Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Zirconium Catalyzed Alkyne Dimerization for Selective *Z*-Enyne Synthesis

Rachel H. Platel, and Laurel L. Schafer*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia,V6T 1Z1

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S1: General Considerations

All reactions were performed under an atmosphere of dry, oxygen free dinitrogen using an MBraun glovebox or standard Schlenk techniques, unless otherwise noted. Dichloromethane was distilled from calcium hydride. Tetrahydrofuran, toluene, hexanes, and pentane were purified and dried by passage through a column of activated alumina and sparged with dinitrogen. Hexamethyldisiloxane was refluxed over sodium, distilled and degassed by 3 freeze-pump-thaw cycles. Benzene-d_6 and toluene-d_8 were degassed by several freeze-pump-thaw cycles and dried over activated 4 Å molecular sieves before use. All organic reagents were purchased from Aldrich and either used as received (for proligand synthesis) or distilled from calcium hydride and stored under an inert atmosphere (for reaction with Zr complexes). $ZrCl_4$ was purchased from Strem and used as received. $Zr(CH_2Ph)_4$, **1**[1] and **2**[2] were prepared according to literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either a Bruker 300 or 400 MHz Avance spectrometer; chemical shifts are given relative to residual protio solvent at 298 K. The single-crystal X-ray structure determination was performed at the Department of Chemistry, University of British Columbia, by Mr. Neal Yonson.

S2: General Procedure for amine screening

A solution of 1,3,5-trimethoxybenzene (333 µL of a 0.5 M solution) in toluene-d_8 was added to a small scintillation vial containing **2** (31 mg, 0.05 mmol). Additional toluene-d_8 (166 µL) was added and then the appropriate amine (0.05 mmol) was added to the solution, which was transferred to a J Young NMR tube. Phenylacetylene (65.3 µL, 0.5 mmol) was added to the NMR tube and the tube was sealed and shaken. A ^{1}H NMR spectrum was acquired and the tube was heated in a 110 °C oil bath for 2 h. Another ^{1}H NMR spectrum was acquired and the percentage yield of (*Z*)-1,4-Diphenylbut-1-en-3-yne calculated by comparison of the signals at 5.76 and 6.39 ppm with the ArC*H* signal of 1,3,5-trimethoxybenzene at 6.09 ppm.

S3: General Procedure for Enyne Synthesis

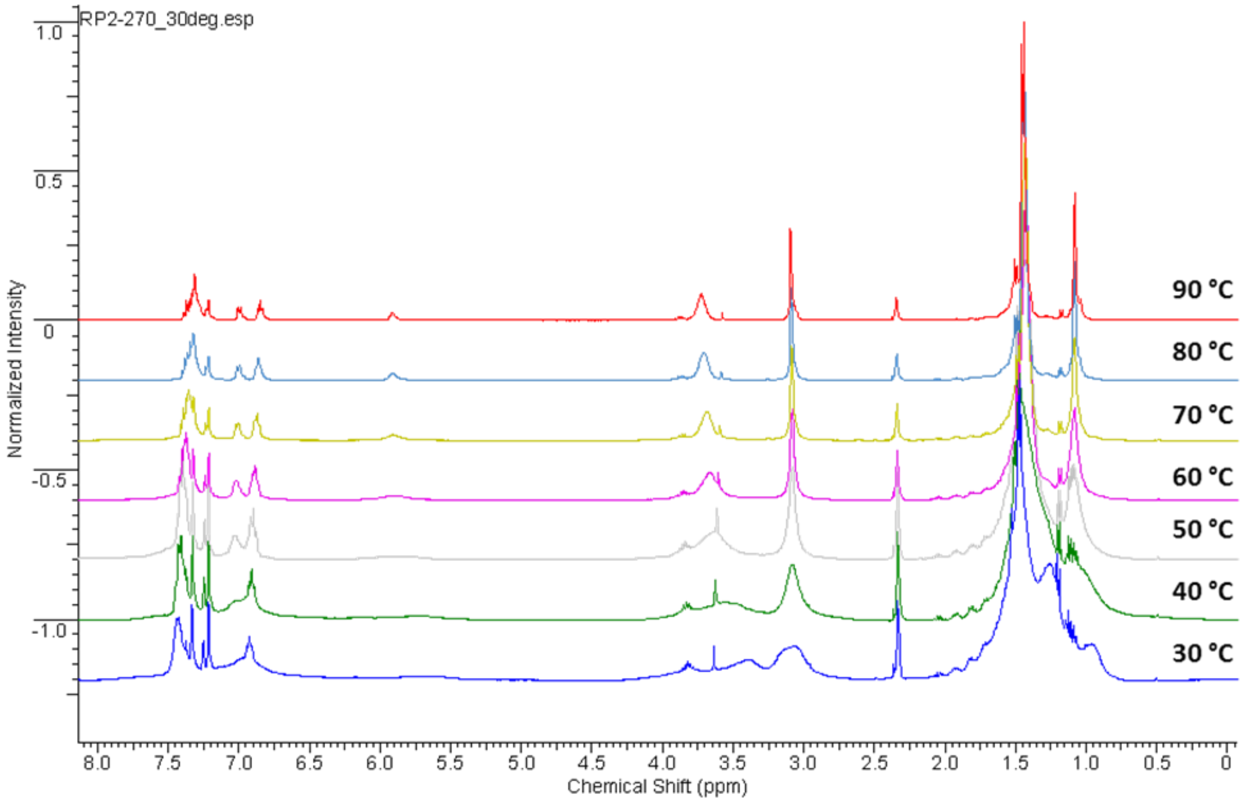
A solution of **2** (62 mg, 0.10 mmol) was prepared in toluene (1 mL). Aniline (9 µL, 0.10 mmol) was added to the solution, which was transferred to an ampoule equipped with a stir bar. The appropriate terminal alkyne (0.5 mmol) was added to the ampoule, which was sealed and heated, with stirring, at 110 °C for the appropriate length of time. After cooling, reaction mixture was transferred directly to a silica column and the enyne was isolated by column chromatography, eluting with hexanes. (*Z*)-1,4-Diphenylbut-1-en-3-yne (**3a**),[3] (*Z*)-1,4-Bis-(*p*-methoxyphenyl)but-1-en-3-yne (**3b**),[3] (*Z*)-1,4-Di-*p*-bromobut-1-en-3-yne (**3c**),[4] (*Z*)-1,4-Di-*o*-tolylbut-1-en-3-yne (**3d**),[5] (*Z*)-1,4-Bis-(*m*-methoxyphenyl)but-1-en-3-yne (**3e**)[6] and (*Z*)-1,4-Di(1-cyclohexenyl)but-1-en-3-yne (**3f**)[7] were characterized by comparison of NMR spectra with literature data.

In the case (**3g**), (*Z*)-1,4-Di(1-cyclohexyl)but-1-en-3-yne has been reported previously.[8] After column chromatography, a mixture of a dimeric and trimeric product in a 1:1 ratio was obtained. ^{1}H (400 MHz, C_6D_6, 25 °C) δ: 5.89 (1H, d, J_{HH} = 12.0 Hz, CyC*H*=, trimer), 5.74 (1H, d, J_{HH} = 10.0 Hz, CyC=C*H*, trimer), 5.59 (1H, dd, J_{HH} = 8.8 Hz, 10.8 Hz, =C*H*C≡CCy, dimer), 5.52 (1H, dd, J_{HH} = 10.8 Hz, 2.0 Hz, CyC*H*=, dimer), 5.29 (1H, dd, J_{HH} = 10.0 Hz, 12.0 Hz, CyC=C*H*, trimer), 3.63 (1H, m, C*H*), 2.88 (2H, m, C*H*), 2.57 (1H, m, C*H*), 2.48 (1H, m, C*H*), 1.95 – 1.80 (7H, m, CH_2), 1.73 – 1.48 (20H, m, CH_2), 1.43 – 1.29 (8H, m, CH_2), 1.26 – 1.03 (15H, m, CH_2); ^{13}C{^{1}H} (100 MHz, C_6D_6, 25 °C) δ: 147.7 (=*C*HCy), 147.5 (=*C*HCy), 137.7 (=*C*HCy), 127.3 (=*C*H), 120.3 (*C*), 108.5 (=*C*HC≡CAr), 99.1 (=CH*C*≡CAr), 98.4 (=CH*C*≡CAr), 79.1 (=CHC≡*C*Ar), 78.2 (=CHC≡*C*Ar), 39.5, 39.4, 36.3, 33.9 33.0 32.9 32.6, 32.5, 30.2, 30.0, 26.4, 26.3 (2), 26.2 (2), 26.1 (2), 24.9, 24.8.

S4: Synthesis of 4

Aniline (13.7 µL, 0.15 mmol) was added to a solution of **2** (0.095 g, 0.15 mmol) in hexanes (2 mL) *via* a micropipette. The resulting solution was transferred to an ampoule, sealed and heated at 60 °C for 1 h. The solvents were removed *in vacuo* to leave a colourless residue. Recrystallization from hexanes at -35 °C gave the product as a colourless powder (0.053 g, 61 %). Crystals for X-ray crystallography were grown from a toluene/hexamethyldisiloxane mixture at -35 °C. ^{1}H NMR (C_7D_8; 90 °C) δ ppm: 7.05 (9H, m, Ar*H*), 6.95 (2H, m, Ar*H*), 6.72 (2H, m, Ar*H*), 6.59 (2H, m, Ar*H*), 5.65 (2H, br s, N*H*), 3.46 (8H, m, C*H*(CH_3)$_2$), 2.83 (8H, s, CH_2), 1.18 (48H, d, J_{HH} = 6.4 Hz, CH(CH_3)$_2$), 0.82 (12H, s, CH_3); ^{13}C{^{1}H} NMR (C_7D_8; 90 °C) δ ppm: 169.7 (CO), 156.5 (Ar*C*), 156.4 (Ar*C*), 127.8 (Ar*C*), 127.4 (Ar*C*), 123.4 (Ar*C*), 121.8 (Ar*C*), 120.3 (br, Ar*C*), 117.9 (br, Ar*C*), 116.9 (Ar*C*), 116.5 (br, Ar*C*), 57.8 (*C*H_2), 47.4 (*C*H(CH_3)$_2$), 37.1 (*C*), 25.8 (*C*H_3), 22.5 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$).

S5: Variable temperature ^{1}H NMR spectra of 4 in toluene-d_8



X-ray structure of **4.** CCDC 896118.

Crystallographic Parameters for **4**

Formula	$C_{69}H_{119}N_{11}O_5Si_2Zr_2$
F_w	1421.37
Crystal Size	0.4 x 0.3 x 0.1
Colour, habit	Colourless, prisms
Crystal System	Orthorhombic
Space Group	*P 21 21 2*
a (Å)	21.592(1)
b (Å)	22.878(1)
c (Å)	16.089(1)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	7948.4(8)
Z	4
ρ_{calc} (Mg m^{-3})	1.188
Radiation	$Mo_{K\alpha}$ (λ = 0.71073 Å)
F(000)	3032
μ (mm^{-1})	0.343
$2\theta_{max}$ (°)	50.2
Total Reflections	99580
Unique Reflections	14120 [R_{int} = 0.0700]
R_1 (F^2, all data)	0.0692
wR_2 (F^2, all data)	0.1603
R_1 (F, $I = 2\sigma(I)$)	0.0479
wR_2 (F, $I = 2\sigma(I)$)	0.1326
Goodness of Fit	1.140
Flack Parameter	-0.0027

Table 2. Bond lengths [Å] and angles [°] for ls319.

C(1)-O(1)	1.303(6)
C(1)-N(1)	1.329(7)
C(1)-N(2)	1.363(7)
C(1)-Zr(01)	2.614(5)
C(2)-N(2)	1.491(6)
C(2)-C(3)	1.520(8)
C(2)-C(4)	1.525(8)
C(5)-N(2)	1.477(7)
C(5)-C(6)	1.519(8)
C(5)-C(7)	1.529(8)
C(8)-N(1)	1.449(7)
C(8)-C(9)	1.542(8)
C(9)-C(12)	1.502(8)
C(9)-C(10)	1.533(8)
C(9)-C(11)	1.546(8)
C(10)-N(3)	1.450(7)
C(13)-O(2)	1.315(6)
C(13)-N(3)	1.330(7)
C(13)-N(4)	1.340(7)
C(13)-Zr(01)	2.634(5)
C(14)-N(4)	1.467(7)
C(14)-C(16)	1.528(8)
C(14)-C(15)	1.529(8)
C(17)-N(4)	1.488(7)
C(17)-C(18)	1.507(9)
C(17)-C(19)	1.523(10)
C(20)-O(3)	1.304(6)
C(20)-N(5)	1.331(7)
C(20)-N(6)	1.343(6)
C(20)-Zr(02)	2.642(5)
C(21)-N(6)	1.490(7)
C(21)-C(22)	1.524(8)
C(21)-C(23)	1.525(8)
C(24)-N(6)	1.490(7)
C(24)-C(26)	1.511(8)
C(24)-C(25)	1.524(8)
C(27)-N(5)	1.447(6)
C(27)-C(28)	1.529(7)
C(28)-C(29)	1.506(8)
C(28)-C(30)	1.537(7)
C(28)-C(31)	1.544(8)
C(29)-N(7)	1.471(7)
C(32)-N(7)	1.303(7)
C(32)-O(4)	1.304(6)
C(32)-N(8)	1.363(7)
C(32)-Zr(02)	2.630(6)
C(33)-N(8)	1.479(7)
C(33)-C(35)	1.510(9)
C(33)-C(34)	1.512(10)
C(36)-C(37)	1.457(13)
C(36)-N(8)	1.486(8)
C(36)-C(38)	1.487(13)
C(39)-N(9)	1.376(7)
C(39)-C(44)	1.407(8)
C(39)-C(40)	1.415(8)
C(40)-C(41)	1.345(9)
C(41)-C(42)	1.416(9)
C(42)-C(43)	1.376(9)
C(43)-C(44)	1.387(8)
C(45)-C(50)	1.369(8)
C(45)-C(46)	1.407(8)
C(45)-N(10)	1.418(7)
C(46)-C(47)	1.382(8)
C(47)-C(48)	1.388(10)
C(48)-C(49)	1.343(9)
C(49)-C(50)	1.389(8)
C(51)-C(52)	1.389(8)
C(51)-C(56)	1.392(8)
C(51)-N(11)	1.417(7)
C(52)-C(53)	1.392(9)
C(53)-C(54)	1.366(11)
C(54)-C(55)	1.393(12)
C(55)-C(56)	1.382(9)
C(200)-Si(2)	1.814(11)
C(201)-Si(2)	1.852(12)
C(202)-Si(2)	1.734(13)
C(203)-Si(1)	1.884(14)
C(204)-Si(1)	1.883(17)
C(205)-Si(1)	1.766(13)
C(500)-C(501)	1.3900
C(500)-C(505)	1.3900
C(501)-C(502)	1.3900
C(501)-C(506)	1.571(18)
C(502)-C(503)	1.3900
C(503)-C(504)	1.3900
C(504)-C(505)	1.3900
N(1)-Zr(01)	2.204(4)
N(3)-Zr(01)	2.202(4)
N(5)-Zr(02)	2.185(4)
N(7)-Zr(02)	2.194(4)
N(9)-Zr(02)	2.176(4)
N(10)-Zr(01)	2.258(4)
N(10)-Zr(02)	2.391(4)
N(11)-Zr(01)	1.975(4)
N(11)-Zr(02)	2.173(4)
O(1)-Zr(01)	2.158(3)
O(2)-Zr(01)	2.186(3)
O(3)-Zr(02)	2.227(3)

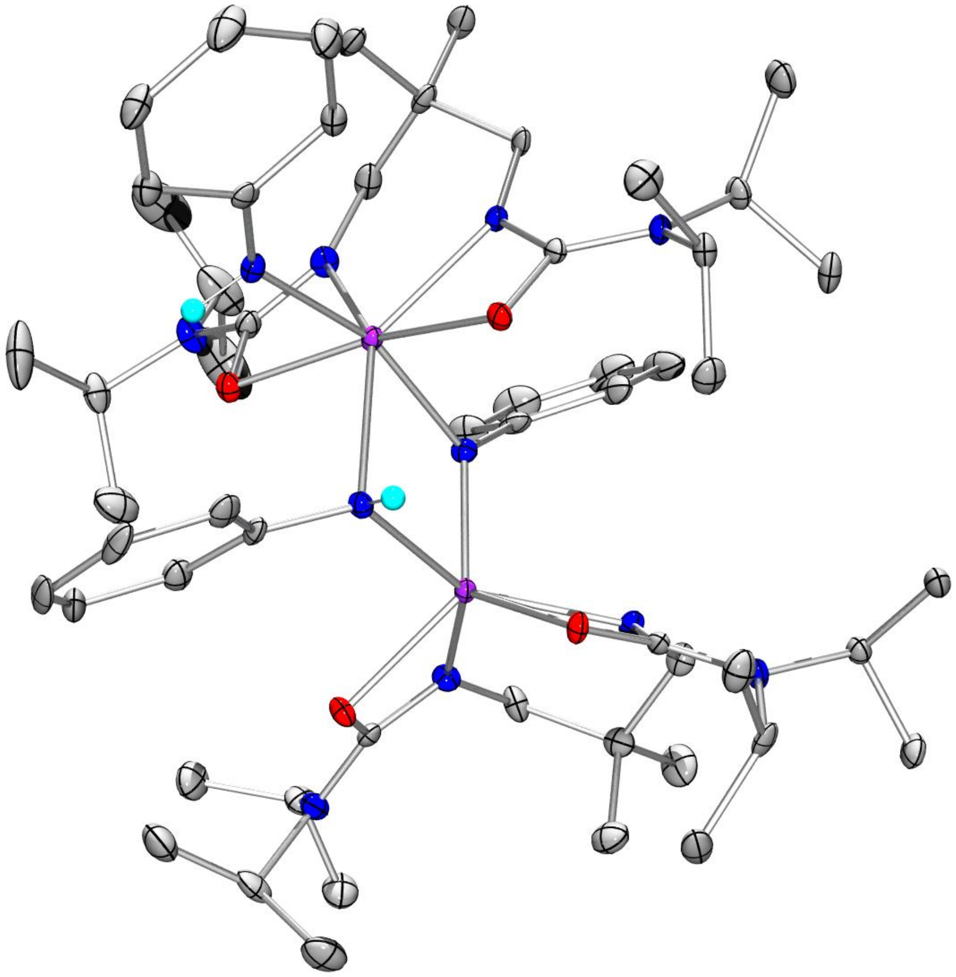
O(4)-Zr(02)	2.212(4)
O(500)-Si(1)	1.637(8)
O(500)-Si(2)	1.645(8)
Zr(01)-Zr(02)	3.3963(7)
C(507)-C(508)	1.3900
C(507)-C(512)	1.3900
C(508)-C(509)	1.3900
C(509)-C(510)	1.3900
C(510)-C(511)	1.3900
C(511)-C(512)	1.3900
C(512)-C(513)	1.41(5)

O(1)-C(1)-N(1)	112.7(4)
O(1)-C(1)-N(2)	118.7(4)
N(1)-C(1)-N(2)	128.6(5)
O(1)-C(1)-Zr(01)	55.3(2)
N(1)-C(1)-Zr(01)	57.4(3)
N(2)-C(1)-Zr(01)	173.8(4)
N(2)-C(2)-C(3)	110.8(4)
N(2)-C(2)-C(4)	113.7(5)
C(3)-C(2)-C(4)	114.0(5)
N(2)-C(5)-C(6)	112.5(4)
N(2)-C(5)-C(7)	109.7(4)
C(6)-C(5)-C(7)	111.8(4)
N(1)-C(8)-C(9)	112.8(4)
C(12)-C(9)-C(10)	111.9(5)
C(12)-C(9)-C(8)	109.9(5)
C(10)-C(9)-C(8)	112.2(5)
C(12)-C(9)-C(11)	110.2(5)
C(10)-C(9)-C(11)	106.4(5)
C(8)-C(9)-C(11)	106.0(5)
N(3)-C(10)-C(9)	112.9(4)
O(2)-C(13)-N(3)	112.5(4)
O(2)-C(13)-N(4)	118.3(4)
N(3)-C(13)-N(4)	129.2(5)
O(2)-C(13)-Zr(01)	55.9(2)
N(3)-C(13)-Zr(01)	56.6(3)
N(4)-C(13)-Zr(01)	174.1(4)
N(4)-C(14)-C(16)	110.9(5)
N(4)-C(14)-C(15)	113.1(5)
C(16)-C(14)-C(15)	111.4(5)
N(4)-C(17)-C(18)	111.1(5)
N(4)-C(17)-C(19)	113.9(5)
C(18)-C(17)-C(19)	112.1(6)
O(3)-C(20)-N(5)	111.2(4)
O(3)-C(20)-N(6)	118.5(4)
N(5)-C(20)-N(6)	130.2(5)
O(3)-C(20)-Zr(02)	57.3(2)
N(5)-C(20)-Zr(02)	55.6(2)
N(6)-C(20)-Zr(02)	166.0(4)
N(6)-C(21)-C(22)	111.1(4)
N(6)-C(21)-C(23)	111.7(4)
C(22)-C(21)-C(23)	111.8(5)
N(6)-C(24)-C(26)	111.6(4)
N(6)-C(24)-C(25)	113.7(4)
C(26)-C(24)-C(25)	112.1(5)
N(5)-C(27)-C(28)	112.4(4)
C(29)-C(28)-C(27)	111.4(5)
C(29)-C(28)-C(30)	106.9(5)
C(27)-C(28)-C(30)	107.0(4)
C(29)-C(28)-C(31)	112.1(5)
C(27)-C(28)-C(31)	110.2(5)
C(30)-C(28)-C(31)	109.0(5)
N(7)-C(29)-C(28)	112.8(5)
N(7)-C(32)-O(4)	112.9(5)
N(7)-C(32)-N(8)	129.6(5)
O(4)-C(32)-N(8)	117.5(5)
N(7)-C(32)-Zr(02)	56.3(3)
O(4)-C(32)-Zr(02)	57.1(3)
N(8)-C(32)-Zr(02)	169.9(4)
N(8)-C(33)-C(35)	111.3(6)
N(8)-C(33)-C(34)	111.9(5)
C(35)-C(33)-C(34)	112.8(7)
C(37)-C(36)-N(8)	113.5(8)
C(37)-C(36)-C(38)	111.5(8)
N(8)-C(36)-C(38)	112.6(7)
N(9)-C(39)-C(44)	122.4(5)
N(9)-C(39)-C(40)	120.8(5)
C(44)-C(39)-C(40)	116.8(5)
C(41)-C(40)-C(39)	121.5(5)
C(40)-C(41)-C(42)	121.3(6)
C(43)-C(42)-C(41)	118.5(6)
C(42)-C(43)-C(44)	120.3(6)
C(43)-C(44)-C(39)	121.6(6)
C(50)-C(45)-C(46)	117.5(5)
C(50)-C(45)-N(10)	121.4(5)
C(46)-C(45)-N(10)	121.1(5)
C(47)-C(46)-C(45)	120.9(6)
C(46)-C(47)-C(48)	119.8(6)
C(49)-C(48)-C(47)	119.0(5)
C(48)-C(49)-C(50)	121.9(6)
C(45)-C(50)-C(49)	120.6(6)
C(52)-C(51)-C(56)	117.3(5)
C(52)-C(51)-N(11)	121.5(5)
C(56)-C(51)-N(11)	121.3(5)
C(51)-C(52)-C(53)	121.0(7)
C(54)-C(53)-C(52)	120.7(7)
C(53)-C(54)-C(55)	119.7(6)
C(56)-C(55)-C(54)	119.2(7)
C(55)-C(56)-C(51)	122.2(7)
C(501)-C(500)-C(505)	120.0
C(500)-C(501)-C(502)	120.0

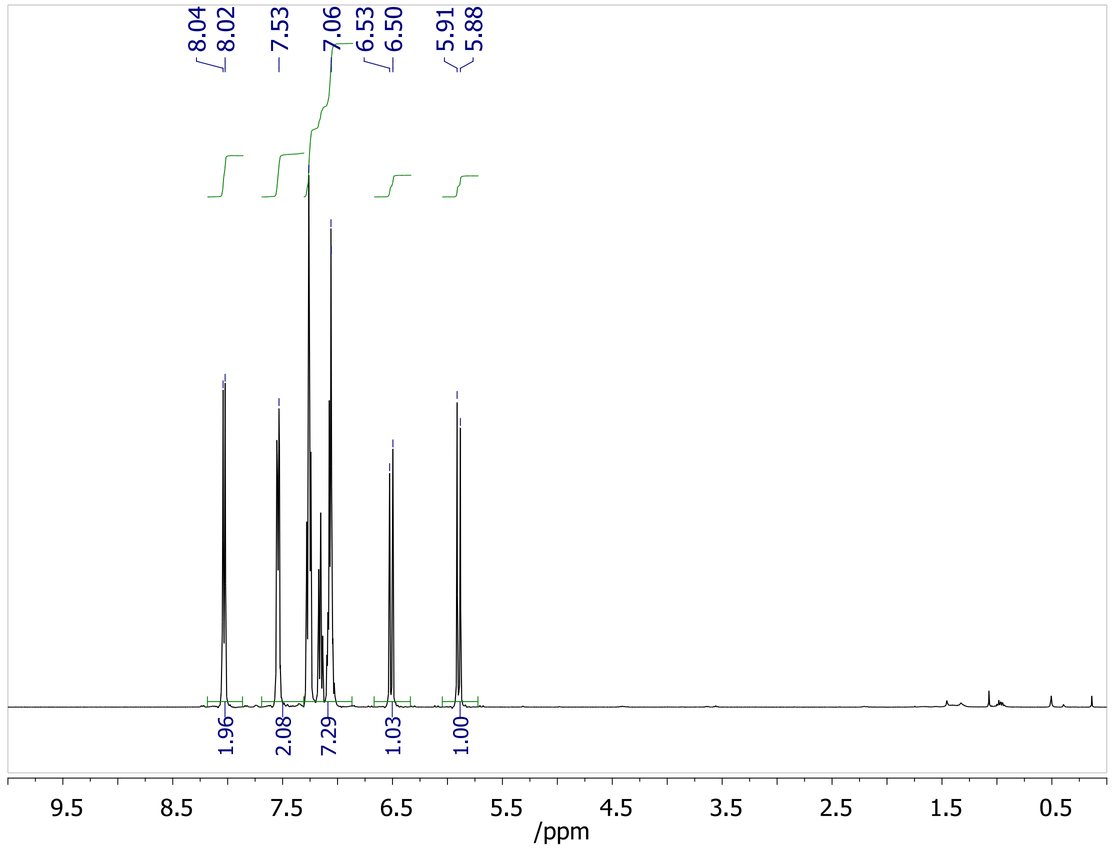
C(500)-C(501)-C(506)	124.2(9)	N(3)-Zr(01)-N(1)	80.20(16)
C(502)-C(501)-C(506)	115.8(9)	N(11)-Zr(01)-N(10)	81.64(16)
C(503)-C(502)-C(501)	120.0	O(1)-Zr(01)-N(10)	87.19(14)
C(502)-C(503)-C(504)	120.0	O(2)-Zr(01)-N(10)	88.28(15)
C(505)-C(504)-C(503)	120.0	N(3)-Zr(01)-N(10)	139.00(16)
C(504)-C(505)-C(500)	120.0	N(1)-Zr(01)-N(10)	140.79(16)
C(1)-N(1)-C(8)	129.7(4)	N(11)-Zr(01)-C(1)	111.34(16)
C(1)-N(1)-Zr(01)	92.1(3)	O(1)-Zr(01)-C(1)	29.77(14)
C(8)-N(1)-Zr(01)	133.4(3)	O(2)-Zr(01)-C(1)	119.68(15)
C(1)-N(2)-C(5)	122.6(4)	N(3)-Zr(01)-C(1)	103.94(16)
C(1)-N(2)-C(2)	119.0(4)	N(1)-Zr(01)-C(1)	30.54(16)
C(5)-N(2)-C(2)	118.4(4)	N(10)-Zr(01)-C(1)	114.83(16)
C(13)-N(3)-C(10)	127.3(4)	N(11)-Zr(01)-C(13)	115.20(16)
C(13)-N(3)-Zr(01)	93.1(3)	O(1)-Zr(01)-C(13)	122.68(15)
C(10)-N(3)-Zr(01)	132.7(3)	O(2)-Zr(01)-C(13)	29.85(15)
C(13)-N(4)-C(14)	121.8(5)	N(3)-Zr(01)-C(13)	30.27(16)
C(13)-N(4)-C(17)	119.7(5)	N(1)-Zr(01)-C(13)	101.81(16)
C(14)-N(4)-C(17)	117.8(4)	N(10)-Zr(01)-C(13)	114.77(16)
C(20)-N(5)-C(27)	129.4(4)	C(1)-Zr(01)-C(13)	114.84(16)
C(20)-N(5)-Zr(02)	94.3(3)	N(11)-Zr(01)-Zr(02)	37.01(12)
C(27)-N(5)-Zr(02)	135.9(3)	O(1)-Zr(01)-Zr(02)	108.76(10)
C(20)-N(6)-C(21)	123.2(4)	O(2)-Zr(01)-Zr(02)	114.71(10)
C(20)-N(6)-C(24)	119.5(4)	N(3)-Zr(01)-Zr(02)	123.21(11)
C(21)-N(6)-C(24)	117.2(4)	N(1)-Zr(01)-Zr(02)	122.53(11)
C(32)-N(7)-C(29)	131.1(5)	N(10)-Zr(01)-Zr(02)	44.63(11)
C(32)-N(7)-Zr(02)	94.1(3)	C(1)-Zr(01)-Zr(02)	120.52(11)
C(29)-N(7)-Zr(02)	134.4(4)	C(13)-Zr(01)-Zr(02)	124.27(11)
C(32)-N(8)-C(33)	121.2(5)	N(11)-Zr(02)-N(9)	161.92(17)
C(32)-N(8)-C(36)	123.2(5)	N(11)-Zr(02)-N(5)	91.29(15)
C(33)-N(8)-C(36)	115.6(5)	N(9)-Zr(02)-N(5)	105.15(17)
C(39)-N(9)-Zr(02)	140.2(4)	N(11)-Zr(02)-N(7)	90.99(17)
C(45)-N(10)-Zr(01)	131.0(3)	N(9)-Zr(02)-N(7)	99.44(17)
C(45)-N(10)-Zr(02)	115.2(3)	N(5)-Zr(02)-N(7)	78.83(16)
Zr(01)-N(10)-Zr(02)	93.82(15)	N(11)-Zr(02)-O(4)	90.75(14)
C(51)-N(11)-Zr(01)	126.9(3)	N(9)-Zr(02)-O(4)	82.16(16)
C(51)-N(11)-Zr(02)	123.2(3)	N(5)-Zr(02)-O(4)	137.89(14)
Zr(01)-N(11)-Zr(02)	109.83(19)	N(7)-Zr(02)-O(4)	59.08(15)
C(1)-O(1)-Zr(01)	94.9(3)	N(11)-Zr(02)-O(3)	94.04(14)
C(13)-O(2)-Zr(01)	94.3(3)	N(9)-Zr(02)-O(3)	88.19(15)
C(20)-O(3)-Zr(02)	93.2(3)	N(5)-Zr(02)-O(3)	59.04(14)
C(32)-O(4)-Zr(02)	93.2(3)	N(7)-Zr(02)-O(3)	137.63(15)
Si(1)-O(500)-Si(2)	148.4(6)	O(4)-Zr(02)-O(3)	162.36(12)
N(11)-Zr(01)-O(1)	120.22(15)	N(11)-Zr(02)-N(10)	74.71(16)
N(11)-Zr(01)-O(2)	127.34(16)	N(9)-Zr(02)-N(10)	88.37(16)
O(1)-Zr(01)-O(2)	110.62(14)	N(5)-Zr(02)-N(10)	132.87(15)
N(11)-Zr(01)-N(3)	96.79(16)	N(7)-Zr(02)-N(10)	144.23(16)
O(1)-Zr(01)-N(3)	126.41(15)	O(4)-Zr(02)-N(10)	87.97(14)
O(2)-Zr(01)-N(3)	60.12(15)	O(3)-Zr(02)-N(10)	76.99(14)
N(11)-Zr(01)-N(1)	95.73(16)	N(11)-Zr(02)-C(32)	88.47(17)
O(1)-Zr(01)-N(1)	60.28(14)	N(9)-Zr(02)-C(32)	93.33(17)
O(2)-Zr(01)-N(1)	121.88(15)	N(5)-Zr(02)-C(32)	108.38(16)

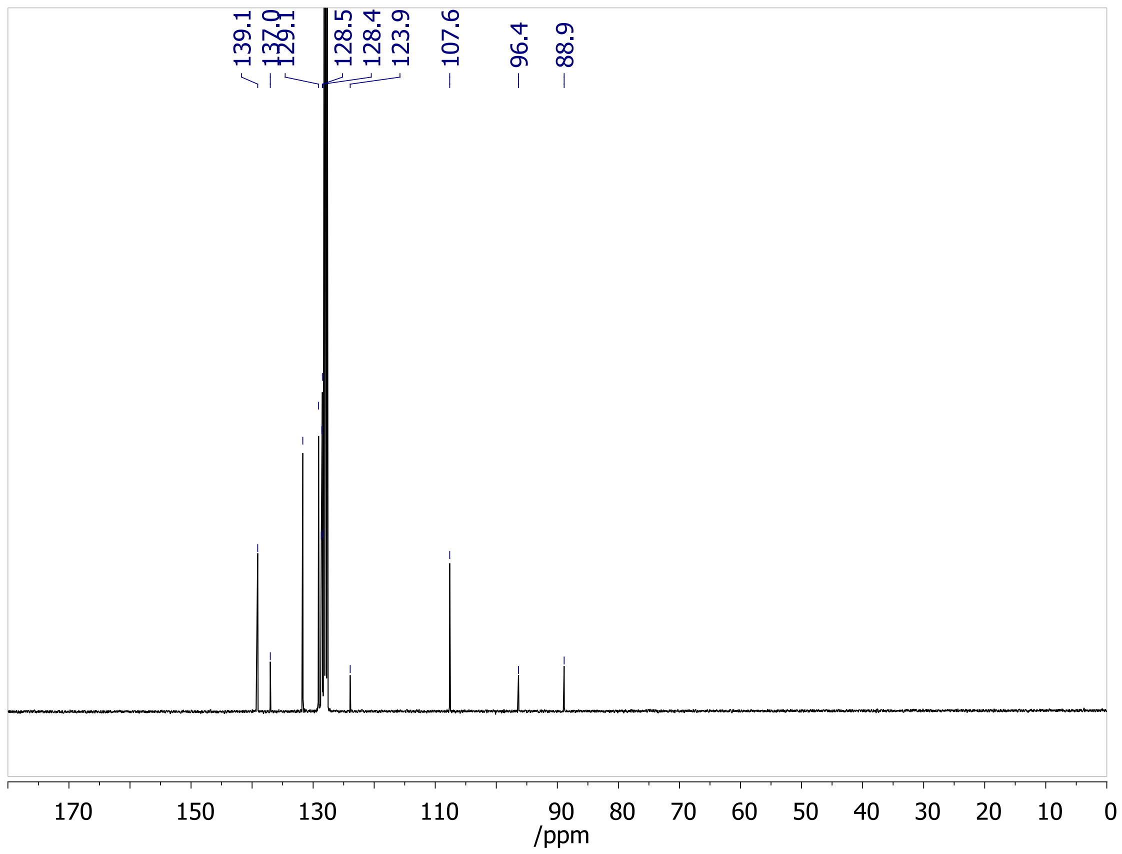
N(7)-Zr(02)-C(32)	29.61(17)
O(4)-Zr(02)-C(32)	29.67(15)
O(3)-Zr(02)-C(32)	167.17(15)
N(10)-Zr(02)-C(32)	115.77(16)
N(11)-Zr(02)-C(20)	88.53(15)
N(9)-Zr(02)-C(20)	101.82(16)
N(5)-Zr(02)-C(20)	30.15(16)
N(7)-Zr(02)-C(20)	108.89(16)
O(4)-Zr(02)-C(20)	167.94(14)
O(3)-Zr(02)-C(20)	29.53(14)
N(10)-Zr(02)-C(20)	103.43(15)
C(32)-Zr(02)-C(20)	138.28(16)
N(11)-Zr(02)-Zr(01)	33.16(12)
N(9)-Zr(02)-Zr(01)	129.66(12)
N(5)-Zr(02)-Zr(01)	113.38(11)
N(7)-Zr(02)-Zr(01)	118.38(13)
O(4)-Zr(02)-Zr(01)	89.72(10)
O(3)-Zr(02)-Zr(01)	85.11(9)
N(10)-Zr(02)-Zr(01)	41.55(11)
C(32)-Zr(02)-Zr(01)	103.51(12)
C(20)-Zr(02)-Zr(01)	96.20(11)
O(500)-Si(1)-C(205)	108.5(6)
O(500)-Si(1)-C(204)	107.3(8)
C(205)-Si(1)-C(204)	105.0(9)
O(500)-Si(1)-C(203)	110.4(6)
C(205)-Si(1)-C(203)	107.5(7)
C(204)-Si(1)-C(203)	117.7(12)
O(500)-Si(2)-C(202)	110.1(5)
O(500)-Si(2)-C(200)	108.9(6)
C(202)-Si(2)-C(200)	106.6(7)
O(500)-Si(2)-C(201)	107.0(5)
C(202)-Si(2)-C(201)	115.3(7)
C(200)-Si(2)-C(201)	108.9(6)
C(508)-C(507)-C(512)	120.0
C(507)-C(508)-C(509)	120.0
C(510)-C(509)-C(508)	120.0
C(511)-C(510)-C(509)	120.0
C(512)-C(511)-C(510)	120.0
C(511)-C(512)-C(507)	120.0
C(511)-C(512)-C(513)	120(3)
C(507)-C(512)-C(513)	119(3)

Symmetry transformations used to generate equivalent atoms

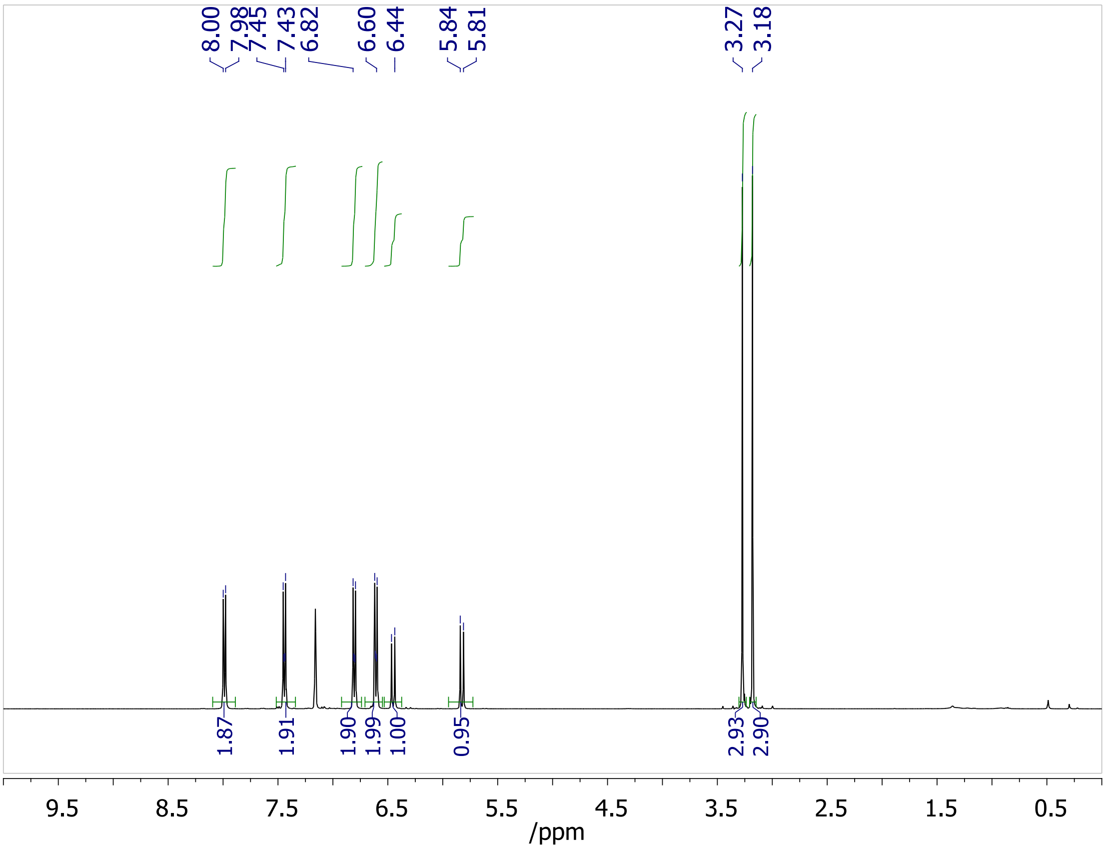


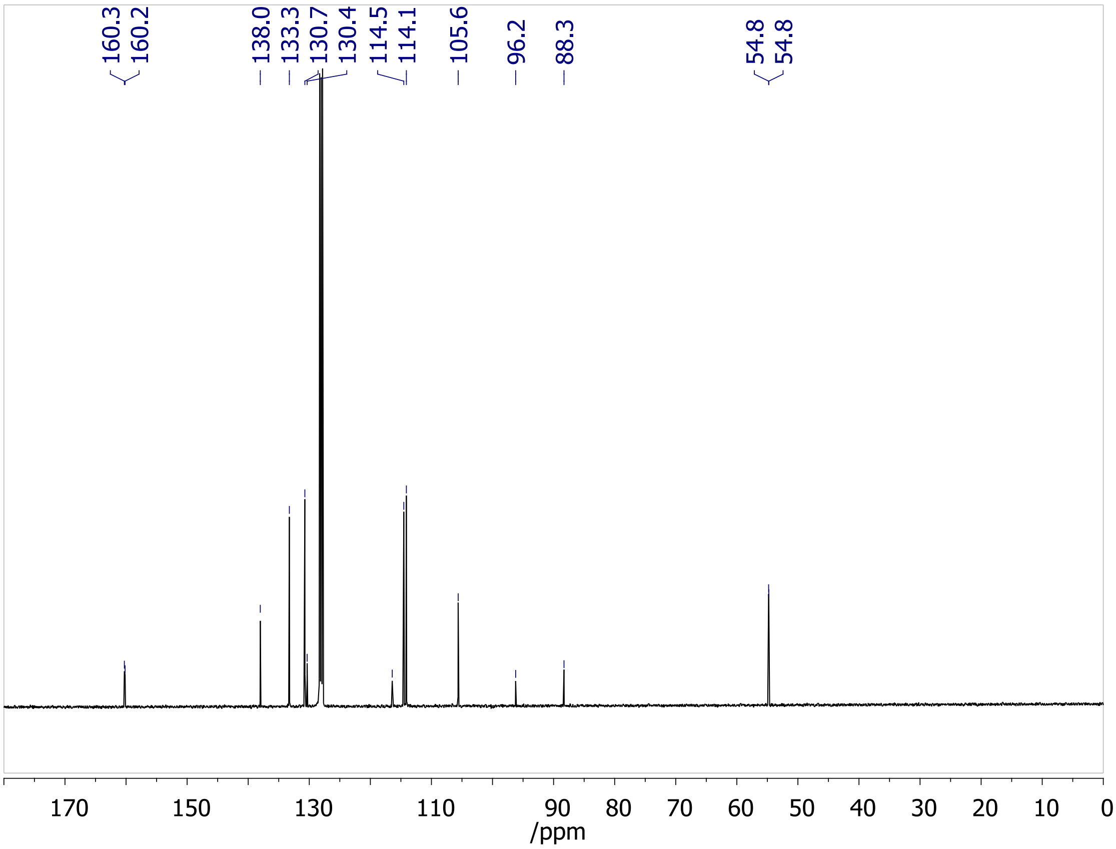
^{1}H and ^{13}C{^{1}H} NMR Spectra of (*Z*)-1,4-Diphenylbut-1-en-3-yne (**3a**) in C_6D_6



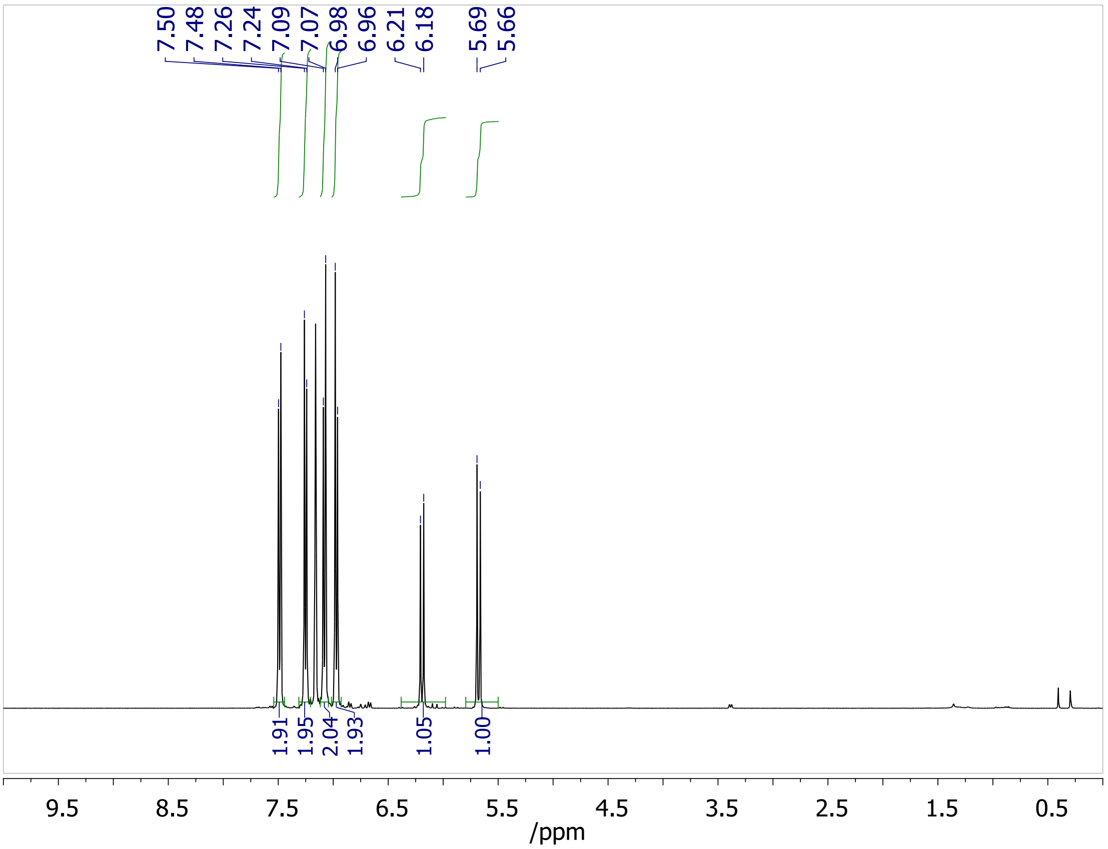


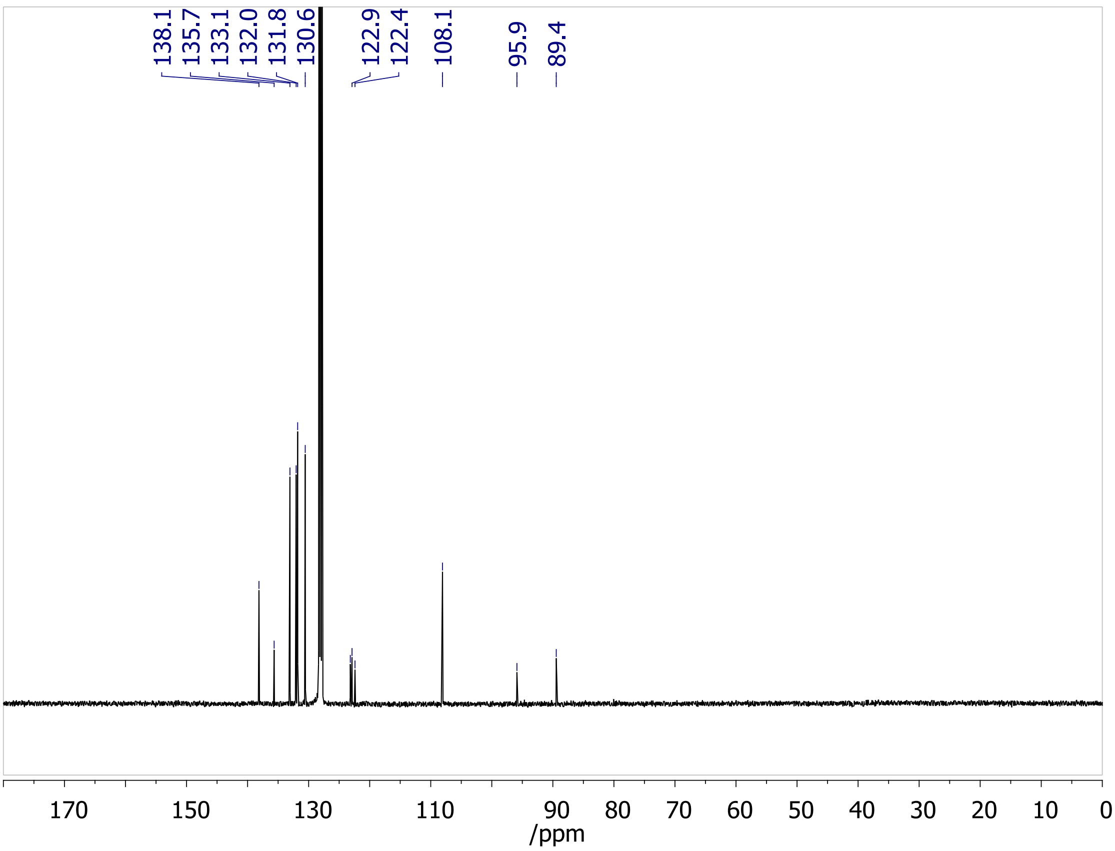
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of (*Z*)-1,4-Bis-(*p*-methoxyphenyl)but-1-en-3-yne (**3b**) in C_6D_6



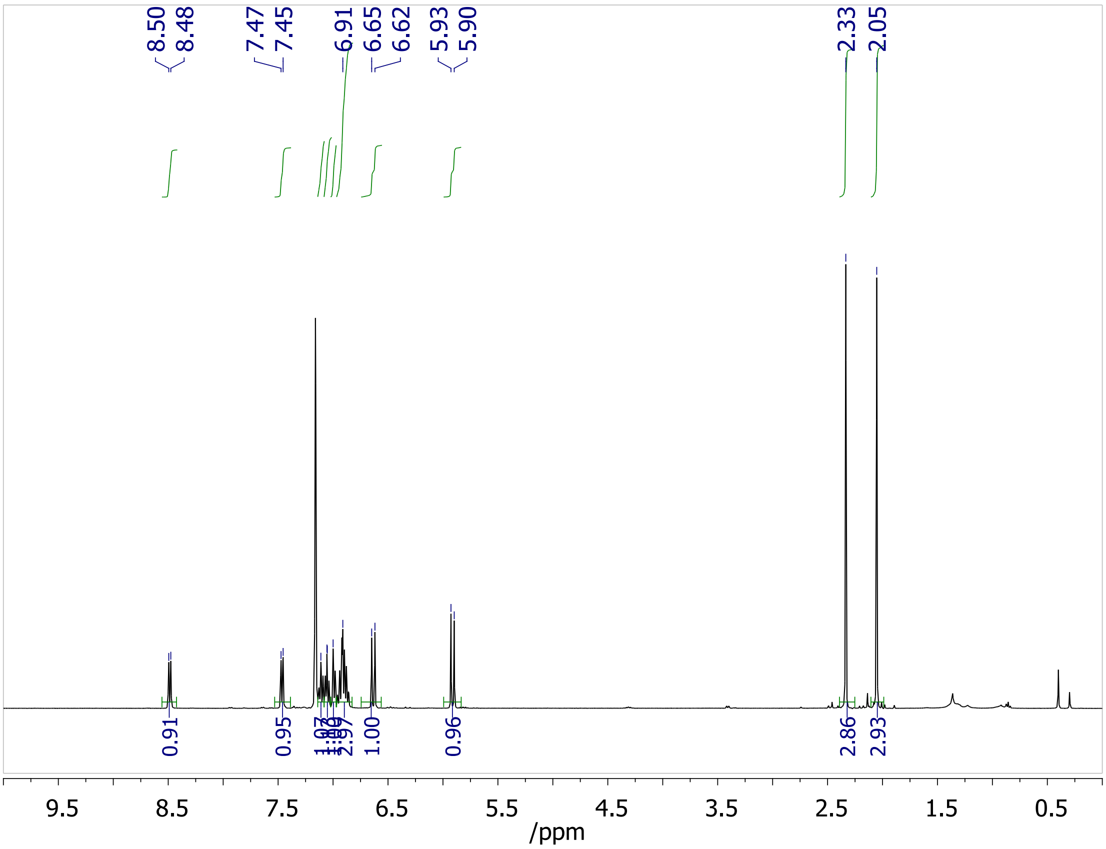


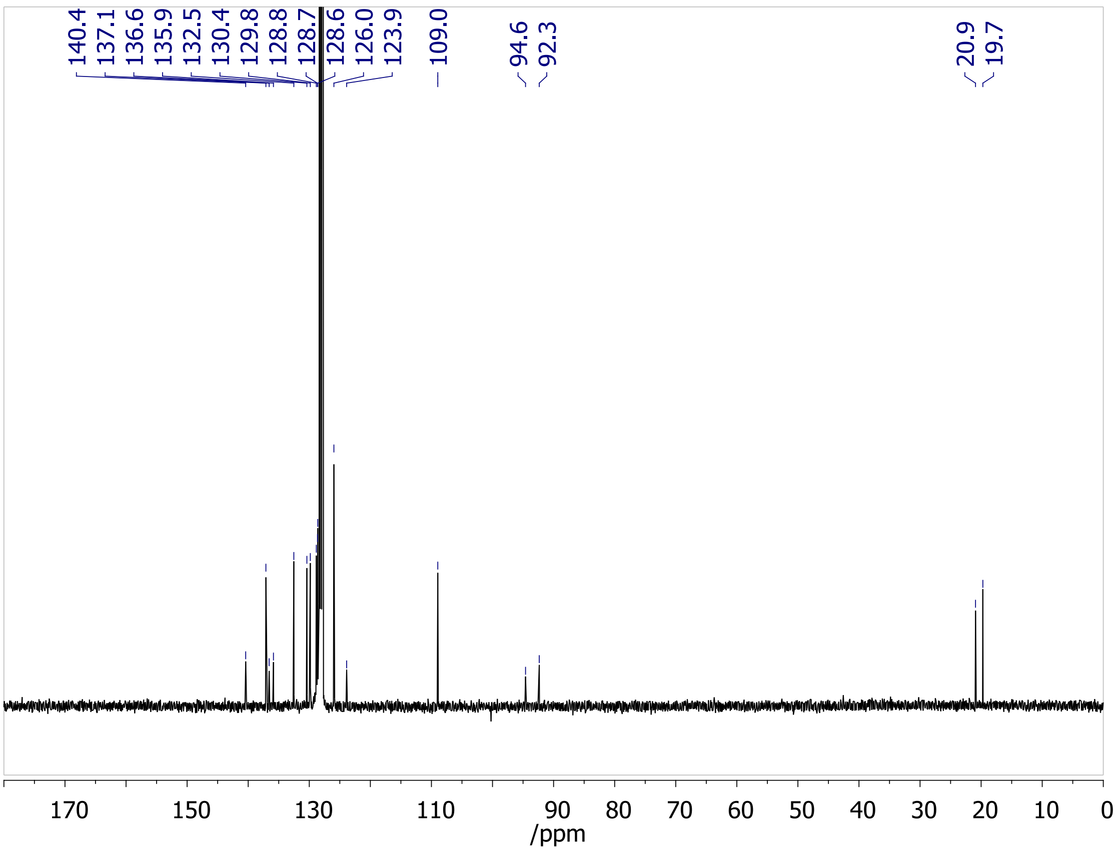
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of (*Z*)-1,4-Di-*p*-bromobut-1-en-3-yne (**3c**) in C_6D_6



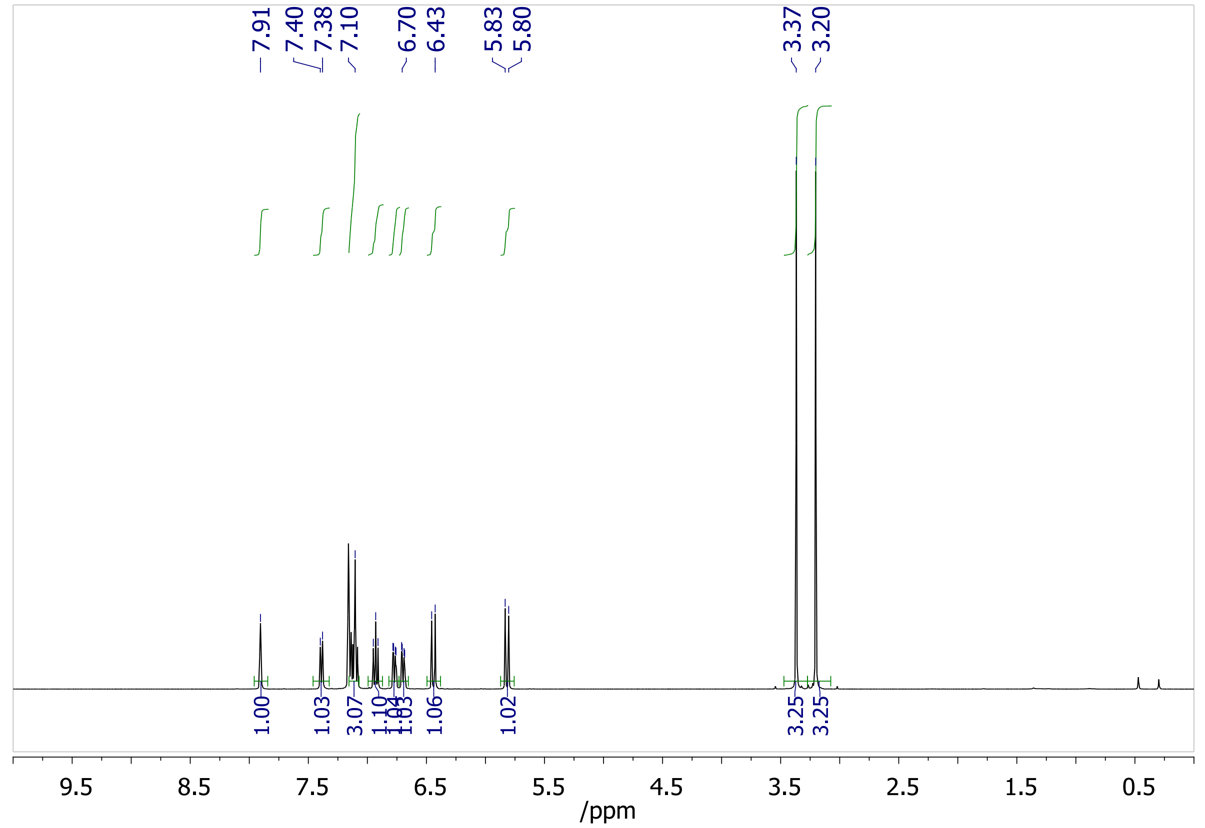


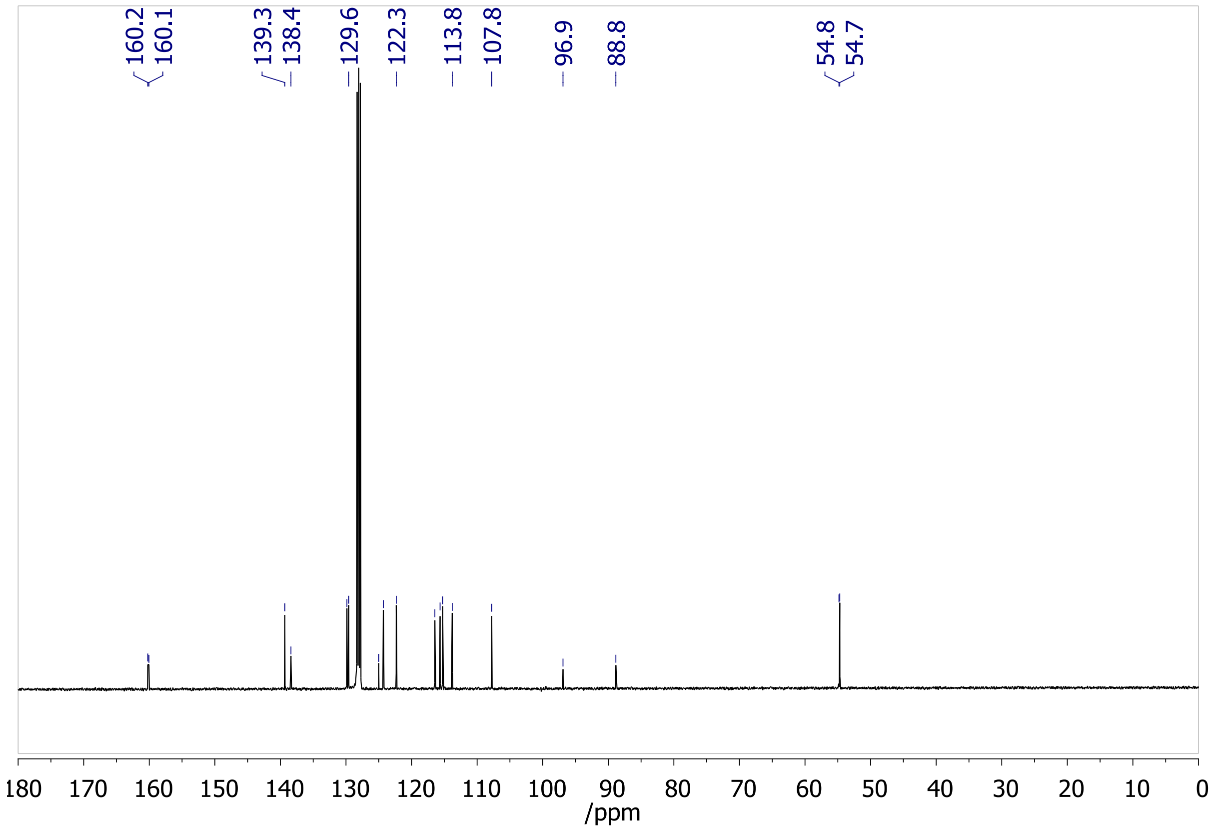
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of (*Z*)-1,4-Di-*o*-tolylbut-1-en-3-yne (**3d**) in C_6D_6



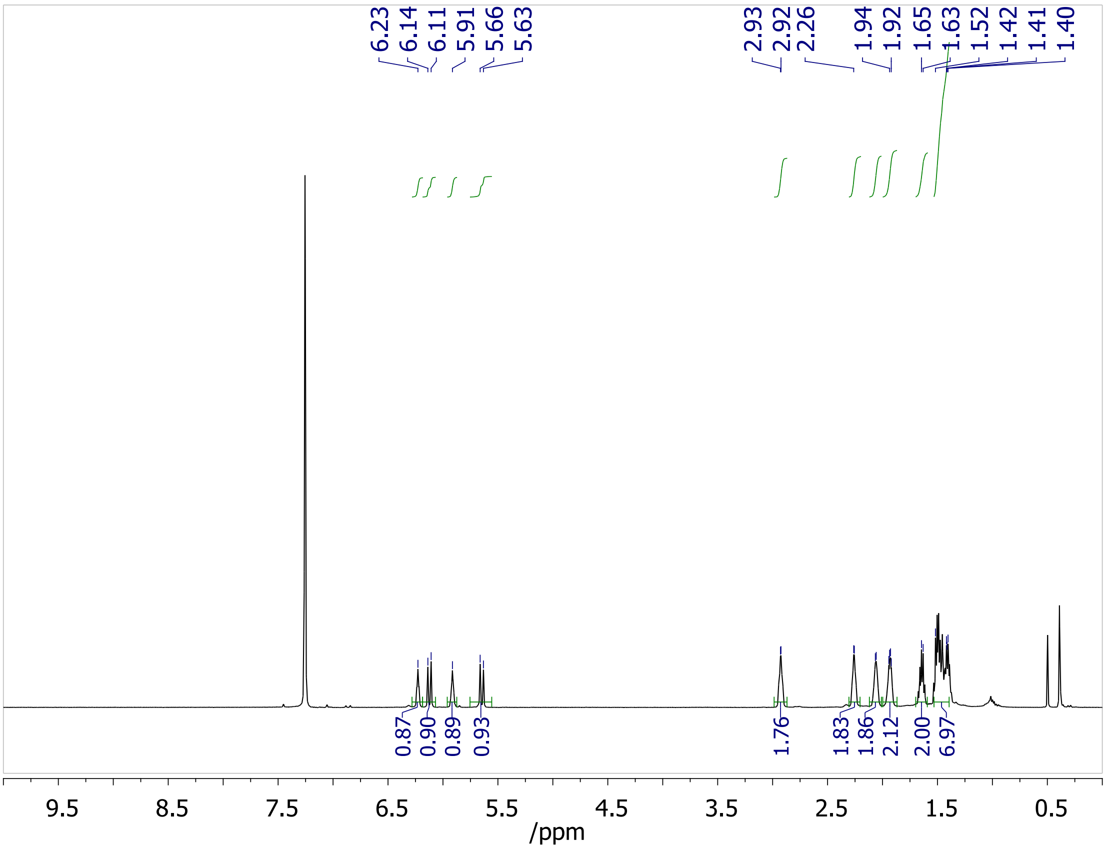


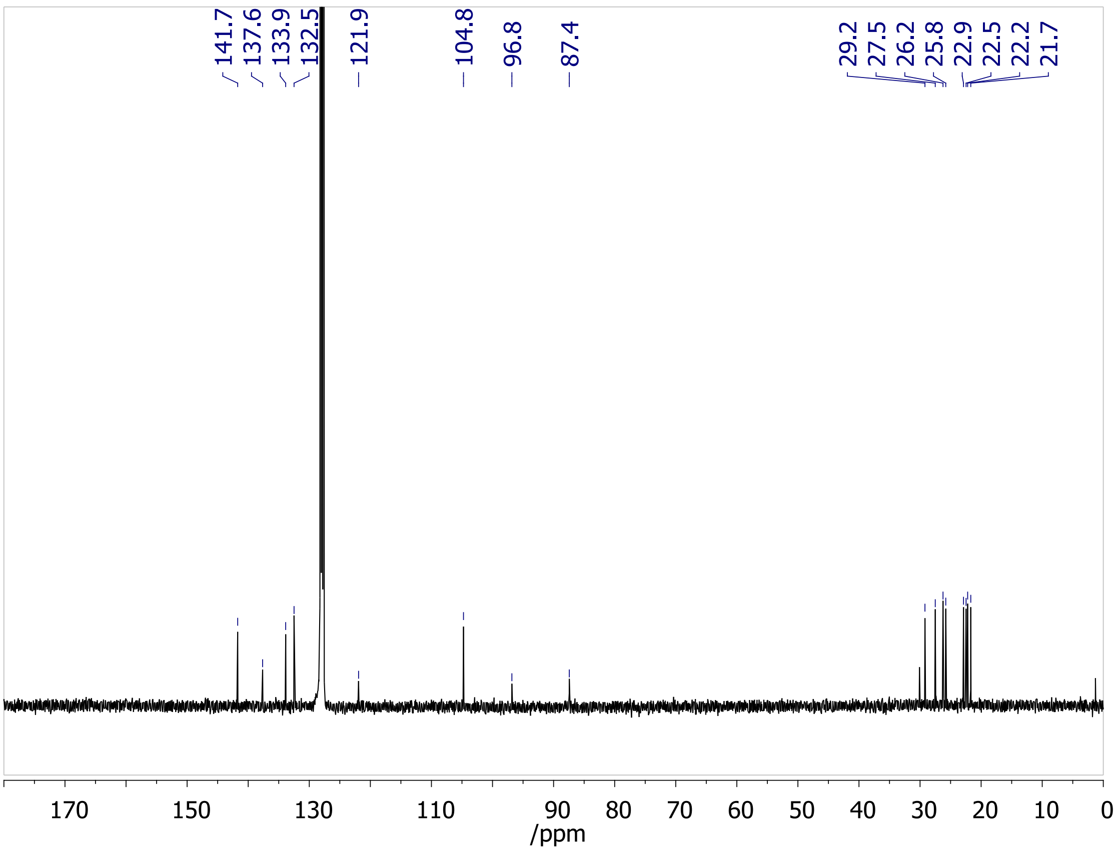
^{1}H and ^{13}C{^{1}H} NMR Spectra of (*Z*)-1,4-Bis-(*m*-methoxyphenyl)but-1-en-3-yne (**3e**) in C_6D_6



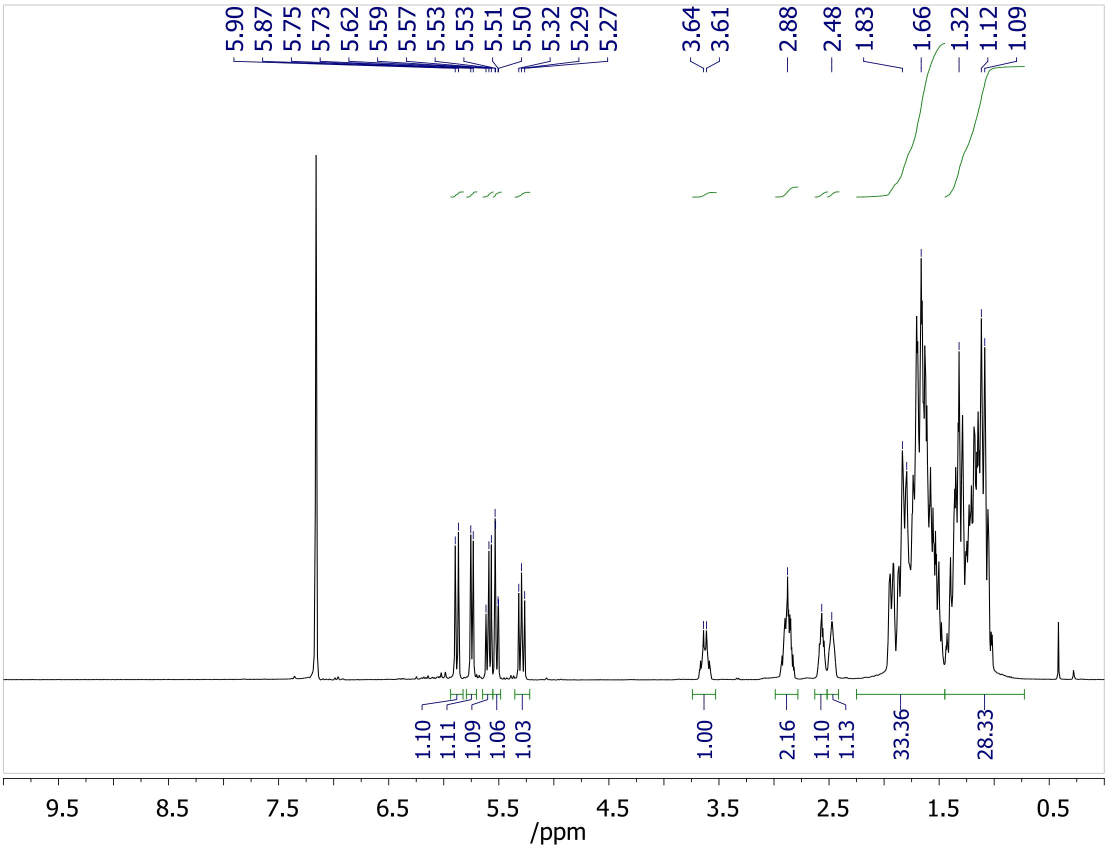


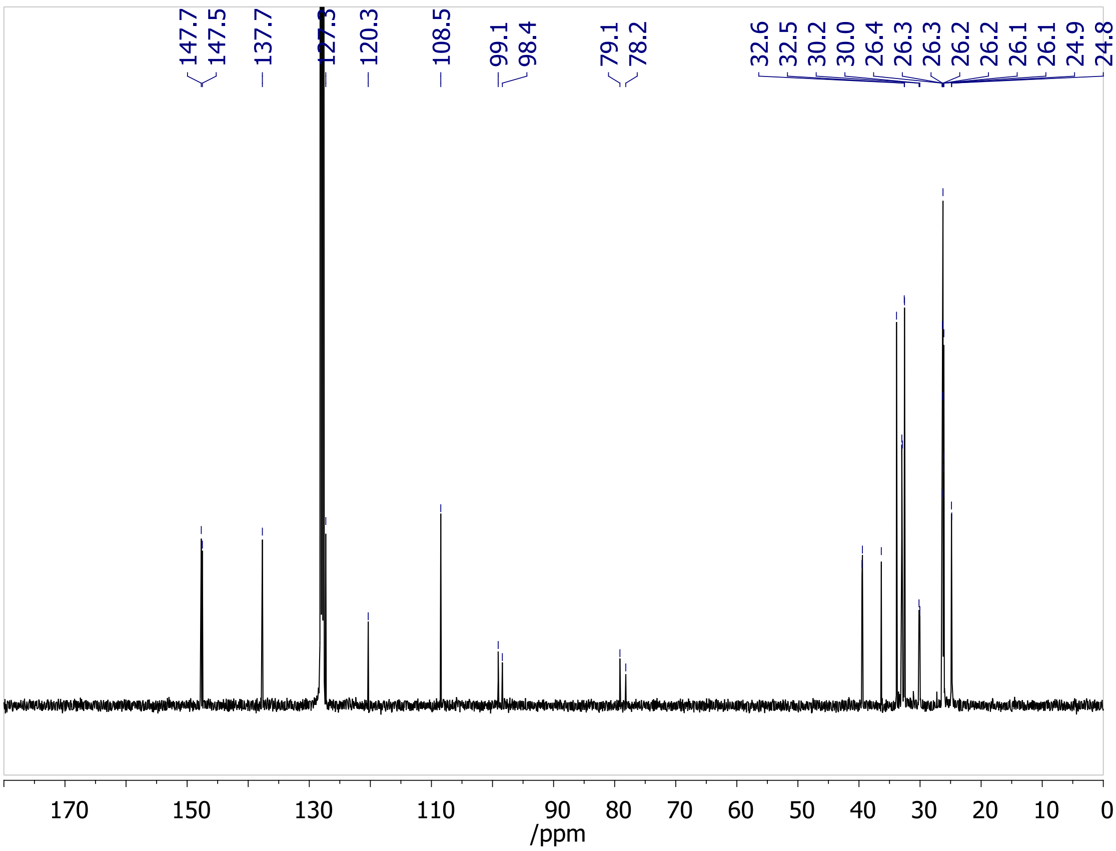
^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of (*Z*)-1,4-Di(1-cyclohexenyl)but-1-en-3-yne (**3f**) in C_6D_6





[1]H and [13]C{[1]H} NMR Spectra of (*Z*)-1,4-Di(1-cyclohexyl)but-1-en-3-yne (**3g**) in C_6D_6





References

1. D. C. Leitch, P. R. Payne, C. R. Dunbar and L. L. Schafer, *J. Am. Chem. Soc.*, 2009, **131**, 18246-18247.
2. D. C. Leitch and L. L. Schafer, *Organometallics*, 2010, **29**, 5162-5172.
3. H. Katayama, H. Yari, M. Tanaka and F. Ozawa, *Chem. Commun.*, 2005, 4336-4338.
4. M. Nishiura, Z. M. Hou, Y. Wakatsuki, T. Yamaki and T. Miyamoto, *J. Am. Chem. Soc.*, 2003, **125**, 1184-1185.
5. S. Z. Ge, V. F. Q. Norambuena and B. Hessen, *Organometallics*, 2007, **26**, 6508-6510.
6. G. C. Midya, S. Paladhi, K. Dhara and J. Dash, *Chem. Commun.*, 2011, **47**, 6698-6700.
7. C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler and F. Stelzer, *Monatsh. Chem.*, 1998, **129**, 221-233.
8. Y. Nishimura, T. Shiraishi and M. Yamaguchi, *Tet. Lett.*, 2008, **49**, 3492-3495.