Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

For

A General Approach to the Formation of Oxygen-Chelated Ruthe-nium Alkylidene Complexes Relying on the Thorpe-Ingold Effect

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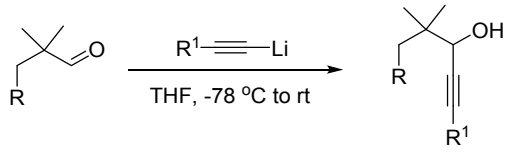
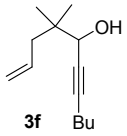
Contents

General Information: Reactions were carried out in oven or flame–dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America or GFS or Oakwood or Strem chemicals unless otherwise noted. Dichloromethane (CH_2Cl_2) and Toluene (PhMe) were distilled over calcium hydride (CaH_2) under nitrogen atmosphere. Flash chromatography was performed using silica gel 60 Å (32−63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040−0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX–500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). ^{1}H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, J, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q–Tof Ultima in the University of Illinois at Urbana–Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana-Champaign.

Experimental Details and Characterization Data

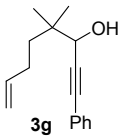


Enynes **3a**–**3c**, **3f**–**3h**, **3j**, **3k** and **3m** were synthesized from the know aldehydes and/or ketones using the alkynyl lithium. The characterization data of **3a**,[1] **3b**[2] and **3c**[3] can be found in reference 1–3.



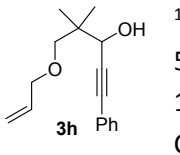
3f

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89–5.81 (m, 1H), 5.08–5.05 (m, 2H), 4.05 (s, 1H), 2.22 (dt, *J* = 2.0 Hz, 7.0 Hz, 2H), 2.18–2.07 (m, 2H), 1.69 (bs, 1H), 1.52–1.47 (m, 2H), 1.45–1.39 (s, 2H), 0.95 (s, 3H), 0.95 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.19, 117.49, 86.76, 79.50, 70.53, 42.83, 38.75, 30.82, 22.67, 22.55, 21.97, 18.41, 13.59; HRMS (ESI**)** calcd for $C_{13}H_{23}O$ $[M+H]^+$ 195.1743, found 195.1751.



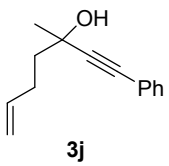
3g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.32–7.31 (m, 3H), 5.89–5.81 (m, 1H), 5.06–5.03 (m, 1H), 4.96–4.94 (m, 1H), 4.32 (s, 1H), 2,12–2.07 (m, 2H), 1.83 (bs, 1H), 1.57–1.52 (m, 2H), 1.05 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.39, 131.70, 128.37, 128.32, 122.78, 114.18, 88.77, 86.08, 70.91, 38.63, 37.56, 28.43, 22.76, 22.54; HRMS (ESI**)** calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found 229.1592.



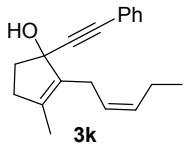
3h

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.31–7.29 (m, 3H), 5.94–5.86 (m, 1H), 5.30–5.27 (m, 1H), 5.20–5.17 (m, 1H), 4.43 (s, 1H), 4.02–4.00 (m, 2H), 3.68 (d, *J* = 8.9 Hz, 1H), 3.62 (bs, 1H), 3.30 (d, *J* = 8.9 Hz, 1H), 1.15 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.41, 131.71, 128.27, 128.23, 123.05, 117.14, 88.90, 85.47, 78.11, 72.53, 70.99, 39.48, 22.25, 21.17; HRMS (ESI**)** calcd for $C_{16}H_{20}O_2$ $[M]^+$ 244.1458, found 244.1462.



3j

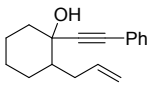
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.32–7.29 (m, 2H), 5.96–5.86 (m, 1H), 5.14–5.08 (m, 1H), 5.03–4.99 (m, 1H), 2.43–2.33 (m, 2H), 1.91–1.83 (m, 2H), 1.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 131.6, 128.3, 128.3, 122.7, 114.9, 92.6, 83.7, 68.5, 42.7, 30.1, 29.4; HRMS (ESI**)** calcd for $C_{14}H_{16}ONa$ $[M+Na]^+$ 223.1099, found 223.1094.



3k

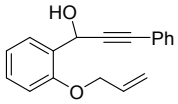
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.32–7.30 (m, 3H), 5.53–5.42 (m, 2H), 3.22 (dd, *J* = 7.1 Hz, 14.7 Hz, 1H), 3.10–3.04 (m, 1H), 2.63–2.57 (m, 1H), 2.47–2.40 (m, 1H), 2.24–2.21 (m, 2H), 2.07–1.97 (m, 2H), 1.38 (s, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.87, 132.82, 131.70, 128.33, 128.17, 126.26, 94.48, 86.06,

84.40, 62.96, 43.34, 40.14, 32.82, 25.95, 25.02, 20.71, 14.20; HRMS (ESI**)** calcd for $C_{18}H_{21}O$ $[M+H]^+$ 249.1640, found 249.1643.



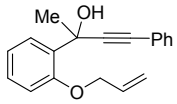
3l

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.32–7.31 (m, 3H), 5.95–5.87 (m, 1H), 5.15–5.04 (m, 1H), 2.74–2.68 (m, 1H), 2.63 (s, 1H), 2.14–2.01 (m, 2H), 1.80–1.50 (m, 5H), 1.32–1.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.31, 131.72, 128.31, 122.96, 116.27, 90.33, 86.59, 73.38, 47.92, 41.61, 41.12, 36.15, 29.64, 25.54, 24.18; HRMS (ESI**)** calcd for $C_{17}H_{20}O$ $[M]^+$ 240.1509, found 240.1518.



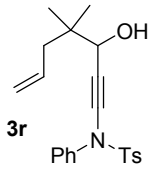
3m

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2H), 7.52–7.46 (m, 2H), 7.35–7.29 (m, 4H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.14–6.05 (m, 1H), 5.99 (d, *J* = 6.6 Hz, 1H), 5.50 (dd, *J* = 1.4, 16.0 Hz, 1H), 5.33 (dd, *J* = 1.2, 8.8 Hz, 1H), 4.68–4.59 (m, 2H), 3.37 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 132.9, 131.8, 129.6, 129.3, 128.4, 128.3, 122.9, 121.2, 117.7, 112.3, 88.8, 85.9, 69.1, 61.8; HRMS (ESI**)** calcd for $C_{18}H_{16}O_2Na$ $[M+Na]^+$ 287.1048, found 287.1052.



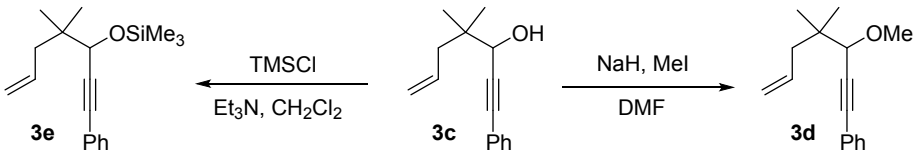
3n

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.61 (m, 1H), 7.47–7.42 (m, 2H), 7.33–7.25 (m, 4H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.15–6.06 (m, 1H), 5.56–5.49 (m, 1H), 5.35–5.30 (m, 1H), 4.72–4.66 (m, 2H), 4.62 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 132.9, 132.6, 131.7, 129.1, 128.2, 128.2, 126.4, 123.1, 121.2, 118.1, 112.9, 92.9, 83.3, 69.4, 29.6; HRMS (ESI**)** calcd for $C_{19}H_{18}O_2Na$ $[M+Na]^+$ 301.1204, found 301.1202.

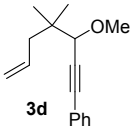


3r

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.32–7.23 (m, 7H), 5.87–5.79 (m, 1H), 5.06–5.03 (m, 2H), 4.21 (s, 1H), 2.41 (s, 3H), 2.19–2.06 (m, 2H), 0.97 (s, 3H), 9,95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 138.8, 134.9, 133.0, 129.6, 129.1, 128.3, 128.2, 126.2, 117.7, 79.8, 70.4, 70.2, 42.9, 39.2, 22.9, 22.8, 21.7; HRMS (ESI**)** calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$ 384.1628, found 384.1626.

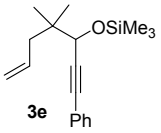


Methyl ether **3d** prepared from **3c** by treating with sodium hydride and then methyl iodide. Silyl ether **3e** prepared by protecting the enyne **3c** with TMSCl.



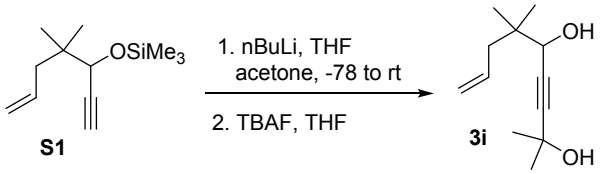
3d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.33–7.31 (m, 3H), 5.91–5.82 (m, 1H), 5.11–5.08 (m, 2H), 3.83 (s, 1H), 3.49 (s, 3H), 2.26–2.17 (m, 2H), 1.06 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.99, 131.75, 128.29, 128.21, 123.10, 117.55, 86.98, 86.94, 79.63, 57.45, 43.22, 38.67, 29.77, 23.33, 22.97; HRMS (ESI**)** calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found 229.1590.



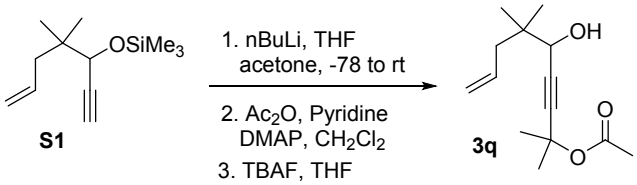
3e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.44 (m, 2H), 7.33–7.31 (m, 3H), 5.91–5.84 (m, 1H), 5.11–5.08 (m, 2H), 4.27 (s, 1H), 2.20 (d, *J* = 7.3 Hz, 2H), 1.02 (s, 3H), 1.01 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.28, 131.52, 128.28, 128.07, 123.35, 117.30, 89.67, 85.53, 70.84, 42.78, 39.24, 22.80, 22.56, 0.25; HRMS (ESI**)** calcd for $C_{18}H_{27}OSi$ $[M+H]^+$ 287.1826, found 287.1823.



S1 **3i**

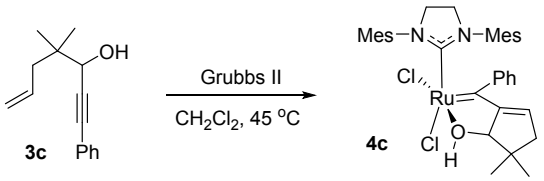
Enyne **3i** prepared from the known propargy silyl ether[4] **S1** in two steps as shown above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87–5.78 (m, 1H), 5.07–5.04 (m, 2H), 4.07 (s, 1H), 2.62 (bs, 1H), 2.37 (bs, 1H), 2.17–2.06 (m, 2H), 1.51 (s, 6H), 0.95 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.92, 117.70, 90.91, 81.58, 69.96, 65.16, 42.82, 38.69, 31.47, 31.41, 22.73, 22.53; HRMS (ESI**)** calcd for $C_{12}H_{19}O$ $[M–H_2O]^+$ 179.1430, found 179.1433.



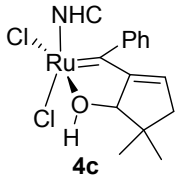
S1 **3q**

Enyne **3q** prepared from the known propargy silyl ether **S1** in three steps as shown above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86−5.77 (m, 1H), 5.08−5.02 (m, 2H), 4.06 (s, 1H), 2.33 (s, 1H), 2.16−2.05 (m, 2H), 1.99 (s, 3H), 1.63 (s, 6H), 0.94 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.34, 135.05, 117.55, 86.88, 83.84, 71.95, 69.87, 42.76, 38.82, 29.04, 28.97, 22.66, 22.54, 21.93; HRMS (ESI) calcd for $C_{14}H_{22}O_3Na$ $[M+Na]^+$ 261.1461 found, 261.1466.

General procedure for the hydroxy- and ether-chelated ruthenium alkylidenes

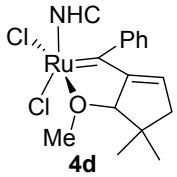


Compund **3c** (16 mg, 0.074 mmol) and Grubbs II (59 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (4 mL) in an air–free sealed tube and heated up to 45 °C over 3 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, EtOAc : CH_2Cl_2 = 1 : 1) to afford **4c** (43.7 mg, 92%) as a green solid.



4c

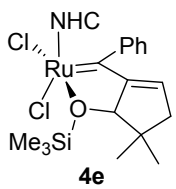
4c (43.7 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.2 Hz, 1H), 7.08–7.06 (m, 3H), 7.00–6.95 (m, 4H), 6.70 (s, 1H), 5.78 (s, 1H), 4.97 (d, *J* = 11.1 Hz, 1H), 4.28–4.23 (m, 2H), 4.12–4.08 (m, 1H), 3.92–3.90 (m, 1H), 2.51 (s, 3H), 2.44 (s, 3H), 2.36 (s, 9H), 2.20 (d, *J* = 11.2 Hz, 1H), 1.84 (m, 5H), 1.20 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 285.24, 216.84, 164.91, 155.07, 140.22, 140.07, 139.01, 138.09, 137.98, 135.65, 135.13, 131.26, 131.03, 130.58, 129.31, 128.49, 127.37, 126.11, 124.29, 112.16, 93.61, 53.10, 51.06, 42.78, 26.42, 21.60, 21.34, 21.08, 20.16, 19.01, 18.57, 18.28; HRMS (ESI**)** calcd for $C_{35}H_{40}Cl_1N_2ORu$ $[M–HCl–H]^+$ 641.1867, found 641.1875.



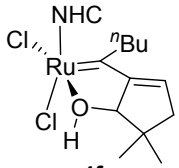
4d

4d (42 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (bs, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.06 (s, 1H), 7.02 (s, 1H), 6.93 (s, 2H) 6.40 (s, 1H), 5.90 (s, 1H), 4.99 (d, *J* = 5.2 Hz, 1H), 4.34 (s, 1H), 4.24–4.18 (m, 2H), 3.88–3.86 (m, 1H), 3.70–3.68 (m, 1H), 2.81 (s, 3H), 2.79 (s, 3H), 2.57 (s, 3H), 2.30 (s, 3H), 2.19 (s, 3H), 1.98–1.94 (m, 1H), 1.86 (s, 3H), 1.85 (s, 3H), 1.68 (m, 1H), 1.18 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 281.29, 214.66, 141.92, 139.66, 139.41, 138.35, 137.51, 135.78, 134.31, 130.75, 130.37, 129.86, 129.46, 128.94, 128.05, 88.58, 86.65, 79.65, 60.73, 52.41, 52.25, 49.50, 46.10, 27.01, 26.38, 14.63, 23.38, 21.26, 20.84, 20.38, 18.96, 18.89, 17.91; HRMS (ESI**)** calcd for $C_{35}H_{39}N_2Ru$ $[M–2Cl–CH_3OH–H]^+$ 589.2151, found 589.2040.

4e (44 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (bs, 1H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.17 (bm, 2H), 7.06 (s, 1H), 7.17 (s, 1H), 6.37 (s, 1H), 5.91 (s, 1H), 4.96 (s, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.25–4.17 (m, 2H), 3.87–3.86 (m, 1H), 3.70–3.68 (m, 1H), 2.79 (s, 3H), 2.58 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 1.94 (dd, *J* = 5.4 Hz, 14.0Hz, 1H), 1.86 (s, 3H), 1.83 (s, 3H), 1.59 (d, *J* = 14.3 Hz, 1H), 1.16 (s, 3H), 0.96 (s, 3H), –0.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 281.44, 214.57, 142.63, 139.69, 139.45, 138.19, 137.43, 135.83, 134.74, 134.13, 133.04, 130.74, 129.87, 129.48, 128.83, 91.47, 79.23, 52.40, 52.34, 50.22, 45.21, 24.17, 22.78, 21.25, 20.87, 20.46, 18.97, 17.85, 0.15; HRMS (ESI**)** calcd for $C_{38}H_{51}Cl_2N_2ORuSi$ $[M+H]^+$ 751.2186, found 751.1168.

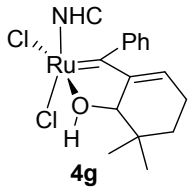


4e



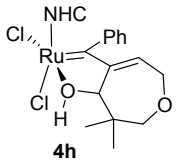
4f

4f (39 mg, 84%, cis:trans: **5:1**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.96 (s, 2H), 6.81 (s, 1H), 5.78 (s, 1H), 4.93 (s, 1H), 4.34–4.30 (m, 1H), 4.11–4.04 (s, 2H), 3.99–3.94 (m, 1H), 3.33–3.30 (m, 2H), 2.76 (s, 3H), 2.51 2.76 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H), 2.21 (s, 3H), 2.11–2.07 (m, 1H), 1.92 (s, 3H), 1.90–1.86 (m, 4H), 1.51–1.47 (m, 1H), 1.08 (s, 3H), 0.90 (s, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 305.80, 218.08, 160.42, 140.33, 139.97, 138.69, 138.52, 137.81, 136.20, 135.97, 136.20, 135.97, 131.17, 130.02, 129.06, 128.51, 107.64, 106.11, 92.16, 52.68, 52.27, 52.17, 50.74, 41.39, 28.43, 26.76, 24.25, 22.73, 21.27, 21.04, 19.92, 19.31, 19.09, 18.46, 13.50; HRMS (ESI**)** calcd for $C_{33}H_{46}Cl_1N_2ORu$ $[M–Cl]^+$ 623.2337, found 623.2346.



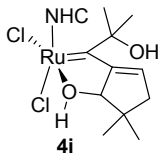
4g

4g (45.6 mg, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 3H), 7.08–6.83 (m, 6H), 6.19 (s, 1H), 4.27–4.17 (m, 3H), 4.06–4.02 (m, 1H), 3.91–3.87 (m, 1H), 2.55 (s, 3H), 2.46 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H), 1.96 (s, 3H), 1.49–1.44 (m, 2H), 1.26–1.20 (m, 2H), 1.10 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 294.66, 216.79, 156.52, 155.68, 140.22, 139.20, 138.17, 137.89, 135.90, 135.03, 131.21, 131.00, 129.21, 128.52, 126.58, 120.91, 84.21, 53.19, 50.94, 35.09, 34.22, 27.76, 24.38, 21.38, 21.14, 20.20, 19.13, 18.86, 18.17, 17.65; HRMS (ESI**)** calcd for $C_{36}H_{41}N_2ORu$ $[M–2HCl–H]^+$ 619.2257, found 619.2269.



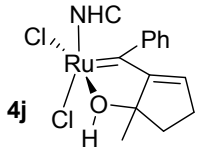
4h

4h (39.7 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11–7.08 (m, 2H), 7.01–6.96 (m, 4H), 6.84 (s, 1H), 6.41 (s, 1H), 6.39 (s, 1H), 5.99 (bs, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 4.34–4.28 (m, 1H), 4.18–3.97 (m, 3H), 3.65 (dd, *J* = 4.5 Hz, 17.5 Hz, 1H), 3.56 (d, *J* = 12.5 Hz), 3.43 (d, *J* = 12.4 Hz, 1H), 3.28 (d, *J* = 17.4 Hz, 1H), 2.76 (d, *J* = 8.7 Hz, 1H), 2.60 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 1.01 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 292.6, 214.3, 160.6, 157.7, 140.2, 139.7, 139.0, 138.6, 137.4, 136.1, 130.7, 130.5, 130.49, 128.9, 128.3, 126.3, 126.30, 122.7, 114.0, 84.2, 80.6, 71.1, 52.9, 51.4, 40.6, 24.8, 21.3, 21.1, 19.9, 19.2, 19.1, 18.8, 18.1; HRMS (ESI**)** calcd for $C_{36}H_{42}Cl_1N_2O_2Ru$ $[M–HCl–H]^+$ 671.1973, found 671.1985.



4i

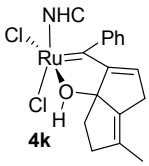
4i (38 mg, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.92 (s, 1H), 6.84 (s, 1H), 6.80 (s, 1H), 5.16 (s, 1H), 4.91 (s, 1H), 4.34–4.37 (bs, 1H), 4.25–4.21 (m, 1H), 4.12–4.07 (m, 2H), 3.70 (s, 1H), 2.51 (s, 3H), 2.32 (s, 3H), 2.28 (s, 6H), 2.26 (s, 3H), 2.25 (s, 3H), 2.04–1.99 (m, 2H), 1.40 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 283.59, 216.98, 159.01, 140.76, 140.22, 138.78, 138.12, 137.65, 135.69, 135.48, 130.65, 130.48, 130.34, 129.99, 129.83, 128.81, 119.51, 116.16, 95.15, 84.13, 52.67, 51.03, 46.74, 41.99, 27.28, 27.05, 26.96, 26.43, 26.21, 25.06, 23.10, 21.60, 21.34, 20.98, 20.07, 18.90, 18.35; HRMS (ESI**)** calcd for $C_{32}H_{43}N_2O_2Ru$ $[M–2HCl]^+$ 589.2377, found 589.2377.



4j

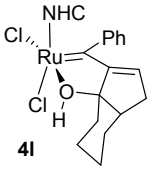
4j (34 mg, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (bs, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.20 (t, J = 8.1 Hz, 2H), 7.11 (s, 1H), 7.07 (s, 1H), 6.25 (s, 1H), 6.10 (s, 1H), 4.32–4.24 (m, 2H), 4.21–4.11 (m, 2H), 3.88–3.71 (m, 2H), 2.79 (s, 3H), 2.66 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.08–2.02 (m, 2H), 1.86 (s, 2H), 1.64 (s, 3H), 1.59–1.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 282.7, 211.6, 142.9, 139.8, 139.1, 138.3, 137.5, 135.4, 134.6, 134.1, 133.7, 131.0, 130.1,

129.8, 128.7, 128.6, 94.7, 81.5, 73.0, 52.4, 52.3, 39.3, 33.9, 29.4, 29.2, 27.0, 26.9, 26.4, 26.2, 25.0, 21.2, 20.8, 19.1, 17.7; HRMS (ESI**)** calcd for $C_{34}H_{39}N_2ORu$ $[M–2HCl]^+$ 593.2106, found 593.2122.



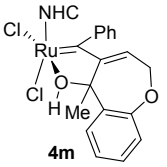
4k

4k (45 mg, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.3 Hz, 2H), 7.24 (m, 3H), 7.13 (s, 1H), 7.03 (s, 1H), 6.24 (s, 1H), 6.11 (s, 1H), 4.81 (d, *J* = 2.3 Hz, 1H), 4.33–4.25 (m, 2H), 3.96–3.90 (m, 1H), 3.84–3.80 (m, 1H), 2.94 (s, 3H), 2.71–2.66 (m, 1H), 2.60 (s, 3H), 2.49 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.15–2.00 (m, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 276.5, 213.3, 166.2, 143.1, 141.9, 140.0, 139.3, 137.6, 135.8, 134.9, 134.5, 132.9, 130.9, 130.80, 130.1, 129.5, 128.7, 87.9, 79.4, 74.3, 52.25, 52.4, 44.3, 35.1, 26.1, 24.9, 21.3, 20.8, 20.4, 19.3, 19.0, 17.8; HRMS (ESI**)** calcd for $C_{37}H_{39}N_2Ru$ $[M–2Cl–H_2O]^+$ 613.2157, found 613.2184.



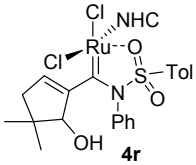
4l

4l (44 mg, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (bm, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.10 (s, 1H), 7.05 (s, 1H), 6.27 (s, 1H), 6.03 (s, 1H), 4.34 (s, 1H), 4.30–4.14 (m, 2H), 3.87–3.69 (m, 2H), 2.83 (s, 3H), 2.64 (s, 3H), 2.41 (bs, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 1.85 (s, 3H), 1.81–1.75 (m, 2H), 1.51–1.28 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 283.37, 212.49, 142.86, 139.66, 139.04, 138.28, 137.56, 135.46, 134.61, 134.17, 133.97, 130.95, 130.73, 130.00, 129.49, 128.73, 128.61, 96.43, 80.84, 73.82, 52.36, 41.03, 36.93, 33.09, 22.93, 21.24, 20.98, 20.84, 20.60, 20.48, 19.31, 19.17, 17.88; HRMS (ESI**)** calcd for $C_{37}H_{43}N_2ORu$ $[M–2Cl–H]^+$ 633.2413, found 633.2411.



4m

This compound could not be isolated in purform owing to its instability towards purification. Yield was calculated to be 58% based on crude nmr. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 9.2 Hz, 1H), 7.34–7.28 (m, 3H), 7.14–7.10 (m, 2H), 7.04–6.98 (m, 2H), 6.96 (s, 1H), 6.62 (s, 1H), 6.60 (s, 1H), 6.52 (s, 1H), 5.74 (d, J = 18 Hz, 1H), 546–5.38 (m, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.36-4.32 (m, 1H), 4.21-4.13 (m, 1H), 3.97-3.85 (m, 2H), 2.71 (s, 3H), 2.49 (s, 3H), 2.37 (m, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 1.72 (s, 3H), 1.37 (s, 3H); ; HRMS (ESI**)** calcd for $C_{39}H_{41}N_2O_2Ru$ $[M–2HCl]^+$ 671.2212, found 671.2203.



4r

4r (44 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.22–7.14 (m, 3H), 7.10–7.02 (m, 4H), 6.86–6.82 (m, 2H), 6.86–6.57 (m, 2H), 5.53 (d, *J* = 2.0 Hz, 1H), 4.31–4.04 (m, 4H), 3.90 (s, 1H), 3.62 (d, *J* = 4.2 Hz, 1H), 2.59 (s, 3H), 2.56 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.79 (d, *J* = 16.6 Hz, 1H), 1.38 (d, *J* = 16.4 Hz, 1H), 0.96 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 262.6, 214.7, 153.9, 146.2, 140.5, 139.0, 138.4, 138.3, 137.2, 137.0, 136.3, 132.9, 130.6, 130.5, 130.0, 129.9, 129.7, 129.3, 129.1, 128.5, 127.8, 122.1, 88.1, 52.7, 51.1, 47.2, 41.7, 27.7, 23.5, 21.8, 21.4, 21.1, 20.5, 19.2, 19.0, 18.7; HRMS (ESI**)** calcd for $C_{43}H_{50}N_3O_4RuS$ $[M–2Cl+CO+H]^+$ 806.2560 found, 806.2483 (Note: sulfonamide–ruthenium alkylidenes can react with fractional amount carbon monoxide in the solvent[5]).

References

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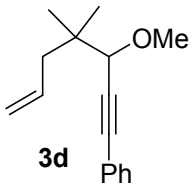
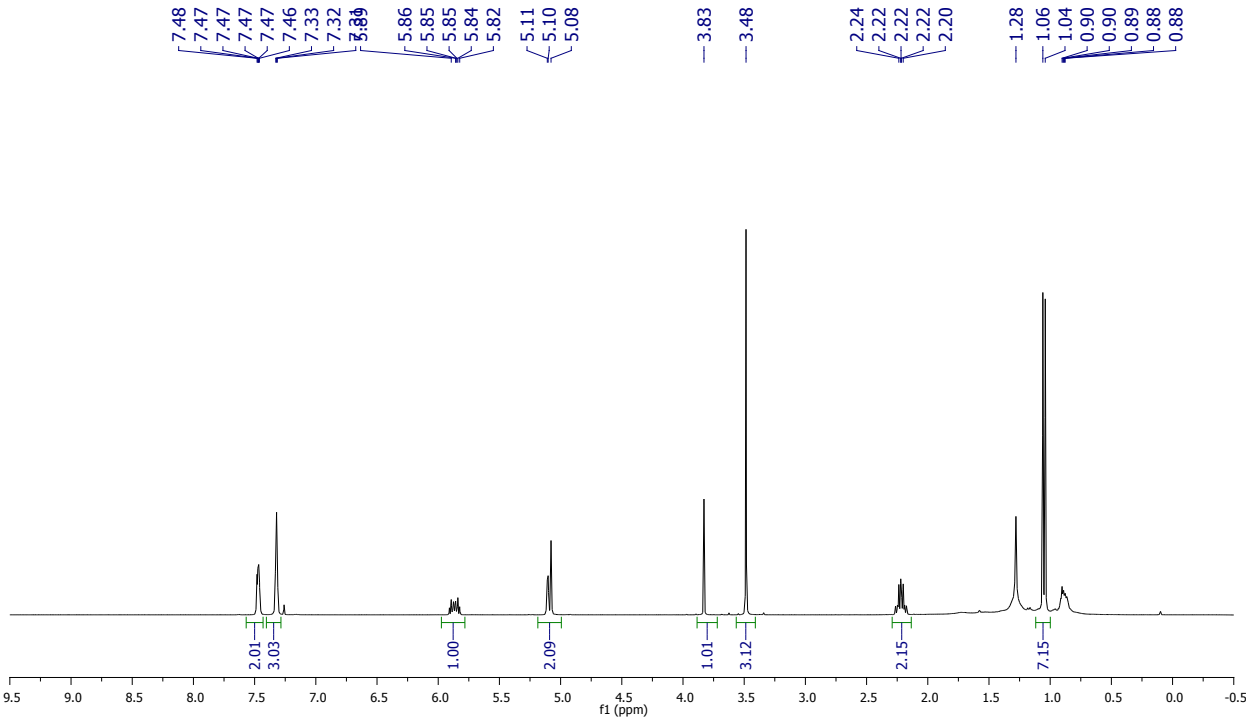
5. Sabbasani, V. R.; Yun, S. Y.; Lee, D. *Org. Chem. Front*. **2016**, *3*, 939.


OMe
Ph

3d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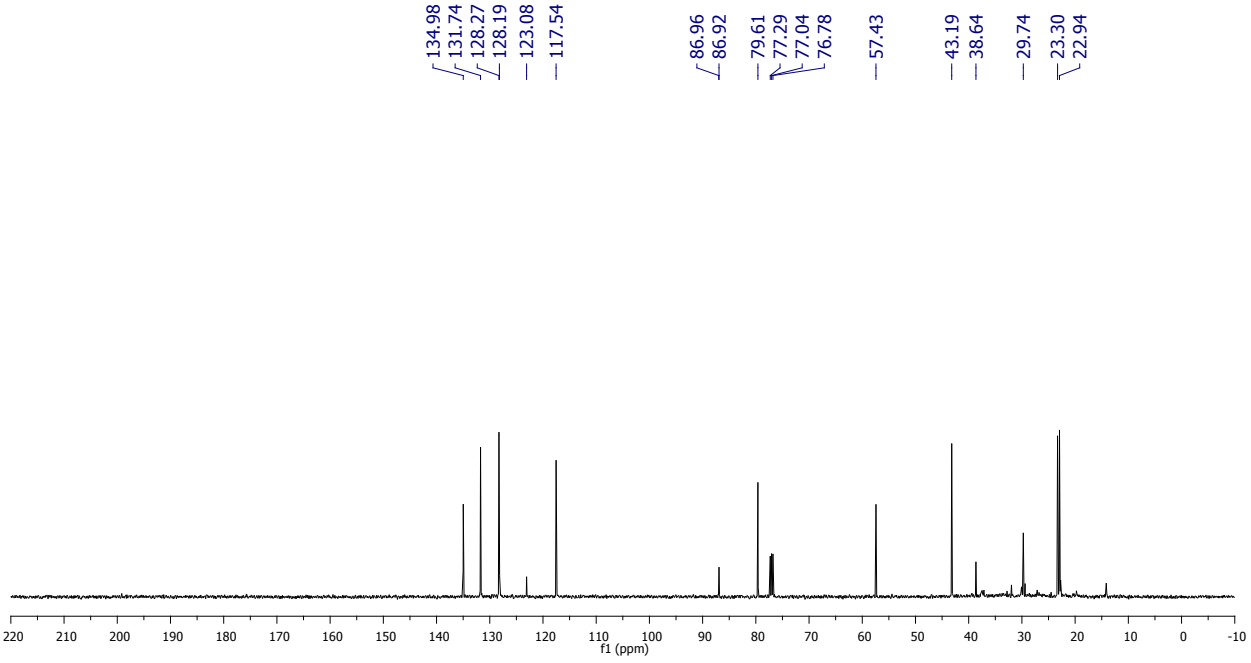
f1 (ppm)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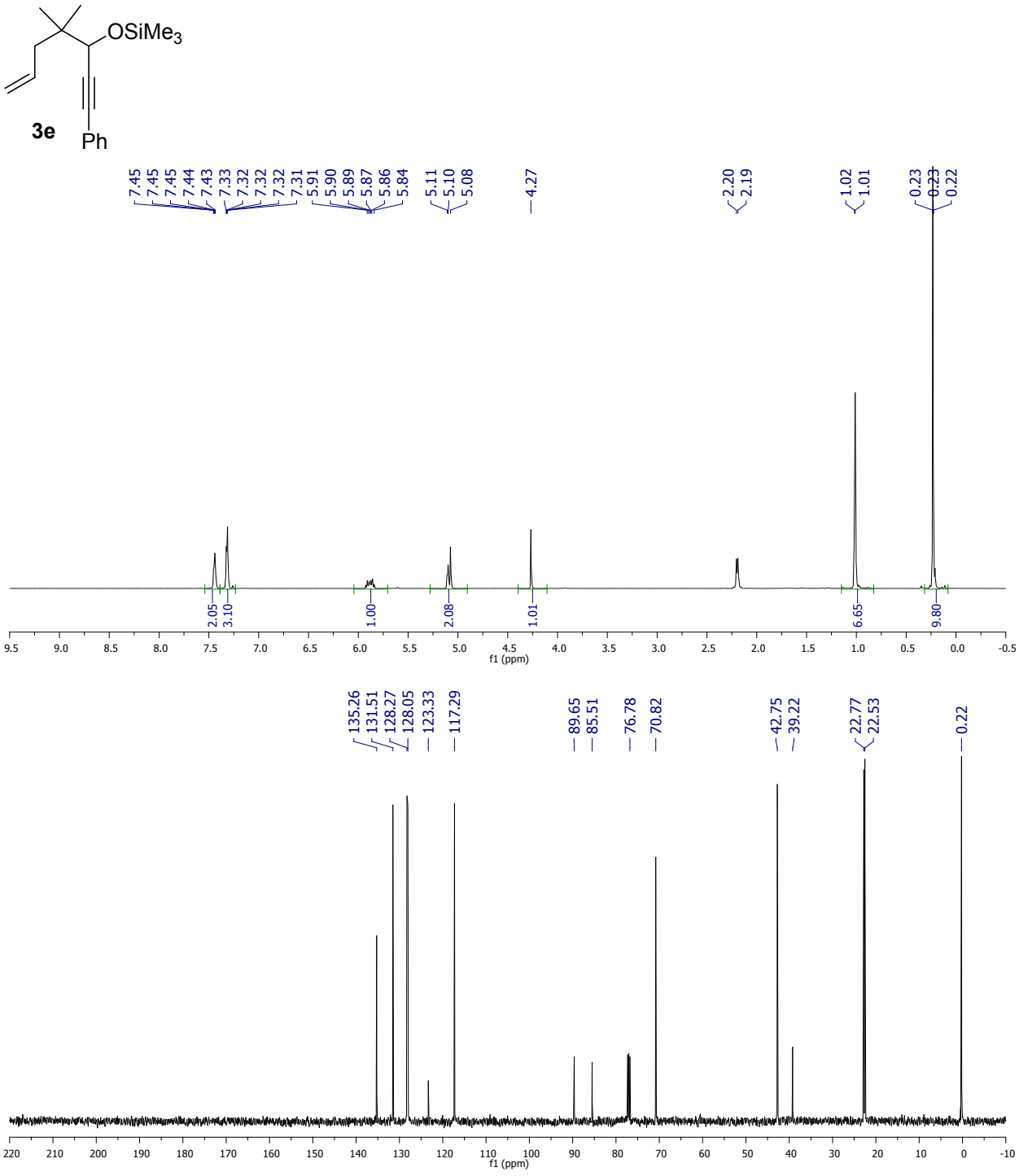
f1 (ppm)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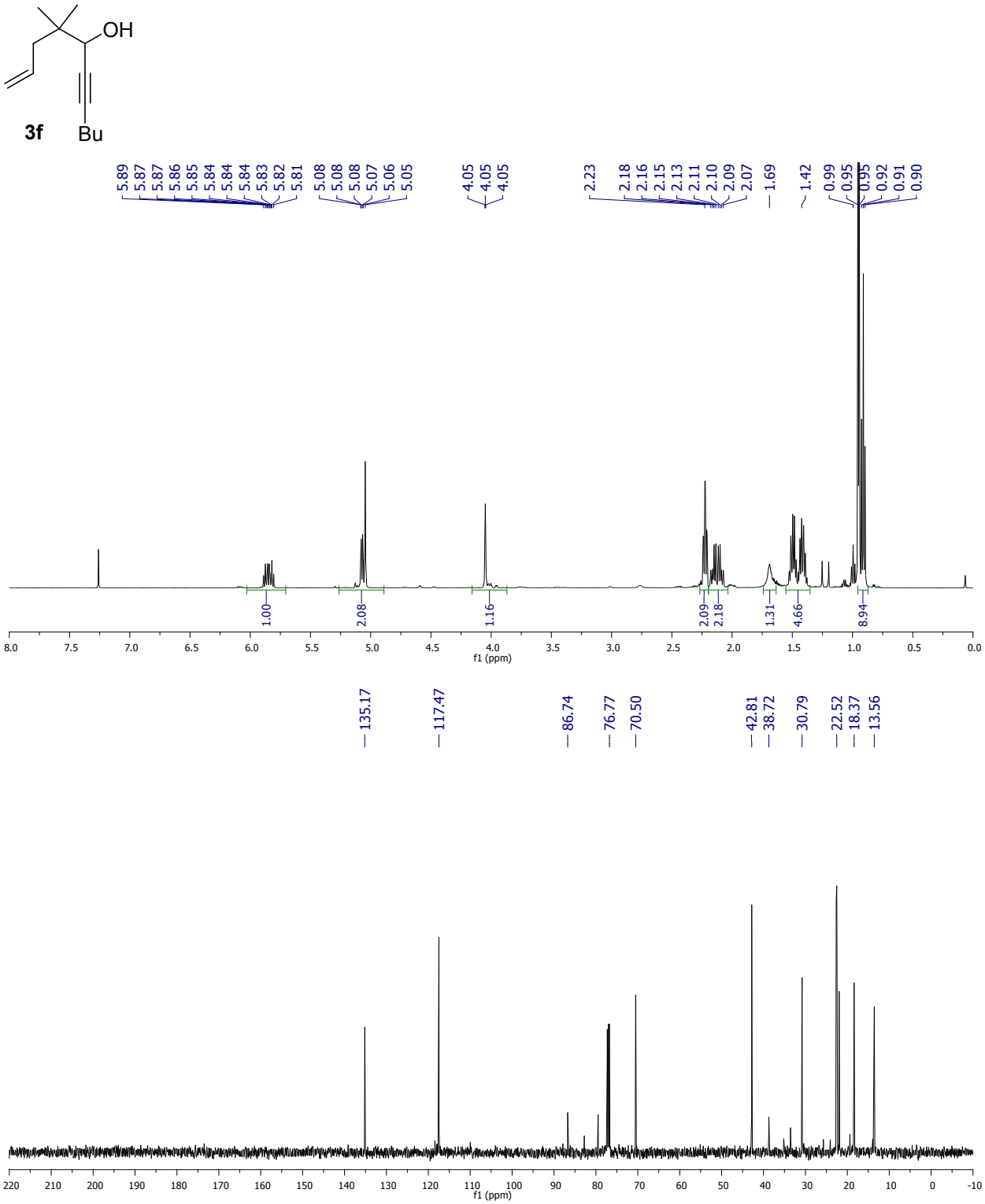
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5.08 5.08 5.08 5.07 5.06 5.05
4.05 4.05 4.05
2.23 2.18 2.16 2.15 2.13 2.11 2.10 2.09 2.07
1.69
1.42
0.99 0.95 0.95 0.92 0.91 0.90
1.00 2.08 1.16 2.09 2.18 1.31 4.66 8.94
f1 (ppm)
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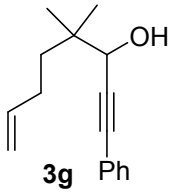
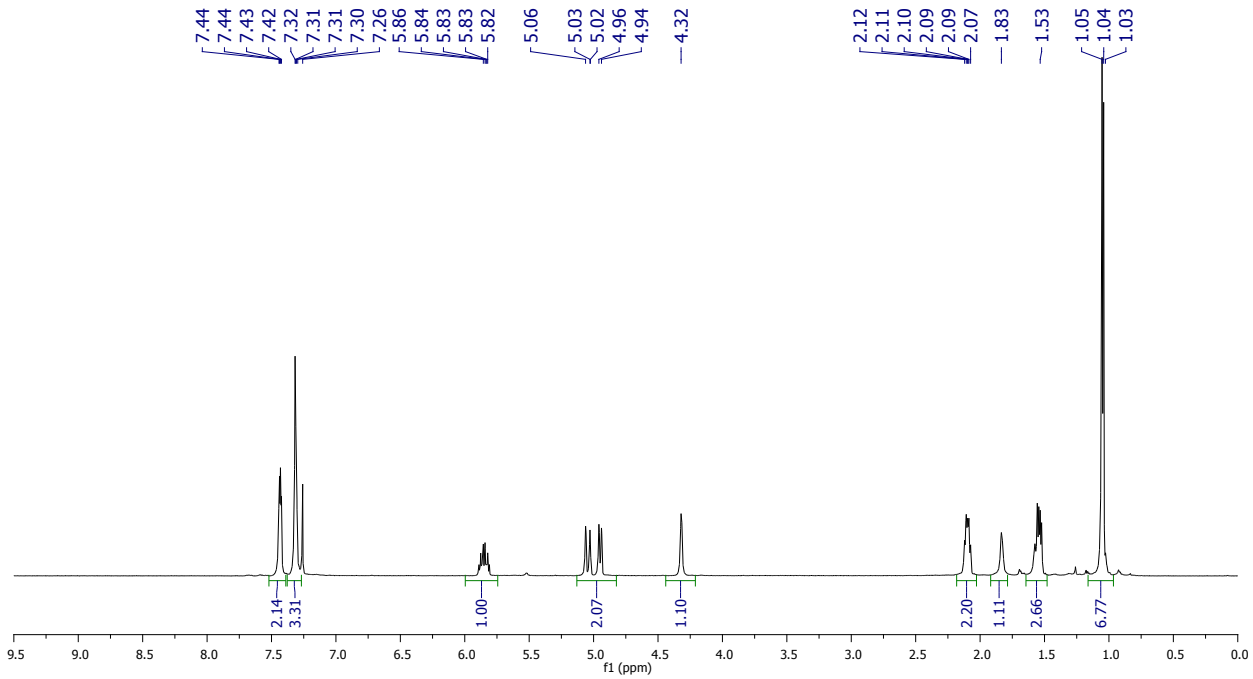
f1 (ppm)


OH
Ph

3g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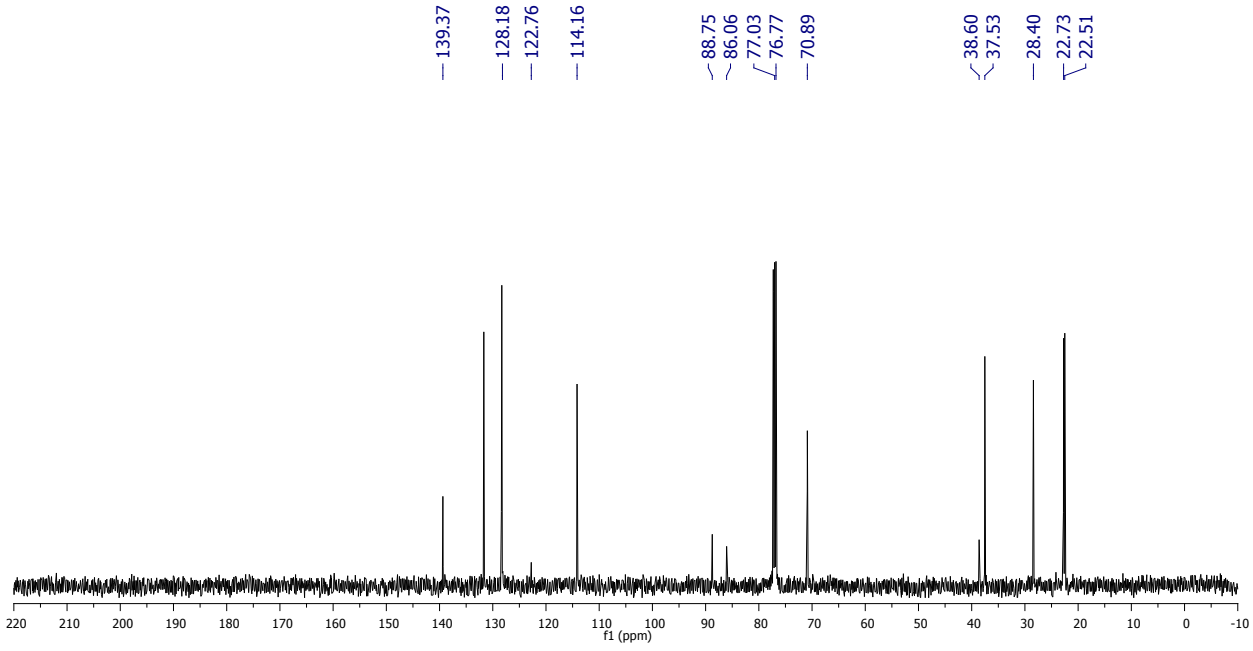
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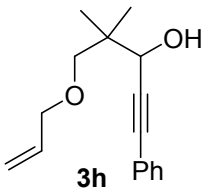
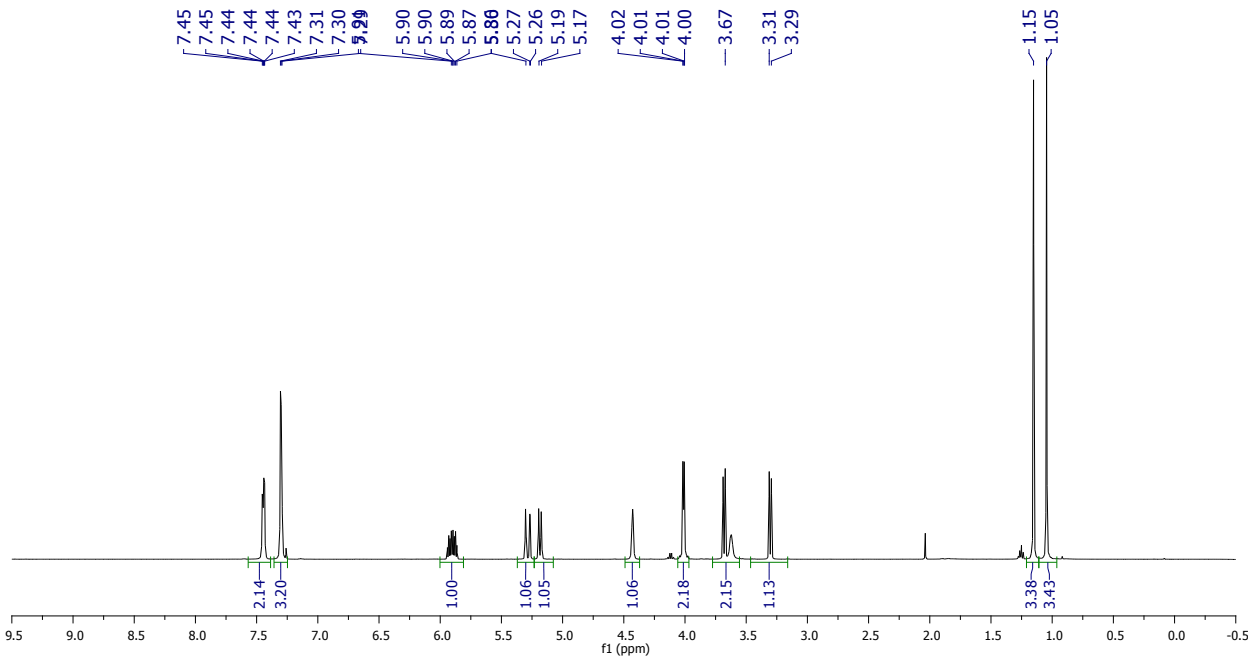
f1 (ppm)


OH
O
Ph

3h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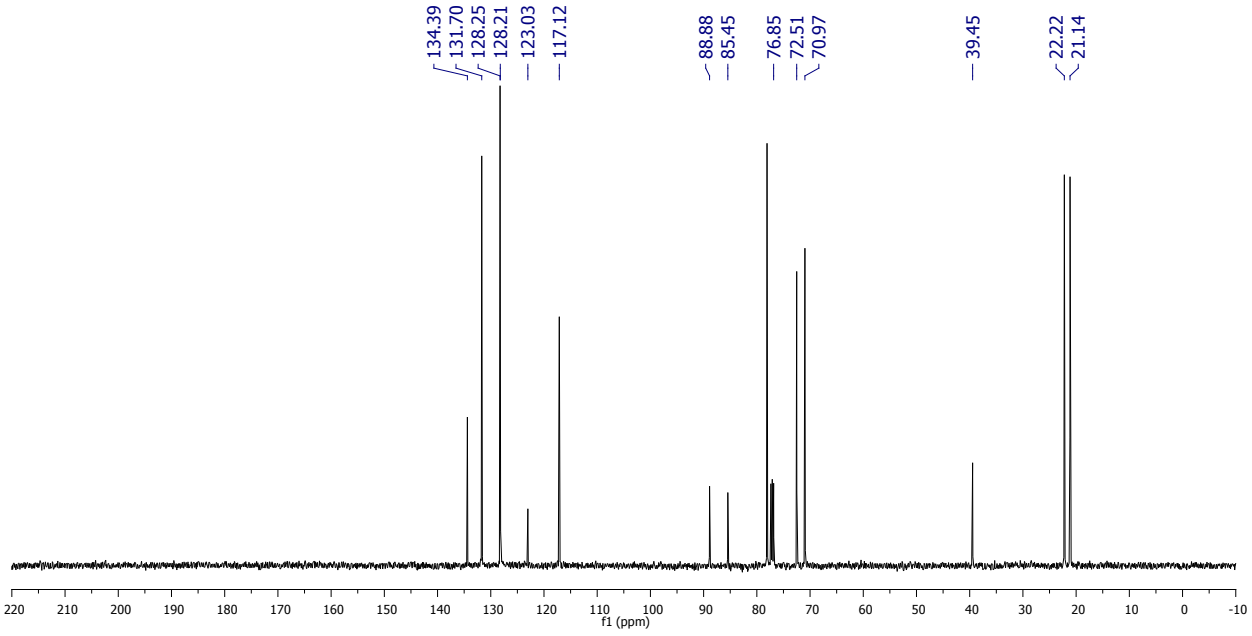
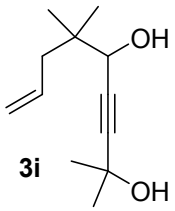
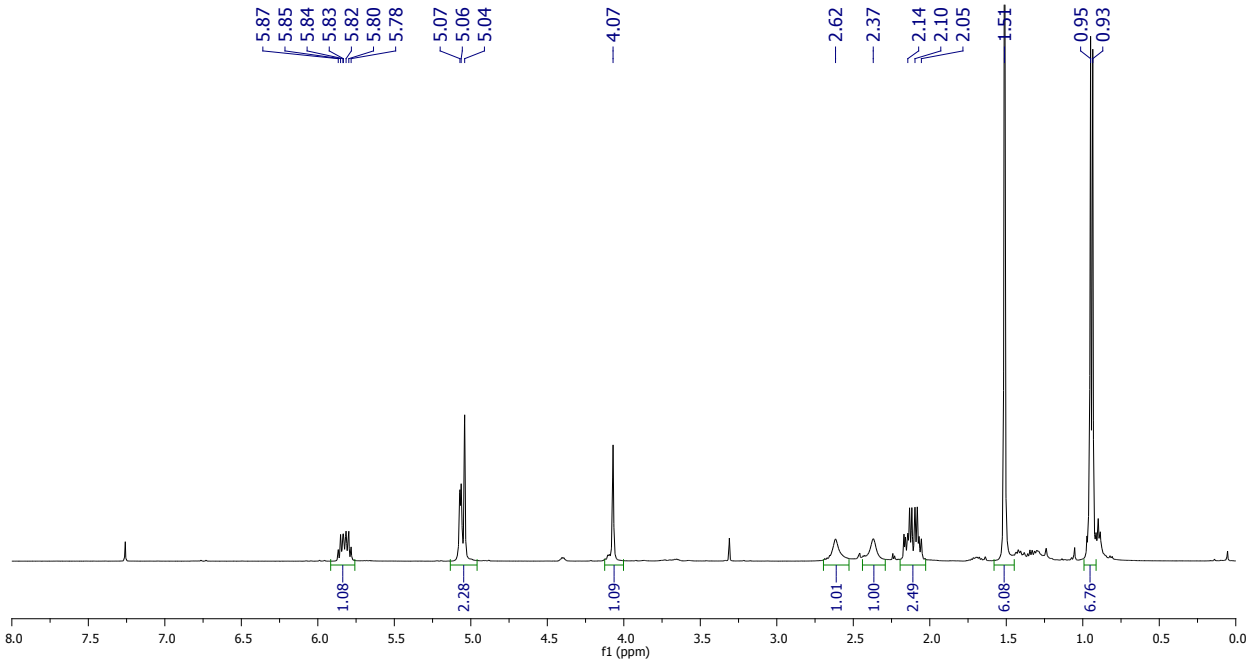
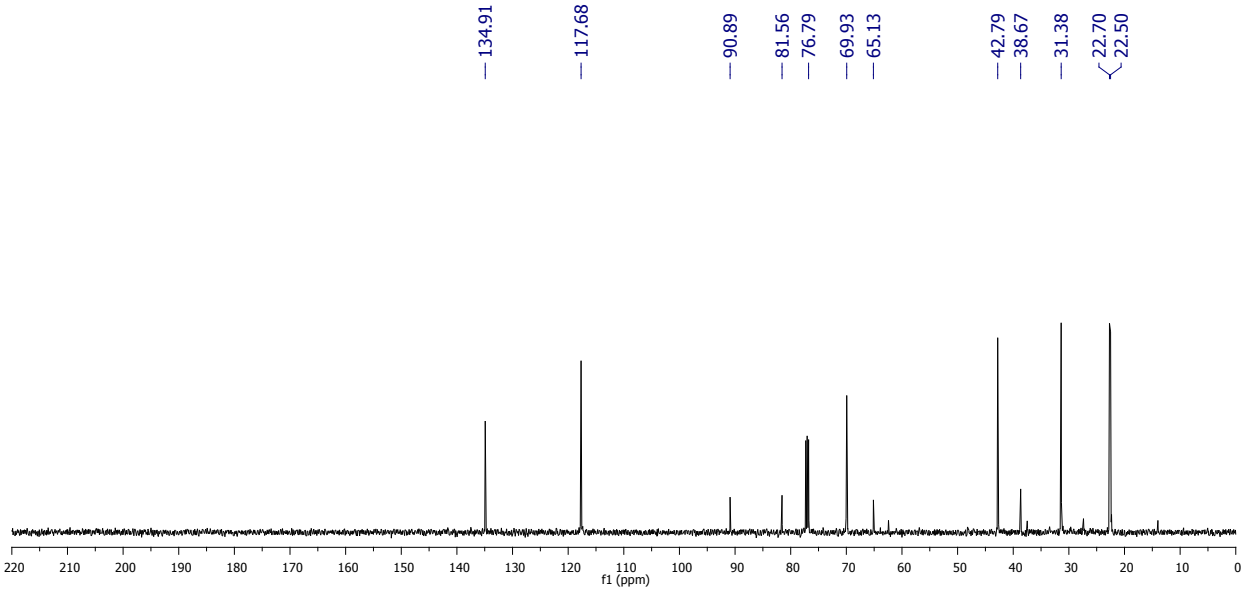
1.13
3.38
3.43
f1 (ppm)

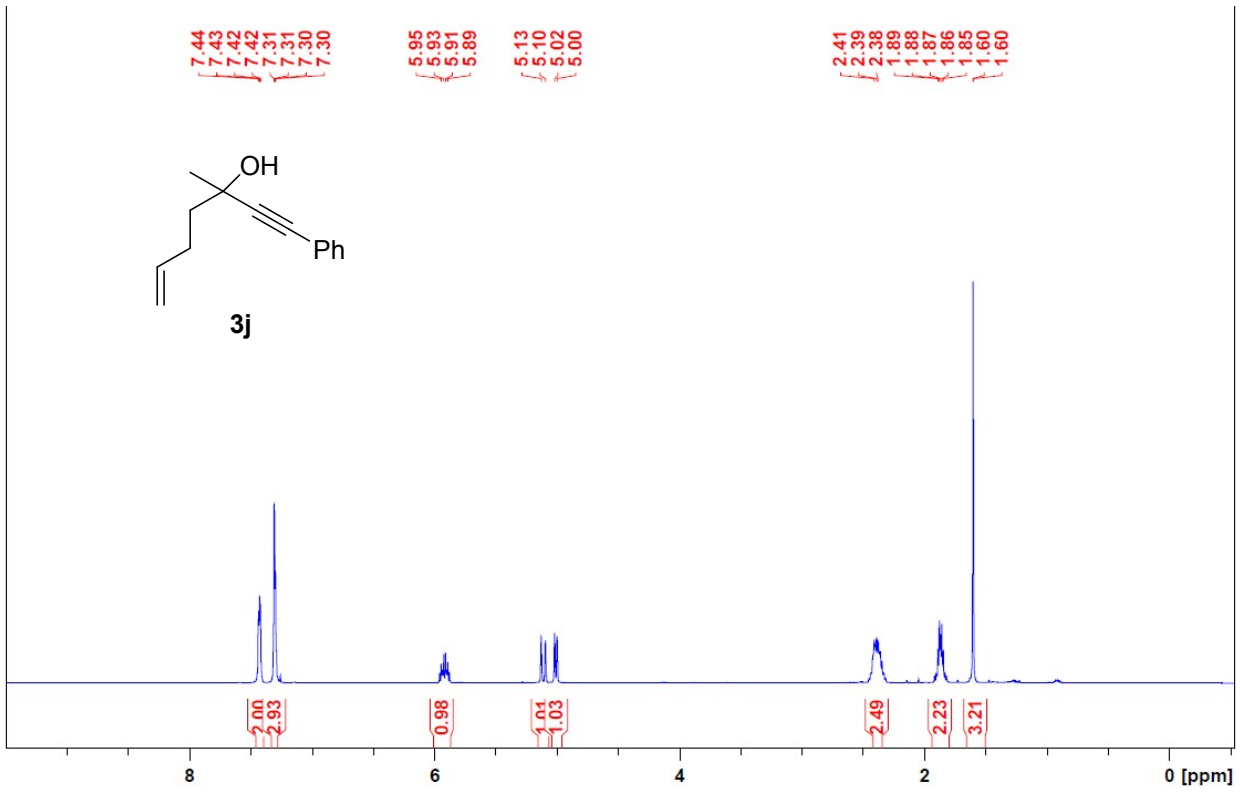

134.39
131.70
128.25
128.21
123.03
117.12
88.88
85.45
76.85
72.51
70.97
39.45
22.22
21.14
f1 (ppm)


OH
OH

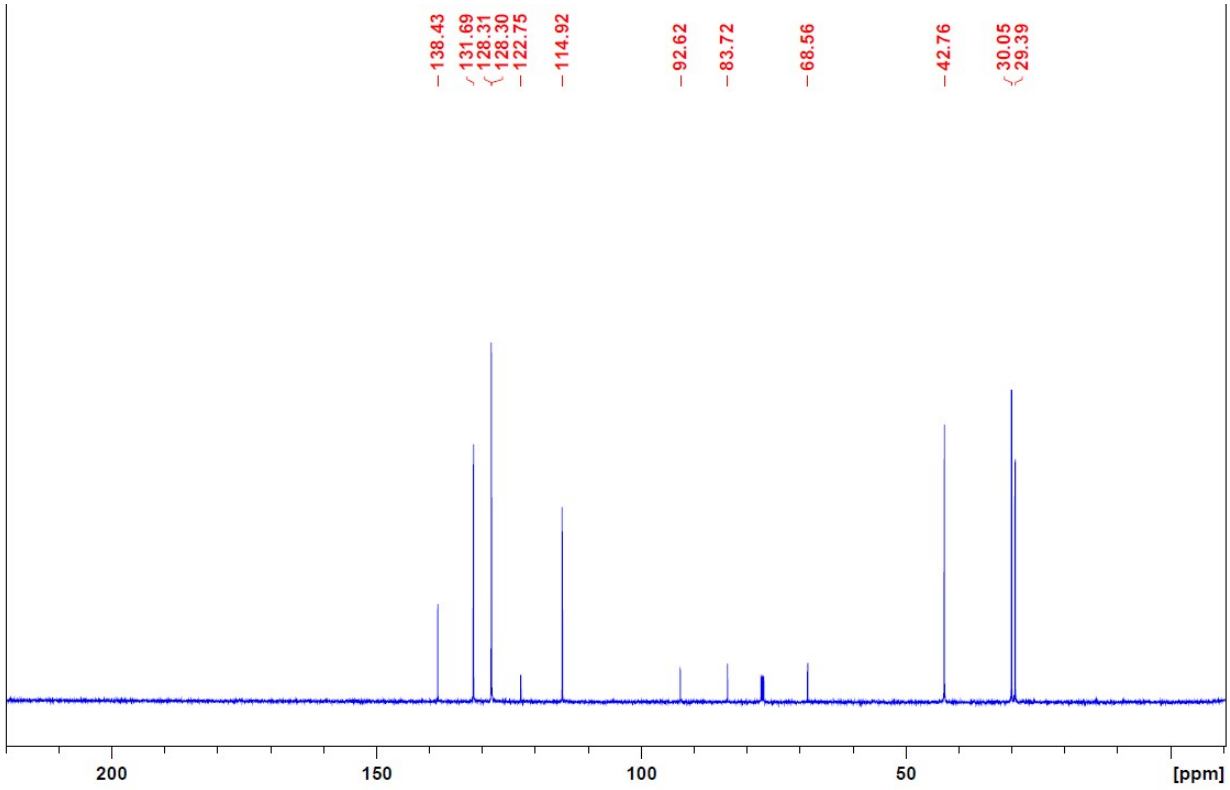
3i

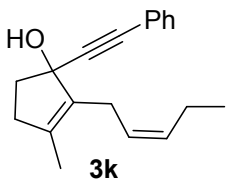

5.87
5.85
5.84
5.83
5.82
5.80
5.78
5.07
5.06
5.04
4.07
2.62
2.37
2.14
2.10
2.05
1.51
0.95
0.93
1.08
2.28
1.09
1.01
1.00
2.49
6.08
6.76
f1 (ppm)


134.91
117.68
90.89
81.56
76.79
69.93
65.13
42.79
38.67
31.38
22.70
22.50
f1 (ppm)

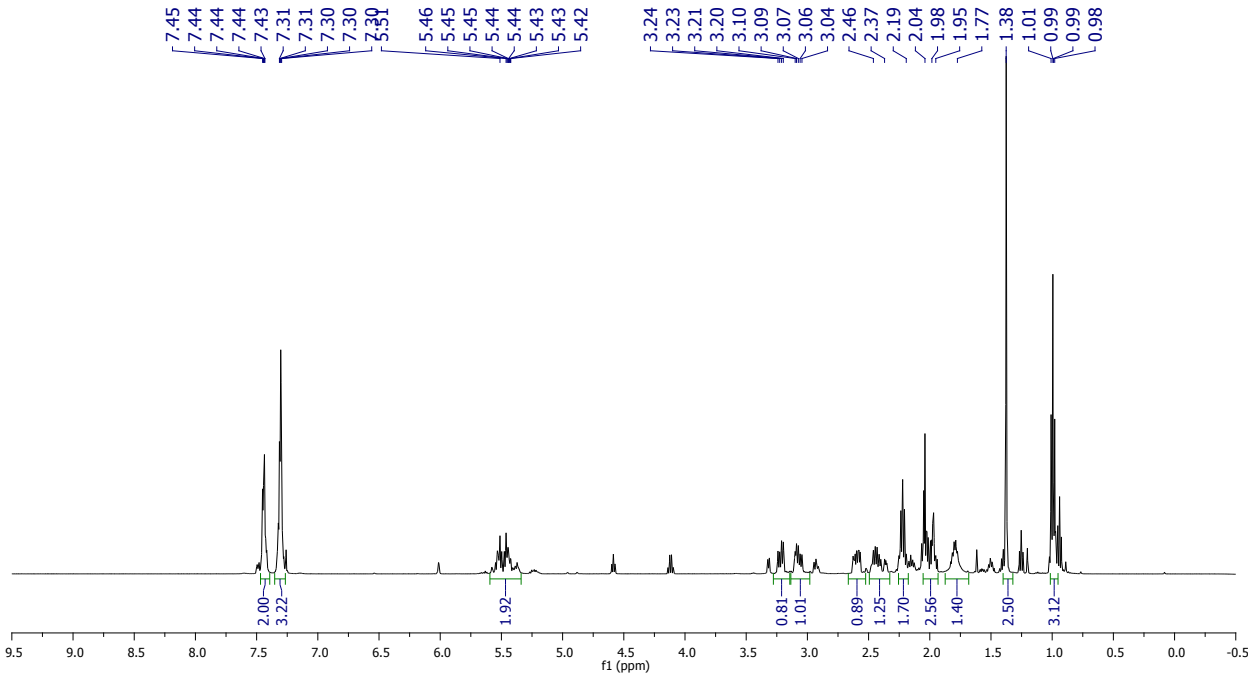

7.44
7.43
7.42
7.42
7.31
7.31
7.30
7.30
5.95
5.93
5.91
5.89
5.13
5.10
5.02
5.00
2.41
2.39
2.38
1.89
1.88
1.87
1.86
1.85
1.60
1.60
OH
Ph
2.00
2.93
0.98
1.01
1.03
2.49
2.23
3.21
8
6
4
2
0 [ppm]

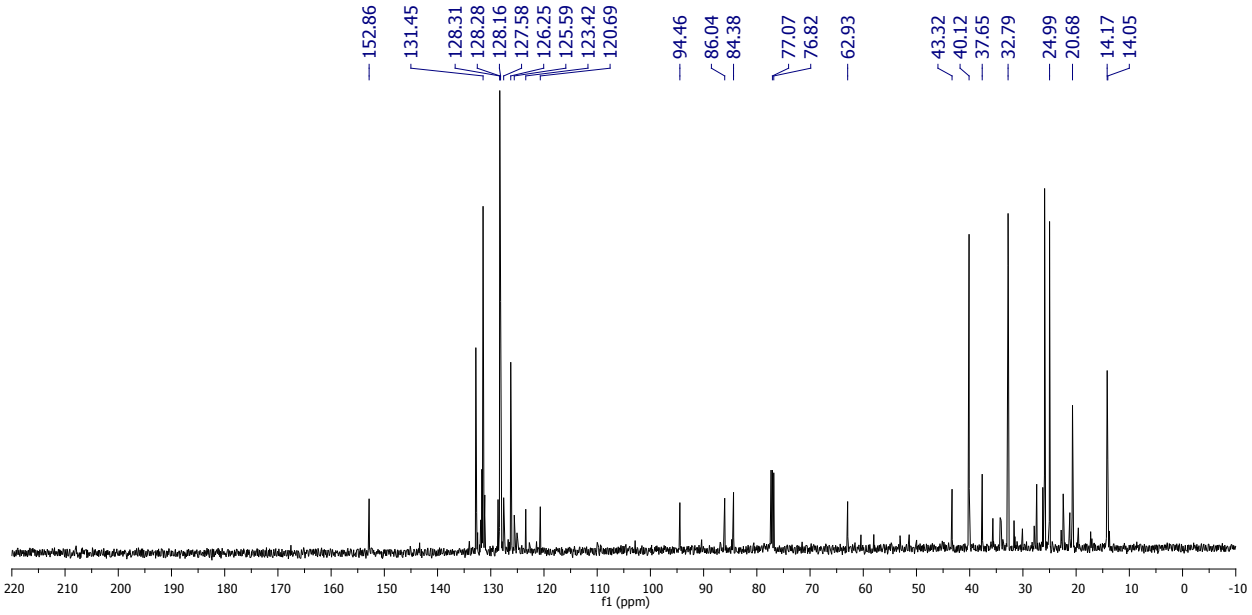
3j

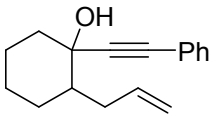

138.43
131.69
128.31
128.30
122.75
114.92
92.62
83.72
68.56
42.76
30.05
29.39
200
150
100
50
[ppm]


HO
Ph

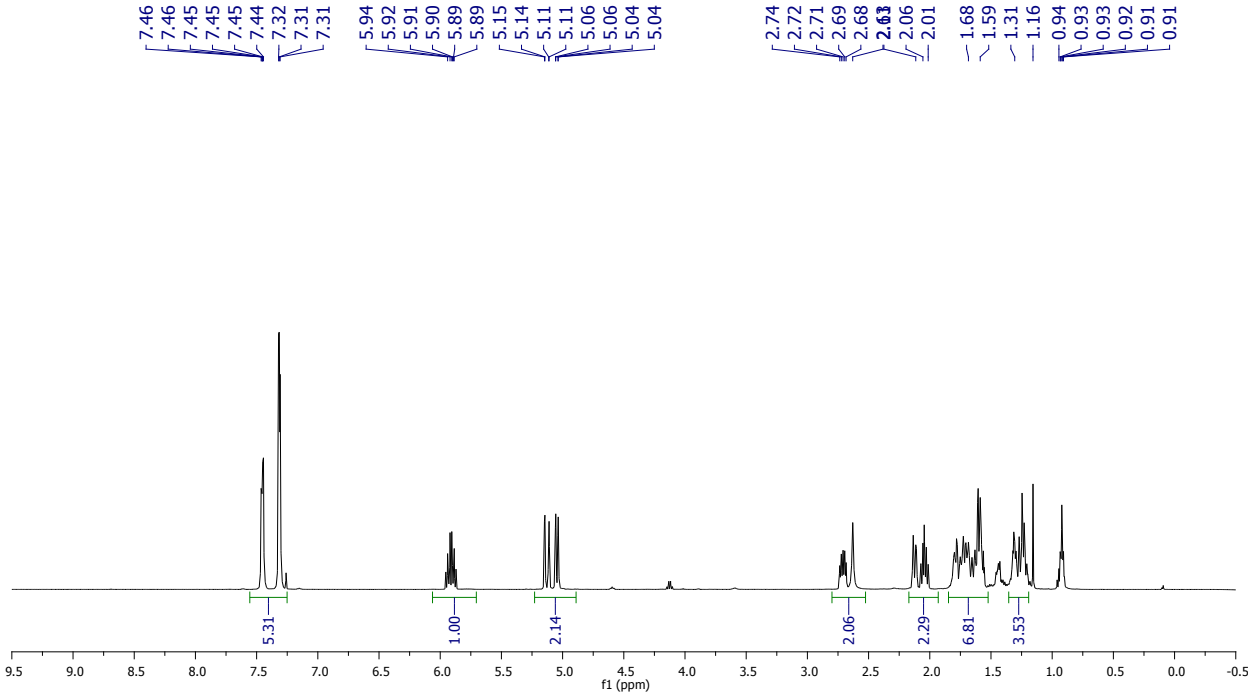
3k

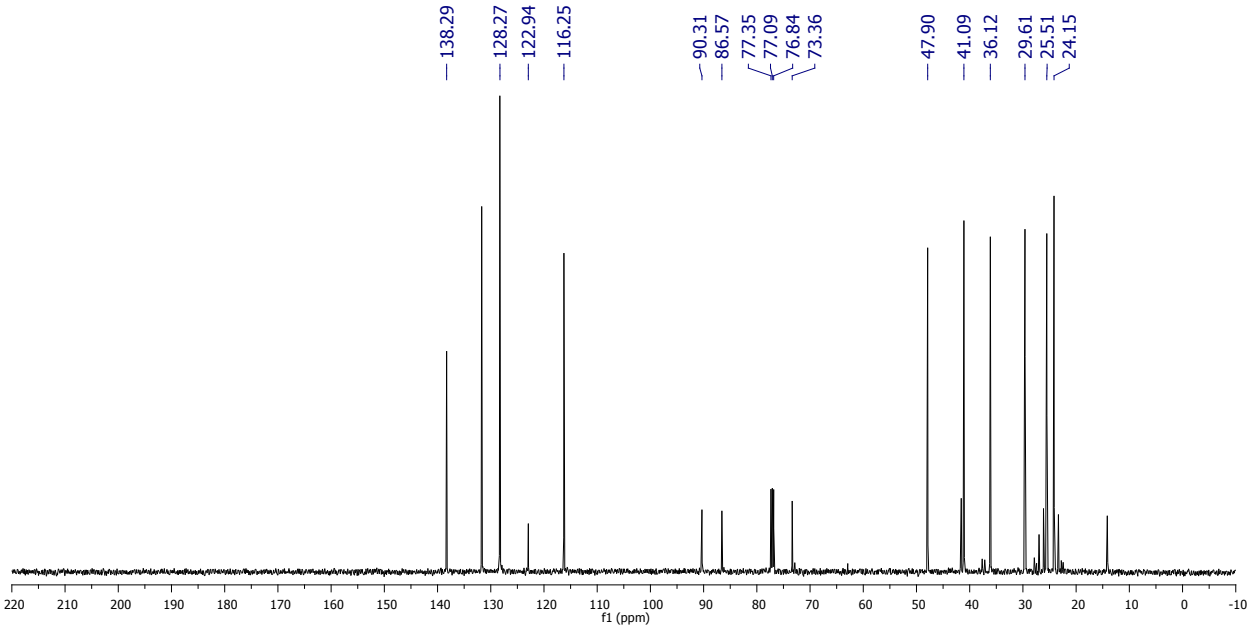

7.45 7.44 7.44 7.44 7.43 7.31 7.31 7.30 7.30 7.30 7.31 5.46 5.45 5.45 5.44 5.44 5.43 5.43 5.42
3.24 3.23 3.21 3.20 3.10 3.09 3.07 3.06 3.04 2.46 2.37 2.19 2.04 1.98 1.95 1.77 1.38 1.01 0.99 0.99 0.98
2.00 3.22 1.92 0.81 1.01 0.89 1.25 1.70 2.56 1.40 2.50 3.12
f1 (ppm)

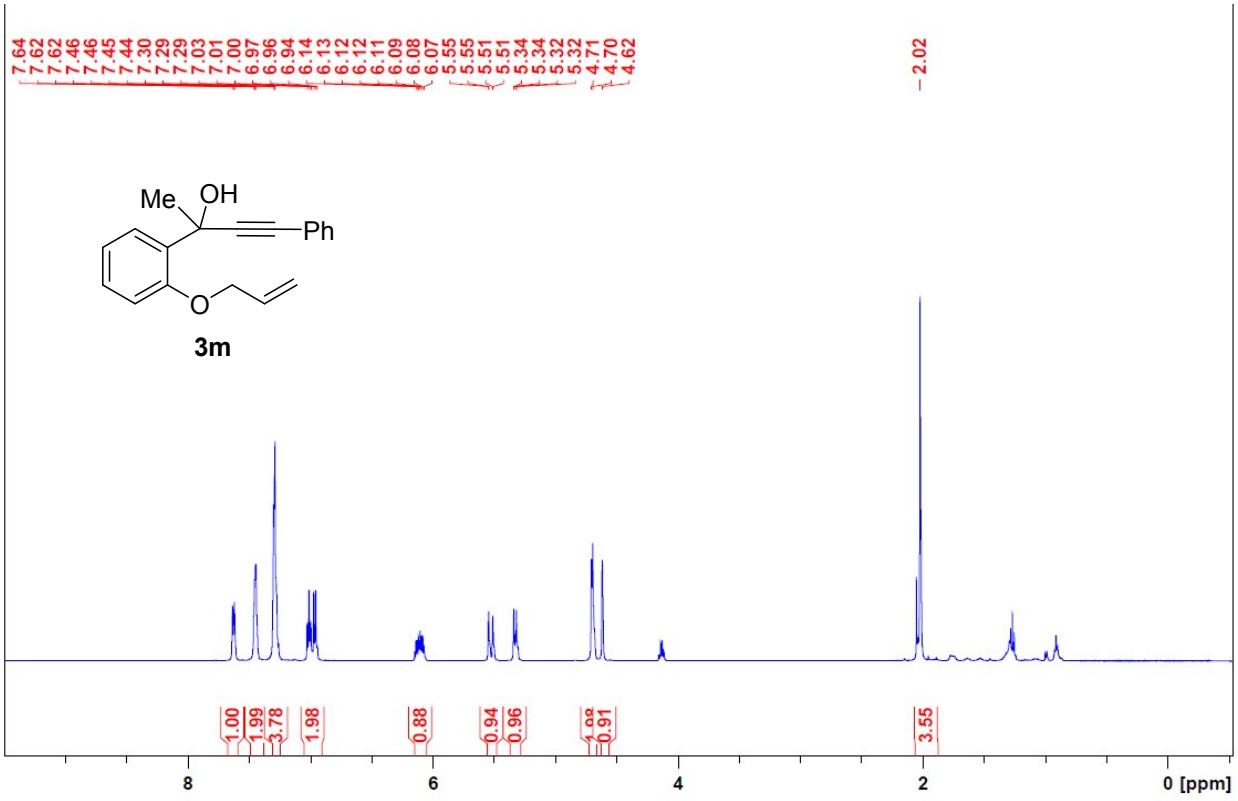

152.86 131.45 128.31 128.28 128.16 127.58 126.25 125.59 123.42 120.69
94.46 86.04 84.38 77.07 76.82 62.93 43.32 40.12 37.65 32.79 24.99 20.68 14.17 14.05
f1 (ppm)

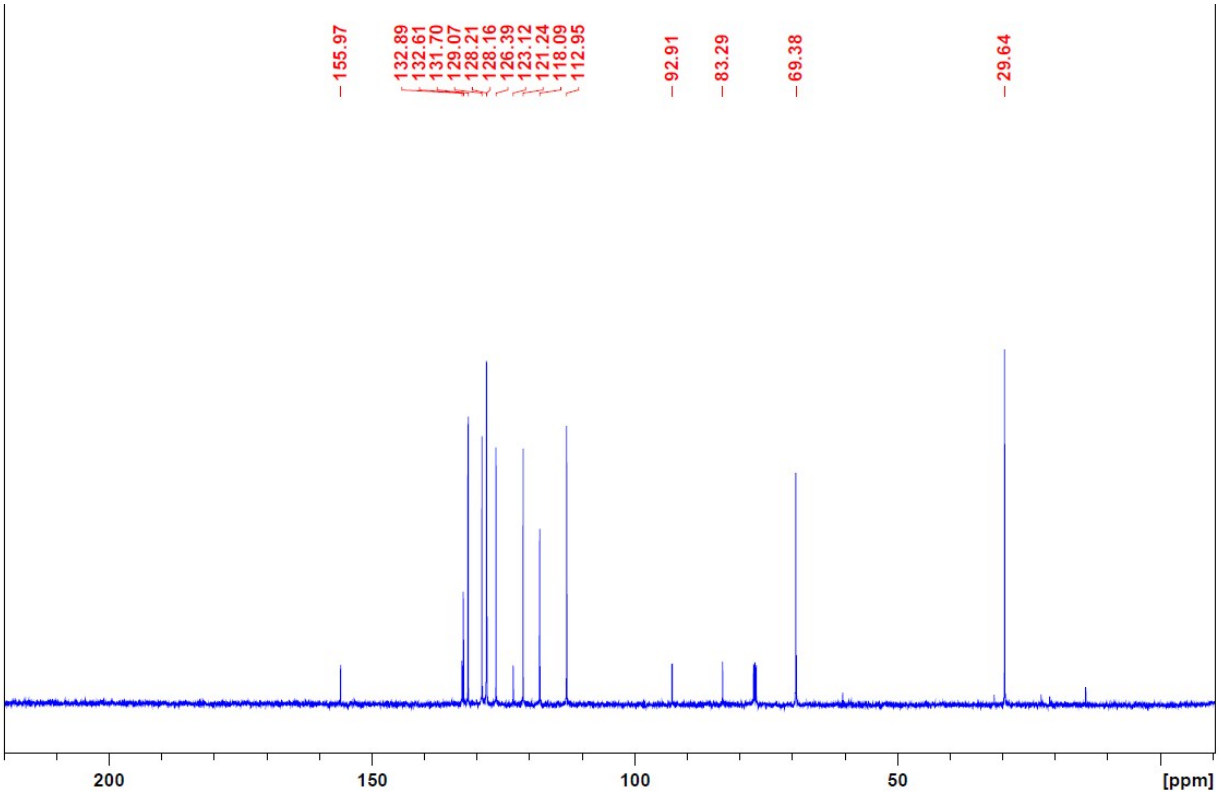

OH
Ph

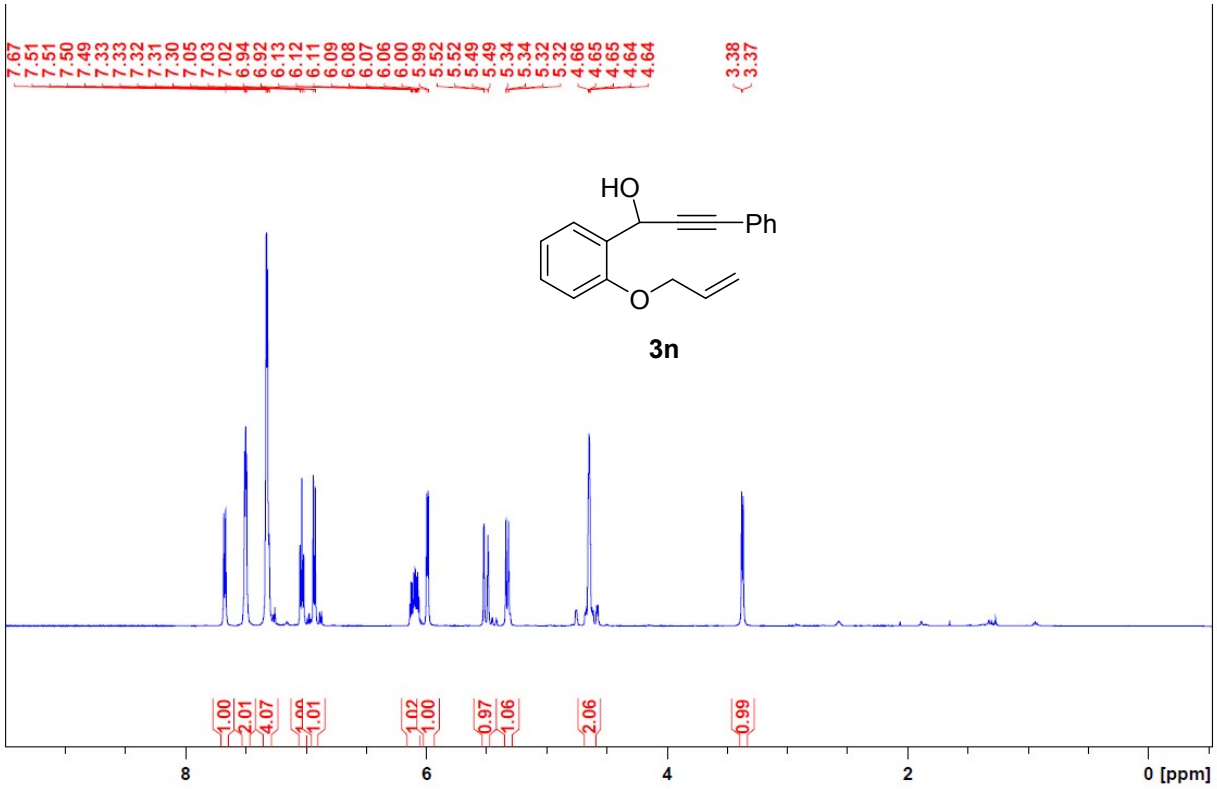
3l


7.46
7.46
7.45
7.45
7.45
7.44
7.32
7.31
7.31
5.94
5.92
5.91
5.90
5.89
5.89
5.15
5.14
5.11
5.11
5.06
5.06
5.04
5.04
2.74
2.72
2.71
2.69
2.68
2.06
2.01
1.68
1.59
1.31
1.16
0.94
0.93
0.93
0.92
0.91
0.91
5.31
1.00
2.14
2.06
2.29
6.81
3.53
f1 (ppm)

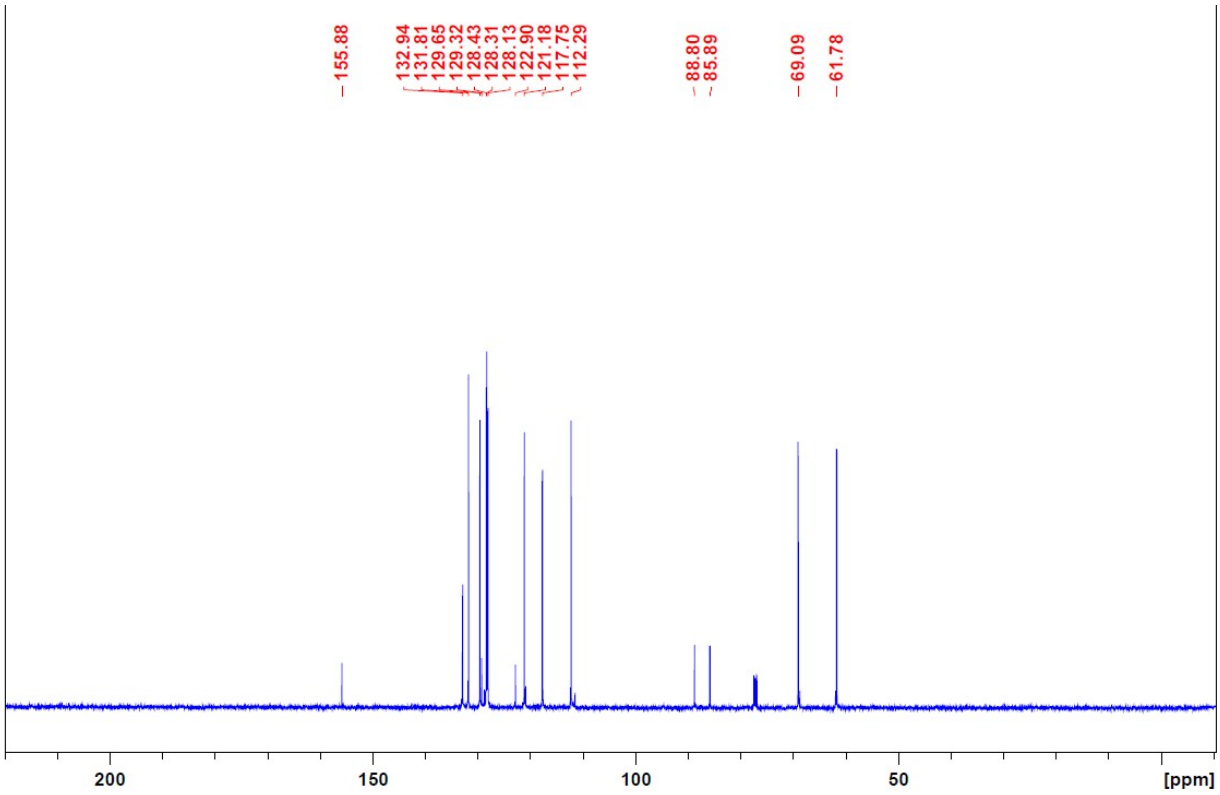

138.29
128.27
122.94
116.25
90.31
86.57
77.35
77.09
76.84
73.36
47.90
41.09
36.12
29.61
25.51
24.15
f1 (ppm)

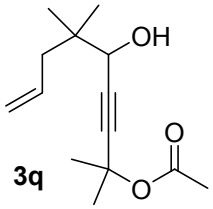

7.64
7.62
7.62
7.46
7.46
7.45
7.44
7.30
7.29
7.29
7.03
7.01
7.00
6.97
6.96
6.94
6.14
6.13
6.12
6.12
6.11
6.09
6.08
6.07
5.55
5.55
5.51
5.51
5.34
5.34
5.32
5.32
4.71
4.70
4.62
2.02
Me
OH
Ph
O
3m
1.00
1.99
3.78
1.98
0.88
0.94
0.96
0.91
3.55
8
6
4
2
0 [ppm]


155.97
132.89
132.61
131.70
129.07
128.21
128.16
126.39
123.12
121.24
118.09
112.95
92.91
83.29
69.38
29.64
200
150
100
50
[ppm]

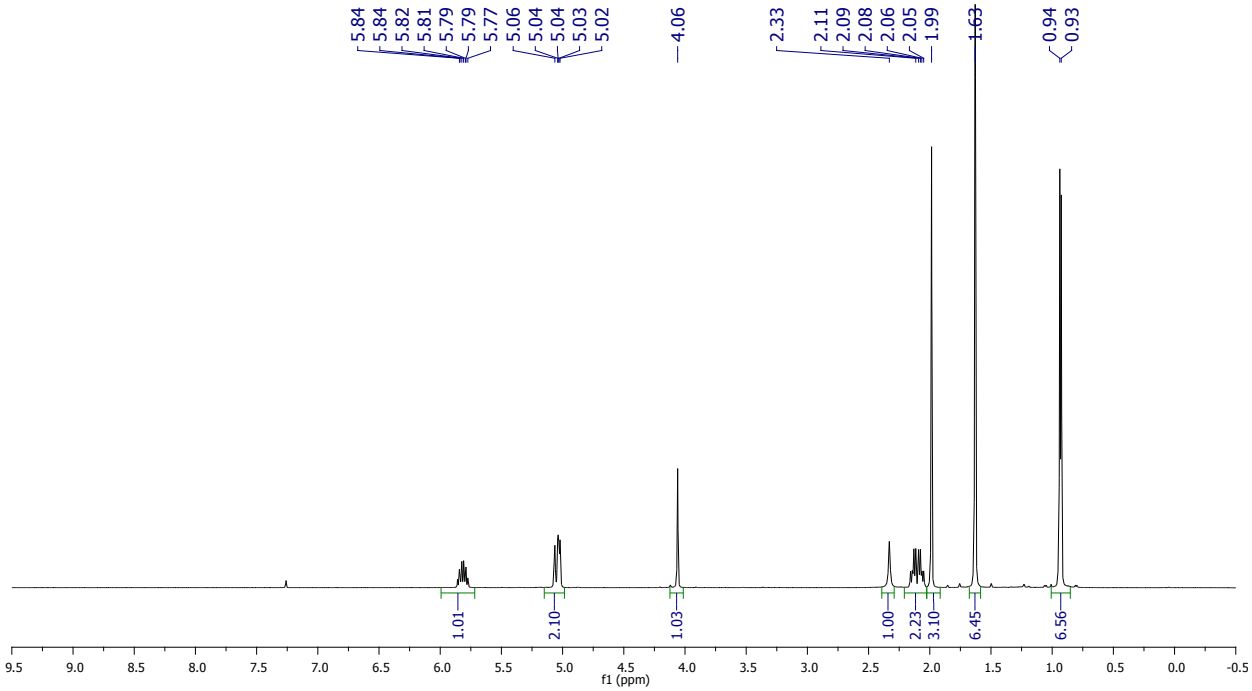

7.67
7.51
7.51
7.50
7.49
7.33
7.32
7.31
7.30
7.05
7.03
7.02
6.94
6.92
6.13
6.12
6.11
6.09
6.08
6.07
6.06
6.00
5.99
5.52
5.52
5.49
5.49
5.34
5.34
5.32
5.32
4.66
4.65
4.65
4.64
4.64
3.38
3.37
HO
Ph
O
1.00
2.01
4.07
1.00
1.01
1.02
1.00
0.97
1.06
2.06
0.99
8
6
4
2
0 [ppm]

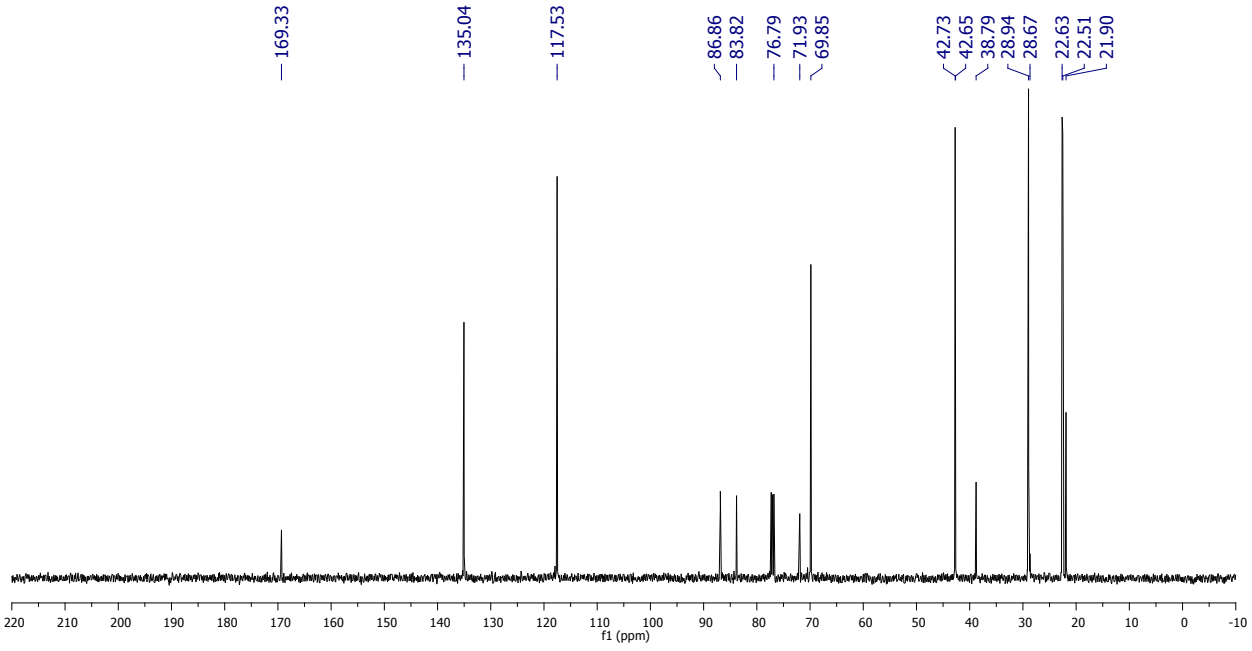
3n

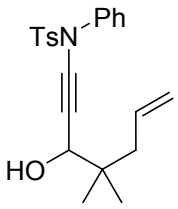

155.88
132.94
131.81
129.65
129.32
128.43
128.31
128.13
122.90
121.18
117.75
112.29
88.80
85.89
69.09
61.78
200
150
100
50
[ppm]


OH
O
O

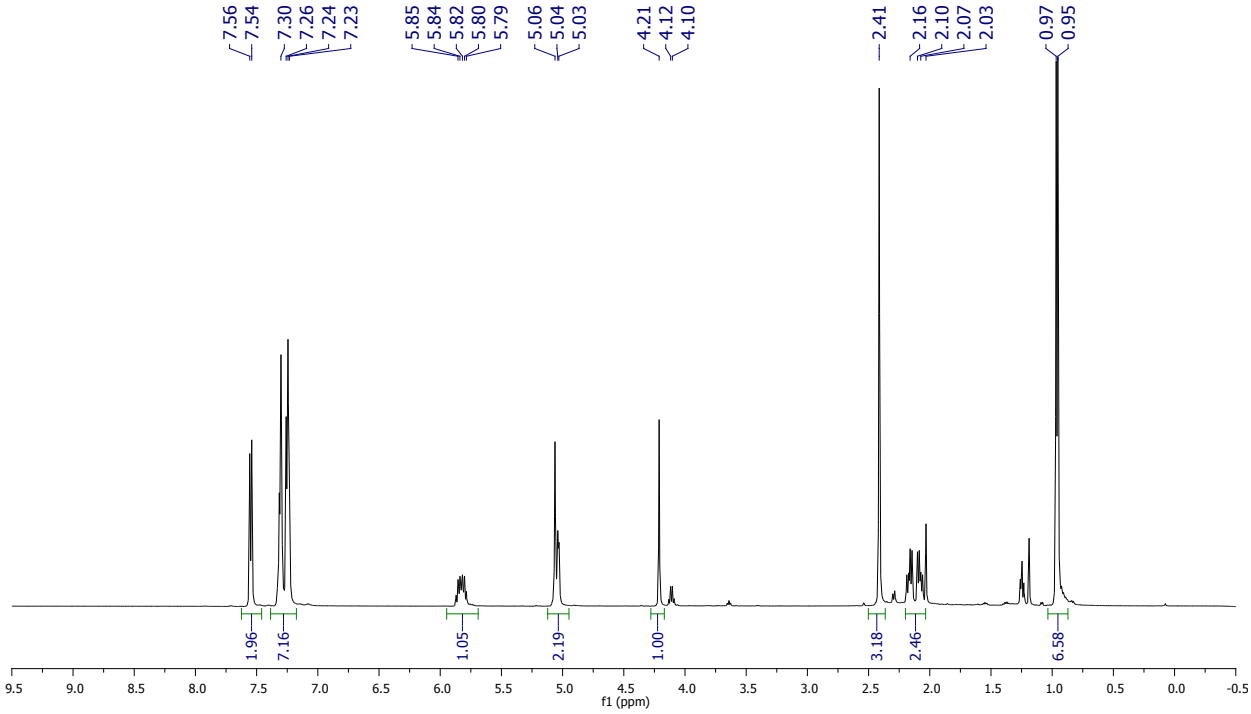
3q

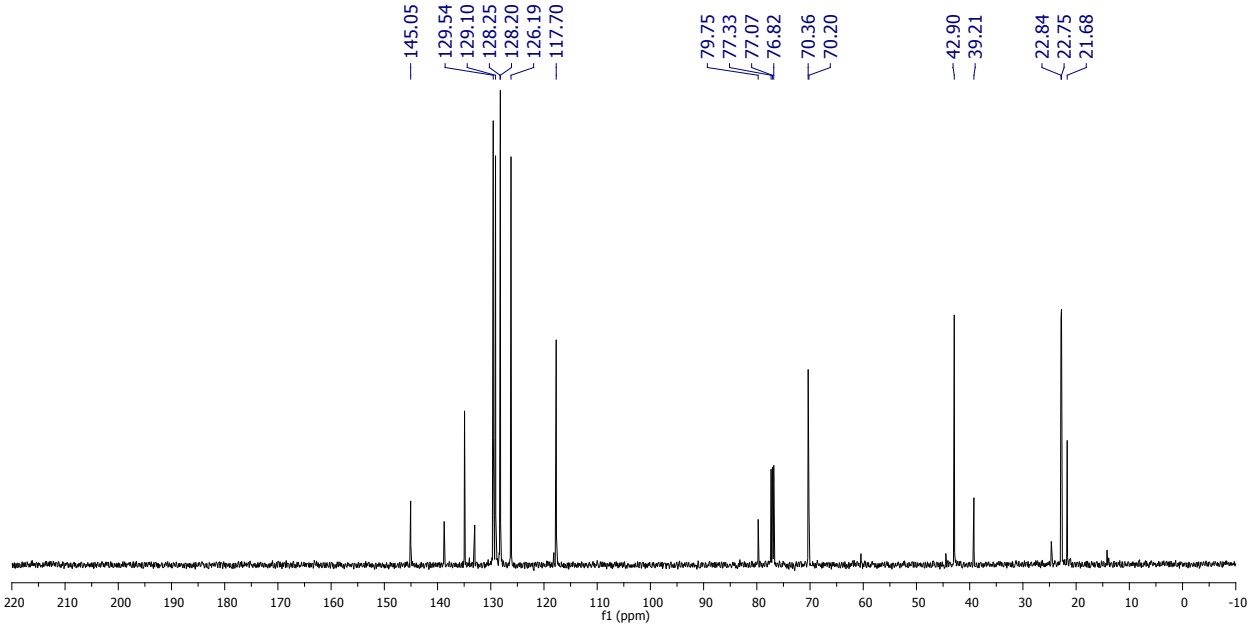

5.84
5.84
5.82
5.81
5.79
5.79
5.77
5.06
5.04
5.04
5.03
5.02
4.06
2.33
2.11
2.09
2.08
2.06
2.05
1.99
1.63
0.94
0.93
1.01
2.10
1.03
1.00
2.23
3.10
6.45
6.56
f1 (ppm)

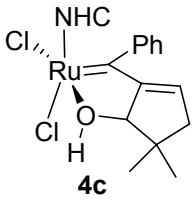

169.33
135.04
117.53
86.86
83.82
76.79
71.93
69.85
42.73
42.65
38.79
28.94
28.67
22.63
22.51
21.90
f1 (ppm)


TsN
Ph
HO

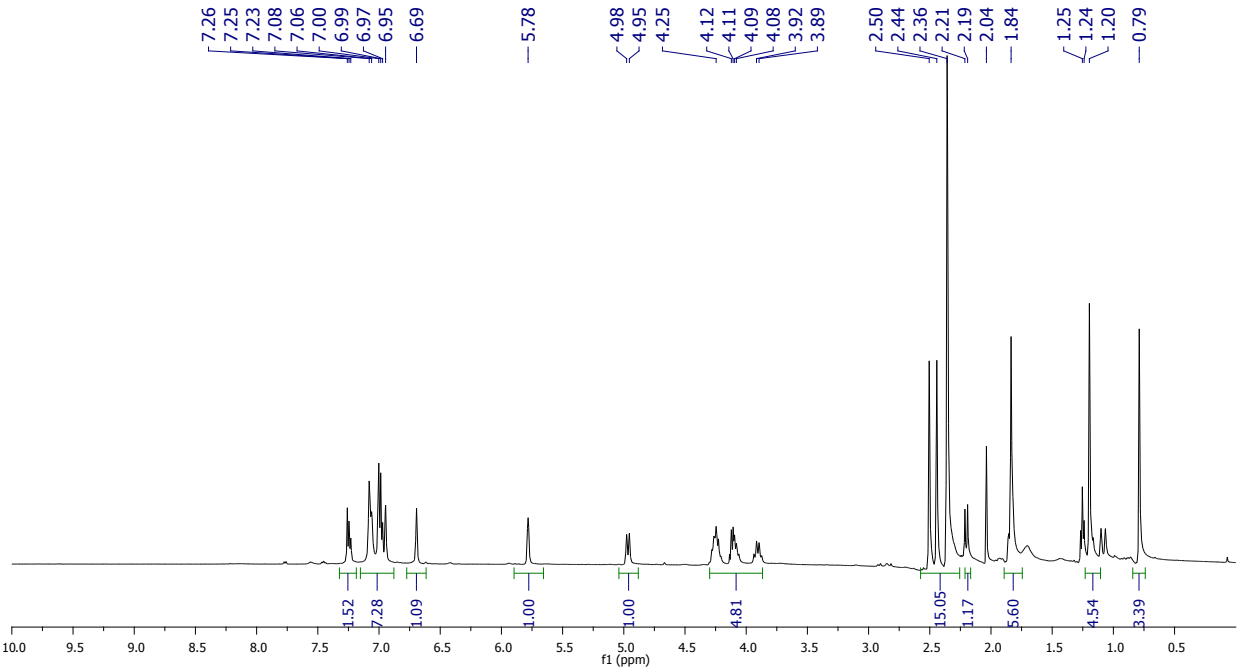
3r

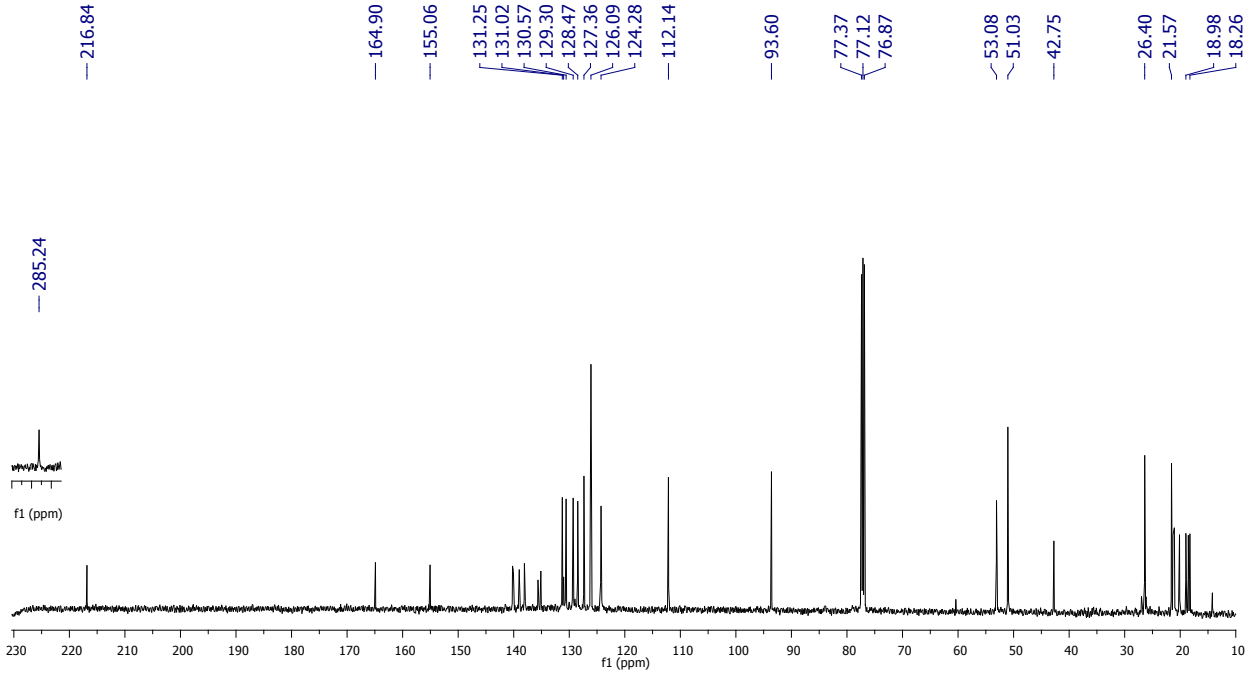

7.56
7.54
7.30
7.26
7.24
7.23
5.85
5.84
5.82
5.80
5.79
5.06
5.04
5.03
4.21
4.12
4.10
2.41
2.16
2.10
2.07
2.03
0.97
0.95
1.96
7.16
1.05
2.19
1.00
3.18
2.46
6.58
f1 (ppm)

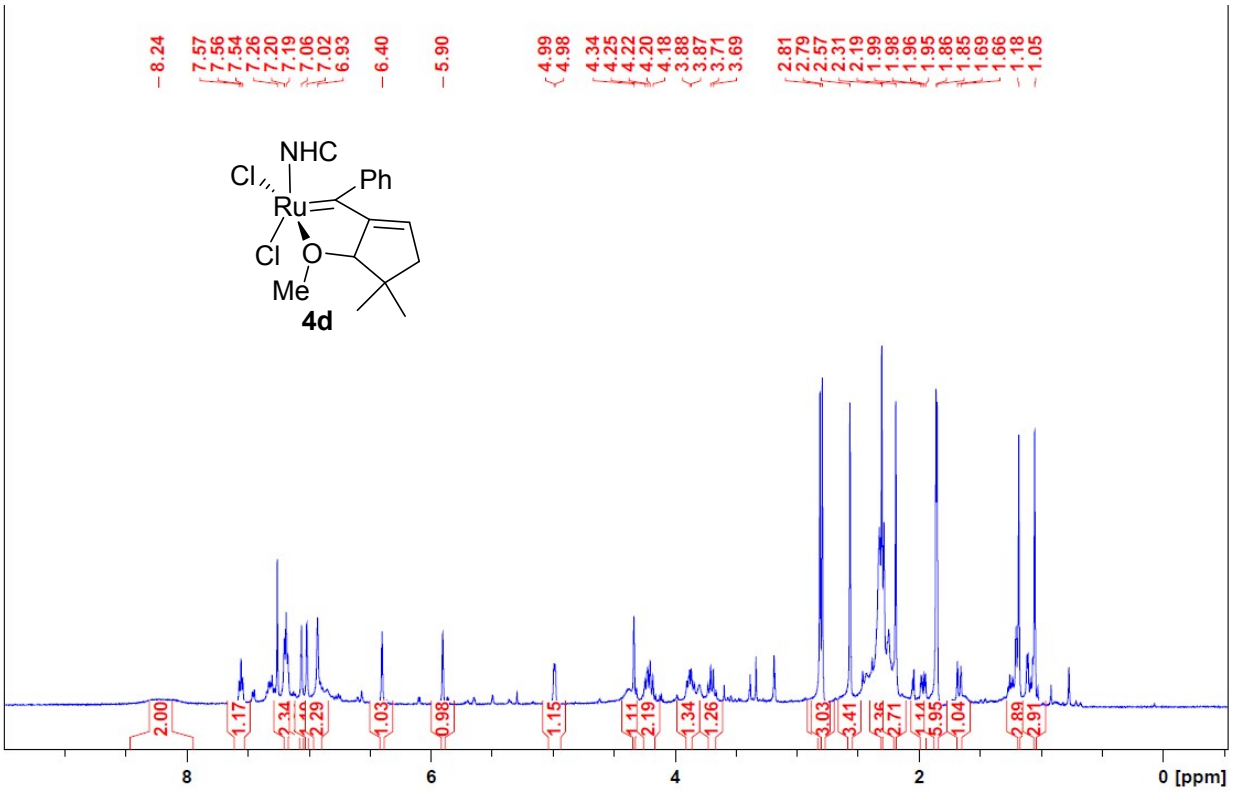

145.05
129.54
129.10
128.25
128.20
126.19
117.70
79.75
77.33
77.07
76.82
70.36
70.20
42.90
39.21
22.84
22.75
21.68
f1 (ppm)

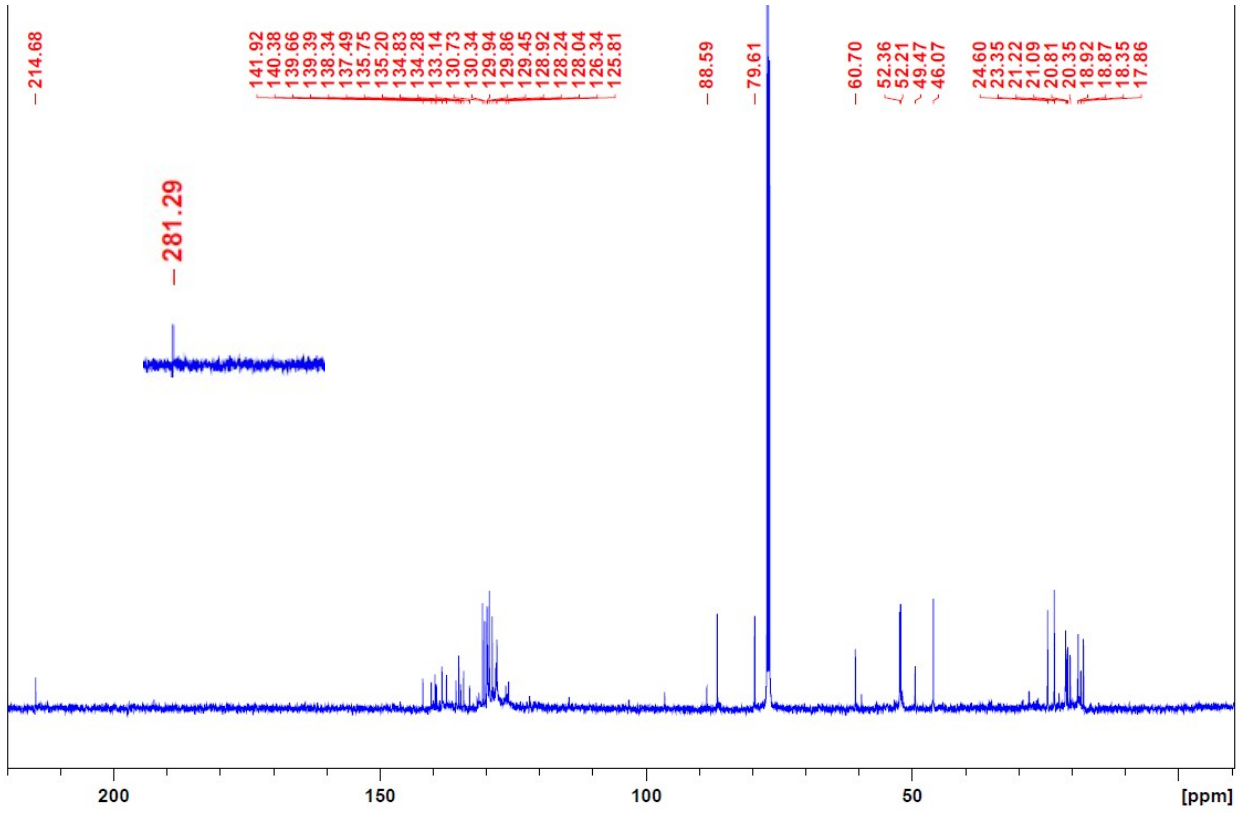

NHC
Cl
Ph
Ru
Cl
O
H

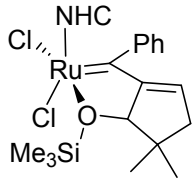
4c


7.26
7.25
7.23
7.08
7.06
7.00
6.99
6.97
6.95
6.69
5.78
4.98
4.95
4.25
4.12
4.11
4.09
4.08
3.92
3.89
2.50
2.44
2.36
2.21
2.19
2.04
1.84
1.25
1.24
1.20
0.79
1.52
7.28
1.09
1.00
1.00
4.81
15.05
1.17
5.60
4.54
3.39
f1 (ppm)

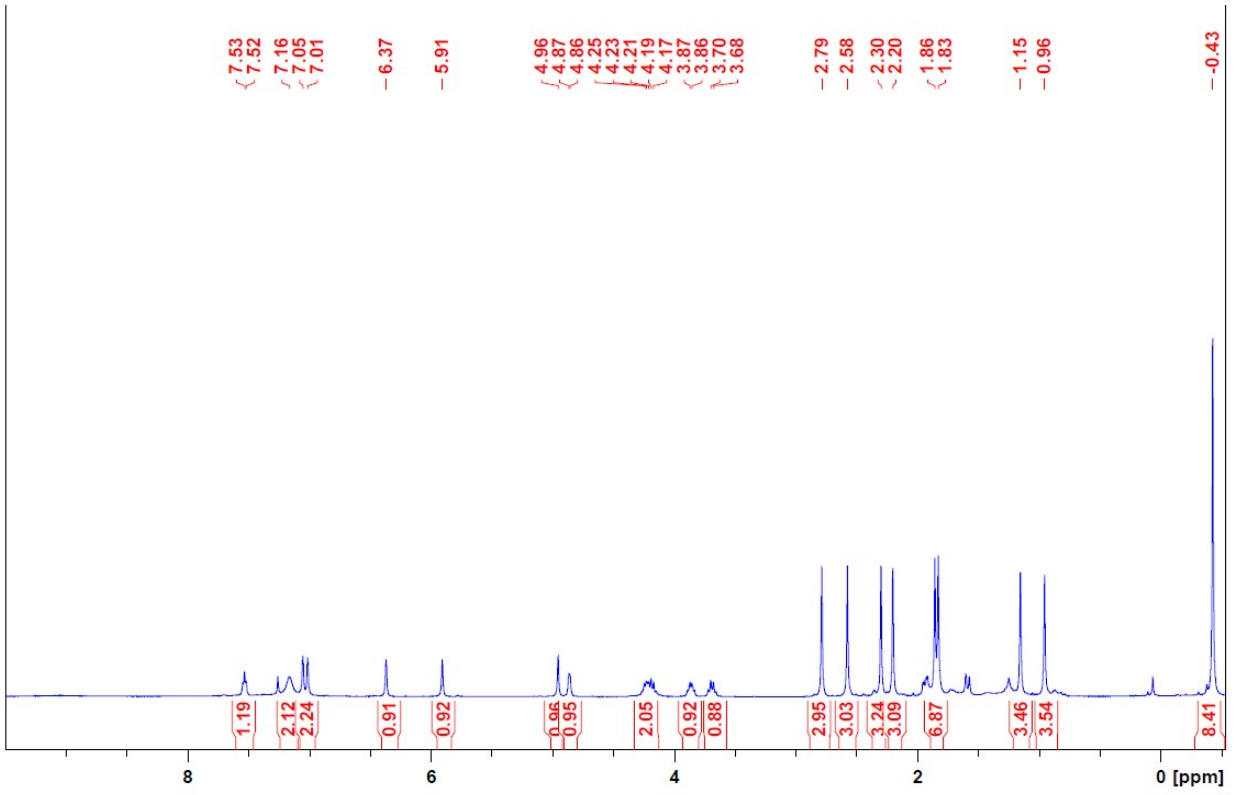

216.84
164.90
155.06
131.25
131.02
130.57
129.30
128.47
127.36
126.09
124.28
112.14
93.60
77.37
77.12
76.87
53.08
51.03
42.75
26.40
21.57
18.98
18.26
285.24
f1 (ppm)
f1 (ppm)

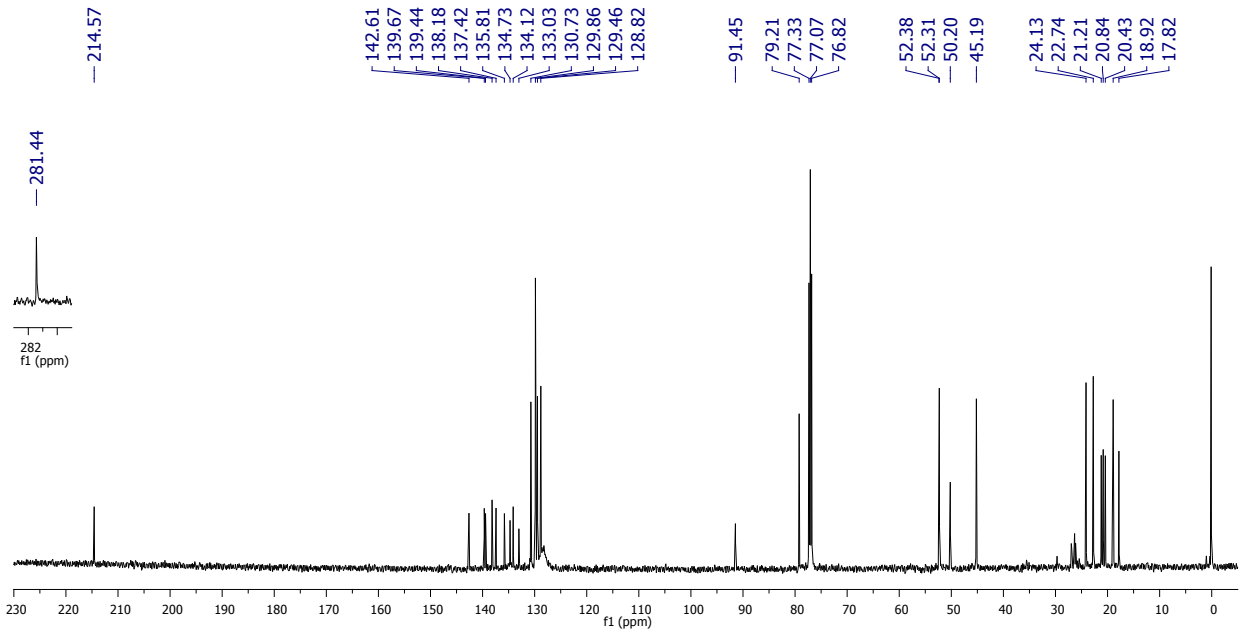

8.24
7.57
7.56
7.54
7.26
7.20
7.19
7.06
7.02
6.93
6.40
5.90
4.99
4.98
4.34
4.25
4.22
4.20
4.18
3.88
3.87
3.71
3.69
2.81
2.79
2.57
2.31
2.19
1.99
1.98
1.96
1.95
1.86
1.85
1.69
1.66
1.18
1.05
NHC
Cl
Ph
Ru
Cl
O
Me
4d
2.00
1.17
2.34
2.29
1.03
0.98
1.15
1.11
2.19
1.34
1.26
3.03
3.41
2.36
2.71
1.14
5.95
1.04
2.89
2.91
8
6
4
2
0 [ppm]

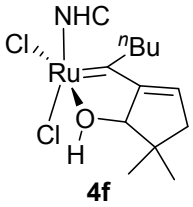

214.68
141.92
140.38
139.66
139.39
138.34
137.49
135.75
135.20
134.83
134.28
133.14
130.73
130.34
129.94
129.86
129.45
128.92
128.24
128.04
126.34
125.81
88.59
79.61
60.70
52.36
52.21
49.47
46.07
24.60
23.35
21.22
21.09
20.81
20.35
18.92
18.87
18.35
17.86
281.29
200
150
100
50
[ppm]


NHC
Cl
Ph
Ru
Cl
O
Me3Si

4e

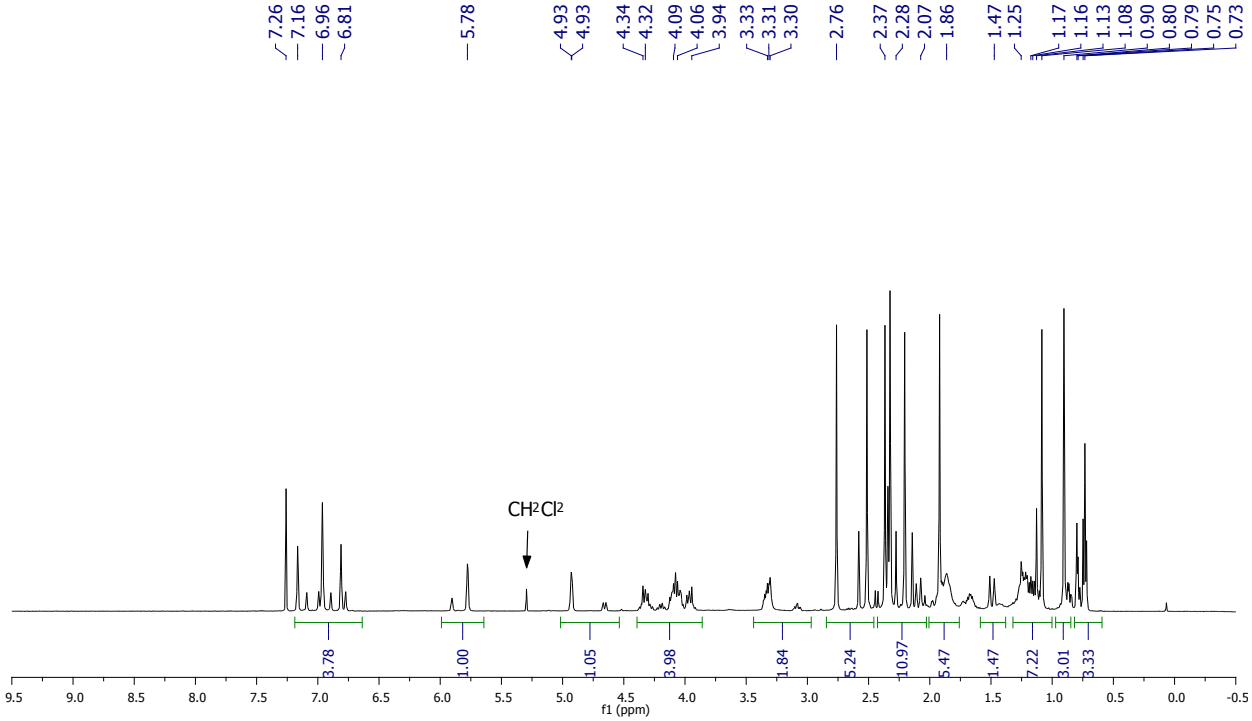

7.53
7.52
7.16
7.05
7.01
6.37
5.91
4.96
4.87
4.86
4.25
4.23
4.21
4.19
4.17
3.87
3.86
3.70
3.68
2.79
2.58
2.30
2.20
1.86
1.83
1.15
0.96
-0.43
1.19
2.12
2.24
0.91
0.92
0.96
0.95
2.05
0.92
0.88
2.95
3.03
3.24
3.09
6.87
3.46
3.54
8.41
8
6
4
2
0 [ppm]

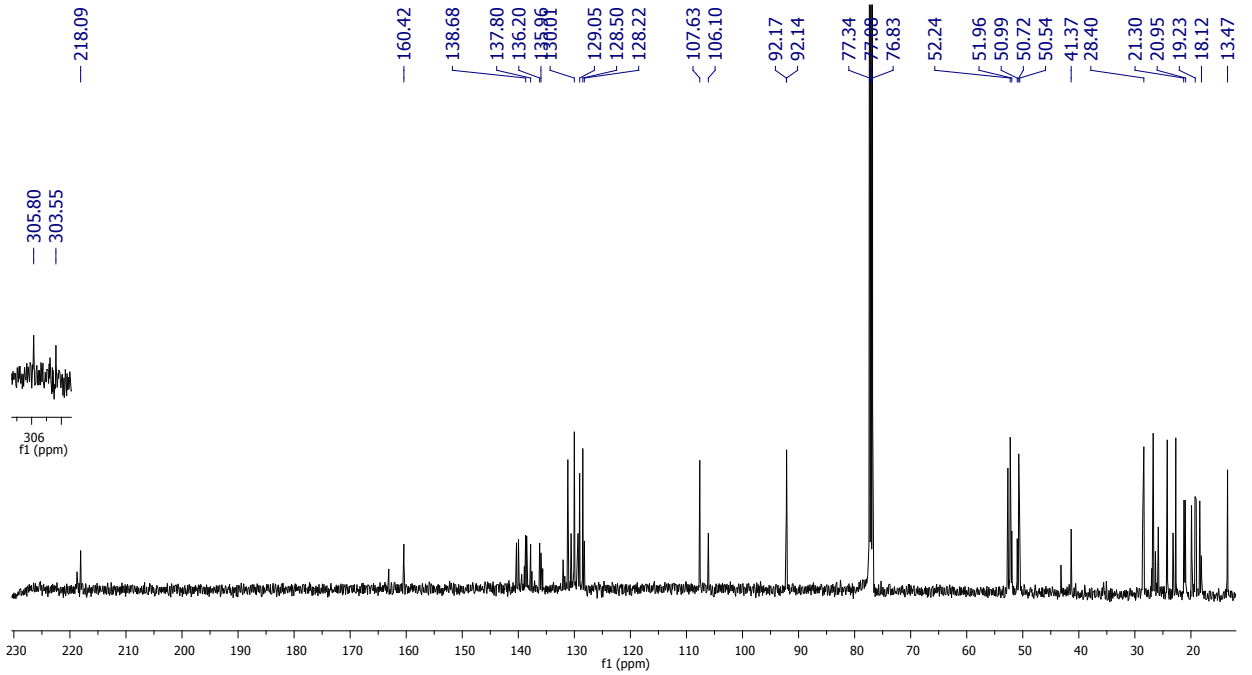

214.57
142.61
139.67
139.44
138.18
137.42
135.81
134.73
134.12
133.03
130.73
129.86
129.46
128.82
91.45
79.21
77.33
77.07
76.82
52.38
52.31
50.20
45.19
24.13
22.74
21.21
20.84
20.43
18.92
17.82
281.44
282
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

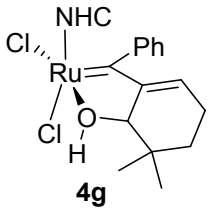


4f

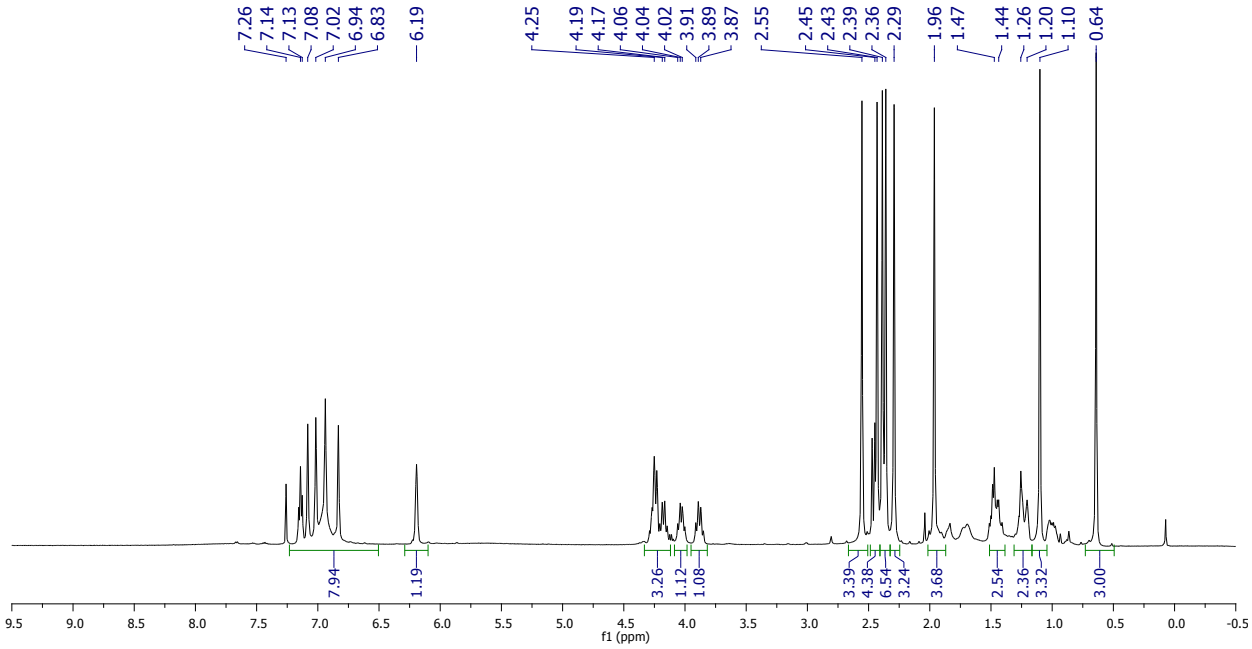
cis:trans: **5:1**

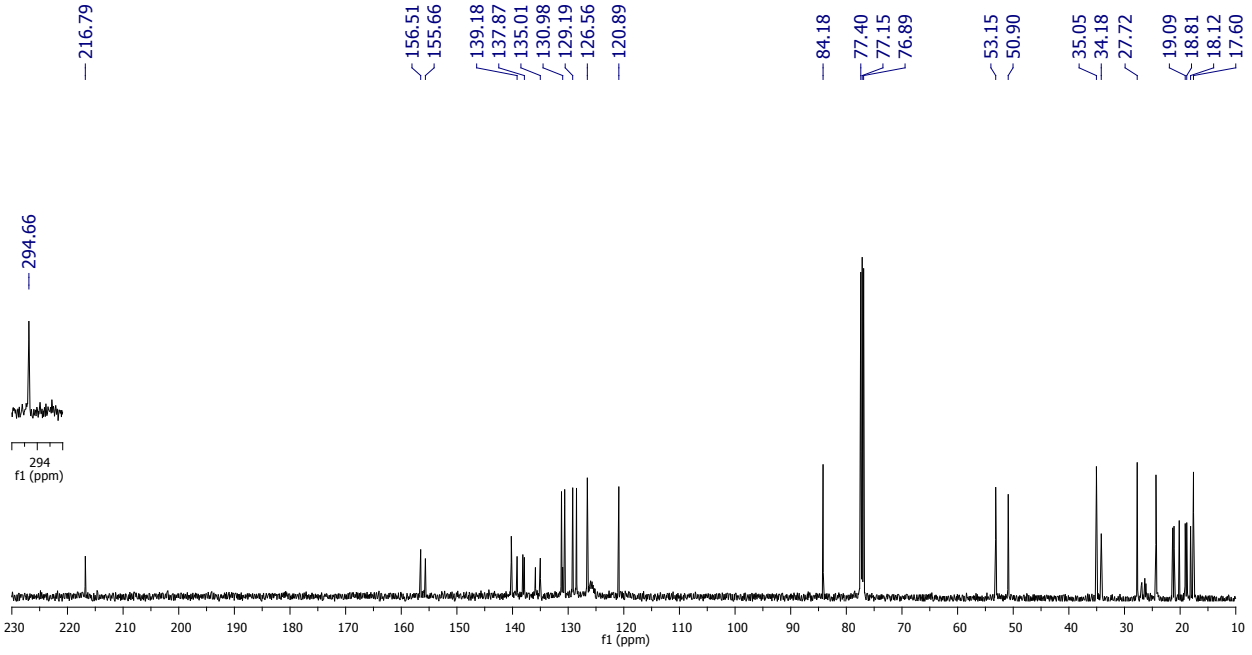


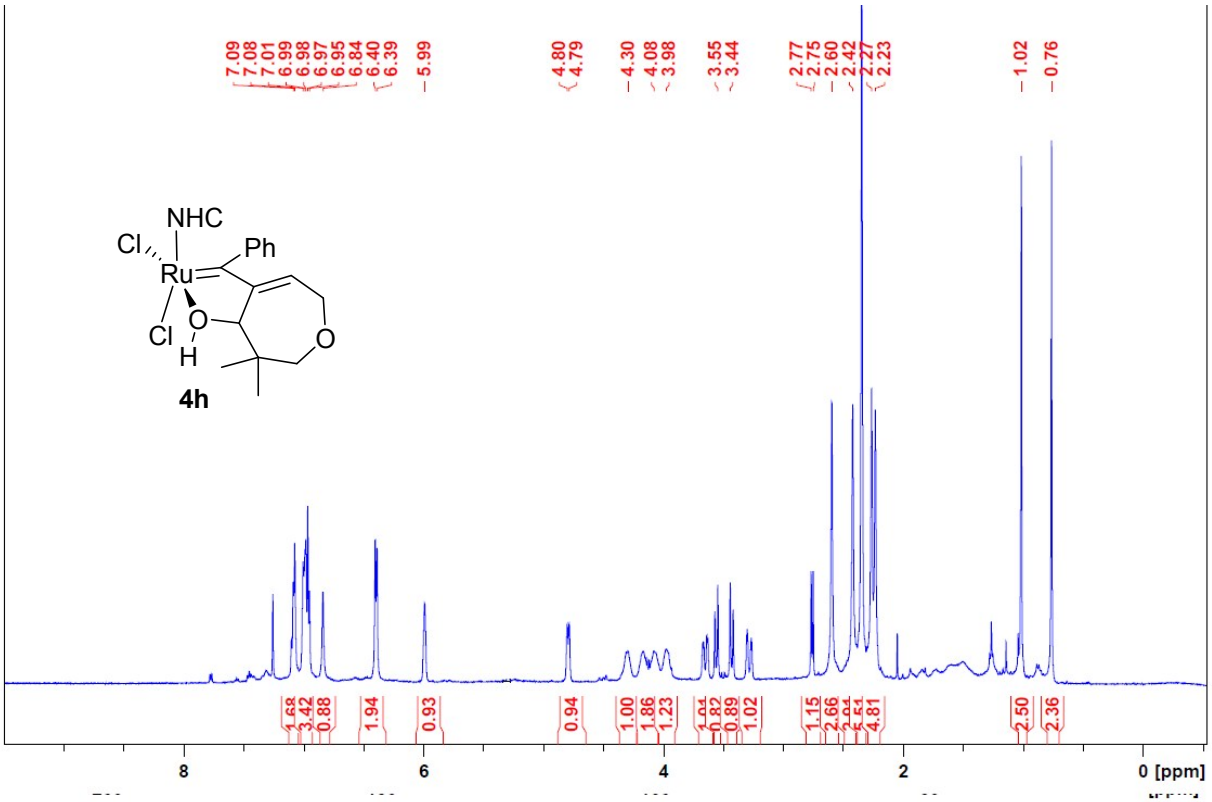


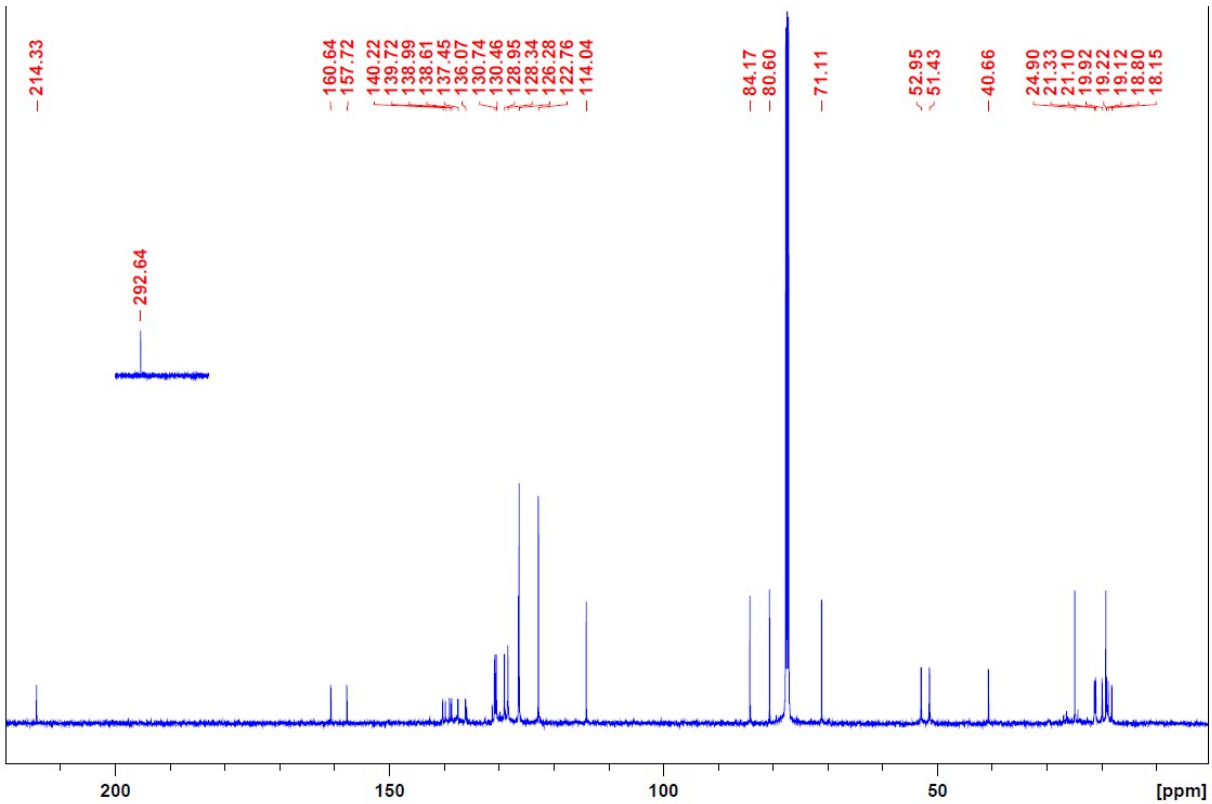

NHC
Cl
Ph
Ru
Cl
O
H

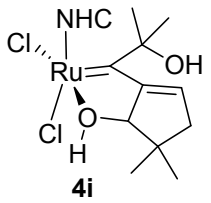
4g


7.26
7.14
7.13
7.08
7.02
6.94
6.83
6.19
4.25
4.19
4.17
4.06
4.04
4.02
3.91
3.89
3.87
2.55
2.45
2.43
2.39
2.36
2.29
1.96
1.47
1.44
1.26
1.20
1.10
0.64
7.94
1.19
3.26
1.12
1.08
3.39
4.38
6.54
3.24
3.68
2.54
2.36
3.32
3.00
f1 (ppm)

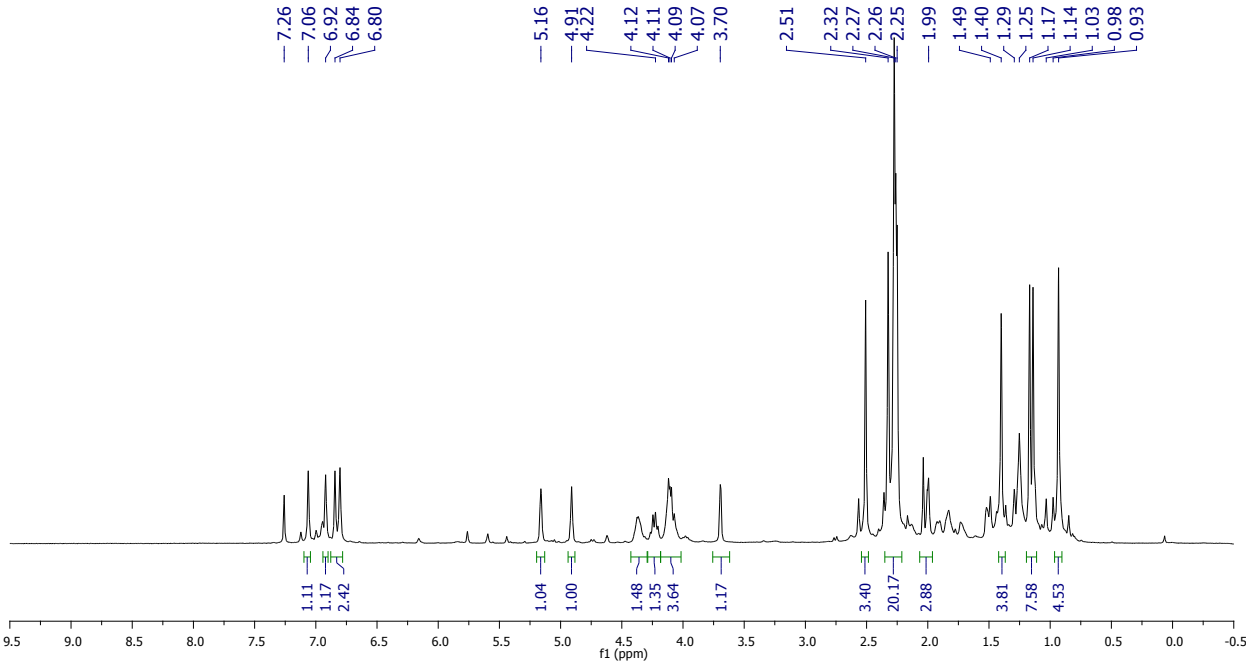

216.79
156.51
155.66
139.18
137.87
135.01
130.98
129.19
126.56
120.89
84.18
77.40
77.15
76.89
53.15
50.90
35.05
34.18
27.72
19.09
18.81
18.12
17.60
294.66
294
f1 (ppm)

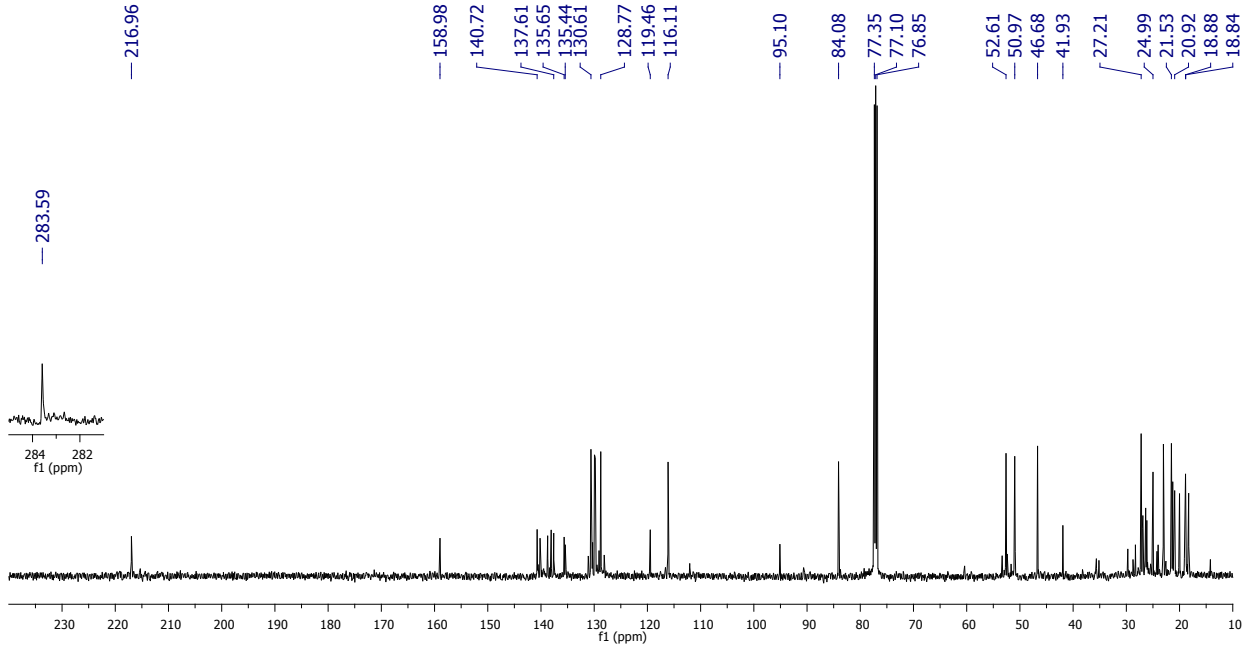

7.09
7.08
7.01
6.99
6.98
6.97
6.95
6.84
6.40
6.39
5.99
4.80
4.79
4.30
4.08
3.98
3.55
3.44
2.77
2.75
2.60
2.42
2.27
2.23
1.02
0.76
NHC
Cl
Ph
Ru
O
Cl
H
O
4h
1.68
3.42
0.88
1.94
0.93
0.94
1.00
1.86
1.23
1.01
0.82
0.89
1.02
1.15
2.66
2.01
5.51
4.81
2.50
2.36
8
6
4
2
0 [ppm]

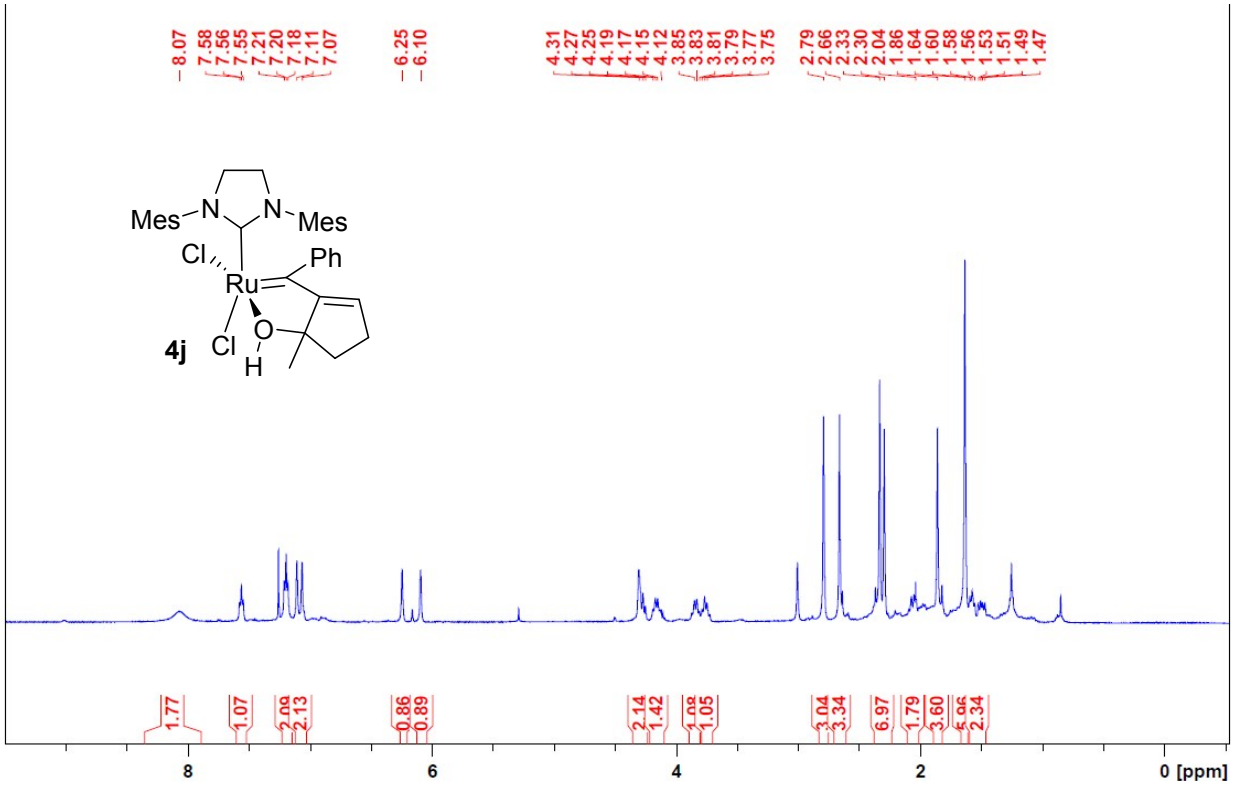

214.33
160.64
157.72
140.22
139.72
138.99
138.61
137.45
136.07
130.74
130.46
128.95
128.34
126.28
122.76
114.04
84.17
80.60
71.11
52.95
51.43
40.66
24.90
21.33
21.10
19.92
19.22
19.12
18.80
18.15
292.64
200
150
100
50
[ppm]

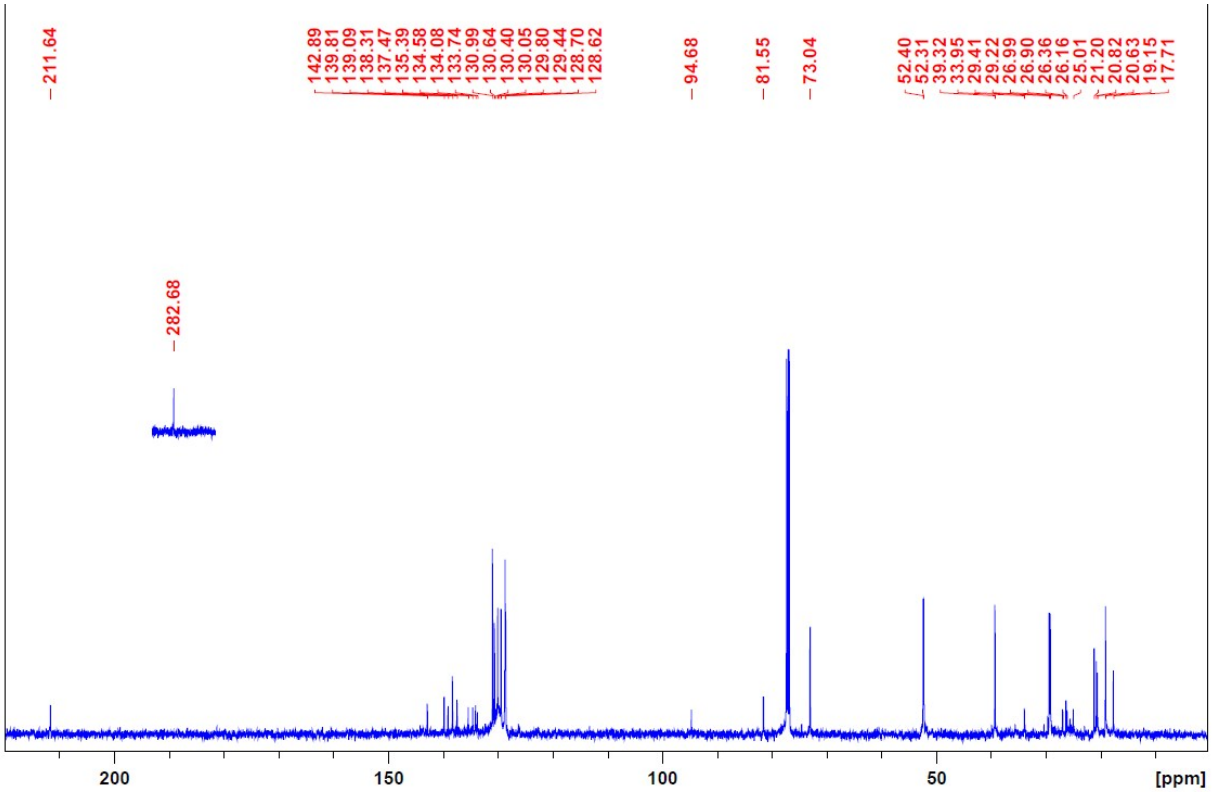

NHC
Cl
Ru
OH
Cl
O
H

4i


7.26
7.06
6.92
6.84
6.80
5.16
4.91
4.22
4.12
4.11
4.09
4.07
3.70
2.51
2.32
2.27
2.26
2.25
1.99
1.49
1.40
1.29
1.25
1.17
1.14
1.03
0.98
0.93
1.11
1.17
2.42
1.04
1.00
1.48
1.35
3.64
1.17
3.40
20.17
2.88
3.81
7.58
4.53
f1 (ppm)


216.96
158.98
140.72
137.61
135.65
135.44
130.61
128.77
119.46
116.11
95.10
84.08
77.35
77.10
76.85
52.61
50.97
46.68
41.93
27.21
24.99
21.53
20.92
18.88
18.84
283.59
284
282
f1 (ppm)
f1 (ppm)


8.07
7.58
7.56
7.55
7.21
7.20
7.18
7.11
7.07
6.25
6.10
4.31
4.27
4.25
4.19
4.17
4.15
4.12
3.85
3.83
3.81
3.79
3.77
3.75
2.79
2.66
2.33
2.30
2.04
1.86
1.64
1.60
1.58
1.56
1.53
1.51
1.49
1.47
Mes
N
N
Mes
Cl
Ph
Ru
Cl
O
H
4j
1.77
1.07
2.09
2.13
0.86
0.89
2.14
1.42
1.02
1.05
3.04
3.34
6.97
1.79
3.60
5.96
2.34
8
6
4
2
0 [ppm]


211.64
142.89
139.81
139.09
138.31
137.47
135.39
134.58
134.08
133.74
130.99
130.64
130.40
130.05
129.80
129.44
128.70
128.62
94.68
81.55
73.04
52.40
52.31
39.32
33.95
29.41
29.22
26.99
26.90
26.36
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20.82
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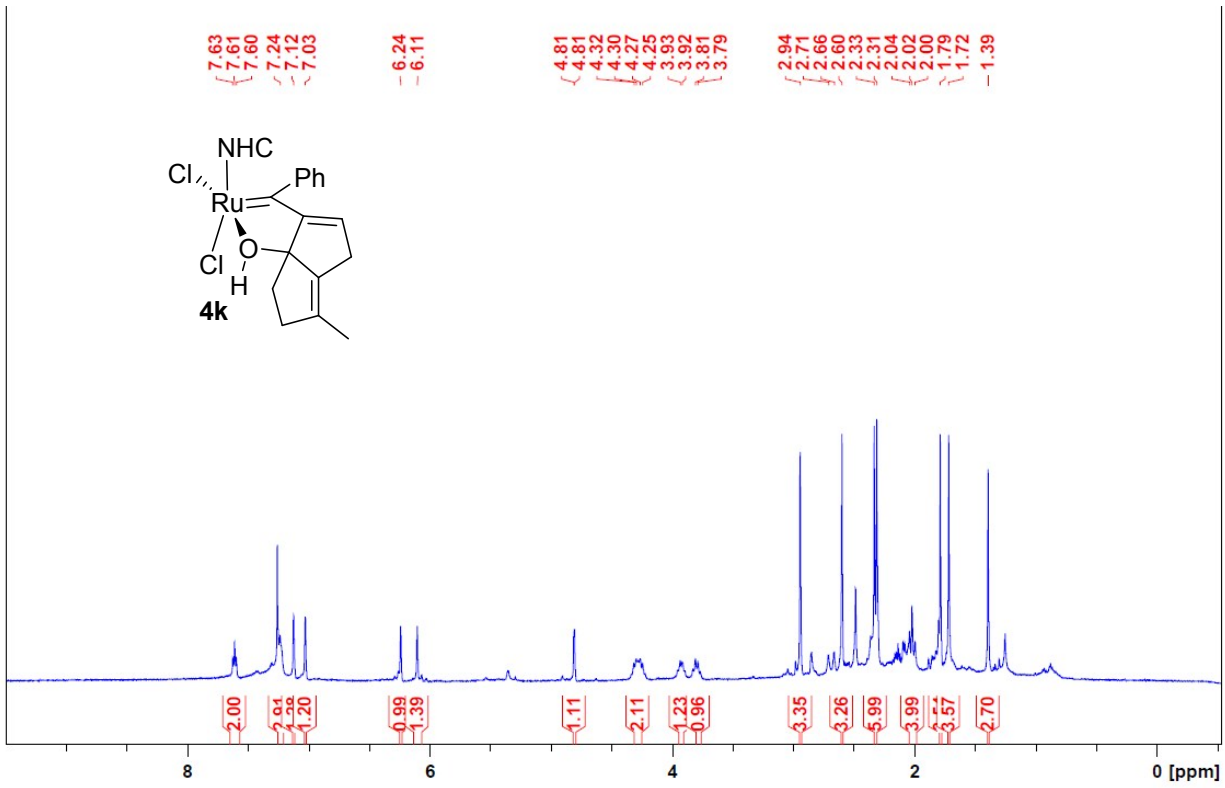
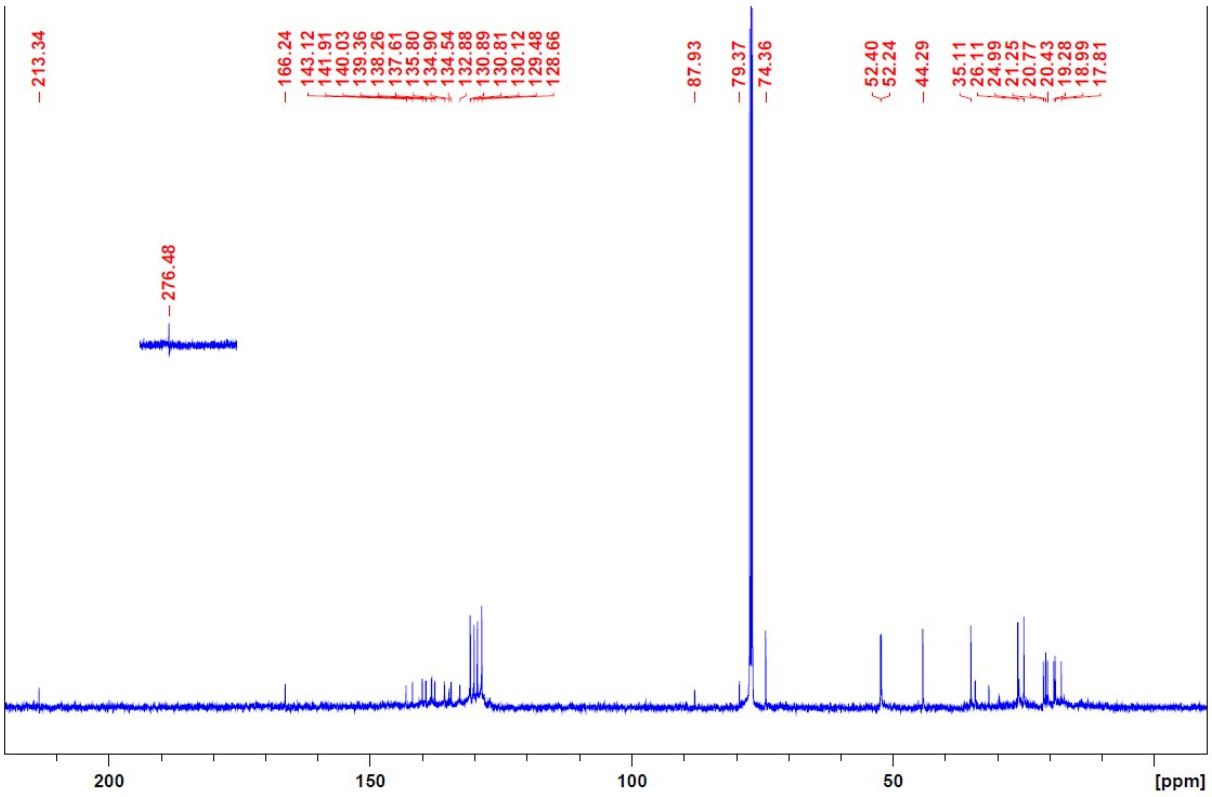
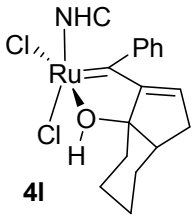
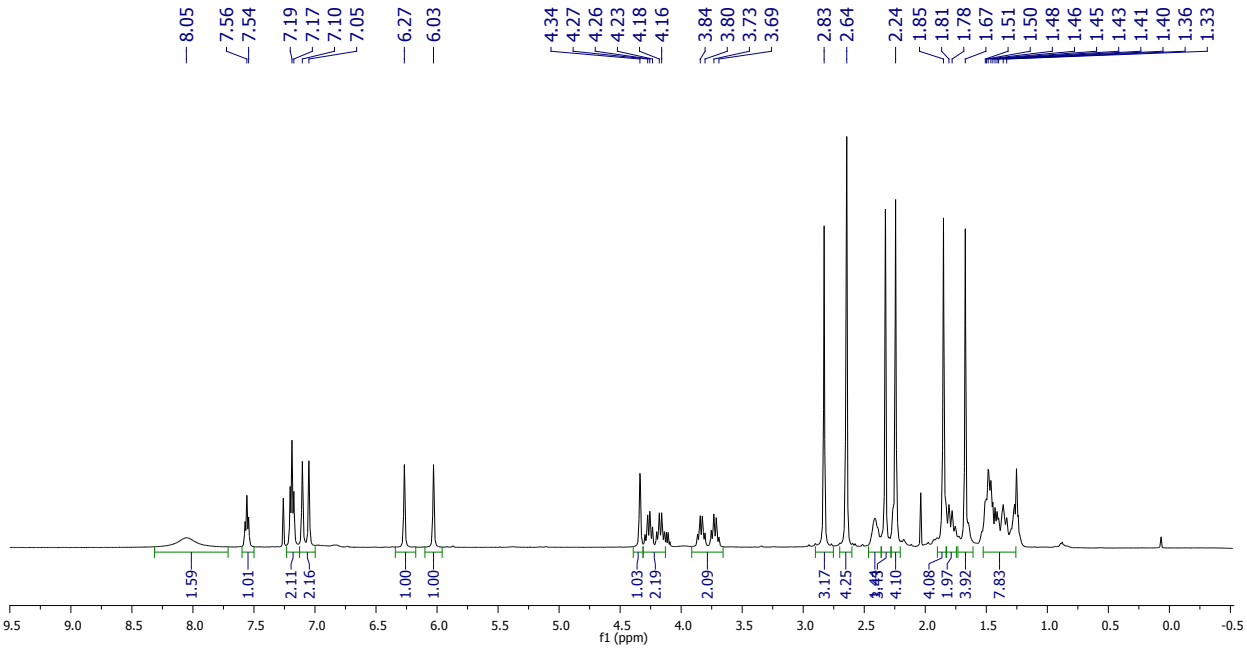
19.15
17.71
282.68
200
150
100
50
[ppm]

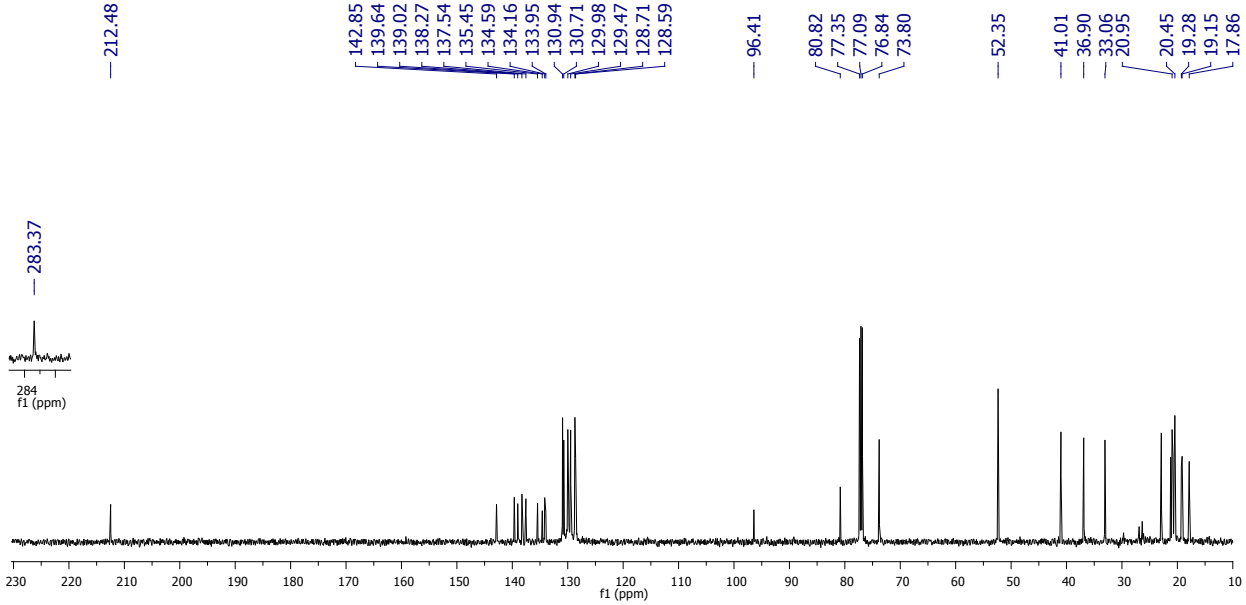

7.63
7.61
7.60
7.24
7.12
7.03
6.24
6.11
4.81
4.81
4.32
4.30
4.27
4.25
3.93
3.92
3.81
3.79
2.94
2.71
2.66
2.60
2.33
2.31
2.04
2.02
2.00
1.79
1.72
1.39
NHC
Cl
Ph
Ru
O
Cl
H
4k
2.00
1.20
0.99
1.39
1.11
2.11
1.23
0.96
3.35
3.26
5.99
3.99
3.57
2.70
8
6
4
2
0 [ppm]

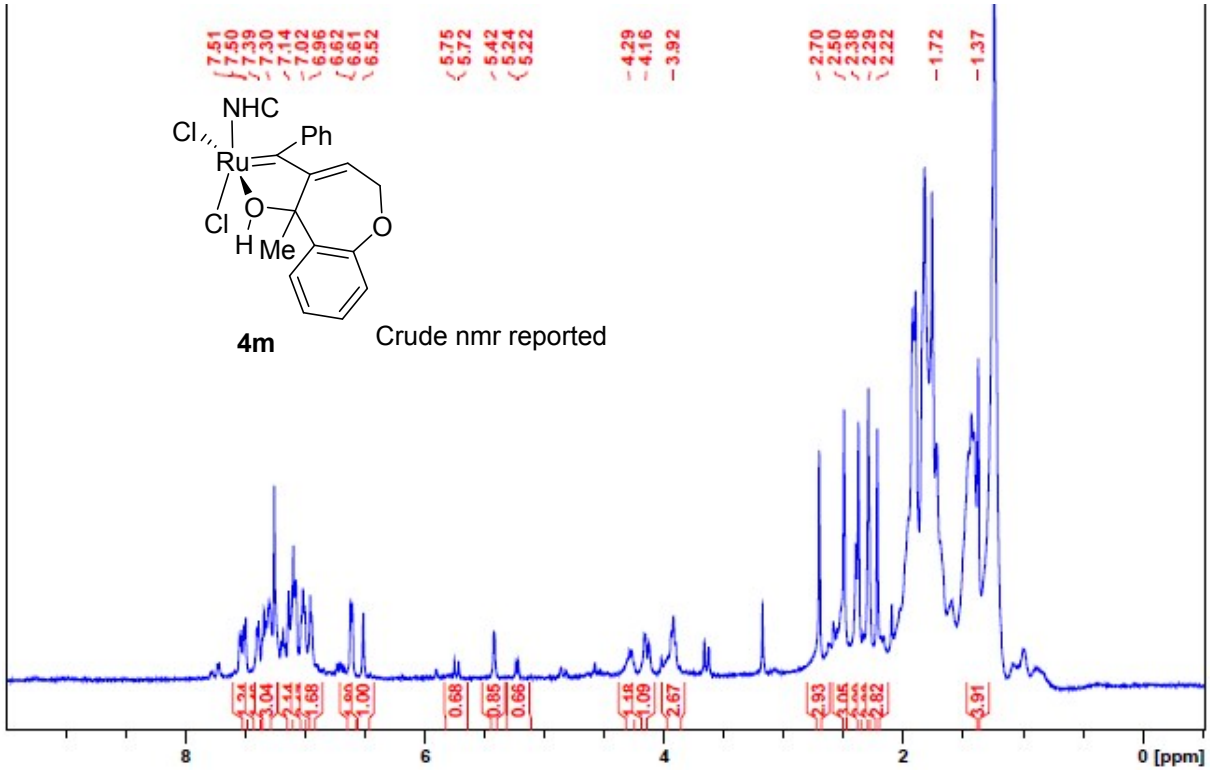

213.34
166.24
143.12
141.91
140.03
139.36
138.26
137.61
135.80
134.90
134.54
132.88
130.89
130.81
130.12
129.48
128.66
87.93
79.37
74.36
52.40
52.24
44.29
35.11
26.11
24.99
21.25
20.77
20.43
19.28
18.99
17.81
276.48
200
150
100
50
[ppm]

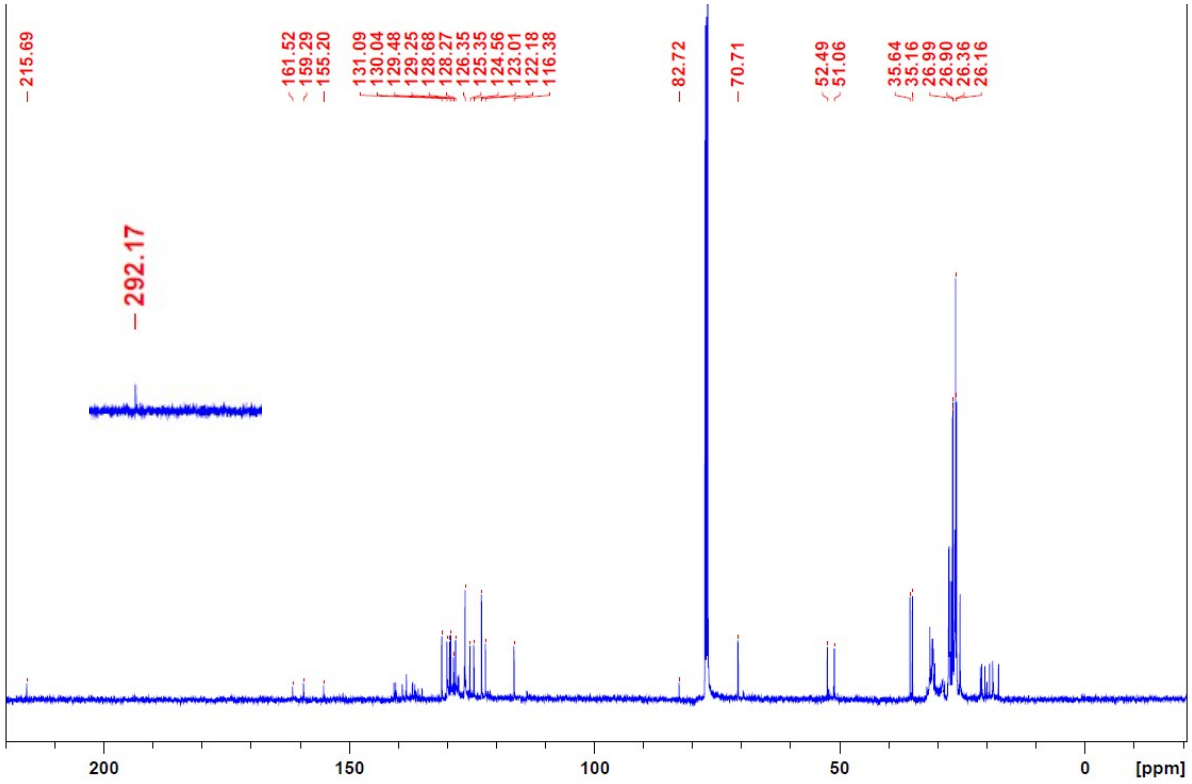

NHC
Cl
Ph
Ru
Cl
O
H

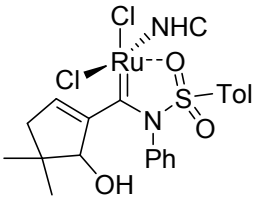
4l


8.05
7.56
7.54
7.19
7.17
7.10
7.05
6.27
6.03
4.34
4.27
4.26
4.23
4.18
4.16
3.84
3.80
3.73
3.69
2.83
2.64
2.24
1.85
1.81
1.78
1.67
1.51
1.50
1.48
1.46
1.45
1.43
1.41
1.40
1.36
1.33
1.59
1.01
2.11
2.16
1.00
1.00
1.03
2.19
2.09
3.17
4.25
4.10
4.08
1.97
3.92
7.83
f1 (ppm)

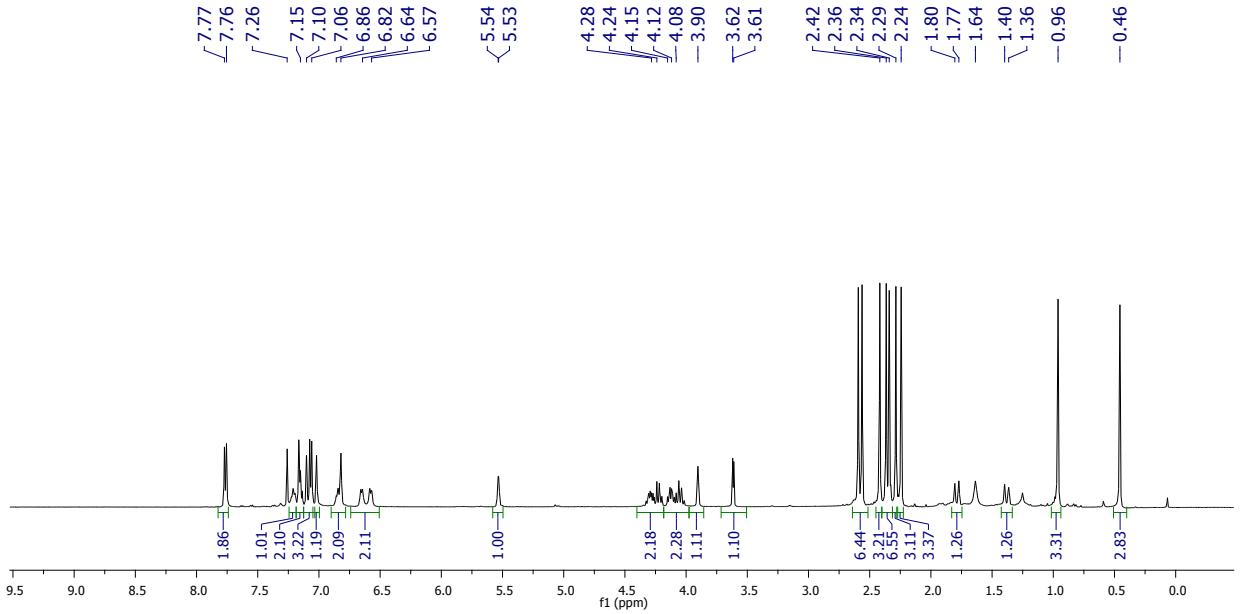

212.48
142.85
139.64
139.02
138.27
137.54
135.45
134.59
134.16
133.95
130.94
130.71
129.98
129.47
128.71
128.59
96.41
80.82
77.35
77.09
76.84
73.80
52.35
41.01
36.90
33.06
20.95
20.45
19.28
19.15
17.86
283.37
284
f1 (ppm)
f1 (ppm)

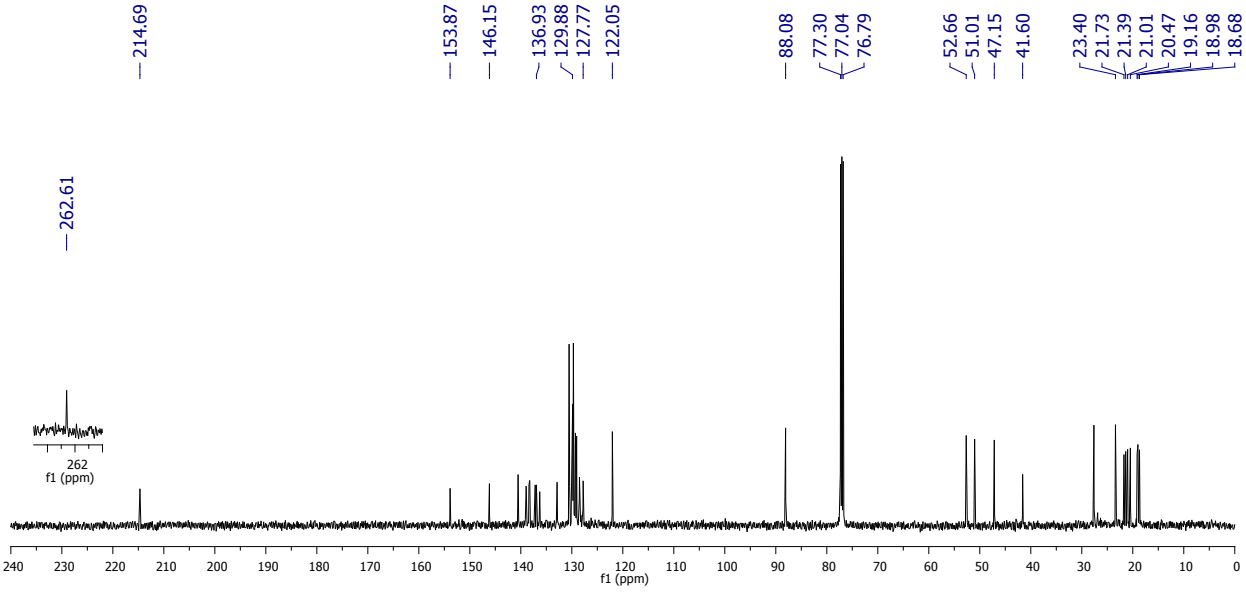

7.51
7.50
7.39
7.30
7.14
7.02
6.96
6.62
6.61
6.52
5.75
5.72
5.42
5.24
5.22
4.29
4.16
3.92
2.70
2.50
2.38
2.29
2.22
1.72
1.37
NHC
Cl
Ph
Ru
Cl
O
H
Me
O
4m
Crude nmr reported
0.68
0.85
0.66
1.09
2.67
2.93
3.91
8
6
4
2
0 [ppm]


215.69
161.52
159.29
155.20
131.09
130.04
129.48
129.25
128.68
128.27
126.35
125.35
124.56
123.01
122.18
116.38
82.72
70.71
52.49
51.06
35.64
35.16
26.99
26.90
26.36
26.16
292.17
200
150
100
50
0
[ppm]


Cl
NHC
Ru
O
Cl
S
Tol
N
O
Ph
OH

4r


7.77
7.76
7.26
7.15
7.10
7.06
6.86
6.82
6.64
6.57
5.54
5.53
4.28
4.24
4.15
4.12
4.08
3.90
3.62
3.61
2.42
2.36
2.34
2.29
2.24
1.80
1.77
1.64
1.40
1.36
0.96
0.46
1.86
1.01
2.10
3.22
1.19
2.09
2.11
1.00
2.18
2.28
1.11
1.10
6.44
3.21
6.55
3.11
3.37
1.26
1.26
3.31
2.83
f1 (ppm)


214.69
153.87
146.15
136.93
129.88
127.77
122.05
88.08
77.30
77.04
76.79
52.66
51.01
47.15
41.60
23.40
21.73
21.39
21.01
20.47
19.16
18.98
18.68
262.61
262
f1 (ppm)
f1 (ppm)

Checked CIF Data of 4f: CCDC 1584832

Datablock: ru_bu_a

Bond precision: C-C = 0.0166 A Wavelength=0.71073

Cell: a=14.573(10) b=14.783(10) c=16.116(10)

alpha=90 beta=104.49(2) gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	3362(4)	3361(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C33 H46 Cl2 N2 O Ru	C33 H46 Cl2 N2 O Ru
Sum formula	C33 H46 Cl2 N2 O Ru	C33 H46 Cl2 N2 O Ru
Mr	658.69	658.69
Dx,g cm-3	1.301	1.302
Z	4	4
Mu (mm-1)	0.652	0.652
F000	1376.0	1376.0
F000'	1372.51	
h,k,lmax	18,19,20	18,19,20
Nref	7712	7324
Tmin,Tmax	0.683,0.878	0.600,0.880
Tmin'	0.670	

Correction method= # Reported T Limits: Tmin=0.600
Tmax=0.880 AbsCorr = MULTI-SCAN

Data completeness= 0.950 Theta(max)= 27.484

R(reflections)= 0.1163(4378) wR2(reflections)= 0.3651(7324)

S = 1.281 Npar= 364

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ..... 0.37 Report

RESPONSE: The investigated single crystal was a small-sized poorly diffracting needle. Numerous datasets were collected on single crystals from different batches, whereof the one of the highest quality is reported herein.

Alert level C

PLAT082_ALERT_2_C High R1 Value ..... 0.12 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 4.1 Ratio
PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 4.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference N7 -- C16 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 -- C21 0.16 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C8 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C15 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C26 Check
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.01658 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C1 - C2 . 1.43 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 4 Note
PLAT012_ALERT_1_G No _shelx_res_checksum Found in CIF ..... Please Check
PLAT019_ALERT_1_G _diffrn_measured_fraction_theta_full/*_max < 1.0 0.989 Report
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.20 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 1 Report
PLAT173_ALERT_4_G The CIF-Embedded .res File Contains DANG Records 2 Report
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C24 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 6 Note
PLAT793_ALERT_4_G Model has Chirality at C10 (Centro SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 3 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
8 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

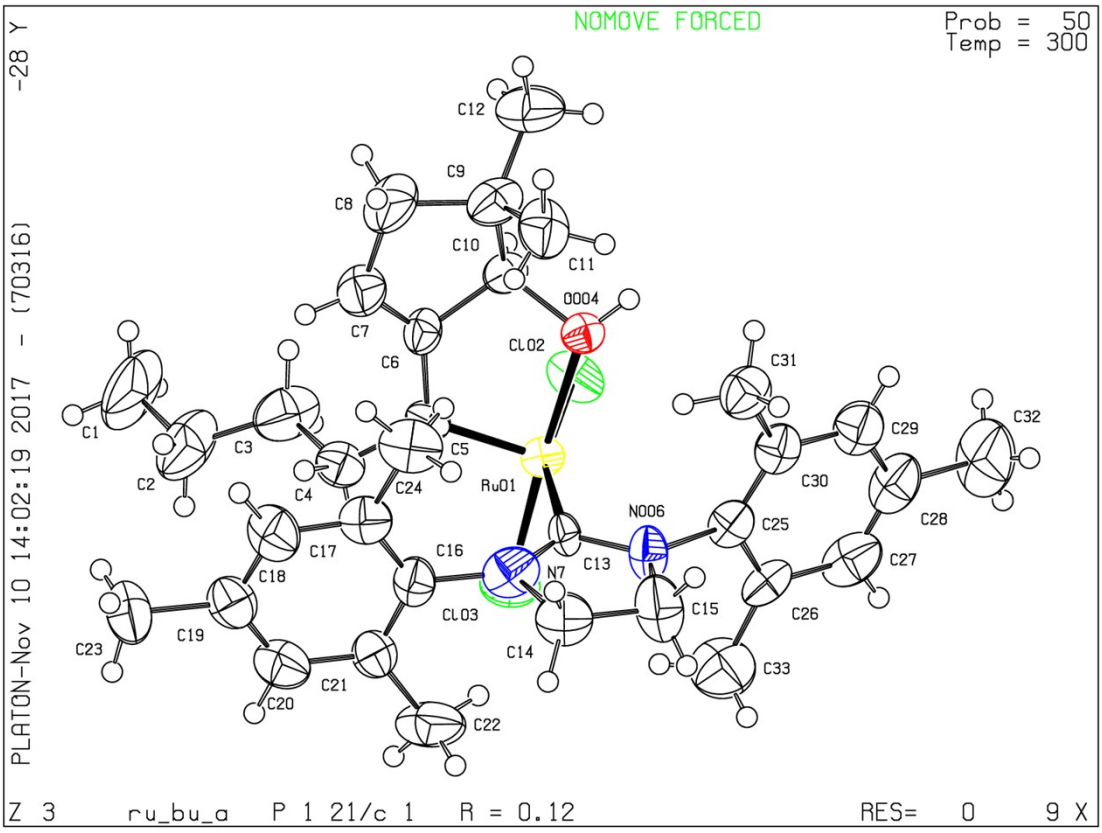
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 09/11/2017; check.def file version of 08/11/2017

Datablock ru_bu_a - ellipsoid plot


NOMOVE FORCED
Prob = 50
Temp = 300
PLATON-Nov 10 14:02:19 2017 - (70316)
-28 Y
C12
C9
C8
C10
C11
O004
C7
C6
CL02
C31
C1
C3
C5
C29
C32
C2
C4
C24
Ru01
C30
N006
C25
C28
C17
C16
C13
C27
C18
N7
C15
CL03
C26
C19
C14
C23
C33
C21
C20
C22
Z 3 ru_bu_a P 1 21/c 1 R = 0.12
RES= 0 9 X

Checked CIF Data of 4g: CCDC 1584833

Datablock: scan_0m_c2_c

Bond precision: C-C = 0.0059 A Wavelength=0.71073

Cell: a=26.317(4) b=17.570(2) c=17.431(2)

alpha=90 beta=110.100(4) gamma=90

Temperature: 200 K

	Calculated	Reported
Volume	7569.0(17)	7569.1(17)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C36 H44 Cl2 N2 O Ru [+ solvent]	C36 H44 Cl2 N2 O Ru
Sum formula	C36 H44 Cl2 N2 O Ru [+ solvent]	C36 H44 Cl2 N2 O Ru
Mr	692.70	692.70
Dx,g cm-3	1.216	1.216
Z	8	8
Mu (mm-1)	0.582	0.582
F000	2880.0	2880.0
F000'	2873.08	
h,k,lmax	31,20,20	31,20,20
Nref	6742	6671
Tmin,Tmax	0.811,0.890	
Tmin'	0.748	

Correction method= Not given

Data completeness= 0.989 Theta(max)= 25.094

R(reflections)= 0.0417(5571) wR2(reflections)= 0.1240(6671)

S = 1.080 Npar= 391

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.58 Report
PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 4.6 Ratio

Alert level G

PLAT012_ALERT_1_G No _shelx_res_checksum Found in CIF ..... Please Check
PLAT014_ALERT_1_G No _shelx_fab_checksum Found in CIF ..... Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 22.62 Why ?
PLAT128_ALERT_4_G Alternate Setting for Input Space Group C2/c I2/a Note
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 1 Note
PLAT793_ALERT_4_G Model has Chirality at C31 (Centro SPGR) S Verify
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE Suppressed ! Info
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 4 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF

prior to submission.

Publication of your CIF in other journals

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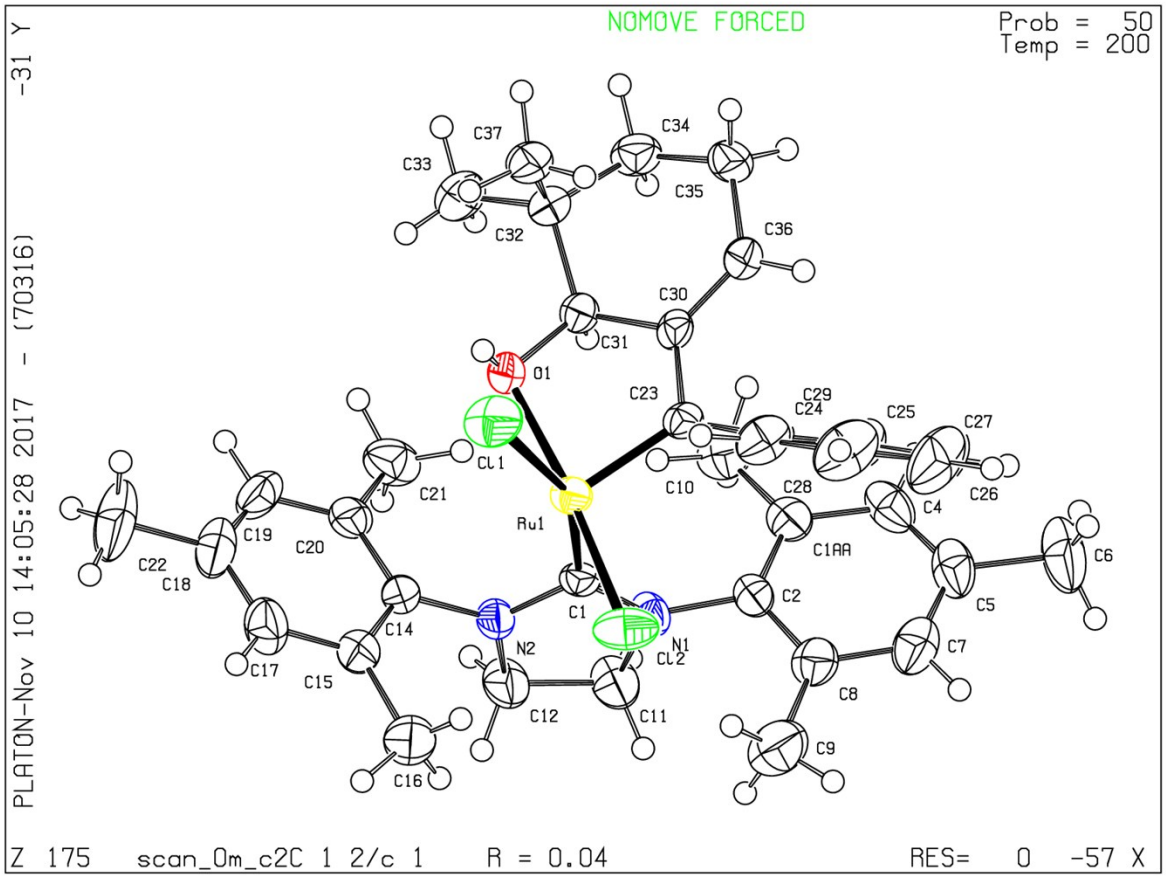
PLATON version of 09/11/2017; check.def file version of 08/11/2017

Datablock scan_0m_c2_c - ellipsoid plot



Checked CIF Data of 4r: CCDC 1584834

Datablock: venkata_p21n_a

Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=13.3662(8) b=19.3514(12) c=18.2778(11)

alpha=90 beta=107.451(2) gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	4510.0(5)	4510.0(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2ybc (x-
Moiety formula	C42 H49 Cl2 N3 O3 Ru S [+ solvent]	C42 H49 Cl2 N3 O3 Ru S
Sum formula	C42 H49 Cl2 N3 O3 Ru S [+ solvent]	C42 H49 Cl2 N3 O3 Ru S
Mr	847.87	847.91
Dx,g cm-3	1.249	1.249
Z	4	4
Mu (mm-1)	0.550	0.550
F000	1760.0	1757.3
F000'	1757.18	
h,k,lmax	16,24,22	16,24,22
Nref	9211	9202
Tmin,Tmax	0.803,0.803	
Tmin'	0.803	

Correction method= Not given

Data completeness= 0.999 Theta(max)= 26.370

R(reflections)= 0.0425(7403) wR2(reflections)= 0.1226(9202)

S = 1.036 Npar= 479

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT126_ALERT_1_C Error in or Uninterpretable Hall Symbol ..... -P 2YBC (X-Z,Y
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 4.0 Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C013 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C01G Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C011 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C016 Check
PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C00U -C01C 1.37 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 3.309 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 4 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check

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Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 52 Report
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT073_ALERT_1_G H-atoms ref, but _hydrogen_treatment Reported as constr Check
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ru01 --Cl02 . 5.4 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ru01 --C00H . 5.3 s.u.
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure 139 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 98 Note
PLAT793_ALERT_4_G Model has Chirality at S004 (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C00Y (Centro SPGR) R Verify
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE Suppressed ! Info
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 2 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 8 Note

PLAT960_ALERT_3_G Number of Intensities with I < - 2*sig(I) ... 5 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 1 Info
PLAT982_ALERT_1_G The Ru-f'= -1.239 Deviates from the IT-value - 1.259 Ch

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relating to CIF submission.

PLATON version of 09/11/2017; check.def file version of 08/11/2017

Datablock venkata_p21n_a - ellipsoid plot