Supporting Information

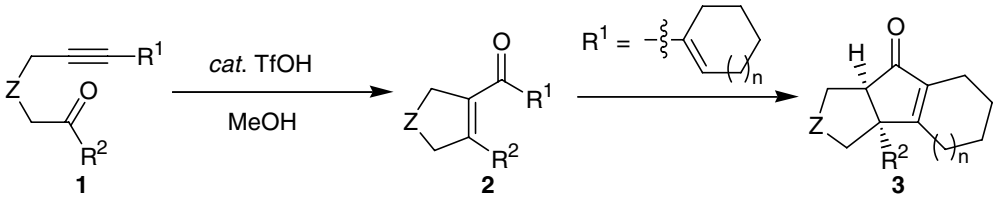
TfOH-Catalyzed Intramolecular Alkyne-Ketone Metathesis Leading to Highly Substituted 5-Membered Cyclic Enones

Tienan Jin,* Fan Yang, Chunli Liu, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University

Sendai 980-8578, Japan

tjin@mail.tains.tohoku.ac.jp; yoshi@mail.tains.tohoku.ac.jp



Contents

General Information: ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 300 MHz, 400 MHz, 500MHz) and BRUKER (600 MHz) spectrometers. 1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spetra reported in ppm (d) relative to the central line of triplet for $CDCl_3$ at 77 ppm. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer; absorptions are reported in cm^{-1}. High-resolution mass spetra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Slica gel 60N (spherical, neutral, 40~100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merck).

Materials: Anhydrous methanol, toluene, DMF, diethylamine (WAKO), $AuCl_3$, $AgSbF_6$, AgOTf, $Pd(PPh_3)_4$, CuI (Aldrich), TfOH (TCI) were purchased and used as received. All of the starting materials **1** were prepared according to the literature procedures.[1, 2] The structure and stereochemistry of starting materials and products were determined by 1D, 2D, NOE.

References

1. T. Jin, Y. Yamamoto, *Org. Lett*, **2008**, *10*, 3137.

2. N. Hamada, K. Kazahaya, H. Shimizu, T. Sato, *Synlett*, **2004**, 1074.

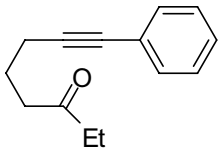
Experimental Procedures of (2) and (3)

Representative procedure for the synthesis of (2-ethyl-cyclopent-1-enyl)-phenyl-methanone (2a)

To a methanol (2 ml, 0.2 M) solution of 8-phenyl-oct-7-yn-3-one **1a** (80 mg, 0.4 mmol) was added 5 mol% of TfOH (1.8 μl, 0.02 mmol) at room temperature in a pressure vial. The mixture was stirred at 80 °C for 4 h. After consumption of **1a** which was monitored by TLC, the reaction mixture was filtered through a short Florisil pad using diethyl ether as an eluent. After concentration, the residue was purified with a silica gel chromatography using hexane/EtOAc as an eluent, gave (2-ethyl-cyclopent-1-enyl)-phenyl-methanone **2a** in 87% yield as a slight yellow oil (70 mg).

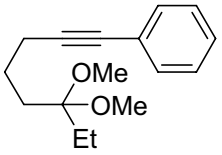
Spectroscopic data of (1)

(2-Ethyl-cyclopent-1-enyl)-phenyl-methanone (1a)



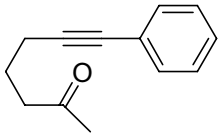
slight yellow oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.41-7.37 (2H, m), 7.29-7.26 (3H, m), 2.58 (2H, t, *J* = 7.2 Hz), 2.47-2.42 (4H, m), 1.92-1.82 (2H, m), 1.05 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.67, 18.64, 22.51, 35.85, 40.70, 81.17, 89,08, 123.63, 127.48, 128.05, 131.34, 210.72; IR(neat) 691, 755, 1114, 1373, 1490, 1712, 2226, 2938 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{16}O$ (M+Na)+ 223.1093. Found 223.1093.

(6,6-Dimethoxy-oct-1-ynyl)-benzene (1a')



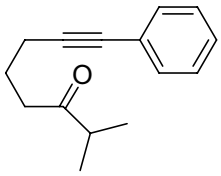
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.35 (2H, m), 7.28-7.25 (3H, m), 3.18 (6H, s), 2.43 (2H, t, *J* = 6.9 Hz), 1.80-1.74 (2H, m), 1.66-1.55 (5H, m), 0.88-0.83 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.91, 19.49, 23.05, 25.03, 30.93, 47.64, 80.98, 89.73, 103.49, 123.86, 127.51, 128.15, 131.44; IR(neat) 690, 755, 910, 1048, 1068, 1127, 1457, 1490, 2232, 2952 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{22}O_2$ (M+Na)+ 269.1512. Found 269.1512.

7-Phenyl-hept-6-yn-2-one (1b)



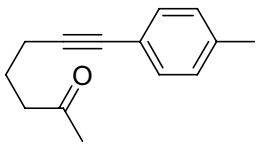
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.35 (2H, m), 7.29-7.24 (3H, m), 2.62 (2H, t, *J* = 7.2 Hz), 2.44 (2H, t, *J* = 6.9 Hz), 2.16 (3H, s), 1.91-1.82 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.67, 22.53, 29.97, 42.21, 81.31, 89.07, 123.67, 127.59, 128.15, 131.45, 208.21; IR(neat) 691, 756, 1158, 1355, 1442, 1490, 1713, 2328 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}O$ (M+Na)+ 209.0937. Found 209.0937.

2-Methyl-8-phenyl-oct-7-yn-3-one (1c)



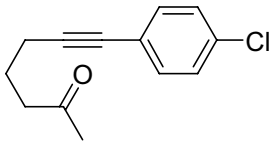
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.35 (2H, m), 7.27-7.25 (3H, m), 2.66-2.56 (3H, m), 2.43 (2H, t, *J* = 6.9 Hz), 1.90-1.81 (2H, m), 1.11 (6H, d, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.19, 18.70, 22.51, 38.72, 40.91, 81.26, 89.21, 123.74, 127.57, 128.15, 131.45, 214.13; IR(neat) 691, 755, 1025, 1084, 1490, 1709, 2336, 2968 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{18}O$ (M+Na)+ 237.1250. Found 237.1250.

7-(*p*-Tolyl)-hept-6-yn-2-one (1d)



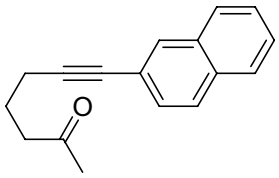
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.25 (2H, m), 7.09-7.06 (2H, m), 2.62 (2H, t, *J* = 7.5 Hz), 2.43 (2H, t, *J* = 6.6 Hz), 2.32 (3H, s), 2.16 (3H, s), 1.90-1.81 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.72, 21.34, 22.63, 30.02, 42.27, 81.38, 88.25, 120.60, 128.93, 131.34, 137.62, 208.34; IR(neat) 816, 1157, 1355, 1509, 1713, 2229, 2942 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{16}O$ (M+Na)+ 223.1093. Found 223.1093.

7-(4-Chloro-phenyl)-hept-6-yn-2-one (1e)



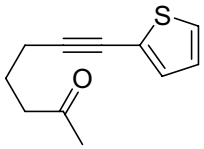
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m), 7.26-7.22 (2H, m), 2.61 (2H, t, *J* = 7.2 Hz), 2.43 (2H, t, *J* = 6.9 Hz), 2.16 (3H, s), 1.90-1.81 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.63, 22.39, 29.92, 42.13, 80.16, 90.16, 122.14, 128.39, 132.64, 133.46, 208.02; IR(neat) 751, 826, 1013, 1090, 1157, 1355, 1489, 1713, 2239, 2936 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{13}ClO$ (M+Na)+ 243.0547. Found 243.0547.

7-(Naphthalen-2-yl)-hept-6-yn-2-one (1f)



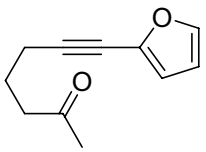
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (1H, s), 7.81-7.74 (3H, m), 7.50-7.43 (3H, m), 2.64 (2H, t, *J* = 7.2 Hz), 2.50 (2H, t, *J* = 6.9 Hz), 2.17 (3H, s), 1.96-1.86 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.74, 22.53, 29.92, 42.18, 81.61, 89.48, 120.96, 126.24, 126.31, 127.45, 127.58, 127.75, 128.50, 130.97, 132.40, 132.90, 208.16; IR(neat) 746, 818, 859, 1157, 1354, 1712, 2227, 2932 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}O$ (M+Na)+ 259.1093. Found 259.1093.

7-(Thiophen-2-yl)-hept-6-yn-2-one (1g)



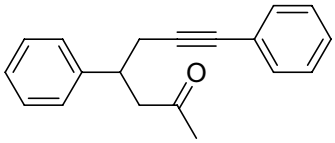
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (1H, dd, *J* = 0.9, 5.1 Hz), 7.09 (1H, dd, *J* = 0.9, 3.6 Hz), 6.91 (1H, dd, *J* = 3.6, 5.1 Hz), 2.58 (2H, t, *J* = 7.2 Hz), 2.44 (2H, t, *J* = 6.9 Hz), 2.13 (3H, s), 1.87-1.78 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.83, 22.25, 29.88, 42.04, 74.35, 93.12, 123.67, 125.95, 126.66, 130.96, 208.01; IR(neat) 689, 840, 1158, 1189, 1356, 1427, 1712, 2939 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}OS$ (M+Na)+ 215.0501. Found 215.0501.

7-(Furan-2-yl)-hept-6-yn-2-one (1h)



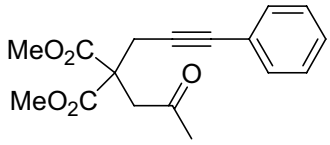
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (1H, m), 7.32-7.31 (1H, m), 6.38-6.37 (1H, m), 2.58 (2H, t, *J* = 7.2 Hz), 2.39 (2H, *J* = 6.9 Hz), 2.15 (3H, s), 1.87-1.77 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.70, 22.46, 29.97, 42.21, 72.08, 90.71, 107.71, 112.57, 142.55, 145.01, 208.21; IR(neat) 733, 787, 871, 1013, 1084, 1159, 1353, 1712, 2236, 2936 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O_2$ (M+Na)+ 199.0730. Found 199.0730.

4,7-Diphenyl-hept-6-yn-2-one (1i)



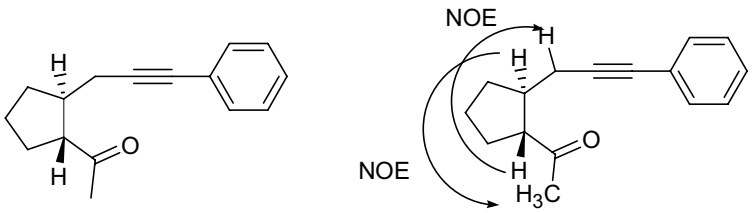
yellow oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.36-7.19 (10H, m), 3.54-3.45 (1H, m), 3.07 (1H, dd, *J* = 6.9, 16.8 Hz), 2.83 (1H, dd, *J* = 7.2, 16.8 Hz), 2.77-2.62 (2H, m), 2.06 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.62, 30.41, 39.52, 48.09, 82.65, 87.61, 123.46, 126.69, 127.23, 127.64, 128.09, 128.35, 131.35, 143.17, 206.977; IR(neat) 691, 755, 1027, 1157, 1356, 1490, 1713, 2229, 2917 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{18}O$ (M+Na)+ 285.1250. Found 285.1250.

2-(2-Oxo-propyl)-2-(3-phenyl-prop-2-ynyl)-malonic acid dimethyl ester (1j)



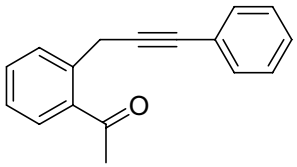
yellow oil; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.34-7.30 (2H, m), 7.26-7.23 (3H, m), 3.72 (6H, s), 3.38 (2H, s), 3.18 (2H, s), 2.16 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.26, 30.18, 45.59, 53.07, 54.68, 83.79, 84.40, 122.94, 128.09, 128.22, 131.57, 169.68, 205.33; IR(neat) 692, 757, 1054, 1199, 1288, 1434, 1739, 2954 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}O_5$ (M+Na)+ 325.1046. Found 325.1046.

1-[2-(3-Phenyl-prop-2-ynyl)-cyclopentyl]-ethanone (1k)



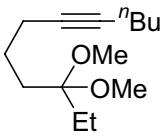
yellow oil; ^{1}H NMR (600 MHz, C_6D_6) δ 7.47-7.44 (2H, m), 7.02-6.95 (3H, m), 2.47-2.38 (2H, m), 2.30-2.22 (2H, m), 1.80 (3H, s), 1.72-1.67 (1H, m), 1.61-1.49 (4H, m), 1.46-1.38 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.28, 24.80, 29.19, 29.88, 31.91, 40.77, 56.97, 81.48, 88.36, 123.57, 127.50, 128.06, 131.32, 210.51; IR(neat) 691, 755, 913, 1164, 1354, 1442, 1490, 1705, 2232, 2953 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}O$ (M+Na)+ 249.1250. Found 249.1250.

1-[2-(3-Phenyl-prop-2-ynyl)-phenyl]-ethanone (1l)



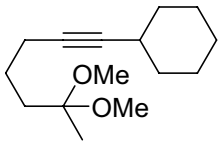
yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, d, J = 8.0 Hz), 7.70 (1H, d, J = 8.0 Hz), 7.49-7.41 (3H, m), 7.34-7.24 (4H, m), 4.15 (2H, s), 2.61 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.41, 29.36, 83.19, 87.62, 123.61, 126.62, 127.72, 128.14, 129.42, 130.08, 131.51, 131.88, 136.62, 136.82, 201.41; IR(neat) 696, 785, 957, 1023, 1071, 1255, 1356, 1444, 1483, 1668 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{14}O$ (M+Na)+ 257.0937. Found 257.0937.

10,10-Dimethoxy-dodec-5-yne (1m')



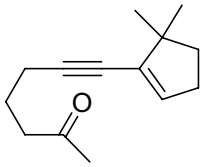
colorless oil; yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (6H, s), 2.18-2.11 (4H, m), 1.70-1.66 (2H, m), 1.62-1.57 (3H, m), 1.62-1.57 (3H, m), 1.46-1.38 (6H, m), 0.89 (3H, t, J = 5.4 Hz), 0.83 (3H, t, J = 5.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.88, 13.59, 18.37, 18.90, 21.92, 23.39, 25.03, 30.94, 31.19, 47.65, 79.59, 80.68, 103.58; IR(neat) 905, 1048, 1068, 1126, 1187, 1458, 2955 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{26}O_2$ (M+Na)+ 249.1825. Found 249.1825.

(6,6-Dimethoxy-hept-1-ynyl)-cyclohexane (1n')



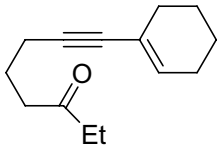
colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17 (6H, s), 2.35-2.24 (1H, m), 2.20-2.15 (2H, m), 1.77-1.68 (6H, m), 1.58-1.26 (11H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.91, 20.99, 24.02, 24.95, 25.91, 29.14, 33.13, 35.57, 47.99, 79.46, 85.10, 101.49; IR(neat) 863, 1054, 1104, 1123, 1173, 1204, 1377, 1448, 2928 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{26}O_2$ (M+Na)+ 261.1825. Found 261.1825.

7-(5,5-Dimethyl-cyclopent-1-enyl)-hept-6-yn-2-one (1o)



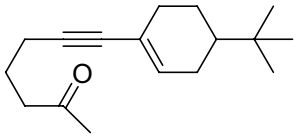
yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79-5.72 (1H, m), 2.59-2.50 (2H, m), 2.37-2.27 (4H, m), 2.11 (3H, s), 1.80-1.64 (4H, m), 1.04-1.03 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.70, 22.70, 26.98, 29.92, 30.26, 38.82, 42.12, 46.65, 76.93, 91.04, 133.46, 133.48, 134.80, 208.12; IR(neat) 824, 1157, 1360, 1715, 2954 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

8-Cyclohex-1-enyl-oct-7-yn-3-one (1p)



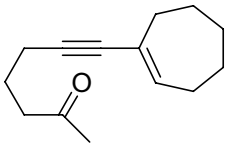
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03-5.96 (1H, m), 2.57-2.31 (6H, m), 2.11-2.02 (4H, m), 1.84-1.74 (2H, m), 1.68-1.51 (4H, m), 1.08-1.02 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.74, 18.62, 21.48, 22.29, 22.77, 25.45, 29.47, 35.95, 40.84, 83.06, 86.08, 120.79, 133.36, 210.99; IR(neat) 842, 918, 1113, 1436, 1713, 2932 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

7-(4-*tert*-Butyl-cyclohex-1-enyl)-hept-6-yn-2-one (1q)



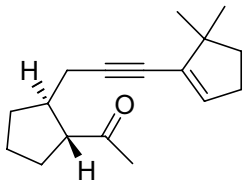
yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (1H, bs), 2.54-2.49 (2H, m), 2.28 (2H, t, *J* = 6.8 Hz), 2.13-2.07 (6H, m), 1.78-1.70 (4H, m), 1.18-1.09 (2H, m), 0.81 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.55, 22.69, 23.70, 27.00, 27.14, 29.89, 30.95, 32.02, 42.18, 43.15, 82.77, 86.19, 120.54, 133.58, 208.16; IR(neat) 834, 1157, 1365, 1715, 2951 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{26}O$ (M+Na)+ 269.1876. Found 269.1876.

7-Cyclohept-1-enyl-hept-6-yn-2-one (1r)



yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15-6.11 (1H, m), 2.51 (2H, t, *J* = 7.2 Hz), 2.29-2.23 (4H, m), 2.15-2.08 (5H, m), 1.76-1.66 (4H, m), 1.51-1.44 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.59, 22.70, 26.42, 26.45, 28.86, 29.88, 32.01, 34.38, 42.22, 84.67, 85.93, 126.96, 138.34, 208.21; IR(neat) 852, 1158, 1356, 1445, 1713, 2922 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

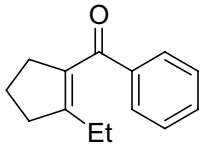
1-{2-[3-(5,5-Dimethyl-cyclopent-1-enyl)-prop-2-ynyl]-cyclopentyl}-ethanone (1s)



yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (1H, m), 2.77-2.70 (1H, m), 2.39-2.25 (5H, m), 2.15 (3H, s), 1.93-1.42 (8H, m), 1.04 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.33, 24.80, 27.03, 29.29, 29.84, 30.29, 31.81, 38.83, 40.83, 46.66, 56.81, 77.23, 90.24, 133.57, 134.80, 210.57 cm^{-1}; IR(neat) 825, 1165, 1359, 1454, 1708, 2953 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{24}O$ (M+Na)+ 267.1719. Found 267.1719.

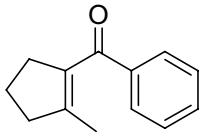
Spectroscopic data of (2)

(2-Ethyl-cyclopent-1-enyl)-phenyl-methanone (2a)



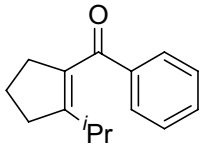
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.74 (2H, m), 7.53-7.48 (H, m), 7.44-7.38 (2H, m), 2.75-2.69 (2H, m), 2.55-2.52 (2H, m), 2.07 (2H, q, *J* = 7.5 Hz m), 1.96-1.86 (2H, m), 0.93 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.37, 22.22, 23.37, 35.83, 36.70, 128.24, 128.66, 132.28, 135.32, 138.92, 154.27, 197.43; IR(neat) 695, 717, 878, 1174, 1275, 1349, 1446, 1640, 2964 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{16}O$ (M+Na)+ 223.1093. Found 223.1093.

(2-Methyl-cyclopent-1-enyl)-phenyl-methanone (2b)



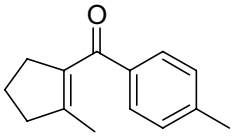
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (2H, m), 7.52-7.46 (1H, m), 7.43-7.37 (2H, m) 2.76-2.71 (2H, m), 2.53-2.47 (2H, m), 1.94-1.84 (2H, m), 1.66-1.64 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.59, 22.07, 35.66, 40.37, 128.25, 128.69, 132.13, 136.04, 139.04, 149.89, 197.02; IR(neat) 695, 719, 881, 1268, 1349, 1446, 1597, 1637, 2912 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}O$ (M+Na)+ 209.0937. Found 209.0937.

(2-Isopropyl-cyclopent-1-enyl)-phenyl-methanone (2c)



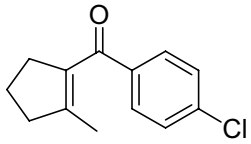
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.78 (2H, m), 7.55-7.50 (1H, m), 7.46-7.41 (2H, m), 2.72-2.62 (3H, m), 2.55-2.49 (2H, m), 1.96-1.86 (2H, m), 0.96 (6H, d, *J* = 6.6 Hz; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.09, 22.44, 28.33, 32.01, 35.95, 128.34, 128.78, 132.51, 134.47, 138.75, 157.10, 198.01; IR(neat) 696, 729, 909,1263, 1447, 1645, 2249, 2961 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{18}O$ (M+Na)+ 237.1250. Found 237.1250.

(2-Methyl-cyclopent-1-enyl)-(*p*-tolyl)-methanone (2d)



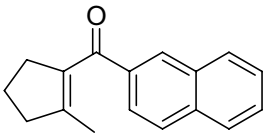
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.68 (2H, m), 7.27-7.23 (2H, m), 2.80-2.73 (2H, m), 2.56-2.50 (2H, m), 2.42 (3H, s), 1.98-1.88 (2H, m), 1.69-1.66 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.61, 21.61, 22.21, 35.86, 40.29, 129.04, 129.07, 136.24, 136.33, 143.03, 148.76, 197.03; IR(neat) 752, 831, .1176, 1269, 1374, 1606, 1636, 2915 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{16}O$ (M+Na)+ 223.1093. Found 223.1093.

(4-Chloro-phenyl)-(2-methyl-cyclopent-1-enyl)-methanone (2e)



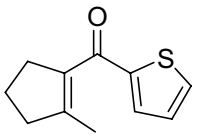
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.67 (2H, m), 7.42-7.372 (2H, m), 2.76-2.69 (2H, m), 2.54-2.49 (2H, m), 1.96-1.86 (2H, m), 1.67-1.66 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.77, 22.12, 35.67, 40.47, 128.66, 130.23, 135.82, 137.40, 138.55, 150.55, 195.70; IR(neat) 758, 841, 1012, 1088, 1268, 1586, 1637, 2912 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{13}ClO$ (M+Na)+ 243.0547. Found 243.0547.

(2-Methyl-cyclopent-1-enyl)-(naphthalen-2-yl)-methanone (2f)



slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (1H, s), 7.94-7.85 (4H, m), 7.59-7.49 (2H, m), 2.87-2.80 (2H, m), 2.59-2.54 (2H, m), 2.02-1.92 (2H, m), 1.70-1.69 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.67, 22.12, 35.82, 40.38, 124.68, 126.49, 127.69, 127.96, 128.16, 129.25, 130.37, 132.49, 135.19, 136.22, 136.26, 149.64, 196.98; IR(neat) 759, 776, 1277, 1355, 1622, 2341, 2911 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}O$ (M+Na)+ 259.1093. Found 259.1093.

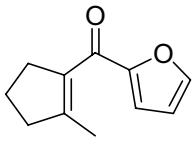
(2-Methyl-cyclopent-1-enyl)-(thiophen-2-yl)-methanone (2g)



slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.61 (2H, m), 7.11-7.08 (1H, m), 2.86-2.79 (2H, m), 2.53-2.48 (2H, m), 1.97-1.90 (2H, m), 1.87-1.86 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.68, 22.53, 35.90, 40.03, 127.82, 132.81, 133.42, 135.56, 145.35, 149.94,

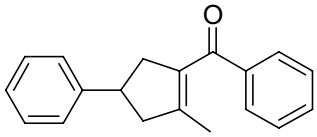
188.23; IR(neat) 718, 791, 1040, 1271, 1412, 1515, 1619, 2913 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}OS$ (M+Na)+ 215.0501. Found 215.0501.

(Furan-2-yl)-(2-methyl-cyclopent-1-enyl)-methanone (2h)



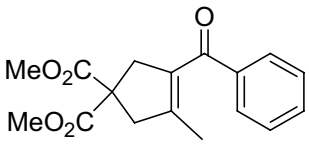
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (1H, m), 7.42-7.41 (1H, m), 7.79-7.78 (1H, m) 2.80-2.75 (2H, m), 2.51-2.47 (2H, m), 1.93-1.86 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.71, 22.39, 35.38, 40.21, 109.48, 128.39, 136.23, 143.58, 147.41, 151.17, 189.02; IR(neat) 756, 806, 872, 1005, 1070, 1162, 1307, 1508, 1560, 1636, 2916 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O_2$ (M+Na)+ 199.0730. Found 199.0730.

(2-Methyl-4-phenyl-cyclopent-1-enyl)-phenyl-methanone (2i)



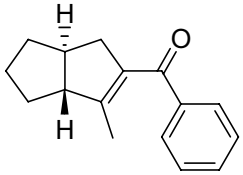
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.73 (2H, m), 7.51-7.37 (3H, m), 7.30-7.15 (5H, m), 3.59-3.48 (1H, m), 3.18-3.10 (1H, m), 2.98-2.28 (2H, m), 2.71-2.63 (1H, m), 1.69 (3H, bs); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.74, 42.04, 43.53, 48.08, 126.13, 126.85, 128.40, 128.47, 128.78, 132.33, 135.17, 139.01, 145.56, 148.80, 196.43; IR(neat) 696, 722, 1250, 1346, 1446, 1597, 1636, 2249, 2914 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{18}O$ (M+Na)+ 285.1250. Found 285.1250.

3-Benzoyl-4-methyl-cyclopent-3-ene-1,1-dicarboxylic acid dimethyl ester (2j)



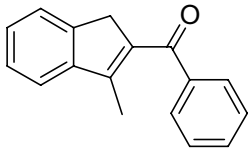
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (2H, m), 7.56-7.50 (1H, m), 7.45-7.40 (2H, m), 3.77 (6H, s), 3.42-3.40 (2H, m), 3.20-3.19 (2H, m), 1.66 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.25, 42.99, 47.19, 52.99, 57.19, 128.50, 128.86, 132.61, 133.02, 138.59, 145.92, 171.99, 195.26; IR(neat) 719, 1071, 1250, 1434, 1641, 1732, 2954 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}O_5$ (M+Na)+ 325.1046. Found 325.1046.

(3-Methyl-1,3a,4,5,6,6a-hexahydro-pentalen-2-yl)-phenyl-methanone (2k)



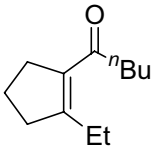
slight yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (2H, m), 7.54-7.48 (1H, m), 7.45-7.39 (2H, m), 3.19-3.14 (1H,m), 3.07-2.98 (1H, m), 2.76-2.65 (1H, m), 2.44-2.38 (1H, m), 1.86-1.71 (2H, m), 1.62-1.55 (6H, m), 1.46-1.36 (1H,m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.30, 25.83, 30.88, 35.39, 39.06, 42.68, 57.04, 128.36, 128.75, 132.26, 134.69, 138.95, 150.18, 197.33; IR(neat) 694, 711, 791, 908, 1174, 1271, 1344, 1446, 1597, 1639, 2941 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}O$ (M+Na)+ 249.1250. Found 249.1250.

(3-Methyl-1H-inden-2-yl)-phenyl-methanone (2l)



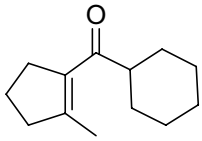
slight yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (2H, m), 7.57-7.44 (5H, m), 7.41-7.38 (2H, m), 3.86-3.85 (2H, m), 2.18-2.16 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.45, 40.15, 121.14, 123.96, 126.75, 127.57, 128.37, 128.75, 132.05, 138.77, 140.07, 143.53, 145.43, 147.93, 195.46; IR(neat) 654, 696, 724, 761, 929, 950, 1270, 1357, 1568, 1614 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{14}O$ (M+Na)+ 257.0937. Found 257.0937.

1-(2-Ethyl-cyclopent-1-enyl)-pentan-1-one (2m)



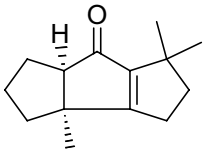
slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65-2.64 (2H, m), 2.56-2.41 (6H, m), 1.85-1.78 (2H, m), 1.59-1.53 (2H, m), 1.35-1.25 (3H, m), 1.08-1.02 (3H, m), 0.93-0.89 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.43, 13.95, 21.72, 22.44, 23.47, 25.85, 34.20, 37.55, 41.90, 134.58, 159.15, 201.20; IR(neat) 1174, 1459, 1610, 1676, 2957 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{20}O$ (M+Na)+ 203.1406. Found 203.1406.

Cyclohexyl-(2-methyl-cyclopent-1-enyl)-methanone (2n)



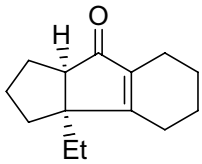
slight yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68-2.65 (2H, m), 2.60-2.56 (1H, m), 2.47-2.43 (2H, m), 2.03 (3H, s), 1.86-1.66 (6H, m), 1.38-1.19 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.60, 21.75, 25.87, 25.98, 28.49, 34.15, 40.71, 48.75, 135.03, 153.47, 204.83; IR(neat) 770, 964, 1163, 1250, 1371, 1447, 1607, 1672, 2851, 2925 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{20}O$ (M+Na)+ 215.1406. Found 215.1406.

3a,6,6-Trimethyl-1,2,3,3a,4,5,6,7a-octahydro-cyclopenta[*a*]pentalen-7-one (3o)



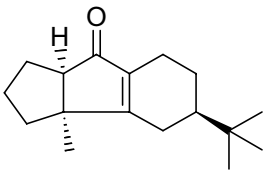
brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (1H, d, *J* = 9.5 Hz), 2.45-2.31 (2H, m), 2.12-2.06 (2H, m), 1.89-1.85 (1H, m), 1.73-1.61 (4H, m), 1.34-1.24 (4H, m), 1.20 (3H, s), 1.17 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.88, 25.29, 25.81, 26.75, 26.90, 29.55, 35.78, 40.55, 44.81, 48.53, 64.55, 154.19, 189.01, 205.41; IR(neat) 840, 966, 989, 1291, 1364, 1383, 1446, 1635, 1682, 2865, 2953 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

3a-Ethyl-2,3,3a,4,5,6,7,8a-octahydro-1H-cyclopenta[*a*]inden-8-one (3p)



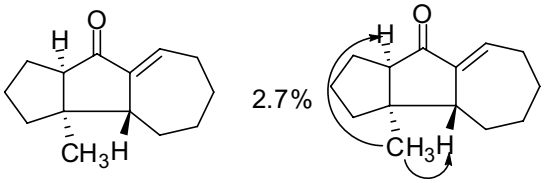
brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (1H, d, *J* = 9.3 Hz), 2.19-2.09 (4H, m), 1.86-1.78 (1H, m), 1.75-1.49 (9H, m), 1.40-1.27 (1H, m),1.23-1.07 (1H, m), 0.70 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.66, 20.00, 21.78, 22.32, 23.75, 24.40, 28.95, 29.32, 34.64, 54.06, 57.04, 139.63, 176.75, 211.06; IR(neat) 946, 986, 1278, 1389, 1448, 1643, 1693, 2932 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

5-*tert*-Butyl-3a-methyl-2,3,3a,4,5,6,7,8a-octahydro-1H-cyclopenta[*a*]inden-8-one (3q)



brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40-2.26 (4H, m), 1.96-1.55 (6H, m), 1.35-0.99 (7H, m), 0.91 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.94, 23.52, 24.44, 24.69, 25.06, 27.24, 29.26, 32.37, 36.03, 44.52, 52.27, 58.66, 138.20, 178.68, 210.36; IR(neat) 729, 918, 1255, 1365, 1391, 1449, 1646, 1693, 2953 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{26}O$ (M+Na)+ 269.1876. Found 269.1876.

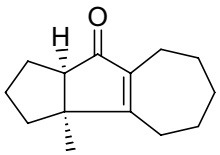
3a-Methyl-1,2,3,3a,3b,4,5,6,7,9a-decahydro-cyclopenta[*a*]azulen-9-one (3r')



NOE experiment

brown oil; ^{1}H NMR (500MHz, $CDCl_3$) δ 6.95-6.92 (1H, m), 2.53-2.42 (2H, m), 2.32-2.29 (1H, m), 2.22-2.16 (1H, m), 2.08-1.99 (2H, m), 1.89-1.61 (6H, m), 1.52-1.25 (4H, m), 1.01 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.03, 24.96, 26.90, 28.35, 29.28, 29.72, 39.61, 48.87, 49.14, 61.15, 139.07, 144.19, 209.29; IR(neat) 1229, 1446, 1643, 1714, 2923 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

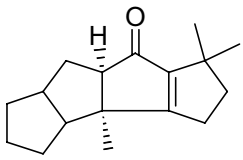
3a-Methyl-1,2,3,3a,4,5,6,7,8,9a-decahydro-cyclopenta[*a*]azulen-9-one (3r)



brown oil;^{1}H NMR (300MHz, $CDCl_3$) δ 2.40 (2H, t, *J* = 5.7 Hz), 2.33-2.23 (3H, m), 1.83-1.70 (5H, m), 1.60-1.40 (5H, m), 1.35-1.10 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.18, 24.08, 24.82, 26.66, 26.88, 29.14, 30.07, 31.90, 35.70, 53.16, 57.34, 142.47, 181.67, 210.53; IR(neat) 731, 972, 1284, 1383, 1445, 1641, 1692, 2922 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}O$ (M+Na)+ 227.1406. Found 227.1406.

3b,6,6-Trimethyl-2,3,3a,3b,4,5,6,7a,8,8a-decahydro-1H-dicyclopenta[*a,f*]pentalen-7-one

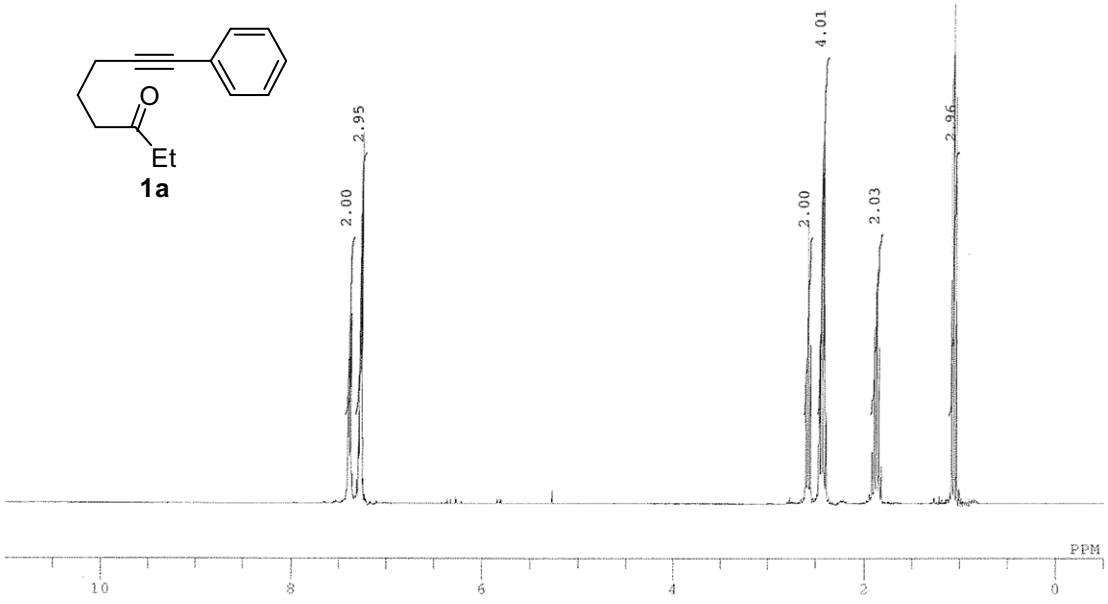
(3s)

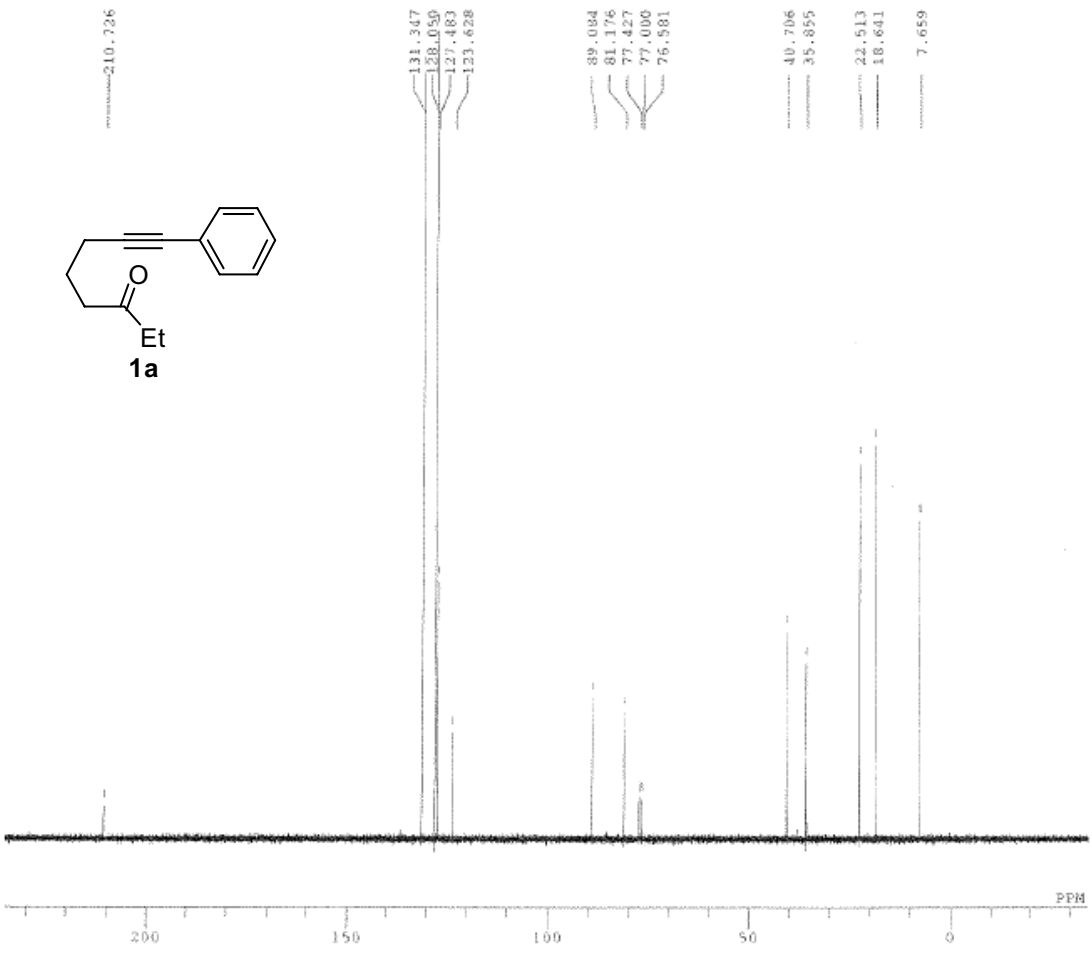


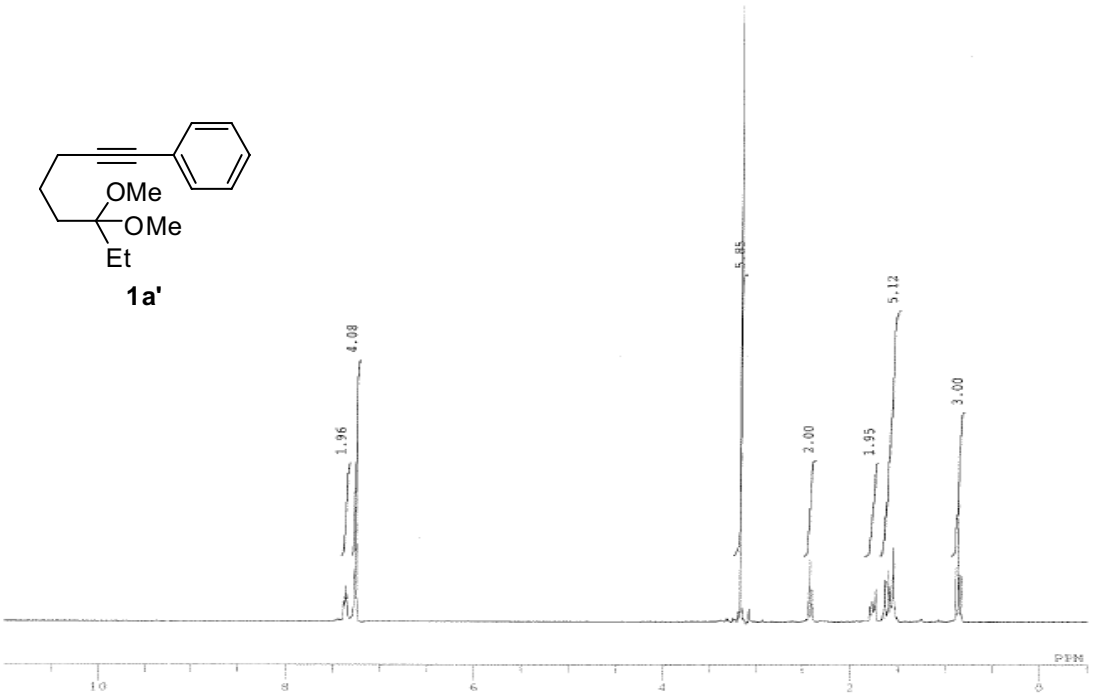
1.7:1 mixture of diastereomers (C_6D_6)

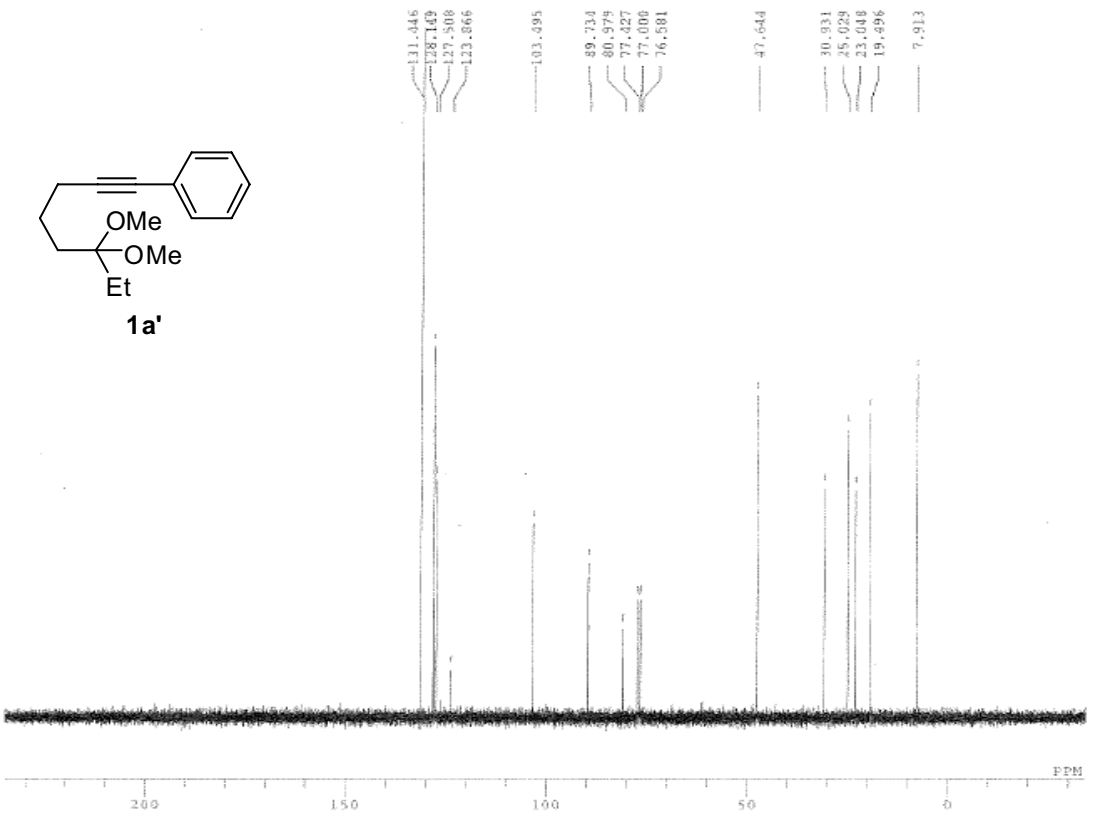
brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78-2.70 (1H, m), 2.63 (1H, d, *J* = 10.0 Hz), 2.44-2.33 (3H, m), 2.25-2.21 (1H, m), 2.12-2.01 (5H, m), 1.96-1.92 (1H, m), 1.87-1.83 (1H, m), 1.78-1.71 (2H, m), 1.61-1.41 (7H, m), 1.30-1.15 (13H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.24, 25.66, 25.75, 26.05, 26.20, 26.62, 26.73, 26.75, 26.90, 27.14, 27.42, 27.77, 29.47, 30.34, 32.76, 35.55, 40.37, 40.42, 43.33, 44.84, 44.87, 48.41, 50.72, 50.74, 51.93, 53.38, 66.10, 67.85, 152.02, 152.29, 187.29, 190.86, 205.83, 205.94 cm^{-1}; IR(neat) 896, 1364, 1384, 1452, 1634, 1687, 2864, 2951 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{24}O$ (M+Na)+ 267.1719. Found 267.1719.

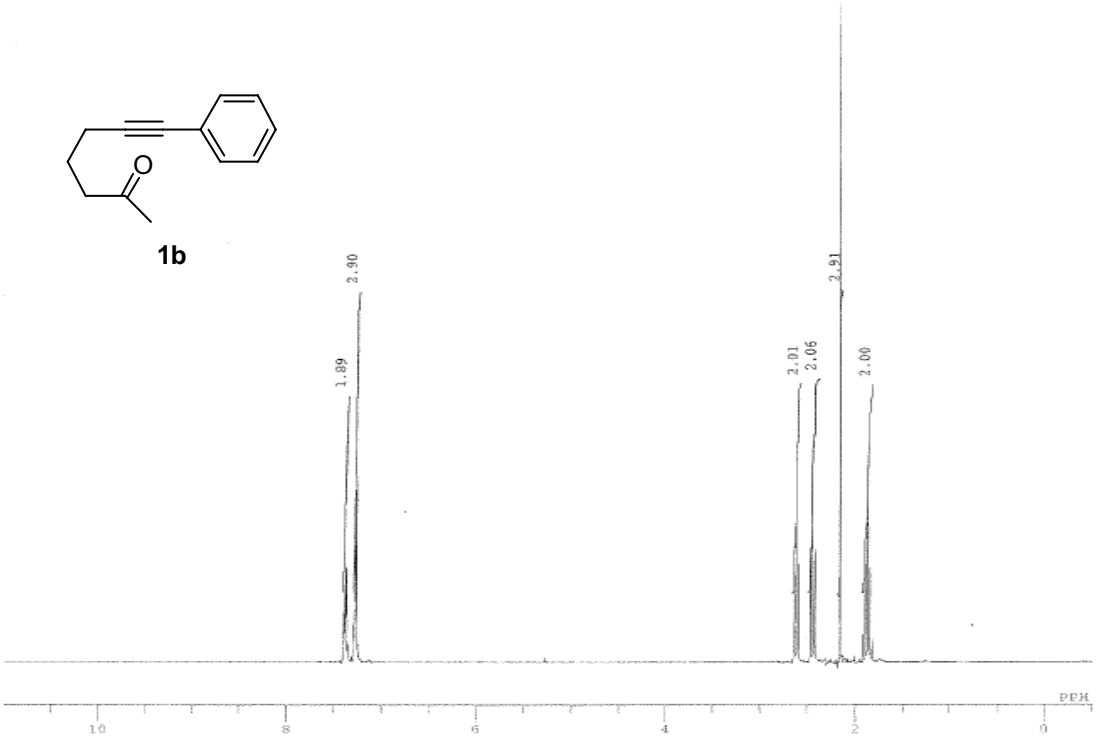
^{1}H NMR and ^{13}C NMR charts of (1), (2), and (3)



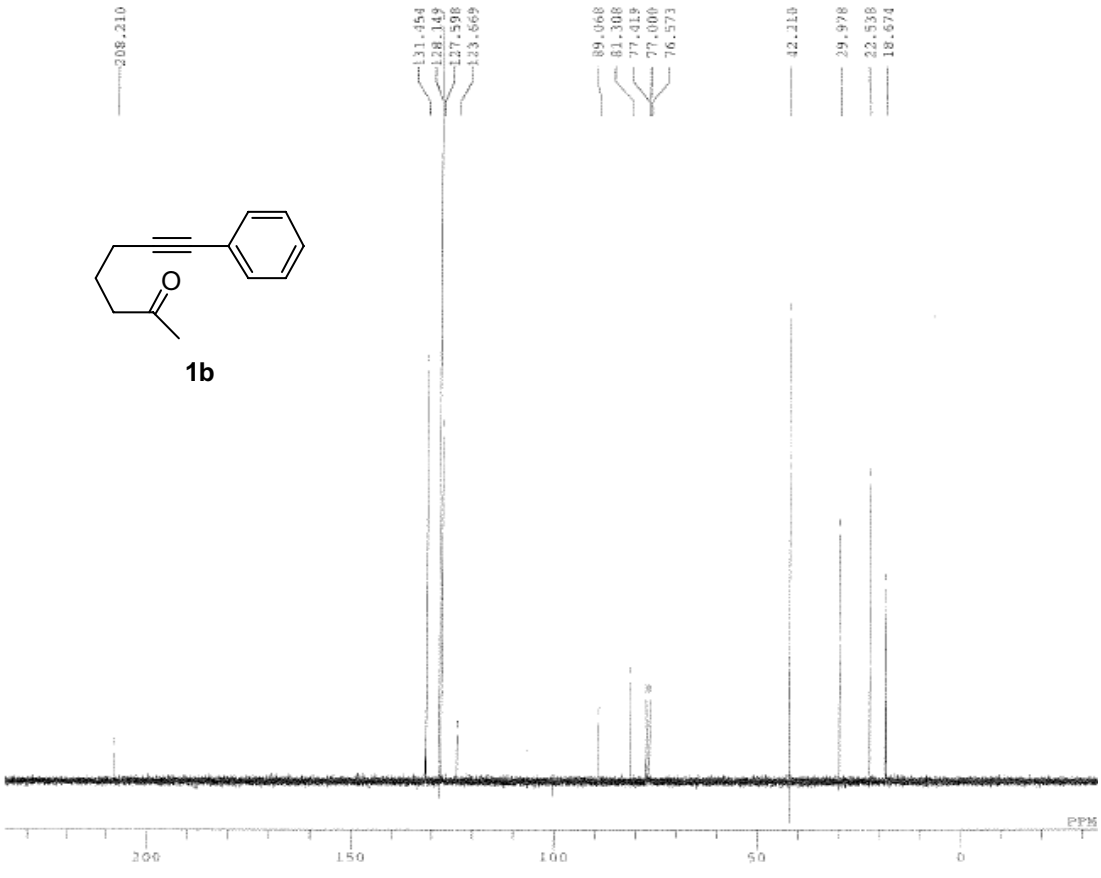

210.726
131.347
128.050
127.483
123.628
89.084
81.176
77.427
77.000
76.581
40.706
35.855
22.513
18.641
7.659
O
Et
1a
PPM
200
150
100
50
0


OMe
OMe
Et
1a'
1.96
4.08
5.85
2.00
1.95
5.12
3.00
PPM
10
8
6
4
2
0


131.446
128.149
127.908
123.866
103.395
99.734
80.974
77.427
77.000
76.581
47.644
30.931
25.029
23.048
19.496
7.913
OMe
OMe
Et
1a'
PPM
200
150
100
50
0


1.89
2.90
2.01
2.06
2.91
2.00
PPM
10
8
6
4
2
0

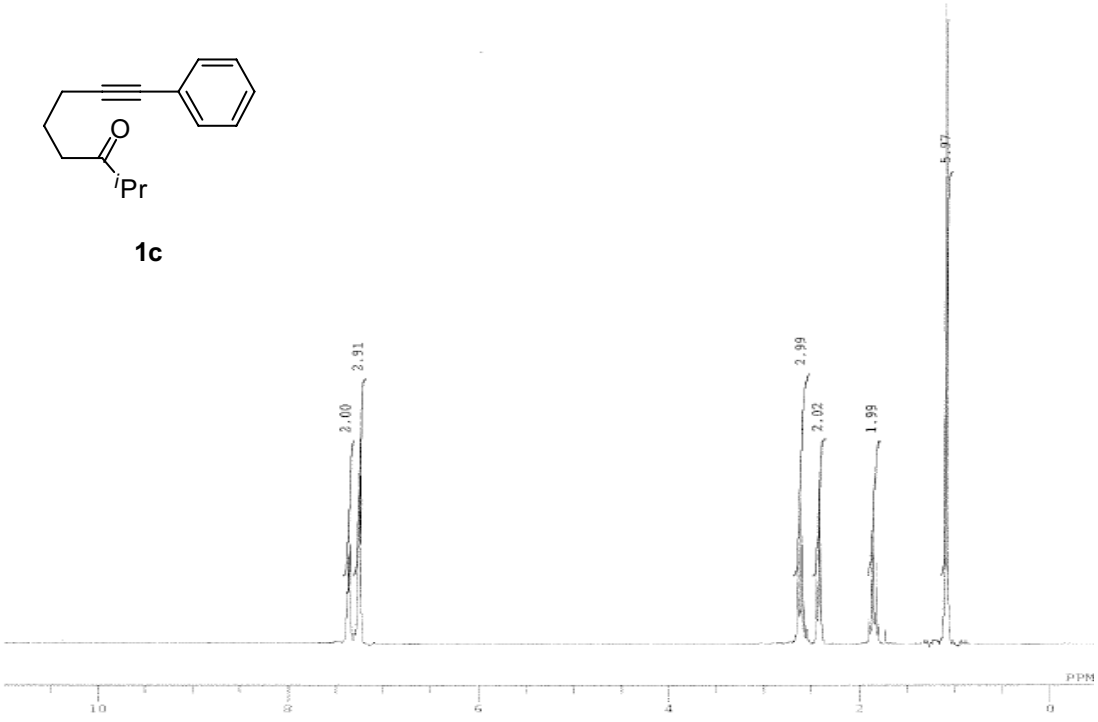
1b

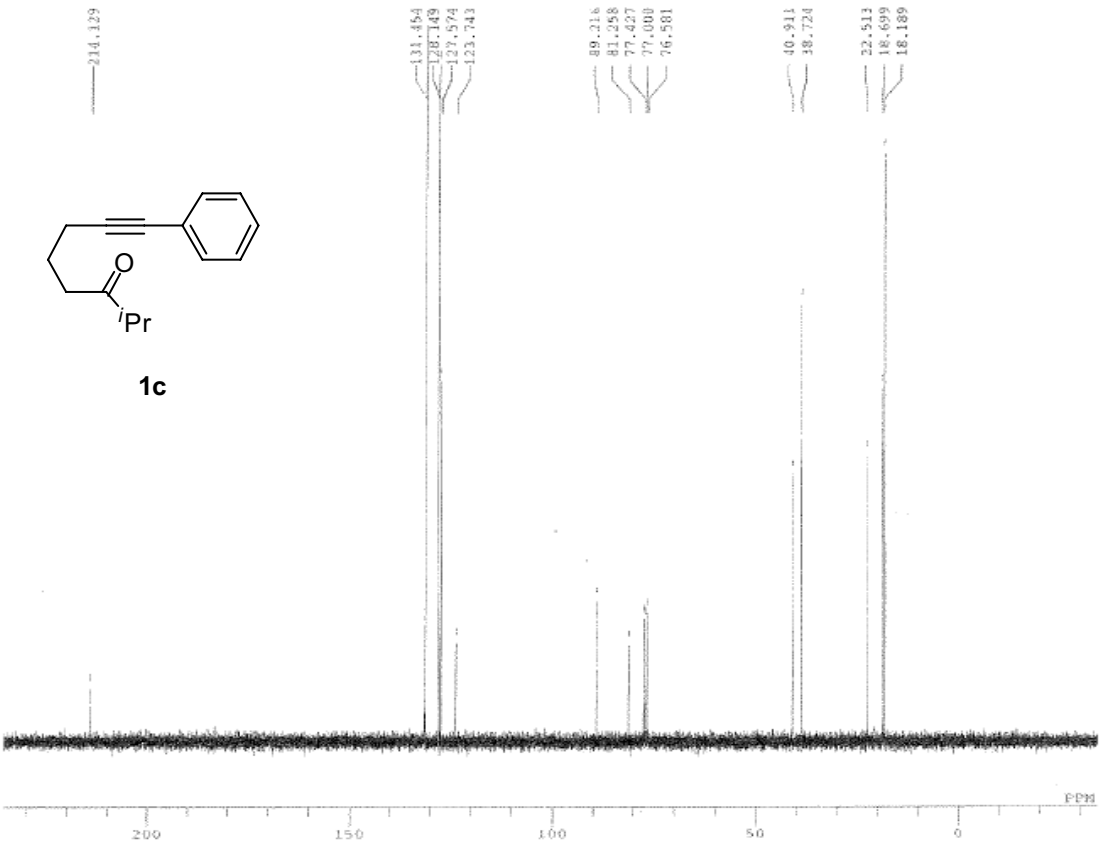

208.210
131.454
128.149
127.598
123.669
89.068
81.308
77.419
77.000
76.573
42.210
29.978
22.538
18.674
PPM
200
150
100
50
0

1b

O
iPr

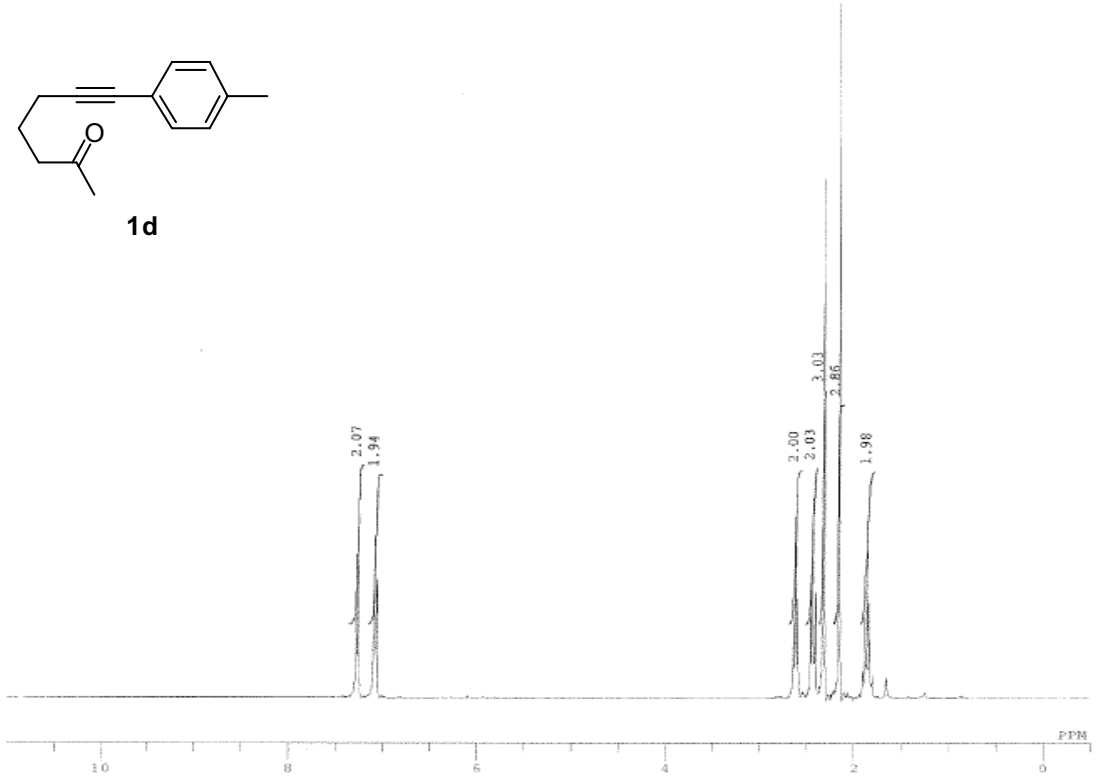
1c


2.00
2.91
2.99
2.02
1.99
5.97
PPM
10
8
6
4
2
0

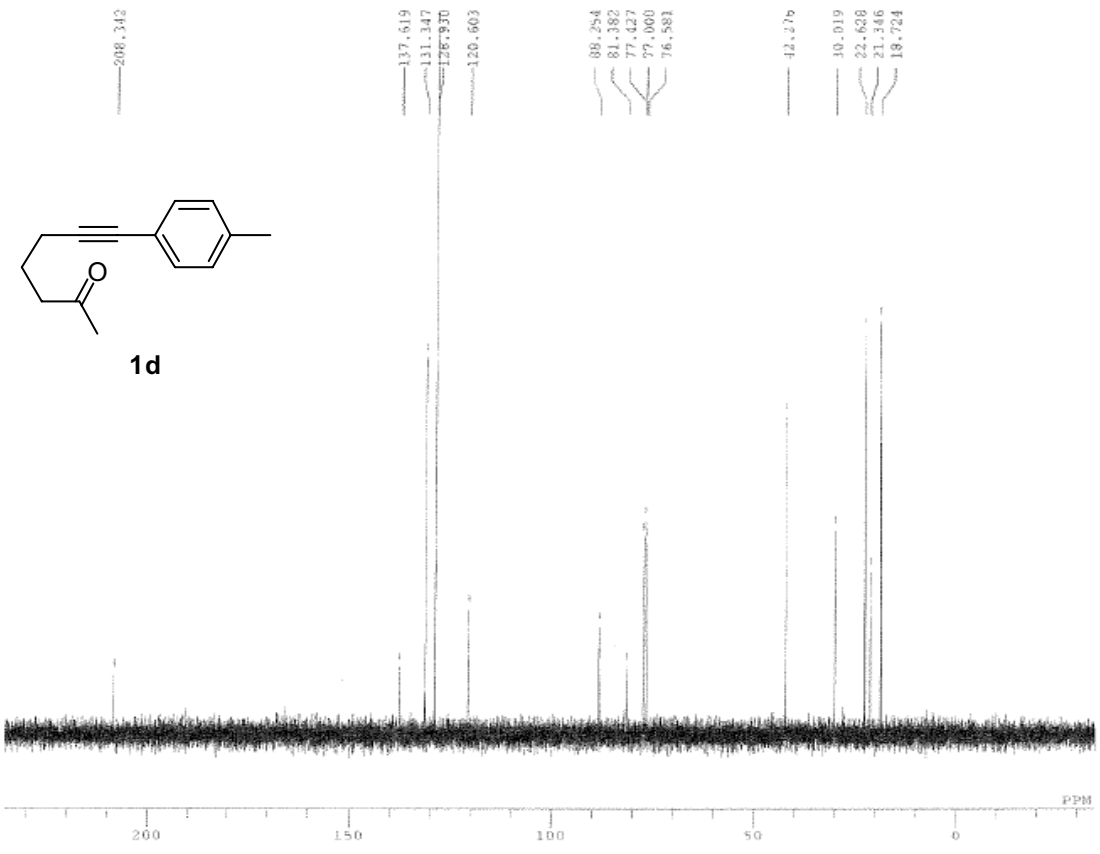

214.129
131.454
128.149
127.574
123.743
89.216
81.458
77.427
77.000
76.581
40.911
38.724
22.513
18.699
18.189
PPM
200
150
100
50
0

O
iPr

1c


2.07
1.94
2.00
2.03
3.03
2.86
1.98
PPM
10
8
6
4
2
0

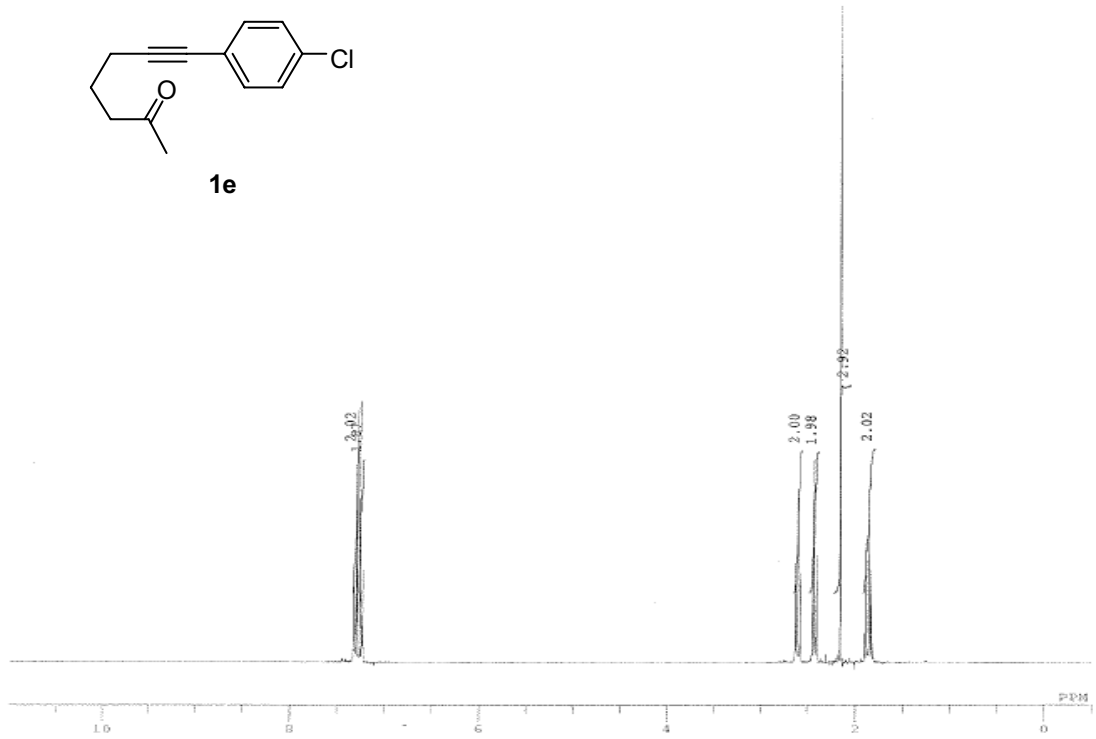
1d

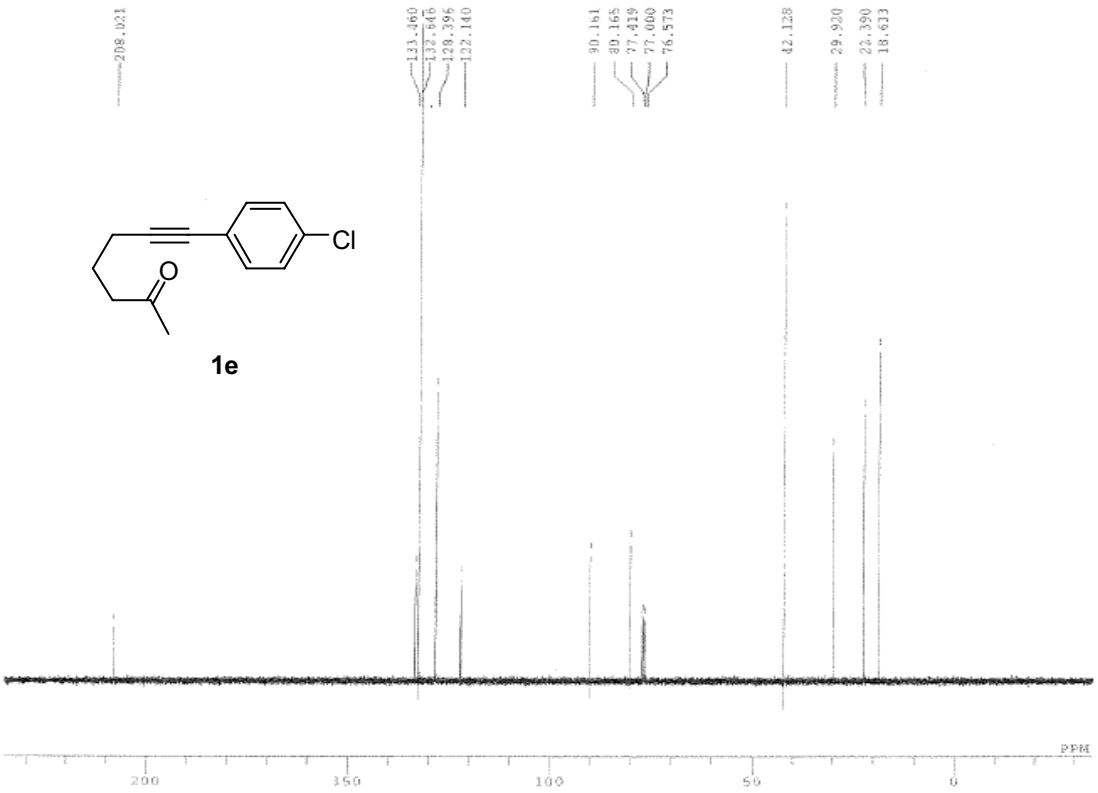

208.342
137.619
131.347
128.930
120.603
89.254
81.382
77.427
77.000
76.581
42.276
30.019
22.628
21.346
18.724
PPM
200
150
100
50
0

1d

Cl
O

1e

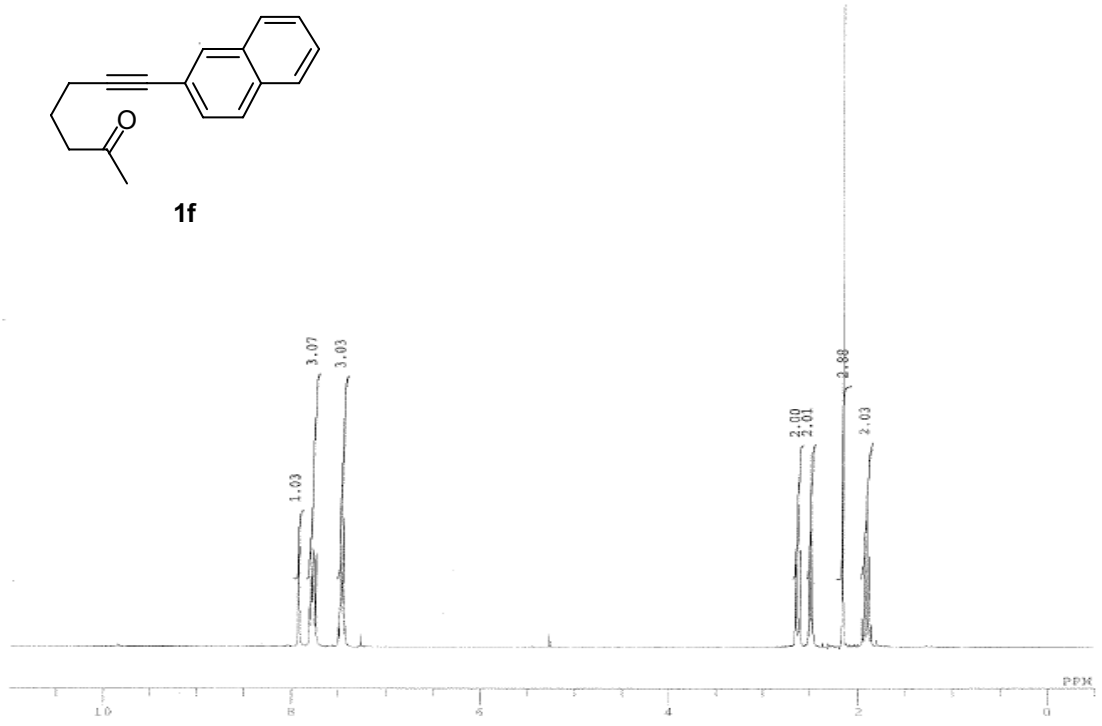

2.02
2.00
1.98
2.92
2.02
PPM
10
8
6
4
2
0


208.021
133.460
132.645
128.396
122.140
90.161
89.165
77.419
77.000
76.573
42.128
29.930
22.390
18.633
PPM
200
150
100
50
0

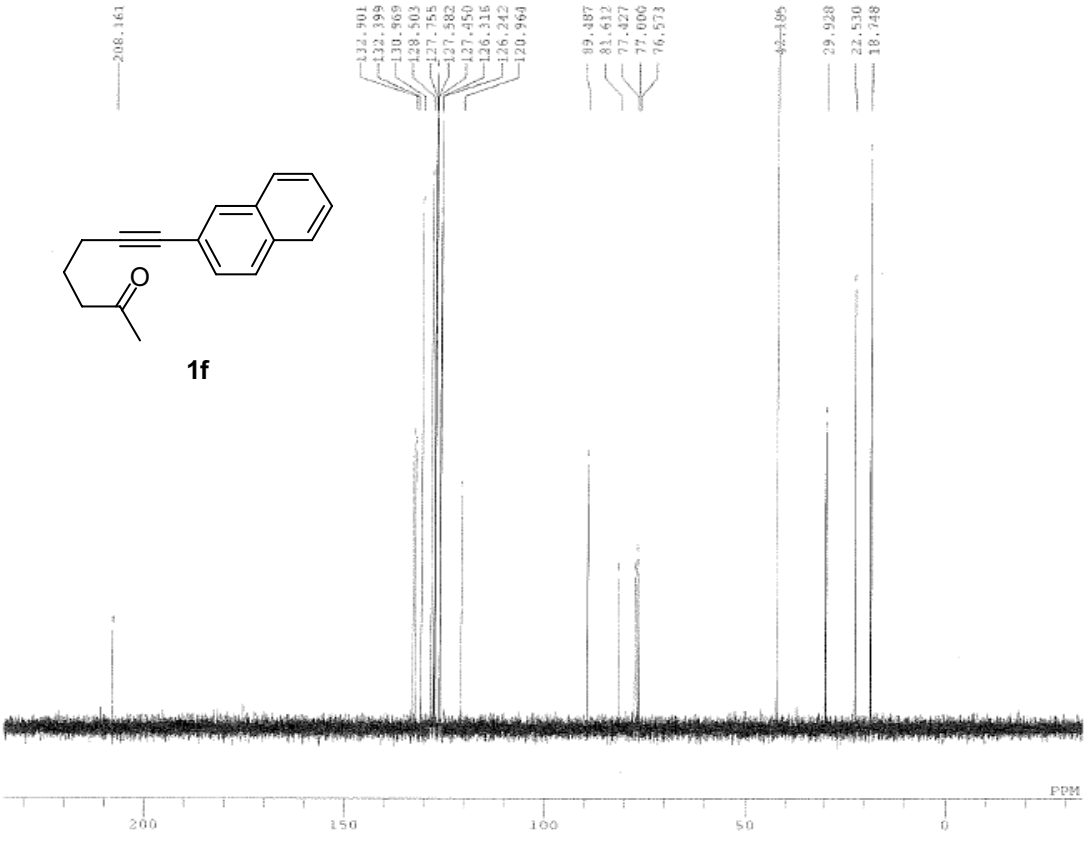
Cl
O

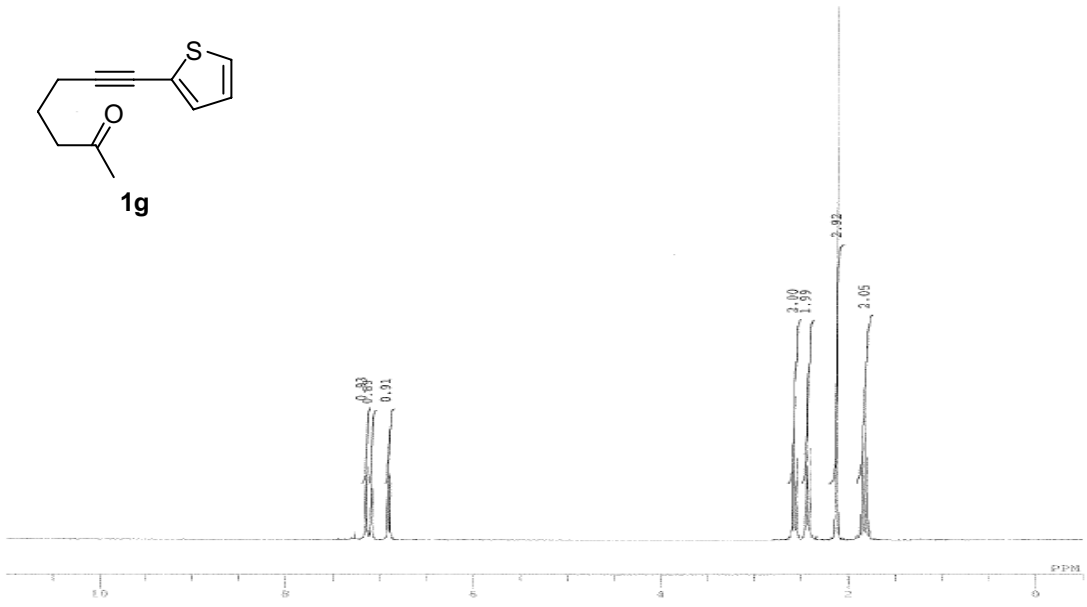
1e

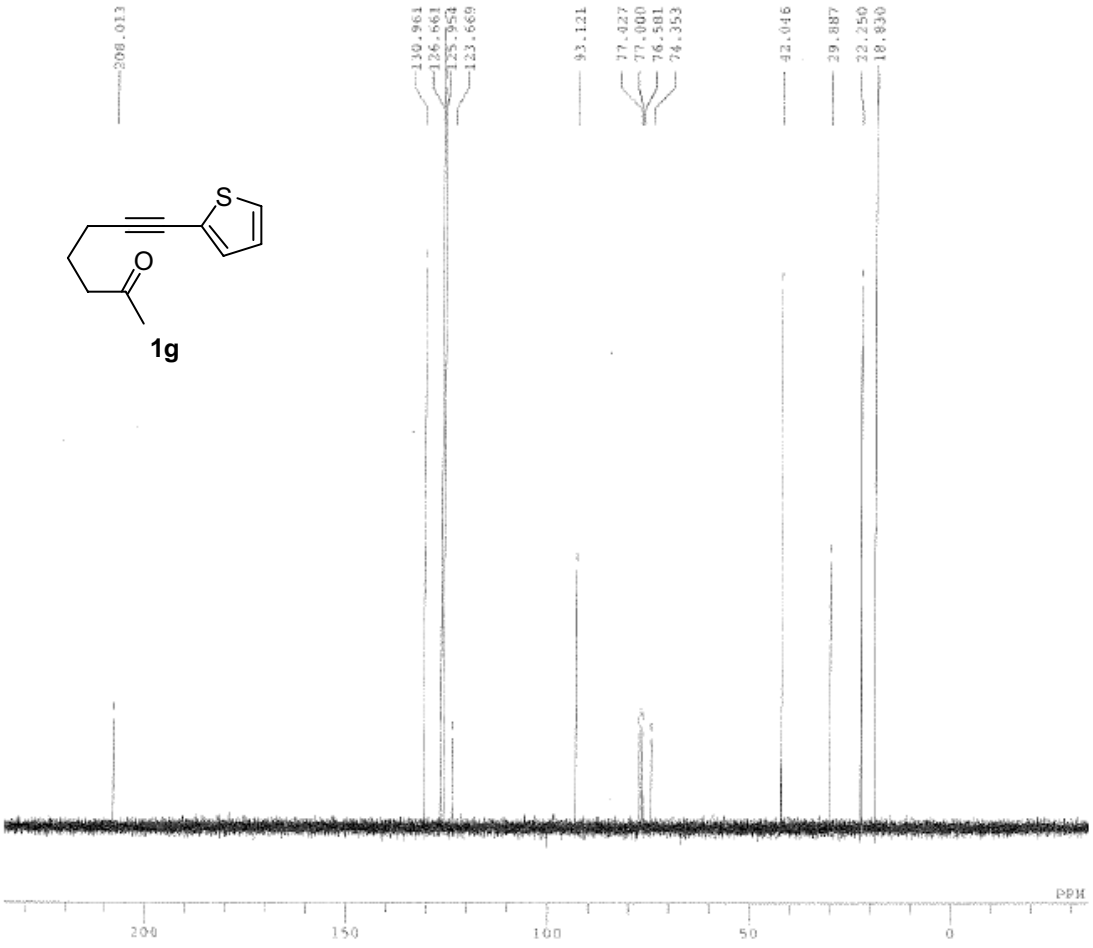
1f


1.03
3.07
3.03
2.00
2.01
3.88
2.03
PPM
10
8
6
4
2
0

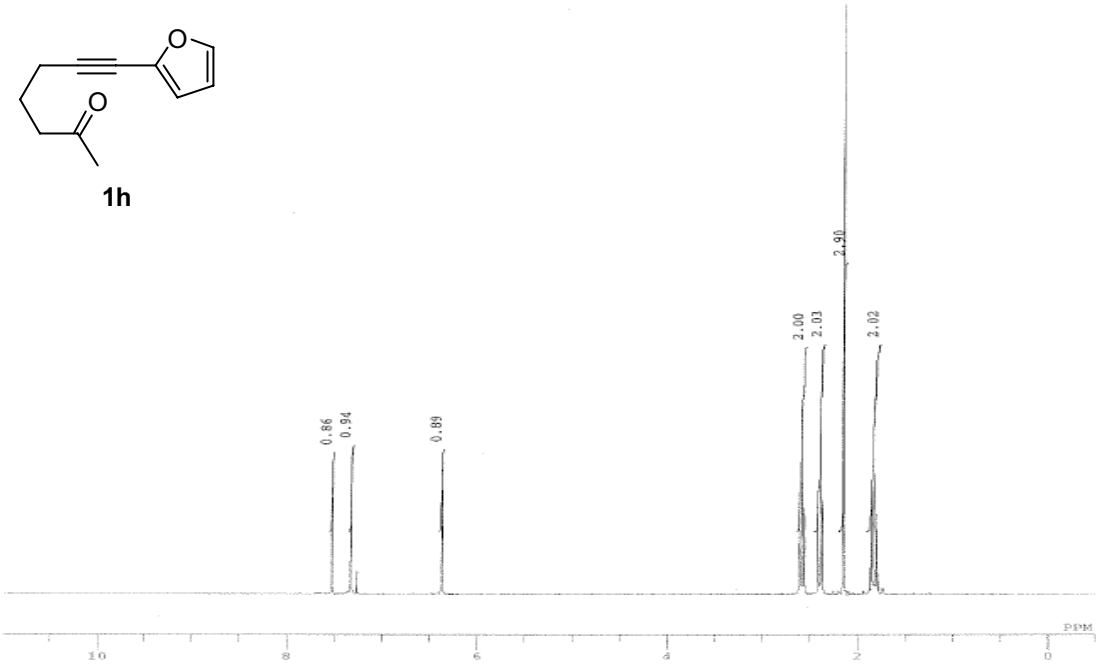
1f


208.161
132.901
132.399
130.969
128.503
127.755
127.582
127.450
126.316
126.242
120.964
89.487
81.612
77.427
77.000
76.573
40.395
29.928
22.530
18.748
PPM
200
150
100
50
0

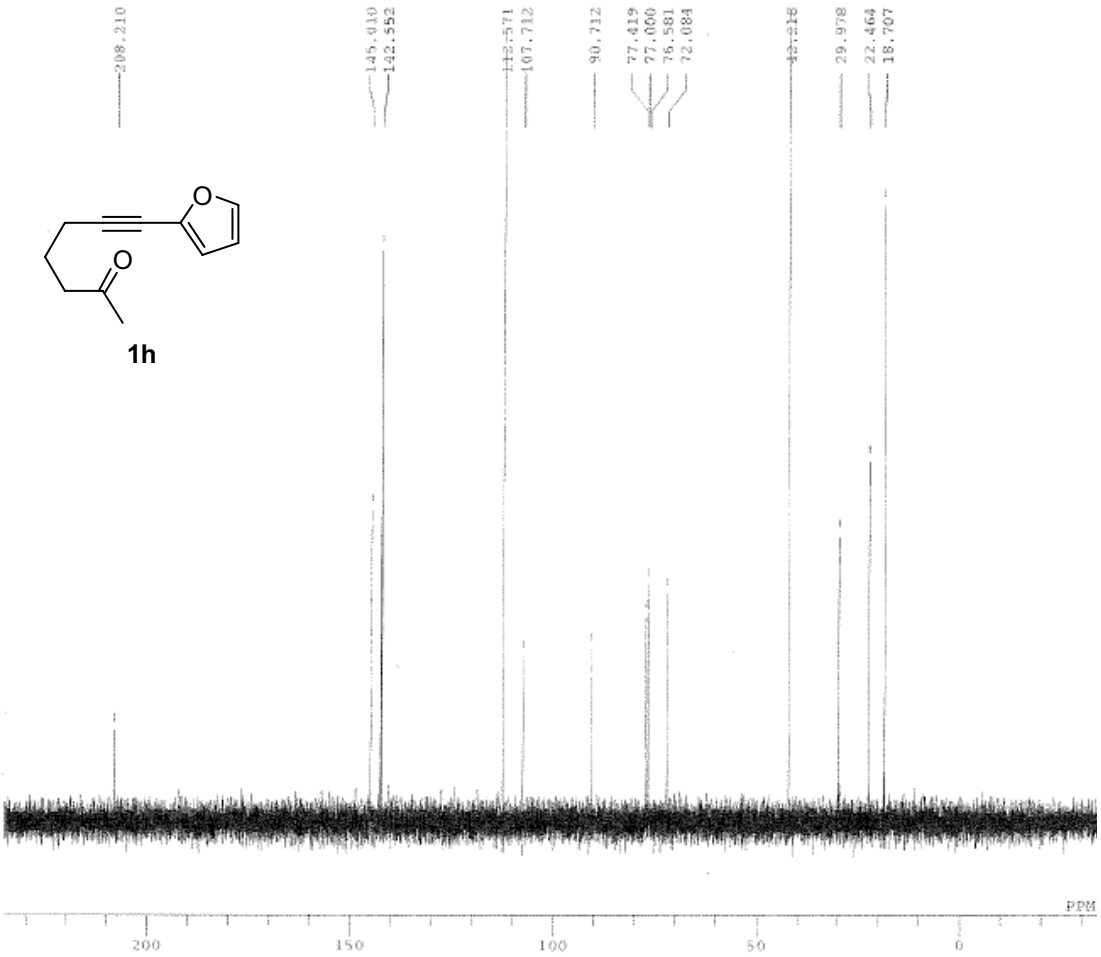

S
O
1g
0.93
0.89
0.91
2.00
1.99
2.92
2.05
PPM

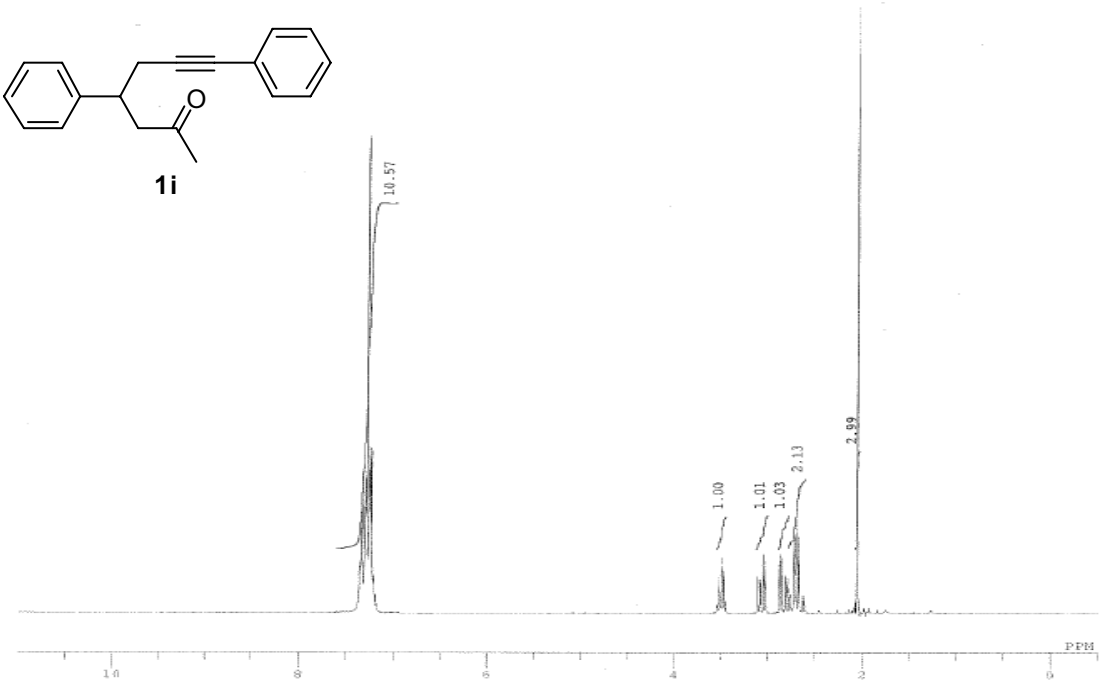

208.013
130.961
126.661
125.954
123.669
93.121
77.427
77.000
76.581
74.353
42.046
29.887
22.250
18.830
S
O
1g
PPM
200
150
100
50
0

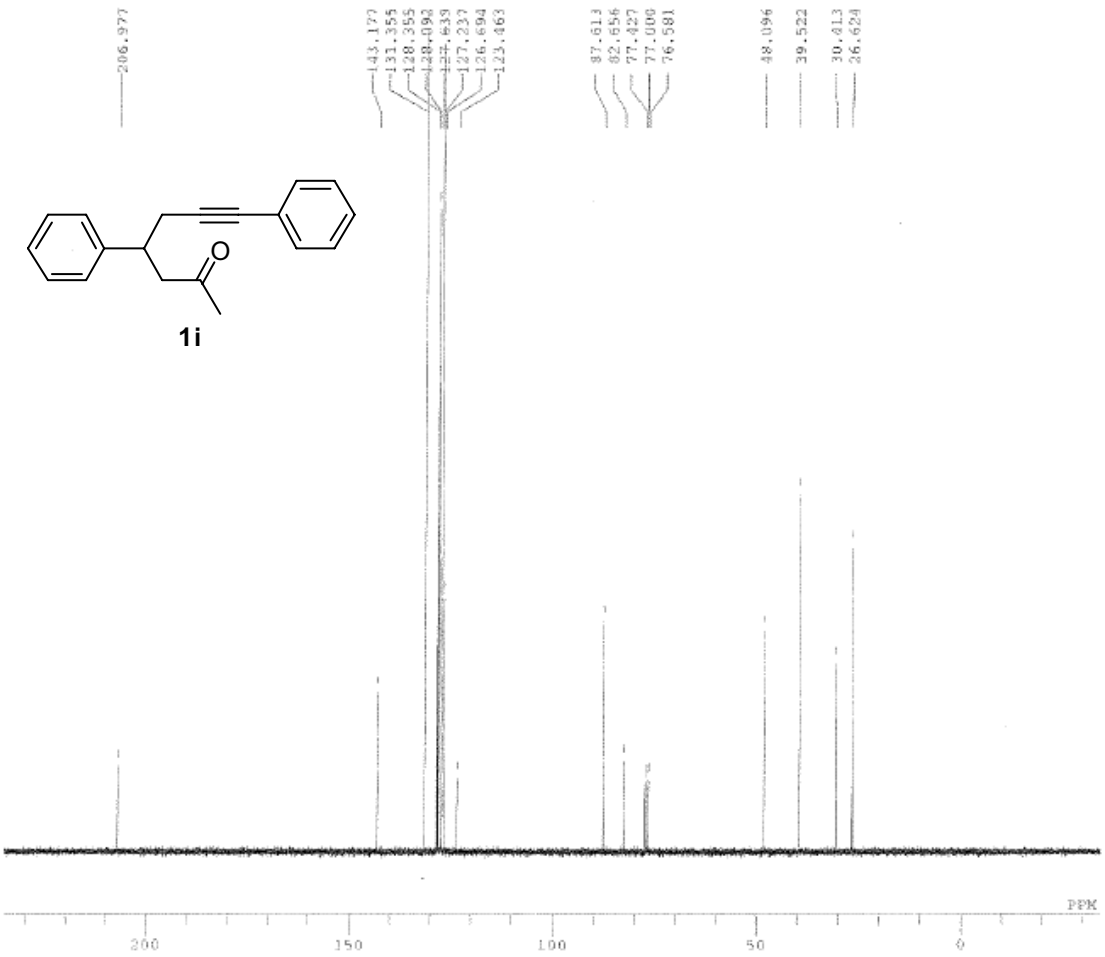
1h


0.86
0.94
0.89
2.00
2.03
2.90
2.02
PPM
10
8
6
4
2
0

1h

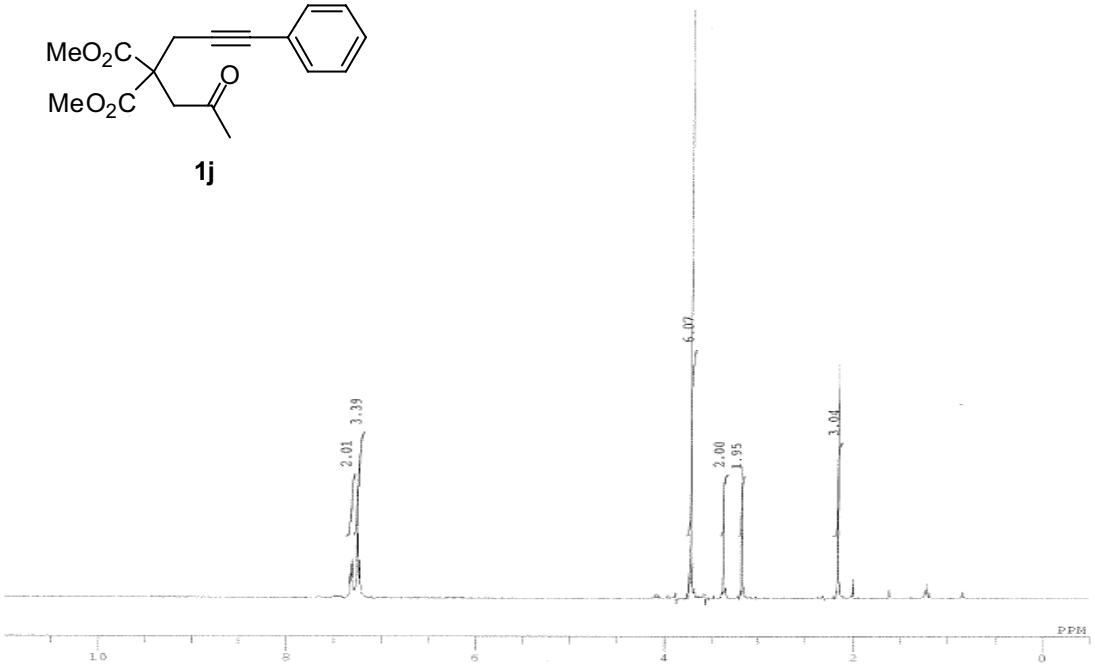

208.210
145.930
142.552
113.571
107.712
90.732
77.419
77.000
76.581
72.084
43.218
29.978
22.464
18.707
PPM
200
150
100
50
0


O
1i
10.57
1.00
1.01
1.03
2.13
2.99
PPM

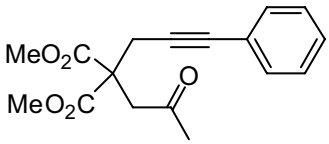

206.977
143.177
131.355
128.355
128.093
128.039
127.237
126.694
123.463
87.613
82.656
77.427
77.000
76.581
48.096
39.522
30.413
26.624
O
1i
PPM

MeO2C
MeO2C
O

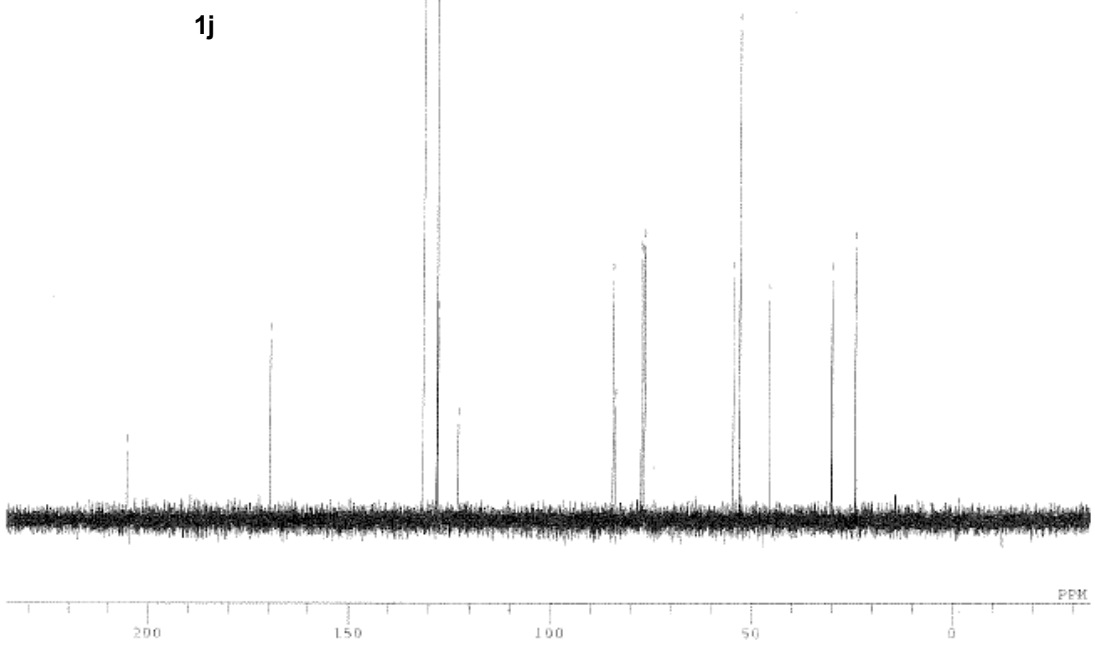
1j

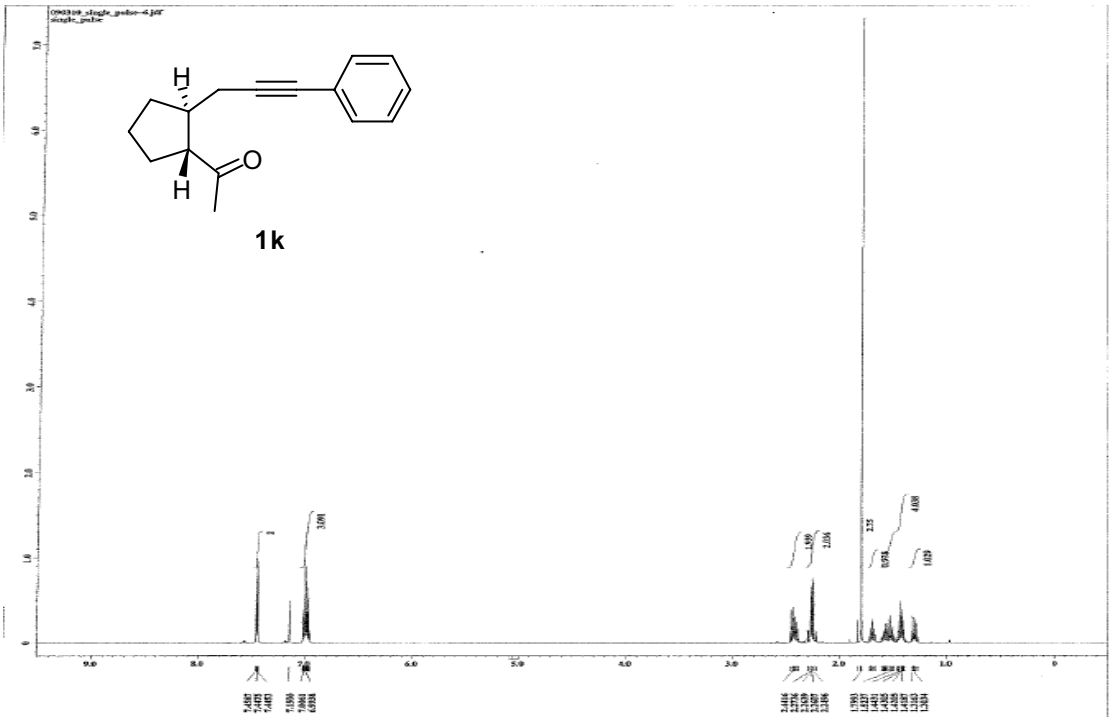

2.01
3.39
6.07
2.00
1.95
3.04
PPM
10
8
6
4
2
0


205.333
169.680
131.569
128.223
128.092
122.945
84.399
83.790
77.427
77.000
76.581
54.681
53.070
45.589
30.183
24.264

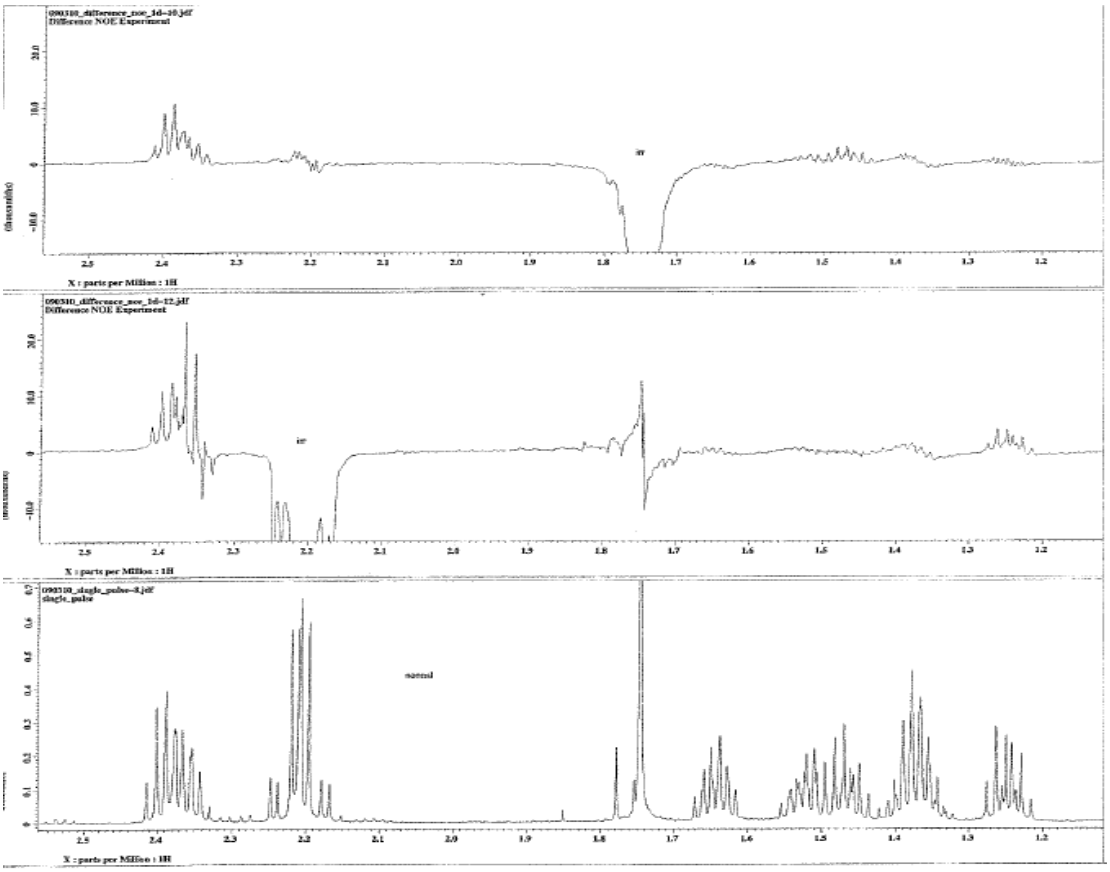

MeO2C
MeO2C
O

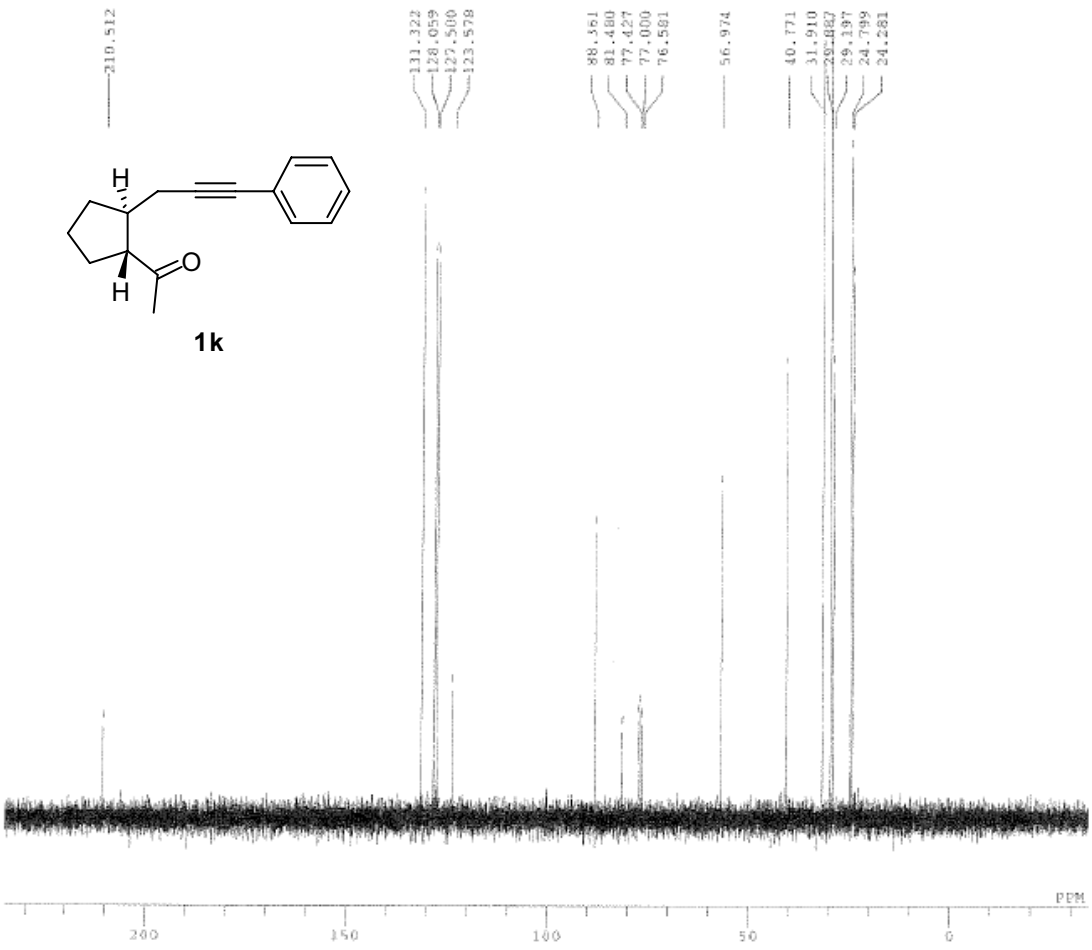
1j


PPM
200
150
100
50
0

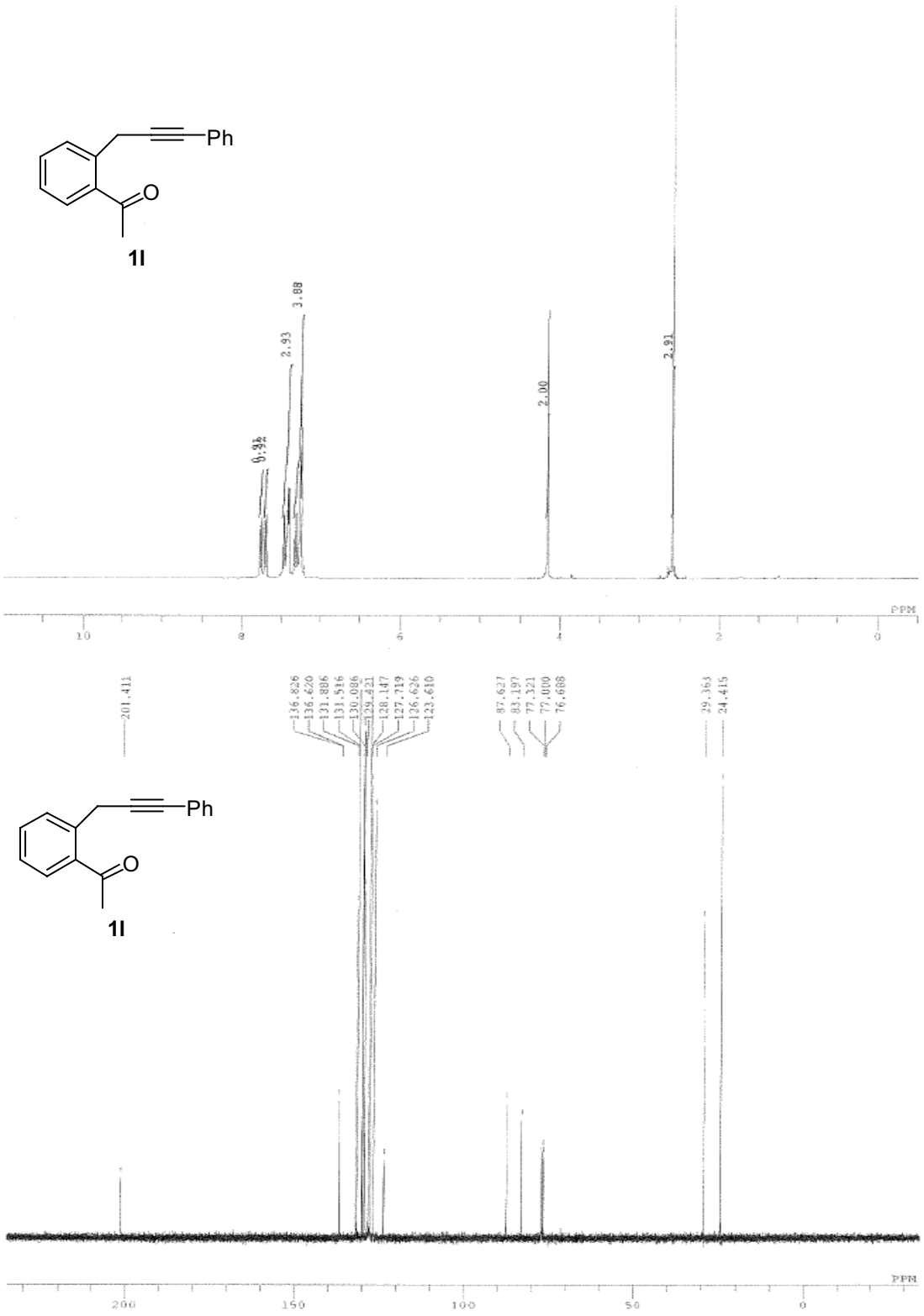


1k



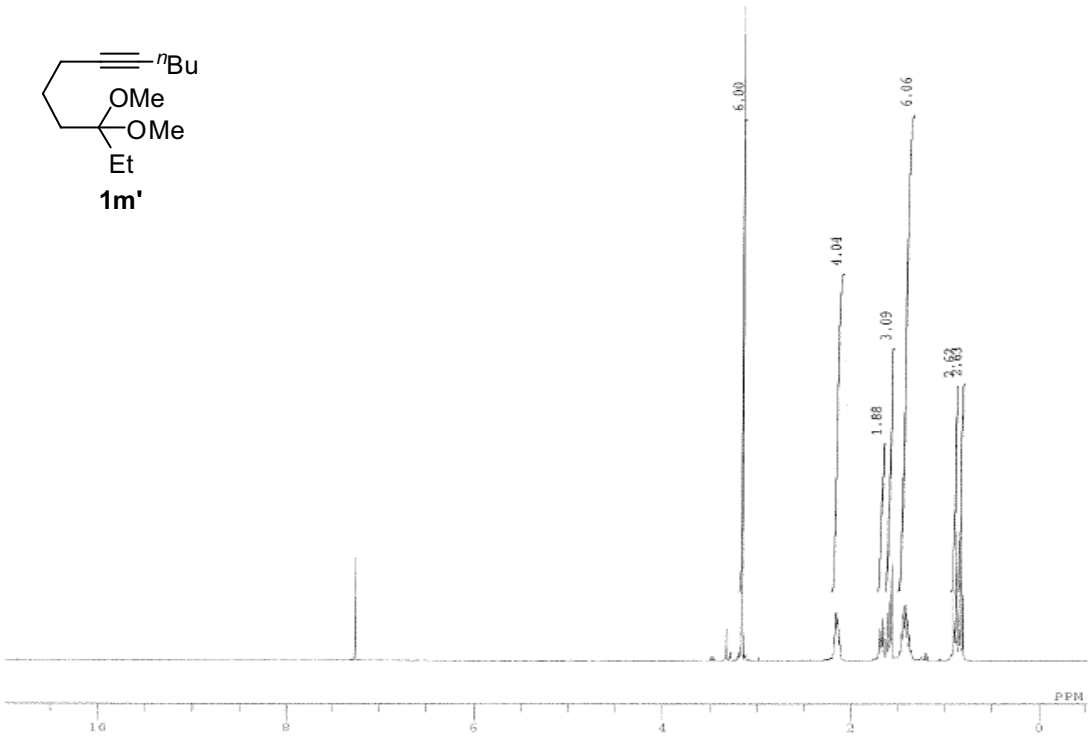

210.512
131.322
128.059
127.500
123.578
88.361
81.480
77.427
77.000
76.581
56.974
40.771
31.910
29.082
29.197
24.799
24.281
H
O
H
PPM
200
150
100
50
0

1k


Ph
O
1l
3.88
2.93
2.00
2.91
PPM
10
8
6
4
2
0
201.411
136.826
136.620
131.886
131.516
130.086
129.421
128.147
127.719
126.626
123.610
87.627
83.197
77.321
77.000
76.688
29.363
24.415
Ph
O
1l
PPM
200
150
100
50
0

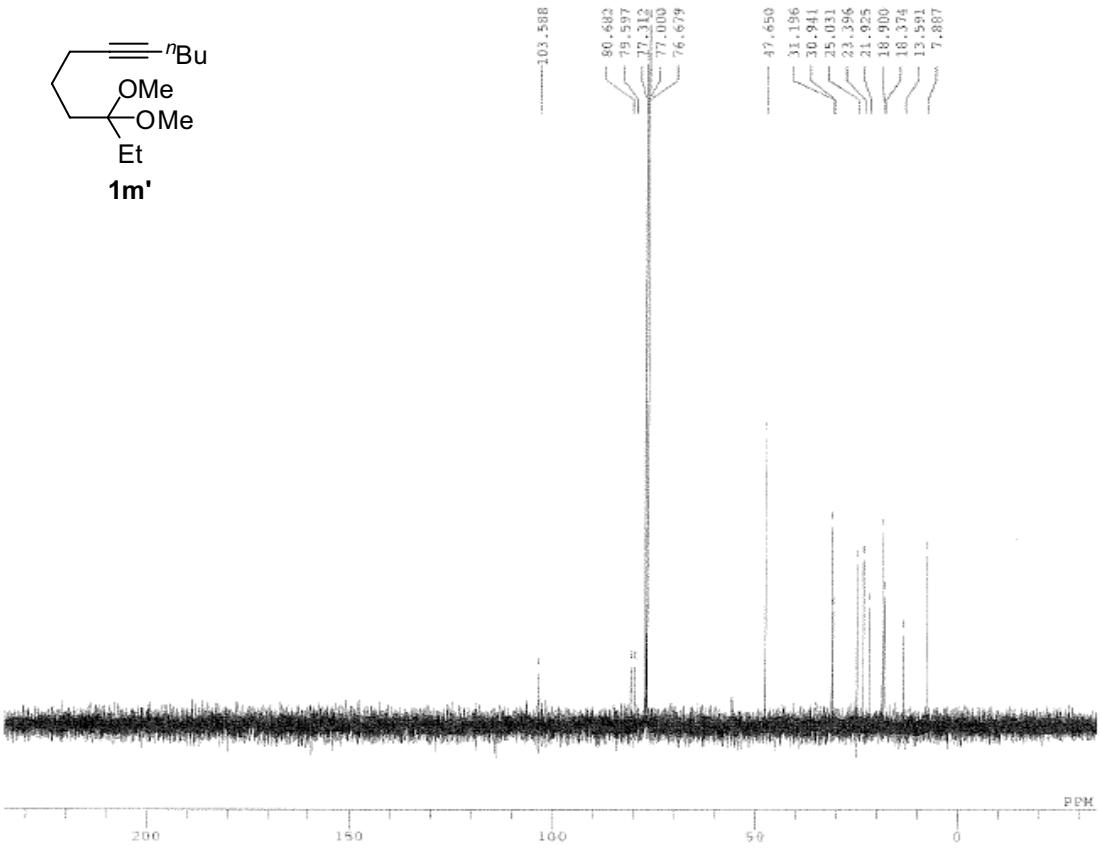
nBu
OMe
OMe
Et

1m'


6.00
4.04
3.09
6.06
1.88
2.62
2.63
PPM
10
8
6
4
2
0

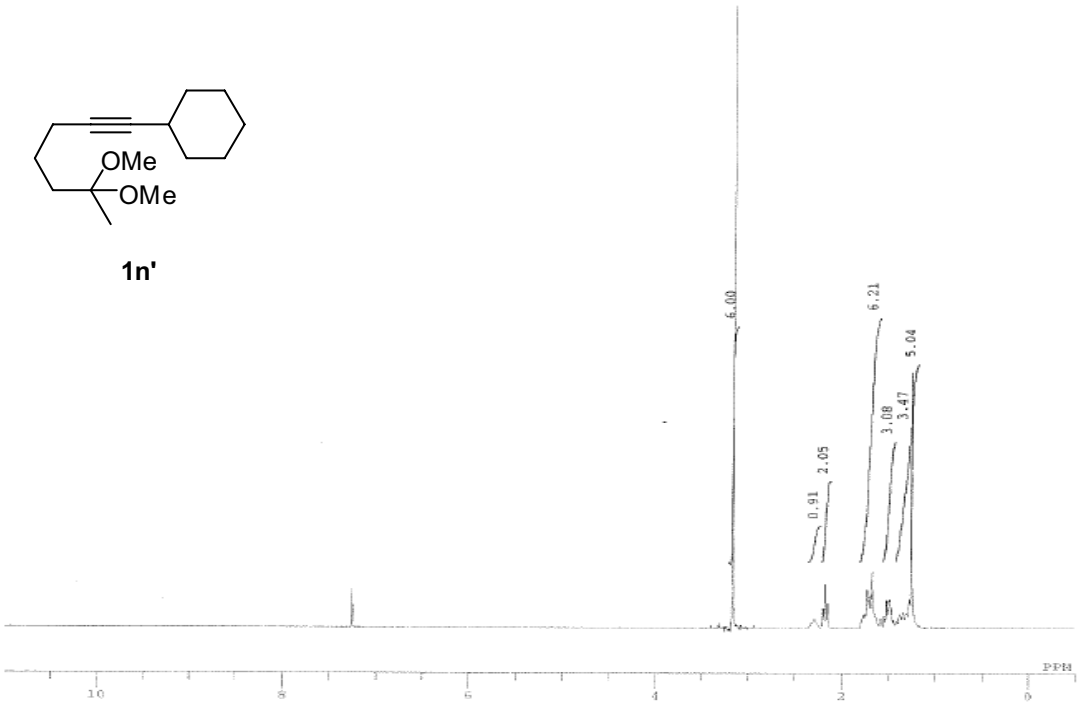
nBu
OMe
OMe
Et

1m'


103.588
80.682
79.597
77.312
77.000
76.679
47.650
31.196
30.941
25.031
23.396
21.925
18.900
18.374
13.591
7.887
PPM
200
150
100
50
0

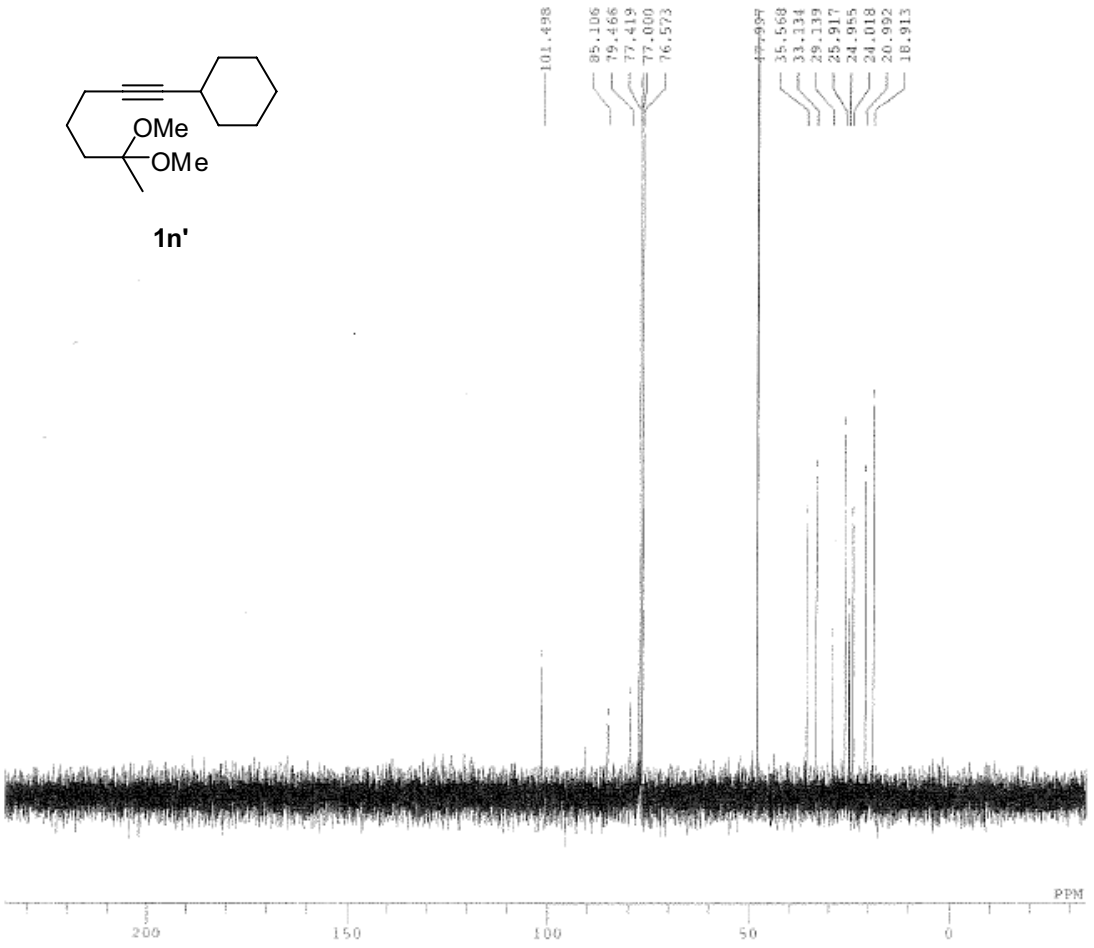
OMe
OMe

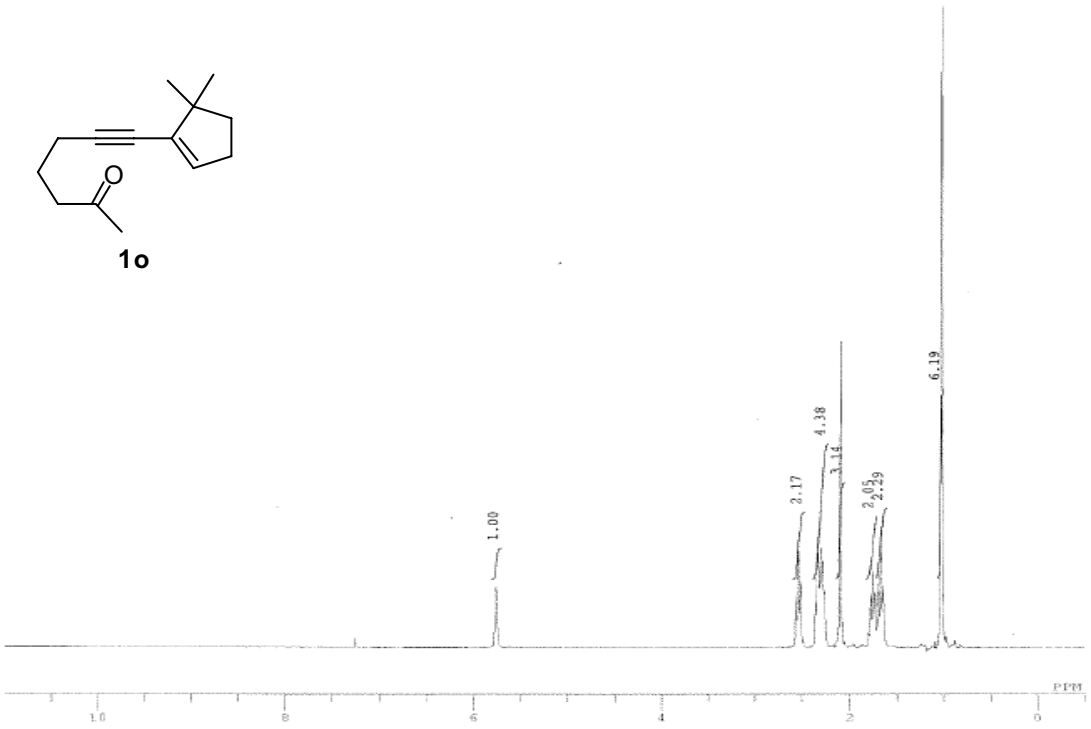
1n'


6.00
0.91
2.05
3.08
3.47
6.21
5.04
PPM
10
8
6
4
2
0

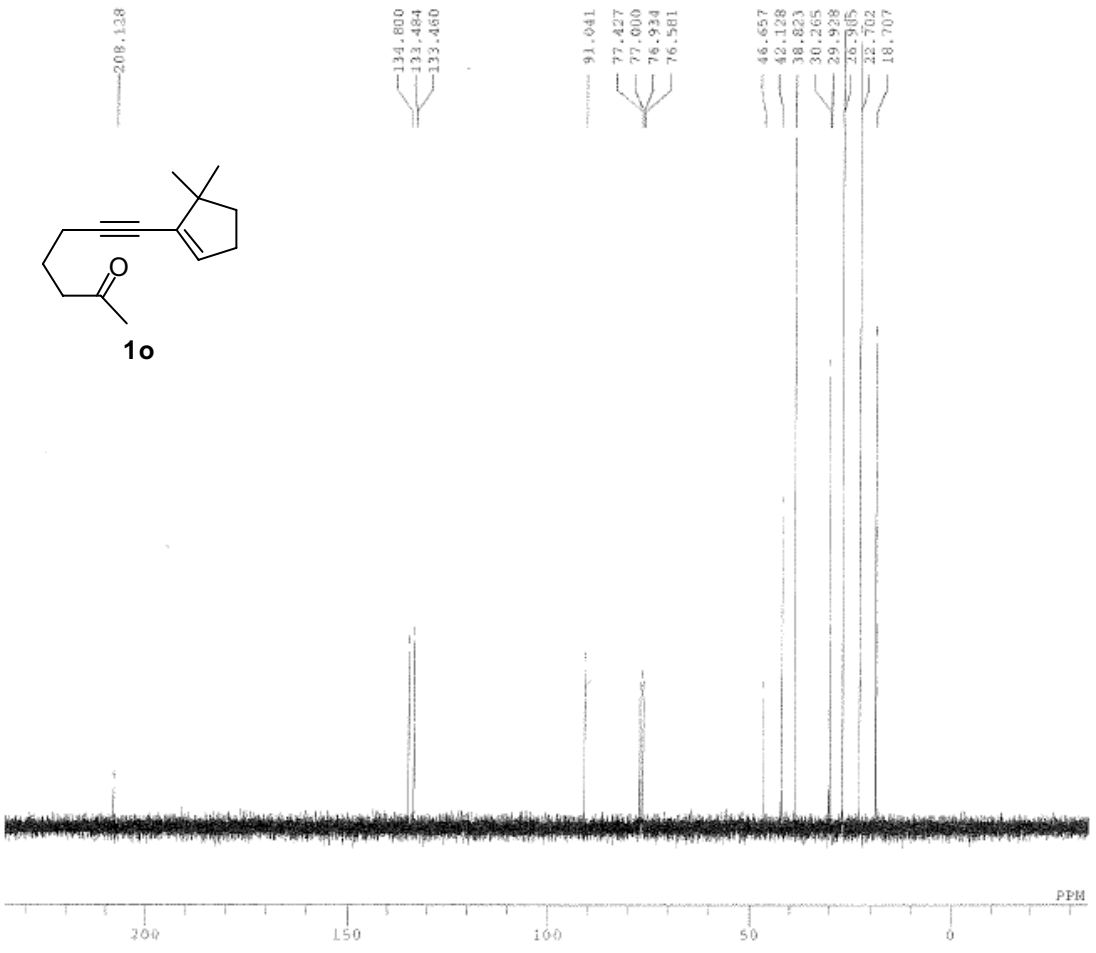
OMe
OMe

1n'

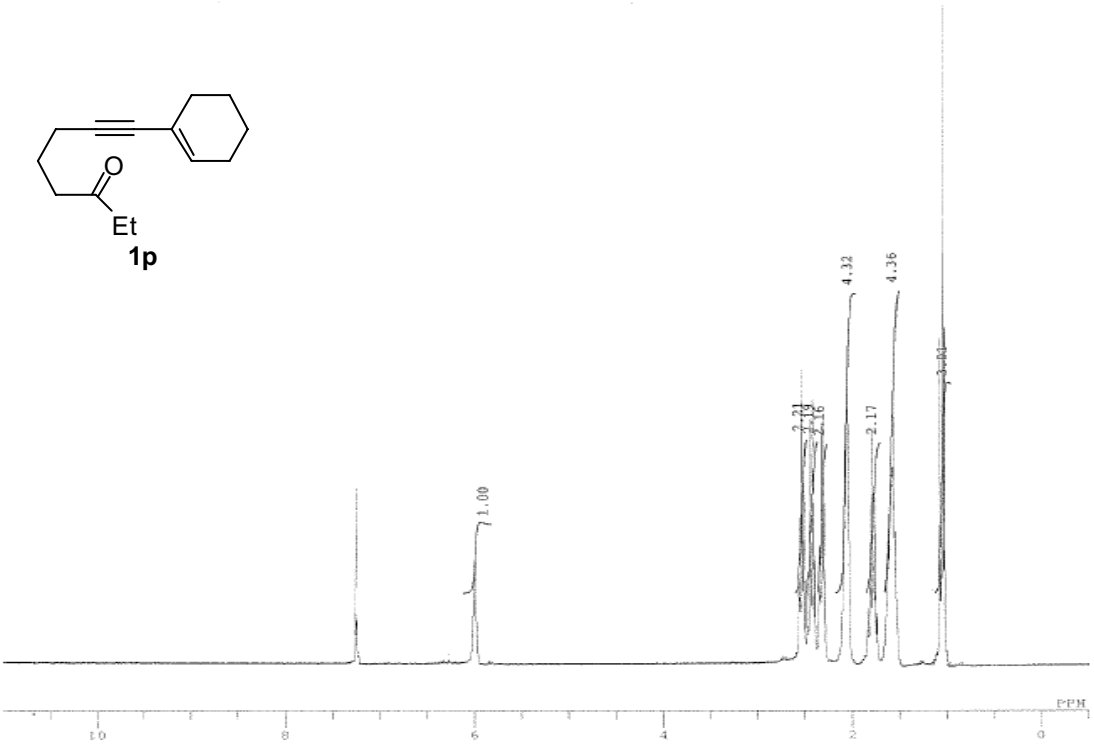

101.498
85.106
79.466
77.419
77.000
76.573
47.994
35.568
33.134
29.139
25.917
24.955
24.018
20.992
18.913
PPM
200
150
100
50
0

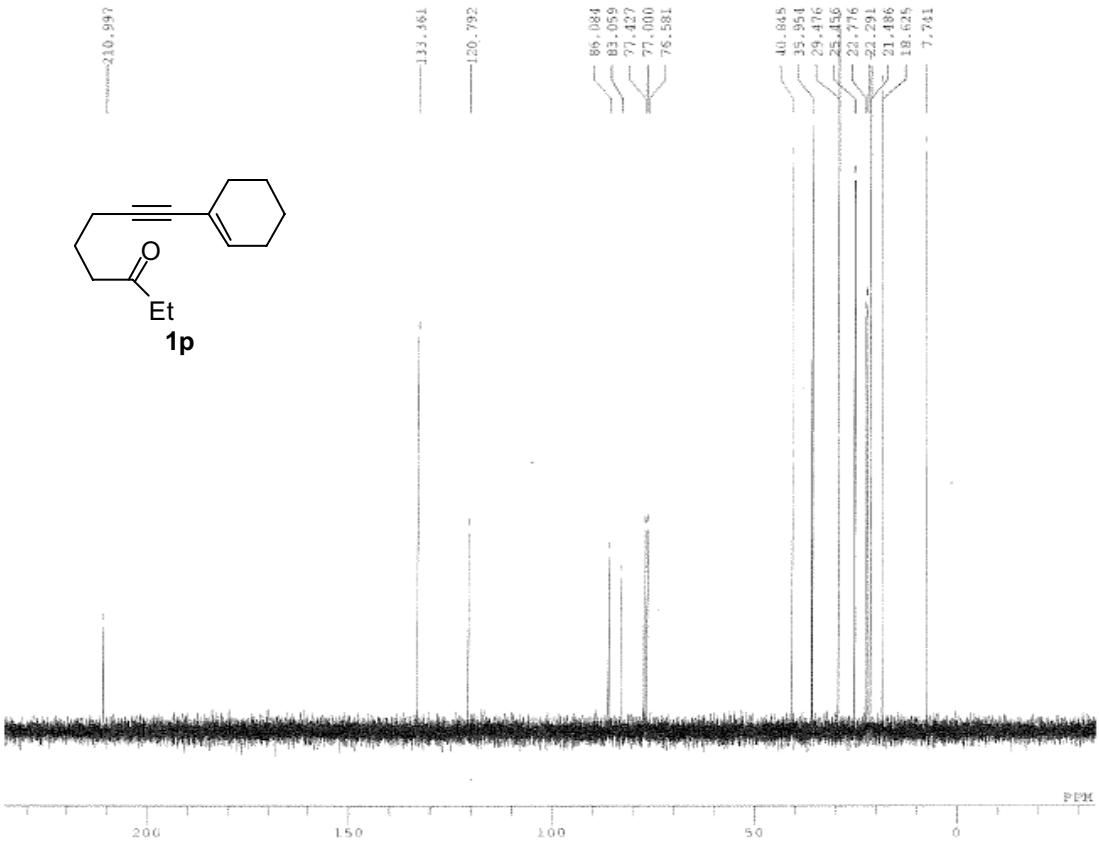

1.00
2.17
4.38
3.14
2.05
2.29
6.19
PPM
1.0
8
6
4
2
0

1o

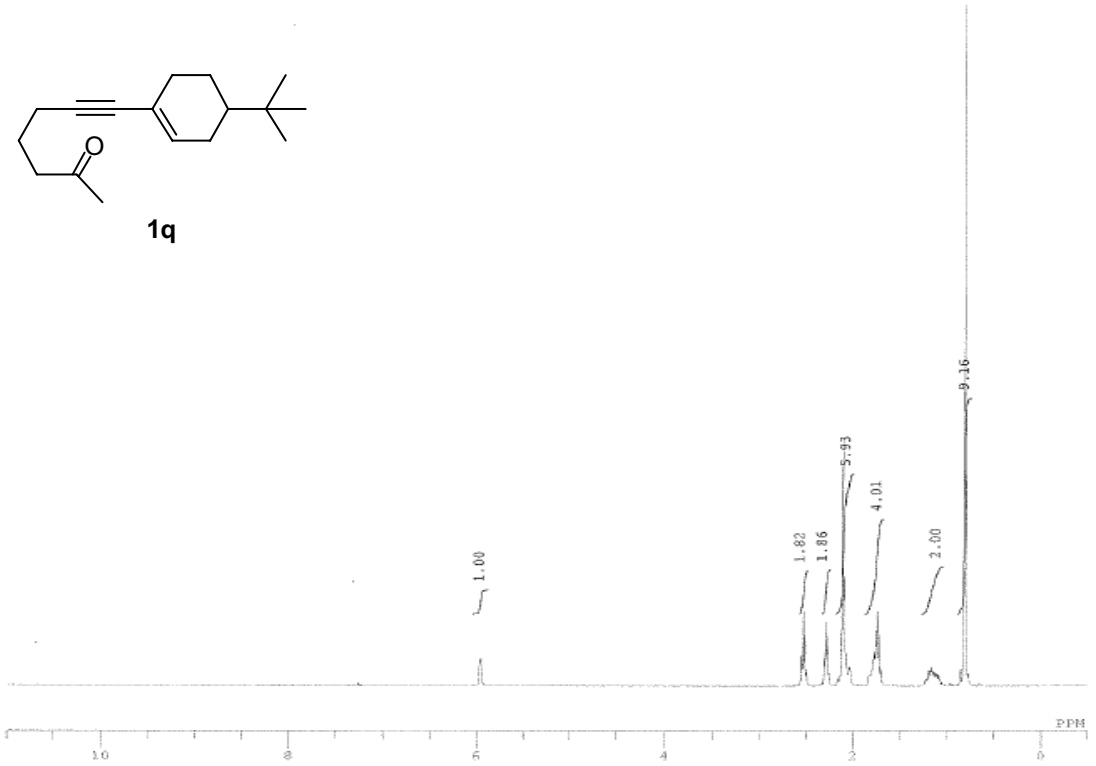

208.138
134.800
133.484
133.460
91.041
77.427
77.000
76.934
76.581
46.657
42.128
38.823
30.265
29.928
26.965
22.702
18.707
PPM
200
150
100
50
0

1o

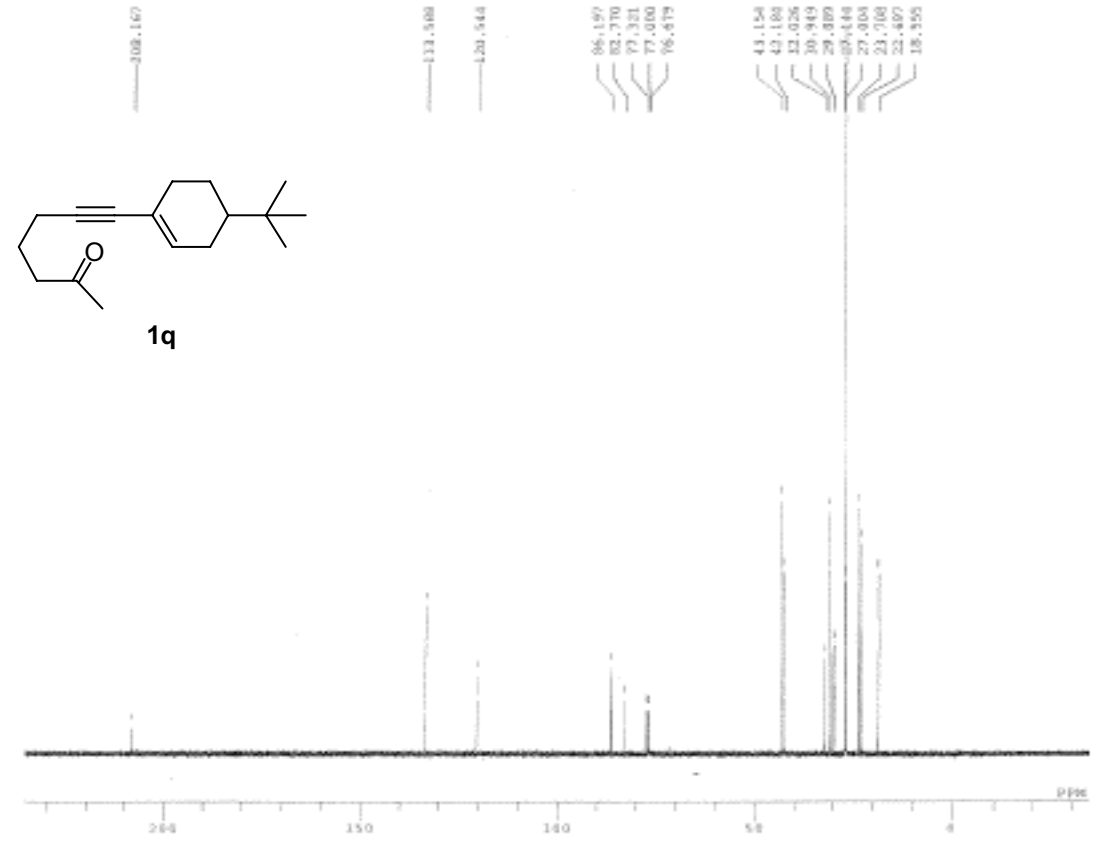

O
Et
1p
4.32
4.36
2.17
1.00
PPM


210.997
133.561
120.792
89.084
83.059
77.427
77.000
76.581
40.845
35.954
29.476
25.456
22.776
22.291
21.486
18.625
7.741
O
Et
1p
PPM

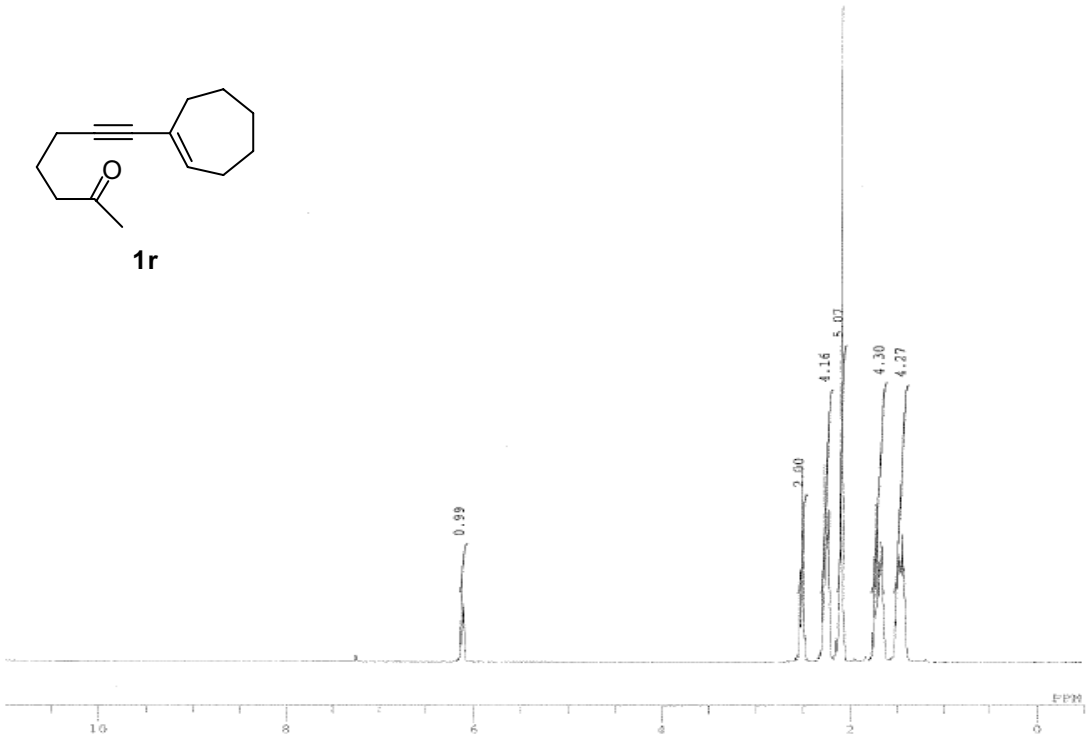
1q



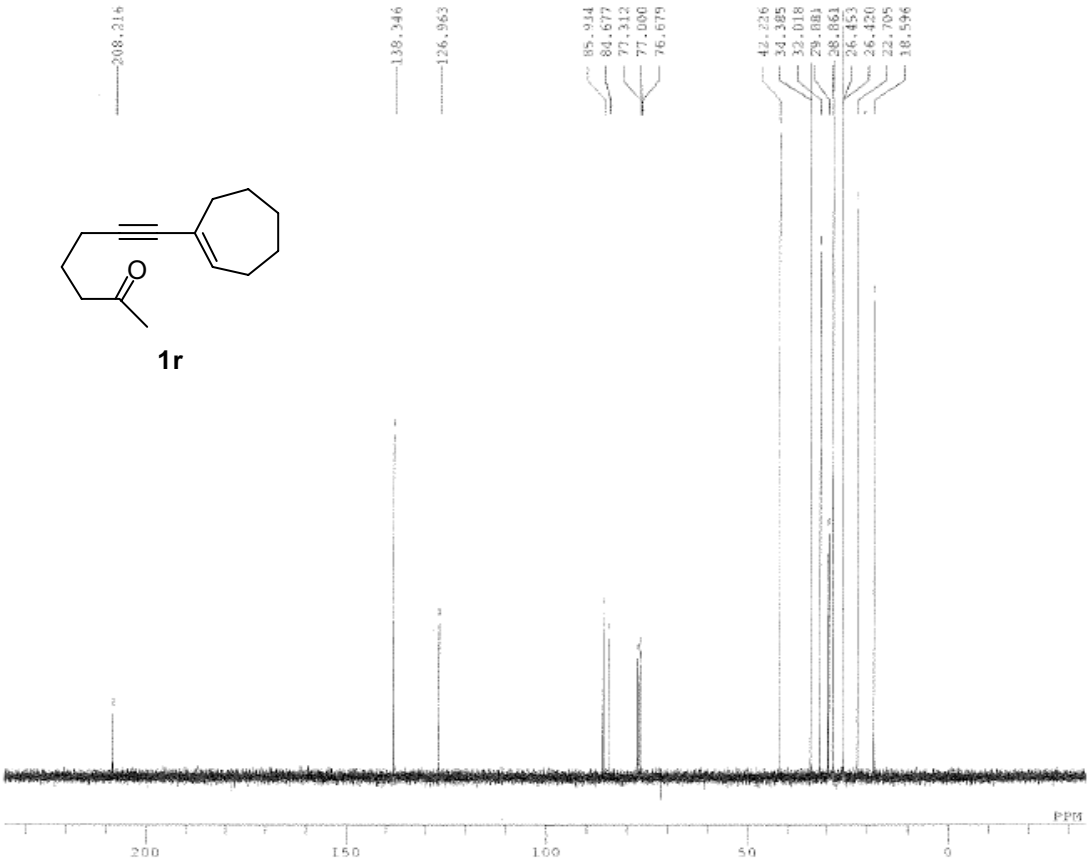
1q



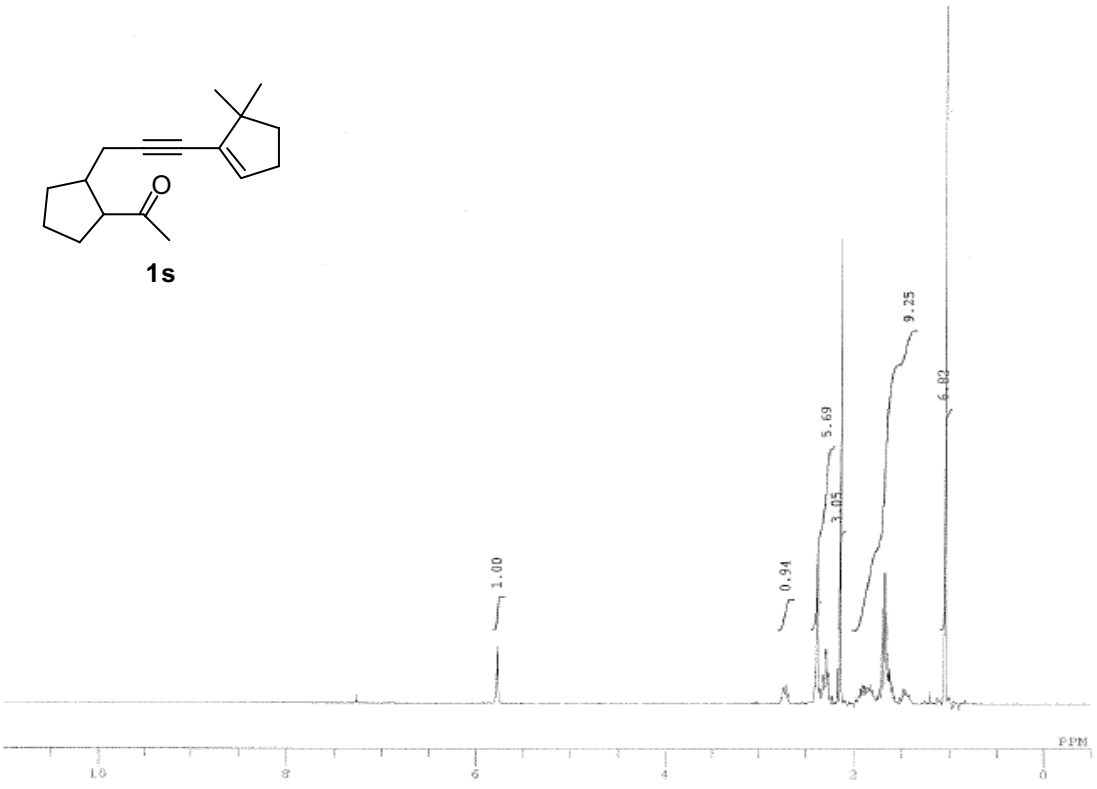
1r


0.99
2.00
4.16
5.07
4.30
4.27
PPM
10
8
6
4
2
0

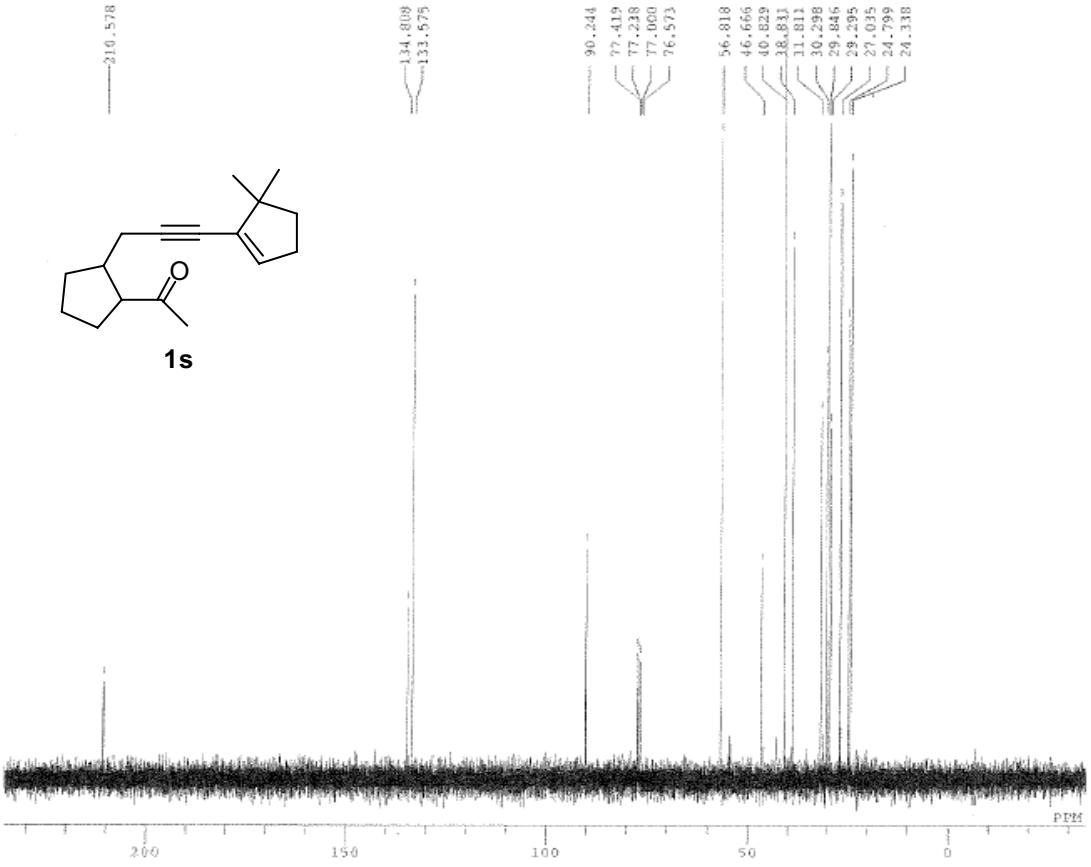
1r


208.216
138.346
126.963
85.934
84.677
77.312
77.000
76.679
42.226
34.385
32.018
29.081
28.861
26.453
26.420
22.705
18.596
PPM
200
150
100
50
0

1s

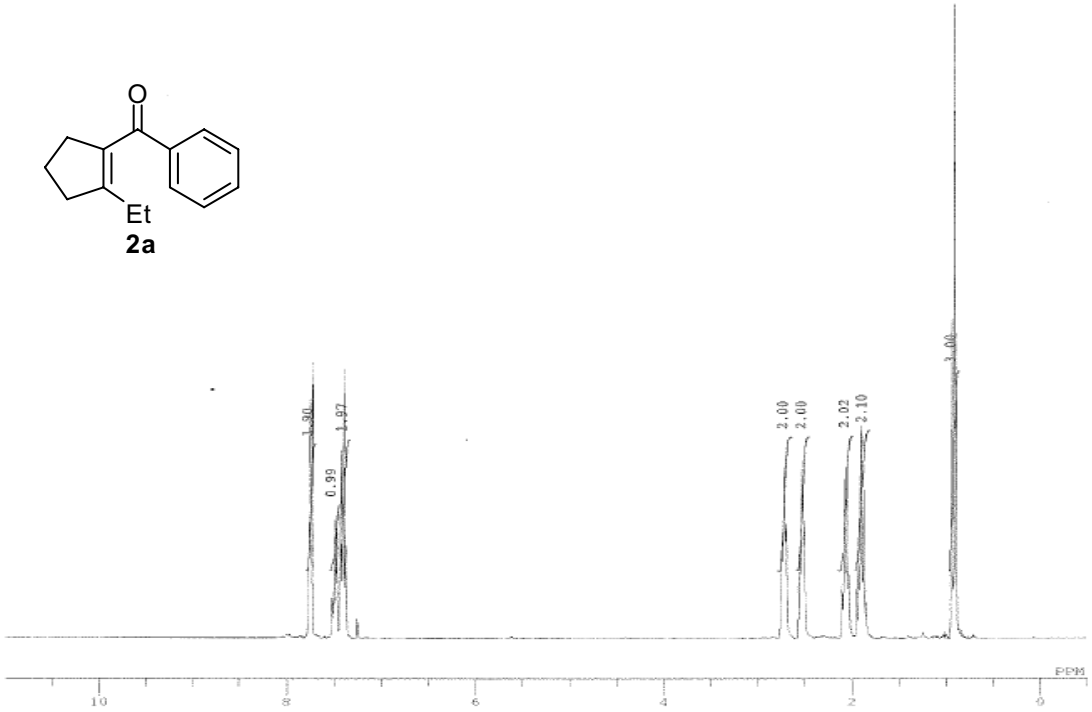

1.00
0.94
3.05
5.69
9.25
6.02
PPM
10
8
6
4
2
0

1s


210.578
134.809
133.575
90.244
77.419
77.238
77.060
76.573
56.818
46.666
40.829
38.831
11.811
30.298
29.846
29.295
27.035
24.799
24.348
PPM
200
150
100
50
0

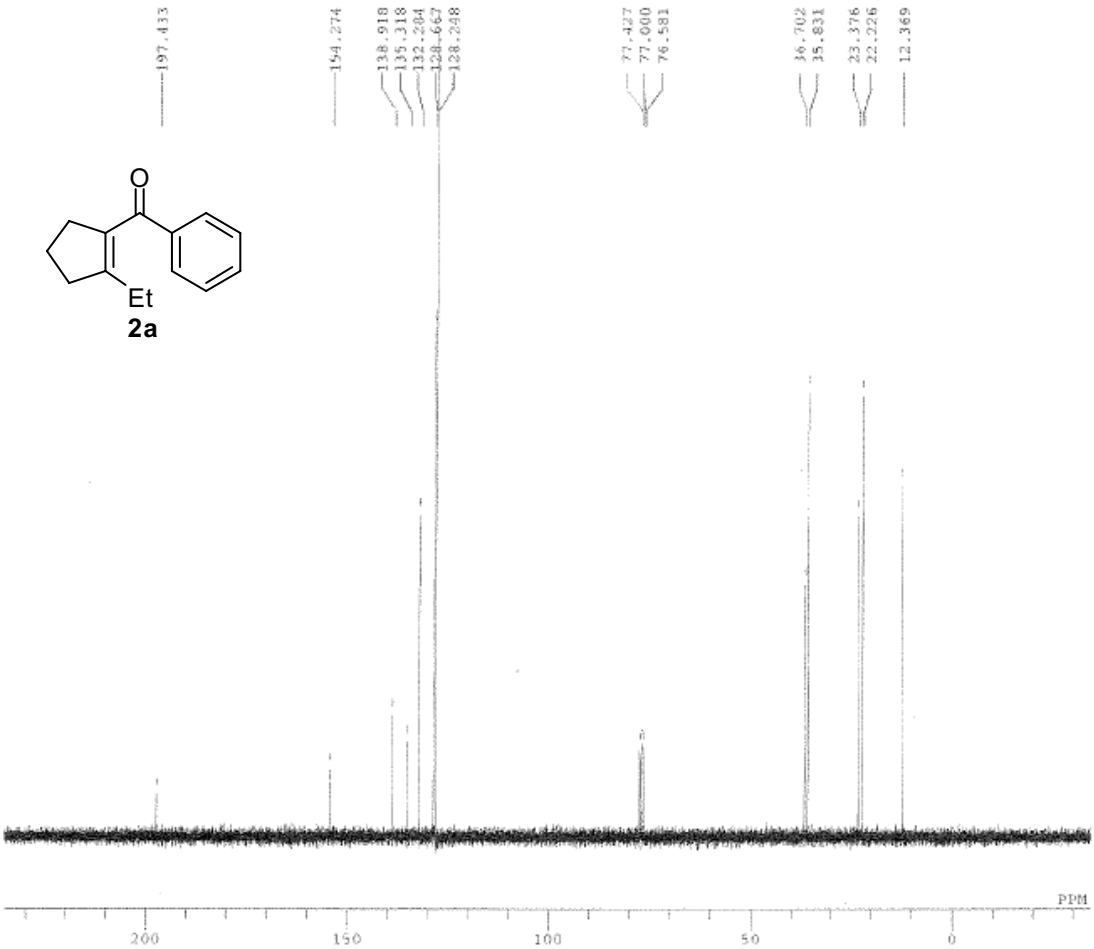
O
Et

2a

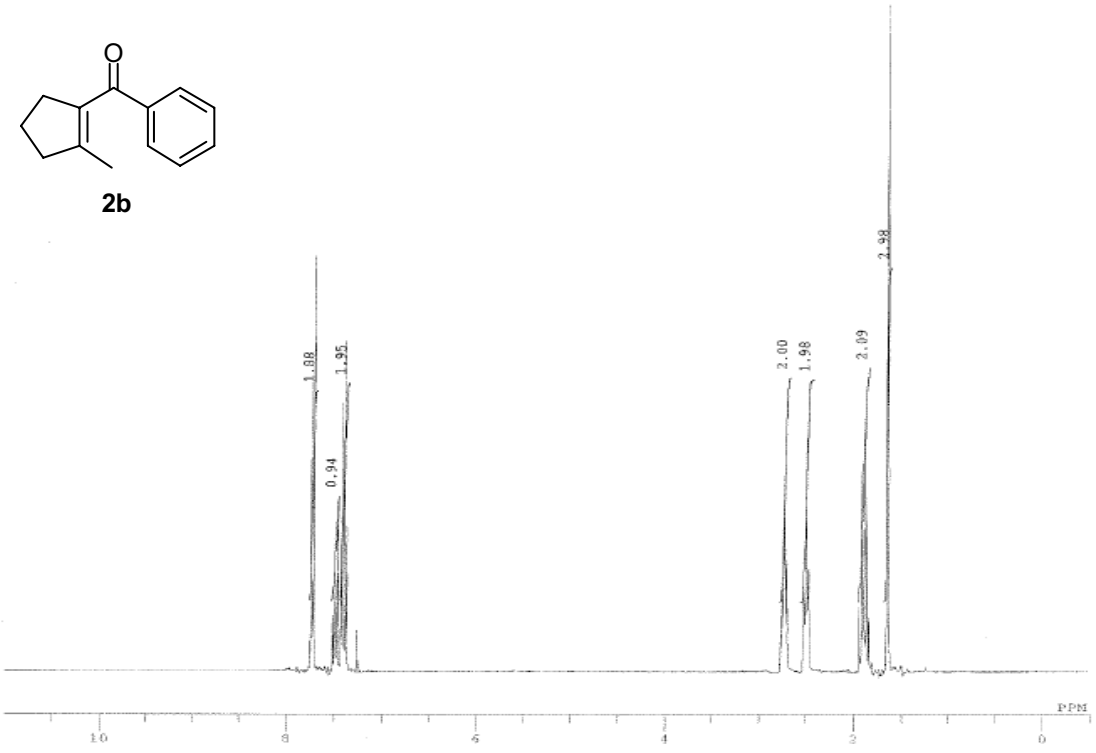

1.00
0.99
1.97
2.00
2.00
2.02
2.10
3.00
PPM
10
8
6
4
2
0

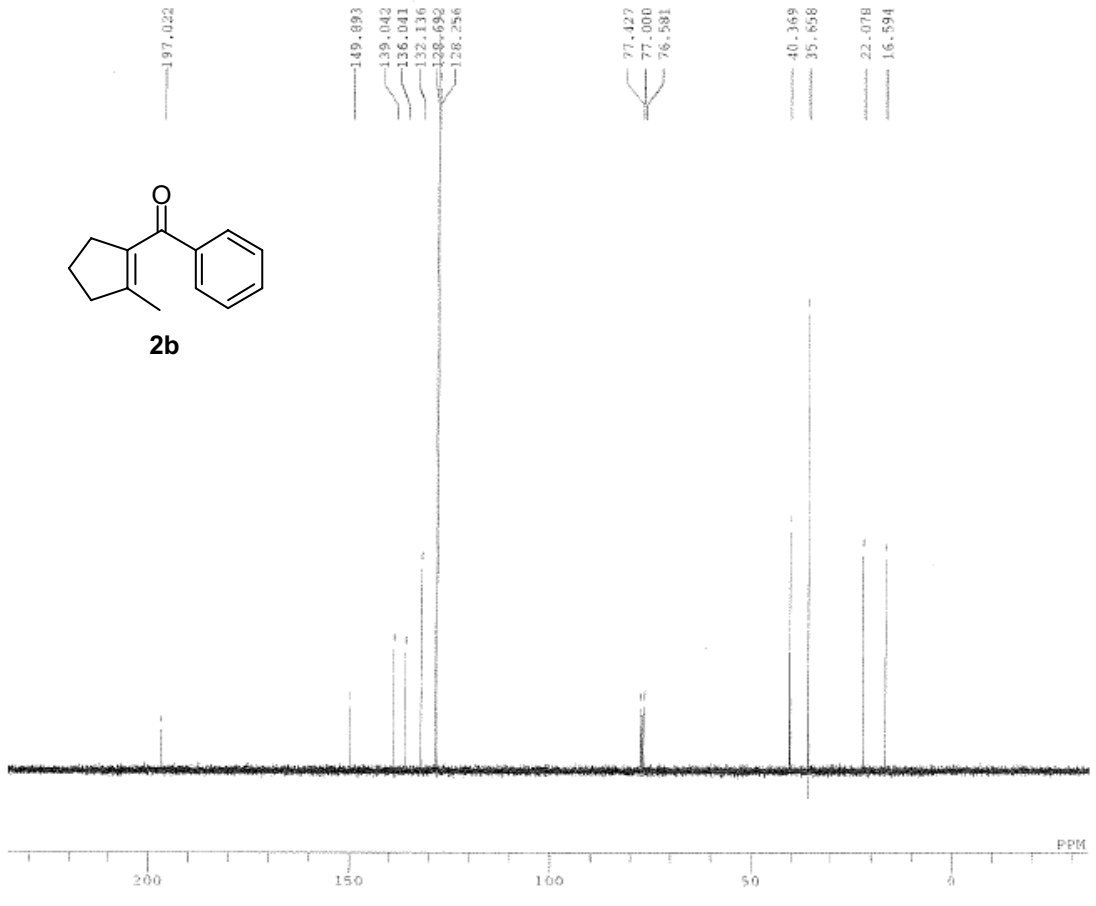
O
Et

2a


197.433
154.274
138.918
135.318
132.204
128.667
128.298
77.427
77.000
76.581
36.702
35.831
23.376
22.226
12.369
PPM
200
150
100
50
0

2b

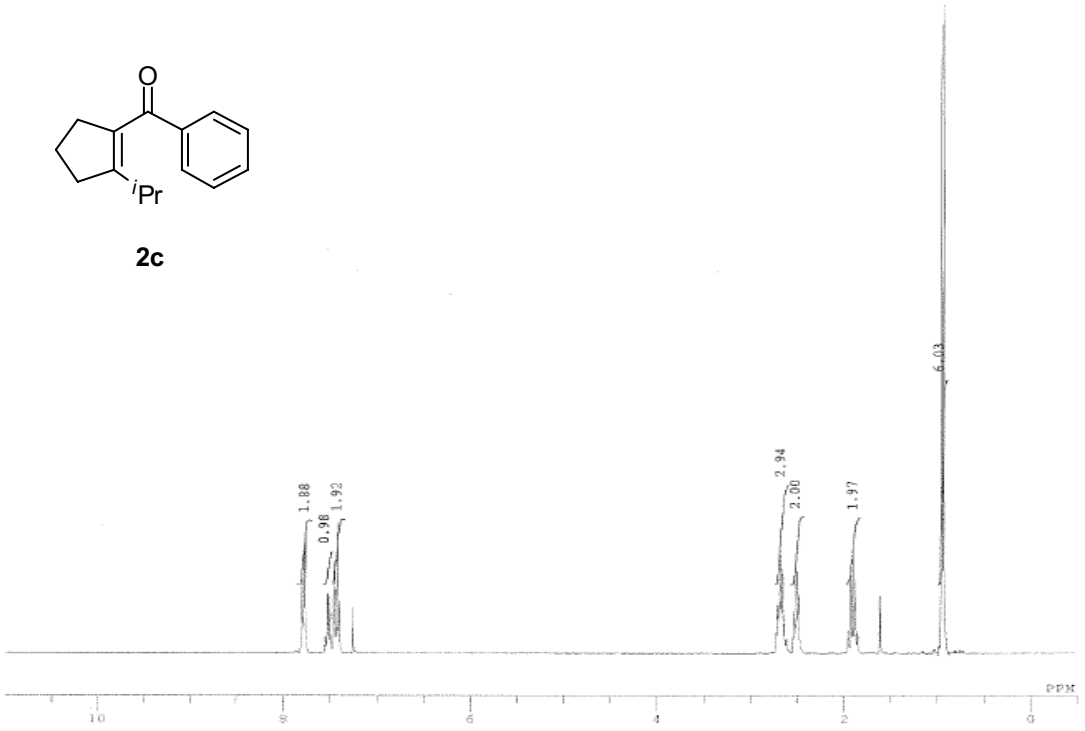

1.08
1.95
0.94
2.00
1.98
2.09
2.98
PPM
10
8
6
4
2
0


197.022
149.893
139.042
136.041
132.136
128.692
128.256
77.427
77.000
76.581
40.369
35.658
22.078
16.594
PPM
200
150
100
50
0

2b

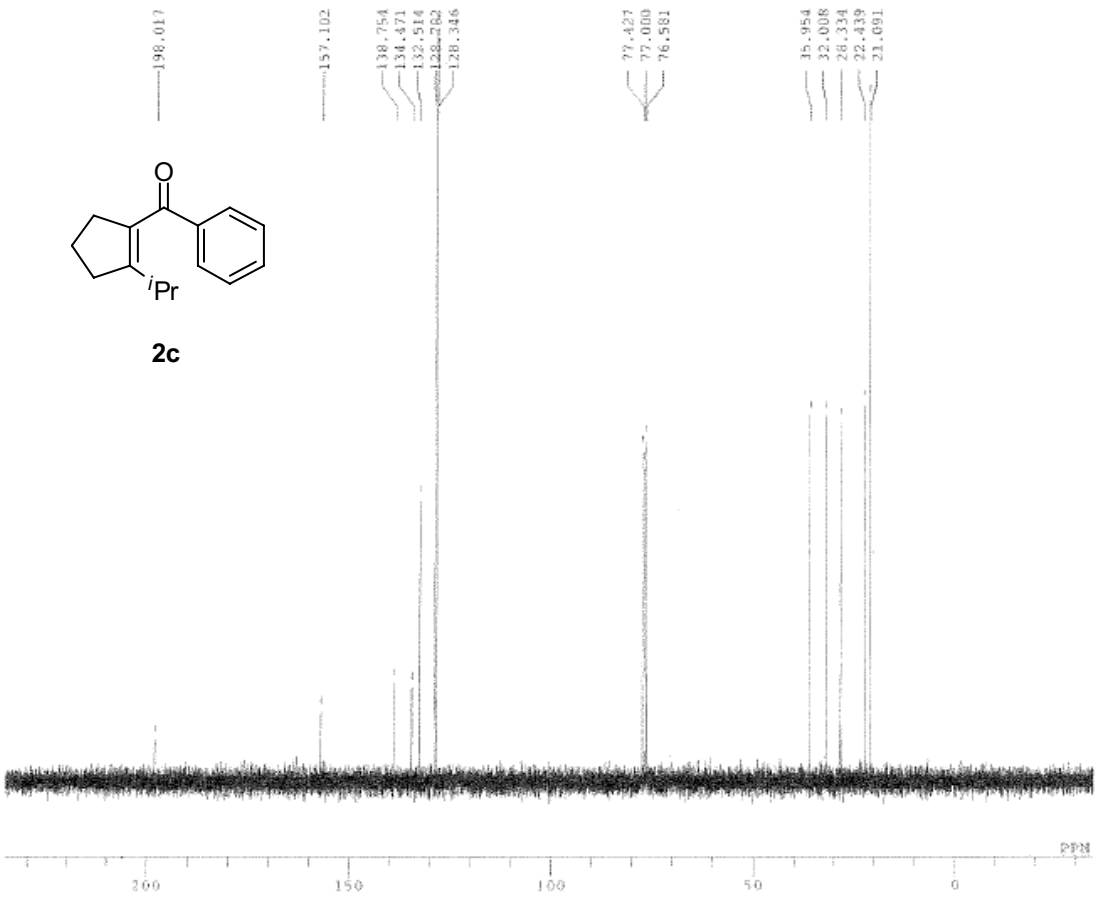
O
iPr

2c

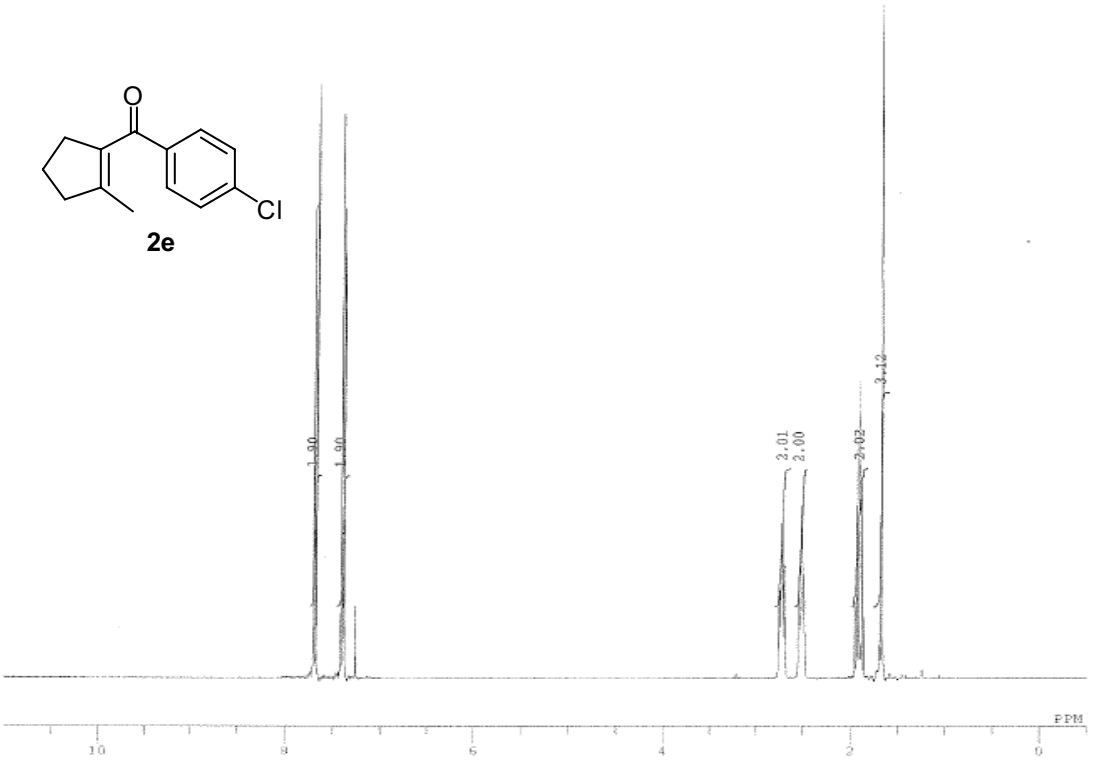

1.88
0.98
1.92
2.94
2.00
1.97
6.03
PPM
10
8
6
4
2
0

O
iPr

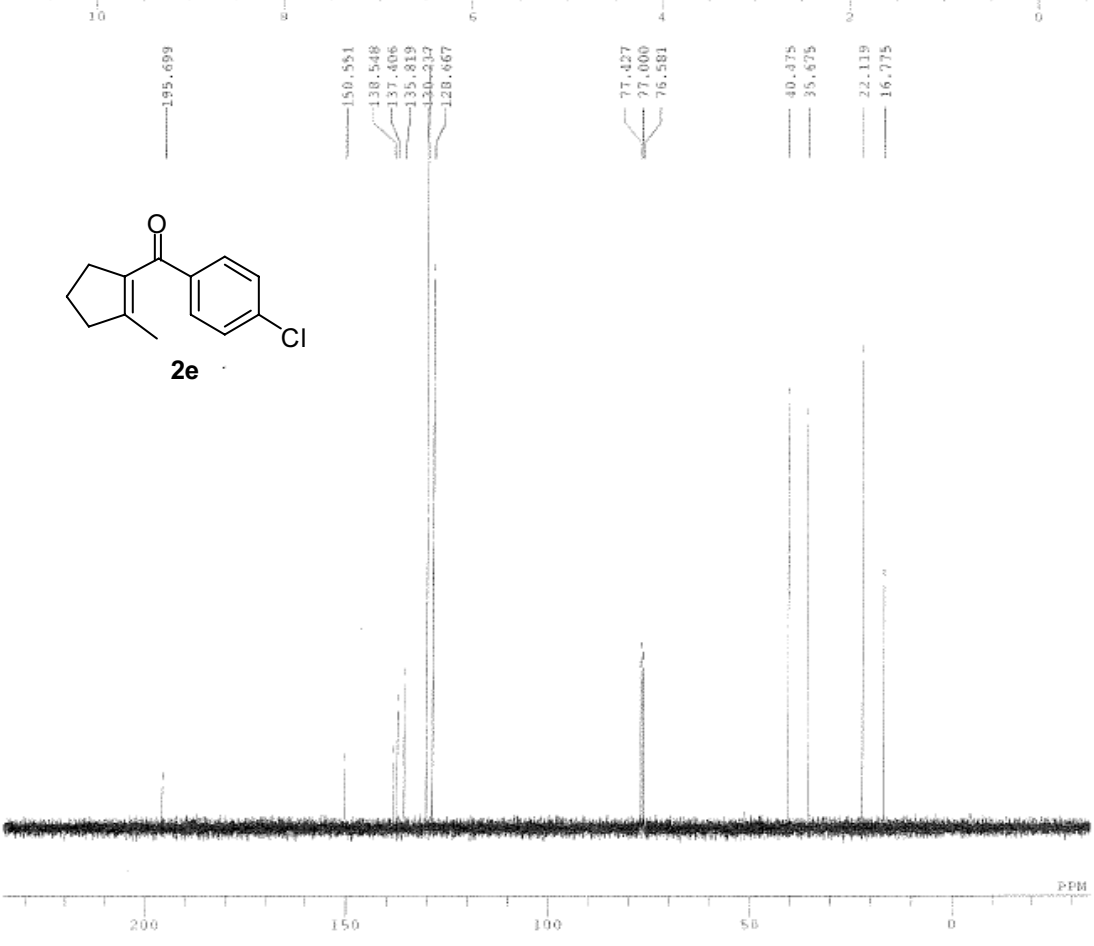
2c


198.017
157.102
138.754
134.471
132.514
128.762
128.346
77.427
77.000
76.581
35.954
32.008
28.334
22.439
21.691
PPM
200
150
100
50
0


2d
2.00
2.24
2.12
2.09
3.00
2.10
3.01
PPM
197.030
148.767
143.037
136.337
136.247
129.070
129.045
77.427
77.000
76.581
40.295
35.864
22.217
21.617
16.611
2d
PPM
200
150
100
50
0

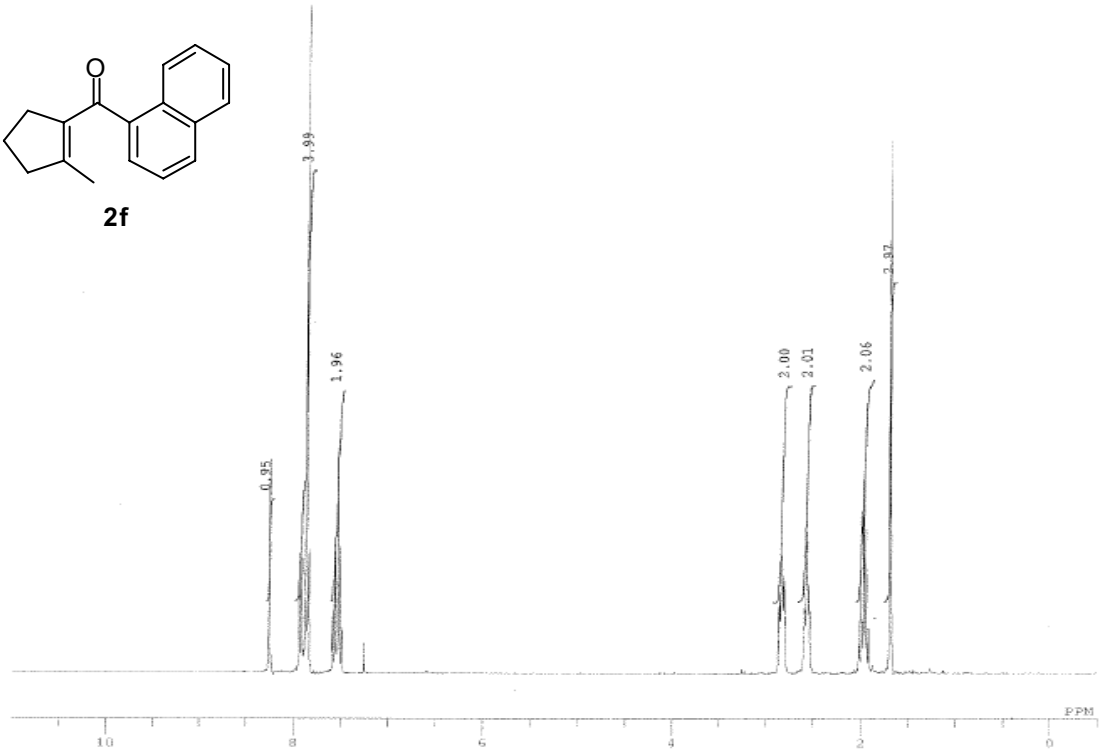

O
Cl
1.90
1.90
2.01
2.00
2.02
3.12
PPM
10
8
6
4
2
0

2e

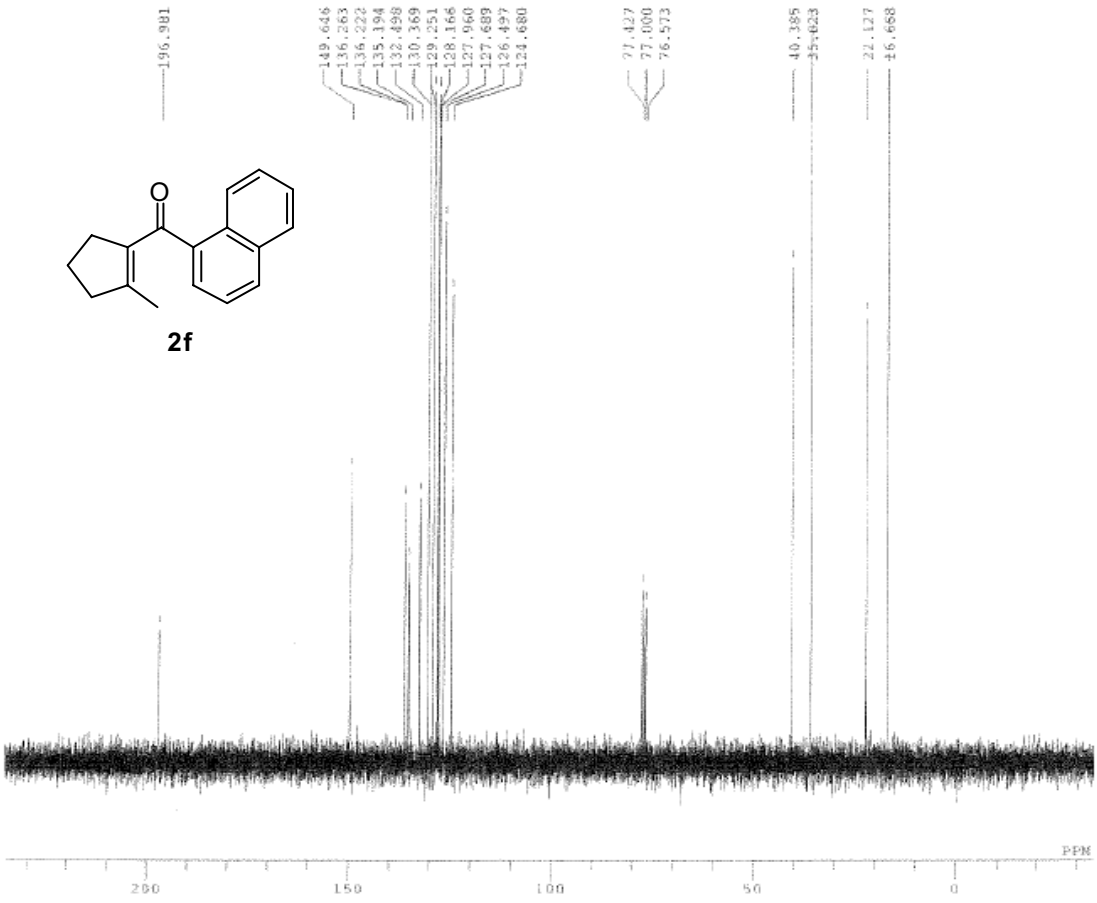

195.699
150.551
138.548
137.406
135.819
130.234
128.667
77.427
77.000
76.581
40.375
35.675
22.119
16.775
O
Cl
PPM
200
150
100
50
0

2e

2f

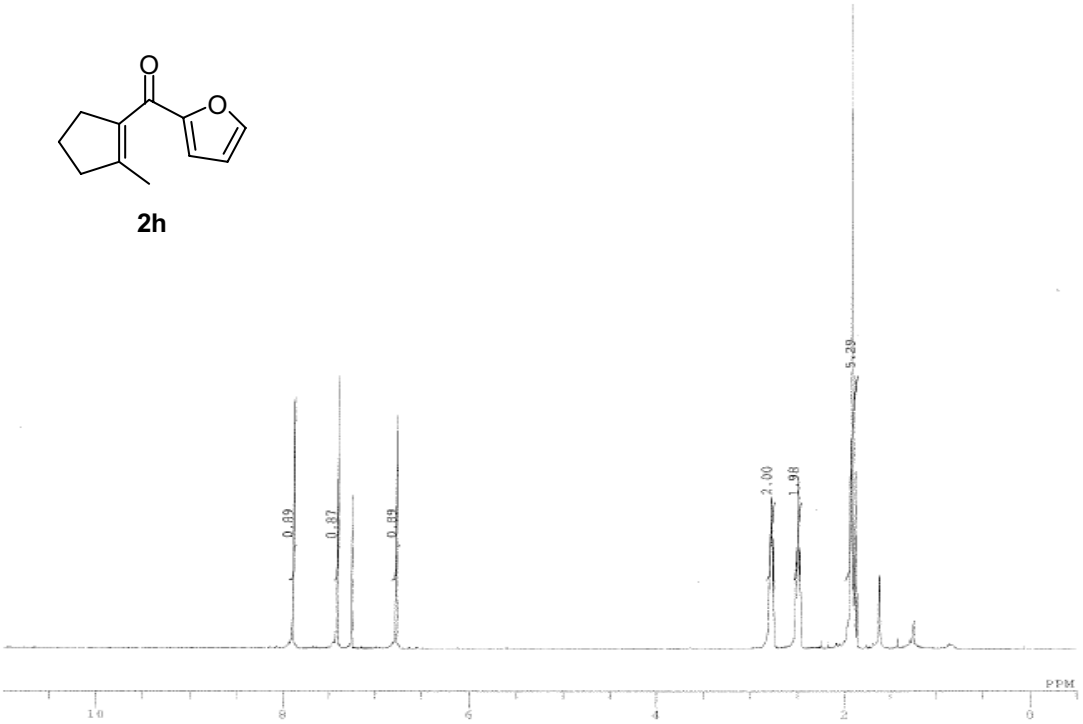

0.95
3.99
1.96
2.00
2.01
2.06
2.87
PPM
10
8
6
4
2
0

2f

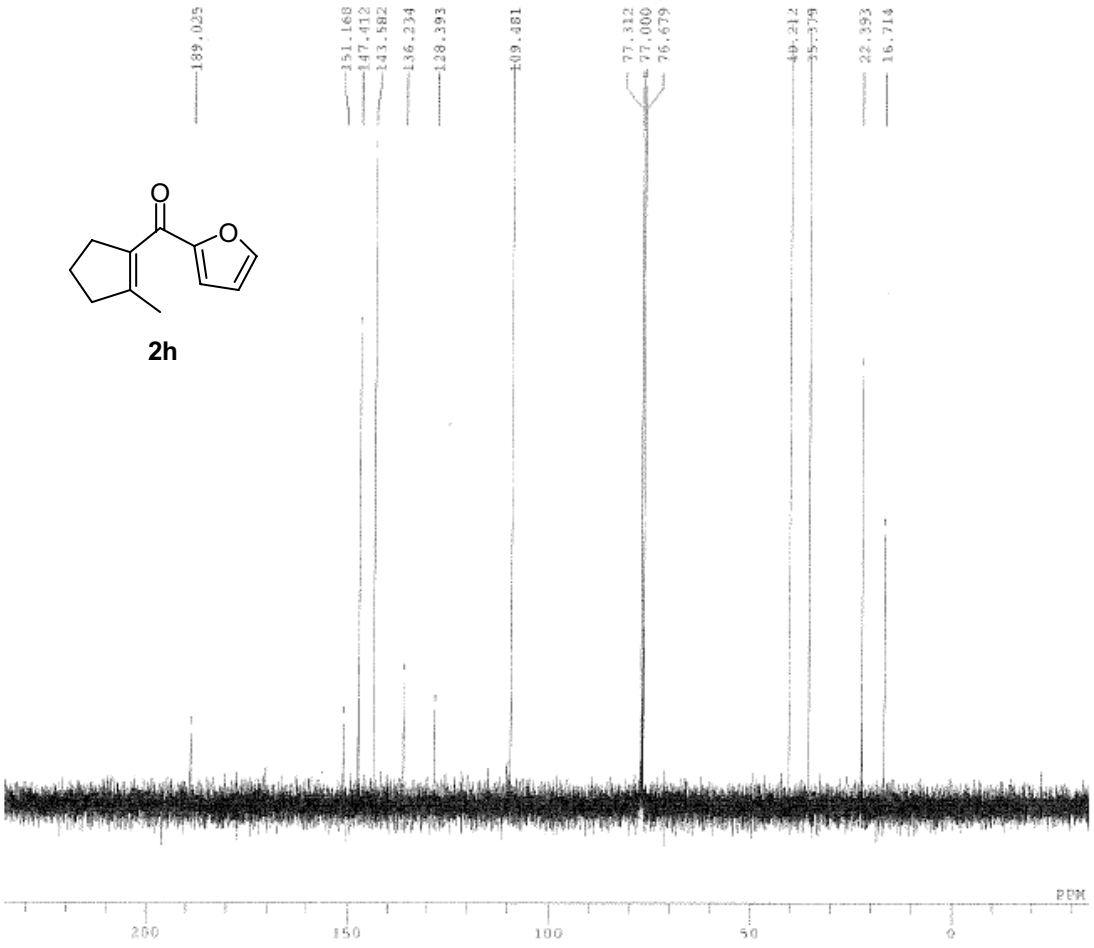

196.981
149.646
136.263
136.222
135.194
132.498
130.369
129.251
128.166
127.960
127.689
126.497
124.680
77.427
77.000
76.573
40.385
35.023
22.127
16.668
PPM
200
150
100
50
0

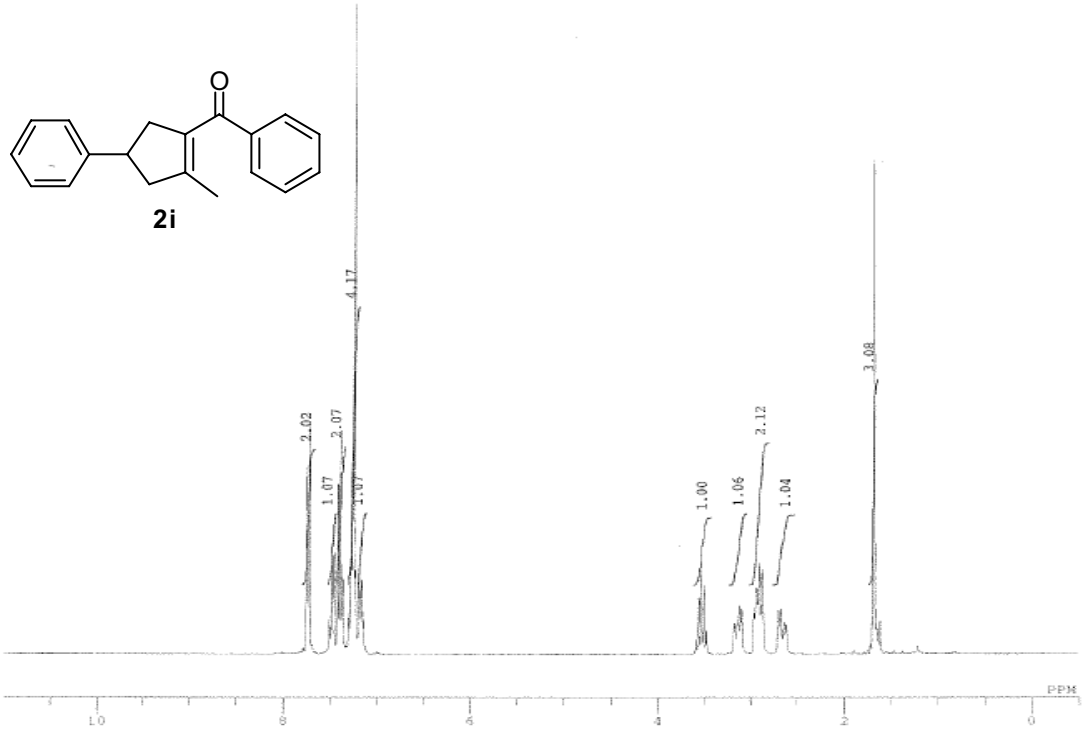

O
S
2g
1.83
0.93
2.00
2.00
1.94
3.04
PPM
10
8
6
4
2
0
188.234
149.942
145.355
135.564
133.427
132.810
127.820
77.427
77.000
76.581
40.032
35.905
22.538
16.685
O
S
2g
PPM
200
150
100
50
0

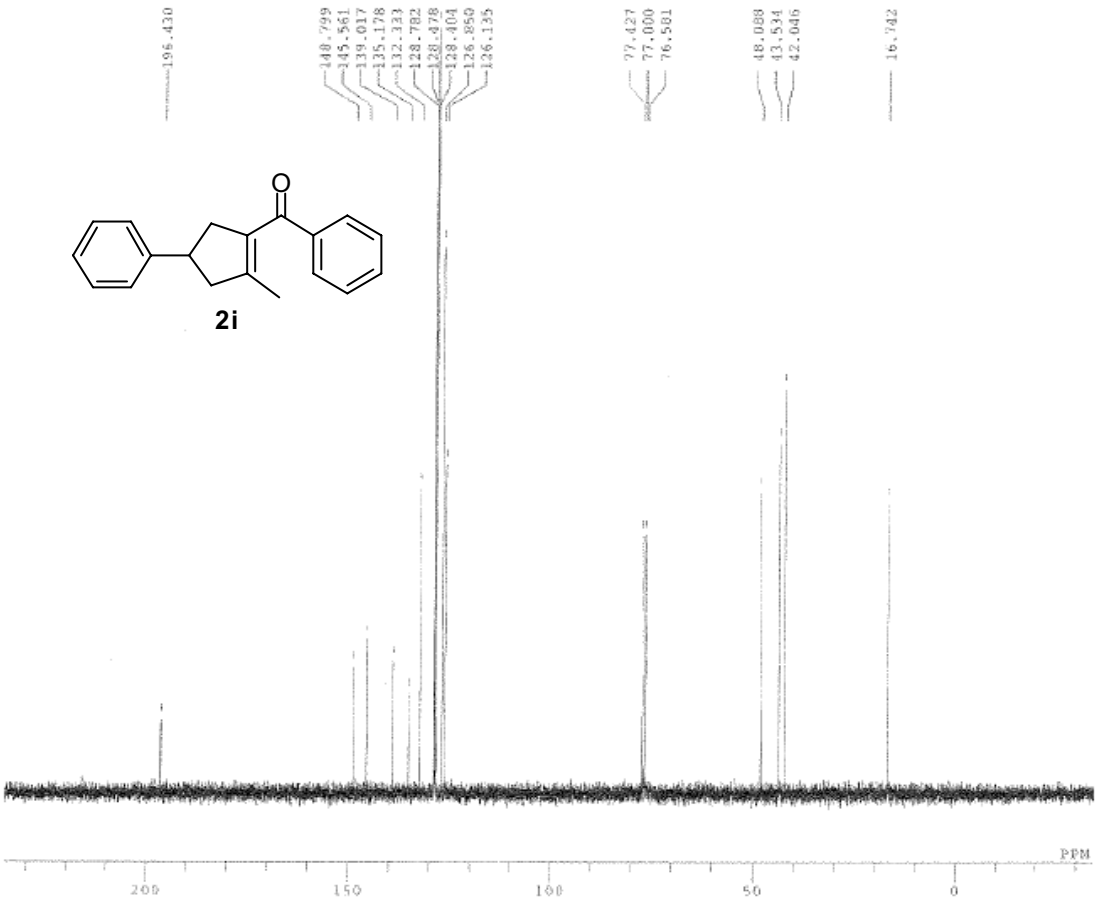
2h

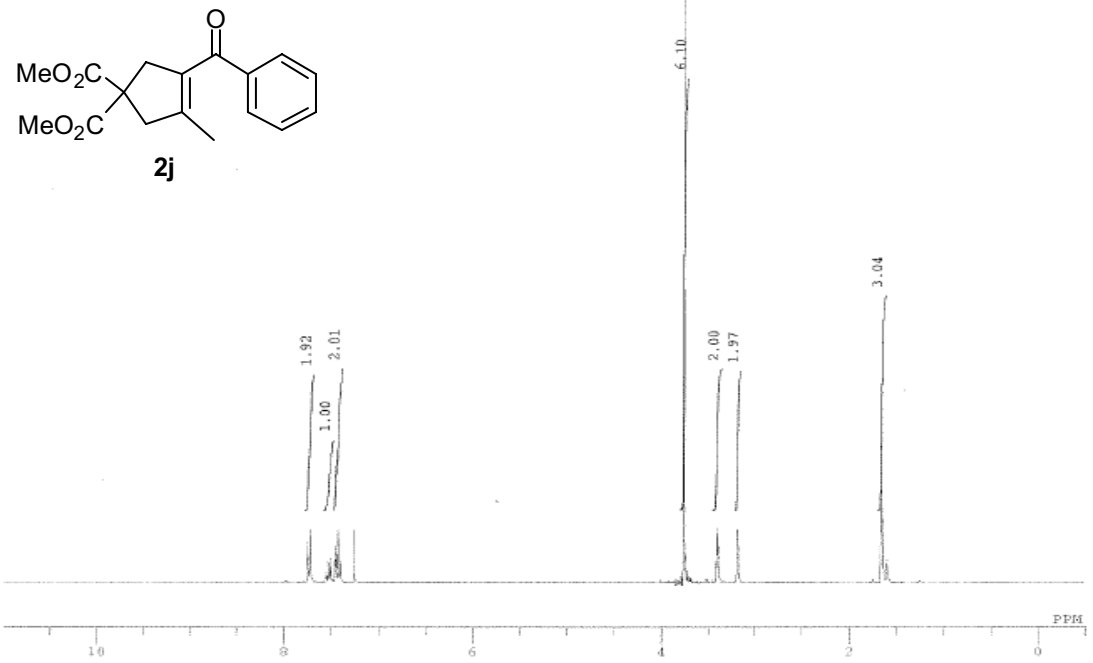

0.89
0.87
0.89
2.00
1.98
5.29
PPM
10
8
6
4
2
0

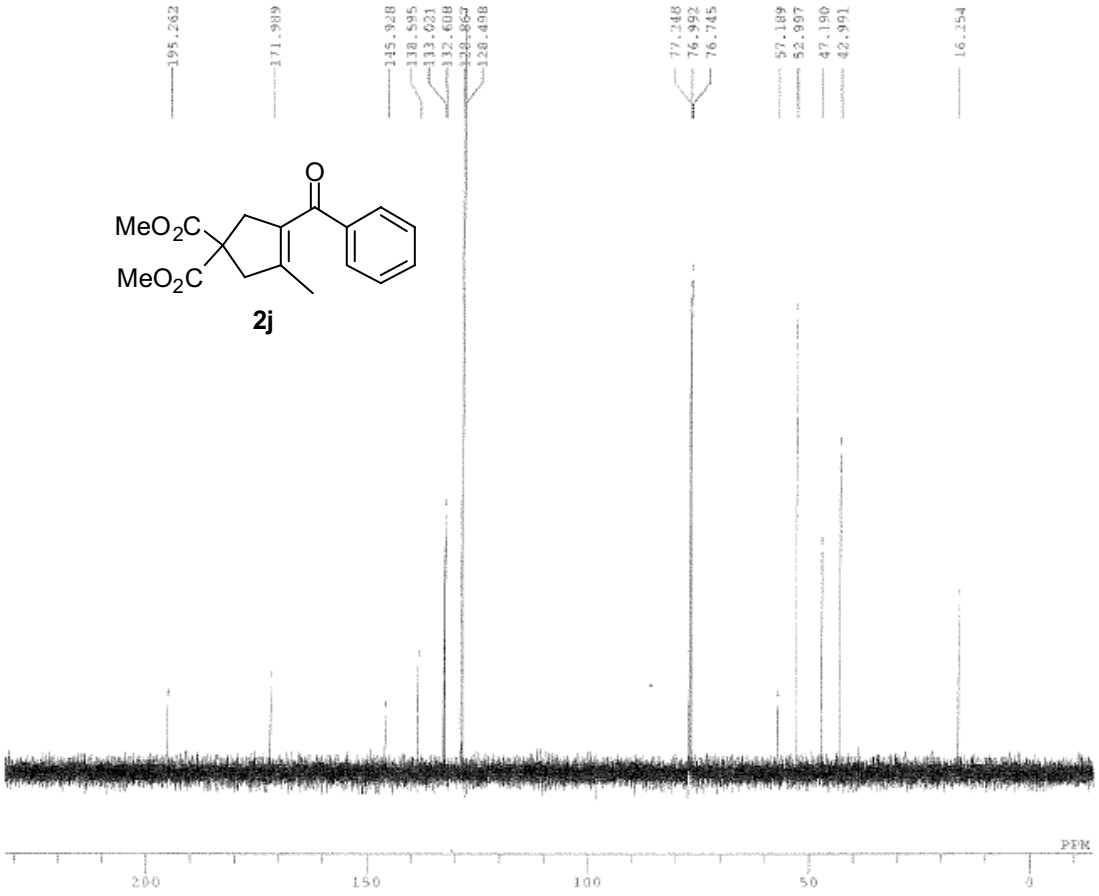
2h


189.025
151.168
147.412
143.582
136.234
128.393
109.481
77.312
77.000
76.679
40.212
35.379
22.393
16.714
PPM
200
150
100
50
0

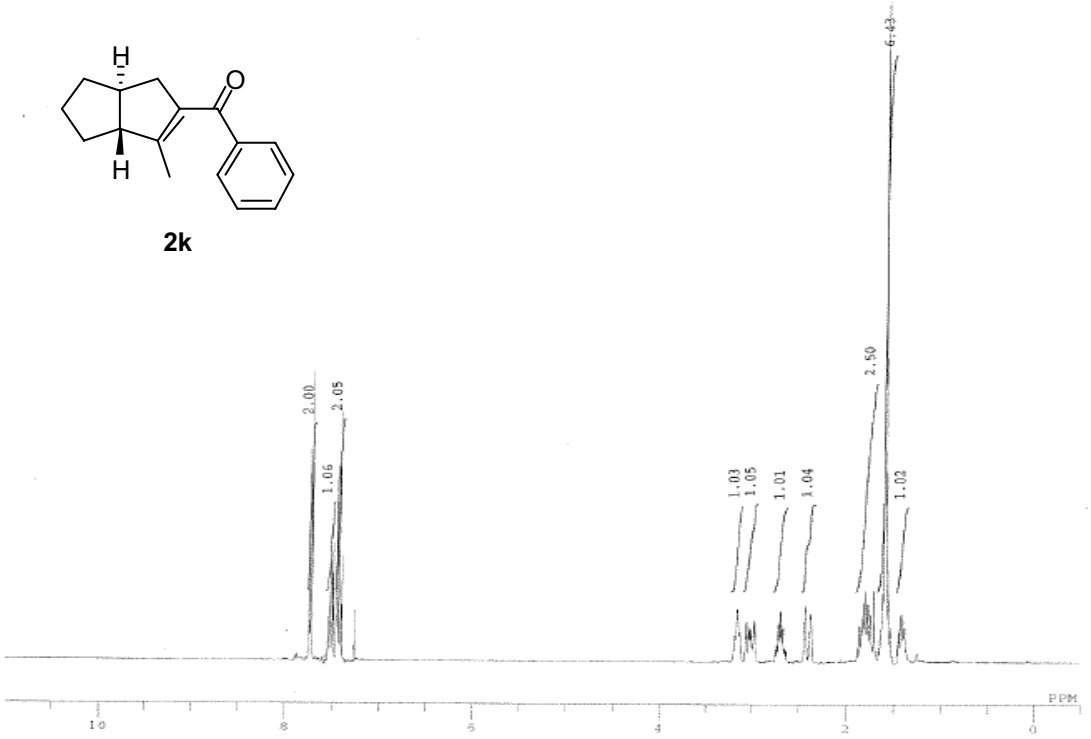

O
2i
2.02
1.07
4.17
2.07
2.07
1.00
1.06
2.12
1.04
3.08
PPM
1.0
6
5
4
3
0


196.430
148.799
145.561
139.017
135.178
132.333
128.782
128.478
128.404
126.850
126.135
77.427
77.000
76.581
48.088
43.534
42.046
16.742
O
2i
PPM
200
150
100
50
0

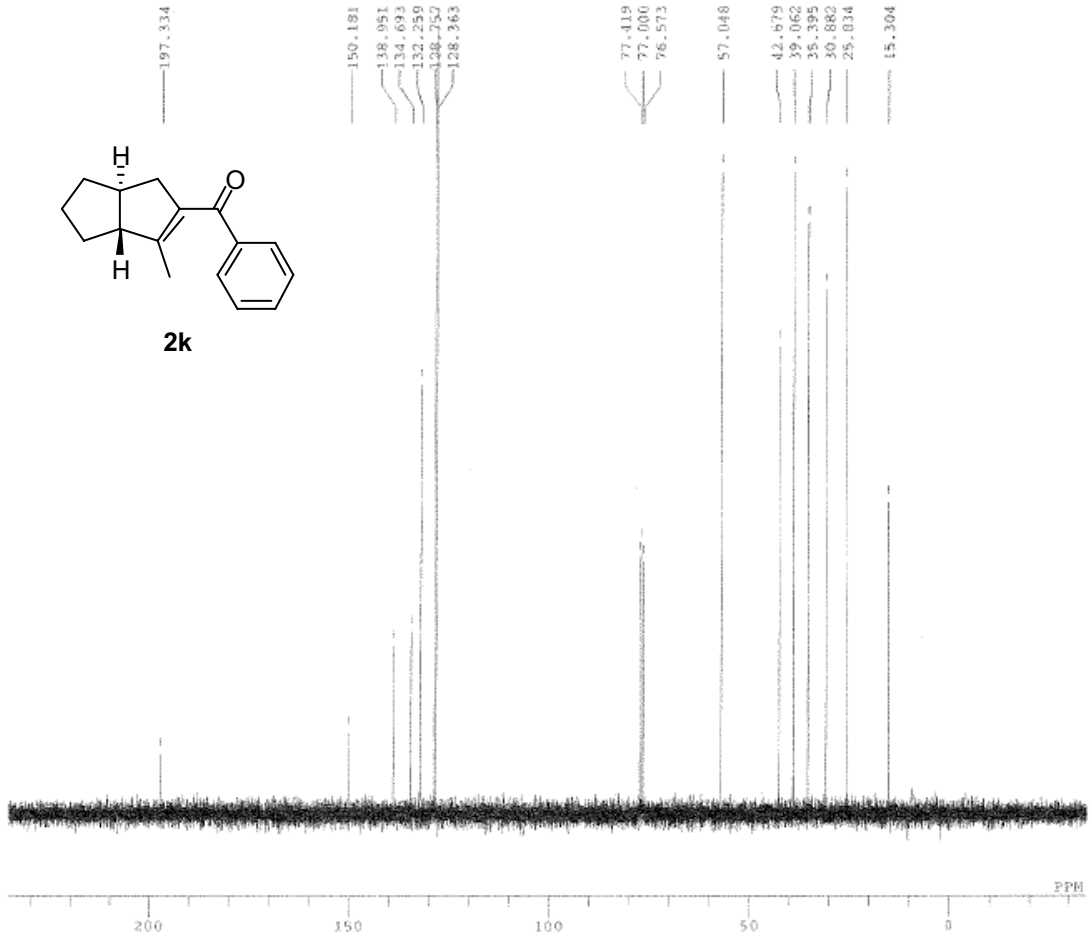

MeO2C
MeO2C
O
2j
6.10
3.04
2.00
1.97
1.92
2.01
1.00
PPM
10
8
6
4
2
0

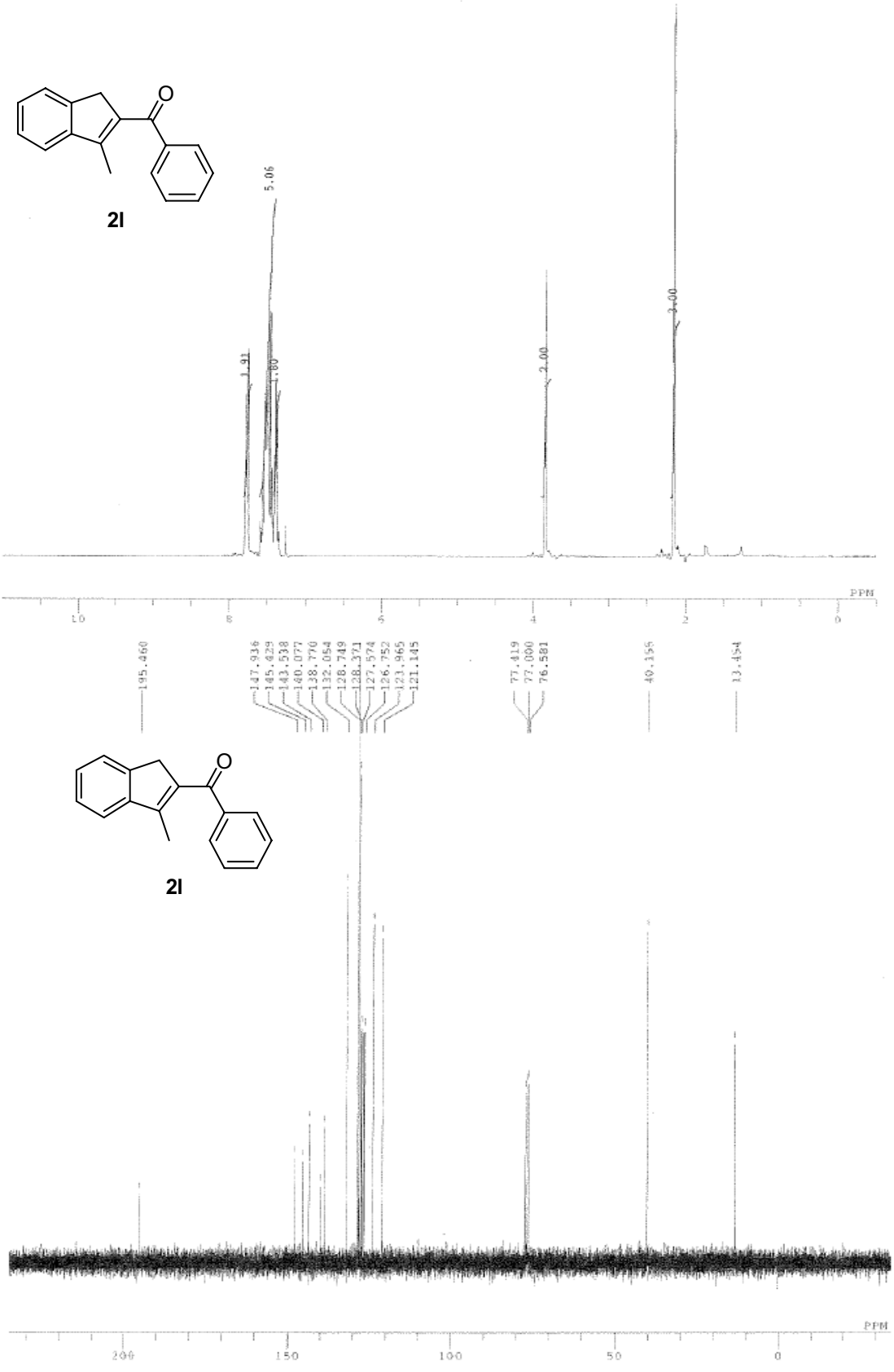

195.262
171.989
145.928
138.595
133.621
132.608
128.498
77.348
76.992
76.745
57.189
52.997
47.190
42.991
16.254
MeO2C
MeO2C
O
2j
PPM
200
150
100
50
0

2k


6.43
2.50
2.00
2.05
1.06
1.03
1.05
1.01
1.04
1.02
PPM
10
8
6
4
2
0

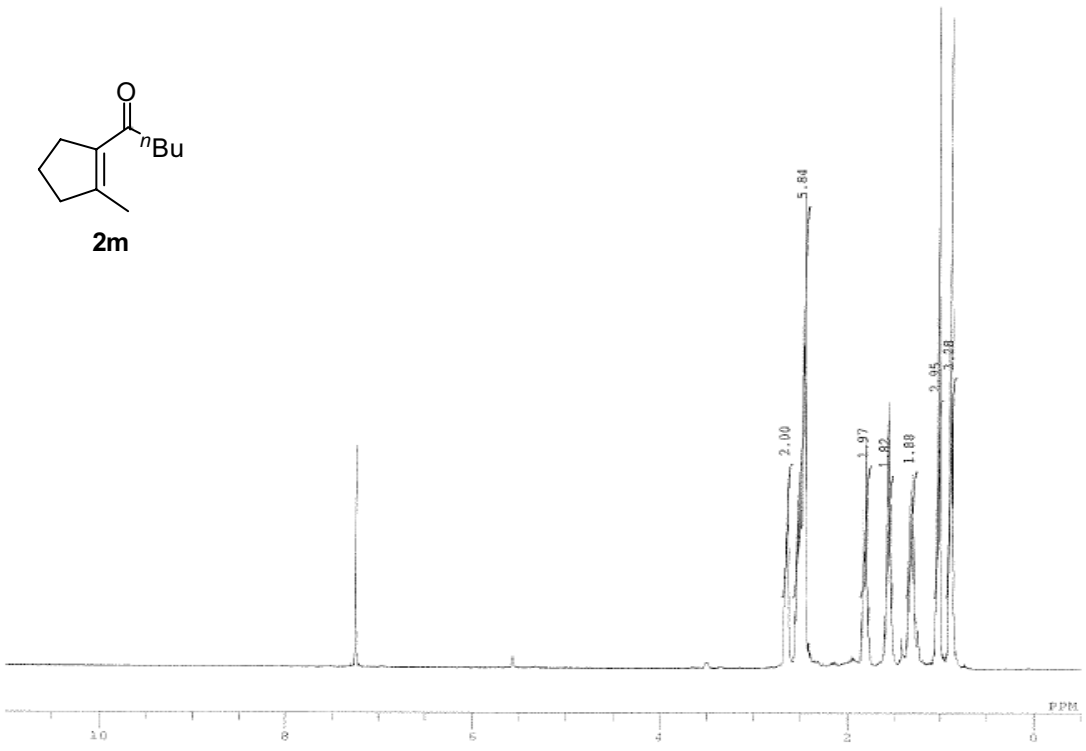
2k

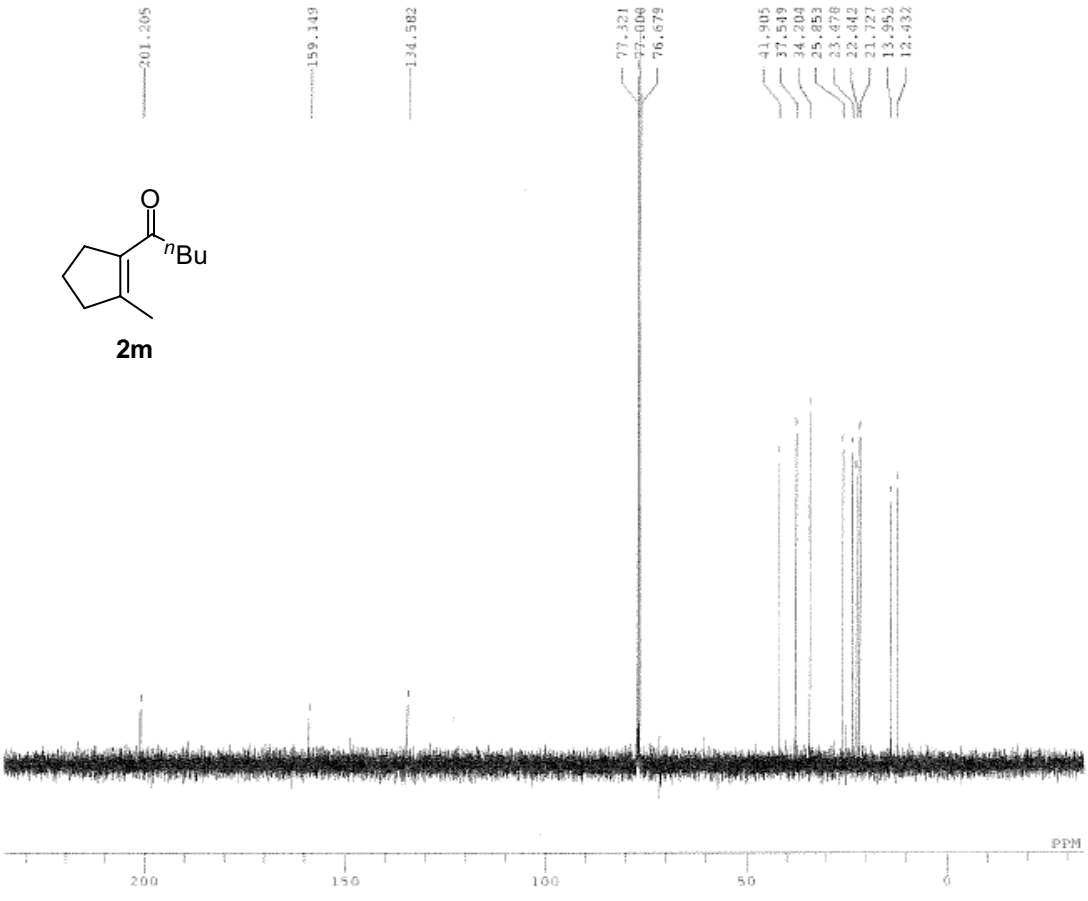

197.334
150.181
138.951
134.693
132.259
128.757
128.363
77.419
77.000
76.573
57.048
42.679
39.062
35.395
30.882
25.834
15.304
PPM
200
150
100
50
0


2l
5.06
1.91
1.80
2.00
3.00
PPM
10
8
6
4
2
0
195.460
147.936
145.429
143.538
140.077
138.770
132.054
128.749
128.371
127.574
126.752
121.965
121.145
77.419
77.000
76.581
40.155
13.454
2l
PPM
200
150
100
50
0

O
nBu

2m

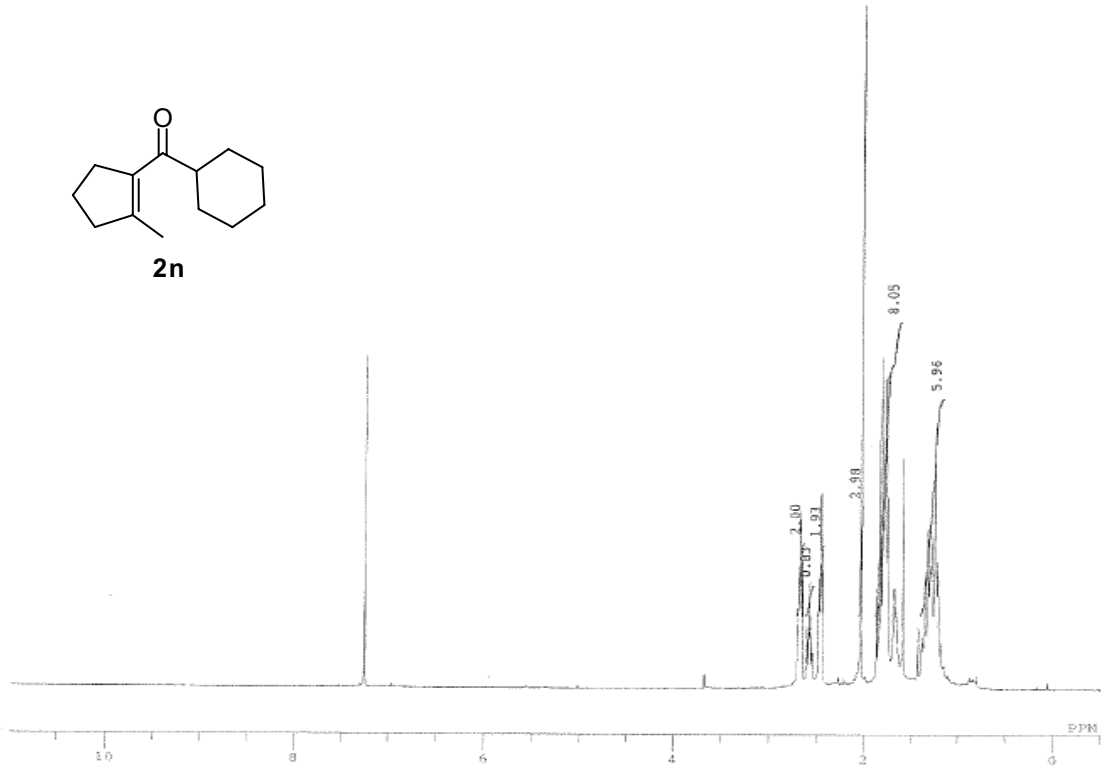

5.84
2.00
1.97
1.82
1.88
3.05
3.28
PPM
10
8
6
4
2
0


201.205
159.149
134.582
77.321
77.004
76.679
41.905
37.549
34.204
25.853
23.478
22.442
21.727
13.952
12.432
PPM
200
150
100
50
0

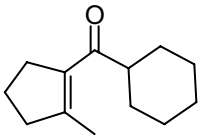
O
nBu

2m

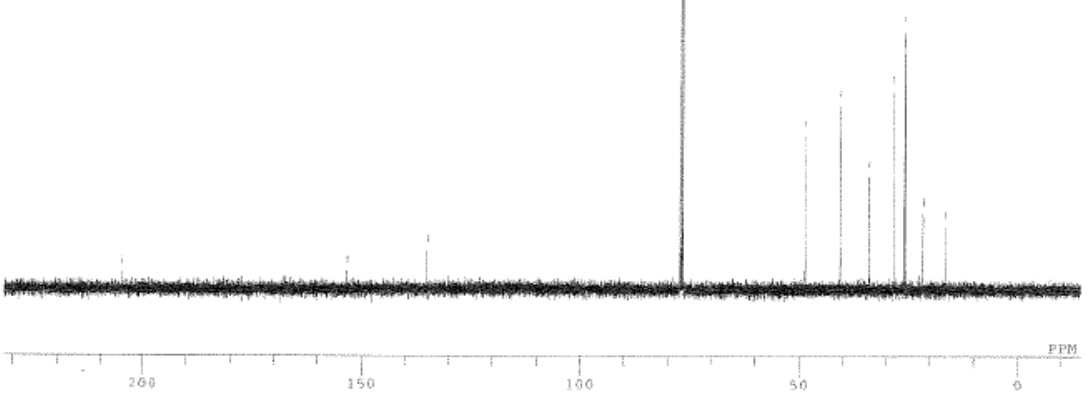
2n


8.05
5.96
3.98
2.00
1.93
0.83
PPM
10
8
6
4
2
0

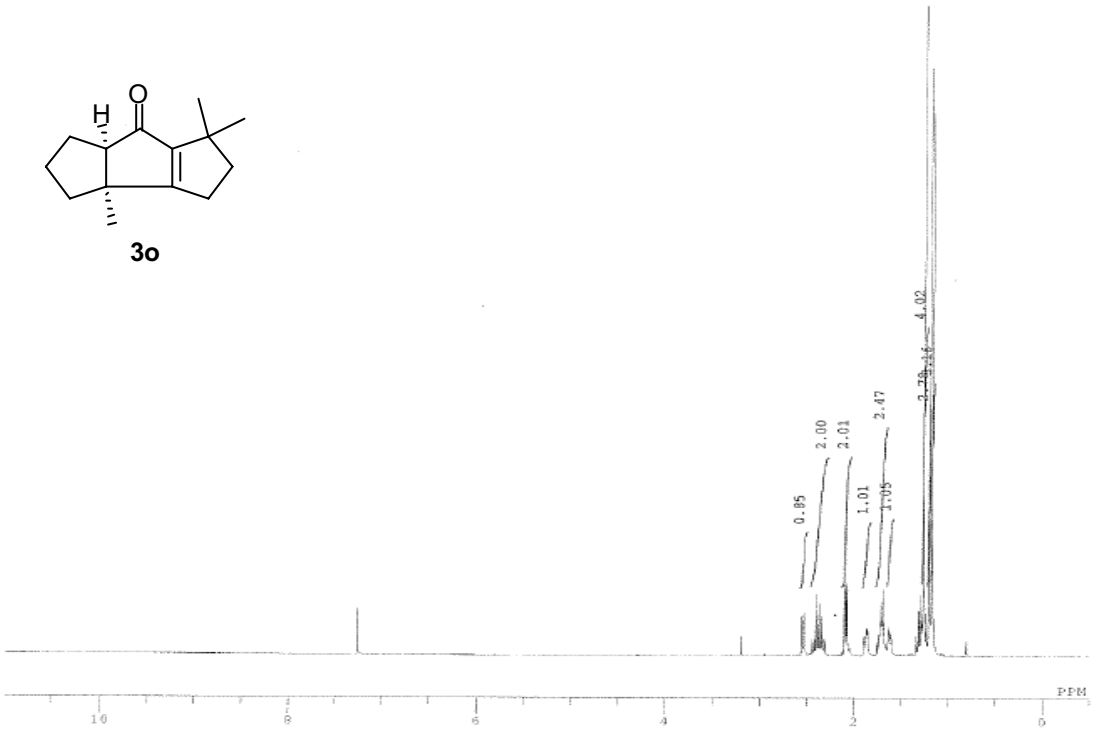

204.833
153.478
135.034
77.255
77.000
76.745
48.754
40.714
34.156
28.492
25.982
25.877
21.753
16.599

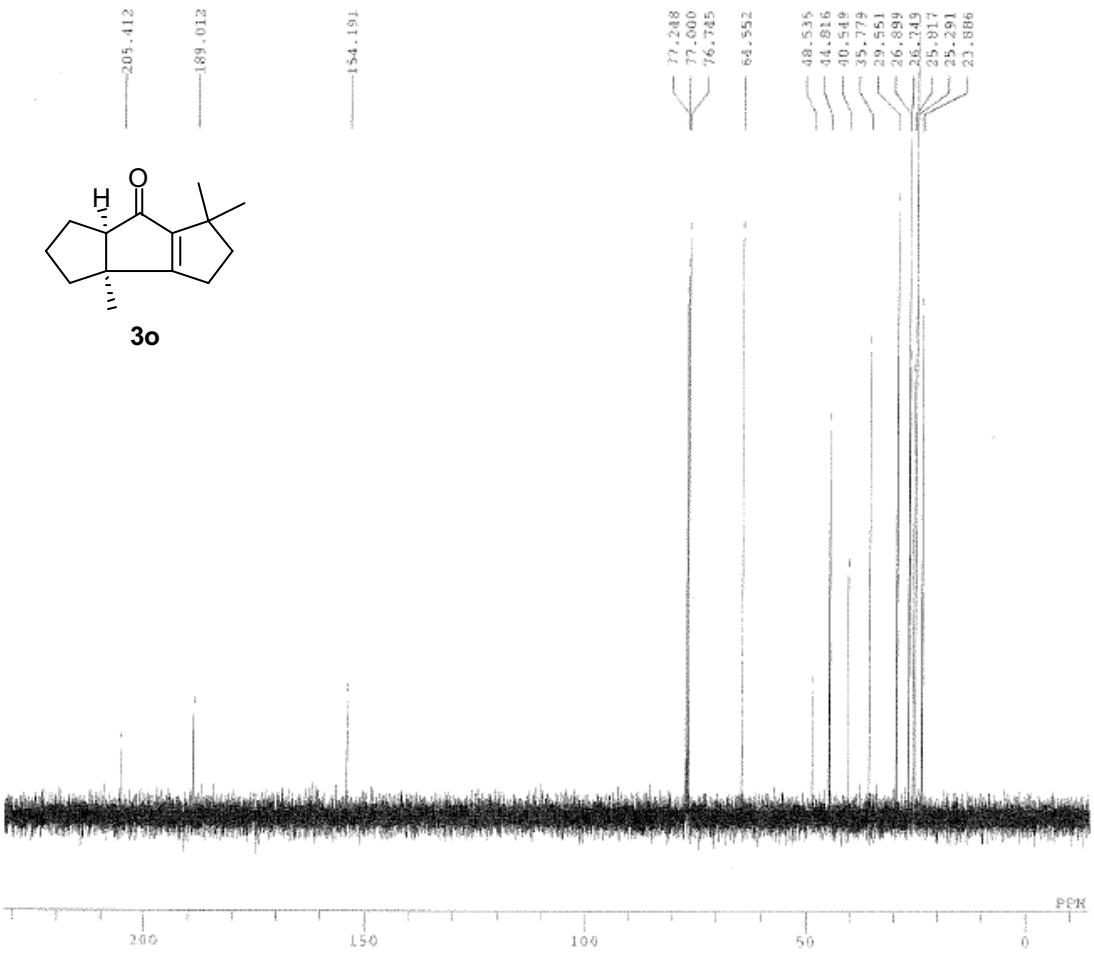


2n


PPM
200
150
100
50
0

3o

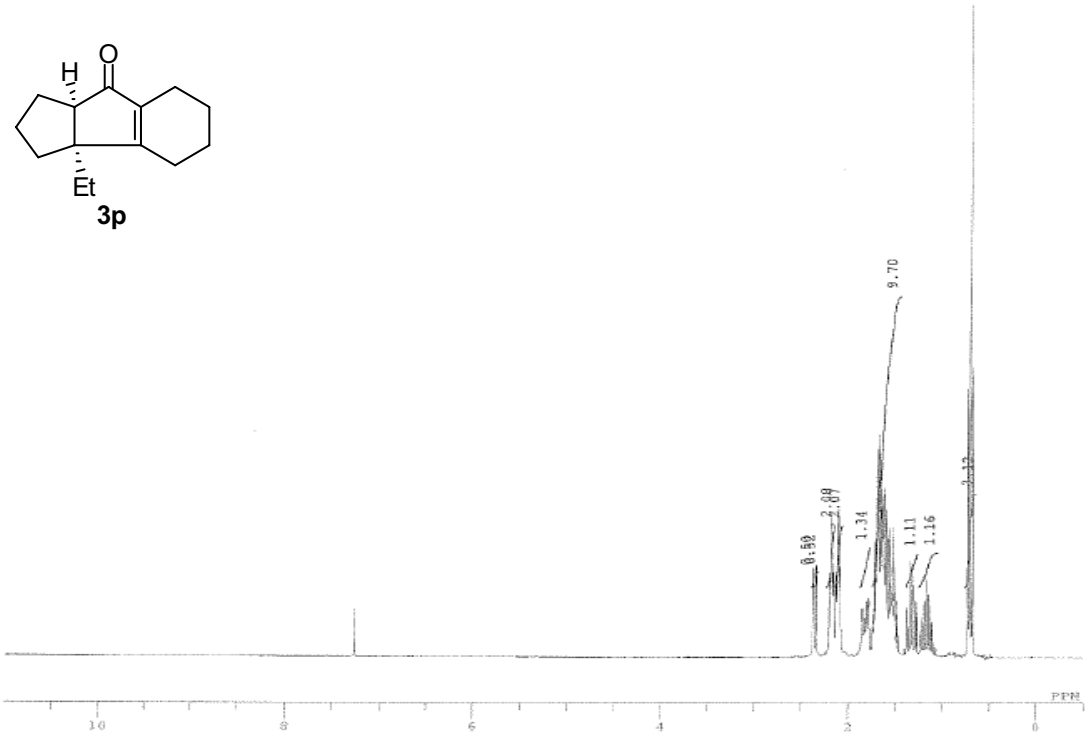

0.85
2.00
2.01
1.01
1.05
2.47
4.02
PPM
10
8
6
4
2
0

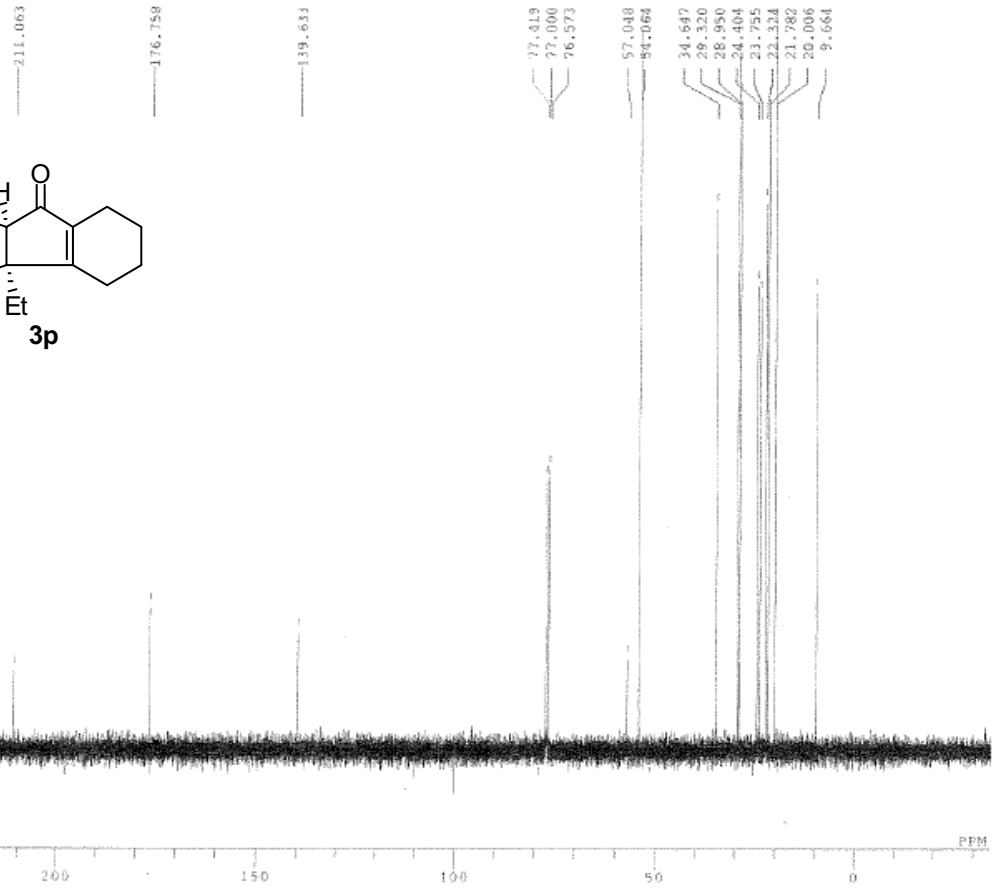

205.412
189.012
154.191
77.248
77.600
76.745
64.552
48.535
44.816
40.549
35.779
29.551
26.889
26.749
25.917
25.291
23.886
PPM
200
150
100
50
0

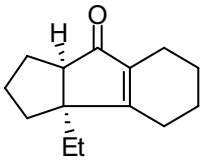
3o

H
O
Et

3p

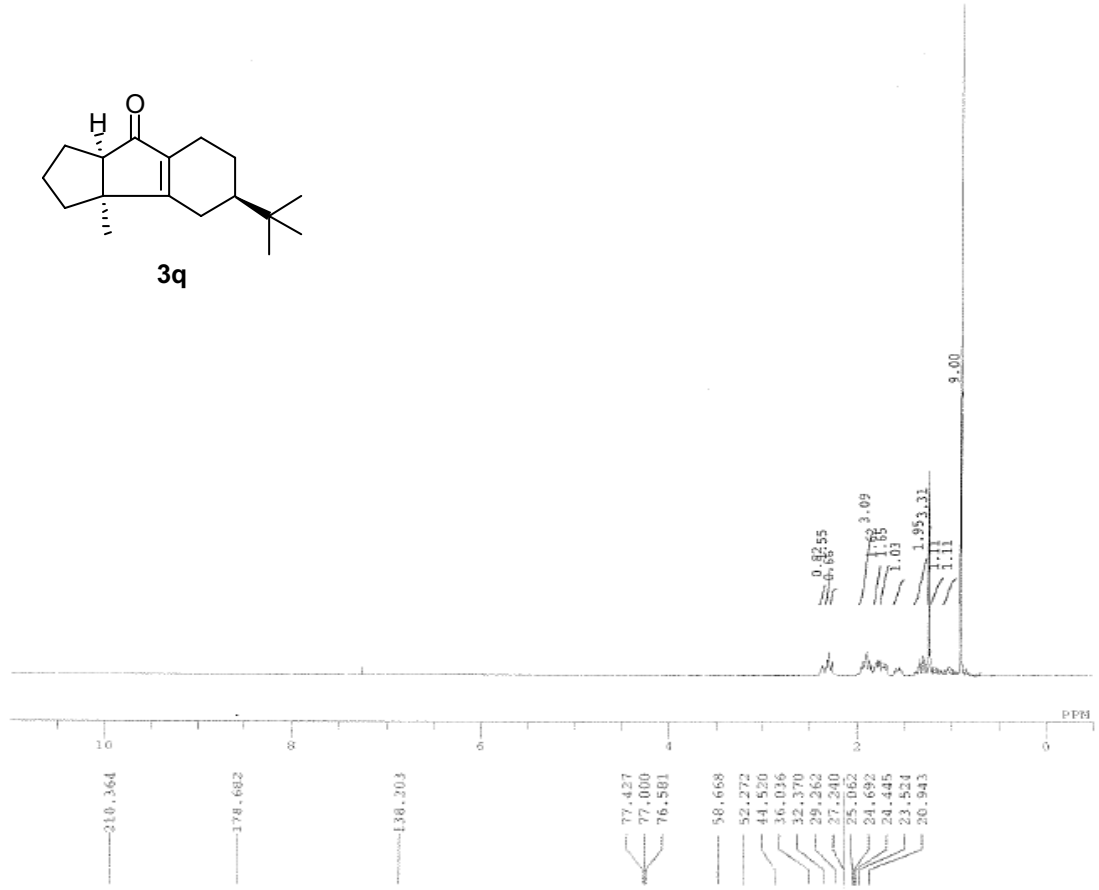

9.70
2.09
2.07
1.34
1.11
1.16
PPM
10
8
6
4
2
0


211.063
176.758
139.631
77.419
77.000
76.573
57.048
54.064
34.647
29.320
28.950
24.404
23.755
22.324
21.782
20.006
9.664
PPM
200
150
100
50
0

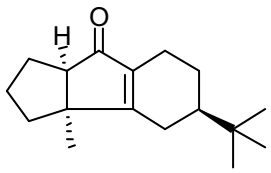

H
O
Et

3p

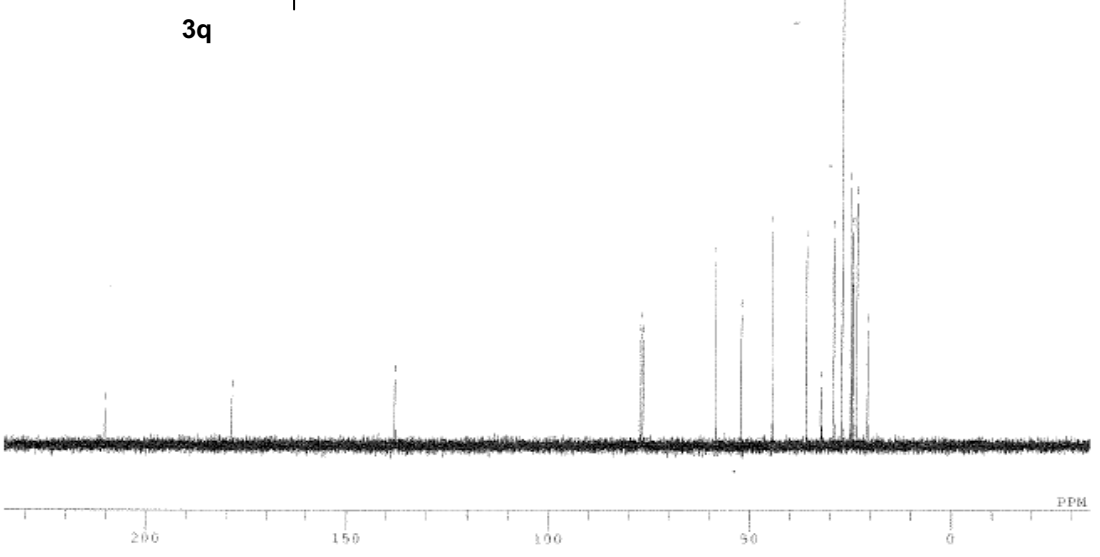
3q


9.00
3.09
1.95
1.03
1.953.31
1.11
1.11
PPM
10
8
6
4
2
0

210.364
178.682
138.203
77.427
77.000
76.581
58.668
52.272
44.530
36.036
32.370
29.262
27.240
25.062
24.692
24.445
23.534
20.943

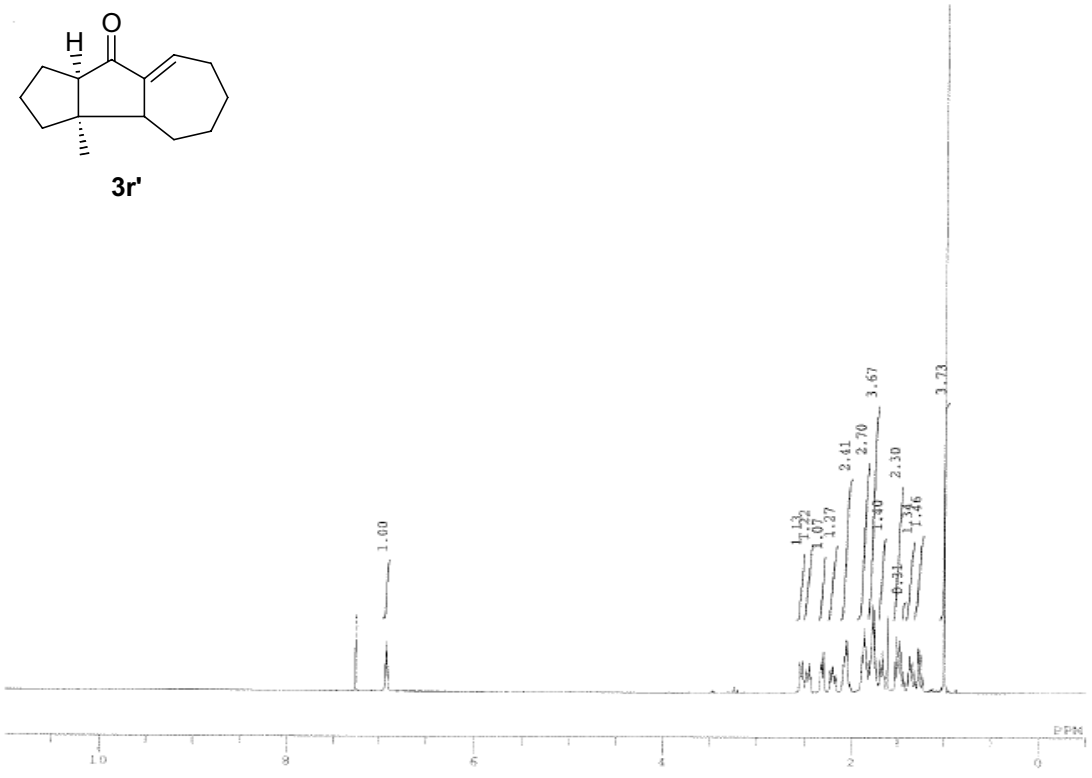


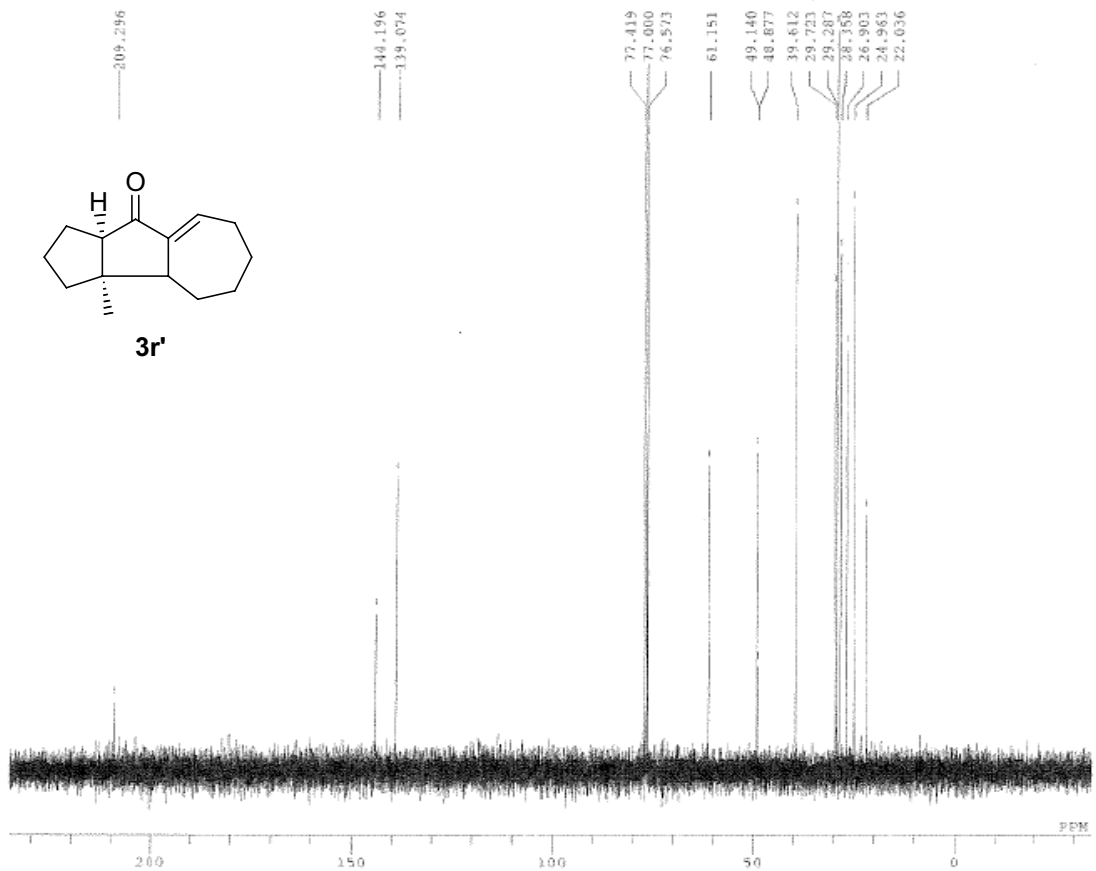
3q


PPM
200
150
100
50
0

H
O

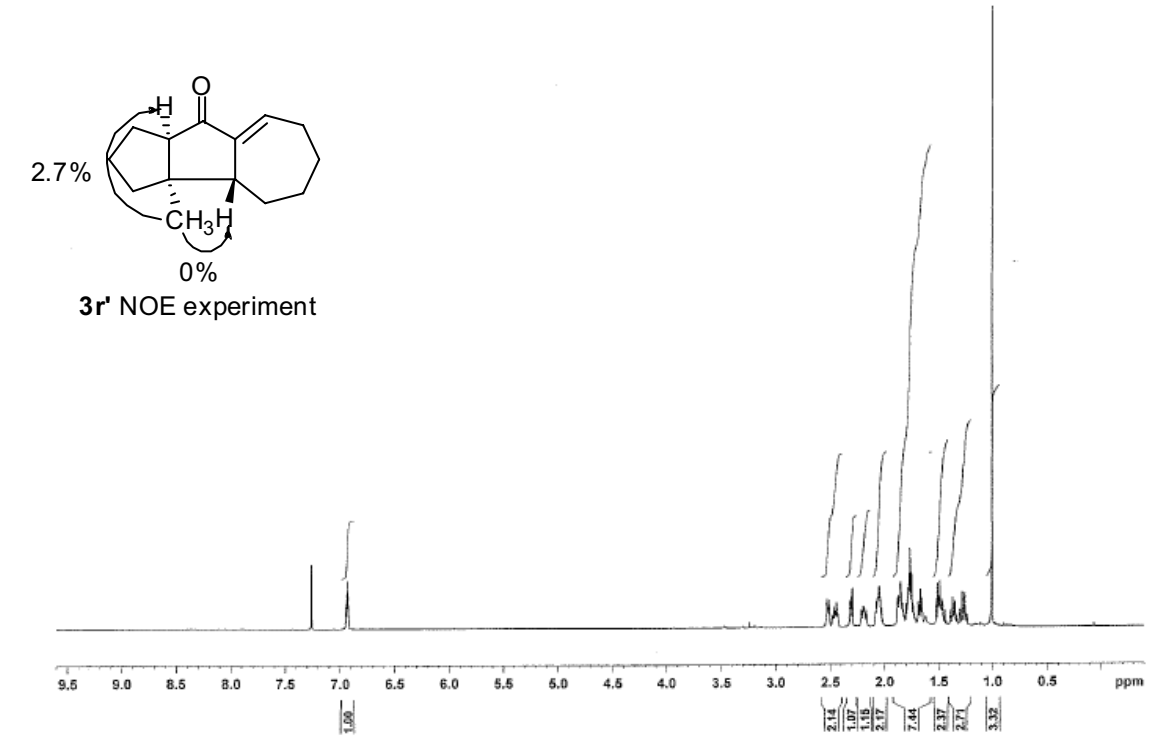
3r'

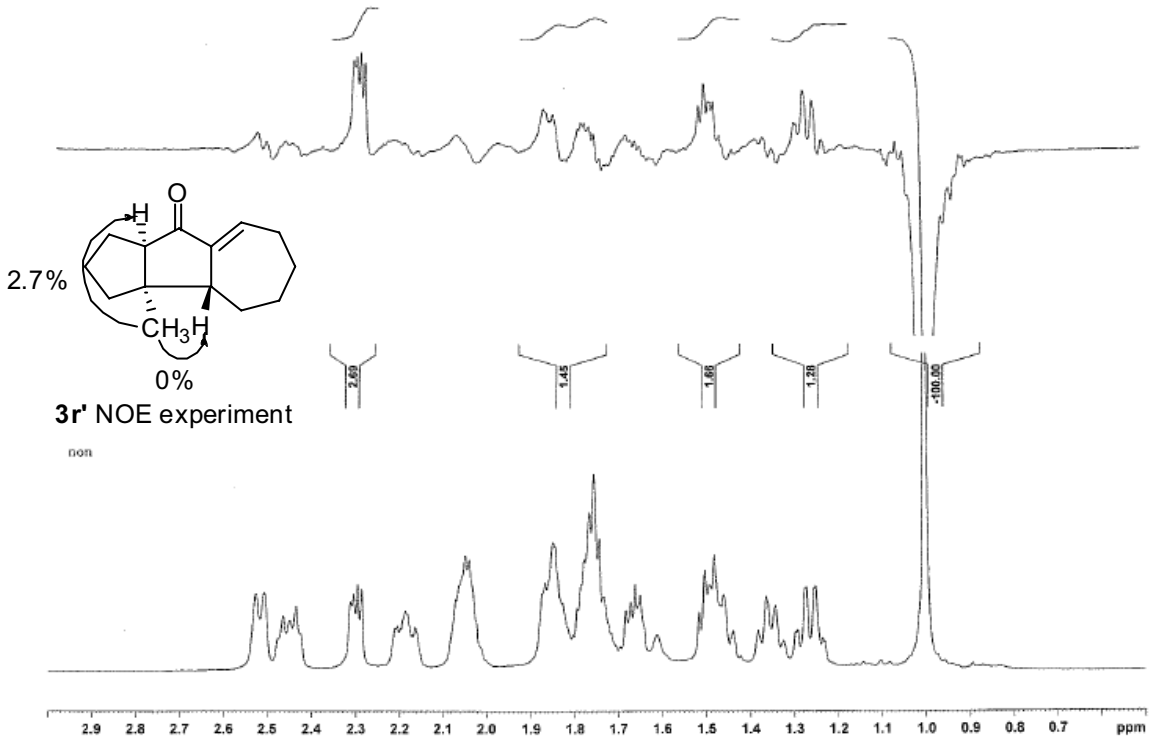

1.00
1.13
1.22
1.24
1.07
1.87
2.41
2.70
1.30
3.67
2.30
1.34
1.46
3.73
PPM
10
8
6
4
2
0


209.296
144.196
139.074
77.419
77.000
76.573
61.151
49.140
48.877
39.612
29.723
29.287
28.358
26.903
24.963
22.036
PPM
200
150
100
50
0

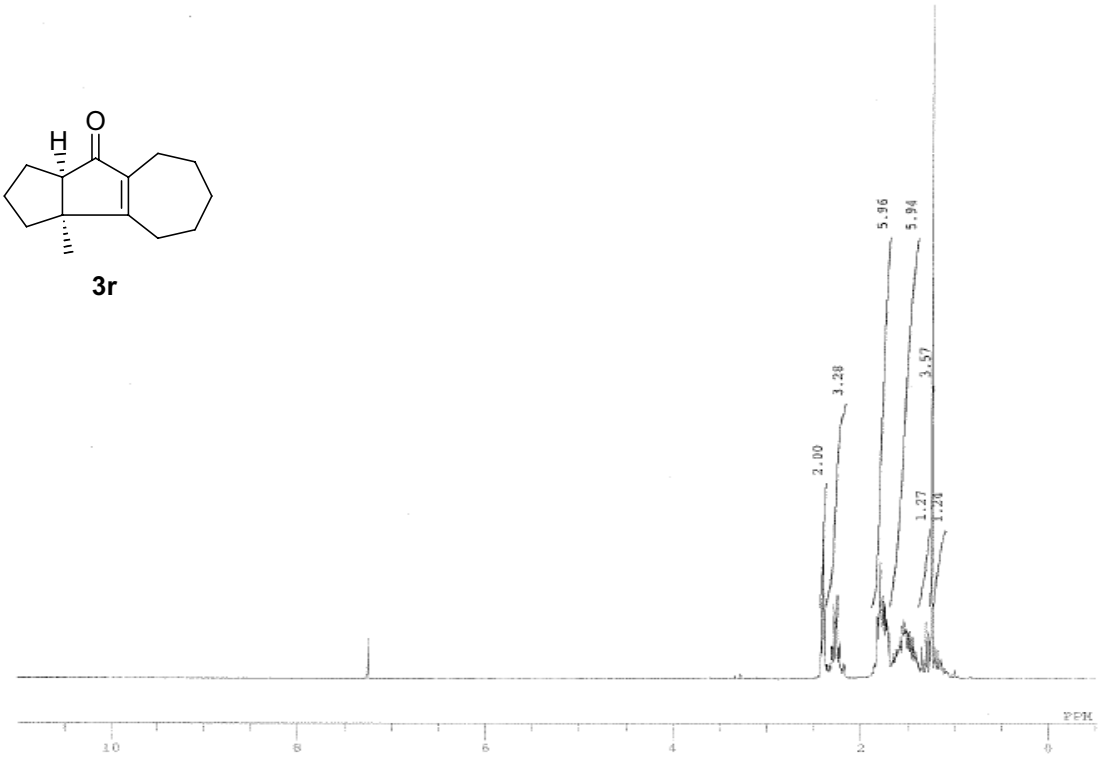
H
O

3r'

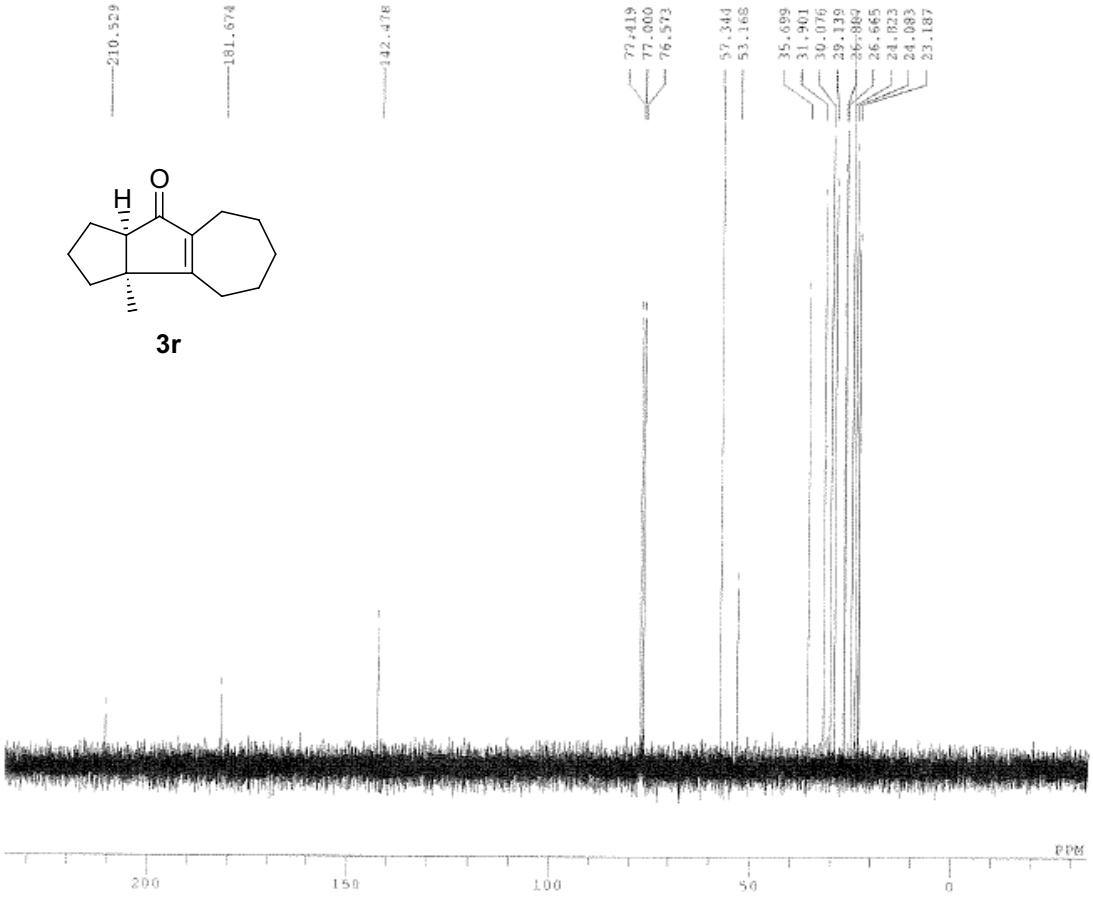

O
H
2.7%
CH3H
0%
3r' NOE experiment
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.14
1.07
1.16
2.17
7.44
2.37
2.71
3.32


O
H
2.7%
CH3H
0%
3r' NOE experiment
non
2.69
1.45
1.88
1.28
-100.00
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 ppm

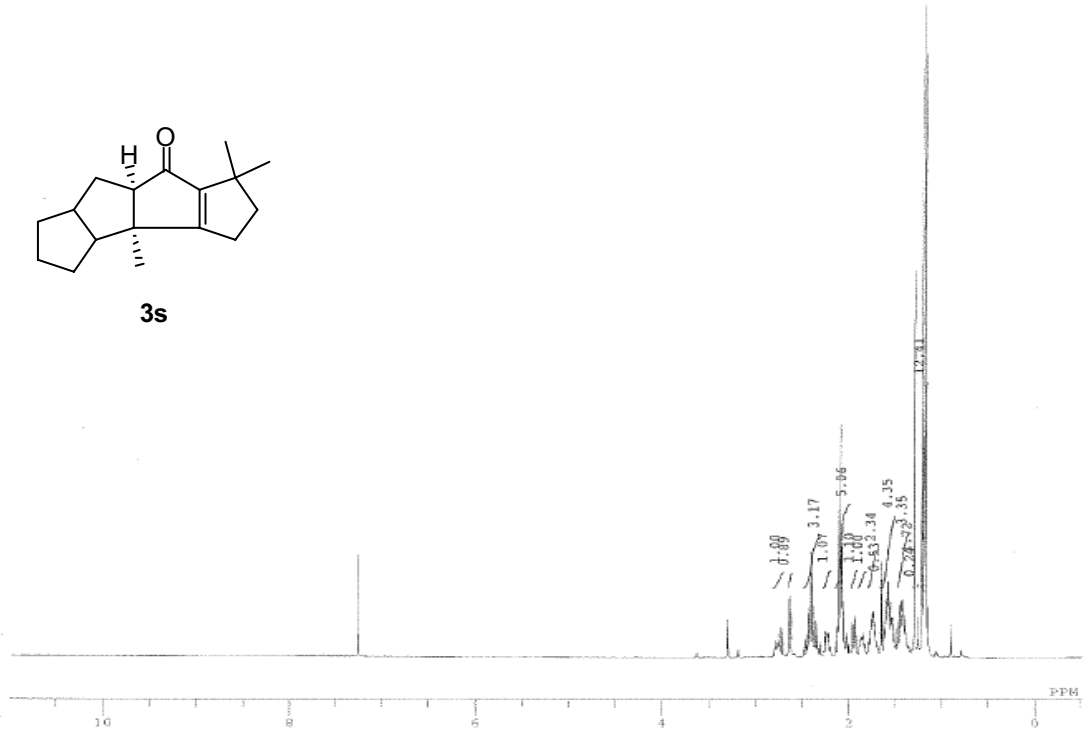
3r


5.96
5.94
3.57
3.28
2.00
1.27
1.26
PPM
10
8
6
4
2
0

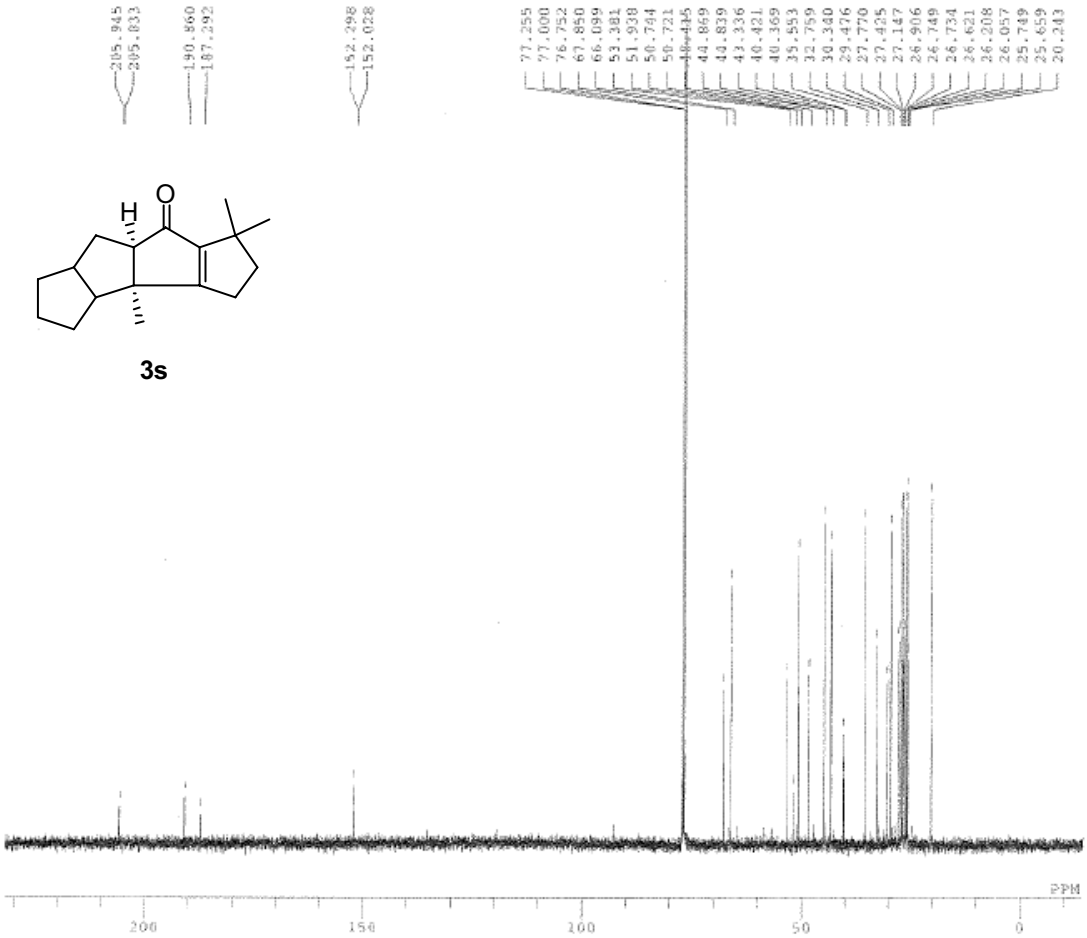
3r


210.529
181.674
142.478
77.419
77.000
76.573
57.344
53.168
35.699
31.901
30.076
29.139
26.864
26.665
24.823
24.083
23.187
PPM
200
150
100
50
0

3s


0.89
3.17
1.07
1.00
1.00
5.06
2.34
4.35
2.35
12.84
PPM
10
8
6
4
2
0

3s


205.945
205.833
190.860
187.292
152.298
152.028
77.255
77.000
76.752
67.850
66.099
53.381
51.938
50.794
50.721
44.869
44.839
43.336
40.421
40.369
35.553
32.759
30.340
29.476
27.770
27.425
27.147
26.906
26.749
26.734
26.621
26.208
26.057
25.749
25.659
20.243
PPM
200
150
100
50
0

3s 1.7:1 mixture of diastereomers (C_6D_6)