[Supporting Information]

Synthesis of Dihydrotropone Derivatives Using an Anionic 8π Electrocyclic Reaction

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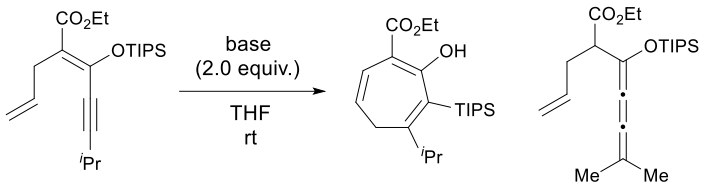
Supplementary Materials

Table S1. Using other base for anionic cyclisation.



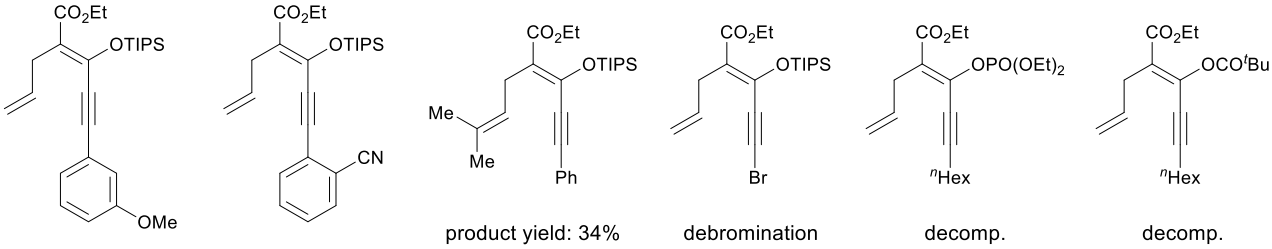
6b **8b** **9b**

entry	base	result (NMR yield)
1	LDA	**8b** (84%)†
2	LHMDS	**6b** (99%) recovered
3	KHMDS	**9b** (58%) + byproducts

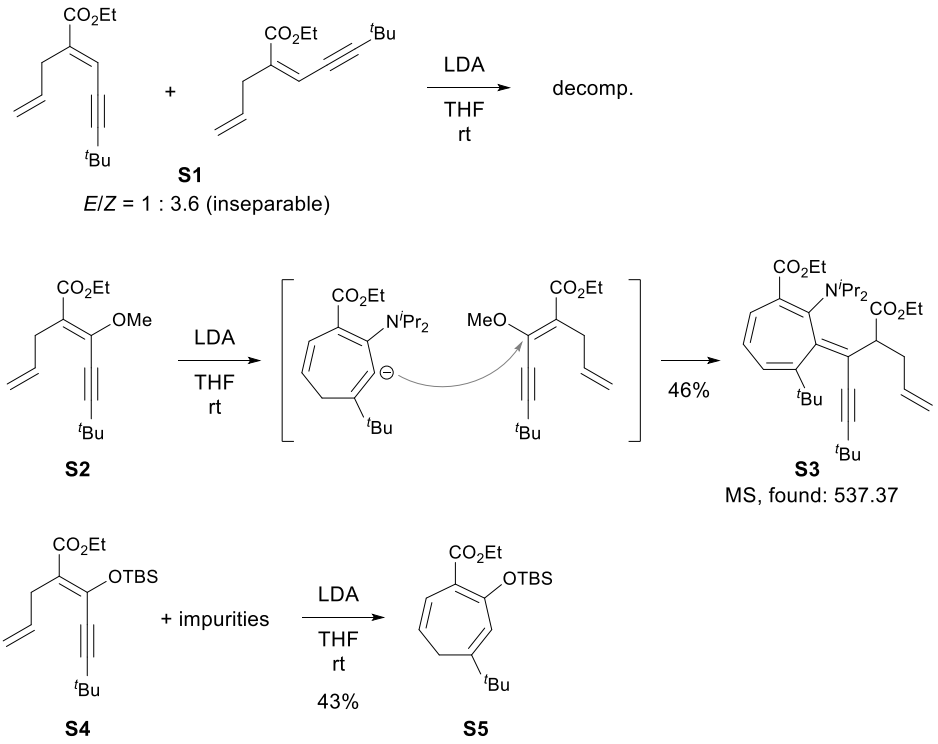
Reactions were conducted on 0.1 mmol scale. † Isolated yield.

Use of LHMDS instead of LDA resulted in almost full recovery of the starting material due to its low basicity (entry 2). When KHMDS was used as the base, undesired deprotonation at the isopropyl group occurred to give cumulene **9b** as the major product (entry 3).

Figure S1. Other unsuccessful substrates.



Scheme S1. Substrates with other *β*-substituents.



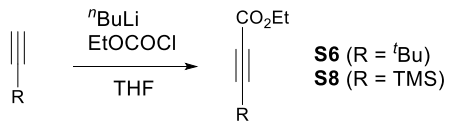
The reaction using dienyne **S1**, lacking a silyloxy group as a substrate, resulted in decomposition of the starting material. The reaction using methoxy-dienyne **S2** gave dimerised product **S3** in moderate yield, which caused by 1,4-addition of nucleophilic species including LDA. Indeed, the use of a OTBS group instead of a OTIPS group was applicable, but the substrate **S4** was labile and easily desilylated, thus not isolated in a pure form. These results indicate that the *β*-OTIPS group is essential to prevent undesired 1,4-addition or desilylation by its large steric hindrance.

General Information

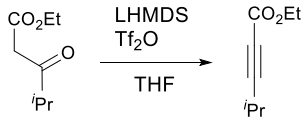
All reactions were performed using flame-dried glassware under a positive pressure of argon unless otherwise noted. Reactions at elevated temperatures were performed under heating in an oil bath. THF was distilled from sodium benzophenone ketyl. Other anhydrous solvents were purchased from chemical companies. $^{i}Pr_2NH$ and Et_3N were distilled from CaH_2 under argon and stored in the presence of NaOH (pellets). All other reagents were used as received from commercial sources without further purification.

The melting points were measured using ASONE ATM-02 apparatus and uncorrected. Specific optical rotations were determined using JASCO P-2200 polarimeter with a 100 mm cell at 589 nm. Enantiomeric excesses were determined by HPLC analysis using JASCO PU-2089 Plus pump, UV-2075 Plus detector, and DAICEL CHIRALPAK AS-H column (0.46 cm ϕ × 25 cm). ^{1}H NMR spectra were recorded on JEOL ECA-500 (500 MHz) in $CDCl_3$ (δ_H 7.26). Chemical shifts are reported in parts per million (ppm), and signal are expressed as broad (br), singlet (s), doublet (d), triplet (t), quartet (q), septet (sept), and multiplet (m). Coupling constants are reported in Hz. ^{13}C NMR spectra were recorded on JEOL ECA-500 (126 MHz) in $CDCl_3$ (δ_C 77.0). HRMS were recorded on JEOL JMS-T100GCV (GC-TOFMS) at the GC-MS & NMR Laboratory, Faculty of Agriculture, Hokkaido University. FT-IR spectra were recorded on JASCO FT/IR-4100 spectrophotometer. Analytical TLC was performed using Silica Gel 60 F_{254} (E. Merck), and PTLC was performed using PLC Silica Gel 60 F_{254} (E. Merck). Reaction components were visualised by illumination with UV light (254 nm) and by staining with 8% ethanolic phosphomolybdic acid, ceric ammonium molybdate in 10% sulfuric acid, or basic potassium permanganate aqueous solution. Flash column chromatography was performed on Chromatorex PSQ60B (Fuji Silysia Chemical Ltd.) or Chromatorex NH-DM2035 (Fuji Silysia Chemical Ltd.).

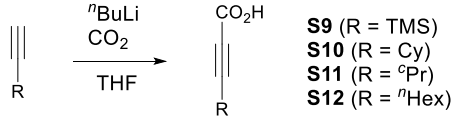
Alkynyl ester **S6**–**8**, [1–3] alkynyl carboxylic acid **S9**–**13**, [4–7] alkyne **S14**,**15**, [8,9] alkenyl ester **S16**–**19**, [10–12] alkenyl carboxylic acid **S20**, [13] and alkenyl malonic acid monoester **S21** [14] were prepared by known or previously reported procedures.



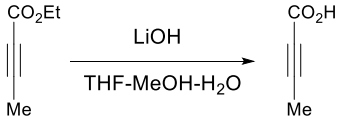
S6 (R = ^{t}Bu)
S8 (R = TMS)



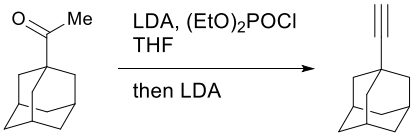
S7



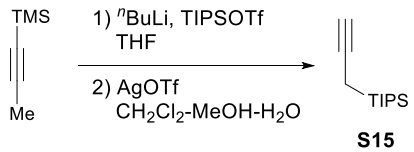
S9 (R = TMS)
S10 (R = Cy)
S11 (R = ^{c}Pr)
S12 (R = ^{n}Hex)



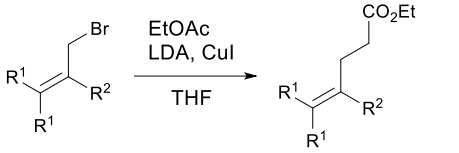
S13



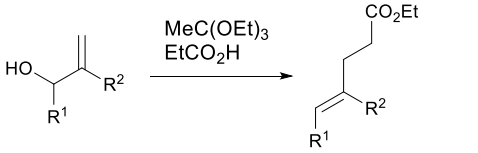
S14



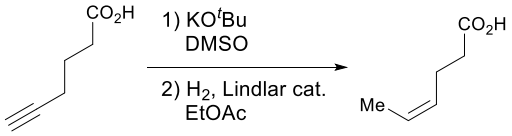
S15



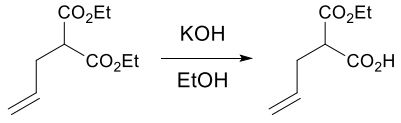
S16 (R^1 = H, R^2 = Me)
S18 (R^1 = Me, R^2 = H)



S17 (R^1,R^2 = -$(CH_2)_3$-)
S19 (R^1 = Me, R^2 = H)



S20

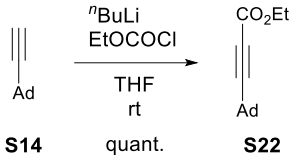


S21

Experimental and Characterisation Details

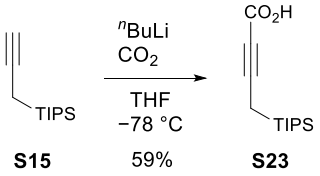
Preparation of Synthetic Fragments

Alkynyl ester S22



To a solution of **S14** (320 mg, 2.00 mmol) in THF (10 mL) was added *n*BuLi (2.65 mol/L in hexane, 792 µL, 2.10 mmol) at −78 °C. The reaction mixture was then warmed up to 0 °C and stirred for 20 min. To this mixture was added ethyl chloroformate (381 µL, 4.00 mmol), and the reaction mixture was warmed up to room temperature and stirred for 20 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL), and the organic layer was diluted with EtOAc (10 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 30:1) to afford **S22** (480 mg, > 2.00 mmol, quant.) as a white solid. The spectral data matched with those reported in literature. [15]

Alkynyl carboxylic acid S23

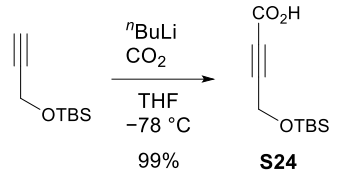


To a solution of **S15** (331 mg, 1.68 mmol) in THF (7.5 mL) was added *n*BuLi (2.65 mol/L in hexane, 582 µL, 1.54 mmol) at −78 °C. After stirring for 20 min, crushed dry ice (excess.) was added, and the reaction mixture was stirred under ambient temperature until no further evolution of CO_2 gas was detected. The reaction was quenched with saturated aqueous NH_4Cl solution (5 mL), and the organic layer was diluted with Et_2O (5.0 mL). Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane only, then EtOAc only) to afford **S23** (238 mg, 0.991 mmol, 59% yield) as a white solid.

S23: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73 (s, 2H), 1.22–1.14 (m, 3H), 1.09 (d, J = 6.9 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 93.7, 72.3, 18.4 (6C), 11.0 (3C), 0.2; FT-IR (ATR) ν 2943, 2867, 2225, 1676, 1283 cm^{-1}; HRMS (FD) calcd for $C_{13}H_{25}O_2Si$ ($[M + H]^+$): 241.1624, found: 241.1615; m.p.

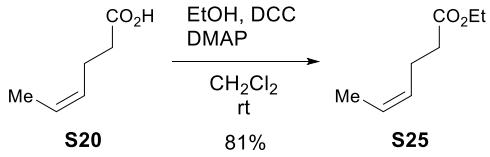
(hexane) 52–55 °C.

Alkynyl carboxylic acid S24



To a solution of *tert*-butyldimethyl(2-propynyloxy)silane (601 µL, 3.00 mmol) in THF (10 mL) was added ^{n}BuLi (2.65 mol/L in hexane, 1.19 mL, 3.15 mmol) at −78 °C. After stirring for 30 min, crushed dry ice (excess.) was added, and the reaction mixture was stirred under ambient temperature until no further evolution of CO_2 gas was detected. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (5.0 mL) and water (10 mL). Two layers were separated, and the aqueous layer was washed with CH_2Cl_2 (5.0 mL × 2). The aqueous layer was then neutralised with 3 M aqueous HCl solution and extracted with CH_2Cl_2 (5.0 mL × 4). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford **S24** (634 mg, 2.96 mmol, 99% yield) as a white solid. The spectral data matched with those reported in literature. [16]

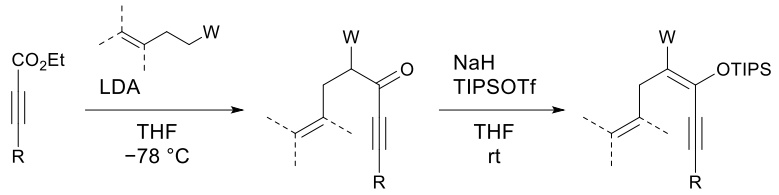
Alkenyl ester S25



To a solution of **S20** (116 mg, 1.01 mmol) in CH_2Cl_2 (5.0 mL) were added successively EtOH (294 µL, 5.05 mmol), 4-dimethylaminopyridine (11.7 mg, 95.8 µmol), and *N*,*N'*-dicyclohexylcarbodiimide (228 mg, 1.10 mmol) at room temperature. After stirring for 14 h, AcOH (578 µL, 10.1 mmol) was added, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (5.0 mL). Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, pentane:Et_2O = 10:1) to afford **S25** (117 mg, 0.823 mmol, 81% yield) as a colourless oil.

S25: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52–5.45 (m, 1H), 5.38–5.32 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 2.38–2.31 (m, 4H), 1.62 (dd, J = 5.7, 1.1 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 128.3, 125.3, 60.2, 34.2, 22.4, 14.2, 12.7; FT-IR (ATR) ν 2980, 2927, 1735, 1161 cm^{-1}; HRMS (FI) calcd for $C_8H_{14}O_2$ (M^+): 142.0994, found: 142.0989.

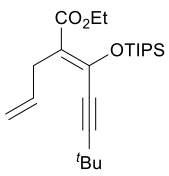
Synthesis of Dienynes: General Procedure A



6a–c, **6e**, **6h**, **6m–q**

An LDA solution (1 mol/L in THF-hexane) was prepared by the addition of ^{n}BuLi (2.65 mol/L in hexane, 755 μL, 2.00 mmol) to a solution of $^{i}Pr_2NH$ (281 μL, 2.00 mmol) in THF (1.25 mL) at 0 °C. The mixture was stirred for 20 min at the same temperature before the use. To another reaction vessel charged with alkenyl ester (1.2 equiv.) in THF (0.2 mol/L) was added the LDA solution (2.4 equiv.) via a syringe at −78 °C. After stirring for 20 min, alkynyl ester (1.0 equiv.) in THF was added, and the mixture was stirred for 10 min at the same temperature. [For synthesis of **6p** and (*E*)-**6q**, alkynyl ester (1.2 eqiv.) and LDA solution (2.4 equiv.) based on alkenyl ester (1.0 equiv.) were used]. Crushed dry ice was added to trap the excessive enolate, and the mixture was stirred under ambient temperature until evolution of CO_2 gas ceased. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the organic layer was diluted with EtOAc. Two layers were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Highly polar components were filtered off through a plug of SiO_2 (hexane:EtOAc = 10:1) to afford ketoester along with a small amount of byproducts.

NaH (60% dispersion in mineral oil, 2.0 equiv.) was washed with hexane and suspended with THF (0.4 mol/L). To this suspension was added above ketoester (1.0 equiv.) in THF via cannula at 0 °C. After stirring for 10 min, TIPSOTf (1.5 equiv.) was added, and the reaction mixture was warmed up to room temperature and stirred for 10 min. The reaction was quenched by the careful addition of saturated aqueous $NaHCO_3$ solution, and the organic layer was diluted with EtOAc. Two layers were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford the product dienyne.

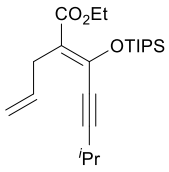


6a

According to the general procedure A, **6a** (154 mg, 0.392 mmol, 79% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), ethyl 4-pentenoate (85.4 μL, 0.600 mmol), alkynyl ester **S6** (76.6 mg, 0.497 mmol), NaH (60% in mineral oil, 40.2 mg, 1.01 mmol), and TIPSOTf (202 μL, 0.750 mmol).

6a: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.1, 10.1, 6.4 Hz, H), 5.06 (ddt, *J* = 17.1, 1.7, 1.6 Hz, 1H), 4.95 (ddt, *J* = 10.1, 1.7, 1.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.13 (ddd, *J* = 6.4,

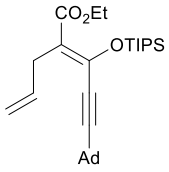
1.6, 1.6 Hz, 2H), 1.36–1.28 (m, 3H), 1.26 (s, 9H), 1.25 (t, J = 7.2 H, 3H), 1.11 (d, J = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.7, 136.0, 115.8, 114.8, 104.7, 76.0, 59.9, 34.6, 30.2 (3C), 28.2, 17.9 (6C), 14.4, 13.0 (3C); FT-IR (ATR) ν 2969, 2945, 2867, 2216, 1716, 1318, 1197 cm^{-1}; HRMS (FD) calcd for $C_{23}H_{40}O_3Si$ (M^+): 392.2747, found: 392.2759.



6b

According to the general procedure A, **6b** (933 mg, 2.46 mmol, 60% yield for 2 steps) was synthesised from $^{i}Pr_2NH$ (1.39 mL, 9.91 mmol), ^{n}BuLi (2.65 mol/L in hexane, 3.74 mL, 9.91 mmol), ethyl 4-pentenoate (706 µL, 4.96 mmol), alkynyl ester **S7** (579 mg, 4.13 mmol), NaH (60% in mineral oil, 249 mg, 6.21 mmol), and TIPSOTf (1.33 mL, 4.96 mmol). Enolate was prepared by the addition of **S7** in THF to an LDA solution.

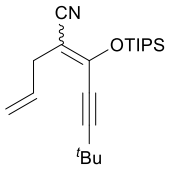
6b: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, J = 17.1, 10.2, 6.4 Hz, 1H), 5.06 (ddt, J = 17.1, 1.7, 1.6 Hz, 1H), 4.95 (ddt, J = 10.2, 1.7, 1.5 Hz, 1H), 4.17 (q, J = 7.3 Hz, 2H), 3.14 (ddd, J = 6.4, 1.6, 1.5 Hz, 2H), 2.73 (sept, J = 6.9 Hz, 1H), 1.34–1.28 (m, 3H), 1.25 (t, J = 7.3 Hz, 3H), 1.20 (d, J = 6.9 Hz, 6H), 1.10 (d, J = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.7, 136.0, 115.7, 114.9, 102.3, 76.5, 59.9, 34.6, 22.1 (2C), 21.2, 17.9 (6C), 14.4, 13.0 (3C); FT-IR (ATR) ν 2944, 2867, 2216, 1715, 1322, 1207 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{38}O_3Si$ (M^+): 378.2590, found: 378.2607.



6c

According to the general procedure A, **6c** (172 mg, 0.365 mmol, 73% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), ethyl 4-pentenoate (85.4 µL, 0.600 mmol), alkynyl ester **S22** (116 mg, 0.501 mmol), NaH (60% in mineral oil, 41.0 mg, 1.03 mmol), and TIPSOTf (202 µL, 0.750 mmol).

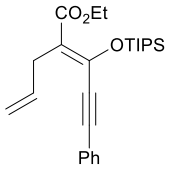
6c: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, J = 16.9, 10.1, 6.5 Hz, 1H), 5.07 (ddt, J = 16.9, 1.9, 1.9 Hz, 1H), 4.95 (ddt, J = 10.1, 1.9, 1.9 Hz, 1H), 4.17 (q, J = 7.3 Hz, 2H), 3.13 (d, J = 6.5 Hz, 2H), 1.98 (br, 3H), 1.88 (br-d, J = 2.9 Hz, 6H), 1.70 (br, 6H), 1.36–1.28 (m, 3H), 1.25 (t, J = 7.3 Hz, 3H), 1.11 (d, J = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 141.0, 136.1, 115.6, 114.8, 104.5, 76.2, 59.9, 42.0 (3C), 36.2 (3C), 34.7, 30.3, 27.7 (3C), 17.9 (6C), 14.4, 13.1 (3C); FT-IR (ATR) ν 2906, 2865, 2213, 1715, 1322, 1133 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{46}O_3Si$ (M^+): 470.3216, found: 470.3232.



6e

According to the general procedure A, **6e** (*E*/*Z* or *Z*/*E* = 3.9:1, 118 mg, 0.342 mmol, 69% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), 4-pentenenitrile (57.9 μL, 0.600 mmol), alkynyl ester **S6** (76.6 mg, 0.497 mmol), NaH (60% in mineral oil, 40.6 mg, 1.01 mmol), and TIPSOTf (202 μL, 0.750 mmol).

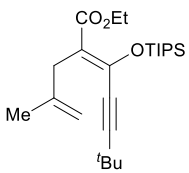
6e (*E*/*Z* mixture): pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82–5.72 (m, 1H), 5.17–5.08 (m, 2H), 2.98 (dt, *J* = 6.5, 1.4 Hz, 2H), 1.37–1.28 (m, 3H), 1.28 (s, 0.20 × 9H), 1.27 (s, 0.80 × 9H), 1.12 (d, *J* = 7.4 Hz, 0.80 × 18H), 1.09 (d, *J* = 7.4 Hz, 0.20 × 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 145.9, 133.4, 133.0, 120.0, 117.9, 117.0, 116.9, 109.0, 104.5, 99.1, 97.2, 74.6, 73.7, 33.7, 31.2, 30.0 (3C, major), 29.9 (3C, minor), 28.3, 28.2, 17.8 (6C, major + minor), 12.73 (3C, minor), 12.68 (3C, major); FT-IR (ATR) *ν* 2947, 2868, 2204, 1588, 1313, 1190 cm^{-1}; HRMS (FD) calcd for $C_{21}H_{35}NOSi$ (M^+): 345.2488, found: 345.2481.



6h

According to the general procedure A, **6h** (260 mg, 63.0 mmol, 63% yield for 2 steps) was synthesised from $^{i}Pr_2NH$ (337 μL, 2.40 mmol), ^{n}BuLi (2.66 mol/L, 902 μL, 2.40 mmol), ethyl 4-pentenoate (171 μL, 1.20 mmol), ethyl phenylpropiolate (164 μL, 1.00 mmol), NaH (60% in mineral oil, 80.0 mg, 2.00 mmol), and TIPSOTf (403 μL, 1.50 mmol). Enolate was prepared by the addition of ethyl phenylpropiolate to an LDA solution.

6h: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.39–7.35 (m, 3H), 5.89 (ddt, *J* = 17.1, 10.2, 6.4 Hz, 1H), 5.12 (ddt, *J* = 17.1, 1.6, 1.6 Hz, 1H), 5.00 (ddt, *J* = 10.2, 1.6, 1.5 Hz, 1H), 4.22 (q, *J* = 7.3 Hz, 2H), 3.27 (ddd, *J* = 6.4, 1.6, 1.5 Hz, 2H), 1.43–1.33 (m, 3H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.15 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 140.1, 135.8, 131.4 (2C), 129.3, 128.6 (2C), 121.8, 117.3, 115.3, 95.2, 85.6, 60.1, 34.7, 17.9 (6C), 14.4, 13.1 (3C); FT-IR (ATR) *ν* 2944, 2867, 2203, 1714, 1325, 1186 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{36}O_3Si$ (M^+): 412.2434, found: 412.2444.

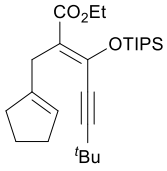


6m

According to the general procedure A, **6m** (136 mg, 0.335 mmol, 67% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), alkenyl ester **S16** (85.5 mg, 0.602 mmol), alkynyl ester **S6** (77.4 mg, 0.502 mmol), NaH (60% in mineral oil, 40.5 mg, 1.01 mmol), and TIPSOTf (202 μL, 0.750 mmol).

6m: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 2H), 4.16 (q, *J* = 7.3 Hz, 2H), 3.11 (s, 2H), 1.73 (s, 3H), 1.36–1.28 (m, 3H), 1.243 (s, 9H), 1.242 (t, *J* = 7.3 Hz, 3H), 1.11 (d, *J* = 7.4 Hz, 18H); ^{13}C

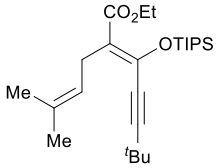
NMR (126 MHz, $CDCl_3$) δ 167.4, 143.7, 140.2, 116.2, 110.5, 104.2, 76.0, 59.9, 38.3, 30.2 (3C), 28.1, 22.4, 17.9 (6C), 14.3, 13.0 (3C); FT-IR (ATR) *v* 2968, 2945, 2867, 2217, 1715, 1200, 1060 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{42}O_3Si$ (M^+): 406.2903, found: 406.2911.



6n

According to the general procedure A, **6n** (149 mg, 0.343 mmol, 68% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), alkenyl ester **S17** (101 mg, 0.600 mmol), alkynyl ester **S6** (77.4 mg, 0.502 mmol), NaH (60% in mineral oil, 39.9 mg, 0.998 mmol), and TIPSOTf (202 μL, 0.750 mmol).

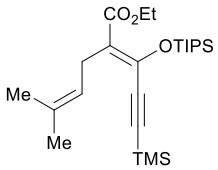
6n: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (br, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.16 (s, 2H), 2.30–2.22 (m, 4H), 1.86–1.80 (m, 2H), 1.37–1.28 (m, 3H), 1.243 (s, 9H), 1.241 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 142.4, 139.9, 124.2, 116.4, 104.3, 76.0, 59.9, 34.9, 32.4, 32.1, 30.2 (3C), 28.1, 23.4, 17.9 (6C), 14.3, 13.0 (3C); FT-IR (ATR) *v* 2945, 2867, 2218, 1715, 1327, 1203, 1055 cm^{-1}; HRMS (FD) calcd for $C_{26}H_{44}O_3Si$ (M^+): 432.3060, found: 432.3053.



6o

According to the general procedure A, **6o** (135 mg, 0.322 mmol, 64% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), alkenyl ester **S18** (93.2 mg, 0.597 mmol), alkynyl ester **S6** (77.0 mg, 0.499 mmol), NaH (60% in mineral oil, 39 .7 mg, 0.993 mmol), and TIPSOTf (202 μL, 0.750 mmol).

6o: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14–5.10 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.09 (d, *J* = 7.4 Hz, 2H), 1.67 (s, 6H), 1.34–1.28 (m, 3H), 1.251 (s, 9H), 1.251 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 139.0, 132.1, 121.9, 117.7, 104.3, 76.0, 59.9, 30.2 (3C), 29.3, 28.1, 25.7, 18.0, 17.9 (6C), 14.3, 13.0 (3C); FT-IR (ATR) *v* 2968, 2867, 2217, 1715, 1316, 1200, 1054 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{44}O_3Si$ (M^+): 420.3060, found: 420.3074.

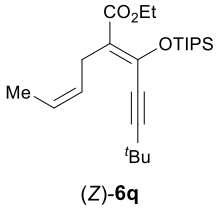


6p

According to the general procedure A, **6p** (265 mg, 0.607 mmol, 61% yield for 2 steps) was synthesised from ^{i}Pr$_2$NH (337 μL, 2.40 mmol), ^{n}BuLi (2.69 mol/L, 892 μL, 2.40 mmol), alkenyl ester **S18** (155 mg, 0.995 mmol), alkynyl ester **S8** (204 mg, 1.20 mmol), NaH (60% in mineral oil, 80.7 mg, 2.02 mmol), and TIPSOTf (403 μL, 1.50 mmol). Enolate was prepared by the addition of **S8** in THF to an LDA solution.

6p: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (t, *J* = 7.1 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.13 (d, *J* = 7.1 Hz, 2H), 1.67 (s, 6H), 1.35–1.28 (m, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.4 Hz,

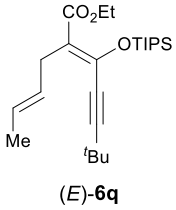
18H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 137.8, 132.4, 121.5, 119.7, 101.6, 100.6, 60.1, 29.4, 25.7, 18.0, 17.9 (6C), 14.3, 13.0 (3C), −0.7 (3C); FT-IR (ATR) *v* 2945, 2868, 2148, 1718, 1204, 843 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{44}O_3Si_2$ (M^+): 436.2829, found: 436.2834.



(*Z*)-**6q**

According to the general procedure A, (*Z*)-**6q** (137 mg, 0.336 mmol, 68% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.48 mL, 1.48 mmol), alkenyl ester **S25** (105 mg, 0.738 mmol), alkynyl ester **S6** (75.6 mg, 0.490 mmol), NaH (60% in mineral oil, 39.2 mg, 0.980 mmol), and TIPSOTf (198 μL, 0.738 mmol).

(*Z*)-**6q**: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49–5.36 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.15 (d, *J* = 6.9 Hz, 2H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.35–1.28 (m, 3H), 1.26 (s, 9H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 139.6, 128.0, 124.4, 117.1, 104.5, 76.0, 59.9, 30.2 (3C), 28.21, 28.15, 18.0, 17.9 (6C), 14.4, 13.0 (3C); FT-IR (ATR) *v* 2968, 2945, 2867, 2216, 1715, 1328, 1190 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{42}O_3Si$ (M^+): 406.2903, found: 406.2918.

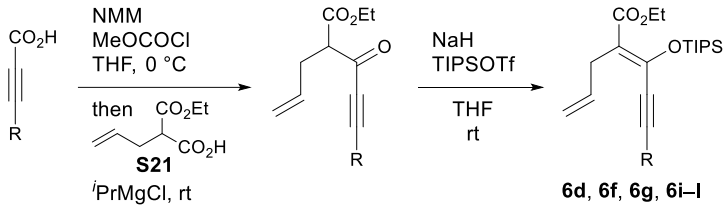


(*E*)-**6q**

According to the general procedure A, (*E*)-**6q** (135 mg, 0.331 mmol, 66% yield for 2 steps) was synthesised from LDA (ca. 1.0 mol/L in THF-hexane, 1.20 mL, 1.20 mmol), alkenyl ester **S19** (71.2 mg, 0.501 mmol), alkynyl ester **S6** (92.5 mg, 0.600 mmol), NaH (60% in mineral oil, 40.5 mg, 1.01 mmol), and TIPSOTf (202 μL, 0.750 mmol).

(*E*)-**6q**: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52–5.39 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.05 (d, *J* = 6.3 Hz, 2H), 1.63 (d, *J* = 5.7 Hz, 3H), 1.35–1.28 (m, 3H), 1.26 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 8.0 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 140.0, 128.3, 125.6, 116.8, 104.5, 76.0, 59.9, 33.5, 30.2 (3C), 28.2, 17.9 (6C), 17.8, 14.4, 13.0 (3C); FT-IR (ATR) *v* 2968, 2944, 2867, 2216, 1715, 1317, 1191 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{42}O_3Si$ (M^+): 406.2903, found: 406.2890.

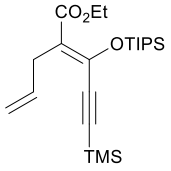
Synthesis of Dienynes: General Procedure B



This procedure is based on the method originally reported by Presset *et al.* [17]

A solution of mixed anhydride in THF was prepared by the addition of *N*-methylmorpholine (1.1 equiv.)

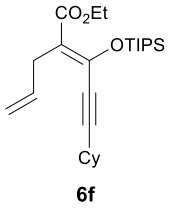
and MeOCOCl (1.1 equiv.) successively to a solution of alkynyl carboxylic acid (1.0 equiv.) in THF (0.5 mol/L) at 0 °C. The mixture was stirred for 15 min at the same temperature before the use. In another flask, malonic acid monoester **S21** (1.5 equiv.) was dissolved in THF (0.75 mol/L), and ^{i}PrMgCl (2.0 mol/L in THF, 3.0 equiv.) was added at 0 °C. After stirring for 5 min, the solution of mixed anhydride in THF was transferred via cannula to this mixture, and the resulting mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic layer was diluted with EtOAc. Two layers were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Highly polar components were filtered off through a plug of SiO_2 (hexane:EtOAc = 10:1) to afford ketoester along with a small amount of byproducts.
NaH (60% dispersion in mineral oil, 2.0 equiv.) was washed with hexane and suspended with THF (0.4 mol/L). To this suspension was added above ketoester (1.0 equiv.) in THF via cannula at 0 °C. After stirring for 10 min, TIPSOTf (1.5 equiv.) was added, and the reaction mixture was warmed up to room temperature and stirred for 10 min. The reaction was quenched by the careful addition of saturated aqueous $NaHCO_3$ solution, and the organic layer was diluted with EtOAc. Two layers were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford the product dienyne.



6d

According to the general procedure B, **6d** (751 mg, 1.84 mmol, 73% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S9** (356 mg, 2.50 mmol), *N*-methylmorpholine (275 µL, 2.50 mmol), MeOCOCl (192 µL, 2.50 mmol), malonic acid monoester **S21** (646 mg, 3.75 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 3.75 mL, 7.50 mmol), NaH (60% in mineral oil, 149 mg, 3.73 mmol), and TIPSOTf (806 µL, 3.00 mmol).

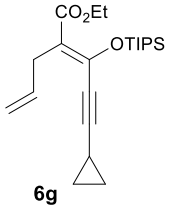
6d: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, J = 17.1, 10.2, 6.5 Hz, 1H), 5.06 (ddt, J = 17.1, 1.6, 1.6 Hz, 1H), 4.97 (ddt, J = 10.2, 1.6, 1.5 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.16 (ddd, J = 6.5, 1.6, 1.5 Hz, 2H), 1.36–1.29 (m, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.10 (d, J = 8.0 Hz, 18H), 0.20 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 139.4, 135.6, 117.7, 115.2, 102.2, 100.3, 60.1, 34.6, 17.9 (6C), 14.3, 13.0 (3C), −0.7 (3C); FT-IR (ATR) ν 2945, 2868, 2150, 1717, 1200, 842 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{40}O_3Si_2$ (M^+): 408.2516, found: 408.2535.



6f

According to the general procedure B, **6f** (160 mg, 0.381 mmol, 76% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S10** (76.2 mg, 0.501 mmol), *N*-methylmorpholine (57.7 μL, 0.525 mmol), MeOCOCl (40.3 μL, 0.525 mmol), malonic acid monoester **S21** (129 mg, 0.750 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 750 μL, 1.50 mmol), NaH (60% in mineral oil, 36.4 mg, 0.910 mmol), and TIPSOTf (183 μL, 0.679 mmol).

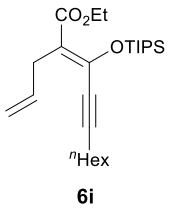
6f: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 17.1, 10.4, 6.4 Hz, 1H), 5.06 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 4.95 (ddt, *J* = 10.4, 1.7, 1.7 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 6.4 Hz, 2H), 2.57–2.52 (m, 1H), 1.85–1.80 (m, 2H), 1.74–1.68 (m, 2H), 1.50–1.43 (m, 2H), 1.35–1.29 (m, 7H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.8, 136.1, 115.7, 114.9, 101.2, 77.1, 59.9, 34.6, 31.9 (2C), 29.7, 25.7, 24.8 (2C), 17.9 (6C), 14.4, 13.1 (3C); FT-IR (ATR) *ν* 2932, 2866, 2213, 1715, 1321, 1204 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{42}O_3Si$ (M^+): 418.2903, found: 418.2917.



6g

According to the general procedure B, **6g** (129 mg, 0.341 mmol, 68% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S11** (54.9 mg, 0.499 mmol), *N*-methylmorpholine (57.7 μL, 0.525 mmol), MeOCOCl (40.3 μL, 0.525 mmol), malonic acid monoester **S21** (129 mg, 0.751 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 750 μL, 1.50 mmol), NaH (60% in mineral oil, 34.0 mg, 0.850 mmol), and TIPSOTf (174 μL, 0.646 mmol).

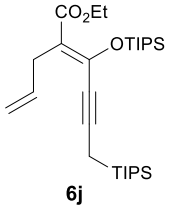
6g: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.05 (ddt, *J* = 17.0, 1.7, 1.6 Hz, 1H), 4.96 (ddt, *J* = 10.2, 1.7, 1.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.13 (ddd, *J* = 6.4, 1.6, 1.6 Hz, 2H), 1.43–1.38 (m, 1H), 1.31–1.26 (m, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H), 0.91–0.87 (m, 2H), 0.78–0.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.7, 136.1, 115.6, 114.8, 100.5, 72.4, 59.9, 34.5, 17.9 (6C), 14.4, 13.0 (3C), 8.5 (2C), 0.1; FT-IR (ATR) *ν* 2945, 2867, 2217, 1714, 1208, 1184, 1126 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{36}O_3Si$ (M^+): 376.2434, found: 376.2420.



6i

According to the general procedure B, **6i** (62.6 mg, 0.149 mmol, 74% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S12** (31.0 mg, 0.201 mmol), *N*-methylmorpholine (24.2 μL, 0.220 mmol), MeOCOCl (16.9 μL, 0.220 mmol), malonic acid monoester **S21** (51.5 mg, 0.299 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 300 μL, 0.600 mmol), NaH (60% in mineral oil, 16.1 mg, 0.403 mmol), and TIPSOTf (80.6 μL, 0.300 mmol).

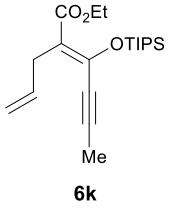
6i: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.1, 10.3, 6.4 Hz, 1H), 5.05 (ddt, *J* = 17.1, 1.7, 1.7 Hz, 1H), 4.95 (ddt, *J* = 10.3, 1.7, 1.7 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.57–1.51 (m, 2H), 1.43–1.37 (m, 2H), 1.33–1.25 (m, 7H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 7.4 Hz, 18H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.6, 136.1, 115.7, 114.9, 97.7, 59.9, 34.5, 31.3, 28.6, 28.0, 22.5, 19.4, 17.9 (6C), 14.4, 14.0, 13.0 (3C) (1 signal overlapped with the solvent signals δ 77.2, 77.0, 76.7); FT-IR (ATR) *v* 2934, 2867, 2220, 1715, 1334, 1205 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{44}O_3Si$ (M^+): 420.3060, found: 420.3040.



6j

According to the general procedure B, **6j** (59.1 mg, 0.117 mmol, 78% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S23** (35.9 mg, 0.149 mmol), *N*-methylmorpholine (18.1 μL, 0.165 mmol), MeOCOCl (12.7 μL, 0.165 mmol), malonic acid monoester **S21** (39.1 mg, 0.227 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 225 μL, 0.450 mmol), NaH (60% in mineral oil, 12.3 mg, 0.308 mmol), and TIPSOTf (60.5 μL, 0.225 mmol).

6j: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.1, 6.3 Hz, 1H), 5.03 (ddt, *J* = 17.0, 1.8, 1.8 Hz, 1H), 4.94 (ddt, *J* = 10.1, 1.8, 1.8 Hz, 1H), 4.16 (q, *J* = 7.3 Hz, 2H), 3.15 (d, *J* = 6.3 Hz, 2H), 1.73 (s, 2H), 1.33–1.26 (m, 3H), 1.25 (t, *J* = 7.3 Hz, 3H), 1.18–1.12 (m, 3H), 1.11 (d, *J* = 7.5 Hz, 18H), 1.08 (d, *J* = 7.0 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 141.1, 136.3, 114.8, 114.7, 97.1, 76.4, 59.8, 34.2, 18.5 (6C), 17.9 (6C), 14.4, 13.1 (3C), 11.1 (3C), 0.4; FT-IR (ATR) *v* 2943, 2867, 2204, 1715, 1205, 1163, 881 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{54}O_3Si_2$ (M^+): 506.3612, found: 506.3607.

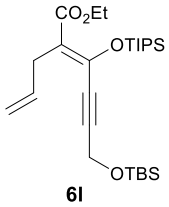


6k

According to the general procedure B, **6k** (59.8 mg, 0.171 mmol, 63% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S13** (75% in Et_2O, 30.2 mg, 0.270 mmol), *N*-methylmorpholine (32.7 μL, 0.297 mmol), MeOCOCl (22.8 μL, 0.297 mmol), malonic acid monoester **S21** (69.2 mg, 0.402 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 406 μL, 0.811 mmol), NaH (60% in mineral oil, 19.6 mg, 0.490 mmol), and TIPSOTf (96.8 μL, 0.360 mmol).

6k: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.0, 9.9, 6.4 Hz, 1H), 5.05 (ddt, *J* = 17.0, 1.7, 1.7 Hz, 1H), 4.96 (ddt, *J* = 9.9, 1.7, 1.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.14 (d, *J* = 6.4 Hz, 2H), 2.01 (s, 3H), 1.31–1.26 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 140.5, 136.2, 115.6, 114.9, 93.2, 76.6, 59.9, 34.4, 17.9 (6C), 14.4, 13.0 (3C), 4.3; FT-IR (ATR) *v* 2945, 2867, 2228, 1715, 1589, 1206 cm^{-1}; HRMS (FI) calcd for $C_{20}H_{34}O_3Si$ (M^+):

350.2277, found: 350.2268.

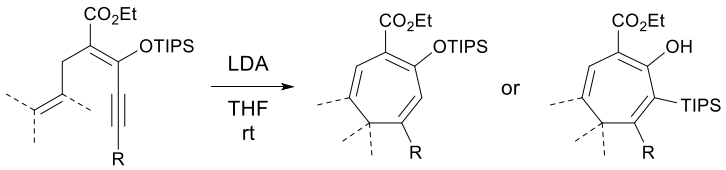


6l

According to the general procedure B, **6l** (146 mg, 0.303 mmol, 61% yield for 2 steps) was synthesised from alkynyl carboxylic acid **S24** (107 mg, 0.499 mmol), *N*-methylmorpholine (57.7 μL, 0.525 mmol), MeOCOCl (40.3 μL, 0.525 mmol), malonic acid monoester **S21** (129 mg, 0.750 mmol), ^{i}PrMgCl (2.0 mol/L in THF, 750 μL, 1.50 mmol), NaH (60% in mineral oil, 34.5 mg, 0.863 mmol), and TIPSOTf (175 μL, 0.651 mmol).

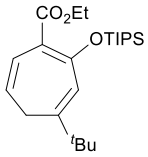
6l: colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.06 (ddt, *J* = 16.9, 1.6, 1.6 Hz, 1H), 4.96 (ddt, *J* = 10.3, 1.6, 1.6 Hz, 1H), 4.45 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 6.4 Hz, 2H), 1.34–1.28 (m, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H), 0.90 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 139.3, 135.7, 117.2, 115.2, 94.2, 80.6, 60.1, 51.8, 34.4, 25.6 (3C), 18.2, 17.9 (6C), 14.3, 13.0 (3C), −5.4 (2C); FT-IR (ATR) *v* 2947, 2867, 1717, 1207, 1093, 833, 777 cm^{-1} (C≡C absorption band was not detected due to very weak intensity); HRMS (FI) calcd for $C_{26}H_{48}O_4Si_2$ (M^+): 480.3091, found: 480.3078.

Synthesis of Cycloheptatrienes: General Procedure C



6a–j, **6m–q** **7a**, **7c–e**, **7m–q** **8b**, **8f–j**

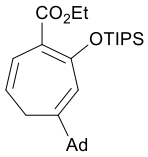
An LDA solution (1 mol/L in THF-hexane) was prepared by the addition of ^{n}BuLi (2.65 mol/L in hexane, 755 μL, 2.00 mmol) to a solution of $^{i}Pr_2NH$ (281 μL, 2.00 mmol) in THF (1.25 mL) at 0 °C. The mixture was stirred for 20 min at the same temperature before the use. To another reaction vessel charged with dienyne (1.0 equiv.) in THF (0.1 mol/L) was added the LDA solution (2.0 equiv.) via a syringe at 0 °C. The reaction mixture was then warmed up to room temperature and stirred for 20 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the organic layer was diluted with EtOAc. Two layers were separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford the product cycloheptatriene.



7a

According to the general procedure C, **7a** (33.0 mg, 84.0 μmol, 84% yield) was synthesised from dienyne **6a** (39.1 mg, 99.6 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

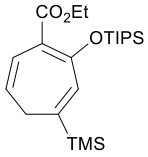
7a: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.5 Hz, 1H), 5.86 (s, 1H), 5.28 (dt, *J* = 9.5, 6.7 Hz, 1H), 4.23 (q, *J* = 7.3 Hz, 2H), 2.35 (d, *J* = 6.7 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H), 1.27–1.20 (m, 3H), 1.12 (s, 9H), 1.10 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 157.9, 153.7, 125.1, 118.6, 117.5, 116.7, 60.2, 36.1, 29.24 (3C), 29.16, 17.9 (6C), 14.4, 13.3 (3C); FT-IR (ATR) *v* 2946, 2867, 1720, 1195, 1058, 881 cm^{-1}; HRMS (FD) calcd for $C_{23}H_{40}O_3Si$ (M^+): 392.2747, found: 392.2762.



7c

According to the general procedure C, **7c** (37.3 mg, 79.2 μmol, 79% yield) was synthesised from dienyne **6c** (47.1 mg, 0.100 mmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

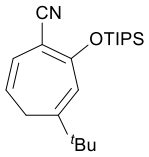
7c: yellow semisolid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.4 Hz, 1H), 5.76 (s, 1H), 5.23 (ddd, *J* = 9.4, 7.0, 7.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.32 (br, 2H), 2.04 (br, 3H), 1.75–1.65 (m, 12H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27–1.20 (m, 3H), 1.10 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 158.1, 153.8, 125.0, 118.2, 117.6, 116.6, 60.2, 41.2 (3C), 37.7, 36.7 (3C), 28.3 (3C), 28.0, 17.9 (6C), 14.4, 13.3 (3C); FT-IR (ATR) *v* 2903, 2865, 2849, 1713, 1204, 1064 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{46}O_3Si$ (M^+): 470.3216, found: 470.3207.



7d

According to the general procedure C, **7d** (38% NMR yield) and **8d** (12% NMR yield) was synthesised from dienyne **6d** (39.4 mg, 96.4 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 193 μL, 0.193 mmol). The major product **7d** was partially isolated by PTLC purification.

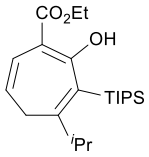
7d: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.3 Hz, 1H), 6.22 (s, 1H), 5.29 (dt, *J* = 9.3, 6.9 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.32 (d, *J* = 6.9 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.26–1.18 (m, 3H), 1.10 (d, *J* = 6.9 Hz, 18H), 0.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 158.0, 144.8, 131.7, 125.0, 118.8, 117.9, 60.4, 30.2, 17.9 (6C), 14.3, 13.2 (3C), −1.9 (3C); FT-IR (ATR) *v* 2946, 2867, 1723, 1206, 1053, 834 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{40}O_3Si_2$ (M^+): 408.2516, found: 408.2506.



7e

According to the general procedure C, **7e** (17.3 mg, 50.1 μmol, 51% yield) was synthesised from dienyne **6e** (34.1 mg, 98.7 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

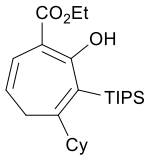
7e: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (d, *J* = 9.1 Hz, 1H), 5.92 (s, 1H), 5.31 (dt, *J* = 9.1, 7.4 Hz, 1H), 2.40 (d, *J* = 7.4 Hz, 2H), 1.28–1.21 (m, 3H), 1.132 (s, 9H), 1.125 (d, *J* = 6.9 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 156.7, 124.1, 120.4, 118.7, 116.9, 97.1, 36.6, 29.2, 29.1 (3C), 17.8 (6C), 13.0 (3C); FT-IR (ATR) *v* 2947, 2868, 2209, 1308, 1228, 878, 837 cm^{-1}; HRMS (FD) calcd for $C_{21}H_{35}NOSi$ (M^+): 345.2488, found: 345.2484.



8b

According to the general procedure C, **8b** (451 mg, 1.19 mmol, 85% yield) was synthesised from dienyne **6b** (530 mg, 1.40 mmol) and LDA (ca. 1.0 mol/L in THF-hexane, 2.80 mL, 2.80 mmol).

8b: yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (dd, *J* = 9.3, 1.4 Hz, 1H), 5.45 (ddd, *J* = 9.3, 7.4, 6.4 Hz, 1H), 4.31–4.22 (m, 2H), 2.89 (dd, *J* = 12.2, 7.4 Hz, 1H), 2.80 (sept, *J* = 6.8 Hz, 1H), 1.87 (ddd, *J* = 12.2, 6.4, 1.4 Hz, 1H), 1.42–1.34 (m, 3H), 1.34 (t, *J* = 7.3 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 7.4 Hz, 9H), 1.03 (d, *J* = 7.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 172.8, 167.5, 124.5, 123.6, 122.7, 103.4, 60.6, 34.3, 29.8, 22.2, 21.6, 19.4 (3C), 19.3 (3C), 14.2, 13.6 (3C); FT-IR (ATR) *v* 2946, 2866, 1637, 1533, 1226, 1067 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{38}O_3Si$ (M^+): 378.2590, found: 378.2576; m.p. (Et_2O) 57–62 °C.

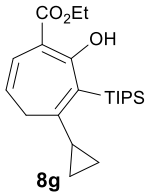


8f

According to the general procedure C, **8f** (33.1 mg, 79.1 μmol, 81% yield) was synthesised from dienyne **6f** (41.1 mg, 98.2 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

8f: yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (dd, *J* = 9.0, 1.4 Hz, 1H), 5.44 (ddd, *J* = 9.0, 7.4, 6.4 Hz, 1H), 4.31–4.21 (m, 2H), 2.90 (dd, *J* = 12.1, 7.4 Hz, 1H), 2.46 (tt, *J* = 11.4, 3.1 Hz, 1H), 1.84 (ddd, *J* = 12.1, 6.4, 1.4 Hz, 1H), 1.82–1.70 (m, 3H), 1.65–1.61 (m, 2H), 1.53–1.19 (m, 8H), 1.34 (t, 7.0 Hz, 3H), 1.08 (d, *J* = 7.4 Hz, 9H), 1.03 (d, *J* = 7.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 172.8, 166.4, 124.7, 123.1, 122.7, 103.5, 60.6, 45.2, 32.2, 31.4, 31.1, 26.05, 26.00, 25.8, 19.5 (3C), 19.4 (3C), 14.2, 13.7 (3C); FT-IR (ATR) *v* 2927, 2864, 1636, 1316, 1228, 1070 cm^{-1}; HRMS (FD) calcd for

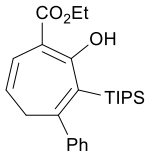
$C_{25}H_{42}O_3Si$ (M^+): 418.2903, found: 418.2922; m.p. (Et_2O) 96–101 °C.



8g

According to the general procedure C, **8g** (21.8 mg, 57.9 μmol, 58% yield) was synthesised from dienyne **6g** (37.6 mg, 99.8 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

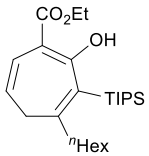
8g: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (d, *J* = 9.3 Hz, 1H), 5.33 (ddd, *J* = 9.3, 7.1, 7.1 Hz, 1H), 4.31–4.21 (m, 2H), 2.14 (dd, *J* = 12.6, 7.1 Hz, 1H), 1.77–1.71 (m, 2H), 1.47–1.38 (m, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.5 Hz, 18H), 0.95–0.87 (m, 2H), 0.85–0.79 (m, 1H), 0.68–0.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 172.8, 162.0, 124.7, 123.5, 122.0, 103.1, 60.6, 27.6, 19.3 (3C), 19.1 (3C), 17.1, 14.2, 13.3 (3C), 9.5, 7.3; FT-IR (ATR) *ν* 2944, 2865, 1635, 1299, 1227, 1072 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{36}O_3Si$ (M^+): 376.2434, found: 376.2420.



8h

According to the general procedure C, **8h** (19.3 mg, 46.8 μmol, 47% yield) was synthesised from dienyne **6h** (40.7 mg, 98.6 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

8h: yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.22 (m, 5H), 6.51 (d, *J* = 9.2 Hz, 1H), 5.72 (ddd, *J* = 9.2, 6.8, 6.8 Hz, 1H), 4.31 (q, *J* = 7.3 Hz, 2H), 2.86 (br, 1H), 2.34 (br, 1H), 1.37 (t, *J* = 7.3 Hz, 3H), 1.25–0.86 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 172.9, 159.2, 144.3, 127.9 (2C), 127.8, 127.5 (2C), 127.2, 123.4, 121.5, 104.1, 60.9, 40.2, 19.5 (6C), 14.2, 13.0 (3C); FT-IR (ATR) *ν* 2946, 2865, 1637, 1315, 1226, 1081 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{36}O_3Si$ (M^+): 412.2434, found: 412.2426; m.p. (Et_2O) 79–81 °C.

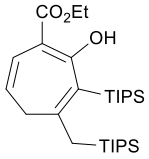


8i

According to the general procedure C, **8i** (36.7 mg, 87.2 μmol, 86% yield) was synthesised from dienyne **6I** (42.5 mg, 0.101 mmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

8i: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 9.1 Hz, 1H), 5.52 (ddd, *J* = 9.1, 7.4, 6.4 Hz, 1H), 4.29–4.23 (m, 2H), 2.78 (dd, *J* = 12.1, 7.4 Hz, 1H), 2.38–2.32 (m, 1H), 2.26–2.20 (m, 1H), 2.05 (ddd, *J* = 12.1, 6.4, 1.4 Hz, 1H), 1.55–1.46 (m, 2H), 1.42–1.29 (m, 12H), 1.05 (d, *J* = 7.4 Hz, 9H), 1.02 (d, *J* = 7.4 Hz, 9H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 172.8, 162.0, 125.1,

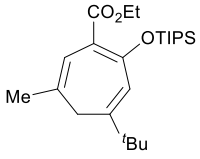
123.0, 122.6, 103.3, 60.6, 38.4, 35.1, 31.7, 29.9, 29.3, 22.5, 19.34 (3C), 19.30 (3C), 14.2, 14.0, 13.5 (3C); FT-IR (ATR) *v* 2928, 2864, 1636, 1315, 1226, 1068 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{44}O_3Si$ (M^+): 420.3060, found: 420.3045.



8j

According to the general procedure C, **8j** (22.4 mg, 44.2 μmol, 88% yield) was synthesised from dienyne **6j** (25.4 mg, 50.1 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 100 μL, 0.100 μmol).

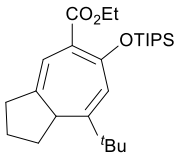
8j: pale yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 9.3 Hz, 1H), 5.56 (ddd, *J* = 9.3, 7.0, 7.0 Hz, 1H), 4.28–4.23 (m, 2H), 2.68 (br, 1H), 2.21 (br, 1H), 2.03 (br-d, *J* = 12.3 Hz, 1H), 1.95 (br-d, *J* = 12.3 Hz, 1H), 1.52–1.43 (m, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.25–1.14 (m, 3H), 1.11–1.04 (m, 36H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.4, 172.7, 161.0, 125.1, 123.5, 122.7, 102.9, 60.5, 37.9, 21.5, 19.5 (6C), 19.0 (6C), 14.3, 14.0 (3C), 11.8 (3C); FT-IR (ATR) *v* 2943, 2866, 1637, 1316, 1227, 1070 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{54}O_3Si_2$ (M^+): 506.3612, found: 506.3625; m.p. (Et_2O) 64–69 °C.



7m

According to the general procedure C, **7m** (32.5 mg, 79.9 μmol, 79% yield) was synthesised from dienyne **6m** (41.0 mg, 0.101 mmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

7m: colourless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, *J* = 1.1 Hz, 1H), 5.83 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 2H), 1.97 (d, *J* = 1.1 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.26–1.17 (m, 3H), 1.14 (s, 9H), 1.09 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 156.3, 152.6, 129.9, 120.7, 118.1, 116.8, 60.2, 36.1, 34.2, 28.8 (3C), 23.5, 17.9 (6C), 14.4, 13.3 (3C); FT-IR (ATR) *v* 2945, 2867, 1720, 1223, 1194, 883 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{42}O_3Si$ (M^+): 406.2903, found: 406.2907.

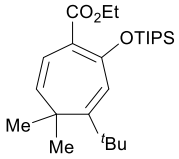


7n

According to the general procedure C, **7n** (38.2 mg, 88.3 μmol, 89% yield) was synthesised from dienyne **6n** (43.1 mg, 99.6 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

7n: pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 6.23 (s, 1H), 5.84 (s, 1H), 4.30–4.23 (m, 1H), 4.21–4.14 (m, 1H), 2.65–2.57 (m, 1H), 2.46–2.33 (m, 3H), 2.12–2.06 (m, 1H), 2.04–1.99 (m, 1H), 1.66–1.56 (m, 1H), 1.30 (t, *J* = 6.9 Hz, 3H), 1.25–1.18 (m, 3H), 1.20 (s, 9H), 1.11 (d, *J* = 7.4 Hz, 9H), 1.08 (d, *J* =

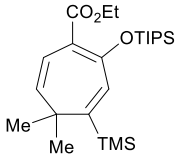
6.9 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 155.9, 152.3, 143.9, 118.9, 117.3, 115.1, 60.3, 45.3, 36.5, 33.5, 30.2 (3C), 29.0, 26.6, 18.0 (3C), 17.9 (3C), 14.4, 13.3 (3C); FT-IR (ATR) *v* 2946, 2867, 1721, 1272, 1200, 883 cm^{-1}; HRMS (FD) calcd for $C_{26}H_{44}O_3Si$ (M^+): 432.3060, found: 432.3039.



7o

According to the general procedure C, **7o** (29.3 mg, 69.6 μmol, 70% yield) was synthesised from dienyne **6o** (42.0 mg, 99.8 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

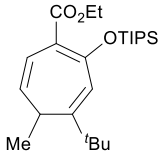
7o: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (d, *J* = 10.3 Hz, 1H), 5.99 (s, 1H), 4.91 (d, *J* = 10.3 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27–1.20 (m, 18H), 1.11 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 157.0, 152.7, 124.2, 122.7, 118.8, 115.3, 60.1, 38.9, 38.5 (2C), 32.0 (3C), 27.2, 18.0 (6C), 14.4, 13.4 (3C); FT-IR (ATR) *v* 2946, 2867, 1720, 1204, 1068, 882 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{44}O_3Si$ (M^+): 420.3060, found: 420.3041.



7p

According to the general procedure C, **7p** (12.7 mg, 29.1 μmol, 58% yield) was synthesised from dienyne **6p** (21.9 mg, 50.1 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 100 μL, 0.100 μmol).

7p: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37 (d, *J* = 10.3 Hz, 1H), 6.25 (s, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.26–1.19 (m, 3H), 1.12 (s, 6H), 1.11 (d, *J* = 7.5 Hz, 18H), 0.21 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 157.4, 153.1, 132.1, 129.5, 122.3, 117.4, 60.4, 38.8 (2C), 26.3, 17.9 (6C), 14.4, 13.4 (3C), 1.8 (3C); FT-IR (ATR) *v* 2947, 2867, 1722, 1203, 835 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{44}O_3Si_2$ (M^+): 436.2829, found: 436.2830.



7q

From (*Z*)-**6q**: According to the general procedure C, **7q** (26.5 mg, 65.2 μmol, 66% yield) was synthesised from dienyne (*Z*)-**6q** (40.3 mg, 99.1 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 μmol).

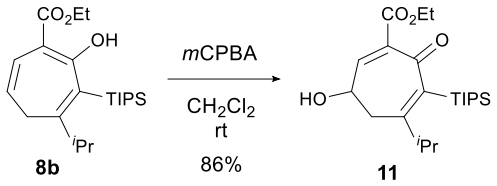
From (*E*)-**6q**: According to the general procedure C, **7q** (14.2 mg, 34.9 μmol, 35% yield) and **10** (isomeric mixture, 5.8 mg, 16 μmol, 16% yield) was synthesised from dienyne (*E*)-**6q** (40.2 mg, 98.8 μmol) and LDA (ca. 1.0 mol/L in THF-hexane, 200 μL, 0.200 mmol).

7q: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 10.2 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.39 (dd, *J* = 10.2, 8.9 Hz, 1H), 4.30–4.24 (m, 1H), 4.20–4.13 (m, 1H), 3.30 (dq, *J* = 8.9, 7.4 Hz, 1H), 1.30

(t, J = 7.3 Hz, 3H), 1.29–1.21 (m, 3H), 1.13 (s, 9H), 1.12 (d, J = 7.0 Hz, 9H), 1.10 (d, J = 7.0 Hz, 9H), 0.80 (d, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 157.7, 156.2, 124.1, 122.8, 117.0, 115.6, 60.2, 37.5, 32.7, 29.3 (3C), 17.9 (6C), 14.4, 13.5, 13.3 (3C); FT-IR (ATR) ν 2946, 2868, 1719, 1197, 1068, 881 cm^{-1}; HRMS (FD) calcd for $C_{24}H_{42}O_3Si$ (M^+): 406.2903, found: 406.2911.

Synthetic Applications

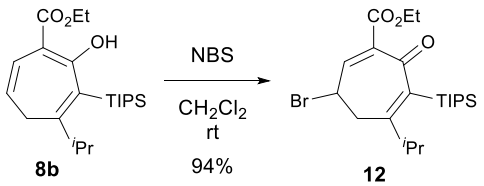
Ketoester 11



To a solution of **8b** (18.9 mg, 49.9 μmol) in CH_2Cl_2 (0.25 mL) was added *m*CPBA (ca. 70%, 12.5 mg, 50.7 μmol) at room temperature. After stirring for 20 min, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution (0.50 mL) and $Na_2S_2O_3{\cdot}5H_2O$ (90 mg). After stirring for 1 h, the two layers were separated, the aqueous layer was extracted with CH_2Cl_2 (0.50 mL × 3). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (1.0 mL × 2), then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:Et_2O = 10:1 to 1:1 gradient) to afford **11** (16.9 mg, 42.8 μmol, 86% yield) as a pale yellow oil.

11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 4.35 (d, J = 11.8 Hz, 1H), 4.26–4.17 (m, 2H), 2.70 (sept, J = 6.8 Hz, 1H), 2.64 (dd, J = 13.6, 11.8 Hz, 2H), 2.48 (d, J = 13.6 Hz, 1H), 2.30 (br, 1H), 1.28 (t, J = 7.0 Hz, 3H), 1.29–1.23 (m, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.10 (d, J = 7.2 Hz, 9H), 1.05 (d, J = 7.2 Hz, 9H), 1.02 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 164.2, 154.4, 149.6, 144.5, 134.7, 68.3, 61.5, 35.7, 35.3, 20.9, 20.8, 19.2 (3C), 19.0 (3C), 13.9, 12.8 (3C); FT-IR (ATR) ν 3464 (br), 2947, 2867, 1720, 1661, 1243, 1042 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{39}O_4Si$ ([M + H]$^+$): 395.2618, found: 395.2607.

Ketoester 12

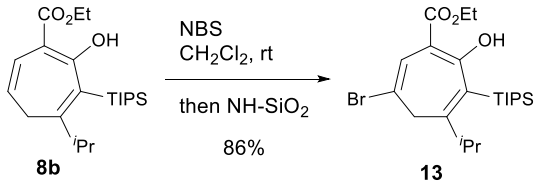


To a solution of **8b** (37.7 mg, 99.6 μmol) in CH_2Cl_2 (0.50 mL) was added NBS (26.7 mg, 0.150 mmol)

at room temperature. After stirring for 30 min, the mixture was concentrated, and the residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 50:1 to 20:1) to afford **12** (42.6 mg, 93.1 μmol, 94% yield) as a pale yellow oil.

12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.78 (dt, *J* = 11.6, 3.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.03 (dd, *J* = 14.5, 11.6 Hz, 1H), 2.81 (dd, *J* = 14.5, 1.7 Hz, 1H), 2.69 (sept, *J* = 6.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.30–1.22 (m, 3H), 1.10 (d, *J* = 7.4 Hz, 12H), 1.06 (d, *J* = 7.4 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 163.4, 154.4, 146.5, 145.8, 133.8, 61.7, 44.9, 36.6, 35.0, 21.5, 20.6, 19.1 (3C), 19.0 (3C), 13.9, 12.8 (3C); FT-IR (ATR) *ν* 2946, 2867, 1720, 1672, 1248, 1042 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{37}BrO_3Si$ (M^+): 456.1695, found: 456.1682.

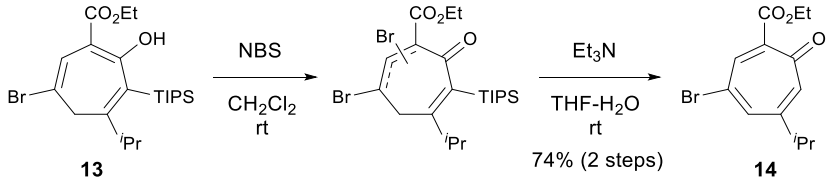
Cycloheptatriene 13



To a solution of **8b** (379 mg, 1.00 mmol) in CH_2Cl_2 (5.0 mL) was added NBS (215 mg, 1.21 mmol) at room temperature After stirring for 30 min, hexane (5.0 mL) was added, and the resulting precipitate was filtered and washed with hexane. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography [SiO_2 (NH-functionalised), hexane:EtOAc = 200:1] to afford **13** (396 mg, 0.866 mmol, 86% yield) as a white solid.

13: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (s, 1H), 4.31–4.22 (m, 2H), 3.11 (dd, *J* = 14.2, 1.4 Hz, 1H), 2.83 (sept, *J* = 6.7 Hz, 1H), 2.69 (dd, *J* = 14.2, 1.1 Hz, 1H), 1.43–1.35 (m, 3H), 1.34 (t, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 7.5 Hz, 9H) 1.04 (d, *J* = 7.5 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 171.6, 166.6, 127.0, 124.7, 112.9, 103.3, 61.0, 38.9, 34.6, 21.7, 20.9, 19.4 (3C), 19.3 (3C), 14.2, 13.5 (3C); FT-IR (ATR) *ν* 2966, 2946, 2867, 1639, 1226, 1067 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{37}BrO_3Si$ (M^+): 456.1695, found: 456.1697; m.p. (EtOAc) 100–105 °C.

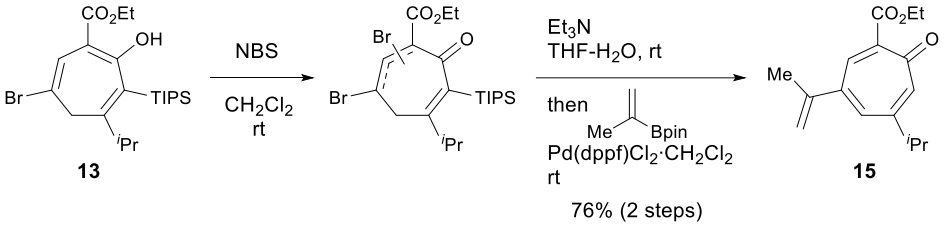
Tropone 14



To a solution of **13** (230 mg, 0.502 mmol) in CH_2Cl_2 (5.0 mL) was added NBS (178 mg, 1.00 mmol) at room temperature. After stirring for 1 h, hexane (5.0 mL) was added, and the resulting precipitate was filtered and washed with hexane. The filtrate was concentrated under reduced pressure, and the residue was filtered through a short plug of SiO_2 (hexane:EtOAc = 10:1) to afford dibromide.
To a solution of above dibromide in THF (4.0 mL) and H_2O (1.0 mL) was added Et_3N (347 µL, 2.50 mmol) at room temperature. After stirring for 15 h, the reaction was quenched with saturated aqueous NH_4Cl solution (5.0 mL), and the organic layer was diluted with EtOAc (5.0 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 20:1 to 5:1) to afford **14** (111 mg, 0.372 µmol, 74% yield for 2 steps) as a yellow oil.

14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.7 Hz, 1H), 7.37 (dd, *J* = 1.7, 1.1 Hz, 1H), 6.91 (d, *J* = 1.1 Hz, 1H), 4.35 (q, *J* = 7.3 Hz, 2H), 2.70 (sept, *J* = 6.9 Hz, 1H), 1.35 (t, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.3, 165.9, 154.6, 141.5, 140.3, 139.3, 137.5, 127.2, 62.2, 37.7, 22.5 (2C), 14.1; FT-IR (ATR) *ν* 2965, 1730, 1624, 1584, 1234 cm^{-1}; HRMS (FD) calcd for $C_{13}H_{15}BrO_3$ (M^+): 298.0205, found: 298.0214.

Tropone 15

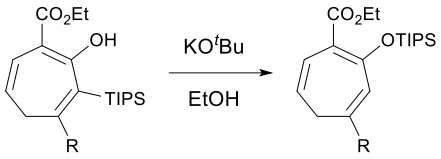


To a solution of **13** (196 mg, 0.428 mmol) in CH_2Cl_2 (4.3 mL) was added NBS (152 mg, 0.853 mmol) at room temperature. After stirring for 45 min, hexane (5.0 mL) was added, and the resulting precipitate was filtered and washed with hexane. The filtrate was concentrated under reduced pressure, and the residue was filtered through a short plug of SiO_2 (hexane:EtOAc = 10:1) to afford dibromide.
To a solution of crude dibromide in THF (3.4 mL) and H_2O (0.85 mL) was added Et_3N (297 µL, 2.14 mmol) at room temperature. After stirring for 15 h, (isopropenyl)Bpin (121 µL, 0.643 mmol) and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (16.9 mg, 20.7 µmol) were added successively, and the reaction mixture was stirred for 1 h. The reaction was quenched with H_2O (3.0 mL), and the organic layer was diluted with EtOAc (3.0 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 10:1 to 3:1) to afford

15 (85.2 mg, 0.327 mmol, 76% yield for 2 steps) as a dark orange oil.

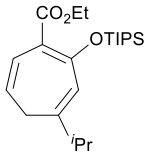
15: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.1 Hz, 1H), 6.97 (dd, *J* = 1.7, 1.1 Hz, 1H), 6.90 (d, *J* = 1.7 Hz, 1H), 5.29 (s, 1H), 5.23 (s, 1H), 4.33 (q, *J* = 7.3 Hz, 2H), 2.73 (sept, *J* = 6.9 Hz, 1H), 2.09 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.2, 167.5, 155.8, 145.2, 144.8, 141.7, 137.0, 135.3, 133.9, 117.1, 61.7, 38.3, 22.7 (2C), 22.0, 14.0; FT-IR (ATR) *v* 2964, 1726, 1634, 1579, 1233, 1044 cm^{-1}; HRMS (FD) calcd for $C_{16}H_{20}O_3$ (M^+): 260.1412, found: 260.1402.

Brook Rearrangement: General Procedure D



8b, **8h**, **8i** **7b**, **7h**, **7i**

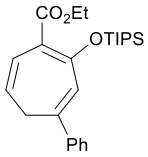
To a solution of vinylsilane (1 equiv.) in EtOH (0.2 mol/L) was added KO^{t}Bu (1.0 mol/L in THF, 0.2 equiv.) at room temperature. The reaction mixture was stirred until full consumption of starting material was observed by TLC. The reaction was quenched with saturated aqueous NH_4Cl solution, and the resulting mixture was extracted four times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford the product silylether.



7b

According to the general procedure D, **7b** (35.7 mg, 94.3 μmol, 94% yield) was synthesised from vinylsilane **8b** (38.0 mg, 0.100 mmol) and KO^{t}Bu (1.0 mol/L in THF, 20.0 μL, 20.0 μmol).

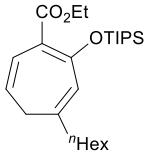
7b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.5 Hz, 1H), 5.79 (s, 1H), 5.27 (dt, *J* = 9.5, 6.9 Hz, 1H), 4.22 (q, *J* = 7.3 Hz, 2H), 2.47 (sept, *J* = 6.7 Hz, 1H), 2.33 (d, *J* = 6.9 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H), 1.27–1.19 (m, 3H), 1.10 (d, *J* = 7.0 Hz, 18H), 1.08 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 157.7, 151.3, 125.3, 118.4, 118.0, 116.7, 60.2, 35.6, 30.4, 21.9 (2C), 17.9 (6C), 14.4, 13.2 (3C); FT-IR (ATR) *v* 2959, 2944, 2867, 1721, 1206 cm^{-1}; HRMS (FD) calcd for $C_{22}H_{38}O_3Si$ (M^+): 378.2590, found: 378.2573.



7h

According to the general procedure D, **7h** (17.0 mg, 41.2 μmol, 93% yield) was synthesised from vinylsilane **8h** (18.2 mg, 44.1 μmol) and KO^{t}Bu (1.0 mol/L in THF, 8.8 μL, 8.8 μmol).

7h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.39–7.36 (m, 2H), 7.33–7.30 (m, 1H), 6.53 (d, *J* = 9.3 Hz, 1H), 6.30 (s, 1H), 5.43 (dt, *J* = 9.3, 7.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.81 (d, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.30–1.23 (m, 3H), 1.12 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 157.2, 139.9, 139.2, 128.7 (2C), 128.1, 127.3 (2C), 125.9, 121.4, 118.3, 117.7, 60.4, 31.4, 17.9 (6C), 14.4, 13.3 (3C); FT-IR (ATR) *v* 2944, 2866, 1718, 1207, 1061 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{36}O_3Si$ (M^+): 412.2434, found: 412.2451.

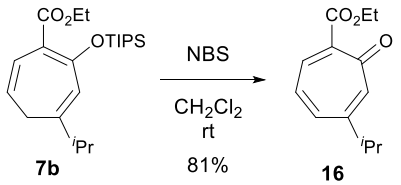


7i

According to the general procedure D, **7i** (18.0 mg, 42.8 μmol, 87% yield) was synthesised from vinylsilane **8i** (20.6 mg, 49.0 μmol) and KO^{t}Bu (1.0 mol/L in THF, 10.0 μL, 10.0 μmol).

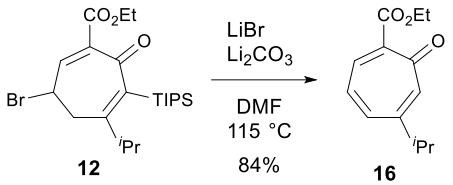
7i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J* = 9.1 Hz, 1H), 5.77 (s, 1H), 5.28 (dt, *J* = 9.1, 7.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.34 (d, *J* = 7.0 Hz, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.50–1.43 (m, 2H), 1.41–1.20 (m, 9H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 157.6, 145.2, 125.4, 120.6, 117.6, 116.9, 60.2, 38.0, 32.1, 31.7, 28.9, 28.6, 22.6, 17.9 (6C), 14.4, 14.1, 13.3 (3C); FT-IR (ATR) *v* 2928, 2866, 1721, 1207, 1060, 882 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{44}O_3Si$ (M^+): 420.3060, found: 420.3050.

Tropone 16



7b **16**

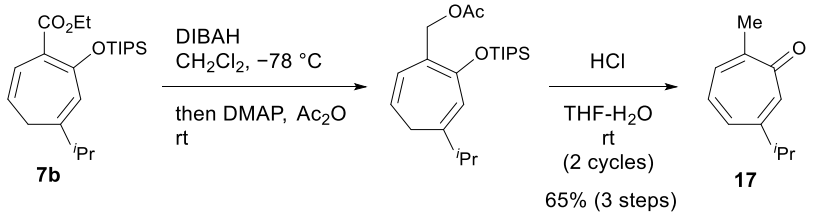
From **7b**: To a solution of **7b** (35.6 mg, 94.0 μmol) in CH_2Cl_2 (0.47 mL) was added NBS (20.2 mg, 0.113 mmol) at −78 °C. The reaction mixture was then warmed up to 0 °C and stirred for 10 min before it was concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 10:1 to 3:1) to afford **16** (16.8 mg, 76.3 μmol, 81% yield) as a yellow oil.



From **12**: To a solution of **12** (44.2 mg, 96.6 μmol) in DMF (0.50 mL) was added successively Li_2CO_3 (21.6 mg, 0.292 mmol) and LiBr (25.8 mg, 0.297 μmol) at room temperature. The reaction mixture was warmed up to 115 °C and stirred for 1 h. After cooling down to room temperature, the reaction was quenched with brine (1.5 mL). Two layers were separated, and the aqueous layer was extracted with Et_2O (0.50 mL × 5). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 3:1) to afford **16** (17.8 mg, 80.8 μmol, 84% yield) as a yellow oil.

16: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.42 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.99–6.97 (m, 2H), 6.91 (dd, *J* = 12.0, 8.6 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.73 (sept, *J* = 6.9 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 167.3, 155.7, 143.0, 139.0, 138.6, 135.3, 131.3, 61.7, 37.7, 22.6 (2C), 14.1; FT-IR (ATR) *v* 2964, 1726, 1633, 1579, 1287, 1230 cm^{-1}; HRMS (FD) calcd for $C_{13}H_{16}O_3$ (M^+): 220.1099, found: 220.1108.

Tropone 17



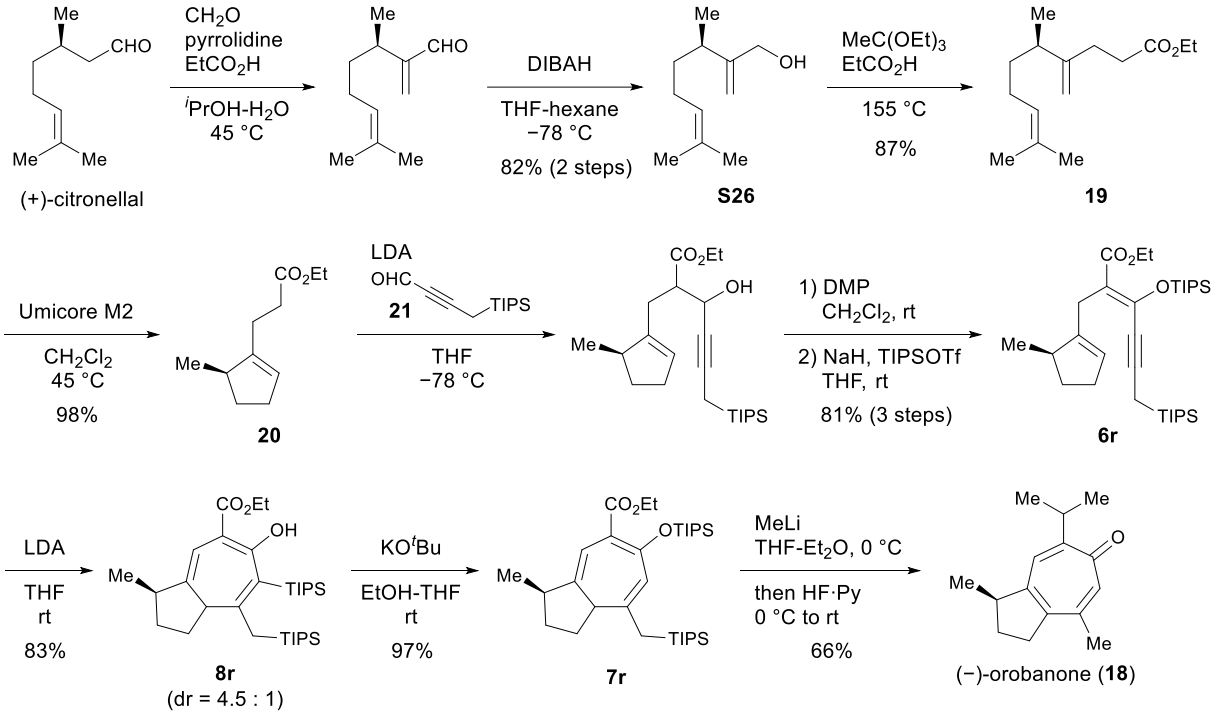
To a solution of **6b** (35.7 mg, 94.3 μmol) in CH_2Cl_2 (0.47 mL) was added DIBAH (1.0 mol/L, 283 μL, 0.283 mmol) at −78 °C. After stirring for 10 min, 4-dimethylaminopyridine (57.8 mg, 0.473 mmol) and Ac_2O (44.5 μL, 0.471 μmol) were added. The reaction mixture was then warmed up to room temperature and stirred for 10 min. The reaction was quenched with 3 M aqueous HCl solution (0.50 mL). After stirring overnight, two layers were separated, and the aqueous layer was extracted with EtOAc (0.50 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford crude acetate.

The crude acetate was dissolved in THF (0.50 mL) and 3 M aqueous HCl solution (0.50 mL). After stirring overnight, the mixture was extracted with EtOAc (0.50 mL × 4). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. This cycle was repeated twice, and the resulting residue was purified by flash column chromatography (SiO_2, hexane:EtOAc =

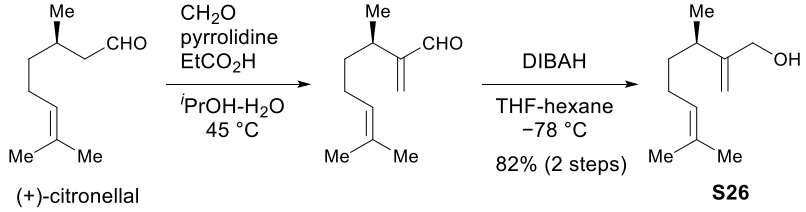
10:1 to 3:1) to afford **17** (9.9 mg, 61 μmol, 65% yield for 3 steps) as a pale yellow oil.

17: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.21 (m, 1H), 7.01 (s, 1H), 6.88–6.83 (m, 2H), 2.75 (sept, J = 6.9 Hz, 1H), 2.24 (d, J = 1.4 Hz, 3H), 1.21 (d, J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 156.1, 151.8, 136.6, 134.5, 134.1, 132.5, 38.0, 22.9 (2C), 22.6; FT-IR (ATR) ν 2962, 1632, 1565, 1471, 794 cm^{-1}; HRMS (FI) calcd for $C_{11}H_{14}O$ (M^+): 162.1045, found: 162.1046.

Total Synthesis of (−)-Orobanone



Alcohol S26

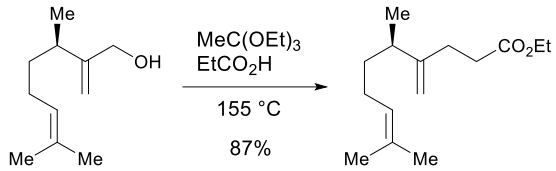


To a solution of (+)-citronellal (907 μL, 5.00 mmol) in ^{i}PrOH (0.50 mL) was added successively CH_2O (37% in H_2O, 387 μL, 5.25 mmol), propionic acid (37.0 μL, 0.500 mmol), and pyrrolidine (41.3 μL, 0.500 mmol) at room temperature. The reaction mixture was warmed up to 45 °C and stirred for 3 h. After cooling down to room temperature, the reaction was quenched with saturated aqueous $NaHCO_3$

solution (2.0 mL), and the organic layer was diluted with Et_2O (2.0 mL). Two layers were separated, and the aqueous layer was extracted with Et_2O (2.0 mL × 4). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was filtered through a short plug of SiO_2 (hexane:EtOAc = 10:1) to afford the product aldehyde.

To a solution of above aldehyde in THF (15 mL) was added DIBAH (1.0 mol/L in hexane, 6.00 mL, 6.00 mmol) at −78 °C. After stirring for 10 min, the reaction was quenched with saturated aqueous Rochelle salt solution (20 mL). The biphasic mixture was warmed up to room temperature and stirred vigorously overnight. Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 10:1 to 3:1) to afford **S26** (694 mg, 4.12 mmol, 82% yield) as a colourless oil. The spectral data matched with those reported in literature. [18]

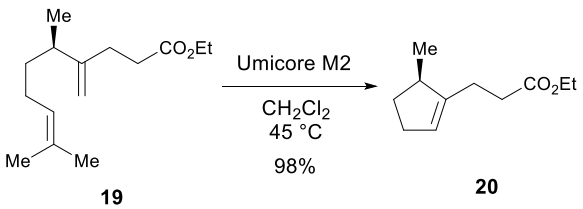
Alkenyl ester S19



S26 **19**

To a solution of **S26** (694 mg, 4.12 mmol) in triethyl orthoacetate (7.52 mL, 41.2 mmol) was added propionic acid (30.6 μL, 0.412 mmol) at room temperature. The reaction mixture was warmed up to 155 °C and stirred under reflux for 3 h with removal of EtOH by distillation. After cooling down to room temperature, the mixture was diluted with Et_2O (5 mL), and the reaction was quenched with 1 M aqueous HCl solution (5.0 mL). After stirring overnight, the mixture was extracted with Et_2O (10 mL × 4). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 50:1 to 30:1) to afford **19** (853 mg, 3.58 mmol, 87% yield) as a colourless oil. The spectral data matched with those reported in literature. [18]

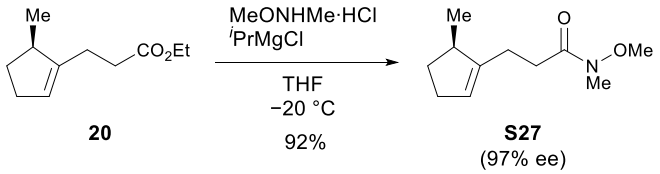
Alkenyl ester 20



19 **20**

To a solution of **19** (853 mg, 3.58 mmol) in CH_2Cl_2 (10 mL) was added Grubbs catalyst® M2 (Umicore, 38.5 mg, 40.6 μmol) at room temperature. The reaction mixture was then warmed up to 45 °C and stirred for 14 h. The resulting mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 50:1) to afford **20** (641 mg, 3.52 mmol, 98% yield) as a pale yellow oil.

20: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, J = 1.7 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 2.60–2.53 (m, 1H), 2.52–2.37 (m, 3H), 2.30–2.13 (m, 3H), 2.12–2.05 (m, 1H), 1.42–1.35 (m, 1H), 1.25 (t, J = 7.0 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 147.2, 123.0, 60.3, 41.4, 32.74, 32.69, 30.6, 24.2, 19.2, 14.2; FT-IR (ATR) ν 2953, 2849, 1736, 1156 cm^{-1}; HRMS (FI) calcd for $C_{11}H_{18}O_2$ (M^+): 182.1307, found: 182.1311; $[\alpha]_D^{22}$ = +17.55 (c 0.315, $CHCl_3$).



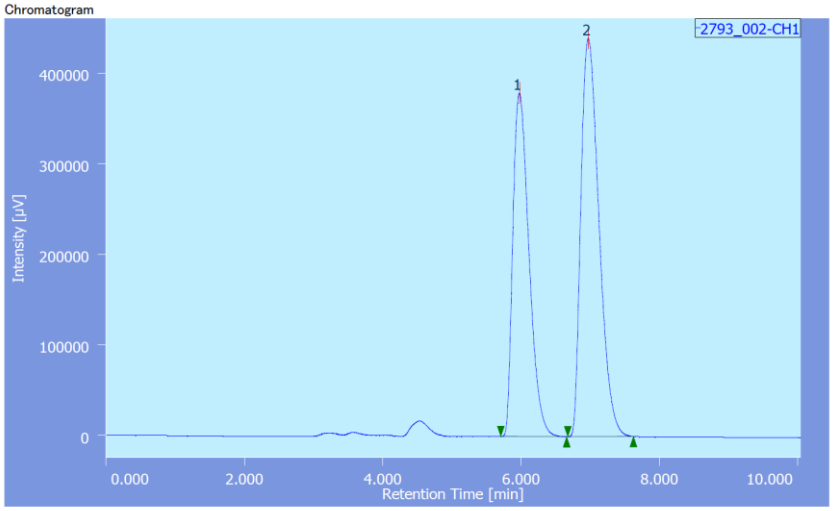
20 **S27** (97% ee)

The enantiomeric excess of **20** was determined after conversion to amide **S27** and HPLC analysis (97% ee).

To a suspension of **20** (17.6 mg, 96.6 μmol) and dimethylhydroxylamine hydrochloride (14.6 mg, 0.150 mmol) in THF (0.50 mL) was added dropwise ^{i}PrMgCl (2.0 mol/L in THF, 0.300 mL, 0.600 mmol) at −20 °C. After stirring for 10 min, the reaction was quenched with saturated aqueous NH_4Cl solution (0.50 mL), and the organic layer was diluted with EtOAc (0.50 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (0.50 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 3:1) to afford **S27** (17.5 mg, 88.7 μmol, 92% yield, 97% ee) as a colourless oil.

S27: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (d, J = 1.7 Hz, 1H), 3.70 (s, 3H), 3.19 (s, 3H), 2.65–2.52 (m, 3H), 2.44–2.38 (m, 1H), 2.32–2.15 (m, 3H), 2.14–2.07 (m, 1H), 1.43–1.37 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 147.9, 122.7, 61.2, 41.5, 32.8, 32.2, 30.6, 30.2, 23.8, 19.3; FT-IR (ATR) ν 2951, 2848, 1664, 1415, 1384, 990 cm^{-1}; HRMS (FD) calcd for $C_{11}H_{19}NO_2$ (M^+): 197.1416, found: 197.1415; $[\alpha]_D^{21}$ = +13.51 (c 0.345, $CHCl_3$).

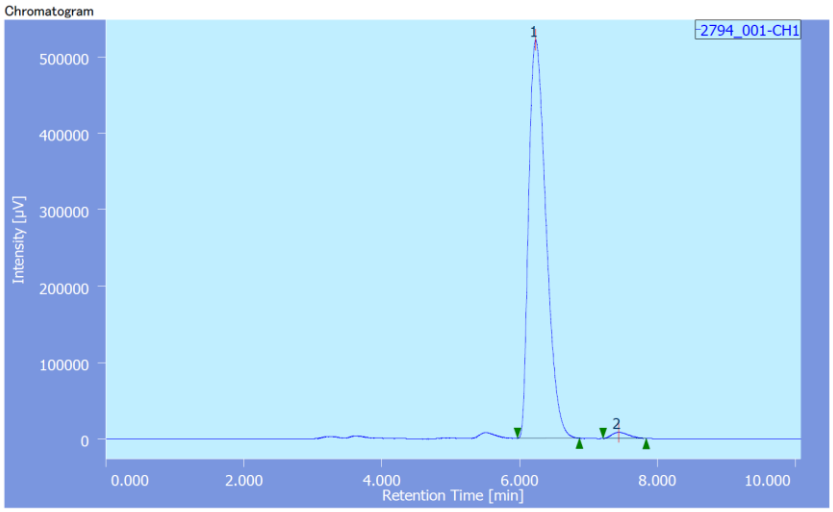
HPLC analysis of *rac*-**S27**



Peak Information

#	tR [min]	Area [μV·sec]	Area%
1	5.975	6156198	43.567
2	6.975	7974367	56.433

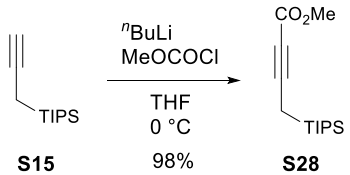
HPLC analysis of **S27**



Peak Information

#	tR [min]	Area [μV·sec]	Area%
1	6.233	9078940	98.480
2	7.433	140152	1.520

Alkynyl ester S28



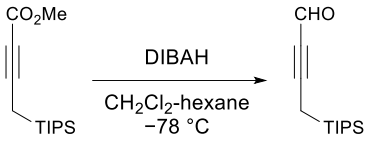
S15 98% **S28**

To a solution of **S15** (819 mg, 4.17 mmol) in THF (12.5 mL) was added ^{n}BuLi (2.65 mol/L in hexane,

1.57 mL, 4.17 mmol) at −78 °C. After stirring for 20 min, methyl chloroformate (384 μL, 5.00 mmol) was added, and the reaction mixture was warmed up to 0 °C and stirred for 10 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL), and the organic layer was diluted with EtOAc (10 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 50:1 to 20:1) to afford **S28** (1.04 g, 4.08 mmol, 98% yield) as a colourless oil.

S28: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 3H), 1.69 (s, 2H), 1.21–1.14 (m, 3H), 1.08 (d, J = 6.9 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 90.5, 72.4, 52.3, 18.4 (6C), 11.0 (3C), −0.2; FT-IR (ATR) ν 2944, 2867, 2225, 1711, 1261, 1073 cm^{-1}; HRMS (FI) calcd for $C_{14}H_{26}O_2Si$ (M^+): 254.1702, found: 254.1690.

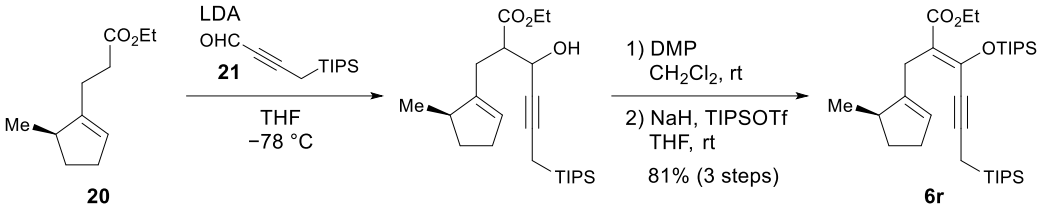
Alkynyl aldehyde 21



To a solution of **S28** (871 mg, 3.42 mmol) in CH_2Cl_2 (12.5 mL) was added DIBAH (1.0 mol/L in hexane, 4.11 mL, 4.11 mmol) at −78 °C. After stirring for 10 min, the reaction was quenched with saturated aqueous Rochelle salt solution (12.5 mL). The biphasic mixture was warmed up to room temperature and stirred vigorously for 2 h. Two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 50:1 to 20:1) to afford **21** (687 mg, 3.06 mmol, 89% yield) as a colourless oil.

21: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 1.80 (s, 2H), 1.22–1.14 (m, 3H), 1.09 (d, J = 6.9 Hz, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 101.4, 82.4, 18.4 (6C), 11.1 (3C), 0.9; FT-IR (ATR) ν 2943, 2867, 2184, 1666, 822 cm^{-1}; HRMS (FI) calcd for $C_{13}H_{24}OSi$ (M^+): 224.1596, found: 224.1588.

Dienyne ester 6r



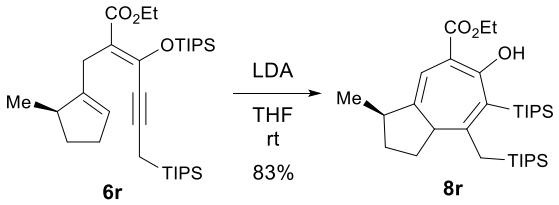
An LDA solution (1 mol/L in THF-hexane) was prepared by the addition of ^{n}BuLi (2.65 mol/L in hexane, 755 μL, 2.00 mmol) to a solution of $^{i}Pr_2NH$ (281 μL, 2.00 mmol) in THF (1.25 mL) at 0 °C. The mixture was stirred for 20 min at the same temperature before the use. To another flask charged with **20** (183 mg, 1.00 mmol) in THF (5.0 mL) was added the LDA solution (1.20 mL, 1.20 mmol) via a syringe at −78 °C. After stirring for 20 min, aldehyde **21** (269 mg, 1.20 mmol) in THF (0.50 mL) was added via cannula, and the mixture was stirred for 10 min at the same temperature. The reaction was quenched with saturated aqueous NH_4Cl solution (5.0 mL), and the organic layer was diluted with EtOAc (5.0 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 20:1 to 3:1) to afford the product *β*-hydroxyester (diastereomeric mixture, 379 mg, 0.931 mmol, 93% yield).

To a solution of above *β*-hydroxyester (379 mg, 0.931 mmol) in CH_2Cl_2 was added Dess-Martin periodinane (473 mg, 1.12 mmol) at 0 °C. The reaction mixture was then warmed up to room temperature and stirred for 30 min. Another Dess-Martin periodinane (118 mg, 0.279 mmol) was added, and the reaction mixture was stirred for 20 min. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution (5.0 mL) and $Na_2S_2O_3·5H_2O$ (770 mg). After stirring vigorously for 50 min, the two layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was filtered through a short plug of SiO_2 (hexane:EtOAc = 10:1) to afford the product *β*-ketoester.

NaH (60% dispersion in mineral oil, 74.7 mg, 1.87 mmol) was washed with hexane (4.0 mL) and suspended with THF (4.0 mL). To this suspension was added above *β*-ketoester in THF (1.0 mL) via cannula at 0 °C. After stirring for 15 min, TIPSOTf (375 μL, 1.40 mmol) was added, and the reaction mixture was warmed up to room temperature and stirred for 15 min. The reaction was quenched by the careful addition of saturated aqueous $NaHCO_3$ solution (5.0 mL), and the organic layer was diluted with EtOAc (5.0 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford **6r** (458 mg, 0.817 mmol, 88% yield for 2 steps) as a yellow oil.

6r: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.56–2.51 (m, 1H), 2.26–2.21 (m, 1H), 2.15–2.03 (m, 2H), 1.71 (s, 2H), 1.41–1.26 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.17–1.08 (m, 3H), 1.11 (d, *J* = 6.9 Hz, 18H), 1.06 (d, *J* = 6.9 Hz, 18H), 1.02 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 146.8, 139.9, 123.2, 115.8, 96.0, 76.4, 59.7, 41.7, 32.9, 30.5, 30.0, 19.3, 18.51 (3C), 18.49 (3C), 18.0 (6C), 14.3, 13.1 (3C), 11.0 (3C), 0.4; FT-IR (ATR) *ν* 2943, 2866, 2205, 1716, 1462, 1173, 881 cm^{-1}; HRMS (FD) calcd for $C_{33}H_{60}O_3Si_2$ (M^+): 560.4081, found: 560.4068; $[\alpha]_D^{21}$= +30.72 (*c* 1.02, $CHCl_3$).

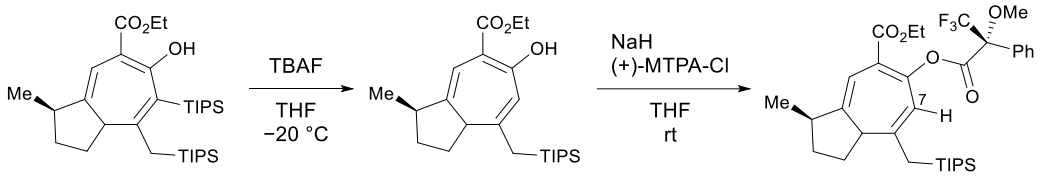
Bicyclic ester 8r



An LDA solution (1 mol/L in THF-hexane) was prepared by the addition of ^{n}BuLi (2.65 mol/L in hexane, 755 μL, 2.00 mmol) to a solution of $^{i}Pr_2NH$ (281 μL, 2.00 mmol) in THF (1.25 mL) at 0 °C. The mixture was stirred for 20 min at the same temperature before the use. To another reaction vessel charged with **6r** (282 mg, 0.502 mmol) in THF (5.0 mL) was added the LDA solution (1.00 mL, 1.00 mmol) via a syringe at 0 °C. The reaction mixture was then warmed up to room temperature and stirred for 20 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (5.0 mL), and the organic layer was diluted with EtOAc (5.0 mL). Two layers were separated, and the aqueous layer was extracted three times with EtOAc (5.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford **8r** (dr = 4.5:1, 234 mg, 0.416 mmol, 83% yield) as a yellow semisolid. The diastereomers were inseparable even after PTLC, and the characterisation data were collected as the mixture.

8r (diasteromeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (t, *J* = 1.7 Hz, 0.82 × 1H), 5.92 (t, *J* = 2.0 Hz, 0.18 × 1H), 4.32–4.26 (m, 1H), 4.25–4.19 (m, 1H), 2.80–2.76 (m, 1H), 2.66–2.59 (m, 0.82 × 1H), 2.34–2.29 (m, 0.18 × 1H), 2.10–1.90 (m, 4H), 1.74–1.66 (m, 1H), 1.48–1.40 (m, 3H), 1.35–1.21 (m, 7H), 1.14–1.02 (m, 39H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 177.5, 172.4, 172.3, 168.1, 167.0, 151.3, 150.8, 127.1, 125.6, 113.1, 110.9, 103.8, 103.4, 60.4, 60.3, 48.6, 48.5, 38.0, 35.9, 35.1, 28.2, 27.3, 22.0, 20.7, 20.2, 19.9, 19.7, 19.4, 19.30, 19.26, 19.22, 17.2, 14.34, 14.31, 13.6, 13.5 (only detected signals were recorded); FT-IR (ATR) *ν* 2944, 2865, 1634, 1370, 1218, 1068, 880 cm^{-1}; HRMS (FD)

calcd for $C_{33}H_{60}O_3Si_2$ (M^+): 560.4081, found: 560.4069; $[\alpha]_D^{22}$= +81.62 (*c* 0.99, $CHCl_3$).

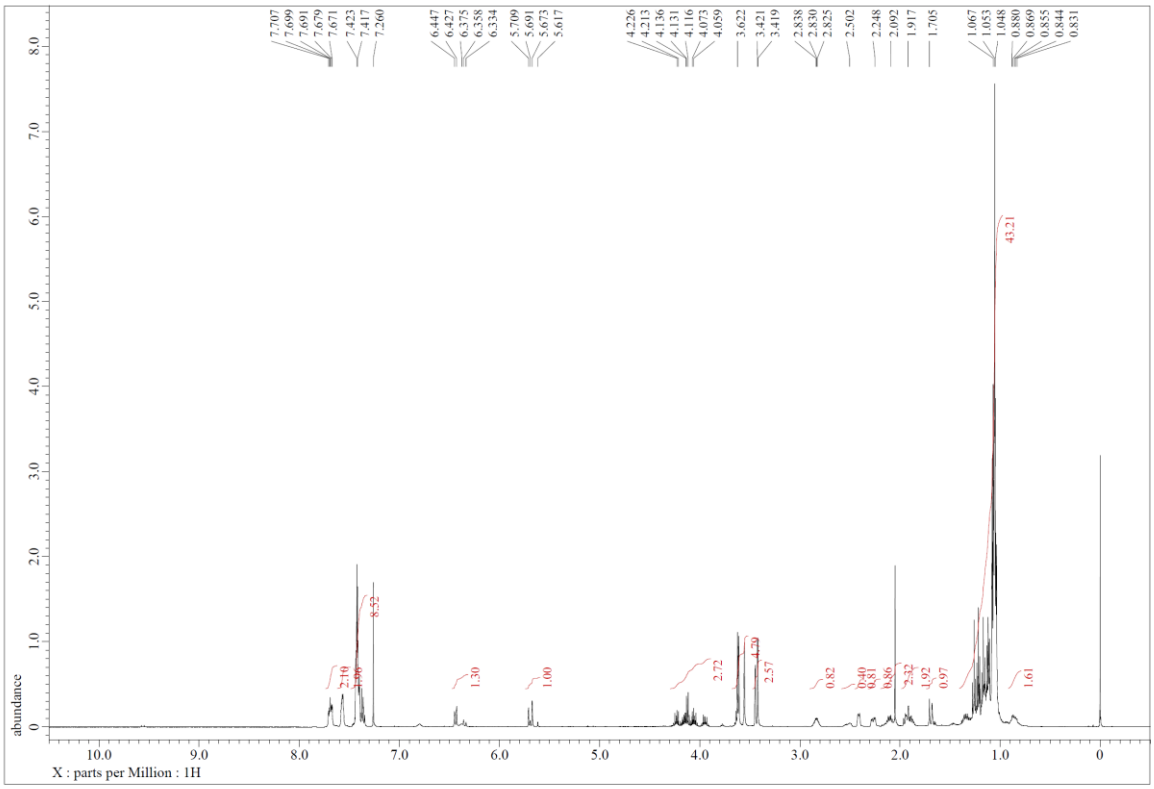


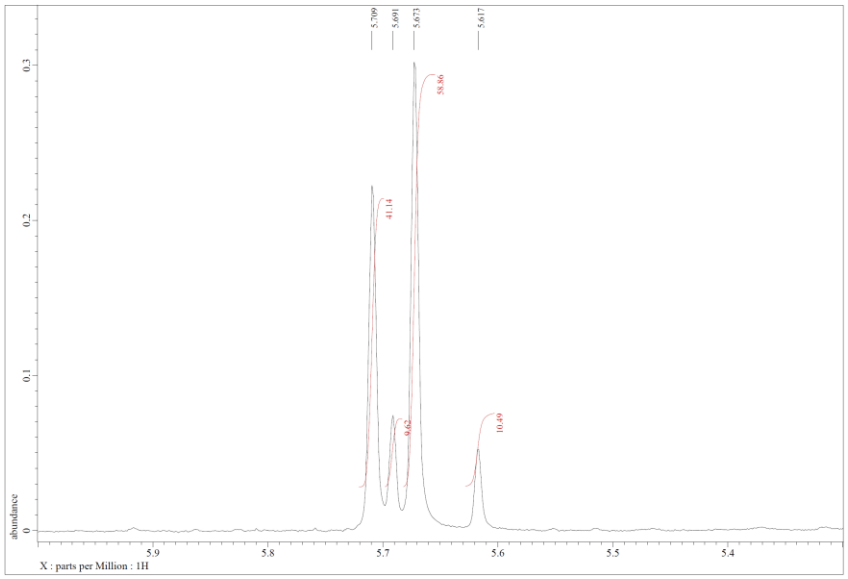
The enantiomeric excess of **8r** was approximately estimated after conversion to a diastereomeric mixture of chiral enol ester **S29** and comparing the integration values of H-7 proton (δ 5.71–5.62 ppm) of the crude product on ^{1}H NMR (ca. 97% ee).

To a solution of **8r** (diastereomeric mixture, 10.8 mg, 19.3 μmol) in THF (0.20 mL) was added tetrabutylammonium fluoride (1.0 mol/L in THF, 30.0 μL, 30.0 μmol) at −20 °C. After stirring for 5 min, the reaction was quenched with saturated aqueous NH_4Cl solution (0.50 mL), and the organic layer was diluted with EtOAc (0.50 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (0.50 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was filtered through a short plug of SiO_2 (hexane:EtOAc = 30:1) to afford the product enol ester.

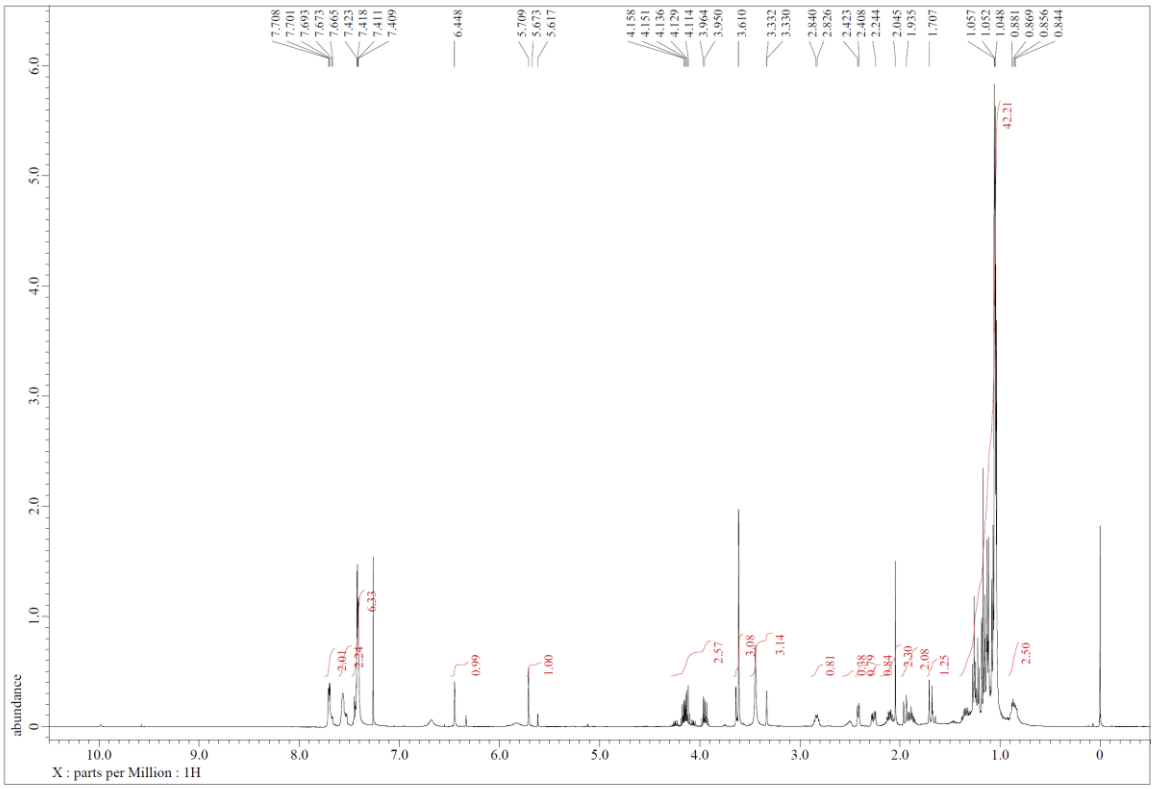
To a solution of above enol ester in THF (0.20 mL) was added NaH (60% dispersion in mineral oil, 2.6 mg, 65 μmol) at 0 °C. After stirring for 10 min, (+)-*α*-methoxy-*α*-(trifluoromethyl)phenylacetyl chloride (7.5 μL, 40 μmol) was added. The reaction mixture was then warmed up to room temperature and stirred for 10 min. The reaction was quenched with saturated aqueous NH_4Cl solution (0.50 mL), and the organic layer was diluted with EtOAc (0.50 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (0.50 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford crude **S29**.

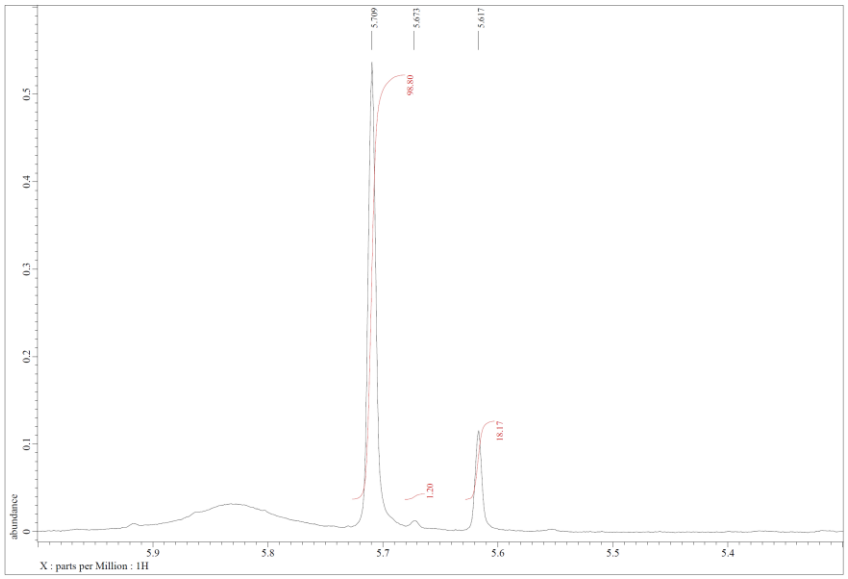
^{1}H NMR spectrum of crude *rac*-**S29** (500 MHz, $CDCl_3$)



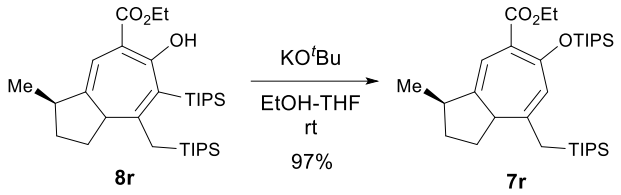


^{1}H NMR spectrum of crude **S29** (500 MHz, $CDCl_3$)





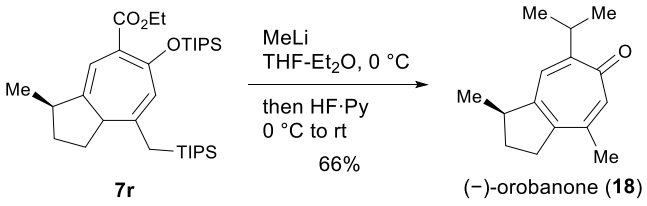
Bicyclic ester 7r



To a suspension of **8r** (84.5 mg, 0.151 mmol) in EtOH (0.75 mL) was added KO^{t}Bu (1.0 mol/L in THF, 150 μL, 0.150 mmol) at room temperature. After stirring for 1.5 h, the reaction was quenched with saturated aqueous NH_4Cl solution (1.0 mL), and the resulting mixture was extracted with Et_2O (1.0 mL × 4). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 100:1) to afford **7r** (dr = 4.6:1, 81.4 mg, 0.145 mmol, 97% yield) as a yellow oil. The diastereomers were inseparable even after PTLC, and the characterisation data were collected as the mixture.

7r (diasteromeric mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (s, 0.82 × 1H), 6.13 (s, 0.18 × 1H), 5.71 (s, 1H), 4.31–4.25 (m, 1H), 4.19–4.13 (m, 1H), 2.82–2.75 (m, 0.82 × 1H), 2.44–2.39 (m, 0.18 × 1H), 2.35 (dd, J = 6.9, 6.9 Hz, 0.18 × 1H), 2.28 (d, J = 8.0 Hz, 0.82 × 1H), 2.19 (dd, J = 13.8, 6.3 Hz, 0.82 × 1H), 2.09–1.95 (m, 1H + 0.18 × 2H), 1.88–1.79 (m, 1H + 0.82 × 1H), 1.67 (d, J = 14.3 Hz, 0.82 × 1H), 1.62 (d, J = 13.7 Hz, 0.18 × 1H), 1.40–1.29 (m, 4H), 1.26–1.15 (m, 6H), 1.11–1.06 (m, 39H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 169.0, 155.1, 154.7, 144.4, 143.7, 142.2, 120.1, 119.4, 117.7, 117.1, 115.2, 114.1, 60.2, 47.0, 46.6, 38.8, 38.5, 35.9, 35.2, 27.6, 26.4, 20.2, 18.7, 18.3, 18.04, 18.00, 15.3, 14.4, 13.8, 13.7, 13.4, 11.53, 11.48 (only detected signals were recorded); FT-IR (ATR) ν 2942, 2865, 1717, 1462, 1213, 881 cm^{-1}; HRMS (FD) calcd for $C_{33}H_{60}O_3Si_2$ (M^+): 560.4081, found: 560.4080; $[\alpha]_D^{22} = -7.397$ (c 1.02, $CHCl_3$).

(−)-orobanone (18)



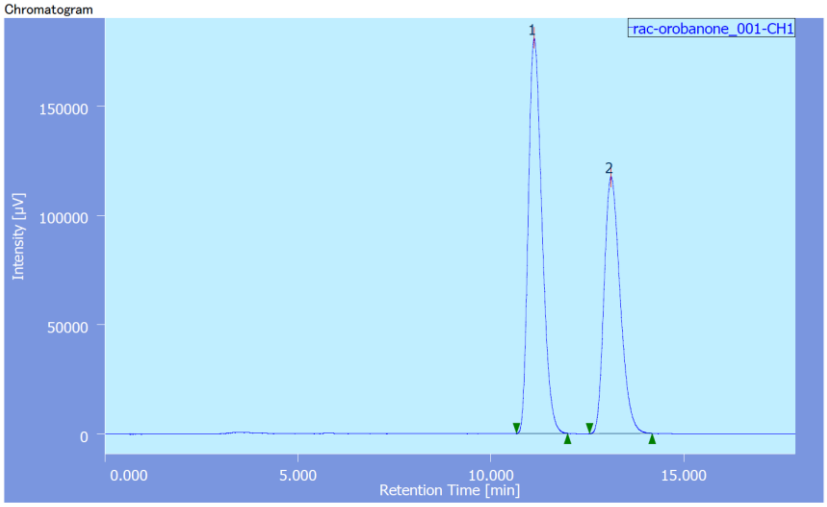
To a solution of **7r** (40.5 mg, 72.2 μmol) in THF (0.72 mL) was added MeLi (1.13 mol/L in Et_2O, 0.319 mL, 0.361 mmol) at −78 °C. The reaction mixture was then warmed up to 0 °C and stirred for 10 min. To this mixture was added dropwise HF·pyridine (HF: 67%, 0.180 mL), and the resulting suspension was stirred vigorously for 30 min at 0 °C. The mixture was then warmed up to room temperature and

stirred for 21 h. The reaction was quenched by the careful addition of saturated aqueous $NaHCO_3$ solution (1.0 mL), and the mixture was neutralised with additional $NaHCO_3$ (powder). EtOAc (1.0 mL) was added, the two layers were separated, and the aqueous layer was extracted with EtOAc (1.0 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane:EtOAc = 10:1 to 3:1) to afford **18** (10.3 mg, 47.6 µmol, 66% yield, 87% ee) as a pale brown solid.

18: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (s, 1H), 7.00 (s, 1H), 3.47 (sept, J = 6.9 Hz, 1H), 3.22–3.15 (m, 1H), 2.92–2.85 (m, 1H), 2.80–2.74 (m, 1H), 2.22 (s, 3H), 2.21 (dddd, J = 12.6, 8.5, 8.5, 6.2 Hz, 1H), 1.59 (dddd, J = 12.6, 8.6, 6.0, 6.0 Hz, 1H), 1.24 (d, J = 7.4 Hz, 3H), 1.18 (d, J = 6.5 Hz, 3H), 1.16 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.4, 158.2, 149.8, 145.6, 144.7, 138.9, 129.8, 44.9, 34.5, 30.7, 29.8, 25.1, 22.6 (2C), 20.5; FT-IR (ATR) ν 2956, 2868, 1614, 1561, 1516, cm^{-1}; HRMS (FI) calcd for $C_{15}H_{20}O$ (M^+): 216.1514, found: 216.1525; m.p. (hexane) 48–53 °C; $[\alpha]_D^{19}$= −4.114 (c 0.25, MeOH).

lit. [20] $[\alpha]_D^{20}$= −5.21 (c 0.15, MeOH)

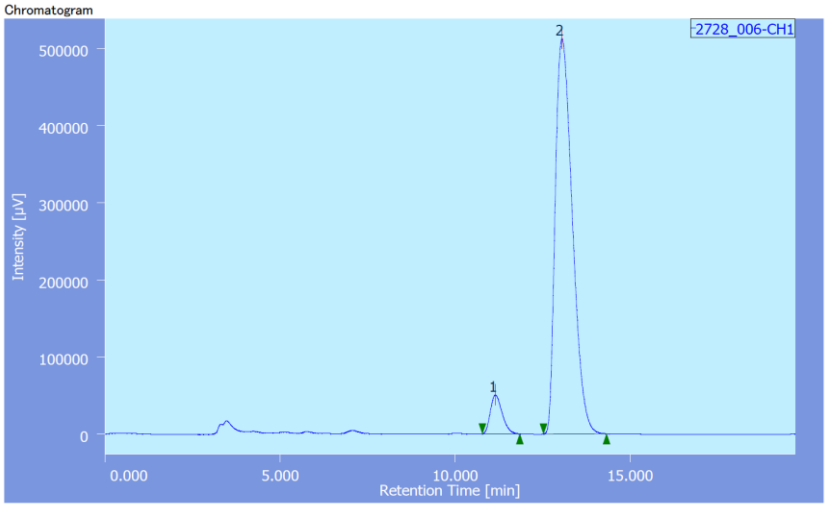
HPLC analysis of *rac*-**18**



Peak Information

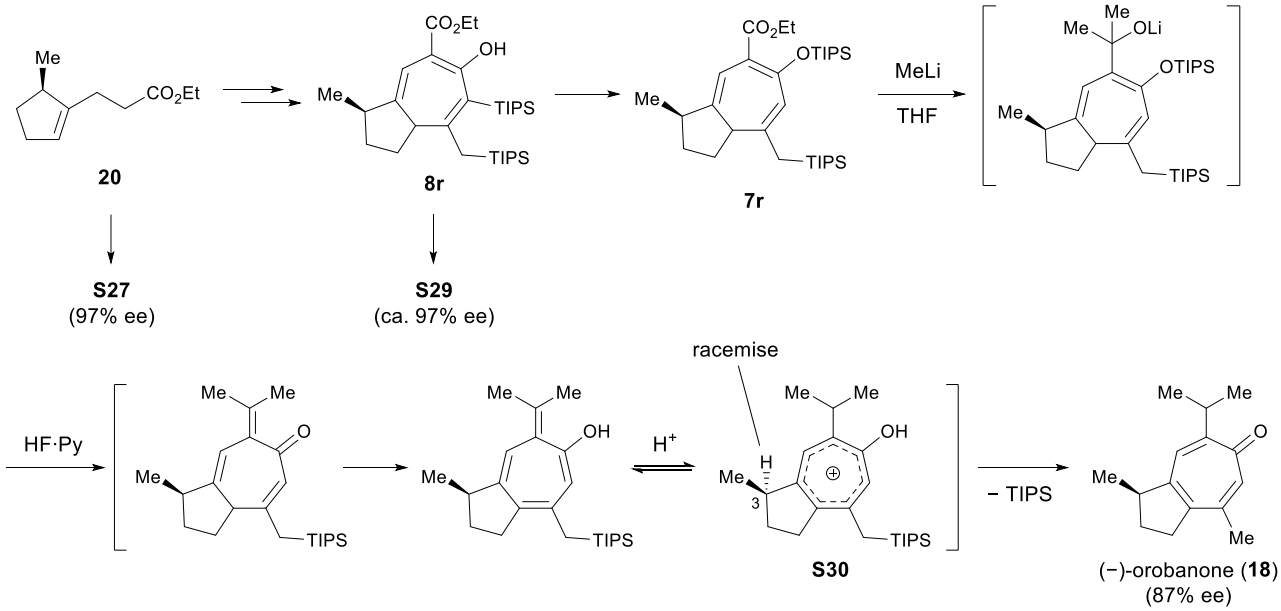
#	tR [min]	Area [µV·sec]	Area%
1	11.117	4441014	56.662
2	13.108	3396721	43.338

HPLC analysis of **18**



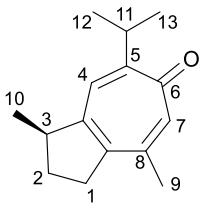
Peak Information

#	tR [min]	Area [μV·sec]	Area%
1	11.142	1183679	6.383
2	13.042	17360268	93.617



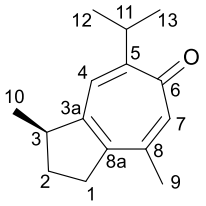
The slight decrease of enantiomeric excess is probably due to the racemisation at C3 position of the tropylium cation intermediate **S30** generated in the final step.

Table S2. Comparison of ^{1}H NMR spectral data.



proton number	^{1}H NMR, δ (ppm)			
	synthetic (500 MHz, $CDCl_3$)	natural [19] (250 MHz, $CHCl_3$)	natural [20] (400/500 MHz, $CDCl_3$)	natural [21] (600 MHz, $CDCl_3$)
1	2.89 (m) 2.77 (m)	2.83	2.82 (m) 2.72 (m)	2.99 (m) 2.87 (m)
2	2.21 (dddd) 1.59 (dddd)	- 1.61	2.14 (dddd) 1.52 (dddd)	2.25 (m) 1.62 (m)
3	3.19 (m)	3.15	3.12 (m)	3.26 (m)
4	7.10 (s)	7.093	7.03 (s)	7.33 (s)
7	7.00 (s)	6.995	6.93 (s)	7.01 (s)
9	2.22 (s)	2.225	2.15 (d)	2.30 (s)
10	1.24 (d)	1.249	1.17 (d)	1.65 (d)
11	3.47 (sept)	3.48	3.40 (sept)	3.39 (sept)
12/13	1.18 (d) 1.16 (d)	1.181 1.165	1.11 (d) 1.09 (d)	1.26 (d) 1.18 (d)

Table S3. Comparison of ^{13}C NMR spectral data.



carbon number	^{13}C NMR, δ (ppm)			
	synthetic (126 MHz, $CDCl_3$)	natural [19] (25.03 MHz, $CDCl_3$)	natural [20] (100/125 MHz, $CDCl_3$)	natural [21] (150 MHz, $CDCl_3$)
1	34.5	34.53	33.52	35.4
2	30.7	30.72	29.71	31.7
3	44.9	44.90	43.88	46.2
3a	145.6	145.61	148.79	152.6
4	129.8	129.78	128.78	132.7
5	158.2	158.19	157.20	159.2
6	185.4	185.41	184.40	187.0
7	138.9	138.90	137.87	139.3
8	149.8	149.78	143.68	148.5
8a	144.7	144.72	144.59	148.6
9	25.1	25.12	24.04	25.4
10	20.5	20.48	19.45	20.8
11	29.8	29.81	28.83	31.2
12/13	22.6	22.59	21.55	22.8
			21.54	22.7

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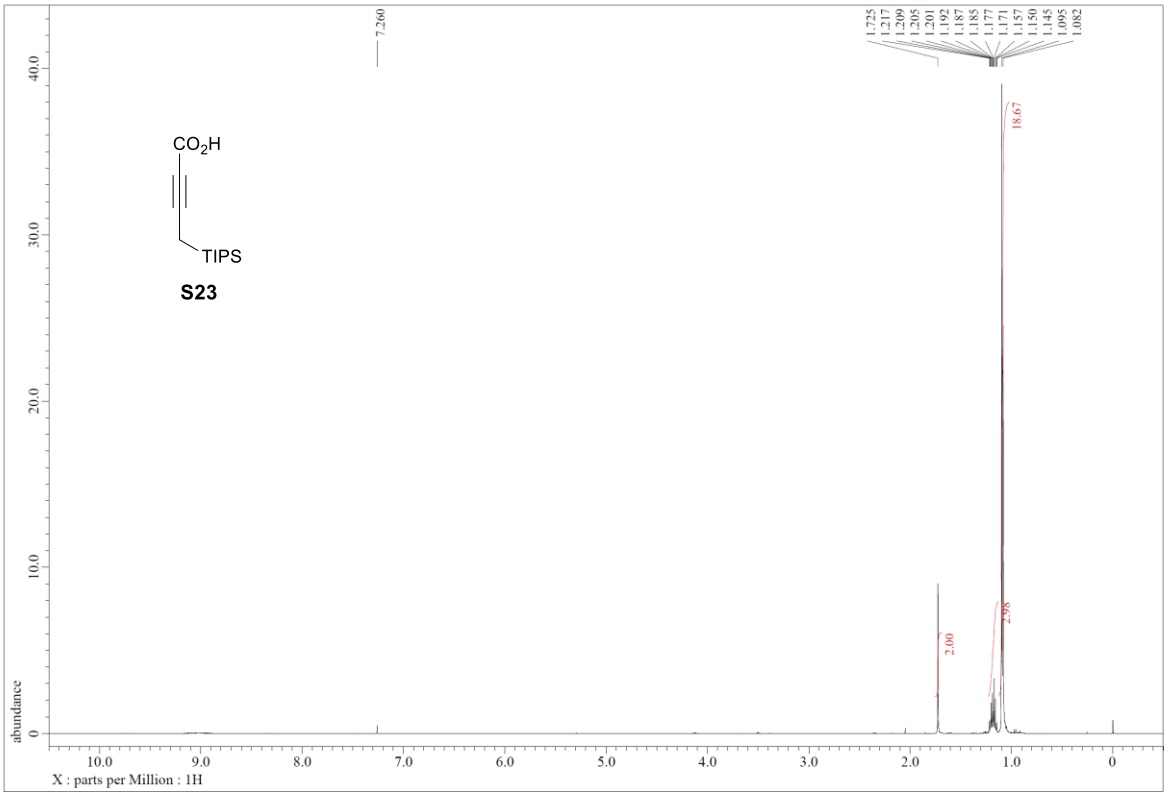
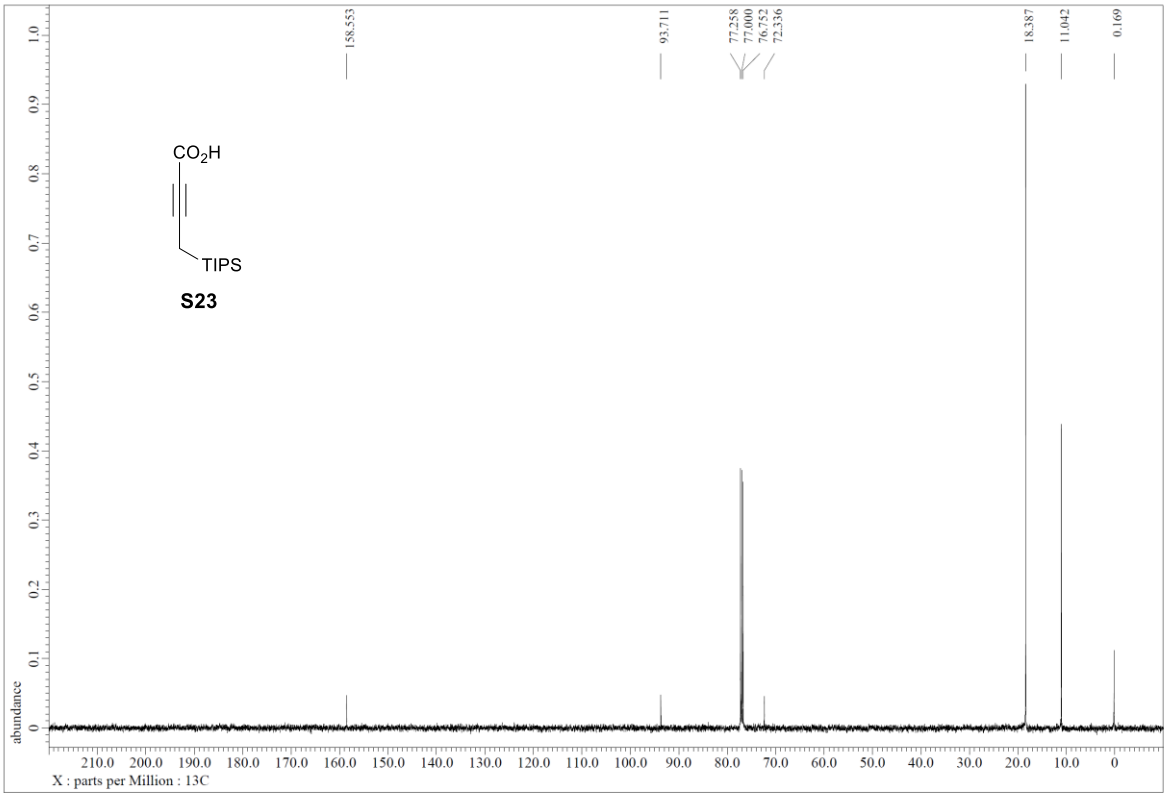
^{1}H and ^{13}C NMR Spectra

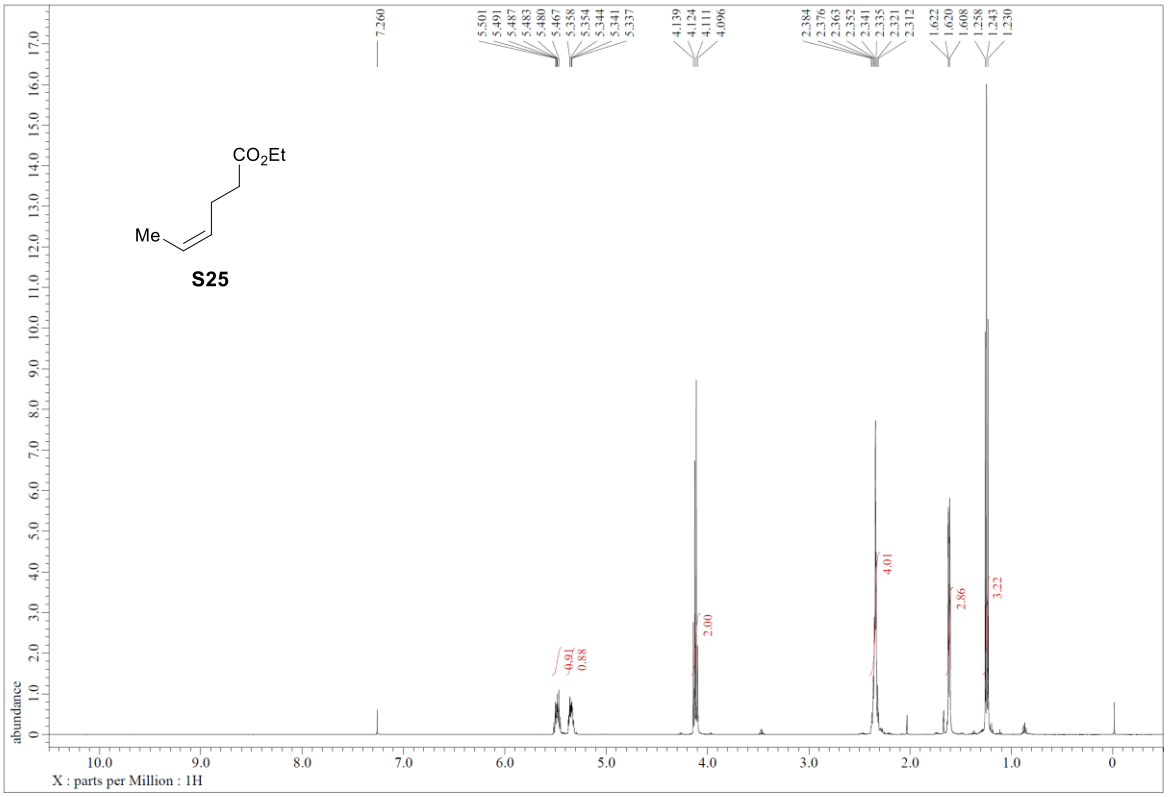
S23 (^{1}H NMR, 500 MHz, $CDCl_3$)



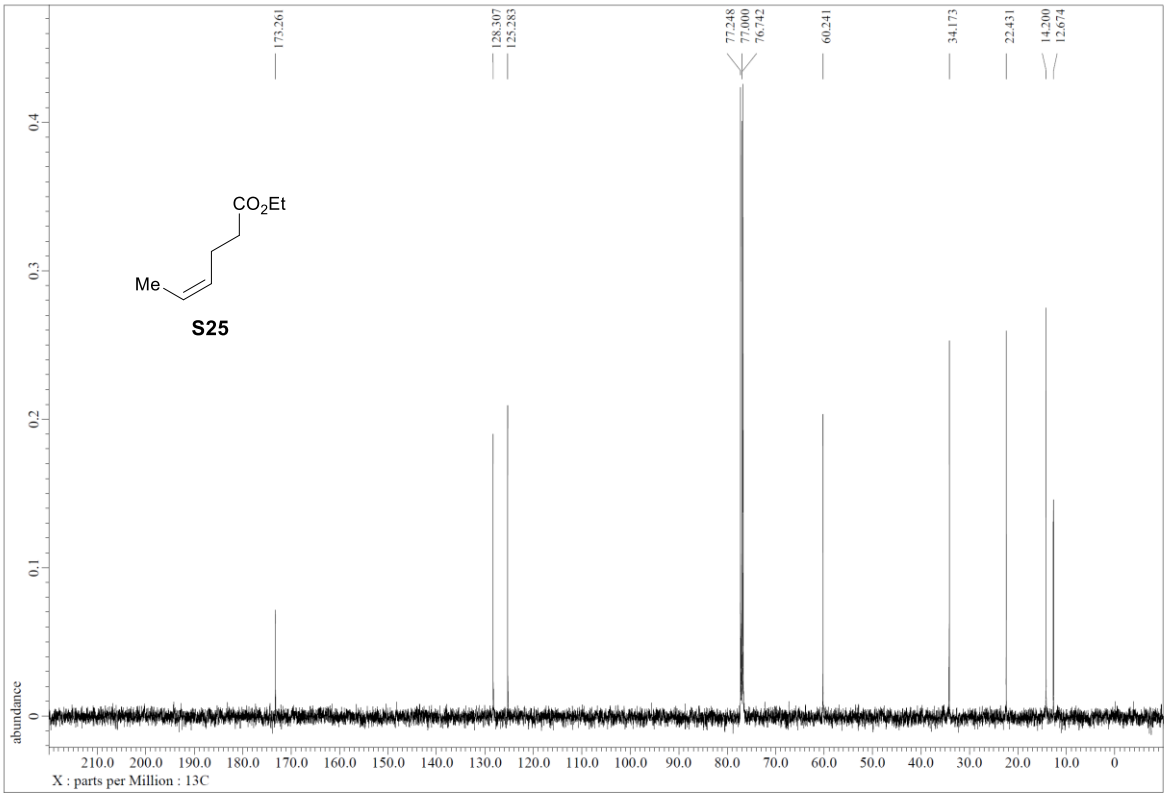
S23 (^{13}C NMR, 126 MHz, $CDCl_3$)



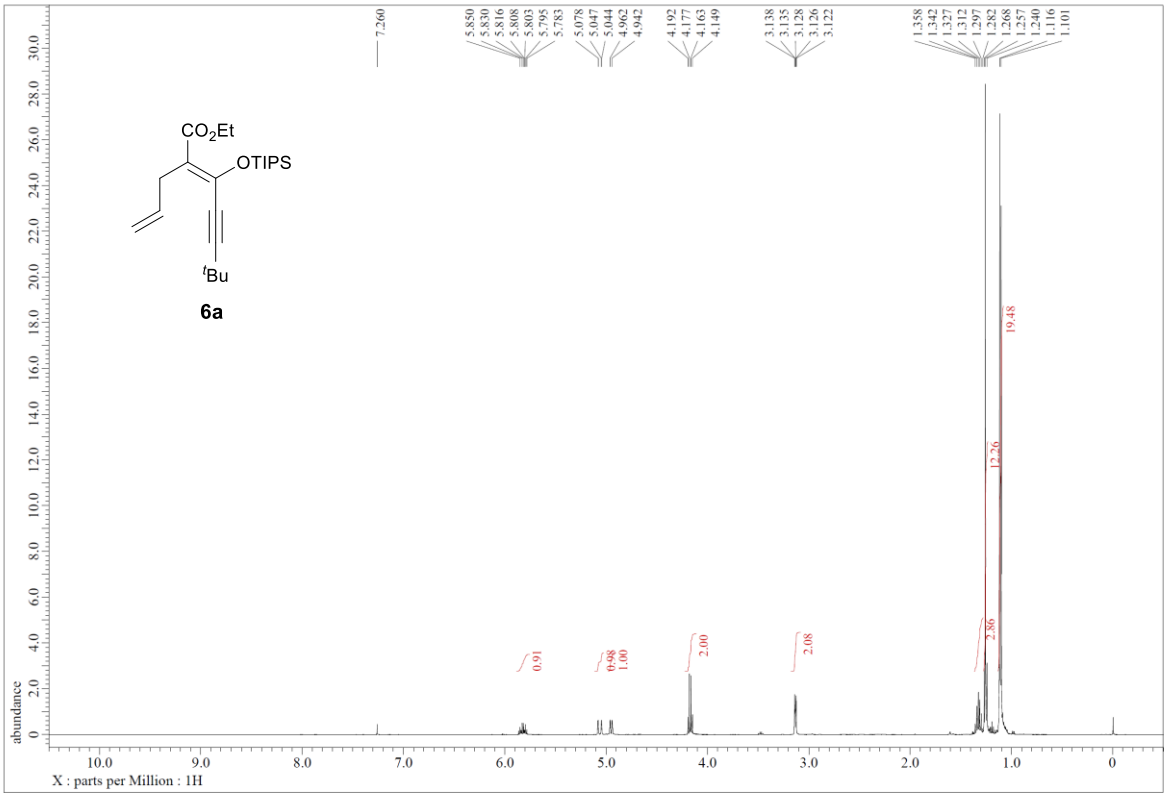
S25 (^{1}H NMR, 500 MHz, $CDCl_3$)



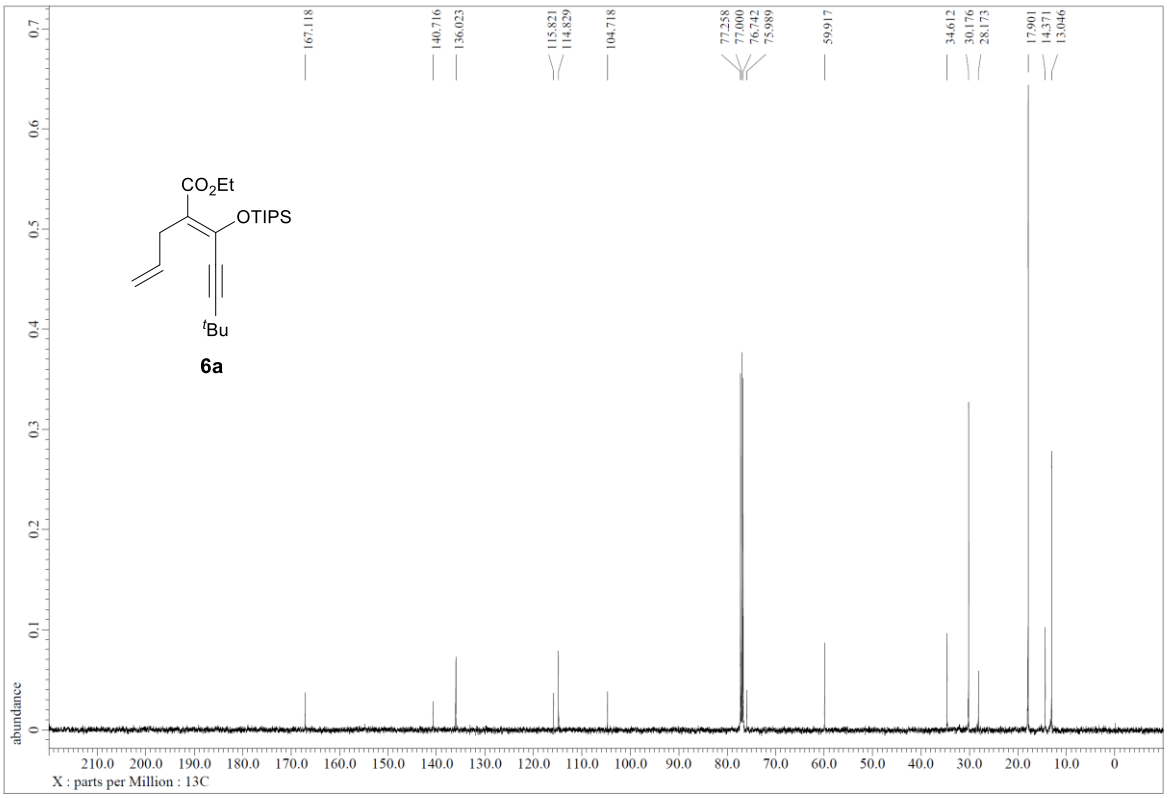
S25 (^{13}C NMR, 126 MHz, $CDCl_3$)



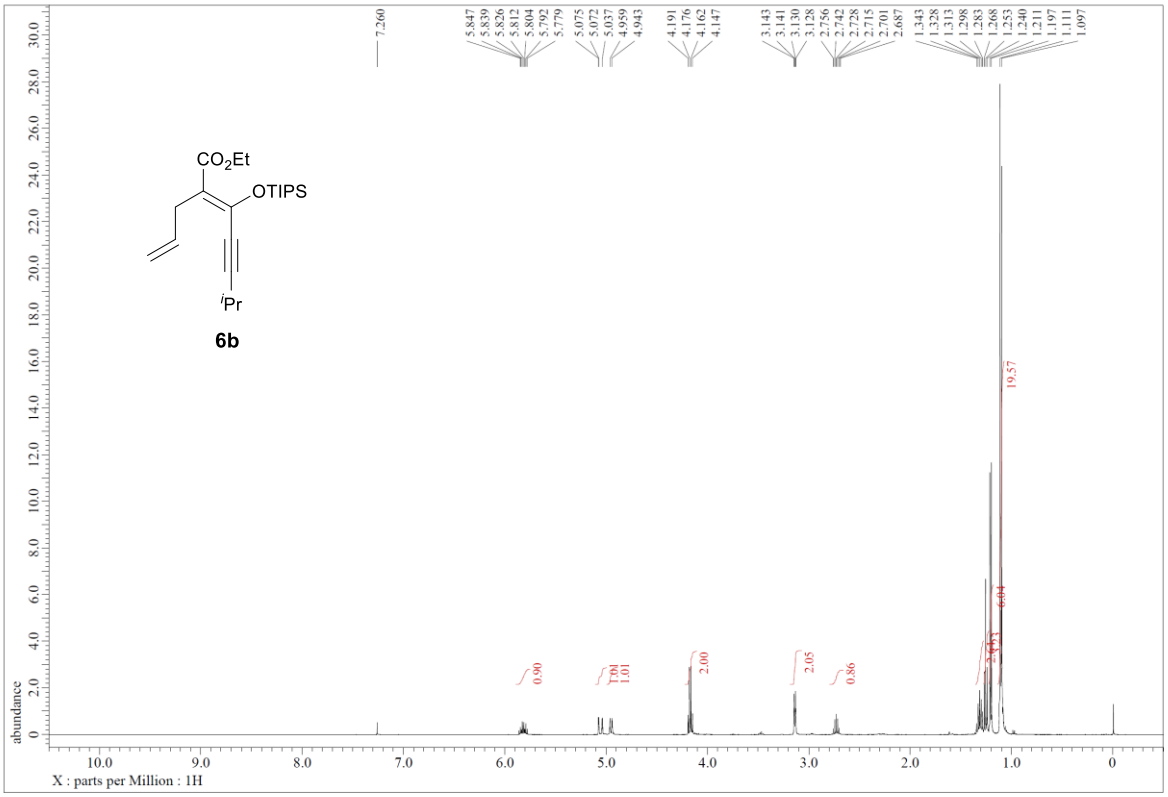
6a (^{1}H NMR, 500 MHz, $CDCl_3$)



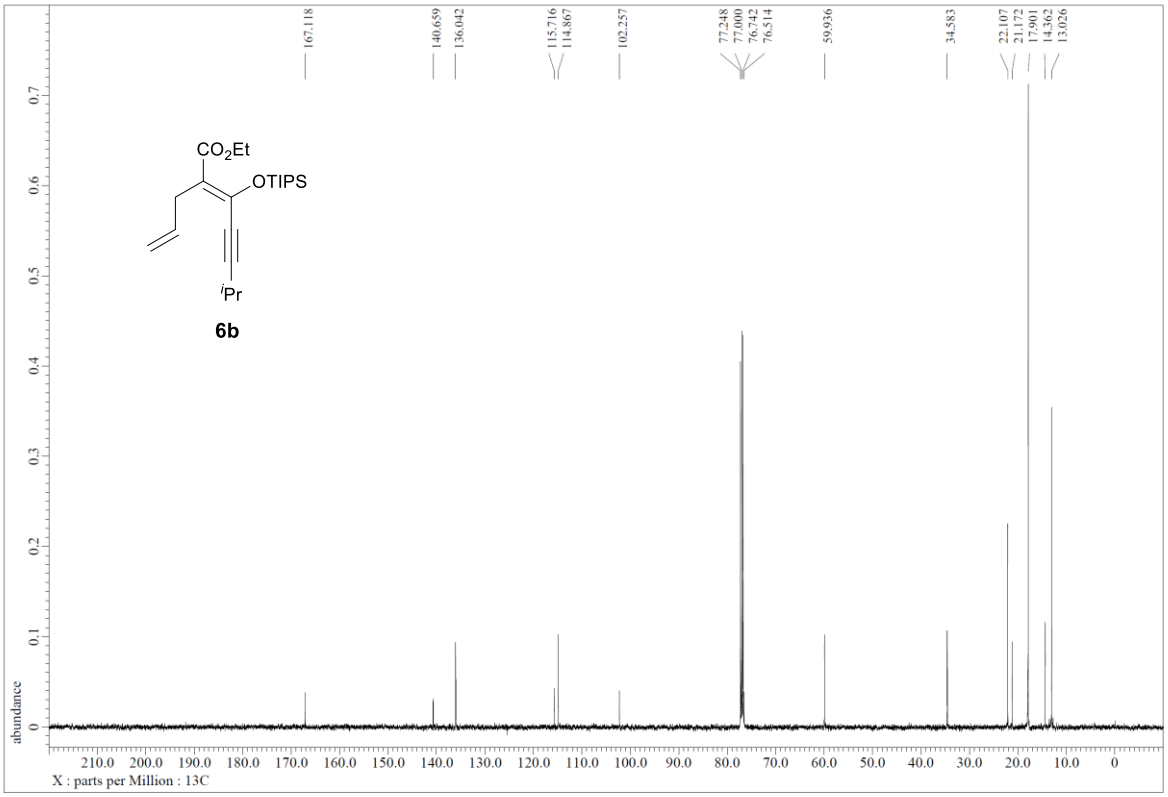
6a (^{13}C NMR, 126 MHz, $CDCl_3$)



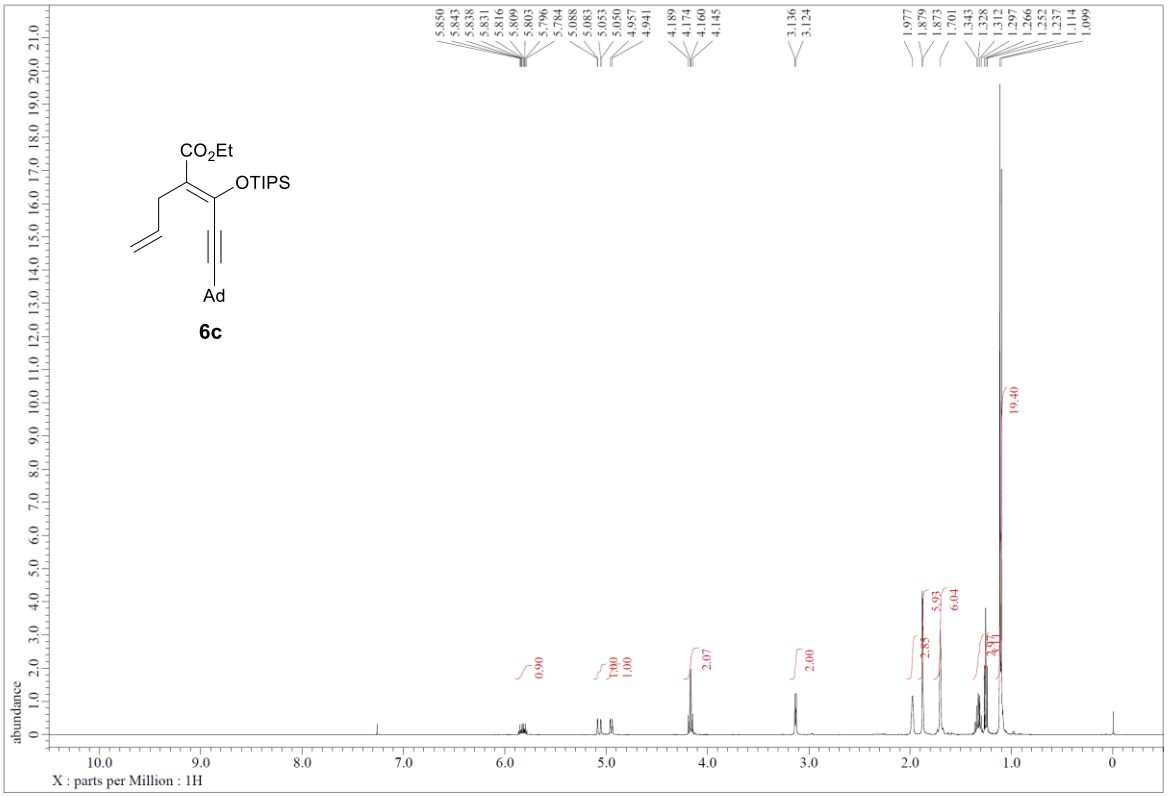
6b (^{1}H NMR, 500 MHz, $CDCl_3$)



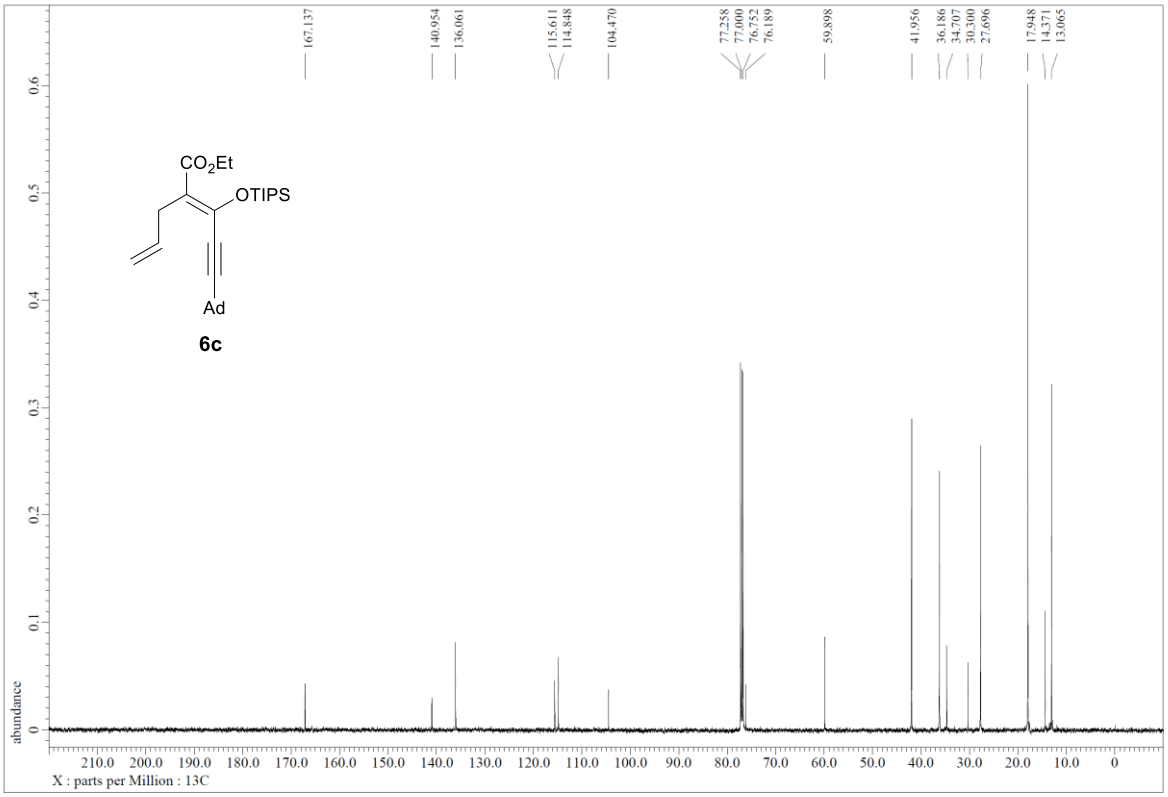
6b (^{13}C NMR, 126 MHz, $CDCl_3$)



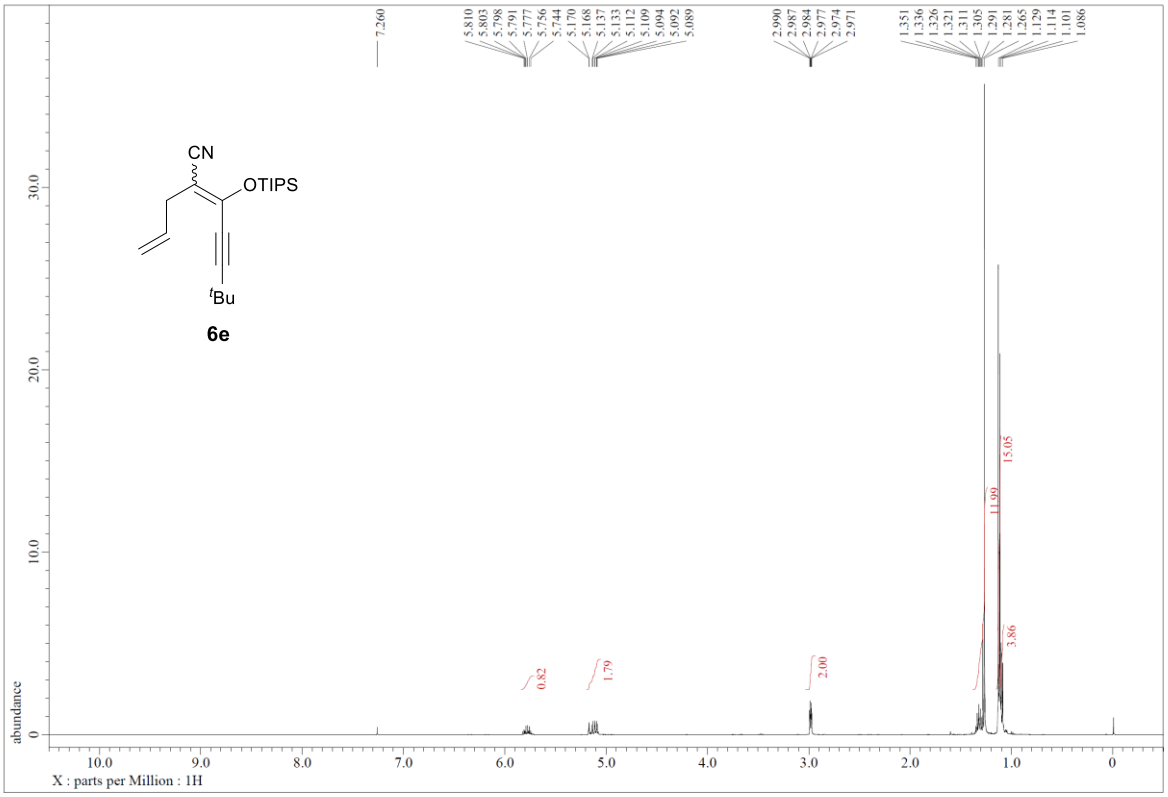
6c (^{1}H NMR, 500 MHz, $CDCl_3$)



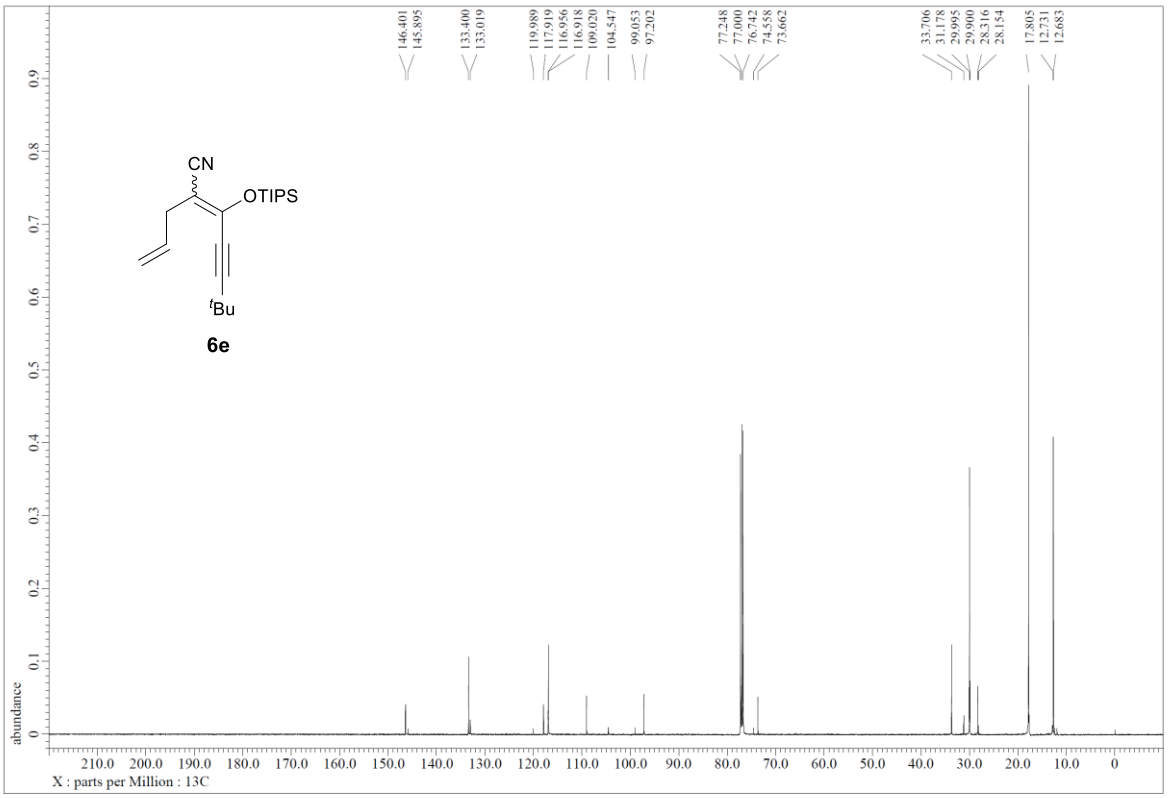
6c (^{13}C NMR, 126 MHz, $CDCl_3$)



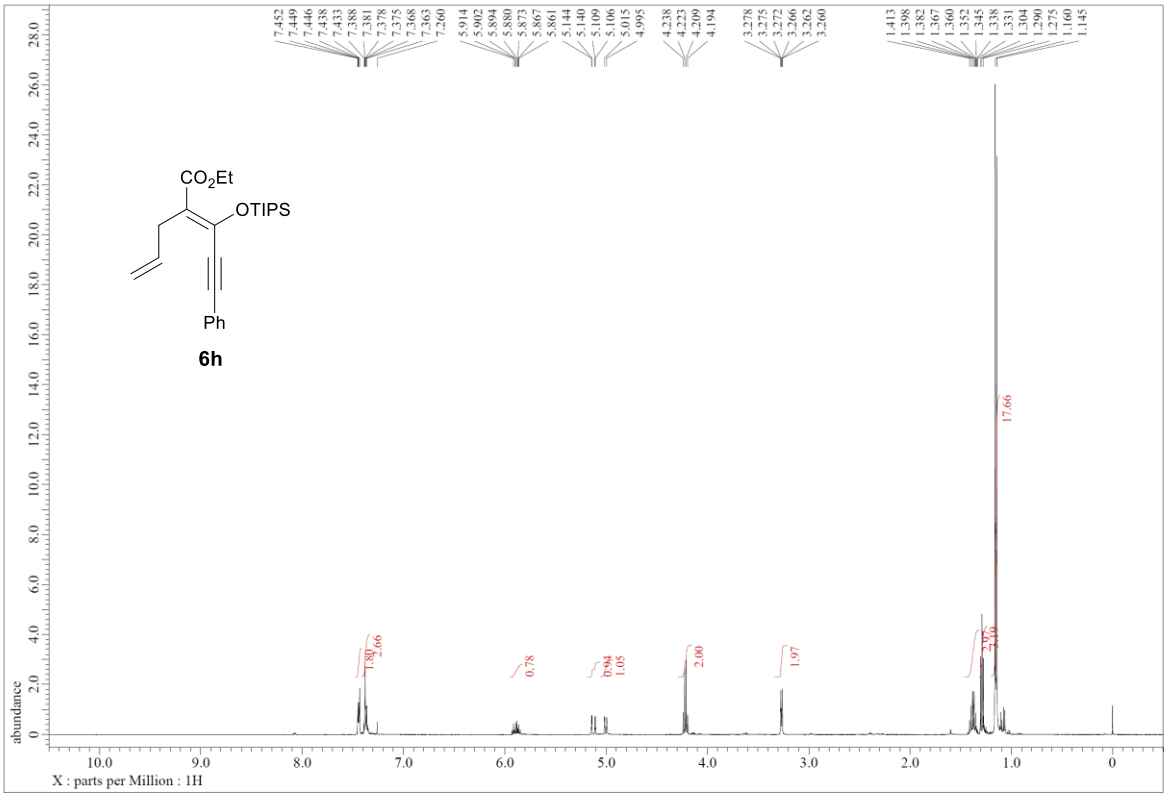
6e (^{1}H NMR, 500 MHz, $CDCl_3$)



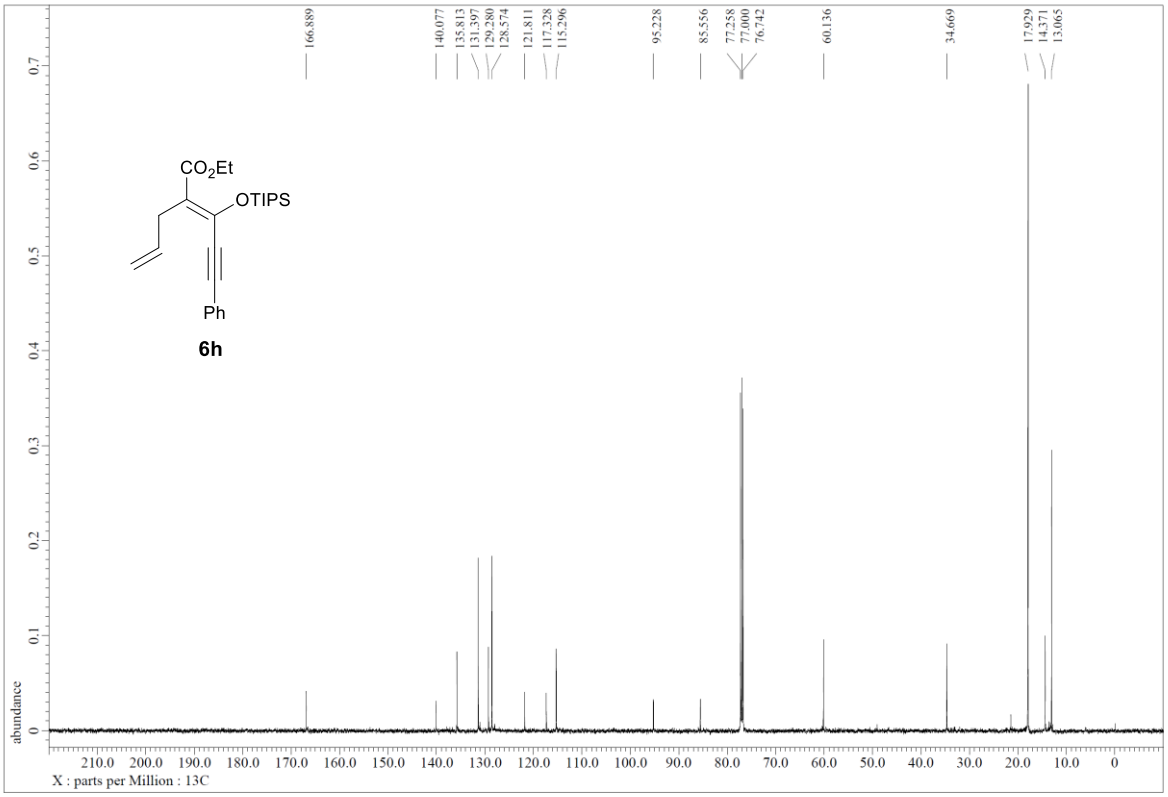
6e (^{13}C NMR, 126 MHz, $CDCl_3$)



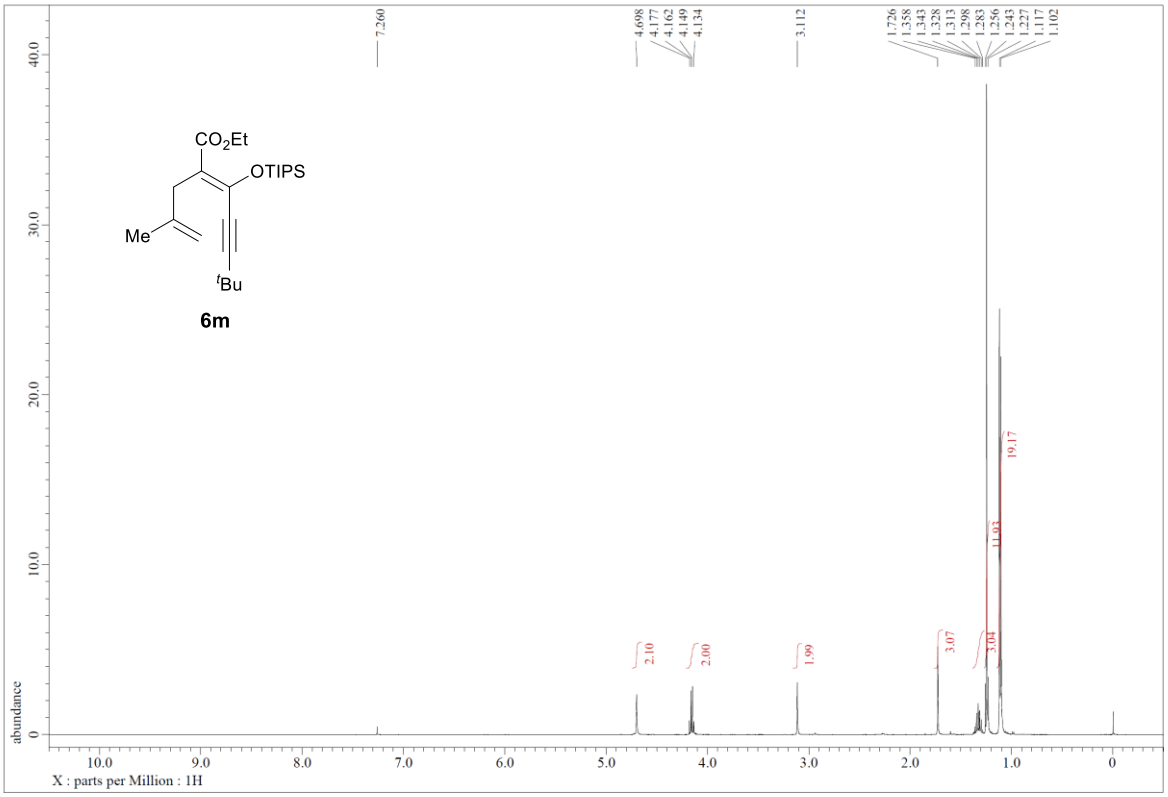
6h (^{1}H NMR, 500 MHz, $CDCl_3$)



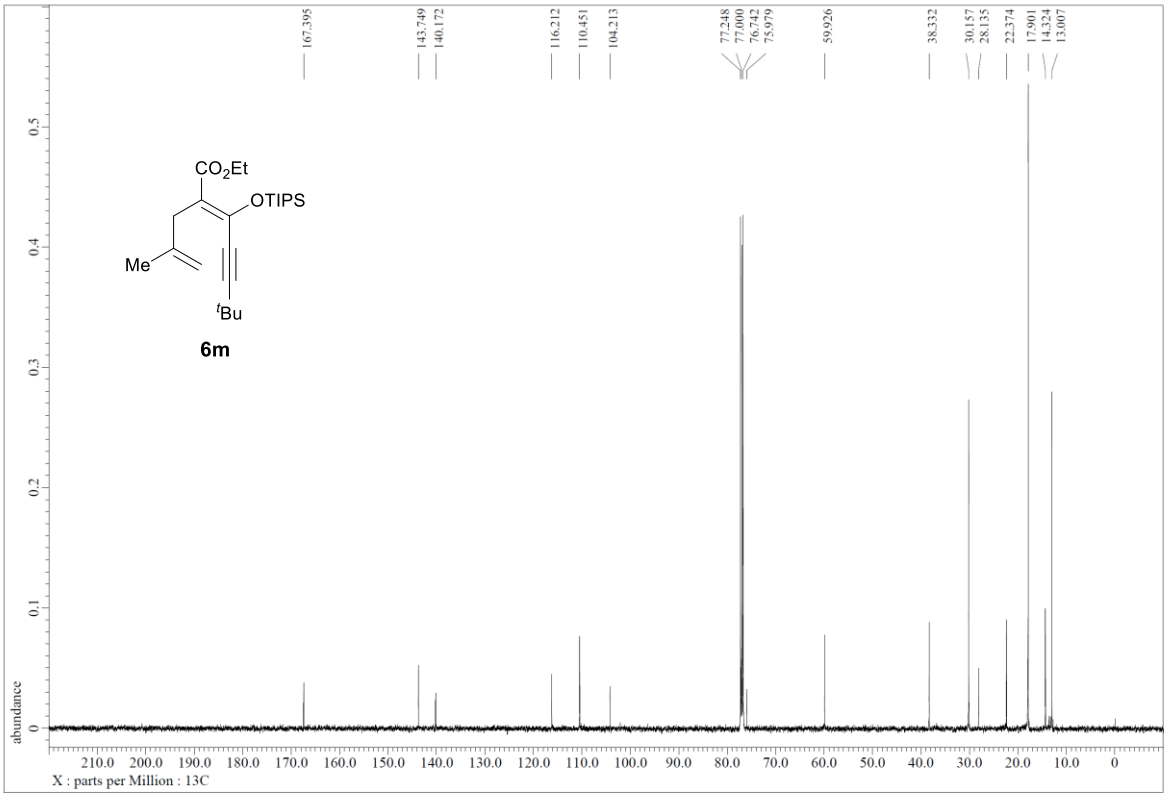
6h (^{13}C NMR, 126 MHz, $CDCl_3$)



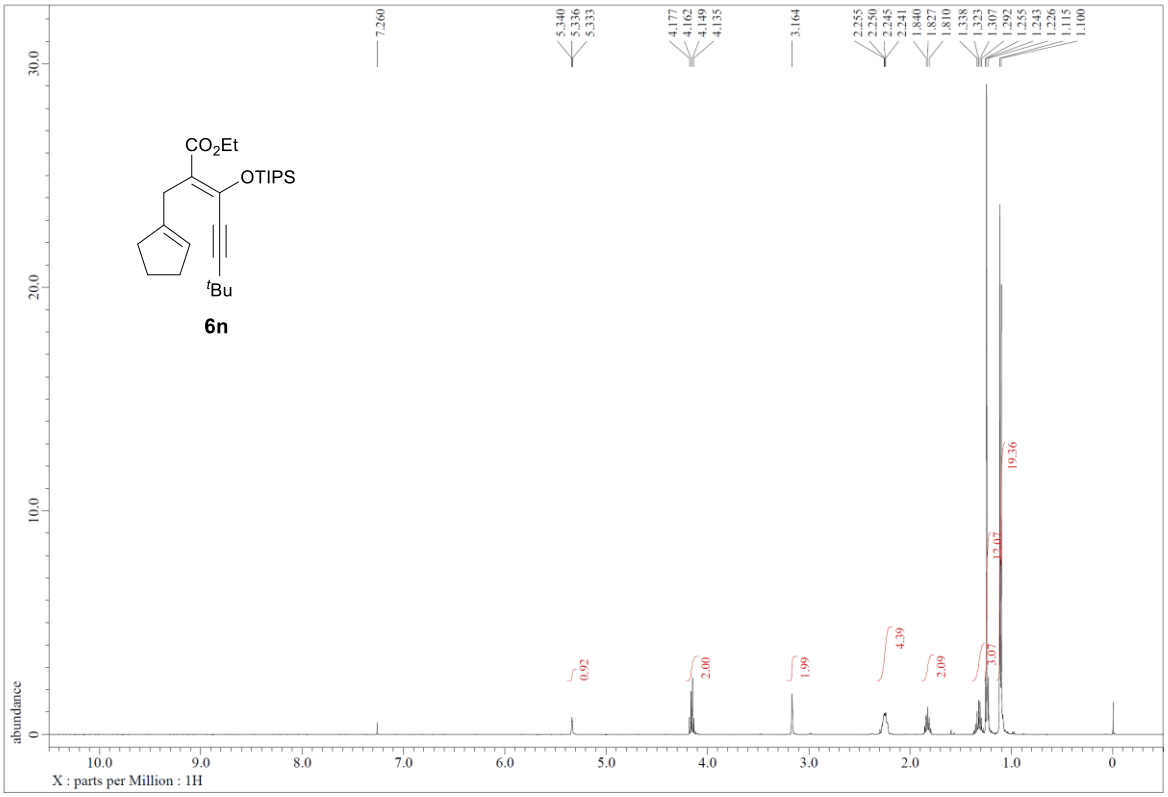
6m (^{1}H NMR, 500 MHz, $CDCl_3$)



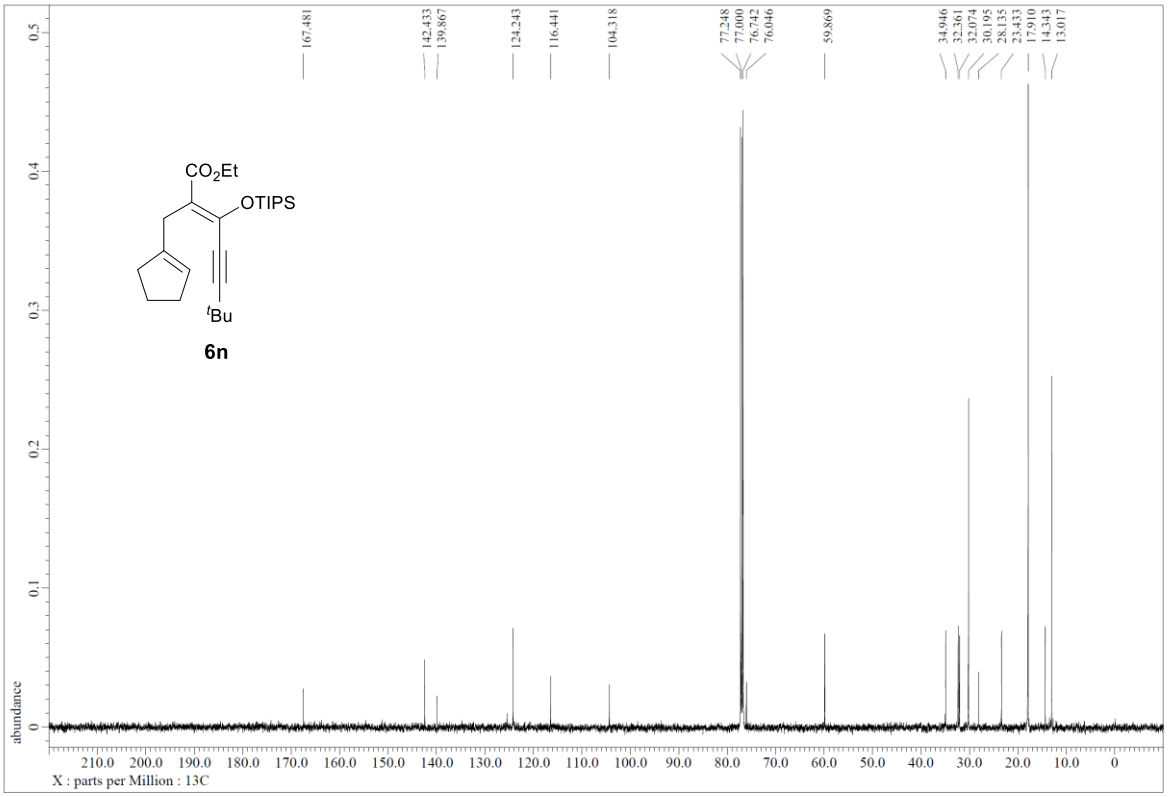
6m (^{13}C NMR, 126 MHz, $CDCl_3$)



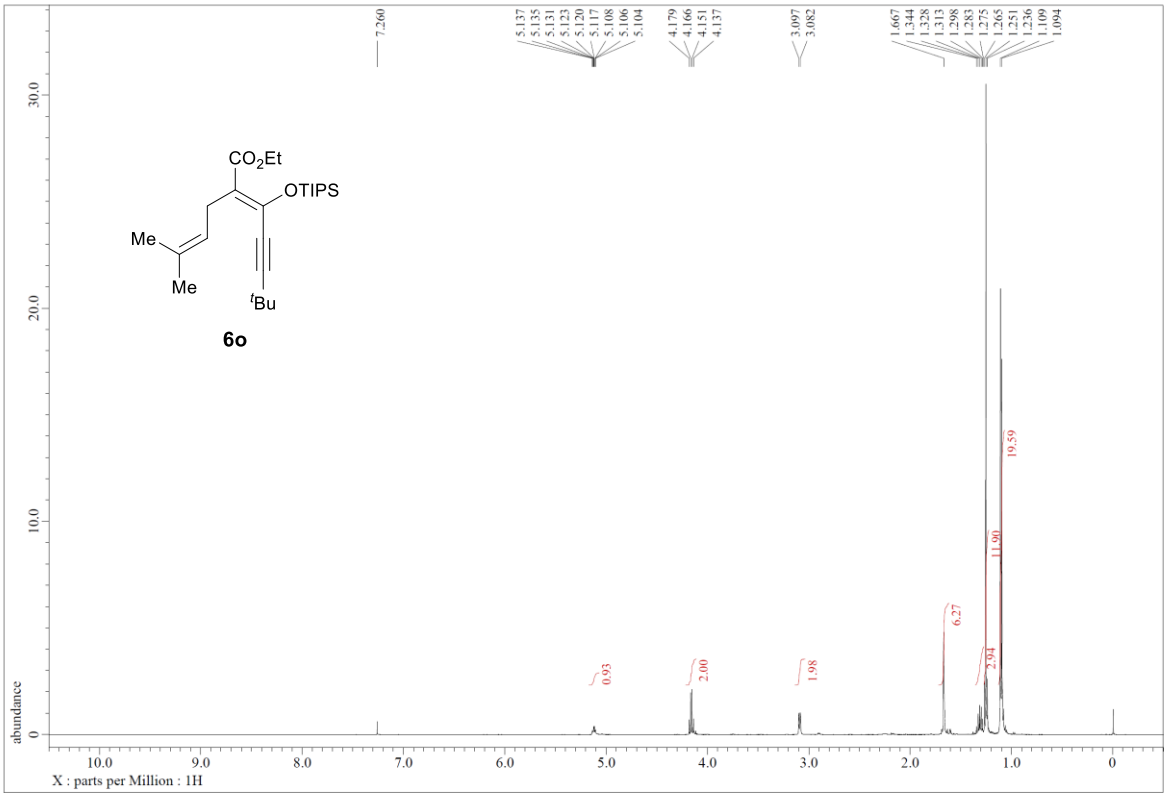
6n (^{1}H NMR, 500 MHz, $CDCl_3$)



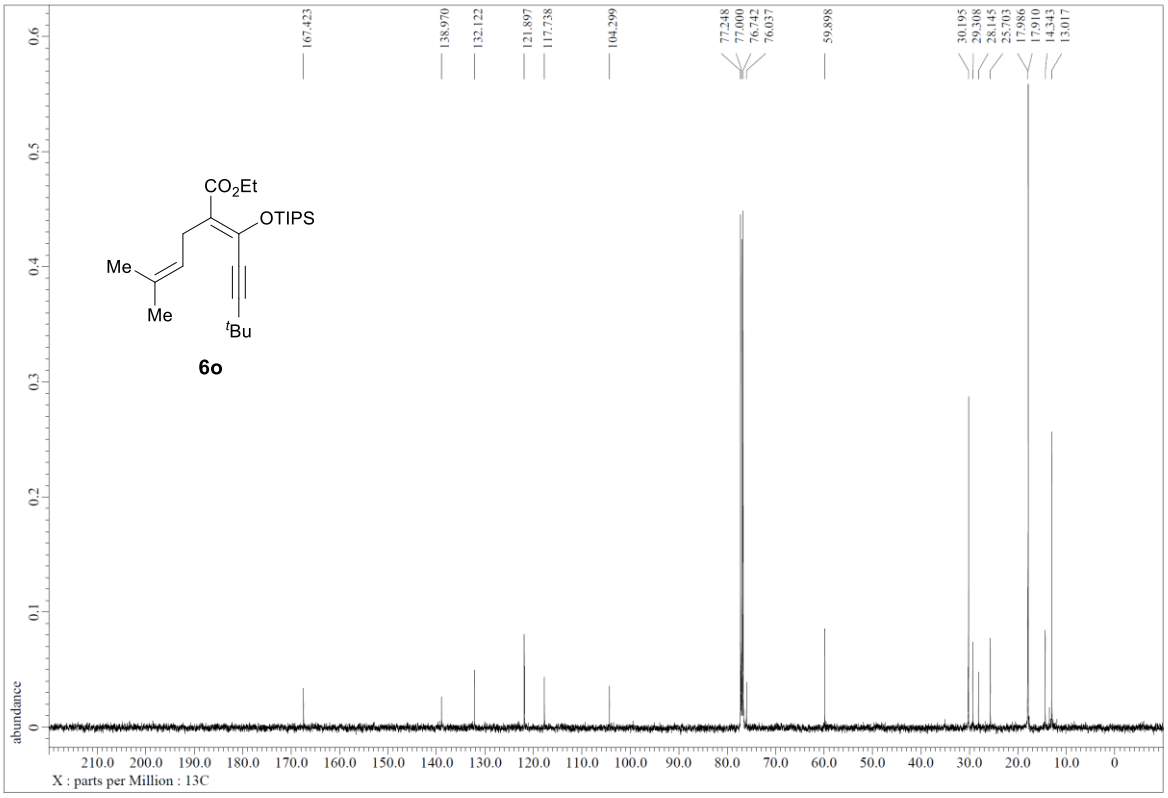
6n (^{13}C NMR, 126 MHz, $CDCl_3$)



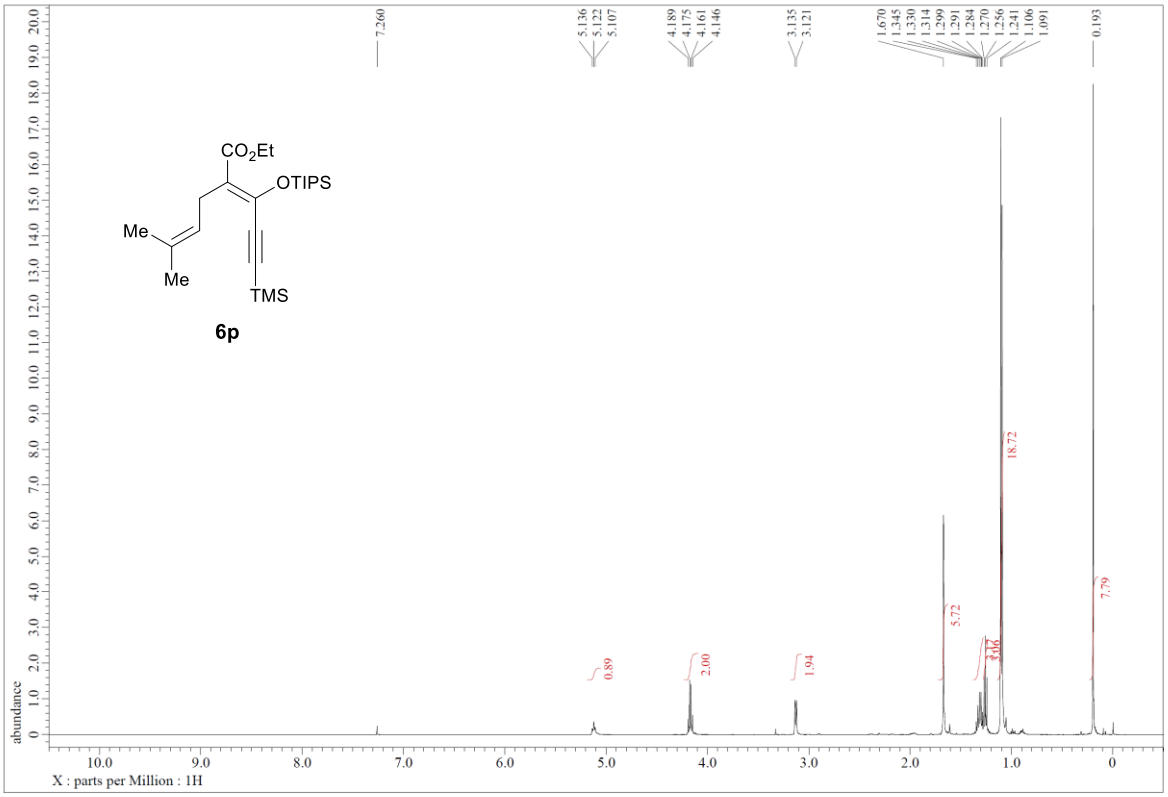
6o (^{1}H NMR, 500 MHz, $CDCl_3$)



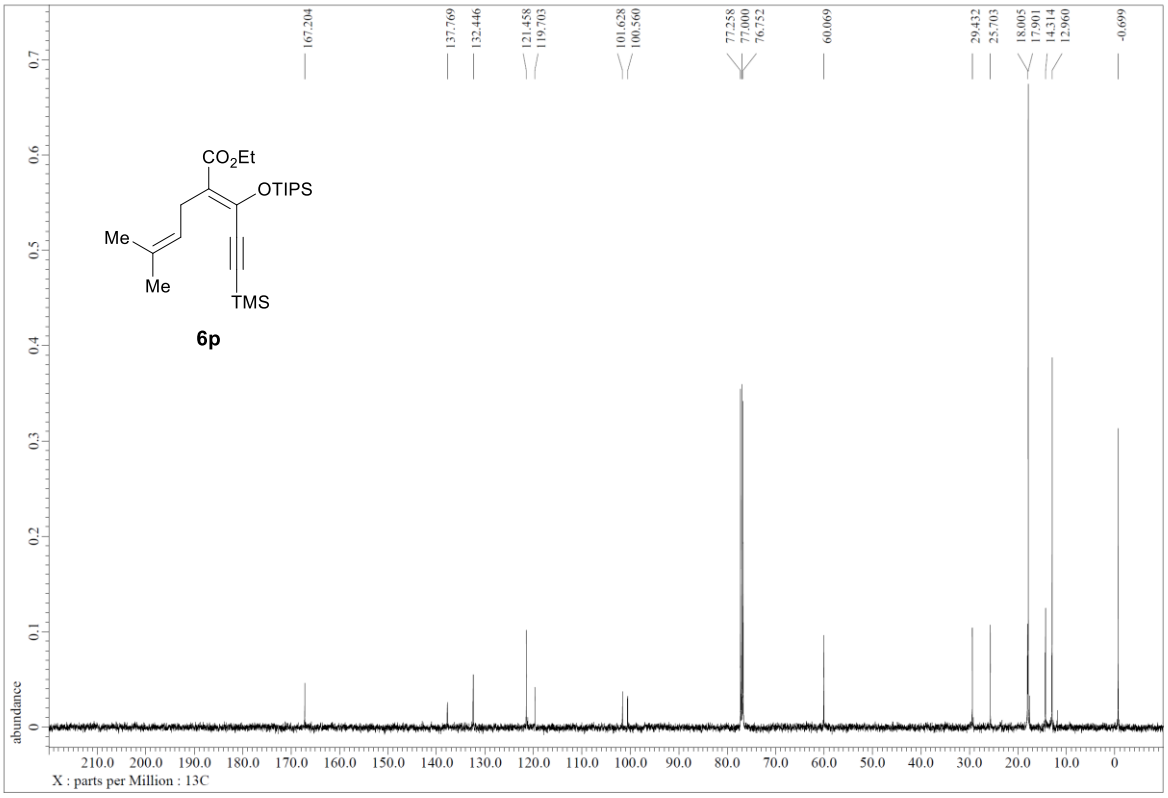
6o (^{13}C NMR, 126 MHz, $CDCl_3$)



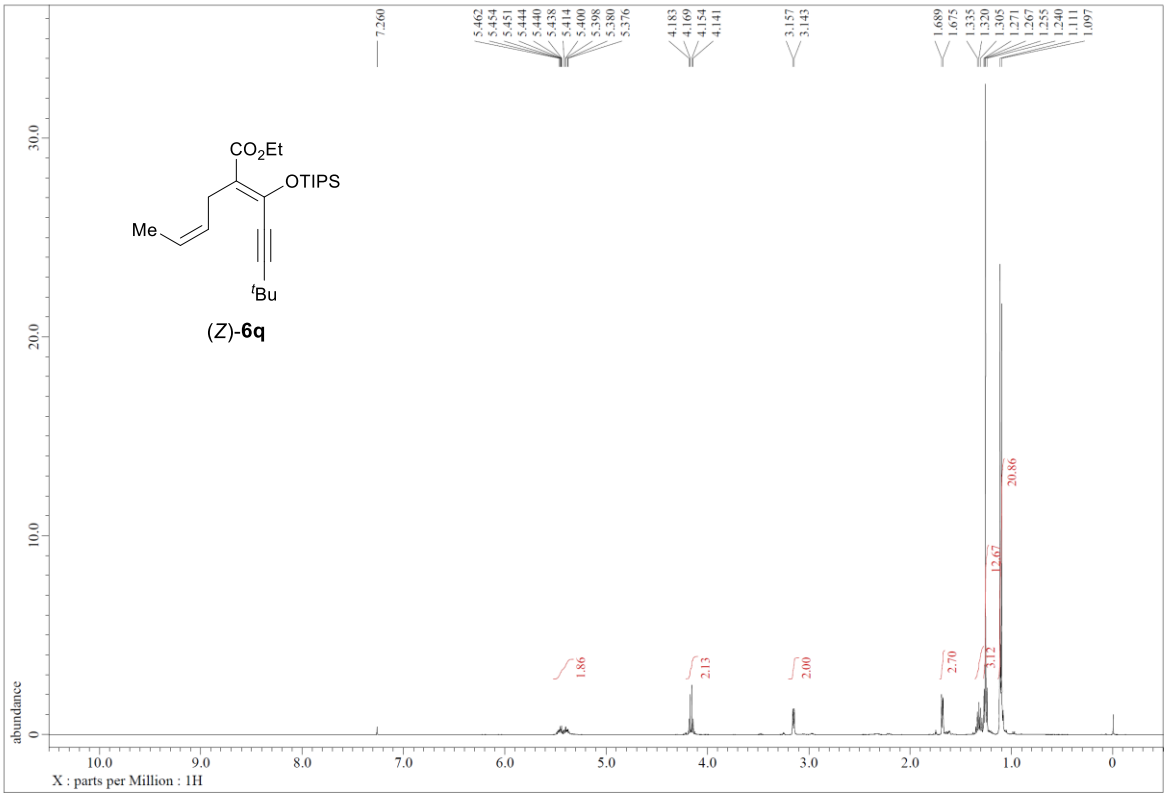
6p (^{1}H NMR, 500 MHz, $CDCl_3$)



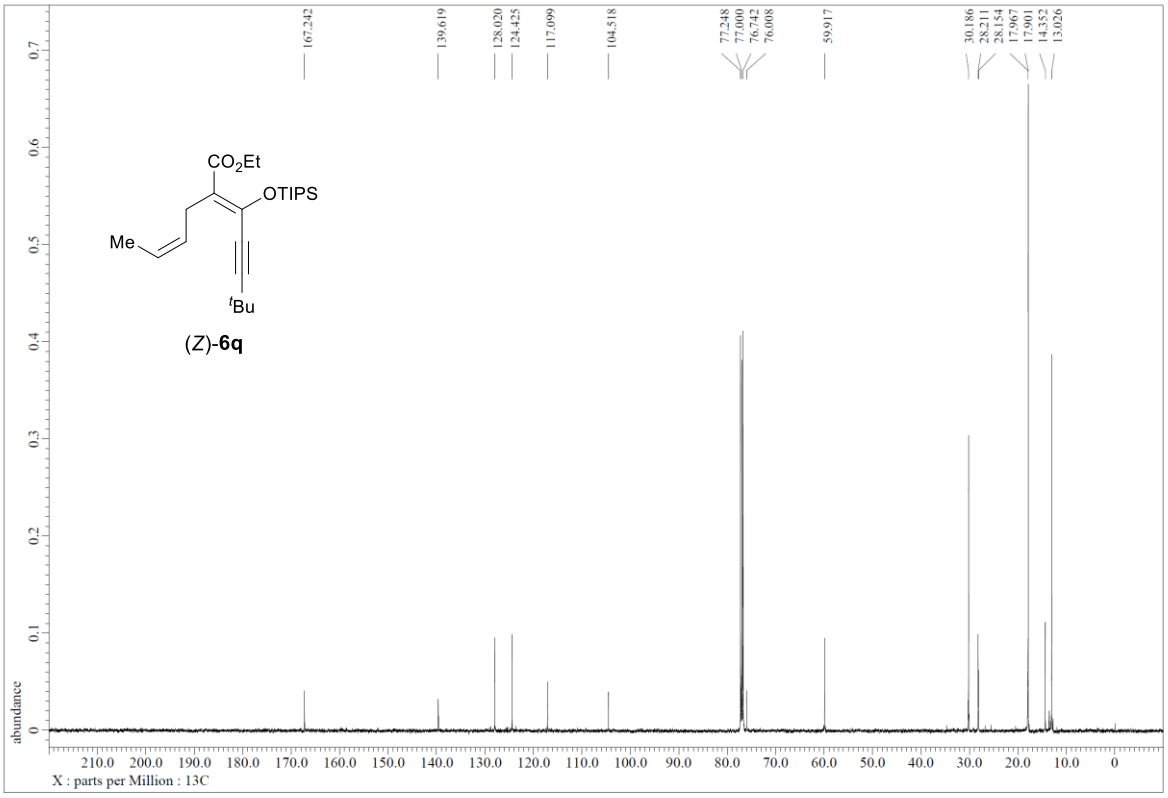
6p (^{13}C NMR, 126 MHz, $CDCl_3$)



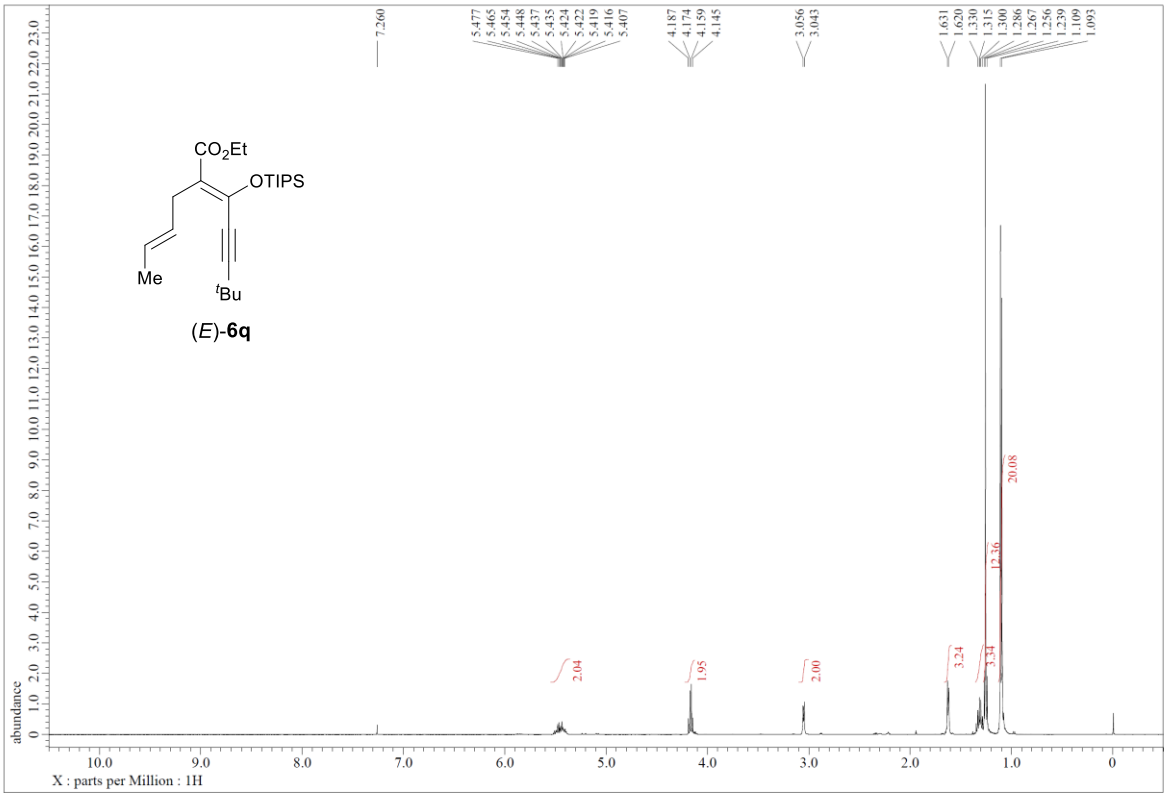
(*Z*)-**6q** (^{1}H NMR, 500 MHz, $CDCl_3$)



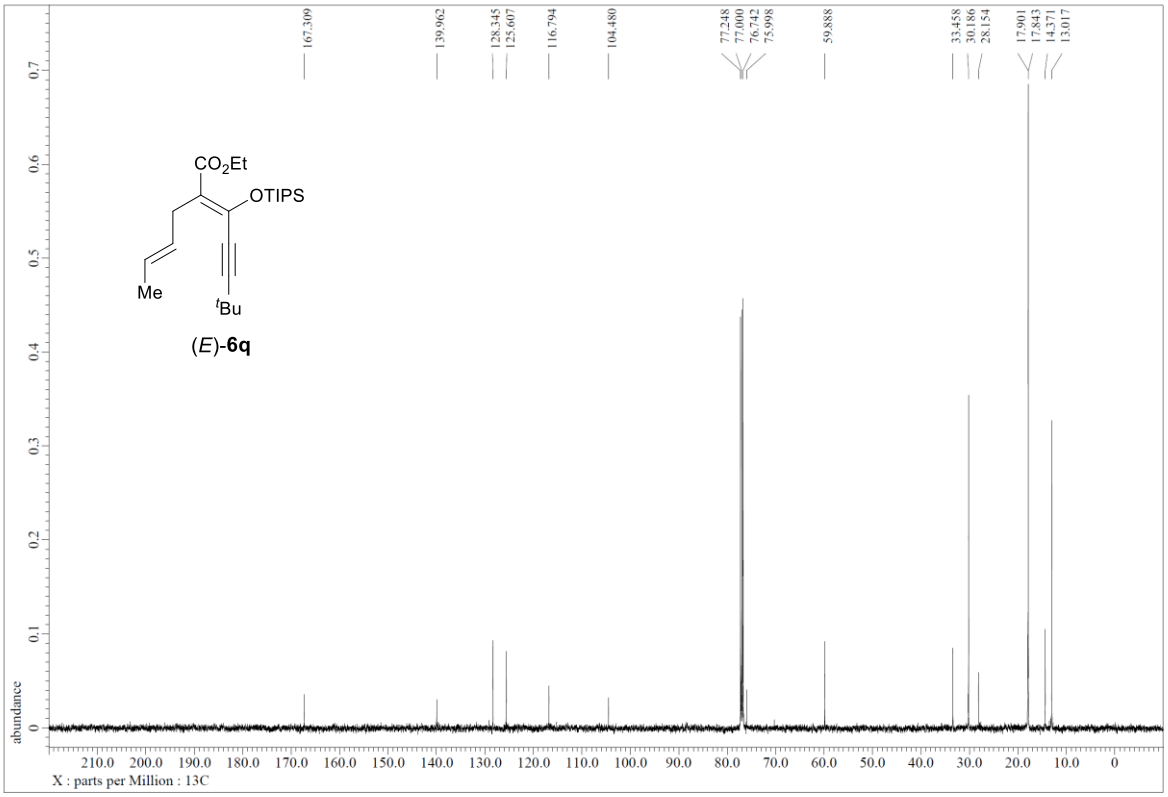
(*Z*)-**6q** (^{13}C NMR, 126 MHz, $CDCl_3$)



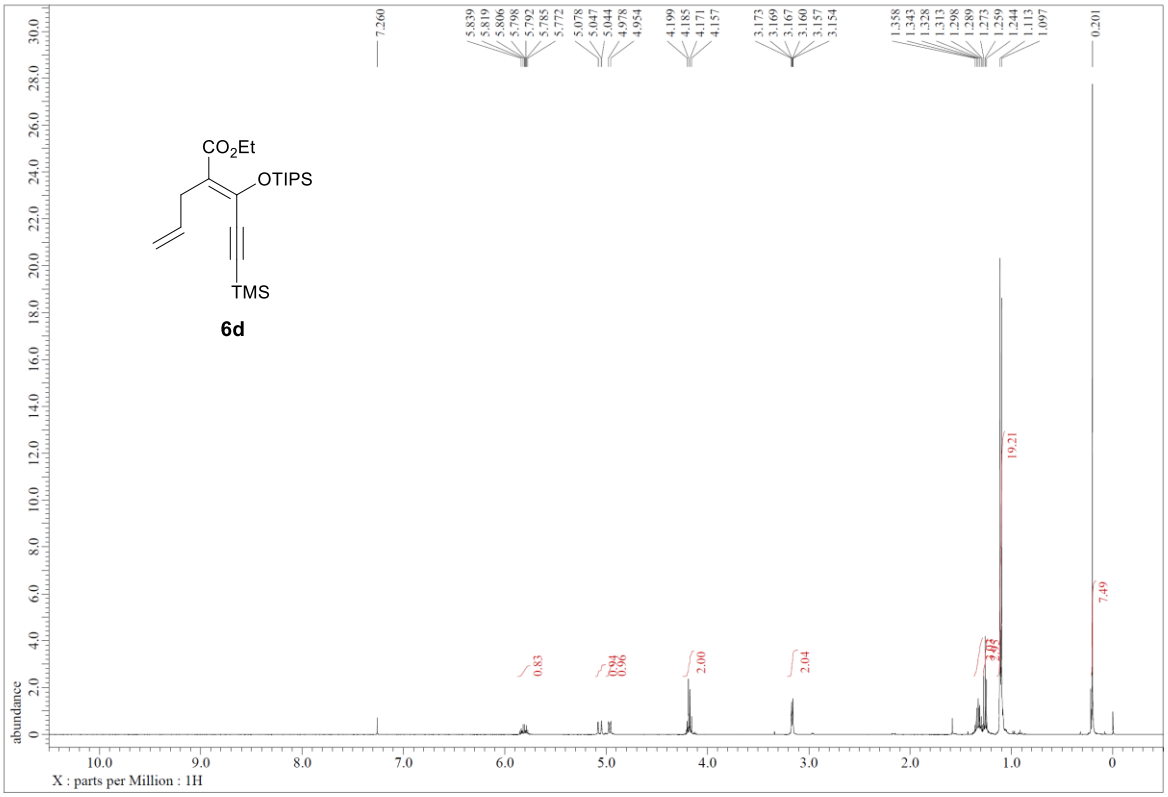
(*E*)-**6q** (^{1}H NMR, 500 MHz, $CDCl_3$)



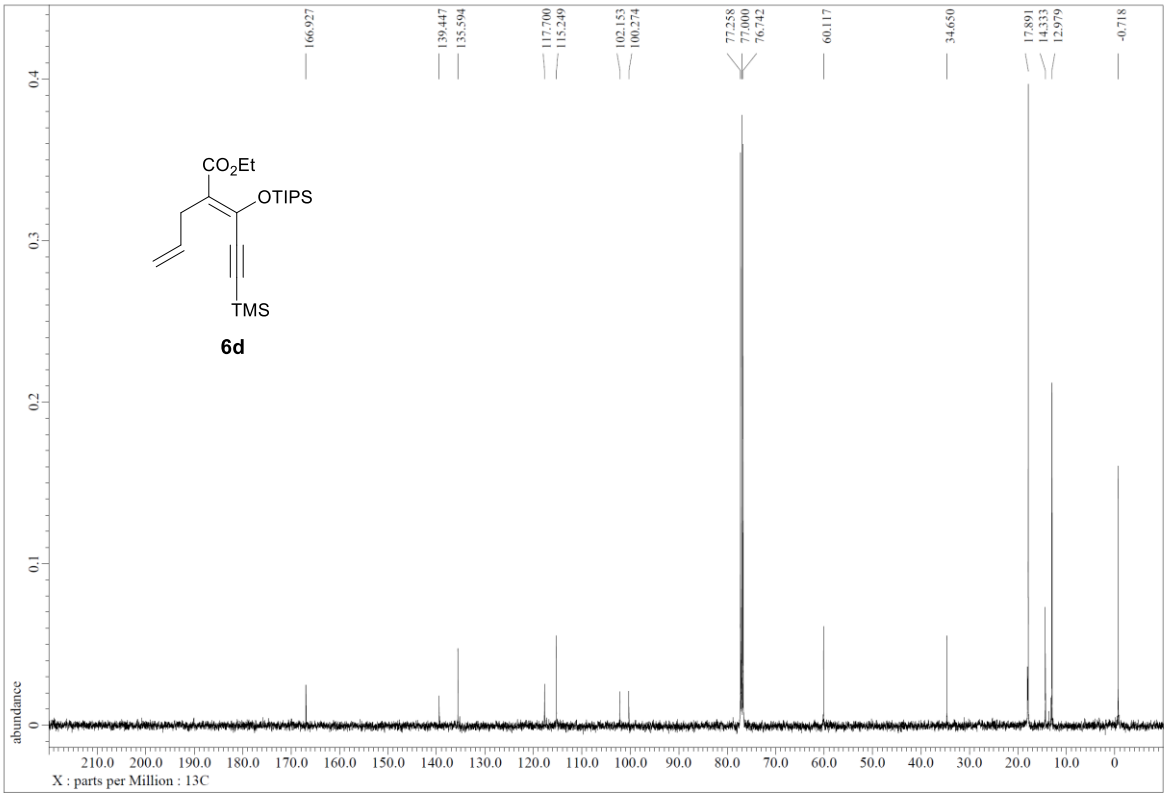
(*E*)-**6q** (^{13}C NMR, 126 MHz, $CDCl_3$)



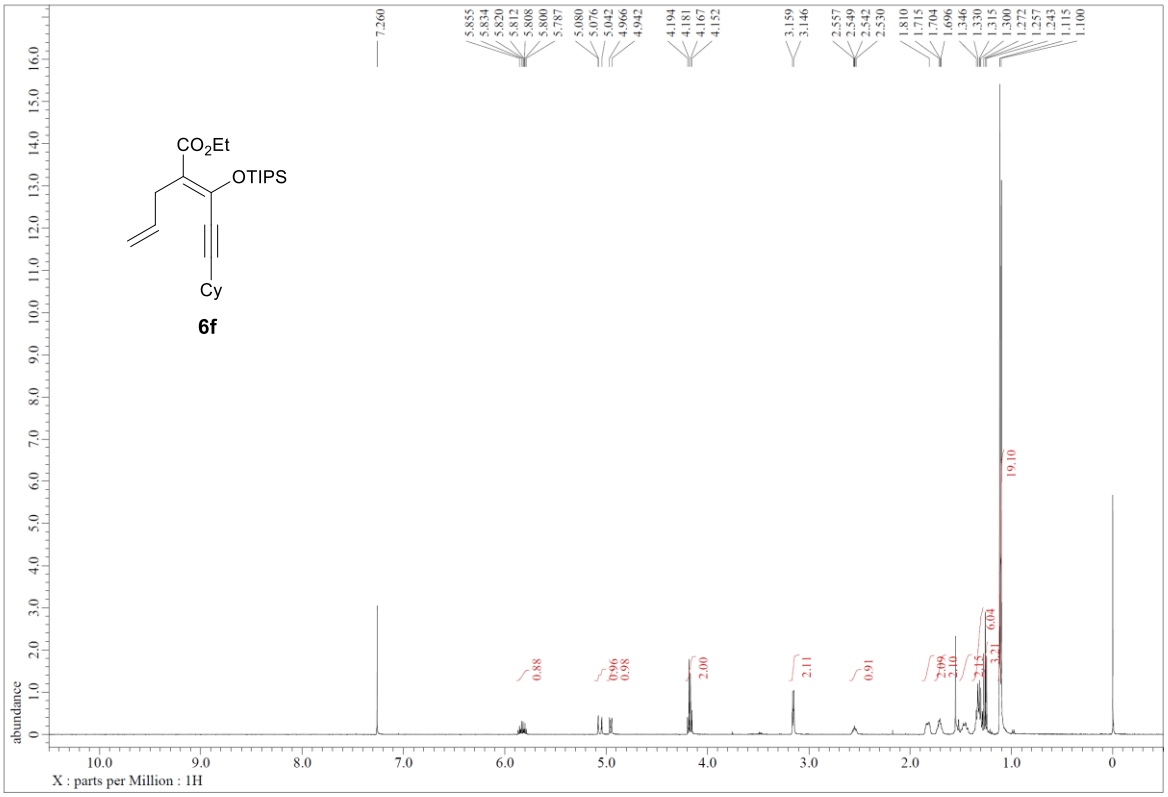
6d (^{1}H NMR, 500 MHz, $CDCl_3$)



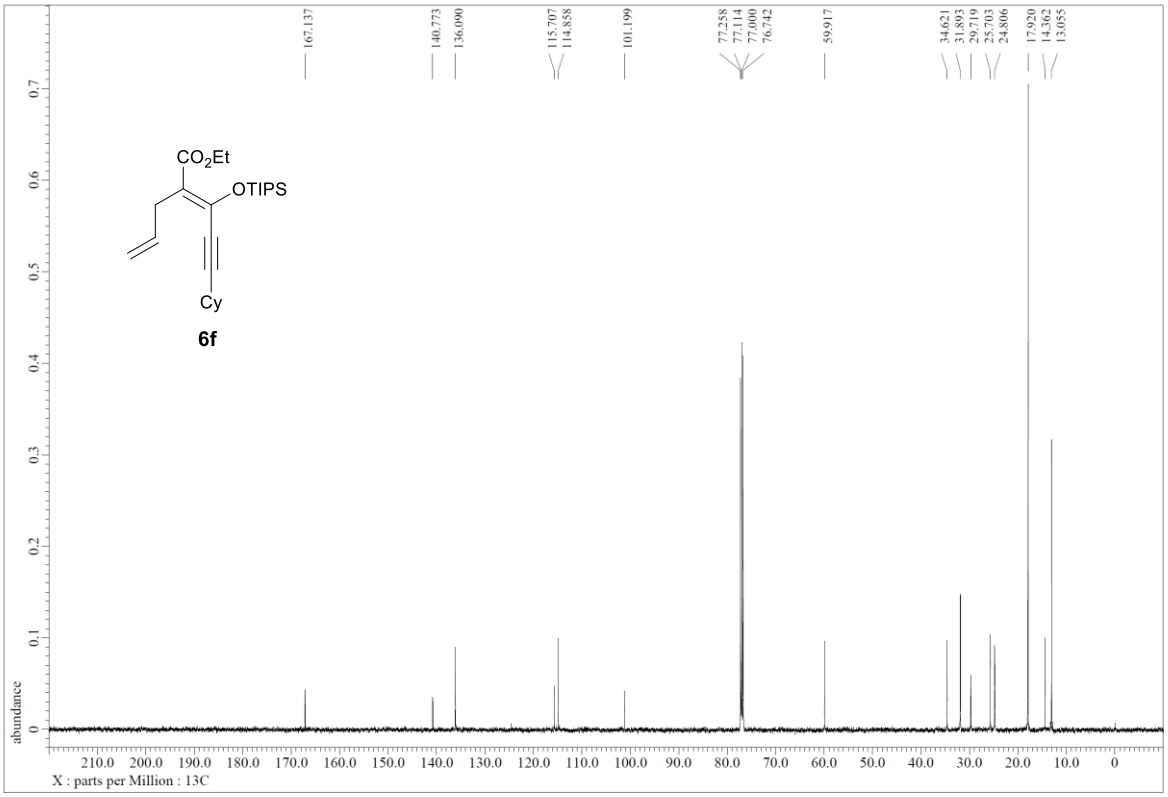
6d (^{13}C NMR, 126 MHz, $CDCl_3$)



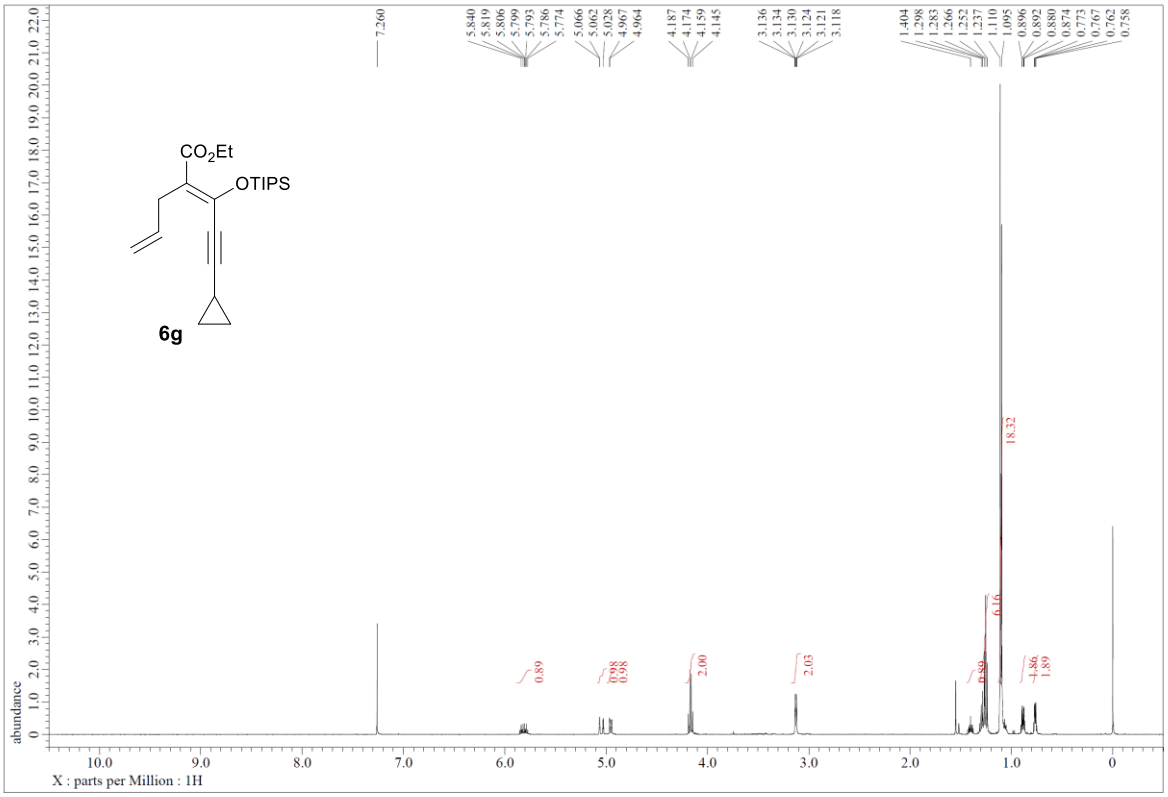
6f (^{1}H NMR, 500 MHz, $CDCl_3$)



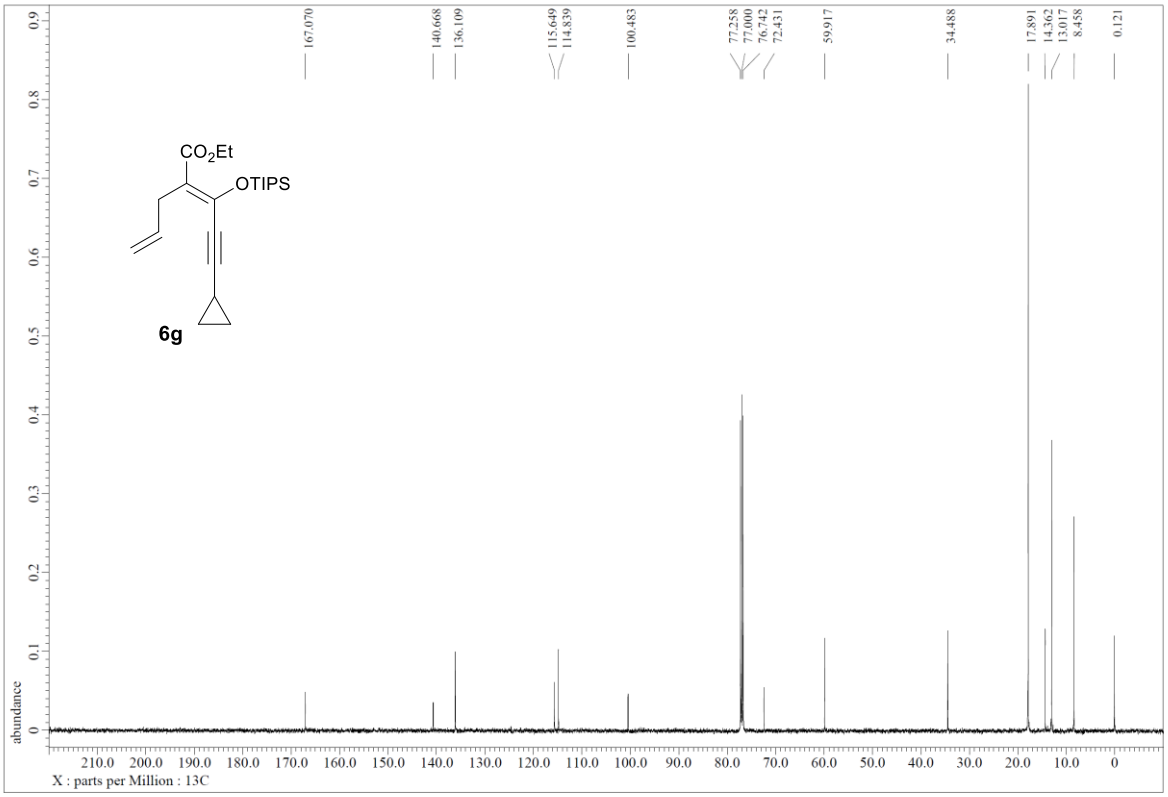
6f (^{13}C NMR, 126 MHz, $CDCl_3$)



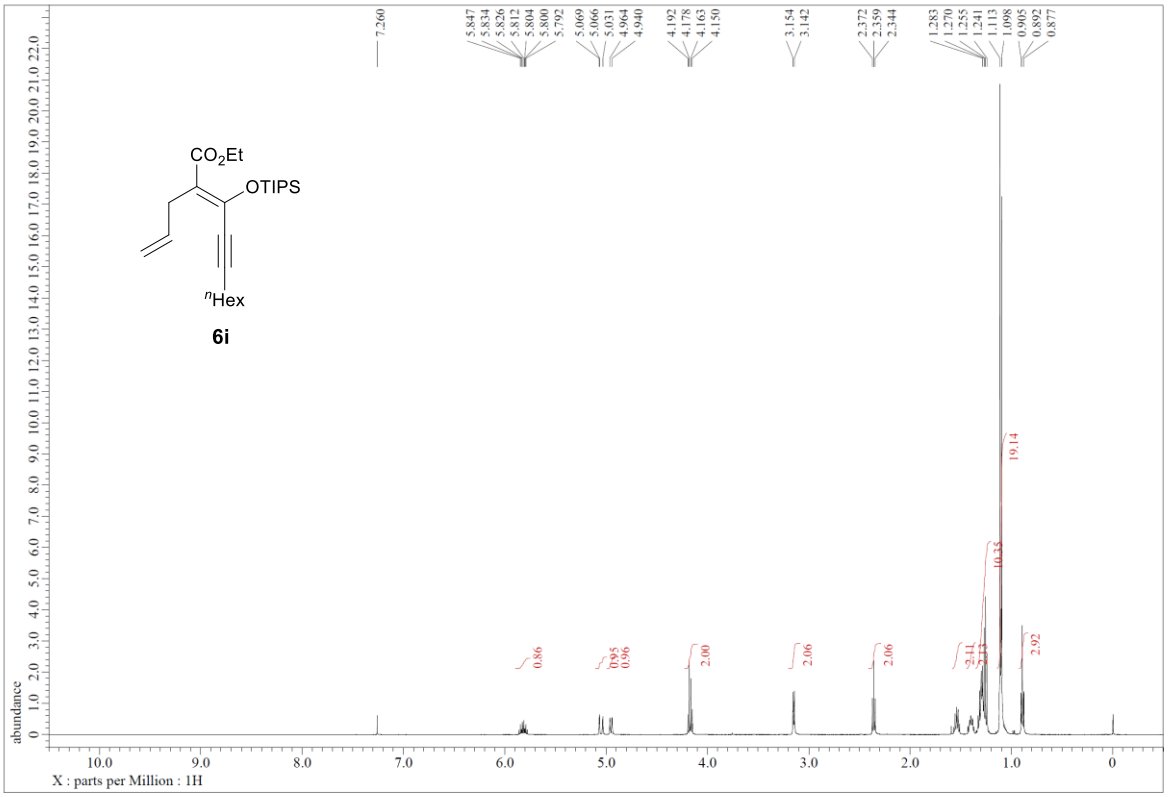
6g (^{1}H NMR, 500 MHz, $CDCl_3$)



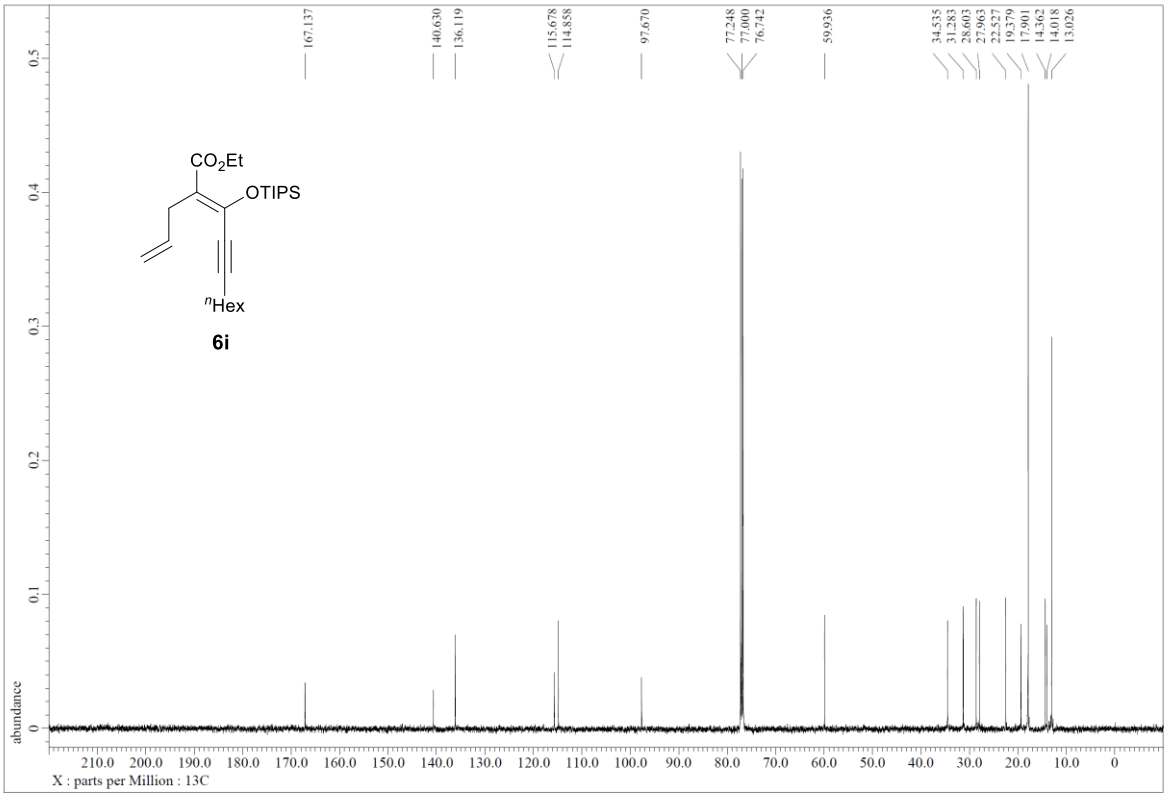
6g (^{13}C NMR, 126 MHz, $CDCl_3$)



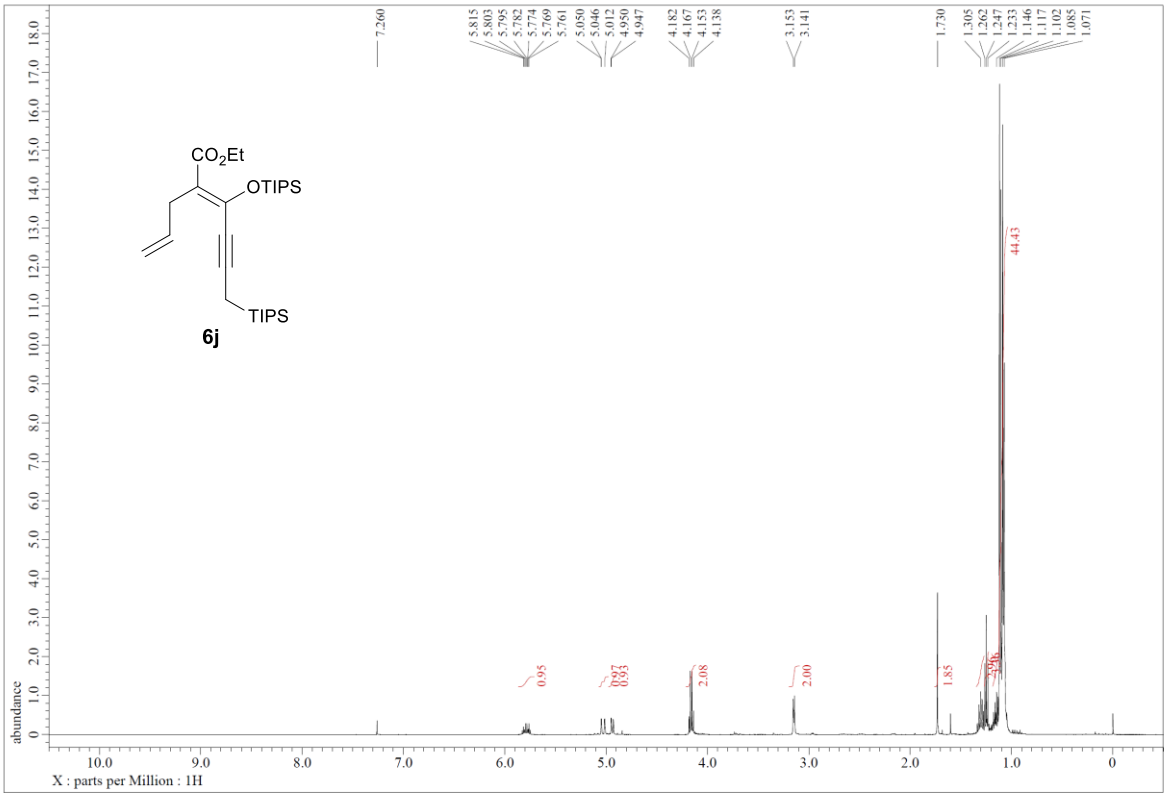
6i (^{1}H NMR, 500 MHz, $CDCl_3$)



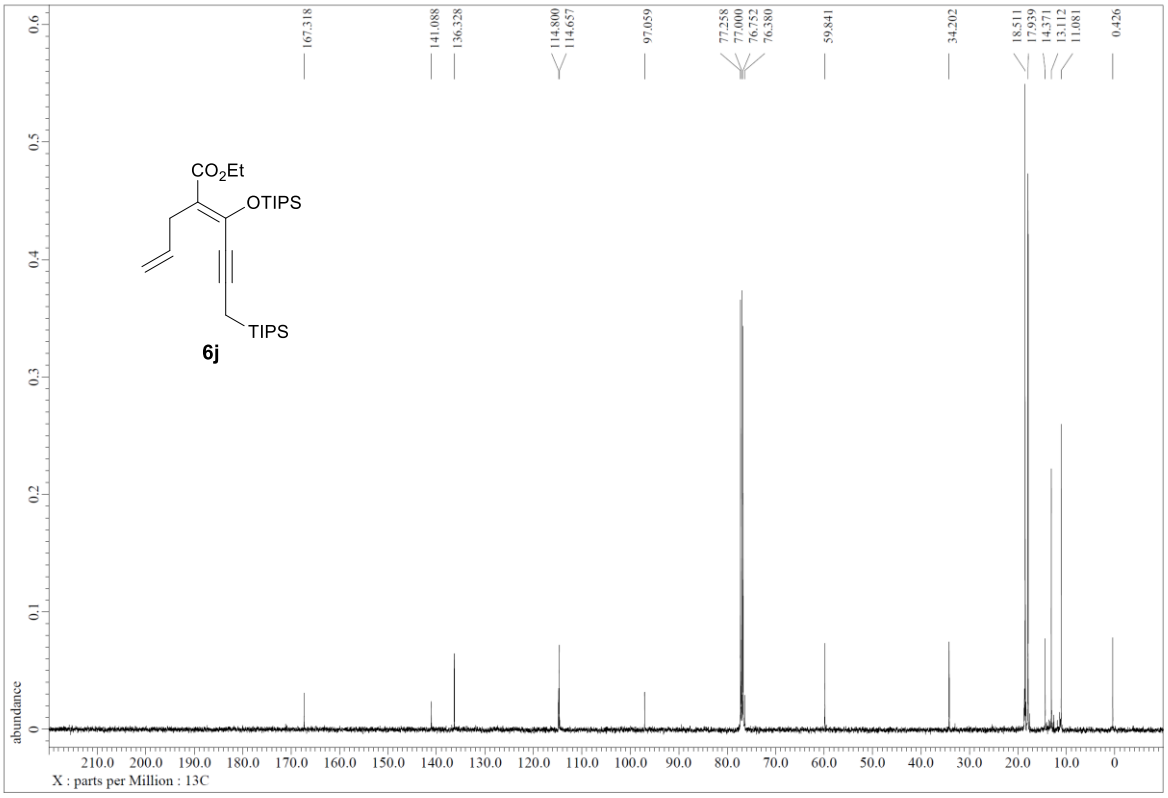
6i (^{13}C NMR, 126 MHz, $CDCl_3$)



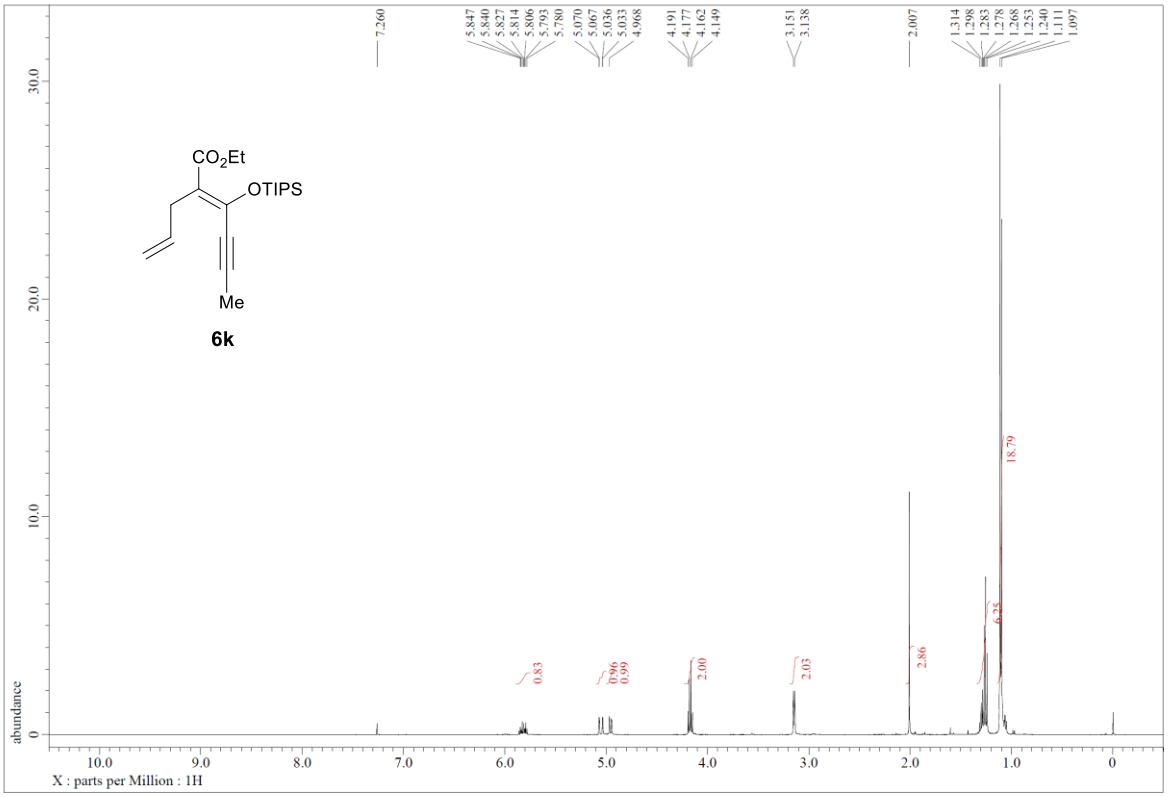
6j (^{1}H NMR, 500 MHz, $CDCl_3$)



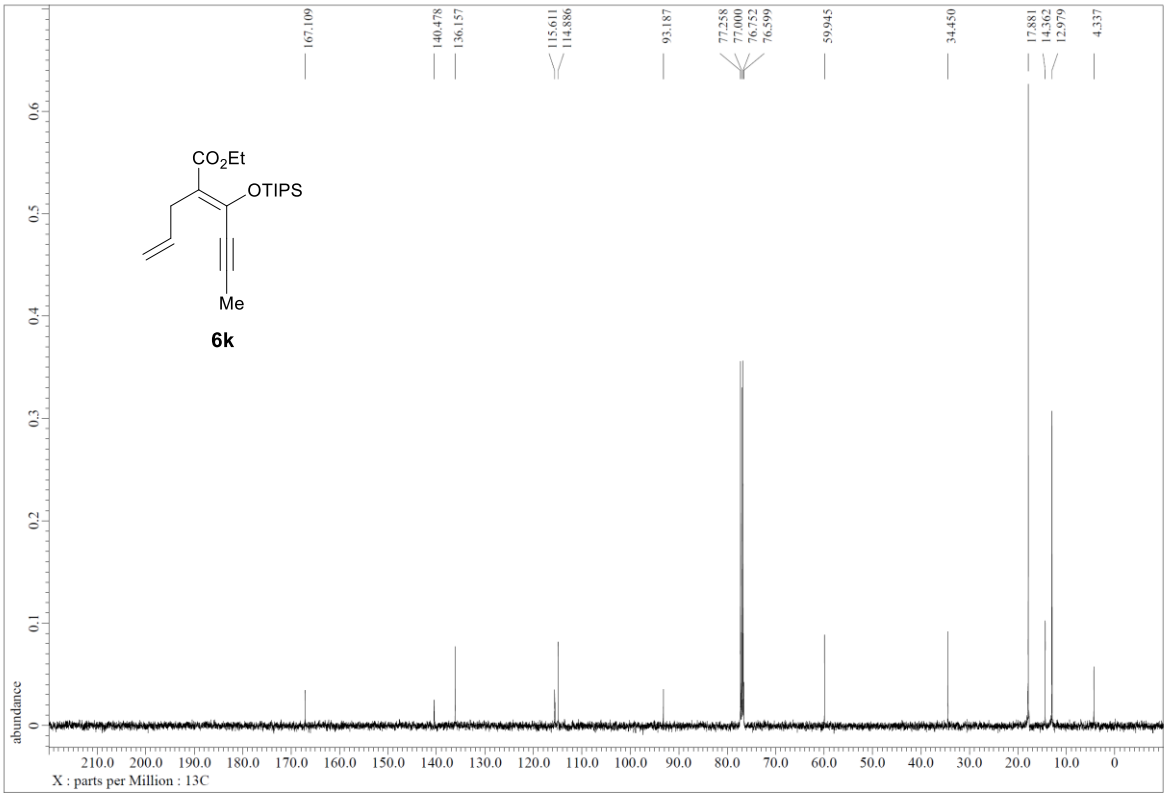
6j (^{13}C NMR, 126 MHz, $CDCl_3$)



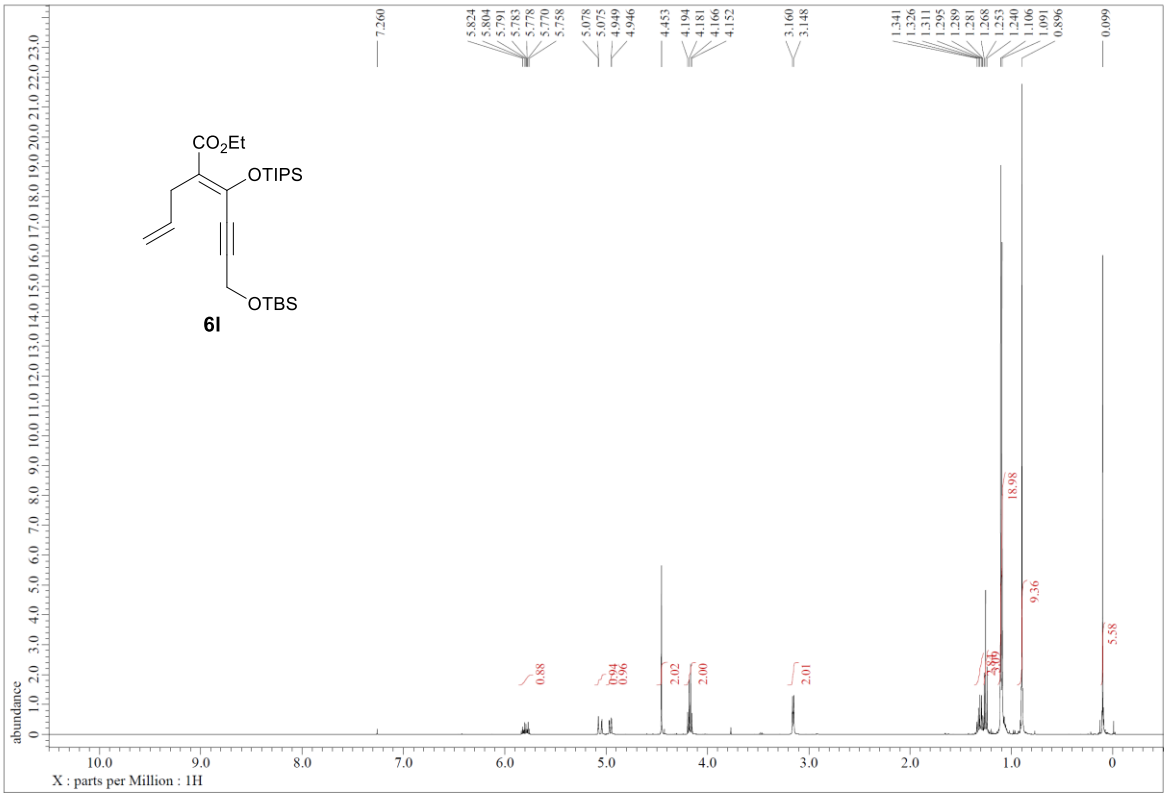
6k (^{1}H NMR, 500 MHz, $CDCl_3$)



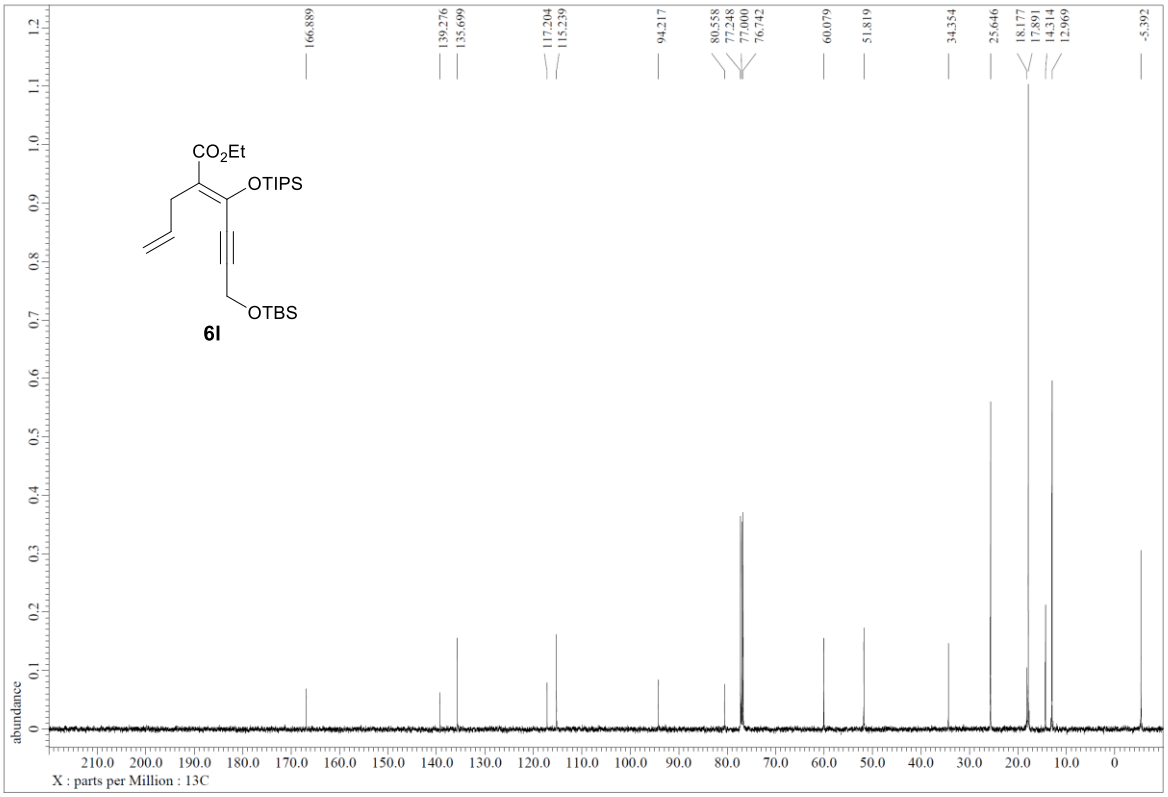
6k (^{13}C NMR, 126 MHz, $CDCl_3$)



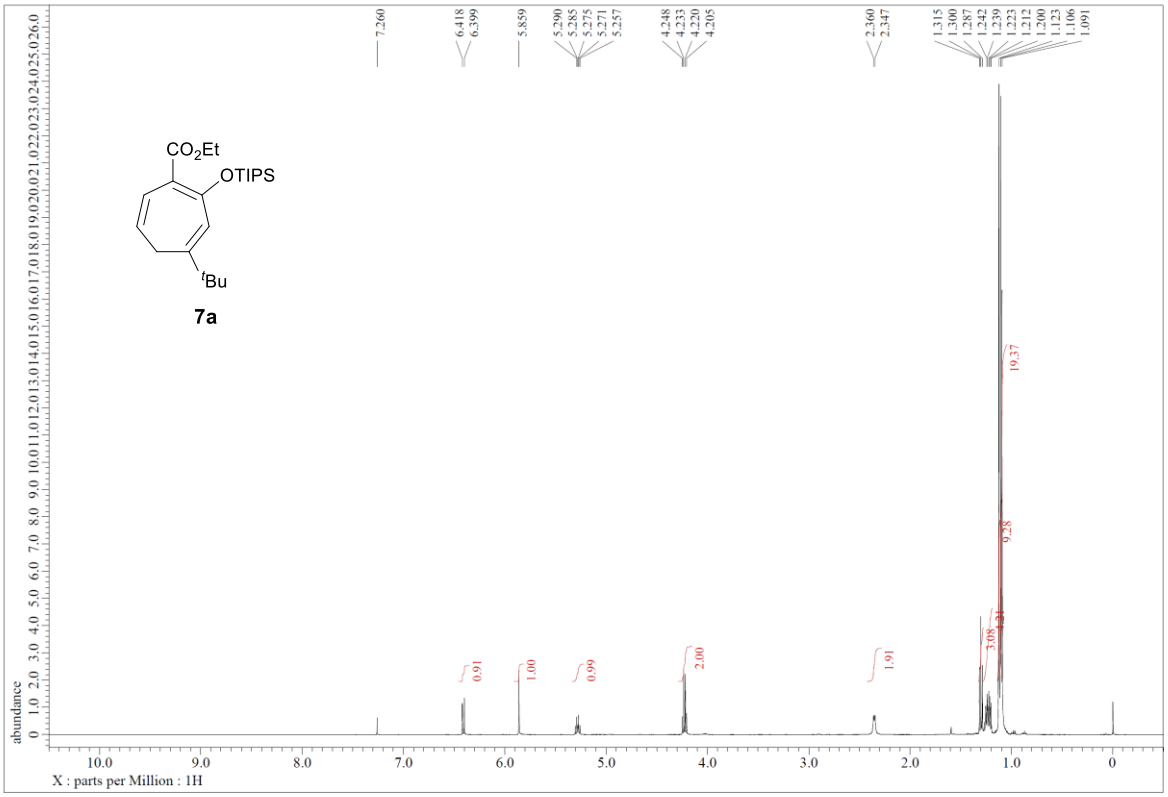
6l (^{1}H NMR, 500 MHz, $CDCl_3$)



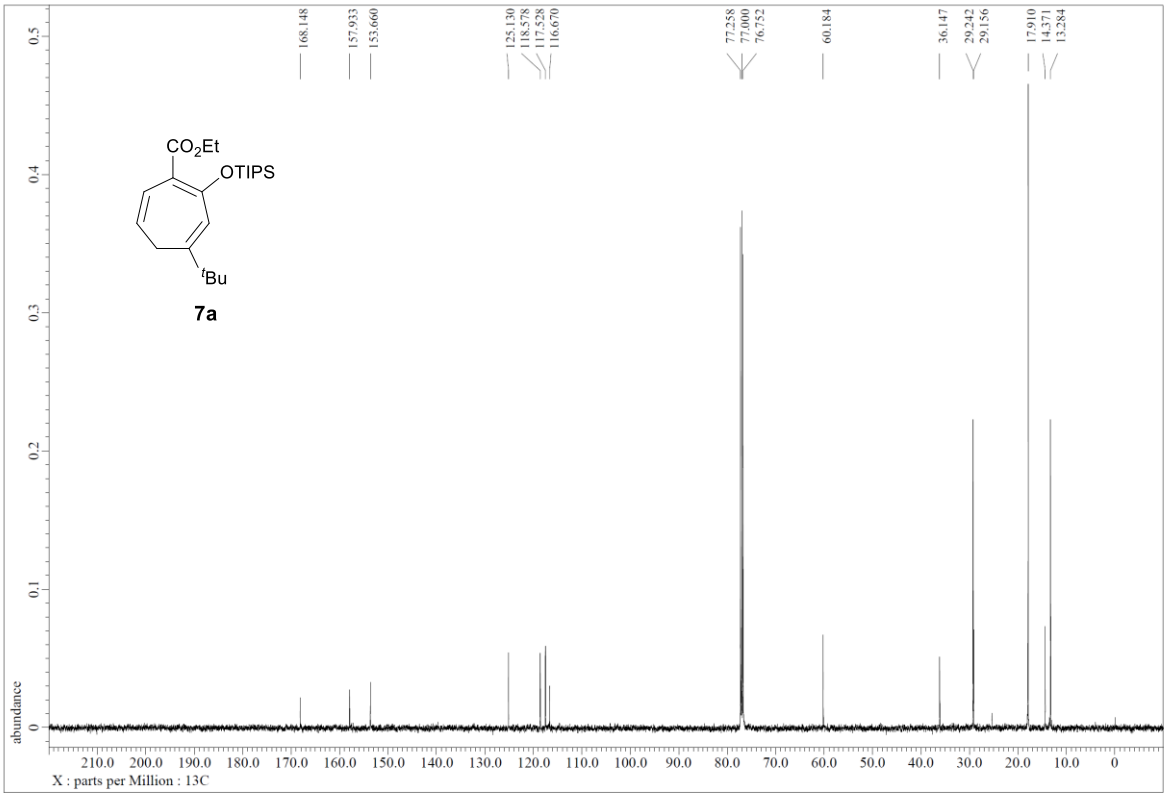
6l (^{13}C NMR, 126 MHz, $CDCl_3$)



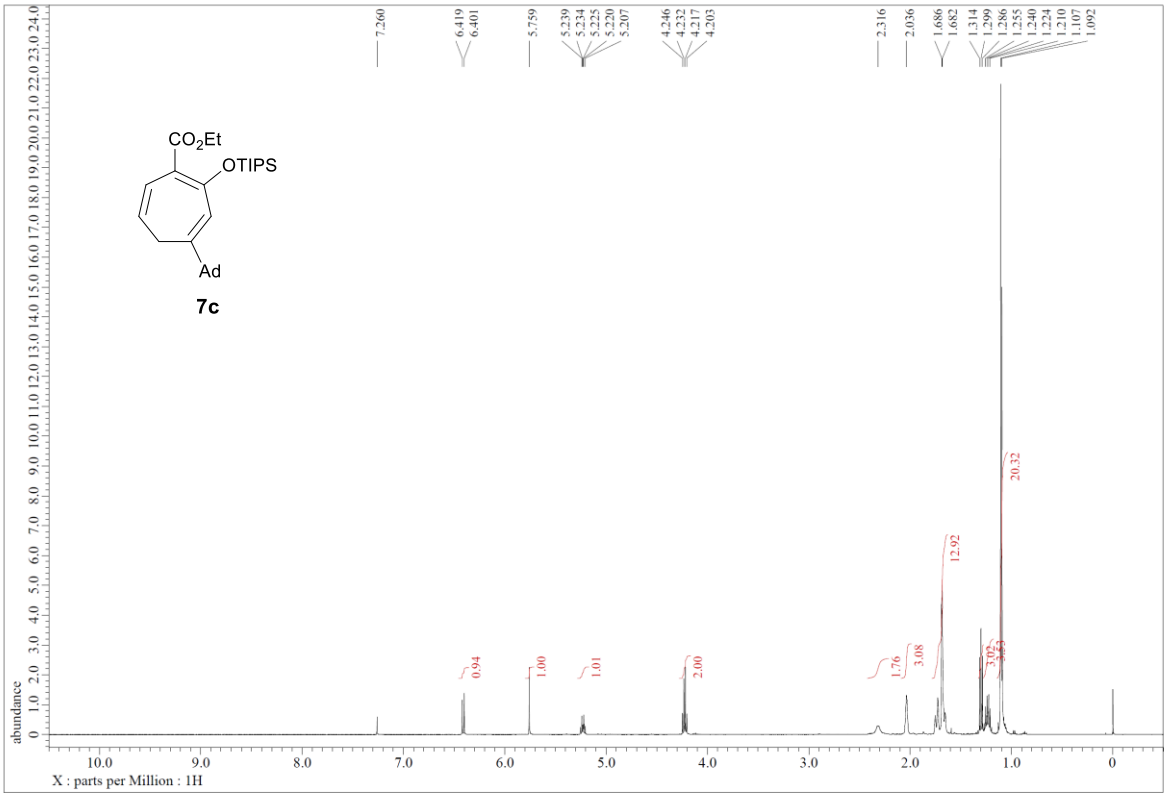
7a (^{1}H NMR, 500 MHz, $CDCl_3$)



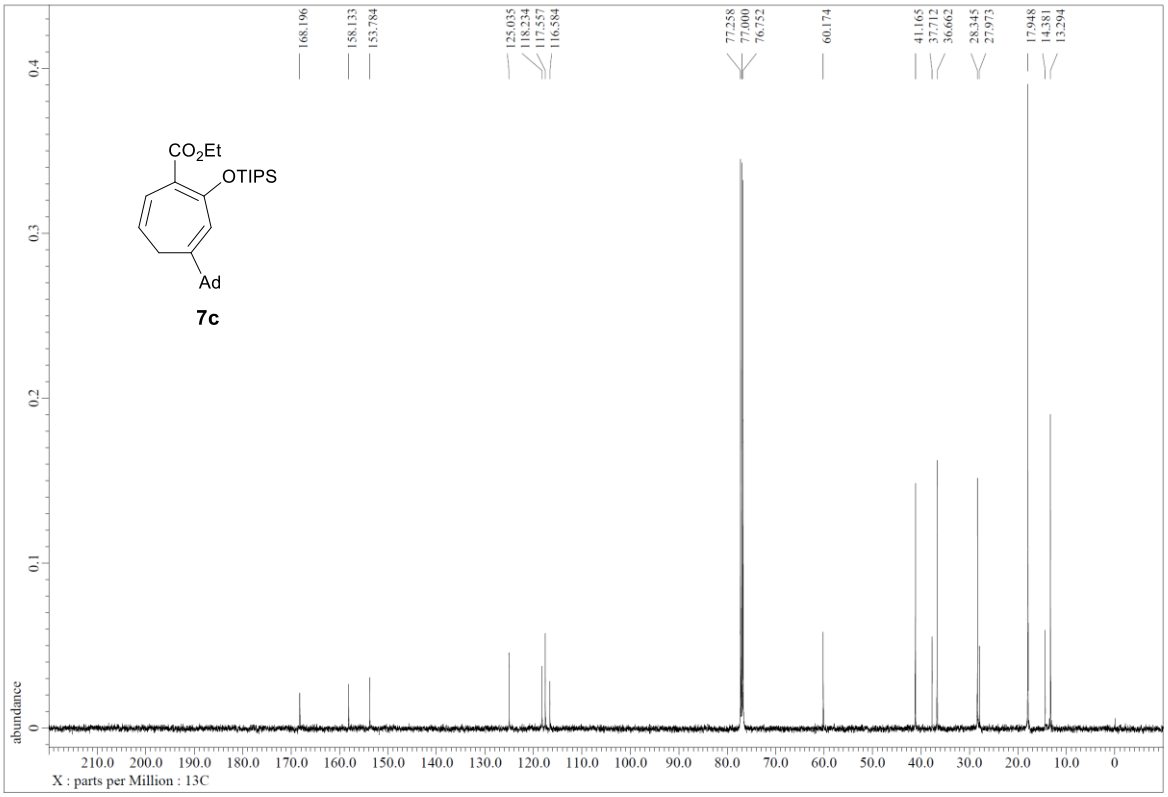
7a (^{13}C NMR, 126 MHz, $CDCl_3$)



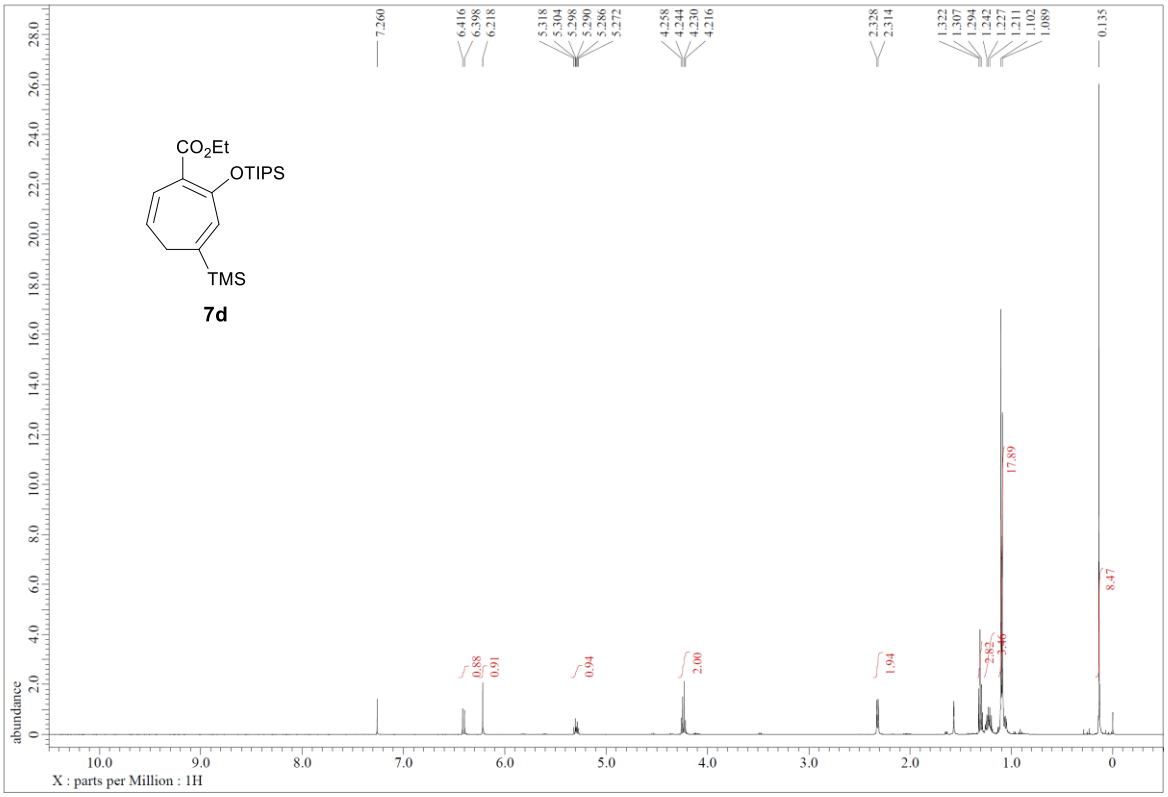
7c (^{1}H NMR, 500 MHz, $CDCl_3$)



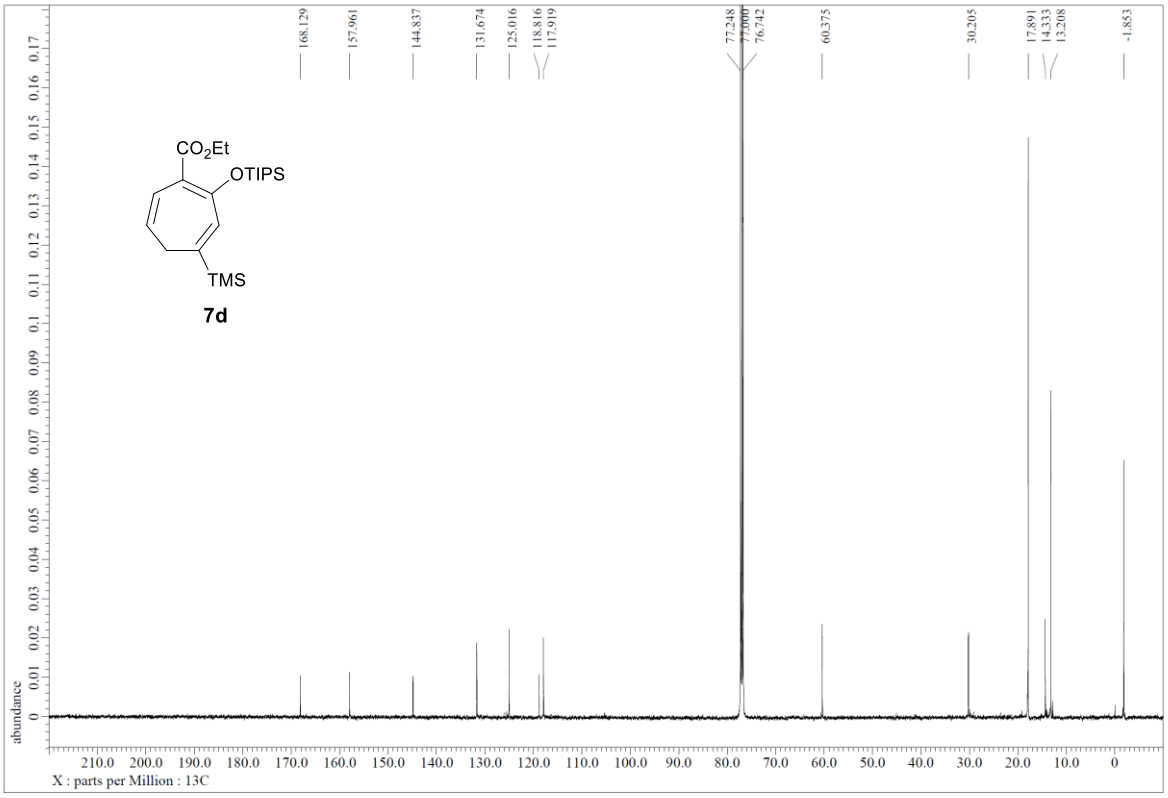
7c (^{13}C NMR, 126 MHz, $CDCl_3$)



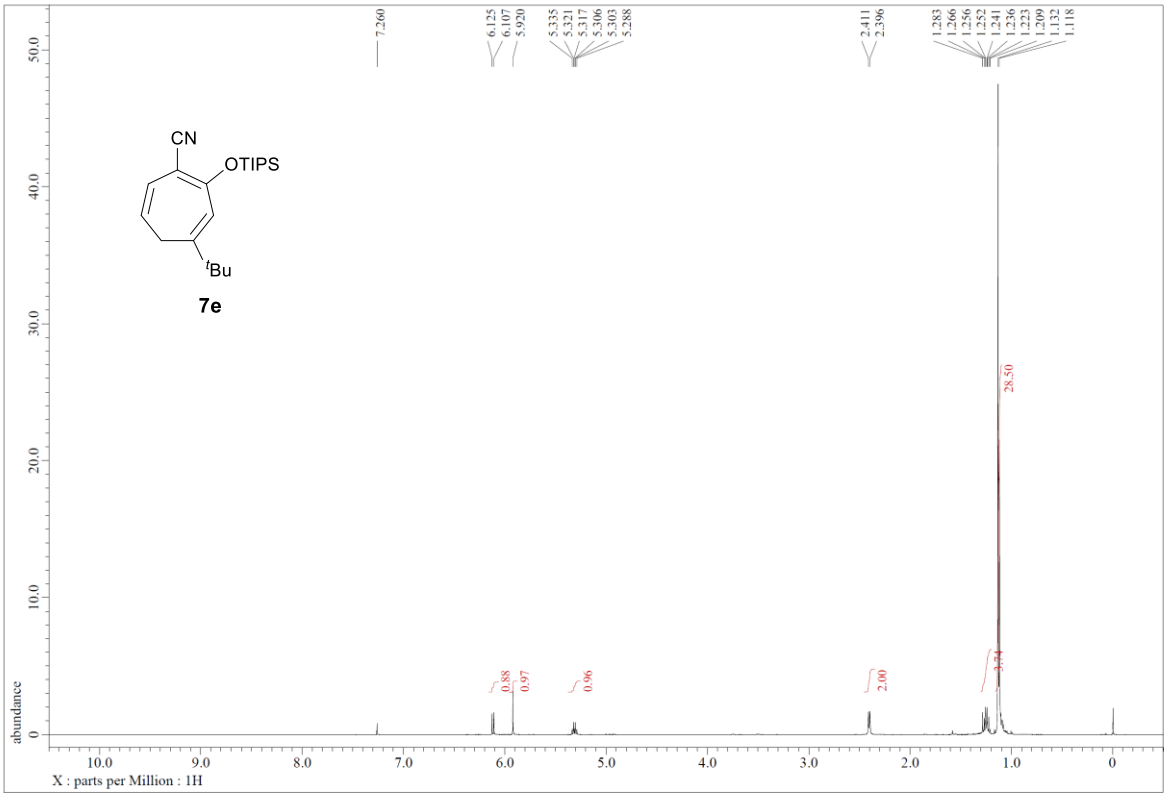
7d (^{1}H NMR, 500 MHz, $CDCl_3$)



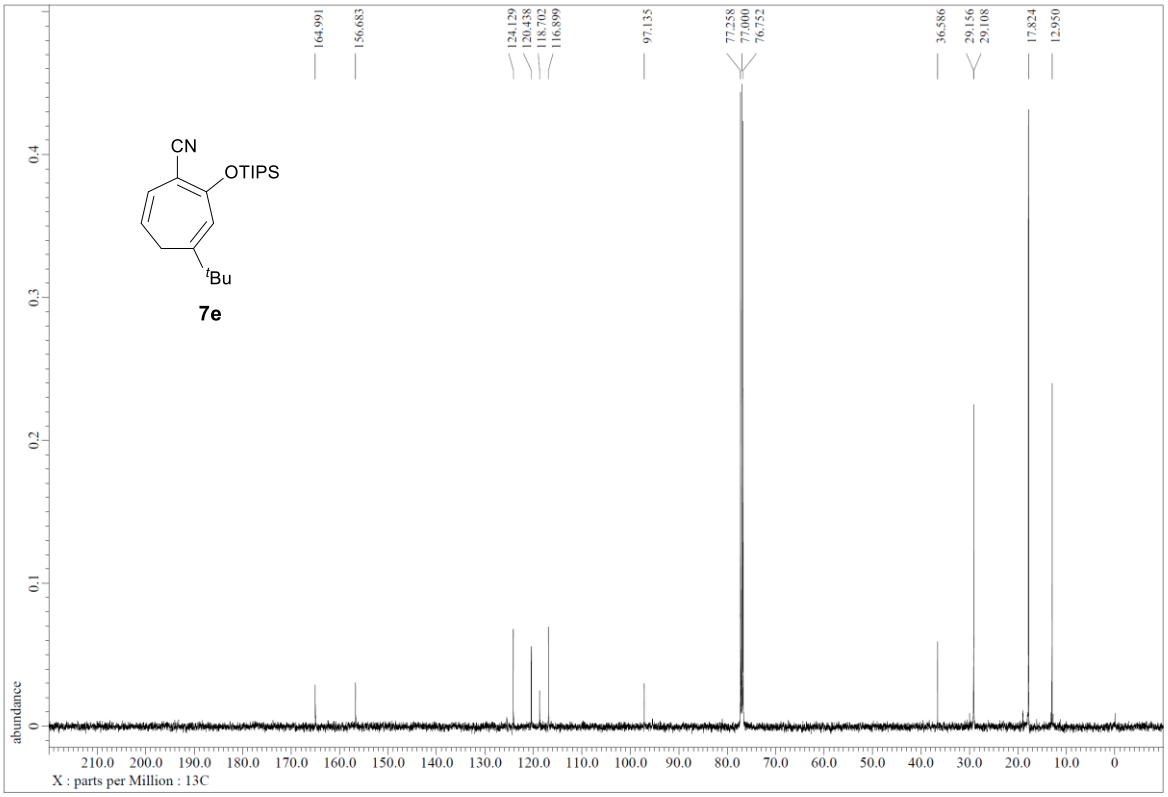
7d (^{13}C NMR, 126 MHz, $CDCl_3$)



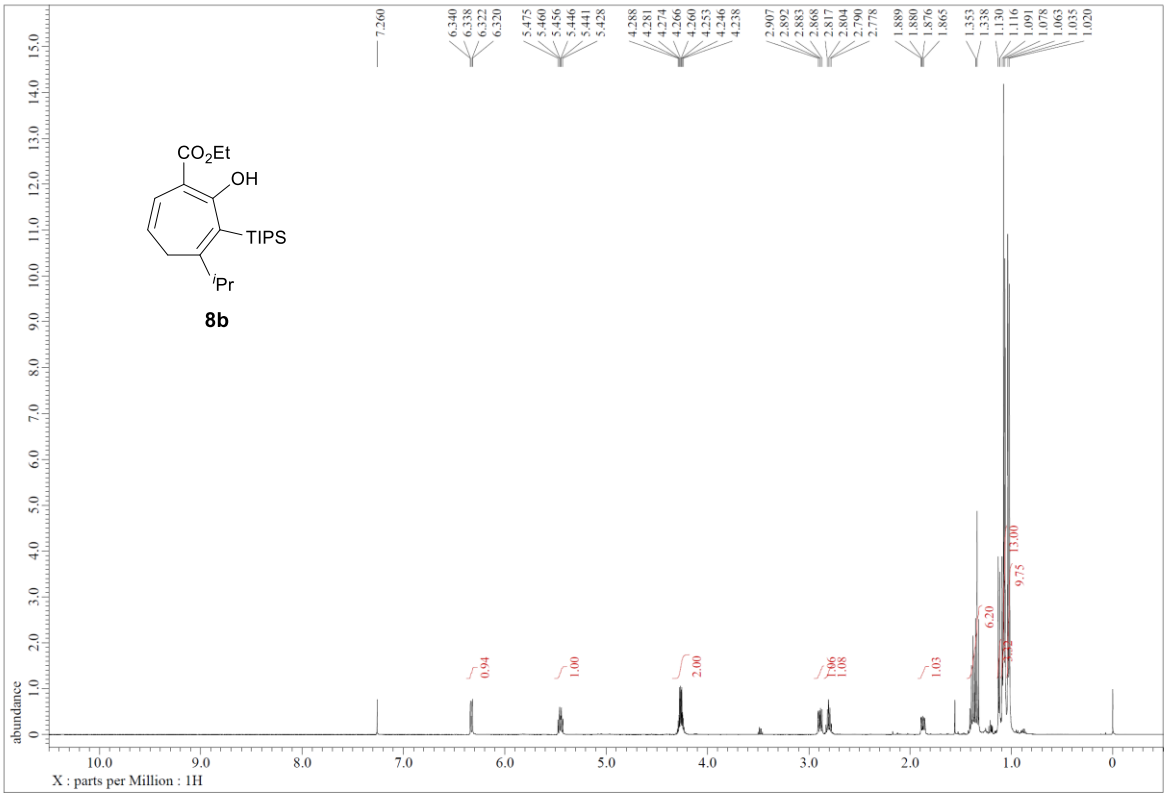
7e (^{1}H NMR, 500 MHz, $CDCl_3$)



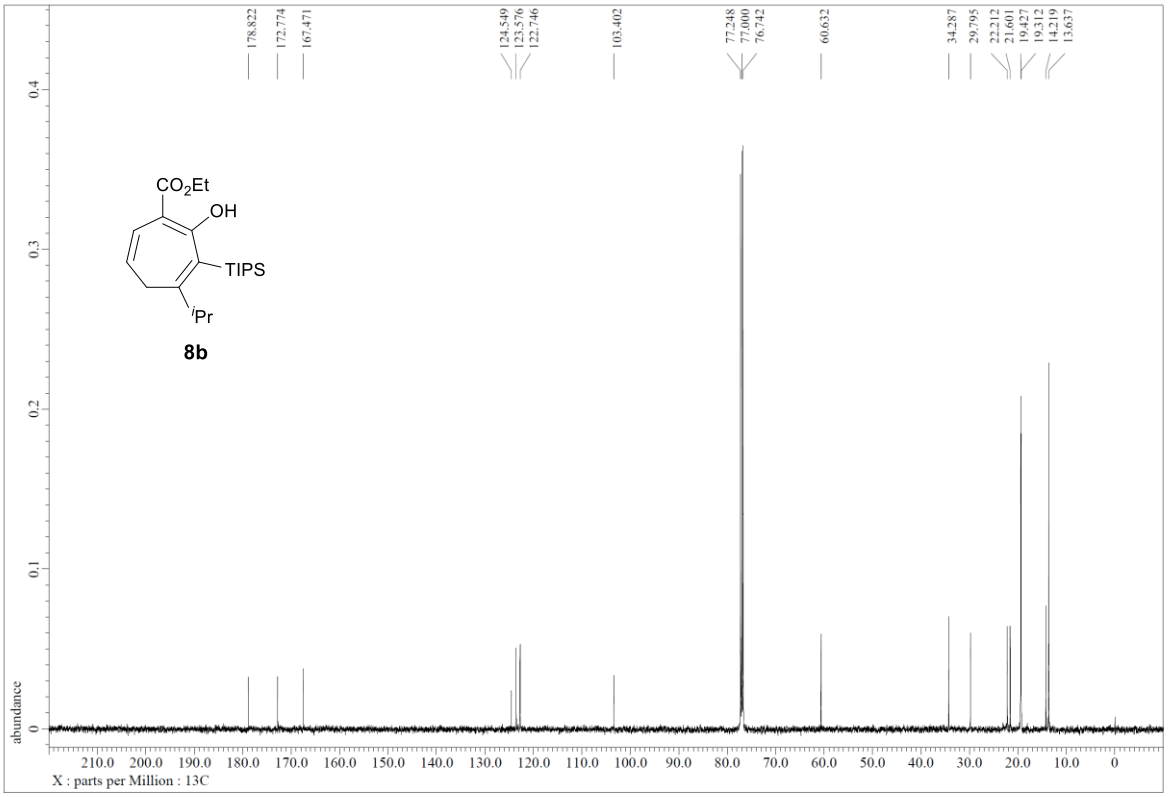
7e (^{13}C NMR, 126 MHz, $CDCl_3$)



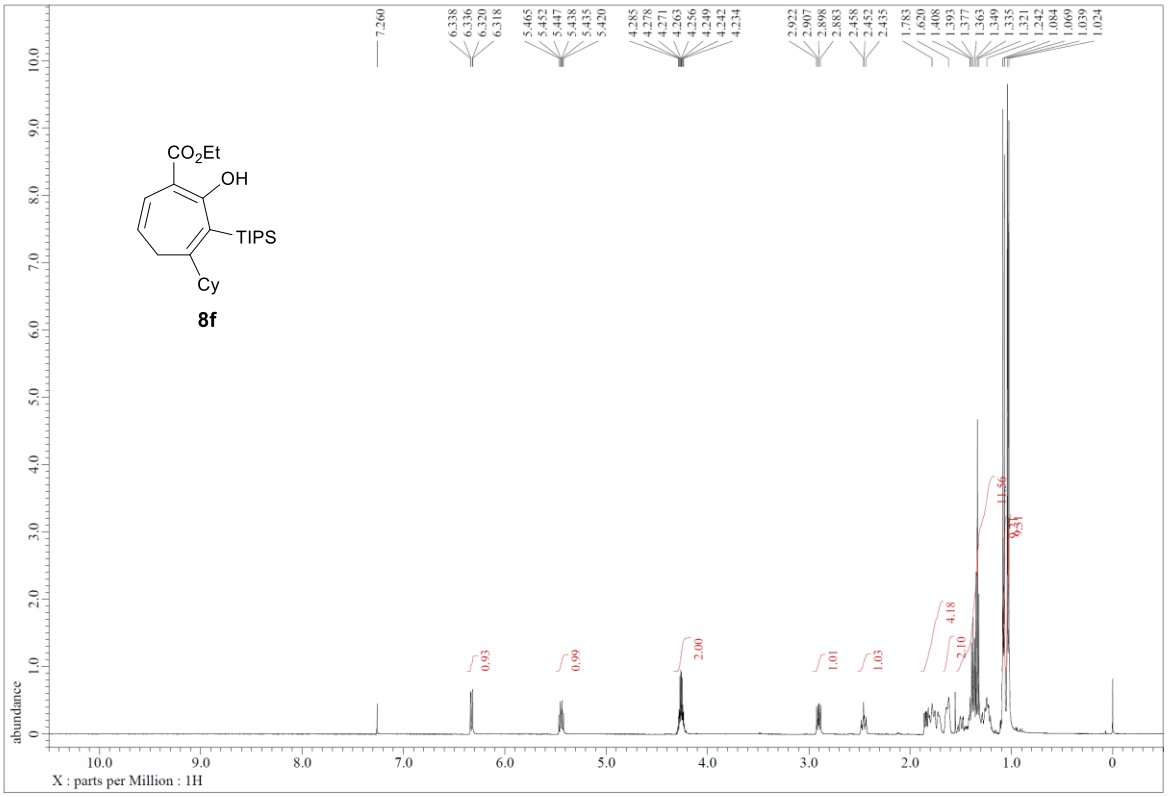
8b (^{1}H NMR, 500 MHz, $CDCl_3$)



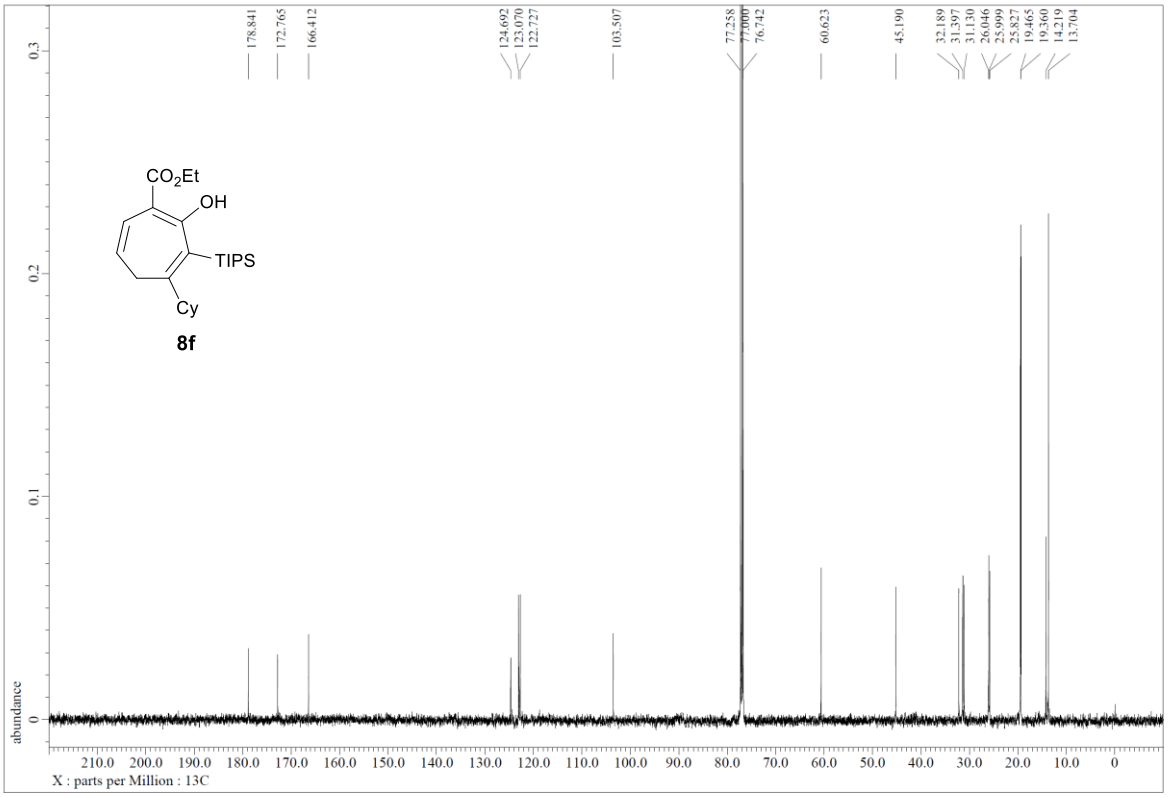
8b (^{13}C NMR, 126 MHz, $CDCl_3$)



8f (^{1}H NMR, 500 MHz, $CDCl_3$)

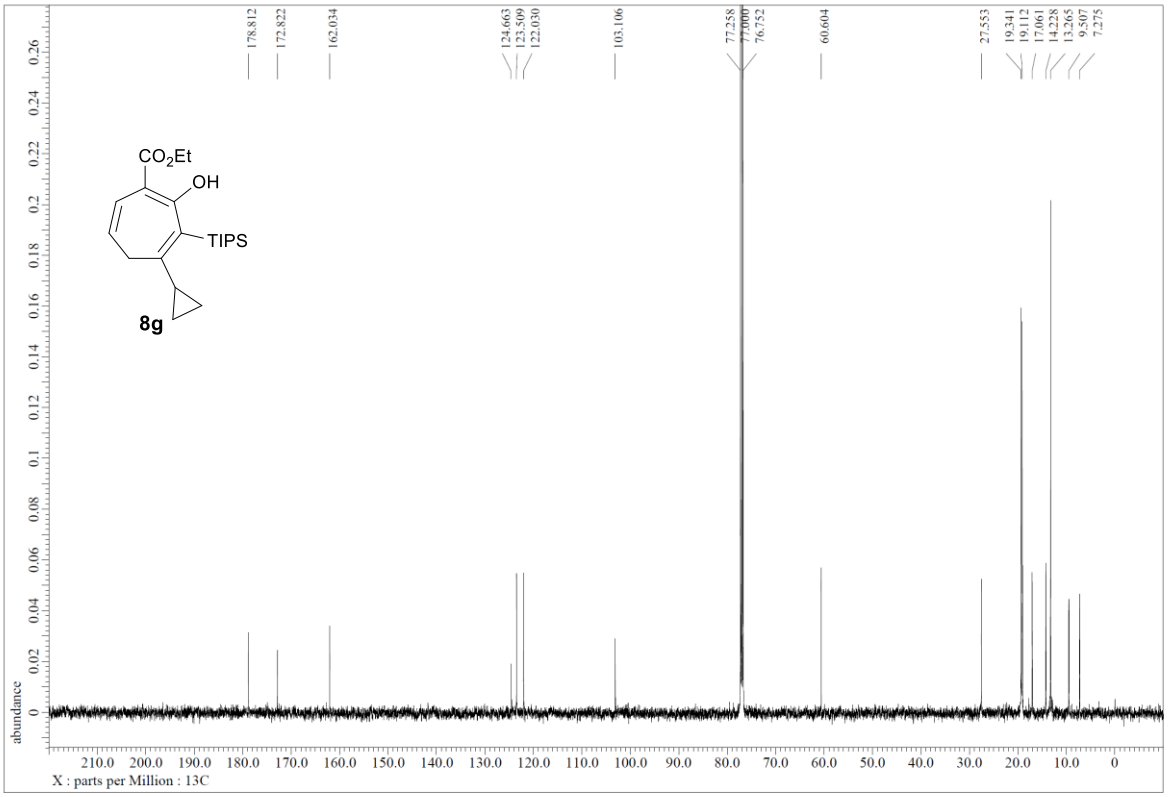


8f (^{13}C NMR, 126 MHz, $CDCl_3$)

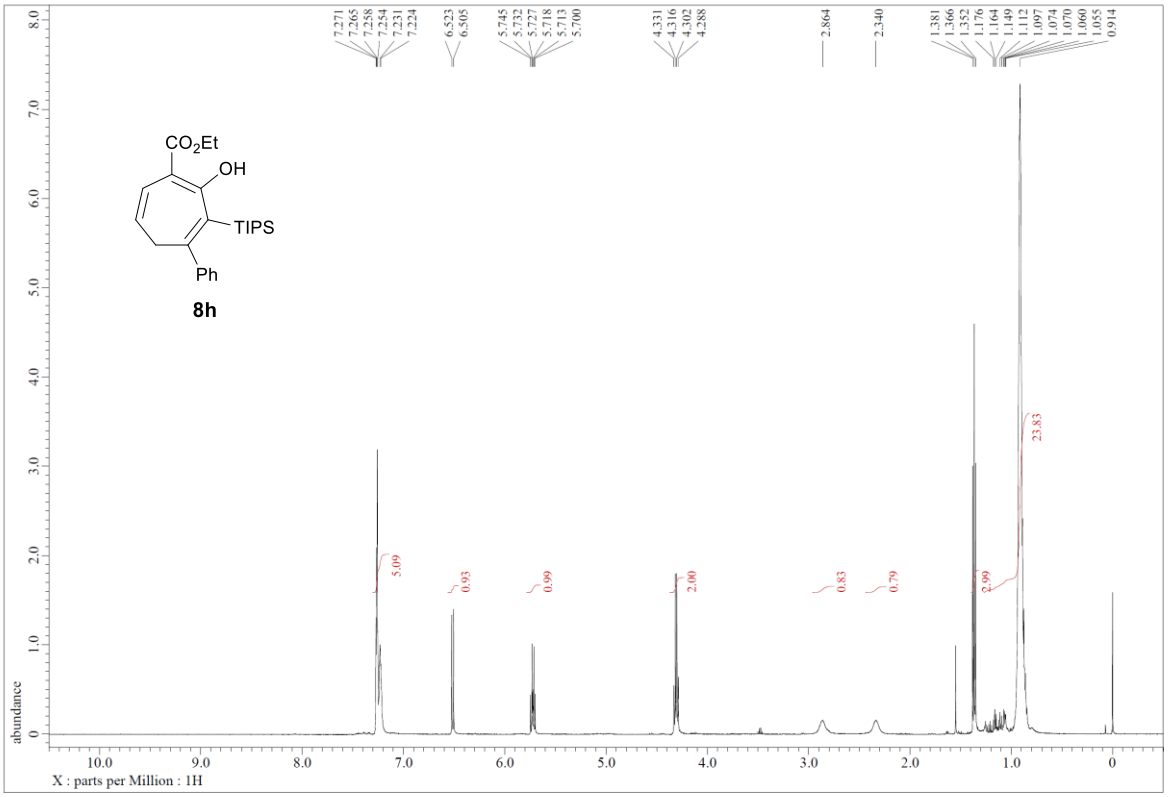


8g (^{1}H NMR, 500 MHz, $CDCl_3$)

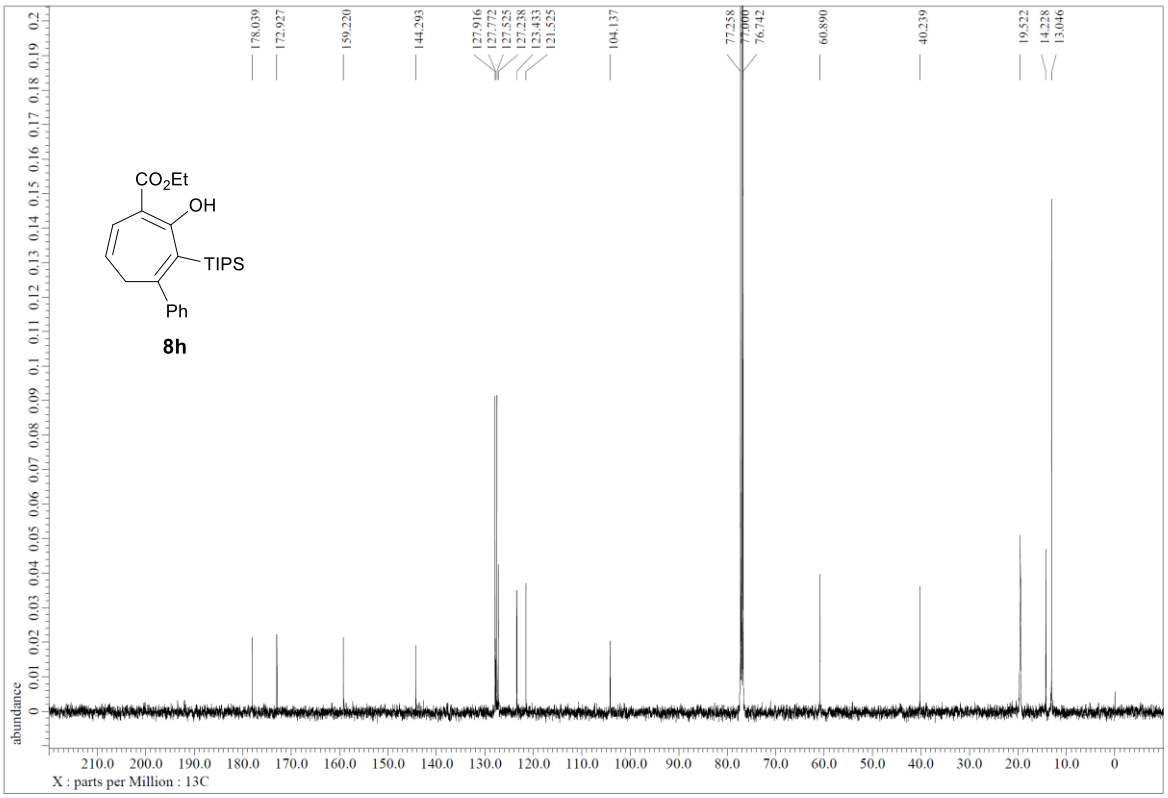
8g (^{13}C NMR, 126 MHz, $CDCl_3$)



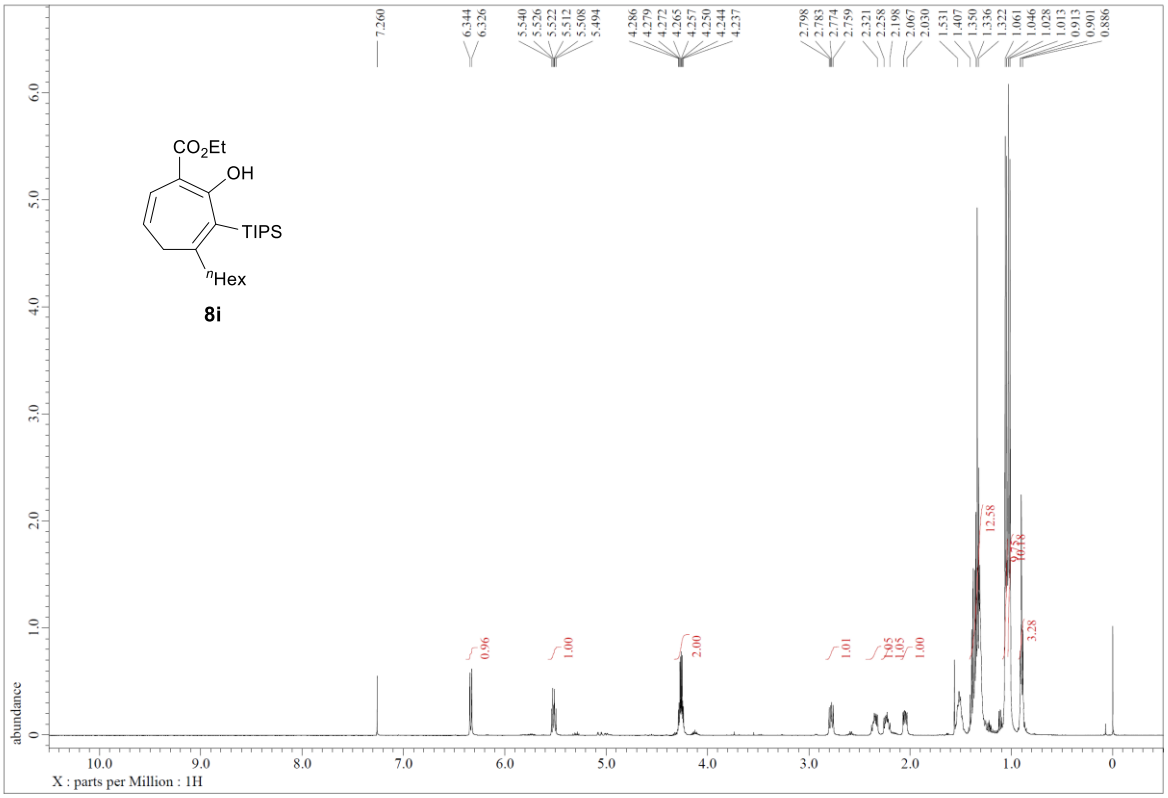
8h (^{1}H NMR, 500 MHz, $CDCl_3$)



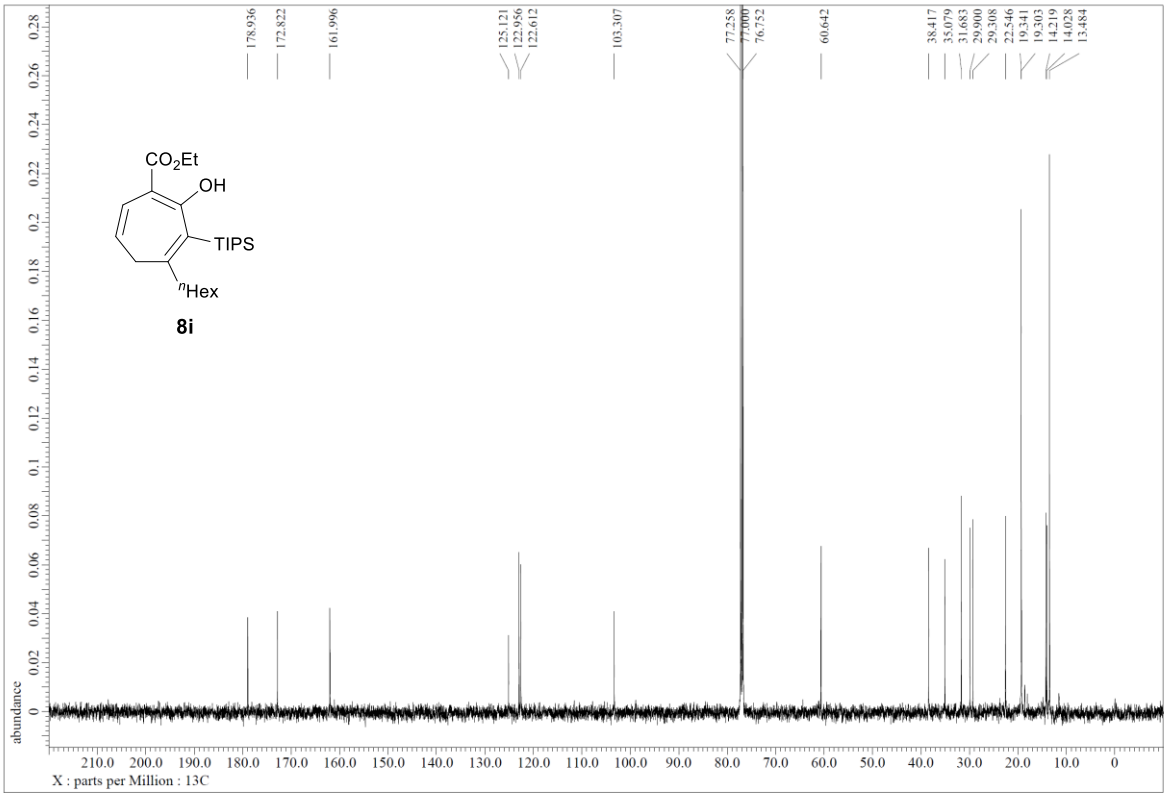
8h (^{13}C NMR, 126 MHz, $CDCl_3$)



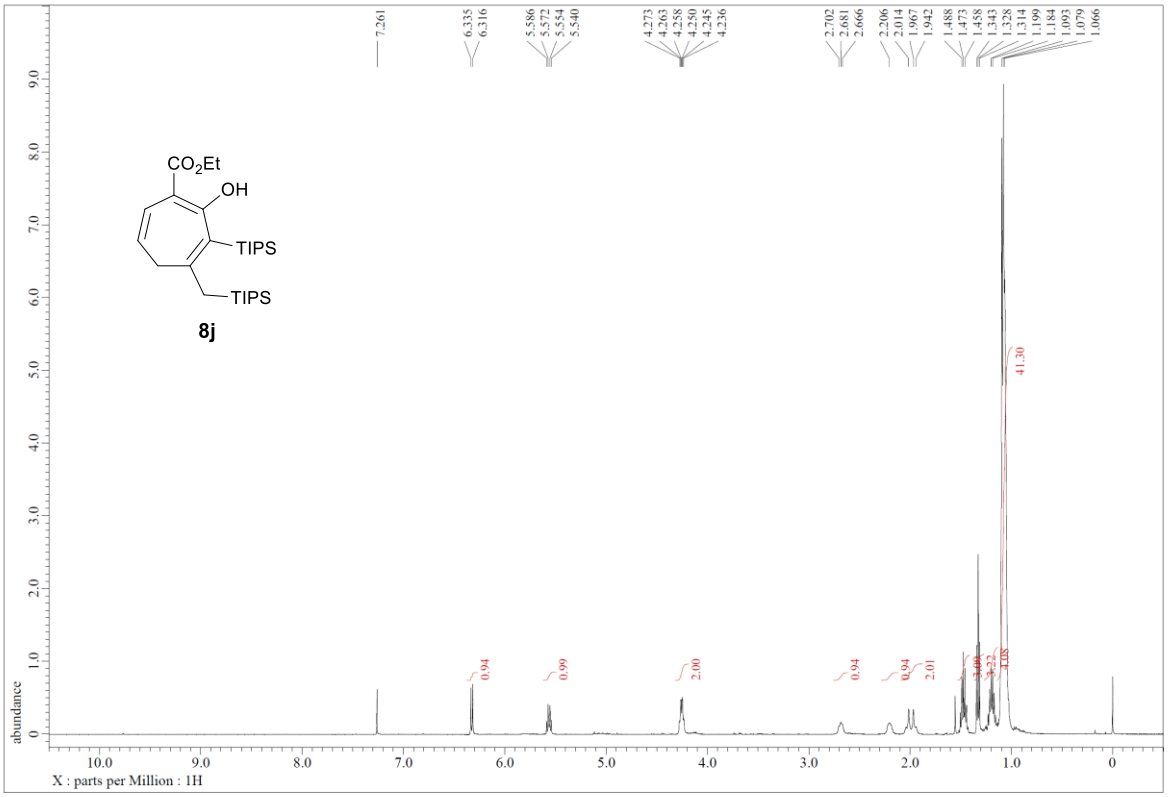
8i (^{1}H NMR, 500 MHz, $CDCl_3$)



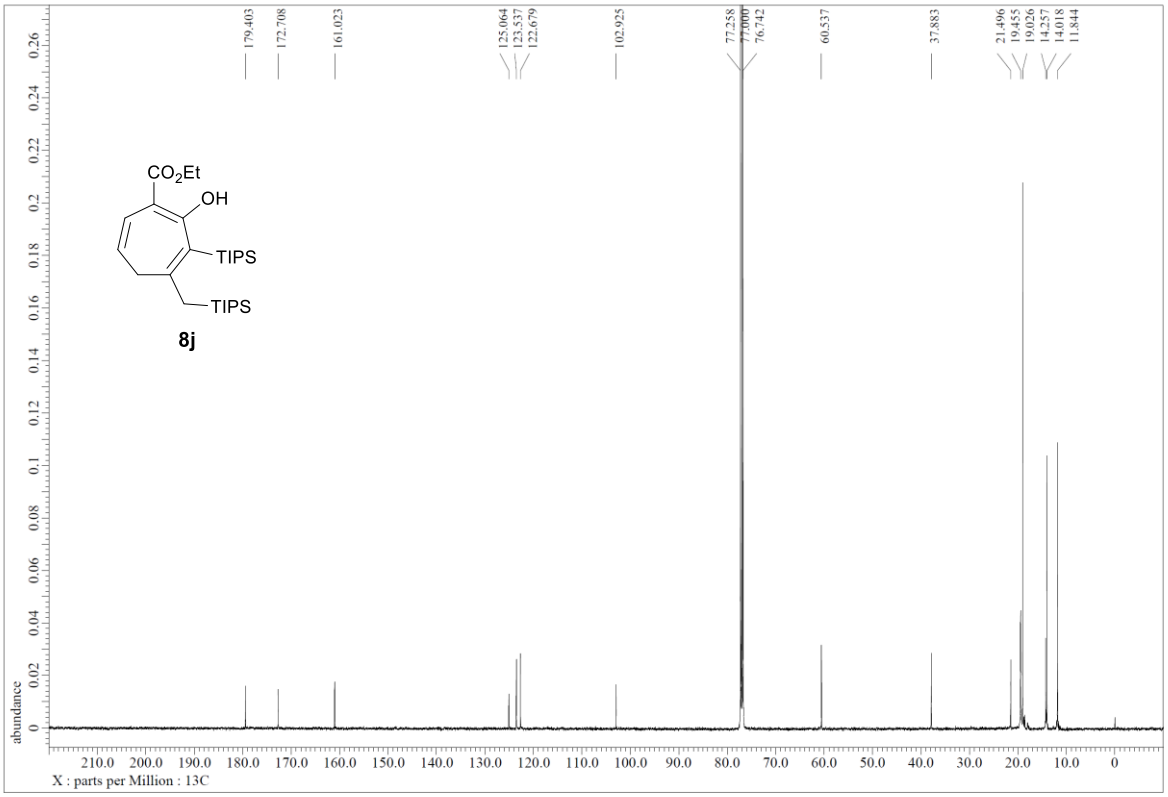
8i (^{13}C NMR, 126 MHz, $CDCl_3$)



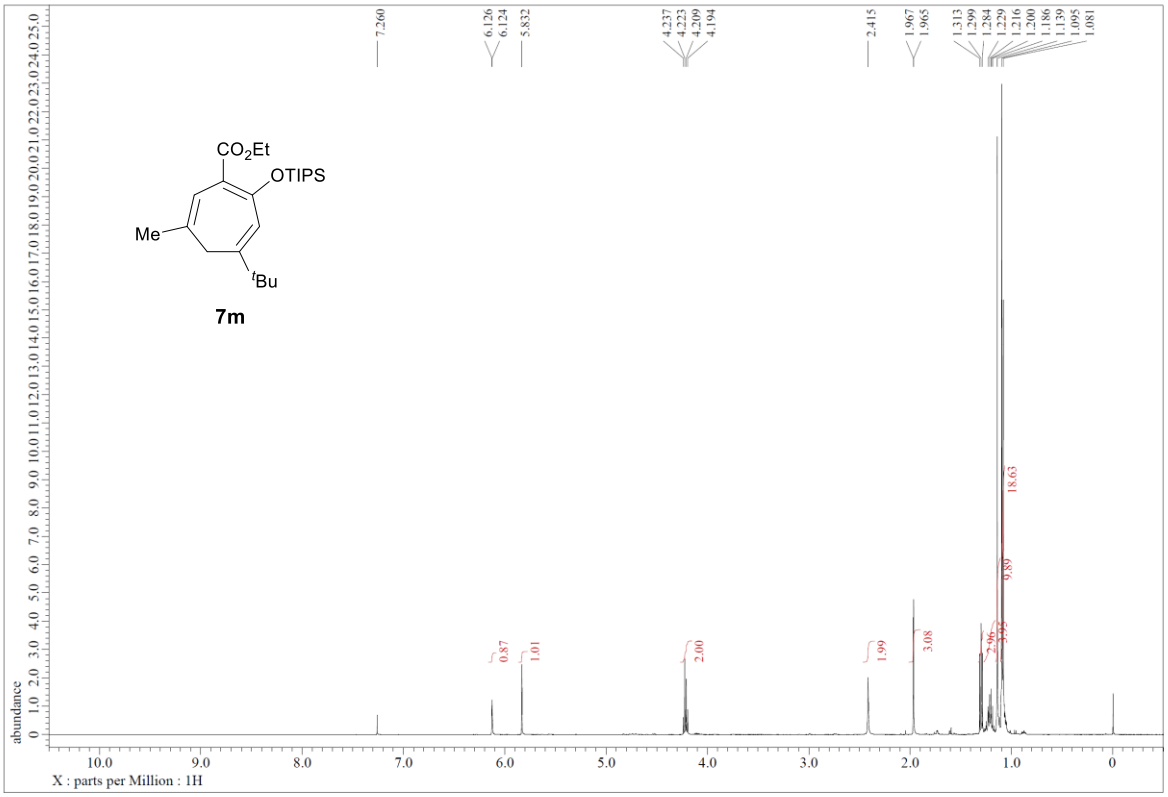
8j (^{1}H NMR, 500 MHz, $CDCl_3$)



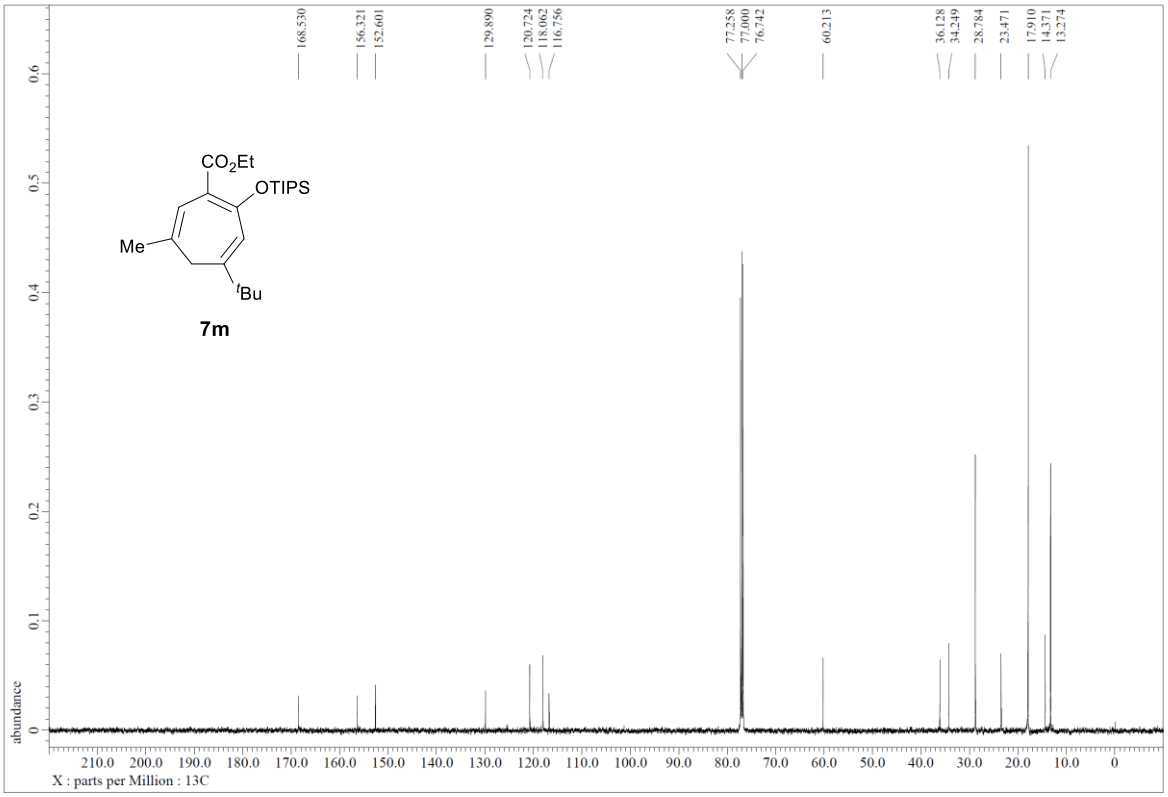
8j (^{13}C NMR, 126 MHz, $CDCl_3$)



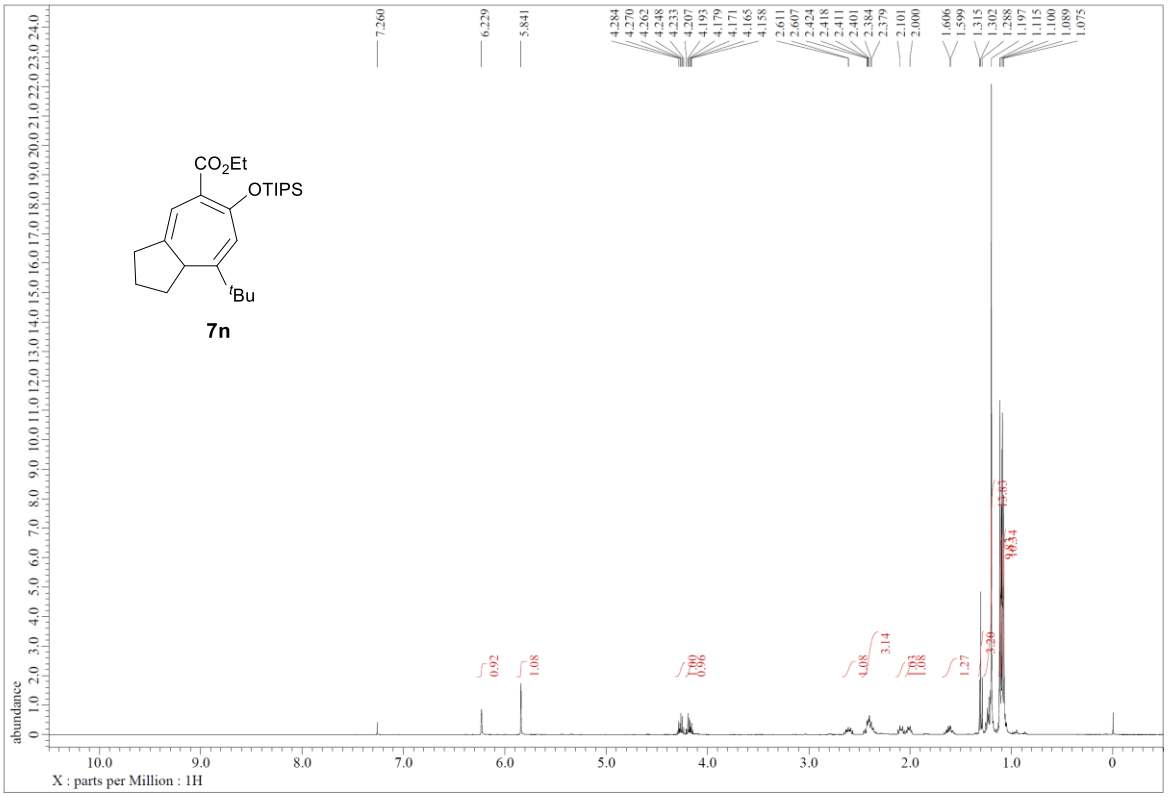
7m (^{1}H NMR, 500 MHz, $CDCl_3$)



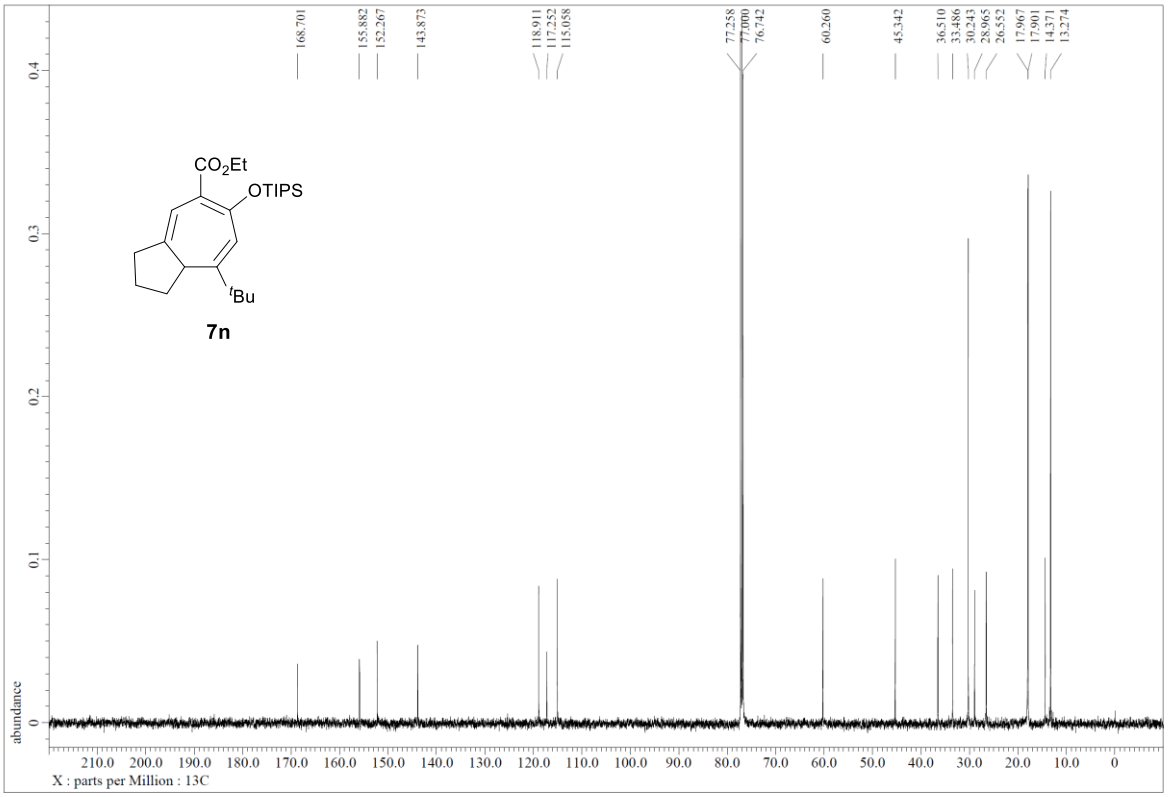
7m (^{13}C NMR, 126 MHz, $CDCl_3$)



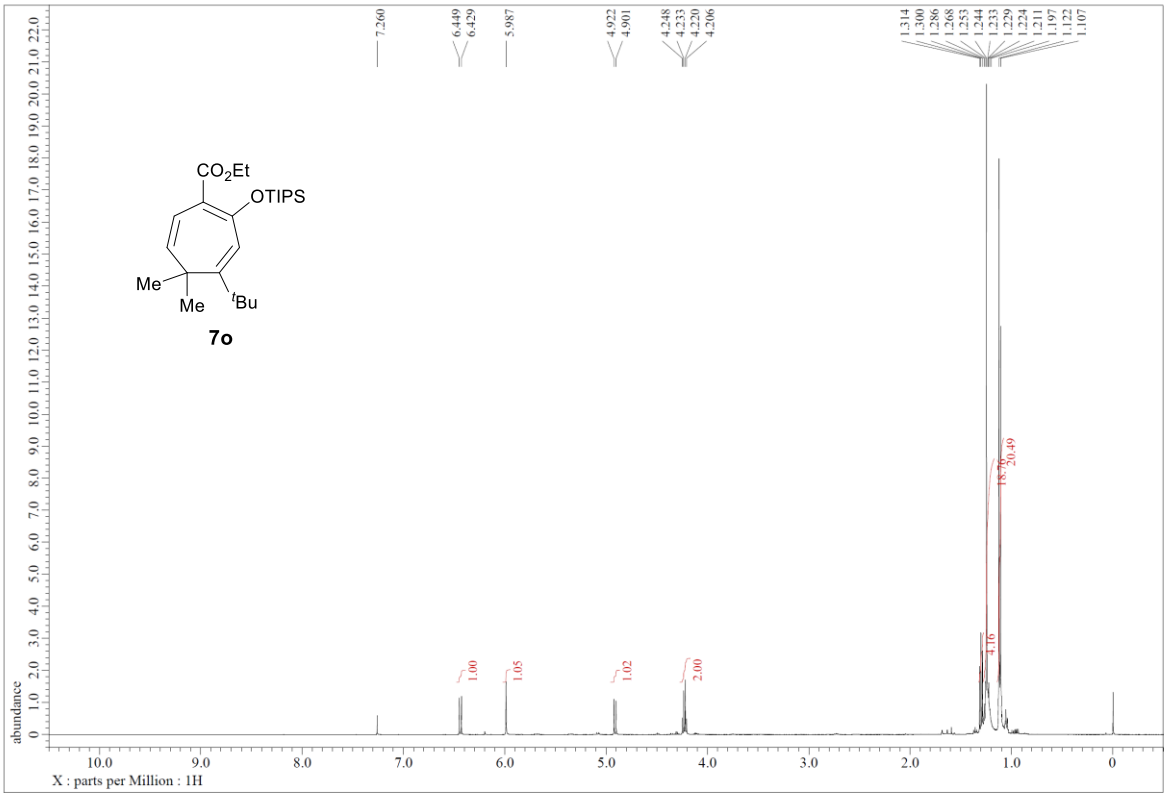
7n (^{1}H NMR, 500 MHz, $CDCl_3$)



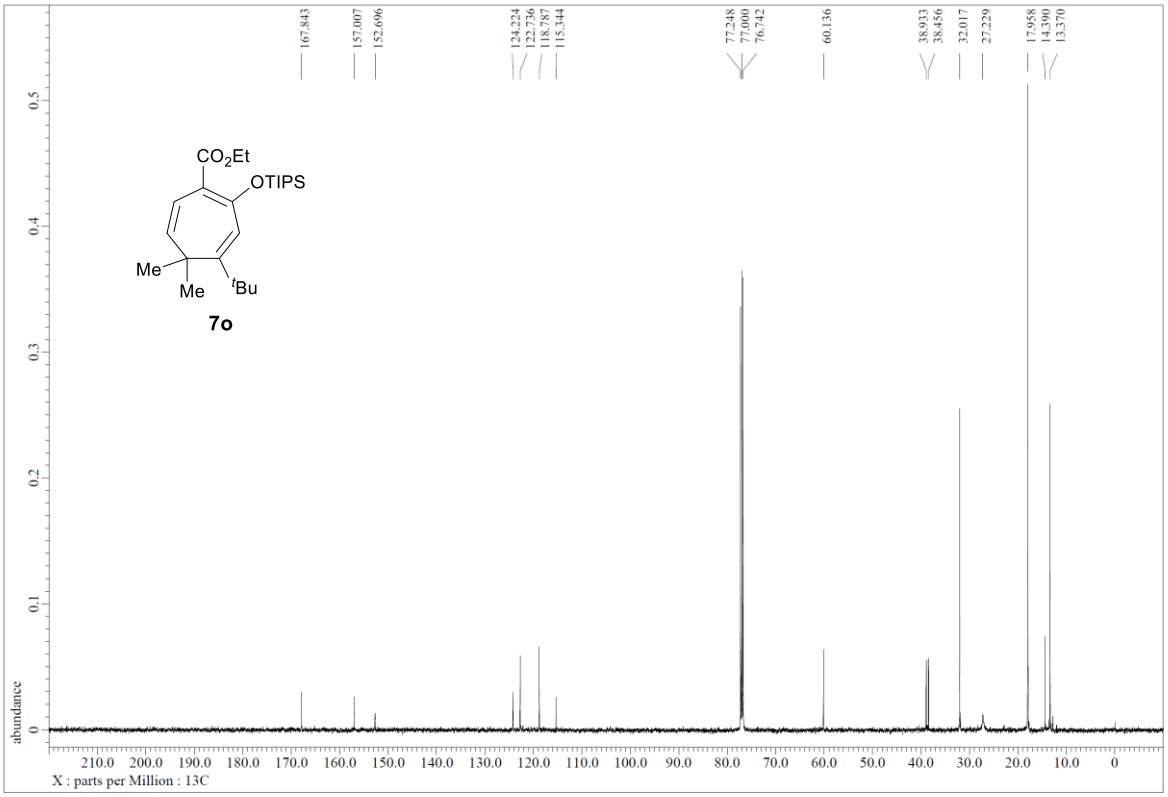
7n (^{13}C NMR, 126 MHz, $CDCl_3$)



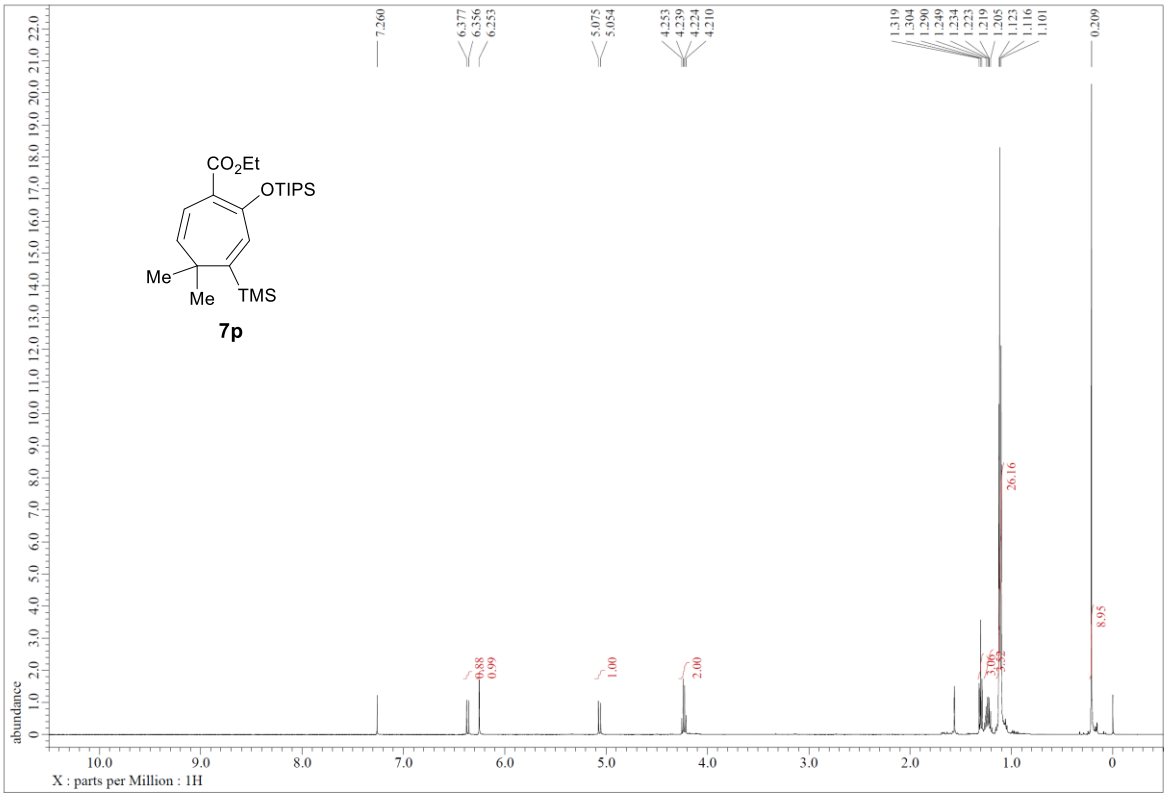
7o (^{1}H NMR, 500 MHz, $CDCl_3$)



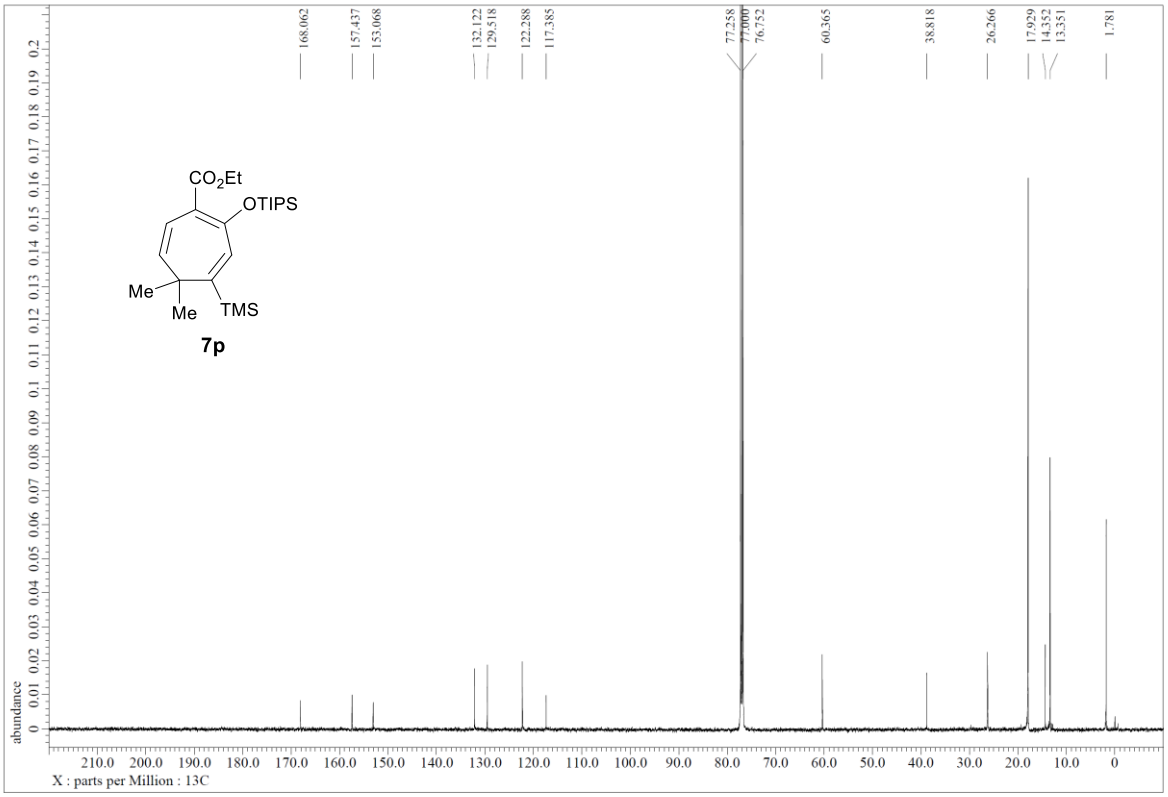
7o (^{13}C NMR, 126 MHz, $CDCl_3$)



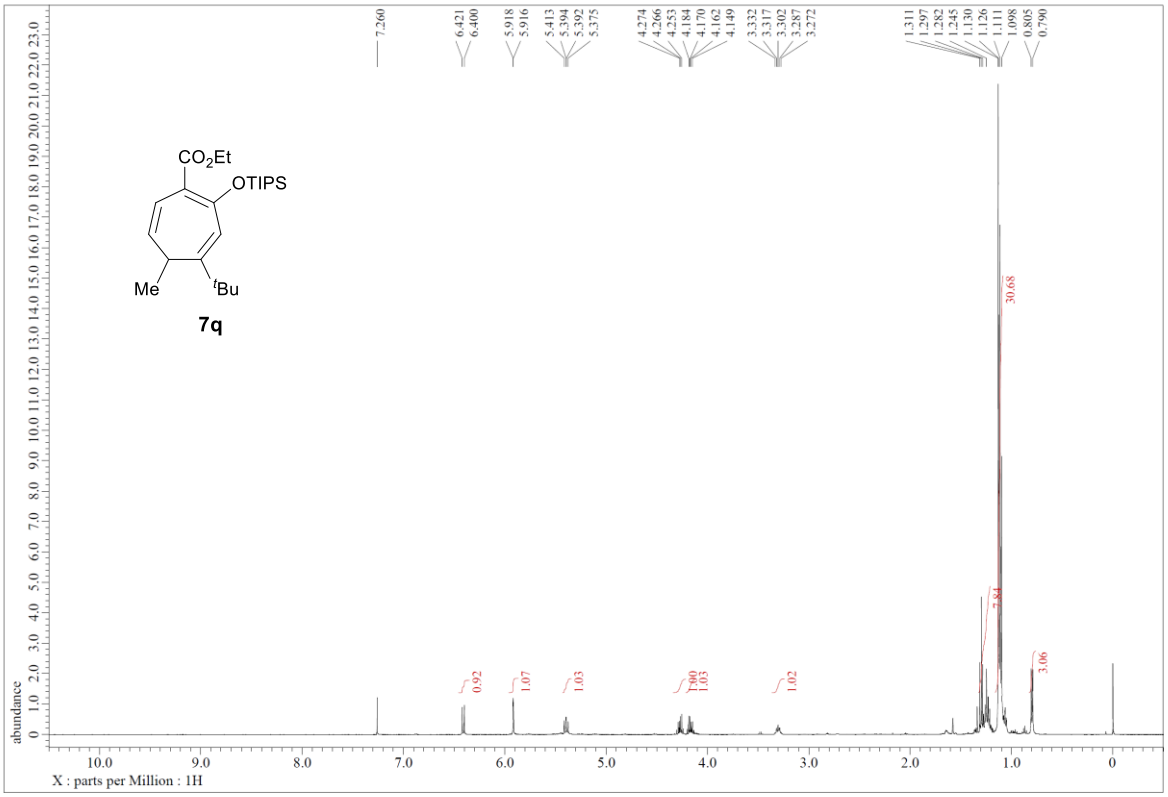
7p (^{1}H NMR, 500 MHz, $CDCl_3$)



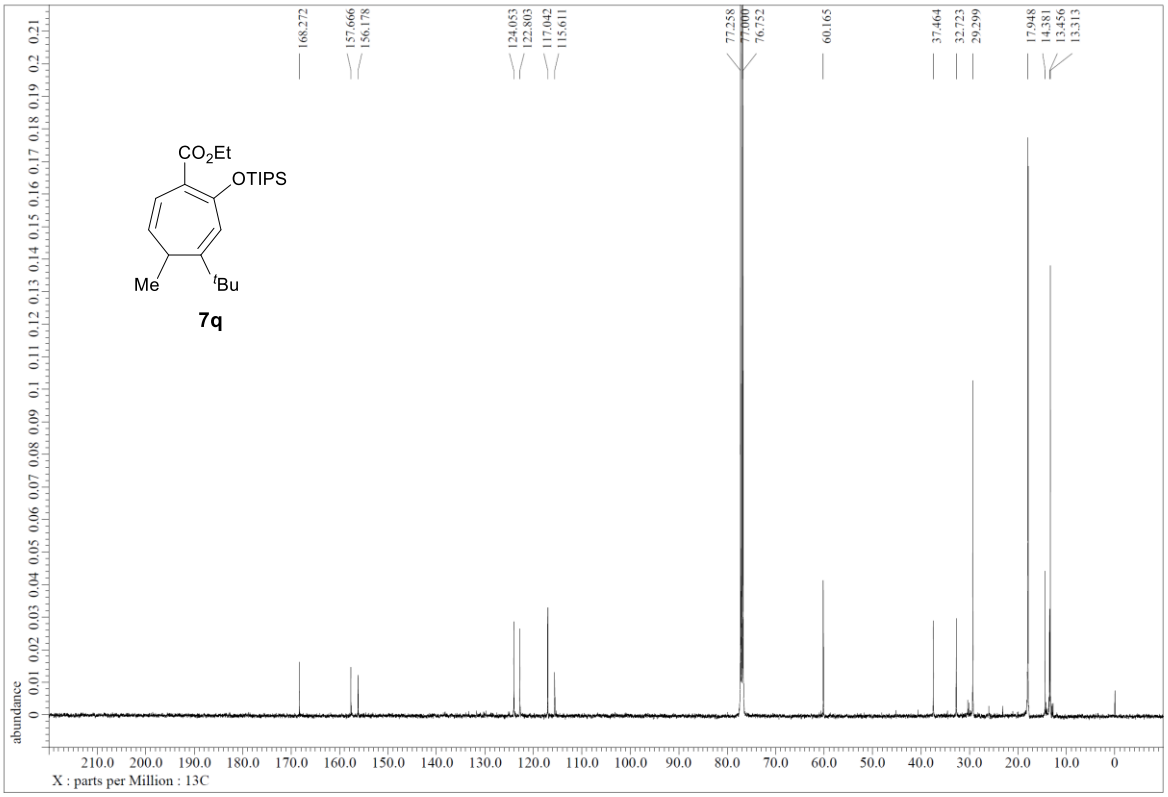
7p (^{13}C NMR, 126 MHz, $CDCl_3$)



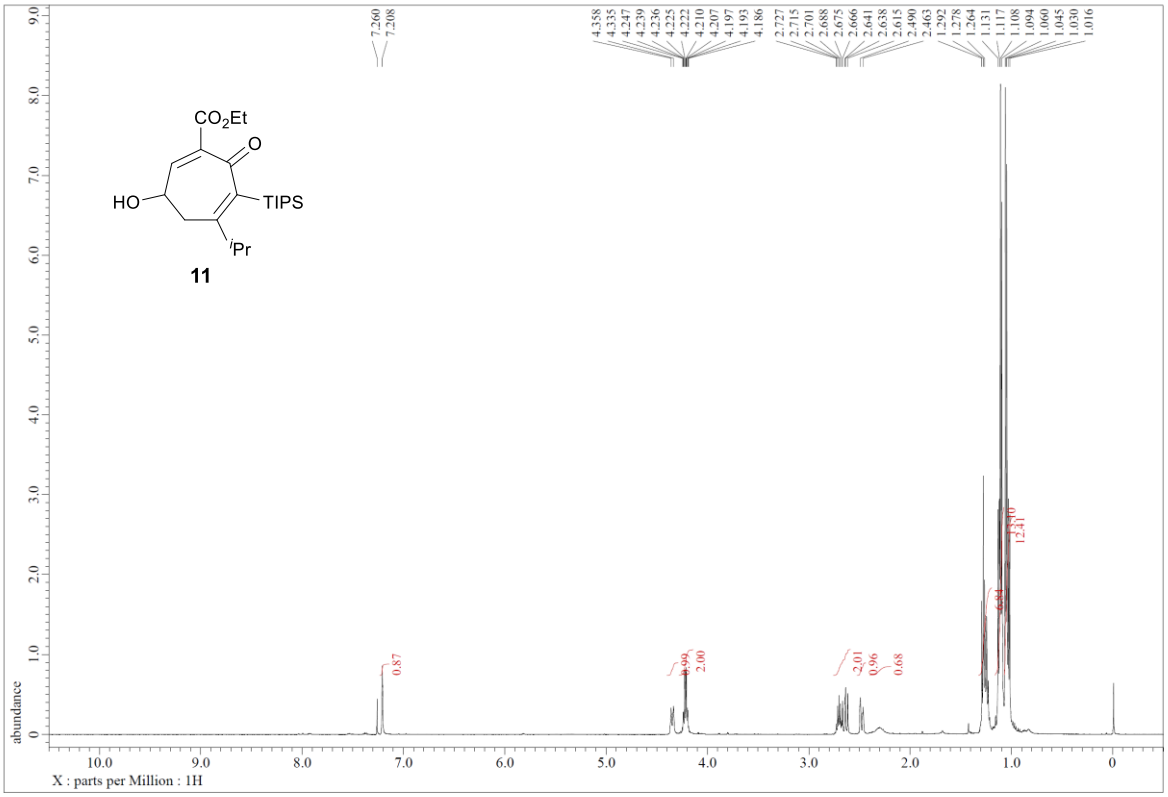
7q (^{1}H NMR, 500 MHz, $CDCl_3$)



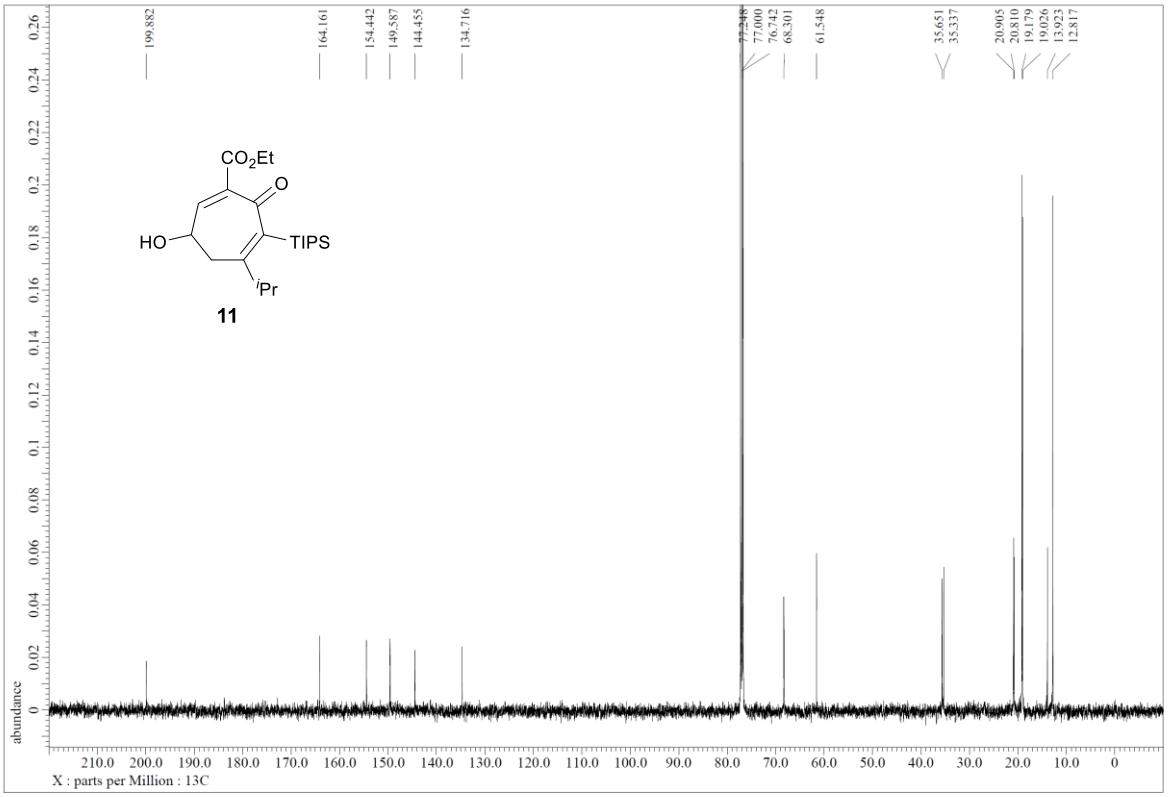
7q (^{13}C NMR, 126 MHz, $CDCl_3$)



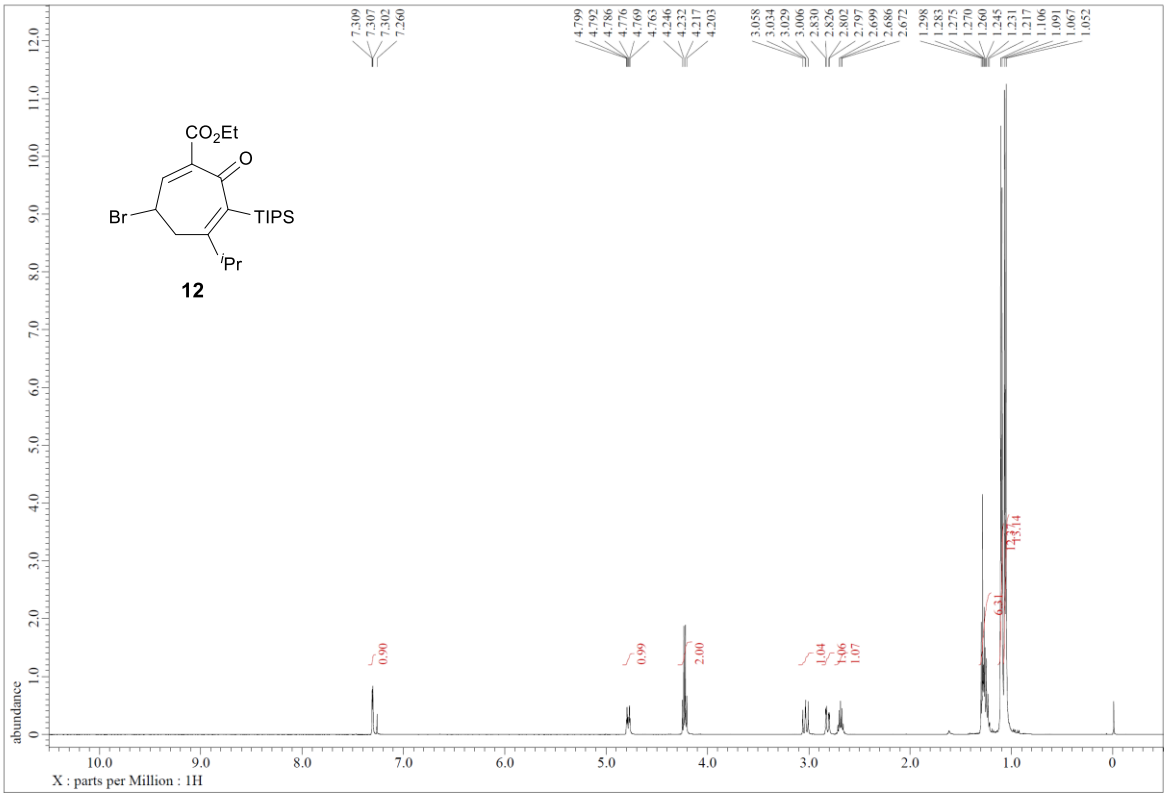
11 (^{1}H NMR, 500 MHz, $CDCl_3$)



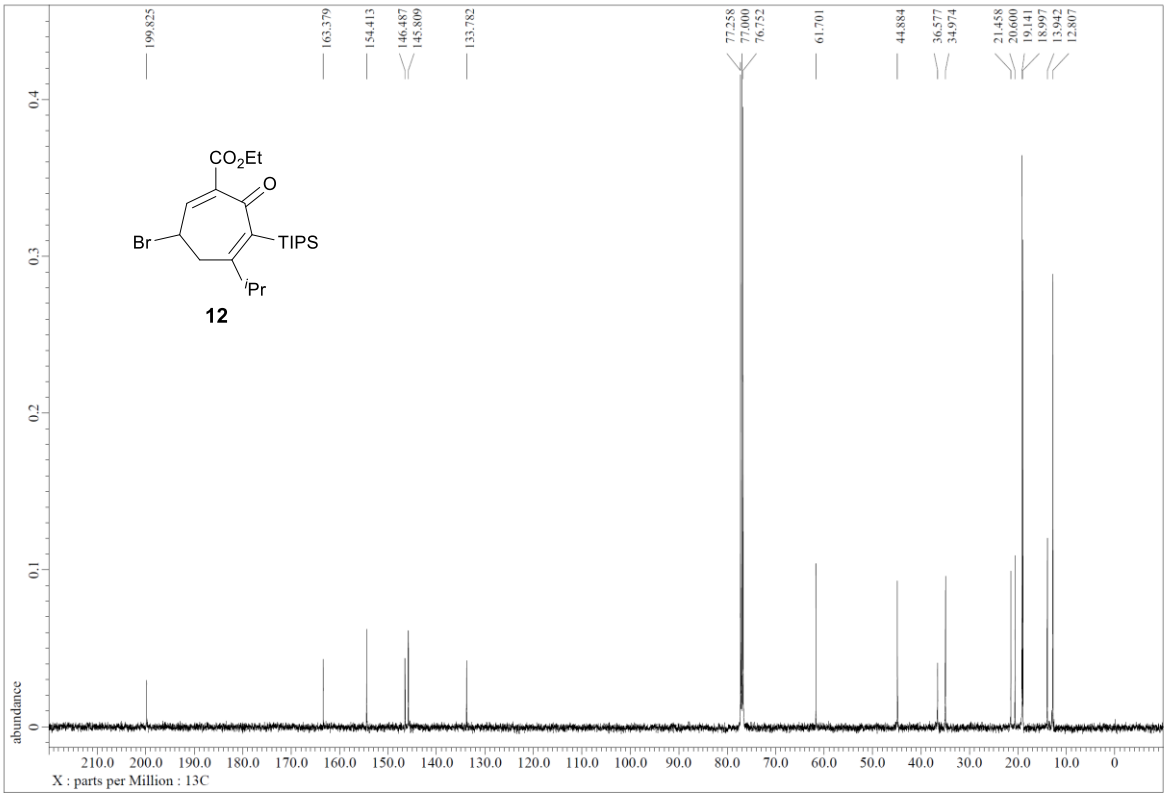
11 (^{13}C NMR, 126 MHz, $CDCl_3$)



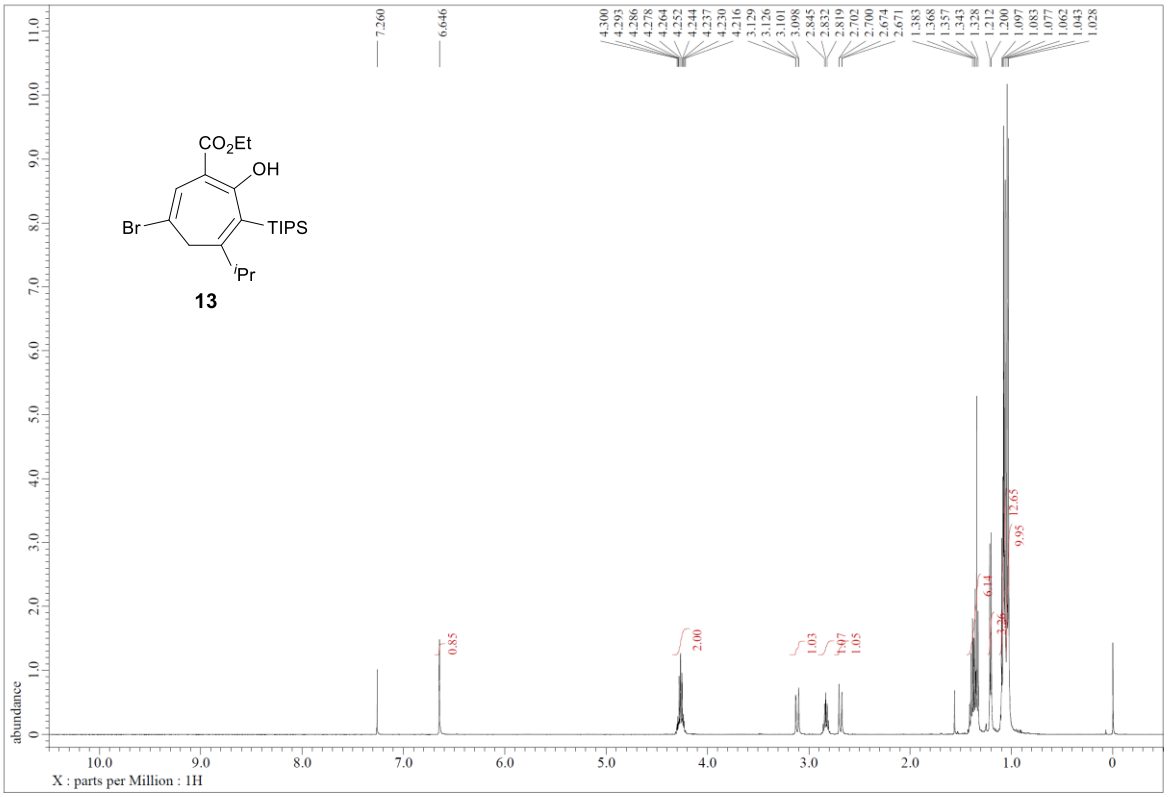
12 (^{1}H NMR, 500 MHz, $CDCl_3$)



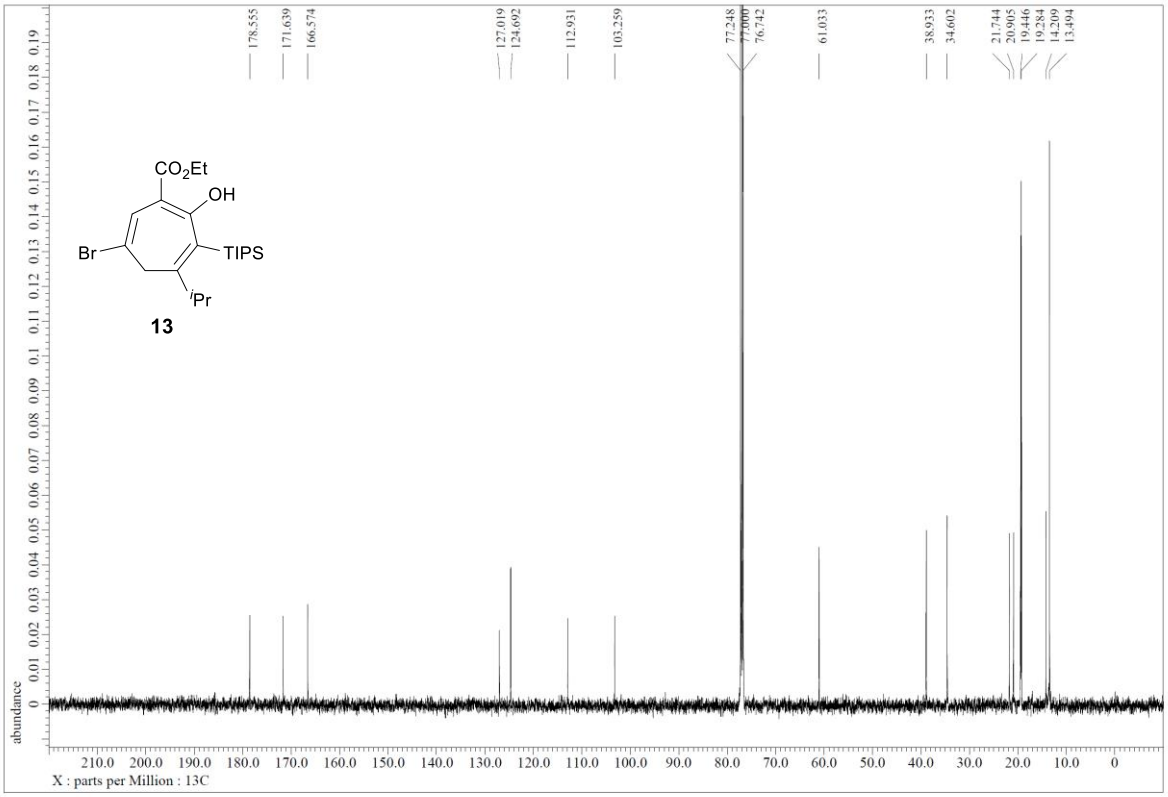
12 (^{13}C NMR, 126 MHz, $CDCl_3$)



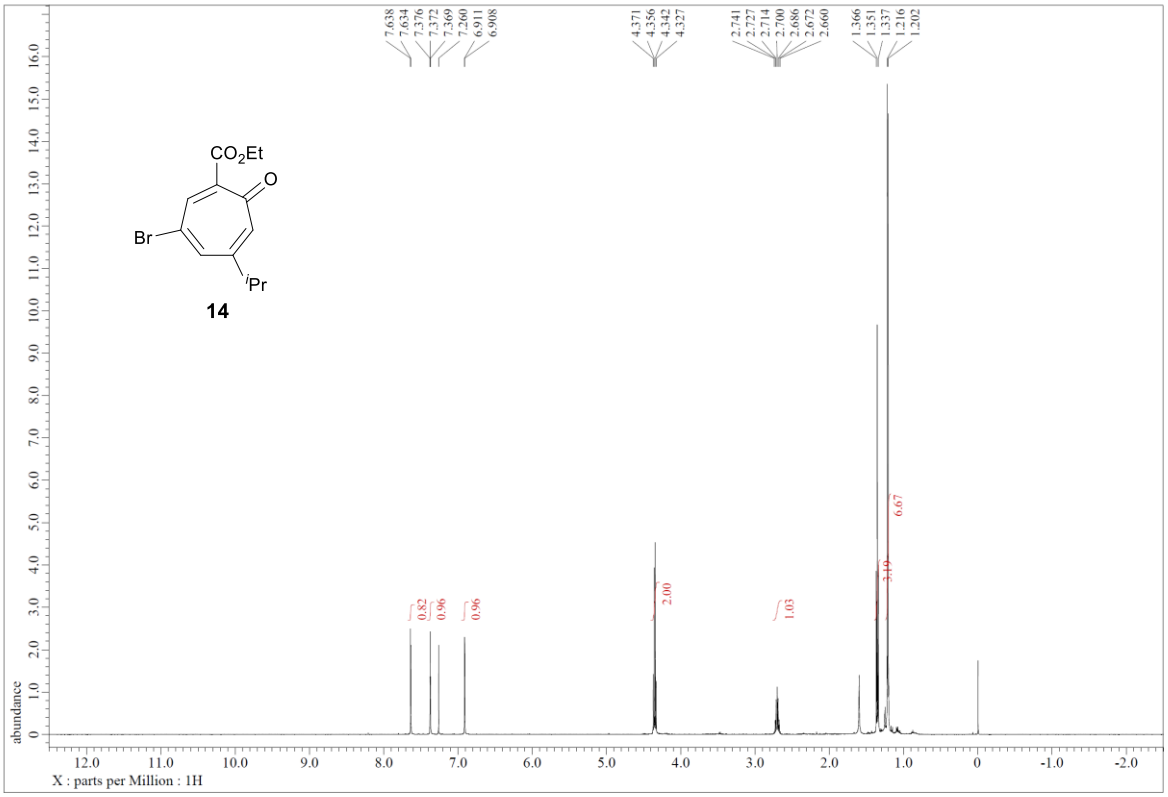
13 (^{1}H NMR, 500 MHz, $CDCl_3$)



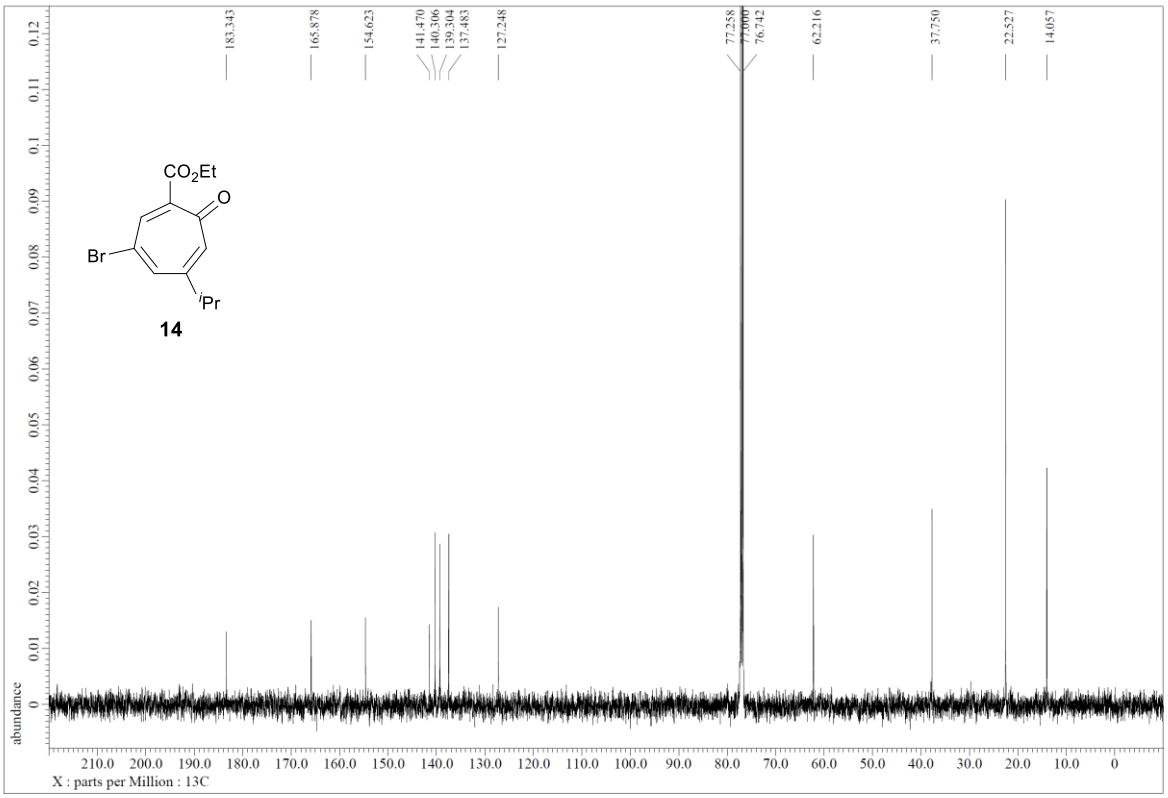
13 (^{13}C NMR, 126 MHz, $CDCl_3$)



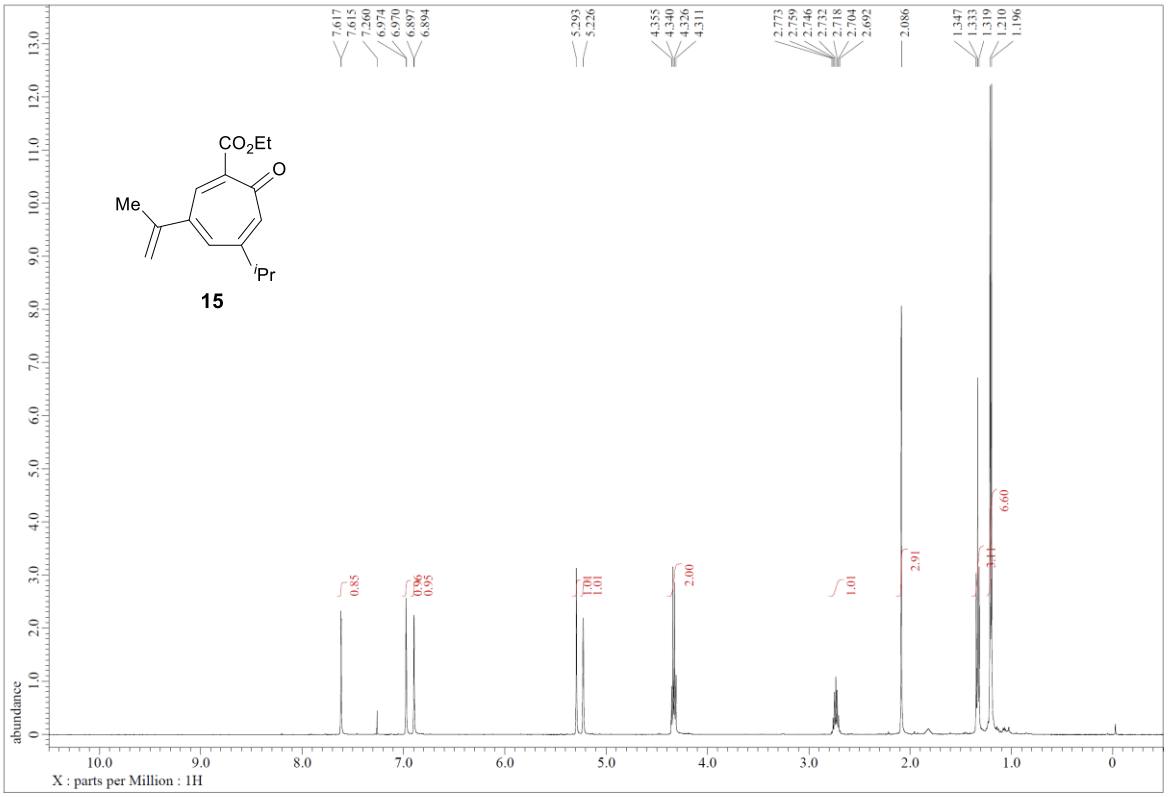
14 (^{1}H NMR, 500 MHz, $CDCl_3$)



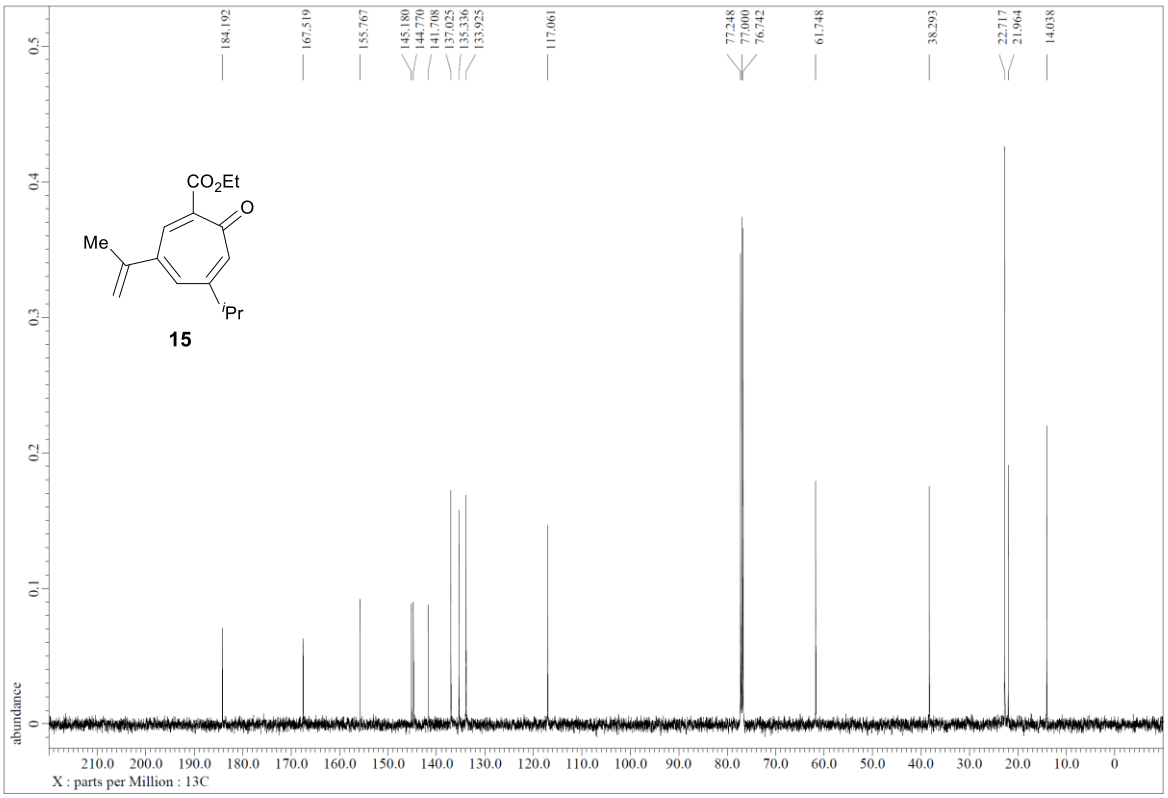
14 (^{13}C NMR, 126 MHz, $CDCl_3$)



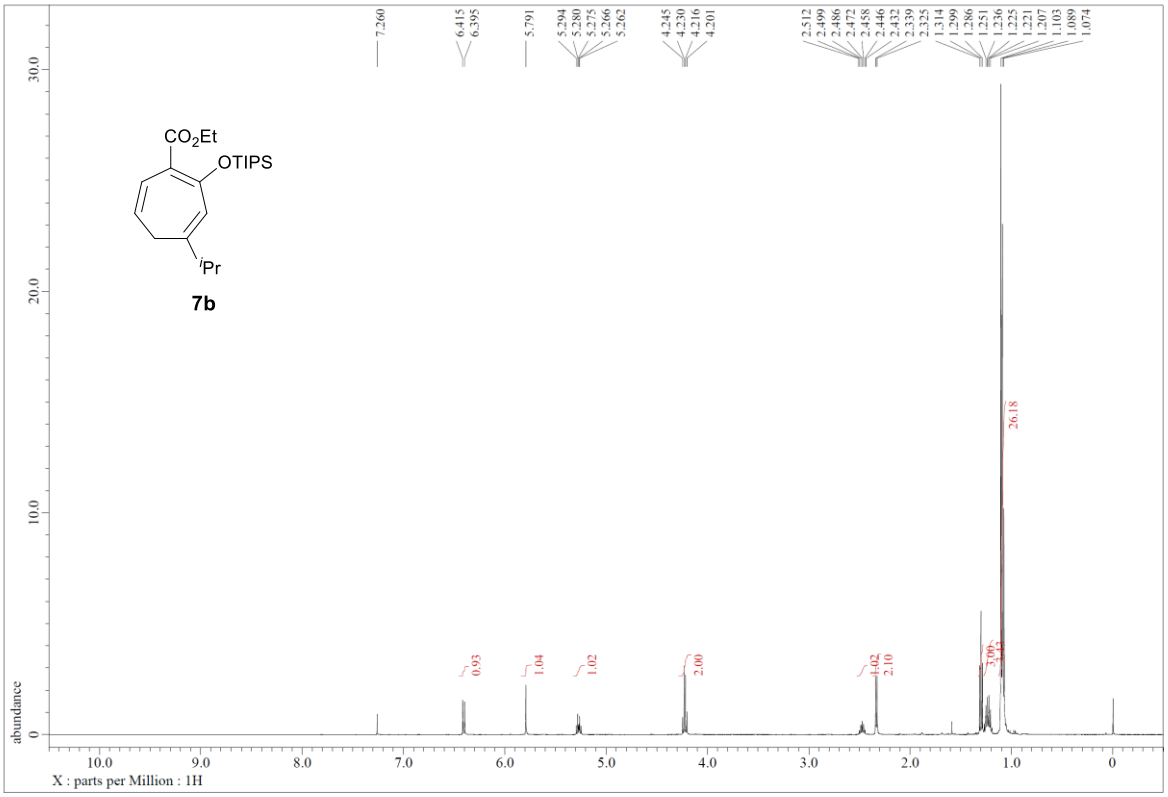
15 (^{1}H NMR, 500 MHz, $CDCl_3$)



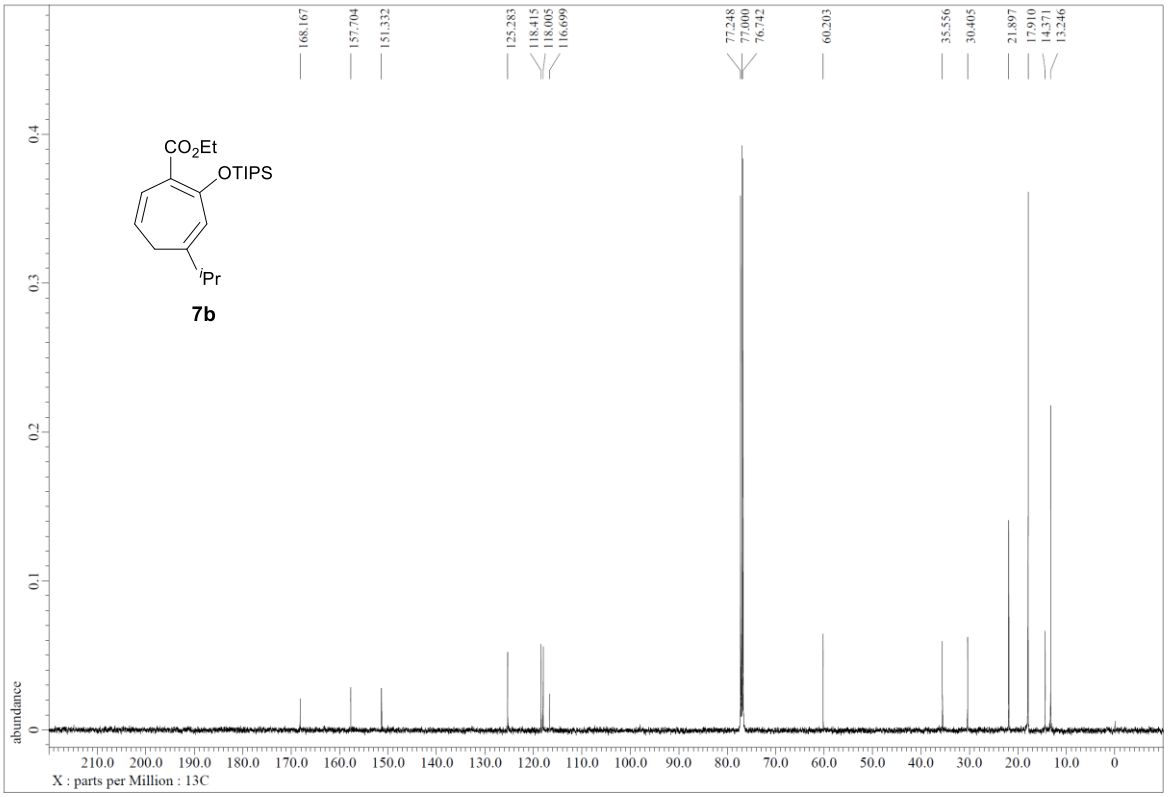
15 (^{13}C NMR, 126 MHz, $CDCl_3$)



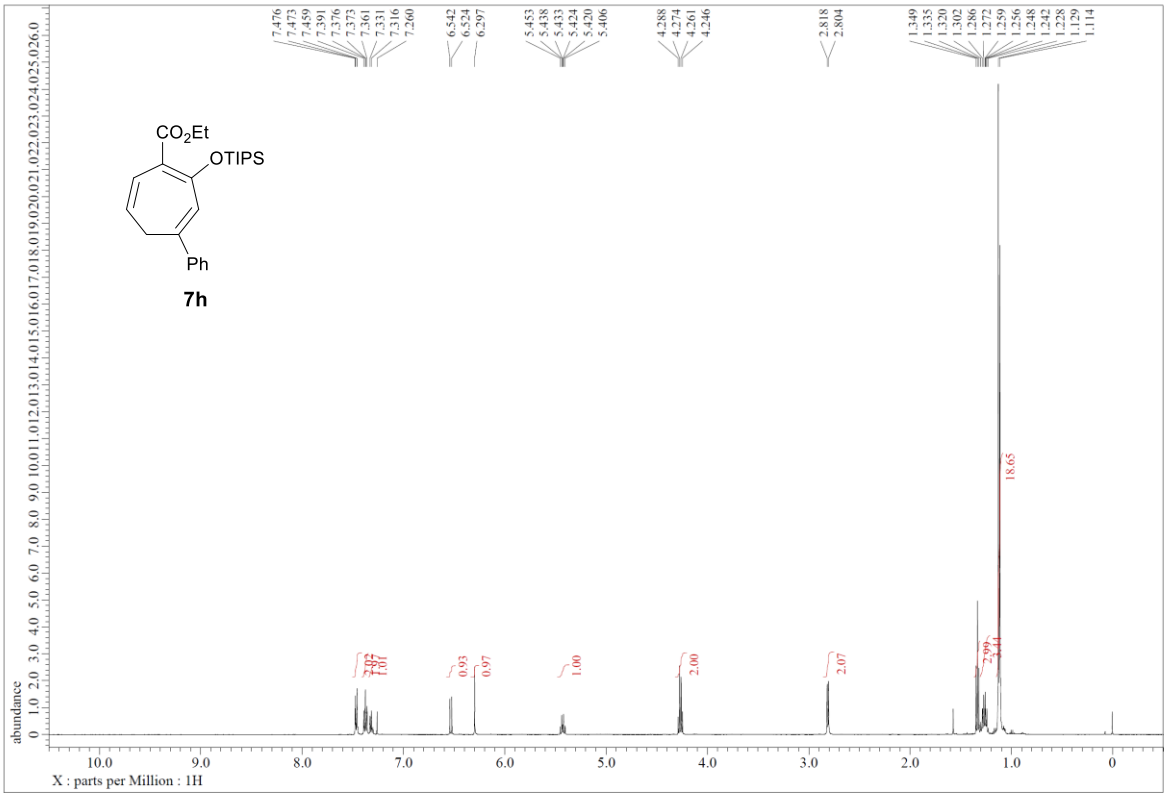
7b (^{1}H NMR, 500 MHz, $CDCl_3$)



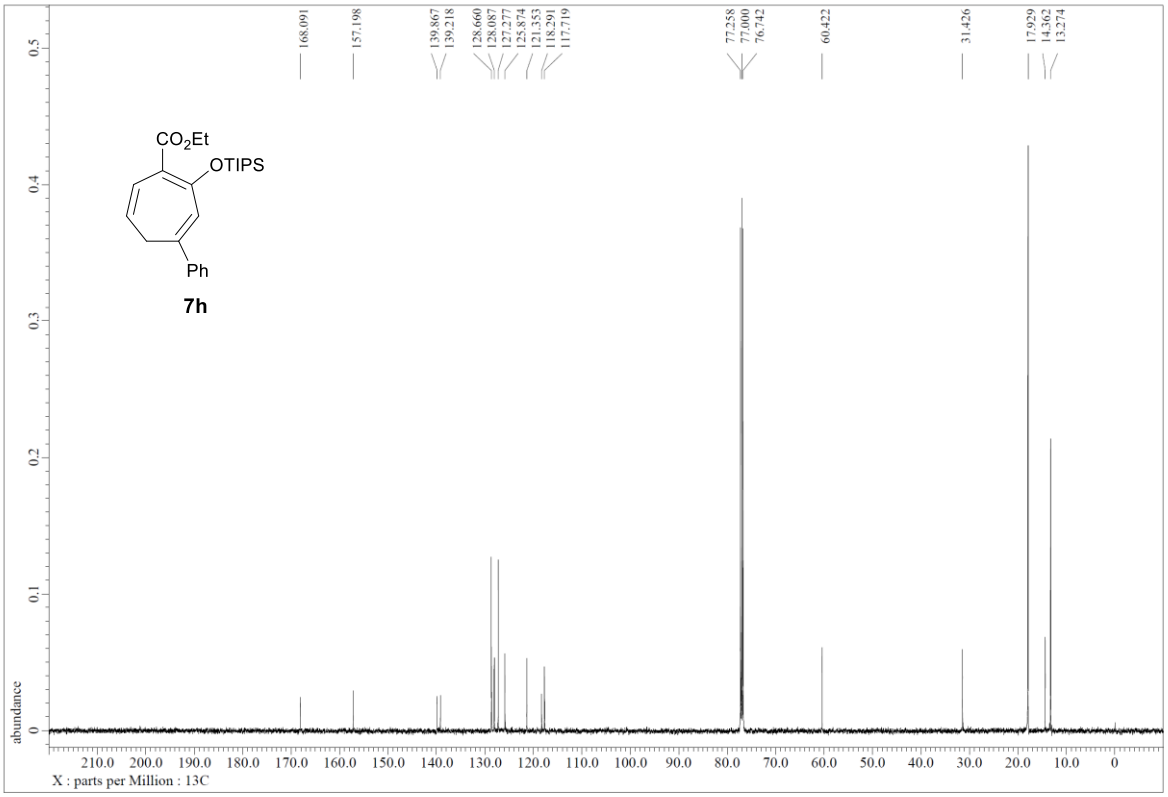
7b (^{13}C NMR, 126 MHz, $CDCl_3$)



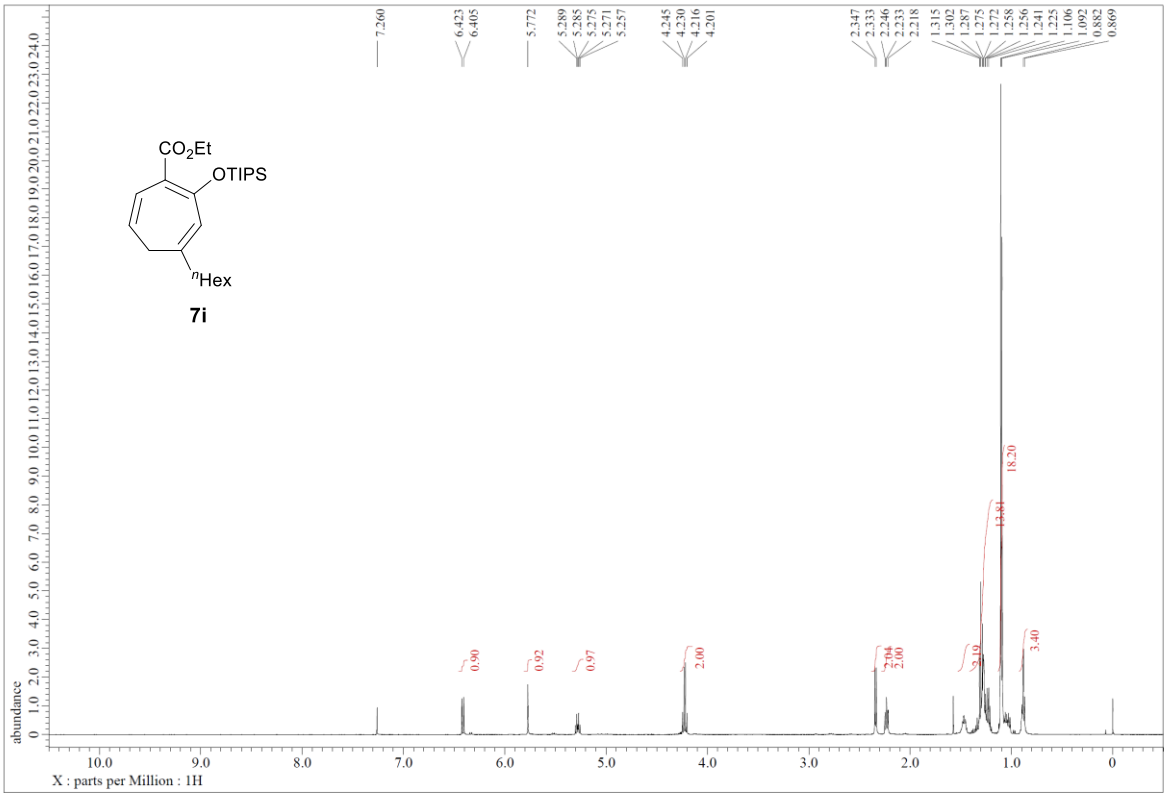
7h (^{1}H NMR, 500 MHz, $CDCl_3$)



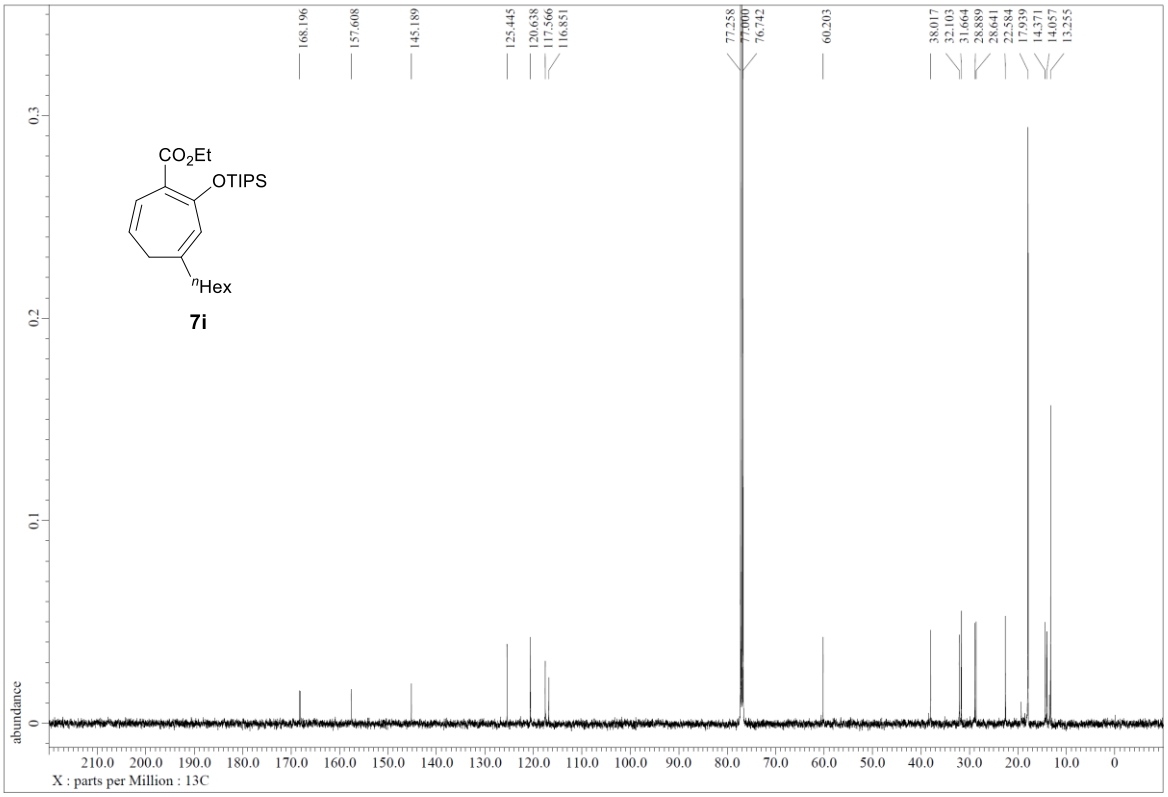
7h (^{13}C NMR, 126 MHz, $CDCl_3$)



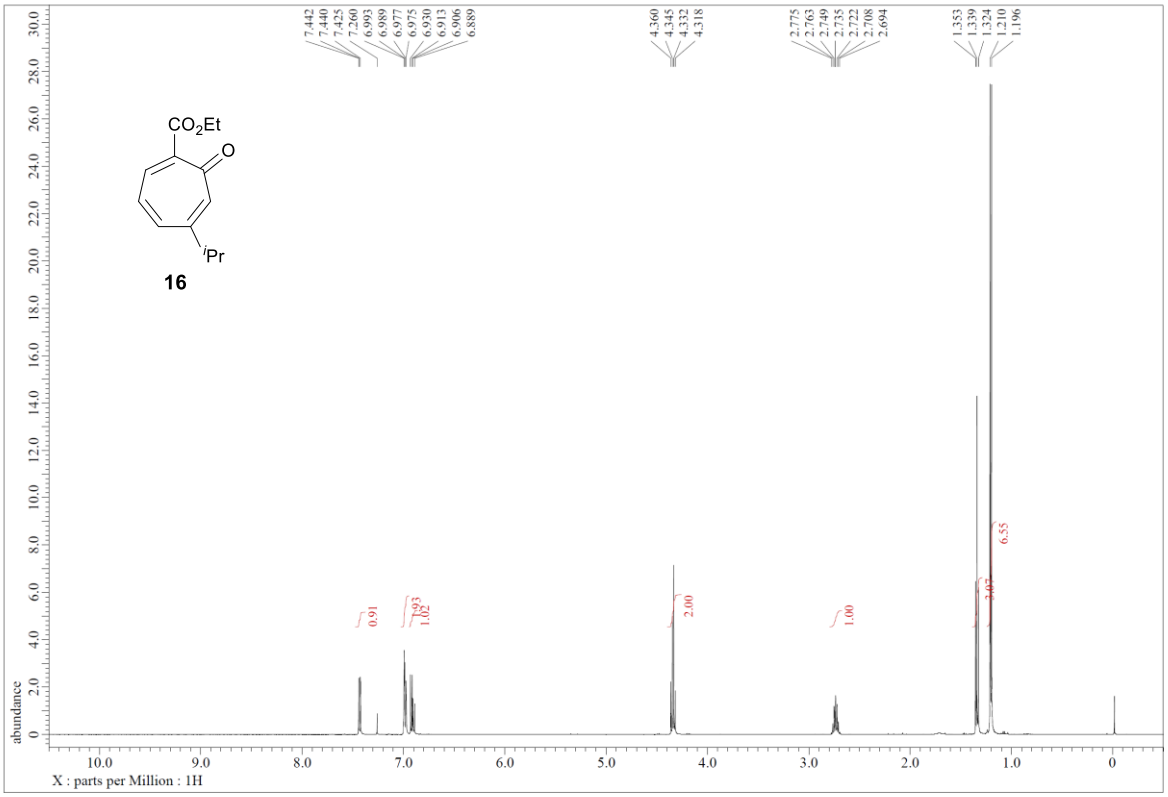
7i (^{1}H NMR, 500 MHz, $CDCl_3$)



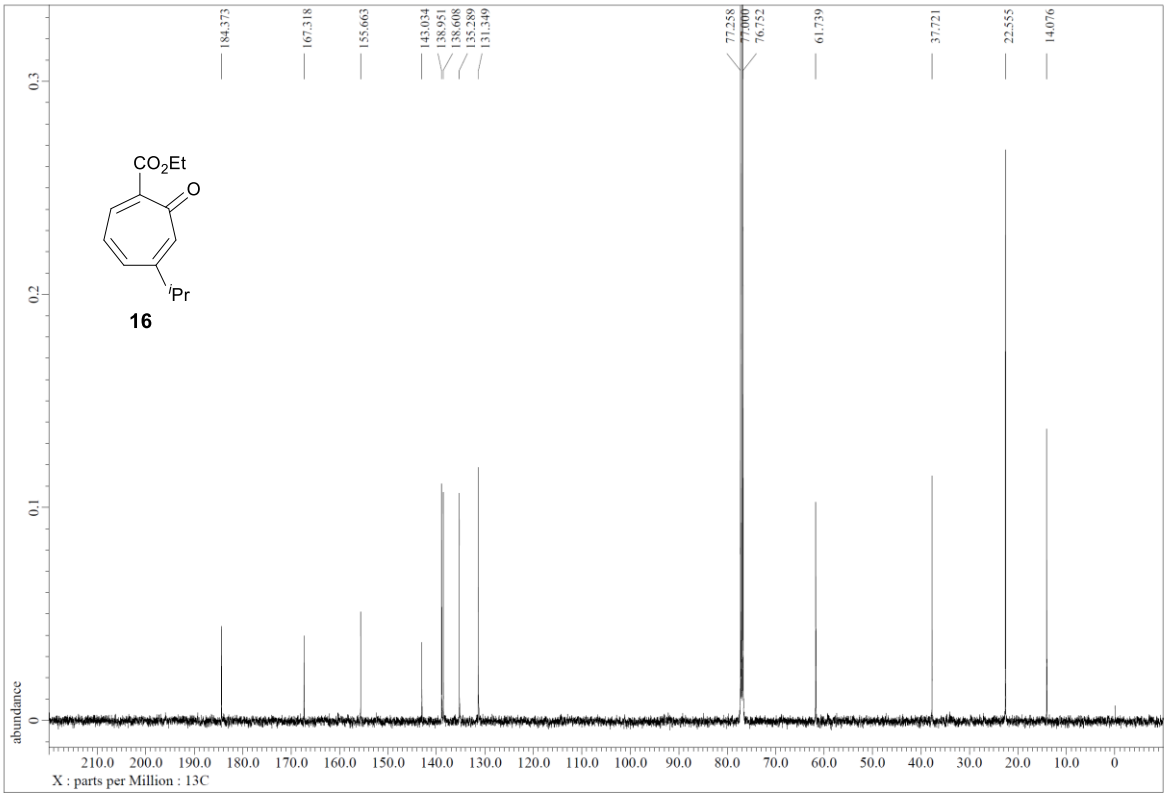
7i (^{13}C NMR, 126 MHz, $CDCl_3$)



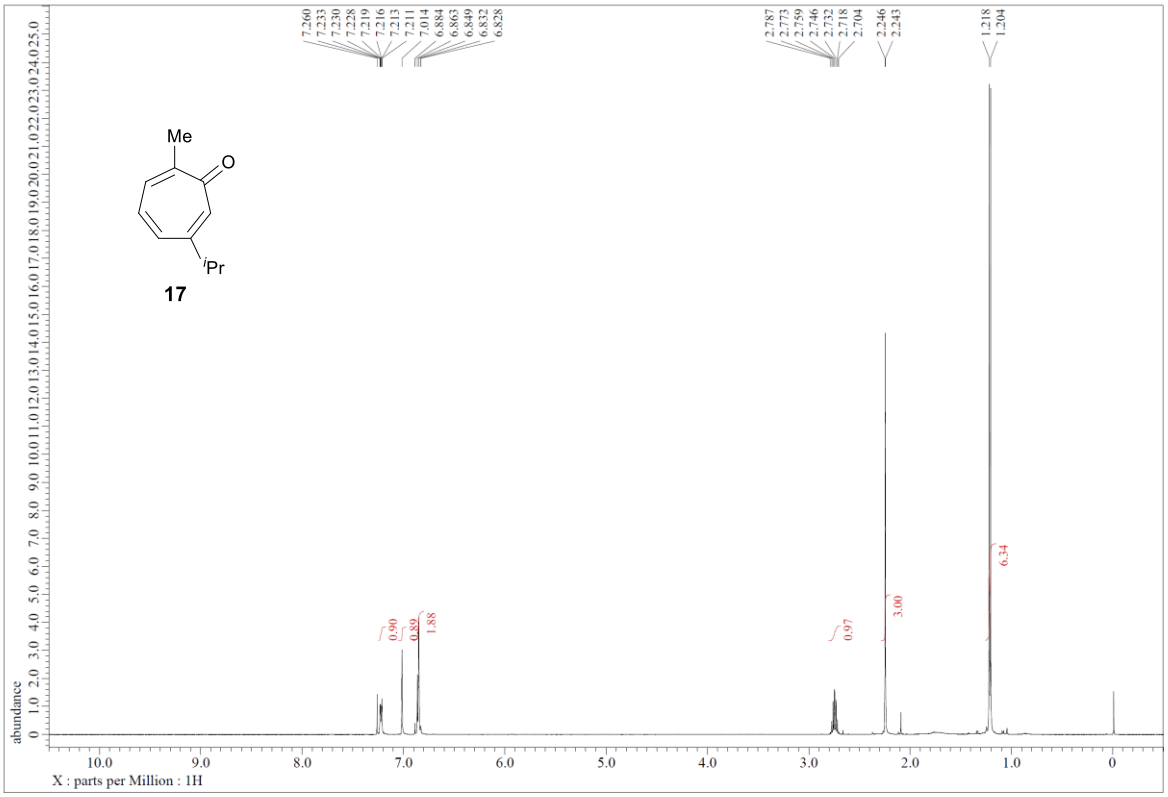
16 (^{1}H NMR, 500 MHz, $CDCl_3$)



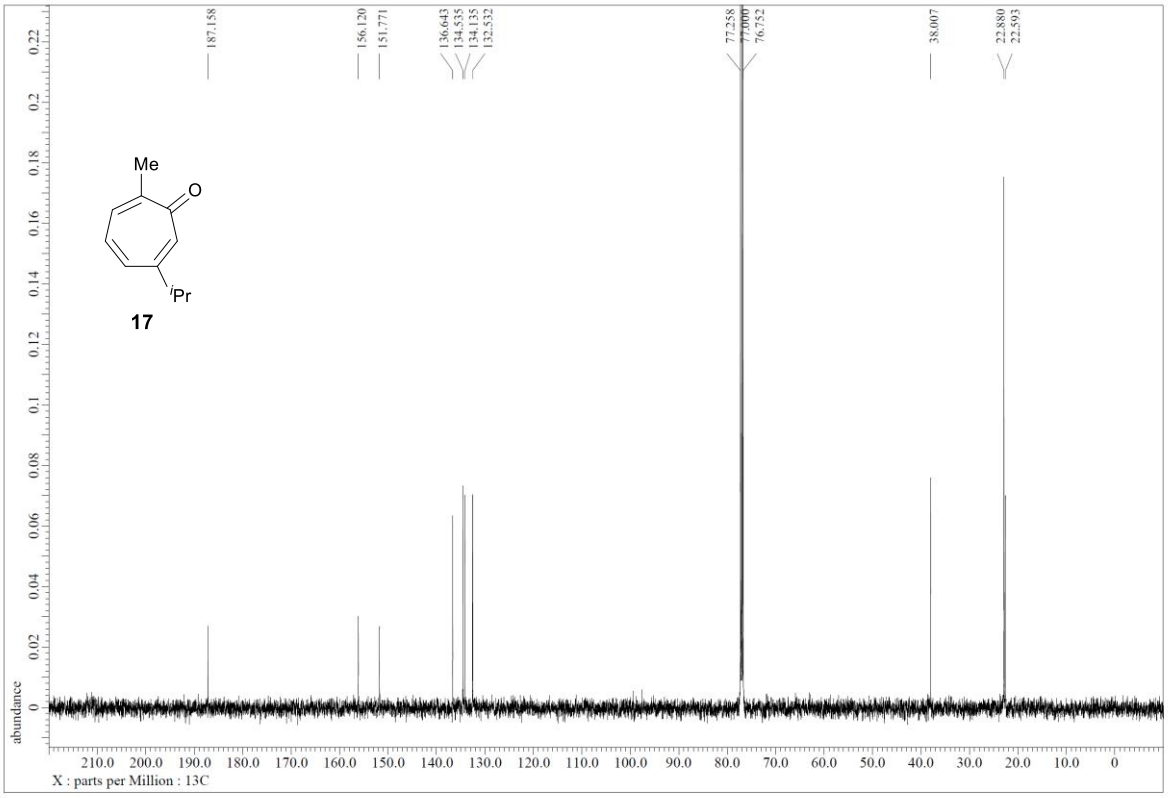
16 (^{13}C NMR, 126 MHz, $CDCl_3$)



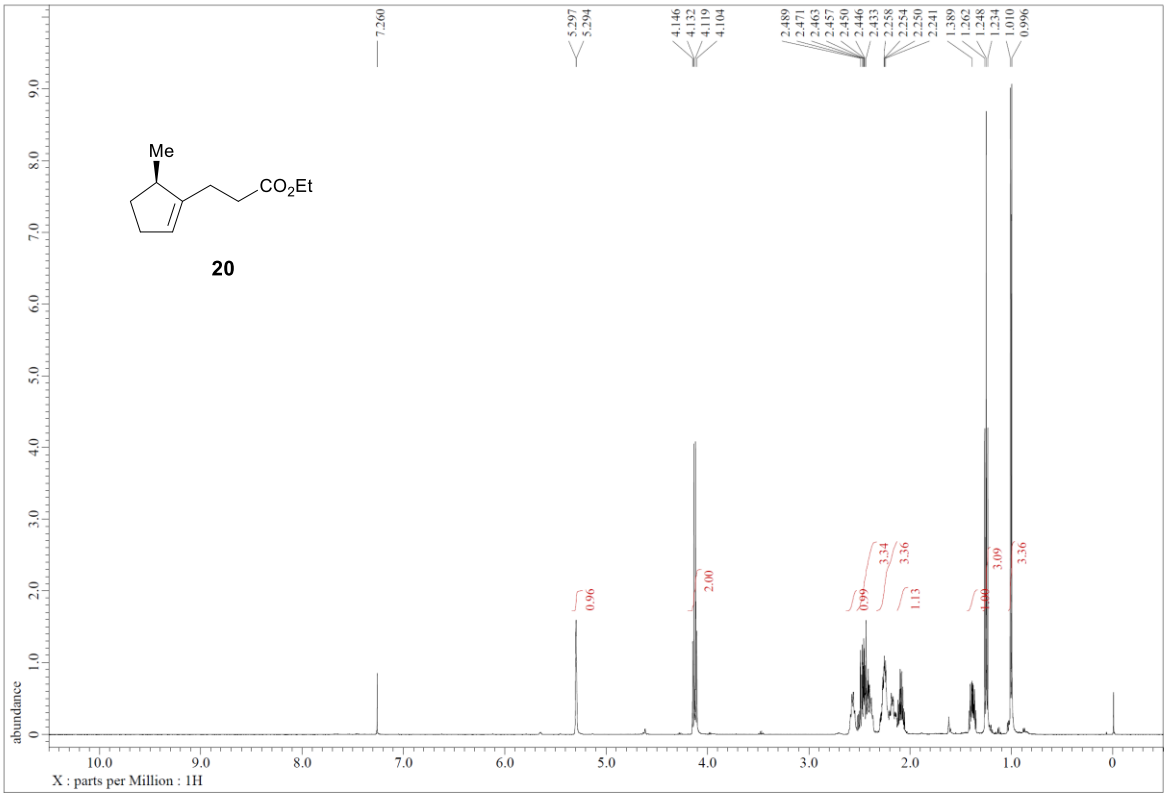
17 (^{1}H NMR, 500 MHz, $CDCl_3$)



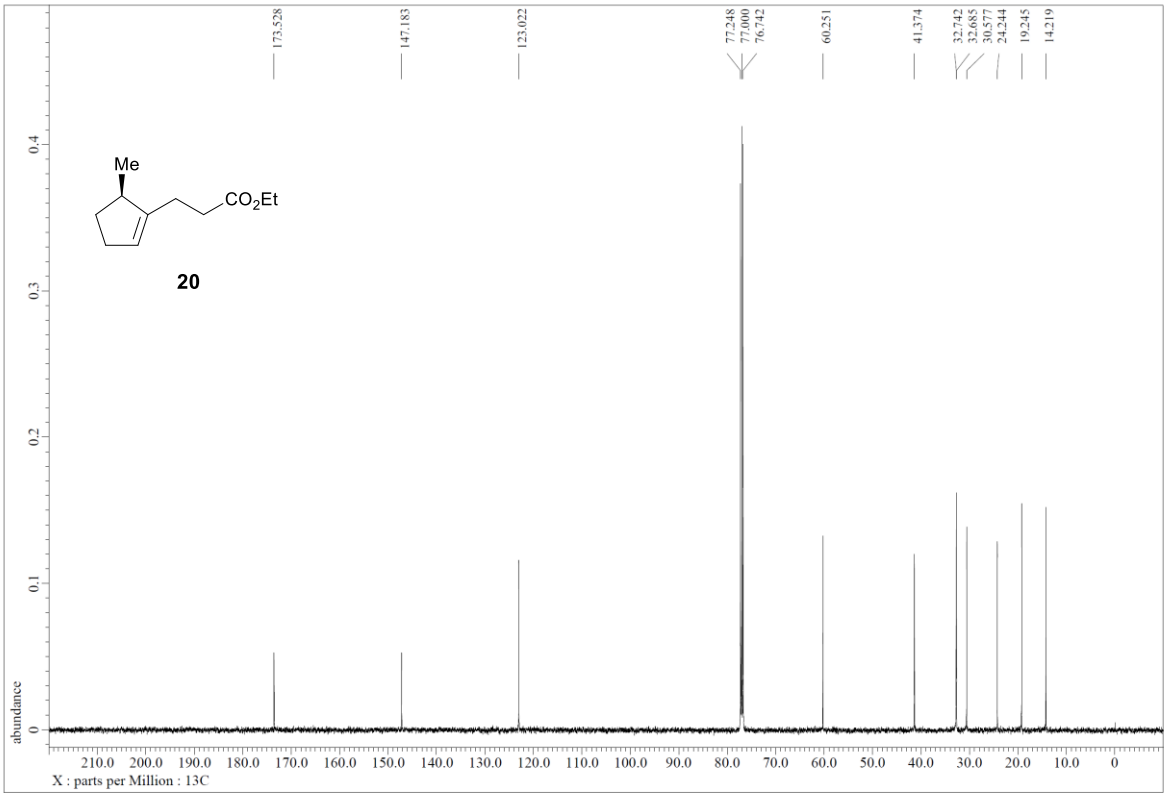
17 (^{13}C NMR, 126 MHz, $CDCl_3$)



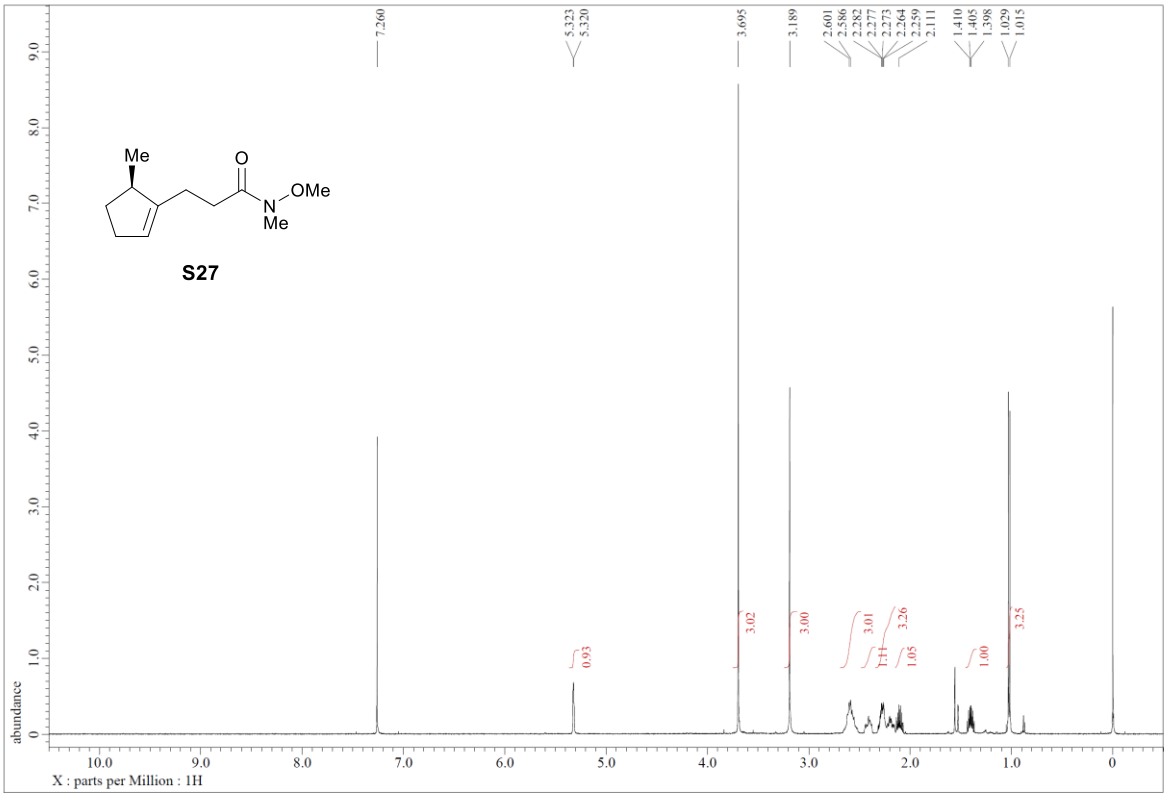
20 (^{1}H NMR, 500 MHz, $CDCl_3$)



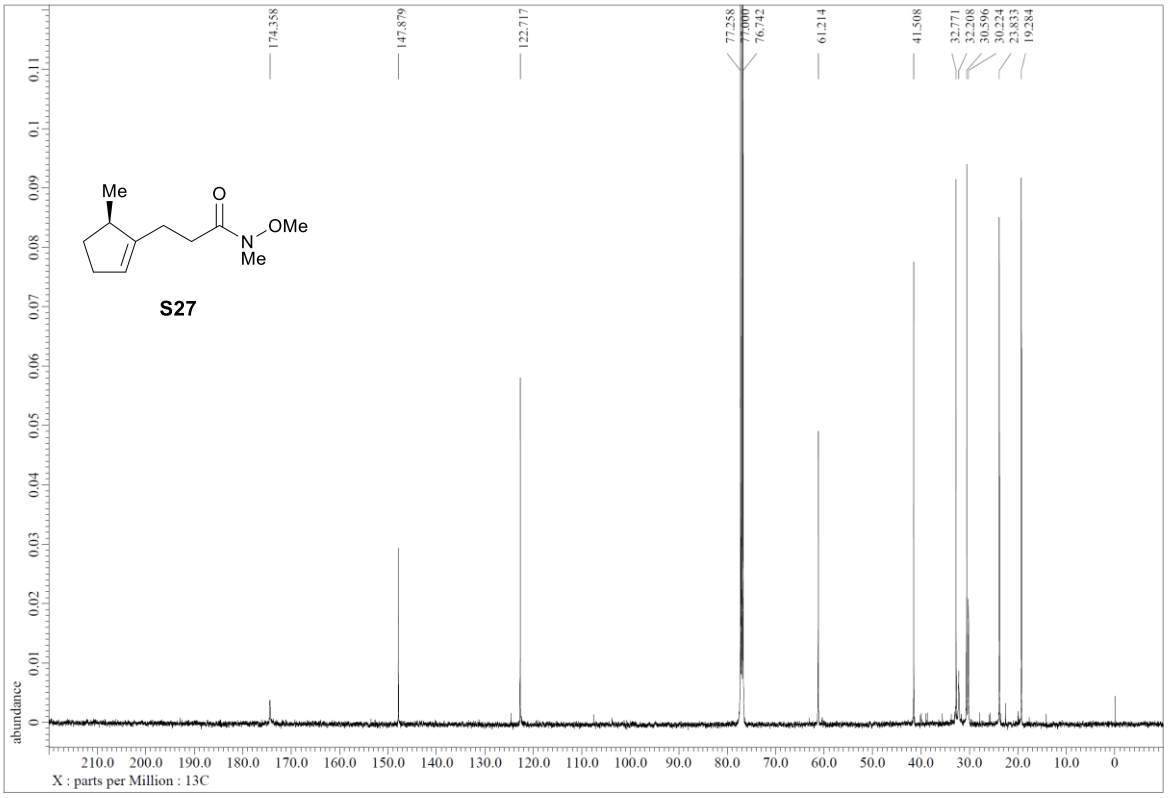
20 (^{13}C NMR, 126 MHz, $CDCl_3$)



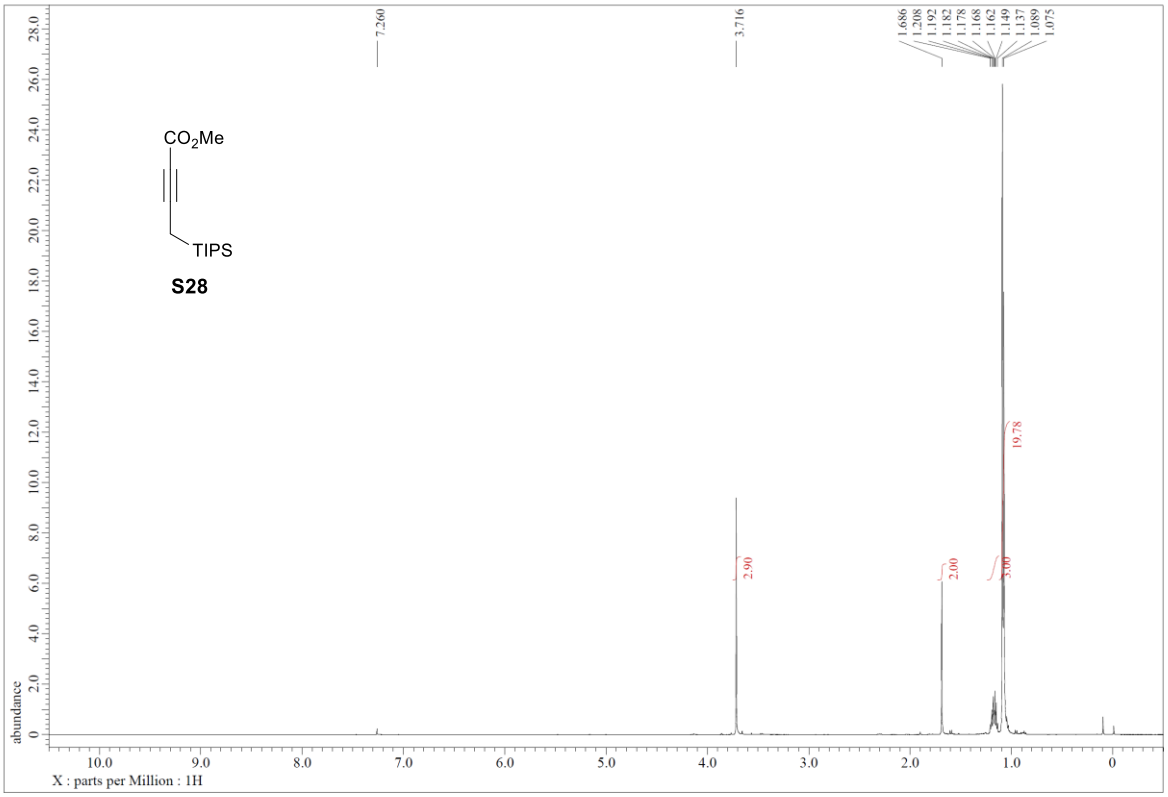
S27 (^{1}H NMR, 500 MHz, $CDCl_3$)



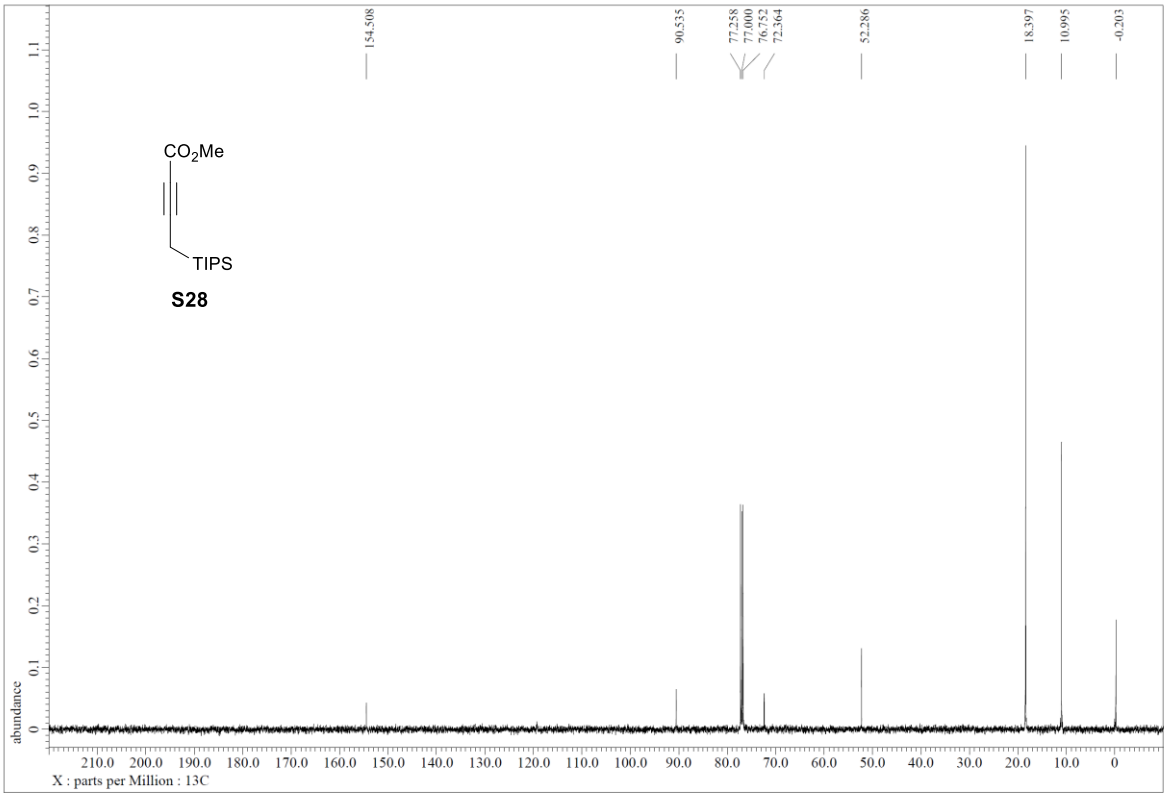
S27 (^{13}C NMR, 126 MHz, $CDCl_3$)



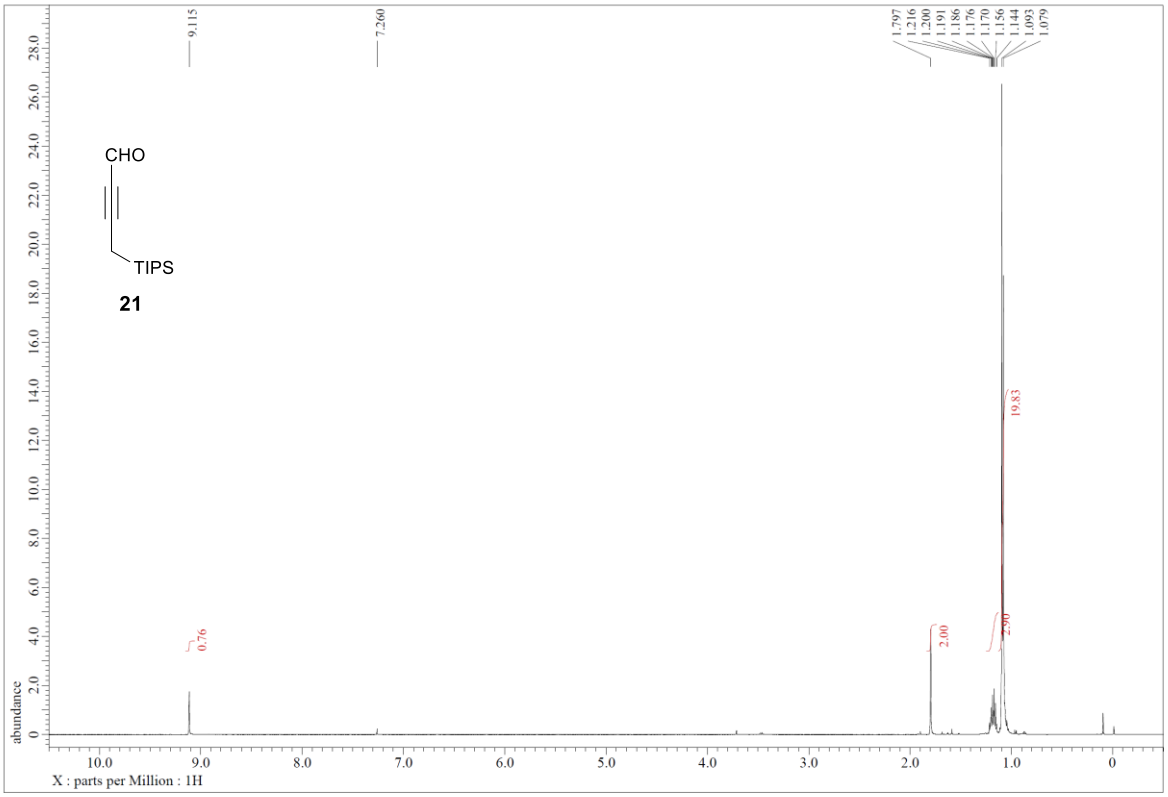
S28 (^{1}H NMR, 500 MHz, $CDCl_3$)



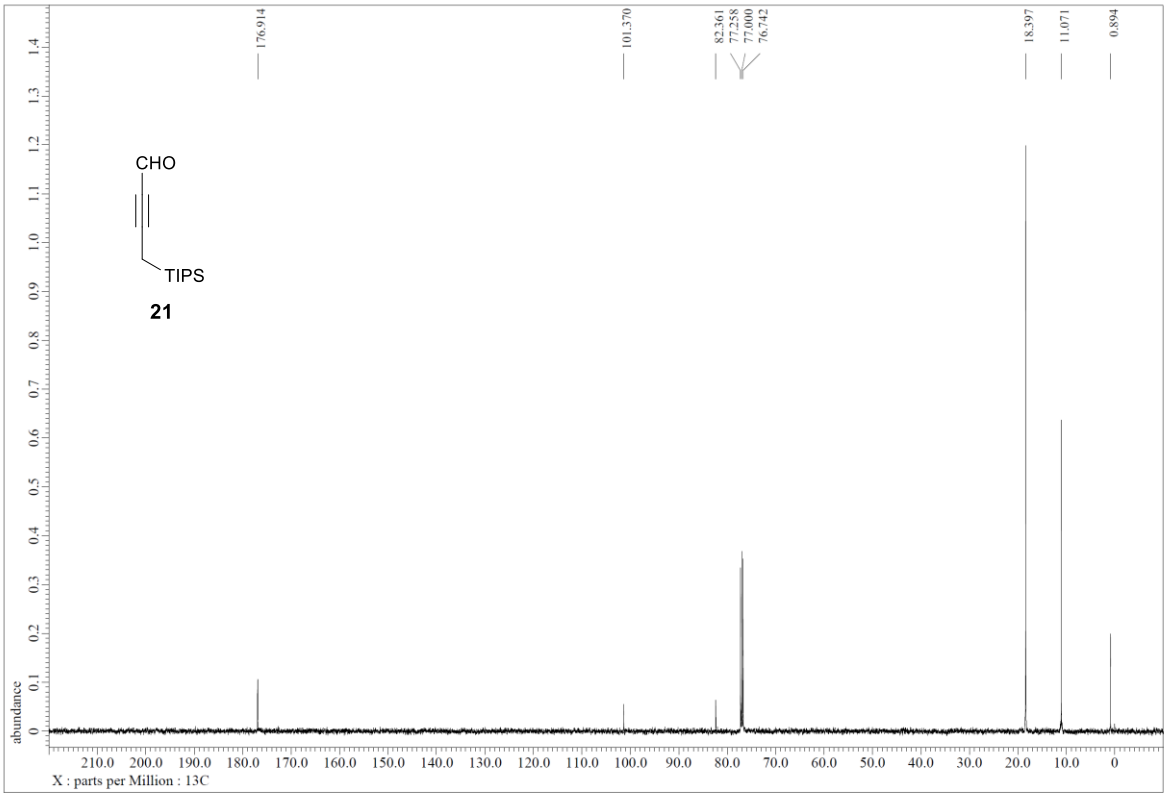
S28 (^{13}C NMR, 126 MHz, $CDCl_3$)



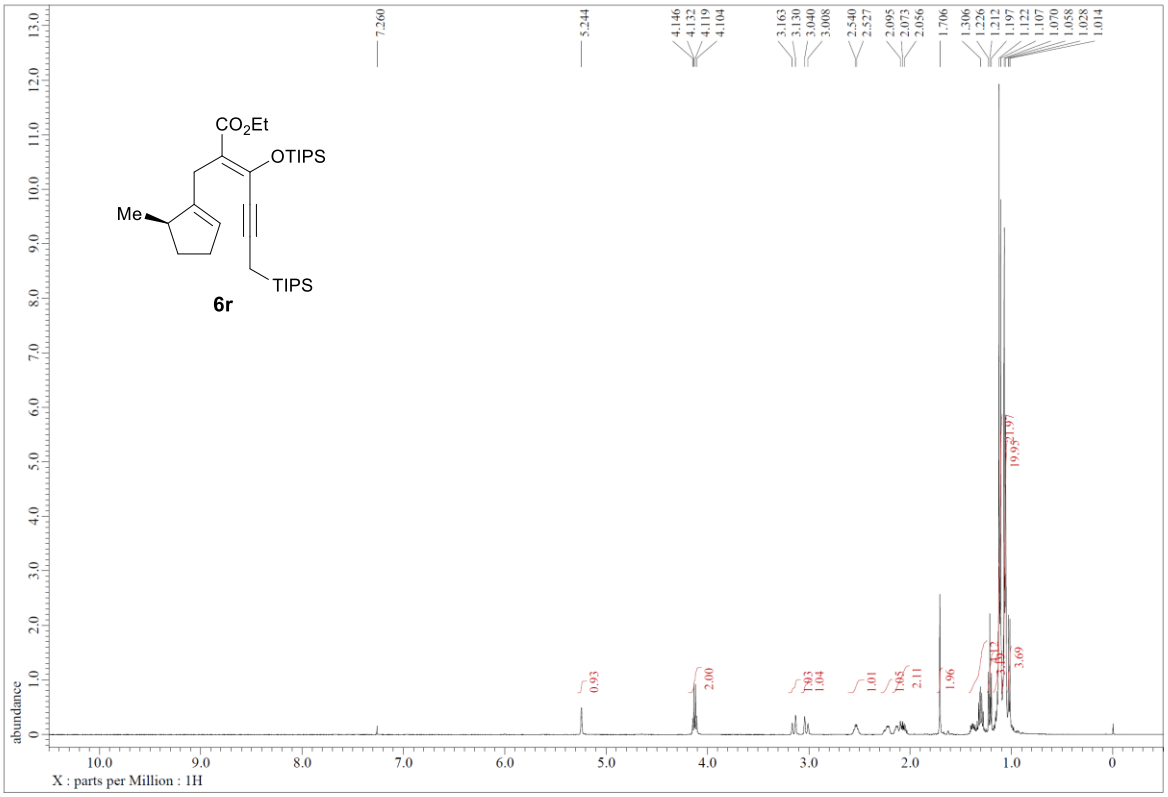
21 (^{1}H NMR, 500 MHz, $CDCl_3$)



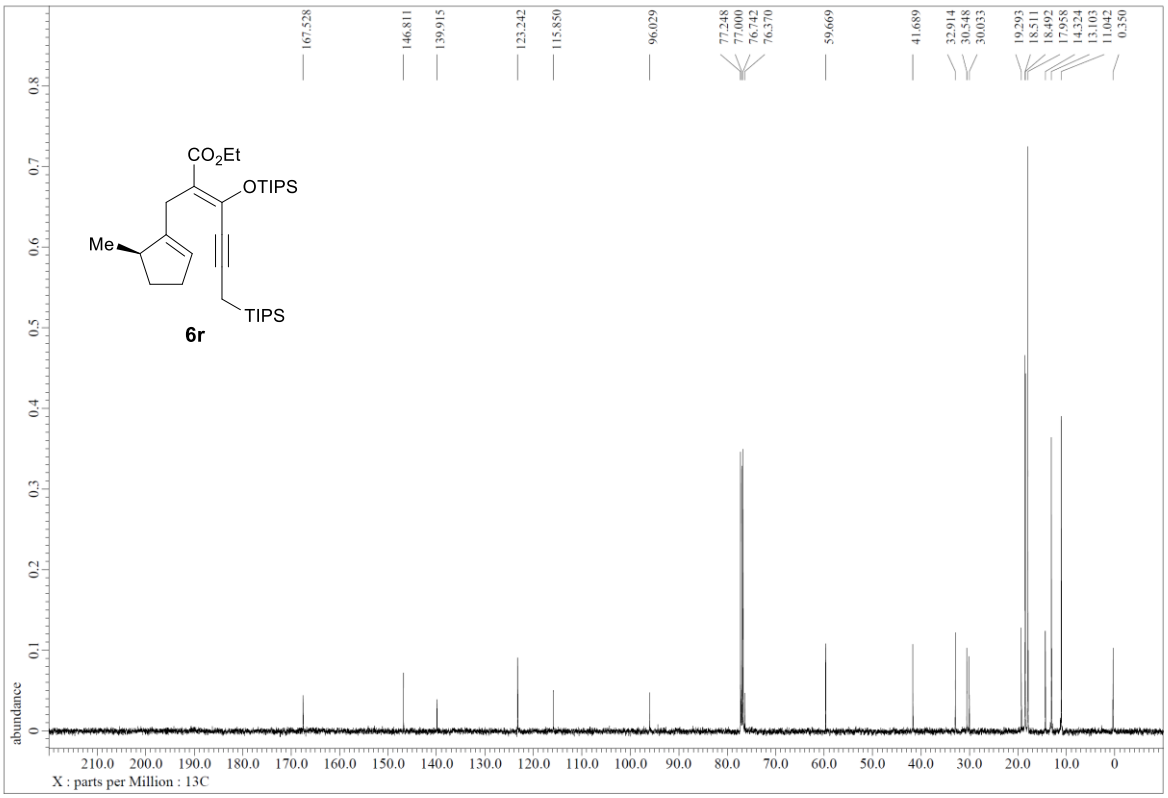
21 (^{13}C NMR, 126 MHz, $CDCl_3$)



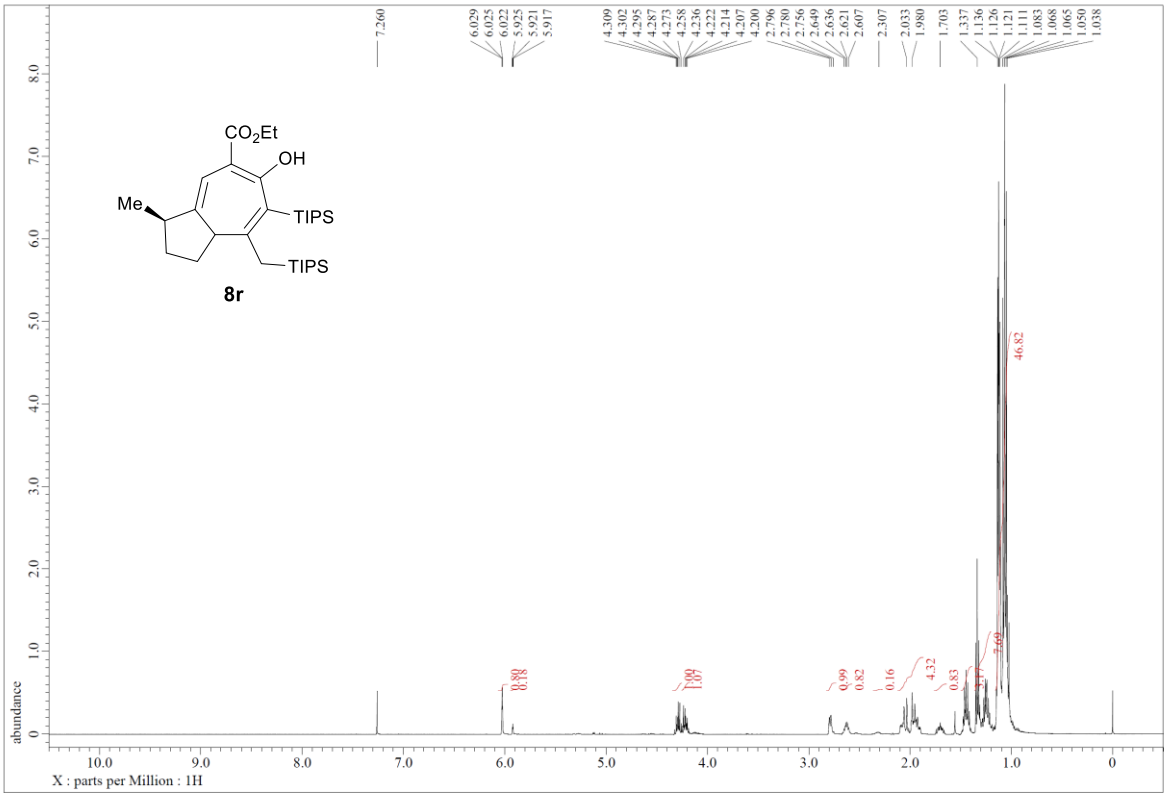
6r (^{1}H NMR, 500 MHz, $CDCl_3$)



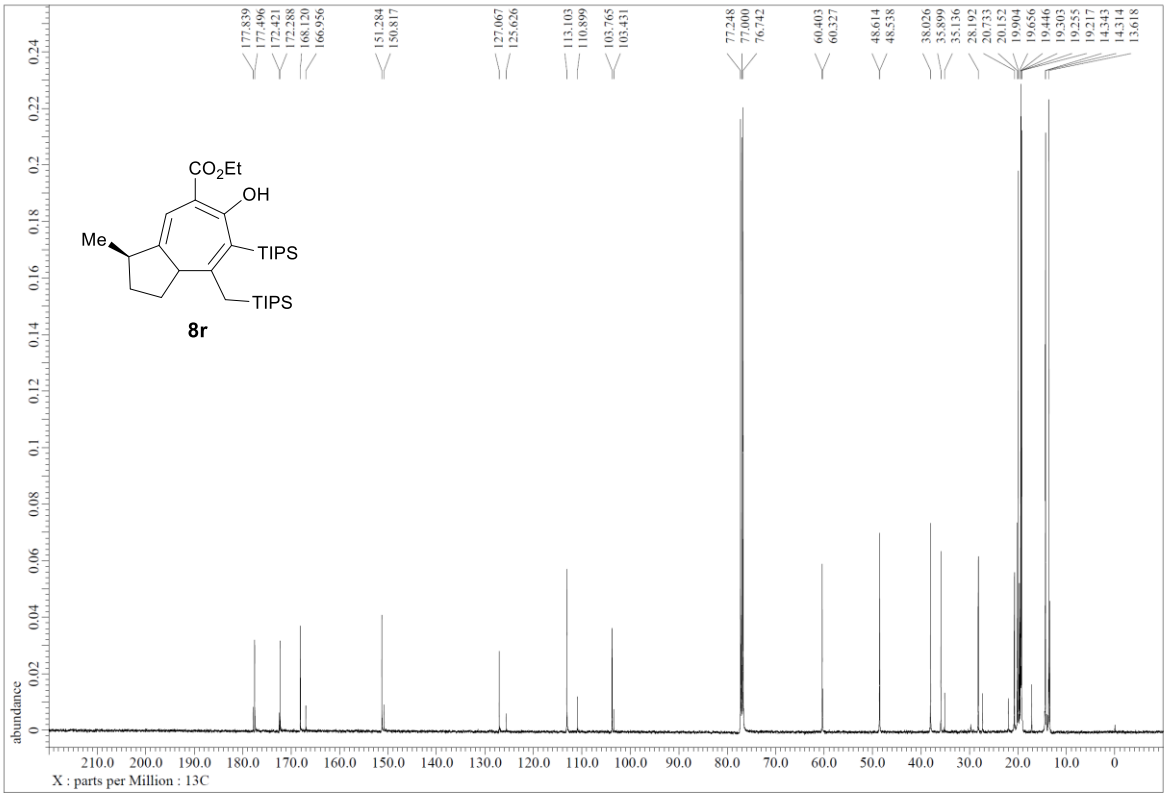
6r (^{13}C NMR, 126 MHz, $CDCl_3$)



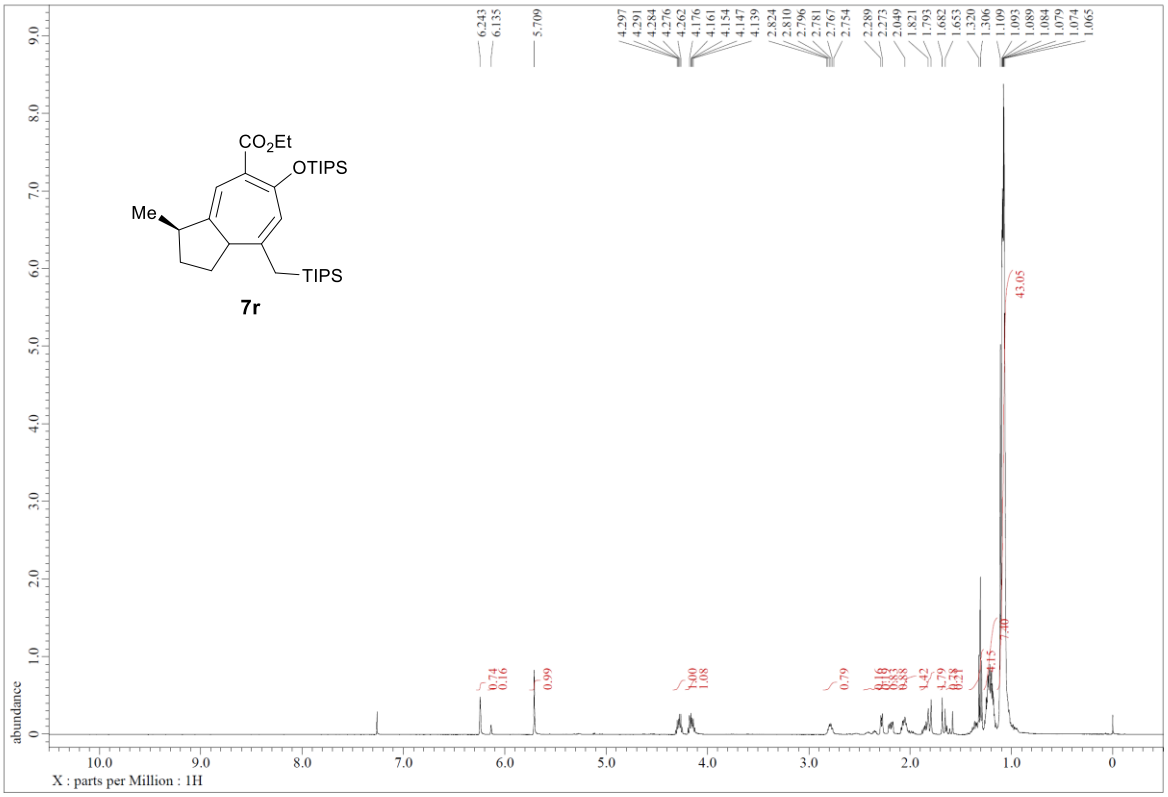
8r (^{1}H NMR, 500 MHz, $CDCl_3$)



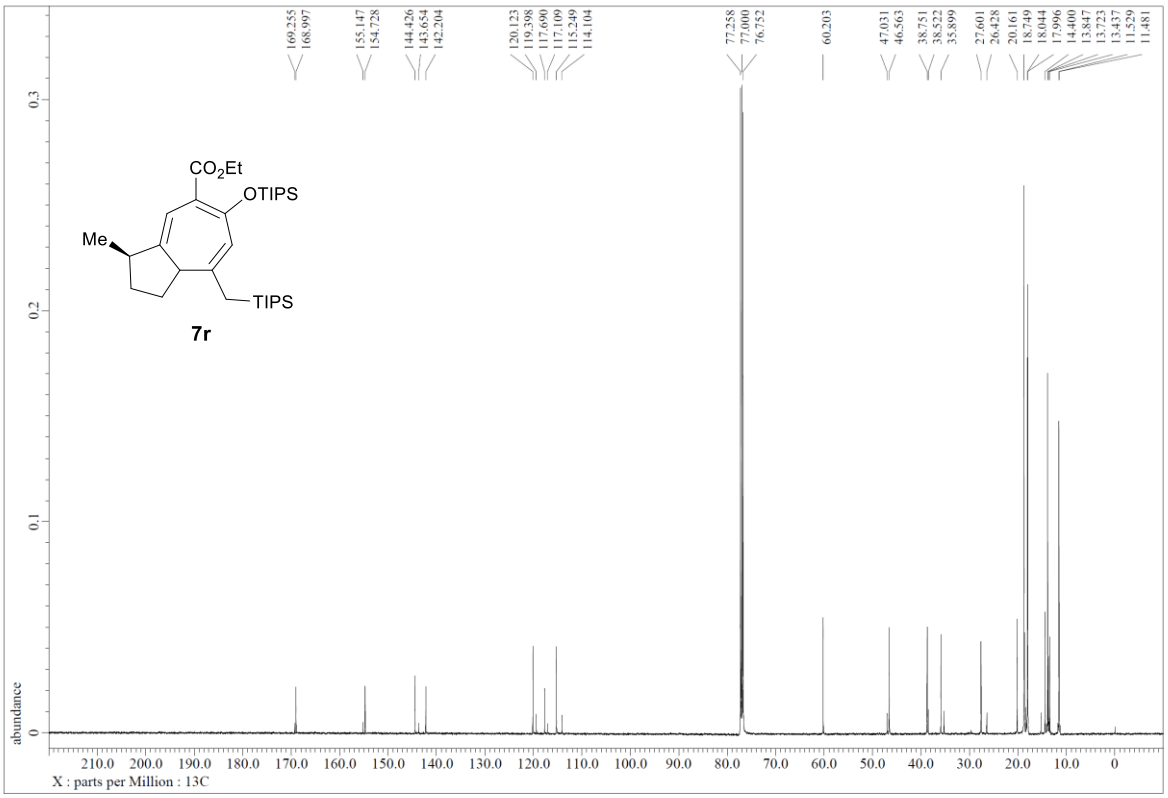
8r (^{13}C NMR, 126 MHz, $CDCl_3$)



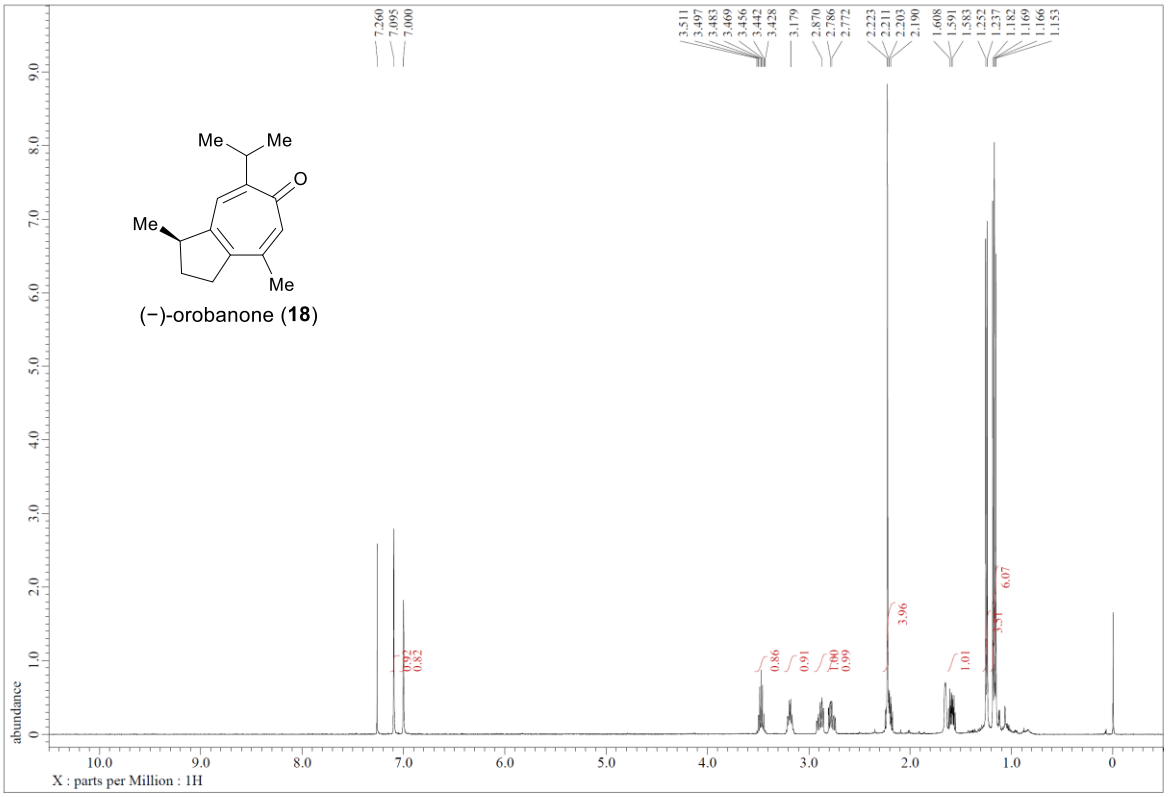
7r (^{1}H NMR, 500 MHz, $CDCl_3$)



7r (^{13}C NMR, 126 MHz, $CDCl_3$)



18 (^{1}H NMR, 500 MHz, $CDCl_3$)



18 (^{13}C NMR, 126 MHz, $CDCl_3$)