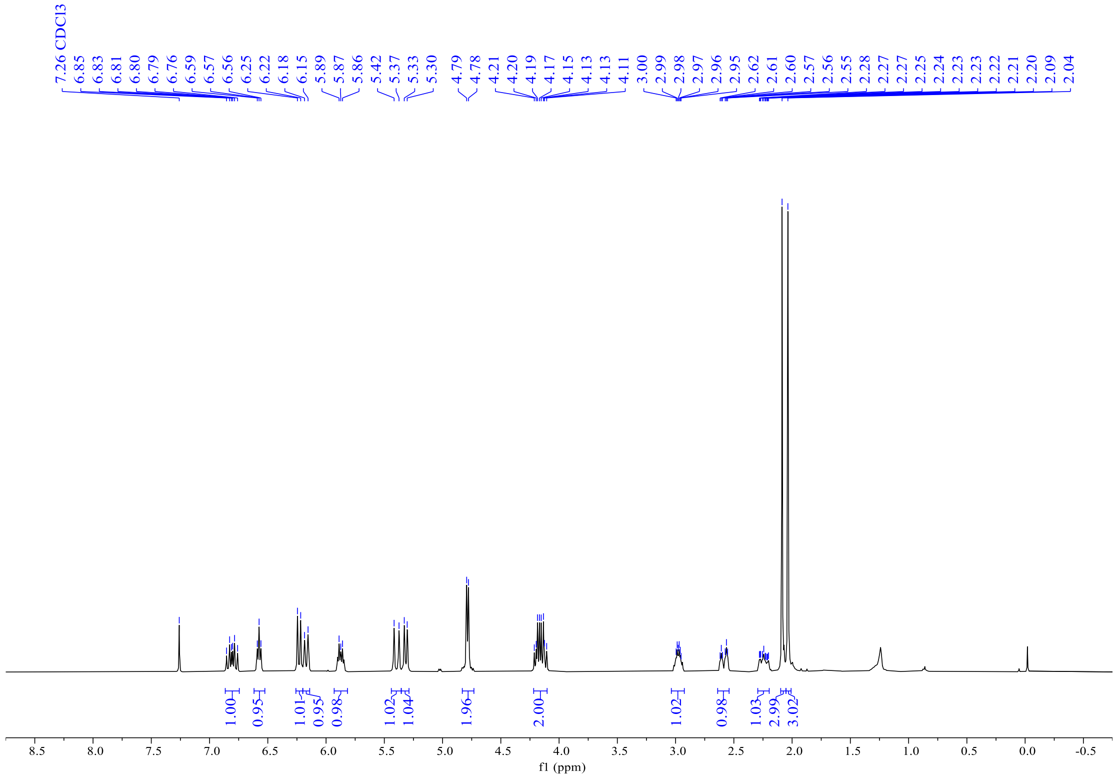
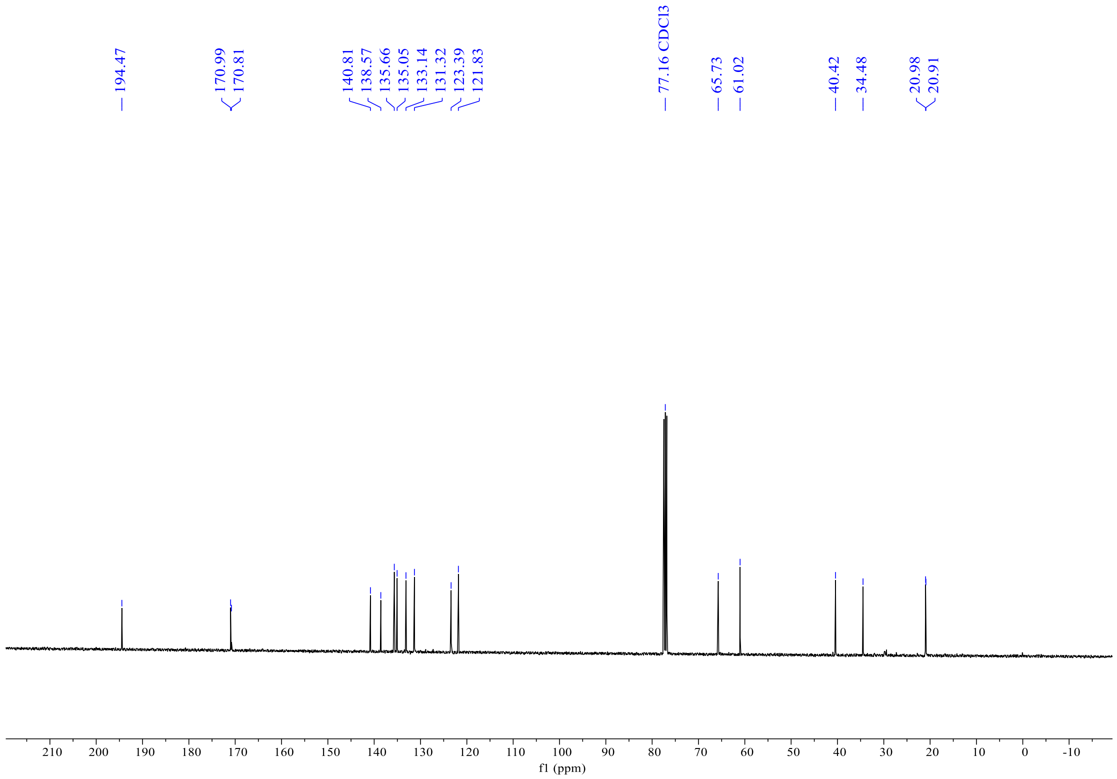
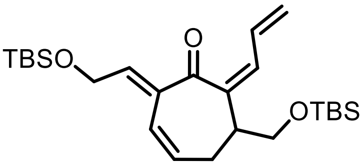
10
0
-10
f1 (ppm)


AcO
O
OAc

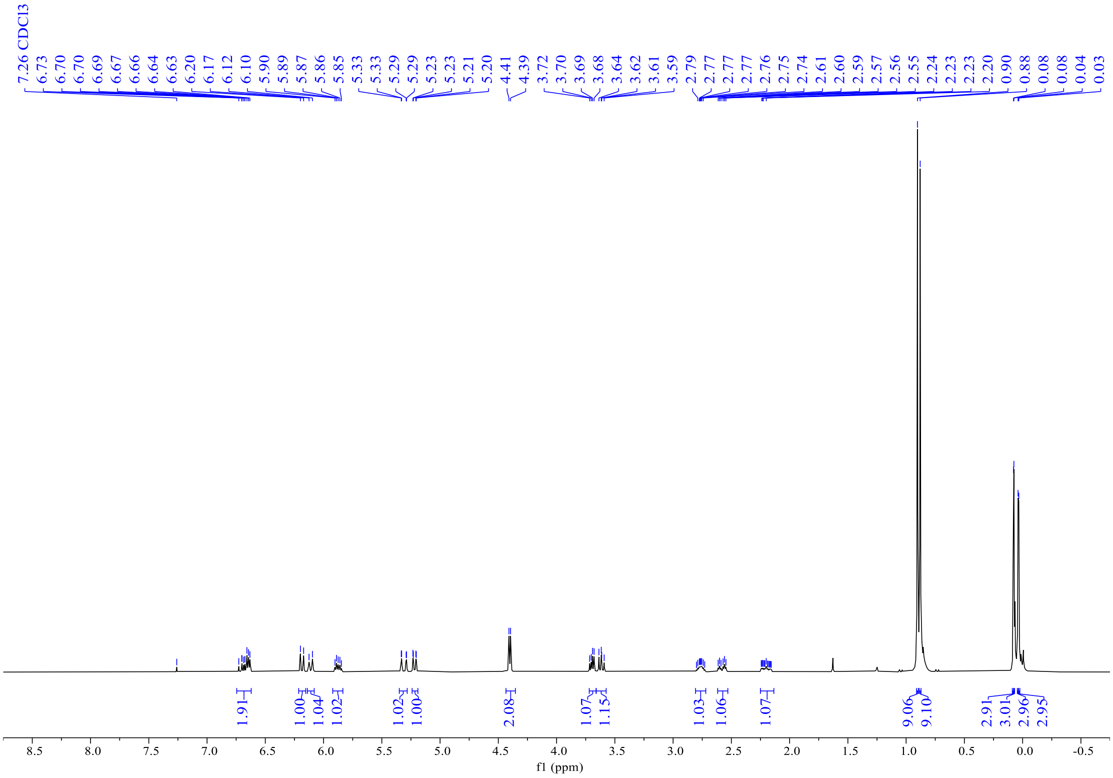
2h

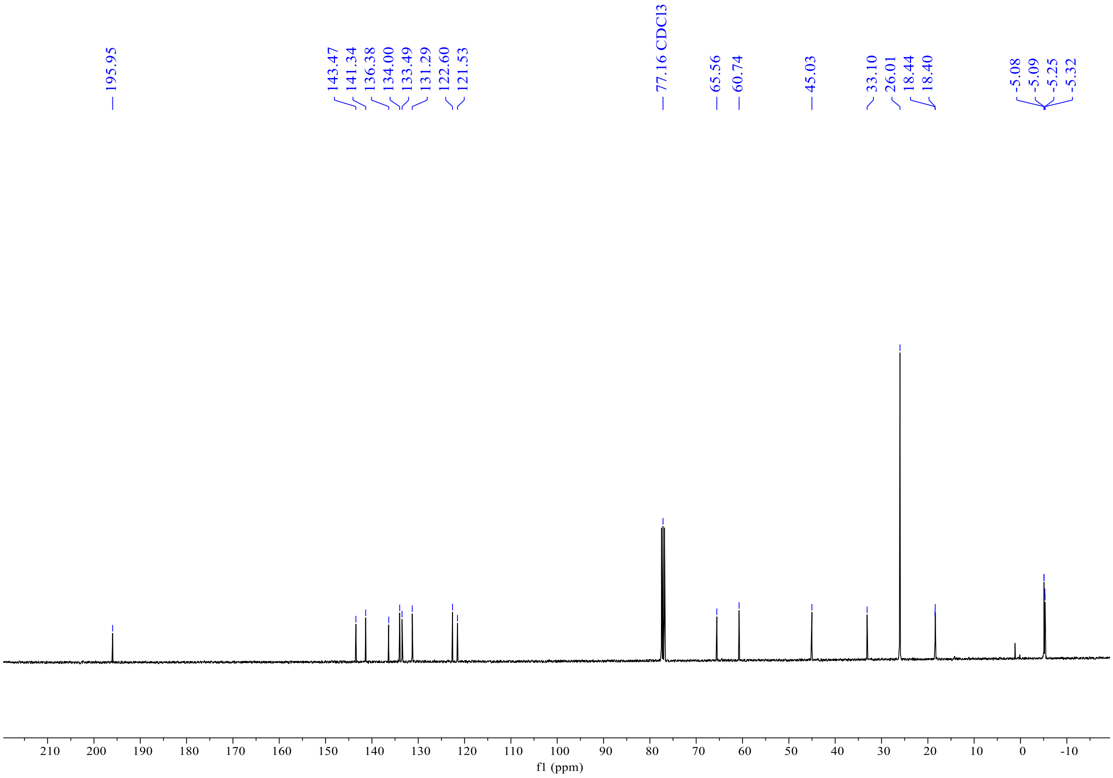

7.26 CDCl3
6.85
6.83
6.81
6.80
6.79
6.76
6.59
6.57
6.56
6.25
6.22
6.18
6.15
5.89
5.87
5.86
5.42
5.37
5.33
5.30
4.79
4.78
4.21
4.20
4.19
4.17
4.15
4.13
4.13
4.11
3.00
2.99
2.98
2.97
2.96
2.95
2.62
2.61
2.60
2.57
2.56
2.55
2.28
2.27
2.27
2.25
2.24
2.23
2.23
2.22
2.21
2.20
2.09
2.04
1.00
0.95
1.01
0.95
0.98
1.02
1.04
1.96
2.00
1.02
0.98
1.03
2.99
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


194.47
170.99
170.81
140.81
138.57
135.66
135.05
133.14
131.32
123.39
121.83
77.16 CDCl3
65.73
61.02
40.42
34.48
20.98
20.91
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
O
OTBS

2i


7.26 CDCl3
6.73
6.70
6.70
6.69
6.67
6.66
6.64
6.63
6.20
6.17
6.12
6.10
5.90
5.89
5.87
5.86
5.85
5.33
5.33
5.29
5.29
5.23
5.23
5.21
5.20
4.41
4.39
3.72
3.70
3.69
3.68
3.64
3.62
3.61
3.59
2.79
2.77
2.77
2.77
2.76
2.75
2.74
2.61
2.60
2.59
2.57
2.56
2.55
2.24
2.23
2.23
2.20
0.90
0.88
0.08
0.08
0.04
0.03
1.91
1.00
1.04
1.02
1.02
1.00
2.08
1.07
1.15
1.03
1.06
1.07
9.06
9.10
2.91
3.01
2.96
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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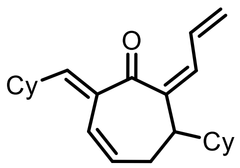
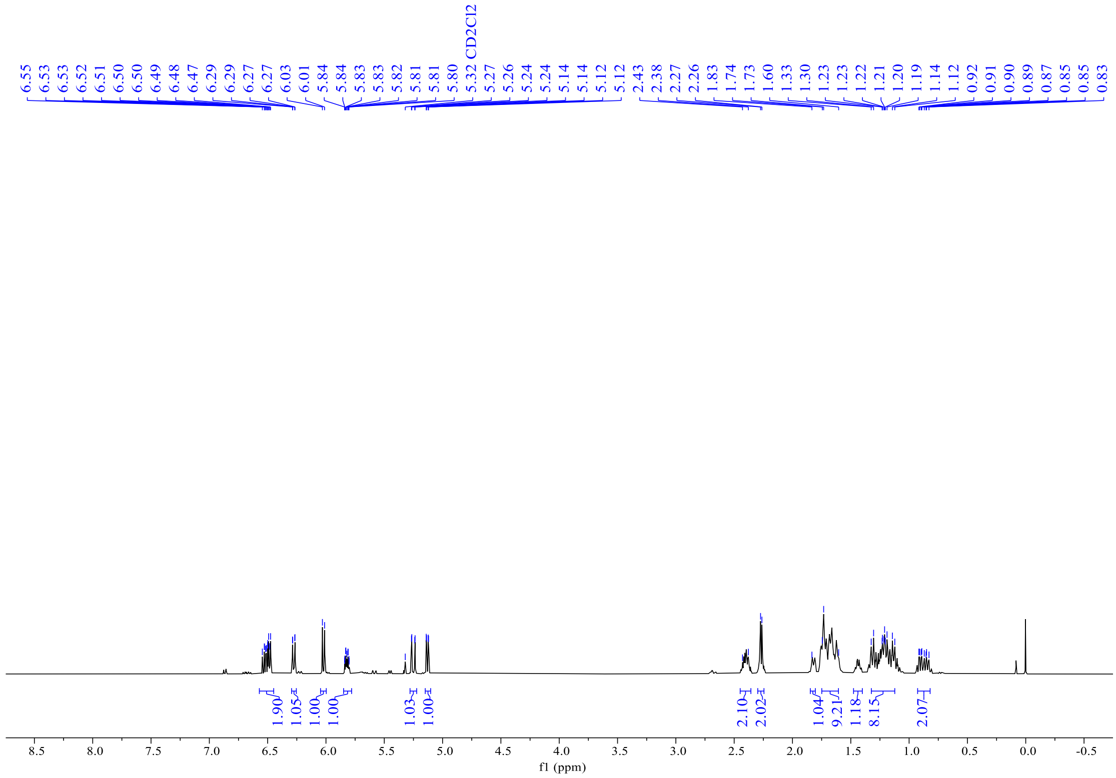
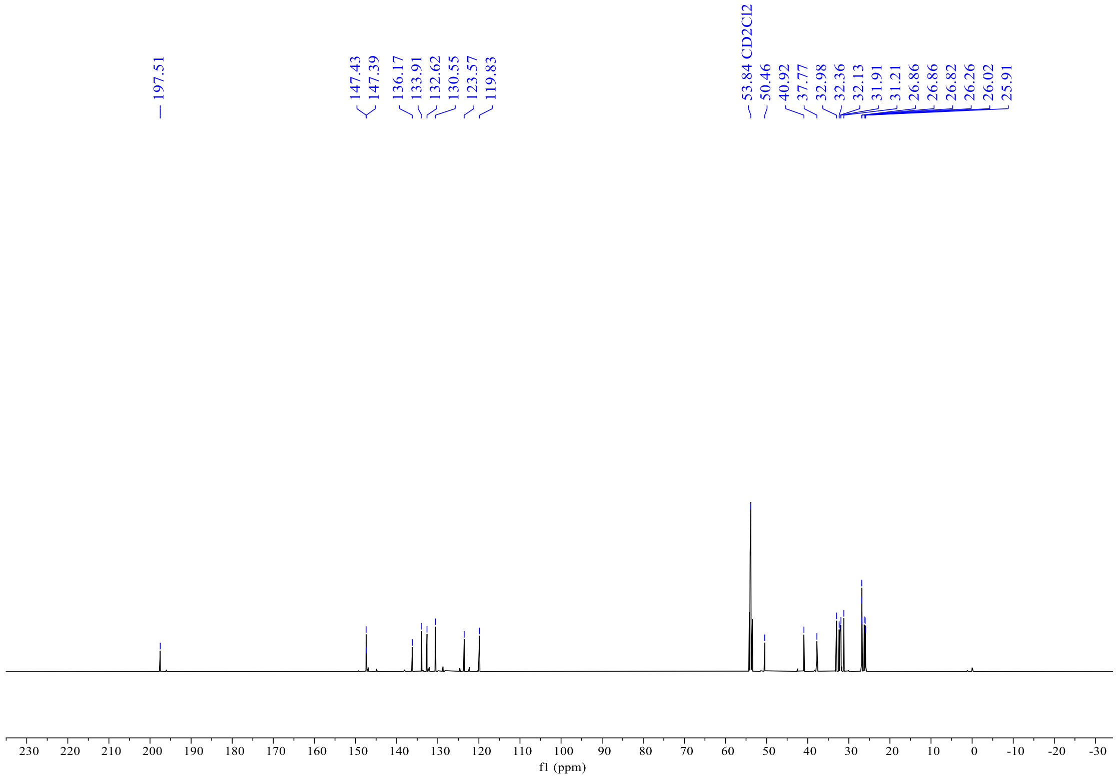
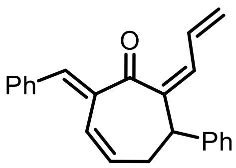
143.47
141.34
136.38
134.00
133.49
131.29
122.60
121.53
77.16 CDCl3
65.56
60.74
45.03
33.10
26.01
18.44
18.40
-5.08
-5.09
-5.25
-5.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Cy
Cy

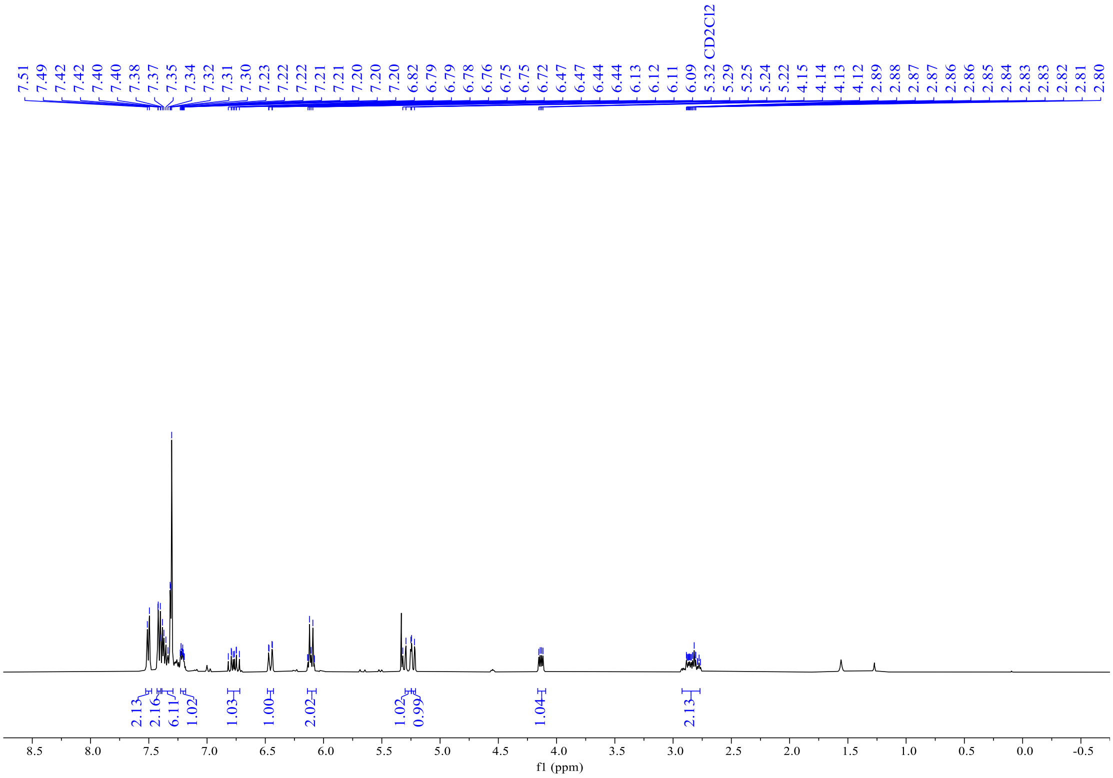
2j


6.55
6.53
6.53
6.52
6.51
6.50
6.50
6.49
6.48
6.47
6.29
6.29
6.27
6.27
6.03
6.01
5.84
5.84
5.83
5.83
5.82
5.81
5.81
5.80
5.32 CD2Cl2
5.27
5.26
5.24
5.24
5.14
5.14
5.12
5.12
2.43
2.38
2.27
2.26
1.83
1.74
1.73
1.60
1.33
1.30
1.23
1.23
1.22
1.21
1.20
1.19
1.14
1.12
0.92
0.91
0.90
0.89
0.87
0.85
0.85
0.83
1.90
1.05
1.00
1.00
1.03
1.00
2.10
2.02
1.04
9.21
1.18
8.15
2.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


197.51
147.43
147.39
136.17
133.91
132.62
130.55
123.57
119.83
53.84 CD2Cl2
50.46
40.92
37.77
32.98
32.36
32.13
31.91
31.21
26.86
26.86
26.82
26.26
26.02
25.91
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)



2k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7.42
7.42
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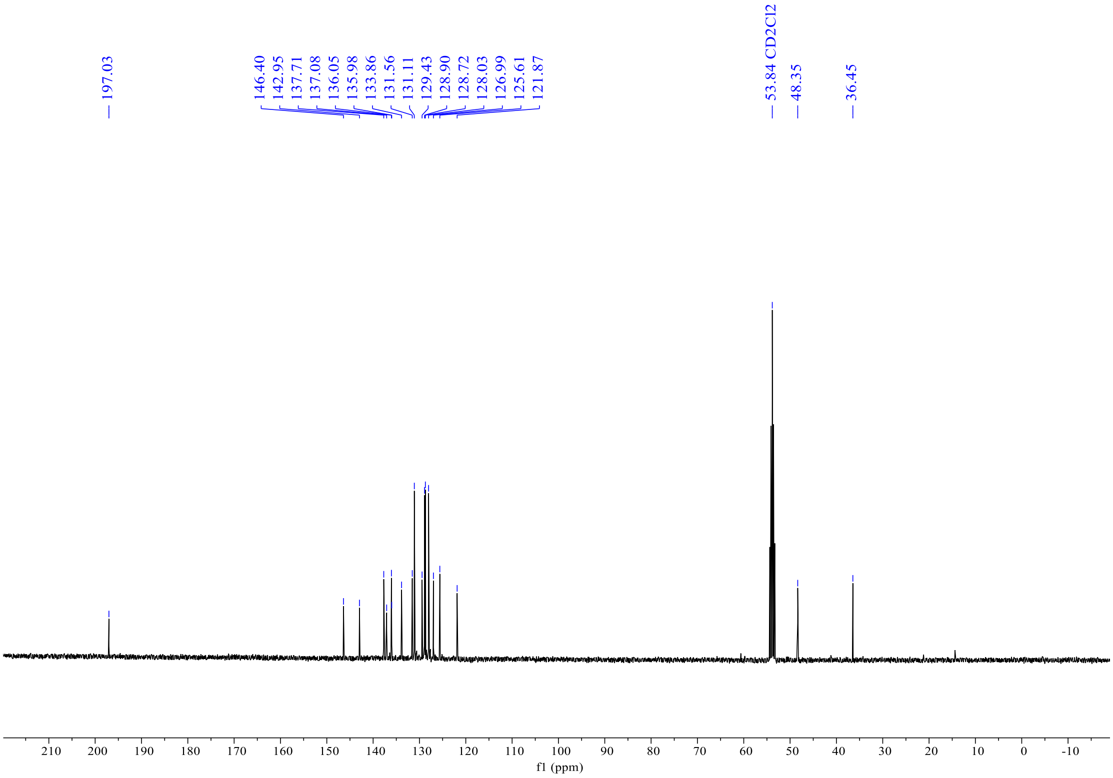
7.40
7.38
7.37
7.35
7.34
7.32
7.31
7.30
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
6.82
6.79
6.79
6.78
6.76
6.75
6.75
6.72
6.47
6.47
6.44
6.44
6.13
6.12
6.11
6.09
5.32 CD2Cl2
5.29
5.25
5.24
5.22
4.15
4.14
4.13
4.12
2.89
2.88
2.87
2.87
2.86
2.86
2.85
2.84
2.83
2.83
2.82
2.81
2.80
2.13
2.16
6.11
1.02
1.03
1.00
2.02
1.02
0.99
1.04
2.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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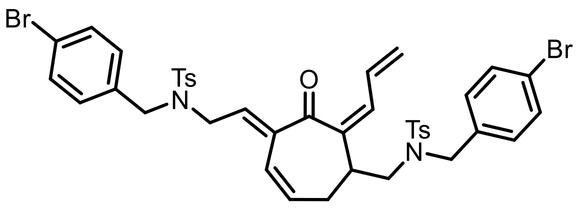
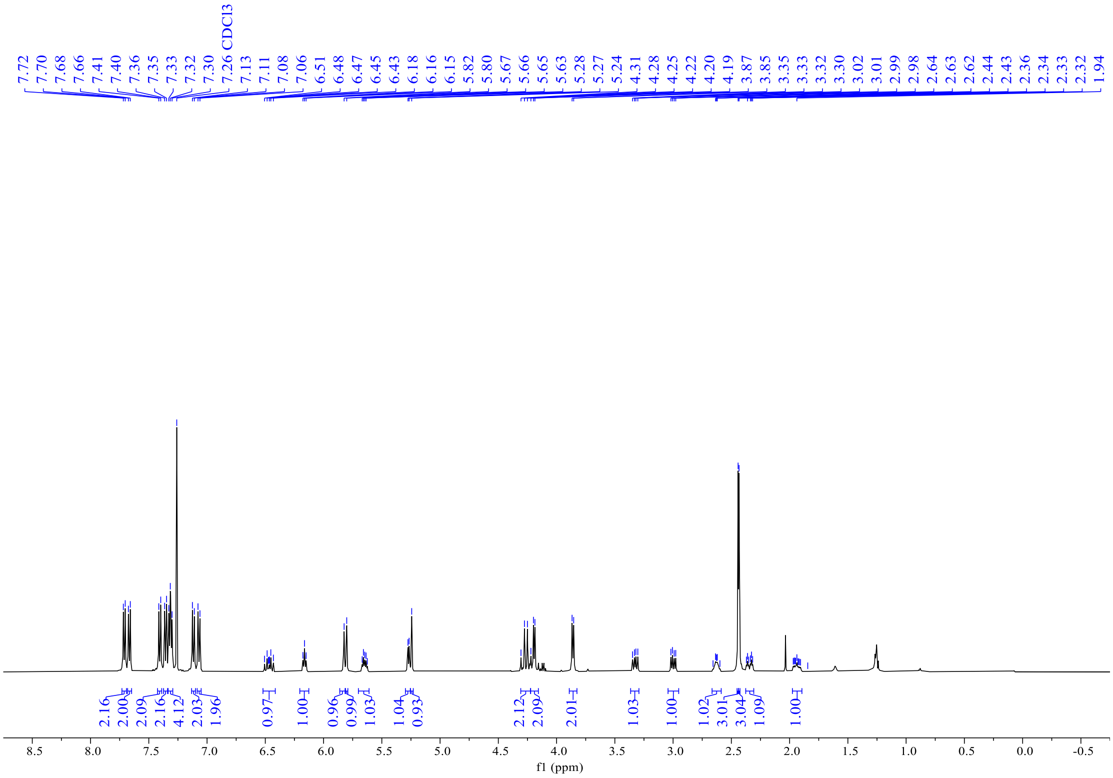
137.71
137.08
136.05
135.98
133.86
131.56
131.11
129.43
128.90
128.72
128.03
126.99
125.61
121.87
53.84 CD2Cl2
48.35
36.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Br
Ts
N
O
Ts
N
Br

2l


7.72
7.70
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7.66
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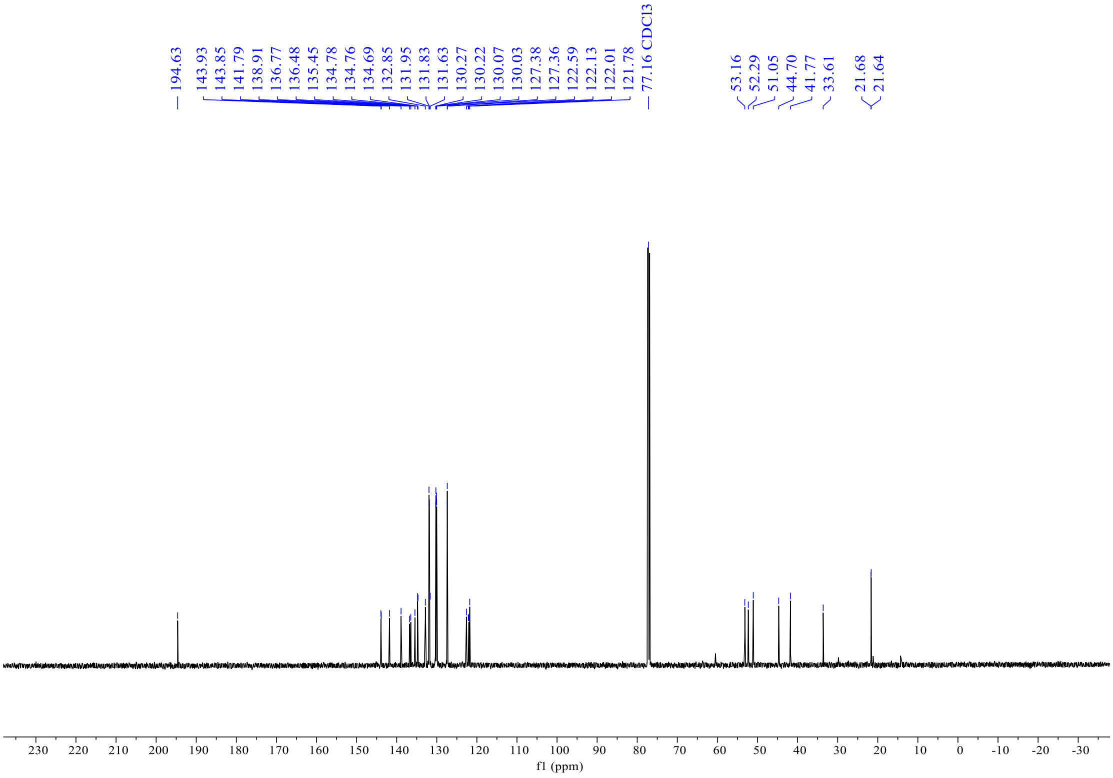
7.40
7.36
7.35
7.33
7.32
7.30
7.26 CDCl3
7.13
7.11
7.08
7.06
6.51
6.48
6.47
6.45
6.43
6.18
6.16
6.15
5.82
5.80
5.67
5.66
5.65
5.63
5.28
5.27
5.24
4.31
4.28
4.25
4.22
4.20
4.19
3.87
3.85
3.35
3.33
3.32
3.30
3.02
3.01
2.99
2.98
2.64
2.63
2.62
2.44
2.43
2.36
2.34
2.33
2.32
1.94
2.16
2.00
2.09
2.16
4.12
2.03
1.96
0.97
1.00
0.96
0.99
1.03
1.04
0.93
2.12
2.09
2.01
1.03
1.00
1.02
3.01
3.04
1.09
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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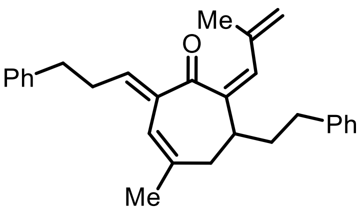
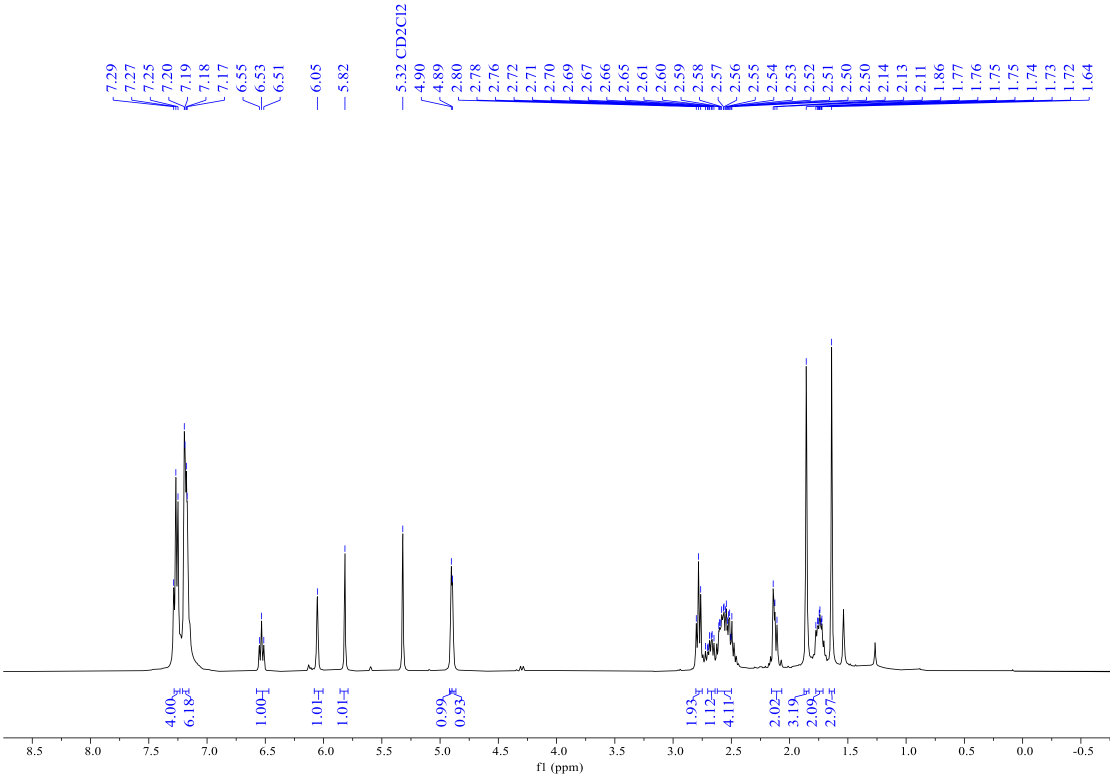
135.45
134.78
134.76
134.69
132.85
131.95
131.83
131.63
130.27
130.22
130.07
130.03
127.38
127.36
122.59
122.13
122.01
121.78
77.16 CDCl3
53.16
52.29
51.05
44.70
41.77
33.61
21.68
21.64
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


Me
O
Ph
Ph
Me

2m


7.29
7.27
7.25
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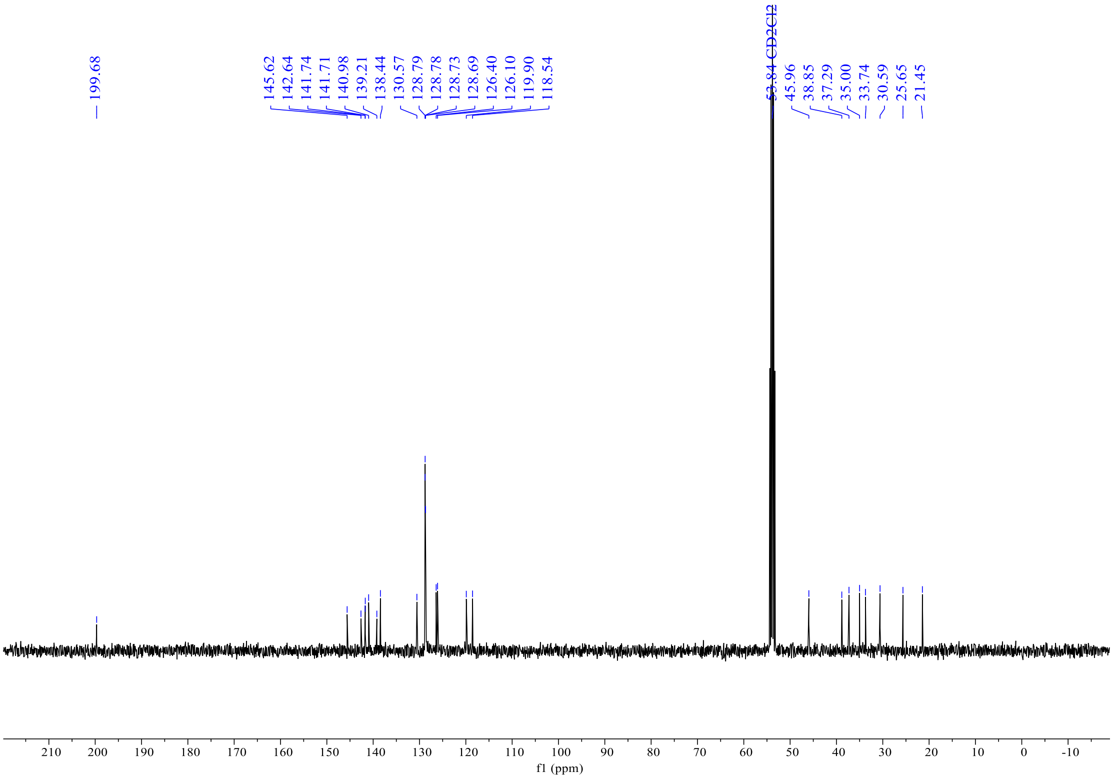
7.19
7.18
7.17
6.55
6.53
6.51
6.05
5.82
5.32 CD2Cl2
4.90
4.89
2.80
2.78
2.76
2.72
2.71
2.70
2.69
2.67
2.66
2.65
2.61
2.60
2.59
2.58
2.57
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.50
2.14
2.13
2.11
1.86
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.64
4.00
6.18
1.00
1.01
1.01
0.99
0.93
1.93
1.12
4.11
2.02
3.19
2.09
2.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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138.44
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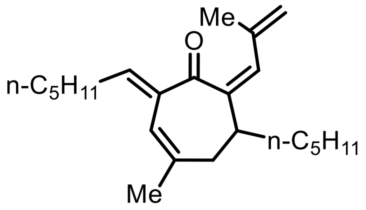
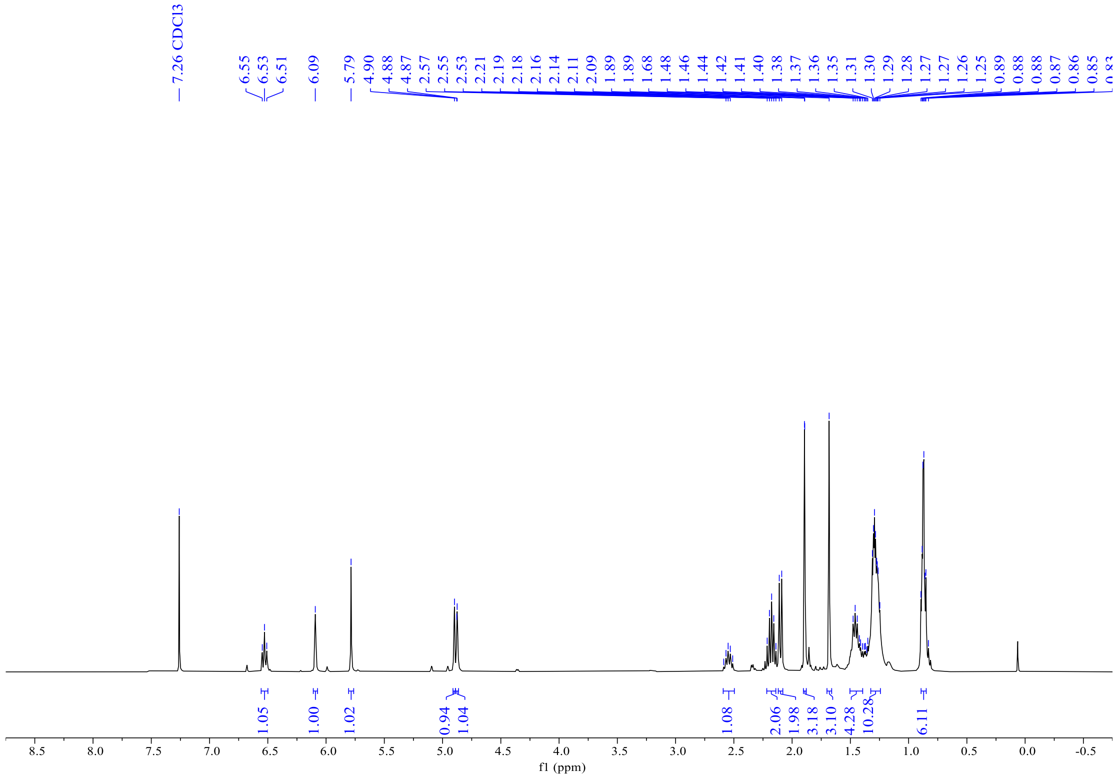
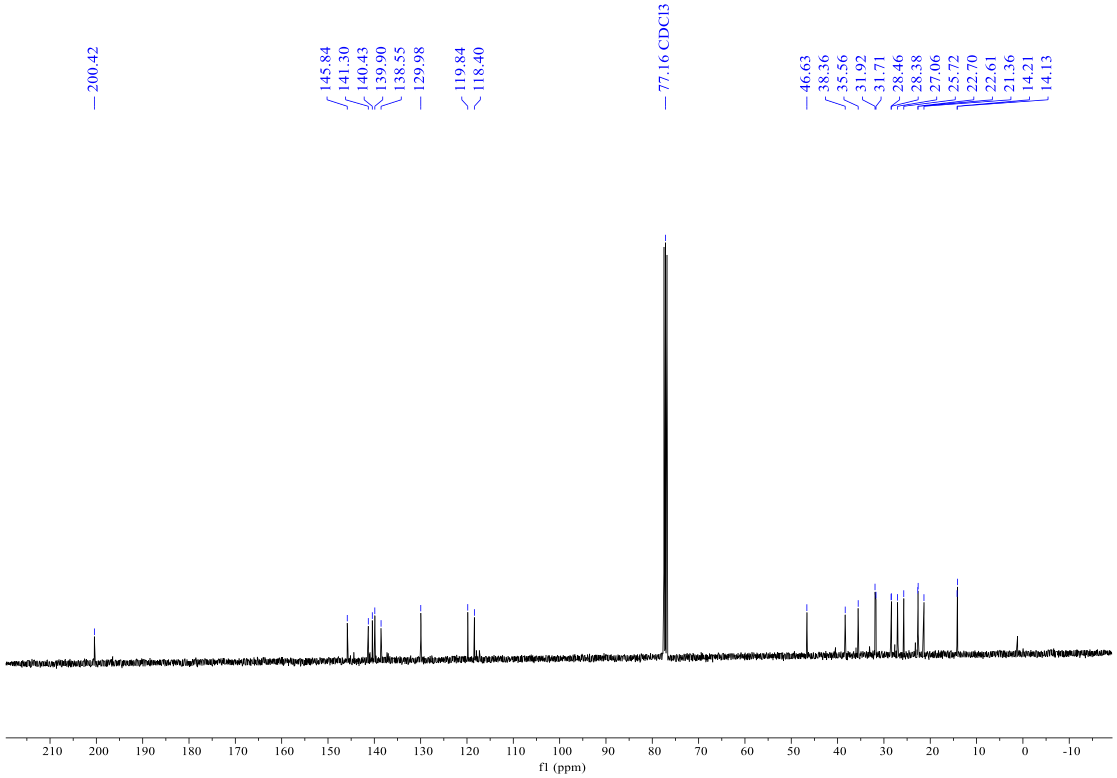
128.79
128.78
128.73
128.69
126.40
126.10
119.90
118.54
53.84 CD2Cl2
45.96
38.85
37.29
35.00
33.74
30.59
25.65
21.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O
n-C5H11
n-C5H11
Me

2n


7.26 CDCl3
6.55
6.53
6.51
6.09
5.79
4.90
4.88
4.87
2.57
2.55
2.53
2.21
2.19
2.18
2.16
2.14
2.11
2.09
1.89
1.89
1.68
1.48
1.46
1.44
1.42
1.41
1.40
1.38
1.37
1.36
1.35
1.31
1.30
1.29
1.28
1.27
1.27
1.26
1.25
0.89
0.88
0.88
0.87
0.86
0.85
1.05
1.00
1.02
0.94
1.04
1.08
2.06
1.98
3.18
3.10
4.28
10.28
6.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


200.42
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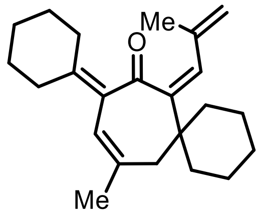
140.43
139.90
138.55
129.98
119.84
118.40
77.16 CDCl3
46.63
38.36
35.56
31.92
31.71
28.46
28.38
27.06
25.72
22.70
22.61
21.36
14.21
14.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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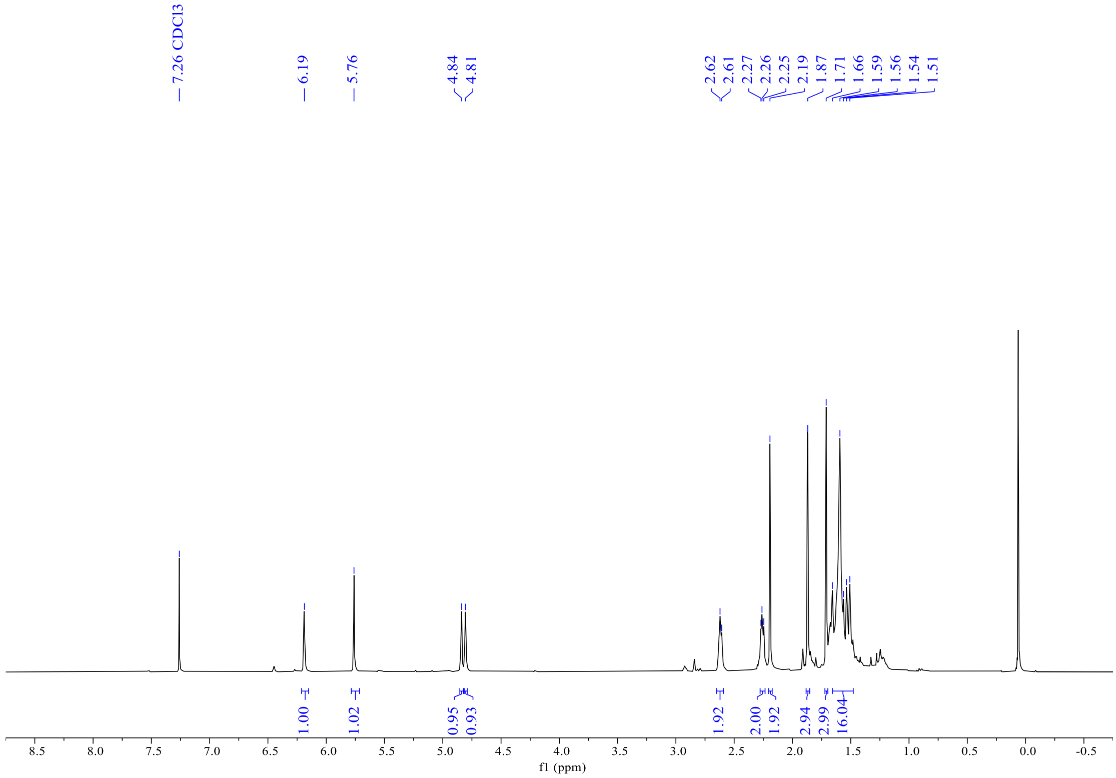
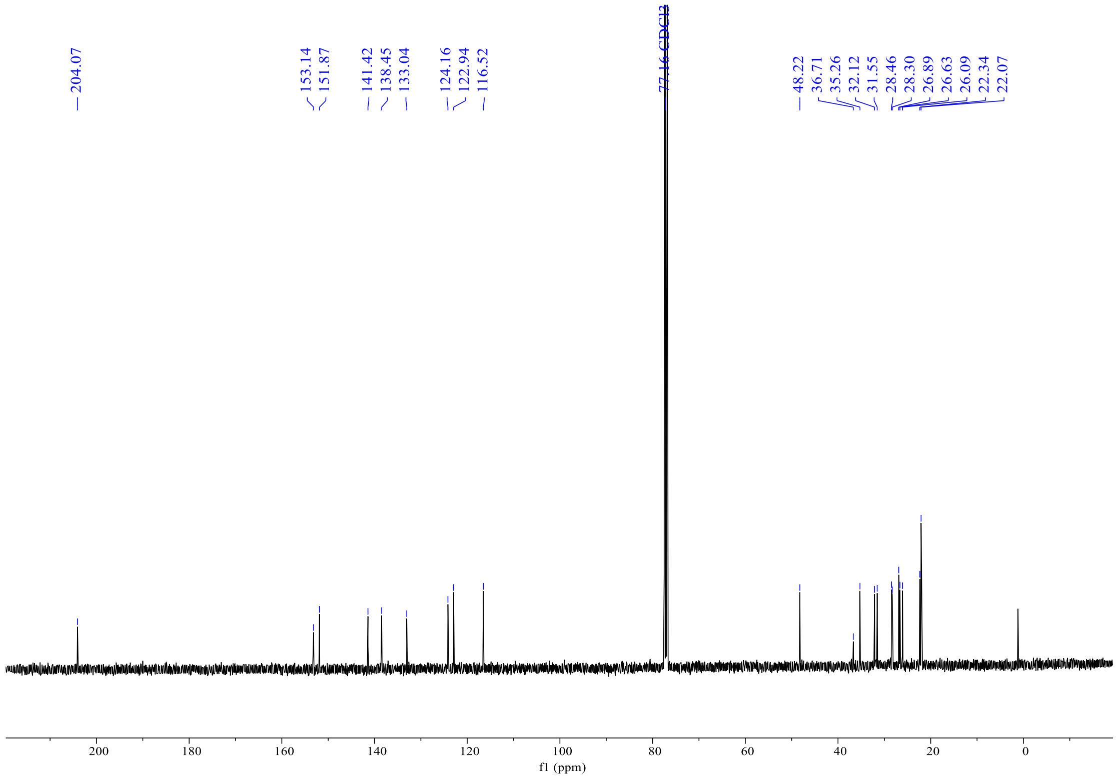
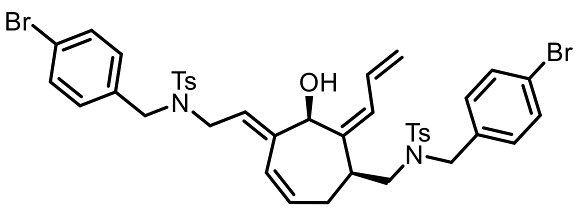
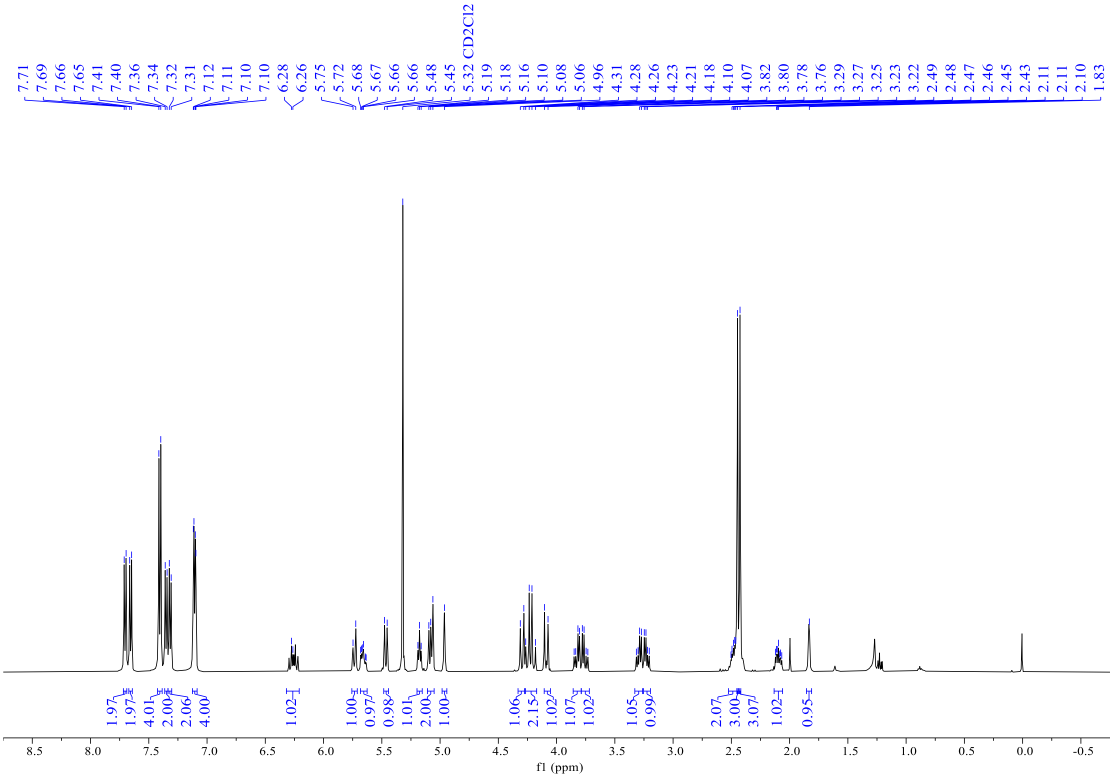

7.26 CDCl3
6.19
5.76
4.84
4.81
2.62
2.61
2.27
2.26
2.25
2.19
1.87
1.71
1.66
1.59
1.56
1.54
1.51
1.00
1.02
0.95
0.93
1.92
2.00
1.92
2.94
2.99
16.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


204.07
153.14
151.87
141.42
138.45
133.04
124.16
122.94
116.52
77.16 CDCl3
48.22
36.71
35.26
32.12
31.55
28.46
28.30
26.89
26.63
26.09
22.34
22.07
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


Br
Ts
N
OH
Ts
N
Br

6l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7.69
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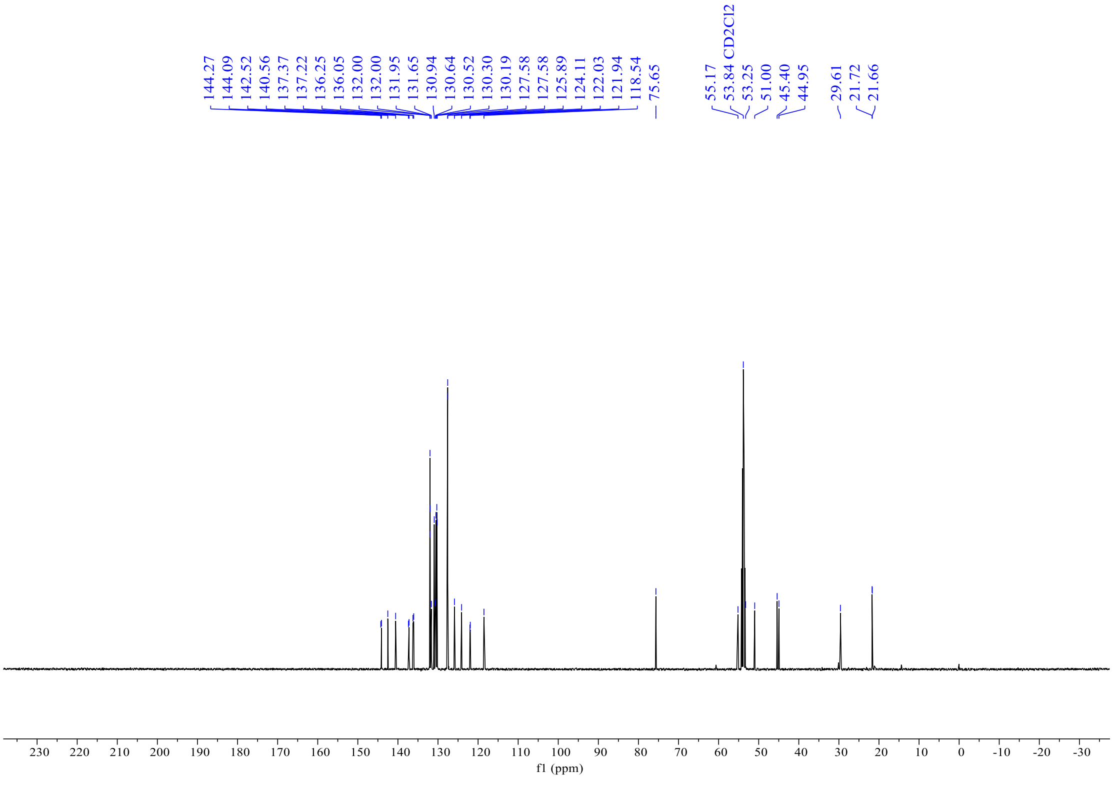
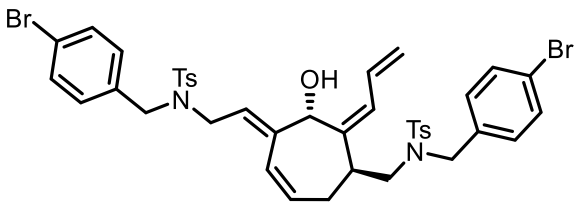
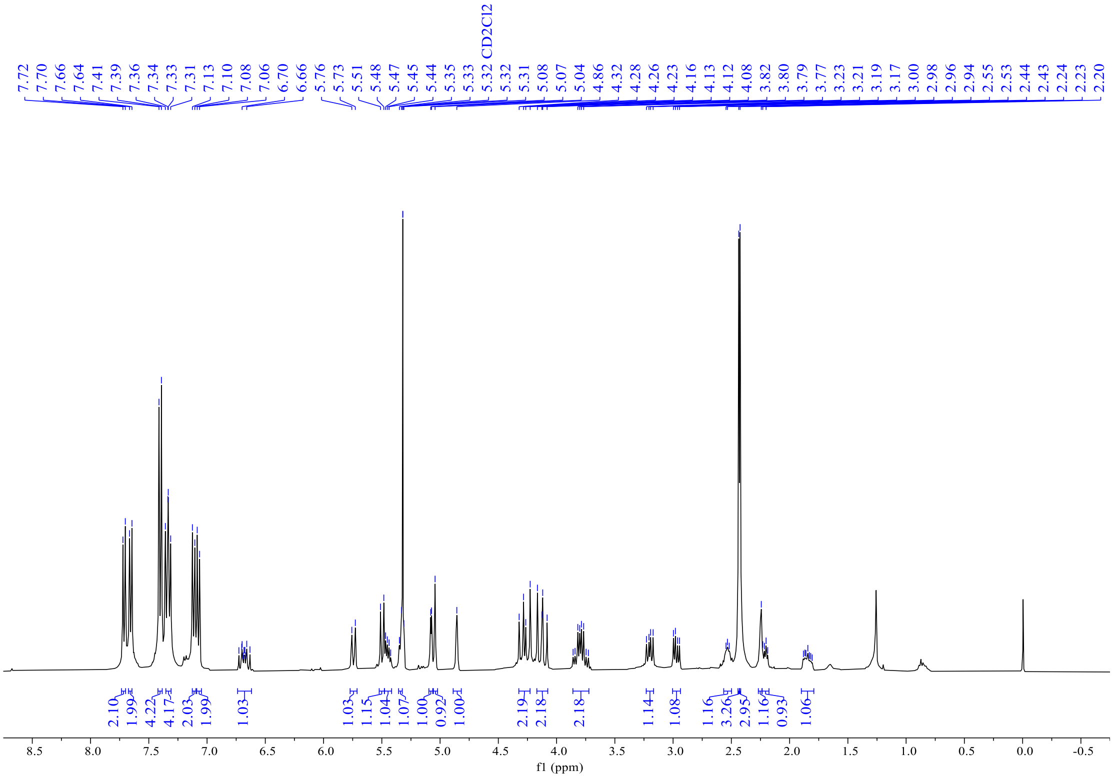
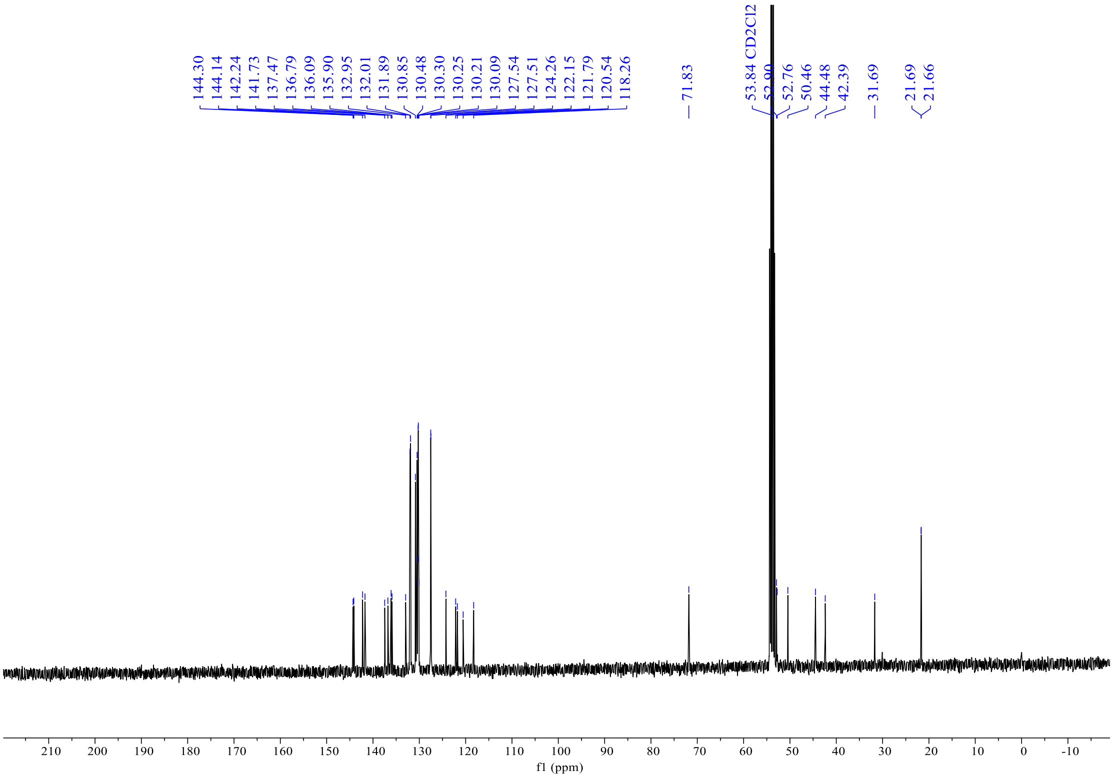
7.65
7.41
7.40
7.36
7.34
7.32
7.31
7.12
7.11
7.10
7.10
6.28
6.26
5.75
5.72
5.68
5.67
5.66
5.66
5.48
5.45
5.32 CD2Cl2
5.19
5.18
5.16
5.10
5.08
5.06
4.96
4.31
4.28
4.26
4.23
4.21
4.18
4.10
4.07
3.82
3.80
3.78
3.76
3.29
3.27
3.25
3.23
3.22
2.49
2.48
2.47
2.46
2.45
2.43
2.11
2.11
2.10
1.83
1.97
1.97
4.01
2.00
2.06
4.00
1.02
1.00
0.97
0.98
1.01
2.00
1.00
1.06
2.15
1.02
1.07
1.02
1.05
0.99
2.07
3.00
3.07
1.02
0.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


144.27
144.09
142.52
140.56
137.37
137.22
136.25
136.05
132.00
132.00
131.95
131.65
130.94
130.64
130.52
130.30
130.19
127.58
127.58
125.89
124.11
122.03
121.94
118.54
75.65
55.17
53.84 CD2Cl2
53.25
51.00
45.40
44.95
29.61
21.72
21.66
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


Br
Ts
N
OH
Ts
N
Br

6l'


7.72
7.70
7.66
7.64
7.41
7.39
7.36
7.34
7.33
7.31
7.13
7.10
7.08
7.06
6.70
6.66
5.76
5.73
5.51
5.48
5.47
5.45
5.44
5.35
5.33
5.32 CD2Cl2
5.32
5.31
5.08
5.07
5.04
4.86
4.32
4.28
4.26
4.23
4.16
4.13
4.12
4.08
3.82
3.80
3.79
3.77
3.23
3.21
3.19
3.17
3.00
2.98
2.96
2.94
2.55
2.53
2.44
2.43
2.24
2.23
2.20
2.10
1.99
4.22
4.17
2.03
1.99
1.03
1.03
1.15
1.04
1.07
1.00
0.92
1.00
2.19
2.18
2.18
1.14
1.08
1.16
3.26
2.95
1.16
0.93
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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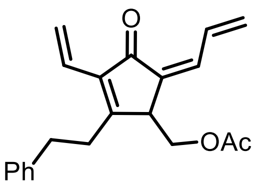
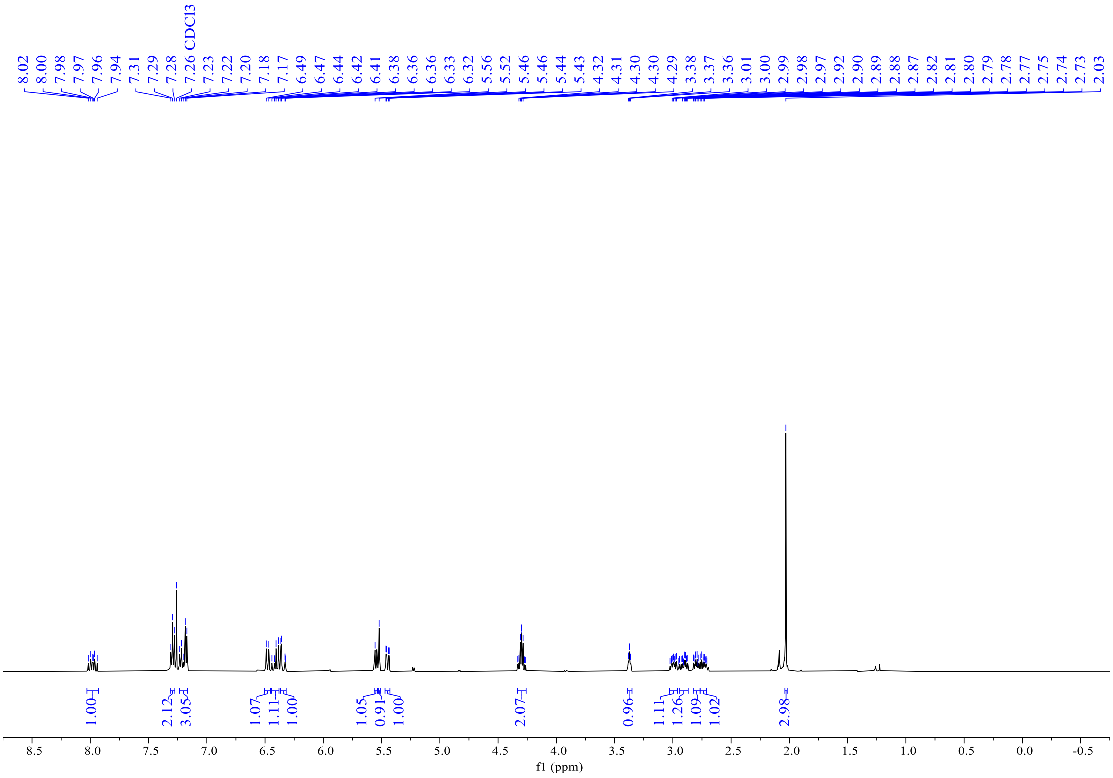
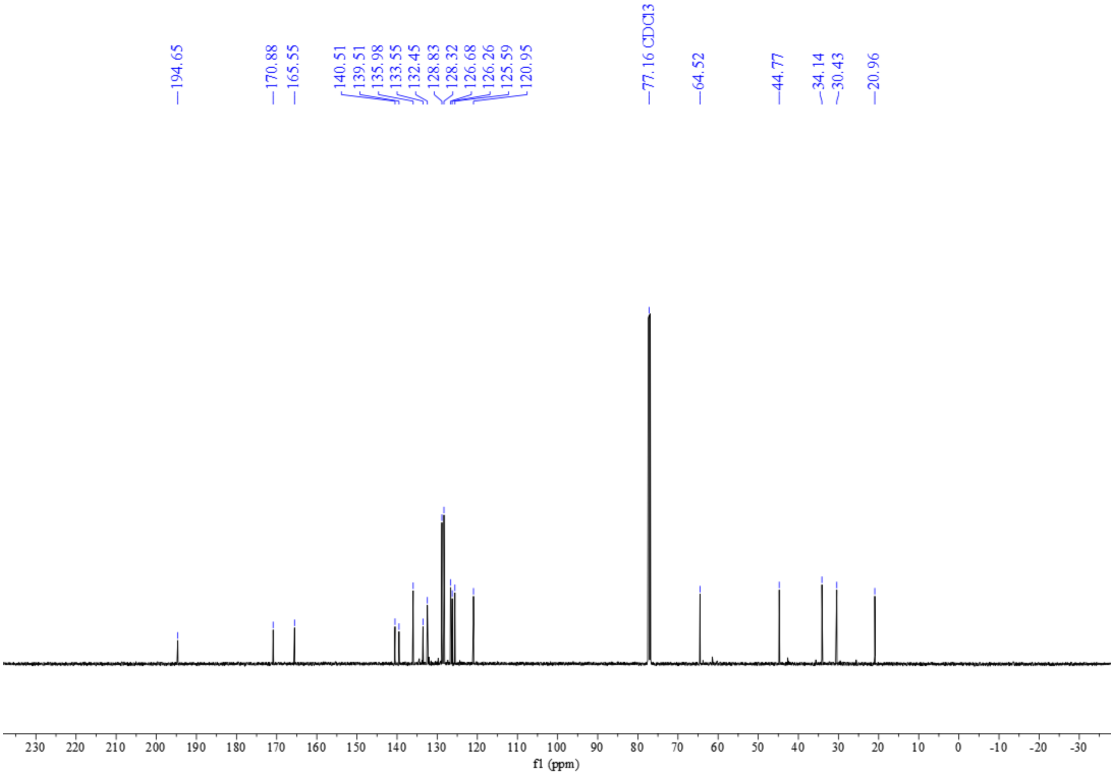
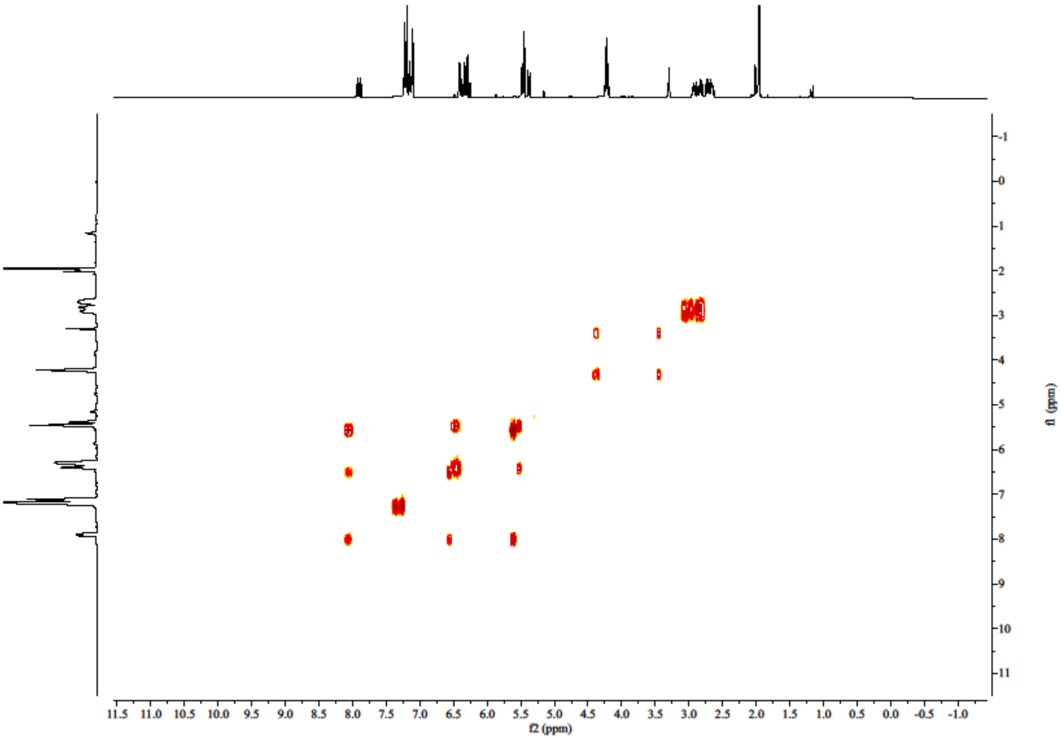
144.14
142.24
141.73
137.47
136.79
136.09
135.90
132.95
132.01
131.89
130.85
130.48
130.30
130.25
130.21
130.09
127.54
127.51
124.26
122.15
121.79
120.54
118.26
71.83
53.84 CD2Cl2
52.90
52.76
50.46
44.48
42.39
31.69
21.69
21.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

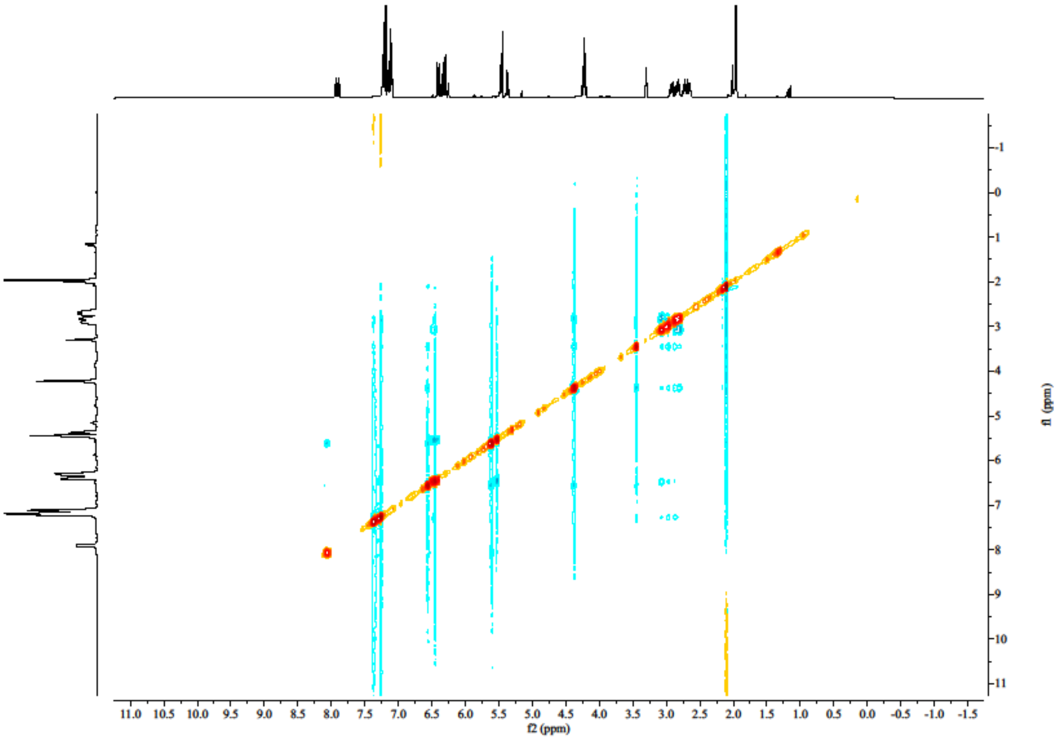

O
OAc
Ph

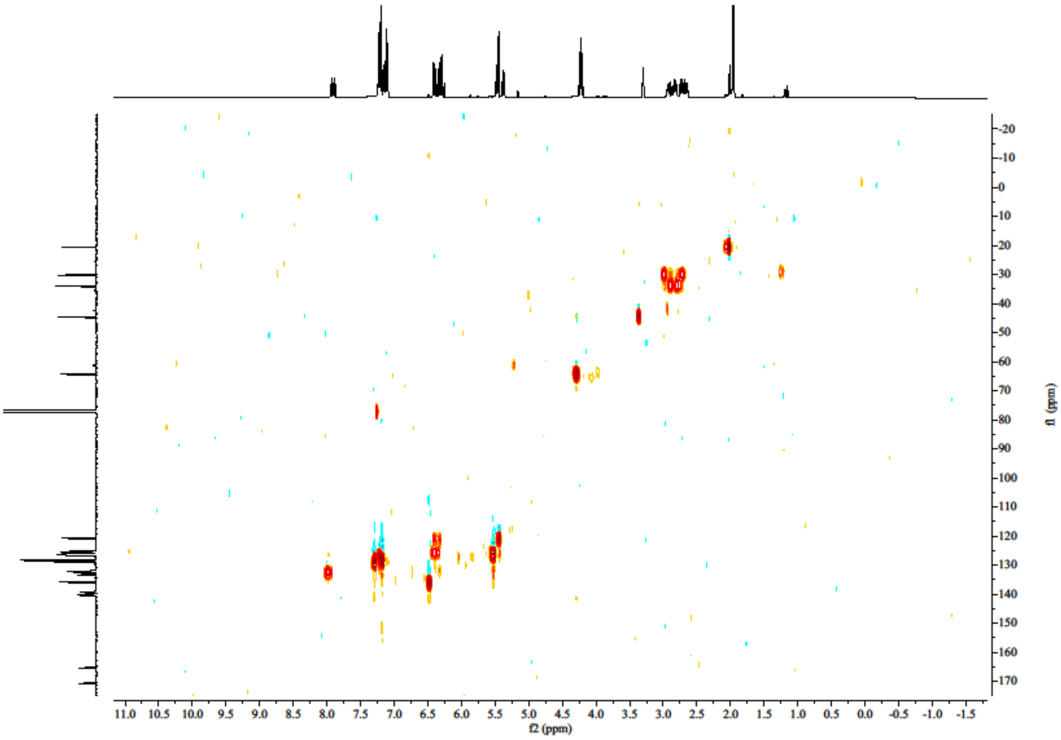
4

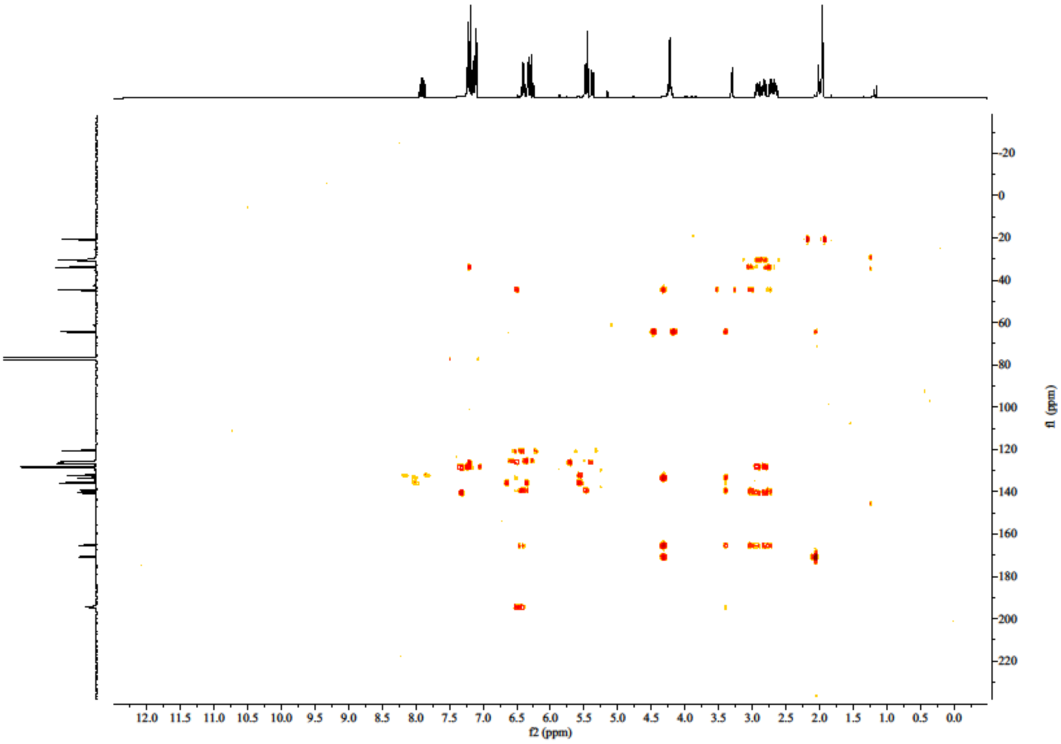

8.02
8.00
7.98
7.97
7.96
7.94
7.31
7.29
7.28
7.26 CDCl3
7.23
7.22
7.20
7.18
7.17
6.49
6.47
6.44
6.42
6.41
6.38
6.36
6.36
6.33
6.32
5.56
5.52
5.46
5.46
5.44
5.43
4.32
4.31
4.30
4.30
4.29
3.38
3.37
3.36
3.01
3.00
2.99
2.98
2.97
2.92
2.90
2.89
2.88
2.87
2.82
2.81
2.80
2.79
2.78
2.77
2.75
2.74
2.73
2.03
1.00
2.12
3.05
1.07
1.11
1.00
1.05
0.91
1.00
2.07
0.96
1.11
1.26
1.09
1.02
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

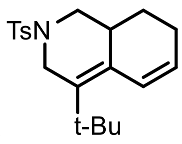

194.65
170.88
165.55
140.51
139.51
135.98
133.55
132.45
128.83
128.32
126.68
126.26
125.59
120.95
77.16 CDCl3
64.52
44.77
34.14
30.43
20.96
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9 10 11
f1 (ppm)

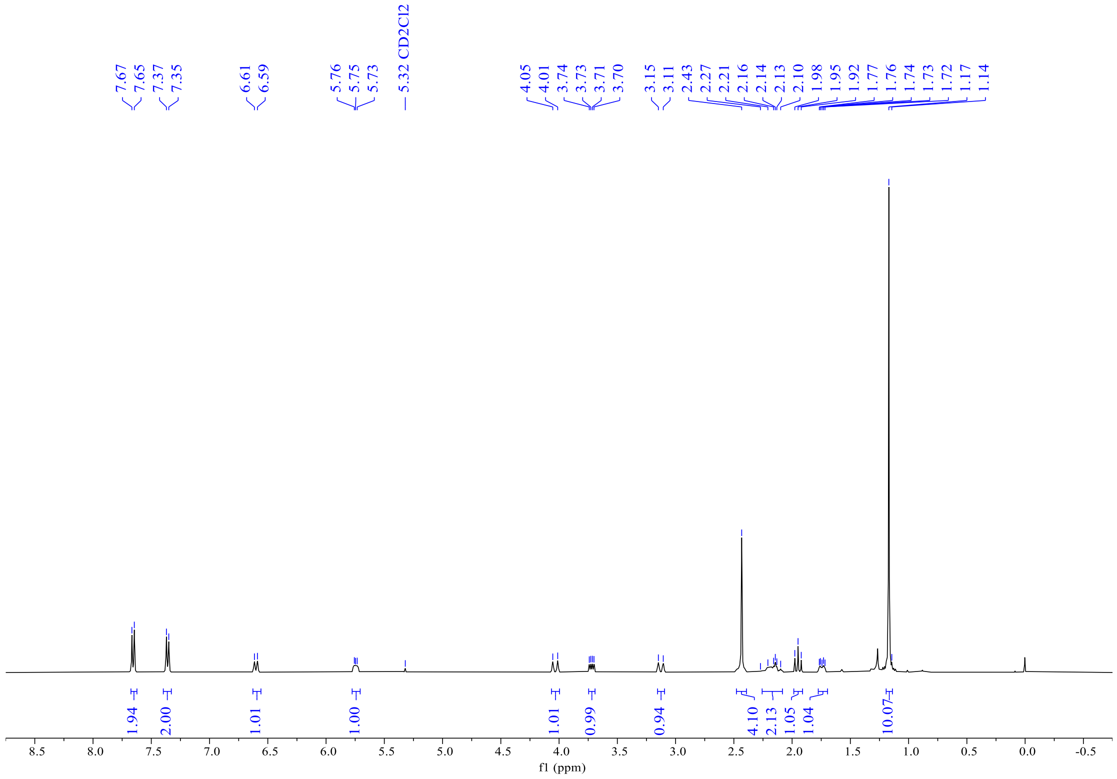

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9 10 11
f1 (ppm)

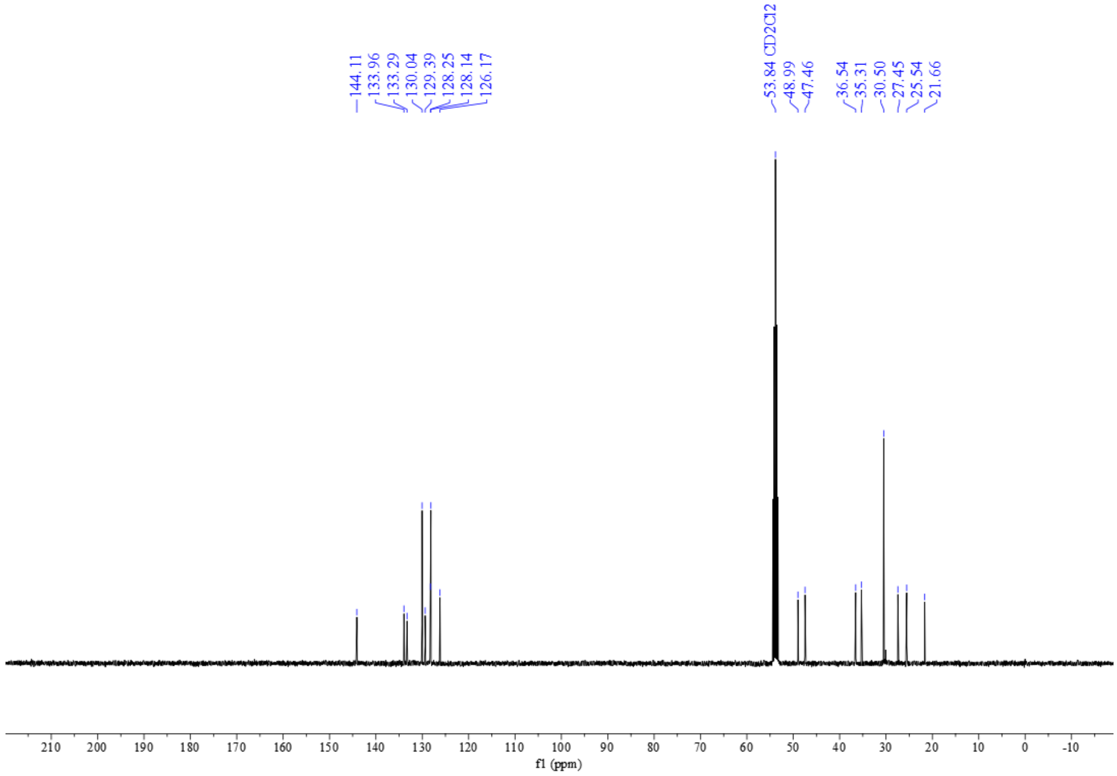

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
-20 0 20 40 60 80 100 120 140 160 180 200 220
f1 (ppm)


TsN
t-Bu

5


7.67
7.65
7.37
7.35
6.61
6.59
5.76
5.75
5.73
5.32 CD2Cl2
4.05
4.01
3.74
3.73
3.71
3.70
3.15
3.11
2.43
2.27
2.21
2.16
2.14
2.13
2.10
1.98
1.95
1.92
1.77
1.76
1.74
1.73
1.72
1.17
1.14
1.94
2.00
1.01
1.00
1.01
0.99
0.94
4.10
2.13
1.05
1.04
10.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


144.11
133.96
133.29
130.04
129.39
128.25
128.14
126.17
53.84 CD2Cl2
48.99
47.46
36.54
35.31
30.50
27.45
25.54
21.66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)