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Enantioselective Nickel-Catalyzed *anti*-Arylmetallative Cyclizations onto Acyclic Electron-Deficient Alkenes

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Contents

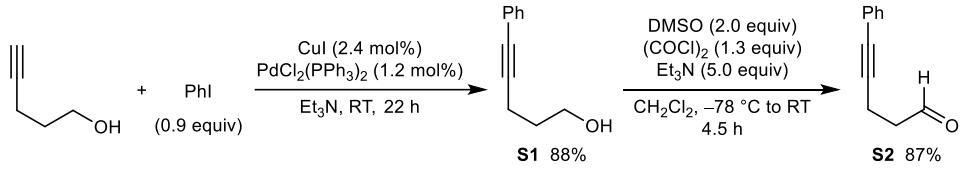
1. General Information

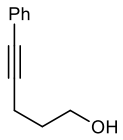
All air-sensitive reactions were carried out under an inert atmosphere using oven-dried apparatus. 2,2,2-Trifluoroethanol (TFE) was purchased from Fluorochem and degassed before use using a stream of argon gas (20 min). All commercially available reagents were used as received unless otherwise stated. Petroleum ether refers to Sigma-Aldrich product 24587 (petroleum ether boiling point 40−60 °C). Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron or Fluorochem 60 Å particle size 40-63 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on Bruker platinum alpha FTIR spectrometer on the neat compound using the attenuated total reflectance technique. NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent (^{1}H) or the solvent itself (^{13}C). ^{19}F NMR spectra were referenced through the solvent lock (^{2}H) signal according to the IUPAC-recommended secondary referencing method following Bruker protocols. All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.26 ppm for ^{1}H NMR spectroscopy and 77.16 ppm for ^{13}C NMR spectroscopy. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. High-resolution mass spectra were recorded using electrospray ionization (ESI) techniques. X-ray diffraction data were collected at 120 K on an Agilent SuperNova diffractometer using CuKα radiation. Solvents (THF, CH_2Cl_2, $CHCl_3$, toluene, Et_3N and DMF) were freshly degassed (20 min with a stream of argon). Ligands **L1**[1] and **L3**[2] was prepared according to a literature procedure. 2-[2-(Diphenylphosphino)ethyl]pyridine (**L2**) or racemic Ph-PHOX[3] were used as achiral ligands to prepare authentic racemic products for obtaining chiral HPLC assays.

2. Preparation of Substrates for Arylative Cyclizations onto Electron-Deficient Alkenes

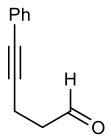
2.1 Preparation of Key Intermediates

5-Phenylpent-4-ynal (S2)



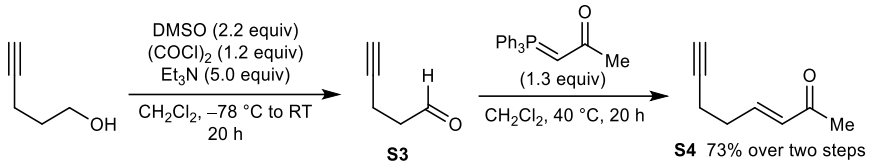


5-Phenylpent-4-yn-1-ol (S1).[4] To a solution of iodobenzene (5.4 mL, 48.0 mmol) in Et_3N (80 mL) under an argon atmosphere at room temperature was added $PdCl_2(PPh_3)_2$ (337 mg, 0.480 mmol) and CuI (183 mg, 0.960 mmol) and the mixture was stirred for 5 min. To the solution was added 4-pentyn-1-ol (3.7 mL, 40.0 mmol) slowly and the reaction was stirred at room temperature for 22 h. The volatiles were removed *in vacuo* and saturated aqueous $NaHCO_3$ (150 mL) was added to the resulting slurry. The mixture was extracted with EtOAc (3 × 100 mL) and the combined organic layers were washed with brine (150 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by automated column chromatography (70% Et_2O/pet. ether) to give the alkyne **S1** (5.61 g, 88%) as a brown oil. The analytical data were consistent with those reported previously.[4]



5-Phenylpent-4-ynal (S2).[5] To a solution of $(COCl)_2$ (1.4 mL, 16.2 mmol) in CH_2Cl_2 (40 mL) at −78 °C was added DMSO (1.8 mL, 25.0 mmol) dropwise over 4 min and the solution was stirred at this temperature for 30 min. A solution of 5-phenylpent-4-yn-1-ol **S1** (2.00 g, 12.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min and the mixture was stirred at −78 °C for 2 h. Et_3N (8.7 mL, 62.4 mmol) was added and the mixture was warmed to room temperature and stirred for 2 h. The reaction was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were washed with 2 M HCl (30 mL), saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (30% EtOAc/pet. ether) to give the aldehyde **S2** (1.72 g, 87%) as an orange oil. The analytical data were consistent with those reported previously.[5]

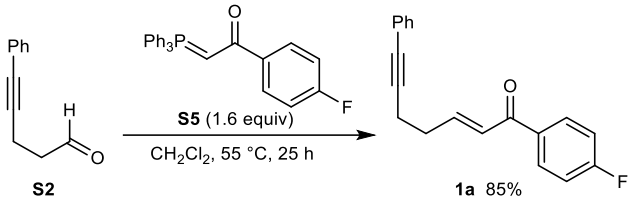
(*E*)-Oct-3-en-7-yn-2-one (S4)[6]



To a solution of $(COCl)_2$ (2.9 mL, 34.5 mmol) in CH_2Cl_2 (65 mL) at −78 °C was added a solution of DMSO (4.6 mL, 65.4 mmol) in CH_2Cl_2 (15 mL) dropwise over 8 min and the solution was stirred at −78 °C for 30 min. A solution of 4-pentyn-1-ol (2.50 g, 29.7 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min and the mixture was stirred at −78 °C for 1 h. Et_3N (20.7 mL, 149 mmol) was added and the mixture was warmed to room temperature and stirred for 20 h. The reaction was diluted with H_2O (15 mL) and the two layers were separated. The aqueous layer was acidified with 1 M HCl and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were washed with 1% HCl saturated with NaCl (50 mL), 5% aqueous $NaHCO_3$ (50 mL), H_2O (75 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and gently concentrated *in vacuo* until *ca.* 5 mL of intermediate **S3** remained. The residue was diluted in CH_2Cl_2 (40 mL) and 1-(triphenylphosphoranylidene)-2-propanone (12.3 g, 38.6 mmol) was added and the reaction was stirred at 40 °C for 20 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (20% EtOAc/pet. ether) to give the enone **S4** (2.66 g, 73% over two steps) as an orange oil. The analytical data were consistent with those reported previously.[6]

2.2 Preparation of Final Arylative Cyclization Precursors

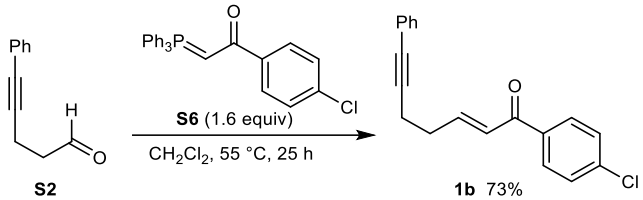
(*E*)-1-(4-Fluorophenyl)-7-phenylhept-2-en-6-yn-1-one (1a)



To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (15 mL) under an argon atmosphere at 55 °C was added the phosphorane **S5**[7] (2.02 g, 5.06 mmol) and the reaction was stirred at 55 °C for 25 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (10% EtOAc/pet. ether) to give the enone **1a** (744 mg, 85%) as a yellow solid. R_f = 0.69 (40% EtOAc/pet. ether); m.p. 58−59 °C (Et_2O); IR 3062, 2912, 1670 (C=O), 1621, 1596, 1505, 1489, 1227, 1155, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03-7.93 (2H, m, Ar**H**), 7.42-7.34 (2H, m, Ar**H**), 7.31-7.26 (3H, m, Ar**H**), 7.15-7.06 (3H, m, 2 × Ar**H** and CH_2C**H**=), 6.98 (1H, d, *J* = 15.4 Hz, CH_2CH=C**H**), 2.69-2.59 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (C), 165.7 (d, $J_{C\text{-}F}$

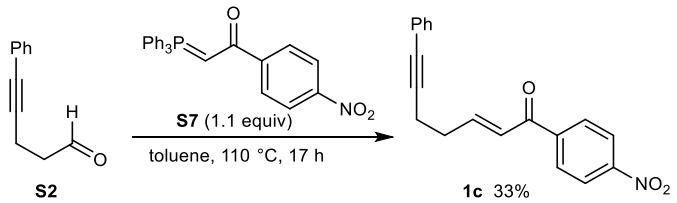
= 254.0 Hz, C), 147.2 (CH), 134.3 (d, $J_{C\text{-}F}$ = 2.9 Hz, C), 131.7 (2 × CH), 131.3 (d, $J_{C\text{-}F}$ = 9.5 Hz, 2 × CH), 128.4 (2 × CH), 128.0 (CH), 126.9 (CH), 123.6 (C), 115.8 (d, $J_{C\text{-}F}$ = 21.9 Hz, 2 × CH), 88.5 (C), 82.0 (C), 32.0 (CH_2), 18.7 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –105.7 (s); HRMS (ESI) Exact mass calculated for $[C_{19}H_{15}OFNa]^+$ $[M+Na]^+$: 301.0999, found 301.0994.

(*E*)-1-(4-Chlorophenyl)-7-phenylhept-2-en-6-yn-1-one (1b)



To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (15 mL) under an argon atmosphere at 55 °C was added the phosphorane **S6**[8] (2.10 g, 5.06 mmol) and the reaction was stirred at 55 °C for 25 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (10% EtOAc/pet. ether) to give the enone **1b** (682 mg, 73%) as an orange solid. R_f = 0.69 (40% EtOAc/pet. ether); m.p. 68−69 °C (Et_2O); IR 3056, 2924, 1666 (C=O), 1615, 1586, 1488, 1090, 818, 754, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.79 (2H, m, Ar**H**), 7.52-7.31 (4H, m, Ar**H**), 7.31-7.26 (3H, m, Ar**H**), 7.12 (1H, dt, *J* = 15.5, 6.4 Hz, CH_2C**H**=), 6.96 (1H, dt, *J* = 15.5, 1.3 Hz, CH_2CH=C**H**), 2.72-2.56 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6 (C), 147.6 (CH), 139.3 (C), 136.2 (C), 131.7 (2 × CH), 130.2 (2 × CH), 129.0 (2 × CH), 128.4 (2 × CH), 128.0 (CH), 126.9 (CH), 123.6 (C), 88.4 (C), 82.1 (C), 32.0 (CH_2), 18.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{15}OClNa]^+$ $[M+Na]^+$: 317.0704, found 317.0704.

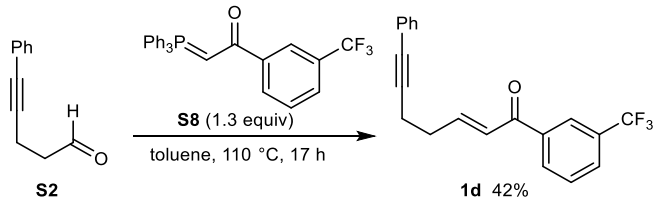
(*E*)-1-(4-Nitrophenyl)-7-phenylhept-2-en-6-yn-1-one (1c)



To a mixture of aldehyde **S2** (273 mg, 1.72 mmol) and the phosphorane **S7**[9] (807 mg, 1.90 mmol) under an argon atmosphere was added toluene (17 mL) and the reaction was stirred at 110 °C for 17 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (15% EtOAc/pentane) to give the enone **1c** (173 mg, 33%) as an orange solid. R_f = 0.53 (30% EtOAc/pet. ether); m.p. 84–85 °C (Et_2O); IR 3083, 2912, 1670 (C=O), 1615, 1599, 1517, 1489, 1347, 1268, 1212 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.21 (2H, m, Ar**H**), 8.09-8.02 (2H, m, Ar**H**), 7.41-7.35 (2H, m, Ar**H**), 7.33-7.27 (3H, m, Ar**H**), 7.21-7.12 (1H, m, CH_2C**H**=), 6.97 (1H, d, *J* = 15.5 Hz, CH_2CH=C**H**), 2.74-2.59 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 189.5 (C), 150.2 (C),

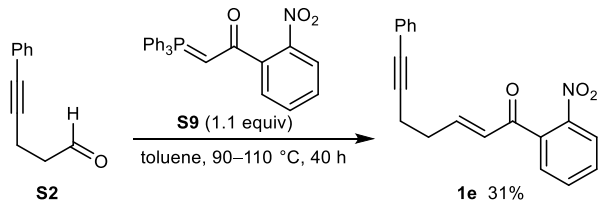
149.5 (CH), 142.8 (C), 131.7 (2 × CH), 129.7 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 127.0 (CH), 123.9 (2 × CH), 123.5 (C), 88.2 (C), 82.3 (C), 32.0 (CH_2), 18.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{15}NO_3Na]^+$ $[M+Na]^+$: 328.0944, found: 328.0959.

(*E*)-7-Phenyl-1-(3-(trifluoromethyl)phenyl)hept-2-en-6-yn-1-one (1d)



To a mixture of aldehyde **S2** (233 mg, 1.47 mmol) and the phosphorane **S8**[10] (857 mg, 1.91 mmol) under an argon atmosphere was added toluene (10 mL) and the reaction was stirred at 110 °C for 17 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (7% EtOAc/pet. ether) followed by a second purification by column chromatography (40% CH_2Cl_2/pet. ether) to give the enone **1d** (204 mg, 42%) as a yellow oil. R_f = 0.59 (30% EtOAc/pet. ether); IR 3065, 2918, 1674 (C=O), 1624, 1490, 1330, 1165, 1123, 1070, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, s, Ar**H**), 8.11 (1H, app dt, *J* = 7.8, 1.4, Hz, Ar**H**), 7.81 (1H, dd, *J* = 7.8, 1.7 Hz, Ar**H**), 7.58 (1H, app t, *J* = 7.8 Hz, Ar**H**), 7.43-7.34 (2H, m, Ar**H**), 7.31-7.26 (3H, m, Ar**H**), 7.21-7.13 (1H, m, CH_2C**H**=), 7.04-6.96 (1H, m, CH_2CH=C**H**), 2.74-2.60 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.4 (C), 148.6 (CH), 138.5 (C), 131.9 (CH), 131.7 (2 × CH), 131.3 (q, $J_{C\text{-}F}$ = 33.1 Hz, C), 129.34 (CH), 129.27 (q, $J_{C\text{-}F}$ = 3.6 Hz, CH), 128.4 (2 × CH), 128.0 (CH), 126.6 (CH), 125.5 (q, $J_{C\text{-}F}$ = 3.7 Hz, CH), 123.9 (q, $J_{C\text{-}F}$ = 272.5 Hz, C), 123.6 (C), 88.3 (C), 82.1 (C), 32.1 (CH_2), 18.6 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 (s, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{20}H_{15}OF_3Na]^+$ $[M+Na]^+$: 351.0967, found 351.0969.

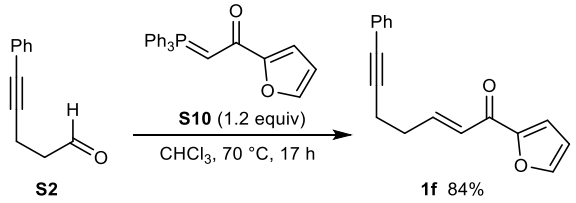
(*E*)-1-(2-Nitrophenyl)-7-phenylhept-2-en-6-yn-1-one (1e)



To a mixture of aldehyde **S2** (300 mg, 1.90 mmol) and the phosphorane **S9**[11] (887 mg, 2.09 mmol) under an argon atmosphere was added toluene (10 mL) and the reaction was stirred at 90 °C for 16 h and then at 110 °C for 24 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (15 to 20% EtOAc/pet. ether) to give the enone **1e** (178 mg, 31%) as a red oil. R_f = 0.19 (20% EtOAc/pet. ether); IR 3034, 2924, 1664 (C=O), 1625, 1528, 1489, 1347, 1286, 757, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, d, *J* = 8.2 Hz, Ar**H**), 7.69 (1H, app t, *J* = 7.5

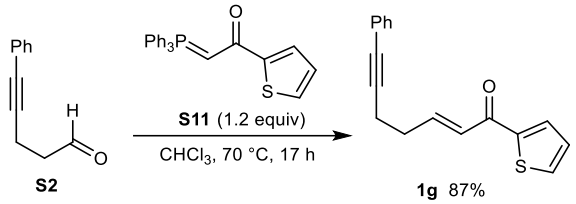
Hz, Ar**H**), 7.60 (1H, app t, *J* = 7.8 Hz, Ar**H**), 7.43 (1H, d, *J* = 7.5 Hz, Ar**H**), 7.39-7.31 (2H, m, Ar**H**), 7.31-7.26 (3H, m, Ar**H**), 6.71-6.39 (2H, m, C**H**=C**H**), 2.65-2.46 (4H, m, C$\mathbf{H}_2$C$\mathbf{H}_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0 (C), 149.2 (CH), 146.9 (C), 136.3 (C), 134.0 (CH), 131.7 (2 × CH), 131.5 (CH), 130.6 (CH), 129.0 (CH), 128.4 (2 × CH), 128.0 (CH), 124.5 (CH), 123.5 (C), 87.9 (C), 82.1 (C), 31.7 (CH_2), 18.5 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{15}NO_3Na]^+$ $[M+Na]^+$: 328.0944, found 328.0945.

(*E*)-1-(Furan-2-yl)-7-phenylhept-2-en-6-yn-1-one (1f)



A solution of aldehyde **S2** (300 mg, 1.90 mmol) and the phosphorane **S10**[12] (843 mg, 2.28 mmol) in $CHCl_3$ (7 mL) under an argon atmosphere at 70 °C was stirred for 17 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (15% EtOAc/pet. ether) to give the enone **1f** (401 mg, 84%) as a brown solid. R_f = 0.35 (30% EtOAc/pet. ether); m.p. 50−51 °C (Et_2O); IR 3120, 2897, 2220 (C≡C), 1654 (C=O), 1615, 1603, 1556, 1463, 1396, 1274 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, d, *J* = 1.7 Hz, Ar**H**), 7.42-7.34 (2H, m, Ar**H**), 7.30-7.25 (3H, m, Ar**H**), 7.25-7.17 (2H, m, CH_2C**H**= and Ar**H**), 6.92 (1H, dt, *J* = 15.6, 1.5 Hz, CH_2CH=C**H**), 6.55 (1H, dd, *J* = 3.6, 1.7 Hz, Ar**H**), 2.68-2.57 (4H, m, C$\mathbf{H}_2$C$\mathbf{H}_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1 (C), 153.4 (C), 146.7 (CH), 146.5 (CH), 131.7 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 126.1 (CH), 123.7 (C), 117.8 (CH), 112.5 (CH), 88.5 (C), 81.9 (C), 32.0 (CH_2), 18.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{17}H_{14}O_2Na]^+$ $[M+Na]^+$: 273.0886, found: 273.0886.

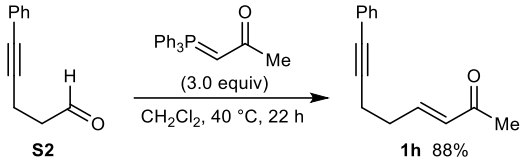
(*E*)-7-Phenyl-1-(thiophen-2-yl)hept-2-en-6-yn-1-one (1g)



A solution of aldehyde **S2** (400 mg, 2.53 mmol) and the phosphorane **S11**[13] (1.17 g, 3.03 mmol) in $CHCl_3$ (9 mL) under an argon atmosphere at 70 °C was stirred for 17 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (15% EtOAc/pet. ether) to give the enone **1g** (586 mg, 87%) as an orange solid. R_f = 0.50 (30% EtOAc/pet. ether); m.p. 65−66 °C (Et_2O); IR 3074, 2923, 1654 (C=O), 1598, 1512, 1489, 1414, 1354, 1234, 969 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* = 3.7 Hz, Ar**H**), 7.65 (1H, d, *J* = 4.9 Hz, Ar**H**), 7.43-7.34 (2H, m, Ar**H**), 7.29-

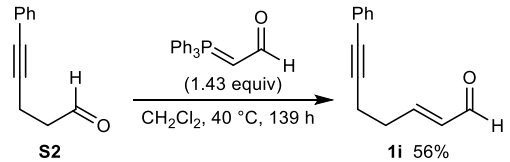
7.25 (3H, m, Ar**H**), 7.22-7.09 (2H, m, Ar**H** and CH_2C**H**=), 6.92 (1H, d, *J* = 15.3 Hz, CH_2CH=C**H**), 2.70-2.57 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3 (C), 146.4 (CH), 145.2 (C), 134.0 (CH), 132.2 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 127.9 (CH), 126.6 (CH), 123.7 (C), 88.5 (C), 81.9 (C), 31.9 (CH_2), 18.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{17}H_{14}OSNa]^+$ $[M+Na]^+$: 289.0658, found: 289.0659.

(*E*)-8-Phenyloct-3-en-7-yn-2-one (1h)



To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (10 mL) under an argon atmosphere at 40 °C was added 1-(triphenylphosphoranylidene)-2-propanone (3.02 g, 9.48 mmol) and the reaction was stirred at 40 °C for 22 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (15% EtOAc/pet. ether) to give the enone **1h** (549 mg, 88%) as a yellow oil. R_f = 0.46 (40% EtOAc/pet. ether); IR 3047, 2924, 2237 (C≡C), 1671 (C=O), 1627, 1490, 1359, 1159, 971, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (2H, m, Ar**H**), 7.31-7.25 (3H, m, Ar**H**), 6.87 (1H, dt, *J* = 16.1, 6.5 Hz, CH_2C**H**=), 6.17 (1H, dt, *J* = 16.1, 1.4 Hz, CH_2CH=C**H**), 2.62-2.56 (2H, m, C**H**$_2$), 2.56-2.49 (2H, m, C**H**$_2$), 2.27 (3H, s, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.5 (C), 145.8 (CH), 132.3 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.0 (CH), 123.6 (C), 88.2 (C), 81.9 (C), 31.7 (CH_2), 27.1 (CH_3), 18.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{14}H_{14}ONa]^+$ $[M+Na]^+$: 221.0937, found: 221.0937.

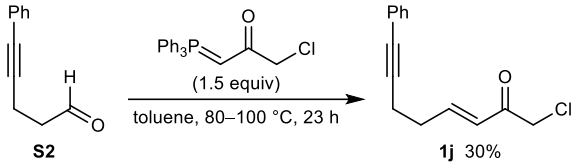
(*E*)-7-Phenylhept-2-en-6-ynal (1i)



To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (5 mL) under an argon atmosphere at 40 °C was added a solution of (triphenylphosphoranylidene)acetaldehyde (1.09 g, 3.57 mmol) in CH_2Cl_2 (6 mL) in 6 portions over 50 min and the reaction was stirred at 40 °C for 70 h. An additional portion of the phosphorane (289 mg, 0.948 mmol) in CH_2Cl_2 (3 mL) was added to the reaction and stirring was continued at 40 °C for 69 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (10% EtOAc/pet. ether) to give the enal **1i** (326 mg, 56%) as a yellow oil. R_f = 0.44 (30% EtOAc/pet. ether); IR 3034, 2912, 2817, 2742, 1684 (C=O), 1489, 1123, 1012, 755, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (1H, d, *J* = 7.8 Hz, C**H**=O), 7.41-7.36 (2H,

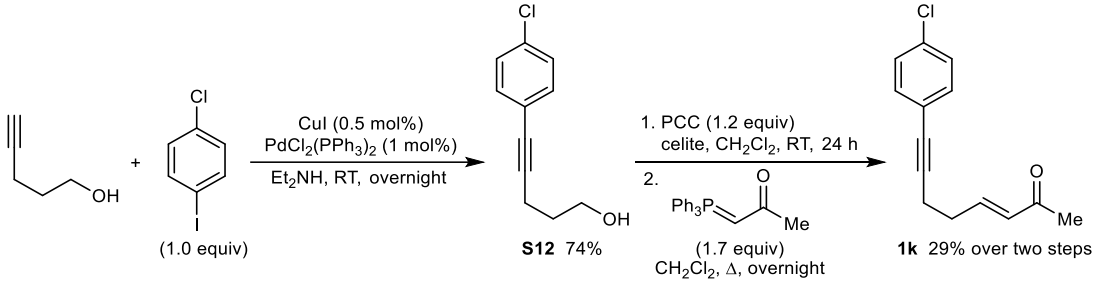
m, Ar**H**), 7.31-7.27 (3H, m, Ar**H**), 7.00-6.85 (1H, m, CH_2C**H**=), 6.23 (1H, dd, *J* = 15.6, 7.8 Hz, CH_2CH=C**H**), 2.69-2.59 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9 (C), 156.0 (CH), 133.9 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.1 (CH), 123.4 (C), 87.8 (C), 82.1 (C), 31.9 (CH_2), 18.4 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{13}H_{12}ONa]^+$ $[M+Na]^+$: 207.0780, found 207.0793.

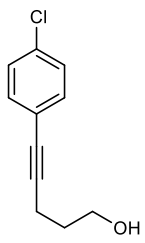
(*E*)-1-Chloro-8-phenyloct-3-en-7-yn-2-one (1j)



To a mixture of aldehyde **S2** (500 mg, 3.16 mmol) and 1-chloro-3-(triphenyl-λ5-phosphanylidene)propan-2-one[14] (1.67 g, 4.74 mmol) under an argon atmosphere was added toluene (15 mL) and the reaction was stirred at 80 °C for 1 h and at 100 °C for 22 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (10% EtOAc/pentane) to give the enone **1j** (223 mg, 30%) as a brown oil. R_f = 0.17 (10% EtOAc/pet. ether); IR 3019, 2928, 1694 (C=O), 1626, 1598, 1489, 1441, 1398, 1192, 968 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.35 (2H, m, Ar**H**), 7.30-7.27 (3H, m, Ar**H**), 7.08 (1H, dt, *J* = 15.9, 6.4 Hz, CH_2C**H**=), 6.44 (1H, dt, *J* = 15.9, 1.5 Hz, CH_2CH=C**H**), 4.22 (2H, s, C**H**$_2$Cl), 2.64-2.55 (4H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 191.1 (C), 148.0 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.1 (CH), 127.2 (CH), 123.5 (C), 88.0 (C), 82.1 (C), 47.2 (CH_2), 31.9 (CH_2), 18.4 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{14}H_{17}OClNa]^+$ $[M+Na]^+$: 255.0547, found: 255.0548.

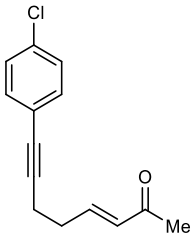
(*E*)-8-(4-Chlorophenyl)oct-3-en-7-yn-2-one (1k)





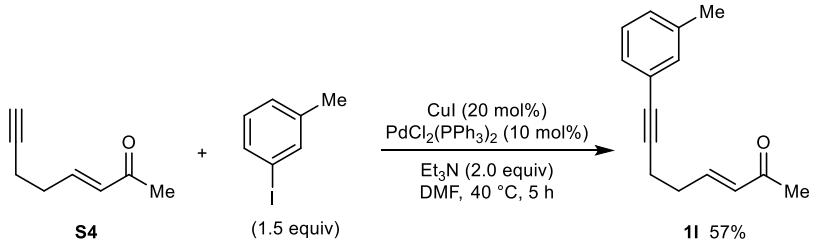
5-(4-Chlorophenyl)pent-4-yn-1-ol (S12).[15] The title compound was prepared by modification of a previously reported procedure.[16] To a solution of 4-chloroiodobenzene (5.68 g, 23.8 mmol), $PdCl_2(PPh_3)_2$ (170 mg, 0.240 mmol) and CuI (23.0 mg, 0.120 mmol) in dry Et_2NH (40 mL) under an argon atmosphere at 0 °C was added 4-pentyn-1-ol (2.2 mL, 23.8 mmol) and the reaction mixture was stirred at room temperature

overnight. The volatiles were removed *in vacuo* and brine was added to the resulting slurry. The mixture was extracted with EtOAc and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (20% EtOAc/pet. ether) to give the alkyne **S12** (3.41 g, 74%) as a brown solid. The analytical data were consistent with those reported previously.[15]



(*E*)-8-(4-Chlorophenyl)oct-3-en-7-yn-2-one (1k). To a solution of alkyne **S12** (2.00 g, 10.3 mmol) in CH_2Cl_2 (30 mL) was added PCC (2.68 g, 12.4 mmol) and celite and the mixture was stirred for 24 h. The reaction mixture was filtered through celite and silica and concentrated *in vacuo* to give the crude product (774 mg) which was carried through to the next step without further purification. To a solution of the aldehyde (774 mg) in CH_2Cl_2 (12 mL) was added 1-(triphenylphosphoranylidene)-2-propanone (3.80 g, 12.0 mmol) and the reaction was stirred at reflux overnight. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (20% EtOAc/pet. ether) to give the enone **1k** (689 mg, 29% over two steps) as a yellow solid. R_f = 0.30 (20% EtOAc/pet. ether); m.p. 50−51 °C (Et_2O); IR 3032, 2945, 2919, 1910, 1667 (C=O), 1488, 1363, 1253, 1087, 827 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m, Ar**H**), 7.27-7.26 (1H, m, Ar**H**), 7.26-7.24 (1H, m, Ar**H**), 6.86 (1H, dt, *J* = 16.0, 6.5 Hz, CH_2C**H**=), 6.18 (1H, dt, *J* = 16.0, 1.5 Hz, CH_2CH=C**H**), 2.61-2.57 (2H, m, C**H**$_2$), 2.55-2.50 (2H, m, C**H**$_2$), 2.27 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5 (C), 145.6 (CH), 134.0 (C), 132.9 (2 × CH), 132.4 (CH), 128.7 (2 × CH), 122.1 (C), 89.3 (C), 80.9 (C), 31.6 (CH_2), 27.2 (CH_3), 18.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{14}H_{13}OClNa]^+$ $[M+Na]^+$: 255.0547, found 255.0547.

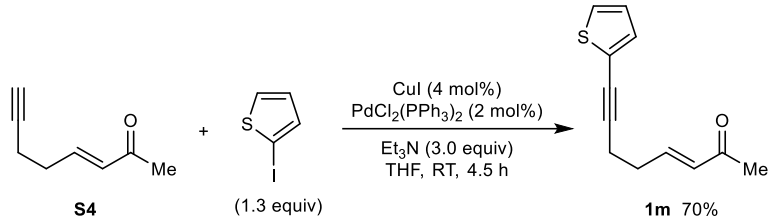
(*E*)-8-(*m*-Tolyl)oct-3-en-7-yn-2-one (1l)



To a solution of $PdCl_2(PPh_3)_2$ (173 mg, 0.246 mmol) and CuI (93.7 mg, 0.492 mmol) in DMF (3 mL) under an argon atmosphere at room temperature was added Et_3N (0.68 mL, 4.91 mmol) and 3-iodotoluene (0.47 mL, 3.68 mmol). A solution of alkyne **S4** (300 mg, 2.46 mmol) in DMF (2 mL) was added and the reaction was stirred at 40 °C for 5 h. The reaction was diluted with 50% brine (50 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (20% EtOAc/pet. ether) and further purified by dissolving the

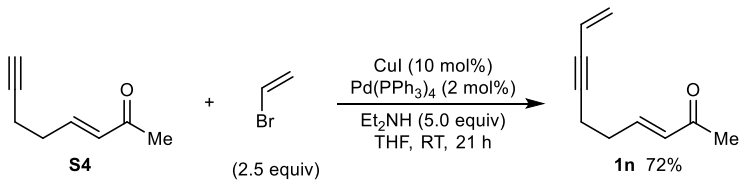
residue in Et_2O and filtering off the solid to give the enone **1l** (297 mg, 57%) as an orange oil. R_f = 0.32 (20% EtOAc/pet. ether); IR 3033, 2919, 1697, 1672 (C=O), 1626, 1358, 1252, 971, 783, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.14 (3H, m, Ar**H**), 7.13-7.06 (1H, m, Ar**H**), 6.88 (1H, dt, *J* = 15.9, 6.5 Hz, CH_2C**H**=), 6.18 (1H, d, *J* = 15.9 Hz, CH_2CH=C**H**), 2.62-2.50 (4H, m, C**H**$_2C$**H**$_2$), 2.32 (3H, s, C**H**$_3$), 2.28 (3H, s, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.6 (C), 145.9 (CH), 138.1 (C), 132.32 (CH), 132.30 (CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 123.4 (C), 87.9 (C), 82.1 (C), 31.7 (CH_2), 27.1 (CH_3), 21.4 (CH_3), 18.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{15}H_{16}ONa]^+$ [M+Na]$^+$: 235.1093, found: 235.1087.

(*E*)-8-(Thiophen-2-yl)oct-3-en-7-yn-2-one (1m)



To a solution of $PdCl_2(PPh_3)_2$ (28.7 mg, 0.041 mmol), CuI (15.6 mg, 0.082 mmol) and alkyne **S4** (250 mg, 2.05 mmol) in THF (5 mL) under an argon atmosphere at room temperature was added Et_3N (0.86 mL, 6.14 mmol) and 2-iodothiophene (559 mg, 2.66 mmol) and the reaction was stirred for 4.5 h. The reaction was filtered through celite (EtOAc) and concentrated *in vacuo*. The residue was purified by column chromatography (20% EtOAc/pet. ether) to give the enone **1m** (293 mg, 70%) as a red oil. R_f = 0.32 (20% EtOAc/pet. ether); IR 3105, 2849, 1671 (C=O), 1626, 1426, 1358, 1253, 1190, 971, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (1H, d, *J* = 5.2 Hz, Ar**H**), 7.12 (1H, d, *J* = 3.6 Hz, Ar**H**), 6.94 (1H, dd, *J* = 5.2, 3.6 Hz, Ar**H**), 6.85 (1H, dt, *J* = 16.1, 6.6 Hz, CH_2C**H**=), 6.16 (1H, d, *J* = 16.1 Hz, CH_2CH=C**H**), 2.65-2.57 (2H, m, C**H**$_2$), 2.56-2.49 (2H, m, C**H**$_2$), 2.27 (3H, s, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.5 (C), 145.6 (CH), 132.4 (CH), 131.4 (CH), 127.0 (CH), 126.5 (CH), 123.6 (C), 92.3 (C), 75.1 (C), 31.5 (CH_2), 27.1 (CH_3), 18.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{12}H_{12}OSNa]^+$ [M+Na]$^+$: 227.0501, found: 227.0500.

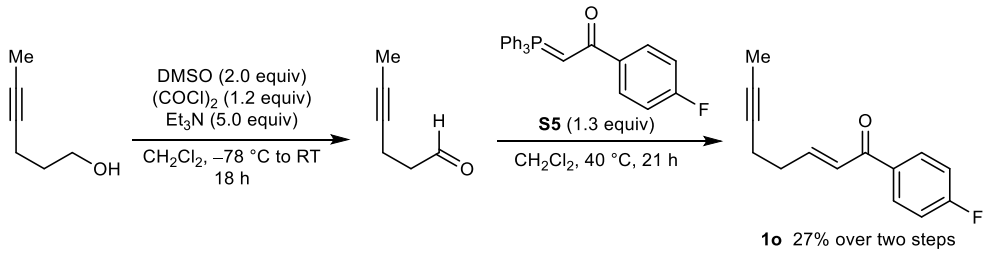
(*E*)-Deca-3,9-dien-7-yn-2-one (1n)



To a mixture of $Pd(PPh_3)_4$ (56.7 mg, 0.049 mmol) and CuI (46.9 mg, 0.246 mmol) under an argon atmosphere at room temperature was added vinyl bromide (1 M in THF, 6.1 mL, 6.10 mmol) and Et_2NH (1.3 mL, 12.3 mmol) and the resulting mixture was stirred for 5 min. A solution of alkyne **S4**

(300 mg, 2.46 mmol) in THF (1.3 mL) was added dropwise and the reaction was stirred at room temperature for 21 h. The reaction was filtered through celite (Et_2O) and concentrated *in vacuo*. The residue was purified by column chromatography (10% EtOAc/pet. ether) to give the enone **1n** (261 mg, 72%) as an orange oil. R_f = 0.37 (20% EtOAc/pet. ether); IR 3009, 2913, 2848, 2225 (C≡C), 1698, 1672 (C=O), 1627, 1359, 1252, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (1H, dt, *J* = 16.2, 6.4 Hz, $CH_2C\mathbf{H}$=), 6.13 (1H, dt, *J* = 16.2, 1.4 Hz, CH_2CH=C**H**), 5.76 (1H, ddt, *J* = 17.6, 11.0, 1.8 Hz, C**H**=CH_2), 5.56 (1H, dd, *J* = 17.6, 2.1 Hz, =C**H**$_a$H$_b$), 5.40 (1H, dd, *J* = 11.0, 2.1 Hz, =CH$_a$**H**$_b$), 2.52-2.42 (4H, m, C**H**$_2$C**H**$_2$), 2.26 (3H, s, C**H**$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 198.6 (C), 145.8 (CH), 132.3 (CH), 126.4 (CH_2), 117.4 (CH), 89.0 (C), 80.6 (C), 31.6 (CH_2), 27.1 (CH_3), 18.5 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{10}H_{13}O]^+$ $[M+H]^+$: 149.0961, found: 149.0965.

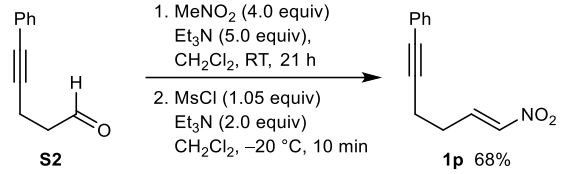
(*E*)-1-(4-Fluorophenyl)oct-2-en-6-yn-1-one (1o)



To a solution of $(COCl)_2$ (0.30 mL, 3.6 mmol) in CH_2Cl_2 (6 mL) at −78 °C was added a solution of DMSO (0.32 mL, 6.0 mmol) in CH_2Cl_2 (2 mL) dropwise over 8 min and the solution was stirred at −78 °C for 30 min. A solution of hex-4-yn-1-ol[17] (294 mg, 3.00 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 5 min and the mixture was stirred at −78 °C for 1 h. Et_3N (2.1 mL, 15.0 mmol) was added and the mixture was warmed to room temperature and stirred for 18 h. The reaction was diluted with H_2O (15 mL) and the two layers were separated. The aqueous layer was acidified with 10 % HCl and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with 10% HCl saturated with NaCl (15 mL), 5% aqueous $NaHCO_3$ (15 mL), H_2O (20 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and gently concentrated by blowing nitrogen over the mixture until *ca.* 2 mL remained. The residue was diluted in CH_2Cl_2 (20 mL) and phosphorane **S5**[1] (1.55 g, 3.9 mmol) was added and the reaction was stirred at 40 °C for 21 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (5% EtOAc/pet. ether) to give the enone **1o** (177 mg, 27% over two steps) as an orange oil. R_f = 0.24 (5% EtOAc/pet. ether); IR 2918, 2848, 1671 (C=O), 1621, 1597, 1506, 1409, 1301, 1229 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-7.93 (2H, m, Ar**H**), 7.19-7.10 (2H, m, Ar**H**), 7.06 (1H, dt, *J* = 15.4, 6.6 Hz, CH_2CH=C**H**), 6.91 (1H, dt, *J* = 15.4, 1.4 Hz, $CH_2C\mathbf{H}$=), 2.55-2.44 (2H, m C**H**$_2$CH=), 2.43-2.31 (2H, m, ≡CC**H**$_2$), 1.78 (3H, t, *J* = 2.5 Hz, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (C), 165.7 (d, $J_{C\text{-}F}$ = 254.2 Hz, C), 147.9 (CH), 134.3 (d, $J_{C\text{-}F}$ = 2.9 Hz, C), 131.3 (d, $J_{C\text{-}F}$ = 9.2 Hz, 2 × CH), 126.4 (CH), 115.8 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2 × CH),

77.6 (C), 77.0 (C), 32.3 (CH_2), 18.0 (CH_2), 3.6 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –105.8 (s); HRMS (ESI) Exact mass calculated for $[C_{14}H_{13}FONa]^+$ $[M+Na]^+$: 239.0843, found: 239.0832.

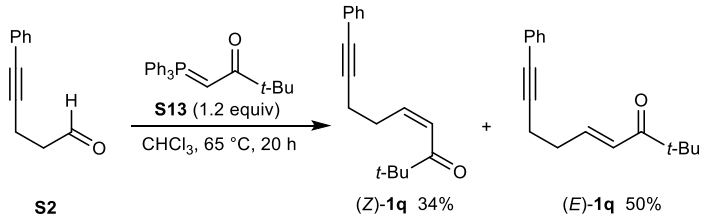
(*E*)-(6-Nitrohex-5-en-1-yn-1-yl)benzene (1p)



S2 **1p** 68%

To a solution of aldehyde **S2** (633 mg, 4.00 mmol) and $MeNO_2$ (0.87 mL, 16.0 mmol) in CH_2Cl_2 (4.0 mL) under an argon atmosphere at room temperature was added Et_3N (2.8 mL, 20.0 mmol) and the reaction was stirred for 21 h. The volatiles were removed *in vacuo* and the resulting solid was dissolved in CH_2Cl_2 (12 mL). To the mixture at −20 °C was added slowly MsCl (0.33 mL, 4.20 mmol) followed by Et_3N (1.1 mL, 8.00 mmol) and the reaction was stirred for 10 min. The reaction was diluted with 1 M HCl (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (15% EtOAc/pentane) to give the nitroalkene **1p** (548 mg, 68%) as a yellow oil. R_f = 0.54 (30% EtOAc/pet. ether); IR 3103, 2914, 1650, 1521, 1489, 1441, 1348, 946, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (6H, m, 5 × Ar**H** and CH_2CH=), 7.11 (1H, d, *J* = 13.4 Hz, CH_2CH=C**H**), 2.66 (2H, t, *J* = 7.0 Hz, ≡CC$\mathbf{H}_2$), 2.62-2.52 (2H, m, C$\mathbf{H}_2$CH=CH); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.6 (CH), 140.4 (CH), 131.7 (2 × CH), 128.5 (2 × CH), 128.3 (CH), 123.2 (C), 87.0 (C), 82.7 (C), 27.8 (CH_2), 18.4 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{12}H_{11}NO_2Na]^+$ $[M+Na]^+$: 224.0682, found: 224.0678.

(*Z*)-2,2-Dimethyl-9-phenylnon-4-en-8-yn-3-one [(*Z*)-(1q)] and (*E*)-2,2-dimethyl-9-phenylnon-4-clen-8-yn-3-one [(*E*)-(1q)]



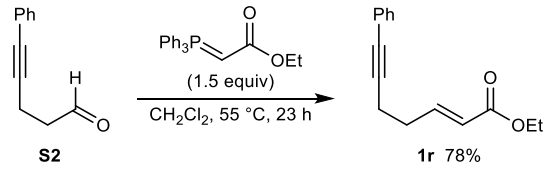
S2 (*Z*)-**1q** 34% (*E*)-**1q** 50%

To a mixture of aldehyde **S2** (400 mg, 2.53 mmol) and the phosphorane **S13**[18] (1.09 g, 3.03 mmol) under an argon atmosphere was added $CHCl_3$ (9 mL) and the reaction was stirred at 65 °C for 20 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (1 to 3% EtOAc/pet. ether) followed by a second purification by column chromatography (1% EtOAc/pentane) to give the enone (*Z*)-**1q** (206 mg, 34%) as a yellow oil followed by the enone (*E*)-**1q** (305 mg, 50%) as an off-white solid.

Data for (Z)-**1q**: R_f = 0.66 (30% EtOAc/pet. ether); IR 3032, 2967, 2869, 1683 (C=O), 1614, 1490, 1476, 1074, 755, 691 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.35 (2H, m, Ar**H**), 7.29-7.24 (3H, m, Ar**H**), 6.49 (1H, dt, *J* = 11.6, 1.8 Hz, CH_2CH=C**H**), 6.29 (1H, dt, *J* = 11.6, 7.1 Hz, CH_2C**H**=), 2.91-2.83 (2H, m, C**H**$_2$C=), 2.54 (2H, t, *J* = 7.0 Hz, C**H**$_2CH_2$C=), 1.15 (9H, s, C(C**H**$_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8 (C), 146.4 (CH), 131.7 (2 × CH), 128.3 (2 × CH), 127.8 (CH), 124.1 (CH), 123.9 (C), 89.3 (C), 81.4 (C), 43.8 (C), 28.8 (CH_2), 26.4 (3 × CH_3), 19.4 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{17}H_{20}ONa]^+$ $[M+Na]^+$: 263.1406, found: 263.1405.

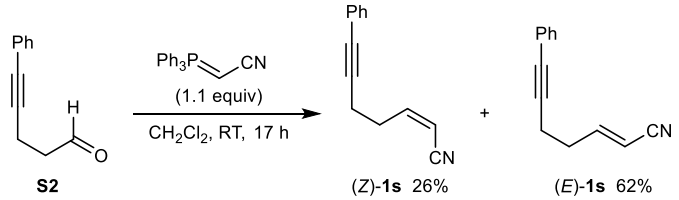
Data for (E)-**1q**: R_f = 0.61 (30% EtOAc/pet. ether); m.p. 38–40 °C (Et_2O); IR 3051, 2969, 2869, 1685 (C=O), 1623, 1490, 1475, 1099, 1070, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.34 (2H, m, Ar**H**), 7.28-7.25 (3H, m, Ar**H**), 6.99 (1H, dt, *J* = 15.3, 6.6 Hz, CH_2C**H**=), 6.62 (1H, dt, *J* = 15.3, 1.5 Hz, CH_2CH=C**H**), 2.58 (2H, td, *J* = 6.6, 1.5 Hz, C**H**$_2CH_2$C=), 2.54-2.49 (2H, m, C**H**$_2$C=), 1.15 (9H, s, C(C**H**$_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3 (C), 144.9 (CH), 131.7 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 125.4 (CH), 123.7 (C), 88.6 (C), 81.7 (C), 43.1 (C), 31.8 (CH_2), 26.3 (3 × CH_3), 18.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{17}H_{20}ONa]^+$ $[M+Na]^+$: 263.1406, found: 263.1407.

Ethyl (*E*)-7-phenylhept-2-en-6-ynoate (1r)



To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (15 mL) under an argon atmosphere at 55 °C was added (carbethoxymethylene)triphenylphosphorane (1.65 g, 4.74 mmol) and the reaction was stirred at 55 °C for 23 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (5 to 10% EtOAc/petroleum ether) to give the enone **1r** (562 mg, 78%) as a yellow oil. The analytical data were consistent with those reported previously.[19]

(*Z*)-7-Phenylhept-2-en-6-ynenitrile [(*Z*)-1s] and (*E*)-7-phenylhept-2-en-6-ynenitrile [(*E*)-1s]



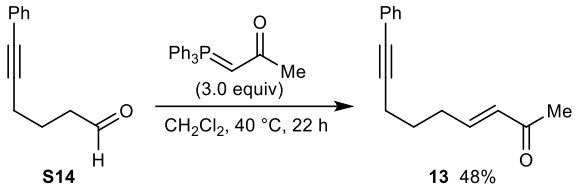
To a solution of aldehyde **S2** (500 mg, 3.16 mmol) in CH_2Cl_2 (25 mL) under an argon atmosphere at room temperature was added (triphenylphosphoranylidene)acetonitrile (1.05 g, 3.48 mmol) and the reaction was stirred at room temperature for 17 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (1 to 4% Et_2O/pentane) to give the α,β-unsaturated nitrile

(*Z*)-**1s** (148 mg, 26%) as a yellow oil followed by the α,β-unsaturated nitrile (*E*)-**1s** (353 mg, 62%) as a yellow oil.

Data for (Z)-**1s**: R_f = 0.27 (2% Et_2O/pentane, 4 elutions); IR 3061, 2910, 2220 (C≡N), 1598, 1490, 1441, 1330, 1128, 1069, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.37 (2H, m, Ar**H**), 7.34-7.26 (3H, m, Ar**H**), 6.73-6.53 (1H, m, CH_2C**H**=), 5.43 (1H, d, *J* = 10.9 Hz, CH_2CH=C**H**), 2.73 (2H, app q, *J* = 6.9 Hz, C**H**$_2$C=), 2.61 (2H, t, *J* = 6.9 Hz, C**H**$_2CH_2$=); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.8 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.1 (CH), 123.4 (C), 115.9 (C), 101.1 (CH), 87.5 (C), 82.3 (C), 30.9 (CH_2), 18.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{13}H_{11}NNa]^+$ $[M+Na]^+$: 204.0784, found: 204.0783.

Data for (E)-**1s**: R_f = 0.19 (2% Et_2O/pentane, 4 elutions); IR 3054, 2912, 2223 (C≡N), 1634, 1598, 1489, 1441, 1344, 1070, 958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (2H, m, Ar**H**), 7.34-7.27 (3H, m, Ar**H**), 6.82 (1H, dt, *J* = 16.4, 6.6 Hz, CH_2C**H**=), 5.48 (1H, dt, *J* = 16.4, 1.6 Hz, CH_2CH=C**H**), 2.62-2.57 (2H, m, C**H**$_2$), 2.56-2.49 (2H, m, C**H**$_2$); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 153.6 (CH), 131.7 (2 × CH), 128.4 (2 × CH), 128.2 (CH), 123.3 (C), 117.3 (C), 101.3 (CH), 87.3 (C), 82.5 (C), 32.4 (CH_2), 18.3 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{13}H_{11}NNa]^+$ $[M+Na]^+$: 204.0784, found: 204.0781.

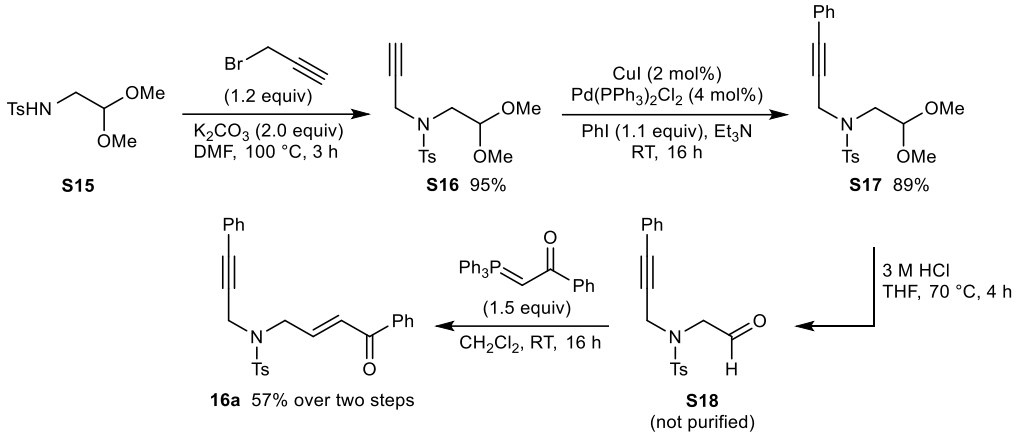
(*E*)-9-Phenylnon-3-en-8-yn-2-one (13)

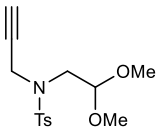


S14 **13** 48%

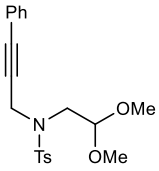
To a solution of aldehyde **S14**[20] (500 mg, 2.90 mmol) in CH_2Cl_2 (10 mL) under an argon atmosphere at 40 °C was added 1-(triphenylphosphoranylidene)-2-propanone (2.77 g, 8.70 mmol) and the reaction was stirred at 40 °C for 22 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (10% EtOAc/petroleum ether) to give the enone **13** (298 mg, 48%) as a yellow oil. The analytical data were consistent with those reported previously.[21]

(*E*)-4-methyl-*N*-(4-oxo-4-phenylbut-2-en-1-yl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (16a)



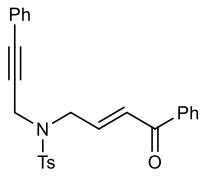


***N*-(2,2-Dimethoxyethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S16).**[22] Propargyl bromide (80% solution in toluene, 6.21 mL, 55.7 mmol) was added dropwise to a stirred mixture of *N*-(2,2-dimethoxyethyl)-4-methylbenzenesulfonamide[23] (**S15**, 12.0 g, 46.4 mmol) and K_2CO_3 (12.3 g, 92.9 mmol) in DMF (230 mL) under argon at room temperature, and the mixture was then stirred at 100 °C for 3 h. The mixture was quenched with H_2O, extracted with Et_2O (3 × 200 mL), washed with 5% aqueous LiCl solution (2 × 100 mL), H_2O (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting residue was triturated with petroleum ether to give the alkyne **S16** (13.1 g, 95%) as a pale orange solid. The analytical data were consistent with those reported previously.[22]



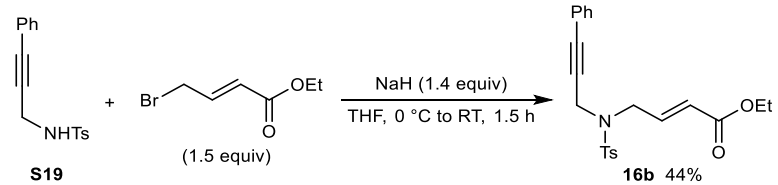
***N*-(2,2-Dimethoxyethyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (S17)**. To a solution of $PdCl_2(PPh_3)_2$ (1.33 g, 1.90 mmol), CuI (726 mg, 3.81 mmol), and alkyne **S6** (28.2 g, 95.1 mmol) in Et_3N (360 mL) under an argon atmosphere at room temperature was added iodobenzene (11.7 mL, 104.7 mmol), and the reaction was stirred for 16 h. The reaction was diluted with EtOAc, washed with 10% aqueous HCl solution, 50% brine (× 3), dried ($MgSO_4$), filtered, and concentrated *in vacuo.* The residue was purified by column chromatography (40 to 60% EtOAc/pet. ether) to give the alkyne **S17** (31.6 g, 89%) as a dark orange solid. R_f = 0.18 (20% EtOAc/pet. ether); m.p. 63–65 °C (Et_2O); IR 2998, 2833, 1595, 1489, 1436, 1331, 1306, 1262, 1159, 1131 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.73 (2H, m, Ar**H**), 7.27-7.20 (5H, m, Ar**H**), 7.10-6.98 (2H, m, Ar**H**), 4.61 (1H, t, *J* = 5.5 Hz, C**H**$(OCH_3)_2$), 4.47 (2H, s, ≡CC**H**$_2$), 3.44 (6H, s, C$(OC\mathbf{H}_3)_2$), 3.34 (2H, d, *J* = 5.5 Hz, C**H**$_2$CH), 2.33 (3H, s, ArC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7 (C), 136.2 (C), 131.6 (2 × CH), 129.7 (2 × CH), 128.5 (CH), 128.2 (2 × CH), 127.9 (2 × CH), 122.4 (C), 104.6 (CH), 85.6 (C), 82.4 (C), 54.9 (2

× CH_3), 47.9 (CH_2), 39.3 (CH_2), 21.6 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{20}H_{23}NO_4SNa]^+$ $[M+Na]^+$: 396.1240, found: 396.1245.



(*E*)-4-Methyl-*N*-(4-oxo-4-phenylbut-2-en-1-yl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (16a). A solution of alkyne **S17** (1.00 g, 2.68 mmol) in a mixture of 3 M aqueous HCl solution (6.3 mL) and THF (8 mL) was stirred at 70 °C for 4 h. The volatiles were removed *in vacuo* and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with H_2O (20 mL), brine (20 mL), dried ($MgSO_4$), filtered, and concentrated in *vacuo* to leave the aldehyde **S18** that was used immediately in the next step without further purification. To a solution of the aldehyde **S18** (877 mg, 2.68 mmol) in CH_2Cl_2 (20 mL) under an argon atmosphere at room temperature was added 1-phenyl-2-(triphenyl-λ-5-phosphanylidene)ethan-1-one (1.53 g, 4.02 mmol) and the reaction was stirred at room temperature for 16 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (20% EtOAc/pentane) to give the enone **16a** (656 mg, 57% over two steps) as an orange solid. R_f = 0.44 (40% EtOAc/petroleum ether); m.p. 82–84 °C (Et_2O); IR 3027, 1722, 1673 (C=O), 1625, 1579, 1490, 1346, 1158, 1091, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94-7.89 (2H, m, Ar**H**), 7.84-7.79 (2H, m, Ar**H**), 7.59-7.55 (1H, m, Ar**H**), 7.45 (2H, t, *J* = 7.7 Hz, Ar**H**), 7.31-7.27 (3H, m, Ar**H**), 7.26-7.21 (2H, m, Ar**H**), 7.14 (1H, dt, *J* = 15.5, 1.7 Hz, CH_2CH=C**H**), 7.12-7.06 (2H, m, Ar**H**), 6.93 (1H, dt, *J* = 15.5, 5.5 Hz, CH_2C**H**=), 4.37 (2H, s, ≡CC**H**$_2$), 4.18 (2H, dd, *J* = 5.5, 1.7 Hz, C**H**$_2$C=), 2.35 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1 (C), 144.1 (C), 141.6 (CH), 137.4 (C), 135.9 (C), 133.3 (CH), 131.7 (2 × CH), 129.9 (2 × CH), 128.81 (2 × CH), 128.80 (2 × CH), 128.75 (CH), 128.4 (CH), 128.3 (2 × CH), 128.0 (2 × CH), 122.1 (C), 86.4 (C), 81.5 (C), 48.2 (CH_2), 38.1 (CH_2), 21.6 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{26}H_{23}NO_3SNa]^+$ $[M+Na]^+$: 452.1291, found: 452.1293.

Ethyl (*E*)-4-{[4-methyl-*N*-(3-phenylprop-2-yn-1-yl)phenyl]sulfonamido}but-2-enoate (16b)[24]

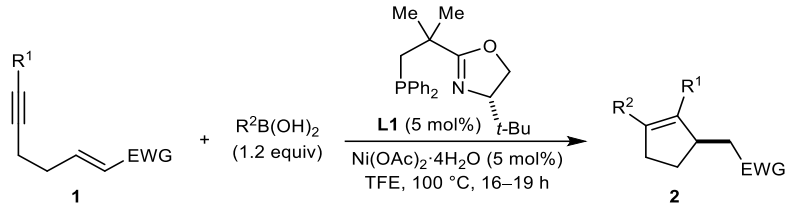


A solution of the *N*-tosyl propargyl amine **S19**[25] (3.00 g, 10.5 mmol) in THF (5 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 588 mg, 14.7 mmol) in THF (25 mL). The resulting solution was warmed to room temperature and stirred for 45 min. Ethyl-4-bromo crotonate (75% purity, 2.9 mL, 15.8 mmol) was added slowly and the resulting solution was stirred at room temperature for 1.5 h. The reaction was quenched with H_2O (50 mL) and extracted

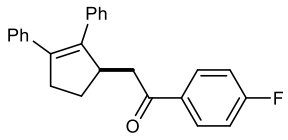
with EtOAc (3 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography (20% to 30% Et_2O/pet. ether) to give the enone **16b** (1.84 g, 44%) as a yellow solid. The analytical data were consistent with those reported previously.[24]

3. Enantioselective Nickel-Catalyzed Arylative Cyclizations onto Electron-Deficient Alkenes

General Procedure C



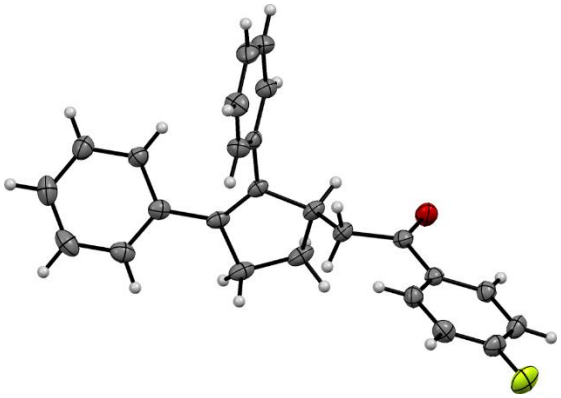
An oven-dried microwave vial fitted with a magnetic stirrer bar was charged with the appropriate substrate **1** (0.30 mmol), boronic acid (0.36 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (3.7 mg, 0.015 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 5.5 mg, 0.015 mmol). The vial was capped with a crimp cap seal and flushed with argon (5 min). Freshly degassed TFE (3 mL, using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 100 °C for 16–19 h. The reaction was cooled to room temperature, diluted with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography to give the arylative cyclization product **2**.

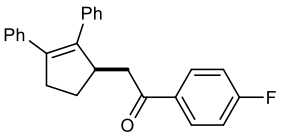


(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-(4-fluorophenyl)ethan-1-one (2a). Prepared according to General Procedure C, using enyne **1a** (83.5 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 16 h. Purification by column chromatography (3% EtOAc/pet. ether) gave **2a** (97.6 mg, 91%) as an off-white solid. R_f = 0.69 (40% EtOAc/pet. ether); m.p. 82−83 °C (Et_2O); IR 3050, 2946, 1804, 1674 (C=O), 1594, 1411, 1359, 1273, 1233, 1153 cm^{-1}; $[\alpha]_D^{25}$ −116.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.83 (2H, m, Ar**H**), 7.30-7.11 (10H, m, Ar**H**), 7.10-7.03 (2H, m, Ar**H**), 3.94-3.77 (1H, m, C**H**CH_2), 3.11 (1H, dddd, *J* = 15.9, 9.2, 6.6, 2.7 Hz, C**H**$_a$H$_b$C=), 3.01 (1H, dd, *J* = 16.6, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.90 (1H, dd, *J* = 16.6, 10.5 Hz, CH$_a$**H**$_b$C=O), 2.73 (1H, dddd, *J* = 15.9, 9.3, 4.8, 1.3 Hz, CH$_a$**H**$_b$C=), 2.42 (1H, app dtd, *J* = 13.3, 8.9, 6.6 Hz, CH_2C**H**$_a$H$_b$CH), 1.76 (1H, app ddt, *J* = 13.3, 9.2, 4.7 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5 (C), 165.8 (d, $J_{C\text{-}F}$ = 254.5 Hz, C), 140.8 (C), 138.2 (C), 137.8 (C), 137.5 (C), 133.7 (d, $J_{C\text{-}F}$ = 3.4 Hz, C), 130.8 (d, $J_{C\text{-}F}$ = 9.4 Hz, 2 × CH), 129.0 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.1 (CH), 126.8 (CH), 115.7 (d, $J_{C\text{-}F}$ = 21.9 Hz, 2 × CH), 46.8 (CH), 42.6 (CH_2), 36.6 (CH_2), 29.1 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –105.6 (s); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}FONa]^+$ $[M+Na]^+$: 379.1469, found 379.1461; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H

column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 10.2 min, t_r (major) = 11.5 min, 99% ee.

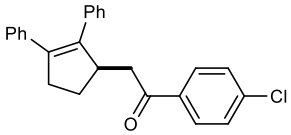
Slow diffusion of pentane into a solution of **2a** in Et_2O gave crystals that were suitable for X-ray crystallography:



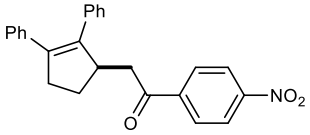


2a
CCDC 2040010
Flack parameter 0.05(10)

ORTEP with ellipsoid probabilities at 50%

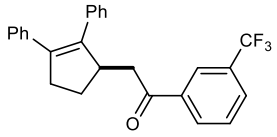


(*R*)-1-(4-Chlorophenyl)-2-(2,3-diphenylcyclopent-2-en-1-yl)ethan-1-one (2b). Prepared according to General Procedure C, using enyne **1b** (88.4 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2b** (75.3 mg, 67%) as an off-white solid. R_f = 0.65 (30% EtOAc/pet. ether); m.p. 37−39 °C (Et_2O); IR 3052, 2946, 1680 (C=O), 1587, 1487, 1399, 1356, 1271, 1092, 757 cm^{-1}; $[\alpha]_D^{25}$ −108.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82-7.75 (2H, m, Ar**H**), 7.41-7.35 (2H, m, Ar**H**), 7.28-7.26 (1H, m, Ar**H**), 7.26-7.11 (9H, m, Ar**H**), 3.90-3.80 (1H, m, C**H**CH_2), 3.11 (1H, dddd, *J* = 15.9, 9.2, 6.6, 2.8 Hz, C**H**$_a$H$_b$C=), 3.00 (1H, dd, *J* = 16.6, 3.2 Hz, C**H**$_a$H$_b$C=O), 2.89 (1H, dd, *J* = 16.6, 10.6 Hz, CH$_a$**H**$_b$C=O), 2.72 (1H, dddd, *J* = 15.9, 9.2, 4.8, 1.4 Hz, CH$_a$**H**$_b$C=), 2.42 (1H, app dtd, *J* = 13.3, 9.0, 6.7 Hz, CH_2C**H**$_a$H$_b$CH), 1.75 (1H, app ddt, *J* = 13.3, 9.1, 4.6 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9 (C), 140.7 (C), 139.5 (C), 138.2 (C), 137.7 (C), 137.5 (C), 135.6 (C), 129.6 (2 × CH), 129.0 (2 × CH), 128.9 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.1 (CH), 126.9 (CH), 46.8 (CH), 42.7 (CH_2), 36.6 (CH_2), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}OClNa]^+$ $[M+Na]^+$: 395.1173, found: 395.1167; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 11.0 min, t_r (major) = 13.1 min, >99% ee.

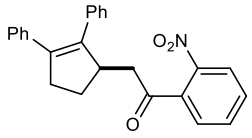


(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-(4-nitrophenyl)ethan-1-one (2c). Prepared according to General Procedure C, using enyne **1c** (91.6 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for

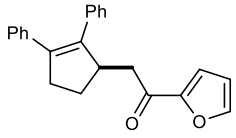
19 h. Purification by column chromatography (10% EtOAc/pentane) gave **2c** (86.6 mg, 75%) as a yellow oil. R_f = 0.44 (20% EtOAc/pet. ether); IR 3077, 2944, 1692 (C=O), 1602, 1525, 1345, 1318, 1273, 761, 698 cm^{-1}; $[\alpha]_D^{20}$ −144.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32-8.15 (2H, m, Ar**H**), 8.04-7.89 (2H, m, Ar**H**), 7.29-7.26 (1H, m, Ar**H**), 7.26-7.09 (9H, m, Ar**H**), 3.93-3.81 (1H, m, C**H**CH_2), 3.18-3.04 (2H, m, C**H**$_a$H$_b$C= and C**H**$_a$H$_b$C=O), 2.96 (1H, dd, *J* = 16.9, 10.2 Hz, CH_a**H**$_b$C=O), 2.74 (1H, dddd, *J* = 15.9, 9.2, 4.9, 1.4 Hz, CH_a**H**$_b$C=), 2.45 (1H, app dtd, *J* = 13.3, 8.9, 6.5 Hz, CH_2C**H**$_a$H$_b$CH), 1.76 (1H, app ddt, *J* = 13.3, 9.2, 4.7 Hz, CH_2CH_a**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6 (C), 150.3 (C), 141.6 (C), 140.3 (C), 138.5 (C), 137.5 (C), 137.3 (C), 129.2 (2 × CH), 129.0 (2 × CH), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.2 (CH), 127.0 (CH), 123.9 (2 × CH), 46.7 (CH), 43.4 (CH_2), 36.6 (CH_2), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}O_3NNa]^+$ $[M+Na]^+$: 406.1414, found: 406.1414; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 11.1 min, t_r (major) = 13.1 min, >99% ee.



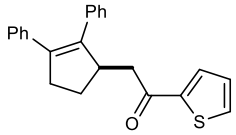
(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-[3-(trifluoromethyl)phenyl]ethan-1-one (2d). Prepared according to General Procedure C, using enyne **1d** (98.5 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (4% EtOAc/pet. ether) gave **2d** (112 mg, 92%) as a light yellow oil. R_f = 0.58 (20% EtOAc/pet. ether); IR 3055, 2927, 1690 (C=O), 1611, 1495, 1440, 1331, 1168, 1128, 695 cm^{-1}; $[\alpha]_D^{25}$ −100.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, s, Ar**H**), 8.02 (1H, d, *J* = 7.9 Hz, Ar**H**), 7.78 (1H, d, *J* = 7.9 Hz, Ar**H**), 7.55 (1H, app t, *J* = 7.9 Hz, Ar**H**), 7.28-7.11 (10H, m, Ar**H**), 3.96-3.79 (1H, m, C**H**CH_2), 3.13 (1H, dddd, *J* = 15.9, 9.2, 6.6, 2.8 Hz, C**H**$_a$H$_b$C=), 3.07 (1H, dd, *J* = 16.6, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.93 (1H, dd, *J* = 16.6, 10.4 Hz, CH_a**H**$_b$C=O), 2.73 (1H, dddd, *J* = 15.9, 9.4, 4.8, 1.4 Hz, CH_a**H**$_b$C=), 2.42 (1H, app dtd, *J* = 13.3, 8.9, 6.7 Hz, CH_2C**H**$_a$H$_b$CH), 1.77 (1H, app ddt, *J* = 13.3, 9.1, 4.6 Hz, CH_2CH_a**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8 (C), 140.5 (C), 138.3 (C), 137.7 (C), 137.3 (C), 131.4 (CH), 131.3 (q, J_{C-F} = 33.0 Hz, C), 129.4 (q, J_{C-F} = 3.7 Hz, CH), 129.3 (CH), 129.0 (2 × CH), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.2 (CH), 126.9 (CH), 125.1 (q, J_{C-F} = 3.7 Hz, CH), 123.8 (q, J_{C-F} = 272.5 Hz, C), 46.9 (CH), 42.9 (CH_2), 36.6 (CH_2), 29.1 (CH_2) (one quaternary carbon signal was not identified); ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 (s, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{26}H_{21}OF_3Na]^+$ $[M+Na]^+$: 429.1437, found: 429.1438; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (99:1 *iso*-hexane:*i*-PrOH, 0.3 mL/min, 280 nm, 25 °C); t_r (major) = 23.0 min, t_r (minor) = 24.5 min, >99% ee.



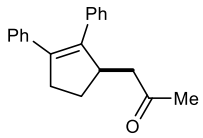
(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-(2-nitrophenyl)ethan-1-one (2e). Prepared according to General Procedure C, using enyne **1e** (91.6 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (10% EtOAc/pet. ether) gave **2e** (37.6 mg, 33%) as an orange solid. R_f = 0.44 (30% EtOAc/pet. ether); m.p. 79−80 °C (Et_2O); IR 3045, 2924, 1706 (C=O), 1598, 1573, 1525, 1439, 1347, 1198, 757 cm^{-1}; $[\alpha]_D^{25}$ −88.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11-8.00 (1H, m, Ar**H**), 7.66-7.60 (1H, m, Ar**H**), 7.58-7.52 (1H, m, Ar**H**), 7.26-7.16 (5H, m, Ar**H**), 7.16-7.07 (6H, m, Ar**H**), 3.94-3.83 (1H, m, C**H**CH_2), 3.13 (1H, dddd, *J* = 15.6, 9.0, 6.2, 2.7 Hz, C**H**$_a$H$_b$C=), 2.89 (1H, dd, *J* = 17.9, 3.1 Hz, C**H**$_a$H$_b$C=O), 2.82-2.69 (2H, m, CH$_a$**H**$_b$C=O and CH$_a$**H**$_b$C=), 2.53 (1H, app dtd, *J* = 13.1, 8.9, 6.2 Hz, CH_2C**H**$_a$H$_b$CH), 2.03-1.97 (1H, m, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1 (C), 145.8 (C), 140.1 (C), 138.6 (C), 138.2 (C), 137.7 (C), 137.3 (C), 134.2 (CH), 130.5 (CH), 129.0 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.6 (CH), 127.1 (CH), 126.8 (CH), 124.5 (CH), 46.9 (CH_2), 46.0 (CH), 36.8 (CH_2), 28.8 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}NO_3Na]^+$ $[M+Na]^+$: 406.1414, found: 406.1416; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 21.1 min, t_r (major) = 22.2 min, 99% ee.



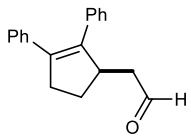
(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-(furan-2-yl)ethan-1-one (2f). Prepared according to General Procedure C, using enyne **1f** (75.1 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (5 to 10% EtOAc/pet. ether) gave **2f** (83.5 mg, 85%) as an off-white solid. R_f = 0.51 (30% EtOAc/pet. ether); m.p. 99−101 °C (Et_2O); IR 3116, 3094, 2944, 1664 (C=O), 1562, 1469, 1397, 1160, 911, 757 cm^{-1}; $[\alpha]_D^{25}$ −132.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (1H, d, *J* = 1.7 Hz, Ar**H**), 7.26-7.23 (2H, m, Ar**H**), 7.22-7.10 (8H, m, Ar**H**), 7.07 (1H, d, *J* = 3.6 Hz, Ar**H**), 6.48 (1H, dd, *J* = 3.6, 1.7 Hz, Ar**H**), 3.89-3.78 (1H, m, C**H**CH_2), 3.11 (1H, dddd, *J* = 15.9, 9.1, 6.5, 2.7 Hz, C**H**$_a$H$_b$C=), 2.88 (1H, dd, *J* = 15.9, 3.6 Hz, C**H**$_a$H$_b$C=O), 2.79 (1H, dd, *J* = 15.9, 10.6 Hz, CH$_a$**H**$_b$C=O), 2.72 (1H, dddd, *J* = 15.9, 9.2, 5.0, 1.4 Hz, CH$_a$**H**$_b$C=), 2.44-2.27 (1H, m, CH_2C**H**$_a$H$_b$CH), 1.79 (1H, app ddt, *J* = 13.5, 9.2, 4.8 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.3 (C), 153.1 (C), 146.3 (CH), 140.8 (C), 138.2 (C), 137.8 (C), 137.4 (C), 129.0 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.0 (CH), 126.8 (CH), 117.1 (CH), 112.2 (CH), 46.9 (CH), 42.6 (CH_2), 36.6 (CH_2), 28.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{23}H_{20}O_2Na]^+$ $[M+Na]^+$: 351.1361, found: 351.1353; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 10.8 min, t_r (major) = 12.8 min, >99% ee.



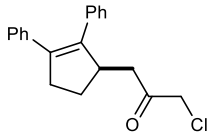
(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)-1-(thiophen-2-yl)ethan-1-one (2g). Prepared according to General Procedure C, using enyne **1g** (79.9 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2g** (83.5 mg, 81%) as an off-white solid. R_f = 0.57 (30% EtOAc/pet. ether); m.p. 130−131 °C (Et_2O); IR 3098, 2925, 1645 (C=O), 1518, 1493, 1412, 1277, 1232, 856, 695 cm^{-1}; $[\alpha]_D^{25}$ −128.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, d, *J* = 5.0 Hz, Ar**H**), 7.56 (1H, d, *J* = 3.8 Hz, Ar**H**) 7.28-7.12 (10H, m, Ar**H**), 7.07 (1H, app t, *J* = 4.4 Hz, Ar**H**), 3.92-3.79 (1H, m, C**H**CH_2), 3.12 (1H, dddd, *J* = 15.9, 9.1, 6.6, 2.7 Hz, C**H**$_a$H$_b$C=), 2.97 (1H, dd, *J* = 15.8, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.84 (1H, dd, *J* = 15.8, 10.7 Hz, CH$_a$**H**$_b$C=O), 2.72 (1H, dddd, *J* = 15.9, 9.3, 4.9, 1.4 Hz, CH$_a$**H**$_b$C=), 2.39 (1H, app dtd, *J* = 13.3, 8.9, 6.5 Hz, CH_2C**H**$_a$H$_b$CH), 1.82 (1H, app ddt, *J* = 13.3, 9.2, 4.7 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1 (C), 144.8 (C), 140.7 (C), 138.2 (C), 137.8 (C), 137.4 (C), 133.6 (CH), 132.0 (CH), 129.0 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.11 (CH), 128.06 (2 × CH), 127.1 (CH), 126.8 (CH), 47.3 (CH), 43.4 (CH_2), 36.6 (CH_2), 28.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{23}H_{20}OSNa]^+$ $[M+Na]^+$: 367.1127, found: 367.1149; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 10.9 min, t_r (major) = 13.1 min, >99% ee.



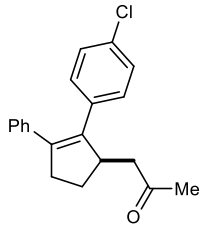
(*R*)-1-(2,3-Diphenylcyclopent-2-en-1-yl)propan-2-one (2h). Prepared according to General Procedure C, using enyne **1h** (59.5 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 16 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2h** (78.2 mg, 94%) as an off-white solid. R_f = 0.59 (40% EtOAc/pet. ether); m.p. 55−57 °C (Et_2O); IR 3021, 2941, 1704 (C=O), 1597, 1488, 1441, 1360, 1158, 769, 694 cm^{-1}; $[\alpha]_D^{25}$ −172.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (3H, m, Ar**H**), 7.20-7.06 (7H, m, Ar**H**), 3.76-3.59 (1H, m, C**H**CH_2), 3.06 (1H, dddd, *J* = 15.8, 9.0, 6.3, 2.7 Hz, C**H**$_a$H$_b$C=), 2.70 (1H, dddd, *J* = 15.8, 9.2, 5.2, 1.5 Hz, CH$_a$**H**$_b$C=), 2.53 (1H, dd, *J* = 16.9, 3.5 Hz, C**H**$_a$H$_b$C=O), 2.44-2.33 (2H, m, CH$_a$**H**$_b$C=O and CH_2C**H**$_a$H$_b$CH), 2.05 (3H, s, C**H**$_3$), 1.67 (1H, app ddt, *J* = 13.8, 9.1, 5.0 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8 (C), 140.7 (C), 138.0 (C), 137.7 (C), 137.5 (C), 129.0 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.0 (CH), 126.8 (CH), 47.9 (CH_2), 46.4 (CH), 36.5 (CH_2), 30.5 (CH_3), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{20}H_{20}ONa]^+$ $[M+Na]^+$: 299.1406, found: 299.1405; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 6.3 min, t_r (major) = 7.7 min, 99% ee.



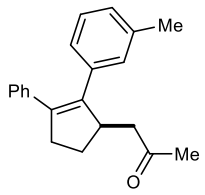
(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)acetaldehyde (2i). Prepared according to General Procedure C, using enyne **1i** (55.3 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2i** (45.5 mg, 58%) as an off-white solid. R_f = 0.59 (30% EtOAc/pet. ether); m.p. 56−57 °C (Et_2O); IR 3077, 3022, 2919, 2839, 2732, 1712 (C=O), 1597, 1489, 1442, 761 cm^{-1}; $[\alpha]_D^{25}$ −180.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (1H, app t, *J* = 2.0 Hz, O=C**H**), 7.30-7.26 (1H, m, Ar**H**), 7.25-7.19 (2H, m, Ar**H**), 7.18-7.07 (7H, m, Ar**H**), 3.77-3.67 (1H, m, C**H**CH_2), 3.09 (1H, dddd, *J* = 15.9, 9.0, 6.3, 2.7 Hz, C**H**$_a$H$_b$C=), 2.75 (1H, dddd, *J* = 15.9, 9.2, 5.1, 1.4 Hz, CH$_a$**H**$_b$C=), 2.55 (1H, ddd, *J* = 16.6, 3.8, 1.5 Hz, C**H**$_a$H$_b$C=O), 2.47-2.35 (2H, m, CH$_a$**H**$_b$C=O and CH_2C**H**$_a$H$_b$CH), 1.76 (1H, app ddt, *J* = 13.7, 9.5, 5.0 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6 (C), 140.1 (C), 138.3 (C), 137.5 (C), 137.3 (C), 128.9 (2 × CH), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.2 (CH), 126.9 (CH), 48.1 (CH_2), 45.4 (CH), 36.6 (CH_2), 28.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{18}ONa]^+$ $[M+Na]^+$: 285.1250, found: 285.1254; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (95:5 *iso*-hexane:*i*-PrOH, 0.4 mL/min, 230 nm, 25 °C); t_r (major) = 17.7 min, t_r (minor) = 18.4 min, >99% ee.



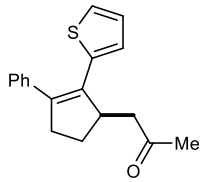
(*R*)-1-Chloro-3-(2,3-diphenylcyclopent-2-en-1-yl)propan-2-one (2j). Prepared according to a modification of General Procedure C, using enyne **1j** (69.8 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (14.9 mg, 0.06 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 22.0 mg, 0.06 mmol) and stirring for 18 h. Purification by column chromatography (3 to 4% EtOAc/pentane) gave **2j** (39.1 mg, 42%) as a yellow solid. R_f = 0.56 (20% EtOAc/pet. ether); m.p. 48–49 °C (Et_2O); IR 3021, 2931, 1731 (C=O), 1717, 1598, 1490, 1442, 1397, 1069, 1030 cm^{-1}; $[\alpha]_D^{20}$ −148.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (1H, m, Ar**H**), 7.26-7.08 (9H, m, Ar**H**), 4.04-3.83 (2H, m, C**H**$_2$Cl), 3.82-3.70 (1H, m, C**H**CH_2), 3.08 (1H, dddd, *J* = 15.9, 8.9, 6.1, 2.7 Hz, C**H**$_a$H$_b$C=), 2.72 (1H, dddd, *J* = 15.9, 9.2, 5.3, 1.6 Hz, CH$_A$**H**$_B$C=), 2.64 (1H, dd, *J* = 17.1, 4.1 Hz, C**H**$_a$H$_b$C=O), 2.56 (1H, dd, *J* = 17.1, 9.7 Hz, CH$_a$**H**$_b$C=O), 2.41 (1H, app dtd, *J* = 13.0, 8.8, 6.1 Hz, CH_2C**H**$_a$H$_b$CH), 1.69 (1H, app ddt, *J* = 13.0, 9.0, 5.2 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3 (C), 140.2 (C), 138.4 (C), 137.5 (C), 137.2 (C), 129.0 (2 × CH), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.2 (CH), 126.9 (CH), 48.6 (CH_2), 46.4 (CH), 44.1 (CH_2), 36.5 (CH_2), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{20}H_{19}OClNa]^+$ $[M+Na]^+$: 333.1017, found: 333.1019; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 8.3 min, t_r (major) = 11.2 min, 99% ee.



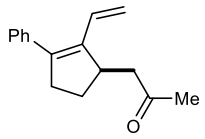
(*R*)-1-[2-(4-Chlorophenyl)-3-phenylcyclopent-2-en-1-yl]propan-2-one (2k). Prepared according to General Procedure C, using enyne **1k** (69.8 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 16 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2k** (64.6 mg, 69%) as an off-white solid. R_f = 0.58 (30% EtOAc/pet. ether); m.p. 84−85 °C (Et_2O); IR 3052, 2928, 1704 (C=O), 1486, 1361, 1157, 1088, 1010, 821, 763 cm^{-1}; $[\alpha]_D^{25}$ −184.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.12 (5H, m, Ar**H**), 7.11-7.02 (4H, m, Ar**H**), 3.71-3.61 (1H, m, C**H**CH_2), 3.05 (1H, dddd, *J* = 16.0, 9.1, 6.4, 2.7 Hz, C**H**$_a$H$_b$C=), 2.69 (1H, dddd, *J* = 16.0, 9.3, 5.2, 1.4 Hz, CH$_a$**H**$_b$C=), 2.49 (1H, dd, *J* = 17.0, 3.5 Hz, C**H**$_a$H$_b$C=O), 2.44-2.33 (2H, m, CH$_a$**H**$_b$C=O and CH_2C**H**$_a$H$_b$CH), 2.07 (3H, s, C**H**$_3$), 1.66 (1H, app ddt, *J* = 13.7, 9.4, 5.0 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5 (C), 139.3 (C), 139.0 (C), 137.4 (C), 135.9 (C), 132.7 (C), 130.3 (2 × CH), 128.8 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.0 (CH), 47.8 (CH_2), 46.1 (CH), 36.7 (CH_2), 30.5 (CH_3), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{20}H_{19}OClNa]^+$ $[M+Na]^+$: 333.1017, found: 333.1029; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 5.9 min, t_r (major) = 6.7 min, 99% ee.



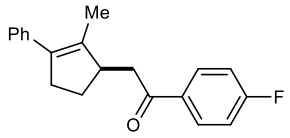
(*R*)-1-[3-Phenyl-2-(m-tolyl)cyclopent-2-en-1-yl]propan-2-one (2l). Prepared according to General Procedure C, using enyne **1l** (63.7 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (6% EtOAc/pet. ether) gave **2l** (63.4 mg, 73%) as a colorless oil. R_f = 0.51 (20% EtOAc/pet. ether); IR 3053, 2924, 1714 (C=O), 1600, 1493, 1443, 1360, 1159, 761, 697 cm^{-1}; $[\alpha]_D^{25}$ −136.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.19-7.08 (6H, m, Ar**H**), 7.05-7.00 (1H, m, Ar**H**), 6.96-6.93 (1H, m, Ar**H**), 6.92-6.86 (1H, m, Ar**H**), 3.71-3.60 (1H, m, C**H**CH_2), 3.05 (1H, dddd, *J* = 15.9, 9.0, 6.3, 2.5 Hz, C**H**$_a$H$_b$C=), 2.70 (1H, dddd, *J* = 15.9, 9.4, 5.1, 1.4 Hz, CH$_a$**H**$_b$C=), 2.53 (1H, dd, *J* = 16.9, 3.4 Hz, C**H**$_a$H$_b$C=O), 2.43-2.32 (2H, m, CH$_a$**H**$_b$C=O and CH_2C**H**$_a$H$_b$CH), 2.27 (3H, s, C**H**$_3$), 2.06 (3H, s, C**H**$_3$), 1.66 (1H, app ddt, *J* = 13.7, 9.4, 5.0 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9 (C), 140.9 (C), 138.1 (C), 137.7 (C), 137.6 (C), 137.5 (C), 129.4 (CH), 128.4 (CH), 128.1 (2 × CH), 128.0 (2 × CH), 127.8 (CH), 126.7 (CH), 126.1 (CH), 47.9 (CH), 46.5 (CH_2), 36.5 (CH_3), 30.5 (CH_2), 29.1 (CH_3), 21.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{21}H_{22}ONa]^+$ $[M+Na]^+$: 313.1563, found: 313.1559; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (99:1 *iso*-hexane:*i*-PrOH, 0.3 mL/min, 280 nm, 25 °C); t_r (major) = 23.6 min, t_r (minor) = 25.6 min, 99% ee.



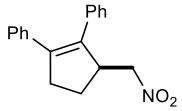
(*R*)-1-[3-Phenyl-2-(thiophen-2-yl)cyclopent-2-en-1-yl]propan-2-one (2m). Prepared according to General Procedure C, using enyne **1m** (61.3 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (8% EtOAc/pet. ether) gave **2m** (41.7 mg, 49%) as an off-white solid. R_f = 0.42 (30% EtOAc/pet. ether); m.p. 68−70 °C (Et_2O); IR 3074, 2925, 2843, 1713 (C=O), 1598, 1491, 1360, 1159, 761, 670 cm^{-1}; $[\alpha]_D^{25}$ −36.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (2H, m, Ar**H**), 7.26-7.21 (3H, m, Ar**H**), 7.12 (1H, dd, *J* = 5.1, 1.1 Hz, Ar**H**), 6.90 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 6.80 (1H, dd, *J* = 3.6, 1.1 Hz, Ar**H**), 3.71-3.56 (1H, m, C**H**CH_2), 2.98 (1H, app dtd, *J* = 16.8, 8.4, 2.6 Hz, C$\mathbf{H}_a$$H_b$C=), 2.75 (1H, dd, *J* = 16.9, 3.0 Hz, C$\mathbf{H}_a$$H_b$C=O), 2.71-2.62 (1H, m, $CH_a$$\mathbf{H}_b$C=), 2.53 (1H, dd, *J* = 16.9, 10.7 Hz, $CH_a$$\mathbf{H}_b$C=O), 2.41-2.26 (1H, m, CH_2C$\mathbf{H}_a$$H_b$CH), 2.14 (3H, s, C$\mathbf{H}_3$), 1.71 (1H, app ddt, *J* = 13.1, 8.5, 3.2 Hz, $CH_2CH_a$$\mathbf{H}_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7 (C), 140.0 (C), 139.0 (C), 138.2 (C), 133.4 (C), 128.5 (2 × CH), 128.2 (2 × CH), 127.4 (CH), 126.9 (CH), 126.1 (CH), 125.1 (CH), 47.6 (CH_2), 46.2 (CH), 37.7 (CH_2), 30.5 (CH_3), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{18}H_{18}OSNa]^+$ $[M+Na]^+$: 305.0971, found: 305.0971; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (95:5 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (major) = 6.2 min, t_r (minor) = 6.7 min, 84% ee.



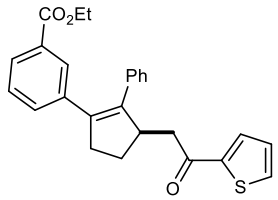
(*R*)-1-(3-Phenyl-2-vinylcyclopent-2-en-1-yl)propan-2-one (2n). Prepared according to General Procedure C, using enyne **1n** (44.5 mg, 0.30 mmol) and phenylboronic acid (43.9 mg, 0.36 mmol) and stirring for 17 h. Purification by column chromatography (20% EtOAc/cyclohexane) gave **2n** (67.4 mg, 99%) as a yellow oil. R_f = 0.50 (30% EtOAc/pet. ether); IR 3083, 2928, 1712 (C=O), 1600, 1492, 1358, 1158, 900, 763, 698 cm^{-1}; $[\alpha]_D^{25}$ +20.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (2H, m, Ar**H**), 7.30-7.25 (3H, m, Ar**H**), 6.64 (1H, dd, *J* = 17.7, 11.0 Hz, C**H**=), 5.24-5.13 (2H, m, =C$\mathbf{H}_2$), 3.56 (1H, app t, *J* = 9.4 Hz, C**H**CH_2), 2.94 (1H, app dt, *J* = 17.5, 8.8 Hz, C$\mathbf{H}_a$$H_b$C=), 2.78 (1H, dd, *J* = 16.9, 2.5 Hz, C$\mathbf{H}_a$$H_b$C=O), 2.64 (1H, app dd, *J* = 17.5, 9.4 Hz, $CH_a$$\mathbf{H}_b$C=), 2.47 (1H, dd, *J* = 16.9, 10.8 Hz, $CH_a$$\mathbf{H}_b$C=O), 2.22-2.11 (1H, m, CH_2C$\mathbf{H}_a$$H_b$CH), 2.18 (3H, s, C$\mathbf{H}_3$), 1.69 (1H, app ddt, *J* = 11.4, 8.1, 1.7 Hz, $CH_2CH_a$$\mathbf{H}_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0 (C), 141.8 (C), 138.8 (C), 137.7 (C), 131.0 (CH), 128.34 (2 × CH), 128.27 (2 × CH), 127.3 (CH), 115.5 (CH_2), 46.8 (CH_2), 40.9 (CH), 36.1 (CH_2), 30.6 (CH_3), 28.8 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{16}H_{18}ONa]^+$ $[M+Na]^+$: 249.1250, found: 249.1241; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 5.4 min, t_r (major) = 6.2 min, 91% ee.



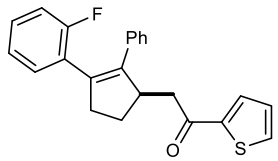
(*R*)-1-(4-Fluorophenyl)-2-(2-methyl-3-phenylcyclopent-2-en-1-yl)ethan-1-one (2o). Prepared according to a modification of General Procedure C, using enyne **1o** (64.9 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 18 h. Purification by column chromatography (3-10% EtOAc/pentane) gave **2o** (27.4 mg, 31%) as a colorless oil. R_f = 0.35 (5% EtOAc/pet. ether); $[\alpha]_D^{25}$ +40.0 (*c* 0.10, $CHCl_3$); IR 3924, 2852, 1681 (C=O), 1595, 1504, 1408, 1272, 1229, 1155, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-7.99 (2H, m, Ar**H**), 7.38-7.27 (4H, m, Ar**H**), 7.26-7.21 (1H, m, Ar**H**), 7.19-7.12 (2H, m, Ar**H**), 3.37-3.21 (2H, m, C**H**C**H**$_a$H$_b$C=O), 2.92 (1H, dd, *J* = 16.1, 9.8 Hz, CH$_a$**H**$_b$C=O), 2.77-2.67 (2H, m, C**H**$_2$C=), 2.26 (1H, app dtd, *J* = 12.8, 8.1, 6.1 Hz, CH$_2$C**H**$_a$H$_b$CH), 1.85 (3H, app q, *J* = 1.8 Hz, C**H**$_3$), 1.63-1.50 (1H, m, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6 (C), 165.8 (d, $J_{C\text{-}F}$ = 254.6 Hz, C), 138.5 (C), 136.6 (C), 136.5 (C), 133.9 (d, $J_{C\text{-}F}$ = 3.1 Hz, C), 130.9 (d, $J_{C\text{-}F}$ = 9.2 Hz, 2 × CH), 128.2 (2 × CH), 127.8 (2 × CH), 126.5 (CH), 115.8 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2 × CH), 47.2 (CH), 42.8 (CH_2), 35.5 (CH_2), 29.5 (CH_2), 14.1 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –105.5 (s); HRMS (ESI) Exact mass calculated for $[C_{20}H_{19}FONa]^+$ $[M+Na]^+$: 317.1312, found: 317.1310; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (95:5 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 254 nm, 25 °C); t_r (minor) = 24.3 min, t_r (major) = 26.4 min, 92% ee.



(*S*)-[3-(Nitromethyl)cyclopent-1-ene-1,2-diyl]dibenzene (2p). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 17 h. Purification by column chromatography (5% EtOAc/pentane) gave **2p** (61.4 mg, 73%) as a yellow solid. R_f = 0.46 (10% EtOAc/pet. ether); m.p. 49−50 °C (Et_2O); IR 3077, 3056, 2919, 2846, 1546, 1490, 1442, 1380, 762, 692 cm^{-1}; $[\alpha]_D^{25}$ −128.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (3H, m, Ar**H**), 7.24-7.06 (7H, m, Ar**H**), 4.37 (1H, dd, *J* = 12.1, 3.8 Hz, C**H**$_a$H$_b$NO$_2$), 4.25 (1H, dd, *J* = 12.1, 10.3 Hz, CH$_a$**H**$_b$NO$_2$), 4.11-3.96 (1H, m, C**H**CH$_2$), 3.17 (1H, dddd, *J* = 16.3, 9.2, 6.8, 2.7 Hz, C**H**$_a$H$_b$C=), 2.78 (1H, dddd, *J* = 16.3, 9.4, 4.5, 1.3 Hz, CH$_a$**H**$_b$C=), 2.39 (1H, app dtd, *J* = 13.5, 9.1, 6.9 Hz, CH$_2$C**H**$_a$H$_b$CH), 2.02 (1H, ddt, *J* = 13.5, 8.8, 4.1 Hz, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (C), 136.9 (C), 136.02 (C), 135.98 (C), 128.9 (2 × CH), 128.7 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.7 (CH), 127.4 (CH), 78.4 (CH_2), 49.9 (CH), 36.4 (CH_2), 26.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{18}H_{17}NO_2Na]^+$ $[M+Na]^+$: 302.1151, found: 302.1149; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (99.5:0.5 *iso*-hexane:*i*-PrOH, 0.3 mL/min, 280 nm, 25 °C); t_r (minor) = 38.0 min, t_r (major) = 39.3 min, >99% ee.



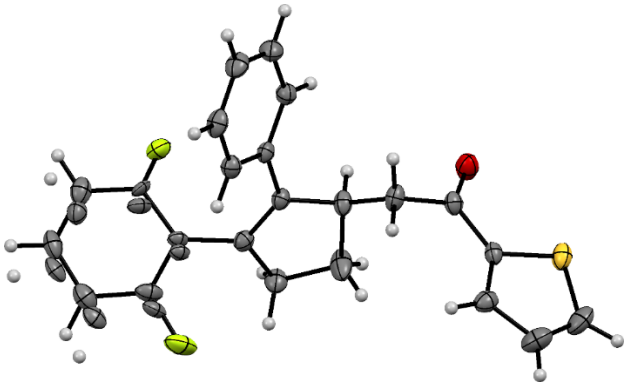
Ethyl (*R*)-3-{3-[2-oxo-2-(thiophen-2-yl)ethyl]-2-phenylcyclopent-1-en-1-yl}benzoate (2q). Prepared according to General Procedure C, using enyne **1g** (79.9 mg, 0.30 mmol) and 3-ethoxycarbonylphenylboronic acid (69.8 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (10% EtOAc/pet. ether) gave **2q** (120 mg, 96%) as a yellow solid. R_f = 0.48 (20% EtOAc/pet. ether); m.p. 83−84 °C (Et_2O); IR 3079, 2929, 1716 (C=O), 1660, 1441, 1280, 1222, 1109, 756, 699 cm^{-1}; $[\alpha]_D^{25}$ −96.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (1H, app t, *J* = 1.7 Hz, Ar**H**), 7.82 (1H, app dt, *J* = 7.6, 1.6 Hz, Ar**H**), 7.60 (1H, dd, *J* = 4.9, 1.1 Hz, Ar**H**), 7.57 (1H, dd, *J* = 3.8, 1.2 Hz, Ar**H**), 7.26-7.17 (5H, m, Ar**H**), 7.17-7.12 (2H, m, Ar**H**), 7.07 (1H, dd, *J* = 5.0, 3.8 Hz, Ar**H**), 4.31 (2H, app qd, *J* = 7.1, 1.9 Hz, OC**H**$_2$), 3.93-3.80 (1H, m, C**H**CH_2), 3.15 (1H, dddd, *J* = 15.8, 9.1, 6.4, 2.8 Hz, C**H**$_a$H$_b$C=), 2.97 (1H, dd, *J* = 15.9, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.86 (1H, dd, *J* = 15.9, 10.7 Hz, CH$_a$**H**$_b$C=O), 2.74 (1H, dddd, *J* = 15.8, 9.2, 4.9, 1.4 Hz, CH$_a$**H**$_b$C=), 2.41 (1H, app dtd, *J* = 13.4, 9.0, 6.5 Hz, CH_2C**H**$_a$H$_b$CH), 1.84 (1H, app ddt, *J* = 13.4, 9.3, 4.8 Hz, CH_2CH$_a$**H**$_b$CH), 1.34 (3H, t, *J* = 7.1 Hz, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9 (C), 166.7 (C), 144.8 (C), 142.1 (C), 138.0 (C), 137.3 (C), 137.1 (C), 133.7 (CH), 132.7 (CH), 132.0 (CH), 130.4 (C), 129.1 (CH), 128.9 (2 × CH), 128.7 (2 × CH), 128.14 (CH), 128.05 (CH), 127.9 (CH), 127.3 (CH), 61.0 (CH_2), 47.3 (CH), 43.3 (CH_2), 36.5 (CH_2), 29.0 (CH_2), 14.4 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{26}H_{24}O_3SNa]^+$ $[M+Na]^+$: 439.1338, found: 439.1331; Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (minor) = 7.5 min, t_r (major) = 9.3 min, >99% ee.

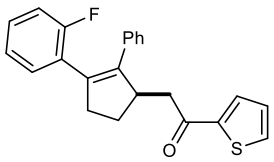


(*R*)-2-[3-(2-Fluorophenyl)-2-phenylcyclopent-2-en-1-yl]-1-(thiophen-2-yl)ethan-1-one (2r). Prepared according to General Procedure C, using enyne **1g** (79.9 mg, 0.30 mmol) and 2-fluorophenylboronic acid (50.4 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2r** (89.8 mg, 83%) as an off-white solid. R_f = 0.73 (30% EtOAc/pet. ether); m.p. 129−131 °C (Et_2O); IR 3079, 2930, 2850, 1657 (C=O), 1484, 1446, 1414, 1204, 755, 698 cm^{-1}; $[\alpha]_D^{25}$ −172.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.55 (2H, m, Ar**H**), 7.24-7.10 (6H, m, Ar**H**), 7.10-7.05 (3H, m, Ar**H**), 7.04-6.91 (1H, m, Ar**H**), 3.99-3.90 (1H, m, C**H**CH_2), 3.19-3.07 (1H, m, C**H**$_a$H$_b$C=), 3.01 (1H, dd, *J* = 16.1, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.90 (1H, dd, *J* = 16.1, 10.7 Hz, CH$_a$**H**$_b$C=O), 2.65 (1H, dddd, *J* = 16.2, 9.3, 5.0, 1.5 Hz, CH$_a$**H**$_b$C=), 2.43 (1H, app dtd, *J* = 13.3, 8.9, 6.5 Hz, CH_2C**H**$_a$H$_b$CH), 1.84 (1H, app ddt, *J* = 13.3, 9.2, 4.8 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0 (C), 160.3 (d, $J_{C\text{-}F}$ = 247.1 Hz, C), 144.8 (C), 143.0 (C), 136.4 (C), 134.3 (C), 133.6 (CH), 132.0 (CH), 131.0 (d, $J_{C\text{-}F}$ = 4.5 Hz, CH), 128.6 (d, $J_{C\text{-}F}$ = 8.1 Hz, CH), 128.5 (2 × CH), 128.3 (2 × CH), 128.1 (CH), 127.1 (CH), 126.3 (d, $J_{C\text{-}F}$ = 15.5 Hz, C), 123.9 (d, $J_{C\text{-}F}$ = 3.6 Hz, CH), 115.8 (d, $J_{C\text{-}F}$ = 22.6 Hz, CH), 45.6

(CH), 43.6 (CH_2), 37.1 (d, J_{C-F} = 2.8 Hz, CH_2), 29.4 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.2 (s); HRMS (ESI) Exact mass calcu lated for $[C_{23}H_{19}FOSNa]^+$ $[M+Na]^+$: 385.1033, found: 385.1037; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (major) = 5.9 min, t_r (minor) = 8.2 min, 99% ee.

Slow evaporation of a solution of **2r** in pentane gave crystals that were suitable for X-ray crystallography:

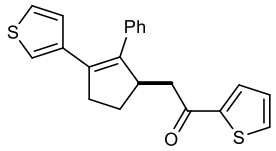




2r
CCDC 2040011
Flack parameter –0.001(6)

ORTEP with ellipsoid probabilities at 50%

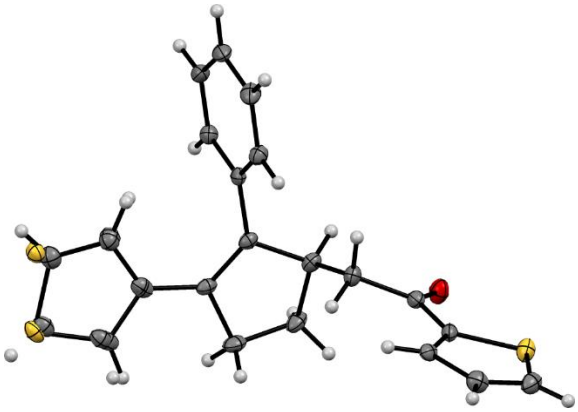
Note: There is conformational disorder in the fluorophenyl ring moiety. Occupancies of the two disorder components were refined and constrained to sum to unity. The geometries of the two disorder components were restrained to be similar (SAME). Rigid bond and similarity restraints were applied to the anisoptropic displacement parameters of the disordered atoms (RIGU, SIMU). Carbon atoms C20 and C20a were constrained to have identical anisotropic displacement parameters (see .cif file for details).

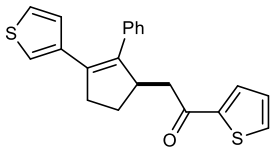


(*R*)-2-[2-Phenyl-3-(thiophen-3-yl)cyclopent-2-en-1-yl]-1-(thiophen-2-yl)ethan-1-one (2s). Prepared according to General Procedure C, using enyne **1g** (79.9 mg, 0.30 mmol) and 3-thienylboronic acid (46.1 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pet. ether) gave **2s** (88.0 mg, 84%) as a yellow solid. R_f = 0.56 (20% EtOAc/pet. ether); m.p. 117−118 °C (Et_2O); IR 3102, 2926, 2847, 1659 (C=O), 1517, 1415, 1310, 1234, 849, 701 cm^{-1}; $[\alpha]_D^{25}$ −56.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, dd, *J* = 4.9, 1.1 Hz, Ar**H**), 7.55 (1H, dd, *J* = 3.8, 1.1 Hz, Ar**H**), 7.38-7.32 (2H, m, Ar**H**), 7.30-7.26 (1H, m, Ar**H**), 7.25-7.20 (2H, m, Ar**H**), 7.06 (2H, dt, *J* = 5.0, 3.1 Hz, Ar**H**), 7.01 (1H, dd, *J* = 3.1, 1.3 Hz, Ar**H**), 6.67 (1H, dd, *J* = 5.0, 1.3 Hz, Ar**H**), 3.84-3.67 (1H, m, C**H**CH_2), 3.08-2.93 (2H, m, C**H**$_a$H$_b$C= and C**H**$_a$H$_b$C=O), 2.86-2.74 (2H, m, CH$_a$**H**$_b$C=O and CH$_a$**H**$_b$C=), 2.40 (1H, app dtd, *J* = 13.2, 8.9, 5.7 Hz, CH_2C**H**$_a$H$_b$CH), 1.78 (1H, app ddt, *J* = 13.2, 9.1, 5.6 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9 (C), 144.8 (C), 140.3 (C), 138.4 (C), 138.2 (C), 133.6 (CH), 132.8 (C), 131.9 (CH), 129.0 (2 × CH), 128.8 (2 × CH), 128.1 (CH), 127.4

(CH), 127.3 (CH), 124.7 (CH), 122.6 (CH), 47.9 (CH), 43.8 (CH_2), 36.0 (CH_2), 29.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{21}H_{18}OS_2Na]^+$ $[M+Na]^+$: 373.0691, found: 373.0692; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (major) = 15.0 min, t_r (minor) = 19.4 min, 99% ee.

Slow evaporation of a solution of **2s** in pentane gave crystals that were suitable for X-ray crystallography:

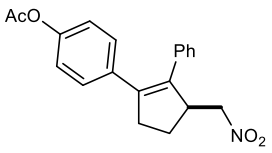




2s
CCDC 2040012
Flack parameter 0.002(5)

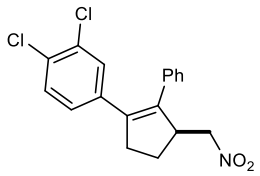
ORTEP with ellipsoid probabilities at 50%

Note: Conformational disorder is observed for the thiophene group attached directly to the cyclopentene ring. The occupancies of the two disorder components were refined and constrained to sum unity, resulting in values of 0.66(1) and 0.34(1) respectively. The geometries of the two disorder components were restrained to be similar (SADI), planar (FLAT) and have 1,2 and 1,3 bond distances set a target values generated by the FragmentDB function in the Software Olex2 v1.3 (DFIX, DANG). Rigid bond and similarity restraints (RIGU, SIMU) were applied to the anisotropic displacement parameters of all atoms in the disordered moieties. The three pairs of overlapping atoms in the disordered moieties were constrained to have identical anisotropic displacement parameters (EADP). All hydrogen atoms in the structure were observed in the electron density map before being geometrically placed and refined using a riding model (see .cif file for details).

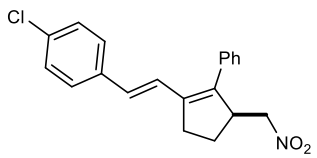


(*S*)-4-[3-(Nitromethyl)-2-phenylcyclopent-1-en-1-yl]phenyl acetate (2t). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), 4-acetoxyphenylboronic acid (108 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pentane) gave **2t** (57.0 mg, 56%) as a colorless oil. R_f = 0.26 (10% EtOAc/pet. ether); IR 3063, 2918, 2858, 1756 (C=O), 1543, 1506, 1369, 1185, 1172, 1010 cm^{-1}; $[\alpha]_D^{25}$ −108.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m, Ar**H**), 7.26-7.23 (1H, m, Ar**H**), 7.18-7.07 (4H, m, Ar**H**), 6.94-6.87 (2H, m, Ar**H**), 4.36 (1H, dd, *J*

= 12.2, 3.8 Hz, C**H**$_a$H$_b$NO$_2$), 4.23 (1H, dd, *J* = 12.2, 10.3 Hz, CH$_a$**H**$_b$NO$_2$), 4.04-3.97 (1H, m, C**H**CH$_2$), 3.13 (1H, dddd, *J* = 16.3, 9.3, 6.7, 2.9 Hz, C**H**$_a$H$_b$C=), 2.76 (1H, dddd, *J* = 16.3, 9.5, 4.6, 1.3 Hz, CH$_a$**H**$_b$C=), 2.38 (1H, app dtd, *J* = 13.4, 9.1, 6.8 Hz, CH$_2$C**H**$_a$H$_b$CH), 2.26 (3H, s, C**H**$_3$), 2.01 (1H, app ddt, *J* = 13.4, 8.8, 4.4 Hz, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.5 (C), 149.8 (C), 139.7 (C), 136.4 (C), 135.9 (C), 134.4 (C), 129.2 (2 × CH), 129.0 (2 × CH), 128.7 (2 × CH), 127.8 (CH), 121.3 (2 × CH), 78.4 (CH$_2$), 50.0 (CH), 36.4 (CH$_2$), 26.6 (CH$_2$), 21.3 (CH$_3$); HRMS (ESI) Exact mass calculated for [C$_{20}$H$_{19}$NO$_4$Na]$^+$ [M+Na]$^+$: 360.1206, found: 360.1203; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t$_r$ (major) = 32.3 min, t$_r$ (minor) = 35.3 min, 98% ee.

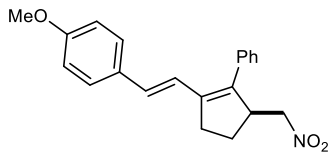


(*S*)-1,2-Dichloro-4-[3-(nitromethyl)-2-phenylcyclopent-1-en-1-yl]benzene (2u). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), 3,4-dichlorophenylboronic acid (115 mg, 0.60 mmol), Ni(OAc)$_2$·4H$_2$O (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 18 h. Purification by column chromatography (10% EtOAc/pentane) gave **2u** (81.2 mg, 78%) as an orange oil. R$_f$ = 0.50 (20% EtOAc/pet. ether); IR 3023, 2924, 2850, 1545, 1469, 1376, 1135, 1028, 762, 698 cm^{-1}; $[\alpha]_D^{25}$ −144.0 (*c* 1.00, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37-7.26 (3H, m, Ar**H**), 7.24-7.16 (2H, m, Ar**H**), 7.15-7.09 (2H, m, Ar**H**), 6.88 (1H, dd, *J* = 8.4, 2.0 Hz, Ar**H**), 4.36 (1H, dd, *J* = 12.2, 3.9 Hz, C**H**$_a$H$_b$NO$_2$), 4.23 (1H, dd, *J* = 12.2, 10.0 Hz, CH$_a$**H**$_b$NO$_2$), 4.09-3.88 (1H, m, C**H**CH$_2$), 3.10 (1H, dddd, *J* = 16.1, 9.3, 6.7, 2.8 Hz, C**H**$_a$H$_b$C=), 2.83-2.76 (1H, m, CH$_a$**H**$_b$C=), 2.40 (1H, app dtd, *J* = 13.6, 8.9, 6.6 Hz, CH$_2$C**H**$_a$H$_b$CH), 2.03 (1H, app ddt, *J* = 13.6, 9.5, 4.5 Hz, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.3 (2 × C), 136.8 (C), 135.3 (C), 132.4 (C), 131.2 (C), 130.1 (CH), 129.9 (CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.3 (CH), 127.6 (CH), 78.2 (CH$_2$), 50.0 (CH), 36.2 (CH$_2$), 26.6 (CH$_2$); HRMS (ESI) Exact mass calculated for [C$_{18}$H$_{15}$NO$_2$Cl$_2$Na]$^+$ [M+Na]$^+$: 370.0372, found: 370.0.374; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t$_r$ (major) = 14.6 min, t$_r$ (minor) = 15.3 min, 99% ee.

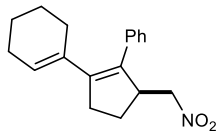


(*S*,*E*)-1-Chloro-4-{2-[3-(nitromethyl)-2-phenylcyclopent-1-en-1-yl]vinyl}benzene (2v). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), *trans*-2-(4-chlorophenyl)vinylboronic acid (109 mg, 0.60 mmol), Ni(OAc)$_2$·4H$_2$O (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 16 h. Purification by column chromatography (5% EtOAc/pentane) gave **2v** (37.1 mg, 36%) as a yellow oil. R$_f$ = 0.67 (30% EtOAc/pet. ether); IR 3025, 2924, 2851, 1545, 1489, 1376, 1090, 961, 810, 700 cm^{-1}; $[\alpha]_D^{25}$ −224.0 (*c*

1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.25 (9H, m, Ar**H**), 6.98 (1H, d, *J* = 16.1 Hz, =C**H**), 6.56 (1H, d, *J* = 16.1 Hz, =C**H**), 4.39 (1H, dd, *J* = 12.1, 3.7 Hz, C**H**$_a$H$_b$NO$_2$), 4.17 (1H, dd, *J* = 12.1, 10.2 Hz, CH$_a$**H**$_b$NO$_2$), 4.12-3.99 (1H, m, C**H**CH$_2$), 2.94 (1H, dddd, *J* = 11.8, 8.9, 6.0, 2.2 Hz, C**H**$_a$H$_b$C=), 2.81-2.73 (1H, m, CH$_a$**H**$_b$C=), 2.40 (1H, app dtd, *J* = 14.4, 8.8, 5.9 Hz, CH$_2$C**H**$_a$H$_b$CH), 2.02-1.89 (1H, m, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8 (C), 139.2 (C), 135.9 (C), 135.4 (C), 133.5 (C), 131.0 (CH), 129.0 (2 × CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.1 (CH), 127.9 (2 × CH), 124.0 (CH), 78.8 (CH_2), 49.0 (CH), 32.1 (CH_2), 26.7 (CH_2); HRMS (ESI) Exact mass calculated for [$C_{20}H_{18}NO_2ClNa$]$^+$ [M+Na]$^+$: 362.0918, found: 362.0916; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 280 nm, 25 °C); t_r (major) = 9.5 min, t_r (minor) = 10.7 min, >99% ee.



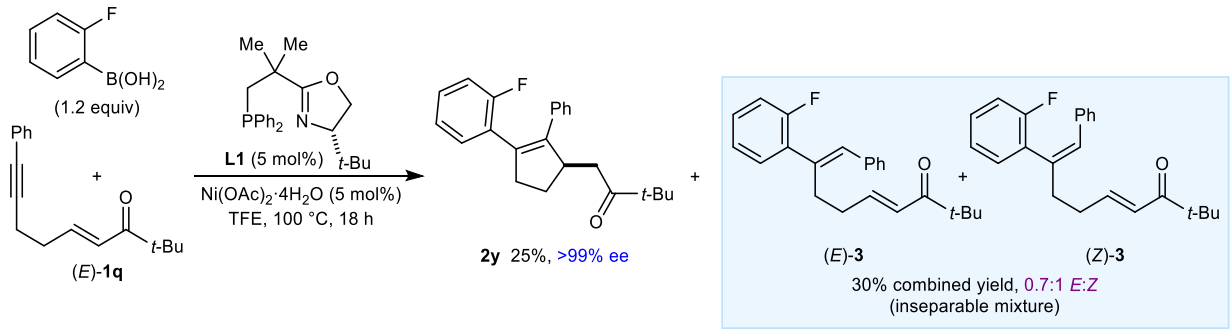
(*S*,*E*)-1-Methoxy-4-[2-(3-(nitromethyl)-2-phenylcyclopent-1-en-1-yl)vinyl]benzene (2w). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), *trans*-2-(4-methoxyphenyl)vinylboronic acid (107 mg, 0.60 mmol), Ni(OAc)$_2$·4H$_2$O (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 18 h. Purification by column chromatography (5% EtOAc/pentane) followed by a second purification by column chromatography (60 to 80% $CHCl_3$/pentane) gave **2w** (25.0 mg, 25%) as a yellow solid. R_f = 0.29 (10% EtOAc/pet. ether); m.p. 70−72 °C ($CHCl_3$); IR 2929, 1601, 1546, 1509, 1377, 1243, 1173, 1031, 961, 700 cm^{-1}; $[\alpha]_D^{25}$ −80.0 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.38 (2H, m, Ar**H**), 7.36-7.27 (5H, m, Ar**H**), 6.91 (1H, d, *J* = 16.1 Hz, =C**H**), 6.86-6.80 (2H, m, Ar**H**), 6.58 (1H, d, *J* = 16.1 Hz, =C**H**), 4.39 (1H, dd, *J* = 12.0, 3.6 Hz, C**H**$_a$H$_b$NO$_2$), 4.16 (1H, dd, *J* = 12.0, 10.3 Hz, CH$_a$**H**$_b$NO$_2$), 4.09-4.00 (1H, m, C**H**CH$_2$), 3.80 (3H, s, C**H**$_3$), 3.01-2.88 (1H, m, C**H**$_a$H$_b$C=), 2.77 (1H, app ddd, *J* = 15.1, 9.2, 5.4 Hz, CH$_a$**H**$_b$C=), 2.38 (1H, dddd, *J* = 14.0, 9.4, 8.3, 6.0 Hz, CH$_2$C**H**$_a$H$_b$CH), 1.94 (1H, app ddt, *J* = 14.2, 9.4, 5.2 Hz, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (C), 139.6 (C), 137.9 (C), 135.7 (C), 131.9 (CH), 130.2 (C), 128.9 (2 × CH), 128.8 (2 × CH), 128.0 (2 × CH), 127.8 (CH), 121.4 (CH), 114.2 (2 × CH), 79.0 (CH_2), 55.4 (CH_3), 49.0 (CH), 32.2 (CH_2), 26.7 (CH_2); HRMS (ESI) Exact mass calculated for [$C_{21}H_{21}NO_3Na$]$^+$ [M+Na]$^+$: 358.1414, found: 358.1418; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 230 nm, 25 °C); t_r (minor) = 15.7 min, t_r (major) = 20.9 min, >99% ee.



(*S*)-[2-(Cyclohex-1-en-1-yl)-5-(nitromethyl)cyclopent-1-en-1-yl]benzene (2x). Prepared according to a modification of General Procedure C, using enyne **1p** (60.4 mg, 0.30 mmol), cyclohex-1-en-1-ylboronic acid (75.6 mg, 0.60 mmol), Ni(OAc)$_2$·4H$_2$O (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring

for 18 h. Purification by column chromatography (5 to 10% EtOAc/pentane) gave **2x** (22.1 mg, 26%) as a colorless oil. R_f = 0.36 (5% EtOAc/pentane); $[\alpha]_D^{25}$ −200.0 (*c* 0.10, $CHCl_3$); IR 2924, 2855, 1544, 1490, 1432, 1377, 1208, 916, 776, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (2H, m, Ar**H**), 7.29-7.20 (3H, m, Ar**H**), 5.71 (1H, tt, *J* = 3.8, 1.7 Hz, $CH_2C\mathbf{H}$=), 4.30 (1H, dd, *J* = 12.1, 3.8 Hz, $C\mathbf{H}_aH_bNO_2$), 4.17 (1H, dd, *J* = 12.1, 10.4 Hz, $CH_a\mathbf{H}_bNO_2$), 3.89-3.79 (1H, m, $C\mathbf{H}CH_2$), 2.85 (1H, dddd, *J* = 16.0, 9.2, 6.7, 2.6 Hz, $C\mathbf{H}_aH_bC$=C), 2.60 (1H, dddd, *J* = 16.0, 9.4, 4.7, 1.2 Hz, $CH_a\mathbf{H}_bC$=C), 2.26 (1H, dtd, *J* = 13.3, 9.0, 6.8 Hz, $CH_2C\mathbf{H}_aH_bCH$), 2.12-2.02 (2H, m, $C\mathbf{H}_2CH$=C), 1.88-1.81 (2H, m, $CH_2CH_a\mathbf{H}_bCH$ and $C\mathbf{H}_aH_bC$=CH), 1.73-1.62 (1H, m, $CH_a\mathbf{H}_bC$=CH), 1.61-1.39 (4H, m, $CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2 (C), 137.4 (C), 134.6 (C), 133.6 (C), 128.6 (2 × CH), 128.4 (2 × CH), 127.8 (CH), 127.3 (CH), 78.7 (CH_2), 50.3 (CH), 35.4 (CH_2), 28.0 (CH_2), 26.6 (CH_2), 25.8 (CH_2), 23.0 (CH_2), 22.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{18}H_{21}NO_2Na]^+$ $[M+Na]^+$: 306.1465, found: 306.1458; Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column (98:2 *iso*-hexane:*i*-PrOH, 0.25 mL/min, 254 nm, 25 °C); t_r (minor) = 47.5 min, t_r (major) = 49.4 min, 98% ee.

(*R*)-1-[-(2-Fluorophenyl)-2-phenylcyclopent-2-en-1-yl]-3,3-dimethylbutan-2-one (2y), (4*E*,8*E*)-8-(2-fluorophenyl)-2,2-dimethyl-9-phenylnona-4,8-dien-3-one [(*E*)-3], and (4*E*,8*Z*)-8-(2-fluorophenyl)-2,2-dimethyl-9-phenylnona-4,8-dien-3-one [(*Z*)-3]

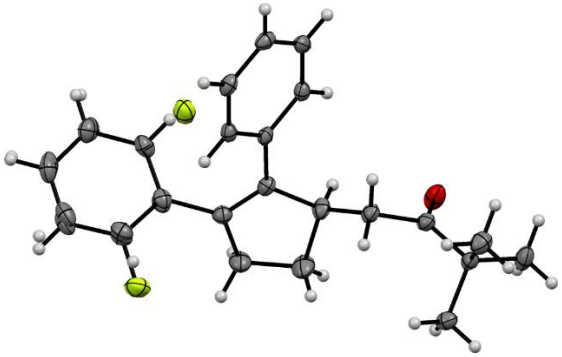


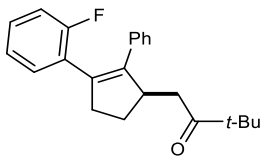
Prepared according to General Procedure A, using enyne (*E*)-**1q** (79.9 mg, 0.30 mmol) and 2-fluorophenylboronic acid (50.4 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (2% EtOAc/pentane) gave **2y** (25.0 mg, 25%) as a white solid followed by a 0.7:1 mixture of inseparable alkyne hydroarylation products (*E*)-**3** and (*Z*)-**3**, respectively, (30.6 mg, 30%) as a colorless oil.

Data for **2y**: R_f = 0.29 (3% EtOAc/pet. ether); m.p. 103–105 °C (Et_2O); IR 3057, 2964, 2868, 1703 (C=O), 1483, 1446, 1365, 1206, 1057, 754 cm^{-1}; $[\alpha]_D^{20}$ −156.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21-7.11 (4H, m, Ar**H**), 7.09-7.03 (2H, m, Ar**H**), 7.02-6.89 (3H, m, Ar**H**), 3.83 (1H, app tdd, *J* = 7.8, 5.5, 3.3 Hz, $C\mathbf{H}CH_2$), 3.11-2.99 (1H, m, $C\mathbf{H}_aH_bC$=), 2.67-2.54 (2H, m, $CH_a\mathbf{H}_bC$= and $C\mathbf{H}_aH_bC$=O), 2.49 (1H, dd, *J* = 17.7, 3.4 Hz, $CH_a\mathbf{H}_bC$=O), 2.40 (1H, app dtd, *J* = 12.9, 8.8, 6.2 Hz,

$CH_2C\mathbf{H}_aH_bCH$), 1.63-1.55 (1H, m, $CH_2CH_a\mathbf{H}_bCH$), 1.06 (9H, s, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7 (C), 160.4 (d, $J_{C\text{-}F}$ = 246.9 Hz, C), 143.5 (C), 136.6 (C), 133.9 (C), 131.1 (d, $J_{C\text{-}F}$ = 4.6 Hz, CH), 128.6 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 127.0 (CH), 126.5 (d, $J_{C\text{-}F}$ = 15.6 Hz, C), 123.9 (d, $J_{C\text{-}F}$ = 3.4 Hz, CH), 115.8 (d, $J_{C\text{-}F}$ = 22.3 Hz, CH), 44.4 (CH), 44.3 (C), 41.0 (CH_2), 37.1 (d, $J_{C\text{-}F}$ = 2.9 Hz, CH_2), 29.9 (CH_2), 26.4 (3 ×CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.3 (s); HRMS (ESI) Exact mass calculated for $[C_{23}H_{25}FONa]^+$ $[M+Na]^+$: 359.1782, found 359.1785; Enantiomeric excess was determined by HPLC using a Chiralpak IC column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 8.0 min, t_r (major) = 9.3 min, >99% ee.

Slow evaporation of a solution of **2y** in pentane gave crystals that were suitable for X-ray crystallography:





2y
CCDC 2040013
Flack parameter 0.07(5)

ORTEP with ellipsoid probabilities at 50%

Note: Conformational disorder is observed in the fluorophenyl moiety. The occupancies of the coplanar disorder components were refined and restrained to sum to unity, having values of 0.92(1) and 0.08(1) each. The geometries of the two components are restrained to be similar (SAME). The anisotropic displacement parameters of the coincident atoms are contrained to be identical (EADP). A rigid bond and similarity restraint was applied to all atoms in the disordered moieties. All hydrogen atoms were observed in the electron density map before being geometrically placed and refined with a riding model (see .cif file for details).

Data for the mixture of (*E*)-**3** and (*Z*)-**3**: R_f = 0.20 (3% EtOAc/pet. ether); IR 3028, 2971, 2929, 1687 (C=O), 1620, 1487, 1475, 1448, 1218, 1106 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{23}H_{25}OFNa]^+$ $[M+Na]^+$: 359.1782, found: 359.1788.

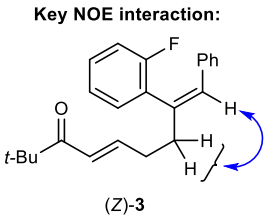
Overlapping NMR signals (integrals refer to the sum of the integrals for each isomer): ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (2H, m, Ar**H**), 7.34-7.27 (5H, m, Ar**H**), 7.17-7.05 (8H, m, Ar**H**), 7.00-6.90 (4H, m, 3 × Ar**H** and $CH_2C\mathbf{H}$= (from (*Z*)-**3**).

Characteristic NMR signals signals for (E)-**3**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (1H, dt, *J* = 15.2, 6.8 Hz, $CH_2C\mathbf{H}$=), 6.64 (1H, s, C=C**H**Ph), 6.36 (1H, dt, *J* = 15.2, 1.6 Hz, C**H**C=O), 2.89 (2H, t, *J* =

7.7 Hz, C**H**$_2$CH$_2$CH=), 2.29-2.21 (2H, m, C**H**$_2$CH=), 1.10 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (C), 160.1 (d, $J_{C\text{-}F}$ = 246.8 Hz, C), 146.28 (CH), 137.7 (C), 137.3 (C), 132.0 (d, $J_{C\text{-}F}$ = 1.5 Hz, CH), 130.6 (d, $J_{C\text{-}F}$ = 4.3 Hz, CH), 129.1 (d, $J_{C\text{-}F}$ = 8.2 Hz, CH), 129.0 (2 × CH), 128.5 (2 × CH), 127.1 (CH), 124.6 (CH), 124.3 (d, $J_{C\text{-}F}$ = 3.4 Hz, CH), 116.2 (CH), 42.9 (C), 31.2 (CH_2), 29.6 (d, $J_{C\text{-}F}$ = 3.4 Hz, CH_2), 26.28 (3 × CH_3) (one quaternary carbon signal was not identified); ^{19}F NMR (376 MHz, $CDCl_3$) δ –114.6 (s).

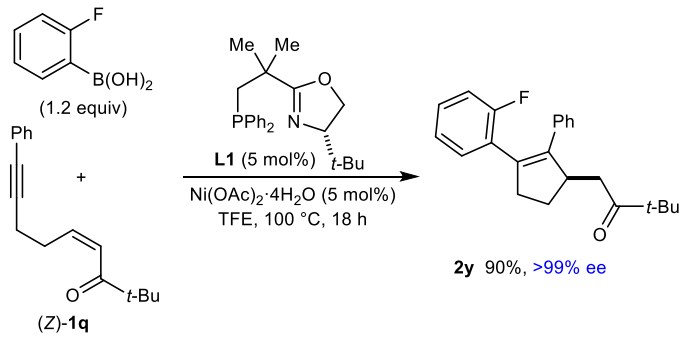
*Characteristic NMR signals signals for (Z)-**3***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (1H, s, C=C**H**Ph), 6.50 (1H, dt, *J* = 15.3, 1.6 Hz, =C**H**C=O), 2.69 (1H, t, *J* = 7.0 Hz, C**H**$_2$CH$_2$CH=), 2.37-2.30 (2H, m, C**H**$_2$CH=), 1.14 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3 (C), 160.0 (d, $J_{C\text{-}F}$ = 245.9 Hz, C), 146.31 (CH), 136.9 (C), 135.8 (C), 131.2 (d, $J_{C\text{-}F}$ = 4.3 Hz, CH), 129.7 (CH), 129.3 (d, $J_{C\text{-}F}$ = 8.0 Hz, CH), 128.7 (2 × CH), 128.1 (2 × CH), 126.8 (CH), 124.8 (CH), 124.5 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 116.0 (CH), 43.0 (C), 38.3 (d, $J_{C\text{-}F}$ = 1.7 Hz, CH_2), 30.9 (CH_2), 26.31 (3 × CH_3) (one quaternary carbon signal was not identified); ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.1 (s)

Assignment of the alkenyl stereochemistries of (*E*)-**3** and (*Z*)-**3** was made based on the following NOE interaction observed in the 2D NOESY spectrum of the mixture, between the alkenyl proton at 6.59 ppm and the methylene protons at 2.69 ppm, which correspond to those (*Z*)-**3**:



(*Z*)-**3**

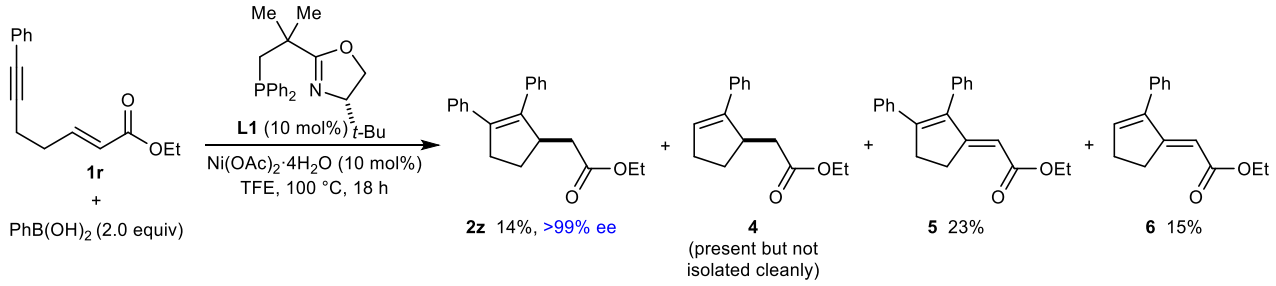
(*R*)-1-[-(2-Fluorophenyl)-2-phenylcyclopent-2-en-1-yl]-3,3-dimethylbutan-2-one (2y)



Prepared according to General Procedure A, using enyne (*Z*)-**1q** (79.9 mg, 0.30 mmol) and 2-fluorophenylboronic acid (50.4 mg, 0.36 mmol) and stirring for 18 h. Purification by column chromatography (3% EtOAc/pentane) gave **2y** (90.8 mg, 90%) as a white solid. For the characterization data, see above. Enantiomeric excess was determined by HPLC using a Chiralpak

IC column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 7.8 min, t_r (major) = 9.2 min, >99% ee.

Ethyl (*R*)-2-(2,3-diphenylcyclopent-2-en-1-yl)acetate (2z), ethyl (*R*)-2-(2-phenylcyclopent-2-en-1-yl)acetate (4), ethyl (*E*)-2-(2,3-diphenylcyclopent-2-en-1-ylidene)acetate (5), and ethyl (*E*)-2-(2-phenylcyclopent-2-en-1-ylidene)acetate (6)

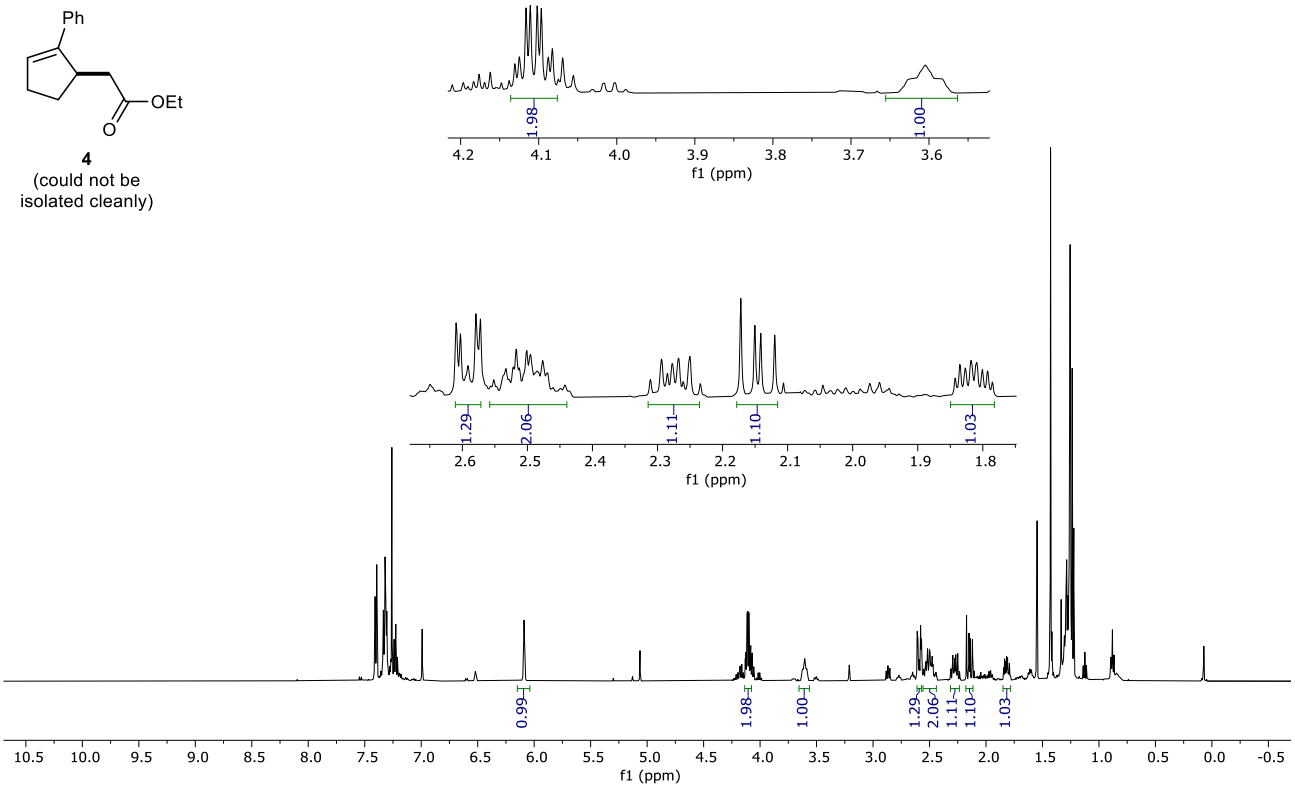


An oven-dried microwave vial fitted with a magnetic stirrer bar was charged with the enyne **1r** (0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol) and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.6 mg, 0.03 mmol). The vial was capped with a crimp cap seal and flushed with argon (5 min). Freshly degassed TFE (3 mL, using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 100 °C for 18 h. The reaction was cooled to room temperature, diluted with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0.5 to 2% EtOAc/pentane) to give a mixture of **2z** and **6** (23.9 mg) followed by **5** (20.7 mg, 23%) as a white solid. A second purification of the mixture of **2z** and **6** by column chromatography (0.5% MeOH/CH_2Cl_2) gave **2z** (13.2 mg, 14%) as a colorless oil, followed by **6** (10.4 mg, 15%) as a white solid. The reductive cyclization product **4** was present in the reaction but could not be isolated cleanly (8.8 mg of very impure material was obtained).

Data for **2z**: R_f = 0.55 (20% EtOAc/pet. ether) and 0.55 (0.5% MeOH/CH_2Cl_2); IR 3054, 2979, 2936, 1729 (C=O), 1599, 1493, 1443, 1370, 1270, 1170 cm^{-1}; $[\alpha]_D^{25}$ −128.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.26-7.19 (3H, m, Ar**H**), 7.19-7.08 (7H, m, Ar**H**), 4.05 (2H, q, *J* = 7.1 Hz, C**H**$_2$CH$_3$), 3.69-3.60 (1H, m, C**H**CH$_2$), 3.09 (1H, dddd, *J* = 15.8, 9.1, 6.4, 2.7 Hz, C**H**$_a$H$_b$C=), 2.71 (1H, dddd, *J* = 15.8, 9.1, 5.0, 1.5 Hz, CH$_a$**H**$_b$C=), 2.44 (1H, dd, *J* = 15.4, 4.1 Hz, C**H**$_a$H$_b$C=O), 2.40-2.34 (1H, m, CH$_2$C**H**$_a$H$_b$CH), 2.21 (1H, dd, *J* = 15.4, 10.5 Hz, CH$_a$**H**$_b$C=O), 1.82 (1H, app ddt, *J* = 13.6, 9.3, 4.9 Hz, CH$_2$CH$_a$**H**$_b$CH), 1.21 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3 (C), 140.7 (C), 138.1 (C), 137.7 (C), 137.5 (C), 129.0 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.0 (CH), 126.8 (CH), 60.4 (CH_2), 47.5 (CH), 38.8 (CH_2), 36.4 (CH_2), 28.8 (CH_2), 14.4 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{21}H_{22}O_2Na]^+$ $[M+Na]^+$: 329.1512, found: 329.1512;

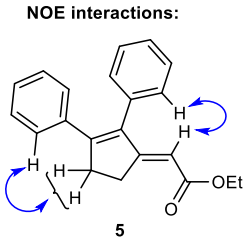
Enantiomeric excess was determined by HPLC using a Chiralpak IC column (99:1 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 280 nm, 25 °C); t_r (minor) = 12.7 min, t_r (major) = 13.1 min, >99% ee.

Diagnostic data for **4**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15-6.04 (1H, m, **H**C=), 4.11 (2H, app qd, *J* = 7.1, 2.8 Hz, C**H**$_2$CH$_3$), 3.66-3.56 (1H, m, C**H**CH$_2$C=O), 2.59 (1H, dd, *J* = 15.3, 3.3 Hz, C**H**$_a$H$_b$C=O), 2.56-2.44 (2H, m, C**H**$_2$C=), 2.31-2.24 (1H, m, CH$_2$C**H**$_a$H$_b$CH), 2.15 (1H, dd, *J* = 15.3, 10.8 Hz, CH$_a$**H**$_b$C=O), 1.87-1.77 (1H, m, CH$_2$CH$_a$**H**$_b$CH); HRMS (ESI) Exact mass calculated for $[C_{15}H_{18}O_2Na]^+$ [M+Na]$^+$: 253.1199, found: 253.1196.



Data for **5**: R_f = 0.50 (20% EtOAc/pet. ether); m.p. 147–149 °C (Et_2O); IR 2971, 2923, 1688 (C=O), 1617, 1605, 1579, 1438, 1371, 1179, 1135 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.31 (3H, m, Ar**H**), 7.21-7.11 (7H, m, Ar**H**), 5.47 (1H, t, *J* = 2.6 Hz, =C**H**C=O), 4.15 (2H, q, *J* = 7.1 Hz, C**H**$_2$CH$_3$), 3.32 (2H, dt, *J* = 7.8, 2.6 Hz, C**H**$_2$C=CH), 3.15-3.10 (2H, m, C**H**$_2$CH$_2$C=CH), 1.26 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9 (C), 168.2 (C), 153.8 (C), 141.6 (C), 136.0 (C), 135.6 (C), 129.7 (2 × CH), 129.1 (2 × CH), 128.5 (2 × CH), 128.4 (CH), 128.2 (2 × CH), 127.7 (CH), 109.0 (CH), 59.6 (CH_2), 35.3 (CH_2), 30.1 (CH_2), 14.6 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{21}H_{20}O_2Na]^+$ [M+Na]$^+$: 327.1356, found: 327.1352.

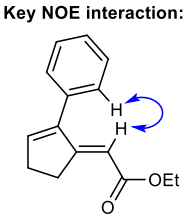
Assignment of the alkene stereochemistry of **5** was made based on the following NOE interactions observed in a series of 1D NOESY experiments:



5

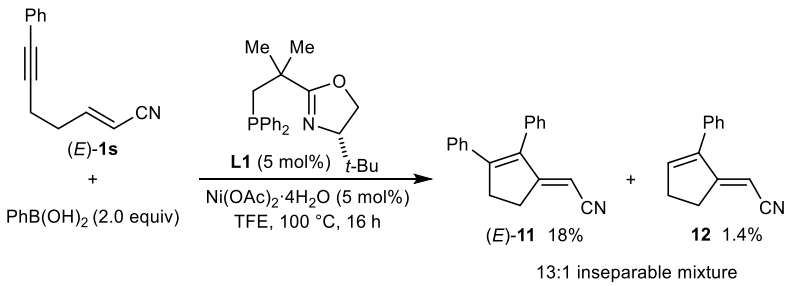
Data for **6**: R_f = 0.55 (20% EtOAc/pet. ether) and 0.45 (0.5% MeOH/CH_2Cl_2); m.p. 49–51 °C (Et_2O); IR 2975, 2904, 1694 (C=O), 1617, 1589, 1490, 1367, 1290, 1172, 1112 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.27 (5H, m, Ar**H**), 6.59 (1H, t, *J* = 2.8 Hz, CH_2C**H**=), 5.79-5.76 (1H, m, =C**H**C=O), 4.16 (2H, q, *J* = 7.1 Hz, C**H**$_2CH_3$), 3.25 (2H, dt, *J* = 7.6, 2.4 Hz, C**H**$_2$C=CH), 2.69 (2H, dt, *J* = 7.6, 2.8 Hz, C**H**$_2CH_2$C=CH), 1.26 (3H, t, *J* = 7.1 Hz, CH_2C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1 (C), 166.6 (C), 146.9 (C), 146.1 (CH), 135.2 (C), 128.6 (2 × CH), 128.5 (2 × CH), 127.9 (CH), 108.8 (CH), 59.7 (CH_2), 32.1 (CH_2), 31.5 (CH_2), 14.6 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{15}H_{16}O_2Na]^+$ [M+Na]$^+$: 251.1043, found: 251.1046.

Assignment of the alkene stereochemistry of **6** was made based on the following NOE interaction observed in the 2D NOESY spectrum:



6

(*E*)-2-(2,3-Diphenylcyclopent-2-en-1-ylidene)acetonitrile [(*E*)-11] and (*E*)-2-(2-phenylcyclopent-2-en-1-ylidene)acetonitrile (12)



Prepared according to a modification of General Procedure A, using enyne (*E*)-**1s** (54.4 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol), and (*S*)-*t*-Bu-NeoPHOX (**L3**, 11.0 mg, 0.03 mmol) and stirring for 16 h. Purification by column chromatography (5% EtOAc/pentane) followed by a second purification by column chromatography

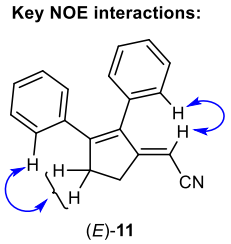
(100% CH_2Cl_2) gave an inseparable 13:1 mixture of (*E*)-**11** and **12** (14.9 mg) as a white solid. The calculated yields of (*E*)-**11** and **12** are 18% and 1.4%, respectively.

R_f = 0.51 (100% CH_2Cl_2); IR 3059, 2918, 2197 (C≡N), 1600, 1561, 1486, 1438, 1364, 1261, 922 cm^{-1}.

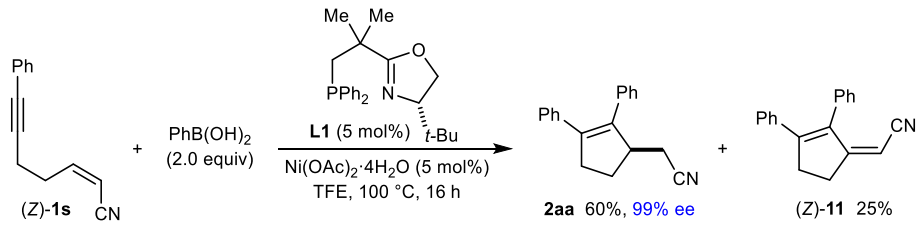
NMR and HRMS data for (*E*)-**11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.35 (3H, m, Ar**H**), 7.26-7.14 (5H, m, Ar**H**), 7.14-7.09 (2H, m, Ar**H**), 4.93-4.81 (1H, m, =C**H**CN), 3.18-3.14 (2H, m, C$\mathbf{H}_2$), 3.14-3.10 (2H, m, C$\mathbf{H}_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4 (C), 154.9 (C), 140.0 (C), 135.3 (C), 134.3 (C), 129.5 (2 × CH), 129.3 (2 × CH), 129.0 (CH), 128.5 (2 × CH), 128.32 (2 × CH), 128.25 (CH), 119.1 (C), 86.1 (CH), 34.4 (CH_2), 29.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{16}N]^+$ $[M+H]^+$: 258.1277, found: 258.1277.

Diagnostic NMR and HRMS data for **12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (1H, t, *J* = 2.9 Hz, **H**C=CPh), 5.20 (1H, t, *J* = 2.7 Hz, =C**H**CN), 3.07 (2H, dt, *J* = 7.8, 2.7 Hz, C$\mathbf{H}_2$C=CHCN), 2.74 (2H, dt, *J* = 7.8, 2.9 Hz, C$\mathbf{H}_2$C=CPh); HRMS (ESI) Exact mass calculated for $[C_{13}H_{11}NNa]^+$ $[M+Na]^+$: 204.0784, found: 204.0782.

Assignment of the alkene stereochemistry of (*E*)-**11** was made based on the following NOE interactions observed in the 2D NOESY spectrum:



(*R*)-2-(2,3-Diphenylcyclopent-2-en-1-yl)acetonitrile (2aa) and (*Z*)-2-(2,3-diphenylcyclopent-2-en-1-ylidene)acetonitrile [(*Z*)-11]



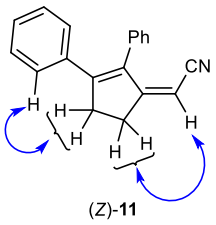
A modification of General Procedure A was followed, using enyne (*Z*)-**1s** (54.4 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol), and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol) and stirring for 16 h. Purification by column chromatography (5% EtOAc/pentane) gave **2aa** (46.8 mg, 60%) as a yellow solid followed by (*Z*)-**11** (19.6 mg, 25%) as an off-white solid.

Data for **2z**: R_f = 0.35 (15% EtOAc/pet. ether); m.p. 66–69 °C (Et_2O); IR 3027, 2954, 2849, 2238 (C≡N), 1598, 1489, 1454, 1442, 1414, 759 cm^{-1}; $[\alpha]_D^{20}$ −128.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (3H, m, Ar**H**), 7.26-7.21 (1H, m, Ar**H**), 7.19-7.10 (6H, m, Ar**H**), 3.59-3.50 (1H, m, C**H**CH_2), 3.22 (1H, dddd, *J* = 16.0, 9.0, 6.1, 2.8 Hz, C**H**$_a$H$_b$C=), 2.78 (1H, dddd, *J* = 16.0, 9.3, 5.1, 1.5 Hz, CH$_a$**H**$_b$C=), 2.54-2.38 (2H, m, CH_2C**H**$_a$H$_b$CH and C**H**$_a$H$_b$CN), 2.28 (1H, dd, *J* = 16.8, 7.9 Hz, CH$_a$**H**$_b$CN), 2.02 (1H, app ddt, *J* = 13.9, 9.5, 5.0 Hz, CH_2CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (C), 138.1 (C), 137.0 (C), 136.5 (C), 128.9 (2 × CH), 128.8 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.5 (CH), 127.3 (CH), 119.1 (C), 47.5 (CH), 36.5 (CH_2), 28.1 (CH_2), 22.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{17}NNa]^+$ $[M+Na]^+$: 282.1253, found: 282.1250; Enantiomeric excess was determined by HPLC using a Chiralpak AS-H column (98:2 *iso*-hexane:*i*-PrOH, 0.4 mL/min, 280 nm, 25 °C); t_r (minor) = 52.7 min, t_r (major) = 56.4 min, 99% ee.

Data for (*Z*)-**11**: R_f = 0.20 (15% EtOAc/pet. ether); m.p. 135-136 °C (Et_2O); IR 3045, 2964, 2197 (C≡N), 1600, 1583, 1561, 1487, 1442, 1375, 765 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46-7.39 (3H, m, Ar**H**), 7.26-7.15 (7H, m, Ar**H**), 5.22-5.06 (1H, m, =C**H**CN), 3.12-3.06 (2H, m, C**H**$_2$CH$_2$C=CH), 2.98-2.92 (2H, m, C**H**$_2$C=CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4 (C), 155.4 (C), 140.0 (C), 135.4 (C), 134.6 (C), 130.0 (2 × CH), 129.04 (2 × CH), 128.96 (CH), 128.7 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 116.1 (C), 85.3 (CH), 34.1 (CH_2), 31.7 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{19}H_{15}NNa]^+$ $[M+Na]^+$: 280.1097, found: 280.1094.

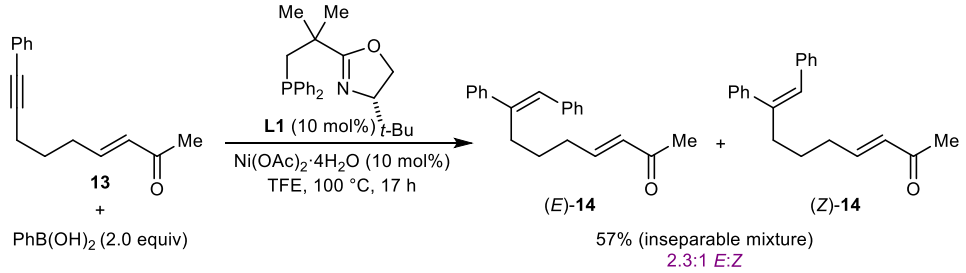
Assignment of the alkene stereochemistry of (*Z*)-**11** was made based on the following NOE interactions observed in the 2D NOESY spectrum:

Key NOE interactions:



(*Z*)-**11**

(3*E*,8*E*)-8,9-Diphenylnona-3,8-dien-2-one [(*E*)-14] and (3*E*,8*Z*)-8,9-diphenylnona-3,8-dien-2-one [(*Z*)-14]



An oven-dried microwave vial fitted with a stirrer bar was charged with the enyne **13** (63.7 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol), and (*S*)-*t*-Bu-NeoPHOX (**L1**, 11.0 mg, 0.03 mmol). The vial was capped with a crimp cap seal and flushed with argon. TFE (3 mL) which had been freshly degassed (using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 100 °C for 17 h. The reaction was cooled to room temperature, quenched with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (10% EtOAc/pentane) to give a 2.3:1 mixture of inseparable alkyne hydroarylation products (*E*)-**14** and (*Z*)-**14**, respectively (50.0 mg, 57%), as a yellow oil.

R_f = 0.41 (20% EtOAc/pet. ether); IR 3021, 2929, 1696, 1672 (C=O), 1625, 1493, 1443, 1359, 1252, 976 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{21}H_{22}ONa]^+$ $[M+Na]^+$: 313.1563, found: 313.1562.

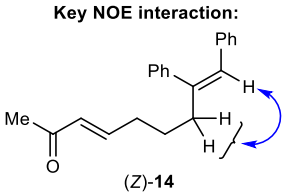
Overlapping NMR signals (integrals refer to the sum of the integrals for each isomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.43 (3H, m, Ar**H**), 7.41-7.27 (12H, m, Ar**H**), 7.26-6.90 (5H, m, Ar**H**), 1.62-1.56 (4H, m, $CH_2C\mathbf{H}_2CH_2C$=).

Characteristic NMR signals for major stereoisomer (*E*)-**14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (1H, s, =C**H**Ph), 6.67 (1H, dt, *J* = 16.0, 6.9 Hz, $CH_2C\mathbf{H}$=CH), 5.96 (1H, dt, *J* = 16.0, 1.6 Hz, CH_2CH=C**H**), 2.80-2.72 (2H, m, $C\mathbf{H}_2CH_2CH_2C$=), 2.21-2.16 (2H, m, $CH_2CH_2C\mathbf{H}_2C$=), 2.16 (3H, s, $C\mathbf{H}_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7 (C), 147.8 (CH), 142.7 (C), 142.4 (C, overlapped with minor stereoisomer (*Z*)-**18**), 138.2 (C), 131.8 (CH), 129.13 (CH), 128.9 (2 × CH), 128.8 (CH), 128.7 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 126.7 (2 × CH), 32.2 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 26.9 (CH_3).

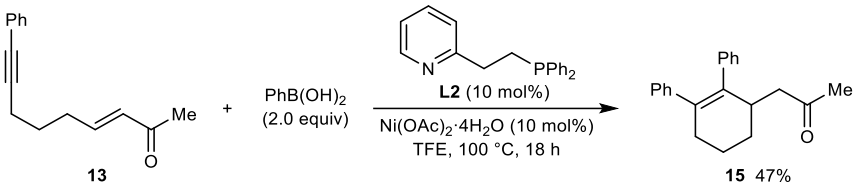
Characteristic NMR signals for minor stereoisomer (*Z*)-**14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81-6.75 (1H, m, $CH_2C\mathbf{H}$=CH), 6.45 (1H, s, =C**H**Ph), 6.07 (1H, dt, *J* = 16.0, 1.6 Hz, CH_2CH=C**H**), 2.57-2.52 (2H, m, $C\mathbf{H}_2CH_2CH_2C$=), 2.30-2.24 (2H, m, $CH_2CH_2C\mathbf{H}_2C$=), 2.23 (1H, s, $C\mathbf{H}_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8 (C), 148.1 (CH), 142.4 (C, overlapped with major stereoisomer (*E*)-**18**), 140.9

(C), 137.3 (C), 131.7 (CH), 129.07 (2 × CH), 128.0 (2 × CH), 127.5 (2 × CH), 127.2 (CH), 127.1 (CH), 126.9 (2 × CH), 126.4 (CH), 40.2 (CH_2), 32.0 (CH_2), 27.0 (CH_3), 26.4 (CH_2).

Assignment of the alkenyl stereochemistries of (*E*)-**14** and (*Z*)-**14** was made based on the following NOE interaction observed in the 2D NOESY spectrum of the mixture, between the alkenyl proton at 6.45 ppm and the methylene protons at 2.57-2.52 ppm, which correspond to those (*Z*)-**14**:



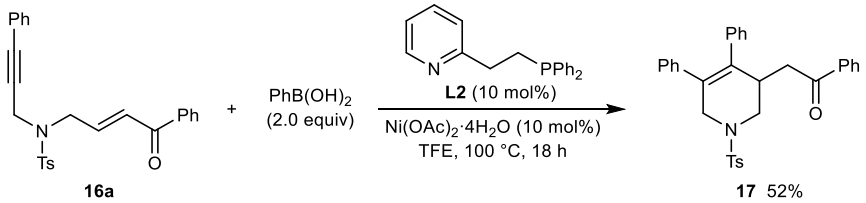
1-[3',4',5',6'-Tetrahydro-(1,1':2',1''-terphenyl)-3'-yl]propan-2-one (15)



An oven-dried microwave vial fitted with a stirrer bar was charged with the enyne **13** (63.7 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol), and pyphos **L2** (8.7 mg, 0.03 mmol). The vial was capped with a crimp cap seal and flushed with argon. TFE (3 mL) which had been freshly degassed (using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 100 °C for 18 h. The reaction was cooled to room temperature, quenched with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (5% EtOAc/pentane) to give **15** (47.1 mg) as a colorless oil containing a small amount of unidentified, inseparable impurities. By using 1,3,5- trimethoxybenzene as the internal standard, the purity of **15** was determined by ^{1}H NMR analysis to be 87% (by weight) and the yield was calculated to be 47%. R_f = 0.49 (20% EtOAc/pet. ether); IR 3019, 2928, 1713 (C=O), 1598, 1490, 1442, 1357, 1158, 1069, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.01 (6H, m, Ar**H**), 7.01-6.90 (4H, m, Ar**H**), 3.34-3.20 (1H, m, C**H**CH_2), 2.65-2.57 (1H, m, =CC**H**$_a$H$_b$), 2.43 (1H, dd, *J* = 16.8, 10.3 Hz, C**H**$_a$H$_b$C=O), 2.33-2.20 (2H, m, CH_a**H**$_b$C=O and =CCH_a**H**$_b$), 1.97 (3H, s, C**H**$_3$), 1.92 (1H, ddd, *J* = 13.1, 5.7, 3.6 Hz, =CCH_2CH_2C**H**$_a$H$_b$), 1.83-1.77 (2H, m, =CCH_2C**H**$_2$), 1.73-1.66 (1H, m, =$CCH_2CH_2CH_a$**H**$_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6 (C), 143.7 (C), 141.9 (C), 137.9 (C), 137.1 (C), 129.9 (2 × CH), 129.2 (2 × CH), 127.8 (2 × CH), 127.7 (2 × CH), 126.1 (CH), 125.9 (CH), 47.4 (CH_2), 35.2 (CH),

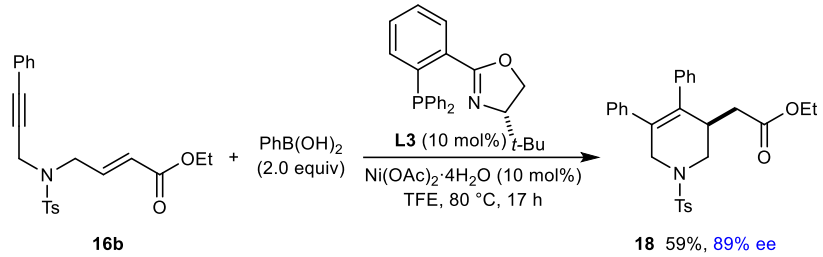
32.4 (CH_2), 30.4 (CH_3), 27.9 (CH_2), 19.6 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{21}H_{22}ONa]^+$ $[M+Na]^+$: 313.1563, found: 313.1567.

2-(4,5-Diphenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-yl)-1-phenylethan-1-one (17)



An oven-dried microwave vial fitted with a stirrer bar was charged with the enyne **16a** (129 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol), and pyphos (**L2**, 8.7 mg, 0.03 mmol). The vial was capped with a crimp cap seal and flushed with argon. TFE (3 mL) which had been freshly degassed (using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 100 °C for 18 h. The reaction was cooled to room temperature, quenched with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under *vacuo*. The residue was purified by column chromatography (10 to 20% EtOAc/pentane) to give **17** (77.7 mg, 52%) as a white solid. R_f = 0.59 (40% EtOAc/pet. ether); m.p. 85–88 °C (Et_2O); IR 3056, 2855, 1681 (C=O), 1597, 1493, 1445, 1342, 1162, 995, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94-7.84 (2H, m, Ar**H**), 7.69-7.64 (2H, m, Ar**H**), 7.55-7.50 (1H, m, Ar**H**), 7.44-7.39 (2H, m, Ar**H**), 7.30-7.27 (2H, m, Ar**H**), 7.16-7.01 (8H, m, Ar**H**), 7.00-6.95 (2H, m, Ar**H**), 4.56 (1H, d, *J* = 16.5 Hz, C**H**$_a$H$_b$C=), 3.88 (1H, dt, *J* = 11.8, 1.4 Hz, NC**H**$_a$H$_b$CH), 3.62-3.53 (2H, m, C**H**$_a$H$_b$C=O and C**H**CH$_2$), 3.25 (1H, dd, *J* = 16.5, 1.9 Hz, CH$_a$**H**$_b$C=), 2.85-2.80 (1H, m, NCH$_a$**H**$_b$CH), 2.76-2.69 (1H, m, CH$_a$**H**$_b$C=O), 2.38 (3H, s, ArC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1 (C), 143.8 (C), 139.6 (C), 138.9 (C), 137.2 (C), 137.0 (C), 133.3 (CH), 133.0 (C), 132.7 (C), 129.8 (2 × CH), 129.74 (2 × CH), 129.68 (2 × CH), 128.6 (2 × CH), 128.24 (4 × CH, two peaks merged into one peak), 128.20 (2 × CH), 127.9 (2 × CH), 127.3 (CH), 127.1 (CH), 49.7 (CH_2), 47.4 (CH_2), 39.7 (CH_2), 36.1 (CH), 21.6 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{32}H_{29}NO_3SNa]^+$ $[M+Na]^+$: 530.1760, found: 530.1750.

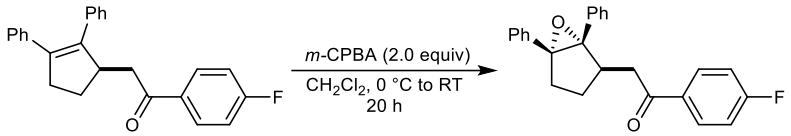
Ethyl (*R*)-2-(4,5-diphenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-yl)acetate (18)



An oven-dried microwave vial fitted with a stirrer bar was charged with the enyne **16b** (119 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (7.5 mg, 0.03 mmol), and (*S*)-*t*-BuPHOX (**L3**, 11.6 mg, 0.03 mmol). The vial was capped with a crimp cap seal and flushed with argon. TFE (3 mL) which had been freshly degassed (using a stream of argon for 20 min) was added, the cap was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 80 °C for 17 h. The reaction was cooled to room temperature, quenched with 50% brine (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (10% EtOAc/pentane) to give **18** (84.1 mg, 59%) as a white solid. R_f = 0.55 (40% EtOAc/pet. ether); m.p. 138–139 °C (Et_2O); IR 2923, 2854, 1729 (C=O), 1705, 1597, 1346, 1163, 1090, 702, 669 cm^{-1}; $[\alpha]_D^{25}$ +128.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76-7.62 (2H, m, Ar**H**), 7.31 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.15-7.05 (6H, m, Ar**H**), 7.01-6.95 (2H, m, Ar**H**), 6.95-6.89 (2H, m, Ar**H**), 4.47 (1H, d, *J* = 16.3 Hz, C**H**$_a$H$_b$C=) 4.13-4.02 (2H, m, C**H**$_2$CH$_3$), 3.97-3.88 (1H, m, NC**H**$_a$H$_b$CH), 3.32-3.17 (2H, m, CH$_a$**H**$_b$C= and C**H**CH$_2$), 2.81 (1H, ddd, *J* = 11.8, 3.6, 1.5 Hz, NCH$_a$**H**$_b$CH), 2.72 (1H, dd, *J* = 17.2, 10.4 Hz, C**H**$_a$H$_b$C=O), 2.42 (3H, s, ArC**H**$_3$), 2.27 (1H, ddd, *J* = 17.2, 2.9, 1.5 Hz, CH$_a$**H**$_b$C=O), 1.22 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6 (C), 143.9 (C), 139.5 (C), 138.8 (C), 136.7 (C), 132.9 (C), 132.7 (C), 129.9 (2 × CH), 129.6 (4 × CH, two peaks merged into one peak), 128.18 (2 × CH), 128.16 (2 × CH), 128.0 (2 × CH), 127.3 (CH), 127.1 (CH), 60.7 (CH_2), 49.7 (CH_2), 47.2 (CH_2), 37.3 (CH), 35.4 (CH_2), 21.7 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{28}H_{29}NO_4SNa]^+$ $[M+Na]^+$: 498.1710, found: 498.1710; Enantiomeric excess was determined by HPLC using a Chiralcel AD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 254 nm, 25 °C); t_r (major) = 21.7 min, t_r (minor) = 24.4 min, 89% ee.

4. Epoxidation of 2a

2-{(1*S*,2*R*,5*R*)-1,5-diphenyl-6-oxabicyclo[3.1.0]hexan-2-yl}-1-(4-fluorophenyl)ethan-1-one (19)

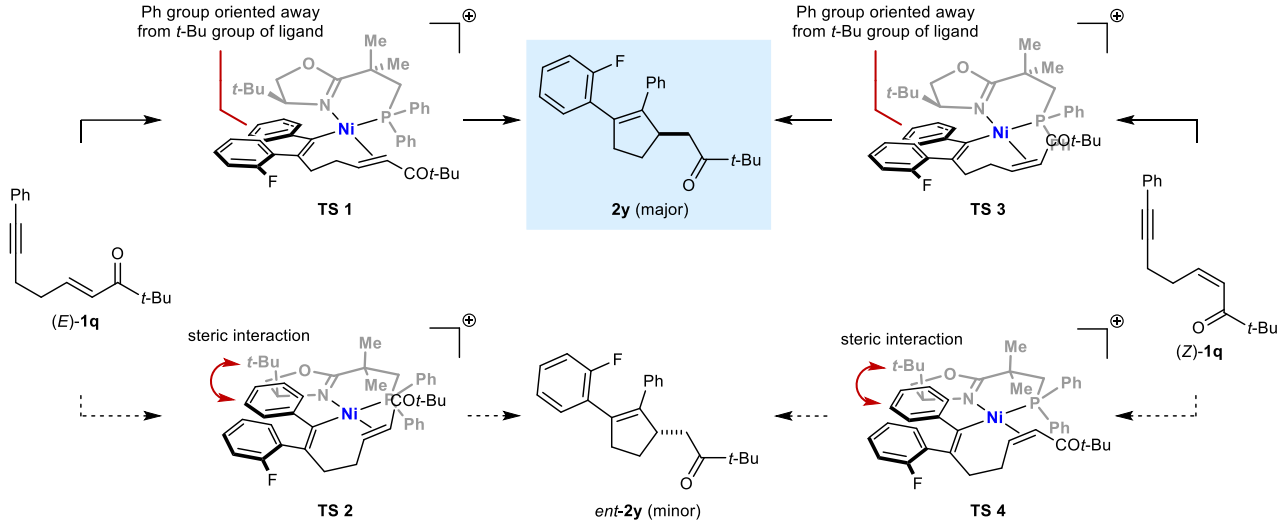


2a **19** 67%

To a solution of alkene **2a** (53.5 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C was added *m*-CPBA (70% purity, 74.0 mg, 0.30 mmol). The resulting solution was slowly warmed to room temperature and stirred for 20 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (2 mL) and the mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (5 to 10% EtOAc/pentane) to give the epoxide **19** as a colorless solid (37.2 mg, 67%). R_f = 0.26 (10% EtOAc/pet. ether); m.p. 76-78 °C ($CHCl_3$); $[\alpha]_D^{25}$ −12.0 (*c* 0.10, $CHCl_3$); IR 2922, 1683 (C=O), 1595, 1504, 1447, 1225, 1155, 966, 908, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.87 (2H, m, Ar**H**), 7.31-7.05 (12H, m, Ar**H**), 3.34-3.25 (1H, m, C**H**CH_2), 3.14 (1H, dd, *J* = 17.1, 10.2 Hz, C**H**$_a$H$_b$C=O), 3.01 (1H, dd, *J* = 17.2, 3.3 Hz, CH$_a$**H**$_b$C=O), 2.50 (1H, ddd, *J* = 14.2, 10.6, 8.3 Hz, C**H**$_a$H$_b$CH$_2$CH), 2.38-2.28 (1H, m, CH$_a$**H**$_b$CH$_2$CH), 2.28-2.20 (1H, m, CH$_2$C**H**$_a$H$_b$CH), 1.36-1.27 (1H, m, CH$_2$CH$_a$**H**$_b$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (C), 165.8 (d, $J_{C\text{-}F}$ = 254.6 Hz, C), 136.1, (C), 134.5 (C), 133.6 (d, $J_{C\text{-}F}$ = 3.0 Hz, C), 130.8 (d, $J_{C\text{-}F}$ = 9.2 Hz, 2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.6 (CH), 127.4 (CH), 127.0 (2 × CH), 126.6 (2 × CH), 115.7 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2 × CH), 76.4 (C), 74.4 (C), 40.2 (CH), 39.6 (CH_2), 32.4 (CH_2), 26.4 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –105.3 (s); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}FO_2Na]^+$ $[M+Na]^+$: 395.1418, found: 395.1421.

5. Stereochemical Model for the Reactions of Substrates (*E*)-1q and (*Z*)-1q with $PhB(OH)_2$

A tentative stereochemical model to explain the observed sense of enantioinduction in the reactions of substrates (*E*)- and (*Z*)-**1q** with $PhB(OH)_2$ is provided below:

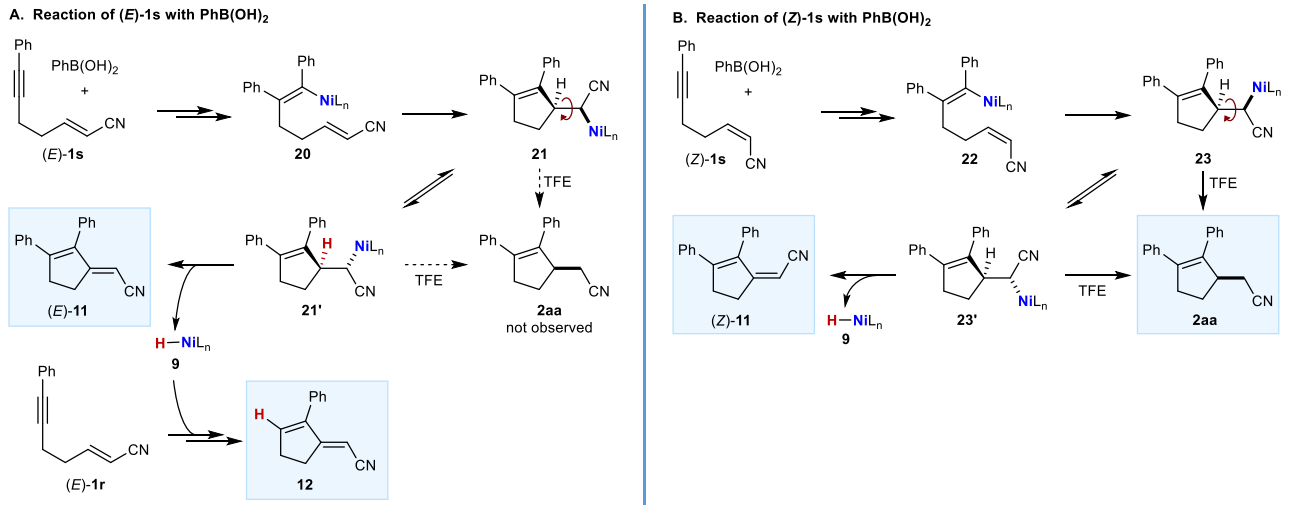


The reaction of (*E*)-**1q** with $PhB(OH)_2$ will lead to square planar nickel intermediates **TS 1** or **TS 2**, in which the alkenyl ligand is *trans* to the phosphorus atom the rather than the nitrogen atom, and where nickel coordinates to one of the two prochiral faces of the alkene of the α,β-unsaturated *t*-butyl ketone. The reason for this arrangement of ligands around nickel is that **TS 1** and **TS 2** are formed by the migratory insertion of the alkyne of (*E*)-**1q** into a phenylnickel species where the electron-rich phenyl ligand is also *trans* to the phosphorus atom rather than the nitrogen atom, because the phosphine is a better π-acceptor than the oxazoline. In **TS 1**, the bound substrate adopts a conformation that orients the phenyl group below the oxazoline ring and away from the bulky *t*-butyl group of the ligand. Cyclization from **TS 1** then leads to the observed major diastereomer **2y**.

In contrast, in **TS 2**, where the other prochiral face of the α,β-unsaturated *t*-butyl ketone is coordinated, the bound substrate adopts a conformation that orients the phenyl group towards the bulky *t*-butyl group of the ligand leading to a highly unfavorable steric interaction. Therefore, this pathway that leads to the minor enantiomer *ent*-**2y** is strongly disfavored.

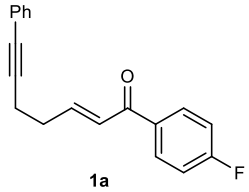
The same considerations apply in the reaction of (*Z*)-**1q** through **TS 3** and **TS 4**; the stereochemistry of the enone does not affect the stereochemical model leading to the enantiomers of **2y**, and in fact, a higher yield of **2y** is observed when using (*Z*)-**1q**.

6. Mechanistic Rationale of the Reactions of Substrates (*E*)-1s and (*Z*)-1s with $PhB(OH)_2$

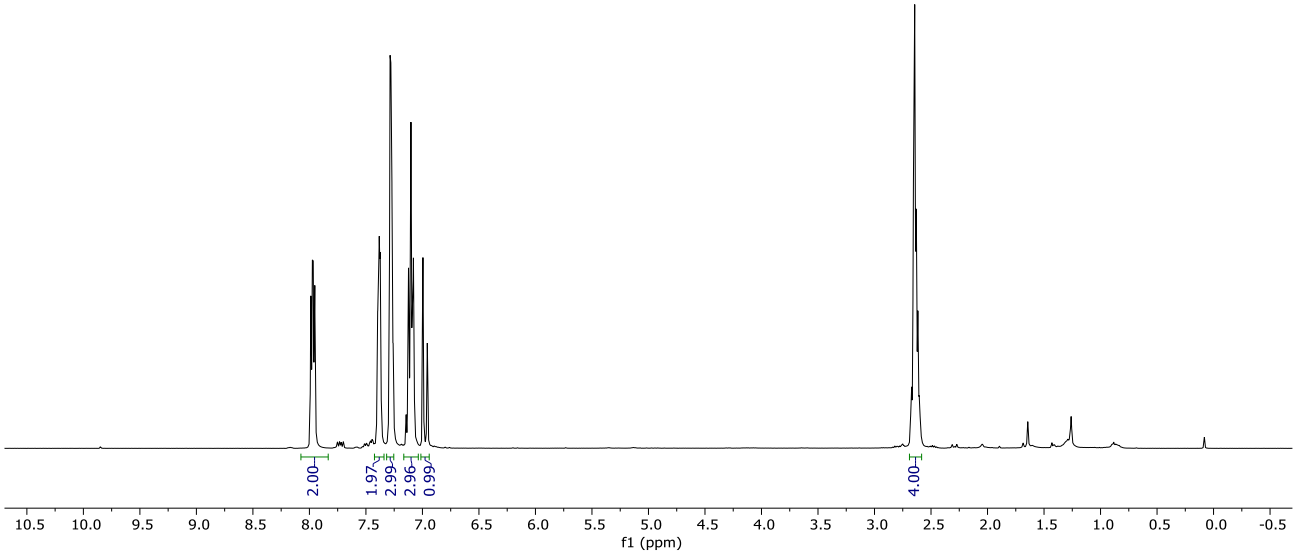


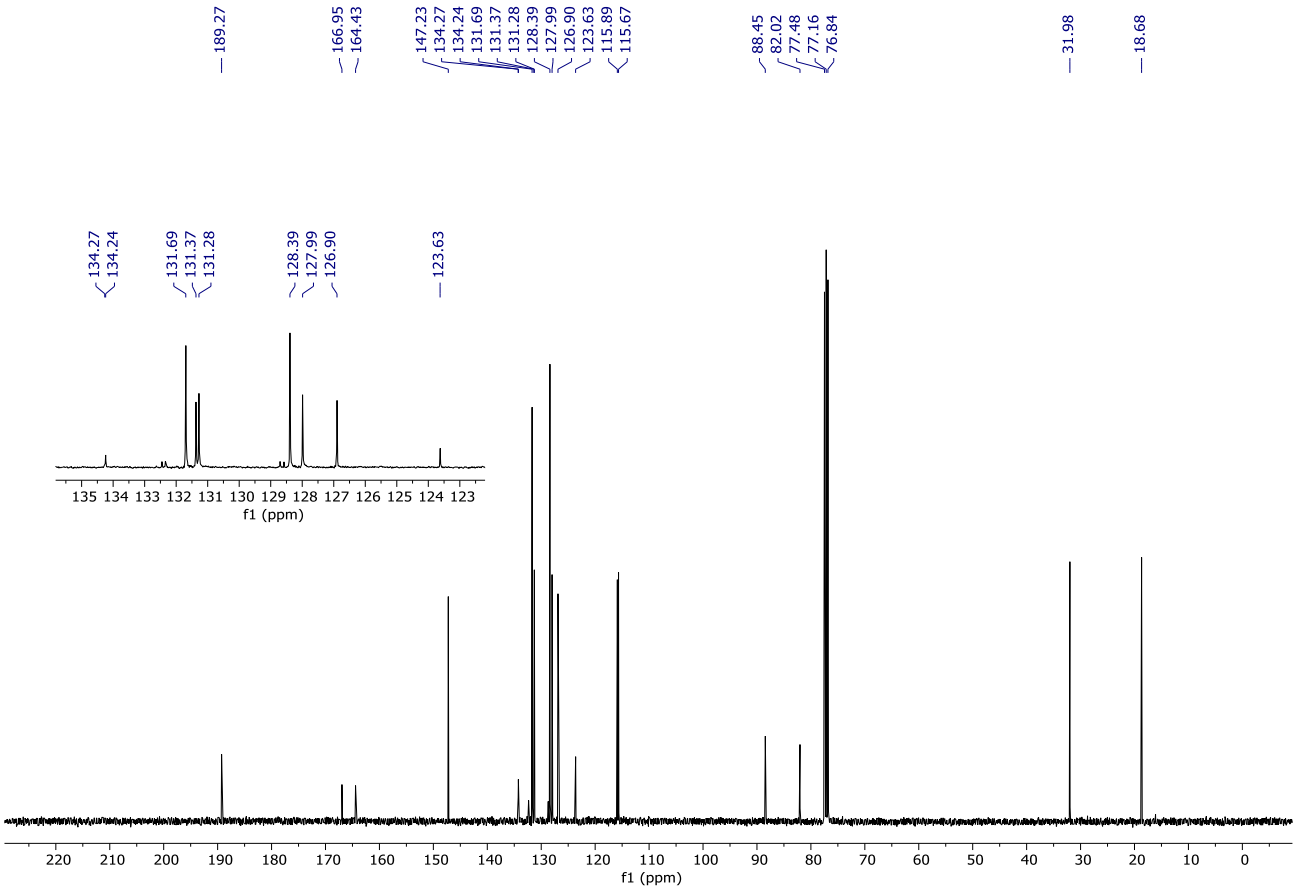
Reaction of (*E*)-**1s** and $PhB(OH)_2$ would, after arylnickelation and reversible *E*/*Z*-isomerization, give alkenylnickel species **20**. A syn-stereospecific migratory insertion of the alkene would then give the α-cyano alkylnickel species **21**. Protodenickelation of **21** by TFE would give, after arylnickelation and reversible *E*/*Z*-isomerization, give the arylative cyclization product **2aa**, but this does not occur to any significant extent. Instead, bond rotation to give **21'** and stereospecific syn-β-hydride elimination gives the conjugated diene (*E*)-**11** along with nickel hydride species **9**, which can then react with the substrate (*E*)-**1s** via alkyne hydronickelation to eventually give diene **12**. A similar sequence starting from (*Z*)-**1s** results in the formation of conjugated diene (*Z*)-**11** *via* **22** and **23**/**23'**, but in this case, significant protodenickelation of **23**/**23'** also occurs to give the desired arylative cyclization product **2aa**. It appears that the different absolute configurations of the stereocenters bearing the carbon–nickel bond in **21** and **23** are responsible for their different propensities to undergo protodenickelation.

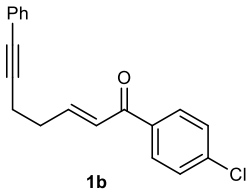
7. NMR Spectra of New Compounds



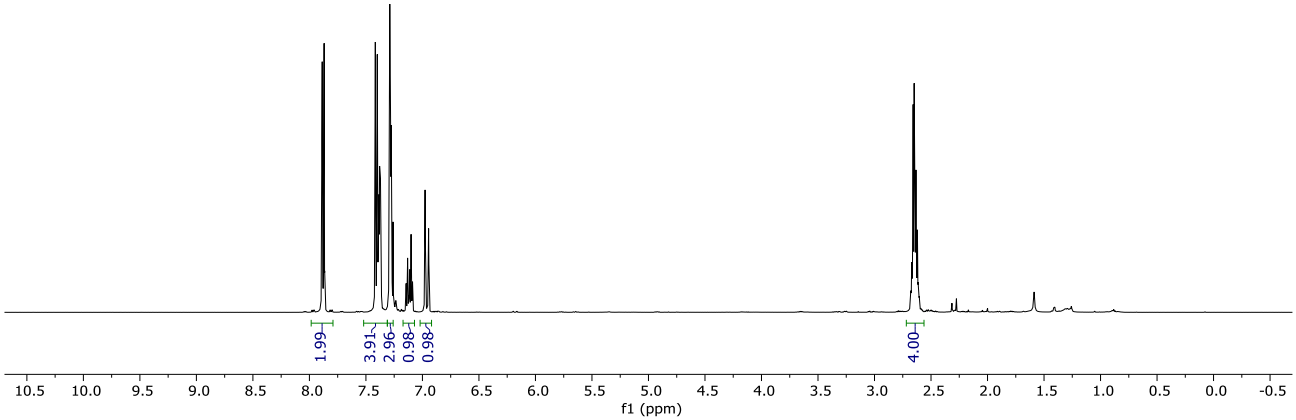
1a






Ph
O
Cl

1b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2.96
0.98
0.98
4.00
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f1 (ppm)

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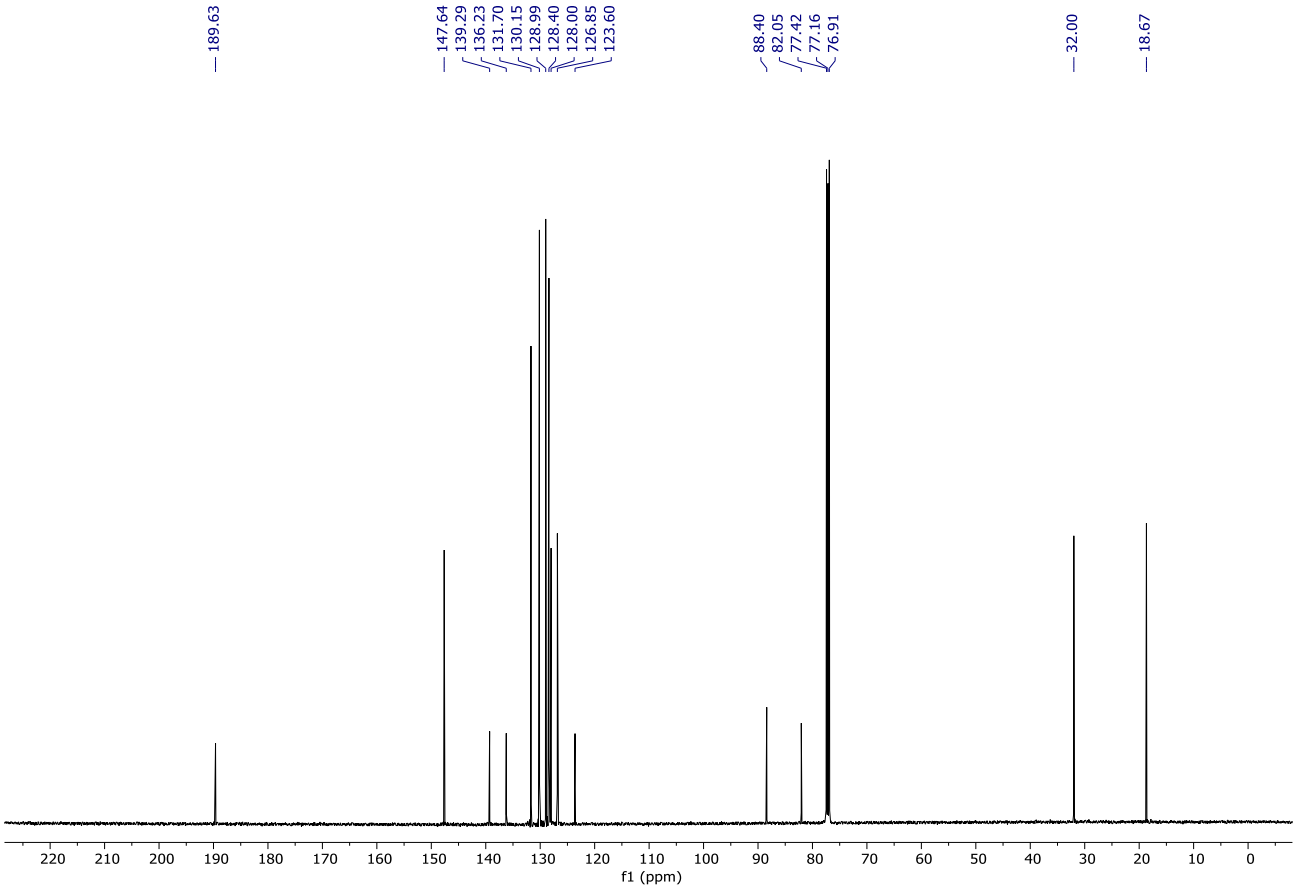
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136.23
131.70
130.15
128.99
128.40
128.00
126.85
123.60
88.40
82.05
77.42
77.16
76.91
32.00
18.67
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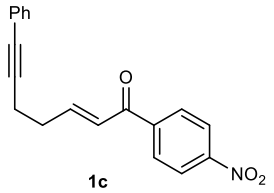
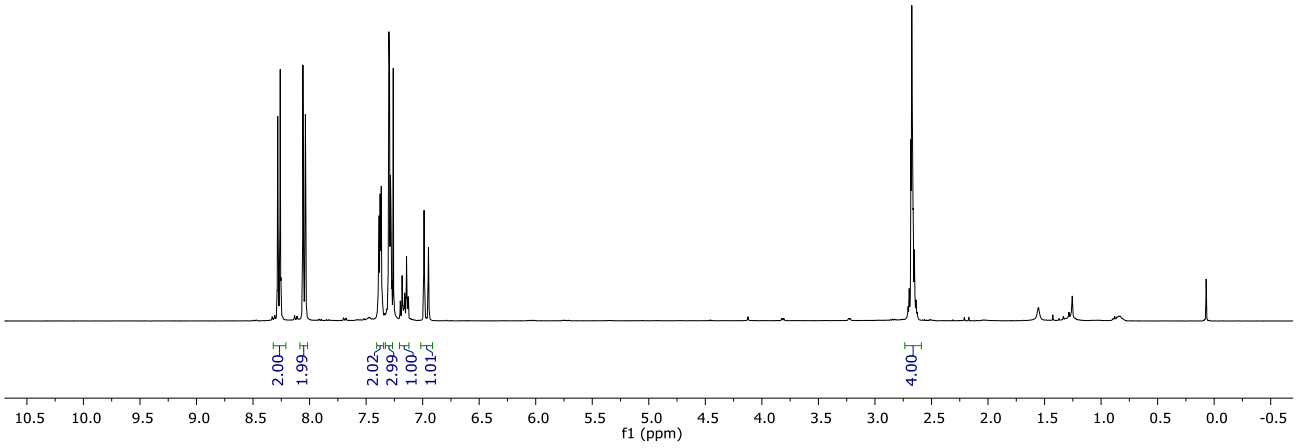
f1 (ppm)


Ph
O
NO2

1c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1.00
1.01
4.00
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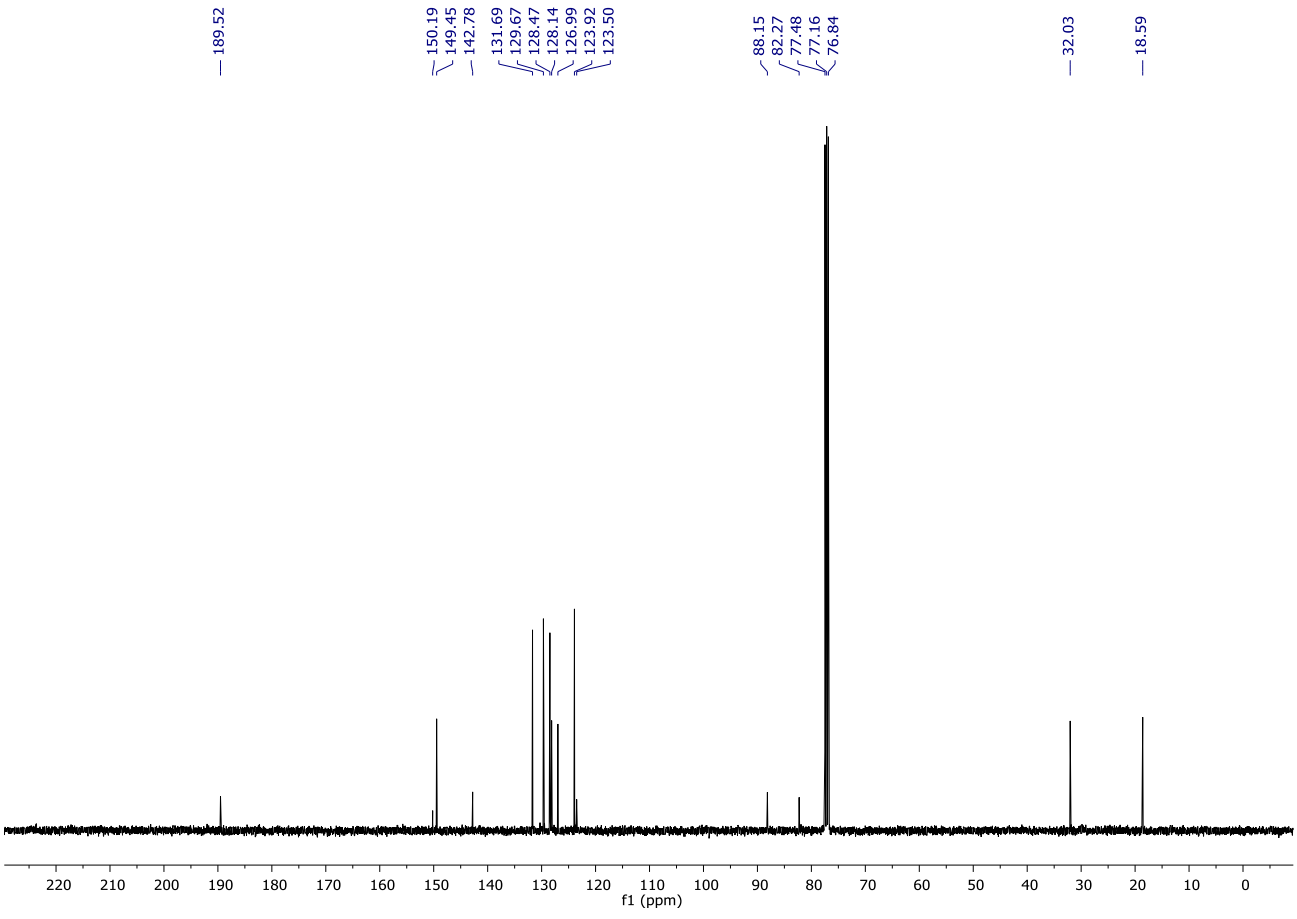
f1 (ppm)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129.67
128.47
128.14
126.99
123.92
123.50
88.15
82.27
77.48
77.16
76.84
32.03
18.59
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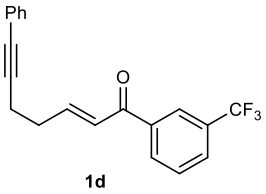
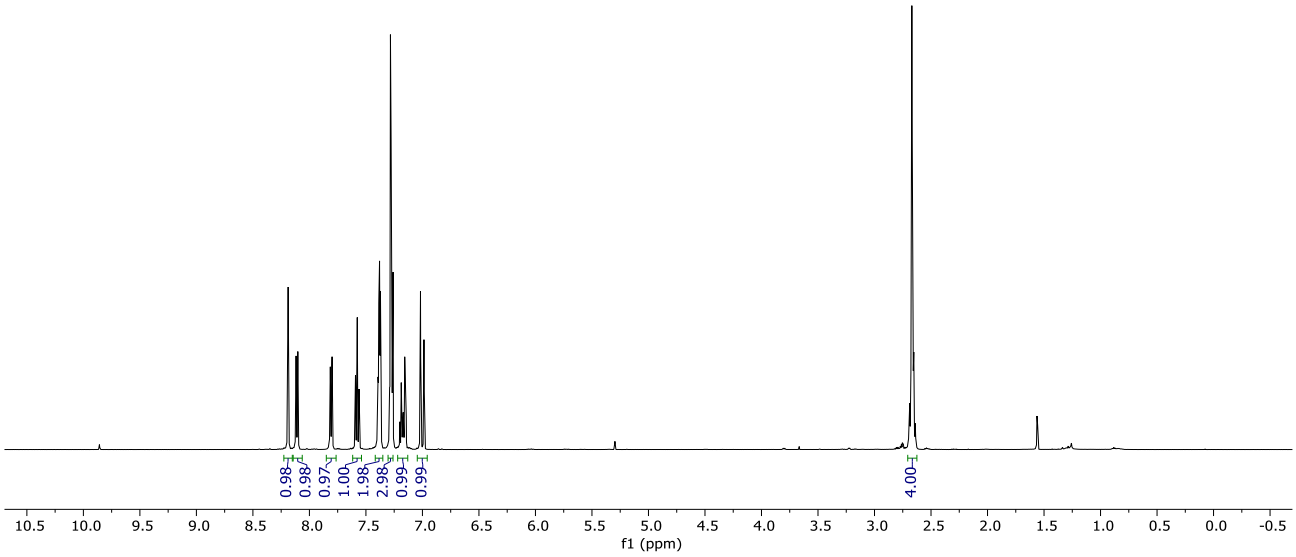
f1 (ppm)


Ph
O
CF3

1d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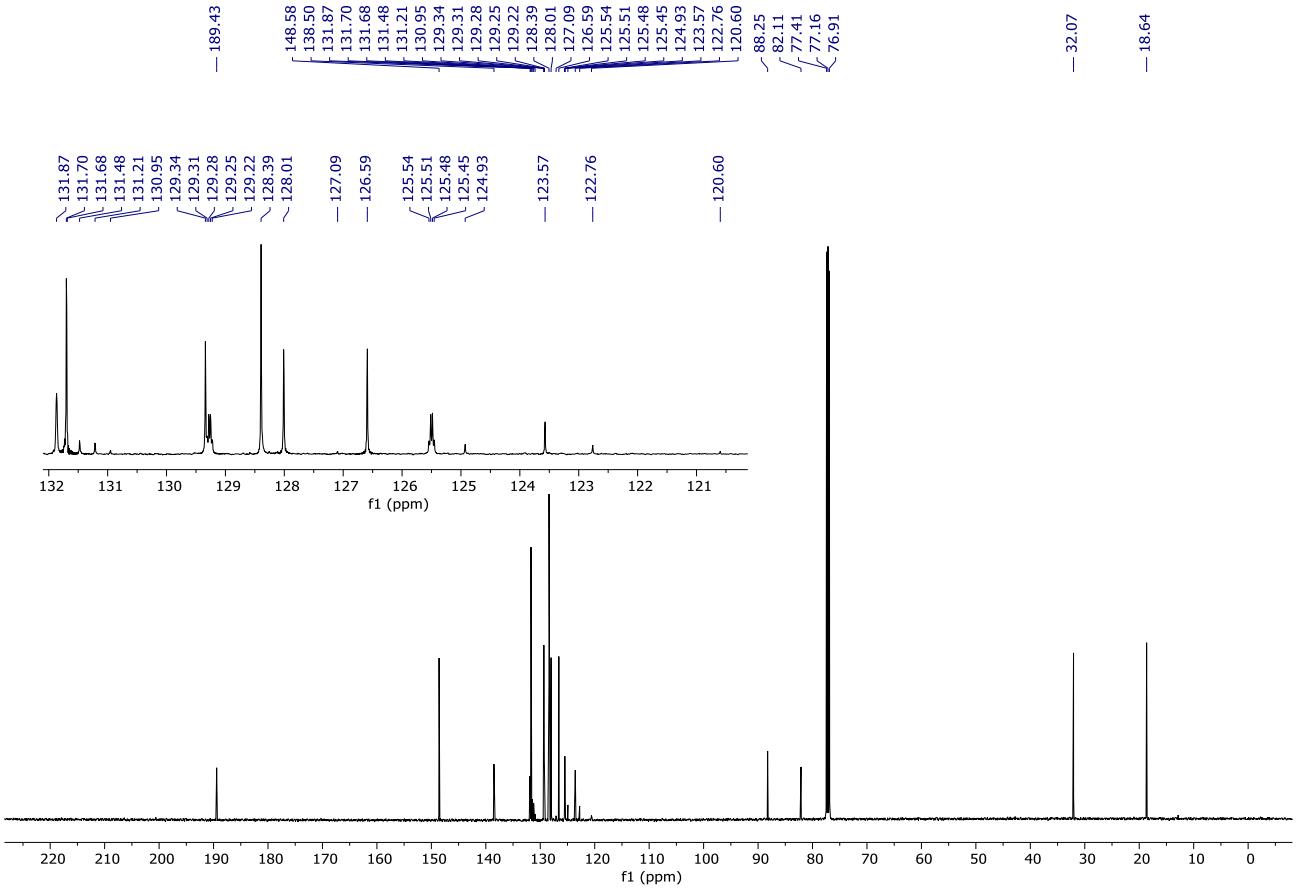
1.98
2.98
0.99
0.99
4.00
f1 (ppm)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131.70
131.68
131.48
131.21
130.95
129.34
129.31
129.28
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129.22
128.39
128.01
127.09
126.59
125.54
125.51
125.48
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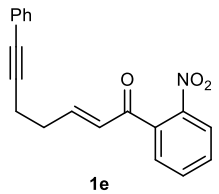
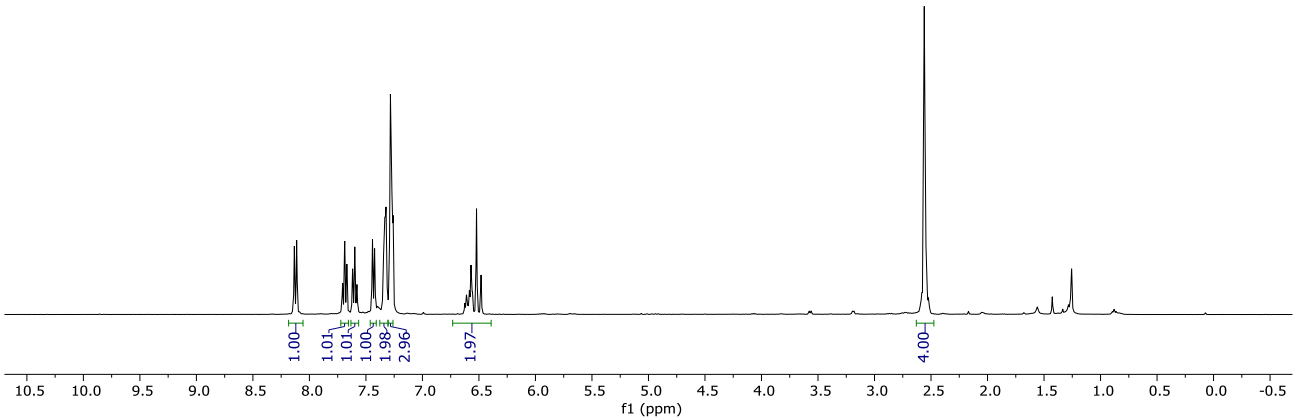
77.16
76.91
32.07
18.64
f1 (ppm)


Ph
O
NO2

1e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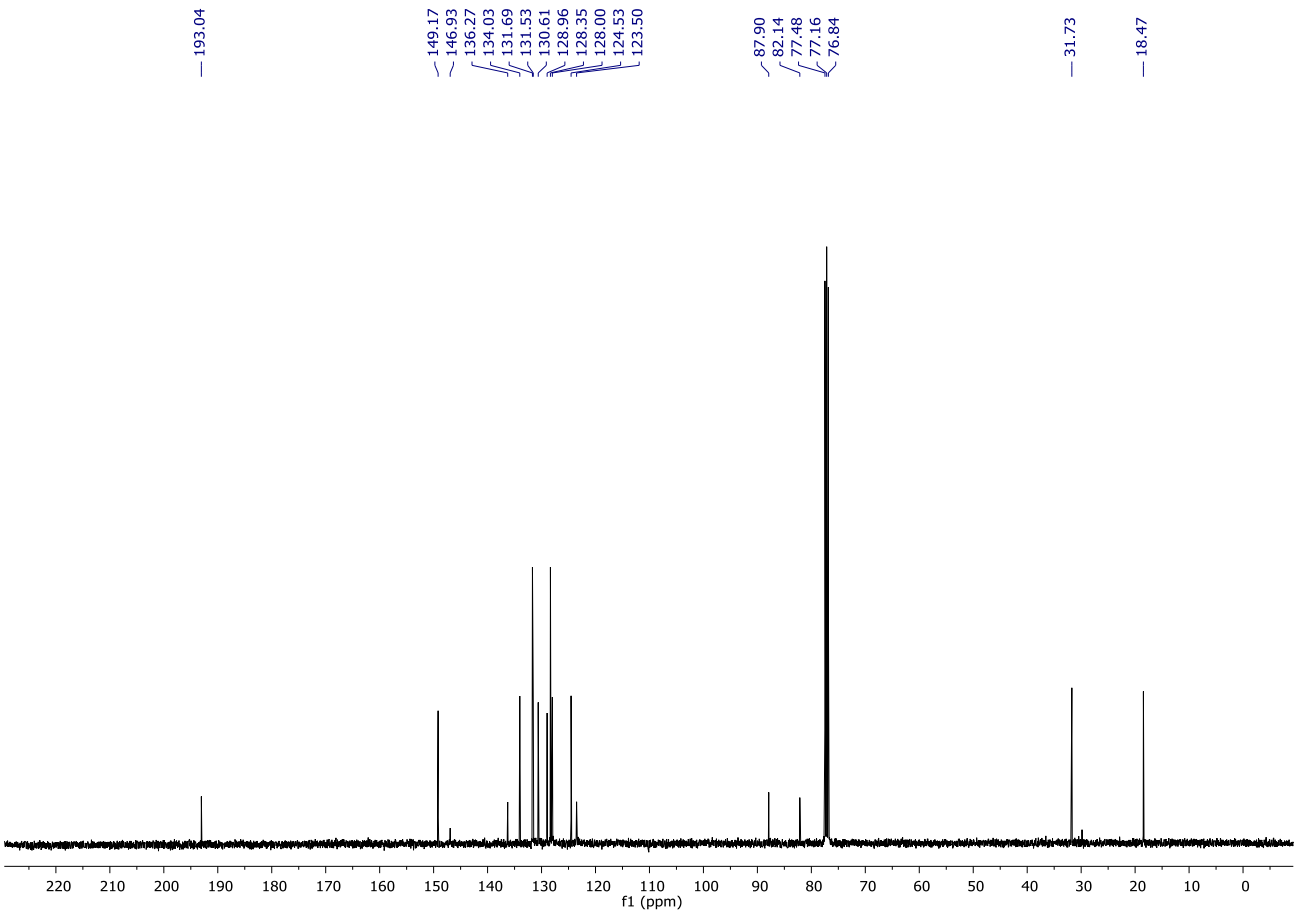
1.01
1.00
1.98
2.96
1.97
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.69
131.53
130.61
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128.35
128.00
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123.50
87.90
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77.48
77.16
76.84
31.73
18.47
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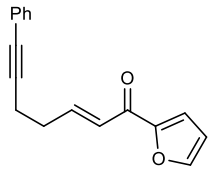
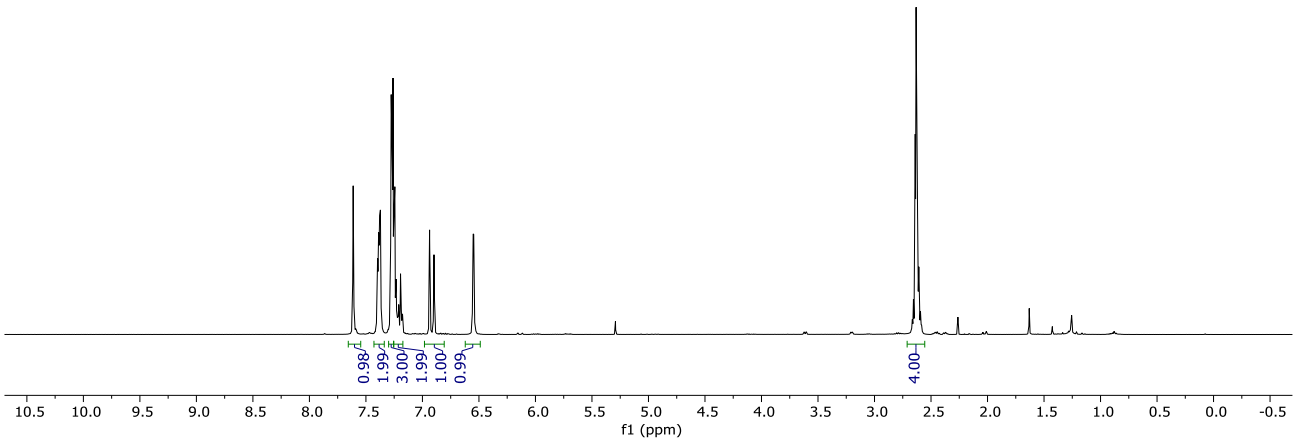
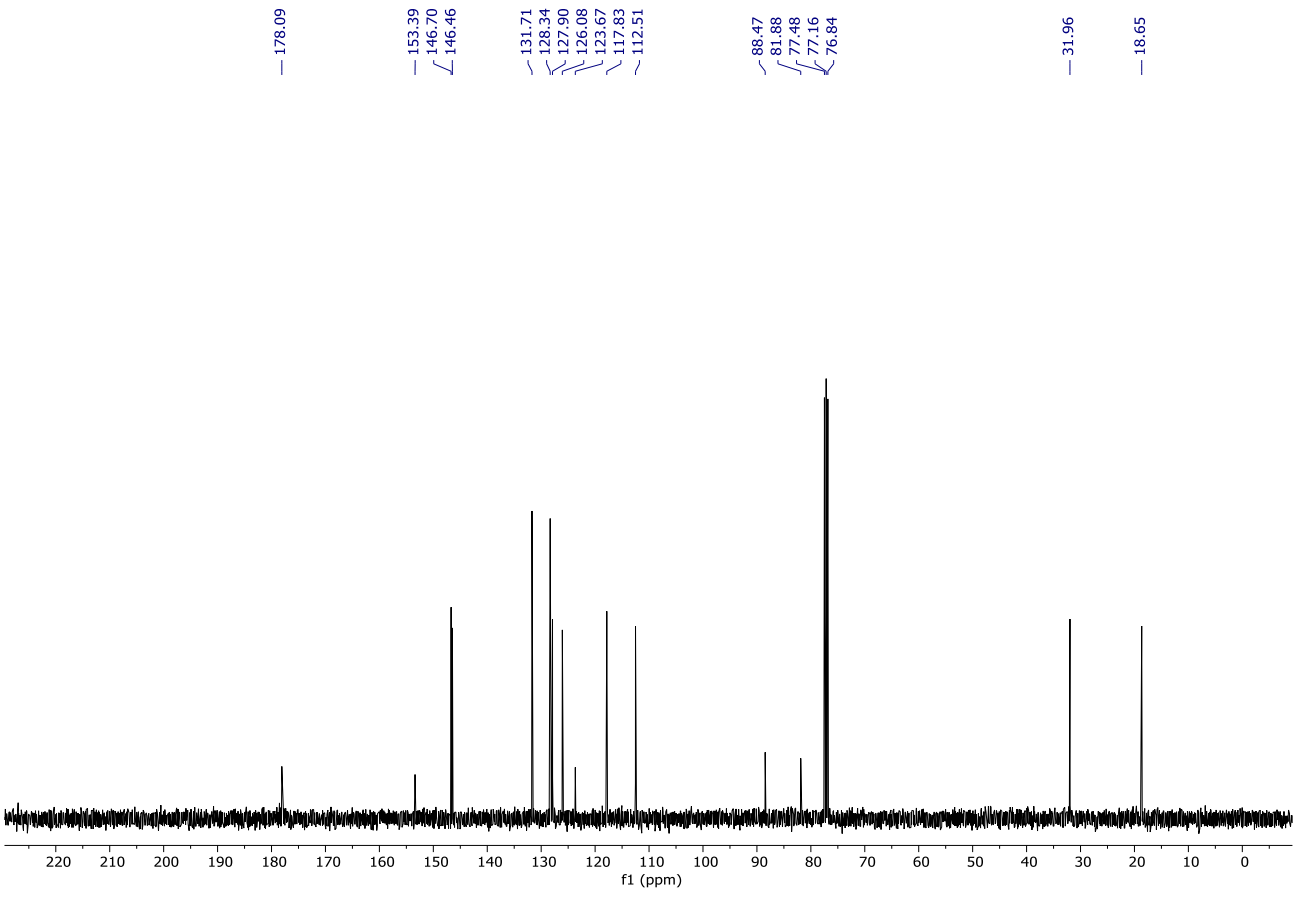
f1 (ppm)


Ph
O
O

1f


0.98
1.99
3.00
1.99
1.00
0.99
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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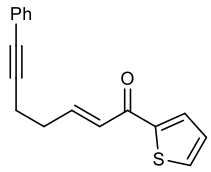
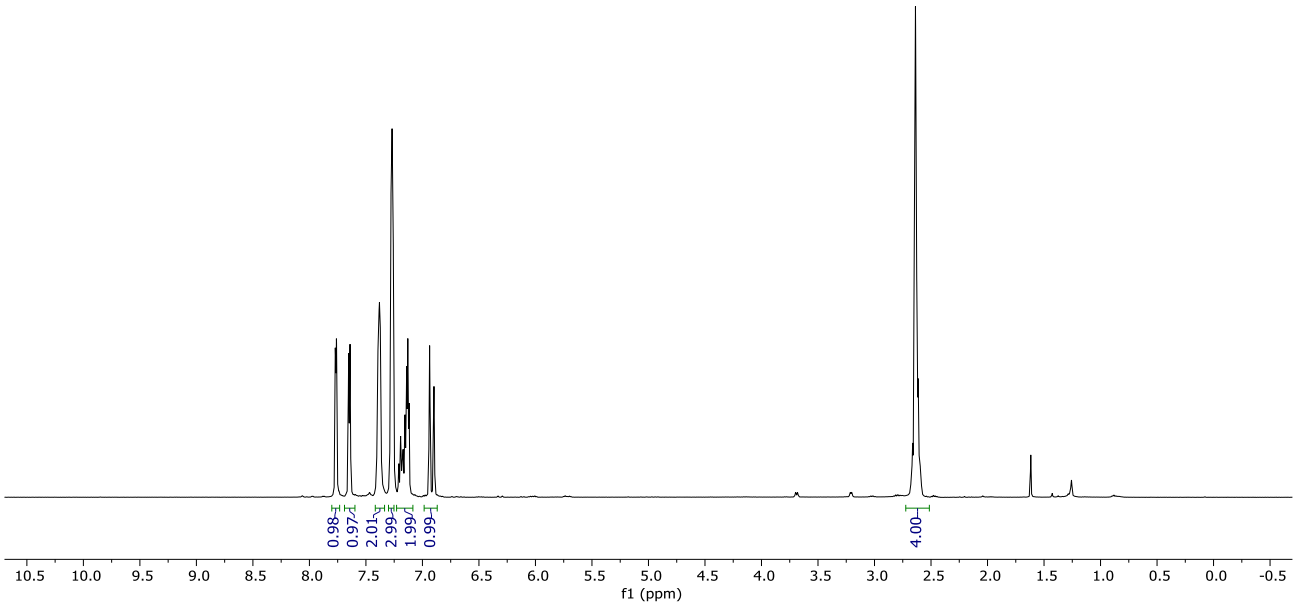
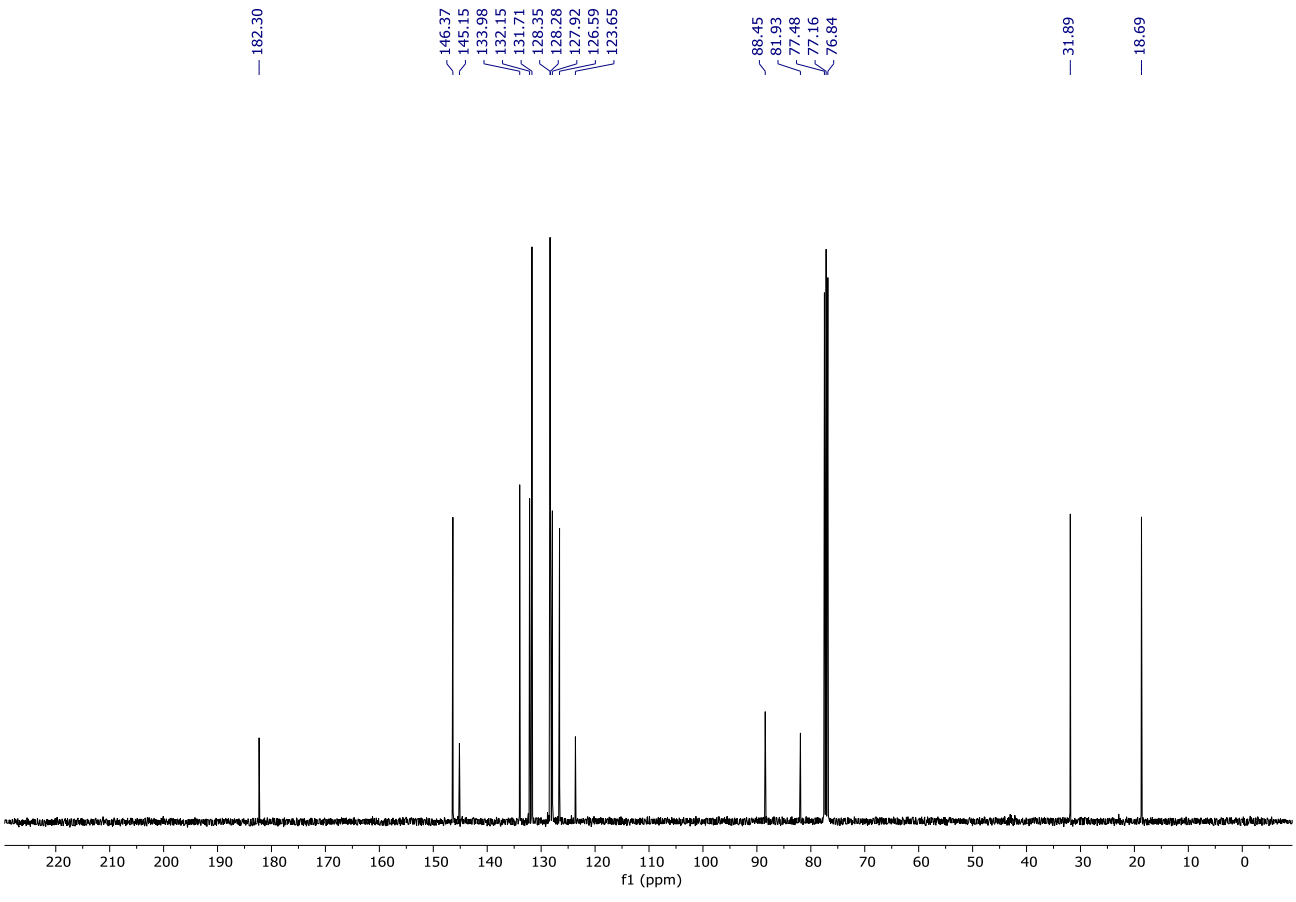
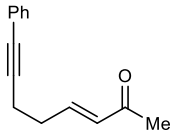
18.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
S

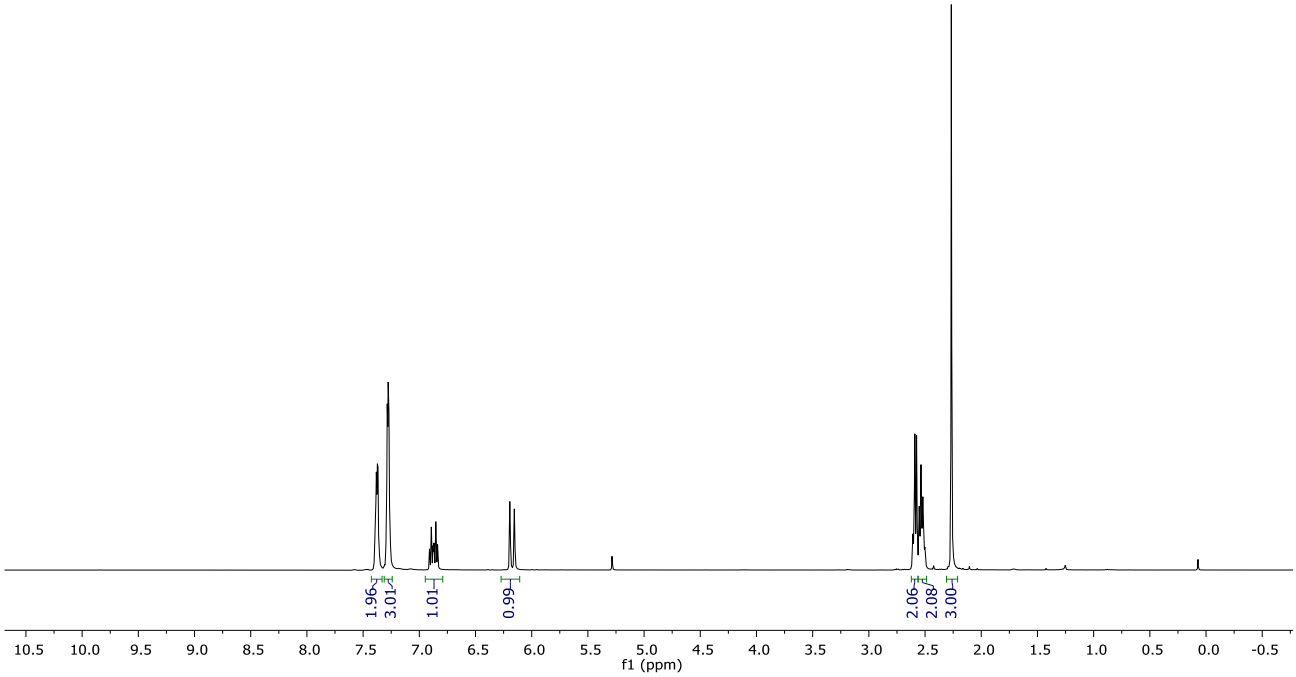
1g

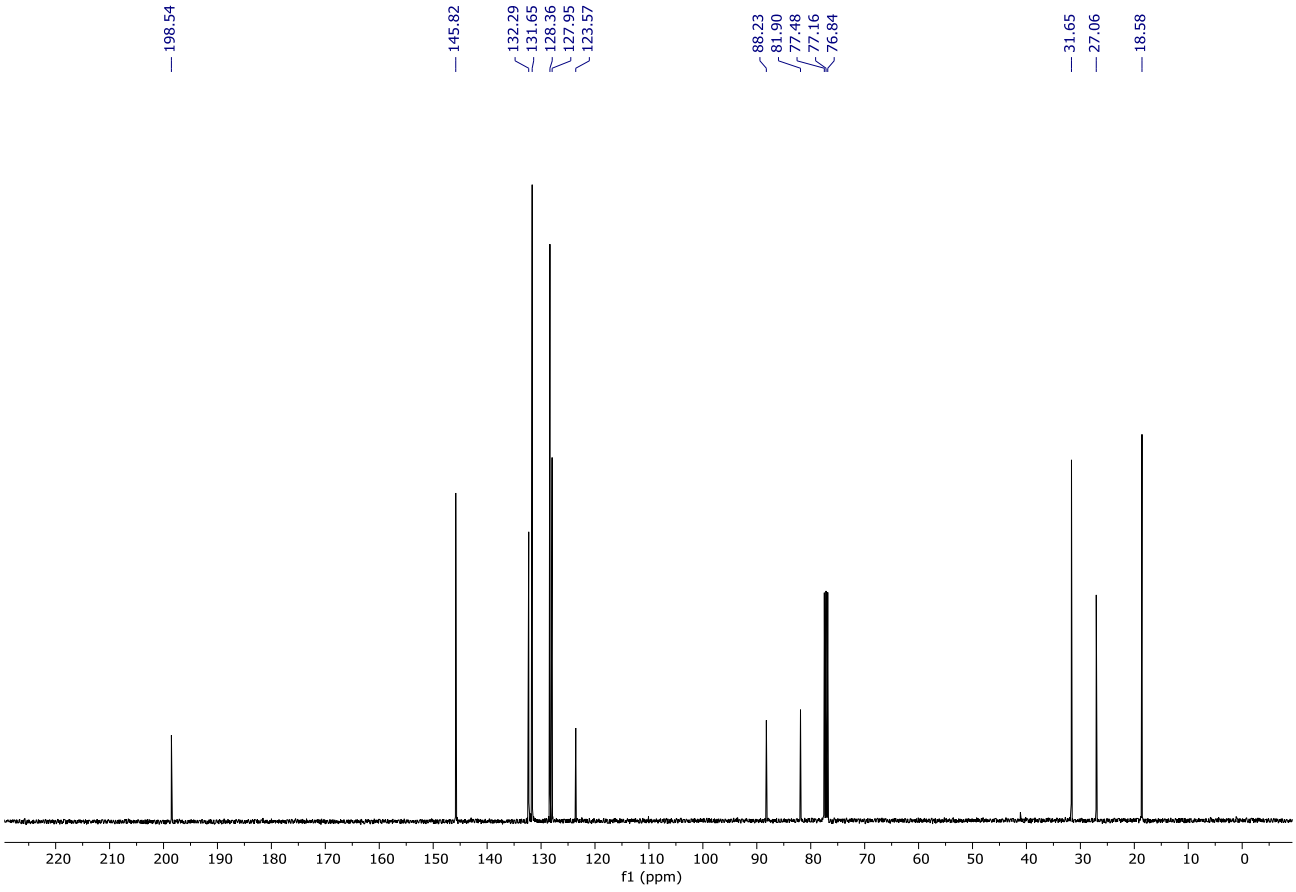

0.98
0.97
2.01
2.99
1.99
0.99
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

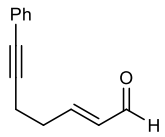

182.30
146.37
145.15
133.98
132.15
131.71
128.35
128.28
127.92
126.59
123.65
88.45
81.93
77.48
77.16
76.84
31.89
18.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
Me

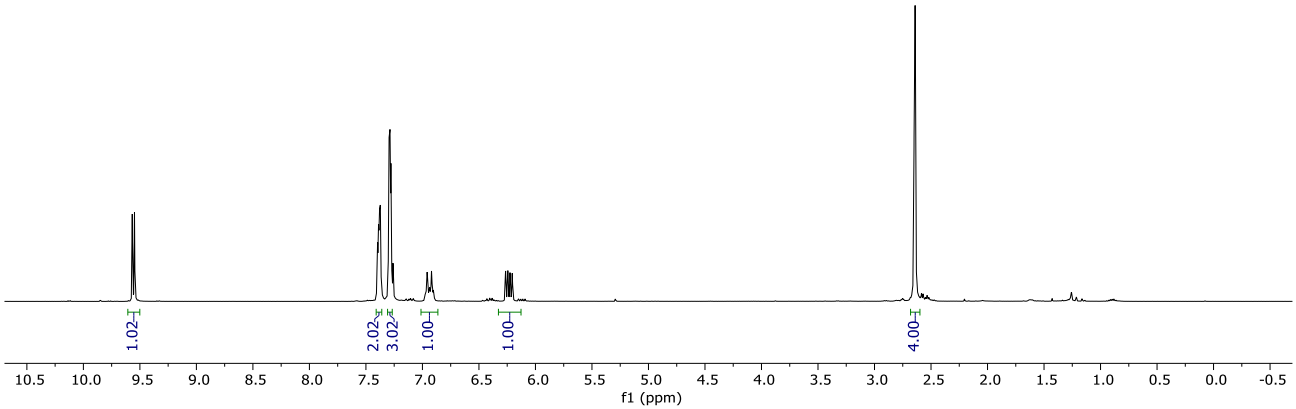
1h

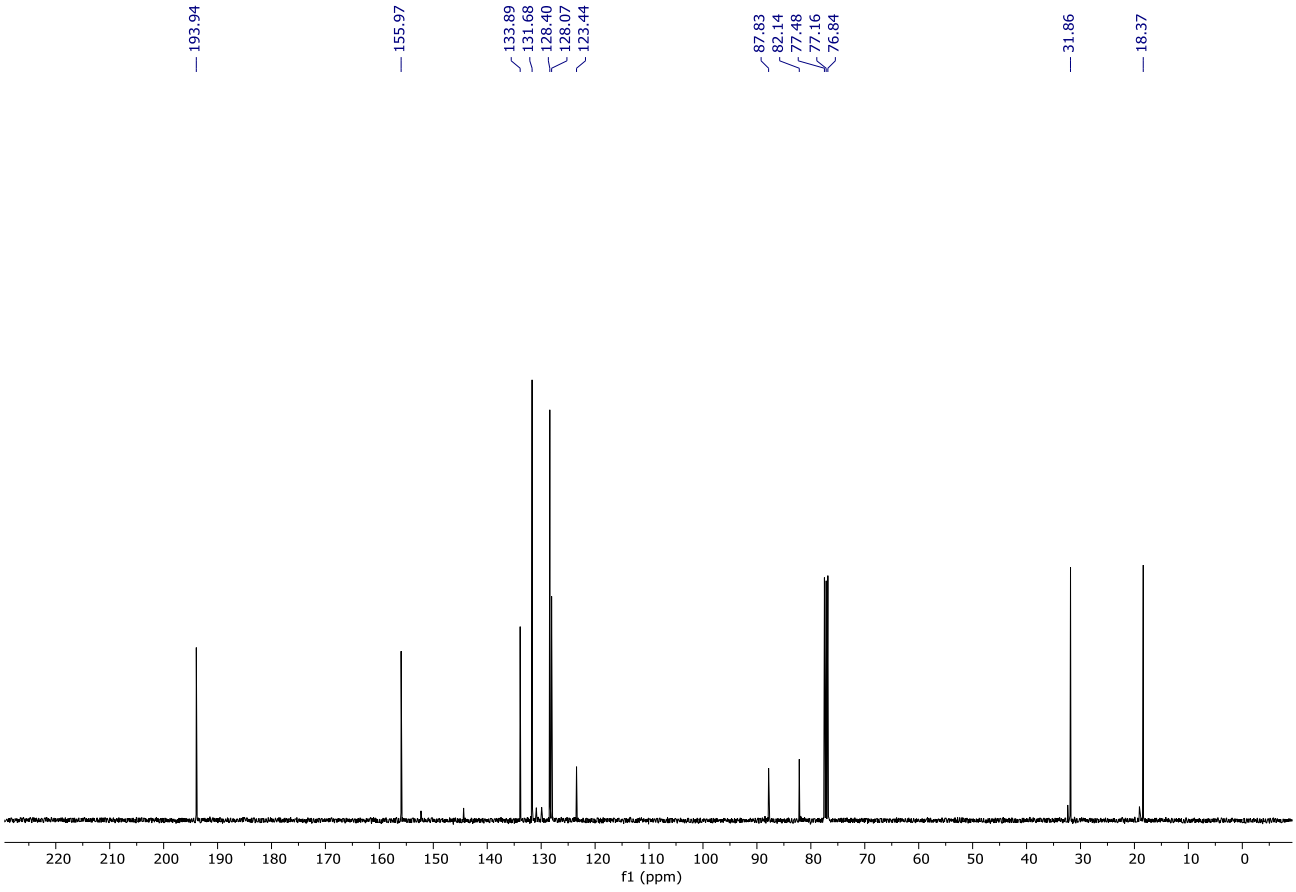

1.96
3.01
1.01
0.99
2.06
2.08
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

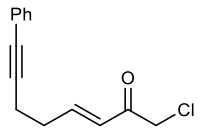

198.54
145.82
132.29
131.65
128.36
127.95
123.57
88.23
81.90
77.48
77.16
76.84
31.65
27.06
18.58
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
H

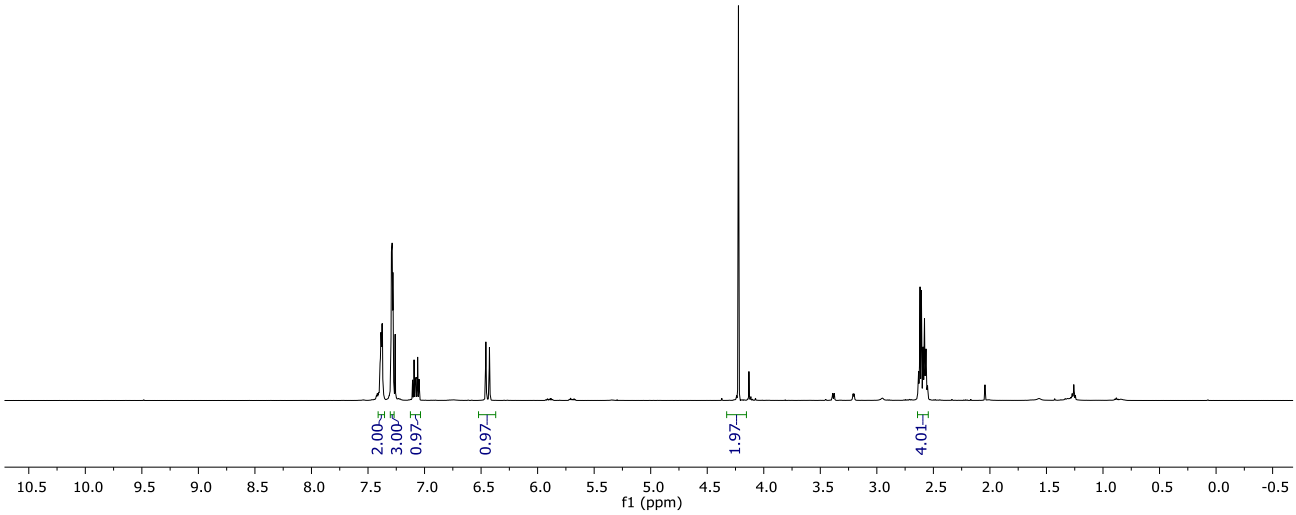
1i

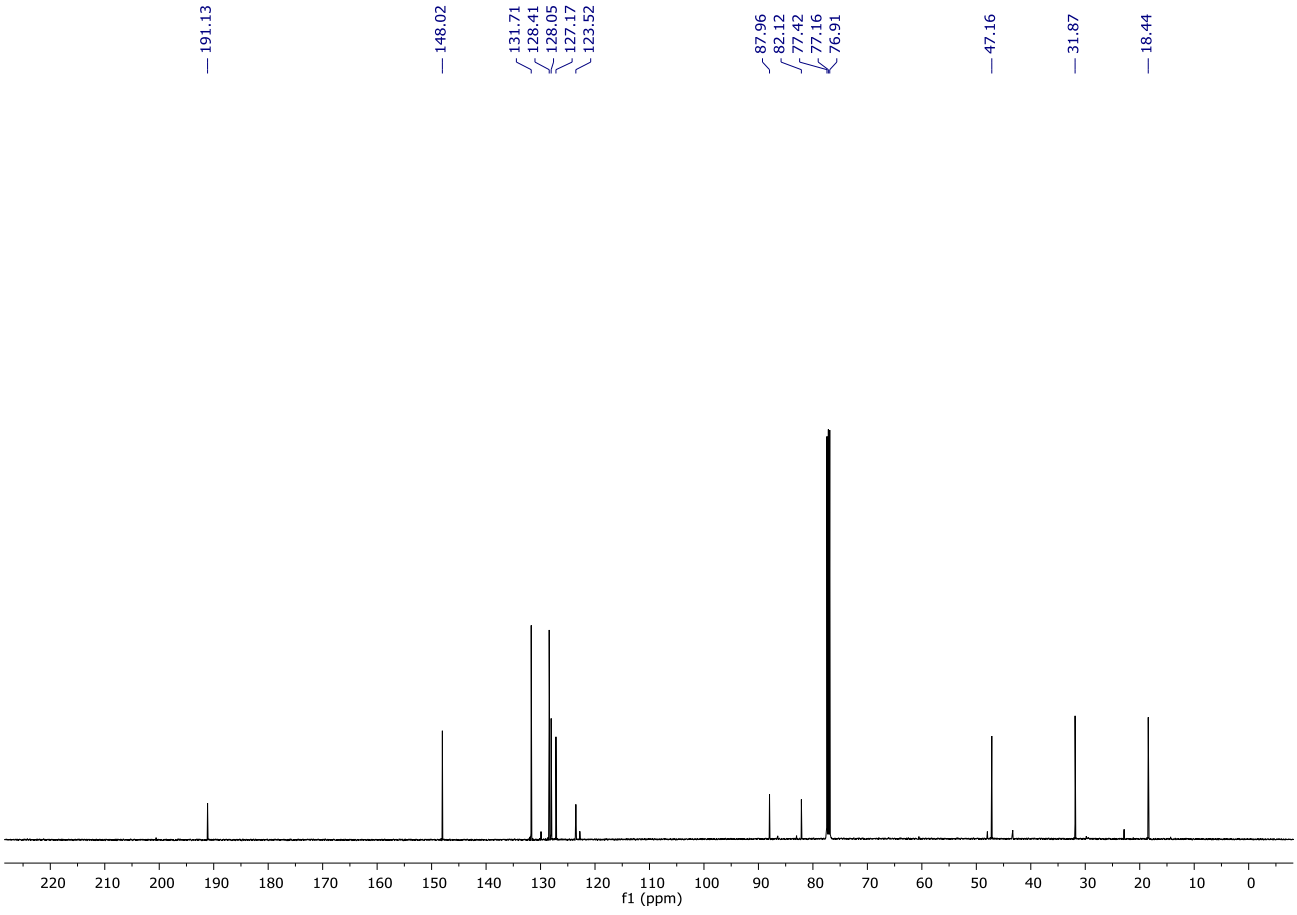

1.02
2.02
3.02
1.00
1.00
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

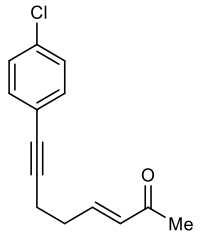

193.94
155.97
133.89
131.68
128.40
128.07
123.44
87.83
82.14
77.48
77.16
76.84
31.86
18.37
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
Cl

1j

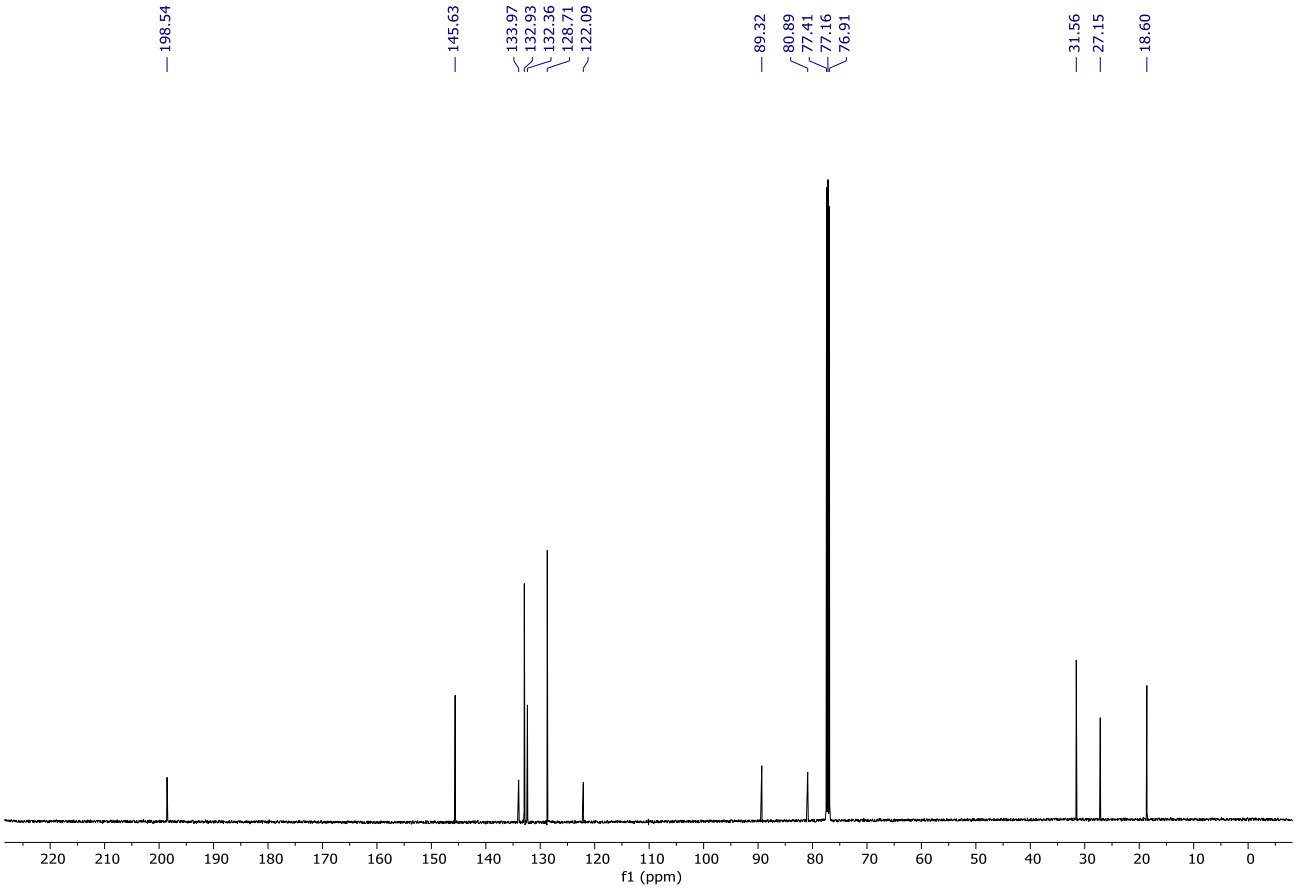

2.00
3.00
0.97
0.97
1.97
4.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

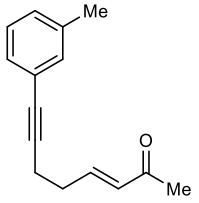

191.13
148.02
131.71
128.41
128.05
127.17
123.52
87.96
82.12
77.42
77.16
76.91
47.16
31.87
18.44
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
O
Me

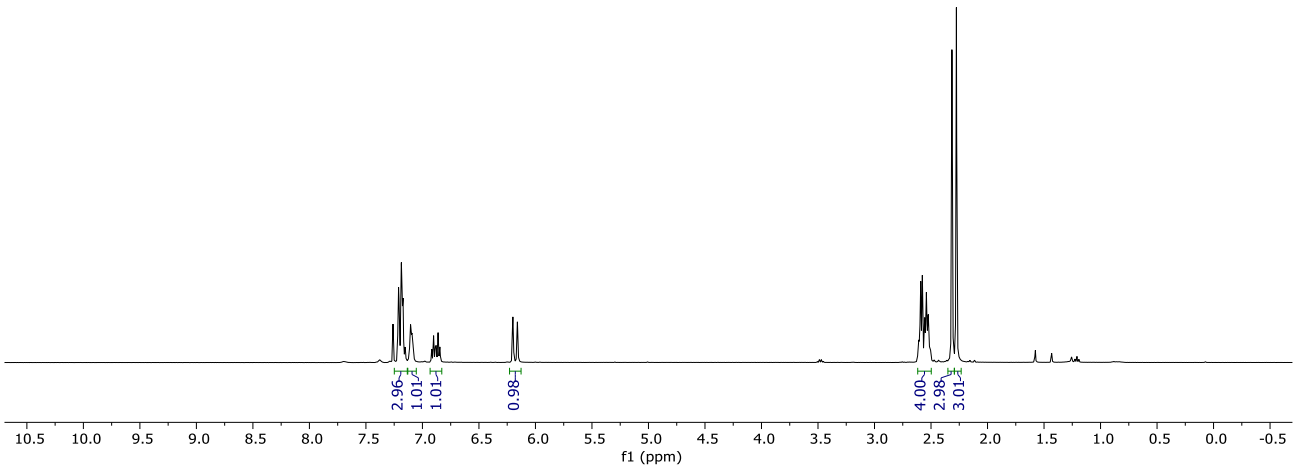
1k

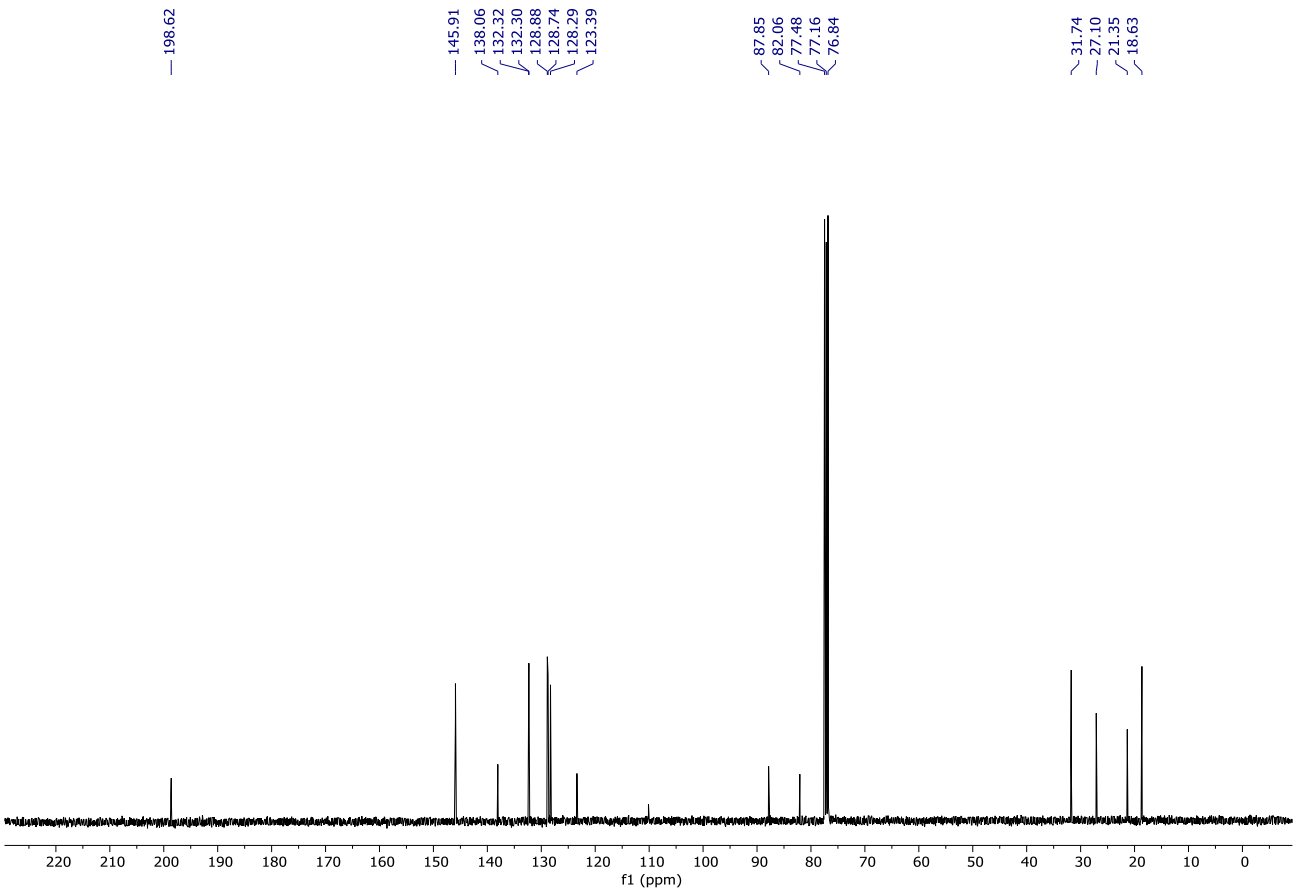
2.01
1.02
0.98
0.99
0.98
2.00
2.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

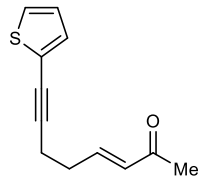

198.54
145.63
133.97
132.93
132.36
128.71
122.09
89.32
80.89
77.41
77.16
76.91
31.56
27.15
18.60
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
Me

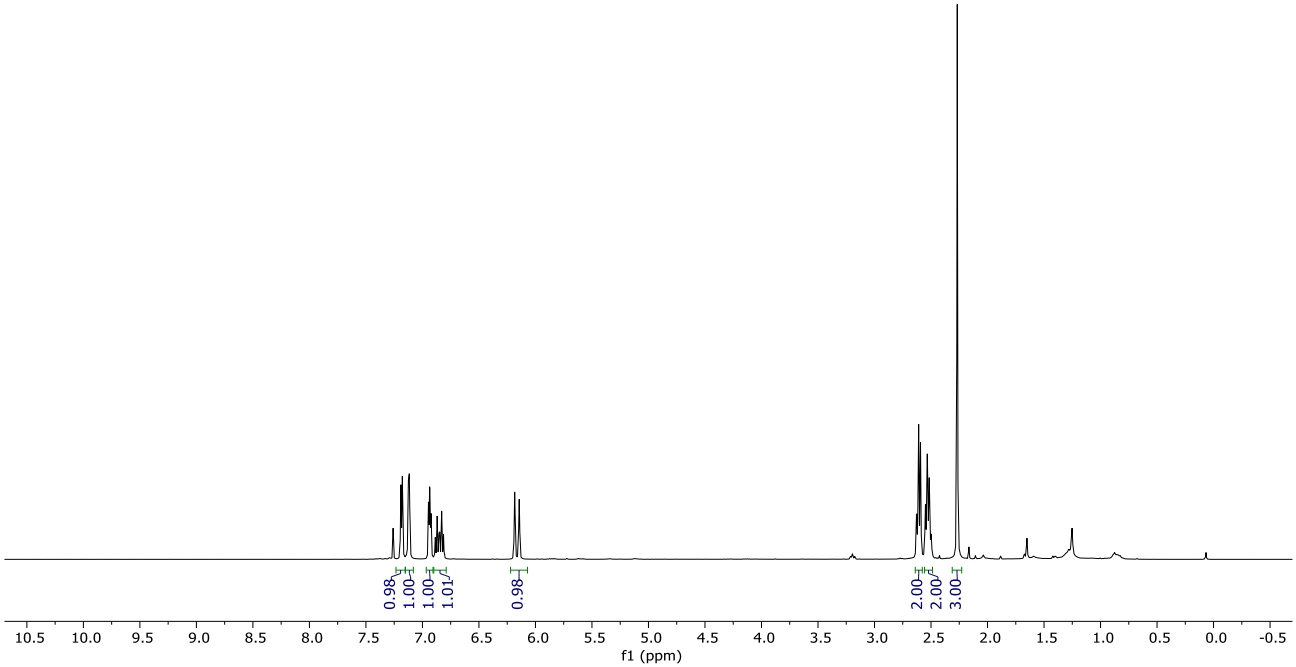
1l

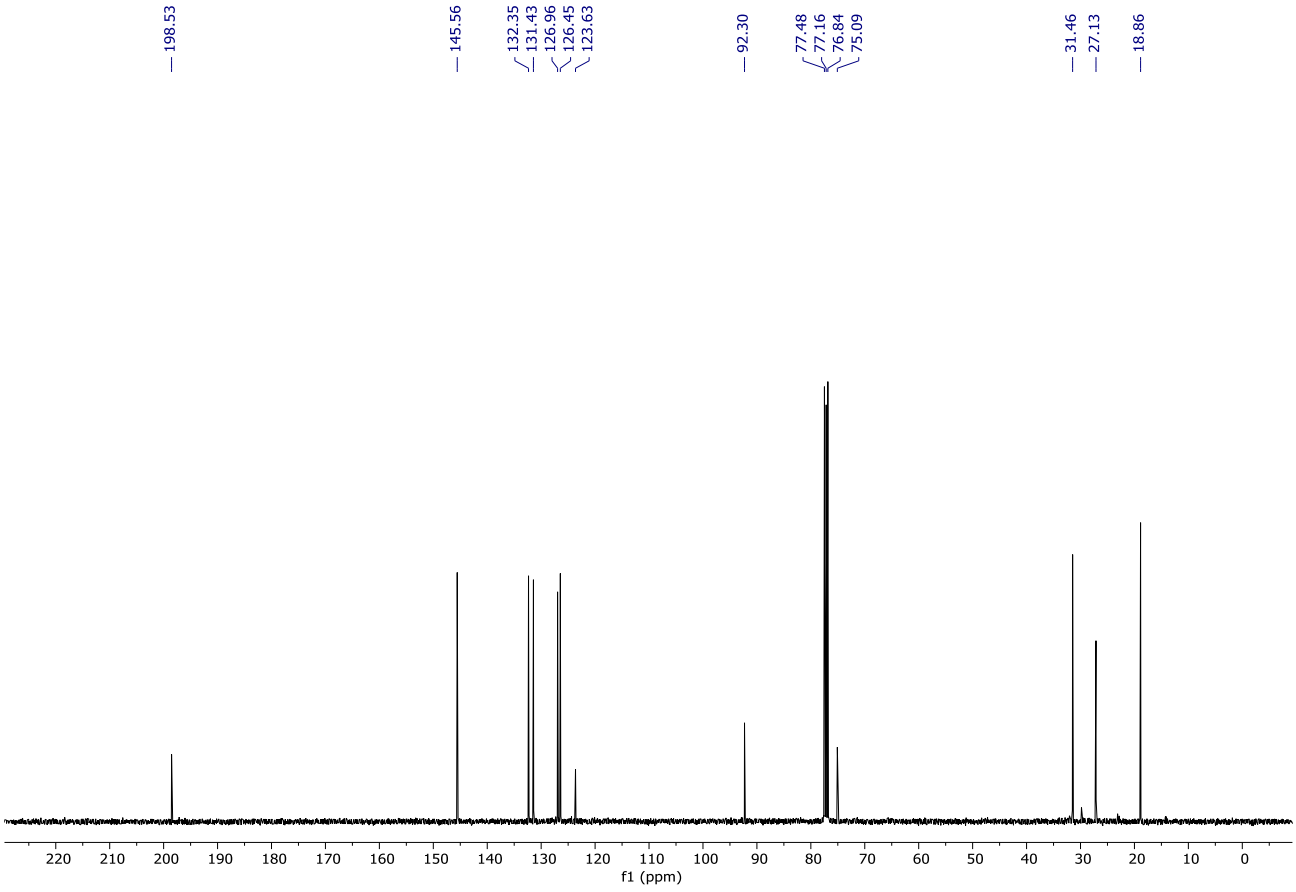

2.96
1.01
1.01
0.98
4.00
2.98
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

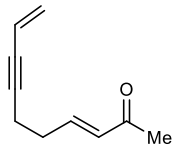

198.62
145.91
138.06
132.32
132.30
128.88
128.74
128.29
123.39
87.85
82.06
77.48
77.16
76.84
31.74
27.10
21.35
18.63
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
O
Me

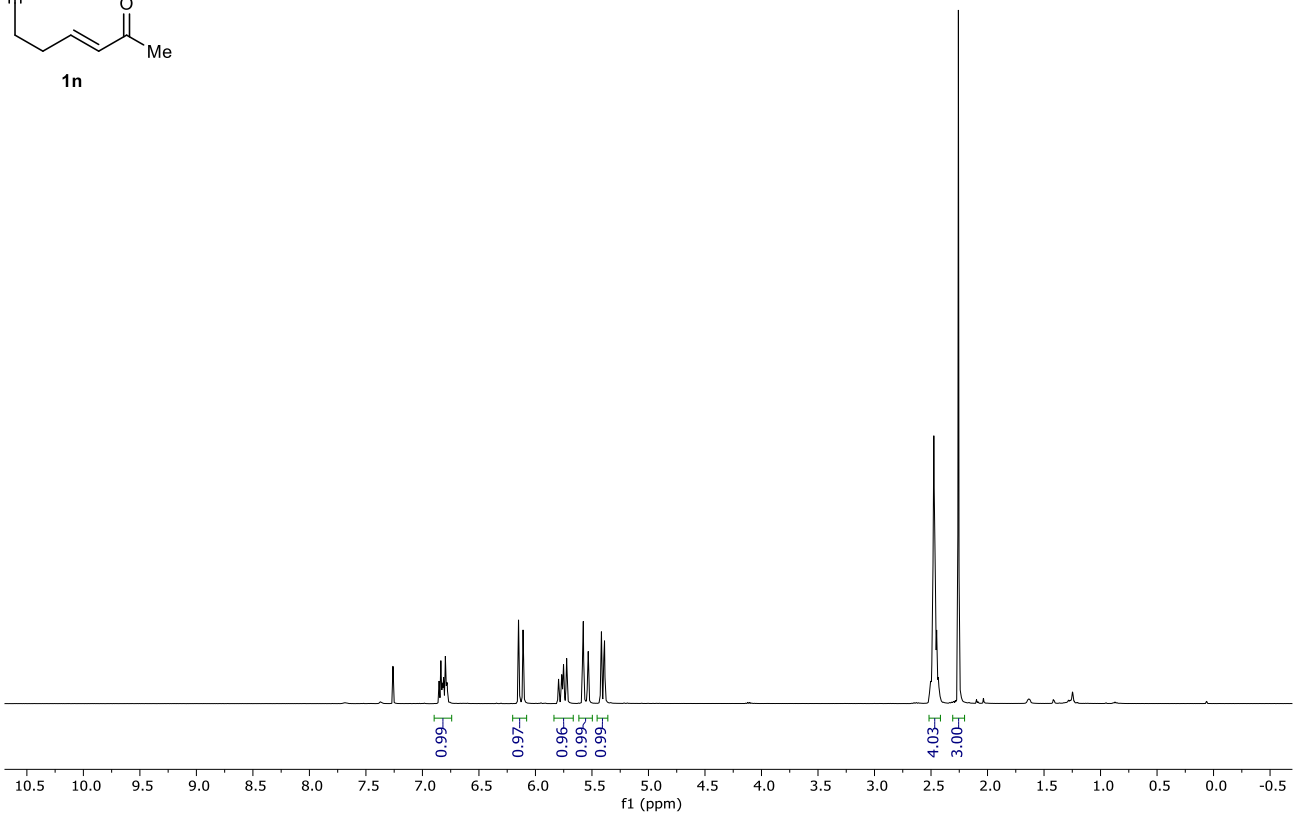
1m

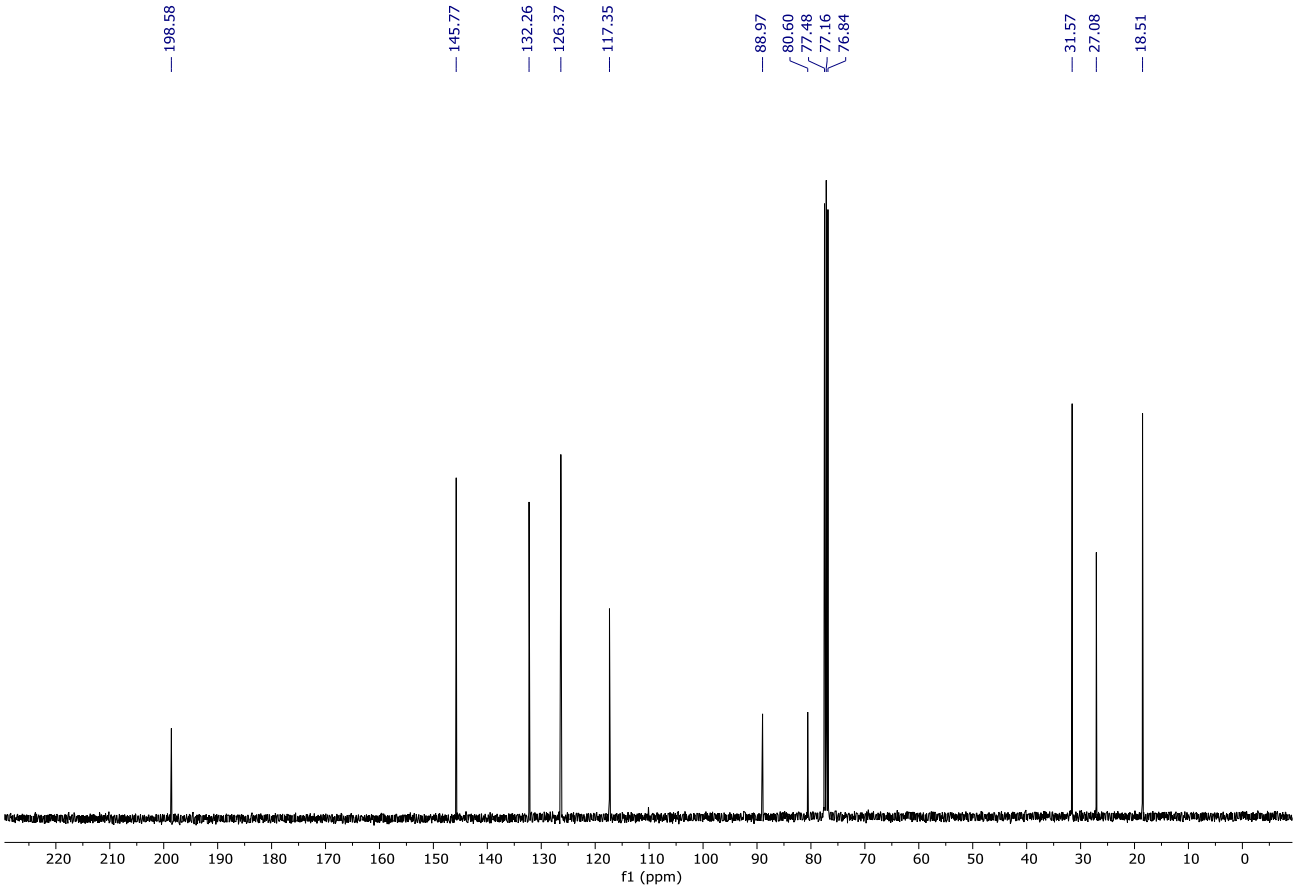

0.98
1.00
1.00
1.01
0.98
2.00
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

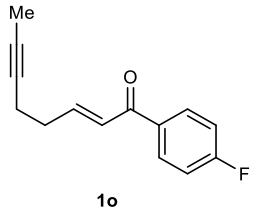

198.53
145.56
132.35
131.43
126.96
126.45
123.63
92.30
77.48
77.16
76.84
75.09
31.46
27.13
18.86
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Me

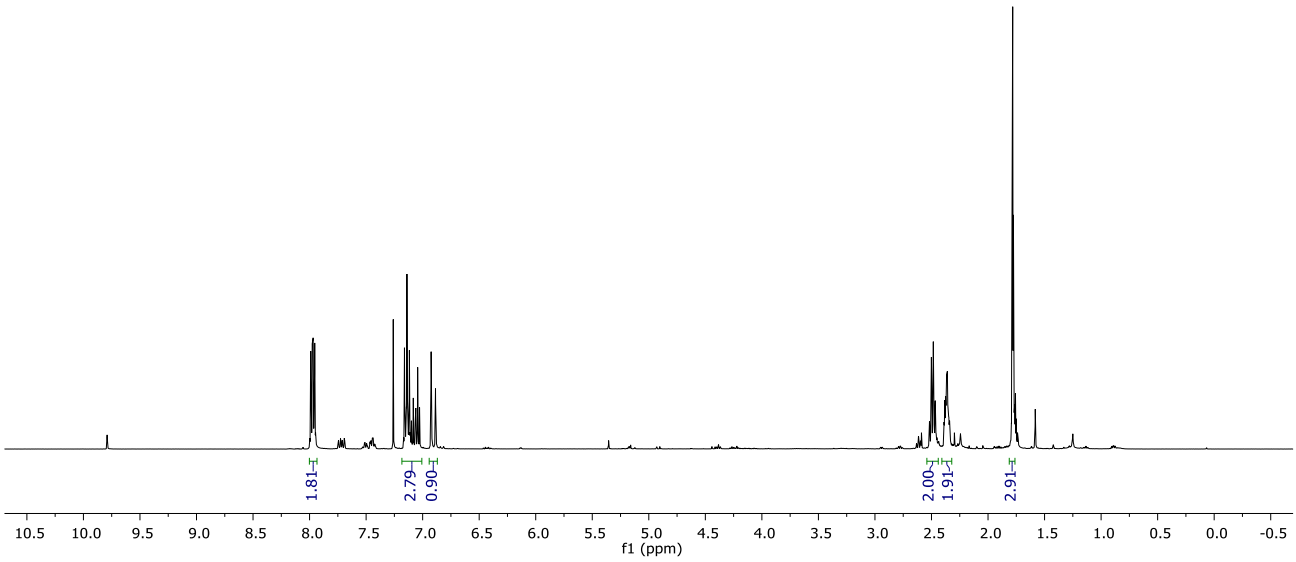
1n

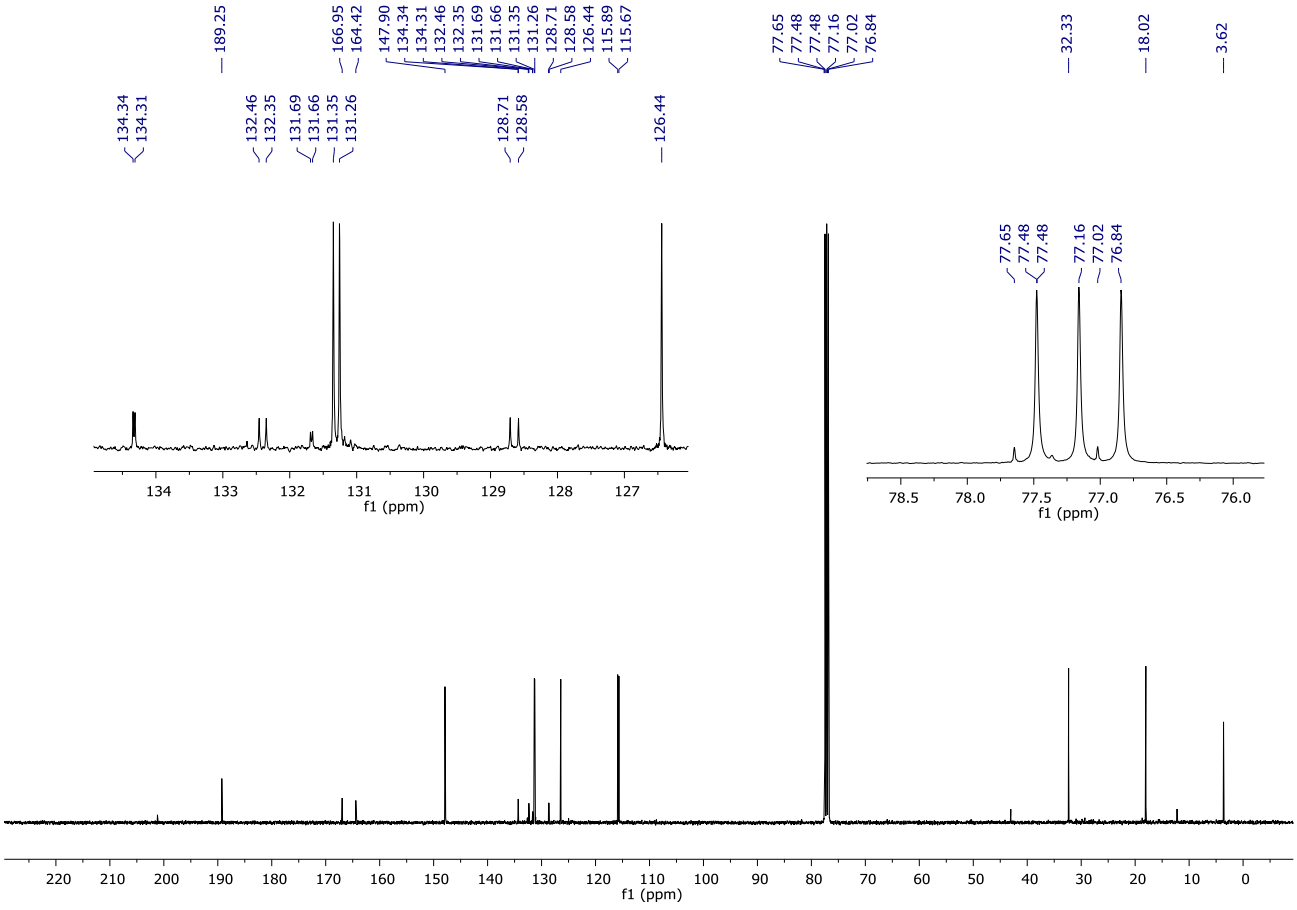

0.99
0.97
0.96
0.99
0.99
4.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

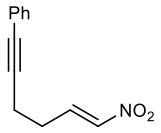

198.58
145.77
132.26
126.37
117.35
88.97
80.60
77.48
77.16
76.84
31.57
27.08
18.51
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
F

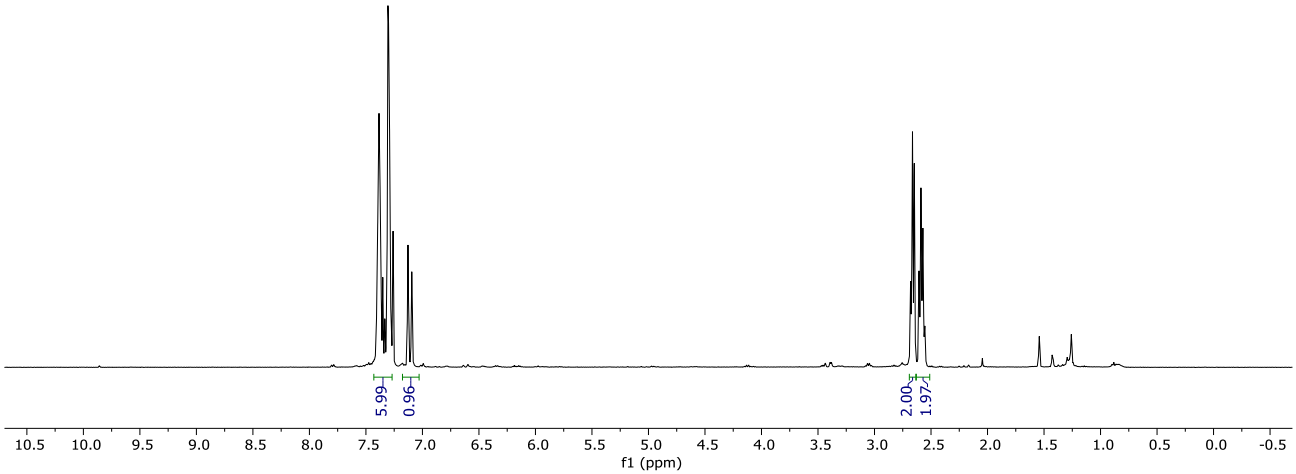
1o

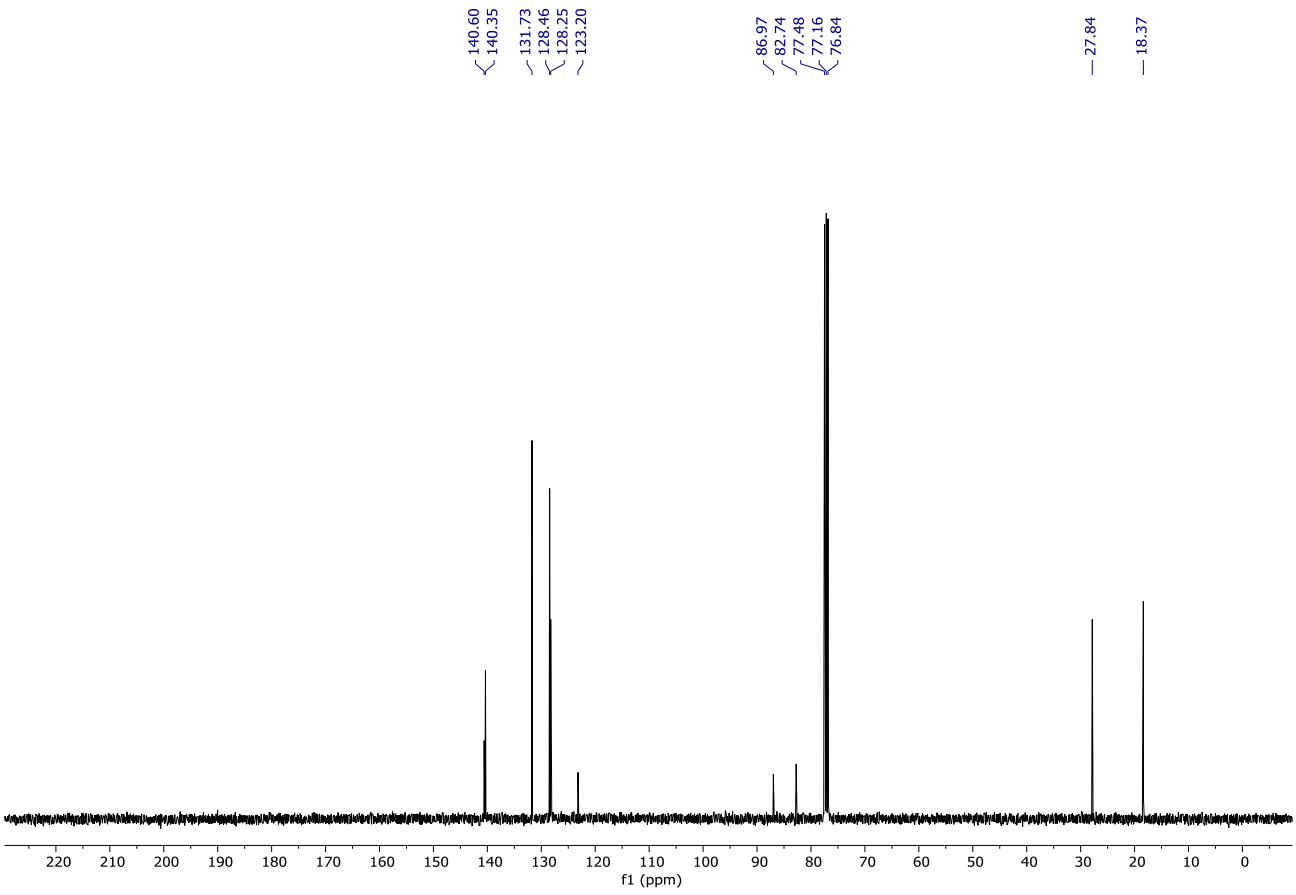

1.81
2.79
0.90
2.00
1.91
2.91
f1 (ppm)

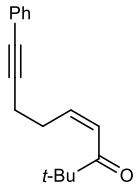

189.25
166.95
164.42
147.90
134.34
134.31
132.46
132.35
131.69
131.66
131.35
131.26
128.71
128.58
126.44
115.89
115.67
77.65
77.48
77.48
77.16
77.02
76.84
32.33
18.02
3.62
f1 (ppm)


Ph
NO2

1p

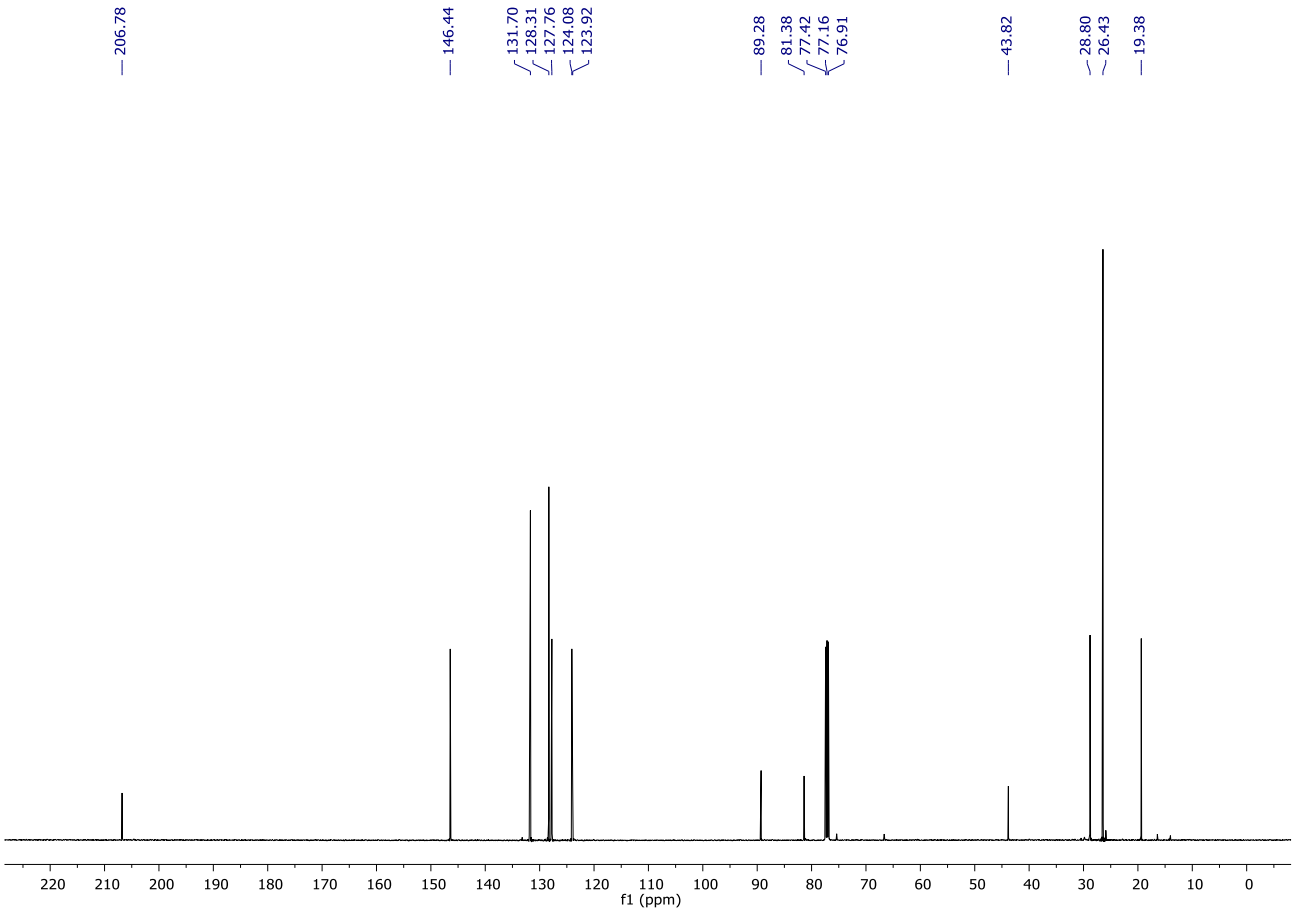

5.99
0.96
2.00
1.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

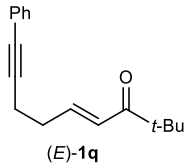

140.60
140.35
131.73
128.46
128.25
123.20
86.97
82.74
77.48
77.16
76.84
27.84
18.37
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
t-Bu
O

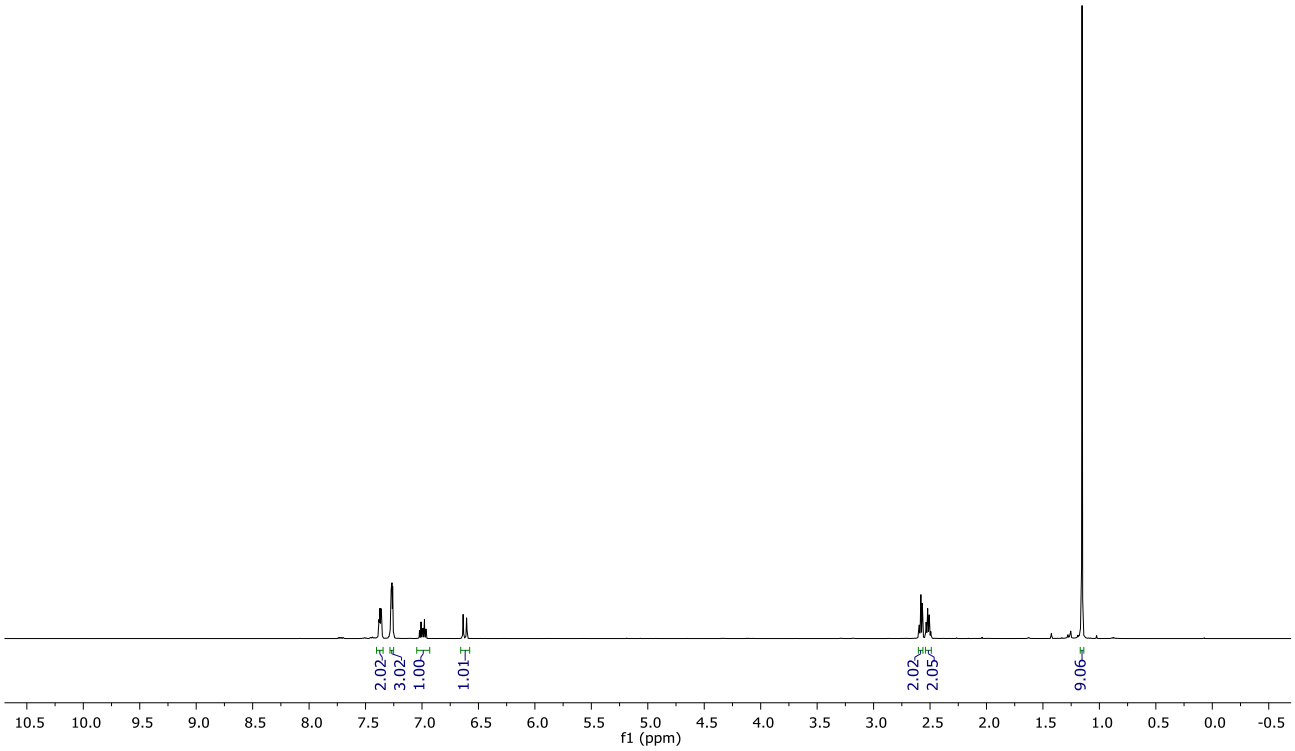
(*Z*)-**1q**

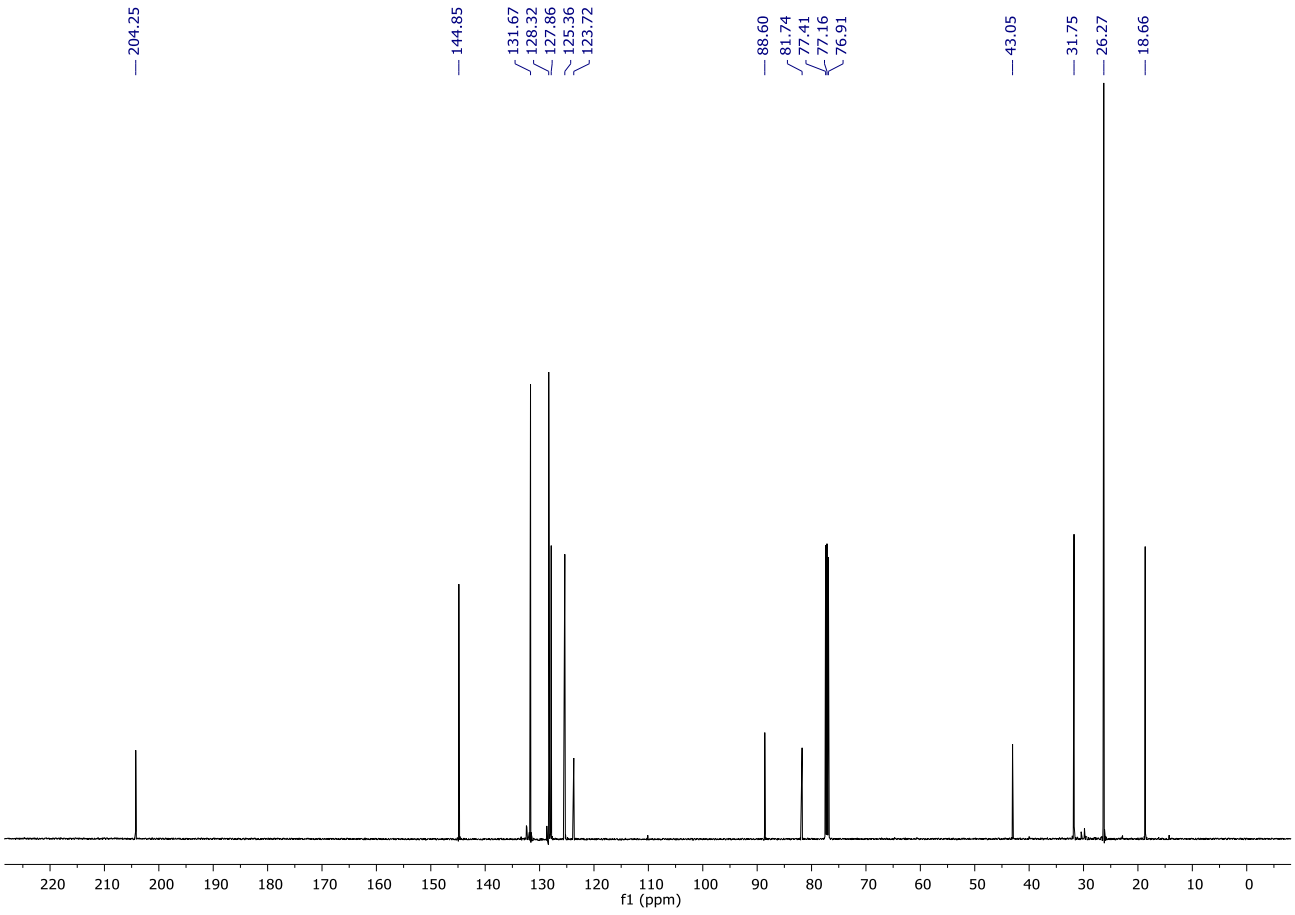
1.99
3.01
0.98
0.98
2.00
2.02
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

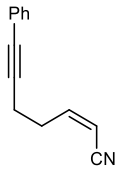

206.78
146.44
131.70
128.31
127.76
124.08
123.92
89.28
81.38
77.42
77.16
76.91
43.82
28.80
26.43
19.38
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
t-Bu

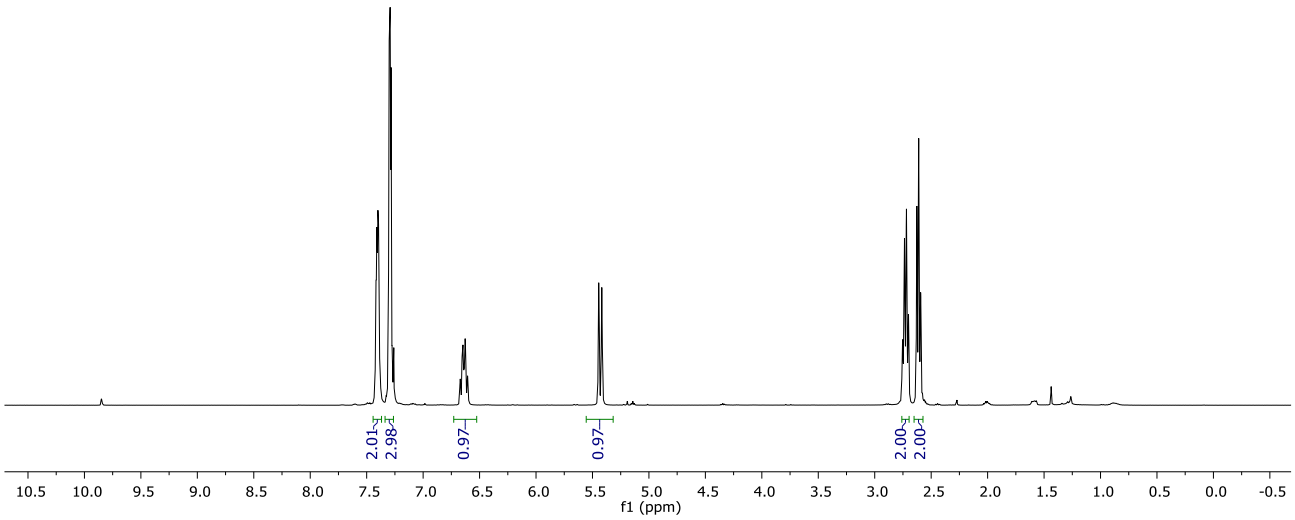
(*E*)-**1q**

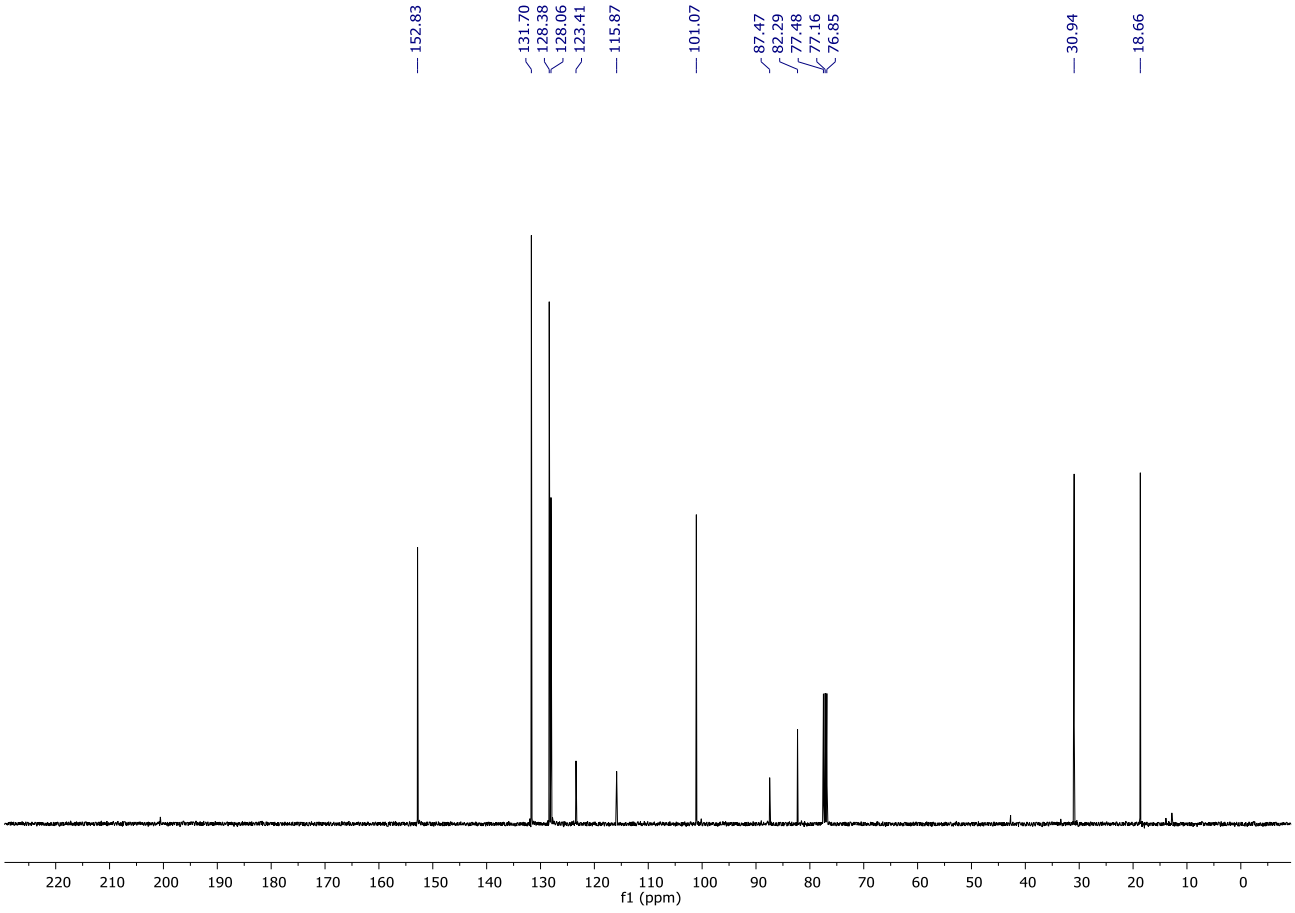

2.02
3.02
1.00
1.01
2.02
2.05
9.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

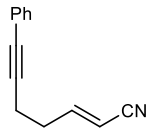

204.25
144.85
131.67
128.32
127.86
125.36
123.72
88.60
81.74
77.41
77.16
76.91
43.05
31.75
26.27
18.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
CN

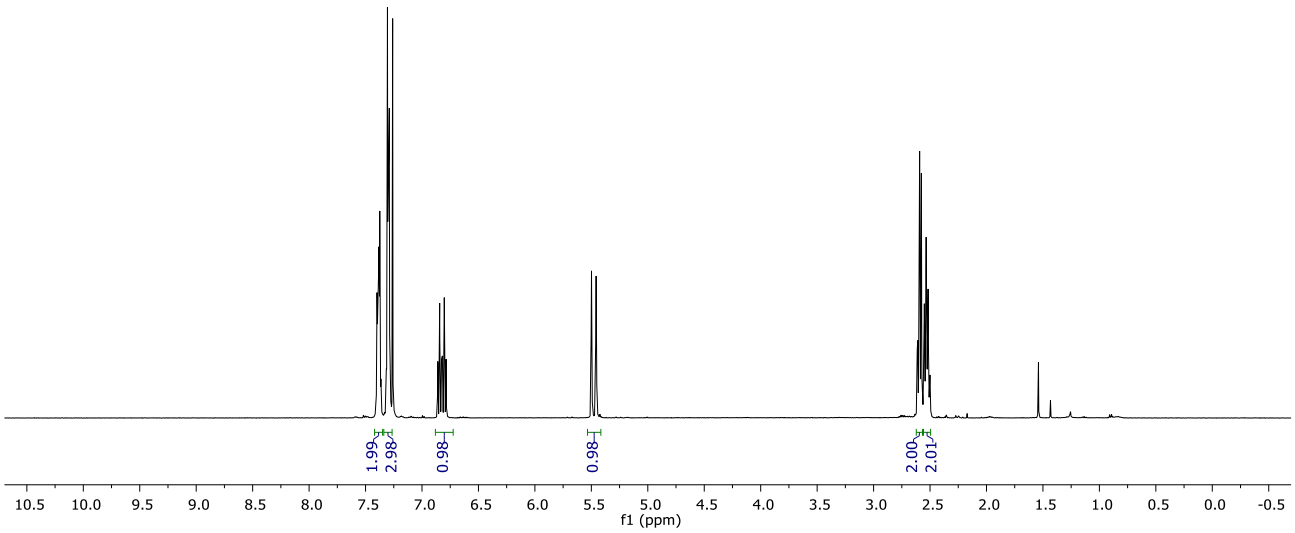
(Z)-**1s**

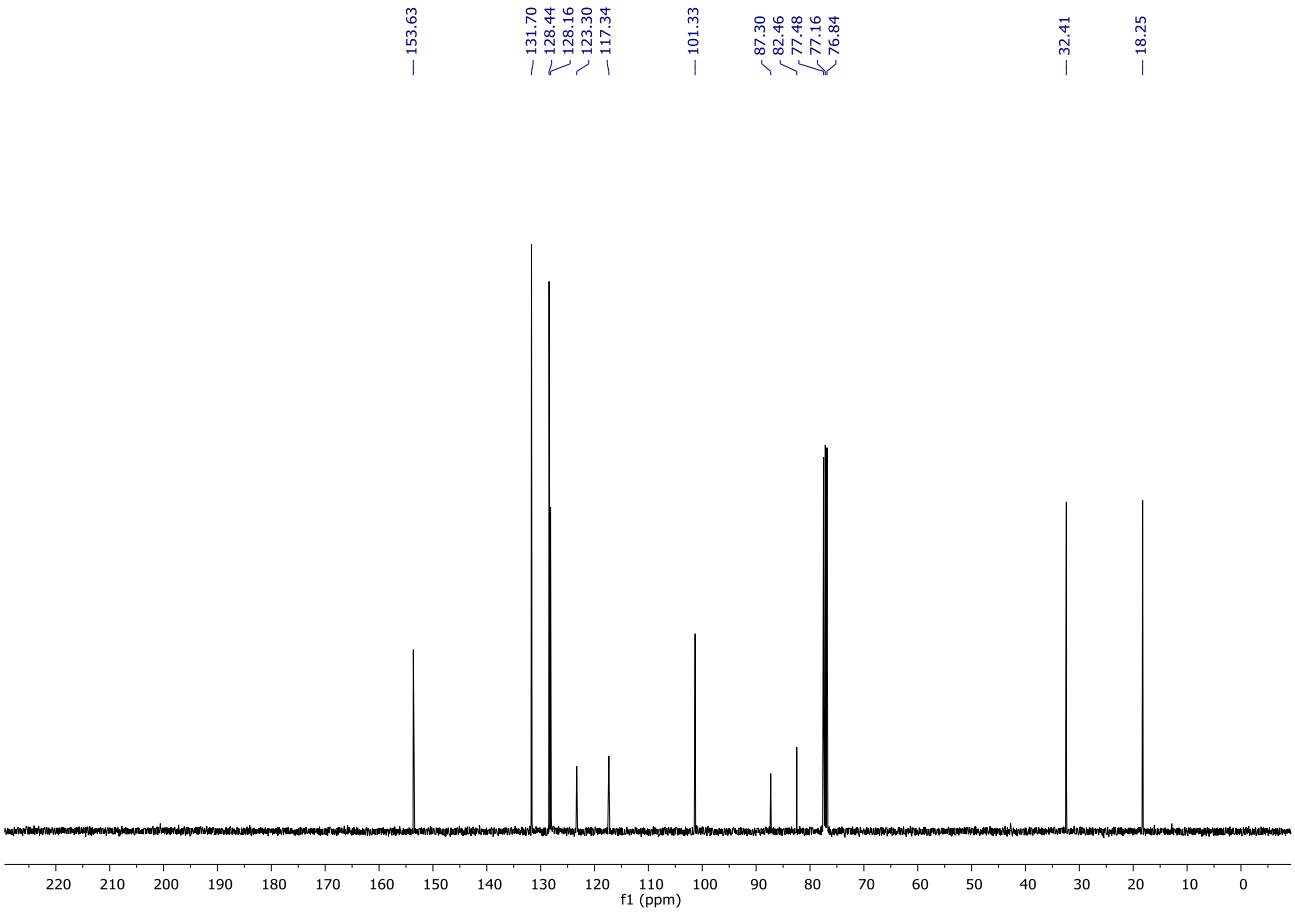

2.01
2.98
0.97
0.97
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

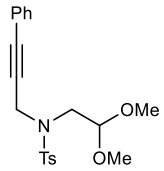

152.83
131.70
128.38
128.06
123.41
115.87
101.07
87.47
82.29
77.48
77.16
76.85
30.94
18.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
CN

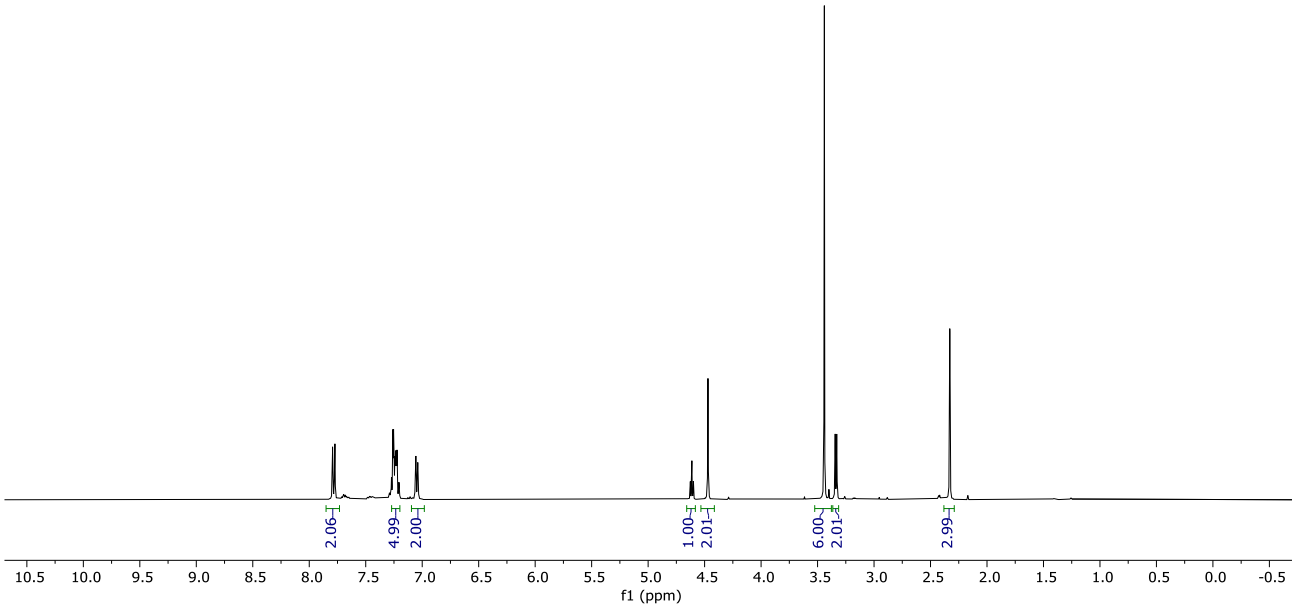
(*E*)-**1s**

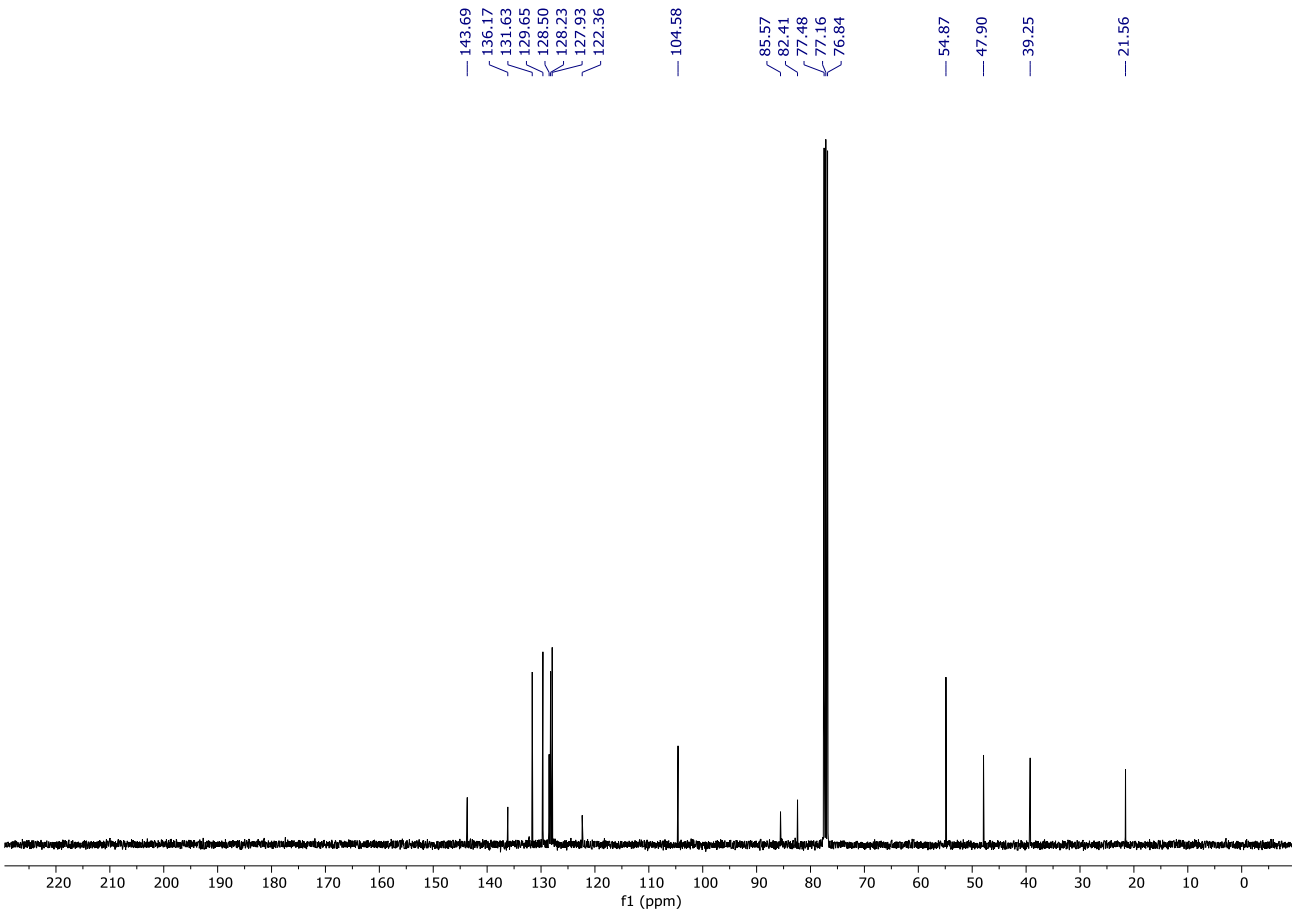

1.99
2.98
0.98
0.98
2.00
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

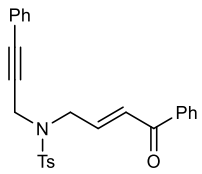

153.63
131.70
128.44
128.16
123.30
117.34
101.33
87.30
82.46
77.48
77.16
76.84
32.41
18.25
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
N
Ts
OMe
OMe

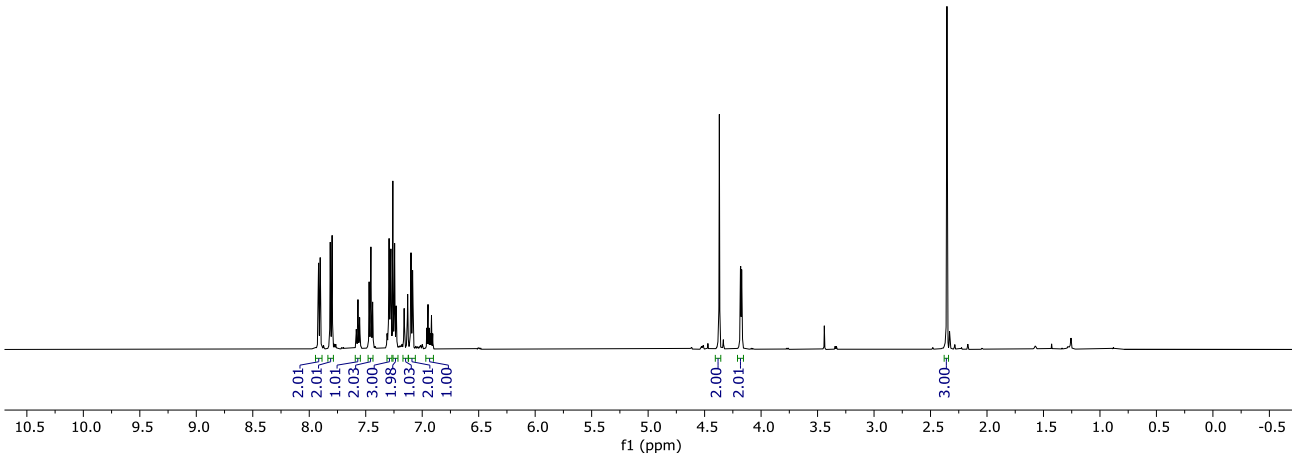
S17

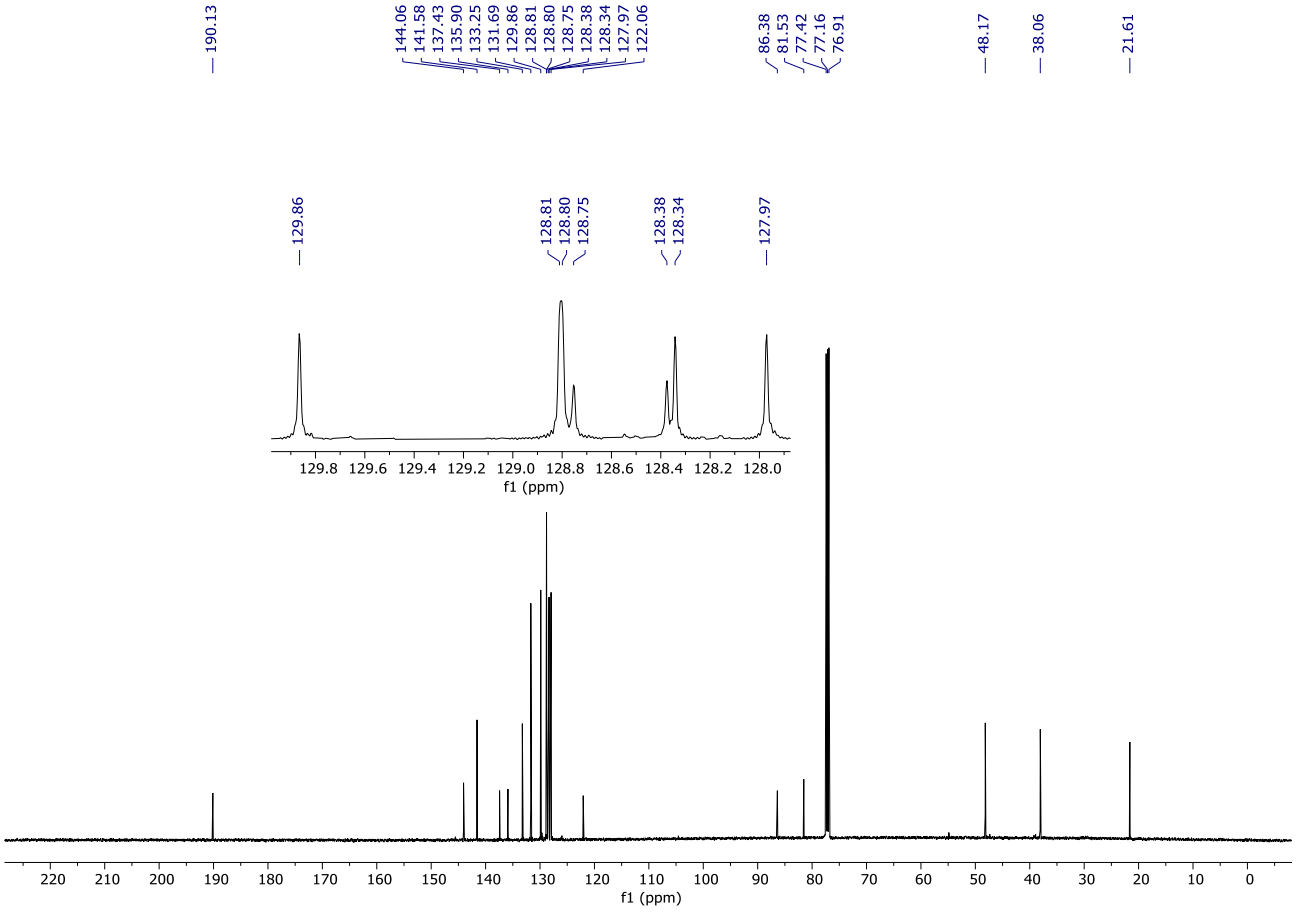

2.06
4.99
2.00
1.00
2.01
6.00
2.01
2.99
f1 (ppm)

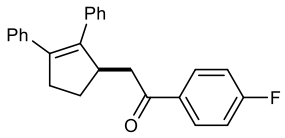

143.69
136.17
131.63
129.65
128.50
128.23
127.93
122.36
104.58
85.57
82.41
77.48
77.16
76.84
54.87
47.90
39.25
21.56
f1 (ppm)


Ph
N
Ts
Ph
O

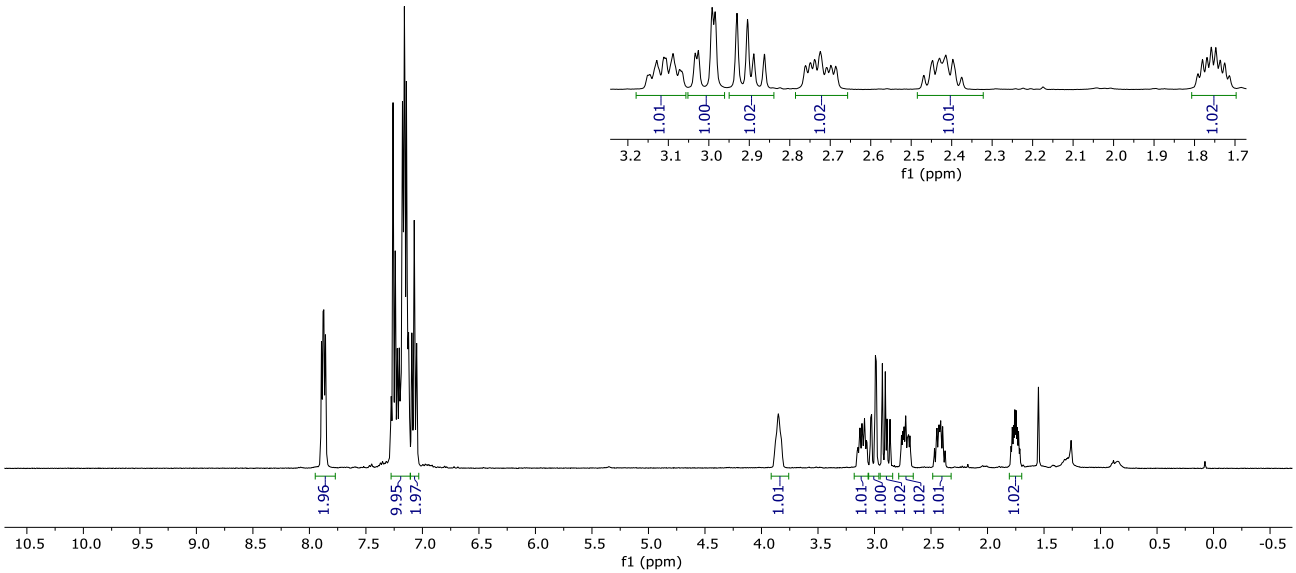
16a

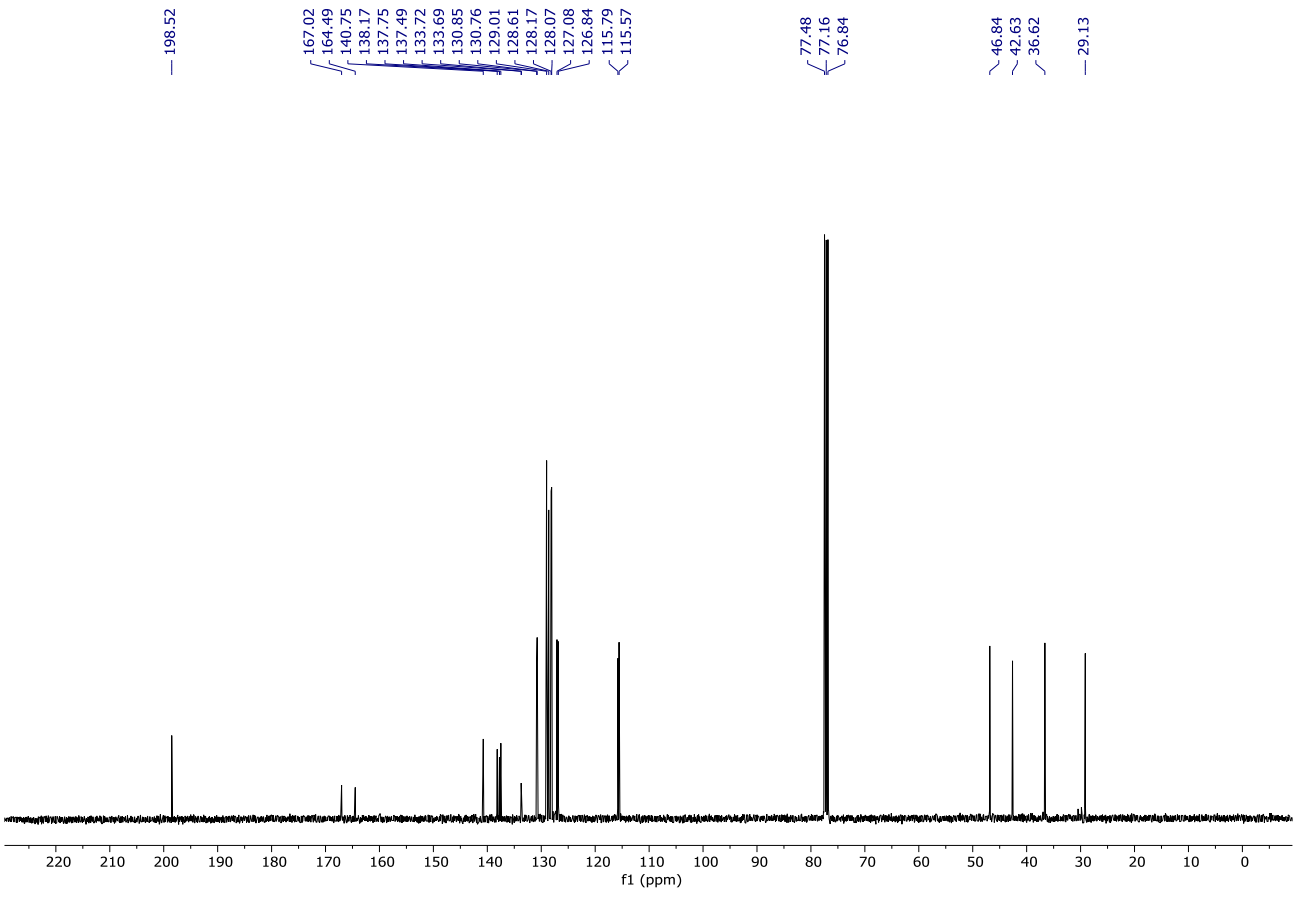

2.01
2.01
1.01
2.03
3.00
1.98
1.03
2.01
1.00
2.00
2.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

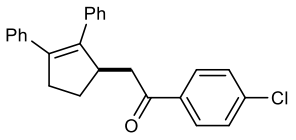

190.13
144.06
141.58
137.43
135.90
133.25
131.69
129.86
128.81
128.80
128.75
128.38
128.34
127.97
122.06
86.38
81.53
77.42
77.16
76.91
48.17
38.06
21.61
129.86
128.81
128.80
128.75
128.38
128.34
127.97
129.8 129.6 129.4 129.2 129.0 128.8 128.6 128.4 128.2 128.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
F
O

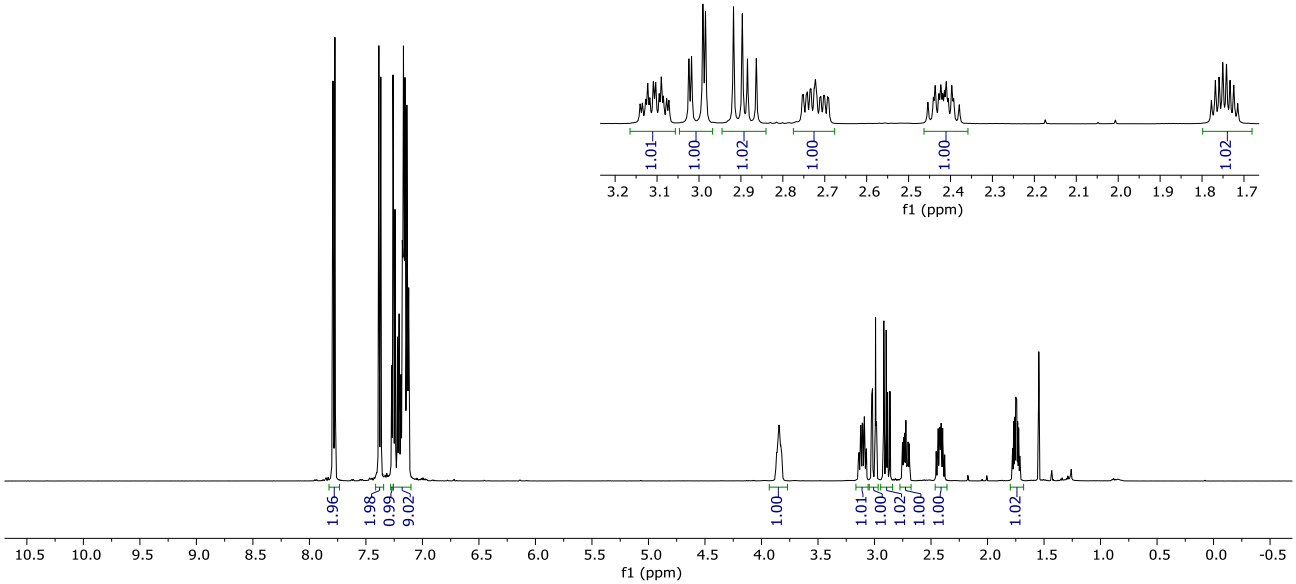
2a

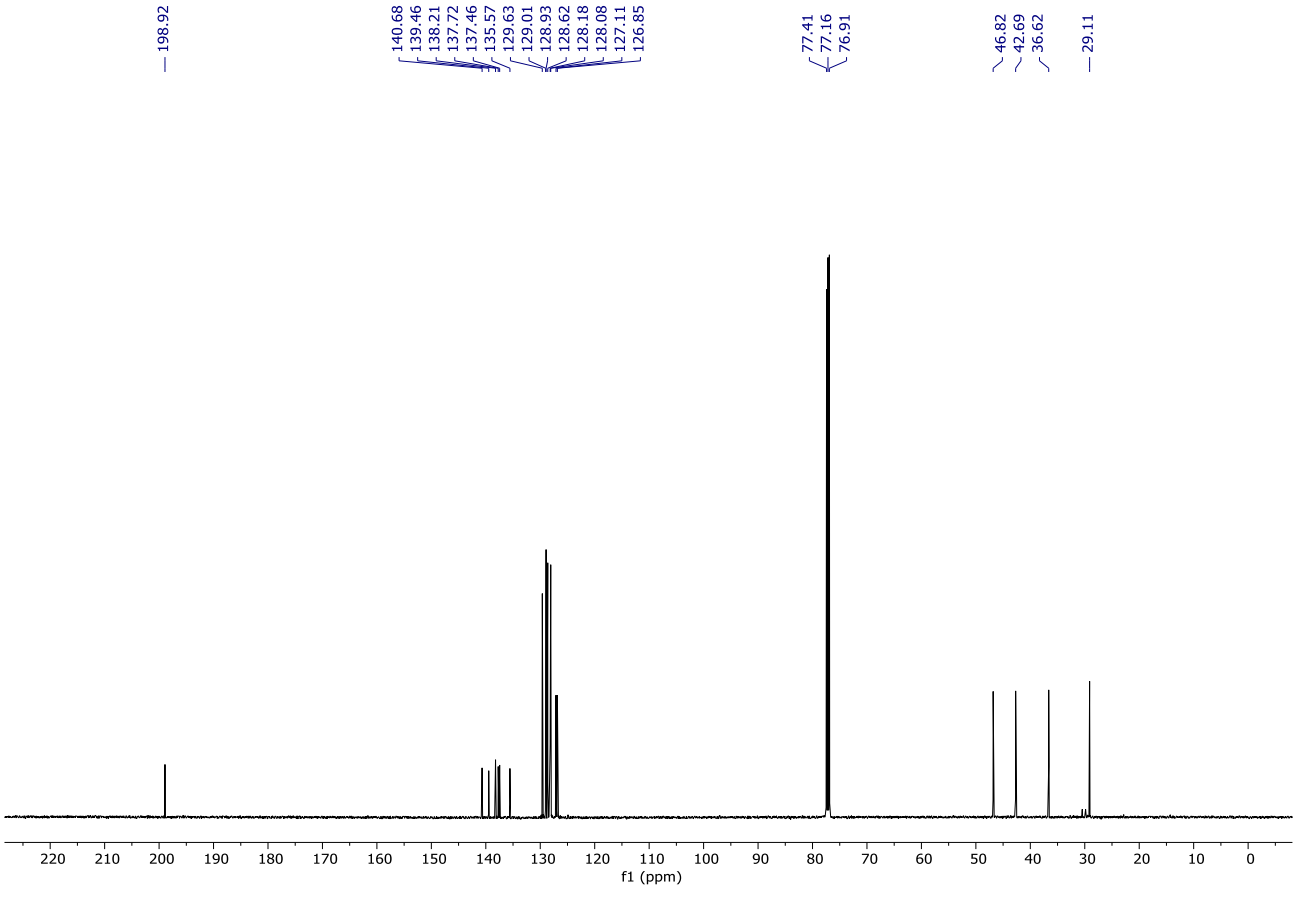

1.01
1.00
1.02
1.02
1.01
1.02
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
1.96
9.95
1.97
1.01
1.01
1.00
1.02
1.02
1.01
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

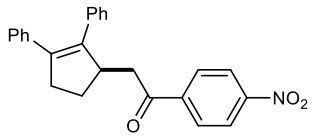

198.52
167.02
164.49
140.75
138.17
137.75
137.49
133.72
133.69
130.85
130.76
129.01
128.61
128.17
128.07
127.08
126.84
115.79
115.57
77.48
77.16
76.84
46.84
42.63
36.62
29.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Cl
O

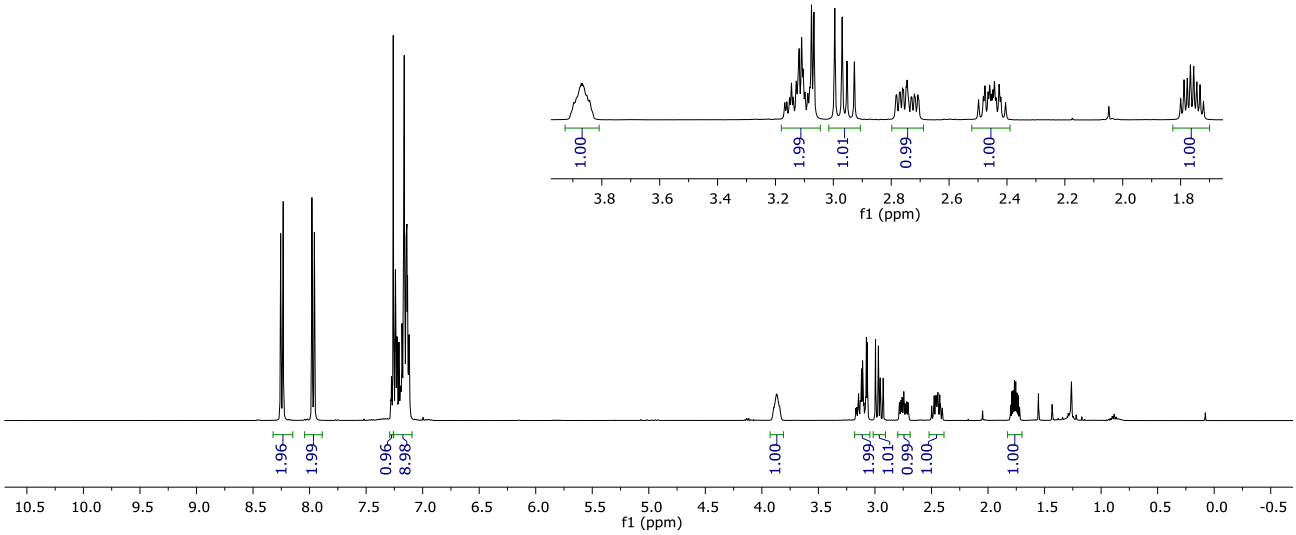
2b

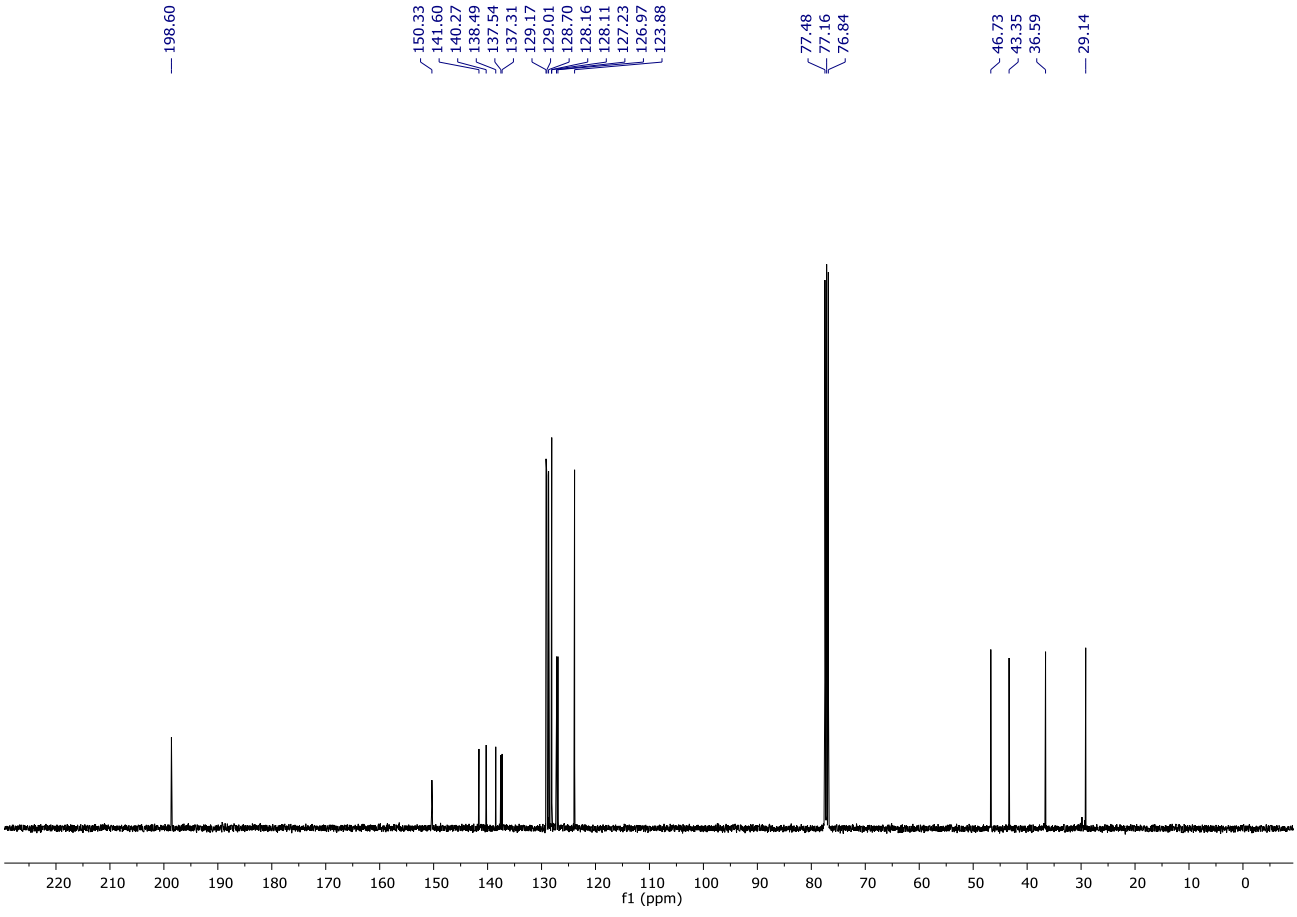

1.01
1.00
1.02
1.00
1.00
1.02
f1 (ppm)
1.96
1.98
0.99
9.02
1.00
1.01
1.00
1.02
1.00
1.00
1.02
f1 (ppm)

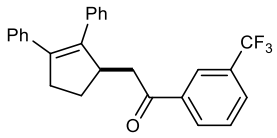

198.92
140.68
139.46
138.21
137.72
137.46
135.57
129.63
129.01
128.93
128.62
128.18
128.08
127.11
126.85
77.41
77.16
76.91
46.82
42.69
36.62
29.11
f1 (ppm)


Ph
Ph
NO2
O

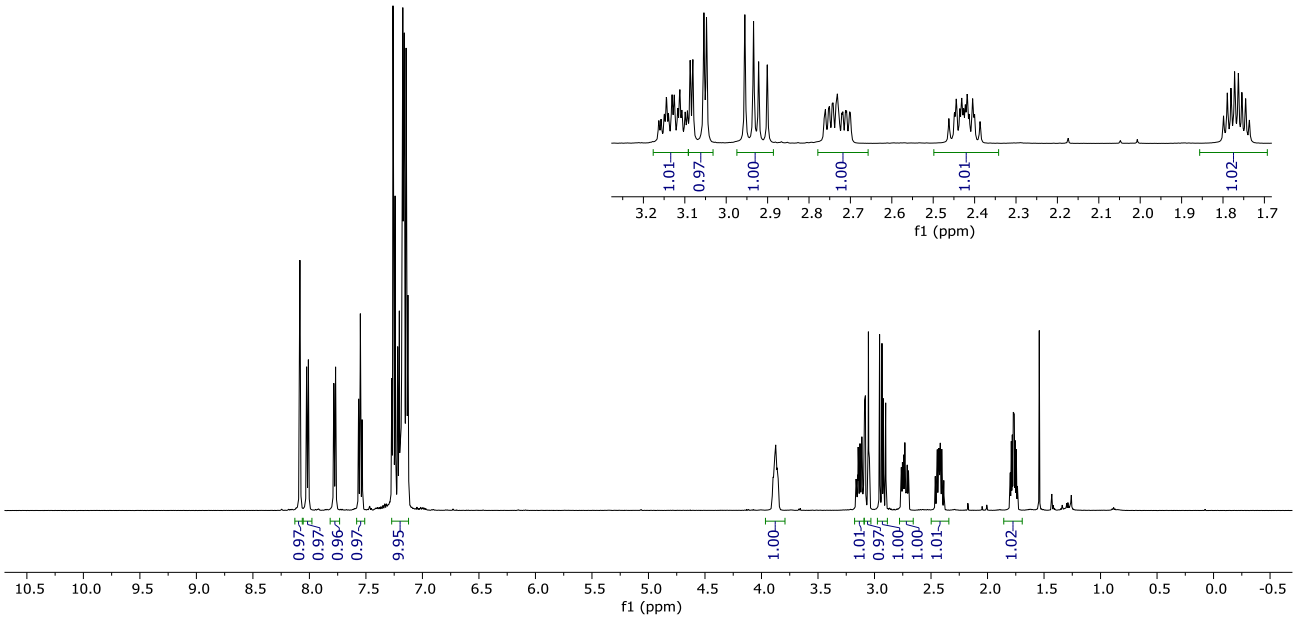
2c

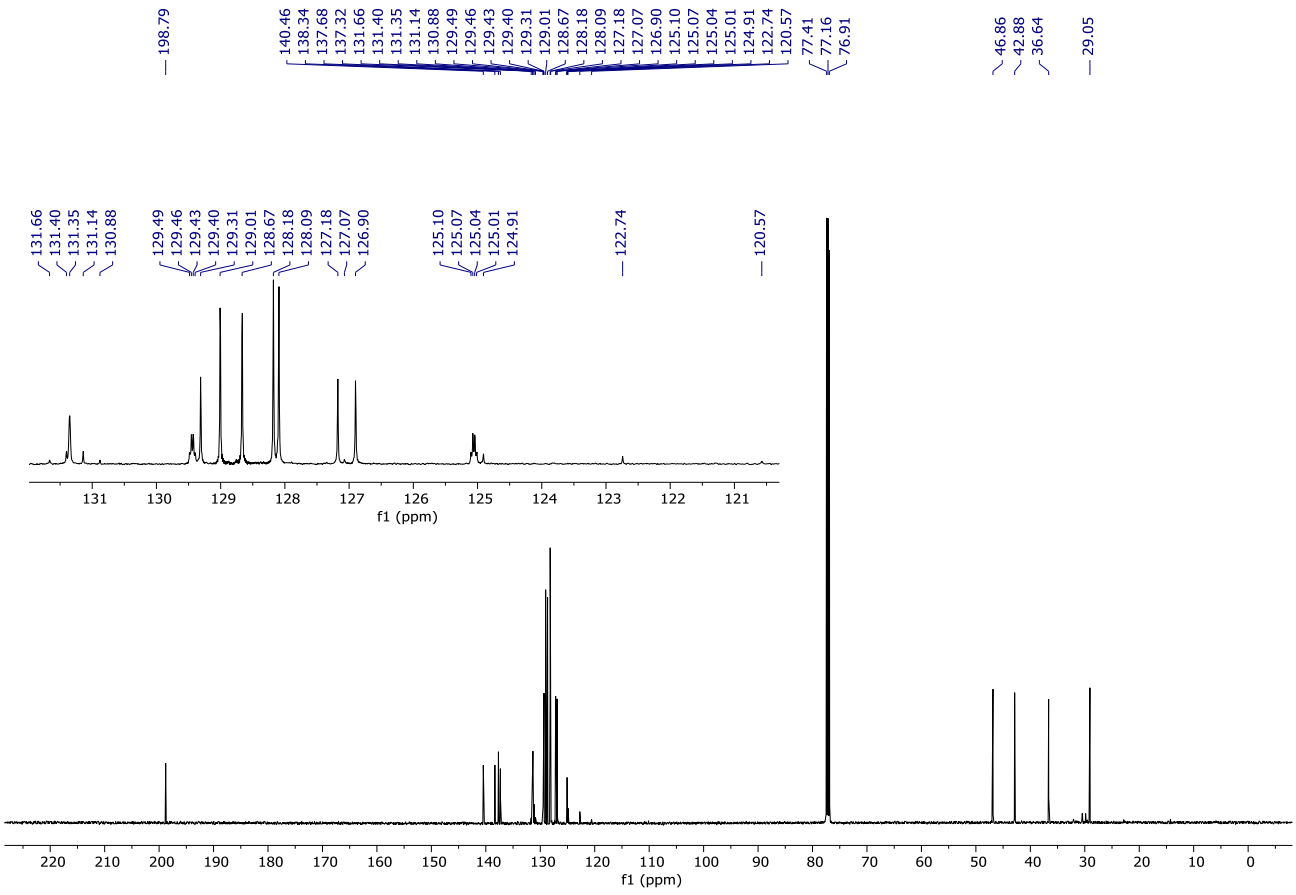

1.00
1.99
1.01
0.99
1.00
1.00
f1 (ppm)
1.96
1.99
0.96
8.98
1.00
1.99
1.01
0.99
1.00
1.00
f1 (ppm)

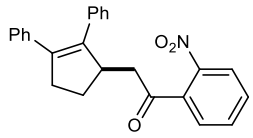

198.60
150.33
141.60
140.27
138.49
137.54
137.31
129.17
129.01
128.70
128.16
128.11
127.23
126.97
123.88
77.48
77.16
76.84
46.73
43.35
36.59
29.14
f1 (ppm)


Ph
Ph
CF3
O

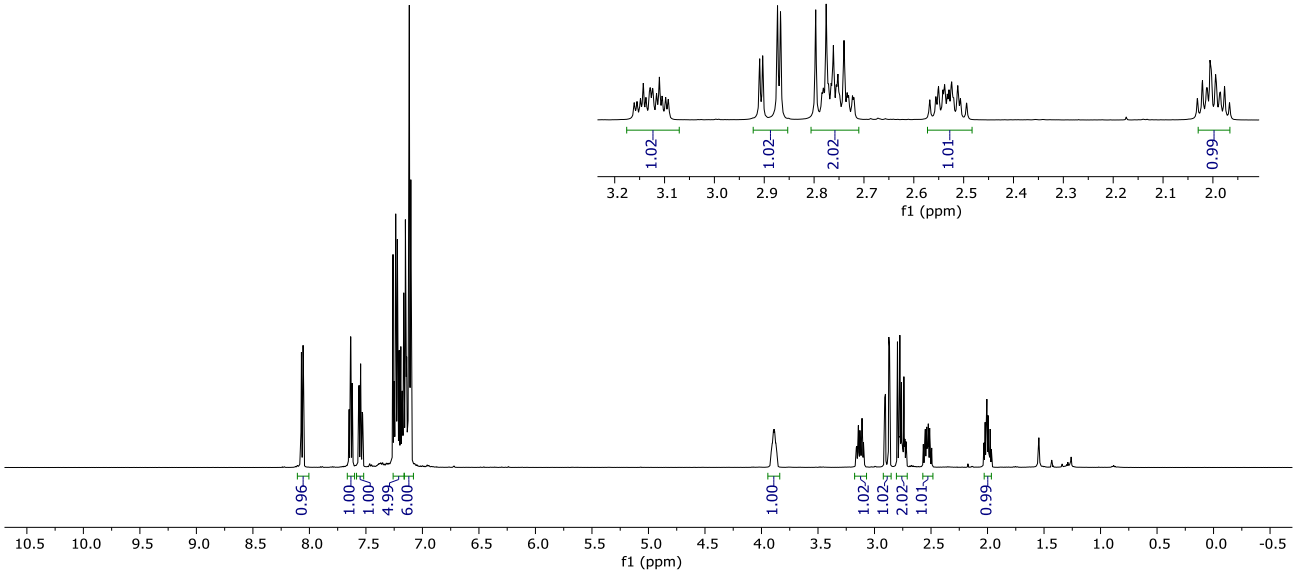
2d

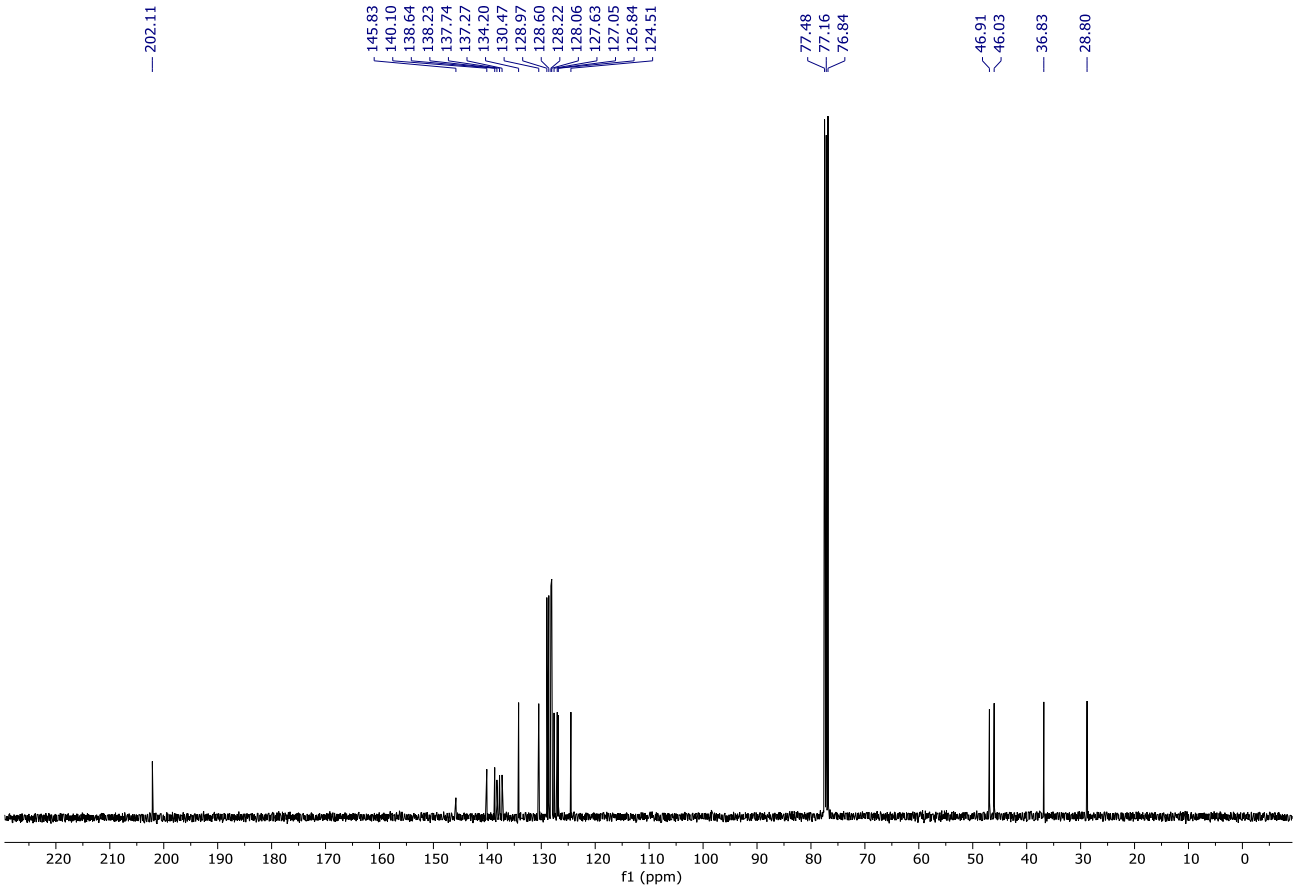

0.97
0.97
0.96
0.97
9.95
1.00
1.01
0.97
1.00
1.01
1.02
f1 (ppm)
1.01
0.97
1.00
1.00
1.01
1.02
f1 (ppm)

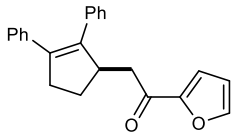

198.79
140.46
138.34
137.68
137.32
131.66
131.40
131.35
131.14
130.88
129.49
129.46
129.43
129.40
129.31
129.01
128.67
128.18
128.09
127.18
127.07
126.90
125.10
125.07
125.04
125.01
124.91
122.74
120.57
77.41
77.16
76.91
46.86
42.88
36.64
29.05
f1 (ppm)
f1 (ppm)


Ph
Ph
O_2N
O

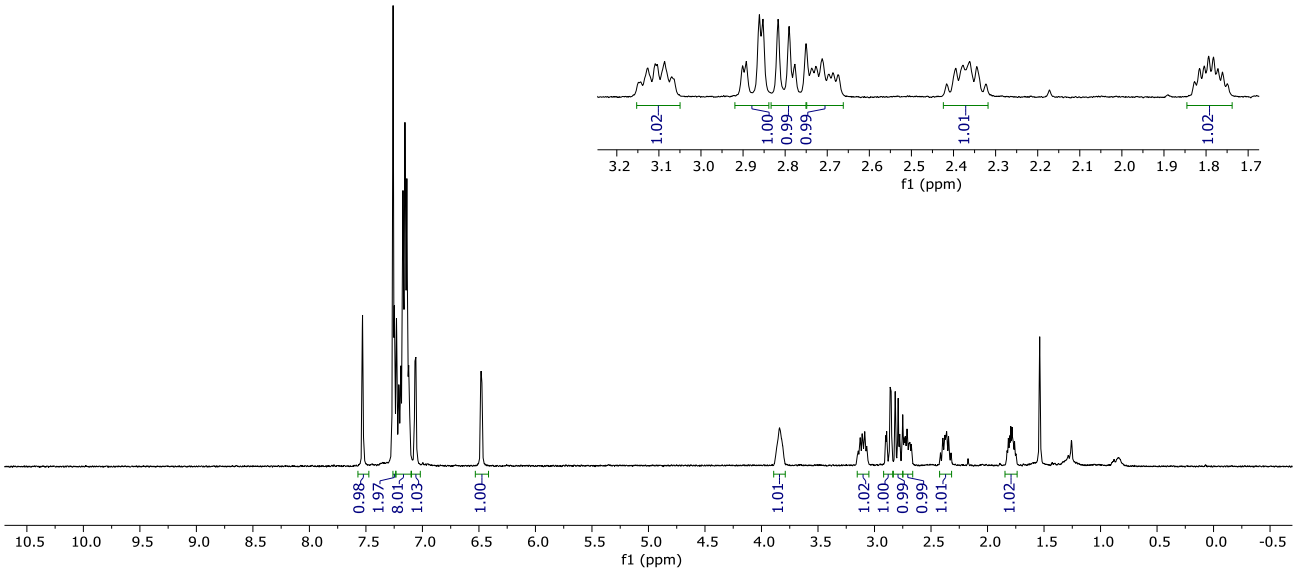
2e

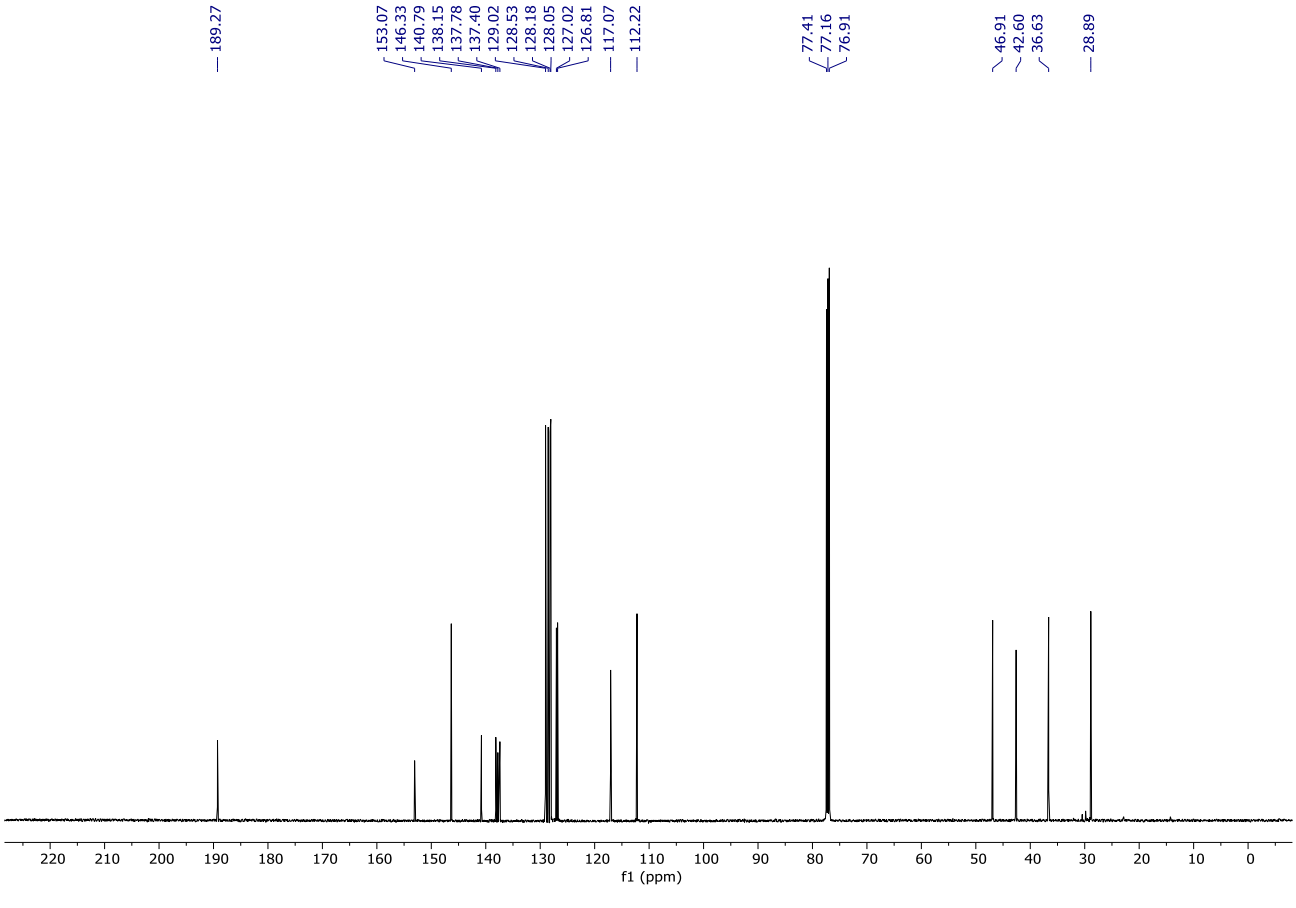

0.96
1.00
1.00
4.99
6.00
1.00
1.02
1.02
2.02
1.01
0.99
f1 (ppm)
1.02
1.02
2.02
1.01
0.99
f1 (ppm)

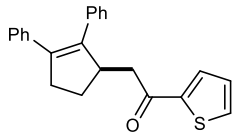

202.11
145.83
140.10
138.64
138.23
137.74
137.27
134.20
130.47
128.97
128.60
128.22
128.06
127.63
127.05
126.84
124.51
77.48
77.16
76.84
46.91
46.03
36.83
28.80
f1 (ppm)


Ph
Ph
O
O

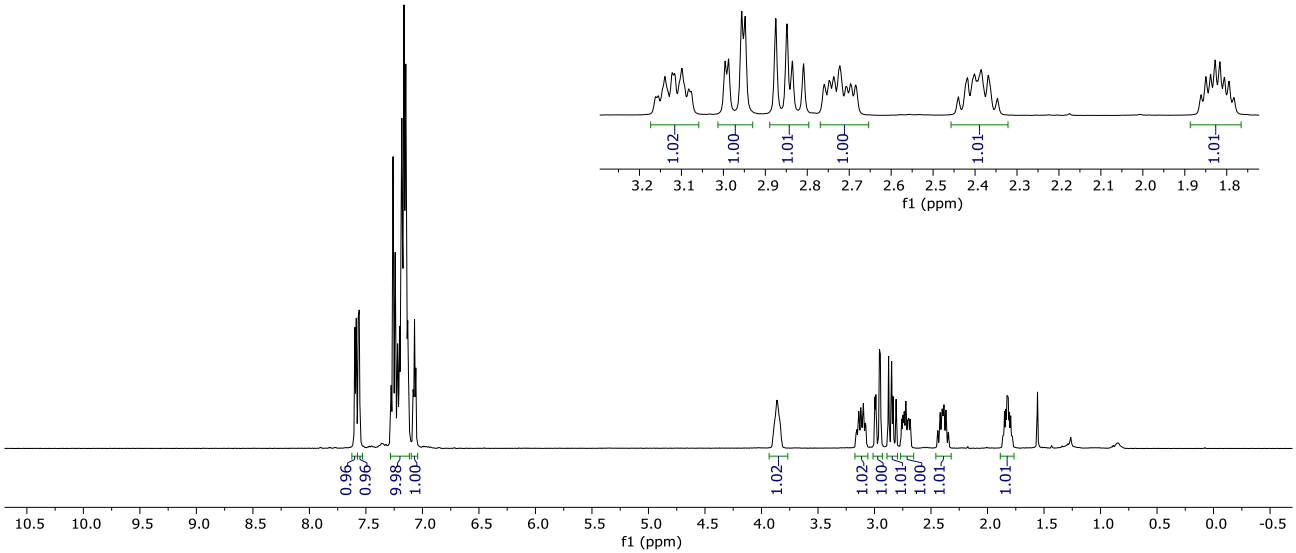
2f

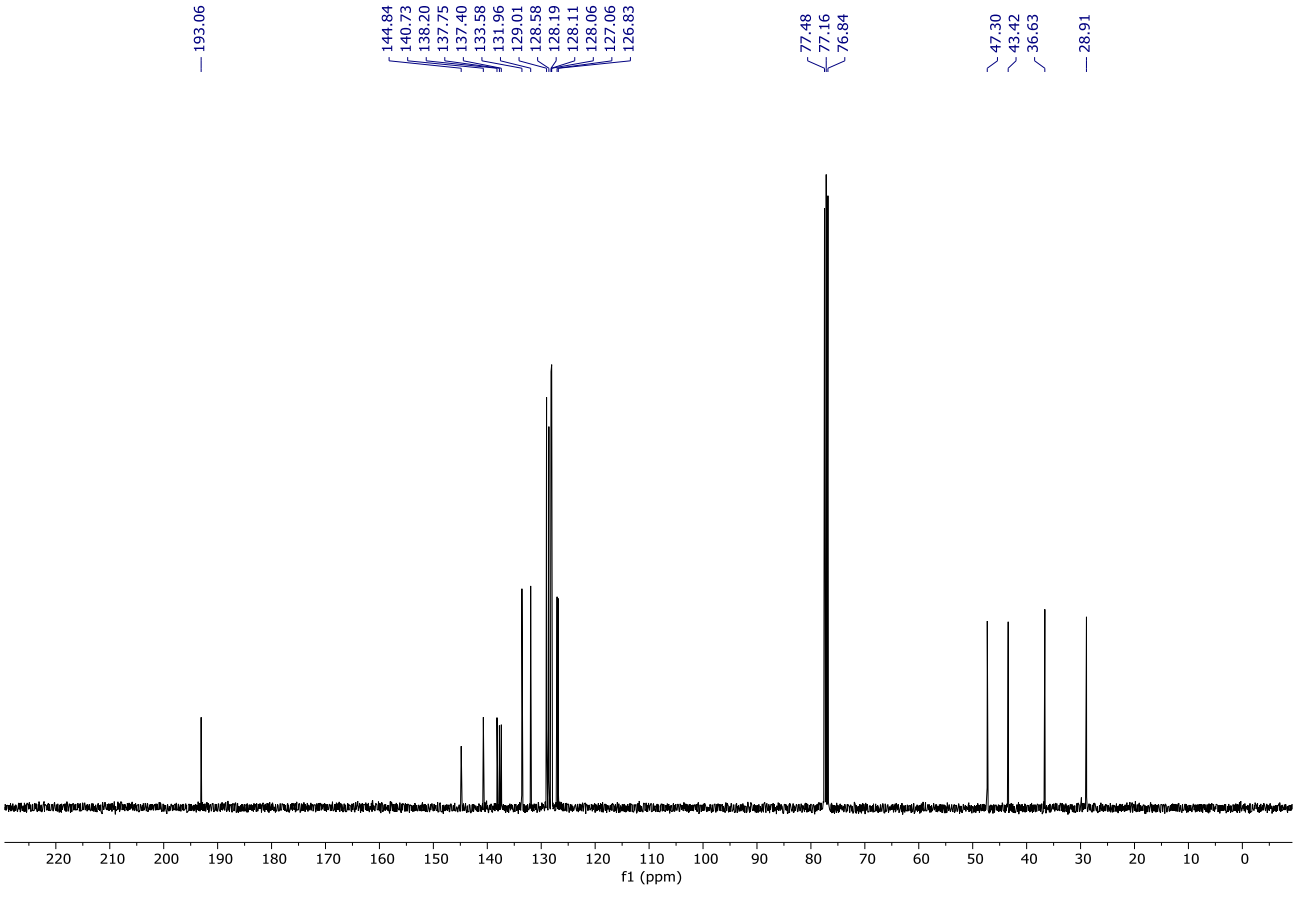

0.98
1.97
8.01
1.03
1.00
1.01
1.02
1.00
0.99
0.99
1.01
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
1.02
1.00
0.99
0.99
1.01
1.02
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)

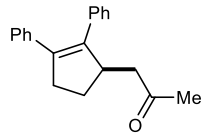

189.27
153.07
146.33
140.79
138.15
137.78
137.40
129.02
128.53
128.18
128.05
127.02
126.81
117.07
112.22
77.41
77.16
76.91
46.91
42.60
36.63
28.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
O
S

2g

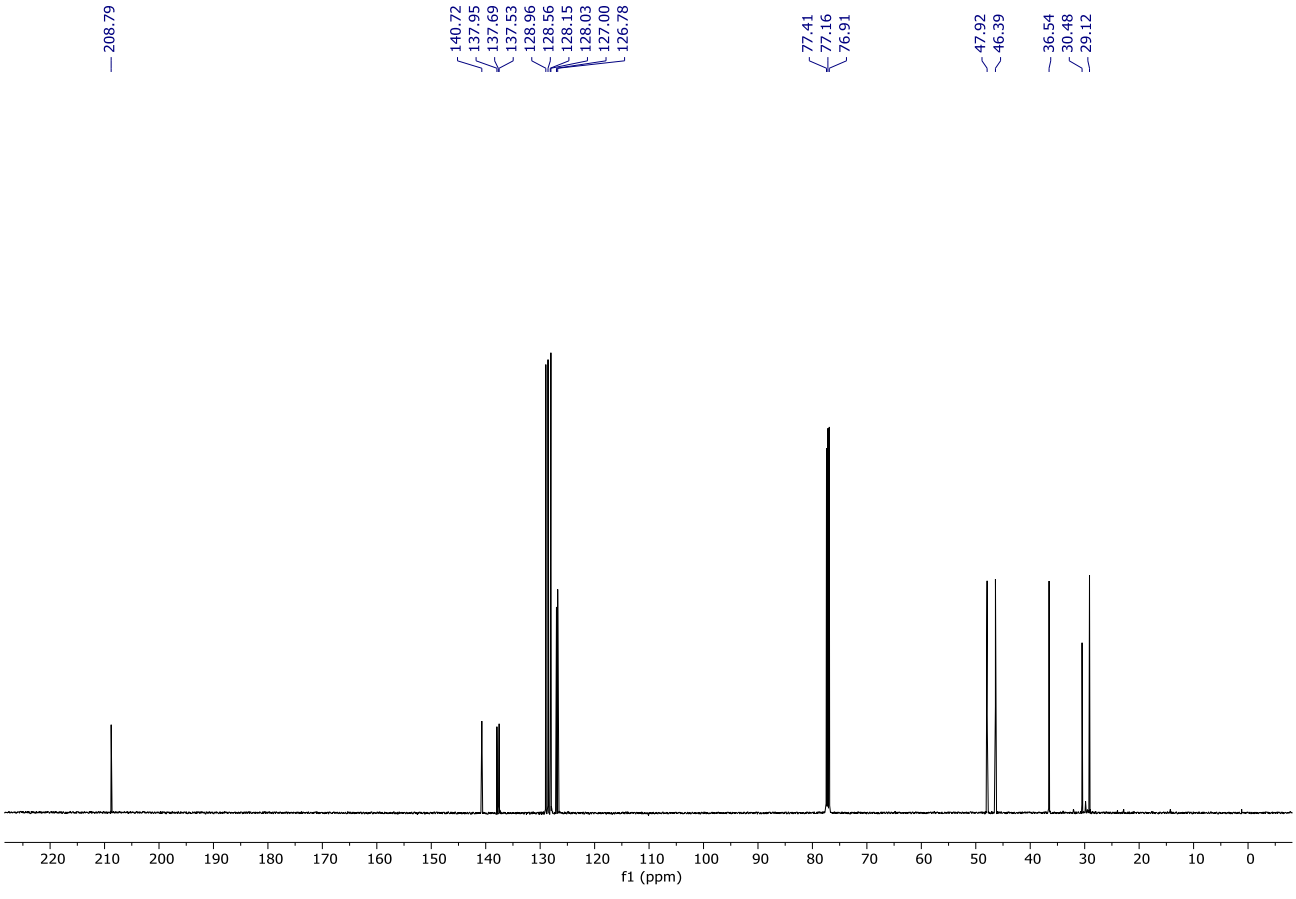

0.96
0.96
9.98
1.00
1.02
1.02
1.00
1.01
1.00
1.01
1.01
f1 (ppm)
1.02
1.00
1.01
1.00
1.01
1.01
f1 (ppm)

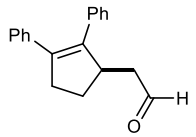

193.06
144.84
140.73
138.20
137.75
137.40
133.58
131.96
129.01
128.58
128.19
128.11
128.06
127.06
126.83
77.48
77.16
76.84
47.30
43.42
36.63
28.91
f1 (ppm)


Ph
Ph
Me
O

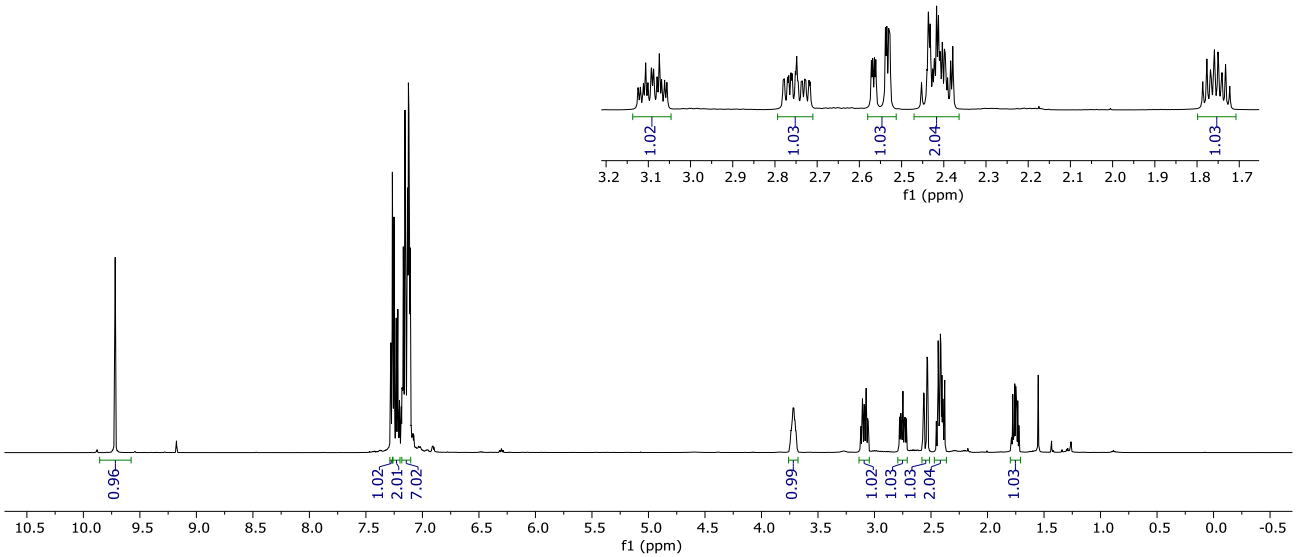
2h

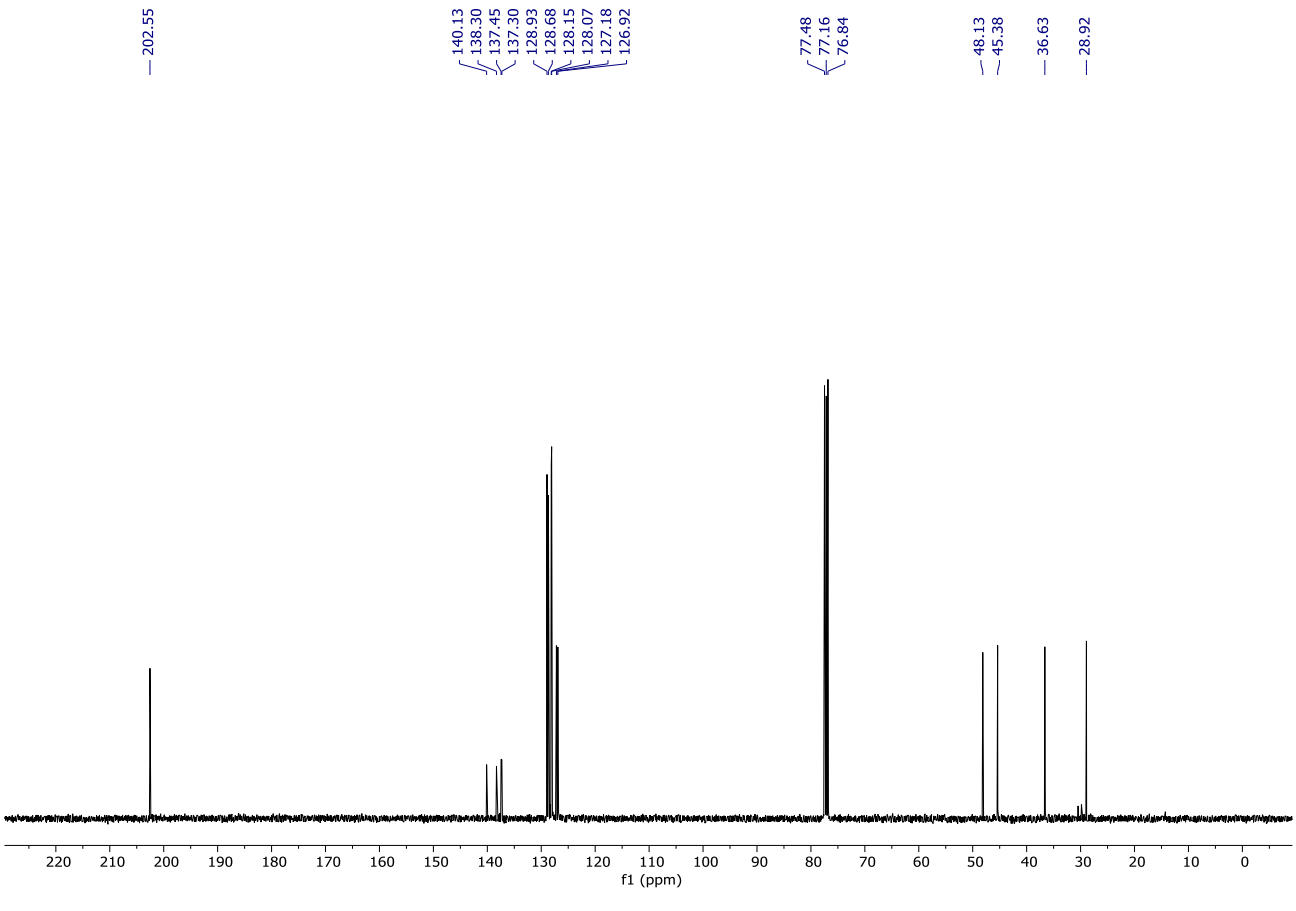
1.01
1.02
1.01
1.98
2.99
1.00
f1 (ppm)
3.02
7.01
1.00
1.01
1.02
1.01
1.98
2.99
1.00
f1 (ppm)

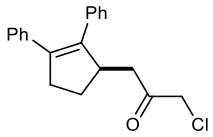

208.79
140.72
137.95
137.69
137.53
128.96
128.56
128.15
128.03
127.00
126.78
77.41
77.16
76.91
47.92
46.39
36.54
30.48
29.12
f1 (ppm)


Ph
Ph
H
O

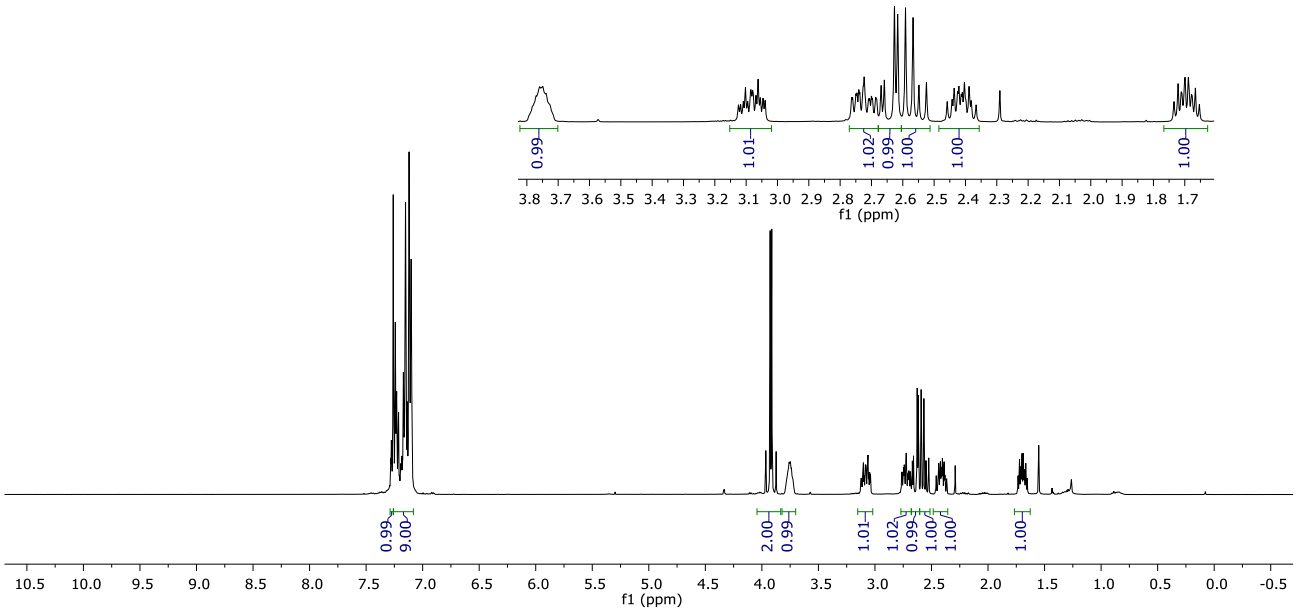
2i

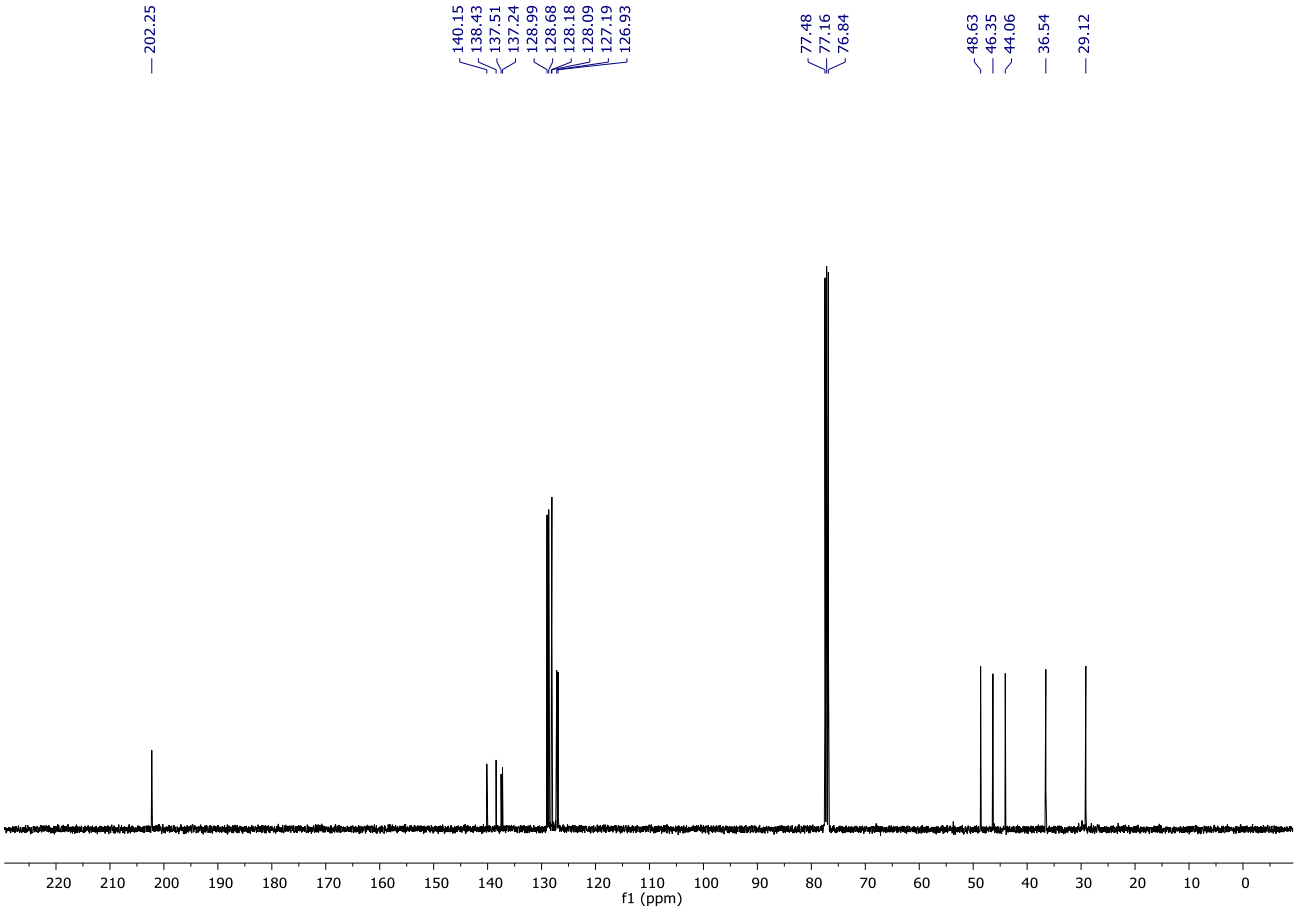

1.02
1.03
1.03
2.04
1.03
f1 (ppm)
0.96
1.02
2.01
7.02
0.99
1.02
1.03
1.03
2.04
1.03
f1 (ppm)

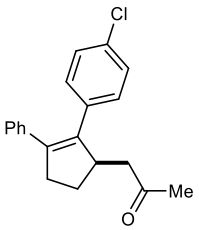

202.55
140.13
138.30
137.45
137.30
128.93
128.68
128.15
128.07
127.18
126.92
77.48
77.16
76.84
48.13
45.38
36.63
28.92
f1 (ppm)


Ph
Ph
O
Cl

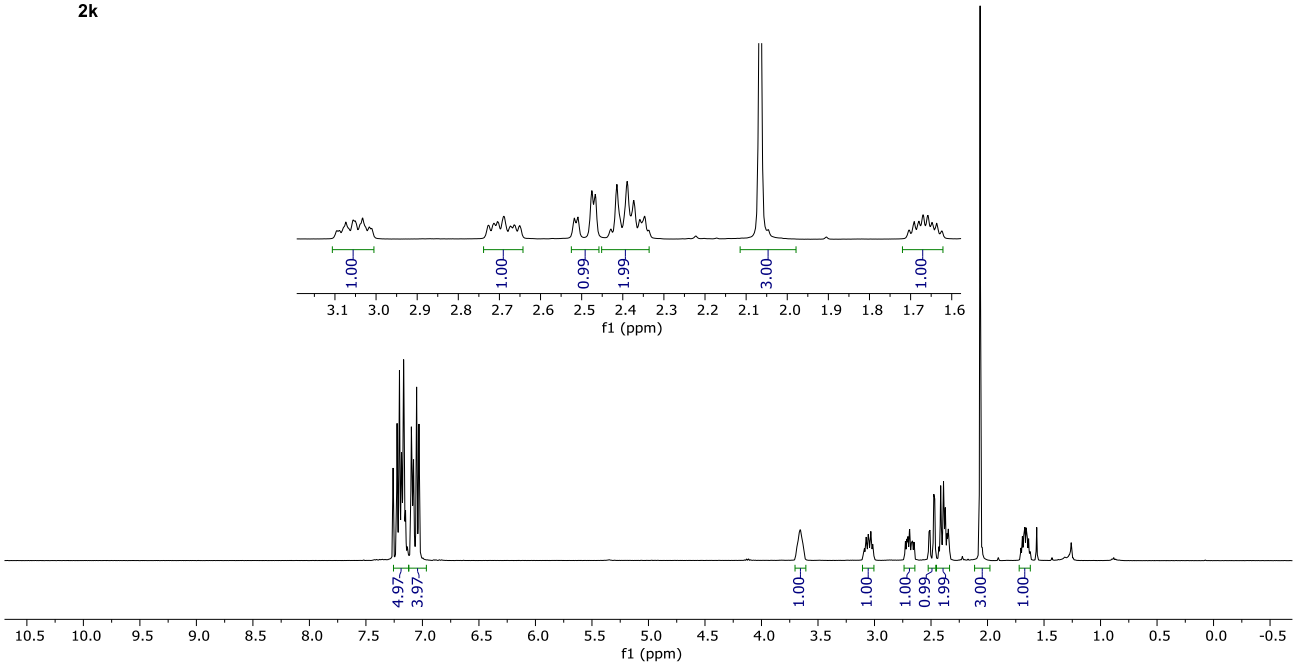
2j

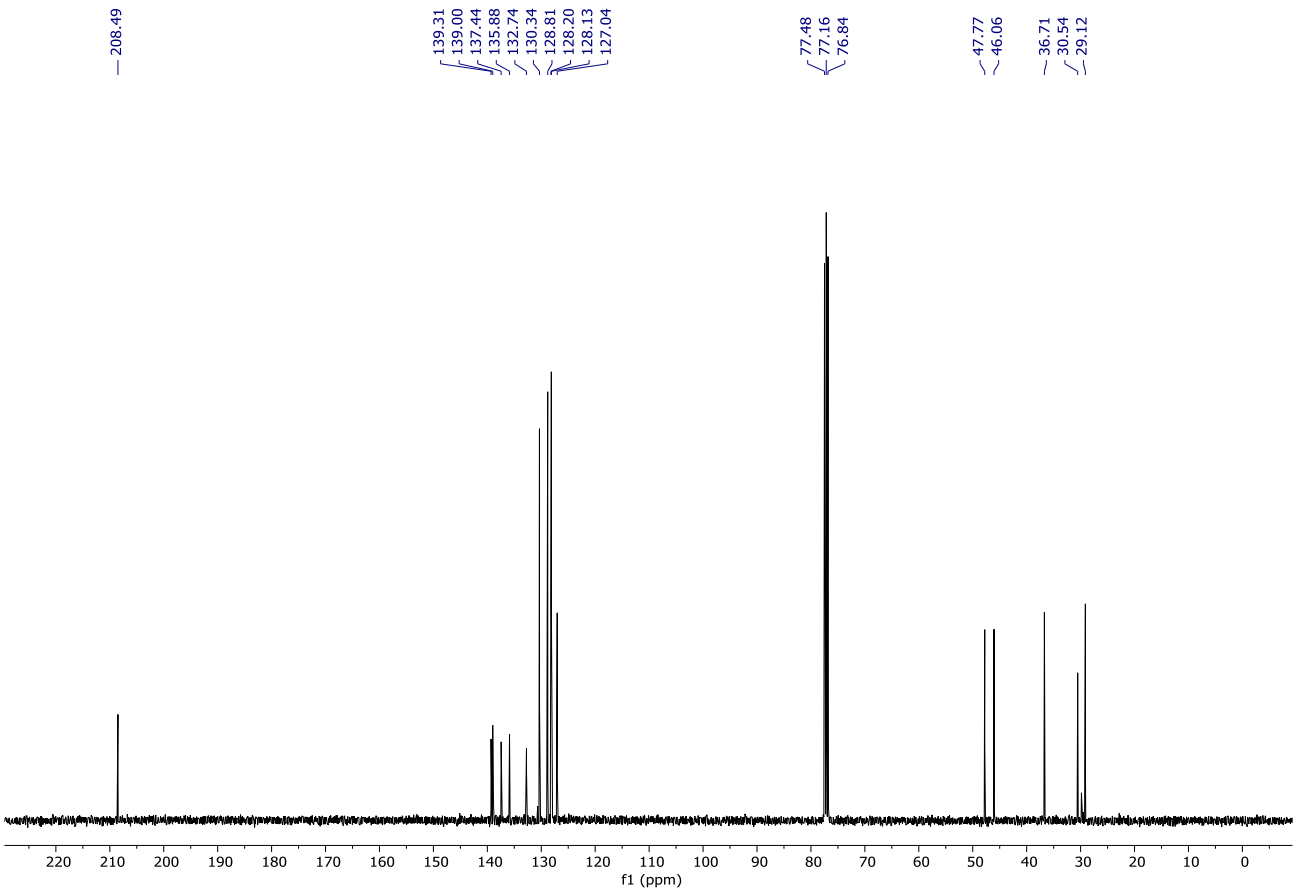

0.99
1.01
1.02
0.99
1.00
1.00
1.00
f1 (ppm)
0.99
9.00
2.00
0.99
1.01
1.02
0.99
1.00
1.00
1.00
f1 (ppm)

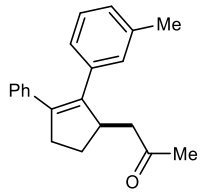

202.25
140.15
138.43
137.51
137.24
128.99
128.68
128.18
128.09
127.19
126.93
77.48
77.16
76.84
48.63
46.35
44.06
36.54
29.12
f1 (ppm)


Cl
Ph
Me
O

2k

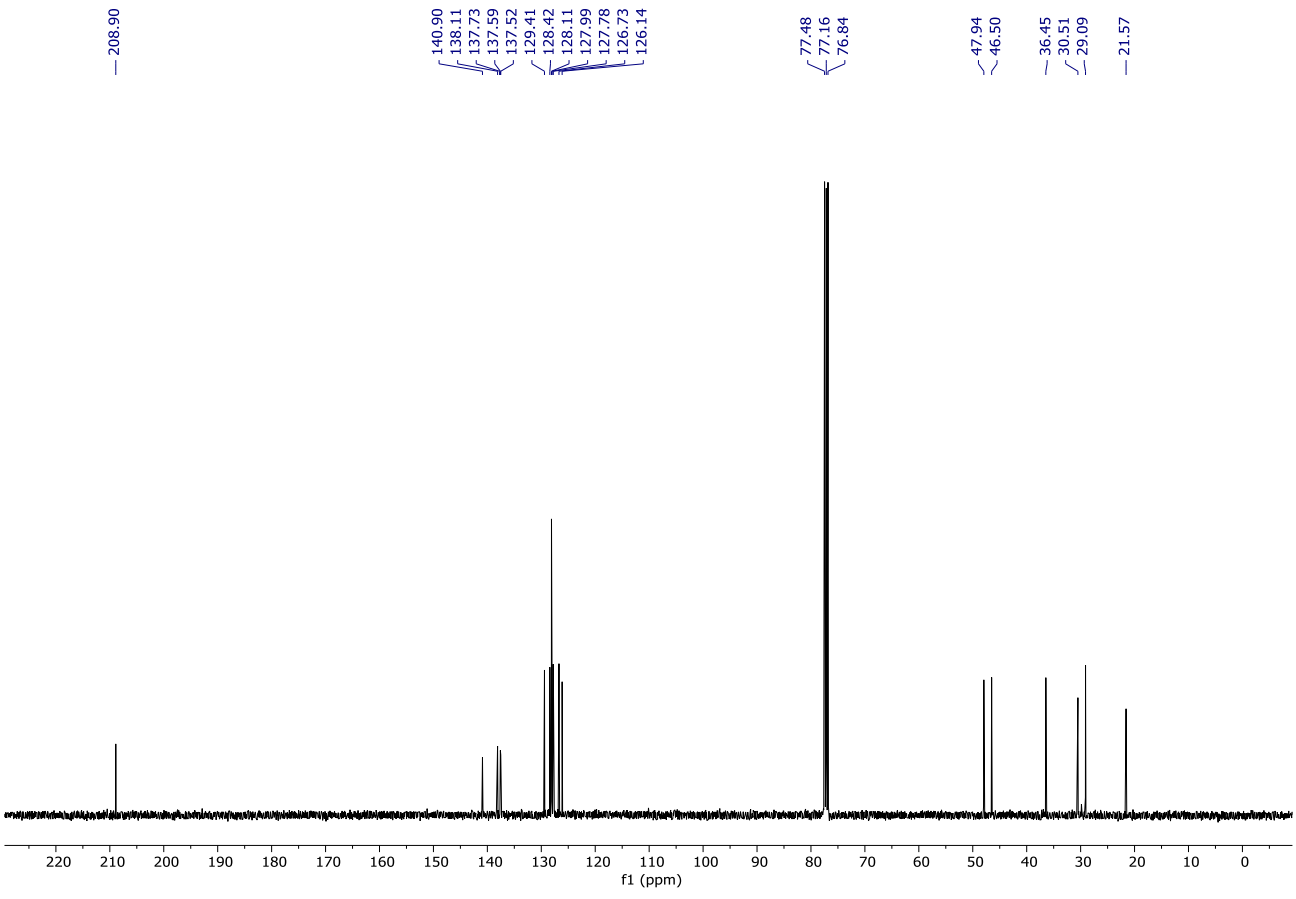

1.00
1.00
0.99
1.99
3.00
1.00
f1 (ppm)
4.97
3.97
1.00
1.00
1.00
0.99
1.99
3.00
1.00
f1 (ppm)

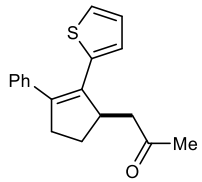

208.49
139.31
139.00
137.44
135.88
132.74
130.34
128.81
128.20
128.13
127.04
77.48
77.16
76.84
47.77
46.06
36.71
30.54
29.12
f1 (ppm)


Me
Ph
Me
O

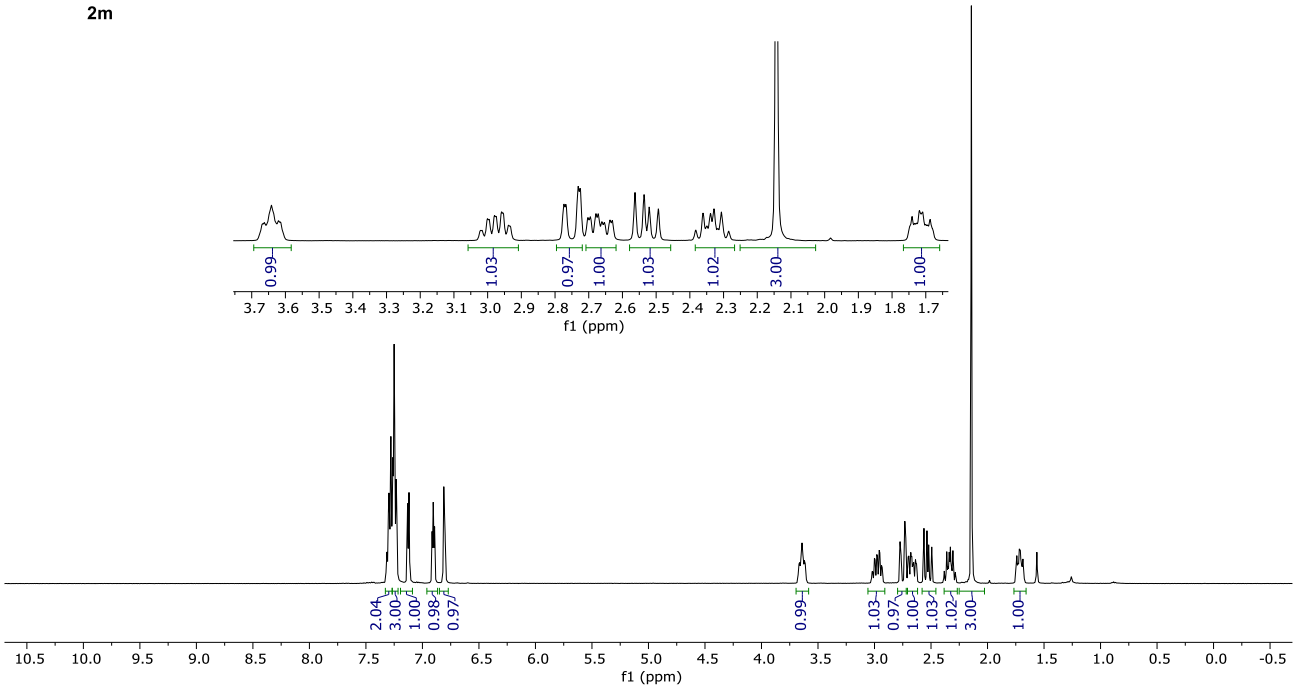
2l

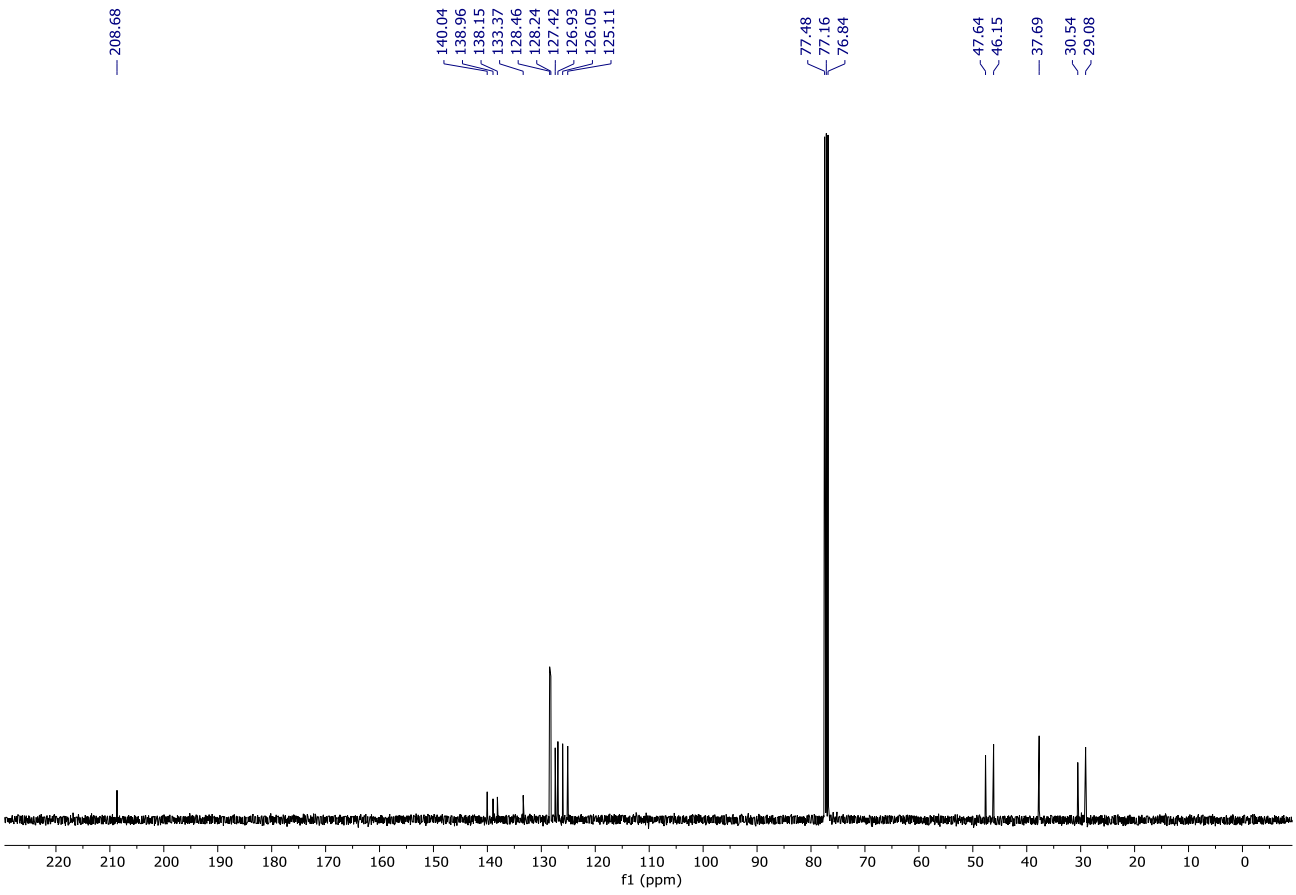
1.01
1.02
1.01
2.02
2.99
2.99
1.01
f1 (ppm)
6.00
0.98
0.99
0.99
1.01
1.01
1.02
1.01
2.02
2.99
2.99
1.01
f1 (ppm)

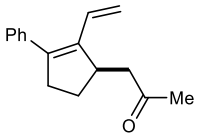

208.90
140.90
138.11
137.73
137.59
137.52
129.41
128.42
128.11
127.99
127.78
126.73
126.14
77.48
77.16
76.84
47.94
46.50
36.45
30.51
29.09
21.57
f1 (ppm)


S
Ph
Me
O

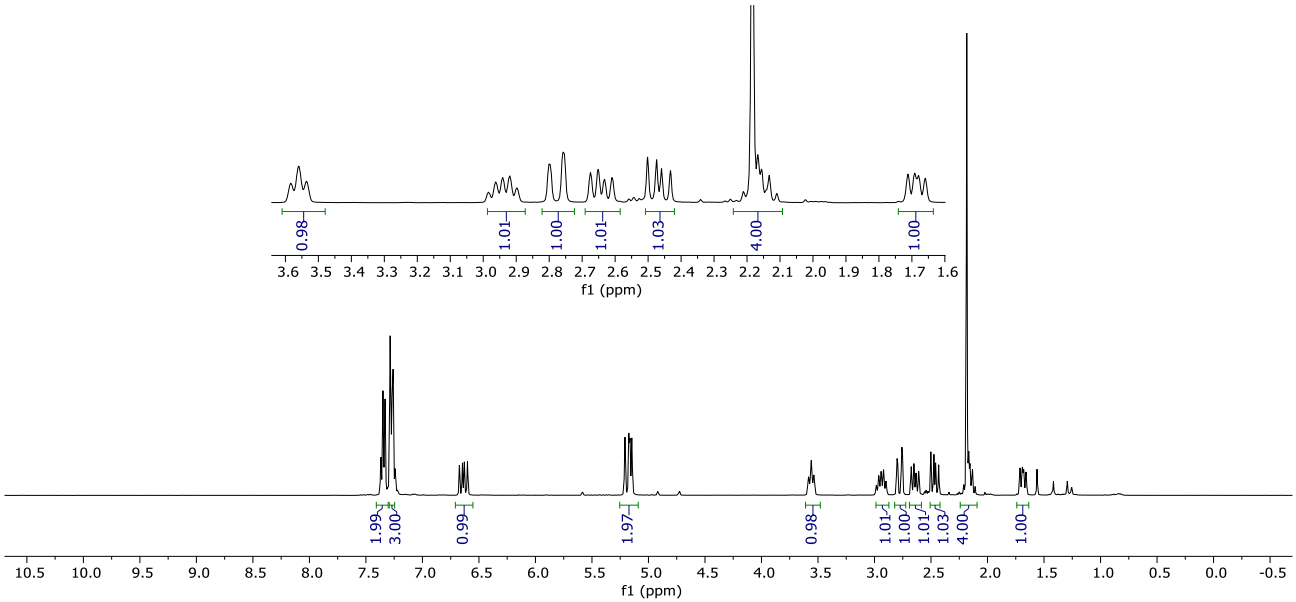
2m

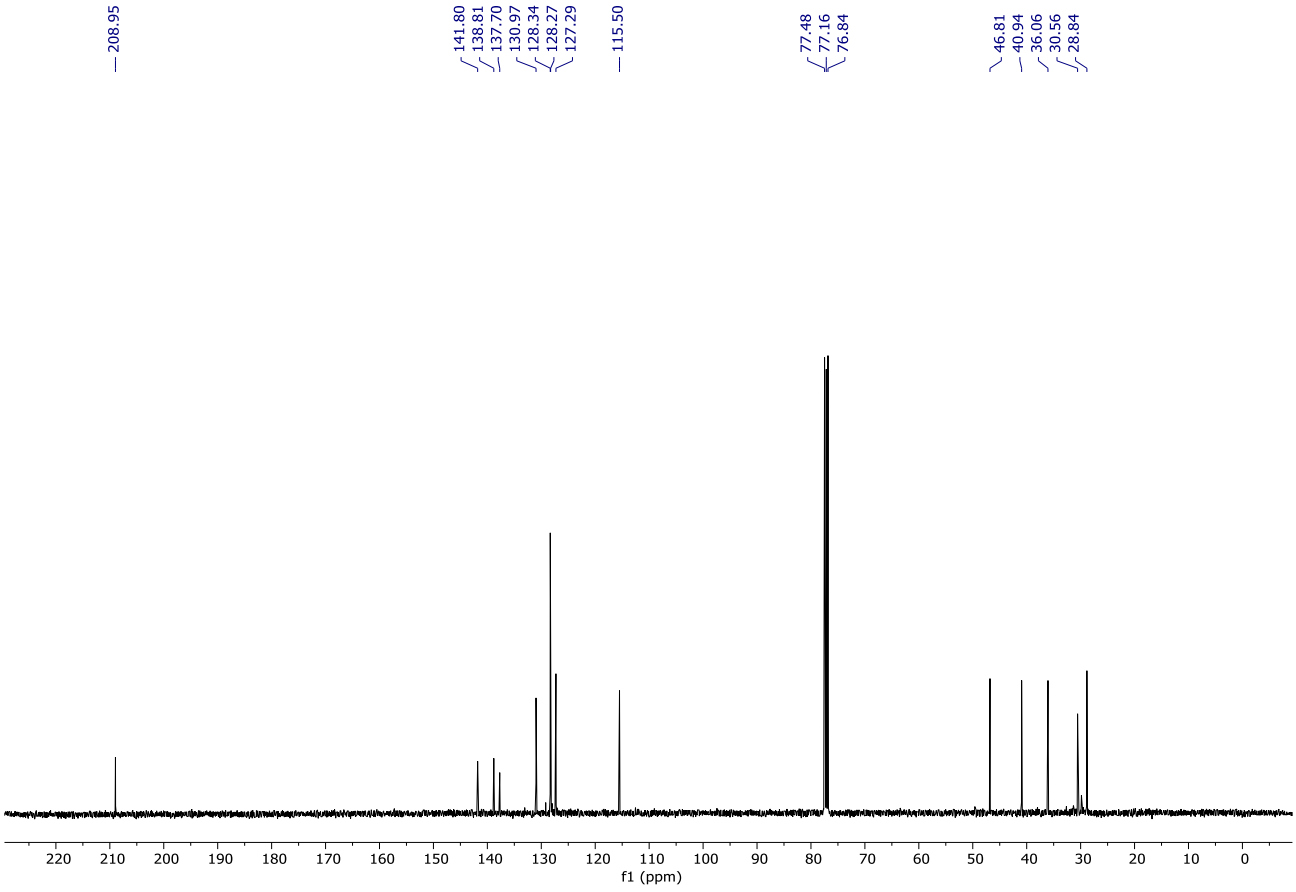

0.99
1.03
0.97
1.00
1.03
1.02
3.00
1.00
f1 (ppm)
2.04
3.00
1.00
0.98
0.97
0.99
1.03
0.97
1.00
1.03
1.02
3.00
1.00
f1 (ppm)

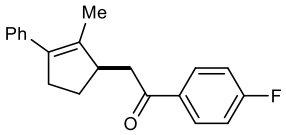

208.68
140.04
138.96
138.15
133.37
128.46
128.24
127.42
126.93
126.05
125.11
77.48
77.16
76.84
47.64
46.15
37.69
30.54
29.08
f1 (ppm)


Ph
Me
O

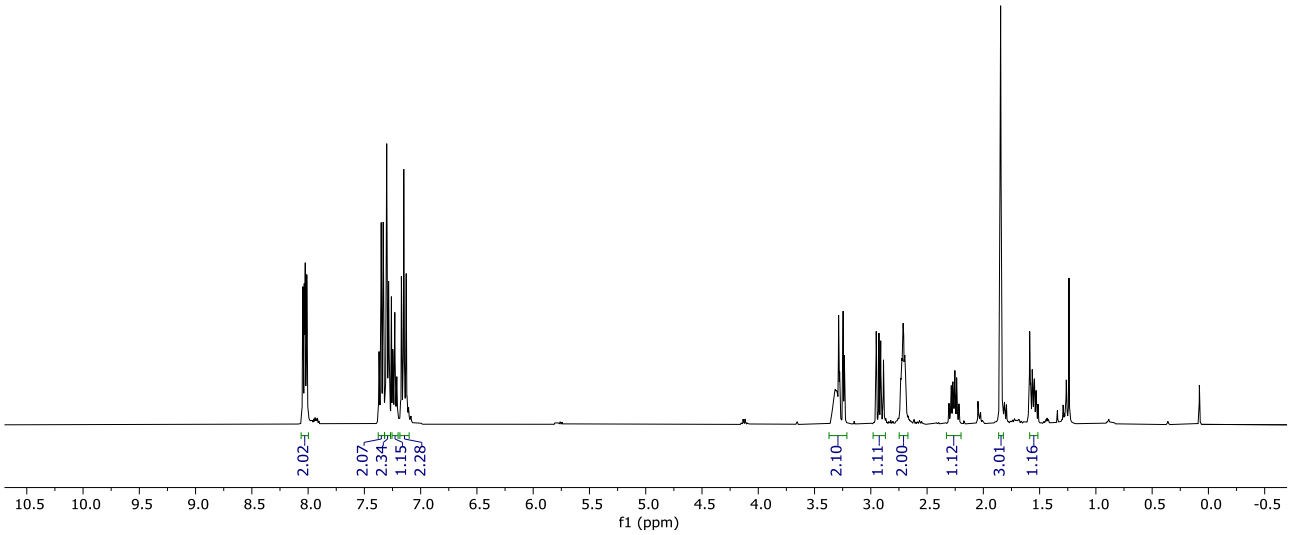
2n

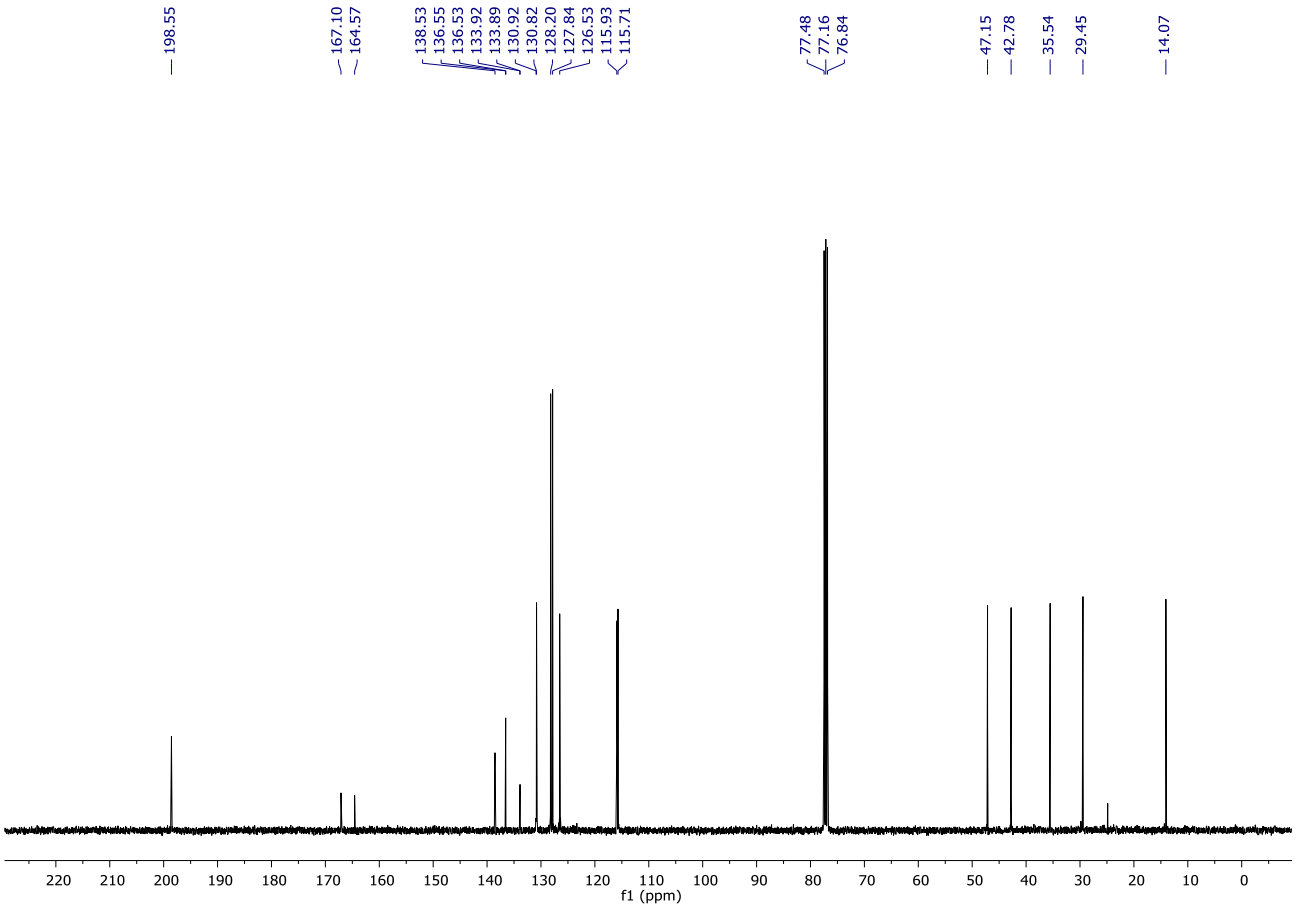

0.98
1.01
1.00
1.01
1.03
4.00
1.00
f1 (ppm)
1.99
3.00
0.99
1.97
0.98
1.01
1.00
1.01
1.03
4.00
1.00
f1 (ppm)

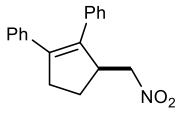

208.95
141.80
138.81
137.70
130.97
128.34
128.27
127.29
115.50
77.48
77.16
76.84
46.81
40.94
36.06
30.56
28.84
f1 (ppm)


Me
Ph
F
O

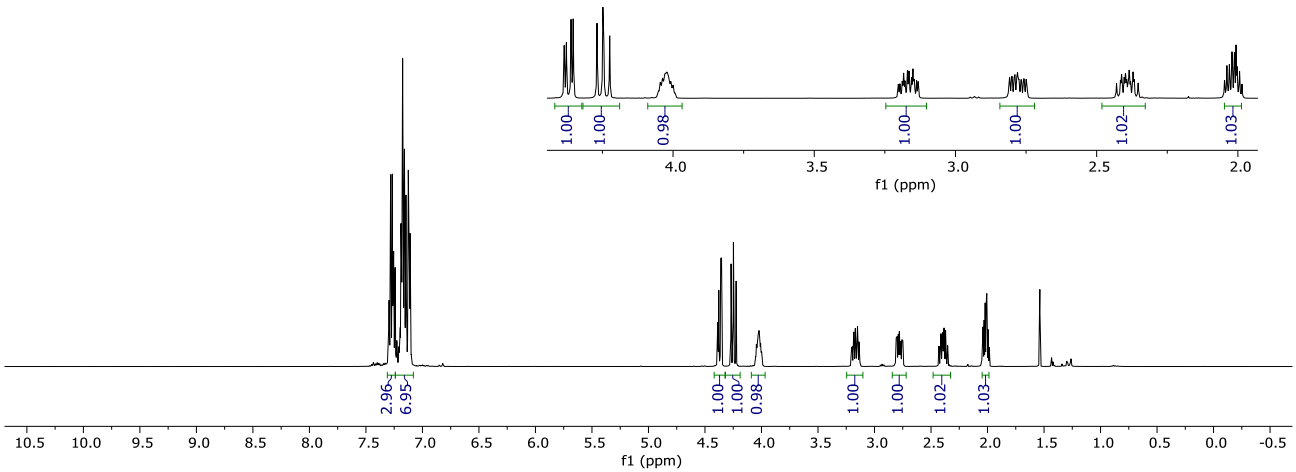
2o

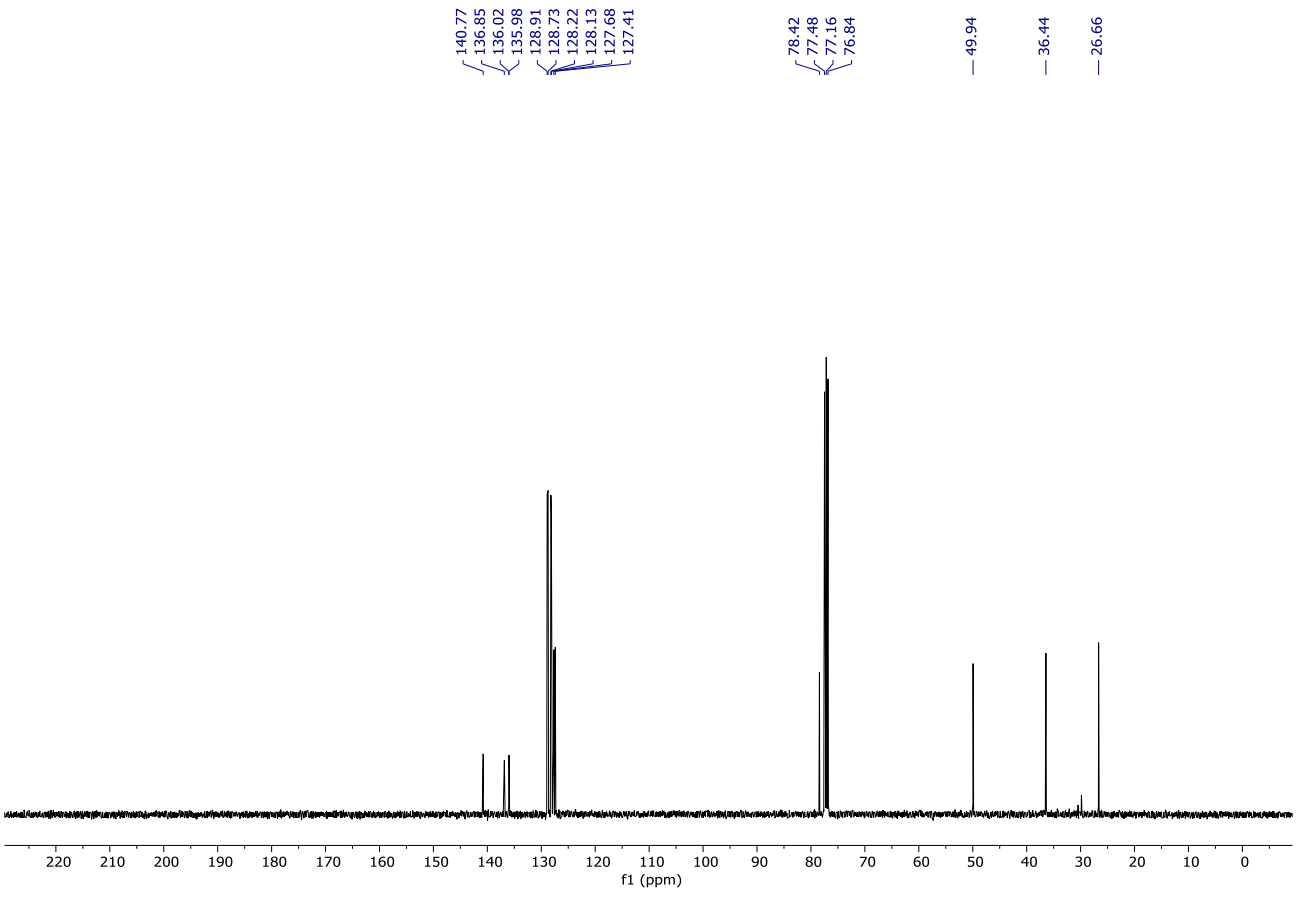

2.02
2.07
2.34
1.15
2.28
2.10
1.11
2.00
1.12
3.01
1.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

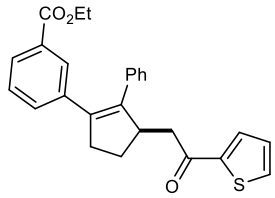

198.55
167.10
164.57
138.53
136.55
136.53
133.92
133.89
130.92
130.82
128.20
127.84
126.53
115.93
115.71
77.48
77.16
76.84
47.15
42.78
35.54
29.45
14.07
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
NO2

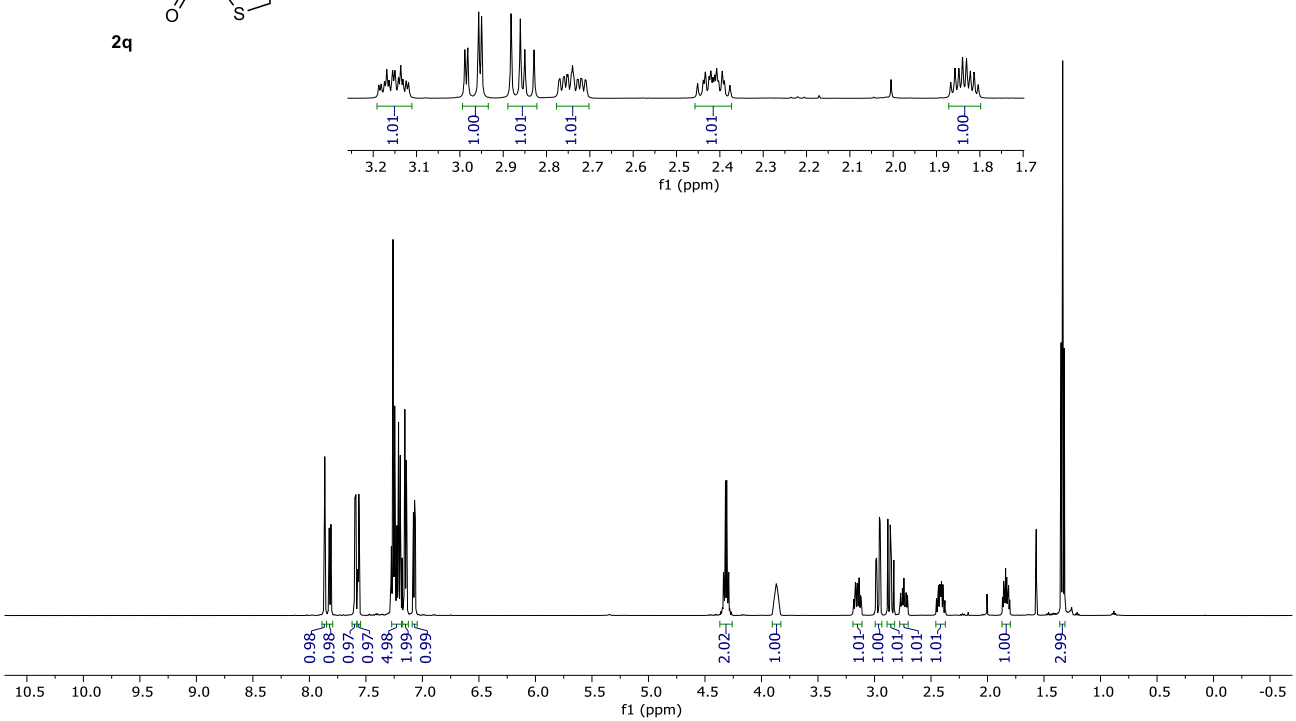
2p

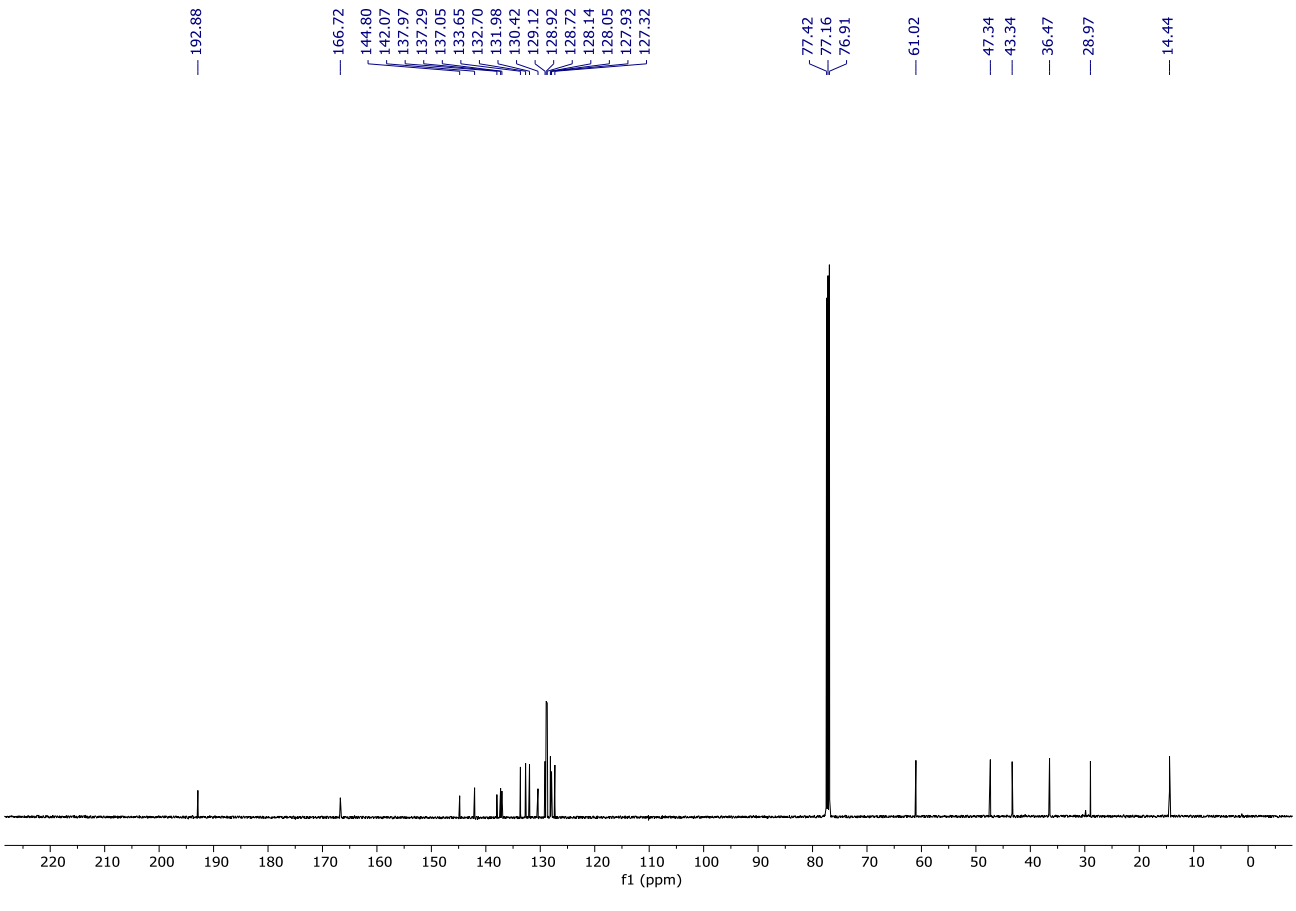

1.00
1.00
0.98
1.00
1.00
1.02
1.03
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
2.96
6.95
1.00
1.00
0.98
1.00
1.00
1.02
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

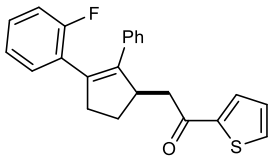

140.77
136.85
136.02
135.98
128.91
128.73
128.22
128.13
127.68
127.41
78.42
77.48
77.16
76.84
49.94
36.44
26.66
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2Et
Ph
O
S

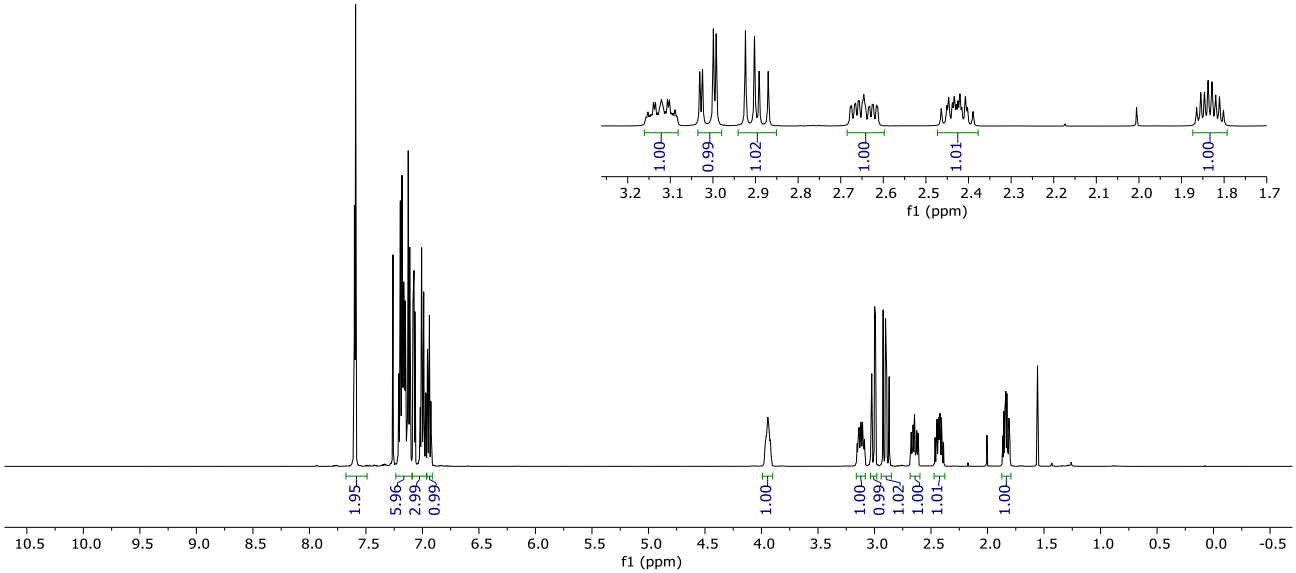
2q

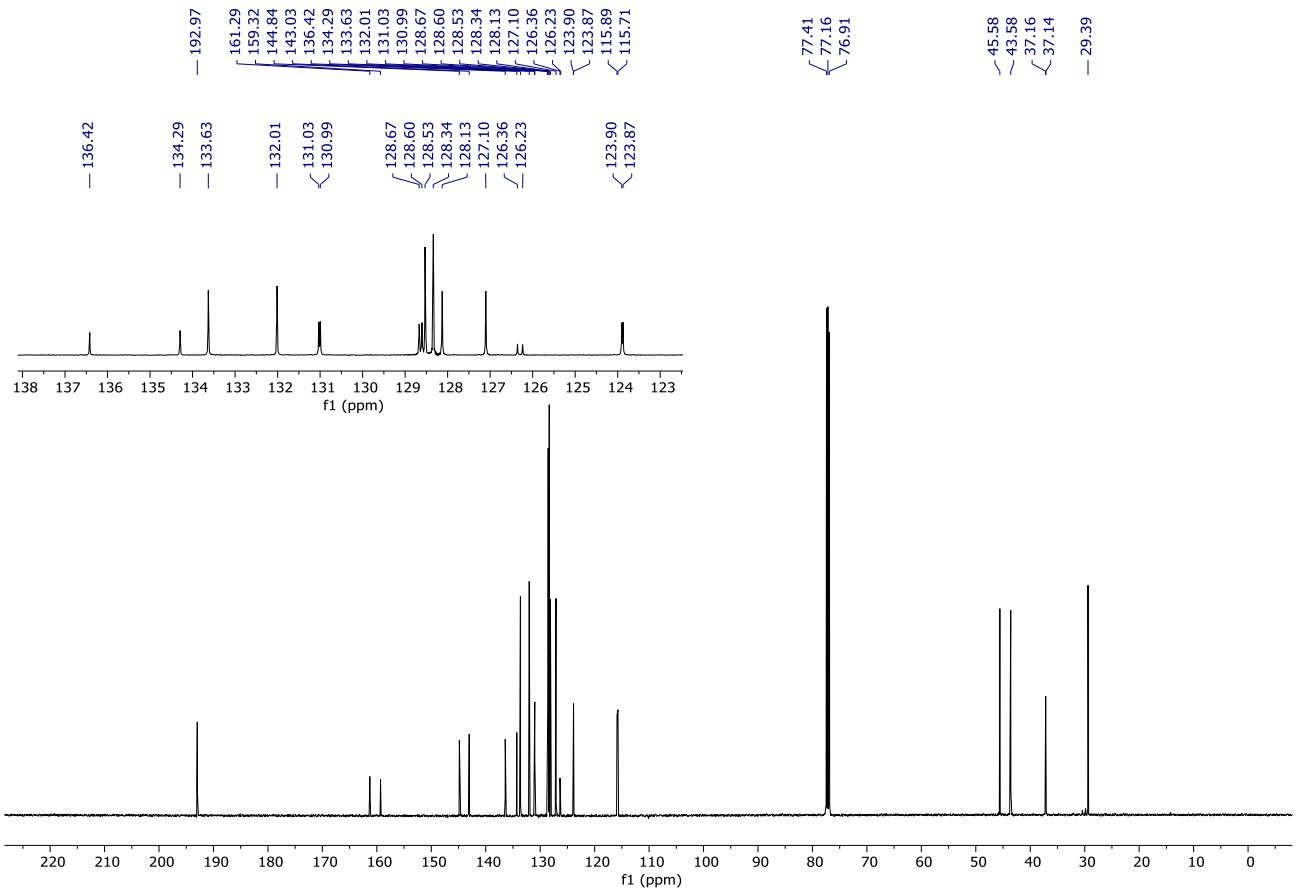

1.01
1.00
1.01
1.01
1.01
1.00
f1 (ppm)
0.98
0.98
0.97
0.97
4.98
1.99
0.99
2.02
1.00
1.01
1.00
1.01
1.01
1.01
1.00
2.99
f1 (ppm)

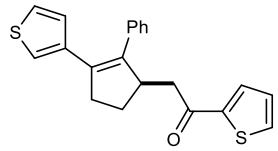

192.88
166.72
144.80
142.07
137.97
137.29
137.05
133.65
132.70
131.98
130.42
129.12
128.92
128.72
128.14
128.05
127.93
127.32
77.42
77.16
76.91
61.02
47.34
43.34
36.47
28.97
14.44
f1 (ppm)


F
Ph
O
S

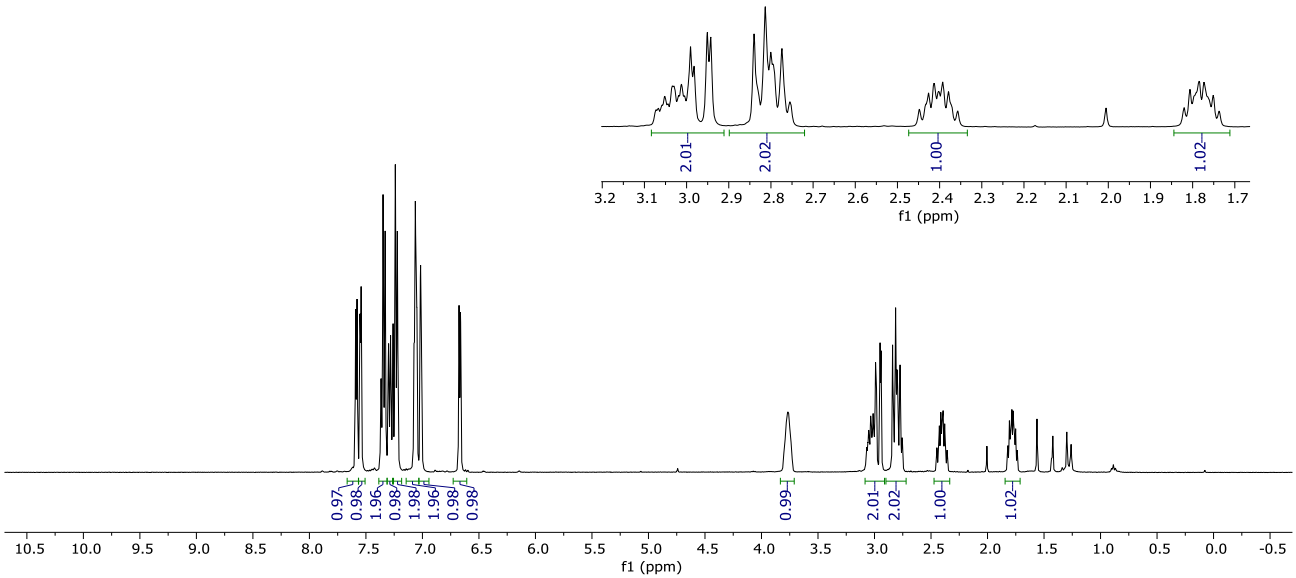
2r

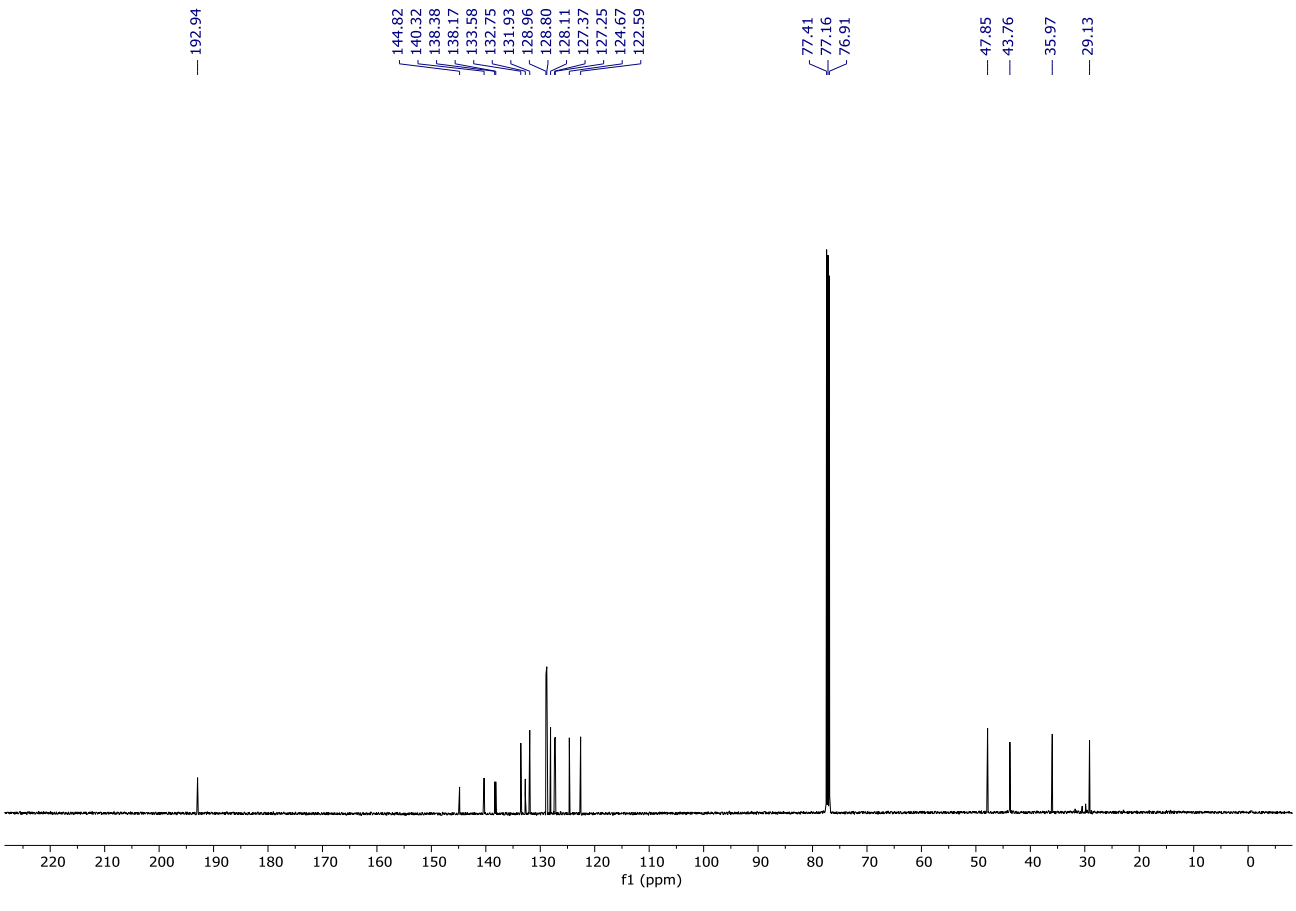

1.95
5.96
2.99
0.99
1.00
1.00
0.99
1.02
1.00
1.01
1.00
f1 (ppm)
1.00
0.99
1.02
1.00
1.01
1.00
f1 (ppm)

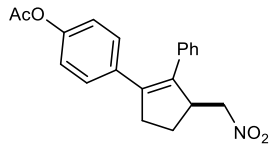

192.97
161.29
159.32
144.84
143.03
136.42
134.29
133.63
132.01
131.03
130.99
128.67
128.60
128.53
128.34
128.13
127.10
126.36
126.23
123.90
123.87
115.89
115.71
77.41
77.16
76.91
45.58
43.58
37.16
37.14
29.39
f1 (ppm)
136.42
134.29
133.63
132.01
131.03
130.99
128.67
128.60
128.53
128.34
128.13
127.10
126.36
126.23
123.90
123.87
f1 (ppm)


S
Ph
O
S

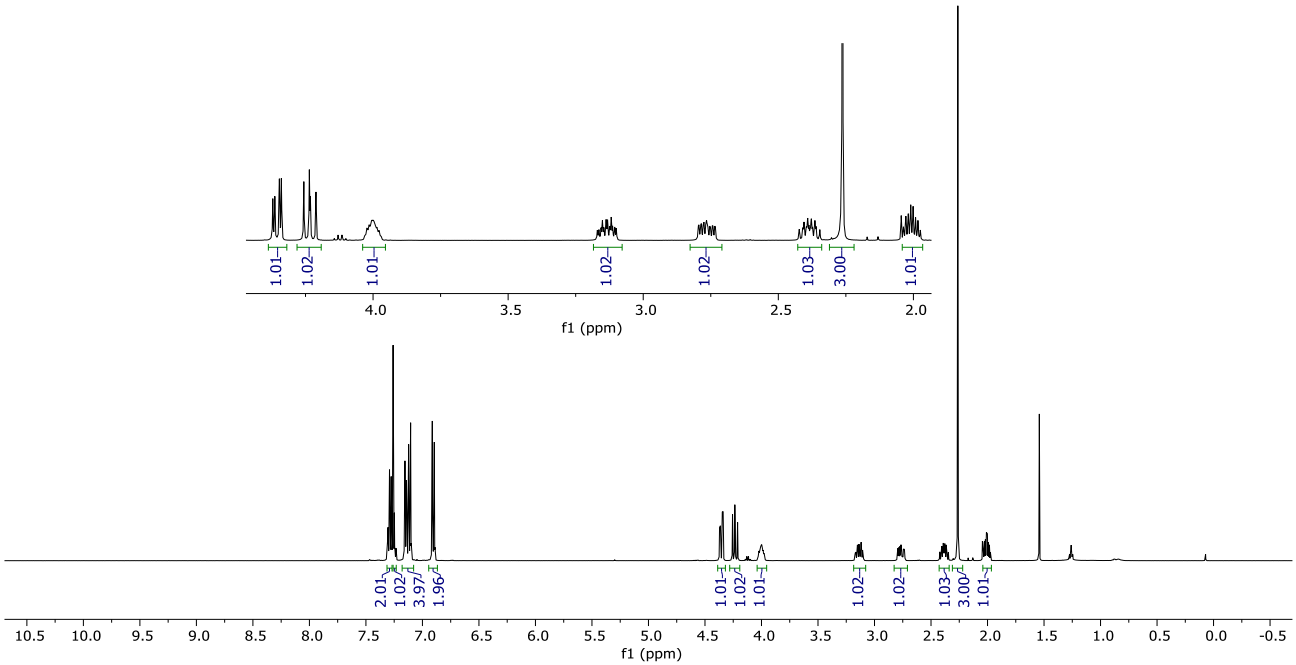
2s

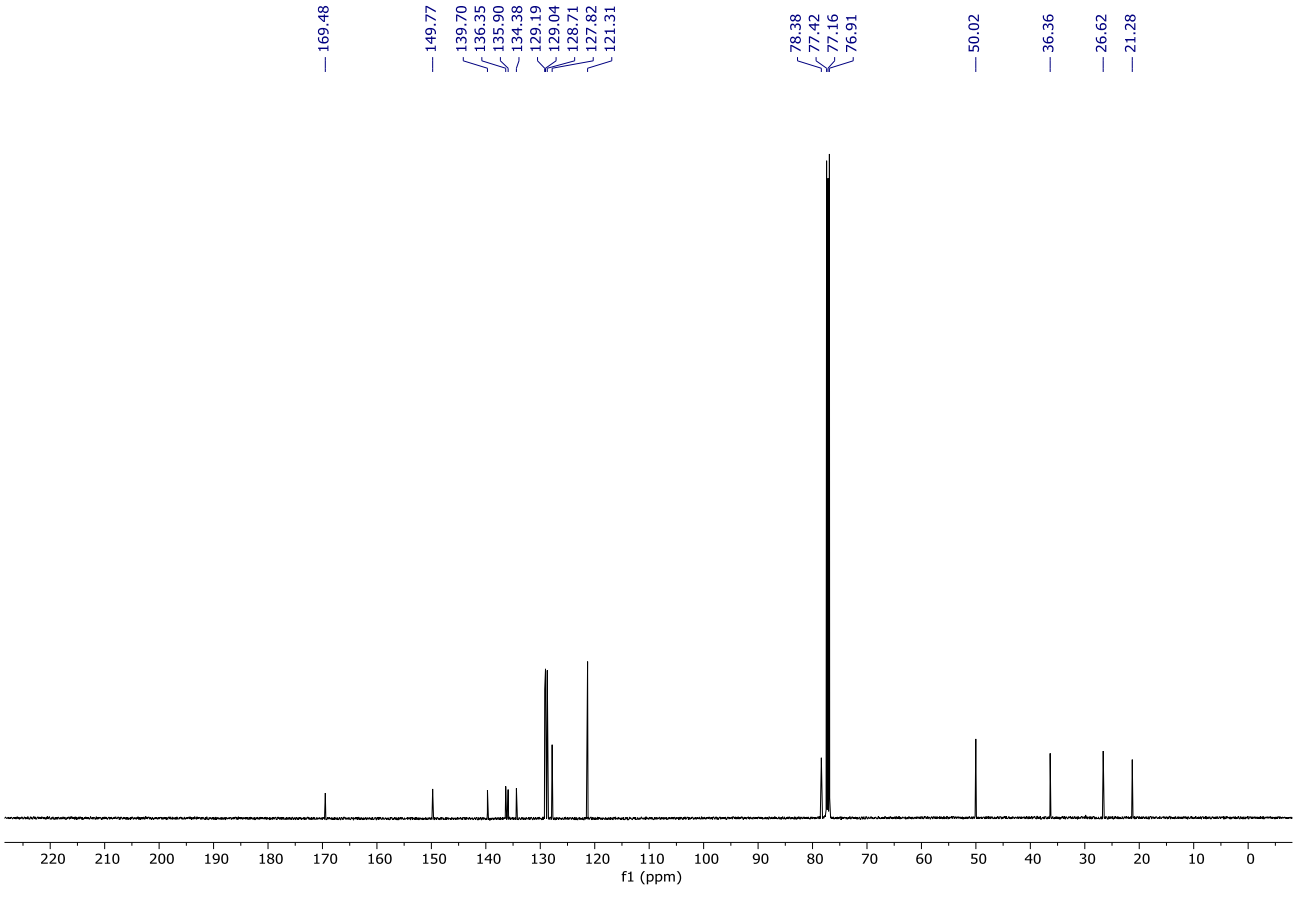

2.01
2.02
1.00
1.02
f1 (ppm)
0.97
0.98
1.96
0.98
1.98
1.96
0.98
0.98
0.99
2.01
2.02
1.00
1.02
f1 (ppm)

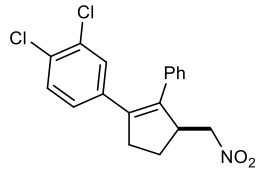

192.94
144.82
140.32
138.38
138.17
133.58
132.75
131.93
128.96
128.80
128.11
127.37
127.25
124.67
122.59
77.41
77.16
76.91
47.85
43.76
35.97
29.13
f1 (ppm)


AcO
Ph
NO2

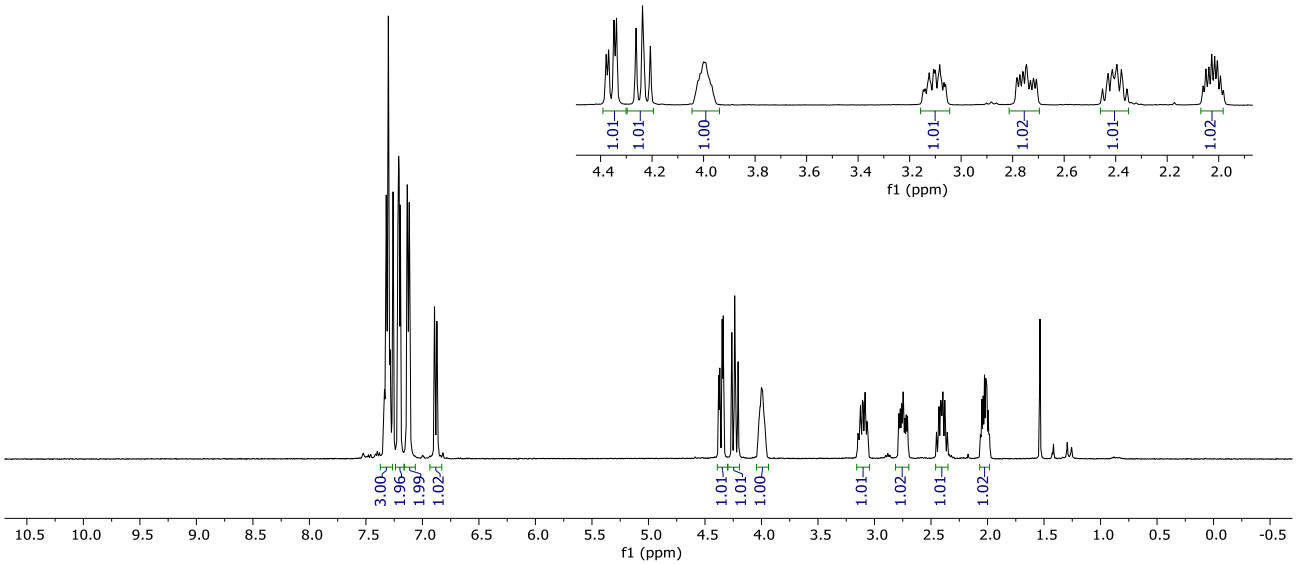
2t

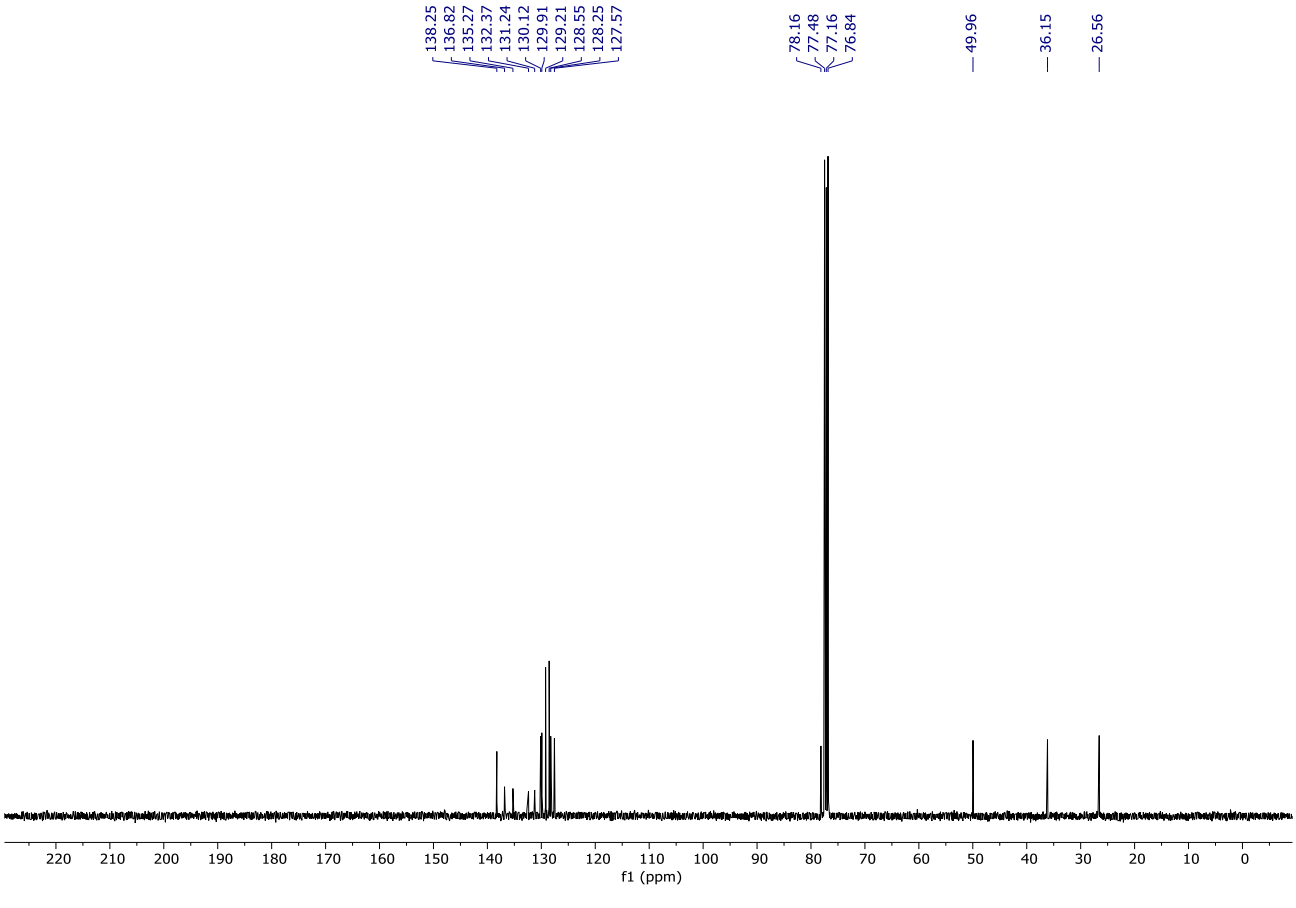

1.01
1.02
1.01
1.02
1.02
1.03
3.00
1.01
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
2.01
1.02
3.97
1.96
1.01
1.02
1.01
1.02
1.02
1.03
3.00
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

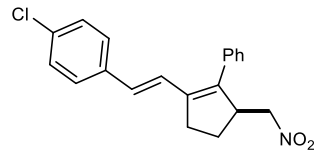

169.48
149.77
139.70
136.35
135.90
134.38
129.19
129.04
128.71
127.82
121.31
78.38
77.42
77.16
76.91
50.02
36.36
26.62
21.28
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
Cl
Ph
NO2

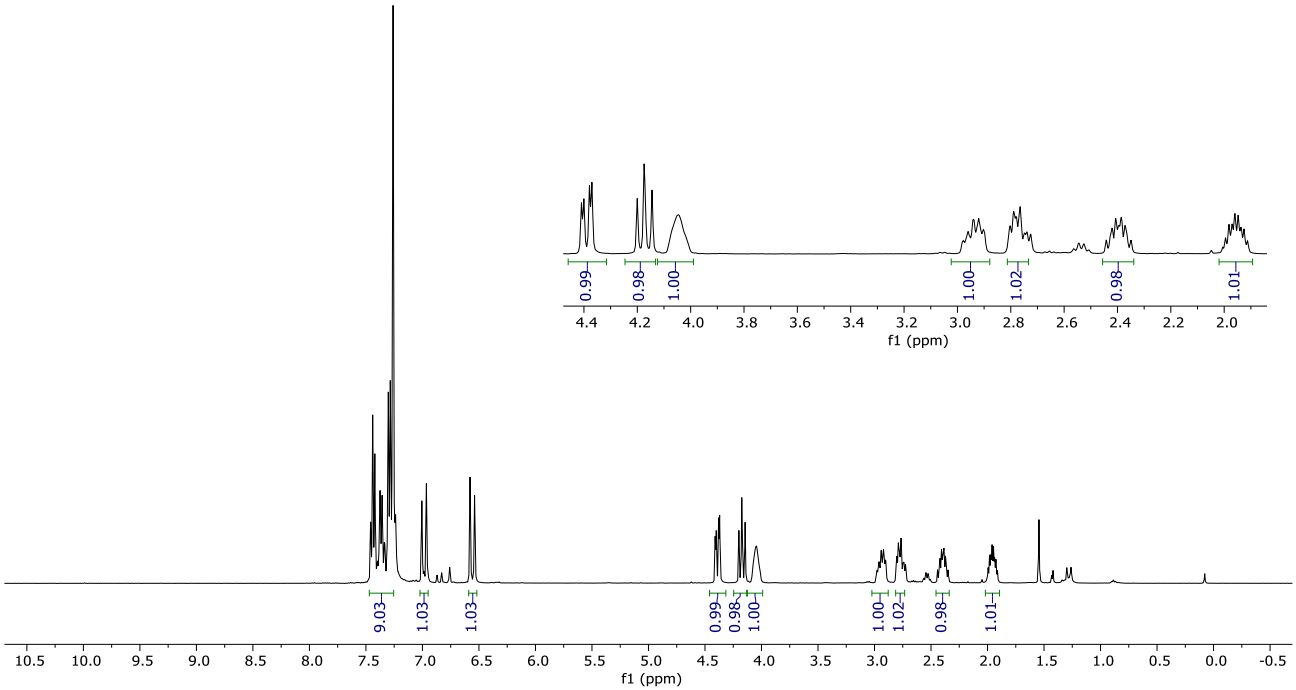
2u

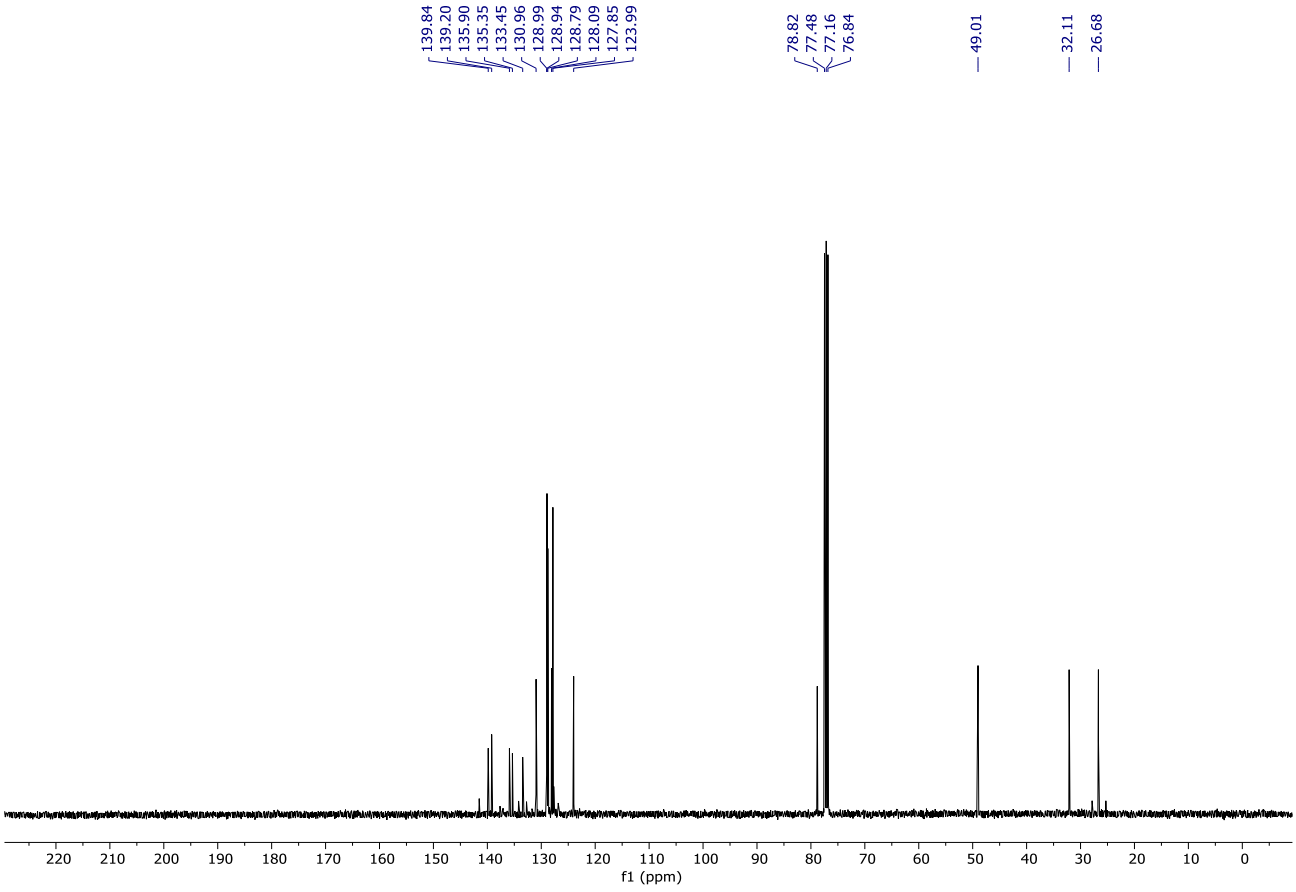

3.00
1.96
1.99
1.02
1.01
1.01
1.00
1.01
1.02
1.01
1.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
1.01
1.01
1.00
1.01
1.02
1.01
1.02
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

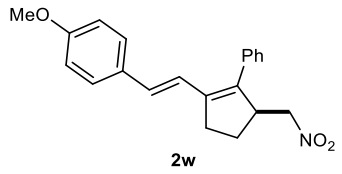

138.25
136.82
135.27
132.37
131.24
130.12
129.91
129.21
128.55
128.25
127.57
78.16
77.48
77.16
76.84
49.96
36.15
26.56
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Ph
NO2

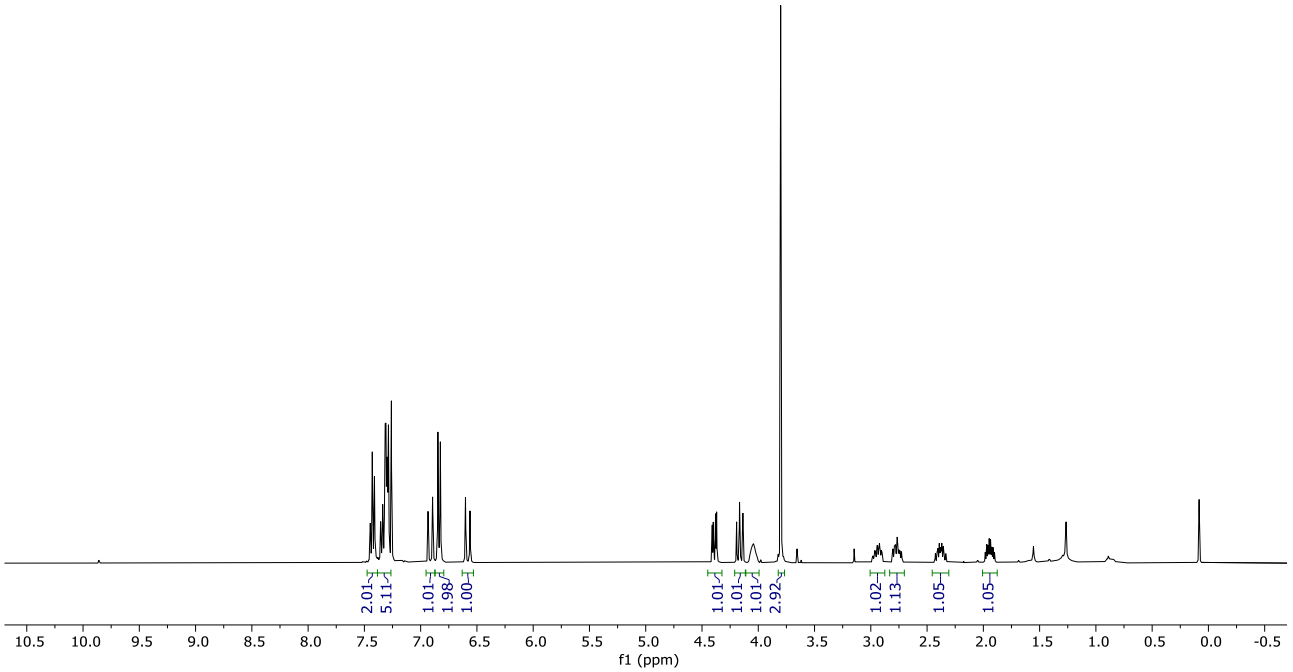
2v

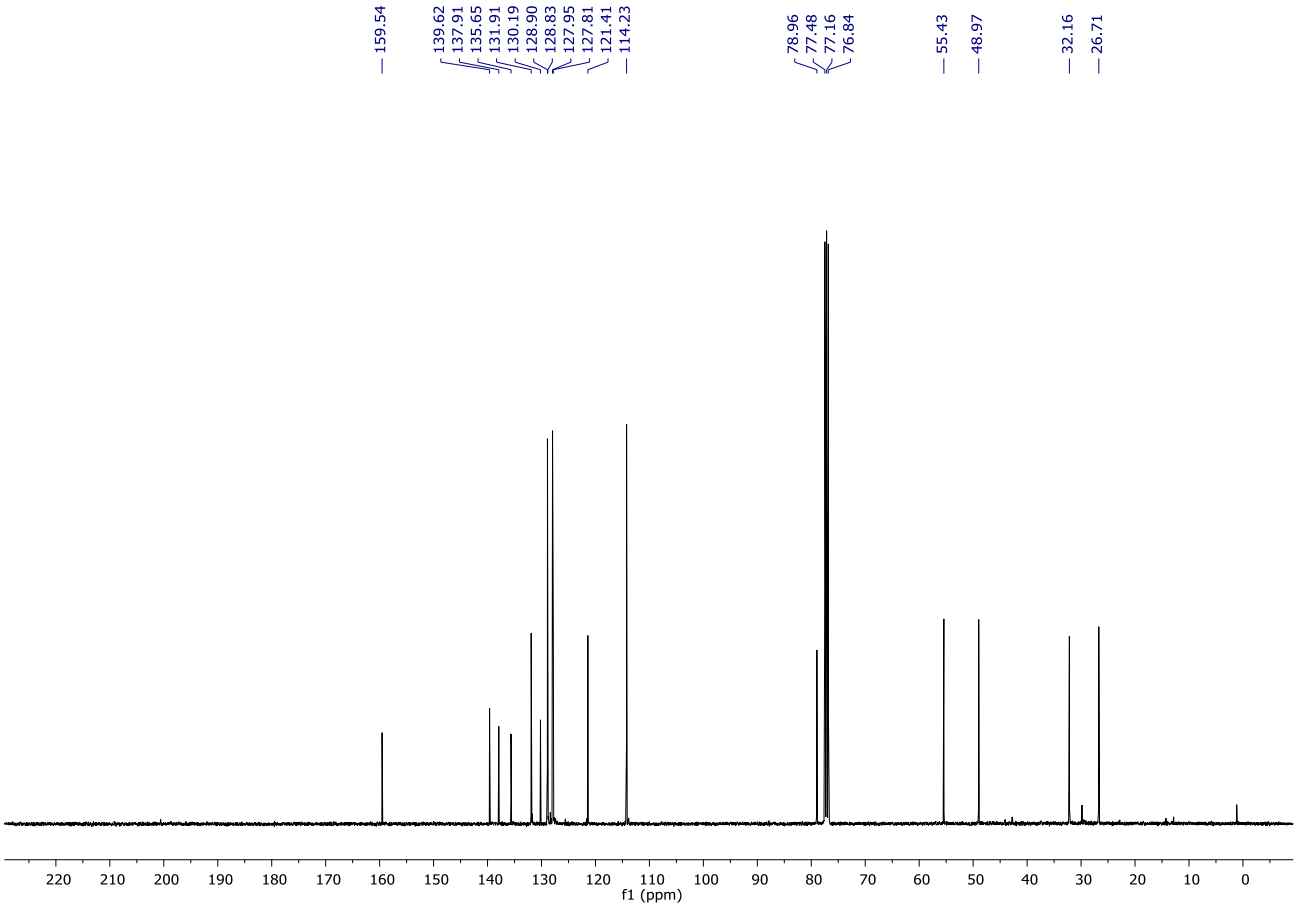

9.03
1.03
1.03
0.99
0.98
1.00
1.00
1.02
0.98
1.01
f1 (ppm)

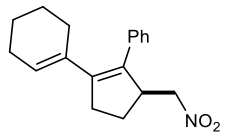

139.84
139.20
135.90
135.35
133.45
130.96
128.99
128.94
128.79
128.09
127.85
123.99
78.82
77.48
77.16
76.84
49.01
32.11
26.68
f1 (ppm)


MeO
Ph
NO2

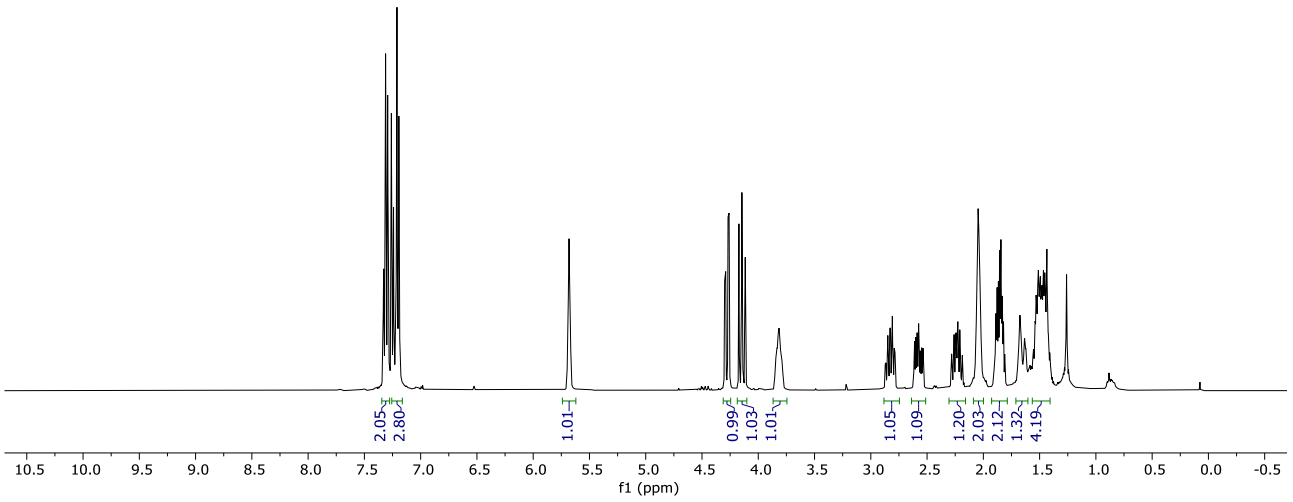
2w

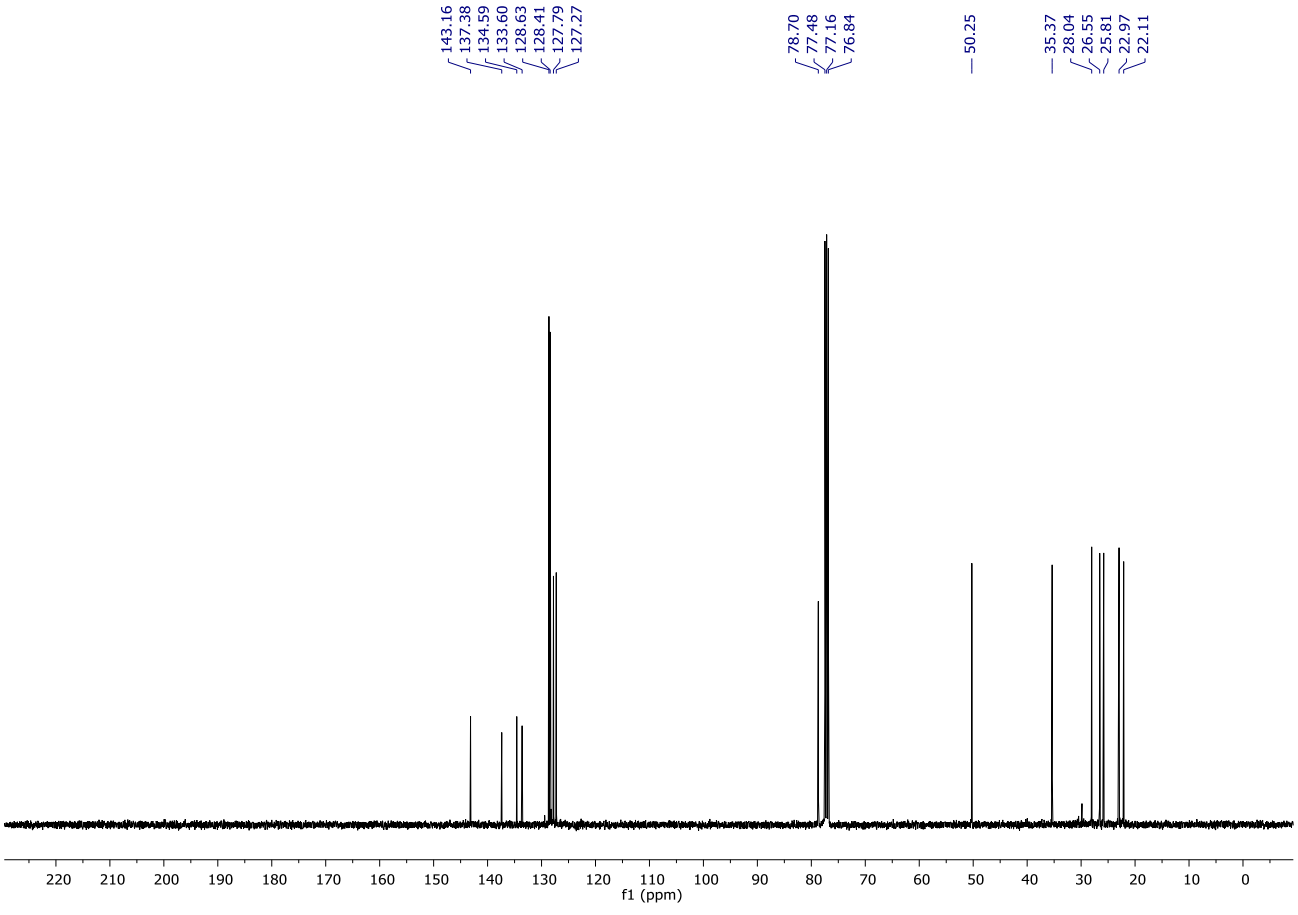

2.01
5.11
1.01
1.98
1.00
1.01
1.01
1.01
2.92
1.02
1.13
1.05
1.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

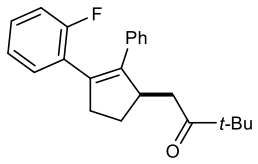

159.54
139.62
137.91
135.65
131.91
130.19
128.90
128.83
127.95
127.81
121.41
114.23
78.96
77.48
77.16
76.84
55.43
48.97
32.16
26.71
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
NO2

2x

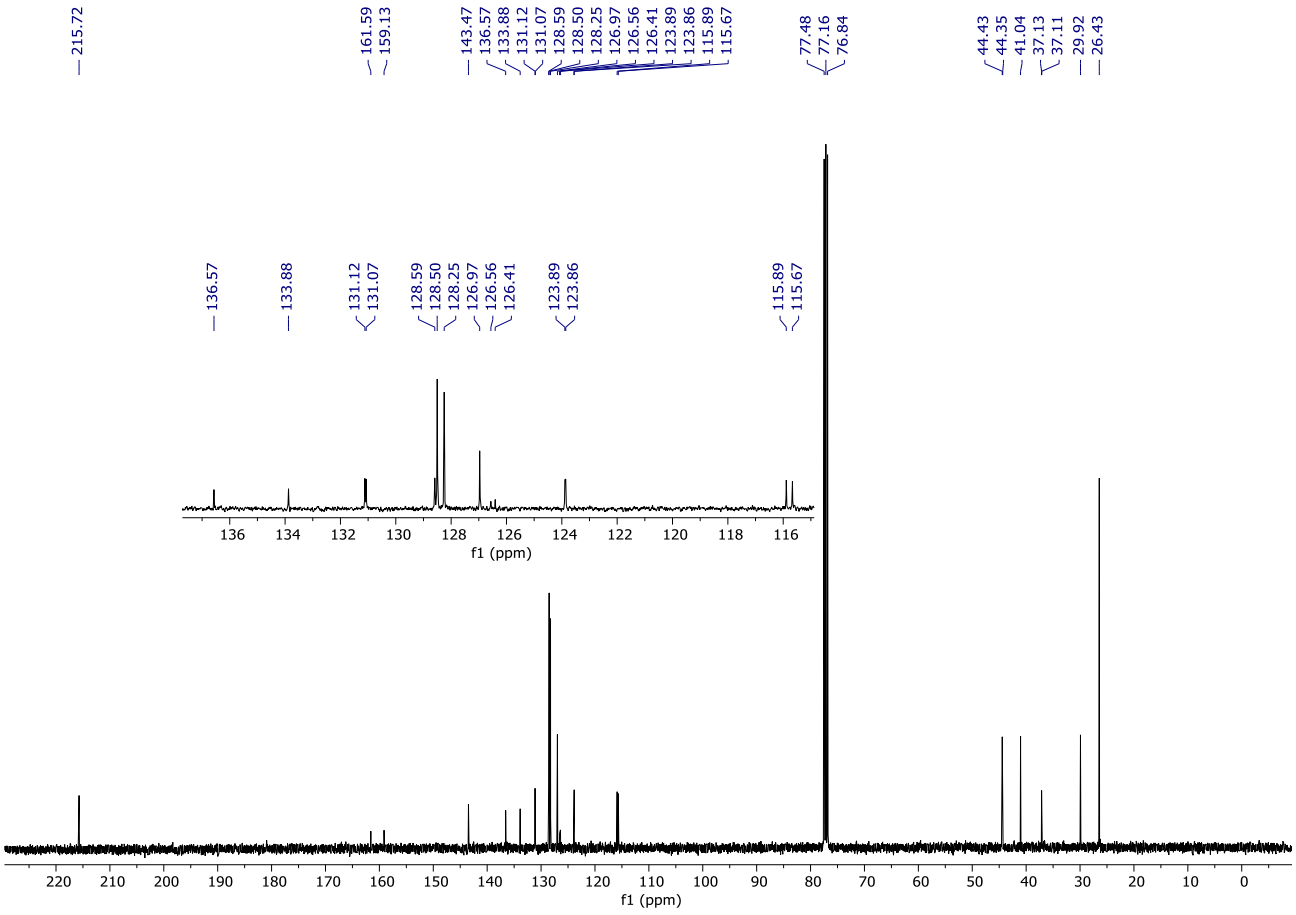

2.05
2.80
1.01
0.99
1.03
1.01
1.05
1.09
1.20
2.03
2.12
1.32
4.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

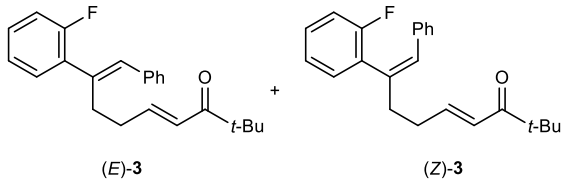

143.16
137.38
134.59
133.60
128.63
128.41
127.79
127.27
78.70
77.48
77.16
76.84
50.25
35.37
28.04
26.55
25.81
22.97
22.11
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
Ph
t-Bu
O

2y

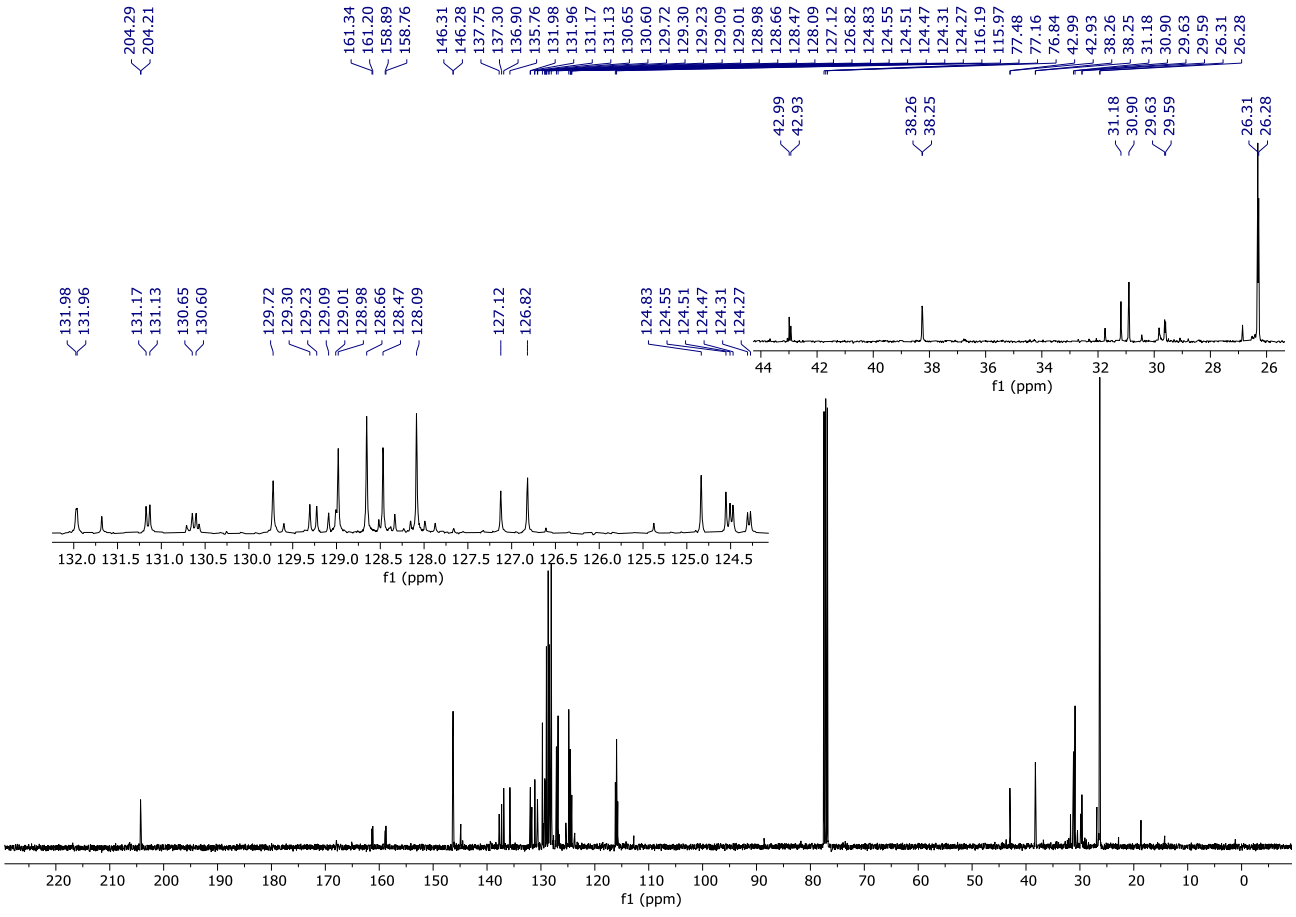
1.00
1.01
2.02
1.00
1.02
0.99
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
3.94
1.97
3.00
1.00
1.01
2.02
1.00
1.02
0.99
9.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

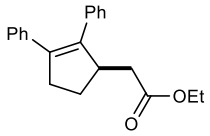

215.72
161.59
159.13
143.47
136.57
133.88
131.12
131.07
128.59
128.50
128.25
126.97
126.56
126.41
123.89
123.86
115.89
115.67
77.48
77.16
76.84
44.43
44.35
41.04
37.13
37.11
29.92
26.43
136.57
133.88
131.12
131.07
128.59
128.50
128.25
126.97
126.56
126.41
123.89
123.86
115.89
115.67
136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



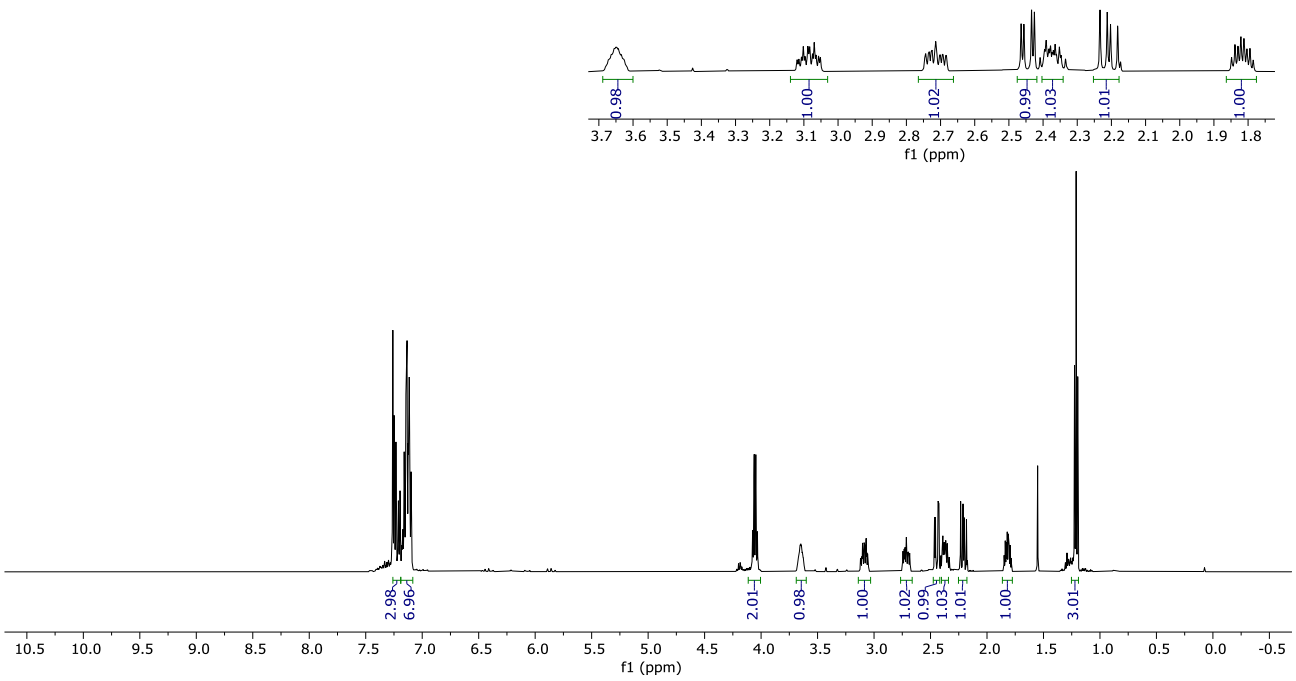
(*E*)-**3** (*Z*)-**3**

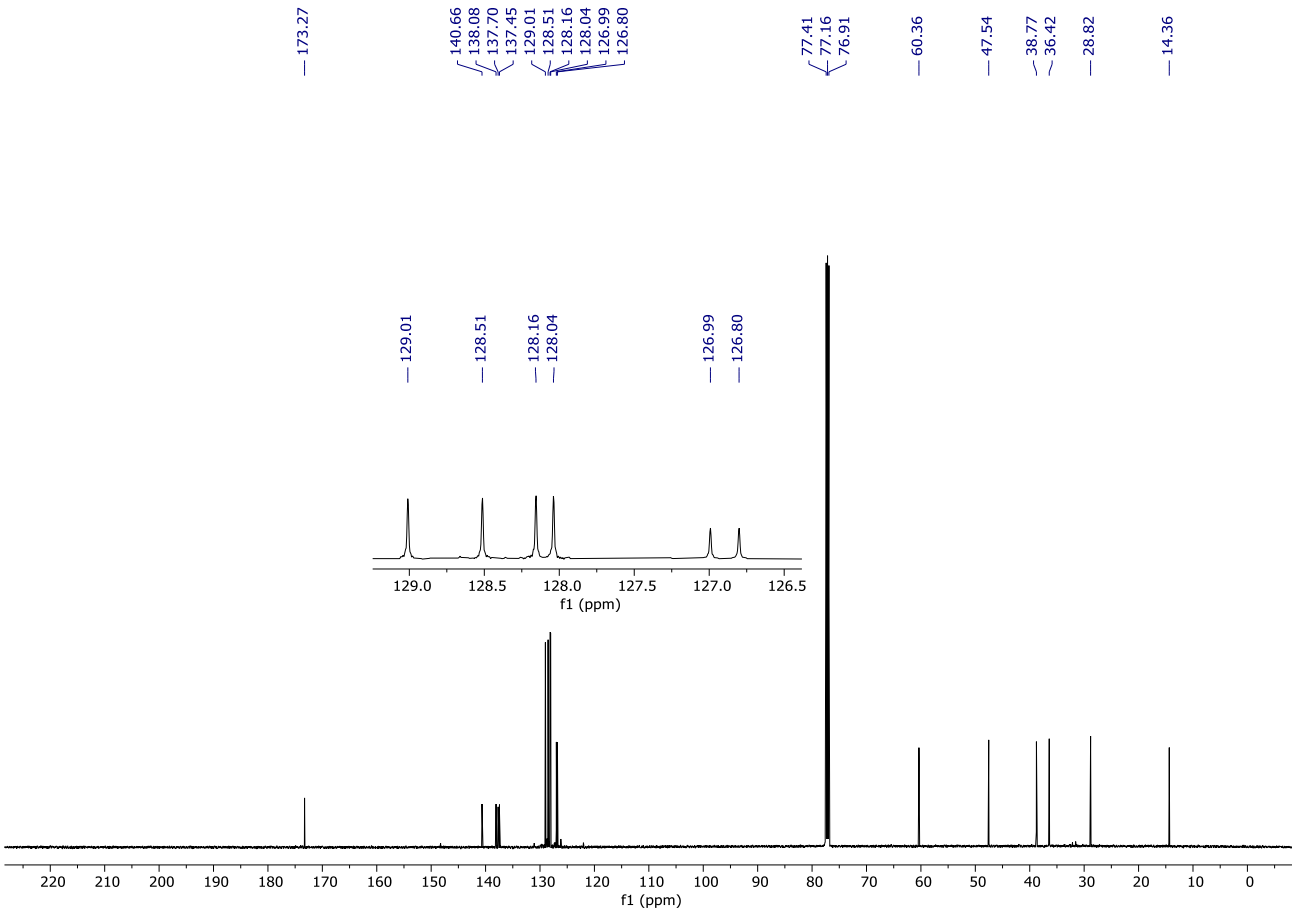
(inseparable mixture)
0.7:1 *E*:*Z*

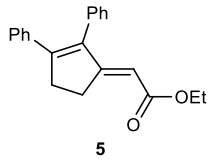



Ph
Ph
OEt
O

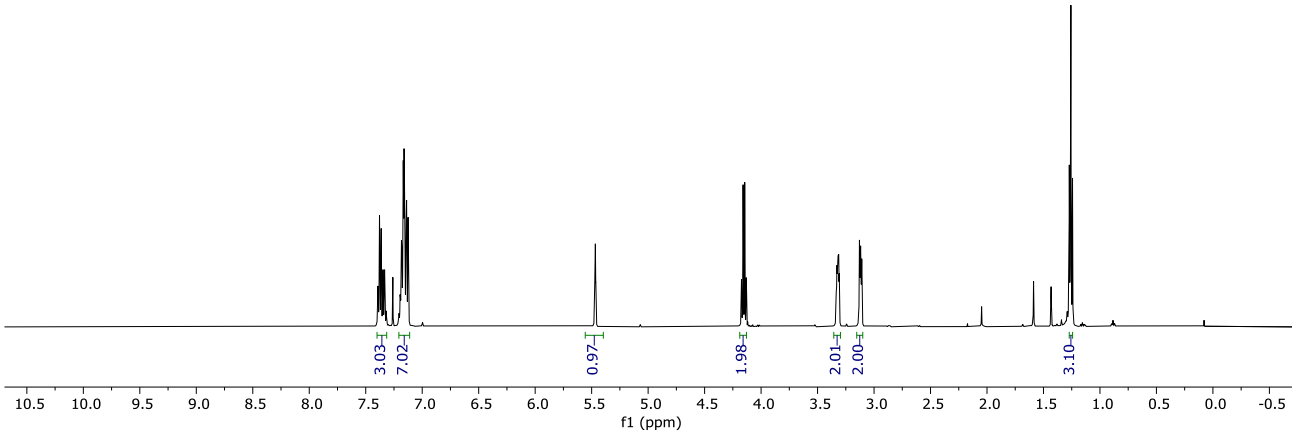
2z

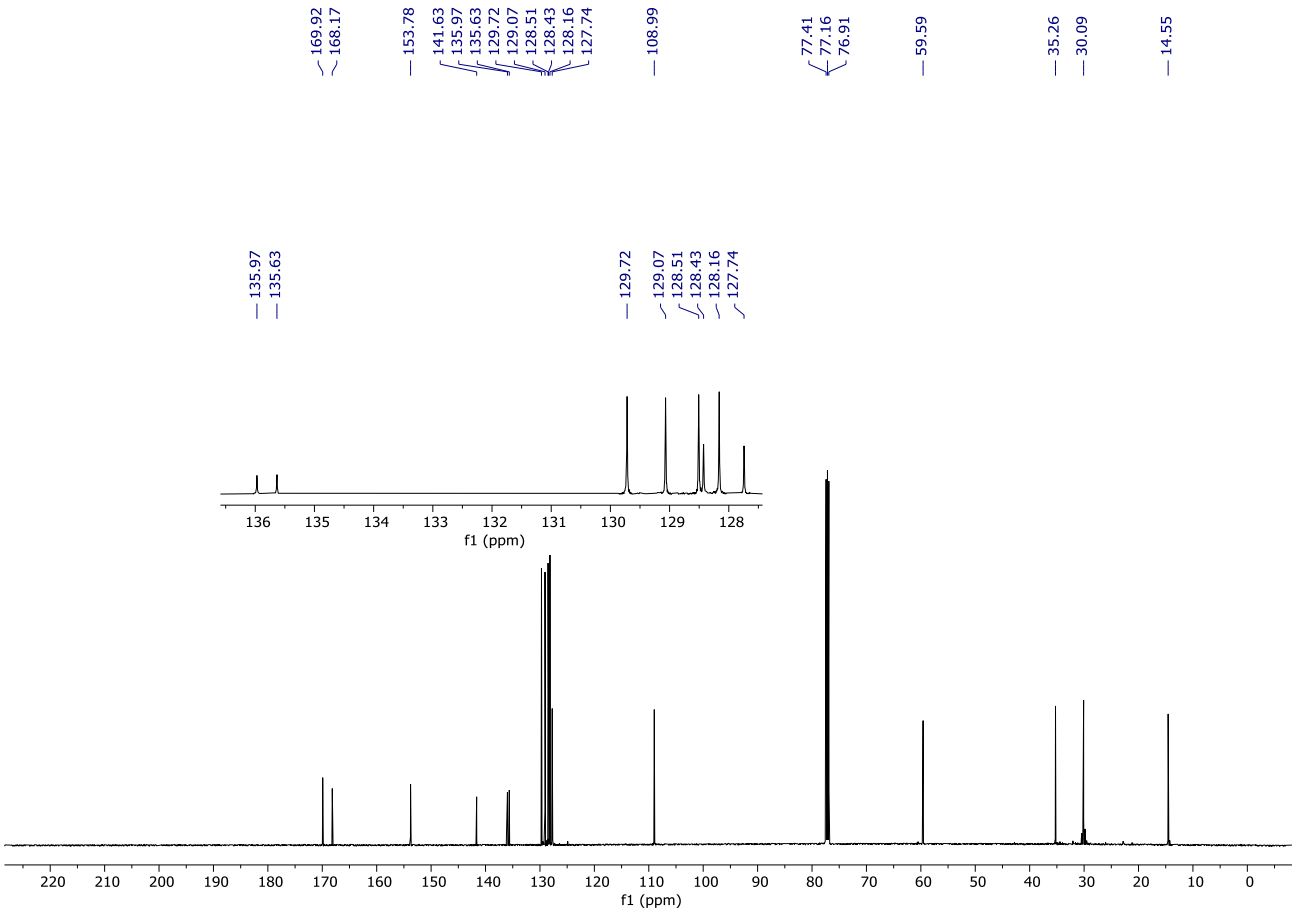

0.98
1.00
1.02
0.99
1.03
1.01
1.00
f1 (ppm)
2.98
6.96
2.01
0.98
1.00
1.02
0.99
1.03
1.01
1.00
3.01
f1 (ppm)

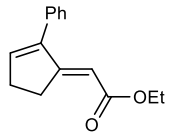

173.27
140.66
138.08
137.70
137.45
129.01
128.51
128.16
128.04
126.99
126.80
77.41
77.16
76.91
60.36
47.54
38.77
36.42
28.82
14.36
129.01
128.51
128.16
128.04
126.99
126.80
f1 (ppm)
f1 (ppm)


Ph
Ph
OEt
O

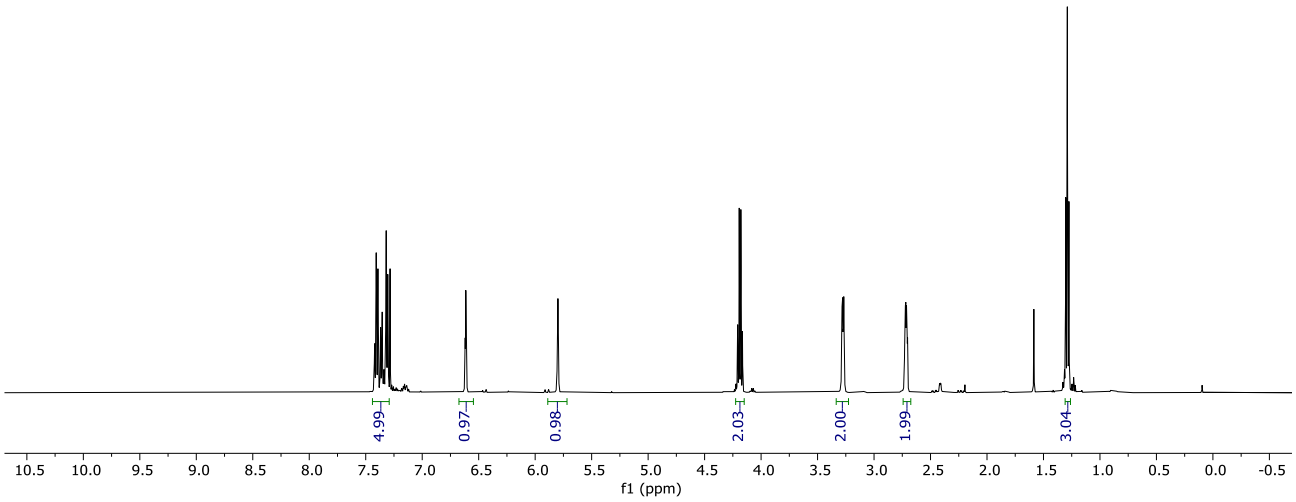
5

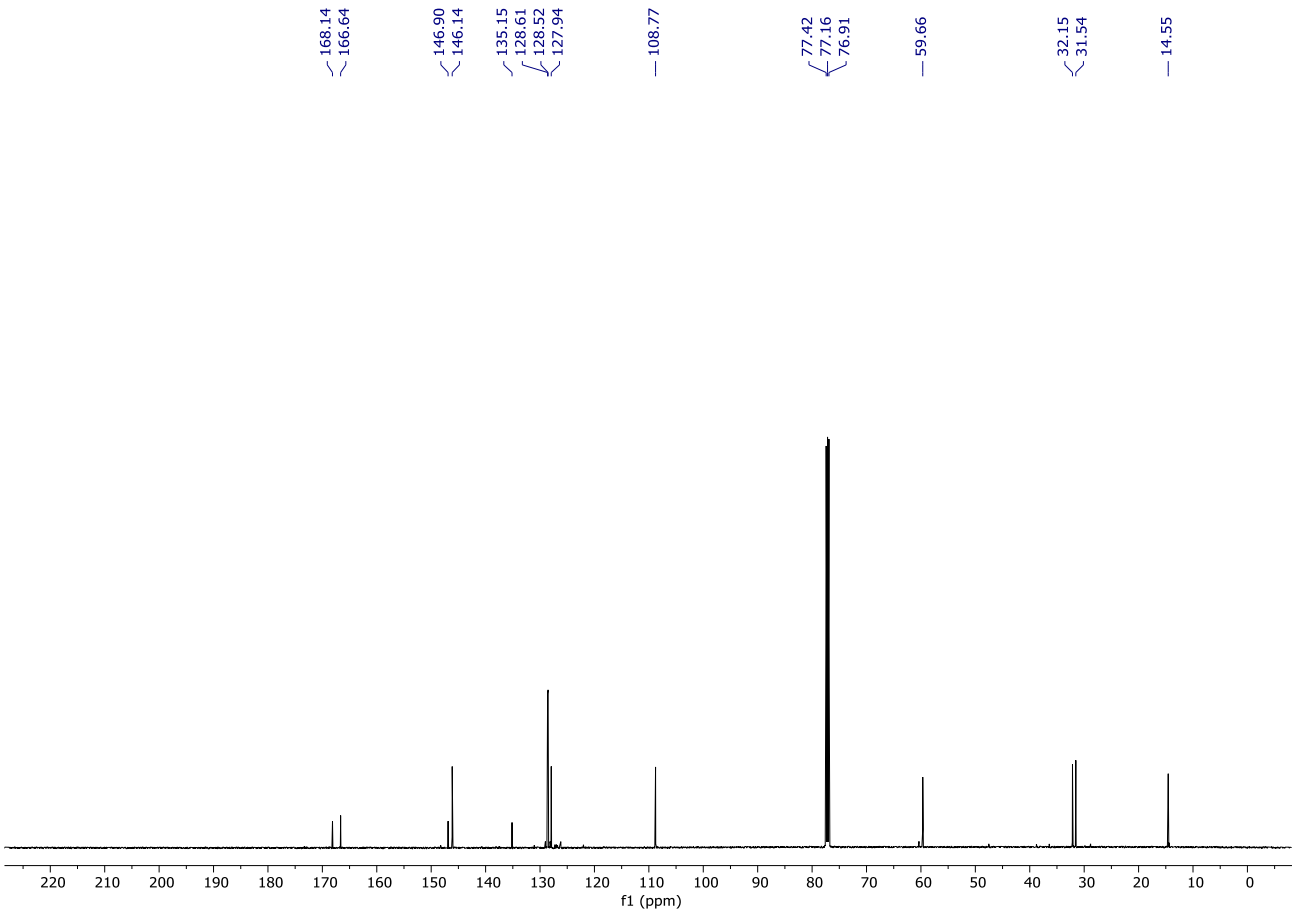

3.03
7.02
0.97
1.98
2.01
2.00
3.10
f1 (ppm)

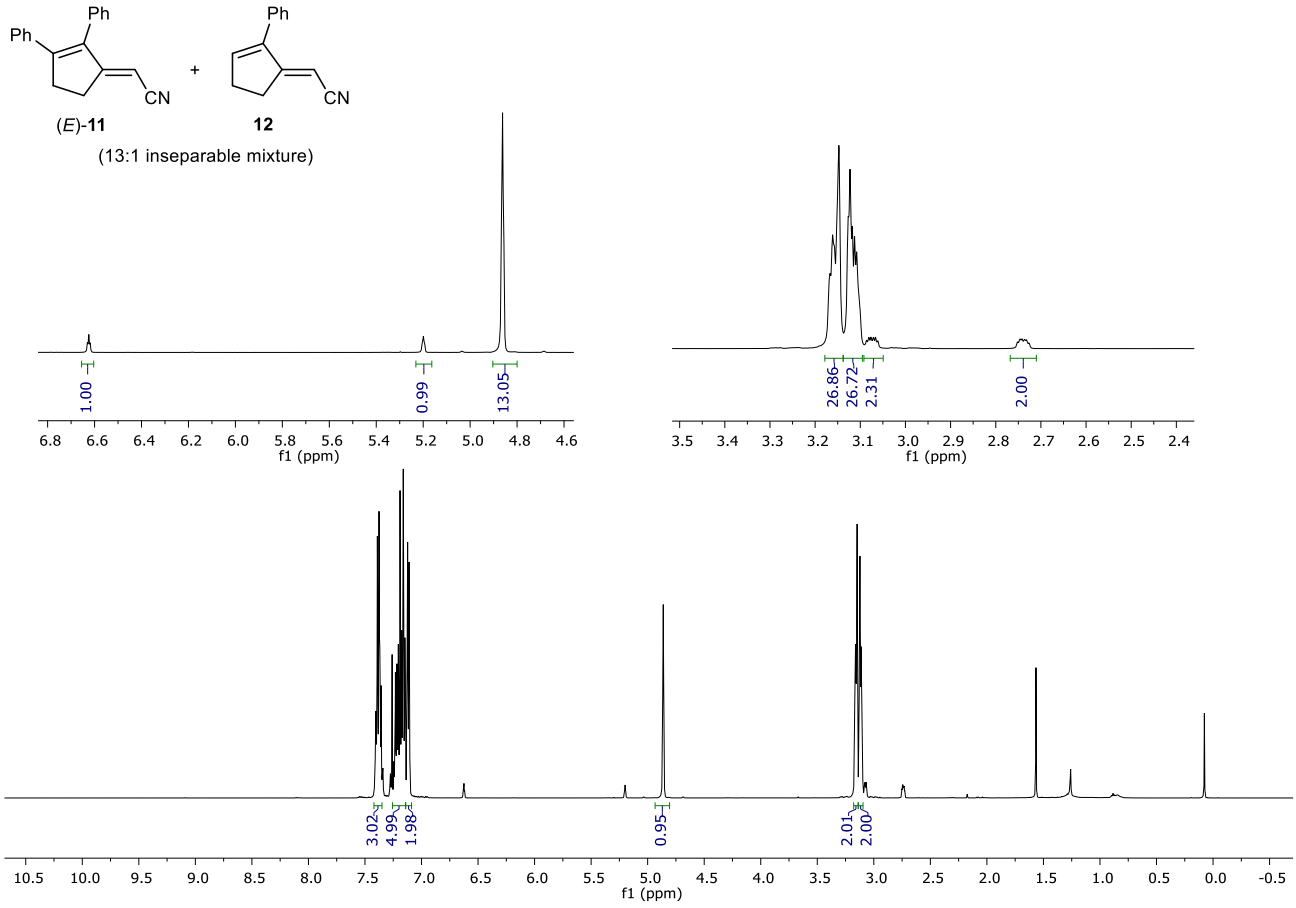

169.92
168.17
153.78
141.63
135.97
135.63
129.72
129.07
128.51
128.43
128.16
127.74
108.99
77.41
77.16
76.91
59.59
35.26
30.09
14.55
f1 (ppm)

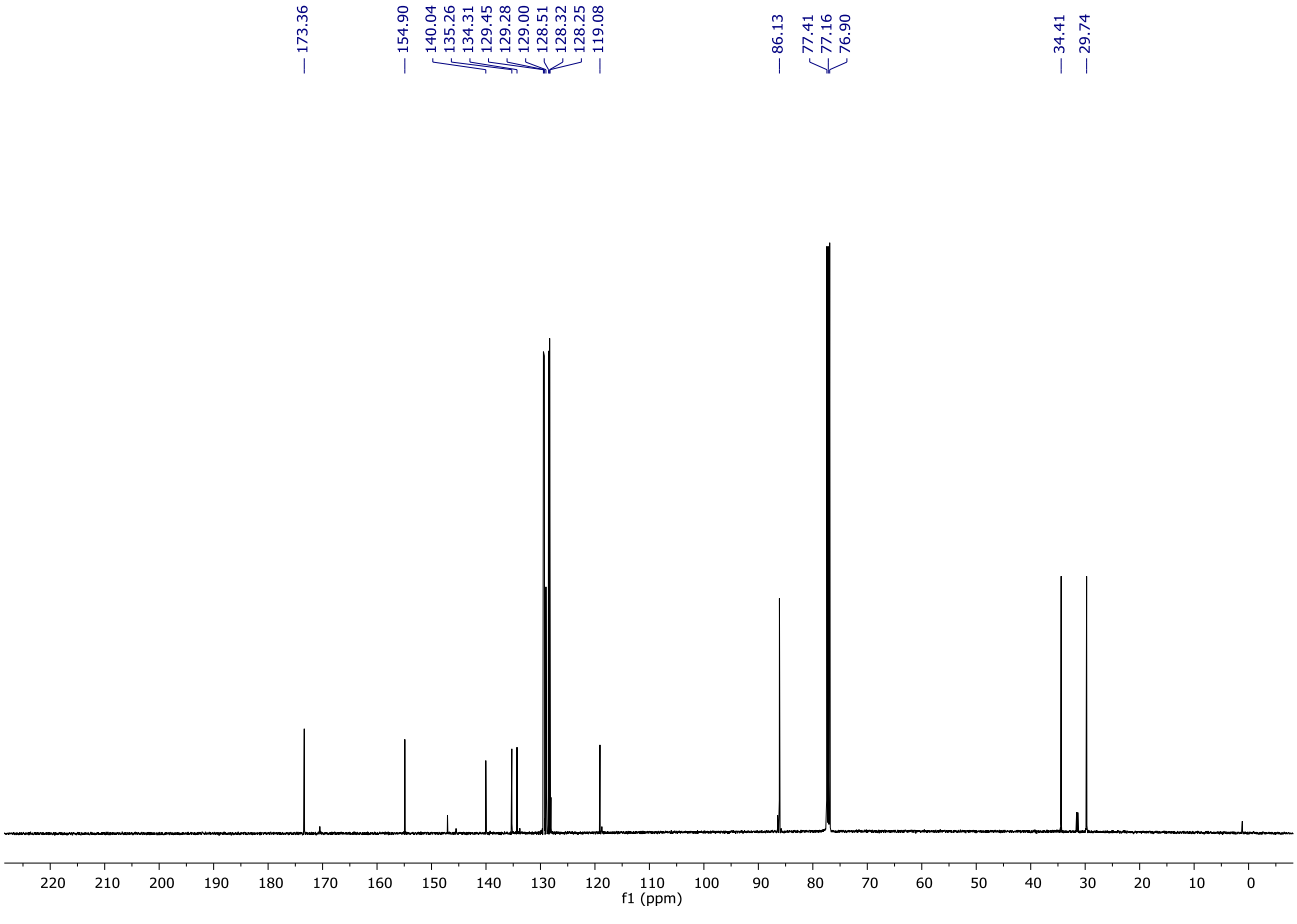

Ph
OEt
O

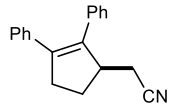
6


4.99
0.97
0.98
2.03
2.00
1.99
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

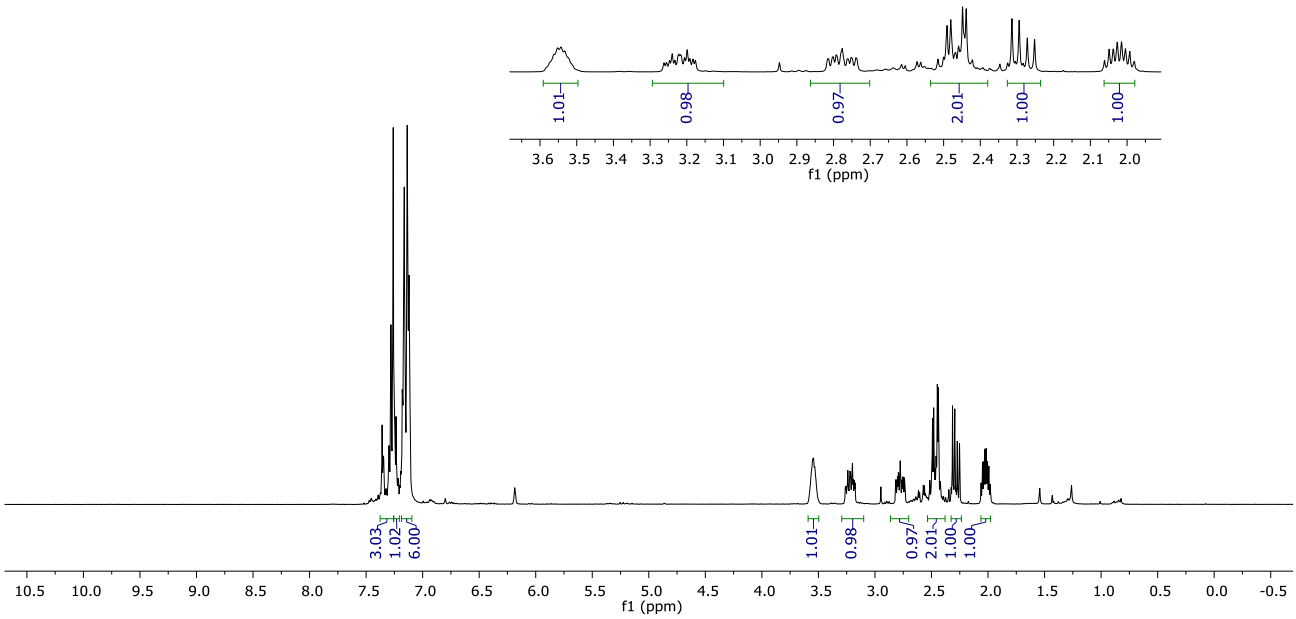

168.14
166.64
146.90
146.14
135.15
128.61
128.52
127.94
108.77
77.42
77.16
76.91
59.66
32.15
31.54
14.55
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

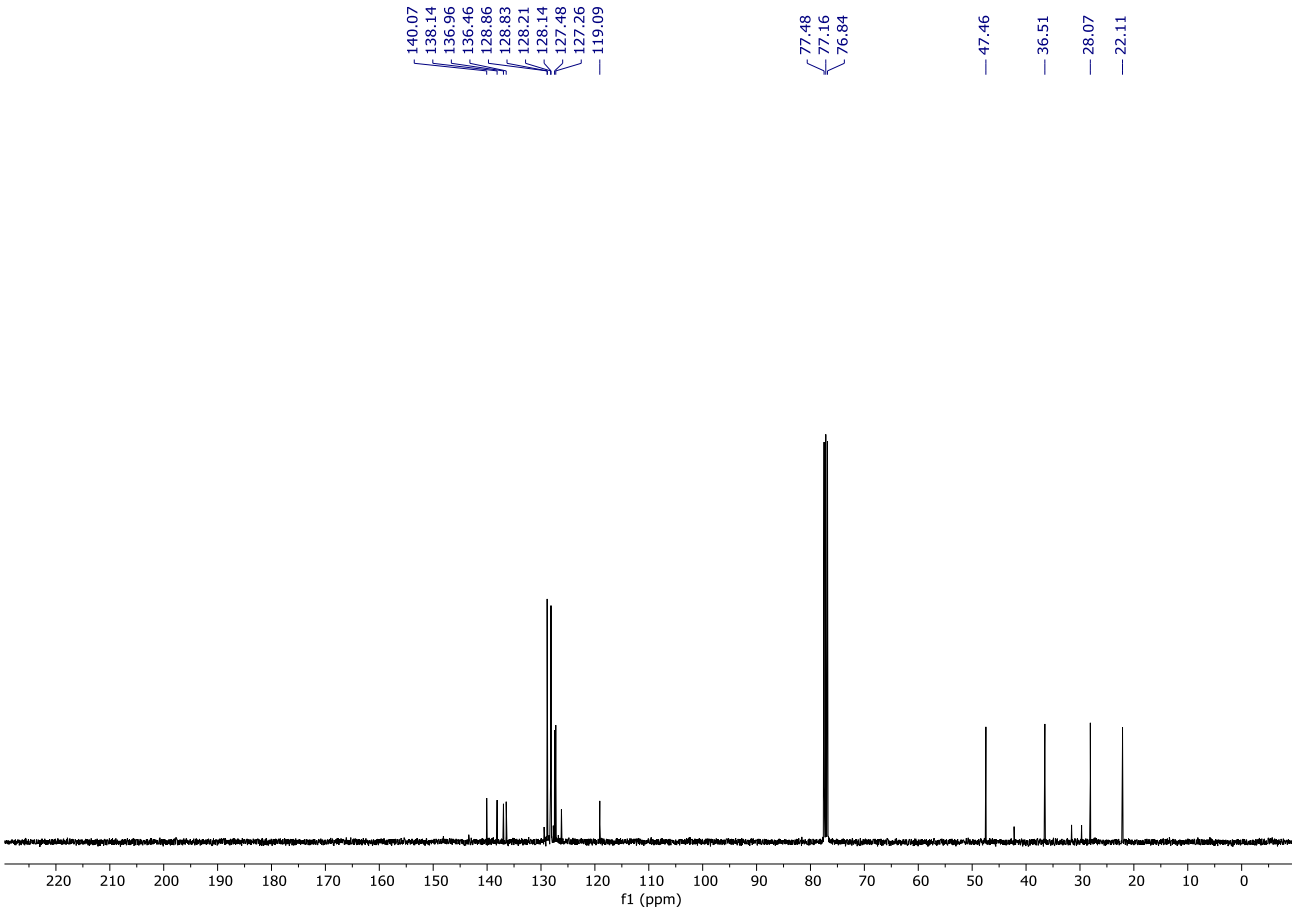

Ph
Ph
CN
+
Ph
CN
(*E*)-**11**
12
(13:1 inseparable mixture)
1.00
0.99
13.05
26.86
26.72
2.31
2.00
f1 (ppm)
3.02
4.99
1.98
0.95
2.01
2.00
f1 (ppm)

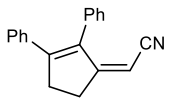

173.36
154.90
140.04
135.26
134.31
129.45
129.28
129.00
128.51
128.32
128.25
119.08
86.13
77.41
77.16
76.90
34.41
29.74
f1 (ppm)


Ph
Ph
CN

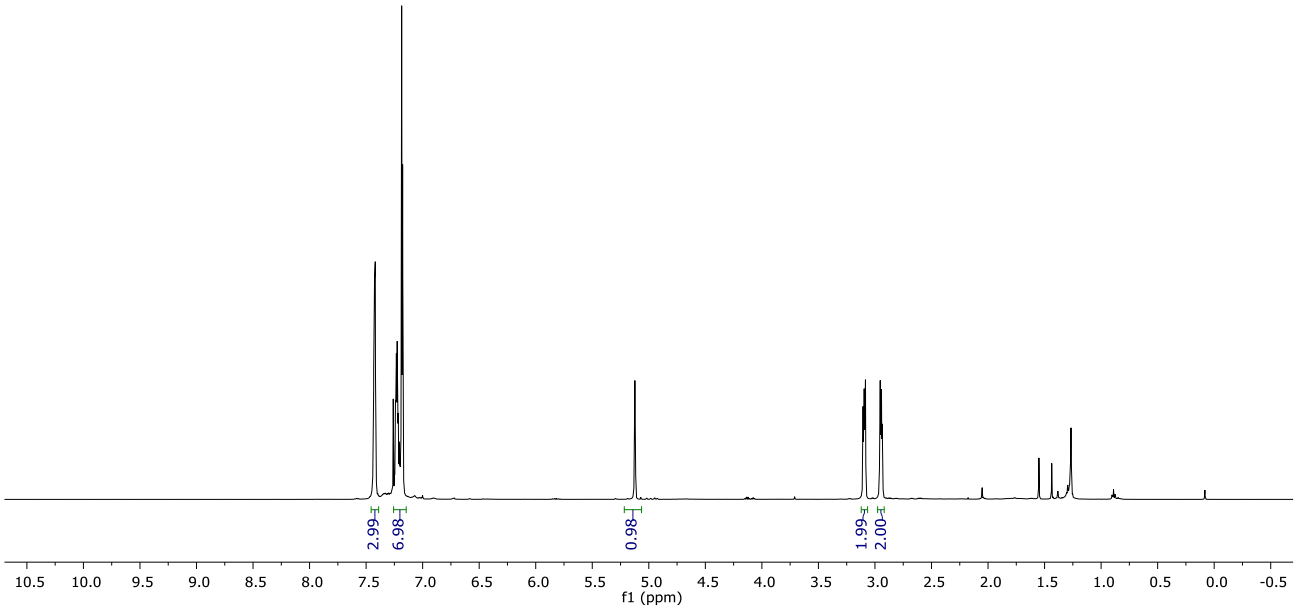
2aa

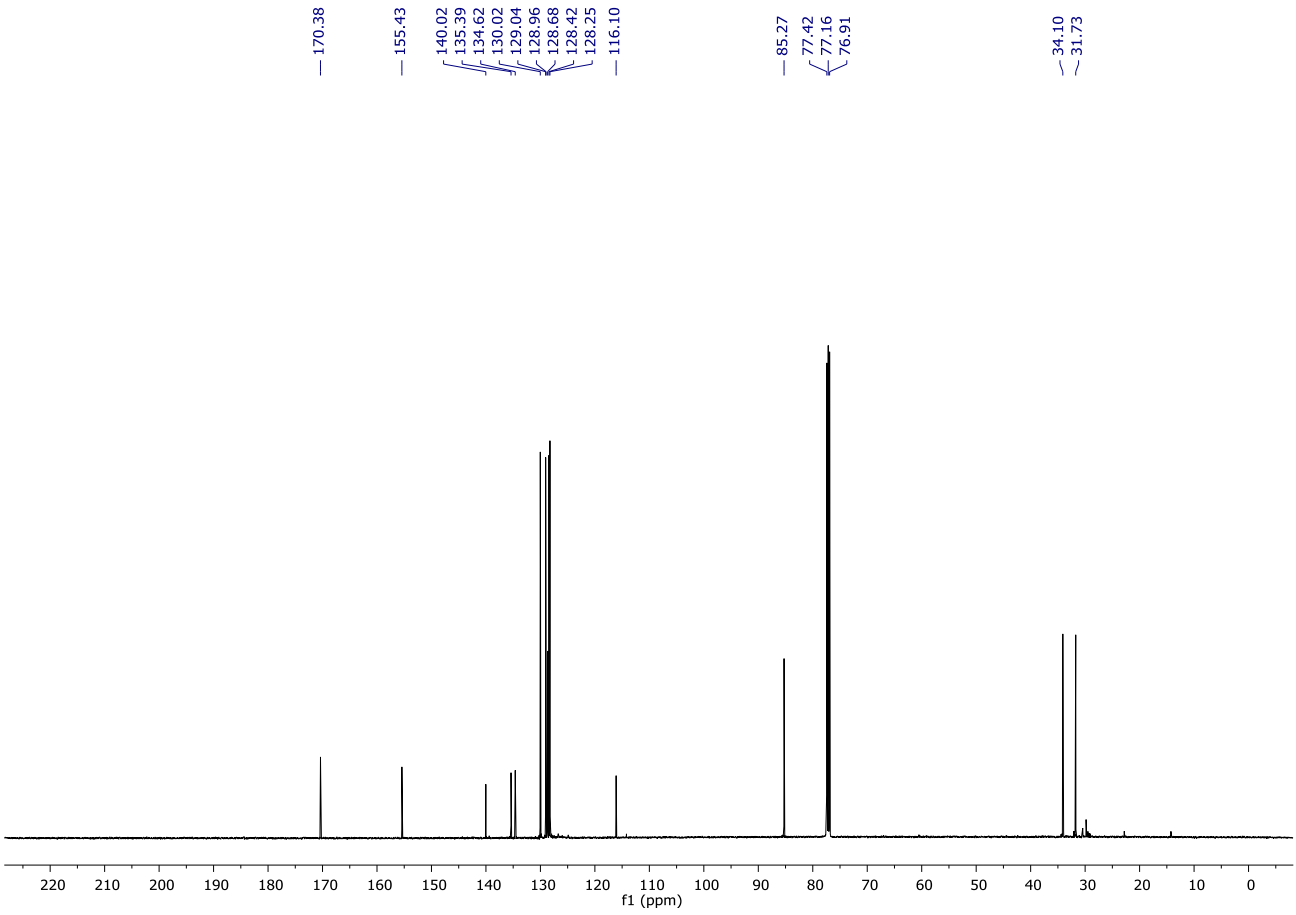

1.01
0.98
0.97
2.01
1.00
1.00
f1 (ppm)
3.03
1.02
6.00
1.01
0.98
0.97
2.01
1.00
1.00
f1 (ppm)

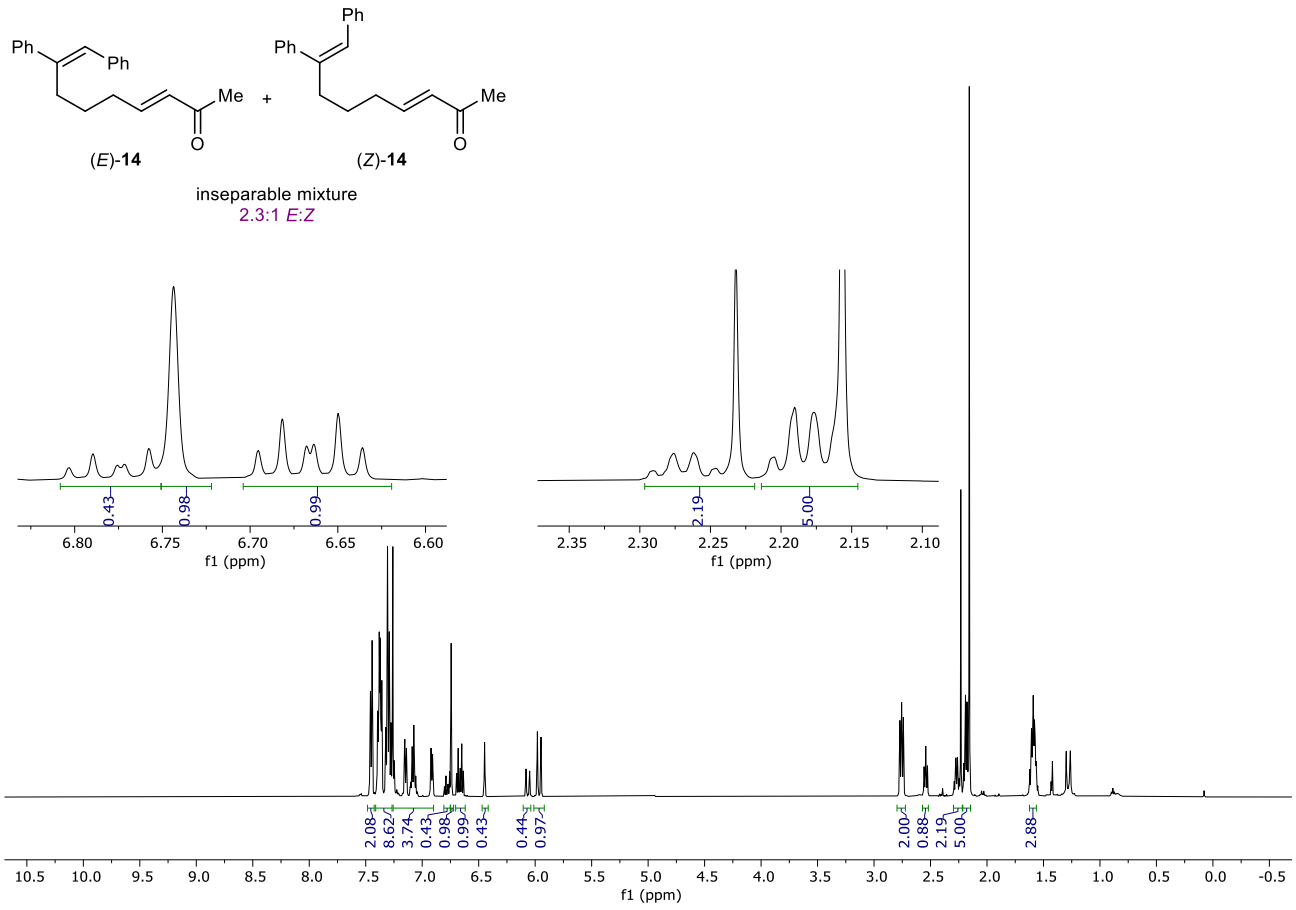

140.07
138.14
136.96
136.46
128.86
128.83
128.21
128.14
127.48
127.26
119.09
77.48
77.16
76.84
47.46
36.51
28.07
22.11
f1 (ppm)

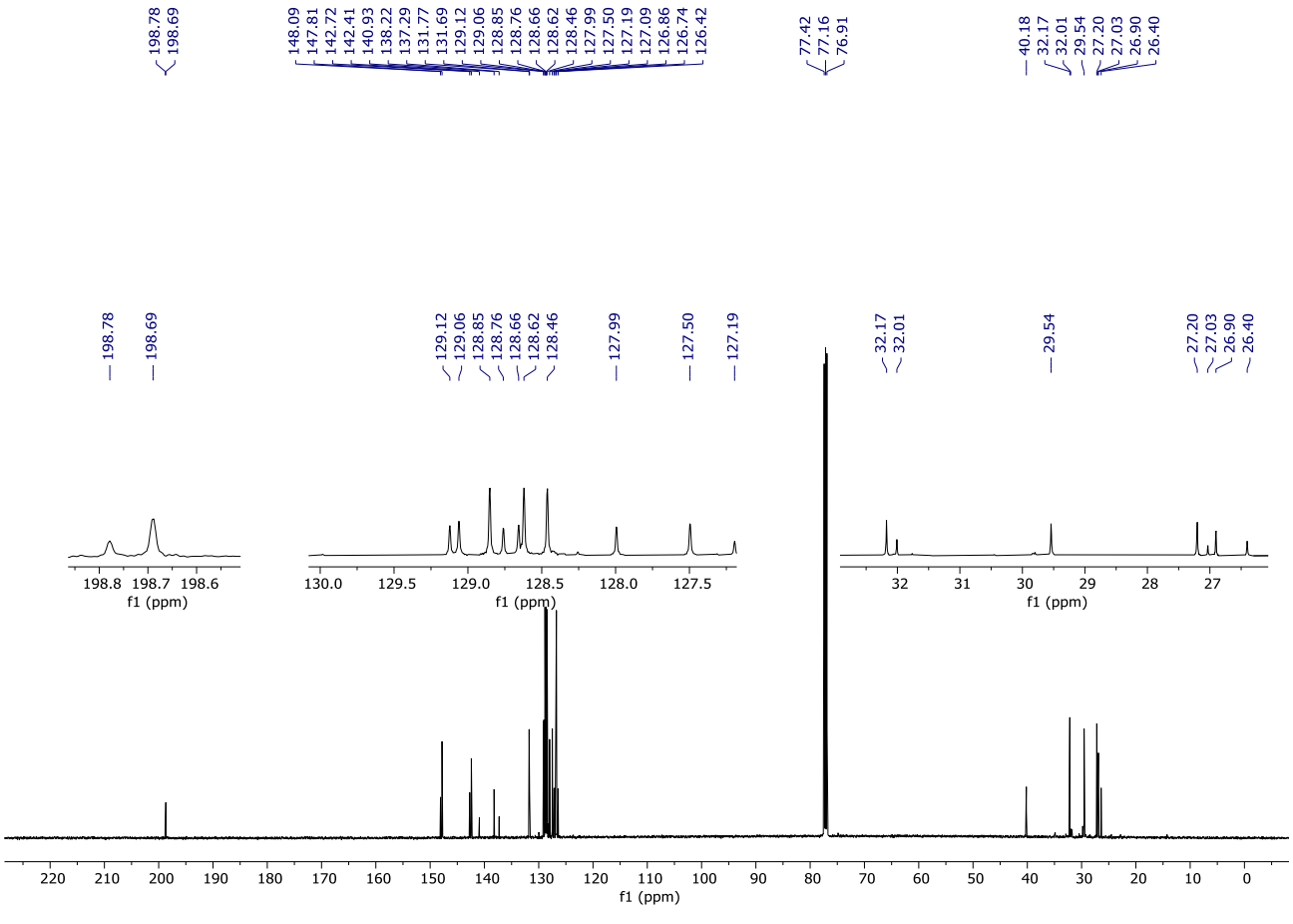

Ph
Ph
CN

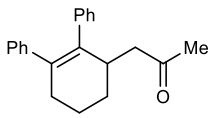
(*Z*)-**11**


2.99
6.98
0.98
1.99
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

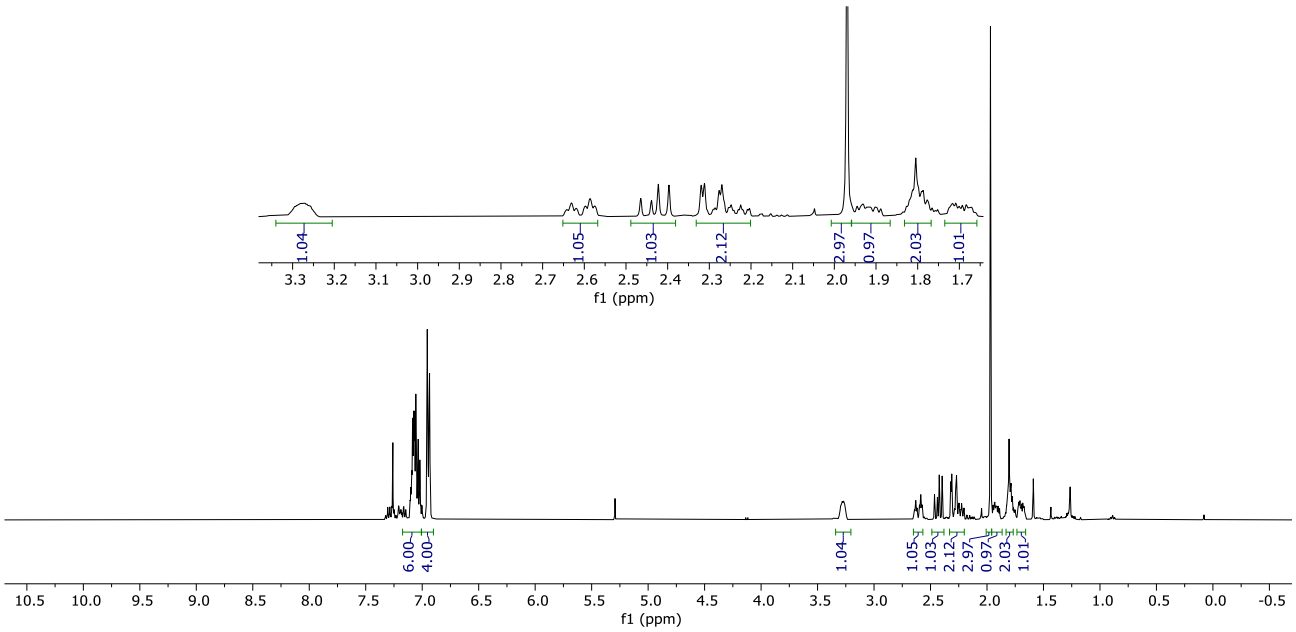

170.38
155.43
140.02
135.39
134.62
130.02
129.04
128.96
128.68
128.42
128.25
116.10
85.27
77.42
77.16
76.91
34.10
31.73
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

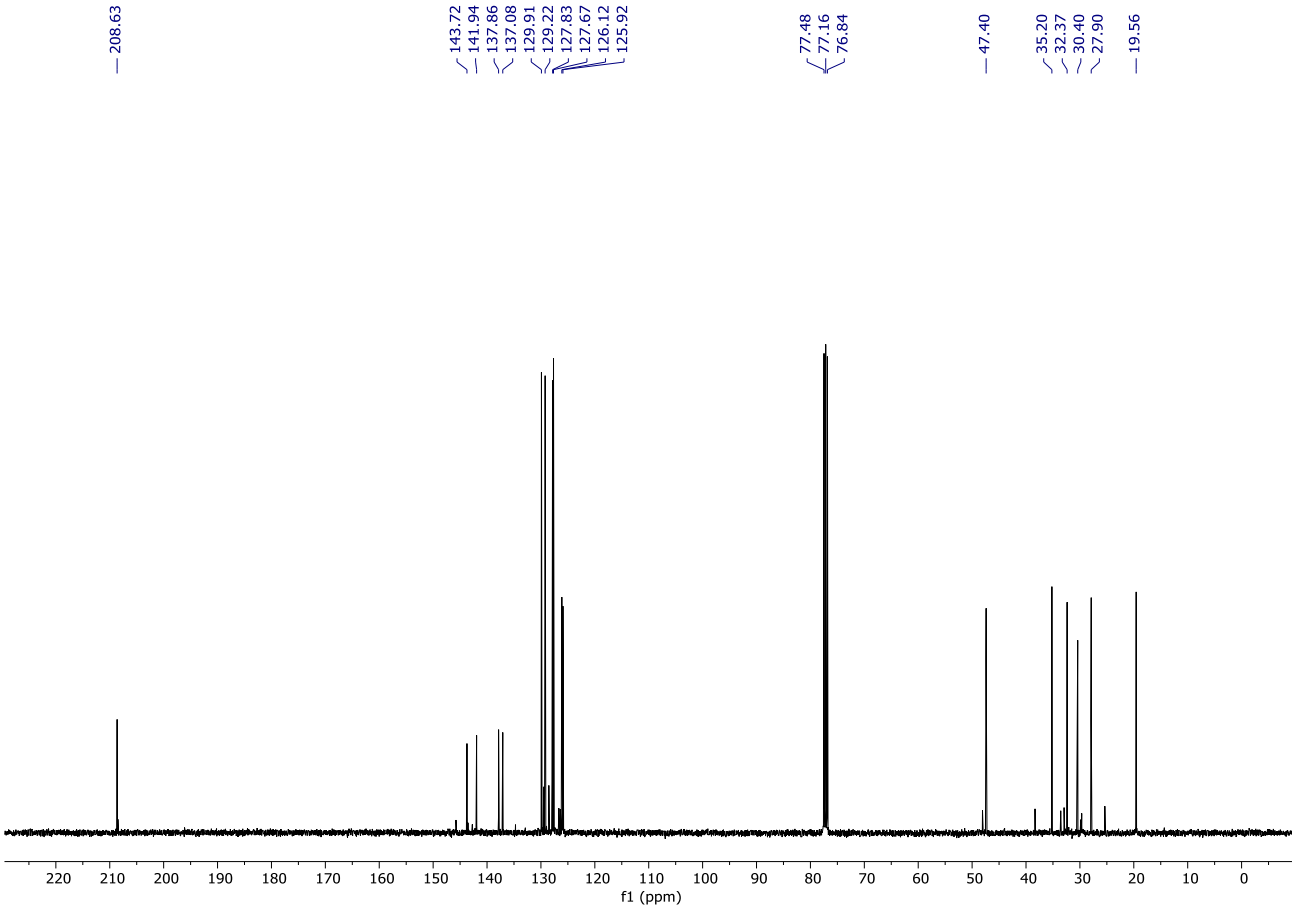

Ph
Ph
Me
O
(E)-14
+
Ph
Ph
Me
O
(Z)-14
inseparable mixture
2.3:1 E:Z
f1 (ppm)

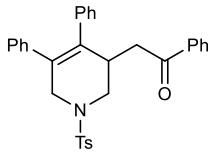

198.78
198.69
148.09
147.81
142.72
142.41
140.93
138.22
137.29
131.77
131.69
129.12
129.06
128.85
128.76
128.66
128.62
128.46
127.99
127.50
127.19
127.09
126.86
126.74
126.42
77.42
77.16
76.91
40.18
32.17
32.01
29.54
27.20
27.03
26.90
26.40
f1 (ppm)


Ph
Ph
Me
O

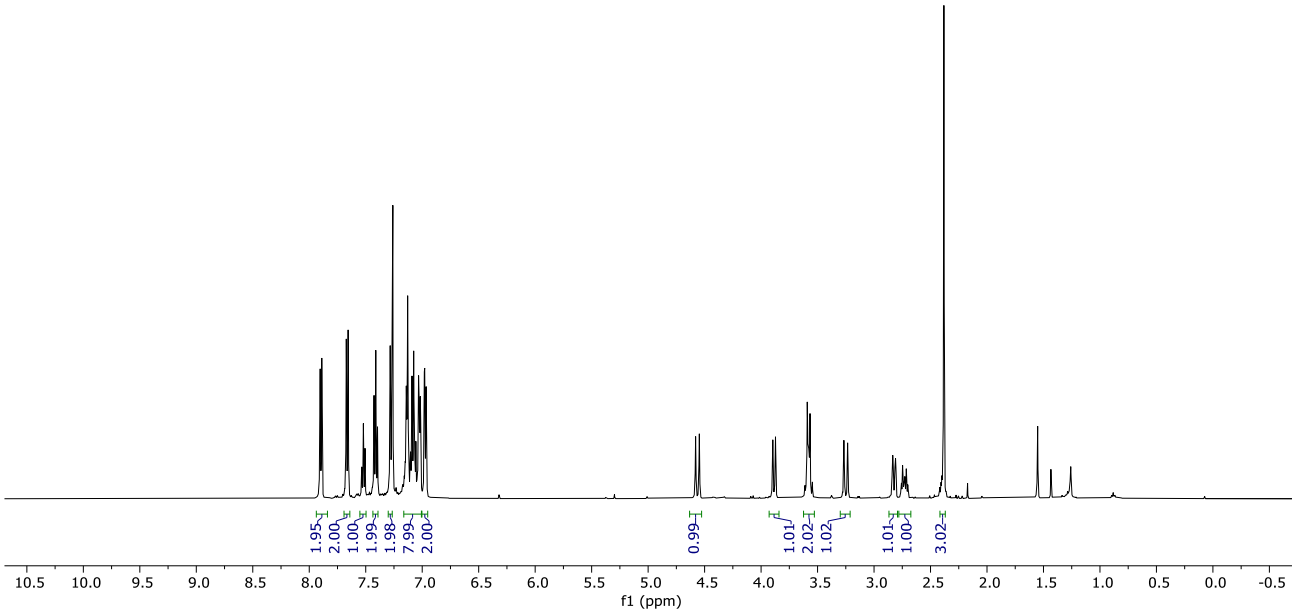
15

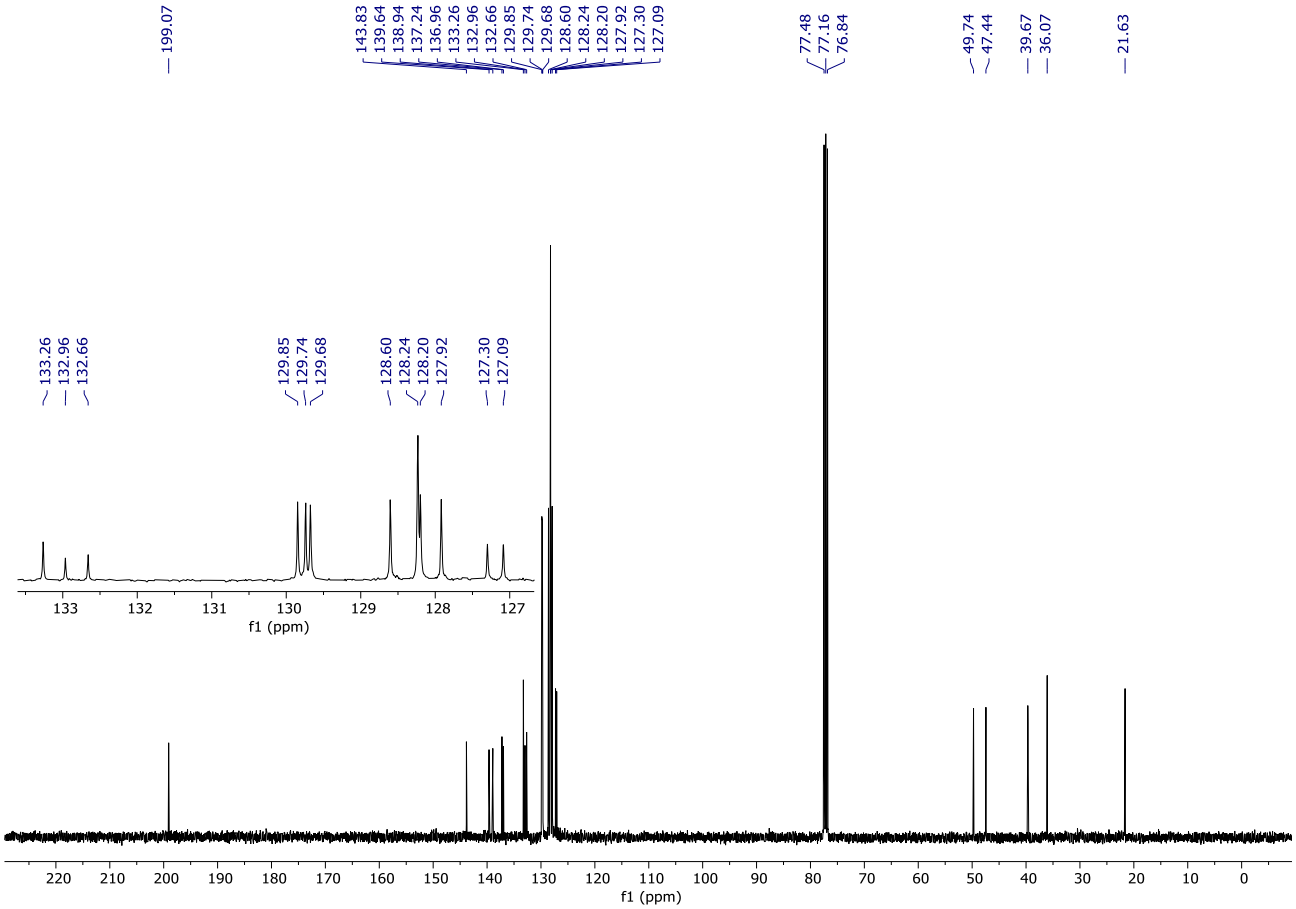

1.04
1.05
1.03
2.12
2.97
0.97
2.03
1.01
f1 (ppm)
6.00
4.00
1.04
1.05
1.03
2.12
2.97
0.97
2.03
1.01
f1 (ppm)

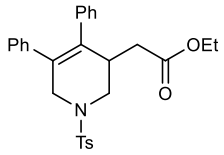

208.63
143.72
141.94
137.86
137.08
129.91
129.22
127.83
127.67
126.12
125.92
77.48
77.16
76.84
47.40
35.20
32.37
30.40
27.90
19.56
f1 (ppm)


Ph
Ph
Ph
O
N
Ts

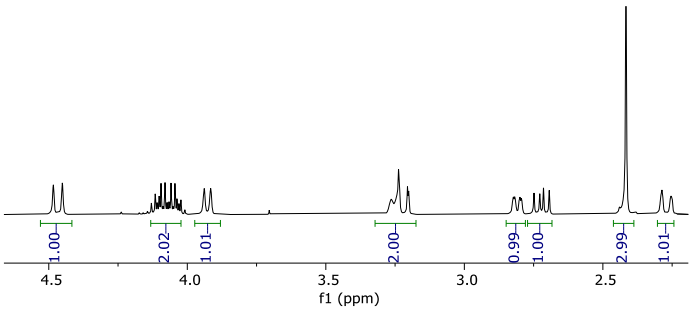
17

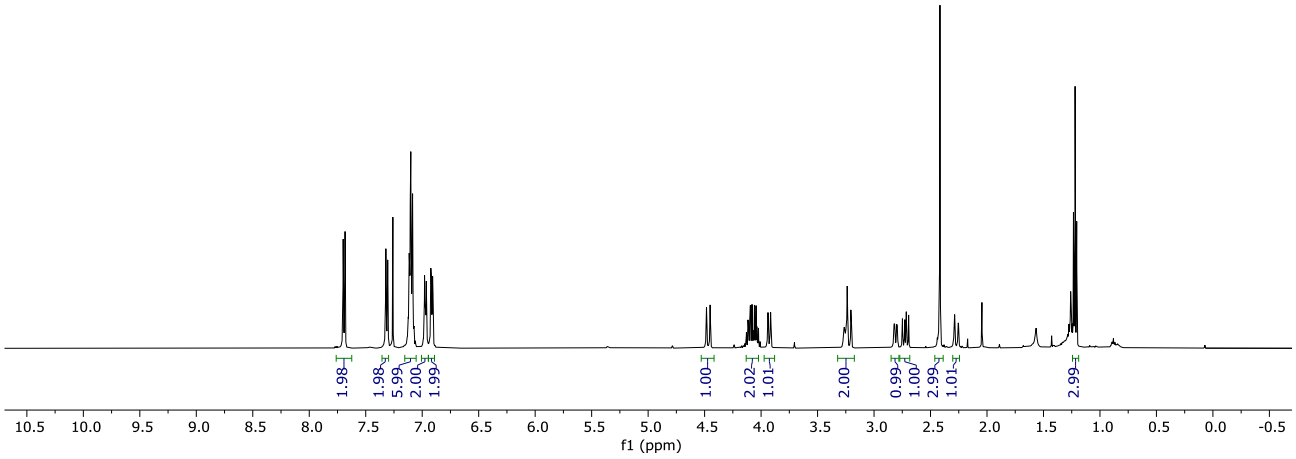

1.95
2.00
1.00
1.99
1.98
7.99
2.00
0.99
1.01
2.02
1.02
1.01
1.00
3.02
f1 (ppm)

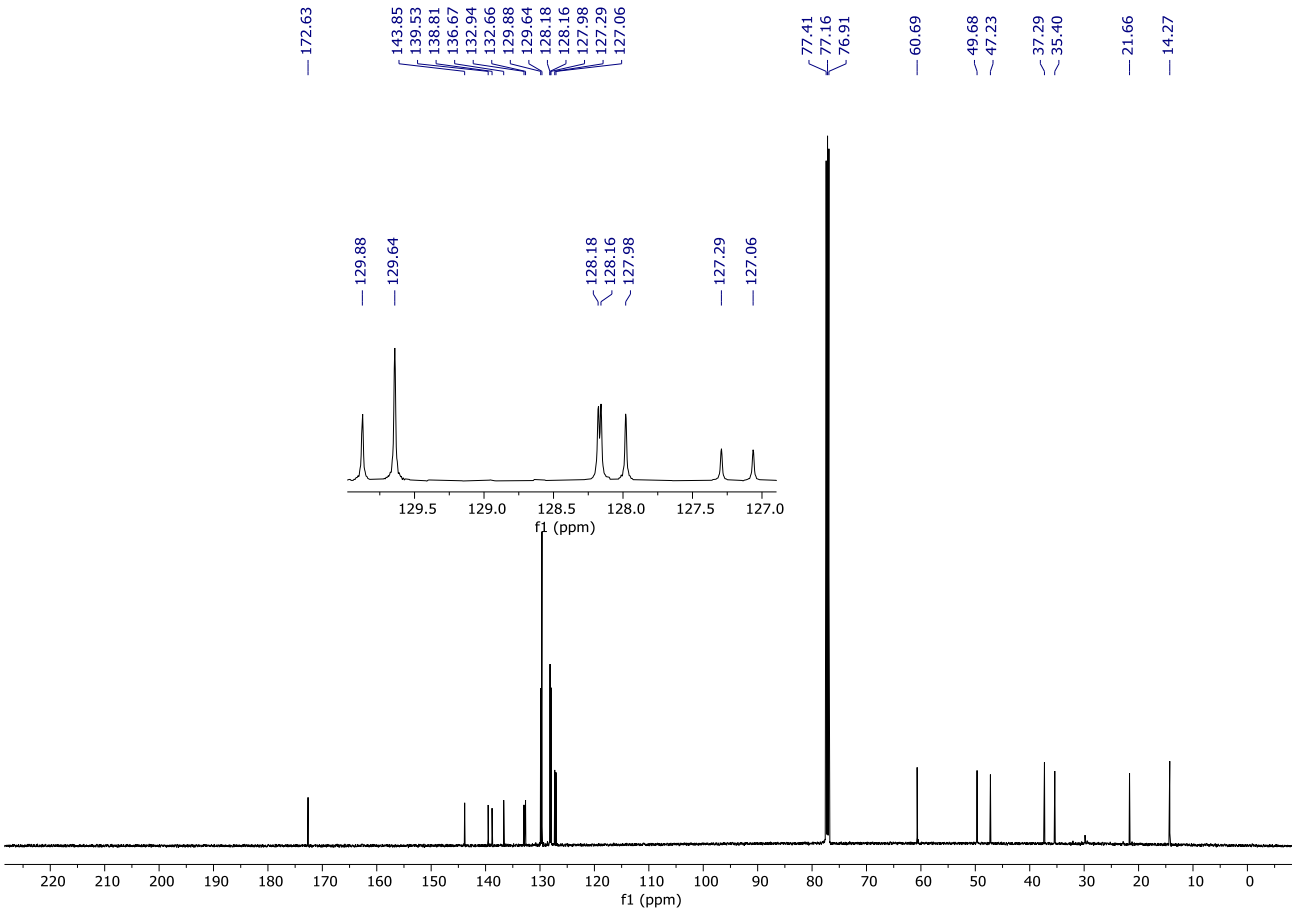

199.07
143.83
139.64
138.94
137.24
136.96
133.26
132.96
132.66
129.85
129.74
129.68
128.60
128.24
128.20
127.92
127.30
127.09
77.48
77.16
76.84
49.74
47.44
39.67
36.07
21.63
f1 (ppm)

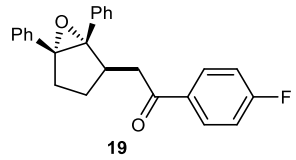

Ph
Ph
OEt
O
N
Ts

18

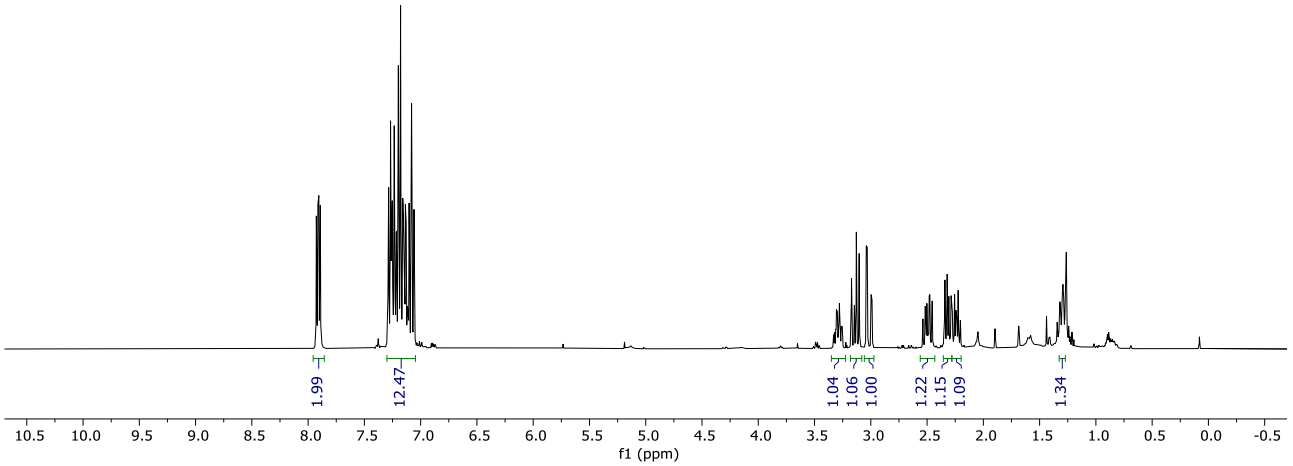

1.00
2.02
1.01
2.00
0.99
1.00
2.99
1.01
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

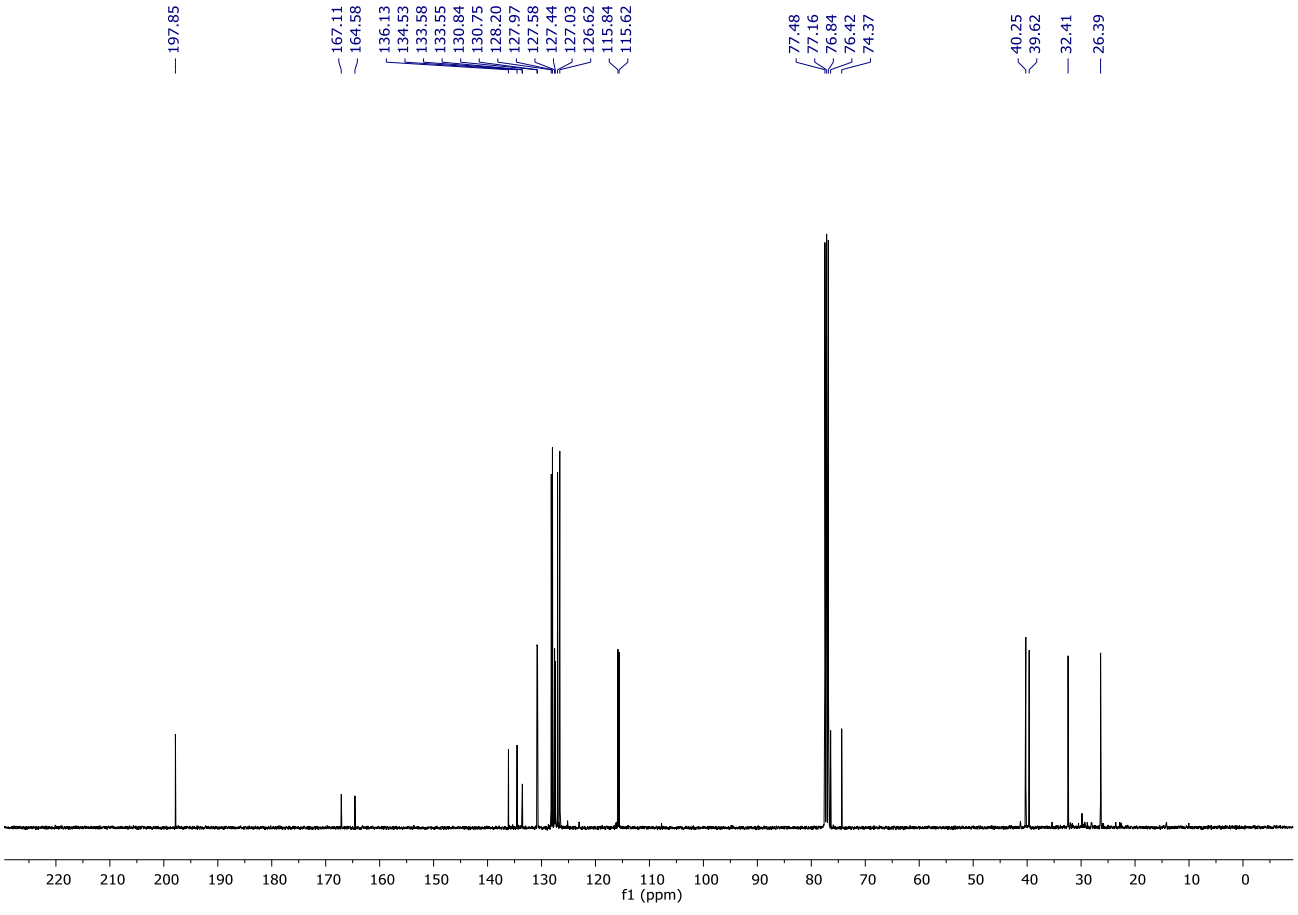

1.98
1.98
5.99
2.00
1.99
1.00
2.02
1.01
2.00
0.99
1.00
2.99
1.01
2.99
f1 (ppm)


172.63
143.85
139.53
138.81
136.67
132.94
132.66
129.88
129.64
128.18
128.16
127.98
127.29
127.06
77.41
77.16
76.91
60.69
49.68
47.23
37.29
35.40
21.66
14.27
129.88
129.64
128.18
128.16
127.98
127.29
127.06
f1 (ppm)
f1 (ppm)

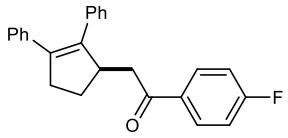

Ph
O
Ph
F
O

19

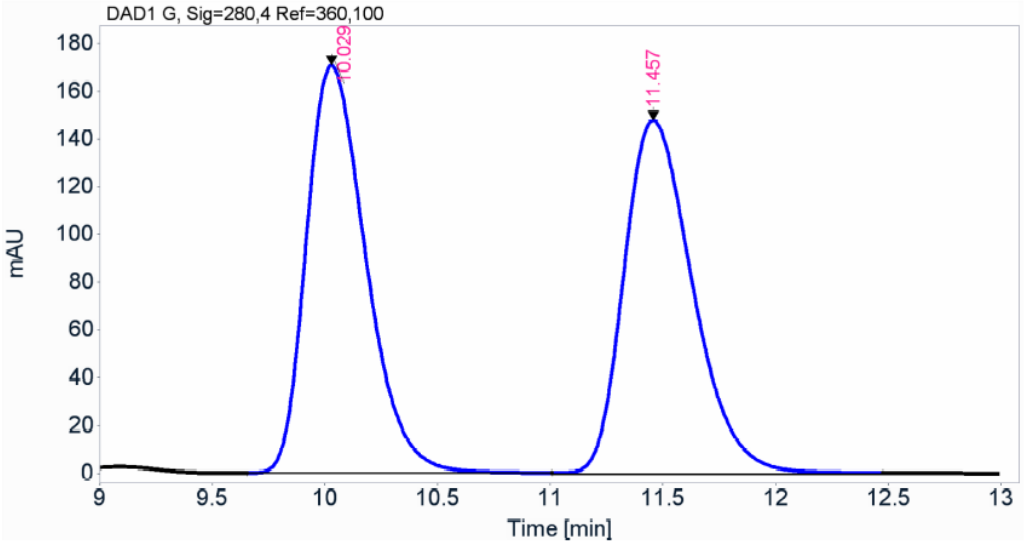

1.99
12.47
1.04
1.06
1.00
1.22
1.15
1.09
1.34
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.85
167.11
164.58
136.13
134.53
133.58
133.55
130.84
130.75
128.20
127.97
127.58
127.44
127.03
126.62
115.84
115.62
77.48
77.16
76.84
76.42
74.37
40.25
39.62
32.41
26.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8. HPLC Traces

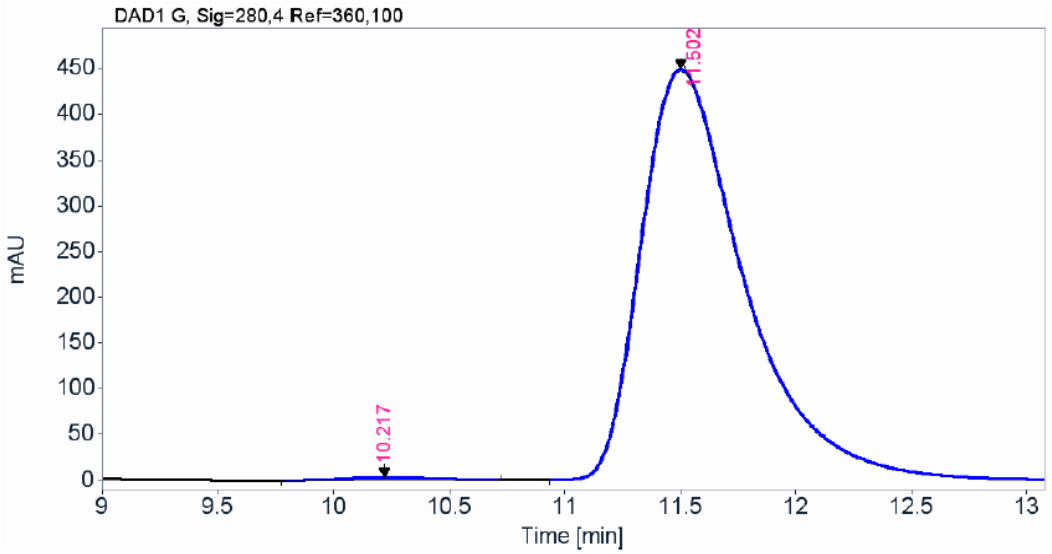


2a



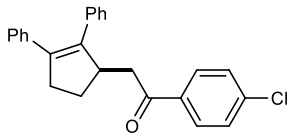
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.029	BB	0.2853	3118.960	170.5840	49.78
11.457	MM	0.3539	3146.153	148.1645	50.22

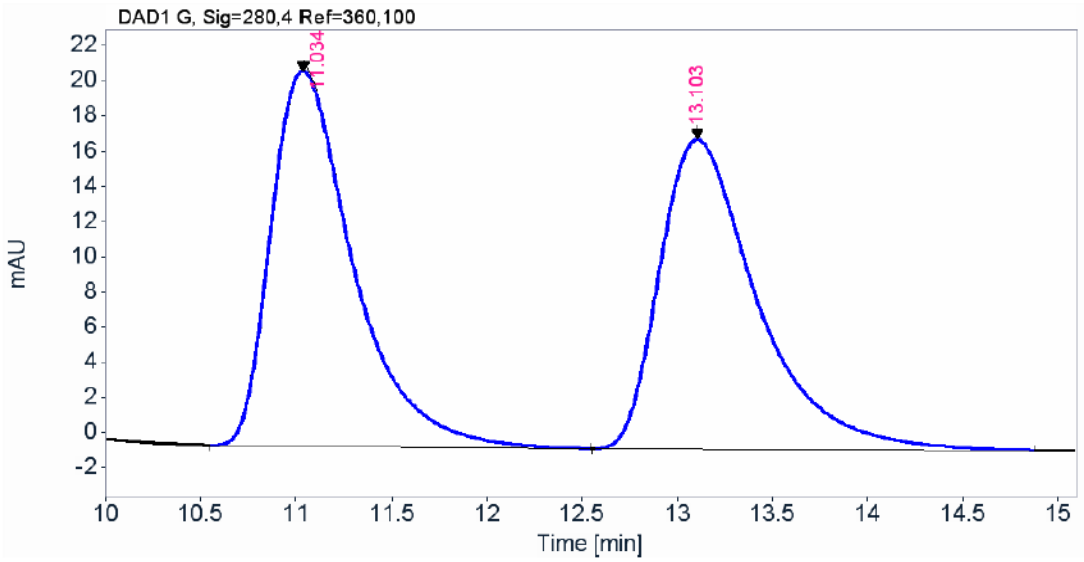


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.217	BB	0.3648	78.173	3.0932	0.56
11.502	BB	0.4683	13926.665	448.4822	99.44

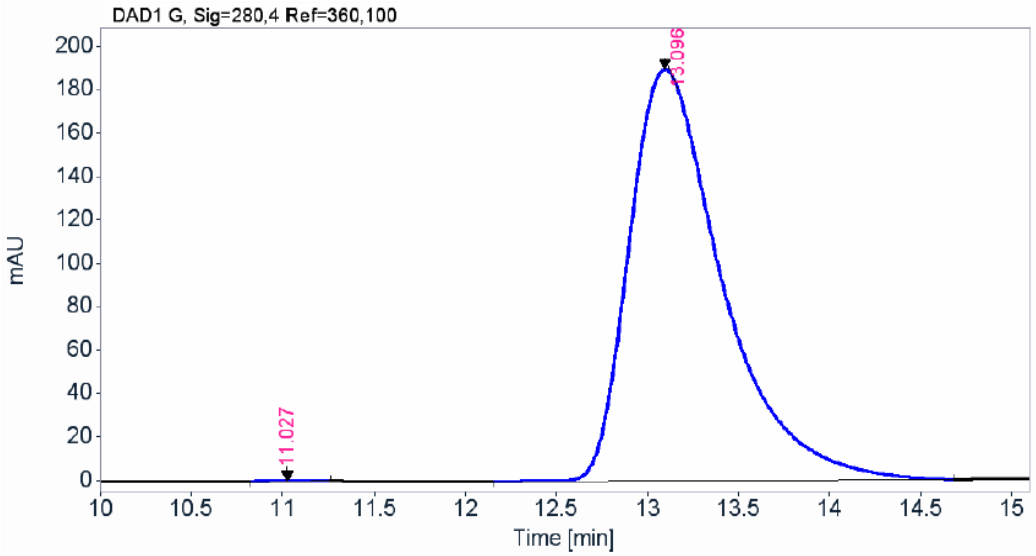


2b



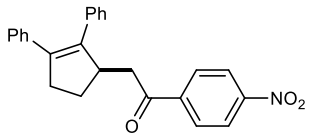
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.034	BB	0.4438	632.276	21.3348	50.22
13.103	BB	0.5450	626.827	17.6228	49.78

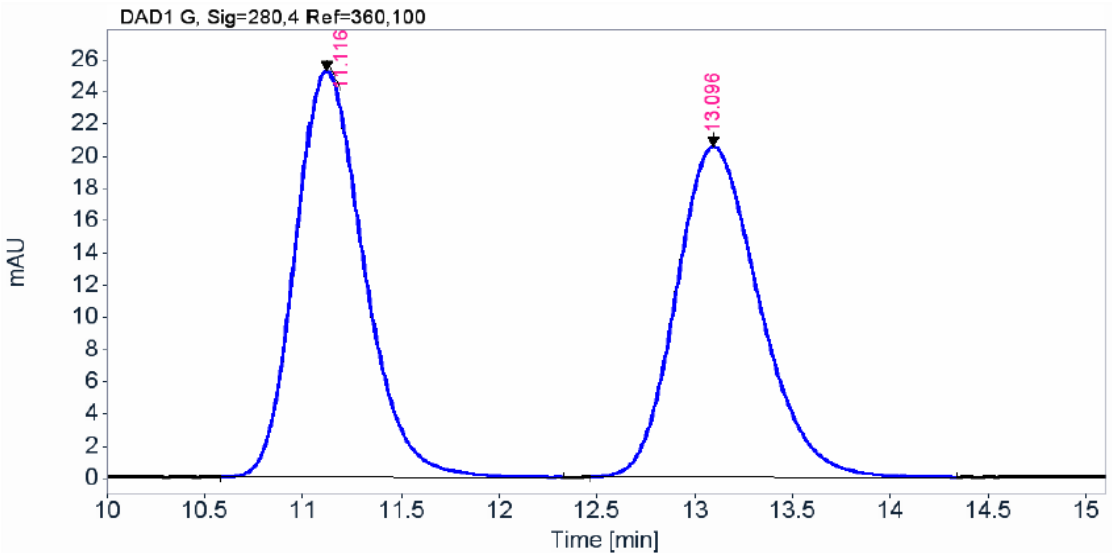


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.027	MM	0.2625	12.040	0.5864	0.18
13.096	BB	0.5371	6712.137	189.5585	99.82

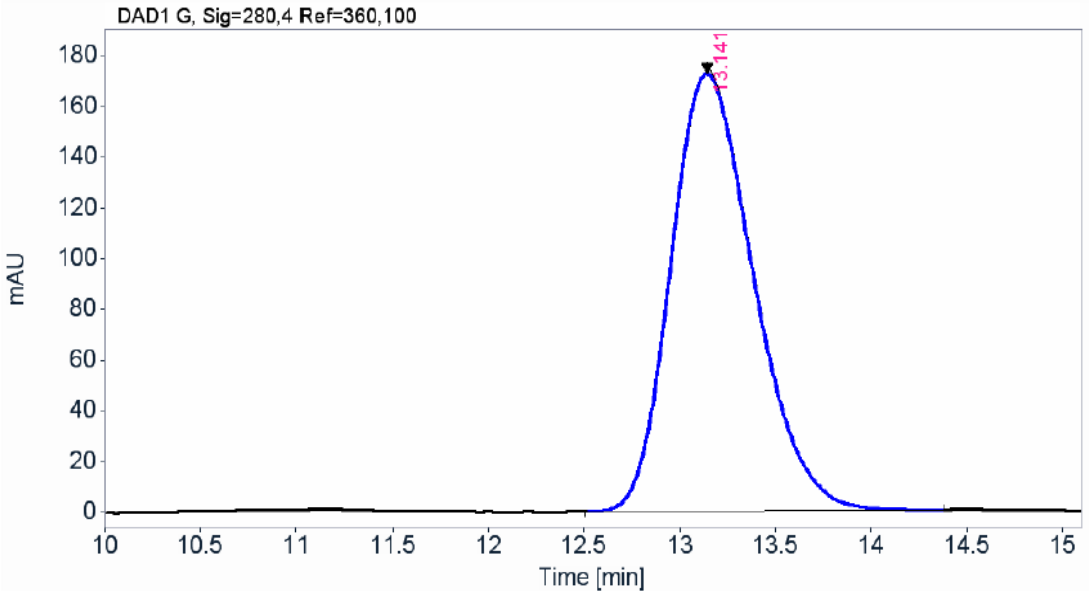


2c



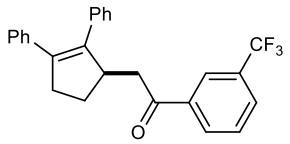
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.116	BB	0.3703	605.605	25.2110	50.05
13.096	BB	0.4539	604.370	20.5005	49.95

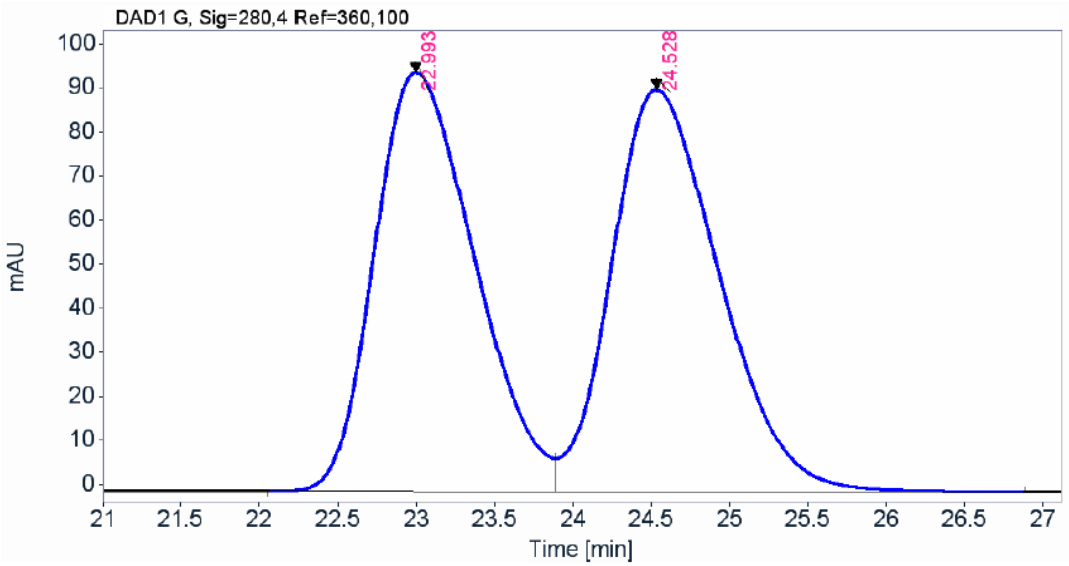


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.141	BB	0.4661	5177.145	172.5381	100.00

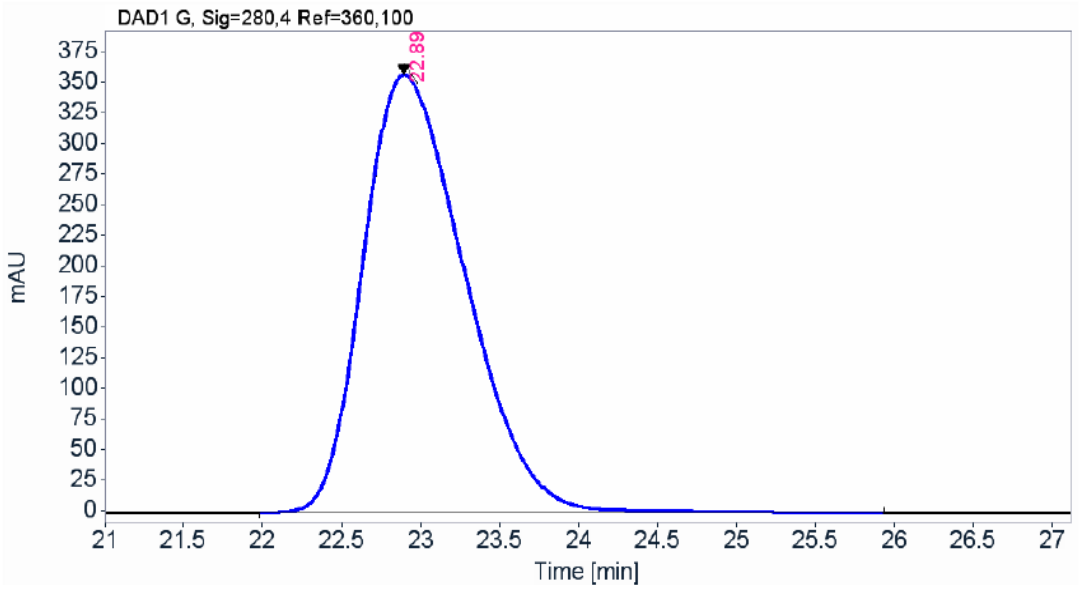


2d



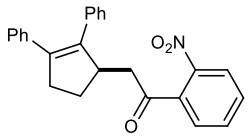
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
22.993	BV	0.6923	4226.570	95.1372	49.20
24.528	VB	0.7502	4363.409	91.2046	50.80

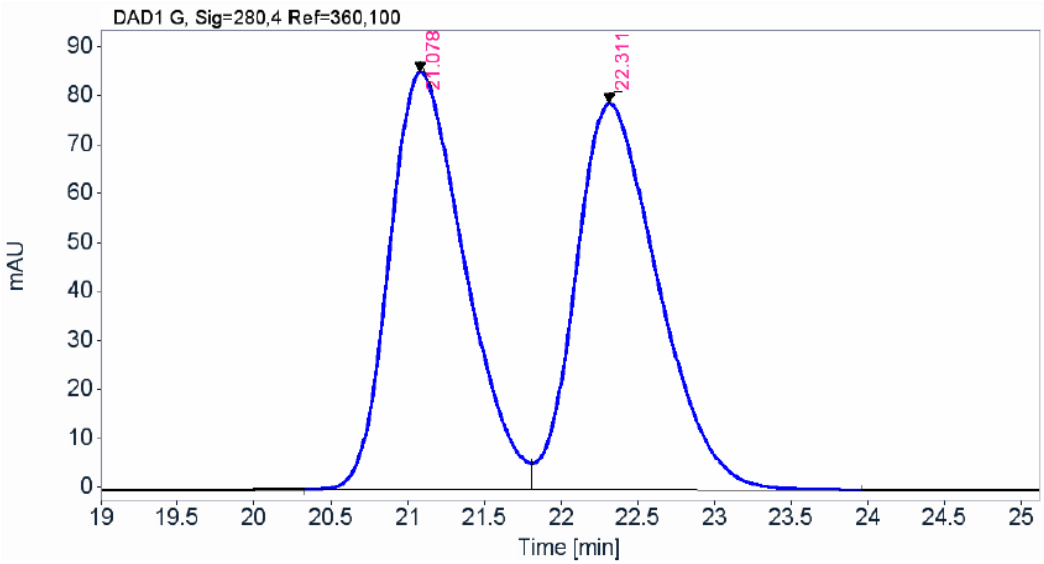


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
22.890	BB	0.6955	16043.541	357.5584	100.00

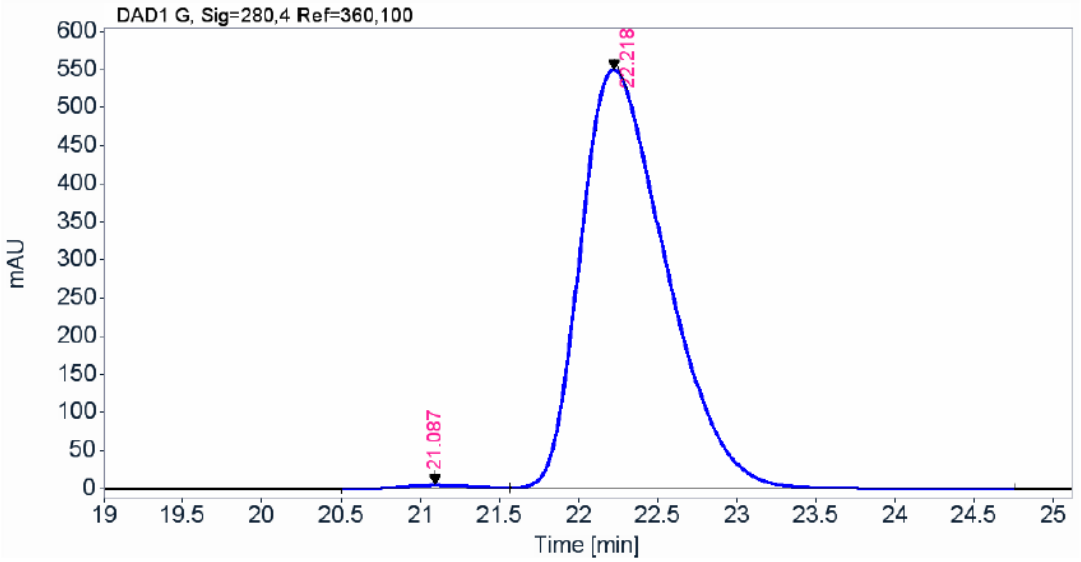


2d



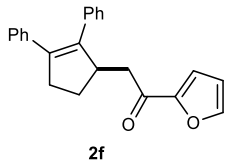
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
21.078	BV	0.5209	2898.109	85.1787	49.60
22.311	VB	0.5659	2944.906	78.8214	50.40

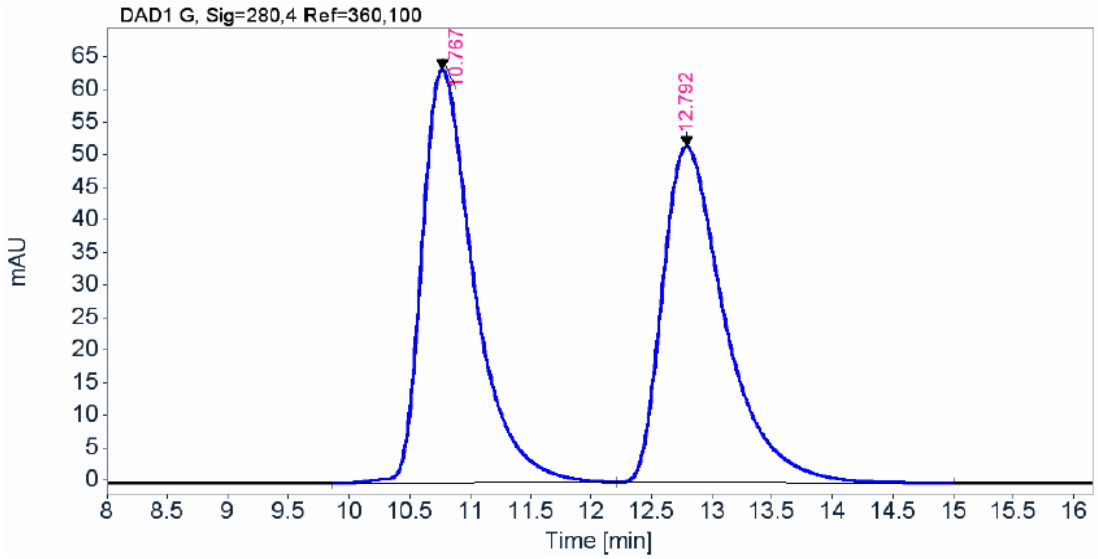


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
21.087	BV	0.4637	156.392	4.8048	0.75
22.218	VB	0.5771	20692.539	549.7675	99.25

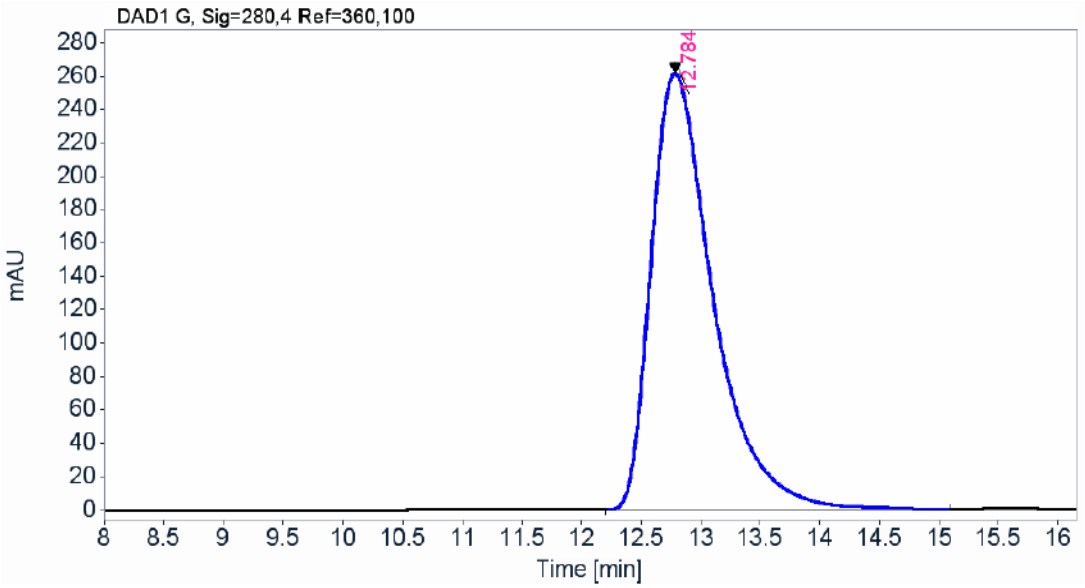


2f



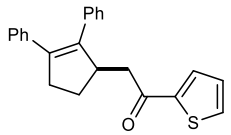
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.767	BB	0.4545	1895.380	63.4434	50.58
12.792	BB	0.5450	1851.974	51.5707	49.42

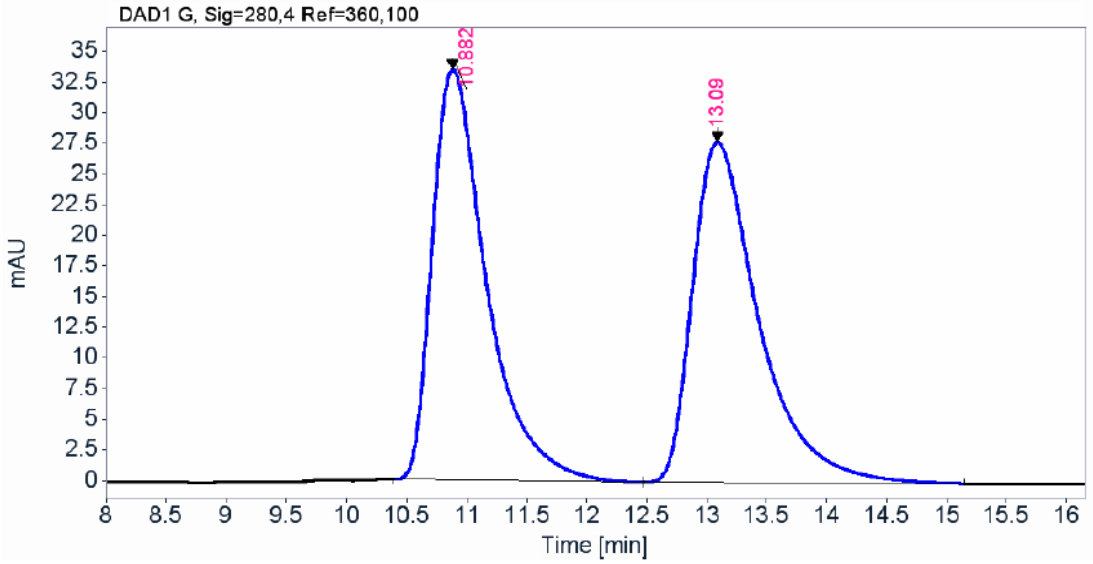


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.784	BB	0.5467	9478.247	261.6157	100.00

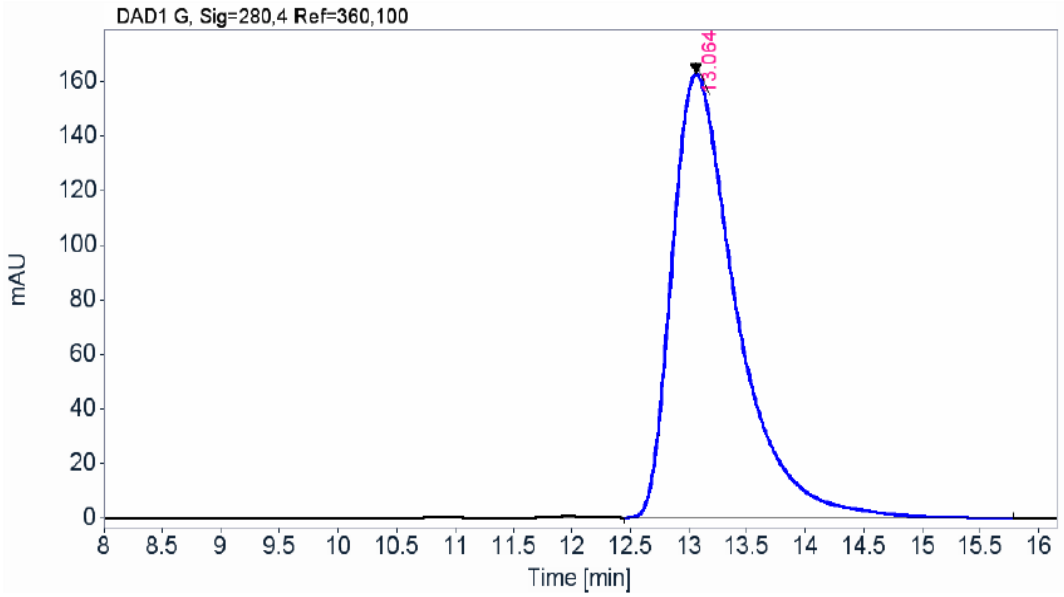


2g



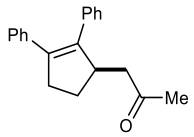
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.882	BB	0.4743	1051.981	33.5021	49.69
13.090	BB	0.5675	1065.284	27.7727	50.31

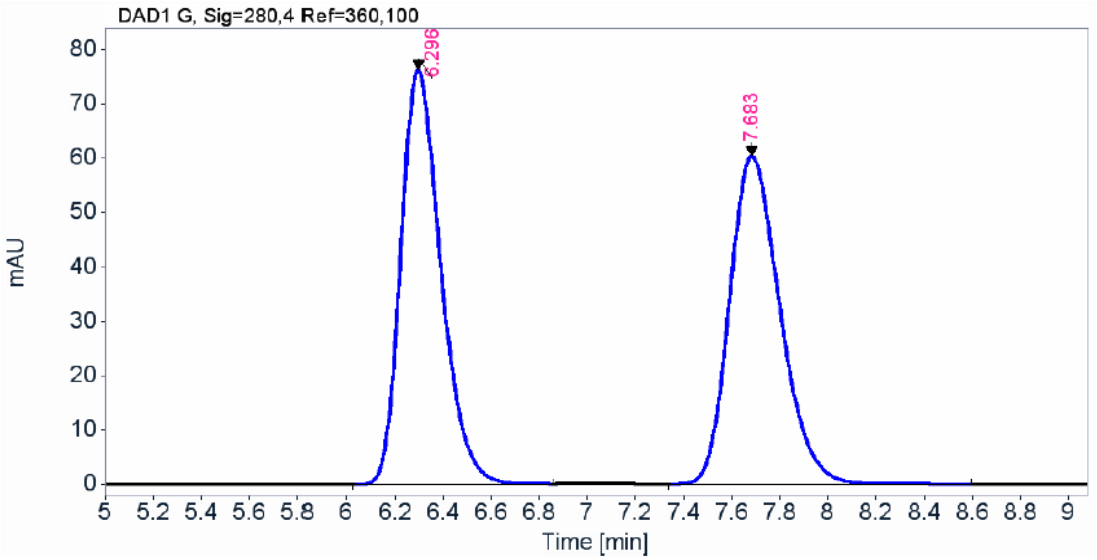


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.064	BB	0.5771	6236.902	162.7421	100.00

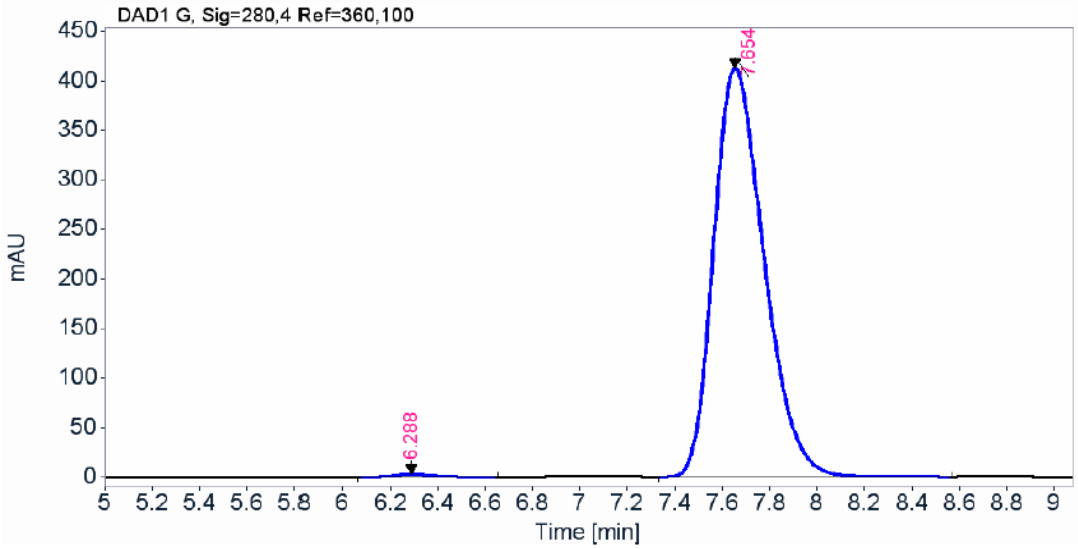


2h



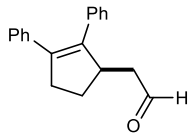
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
6.296	BB	0.1762	879.297	76.4348	49.97
7.683	BB	0.2238	880.402	60.5037	50.03

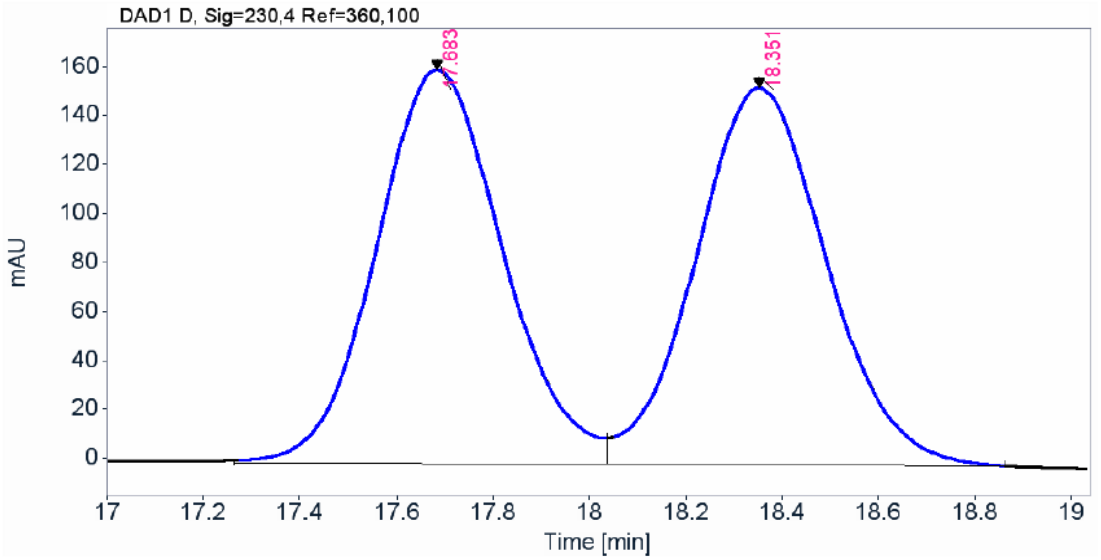


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
6.288	BB	0.1784	33.529	2.9102	0.55
7.654	BB	0.2282	6088.825	412.6321	99.45

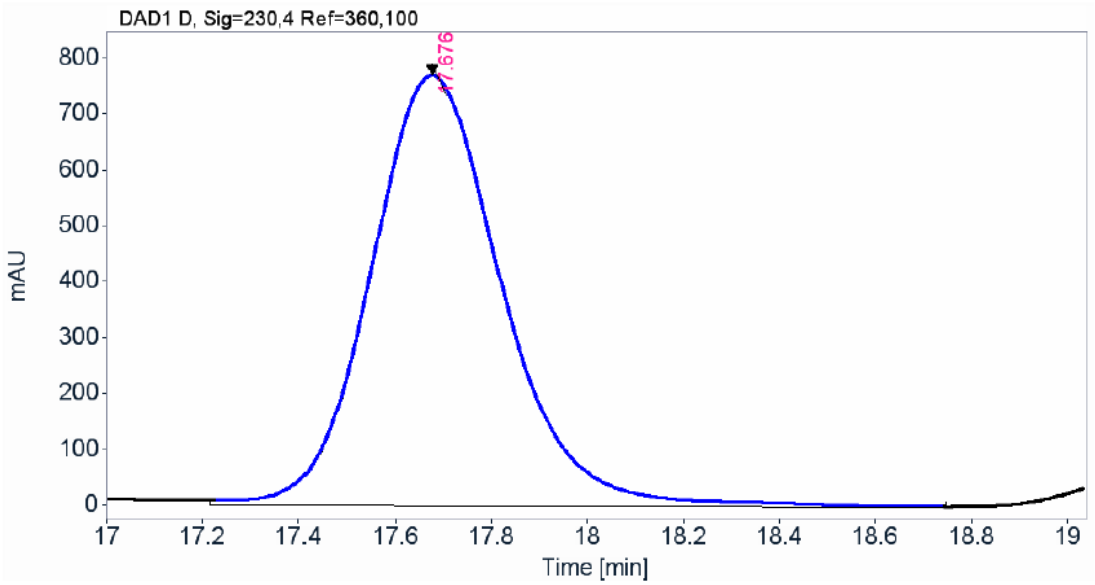


2i



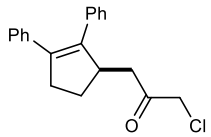
Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
17.683	MF	0.3032	2926.291	160.8415	50.26
18.351	FM	0.3134	2896.092	153.9929	49.74

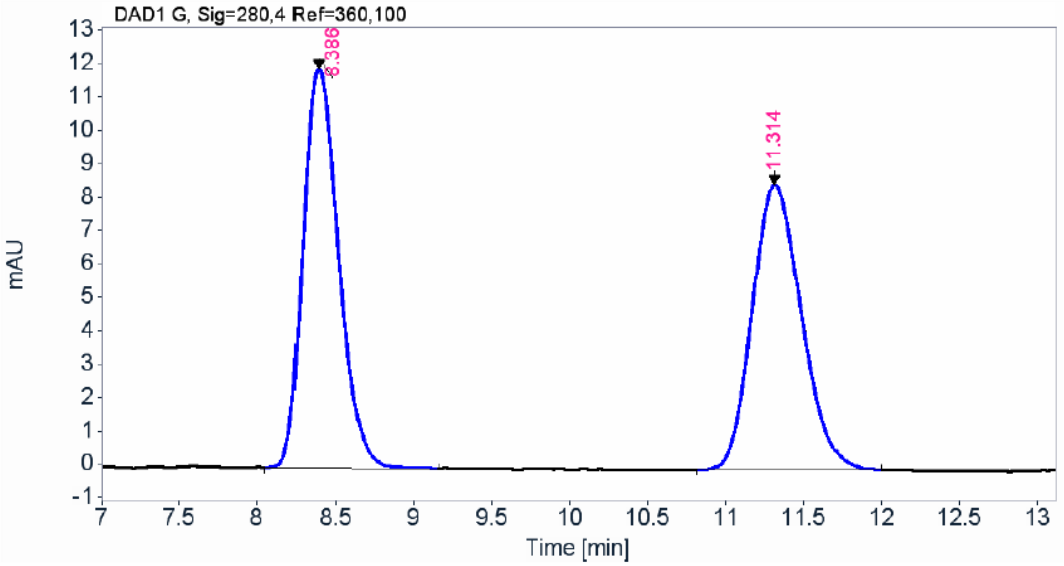


Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
17.676	VB	0.2906	14573.796	770.5792	100.00

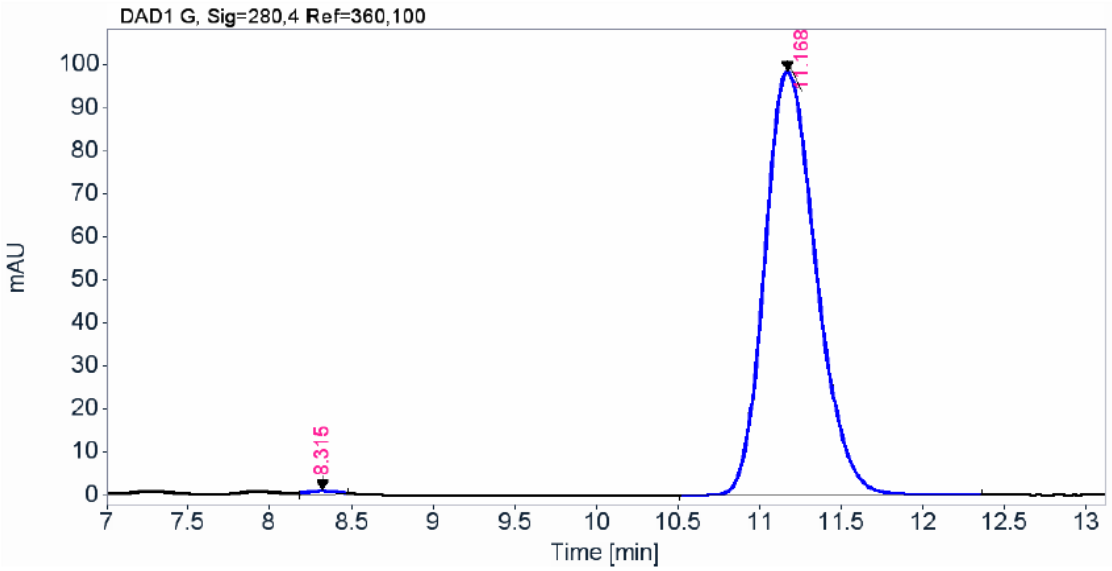


2j



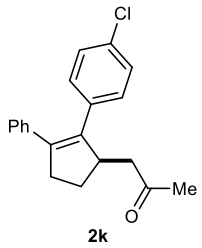
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.386	BB	0.2410	187.284	11.9402	49.96
11.314	BB	0.3344	187.576	8.5334	50.04

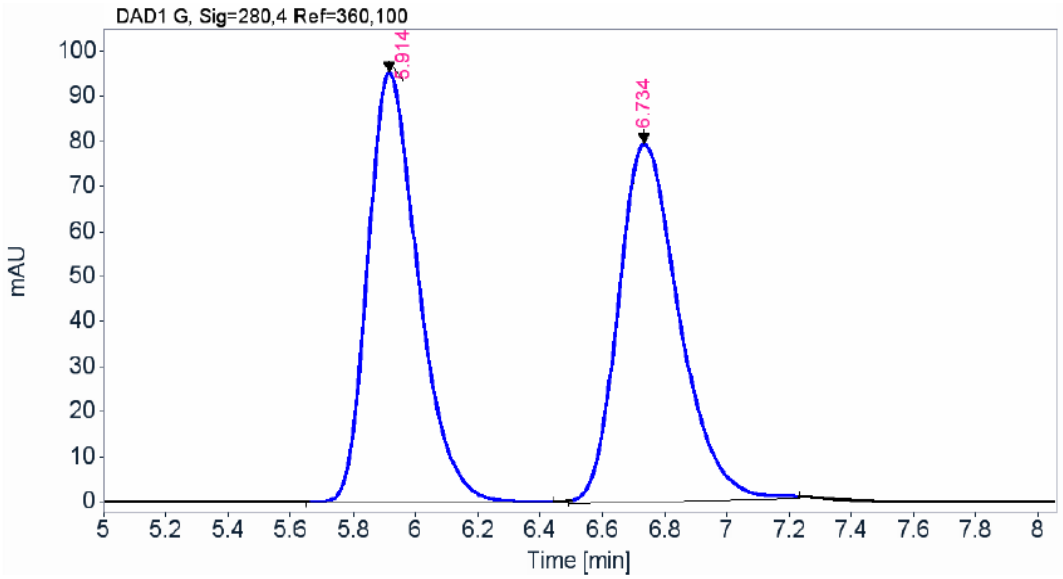


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.315	MM	0.2190	12.330	0.9385	0.57
11.168	BB	0.3415	2157.306	98.4891	99.43

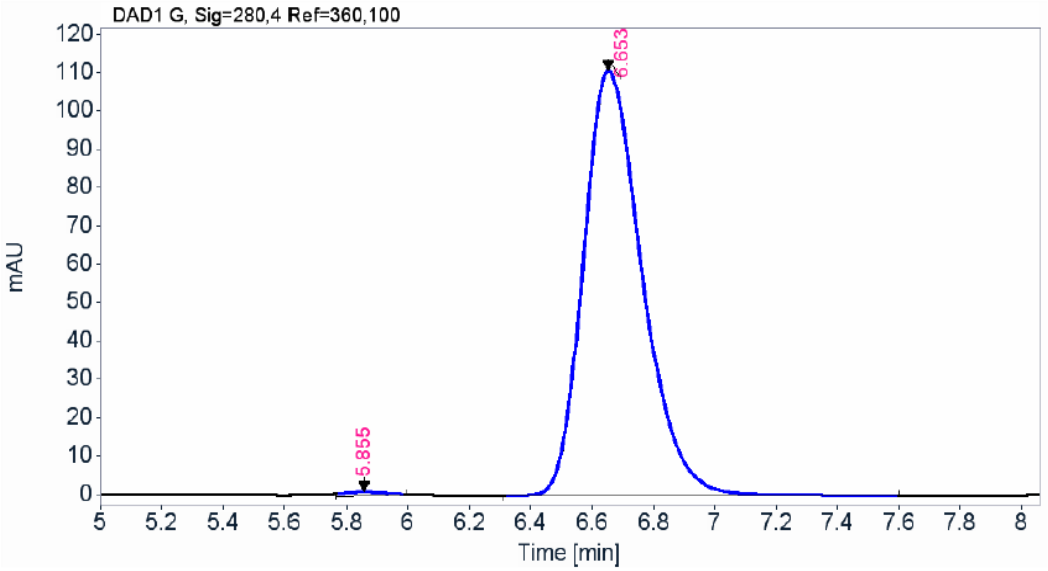


2k



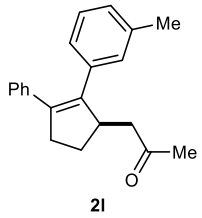
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.914	BB	0.1729	1071.293	95.4702	49.70
6.734	MM	0.2270	1084.264	79.5940	50.30

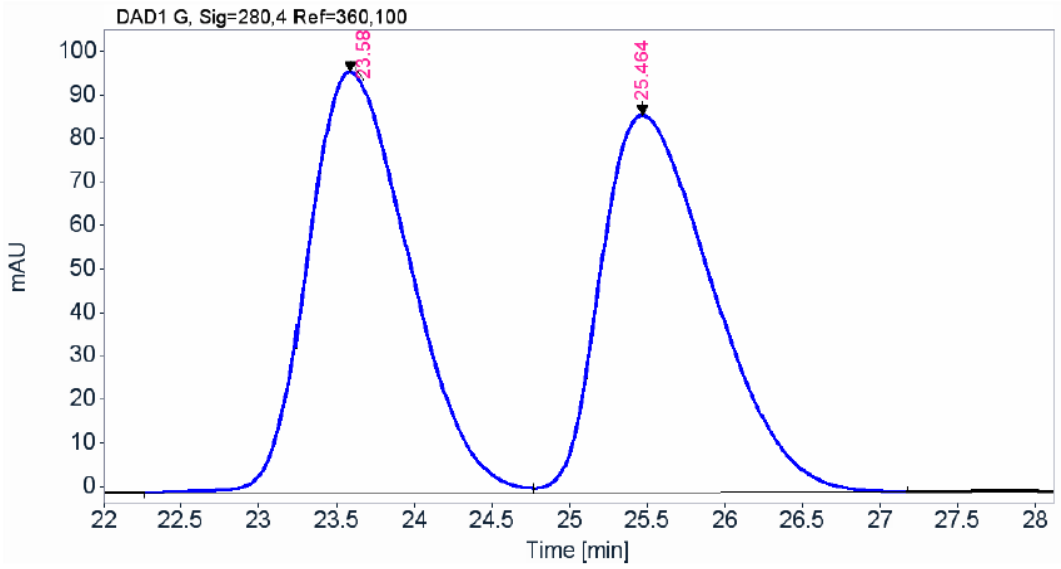


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.855	MM	0.1634	10.888	1.1104	0.73
6.653	BB	0.2053	1475.608	110.8442	99.27

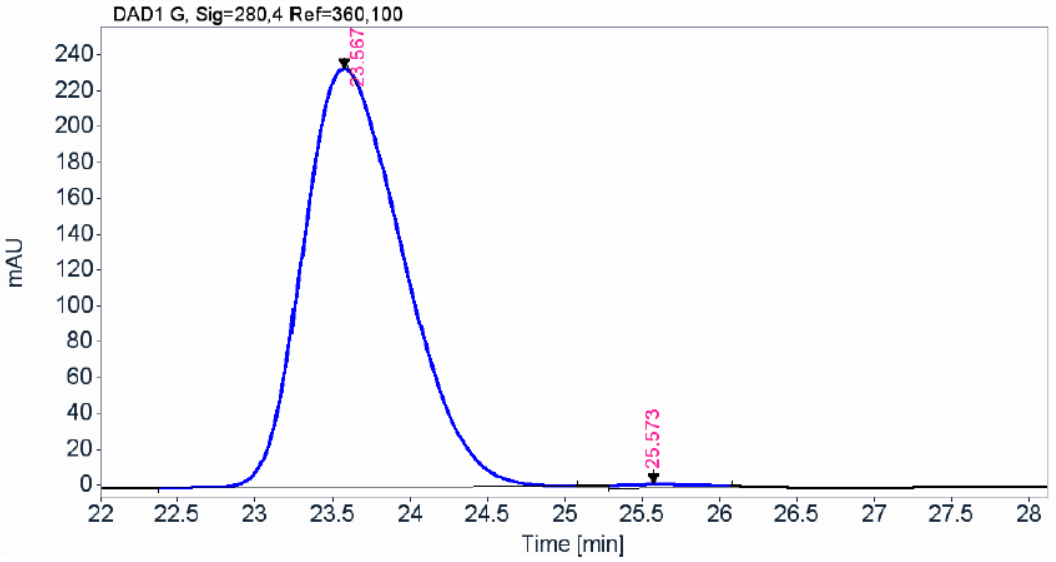


2l



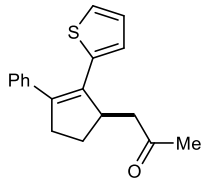
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
23.580	BV	0.7173	4352.182	96.6605	50.23
25.464	VB	0.7813	4311.564	86.5309	49.77

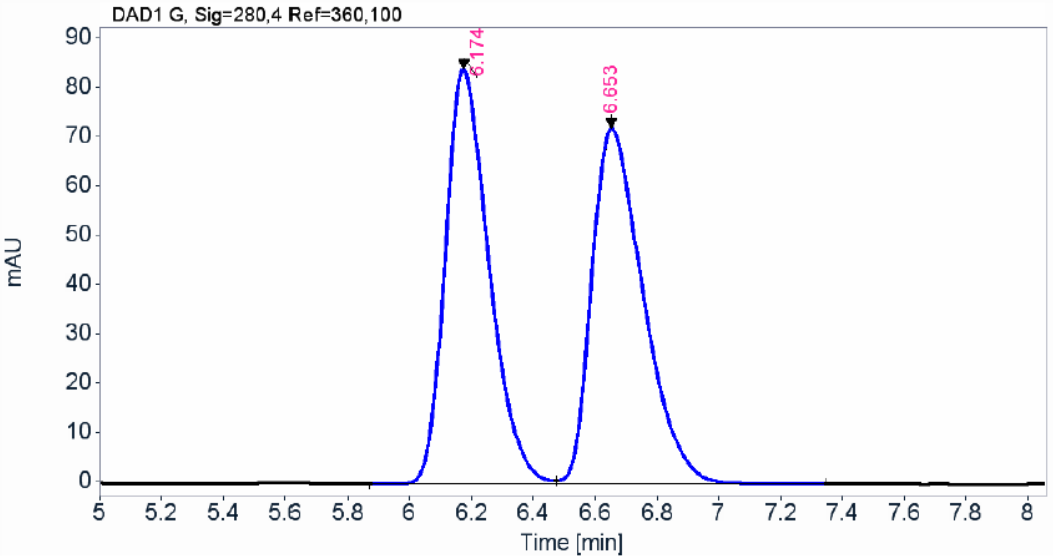


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
23.567	BB	0.6941	10436.622	233.2352	99.28
25.573	MM	0.4346	75.918	2.0995	0.72

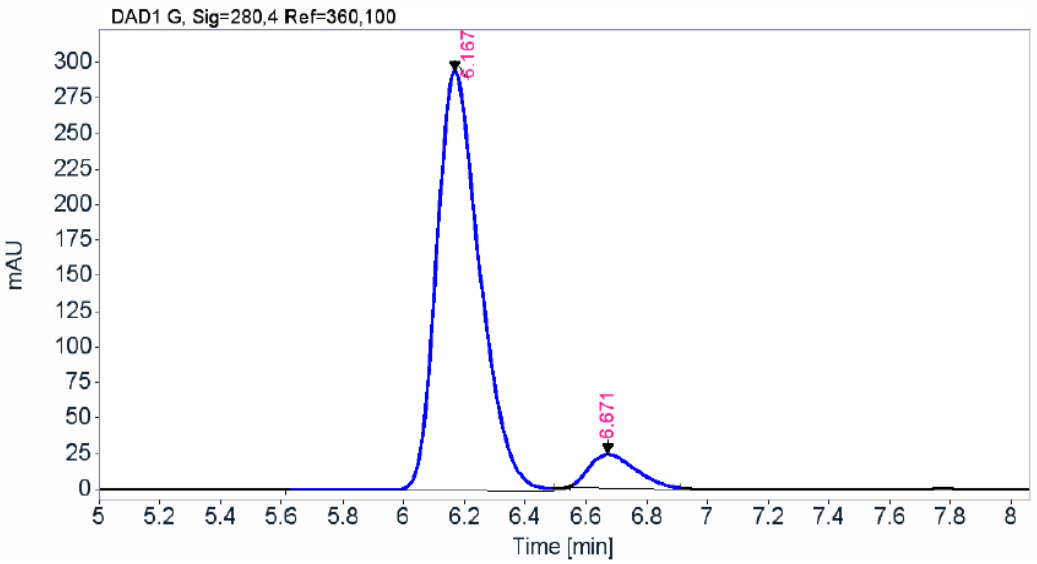


2m



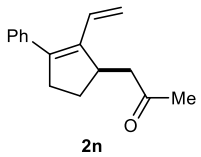
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
6.174	BV	0.1487	827.343	84.1710	49.76
6.653	VB	0.1772	835.363	72.0672	50.24

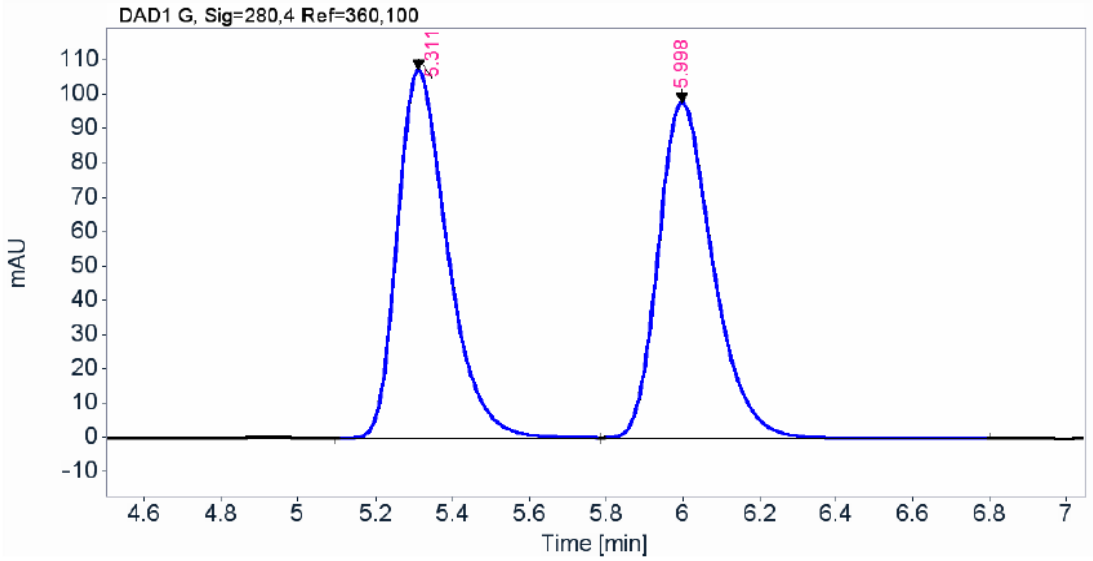


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
6.167	MM	0.1650	2925.138	295.4926	91.75
6.671	MM	0.1812	262.898	24.1824	8.25

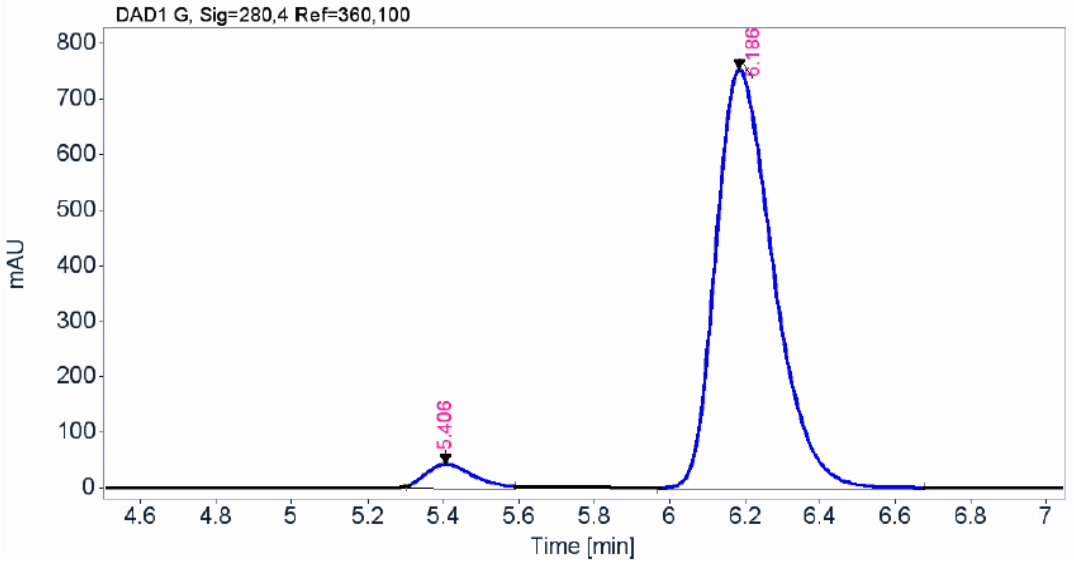


2n



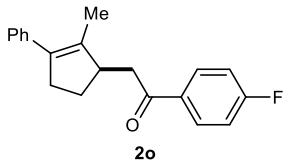
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.311	BB	0.1373	970.374	107.5104	50.06
5.998	BB	0.1513	968.103	97.9234	49.94

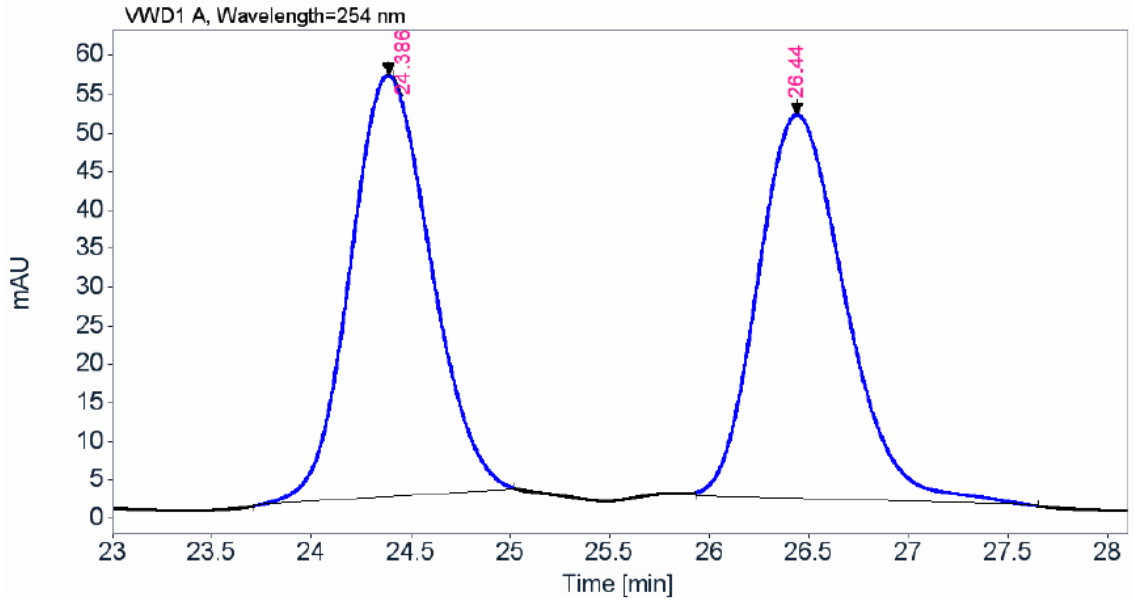


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.406	MM	0.1516	391.831	43.0827	4.64
6.186	MM	0.1773	8051.293	756.6624	95.36

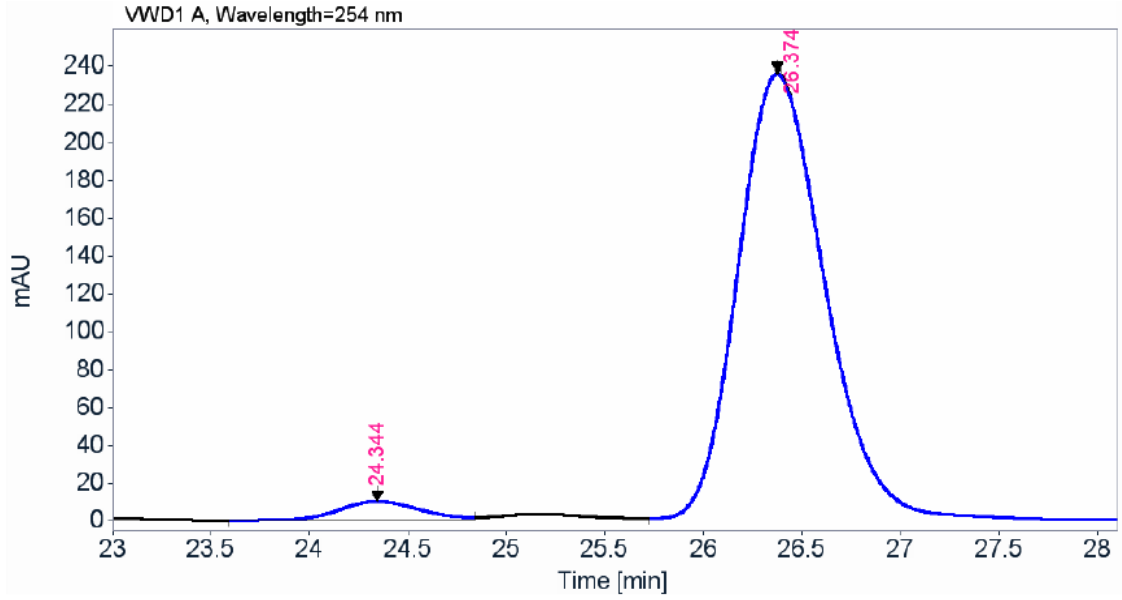


2o



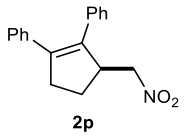
Signal: VWD1 A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
24.386	MM	0.4674	1535.666	54.7579	50.38
26.440	MM	0.5061	1512.308	49.8009	49.62

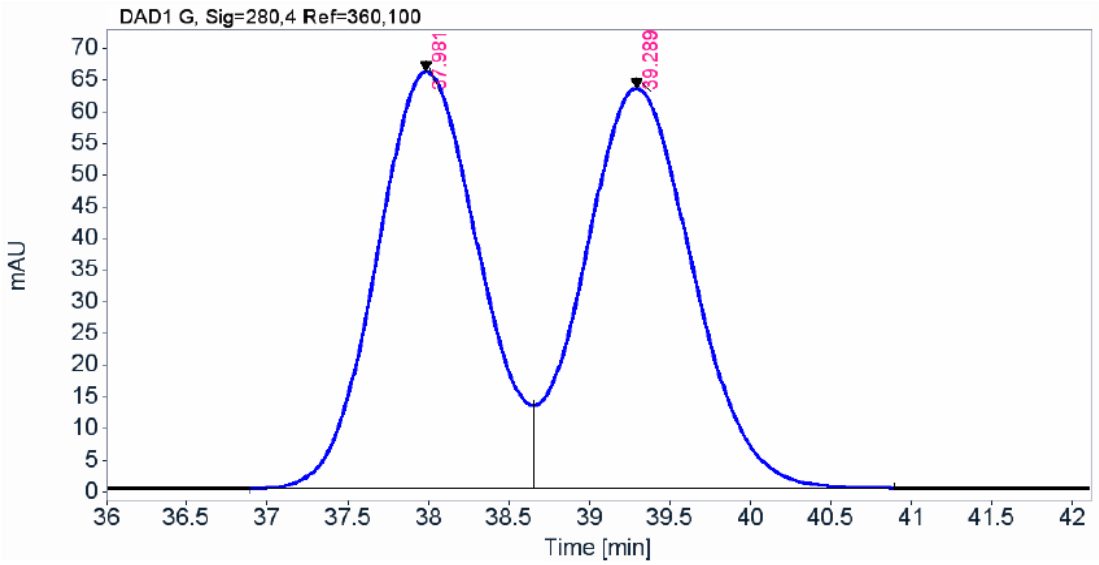


Signal: VWD1 A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
24.344	BV	0.4488	294.824	10.0933	3.90
26.374	VB	0.4774	7264.661	235.8041	96.10

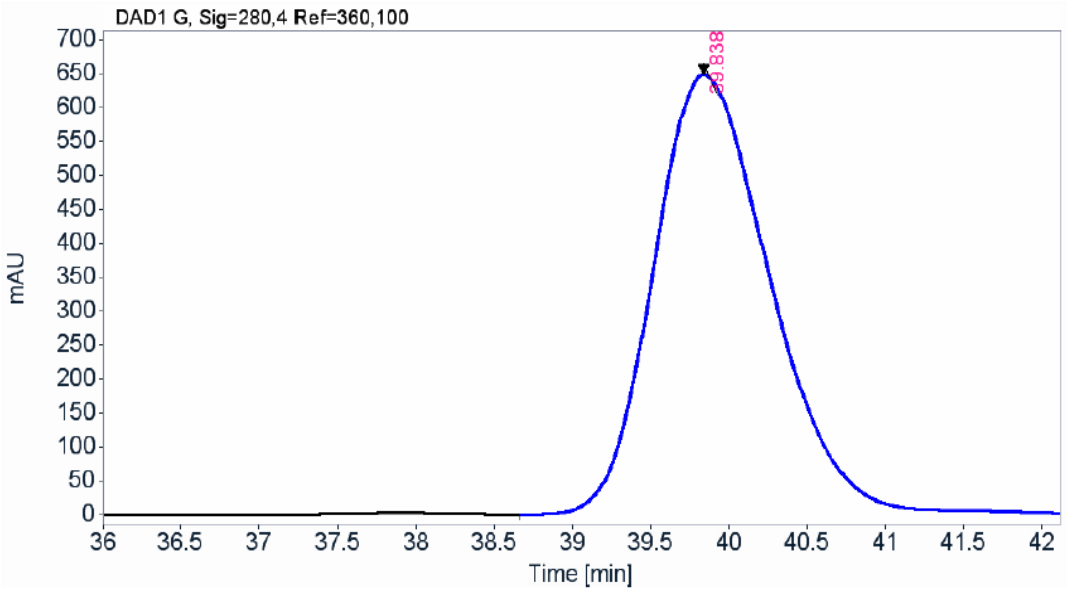


2p



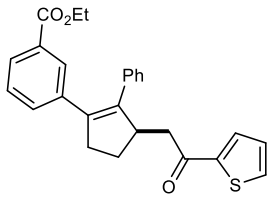
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
37.981	BV	0.6852	2902.111	65.7126	49.38
39.289	VB	0.7247	2975.069	63.0321	50.62

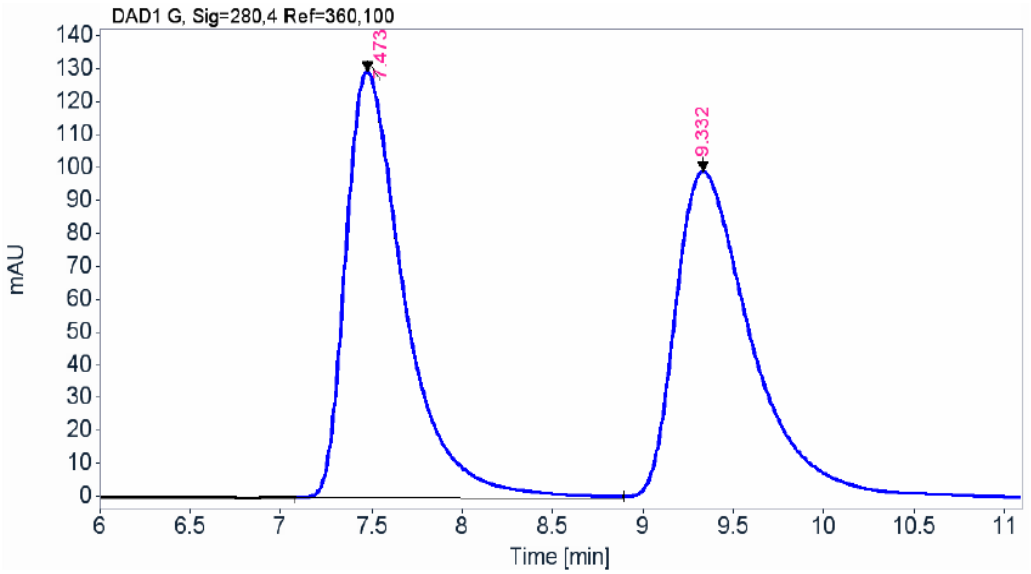


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
39.838	BB	0.8075	33657.621	648.4880	100.00

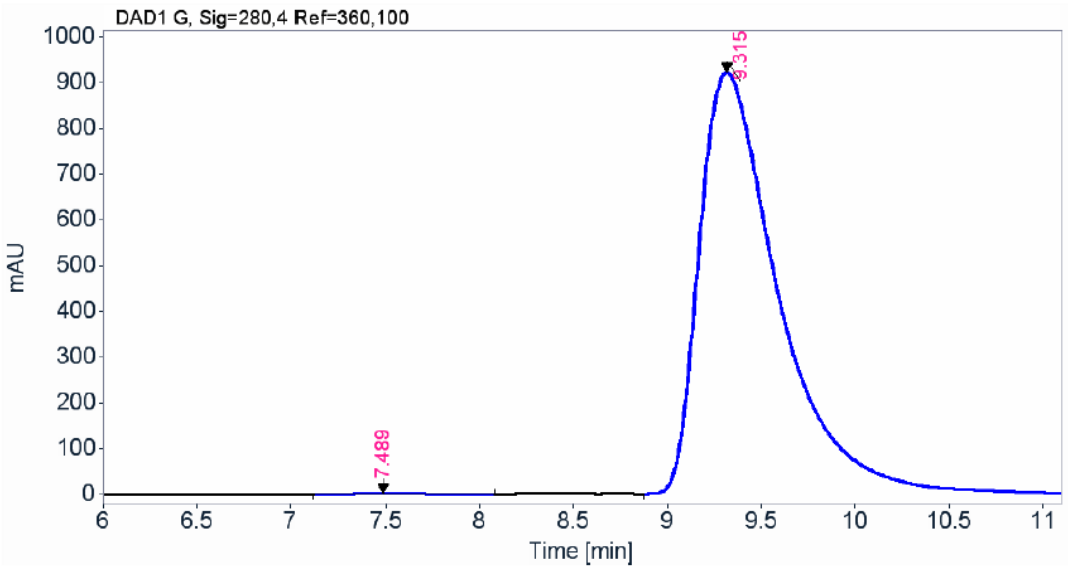


2q



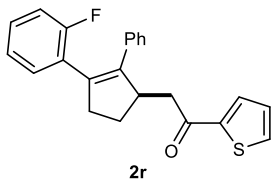
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.473	BV	0.3406	2912.981	129.4387	49.98
9.332	VB	0.4408	2915.487	99.2211	50.02

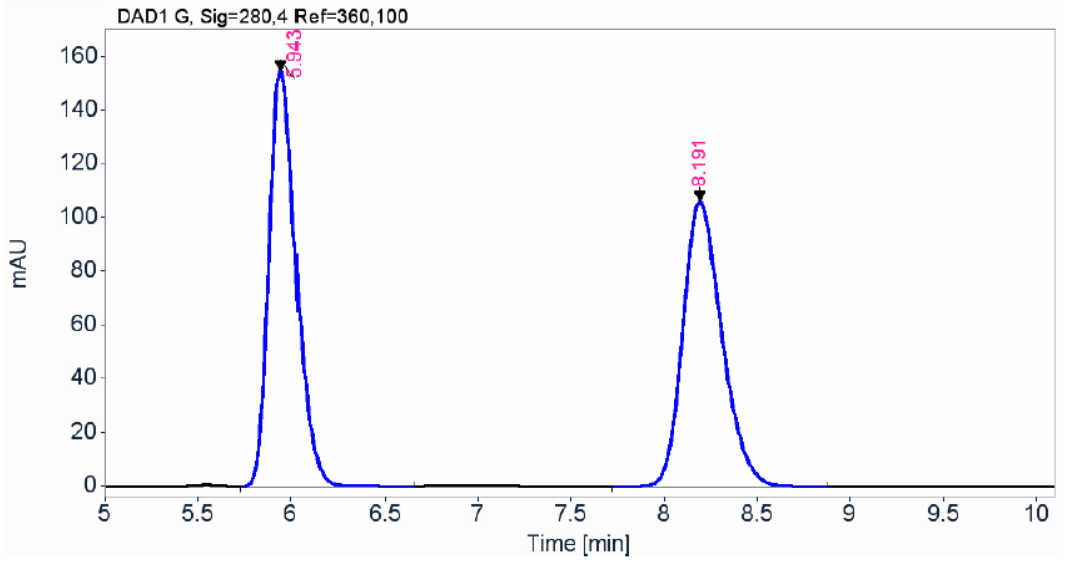


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.489	BB	0.3332	52.085	2.2242	0.19
9.315	BB	0.4405	27018.459	920.2887	99.81

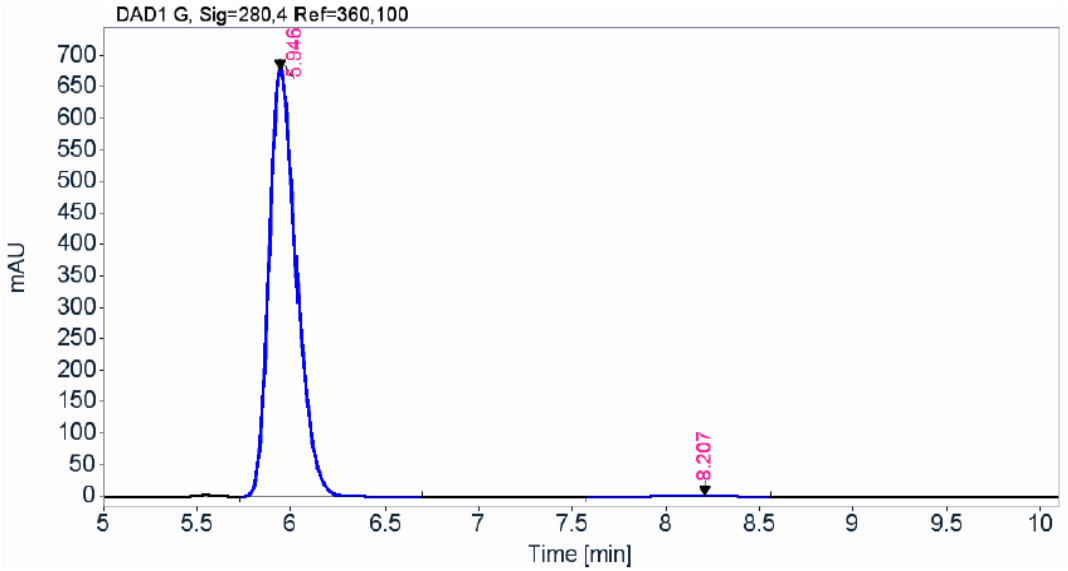


2r



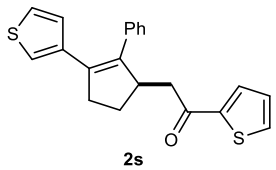
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.943	BB	0.1519	1539.361	155.0000	49.81
8.191	BB	0.2245	1551.299	106.1541	50.19

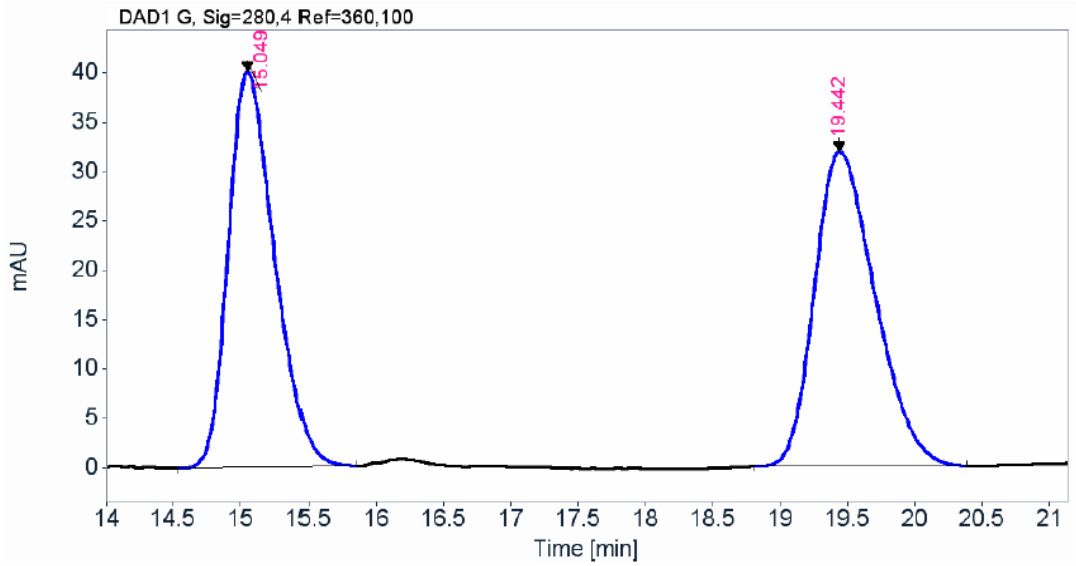


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
5.946	VB	0.1522	6755.389	678.4076	99.31
8.207	BB	0.3108	46.927	2.0216	0.69

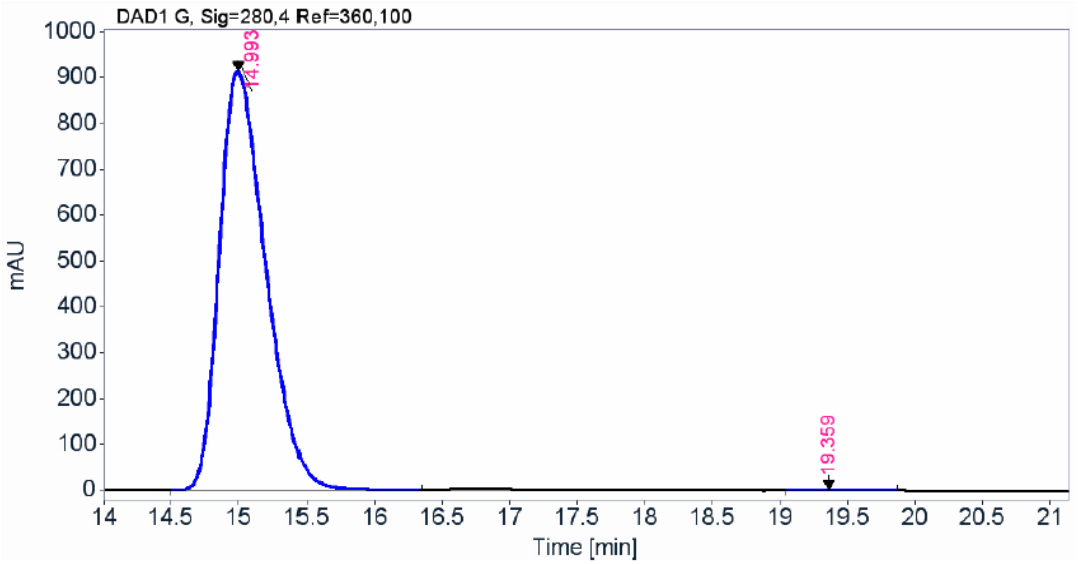


2s



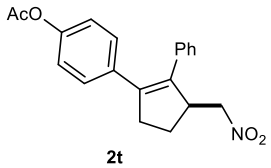
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
15.049	BB	0.3632	952.906	40.0986	48.82
19.442	BB	0.4830	998.948	31.9308	51.18

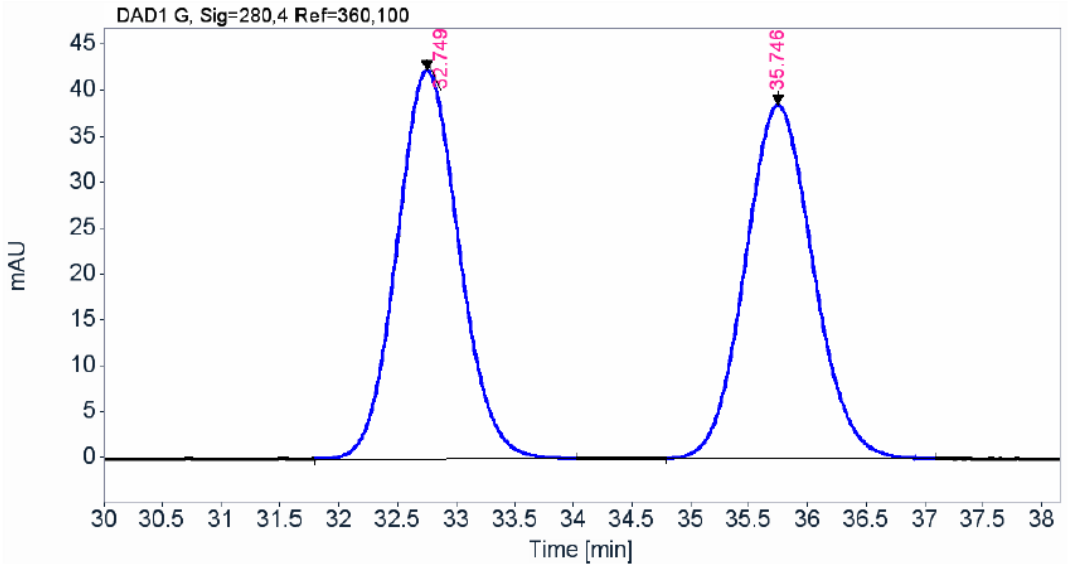


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
14.993	BB	0.3622	21811.531	914.5707	99.45
19.359	MM	0.7144	121.449	2.8332	0.55

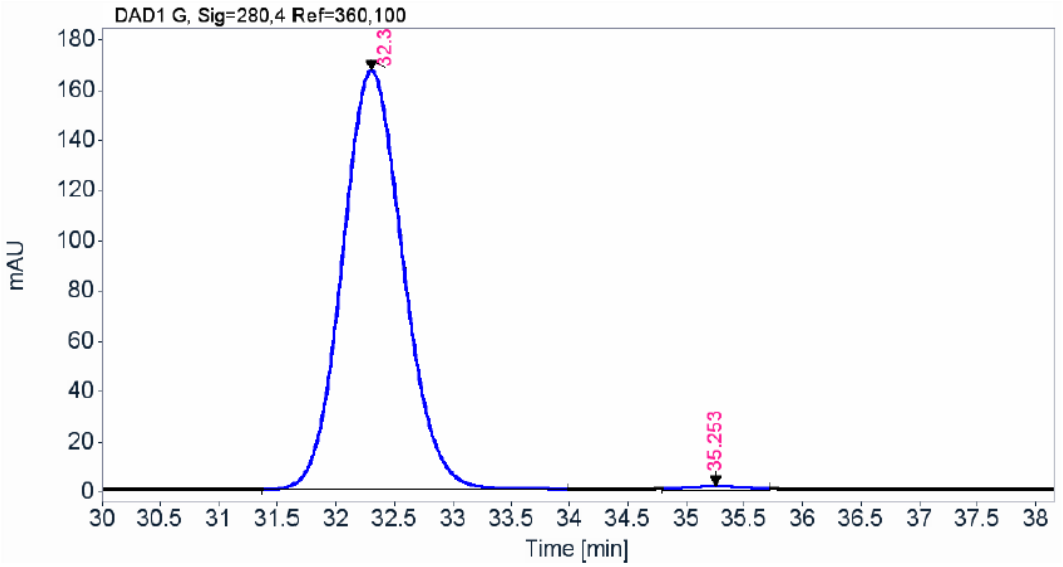


2t



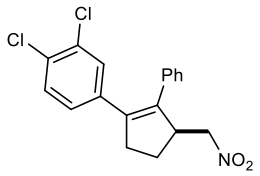
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
32.749	BB	0.5743	1558.852	42.2686	50.07
35.746	BB	0.5817	1554.578	38.4475	49.93

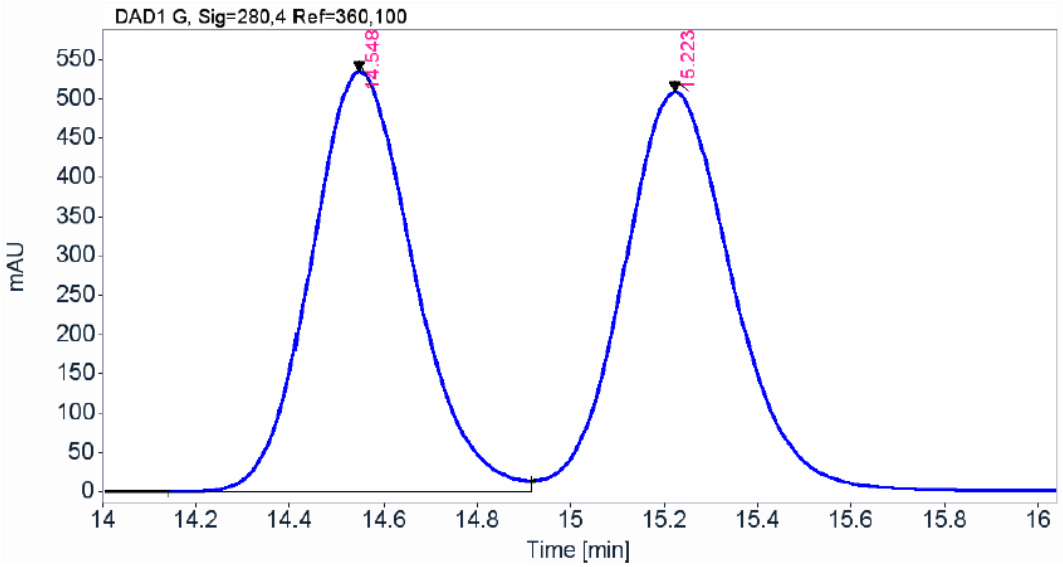


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
32.300	BB	0.5614	6018.979	166.6482	99.01
35.253	MM	0.6826	59.991	1.4648	0.99

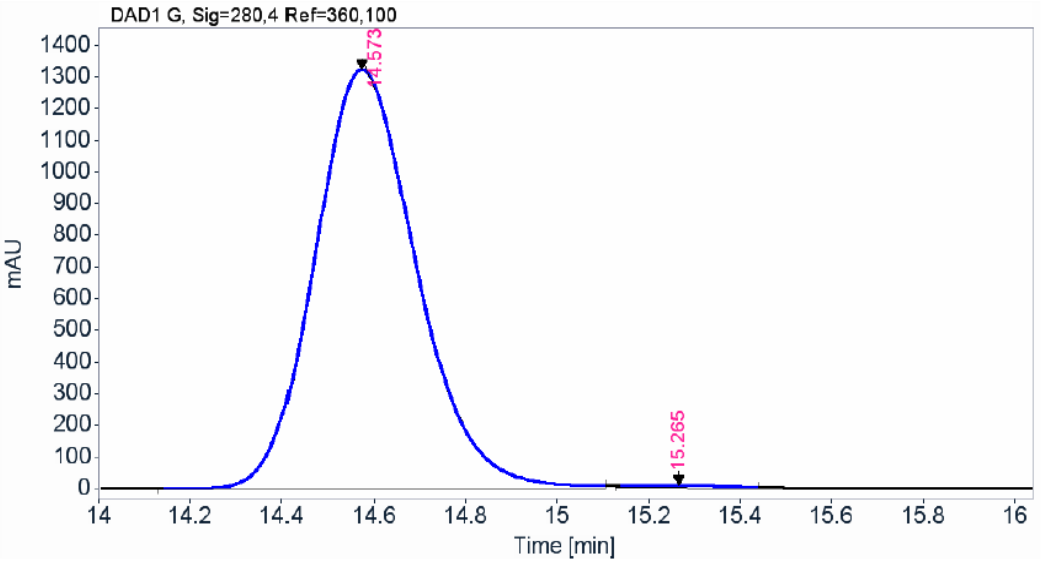


2u



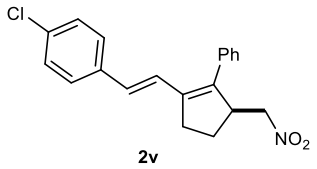
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
14.548	BV	0.2350	8105.860	534.1840	49.54
15.223	VB	0.2496	8255.524	508.0874	50.46

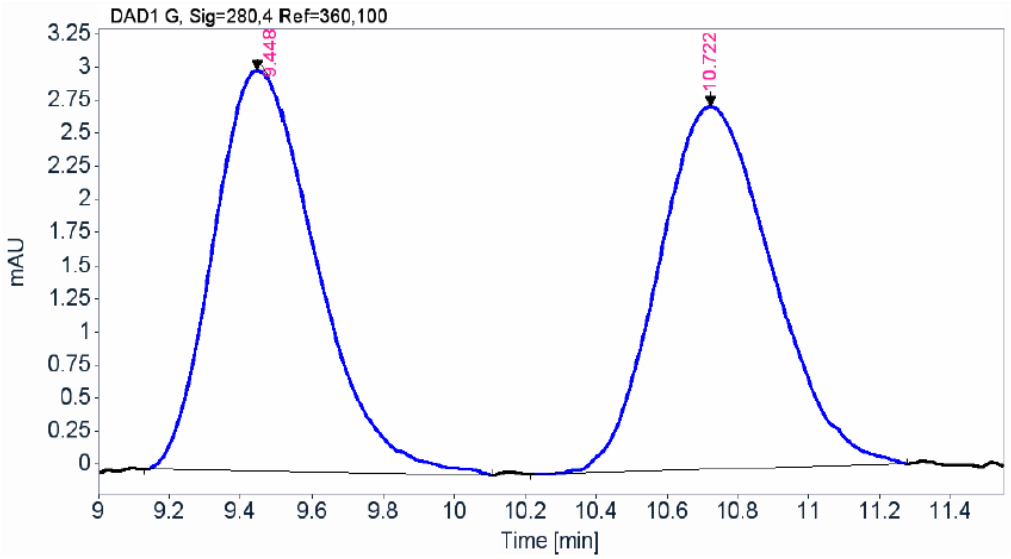


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
14.573	BV	0.2377	20380.799	1323.2819	99.33
15.265	MM	0.2451	136.902	9.3094	0.67

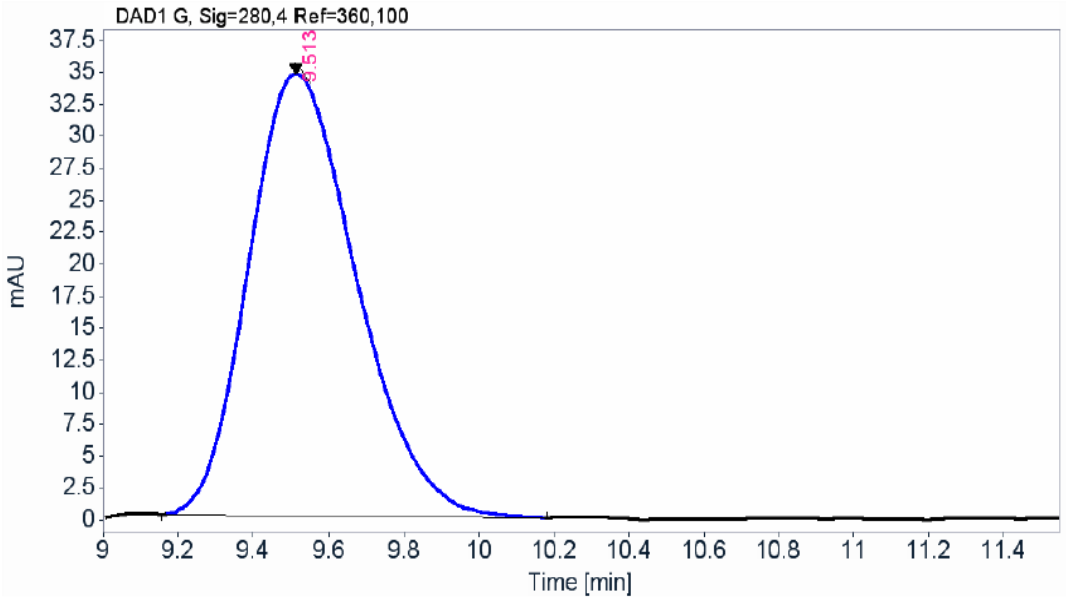


2v



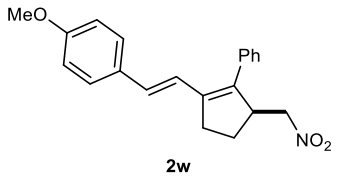
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.448	BB	0.3055	60.073	3.0278	49.70
10.722	BB	0.3388	60.808	2.7412	50.30

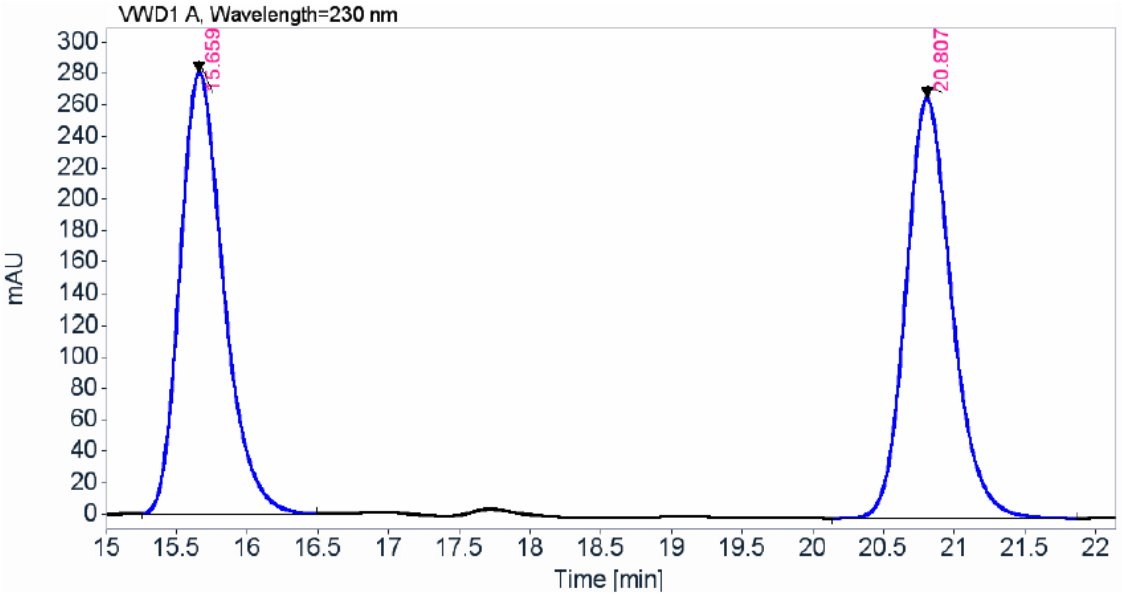


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.513	BB	0.3089	682.513	34.4841	100.00

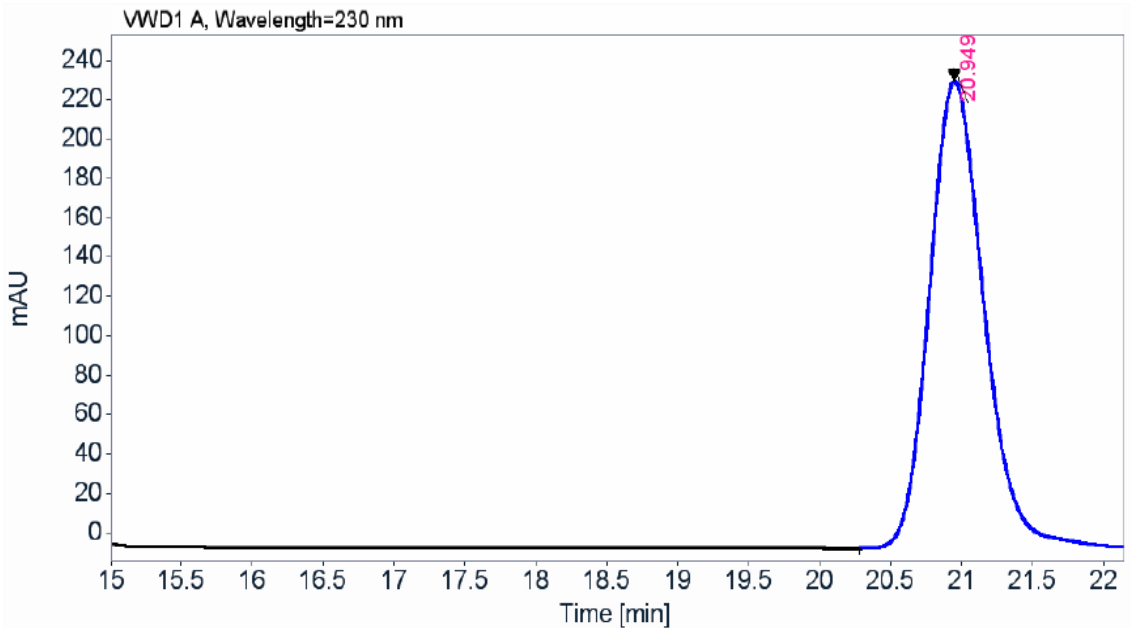


2w



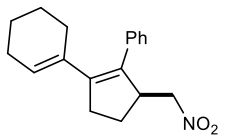
Signal: VWD1 A, Wavelength=230 nm

RT [min]	Type	Width [min]	Area	Height	Area%
15.659	MM	0.3562	6003.450	280.8818	49.89
20.807	BV	0.3476	6030.105	266.8730	50.11

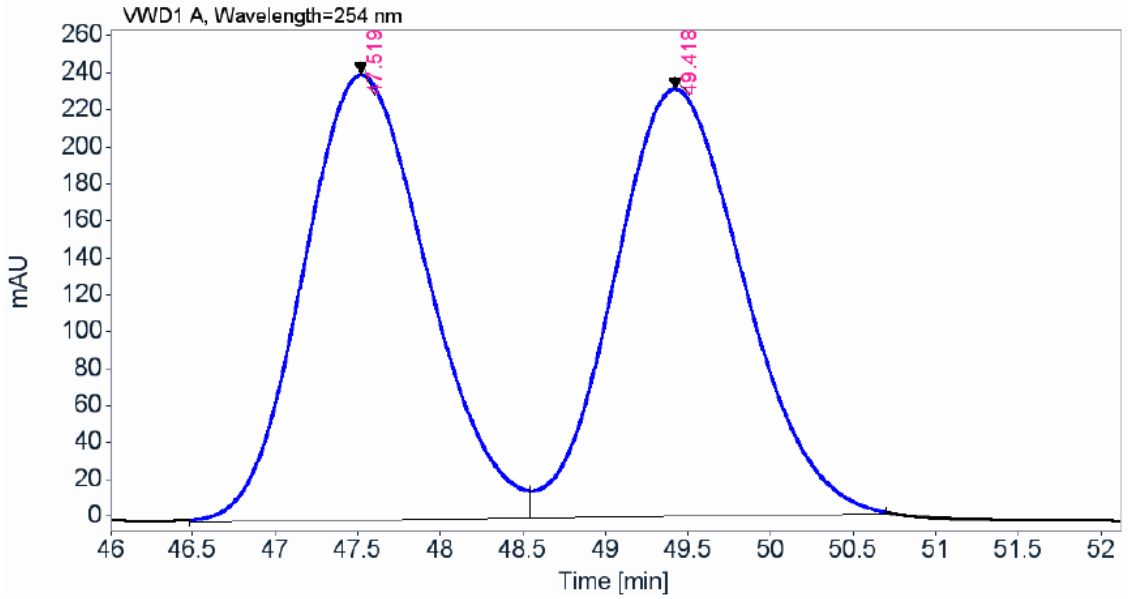


Signal: VWD1 A, Wavelength=230 nm

RT [min]	Type	Width [min]	Area	Height	Area%
20.949	MM	0.4430	6304.397	237.2025	100.00

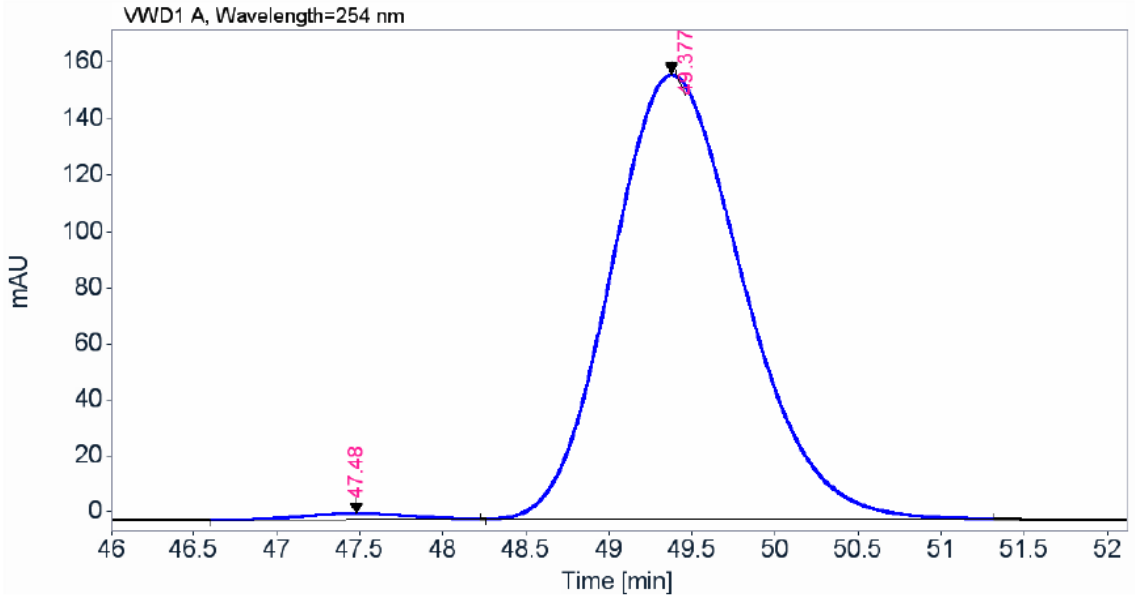


2x



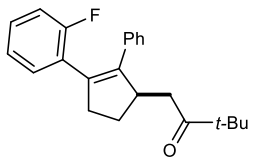
Signal: VWD1 A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
47.519	MF	0.8746	12657.973	241.2190	50.05
49.418	FM	0.9094	12630.399	231.4800	49.95

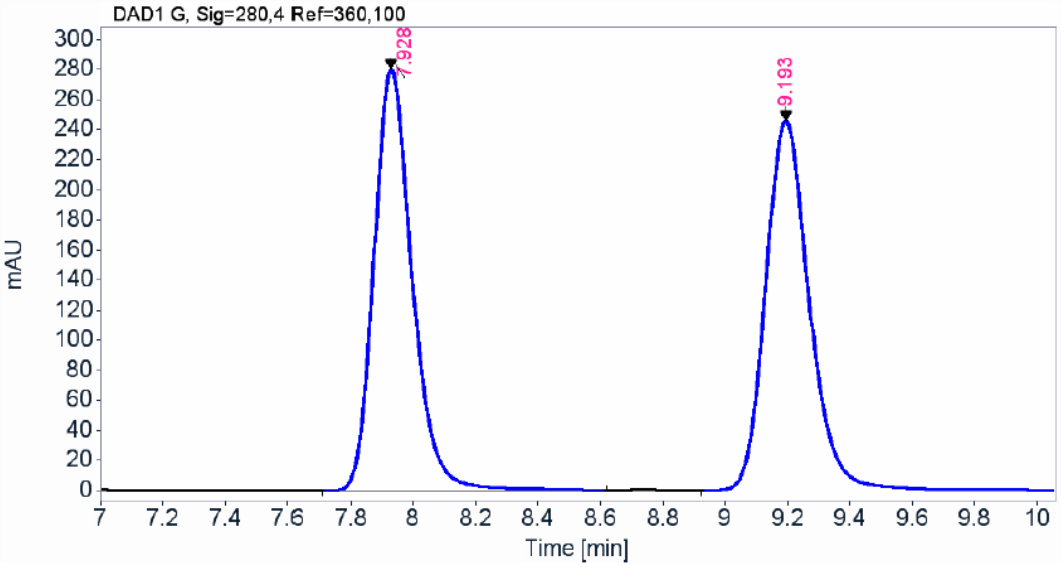


Signal: VWD1 A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
47.480	BB	0.6803	99.392	2.1908	1.13
49.377	MM	0.9167	8721.890	158.5746	98.87



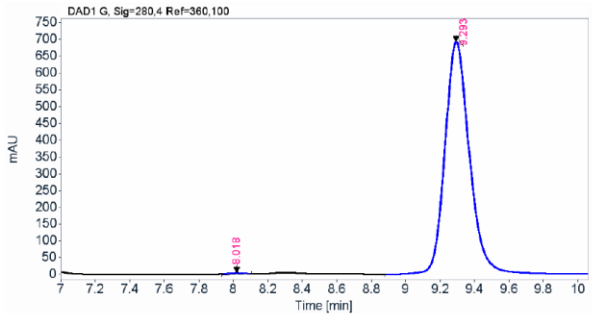
2y



Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.928	BB	0.1292	2384.344	280.5400	49.81
9.193	BB	0.1499	2402.532	246.1131	50.19

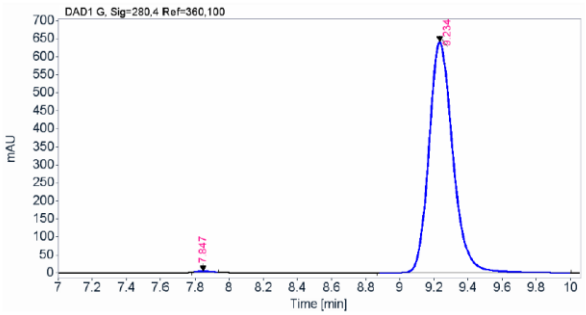
From arylative cyclization of (*E*)-**1q**:



Signal: DAD1 G, Sig=280,4 Ref=360,100

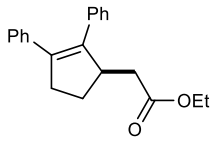
RT [min]	Type	Width [min]	Area	Height	Area%
8.018	MM	0.1147	25.467	3.6993	0.37
9.293	BB	0.1514	6859.086	693.4888	99.63

From arylative cyclization of (*Z*)-**1q**:

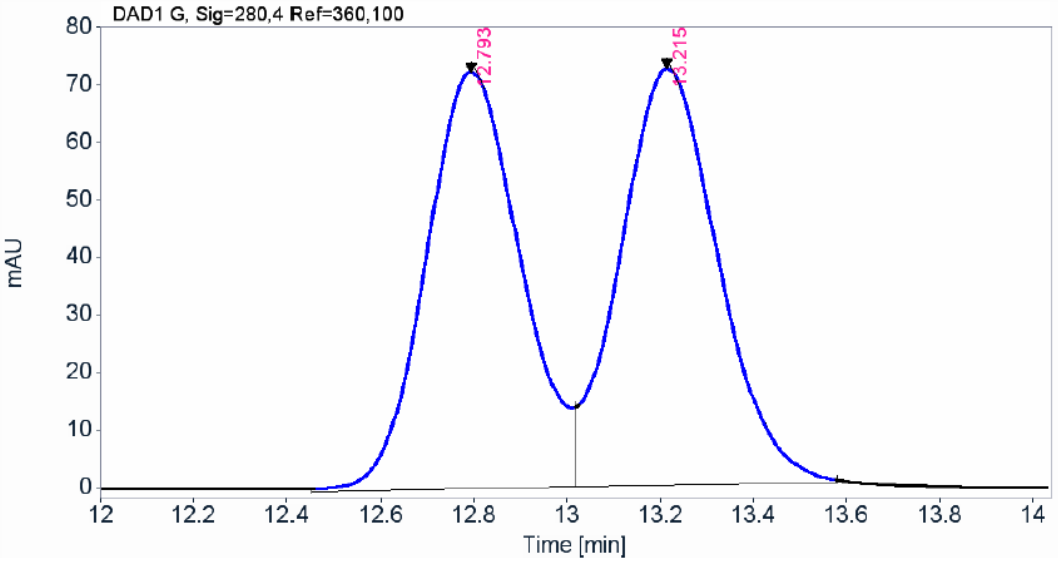


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.847	MM	0.1063	23.302	3.6538	0.37
9.234	BV	0.1498	6255.443	641.2622	99.63

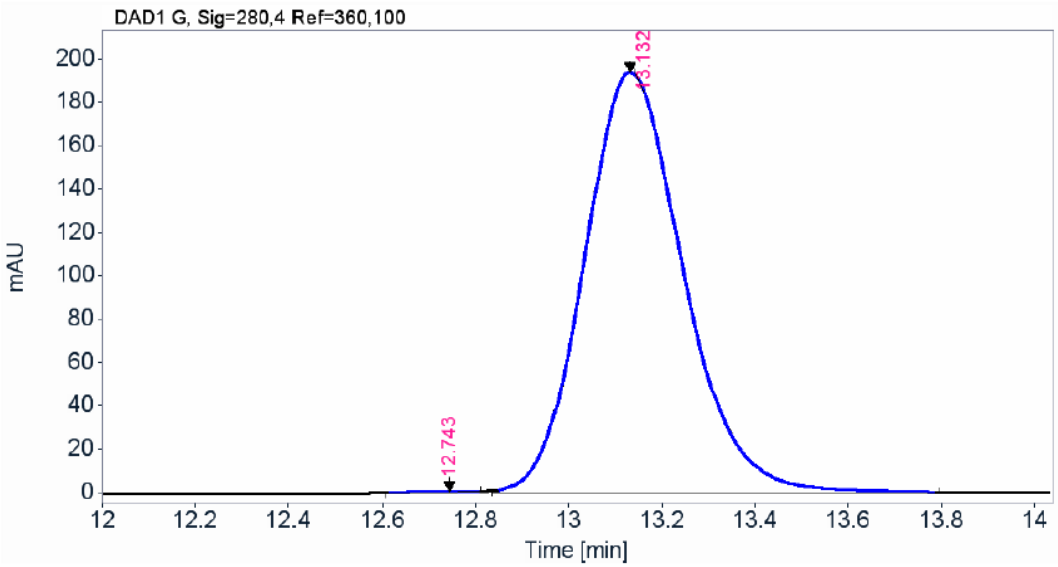


2z



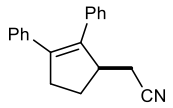
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.793	MF	0.2355	1023.828	72.4660	49.21
13.215	FM	0.2428	1056.608	72.5407	50.79

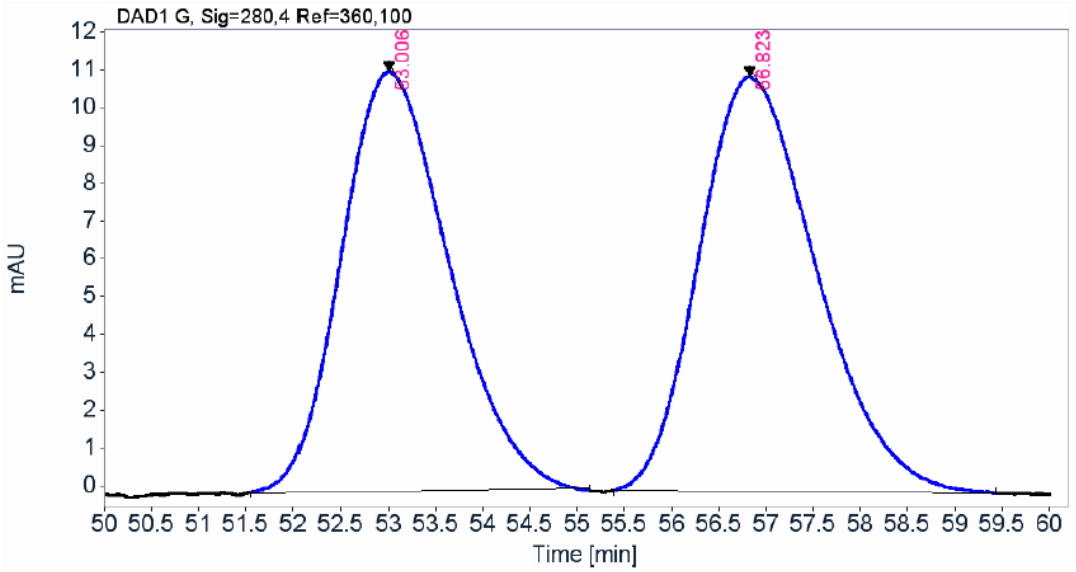


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.743	MM	0.2016	6.436	0.5321	0.22
13.132	MM	0.2463	2867.054	194.0399	99.78

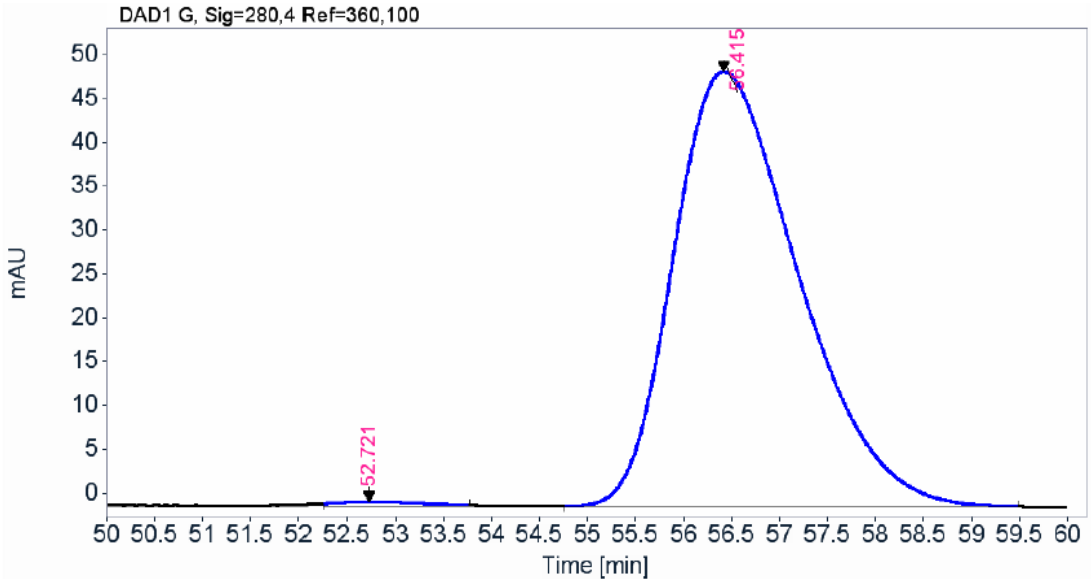


2aa



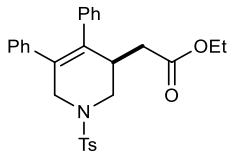
Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
53.006	MM	1.3172	875.715	11.0802	48.08
56.823	BB	1.0209	945.624	10.9571	51.92

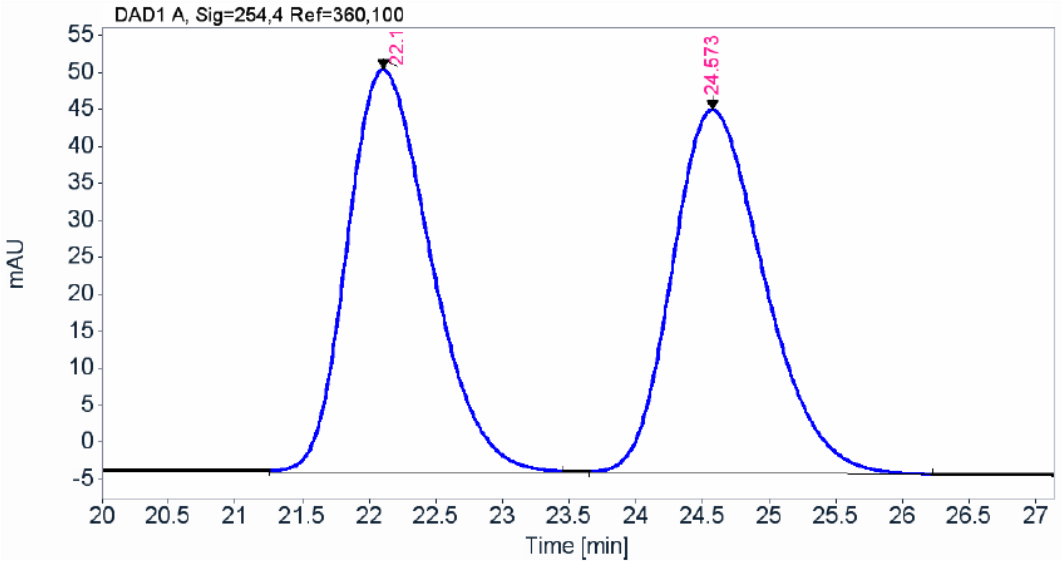


Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
52.721	MM	1.0785	32.474	0.5018	0.72
56.415	BB	1.3410	4480.695	49.6434	99.28

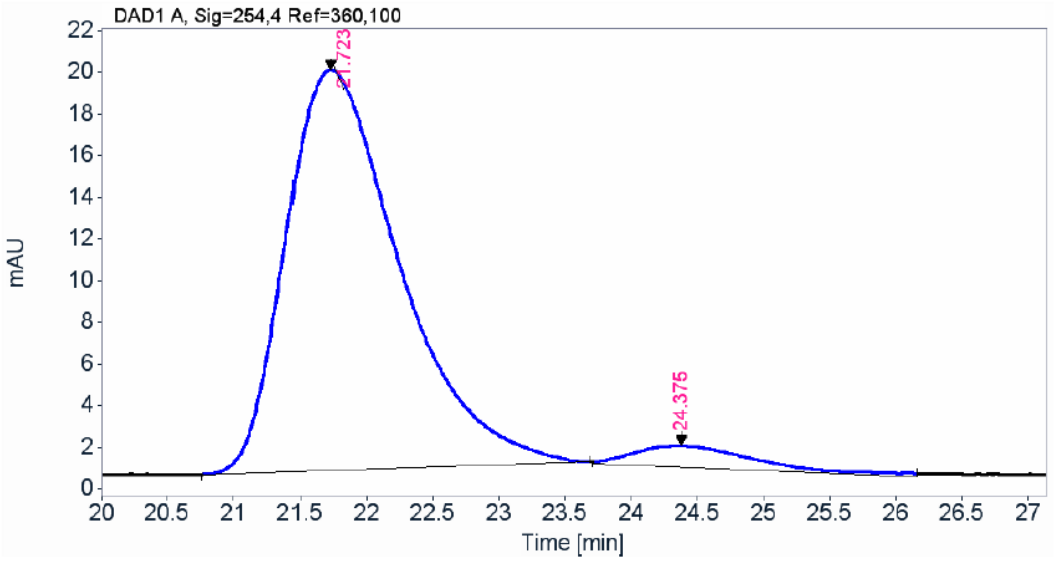


18



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
22.100	MM	0.7243	2368.143	54.4934	50.11
24.573	MM	0.7999	2357.306	49.1141	49.89



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
21.723	BB	0.8618	1139.426	19.2141	94.56
24.375	MM	1.0588	65.582	1.0323	5.44

9. References

1. M. G. Schrems, A. Pfaltz, *Chem. Commun.* **2009**, 6210-6212.
2. M. R. Krout, J. T. Mohr, B. M. Stoltz, *Org. Synth.* **2009**, *86*, 181.
3. S. M. Gillbard, C.-H. Chung, S. N. Karad, H. Panchal, W. Lewis, H. W. Lam, *Chem. Commun.* **2018**, *54*, 11769-11772.
4. J. J. Farndon, T. A. Young, J. F. Bower, *J. Am. Chem. Soc.* **2018**, *140*, 17846-17850.
5. R. Jana, J. A. Tunge, *J. Org. Chem.* **2011**, *76*, 8376-8385.
6. H. Wu, S. Radomkit, J. M. O'Brien, A. H. Hoveyda, *J. Am. Chem. Soc.* **2012**, *134*, 8277-8285.
7. E. Venkateswararao, M.-S. Kim, V. K. Sharma, K.-C. Lee, S. Subramanian, E. Roh, Y. Kim, S.-H. Jung, *Eur. J. Med. Chem.* **2013**, *59*, 31-38.
8. D. Belmessieri, L. C. Morrill, C. Simal, A. M. Z. Slawin, A. D. Smith, *J. Am. Chem. Soc.* **2011**, *133*, 2714-2720.
9. E. Marqués-López, R. P. Herrera, T. Marks, W. C. Jacobs, D. Könning, R. M. de Figueiredo, M. Christmann, *Org. Lett.* **2009**, *11*, 4116-4119.
10. A. R. Burns, J. Solana González, H. W. Lam, *Angew. Chem., Int. Ed.* **2012**, *51*, 10827-10831.
11. Z. Lin, Z. Hu, X. Zhang, J. Dong, J.-B. Liu, D.-Z. Chen, X. Xu, *Org. Lett.* **2017**, *19*, 5284-5287.
12. S. J. Sabounchei, V. Jodaian, S. Salehzadeh, S. Samiee, A. Dadrass, M. Bayat, H. R. Khavasi, *Helv. Chim. Acta* **2010**, *93*, 1105-1119.
13. A. R. Burns, A. G. E. Madec, D. W. Low, I. D. Roy, H. W. Lam, *Chem. Sci.* **2015**, *6*, 3550-3555.
14. S. Lanaspèze, R. Neier, *Monatsh. Chem.* **2005**, *136*, 597-607.
15. G. Abbiati, A. Contini, D. Nava, E. Rossi, *Tetrahedron* **2009**, *65*, 4664-4670.
16. L. Bai, J. Liu, W. Hu, K. Li, Y. Wang, X. Luan, *Angew. Chem., Int. Ed.* **2018**, *57*, 5151-5155.
17. S. Hötling, B. Haberlag, M. Tamm, J. Collatz, P. Mack, J. L. M. Steidle, M. Vences, S. Schulz, *Chem. Eur. J.* **2014**, *20*, 3183-3191.
18. J. Ryan, M. Šiaučiulis, A. Gomm, B. Maciá, E. O'Reilly, V. Caprio, *J. Am. Chem. Soc.* **2016**, *138*, 15798-15800.
19. M. W. Grafton, S. A. Johnson, L. J. Farrugia, A. Sutherland, *Tetrahedron* **2014**, *70*, 7133-7141.
20. C. Körner, P. Starkov, T. D. Sheppard, *J. Am. Chem. Soc.* **2010**, *132*, 5968-5969.
21. K. Li, A. Alexakis, *Chem. Eur. J.* **2007**, *13*, 3765-3771.
22. M. Ishizaki, O. Hoshino, *Tetrahedron* **2000**, *56*, 8813-8819.
23. R. Tanaka, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2010**, *132*, 1238-1239.
24. M. Mori, Y. Kozawa, M. Nishida, M. Kanamaru, K. Onozuka, M. Takimoto, *Org. Lett.* **2000**, *2*, 3245-3247.
25. K. R. Strom, A. C. Impastato, K. J. Moy, A. J. Landreth, J. K. Snyder, *Org. Lett.* **2015**, *17*, 2126-2129.