Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Broad Scope Gold(I)-Catalysed Polyenyne Cyclisations for the Formation of up to Four Carbon-Carbon Bonds

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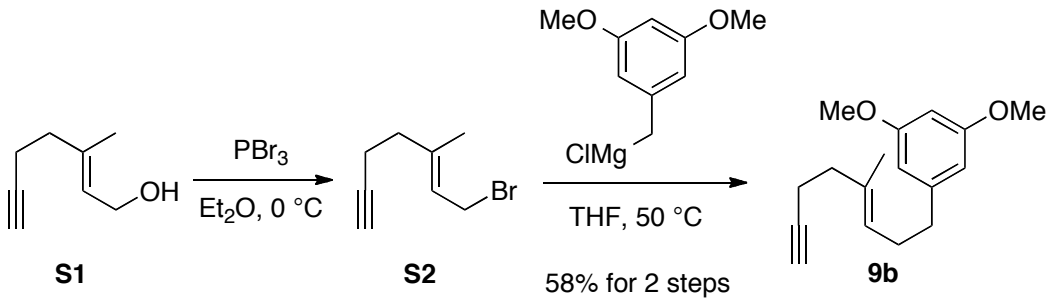
1. General Methods.

All reactions were carried out in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234). Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 µm). NMR spectra were recorded at 23 ºC on Bruker Avance 300, 400 or 500 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI and APCI) or on an Autoflex Broker Daltonics (MALDI and LDI). Melting points were determined using a Büchi melting point apparatus. Crystal structure determinations were carried out using a Bruker-Nonius diffractomer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKa radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = −173 °C). Full-sphere data collection was used with w and j scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implement in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters. HPLC analysis was carried out on an Agilent Tehcnologies instrument HPLC 1100 series with VWD detector or HPLC 1200 series with DAD detector.

2. Procedures for the Preparation of Substrates for Polycyclisations.

(*E*)-1,3-dimethoxy-5-(4-methyloct-3-en-7-yn-1-yl)benzene (9b)



Phosphorus tribromide (33 μL, 0.35 mmol) was added dropwise to a solution of **S1**[1] in Et_2O (7 mL) at 0 °C and the mixture was stirred at this temperature for 30 min before 10 mL of water was added. The aqueous layer was extracted with Et_2O (5 mL) and the combined organic layer was washed sequentially with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous

Na_2SO_4. The solvent was evaporated to give **S2** as colorless oil which was used without further purification.

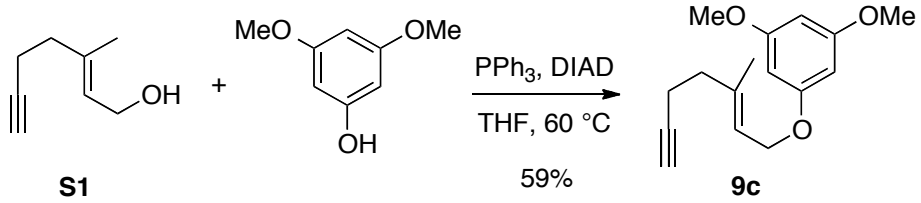
To **S2** (prepared in the last step) was added (3,5-dimethoxybenzyl)magnesium chloride (5.2 mL, 0.2 M in THF, 1.04 mmol) at 0 °C and the mixture was stirred at 50 °C for 5 h before it was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (5 mL) and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 30:1) to give **9b** (103.2 mg, 58% for two steps) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 2.3 Hz, 2H), 6.33 (t, J = 2.3 Hz, 1H), 5.28 (ddq, J = 8.4, 7.1, 1.3 Hz, 1H), 3.81 (s, 6H), 2.62 (dd, J = 8.9, 6.7 Hz, 2H), 2.39 - 2.27 (m, 4H), 2.27 - 2.20 (m, 2H), 1.98 (t, J = 2.5 Hz, 1H), 1.62(s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.67, 144.7, 134.0, 124.9, 106.6, 97.7, 84.4, 68.4, 55.2, 38.4, 36.3, 29.7, 17.6, 15.8.

HRMS-ESI calculated for $C_{17}H_{23}O_2$ $[M+H]^+$: 259.1693; found: 259.1697.

(*E*)-1,3-dimethoxy-5-((3-methylhept-2-en-6-yn-1-yl)oxy)benzene (9c)



S1 **9c**

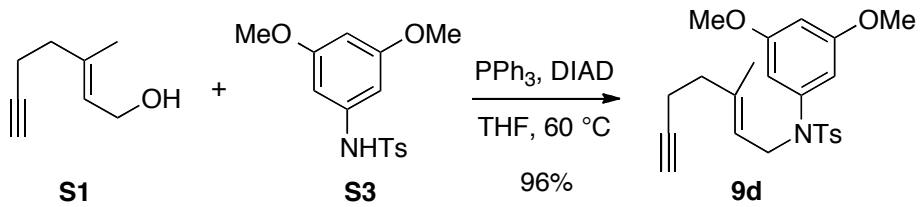
Diisopropyl azodicarboxylate (0.13 mL, 0.66 mmol) was added dropwise to a solution of **S1** (54 mg, 0.44 mmol), 3,5-dimethoxyphenol (101 mg, 0.66 mmol) and triphenylphosphine (171 mg, 0.66 mmol) in THF (5 mL) at 0 °C and the mixture was stirred at 60 °C for 3 h. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/CH_2Cl_2 2:1) to give **9c** (66.8 mg, 59%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, *J* = 2.1 Hz, 2H), 6.12 - 6.10 (m, 1H), 5.57 (ddt, *J* = 7.8, 5.2, 1.3 Hz, 1H), 4.62 - 4.44 (m, 2H), 3.79 (s, 6H), 2.42 - 2.35 (m, 2H), 2.35 - 2.30 (m, 2H), 1.99 (t, *J* = 2.5 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 160.7, 139.1, 120.7, 93.6, 93.0, 83.8, 68.8, 64.7, 55.3, 38.1, 17.2, 16.5.

HRMS-ESI calculated for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: 283.1305; found: 283.1292.

(*E*)-*N*-(3,5-dimethoxyphenyl)-4-methyl-*N*-(3-methylhept-2-en-6-yn-1-yl)benzenesulfonamide (9d)



9d was prepared by the same method as **9c** from **S1** and **S3**.

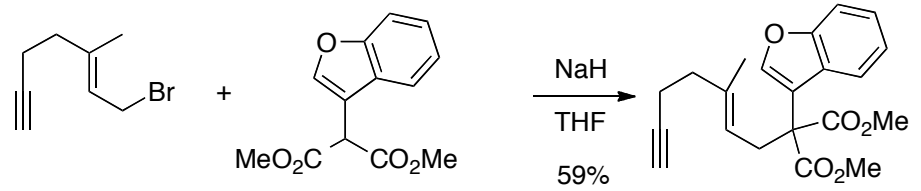
M.p.: 92-94 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.35 - 7.15 (m, 2H), 6.37 (d, *J* = 2.3 Hz, 1H), 6.22 (d, *J* = 2.3 Hz, 2H), 5.19 (ddt, *J* = 6.9, 5.6, 1.3 Hz, 1H), 4.26 - 4.03 (m, 2H), 3.71 (s, 6H), 2.44 (s, 3H), 2.22 - 2.07 (m, 4H), 1.88 (t, *J* = 2.5 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 143.4, 141.1, 138.4, 135.7, 129.4, 127.8, 120.1, 107.0, 100.0, 83.6, 68.7, 55.4, 48.5, 38.0, 21.5, 17.2, 16.0.

HRMS-ESI calculated for $C_{23}H_{27}NNaO_4S$ $[M+Na]^+$: 436.1553; found: 436.1536.

(*E*)-dimethyl 2-(benzofuran-3-yl)-2-(3-methylhept-2-en-6-yn-1-yl)malonate (9e)



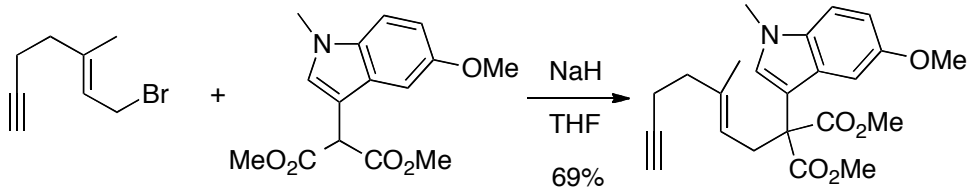
NaH (10.6 mg, 60% dispersion in mineral oil, 0.26 mmol) was added to a solution of **S4**[2] (54.6 mg, 0.22 mmol) in THF (3 mL) at 0 °C and the mixture was stirred at this temperature for 30 min. A solution of **S2** (49.4 mg, 0.26 mmol) in THF (3 mL) was added and the reaction mixture was stirred at 23 °C for 24 h before it was quenched with water (10 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 7:1) to give **9e** (45.9 mg, 59%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 - 7.49 (m, 2H), 7.31 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.23 (ddd, J = 8.1, 7.2, 1.0 Hz, 1H), 5.08 (tq, J = 7.4, 1.3 Hz, 1H), 3.76 (s, 6H), 3.17 - 3.12 (m, 2H), 2.23 - 2.11 (m, 4H), 1.93 (t, J = 2.5 Hz, 1H), 1.52 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 155.0, 144.2, 137.8, 126.0, 124.3, 122.6, 120.6, 119.0, 116.1, 111.6, 83.9, 68.6, 57.1, 52.8, 38.4, 33.5, 17.5, 15.9.

HRMS-ESI calculated for $C_{21}H_{22}NaO_5$ $[M+Na]^+$: 377.1359; found: 377.1372.

(*E*)-dimethyl 2-(5-methoxy-1-methyl-1*H*-indol-3-yl)-2-(3-methylhept-2-en-6-yn-1-yl)malonate (9f)



S2 **S5** **9f**

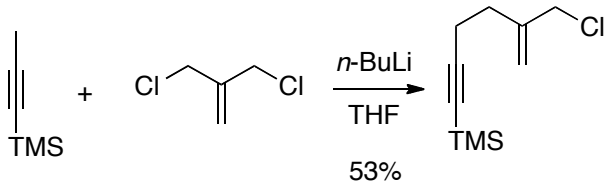
9f was prepared by the same method as **9e** from **S2** and **S5**[3].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.20 (dd, J = 8.9, 0.5 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.90 (dd, J = 8.8, 2.4 Hz, 1H), 5.16 (tdd, J = 7.2, 2.7, 1.4 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.74 (s, 6H), 3.17 - 3.14 (m, 2H), 2.24 - 2.14 (m, 4H), 1.94 (t, J = 2.4 Hz, 1H), 1.57 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 153.9, 136.9, 132.4, 129.1, 126.6, 120.1, 111.8, 110.1, 109.3, 102.3, 84.1, 68.5, 57.8, 55.9, 52.6, 38.5, 34.1, 33.1, 17.7, 16.0.

HRMS-ESI calculated for $C_{23}H_{27}NNaO_5$ $[M+Na]^+$: 420.1781; found: 420.1796.

(5-(chloromethyl)hex-5-en-1-yn-1-yl)trimethylsilane (S6)



S6

n-BuLi (12 mL, 2.5 M in hexanes, 30 mmol) was added dropwise to a solution of 1-(trimethylsilyl)propyne (4.4 mL, 30 mmol) in THF (300 mL) at -40 °C and the mixture was kept at this temperature for 45 min before it was cooled to -78 °C and 3-chloro-2-(chloromethyl)prop-1-ene (3.47 mL, 30 mmol) was added and the reaction mixture was allowed to warmed up to -20 °C during 3 h before it was quenched with saturated aqueous NH_4Cl (300 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (400 mL) and brine (400 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue

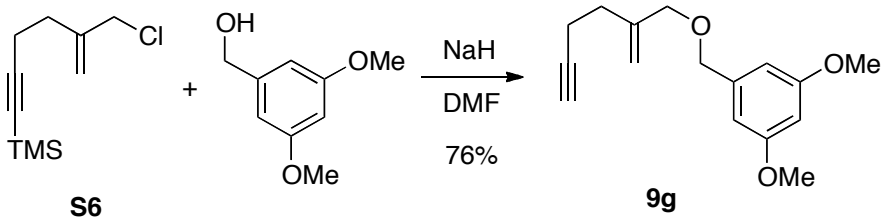
was purified by flash column chromatography (cyclohexane) to give **S6** (3.20 g, 53%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (d, J = 1.0 Hz, 1H), 5.04 (d, J = 1.1 Hz, 1H), 4.10 (d, J = 1.0 Hz, 2H), 2.43 (m, 4H), 0.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 115.5, 106.1, 85.4, 48.0, 32.0, 18.7, 0.1.

HRMS-APCI calculated for $C_{10}H_{18}ClSi$ $[M+H]^+$: 201.0861; found: 201.0858.

1,3-dimethoxy-5-(((2-methylenehex-5-yn-1-yl)oxy)methyl)benzene (9g)



S6 **9g**

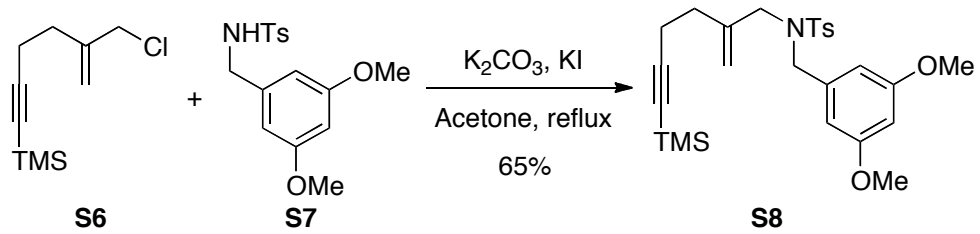
NaH (13.8 mg, 60% dispersion in mineral oil, 0.35 mmol) was added to a solution of 3,5-dimethoxybenzyl alcohol (58.0 mg, 0.35 mmol) in DMF (2 mL) at 0 °C and the mixture was stirred at this temperature for 20 min. A solution of **S6** (63 mg, 0.31 mmol) in DMF (1 mL) was added and the reaction mixture was stirred at 23 °C for 1.5 h before it was quenched with water (5 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 20:1) to give **9g** (58.0 mg, 76%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, J = 2.3 Hz, 2H), 6.41 (t, J = 2.3 Hz, 1H), 5.14 (t, J = 1.3 Hz, 1H), 5.04 (d, J = 1.8 Hz, 1H), 4.46 (s, 2H), 4.00 (d, J = 1.2 Hz, 2H), 3.81 (s, 6H), 2.43 - 2.35 (m, 4H), 1.98 (t, J = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 144.1, 140.7, 113.2, 105.3, 99.7, 83.9, 72.9, 71.9, 68.6, 55.3, 32.1, 17.1.

HRMS-ESI calculated for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: 283.1305; found: 283.1311.

***N*-(3,5-dimethoxybenzyl)-4-methyl-*N*-(2-methylene-6-(trimethylsilyl)hex-5-yn-1-yl)benzenesulfonamide (S8)**



S6 **S7** **S8**

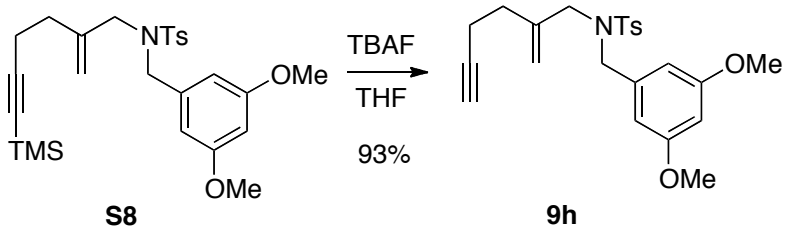
To a solution of **S6** (360 mg, 1.79 mmol) and **S7** (632 mg, 1.97 mmol) in acetone (20 mL) was added K_2CO_3 (272 mg, 1.97 mmol) and KI (29.7 mg, 0.18 mmol) at 23 °C. The mixture was set to reflux for 24 h before the solvent was evaporated. The residue was taken up in Et_2O (20 mL) and washed sequentially with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 5:1) to give **S8** (566 mg, 65%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.35 - 7.30 (m, 2H), 6.34 (t, J = 2.3 Hz, 1H), 6.29 (d, J = 2.3 Hz, 2H), 4.94 (d, J = 1.7 Hz, 1H), 4.87 (d, J = 1.1 Hz, 1H), 4.29 (s, 2H), 3.74 (s, 2H), 3.71 (s, 6H), 2.45 (s, 3H), 2.28 - 2.23 (m, 2H), 2.13 (t, J = 7.3 Hz, 2H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 143.3, 141.8, 138.2, 137.5, 129.7, 127.2, 115.1, 106.5, 106.4, 99.9, 85.1, 55.3, 52.0, 50.8, 31.9, 21.5, 18.3, 0.1.

HRMS-ESI calculated for $C_{26}H_{35}NNaO_4SSi$ $[M+Na]^+$: 508.1948; found: 508.1948.

***N*-(3,5-dimethoxybenzyl)-4-methyl-*N*-(2-methylenehex-5-yn-1-yl)benzenesulfonamide (9h)**



S8 **9h**

Tetrabutylammonium fluoride (1.3 mL, 1.0 M in THF, 1.3 mmol) was added dropwise to a solution of **S8** (530 mg, 1.09 mmol) in THF (11 mL) at 0 °C. The reaction mixture was then stirred at 23 °C for 30 min before it was quenched with saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with Et_2O (10 mL) and the combined organic layer was washed sequentially with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 5:1) to give **9h** (419 mg, 93%) as a white solid.

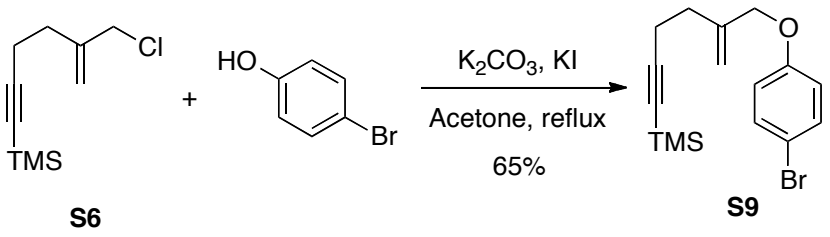
M.p.: 76-77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.35 - 7.31 (m, 2H), 6.34 (t, J = 2.3 Hz, 1H), 6.29 (d, J = 2.3 Hz, 2H), 4.97 - 4.94 (m, 1H), 4.90 - 4.87 (m, 1H), 4.29 (s, 2H), 3.75 (s, 2H), 3.71 (s, 6H), 2.45 (s, 3H), 2.27 - 2.21 (m, 2H), 2.17 - 2.10 (m, 2H), 1.94 (t, J = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 143.3, 141.8, 138.2, 137.4, 129.7, 127.2, 115.1, 106.4, 99.9, 83.6, 68.7, 55.3, 52.1, 50.9, 31.7, 21.5, 16.8.

HRMS-ESI calculated for $C_{23}H_{27}NNaO_4S$ $[M+Na]^+$: 436.1553; found: 436.1549.

(5-((4-bromophenoxy)methyl)hex-5-en-1-yn-1-yl)trimethylsilane (S9)



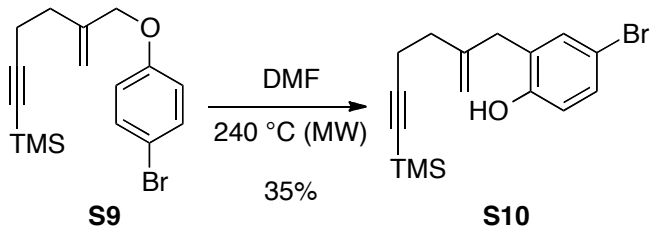
S9 was prepared by the same method as **S8** from **S6** and 4-bromophenol.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.37 (m, 2H), 6.85 - 6.81 (m, 2H), 5.20 (dd, J = 1.3, 0.7 Hz, 1H), 5.09 (q, J = 1.1 Hz, 1H), 4.49 (t, J = 1.1 Hz, 2H), 2.49 - 2.43 (m, 2H), 2.42 - 2.36 (m, 2H), 0.16 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.77, 142.80, 132.22, 116.60, 113.60, 113.02, 106.40, 85.33, 70.92, 32.11, 18.87, 0.11.

HRMS-APCI calculated for $C_{16}H_{22}BrOSi$ $[M+H]^+$: 337.0618; found: 337.0615.

4-bromo-2-(2-methylene-6-(trimethylsilyl)hex-5-yn-1-yl)phenol (S10)



A 5 ml microwave vial was charged with a solution of **S9** (200 mg, 0.59 mmol) in DMF (2 mL). The vial was purged with Argon and then fitted with a septa and vial seal. The reaction was then heated to 240 °C under microwave conditions for 2 hours.

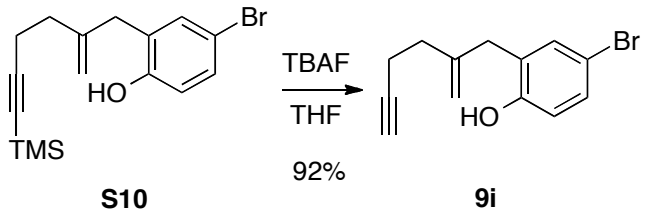
The reaction mixture was poured into water (10 mL) and extracted with Et_2O. The combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 10:1) to give **S10** (70 mg, 35%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 - 7.22 (m, 2H), 6.76 (d, J = 8.5 Hz, 1H), 5.27 (s, 1H), 5.01 (q, J = 1.2 Hz, 1H), 4.87 (t, J = 1.5 Hz, 1H), 3.39 (s, 2H), 2.50 - 2.43 (m, 2H), 2.29 (m, 2H), 0.18 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 145.4, 133.5, 130.9, 126.9, 118.0, 113.3, 112.7, 106.3, 86.1, 37.5, 34.3, 18.9, 0.1.

HRMS-ESI calculated for $C_{16}H_{20}BrOSi$ $[M-H]^-$: 335.0472; found: 335.0461.

4-bromo-2-(2-methylenehex-5-yn-1-yl)phenol (9i)



S10 **9i**

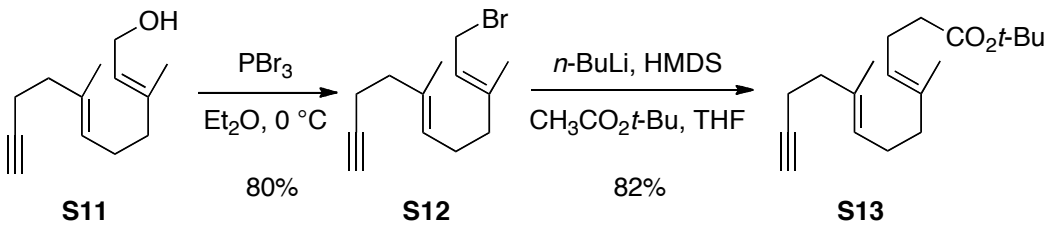
9i was prepared by the same method as **9h** from **S10**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 - 7.24 (m, 2H), 6.75 (d, J = 8.4 Hz, 1H), 5.19 (s, 1H), 5.04 (q, J = 1.2 Hz, 1H), 4.92 (q, J = 1.4 Hz, 1H), 3.39 (s, 2H), 2.43 (tdd, J = 7.1, 2.6, 0.8 Hz, 2H), 2.30 (t, J = 7.0 Hz, 2H), 2.05 (t, J = 2.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 145.3, 133.5, 130.9, 126.9, 117.9, 113.3, 112.8, 83.6, 69.3, 37.5, 34.1, 17.2.

HRMS-ESI calculated for $C_{13}H_{12}BrO$ $[M-H]^-$: 263.0077; found: 263.0080.

(4*E*,8*E*)-*tert*-butyl 5,9-dimethyltrideca-4,8-dien-12-ynoate (S13)



S11 **S12** **S13**

S12 was prepared by the same method as **S2** from **S11**[4].

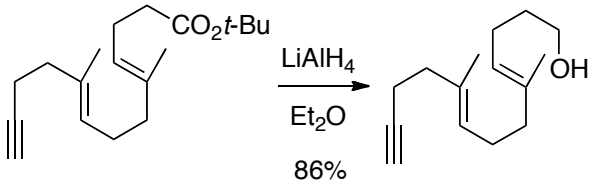
n-BuLi (2.5 mL, 2.5 M in hexanes, 6.3 mmol) was added dropwise to a solution of hexamethyldisilazane (1.37 mL, 6.6 mmol) in THF (15 mL) at -78 °C and the mixture was kept at 0 °C for 30 min before it was re-cooled to -78 °C and *tert*-butyl acetate (0.44 mL, 3.3 mmol) was added. After 1 h, a solution of **S12** (762 mg, 2.99 mmol) in THF (5 mL) was added and the reaction mixture was stirred at 0 °C for 30 min before it was quenched with saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 20:1) to give **S13** (711 mg, 82%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19 (tq, J = 7.1, 1.4 Hz, 1H), 5.12 (ddt, J = 6.9, 5.5, 1.3 Hz, 1H), 2.32 - 2.19 (m, 8H), 2.10 (m, 2H), 2.01 (m, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.68 - 1.59 (m, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 144.7, 134.0, 124.9, 106.6, 97.7, 84.4, 68.4, 55.2, 38.4, 36.3, 29.7, 17.6, 15.8.

HRMS-ESI calculated for $C_{19}H_{30}NaO_2$ $[M+Na]^+$: 313.2138; found: 313.2136.

(4*E*,8*E*)-5,9-dimethyltrideca-4,8-dien-12-yn-1-ol (9j)



S13 **9j**

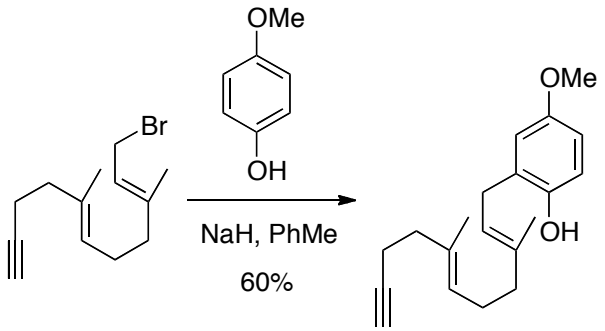
A solution of S13 (100 mg, 0.34 mmol) in Et_2O (4 mL) was added dropwise to a solution of $LiAlH_4$ (26.2 mg, 0.69 mmol) in Et_2O (2 mL) at 0 °C and the mixture was kept at this temperature for 1 h before it was quenched with 10% aqueous NaOH (10 mL) at 0 °C. The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 8:1) to give **9j** (65 mg, 86%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (m, 2H), 3.67 (t, J = 6.5 Hz, 2H), 2.33 - 2.26 (m, 2H), 2.25 - 2.20 (m, 2H), 2.15 - 2.07 (m, 4H), 2.03 (m, 2H), 1.97 (t, J = 2.6 Hz, 1H), 1.68 - 1.61 (m, 8H), 1.40 (br m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.3, 125.5, 123.9, 84.4, 68.3, 62.7, 39.5, 38.4, 32.7, 26.5, 24.3, 17.6, 16.0, 15.8.

HRMS-APCI calculated for $C_{15}H_{25}O$ $[M+H]^+$: 221.1900; found: 221.1896.

2-((2*E*,6*E*)-3,7-dimethylundeca-2,6-dien-10-yn-1-yl)-4-methoxyphenol (9k)



S12 **9k**

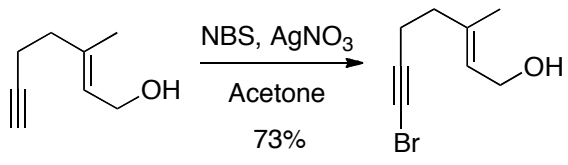
NaH (10.8 mg, 60% dispersion in mineral oil, 0.27 mmol) was added to a solution of 4-methoxyphenol (33.5 mg, 0.27 mmol) in PhMe (2 mL) at 23 °C and the mixture was stirred at this temperature for 15 min. A solution of **S12** (64 mg, 0.25 mmol) in PhMe (1 mL) was added and the reaction mixture was stirred at 23 °C for 15 h before it was quenched with water (5 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 7:1) to give **9k** (45 mg, 60%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (dd, J = 8.5, 0.6 Hz, 1H), 6.72 - 6.66 (m, 2H), 5.33 (tq, J = 7.2, 1.3 Hz, 1H), 5.18 (dddd, J = 6.8, 5.4, 2.7, 1.2 Hz, 1H), 4.79 (s, 1H), 3.78 (s, 3H), 3.35 (d, J = 7.2 Hz, 2H), 2.32 - 2.25 (m, 2H), 2.25 - 2.08 (m, 6H), 1.96 (t, J = 2.5 Hz, 1H), 1.79 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 148.2, 138.3, 133.8, 128.1, 125.0, 121.6, 116.3, 115.7, 112.0, 84.5, 68.3, 55.7, 39.5, 38.3, 29.9, 26.3, 17.5, 16.2, 15.9.

HRMS-ESI calculated for $C_{20}H_{26}NaO_2$ $[M+Na]^+$: 321.1830; found: 321.1821.

(*E*)-7-bromo-3-methylhept-2-en-6-yn-1-ol (S14)



S1 **S14**

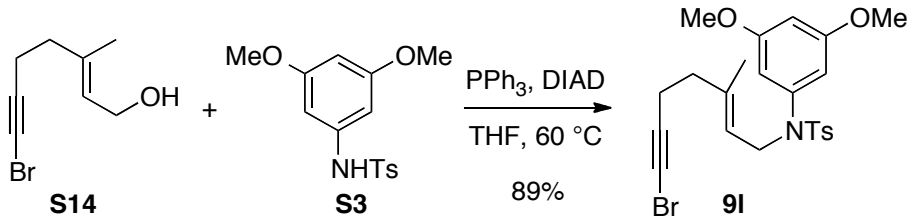
N-bromosuccinimide (117 mg, 0.66 mmol) and silver nitrate (11.2 mg, 66 μmol) were added sequentially to a solution of **S1** (74.2 mg, 0.6 mmol) in acetone (2 mL) at 23 °C and the resulting mixture was stirred at this temperature for 1 h. The solvent was evaporated and the residue was taken up in Et_2O (10 mL) and washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 4:1) to give **S14** (88.7 mg, 73%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (tdd, J = 6.9, 2.7, 1.3 Hz, 1H), 4.18 (d, J = 6.9 Hz, 2H), 2.40 - 2.30 (m, 2H), 2.25 (m, 2H), 1.69 (s, 3H), 1.31 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 124.8, 79.6, 59.3, 38.4, 37.9, 18.5, 16.1.

HRMS-ESI calculated for $C_8H_{11}BrNaO$ $[M+Na]^+$: 224.9885; found: 224.9888.

(*E*)-*N*-(7-bromo-3-methylhept-2-en-6-yn-1-yl)-*N*-(3,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (9l)



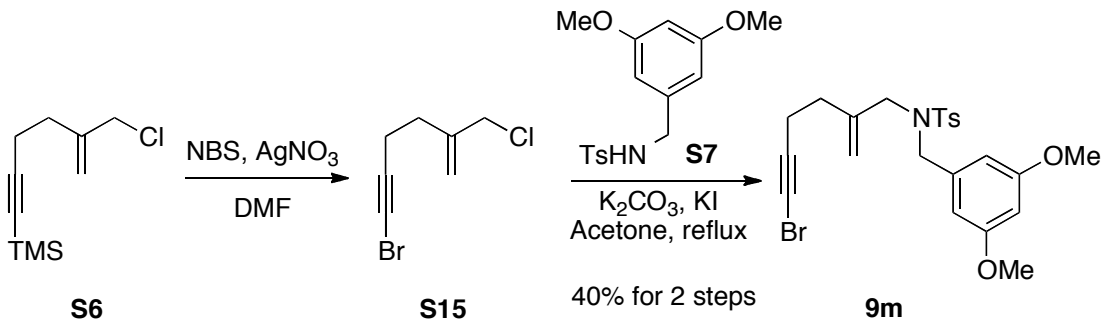
9l was prepared by the same method as **9c** from **S14** and **S3**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 2H), 7.32 - 7.23 (m, 2H), 6.39 (t, J = 2.3 Hz, 1H), 6.22 (d, J = 2.3 Hz, 2H), 5.18 (tq, J = 6.9, 1.2 Hz, 1H), 4.20 - 4.10 (m, 2H), 3.73 (s, 6H), 2.45 (s, 3H), 2.22 - 2.16 (m, 2H), 2.12 (dd, J = 8.6, 5.2 Hz, 2H), 1.56 - 1.53 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 143.4, 141.2, 138.4, 135.7, 129.4, 127.8, 120.1, 107.0, 100.1, 79.5, 55.4, 48.5, 38.3, 37.8, 21.6, 18.6, 16.2.

HRMS-ESI calculated for $C_{23}H_{26}BrNNaO_4S$ $[M+Na]^+$: 514.0653; found: 514.0658.

***N*-(6-bromo-2-methylenehex-5-yn-1-yl)-*N*-(3,5-dimethoxybenzyl)-4-methylbenzenesulfonamide (9m)**



N-bromosuccinimide (100.7 mg, 0.56 mmol) and silver nitrate (8.7 mg, 0.05 mmol) were added sequentially to a solution of **S6** (103.4 mg, 0.51 mmol) in DMF (2 mL) at 23 °C and the resulting mixture was stirred at this temperature for 1 h. The mixture was diluted with water (10 mL) and extracted with Et_2O (10 mL). The organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated to give **S15** as colorless oil which was used without further purification.

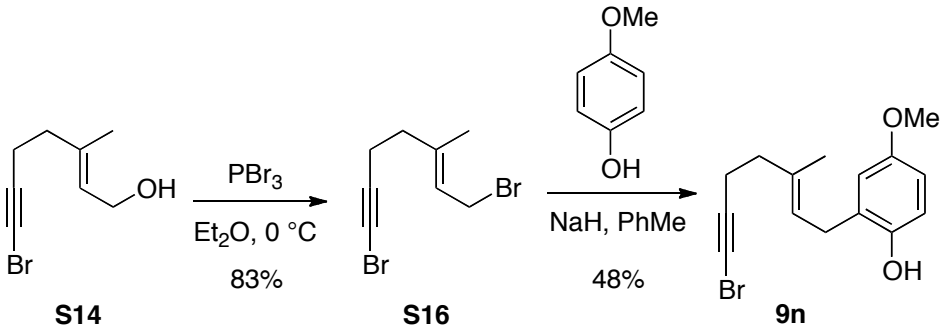
To a solution of **S15** (62.3 mg, 0.3 mmol) and **S7** (115.6 mg, 0.36 mmol) in acetone (5 mL) was added K_2CO_3 (49.7 mg, 0.36 mmol) and KI (5.0 mg, 0.03 mmol) at 23 °C. The mixture was set to reflux for 24 h before the solvent was evaporated. The residue was taken up in Et_2O (10 mL) and washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 5:1) to give **9m** (100 mg, 40% from) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 - 7.72 (m, 2H), 7.35 - 7.31 (m, 2H), 6.35 (t, J = 2.3 Hz, 1H), 6.29 (d, J = 2.3 Hz, 2H), 4.92 (d, J = 1.5 Hz, 1H), 4.87 (d, J = 1.4 Hz, 1H), 4.28 (s, 2H), 3.73 (s, 2H), 3.72 (s, 6H), 2.45 (s, 3H), 2.24 (td, J = 7.2, 1.0 Hz, 2H), 2.10 (t, J = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 143.4, 141.7, 138.2, 137.4, 129.7, 127.2, 115.3, 106.4, 99.9, 79.4, 55.3, 52.1, 51.0, 38.4, 31.4, 21.5, 18.0.

HRMS-ESI calculated for $C_{23}H_{26}BrNNaO_4S$ $[M+Na]^+$: 514.0658; found: 514.0652.

(*E*)-2-(7-bromo-3-methylhept-2-en-6-yn-1-yl)-4-methoxyphenol (9n)



S16 was prepared by the same method as **S2** from **S14**.

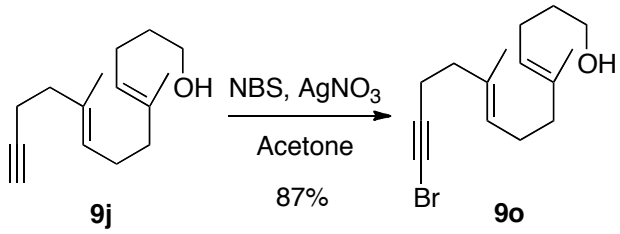
9n was prepared by the same method as **9k** from **S16** and 4-methoxyphenol.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, J = 8.6 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 6.68 (dd, J = 8.6, 3.1 Hz, 1H), 5.40 (tq, J = 7.2, 1.3 Hz, 1H), 4.68 (s, 1H), 3.78 (s, 3H), 3.37 (d, J = 7.1 Hz, 2H), 2.40 - 2.35 (m, 2H), 2.29 (m, 2H), 1.79 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 148.0, 136.1, 128.0, 123.1, 116.4, 115.7, 112.1, 79.6, 55.7, 38.6, 38.1, 29.7, 18.7, 16.0.

HRMS-ESI calculated for $C_{15}H_{17}BrNaO_2$ $[M+Na]^+$: 331.0311; found: 331.0317.

(4*E*,8*E*)-13-bromo-5,9-dimethyltrideca-4,8-dien-12-yn-1-ol (9o)



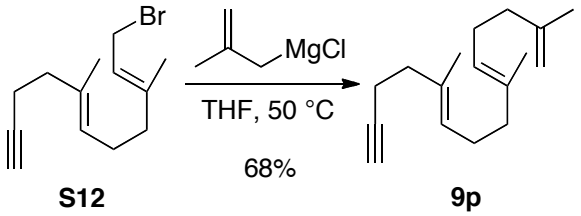
9o was prepared by the same method as **S14** from **9j**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (m, 2H), 3.67 (t, J = 6.5 Hz, 2H), 2.34 - 2.27 (m, 2H), 2.24 - 2.18 (m, 2H), 2.15 - 2.06 (m, 4H), 2.06 - 2.00 (m, 2H), 1.72 - 1.63 (m, 2H), 1.64 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 133.1, 125.7, 123.9, 80.1, 62.8, 39.5, 38.2, 37.9, 32.8, 26.5, 24.3, 18.9, 16.0, 15.8.

HRMS-ESI calculated for $C_{15}H_{23}BrNaO$ $[M+Na]^+$: 321.0832; found: 321.0836.

(5*E*,9*E*)-2,6,10-trimethyltetradeca-1,5,9-trien-13-yne (9p)



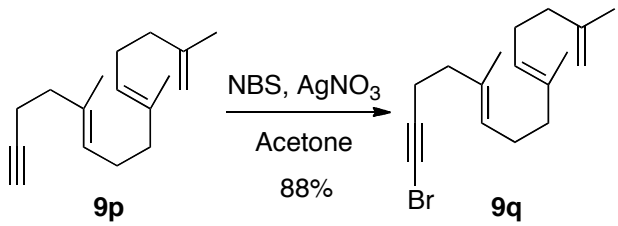
To a solution of **S12** (368 mg, 1.44 mmol) in THF (10 mL) was added (2-methylallyl)magnesium chloride (4.3 mL, 0.5 M in THF, 2.16 mmol) at 0 °C and the mixture was stirred at 50 °C for 8 h before it was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (5 mL) and the combined organic layer was washed sequentially with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane) to give **9p** (225 mg, 68%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (ddq, J = 7.0, 5.6, 1.3 Hz, 1H), 5.15 (tq, J = 6.9, 1.3 Hz, 1H), 4.74 (ddq, J = 2.8, 2.0, 0.9 Hz, 1H), 4.71 (dq, J = 2.1, 1.1 Hz, 1H), 2.29 (tdd, J = 6.9, 2.5, 1.1 Hz, 2H), 2.23 (ddt, J = 8.3, 7.0, 1.3 Hz, 2H), 2.19 - 2.09 (m, 4H), 2.09 - 2.00 (m, 4H), 1.97 (t, J = 2.5 Hz, 1H), 1.76 - 1.74 (s, 3H), 1.65 - 1.62 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 135.0, 133.1, 125.6, 124.2, 109.8, 84.5, 68.3, 39.5, 38.4, 37.8, 26.5, 26.2, 22.5, 17.6, 16.0, 15.8.

HRMS-APCI calculated for $C_{17}H_{27}$ $[M+H]^+$: 231.2107; found: 231.2100.

(5*E*,9*E*)-14-bromo-2,6,10-trimethyltetradeca-1,5,9-trien-13-yne (9q)



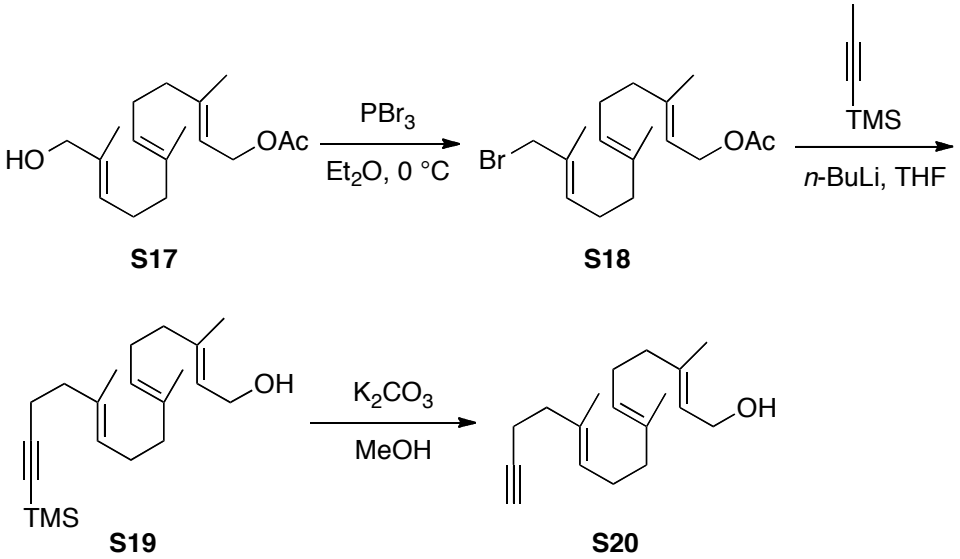
9q was prepared by the same method as **S14** from **9p**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 - 5.09 (m, 2H), 4.72 (ddd, J = 11.6, 2.3, 1.2 Hz, 2H), 2.30 (m, 2H), 2.23 - 1.99 (m, 10H), 1.75 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 135.0, 132.9, 125.8, 124.2, 109.8, 80.1, 39.5, 38.2, 37.9, 37.8, 26.5, 26.2, 22.5, 18.9, 16.0, 15.8.

HRMS-APCI calculated for $C_{17}H_{26}Br$ $[M+H]^+$: 309.1212; found: 309.1216.

(2*E*,6*E*,10*E*)-3,7,11-trimethylpentadeca-2,6,10-trien-14-yn-1-ol (S20)



S18 was prepared by the same method as **S2** from **S17**[5] (2.04 g, 7.3 mmol).

n-BuLi (11.7 mL, 2.5 M in hexanes, 29.2 mmol) was added dropwise to a solution of 1-(trimethylsilyl)propyne (4.3 mL, 29.2 mmol) in THF (80 mL) at -40 °C and the mixture was kept at this temperature for 45 min before it was cooled to -60 °C and a solution of **S18** (prepared in the last step) in THF (20 mL) was added and the reaction mixture was stirred at -60 °C for 1 h before it was quenched with saturated aqueous NH_4Cl (100 mL). The aqueous layer was extracted with Et_2O and the combined organic layer was washed sequentially with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was subjected to the next step without further purification.

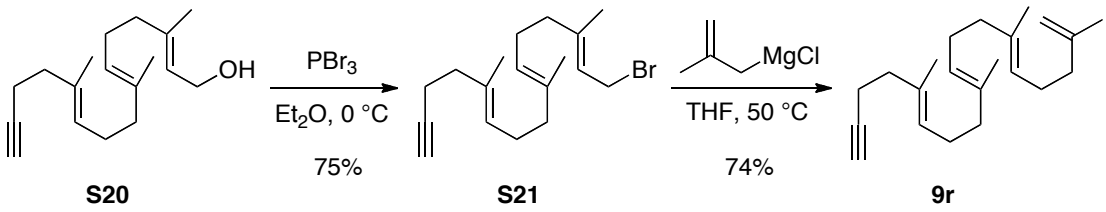
K_2CO_3 (4.03 g, 29.2 mmol) was added to a solution of the residue above in MeOH (40 mL) at 23 °C and the mixture was stirred at this temperature for 12 h. The solvent was evaporated and the residue was taken up in Et_2O (20 mL) and washed sequentially with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 7:1) to give **S20** (930 mg, 49% for three steps) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (m, 1H), 5.20 (m, 1H), 5.14 (m, 1H), 4.18 (d, J = 6.9 Hz, 2H), 2.29 (m, 2H), 2.26 - 2.20 (m, 2H), 2.18 - 1.99 (m, 8H), 1.97 (t, J = 2.5 Hz, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 135.2, 133.2, 125.5, 123.9, 123.4, 84.4, 77.2, 68.3, 59.4, 39.5, 38.4, 26.6, 26.3, 17.6, 16.3, 16.0, 15.8.

HRMS-APCI calculated for $C_{18}H_{29}O$ $[M+H]^+$: 261.2218; found: 261.2215.

(5*E*,9*E*,13*E*)-2,6,10,14-tetramethyloctadeca-1,5,9,13-tetraen-17-yne (9r)



S21 was prepared by the same method as **S2** from **S20**.

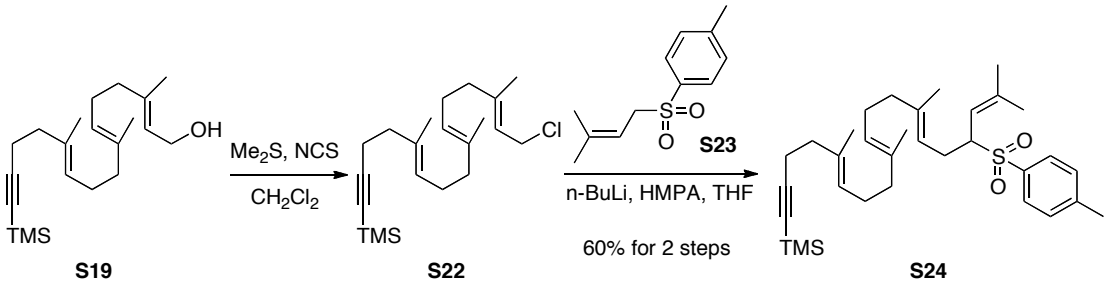
9r was prepared by the same method as **9p** from **S21**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 - 5.11 (m, 3H), 4.74 - 4.69 (m, 2H), 2.33 - 2.26 (m, 2H), 2.25 - 2.21 (m, 2H), 2.17 - 1.98 (m, 12H), 1.96 (t, J = 2.5 Hz, 1H), 1.75 (s, 3H), 1.63 (s, 6H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 135.1, 134.7, 133.1, 125.6, 124.4, 124.1, 109.7, 84.4, 68.3, 39.7, 39.6, 38.4, 37.8, 26.6, 26.2, 22.5, 17.6, 16.0, 15.8.

HRMS-APCI calculated for $C_{22}H_{35}$ $[M+H]^+$: 299.2733; found: 299.2745.

Trimethyl((5*E*,9*E*,13*E*)-5,9,13,18-tetramethyl-16-tosylnonadeca-5,9,13,17-tetraen-1-yn-1-yl)silane (S24)



Dimethyl sulfide (0.28 mL, 3.75 mmol) was added to a solution of *N*-chlorosuccinimide (459 mg, 3.44 mmol) in CH_2Cl_2 (10 mL) at -30 °C and the reaction mixture was stirred at this temperature for 15 min. A solution of **S19** (1.04 g, 3.13 mmol) in CH_2Cl_2 (5 mL) was added slowly and the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. the reaction was quenched by the addition of water (20 mL) and the organic layer was washed sequentially with water (20×3 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was subjected to the next step without further purification.

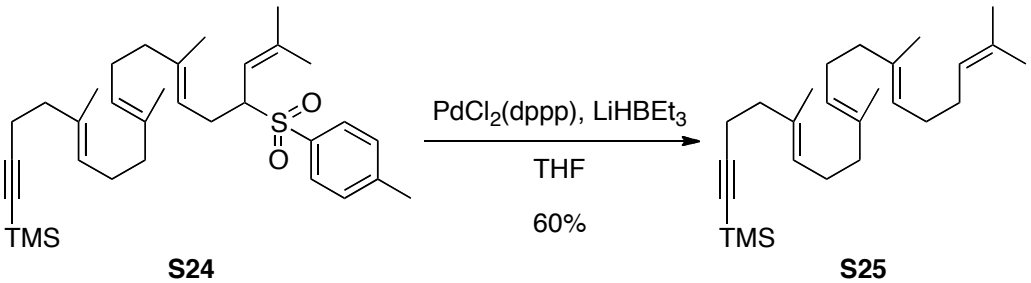
n-BuLi (1.5 mL, 2.5 M in hexanes, 3.76 mmol) and hexamethylphosphoramide (0.71 mL, 4.07 mmol) was added sequentially to a solution of **S23**[6] (701 mg, 3.13 mmol) in THF (8 mL) at -20 °C and the mixture was kept at this temperature for 30 min before it was cooled to -78 °C and a solution of **S22** (prepared in the last step) in THF (5 mL) was added and the reaction mixture was stirred at -78 °C for 1 h. The cooling bath was removed and the mixture was stirred at room temperature for another 1 h before it was quenched with saturated aqueous NH_4Cl (40 mL). The aqueous layer was extracted with Et_2O (30 mL) and the combined organic layer was washed sequentially with water (40 mL) and brine (40 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 10:1) to give **S24** (1.01 g, 60% for 2 steps) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 - 7.70 (m, 2H), 7.34 - 7.30 (m, 2H), 5.19 - 5.13 (m, 1H), 5.07 (tt, J = 5.6, 3.0 Hz, 1H), 4.98 (dddd, J = 7.5, 4.7, 3.0, 1.5 Hz, 2H), 3.70 (td, J = 10.6, 3.4 Hz, 1H), 2.89 - 2.79 (m, 1H), 2.45 (s, 3H), 2.39 - 2.25 (m, 3H), 2.19 (dd, J = 8.3, 6.7 Hz, 2H), 2.12 - 1.93 (m, 8H), 1.69 (d, J = 1.5 Hz, 3H), 1.63 - 1.57 (m, 9H), 1.23 (d, J = 1.4 Hz, 3H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.5, 138.5, 135.2, 135.0, 133.4, 129.3, 129.1, 125.5, 124.0, 118.7, 117.3, 107.4, 84.5, 65.0, 39.7, 39.6, 38.7, 26.6, 26.6, 26.6, 25.8, 21.6, 19.2, 18.1, 16.4, 16.0, 15.8, 0.2.

HRMS-APCI calculated for $C_{33}H_{51}O_2SSi$ $[M+H]^+$: 539.3379; found: 539.3376.

Trimethyl((5*E*,9*E*,13*E*)-5,9,13,18-tetramethylnonadeca-5,9,13,17-tetraen-1-yn-1-yl)silane (S25)



S24 **S25**

To a solution of **S24** (812 mg, 1.51 mmol) in THF (15 mL) was added $PdCl_2$(dppp) (89 mg, 0.151 mmol) at 0 °C. Lithium triethylborohydride ($LiHBEt_3$, 1.0 M solution in THF, 5 mL, 5.0 mmol) was then added slowly to the solution over a 1 min period. The reaction mixture was stirred for an additional 4 h at 0 °C and then diluted with Et_2O (20 mL), followed by the addition of saturated NH_4Cl (40 mL).. The organic layer was washed sequentially with water (40 mL×2), and brine (40 mL), dried over

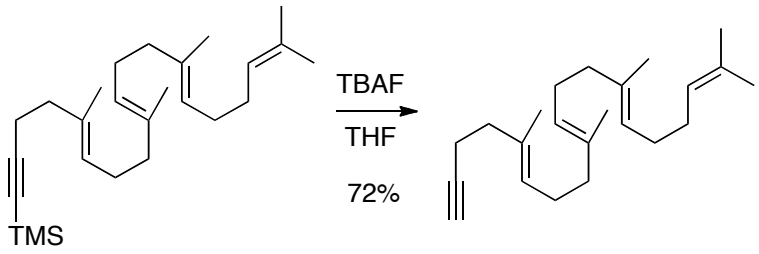
anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane) to give **S25** (349 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 - 5.10 (m, 4H), 2.32 (ddd, J = 7.8, 6.9, 1.2 Hz, 2H), 2.24 - 2.18 (m, 2H), 2.14 - 2.06 (m, 4H), 2.06 - 1.97 (m, 8H), 1.71 (d, J = 1.5 Hz, 3H), 1.64 - 1.61 (m, 12H), 0.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 134.8, 133.3, 131.4, 125.6, 124.5, 124.4, 124.3, 107.4, 84.5, 39.7, 39.6, 38.7, 28.4, 28.3, 26.6, 25.7, 19.2, 17.7, 16.0, 16.0, 15.8, 0.2.

HRMS-APCI calculated for $C_{26}H_{45}Si$ $[M+H]^+$: 385.3290; found: 385.3296.

(5*E*,9*E*,13*E*)-5,9,13,18-tetramethylnonadeca-5,9,13,17-tetraen-1-yne (S26)



S25 **S26**

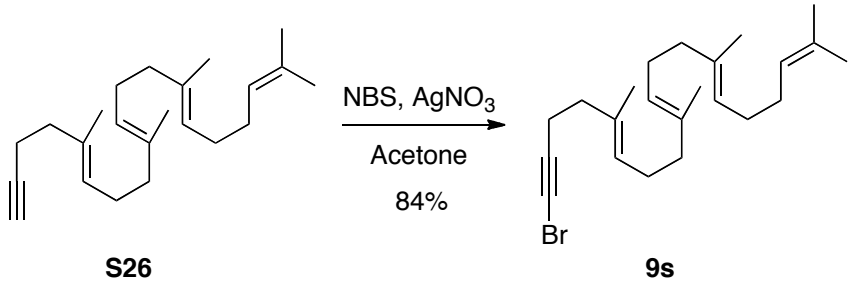
S26 was prepared by the same method as **9h** from **S25**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 - 5.12 (m, 4H), 2.30 (dddd, J = 7.9, 6.8, 2.5, 1.6 Hz, 2H), 2.25 - 2.20 (m, 2H), 2.15 - 2.07 (m, 4H), 2.05 - 1.99 (m, 8H), 1.96 (t, J = 2.6 Hz, 1H), 1.71 (d, J = 1.5 Hz, 3H), 1.64 – 1.62 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 134.7, 133.1, 131.4, 125.6, 124.5, 124.4, 124.3, 84.4, 68.3, 39.7, 39.6, 38.4, 28.4, 28.3, 26.6, 26.6, 25.7, 17.7, 17.6, 16.0, 16.0, 15.8.

HRMS-APCI calculated for $C_{23}H_{37}$ $[M+H]^+$: 313.2895; found: 313.2899.

(5*E*,9*E*,13*E*)-1-bromo-5,9,13,18-tetramethylnonadeca-5,9,13,17-tetraen-1-yne (9s)



S26 **9s**

9s was prepared by the same method as **S14** from **S26**.

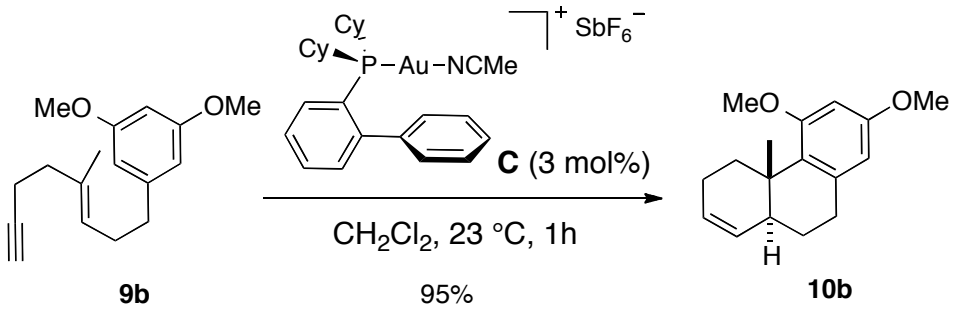
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 - 5.10 (m, 4H), 2.36 - 2.25 (m, 2H), 2.25 - 2.16 (m, 2H), 2.15 - 2.06 (m, 4H), 2.06 - 1.98 (m, 8H), 1.71 (s, 3H), 1.63 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 134.7, 132.9, 131.5, 125.8, 124.5, 124.4, 124.3, 80.1, 39.7, 39.5, 38.2, 37.9, 28.4, 28.3, 26.7, 26.6, 25.7, 18.9, 17.7, 16.0, 16.0, 15.8.

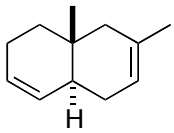
HRMS-ESI calculated for $C_{23}H_{35}BrNa$ $[M+Na]^+$: 413.1822; found: 413.1825.

3. Procedures for Gold(I)-Catalyzed Polycyclisations

Representative procedure for gold(I)-catalyzed polycyclisations



C (4.9 mg, 6 μmol) was added to a solution of **9b** (51.6 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at 23 °C for 1 h. The solvent was evaporated and the residue was purified by flash column chromatography (cyclohexane/EtOAc 30:1) to give **10b** (49 mg, 95%) as colorless oil.

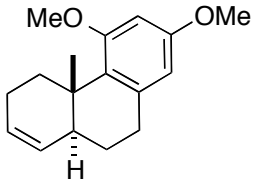


10a

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 - 5.60 (m, 1H), 5.43 - 5.36 (m, 2H), 2.18 - 1.93 (m, 4H), 1.91 - 1.82 (m, 1H), 1.78 - 1.63 (m, 2H), 1.68 (m, 3H), 1.54 - 1.37 (m, 2H), 0.81 - 0.78 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 130.2, 126.1, 120.5, 45.9, 39.5, 36.7, 31.0, 28.7, 24.0, 23.2, 15.8.

HRMS-ESI calculated for $C_{12}H_{19}$ $[M+H]^+$: 163.1488; found: 163.1494.

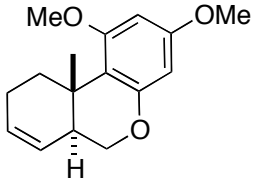


10b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (d, J = 2.6 Hz, 1H), 6.27 (dt, J = 2.6, 0.8 Hz, 1H), 5.70 (dq, J = 9.9, 3.7 Hz, 1H), 5.48 (dq, J = 9.7, 2.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.16 (ddt, J = 13.2, 6.6, 1.3 Hz, 1H), 3.01 (dddt, J = 17.1, 12.1, 7.1, 1.0 Hz, 1H), 2.87 - 2.77 (m, 1H), 2.41 (dddd, J = 12.3, 6.1, 3.1, 1.9 Hz, 1H), 2.34 - 2.12 (m, 2H), 1.75 (tdd, J = 13.1, 12.1, 5.7 Hz, 1H), 1.64 (ddt, J = 8.7, 4.2, 1.4 Hz, 1H), 1.54 - 1.44 (m, 1H), 1.18 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.0, 139.0, 131.2, 127.8, 127.0, 105.2, 97.3, 55.1, 55.0, 44.0, 36.5, 32.4, 32.3, 24.6, 24.5, 17.0.

HRMS-ESI calculated for $C_{17}H_{23}O_2$ $[M+H]^+$: 259.1693; found: 259.1687.

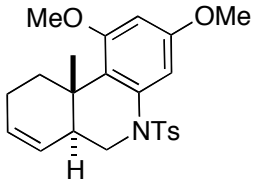


10c

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 - 6.00 (m, 2H), 5.84 - 5.76 (m, 1H), 5.38 (dq, J = 9.8, 2.2 Hz, 1H), 4.10 (dd, J = 10.3, 4.0 Hz, 1H), 3.99 (dd, J = 12.5, 10.3 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.10 - 3.01 (m, 1H), 2.71 (ddqd, J = 12.8, 5.8, 3.4, 1.9 Hz, 1H), 2.29 - 2.18 (m, 2H), 1.56 - 1.49 (m, 1H), 1.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.1, 155.7, 129.2, 123.6, 113.6, 94.0, 92.1, 66.2, 55.2, 55.2, 41.5, 33.2, 31.8, 24.2, 17.9.

HRMS-ESI calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485; found: 261.1473.



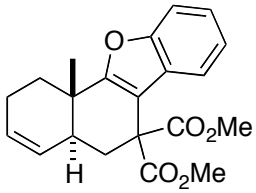
10d

M.p.: 111-112 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.24 - 7.18 (m, 3H), 6.24 (d, J = 2.5 Hz, 1H), 5.73 (dq, J = 9.9, 3.3 Hz, 1H), 5.35 (dq, J = 9.8, 2.1 Hz, 1H), 4.02 (dd, J = 11.9, 4.3 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.24 (dd, J = 13.6, 11.9 Hz, 1H), 3.00 (dt, J = 13.4, 4.4 Hz, 1H), 2.38 (s, 3H), 2.35 - 2.31 (m, 1H), 2.09 (m, 2H), 1.29 (m, 1H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 158.1, 143.7, 137.8, 135.7, 129.5, 128.6, 127.3, 124.9, 120.3, 100.3, 96.1, 55.3, 55.3, 47.7, 40.9, 35.0, 31.8, 23.7, 21.5, 16.3.

HRMS-ESI calculated for $C_{23}H_{27}NNaO_4S$ $[M+Na]^+$: 436.1553; found: 436.1533.

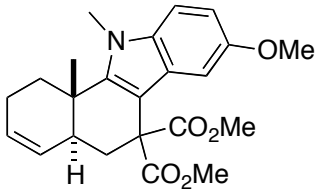


10e

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 - 7.52 (m, 1H), 7.47 - 7.42 (m, 1H), 7.26 - 7.20 (m, 2H), 5.73 (ddd, J = 10.2, 4.3, 2.7 Hz, 1H), 5.56 (dq, J = 9.9, 2.0 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.76 (dd, J = 14.0, 4.9 Hz, 1H), 2.66 (dd, J = 13.6, 2.6 Hz, 1H), 2.37 - 2.16 (m, 4H), 1.82 - 1.70 (m, 1H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 170.8, 163.7, 154.4, 127.6, 127.4, 123.2, 122.6, 121.3, 111.1, 107.7, 55.2, 52.9, 52.7, 40.0, 34.5, 32.6, 30.6, 22.9, 18.3.

HRMS-ESI calculated for $C_{21}H_{22}NaO_5$ $[M+Na]^+$: 377.1359; found: 377.1373.



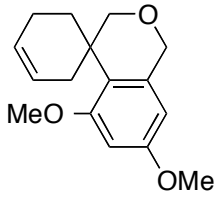
10f

M.p.: 165-168 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.9 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.88 (dd, J = 8.9, 2.5 Hz, 1H), 5.76 (dq, J = 9.9, 3.3 Hz, 1H), 5.56 (dq, J = 9.9, 2.1 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 2.78 (m, 1H), 2.61 (m, 2H), 2.35 - 2.23 (m, 3H), 1.86 (m, 1H), 1.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 171.8, 154.2, 145.9, 133.1, 129.1, 126.9, 126.5, 111.1, 109.4, 104.6, 103.2, 56.3, 56.1, 52.7, 52.6, 41.3, 35.3, 33.2, 32.7, 32.1, 23.6, 17.5.

HRMS-ESI calculated for $C_{23}H_{28}NO_5$ $[M+H]^+$: 398.1962; found: 398.1963.

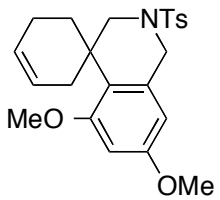


10g

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37 (d, J = 2.5 Hz, 1H), 6.20 - 6.09 (m, 1H), 5.73 (s, 2H), 4.77 - 4.63 (m, 2H), 3.95 (d, J = 11.4 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.62 (dd, J = 11.3, 1.3 Hz, 1H), 2.90 - 2.82 (m, 1H), 2.75 (ddd, J = 13.3, 10.2, 9.1 Hz, 1H), 2.12 - 2.01 (m, 3H), 1.50 - 1.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 158.6, 137.5, 126.4, 125.4, 122.5, 99.9, 98.1, 73.8, 70.0, 55.2, 55.0, 34.5, 31.5, 27.4, 22.0.

HRMS-ESI calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485; found: 261.1475.



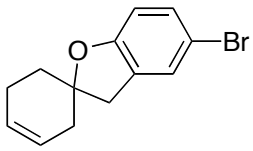
10h

M.p.: 176-178 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.39 - 7.35 (m, 2H), 6.35 (d, J = 2.5 Hz, 1H), 6.20 - 6.16 (m, 1H), 5.80 - 5.74 (m, 1H), 5.74 - 5.67 (m, 1H), 4.24 - 4.16 (m, 1H), 4.04 (dd, J = 14.5, 1.1 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.19 (dd, J = 11.5, 1.5 Hz, 1H), 3.04 - 2.96 (m, 2H), 2.70 (ddd, J = 13.3, 11.8, 6.5 Hz, 1H), 2.46 (s, 3H), 2.18 (m, 1H), 2.13 - 2.02 (m, 1H), 1.94 (ddd, J = 18.5, 4.2, 2.2 Hz, 1H), 1.52 - 1.44 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 158.6, 143.6, 134.3, 133.0, 129.7, 127.9, 125.9, 125.3, 122.8, 102.1, 98.5, 55.2, 55.1, 52.4, 50.0, 36.9, 31.8, 27.7, 21.9, 21.5.

HRMS-ESI calculated for $C_{23}H_{27}NNaO_4S$ $[M+Na]^+$: 436.1553; found: 436.1558.

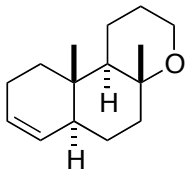


10i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.20 (m, 2H), 6.66 (d, J = 8.4 Hz, 1H), 5.80 (m, 1H), 5.66 (m, 1H), 3.07 - 2.95 (m, 2H), 2.52 - 2.28 (m, 3H), 2.25 - 2.14 (m, 1H), 2.01 (dtd, J = 12.9, 6.3, 1.2 Hz, 1H), 1.81 (dtd, J = 12.9, 6.4, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 130.7, 129.1, 128.1, 126.8, 123.8, 111.6, 111.1, 87.6, 40.8, 37.1, 32.4, 23.4.

HRMS-APCI calculated for $C_{13}H_{14}BrO$ $[M+H]^+$: 265.0223; found: 265.0219.

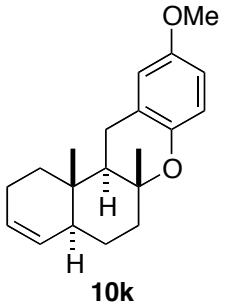


10j

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (dq, J = 9.9, 3.2 Hz, 1H), 5.35 (dq, J = 9.8, 2.1 Hz, 1H), 3.75 (ddd, J = 11.9, 9.6, 7.0 Hz, 1H), 3.70 - 3.63 (m, 1H), 2.09 (dh, J = 6.7, 3.2, 2.3 Hz, 2H), 2.00 (dddd, J = 14.1, 4.8, 3.3, 1.4 Hz, 1H), 1.81 - 1.64 (m, 5H), 1.59 - 1.38 (m, 4H), 1.36 - 1.26 (m, 4H), 1.22 - 1.13 (m, 1H), 0.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 130.3, 125.8, 75.0, 61.0, 55.1, 46.2, 41.2, 35.0, 34.4, 27.7, 25.6, 23.2, 20.7, 18.3, 11.6.

HRMS-APCI calculated for $C_{15}H_{25}O$ $[M+H]^+$: 221.1900; found: 221.1890.



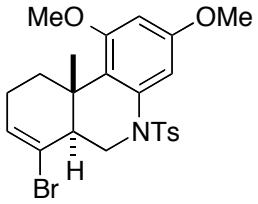
10k

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 - 6.67 (m, 2H), 6.65 (dd, J = 2.8, 1.0 Hz, 1H), 5.60 (dq, J = 9.9, 3.5 Hz, 1H), 5.42 (dq, J = 9.8, 2.0 Hz, 1H), 3.77 (s, 3H), 2.75 (dd, J = 16.4, 5.2 Hz, 1H), 2.70 - 2.63 (m, 1H), 2.17 - 2.11 (m, 2H), 2.08 (ddt, J = 12.6, 10.3, 3.1 Hz, 2H), 1.86 - 1.79 (m, 1H), 1.79 - 1.71 (m, 2H), 1.63 (ddt, J = 13.9, 4.3,

3.1 Hz, 1H), 1.48 (td, J = 13.4, 3.3 Hz, 1H), 1.34 - 1.30 (m, 1H), 1.29 (d, J = 1.0 Hz, 3H), 0.83 (d, J = 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 147.4, 130.1, 125.8, 123.0, 117.6, 114.3, 113.1, 55.7, 49.4, 45.9, 40.4, 34.9, 34.8, 25.2, 23.1, 23.0, 21.4, 11.4.

HRMS-ESI calculated for $C_{20}H_{26}NaO_2$ $[M+Na]^+$: 321.1825; found: 321.1810.

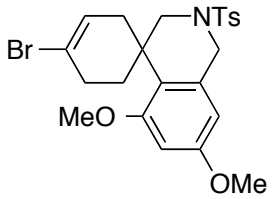


10l

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 - 7.59 (m, 2H), 7.27 - 7.23 (m, 2H), 7.22 (d, J = 2.5 Hz, 1H), 6.28 (d, J = 2.5 Hz, 1H), 6.11 (dt, J = 5.4, 3.0 Hz, 1H), 4.68 (dd, J = 13.0, 3.5 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.27 (t, J = 12.8 Hz, 1H), 3.09 - 3.00 (m, 1H), 2.46 - 2.42 (m, 1H), 2.40 (s, 3H), 2.22 - 2.12 (m, 1H), 2.08 (dtdd, J = 13.8, 7.8, 3.9, 2.3 Hz, 1H), 1.18 (ddd, J = 13.5, 11.6, 6.6 Hz, 1H), 0.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 158.4, 143.8, 137.8, 136.2, 130.6, 129.6, 127.3, 120.9, 119.0, 100.7, 96.6, 55.4, 55.3, 47.1, 46.2, 38.1, 31.3, 25.8, 21.6, 17.2.

HRMS-ESI calculated for $C_{23}H_{26}BrNNaO_4S$ $[M+Na]^+$: 514.0658; found: 514.0651.

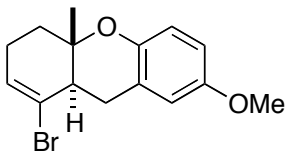


10m

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 - 7.74 (m, 2H), 7.41 - 7.37 (m, 2H), 6.35 (d, J = 2.5 Hz, 1H), 6.18 (d, J = 2.5 Hz, 1H), 6.13 - 6.09 (m, 1H), 4.18 (d, J = 14.5 Hz, 1H), 4.09 (d, J = 14.4 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.51 (ddt, J = 18.0, 4.6, 2.5 Hz, 1H), 3.23 (d, J = 12.0 Hz, 1H), 2.98 (d, J = 11.9 Hz, 1H), 2.64 - 2.54 (m, 1H), 2.47 (s, 3H), 2.36 - 2.25 (m, 1H), 2.25 - 2.19 (m, 1H), 2.19 - 2.11 (m, 1H), 1.61 - 1.57 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 159.0, 143.8, 134.4, 133.0, 129.8, 127.8, 127.0, 121.0, 120.8, 102.2, 98.4, 55.3, 55.2, 52.2, 49.8, 41.4, 39.6, 26.3, 24.0, 21.6.

HRMS-ESI calculated for $C_{23}H_{26}BrNNaO_4S$ $[M+Na]^+$: 514.0658; found: 514.0664.

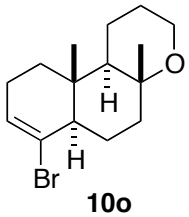


10n

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, J = 8.8 Hz, 1H), 6.74 (dd, J = 9.0, 3.0 Hz, 1H), 6.71 - 6.69 (m, 1H), 6.12 (dt, J = 5.0, 2.9 Hz, 1H), 3.79 (s, 3H), 3.07 (dd, J = 16.3, 5.3 Hz, 1H), 2.90 - 2.82 (m, 1H), 2.61 (ddt, J = 16.2, 13.6, 1.0 Hz, 1H), 2.37 - 2.18 (m, 2H), 2.01 (m, 1H), 1.93 (m, 1H), 1.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 147.1, 129.1, 123.7, 122.5, 117.8, 114.2, 114.0, 76.0, 55.7, 45.0, 34.8, 28.9, 25.7, 16.3.

HRMS-ESI calculated for $C_{15}H_{17}BrNaO_2$ $[M+Na]^+$: 331.0311; found: 331.0314.

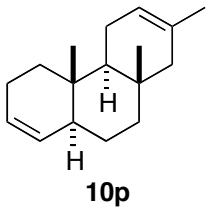


10o

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (dt, J = 4.3, 3.3 Hz, 1H), 3.77 - 3.70 (m, 1H), 3.69 - 3.64 (m, 1H), 2.35 - 2.28 (m, 1H), 2.16 - 2.10 (m, 3H), 1.84 - 1.75 (m, 2H), 1.70 - 1.66 (m, 2H), 1.46 - 1.41 (m, 2H), 1.37 - 1.33 (m, 1H), 1.34 (d, J = 0.9 Hz, 3H), 1.30 - 1.27 (m, 1H), 1.24 - 1.21 (m, 1H), 0.75 (d, J = 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 128.2, 126.9, 74.5, 60.9, 54.8, 51.2, 41.0, 37.9, 33.8, 27.5, 25.3, 25.1, 20.5, 18.6, 11.9.

HRMS-ESI calculated for $C_{15}H_{23}BrNaO$ $[M+Na]^+$: 321.0832; found: 321.0838.

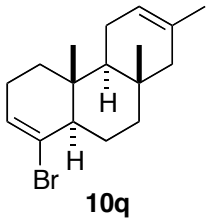


10p

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (ddt, J = 10.0, 4.3, 3.2 Hz, 1H), 5.38 (ddt, J = 9.8, 4.2, 1.8 Hz, 2H), 2.08 (dddd, J = 10.2, 7.1, 4.2, 2.1 Hz, 3H), 1.90 (ddddd, J = 15.3, 13.9, 6.4, 3.5, 2.0 Hz, 3H), 1.78 - 1.71 (m, 1H), 1.67 - 1.60 (m, 4H), 1.58 - 1.54 (m, 1H), 1.51 (dd, J = 13.1, 3.0 Hz, 1H), 1.41 - 1.34 (m, 1H), 1.31 - 1.25 (m, 1H), 1.22 - 1.16 (m, 1H), 1.16 - 1.10 (m, 1H), 0.96 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.2, 131.4, 125.4, 120.2, 51.6, 49.9, 46.8, 42.4, 35.3, 35.0, 33.6, 24.7, 23.7, 23.4, 22.9, 20.9, 11.9.

HRMS-APCI calculated for $C_{17}H_{27}$ $[M+H]^+$: 231.2113; found: 231.2111.

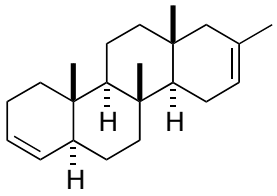


10q

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 - 6.01 (m, 1H), 5.38 - 5.34 (m, 1H), 2.21 - 2.16 (m, 1H), 2.14 - 2.04 (m, 4H), 2.01 (m, 1H), 1.90 (m, 1H), 1.82 - 1.76 (m, 1H), 1.71 (dt, J = 13.3, 3.2 Hz, 1H), 1.64 (s, 3H), 1.56 (m, 1H), 1.47 (dd, J = 13.1, 3.1 Hz, 1H), 1.21 (m, 3H), 0.96 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 132.3, 128.3, 128.0, 119.9, 52.1, 51.4, 49.9, 42.1, 38.1, 34.6, 33.3, 25.2, 24.0, 23.7, 23.2, 20.8, 12.3.

HRMS-APCI calculated for $C_{17}H_{26}Br$ $[M+H]^+$: 309.1212; found: 309.1214.

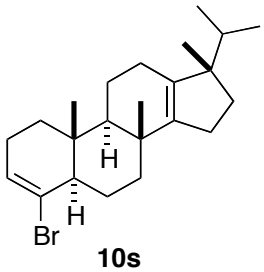


10r

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (m, 1H), 5.34 (m, 2H), 2.09 (m, 2H), 2.02 - 1.74 (m, 6H), 1.73 - 1.61 (m, 6H), 1.51 - 1.32 (m, 4H), 1.26 - 1.16 (m, 2H), 1.13 - 1.06 (m, 1H), 1.05 - 0.93 (m, 4H), 0.93 - 0.83 (m, 4H), 0.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 131.2, 125.5, 119.9, 58.5, 53.5, 51.3, 46.4, 43.5, 40.6, 37.8, 35.5, 35.3, 33.2, 24.3, 23.7, 23.6, 22.7, 20.4, 17.8, 17.0, 12.3.

HRMS-APCI calculated for $C_{22}H_{35}$ $[M+H]^+$: 299.2733; found: 299.2730.



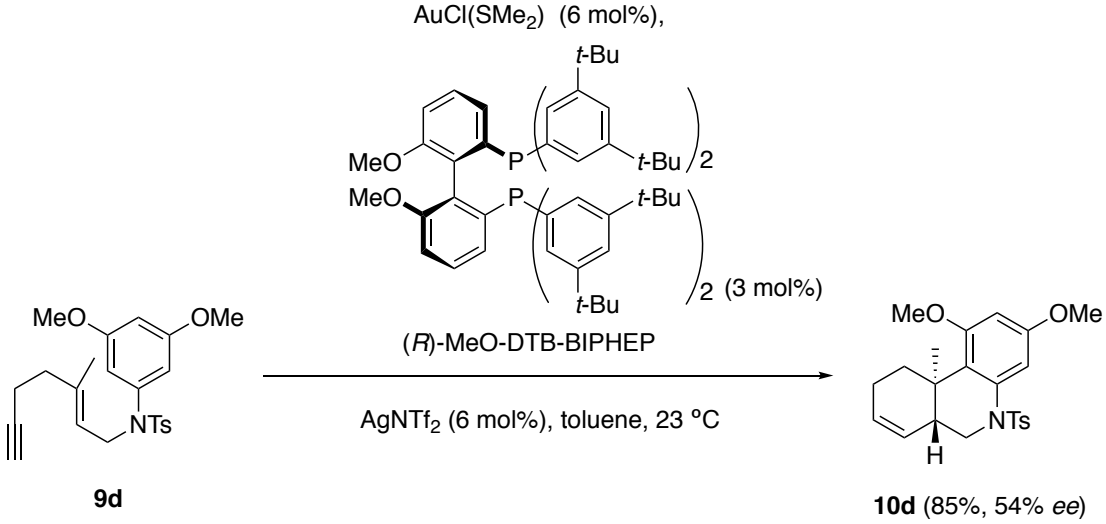
10s

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (q, J = 3.6 Hz, 1H), 2.26 - 2.06 (m, 4H), 2.06 - 1.97 (m, 2H), 1.93 - 1.87 (m, 1H), 1.84 - 1.75 (m, 4H), 1.60 (m, 1H), 1.52 - 1.44 (m, 2H), 1.31 - 1.26 (m, 2H), 1.25 - 1.20 (m, 2H), 1.14 (m, 1H), 1.03 (s, 3H), 0.97 (s, 3H), 0.86 (s, 3H), 0.85 (d, J = 7.1 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 137.6, 128.0, 127.9, 53.8, 52.3, 51.7, 38.5, 38.0, 36.3, 34.6, 33.5, 30.2, 27.7, 25.3, 25.3, 24.3, 23.4, 20.8, 18.4, 18.2, 17.6, 12.5.

HRMS-ESI calculated for $C_{23}H_{35}BrNa$ $[M+Na]^+$: 413.1822; found: 413.1826.

4. Procedures for Enantioselective Cyclisations



9d

10d (85%, 54% *ee*)

Chloro(dimethylsulfide)gold(I) (1.8 mg, 6 μmol) was added to a solution of (R)-MeO-DTBM-BIPHEP (3.0 mg, 3 μmol) in toluene (0.5 mL) and the mixture was stirred at 23 °C for 30 min before silver bis(trifluoromethanesulfonyl)imide (2.3 mg, 6 μmol) was added. The mixture was stirred at this temperature for another 30 min and a solution of **9d** (41 mg, 0.1 mmol) in toluene (0.5 mL) was added. The mixture was stirred at 23 °C for 1 h before it was filtered through a pad of Celite and purified by preparative TLC. The purified product was analyzed on HPLC.

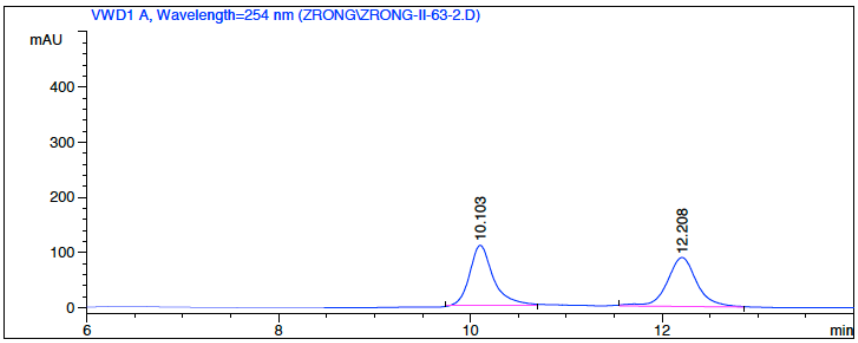
Identical procedure was applied for the reaction of **9f** to form **10f**.

HPLC analysis of racemic **10d**.

```
Data File C:\HPCHEM\1\DATA\ZRONG\ZRONG-II-63-2.D
Sample Name: ZRONG-II-63-2

    ========================================================================
    Acq. Operator   : ZHOUTING
    Acq. Instrument : HPLC1100                      Location : Vial 71
    Injection Date  : 3/5/2015 3:33:19 PM
                                                   Inj Volume : 5 µl
    Acq. Method     : C:\HPCHEM\1\DATA\KATYA\MASHA.M
    Last changed    : 3/5/2015 3:28:03 PM by ZHOUTING
                      (modified after loading)
    Analysis Method : C:\HPCHEM\1\DATA\ZRONG\ZRONG-II-63-2.D\DA.M (MASHA.M)
    Last changed    : 1/26/2017 4:54:10 PM by MASHA
    Method Info     : STANDARD FLAVANONE IB

    Sample Info     : chiralpack IA
                      95:5 hex:ipa
                      1.0 ml/min
```

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    ========================================================================
                           Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      10/28/2004 1:11:56 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime  Type    Width     Area      Area     Name
      #   [min]           [min]  mAU   *s       %
    ----|-------|------|-------|----------|--------|--------------------
       1  10.103 MM      0.2917 1922.37549  50.1159 ?
       2  12.208 MM      0.3594 1913.48779  49.8841 ?

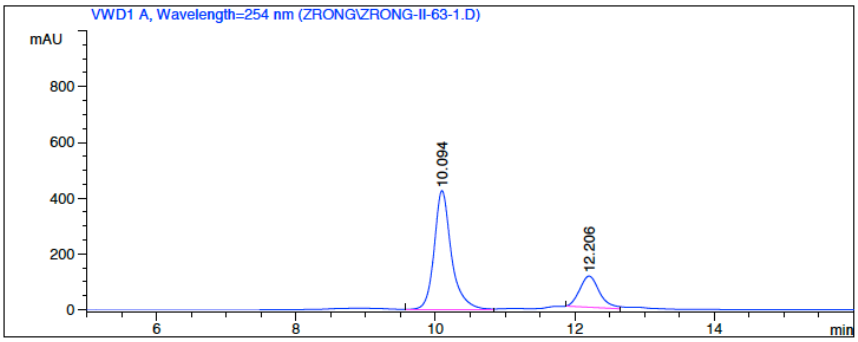
    Totals :                   3835.86328
```

HPLC analysis of enantioenriched **10d**.

```
Data File C:\HPCHEM\1\DATA\ZRONG\ZRONG-II-63-1.D
Sample Name: ZRONG-II-63-1

    ======================================================================
    Acq. Operator   : ZHOUTING
    Acq. Instrument : HPLC1100                      Location : Vial 81
    Injection Date  : 3/5/2015 3:54:37 PM
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\HPCHEM\1\DATA\KATYA\MASHA.M
    Last changed    : 3/5/2015 3:51:54 PM by ZHOUTING
                      (modified after loading)
    Analysis Method : C:\HPCHEM\1\DATA\ZRONG\ZRONG-II-63-1.D\DA.M (MASHA.M)
    Last changed    : 1/26/2017 4:17:38 PM by MASHA
                      (modified after loading)
    Method Info     : STANDARD FLAVANONE IB

    Sample Info     : chiralpack IA
                      95:5 hex:ipa
                      1.0 ml/min
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      10/28/2004 1:11:56 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime  Type   Width     Area      Area    Name
      #   [min]          [min]  mAU   *s       %
    ----|-------|------|-------|----------|--------|--------------------
       1  10.094 VV      0.2607 7396.45166  76.9948 ?
       2  12.206 MM      0.3297 2209.97461  23.0052 ?

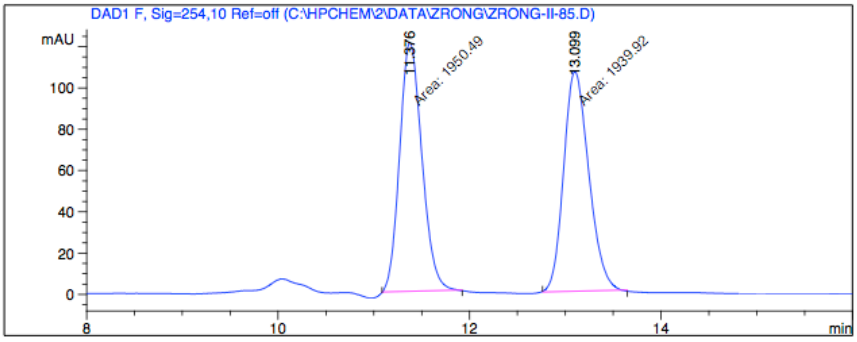
    Totals :                   9606.42627
```

HPLC analysis of racemic **10f**.

```
Data File C:\HPCHEM\2\DATA\ZRONG\ZRONG-II-85.D
Sample Name: ZRONG-II-85

    ======================================================================
    Acq. Operator   : ZHOUTING
    Acq. Instrument : AG1200HPLC                    Location : Vial 41
    Injection Date  : 4/16/2015 4:21:47 PM
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\HPCHEM\2\METHODS\MICHAEL.M
    Last changed    : 4/16/2015 3:55:06 PM by ZHOUTING
                      (modified after loading)
    Analysis Method : C:\HPCHEM\2\DATA\ZRONG\ZRONG-II-85.D\DA.M (MICHAEL.M)
    Last changed    : 1/28/2017 2:11:19 PM by GZ
                      (modified after loading)
    Method Info     : STANDARD FLAVANONE IA

    Sample Info     : CHIRALCEL IA
                      90:10 Hex:IPA
                      1 ml/min
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.376 MM    0.2696 1950.49011  120.55746  50.1358
       2  13.099 MM    0.3038 1939.92041  106.42841  49.8642

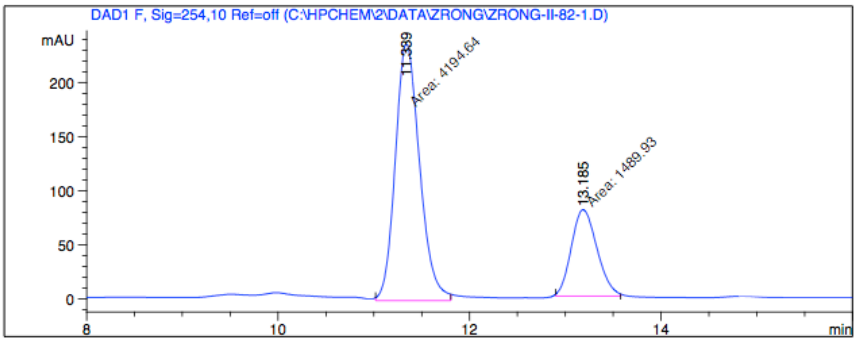
    Totals :                  3890.41052  226.98586
```

HPLC analysis of enantioenriched **10f**.

```
Data File C:\HPCHEM\2\DATA\ZRONG\ZRONG-II-82-1.D
Sample Name: ZRONG-II-82-1

    ======================================================================
    Acq. Operator   : Zhouting
    Acq. Instrument : AG1200HPLC                      Location : Vial 71
    Injection Date  : 4/19/2015 5:07:38 PM
                                                    Inj Volume : 5 µl
    Acq. Method     : C:\HPCHEM\2\METHODS\JAVI.M
    Last changed    : 4/19/2015 4:54:16 PM by Javi
                      (modified after loading)
    Analysis Method : C:\HPCHEM\2\DATA\ZRONG\ZRONG-II-82-1.D\DA.M (JAVI.M)
    Last changed    : 1/28/2017 2:18:42 PM by GZ
                      (modified after loading)
    Method Info     : STANDARD FLAVANONE IA

    Sample Info     : CHIRALCEL IA
                      90:10 Hex:IPA
                      1 ml/min
```

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    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.339 MM    0.2942 4194.64258  237.66092  73.7900
       2  13.185 MM    0.3105 1489.92896   79.96814  26.2100

    Totals :                  5684.57153  317.62906
```

5. Crystal Data

Compound 10f

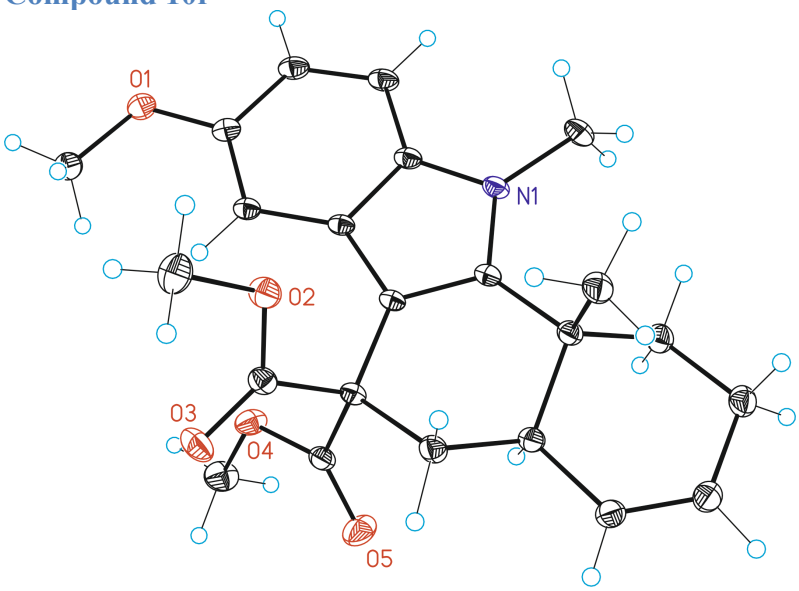

Table 1. Crystal data and structure refinement for mo_zrii7.

Identification code	mo_zrii7	
Empirical formula	C23 H27 N O5	
Formula weight	397.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.8767(14)Å	a= 90°.
	b = 23.638(3)Å	b = 102.363(4)°.
	c = 8.6175(12)Å	g = 90°.
Volume	1965.2(5) $Å^3$	
Z	4	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	848	
Crystal size	0.20 x 0.08 x 0.04 mm^3	
Theta range for data collection	1.723 to 33.188°.	
Index ranges	-15<=h<=15,-36<=k<=36,-13<=l<=12	
Reflections collected	59094	
Independent reflections	7505[R(int) = 0.0271]	
Completeness to theta =33.188°	99.8%	
Absorption correction	Empirical	

Max. and min. transmission	0.996 and 0.766
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7505/ 0/ 267
Goodness-of-fit on F^2	1.127
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1255
R indices (all data)	R1 = 0.0530, wR2 = 0.1284
Largest diff. peak and hole	0.629 and -0.338 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for mo_zrii7.

Bond lengths----	
N1-C1	1.3850(13)
N1-C16	1.3877(12)
N1-C17	1.4571(13)
O1-C4	1.3748(12)
O1-C18	1.4229(13)
O2-C21	1.3338(12)
O2-C22	1.4460(13)
O3-C21	1.2098(12)
O4-C19	1.3390(12)
O4-C20	1.4461(13)
O5-C19	1.2037(12)
C1-C2	1.4012(13)
C1-C6	1.4110(13)
C2-C3	1.3786(15)
C3-C4	1.4110(14)
C4-C5	1.3862(13)
C5-C6	1.4121(13)
C6-C7	1.4361(12)
C7-C16	1.3841(13)
C7-C8	1.5127(12)
C8-C21	1.5279(13)
C8-C19	1.5390(13)
C8-C9	1.5490(13)
C9-C10	1.5252(14)
C10-C11	1.5066(14)
C10-C15	1.5491(13)
C11-C12	1.3343(14)

C12-C13	1.4994(15)
C13-C14	1.5340(15)
C14-C15	1.5469(14)
C15-C16	1.5104(13)
C15-C23	1.5485(14)

Angles----------

C1-N1-C16	108.44(8)
C1-N1-C17	122.56(8)
C16-N1-C17	129.00(9)
C4-O1-C18	116.95(8)
C21-O2-C22	114.88(8)
C19-O4-C20	115.16(8)
N1-C1-C2	129.34(9)
N1-C1-C6	108.72(8)
C2-C1-C6	121.93(9)
C3-C2-C1	117.57(9)
C2-C3-C4	121.34(9)
O1-C4-C5	124.60(9)
O1-C4-C3	113.94(8)
C5-C4-C3	121.46(9)
C4-C5-C6	117.99(8)
C1-C6-C5	119.67(8)
C1-C6-C7	106.16(8)
C5-C6-C7	134.15(8)
C16-C7-C6	107.67(8)
C16-C7-C8	123.98(8)
C6-C7-C8	128.29(8)
C7-C8-C21	113.76(7)
C7-C8-C19	110.59(7)
C21-C8-C19	107.39(7)
C7-C8-C9	110.43(7)
C21-C8-C9	105.34(7)
C19-C8-C9	109.10(7)
C10-C9-C8	110.29(8)
C11-C10-C9	113.31(8)
C11-C10-C15	112.27(8)
C9-C10-C15	112.36(8)

C12-C11-C10	122.24(9)
C11-C12-C13	122.75(9)
C12-C13-C14	113.29(8)
C13-C14-C15	111.47(8)
C16-C15-C14	115.17(8)
C16-C15-C23	107.98(8)
C14-C15-C23	110.55(8)
C16-C15-C10	105.61(7)
C14-C15-C10	105.58(7)
C23-C15-C10	111.89(8)
C7-C16-N1	108.99(8)
C7-C16-C15	124.70(8)
N1-C16-C15	125.98(8)
O5-C19-O4	123.32(9)
O5-C19-C8	124.67(9)
O4-C19-C8	112.00(8)
O3-C21-O2	124.11(9)
O3-C21-C8	123.35(9)
O2-C21-C8	112.39(8)

Table 3. Torsion angles [°] for mo_zrii7.

C16-N1-C1-C2	-179.11(10)
C17-N1-C1-C2	1.55(16)
C16-N1-C1-C6	1.19(10)
C17-N1-C1-C6	-178.15(9)
N1-C1-C2-C3	-178.90(9)
C6-C1-C2-C3	0.77(14)
C1-C2-C3-C4	0.88(15)
C18-O1-C4-C5	0.30(14)
C18-O1-C4-C3	-179.68(9)
C2-C3-C4-O1	178.84(9)
C2-C3-C4-C5	-1.14(15)
O1-C4-C5-C6	179.75(9)
C3-C4-C5-C6	-0.27(14)
N1-C1-C6-C5	177.55(8)
C2-C1-C6-C5	-2.18(14)

N1-C1-C6-C7	-1.04(10)
C2-C1-C6-C7	179.23(9)
C4-C5-C6-C1	1.87(13)
C4-C5-C6-C7	179.99(9)
C1-C6-C7-C16	0.51(10)
C5-C6-C7-C16	-177.79(10)
C1-C6-C7-C8	177.88(9)
C5-C6-C7-C8	-0.42(17)
C16-C7-C8-C21	129.70(9)
C6-C7-C8-C21	-47.28(12)
C16-C7-C8-C19	-109.36(10)
C6-C7-C8-C19	73.66(11)
C16-C7-C8-C9	11.50(12)
C6-C7-C8-C9	-165.47(9)
C7-C8-C9-C10	-40.96(10)
C21-C8-C9-C10	-164.20(8)
C19-C8-C9-C10	80.78(9)
C8-C9-C10-C11	-164.69(8)
C8-C9-C10-C15	66.75(10)
C9-C10-C11-C12	-155.31(10)
C15-C10-C11-C12	-26.70(13)
C10-C11-C12-C13	4.21(16)
C11-C12-C13-C14	-12.11(14)
C12-C13-C14-C15	42.71(11)
C13-C14-C15-C16	-179.11(8)
C13-C14-C15-C23	58.16(10)
C13-C14-C15-C10	-63.03(10)
C11-C10-C15-C16	176.39(8)
C9-C10-C15-C16	-54.50(10)
C11-C10-C15-C14	53.95(10)
C9-C10-C15-C14	-176.94(8)
C11-C10-C15-C23	-66.37(10)
C9-C10-C15-C23	62.74(10)
C6-C7-C16-N1	0.21(10)
C8-C7-C16-N1	-177.31(8)
C6-C7-C16-C15	174.01(8)
C8-C7-C16-C15	-3.50(14)
C1-N1-C16-C7	-0.86(11)

C17-N1-C16-C7	178.42(10)
C1-N1-C16-C15	-174.57(8)
C17-N1-C16-C15	4.72(16)
C14-C15-C16-C7	139.83(9)
C23-C15-C16-C7	-96.09(10)
C10-C15-C16-C7	23.75(12)
C14-C15-C16-N1	-47.42(13)
C23-C15-C16-N1	76.66(11)
C10-C15-C16-N1	-163.49(9)
C20-O4-C19-O5	2.32(15)
C20-O4-C19-C8	-178.55(9)
C7-C8-C19-O5	112.58(11)
C21-C8-C19-O5	-122.77(11)
C9-C8-C19-O5	-9.07(14)
C7-C8-C19-O4	-66.53(10)
C21-C8-C19-O4	58.12(10)
C9-C8-C19-O4	171.82(8)
C22-O2-C21-O3	-2.27(14)
C22-O2-C21-C8	-177.90(8)
C7-C8-C21-O3	152.50(9)
C19-C8-C21-O3	29.79(12)
C9-C8-C21-O3	-86.41(11)
C7-C8-C21-O2	-31.83(11)
C19-C8-C21-O2	-154.55(8)
C9-C8-C21-O2	89.26(9)

Compound 10h

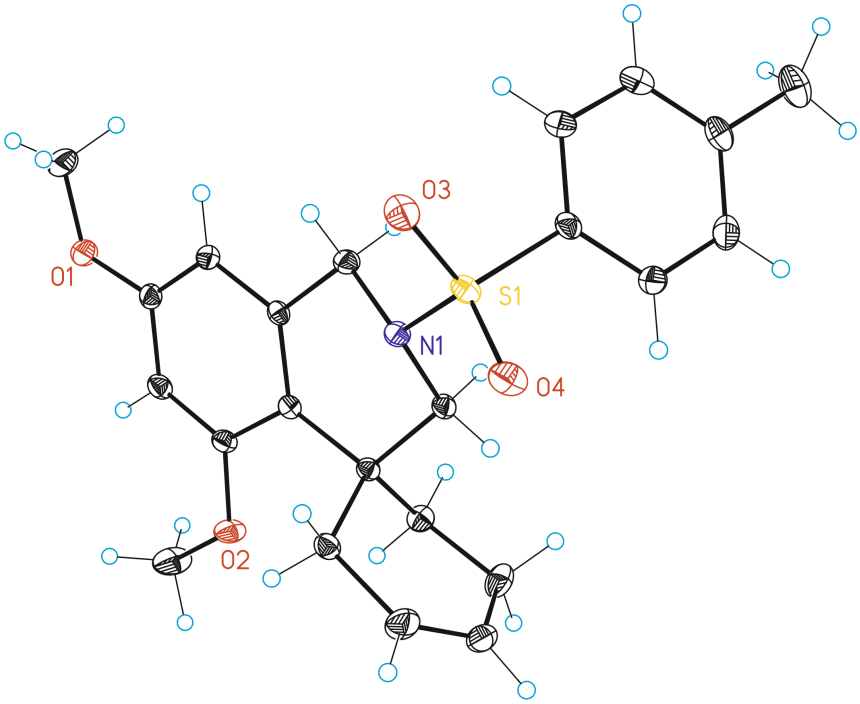

Table 1. Crystal data and structure refinement for mo_zri185_0m.

Identification code	mo_zri185_0m	
Empirical formula	C23 H27 N O4 S	
Formula weight	413.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.4223(6)Å	a= 90°.
	b = 20.6490(13)Å	b = 105.9641(19)°.
	c = 10.9082(8)Å	g = 90°.
Volume	2040.5(2) Å^3	
Z	4	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.189 mm^{-1}	
F(000)	880	
Crystal size	0.35 x 0.35 x 0.30 mm^3	
Theta range for data collection	1.972 to 32.427°.	
Index ranges	-13<=h<=8,-15<=k<=31,-14<=l<=16	
Reflections collected	14366	
Independent reflections	6481[R(int) = 0.0237]	

Completeness to theta =32.427°	88.0%
Absorption correction	Empirical
Max. and min. transmission	0.946 and 0.885
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6481/ 0/ 269
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1059
R indices (all data)	R1 = 0.0510, wR2 = 0.1111
Largest diff. peak and hole	0.428 and -0.493 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for mo_zri185_0m.

Bond lengths----	
S1-O4	1.4318(10)
S1-O3	1.4357(9)
S1-N1	1.6377(10)
S1-C17	1.7598(12)
N1-C8	1.4650(15)
N1-C7	1.4685(14)
O1-C11	1.3588(14)
O1-C15	1.4224(16)
O2-C13	1.3713(14)
O2-C16	1.4245(15)
C1-C14	1.5264(15)
C1-C7	1.5397(15)
C1-C2	1.5453(16)
C1-C6	1.5453(16)
C2-C3	1.5007(18)
C3-C4	1.3664(19)
C4-C5	1.4554(19)
C5-C6	1.5166(17)
C8-C9	1.5117(15)
C9-C14	1.3960(15)
C9-C10	1.3994(16)
C10-C11	1.3832(16)
C11-C12	1.3965(16)
C12-C13	1.3802(16)
C13-C14	1.4213(15)

C17-C18	1.3919(17)
C17-C22	1.3938(16)
C18-C19	1.3875(18)
C19-C20	1.3952(19)
C20-C21	1.3936(19)
C20-C23	1.5065(19)
C21-C22	1.3859(18)

Angles----------

O4-S1-O3	119.61(6)
O4-S1-N1	106.97(5)
O3-S1-N1	106.90(5)
O4-S1-C17	107.64(6)
O3-S1-C17	108.29(6)
N1-S1-C17	106.78(5)
C8-N1-C7	110.10(9)
C8-N1-S1	116.60(7)
C7-N1-S1	116.84(8)
C11-O1-C15	116.82(10)
C13-O2-C16	117.33(10)
C14-C1-C7	109.36(9)
C14-C1-C2	110.41(9)
C7-C1-C2	109.00(9)
C14-C1-C6	112.69(9)
C7-C1-C6	105.86(9)
C2-C1-C6	109.37(9)
C3-C2-C1	112.93(10)
C4-C3-C2	121.84(12)
C3-C4-C5	123.30(12)
C4-C5-C6	115.43(11)
C5-C6-C1	111.92(10)
N1-C7-C1	110.68(9)
N1-C8-C9	109.63(9)
C14-C9-C10	122.90(10)
C14-C9-C8	121.78(10)
C10-C9-C8	115.32(9)
C11-C10-C9	118.99(10)
O1-C11-C10	125.26(11)

O1-C11-C12	114.52(10)
C10-C11-C12	120.21(11)
C13-C12-C11	119.91(10)
O2-C13-C12	121.53(10)
O2-C13-C14	116.58(10)
C12-C13-C14	121.88(10)
C9-C14-C13	115.99(10)
C9-C14-C1	121.90(10)
C13-C14-C1	122.07(10)
C18-C17-C22	120.40(11)
C18-C17-S1	119.29(9)
C22-C17-S1	120.25(9)
C19-C18-C17	119.39(11)
C18-C19-C20	121.20(12)
C21-C20-C19	118.34(12)
C21-C20-C23	120.33(12)
C19-C20-C23	121.33(13)
C22-C21-C20	121.40(12)
C21-C22-C17	119.26(12)

Table 3. Torsion angles [°] for mo_zri185_0m.

O4-S1-N1-C8	176.01(8)
O3-S1-N1-C8	46.78(10)
C17-S1-N1-C8	-68.96(9)
O4-S1-N1-C7	-50.82(10)
O3-S1-N1-C7	179.95(8)
C17-S1-N1-C7	64.21(9)
C14-C1-C2-C3	171.69(10)
C7-C1-C2-C3	-68.16(12)
C6-C1-C2-C3	47.14(13)
C1-C2-C3-C4	-20.97(18)
C2-C3-C4-C5	2.2(2)
C3-C4-C5-C6	-11.62(18)
C4-C5-C6-C1	39.40(15)
C14-C1-C6-C5	179.88(10)
C7-C1-C6-C5	60.39(12)

C2-C1-C6-C5	-56.91(13)
C8-N1-C7-C1	-70.83(12)
S1-N1-C7-C1	153.15(8)
C14-C1-C7-N1	45.99(12)
C2-C1-C7-N1	-74.81(11)
C6-C1-C7-N1	167.64(9)
C7-N1-C8-C9	55.82(12)
S1-N1-C8-C9	-168.05(8)
N1-C8-C9-C14	-22.40(15)
N1-C8-C9-C10	158.67(10)
C14-C9-C10-C11	-1.13(17)
C8-C9-C10-C11	177.78(10)
C15-O1-C11-C10	-6.79(18)
C15-O1-C11-C12	171.95(12)
C9-C10-C11-O1	179.97(11)
C9-C10-C11-C12	1.29(17)
O1-C11-C12-C13	-177.64(11)
C10-C11-C12-C13	1.17(18)
C16-O2-C13-C12	5.34(18)
C16-O2-C13-C14	-176.30(12)
C11-C12-C13-O2	174.37(11)
C11-C12-C13-C14	-3.91(18)
C10-C9-C14-C13	-1.41(17)
C8-C9-C14-C13	179.74(10)
C10-C9-C14-C1	-179.23(10)
C8-C9-C14-C1	1.93(17)
O2-C13-C14-C9	-174.41(10)
C12-C13-C14-C9	3.95(17)
O2-C13-C14-C1	3.40(17)
C12-C13-C14-C1	-178.24(11)
C7-C1-C14-C9	-13.22(15)
C2-C1-C14-C9	106.71(12)
C6-C1-C14-C9	-130.66(11)
C7-C1-C14-C13	169.10(10)
C2-C1-C14-C13	-70.97(13)
C6-C1-C14-C13	51.66(14)
O4-S1-C17-C18	28.37(11)
O3-S1-C17-C18	159.00(10)

N1-S1-C17-C18	-86.20(10)
O4-S1-C17-C22	-154.36(10)
O3-S1-C17-C22	-23.73(11)
N1-S1-C17-C22	91.07(10)
C22-C17-C18-C19	0.08(18)
S1-C17-C18-C19	177.35(10)
C17-C18-C19-C20	0.46(19)
C18-C19-C20-C21	-0.25(19)
C18-C19-C20-C23	-179.94(12)
C19-C20-C21-C22	-0.51(19)
C23-C20-C21-C22	179.18(12)
C20-C21-C22-C17	1.04(19)
C18-C17-C22-C21	-0.82(18)
S1-C17-C22-C21	-178.06(9)

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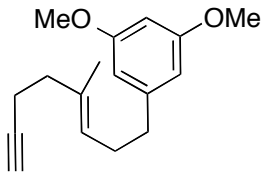
7. ^{1}H NMR and ^{13}C NMR Spectra



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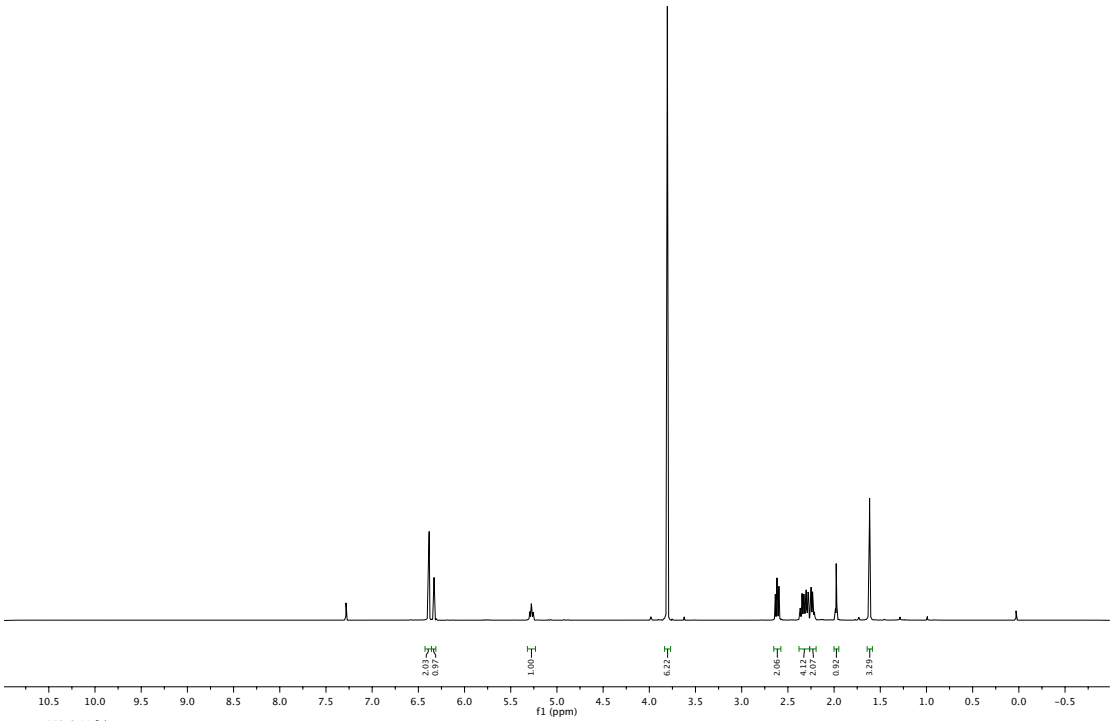

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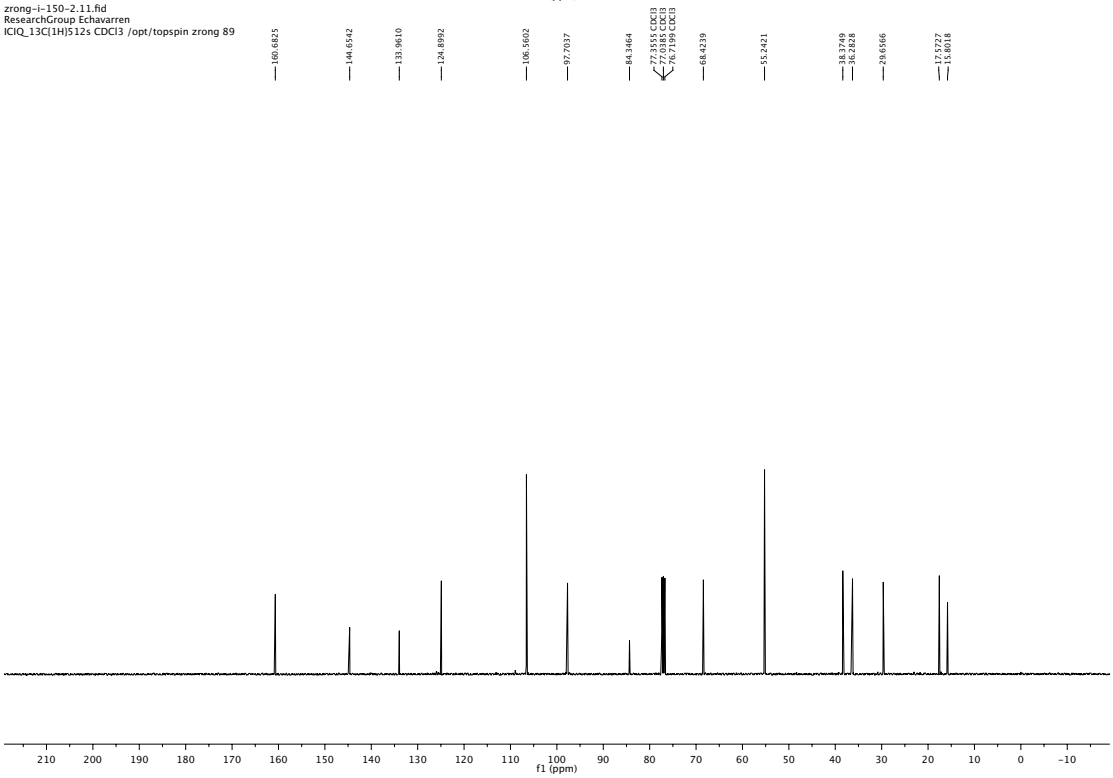

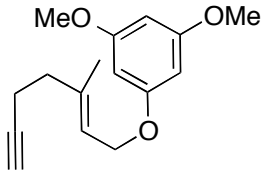

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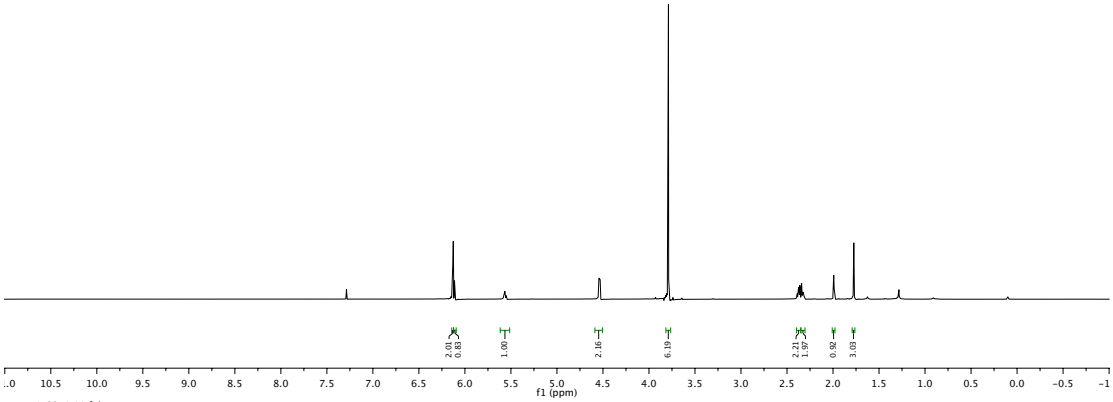

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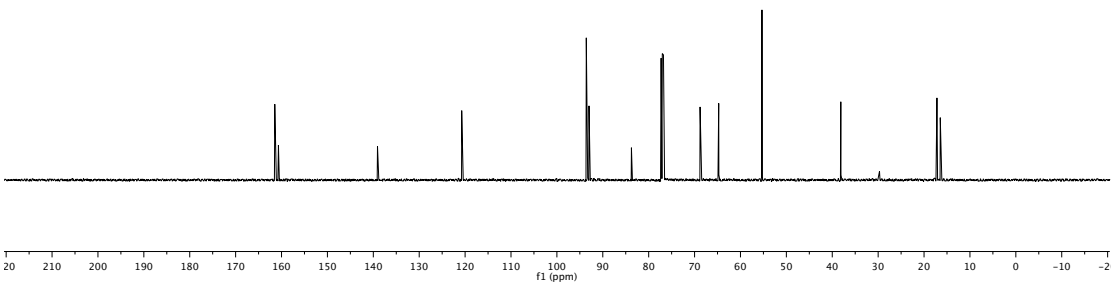

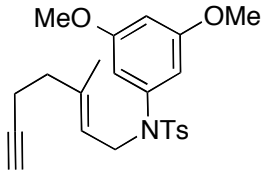

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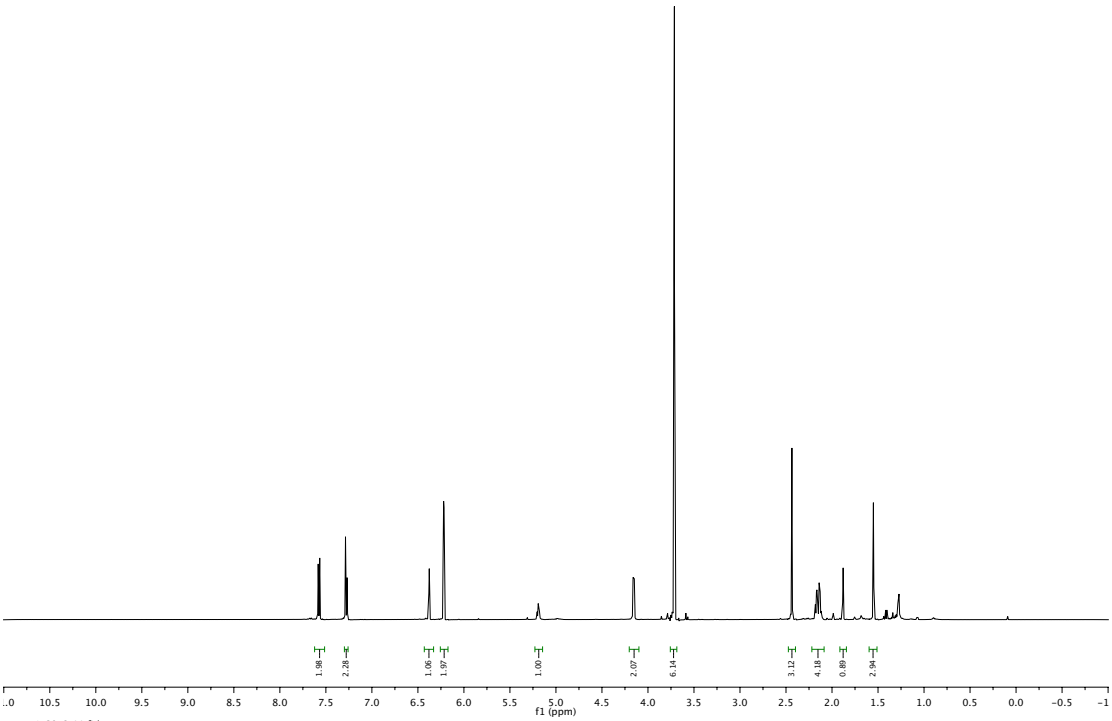

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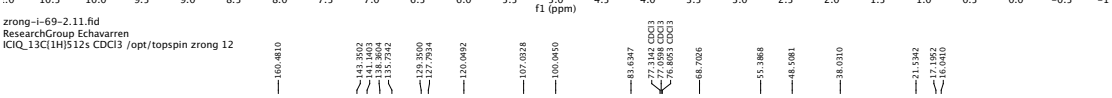

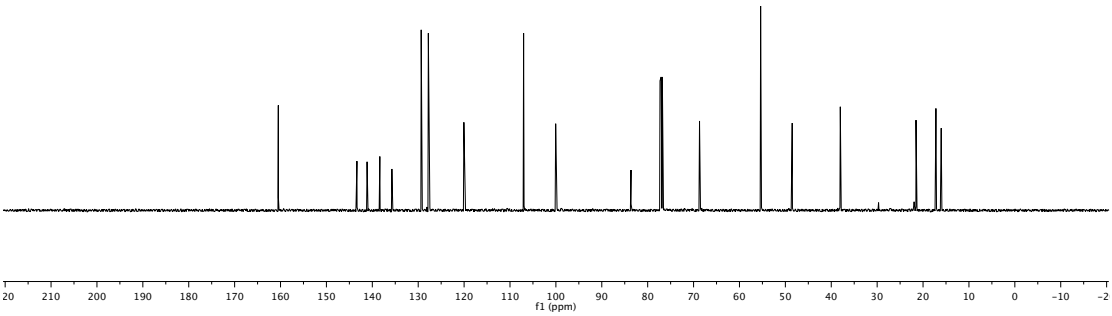

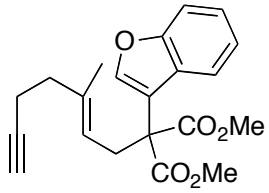

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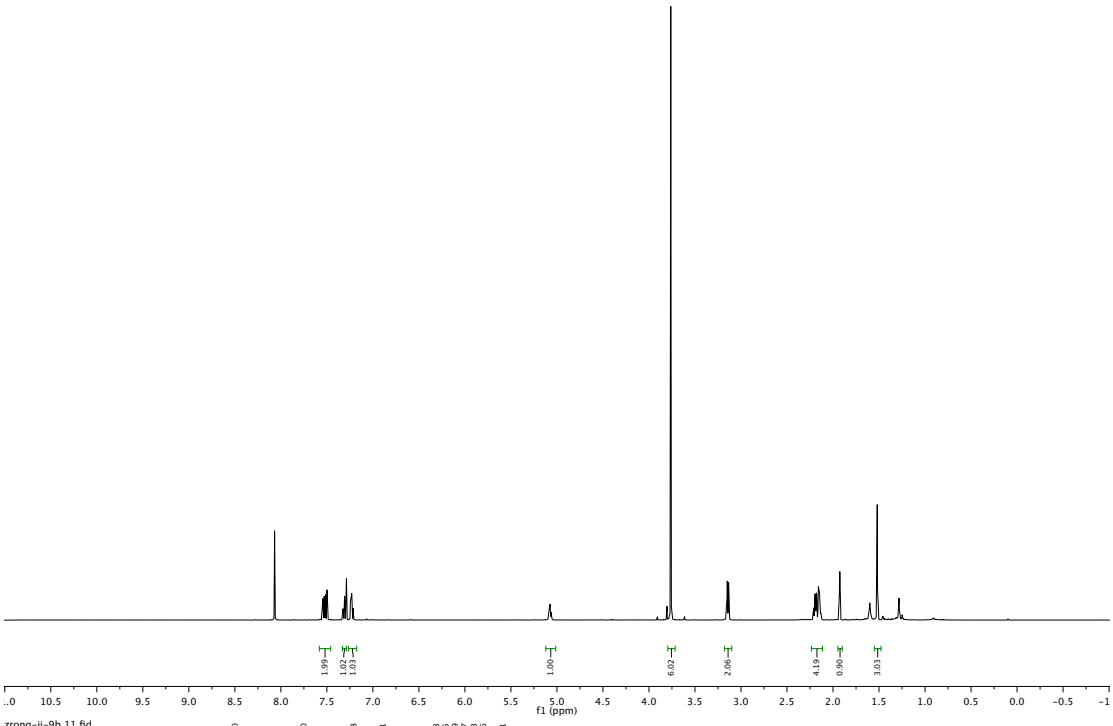

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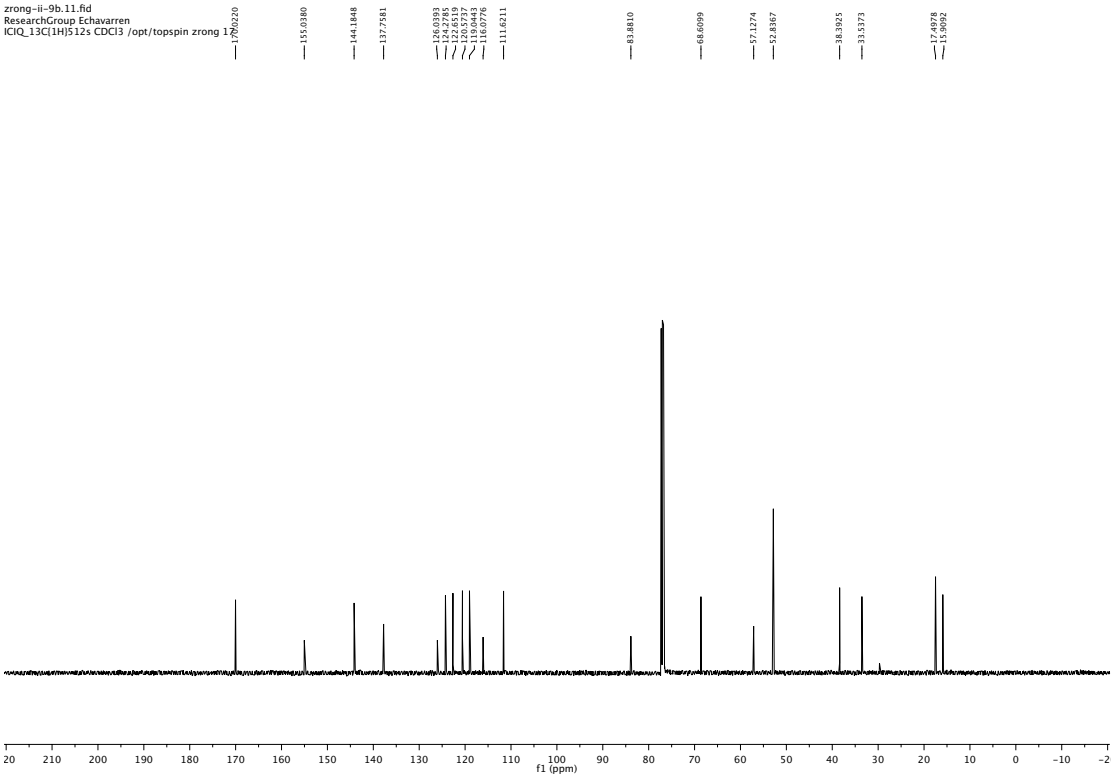

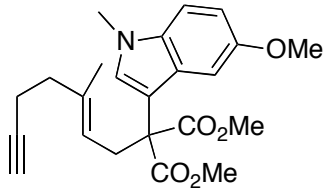

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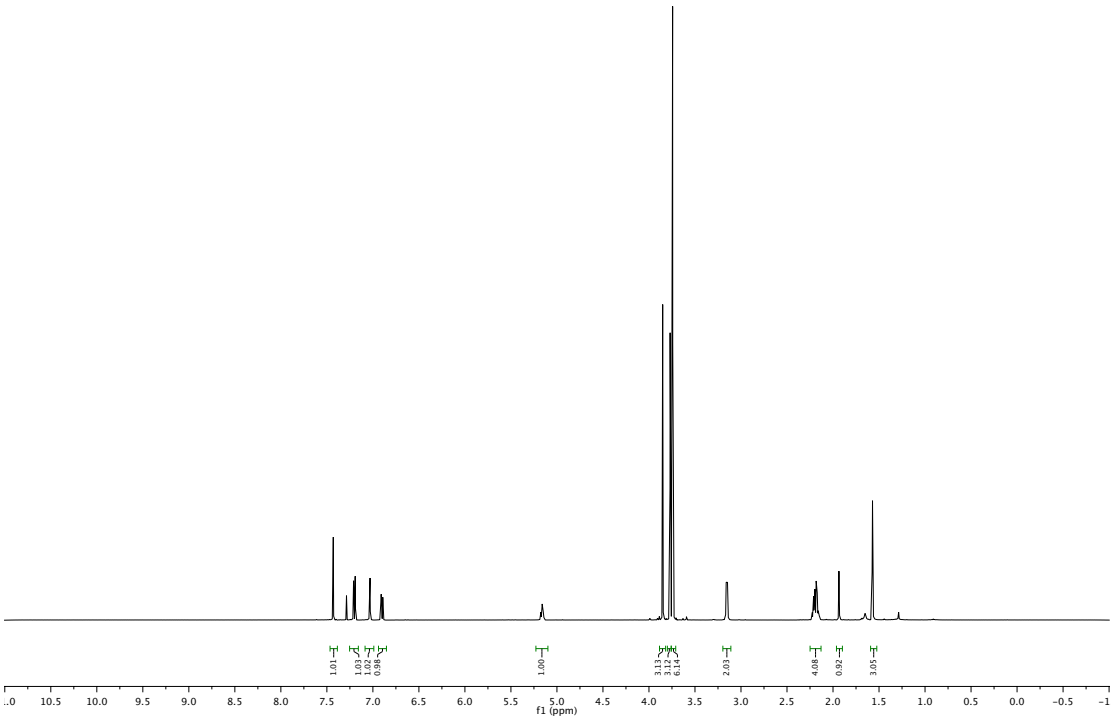
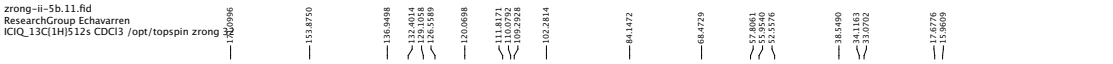
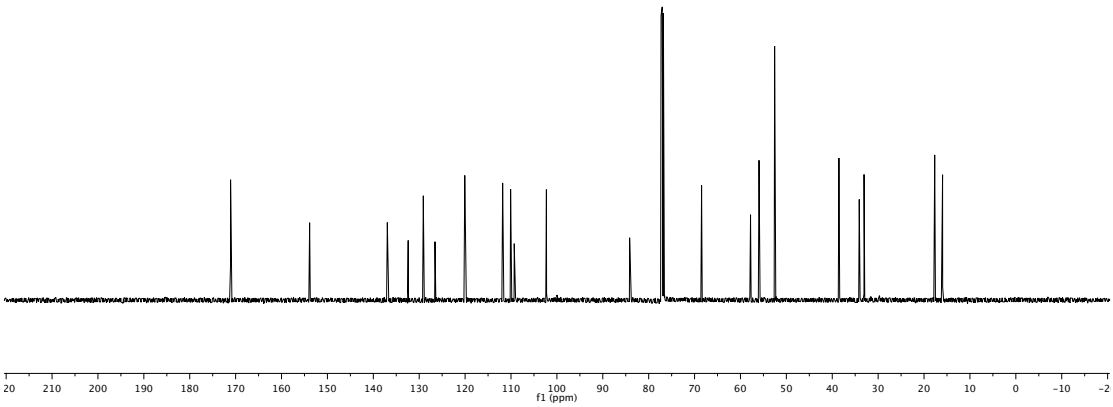
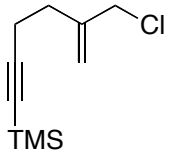
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 32



zrong-ii-5b.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 32

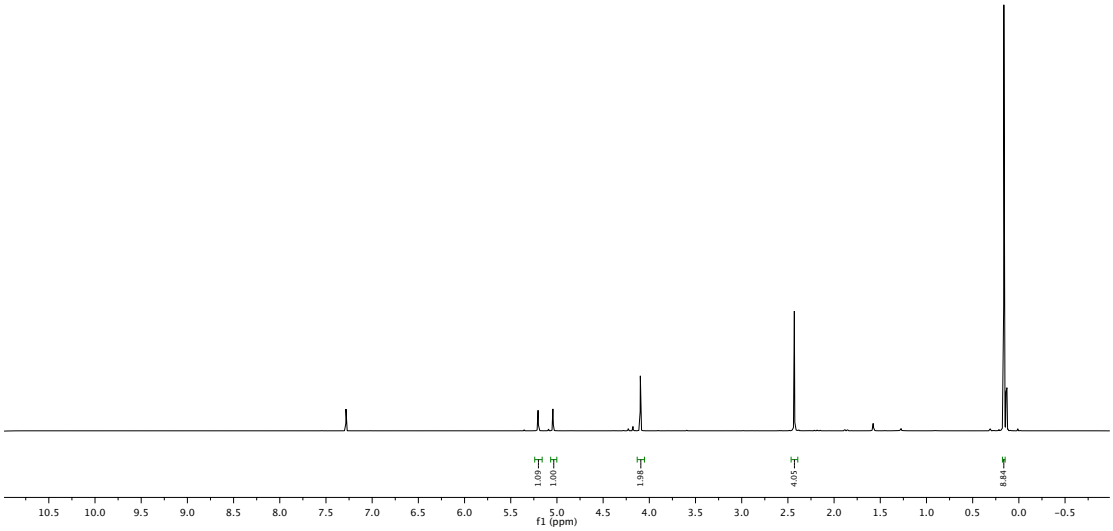




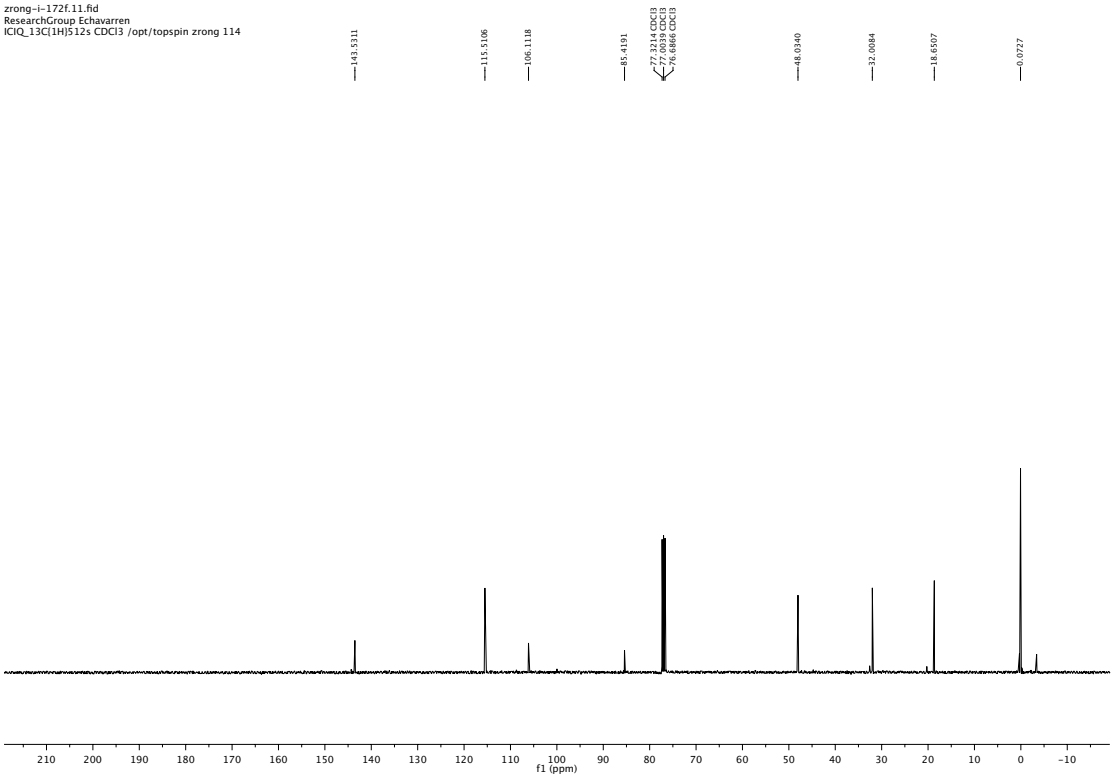


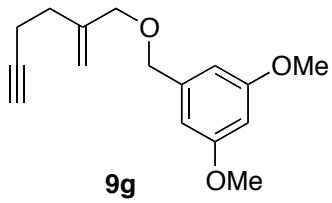
S6

zrong-i-172f.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 114



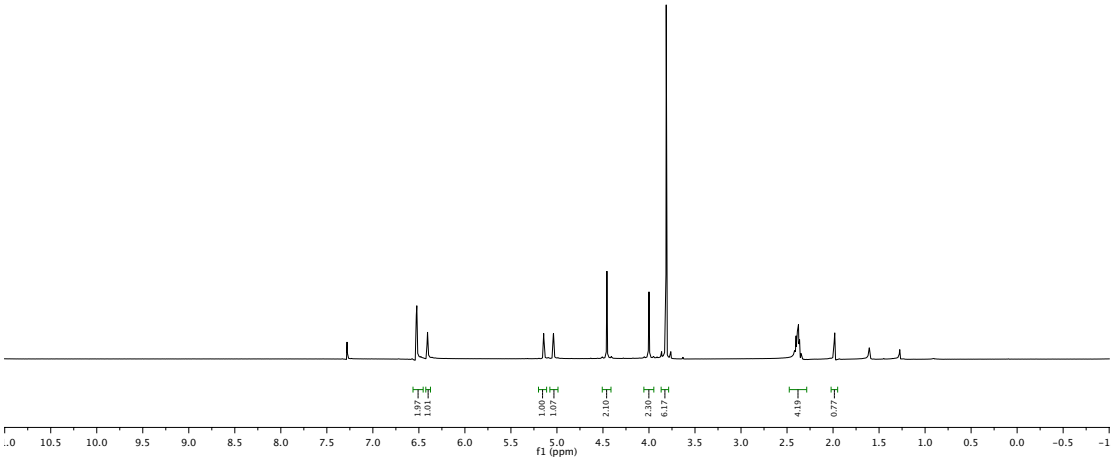
zrong-i-172f.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 114





9g

zrong-i-192.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 23



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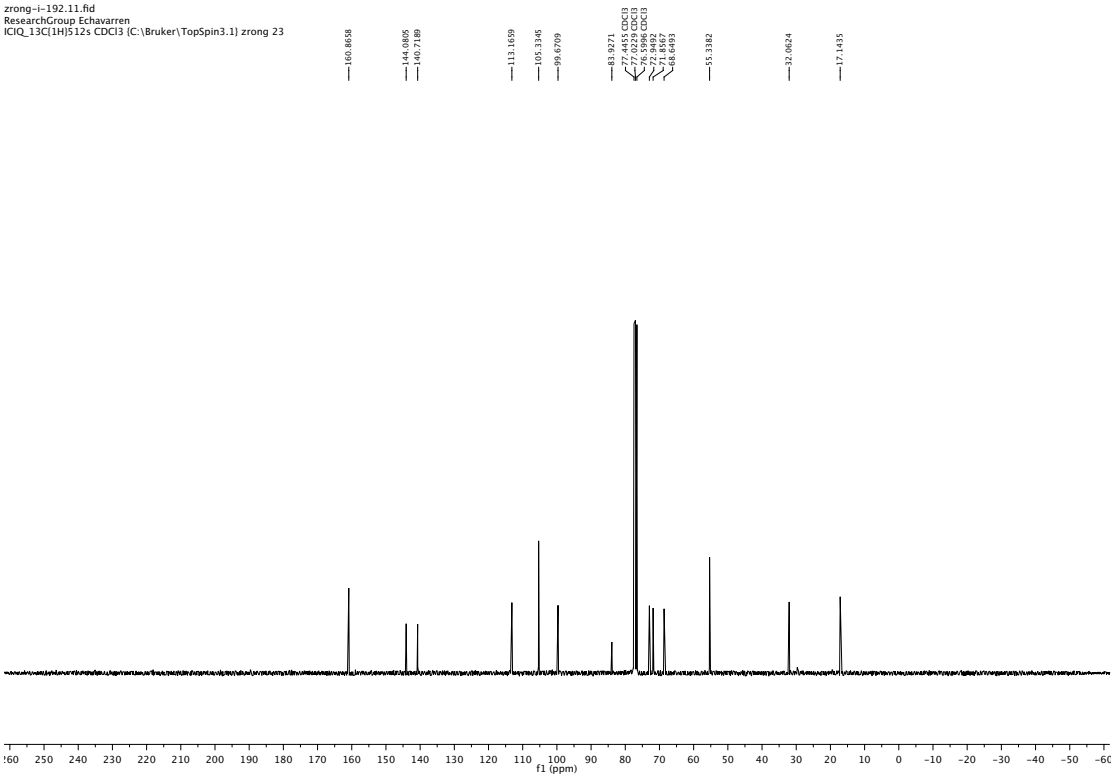
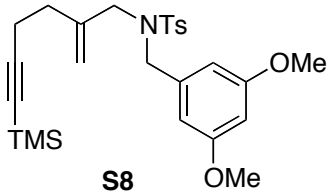
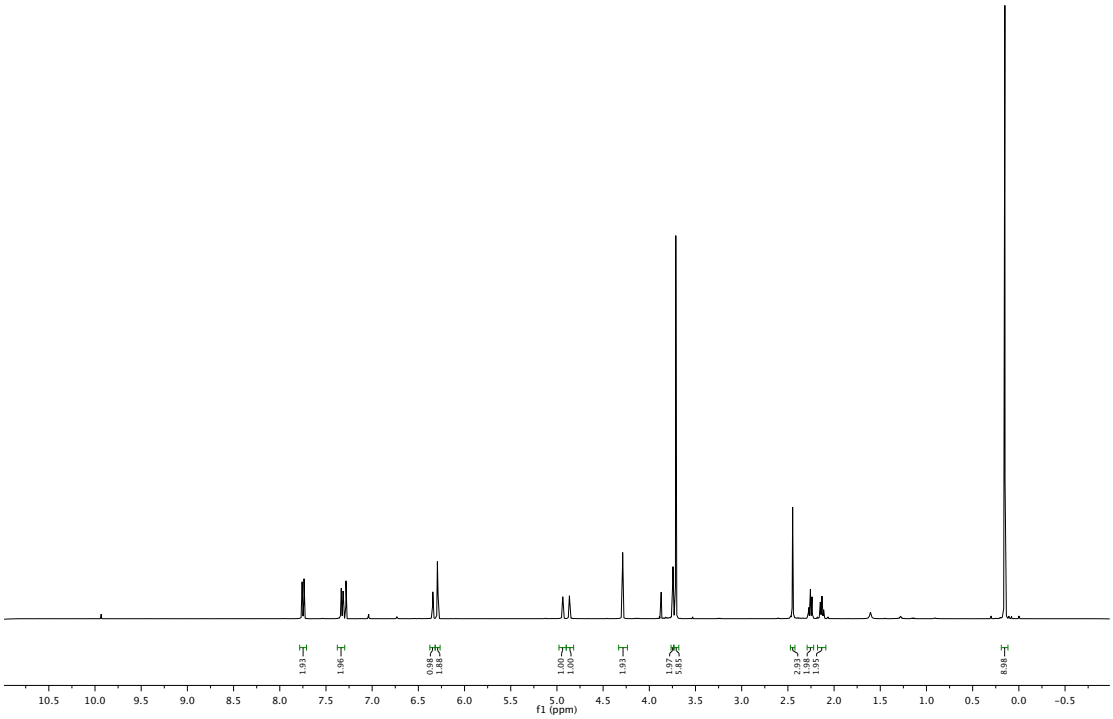
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 {C:\Bruker\TopSpin3.1} zrong 23





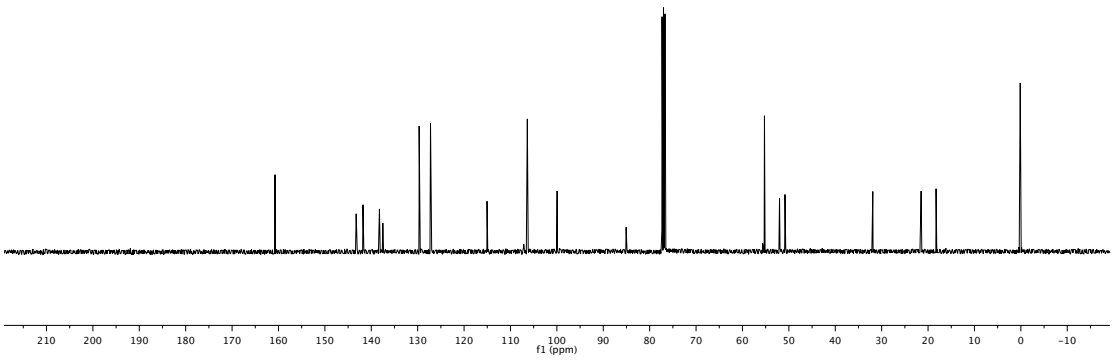
S8

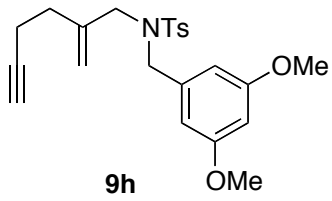
zrong-i-183.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 110



zrong-i-183.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 110

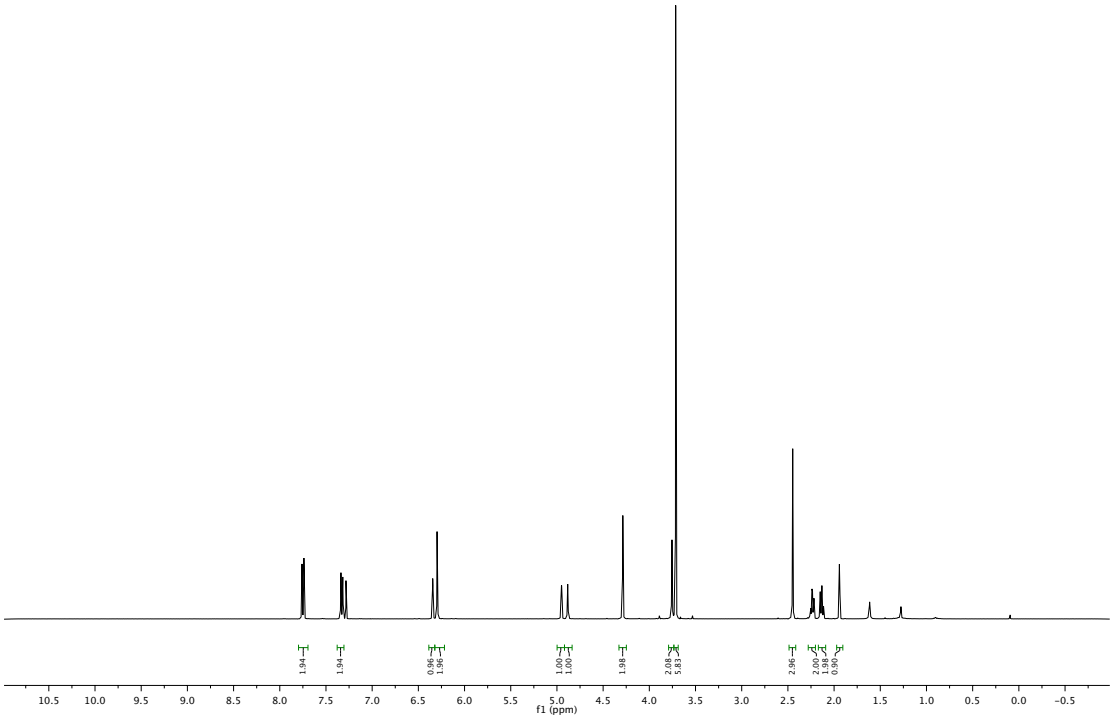
160.7481
143.2557
141.7908
138.2421
137.5046
129.6856
127.2342
115.0514
106.4726
106.3674
99.9448
85.0736
77.3335 CDCl3
77.0157 CDCl3
76.6999 CDCl3
55.2605
52.0104
50.0835
31.9101
21.4950
18.2714
0.1319





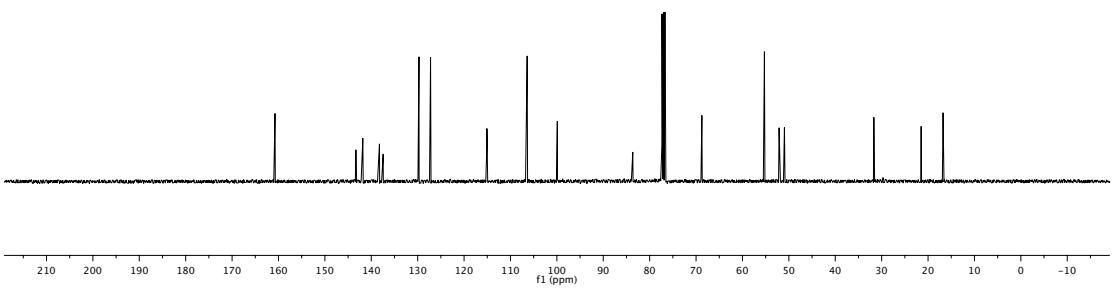
9h

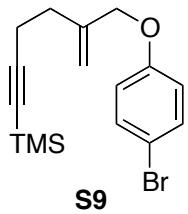
zrong-i-184.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 80



zrong-i-184.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 80

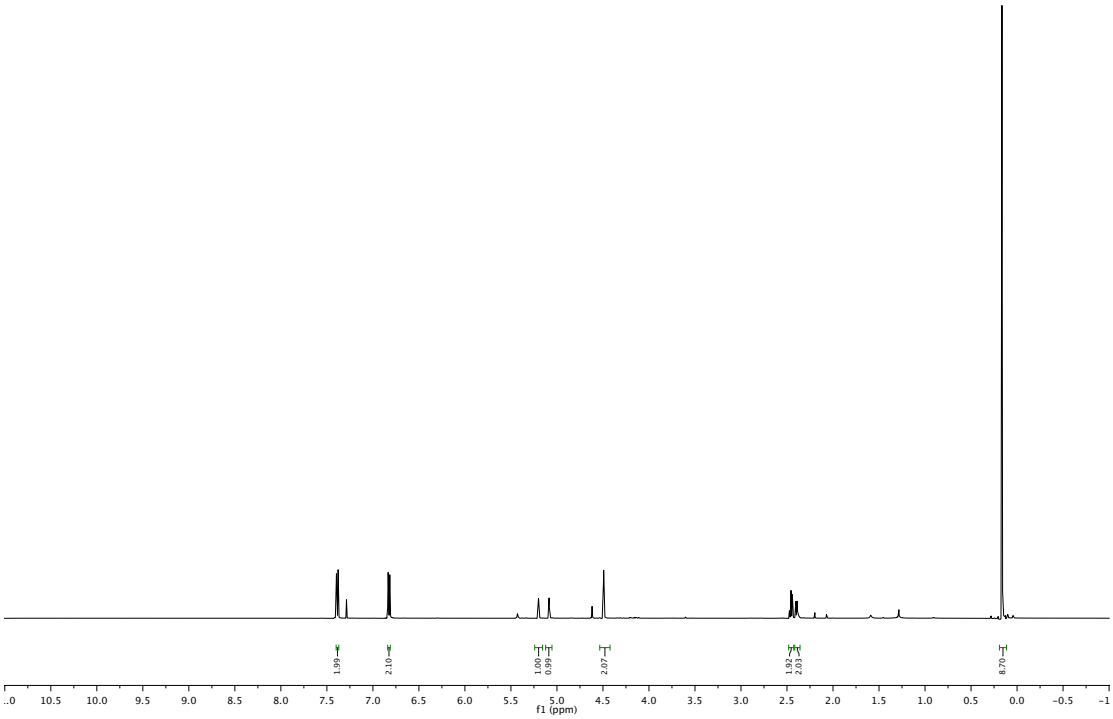
160.7524
143.3145
141.8290
138.2374
137.4389
129.7186
127.2241
115.0754
106.4046
99.9059
83.6395
77.3441 CDCl3
77.0257 CDCl3
76.7080 CDCl3
68.7482
55.2662
52.1064
50.0311
31.6802
21.4909
16.7672





S9

zrong-i--174s.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 18



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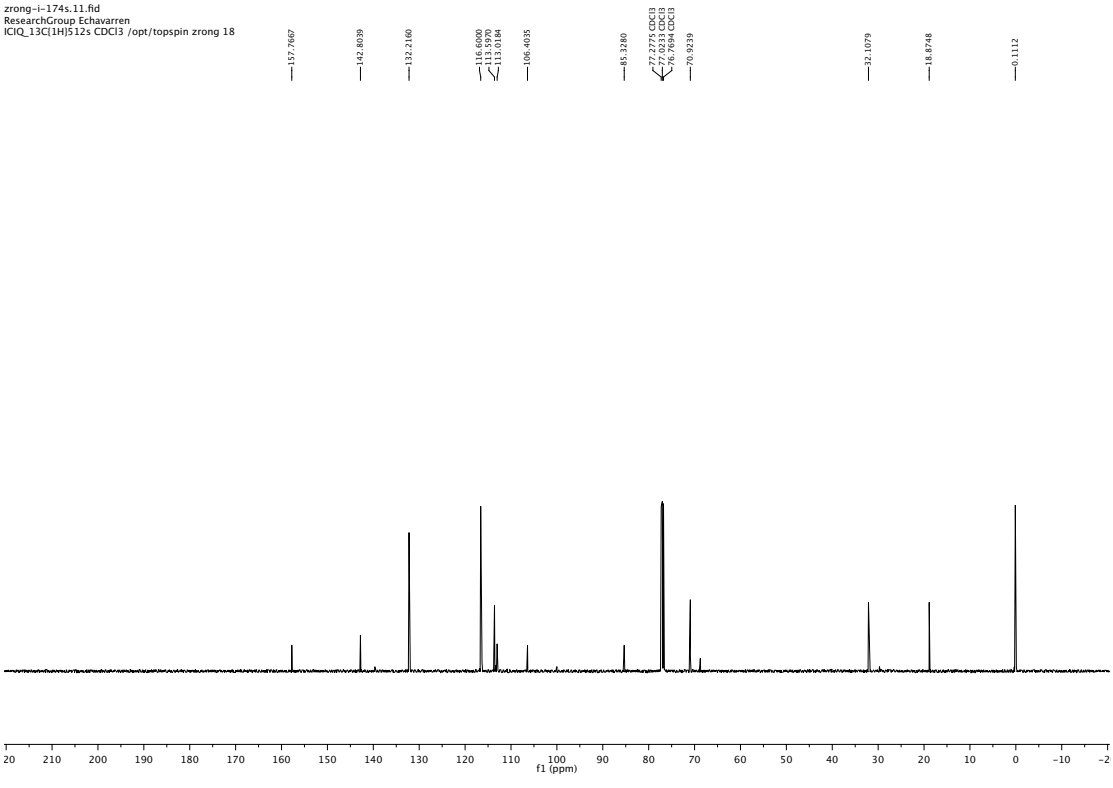
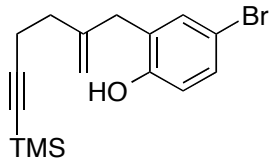
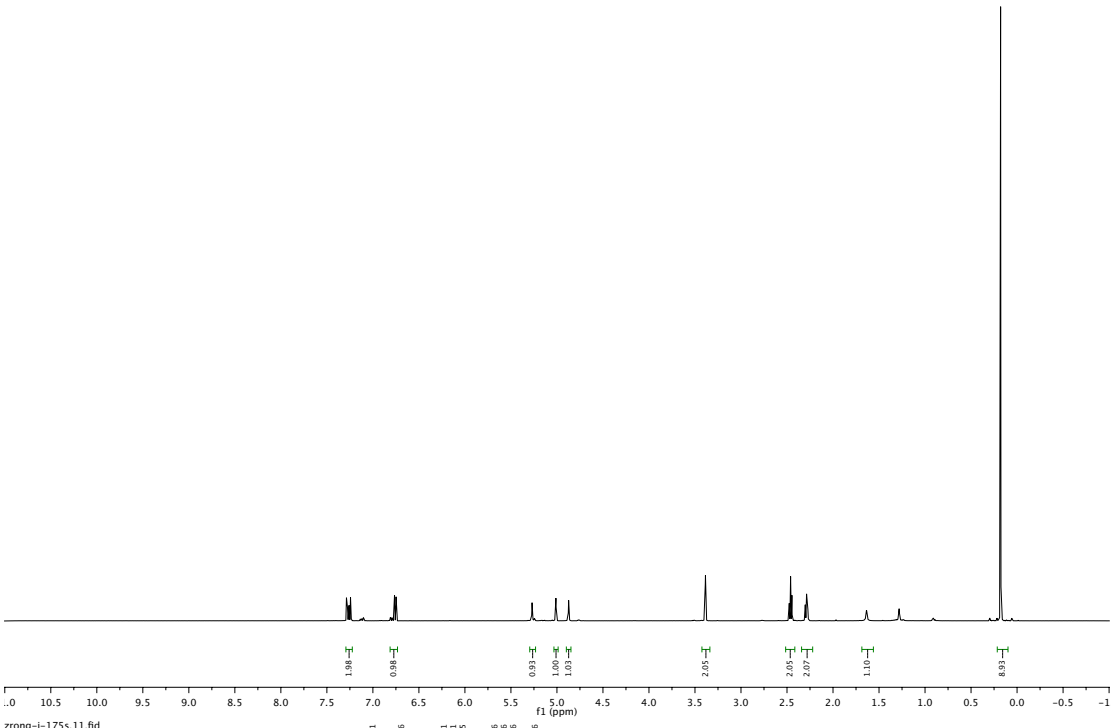
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 18





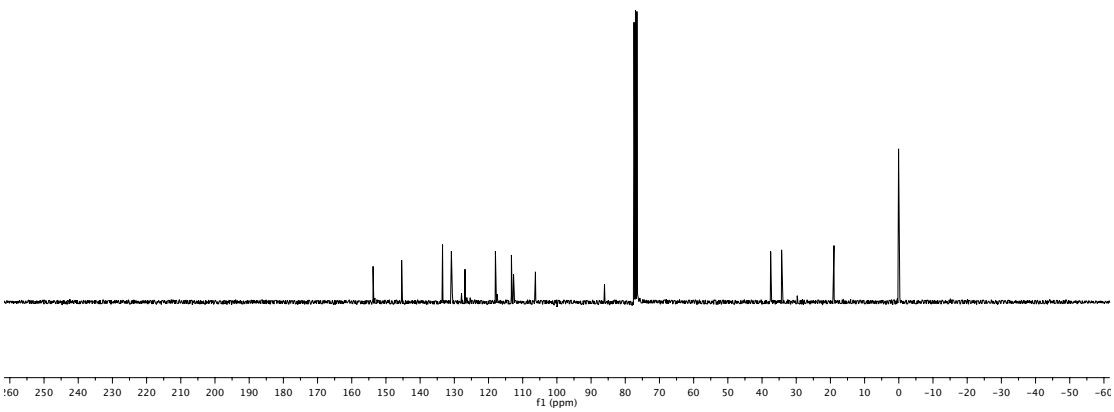
S10

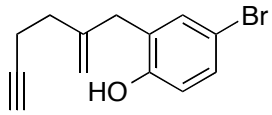
zrong-i-175s.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 52



zrong-i-175s.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 {C:\Bruker\TopSpin3.1} zrong 52

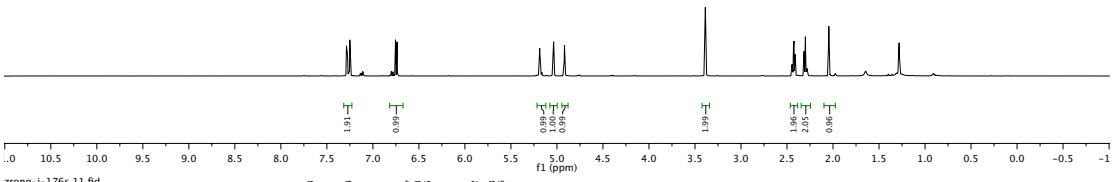
153.7681
145.4026
133.4451
130.8561
126.8745
117.3776
115.1035
112.6796
106.2806
86.0729
37.4803
34.2736
18.9541
0.0645





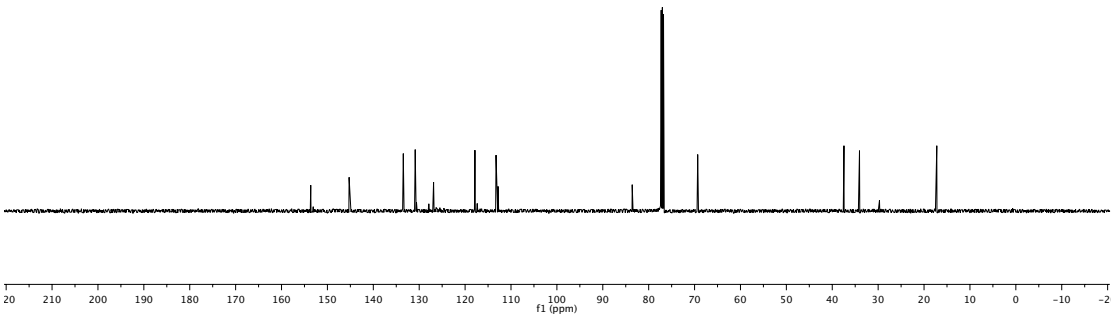
9i

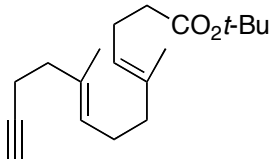
zrong-i-176s.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 15



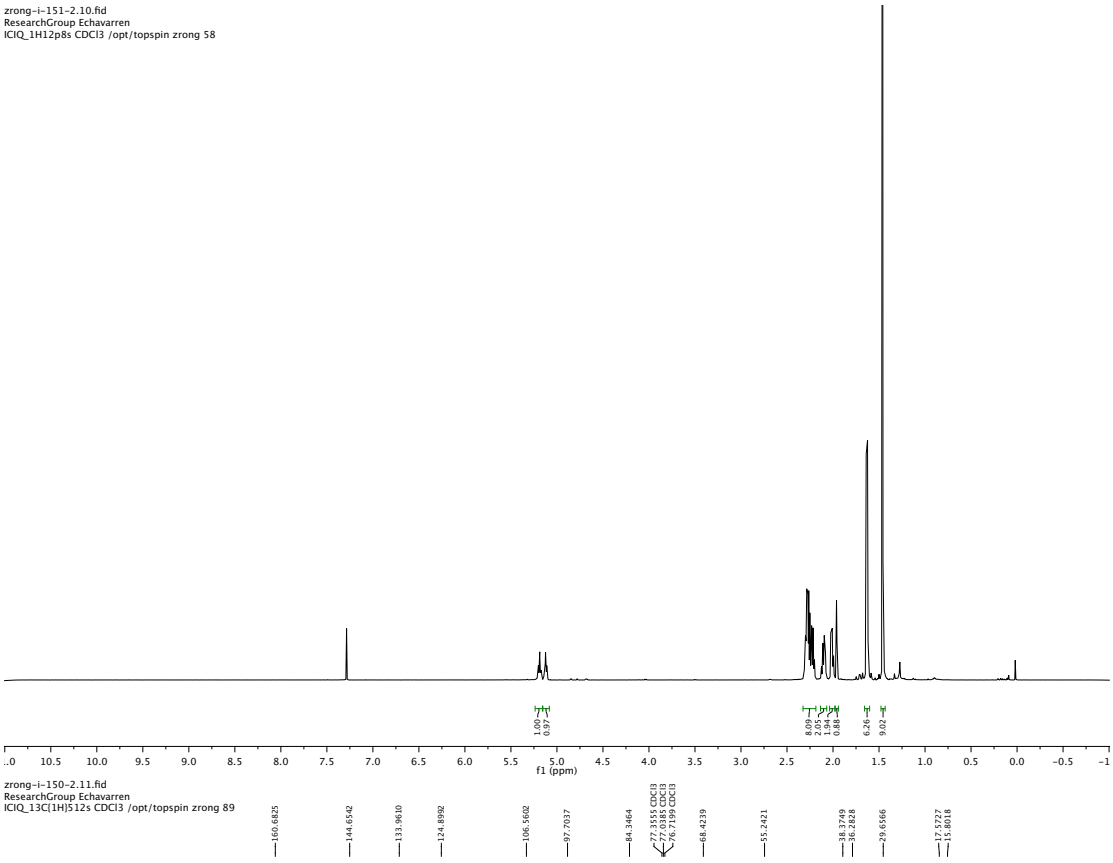
zrong-i-176s.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 15

153.6313
145.2764
133.4687
130.8723
126.8685
117.8582
113.2603
112.8066
83.5905
69.3157
37.4506
34.0670
17.2249




CO2t-Bu

S13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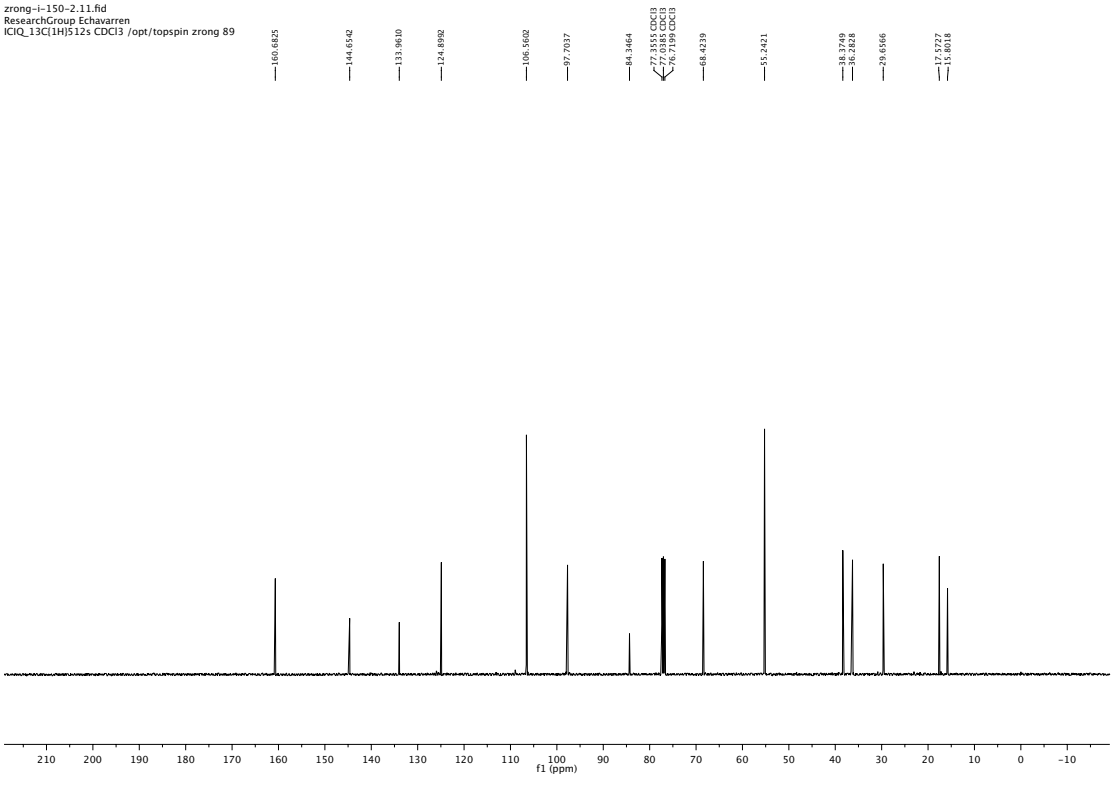
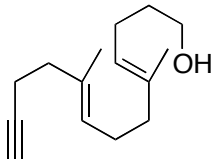
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 58
1.00
0.97
8.09
2.05
1.94
0.88
6.26
9.02
f1 (ppm)


zrong-i-150-2.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 89
160.6825
144.6542
133.9610
124.8992
106.5602
97.7037
84.3464
77.3515 CDCl3
77.0388 CDCl3
76.7189 CDCl3
68.4239
55.2421
38.3749
36.2828
29.6566
17.5727
15.8018
f1 (ppm)



9j

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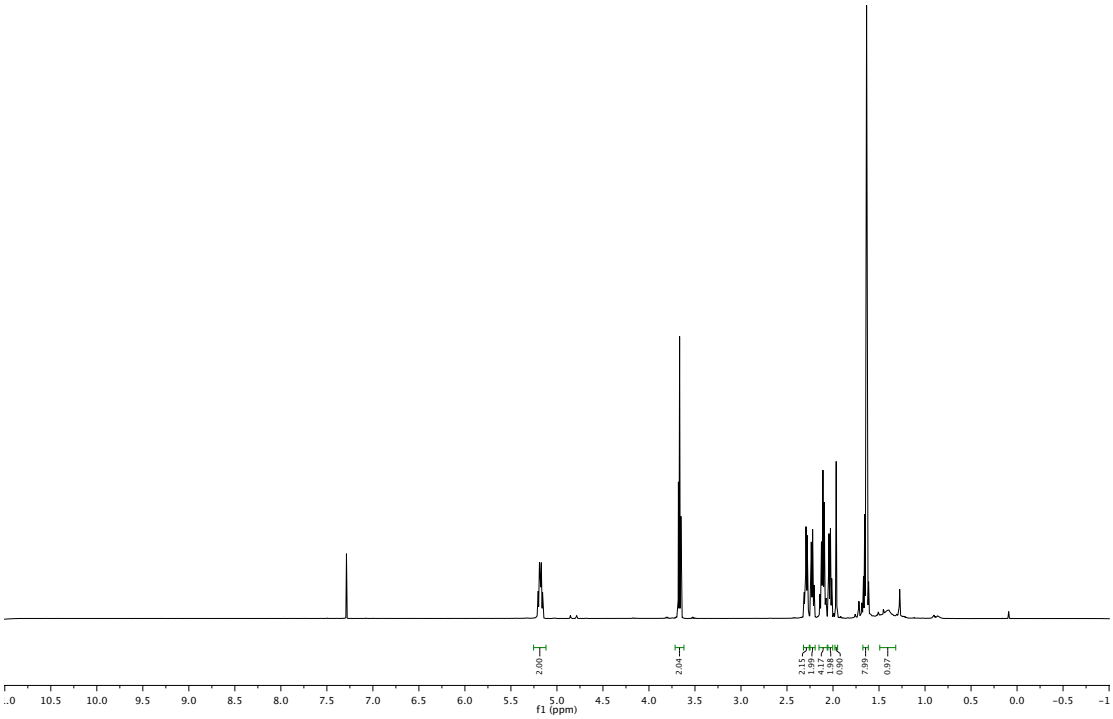
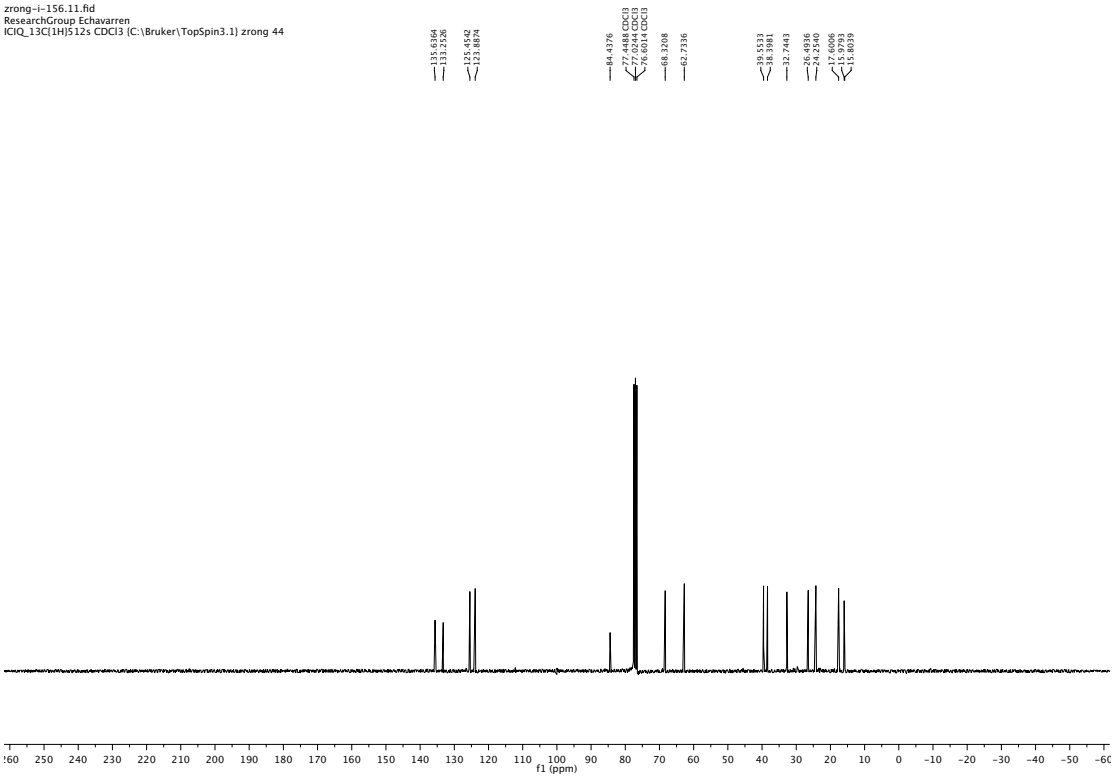
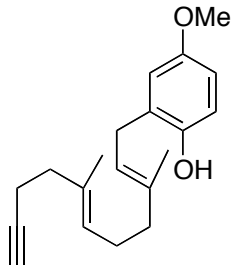
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 44



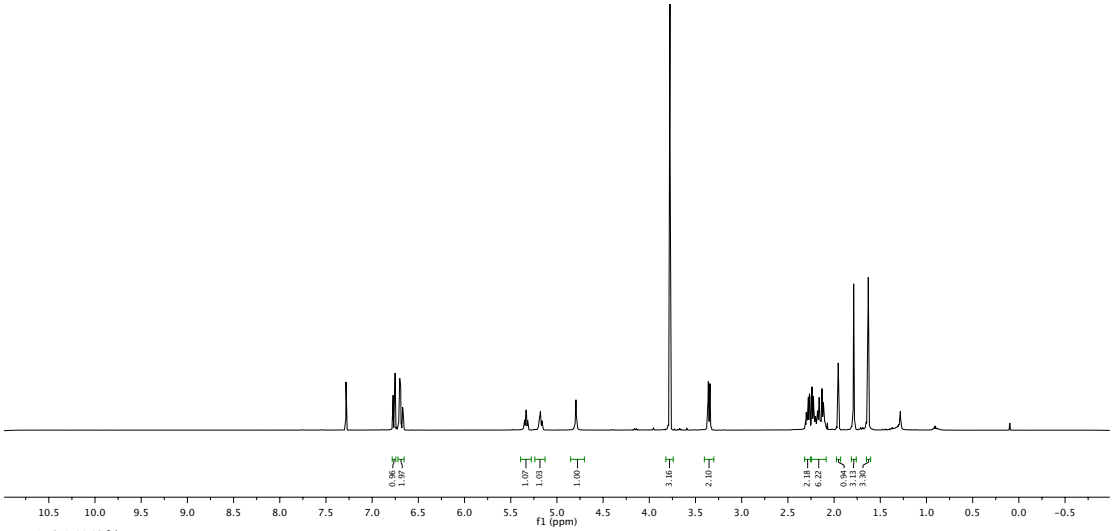
zrong-i-156.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 {C:\Bruker\TopSpin3.1} zrong 44





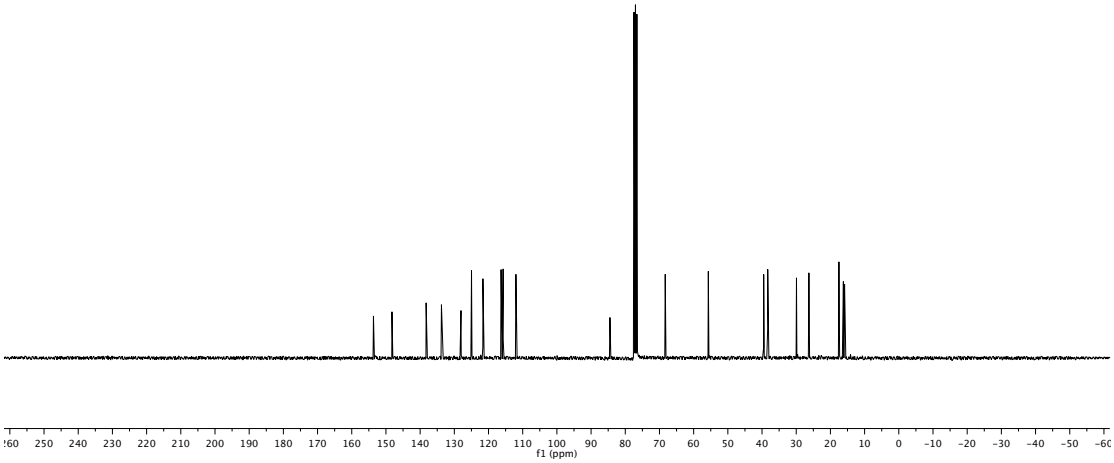
9k

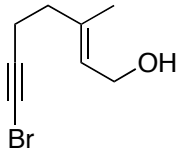
zrong-i-49-1.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 80



zrong-i-49-1_11.10.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 (C:\Bruker\TopSpin3.1) zrong 20

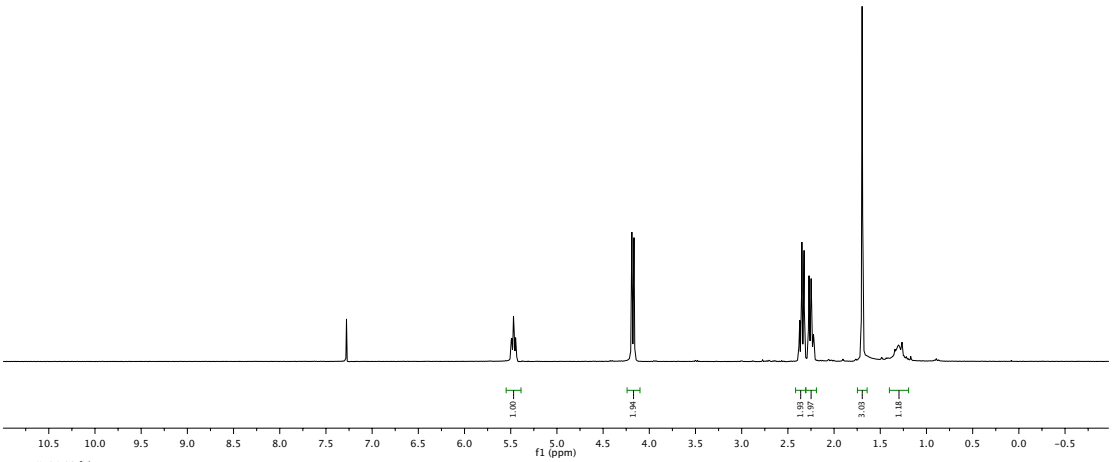
153.6495
148.2371
138.2451
133.7682
128.0511
124.9721
121.6369
116.1577
115.7237
111.9836
84.4806
77.4475 CDCl3
77.0042 CDCl3
76.6065 CDCl3
68.3128
55.7090
39.5154
28.3368
29.9253
26.2915
17.5148
17.2138
15.9604



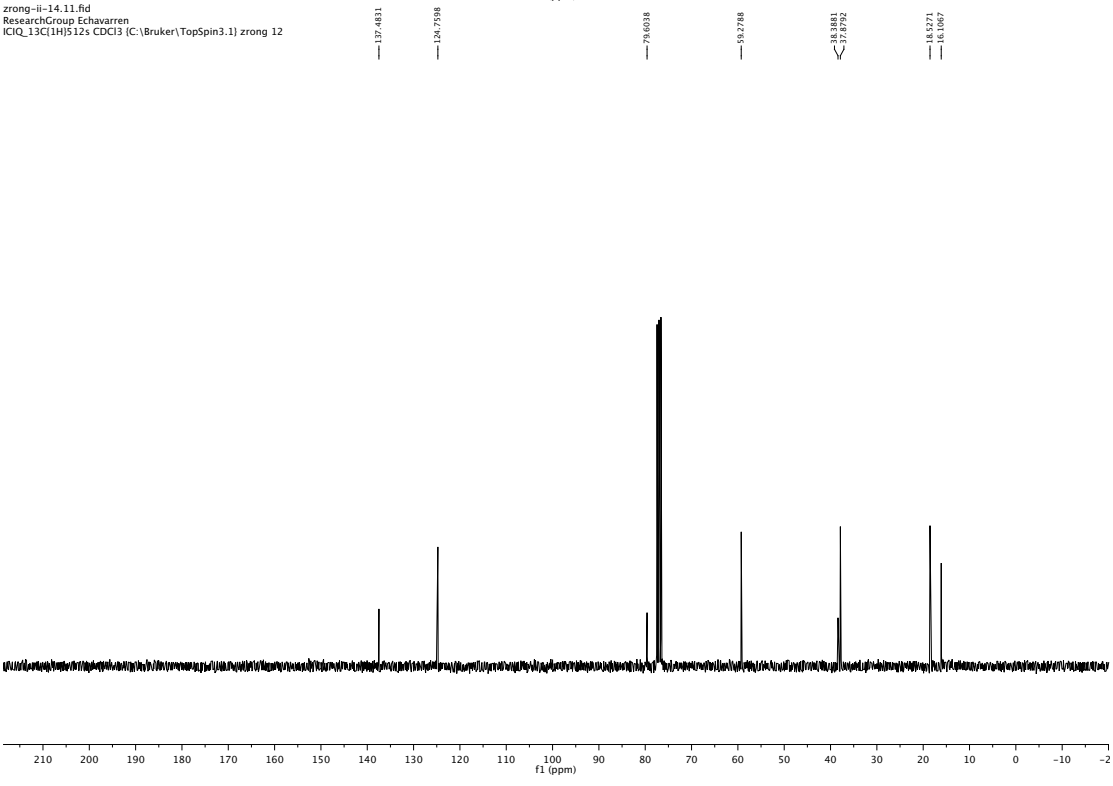


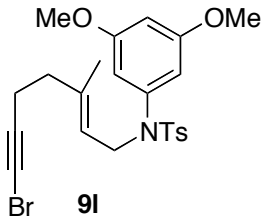
S14

zrong-ii-14.10.fid
ResearchGroup Echavarren
ICIQ_1H20p8s CDCl3 (C:\Bruker\TopSpin3.1) zrong 12



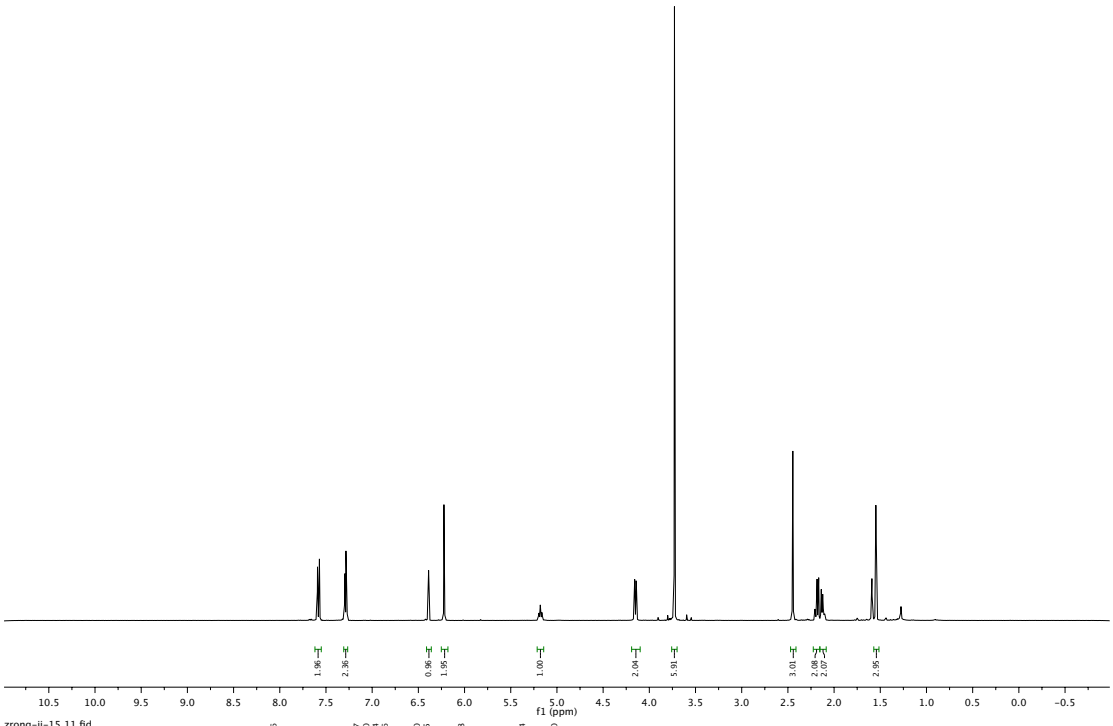
zrong-ii-14.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 (C:\Bruker\TopSpin3.1) zrong 12



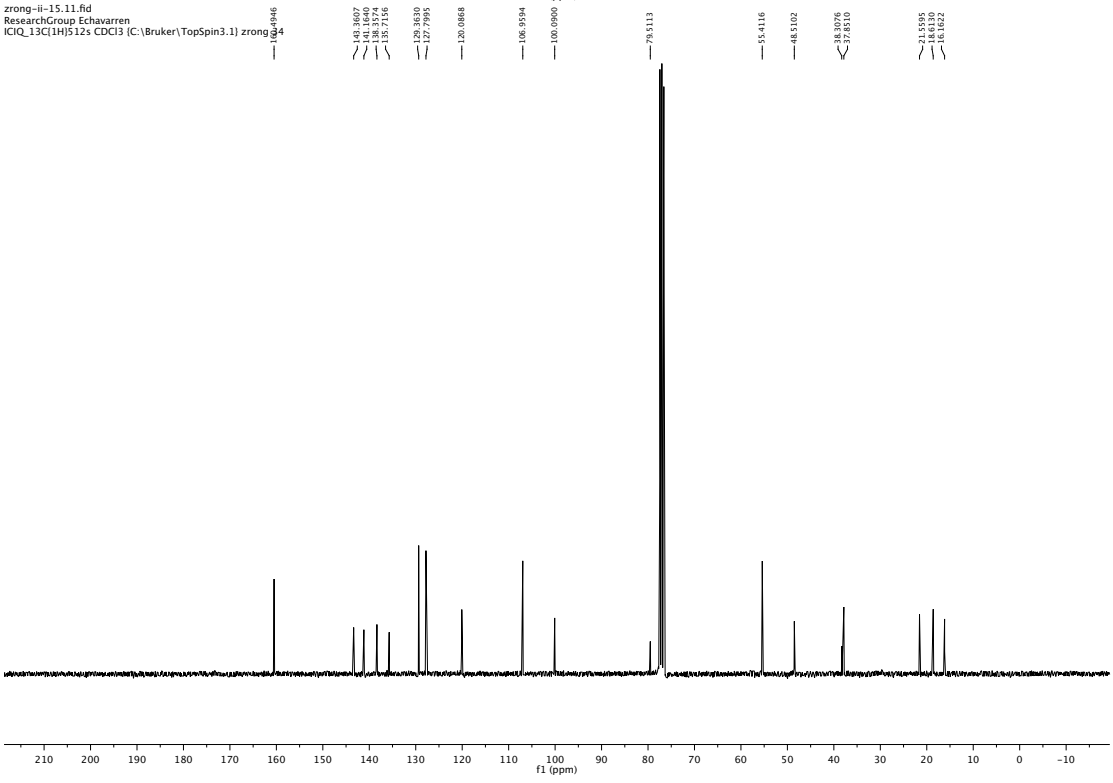


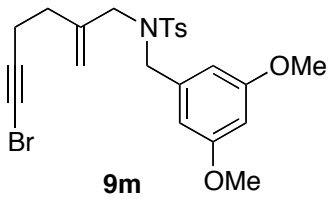
9l

zrong-ii-15.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 94



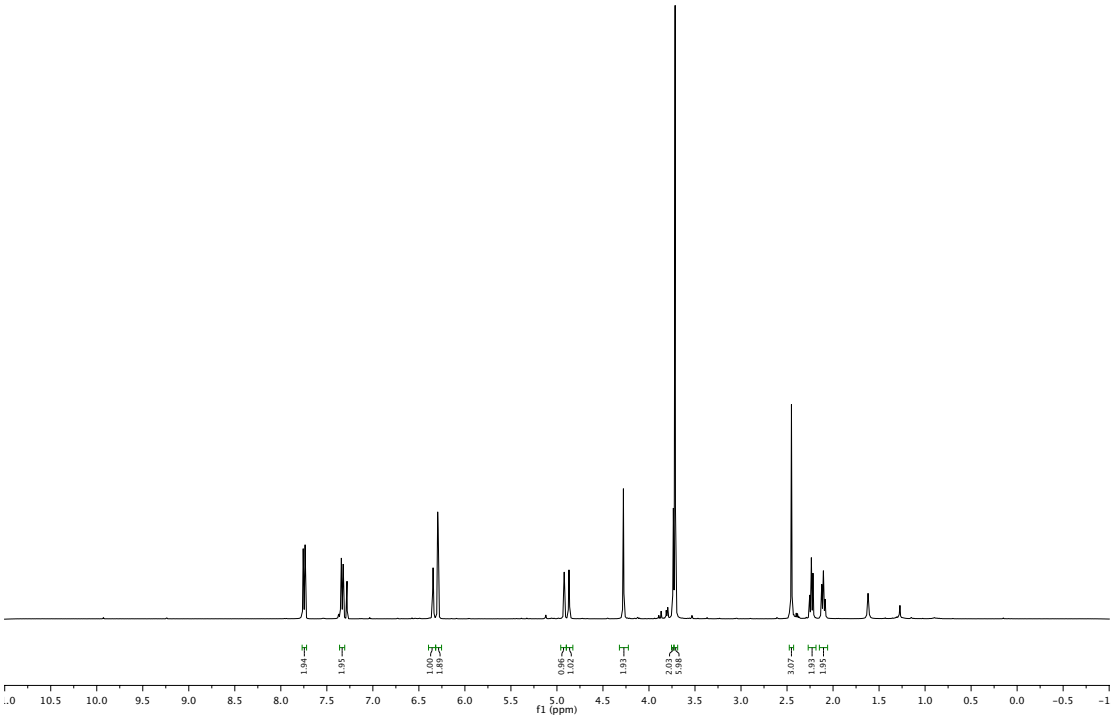
zrong-ii-15.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 {C:\Bruker\TopSpin3.1} zrong 94



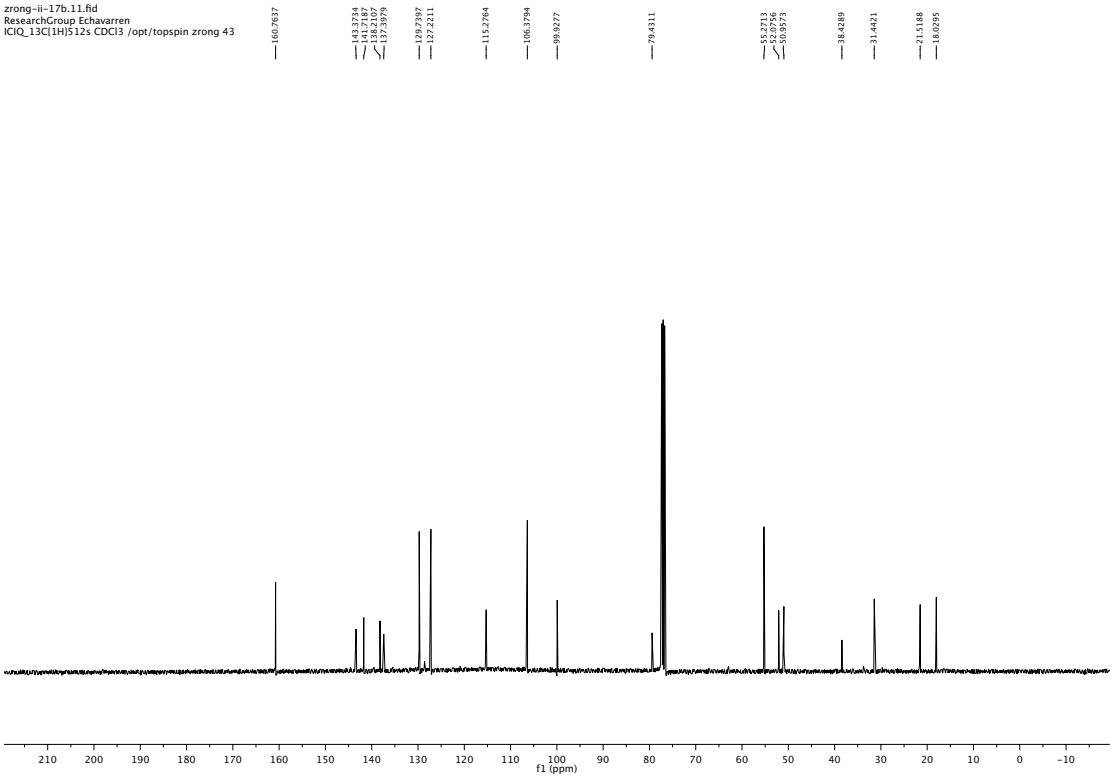


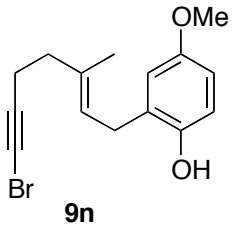
9m

zrong-ii-17b.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 43



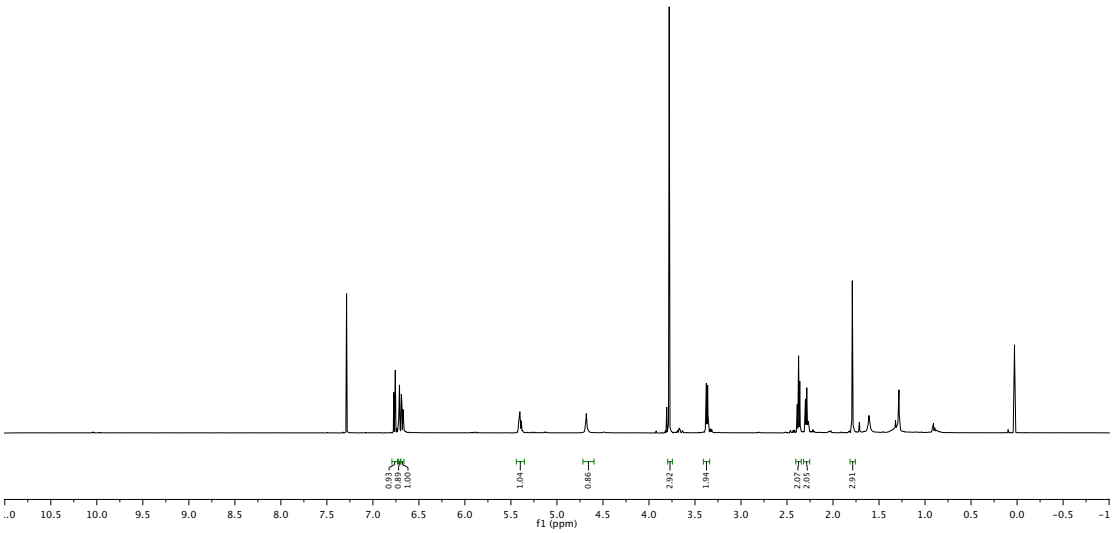
zrong-ii-17b.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 43





9n

AB-ZR-008-prod.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin abermejo 5



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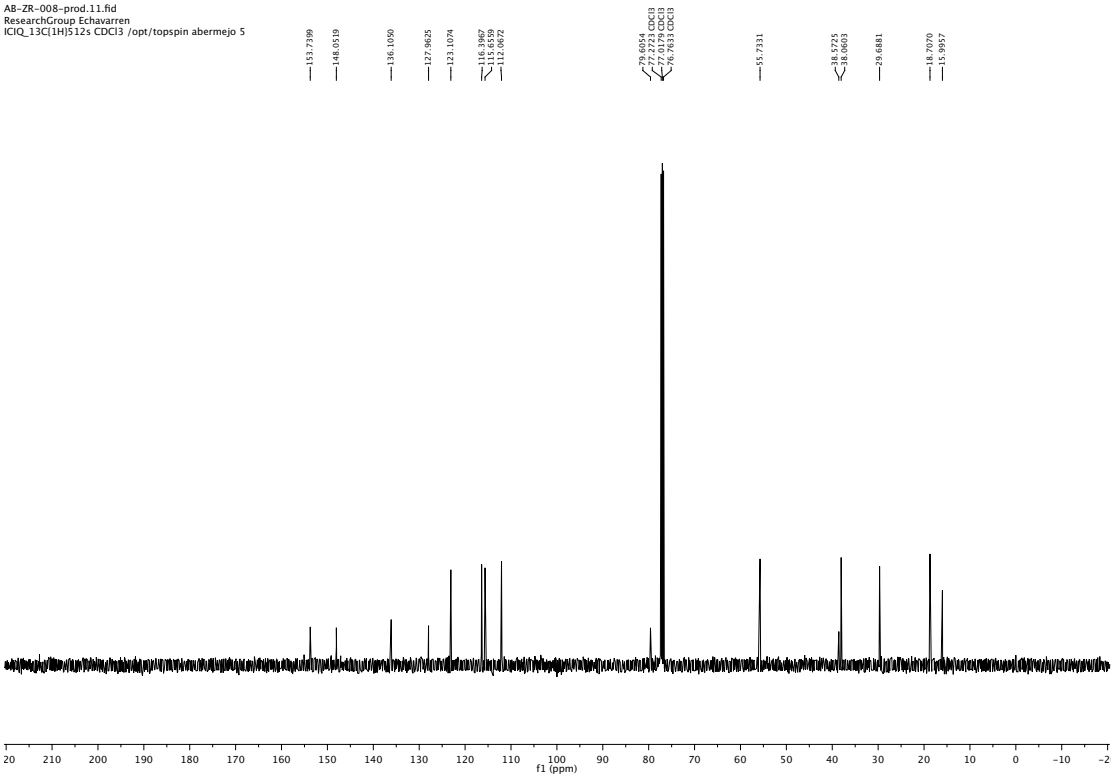
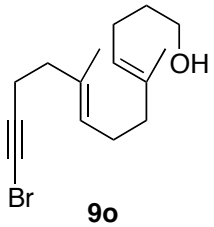
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin abermejo 5





9o

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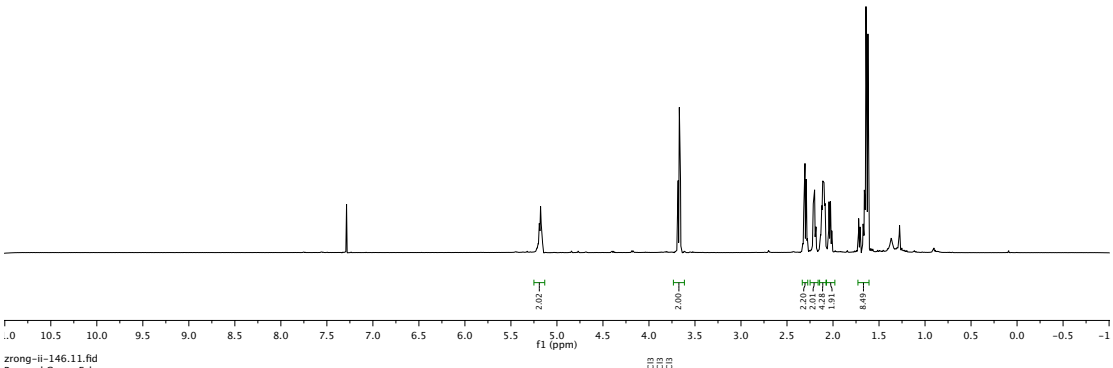
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 52



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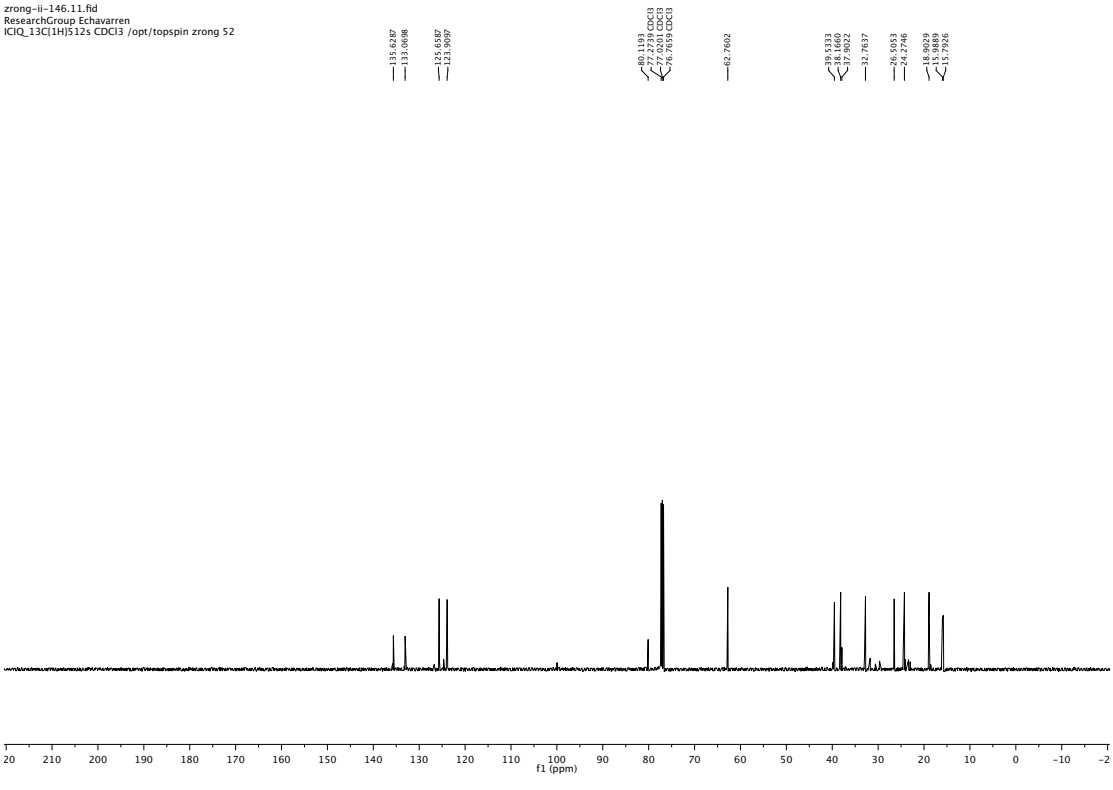
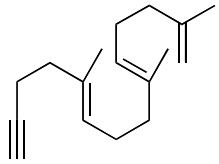
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 52





9p

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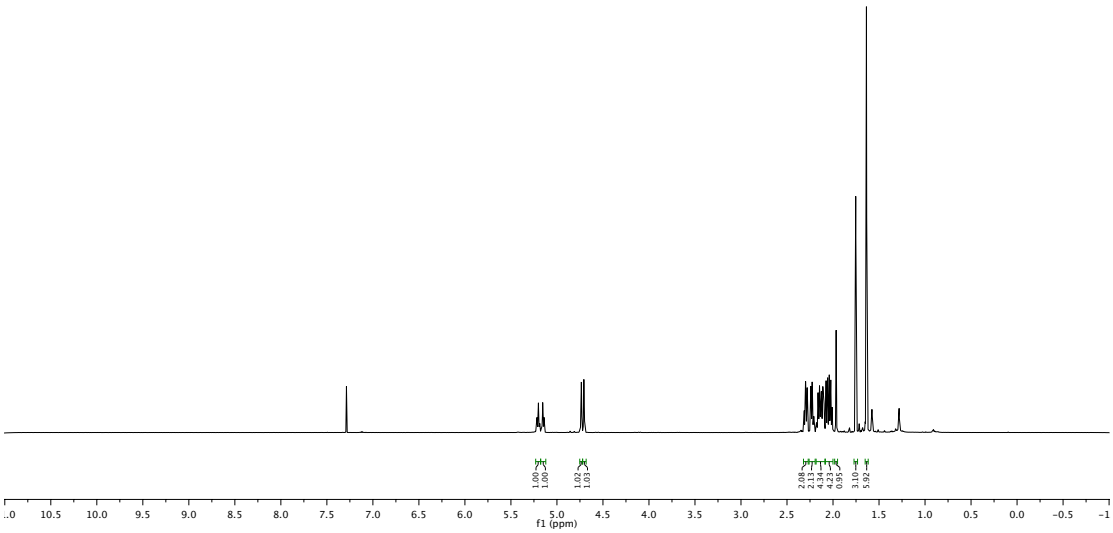
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 58



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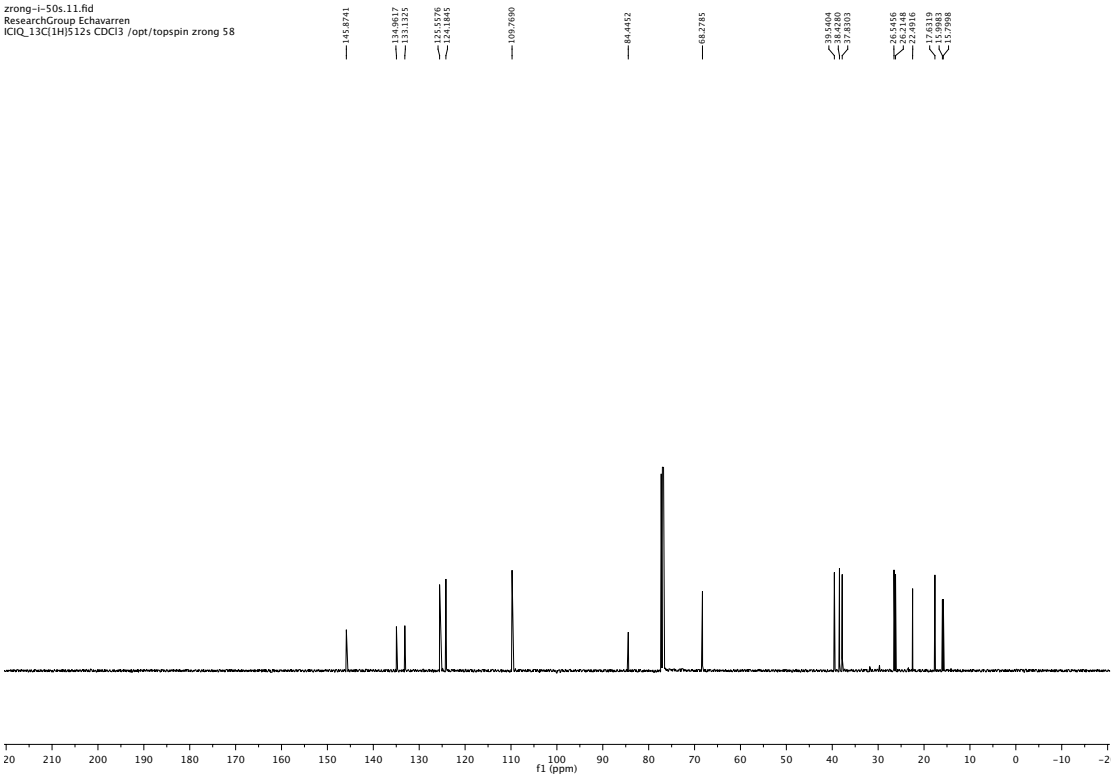
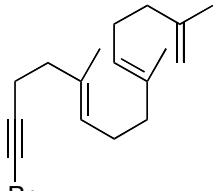
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 58





9q

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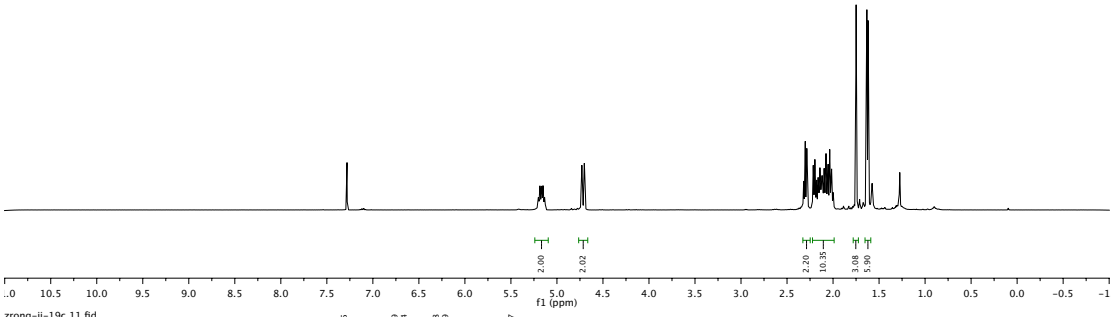
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 29



zrong-ii-19c.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 29

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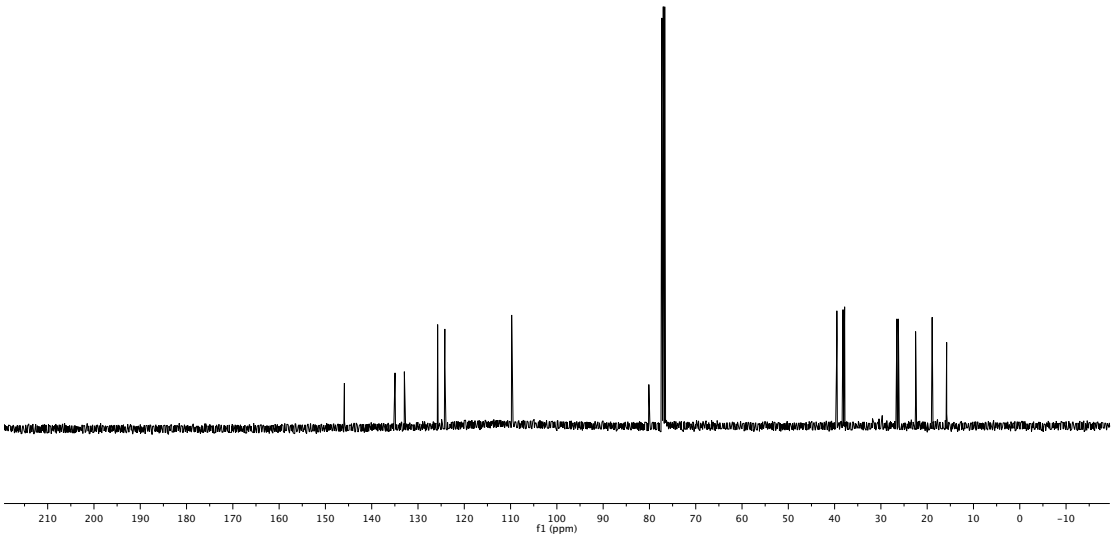

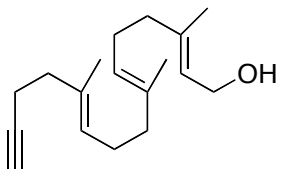

S20

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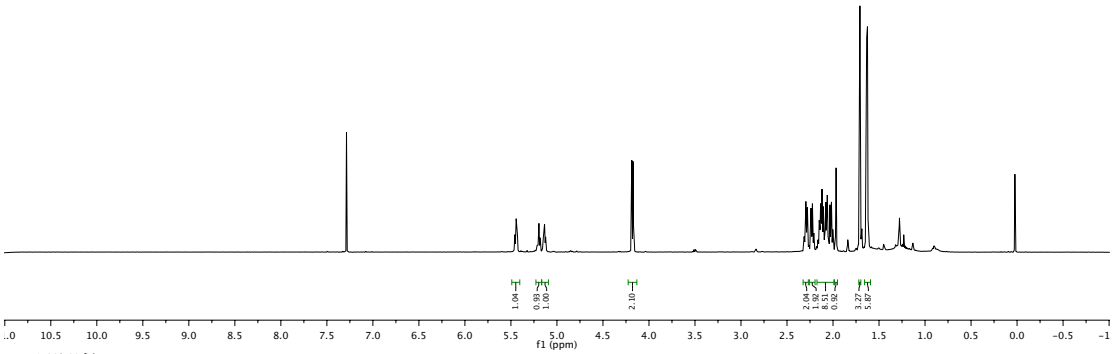
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 26



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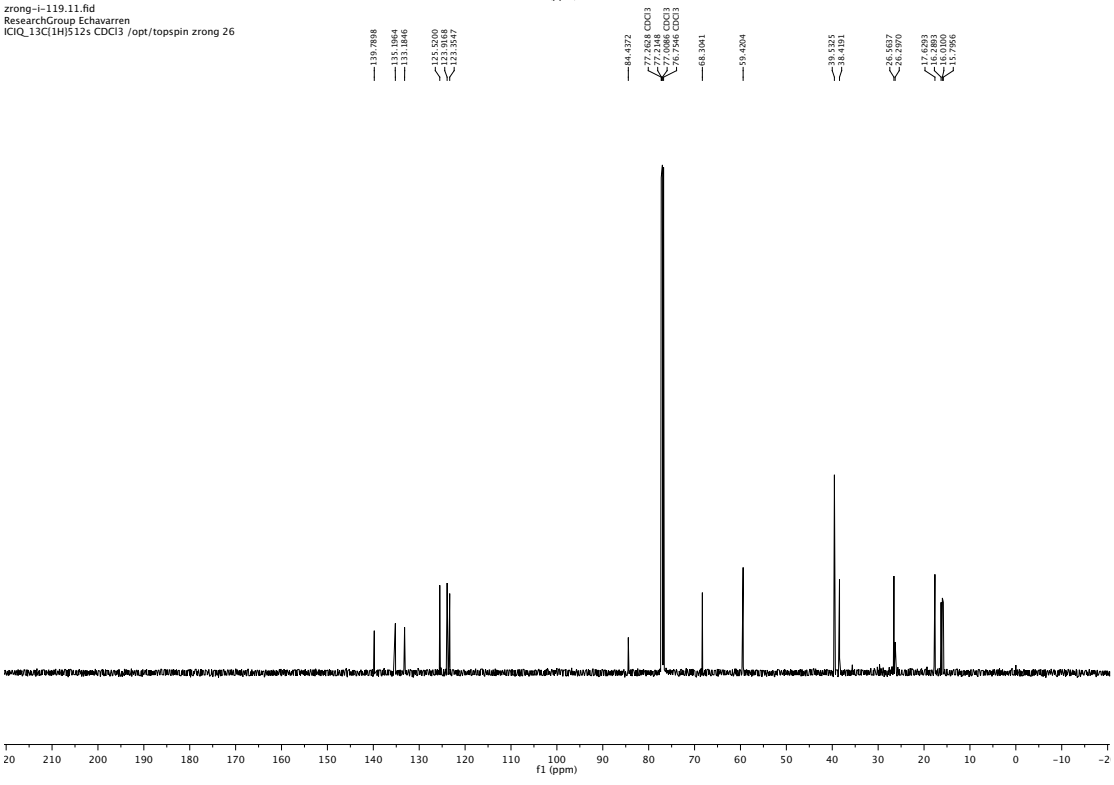
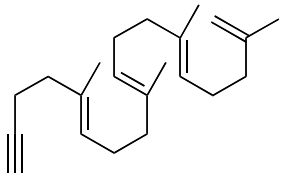
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 26





9r

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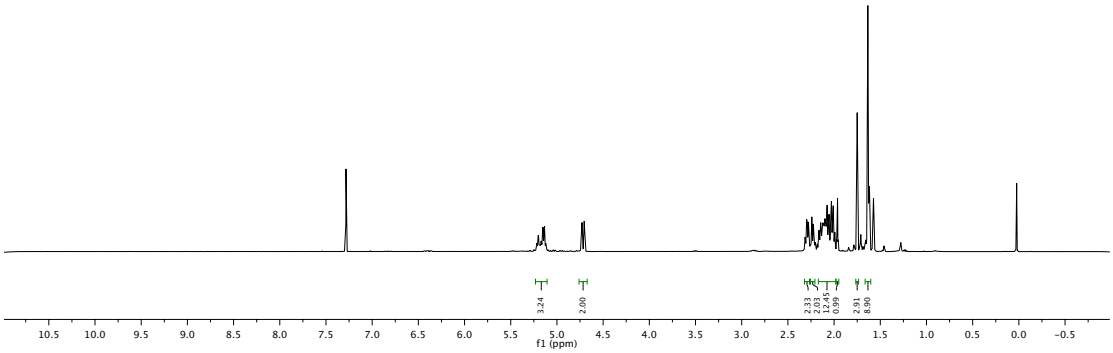
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 85



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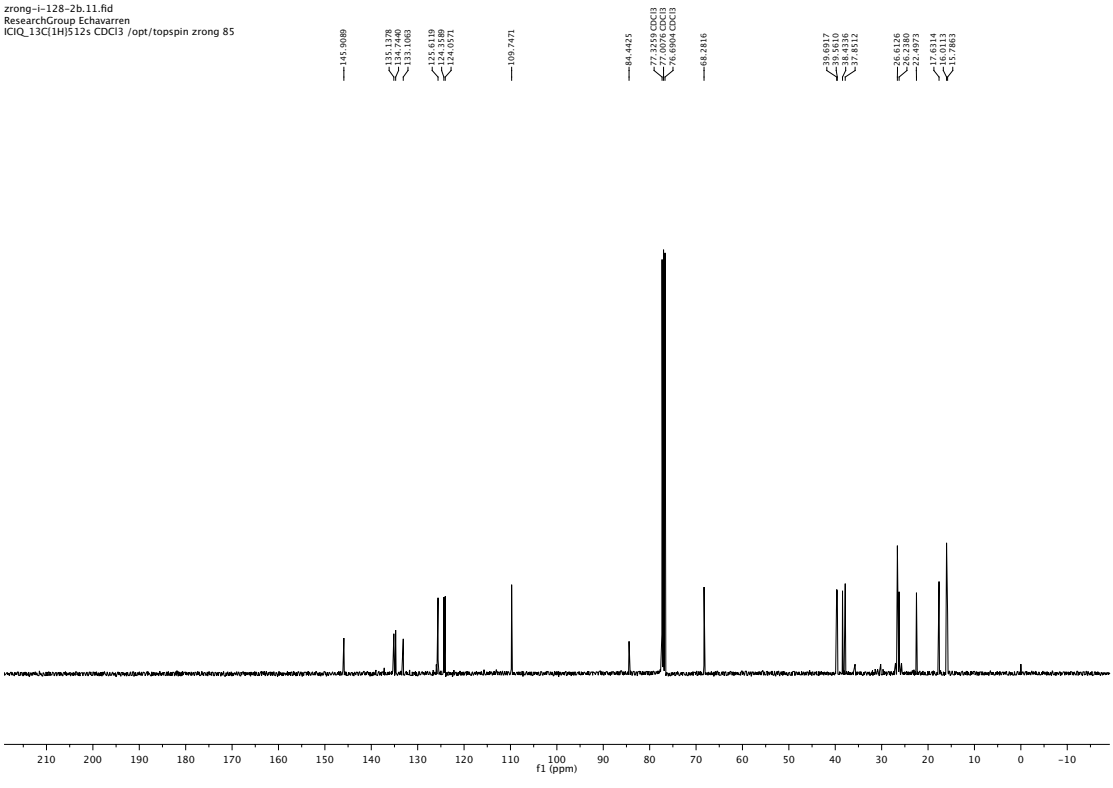
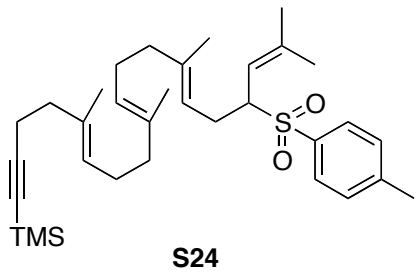
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 85





S24

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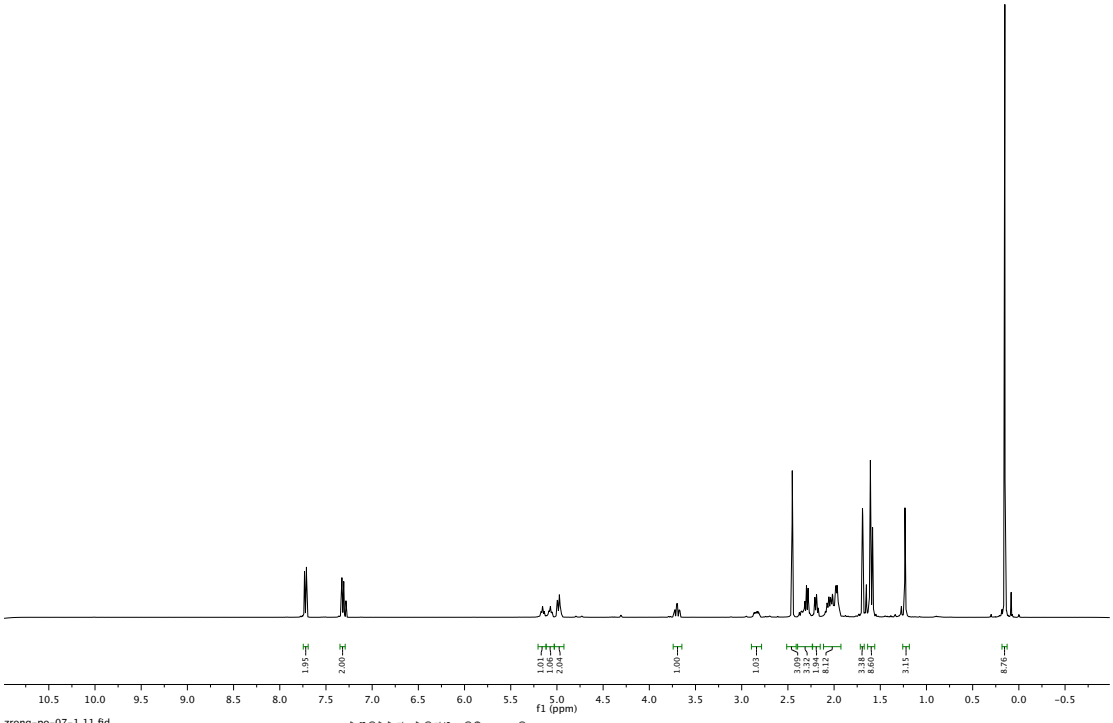
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 66



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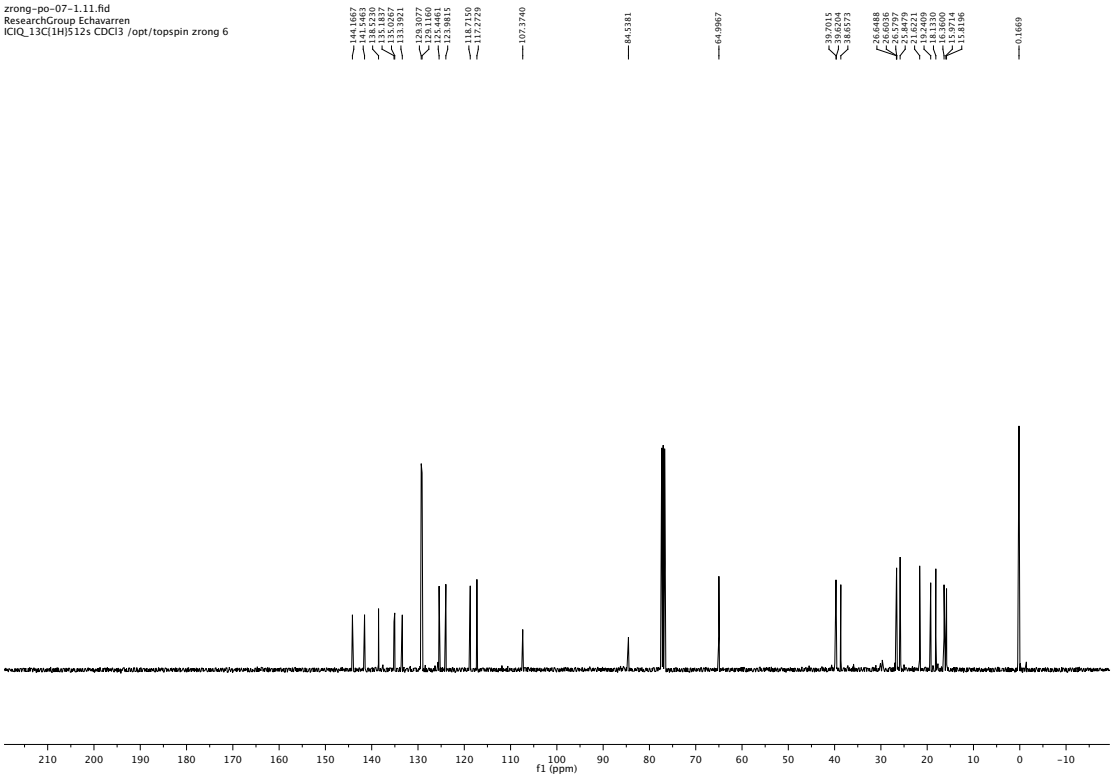
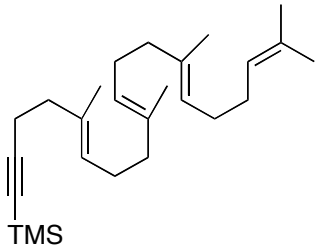
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 6





S25

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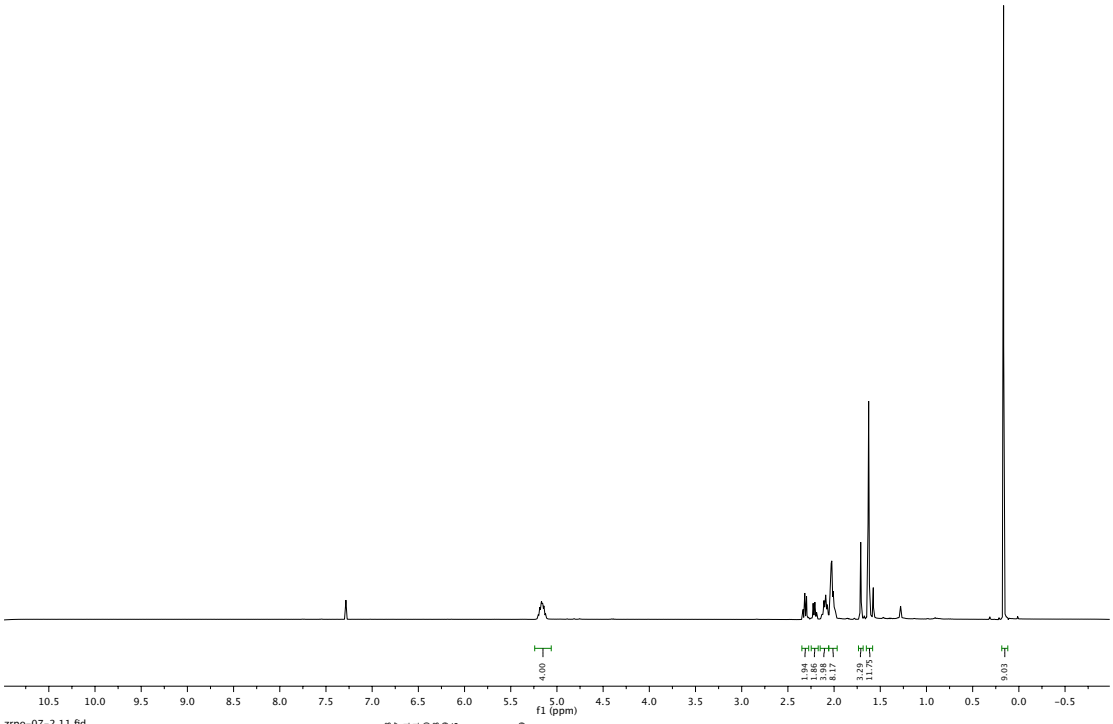
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 97



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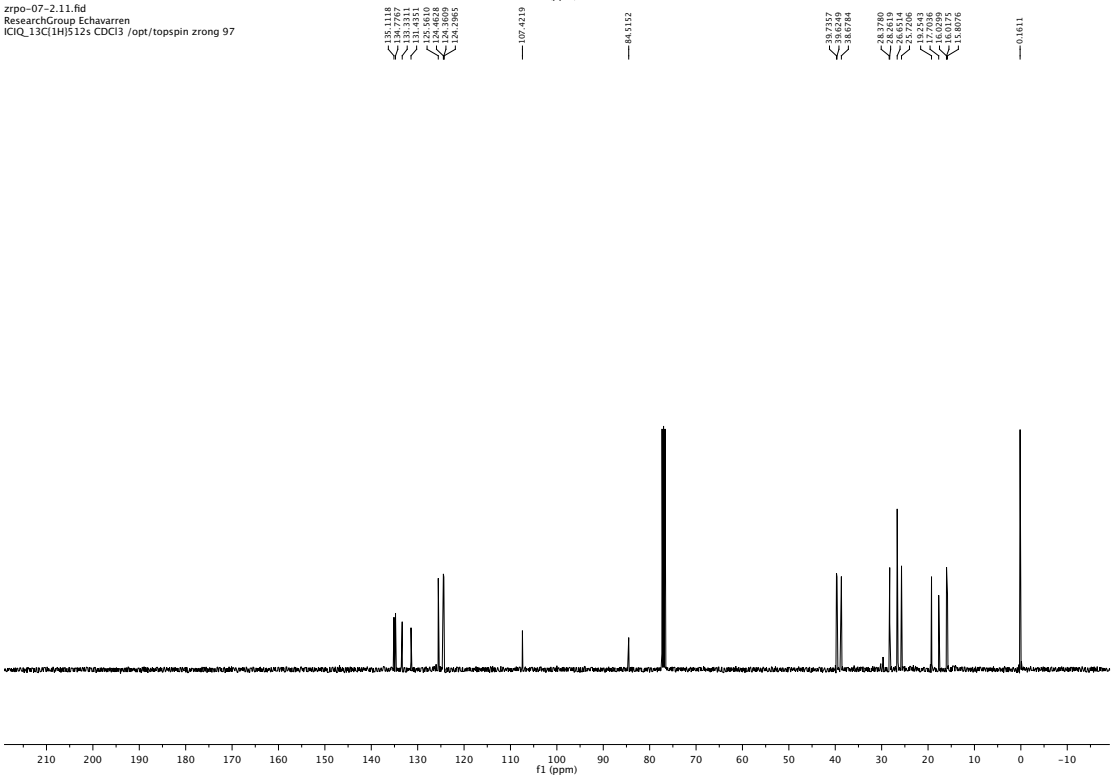
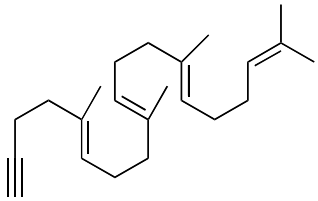
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 97





S26

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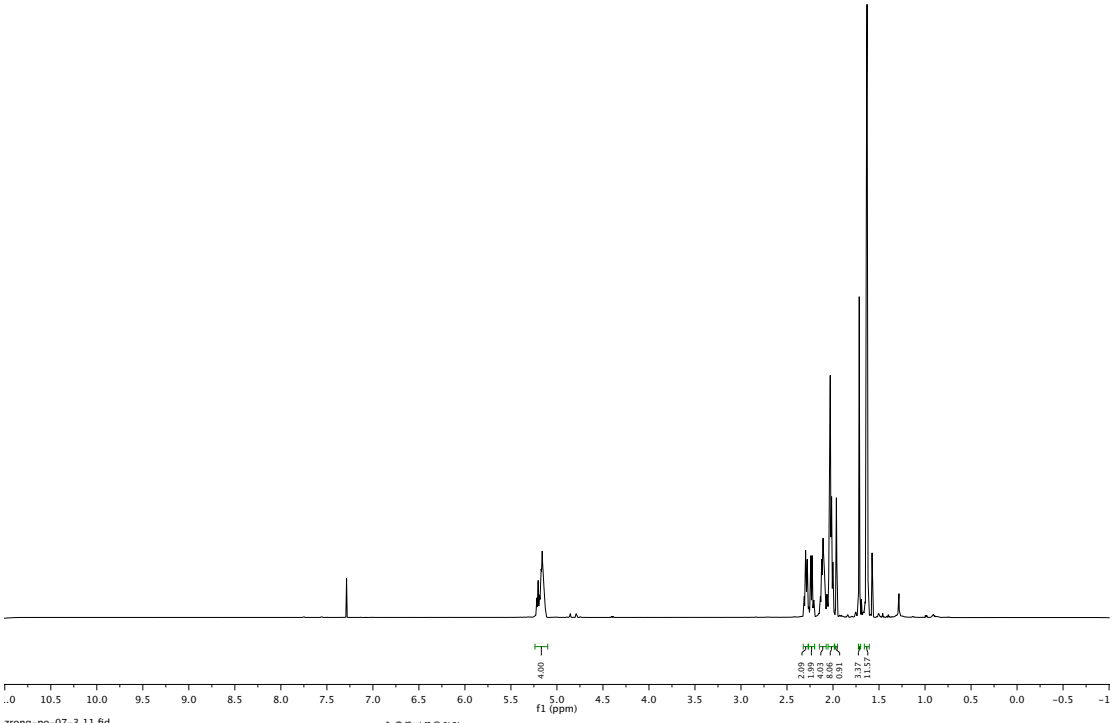
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 50



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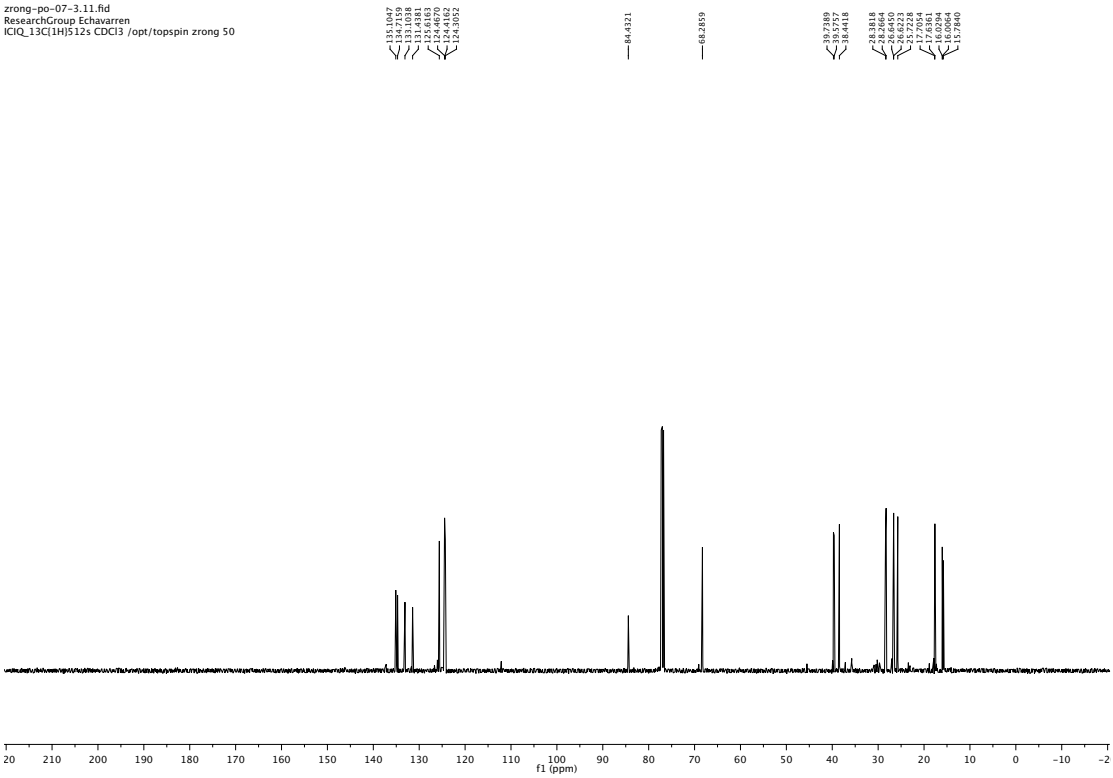
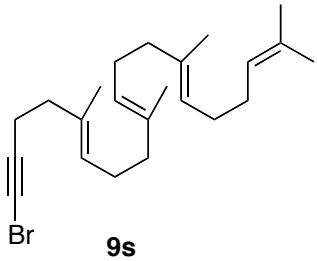
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 50





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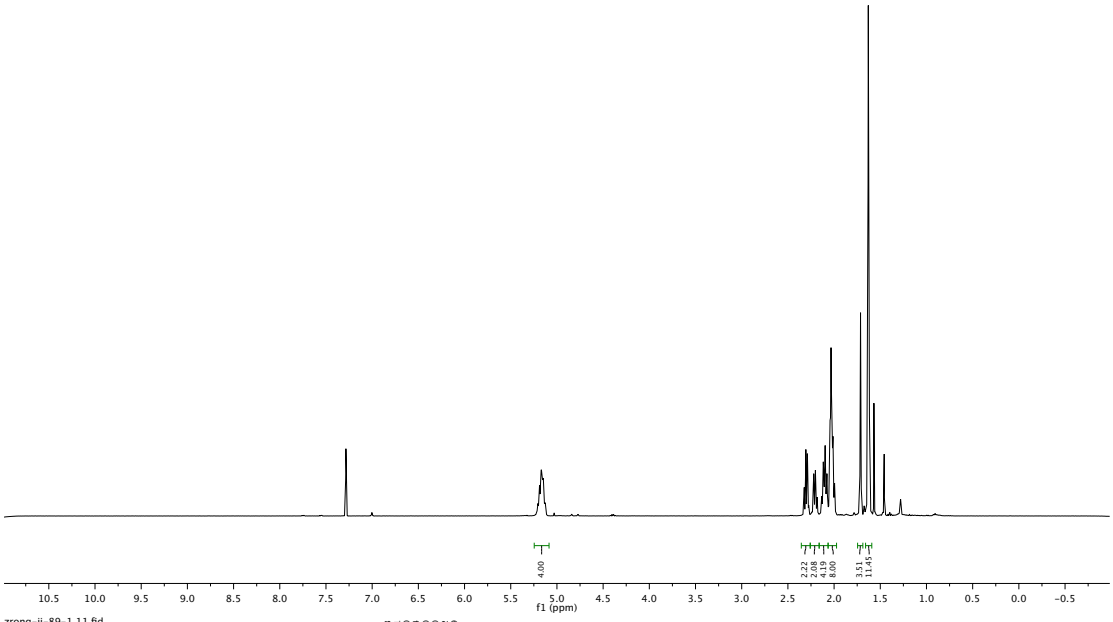
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 110



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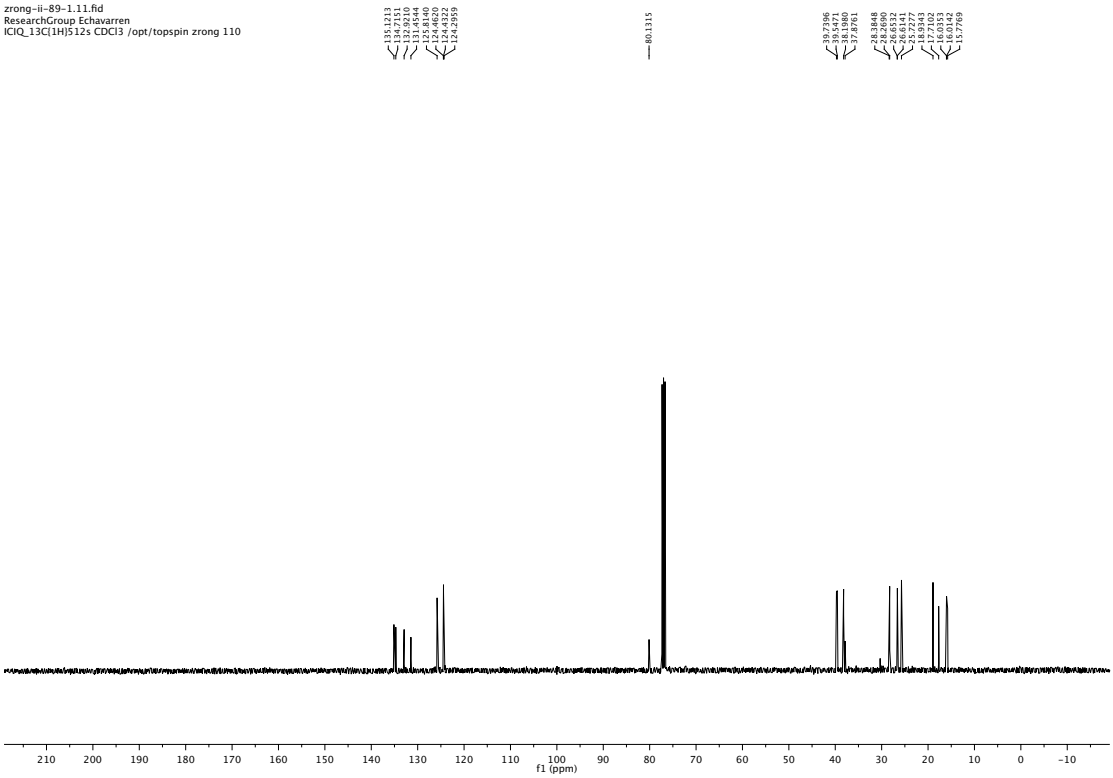
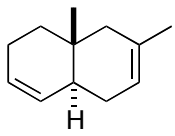
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 110





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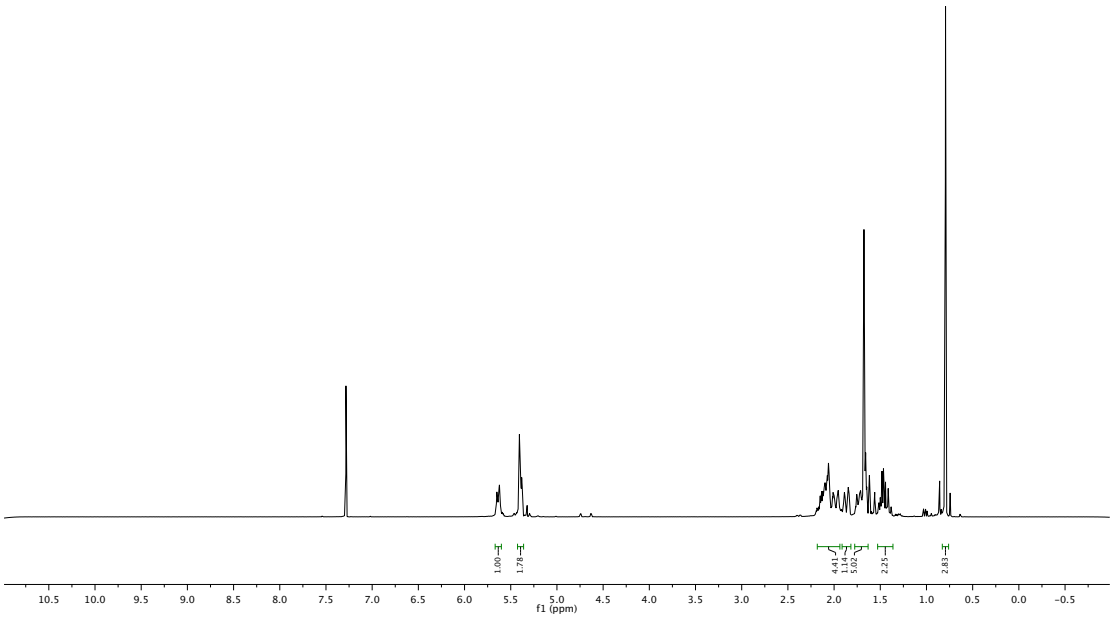
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 106



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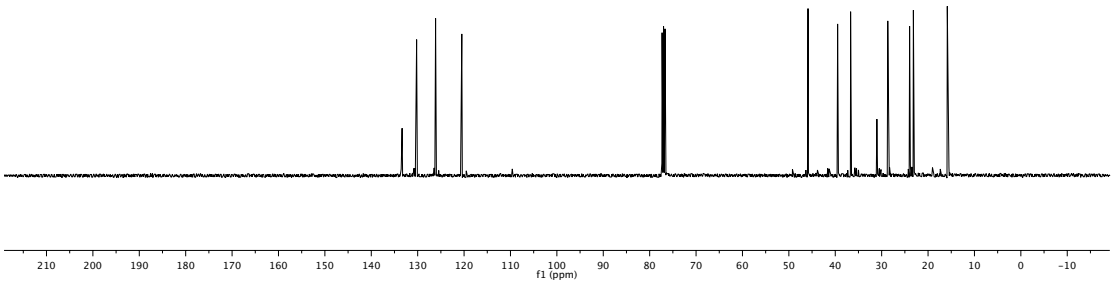
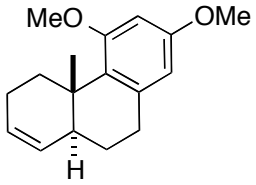
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 106





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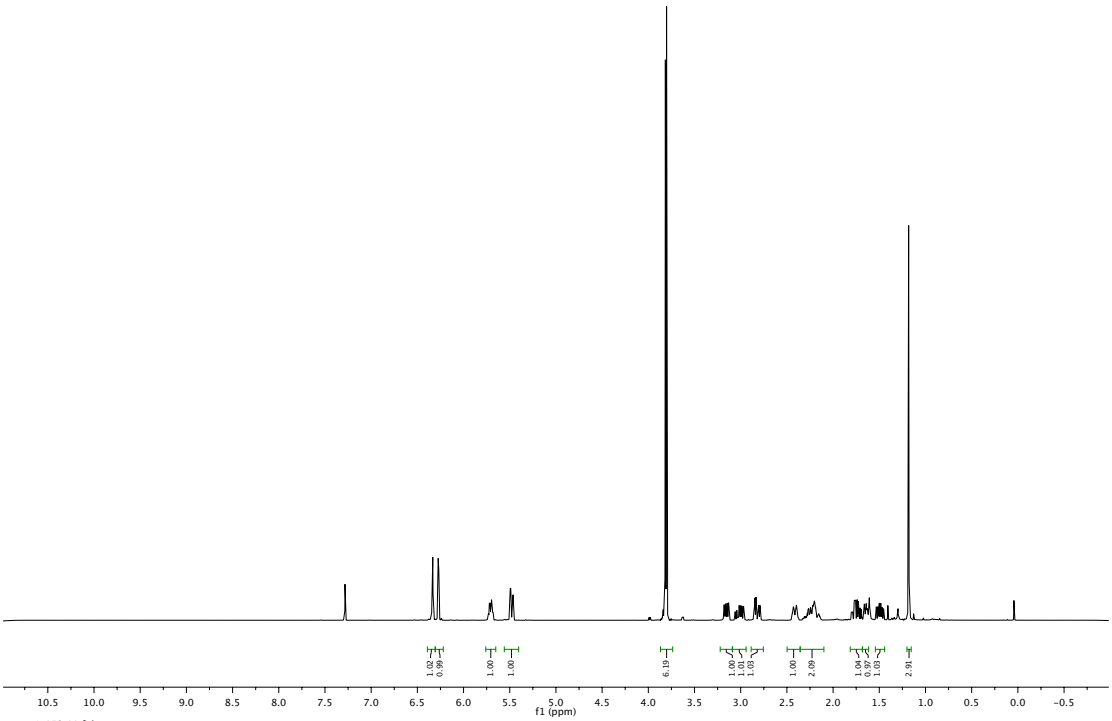
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 104



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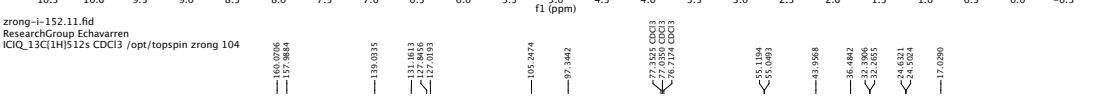
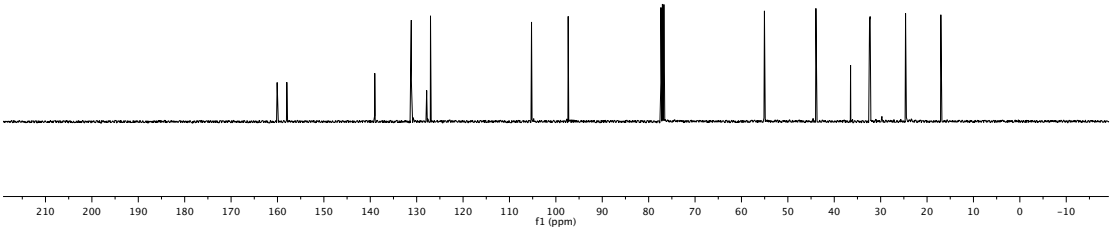
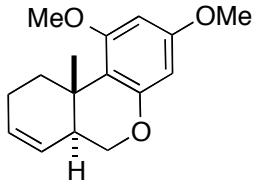
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 104







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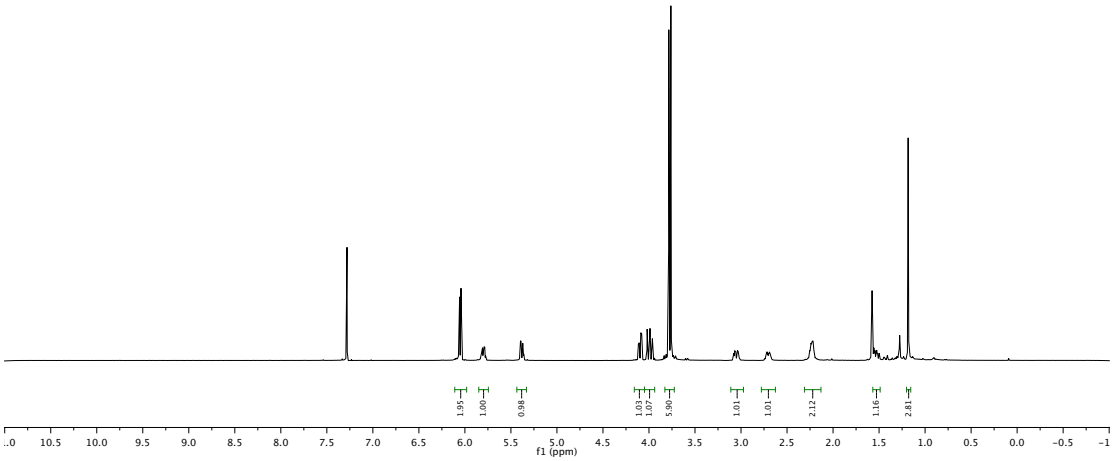
ResearchGroup Echavarren
ICIQ_1H12p32s CDCl3 /opt/topspin zrong 49



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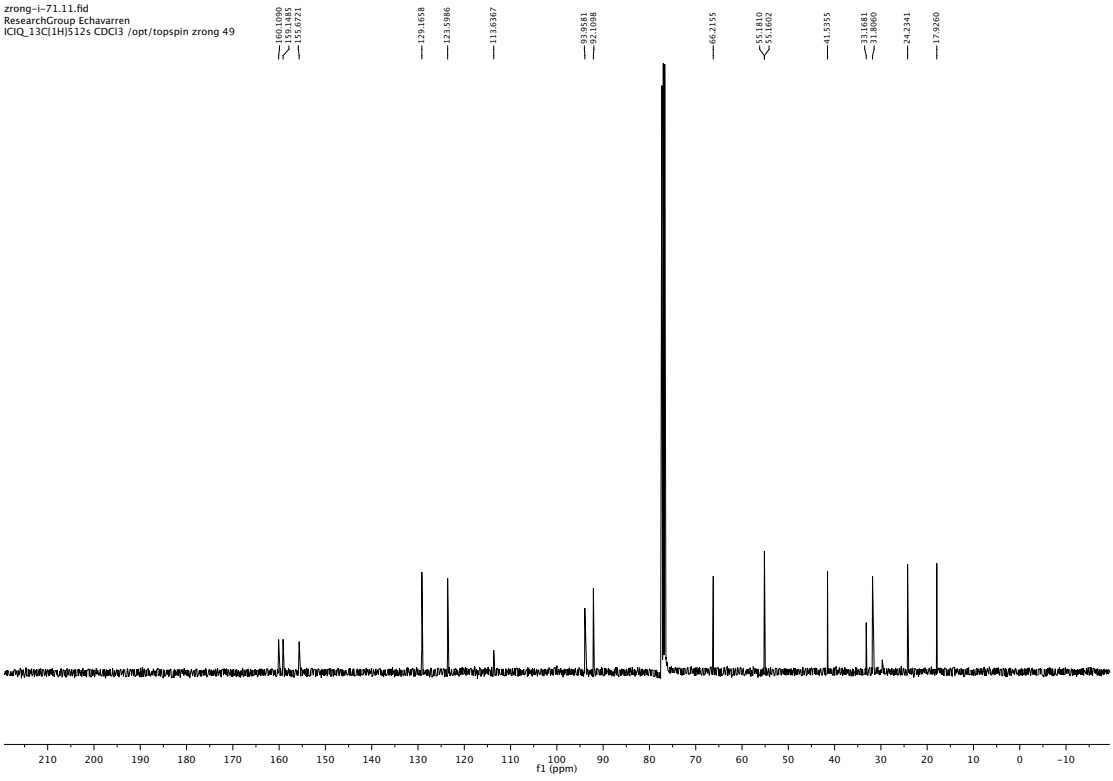
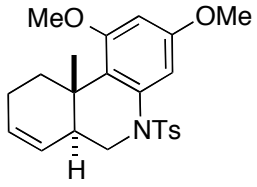
ResearchGroup Echavarren
ICIQ_13C(1H)512s CDCl3 /opt/topspin zrong 49





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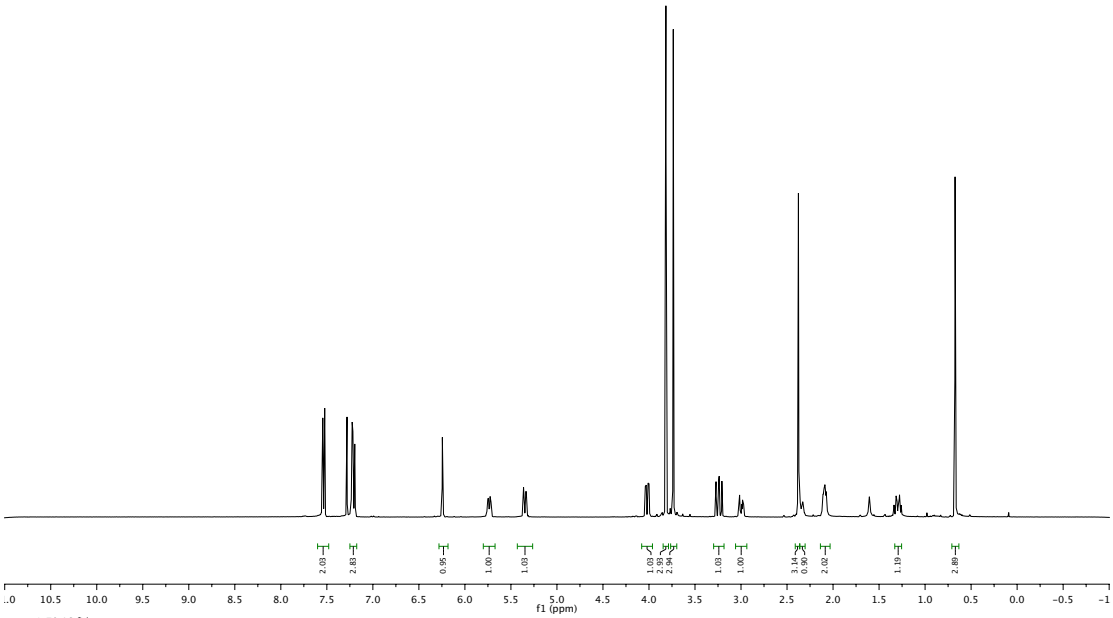
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 51



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ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 51

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120.3069
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77.3429 CDCl3
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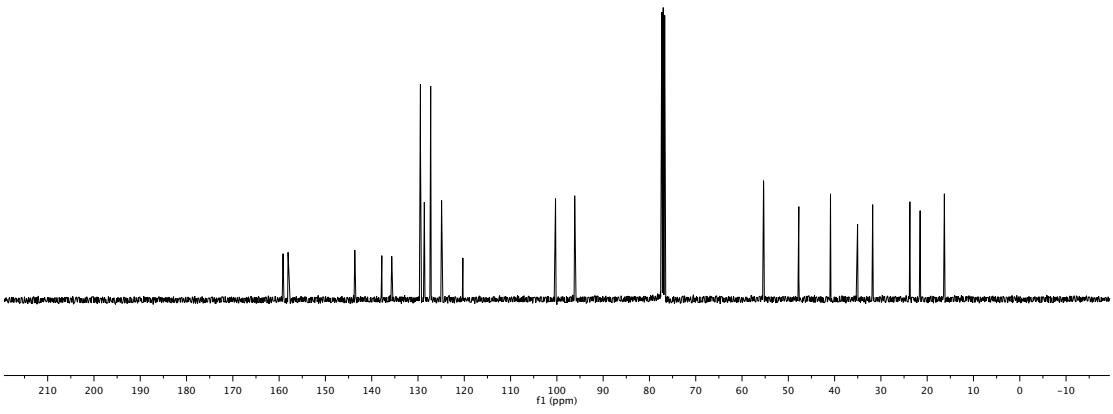

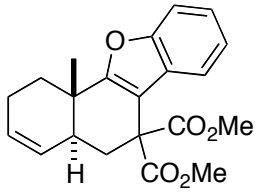

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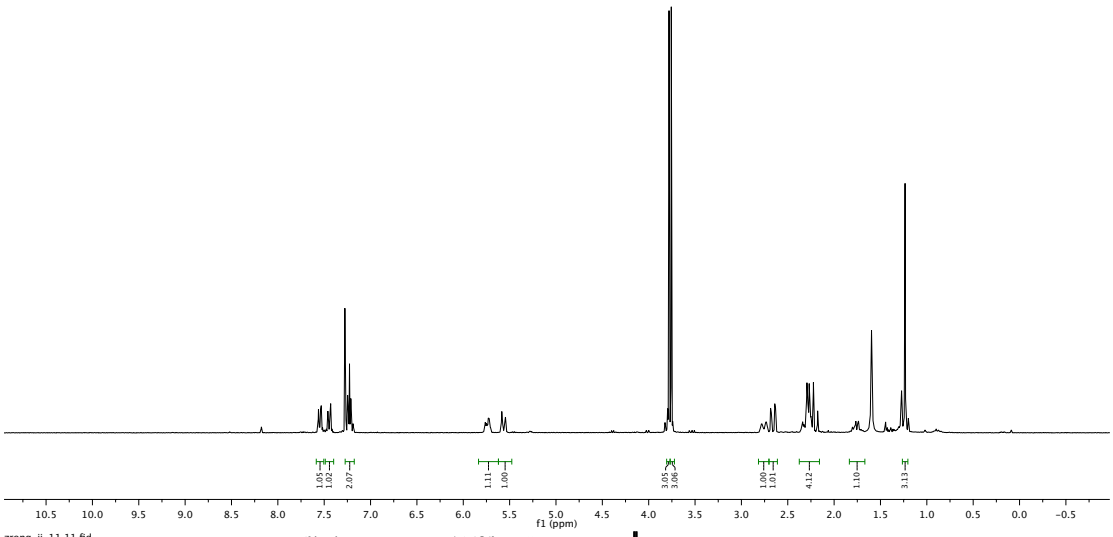
ResearchGroup Echavarren
ICIQ_1H20p8s CDCl3 {C:\Bruker\TopSpin3.1} zrong 24



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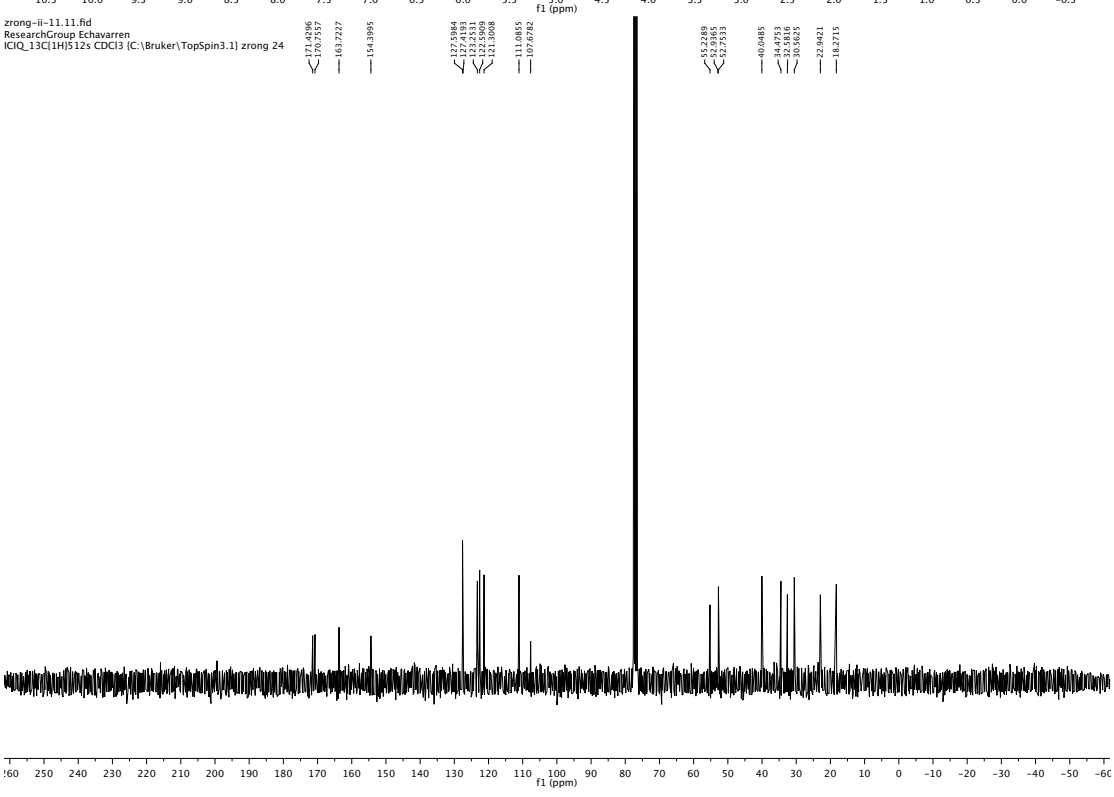
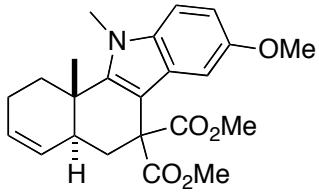
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 {C:\Bruker\TopSpin3.1} zrong 24





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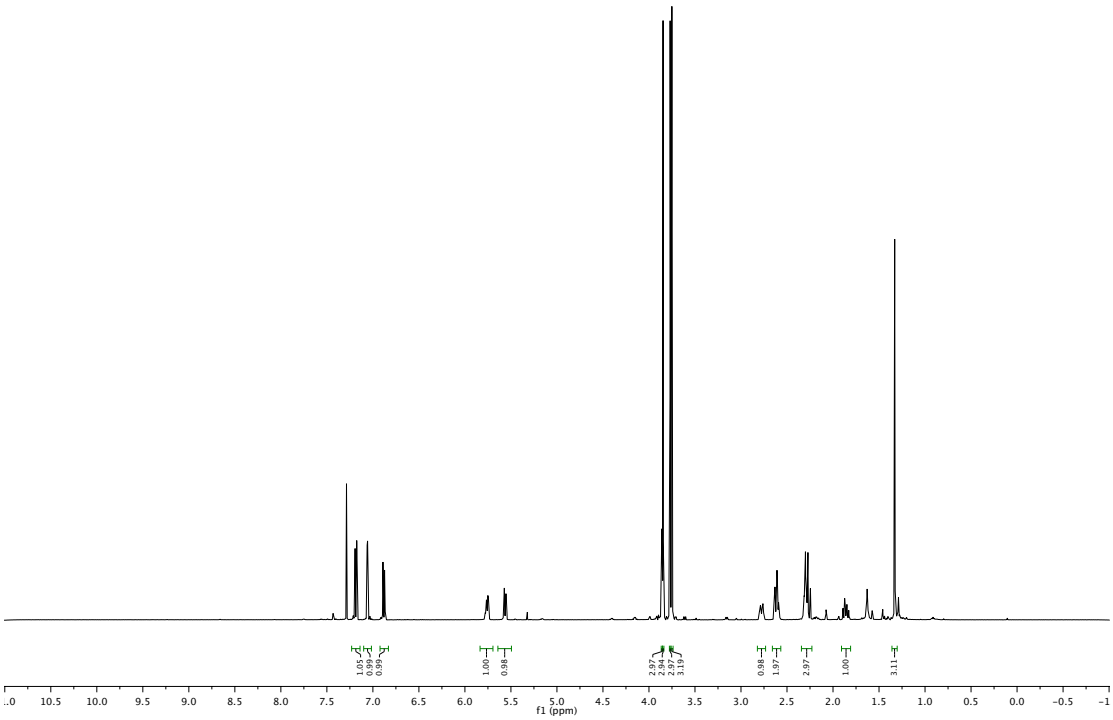
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 11



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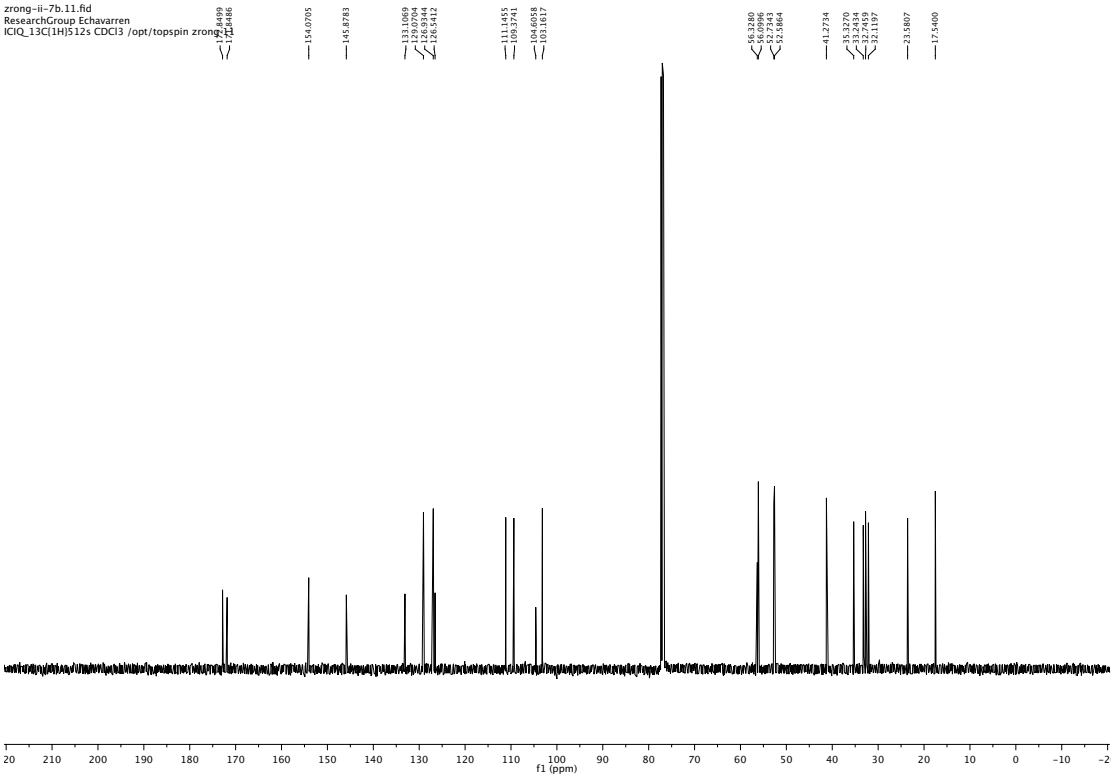
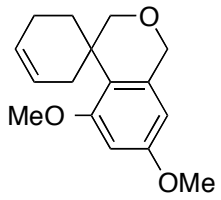
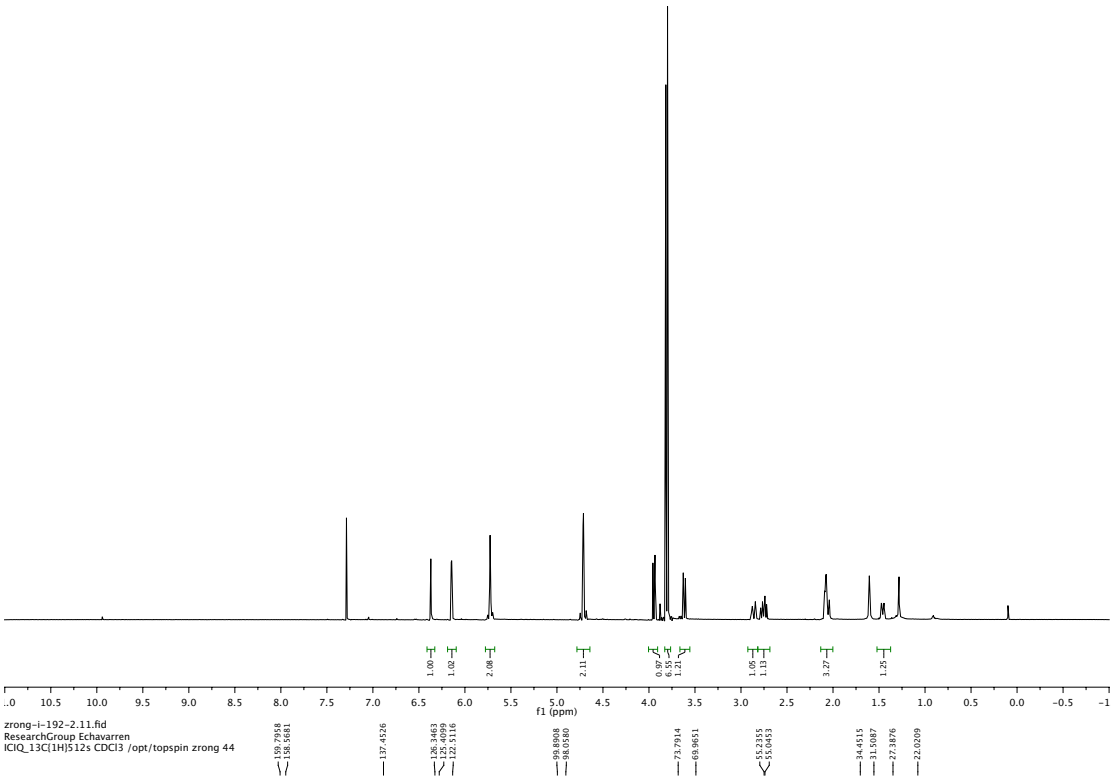
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong





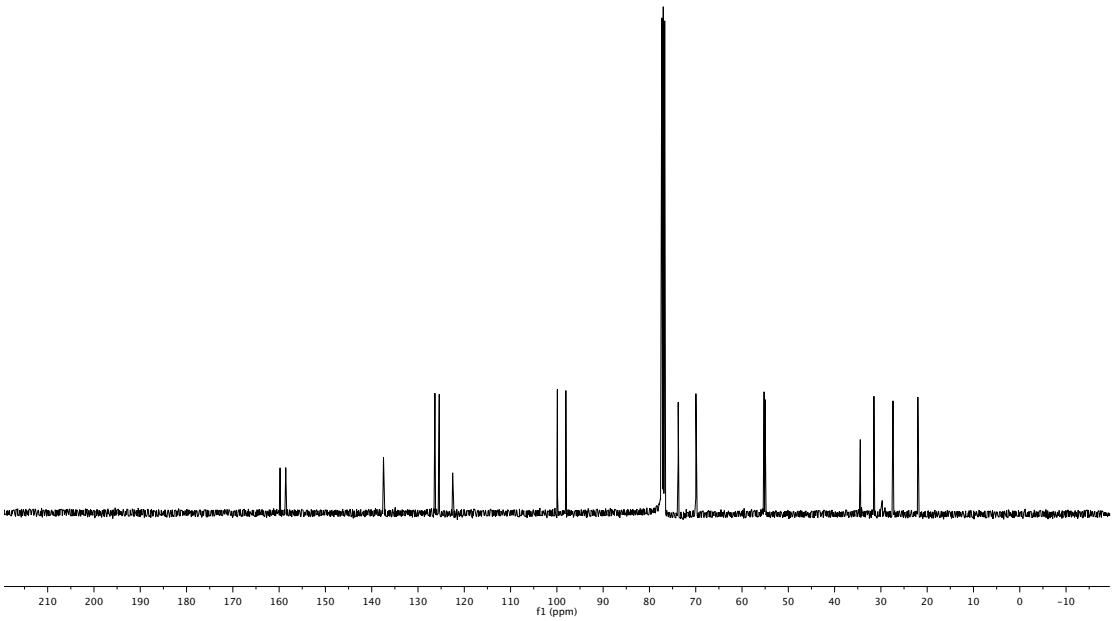
10g

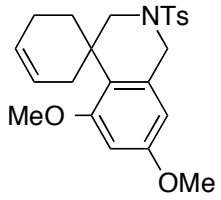
zrong-i-192-2.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 44



zrong-i-192-2.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 44

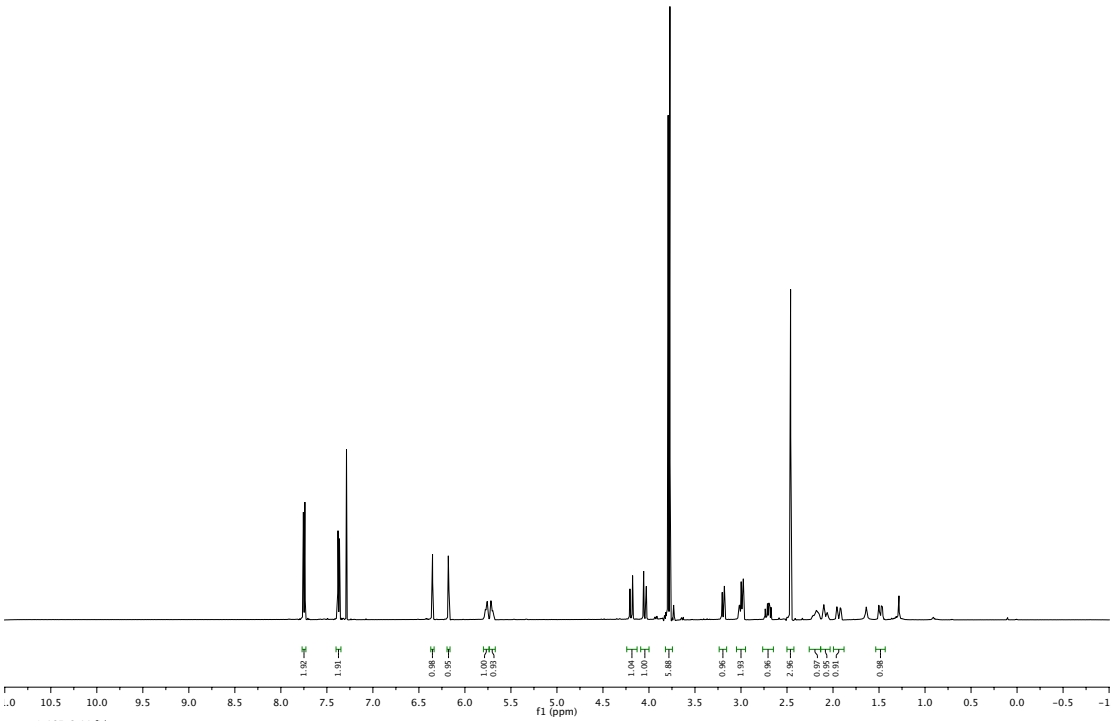
159.7958
158.5681
137.4526
126.3463
125.4099
122.5116
99.8908
98.0580
73.7914
69.9651
55.3255
55.0453
34.4515
31.5087
27.3876
22.0209





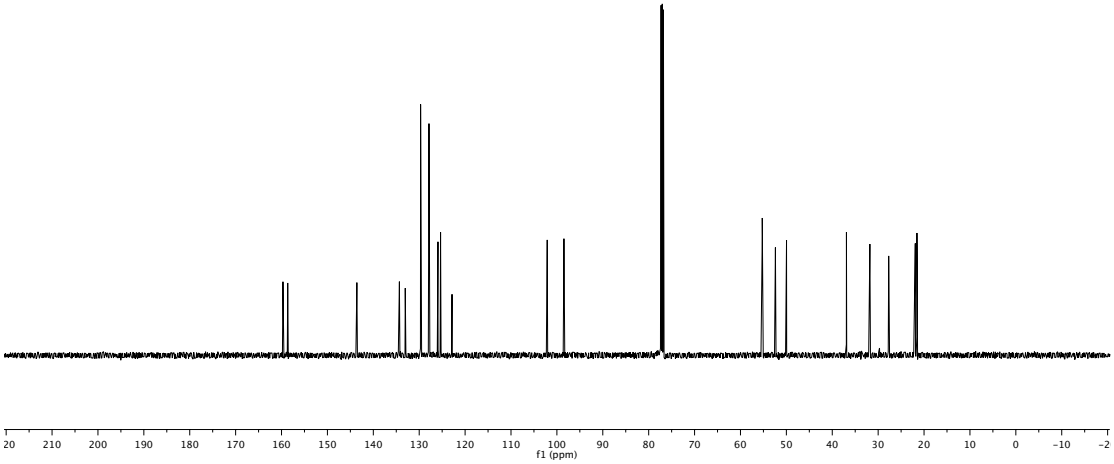
10h

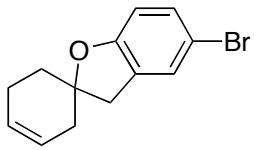
zrong-i-185-2.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 31



zrong-i-185-2.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 31

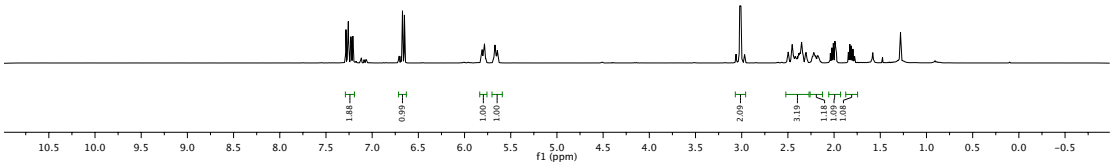
159.6880
158.6494
143.5811
134.3166
133.1043
129.6864
127.8737
127.5638
125.3457
122.8494
102.1098
98.4642
77.2981 CDCl3
77.0444 CDCl3
76.7889 CDCl3
55.3207
55.1137
52.3874
49.9646
36.9113
31.8032
27.7003
21.9101
21.5498





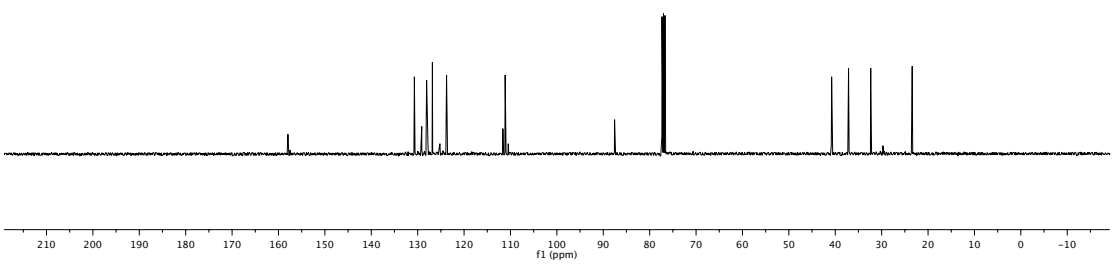
10i

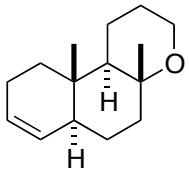
zrong-i-177s.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 89



zrong-i-177s.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 89

157.9663
130.7108
130.2114
128.0729
126.8260
123.7753
111.6381
111.1446
87.5611
40.7777
37.1351
32.3489
23.6147





10j

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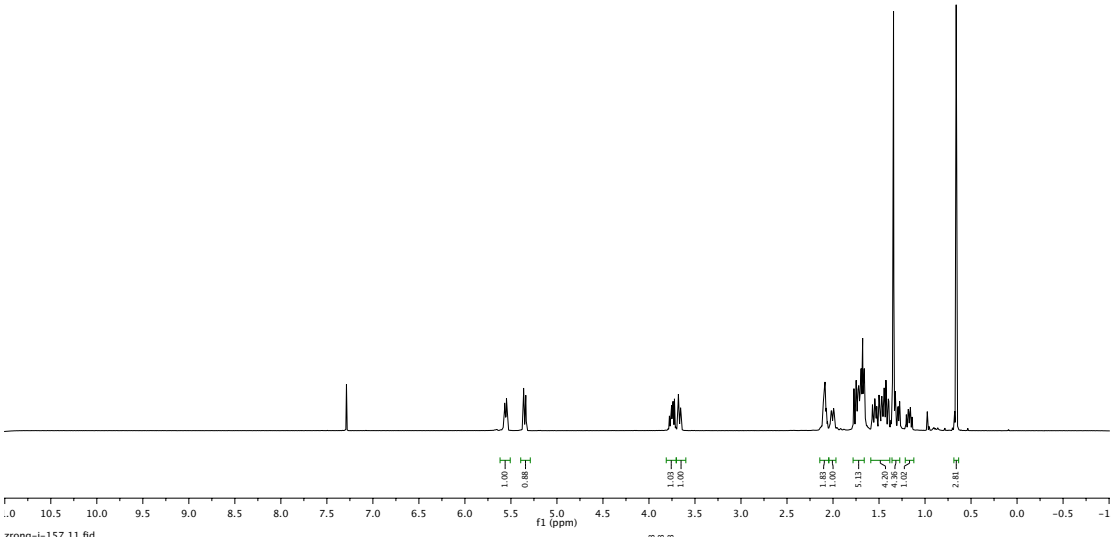
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 23



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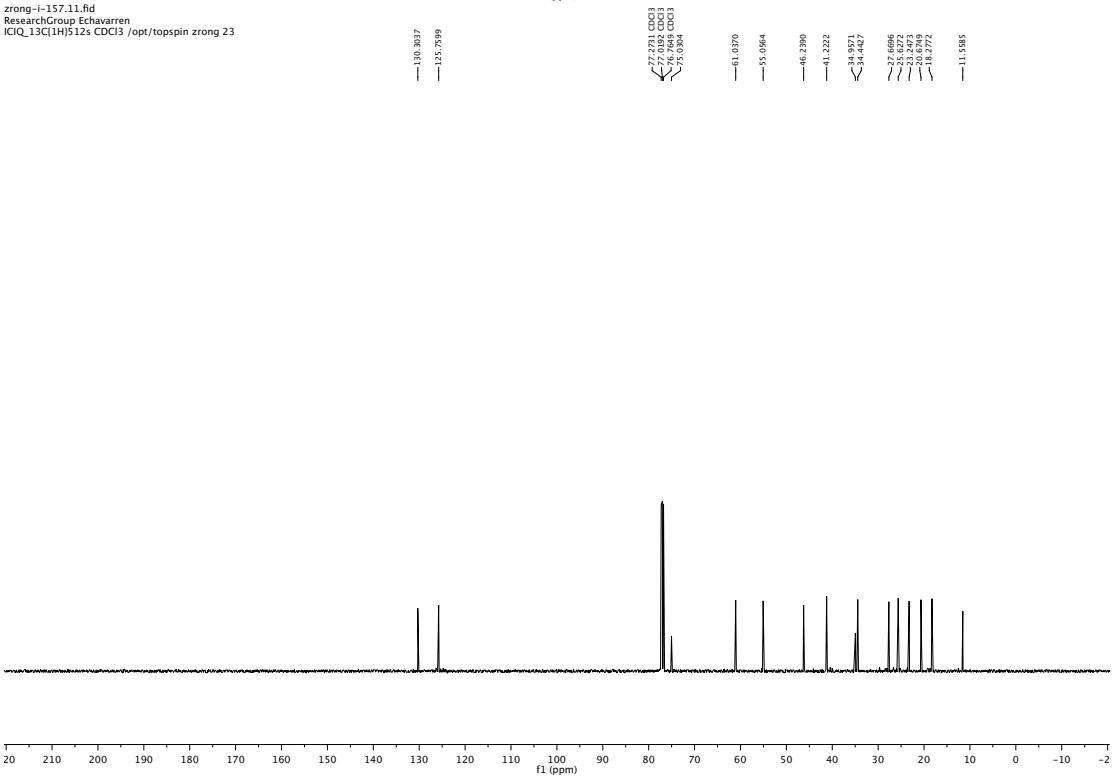
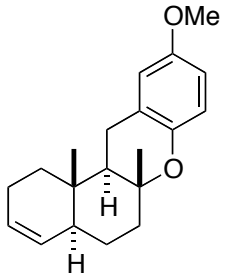
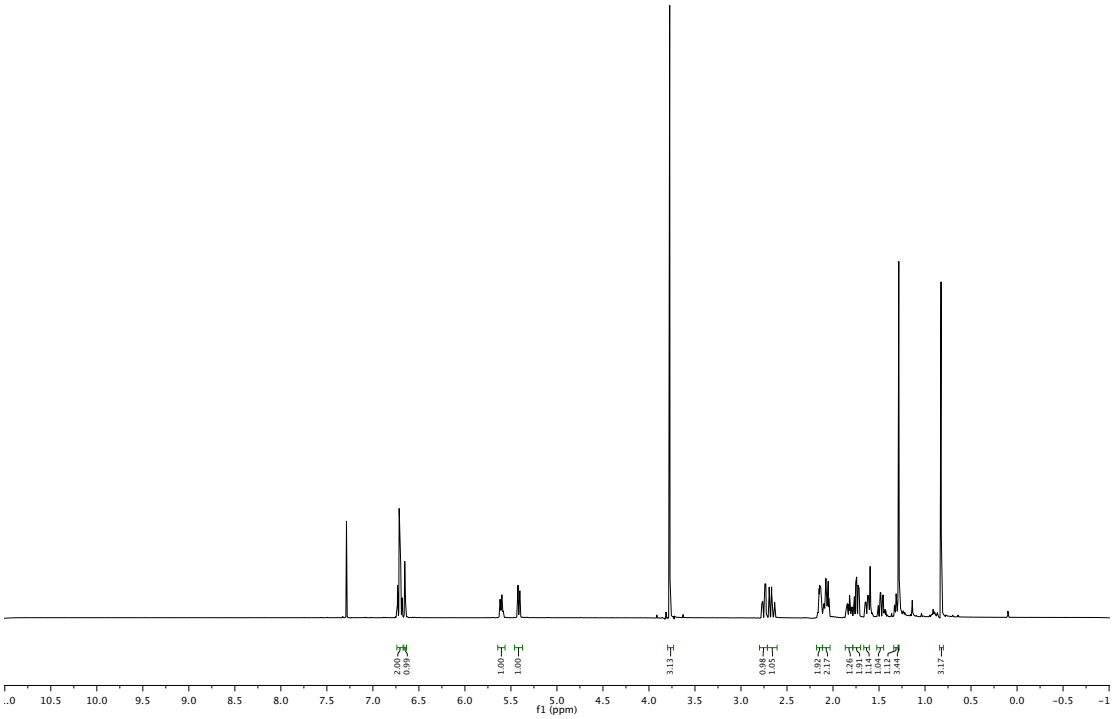
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 23





10k

zrong-i-53s.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 50



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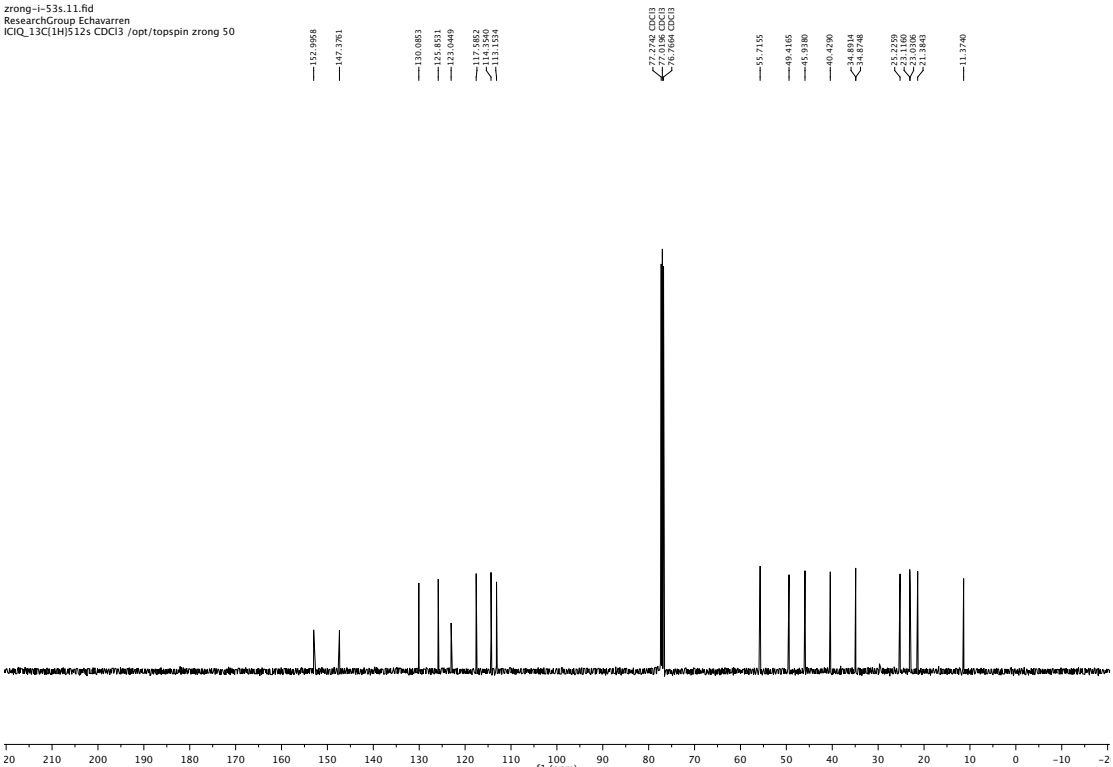
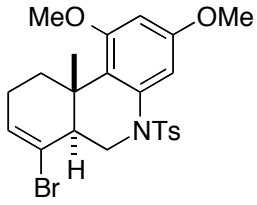
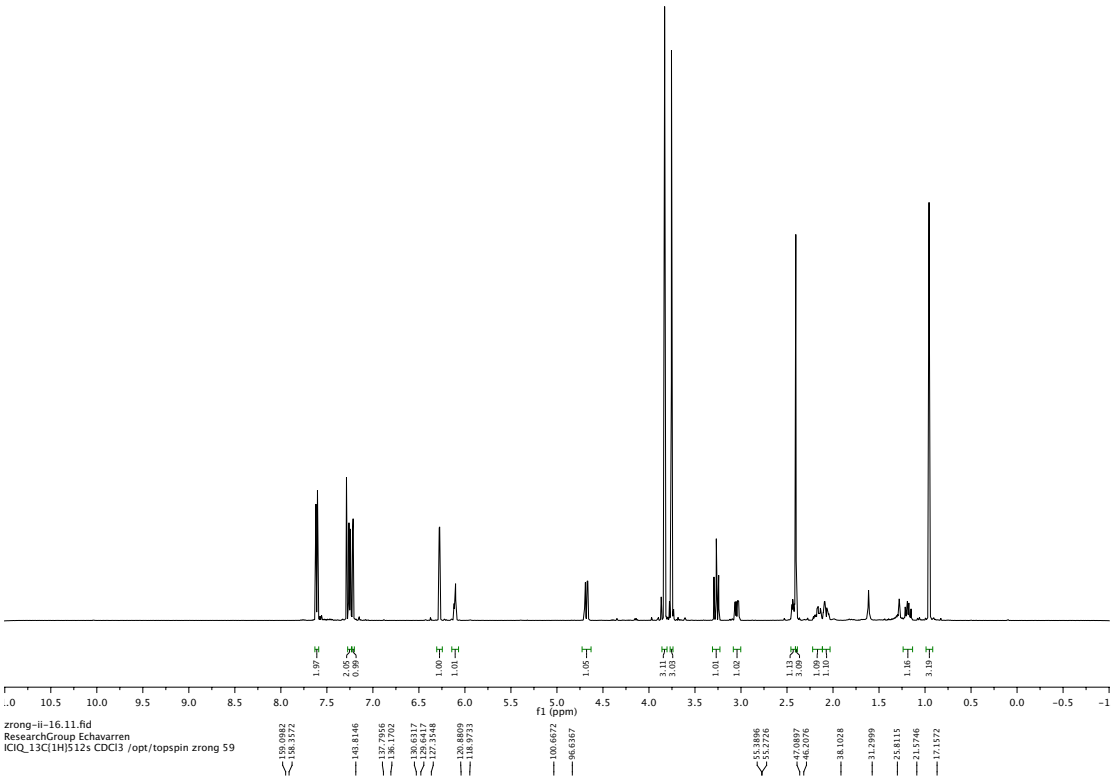
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 50





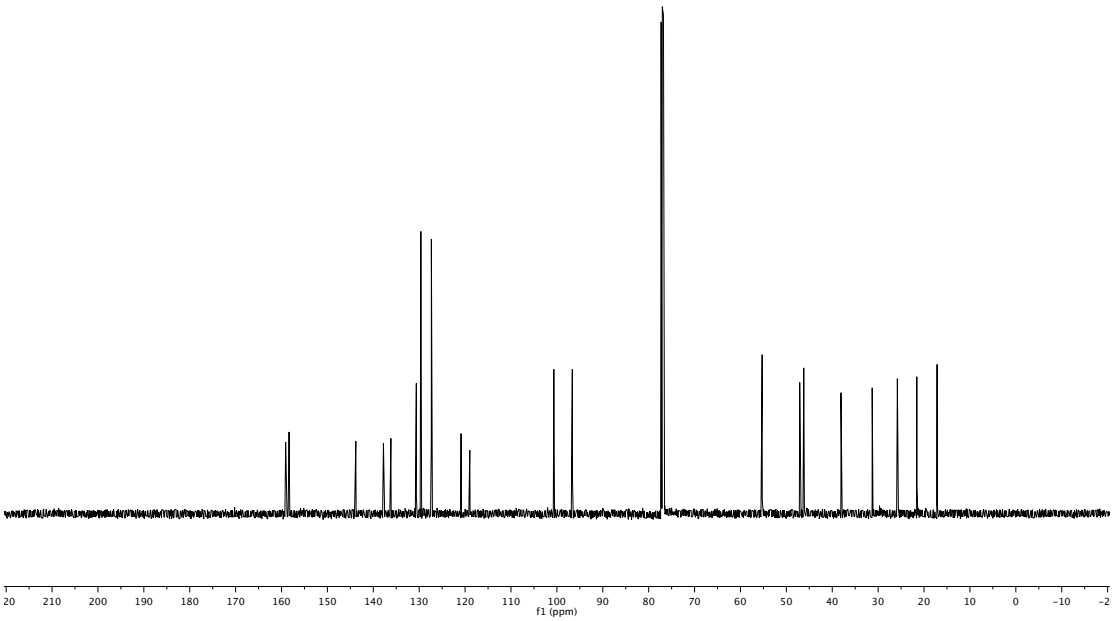
10l

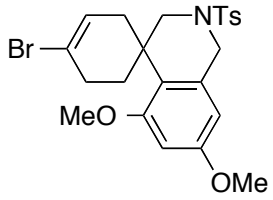
zrong-ii-16.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 59



zrong-ii-16.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 59

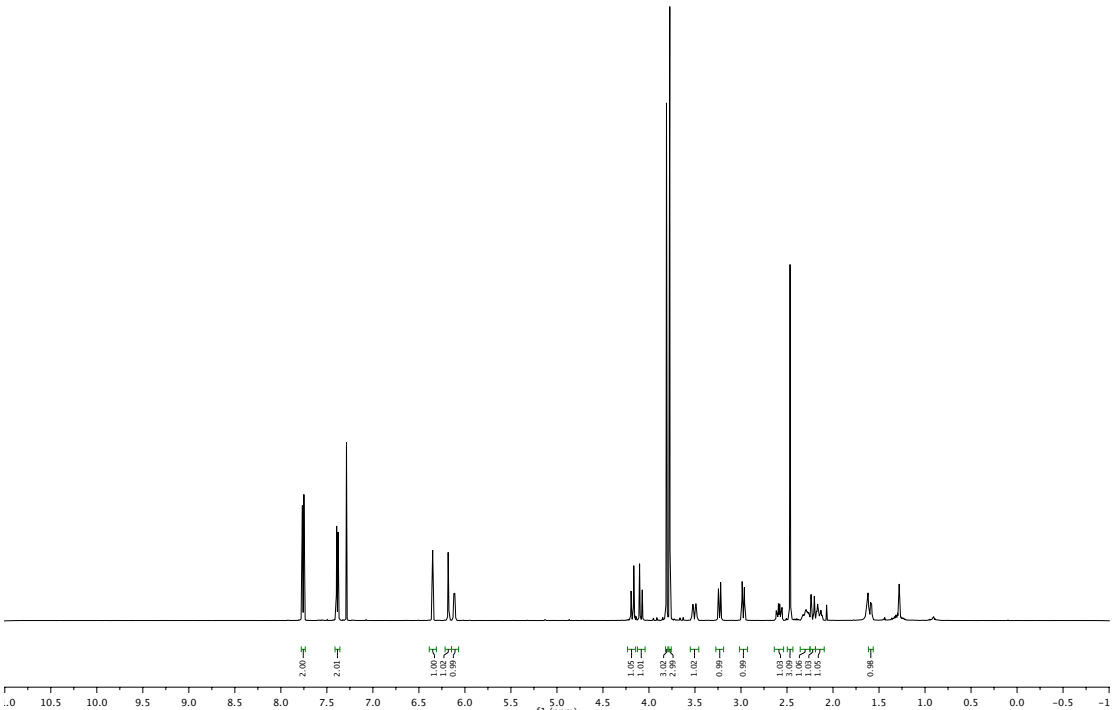
159.0982
158.3572
143.8146
137.7955
136.1702
130.6317
130.4477
127.3548
120.8809
118.9733
100.6672
96.6367
55.3896
55.2726
47.0897
46.2076
38.1028
31.2999
25.8115
21.5746
17.1572





10m

zrong-ii-18b.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 47



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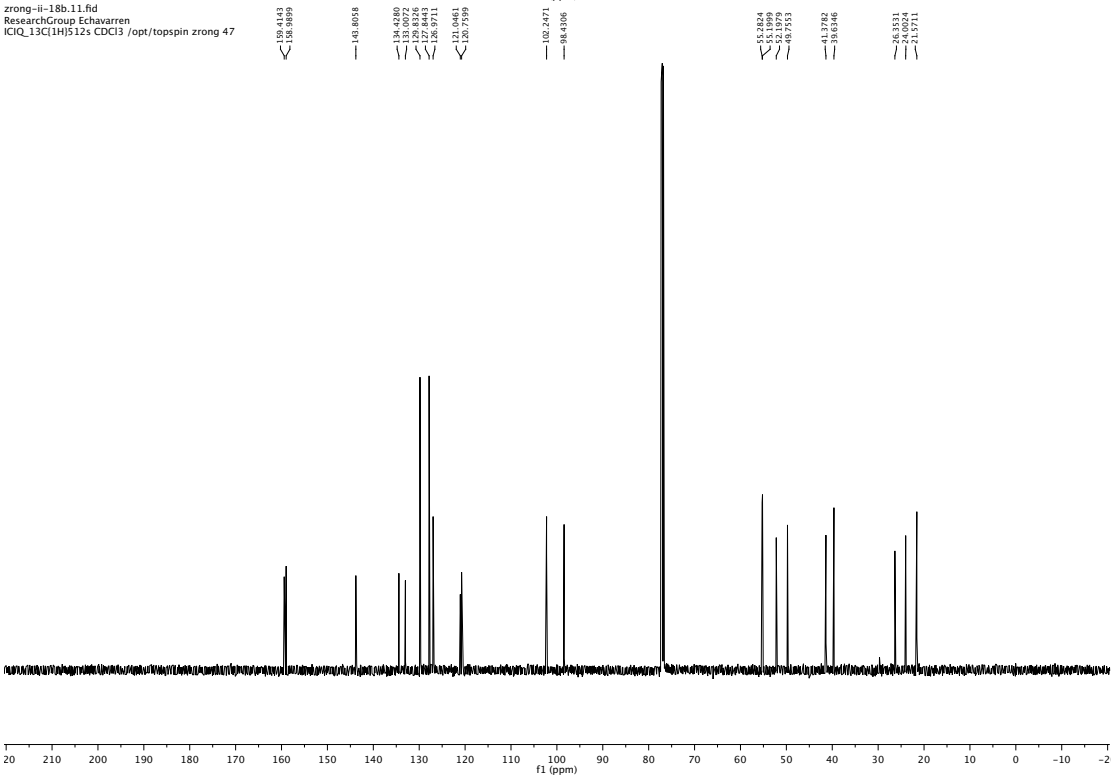
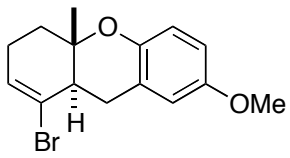
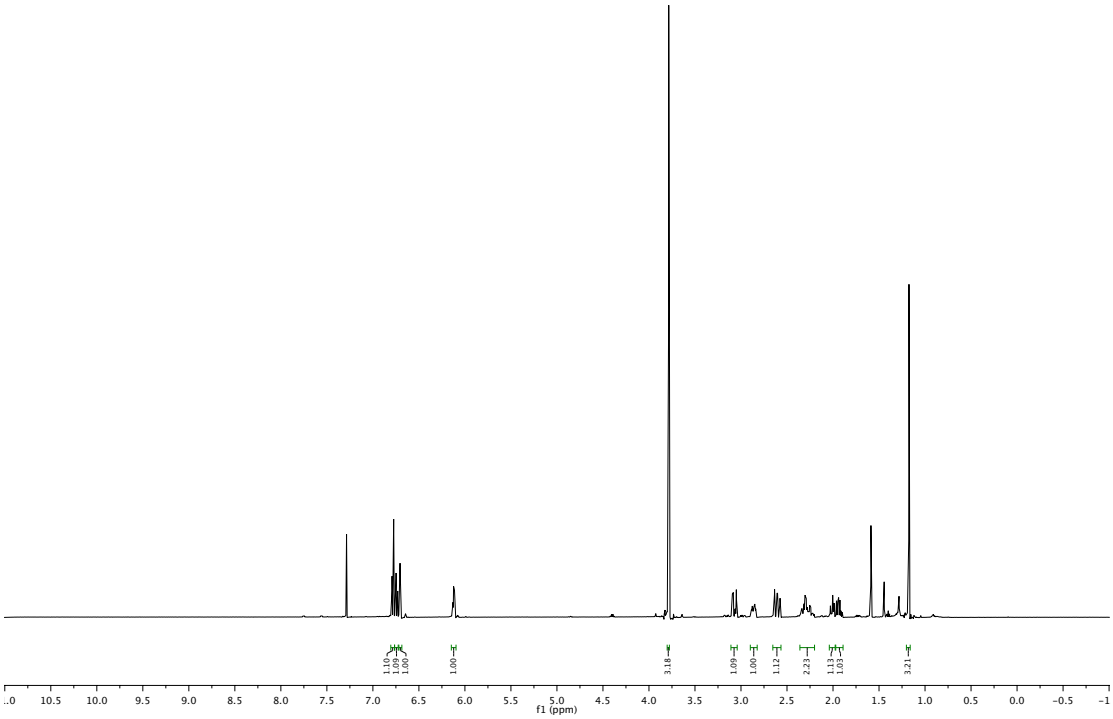
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 47





10n

zrong-ii-161.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 57



zrong-ii-161.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 57

153.2987
147.1383
129.1153
123.7002
122.4847
117.7810
114.1825
114.0112
76.0060
55.7099
45.0029
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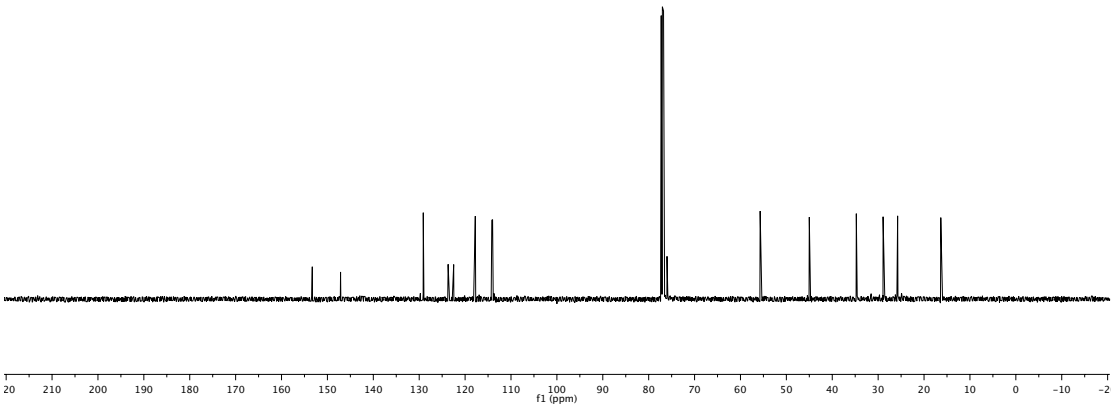

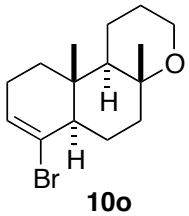

10o

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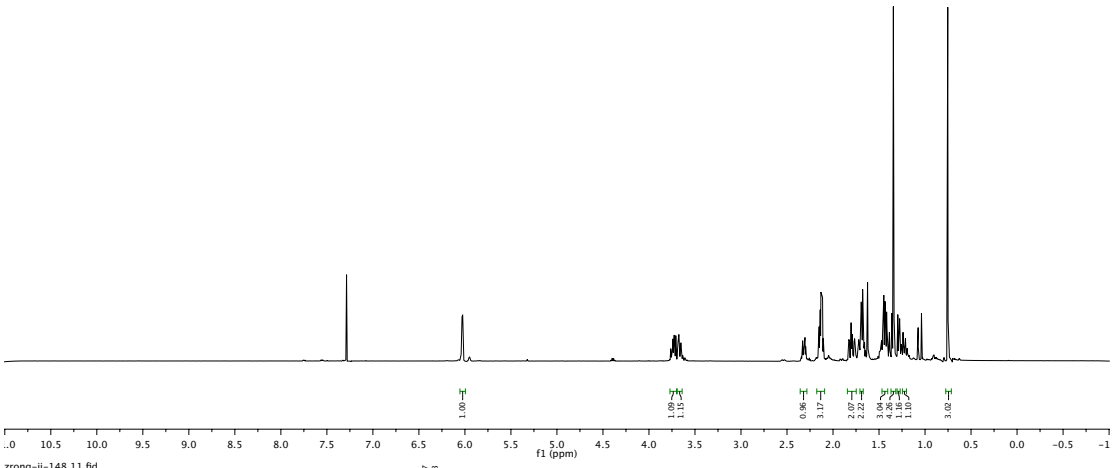
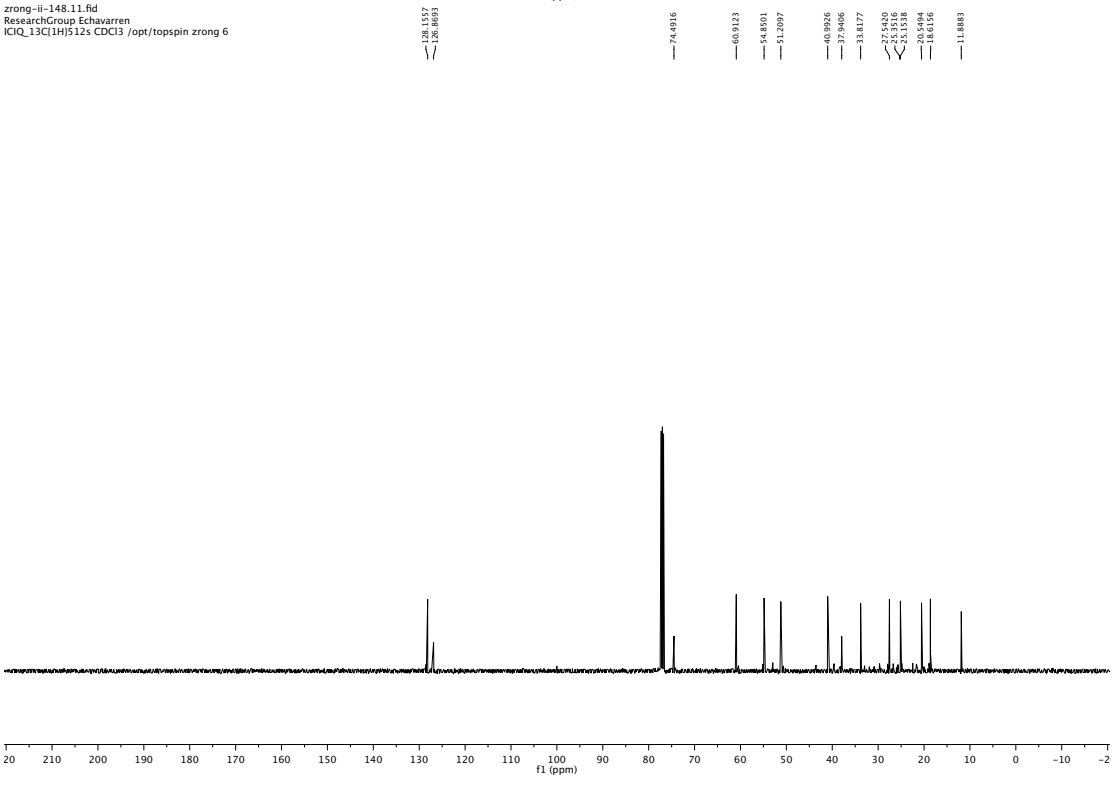
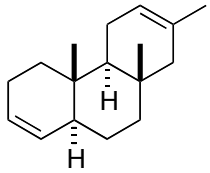
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 6



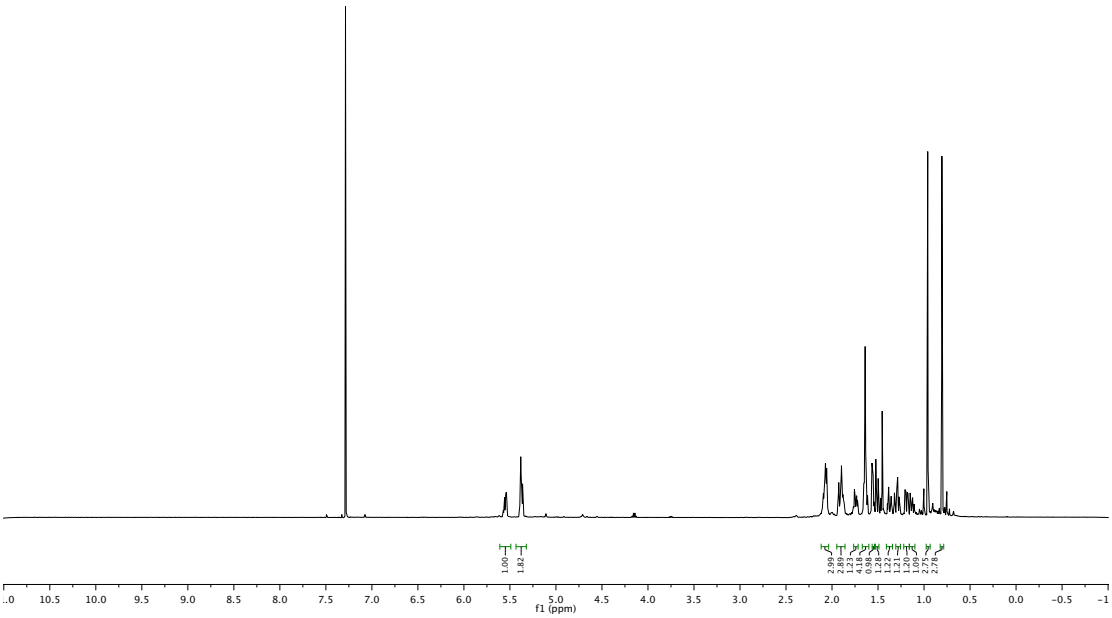
zrong-ii-148.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 6



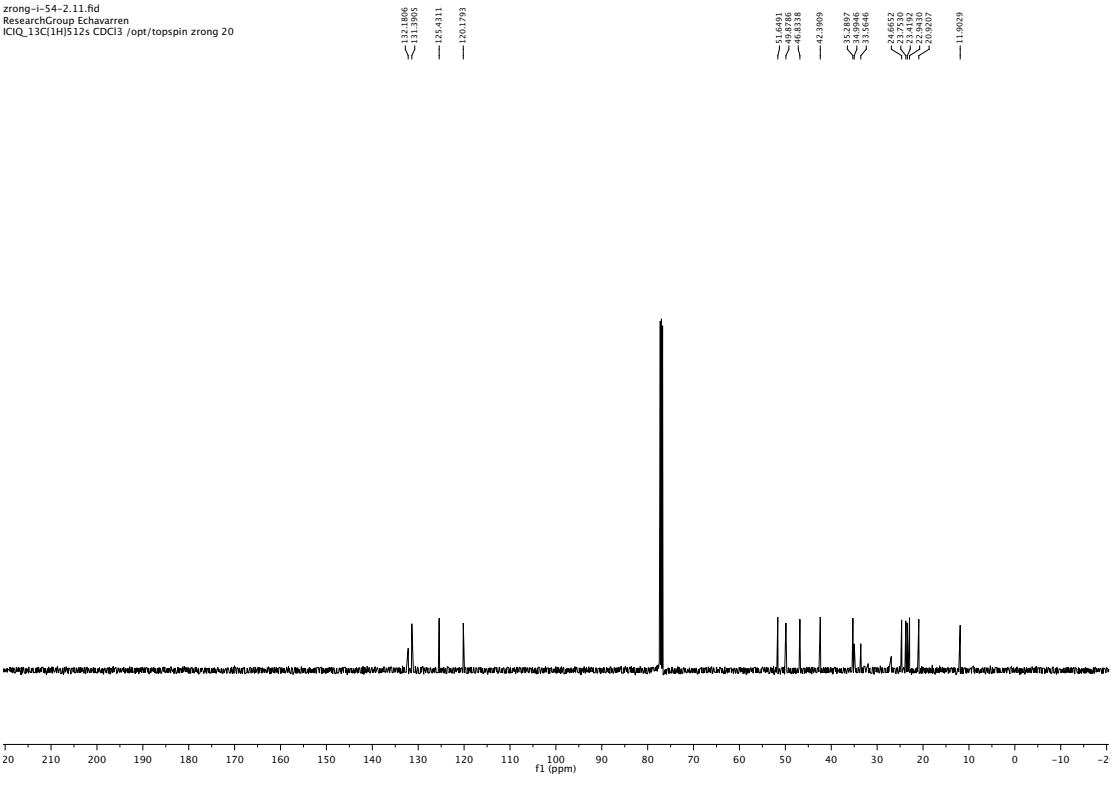


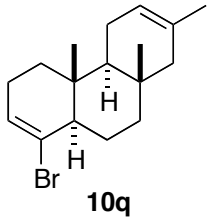
10p

zrong-i-54-2.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 20



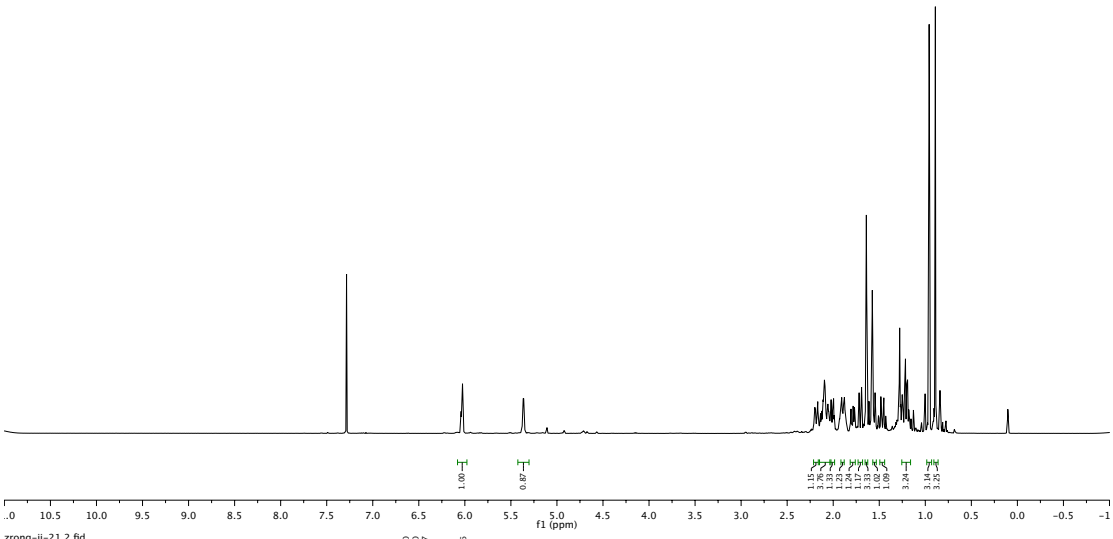
zrong-i-54-2.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 20





10q

zrong-ii-21.1.fid
1H Experiment



zrong-ii-21.2.fid
13C{1H} Experiment

132.2580
128.2710
127.9977
119.8896
52.0813
51.1081
49.8825
42.1017
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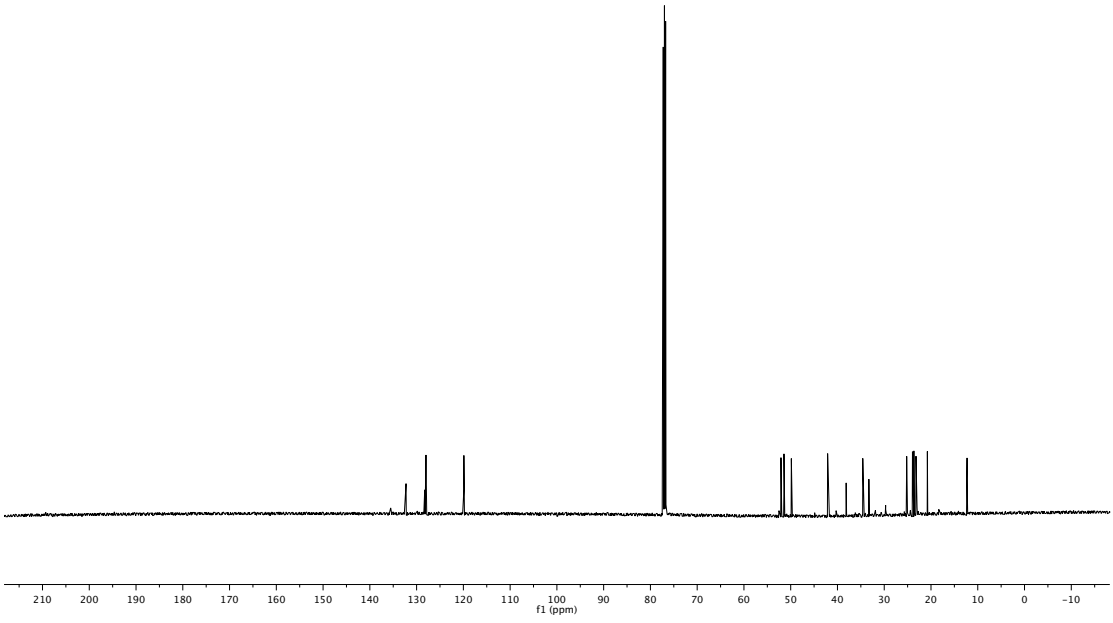
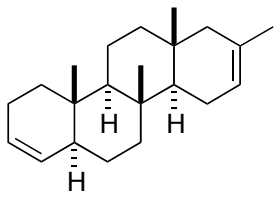
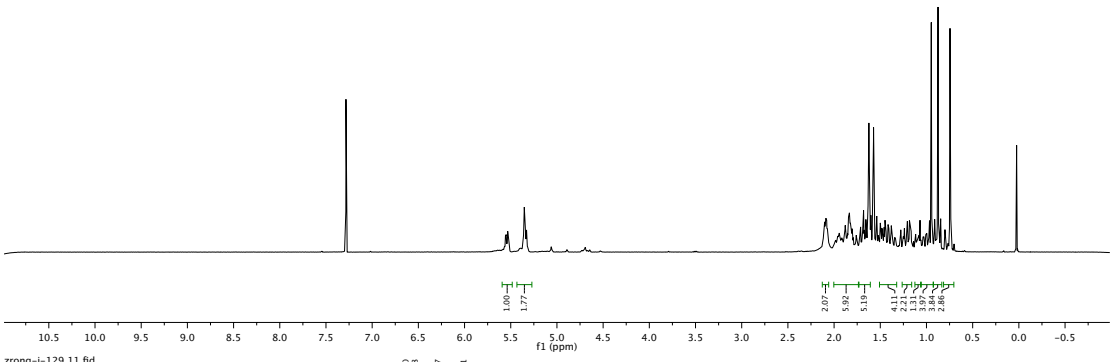
34.5882
33.2852
25.1957
23.9610
23.6579
23.3963
20.7739
12.2855



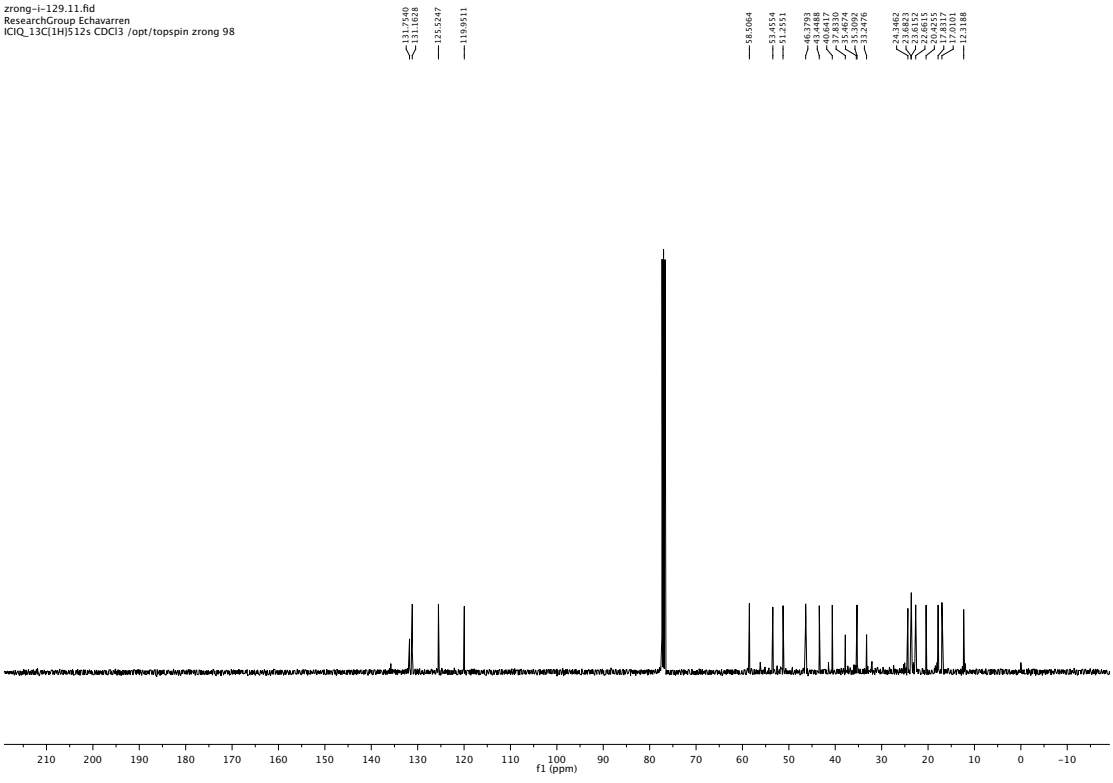


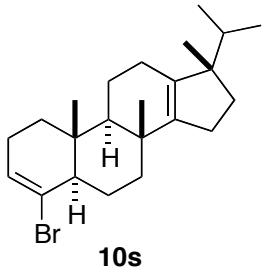
10r

zrong-i-129.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 98



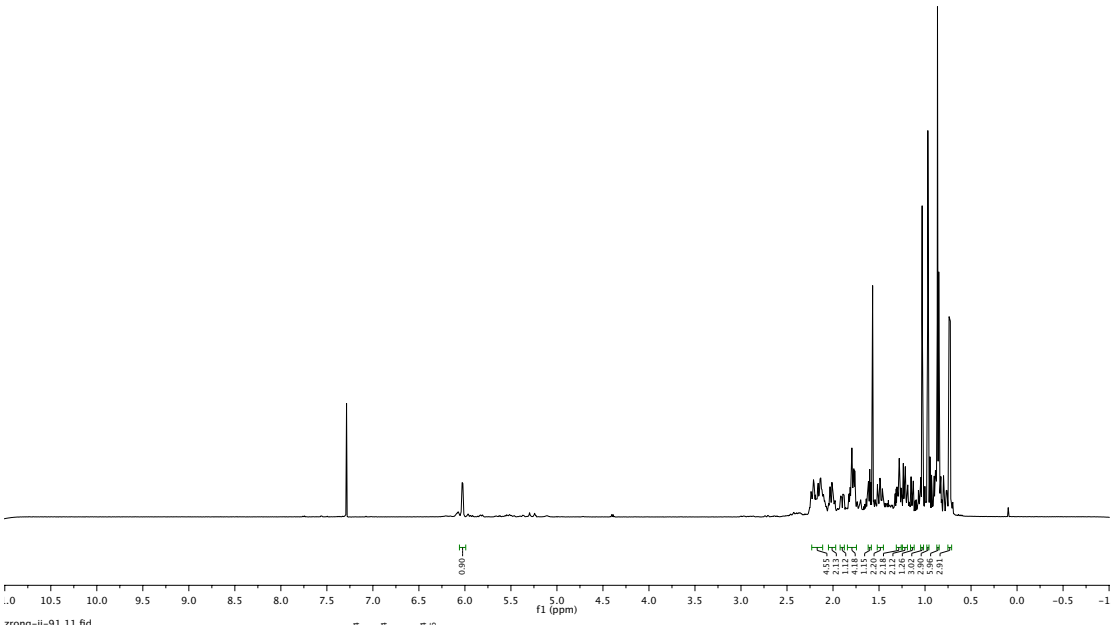
zrong-i-129.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 98





10s

zrong-ii-91.10.fid
ResearchGroup Echavarren
ICIQ_1H12p8s CDCl3 /opt/topspin zrong 1



zrong-ii-91.11.fid
ResearchGroup Echavarren
ICIQ_13C{1H}512s CDCl3 /opt/topspin zrong 1