Iron Catalyzed Regioselective Dimerization of Terminal Aryl Alkynes

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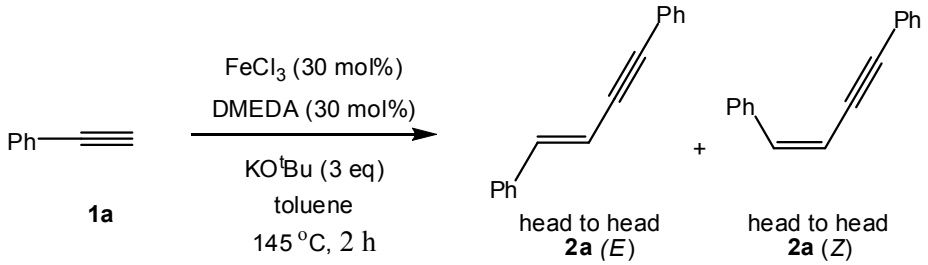
Supporting Information

Contents

1.0 General Information:

All experiments were carried out under an inert atomosphere of argon in flame-dried microwave vials. Solvents were dried using standard procedures reported in Perrin, D. D.; Armarego, W. L. F., Purification of Laboratory Chemicals, 3rd edition, Pergamon Press, Oxford, 1988. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100-200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in $CDCl_3$. **^{1}H NMR** spectra were recorded at 500 MHz using Brüker ADVANCE 500 MHz and JEOL 400 MHz instruments at 278K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard ($CDCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). **^{13}C NMR** spectra were recorded on either a JEOL-400 (100 MHz), or a Brüker ADVANCE 500 MHz (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.23 ppm). Infrared (**FTIR**) spectra were recorded on a Perkin Elmer spectrophotometer with the KBr disk and KBr plate techniques for solid and liquid samples, ν_{max} cm^{-1}.

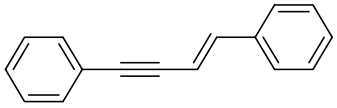
2.0 Dimerization of phenyl acetylene (1a):



Procedure: To an oven dried microwave vial, equipped with magnetic stirrer, under argon atmosphere, KO^{t}Bu (330 mg, 2.94 mmol, 3 equiv), 4 mL of anhydrous toluene and then anhydrous $FeCl_3$ (48 mg, 0.29 mmol, 0.3 equiv) were added. After performing three argon/vacuum cycles under stirring, DMEDA (26 mg, 0.29 mmol, 0.3 equiv) followed by phenyl acetylene **1a** (100 mg, 0.98 mmol, 1 equiv) were added. The mixture was heated at 145 ^{o}C for 2 h. After cooling, the solvent was removed and the crude product was purified by silica gel column chromatography using distilled *n*-hexanes as eluant to give (*E*+*Z*)-1,4-diphenylbut-1-ene-3-yne (**2a**, 73 mg, 73% yield) as colorless solid.

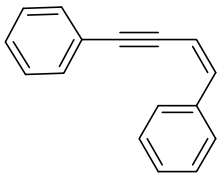
1,4-Diphenylbut-1-ene-3-yne(2a): colorless solid; FT-IR (neat): 2921, 2834, 2360, 2340, 1603, 1506, 1460, 1286, 1250, 1175, 1107; ESI-MS: calcd for $C_{16}H_{13}$ $[M+H]^+$: 205.1017; found, 204.7435.

(*E*)- isomer (2a):[1]



^{1}H NMR (500 MHz): 7.50-7.48 (m, 2H), 7.45-7.43 (m, 2H), 7.37-7.29 (m, 6H), 7.06 (d, J = 16.24 Hz, 1H), 6.40 (d, J = 16.23 Hz, 1H); ^{13}C NMR (125 MHz): 141.3, 136.3, 131.5, 128.7, 128.6, 128.3, 128.2, 126.3, 123.4, 108.1, 91.7, 88.9.

(*Z*)-isomer (2a):[2]

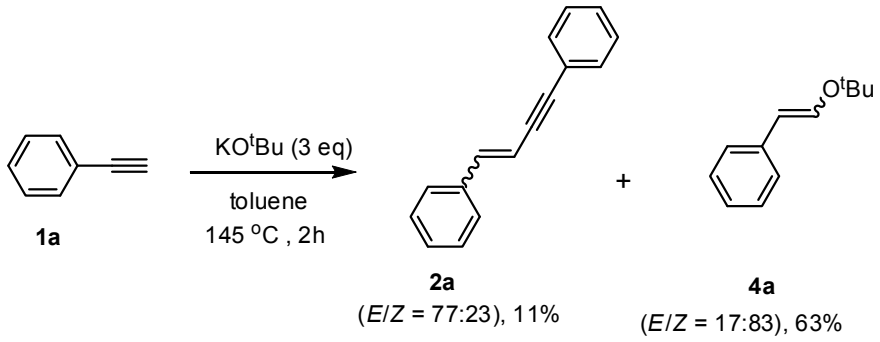


[1] a) M. Rubina and V. Gevorgyan, *J. Am. Chem. Soc*., 2001, **123**, 11107. b) M. Bassetti, C. Pasquini, A. Raneri, D. Rosato, *J. Org. Chem.,* 2007, **72**, 4558. c) S. Ge, V. F. Q. Norambuena and B. Hessen, *Organometallics* 2007, **26**, 6508.

[2] a) M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki and T.Miyamoto, *J. Am. Chem. Soc.*, 2003, **125**, 1184. b) C. S. Yi and N. Liu, Organometallics, 1996, **15**, 3968. c) K. Komeyama, T. Kawabata, K. Takehira and K. Takaki, *J. Org. Chem*. 2005, **70**, 7260.

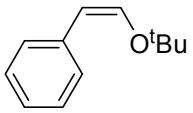
Data from a mixture of *E*/*Z* = 66/34; ^{1}H NMR (500 MHz): 7.93 (d, *J* = 7.4 Hz, 2H), 7.52-7.28 (m, 8H, merged with *E* isomer), 6.71 (d, *J* = 11.9 Hz, 1H), 5.93 (d, *J* = 11.9 Hz, 1H); ^{13}C NMR (125 MHz): 138.7, 136.6, 131.5, 128.8, 128.5, 128.4, 128.3, 128.3, 123.5, 107.4, 95.8, 88.2.

Reaction of phenyl acetylene without added $FeCl_3$:



Procedure: To an oven-dried argon-flushed microwave vial, equipped with magnetic stirrer, KO^{t}Bu (330 mg, 2.94 mmol, 3 equiv), 4 mL of toluene followed by phenyl acetylene (100 mg, 0.98 mmol, 1 equiv) were added. The mixture was heated at 145 °C for 2 h. After cooling the solvent was removed and crude product was purified by silica gel column chromatography using distilled *n*-hexanes as eluant to give (*E*+*Z*)-1,4-diphenylbut-1-ene-3yne (**2a**, 11 mg, 11% yield) and (*E*+*Z*)-(2-tert-butoxyvinyl)benzene (**4a**, 63 mg, 63% yield) as colorless solid.

(*Z*)-(2-tert-butoxyvinyl)benzene (4a):[3]



^{1}H NMR (500MHz): 7.63-7.61 (m, 2H), 7.29-7.25 (m, 2H), 7.13-7.10 (m, 1H), 6.45 (d, *J* = 7.1 Hz, 1H), 5.24 (d, *J* = 7.1 Hz, 1H), 1.4 (s, 9H); ^{13}C NMR (125 MHz): 140.9, 136.5, 128.1, 125.3, 105.7, 28.1; FT-IR (neat): 3404, 2922, 2852, 1609, 1449, 1374, 1267, 1086, 1041.

[3] M. Newcomb, M.-H. Le Tadic-Biadatti, D. L. Chestney, E. S. Roberts and P. F. Hollenberg, *J. Am. Chem. Soc.,* 1995, **117,** 12085.

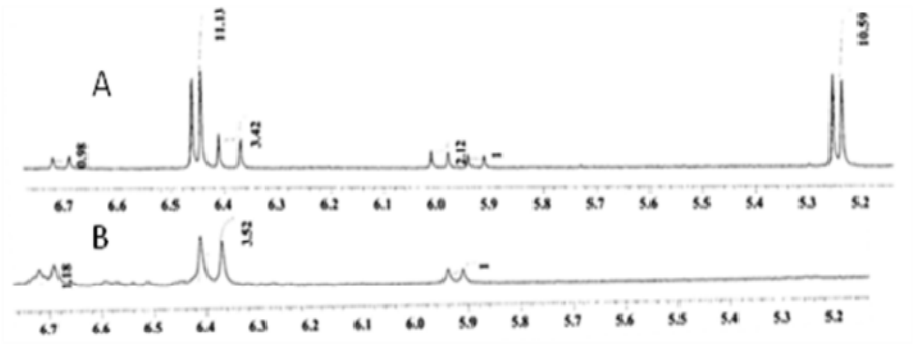
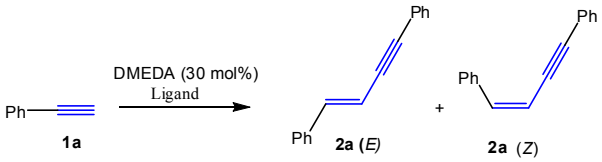


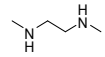
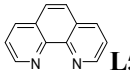
Figure 1: Selected ^{1}H NMR spectrum of unpurified reaction mixture of dimerization of phenyl acetylene **1a** using (A) KO^{t}Bu; (B) $FeCl_3$, **L**, KO^{t}Bu.

3.0 Dimerization of phenyl acetylene (1a) using different ligands:

Various bidentate ligands **L1** to **L6** were also examined for this dimerization reaction (Table 1). Ligands **L2** to **L3** gave head-to-head dimer **2a** in good yields (Table 1, entries 2 and 3). While product **2a** was isolated in moderate yields using 2,2'-bipyridine, **L3** (entry 5) and 1,10-phenanthroline, **L5** (entry 6). The reaction also proceeded using 8-hydroxyquinoline, **L6** to give compound **2a** in 58% yield (entry 7).

Table 1. Iron catalyzed dimerization of phenyl acetylene **1a** using different ligands[a]



Entry	Ligand (30 mol%)	Ratio (*E*/*Z*),[b] Yield[c] (%) of **2a**
1	No ligand	77:23, 42
2	 **L**	78:22, 73
3	 **L2**	75:25, 60
4	 **L3**	77:23, 68
5	 **L4**	75:25, 45
6	 **L5**	76:24, 43
7	 **L6**	83:17, 58

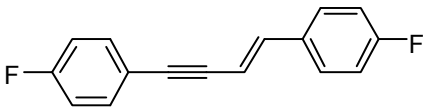
[a]All reactions were carried out using 30 mol% of $FeCl_3$, 3 equiv of KO^{t}Bu in toluene, [b]*E*:*Z* ratios were determined by ^{1}H NMR analysis of crude reaction mixture, [c]isolated yields after chromatography.

4.0 General procedure for dimerization of aryl acetylenes 1:

To an oven dried microwave vial, equipped with magnetic stirrer, under argon atmosphere, KO^{t}Bu (3 equiv), anhydrous toluene (4 mL/1 mmol) and then anhydrous $FeCl_3$ (0.3 equiv) were added. After performing three argon/vacuum cycles under stirring, DMEDA (0.3 equiv) followed by aryl acetylene **1** (1 equiv) were added. The mixture was heated at 145 ^oC for 2 h. After cooling, the solvent was removed and the crude product was purified by silica gel column chromatography using distilled *n*-hexanes/EtOAc (100:0 to 90:10) as eluant to give the corresponding enynes **2**.

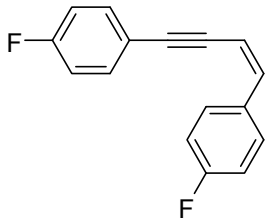
1,4-Di-*p*-fluorophenylbut-1-en-3-yne (2b): obtained as a colorless solid; Data from a mixture of *E*/*Z* = 66/34; FT-IR (neat): 3717, 2928, 2855, 2360, 2336, 1598, 1513, 1230, 1091, 1040; ESI-MS: calcd for $C_{16}H_{11}F_2$ $[M+H]^+$: 241.0829; found, 241.1038.

(*E*)-isomer (2b):[4]



^{1}H NMR (400 MHz): 7.48-7.37 (m, 4H), 7.09-6.97 (m, 5H, overlapped with one vinyl proton), 6.27 (d, *J* = 16.2, 1H); ^{13}C NMR (125 MHz): data from a mixture of *E*/*Z* = 66/34 ; 162.9 (d, *J* = 248.9 Hz), 162.4 (d, *J* = 249.7 Hz), 140.0, 133.3 (d, *J* = 8.3 Hz), 130.4 (d, *J* = 8.0 Hz), 127.9 (d, *J* = 8.1 Hz), 119.4 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.9 Hz), 107.7 (d, *J* = 2.1 Hz), 90.6, 88.3.

(*Z*)-isomer (2b):[4,2c]

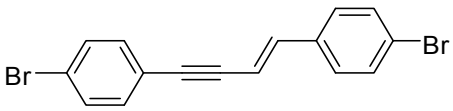


^{1}H NMR (400 MHz): 7.89 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.45 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.09-7.01 (m, 4H), 6.66 (d, *J* = 11.9 Hz, 2H), 5.88 (d, *J* = 11.9 Hz, 2H), ^{13}C NMR (125 MHz): data from a mixture of isomers containing *E*/*Z* = 66/34; 162.6 (d, *J* = 249.9 Hz), 162.5 (d, *J* = 248.9 Hz), 137.4, 133.3 (d, *J* = 8.2 Hz), 132.7 (d, *J* = 3.5 Hz), 132.5 (d, *J* = 3.1 Hz), 119.4 (d, *J* = 3.9 Hz), 115.6 (d, *J* = 21.9 Hz), 115.2 (d, *J* = 21.5 Hz), 106.9, 94.6, 87.6.

[4] a) A. Hijazi, K. Parkhomenko, J. P. Djukic, A. Chemmi and M. Pfeffer, *Adv. Synth. Catal*., 2008, **350**, 1493. b) W. Weng, C. Guo, R. Çelenligil-Çetin, B. M. Foxman and O. V. Ozerov, *Chem. Commun.,* 2006, 197. c) C. C. Lee, Y. C. Lin, Y. H. Liu and Y. Wang, *Organometallics,* 2005, **24**, 136. d) X. Chen, P. Xue, H. H. Y. Sung, I. D. Williams, M. Peruzzini, C. Bianchini and G. Jia, *Organometallics* 2005, **24***,* 4330.

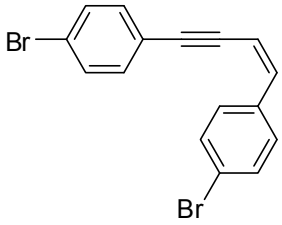
1,4-Di-*p*-bromophenylbut-1-en-3-yne (2c):[4c] obtained as a colorless solid; data from mixture of isomers containing *E*/*Z* = 59/41; FT-IR (neat): 3719, 2920, 2851,2363, 2333, 1600, 1484, 1070; ESI-MS: calcd for $C_{16}H_{10}Br_2$ $[M]^+$: 359.9149; found, 359.4942.

(*E*)-isomer (2c):[4c]



^{1}H NMR (500 MHz): 7.49-7.45 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (125 MHz): 140.3, 135.1, 132.8, 131.9, 131.7, 127.8, 122.7, 122.5, 122.1, 108.6, 89.7, 88.9.

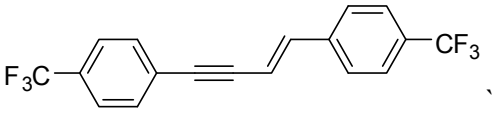
(*Z*)-isomer (2c):



^{1}H NMR (500 MHz): 7.76 (d, *J* = 8.5 Hz, 2H), 7.52-7.50 (m, 4 H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 11.9 Hz, 1H), 5.91 (d, *J* = 11.9 Hz, 1H), ^{13}C NMR (125 MHz): 137.8, 135.3, 132.9, 131.8, 131.5, 130.2, 122.9, 122.6, 122.2, 107.9, 95.4, 91.2.

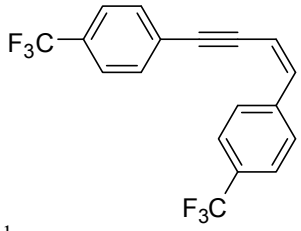
1,4-Di-*p*-trifluoromethylphenylbut-1-ene-3-yne (2d): obtained as a colorless solid; data from a mixture of *E*/*Z* = 75:25; FT-IR (neat): 3388, 2918, 2851, 2367, 2193, 1606, 1401, 1323, 1175, 1130, 1069; ESI-MS: calcd for $C_{18}H_{10}F_6Na$ $[M+Na]^+$: 363.0584; found, 362.5938.

(*E*)-isomer (2d):[1a,1b]



^{1}H NMR (500 MHz): 7.62-7.54 (m, 8H), 7.10 (d, *J* = 16.5 Hz, 1H), 6.47 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (125 MHz); 140.6, 139.3, 131.8, 130.4 (q, *J* = 32.2 Hz), 130.0 (q, *J* = 32.4 Hz), 126.9, 125.8, 125.8 (d, *J* = 4.1 Hz), 125.3 (d, *J* = 4.0 Hz), 122.9 (q, *J* = 270.3 Hz), 122.8 (q, *J* = 270.6 Hz), 110.2, 91.5, 90.5

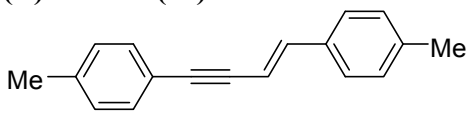
(*Z*)-isomer (2d):[2a]



^{1}H NMR (500 MHz): 7.99 (d, J = 7.9 Hz, 2H), 7.62-7.54 (m, 6H), 6.80 (d, J = 12.2 Hz, 1H), 6.05 (d, J = 12.2 Hz, 1H). ^{13}C NMR (125 MHz): 139.5, 138.1, 131.7, 130.3 (q, J = 32.2 Hz), 130.1 (merged with *E* isomer), 128.8, 126.5, 125.3 (q, J = 4.0 Hz), 124.9 (q, J = 4.0 Hz), 123.8, 114.1, 109.4, 95.1, 89.6 peaks for CF_3 – could not be assigned clearly.

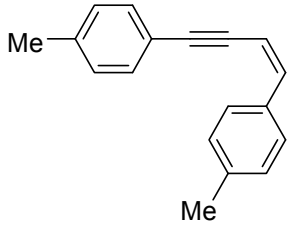
1,4-Di-*p*-methylphenylbut-1-en-3-yne (2e): obtained as a colorless solid; data from a mixture of *E*/*Z* = 76:24; FT-IR (neat): 3415, 2924, 2360, 1602, 1426, 1215, 1105, 1041; ESI-MS: calcd for $C_{18}H_{17}$ $[M+H]^+$: 233.1330; found, 233.0537.

(*E*)-isomer (2e):[4a,5]



^{1}H NMR (500 MHz): 7.35 (d, J = 10.04 Hz, 4H), 7.18-7.12 (m, 4H), 6.99 (d, J = 16.5 Hz, 1H), 6.33 (d, J =16.5 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz): 140.8, 138.6, 138.2, 133.7, 131.4, 129.4, 129.0, 126.2, 120.4, 107.2, 91.6, 88.5, 21.5, 21.3.

(*Z*)- isomer (2e):[2a,2c,5]

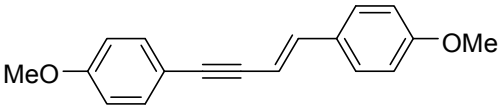


^{1}H NMR (500 MHz): 7.84 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.20-7.16 (m, 4H), 6.65 (d, J = 12.0 Hz, 1H), 5.85 (d, J = 12.1 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz): 138.4, 138.2, 134.0, 131.3, 129.2, 129.0, 128.7, 120.5, 106.5, 95.9, 87.9, 21.5, 21.4.

1,4-Di-*p*-methoxyphenylbut-1-ene-3-yne (2f): obtained as a colorless solid; data from a mixture of *E*/*Z* = 78:22; FT-IR (neat): 2931, 2854, 2360, 2340, 1603, 1506, 1460, 1286, 1250, 1175, 1107, 1027; ESI-MS: calcd for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150; found, 264.6864.

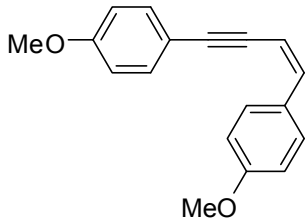
[5] C.Yang and S. P.Nolan, *J. Org. Chem.,* 2002, **67**, 591.

(*E*)-isomer (2f):[1b, 4a]



^{1}H NMR (400 MHz): 7.38 (dd, *J* = 9.2 Hz, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.88-6.82 (m, 4H), 6.23 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.821 (s, 3H); ^{13}C NMR (125 MHz): 160.0, 159.5, 140.1, 132.9, 130.2, 129.8, 127.5, 115.8, 114.0, 106.0, 91.0, 87.9, 55.3, 55.2 (overlapped with *Z*-isomer).

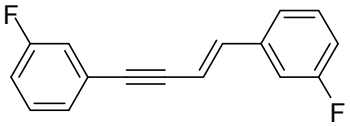
(*Z*)- isomer (2f):[2a,2c]



^{1}H NMR (500 MHz): 7.89 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 6.92-6.88 (m, 4H), 6.60 (d, *J* = 11.8 Hz, 1H), 5.79 (d, *J* = 11.9 Hz, 1H), 3.84 (s, 3H), 3.83(s, 3H); ^{13}C NMR (125 MHz): 159.7, 159.6, 137.4, 132.8, 129.4, 127.4, 115.8, 114.1, 113.7, 105.2, 95.4, 87.4, 55.3, 55.2 (overlapped with *E*-isomer).

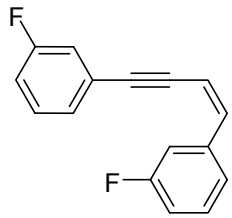
(*E*)-1,4-Di-*m*-fluorophenylbut-1-ene-3-yne (2g): obtained as a light yellow oil, data from a mixture of *E*/*Z* = 70:30); FT-IR (neat): 3401, 3016, 2925, 2853, 2395,2193, 1934, 1607, 1581, 1486, 1268, 1178, 1152, 1075; ESI-MS: calcd for $C_{16}H_{10}F_2$ $[M+H]^+$: 241.0829; found, 241.8726.

(*E*)-isomer (2g):[1b]



^{1}H NMR (500 MHz): 7.33-7.25 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.15-7.11 (m, 2H), 7.01(d, *J* = 15.8 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (500 MHz): 163.2 (d, *J* = 307.3 Hz), 162.3 (d, *J* = 308.7 Hz), 140.5 (d, *J* = 3.1 Hz), 138.5 (d, *J* = 9.6 Hz), 130.1 (d, *J* = 41.3 Hz), 130.0 (d, *J* = 41.3 Hz), 127.5 (d, *J* = 3.5 Hz), 125.2, 122.4 (d, *J* = 3.1 Hz), 118.5 (d, *J* = 28.5 Hz), 115.8 (d, *J* = 26.6 Hz), 115.7 (d, *J* = 26.7 Hz), 112.5 (d, *J* = 27.5 Hz), 109.3, 91.3 (d, *J* = 3.8 Hz), 89.5.

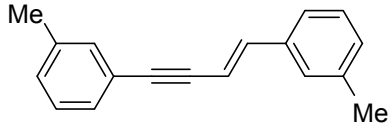
(*Z*)- isomer (2g):



^{1}H NMR (500 MHz): 7.78 (d, *J* =11 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.38-7.27 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 1H), 7.09-7.02(m, 2H), 6.70 (d, *J*=12.2 Hz, 1H), 5.95 (d, *J*=12.2 Hz, 1H).

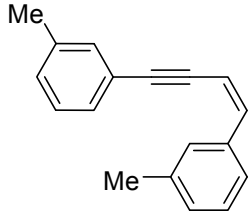
1,4-Di-*m*-methylphenylbut-1-en-3-yne (2h): obtained as a light yellow oil, data from a mixture of *E*/*Z* 74:26; FT-IR (neat): 3427, 3021, 2922, 2855, 2387, 2361, 1601, 1484, 1457, 1090, 1039; ESI-MS: calcd for $C_{18}H_{16}Na$ $[M+Na]^+$: 255.1150; found, 254.7116.

(*E*)- isomer (2h):[4a,6]



^{1}H NMR (500 MHz): 7.30-7.18 (m, 6H), 7.12-7.09 (m, 2H), 6.99 (d, *J* =16.5 Hz, 1H), 6.36 (d, *J* = 16.5 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz): 141.3, 138.3, 138.0, 136.3, 132.1, 129.4, 129.1, 128.6, 128.6, 128.2,127.0,123.4,123.3, 108.0, 91.8, 88.6, 21.4, 21.2.

(Z)-isomer (2h):

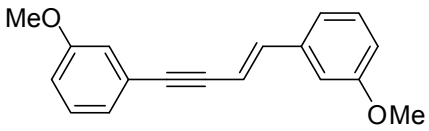


^{1}H NMR (500 MHz): 7.80 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.22-7.18 (m, 4H), 7.09-7.04 (m, 2H), 6.66 (d, *J* = 11.9 Hz, 1H), 5.89 (d, *J* = 11.9 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz): 138.7, 138.1, 137.7, 136.5, 132.0, 129.3, 129.2, 128.6, 128.5, 128.3, 127.3, 125.2, 123.5, 107.2, 96.0, 88.2, 21.5(2C).

[6] A. Kawata, Y. Kuninobu and K. Takai, *Chem. Lett.,* 2009, *38*, 836.

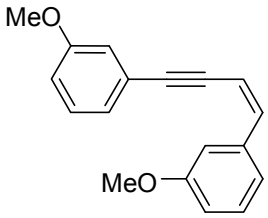
1,4-Di-*m*-methoxyphenylbut-1-ene-3-yne (2i): obtained as a light yellow oil, data from a mixture of *E*/*Z* = 79:21; FT-IR (neat): 3438, 3020, 2926, 2854, 2398, 2348, 2254, 1596, 1466, 1216, 1156, 1048; ESI-MS: calcd for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150; found, 264.6788.

(*E*)-isomer (2i):



^{1}H NMR (500 MHz): 7.30-6.82 (m, 9H, merged with *Z*-isomer & one vinyl proton), 6.37 (d, *J* = 16.5 Hz, 1H), 3.81 (2s, 6H); ^{13}C NMR (100 MHz): 159.5, 159.3, 141.3, 137.7, 129.7, 129.2, 124.1, 121.8, 119.2, 116.2, 114.9, 114.3, 111.6, 108.4, 91.8, 88.6, 55.2, 55.2.

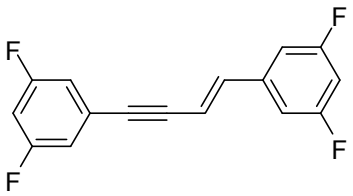
(*Z*)-isomer (2i):



^{1}H NMR (500 MHz) : 7.67 (s, 1H), 7.38 (d, *J* = 8.0 Hz , 1H), 7.30-6.82 (m, 6H, merged with *E*-isomer), 6.68 (d, *J* = 12.0 Hz, 1H), 5.91 (d, *J* = 12.0 Hz, 1H), 3.82 (2s, 6H); ^{13}C NMR (125 MHz): 159.8, 159.4, 138.7, 129.3, 129.2, 124.3, 123.9, 121.6, 119.2, 116.1, 114.8, 114.5, 113.2, 107.5, 96.1, 88.0, 55.3, 55.2.

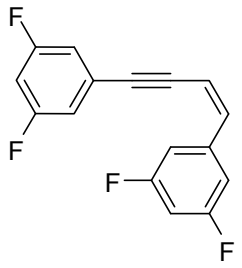
5,5'-(but-1-en-3-yne-1,4-diyl)bis(1,3-difluorobenzene) (2j): obtained as a colorless solid, data from a mixture of *E*/*Z* = 73:27. IR (neat): 3419, 2919, 2843, 2356, 1618, 1586, 1320, 1121; ESI-MS: calcd for $C_{16}H_{12}F_4N$ $[M+ NH_4]^+$: 294.0906; found, 294.6606.

(*E*)-isomer (2j):



^{1}H NMR (400 MHz): 6.99-6.91 (m, 5H, merged with doublet), 6.96 (d, *J* = 15.8 Hz, 1H), 6.85-6.74 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz): 163.3 (d, *J* = 310.9 Hz), 163.2 (d, *J* = 310.6 Hz), 163.0 (d, *J* = 311.4 Hz), 162.6 (d, *J* = 311.3 Hz), 140.1, 139.1, 137.5, 114.5 (d, *J* = 33.6 Hz), 110.2, 109.0 (d, *J* = 32.3 Hz), 104.4 (d, *J* = 73.3 Hz), 90.8 (t, *J* = 4.9 Hz), 89.6.

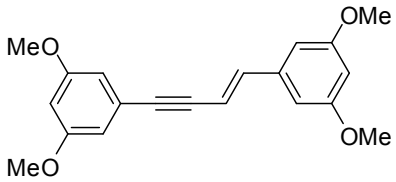
(*Z*)-isomer (2j):



^{1}H NMR (400 MHz): 7.41 (d, *J* = 6.7 Hz, 2H), 7.02-6.95 (m, 2H), 6.85-6.77 (m, 2H), 6.67 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 11.6 Hz, 1H).

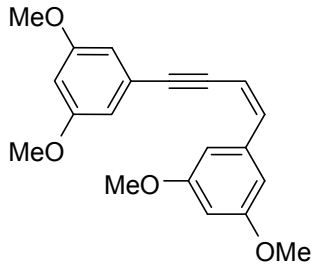
5,5'-(but-1-en-3-yne-1,4-diyl)bis(1,3-dimethoxybenzene) (2k):[7] obtained as a colorless solid, data from a mixture of *E*/*Z* = 70:30. FT-IR (neat): 3439, 3003, 2925, 2849, 2344, 2201, 1593, 1454, 1205, 1157, 1065; ESI-MS: calcd for $C_{20}H_{20}O_4$ $[M]^+$: 224.1362; found, 224.5921.

(*E*)-isomer (2k):



^{1}H NMR (500 MHz): 6.97 (d, *J* = 15.9 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 2H), 6.57 (d, *J* = 2.5 Hz, 2H), 6.46-6.44 (m, 2H), 6.34 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz): 161.0, 160.6, 141.6, 138.2, 124.6, 109.3, 109.2, 108.6, 106.7, 104.4, 101.8, 101.3, 100.9, 92.0, 88.3, 55.4, 55.3.

(*Z*)-isomer (2k):



^{1}H NMR (400 MHz): δ =7.14 (d, *J* = 2.3 Hz, 2H), 6.65 (d, *J* = 2.3 Hz, 2H), 6.46-6.42 (m, 2H), 6.64 (d, 1H merged with aromatic protons), 5.90 (d, *J* = 11.9, 1H), 3.79 (s, 3H, merged with *E*-isomer), 3.78 (s, 3H).

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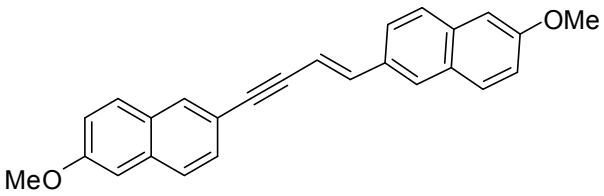
[7] C. Pasquini and M. Bassetti *Adv. Synth. Catal.,* 2010, **352**, 2405.

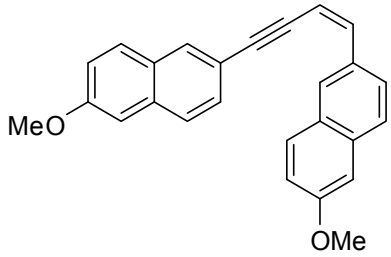
1,4-Di(2-methoxy-6-naphthyl)-1-buten-3-yne (2l):[7] , obtained as a colorless solid; data from a mixture of *E*/*Z* = 37:63; FT-IR (neat): 3017, 2924, 2362, 2336, 1602, 1216, 1026, 769; ESI-MS: calcd for $C_{26}H_{20}O_2$ $[M]^+$: 364.1463; found, 363.4777.

(*E*)-isomer (2l):



^{1}H NMR (400 MHz): 7.93 (s, 1H), 7.76-7.67 (m, 5H), 7.60 (d, *J* = 8.2, 1H), 7.50 (d, *J* = 8.4 Hz, 1.7 Hz, 2H), 7.11-7.16 (m, 5H), 6.49 (d, *J* = 16.0 Hz, 1H), 3.94, 3.93 (2s, 6H); ^{13}C NMR (100 MHz): 158.2, 158.1, 141.2, 139.3, 134.7, 134.1, 131.9, 131.2, 129.8, 129.3, 129.0, 128.9, 127.3, 126.8, 126.7, 123.4, 119.4, 119.2, 118.4, 107.4, 106.0, 92.4, 89.0, 55.4; FT-IR (neat): 3017, 2924, 2362, 2336, 1602, 1216, 1026.

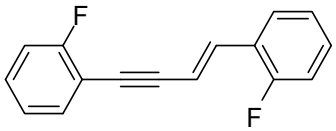
(*Z*)-isomer (2l):



^{1}H NMR (500 MHz): 8.34 (s, 1H), 8,14 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (s, 1H), 7.76 (dd, *J* = 8.6, 2.7 Hz, 2H), 7.73-7.71 (m, 2H), 7.55 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.17 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.15-7.12 (m, 2H), 6.83 (d, *J* = 11.9 Hz, 1H), 5.98 (d, *J* = 11.8 Hz, 1H), 3.94, 3.94 (2s, 6H); ^{13}C NMR (125 MHz): 158.4, 158.2, 138.5, 134.5, 134.2, 132.3, 131.1, 129.9, 129.4, 128.7 , 128.6, 128.4, 127.0, 126.9, 126.6, 119.5, 119.1, 118.5, 106.8, 105.9, 105.8, 96.5, 88.5, 55.4.

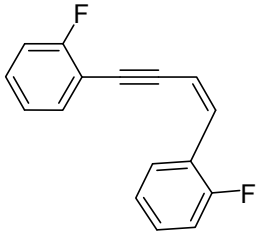
1,4-Di-*o*-fluorophenylbut-1-en-3-yne (2m):[1a] obtained as a colorless light yellow oil; data from a mixture of *E*/*Z* = 50:50; FT-IR (neat): 3041, 3075, 2924, 2854, 2371, 2348, 2208, 1610, 1586, 1490, 1456, 1230, 1154, 1104, 1034. ESI-MS: calcd. for $C_{16}H_{10}F_2$ $[M]^+$: 240.0751; found, 239.9556.

(*E*)-isomer (2m):



^{1}H NMR (400 MHz): 7.52-7.45 (m, 2H), 7.35-7.28 (m, 2H), 7.21 (d, *J* =16.4, 2H), 7.15-7.04 (m, 4H), 6.51 (d, *J* =16.42, 2H): ^{13}C NMR (125 MHz): 162.2 (d, *J* = 280 Hz), 160.2 (d, *J* = 281.1 Hz), 134.5, 134.3, 133.4, 131.1 (d, *J* = 10.0 Hz), 130 (d, *J* = 10.1 Hz), 127.3 (d, *J* = 4.1 Hz), 124.3 (d, *J* = 4.2 Hz). 124.2 (d, *J* = 14.9 Hz), 124.0 (d, *J* = 4.6 Hz), 116.1 (d, *J* = 27.5 Hz), 115.6 (d, *J* = 26.08 Hz), 111.9 (d, *J* = 19.5 Hz), 110.4 (d, *J* = 8.6 Hz), 93.8 (d, *J* = 3.9 Hz), 85.5.

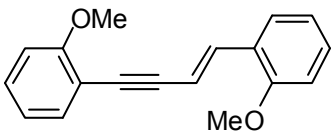
(*Z*)-isomer (2m):



^{1}H NMR (500 MHz): 8.63 (td, *J* = 7.8, 1.6 Hz, 1H), 7.47 (m, 1H), 7.29 (m, 2H), 7.07-7.19 (m, 4H), 7.01 (d, *J* = 12.1 Hz, 1H), 6.04 (d, *J* = 12.1 Hz, 1H).

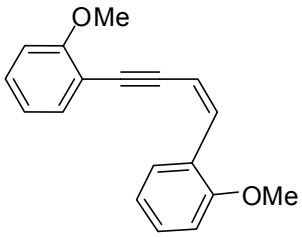
1,4-Di-*o*-methoxyphenylbut-1-ene-3-yne) (2n):[1b,1c] obtained as a colorless light yellow oil; data from a mixture of *E*/*Z* = 37:63; FT-IR (neat): 3436, 2925, 2835, 2545, 2402, 2181, 2051, 1897, 1594, 1482, 1460, 1240, 1159, 1107, 1024; ESI-MS: calcd for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150; found, 264.6672.

(*E*)-isomer (2n):



^{1}H NMR (500 MHz): 7.45 (d, *J* = 9.36 Hz, 2H), 7.36 (d, *J* = 16.5 Hz, 1H), 6.93-6.88 (m, 6H), 6.53 (d, *J* = 16.5 Hz, 1H), 3.91, 3.87 (2s, 6H) ; ^{13}C NMR (125 MHz): 159.7, 157.0, 136.4, 133.5, 129.5, 126.8, 125.5, 120.5, 120.7, 112.8, 111.0, 109.0, 93.8, 87.5, 55.5 (one peak for - OMe group is merged).

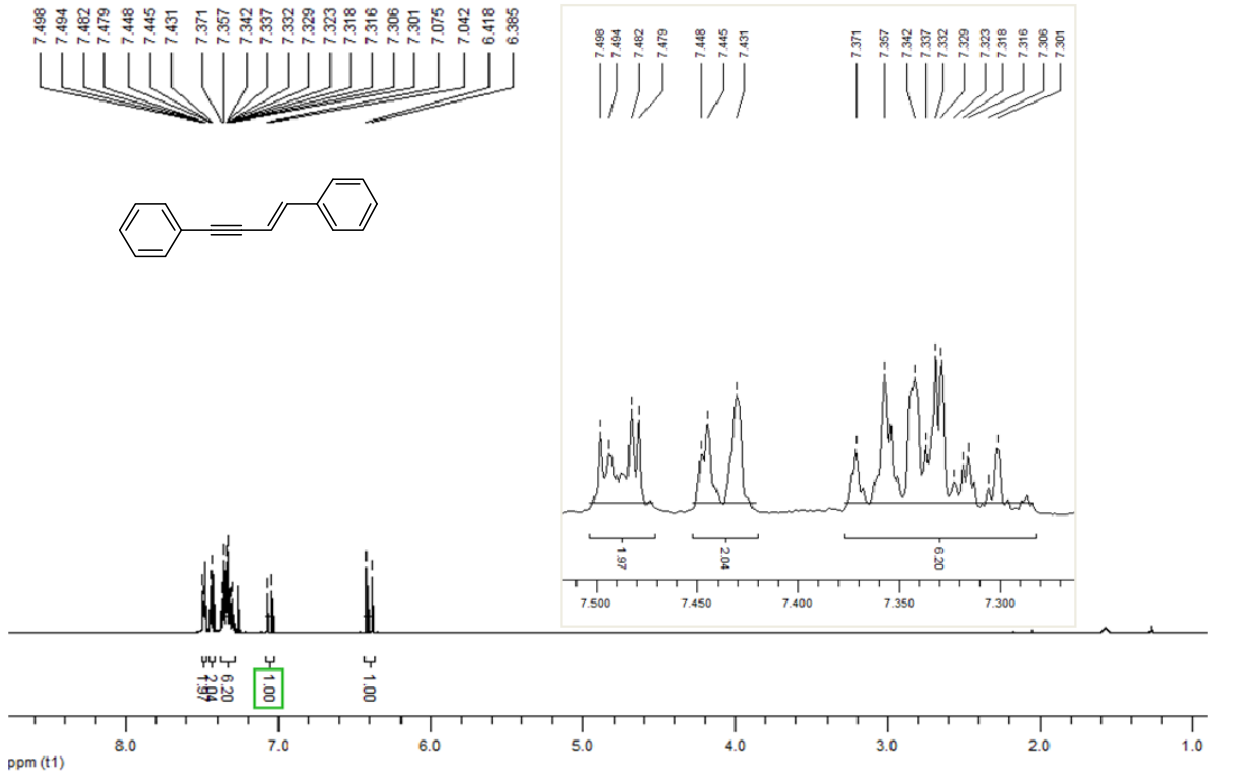
(*Z*)-isomer (2n):[1c]

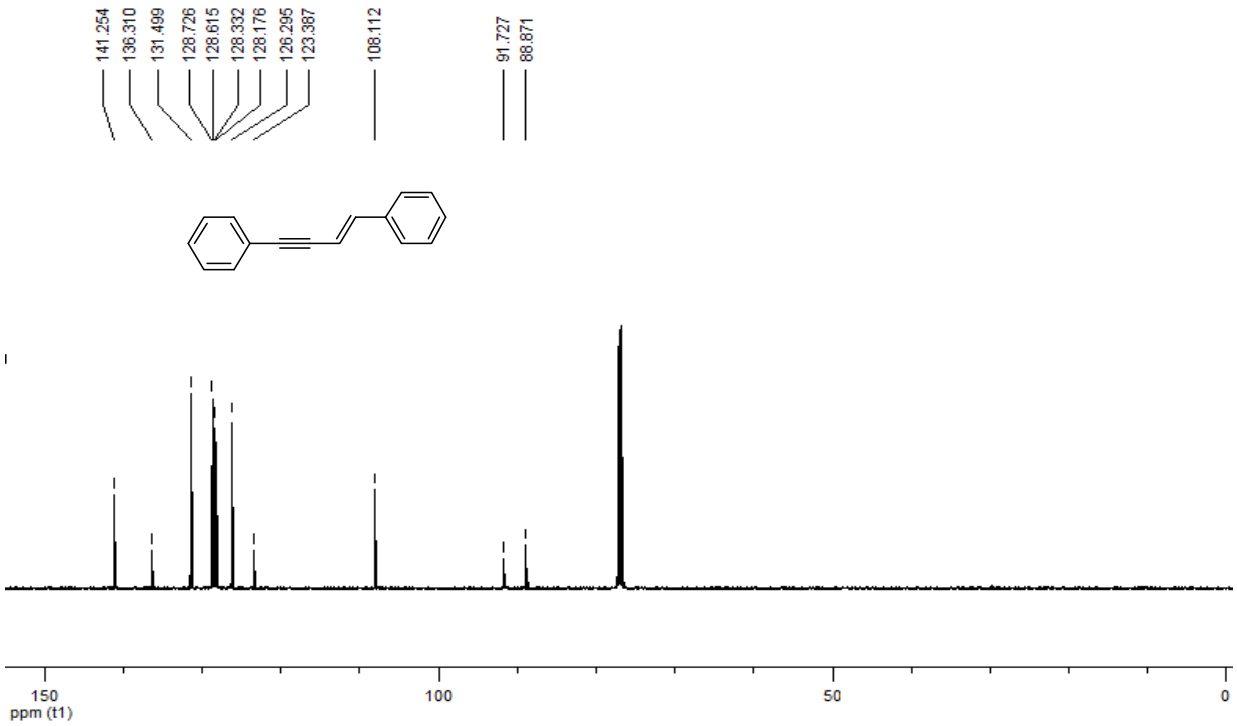


^{1}H NMR (500 MHz): δ =8.7 (m , 1H), 7.40 (m,1H), 7.29 (m, 2H), 7.13 (d, *J* = 12.2 Hz, 1H), 7.0 (t, *J* = 9.5 Hz , 1H), 6.85 - 6.92 (m, 3H), 5.98 (d, *J* = 12.2 Hz, 1H), 3.86, 3.92 (2s, 6H); ^{13}C NMR (100 MHz): 160.1, 156.9, 133.3, 132.1, 129.7, 129.6, 128.8, 125.6, 120.5, 120.1, 112.9, 110.5, 110.4, 107.0, 92.6, 92.2, 55.8, 55.5.

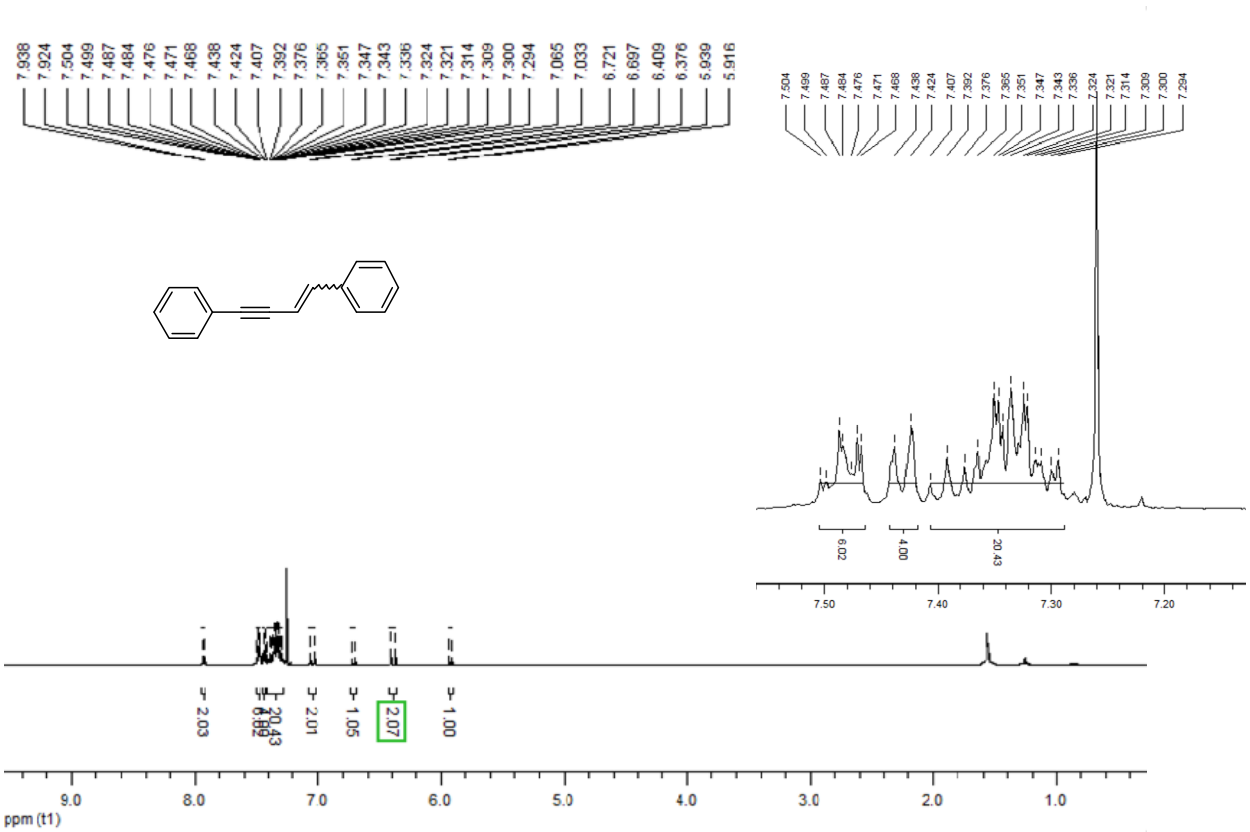
4.0 NMR spectra of compounds:

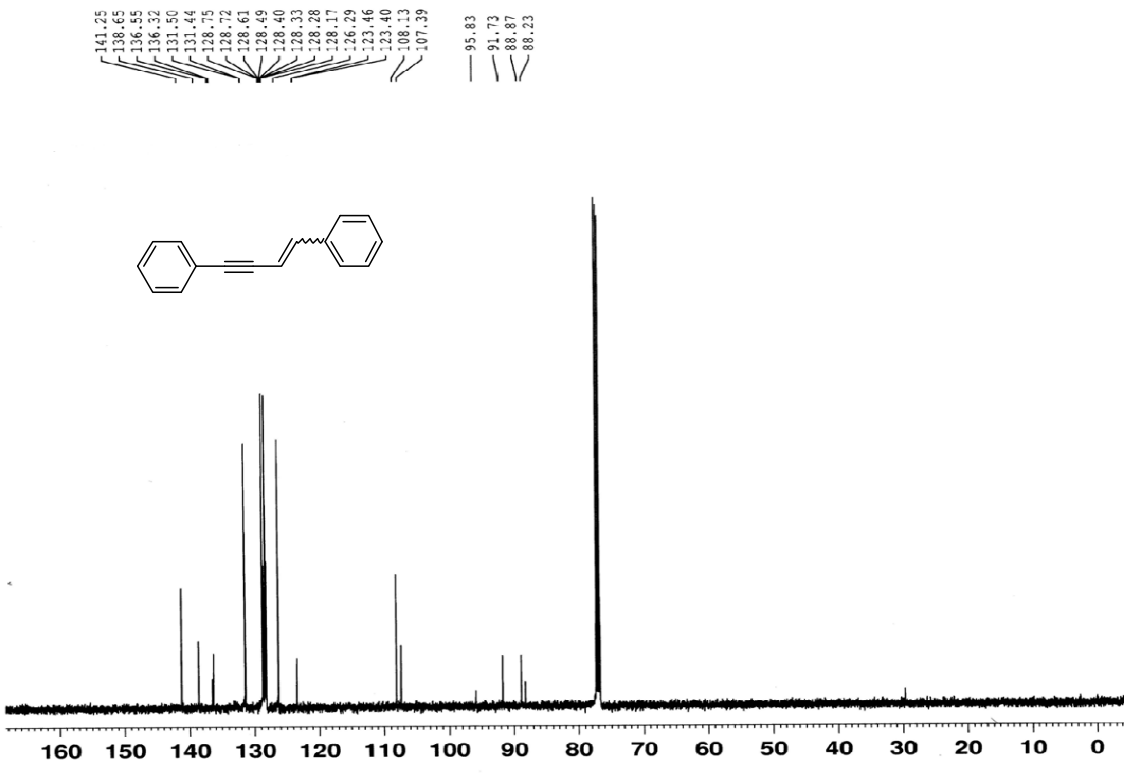
^{1}H and ^{13}C NMR for 2a (*E*):



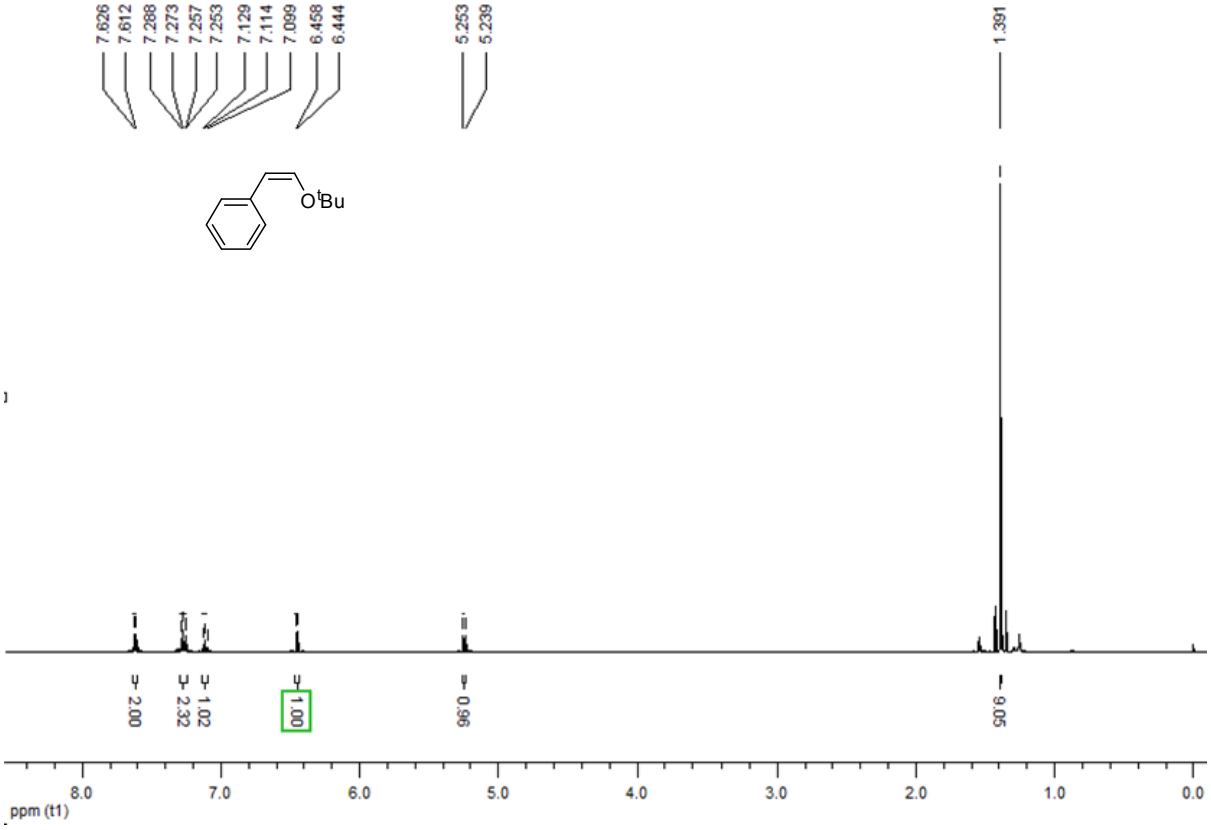


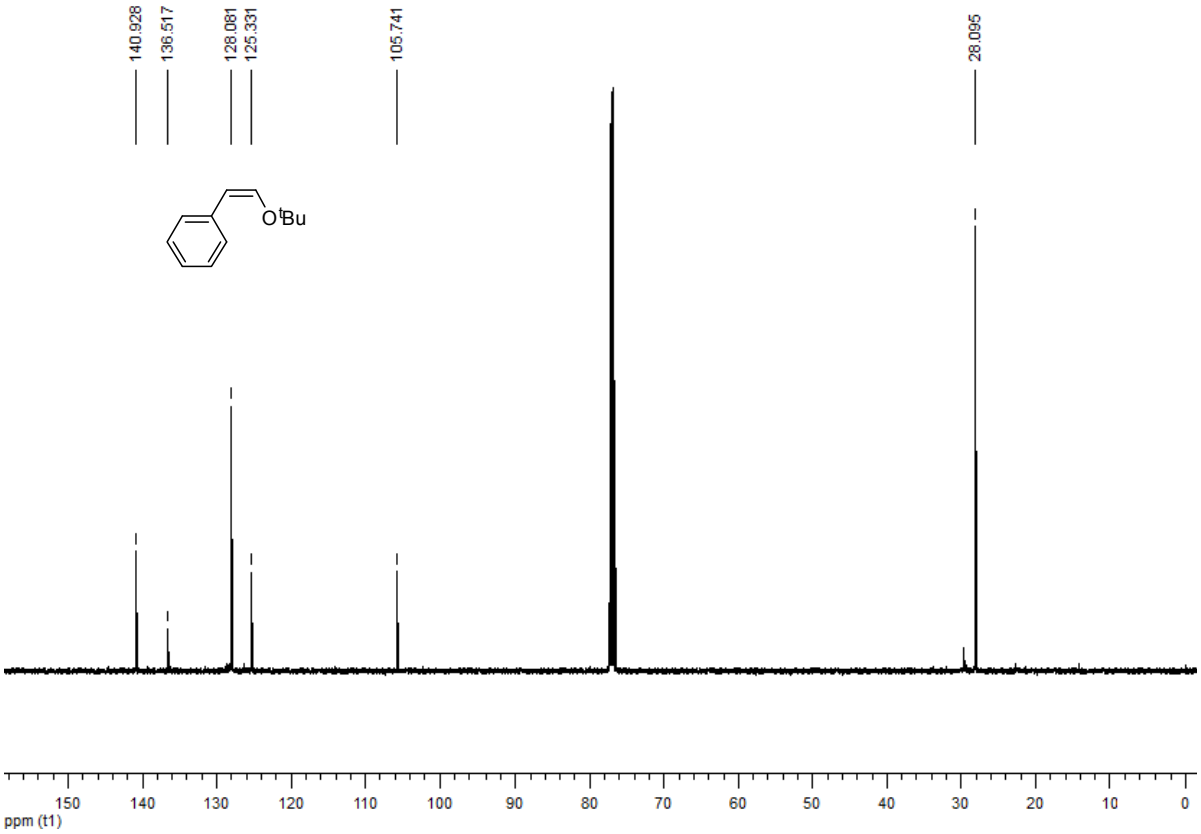
^{1}H and ^{13}C NMR for 2a (*E*/*Z* = 66/34):



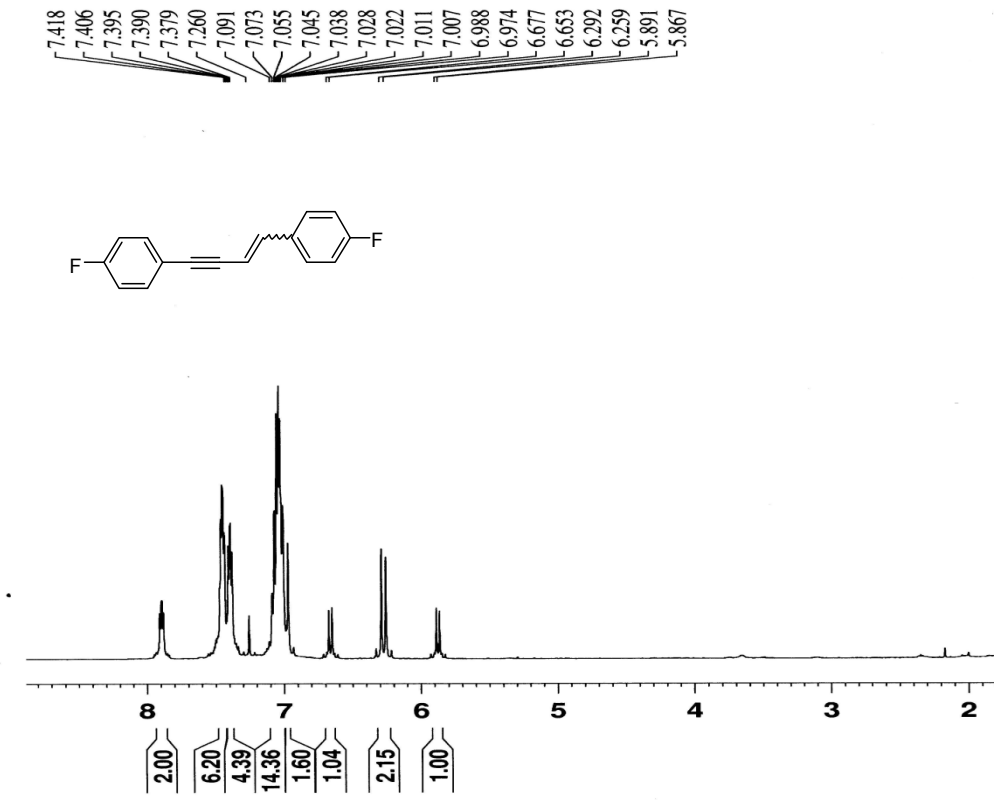


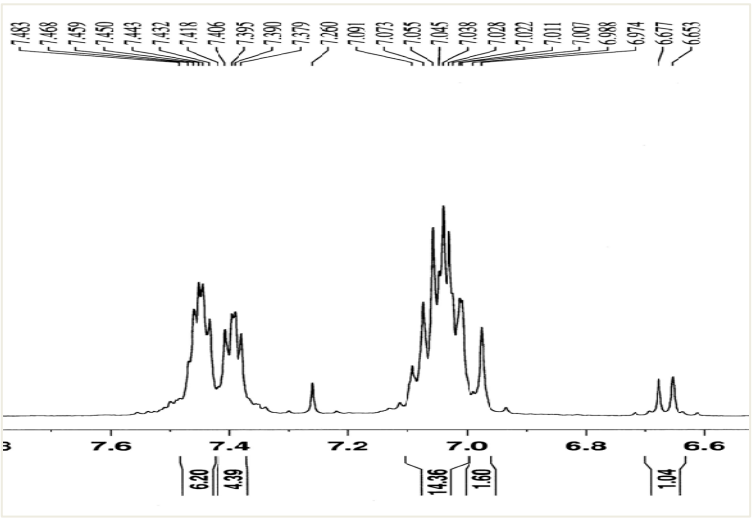
^{1}H and ^{13}C NMR for 4a (*Z*):



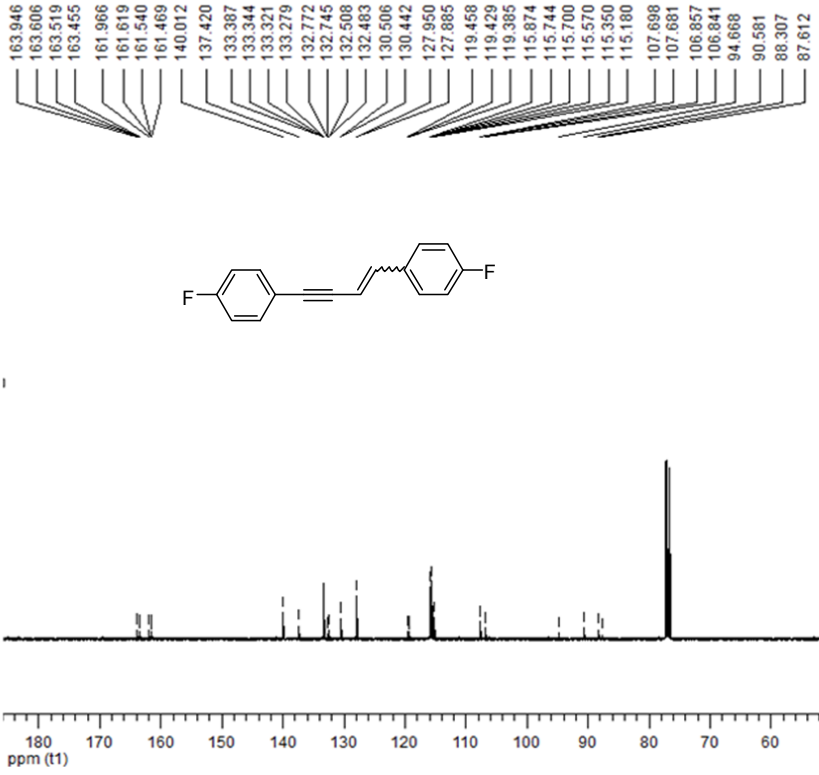


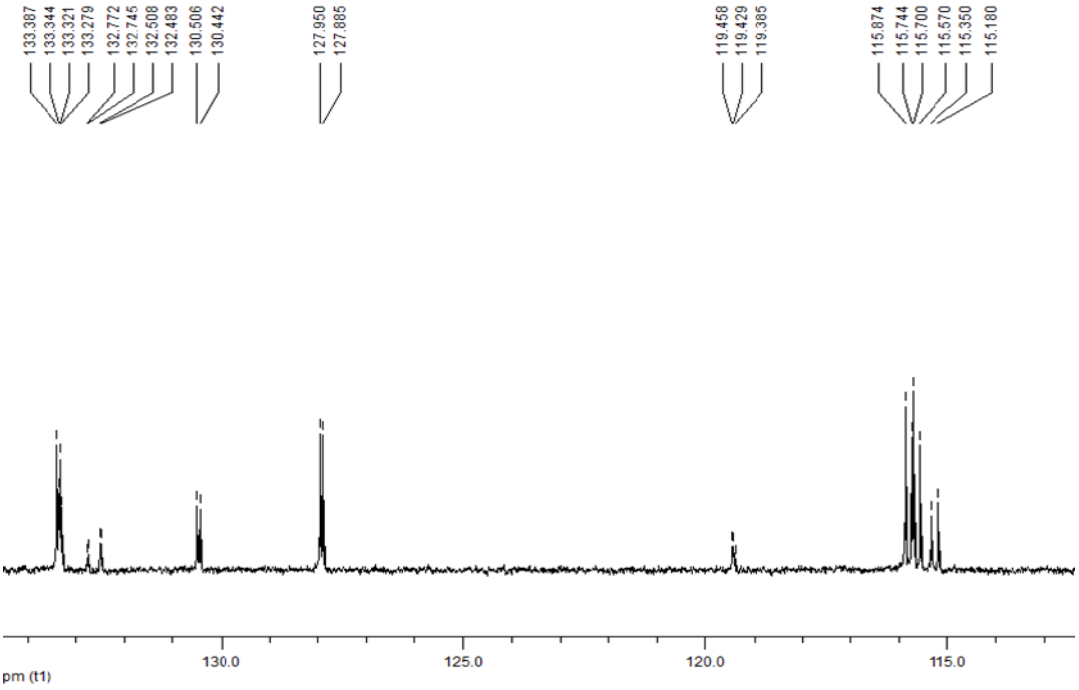
^{1}H NMR of 2b (*E*/*Z* = 66/34):



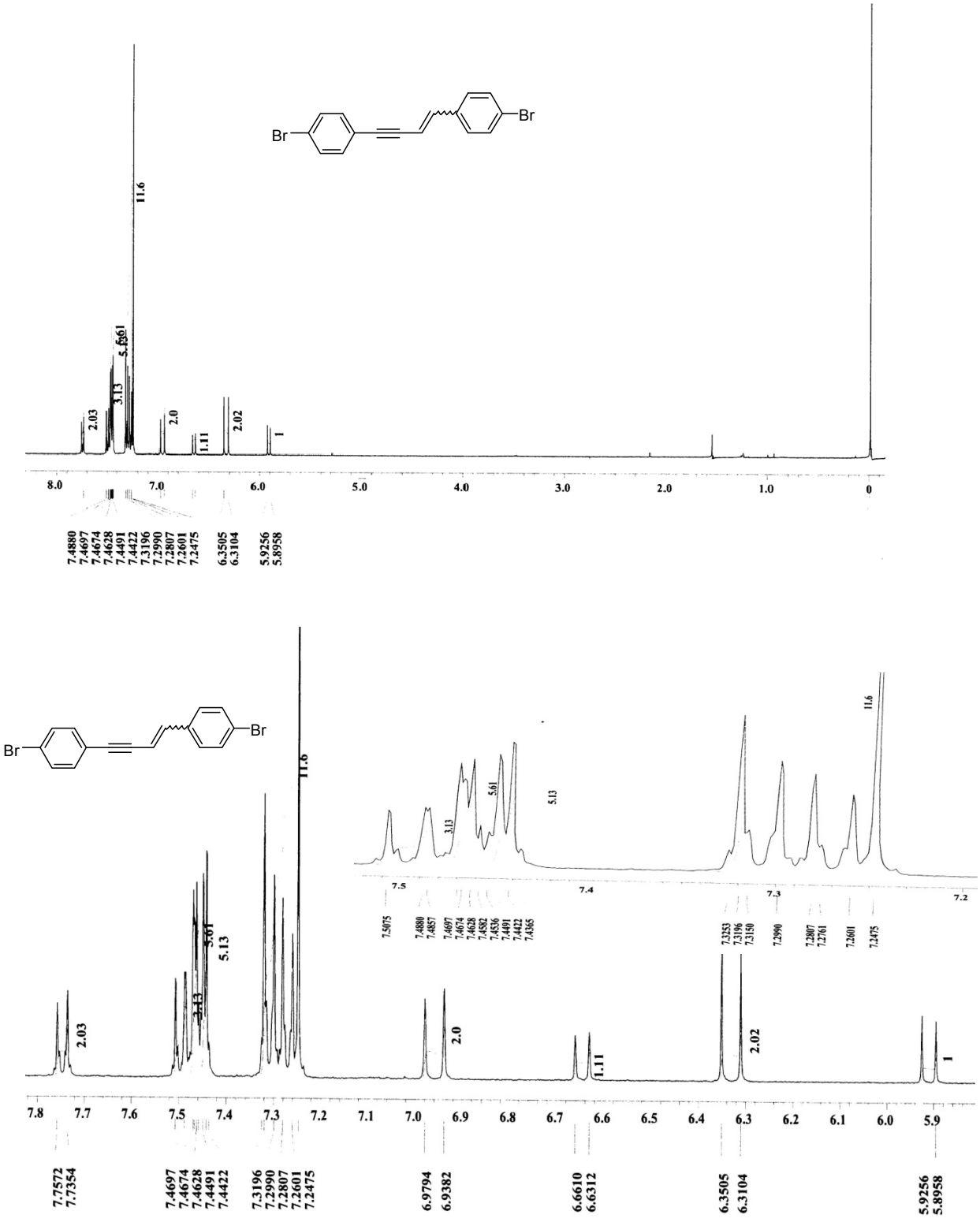


^{13}C NMR for 2b (*E*/*Z* = 66/34):

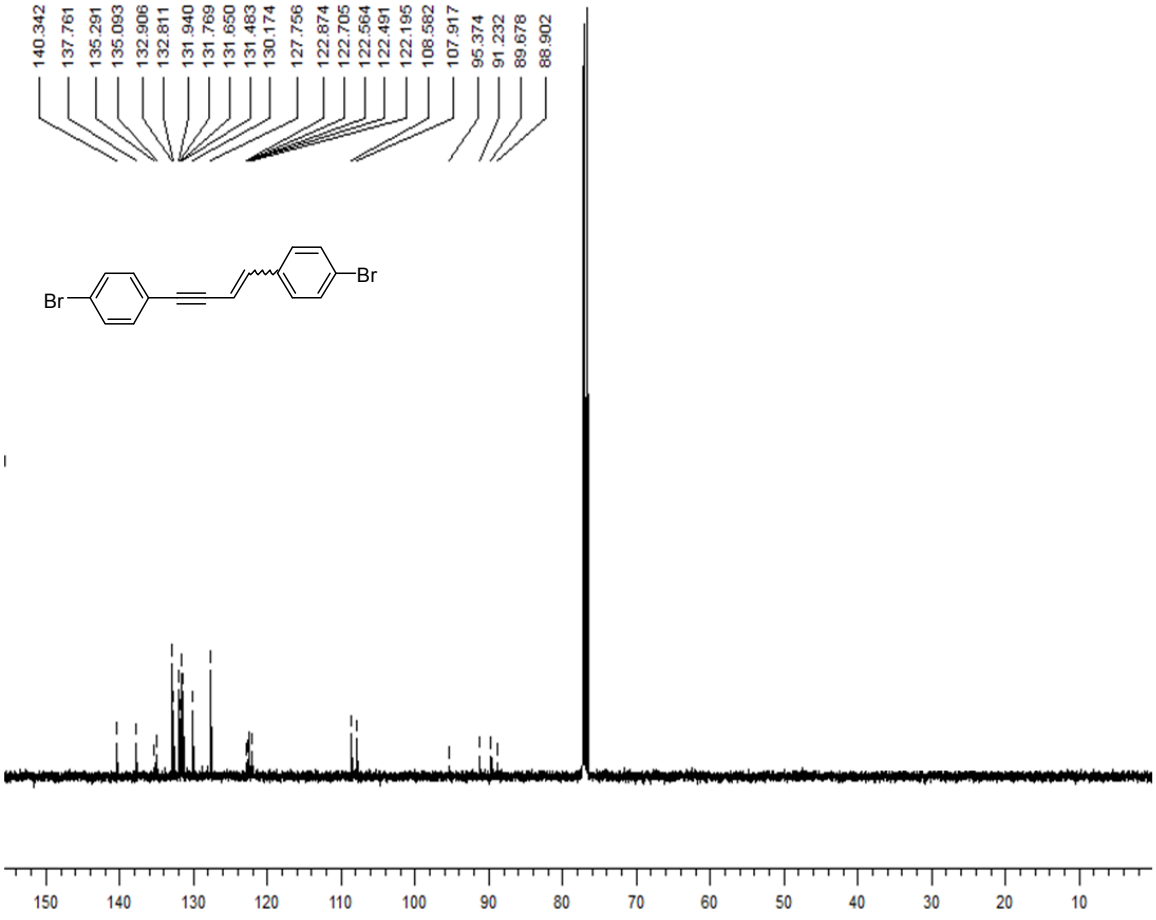


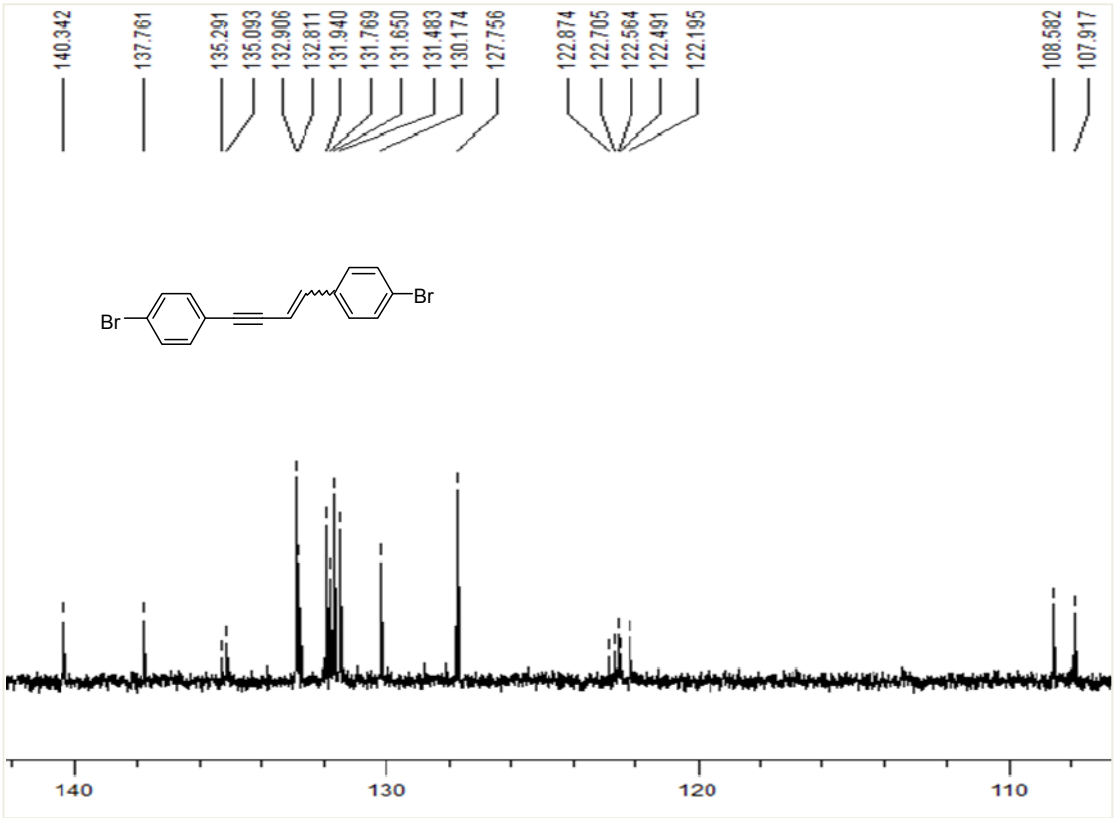


^{1}H NMR for 2c (*E*/*Z* = 67/33):

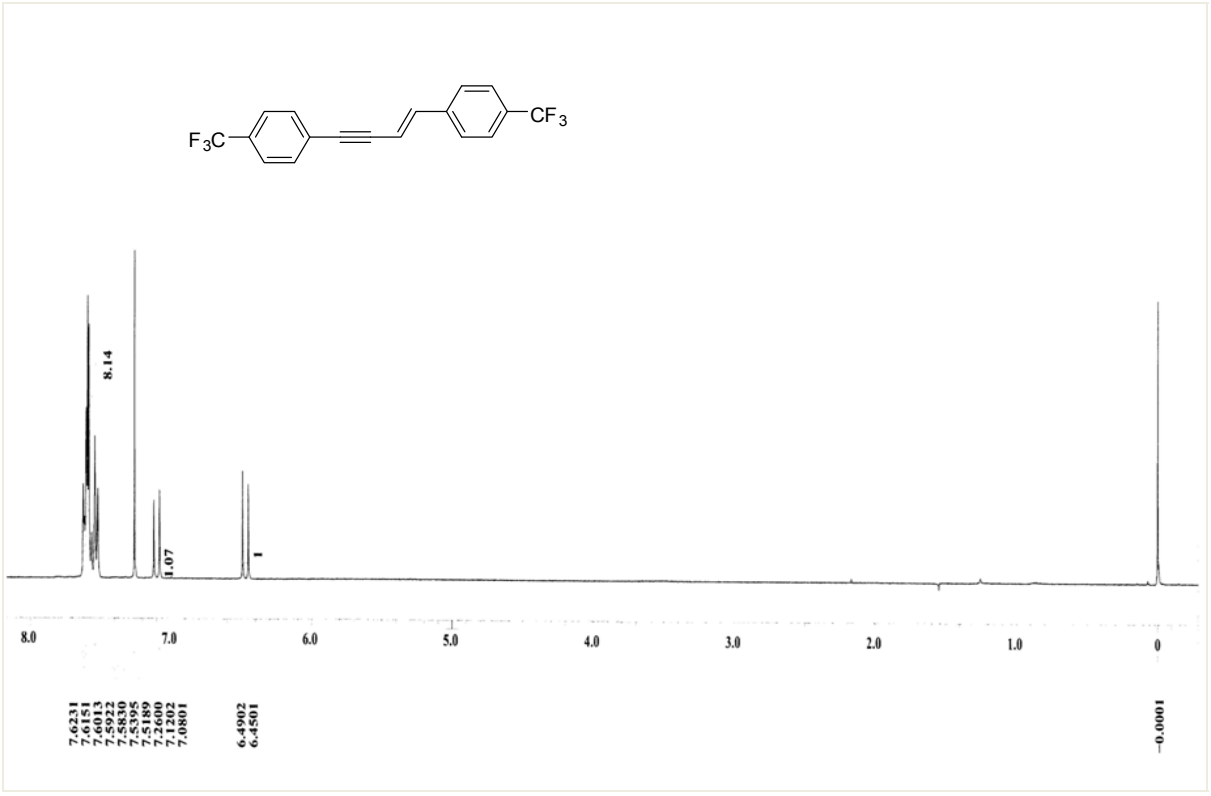


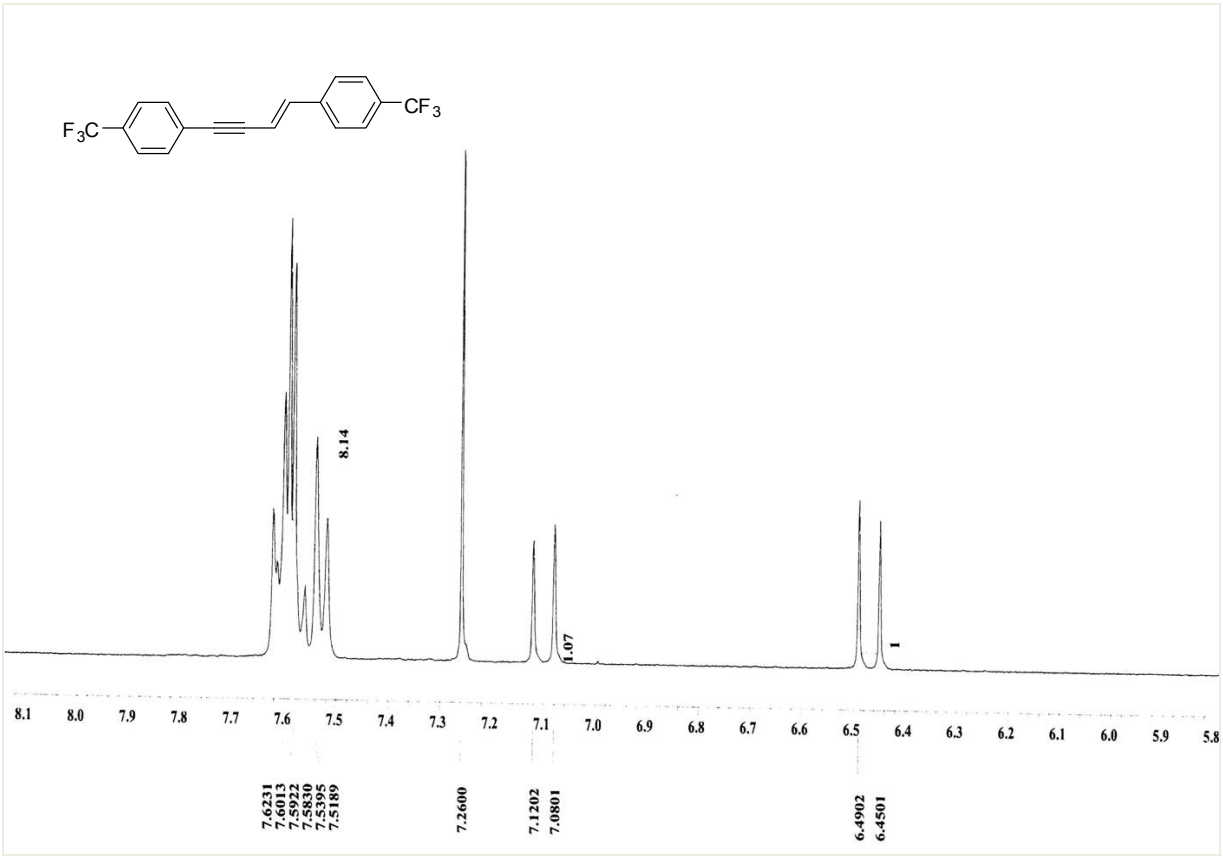
^{13}C NMR for 2c (*E*/*Z* = 67/33):



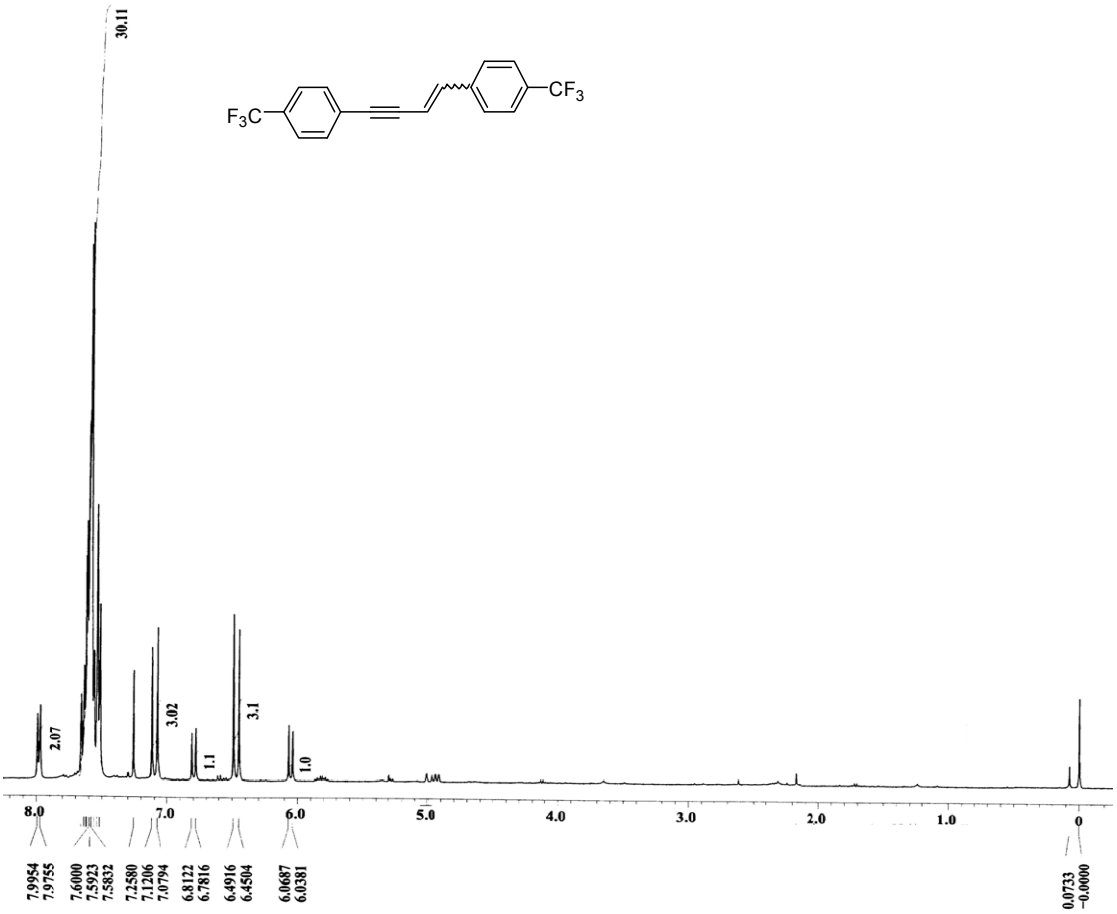


^{1}H NMR for 2d (*E*):

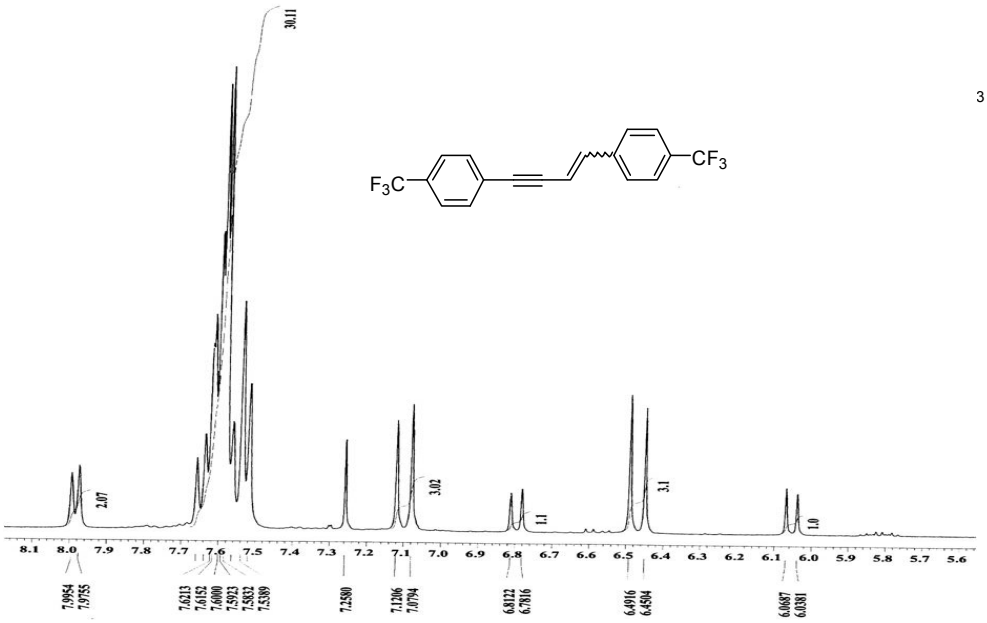




^{1}H NMR for 2d (*E*/*Z* = 75/25):

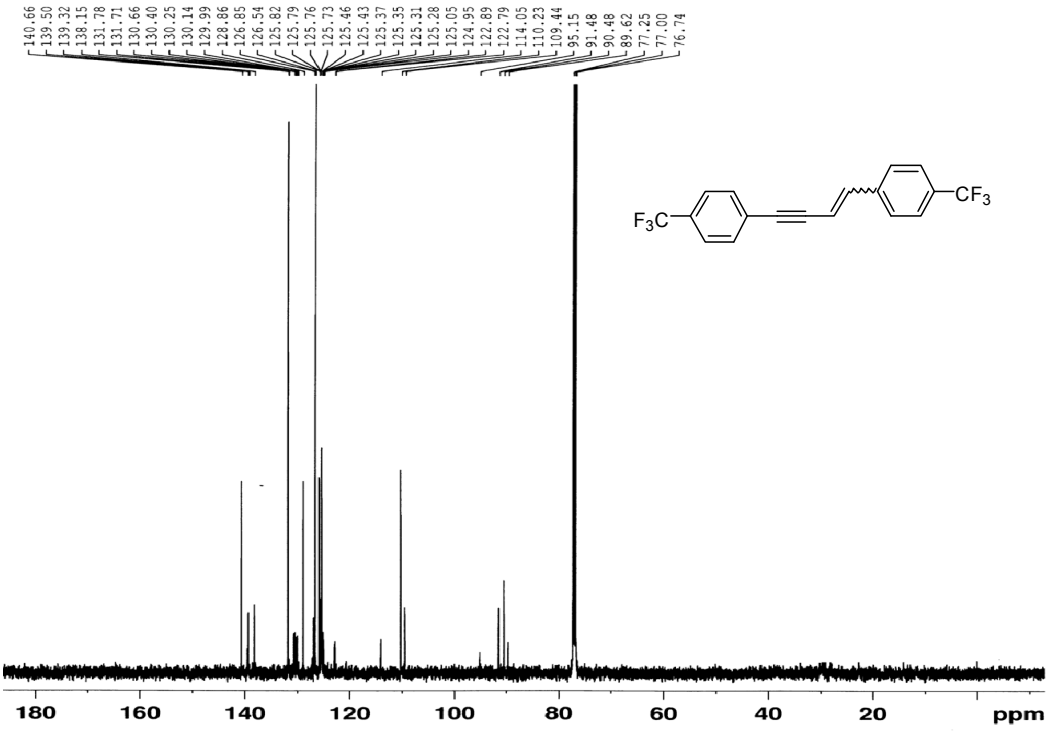


^{1}H and ^{13}C NMR for 2d (*E*/*Z* = 75/25):

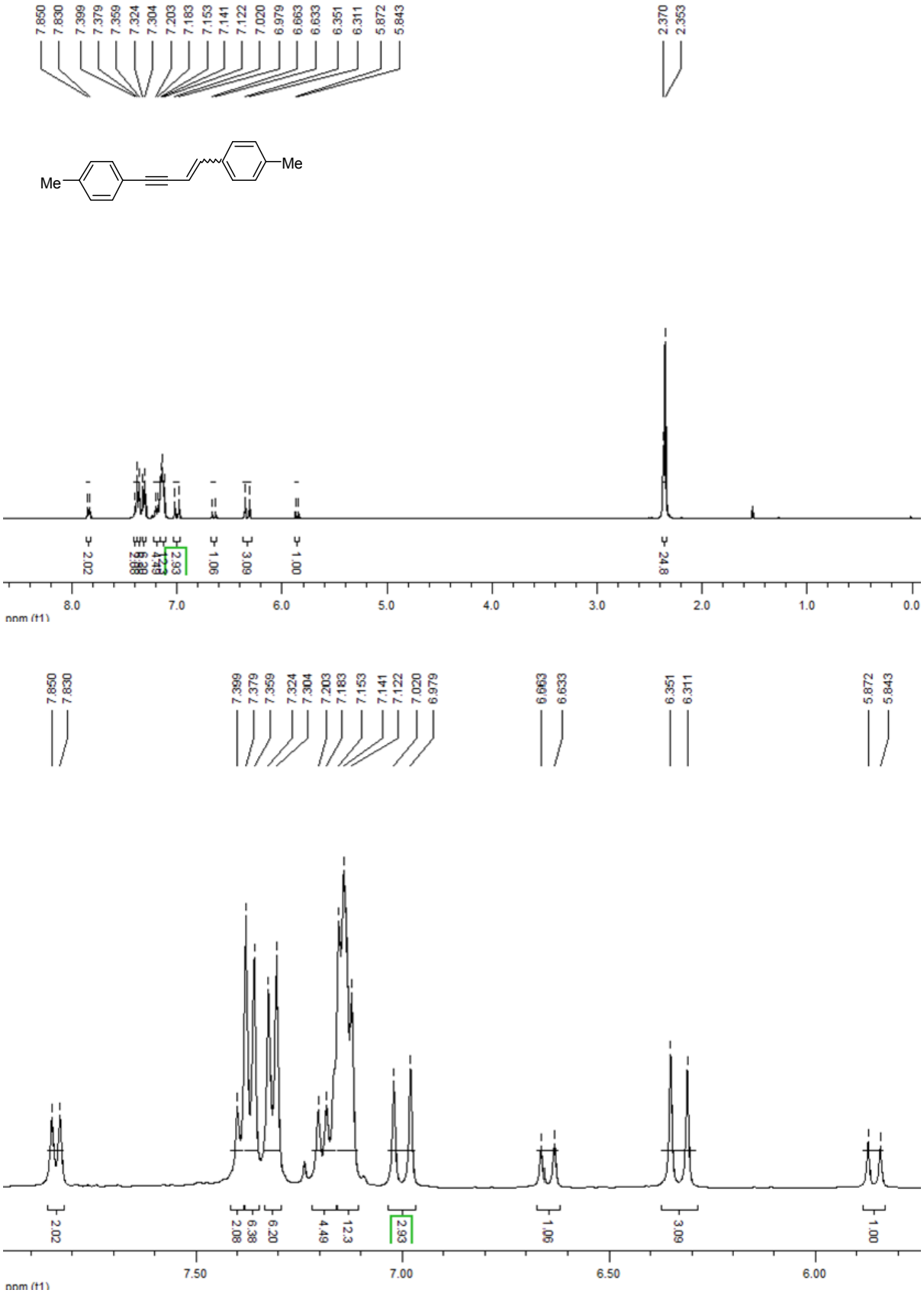


3

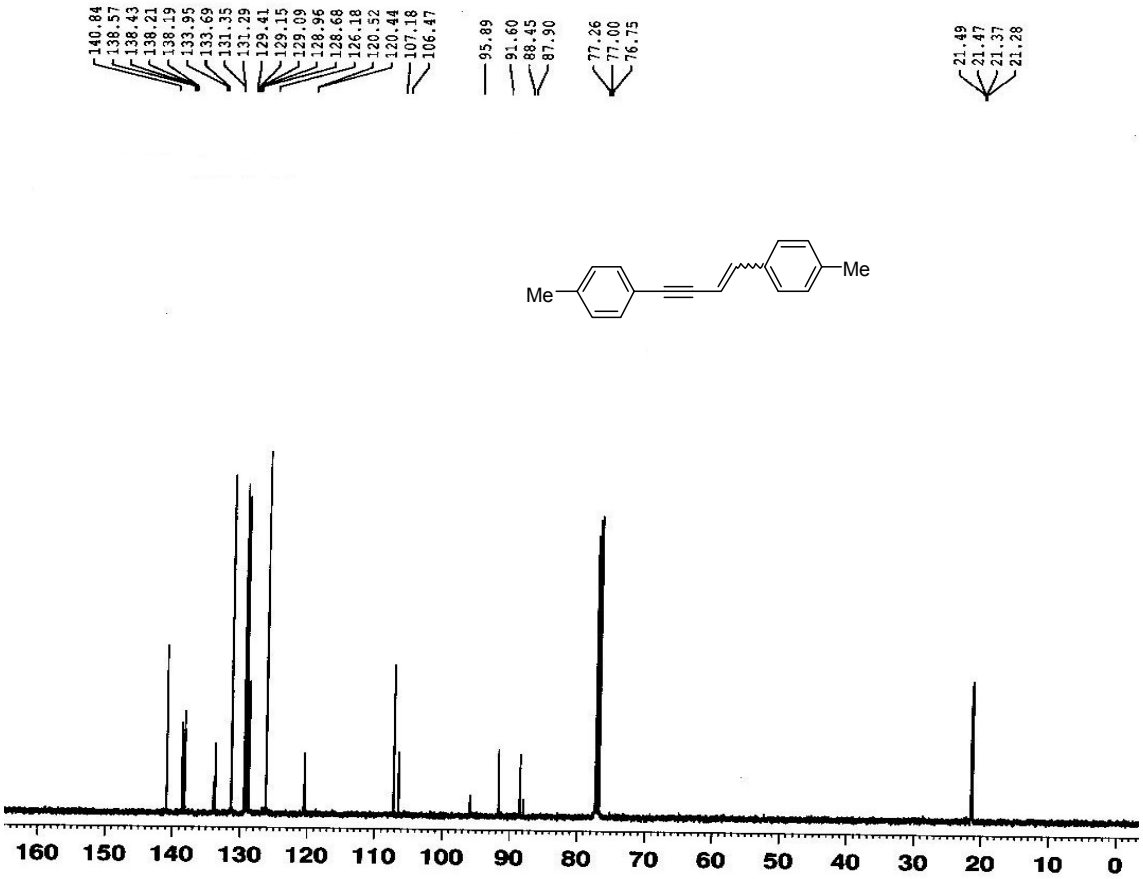
^{13}C NMR for 2d (*E*/*Z* = 75/25):



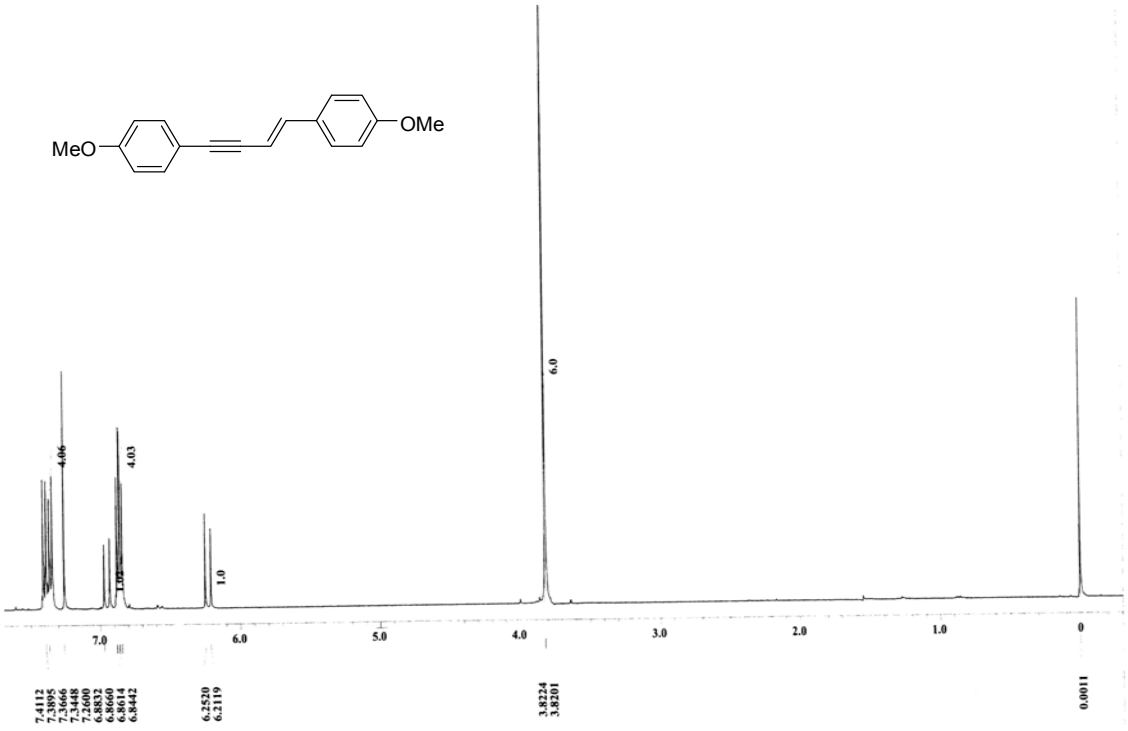
^{1}H NMR for 2e (*E*/*Z* = 76/24):

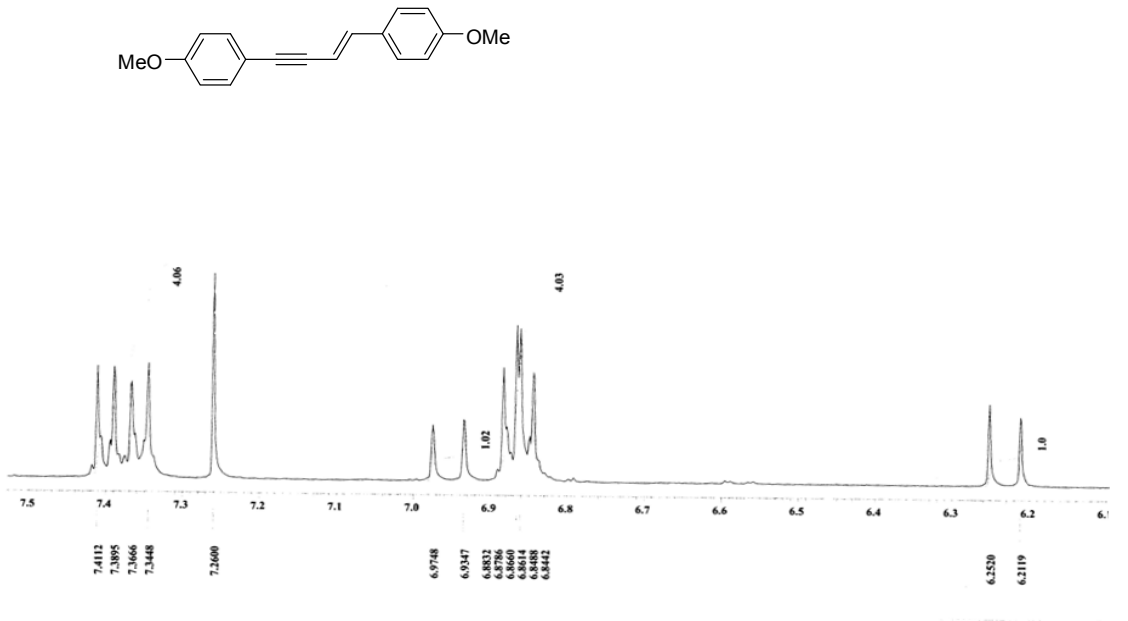


^{13}C NMR for 2e (*E*/*Z* = 76/24):

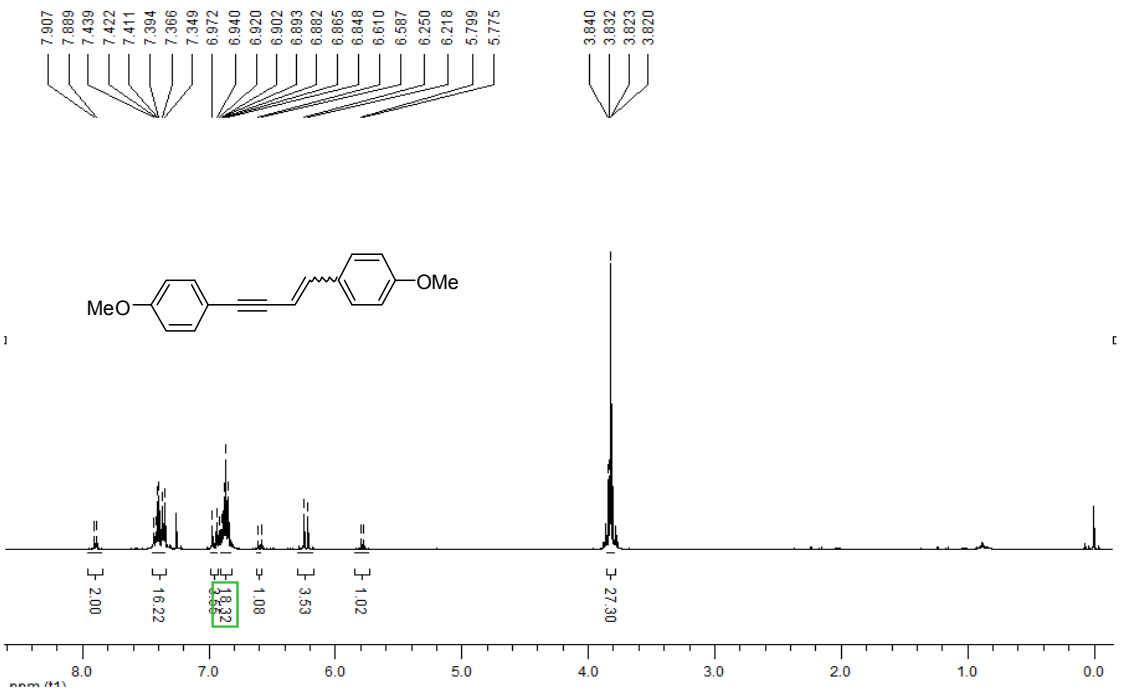


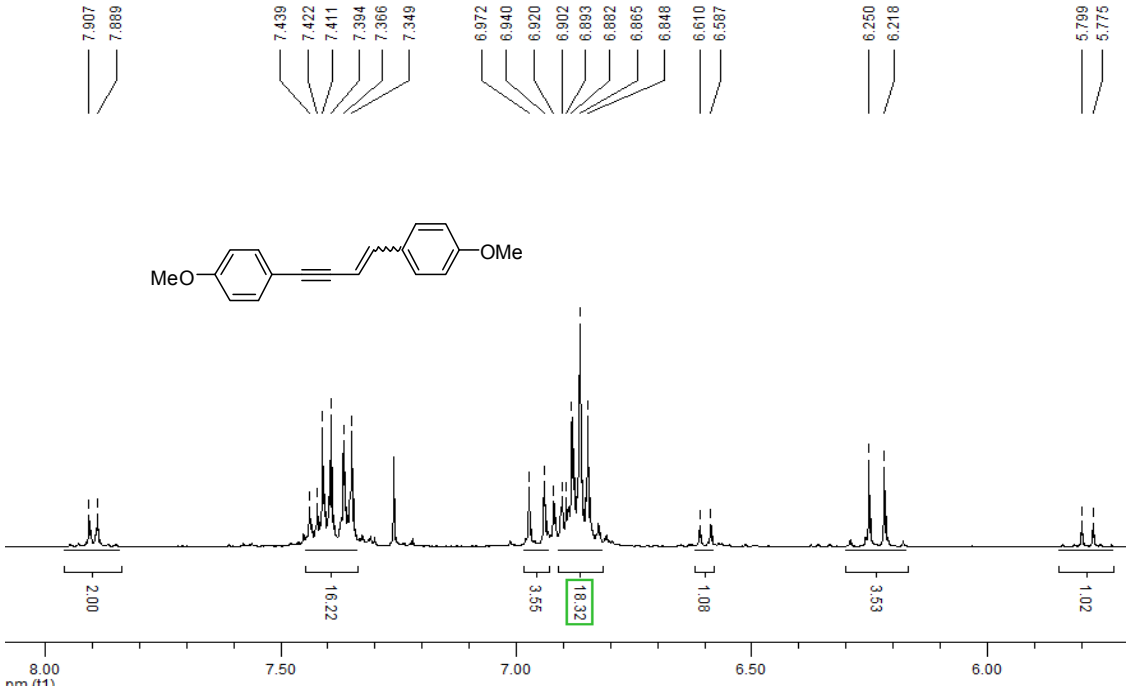
^{1}H NMR for 2f (*E*):

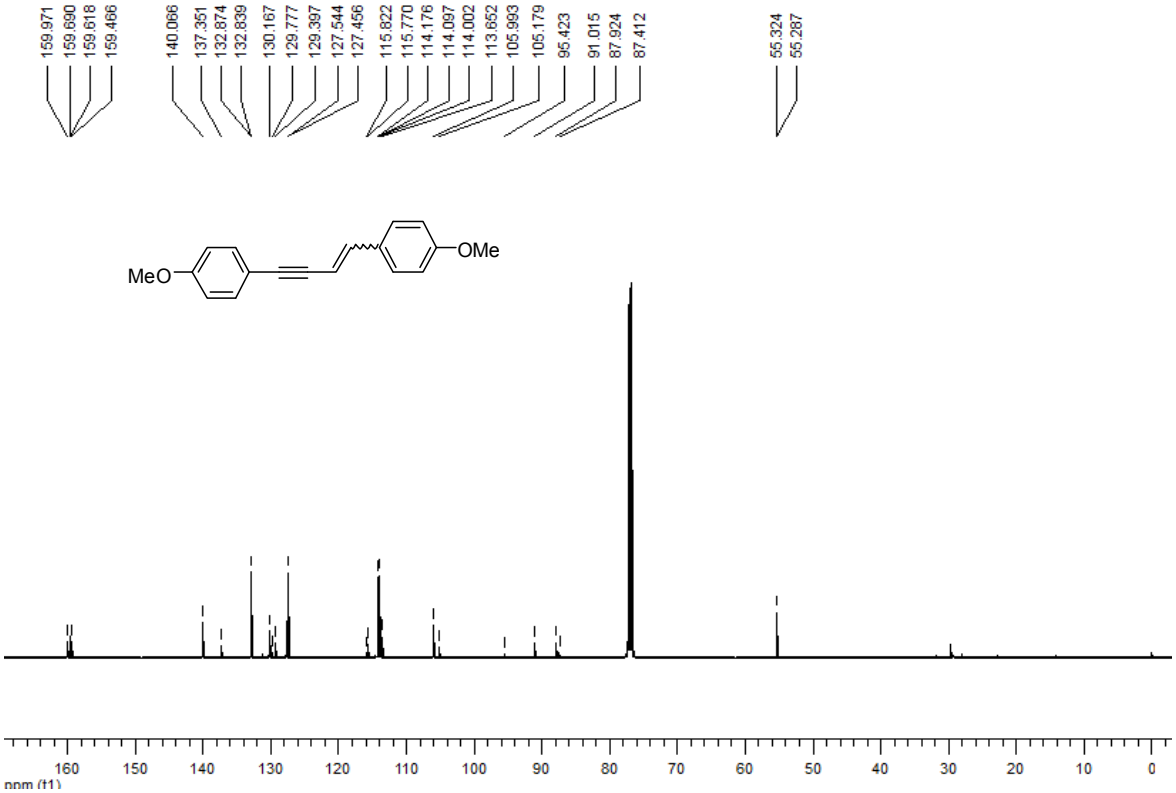


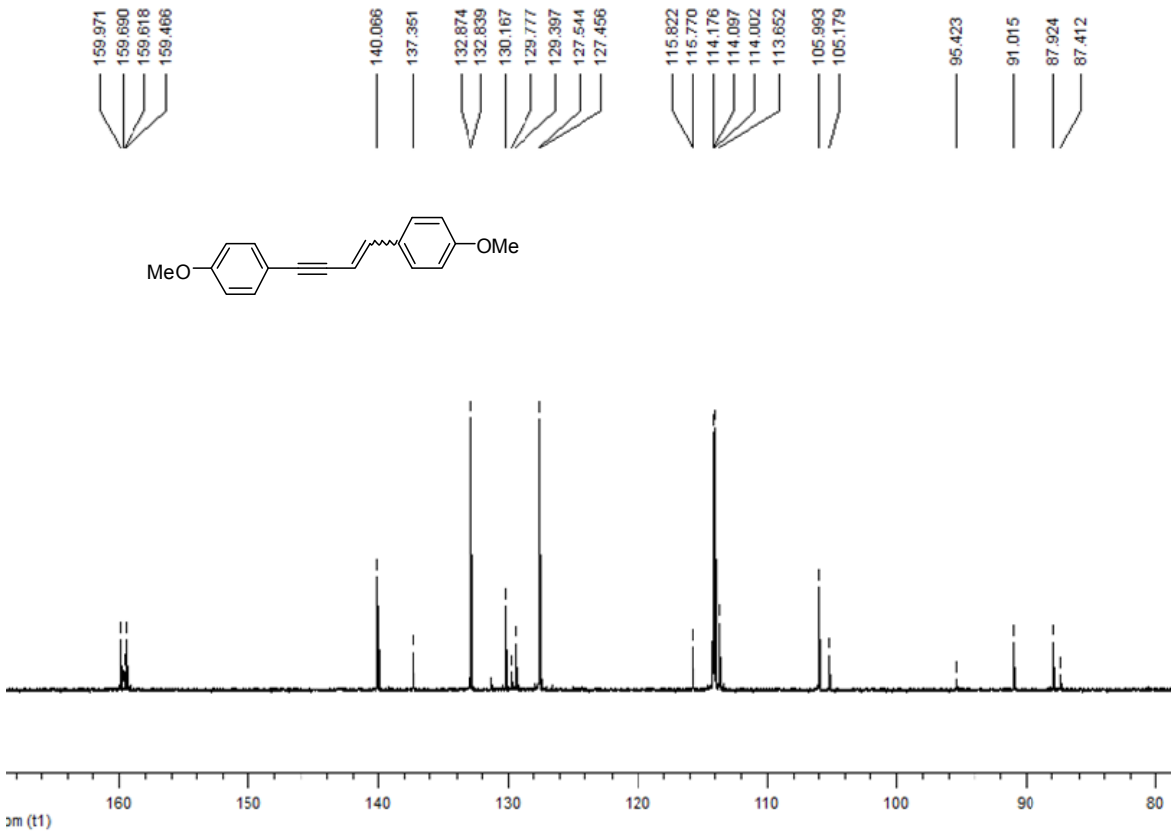


^{1}H and ^{13}C NMR for 2f (*E*/*Z* = 78/22):

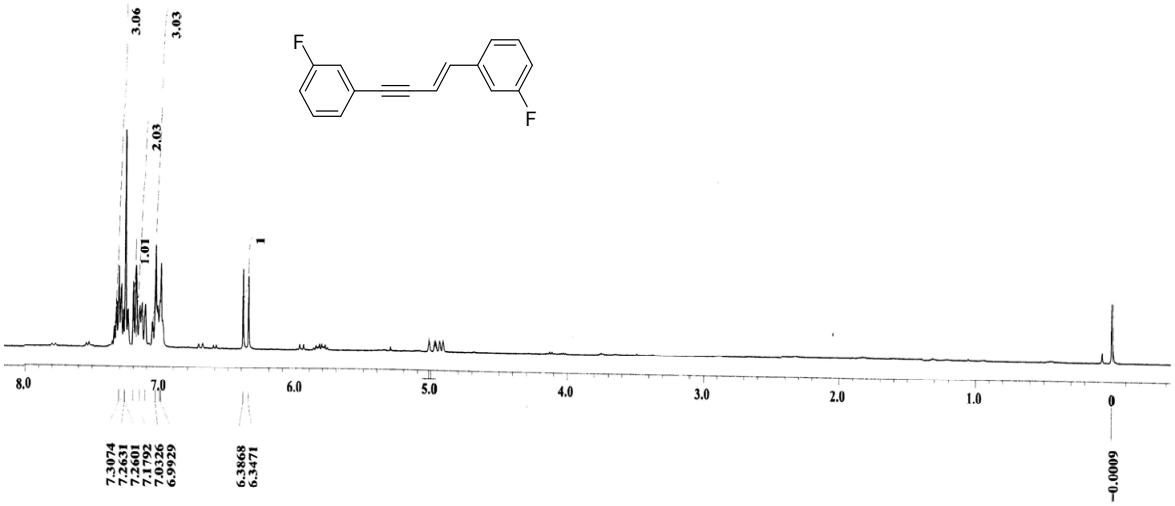


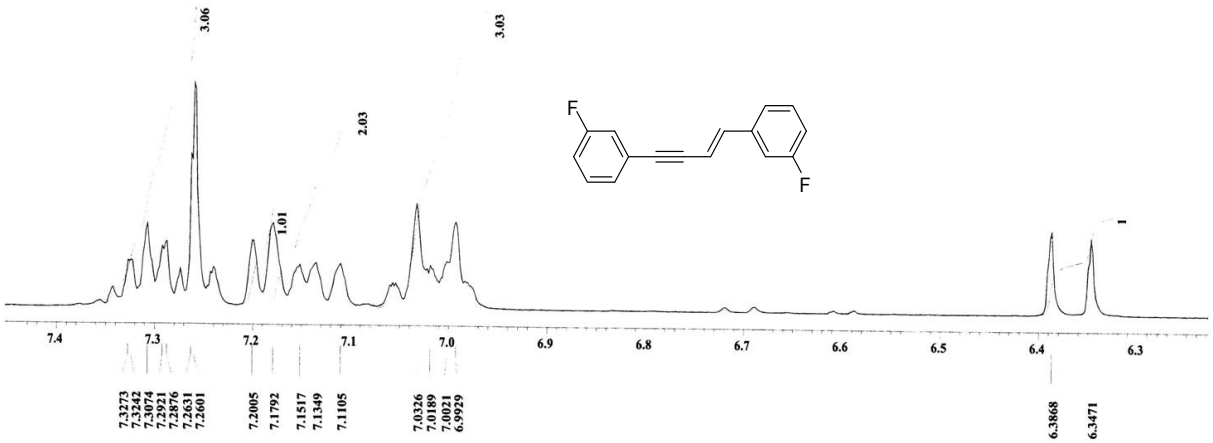



159.971
159.690
159.618
159.466
140.066
137.351
132.874
132.839
130.167
129.777
129.397
127.544
127.456
115.822
115.770
114.176
114.097
114.002
113.652
105.993
105.179
95.423
91.015
87.924
87.412
55.324
55.287
MeO
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

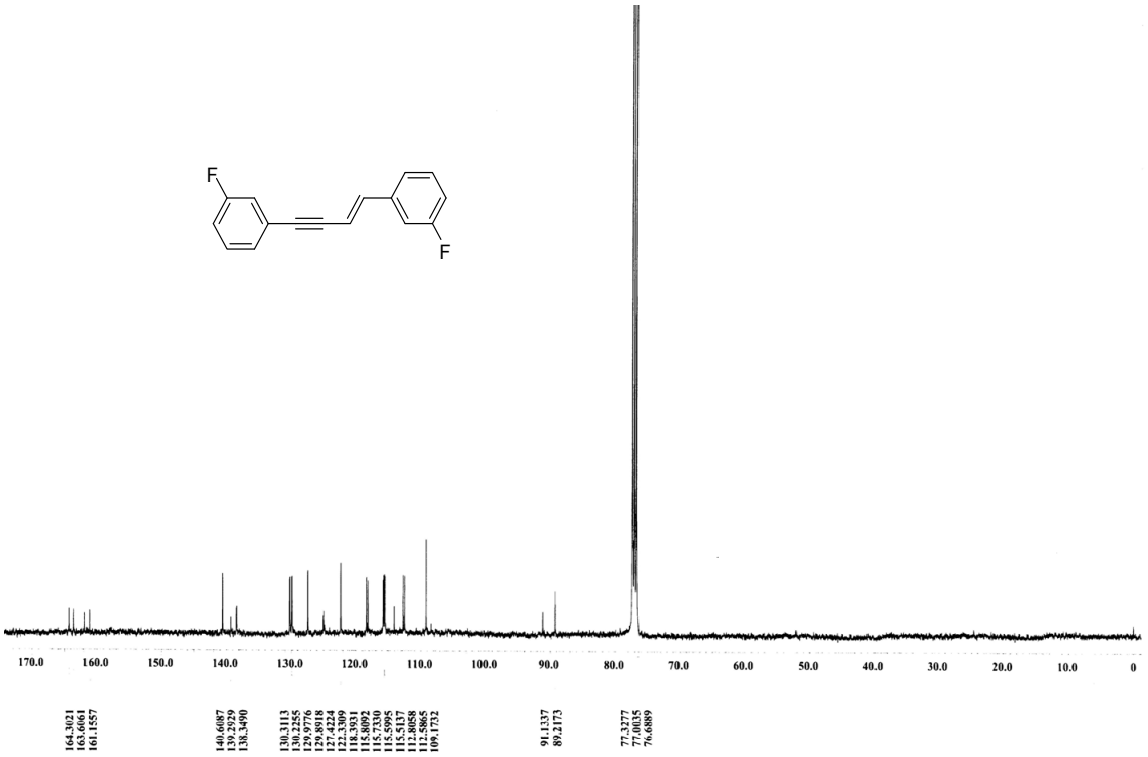

159.971
159.690
159.618
159.466
140.066
137.351
132.874
132.839
130.167
129.777
129.397
127.544
127.456
115.822
115.770
114.176
114.097
114.002
113.652
105.993
105.179
95.423
91.015
87.924
87.412
MeO
OMe
160
150
140
130
120
110
100
90
80
ppm (t1)

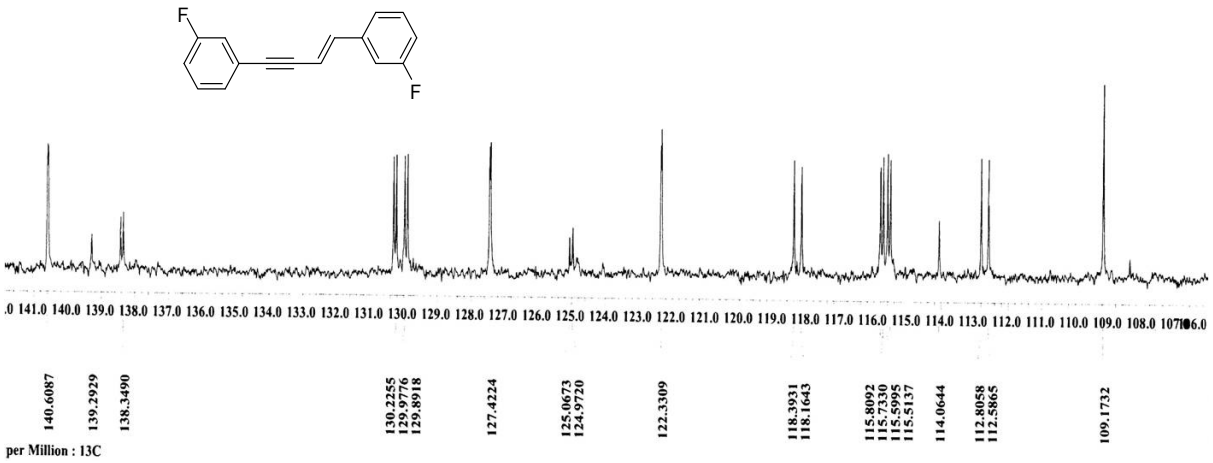
^{1}H NMR for 2g (*E*):



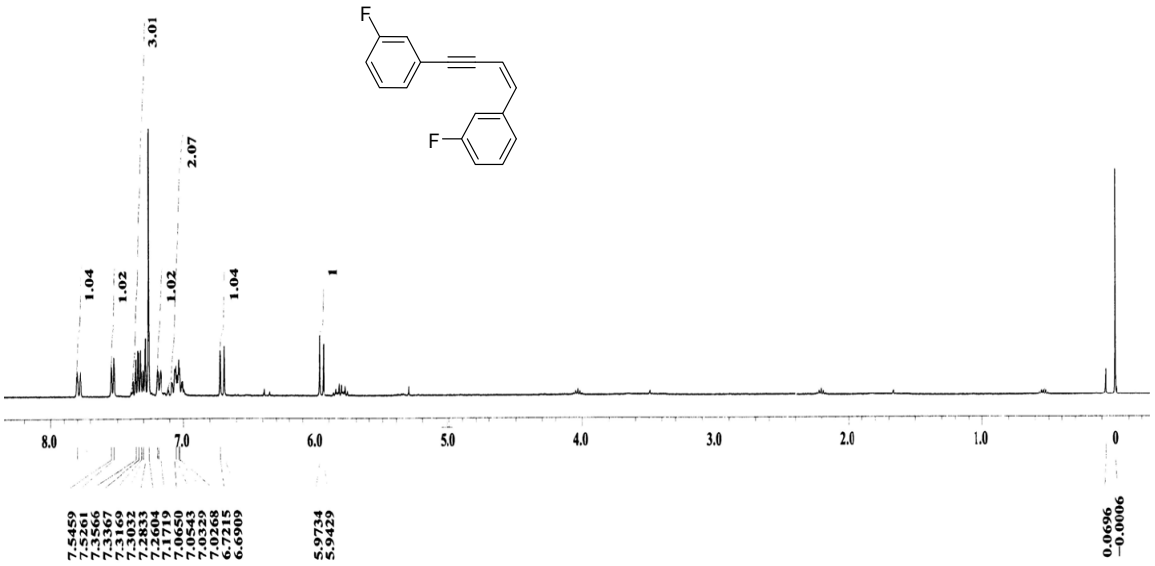


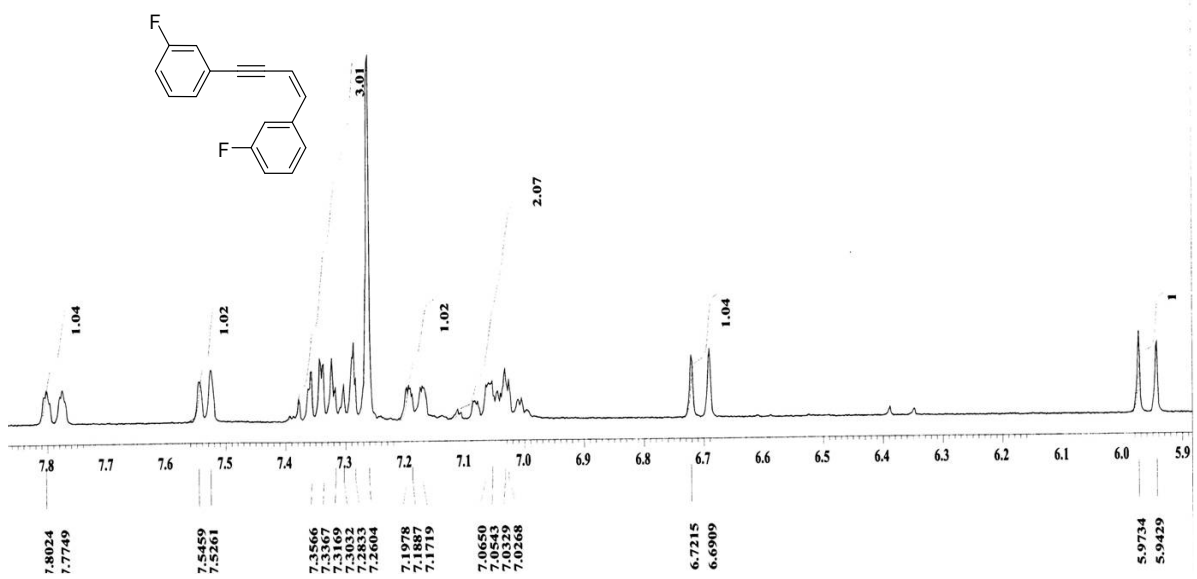
^{13}C NMR for 2g (*E*):



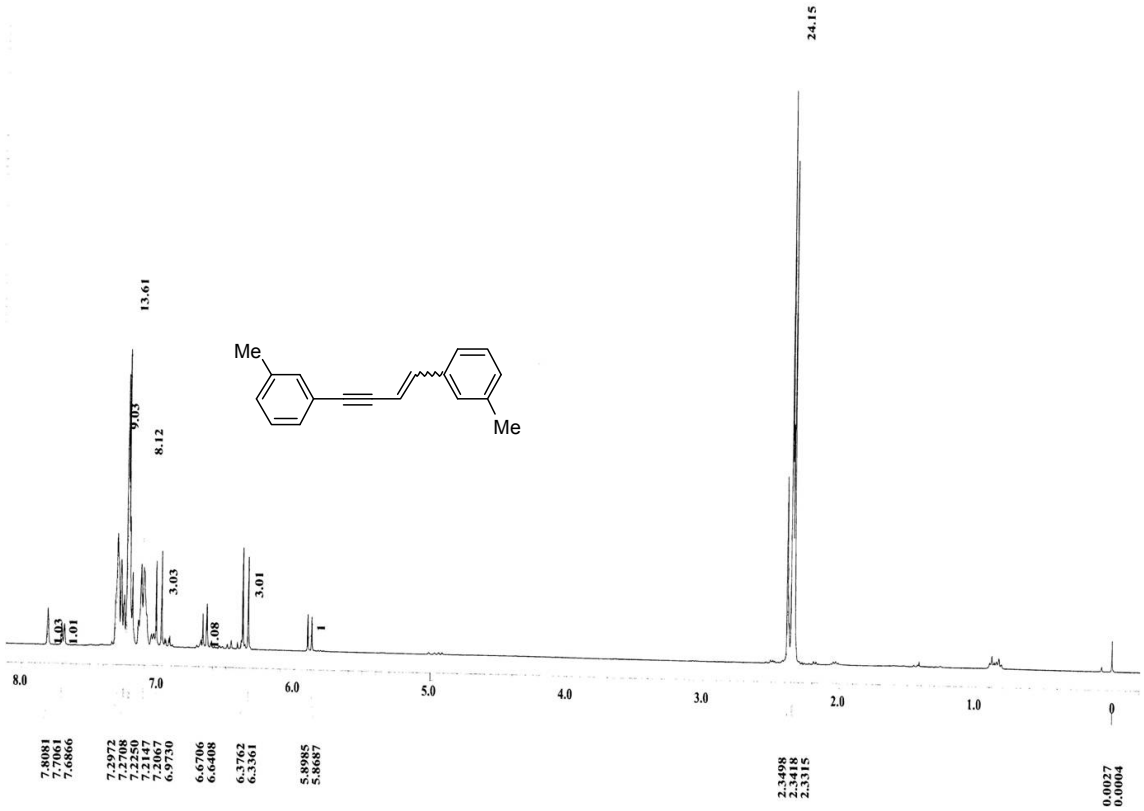


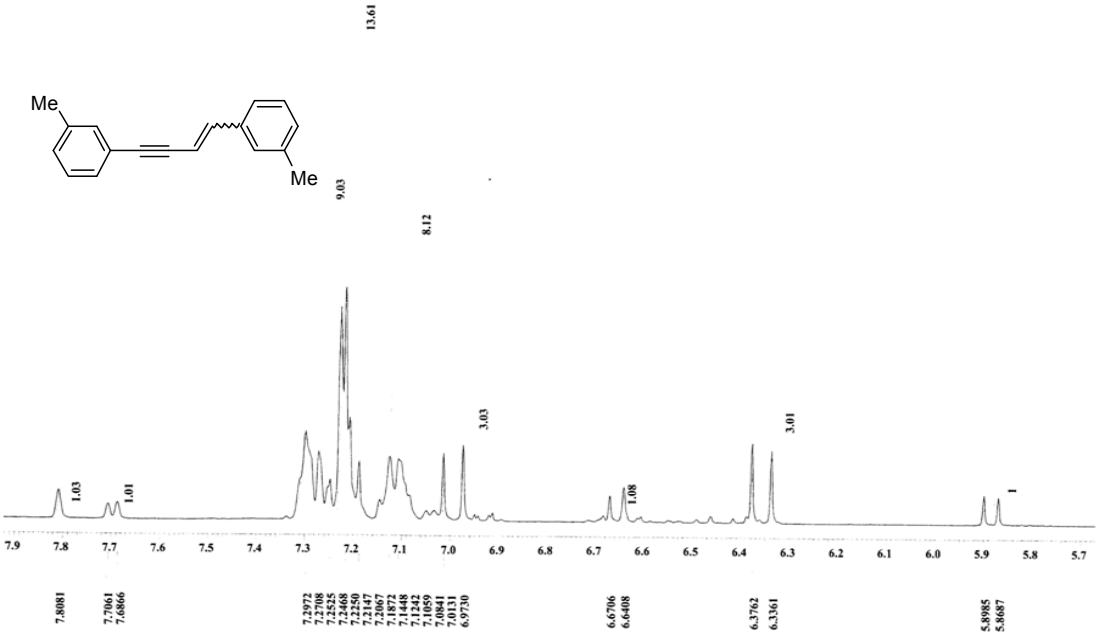
^{1}H NMR for 2g (*Z*):



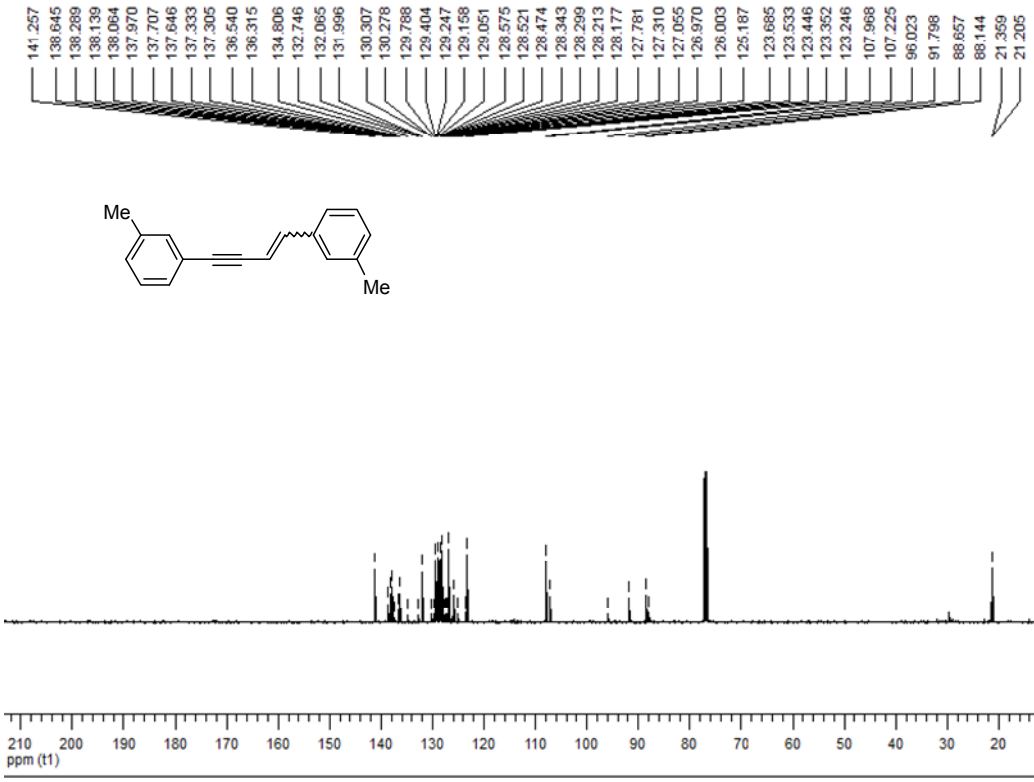


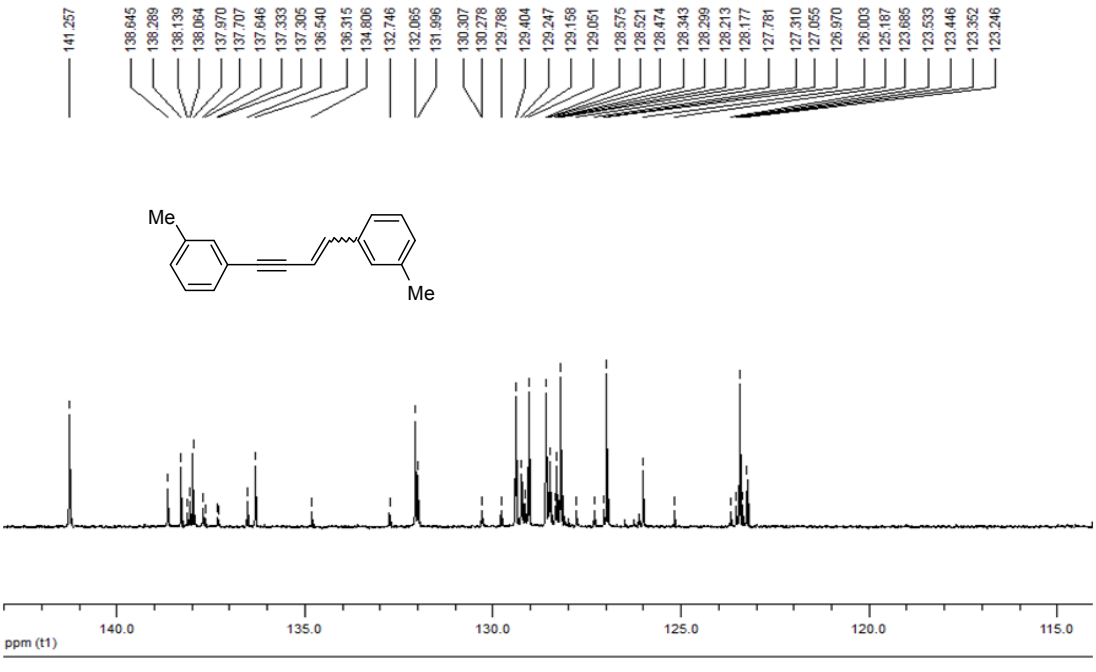
^{1}H NMR for 2h (*E*/*Z* = 75/25):



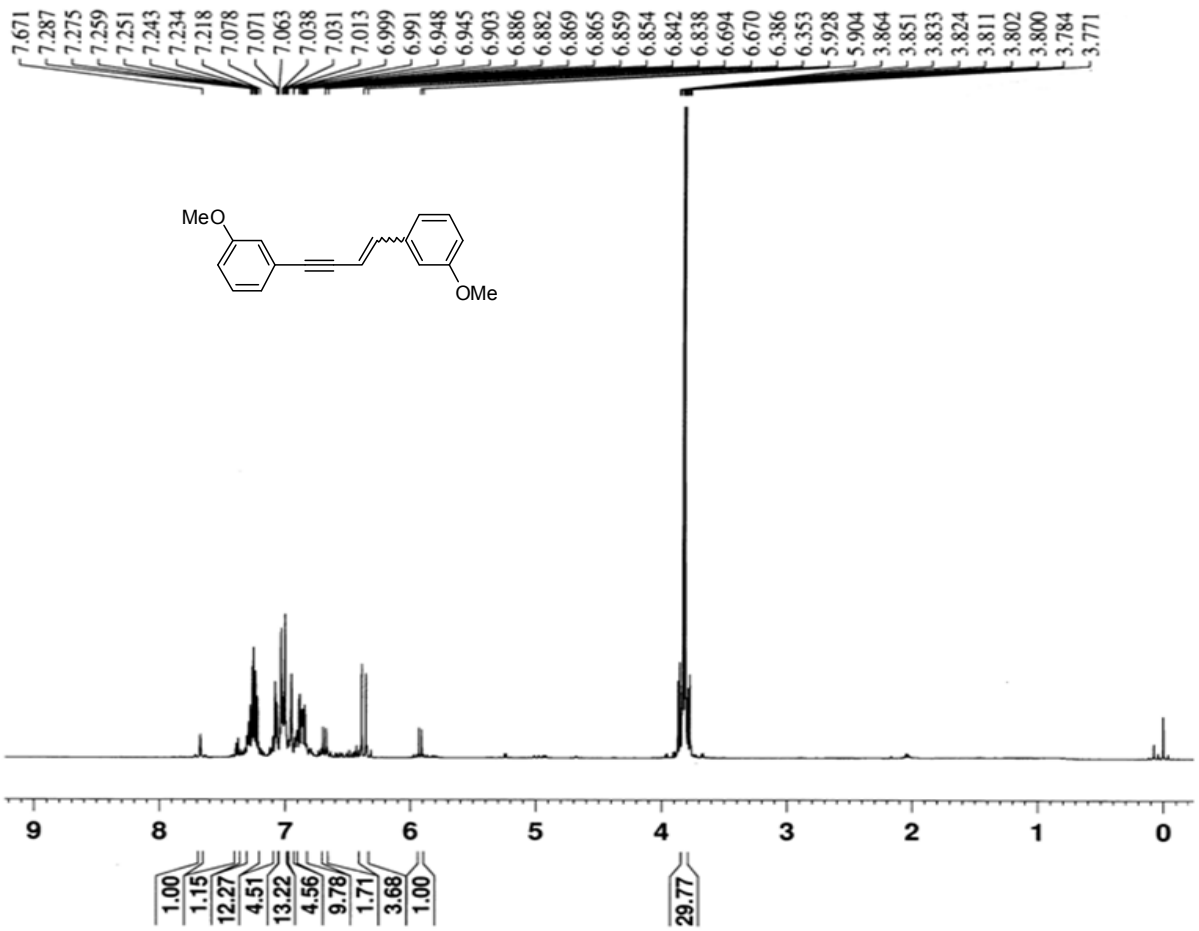


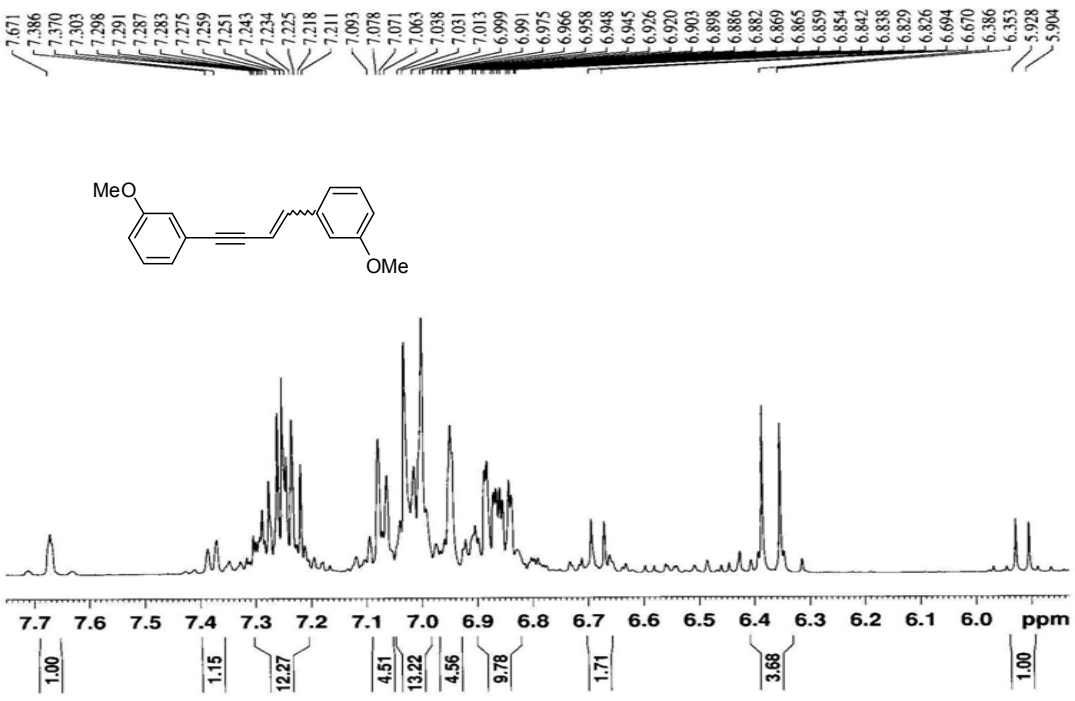
^{1}H and ^{13}C NMR for 2h (*E*/*Z* = 75/25):



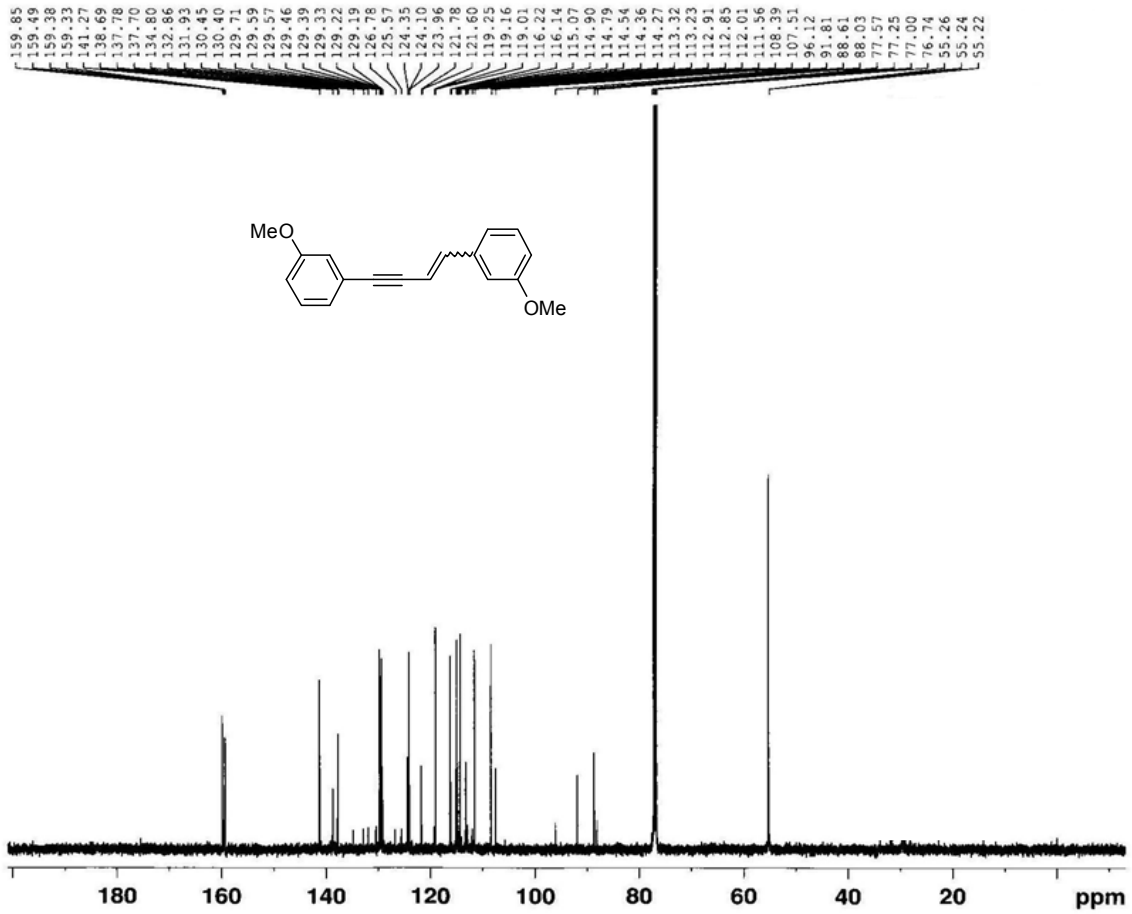


^{1}H NMR for 2i (*E*/*Z* = 79/21):

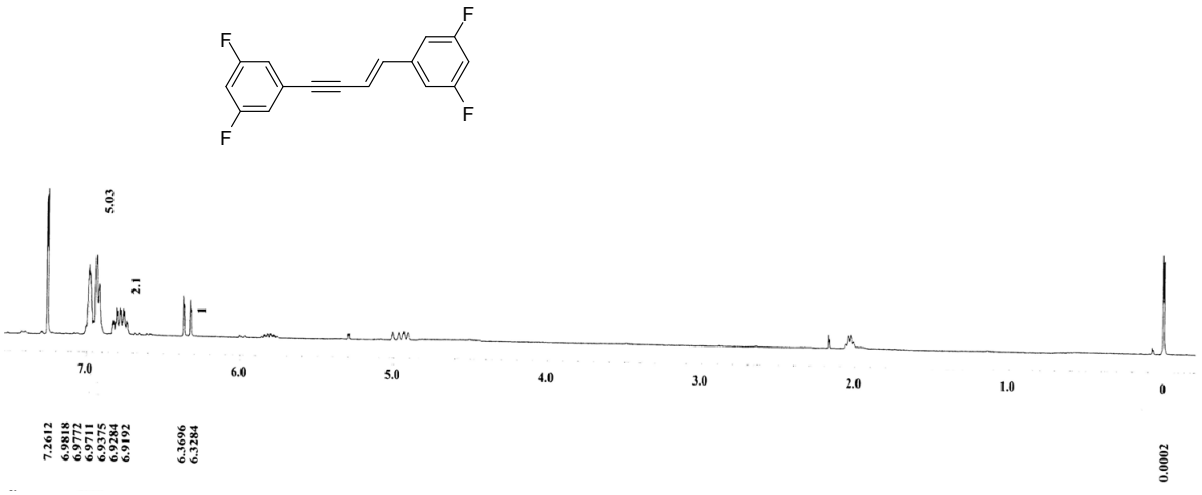


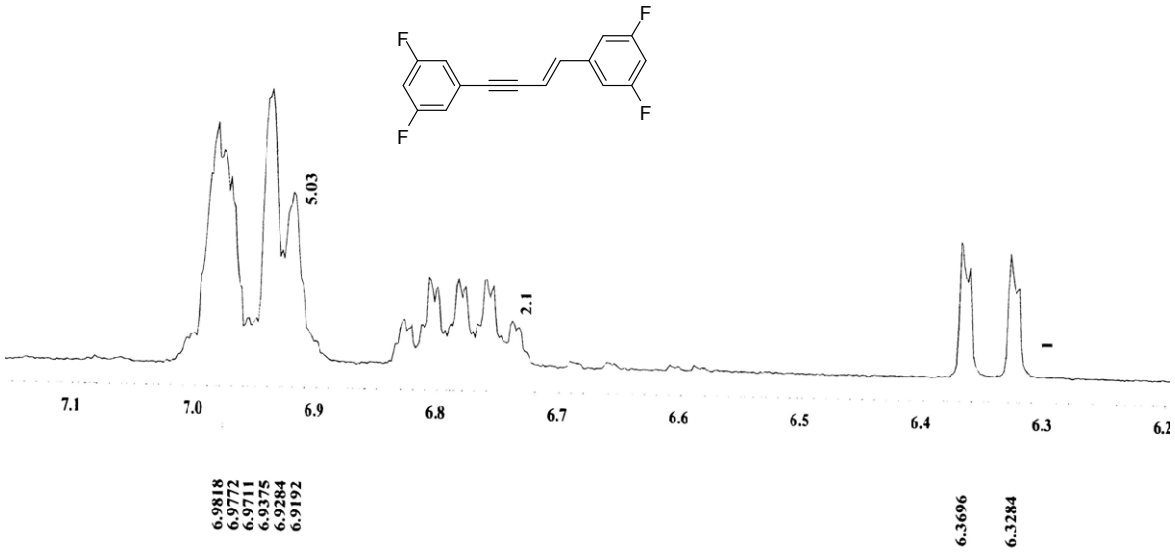


^{13}C NMR for 2i (*E*/*Z* = 79/21):

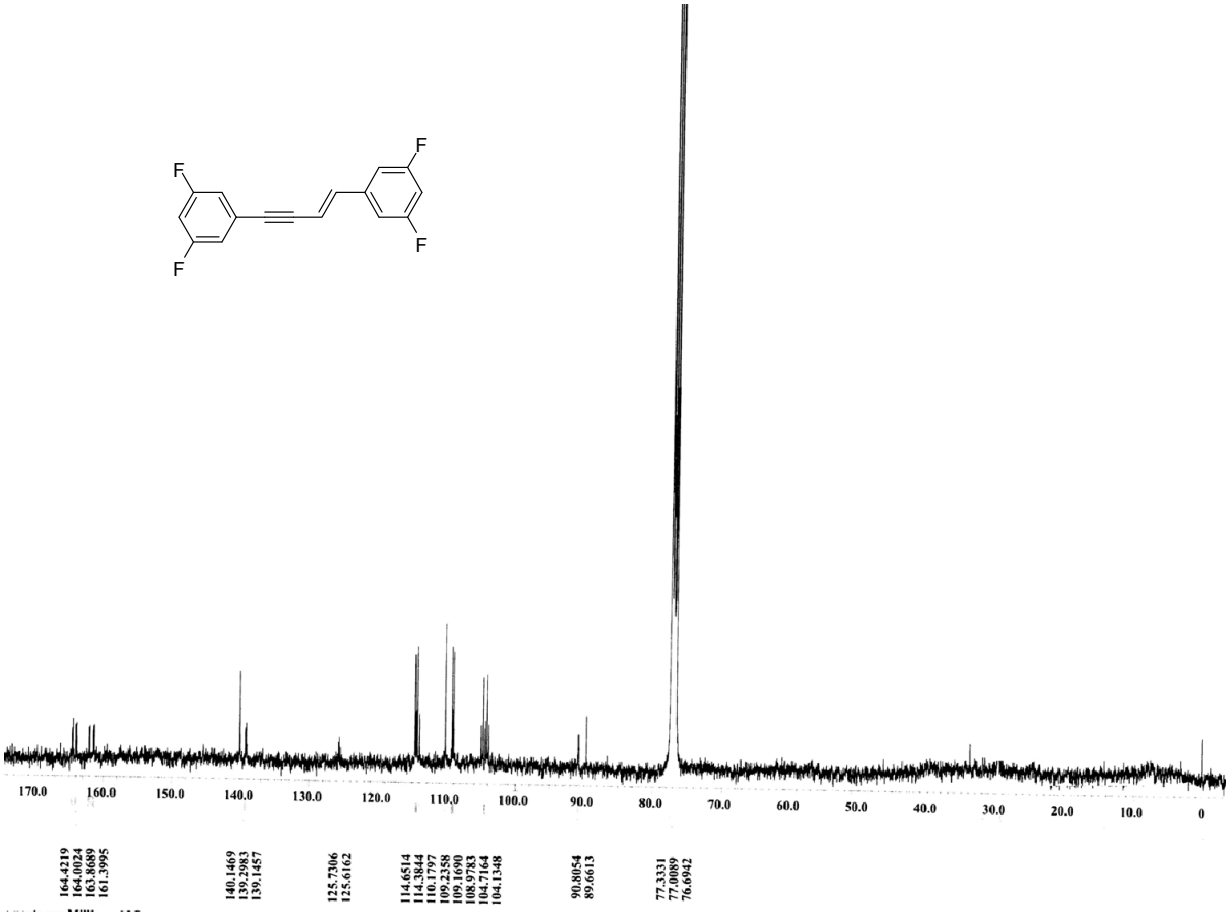


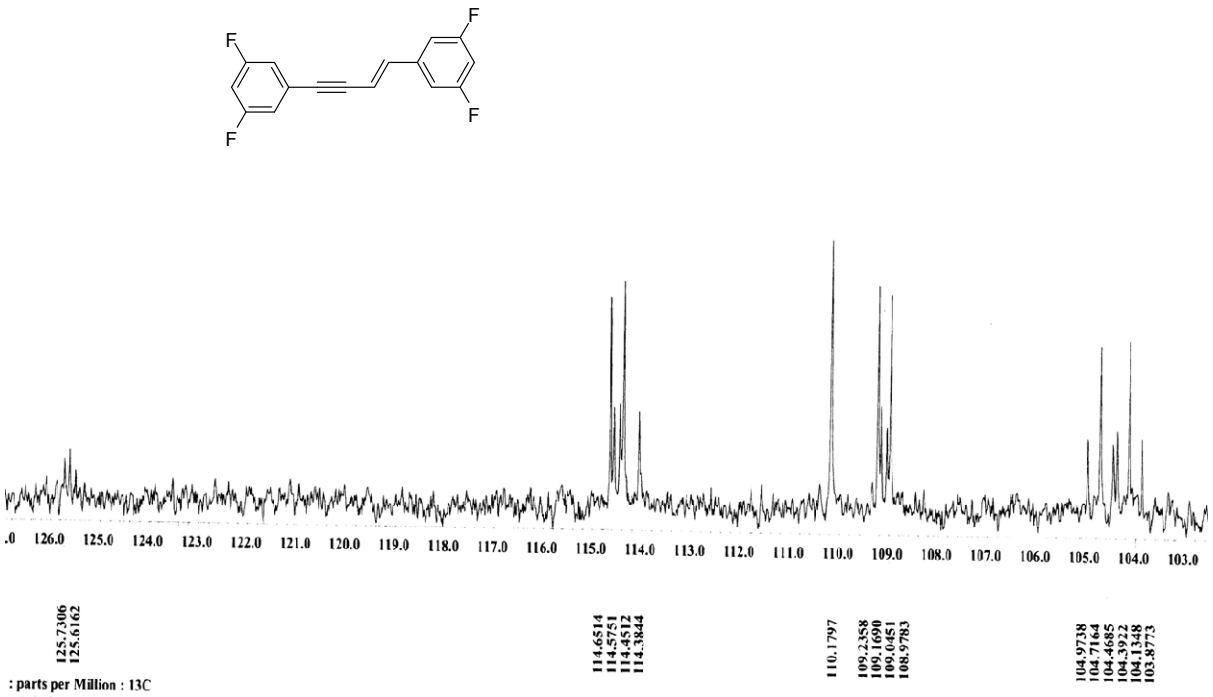
^{1}H NMR for 2j (*E*):



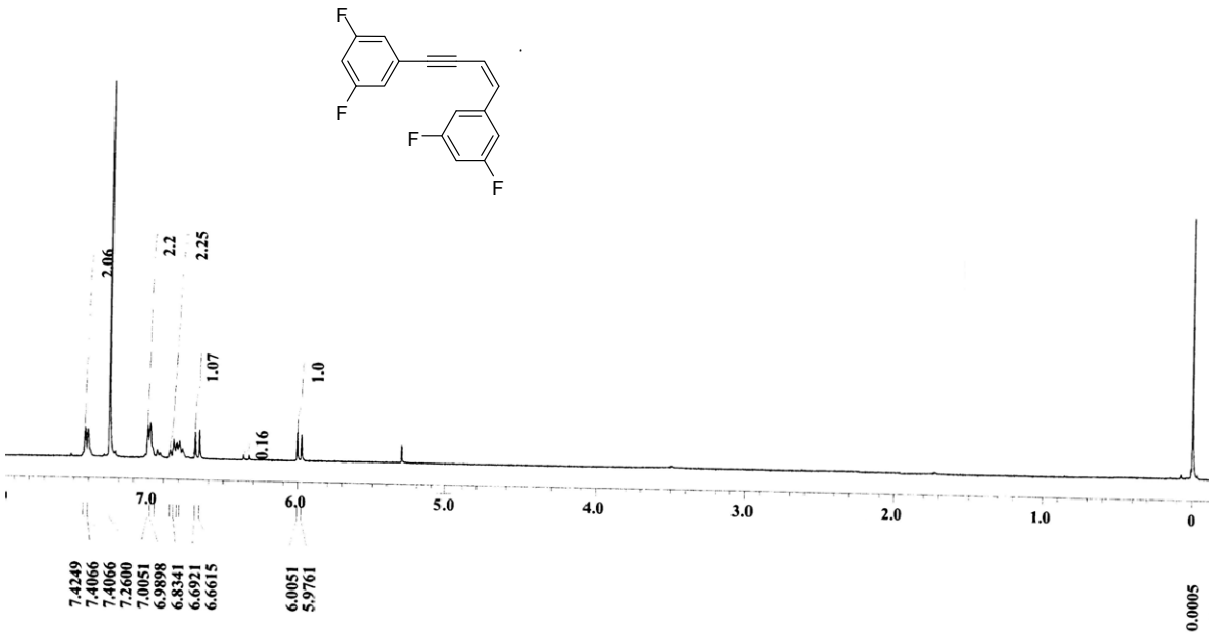


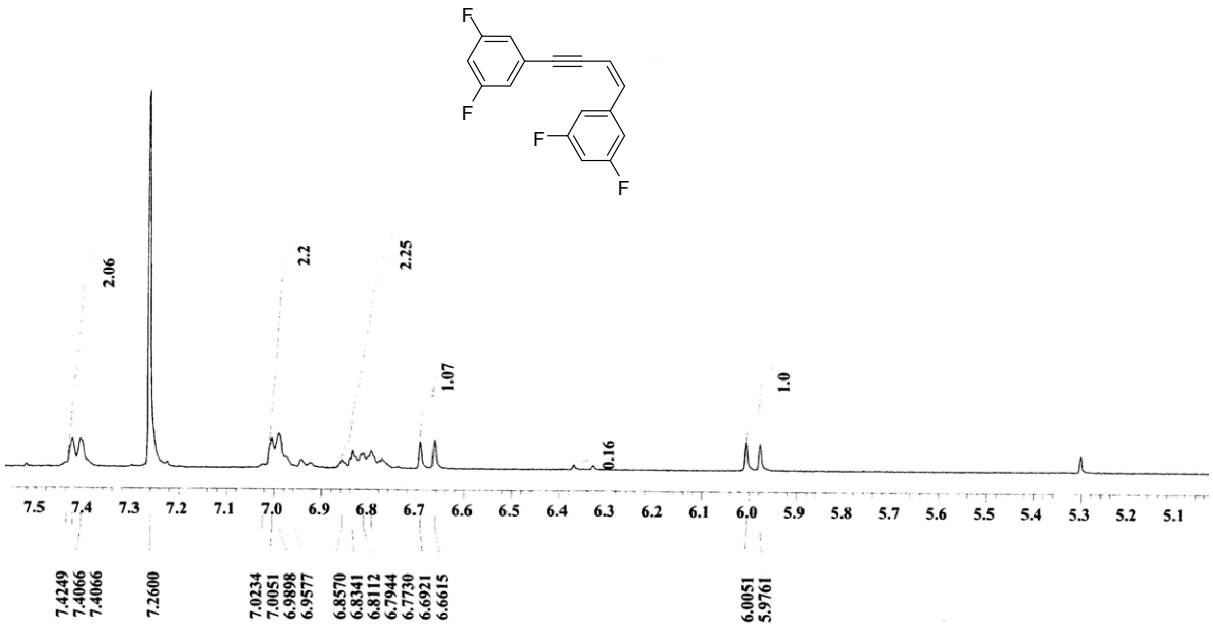
^{13}C NMR for 2j (*E*):



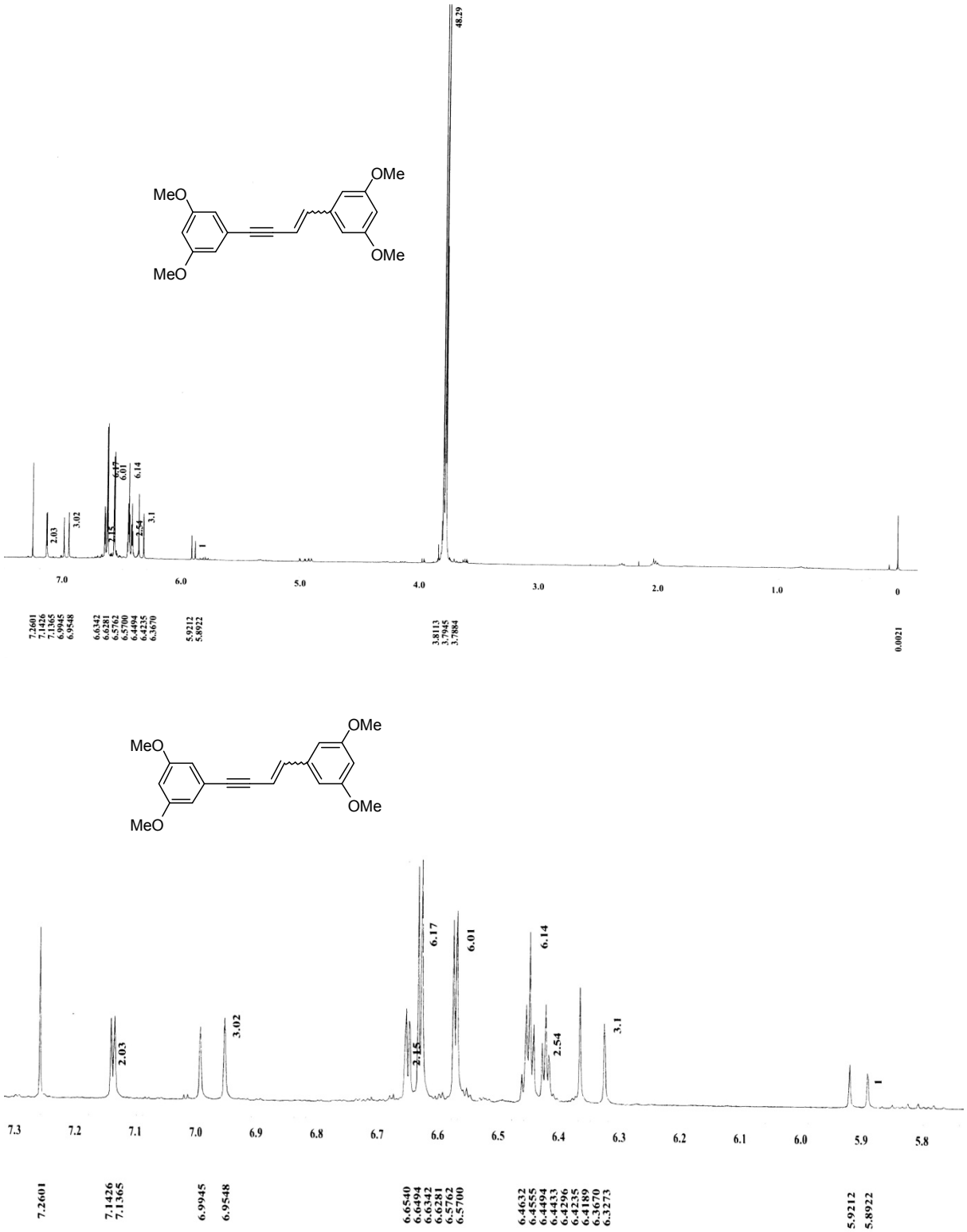


^{1}H NMR for 2j (*Z*):

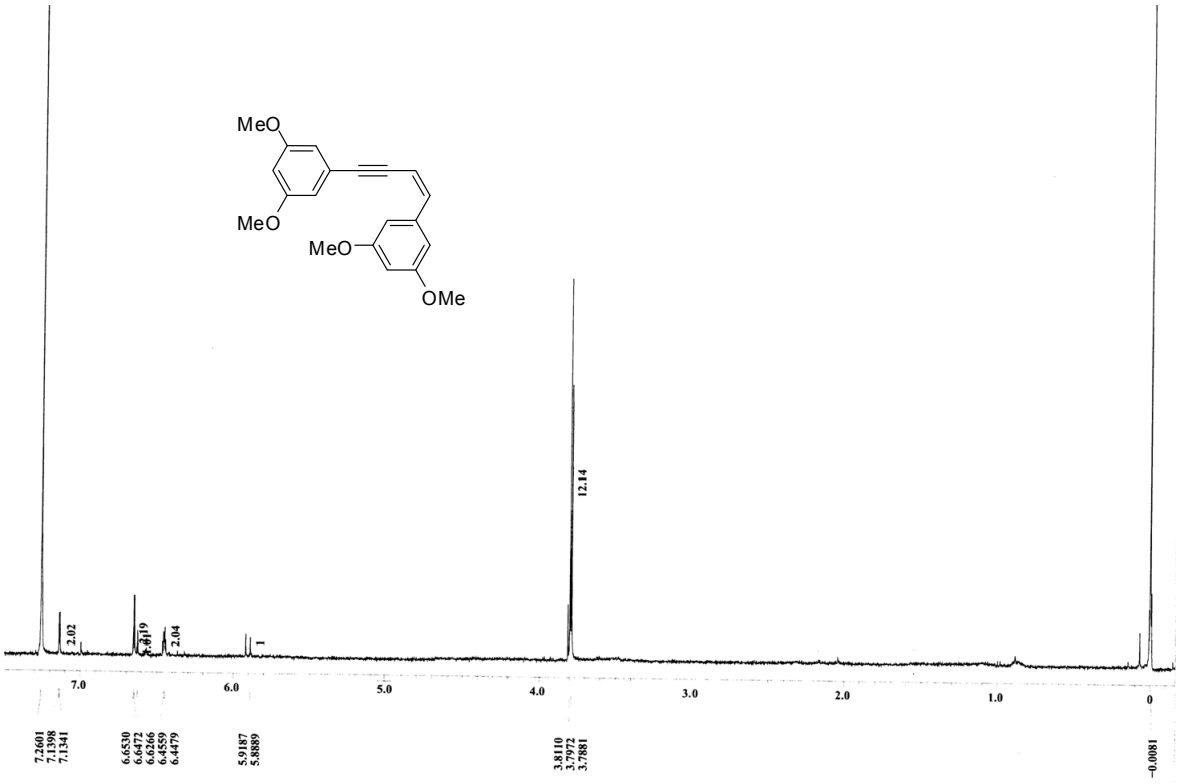


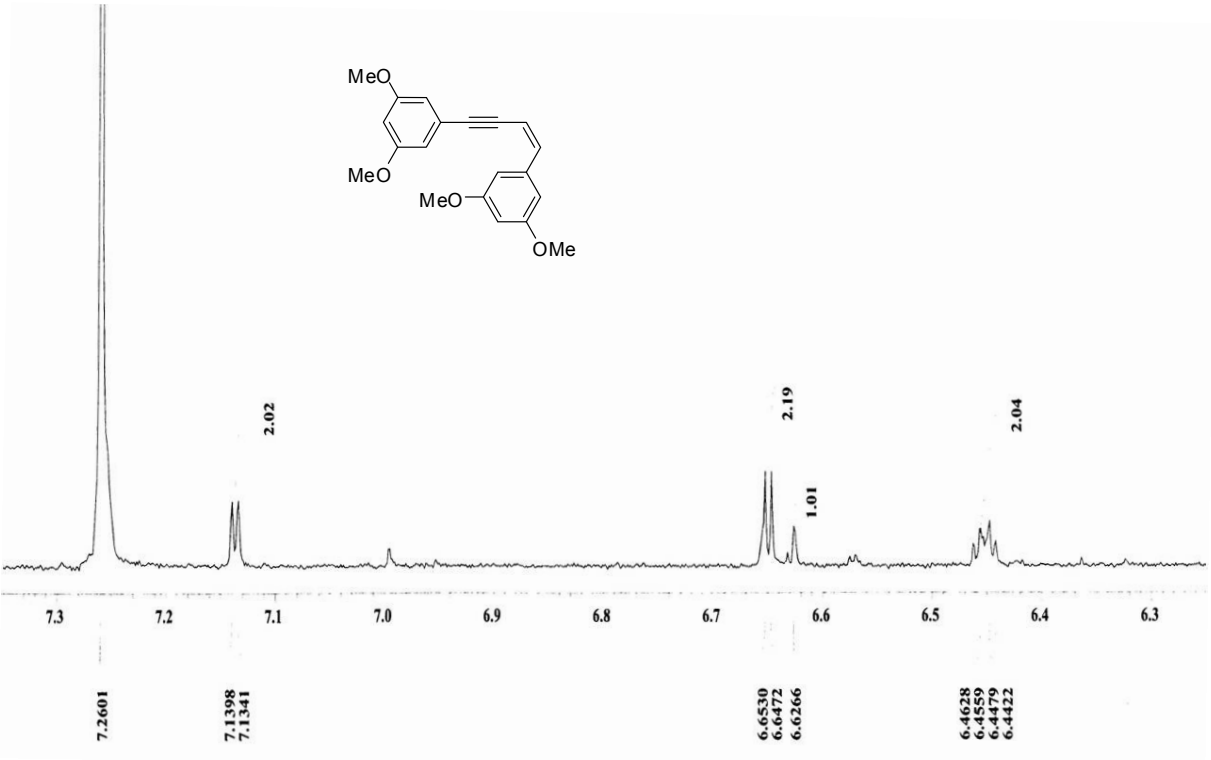


^{1}H NMR of 2k (*E*/*Z* = 75/35):

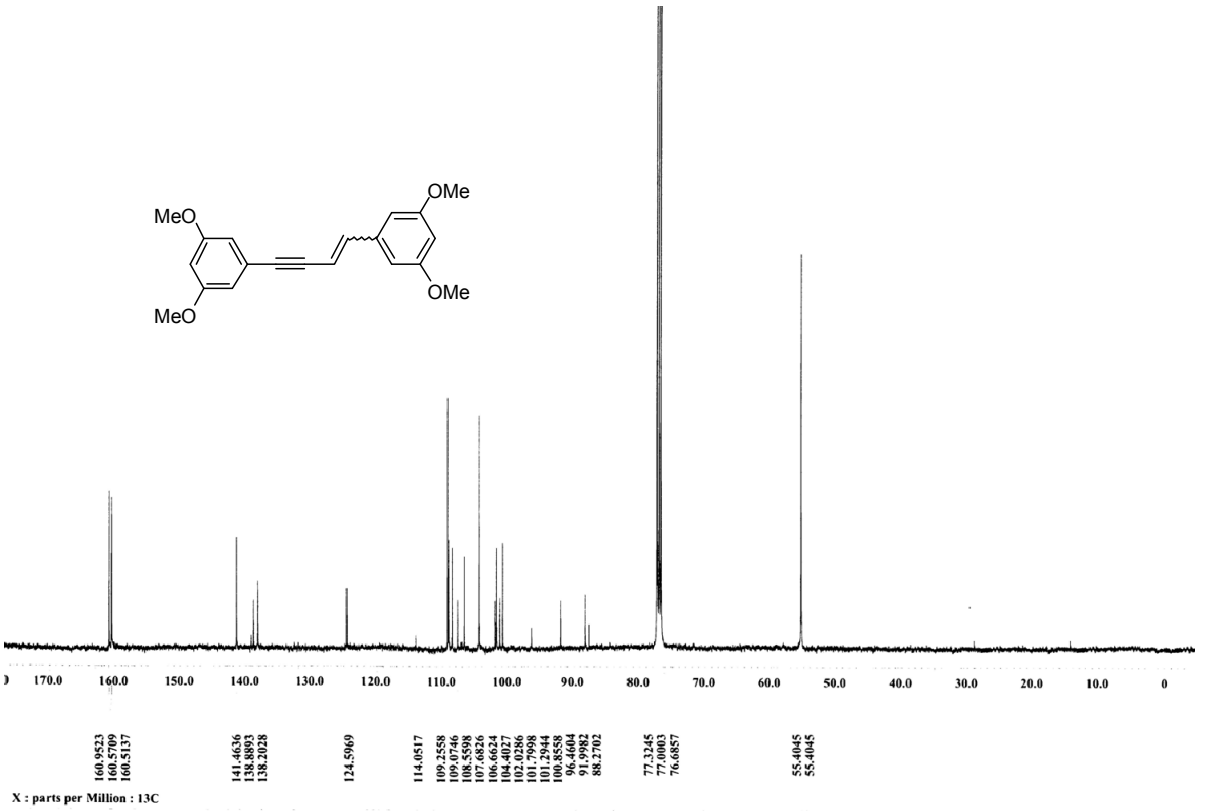


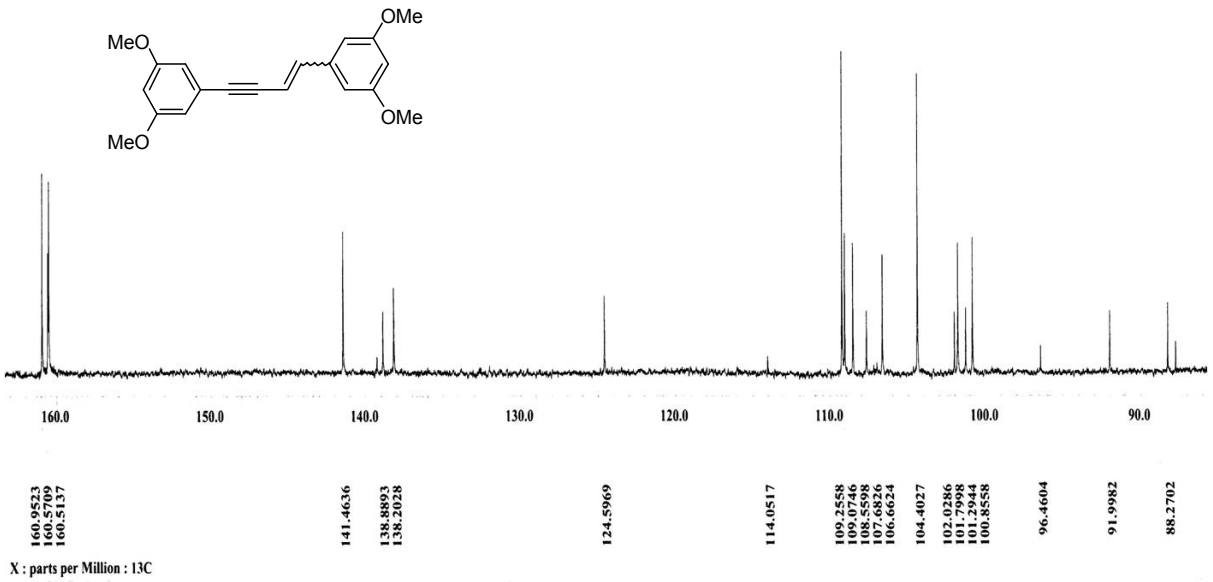
^{1}H NMR of 2k (*Z*):


MeO
MeO
MeO
OMe
12.14
2.02
2.19
2.04
1
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2601
7.1398
7.1341
6.6530
6.6472
6.6266
6.4559
6.4479
5.9187
5.8889
3.8110
3.7972
3.7881
-0.0081

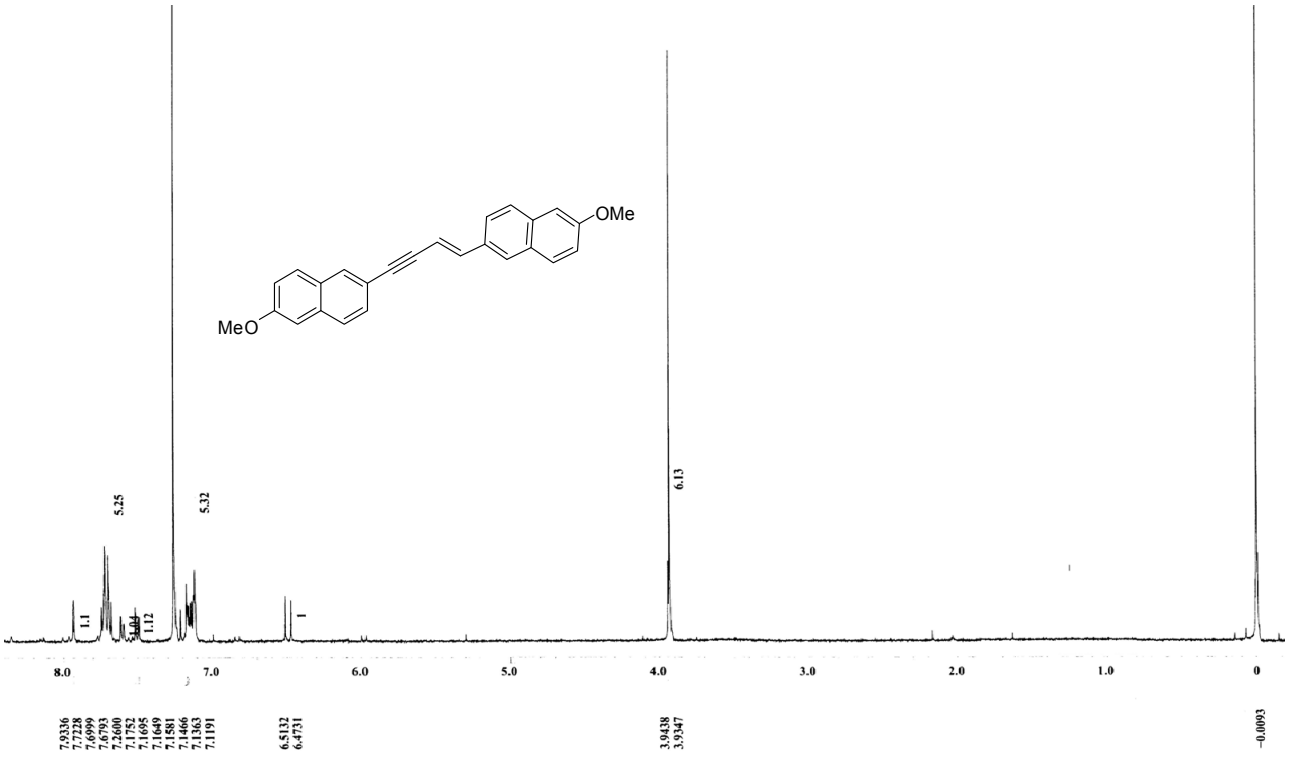

MeO
MeO
MeO
OMe
2.02
2.19
1.01
2.04
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
7.2601
7.1398
7.1341
6.6530
6.6472
6.6266
6.4628
6.4559
6.4479
6.4422

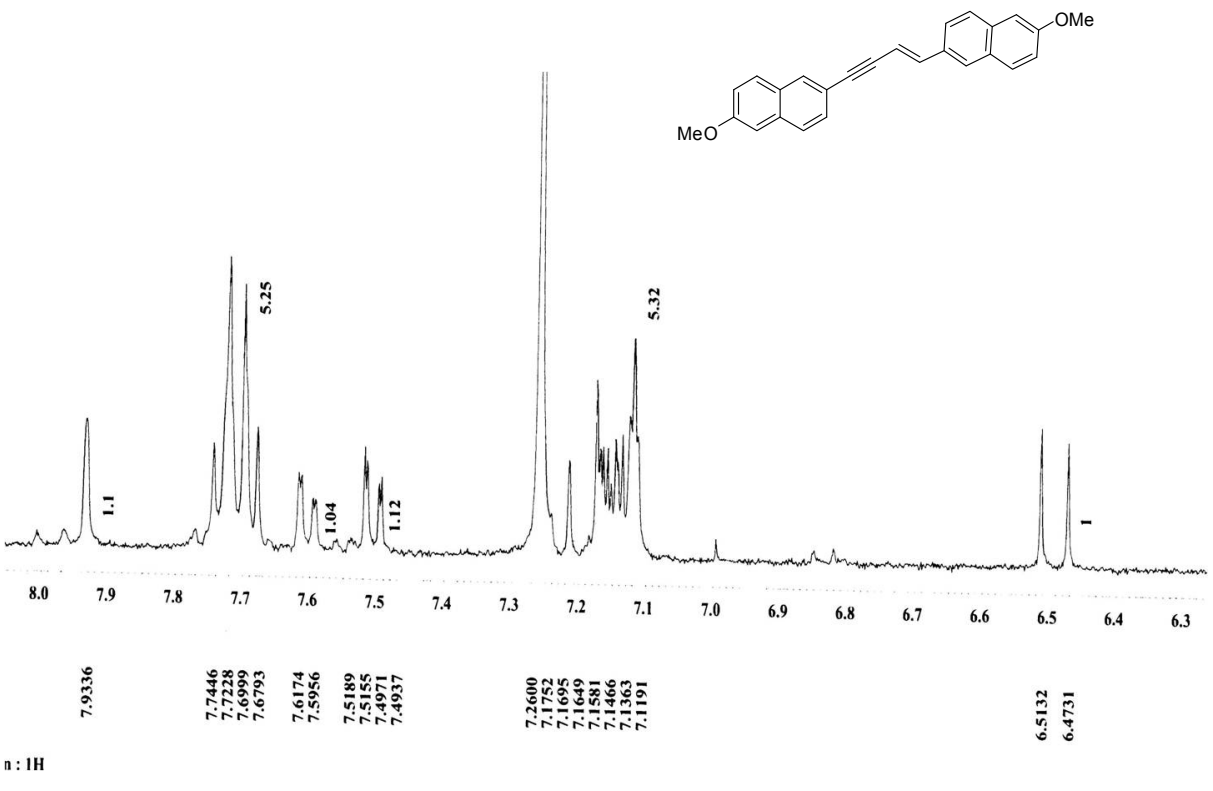
^{13}C NMR of 2k (*E*/*Z* = 75/25):



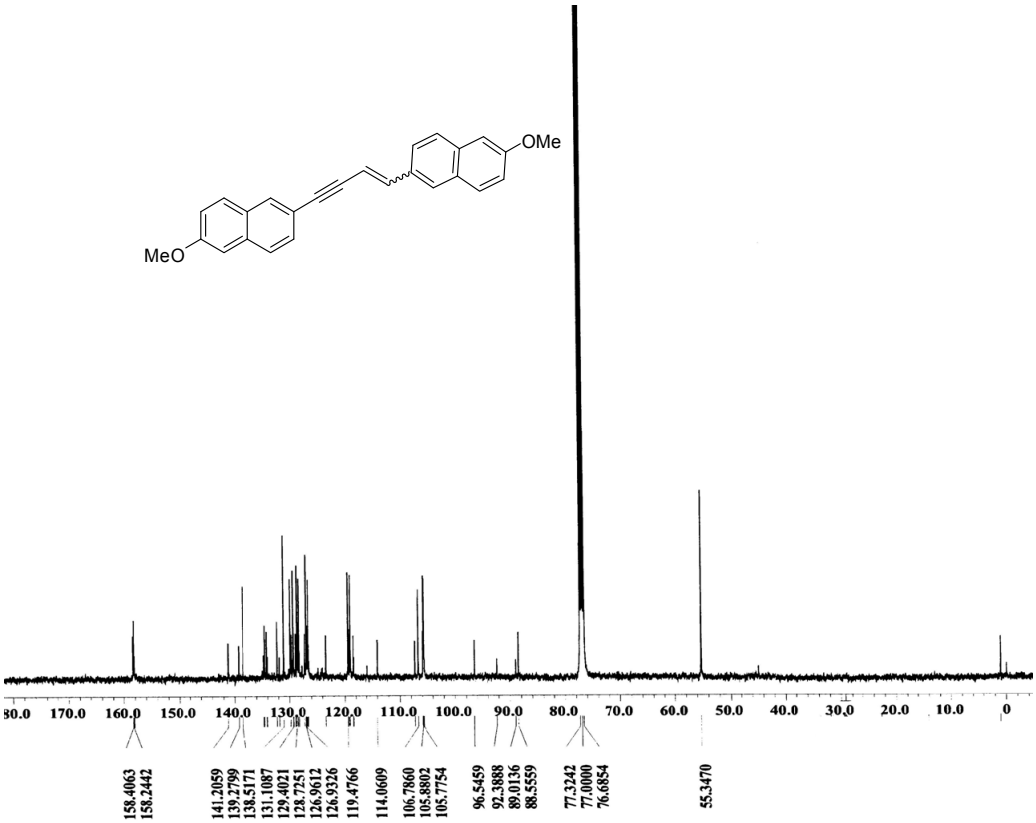


^{1}H NMR for 2l (*E*):

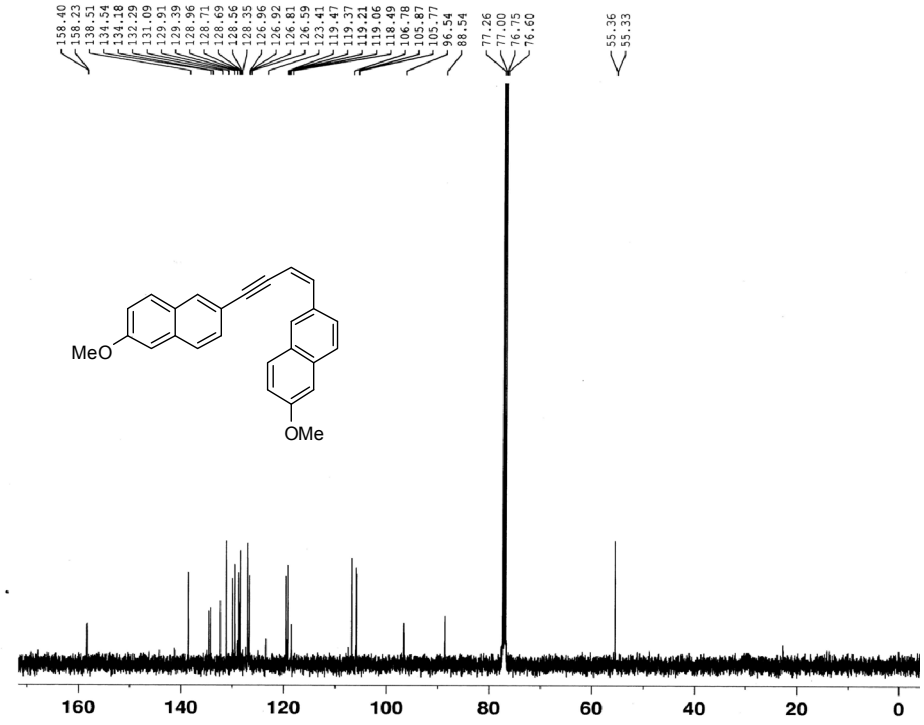




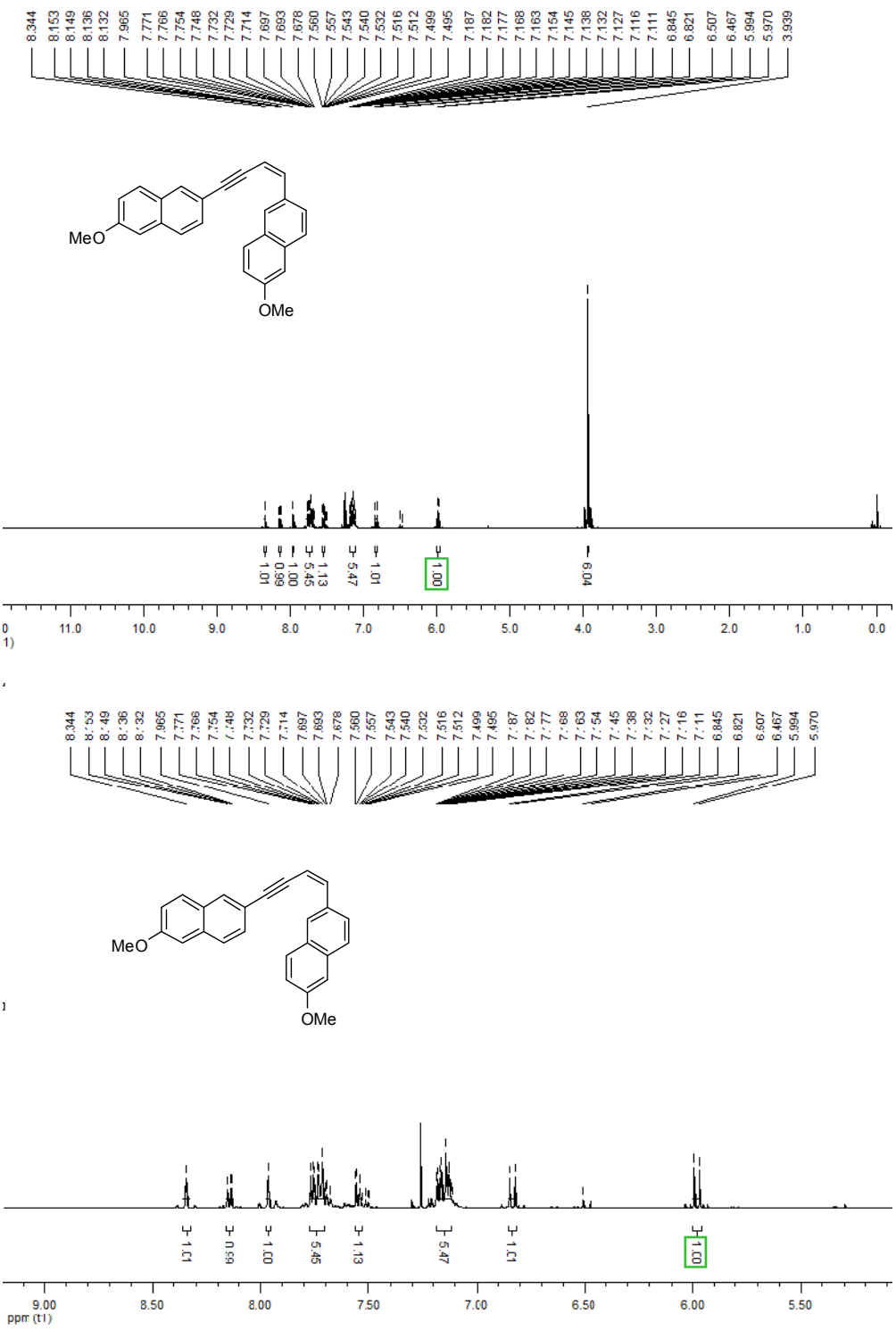
^{13}C NMR for 2l (*E*/*Z* = 37/63):



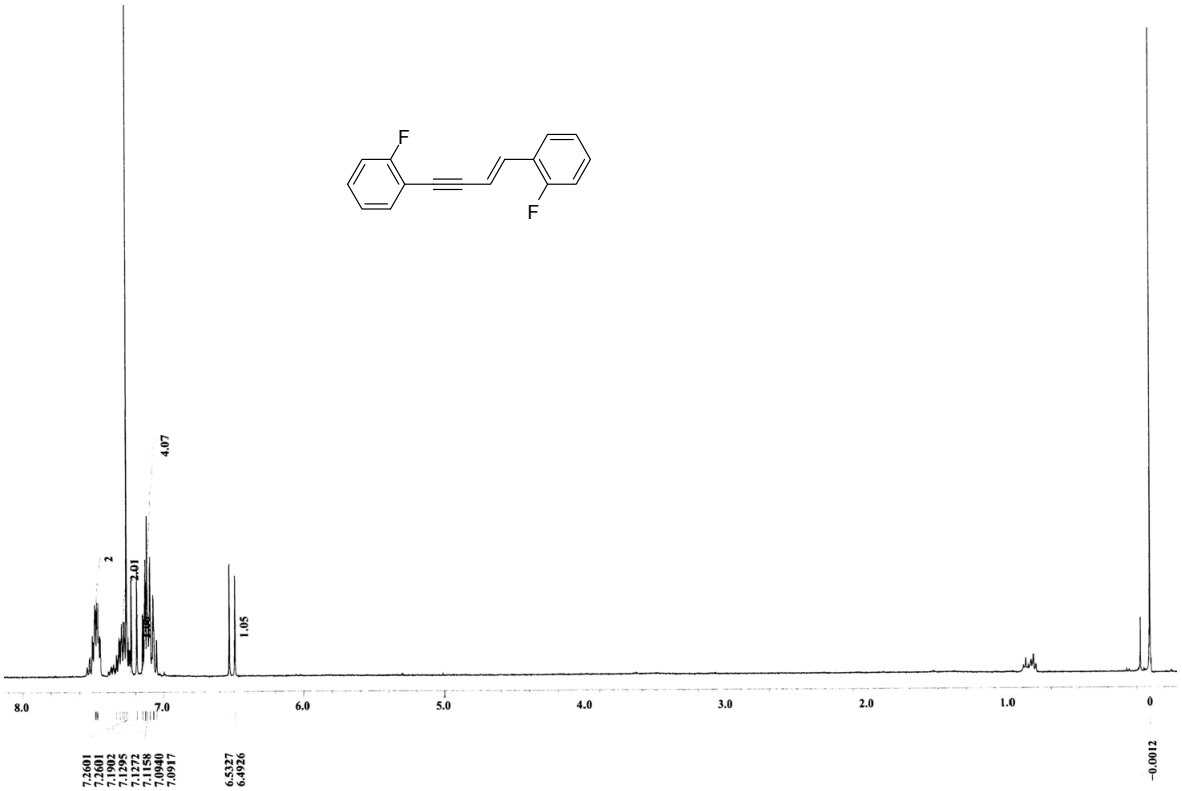
^{13}C NMR for 2l (major *Z* isomer):

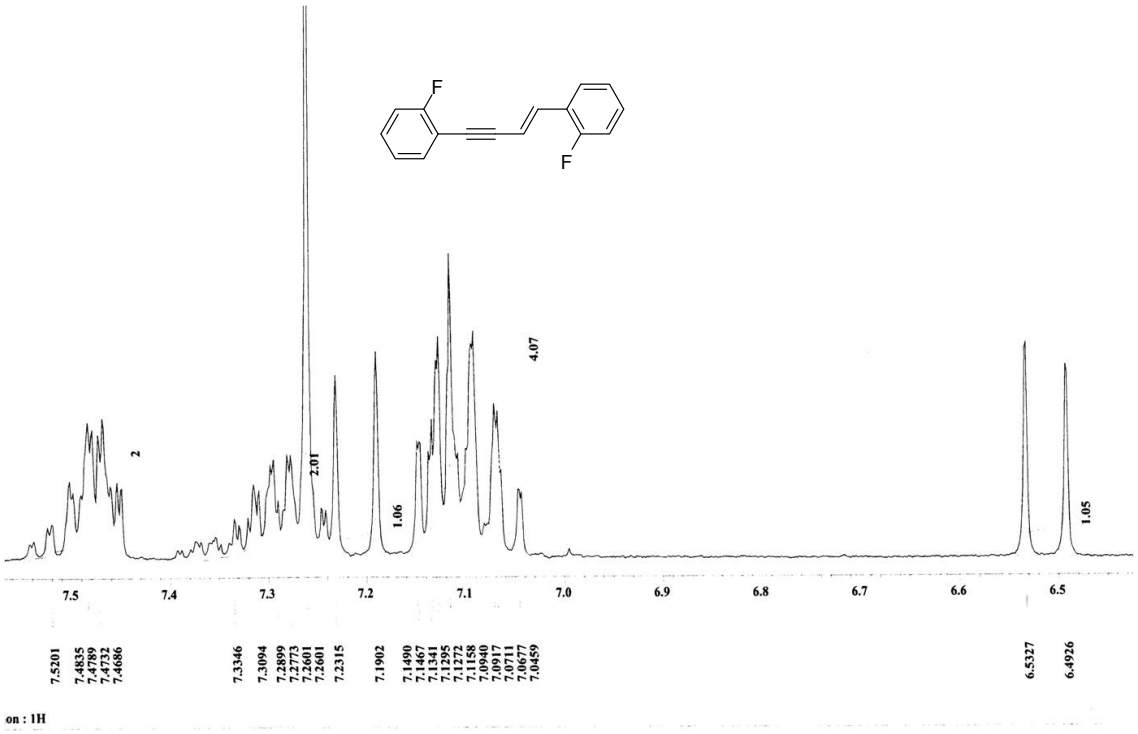


^{1}H NMR for 2l (major *Z* isomer):

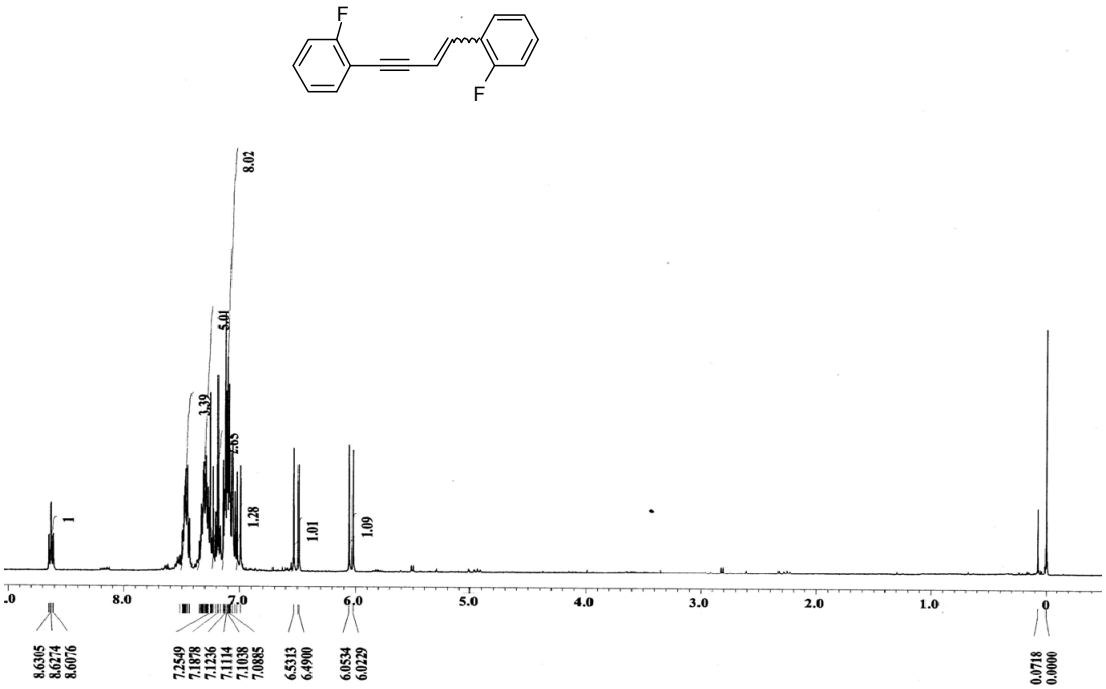


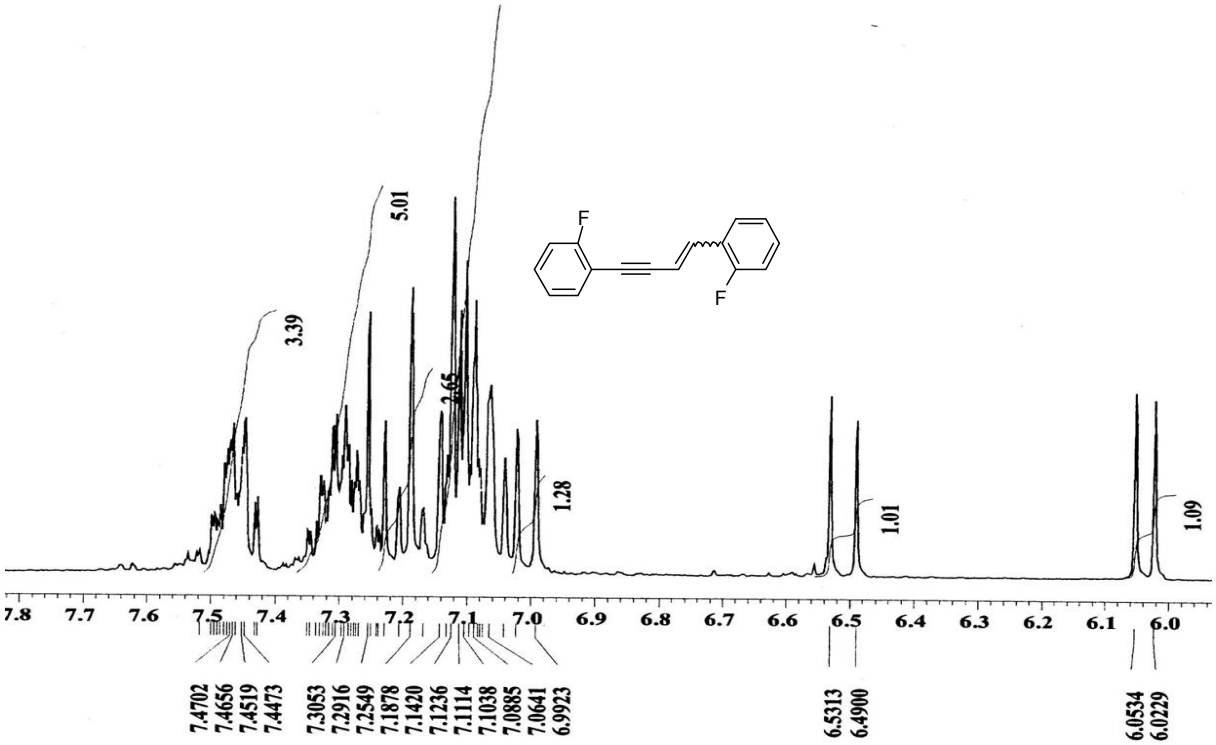
^{1}H NMR for 2m (*E*):



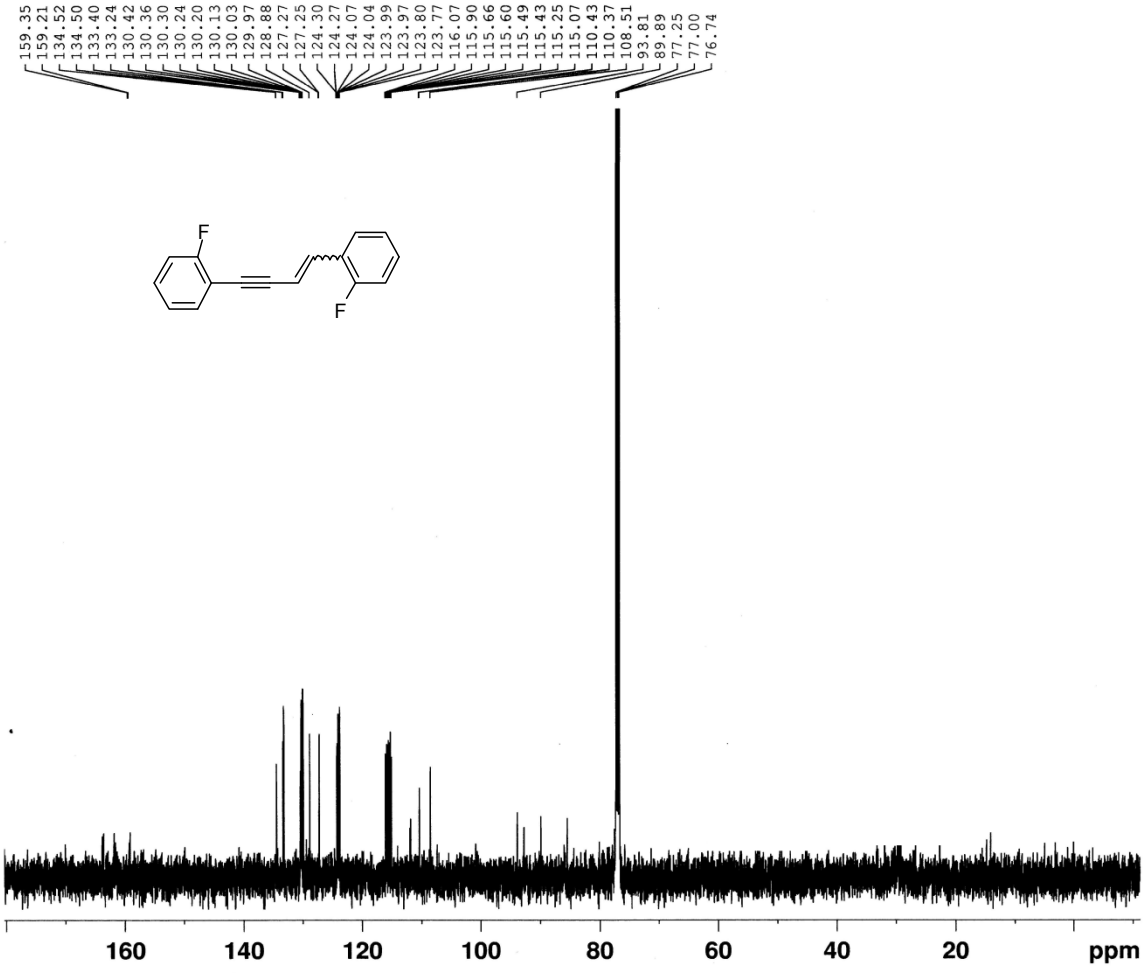


^{1}H NMR for 2m (*E*/*Z* = 50/50):

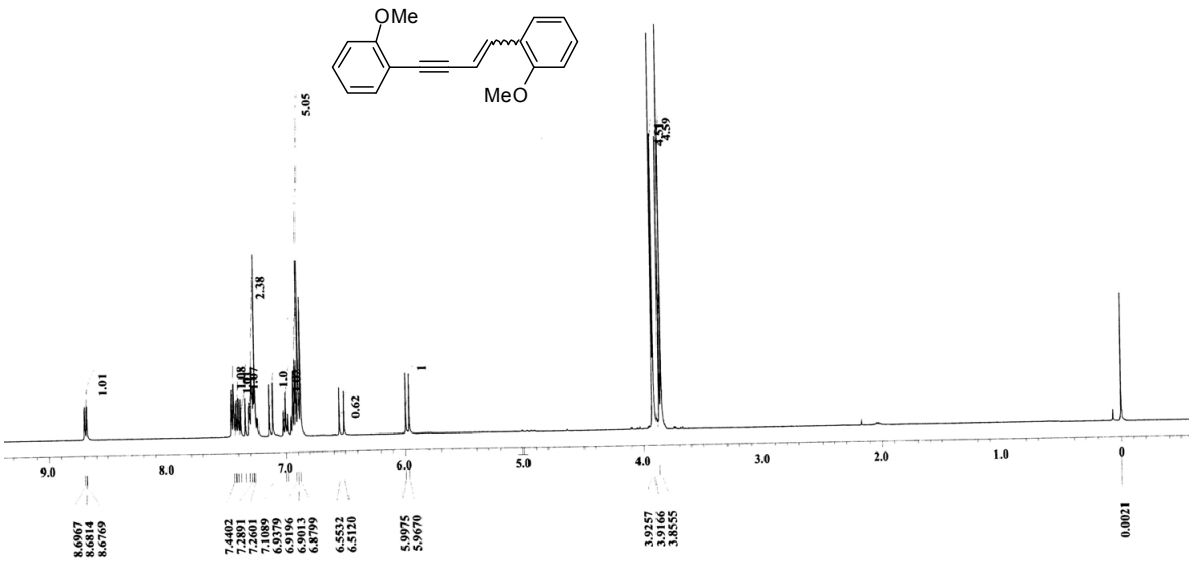


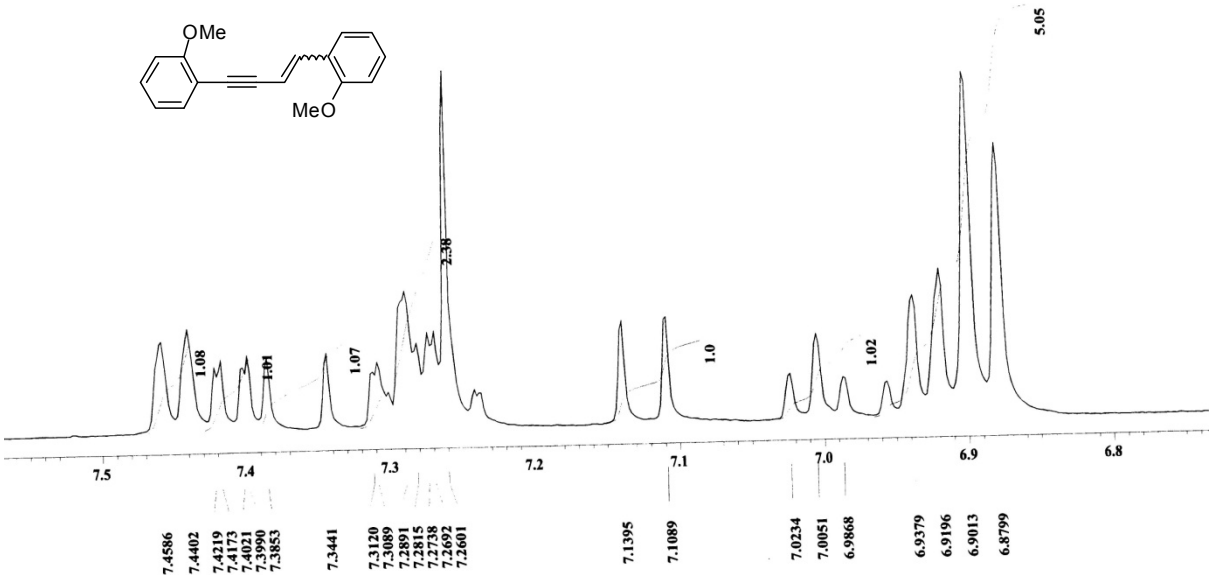


^{1}H and ^{13}C NMR for 2m (*E*/*Z* = 50/50):



^{1}H NMR for 2n (*E*/*Z* = 38/62):





^{13}C NMR for 2n (*E*/*Z* = 38/62):