

Supporting Information for

CuSO₄-H-phosphonate catalyzed highly stereo- and regio-selective dimerization of terminal alkynes

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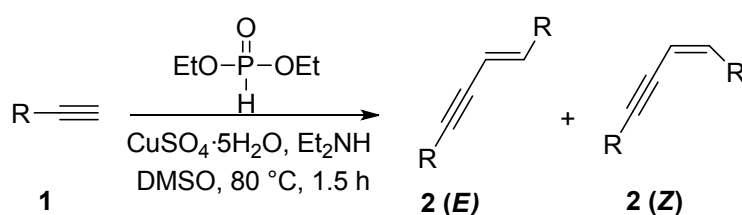
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1. General information

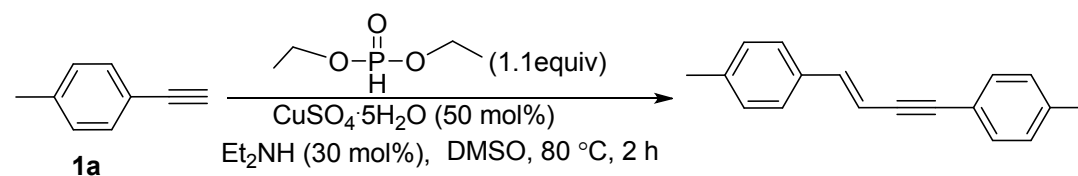
Solvents were freshly distilled from respective drying agents before use. TLC was performed on silica gel plates and preparative chromatograph on columns of silica gel (200-300 mesh). ^1H and ^{13}C spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 400.13, 100.61 MHz respectively, All NMR spectra were recorded in CDCl_3 at room temperature (20 ± 3 °C). ^1H and ^{13}C chemical shifts are quoted in parts per million downfield from TMS.

2. Experimental procedures for the synthesis of conjugated enynes (2a-2q)



terminal alkynes **1** (2.5 mmol), diethyl phosphonate 2.7 mmol (1.1 equiv), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1.25 mmol (0.5 equiv), HNEt_2 0.75 mmol (0.3 equiv) in DMSO (5.0 mL) at $80\text{ }^\circ\text{C}$ for 1.5 h, the solvent was evaporated under vacuum, and the residue was quenched with water (5.0 mL), extracted with dichloromethane ($3 \times 5.0\text{ mL}$). The combined organic layers were washed with brine (15.0 mL) and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated in vacuo. The crude product was purified with pure petroleum ether by silica gel chromatography to give the desired product.

3. The pH of the reaction was also monitored as the reaction progressed through time

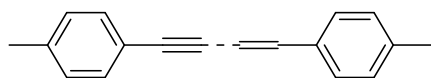


T (min)	0	5	10	30	45	60	75	90	105	130
pH	10.99	6.10	5.56	5.31	4.86	4.53	4.53	4.45	4.49	4.47

Reaction condition: **1a** (2.5 mmol), DEPPEH (1.1 equiv), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1.25 mmol (0.5 equiv), HNEt_2 0.75 mmol (0.3 equiv) in DMSO (5.0 mL) at $^\circ\text{C}$ for 2 h.

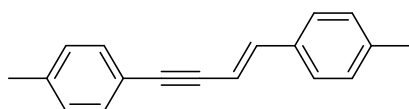
4. Characterization data for products (2a-2t)

The Characterization data of 2a:



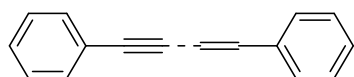
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.963-7.942 (d, 0.72H), 7.510-7.470 (t, 3H), 7.412-7.392 (d, 2H), 7.303-7.283 (d, 0.39H), 7.258-7.214 (m, 5H), 7.121-7.081 (d, 1H, $J=16.0$ Hz), 6.759-6.729 (d, 0.37H, $J=9.0$ Hz), 6.451-6.411 (d, 1H, $J=16.0$ Hz), 5.978-5.949 (d, 0.36H, $J=9.0$ Hz), 2.469-2.442 (t, 8.26H). ^{13}C NMR (100MHz, CDCl_3) δ : 140.97, 138.67, 138.55, 138.36, 138.30, 134.09, 133.80, 132.50, 131.49, 131.42, 129.55, 129.33, 129.30, 129.23, 129.10, 128.83, 120.60, 107.31, 106.59, 96.08, 91.79, 88.65, 88.09, 21.59, 21.41.

The Characterization data of 2a (E): The data was obtained by recrystallization from a mixture of E/Z



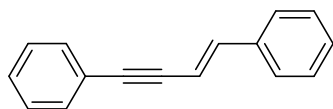
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.445-7.364 (m, 4H), 7.197 (s, 4H), 7.084-7.043 (d, 1H, $J=16.0$ Hz), 6.415-6.374 (d, 1H, $J=16.0$ Hz), 2.412 (s, 6H). ^{13}C NMR (100MHz, CDCl_3) δ : 140.92, 138.65, 138.27, 133.76, 131.44, 129.50, 129.18, 126.26, 120.51, 107.25, 91.70, 88.56, 21.56, 21.37.

The Characterization data of 2b:



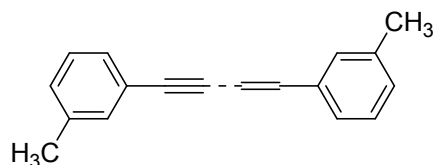
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 8.026-8.007 (d, 0.83H), 7.591-7.504 (m, 2.89H), 7.486-7.430 (m, 2.64H), 7.426-7.399 (m, 4.30H), 7.393-7.358 (m, 3.75H), 7.148-7.107 (d, 1H, $J=16.0$ Hz), 6.792-6.762 (d, 0.42H, $J=9.0$ Hz), 6.490-6.449 (d, 1H, $J=16.0$ Hz), 6.020-5.991 (d, 1H, $J=9.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 141.35, 138.76, 136.63, 136.39, 131.61, 131.54, 128.86, 128.83, 128.71, 128.61, 128.51, 128.46, 128.44, 128.39, 128.28, 126.40, 123.54, 123.50, 108.21, 107.48, 95.97, 91.88, 89.03.

The Characterization data of 2b (E): The data was obtained by recrystallization from a mixture of E/Z



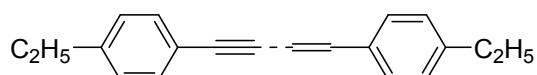
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.522 (s, 1H), 7.5176 (s, 1H), 7.503-7.500 (d, 2H), 7.470-7.452 (d, 2H), 7.398-7.380 (d, 2H), 7.367-7.350 (m, 3H), 7.341-7.323 (d, 1H), 7.101-7.061 (d, 1H, $J=16.0$ Hz), 6.444-6.403 (d, 1H, $J=16.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 141.29, 136.35, 131.54, 128.76, 128.65, 128.36, 128.21, 126.33, 123.43, 108.15, 91.76, 88.90.

The Characterization data of 2c:



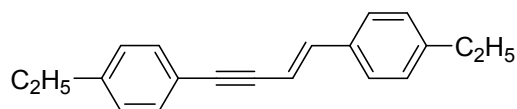
Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ : 7.810 (s, 0.26H), 7.709-7.689 (d, 0.26H), 7.298-7.293 (d, 1.58H), 7.271 (s, 1.02H), 7.269-7.246 (t, 1.78H), 7.224-7.186 (m, 2.69H), 7.143-7.081 (m, 2.58H), 7.012-6.972 (d, 1H, $J=16.0$ Hz), 6.668-6.638 (d, 0.27H, $J=9.0$ Hz), 6.377-6.336 (d, 1H, $J=16.0$ Hz), 5.899-5.869 (d, 0.27H, $J=9.0$ Hz), 2.381 (s, 0.85H), 2.346 (s, 2.77H), 2.339 (s, 0.8H), 2.328 (s, 3H). ^{13}C NMR (100MHz, CDCl_3) δ : 141.32, 138.71, 137.35, 138.13, 137.04, 137.77, 136.59, 136.36, 132.13, 132.06, 129.47, 129.45, 129.12, 128.67, 128.64, 128.54, 128.37, 128.28, 128.25, 127.04, 123.51, 123.30, 108.02, 107.28, 96.10, 91.87, 88.73, 88.22, 22.72, 21.56, 21.43, 21.28.

The Characterization data of 2d:



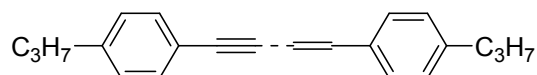
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.938-7.917 (d, 1.40H), 7.487-7.386 (m, 5.5H), 7.263-7.201 (m, 6.24H), 7.085-7.044 (d, 1.02H, $J=16.0$ Hz), 6.722-6.692 (d, 0.71H, $J=9.0$ Hz), 6.416-6.375 (d, 1.00H, $J=16.0$ Hz), 5.932-5.902 (d, 0.70H, $J=9.0$ Hz), 2.751-2.673 (m, 6.92H), 1.326-1.272 (m, 10.63H). ^{13}C NMR (100MHz, CDCl_3) δ : 145.01, 144.86, 144.80, 144.56, 140.92, 138.27, 134.26, 134.00, 131.51, 131.46, 128.85, 128.30, 128.03, 127.96, 127.84, 126.34, 120.82, 120.72, 107.31, 106.56, 96.02, 91.71, 88.53, 87.97, 28.90, 28.87, 28.83, 28.74, 15.51, 15.42, 15.38.

The Characterization data of 2d (*E*): The data was obtained by recrystallization from a mixture of *E/Z*



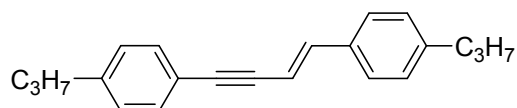
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.430-365 (m, 4H), 7.215-7.058 (m, 4H), 7.058-7.017 (d, 1H, $J=16$ Hz), 6.389-6.348 (d, 1H, $J=16.0$ Hz), 2.709-2.653 (m, 4H), 1.287-1.249 (t, 6H). ^{13}C NMR (100MHz, CDCl_3) δ : 144.99, 144.54, 140.88, 133.98, 131.48, 128.27, 127.92, 126.30, 120.68, 107.28, 91.65, 88.48, 28.84, 28.70, 15.46, 15.34.

The Characterization data of 2e:



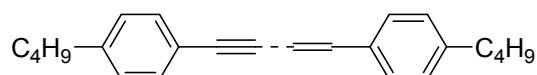
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 8.074-8.054 (d, 0.58H), 7.614-7.569 (t, 2.66H), 7.488-7.468 (d, 2.1H), 7.377-7.278 (m, 5.5H), 7.202-7.162 (d, 1H, $J=16.0$ Hz), 6.821-6.791 (d, 0.29H, $J=9.0$ Hz), 6.536-6.496 (d, 1H, $J=16.0$ Hz), 6.051-6.021 (d, 0.28H, $J=9.0$ Hz), 2.787-2.714 (m, 5.16H), 1.825-1.769 (m, 5.21H), 1.127-1.090 (t, 7.68H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.51, 143.40, 143.35, 143.08, 141.05, 138.43, 134.45, 131.60, 131.52, 129.02, 128.94, 128.78, 128.70, 128.59, 126.40, 121.03, 120.98, 107.47, 106.66, 96.32, 91.98, 88.85, 88.28, 38.14, 38.03, 24.64, 24.54, 14.04, 13.99.

The Characterization data of 2e (E): The data was obtained by recrystallization from a mixture of E/Z



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.478-7.356 (m, 4H), 7.191-7.155 (m, 4H), 7.053-7.013 (d, 1H, $J=16.0$ Hz), 6.388-6.347 (d, 1H, $J=16.0$ Hz), 2.634-2.596 (t, 4H), 1.717-1.625 (m, 4H), 0.995-0.950 (m, 6H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.45, 143.02, 140.89, 133.98, 131.38, 128.86, 128.52, 126.21, 120.70, 107.27, 91.66, 88.52, 37.98, 37.85, 24.44, 24.34, 13.82, 13.77.

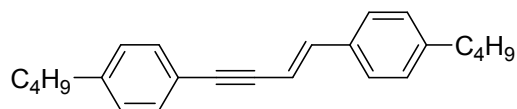
The Characterization data of 2f:



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.943-7.923 (d, 0.7H), 7.489-7.441 (m, 2.79H), 7.403-7.383 (d, 2.16H), 7.273-7.188 (m, 5.6H), 7.088-7.048 (d, 1H, $J=16.0$ Hz), 6.724-6.694 (d, 0.33H, $J=9.0$ Hz), 6.423-6.383 (d, 1H, $J=16.0$ Hz), 5.938-5.908 (d, 0.33H, $J=9.0$ Hz), 2.708-2.647 (m,

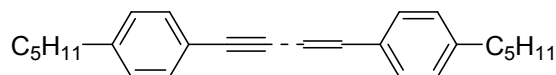
5.65H), 1.169-1.617 (m, 5.55H), 1.459-1.391 (m, 5.67H), 1.017-0.976 (m, 8H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.70, 143.57, 143.51, 143.27, 140.93, 138.28, 134.24, 133.97, 131.45, 131.39, 128.86, 128.79, 128.60, 128.52, 128.42, 126.27, 120.80, 107.29, 106.52, 96.11, 91.74, 88.59, 88.03, 35.67, 35.53, 33.58, 33.47, 22.43, 22.40, 14.03.

The Characterization data of 2f (E): The data was obtained by recrystallization from a mixture of *E/Z*



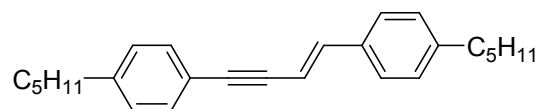
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.441-7.369 (m, 4H), 7.206-7.173 (m, 4H), 7.071-7.030 (d, 1H, $J=16.0$ Hz), 6.405-6.365 (d, 1H, $J=16.0$ Hz), 2.672-2.633 (t, 4H), 1.679-1.603 (m, 4H), 1.432-1.372 (m, 4H), 0.996-0.959 (t, 6H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.69, 143.26, 140.91, 133.95, 131.42, 128.84, 128.50, 126.25, 120.67, 107.27, 91.71, 88.55, 35.64, 35.51, 33.55, 33.44, 22.40, 22.37, 14.00.

The Characterization data of 2g:



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.898-7.877 (d, 0.86H), 7.444-7.396 (m, 2.88H), 7.370-7.349 (d, 2.11H), 7.233-7.151 (m, 5.71H), 7.047-7.006 (d, 1H, $J=16.0$ Hz), 6.689-6.659 (d, 0.42H, $J=9.0$ Hz), 6.382-6.342 (d, 1H, $J=16.0$ Hz), 5.897-5.867 (d, 0.42H, $J=9.0$ Hz), 2.640-2.602 (t, 5.54), 1.671-1.597 (m, 5.86H), 1.356-1.315 (m, 11.51H), 0.934-0.901 (m, 8.60H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.73, 143.59, 143.52, 143.30, 140.89, 138.23, 134.18, 133.92, 131.39, 131.34, 128.81, 128.73, 128.55, 128.48, 128.37, 126.22, 120.73, 120.62, 107.22, 106.47, 96.04, 91.67, 88.52, 87.96, 35.91, 35.89, 35.85, 35.76, 31.50, 31.46, 31.07, 30.98, 30.96, 22.55, 14.05.

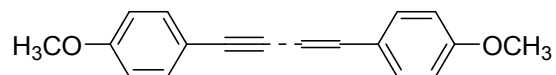
The Characterization data of 2g (E): The data was obtained by recrystallization from a mixture of *E/Z*



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.417-7.352 (m, 4H), 7.189-7.153 (m, 4H), 7.048-7.008 (d, 1H, $J=16.0$ Hz), 6.383-6.343 (d, 1H, $J=16.0$ Hz), 2.644-2.606 (t, 4H), 1.675-1.601 (m, 4H), 1.391-1.319 (m, 8H), 0.937-0.903 (t, 6H). ^{13}C NMR (100MHz, CDCl_3) δ : 143.70, 143.27,

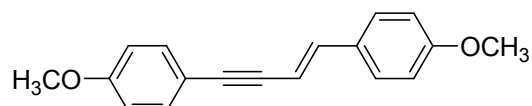
140.88, 133.94, 131.40, 128.80, 128.46, 126.22, 120.67, 107.26, 91.68, 88.53, 35.89, 35.76, 31.51, 31.47, 31.06, 30.94, 22.56, 22.55, 14.04.

The Characterization data of 2h:



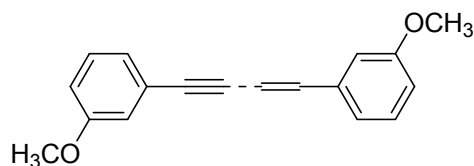
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.955-7.934 (d, 1.97H), 7.486-7.436 (m, 4.2H), 7.400-7.378 (d, 1.8H), 7.016-6.963 (m, 2.25H), 6.940-6.931 (d, 2.02H), 6.913-6.874 (m, 4.35H), 6.651-6.622 (d, 0.92H, *J*=9.0 Hz), 6.295-6.254 (d, 0.91H, *J*=16.0 Hz), 5.846-5.816 (d, 1H, *J*=9.0), 3.865-3.841 (t, 11.70H). ¹³C NMR (100MHz, CDCl₃) δ: 159.98, 159.66, 159.64, 159.47, 140.10, 137.40, 132.91, 132.88, 129.78, 129.36, 127.59, 125.03, 115.79, 115.76, 114.19, 114.13, 114.03, 113.68, 105.98, 105.17, 95.52, 91.10, 88.01, 87.48, 55.34, 55.32.

The Characterization data of 2h (*E*): The data was obtained by recrystallization from a mixture of *E/Z*



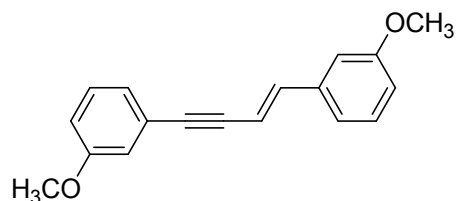
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.447-7.425 (d, 2H), 7.396-7.375 (d, 2H), 7.008-6.968 (d, 1H, *J*=16.0 Hz), 6.911-6.897 (d, 2H), 6.890-6.875 (d, 2H), 6.286-6.246 (d, 1H, *J*=16.0 Hz), 3.843 (s, 6H). ¹³C NMR (100MHz, CDCl₃) δ: 159.96, 159.45, 140.09, 132.90, 129.36, 127.58, 115.74, 114.17, 114.01, 105.97, 91.07, 87.97, 55.35, 55.31.

The Characterization data of 2i:



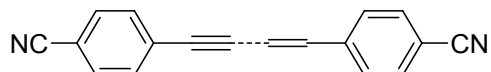
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.752 (s, 0.32H), 7.747-7.742 (d, 0.33H), 7.367-7.347 (d, 2.24H), 7.328-7.290 (m, 0.33H), 7.271-7.134 (m, 1.35H), 7.097-7.057 (m, 3.40H), 7.009-7.004 (d, 1H), 6.947-6.888 (m, 2.74H), 6.751-6.722 (d, 0.32H, *J*=9.0 Hz), 6.455-6.414 (d, 1H, *J*=16.0 Hz), 5.993-5.963 (d, 0.32H, *J*=9.0 Hz), 3.861-3.849 (t, 7.88H). ¹³C NMR (100MHz, CDCl₃) δ: 159.91, 159.56, 159.45, 159.40, 141.36, 138.78, 137.85, 137.75, 129.79, 129.56, 129.48, 129.31, 124.44, 124.42, 124.16, 124.01, 121.86, 119.06, 116.32, 115.12, 114.93, 114.84, 114.34, 113.31, 111.63, 108.46, 107.56, 96.24, 91.94, 88.75, 88.15, 55.25, 55.26.

The Characterization data of 2i (E): The data was obtained by recrystallization from a mixture of *E/Z*



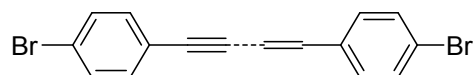
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.293 (s, 1H), 7.273-7.267 (d, 1H), 7.247-7.111 (d, 1H, *J*=16.0 Hz), 7.092-7.027 (s, 3H), 6.979-6.975 (d, 1H), 6.920-6.867 (m, 2H), 6.422-6.381 (s, 1H), 3.857-3.843 (d, 6H). ¹³C NMR (100MHz, CDCl₃) δ: 159.85, 159.33, 141.31, 137.72, 129.75, 129.43, 124.36, 124.13, 119.04, 116.22, 114.93, 114.29, 111.57, 108.41, 91.84, 88.64, 55.29, 55.28.

The Characterization data of 2j:



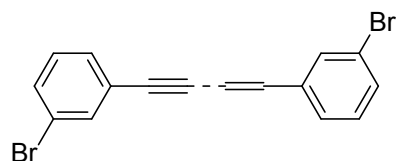
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.971-7.950 (d, 3H), 7.707-7.634 (m, 7H), 7.570-7.521 (m, 4H), 7.114-7.073 (d, 1H, *J*=16.0 Hz), 6.831-6.802 (d, 1.62H, *J*=9.0 Hz), 6.525-6.485 (d, 1H, *J*=16.0 Hz), 6.133-6.103 (d, 1.65H, *J*=9.0 Hz). ¹³C NMR (100MHz, CDCl₃) δ: 140.72, 140.30, 140.09, 138.22, 133.06, 132.63, 132.24, 132.19, 132.12, 132.10, 132.03, 127.77, 127.55, 126.90, 118.67, 118.61, 118.41, 118.32, 112.14, 111.93, 111.83, 111.19, 110.37, 95.52, 92.25, 92.05, 91.23.

The Characterization data of 2k:



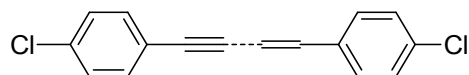
White solid; ¹H NMR (400 MHz, CDCl₃) δ: 7.795-7.774 (d, 1H), 7.546-7.480 (m, 6H), 7.358-7.292 (m, 5H), 7.015-6.974 (d, 1H, *J*=16.0 Hz), 6.696-6.666 (d, 0.54H, *J*=9.0 Hz), 6.386-6.346 (d, 1H, *J*=16.0 Hz), 5.964-5.934 (d, 0.64H, *J*=9.0 Hz). ¹³C NMR (100MHz, CDCl₃) δ: 140.36, 137.78, 135.31, 135.11, 133.84, 132.93, 132.83, 131.96, 131.83, 131.79, 131.67, 131.50, 130.19, 127.78, 122.90, 122.73, 122.59, 122.51, 122.22, 122.12, 108.60, 107.94, 95.40, 91.26, 89.70, 88.93.

The Characterization data of 2l:



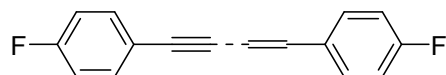
Light yellow solid; ^1H NMR (400 MHz, CDCl_3) δ : 8.332 (s, 0.14H), 7.771-7.651 (t, 1.66H), 7.583 (s, 1.55H), 7.489-7.410 (m, 3.83H), 7.362-7.343 (d, 1.04H), 7.253-7.202 (m, 2.39H), 6.998-6.958 (d, 1H, $J=16$ Hz), 6.698-6.668 (d, 0.14H, $J=9$ Hz), 6.396-6.356 (d, 1H, $J=16$ Hz), 5.984-5.954 (d, 0.14H, $J=9$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 140.29, 138.31, 138.21, 137.72, 135.15, 134.27, 132.62, 131.77, 131.63, 131.52, 131.12, 130.72, 130.29, 130.13, 129.93, 129.83, 129.66, 129.18, 127.67, 125.20, 125.02, 123.57, 123.00, 122.29, 122.24, 109.31, 108.57, 95.00, 91.00, 89.69, 88.98.

The Characterization data of 2m:



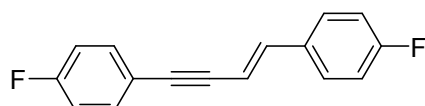
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.865-7.843 (d, 0.53H), 7.464-7.427 (d, 0.25H), 7.410-7.382 (m, 3H), 7.366-7.321 (m, 6H), 7.028-6.988 (d, 1H, $J=16.0$ Hz), 6.708-6.678 (d, 0.28H, $J=9.0$ Hz), 6.376-6.336 (d, 1H, $J=16.0$ Hz), 5.960-5.930 (d, 0.64H, $J=9.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 140.26, 137.69, 134.91, 134.69, 134.49, 134.35, 134.21, 133.71, 132.73, 132.64, 129.95, 129.00, 128.91, 128.86, 128.75, 128.54, 127.51, 121.77, 121.68, 108.49, 107.77, 95.24, 91.13, 89.54, 88.78.

The Characterization data of 2n:



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.939-7.904 (m, 0.62H), 7.500-7.401 (m, 4.71H), 7.123-6.997 (m, 6.49H), 6.706-6.676 (d, 0.32H, $J=9.0$ Hz), 6.322-6.282 (d, 1H, $J=16.0$ Hz), 5.921-5.891 (d, 0.31H, $J=9.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 163.72, 161.73, 161.38, 161.30, 161.23, 140.04, 137.45, 134.60, 134.52, 133.43, 133.39, 133.34, 133.31, 132.79, 132.75, 132.51, 132.48, 130.55, 130.47, 127.99, 127.91, 119.46, 119.43, 119.39, 116.05, 115.93, 115.81, 115.71, 115.59, 115.41, 115.20, 107.70, 107.68, 106.87, 106.85, 94.72, 90.62, 88.34, 87.64.

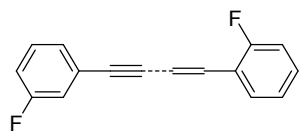
The Characterization data of 2n (E): The data was obtained by recrystallization from a mixture of E/Z



White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.558-7.480 (m, 2H), 7.472-7.398 (m, 2H), 7.085-7.079 (d, 1H), 7.079-7.042 (m, 3H), 7.036-6.997 (d, 1H, $J=16.0$ Hz), 6.322-6.282 (d, 1H, $J=16.0$ Hz).

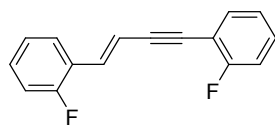
Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 164.33, 164.21, 163.72, 161.82, 161.74, 161.24, 140.04, 134.60, 134.52, 133.43, 133.35, 132.53, 132.49, 128.00, 127.91, 119.49, 119.45, 117.84, 117.81, 116.04, 115.92, 115.81, 115.71, 115.59, 115.19, 107.72, 107.69, 90.64, 88.37, 80.47, 73.59.

The Characterization data of 2o:



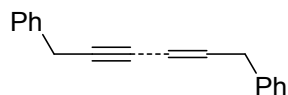
light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ : 7.888-7.852 (tt, 0.29H), 7.604-7.7.584 (d, 0.29H), 7.421-7.382 (m, 0.32H), 7.364 (s, 0.28H), 7.349-7.344 (d, 1H), 7.329-7.309 (m, 2H), 7.254-7.207 (m, 2H), 7.181-7.146 (m, 1H), 7.109-7.070 (m, 1H), 7.047-7.021 (m, 2H), 6.751-6.721 (d, 0.29H, $J=9.0$ Hz), 6.429-6.388 (d, 1H, $J=16.0$ Hz), 6.020-5.991 (d, 0.29H, $J=9.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 163.97 (d), 163.69 (d), 161.92 (d), 161.53 (d), 140.65, 138.56 (t), 138.04 (d), 130.34 (d), 130.17 (d), 130.03 (d), 129.86 (d), 127.54 (d), 127.45 (d), 125.10 (t), 124.95 (t), 122.39 (d), 118.45 (d), 118.34 (d), 116.10 (d), 115.84 (d), 115.75 (d), 115.62, 115.54 (d), 115.14 (d), 112.85, 112.64, 109.24, 108.41, 95.52, 95.49 (d), 91.28, 89.42 (d).

The Characterization data of 2p (*E*):



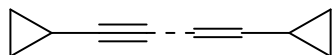
White solid; ^1H NMR (400 MHz, CDCl_3) δ : 7.632-7.513 (m, 3H), 7.463-7.406 (m, 2 H), 7.310-7.236 (m, 4H), 6.491-6.450 (d, 1H, $J=16.0$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 137.85, 135.85, 134.25, 133.38, 130.03, 129.71, 129.40, 129.35, 127.02, 126.52, 126.22, 123.19, 110.42, 93.72, 89.23.

The Characterization data of 2q:



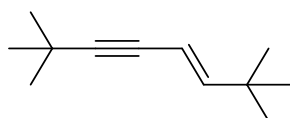
light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ : 7.30-7.28 (m, 2H), 7.25-7.18 (m, 12 H), 7.16-7.07 (m, 7H), 6.21-6.14 (m, 0.62 H), 5.98-5.91(m, 1H), 5.56-5.53 (d, 1H, $J=10.8$ Hz), 5.49-5.45 (d, 1H, $J=16.0$ Hz), 3.71 (s, 2H), 3.61 (s, 1H), 3.59-3.58 (m, 4H), 3.35-3.33 (d, 1H, $J=6.8$ Hz) ^{13}C NMR (100MHz, CDCl_3) δ : 141.97, 141.0, 139.93, 139.11, 136.91, 135.60, 128.72, 128.67, 128.54, 127.99, 127.95, 126.90, 126.65, 126.61, 126.38, 126.20, 111.11, 110.18, 91.99, 86.79, 81.05, 79.39, 75.60, 67.32, 39.26, 36.51.

The Characterization data of 2r:



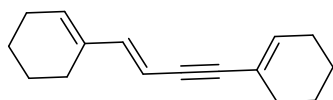
light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ : 5.574-5.514 (m, 1H, $J=16.0$ Hz), 5.503-5.461 (m, 1H, $J=16.0$ Hz), 5.539-5.301 (m, 1H, $J=9.0$ Hz), 5.189-5.138 (m, 1H, $J=9.0$ Hz), 1.984-1.936 (m, 1H), 1.469-1.296 (m, 3H), 0.884-0.662 (m, 12H), 0.483-0.416 (m, 4H). ^{13}C NMR (100MHz, CDCl_3) δ :147.24, 146.79, 106.90, 106.48, 96.73, 91.73, 74.52, 72.93, 14.49, 12.93, 8.60, 8.41, 7.58, 7.41, 0.34, 0.12.

The Characterization data of 2s (E):



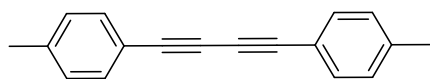
Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ : 6.109-6.069 (d, 1H, $J=16.0$ Hz), 5.436-5.395 (d, 1H, $J=16.0$ Hz), 1.249 (s, 9H), 1.027 (s, 9H). ^{13}C NMR (100MHz, CDCl_3) δ :153.21, 105.30, 97.19, 76.68, 31.10, 30.60, 29.09.

The Characterization data of 2t:



light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ :6.59-6.55 (d, 1H, $J=16.0$ Hz), 6.13 (d, 1H, $J=9.2$ Hz),5.84 (s, 1H), 5.64-5.60 (d, 1H, $J=16.0$ Hz), 2.17 (s, 4H), 2.13 (s, 4H), 1.69-1.62 (m, 4H), 1.61-1.58 (m, 4H); ^{13}C NMR (100MHz, CDCl_3) δ :144.05, 135.63, 134.30, 131.97, 121.06, 104.31, 92.44, 86.90, 61.54, 58.45, 29.68, 29.28, 26.08, 25.75, 23.87, 22.36, 22.31, 22.26, 21.53, 18.40.

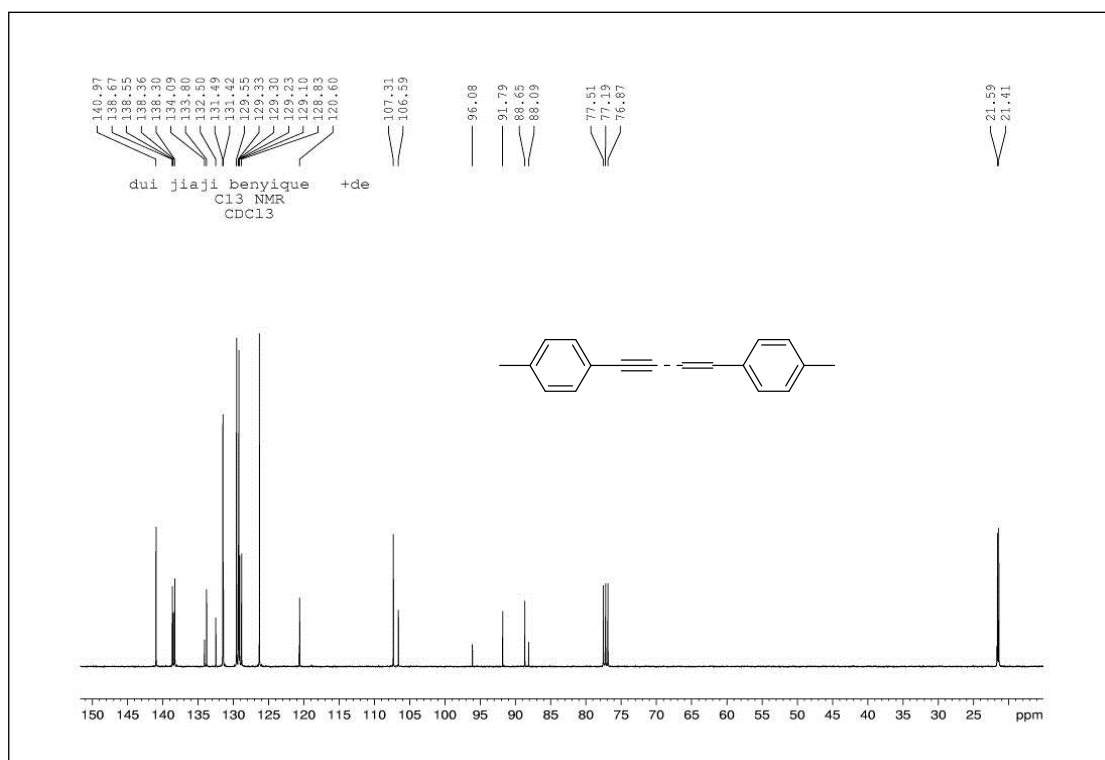
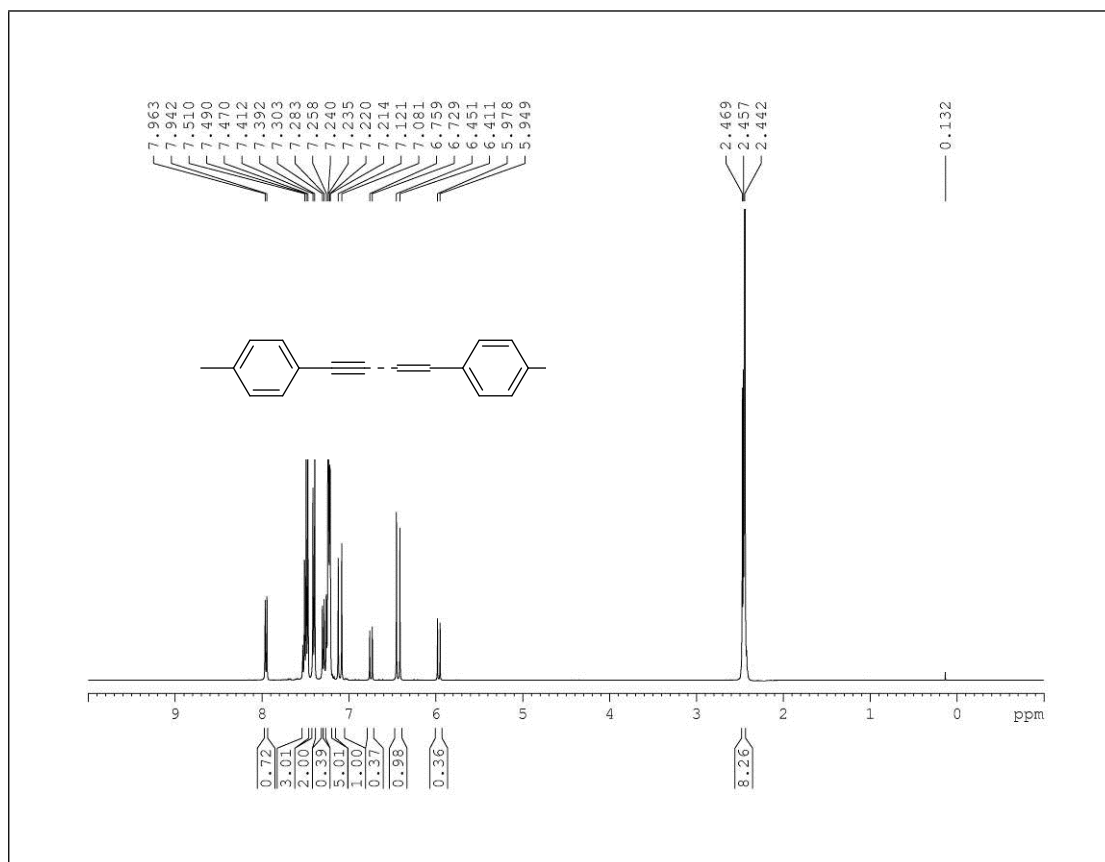
The Characterization data of 3b



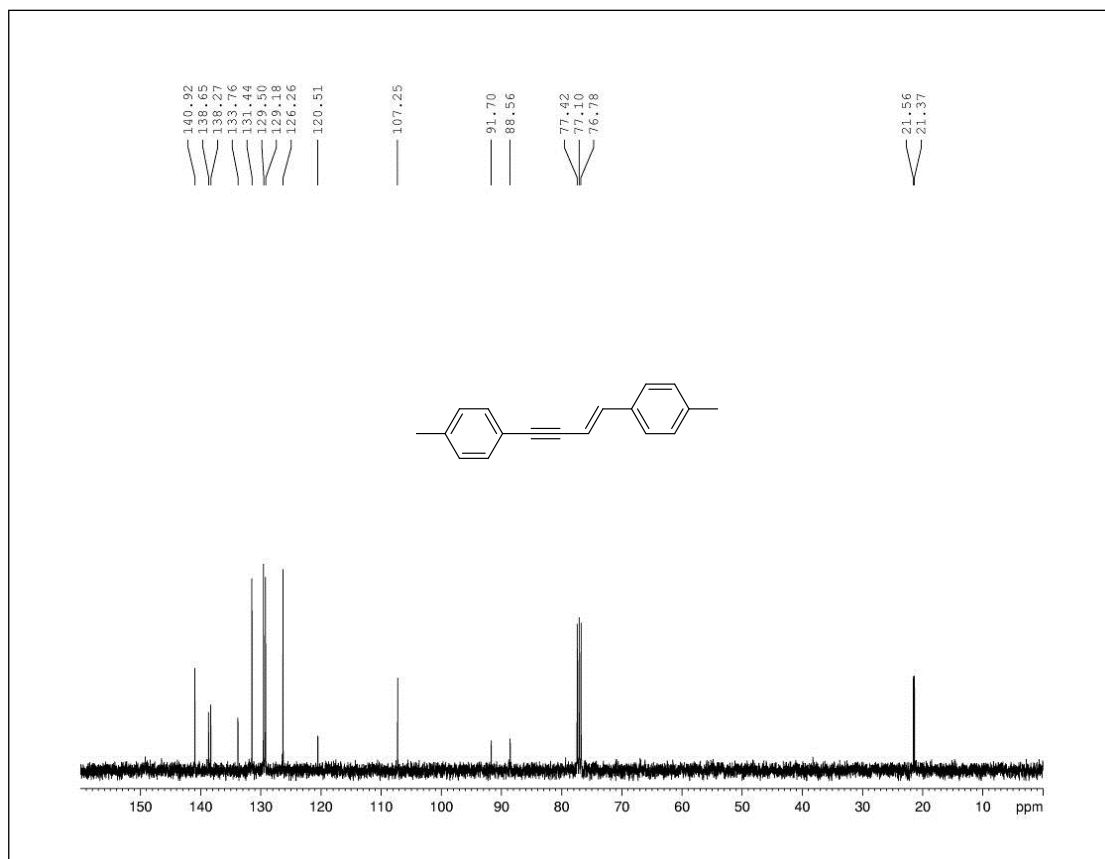
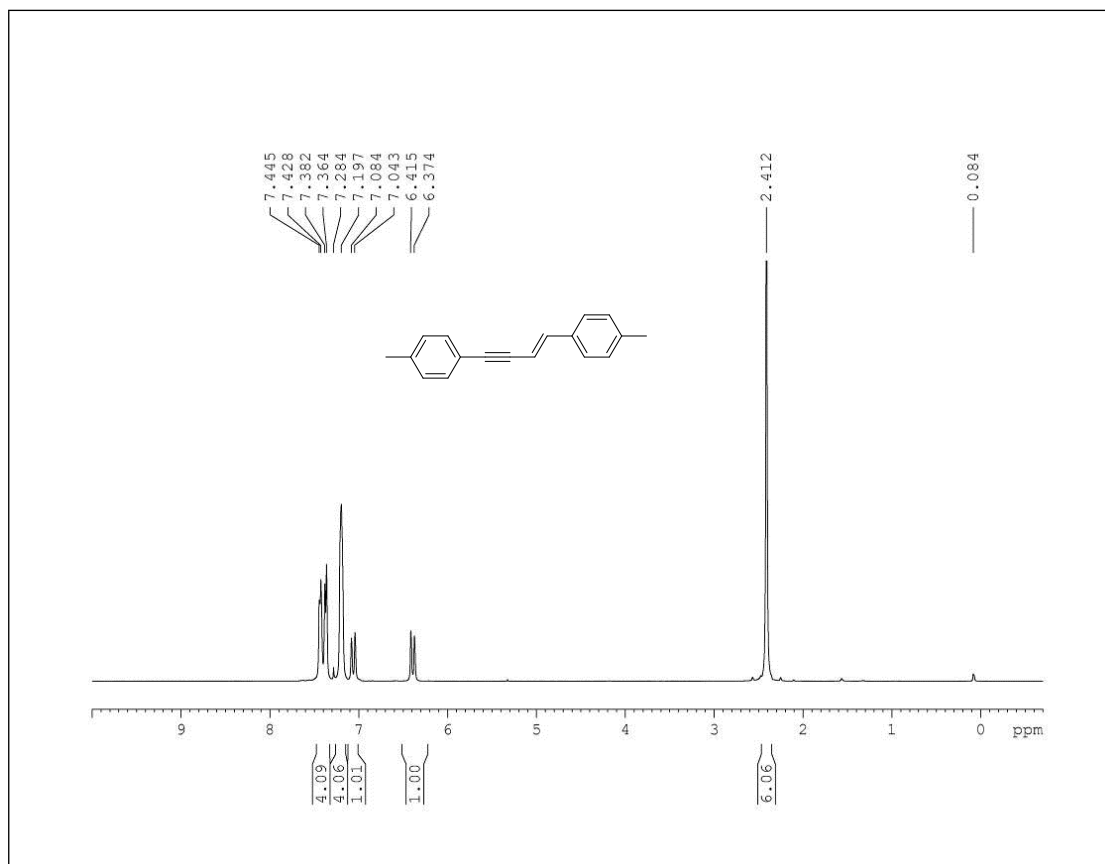
White solid; ^1H NMR (400MHz, CDCl_3) δ : 7.45-7.43 (d, $J= 8.0$ Hz, 4H), 7.17-7.15 (d, $J= 8.0$ Hz, 4H),2.39 (s,6H). ^{13}C NMR (100MHz, CDCl_3) δ : 139.52, 132.40, 129.23, 118.78, 81.55, 73.44, 21.65.

5. ^1H NMR, and ^{13}C NMR copies of products

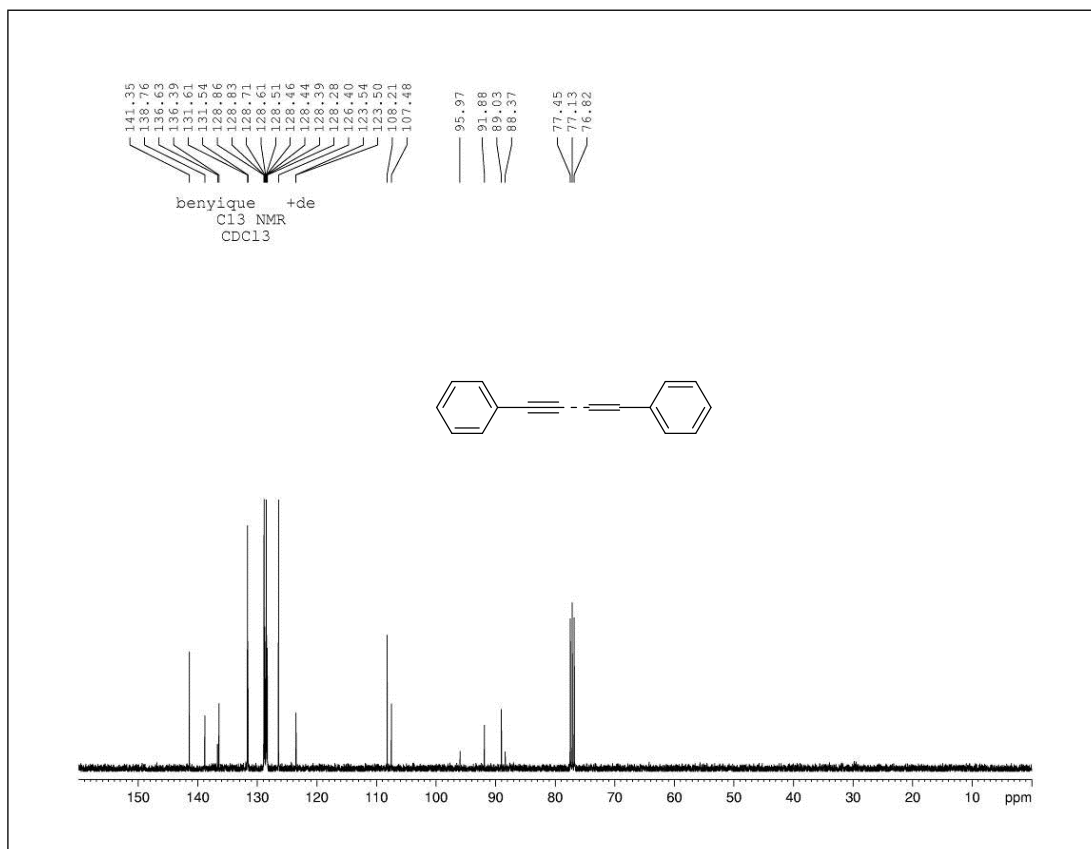
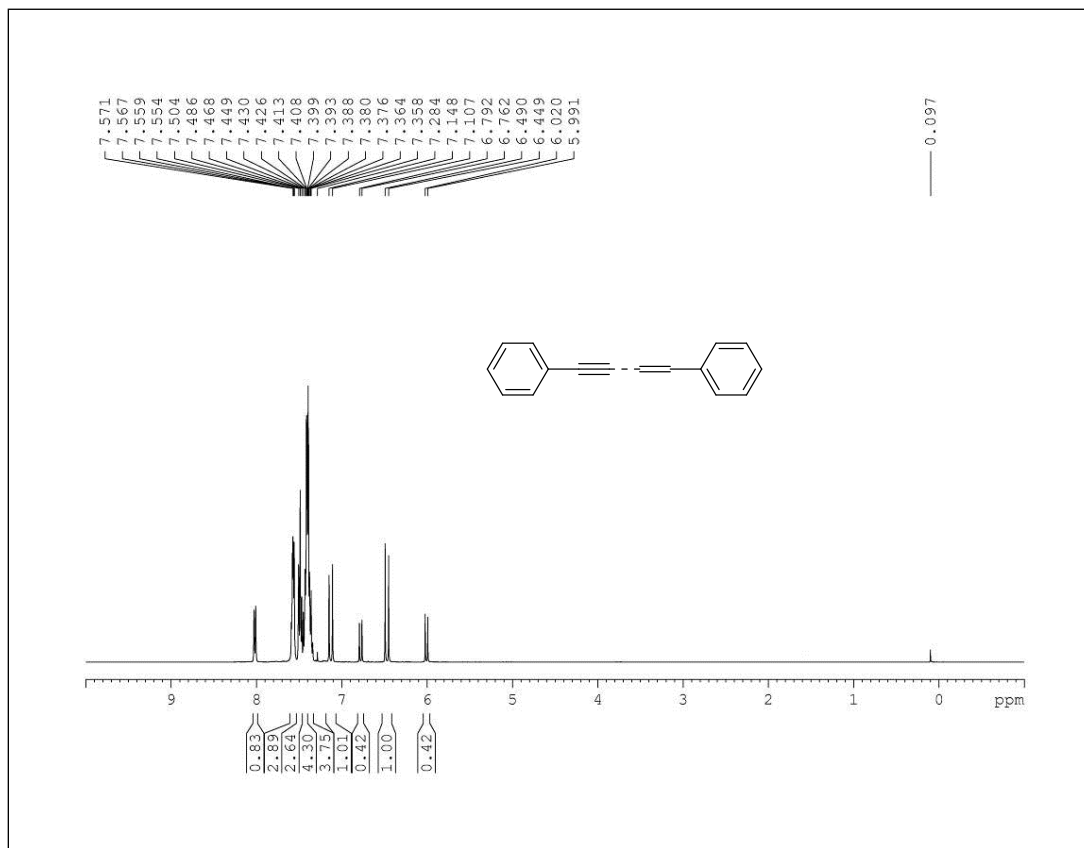
The copies of product 2a (*E/Z*=74:26)



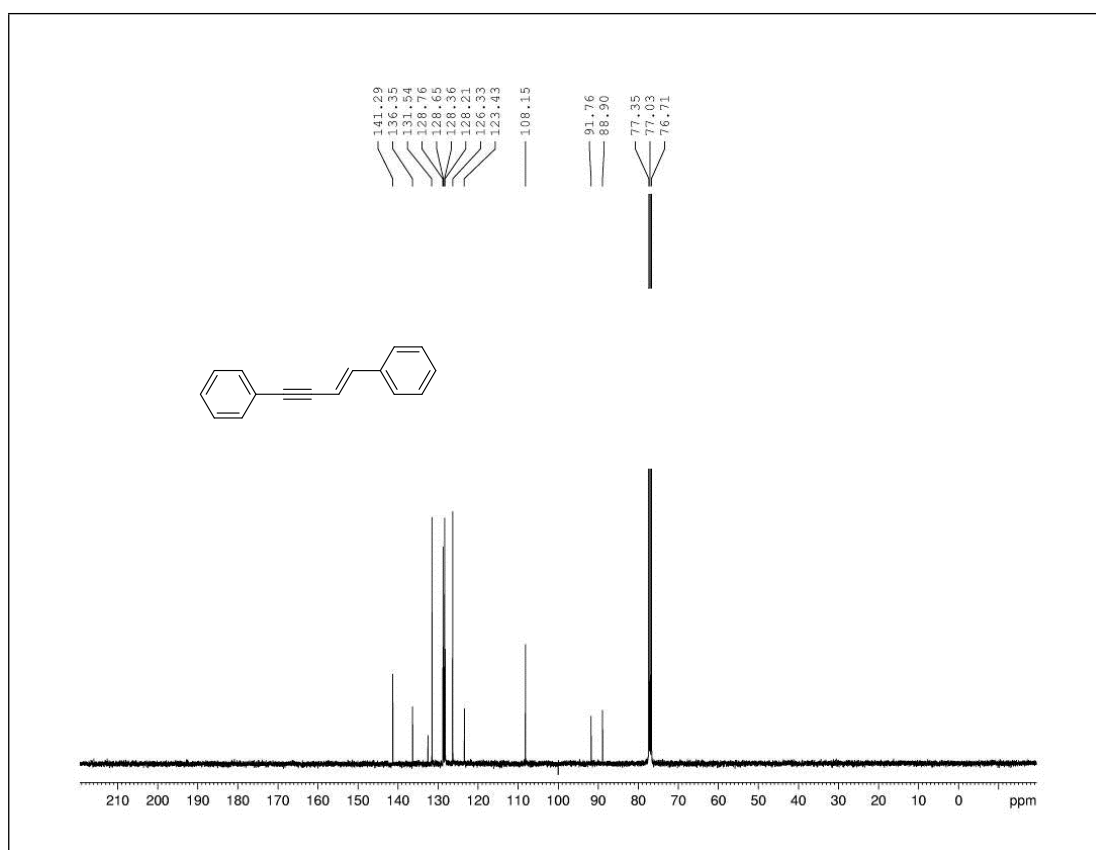
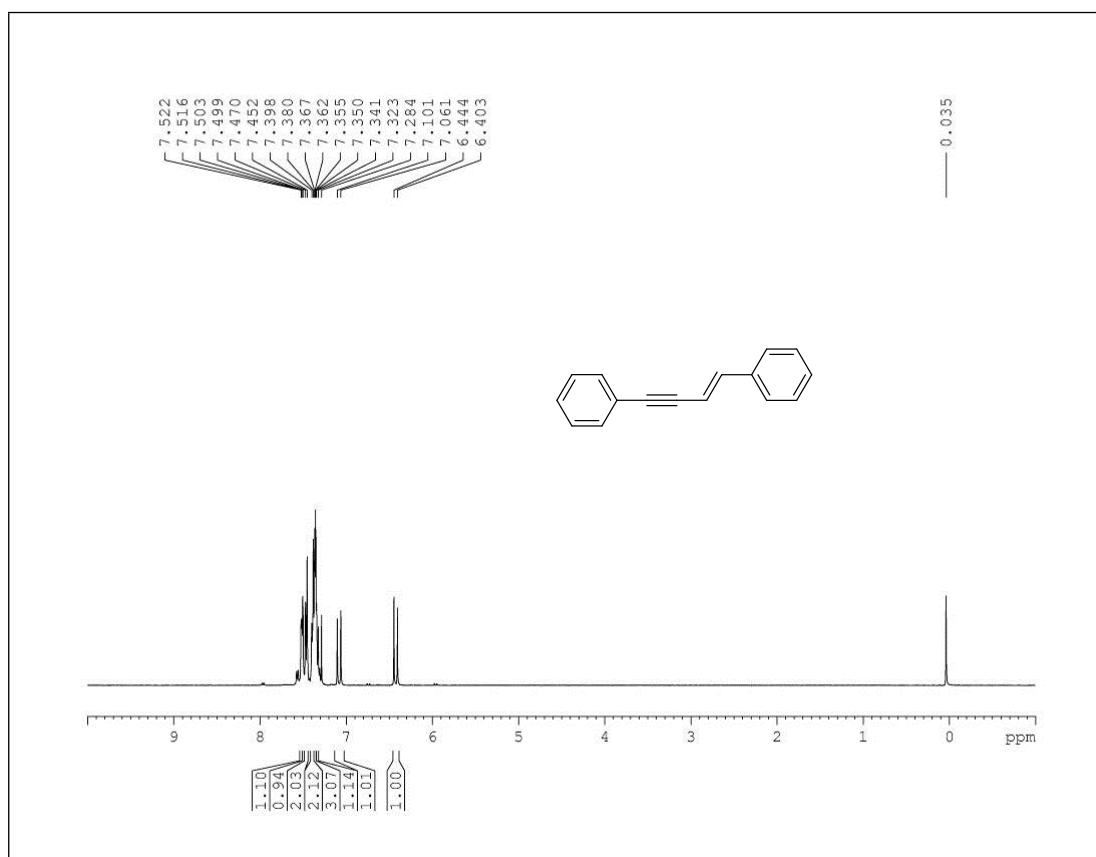
The copies of product 2a (*E*)



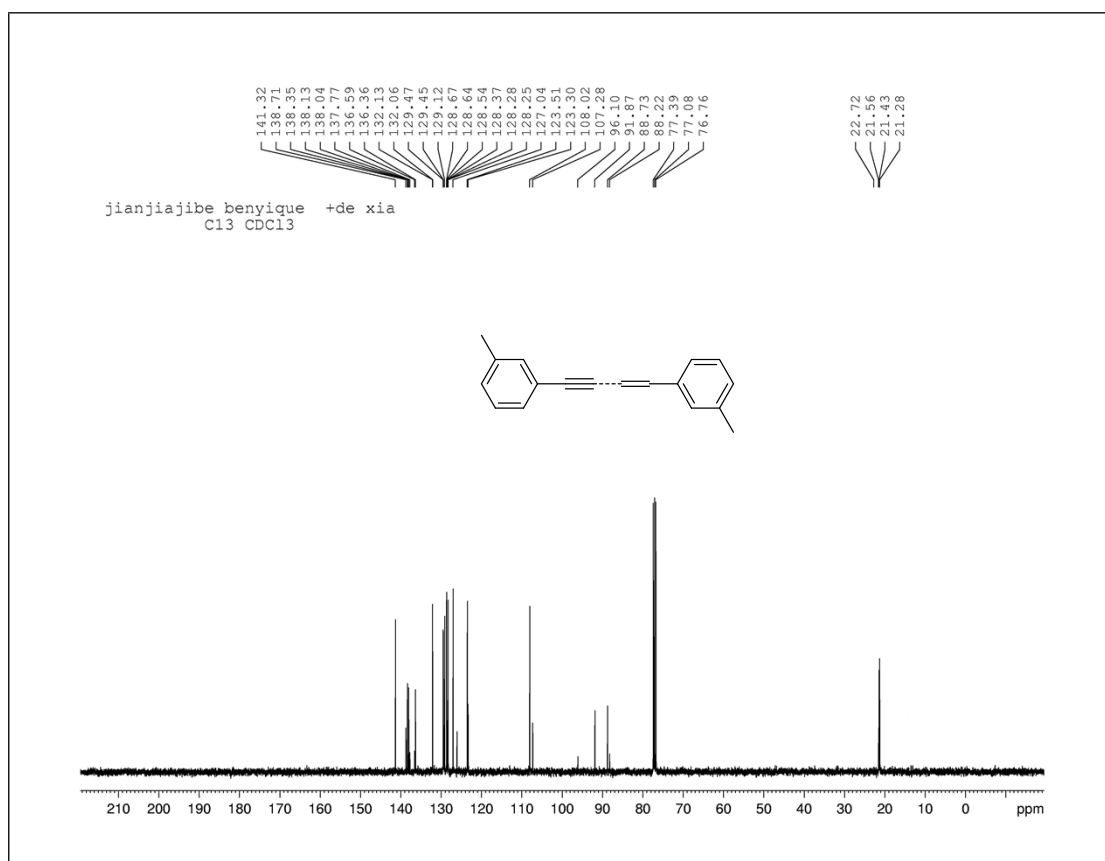
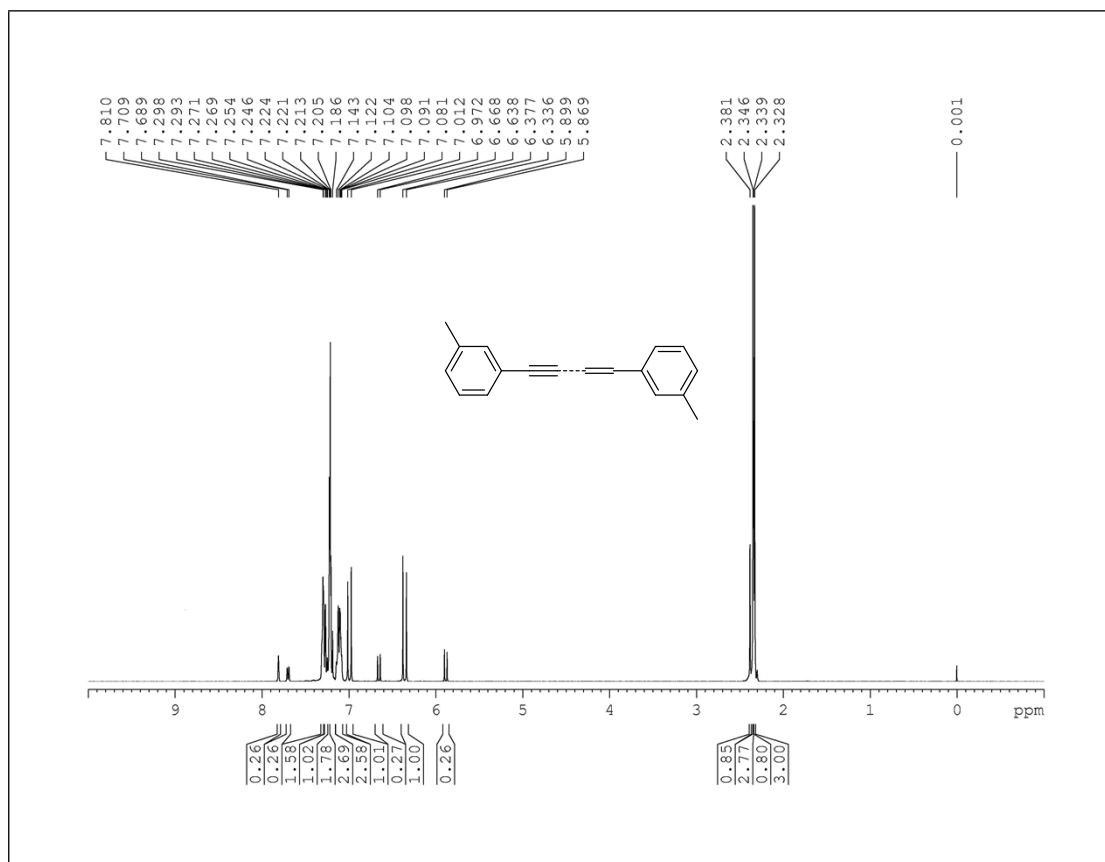
The copies of product 2b (*E/Z*=71:29)



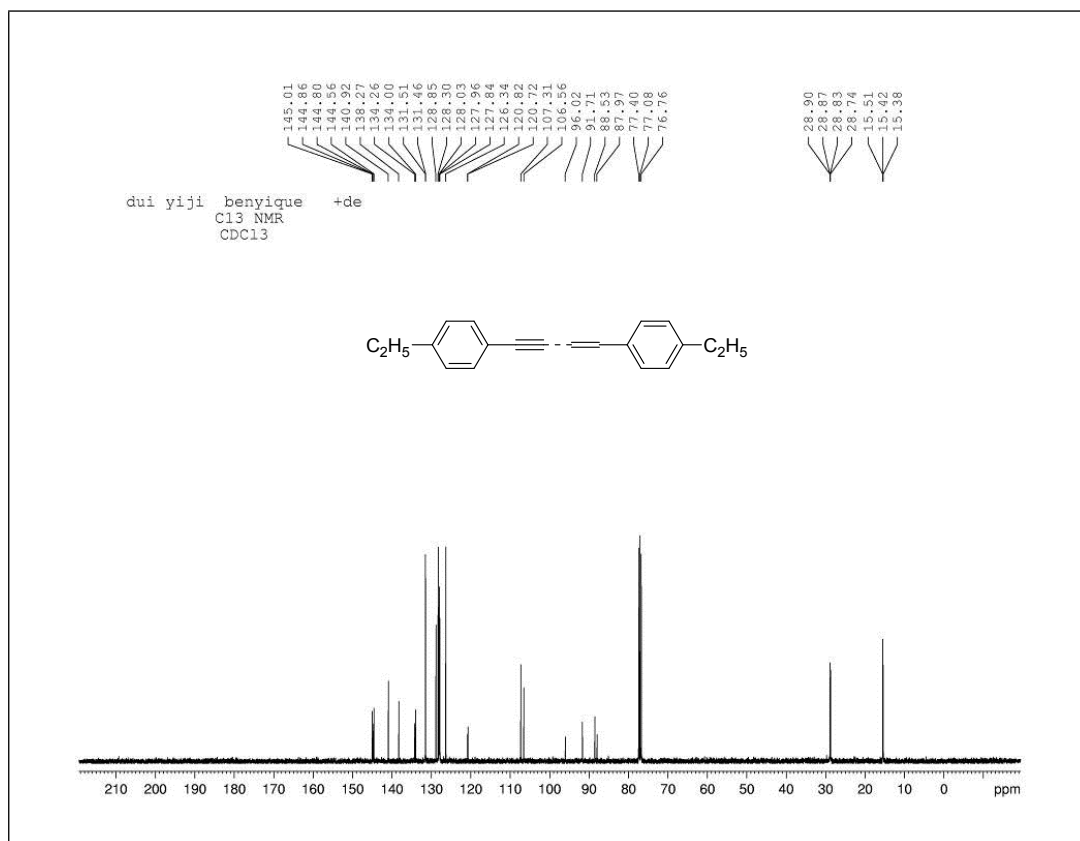
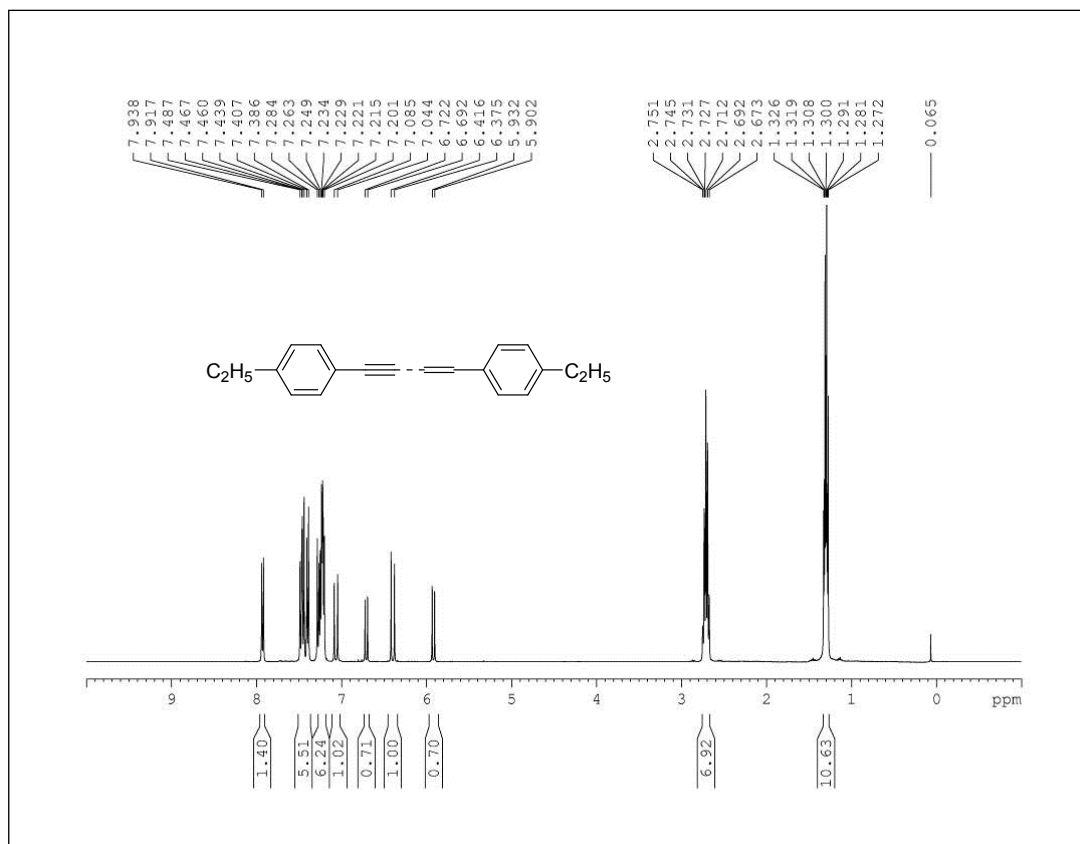
The copies of product 2b (*E*)



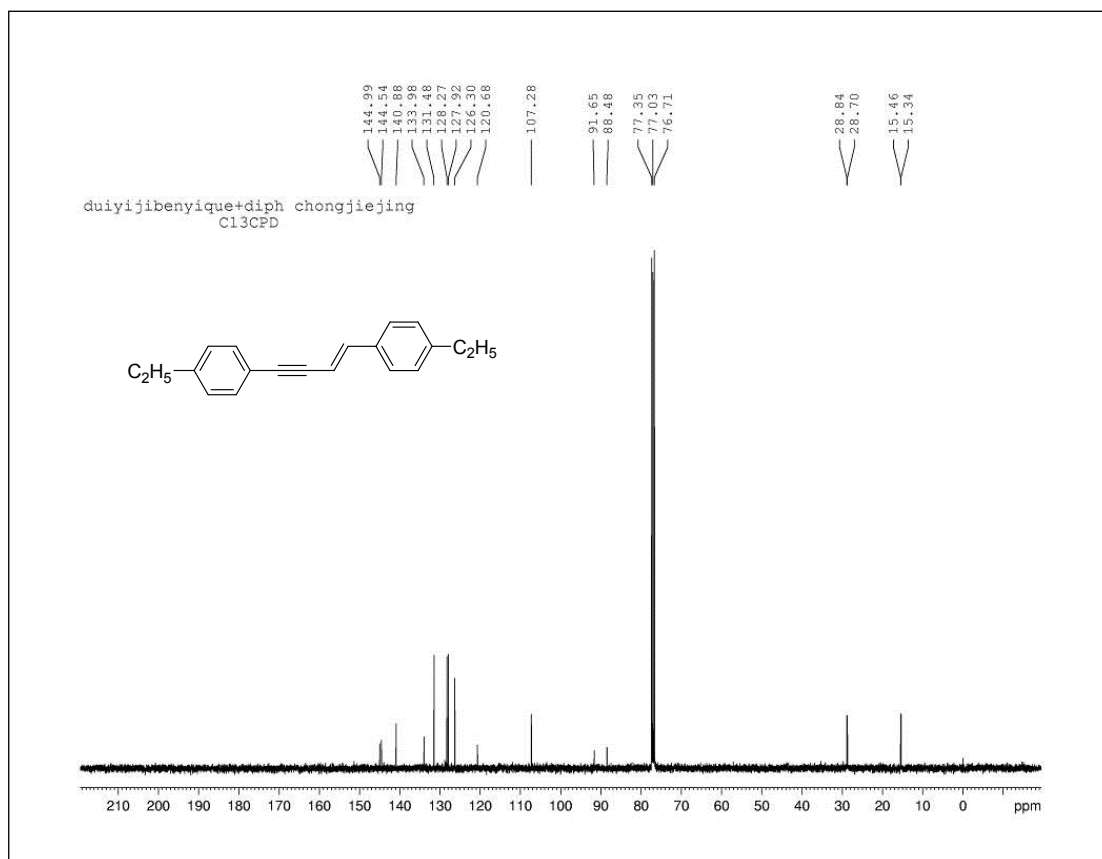
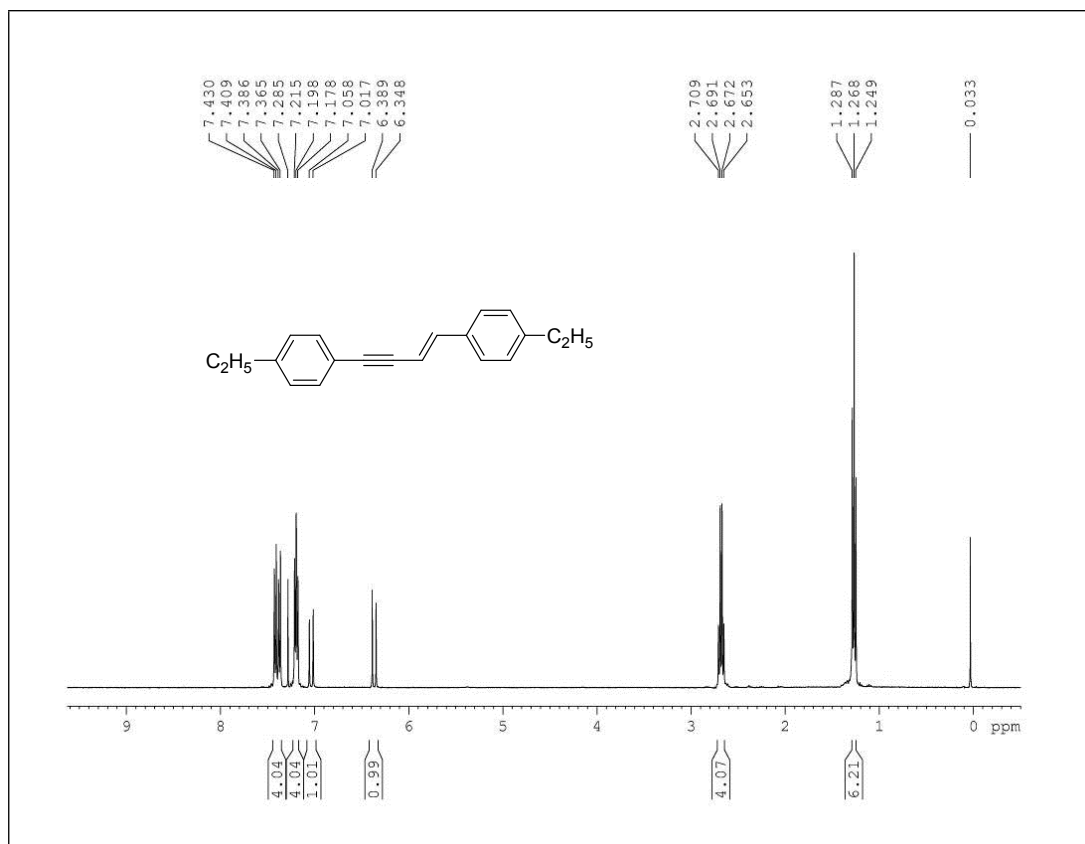
The copies of product 2c (*E/Z*=79:21)



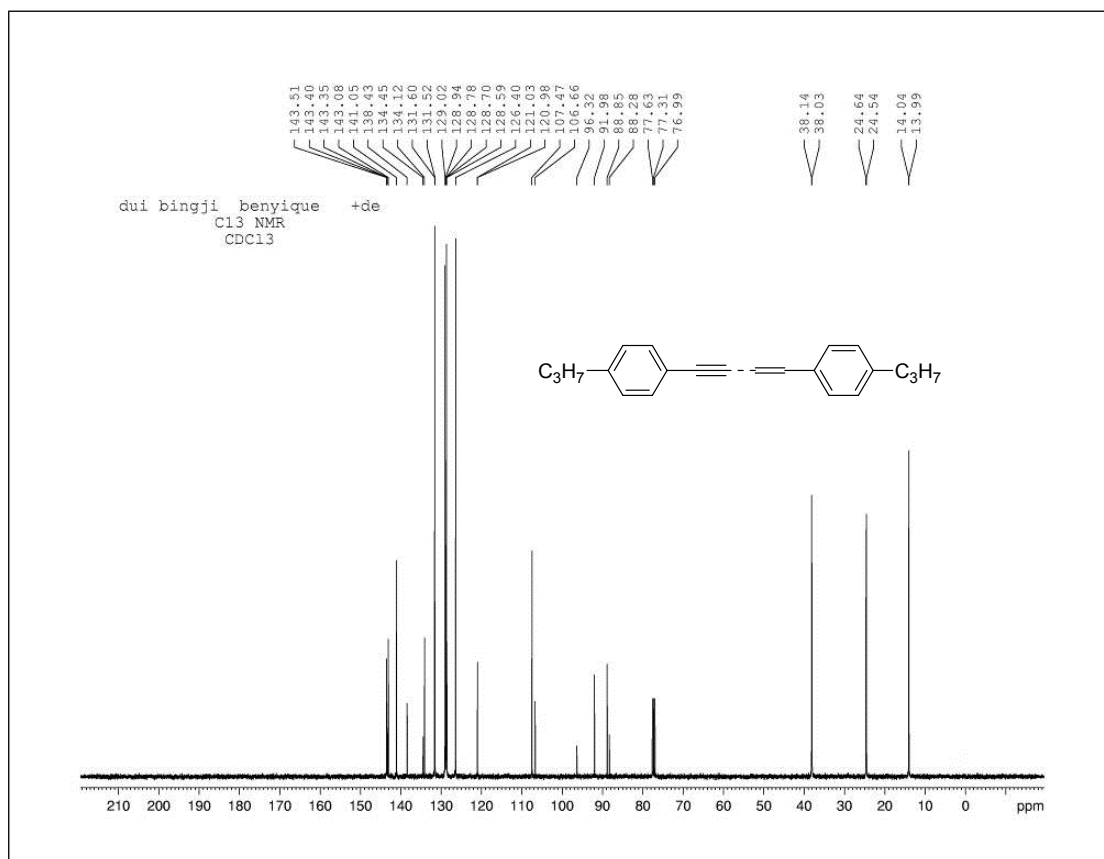
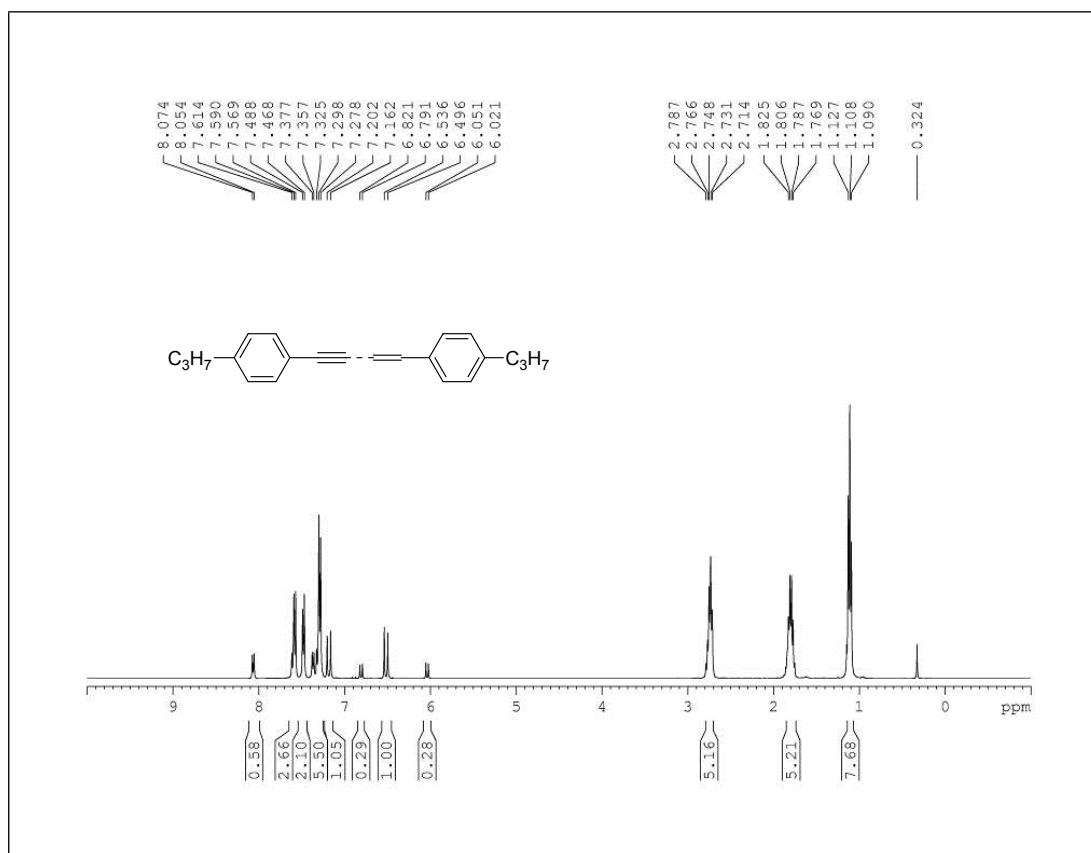
The copies of product 2d (*E/Z*=59:41)



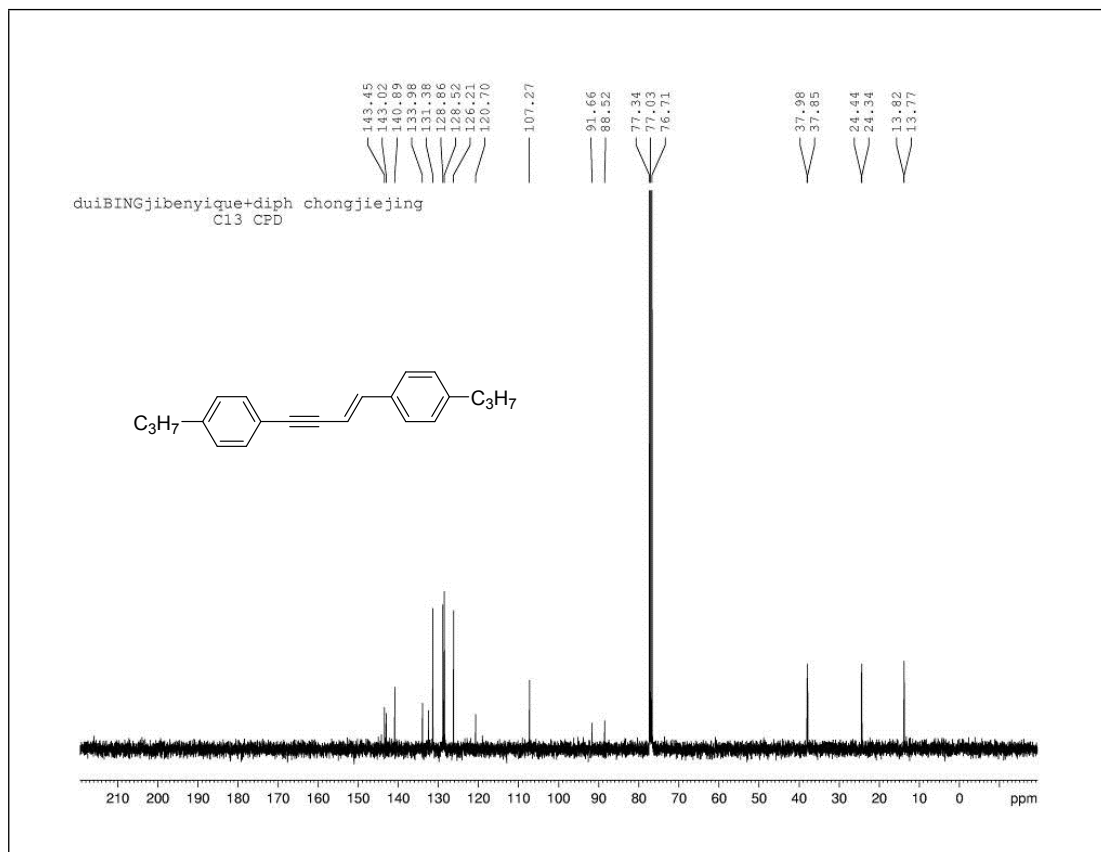
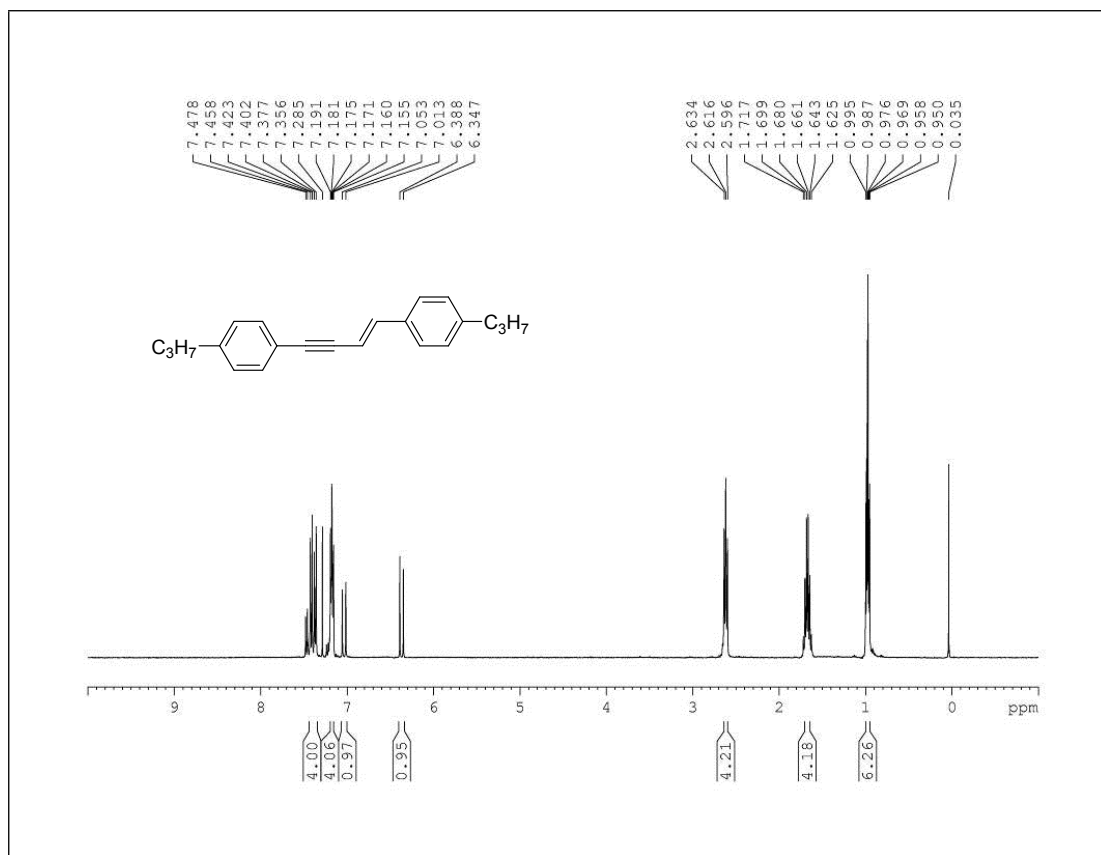
The copies of product 2d (*E*)



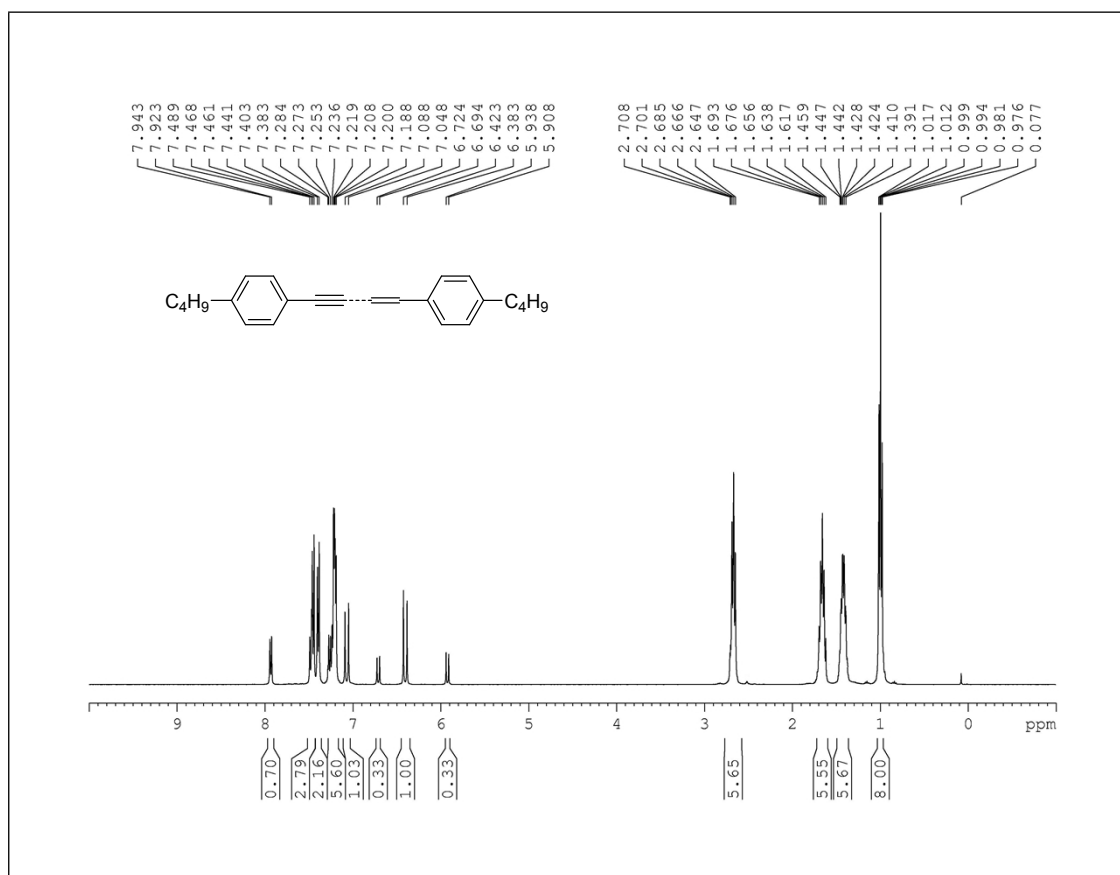
The copies of product 2e (*E/Z*=78:22)

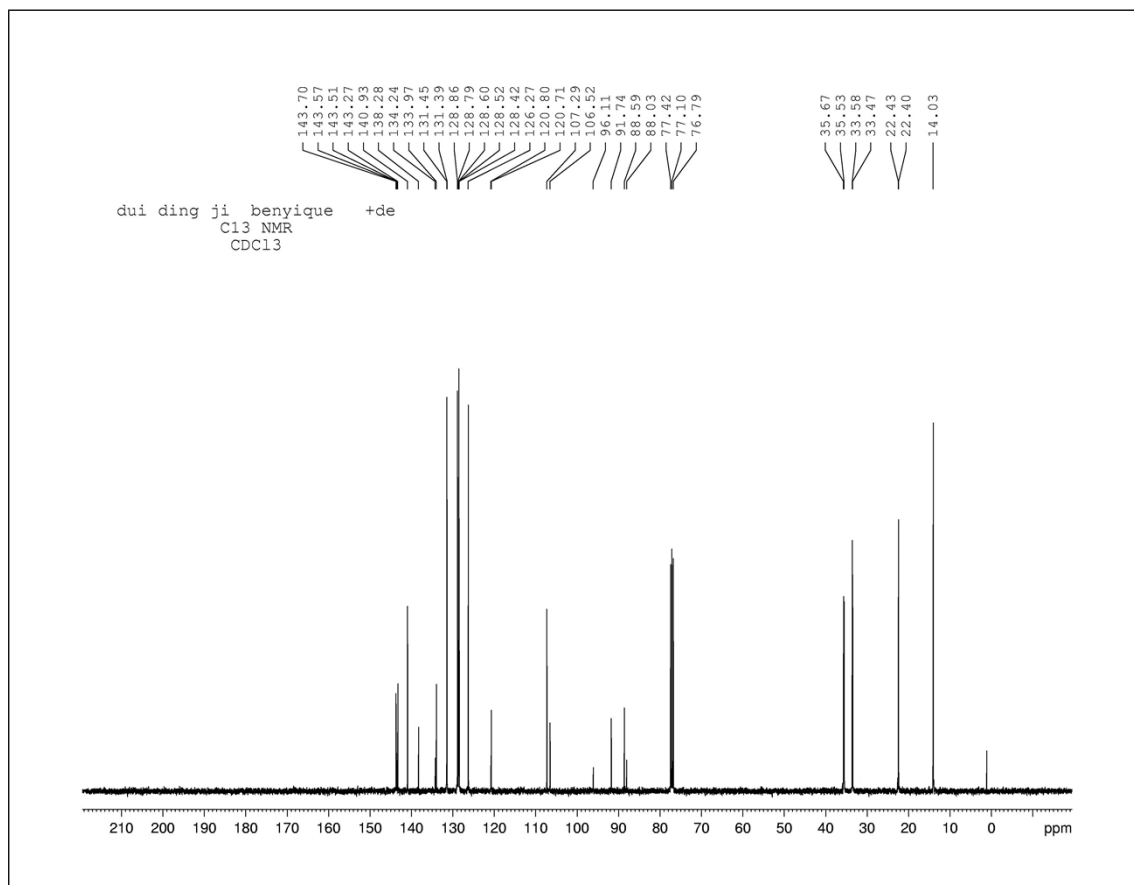


The copies of product 2e (*E*)

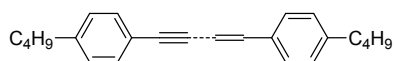


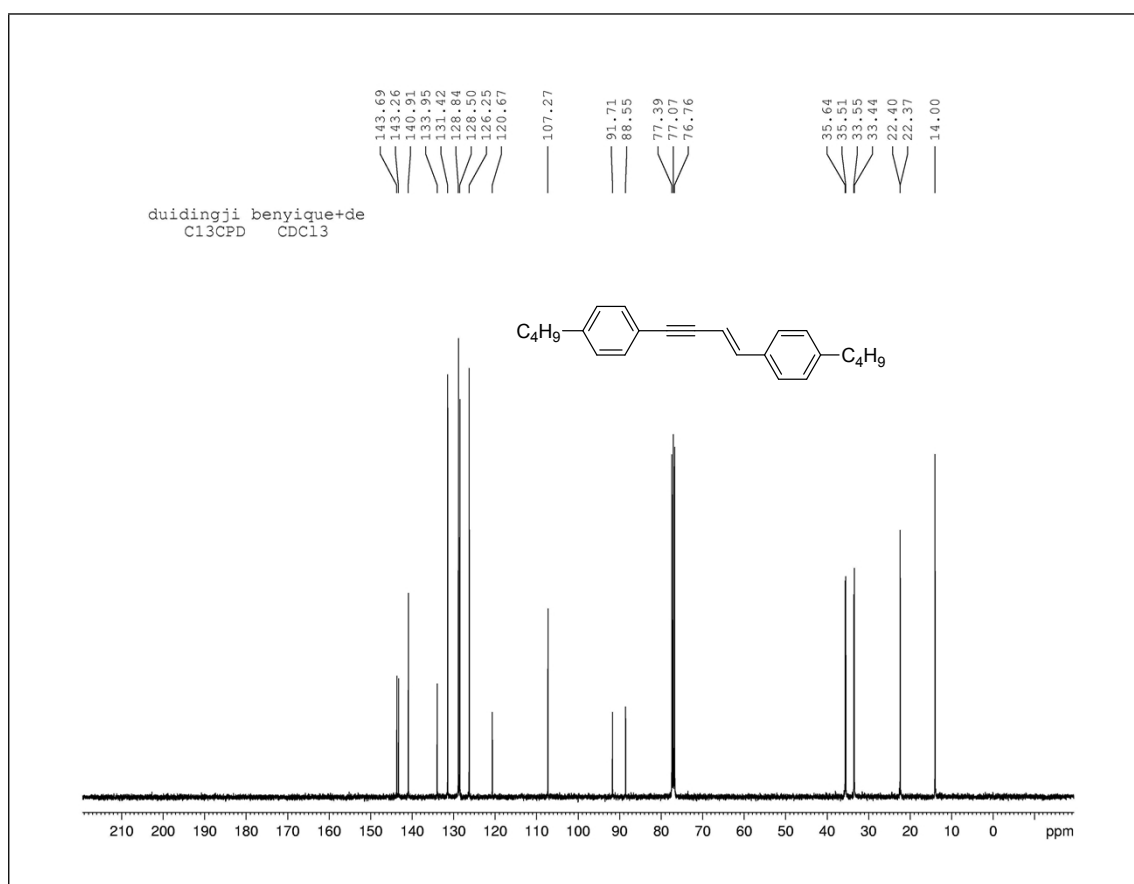
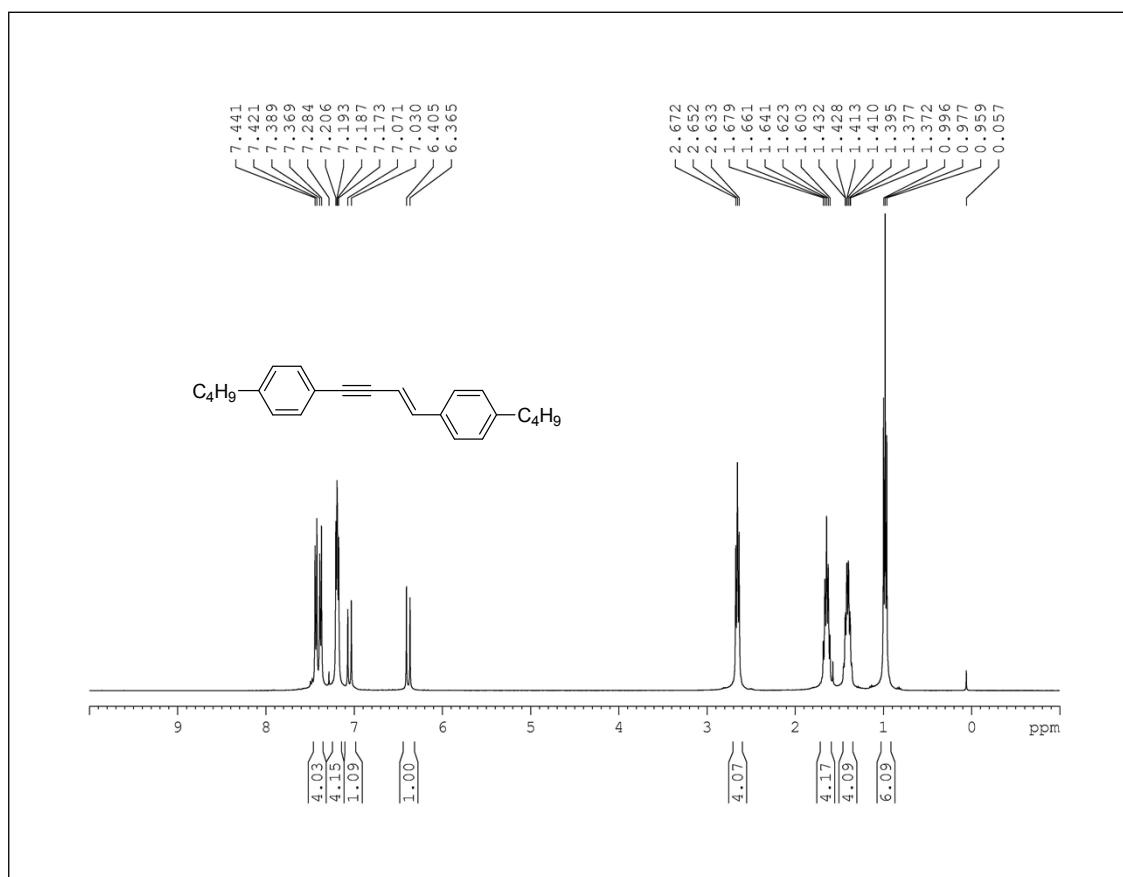
The copies of product 2f (*E/Z*=75:25)



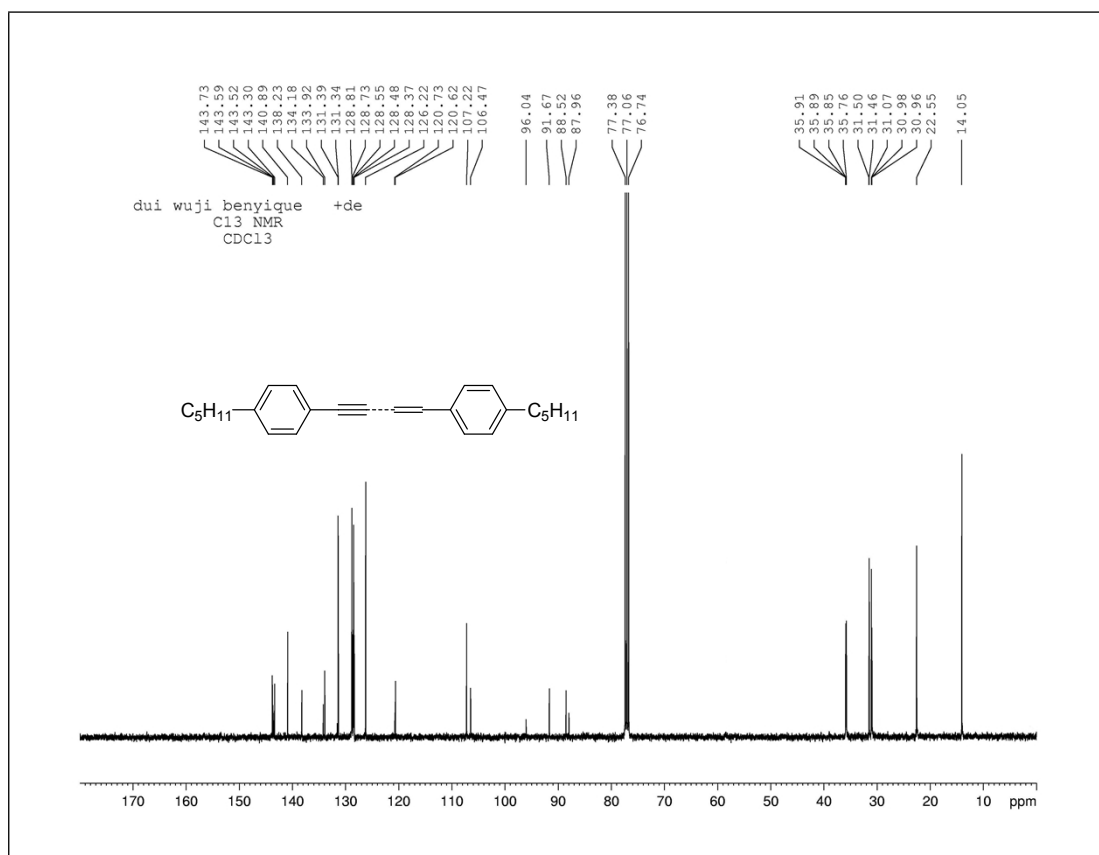
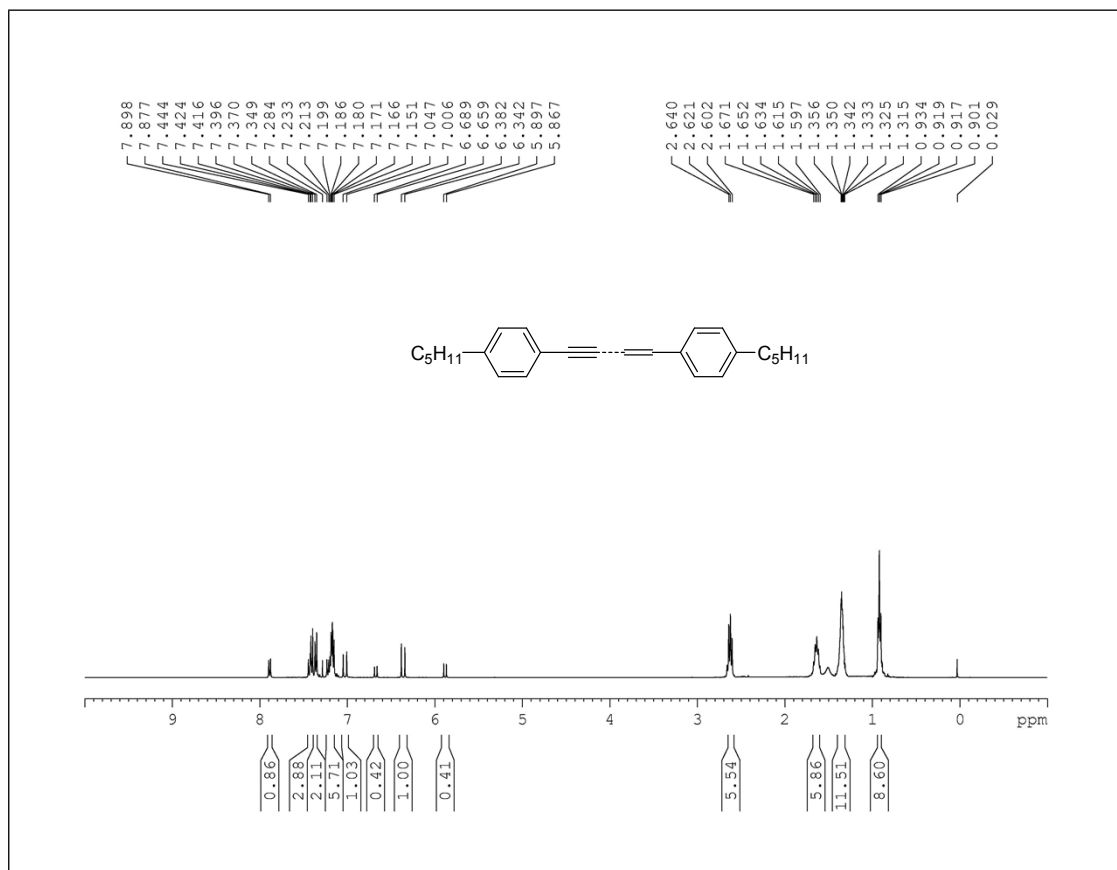


The copies of product 2f (*E*)

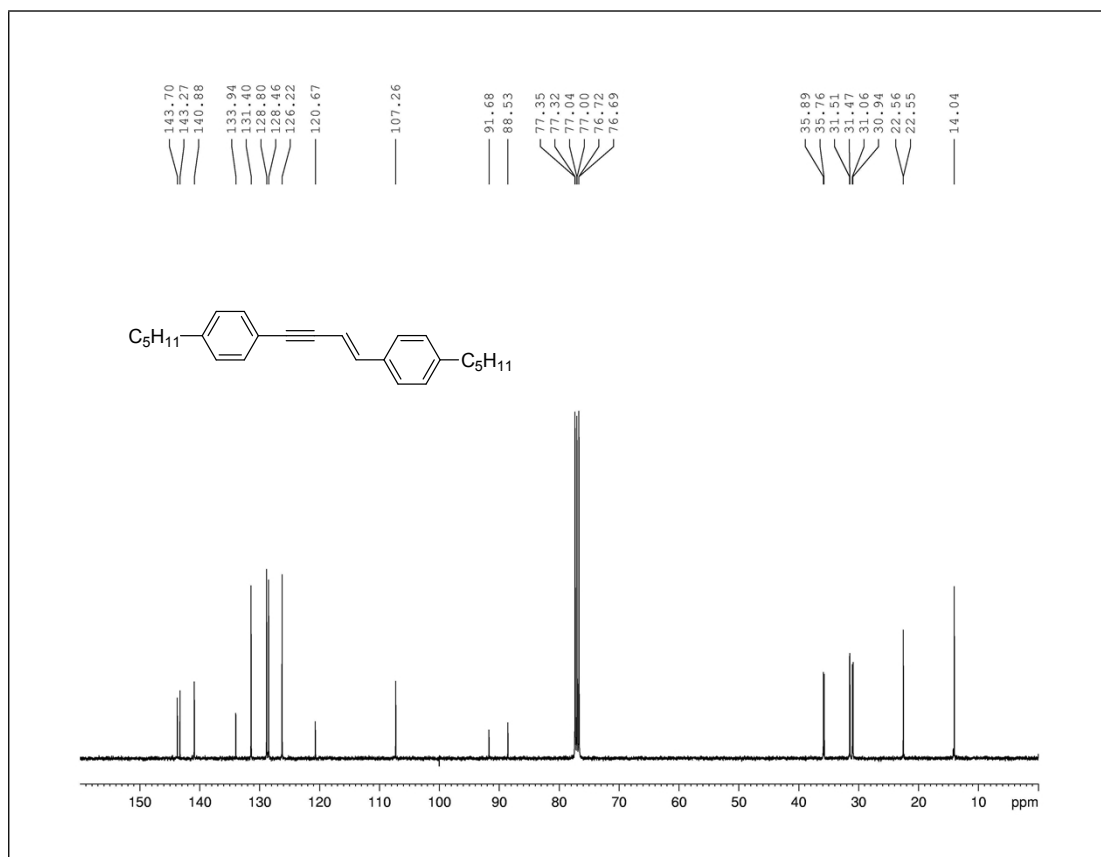
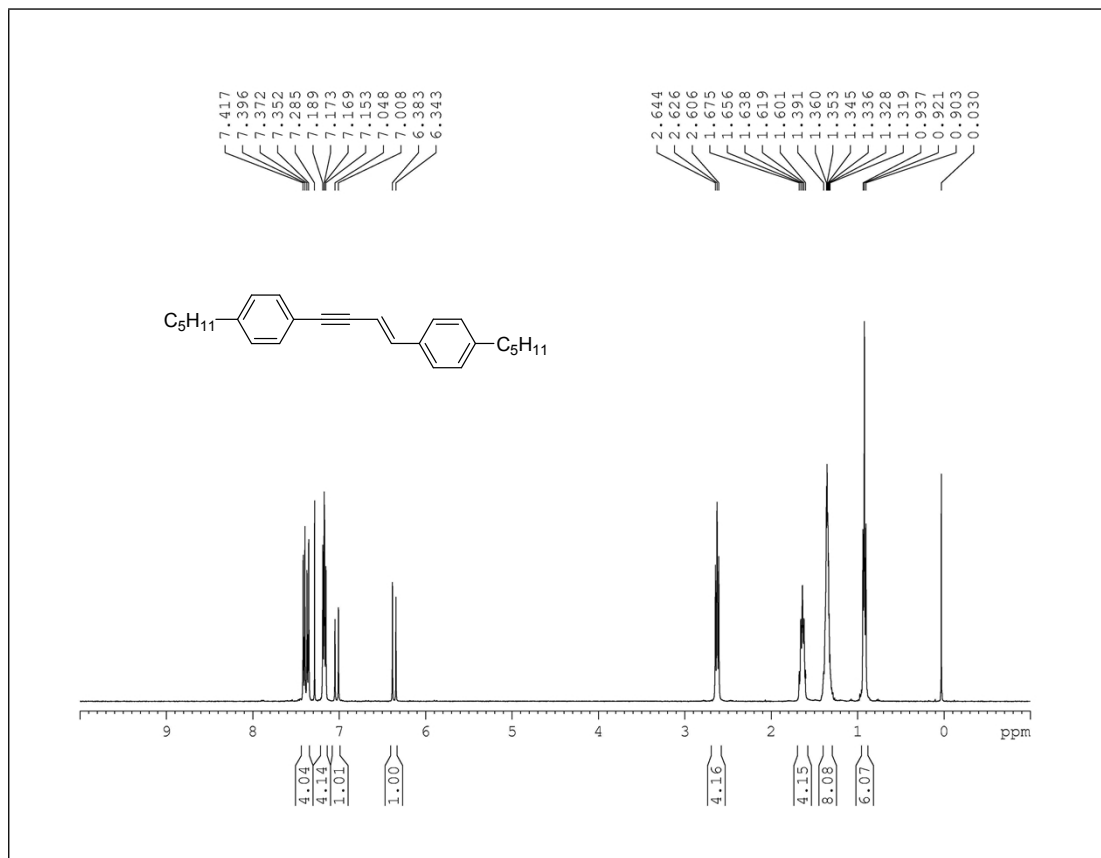




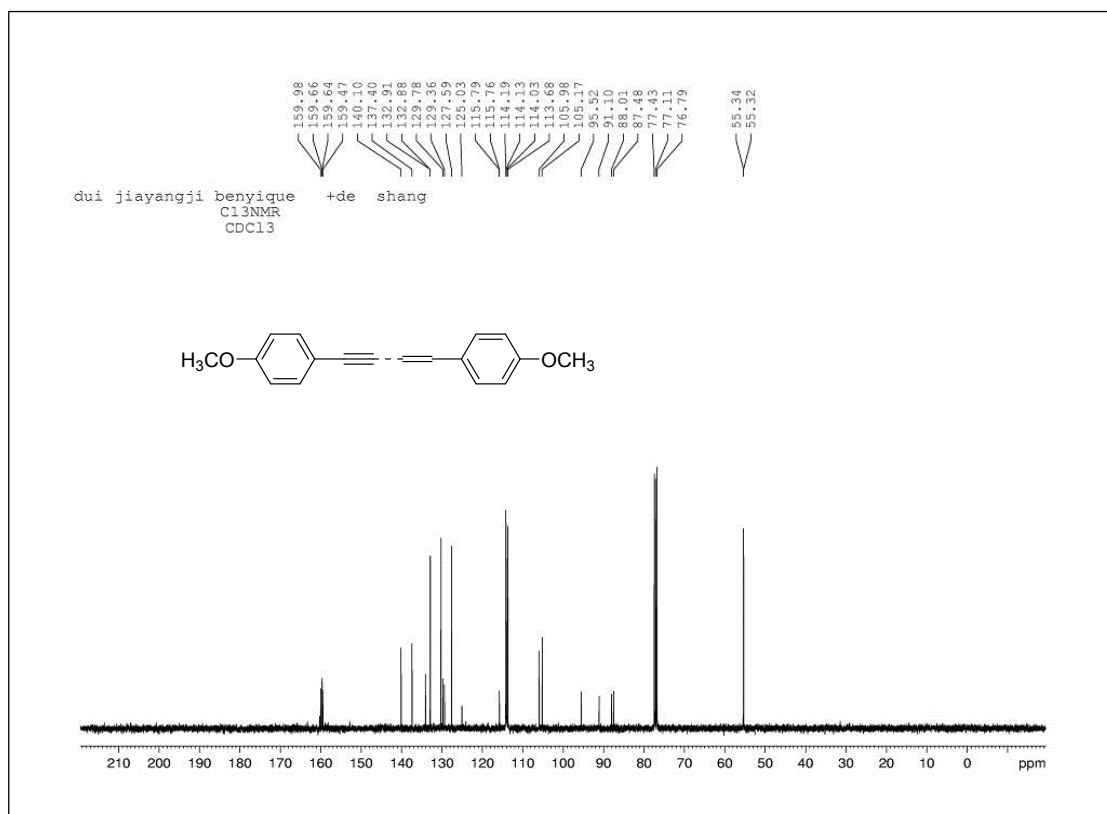
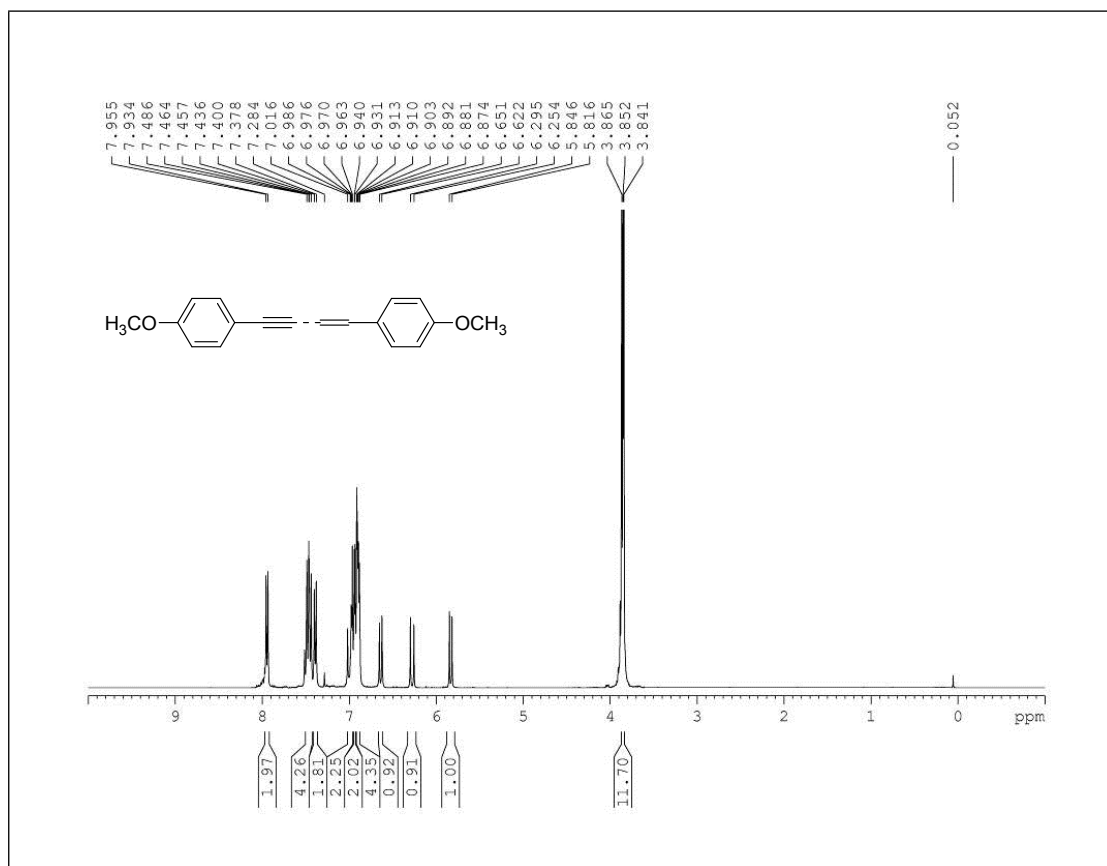
The copies of product 2g (E/Z=71:29)



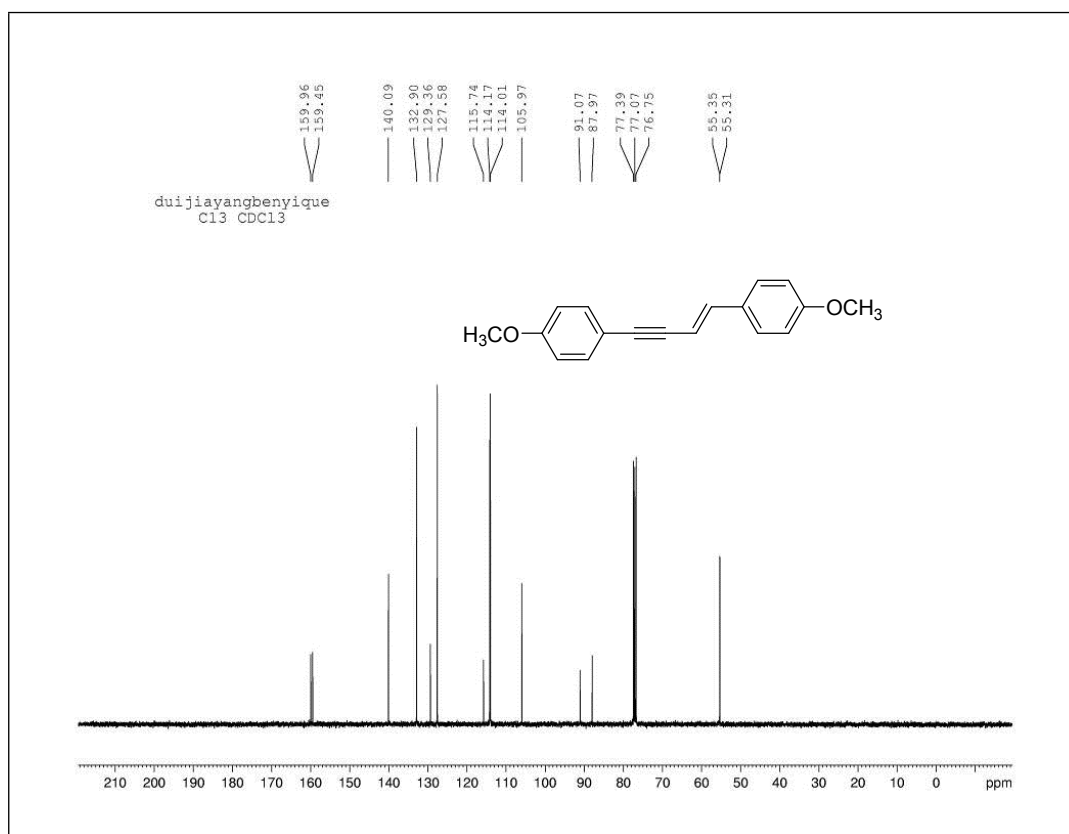
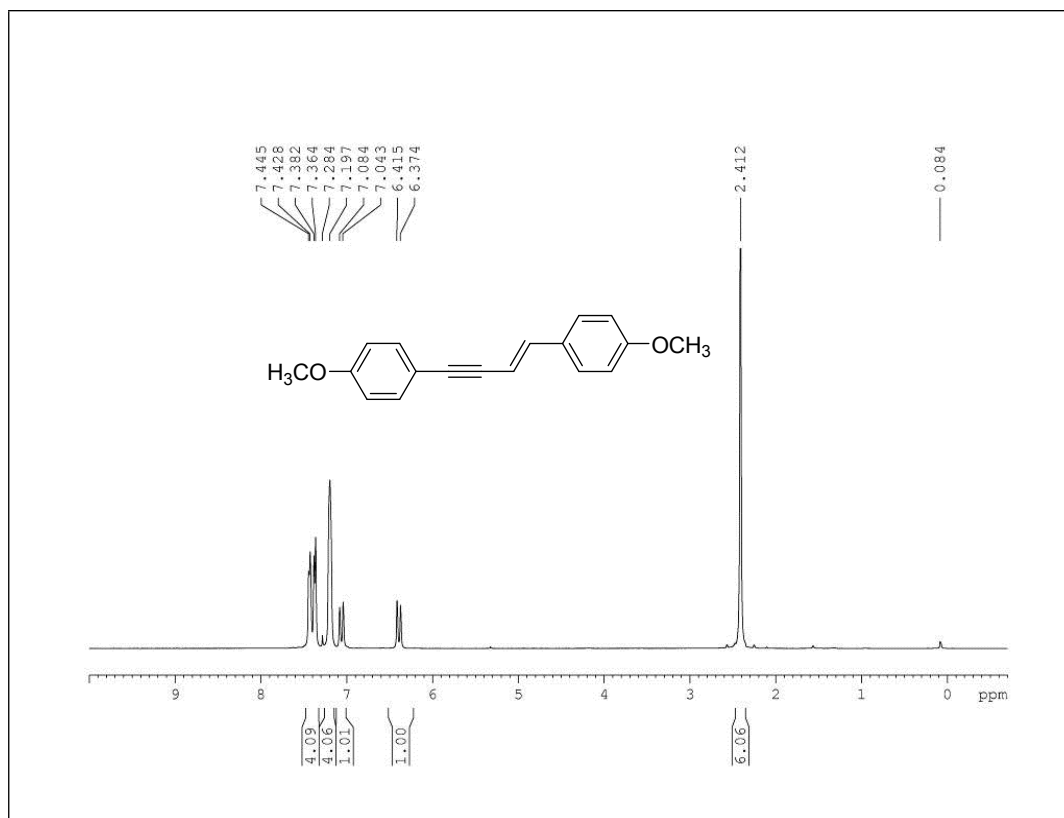
The copies of product 2g (*E*)



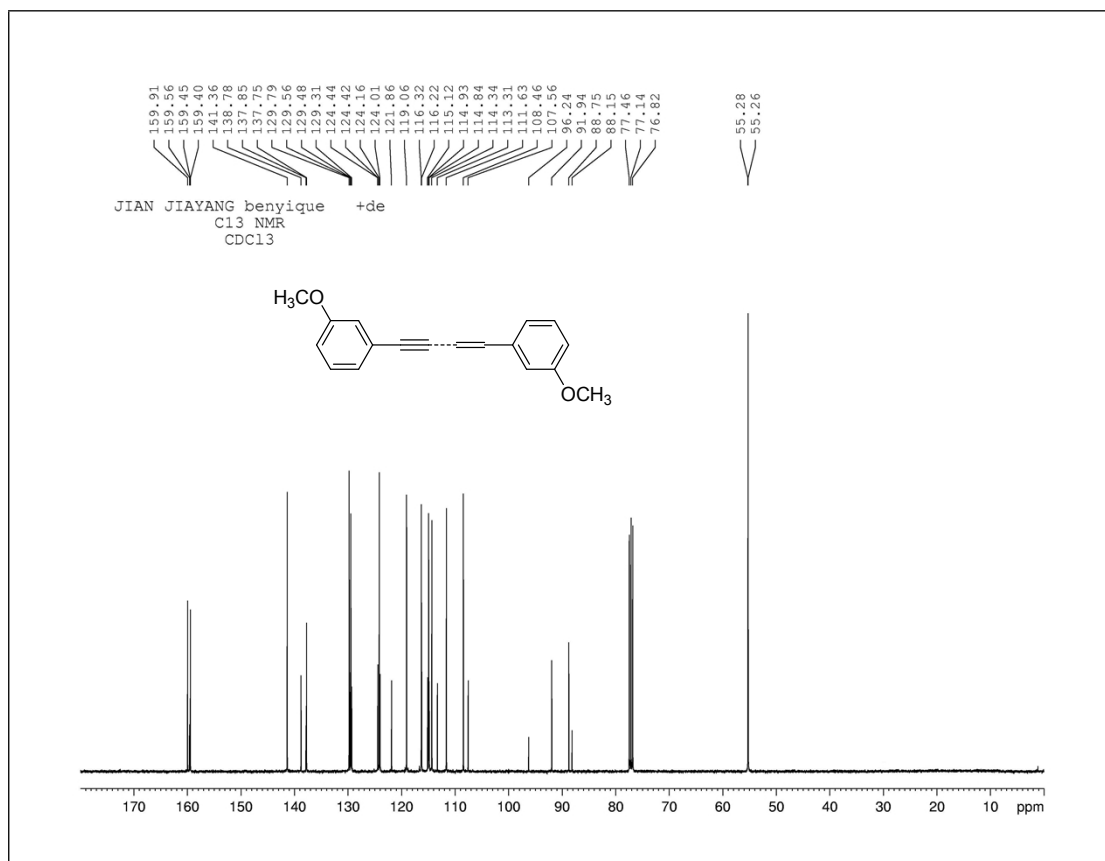
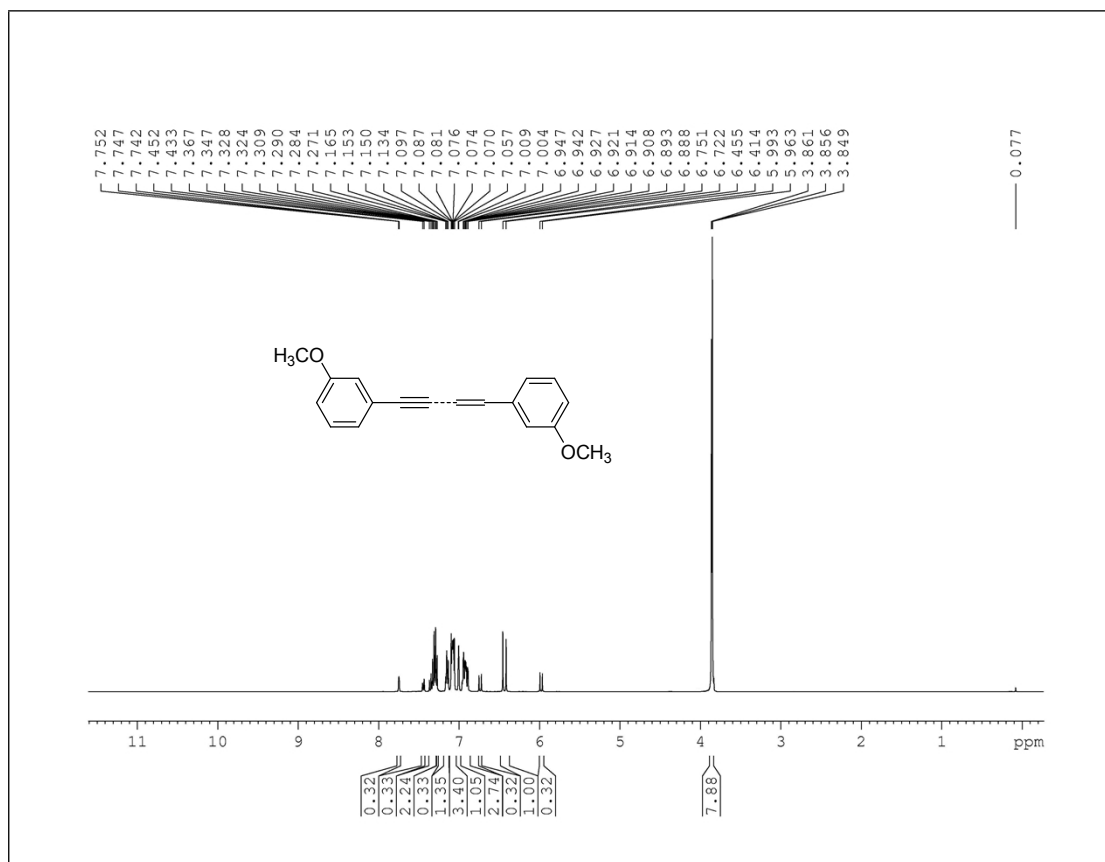
The copies of product 2h (*E/Z*=1:1)



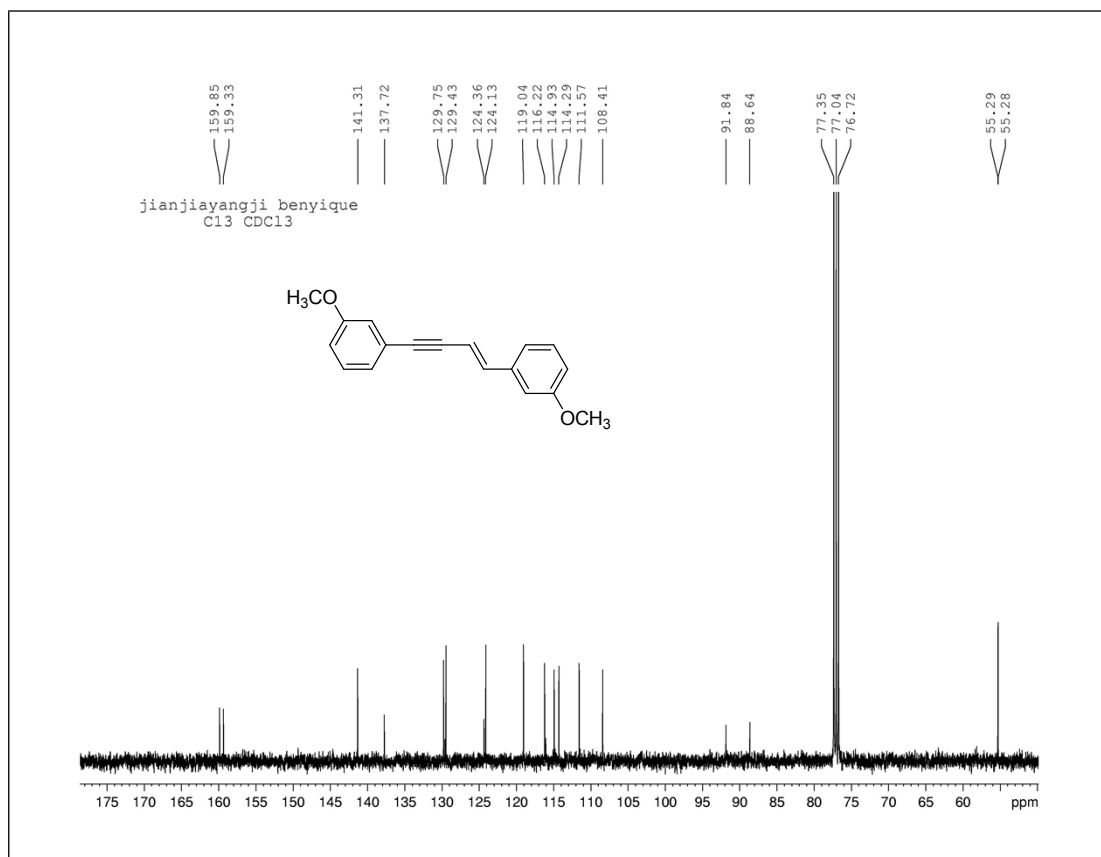
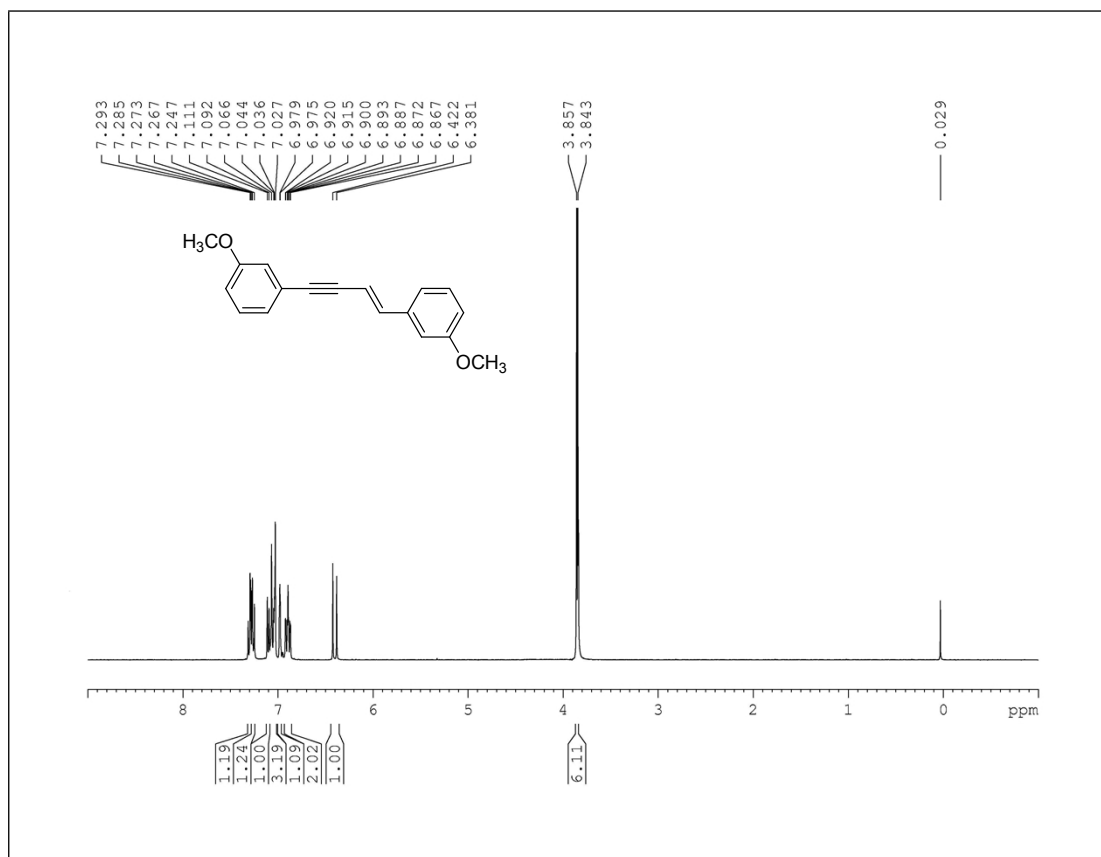
The copies of product 2h (*E*)



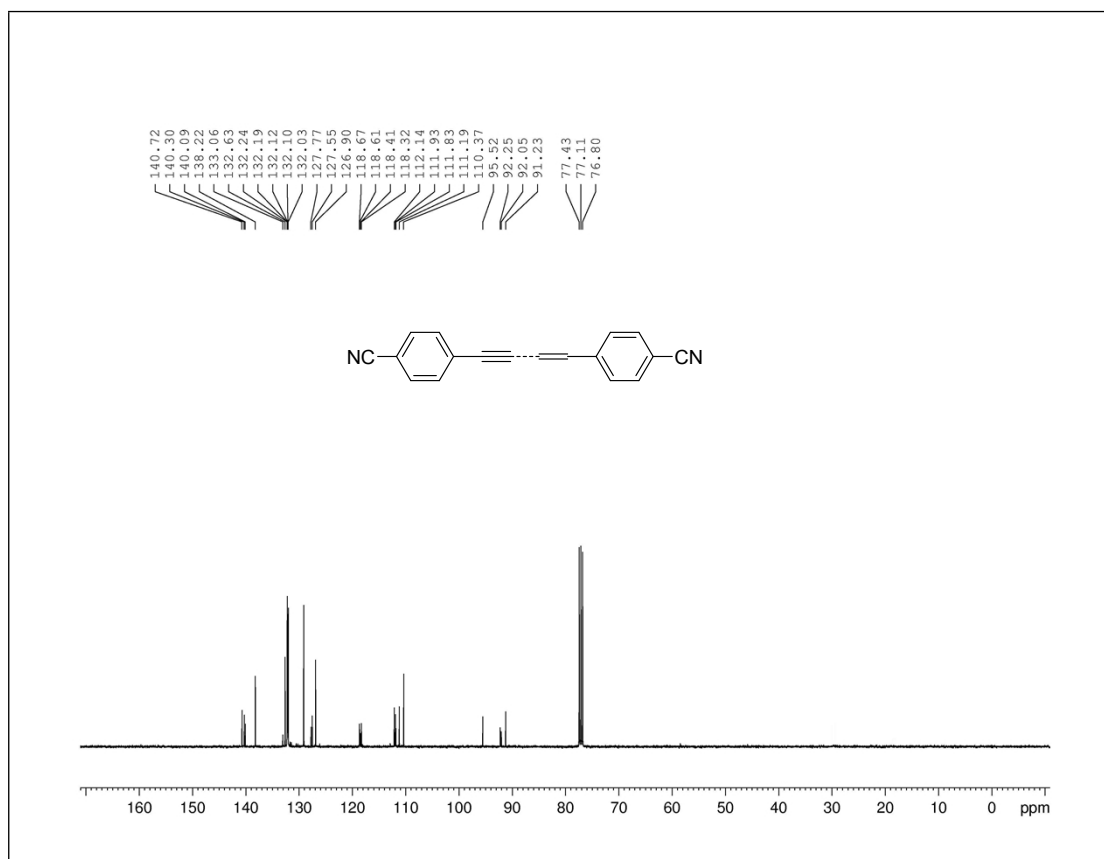
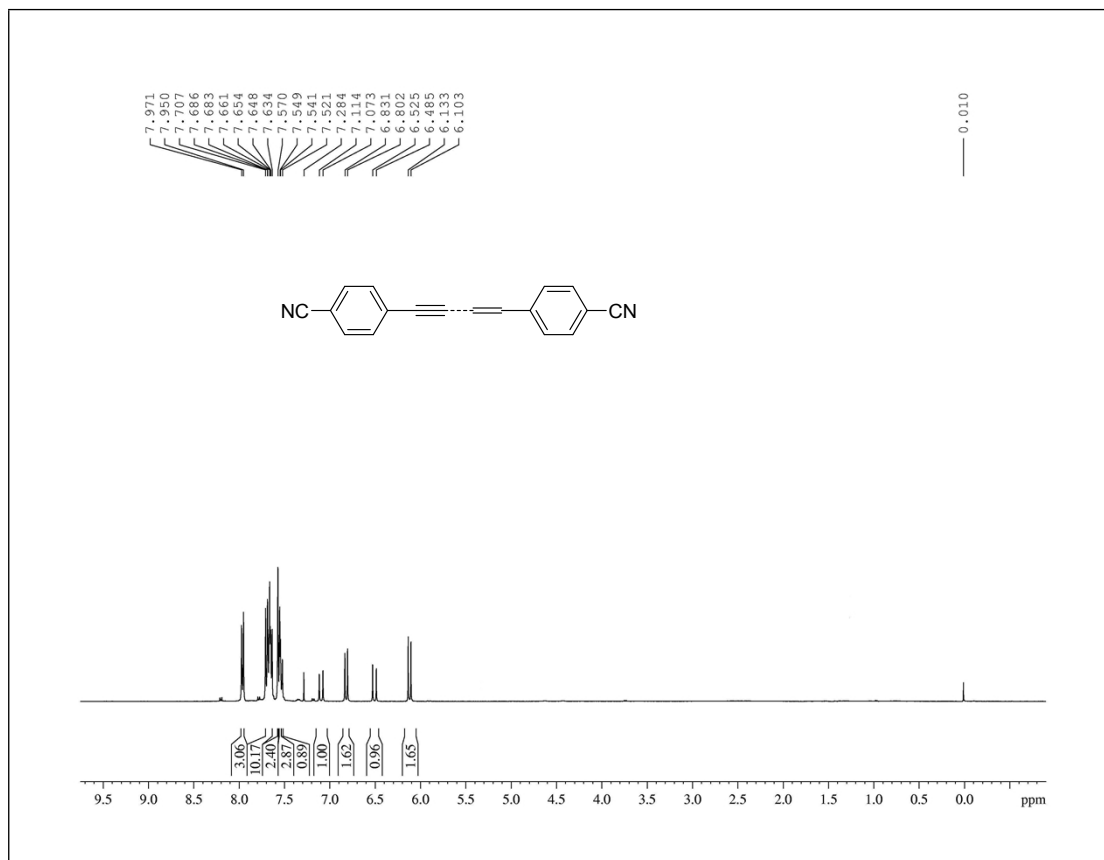
The copies of product 2i (*E/Z*=75:25)



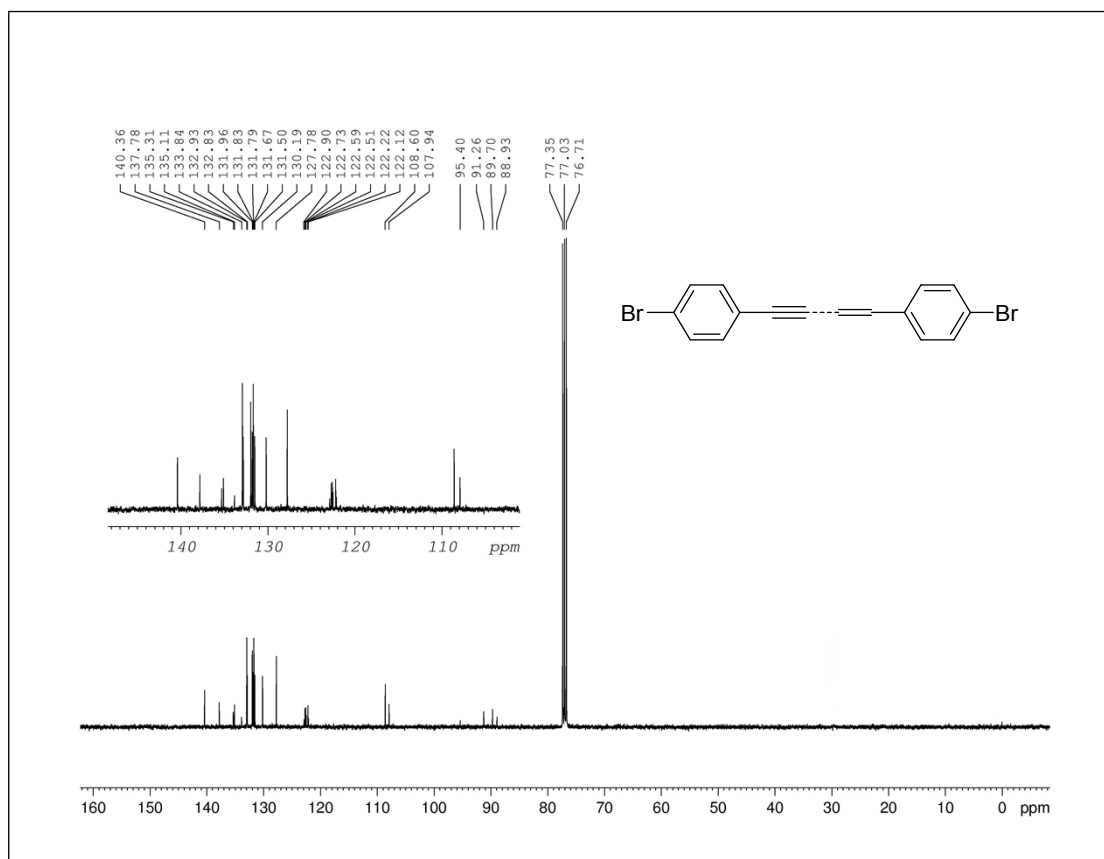
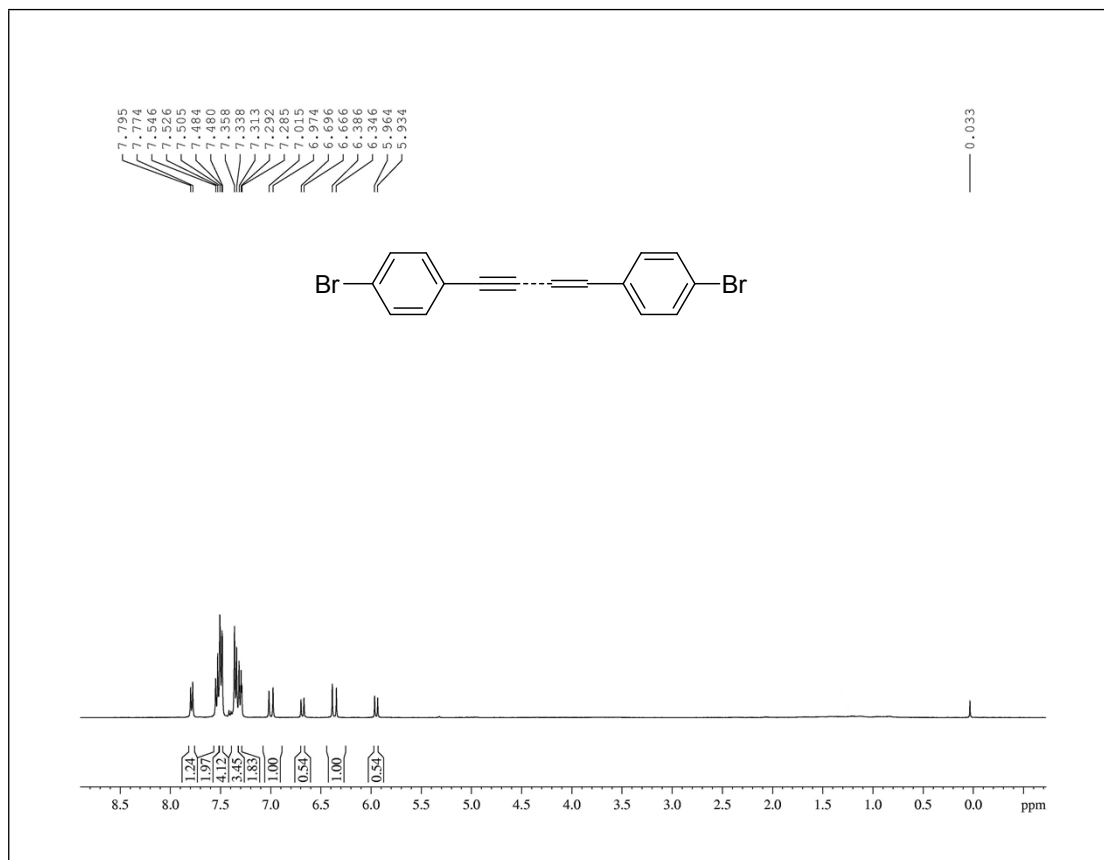
The copies of product 2i (*E*)



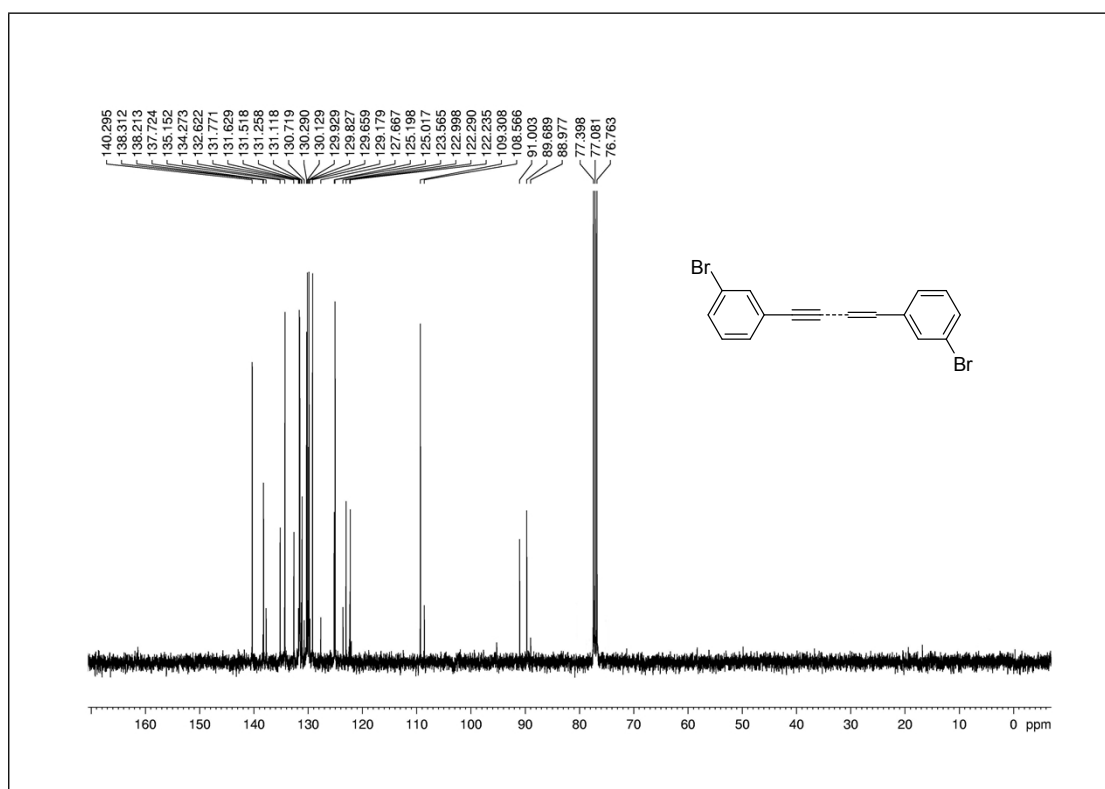
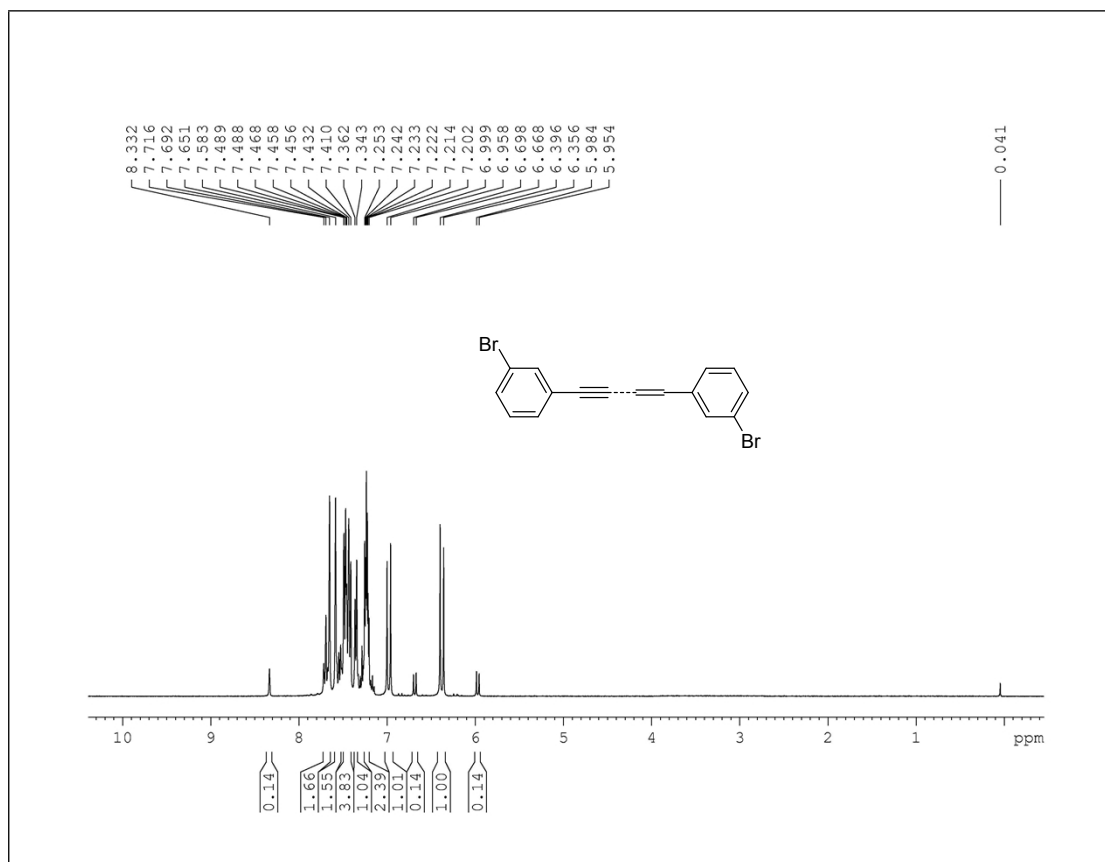
The copies of product 2j (*E/Z*=38:62)



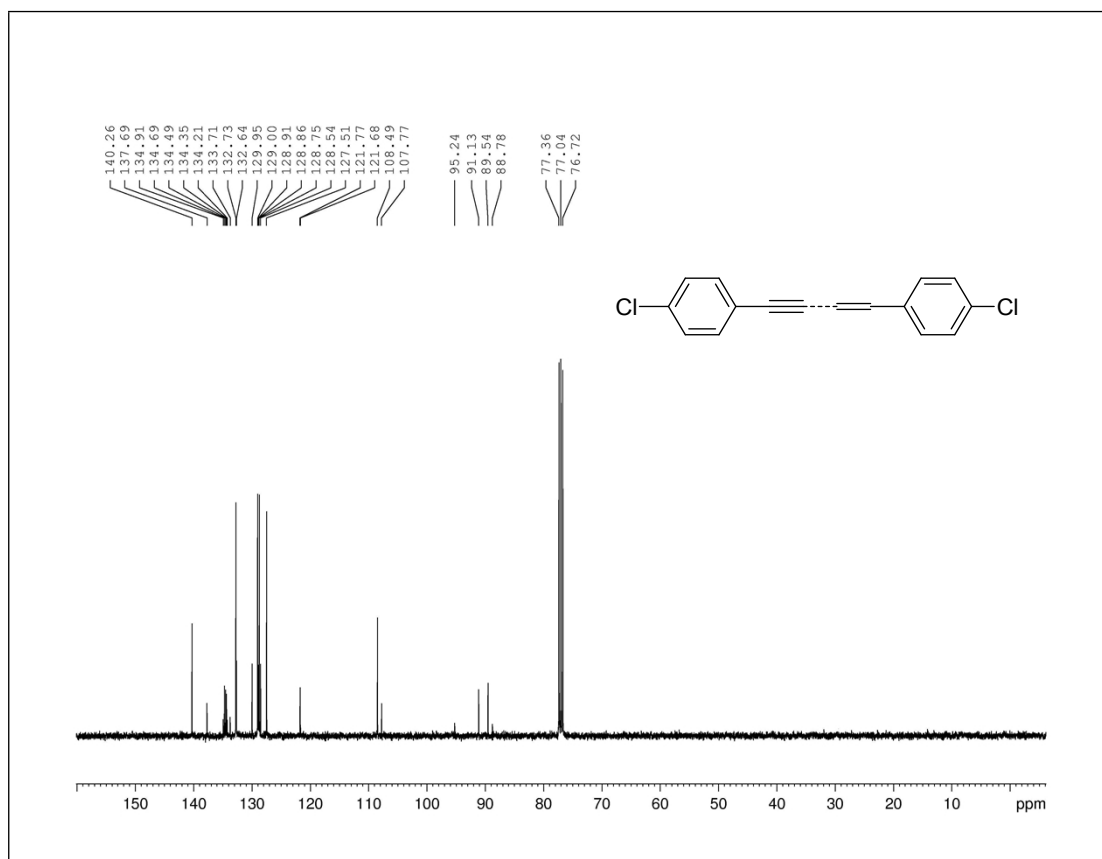
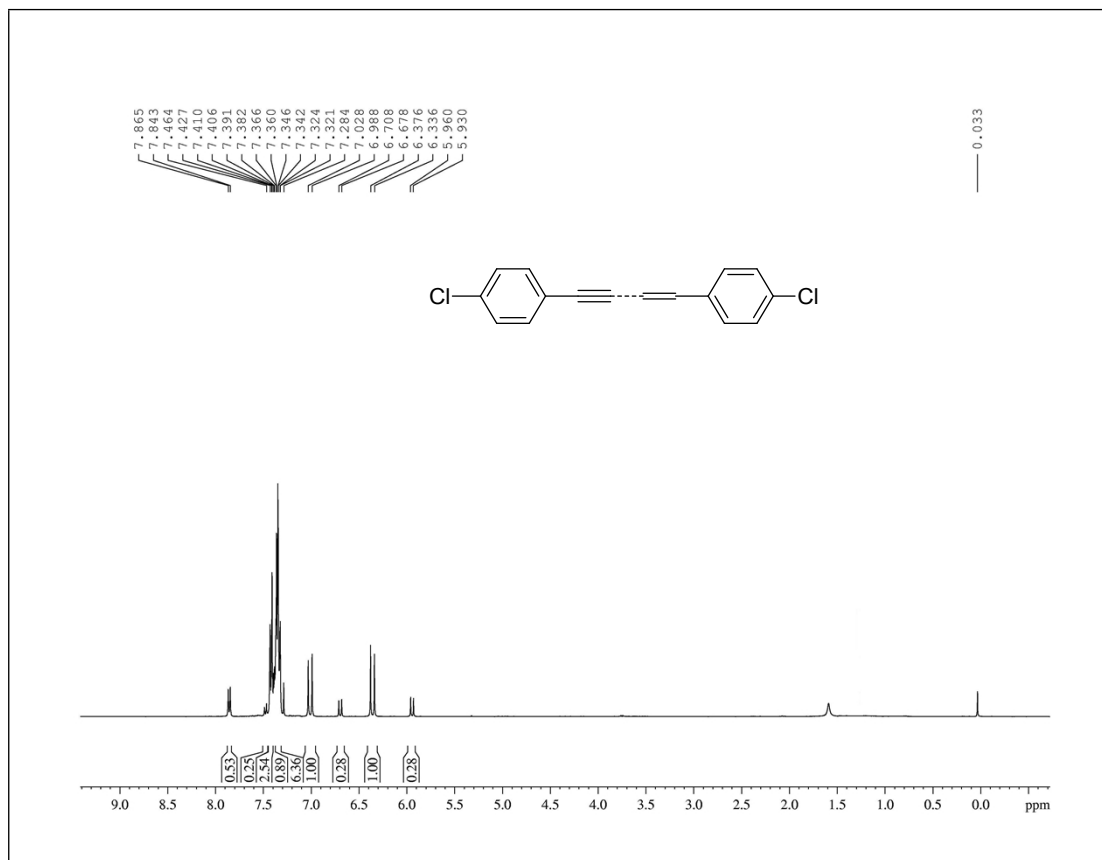
The copies of product 2k (*E/Z*=65:25)



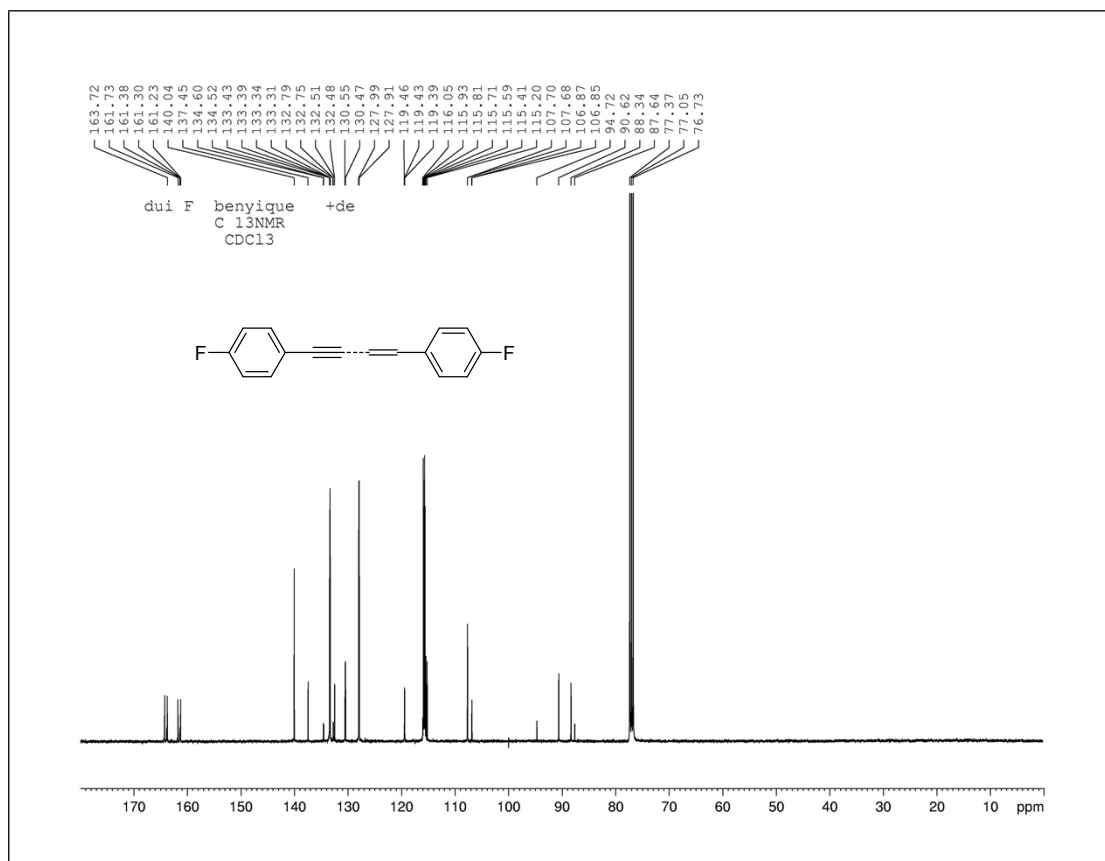
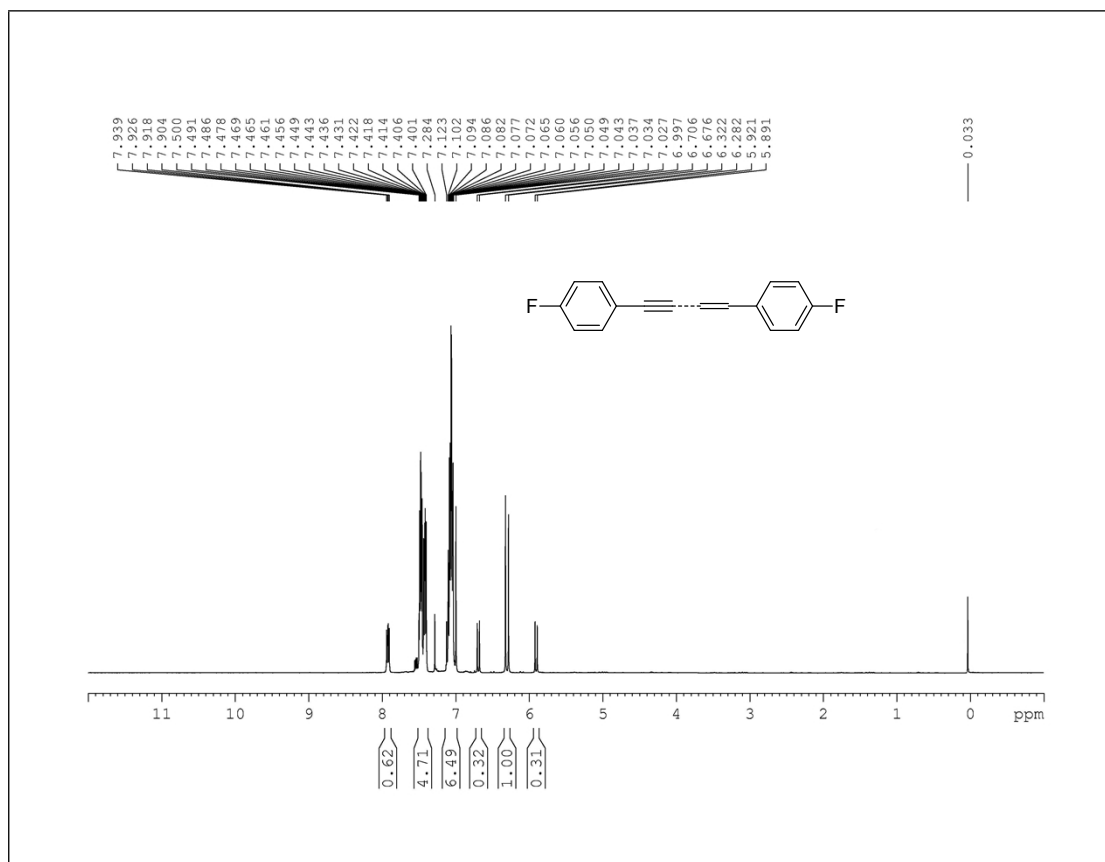
The copies of product 2l (*E/Z*=88:12)



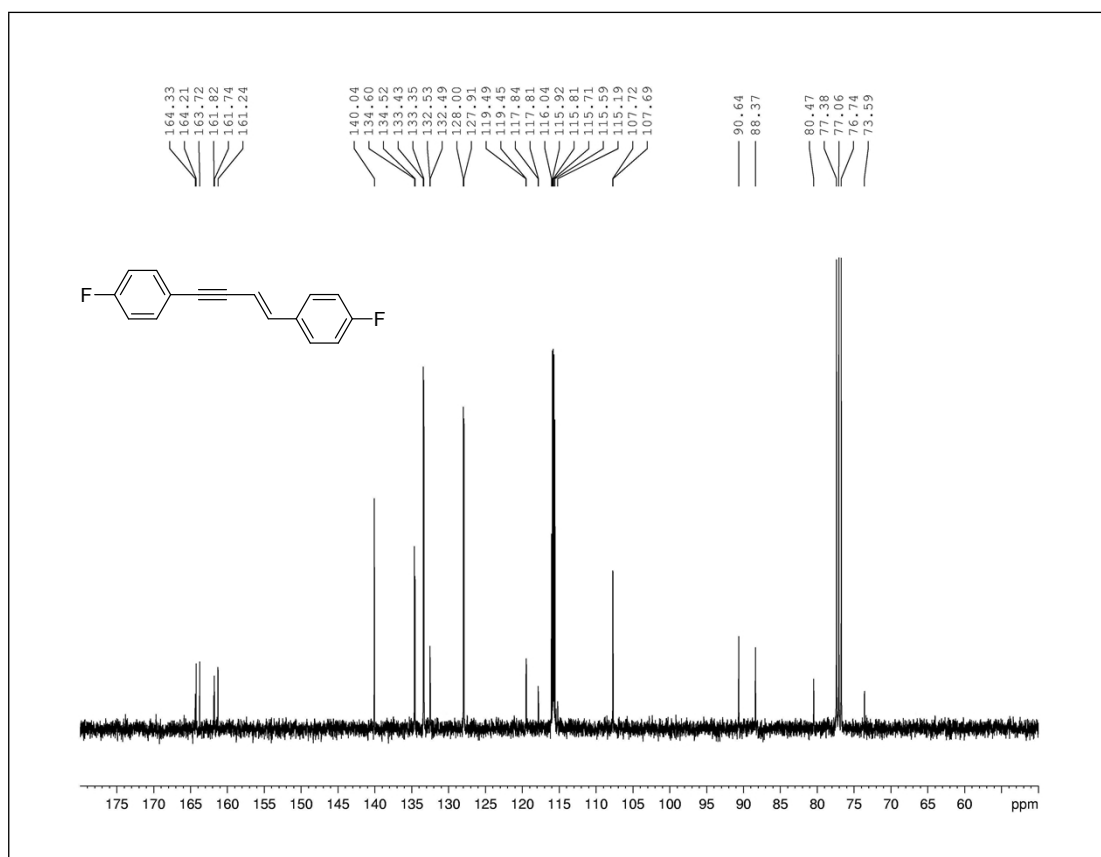
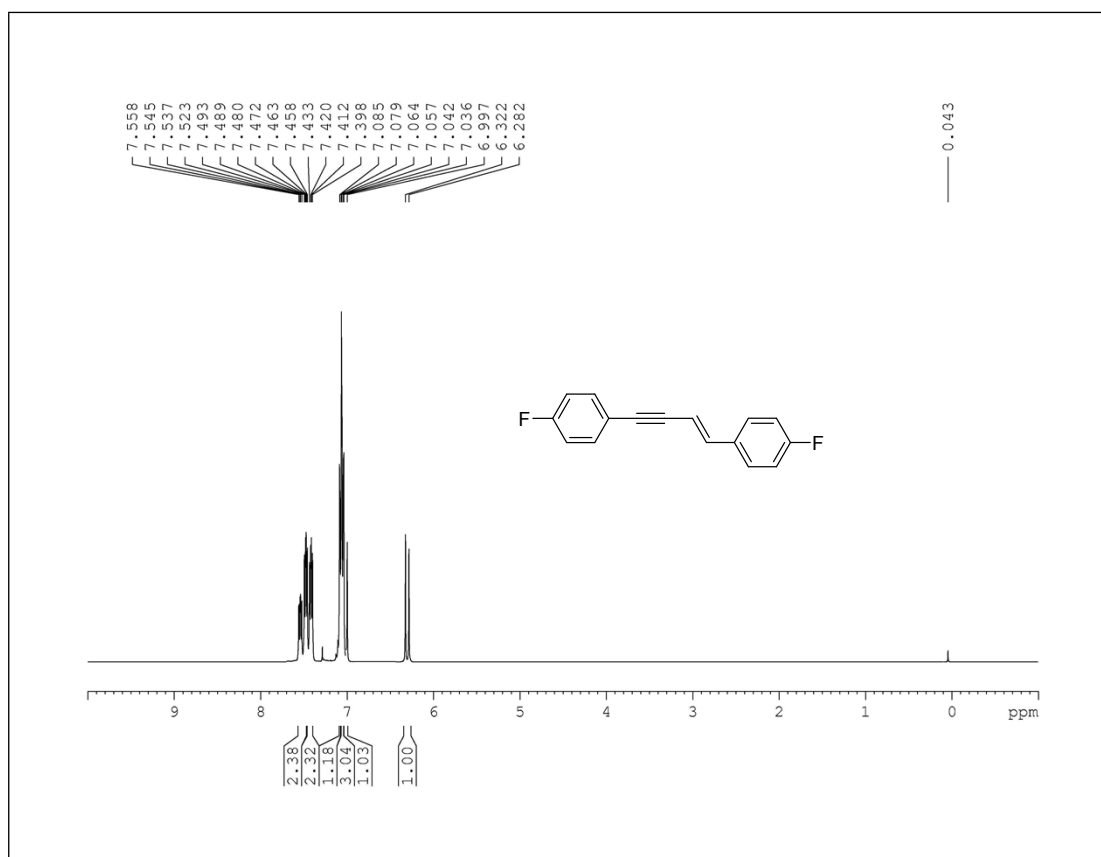
The copies of product 2m (*E/Z*=78:22)



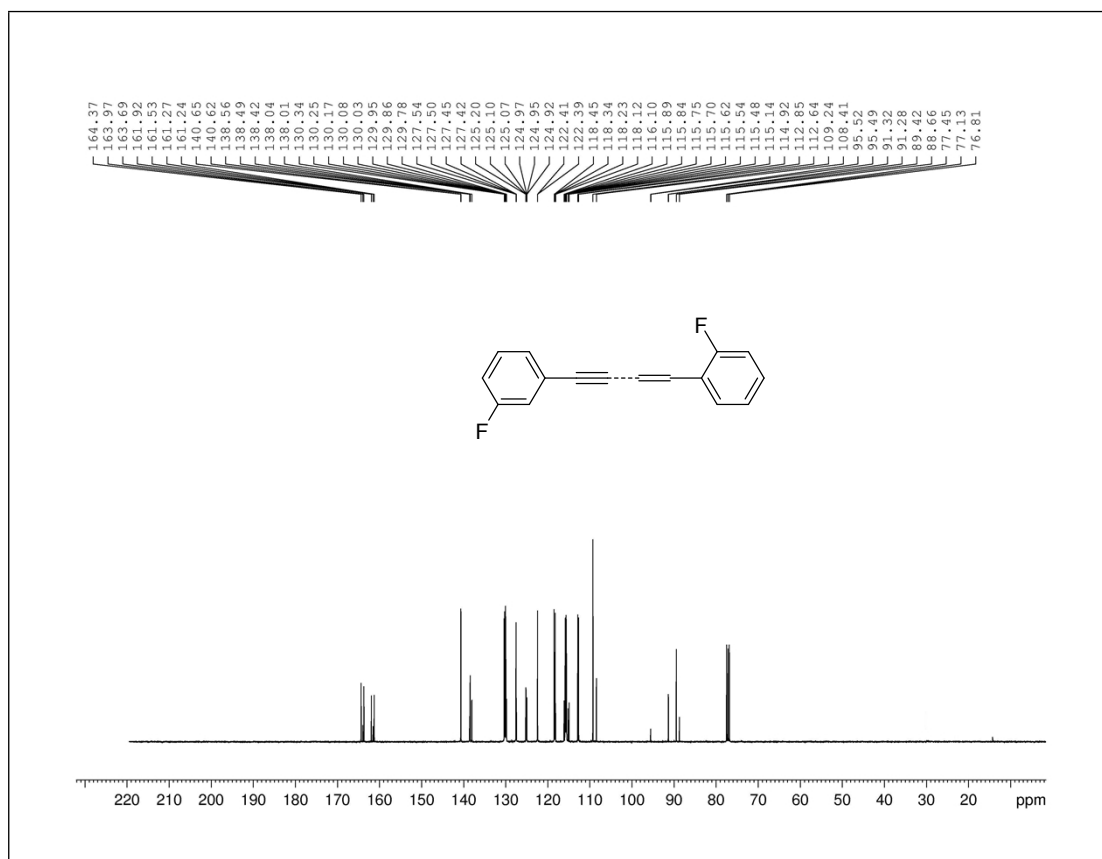
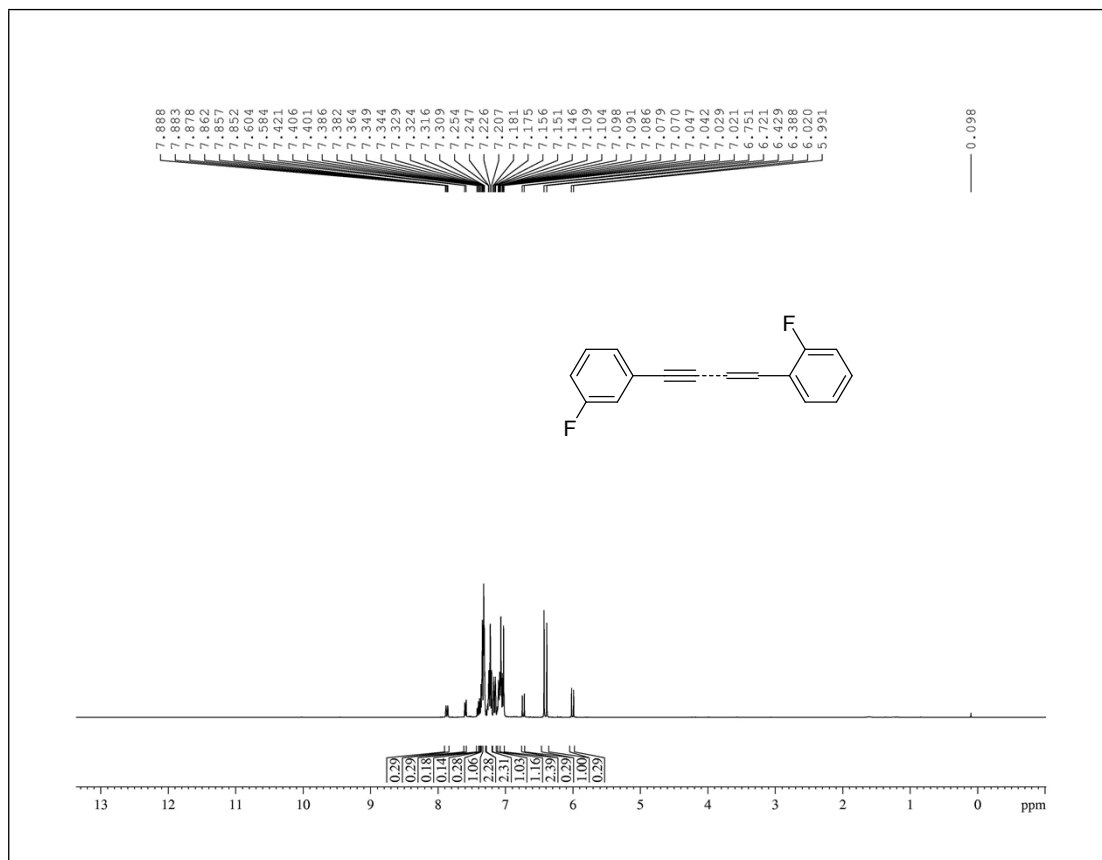
The copies of product 2n (*E/Z*=76:24)



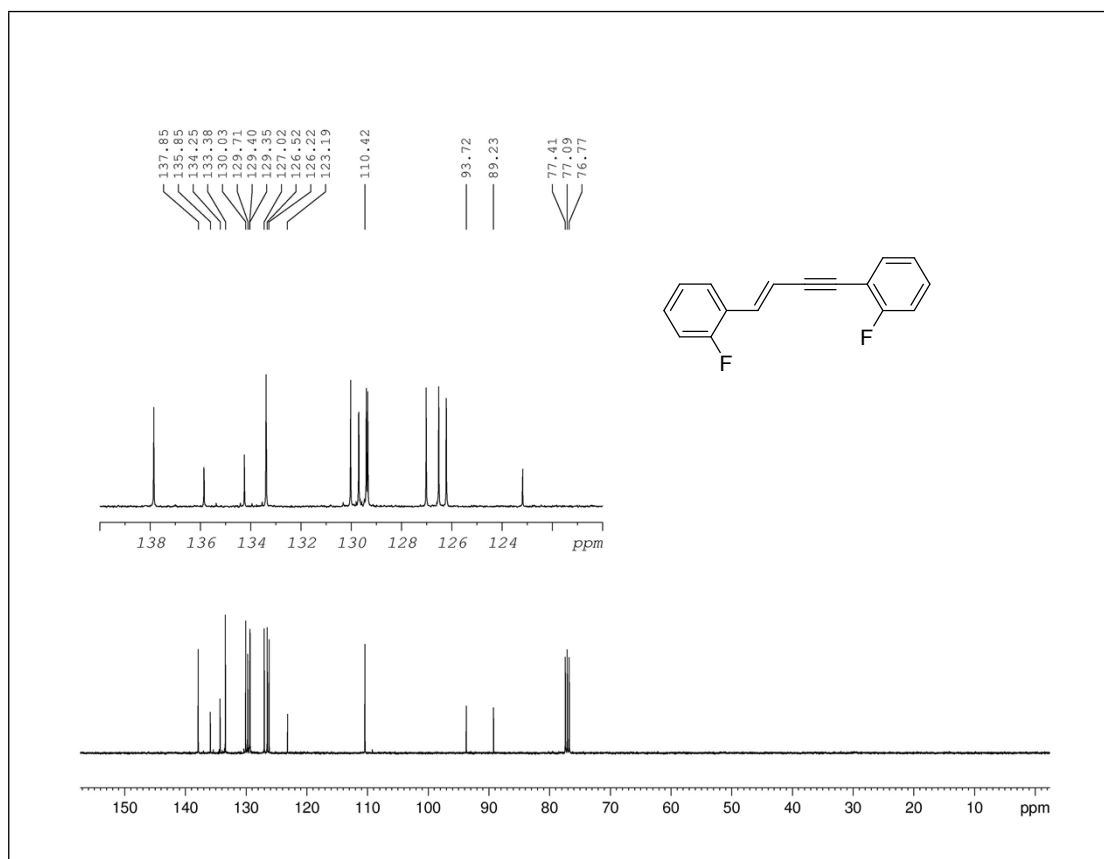
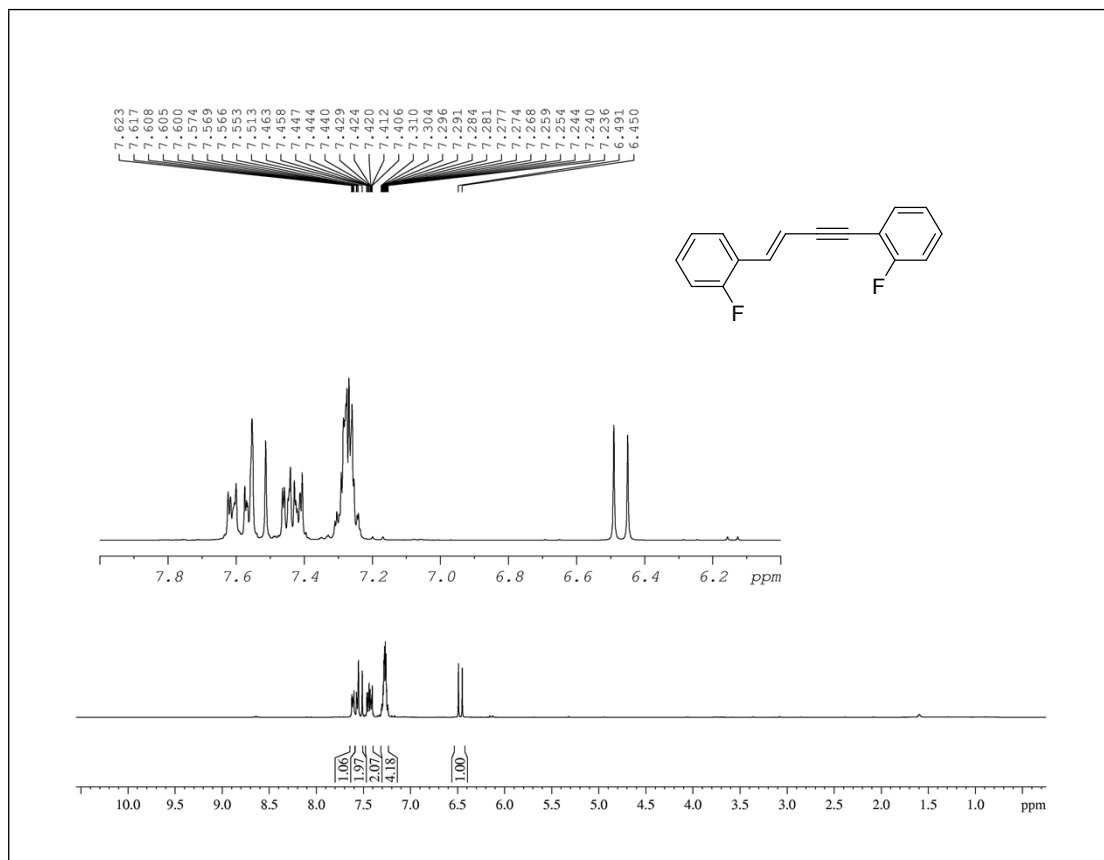
The copies of product (*E*)



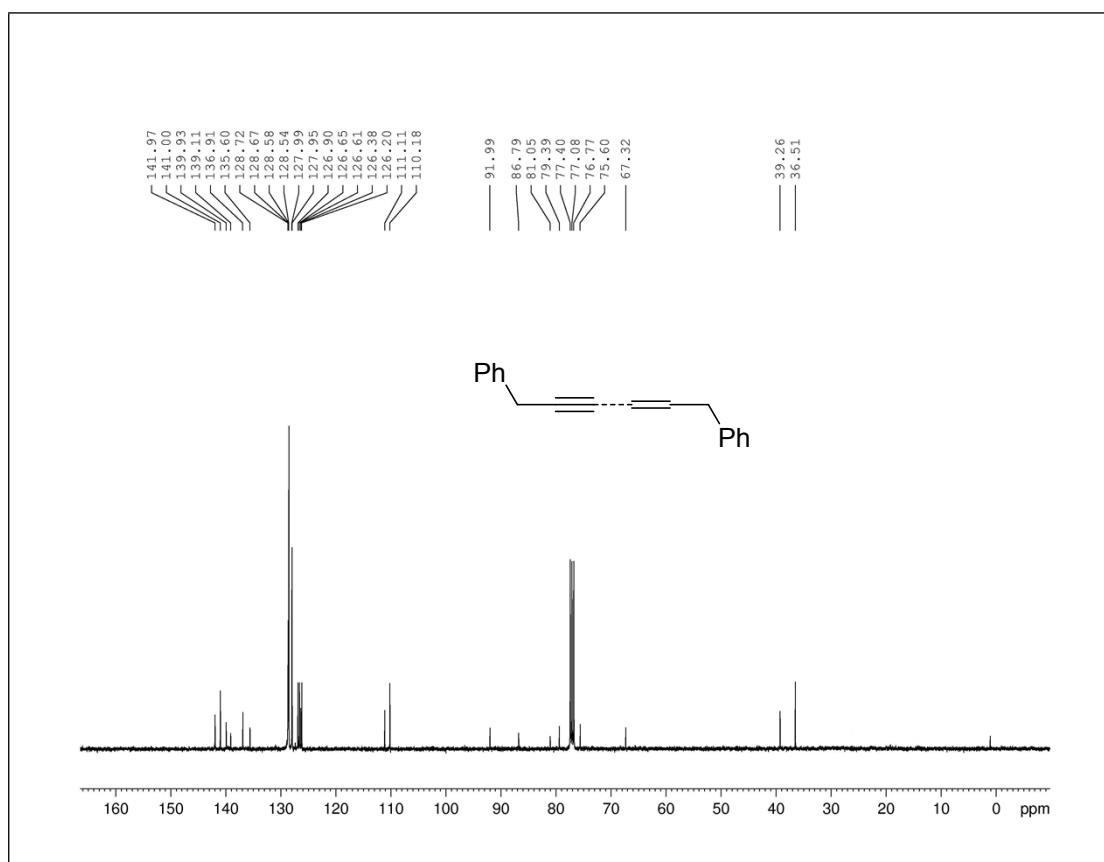
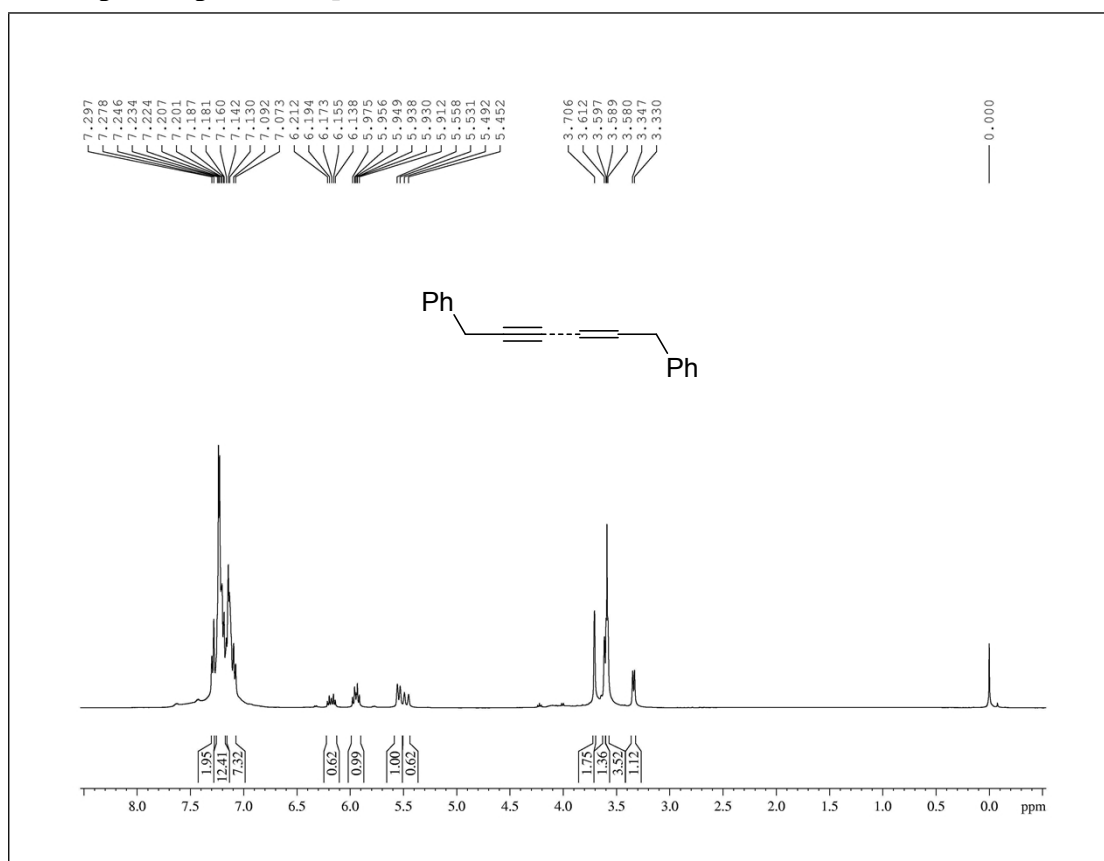
The copies of product 2o (*E/Z*=76:24)



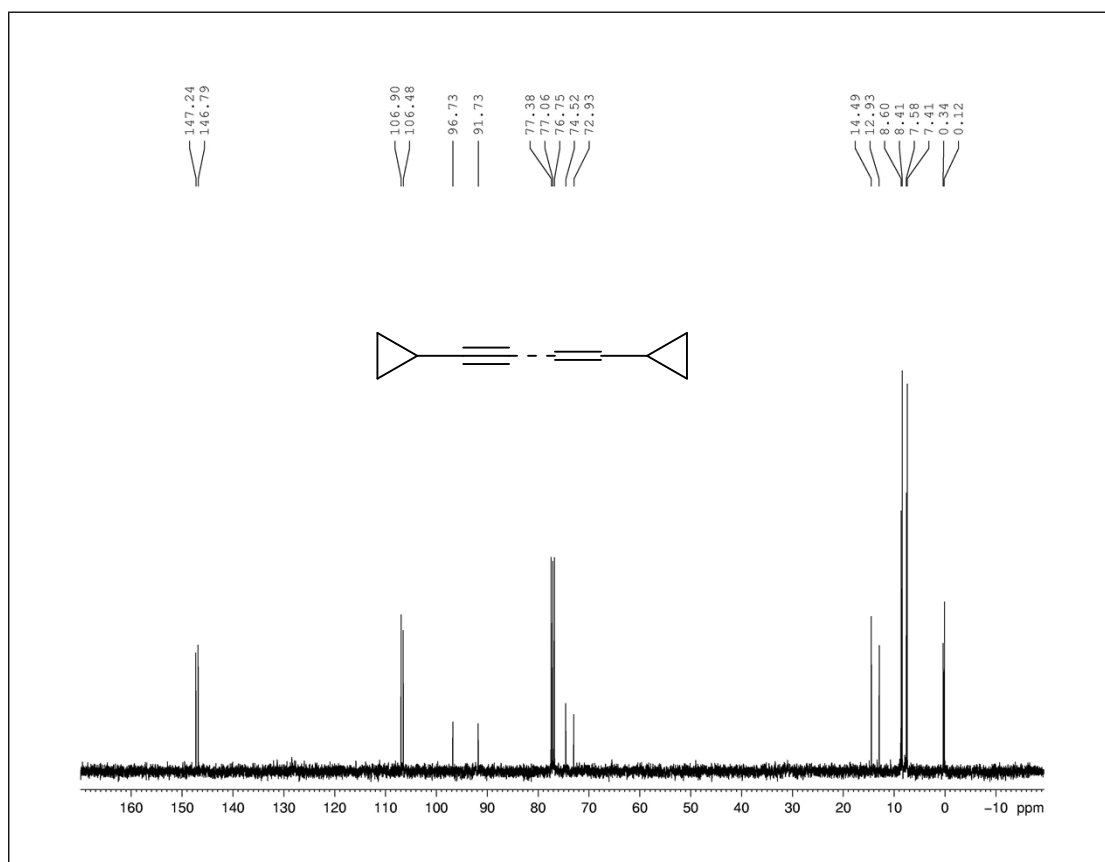
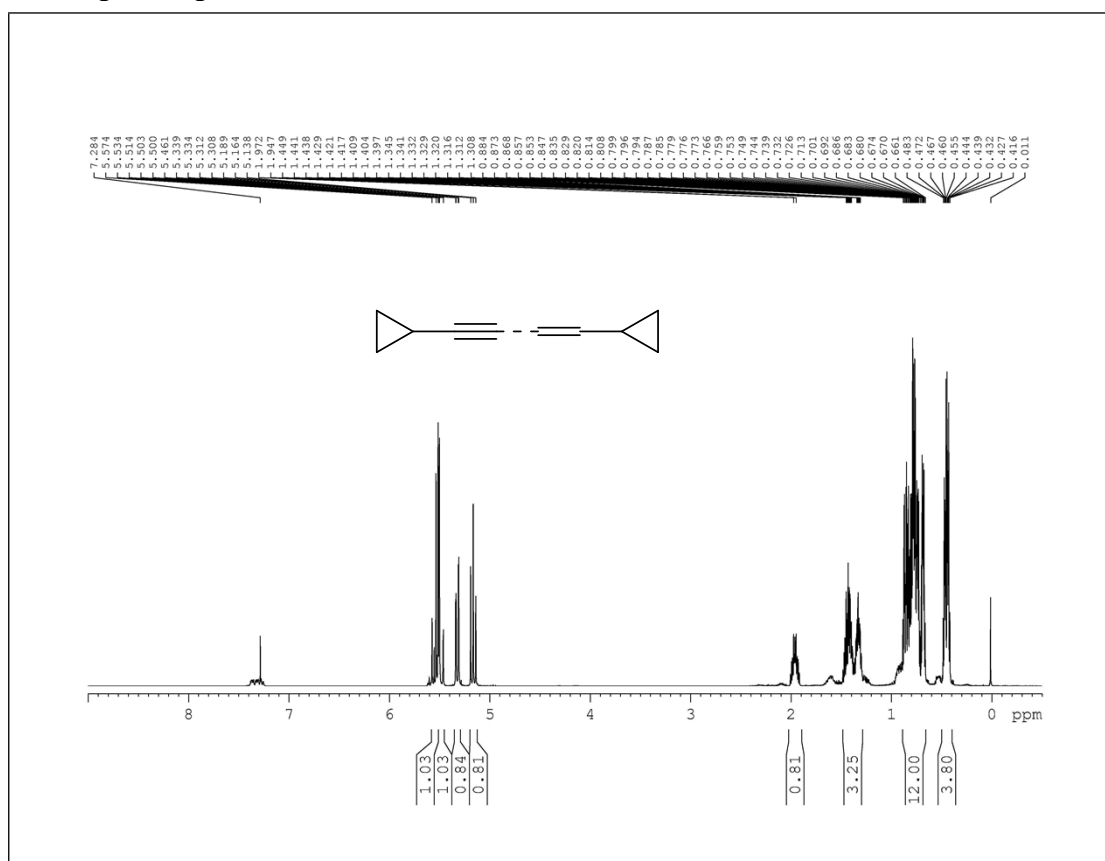
The copies of product 2p (*E*)



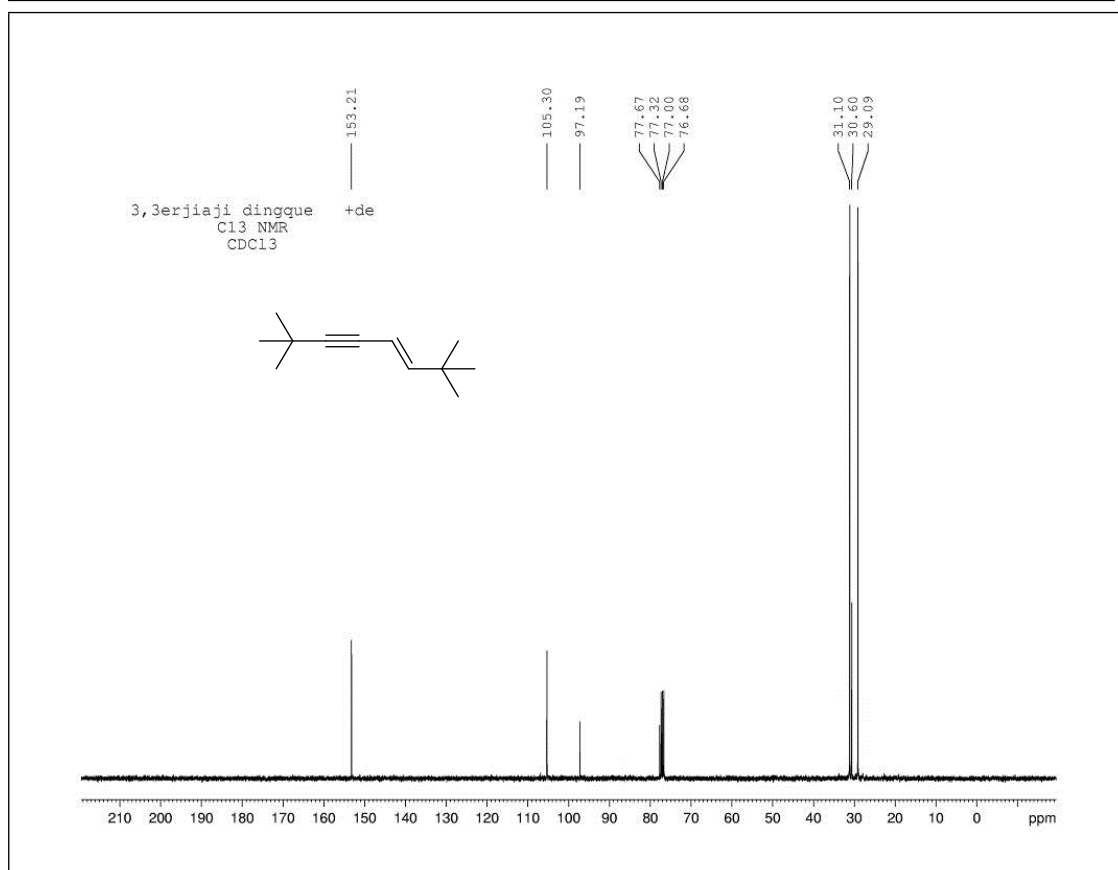
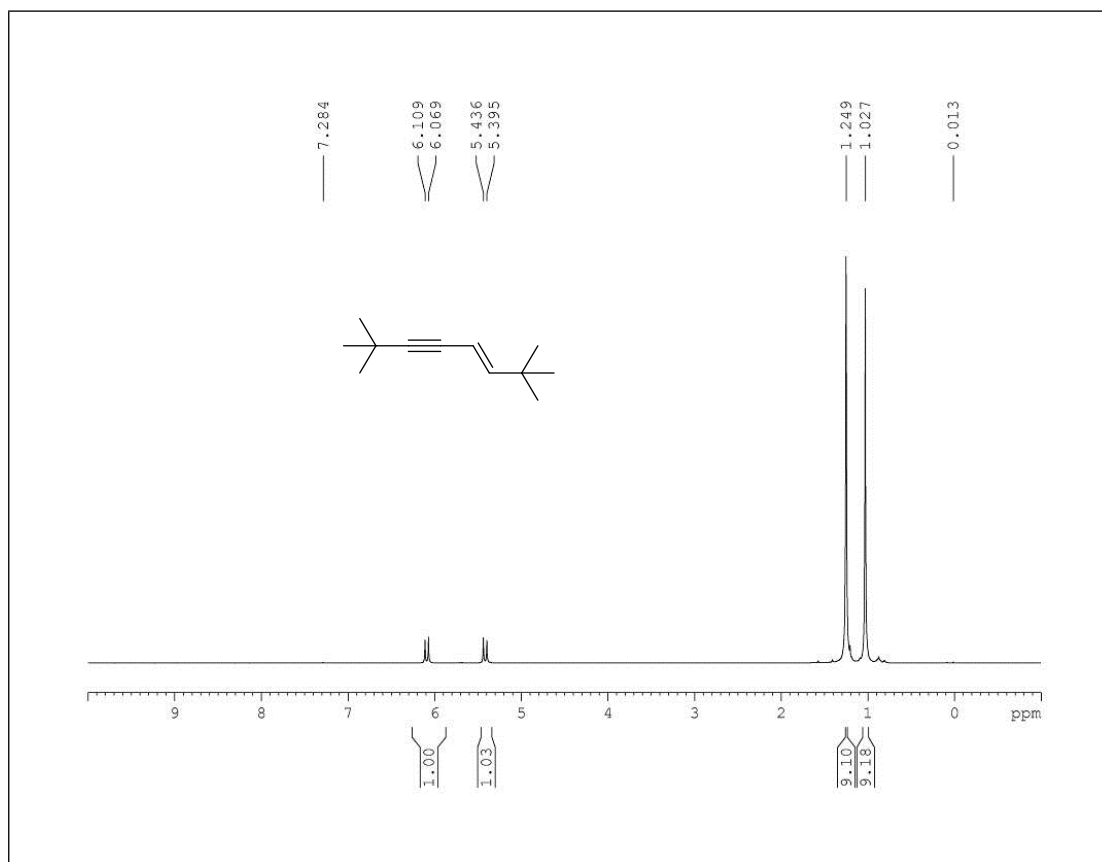
The copies of product 2q:



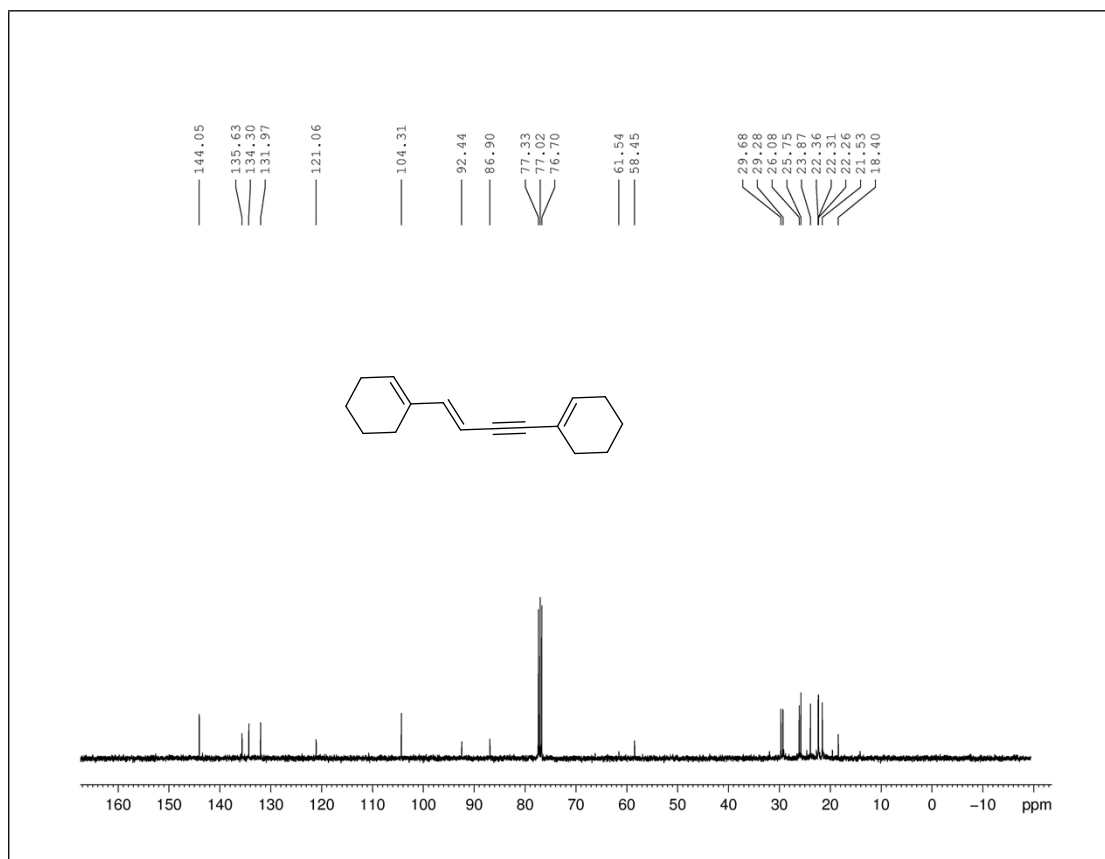
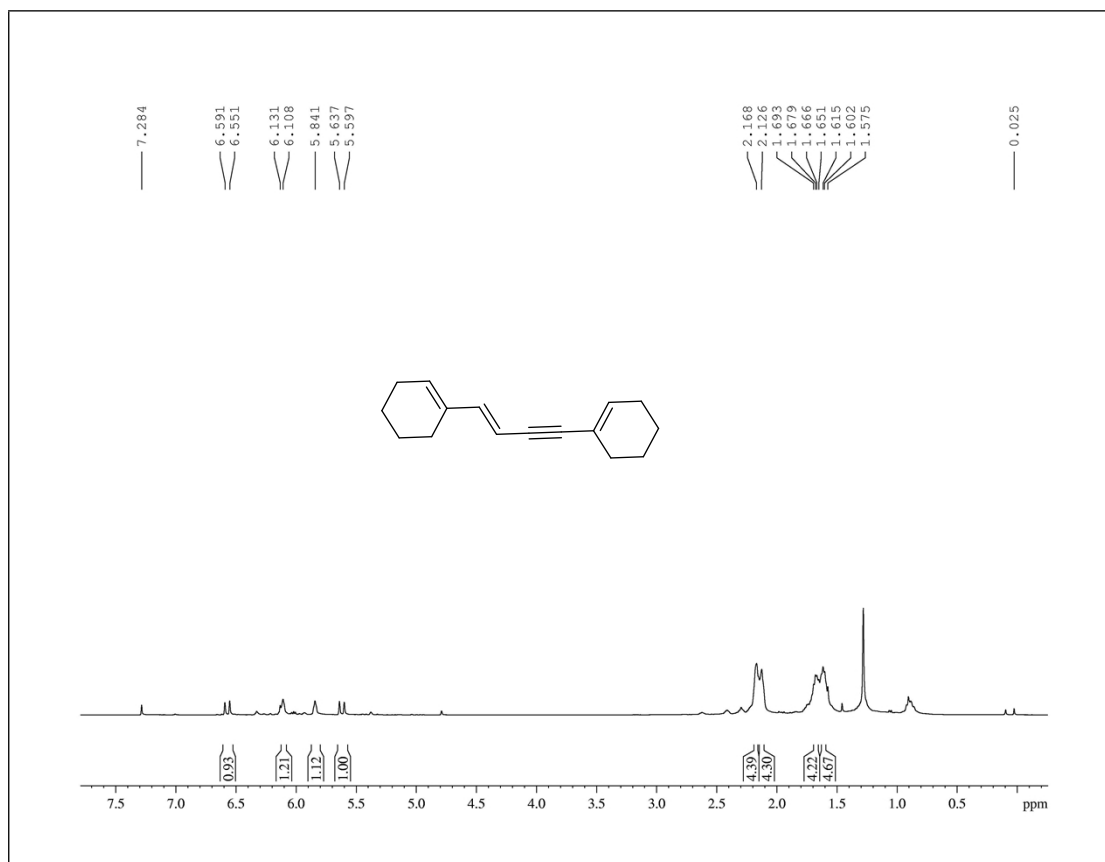
The copies of product 2r:



The copies of product 2s (*E*)



The copies of product 2t:



The copies of product 3b

