Conversion of propargyl alcohols to chloroallenes and aryl alkynes using the $TiCl_4/R_3N$ reagent system

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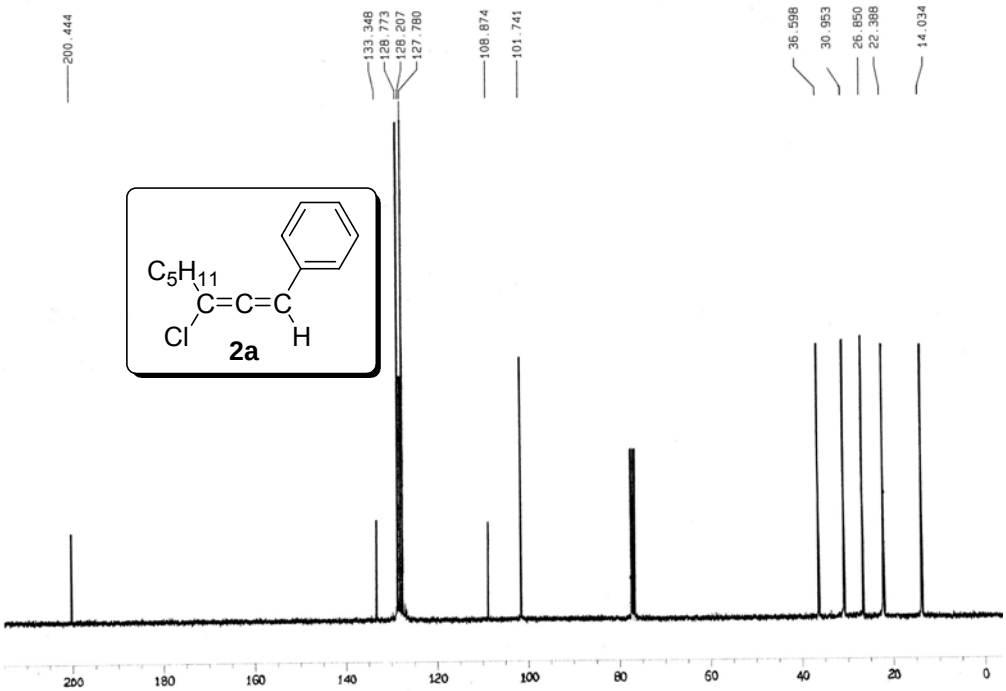
Spectral data for the products 2b, 2c, 5b-5e and 6:

Spectral data for products **2b – 2c**: For **2b**. IR (Neat): 2951, 1939, 1499 cm^{-1}; ^{13}C-NMR(100 MHz, $CDCl_3$, δ ppm): 13.9, 22.3, 28.4, 28.6, 31.2, 97.3, 108.9, 128.0,128.1, 128.4, 129.4, 132.5, 134.9, 138.6, 194.1, 211.1. (400 MHz, $CDCl_3$, δ ppm) ^1H-NMR : 8.1-7.25 (m, 10H), 2.21 (d, 2H, *J* = 5.6 Hz), 1.43-1.24 (m, 6H), 0.85 (t, 3H, *J* = 7.2 Hz); MS (EI) m/z 324 (M^+); Anal. Calcd for $C_{21}H_{21}ClO$: C, 77.64, H, 6.52, Found: C, 77.59, H, 6.56. **2c**. IR (Neat): 3059, 2974, 1963, 1491cm^{-1}; ^{13}C-NMR(100 MHz, $CDCl_3$, δ ppm) 100.6, 112.3, 127.5, 128, 128.1, 128.3, 128.7, 129, 129.4, 129.9, 132.1, 132.9, 133.1, 138.0, 192.8, 212.4; ^1H-NMR: (400 MHz, $CDCl_3$, δ ppm) 7.58-7.18 (m, 15H); MS (EI) m/z = 330 (M^+). Anal. Calcd for $C_{22}H_{15}ClO$: C, 79.88, H, 4.57, Found: C, 77.93, H, 4.6.

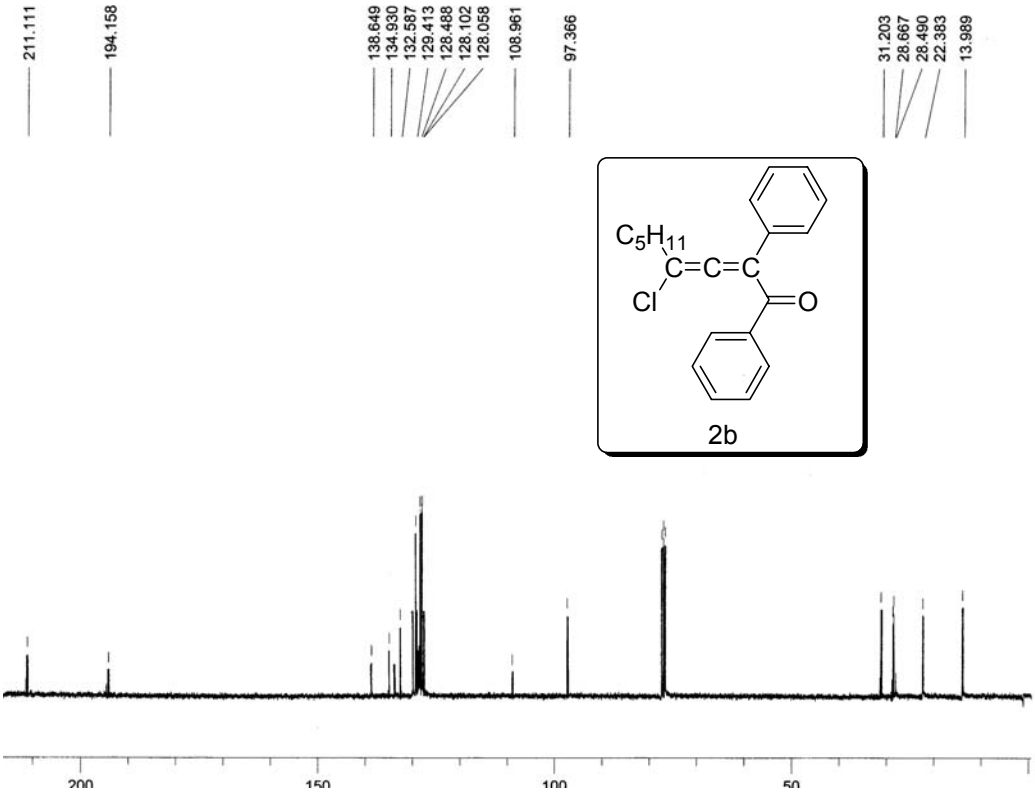
Spectral data for products **5b-5e** and **6**: For product **5b** (0.28 g, 71%) IR (Neat): 3450, 2930, 2057, 1583 cm^{-1}; ^{13}C-NMR: (100 MHz, $CDCl_3$, δ ppm) 14.0, 19.0, 22.2, 24.6, 26.6, 28.7, 31.1, 40.1, 54.7, 81, 85.3, 114.2, 123.8, 124.4, 124.7, 124.8, 125.2, 125.9, 126.5, 126.8, 128.0, 128.3, 129.6, 132.1, 142.1, 150.5; ^1H-NMR: (400 MHz, $CDCl_3$, δ ppm) 8.32 (d, 1H, *J* = 7.9 Hz), 8.10 (d, 1H, *J* = 8.1 Hz), 7.56-7.07 (m, 9H), 5.66 (s, 1H), 2.32 (t, 4H, *J* = 6.3 Hz), 1.88-1.59 (m, 6H), 1.57 (t, 2H, *J* = 7.1 Hz), 1.46-1.33 (m, 6H), 0.93 (t, 3H, *J* = 7.1 Hz); MS (EI) m/z 395 (M^+); Anal. Calcd for $C_{29}H_{33}N$: C, 88.05, H, 8.41, N, 3.54; Found: C, 88.11, H, 8.44, N, 3.54. For the product **5c** (0.28 g, 73%). IR (Neat): 3403, 3051, 2071, 1641 cm^{-1} ^{13}C-NMR: (100 MHz, $CDCl_3$, δ ppm) 12.6, 14.0, 19.0, 22.2, 28.7, 31.2, 39.3, 44.3, 81.5, 84.7, 112.4, 124.5, 125.4, 125.8, 126.2, 127.5, 128.6, 128.8, 129.3, 131.2, 134.1, 138.5, 146.5; ^1H-NMR: (400 MHz, $CDCl_3$, δ ppm) 8.23 (d, 1H, *J* = 4.3 Hz), 8.22-7.26 (m, 8H), 6.55 (d, 2H, *J* = 7.8 Hz), 5.67 (s, 1H),

3.36-3.31 (q, 4H, *J* = 6.9 Hz), 2.30 (t, 2H, *J* = 6.8 Hz), 1.61-1.33 (m, 6H), 1.18 (t, 6H, *J* = 7.8 Hz), 0.94 (t, 3H, *J* = 7.8 Hz). MS (EI) m/z = 383 (M^+); Anal. Calcd for Mf;$C_{28}H_{33}N$ C, 87.67, H, 8.67, N, 3.65; Found: C, 87.59, H, 8.65, N, 3.70. For the product **5d** (0.32 g, 77%). IR (Neat): 2970, 2032, 1608, 1516 cm^{-1}; ^{13}C-NMR(100 MHz, $CDCl_3$, δ ppm): 12.7, 44.3, 55.2, 84.5, 96.4, 111.0, 124.0, 126.5, 127.8, 127.9, 128.2, 129.2, 130.0, 131.6, 131.8, 146.2, 146.5; ^{1}H-NMR(400 MHz, $CDCl_3$, δ ppm): 7.58-7.18 (m, 17H), 6.67 (d, 2H, *J* = 7.1 Hz), 3.42-3.39 (q, 4H, *J* = 5.8 Hz), 1.22 (t, 6H, *J* = 5.8 Hz).; MS (EI) m/z 415 (M^+); Anal. Calcd for $C_{31}H_{29}N$: C, 89.60, H, 7.03, N, 3.07. Found: C, 89.54, H, 6.99, N, 3.04. For the product **5e** (0.29 g, 73%). IR (Neat): 2978, 2097, 1598, 1506 cm^{-1} ^{13}C-NMR(100 MHz, $CDCl_3$, δ ppm): 10.9, 38.0, 42.6, 82.7, 89.6, 110.1, 122.1, 122.6, 123.7, 123.8, 124.2, 124.6, 125.8, 126.01, 126.04, 126.4, 127.0, 127.1, 129.4, 129.9, 132.4, 136.0, 144.9; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.13 (d, 1H, *J* = 1.6 Hz), 7.30-7.14 (m, 13H), 6.52 (d, 2H, *J* = 8.8 Hz), 5.75 (s, 1H), 3.2 (q, 4H, *J* = 6.8 Hz), 1.01 (t, 6H, *J* = 6.8 Hz); MS (EI) m/z 389 (M^+). Anal. Calcd for $C_{29}H_{27}N$: C,89.42, H,6.99, N,3.60. Found: C, 89.47, H,6.99, N, 3.62. For the product **6** (0.34 g, 78%). IR (Neat): 3429, 2930, 1968, 1574 cm^{-1}; ^{13}C-NMR(100 MHz, $CDCl_3$, δ ppm): 45.3, 110.0, 112.1, 113.8, 124.4, 125.1, 125.8, 126.9, 127.0, 127.1, 127.4, 127.6, 128.1, 128.3, 128.5, 128.60, 128.64, 129.1, 129.3, 133.3, 136.5, 136.9, 151.0, 208.1; ^{1}H-NMR(400 MHz, $CDCl_3$, δ ppm): 8.19 (d, 2H, *J* = 8.8 Hz), 7.79 (d, 2H, *J* = 8.4 Hz), 7.40-7.01 (m, 17H), 2.84 (s, 6H); MS (EI) m/z 437 (M^+); Anal. Calcd for $C_{33}H_{27}N$: C, 90.58, H, 6.22, N, 3.20. Found: C, 90.63, H, 6.20, N, 3.24.

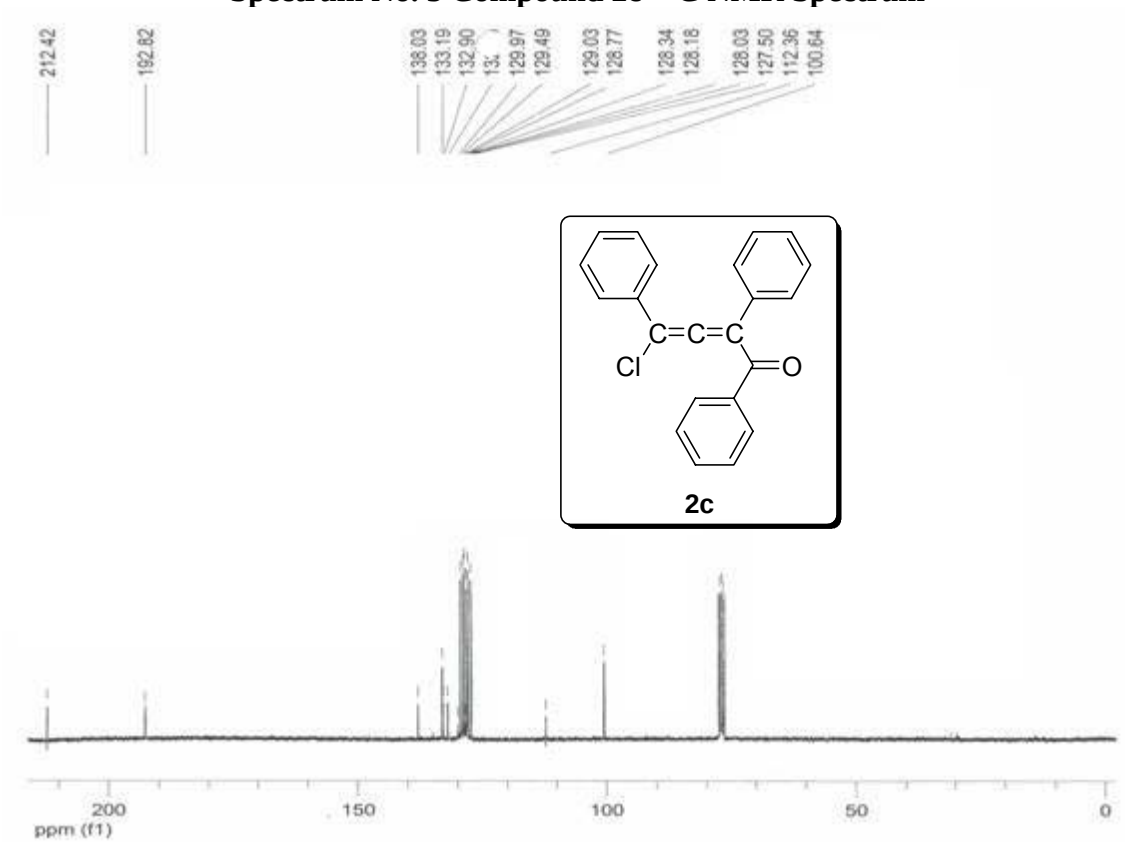
Spectrum No.1 Compound 2a ^{13}C NMR Spectrum



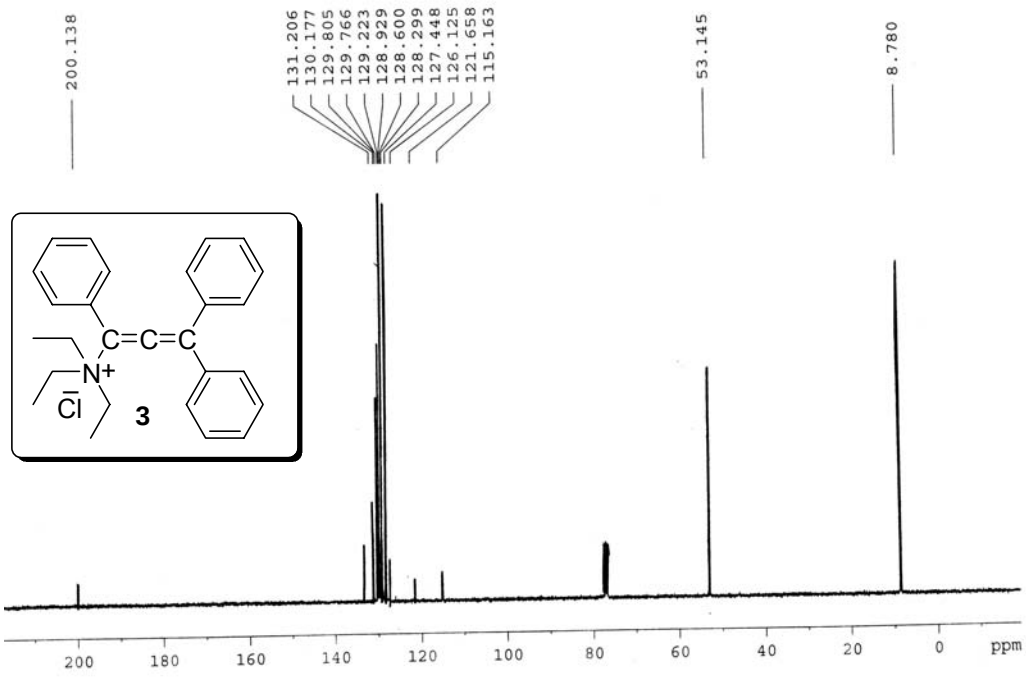
Spectrum No.2 Compound 2b ^{13}C NMR Spectrum



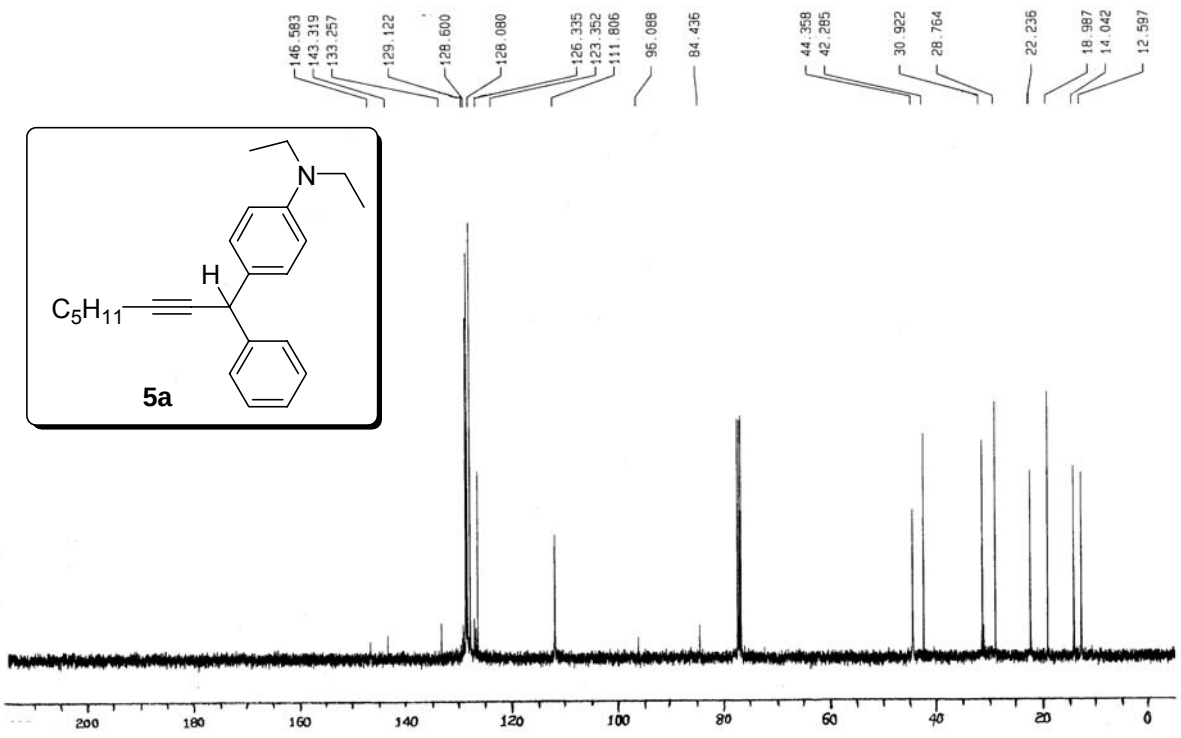
Spectrum No. 3 Compound 2c ^{13}C NMR Spectrum



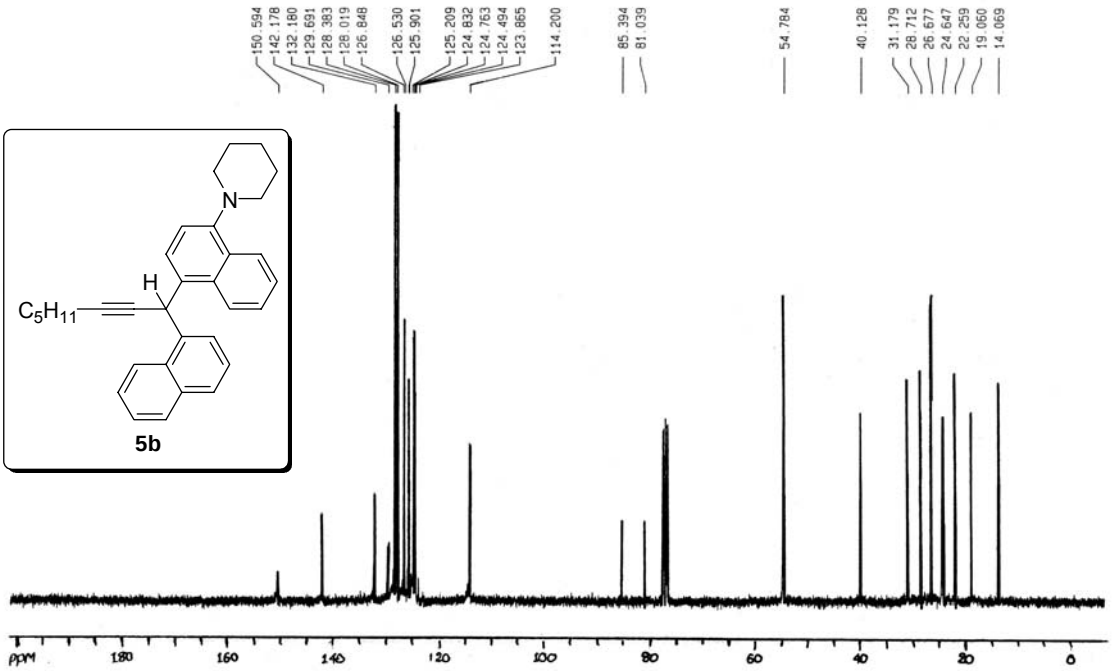
Spectrum No. 4 Compound 3 ^{13}C NMR Spectrum



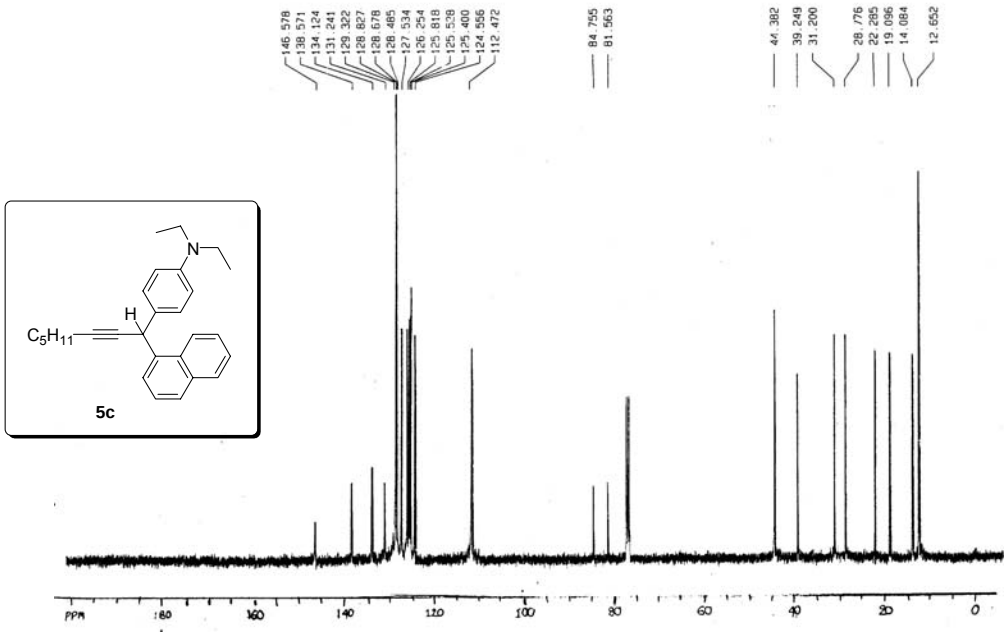
Spectrum No.5 Compound 5a ^{13}C NMR Spectrum



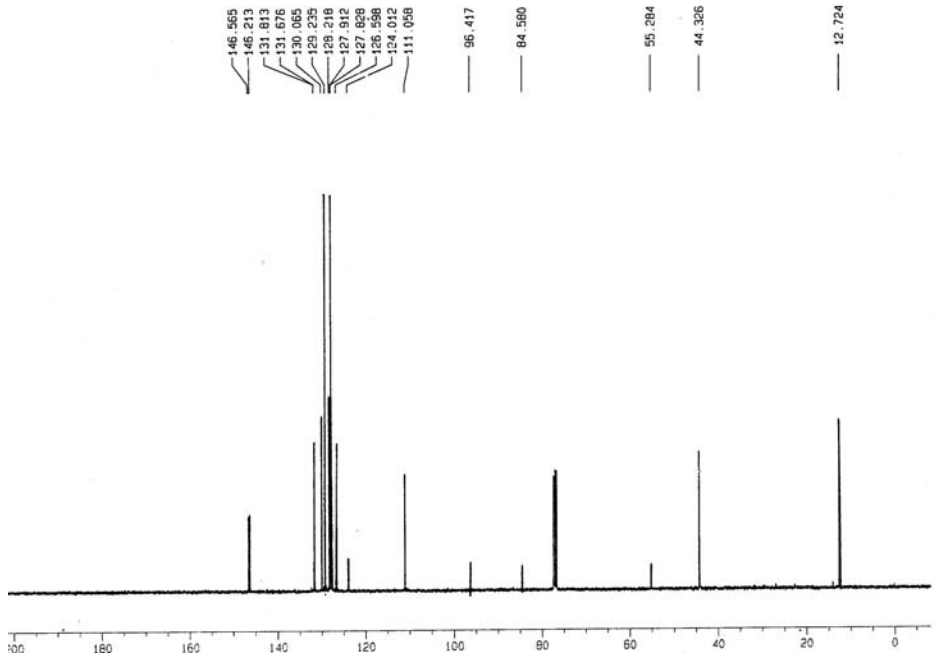
Spectrum No. 6 Compound 5b ^{13}C NMR Spectrum



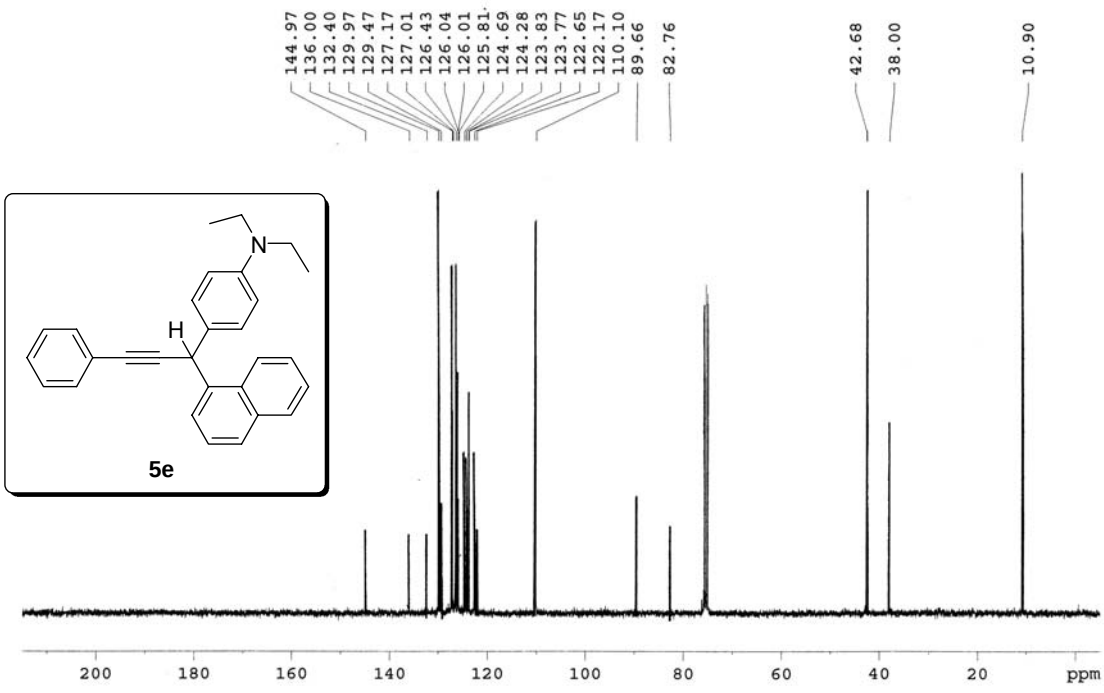
Spectrum No. 7 Compound 5c ^{13}C NMR Spectrum



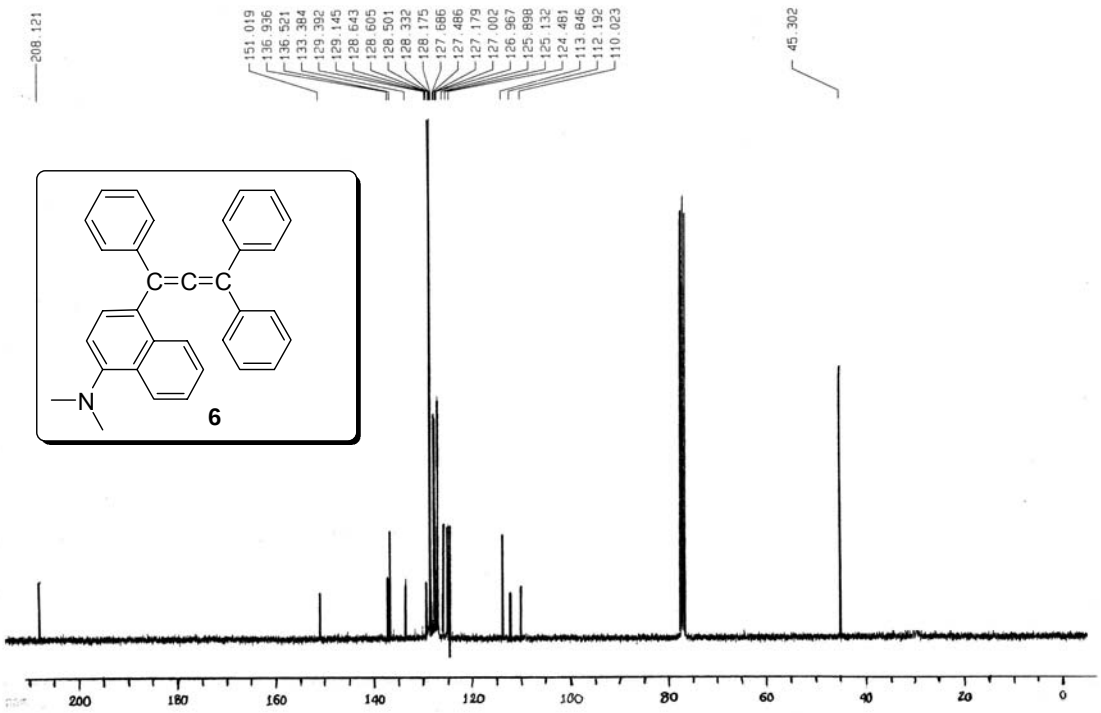
Spectrum No. 8 Compound 5d ^{13}C NMR Spectrum



Spectrum No. 9 Compound 5e ^{13}C NMR Spectrum



Spectrum No. 10 Compound 6 ^{13}C NMR Spectrum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151.019
136.936
136.521
133.384
129.392
129.145
128.643
128.605
128.501
128.332
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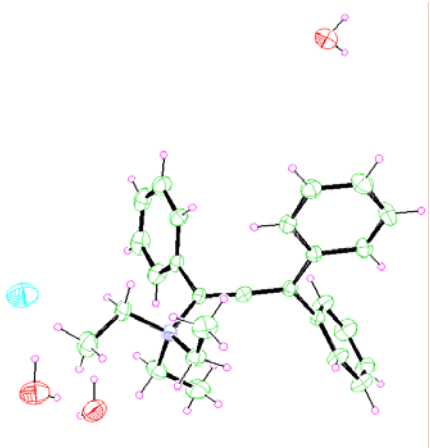
127.686
127.486
127.179
127.002
126.967
125.898
125.132
124.481
113.846
112.192
110.023
45.302
C=C=C
N
6
200
180
160
140
120
100
80
60
40
20
0

Figure S1. ORTEP diagram of the allenyl triethylamine salt **3**. (thermal ellipsoids are drawn at 20% probability).



Crystal Data for Allenyl triethylamine salt (3) $C_{27}H_{36}ClNO_3$, MW = 458.03, monoclinic, space group: $P2_1/n$, a = 9.1453(18) Å, b = 9.8672(5) Å, c = 17.0435(9) Å, β = 99.15(3)^o, V = 2606.5(2) Å ^{3}, Z = 42, ρ_c = 1.143 Mgm^{-3}, μ = 0.100 mm^{-1}, T = 298 K. Of the 24177 reflections collected, 4574 were unique [R_{int} = 0.0401]. Refinement on all data converged at R_1 = 0.0821, wR_2 = 0.2610.

Interestingly, we have found that allenyl triethylamine salt **3** have three water molecules. The three water molecules interacting with chloride anion via non-covelent interactions to form a discrete cyclic hexameric, chair form water clusters.

Figure S2. Cubical water clusters around allenyl triethylamine salt **3**.

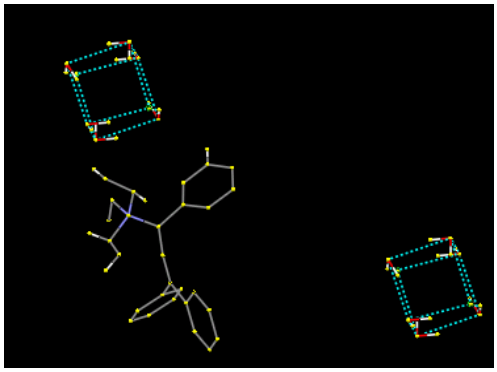


Figure S3. Water cluster formation by chloride ions in allenyl triethylamine salt **3**.

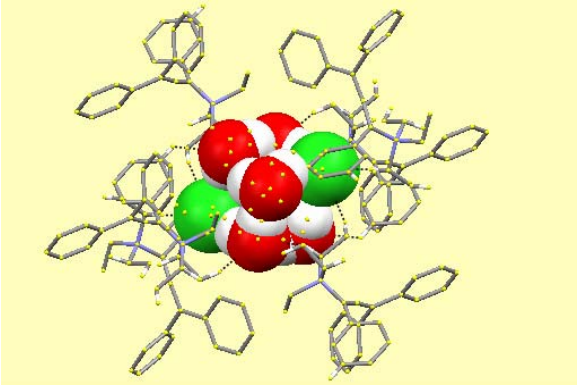
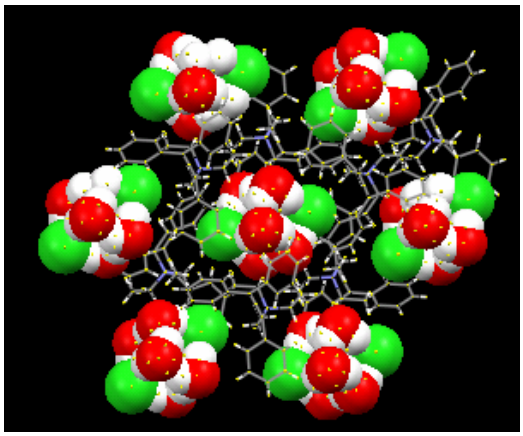



Figure S4. Water clusters formation around allenyl triethylamine salt **3**.