Supporting Information

for

Phosphites as Ligands in Ruthenium-Benzylidene Catalysts for Olefin Metathesis

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General Information

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk and/or glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} 1D and 2D Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer using the residual solvent peak as reference ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CH_2Cl_2, δ_H = 5.32 ppm, δ_C = 54.00 ppm) at 298K. Gas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). Flash chromatography was conducted using 40-63 μm silica. Analytical TLCs were performed on Merck pre-coated silica 60-F_{254} plates. Elemental analyses were performed by the University of St Andrews Analytical Services.

Substrate synthesis

{1-(2-methylallyloxy)prop-2-yne-1,1-diyl}dibenzene (24)

To a suspension of sodium hydride (95%, 0.63g, 25 mmol), in dry DMF (50mL) at 0°C, 1,1-diphenyl-2-propyn-1-ol (5.21g, 25 mmol) was added portion wise. 15 min after the end of the gas evolution, 2-chloro-2-methylprop-1-ene (3.7 mL, 37.5 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 3 h. The reaction was then quenched by addition of water and Et_2O was added. The organic layer was washed with a saturated solution of sodium carbonate and brine, and dried over sodium sulfate, filtered and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (pentane/EtOAc 95:5) to afford the title compound as a pale yellow oil (2.149 g, 33%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298K) δ_H (ppm) = 1.87 (s, 3H, CH_3), 2.95 (s, 1H, C≡CH), 4.02 (s, 1H, CH_2), 4.99 (br. s, 1H, C=CH), 5.20 (br. s, 1H, C=CH), 7.30-7.42 (m, 6H, Ph), 7.66-7.70 (m, 4H, Ph); ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K) δ_C (ppm) = 20.1, 68.6, 77.8, 80.0, 83.4, 111.4, 126.7, 127.8, 128.3, 142.4, 143.4; HRMS (CI) calcd. $C_{19}H_{19}O$: $(M + H)^+$, 263.1430; found: $(M + H)^+$, 263.1433.

Procedures for catalysis

Substrates **4**[1], **6**[2], **8**[3], **10**[4], **12**[5], **14**[5], **16**[6], **18**[4], **20**[2], **22**[2], **26**[7] and **28**[8] were synthesised according to literature procedures. Compound **2** and methyl acrylate were obtained from commercial sources. NMR spectra of the RCM products **3**[2], **5**[2], **7**[2], **9**[2], **11**[2], **13**[2], **15**[2], **17**[2], **19**[2], **21**[2], **23**[2], **25**[9] and CM products **27**[10] and **29**[11] were compared to previously reported analyses.

Procedure for Figure 3 – Kinetic study of the catalysts

In a glovebox, to a Schlenk flask charged with diallyl malonate (60.1 mg, 0.25 mmol), 0.5 mL of a Ru pre-catalyst solution (1 mol% in 1 mL CH_2Cl_2) was added, followed by addition of 2 mL of CH_2Cl_2. Outside the glovebox, the reaction mixture was stirred under an Argon atmosphere. An aliquot was removed every 10 min for a period of 2 h. The aliquot was immediately quenched with ethyl vinyl ester after removal from reaction flask. Evolution of the reaction was followed by gas chromatography and conversion was determined by integral ratios.

General procedure for the metathesis reaction – Tables 1 and 2

A 5 mL screwcap-vial fitted with a septum equipped with a magnetic stirring bar was charged with the olefin (0.25 mmol) and the catalyst (for loadings ≥ 1 mol %). The vials were flushed with Argon, closed and were introduced into a glovebox. For loadings ≤ 1 mol %, a stock solution of the pre-catalyst was prepared by dissolution in 1 mL of solvent and the appropriate volume of catalyst stock solution was injected into the reaction vial containing a solution of the substrate (total volume of 0.5 mL, 0.5 M solution with respect to substrate); for catalyst loadings ≥ 1 mol %, 0.5 mL of solvent was added to the reaction vial. The reaction mixture was heated at the appropriate temperature for 8 hours. The solvent was then evaporated and the resulting product was analysed by gas chromatography (conversion determined by integrals ratios) and/or purified by flash chromatography.

Synthesis of the pre-catalysts

A Schlenk flask was charged with $[RuCl_2(=CHPh)(Py)_2(SIMes)]$ (**G-III**), dichloromethane (5 mL) and $P(OR)_3$ (1.1 eq.) were added. The reaction was stirred 1 h at room temperature and the solvent removed *in vacuo*. The resulting solid was washed with cold pentane and dried *in vacuo* to afford the analytically pure product. Quality crystals were grown by cooling of a saturated solution of the complexes in pentane at -35°C.

Dichloro-{*N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazolin-2-ylidene}(benzylidene) (triisopropylphosphite) ruthenium (1a)

Using 500mg of **G-III** (0.688 mmol), the procedure afforded 414.9 mg (78%) of the analytically pure product as a green powder.

^{1}H NMR ($CDCl_3$, 300 MHz, 298K) δ (ppm) = 0.90 (d, $^3J_{H-H}$ = 6.0 Hz, 18H, CH-C*H*$_3$), 2.07 (s, 3H, Mes-CH_3), 2.26 (s, 6H, Mes-CH_3), 2.32 (s, 3H, Mes-CH_3), 2.68 (s, 6H, Mes-CH_3), 3.88-4.10 (m, 7H, C^4-H_2, C^5-H_2, C*H*-CH_3), 6.46 (s, 2H, Ar-H), 6.99 (s, 2H, Ar-H), 7.14 (t, $^3J_{H-H}$ = 7.7Hz, 2H, Ar-H), 7.47 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar-H), 7.86 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-H), 18.84 (d, $^3J_{H-P}$ = 1.5 Hz, Ru=CH-Ph).

^{13}C-{^{1}H} NMR (CD_2Cl_2, 100.6 MHz, 298 K) δ (ppm) = 18.7 (Mes-CH_3), 20.4 (Mes-CH_3), 21.2 (Mes-CH_3), 21.4 (Mes-CH_3), 24.1 (d, $^3J_{C-P}$ = 4.0 Hz, CH-*C*H$_3$), 51.9 (d, $^4J_{C-P}$ = 4 Hz, C^4), 52.3 (d, $^4J_{C-P}$ = 5.5 Hz, C^5) 69.5 (d, $^2J_{C-P}$ = 1.8 Hz, *C*H-CH_3), 127.8 (Ar-CH), 129.7 (Ar -CH), 129.9 (Ar -CH), 130.6 (Ar-CH), 132.3 (Ar-CH), 135.5 (Ar-C), 137.4 (Ar-C), 137.5 (Ar-C), 138.4 (Ar-C), 138.7 (Ar-C), 139.5 (Ar-C), 151.5 (d, $^3J_{C-P}$ = 7.2 Hz, Ar-C), 218.9 (d, $^2J_{C-P}$ = 138.4 Hz, $C^{carbene}$), 309.6 (d, $^2J_{C-P}$ =15.2 Hz, Ru=CH-Ph).

^{31}P-{^{1}H} NMR (CD_2Cl_2, 162 MHz, 298K) δ (ppm) = 125.4.

Anal. calcd for $C_{37}H_{54}Cl_2N_2O_3PRu$: C, 57.14; H, 7.00; N, 3.60. Found: C, 57.15; 7.26; 3.85.

Dichloro-{*N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazolin-2-ylidene}(benzylidene) (triethylphosphite) ruthenium (1b)

Using 150mg of **G-III** (0.205 mmol), the procedure afforded 104.0 mg (70%) of the analytically pure product as a green powder.

^{1}H NMR (CD_2Cl_2, 400 MHz, 298K) δ (ppm) = 0.91 (t, $^3J_{H-H}$ = 7.0 Hz, 9H, CH_2-C*H*$_3$), 2.10 (s, 3H, Mes-CH_3), 2.21 (s, 6H, Mes-CH_3), 2.30 (s, 3H, Mes-CH_3), 2.61 (s, 6H, Mes-CH_3), 3.36 (qd, $^3J_{H-H}$ = 7.2 Hz, $^3J_{H-P}$ = 7.2 Hz, 6H, C*H*$_2$-CH_3), 3.90-3.96 (m, 2H, C^4-H_2), 4.04-4.09 (m, 2H, C^5-H_2), 6.49 (s, 2H, Ar-H), 6.96 (s, 2H, Ar-H), 7.17 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, Ar-H), 7.50 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar-H), 7.86 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, Ar-H), 18.77 (d, $^2J_{H-P}$ = 1.9 Hz, Ru=CH-Ph).

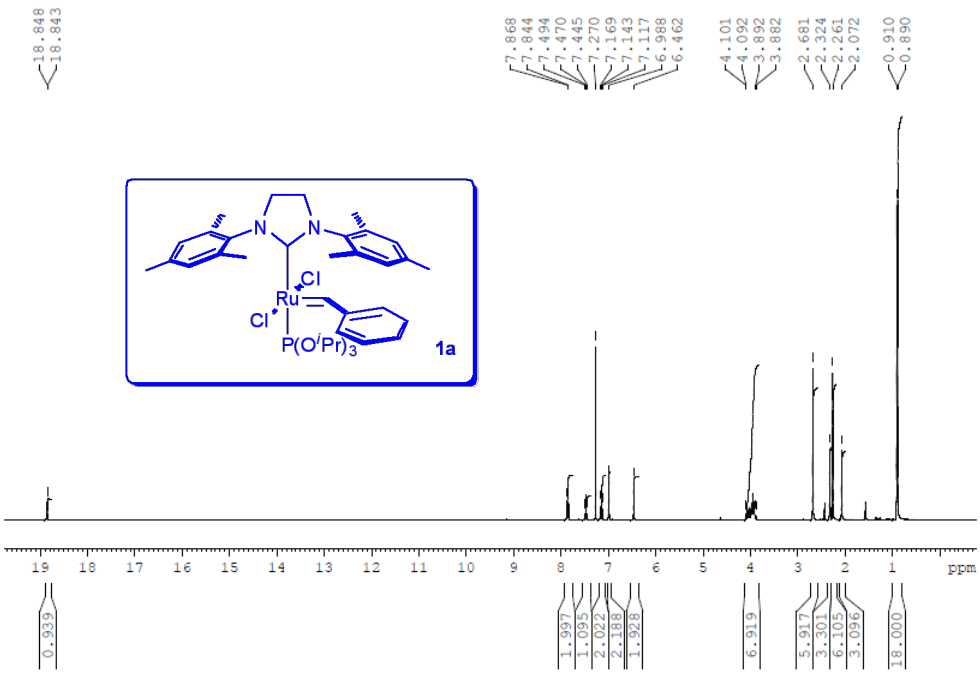
^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 298 K) δ (ppm) = 16.3 (d, $^3J_{C-P}$ = 6.6 Hz, CH_2-*C*H$_3$), 18.6 (Mes-CH_3), 20.5 (Mes-CH_3), 21.2 (Mes-CH_3), 21.3 (Mes-CH_3), 52.0 (d, $^4J_{C-P}$ = 4.0 Hz, C^4), 52.2 (d, $^4J_{C-P}$ = 5.4 Hz, C^5), 61.0 (d, $^2J_{C-P}$ = 1.4 Hz, *C*H$_2$-CH_3), 127.9 (Ar-CH), 129.7 (Ar-CH), 130.5 (Ar-CH), 130.8 (Ar-CH), 132.2 (Ar-CH), 137.4 (Ar-C), 138.4 (Ar-C), 139.0 (Ar-C), 139.8 (Ar-C), 151.6 (d, $^3J_{C-P}$ = 6.5 Hz, Ar-C), 218.9 (d, $^2J_{C-P}$ = 136.0 Hz, $C^{carbene}$), 309.3 (d, $^2J_{C-P}$ = 17.7 Hz, Ru=CH-Ph).

^{31}P-{^{1}H} NMR (CD_2Cl_2, 162 MHz, 298K) δ (ppm) = 130.8.

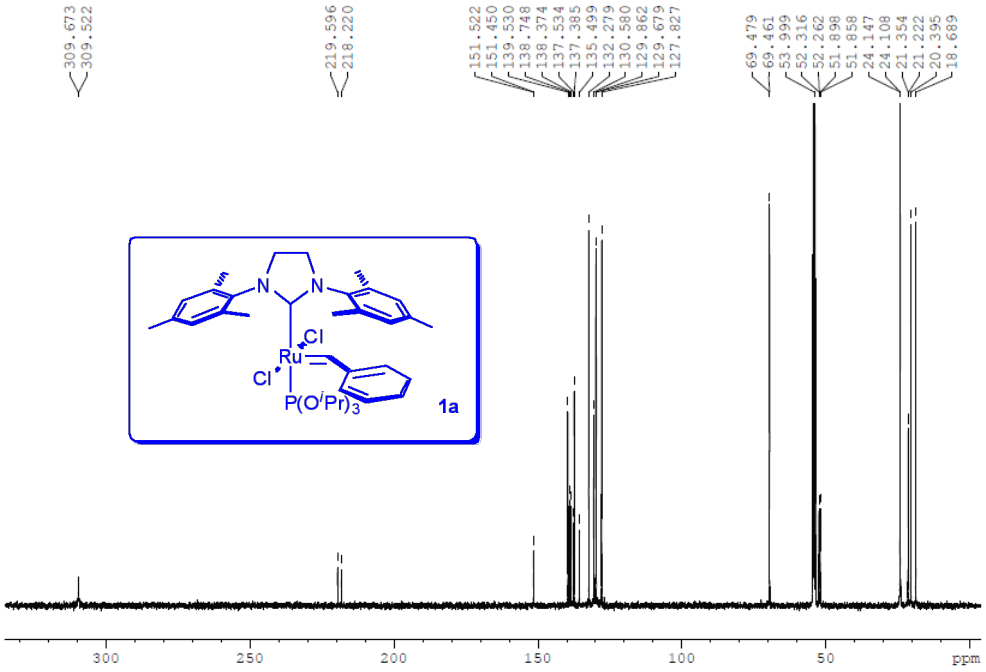
Anal. calcd for $C_{34}H_{47}Cl_2N_2O_3PRu$: C, 55.58; H, 6.45; N, 3.81. Found: C, 55.97; H, 6.41; N, 4.17.

NMR spectra of the complexes

^{1}H NMR ($CDCl_3$) of 1a



^{13}C-{^{1}H} NMR (CD_2Cl_2) of 1a



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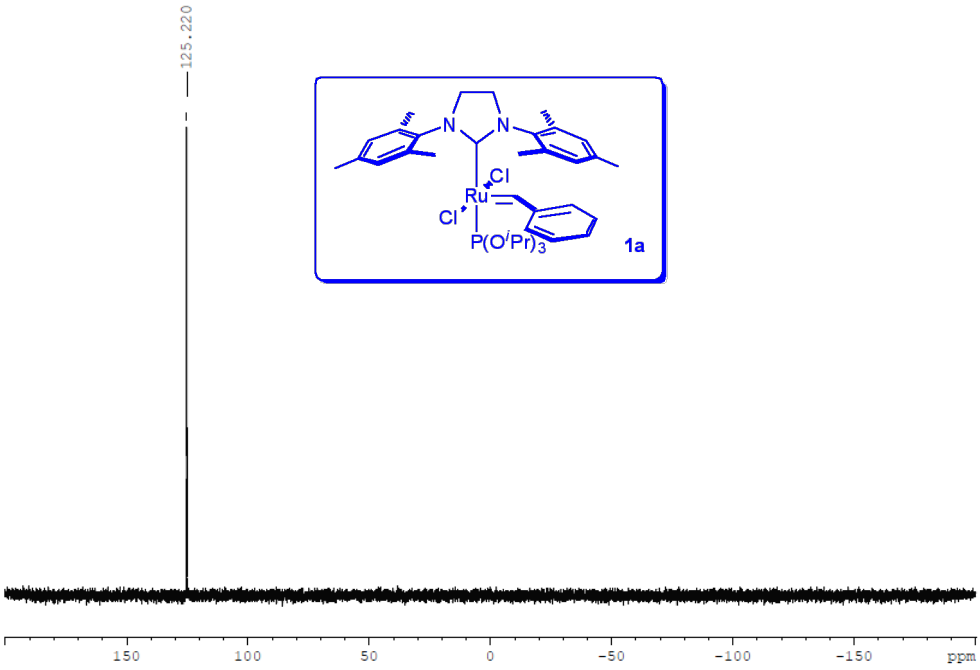
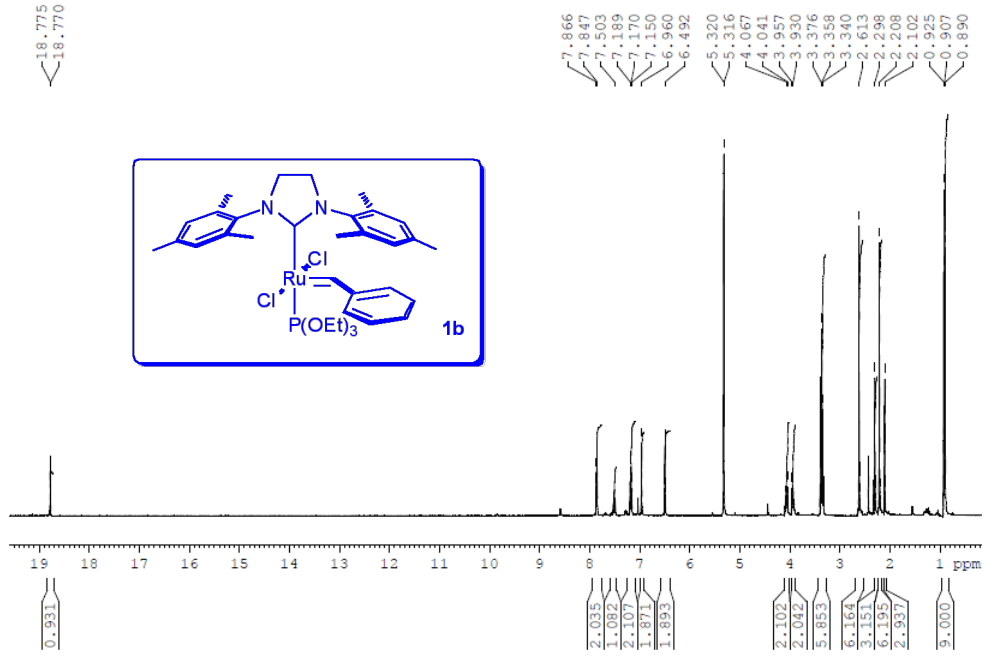
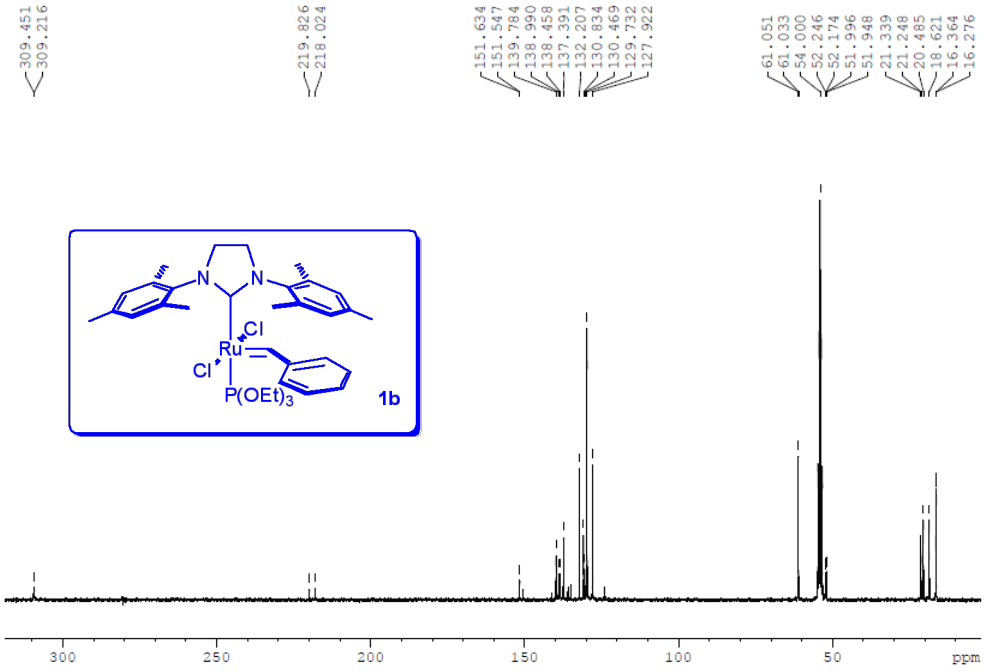


^{1}H NMR (CD_2Cl_2) of 1b



^{13}C-{^{1}H} NMR (CD_2Cl_2) of 1b



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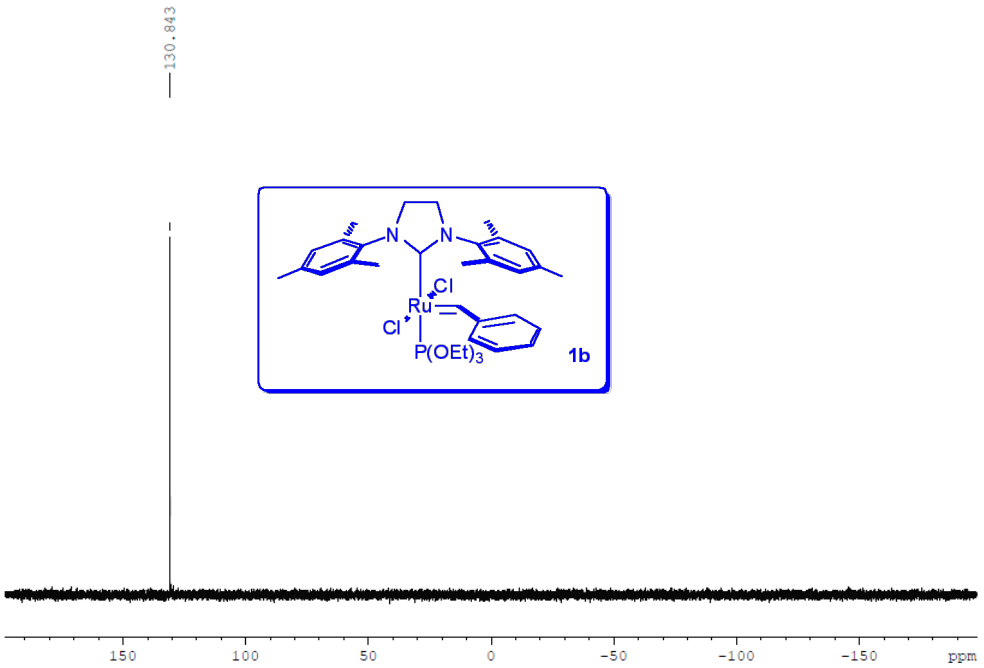
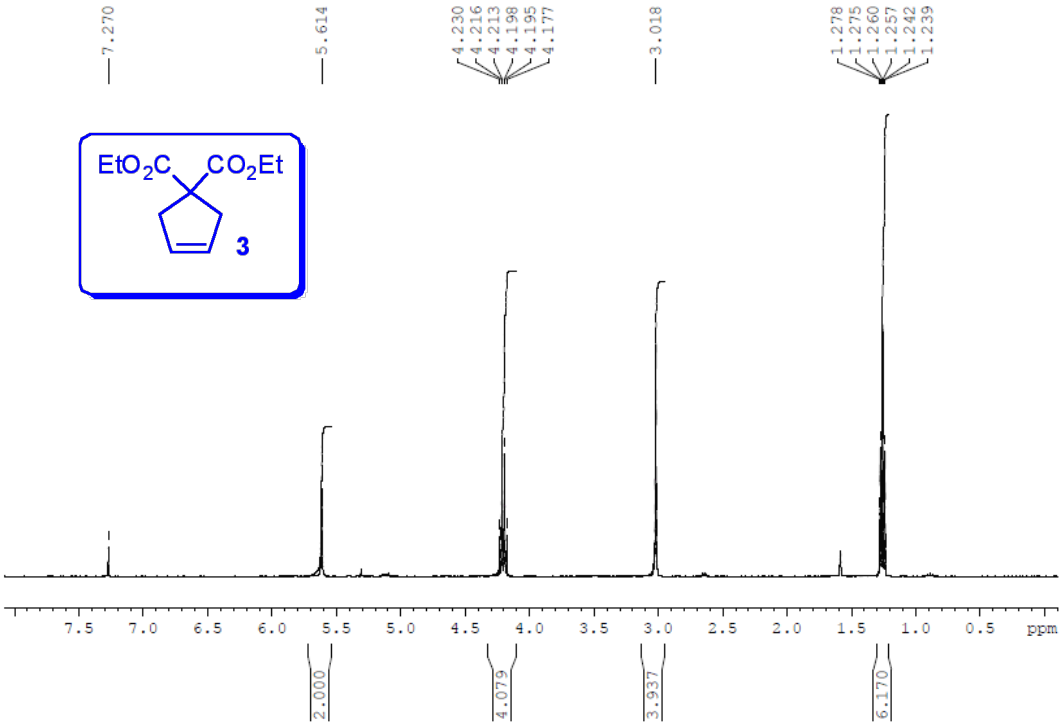
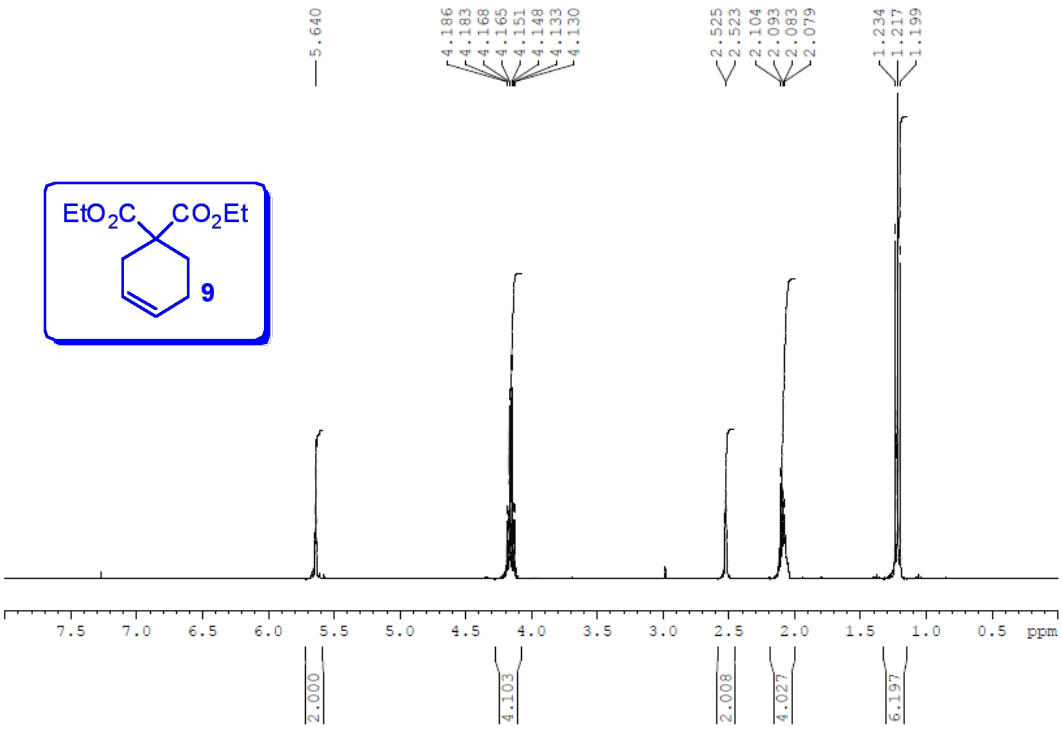


NMR spectra of the Metathesis products

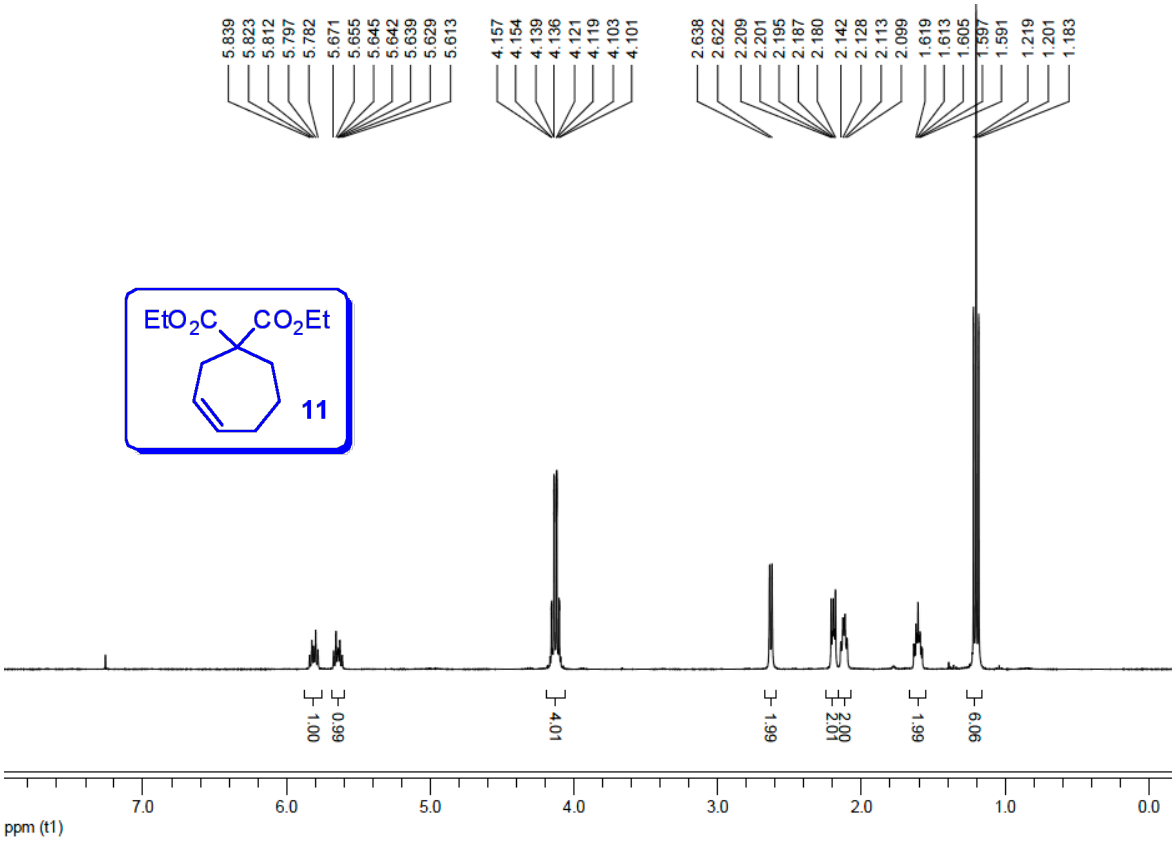
^{1}H NMR ($CDCl_3$) of 3 (Table 2, Entry 1)



^{1}H NMR ($CDCl_3$) of 9 (Table 2, Entry 2)

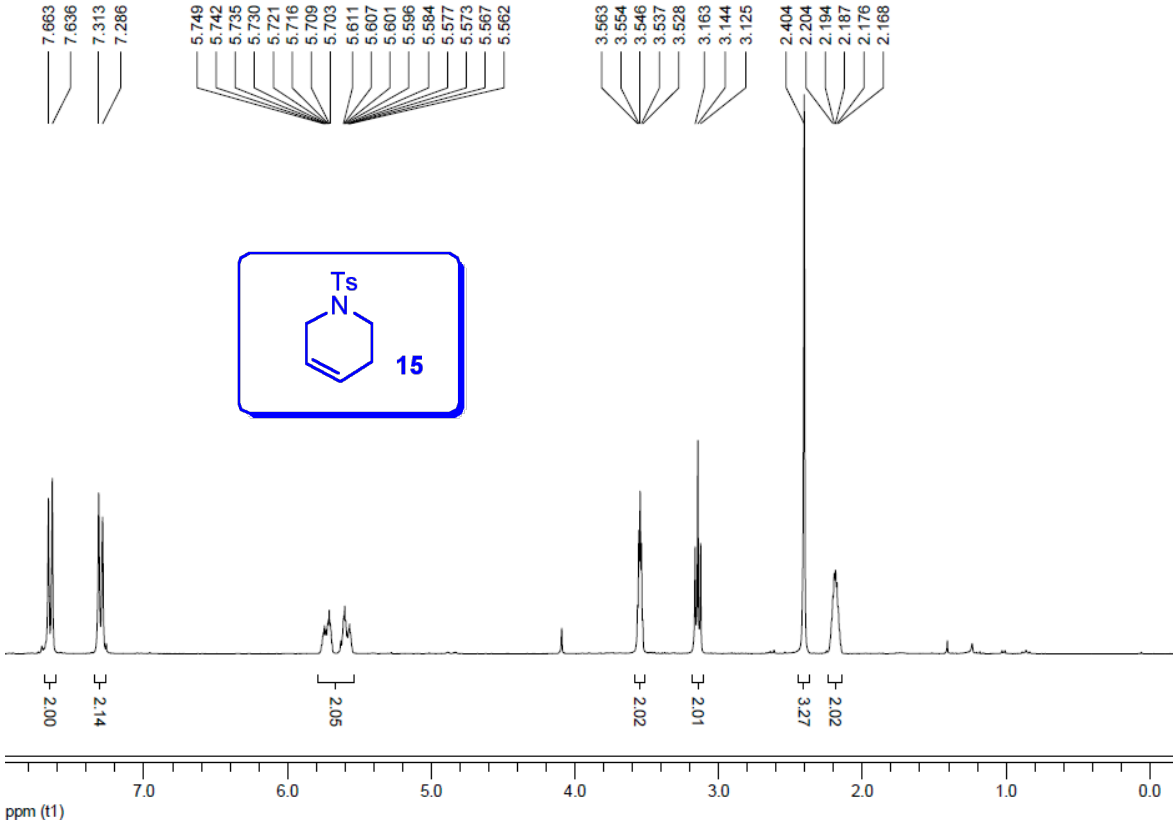


^{1}H NMR ($CDCl_3$) of 11 (Table 2, Entry 3)

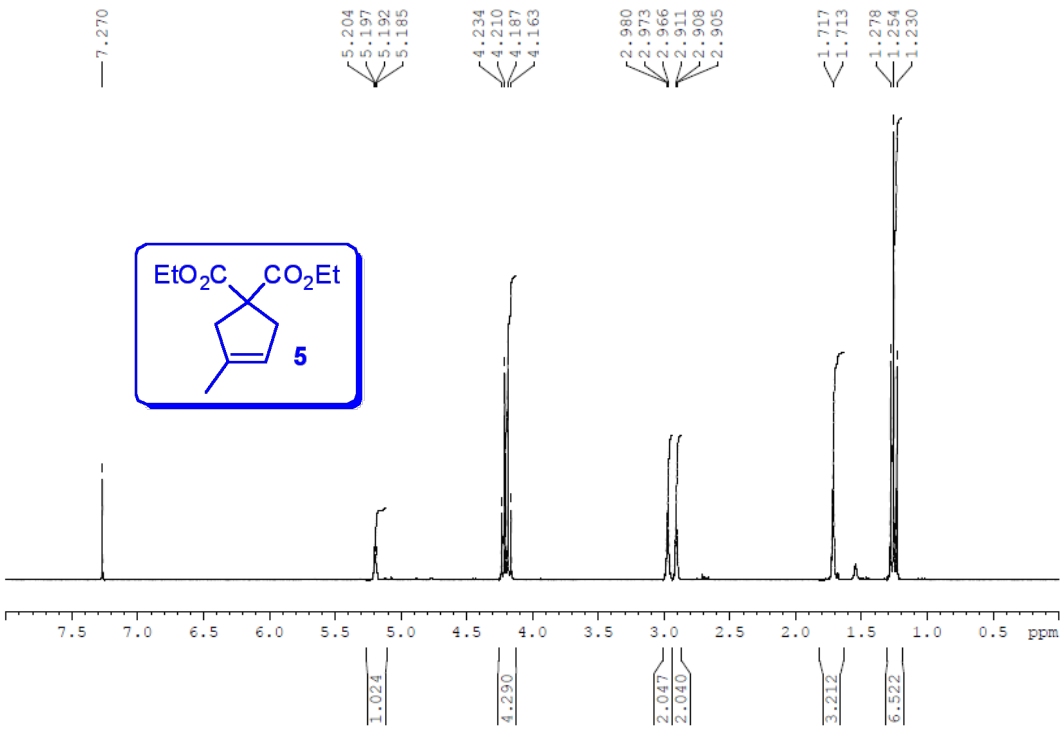


^{1}H NMR ($CDCl_3$) of 13 (Table 2, Entry 4)

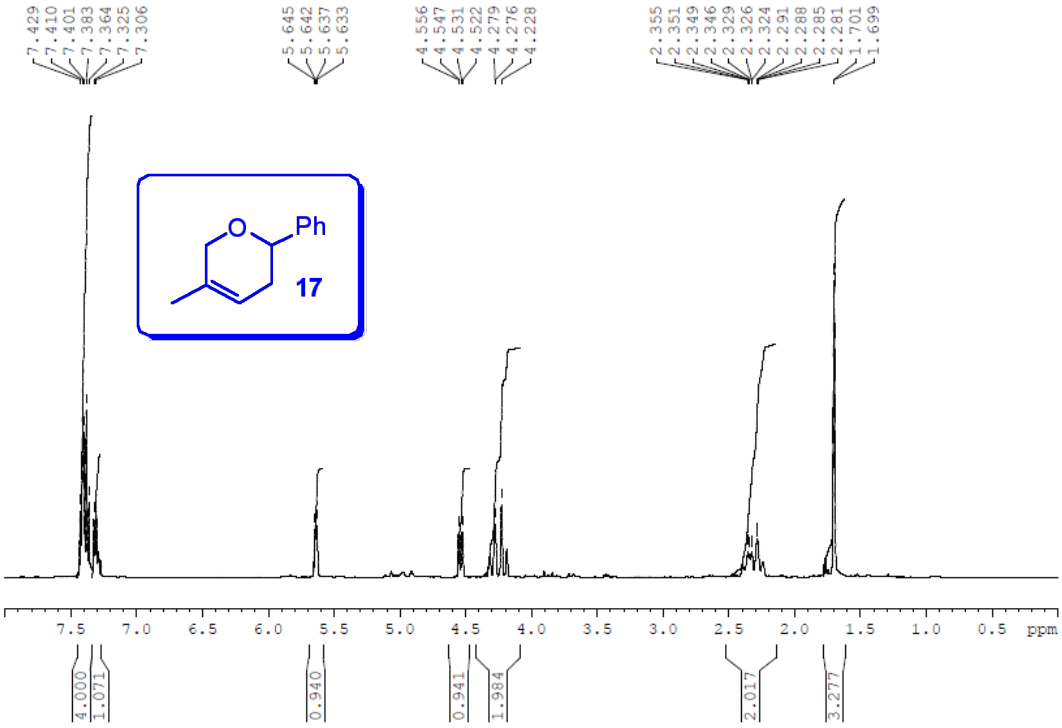
^{1}H NMR ($CDCl_3$) of 15 (Table 2, Entry 5)



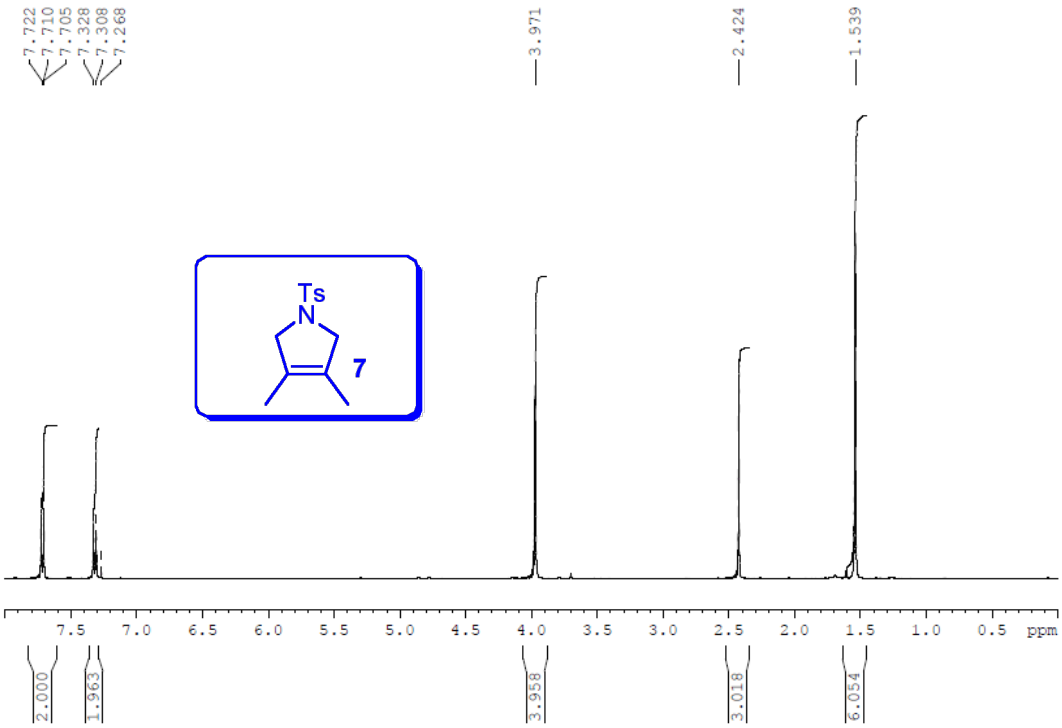
^{1}H NMR ($CDCl_3$) of 5 (Table 2, Entry 6)



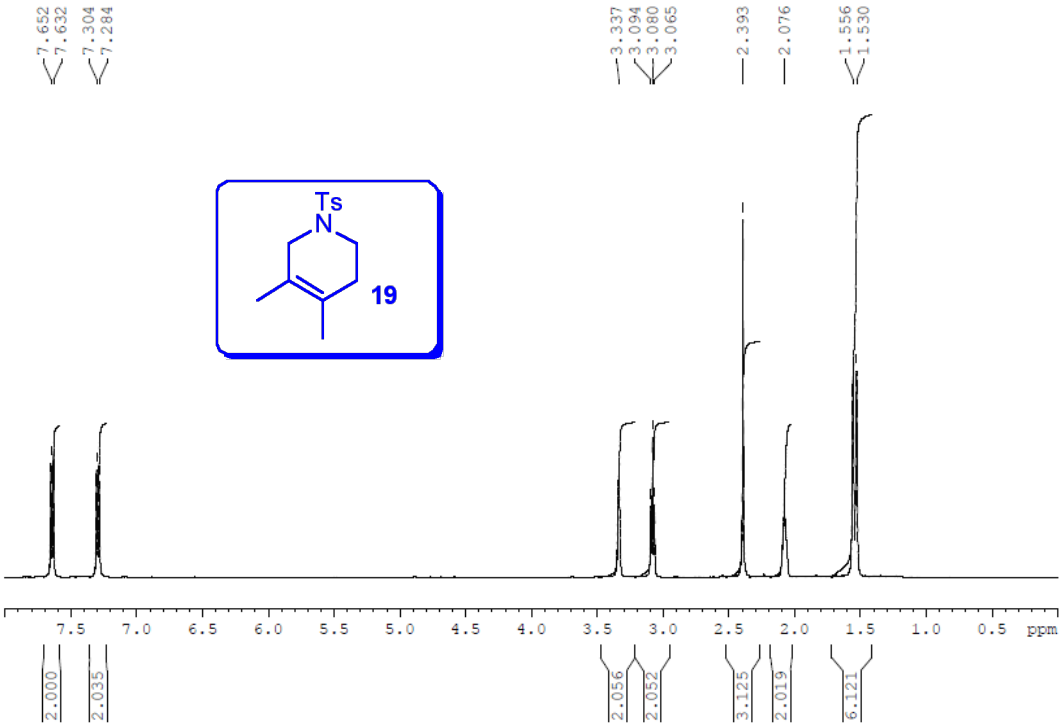
^{1}H NMR ($CDCl_3$) of 17 (Table 2, Entry 7)



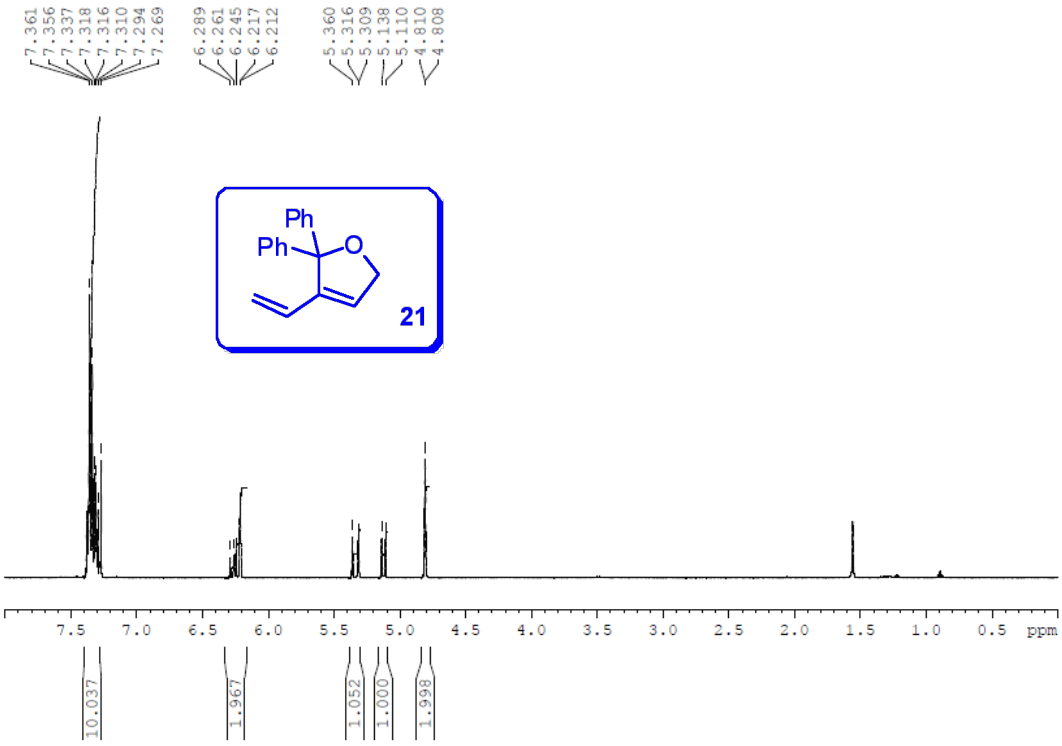
^{1}H NMR ($CDCl_3$) of 7 (Table 2, Entry 8)



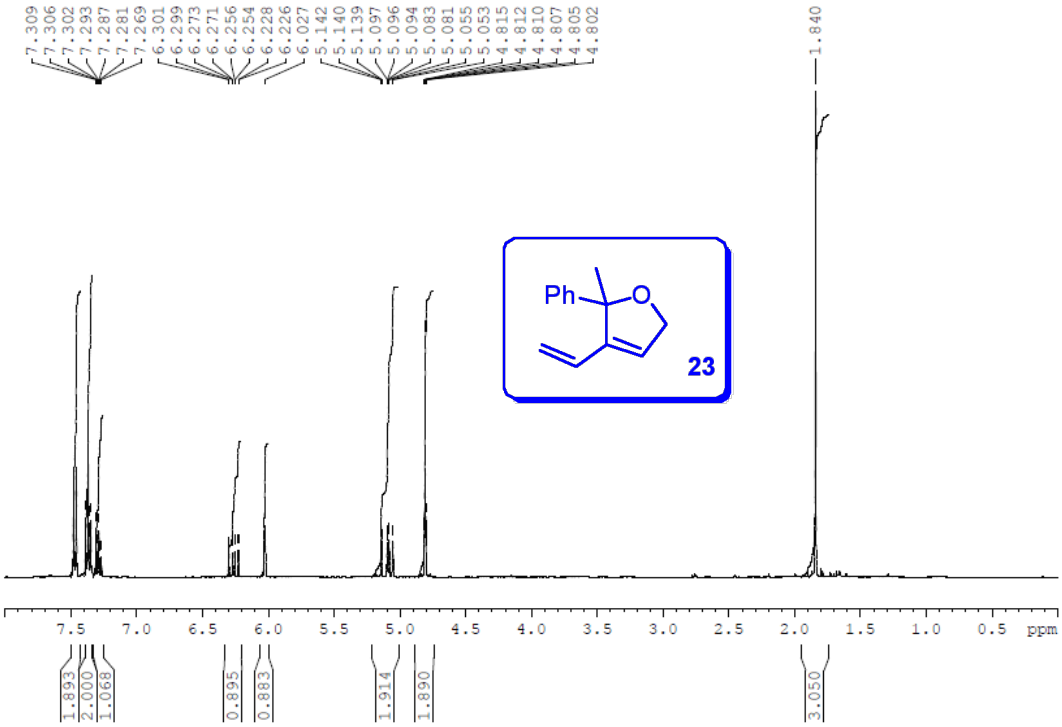
^{1}H NMR ($CDCl_3$) of 19 (Table 2, Entry 9)



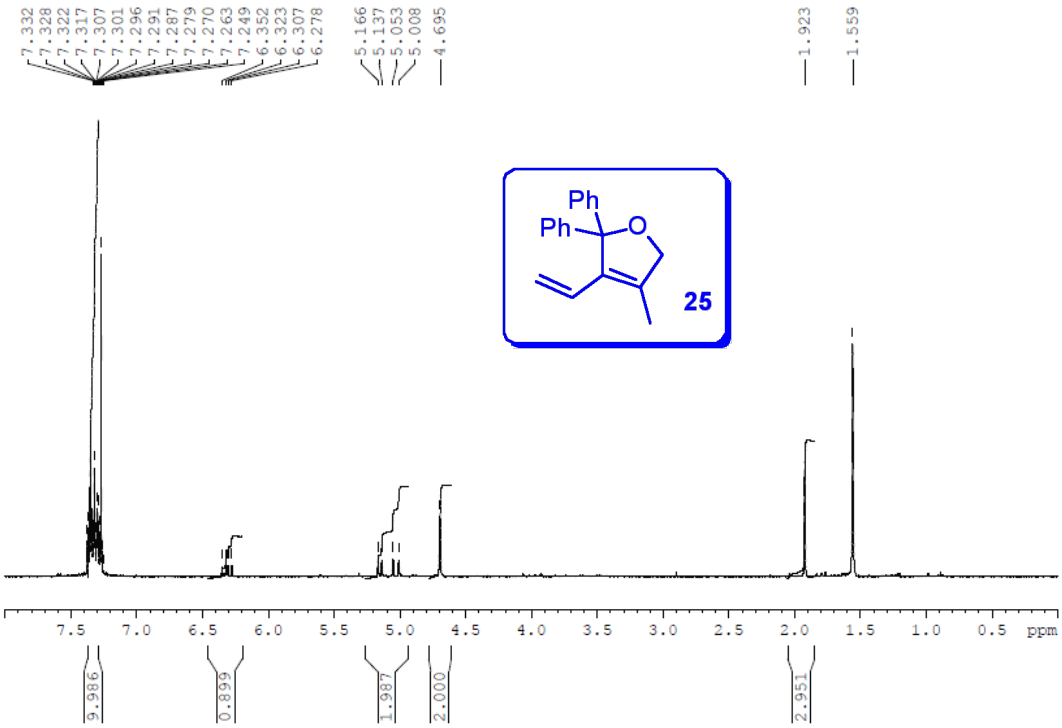
^{1}H NMR ($CDCl_3$) of 21 (Table 2, Entry 10)



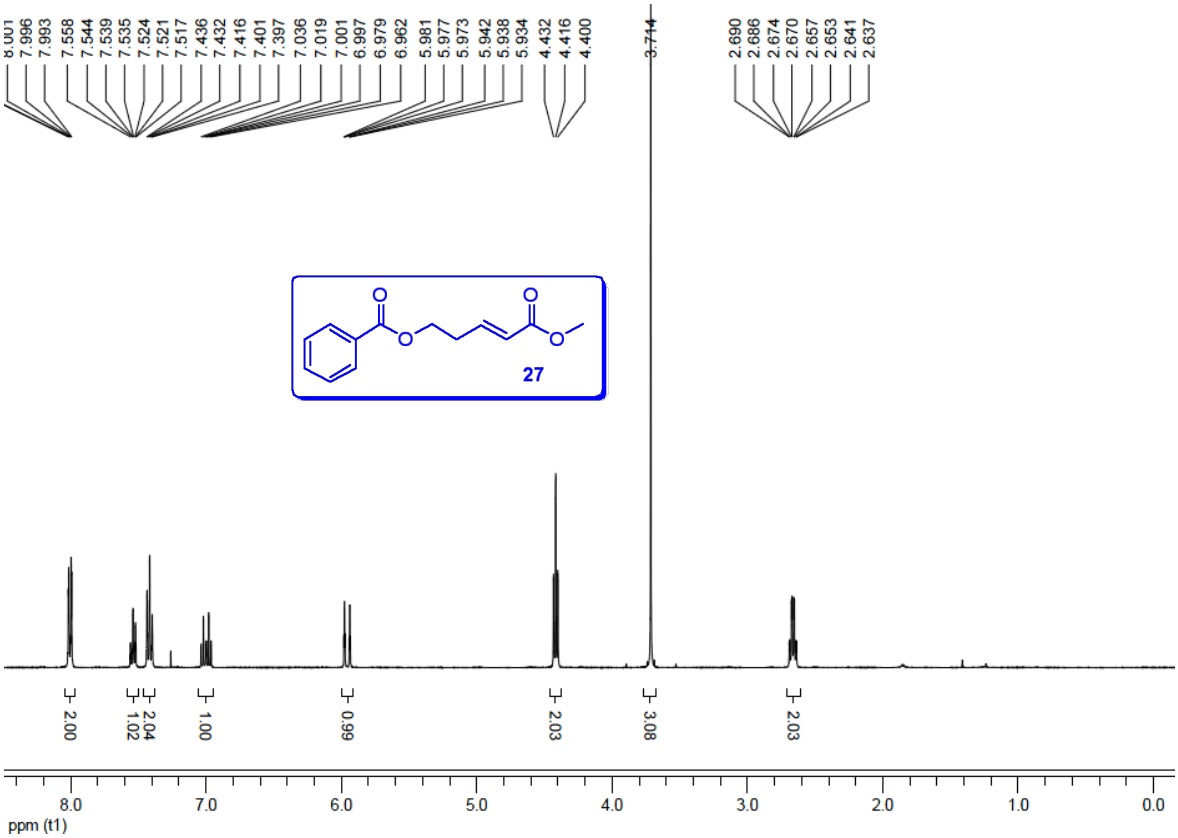
^{1}H NMR ($CDCl_3$) of 23 (Table 2, Entry 11)



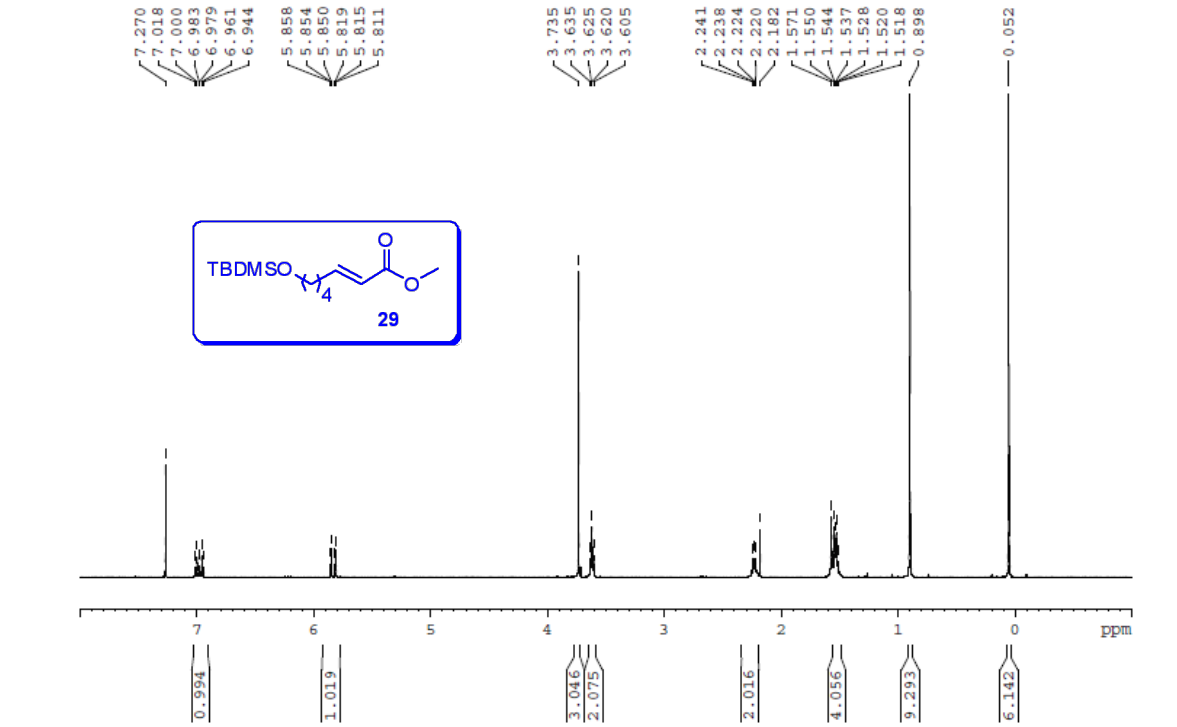
^{1}H NMR ($CDCl_3$) of 25 (Table 2, Entry 12)



^{1}H NMR ($CDCl_3$) of 27 (Table 2, Entry 13)



^{1}H NMR ($CDCl_3$) of 29 (Table 2, Entry 14)



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