

Supplementary Information

for

***Regio- and Diastereoselective Reaction of Chiral Secondary
Alkylcopper Reagents with Propargylic Phosphates: Preparation of
Chiral Allenes***

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1 General

All reactions were carried out with magnetic stirring and under argon atmosphere in glassware dried with a heat gun. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon three times prior to use. Unless otherwise indicated, yields as stated are isolated yields of compounds and are estimated to be >95% pure as determined by ¹H-NMR (25 °C) and capillary gas chromatography. The ratio of diastereoisomers was determined by ¹H-NMR, ¹³C-NMR spectroscopy or capillary GC.

1.1 Solvents

All solvents were dried according to standard methods by distillation over drying agents as stated below and were stored under argon atmosphere. Solvents for column chromatography were distilled on a vacuum evaporator prior to use.

CH₂Cl₂ was predried over CaCl₂ and distilled from CaH₂.

EtOH was treated with phthalic anhydride (25 g/L) and sodium, heated to reflux for 6 h and distilled.

Diethyl ether was predried over calcium hydride and dried with the solvent purification system SPS-400-2 from INNOVATIVE TECHNOLOGIES INC.

MeOH was heated to reflux over magnesium methoxide and distilled.

THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen.

1.2 Chromatography

Gas chromatography was performed with machines of *Agilent* Technologies 7890, using a column of type HP 5 (*Agilent* 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 μm) or *Hewlett-Packard* 6890 or 5890 series II, using a column of type HP 5 (*Hewlett-Packard*, 5% phenylmethylpolysiloxane; length: 15 m; diameter: 0.25 mm; film thickness: 0.25 μm).

Chiral gas chromatography (GC) was performed on the following column: Chirasil-Dex CB, Varian, CP7502 (25.0 m x 250 μm x 0.25 μm), Average velocity 20, H₂-flux.

Flash column chromatography was performed using SiO₂ (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not specially indicated.

Thin layer chromatography (TLC) was performed using SiO₂ pre-coated aluminium plates (Merck 60, F-254). The chromatograms were examined by 254 nm UV irradiation.

1.3 Reagents

All reagents were obtained from commercial sources and used without further purification unless otherwise stated. Liquid reagents were distilled prior to use.

The concentration of *t*-BuLi (ca. 2M in *n*-pentane) was determined by titration with dry 2-propanol and 1,10-phenanthroline as indicator in THF.

1.4 Analytic data

¹H-NMR and ¹³C-NMR spectra were recorded on VARIAN Mercury 200, BRUKER ARX 300, VARIAN VXR 300 S and Bruker AMX 600 instruments. Chemical shifts are reported as δ-values in ppm relative to the solvent peak in CDCl₃ (residual chloroform: δ 7.25 ppm for ¹H-NMR, δ 77.0 ppm

for ^{13}C -NMR). Abbreviations for signal coupling are as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) as well as br (broad).

Mass spectroscopy (MS): High resolution (HRMS) and low resolution (LRMS) spectra were recorded on a FINNIGAN MAT 95Q instrument. Electron impact ionization (EI) was conducted with an ionization energy of 70 eV.

Infrared spectra (IR) were recorded from 4500 cm^{-1} to 650 cm^{-1} on a PERKIN ELMER Spectrum BX-59343 instrument. For detection a SMITHS DETECTION DuraSamplIR II Diamond ATR sensor was used and the absorption bands are reported in wavenumbers. The abbreviations for intensity are as follows: vs (very strong; maximum intensity), s (strong; above 75% of max. intensity), m (medium; from 50% to 75% of max. intensity), w (weak; below 50% of max. intensity) as well as br (broad).

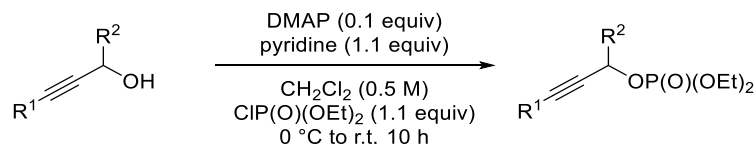
Optical rotation values were recorded on a *Perkin Elmer 241* or *Anton Paar MCP 200* polarimeter. The specific rotation is calculated as follows:

$$[\alpha]_{\lambda}^{\phi} = \frac{[\alpha] \cdot 100}{c \cdot d}$$

Thereby, the wavelength λ is reported in nm and the measuring temperature ϕ in $^{\circ}\text{C}$. α represents the recorded optical rotation, c the concentration of the analyte in 10 mg/mL and d the length of the cuvette in dm. Thus, the specific rotation is given in $10^{-1} \cdot \text{deg} \cdot \text{cm}^2 \cdot \text{g}^{-1}$. Usage of the sodium D line ($\lambda = 589\text{ nm}$) is indicated by D instead of the wavelength in nm. The respective concentration as well as the solvent is reported at the relevant section of the experimental section.

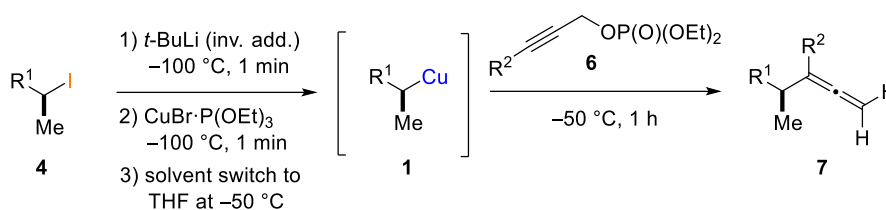
2 Typical procedures

2.1 Typical procedure for the phosphorylation of propargylic alcohols (TP1)^[1]



According to literature,^[1] a dry and Ar-flushed Schlenk-flask was charged with a solution of propargylic alcohol (1.0 equiv), DMAP (0.1 equiv) and pyridine (1.1 equiv) in DCM (0.5 M). After cooling to 0 °C, diethyl chlorophosphate (1.1 equiv) was added dropwise. The solution was allowed to warm to rt and stirred for 10 h. The reaction mixture was quenched with water and extracted with diethyl ether (3 x 25 mL) and purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether (1/2) to afford the desired propargylic phosphate as a colourless oil.

2.2 Typical procedure for the preparation of allenes (TP2)



A dry and Ar-flushed *Schlenk*-tube was cooled to -100 °C and charged with a solution of *t*-BuLi (0.22 mmol, 2.2 equiv) together with a mixture of diethyl ether (1.00 mL) and *n*-pentane (1.50 mL). A solution of iodide **4** (0.10 mmol, 1.0 equiv) in diethyl ether (0.40 mL) was added dropwise for 1 min. After stirring for 10 sec, a solution of CuBr·P(OEt)₃ (0.065 mL, 3 m in diethyl ether, 0.20 mmol, 2.0 equiv) was added and the reaction mixture was stirred for 1 min at -100 °C to observe the color change from yellow to green. The *Schlenk*-tube was transferred to a cooling bath (-50 °C) and the solvent was pumped away under high vacuum. After 10 min, precooled THF (2 mL) and then the propargylic electrophile **6** (0.30 mmol, 3.0 equiv) were added. The reaction mixture was stirred for 1 h at -50 °C. After quenching the reaction mixture with aq. NH₃ solution, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried over MgSO₄ and the solvents were evaporated. The obtained crude product was purified by column chromatography on silica gel to afford alkenes of type **7**.

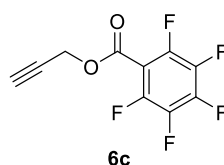
3 Synthesis of starting materials and electrophiles

3.1 Alkyl Iodides

The iodides (*syn*-**4a**^[2a], *anti*-**4a**^[2a], *anti*-**4b**^[2b], *syn*-**4b**^[2b], *anti*-**4c**^[2c], *syn*-**4c**^[2c], (*R*)-**4d**^[2d], (*S*)-**4d**^[2d], (*S*)-**4e**^[2d], (*R*)-**4e**^[2d]) were prepared according to literature known procedures.

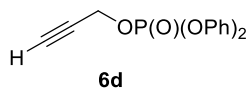
3.2 Electrophiles

The propargyl phosphates were prepared according to literature as described in **TP1**.^[1] Propargyl bromide **6a** is commercially available as a solution in toluene (Sigma Aldrich). Propargyl acetate **6b** is also commercially available (Sigma-Aldrich).



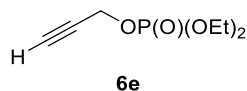
The propargyl pentafluorobenzoate **6c** was prepared according to literature from propargyl alcohol (560 mg, 0.59 mL, 10 mmol).^[3] The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6c** (7.8 mmol, 1.95 g, 78% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 4.97 (d, *J* = 2.5 Hz, 2H), 2.58 (t, *J* = 2.5 Hz, 1H).



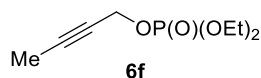
The propargyl diphenylphosphate **6d** was prepared according to literature from propargyl alcohol (560 mg, 0.59 mL, 10 mmol).^[4] The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6d** (8.5 mmol, 2.45 g, 85% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.40–7.29 (m, 4H), 7.28–7.15 (m, 6H), 4.85 (dd, *J* = 10.7, 2.5 Hz, 2H), 2.60 (t, *J* = 2.5 Hz, 1H).



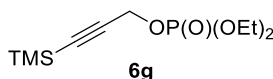
The propargyl diethylphosphate **6e** was prepared according to **TP1** from propargyl alcohol (560 mg, 0.59 mL, 10 mmol).^[5] The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6e** (8.2 mmol, 1.57 g, 82% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = δ 4.66 (dd, *J* = 10.1, 2.5 Hz, 2H), 4.22–4.01 (m, 2H), 2.56 (t, *J* = 2.5 Hz, 1H), 1.35 (td, *J* = 7.1, 1.0 Hz, 6H).



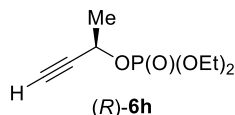
The propargyl phosphate **6f** was prepared according to **TP1** from but-2-yn-1-ol (700 mg, 0.75 mL, 10 mmol). The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6f** (8.9 mmol, 1.83 g, 89% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 4.64 (q, *J* = 2.4 Hz, 1H), 4.62 (q, *J* = 2.4 Hz, 1H), 4.19–4.07 (m, 4H), 1.87 (t, *J* = 2.4 Hz, 3H), 1.35 (td, *J* = 7.1, 0.9 Hz, 6H).



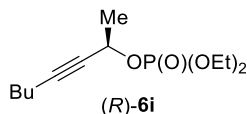
The propargyl phosphate **6g** was prepared according to **TP1** from 3-(trimethylsilyl)prop-2-yn-1-ol (1.28 g, 1.48 mL, 10 mmol). The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6g** (6.2 mmol, 1.54 g, 62% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = δ 4.65 (d, *J* = 10.0 Hz, 2H), 4.20–4.06 (m, 4H), 1.35 (td, *J* = 7.1, 1.0 Hz, 6H), 0.17 (s, 9H).



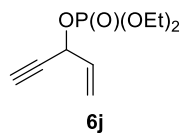
The chiral propargyl phosphate (*R*)-**6h** was prepared according to **TP1** from (*R*)-but-3-yn-2-ol (TCI, mind. er = 99:1; 700 mg, 0.73 mL, 10 mmol). The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford (*R*)-**6h** (6.4 mmol, 1.31 g, 64% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 5.18–5.00 (m, 1H), 4.20–4.03 (m, 4H), 2.55 (d, *J* = 2.1 Hz, 1H), 1.59 (dd, *J* = 6.7, 0.8 Hz, 3H), 1.35 (tdd, *J* = 7.1, 2.9, 1.1 Hz, 6H).



The chiral propargyl phosphate (*R*)-**6i** was prepared according to **TP1** from (*R*)-oct-3-yn-2-ol (1.26 g, 10 mmol). The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford (*R*)-**6i** (5.8 mmol, 1.52 g, 58% yield) as a colourless oil.

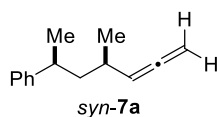
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 5.15–5.03 (m, 1H), 4.18–4.04 (m, 4H), 2.20 (td, *J* = 7.0, 2.0 Hz, 2H), 1.54 (dd, *J* = 6.5, 0.8 Hz, 3H), 1.50–1.37 (m, 4H), 1.36–1.29 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H).



The electrophile **6j** was prepared according to **TP1** from pent-1-en-4-yn-3-ol^[6] (820 mg, 10 mmol). The crude product was purified by flash column chromatography on silica gel with *n*-pentane/diethyl ether = 1/2 to afford **6j** (3.5 mmol, 0.76 g, 35% yield) as a colourless oil.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 5.97 (ddd, J = 17.0, 10.2, 5.7 Hz, 1H), 5.65–5.54 (m, 1H), 5.51–5.43 (m, 1H), 5.35 (dt, J = 10.2, 1.1 Hz, 1H), 4.25–3.94 (m, 4H), 2.68 (d, J = 2.2 Hz, 1H), 1.35 (qd, J = 7.1, 1.1 Hz, 6H).

4 Characterization of allenes



The allene *syn-7a* was prepared according to **TP2** from the alkyl iodide *syn*-(4-iodopentan-2-yl) benzene (*syn-4a*, 27.4 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford *syn-7a* (0.046 mmol, 8.6 mg, 46% yield, dr = 6:94) as a colorless oil.

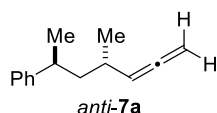
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.32–7.27 (m, 2H), 7.21–7.15 (m, 3H), 5.02 (q, J = 6.7 Hz, 1H), 4.69 (dd, J = 6.6, 2.7 Hz, 2H), 2.83 (q, J = 7.2 Hz, 1H), 2.13–2.00 (m, 1H), 1.75–1.61 (m, 1H), 1.53–1.42 (m, 1H), 1.23 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 207.6, 147.8, 128.5, 127.1, 126.0, 96.2, 75.7, 45.8, 37.5, 30.7, 22.4, 20.6.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2959 (m), 2924 (vs), 2853 (m), 2360 (w), 2341 (w), 1955 (w), 1738 (w), 1493 (w), 1454 (m), 1377 (w), 1243 (w), 867 (w), 842 (m), 762 (m), 700 (s).

MS m/z (%): 171 (15), 157 (23), 144 (40), 143 (22), 129 (100), 128 (14), 118 (49), 117 (43), 115 (13), 105 (63), 103 (22), 91, (49), 79 (24), 78 (10), 77 (21).

HRMS (EI) m/z : calcd. for C₁₃H₁₅ [M⁺-Me]: 171.1174; found 171.1166.



The allene *anti-7a* was prepared according to **TP2** from the alkyl iodide *anti*-(4-iodopentan-2-yl) benzene (*anti-4a*, 27.4 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford *anti-7a* (0.055 mmol, 10.2 mg, 55% yield, dr = 98:2) as a colorless oil.

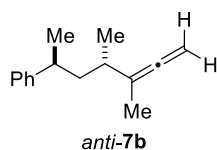
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.34–7.26 (m, 2H), 7.20–7.17 (m, 3H), 5.04 (dt, *J* = 7.3, 6.6 Hz, 1H), 4.70–4.66 (m, 2H), 2.92–2.75 (m, 1H), 2.04–1.86 (m, 1H), 1.64–1.53 (m, 2H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 207.7, 147.5, 128.5, 128.5, 127.3, 126.0, 95.8, 75.6, 46.1, 37.8, 31.0, 22.9, 21.4.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3062 (vw), 3028 (w), 2960 (m), 2924 (m), 2870 (w), 2846 (w), 2360 (vw), 1956 (w), 1604 (w), 1494 (m), 1452 (m), 1376 (w), 1030 (w), 868 (w), 842 (m), 762 (m), 700 (vs).

MS *m/z* (%): 157 (17), 144 (41), 143 (20), 130 (11), 129 (100), 128 (12), 118 (32), 117 (32), 115 (12), 105 (59), 103 (23), 91 (46), 79 (26), 78 (11), 77 (23).

HRMS (EI) *m/z*: calcd. for C₁₄H₁₇ [M⁺-H]: 185.1330; found 185.1323.



The allene *anti-7b* was prepared according to **TP2** from the alkyl iodide *anti*-(4-iodopentan-2-yl) benzene (*anti-4a*, 27.4 mg, 0.1 mmol) and electrophile **6f** (62 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford *anti-7b* (0.065 mmol, 13.0 mg, 65% yield, dr = 97:3) as a colorless oil.

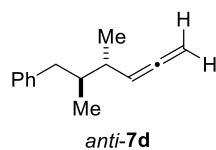
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.32–7.26 (m, 2H), 7.22–7.11 (m, 3H), 4.59 (qd, *J* = 3.2, 1.6 Hz, 2H), 2.83–2.70 (m, 1H), 1.88–1.78 (m, 1H), 1.74–1.65 (m, 1H), 1.63 (t, *J* = 3.1 Hz, 3H), 1.54–1.47 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 205.8, 147.8, 128.4, 127.3, 126.0, 102.5, 74.4, 44.1, 37.8, 35.1, 22.8, 20.1, 16.2.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3062 (vw), 3028 (w), 2960 (m), 2924 (m), 2870 (w), 2846 (w), 2360 (vw), 1956 (w), 1604 (w), 1494 (m), 1452 (m), 1376 (w), 1054 (w), 1030 (w), 868 (w), 842 (m), 762 (m), 700 (vs).

MS *m/z* (%): 185 (13), 171 (18), 158 (52), 157 (26), 144 (11), 143 (100), 129 (14), 128 (15), 118 (68), 117 (52), 115 (14), 105 (59), 103 (22), 91 (40), 79 (35), 78 (11), 77 (26), 67 (24).

HRMS (EI) *m/z*: calcd. for C₁₄H₁₇ [M⁺-Me]: 185.1330; found 185.1321.



The allene *anti-7d* was prepared according to **TP2** from the alkyl iodide *anti*-(3-iodo-2-methylbutyl)benzene (*anti-4b*, 27.4 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford *anti-7d* (0.058 mmol, 10.8 mg, 58% yield, dr = 98:2) as a colorless oil.

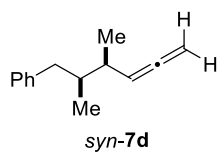
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.31–7.27 (m, 2H), 7.20–7.13 (m, 3H), 5.12 (q, *J* = 6.8 Hz, 1H), 4.75–4.69 (m, 2H), 2.73 (dd, *J* = 13.4, 5.8 Hz, 1H), 2.33 (dd, *J* = 13.3, 8.9 Hz, 1H), 2.29–2.20 (m, 1H), 1.87–1.74 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 208.6, 141.8, 129.3, 128.3, 125.8, 93.0, 75.3, 40.7, 40.7, 36.9, 17.6, 15.5.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3028 (w), 2960 (s), 2924 (m), 2870 (w), 2366 (vw), 1956 (w), 1604 (w), 1494 (m), 1454 (m), 1376 (w), 1112 (w), 1048 (w), 1022 (w), 844 (m), 762 (m), 700 (vs).

MS *m/z* (%): 171 (19), 157 (21), 144 (11), 143 (24), 129 (13), 119 (11), 118 (43), 117 (15), 92 (15), 91 (100), 67 (14), 57 (10), 43 (35), 41 (25), 42 (21).

HRMS (EI) *m/z*: calcd. for C₁₄H₁₈: 186.1409; found 186.1394.



The allene *syn-7d* was prepared according to **TP2** from the alkyl iodide *syn*-(3-iodo-2-methylbutyl)benzene (*syn-4b*, 27.4 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford *syn-7d* (0.042 mmol, 9.2 mg, 42% yield, dr = 6:94) as a colorless oil.

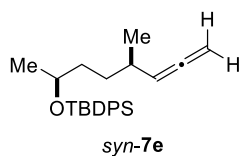
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.30–7.25 (m, 2H), 7.20–7.06 (m, 3H), 5.11 (q, J = 6.7 Hz, 1H), 4.71 (dd, J = 6.8, 3.1 Hz, 2H), 2.79 (dd, J = 13.4, 5.3 Hz, 1H), 2.38–2.28 (m, 1H), 2.23–2.15 (m, 1H), 1.82–1.71 (m, 1H), 1.03 (dd, J = 6.9, 3.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 208.5, 142.0, 129.5, 128.5, 128.5, 126.0, 95.2, 75.7, 41.0, 40.5, 37.3, 15.8, 15.8.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3029 (w), 2959 (s), 2921 (m), 2872 (w), 2354 (vw), 1948 (w), 1604 (w), 1494 (m), 1379 (w), 1115 (w), 1047 (w), 1022 (w), 843 (m), 772 (m), 702 (vs).

MS m/z (%): 171 (30), 157 (39), 144 (13), 143 (53), 129 (40), 118 (57), 117 (57), 115 (12), 91 (100).

HRMS (EI) m/z : calcd. for C₁₄H₁₇ [M⁺-H]: 185.1330; found 185.1322.



The allene *syn-7e* was prepared according to **TP2** from the alkyl iodide *syn*-(*tert*-butyl((5-iodohexan-2-yl)oxy)diphenylsilane) benzene (*syn-4c*, 46.6 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with diethyl ether/pentane = 1/300 to afford *syn-7e* (0.044 mmol, 16.6 mg, 44% yield, dr = 4:96) as a colorless oil.

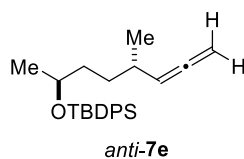
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.71–7.66 (m, 4H), 7.45–7.34 (m, 6H), 4.99 (q, *J* = 6.7 Hz, 1H), 4.69–4.61 (m, 2H), 3.83 (q, *J* = 6.0 Hz, 1H), 2.09–1.95 (m, 1H), 1.55–1.37 (m, 2H), 1.35–1.24 (m, 2H), 1.08–1.03 (m, 12H), 0.94 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 207.6, 136.0, 135.0, 134.7, 129.6, 129.5, 127.6, 127.5, 96.1, 75.5, 69.9, 37.0, 33.0, 32.7, 27.2, 23.4, 20.4, 19.4.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3071 (w), 3050 (w), 2963 (m), 2931 (m), 2858 (m), 2362 (w), 2334 (vw), 1956 (w), 1590 (vw), 1473 (w), 1462 (w), 1428 (m), 1390 (w), 1377 (w), 1362 (w), 1133 (m), 1111 (s), 1058 (m), 1030 (w), 1006 (w), 998 (m), 868 (w), 842 (w), 822 (m), 739 (m), 701 (vs), 687 (w).

MS *m/z* (%): 321 (36), 199 (100), 183 (13), 181 (10), 135 (11), 77 (6).

HRMS (EI) *m/z*: calcd for C₂₁H₂₅OSi [M⁺-*t*-Bu]: 321.1675; found 321.1661.



The allene *anti-7e* was prepared according to **TP2** from the alkyl iodide *anti*-(*tert*-butyl((5-iodohexan-2-yl)oxy)diphenylsilane) benzene (*anti-4c*, 46.6 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with diethyl ether/pentane = 1/300 to afford *anti-7e* (0.050 mmol, 18.9 mg, 50% yield, dr = 95:5) as a colorless oil.

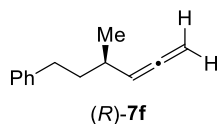
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.71–7.63 (m, 4H), 7.45–7.32 (m, 6H), 4.97 (q, *J* = 6.5 Hz, 1H), 4.69–4.59 (m, 2H), 3.82 (h, *J* = 6.0 Hz, 1H), 2.03 (dt, *J* = 6.7, 3.4 Hz, 1H), 1.56–1.29 (m, 4H), 1.08–1.02 (m, 12H), 0.94 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 207.6, 136.0, 135.1, 134.7, 129.6, 129.5, 127.6, 127.5, 96.1, 96.1, 75.5, 75.5, 69.9, 69.8, 37.0, 33.0, 32.7, 32.6, 27.2, 23.4, 20.5, 20.4, 19.4.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3071 (w), 3050 (vw), 2962 (m), 2930 (m), 2858 (m), 2360 (w), 2333 (vw), 1955 (w), 1590 (vw), 1473 (w), 1462 (w), 1428 (m), 1390 (w), 1377 (w), 1362 (w), 1132 (m), 1110 (s), 1059 (m), 1029 (w), 1006 (w), 998 (m), 868 (w), 842 (w), 822 (m), 739 (m), 701 (vs), 687 (m)

MS *m/z* (%): 321 (10), 199 (100), 135 (8), 77 (5).

HRMS (EI) *m/z*: calcd for C₂₁H₂₅OSi [M⁺-*t*-Bu]: 321.1675; found 321.1665.



The chiral allene (*R*)-**7f** was prepared according to **TP2** from the alkyl iodide (*R*)-(3-iodobutyl) benzene ((*R*)-**4d**, 26.0 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford (*R*)-**7f** (0.041 mmol, 7.1 mg, 41% yield, er = 93:7) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = -20.0$ ($c = 0.5$, CHCl_3).

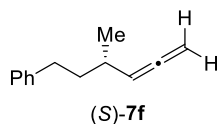
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ [ppm] = 7.30–7.26 (m, 2H), 7.21–7.15 (m, 3H), 5.10 (q, $J = 6.7$ Hz, 1H), 4.73 (dd, $J = 6.7, 2.7$ Hz, 2H), 2.75–2.56 (m, 2H), 2.27–2.08 (m, 1H), 1.80–1.59 (m, 2H), 1.06 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , 101 MHz): δ [ppm] = 207.7, 142.8, 128.6, 128.4, 125.8, 95.9, 75.8, 39.0, 33.7, 32.6, 20.7.

IR (ATR): $\tilde{\nu}[\text{cm}^{-1}] = 3063$ (w), 3027 (w), 2961 (m), 2924 (m), 2856 (w), 1955 (m), 1604 (w), 1497 (m), 1454 (m), 1376 (w), 1031 (w), 868 (m), 842 (s), 746 (m), 722 (w), 698 (vs).

MS m/z (%): 157 (13), 144 (11), 143 (36), 129 (45), 128 (13), 115 (12), 104 (63), 103 (11), 91 (100), 79 (25), 78 (16), 77 (20), 67 (13), 65 (22).

HRMS (EI) m/z : calcd for $\text{C}_{13}\text{H}_{16}$: 172.1252; found 172.1242.



The chiral allene (*S*)-**7f** was prepared according to **TP2** from the alkyl iodide (*S*)-(3-iodobutyl) benzene ((*S*)-**4d**, 26.0 mg, 0.1 mmol) and electrophile **6e** (58 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford (*S*)-**7f** (0.048 mmol, 8.3 mg, 48% yield, er = 10:90) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +22.0$ ($c = 0.3$, CHCl_3).

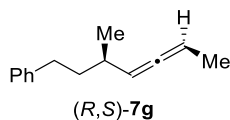
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ [ppm] = 7.33–7.24 (m, 2H), 7.22–7.13 (m, 3H), 5.10 (q, $J = 6.7$ Hz, 1H), 4.73 (dd, $J = 6.6, 2.7$ Hz, 2H), 2.76–2.55 (m, 2H), 2.25–2.10 (m, 1H), 1.75–1.59 (m, 2H), 1.06 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , 101 MHz): δ [ppm] = 207.7, 142.8, 128.6, 128.4, 125.8, 95.9, 75.8, 39.0, 33.7, 32.6, 20.7.

IR (ATR): $\tilde{\nu}[\text{cm}^{-1}] = 3028$ (w), 2961 (m), 2925 (m), 2855 (w), 1955 (m), 1604 (w), 1497 (w), 1454 (m), 1377 (w), 1031 (w), 907 (s), 868 (m), 843 (m), 731 (vs), 698 (vs).

MS m/z (%): 157 (15), 143 (40), 129 (48), 128 (14), 115 (14), 104 (65), 103 (12), 91 (100), 79 (21), 78 (15), 77 (16), 65 (19).

HRMS (EI) m/z : calcd for $\text{C}_{13}\text{H}_{16}$: 172.1252; found 172.1243.



The chiral allene (*R,S*)-**7g** was prepared according to **TP2** from the alkyl iodide (*R*)-(3-iodobutyl)benzene ((*R*)-**4d**, 26.0 mg, 0.1 mmol) and electrophile (*R*)-**6h** (62 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford (*R,S*)-**7g** (0.043 mmol, 8.0 mg, 43% yield, dr = 92:8) as a colorless oil.

$[\alpha]_D^{20} = +18.0$ (c = 0.8, CHCl₃).

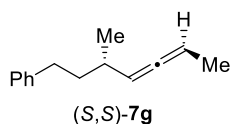
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.31–7.26 (m, 2H), 7.22–7.13 (m, 3H), 5.17–5.08 (m, 1H), 5.07–5.01 (m, 1H), 2.74–2.51 (m, 2H), 2.16 (dtd, $J = 13.5, 6.7, 2.6$ Hz, 1H), 1.67 (dd, $J = 6.9, 3.3$ Hz, 3H), 1.65–1.58 (m, 2H), 1.04 (d, $J = 6.8$ Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 203.9, 143.0, 128.6, 128.6, 128.4, 125.7, 96.2, 86.6, 39.0, 33.7, 33.1, 20.9, 14.9.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3027 (m), 2960 (s), 2925 (s), 2856 (m), 1497 (m), 1455 (m), 1373 (w), 872 (m), 745 (m), 720 (m), 698 (vs).

MS m/z (%): 171 (16), 158 (10), 157 (51), 143 (43), 129 (58), 115 (13), 104 (24), 91 (100), 82 (70), 79 (25), 77 (15), 67 (79), 65 (11).

HRMS (EI) m/z : calcd for C₁₄H₁₉: 186.1409; found 186.1400.



The allene (*S,S*)-**7g** was prepared according to **TP2** from the alkyl iodide (*S*)-(3-iodobutyl)benzene ((*S*)-**4d**, 26.0 mg, 0.1 mmol) and electrophile (*R*)-**6h** (62 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford (*S,S*)-**7g** (0.049 mmol, 9.1 mg, 49% yield, dr = 12:88) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = -16.0$ ($c = 0.3$, CHCl_3).

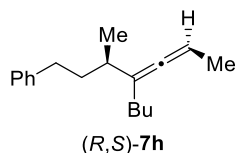
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ [ppm] = 7.33–7.26 (m, 2H), 7.22–7.15 (m, 3H), 5.11 (td, $J = 6.7, 2.5$ Hz, 1H), 5.02 (dq, $J = 6.4, 3.2$ Hz, 1H), 2.75–2.55 (m, 2H), 2.22–2.07 (m, 1H), 1.68 (dd, $J = 6.9, 3.2$ Hz, 3H), 1.66–1.58 (m, 2H), 1.04 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CDCl_3 , 101 MHz): δ [ppm] = 203.9, 143.0, 128.6, 128.6, 128.4, 125.7, 96.1, 86.5, 39.0, 33.7, 33.3, 20.8, 15.0.

IR (ATR): $\tilde{\nu}[\text{cm}^{-1}] = 3027$ (w), 2959 (m), 2924 (m), 2856 (w), 1604 (w), 1496 (w), 1455 (m), 1372 (w), 1031 (w), 872 (m), 761 (w), 745 (m), 717 (m), 698 (vs).

MS m/z (%): 157 (26), 143 (23), 129 (35), 104 (20), 91 (100), 82 (70), 79 (28), 77 (21), 67 (83), 65 (17).

HRMS (EI) m/z : calcd for $\text{C}_{14}\text{H}_{18}$: 186.1409; found 186.1401.



The allene (*R,S*)-**7h** was prepared according to **TP2** from the alkyl iodide (*R*)-(3-iodobutyl)benzene ((*R*)-**4d**, 26.0 mg, 0.1 mmol) and electrophile (*R*)-**6i** (79 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford (*R,S*)-**7h** (0.059 mmol, 14.3 mg, 59% yield, dr = 91:9) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +15.2$ ($c = 0.9$, CHCl_3).

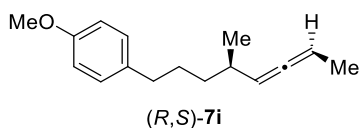
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ [ppm] = 7.31–7.26 (m, 2H), 7.23–7.14 (m, 3H), 5.16–5.02 (m, 1H), 2.73–2.50 (m, 2H), 2.02–1.88 (m, 2H), 1.80–1.70 (m, 1H), 1.67 (d, $J = 6.9$ Hz, 3H), 1.62–1.53 (m, 1H), 1.47–1.19 (m, 5H), 1.04 (d, $J = 6.9$ Hz, 3H), 0.95–0.85 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , 101 MHz): 201.2, 143.3, 128.5, 128.4, 125.7, 108.4, 87.4, 37.8, 36.6, 34.3, 33.8, 30.8, 30.2, 22.6, 22.5, 20.3, 15.3, 14.2.

IR (ATR): $\tilde{\nu}[\text{cm}^{-1}] = 3064$ (w), 3027 (w), 2957 (s), 2926 (vs), 2871 (m), 2858 (m), 2360 (w), 2340 (w), 2334 (w), 1604 (w), 1496 (w), 1455 (m), 1372 (w), 1031 (w), 770 (w), 746 (m), 698 (s).

MS m/z (%): 242 (16), 138 (15), 123 (13), 105 (11), 96 (28), 91 (17), 74 (93), 59 (100), 45 (44), 32 (50).

HRMS (EI) m/z : calcd for $\text{C}_{18}\text{H}_{26}$: 242.2035; found 242.2030.



The allene (*R,S*)-**7i** was prepared according to **TP2** from the alkyl iodide (*R*)-1-(4-iodopentyl)-4-methoxybenzene ((*R*)-**4e**, 30.4 mg, 0.1 mmol) and electrophile (*R*)-**6h** (62 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane/diethyl Ether = 300/1 to afford (*R,S*)-**7i** (0.052 mmol, 11.2 mg, 52% yield, dr = 93:7) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = -6.8$ (c = 0.8, CHCl₃).

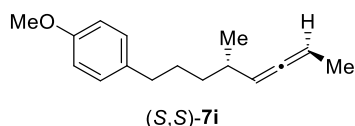
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.13–7.05 (m, 2H), 6.89–6.73 (m, 2H), 5.06 (pd, $J = 6.8, 2.4$ Hz, 1H), 4.97 (tt, $J = 6.4, 3.2$ Hz, 1H), 3.79 (s, 3H), 2.54 (t, $J = 7.7$ Hz, 2H), 2.13 (pd, $J = 6.8, 2.5$ Hz, 1H), 1.64 (dd, $J = 7.0, 3.2$ Hz, 3H), 1.64–1.55 (m, 2H), 1.40–1.20 (m, 2H), 0.98 (d, $J = 6.7$ Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 203.7, 157.7, 135.0, 129.4, 113.8, 96.4, 86.3, 55.4, 36.8, 35.2, 33.6, 29.5, 20.7, 14.9.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2956 (m), 2922 (vs), 2891 (m), 2875 (m), 2851 (s), 1613 (m), 1513 (vs), 1465 (m), 1442 (m), 1303 (m), 1246 (m), 1178 (m), 1040 (m), 808 (w), 722 (w).

MS m/z (%): 148 (32), 147 (43), 134 (53), 122 (13), 121 (100), 91 (11), 74 (30), 59 (34), 45 (16), 43 (18).

HRMS (EI) m/z : calcd for C₁₆H₂₂O: 230.1671; found 230.1663.



The allene (*S,S*)-**7i** was prepared according to **TP2** from the alkyl iodide (*S*)-1-(4-iodopentyl)-4-methoxybenzene ((*S*)-**4e**, 30.4 mg, 0.1 mmol) and electrophile (*R*)-**6h** (62 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane/diethyl ether = 300/1 to afford (*S,S*)-**7i** (0.054 mmol, 12.4 mg, 54% yield, dr = 12:88) as a colorless oil.

$[\alpha]_{\text{D}}^{20} = +9.2$ (c = 1.0, CHCl₃).

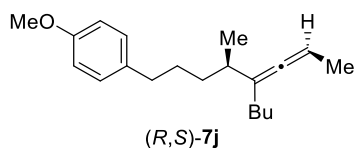
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.12–7.05 (m, 2H), 6.88–6.77 (m, 2H), 5.10–5.03 (m, 1H), 5.02–4.89 (m, 1H), 3.79 (s, 3H), 2.54 (t, *J* = 7.8 Hz, 2H), 2.24–1.96 (m, 1H), 1.64 (dd, *J* = 6.9, 3.2 Hz, 3H), 1.62–1.57 (m, 2H), 1.43–1.28 (m, 2H), 0.98 (d, *J* = 6.7 Hz, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 203.7, 157.7, 135.1, 129.4, 113.8, 96.4, 86.4, 55.4, 36.9, 35.3, 33.4, 29.6, 20.8, 14.9.

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2955 (m), 2927 (s), 2892 (m), 2856 (m), 2837 (w), 1613 (m), 1513 (vs), 1463 (m), 1446 (m), 1442 (m), 1300 (m), 1245 (vs), 1177 (m), 1040 (m), 828 (m), 807 (w), 724 (w).

MS *m/z* (%): 173 (18), 159 (15), 148 (10), 147 (94), 134 (90), 121 (100), 119 (14), 117 (16), 91 (39), 77 (11).

HRMS (EI) *m/z*: calcd for C₁₆H₂₂O: 230.1671; found 230.1664.



The allene (*R,S*)-**7j** was prepared according to **TP2** from the alkyl iodide (*R*)-1-(4-iodopentyl)-4-methoxybenzene (*R*)-**4e**, 30.4 mg, 0.1 mmol) and electrophile (*R*)-**6i** (79 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane/diethyl ether = 200/1 to afford (*R,S*)-**7j** (0.051 mmol, 13.9 mg, 51% yield, dr = 92:8) as a colorless oil.

$[\alpha]_D^{20} = -5.0$ (c = 0.4, CHCl₃).

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.09 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.88–6.74 (m, 2H), 5.03 (tdd, *J* = 6.8, 5.2, 3.6 Hz, 1H), 3.79 (s, 3H), 2.53 (dt, *J* = 8.0, 6.4 Hz, 2H), 2.01–1.92 (m, 1H), 1.90–1.82 (m, 2H), 1.61 (dd, *J* = 6.8, 1.3 Hz, 3H), 1.47–1.40 (m, 1H), 1.36–1.21 (m, 7H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.92–0.74 (m, 3H).

¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 201.3, 157.7, 135.2, 129.4, 113.8, 108.7, 87.1, 55.4, 36.8, 35.3, 31.6, 30.3, 30.2, 29.5, 22.7, 22.6, 20.2, 15.3, 14.2.

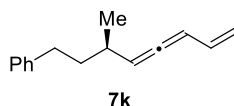
IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2956 (m), 2929 (s), 2870 (w), 2858 (m), 2835 (w), 2359 (m), 2342 (w), 1613 (w), 1513 (vs), 1464 (w), 1442 (w), 1300 (w), 1246 (vs), 1176 (w), 1040 (m), 828 (w), 817 (w), 807 (w).

MS *m/z* (%): 148 (66), 147 (100), 134 (65), 121 (78), 91 (19), 81 (18).

HRMS (EI) *m/z*: calcd for C₂₀H₃₀O: 286.2297; found 286.2292.

Regioselective addition of secondary alkylcopper reagent **1d** to allylic and propargylic moiety containing phosphate **6f**:

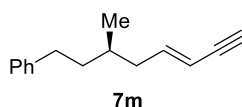
(3-methylocta-4,5,7-trien-1-yl)benzene **7k** and (*E*)-(3-methyloct-5-en-7-yn-1-yl)benzene **7m** was prepared according to **TP2** from the alkyl iodide (3-iodobutyl)benzene (**1e**, 26.0 mg, 0.1 mmol) and electrophile **6j** (65 mg, 0.3 mmol). The crude product was purified by flash column chromatography on silica gel with pentane to afford **7k** (0.022 mmol, 4.4 mg, 22% yield) and **7m** (0.036 mmol, 7.1 mg, 36% yield) as colorless oils.



¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.31–7.26 (m, 2H), 7.21–7.13 (m, 3H), 6.23–6.12 (m, 1H), 5.90–5.82 (m, 1H), 5.35–5.25 (m, 1H), 5.18 (d, J = 17.0 Hz, 1H), 5.02–4.93 (m, 1H), 2.78–2.48 (m, 2H), 2.22 (dq, J = 11.2, 4.6, 3.3 Hz, 1H), 1.78–1.58 (m, 2H), 1.11–1.02 (m, 3H).

IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2952 (m), 2922 (vs), 2853 (s), 2360 (w), 2342 (w), 1457 (m), 1376 (w), 1261 (w), 1099 (w), 1019 (w), 800 (w).

HRMS (EI) m/z : calcd for C₁₅H₁₇ [M⁺-H]: 197.1330; found 197.1324.



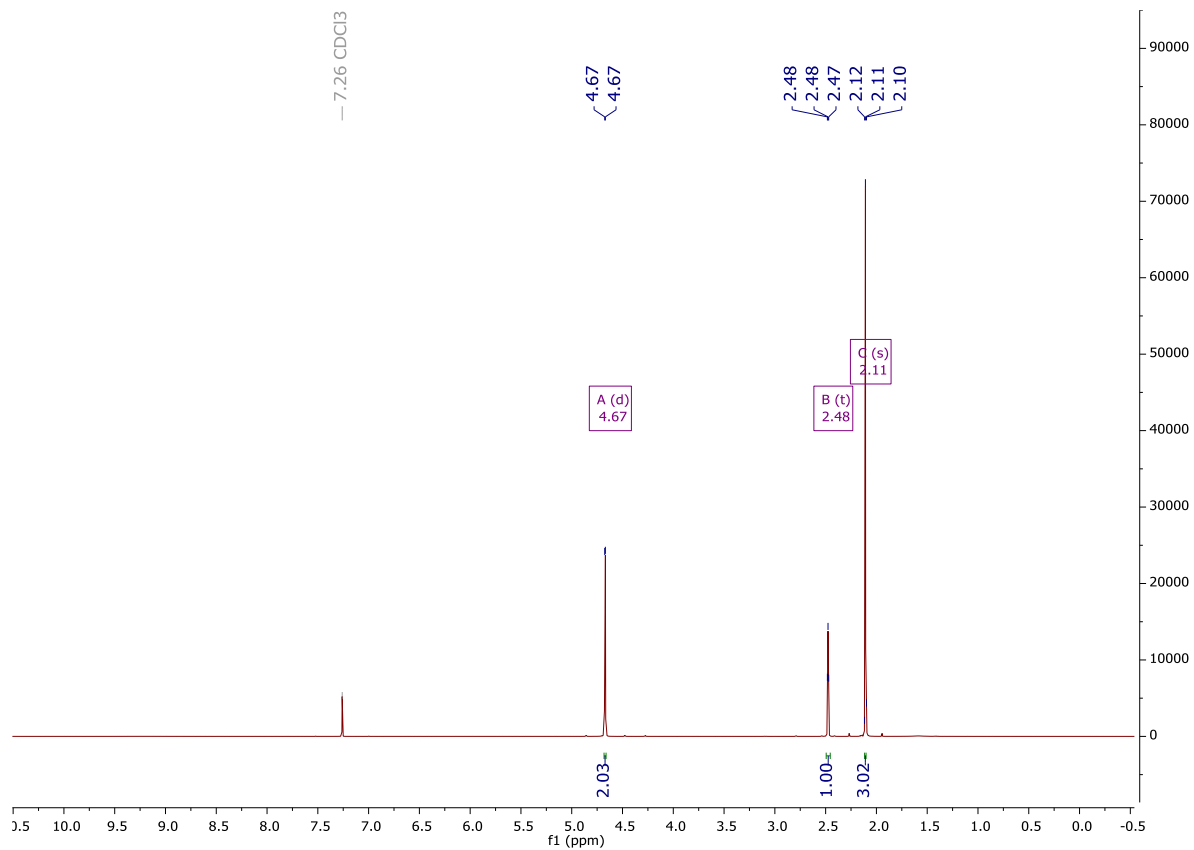
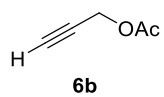
¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 7.31–7.26 (m, 2H), 7.22–7.13 (m, 3H), 6.08–5.93 (m, 1H), 5.57–5.46 (m, 1H), 3.08 (s, 1H), 2.73–2.53 (m, 2H), 2.45–2.34 (m, 1H), 2.32–2.15 (m, 1H), 1.72–1.59 (m, 2H), 1.53–1.40 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H).

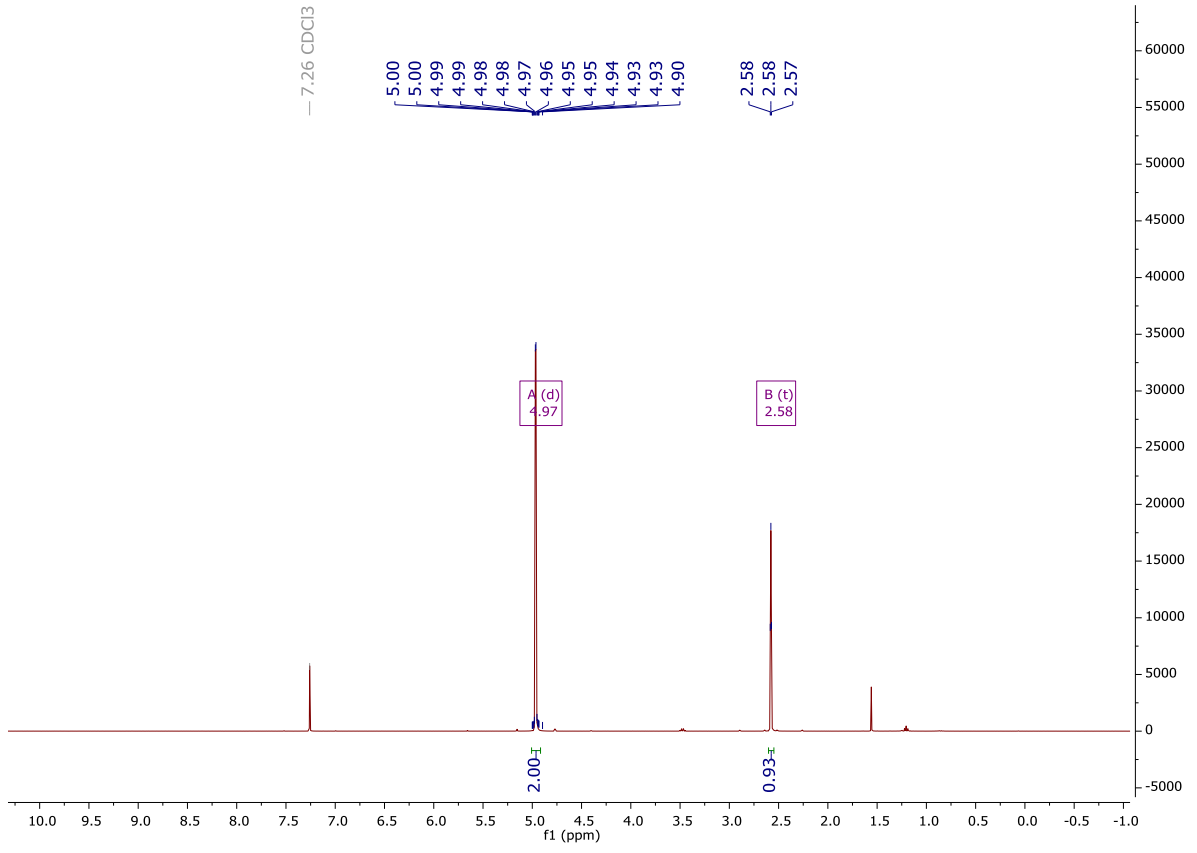
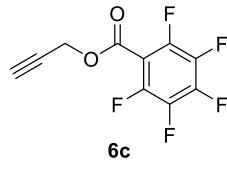
¹³C{¹H}-NMR (CDCl₃, 101 MHz): δ [ppm] = 144.9, 143.1, 128.7, 128.7, 128.6, 126.0, 109.4, 81.7, 81.0, 38.8, 37.6, 33.8, 33.0, 19.9.

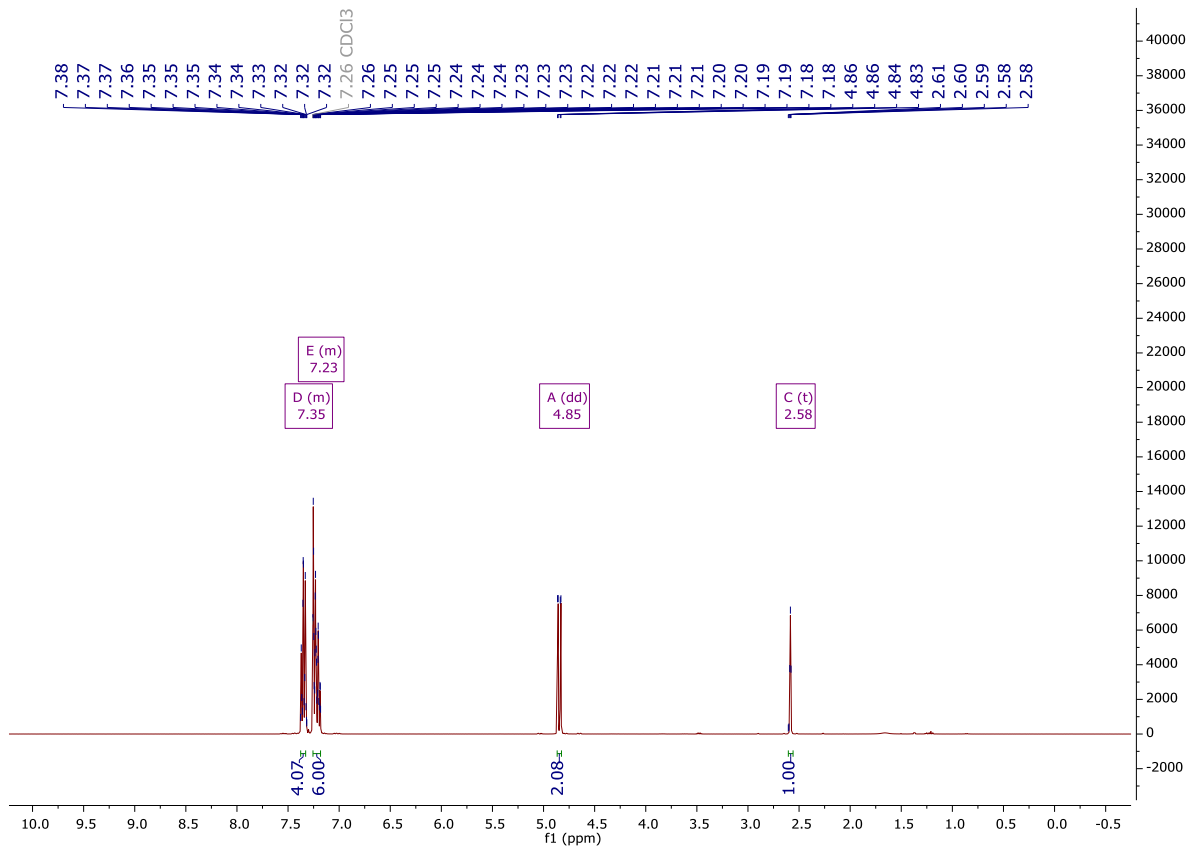
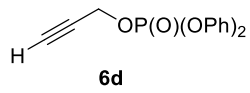
IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3300 (m), 3026 (m), 2955 (m), 2925 (s), 2871 (m), 2859 (m), 2360 (vs), 2341 (s), 2333 (s), 1496 (w), 1455 (m), 1378 (w), 746 (m), 698 (s), 668 (m), 656 (m).

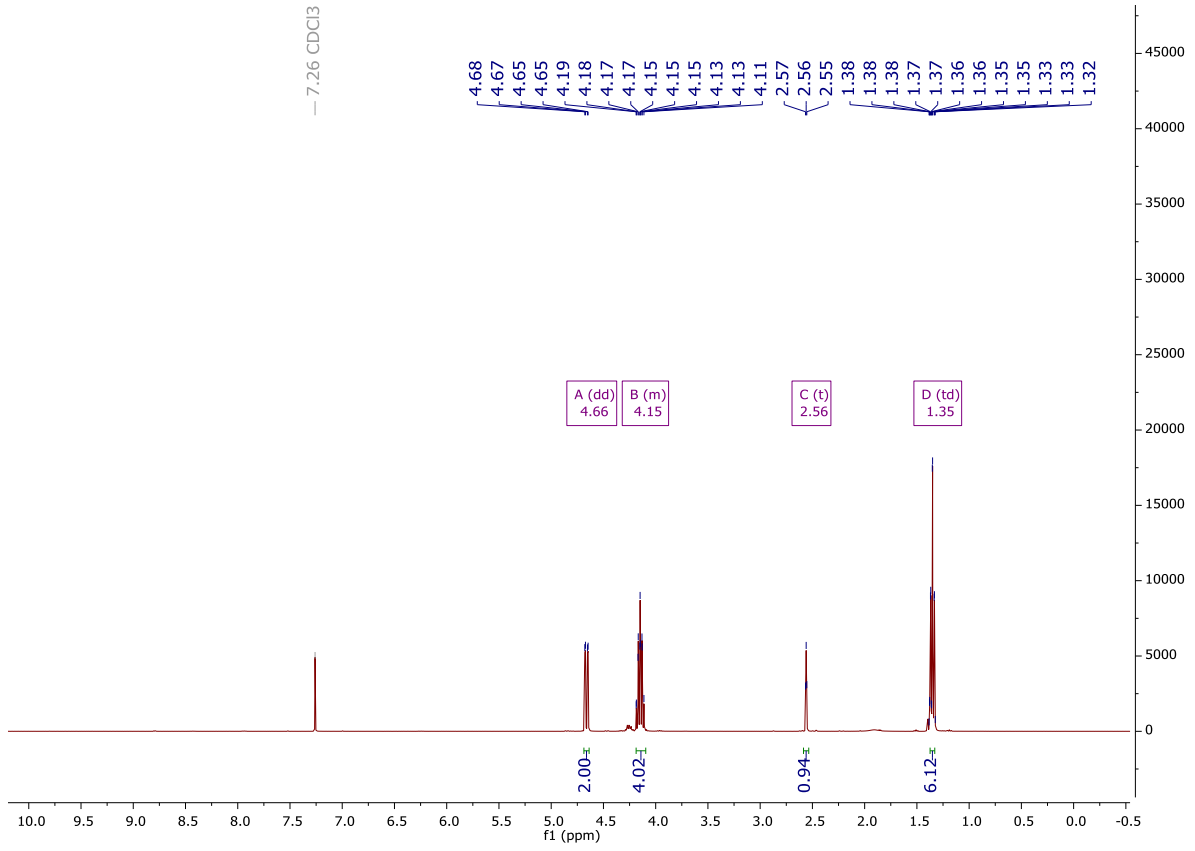
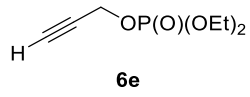
HRMS (EI) m/z : calcd for C₁₅H₁₇ [M⁺-H]: 197.1330; found 197.1325.

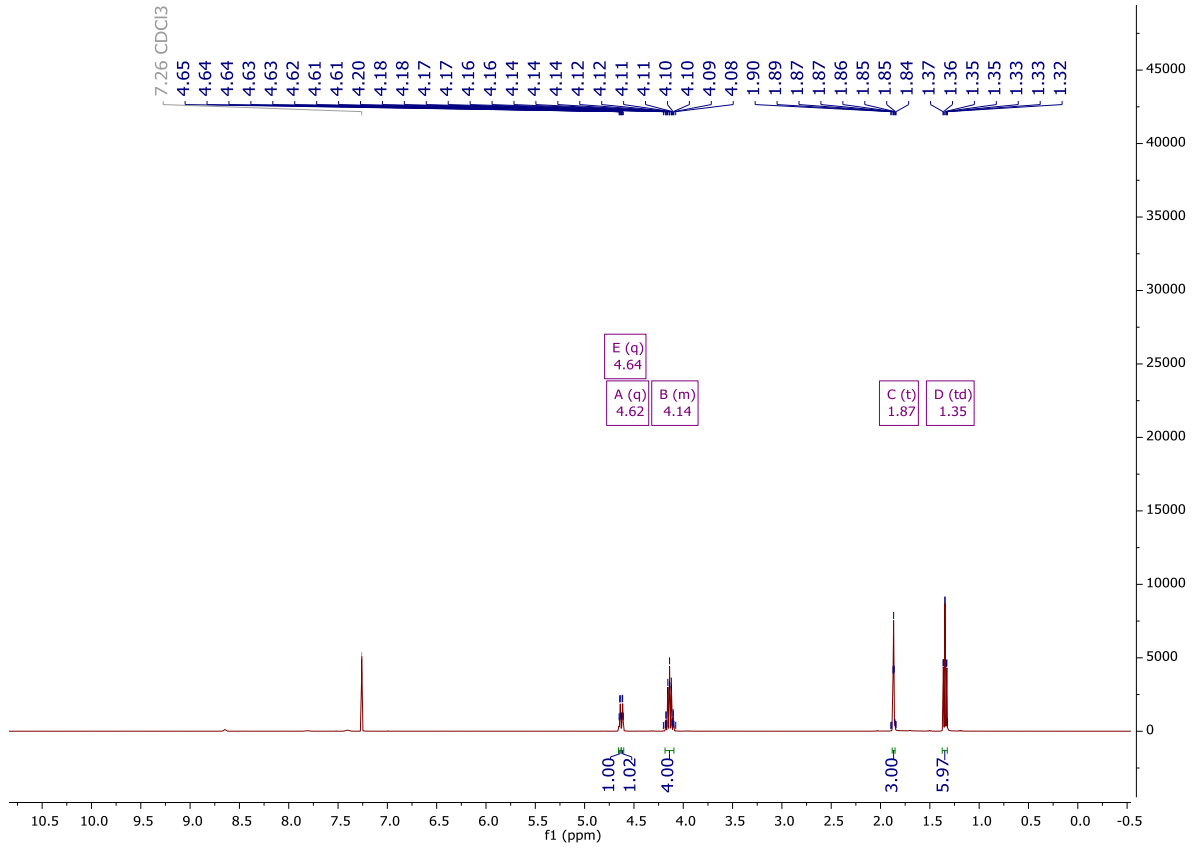
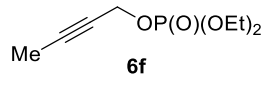
5 NMR Spectra

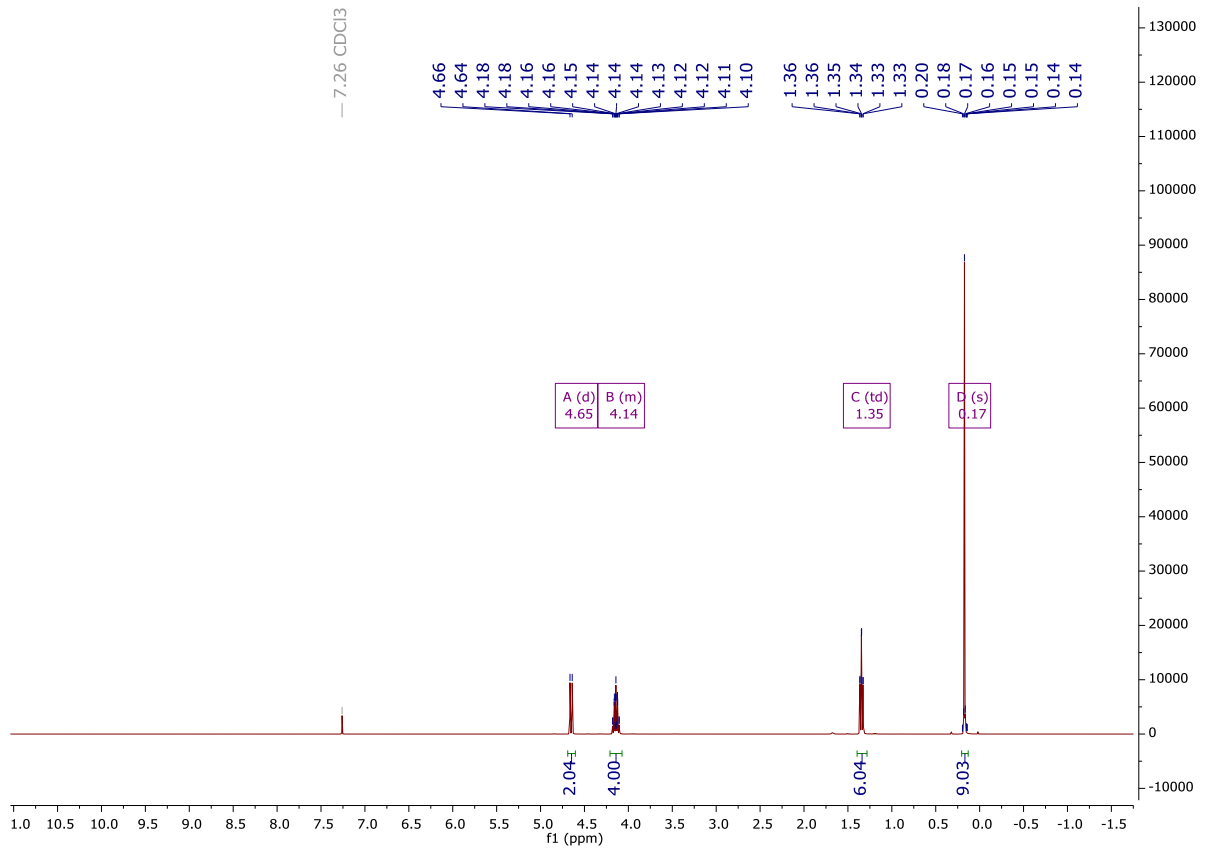
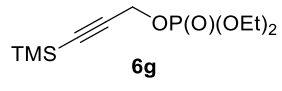


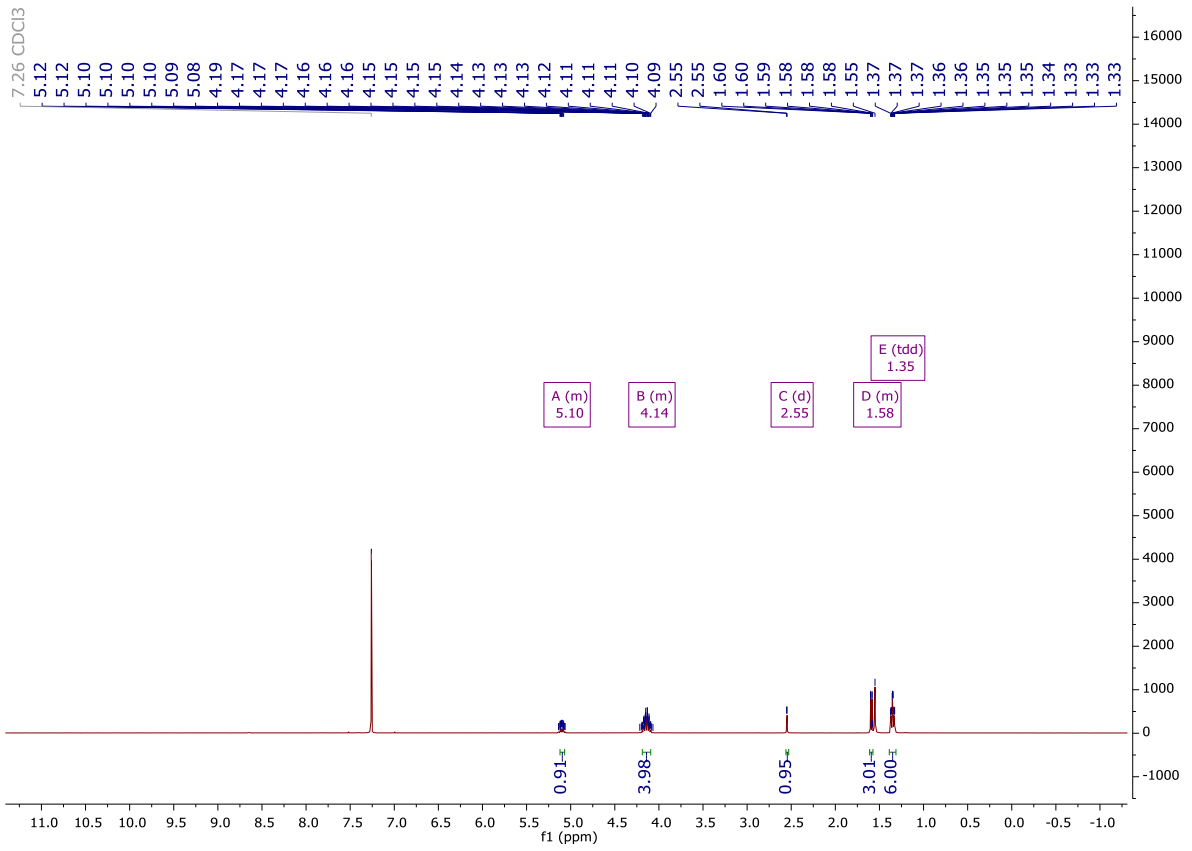
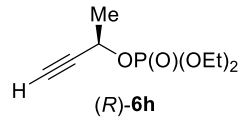


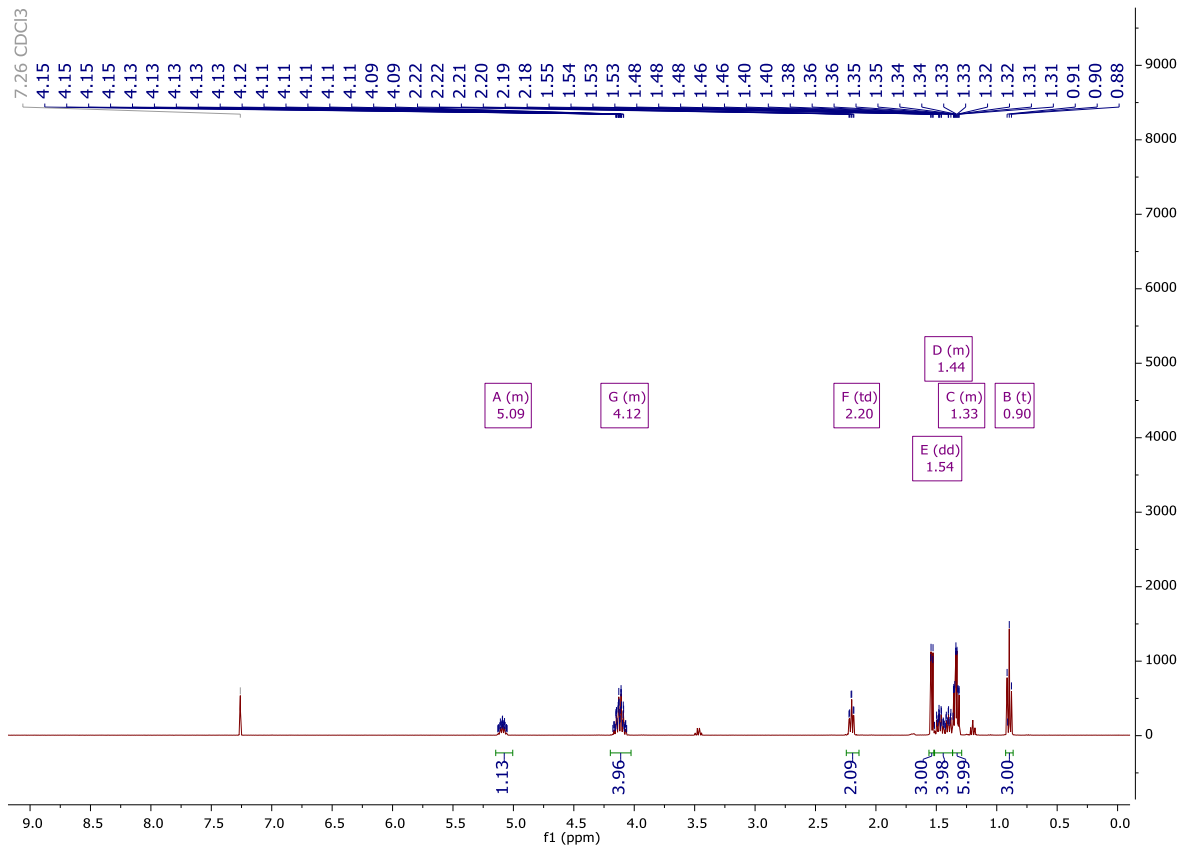
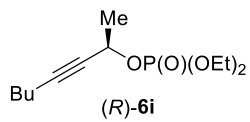


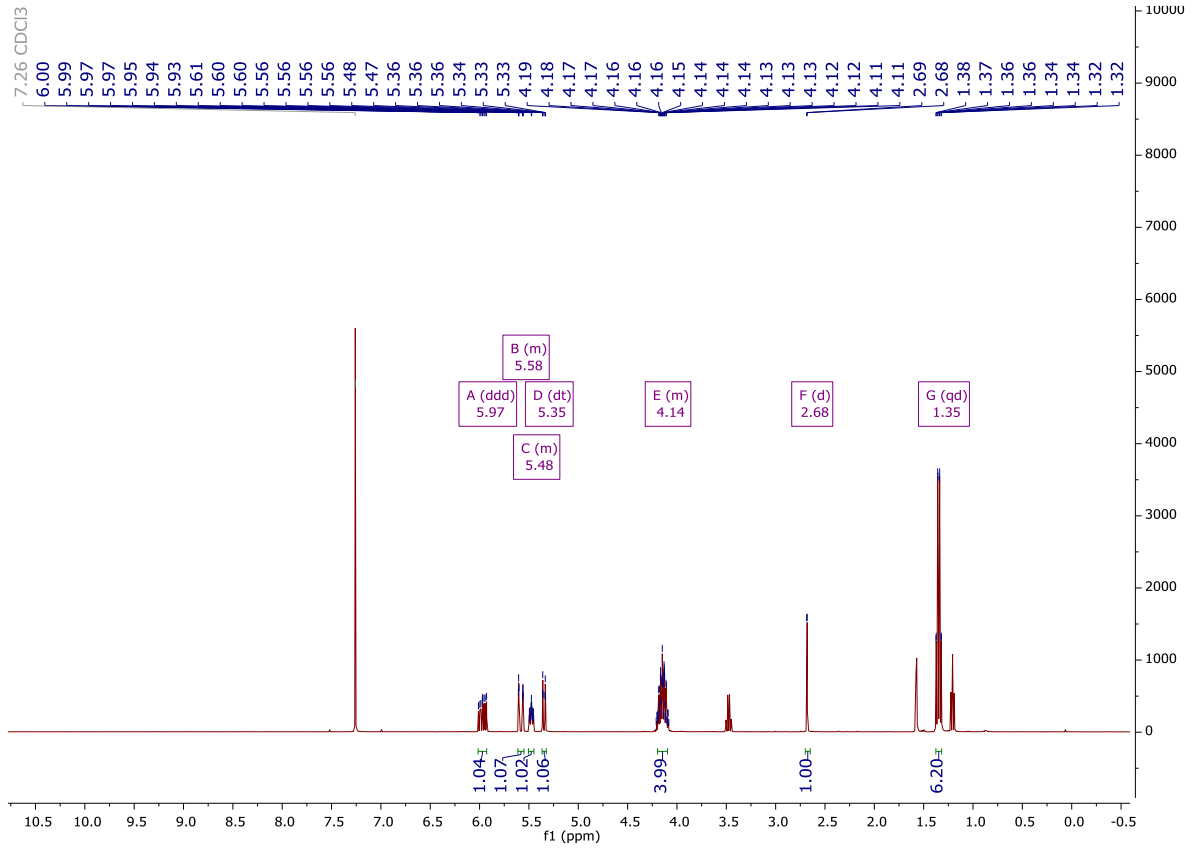
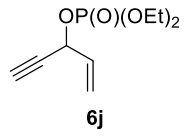


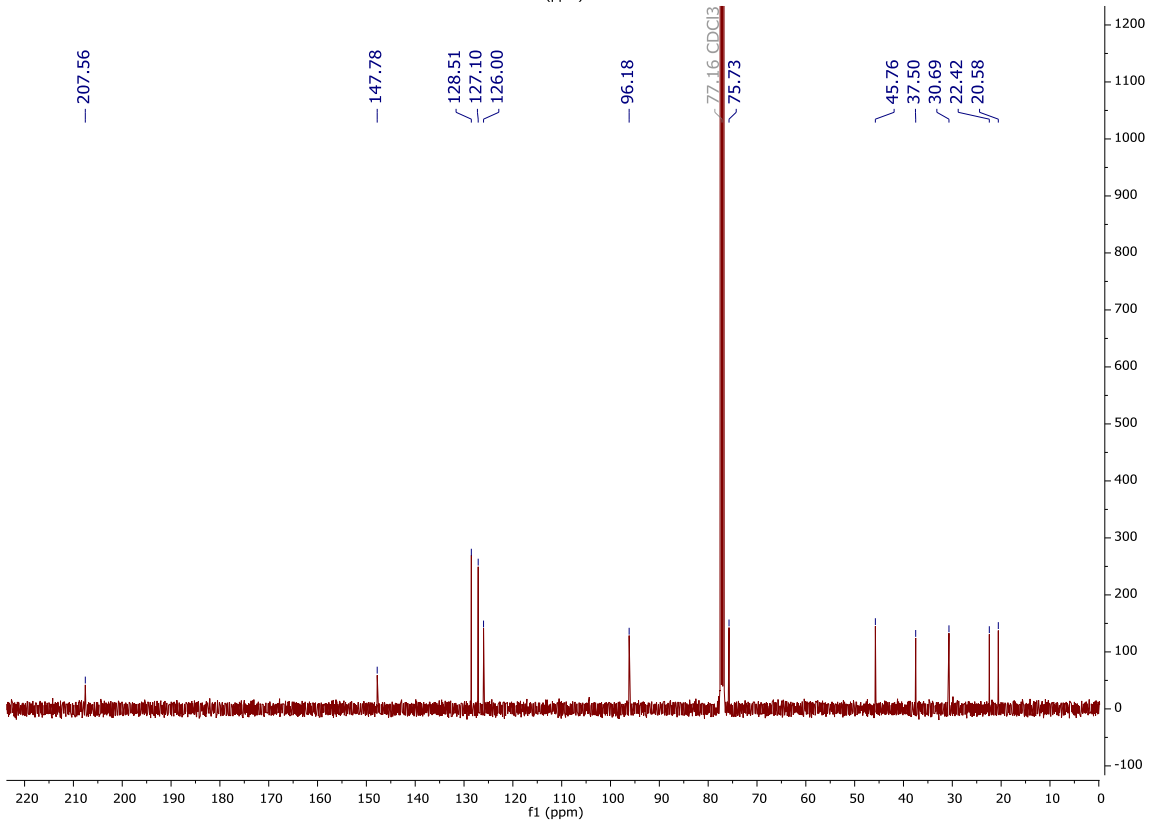
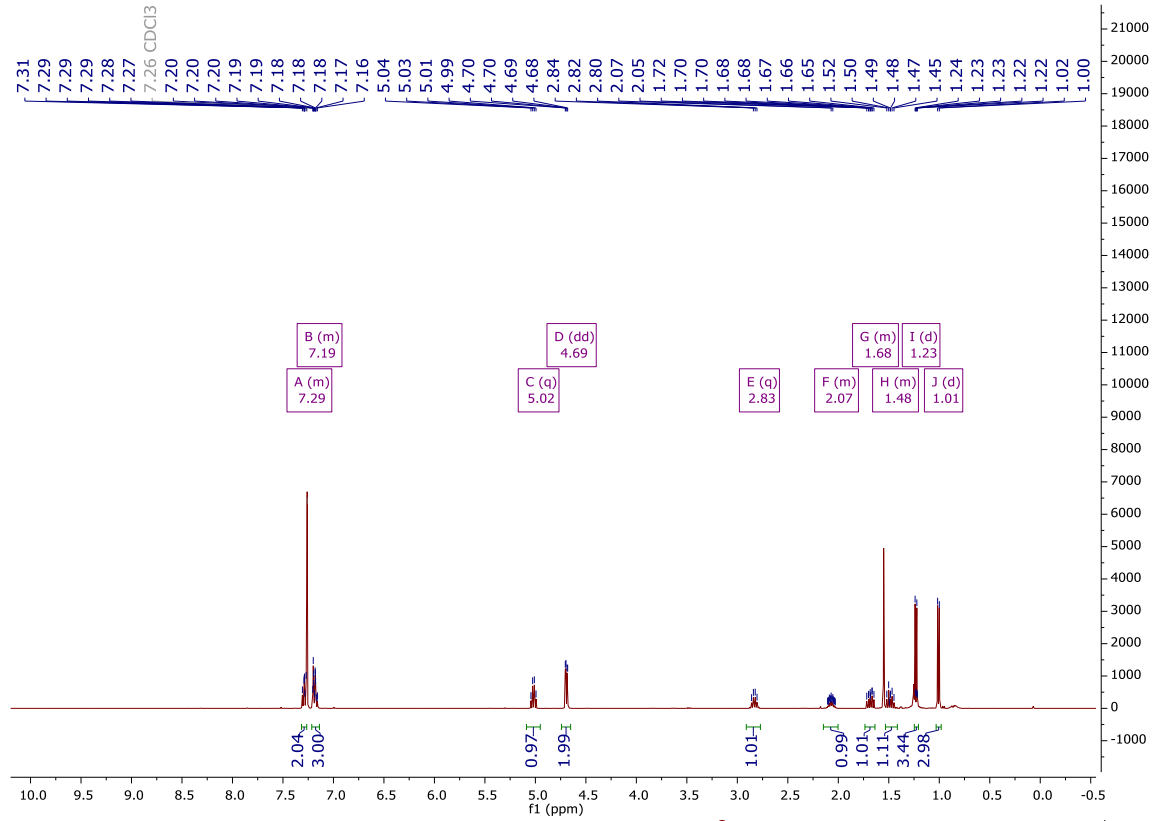
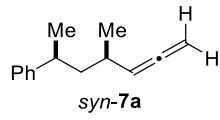


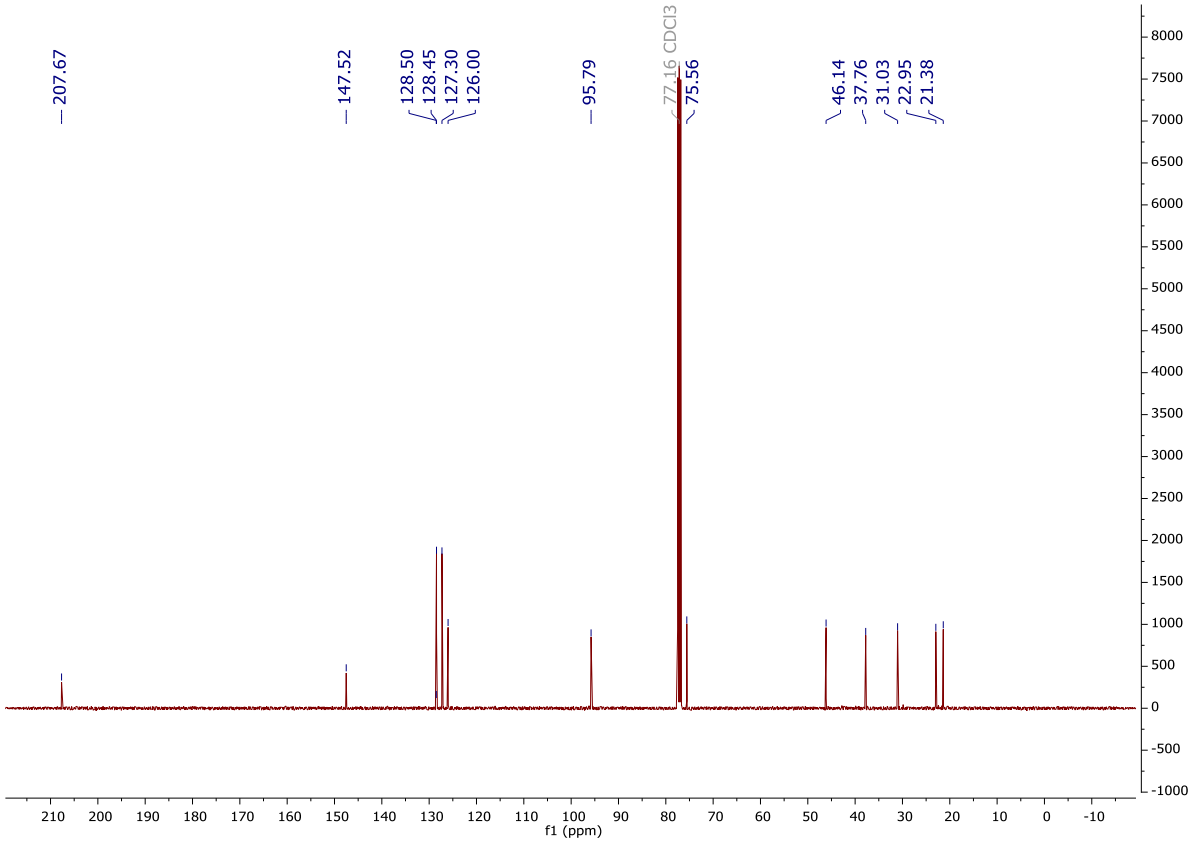
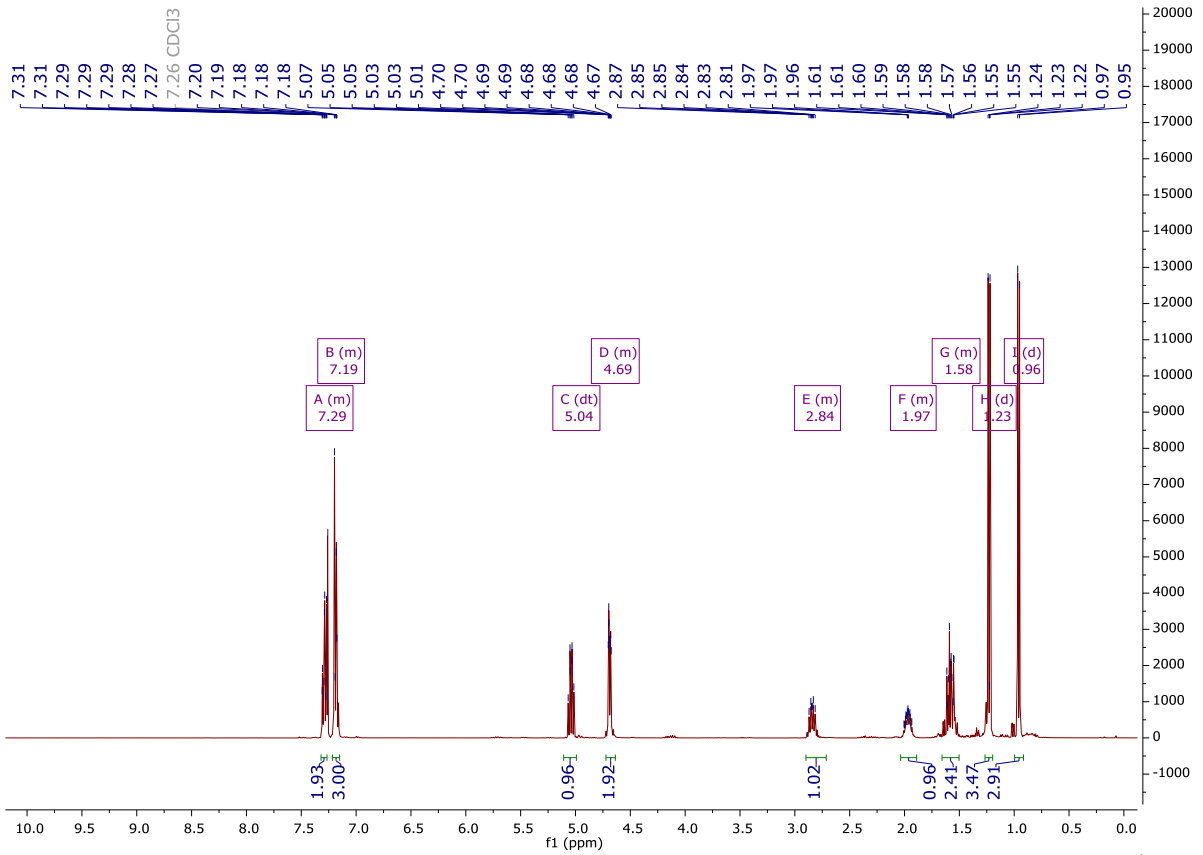
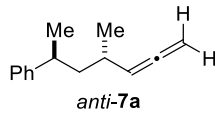


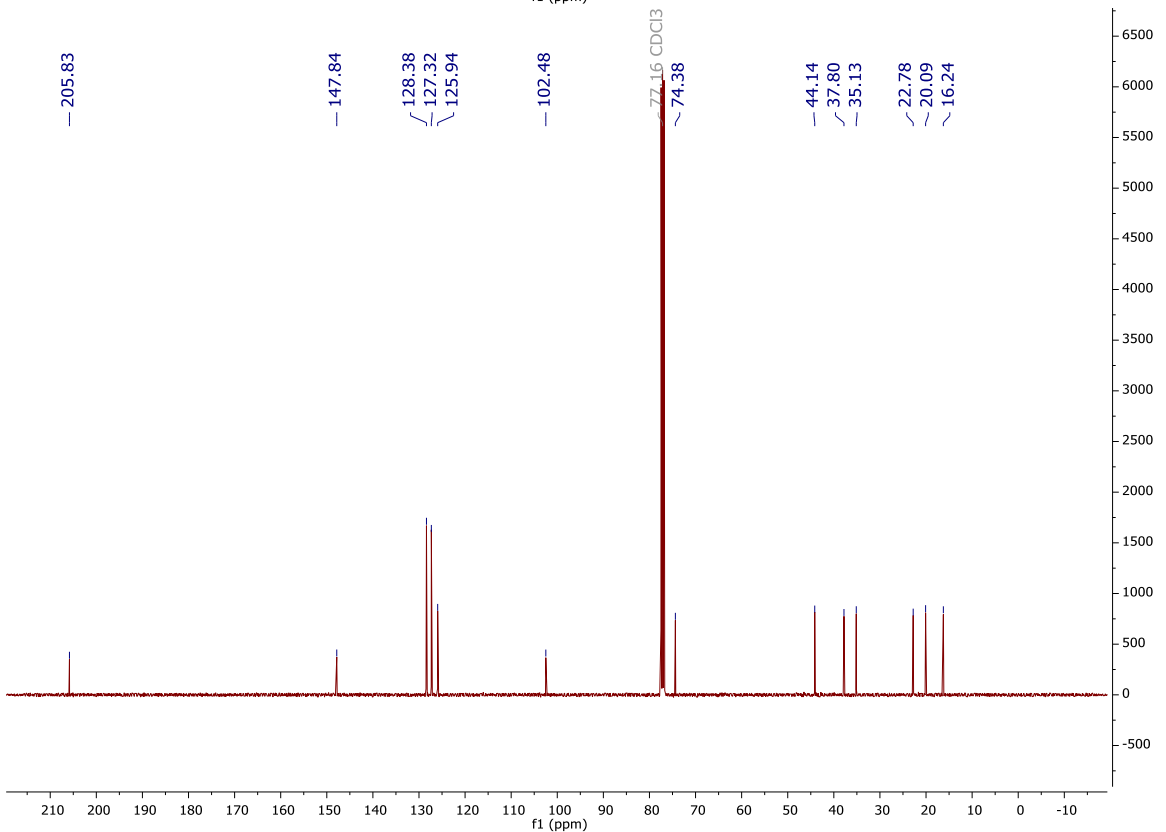
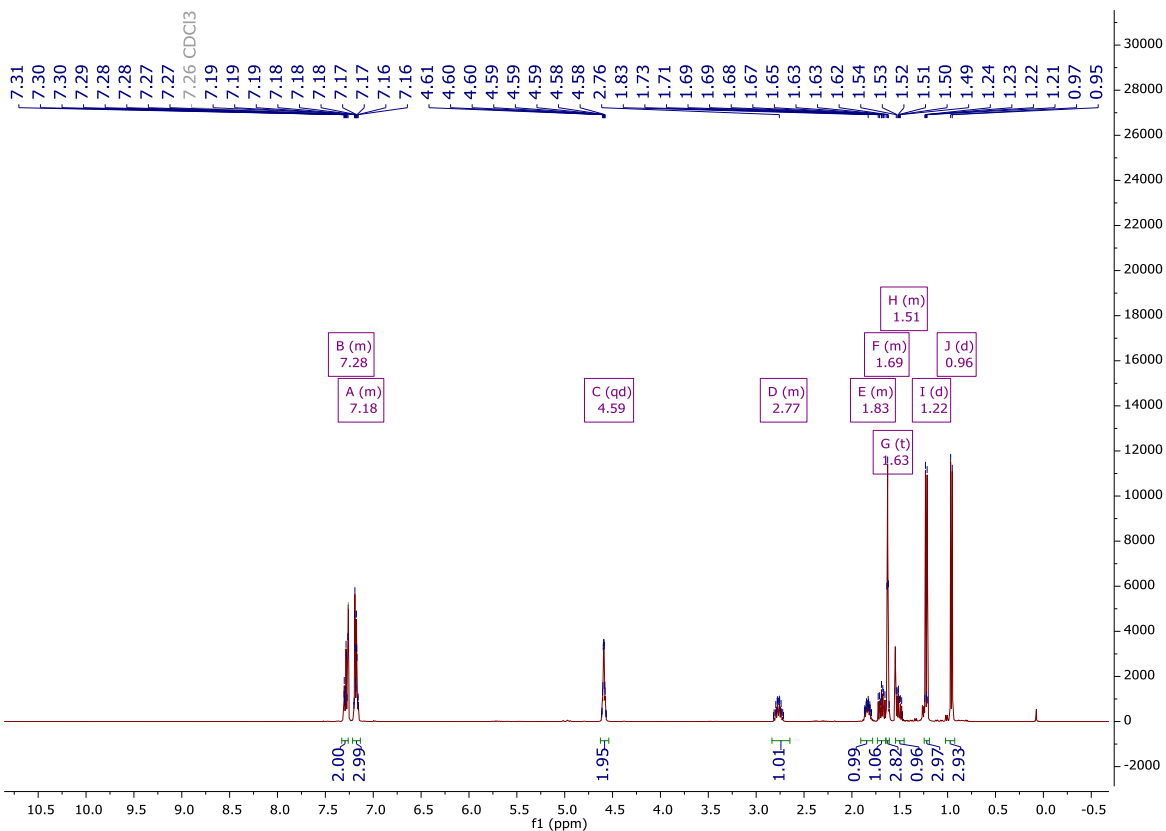
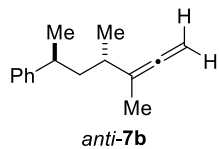


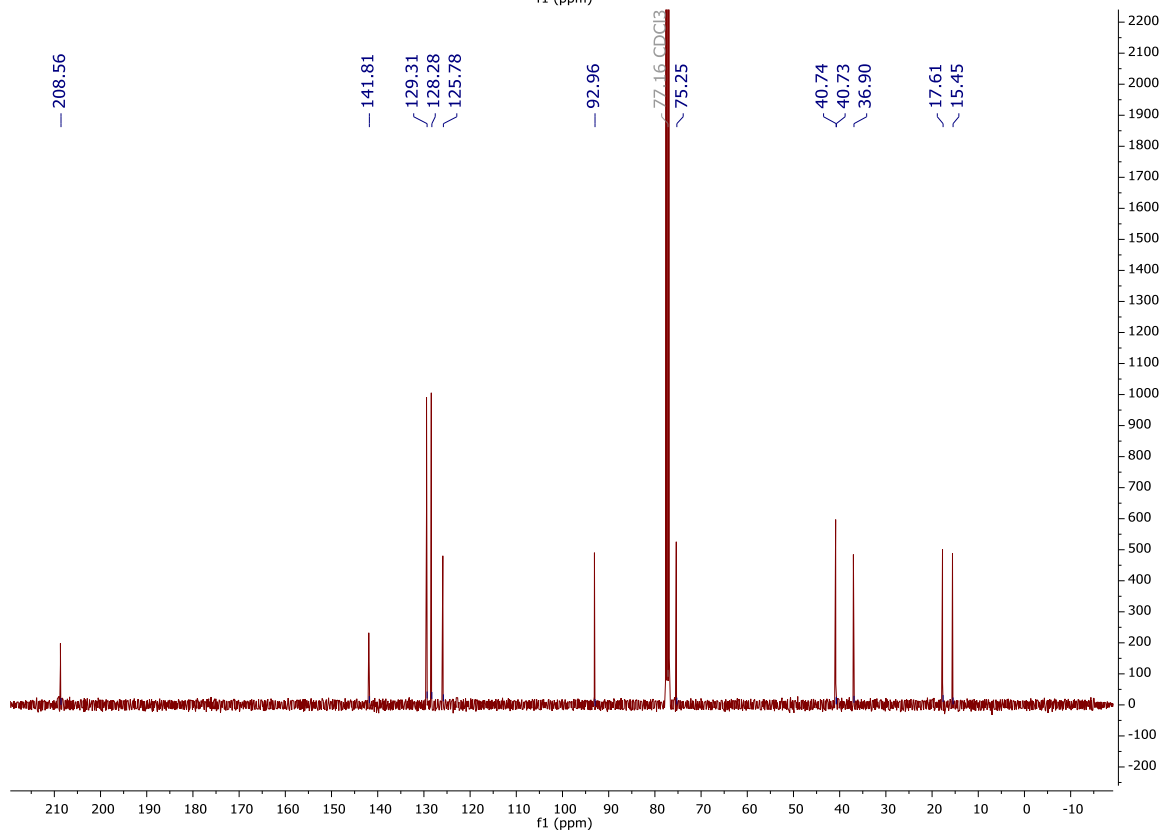
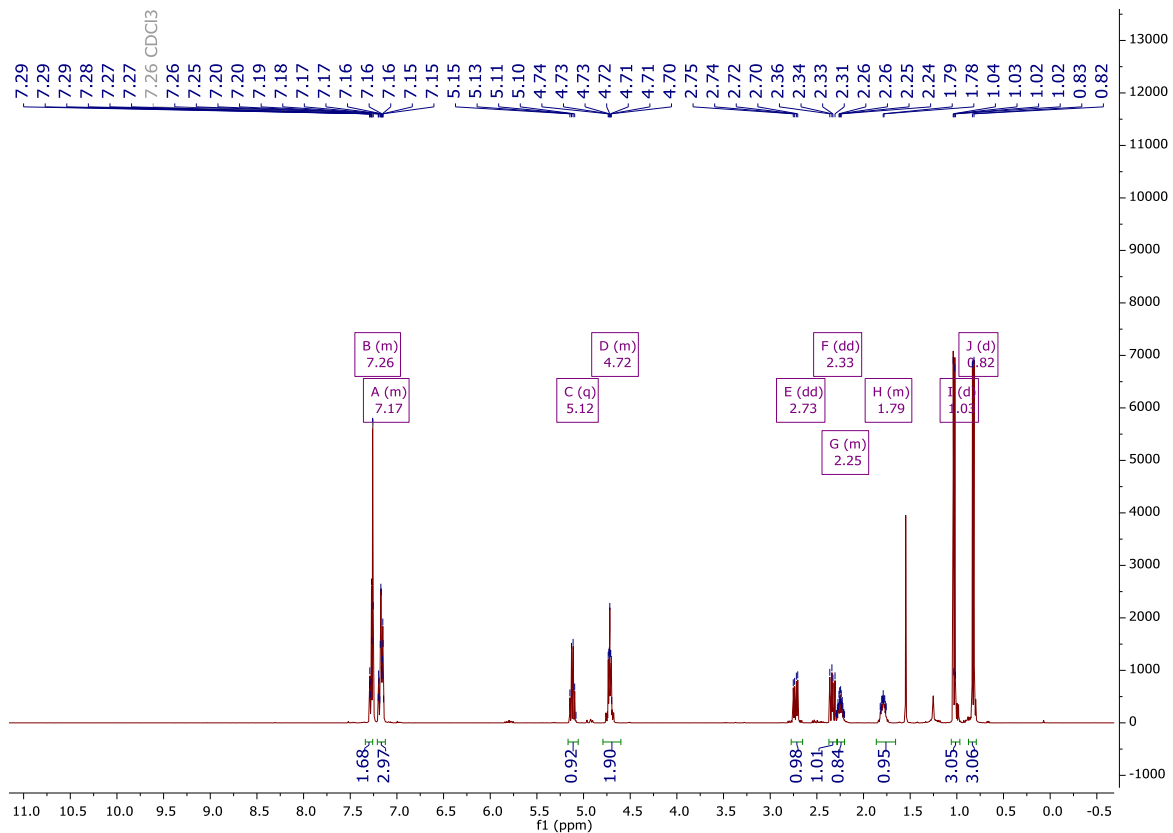
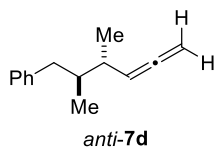


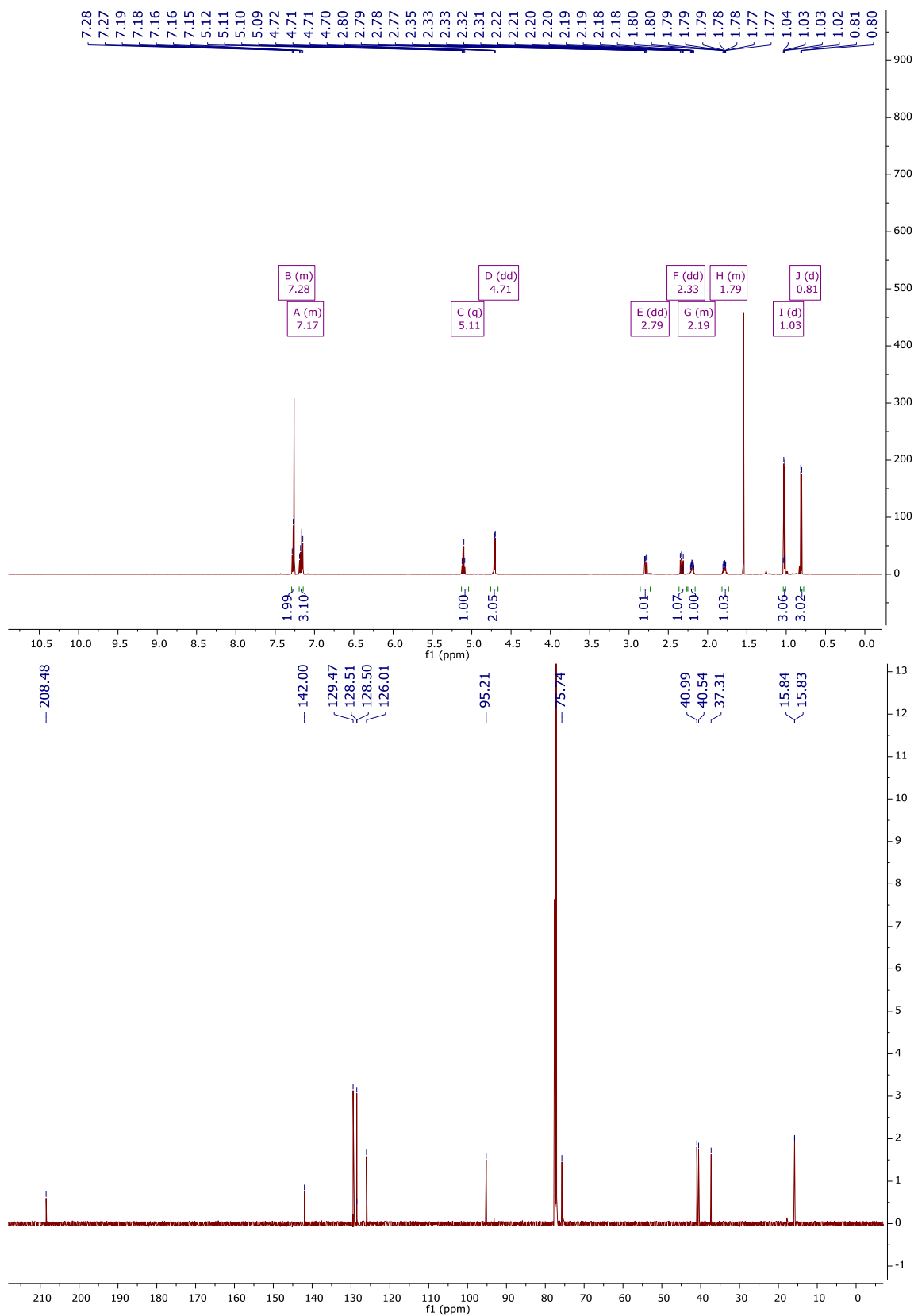
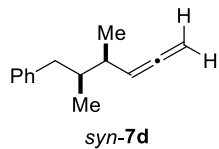


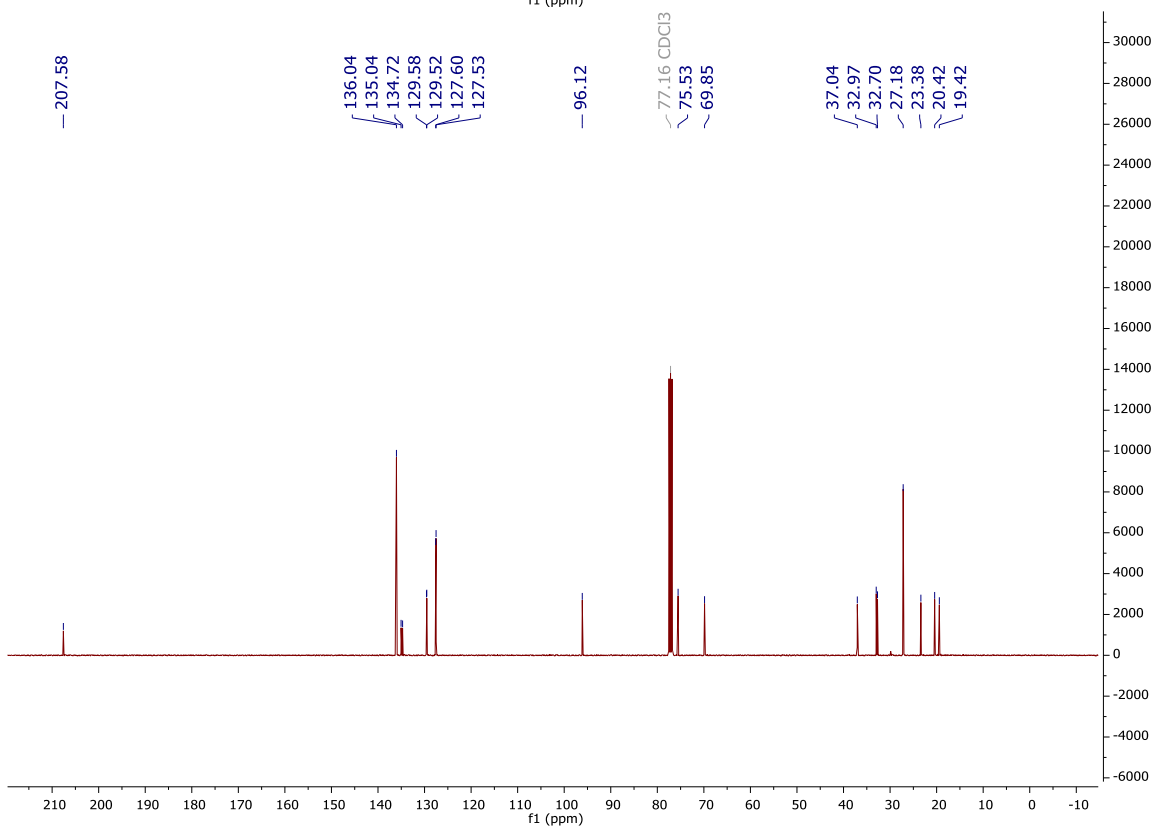
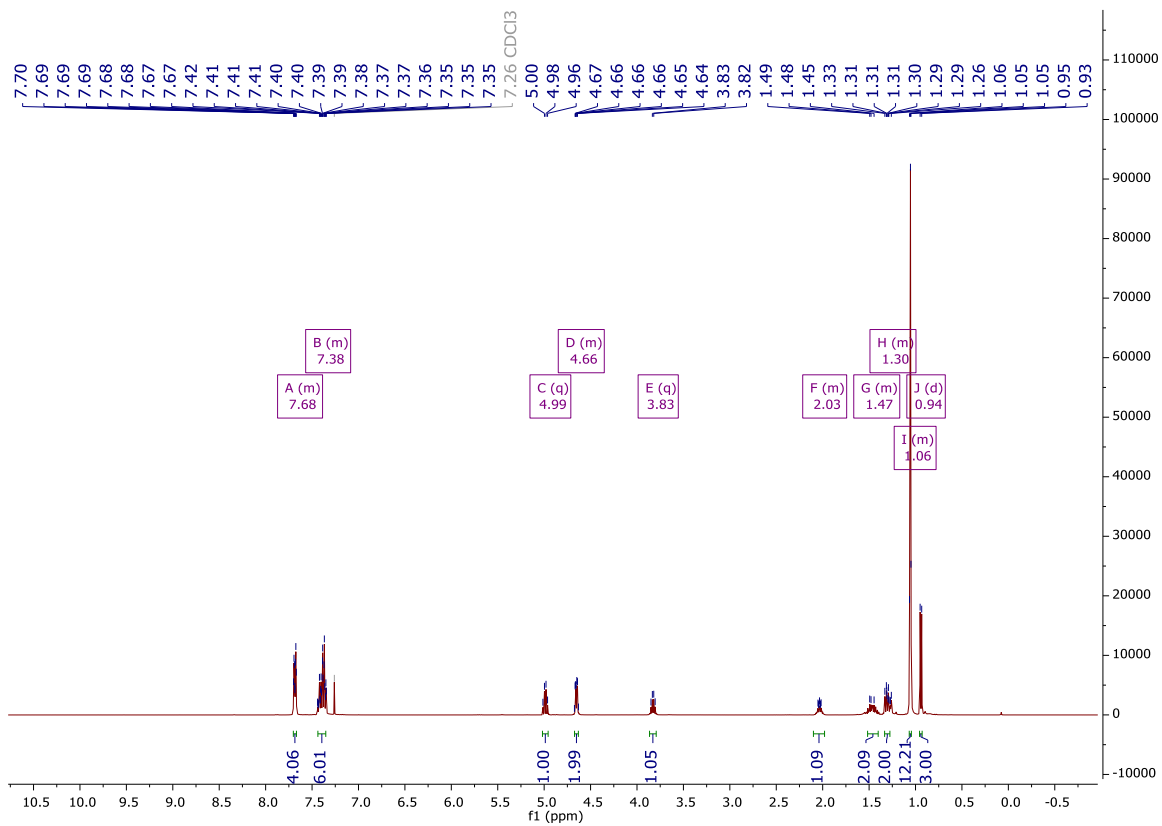
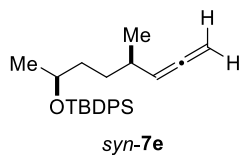


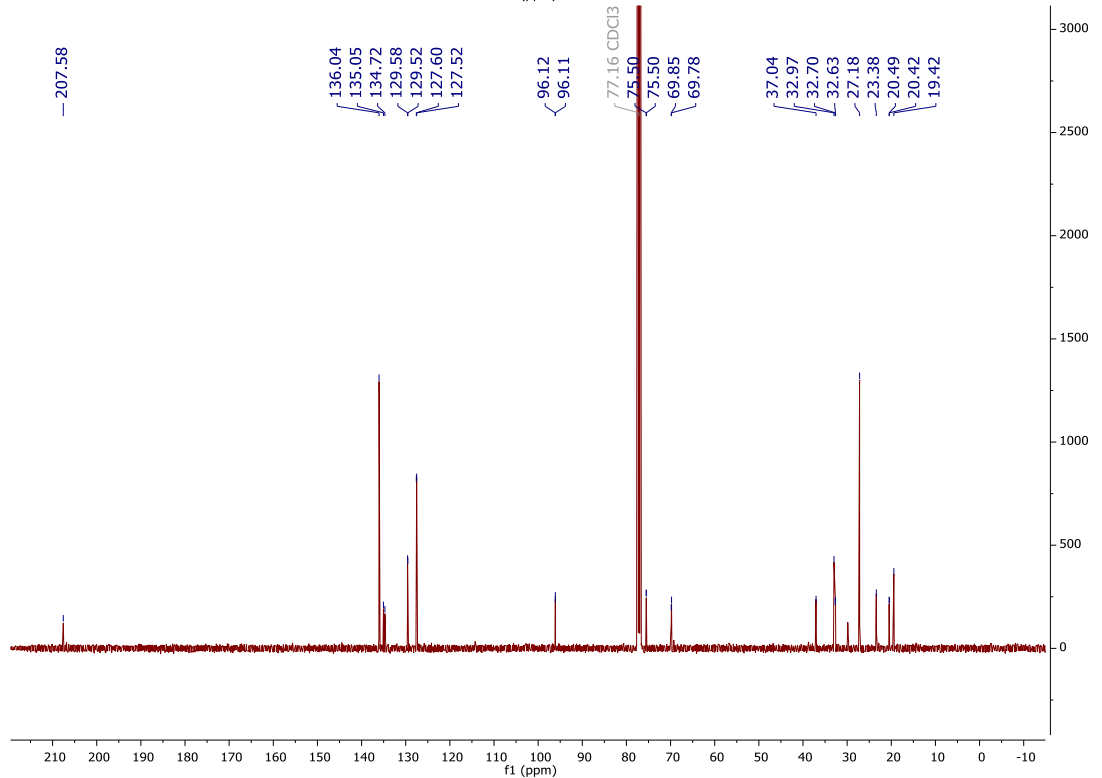
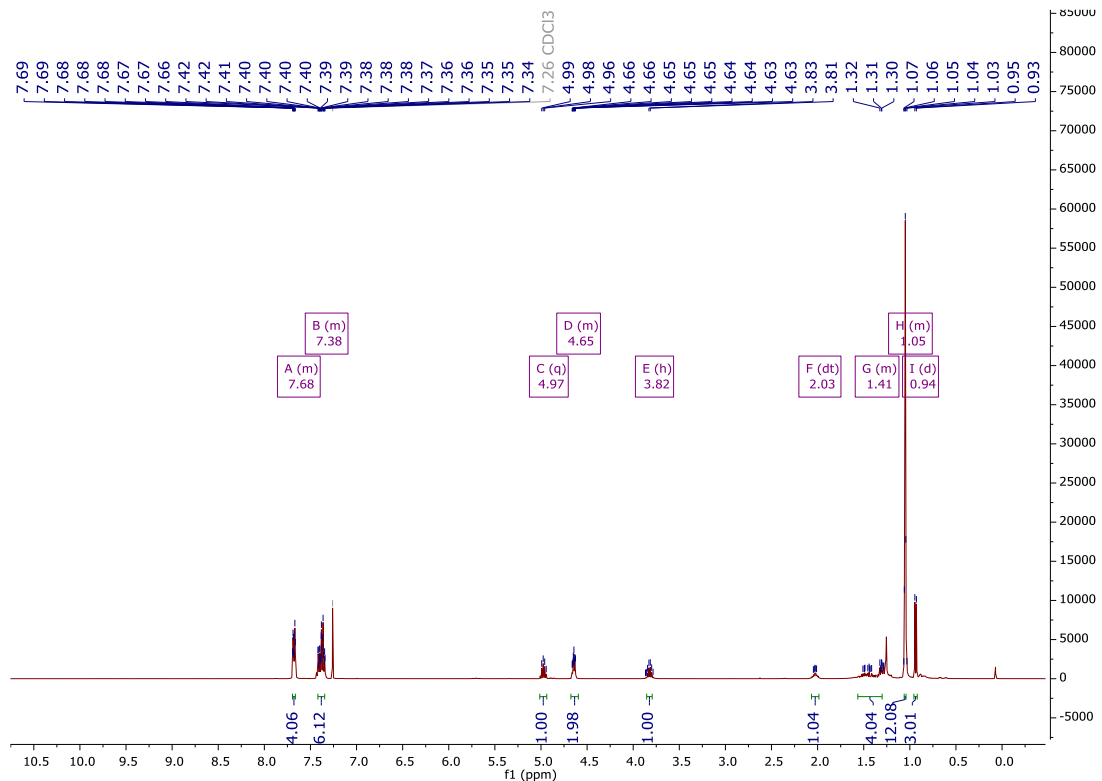
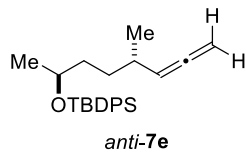


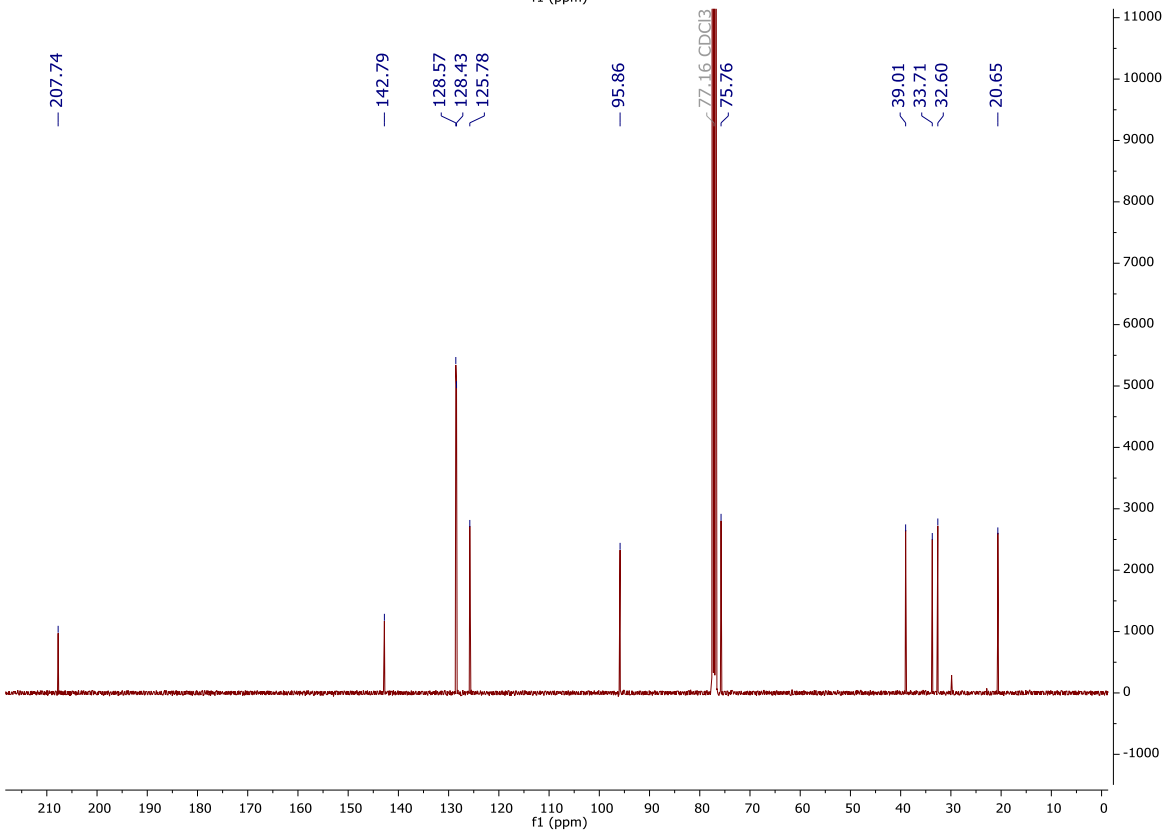
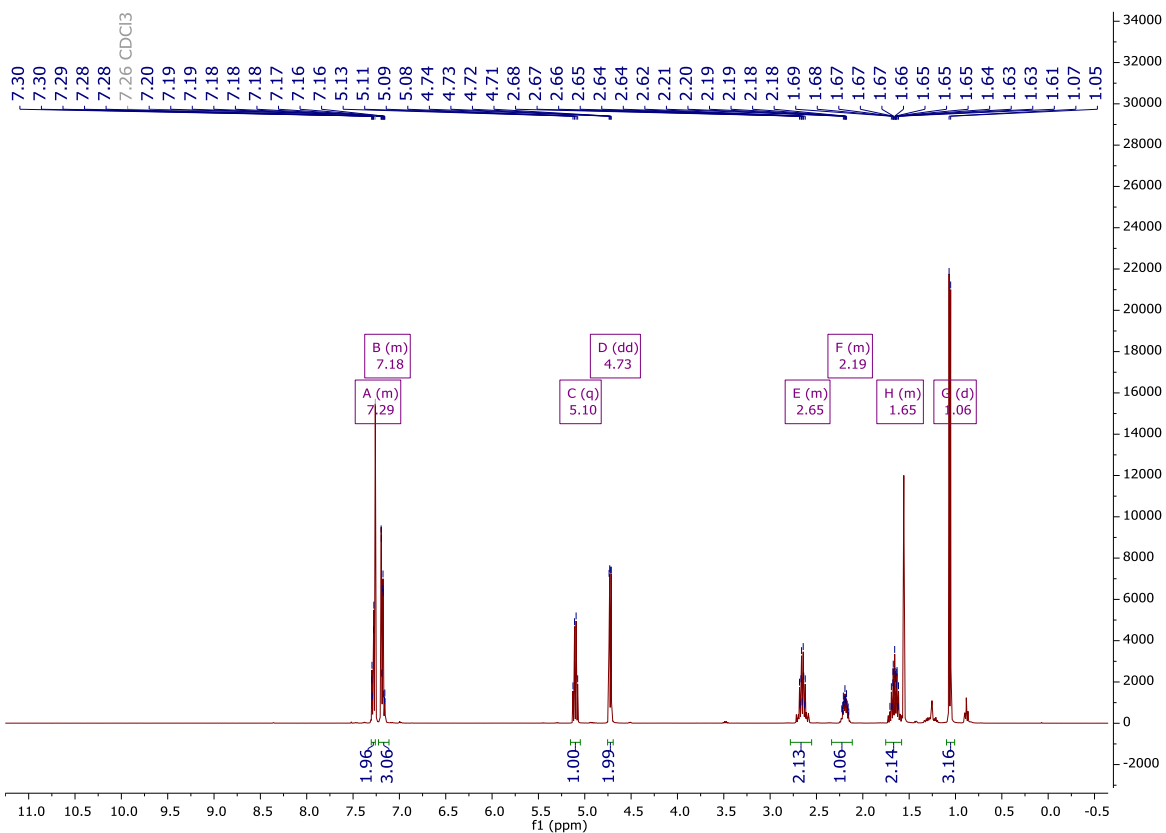
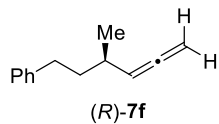


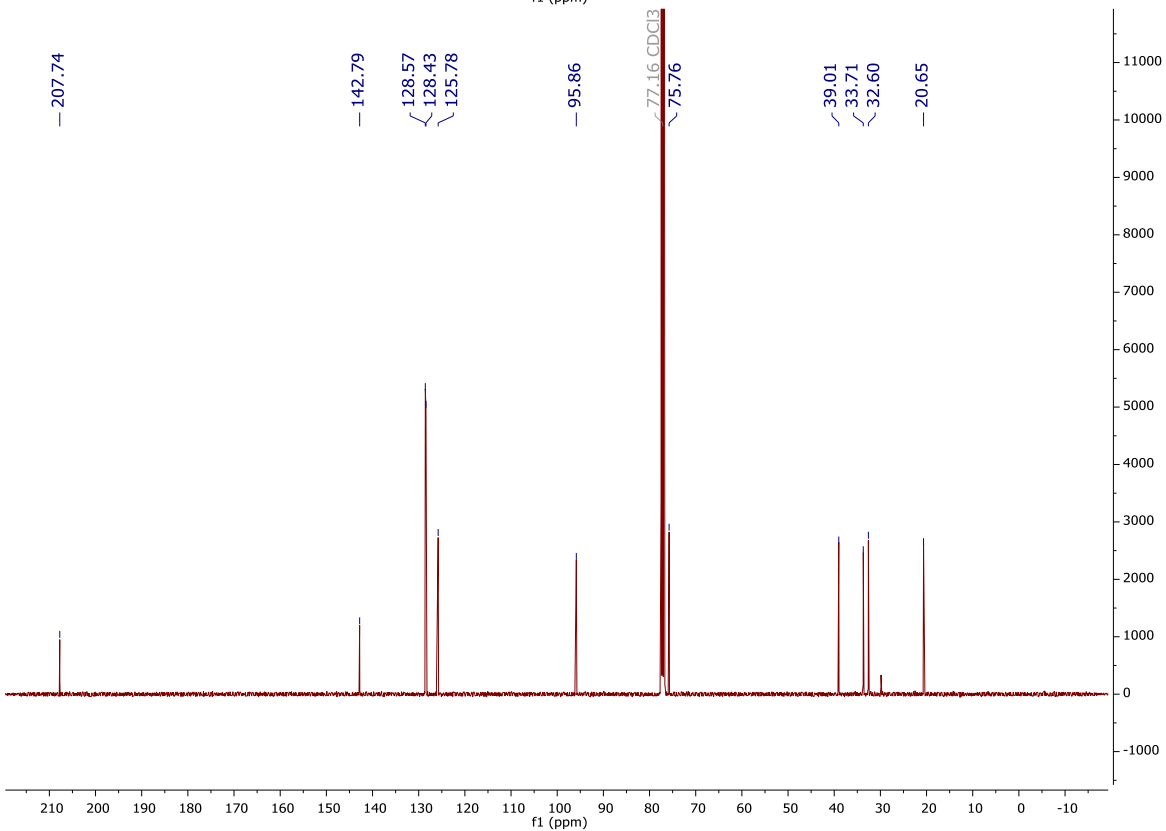
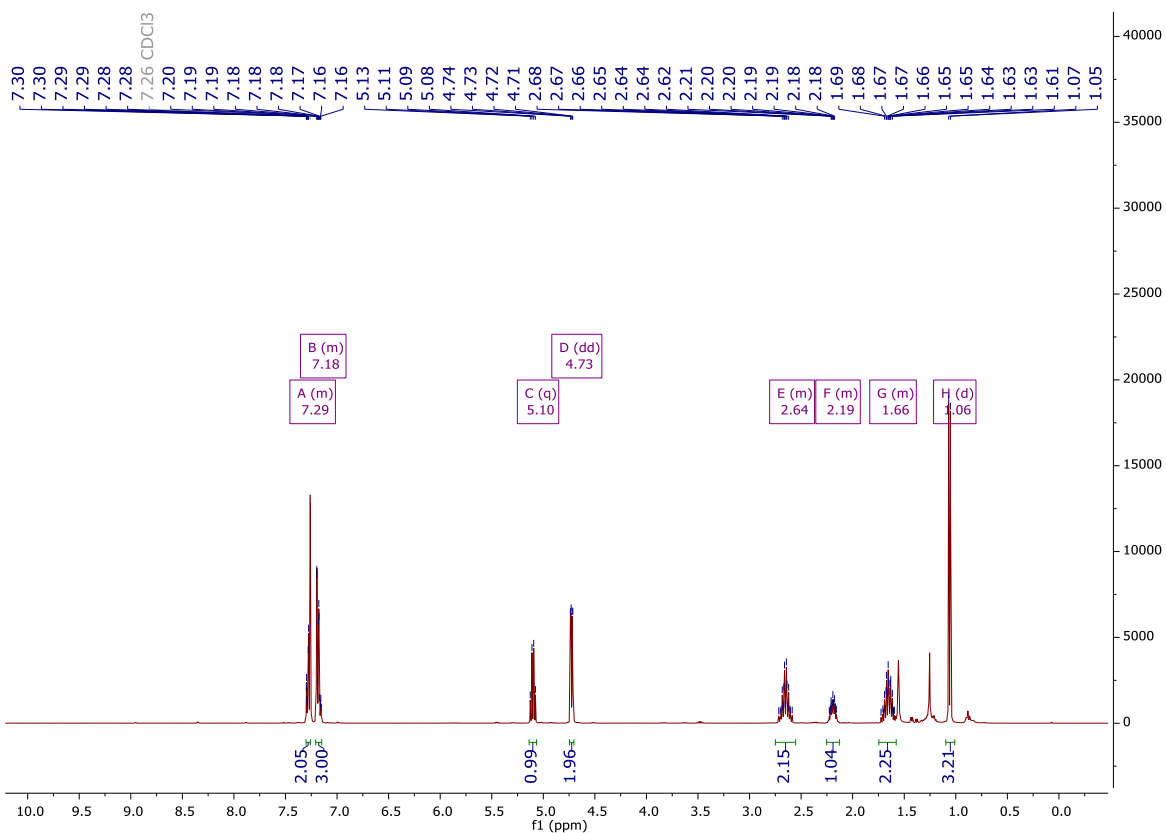
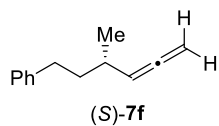


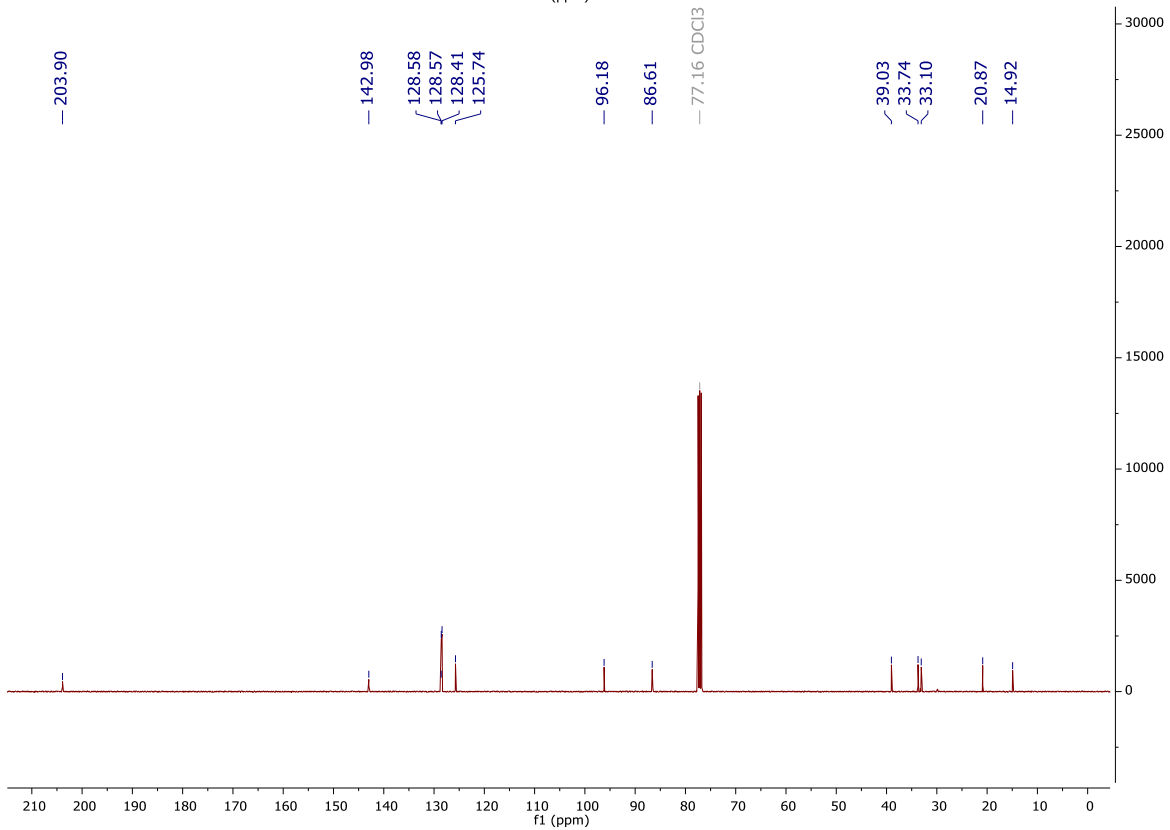
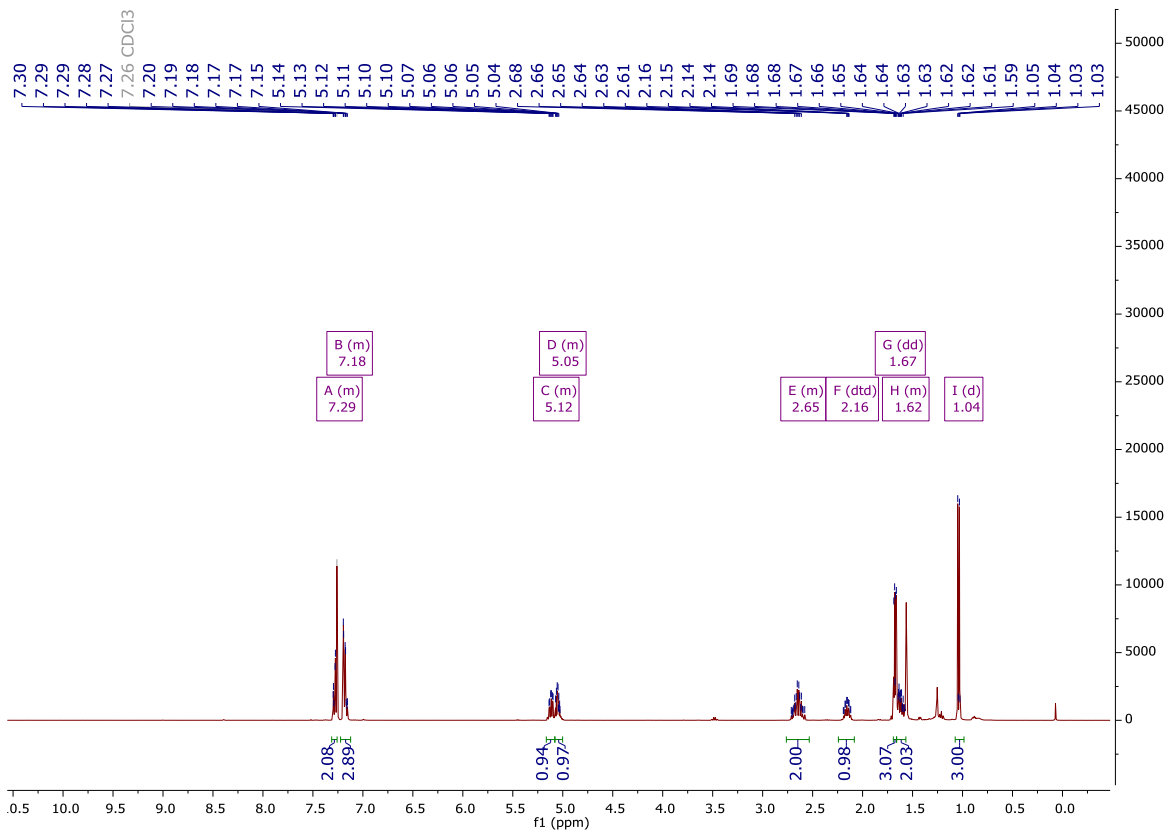
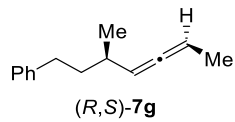


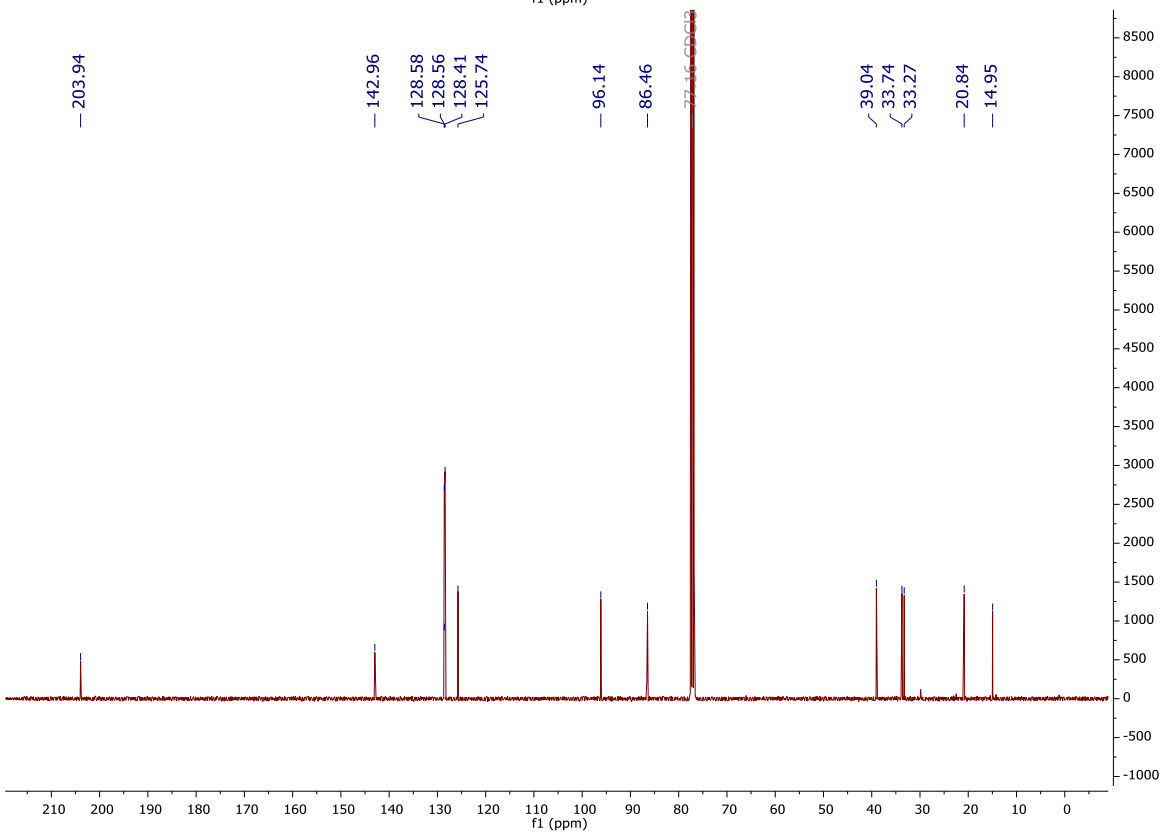
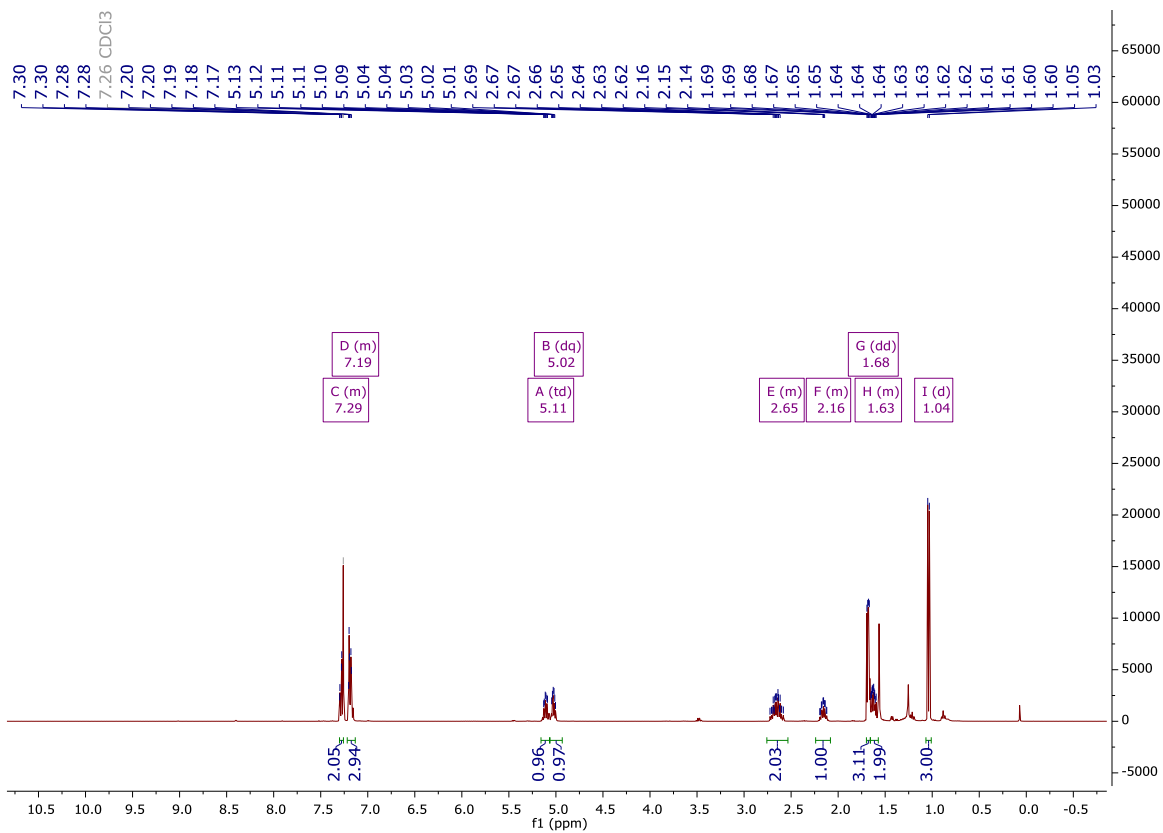
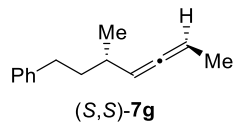


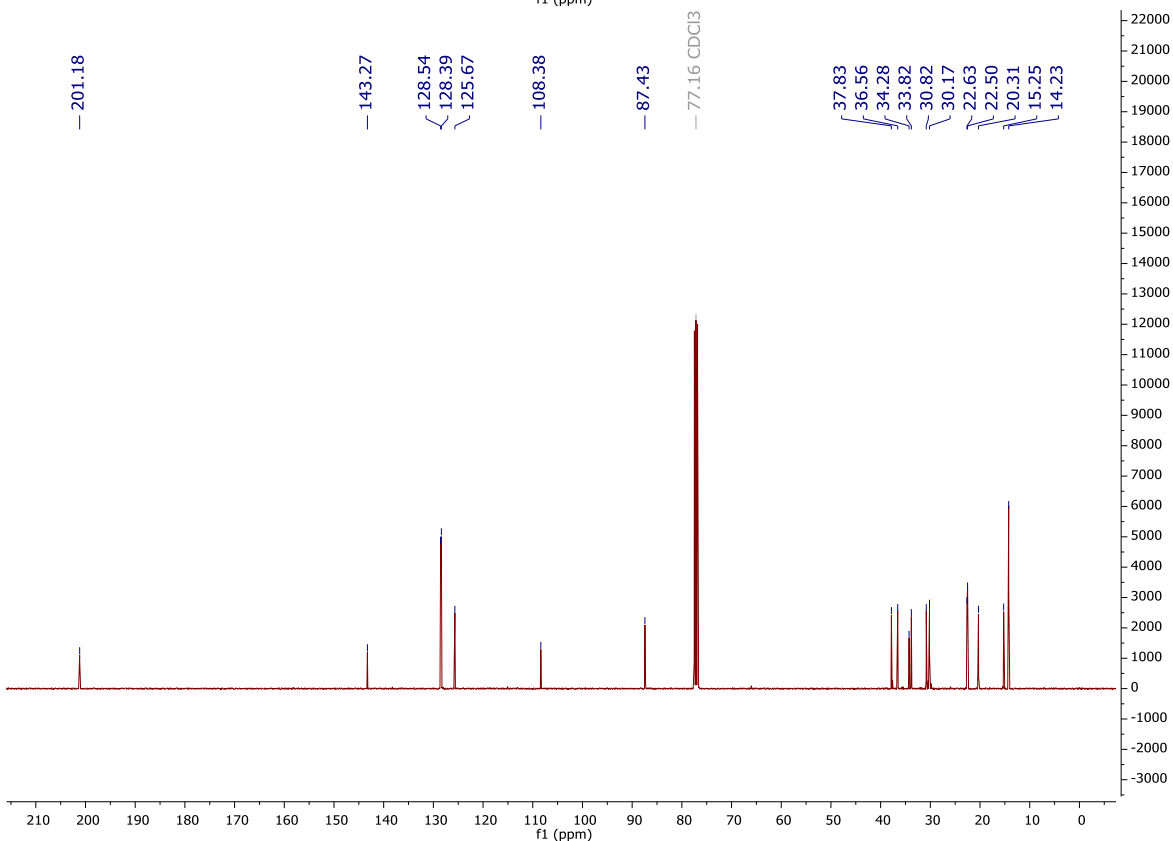
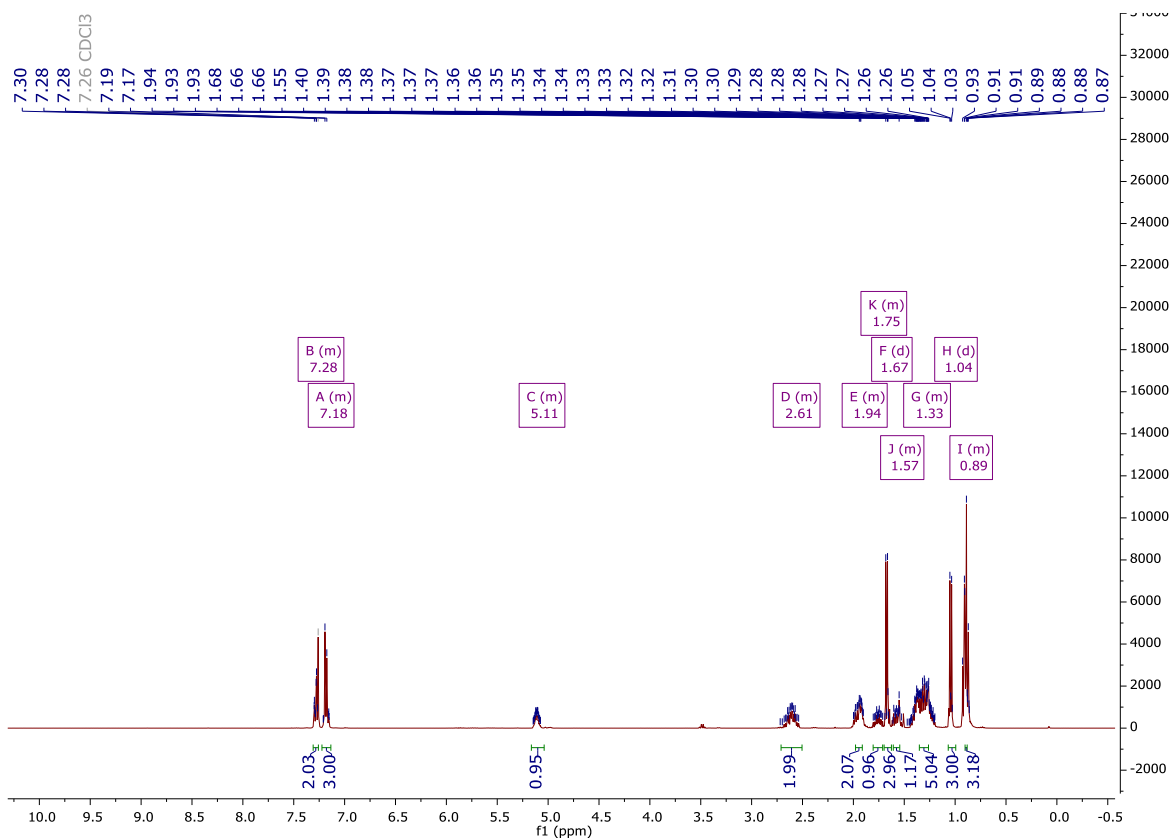
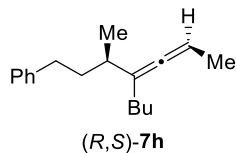


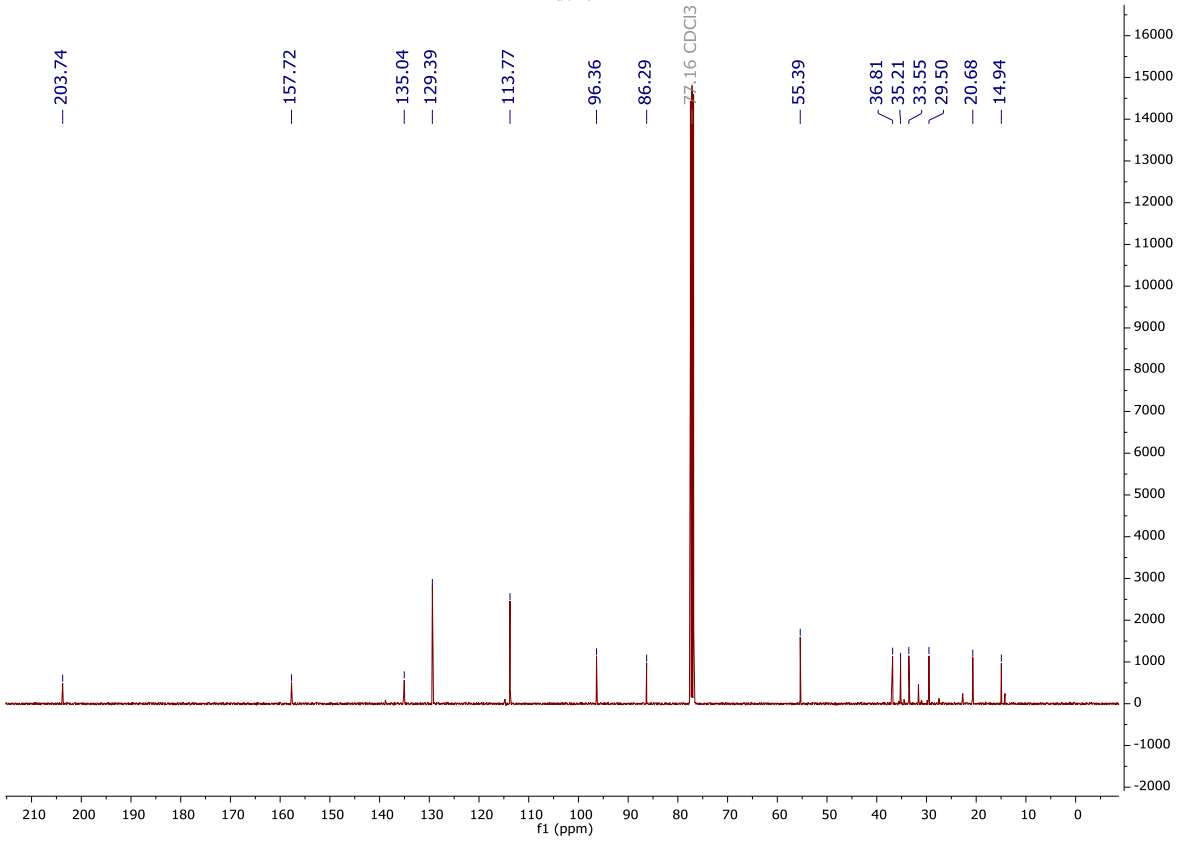
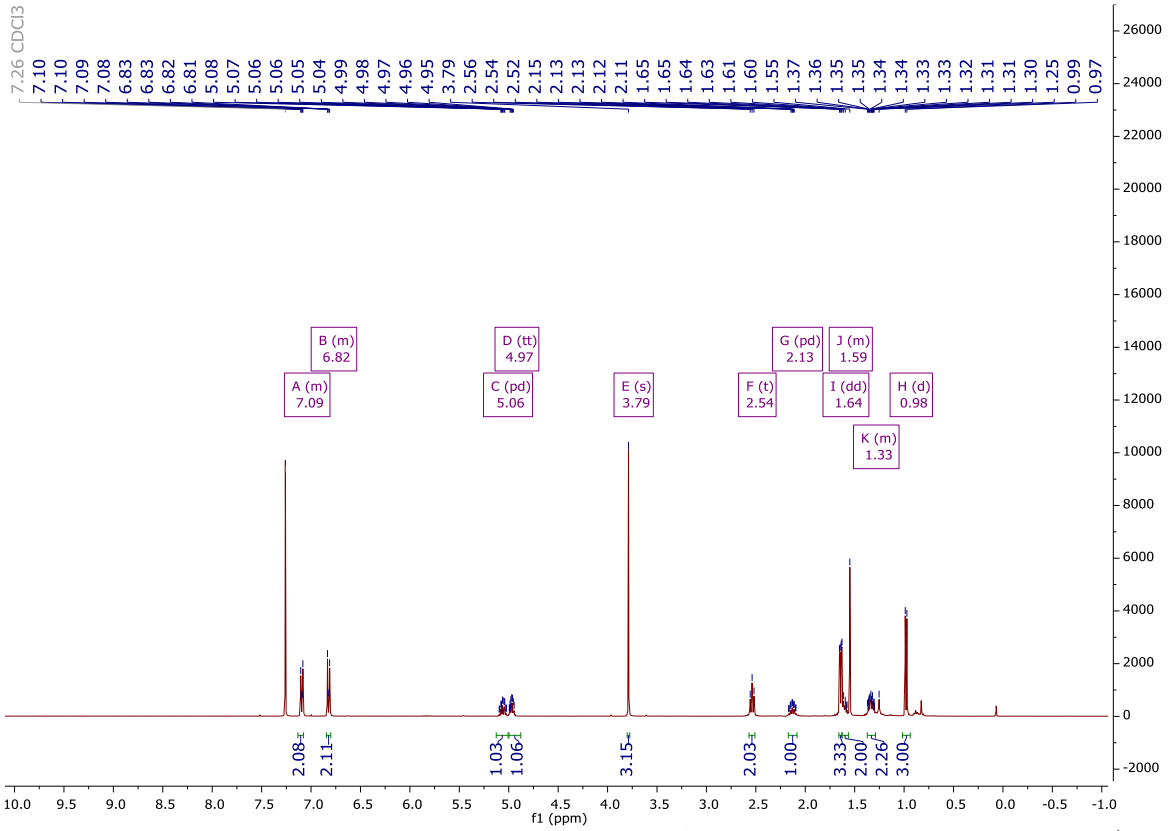
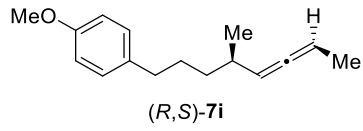


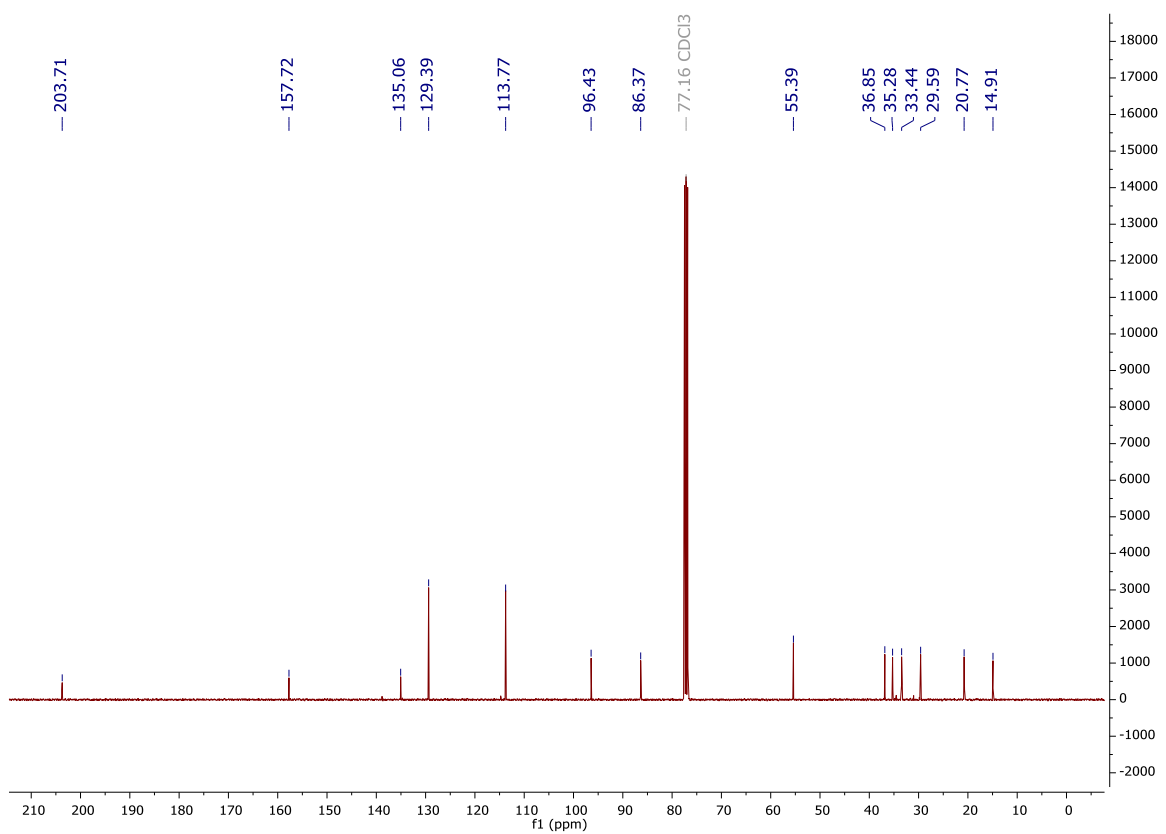
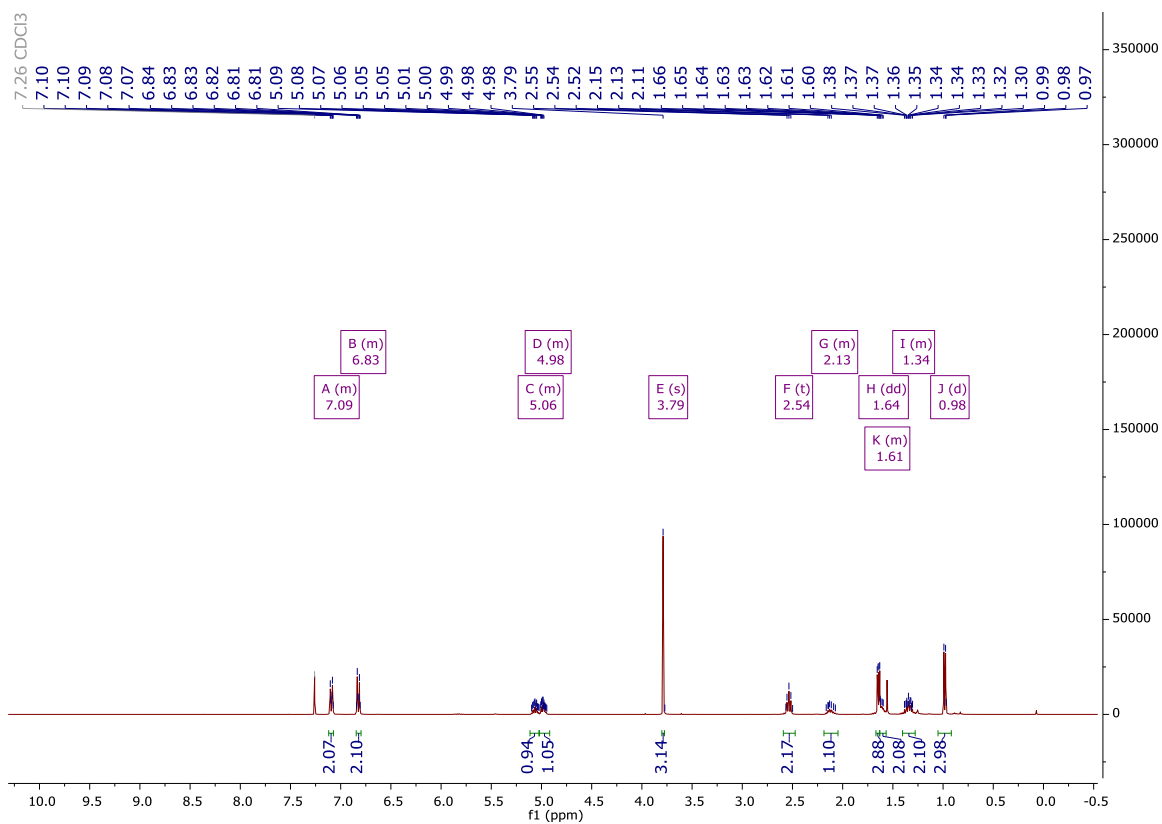
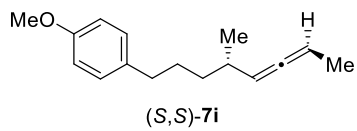


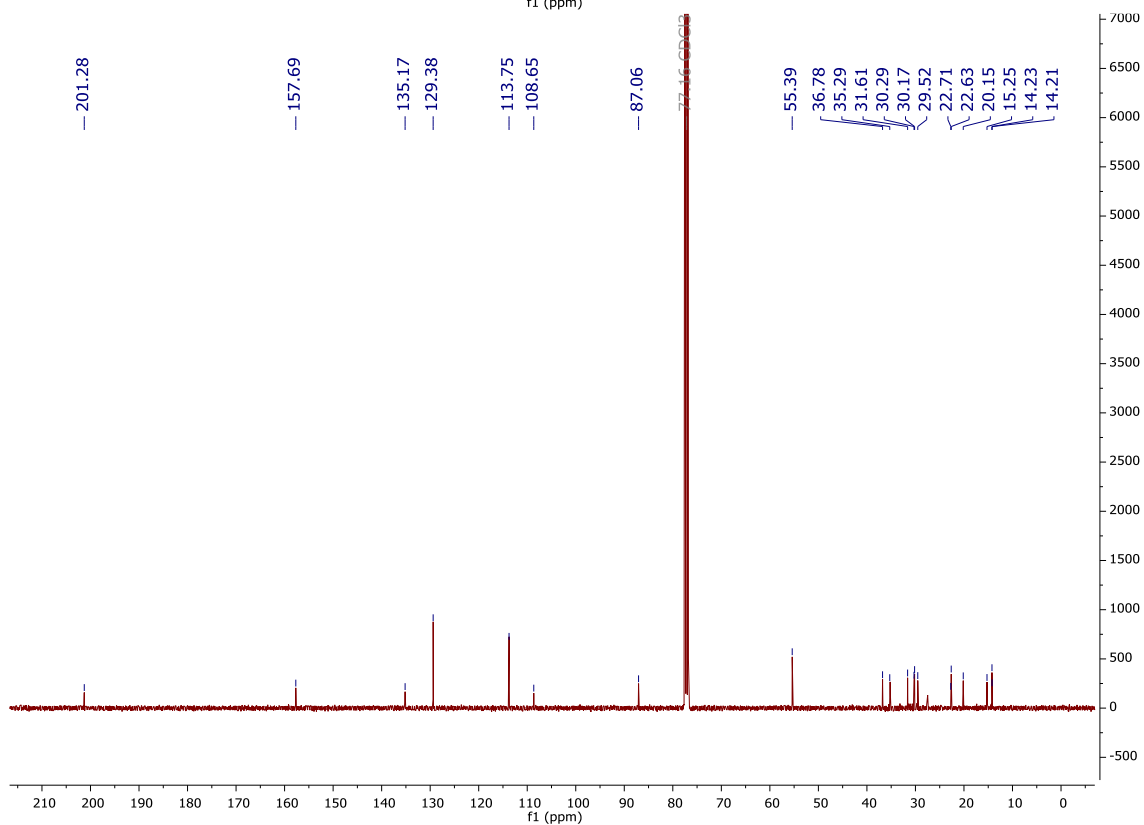
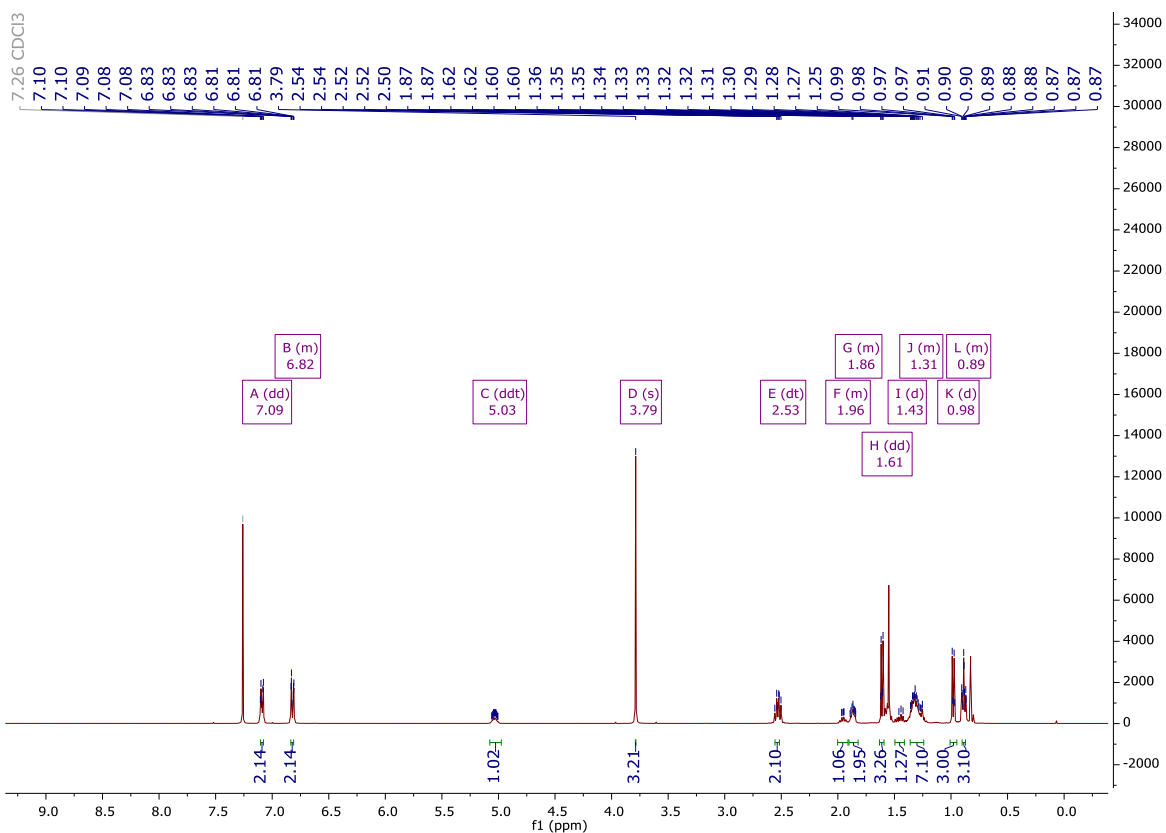
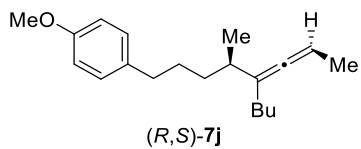


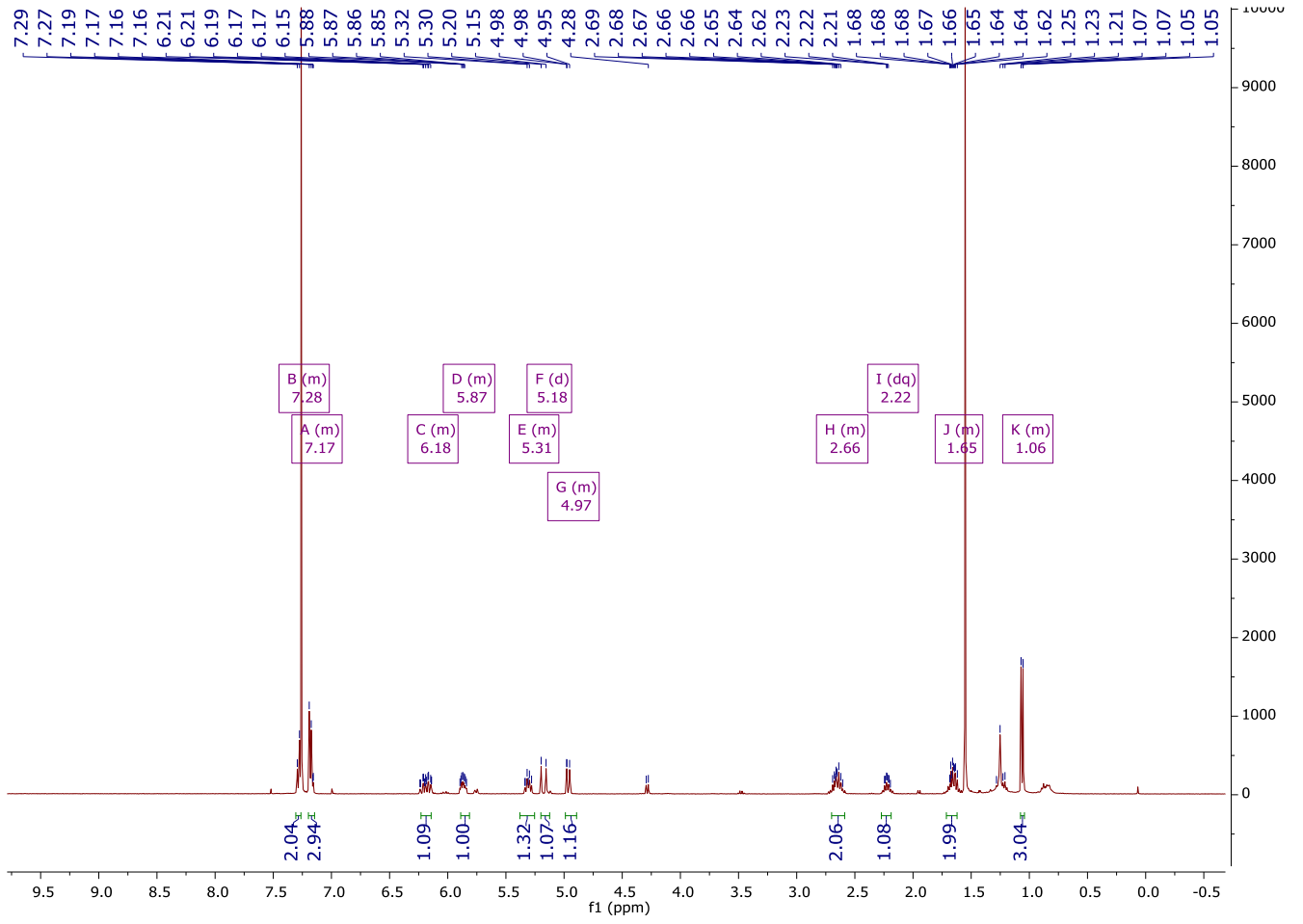
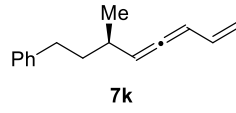


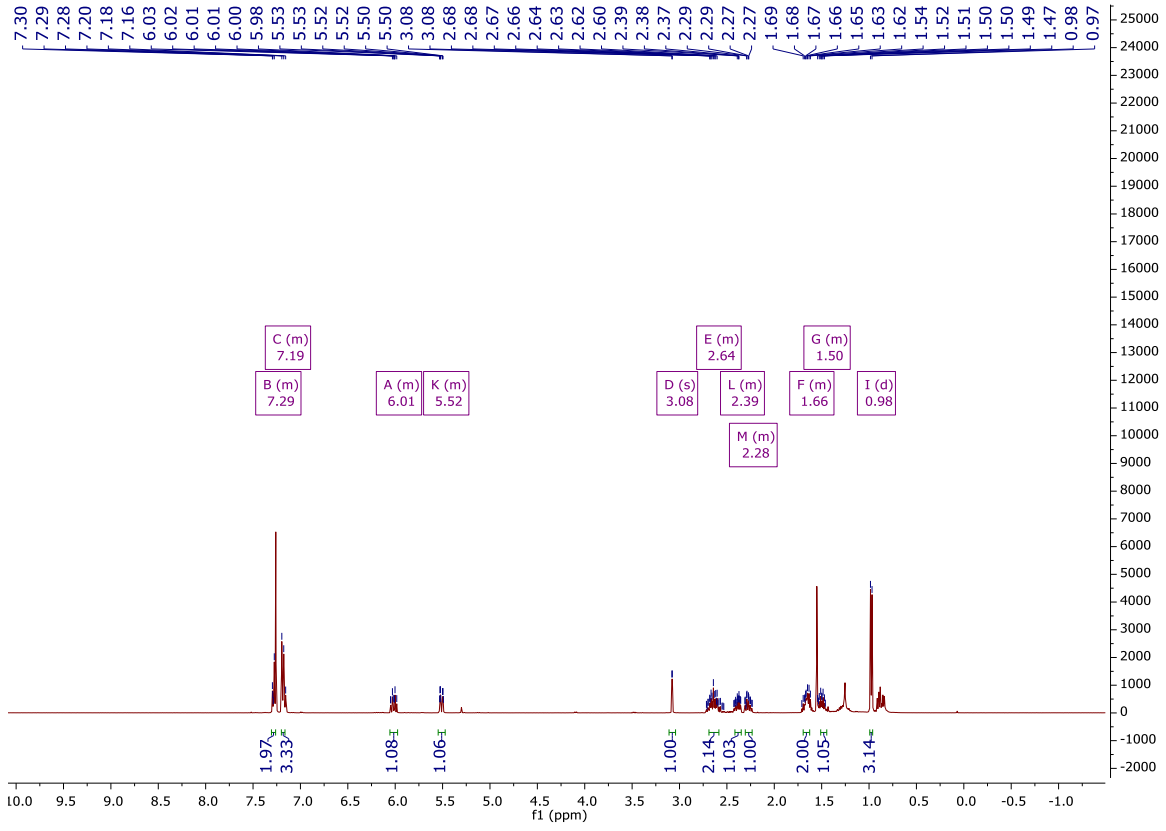
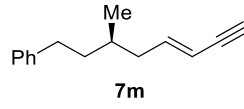










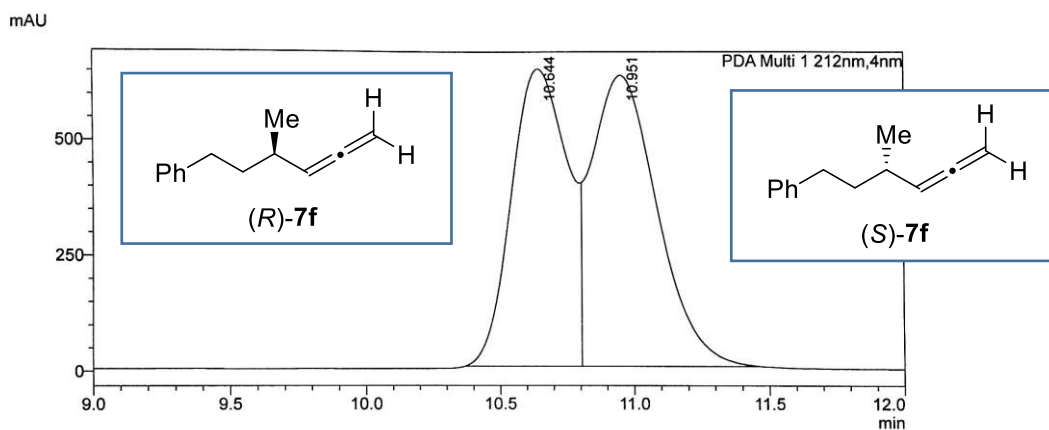


6 Chiral chromatograms for determination of er

The er of (*R*)-**7f** was determined by chiral HPLC analysis.

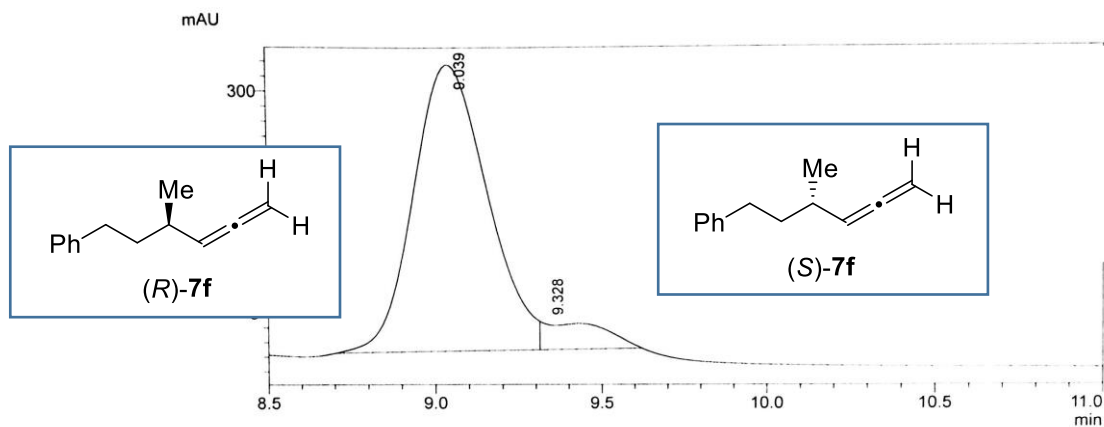
HPLC (column: OB-H; 100% *n*-heptane, 0.2 mL/min): t_R (min) = 10.7 (*R*), 10.9 (*S*).er = 93:7.

Racemate:



Peak#	Ret. Time	Area	Height	Conc.
1	10.644	9599378	646219	47.588
2	10.951	10572420	631868	52.412
Total		20171797	1278087	

(*R*)-Enantiomer:



<Peak Table>

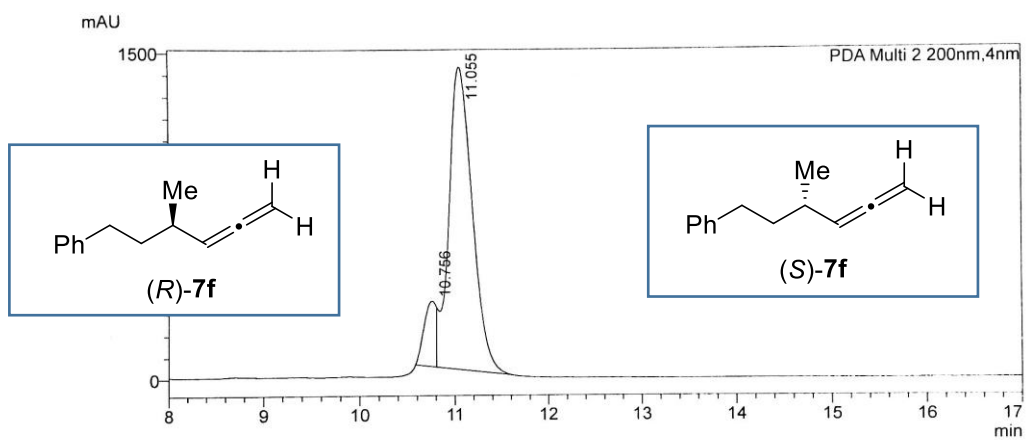
PDA Ch1 212nm

Peak#	Ret. Time	Area	Height	Area%
1	9.039	5969550	387634	92.661
2	9.328	472824	36206	7.339

(S)-Enantiomer:

The er of (S)-7f was determined by chiral HPLC analysis.

HPLC (column: OB-H; 100% *n*-heptane, 0.2 mL/min): t_R (min) = 10.7 (*R*), 11.0 (*S*).er = 10:90.



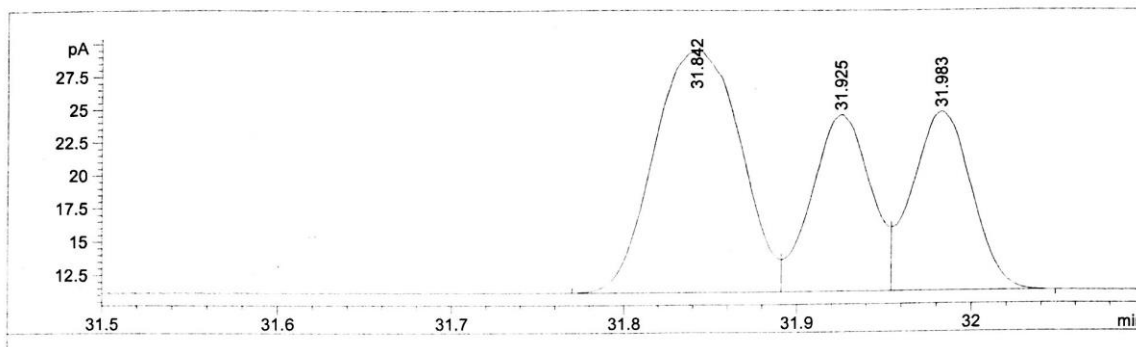
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.
1	10.756	2720167	303673	10.136
2	11.055	24117079	1393325	89.864
Total		26837246	1696998	

The er of (*R,S*)-**7g** was determined by chiral GC analysis.

GC (Supelco β -Dex 120), 50 °C (5 min), ramp of 5 °C/ min to 180 °C, hold 20 min; t_R (min) = 31.84 ((*R,S*)- and (*S,S*)-enantiomer; major), 31.93 ((*R,R*)-enantiomer; minor), 31.98 ((*S,R*)-enantiomer; minor). er = 99:1.

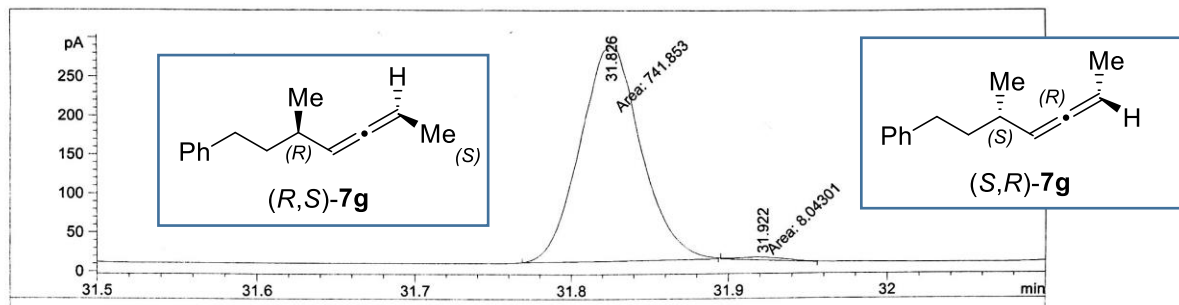
Racemate:



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.842	BV	0.0563	63.04992	18.25036	49.95659
2	31.925	VV	0.0364	31.25006	13.32911	24.76049
3	31.983	VB	0.0355	31.90942	13.53003	25.28292

Totals : 126.20940 45.10949

(*R,S*)-Enantiomer:



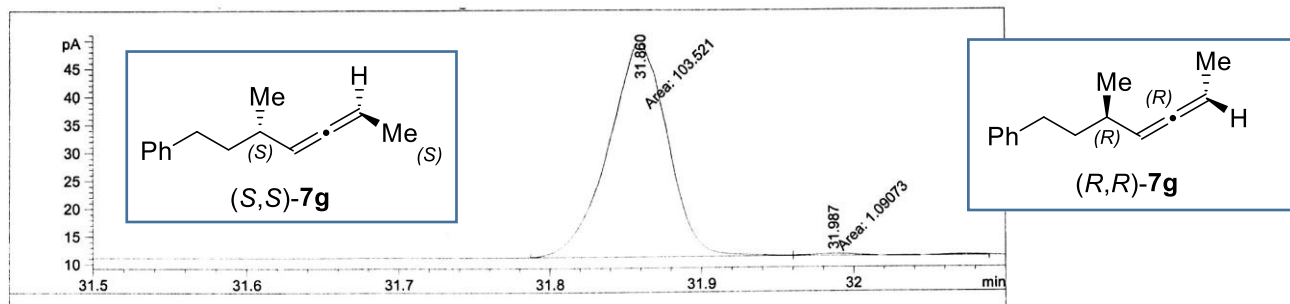
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.826	MM	0.0449	741.85333	275.44794	98.92745
2	31.922	MM	0.0360	8.04301	3.72782	1.07255

Totals : 749.89634 279.17576

(S,S)-Enantiomer:

The er of (S,S)-**7g** was determined by chiral GC analysis.

GC (Supelco β -Dex 120), 50 °C (5 min), ramp of 5 °C/ min to 180 °C, hold 20 min; t_R (min) = 31.60 ((R,S)- and (S,S)-enantiomer; major), 31.98 ((R,R)-enantiomer; minor), 31.98 ((S,R)-enantiomer; minor). er = 99:1.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.860	MF	0.0454	103.52133	38.00557	98.95735
2	31.987	FM	0.0511	1.09073	3.55708e-1	1.04265

Totals : 104.61207 38.36128

7 Computational Calculations

All calculations were conducted with the program package GAUSSIAN16.^[7]

Calculation of Gibbs Free Energies:

Optimizations of minimum geometries were performed using the B3LYP functional^[8–11] with the 6-311+G(d,p) basis set^[12] for atoms C, H, O, and P, and the LANL2DZ^[13] effective core potential for Cu. Solvent effects were accounted for through the Polarizable Continuum Model (PCM)^[14–16], using the adequate dielectric constant according to the solution used in the experiment (THF for *anti-9* and tetralin for *anti-10*; *anti-8* was calculated in both solutions). Tetralin was used because its dielectric constant corresponds to a 3:2 mixture of ether and pentane. The minimum structures were verified by a frequency analysis on the same level of theory by the absence of negative modes. For each geometry, a thermochemical analysis was performed at -100°C , -50°C and -10°C , according to experiments. The Gibbs free energy G_{solv} in solution was extracted from the thermochemistry output for each structure (“Sum of electronic and thermal Free Energies”) and is indicated below. To obtain the ΔG_{solv} values used in the main manuscript, they are compared to the Gibbs free energy of *anti-8*, which was the most stable structure, according to

$$\Delta G_{\text{solv}} = G_{\text{solv}} - G_{\text{solv}}^{\text{ref}} . \quad (1)$$

Calculation of transition state barriers:

The transition state *ts-8* for the epimerization between *syn-8* and *anti-8* was optimized on the same level of electronic structure theory as above. The PCM was not included in this calculation, since the transition state optimization did not converge using the PCM. Energies for the epimerization are therefore given using the gas phase optimized geometries with single point calculations considering the PCM. The relative energy between *syn-8* and *anti-8* is changed by 0.5 kcal/mol when switching off the PCM and the transition state barrier is way higher than this difference (above 50 kcal/mol). The statement of the barrier being too high for epimerization at the investigated temperatures holds. The transition state was further verified by displacing the *ts-8* structure along this mode’s displacement vector in positive and negative direction, and subsequent geometry optimizations leading to *syn-8* and *anti-8*, respectively. For comparison *ts-9* and *ts-10*, the transition states for the epimerization of *anti-9* and *anti-10* to *syn-9* and *syn-10*, respectively, were optimized, as well. In these calculations the PCM was included in the optimization itself. Both barriers are slightly higher (around 4 kcal/mol) than the barrier for the epimerization of structure *anti-8*.

Calculation of bond energies:

Bond dissociation energies (BDEs) of the Cu-C bond at the stereocenter were calculated from the enthalpies of formation of the participating molecular moieties according to

$$\Delta H^{\circ}(298\text{K}) = \sum_{\text{products}} \Delta H_{\text{prod}}^{\circ}(298\text{K}) - \Delta H_{\text{reactant}}^{\circ}(298\text{K}) . \quad (2)$$

In all species investigated here, $\Delta H_{\text{reactant}}^{\circ}$ is the enthalpy of formation of the complete molecule (AB), and $\Delta H_{\text{prod}}^{\circ}(298\text{K})$ are the enthalpies of formation of the two radicals (A + B) after homolytic bond cleavage. These values can be extracted from the GAUSSIAN thermochemistry output (“Sum of electronic and thermal enthalpies”).

To calculate BDEs, all molecules (AB) were optimized at the UB3LYP/6-311+G* level with subsequent frequency analysis. Afterwards, both radicals A and B were optimized separately using the same method to account for relaxation effects and extracting $\Delta H_{\text{prod}}^{\circ}(298\text{K})$ from the thermochemistry

output. BDEs were calculated according to Equation 2 and values are given in Table 2, together with the bond length of the bond before cleavage. All BDEs are well above thermally accessible energies at room temperature.

Table 1: Gibbs free energies (ΔG_{solv}) of investigated molecular species. ΔG_{solv} is given according to Equation 1, with *anti-8* as the reference. ΔG_{solv} of the transition state barriers *ts-8*, *ts-9* and *ts-10* is given with the respective *anti-8*, *anti-9* and *anti-10* structures as reference.

Molecule	ΔG_{solv} (+25 °C) [kcal/mol]	ΔG_{solv} (-100 °C) [kcal/mol]	ΔG_{solv} (-50 °C) [kcal/mol]	ΔG_{solv} (-10 °C) [kcal/mol]
<i>anti-8</i>	0.0	0.0	0.0	0.0
<i>ts-8</i>	51.9	52.4	52.2	52.1
<i>syn-8</i>	2.9	2.7	2.8	2.8
<i>anti-9</i>	4.6	5.0	4.7	4.6
<i>ts-9</i>	55.7	55.6	55.7	55.7
<i>anti-10</i>	6.8	6.8	6.8	6.8
<i>ts-10</i>	57.4	57.1	57.2	57.3
no coordination	11.9	16.2	14.4	13.0

Table 2: Bond dissociation energies (BDEs) of the Cu-C bond of investigated molecular species. BDE values are calculated according to Equation 2.

Molecule	Bond type	Bond length [pm]	BDE (25 °C) [kcal/mol]	BDE (-50 °C) [kcal/mol]
<i>anti-8</i>	Cu-C	198.5	-53.9	-54.0
<i>anti-9</i>	Cu-C	195.8	-51.3	-51.3
<i>anti-10</i>	Cu-C	195.9	-50.6	-50.7

Optimized molecular geometries:

anti-8

B3LYP // 6-311+G(d,p) (C,H,P,O) // LANL2DZ (Cu) // PCM (Tetrahydrofuran) // 298.15 °C

Sum of electronic and thermal Free Energies = -1429.0303 a.u.

C	-3.694868	-1.176985	-0.566547
C	-2.241846	-0.677807	-0.284884
H	-2.219448	-0.326846	0.755344
H	-2.079298	0.215041	-0.902323
C	-1.096588	-1.683810	-0.512617
H	-1.115531	-1.997783	-1.566222
C	-1.237517	-2.946976	0.357122
H	-1.232401	-2.702230	1.426519
H	-2.166395	-3.508101	0.166994
H	-0.412278	-3.646251	0.187119
C	-4.705994	-0.125020	-0.142358
C	-4.875364	1.068136	-0.860232
C	-5.480498	-0.305965	1.010634
C	-5.784710	2.038806	-0.443332
H	-4.292635	1.243210	-1.758215
C	-6.392061	0.661780	1.433977
H	-5.368448	-1.221348	1.583924
C	-6.548768	1.840738	0.707307
H	-5.898280	2.951561	-1.018826
H	-6.980947	0.492331	2.329277
H	-7.257948	2.594631	1.030714
Cu	0.674723	-0.816241	-0.291439
C	-3.886492	-1.614924	-2.028025
H	-4.914239	-1.942492	-2.209460
H	-3.666055	-0.799948	-2.724736
H	-3.219018	-2.444277	-2.273023
H	-3.874380	-2.053251	0.065183
P	2.735723	0.167099	-0.051706
O	2.872084	1.380850	1.039697
O	4.000454	-0.737531	0.423439
O	3.291092	0.745821	-1.449521
C	4.604782	1.358056	-1.629397
H	4.738796	2.126430	-0.864336
H	5.360499	0.584075	-1.485996
C	4.657000	1.942233	-3.025000
H	3.892200	2.710635	-3.157078
H	5.636748	2.397724	-3.193868
H	4.504739	1.165282	-3.777113
C	3.966349	-1.475951	1.674242
H	4.027282	-0.759944	2.497384
H	3.014741	-2.012931	1.747515
C	5.137545	-2.435666	1.686429
H	6.082470	-1.894138	1.603729
H	5.142780	-2.995409	2.625596
H	5.066987	-3.146552	0.860559
C	1.819015	2.371759	1.187539
H	1.972981	3.148201	0.433202
H	0.848534	1.899508	1.002141
C	1.890801	2.944106	2.587989

H	2.867247	3.397946	2.771701
H	1.124671	3.714574	2.709825
H	1.720054	2.166689	3.335802

anti-8

B3LYP // 6-311+G(d,p) (C,H,P,O) // LANL2DZ (Cu) // 298.15 °C
 Sum of electronic and thermal Free Energies = -1429.0209 a.u.

C	3.700825	-1.169149	0.574885
C	2.249134	-0.672176	0.281392
H	2.231634	-0.330893	-0.762298
H	2.083736	0.226433	0.889657
C	1.101981	-1.675696	0.511660
H	1.119307	-1.983098	1.567518
C	1.247637	-2.945546	-0.348162
H	1.245894	-2.708513	-1.419362
H	2.176511	-3.504610	-0.151011
H	0.421859	-3.643984	-0.176907
C	4.714992	-0.123596	0.142045
C	4.880536	1.079907	0.844119
C	5.496489	-0.321432	-1.003897
C	5.793057	2.044424	0.418661
H	4.292354	1.268729	1.735744
C	6.411208	0.640135	-1.435679
H	5.387656	-1.244687	-1.565048
C	6.564116	1.829579	-0.724740
H	5.903169	2.965447	0.981427
H	7.005083	0.457853	-2.325105
H	7.275221	2.578702	-1.054841
Cu	-0.670985	-0.811290	0.272943
C	3.886056	-1.588603	2.042682
H	4.911638	-1.919009	2.231726
H	3.667259	-0.763436	2.727792
H	3.214363	-2.411982	2.296325
H	3.882320	-2.053284	-0.045094
P	-2.738642	0.160495	0.044493
O	-2.899415	1.383330	-1.031135
O	-4.000161	-0.752040	-0.424439
O	-3.281693	0.718583	1.456513
C	-4.589332	1.342632	1.653223
H	-4.721518	2.118609	0.896111
H	-5.353438	0.576927	1.510648
C	-4.624529	1.916156	3.053495
H	-3.851891	2.676849	3.184924
H	-5.598560	2.379792	3.232093
H	-4.475678	1.132234	3.799228
C	-3.970986	-1.484087	-1.681276
H	-4.042150	-0.763835	-2.499544
H	-3.016947	-2.014560	-1.763764
C	-5.136716	-2.450057	-1.690578
H	-6.084445	-1.914820	-1.598783
H	-5.144482	-3.003422	-2.633377
H	-5.056090	-3.166413	-0.870246

C	-1.860530	2.391713	-1.177732
H	-2.009443	3.148930	-0.403653
H	-0.881800	1.926517	-1.022313
C	-1.967947	2.992773	-2.563511
H	-2.952149	3.441293	-2.716669
H	-1.212251	3.773694	-2.683310
H	-1.804740	2.233678	-3.331624

anti-9

B3LYP // 6-311+G(d,p) (C,H,O) // LANL2DZ (Cu) // PCM (Tetrahydrofuran) // 298.15 °C
 Sum of electronic and thermal Free Energies = -856.7173 a.u.

C	2.533305	1.098613	-0.286072
C	1.093242	0.530337	-0.079506
H	1.076444	0.043066	0.904011
H	0.951093	-0.274067	-0.811898
C	-0.074674	1.532664	-0.175773
H	-0.055910	1.987991	-1.176250
C	0.034508	2.668900	0.858148
H	0.035270	2.282377	1.884461
H	0.951031	3.269586	0.745518
H	-0.807118	3.364362	0.781157
C	3.569691	0.023026	-0.004667
C	3.766901	-1.057988	-0.876978
C	4.341272	0.066051	1.163909
C	4.700464	-2.053849	-0.593035
H	3.186794	-1.125454	-1.791010
C	5.276758	-0.928005	1.454767
H	4.207939	0.892456	1.855558
C	5.461189	-1.994127	0.575581
H	4.834787	-2.878003	-1.285710
H	5.862096	-0.866930	2.366144
H	6.188411	-2.767650	0.796105
Cu	-1.802477	0.615031	-0.087659
C	2.715910	1.733290	-1.675004
H	3.735852	2.106377	-1.806169
H	2.515860	1.014172	-2.475598
H	2.030309	2.573077	-1.809777
H	2.692494	1.885574	0.458413
O	-3.562638	-0.326899	-0.017554
C	-4.553753	-0.318513	-1.089100
C	-4.042071	-1.105901	1.120203
C	-5.823854	-0.875326	-0.454617
H	-4.648358	0.705763	-1.449385
H	-4.183626	-0.955209	-1.897106
C	-5.271612	-1.844862	0.601891
H	-3.232514	-1.760776	1.442336
H	-4.288873	-0.409879	1.926282
H	-6.464381	-1.364667	-1.189459
H	-6.395813	-0.074731	0.021777
H	-4.981707	-2.791556	0.138502
H	-5.984074	-2.057448	1.399968

anti-10

B3LYP // 6-311+G(d,p) (C,H,O) // LANL2DZ (Cu) // PCM (Tetralin) // 298.15 °C

Sum of electronic and thermal Free Energies = -857.9087 a.u.

C	-2.078435	0.882238	1.248324
C	-0.534165	1.112083	1.277487
H	-0.281744	1.719568	0.399020
H	-0.055053	0.138968	1.113138
C	0.049821	1.770670	2.543054
H	-0.180244	1.129420	3.405563
C	-0.548592	3.162520	2.817904
H	-0.366827	3.851870	1.984711
H	-1.638032	3.139953	2.978414
H	-0.110144	3.619148	3.710574
C	-2.509726	0.372285	-0.116949
C	-2.211592	-0.929240	-0.546538
C	-3.195276	1.209959	-1.005792
C	-2.587029	-1.375439	-1.812541
H	-1.681017	-1.605999	0.114564
C	-3.573400	0.770031	-2.274737
H	-3.438139	2.222283	-0.697067
C	-3.270662	-0.527280	-2.684417
H	-2.346187	-2.387971	-2.119045
H	-4.106391	1.440352	-2.940766
H	-3.564551	-0.874569	-3.668736
Cu	2.007033	1.813022	2.482695
C	-2.553658	-0.033359	2.388882
H	-3.633500	-0.199410	2.335973
H	-2.061845	-1.010561	2.352089
H	-2.327568	0.410676	3.361059
H	-2.563307	1.854568	1.384179
O	4.037921	1.895314	2.382938
C	4.889631	0.998956	3.134363
H	4.914505	0.023762	2.638500
H	5.901454	1.418101	3.125410
C	4.368958	0.875869	4.552215
H	3.354472	0.469876	4.565129
H	5.013706	0.197685	5.117745
H	4.362198	1.846561	5.052330
C	4.625780	2.423113	1.169242
H	3.970210	3.244113	0.876790
H	5.603672	2.842876	1.428466
C	4.740957	1.397500	0.052417
H	3.763589	0.969971	-0.183702
H	5.125090	1.887684	-0.846642
H	5.426788	0.586442	0.306995

syn-8

B3LYP // 6-311+G(d,p) (C,H,P,O) // LANL2DZ (Cu) // 298.15 °C

Sum of electronic and thermal Free Energies = -1429.0264 a.u.

C	3.551191	-1.134768	-0.455345
C	2.260659	-0.897398	0.382029
H	1.971399	0.142613	0.192193
H	2.519691	-0.930621	1.449733
C	1.079550	-1.866986	0.113759
C	4.558599	-0.018187	-0.224258
C	5.218545	0.132455	1.004430
C	4.838597	0.911600	-1.233393
C	6.124927	1.170690	1.213929
H	5.024177	-0.568592	1.809170
C	5.745036	1.953717	-1.030389
H	4.341091	0.816242	-2.193885
C	6.393198	2.087799	0.196305
H	6.623120	1.264283	2.173122
H	5.944642	2.658090	-1.831005
H	7.099047	2.894823	0.358523
Cu	-0.667131	-0.923035	0.092982
C	4.182480	-2.522273	-0.246014
H	5.077199	-2.638661	-0.865105
H	4.473113	-2.680940	0.796608
H	3.479220	-3.311191	-0.520339
H	3.251295	-1.073917	-1.509232
P	-2.691677	0.160168	0.052654
O	-2.752245	1.653153	-0.614725
O	-3.938551	-0.517841	-0.741016
O	-3.316782	0.294074	1.533072
C	-4.620364	0.885486	1.831696
H	-4.677125	1.863008	1.347939
H	-5.389950	0.237629	1.409226
C	-4.745395	0.998047	3.335852
H	-3.965408	1.642855	3.746627
H	-5.717794	1.429477	3.588632
H	-4.672770	0.015516	3.807204
C	-3.841281	-0.840038	-2.156451
H	-3.853425	0.094396	-2.722220
H	-2.890368	-1.349519	-2.342644
C	-5.015508	-1.723762	-2.520370
H	-5.960884	-1.213564	-2.322693
H	-4.972630	-1.967140	-3.585314
H	-4.992951	-2.655935	-1.951904
C	-1.686990	2.618678	-0.390724
H	-1.872376	3.114987	0.565322
H	-0.729448	2.091926	-0.326343
C	-1.690976	3.610171	-1.535373
H	-2.654127	4.121099	-1.602706
H	-0.914268	4.361842	-1.371057
H	-1.491794	3.109732	-2.485521
C	1.051570	-3.056354	1.096470
H	1.991259	-3.629258	1.121884
H	0.861371	-2.723357	2.123359

H	0.254456	-3.764534	0.844239
H	1.203788	-2.274137	-0.901659

ts-8

B3LYP // 6-311+G(d,p) (C,H,P,O) // LANL2DZ (Cu) // 298.15 °C

Sum of electronic and thermal Free Energies = -1428.9325 a.u.

C	-3.883979	-0.306324	-0.683391
C	-2.811056	0.210288	0.335418
H	-3.143236	-0.115351	1.341815
H	-2.859659	1.308511	0.342777
C	-1.401821	-0.251919	0.043226
H	-0.746045	0.657234	0.034884
C	-1.110021	-1.680357	0.511591
H	-1.451174	-1.894728	1.544368
H	-1.627882	-2.402990	-0.140160
H	-0.054719	-2.035573	0.462338
C	-5.295116	-0.068122	-0.170225
C	-5.801345	1.230652	0.013998
C	-6.131045	-1.145689	0.161824
C	-7.091994	1.442621	0.504662
H	-5.180218	2.089438	-0.229781
C	-7.425079	-0.941840	0.652523
H	-5.761341	-2.161412	0.032199
C	-7.912500	0.355970	0.826190
H	-7.458253	2.458426	0.636915
H	-8.050409	-1.797336	0.898435
H	-8.917626	0.520189	1.207101
C	-3.660632	0.293948	-2.081520
H	-4.349509	-0.138038	-2.818097
H	-3.814101	1.381501	-2.078181
H	-2.629074	0.100657	-2.396498
H	-3.752216	-1.394278	-0.767177
Cu	0.710184	-0.138902	0.410883
P	2.889231	0.045093	0.204974
O	3.599942	-1.377158	0.547939
C	5.032344	-1.589622	0.621014
H	5.502674	-1.181037	-0.281177
H	5.414049	-1.049847	1.495253
C	5.282862	-3.081778	0.748234
H	4.896658	-3.618248	-0.124781
H	6.360067	-3.272393	0.824710
H	4.795342	-3.480577	1.643732
O	3.577784	1.161904	1.150746
C	4.745021	1.977880	0.854816
H	5.630554	1.332896	0.822420
H	4.612555	2.433759	-0.129722
C	4.862686	3.021990	1.950046
H	5.738476	3.654874	1.762116
H	3.972752	3.659152	1.975351
H	4.978982	2.550698	2.931581
O	3.509625	0.501956	-1.243682
C	2.993057	-0.066337	-2.475981

H	3.416732	-1.070386	-2.597158
H	1.901786	-0.158473	-2.399937
C	3.389506	0.844064	-3.623770
H	4.478533	0.944032	-3.688230
H	3.024813	0.424160	-4.568660
H	2.953548	1.840720	-3.498618

ts-9

B3LYP // 6-311+G(d,p) (C,H,O) // LANL2DZ (Cu) // PCM (Tetrahydrofuran) // 298.15 °C
Sum of electronic and thermal Free Energies = -856.6285 a.u.

C	-2.680544	0.799771	-0.689453
C	-1.436370	0.437883	0.180210
H	-1.566580	-0.615325	0.502525
H	-1.484779	1.039904	1.096312
C	-0.100475	0.665919	-0.537962
H	0.574586	0.901893	0.370934
C	0.221942	-0.539823	-1.444073
H	0.123756	-1.543591	-0.980131
H	-0.488463	-0.537171	-2.280259
H	1.206692	-0.502079	-1.937217
C	-3.947381	0.156271	-0.148216
C	-4.452634	0.484311	1.118965
C	-4.643077	-0.799269	-0.899210
C	-5.608417	-0.117986	1.613626
H	-3.938420	1.219503	1.728837
C	-5.801906	-1.405621	-0.410759
H	-4.271571	-1.071913	-1.882392
C	-6.290437	-1.066923	0.849981
H	-5.978097	0.153662	2.596831
H	-6.321372	-2.141136	-1.015920
H	-7.190307	-1.534815	1.233664
C	-2.843096	2.320280	-0.849182
H	-3.660316	2.563461	-1.535144
H	-3.059511	2.797491	0.112439
H	-1.918300	2.750584	-1.238148
H	-2.515288	0.379017	-1.687395
Cu	2.055856	0.313312	0.059551
O	3.984370	0.037648	0.107601
C	4.986437	1.100365	-0.015964
C	4.629379	-1.261229	0.313922
C	6.293970	0.451066	0.420111
H	5.006659	1.416953	-1.061304
H	4.667995	1.930987	0.612945
C	6.100310	-1.015476	0.002549
H	4.467620	-1.552996	1.354301
H	4.146374	-1.979522	-0.348024
H	6.417037	0.528434	1.503323
H	7.155567	0.918045	-0.058195
H	6.748428	-1.701398	0.549086
H	6.290929	-1.138845	-1.066483

ts-10

B3LYP // 6-311+G(d,p) (C,H,O) // LANL2DZ (Cu) // PCM (Tetralin) // 298.15 °C

Sum of electronic and thermal Free Energies = -857.8173 a.u.

C	2.493225	-0.821068	-0.410167
C	1.271576	-0.153399	0.296045
H	1.427218	0.942848	0.239187
H	1.324633	-0.409694	1.361417
C	-0.072843	-0.589850	-0.288887
H	-0.737381	-0.557745	0.655013
C	-0.411709	0.241532	-1.540165
H	-0.299062	1.342691	-1.448726
H	0.277192	-0.055151	-2.341296
H	-1.407845	0.051821	-1.975836
C	3.790934	-0.104226	-0.075370
C	4.291124	-0.067120	1.234663
C	4.521268	0.558751	-1.069071
C	5.474826	0.603178	1.537321
H	3.750181	-0.568509	2.030121
C	5.708267	1.230942	-0.773744
H	4.154045	0.547045	-2.090868
C	6.191257	1.255956	0.533129
H	5.839712	0.616086	2.559081
H	6.254198	1.733807	-1.565118
H	7.113206	1.776529	0.767718
C	2.569646	-2.324541	-0.100523
H	3.361659	-2.811378	-0.677747
H	2.772856	-2.499869	0.961308
H	1.611875	-2.789958	-0.342336
H	2.343135	-0.714599	-1.490452
Cu	-2.222963	-0.142150	0.147045
O	-4.206405	-0.016547	0.055826
C	-4.846663	1.235901	-0.301629
H	-5.855879	1.218054	0.120494
H	-4.925438	1.284383	-1.393084
C	-4.990076	-1.185834	-0.305000
H	-5.993190	-1.044044	0.107852
H	-5.063301	-1.228004	-1.397082
C	-4.338950	-2.429806	0.258913
H	-4.929607	-3.304945	-0.023677
H	-3.329085	-2.569951	-0.138710
H	-4.288236	-2.388270	1.348957
C	-4.046603	2.395505	0.251065
H	-3.033395	2.415617	-0.161645
H	-4.535369	3.333837	-0.023846
H	-3.983416	2.347395	1.339988

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