Supporting Information

Highly efficient and practical synthesis of functionalized 1,5-dienes *via* Pd(II)-catalyzed halohomoallylation of alkynes

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I. General method

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. GC–MS was obtained using electron ionization. HRMS (EI) was carried out on a MAT 95XP (Thermo). TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. The ionic liquids ([Bmim]Cl,[1] [Bmim]BF_4,[2] [Bmim]PF_6,[2] [C_2OHmim]Cl,[3] [BuPy]Cl,[1] [C_2O_2mim]Cl[4] and [C_2O_2mim]Br[4]) were synthesized using the procedure reported by other authors. The bromoalkynes[5] and chloroalkynes[6] were prepared according to the literature. Other reagents were purchased as reagent grade and used without further purification.

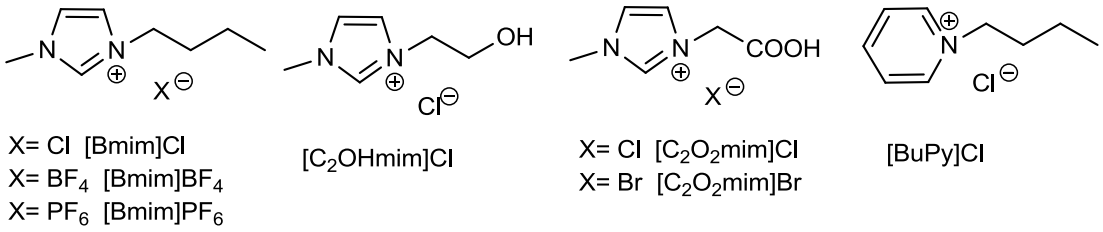

Fig. 1 Ionic liquids applied in this work.

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[3] L. C. Branco, J. N. Rosa, J. J. Moura Ramos and C. A. M. Afonso, *Chem. Eur. J.*, 2002, **8**, 3671.

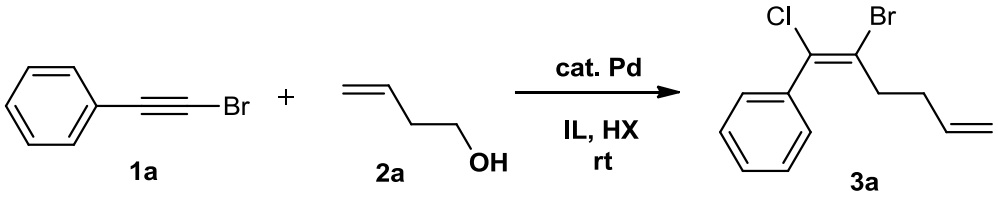
[4] C.-X. Miao, L.-N. He, J.-Q. Wang and J.-L. Wang, *Adv. Synth. Catal.*, 2009, **351**, 2209.

[5] (a)Y. Li, X. Liu, H. Jiang, B. Liu, Z. Chen and P. Zhou, *Angew. Chem., Int. Ed.*, 2011, **50**, 6341; (b) Y. Li, J. Zhao, H. Chen, B. Liu and H. Jiang, *Chem. Commun.*, 2012, **48**, 3545.

[6] Y. Sasson and O. W. Webster, *J. Chem. Soc., Chem. Commun.*, 1992, 1200.

II. Optimization of the reaction conditions

Table 1 Optimization of the Reaction Conditions[a]



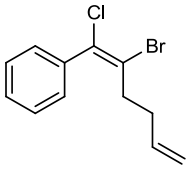
Entry	Ionic liquid	HA (mL)	Pd catalyst	GC yield (%)	Z/E
1	[Bmim]Cl	-	$PdCl_2$	0	-
2	[Bmim]Cl	HCl (0.1)	-	0	-
3	[Bmim]Cl	HCl (0.1)	$PdCl_2$	46	98/2
4[b]	[Bmim]Cl	HCl (0.1)	$PdCl_2$	48	98/2
5	[Bmim]Cl	HCl (0.1)	$PdBr_2$	43	98/2
6	[Bmim]Cl	HCl (0.1)	$Pd(OAc)_2$	35	98/2
7	[Bmim]Cl	HCl (0.1)	$Pd(PPh_3)_4$	0	-
8	[Bmim]Cl	HCl (0.1)	$Pd(PPh_3)_2Cl_2$	29	98/2
9	[Bmim]Cl	HCl (0.15)	$PdCl_2$	83	98/2
10	[Bmim]Cl	HCl (0.25)	$PdCl_2$	92	> 98/2
11[c]	[Bmim]Cl	HCl (0.25)	$PdCl_2$	90	> 98/2
12	$[Bmim]BF_4$	HCl (0.25)	$PdCl_2$	71	87/13
13	$[Bmim]PF_6$	HCl (0.25)	$PdCl_2$	70	79/21
14	$[C_2OHmim]Cl$	HCl (0.25)	$PdCl_2$	63	94/6
15	$[C_2O_2mim]Cl$	HCl (0.25)	$PdCl_2$	72	95/5
16	-	HCl (0.25)	$PdCl_2$	72	66/34
17	HOAc	HCl (0.25)	$PdCl_2$	80	67/33
18	H_2O	HCl (0.25)	$PdCl_2$	51	55/45
19	CH_3CN	HCl (0.25)	$PdCl_2$	trace	-
20	[Bmim]Cl	HOAc	$PdCl_2$	trace	-

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol) and Pd catalyst (3 mol%) in 1 mL of solvents under the atmosphere of air at room temperature. Reaction was monitored by TLC for the completion of the reaction. The ratios of 1Z/1E were determined by GC. [b] 5mol% $PdCl_2$ was used. [c] 1.0 equivalent $CuCl_2$ was used.

III. General procedure for the synthesis of 3 and 4

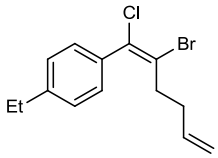
A mixture of alkynes **1** (0.5 mmol), **2** (0.6 mmol), palladium chloride (3.2 mg, 3 mol%), ionic liquid (0.5 mL), HX (0.25 mL) in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred under the atmosphere of air at room temperature. After the reaction was completed, 10 mL ethyl acetate (3×10 mL) was added into the tube. The combined organic layers were washed with brine to neutral, dried over $MgSO_4$, and concentrated in vacuum. Purification of the residue on a preparative TLC afforded the desired products.

IV. Analytical data for compounds 3 and 4



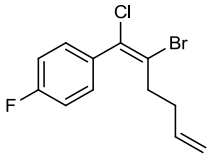
(Z)-(2-bromo-1-chlorohexa-1,5-dien-1-yl)benzene (3a)

Yield: 83% (112.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 5.71-5.61 (m, 1H), 4.99 (dd, J =10.2, 1.2 Hz, 1H), 4.96 (dd, J =17.2, 1.2 Hz, 1H), 2.54-2.48 (m, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.2, 131.5, 128.9, 128.7, 128.6, 126.7, 115.9, 37.5, 32.9 ppm; ν_{max}(KBr)/cm^{-1} 3076, 2980, 1635, 1445, 1490, 718 ; MS (EI) m/z 115, 150, 155, 191, 193, 231, 232, 270; HRMS(EI) calcd for $C_{12}H_{12}ClBr$ 269.9811, found 269.9804.



(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-ethylbenzene (3b)

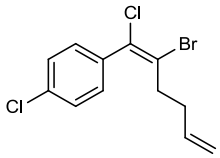
Yield: 90% (134.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 4H), 5.73-5.62 (m, 1H), 5.01 (dd, J =10.4, 1.2 Hz, 1H), 4.97 (dd, J =16.4, 1.2 Hz, 1H), 2.66 (q, J =7.6 Hz, 2H), 2.55-2.52 (m, 2H), 2.37-2.32 (m, 2H), 1.25 (t, J =7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.3, 134.7, 131.7, 128.6, 128.0, 126.2, 115.9, 37.5, 33.0, 28.6, 15.3 ppm; ν_{max}(KBr)/cm^{-1} 3077, 2960, 1600, 1456, 760 ; MS (EI) m/z 115, 128, 149, 150, 178, 229, 231, 257, 259, 271, 298; HRMS(EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0121.



(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-fluorobenzene (3c)

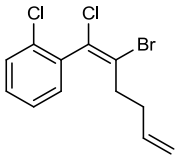
Yield: 88% (126.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.08-7.04 (m, 2H), 5.71-5.60 (m, 1H), 5.01 (dd, J =10.0, 1.2 Hz, 1H), 4.97 (dd, J =17.2, 1.2 Hz, 1H), 2.52-2.49 (m, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (J =248.1 Hz), 136.0, 133.4 (J =3.5Hz), 130.7 (J =8.3 Hz), 130.5, 127.0,

116.1, 115.7 (J =21.7 Hz), 37.5, 32.8 ppm; ν_{max}(KBr)/cm^{-1} 3079, 2926, 1640, 1595, 730 ; MS (EI) m/z 133, 168, 170, 209, 211, 249, 251, 288; HRMS(EI) calcd for $C_{12}H_{11}FClBr$ 287.9717, found 287.9711.



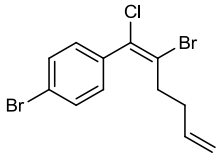
(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-chlorobenzene (3d)

Yield: 86% (130.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.27-7.26 (m, 2H), 5.71-5.60 (m, 1H), 5.03 (dd, J =9.6, 0.8 Hz, 1H), 4.98 (dd, J =16.4, 0.8 Hz, 1H), 2.53-2.49 (m, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.8, 134.9, 130.3, 130.1, 128.8, 127.3, 116.2, 37.5, 32.9 ppm; ν_{max}(KBr)/cm^{-1} 3081, 2924, 1640, 1489, 745 ; MS (EI) m/z 114, 149, 151, 184, 186, 189, 225, 229, 263, 265, 267, 304; HRMS(EI) calcd for $C_{12}H_{11}Cl_2Br$ 303.9421, found 303.9415.



(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-chlorobenzene (3e)

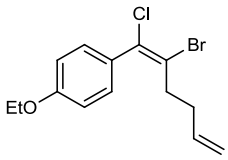
Yield: 81% (123.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.33-7.23 (m, 3H), 5.68-5.58 (m, 1H), 4.97 (dd, J =10.2, 0.8 Hz, 1H), 4.94 (dd, J =16.4, 0.8 Hz, 1H), 2.44-2.34 (m, 2H), 2.32-2.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 136.1, 133.2, 130.7, 130.5, 130.1, 128.5, 128.1, 127.1, 116.0, 37.5, 32.5 ppm; ν_{max}(KBr)/cm^{-1} 3080, 2929, 1640, 1480, 740 ; MS (EI) m/z 63, 75, 87, 99, 114, 149, 151, 183, 185, 189, 225, 229, 265, 267, 304; HRMS(EI) calcd for $C_{12}H_{11}Cl_2Br$ 303.9421, found 303.9418.



(Z)-1-bromo-4-(2-bromo-1-chlorohexa-1,5-dien-1-yl)benzene (3f)

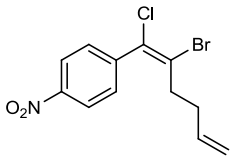
Yield: 89% (154.8 mg)as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.52 (m, 2H), 7.20-7.15 (m, 2H), 5.70-5.60 (m, 1H), 5.01 (dd, J =10.0, 1.2 Hz, 1H), 4.98 (dd, J =17.2, 1.2 Hz, 1H), 2.53-2.49 (m, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.9, 131.8, 130.3, 128.2, 127.3, 123.2, 116.2, 37.5, 32.9 ppm;

ν_{max}(KBr)/cm^{-1} 3080, 2921, 1643, 1480, 735 ; MS (EI) m/z 114, 149, 151, 190, 228, 230, 232, 271, 309, 348; HRMS(EI) calcd for $C_{12}H_{11}ClBr_2$ 347.8916, found 347.8913.



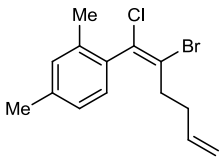
(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-ethoxybenzene (3g)

Yield: 77% (120.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2H), 6.88-6.85 (m, 2H), 5.72-5.62 (m, 1H), 5.00 (dd, J =10.4, 1.6 Hz, 1H), 4.97 (dd, J =16.8, 1.6 Hz, 1H), 4.04 (q, J =7.2 Hz, 2H), 2.55-2.51 (m, 2H), 2.36-2.31 (m, 2H), 1.42 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.3, 131.6, 130.0, 129.5, 126.1, 115.8, 114.4, 63.6, 37.5, 32.9, 14.8 ppm; ν_{max}(KBr)/cm^{-1} 3079, 2921, 1640, 1475, 752 ; MS (EI) m/z 89, 102, 159, 166, 168, 246, 248, 273, 275, 314; HRMS(EI) calcd for $C_{14}H_{16}OClBr$



(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-nitrobenzene (3h)

Yield: 72% (113.4 mg)as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 2H), 7.56-7.51 (m, 2H), 5.70-5.60 (m, 1H), 5.04 (dd, J =10.0, 1.2 Hz, 1H), 5.00 (dd, J =16.8, 1.2 Hz, 1H), 2.55-2.51 (m, 2H), 2.39-2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.6, 135.6, 129.9, 128.9, 128.8, 123.8, 116.6, 37.5, 32.8 ppm; ν_{max}(KBr)/cm^{-1} 3081, 2923, 1640, 1481, 743 ; MS (EI) m/z 114, 130, 149, 151, 178, 200, 228, 230, 236, 257, 259, 276, 300, 315; HRMS(EI) calcd for $C_{12}H_{11}ClBrNO_2$ 314.9662, found 314.9656.

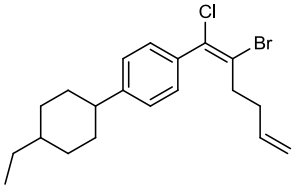


(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-2,4-dimethylbenzene (3i)

Yield: 86% (128.1 mg) as a yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-7.03 (m, 2H), 6.99-6.98 (m, 1H), 5.66-5.56 (m, 1H), 4.98 (dd, J =10.0, 1.2 Hz, 1H), 4.94 (dd, J =17.2, 1.2 Hz, 1H), 2.39-2.34 (m, 2H), 2.32 (s, 3H), 2.30-2.27 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 136.4, 136.1, 133.9, 131.3, 130.9, 128.9, 126.8, 126.6, 115.9, 37.3, 32.6, 21.2, 19.3 ppm; ν_{max}(KBr)/cm^{-1} 3080, 2924, 1645, 1458, 745 ; MS (EI)

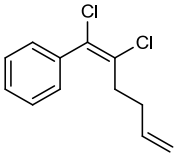
m/z 115, 128, 143, 178, 180, 219, 257, 259, 298; HRMS(EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0119.

314.0073, found 314.0066.



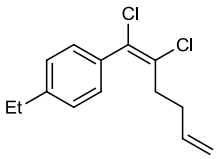
(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-(4-ethylcyclohexyl)benzene (3j)

Yield: 66% (125.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 4H), 5.73-5.63 (m, 1H), 5.00 (dd, J =10.0, 1.2 Hz, 1H), 4.97 (dd, J =16.8, 1.6 Hz, 1H), 2.56-2.50 (m, 2H), 2.37-2.32 (m, 2H), 1.91-1.88 (m, 4H), 1.49-1.39 (m, 2H), 1.31-1.18 (m, 4H), 1.09-1.00 (m, 2H), 0.909 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.3, 134.7, 131.7, 128.6, 126.9, 126.3, 115.9, 44.4, 39.0, 37.5, 34.2, 33.1, 33.0, 29.9, 11.5 ppm; ν_{max}(KBr)/cm^{-1} 3080, 2922, 1640, 1500, 751; MS (EI) m/z 69, 111, 115, 128, 141, 163, 192, 225, 271, 303, 380; HRMS(EI) calcd for $C_{20}H_{26}ClBr$ 380.0906, found 380.0900.



(Z)-(1,2-dichlorohexa-1,5-dien-1-yl)benzene (3k)

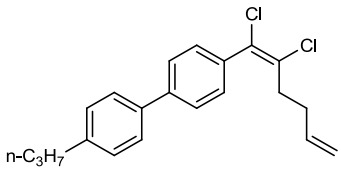
Yield: 71% (80.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 5H), 5.72-5.62 (m, 1H), 5.00 (dd, J =10.4, 1.2 Hz, 1H), 4.97 (dd, J =16.8, 1.2 Hz, 1H), 2.47-2.44 (m, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.3, 133.3, 129.9, 128.9, 128.6, 128.5, 115.9, 35.5, 31.9 ppm; ν_{max}(KBr)/cm^{-1} 3078, 2982, 1635, 1490, 718 ; MS (EI) m/z 115, 149, 151, 155, 163, 191, 193, 226; HRMS(EI) calcd for $C_{12}H_{12}Cl_2$ 226.0316, found 226.0310.



(Z)-1-(1,2-dichlorohexa-1,5-dien-1-yl)-4-ethylbenzene (3l)

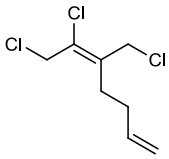
Yield: 78% (99.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 4H), 5.74-5.64 (m, 1H), 5.01 (dd, J =10.4, 1.2 Hz, 1H), 4.97

(dd, *J* =16.4, 1.2 Hz, 1H), 2.66 (q, *J* =7.6 Hz, 2H), 2.48-2.45 (m, 2H), 2.37-2.32 (m, 2H), 1.25 (t, *J* =7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.4, 134.5, 132.9, 128.9, 127.9, 127.4, 115.9, 35.5, 31.9, 28.6, 15.3 ppm; ν_{max}(KBr)/cm^{-1} 3079, 2960, 1600, 1456, 760 ; MS (EI) m/z 115, 128, 149, 151, 185, 187, 213, 215, 225, 227, 254; HRMS(EI) calcd for $C_{14}H_{16}Cl_2$ 254.0629, found 254.0622.



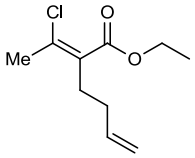
(Z)-4-(1,2-dichlorohexa-1,5-dien-1-yl)-4'-propyl-1,1'-biphenyl (3m)

Yield: 74% (127.2 mg) as a yellow solid;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.51 (d, *J* =7.2 Hz, 2H), 7.38 (d, *J* =8.4 Hz, 2H), 7.26 (d, *J* =8.4 Hz, 2H), 5.75-5.65 (m, 1H), 5.02 (dd, *J* =10.4, 1.2 Hz, 1H), 4.98 (dd, *J* =16.8, 1.2 Hz, 1H), 2.63 (t, *J* =7.6 Hz, 2H), 2.53-2.50 (m, 2H), 2.40-2.34 (m, 2H), 1.73-1.64 (m, 2H), 0.97 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.8, 137.5, 136.3, 135.7, 133.4, 129.3, 129.0, 128.6, 127.0, 126.9, 116.0, 37.7, 35.6, 32.0, 24.5, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 3081, 2927, 1640, 1504, 753; MS (EI) m/z 96, 142, 152, 190, 207, 225, 238, 261, 263, 268, 303, 305, 344; HRMS(EI) calcd for $C_{21}H_{22}Cl_2$ 344.1099, found 344.1093.



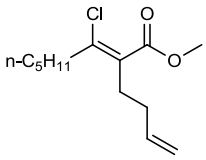
(Z)-6,7-dichloro-5-(chloromethyl)hepta-1,5-diene (3n)

Yield: 78% (82.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.09 (dd, *J* =3.2, 1.2 Hz, 1H), 5.04 (dd, *J* =10.2, 2.8 Hz, 1H), 4.30 (s, 2H), 4.27 (s, 2H), 2.48-2.45 (m, 2H), 2.31-2.25 (m, 2H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.4, 130.1, 116.3, 44.9, 43.8, 32.3, 30.5 ppm; ν_{max}(KBr)/cm^{-1} 3081, 2924, 1520, 1272, 733 ; MS (EI) m/z 71, 81, 95, 97, 123, 130, 158, 160, 212; HRMS(EI) calcd for $C_8H_{11}Cl_3$ 211.9926, found 211.9919.



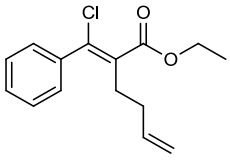
(Z)-ethyl 2-(1-chloroethylidene)hex-5-enoate (3o)

Yield: 89% (89.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.05 (dd, J =8.8, 1.2 Hz, 1H), 5.00 (dd, J =15.6, 1.2 Hz, 1H), 4.26 (q, J =7.2 Hz, 2H), 2.42 (t, J =7.2 Hz, 2H), 2.22-2.18 (m, 2H), 2.17 (s, 3H), 1.33 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 136.8, 131.7, 130.5, 115.7, 61.0, 32.3, 30.5, 22.8, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 2923, 2857, 1630, 1369, 714 ; MS (EI) m/z 55, 77, 79, 91, 97, 121, 138, 157, 166, 202; HRMS(ESI) calcd for $C_{10}H_{15}ClO_2$ 202.0761, found 202.0753.



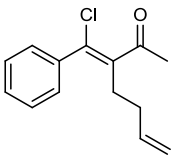
(Z)-methyl 2-(but-3-en-1-yl)-3-chlorooct-2-enoate (3p)

Yield: 85% (103.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77-5.67 (m, 1H), 4.98 (dd, J =10.0, 1.2 Hz, 1H), 4.93 (dd, J =16.4, 1.2 Hz, 1H), 3.72 (3,3H), 2.36-2.31 (m, 4H), 2.12-2.07 (m, 2H), 1.57-1.49 (m, 2H), 1.26-1.18 (m, 4H), 0.84 (t, J =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 136.8, 136.7, 130.3, 115.7, 51.9, 35.3, 32.6, 31.0, 30.3, 27.1, 22.4, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 3080, 2930, 1696, 1640, 750 ; MS (EI) m/z 55, 79, 91, 107, 133,179, 244; HRMS(EI) calcd for $C_{13}H_{21}ClO_2$ 244.1230, found 244.1227.



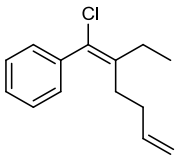
(Z)-ethyl 2-(chloro(phenyl)methylene)hex-5-enoate (3q)

Yield: 83% (109.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 5H), 5.74-5.64 (m, 1H), 4.98 (dd, J =8.4, 0.8 Hz, 1H), 4.95 (dd, J =10.8, 0.8 Hz, 1H), 4.35 (q, J =7.2 Hz, 2H), 2.40-2.36 (m, 2H), 2.19-2.14 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 137.2, 136.7, 132.8, 131.9, 129.0, 128.5, 128.4, 115.7, 61.3, 32.3, 31.3, 14.2 ppm; ν_{max}(KBr)/cm^{-1} 3074, 2980, 2930, 1725, 1634, 1480, 1443, 716; MS (EI) m/z 115, 128, 143, 163, 178, 180, 219, 264 ; HRMS(EI) calcd for $C_{15}H_{17}ClO_2$ 264.0917, found 264.0914.



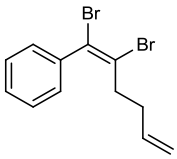
(Z)-3-(chloro(phenyl)methylene)hept-6-en-2-one (3r)

Yield: 72% (84.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 5.71-5.61 (m, 1H), 4.98 (dd, J =8.8, 0.8 Hz, 1H), 4.96 (dd, J =10.4, 0.8 Hz, 1H), 2.52 (s, 3H), 2.38-2.35 (m, 2H), 2.15-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 140.5, 137.2, 136.7, 129.1, 128.6, 128.5, 115.9, 32.3, 31.4, 30.8 ppm; ν_{max}(KBr)/cm^{-1} 3078, 2980, 1725, 1634, 1600, 1480, 1442, 736; MS (EI) m/z 109, 115, 129, 153, 155, 157, 183, 193, 199, 205, 234 ; HRMS(EI) calcd for $C_{14}H_{15}ClO$ 234.0811, found 234.0805.



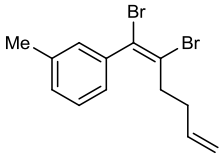
(E)-(1-chloro-2-ethylhexa-1,5-dien-1-yl)benzene (3s)

Yield: 81% (89.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.2 Hz, 2H), 5.80-5.70 (m, 1H), 4.99 (dd, J =10.8, 1.2 Hz, 1H), 4.95 (dd, J =16.0, 1.2 Hz, 1H), 2.57-2.49 (m, 4H), 2.04 (q, J =7.6 Hz, 2H), 1.21 (t, J =7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.6, 135.9, 132.9, 128.6, 128.0, 126.8, 115.2, 34.2, 32.2, 29.0, 13.0 ppm; ν_{max}(KBr)/cm^{-1} 3079, 2966, 1640, 1454, 750 ; MS (EI) m/z 51, 77, 91, 103, 128, 143, 179, 185, 207, 220; HRMS(EI) calcd for $C_{14}H_{17}Cl$ 220.1019, found 220.1017.



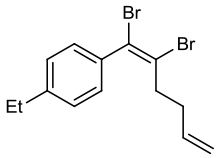
(Z)-(1,2-dibromohexa-1,5-dien-1-yl)benzene (4a)

Yield: 84% (131.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.69-5.59 (m, 1H), 4.99 (dd, J =10.2, 1.2 Hz, 1H), 4.96 (dd, J =17.2, 1.2 Hz, 1H), 2.50-2.46 (m, 2H), 2.35-2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.1, 129.8, 128.8, 128.7, 128.5, 123.0, 116.0, 38.0, 33.0 ppm; ν_{max}(KBr)/cm^{-1} 3077, 2983, 1635, 1493, 736 ; MS (EI) m/z 91, 115, 155, 195, 197, 235, 275, 314; HRMS(EI) calcd for $C_{12}H_{12}Br_2$ 313.9306, found 313.9301.



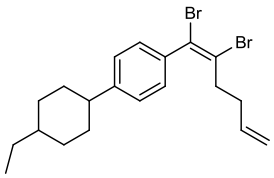
(Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-3-methylbenzene (4b)

Yield: 81% (132.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J =4.8 Hz, 2H), 7.13-7.07 (m, 3H), 5.71-5.61 (m, 1H), 5.00 (dd, J =10.4, 1.2 Hz, 1H), 4.96 (dd, J = 17.2, 1.2 Hz, 1H), 2.54-2.46 (m, 2H), 2.38-2.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.3, 136.2, 129.5, 129.2, 128.4, 125.7, 123.2, 115.9, 38.0, 33.0, 21.3 ppm; ν_{max}(KBr)/cm^{-1} 3079, 2929, 1640, 1505, 768 ; MS (EI) m/z 115, 129, 141, 154, 169, 250, 252, 287, 289, 328; HRMS(EI) calcd for $C_{13}H_{14}Br_2$ 327.9462, found 327.9456.



(Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-4-ethylbenzene (4c)

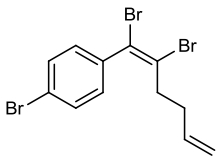
Yield: 85% (148.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.16 (m, 4H), 5.71-5.61 (m, 1H), 5.00 (dd, J =10.4, 1.2 Hz, 1H), 4.96 (dd, J =16.4, 1.2 Hz, 1H), 2.65 (q, J = 7.6 Hz, 2H), 2.51-2.48 (m, 2H), 2.36-2.30 (m, 2H), 1.25 (t, J =7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 136.7, 136.2, 129.5, 128.6, 128.0, 123.3, 115.9, 38.0, 33.0, 28.6, 15.2 ppm; ν_{max}(KBr)/cm^{-1} 3078, 2969, 1611, 1456, 762 ; MS (EI) m/z 115, 128, 143, 155, 169, 195, 223, 224, 305, 342; HRMS(EI) calcd for $C_{14}H_{16}Br_2$ 341.9619, found 341.9615.



(Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-4-(4-ethylcyclohexyl)benzene (4d)

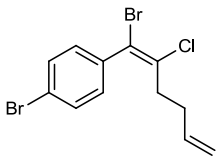
Yield: 71% (150.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.16 (m, 4H),

5.71-5.61 (m, 1H), 5.02 (dd, *J* =10.4, 1.2 Hz, 1H), 4.96 (dd, *J* =17.2, 1.6 Hz, 1H), 2.56-2.43 (m, 2H), 2.36-2.30 (m, 2H), 1.90-1.88 (m, 4H), 1.49-1.40 (m, 2H), 1.30-1.20 (m, 4H), 1.09-0.99 (m, 2H), 0.91 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 136.7, 136.3, 129.4, 128.6, 126.9, 123.4, 115.9, 44.4, 39.1, 38.0, 34.1, 33.1, 33.0, 30.0, 11.5 ppm; ν_{max}(KBr)/cm^{-1} 3081, 2979, 1644, 1500, 746; MS (EI) m/z 111, 127, 153, 169, 195, 242, 265, 304, 373, 424; HRMS(EI) calcd for $C_{20}H_{26}Br_2$ 424.0401, found 424.0395.



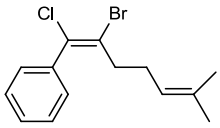
(Z)-1-bromo-4-(1,2-dibromohexa-1,5-dien-1-yl)benzene (4e)

Yield: 89% (174.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.20-7.15 (m, 2H), 5.69-5.59 (m, 1H), 5.01 (dd, J =10.6, 1.2 Hz, 1H), 4.98 (dd, *J* =16.8, 1.2 Hz, 1H), 2.53-2.45 (m, 2H), 2.35-2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.9, 131.8, 130.4, 130.3, 123.0, 121.6, 116.2, 37.9, 32.9 ppm; ν_{max}(KBr)/cm^{-1} 3074, 2981, 1636, 1490, 1435, 711 ; MS (EI) m/z 88, 114, 115, 154, 193, 235, 274, 315, 352, 392; HRMS(EI) calcd for $C_{12}H_{11}Br_3$ 391.8411, found 391.8403.



(Z)-1-bromo-4-(1-bromo-2-chlorohexa-1,5-dien-1-yl)benzene (4f)

Yield: 73% (127.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 5.70-5.60 (m, 1H), 5.01 (dd, J =10.6, 1.2 Hz, 1H), 4.98 (dd, *J* =17.2, 1.2 Hz, 1H), 2.43-2.39 (m, 2H), 2.35-2.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.7, 136.0, 131.8, 130.7, 123.0, 118.4, 116.2, 35.8, 31.9 ppm; ν_{max}(KBr)/cm^{-1} 3075, 2983, 1635, 1495, 713 ; MS (EI) m/z 99, 114, 149, 152, 155, 190, 192, 230, 232, 269, 271, 307, 309, 348; HRMS(EI) calcd for $C_{12}H_{11}ClBr_2$ 347.8916, found 347.8914.



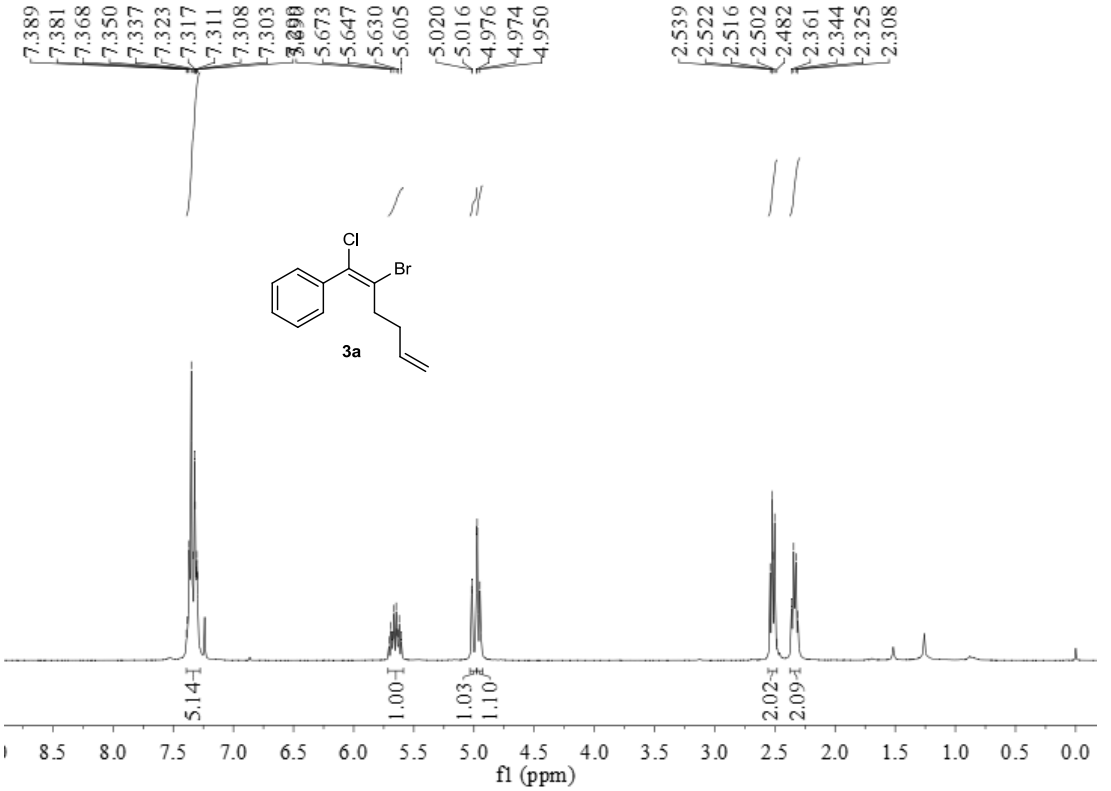
(Z)-(2-bromo-1-chloro-6-methylhepta-1,5-dien-1-yl)benzene (3v)

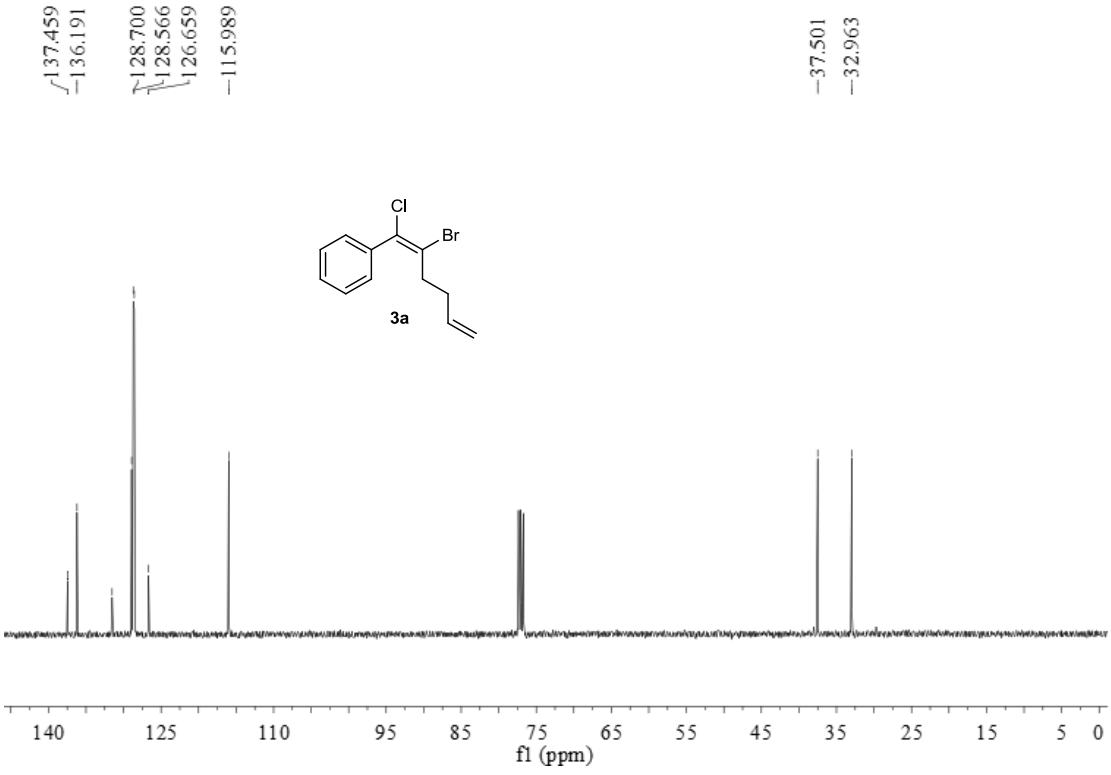
Yield: 81% (120.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.39-7.35 (m, 3H), 7.32-7.30 (m, 2H), 4.98-4.91 (m, 1H), 2.46-2.41 (m, 2H), 2.28-2.23 (m, 2H), 1.65 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 133.4, 131.1, 128.8, 128.7, 128.5, 127.2, 121.9, 38.2, 27.4, 25.7, 17.6 ppm; ν_{max}(KBr)/cm^{-1} 3029, 2926, 1635, 1442, 710; MS (EI) m/z 69, 115, 150, 152, 183, 220, 223, 231, 263, 298; HRMS(EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0122.

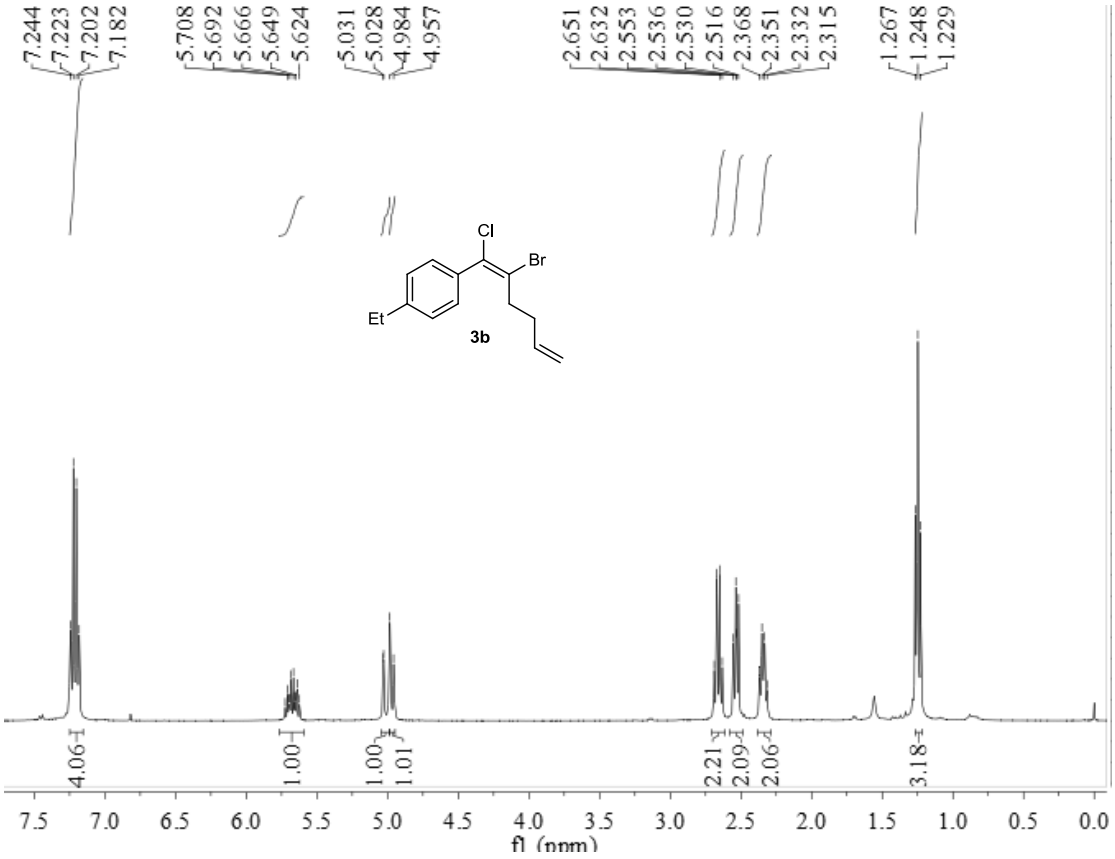
V. ^{1}H and ^{13}C NMR spectra of compounds 3 and 4

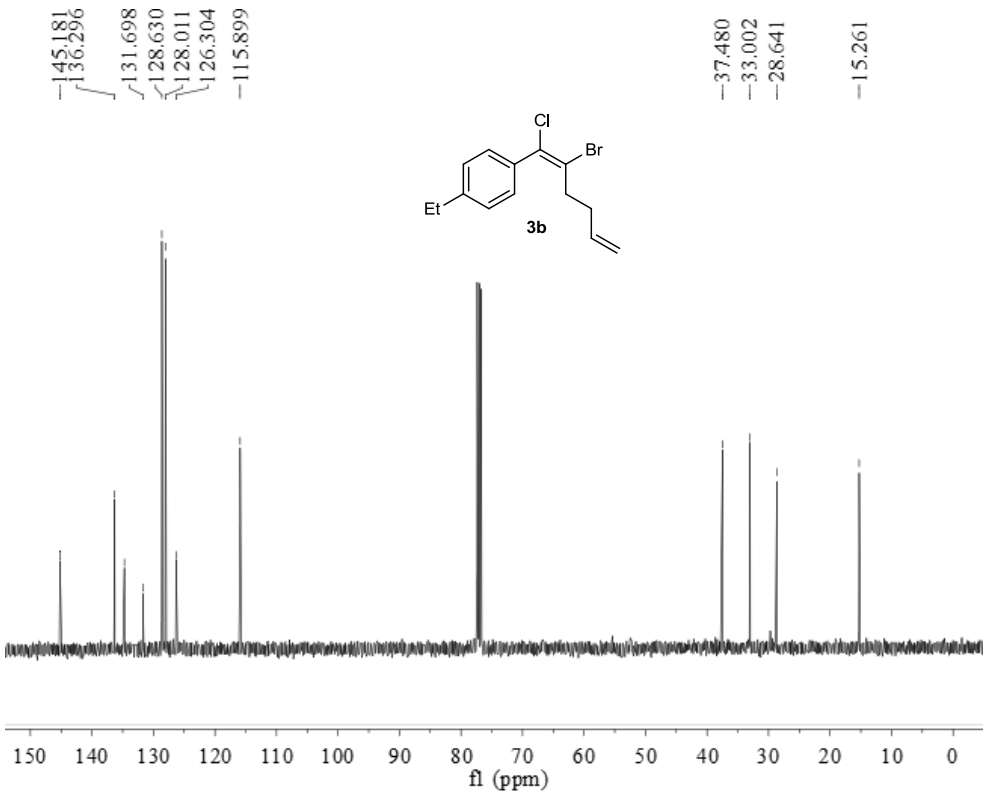
^{1}H NMR and ^{13}C NMR of (Z)-(2-bromo-1-chlorohexa-1,5-dien-1-yl)benzene (3a)



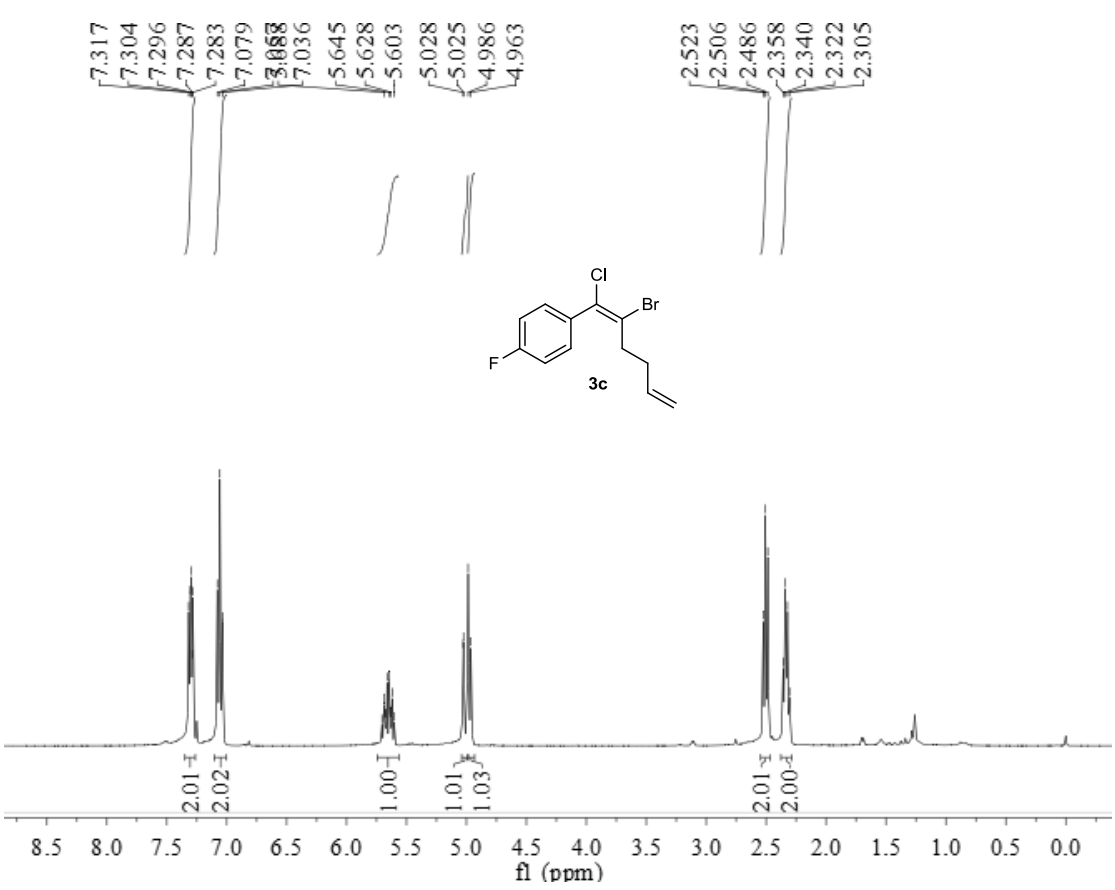


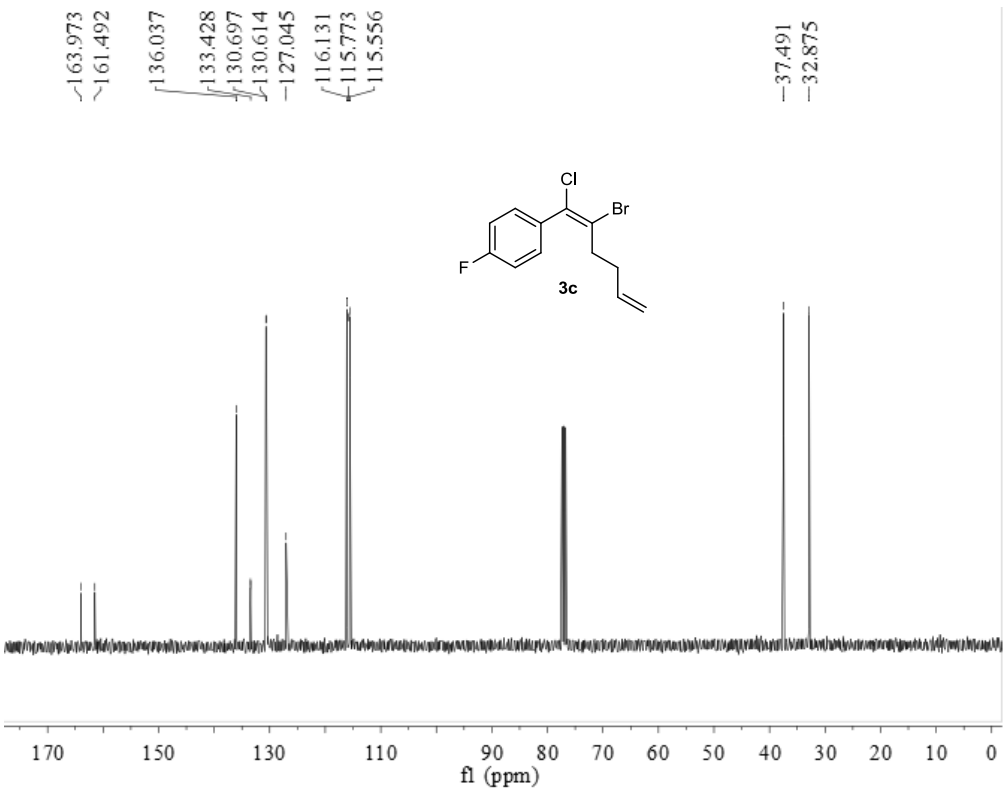
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-ethylbenzene (3b)



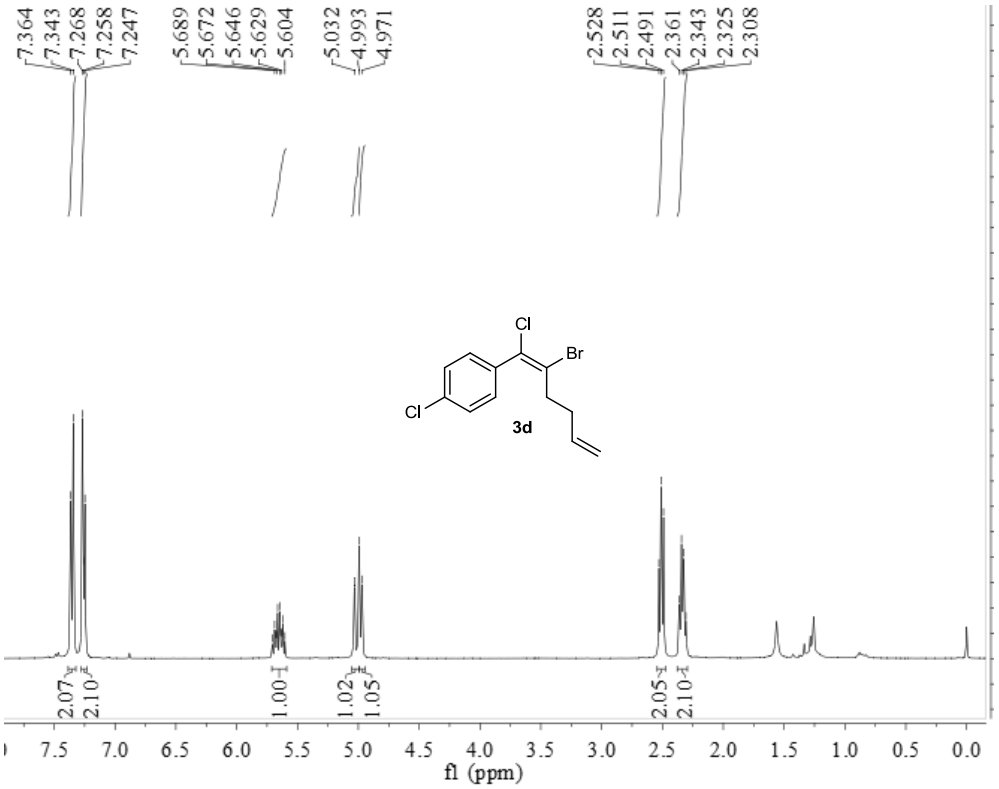


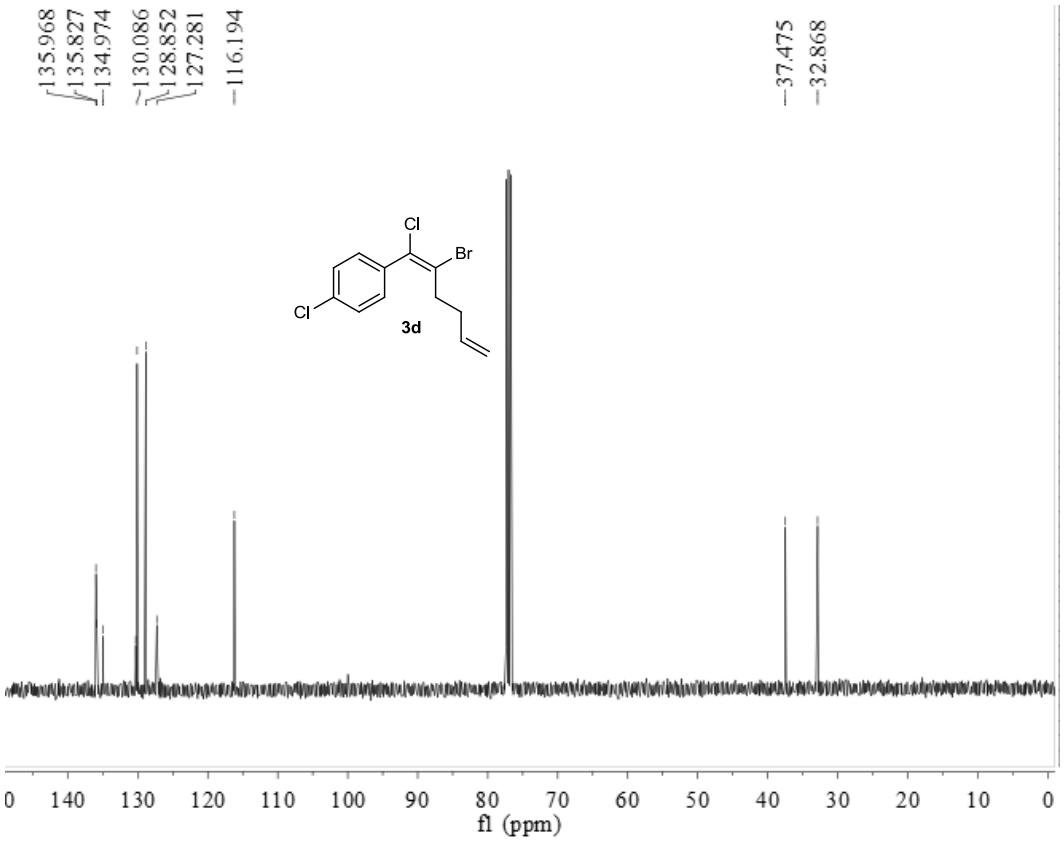
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-fluorobenzene (3c)



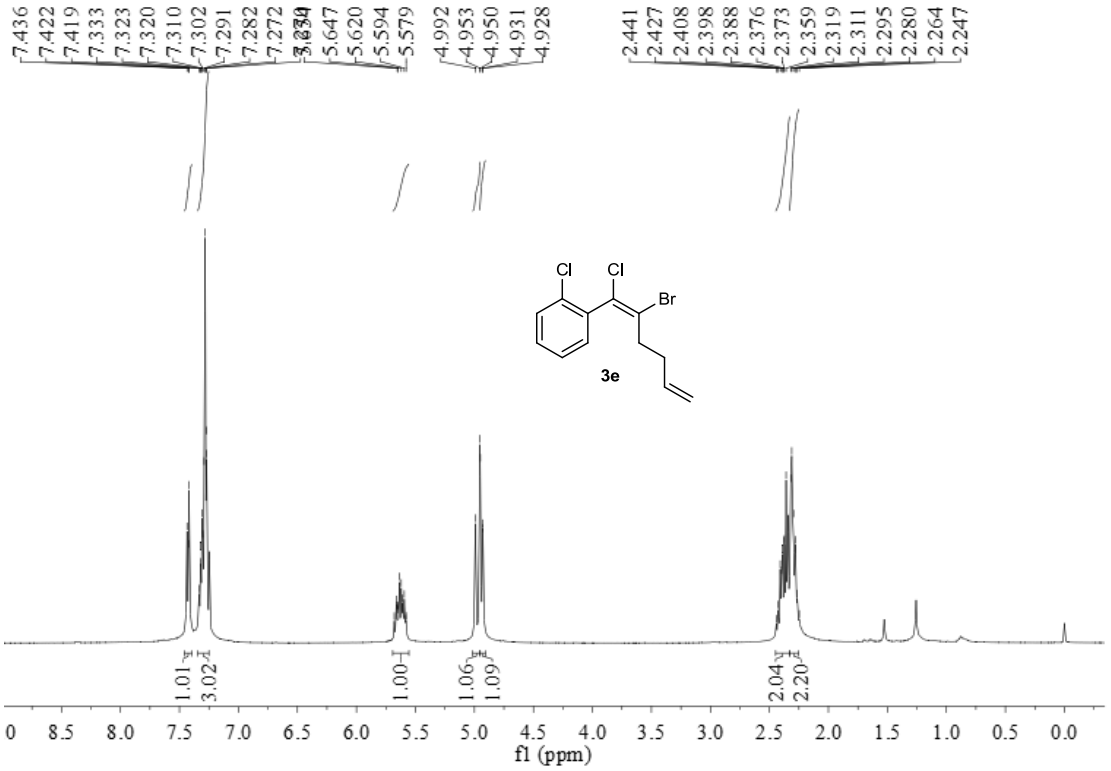


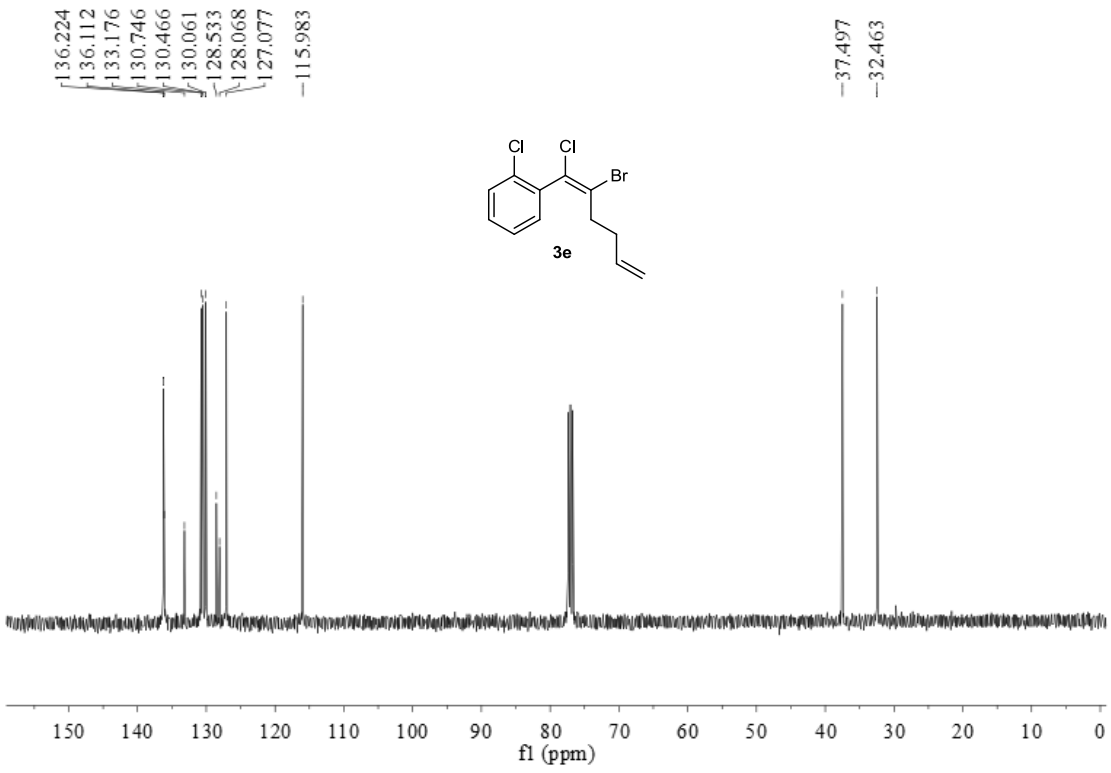
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-chlorobenzene (3d)



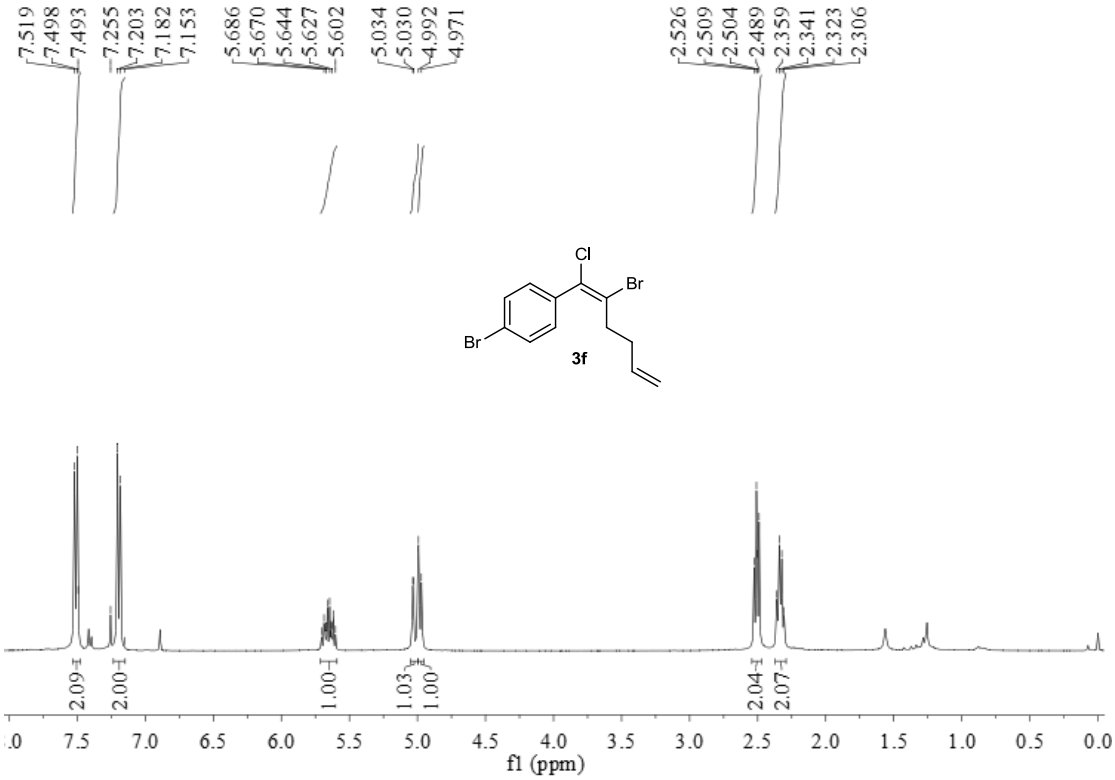


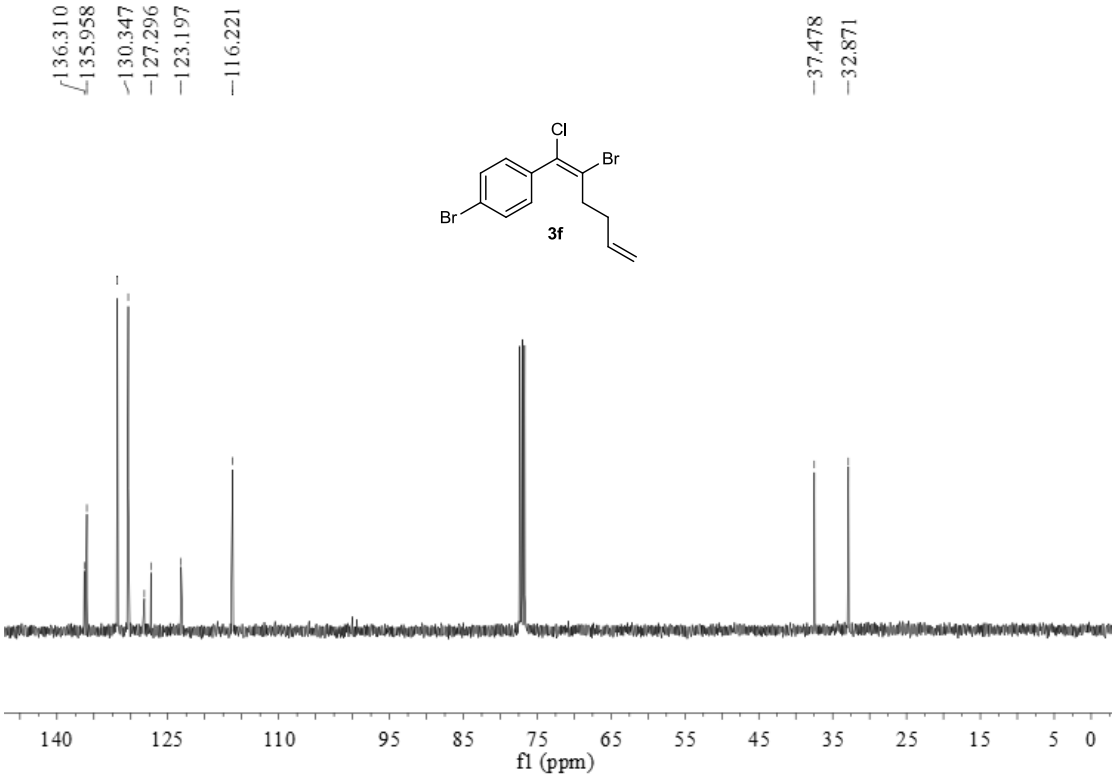
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-chlorobenzene (3e)



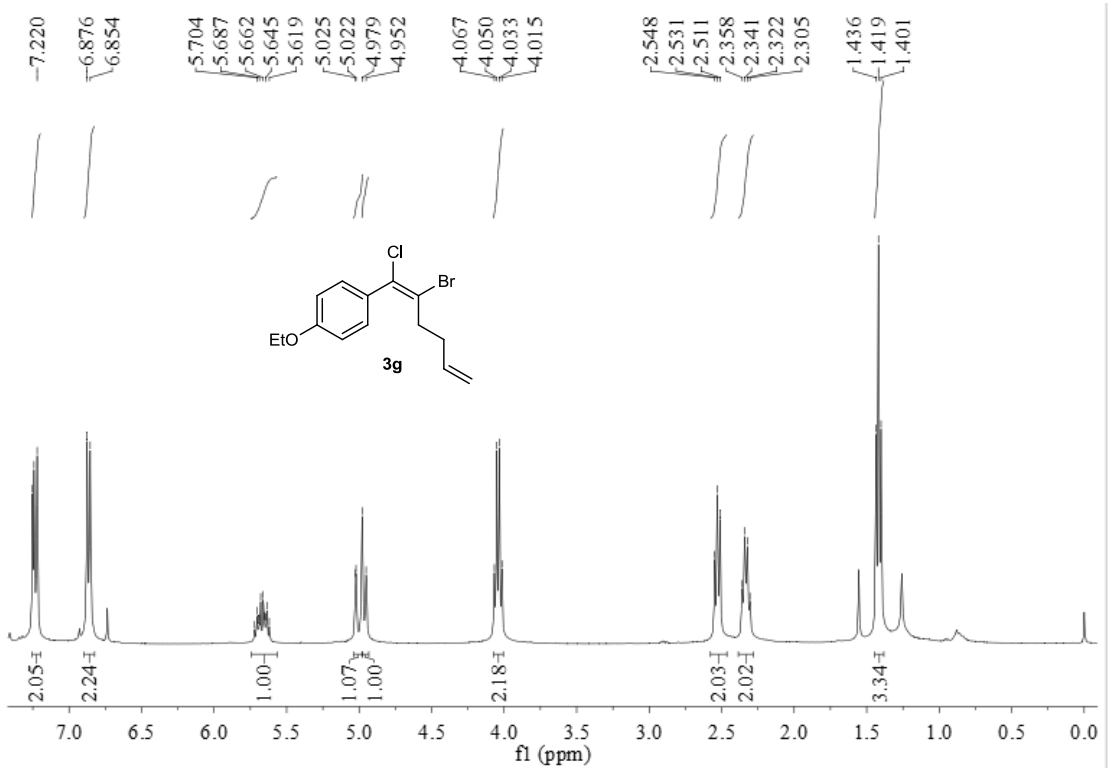


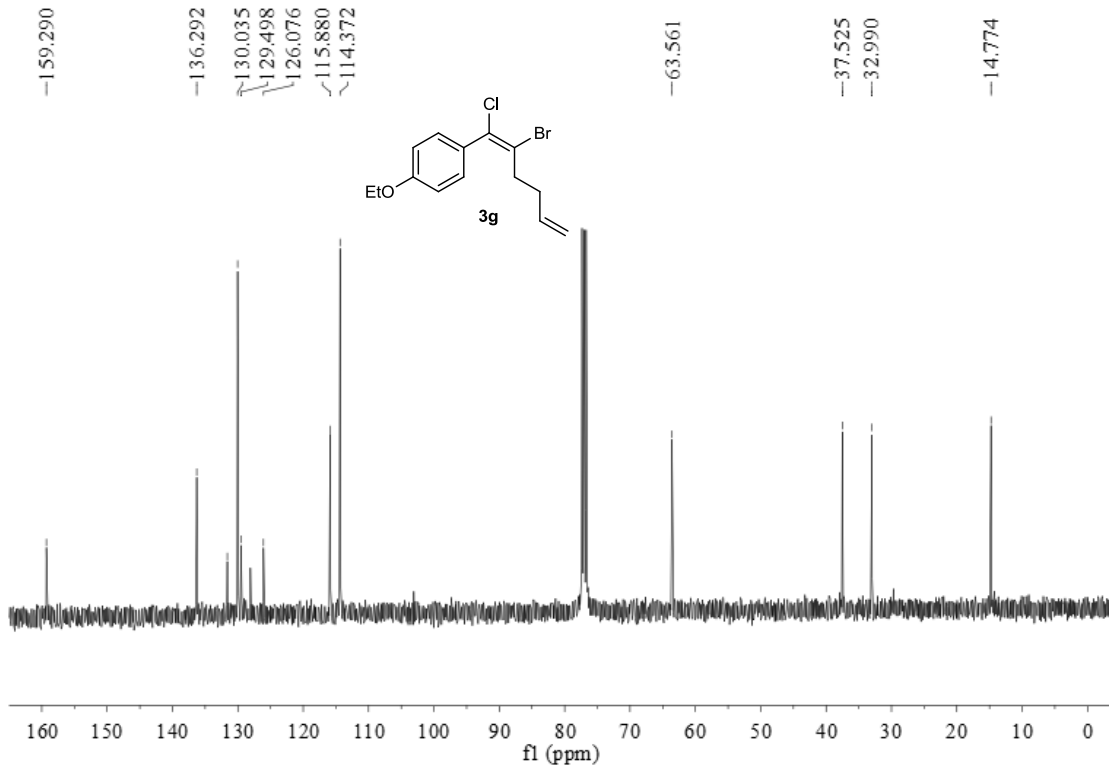
^{1}H NMR and ^{13}C NMR of (Z)-1-bromo-4-(2-bromo-1-chlorohexa-1,5-dien-1-yl)benzene (3f)



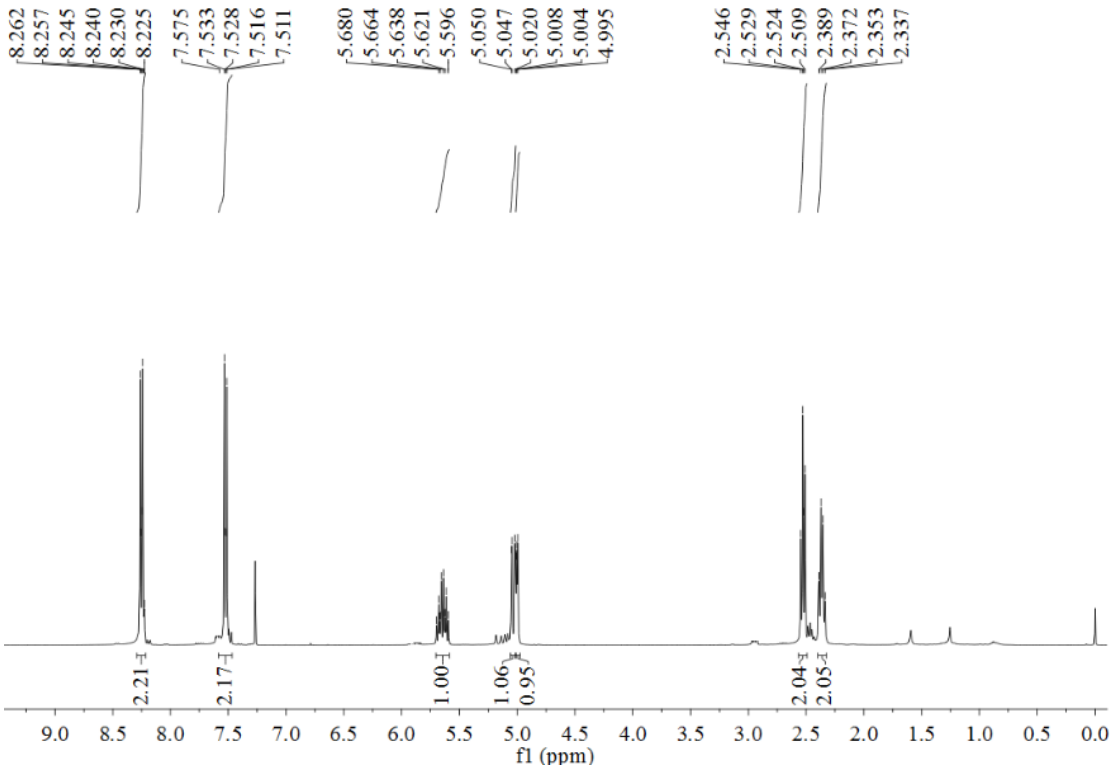


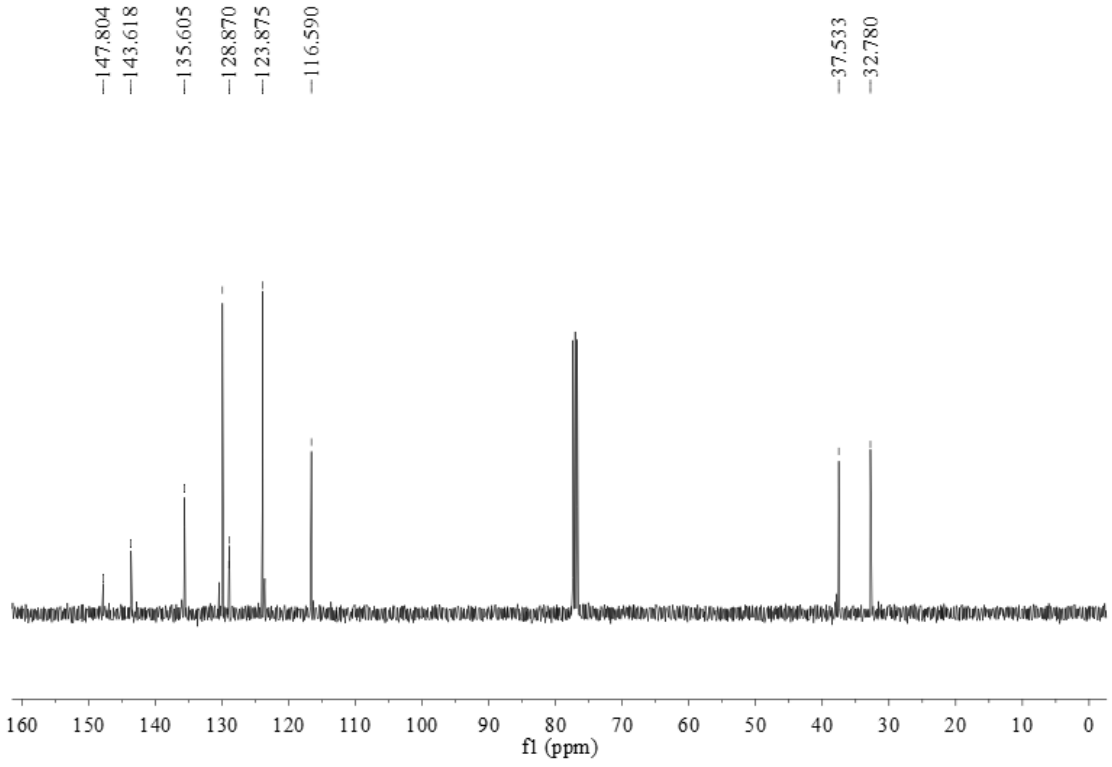
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-ethoxybenzene (3g)





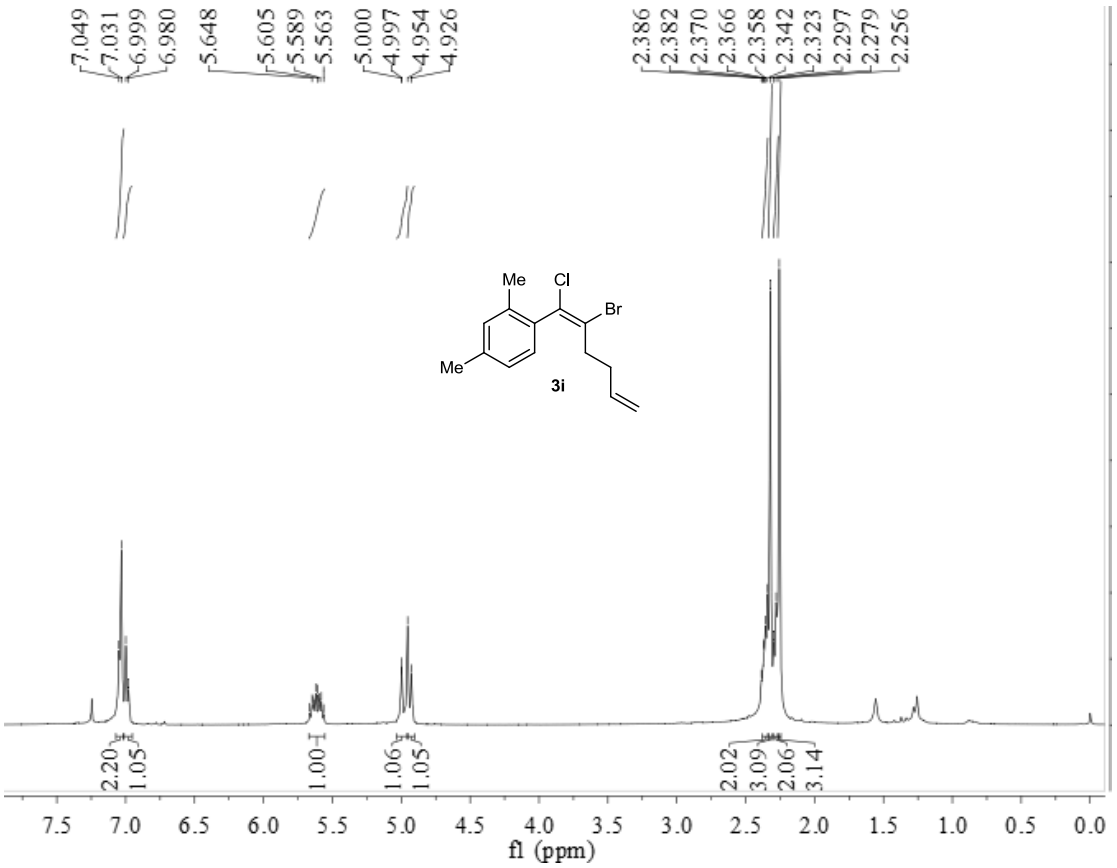
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-nitrobenzene (3h)

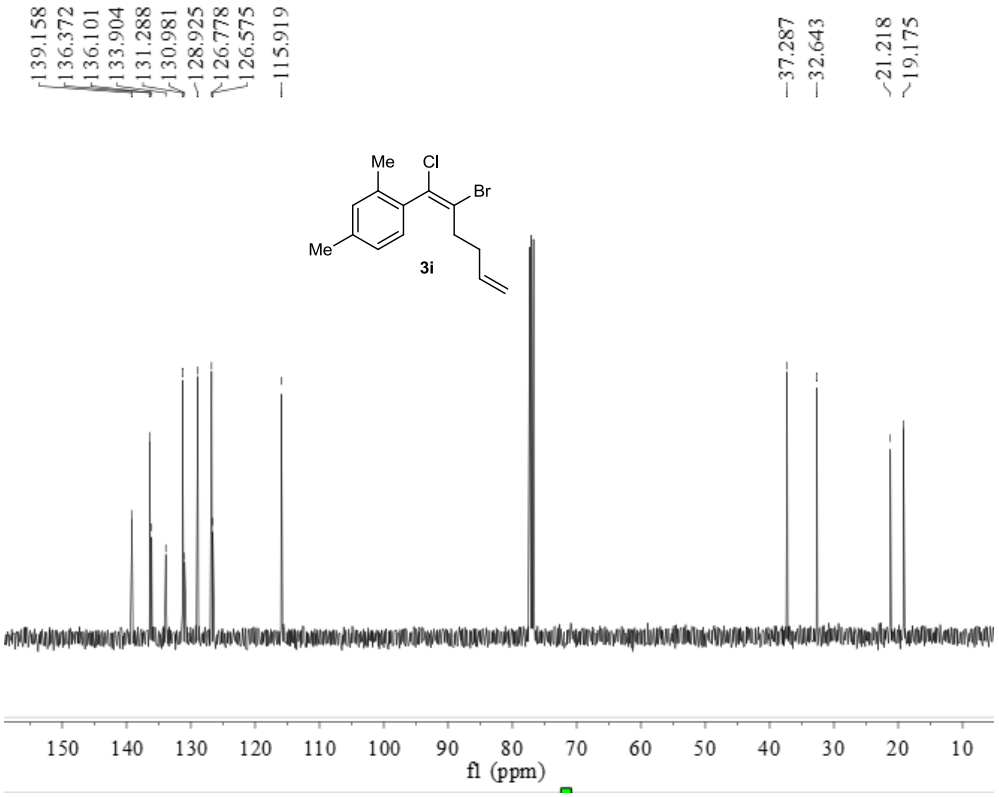




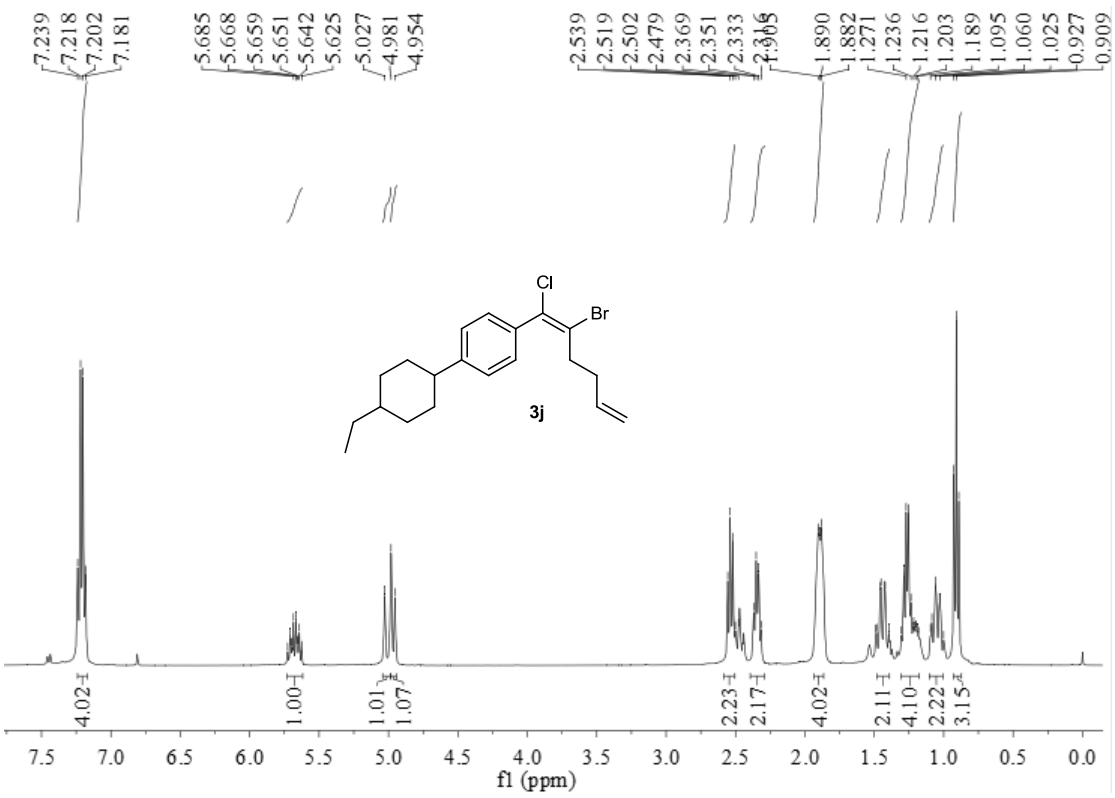
^{1}H NMR and ^{13}C NMR of (Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-2,4-dimethylbenzene

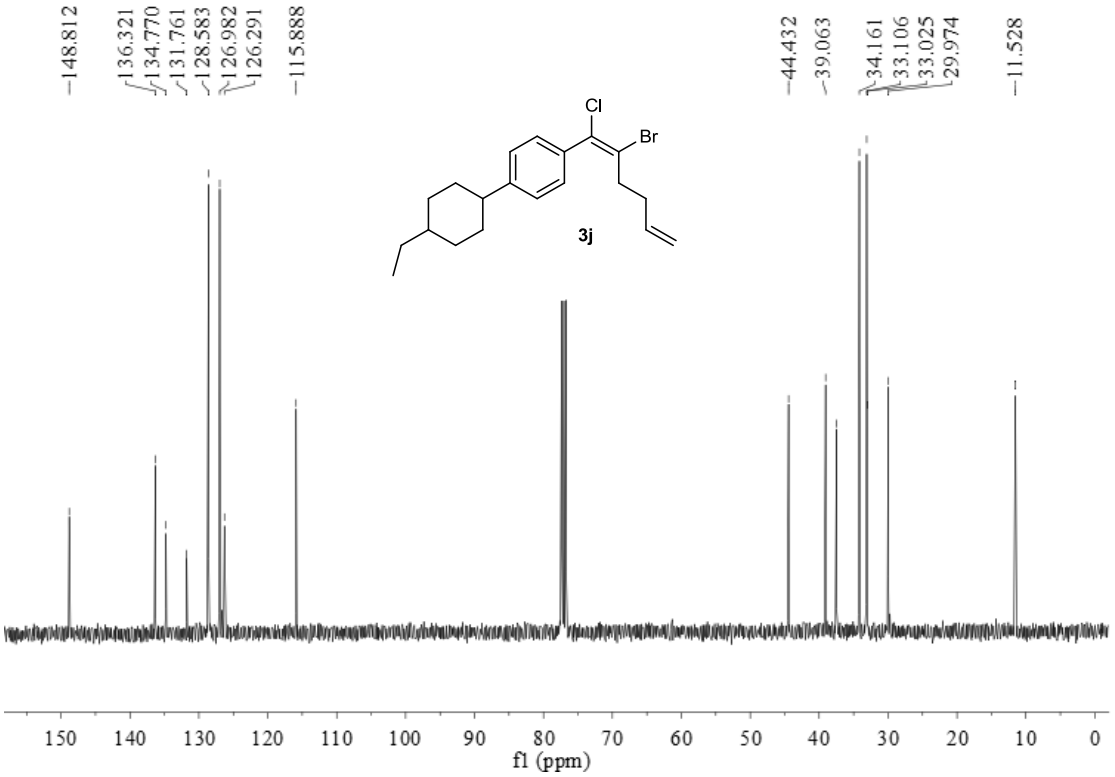
(3i)



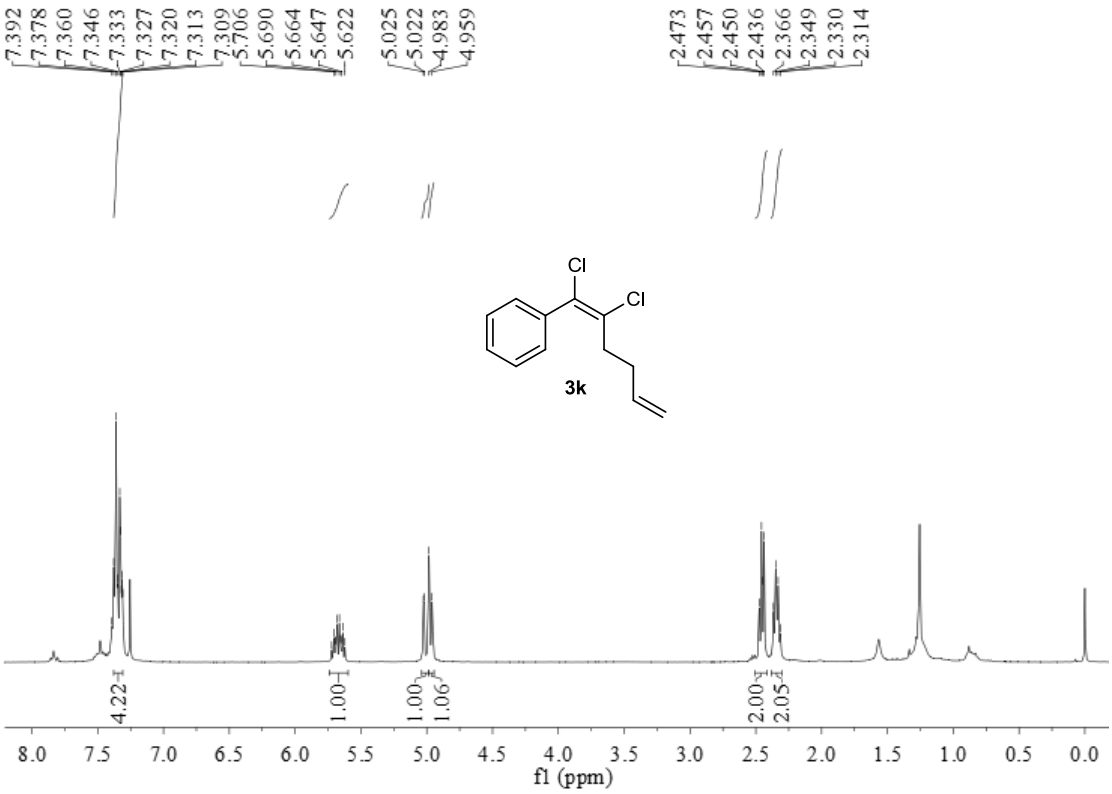


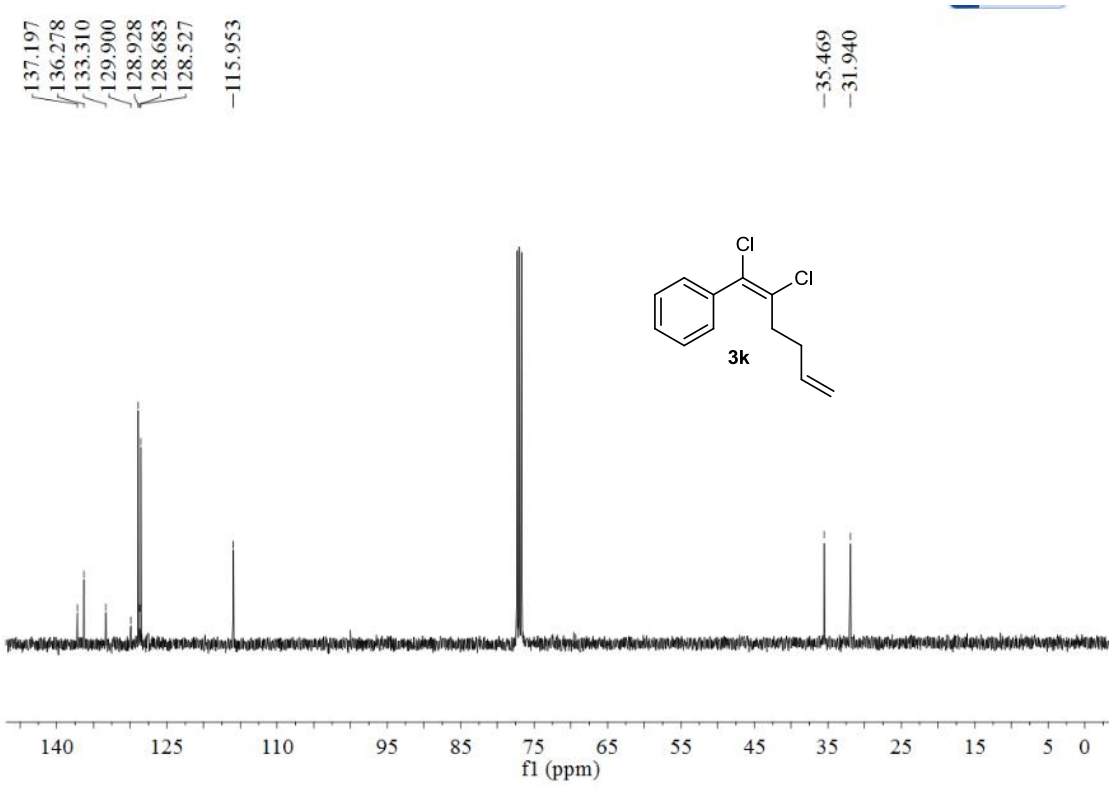
(Z)-1-(2-bromo-1-chlorohexa-1,5-dien-1-yl)-4-(4-ethylcyclohexyl)benzene (3j)



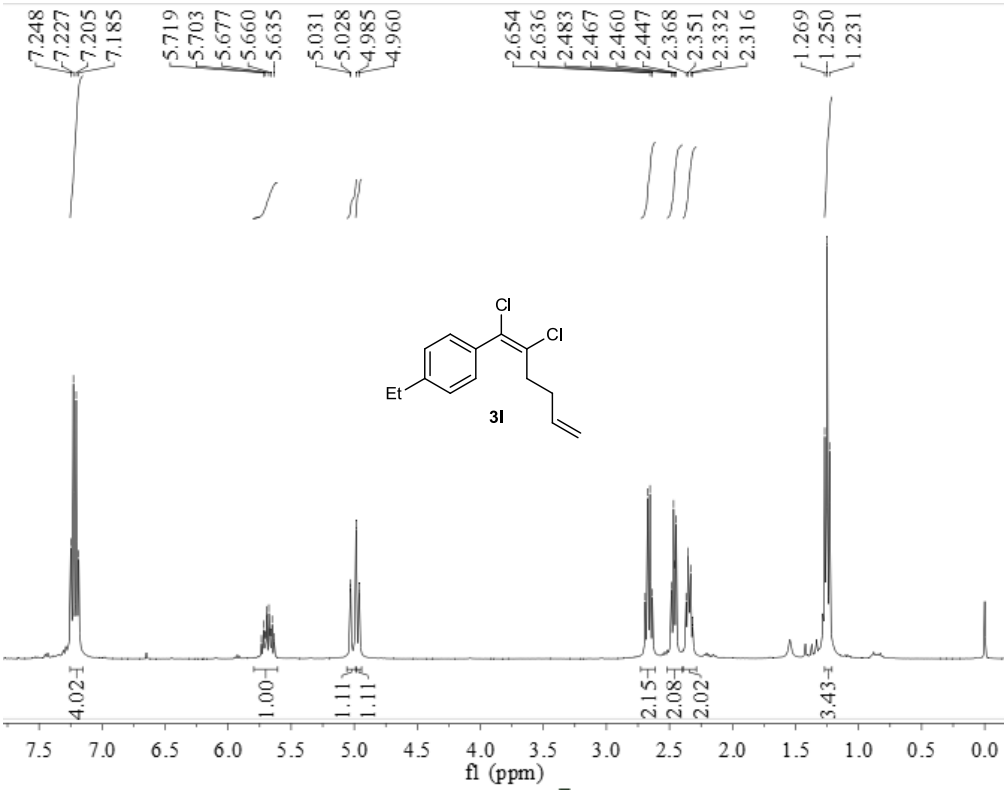


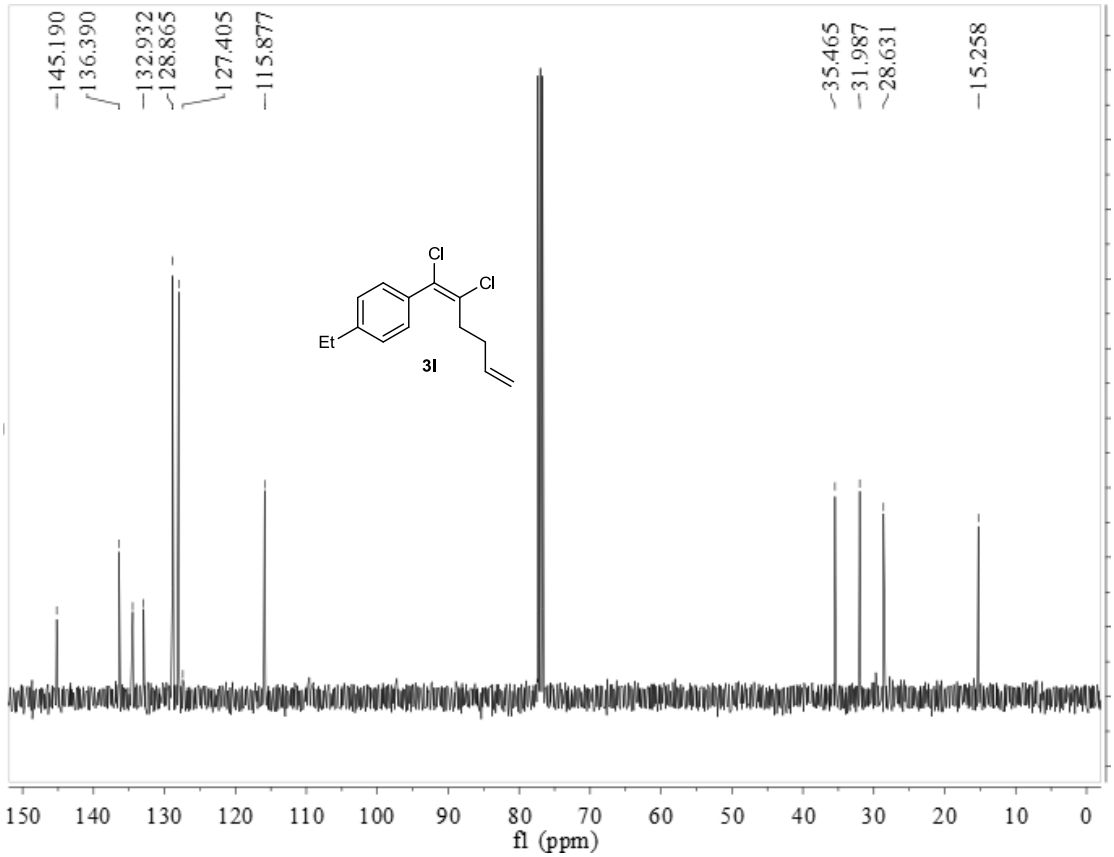
^{1}H NMR and ^{13}C NMR of (Z)-(1,2-dichlorohexa-1,5-dien-1-yl)benzene (3k)



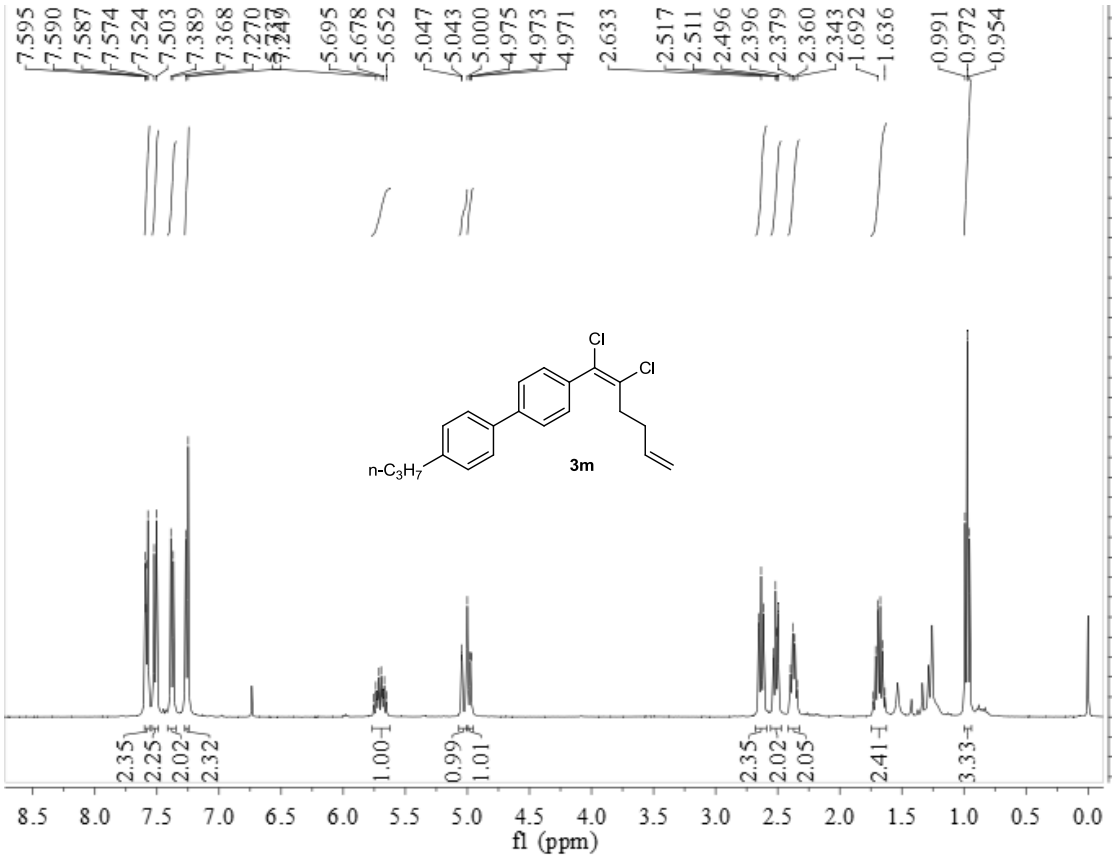


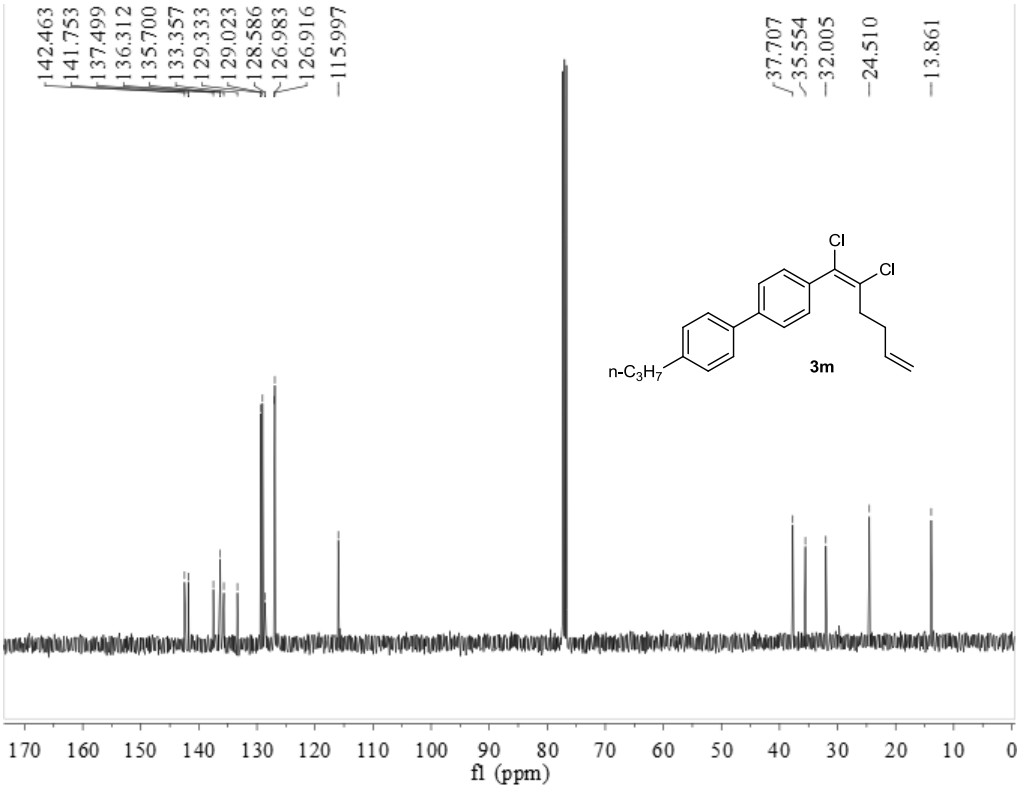
^{1}H NMR and ^{13}C NMR of (Z)-1-(1,2-dichlorohexa-1,5-dien-1-yl)-4-ethylbenzene (3l)



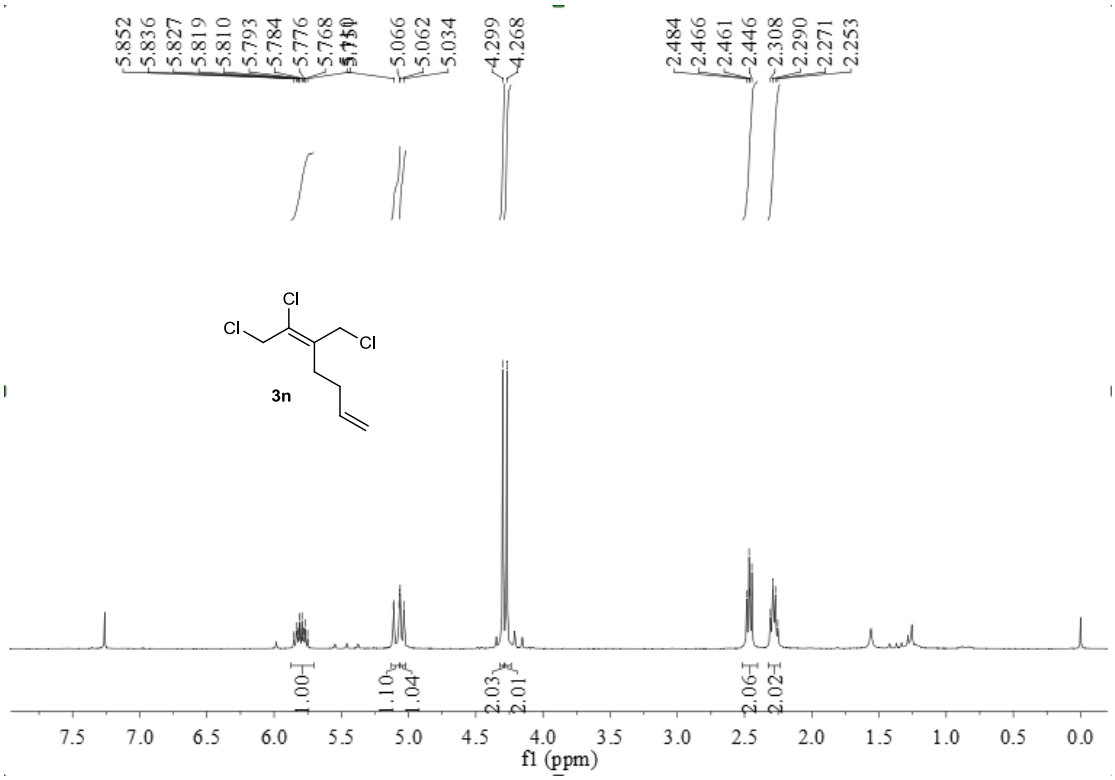


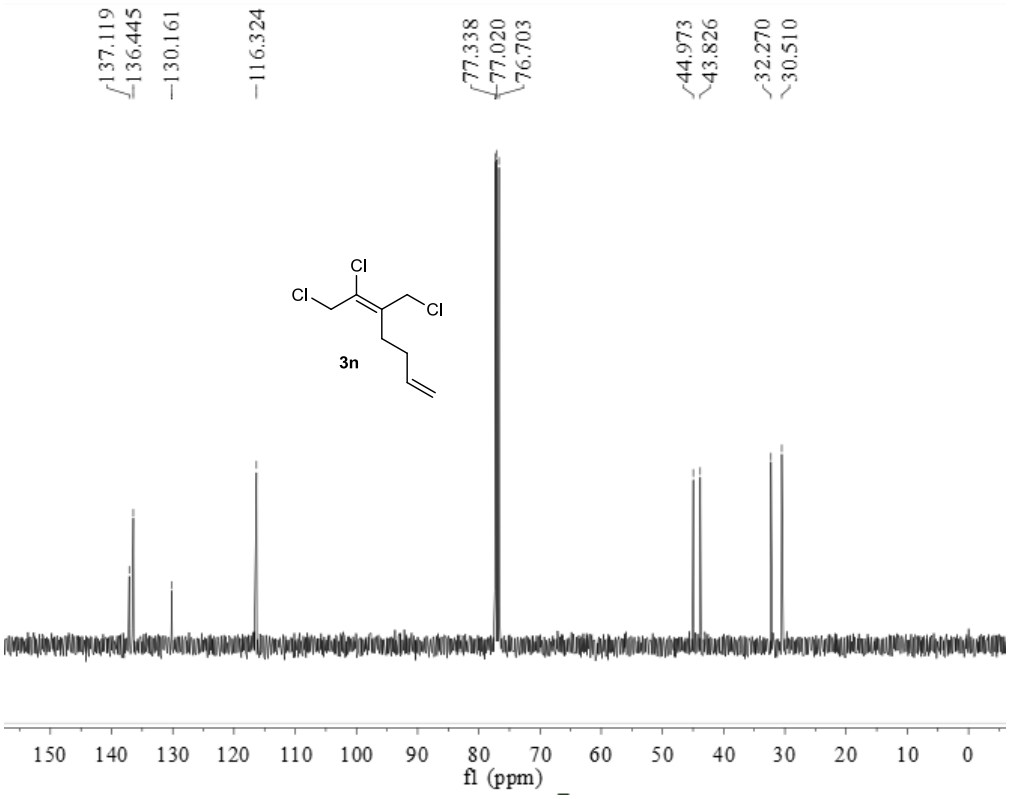
^{1}H NMR and ^{13}C NMR of (Z)-4-(1,2-dichlorohexa-1,5-dien-1-yl)-4'-propyl-1,1'-biphenyl (3m)



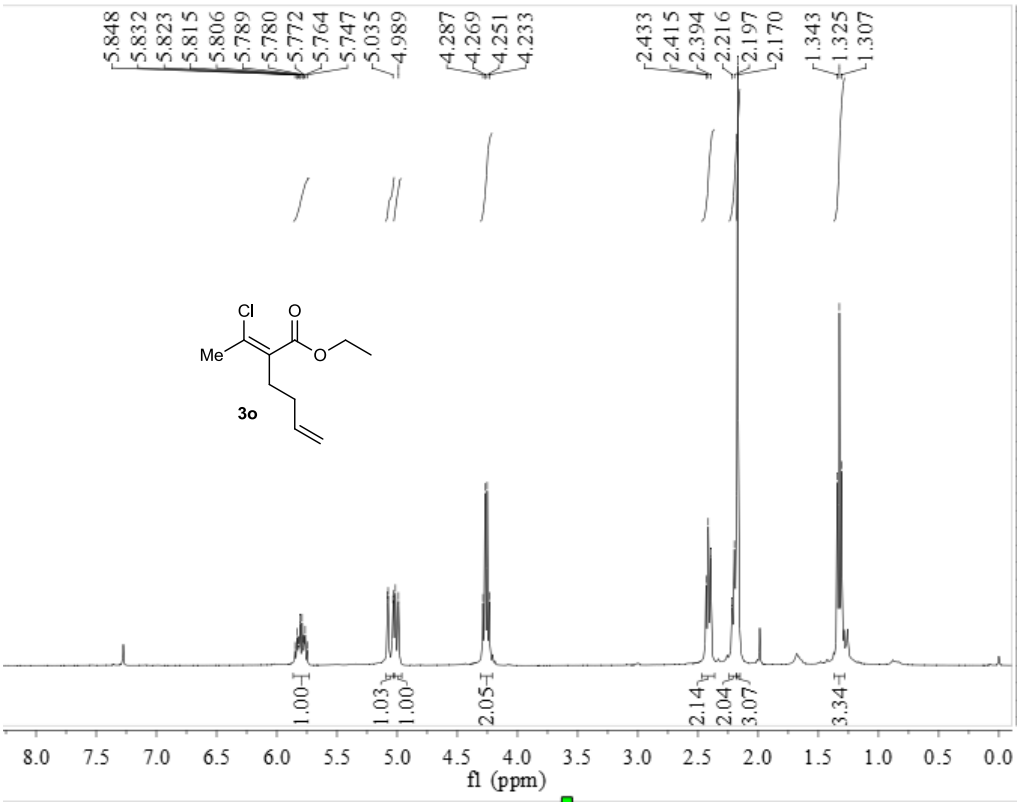


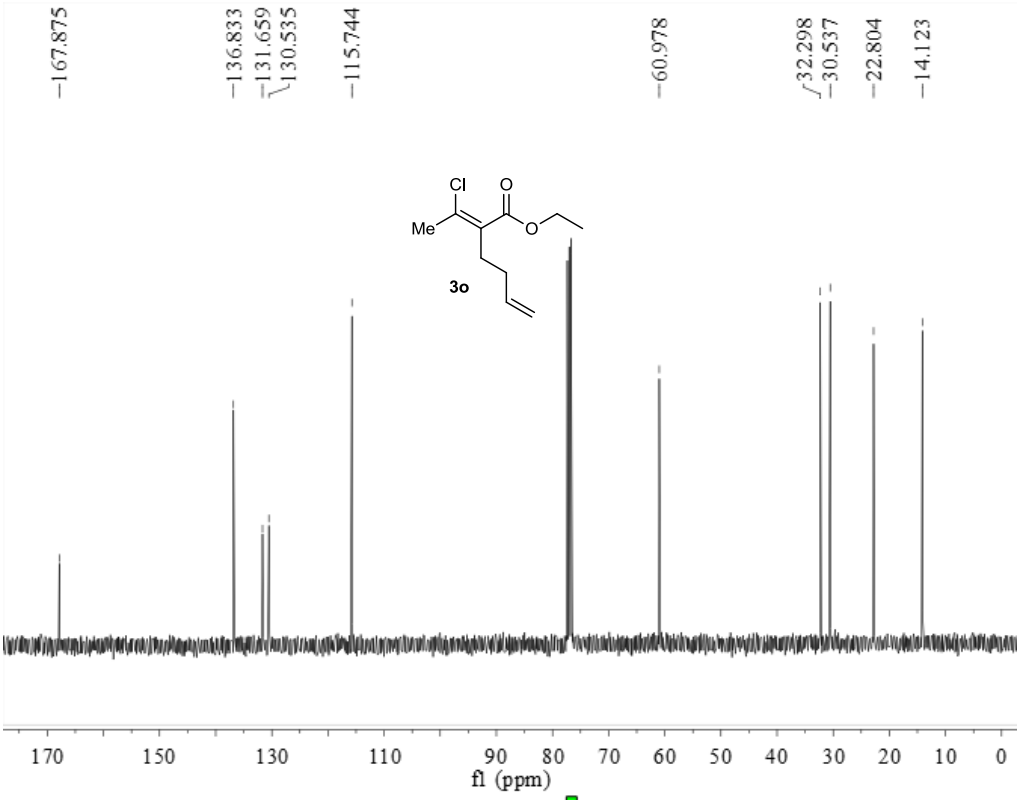
^{1}H NMR and ^{13}C NMR of (Z)-6,7-dichloro-5-(chloromethyl)hepta-1,5-diene (3n)



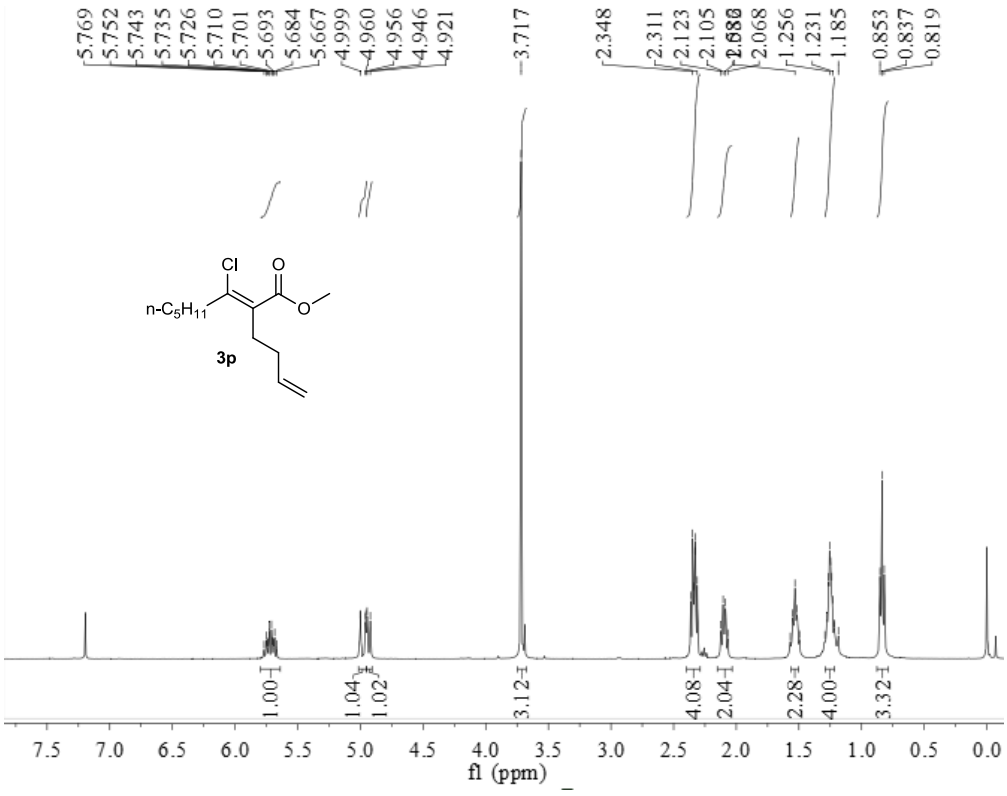


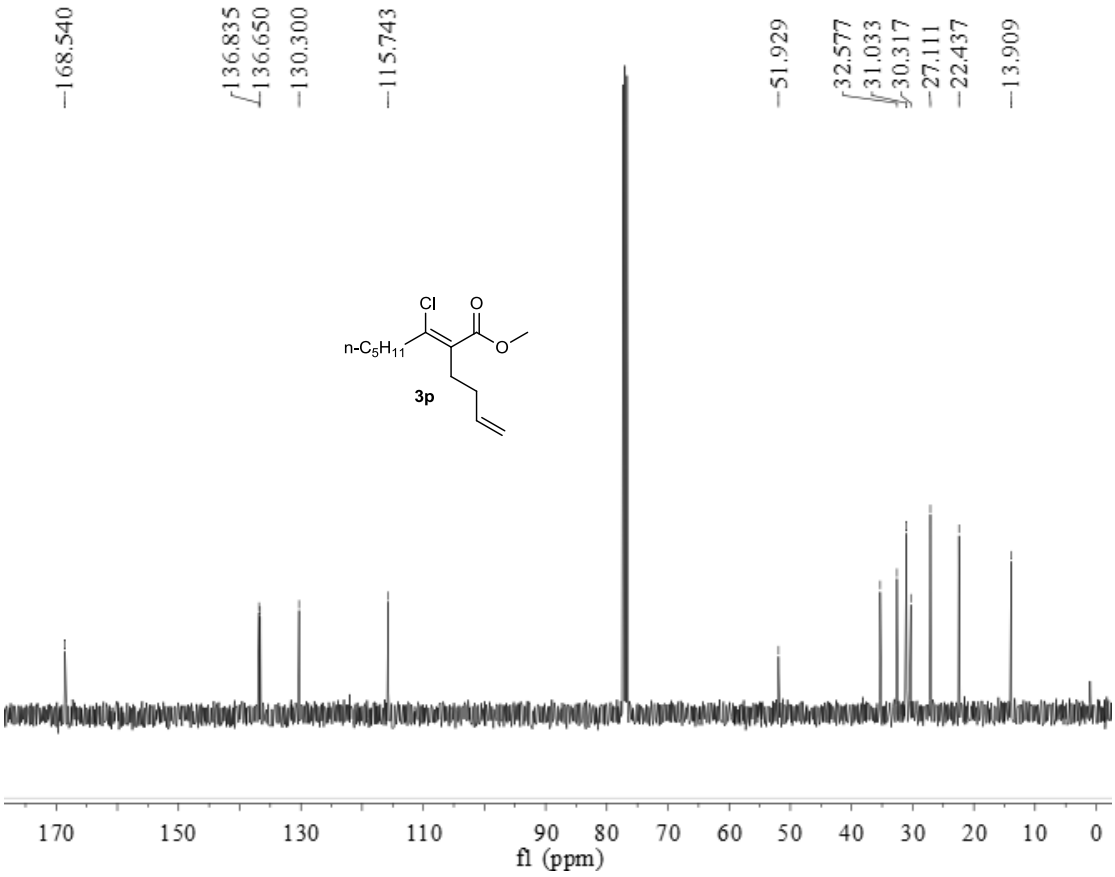
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 2-(1-chloroethylidene)hex-5-enoate (3o)



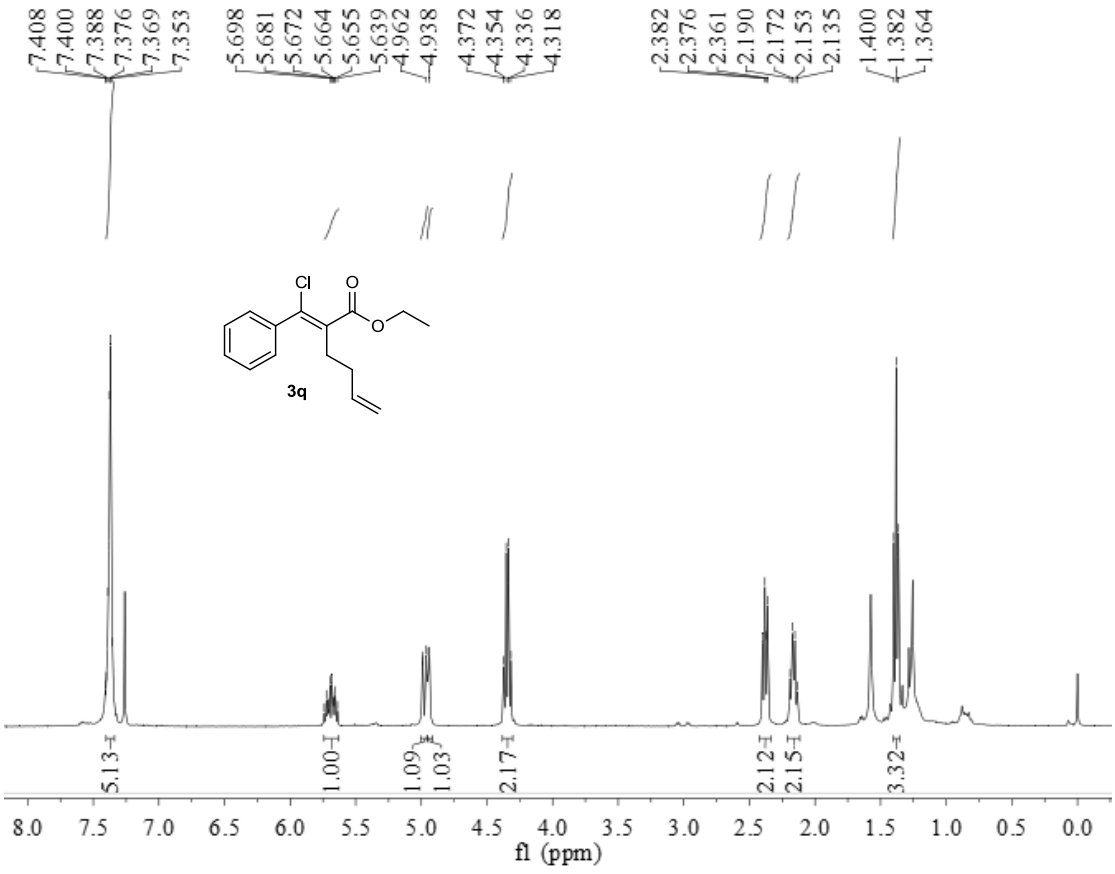


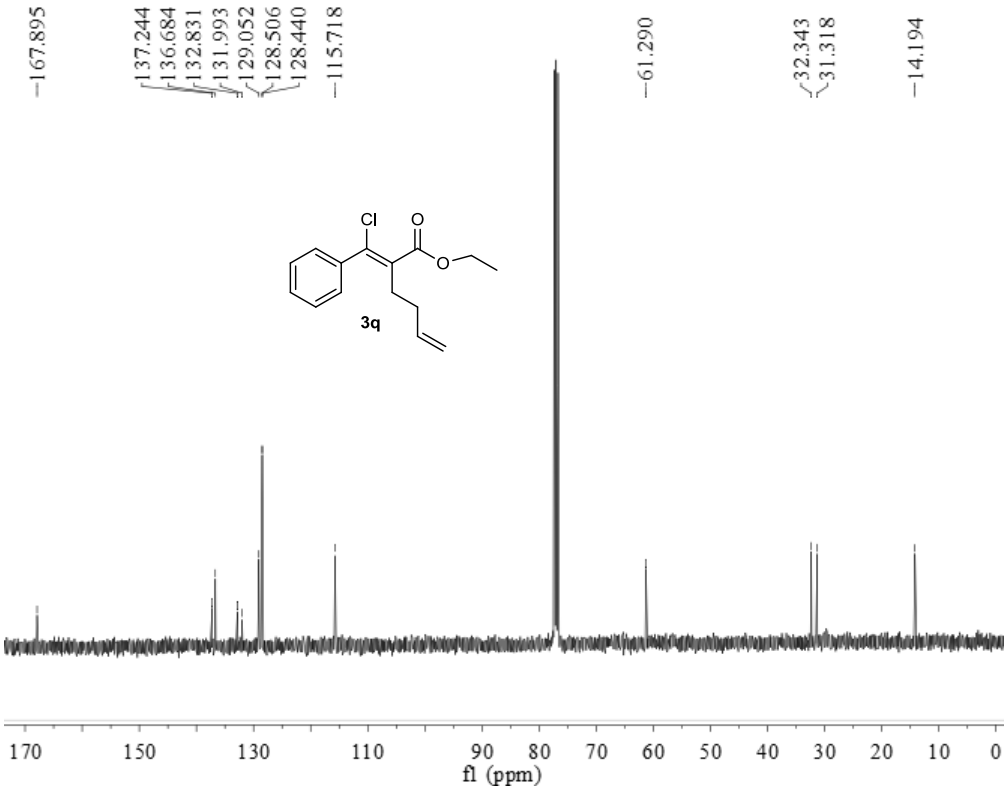
^{1}H NMR and ^{13}C NMR of (Z)-methyl 2-(but-3-en-1-yl)-3-chlorooct-2-enoate (3p)



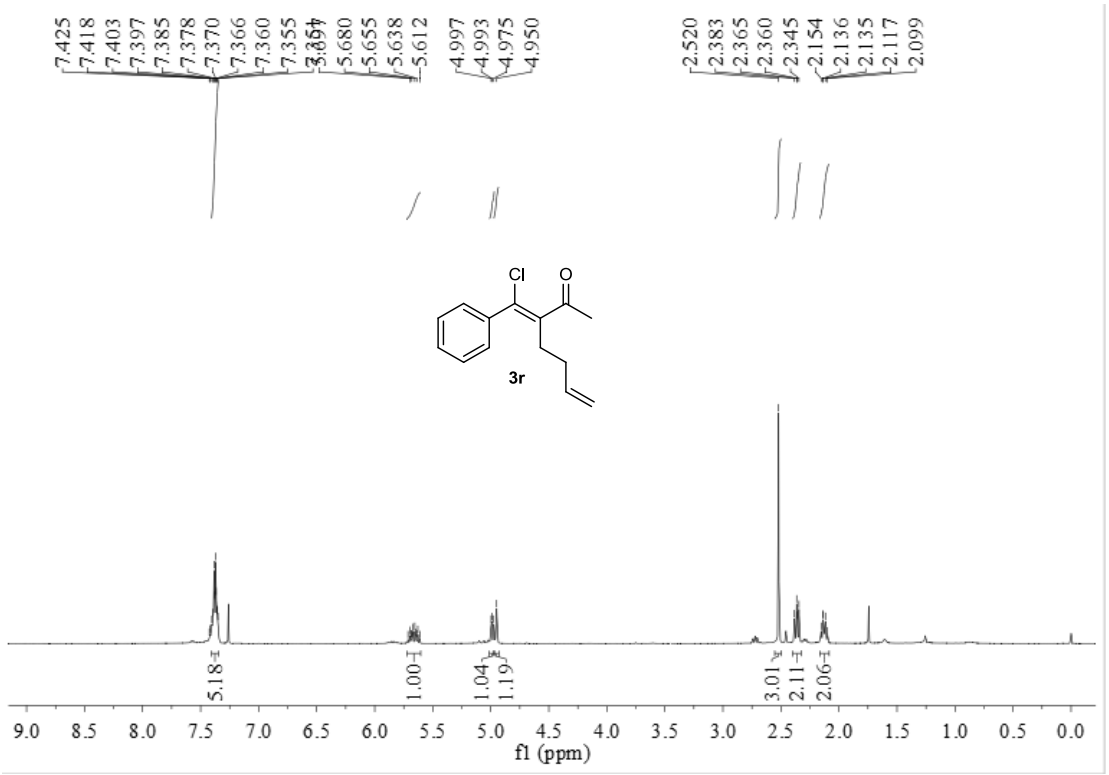


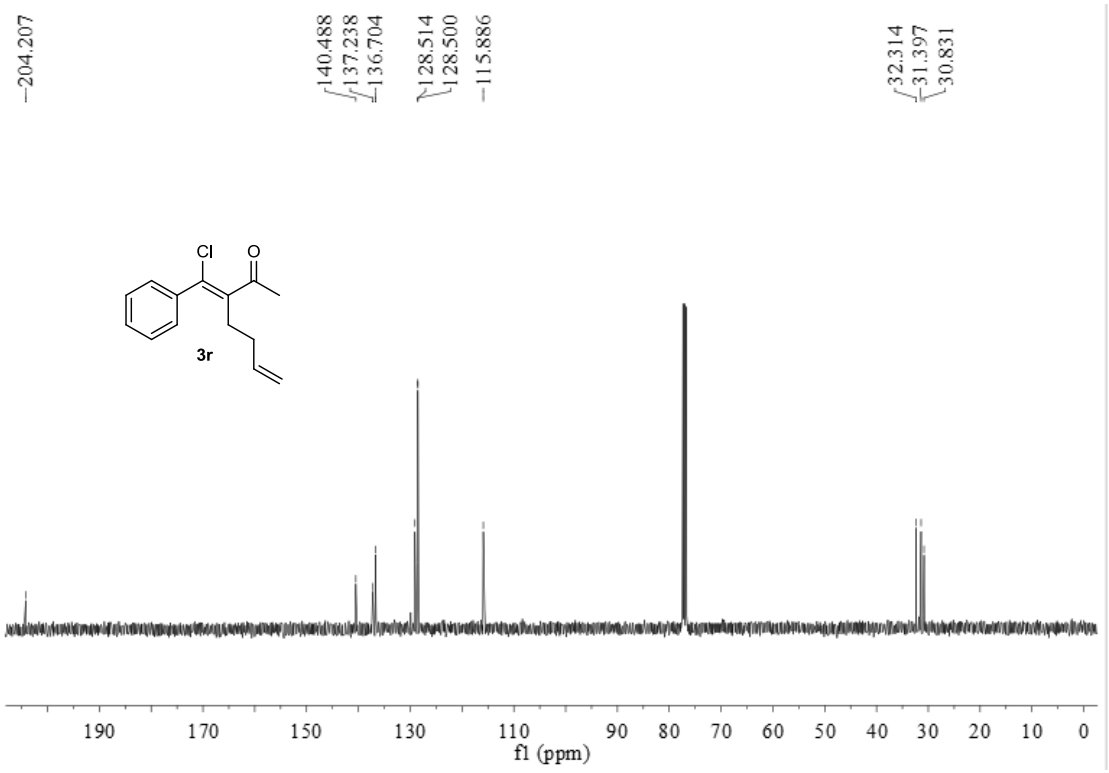
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 2-(chloro(phenyl)methylene)hex-5-enoate (3q)



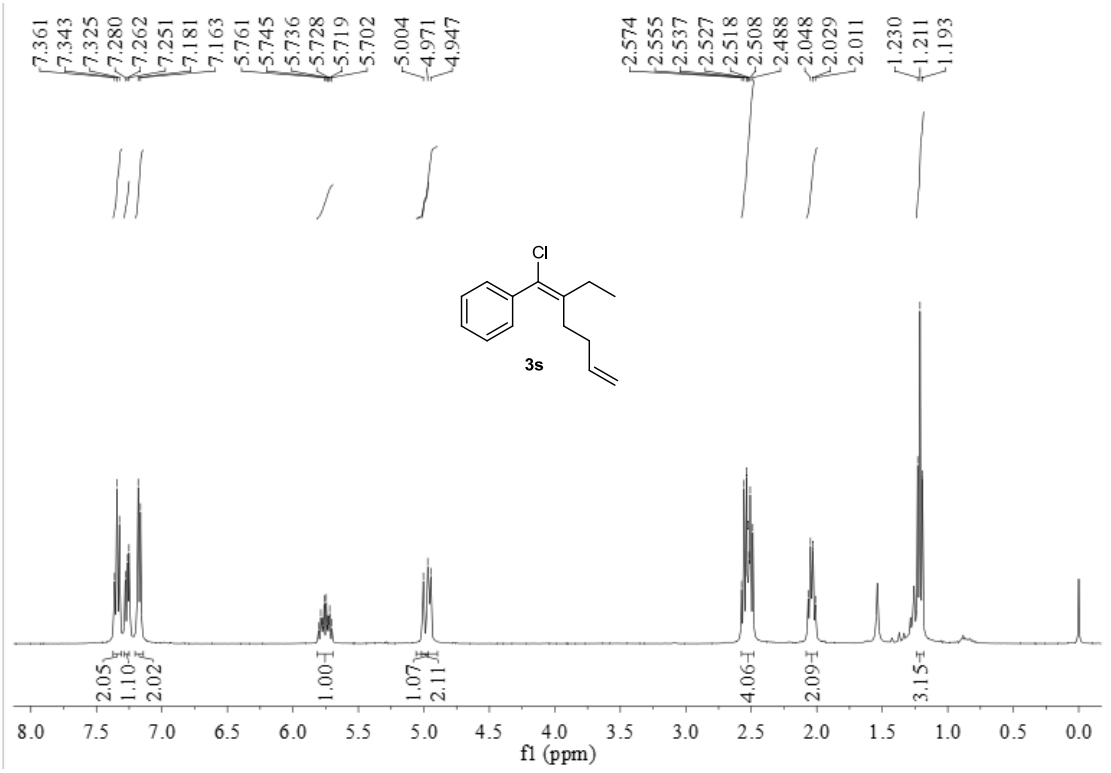


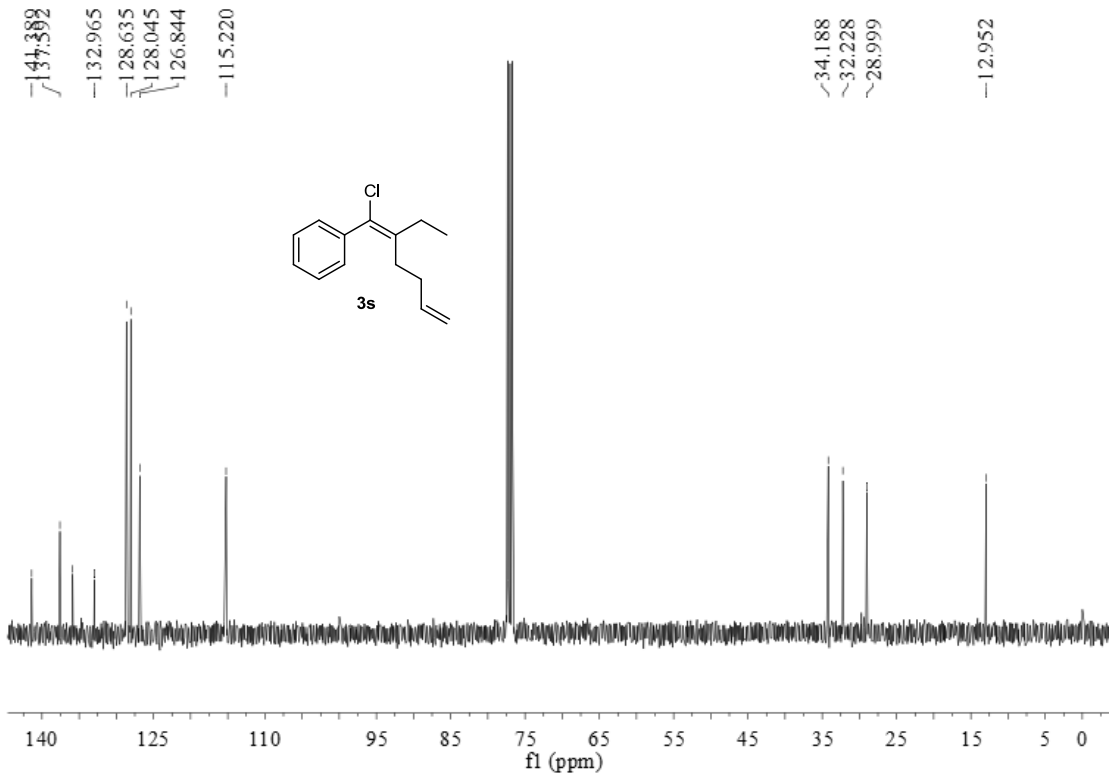
^{1}H NMR and ^{13}C NMR of (Z)-3-(chloro(phenyl)methylene)hept-6-en-2-one (3r)



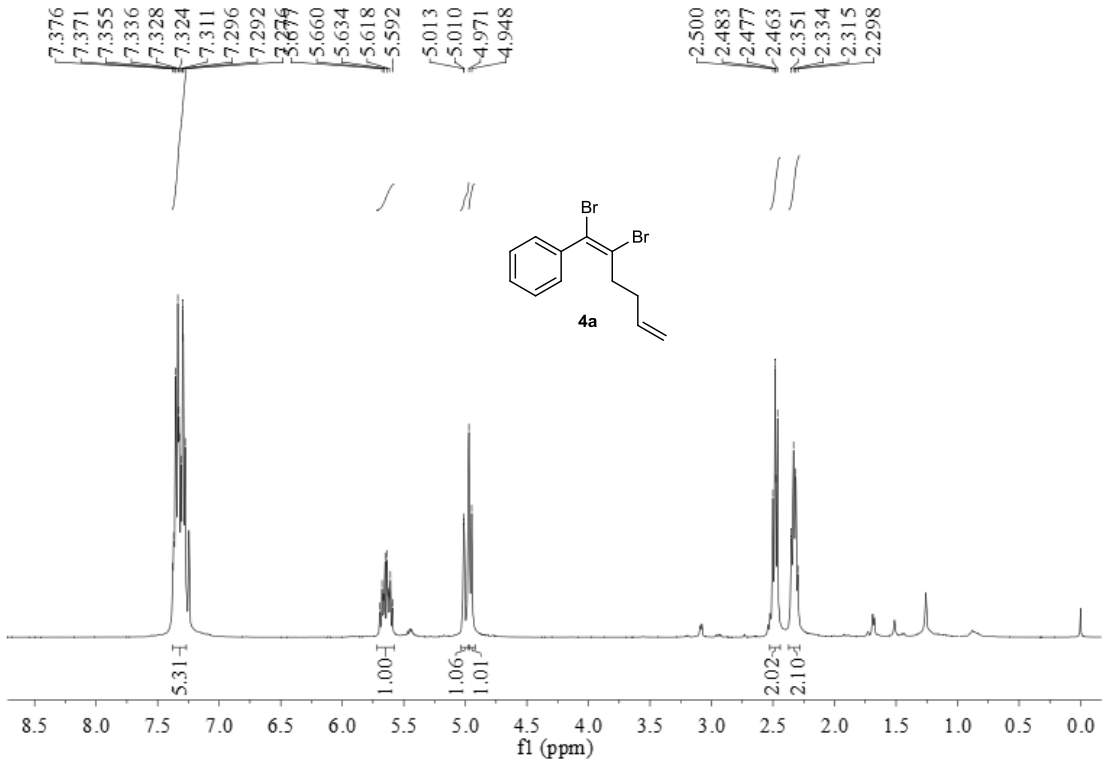


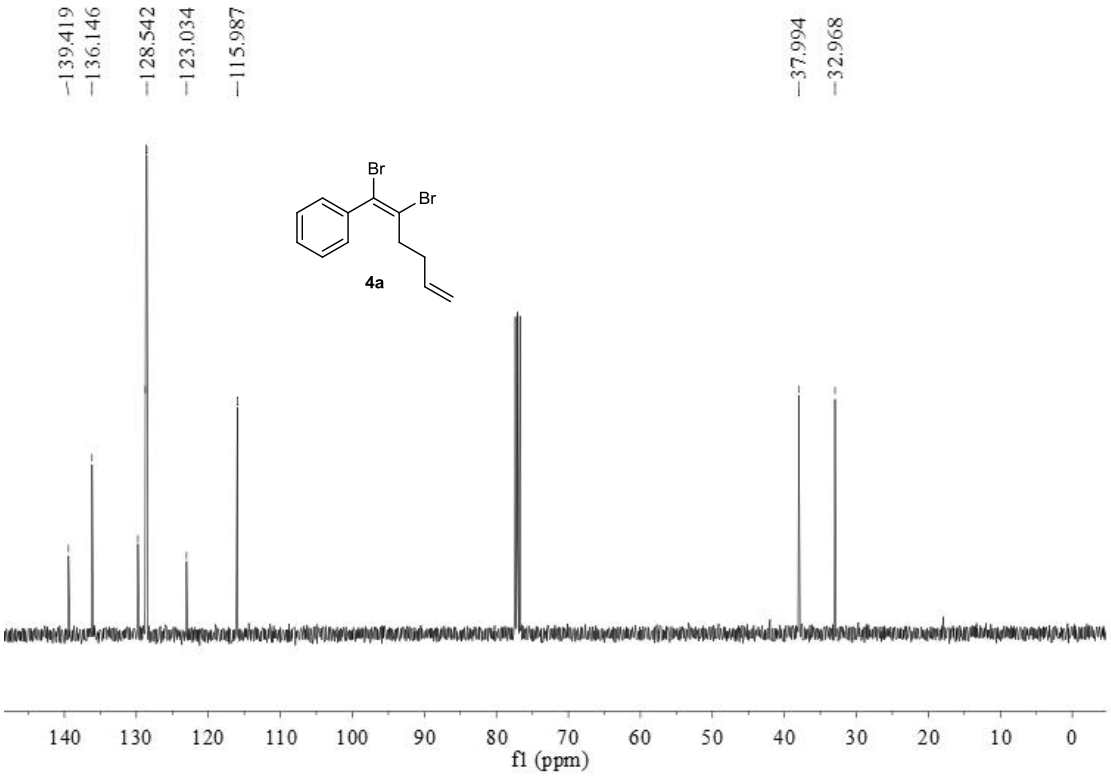
^{1}H NMR and ^{13}C NMR of (E)-(1-chloro-2-ethylhexa-1,5-dien-1-yl)benzene (3s)



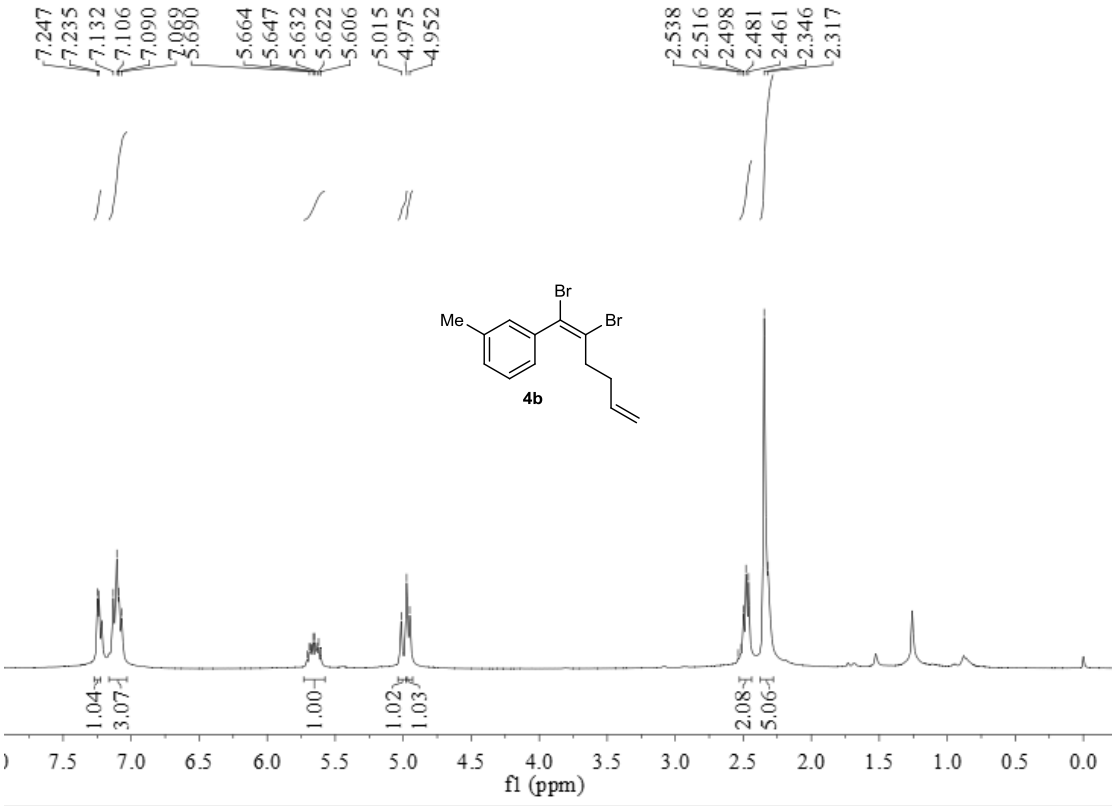


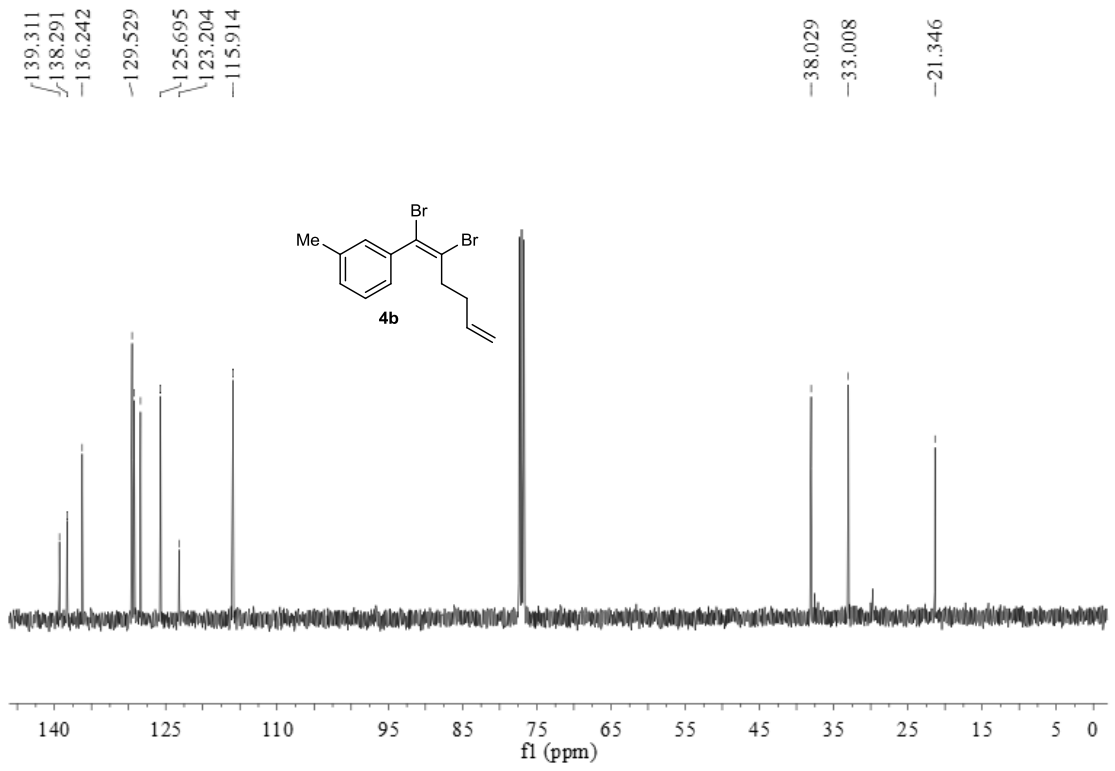
^{1}H NMR and ^{13}C NMR of (Z)-(1,2-dibromohexa-1,5-dien-1-yl)benzene (4a)



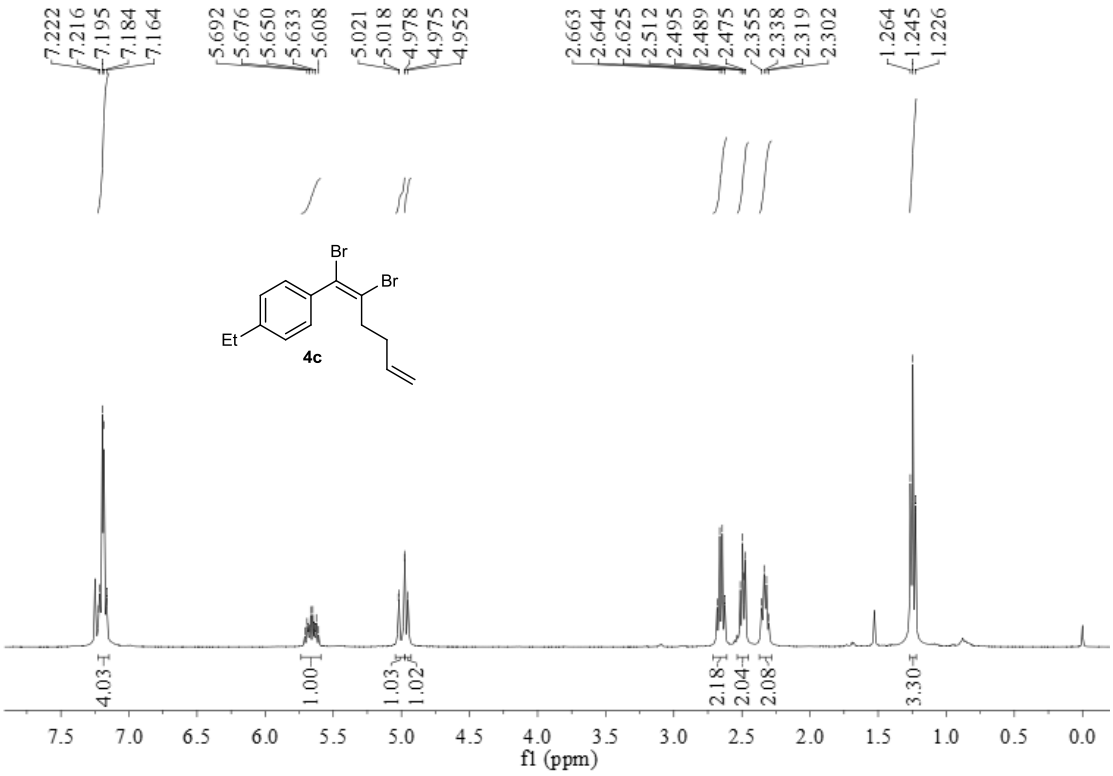


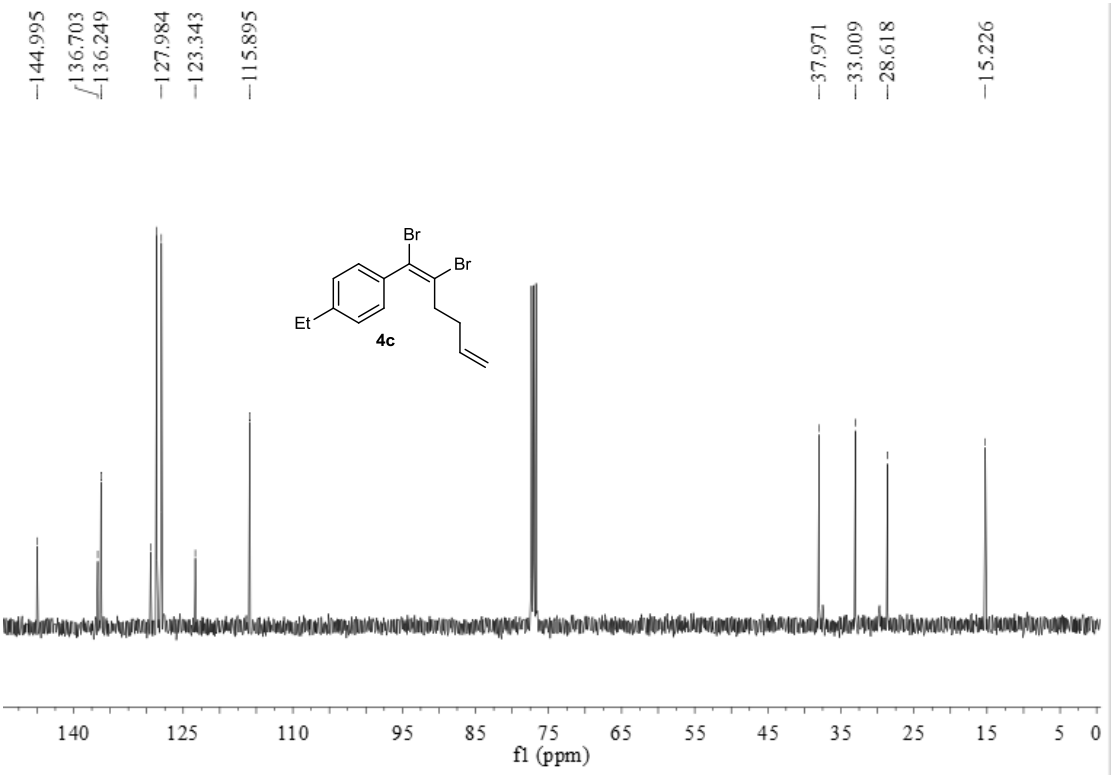
^{1}H NMR and ^{13}C NMR of (Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-3-methylbenzene (4b)



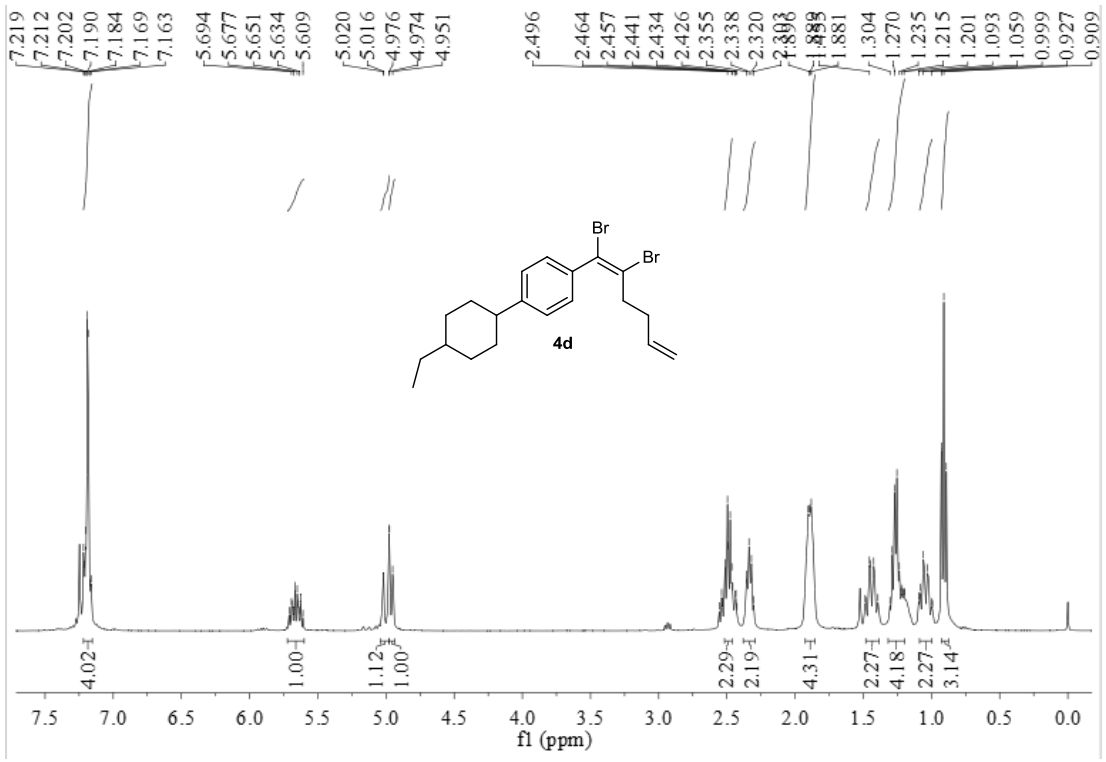


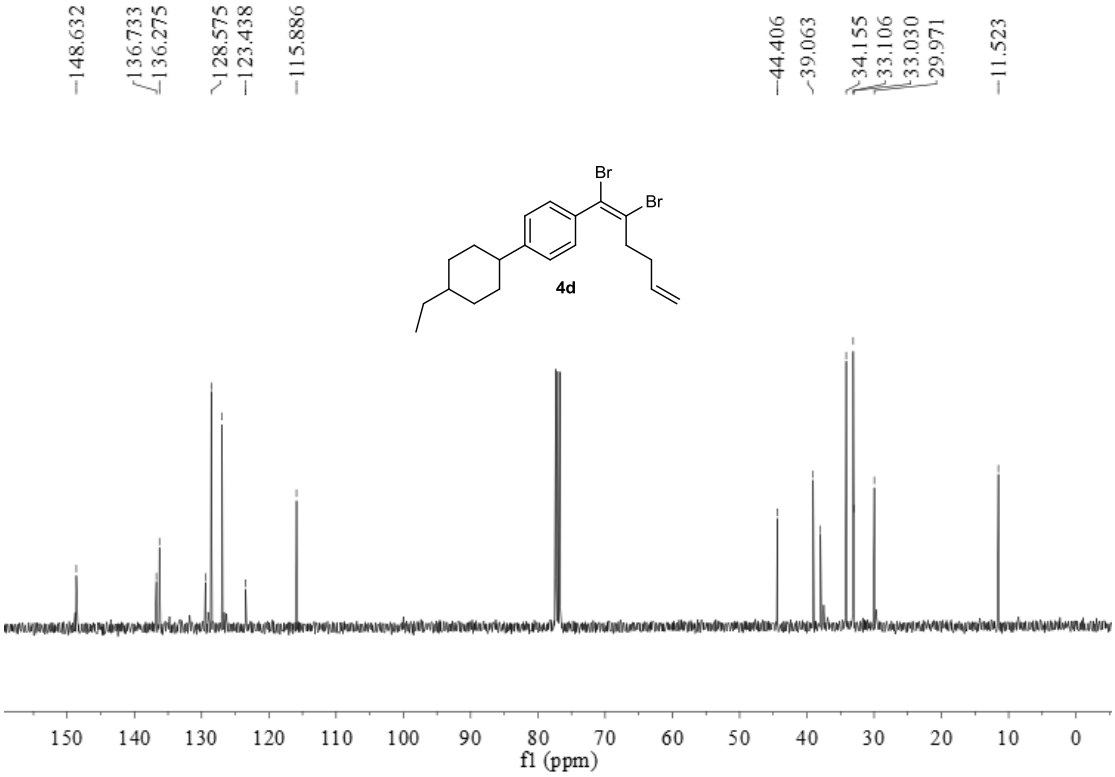
^{1}H NMR and ^{13}C NMR of (Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-4-ethylbenzene (4c)



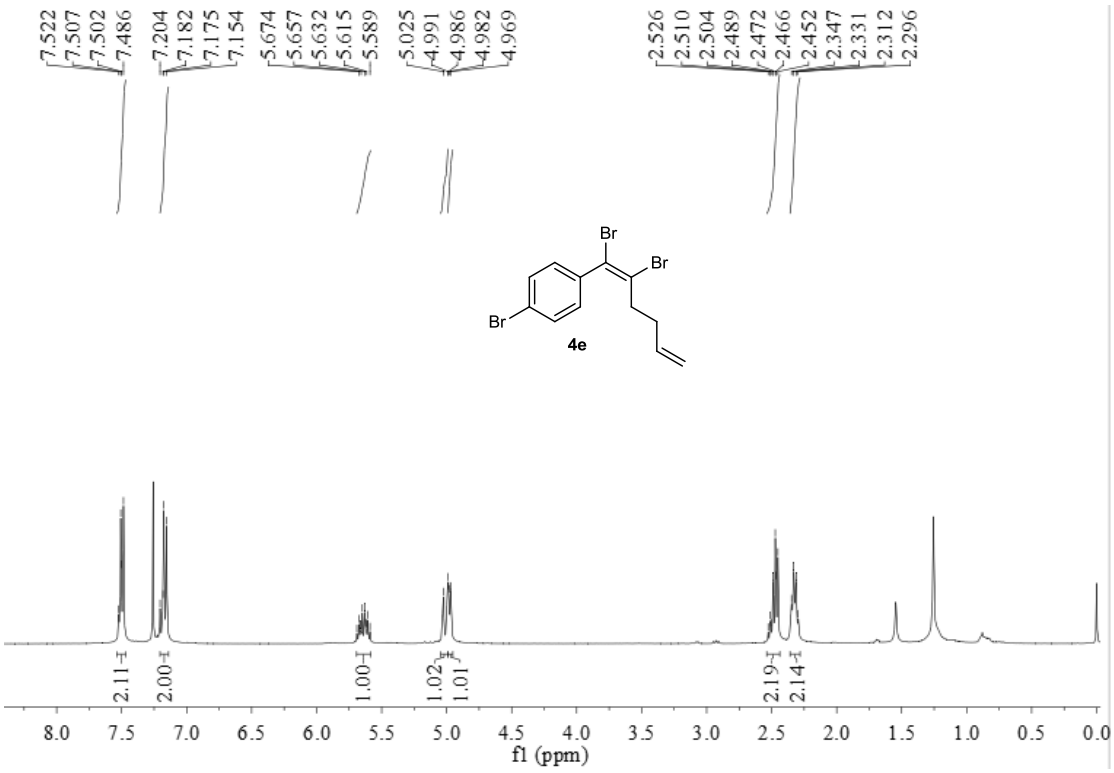


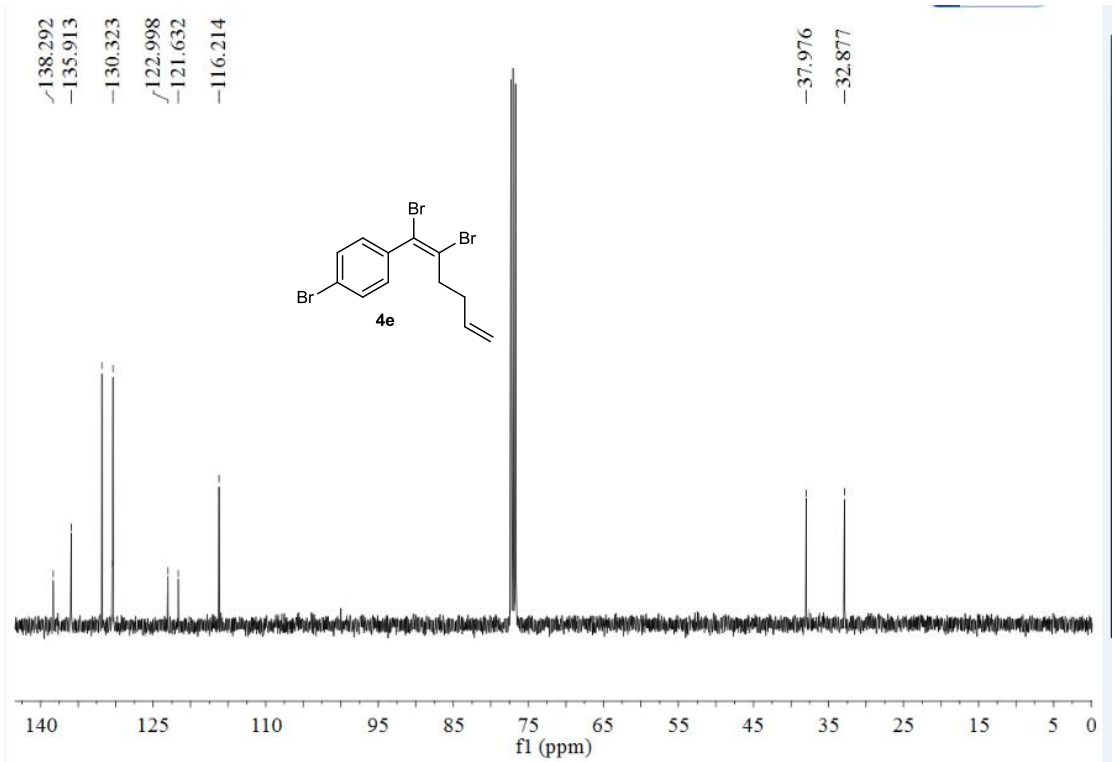
^{1}H NMR and ^{13}C NMR of (Z)-1-(1,2-dibromohexa-1,5-dien-1-yl)-4-(4-ethylcyclohexyl)-benzene (4d)



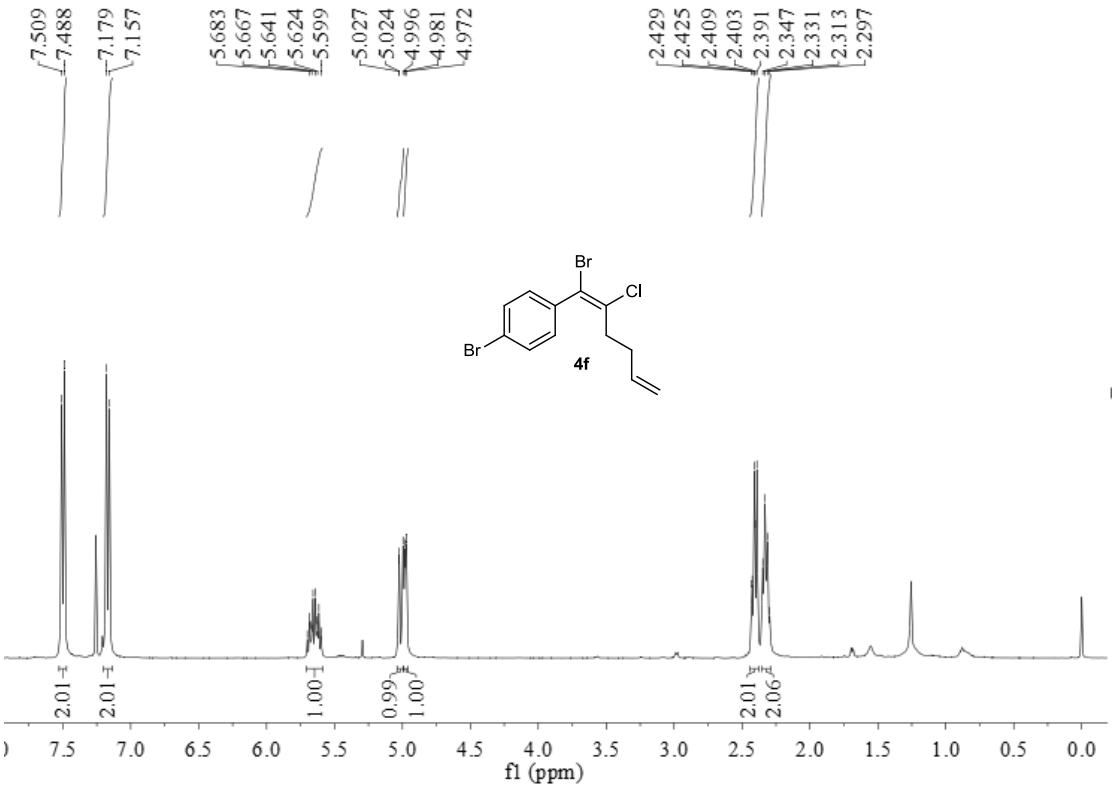


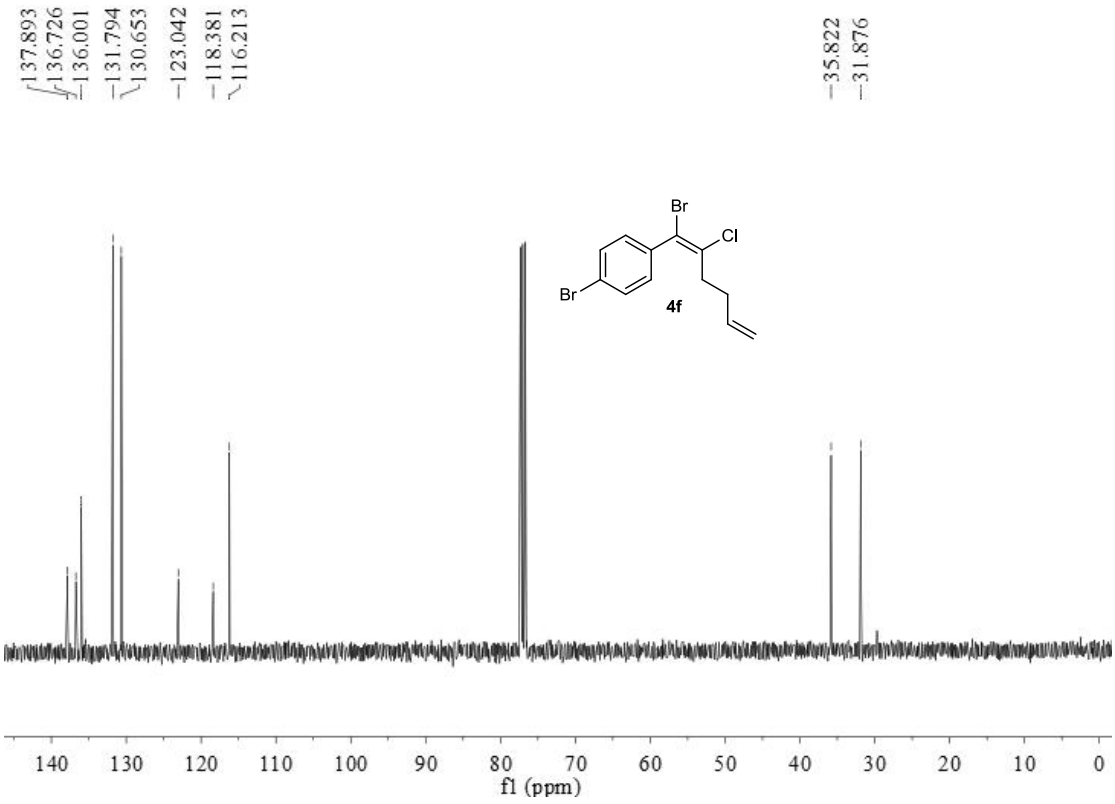
^{1}H NMR and ^{13}C NMR of (Z)-1-bromo-4-(1,2-dibromohexa-1,5-dien-1-yl)benzene (4e)



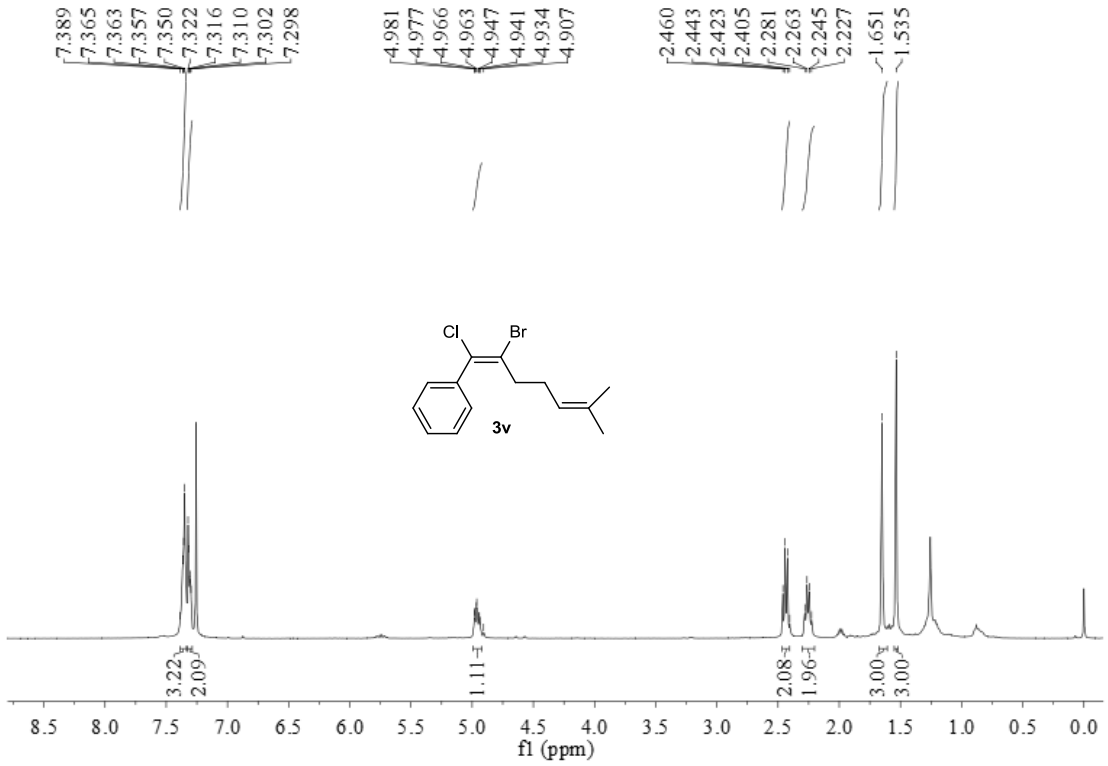


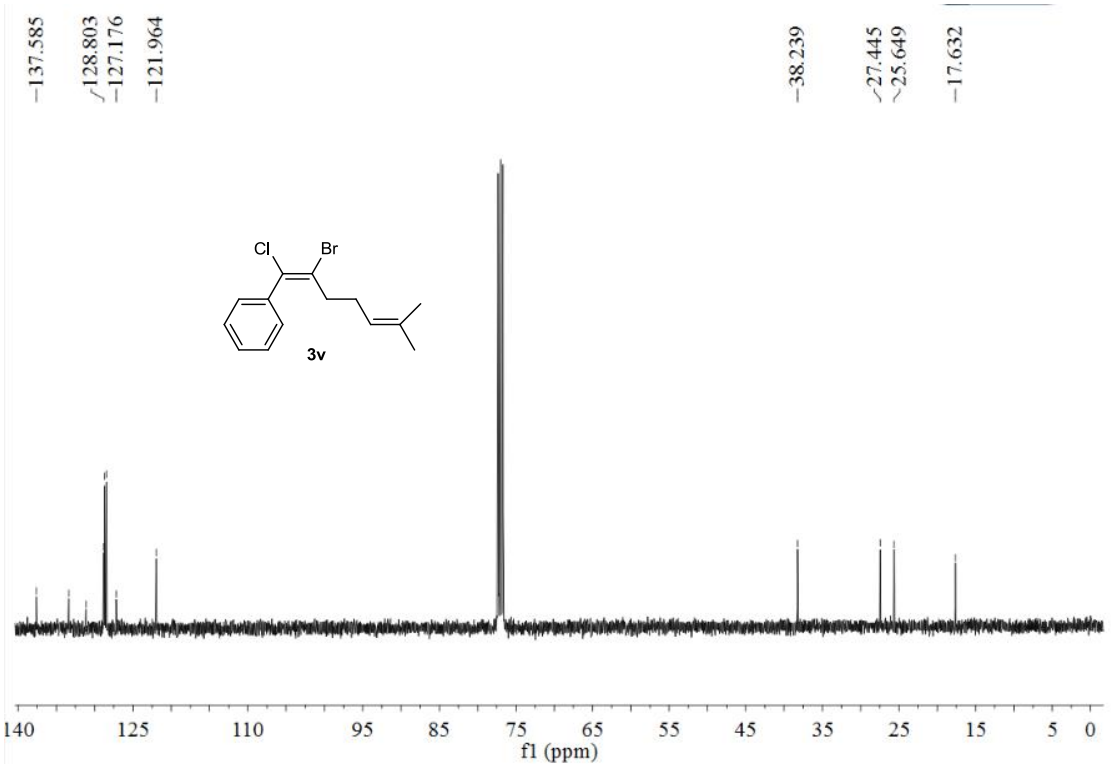
^{1}H NMR and ^{13}C NMR of (Z)-1-bromo-4-(1-bromo-2-chlorohexa-1,5-dien-1-yl)benzene (4f)





^{1}H NMR and ^{13}C NMR of (Z)-(2-bromo-1-chloro-6-methylhepta-1,5-dien-1-yl)benzene (3v)





VI Studies on stereochemistry of 3a