ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

On the Diels–Alder dimerisation of cross-conjugated trienes

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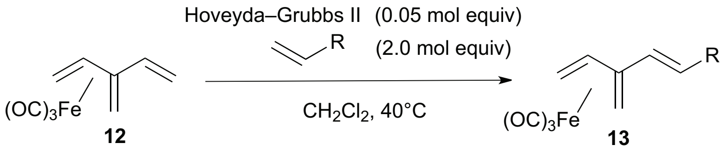
1 Experimental Section

1.1 General methods

^{1}H NMR spectra were recorded under standard conditions at 800 MHz, 600 MHz, 500 MHz, 400 MHz and 300 MHz using a Bruker AVANCE 800, Bruker AVANCE 600, a Varian Unity INOVA 500, Varian MR400 or Varian Mercury 300 spectrometer. Residual chloroform (δ 7.26 ppm) was used as an internal reference for ^{1}H NMR spectra measured in chloroform-*d*. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignment of proton signals was assisted by COSY, 1D-nOe, and NOESY experiments when necessary. ^{13}C NMR spectra were recorded at 200 MHz, 150 MHz, 125 MHz, 100 MHz or 75 MHz using a Bruker AVANCE 800, Bruker AVANCE 600, a Varian Unity INOVA 500, Varian MR400 or Varian Mercury 300 spectrometer. Chloroform-*d* (δ 77.1 ppm) was used as an internal reference for ^{13}C NMR spectra recorded in this solvent. Assignment of carbon signals was assisted by DEPT, HMBC, or HSQC experiments. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer as neat films on NaCl plates for oils or as potassium bromide discs for solid products. Low resolution mass spectra were recorded on a Finnigan Polaris Q ion trap mass spectrometer using electron impact (EI+) ionisation mode at 40 or 70 eV, or a VG Quattro II triple quadrupole MS for electrospray ionisation (ESI). High resolution mass spectra were recorded on a VG Autospec mass spectrometer operating at 70 eV for EI, or a Bruker Apex3 4.7T FTICR-MS for ESI. Melting points were measured on a Reichert melting point stage and are uncorrected. Analytical high performance liquid chromatography (HPLC) was performed using a Shimadzu Prominence LC-20AD chromatography pump and SIL-20A autosampler, on an Alltima Silica 5 μm column (250 mm, 4.6 mm ID). Preparative HPLC was performed using a Waters 600E instrument on an Altima silica 5 μm (250 mm, 22 mm ID), an Altima silica 5 μm (250 mm, 10 mm ID), or a Waters silica 5 μm (150 mm, 19 mm ID) column unless otherwise specified. Analytical TLC was performed with Merck silica gel plates, precoated with silica gel 60 F254 (0.2 mm). Flash chromatography employed Merck Kiesegel 60 (230–400 mesh) silica gel. UV-Vis spectra recorded using a Shimadzu UV-Visible 2450 spectrometer. A LAUDA ecoline 006 constant temperature bath with a LAUDA E300 temperature controller was used for the dimerisation studies.

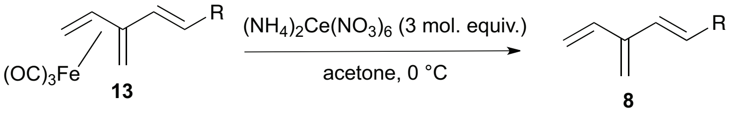
Reactions were conducted under a positive pressure of dry nitrogen in oven-dried glassware. Solvents were dried using a solvent purification system based on that described by Pangborn and co-workers,[1] dried over sodium wire and distilled from sodium benzophenone ketyl, or dried using standard methods. Petrol refers to bp 40–60 °C petroleum spirits unless otherwise stated. Commercially available chemicals were purified by standard procedures[2] or used as purchased.

General procedure 1 (**GP-1**): for the cross metathesis of irontricarbonyl[3]dendralene



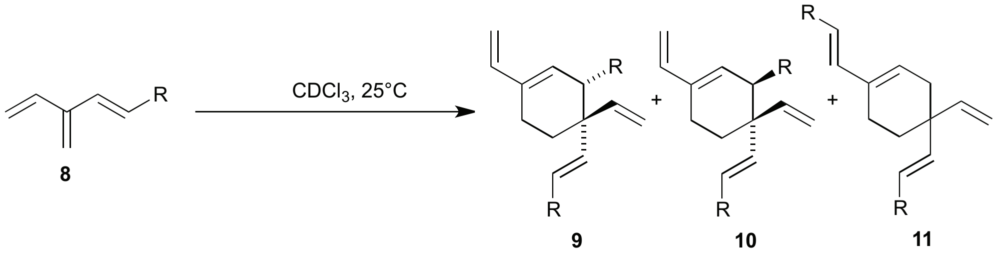
A solution of irontricarbonyl[3]dendralene[3] **12** (1.0 mol equiv.) and the vinylic cross-metathesis partner (2.0 mol equiv) in CH_2Cl_2 (0.1 M) was added *via* cannula to a flask containing Hoveyda–Grubbs second generation catalyst (0.05 mol equiv.) under nitrogen. The resulting mixture was then heated to reflux with stirring for 16 h, and protected from light by aluminium foil. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography affording the *substituted [3]dendralene complex* **13**.

General procedure 2 (**GP-2**): for the decomplexation of irontricarbonyl[3]dendralenes with cerium ammonium nitrate.



To a rapidly stirred solution of the tricarbonyliron complex **13** in acetone or acetone-d_6 (0.02–0.05 M) at 0 °C was added cerium ammonium nitrate (3.0 mol equiv.) as a solid. The solution was left stirring, open to air, for 15 minutes or until completion, as determined by TLC. The orange solution was quenched by addition of saturated NH_4Cl (0.5 vol equiv. relative to the solvent) and diluted with isopentane (*ca.* 3 vol equiv. relative to acetone). The two layers were separated and the organic layer was washed with water and dried ($MgSO_4$). If the decomplexed compound was stable to isolation (i.e. for **8e**) then the solvent was removed under reduced pressure and the residue was purified by flash chromatography. If the compound was unstable towards isolation (i.e. for **8a–d**) then the isopentane solution of the compound was added to a small volume of $C_2D_2Cl_4$ and the isopentane was rapidly removed under reduced pressure (20 mbar) at 0 °C, then at higher vacuum (1–2 mbar) for one minute, and the deuterated solution could be stored over extended periods at –78 °C without change. For compounds **8a,d** $CDCl_3$ could be used in the place of isopentane to carry out the extraction, in these cases the $CDCl_3$ volume was carefully reduced on a rotary evaporator until approximately 0.5 mL remained. These solutions could then be treated in the same way as the $C_2D_2Cl_4$ solution above.

General procedure 3 (**GP-3**): for the monitoring of the dimerisation of unstable terminally substituted dendralenes.



A *ca.* 0.4–0.6 mL volume solution of approximately 0.05 M concentration was made up of the dendralene **8** in $CDCl_3$ or $C_2D_2Cl_4$ in an NMR tube. To this solution was added 0.050 mL of a 0.166M (0.00833 mmol) standard solution of methylsulfonylmethane in $CDCl_3$ as an internal standard. The combined solution was mixed thoroughly and a ^1H NMR spectrum was recorded. The NMR spectrum was used to determine an accurate concentration of dendralene in solution by comparison of the internal standard with the peaks due to the dendralene, and the solution was diluted to 0.030 M with the appropriate volume of $CDCl_3$ or $C_2D_2Cl_4$. A ^1H NMR spectrum of the diluted spectrum was taken to confirm the calculated concentration, and this spectrum was used as an 'initial concentration measurement' or 't_0 concentration.' The solution was held at 25.0 °C in a constant temperature bath and ^1H NMR spectra were collected regularly to measure the rate of dimerisation of the unstable dendralene and derive a half-life. The experiment was stopped at 4 × $t_{1/2}$ or if the concentration of analyte fell below the measurement error of the detection method.[4] The recorded ^1H NMR spectra were used to calculate the instantaneous concentration of the solution which was then correlated with the precise time that the spectrum was recorded. The resulting data was plotted on a scatter plot using Microsoft Excel with the x-axis as time (hours) and the y-axis as 1/[concentration] (L mol^{-1}). The gradient is thus k as in:

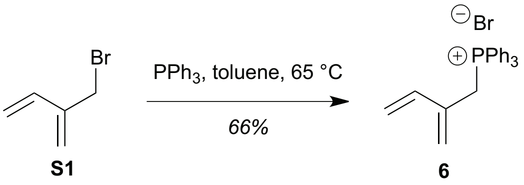
$$\frac{1}{[dendralene]} = \frac{1}{[dendralene]_0} + kt$$

and $t_{1/2}$ is determined *via*: [5]

$$t_{1/2} = \frac{1}{k[dendralene]_0}$$

1.2 Preparation of terminally-substituted [3]dendralenes

Phosphonium salt **6**

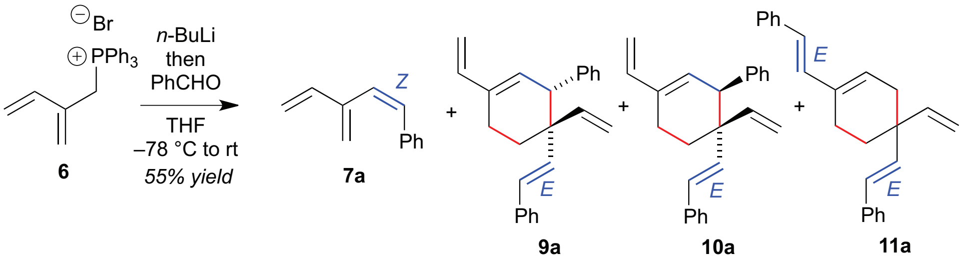


A solution of 2-(bromomethyl)buta-1,3-diene **S1**[6] (1.30 g, 8.84 mmol, 1.0 mol equiv.) and PPh_3 (2.55 g, 9.73 mmol, 1.1 mol equiv.) in PhMe (15 mL), was heated to 65 °C for 14 h. The mixture was allowed to cool to rt and the solvent was removed under reduced pressure. Purification of the crude material by re crystallisation from CH_2Cl_2/THF afforded **6** as colourless cubes (2.39 g, 5.84 mmol, 66%) mp 207–210 °C (CH_2Cl_2/THF).

^{1}H NMR (500 MHz, CD_3OD): δ 7.93–7.69 (15H, m), 6.27 (1H, dd, J = 17.6, 11.0 Hz), 5.42 (1H, d, J = 5.4 Hz), 5.11 (1H, d, J = 17.6 Hz), 5.10 (1H, d, J = 5.4 Hz), 4.89 (1H, d, J = 11.0 Hz), 4.48 (2H, dd, J = 15.6, 1.0 Hz) ppm; ^{13}C NMR (125 MHz, CD_3OD) δ 137.2 (J (^{13}C–^{31}P) = 15.1 Hz), 135.3 (J (^{13}C–^{31}P) = 11.0 Hz), 134.2 (J (^{13}C–^{31}P) = 38.0 Hz) (two coincident signals), 130.2 (J (^{13}C–^{31}P) = 49.0 Hz), 123.4 (J (^{13}C–^{31}P) = 38.0 Hz), 118.3 (J (^{13}C–^{31}P) = 208 Hz), 115.8, and 24.8 (J (^{13}C–^{31}P) = 203 Hz) ppm.

IR (KBr disk) ν = 1437, 1109 cm^{-1}; MS (ESI): m/z 329 [M–Br]$^+$; HRMS (ESI): calculated for $C_{23}H_{22}P$ [M–Br]$^+$: 329.1459; found 329.1443.

Wittig olefination of **6** with benzaldehyde to prepare **7a**, **9a**, **10a**, and **11a**



To a rapidly stirred suspension of the phosphonium salt **6** (262 mg, 0.64 mmol, 1.3 mol equiv.) in THF (0.1 M) at –78 °C was added n-BuLi (0.358 mL, 1.65 M in hexane, 1.2 mol equiv.). The mixture was allowed to stir at this temperature for 30 min., warmed to rt over 20 min., then returned to –78 °C. To this mixture was added (dropwise *via* cannula) a solution of benzaldehyde (52 mg, 0.49 mmol) in THF (2.5 mL). The mixture was stirred at –78 °C for 2 hours, then warmed to rt and stirred for a further 12 hours. The reaction mixture was poured into a cold mixture of saturated NH_4Cl and Et_2O. The layers were separated and the aqueous layer was extracted with ether. The ethereal layers were combined, washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified first by flash chromatography (silica gel, 5:95 Et_2O/hexane) then by HPLC (Porasil preparative column, 0.5:99.5 EtOAc/hexane).

Analysis of the crude mixture by ^{1}H NMR spectroscopy indicated the ratio of products was 61:37:2 for **9a**:**10a**:**11a** respectively.

Z dendralene **7a** was isolated as a colourless oil (15.2 mg, 0.10 mmol, 20%);

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.40–7.35 (2H, m), 7.28–7.15 (3H, m), 6.57 (1H, d, *J* = 12.2 Hz), 6.46 (1H, dd, *J* = 17.7, 10.7 Hz), 6.18 (1H, d, *J* = 12.6 Hz), 5.35 (1H, d, *J* = 17.6 Hz) and 5.19–5.09 (3H, m) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 144.1, 137.7, 137.0, 131.9, 129.0, 128.1, 128.0, 127.2, 118.3 and 115.9 ppm.

IR (thin film) *v* = 3008, 1584, 1493, 1448 cm^{-1}; MS (70 eV, EI): *m/z* (%): 156 (100) $[M]^{+\bullet}$; HRMS (70 eV, EI): calc for $C_{12}H_{12}$ $[M]^{\bullet}$: 156.0939; found 156.0940.

A mixture of dimers **9a** and **10a** were isolated as a colourless oil (26.8 mg, 0.09 mmol, 35%, **9a**:**10a**, 62:38).

^{1}H NMR (500 MHz; $CDCl_3$): *δ* 7.42–7.19 (m, 10H **9a**, 10H **10a**), 6.53-6.46 (m, 2H **9a** 2H **10a**), 6.35 (d, *J* = 16.4 Hz, 1H **10a**), 6.22 (d, *J* = 16.3 Hz, 1H **9a**), 6.06 (d, *J* = 16.4 Hz, 1H **9a**), 6.01 (dd, *J* = 17.6, 10.9 Hz, 1H **10a**), 5.88–5.83 (m, 1H **9a**, 1H **10a**), 5.27–5.19 (m, 2H **9a**, 2H **10a**), 5.07 (br d, *J* = 10.5 Hz, 1H **9a**, 1H **10a**), 4.97 (d, *J* = 10.8 Hz, 1H **10a**), 4.90 (d, *J* = 17.5 Hz, 1H **9a**), br 3.66 (s, 1H **9a**, 1H **10a**), 2.49–2.44 (m, 1H **9a**, 1H **10a**), 2.38–2.30 (m, 1H **9a**, 1H **10a**), 2.08–1.87 (m, 2H **9a**, 2H **10a**) ppm; ^{13}C NMR (125 MHz, $CDCl_3$, d1 = 60 s): *δ* 143.9, 142.6, 141.4, 141.3, 139.5 (two coincident signals), 138.0, 137.9, 136.5, 136.4, 136.3, 135.3, 131.1 (two coincident signals), 130.4 (two coincident signals), 128.8, 128.7 (two coincident signals), 128.5, 127.8 (two coincident signals), 127.2, 127.0, 126.7 (two coincident signals), 126.3 (two coincident signals), 126.2, 114.1, 113.9, 111.5 (two coincident signals), 51.7, 51.3, 45.3, 29.4, 29.3 and 21.5 (two coincident signals) ppm.

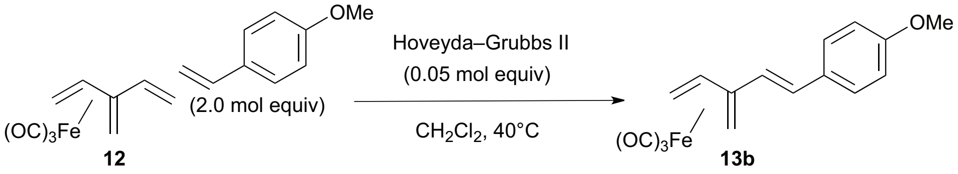
IR (thin film) *v* = 3026, 1642, 1603, 1494, 1450 cm^{-1}; MS (70 eV, EI): *m/z* (%): 312 (58) $[M]^{+\bullet}$, 156 (100); HRMS (70 eV, EI): calc for $C_{24}H_{24}$ $[M]^{+\bullet}$: 312.1878; found 312.1873.

11a was isolated as a colourless oil (2.5% yield calculated *via* ^{1}H NMR).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.44–7.17 (10H, m), 6.80 (1H, d, *J* = 16.1 Hz), 6.44 (1H, d, *J* = 16.1 Hz), 6.38, (1H, d, *J* = 16.3 Hz), 6.22 (1H, d, *J* = 16.3 Hz), 5.95–5.92 (1H, m), 5.90 (1H, dd, *J* = 17.6, 10.7 Hz), 5.13–5.06 (2H, m), 2.44–2.21 (4H, m) and 1.92–1.84 (2H, m) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 144.2, 137.9, 137.8, 136.4, 135.5, 131.9, 128.7, 128.6, 128.2, 128.1, 127.2, 127.1, 126.3 (two coincident signals), 125.5, 113.1, 41.7, 35.4, 32.1 and 22.2 ppm.

IR (thin film) *v* = 2920, 1634, 1447 cm^{-1}; MS (70 eV, EI): *m/z* (%): 312 (24) $[M]^{+\bullet}$, 156 (100); HRMS (70 eV, EI): calc for $C_{24}H_{24}$ $[M]^{+\bullet}$: 312.1878; found 312.1879.

Tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-methoxybenzene)iron (**13b**)

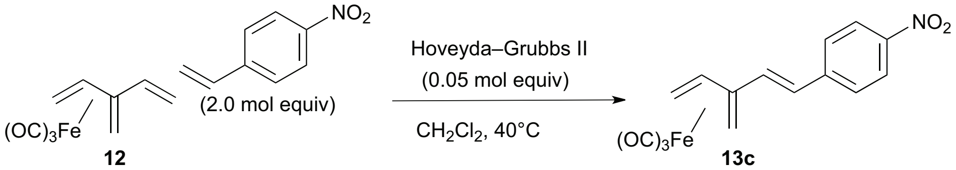


Prepared via **GP-1** using **12** (453 mg, 2.06 mmol, 1.0 mol equiv.), *p*-methoxystyrene (557 mg, 4.0 mmol, 2.0 mol equiv.), Hoveyda–Grubbs second generation catalyst (85 mg, 0.12 mmol, 0.06 mol equiv.), and CH_2Cl_2 (20 mL). The yellow solid was purified by flash column chromatography (silica gel, 5:95 ethyl acetate/hexane) affording the *title compound* as a yellow crystalline solid (451 mg, 67% yield); R_f 0.43 (5:95 ethyl acetate/hexane); mp: 75–78 °C (ether/hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.5 Hz, 2H), 6.90–6.86 (m, 3H), 6.76 (d, J = 5.8 Hz, 1H), 5.51 (m, 1H), 3.83 (s, 3H), 2.32 (dd, J = 2.6, 1.5 Hz, 1H), 1.83 (dd, J = 6.8, 2.4 Hz, 1H), 0.38 (dd, J = 9.1, 2.3 Hz, 1H), 0.21 (d, J = 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1 (q), 159.7 (q), 129.2 (q), 129.0 (CH), 128.1 (CH), 126.3 (CH), 114.2 (CH), 102.1 (q), 85.2 (CH), 55.4 (CH_3), 39.8 (CH_2), 37.5 (CH_2) ppm.

IR (KBr disc): ν_{max} = 2042, 1994, 1979, 1958, 1603 cm^{-1}; MS (EI): *m/z* (%): 356.0 (5), 326.1 ([*M*]$^{+\bullet}$, 14), 298.1 (56), 270.1 (70), 242.0 (100), 56.0 ([*Fe*]$^{+\bullet}$, 30); HRMS (EI): calculated for $C_{16}H_{14}FeO_4$ [*M*]$^{+\bullet}$: 326.0241; found 326.0242.

Tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-nitrobenzene)iron (**13c**)

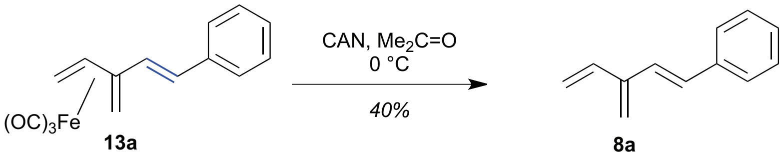


Prepared via **GP-1** using **12** (454 mg, 2.06 mmol, 1.0 mol equiv.), *p*-nitrostyrene (550 mg, 4.0 mmol, 2.0 mol equiv.), Hoveyda–Grubbs second generation catalyst (63 mg, 0.10 mmol, 0.05 mol equiv.), and CH_2Cl_2 (20 mL). The yellow solid was purified by flash column chromatography (silica gel, 20:80 CH_2Cl_2/hexane) affording the *title compound* as a bright yellow crystalline solid (366 mg, 52% yield); R_f 0.12 (20:80 CH_2Cl_2/hexane); mp: 108–110 °C ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 16.1 Hz, 1H) , 6.93 (d, J = 15.8 Hz, 1H), 5.51 (t, J = 8.1 Hz, 1H), 2.29 (dd, J = 2.9, 1.5 Hz, 1H), 1.92 (dd, J = 7.0, 2.6 Hz, 1H), 0.48 (dd, J = 9.5, 2.6 Hz, 1H), 0.25 (d, J = 2.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5 (q), 147.1 (q), 142.9 (q), 133.7 (CH), 127.2 (CH), 126.5 (CH), 124.2 (CH), 99.2 (q), 87.3 (CH), 40.9 (CH_2), 37.3 (CH_2) ppm.

IR (KBr disc): ν_{max} = 2928, 2045, 1976, 1593, 1519, 1340 cm^{-1}; MS (EI): *m/z* (%): 341.0 ([*M*]$^{+\bullet}$, 14), 313.0 (34), 285.0 (100), 257.0 (22), 227.0 (73), 55.9 ([*Fe*]$^{+\bullet}$, 40); HRMS (EI): calculated for $C_{15}H_{11}FeNO_5$ [*M*]$^{+\bullet}$: 340.9987; found 340.9992.

(*E*)-(3-methylenepenta-1,4-dien-1-yl)benzene (**8a**)

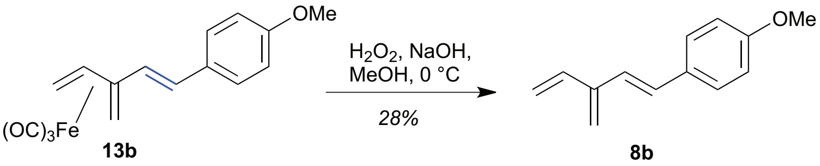


Tricarbonyl[(4-6η^4)-(*E*)-(3-methylenepenta-1,4-dien-1-yl)benzene)iron **13a** (18 mg, 0.0615 mmol, 1.0 mol equiv.), cerium ammonium nitrate (101 mg, 0.185 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $CDCl_3$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $CDCl_3$ solution (0.0245 mmol, 40% yield); R_f 0.35 (2:98 CH_2Cl_2/pentane).

^{1}H NMR (800 MHz; CDCl3): *δ* 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 8.0, 7.3 Hz, 2H), 7.17–7.15 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 16.2 Hz, 1H), 6.46 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.18–5.11 (m, 3H) ppm; ^{13}C NMR (200 MHz; $CDCl_3$): *δ* 144.1 (q), 137.0 (q), 135.8 (CH), 130.1 (CH), 128.4 (CH), 127.49 (CH), 127.41 (CH), 126.3 (CH), 115.7 (CH2), 115.3 (CH2) ppm.

MS (EI): *m/z* (%): 312.2 (2[*M*]$^{+\bullet}$, 22), 156.1 ([*M*]$^{+\bullet}$, 100), 141.1 (51), 128.1 (42), 115.0 (28); HRMS (EI): calculated for $C_{12}H_{12}$ [*M*]$^{+\bullet}$: 156.0939; found 156.0935.

(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-methoxybenzene (**8b**)

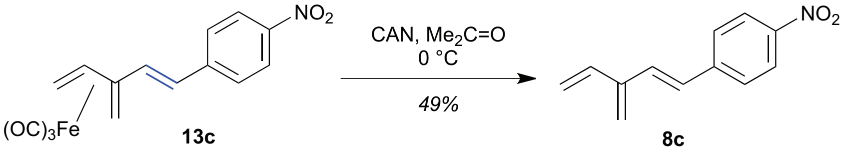


To a rapidly stirred solution of tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-methoxybenzene)iron **13b** (14 mg, 0.042 mmol, 1.0 mol equiv.) in methanol (0.01–0.05 M) (dissolution was aided by heating) was added 30% aqueous hydrogen peroxide (0.26 mL, 6.0 mL/mmol). The solution was cooled to 0 °C. NaOH (10 mg, 0.25 mmol, 6.0 mol equiv.) was added dropwise as a solution in MeOH, and the mixture was left stirring, open to air, for 30 minutes. The brown suspension was quenched by addition of saturated aqueous $Na_2S_2O_3$ (1 vol equiv. relative to the hydrogen peroxide) and diluted with isopentane (*ca.* 2 vol equiv. relative to the methanol). The two layers were separated and the organic layer was washed with water and dried ($MgSO_4$), then filtered. The isopentane solution of **8b** was added to a small volume of $C_2D_2Cl_4$ (0.5 mL) and the isopentane was removed under reduced pressure (20 mbar) at 0 °C on a rotary evaporator, then the remaining traces of isopentane were removed by increasing the vacuum to 1–2 mbar for one minute. The $C_2D_2Cl_4$ solution could be stored over extended periods at −78 °C without change. The *title compound* was characterised as a yellow $C_2D_2Cl_4$ solution (0.0153 mmol, 28% yield); R_f 0.44 (5:95 Et_2O/pentane).

^{1}H NMR (400 MHz; $C_2D_2Cl_4$): δ 7.40 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.74 (app d, J = 4.4 Hz, 2H), 6.57 (dd, J = 17.2, 10.8 Hz, 1H), 5.52 (d, J = 17.8 Hz, 1H), 5.24 (app dd, J = 11.1, 0.7 Hz, 3H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz; $C_2D_2Cl_4$): δ 160.6 (q), 145.5 (q), 137.4 CH), 131.20 (q), 131.09 (CH), 129.2 (CH), 127.0 (CH), 117.5 (CH_2), 116.5 (CH_2), 115.5 (CH), 56.8 (CH_3) ppm.

MS (EI): m/z (%): 186.1 ($[M]^{+\bullet}$, 100), 155.1 (56), 86.0 (75); HRMS (EI): calculated for $C_{13}H_{14}O$ $[M]^{+\bullet}$: 186.1045; found 186.1048.

(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-nitrobenzene (**8c**)

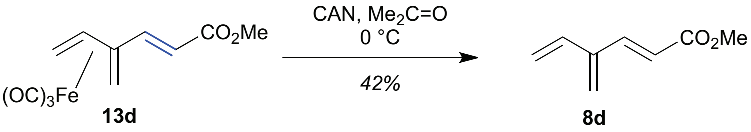


Tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-nitrobenzene]iron **13c** (22 mg, 0.064 mmol, 1.0 mol equiv.), cerium ammonium nitrate (106 mg, 0.19 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $C_2D_2Cl_4$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $C_2D_2Cl_4$ solution (0.0314 mmol, 49% yield); R_f 0.10 (25:75 CH_2Cl_2/pentane).

^{1}H NMR (800 MHz, $C_2D_2Cl_4$): δ 8.18 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 16.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.55 (dd, J = 17.4, 10.8 Hz, 1H), 5.52 (dd, J = 17.4, 1.1 Hz, 1H), 5.38 (d, J = 14.0 Hz, 2H), 5.28 (d, J = 10.9 Hz, 1H) ppm; ^{13}C NMR (200 MHz, $C_2D_2Cl_4$): δ 146.5 (q), 143.7 (q), 143.5 (q), 134.9 (CH), 132.5 (CH), 127.9 (CH), 126.9 (CH), 124.0 (CH), 118.3 (CH_2), 116.9 (CH_2) ppm.

MS (EI): m/z (%): 201.1 ($[M]^{+\bullet}$, 99), 154.1 (100), 128.1 (73), 77.0 (48); HRMS (EI): calculated for $C_{12}H_{11}NO_2$ $[M]^{+\bullet}$: 201.0790; found 201.0788.

(*E*)-methyl 4-methylene-2,5-hexadienoate (**8d**)

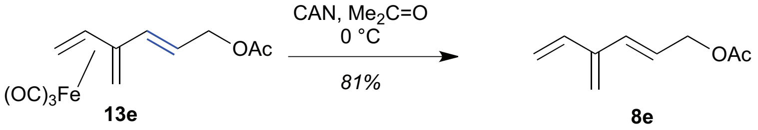


Tricarbonyl[(4-6η^4)-(*E*)-methyl 4-methylene-2,5-hexadienoate)iron **13d** (15 mg, 0.055 mmol, 1.0 mol equiv.), cerium ammonium nitrate (91 mg, 0.17 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $CDCl_3$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $CDCl_3$ solution (0.0235 mmol, 42% yield); R_f 0.15 (25:75 diethyl ether/pentane).

^{1}H NMR (300 MHz; $CDCl_3$): δ 7.20 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 17.4, 10.9 Hz, 1H), 5.88 (d, J = 15.9 Hz, 1H), 5.32–5.20 (m, 3H), 5.04 (d, J = 10.9 Hz, 1H), 3.56 (s, 3H) ppm; ^{13}C NMR (75 MHz; $CDCl_3$): δ 206.8 (q), 143.6 (CH), 142.1 (q), 134.0 (CH), 121.0 (CH_2), 119.6 (CH), 116.9 (CH_2), 51.3 (CH_3) ppm.

MS (EI): m/z (%): 138.1 ([M]$^{+\bullet}$, 23) , 118.0 (68) , 79.1 (100); HRMS (EI): calculated for $C_8H_{10}O_2$ [M]$^{+\bullet}$: 138.0681; found 138.0681.

(*E*)-1-Acetoxy-4-methylene-2,5-hexadiene (**8e**)



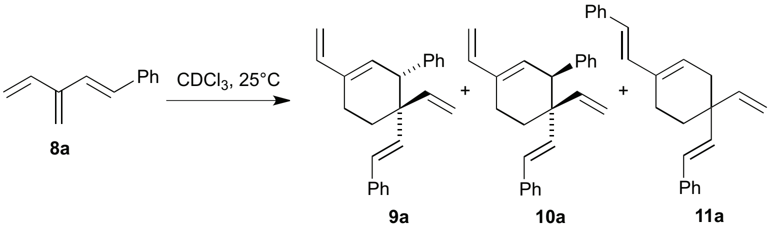
Tricarbonyl[(4-6η^4)-(*E*)-1-acetoxy-4-methylene-2,5-hexadiene]iron **13e** (58 mg, 0.20 mmol, 1.0 mol equiv.), cerium ammonium nitrate (329 mg, 0.60 mmol, 3.0 mol equiv.), and acetone (8 mL) were combined according to **GP-2**. The yellow oil was purified by flash column chromatography (silica gel, 5:95 diethyl ether/pentane) affording the *title compound* as a colourless oil (25 mg, 81 % yield); R_f 0.17 (5:95 diethyl ether/pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (dd, J = 17.2, 10.6 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 5.94 (dt, J = 15.8, 6.3 Hz, 1H), 5.39 (d, J = 17.5 Hz, 1H), 5.18–5.14 (m, 3H), 4.64 (d, J = 6.1 Hz, 2H), 2.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9 (q), 143.4 (q), 135.8 (CH), 132.9 (CH), 125.1 (CH), 116.5 (CH_2), 116.1 (CH_2), 65.0 (CH_2), 21.1 (CH_3) ppm; IR (thin film): ν_{max} = 3090, 2940, 1742, 1239, 968, 899 cm^{-1}.

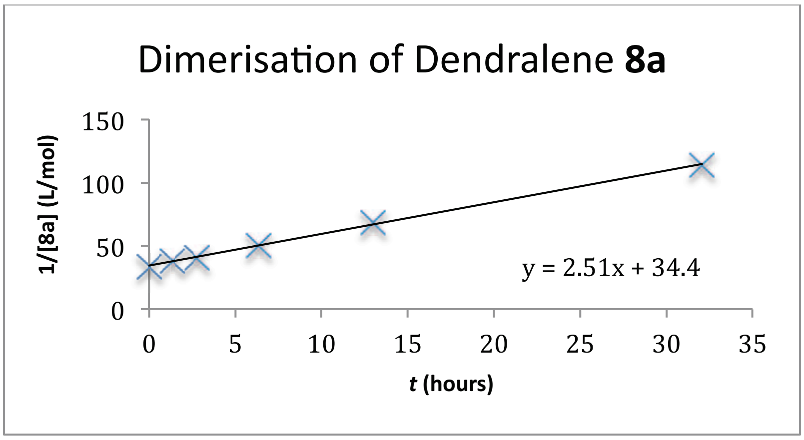
MS (EI): m/z (%): 152.0 ([M]$^{+\bullet}$, 13), 110.0 (12), 95.0 (20), 91.0 (100), 83.9 (45); HRMS (EI): calculated for $C_9H_{12}O_2$ [M]$^{+\bullet}$: 152.0837; found 152.0838.

1.3 Dimerisation of terminally-substituted [3]dendralenes

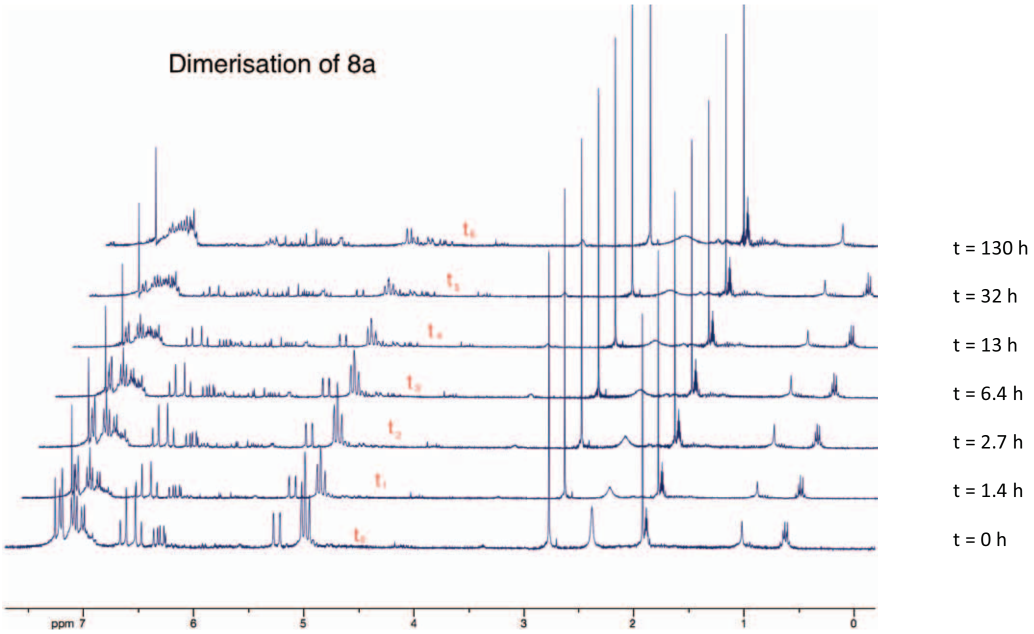
DIMERISATION OF **8a**



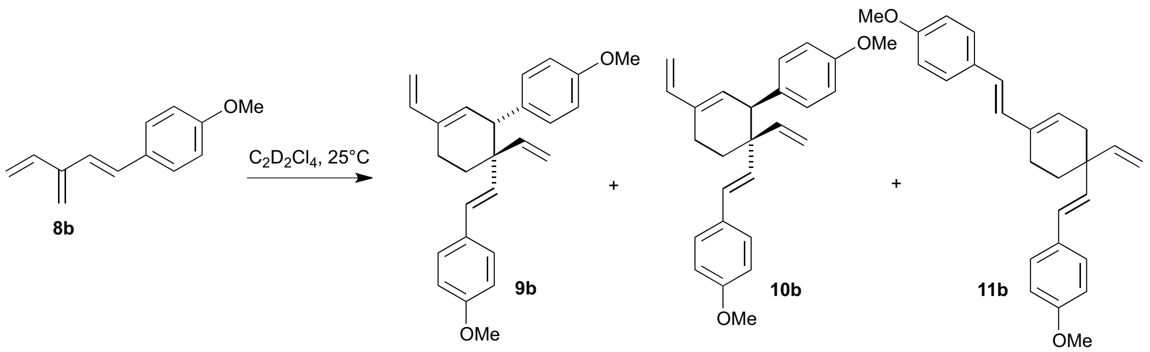
A solution of **8a** in $CDCl_3$ (0.80 mL, 0.0307 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 0.82 mL by addition of $CDCl_3$ to give a 0.030 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 13 hours at a concentration of 0.030 mol L^{-1}.



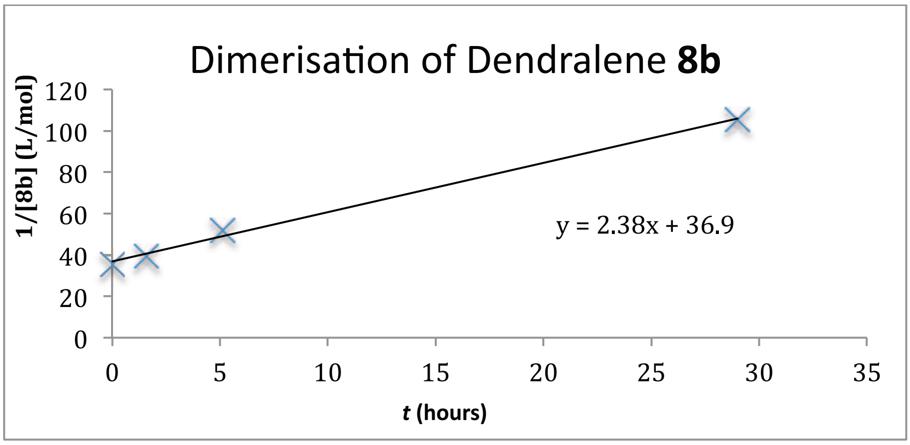
The loss of **8a** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **9a**, **10a**, and **11a**. The ratio of **9a**:**10a**:**11a** is consistent with that obtained in the Wittig reaction of **6** with benzaldehyde.



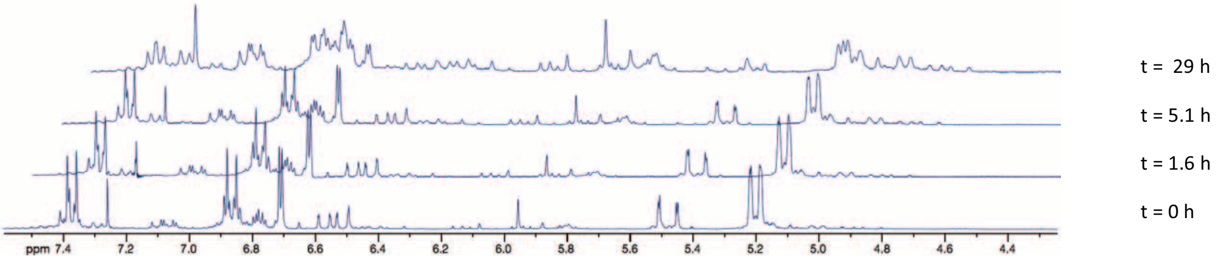
DIMERISATION OF **8b**



A solution of **8b** in $C_2D_2Cl_4$ (0.55 mL, 0.0773 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 1.42 mL by addition of $CDCl_3$ to give a 0.028 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 15 hours at a concentration of 0.028 mol L^{-1}.



The loss of **8b** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **9b**, **10b**, and **11b.** By ^{1}H NMR spectroscopy, the ratio of products **9b**:**10b**:**11b** was 59:33:8 respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 1:99 to 5:95 EtOAc/hexane) followed by HPLC (Porasil preparative column, 5:95 EtOAc/hexane). Dimer **9b** was isolated as a colourless oil (0.011 mmol, 57% by ^{1}H NMR spectroscopy); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.15 (2H, d, J = 8.8 Hz), 7.13 (2H, d, J = 8.8 Hz), 6.68 (2H, d, J = 8.8 Hz), 6.62 (2H, d, J = 8.8 Hz), 6.50 (1H, dd, J = 17.5, 10.9 Hz), 6.17 (1H, d, J = 16.3 Hz), 5.99, (1H, dd, J = 17.5, 10.8 Hz), 5.91 (1H, d, J = 16.3 Hz), 5.85 (1H, d, J = 4.1 Hz), 5.27–5.15 (3H, m), 5.06 (1H, d, J = 10.9 Hz), 3.80 (6H, s), 3.59 (1H, br s), 2.51–2.24 (2H, m) and 2.04–1.80 (2H, m) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 158.8, 158.3, 144.3, 139.6, 136.0, 133.4, 133.3, 131.5, 131.4, 130.8, 121.1, 127.2, 113.9, 113.7, 113.1, 111.2, 55.3 (two coincident signals), 50.5, 45.2, 29.2 and 21.5 ppm.

IR (thin film) v = 1607, 1510, 1247 cm^{-1}; MS (70 eV, EI): m/z (%): 372 (91) [M]$^+$, 186 (95), 155 (100); HRMS (70 eV, EI): calc for $C_{26}H_{28}O_2$ [M]$^+$: 372.2089; found 372.2088;

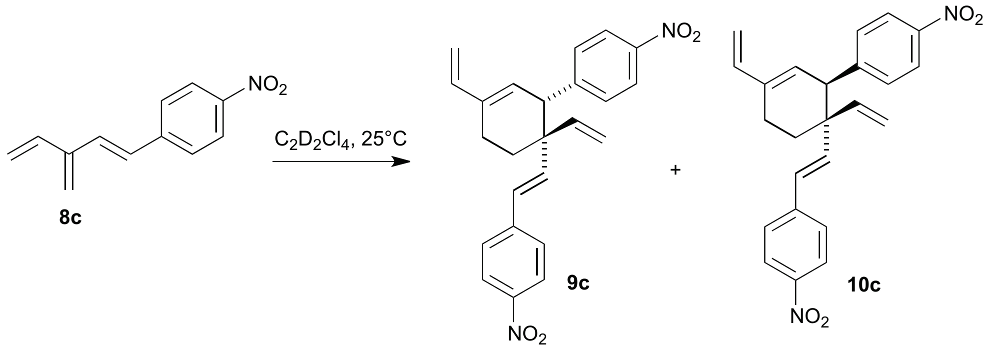
And dimer **10b** was isolated as a colourless oil (0.0064 mmol, 32% by ^{1}H NMR spectroscopy); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.32 (2H, d, J = 9.1 Hz), 7.09 (2H, d, J = 9.1 Hz), 6.90–6.81 (4H, m), 6.47 (1H, dd, J = 17.4, 10.8 Hz), 6.39 (1H, d, J = 16.5 Hz), 6.15, (1H, d, J = 16.5 Hz), 5.83 (2H, dd, J = 17.5, 10.8 Hz), 5.20 (1H, d, J = 17.8 Hz), 5.03 (1H, d, J = 10.8 Hz), 4.94 (1H, dd, J = 10.9, 1.5 Hz), 4.87 (1H, dd, J = 17.5, 1.5 Hz), 3.82 (3H, s), 3.81 (3H, s), 3.58 (1H, br s), 2.49–2.24 (2H, m) and 2.04–1.85 (2H, m) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 158.9 (two coincident signals), 144.5, 135.5, 134.4, 130.8, 130.6, 130.0, 127.4 (two coincident signals), 127.2, 124.9, 114.1, 114.0, 113.9, 112.8, 55.4 (two coincident signals), 41.6, 35.5, 32.2 and 22.3 ppm.

IR (thin film) v = 1510, 1247 cm^{-1}; MS (70 eV, EI): m/z (%): 372 (57) [M]$^{+\bullet}$, 186 (100), 155 (53); HRMS (70 eV, EI): calc for $C_{26}H_{28}O_2$ [M]$^{+\bullet}$: 372.2089; found 372.2090.

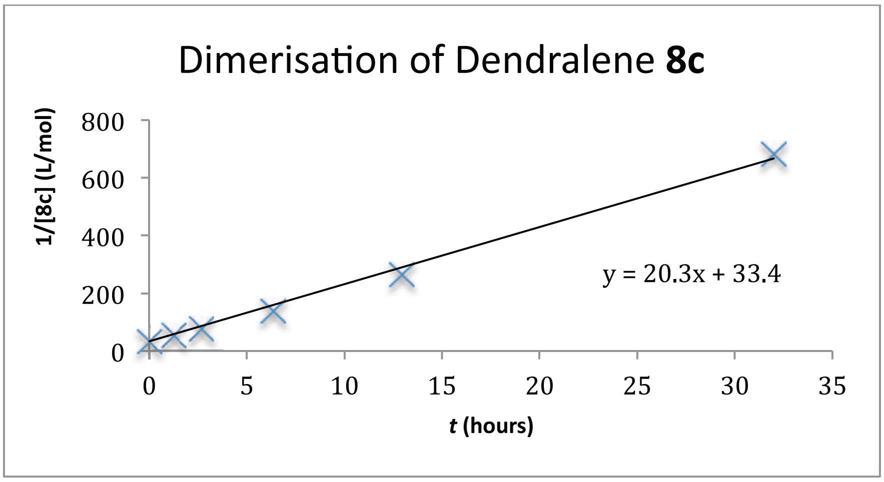
And **11b** as a colourless oil (0.0016 mmol, 8% by ^{1}H NMR spectroscopy); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.31 (4H, pseudo t, J = 8.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.9 Hz), 6.66 (1H, d, J = 16.0 Hz), 6.38 (1H, d, J = 16.0 Hz), 6.31 (1H, d, J = 16.4 Hz), 6.06 (1H, d, J = 16.4 Hz), 5.92–5.82 (2H, m), 5.09 (1H, dd, J = 4.5, 1.2 Hz), 5.04 (1H, dd, J = 10.9, 1.3 Hz), 3.80 (3H, s), 3.79 (3H, s), 2.38–2.27 (4H, m) and 1.84 (2H, t, J = 6.3 Hz) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ 158.9 (two coincident signals), 144.5, 135.5, 134.4, 130.8, 130.6, 130.0, 127.4 (two coincident signals), 127.2, 124.9, 114.1, 114.0, 113.9, 112.8, 55.4 (two coincident signals), 41.6, 35.5, 32.2 and 22.3 ppm.

IR (thin film) v = 1510, 1247 cm^{-1}; MS (70 eV, EI): m/z (%): 372 (57) [M]$^{+\bullet}$, 186 (100), 155 (53); HRMS (70 eV, EI): calculated for $C_{26}H_{28}O_2$ [M]$^{+\bullet}$: 372.2089; found 372.2090.

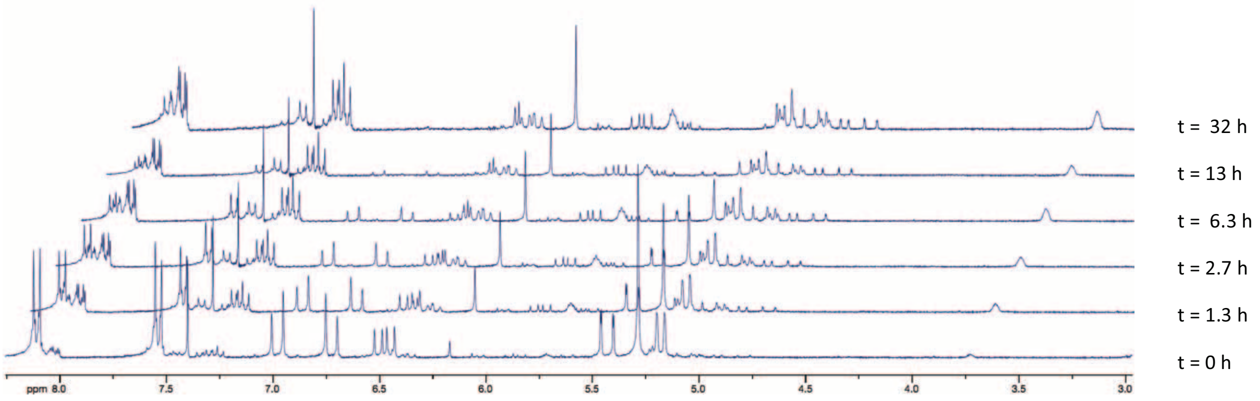
DIMERISATION OF **8c**



A solution of **8c** in $C_2D_2Cl_4$ (1.05 mL, 0.030 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was treated according to **GP-3**. The observed half-life was 1.7 hours at a concentration of 0.030 mol L^{-1}.



The loss of **8c** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **9c** and **10c**. By ^1H NMR spectroscopy, the ratio of products **9c**:**10c** was 56:44 respectively.



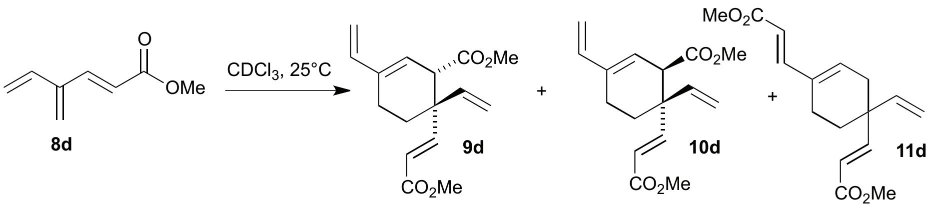
The crude mixture of dimers was purified by flash column chromatography (silica gel, 5:95 EtOAc/hexane). Dimer **9c** was isolated as a colourless oil (0.0087 mmol, 55% by ^{1}H NMR spectroscopy); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (2H, d, *J* = 8.9 Hz), 8.10 (2H, d, *J* = 8.9 Hz), 7.32 (2H, d, *J* = 8.9 Hz), 7.27 (2H, d, *J* = 8.9 Hz), 6.46 (1H, dd, *J* = 17.6, 11.0 Hz), 6.23 (1H, d, *J* = 16.4 Hz), 6.18 (1H, d, *J* = 16.4 Hz), 5.92 (1H, dd, *J* = 17.6, 10.9 Hz), 5.78 (1H, brd, *J* = 3.9 Hz), 5.30 (1H, d, *J* = 11.0 Hz), 5.27 (1H, d, *J* = 17.6 Hz), 5.20 (1H, d, *J* = 17.6 Hz), 5.12 (1H, d, *J* = 10.9 Hz), 3.76 (1H, br s), 2.50–2.55 (1H, m), 2.39–2.31 (1H, m) and 2.01–1.90 (2H, m) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.1, 147.1, 147.0, 143.8, 142.4, 139.2, 138.9, 137.6, 131.2, 128.7, 128.2, 126.7, 124.3, 123.2, 115.5, 113.0, 51.1, 45.7, 29.1 and 21.5 ppm.

IR (thin film) *v* = 1595, 1514, 1344 cm^{-1}; MS (70 eV, EI): *m/z* (%): 402 (28) $[M]^{+\bullet}$, 201 (100), 155 (52); HRMS (70 eV, EI): calc for $C_{24}H_{22}N_2O_4$ $[M]^{+\bullet}$: 402.1580; found 402.1586;

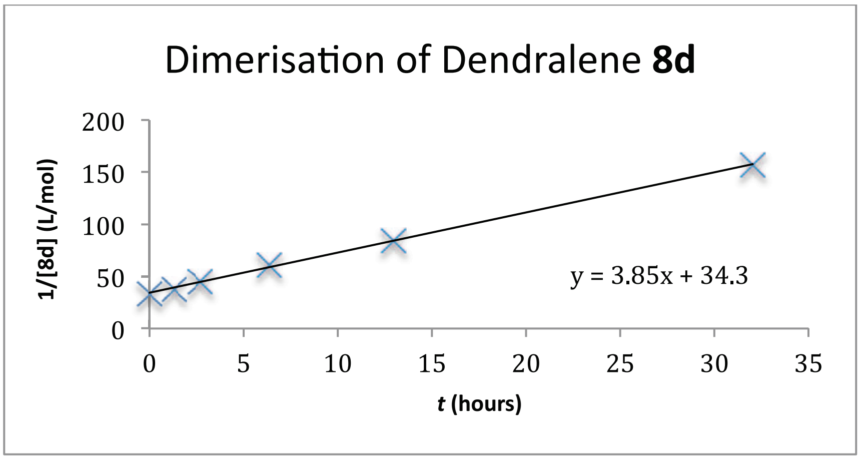
Dimer **10c** was isolated as a colourless oil (0.0068 mmol, 43% by ^{1}H NMR spectroscopy); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (2H, d, *J* = 8.7 Hz), 8.14 (2H, d, *J* = 8.7 Hz), 7.48 (2H, d, *J* = 8.7 Hz), 7.31 (2H, d, *J* = 8.7 Hz), 6.52 (1H, d, *J* = 16.5 Hz), 6.45, (1H, d, *J* = 16.5 Hz), 6.46 (1H, dd. *J* = 17.6, 10.8 Hz), 5.81–5.77 (1H, m), 5.74 (1H, dd, *J* = 17.6, 10.8 Hz), 5.26 (1H, d, *J* = 17.6 Hz), 5.11 (1H, d, *J* = 10.8 Hz), 5.00 (1H, dd, *J* = 10.8, 1.0 Hz), 4.86 (1H, dd, *J* = 17.6, 1.0 Hz), 3.75 (1H, br s), 2.54–2.46 (1H, m), 2.36–2.27 (1H, m) and 2.03–1.91 (2H, m) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0, 147.2, 147.1, 144.0, 141.2, 140.6, 138.9, 137.8, 131.3, 128.6, 128.1, 127.0, 124.3, 123.2, 115.6, 113.1, 51.3, 45.9, 29.0 and 21.6 ppm.

IR (thin film) *v* = 1595, 1515, 1343 cm^{-1}; MS (70 eV, EI): *m/z* (%): 402 (31) $[M]^{+\bullet}$, 201 (100), 155 (59); HRMS (70 eV, EI): calc for $C_{24}H_{22}N_2O_4$ $[M]^{+\bullet}$: 402.1580; found 402.1584.

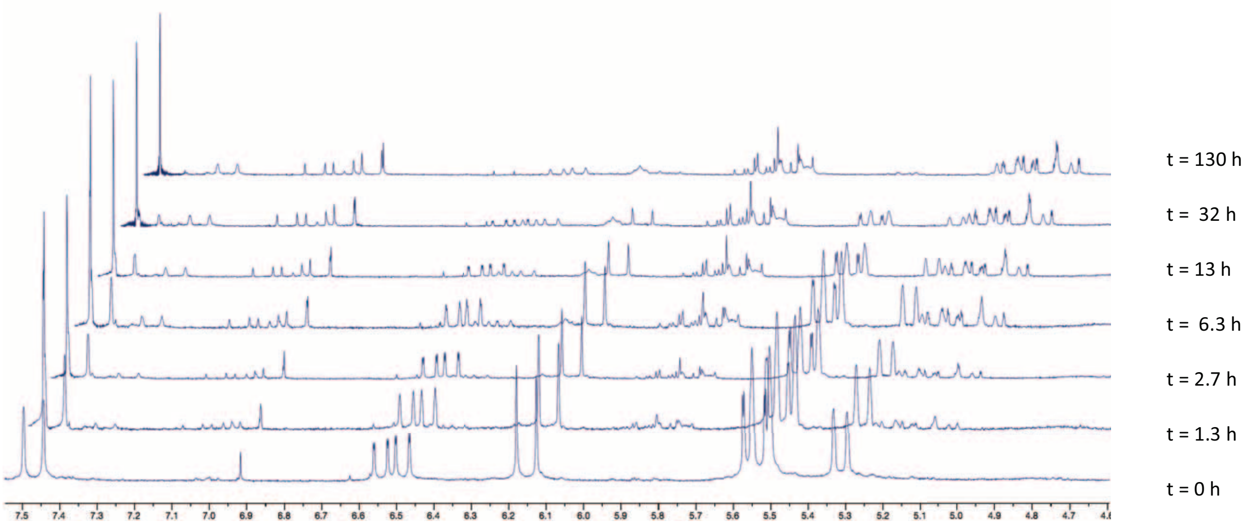
DIMERISATION OF **8d**



A solution of **8d** in $CDCl_3$ (0.55 mL, 0.043 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 0.78 mL by addition of $CDCl_3$ to give a 0.030 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 8.6 hours at a concentration of 0.030 mol L^{-1}.



The loss of **8d** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **9d**, **10d**, and **11d**. By ^{1}H NMR spectroscopy, the ratio of products **9d**:**10d**:**11d** was 28:22:50 respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 10:90 ethyl acetate/hexane) affording a mixture of **9d** and **10d** as a colourless oil (0.0057 mmol, 49% by ^{1}H NMR spectroscopy); R_f 0.30 (10:90 ethyl acetate/hexane).

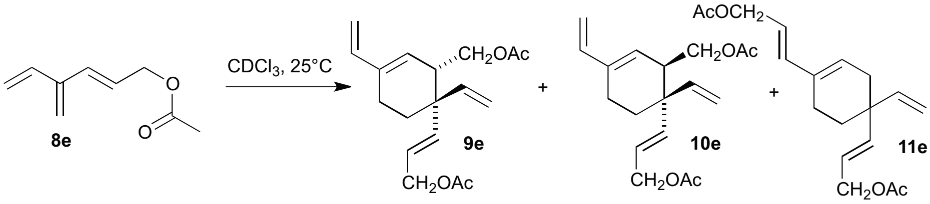
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 16.0 Hz, 1H), 6.96 (d, J =16.0 Hz, 1H), 6.36 (dd, J = 17.5, 10.8 Hz, 2H), 5.90–5.77 (m, 4H), 5.71 (app. d, J = 3.5 Hz, 2H), 5.21–5.02 (m, 8H), 3.72 (app. d, J = 2.8 Hz, 6H), 3.64 (s, 6H), 3.39 (br. s, 2H), 2.39–2.04 (m, 6H), 1.83–1.73 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.2 (two coincident signals), 167.0, 166.9, 152.5, 151.6, 140.8, 139.8, 138.6, 138.5, 138.2, 138.1, 123.4, 123.3, 120.5, 120.2, 115.8, 115.1, 112.7, 112.7, 51.9, 51.8, 51.6, 51.5, 49.9, 49.8, 43.7, 43.6, 28.5, 28.1, 21.0, 21.0 ppm.

IR (thin film): ν_{max} = 3154, 2953, 1718, 908 cm^{-1}; MS (EI): m/z: 276.1 ($[M]^{+\bullet}$); HRMS (EI): calculated for $C_{16}H_{20}O_4$ $[M]^{+\bullet}$: 276.1362; found 276.1365.

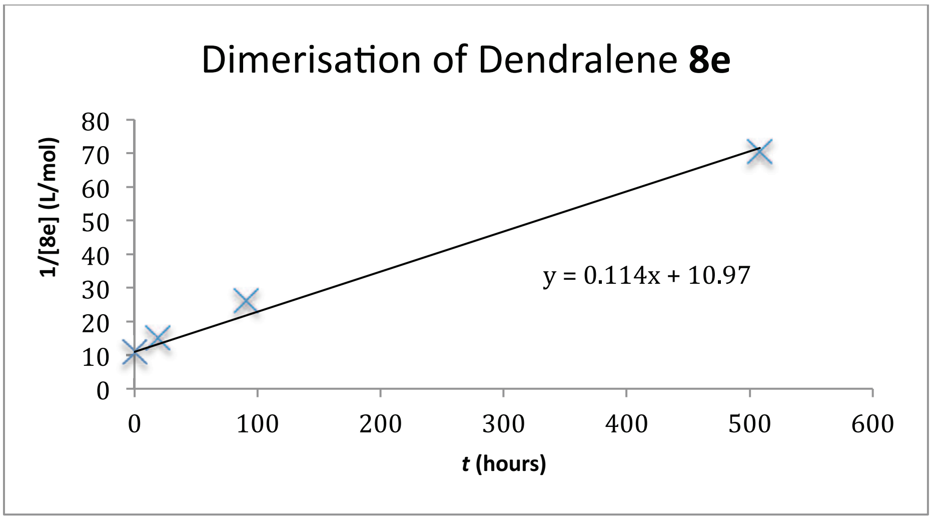
11d was isolated as a colourless oil (0.0057 mmol, 49% by ^{1}H NMR spectroscopy); R_f 0.22 (10:90 ethyl acetate/hexane); ^{1}H NMR (300 MHz; CDCl$_3$): δ 7.27 (d, J = 15.6 Hz, 1H), 6.88 (d, J = 16.0 Hz, 1H), 6.14 (s, 1H), 5.79–5.68 (m, 3H), 5.06 (app dd, J = 33.3, 14.1 Hz, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 2.35 (br s, 2H), 2.16 (br s, 2H), 1.79 (t, J = 6.5 Hz, 2H) ppm; ^{13}C NMR (75 MHz; CDCl$_3$): δ 167.1 (q, two coincident signals), 153.2 (CH), 147.0 (CH), 141.5 (CH), 135.0 (CH), 134.3 (CH), 119.5 (CH), 115.3 (CH), 114.5 (CH$_2$), 51.59 (CH$_3$), 51.53 (CH$_3$), 41.6 (q), 34.4 (CH$_2$), 30.9 (CH$_2$), 21.5 (CH$_2$) ppm.

IR (thin film): ν_{max} = 3153, 2953, 1717 cm^{-1}; MS (EI): m/z (%): 276.1 ([M]$^{+\bullet}$, 6), 244.1 (36), 216.1 (20), 137.1 (11), 79.1 (100); HRMS (EI): calculated for $C_{16}H_{20}O_4$ [M]$^{+\bullet}$: 276.1362; found 276.1365.

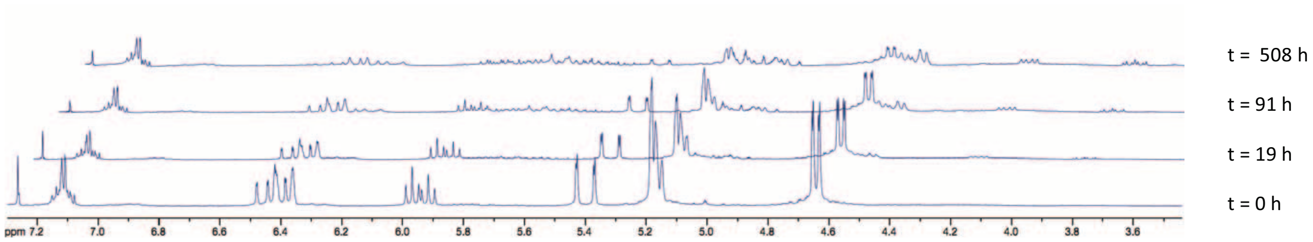
DIMERISATION OF **8e**



A solution of **8e** in CDCl$_3$ (0.45 mL, 0.091 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was treated according to **GP-3**. The observed half-life was 92 hours at a concentration of 0.091 mol L^{-1}.



The loss of **8e** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **9e**, **10e**, and **11e**. By ^{1}H NMR spectroscopy, the ratio of products was 36:25:39 for **9e**:**10e**:**11e** respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 2:98 to 5:95 ethyl acetate/hexane) affording a mixture of all three dimers **9e–11e** as a colourless oil; R_f 0.46 (10:90 EtOAc/hexane). Separation was achieved by reverse phase HPLC (60:40 acetonitrile/water, Waters XBridge Prep C18 5 μm OBD 19 × 150 mm).

9e was isolated as a colourless oil (0.0066 mmol, 32% by ^{1}H NMR spectroscopy); retention time 8.9 minutes (17 mL/minute, 60:40 acetonitrile/water), ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.36 (dd, J = 17.5, 10.8 Hz, 1H), 5.90 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 15.9 Hz, 1H), 5.70–5.69 (m, 1H), 5.59 (dt, J = 15.9, 6.3 Hz, 1H), 5.15–5.06 (m, 3H), 4.99 (d, J = 10.7 Hz, 1H), 4.53 (dd, J = 6.3, 1.0 Hz, 2H), 4.18 (dd, J = 10.9, 5.0 Hz, 1H), 3.83 (dd, J = 11.0, 8.2 Hz, 1H), 2.56 (t, J = 2.6 Hz, 1H), 2.18 (t, J = 2.1 Hz, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 1.83–1.69 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 170.9, 142.8, 139.1, 137.7, 136.7, 127.9, 124.3, 114.2, 111.8, 65.36, 65.23, 43.1, 42.5, 30.6, 29.8, 21.26, 21.10 ppm.

IR (thin film): ν_{max} = 2929, 1733, 908 cm^{-1}; MS (EI): m/z (%): 304.2 ($[M]^{+\bullet}$, 2), 244.1 (30), 184.1 (51), 92.1 (100); HRMS (EI): calculated for $C_{18}H_{24}O_4$ $[M]^{+\bullet}$: 304.1675; found 304.1676.

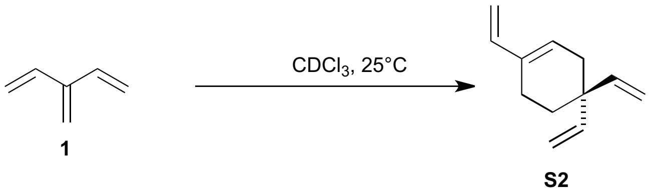
10e was collected as a *ca.* 1:1 mixture with **9e**, as a colourless oil (0.0045 mmol **10e**, yield of **10e** 22% by ^{1}H NMR spectroscopy); retention time 8.4 minutes (17 mL/minute, 60:40 acetonitrile/water), ^{1}H (300 MHz; $CDCl_3$): δ 6.37 (dd, J = 17.5, 10.7 Hz, 2H), 5.95–5.75 (m, 4H), 5.70–5.54 (m, 4H), 5.16–4.98 (m, 8H), 4.54 (t, J = 6.9 Hz, 4H), 4.18 (ddd, J = 10.9, 4.9, 0.6 Hz, 2H), 3.83 (ddd, J = 11.1, 8.2, 3.1 Hz, 2H), 2.55 (br s, 2H), 2.19 (br s, 4H), 2.06–2.05 (m, 12H), 1.86–1.67 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2 (two coincident peaks), 171.1, 170.9, 142.8 (two coincident peaks), 140.3, 140.1, 139.1, 137.8 (two coincident peaks), 136.7, 136.7, 127.9 (two coincident peaks), 124.4, 123.5, 115.2, 114.2, 111.8 (two coincident peaks), 65.5, 65.4, 65.3, 65.2, 43.2, 43.1, 42.6, 42.5, 30.60, 30.5, 29.8 (two coincident peaks), 21.3 (two coincident peaks), 21.1 (two coincident peaks) ppm.

IR (thin film): ν_{max} = 2929, 1733, 908 cm^{-1}; MS (EI): m/z (%): 304.2 ($[M]^{+\bullet}$, 38), 288.1 (100); HRMS (EI): calculated for $C_{18}H_{24}O_4$ $[M]^{+\bullet}$: 304.1675; found 304.1676.

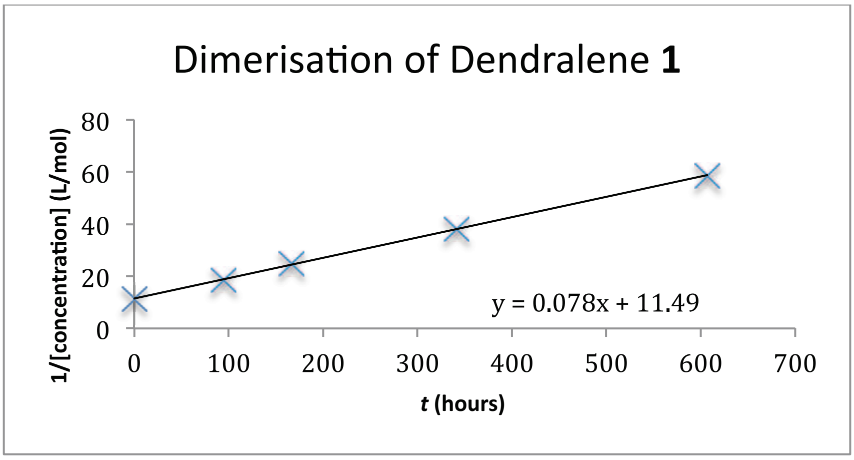
11e was isolated as a colourless oil (0.0071 mmol, 35% by ^{1}H NMR spectroscopy); retention time 7.8 minutes (17 mL/minute, 60:40 acetonitrile/water); ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.26 (d, J = 15.7 Hz, 1H), 5.78–5.68 (m, 3H), 5.60 (dt, J = 15.5, 6.8 Hz, 1H), 5.51 (dt, J = 15.7, 6.3 Hz, 1H), 5.05–4.94 (m, 2H), 4.59 (d, J = 6.7 Hz, 2H), 4.52 (dt, J = 6.3, 1.3 Hz, 2H), 2.21 (s, 2H), 2.13-2.10 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.69 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$): δ 171.0, 171.0, 143.4, 141.3, 137.4, 134.3, 128.4, 122.4, 119.6, 113.2, 65.53, 65.36, 41.2, 34.7, 31.5, 29.8, 21.9, 21.1 ppm.

IR (thin film): ν_{max} =2924, 2951, 1732, 909 cm^{-1}; MS (EI): *m/z* (%): 304.2 ([*M*]$^{+\bullet}$, 4), 262.1 (100); HRMS (EI): calculated for $C_{18}H_{24}O_4$ [*M*]$^{+\bullet}$: 304.1675; found 304.1678.

DIMERISATION OF **1** TO GIVE **S2**



A solution of **1** in $CDCl_3$ (0.55 mL, 0.38 mol L^{-1}) containing methylsulfonylmethane as an internal standard (1 mmol) was diluted to 2.45 mL by addition of $CDCl_3$ to give a 0.087 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 150 hours at a concentration of 0.087 mol L^{-1}. All spectroscopic data for **S2** corresponded to that reported in the literature.[7]



2 References

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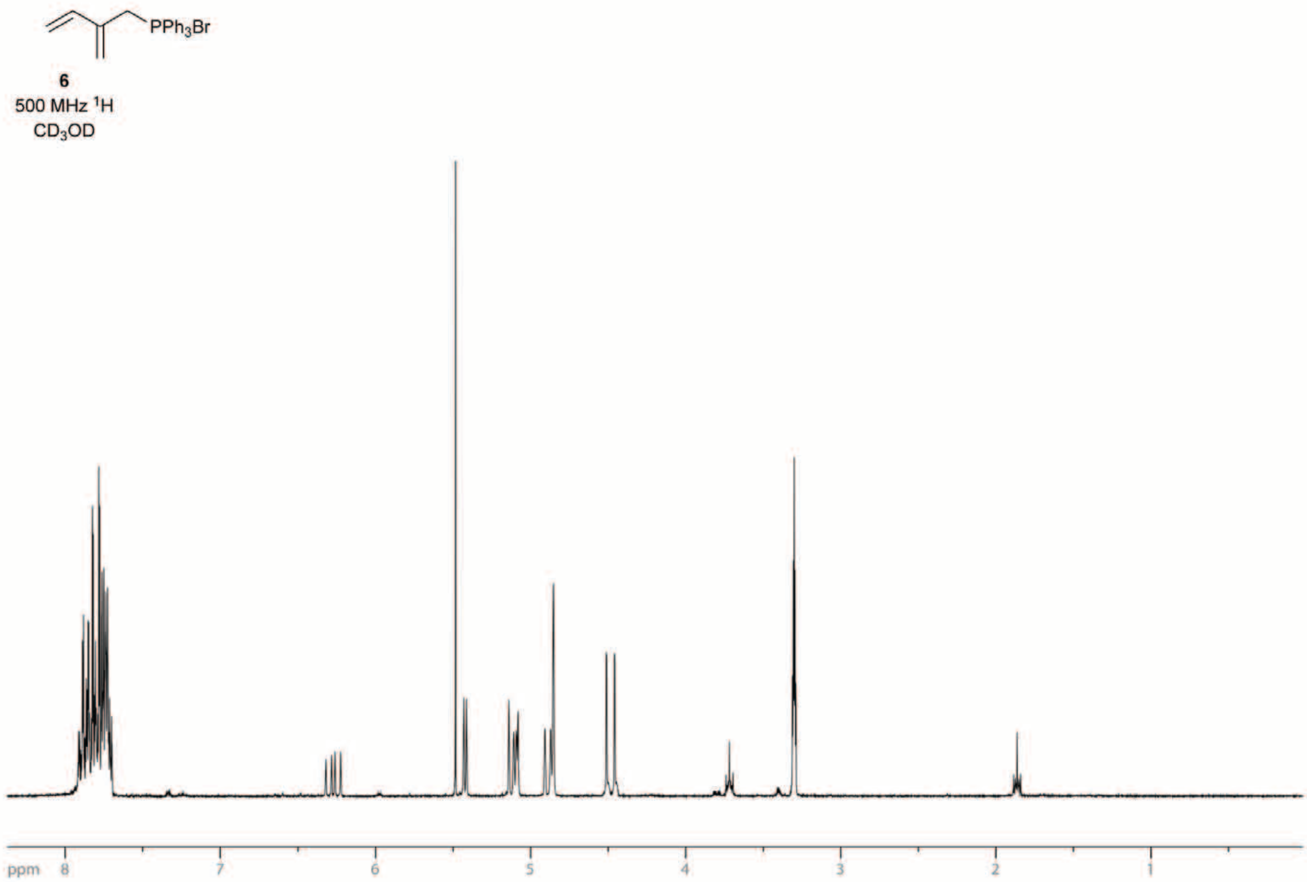
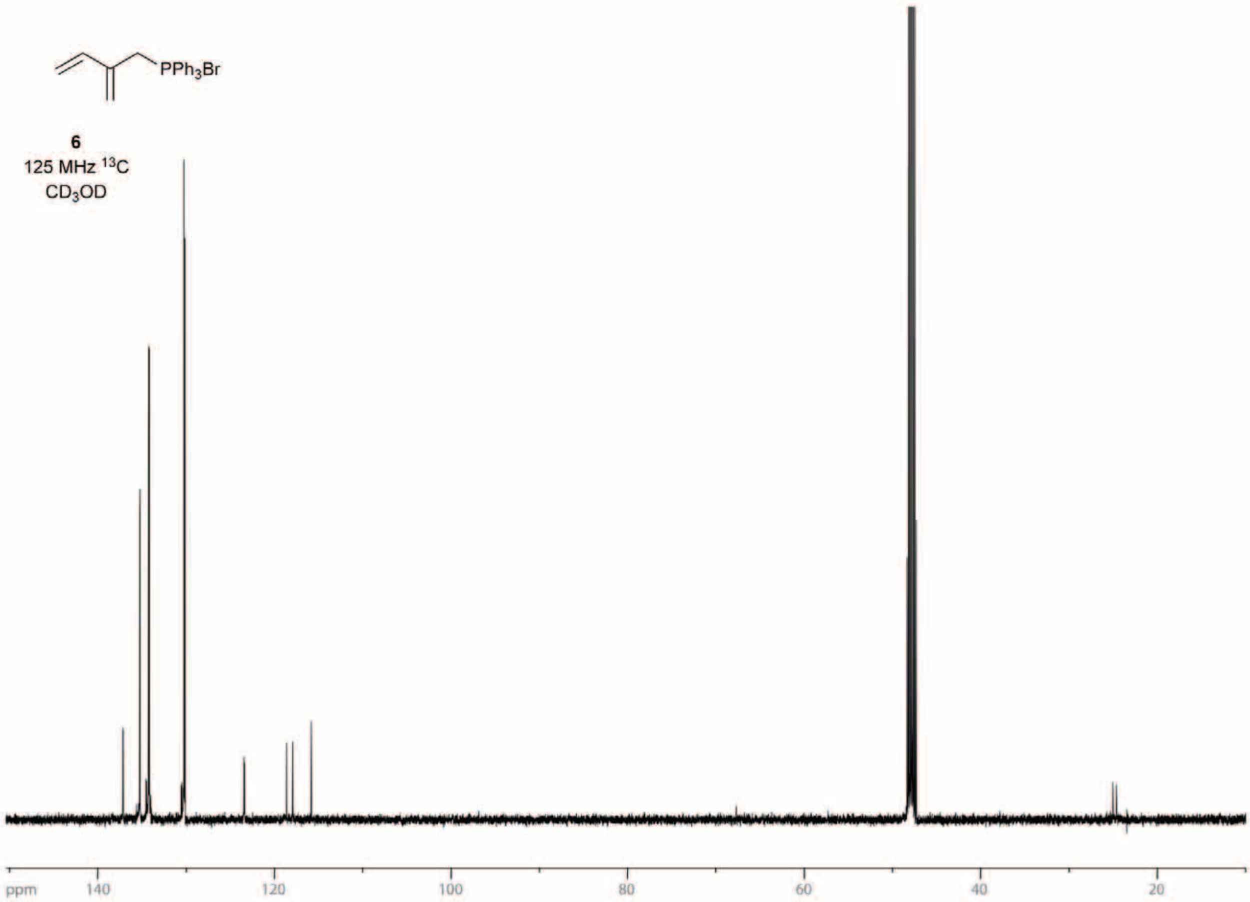
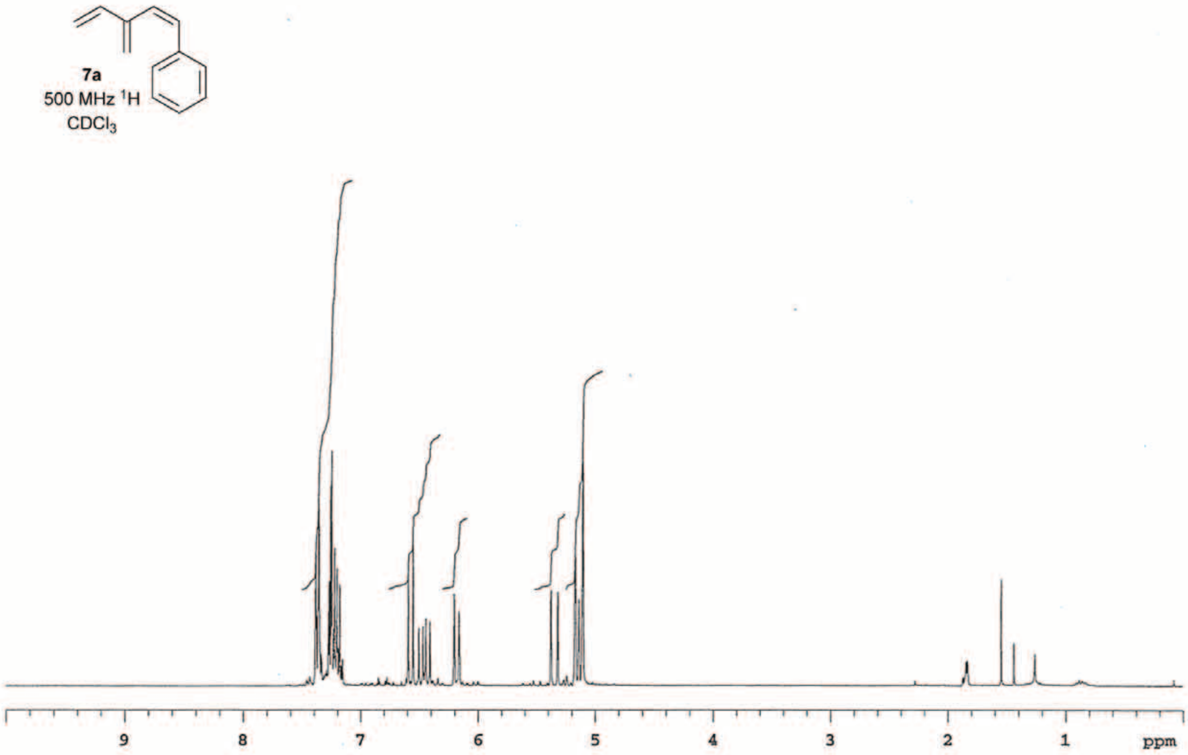
[6] (*a*) R. C. Krug and T. F. Yen, *J. Org. Chem.*, 1956, **21**, 1082–1086; (*b*) R. G. Riley, R. M. Silverstein, J. A. Katzenellenbogen and R. S. Lenox, *J. Org. Chem.*, 1974, **39**, 1957–1958.

[7] (*a*) T. A. Bradford, A. D. Payne, A. C. Willis, M. N. Paddon-Row and M. S. Sherburn, *J. Org. Chem.*, 2010, **75**, 491–494; (*b*) W. S. Trahanovsky and K. A. Koeplinger, *J. Org. Chem.*, 1992, **57**, 4711–4716.

3 ^{1}H and ^{13}C NMR Spectra of Compounds 6, 7a, 8a–11e and 13b,c



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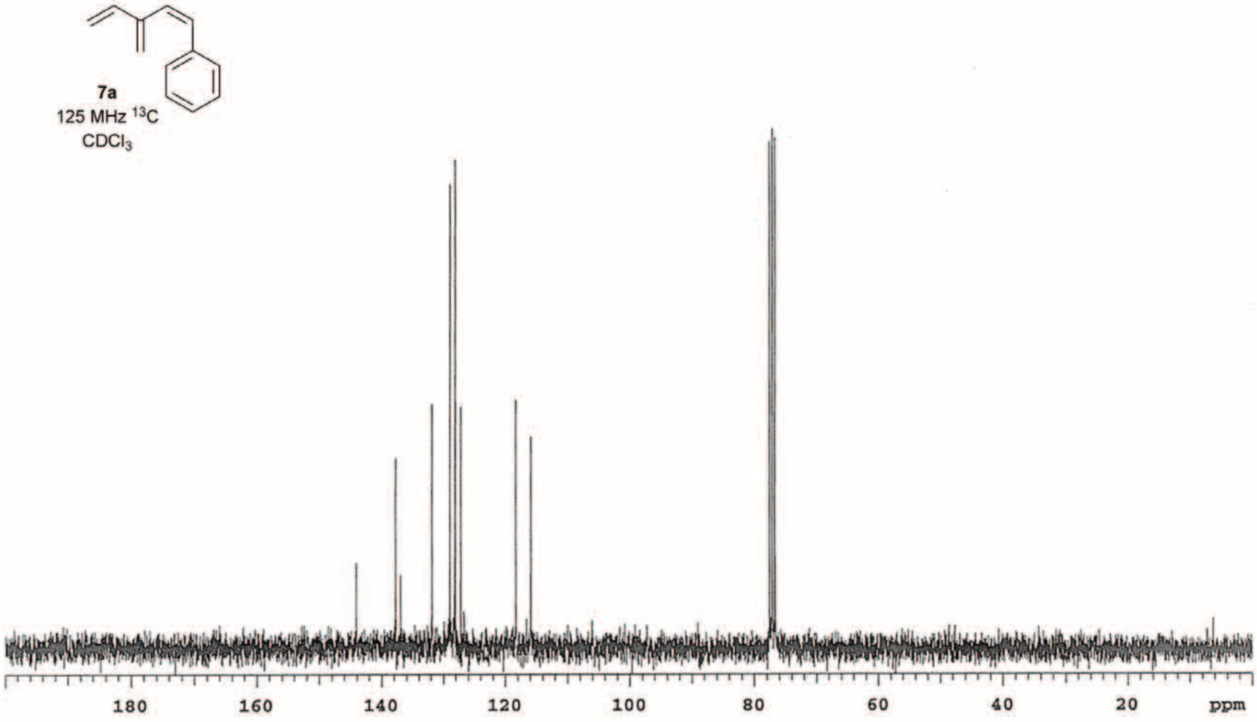
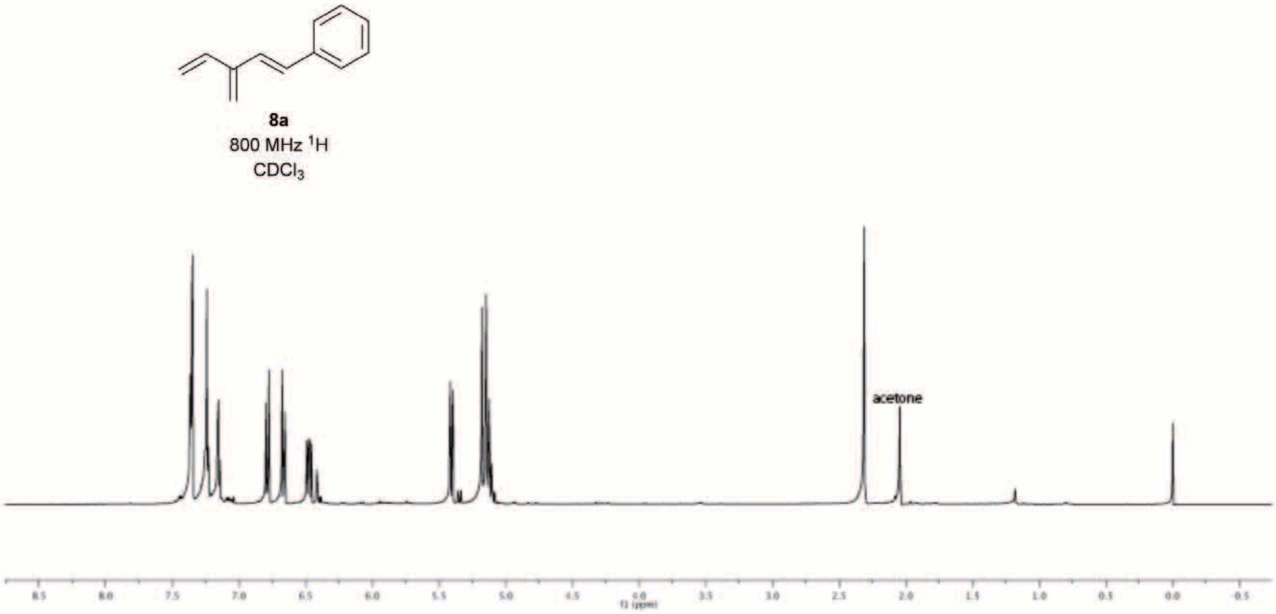
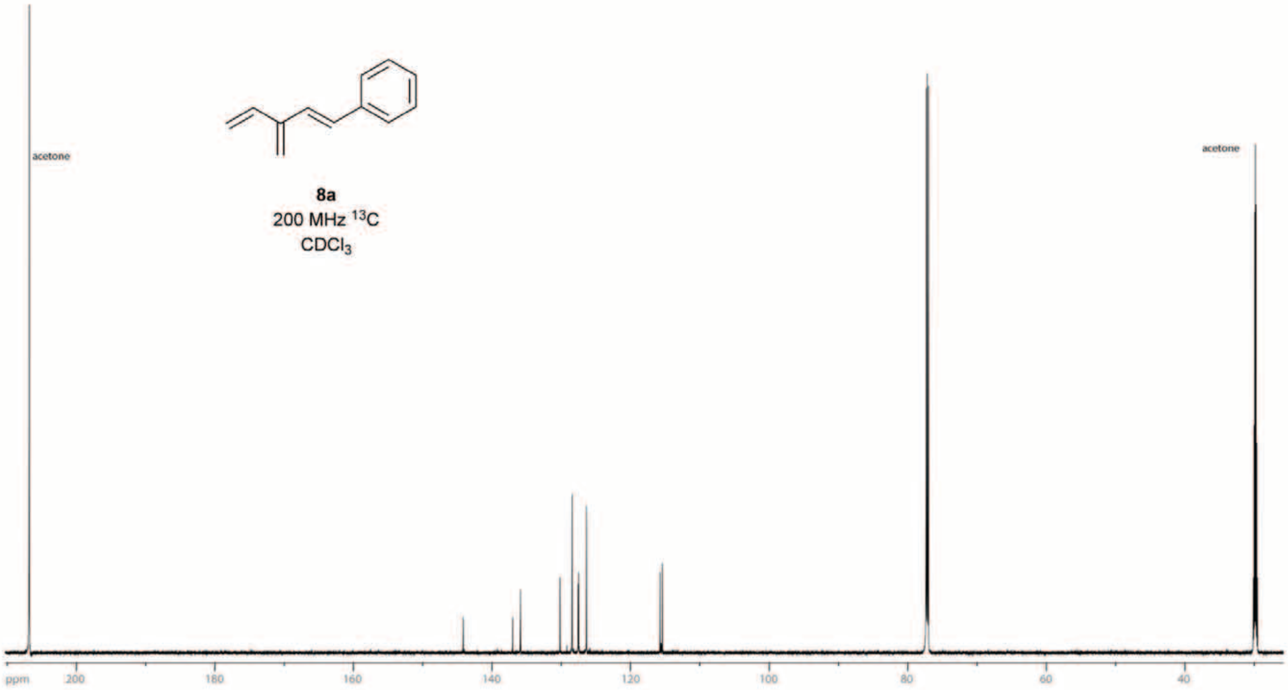
CDCl$_3$
9
8
7
6
5
4
3
2
1
ppm


7a
125 MHz ^{13}C
CDCl$_3$
180
160
140
120
100
80
60
40
20
ppm


8a
800 MHz ^{1}H
CDCl$_3$
acetone
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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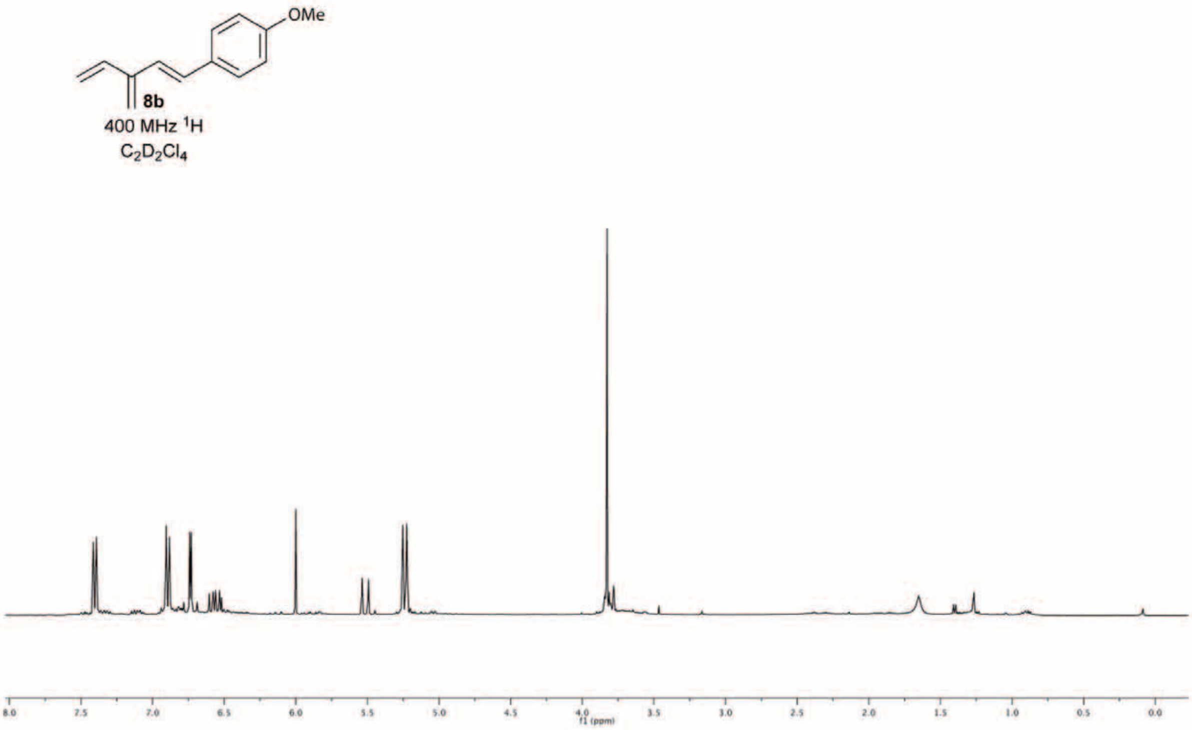
CDCl$_3$
acetone
acetone
ppm
200
180
160
140
120
100
80
60
40


OMe
8b
400 MHz ^{1}H
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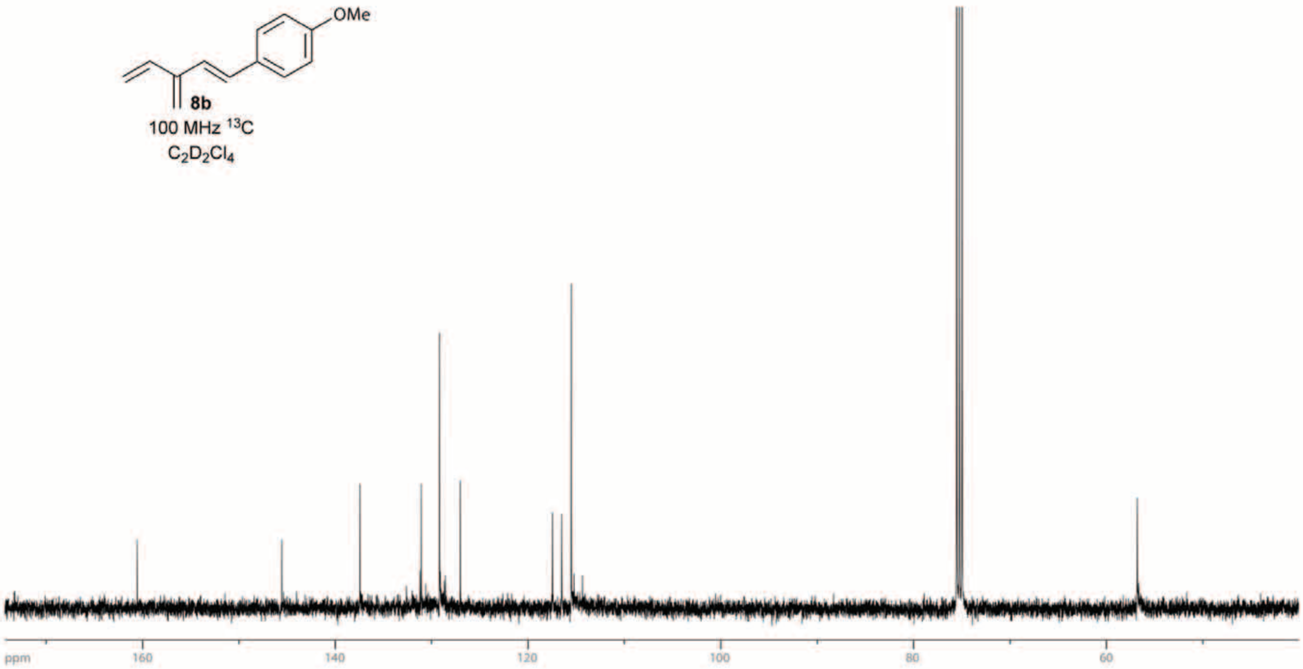
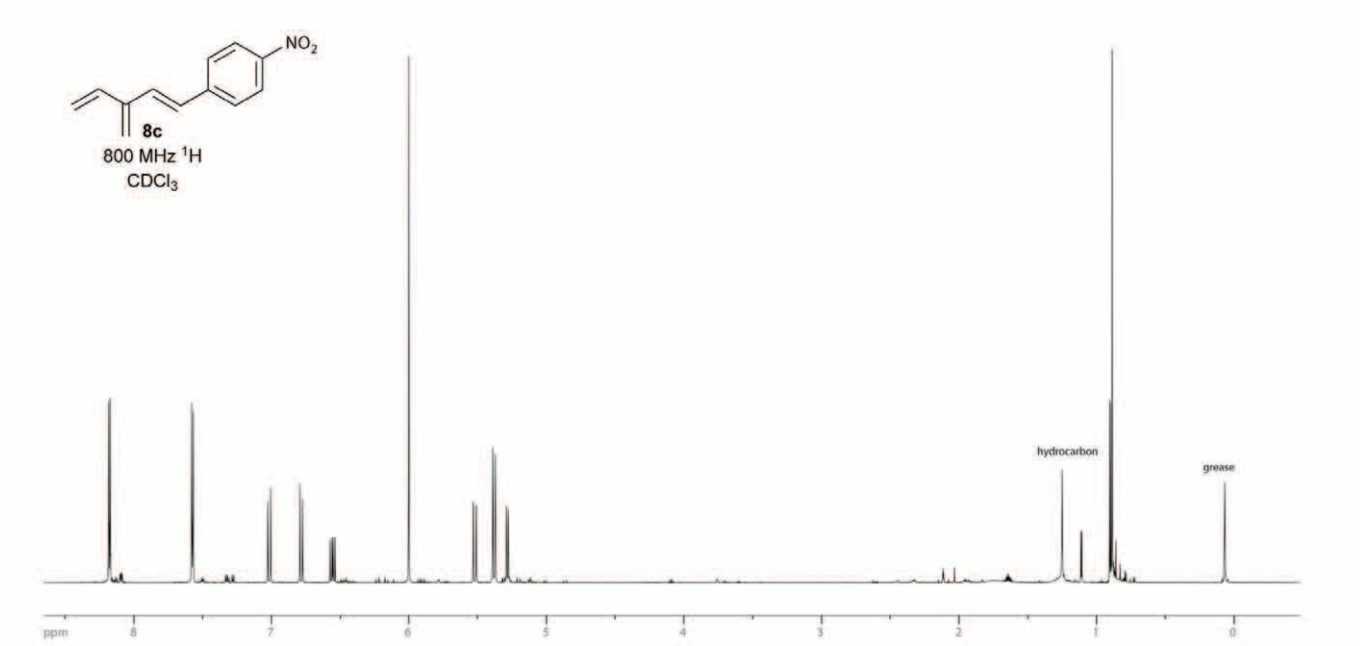
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


OMe
8b
100 MHz ^{13}C
$C_2D_2Cl_4$
ppm
160
140
120
100
80
60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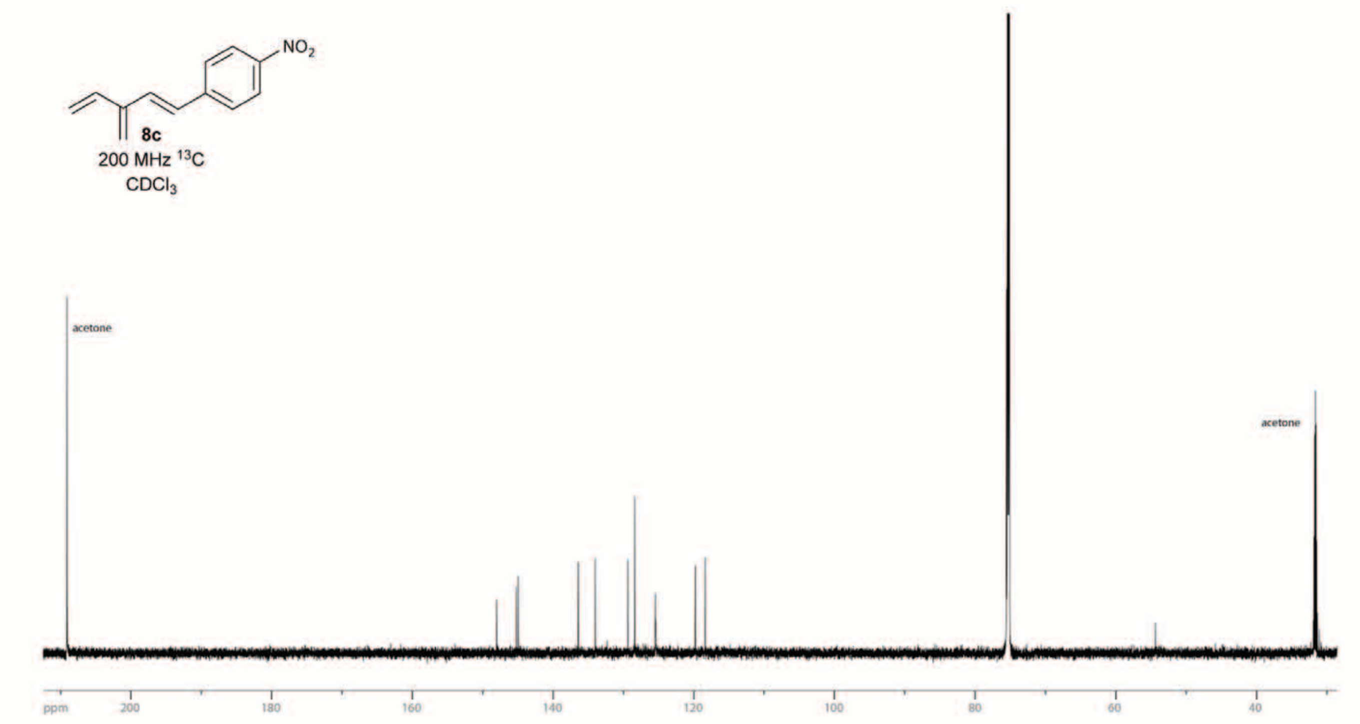
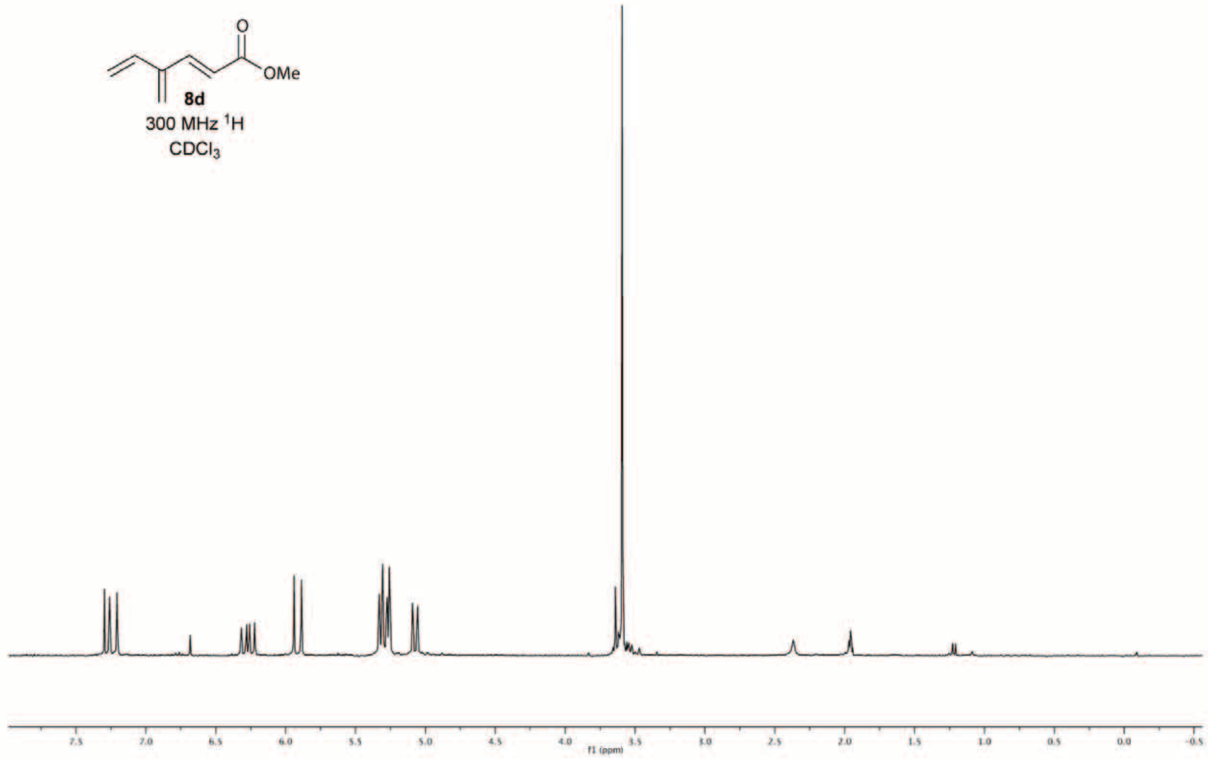
8c
800 MHz ^{1}H
CDCl$_3$
hydrocarbon
grease
ppm
8
7
6
5
4
3
2
1
0


NO$_2$
8c
200 MHz ^{13}C
CDCl$_3$
acetone
acetone
ppm
200
180
160
140
120
100
80
60
40


O
OMe
8d
300 MHz ^{1}H
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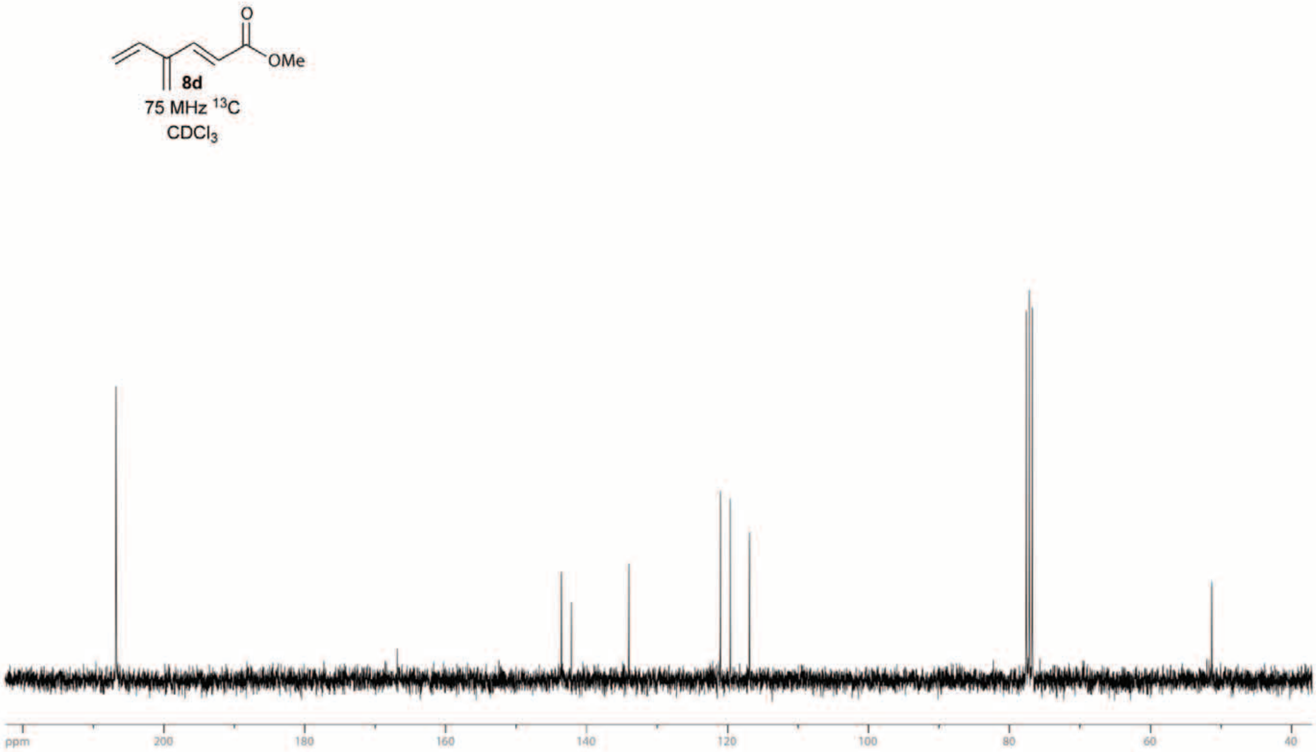
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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OMe
8d
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ppm
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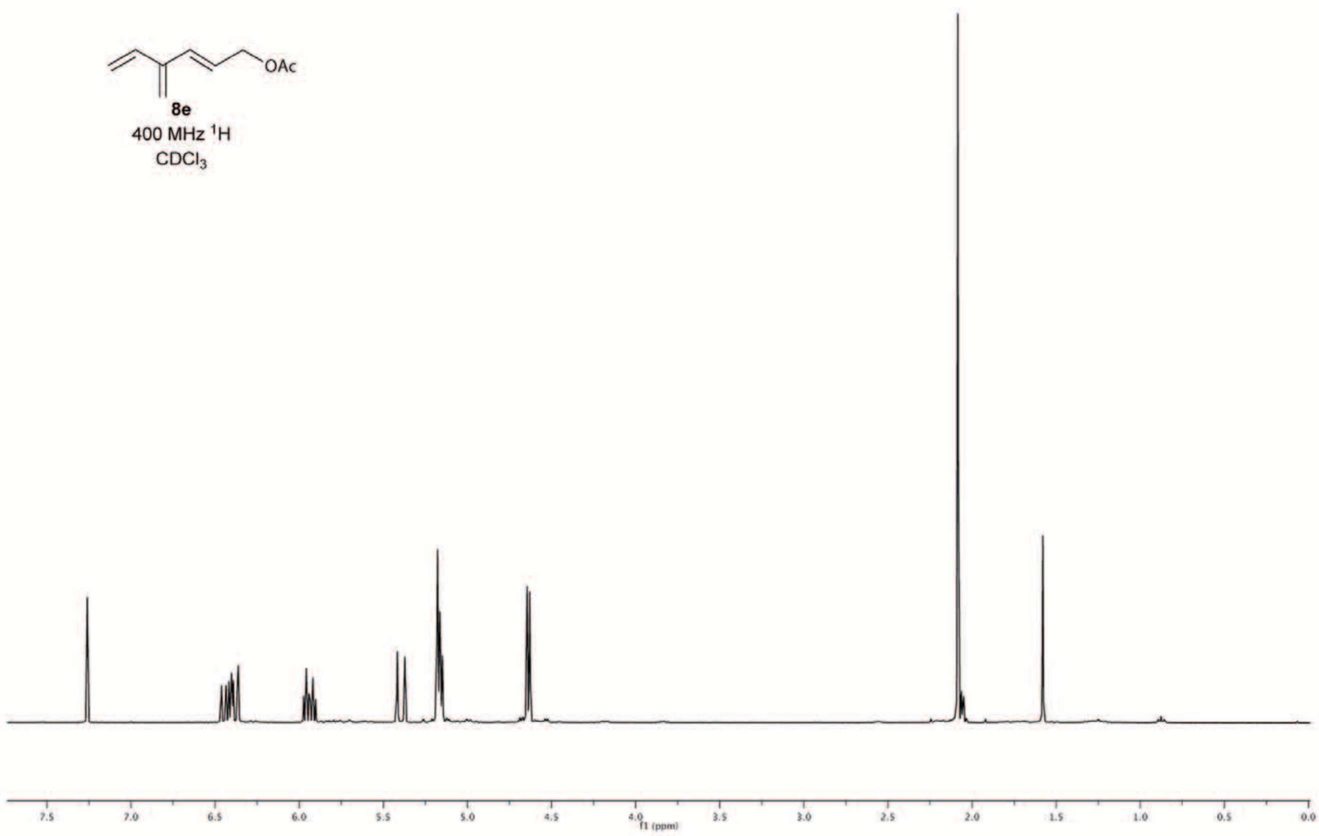
140
120
100
80
60
40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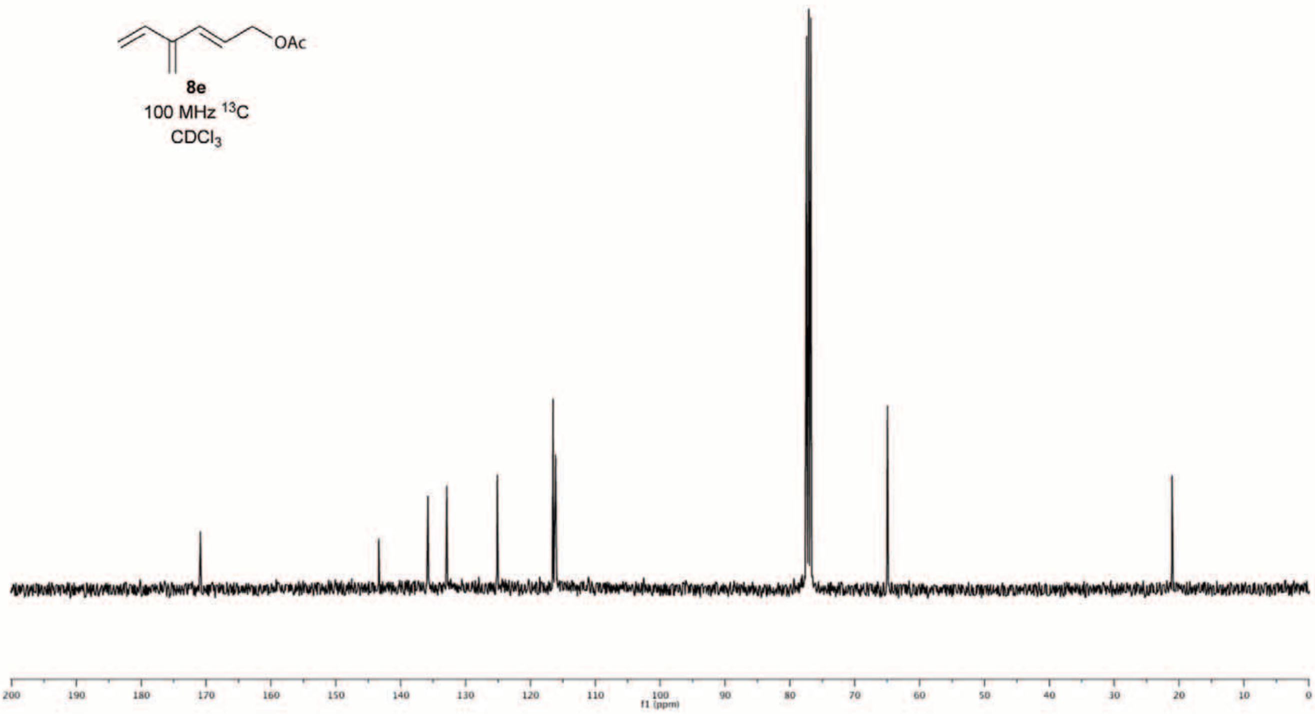
$CDCl_3$
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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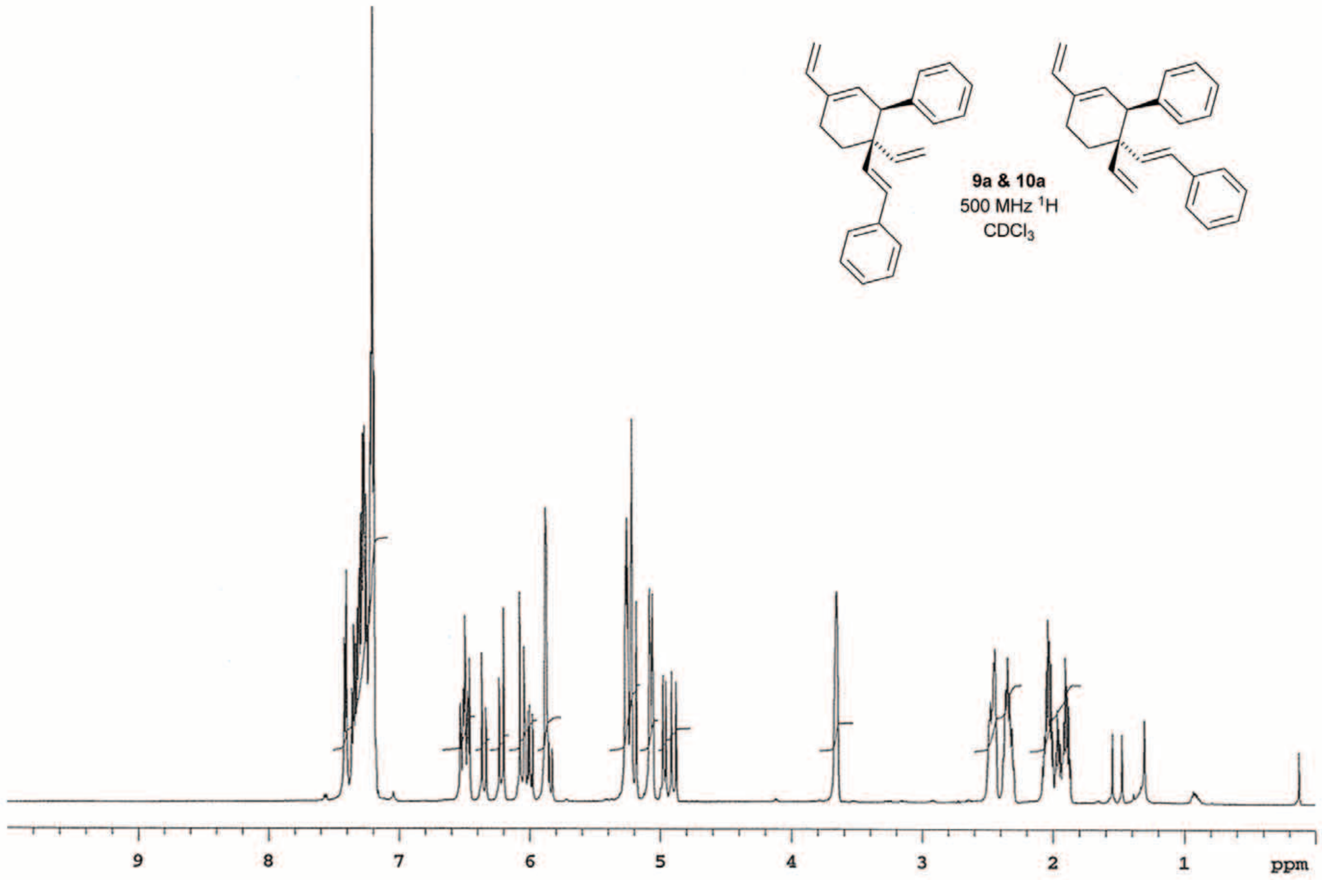
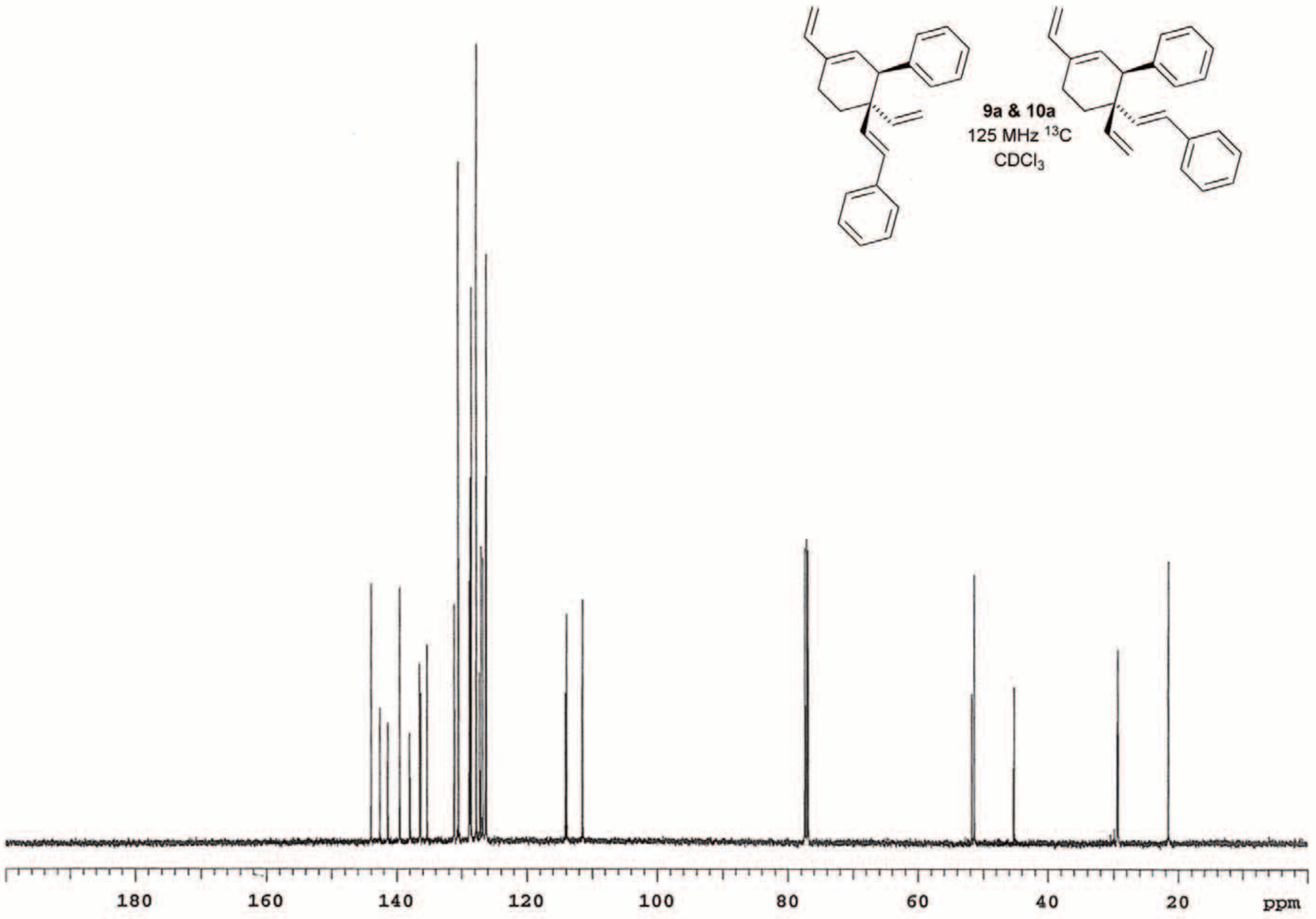
8e
100 MHz ^{13}C
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9a & 10a
500 MHz ^{1}H
CDCl$_3$
9
8
7
6
5
4
3
2
1
ppm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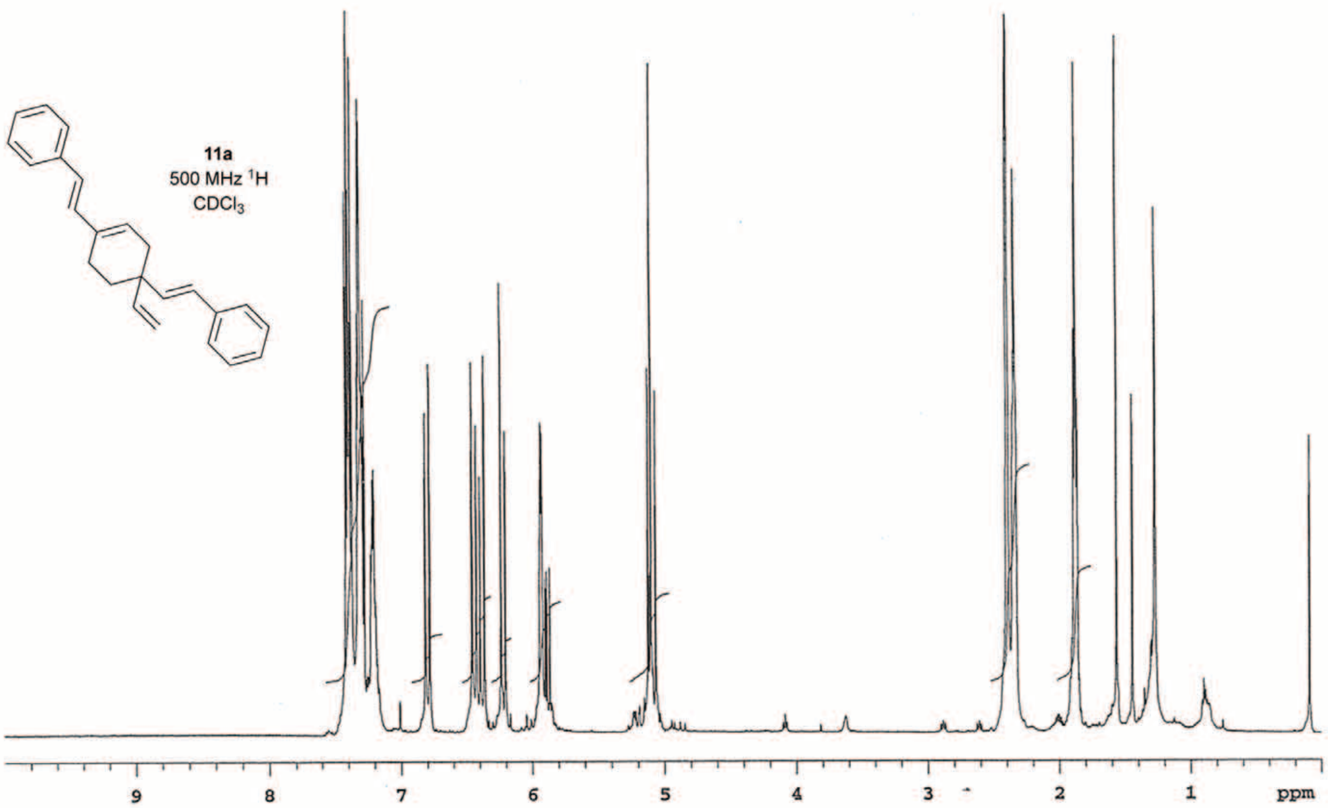
125 MHz ^{13}C
CDCl$_3$
180
160
140
120
100
80
60
40
20
ppm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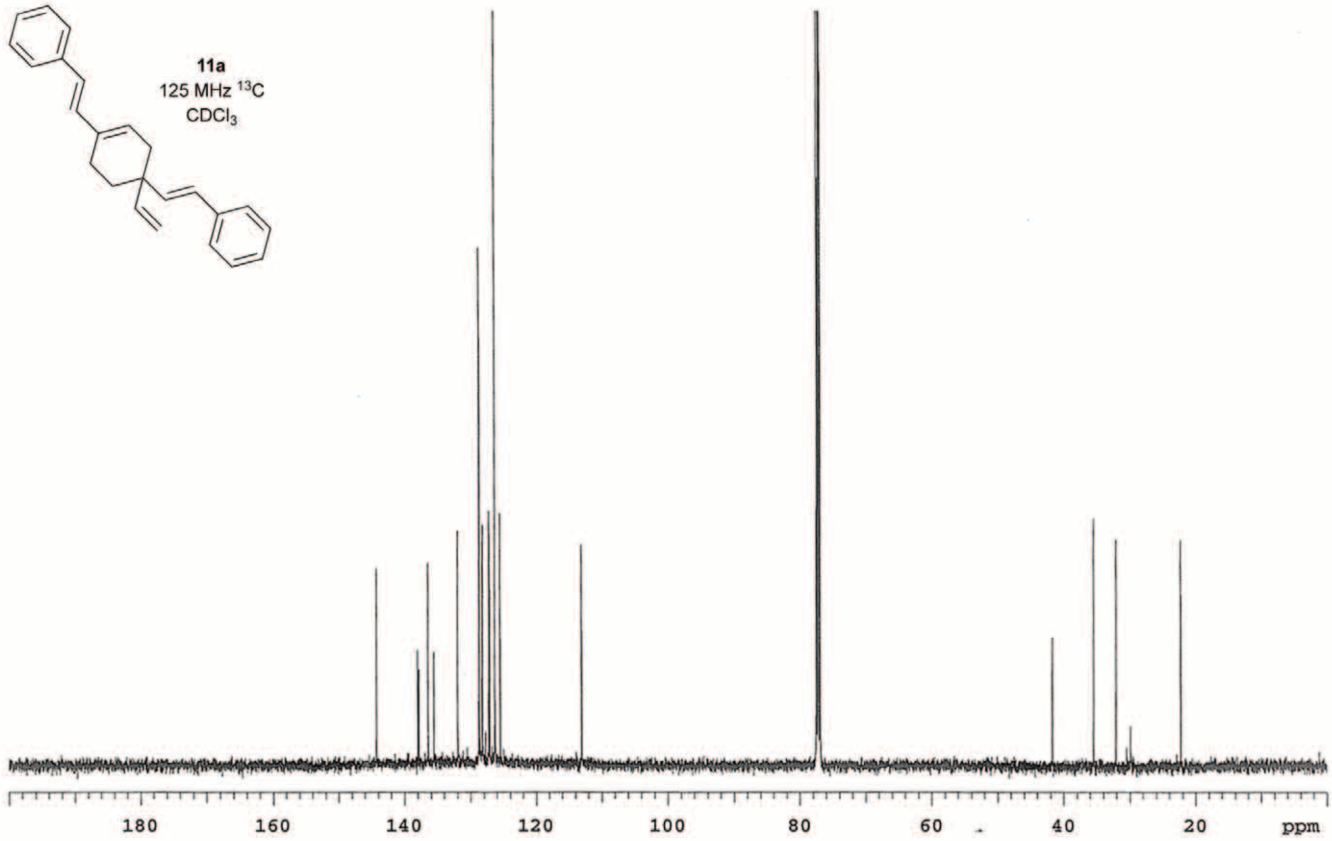
500 MHz ^{1}H
$CDCl_3$
9
8
7
6
5
4
3
2
1
ppm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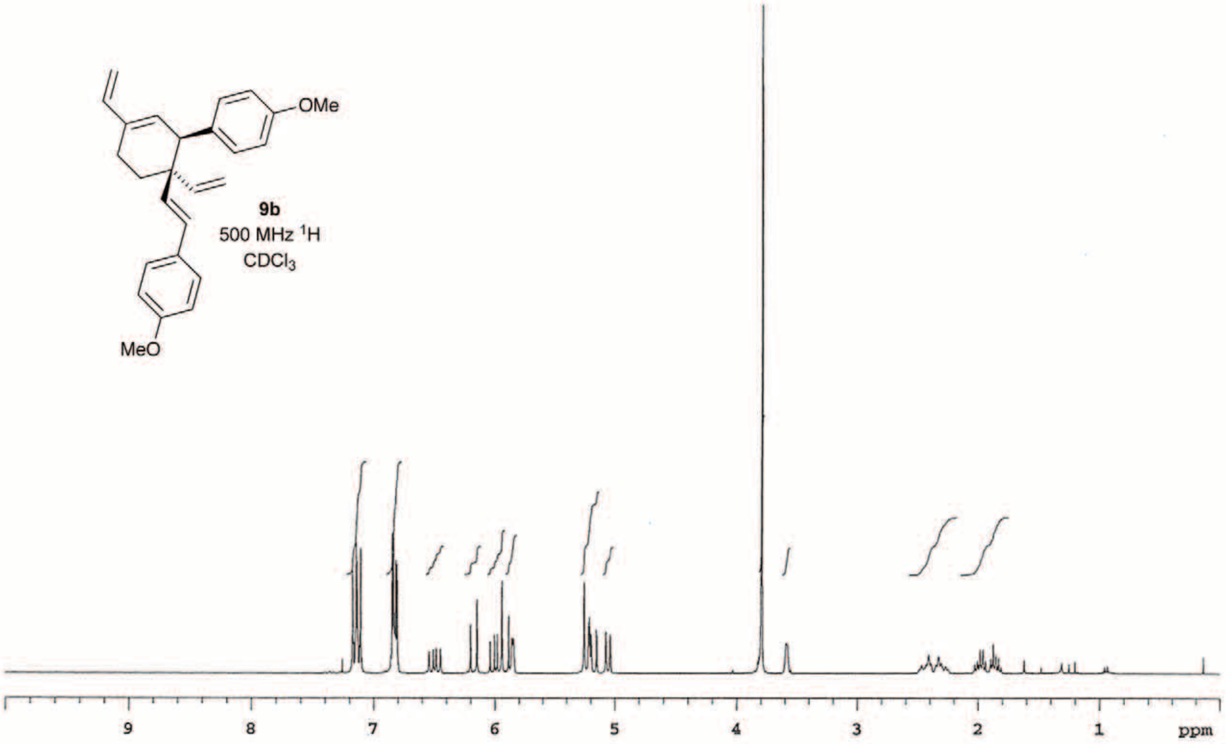
160
140
120
100
80
60
40
20
ppm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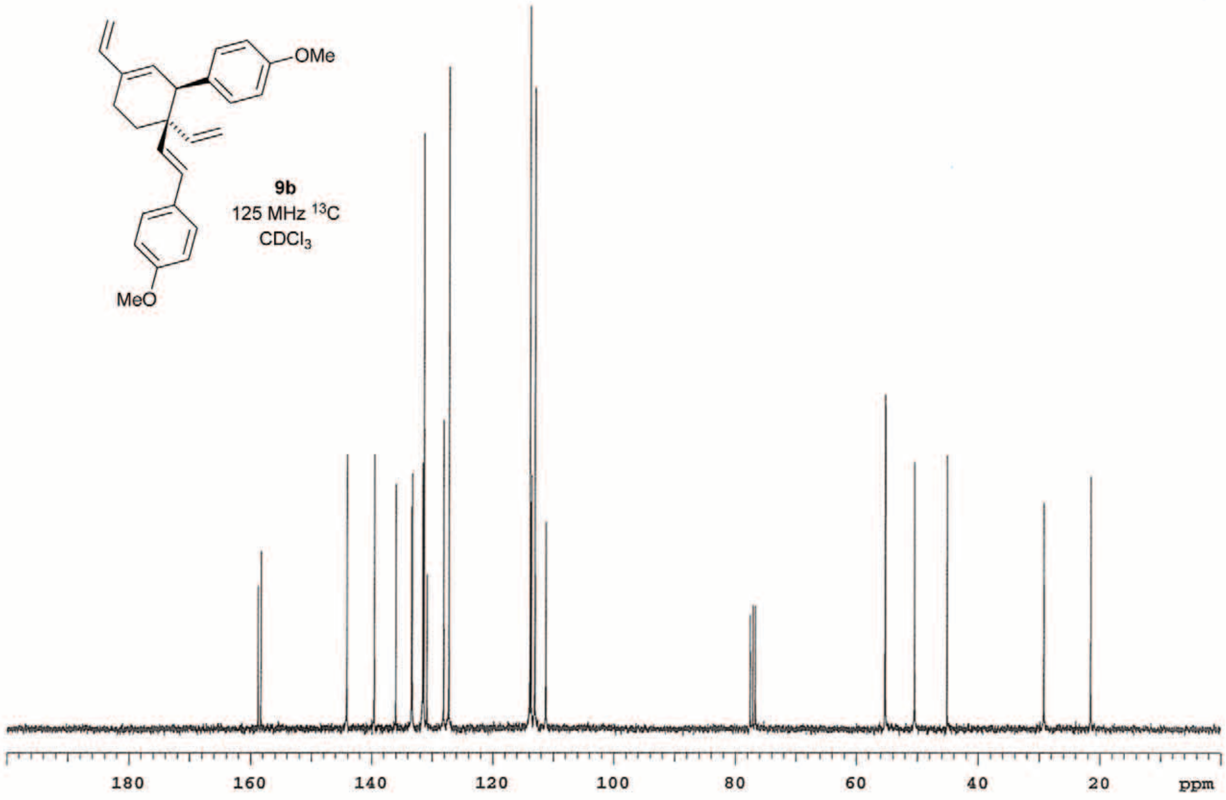
MeO
9b
500 MHz ¹H
CDCl₃
9
8
7
6
5
4
3
2
1
ppm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MeO
9b
125 MHz ¹³C
CDCl₃
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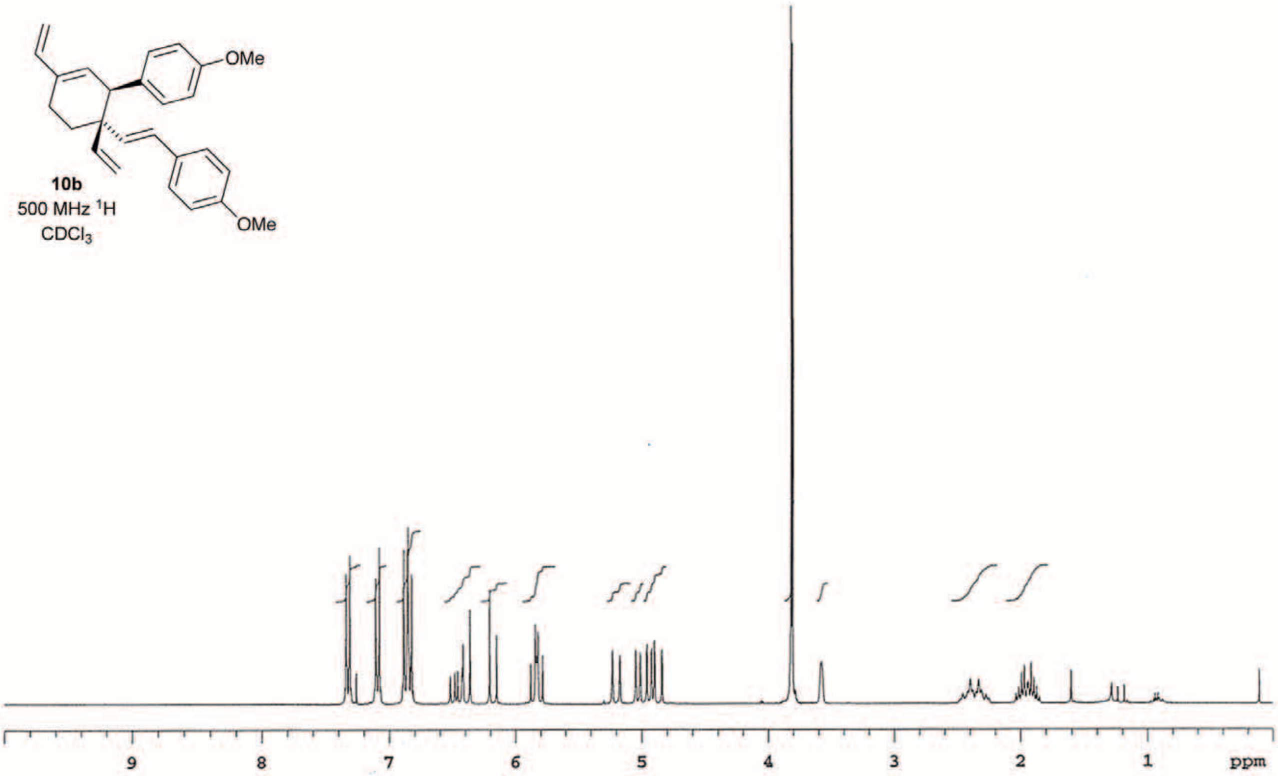
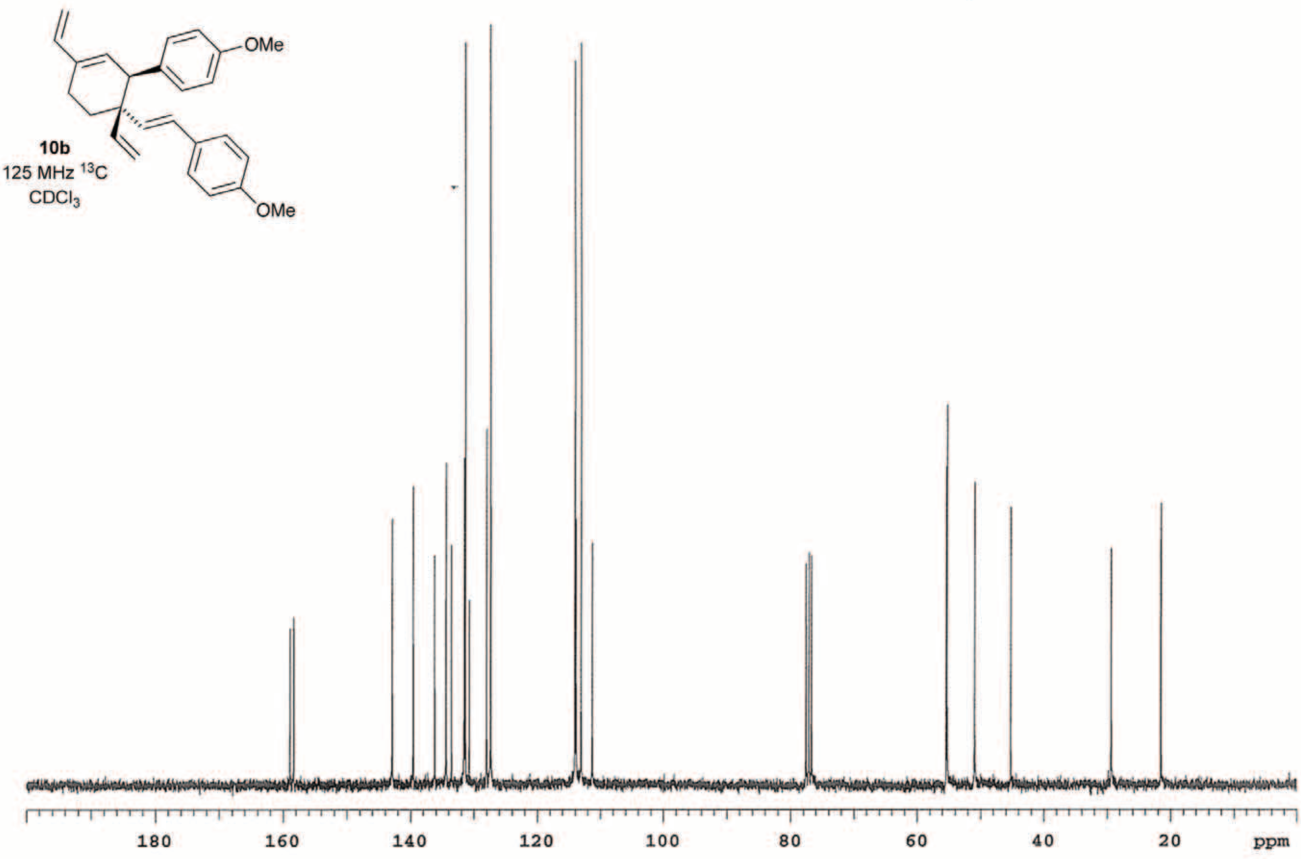
160
140
120
100
80
60
40
20
ppm


OMe
OMe
10b
500 MHz ¹H
CDCl₃
9
8
7
6
5
4
3
2
1
ppm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OMe
10b
125 MHz ¹³C
CDCl₃
180
160
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120
100
80
60
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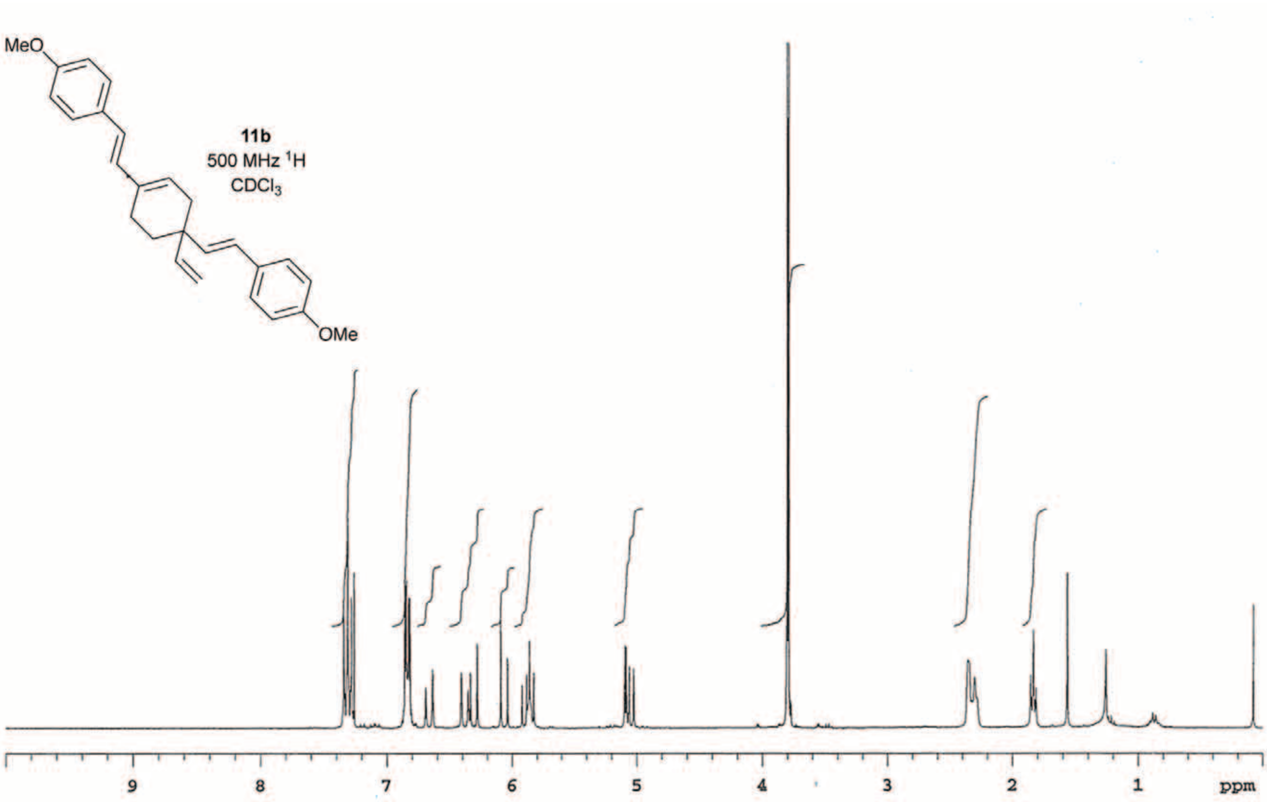
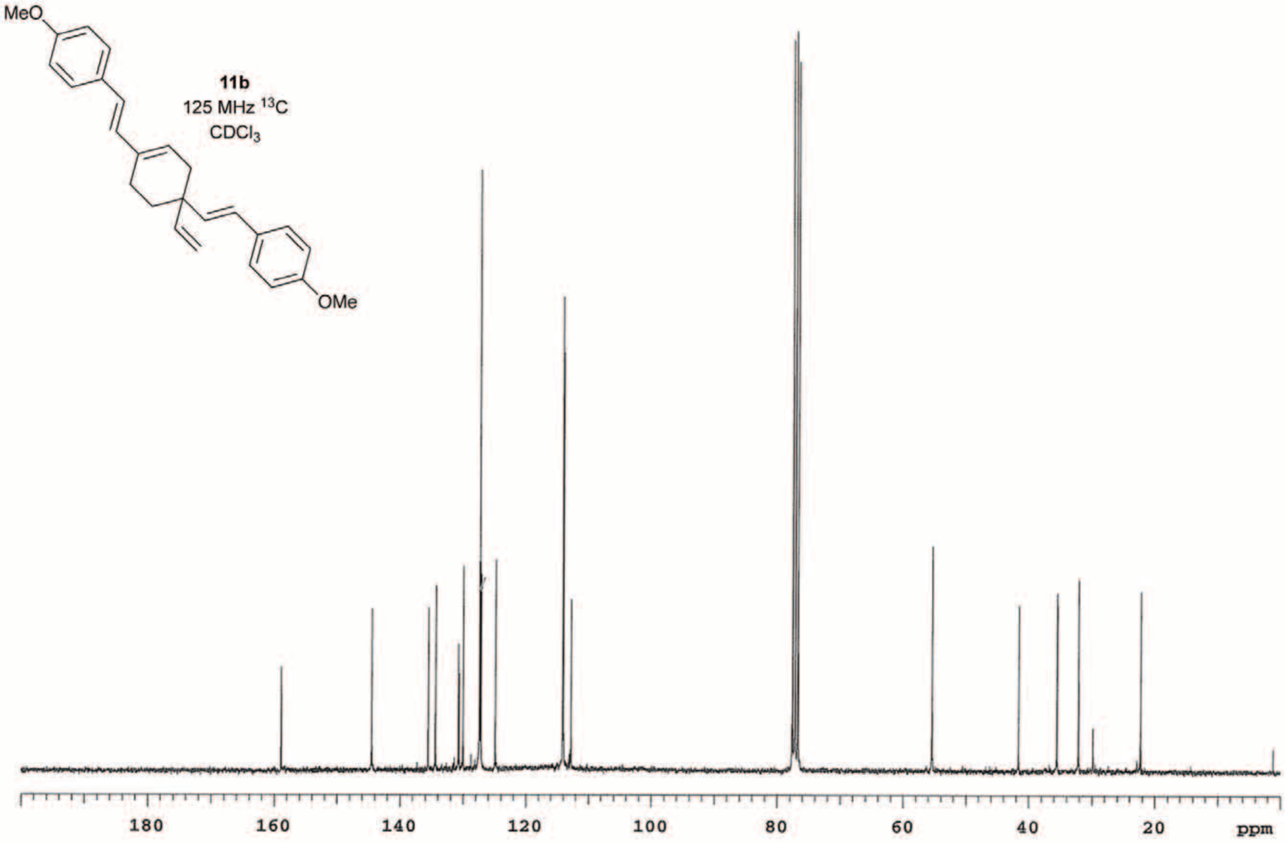
20
ppm


MeO
OMe
11b
500 MHz ^{1}H
$CDCl_3$
9
8
7
6
5
4
3
2
1
ppm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120
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80
60
40
20
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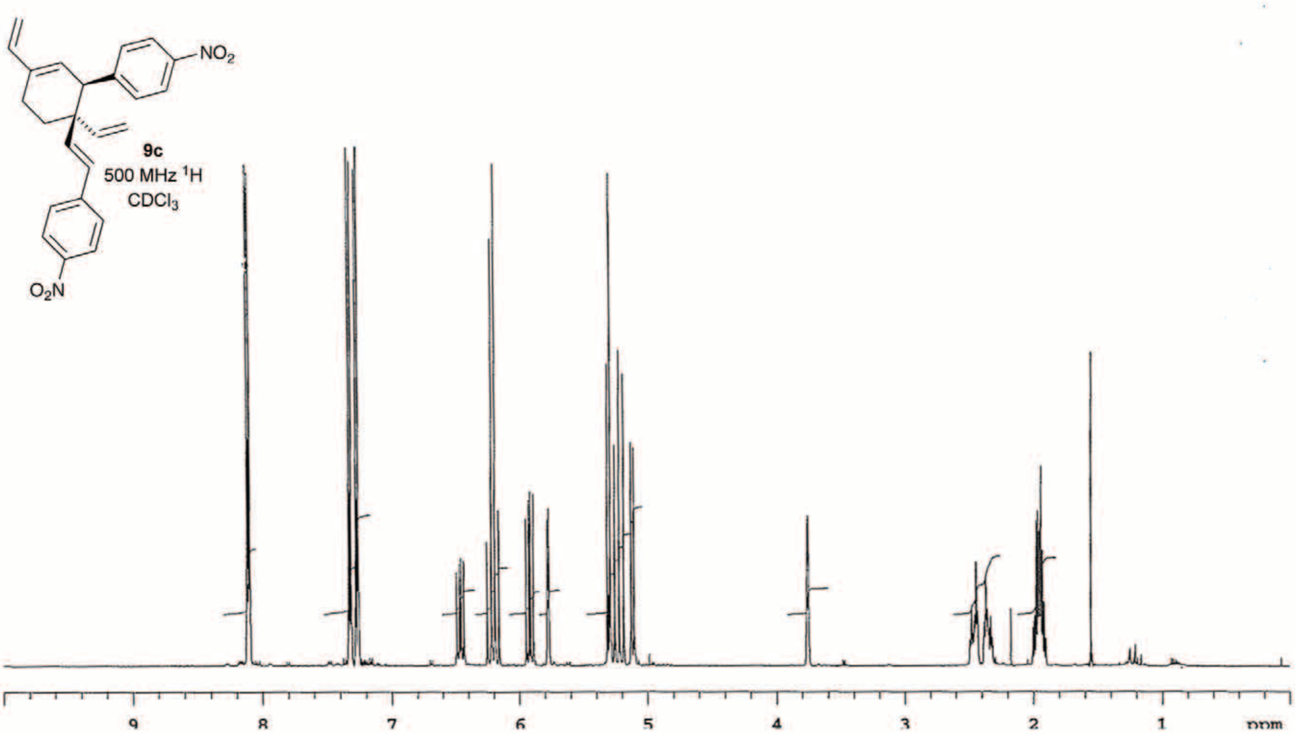
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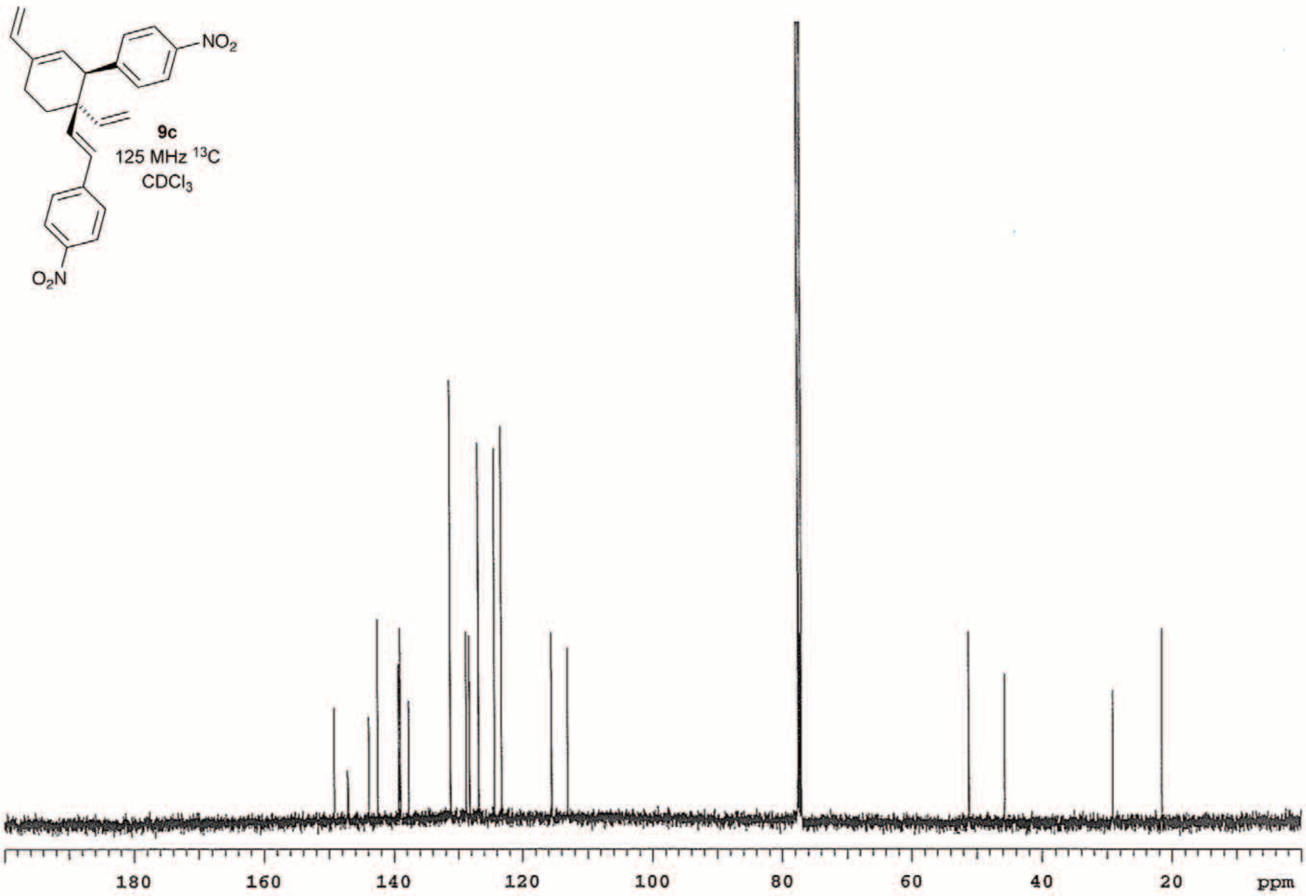
CDCl3
9
8
7
6
5
4
3
2
1
ppm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125 MHz 13C
CDCl3
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140
120
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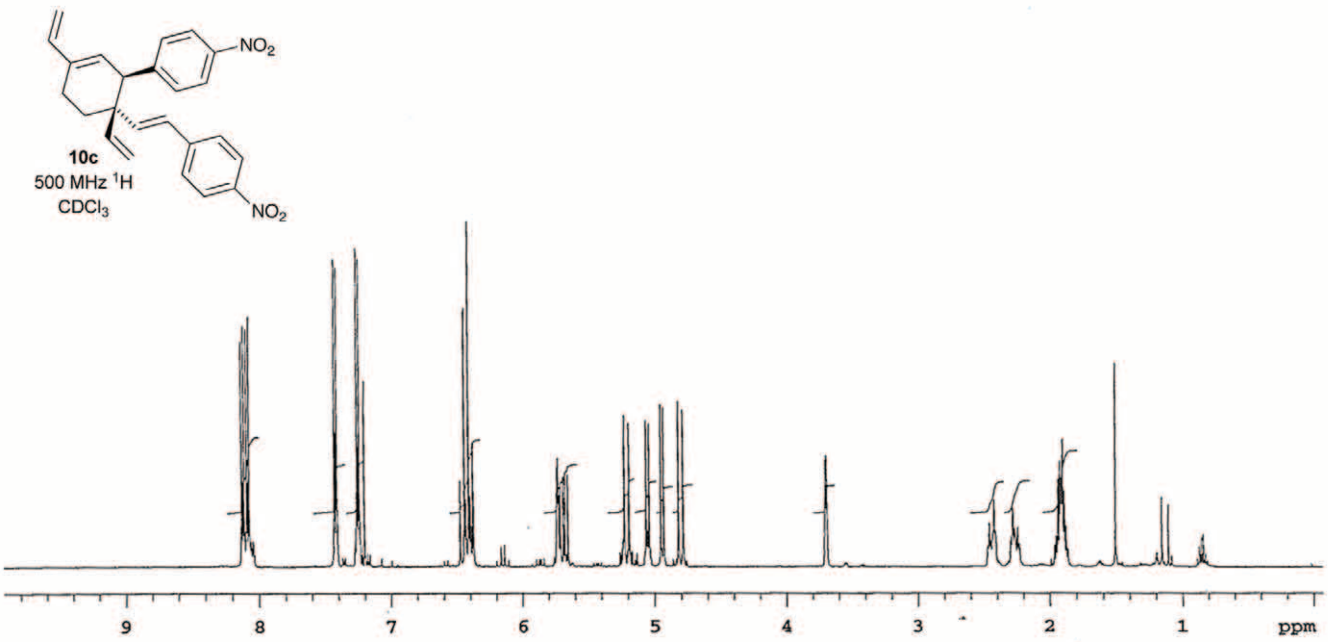
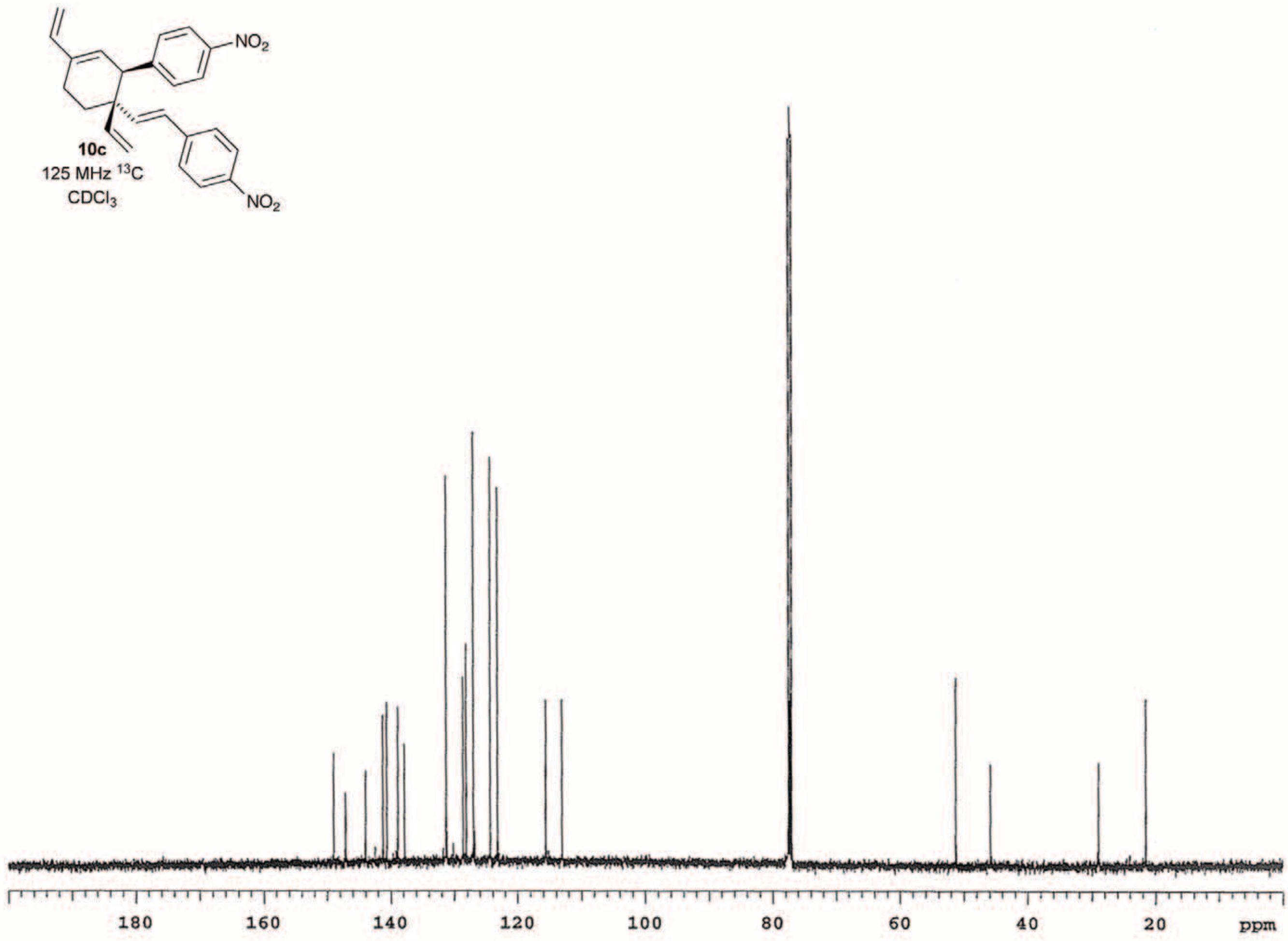
80
60
40
20
ppm


NO$_2$
NO$_2$
10c
500 MHz ^{1}H
CDCl$_3$
9
8
7
6
5
4
3
2
1
ppm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CDCl$_3$
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160
140
120
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80
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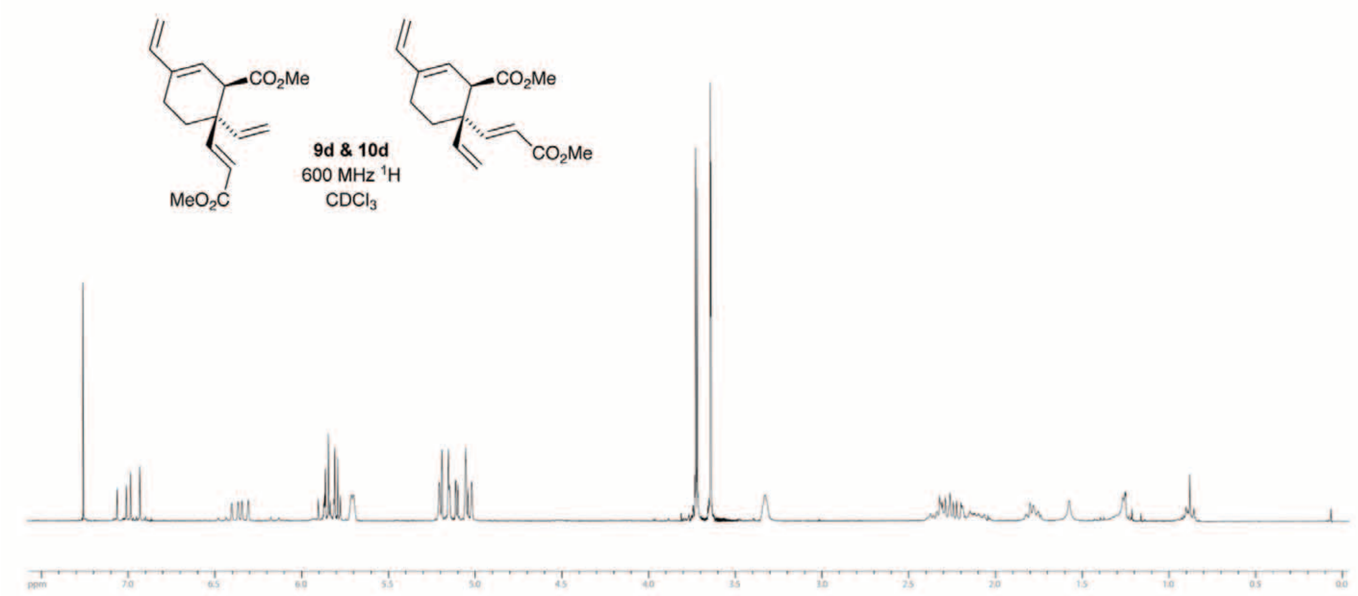
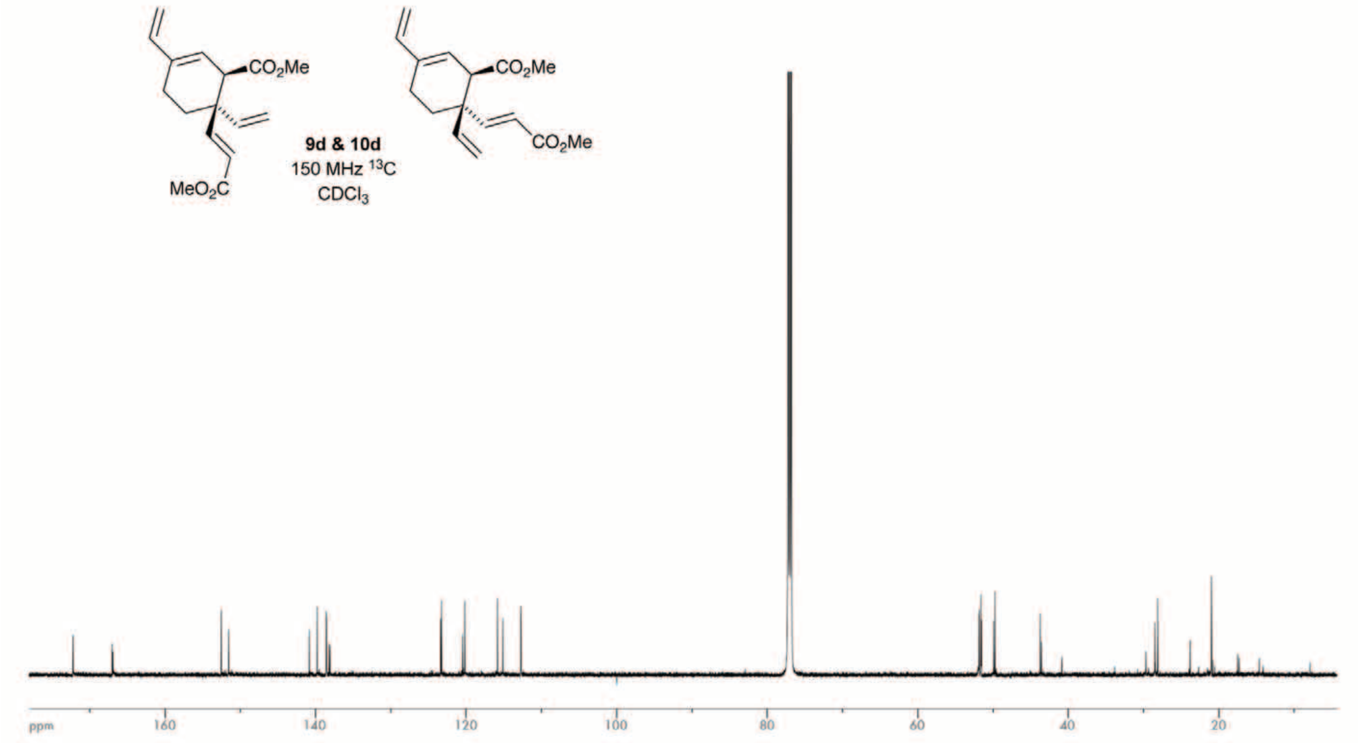
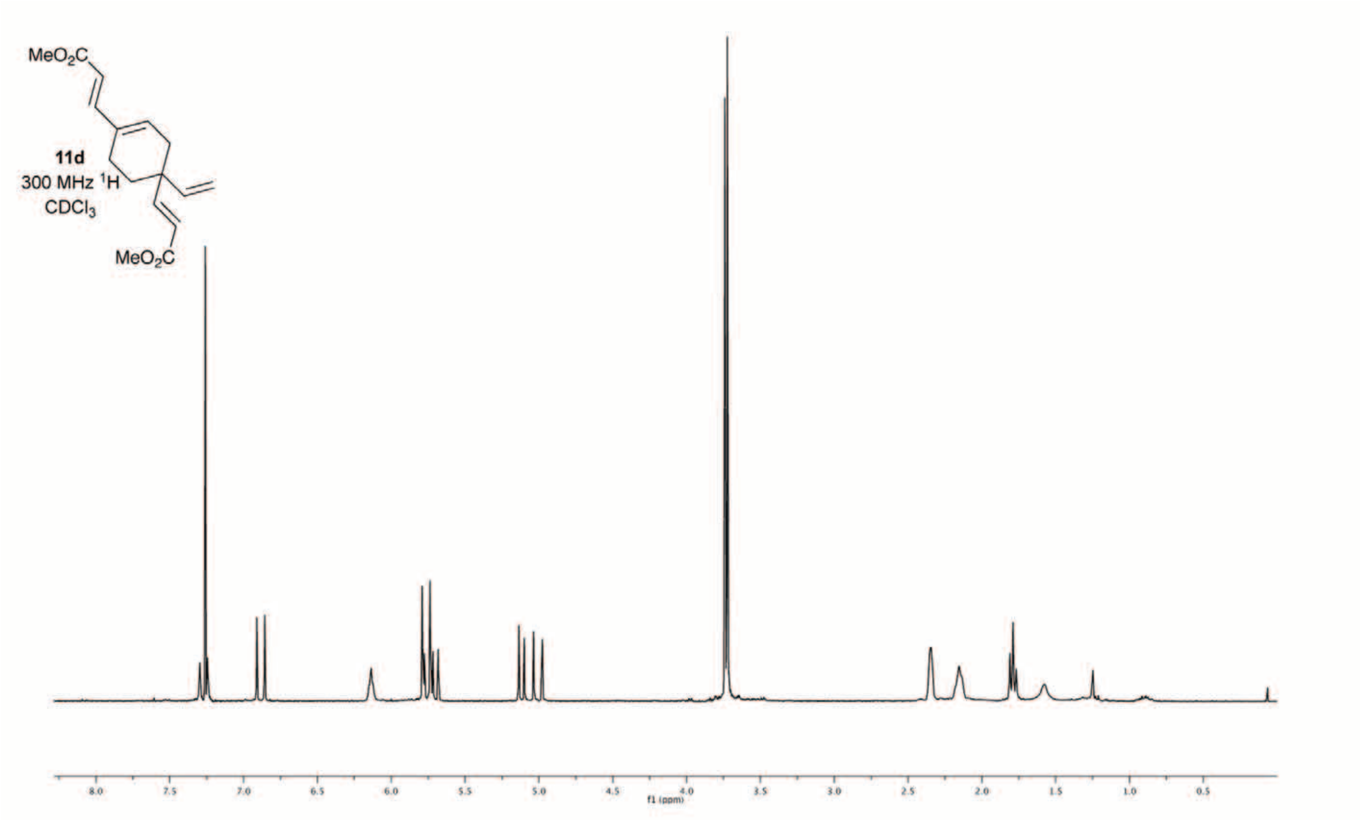
20
ppm

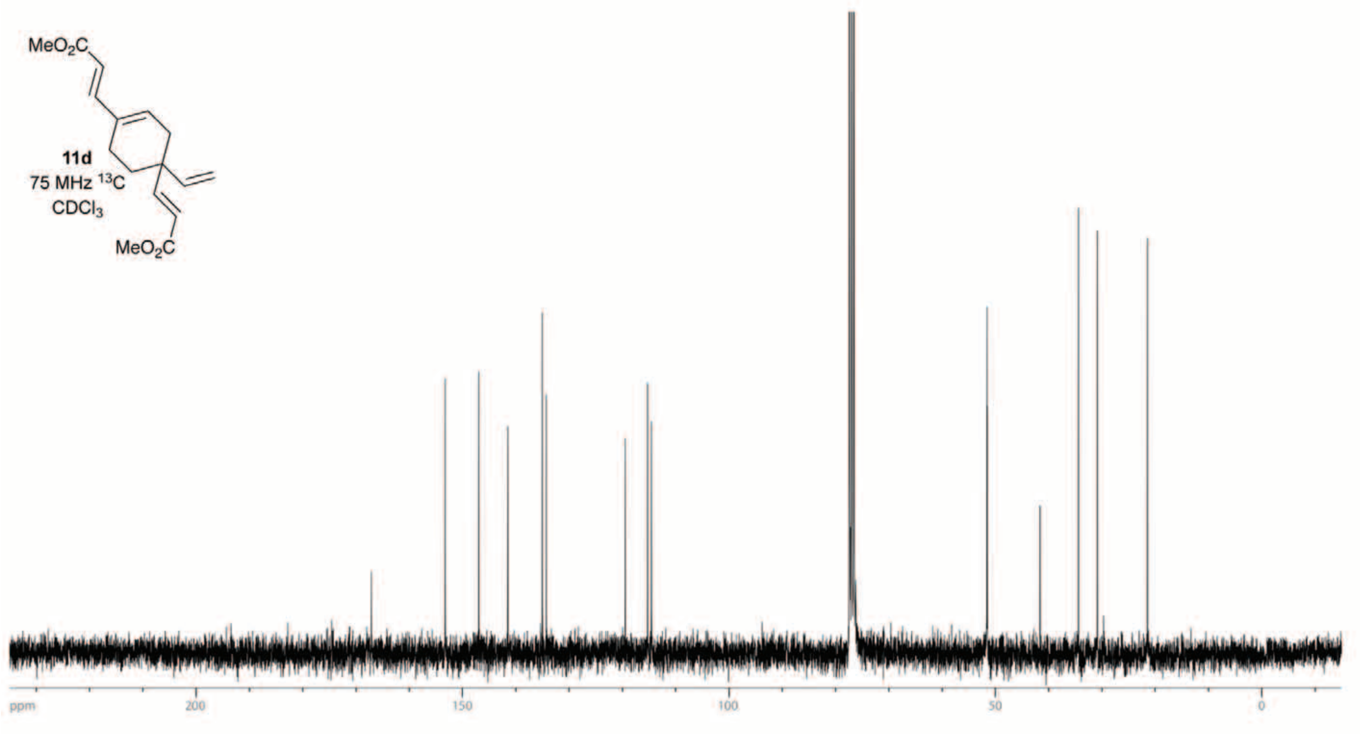


9d & 10d
600 MHz ^1H
$CDCl_3$



9d & 10d
150 MHz ^{13}C
$CDCl_3$


MeO2C
11d
300 MHz 1H
CDCl3
MeO2C
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
f1 (ppm)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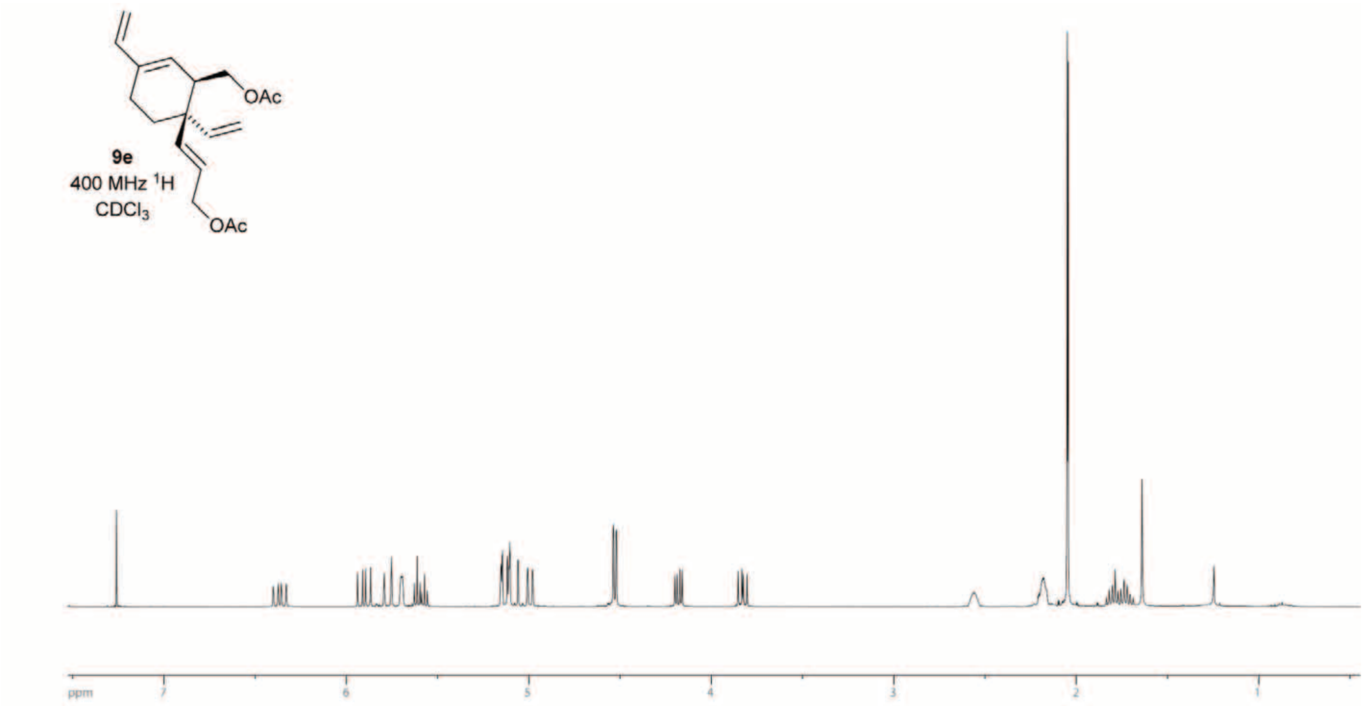
11d
75 MHz 13C
CDCl3
MeO2C
ppm
200
150
100
50
0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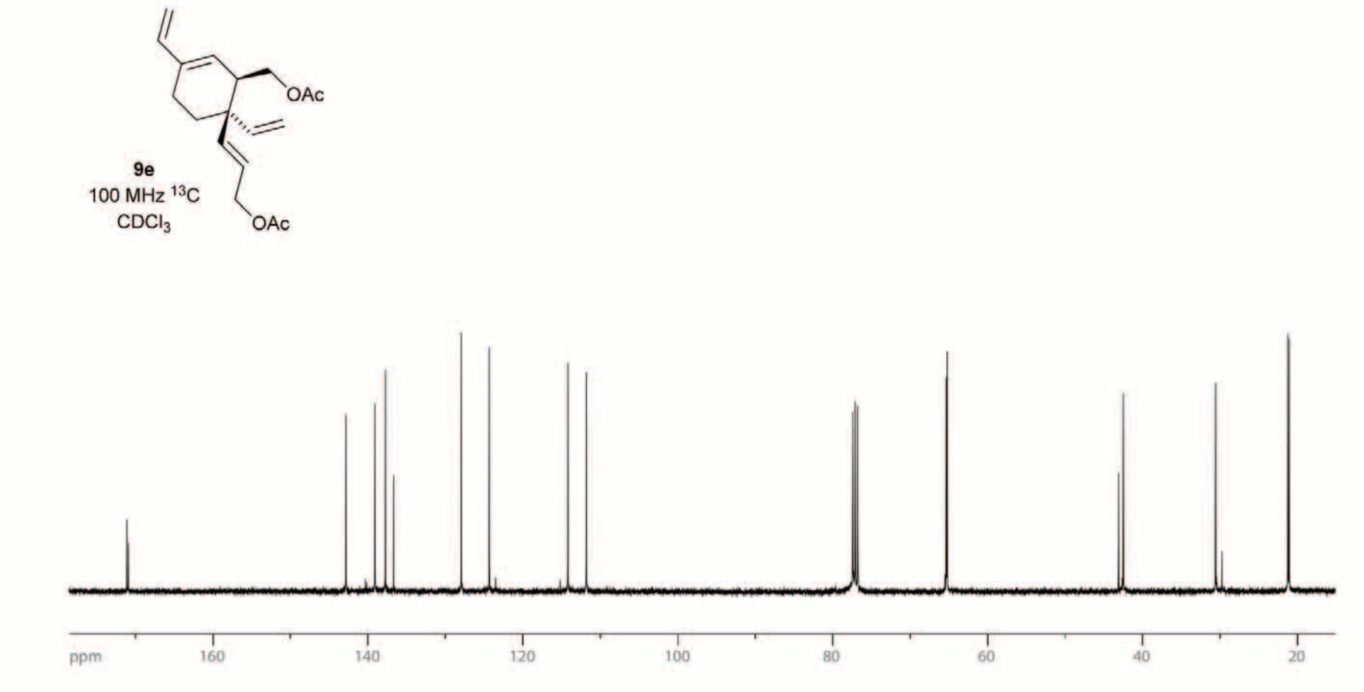
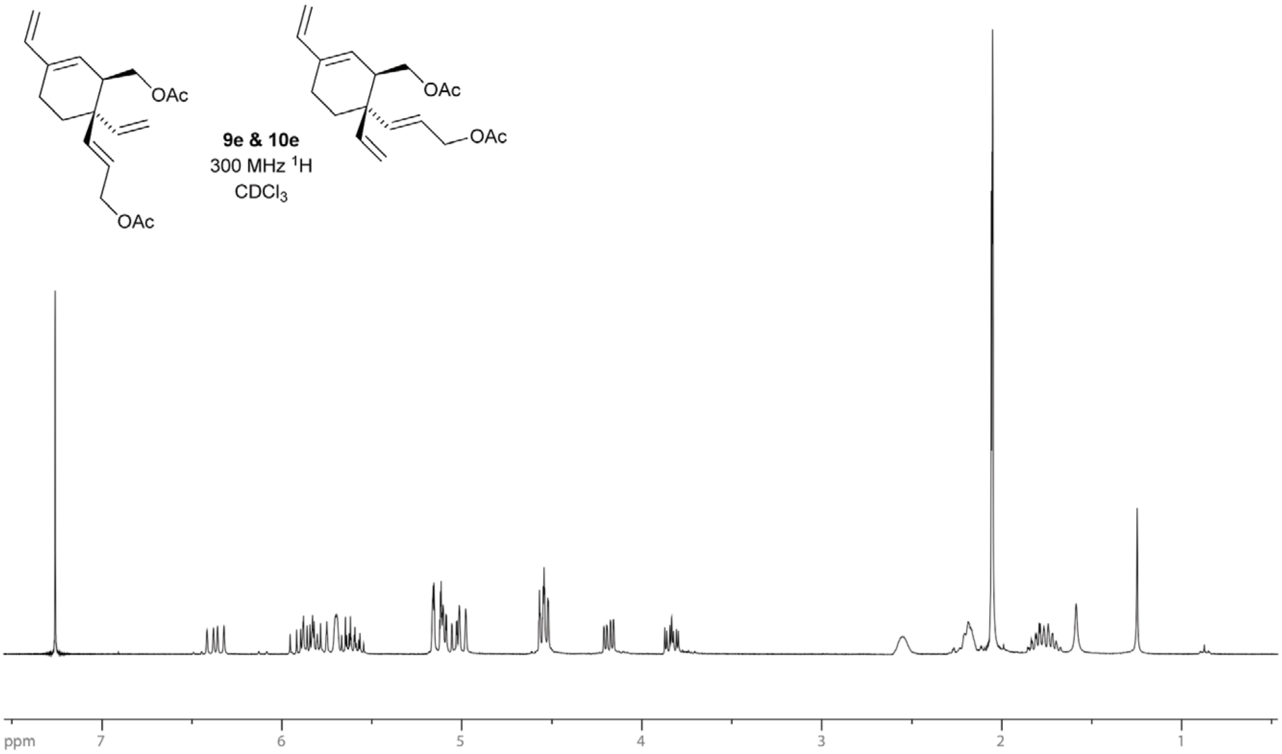
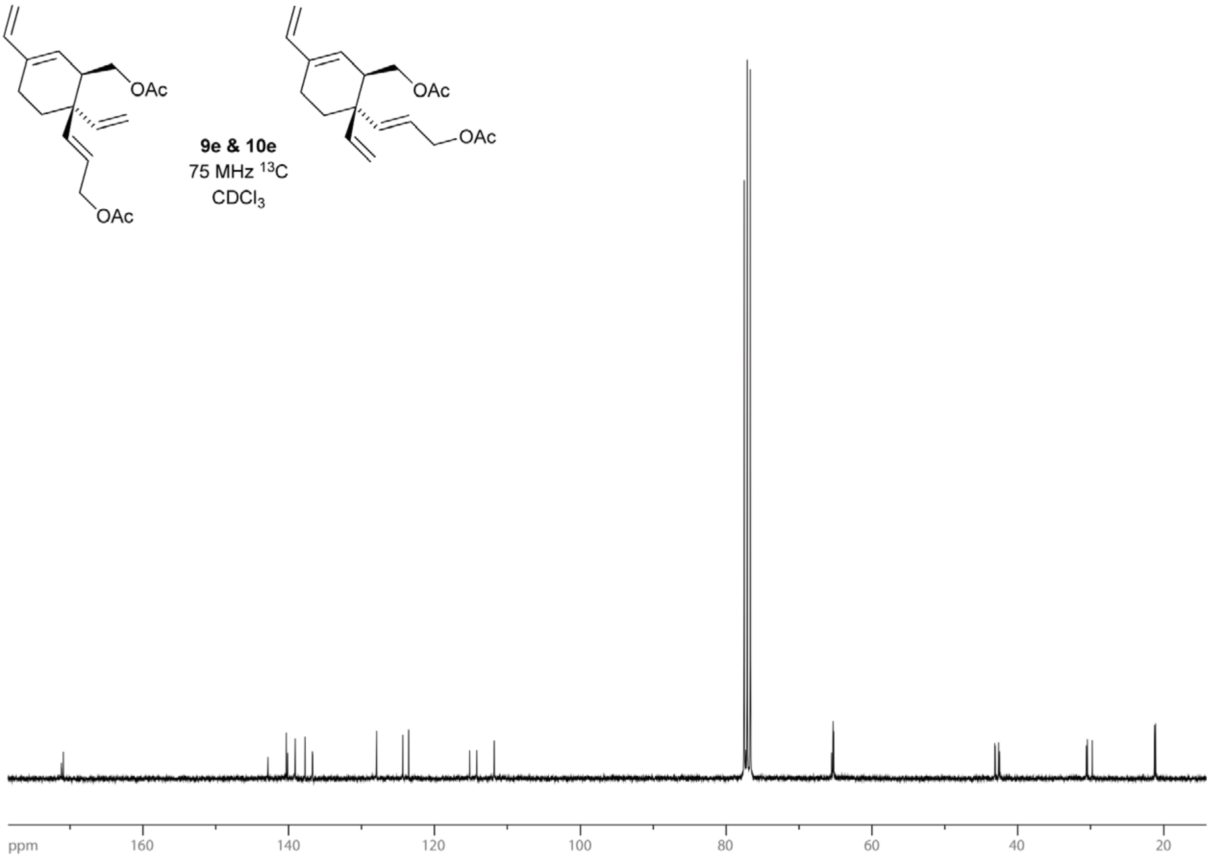
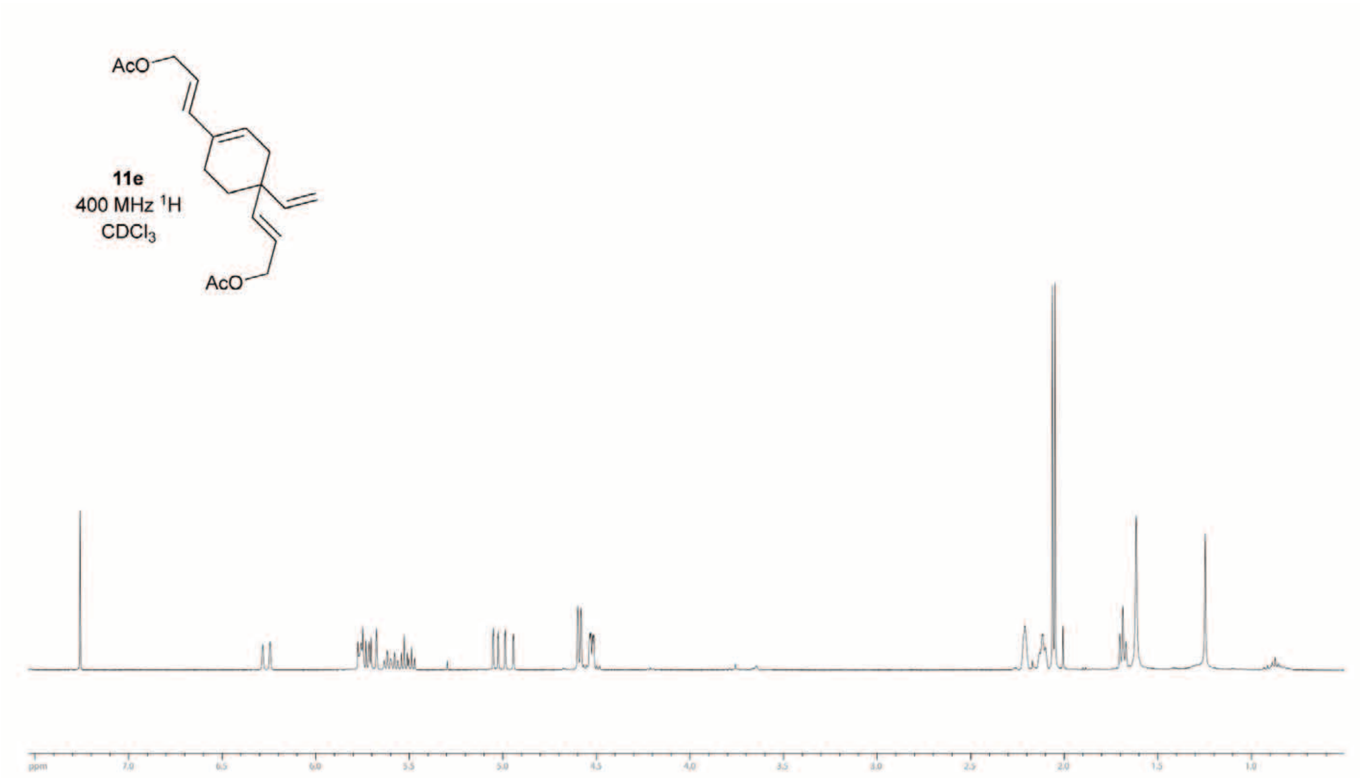
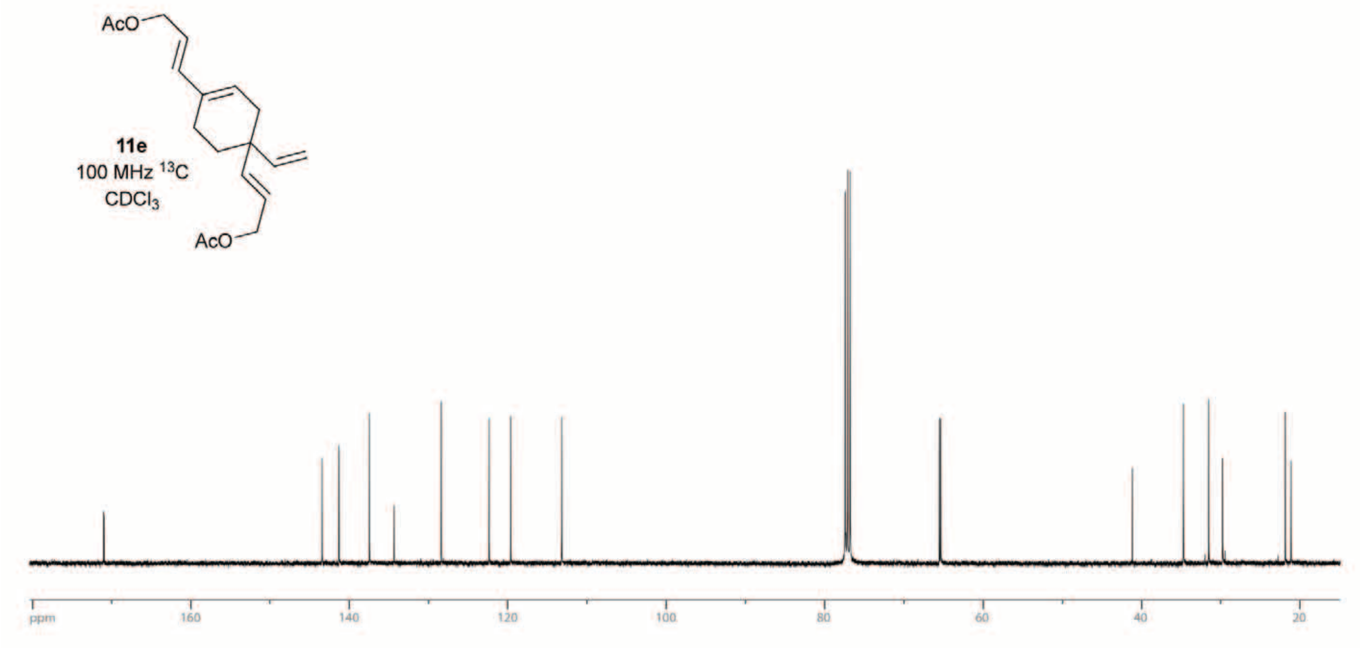
OAc
9e
400 MHz ^{1}H
CDCl$_3$
ppm
7
6
5
4
3
2
1

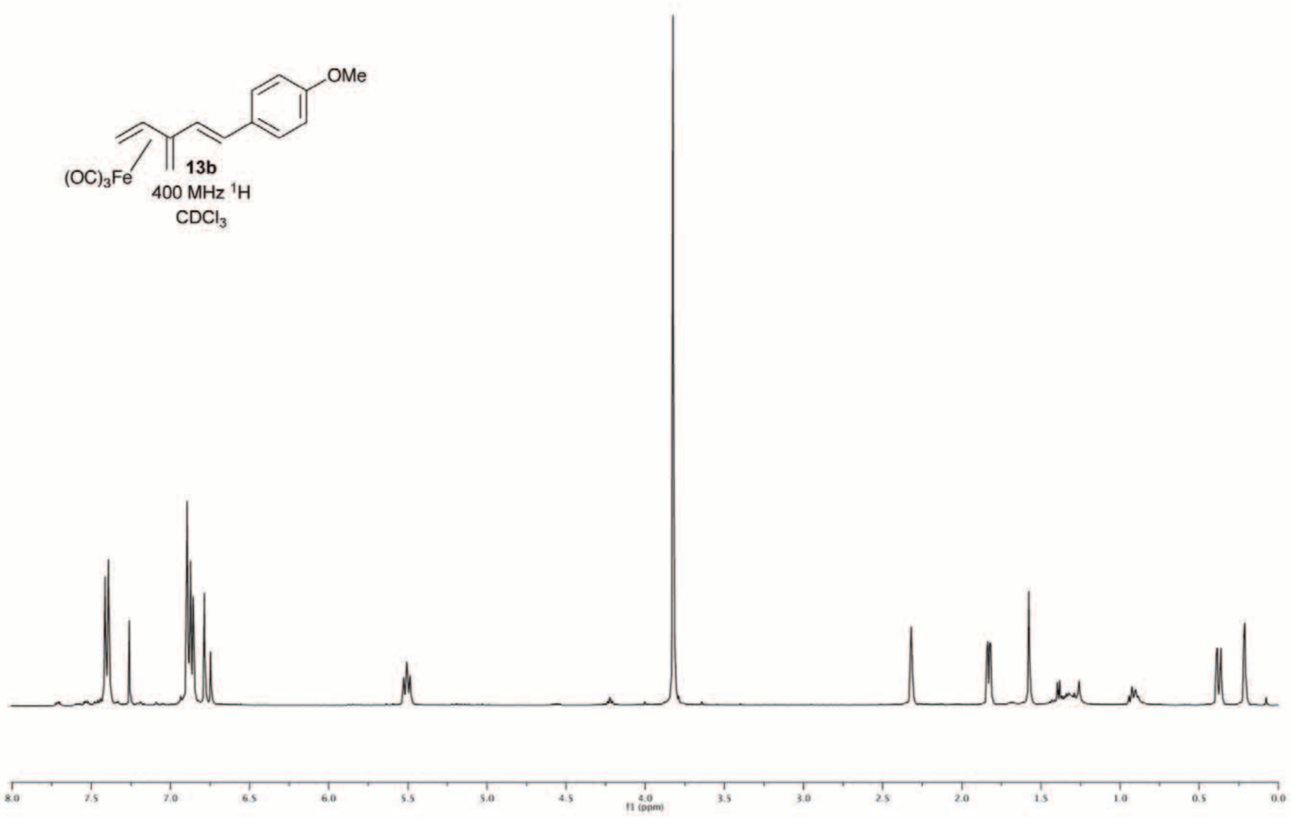

OAc
OAc
9e
100 MHz ^{13}C
CDCl$_3$
ppm
160
140
120
100
80
60
40
20

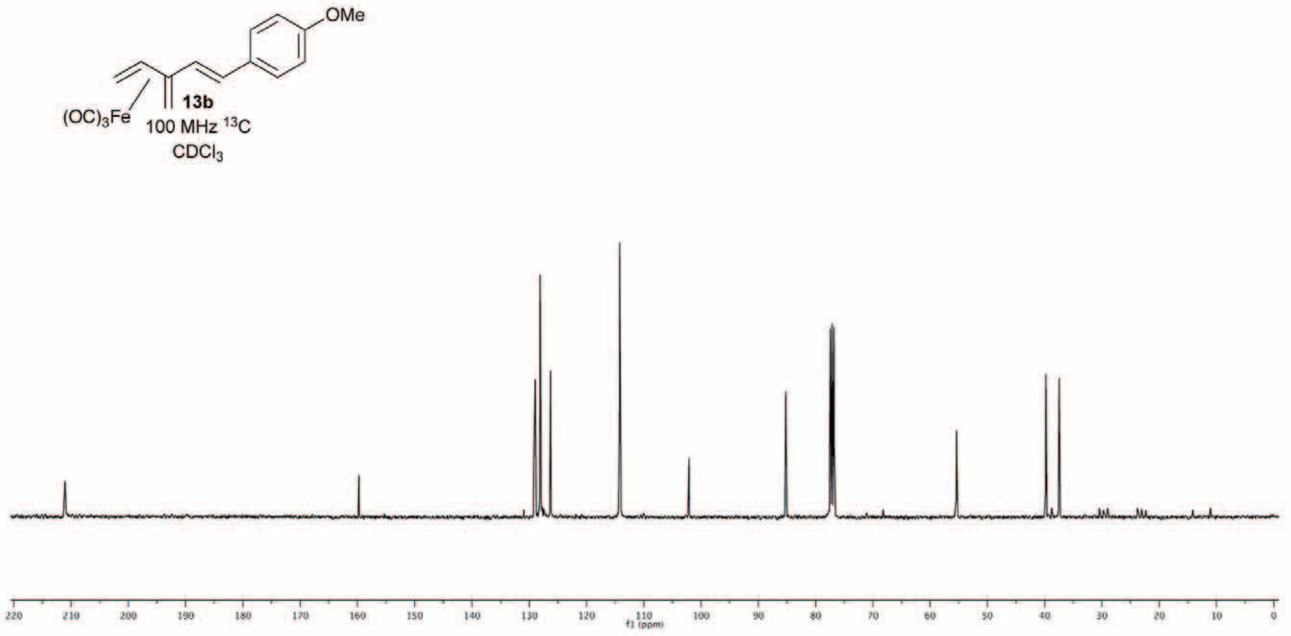

OAc
OAc
OAc
OAc
9e & 10e
300 MHz ^{1}H
$CDCl_3$
ppm
7
6
5
4
3
2
1

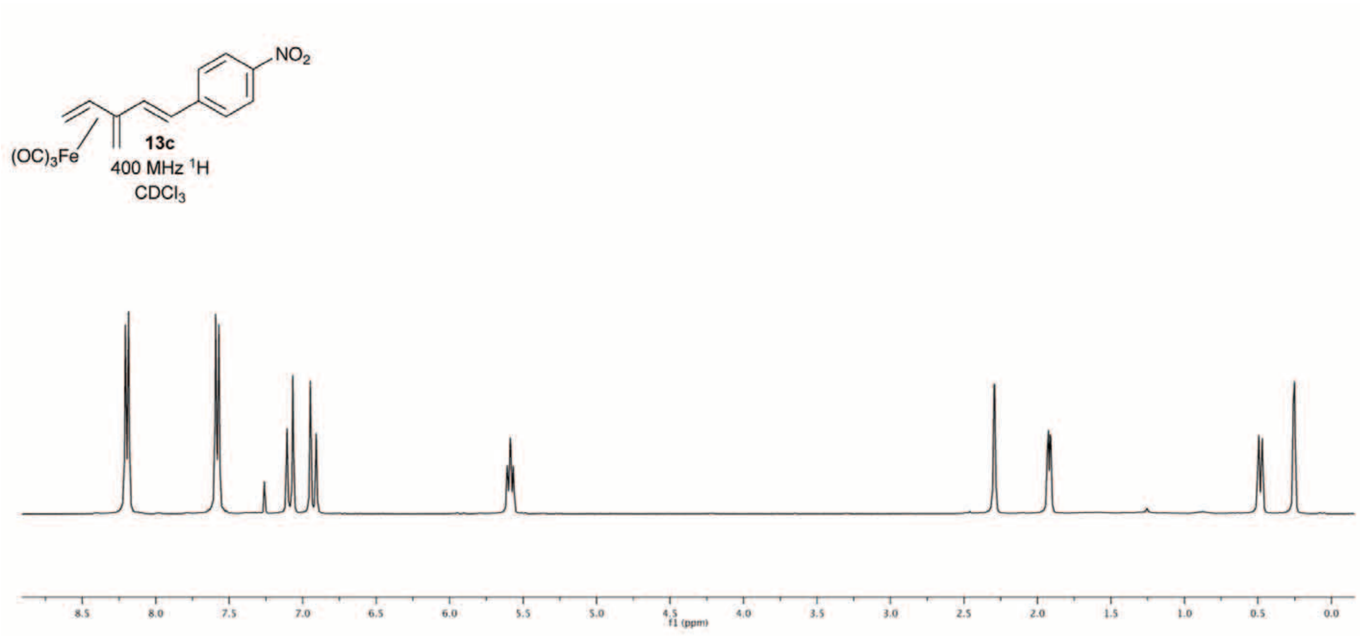

OAc
OAc
OAc
OAc
9e & 10e
75 MHz ^{13}C
$CDCl_3$
ppm
160
140
120
100
80
60
40
20

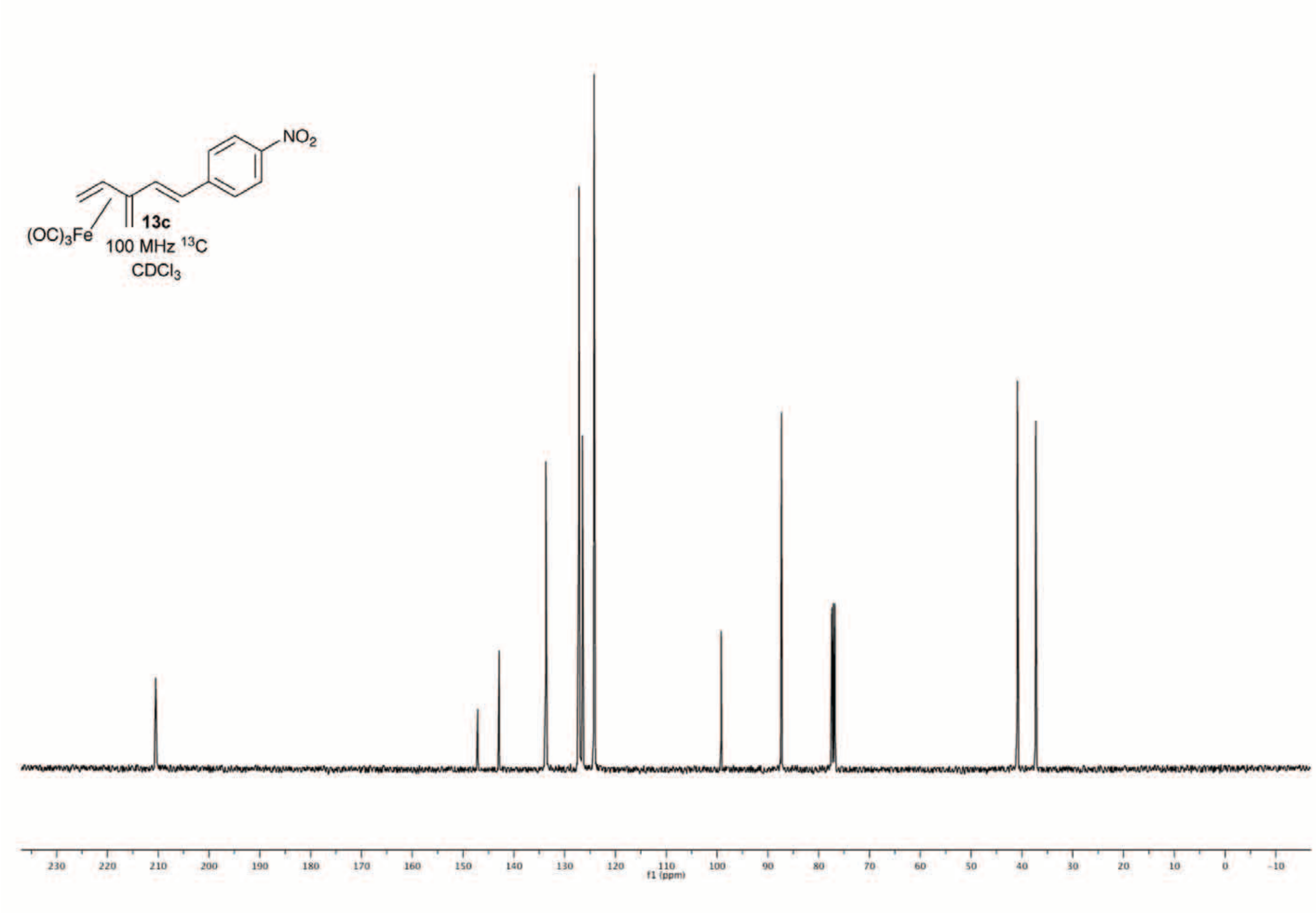

AcO
AcO
11e
400 MHz ^{1}H
$CDCl_3$
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


AcO
AcO
11e
100 MHz ^{13}C
$CDCl_3$
ppm
160
140
120
100
80
60
40
20


OMe
(OC)$_3$Fe
13b
400 MHz ^{1}H
CDCl$_3$
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
f1 (ppm)


OMe
(OC)$_3$Fe
13b
100 MHz ^{13}C
CDCl$_3$
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)


NO$_2$
(OC)$_3$Fe
13c
400 MHz ^{1}H
CDCl$_3$
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
f1 (ppm)


NO$_2$
(OC)$_3$Fe
13c
100 MHz ^{13}C
CDCl$_3$
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)