Supporting Information

Copper immobilized on nano-silica triazine dendrimer (Cu(II)-TD@nSiO$_2$) catalyzed synthesis of symmetrical and unsymmetrical 1,3-diynes under aerobic conditions and ambient temperature

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1. Experimental Section

Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D instrument in the range of 400-4000 cm^{-1}. ^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using $CDCl_3$ as solvent. Mass spectra were recorded on a Platform II spectrometer from Micromass; EI mode at 70 eV. Elemental analysis was done on a LECO, CHNS-932 analyzer. The Cu content of the catalyst was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES), using a Jarrell-Ash 1100 ICP analyzer. The Cu(II)-TD@nSiO_2 catalyst was prepared according to the reported procedure.[1]

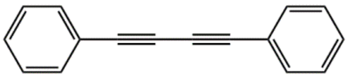
*Typical procedure for synthesis of symmetrical 1,3-diyne **2a***

A mixture of phenylacetylene **1a** (1 mmol), Cu(II)-TD@nSiO_2 (0.6 mol%), DBU (20 mol%) in acetonitrile (2 mL) was stirred under aerobic conditions at room temperature for 1.5 h. After completion of the reaction, as indicated by TLC (eluent: petroleum ether/ethyl acetate, 20:1), the catalyst was separated by centrifugation and washed with acetonitrile (5 mL). The solvent was evaporated and the residue was purified on a small bed of silica gel using petroleum ether/ethyl acetate (20:1) as eluent to afford the corresponding 1,3-diyne **2a** in 99% yield.

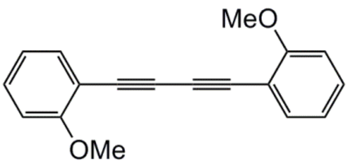
*Typical procedure for synthesis of unsymmetrical 1,3-diyne **3an***

A mixture of phenylacetylene **1a** (1 mmol) and ethyl propiolate **1n** (0.5 mmol), Cu(II)-TD@nSiO_2 (0.6 mol%) and DBU (20 mol%) in acetonitrile (2 mL) was stirred under aerobic conditions at room temperature for 2 h. The progress of the reaction was monitored by TLC (eluent:petroleum ether/ethyl acetate, 20:1). After completion of the reaction, the catalyst was separated by centrifugation and washed with acetonitrile (5 mL). Evaporation of the solvent followed by purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the desired unsymmetrical 1,3-diyne 3an in 89% yield.

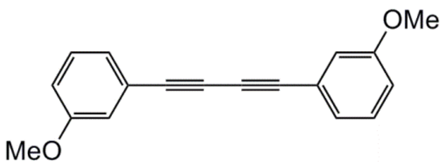
2. Spectroscopic data of the products 2a-2n (Table 2) and 3an-3dk (Table 4):



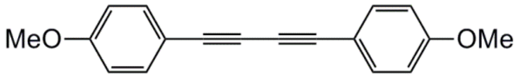
1,4-Diphenylbuta-1,3-diyne (Table 2, 2a):[2] Yield 99%. Mp 86-87 ^{o}C. IR (KBr): ν_{max} = 3077, 2924, 2146, 1590, 1482, 914, 754, 684, 524 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, ^{1}J = 8.0, ^{2}J = 1.6 Hz, 4H), 7.37-7.30 (m, 6H). MS: *m/z* (%): 204.13 ($[M+2]^+$, 2.40), 202.11 ($[M^+]$, 90.77), 200.11 (34.87), 174.09 (10.90), 150.11 (43.08), 122.07 (30.00), 110.06 (36.92), 98.05 (63.59), 74.04 (73.33), 63.09 (85.64), 50.10 (100.00).



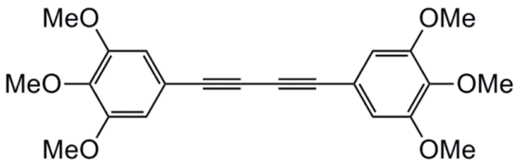
1,4-Bis(2-methoxyphenyl)buta-1,3-diyne (Table 2, 2b):[3] Yield 97%. Mp 136-138 ^{o}C. IR (KBr): ν_{max} = 3064, 3001, 2137, 1590, 1485, 1248, 1019, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, ^{1}J = 7.6, ^{2}J = 1.6 Hz, 2H), 7.27 (td, ^{1}J = 7.6, ^{2}J = 1.6 Hz, 2H), 6.86 (dd, ^{1}J = 7.6, ^{2}J = 7.2 Hz, 4H), 3.82 (s, 6H). MS: *m/z* (%): 262.04 ($[M^+]$, 71.03), 247.11 (15.10), 235.69 (31.12), 172.04 (30.11), 108.05 (47.88), 69.13 (27.10), 57.15 (85.14), 41.15 (100.00).



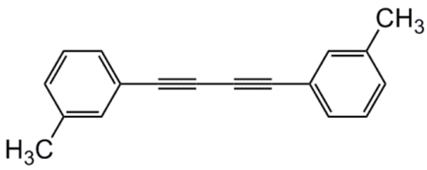
1,4-Bis(3-methoxyphenyl)buta-1,3-diyne (Table 2, 2c):[4] Yield 98%. Mp 92-93 ^{o}C. IR (KBr): ν_{max} = 3071, 2926, 2218, 1594, 1462, 1261, 1048, 782, 684 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, J = 8.0 Hz, 2H), 7.13 (dt, ^{1}J = 8.0, ^{2}J = 1.2 Hz, 2H), 7.04 (dd, ^{1}J = 4.0, ^{2}J = 1.6 Hz, 2H), 6.94 (ddd, ^{1}J = 8.0, ^{2}J = 3.6, ^{3}J = 1.2 Hz, 2H), 3.80 (s, 6H). MS: *m/z* (%): 263.13 ($[M+1]^+$, 5.86), 262.04 ($[M^+]$, 37.11), 218.98 (14.18), 189.09 (15.21), 176.00 (21.39), 150.05 (21.39), 111.03 (32.73), 85.08 (34.28), 71.07 (54.38), 57.07 (100.00), 43.12 (81.44).



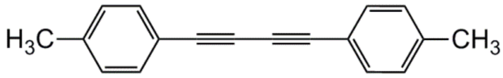
1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (Table 2, 2d):[2] Yield 99%. Mp 139-141 ºC. IR (KBr): v_{max} = 2999, 2929, 2134, 1597, 1500, 1250, 1023, 835, 534 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dt, ^1J = 8.4, ^2J = 2.4 Hz, 4H), 6.87 (dt, ^1J = 7.2, ^2J = 2.0 Hz, 4H), 3.82 (s, 6H). MS: *m/z* (%): 263.03 ($[M+1]^+$, 18.07), 262.04 ($[M^+]$, 89.11), 246.99 (53.47), 219.03 (18.32), 204.03 (14.60), 176.04 (33.17), 149.01 (42.08), 111.05 (21.78), 85.12 (19.31), 63.08 (32.18), 57.13 (73.21), 43.16 (100.00).



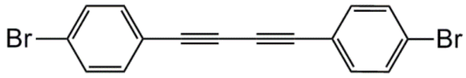
1,4-Bis(3,4,5-trimethoxyphenyl)buta-1,3-diyne (Table 2, 2e):[5] Yield 94%. Mp 200-202 ºC. IR (KBr): v_{max} = 3092, 2959, 2928, 2141, 1573, 1462, 1272, 1127, 992, 819, 712 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, ^1J = 8.4, ^2J = 3.2 Hz, 2H), 7.54 (dd, ^1J = 8.4, ^2J = 3.2 Hz, 2H), 3.87 (s, 6H), 3.86 (s, 12H). MS: *m/z* (%): 384.03 ($[M+2]^+$, 4.49), 383.04 ($[M+1]^+$, 22.18), 382.01 ($[M^+]$, 100.00), 367.01 (38.03), 308.98 (6.56), 221.06 (3.57), 191.10 (12.15), 139.11 (13.73), 111.06 (29.23), 69.04 (48.59), 53.06 (73.94), 41.12 (92.75).



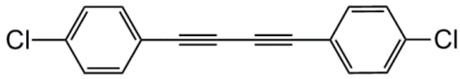
1,4-Di-*m*-tolylbuta-1,3-diyne (Table 2, 2f):[2] Yield 98%. Mp 73-74 ºC. IR (KBr): v_{max} = 3033, 2917, 2138, 1645, 1591, 1478, 1038, 903, 787, 684 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (s, 2H), 7.24 (s, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.26 (s, 6H). MS: *m/z* (%): 231.08 ($[M+1]^+$, 19.72), 230.67 ($[M^+]$, 100.00), 215.05 (11.00), 202.05 (7.79), 163.05 (10.12), 115.06 (20.42), 77.10 (18.66), 63.09 (50.70), 51.11 (63.38), 43.18 (67.61).



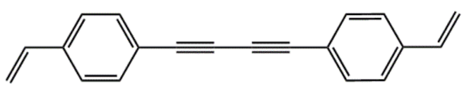
1,4-Di-*p*-tolylbuta-1,3-diyne (Table 2, 2g):[2] Yield 98%. Mp 183-184 ^{o}C. IR (KBr): ν_{max} = 3077, 2959, 2925, 2133, 1500, 1273, 1120, 809, 521 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42 (d, J = 8.0 Hz, 4H), 7.14 (d, J = 8.0 Hz, 4H), 2.36 (s, 6H). MS: *m/z* (%): 232.17 ([M+2]$^+$, 1.23), 230.67 ([M$^+$], 63.68), 215.15 (12.15), 202.13 (8.14), 189.13 (6.57), 167.07 (65.09), 149.02 (97.17), 113.17 (37.26), 104.07 (50.94), 83.11 (41.51), 70.11 (84.43), 57.10 (100.00), 41.13 (96.23).



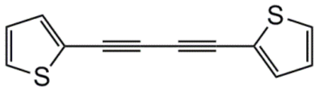
1,4-Bis(4-bromophenyl)buta-1,3-diyne (Table 2, 2h):[6] Yield 92%. Mp 260-261 ^{o}C. IR (KBr): ν_{max} = 3090, 2924, 1624, 1119, 824 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.50 (dt, ^{1}J = 8.4, ^{2}J = 2.0 Hz, 4H), 7.39 (dt, ^{1}J = 7.2, ^{2}J = 2.4 Hz, 4H). MS: *m/z* (%): 361.76 ([M+4]$^+$, 0.31), 359.75 ([M+2]$^+$, 0.54), 357.81 ([M$^+$], 0.41), 335.72 (0.55), 279.12 (1.43), 167.05 (6.27), 149.03 (21.74), 111.11 (6.52), 83.12 (17.32), 69.13(27.45), 57.15 (80.43), 43.20 (100.00).

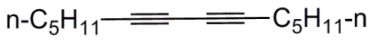


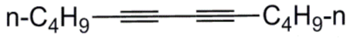
1,4-Bis(4-chlorophenyl)buta-1,3-diyne (Table 2, 2i):[5] Yield 94%. Mp 250-251 ^{o}C. IR (KBr): ν_{max} = 3084, 2929, 2141, 1590, 1110, 846, 530 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (d, J = 7.6 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H). MS: *m/z* (%): 273.03 ([M+2]$^+$, 0.73), 271.03 ([M$^+$], 0.41), 235.72 (20.18), 201.04 (43.12), 171.05 (18.24), 140.03 (21.11), 111.02 (33.52), 83.12 (17.32), 71.12 (34.59), 57.05 (68.54), 43.11 (100.00).

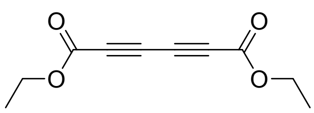


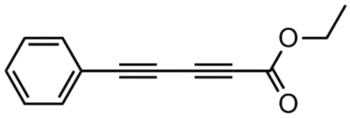
1,4-Bis(4-vinylphenyl)buta-1,3-diyne (Table 2, 2j): Yield 90%. Mp 113-115 ^{o}C. IR (KBr): ν_{max} = 3097, 3054, 2939, 2124, 1643, 1594, 1020, 909, 540 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42 (dd, ^{1}J = 8.4, ^{2}J = 2.0 Hz, 4H), 7.31 (d, J = 8.4 Hz, 4H), 6.66 (dd, ^{1}J = 10.8, ^{2}J = 6.8 Hz, 2H), 5.7 (dd, ^{1}J = 18.0, ^{2}J = 0.4 Hz, 2H), 5.26 (dd, ^{1}J = 10.8, ^{2}J = 0.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.38, 136.07, 132.71, 126.24, 120.98, 115.47, 82.01, 74.63. MS: *m/z* (%): 255.08 ($[M+1]^+$, 11.40), 254.06 ($[M^+]$, 79.08), 228.11 (10.11), 200.08 (23.35), 154.10 (21.44), 126.07 (44.68), 102.09 (50.94), , 72.24 (82.41), 57.07 (100.00), 41.10 (76.23). Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.21 H, 5.58.


1,4-Di(thiophene-2-yl)buta-1,3-diyne (Table 2, 2k): [2] Yield 97%. Mp 89-90 ^{o}C. IR (KBr): v_{max} = 3100, 2920, 2198, 2136, 1617, 1220, 836, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.09 (m, 4H), 6.85 (t, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.42, 128.93, 127.23, 121.93,77.76, 76.64.

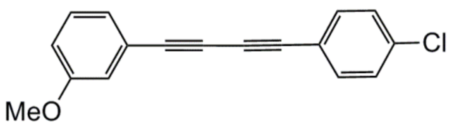

Tetradeca-6,8-diyne (Table 2, 2l):[7] Yield 86%. Oil. IR (KBr): v_{max} = 3050, 2964, 2936, 2219, 1473, 1362, 1150 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (t, *J* = 7.2 Hz, 4H), 1.48 (quin, *J* = 7.2 Hz, 4H), 1.32-1.26 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 6H). MS: *m/z* (%): 190.14 ($[M]^+$, 0.96), 181.04 (1.72), 119.06 (28.08), 105.04 (55.07), 91.01 (100.00), 79.08 (50.00), 55.08 (42.93), 41.12 (92.75).

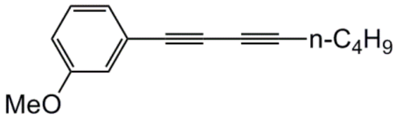

Dodeca-5,7-diyne (Table 2, 2m):[8] Yield 87%. Oil. IR (KBr): v_{max} = 2960, 2932, 2232, 1462, 1255, 1168 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (t, *J* = 7.6 Hz, 4H), 1.45-1.38 (m, 4H), 1.35-1.29 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 6H).


Diethyl hexa-2,4-diynedioate (Table 2, 2n):[9] Yield 86%. Oil. IR (KBr): v_{max} = 2957, 2926, 2147, 1725, 1462, 1243, 1120, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28 (q, *J* = 7.2 Hz, 4H), 1.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.24, 71.60, 67.09, 61.67, 13.54.

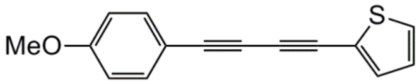
 **Ethyl 5-phenylpenta-2,4-diynoate (Table 4, 3an):**[10] Yield 89%. Oil. IR (KBr): ν_{max} = 3066, 2926, 2226, 2149, 1737, 1602, 1214, 1071, 756, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, ^{1}J = 8.0, ^{2}J = 1.2 Hz, 2H), 7.31 (td, ^{1}J = 7.6, ^{2}J = 1.6 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 1.28(t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.87, 133.09, 130.45, 128.61, 117.14, 78.64, 76.69, 62.47, 28.93, 14.00.

 **1-Methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (Table 4, 3ad):**[11] Yield 95%. Mp 88-90 °C. IR (KBr): ν_{max} = 3050, 2986, 2211, 2138, 1595, 1486, 1247, 1026, 826, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (dd, ^{1}J = 8.0, ^{2}J = 1.6 Hz, 2H), 7.34 (dt, ^{1}J = 8.4, ^{2}J = 2.0 Hz, 2H), 7.20 (m, 2H), 7.10 (s, 1H), 6.72 (dt, ^{1}J = 7.2, ^{2}J = 1.6 Hz, 2H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.38, 134.13, 132.44, 129.03, 128.42, 122.03, 114.17, 81.82, 81.03, 74.17, 72.74, 55.35.

 **1-((4-Chlorophenyl)buta-1,3-diyn-1-yl)-3-methoxybenzene (Table 4 , 3ci):** Yield 93%. Mp 102-103 °C. IR (KBr): ν_{max} = 3064, 2955, 2211, 2151, 1591, 1248, 1036, 822, 777 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dt, ^{1}J = 8.4, ^{2}J = 2.0 Hz, 2H), 7.35 (dd, ^{1}J = 8.4, ^{2}J = 2.0 Hz, 2H), 7.28(d, J = 4.0 Hz, 1H),7.16 (dt, ^{1}J = 7.6, ^{2}J = 1.2 Hz, 1H), 7.07(dd, ^{1}J = 4.0, ^{2}J = 1.6 Hz, 1H), 6.97 (ddd, ^{1}J = 8.0, ^{2}J = 3.6,^{3}J = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.31, 135.41, 133.69, 129.59, 128.88, 125.10, 122.53, 120.27, 117.10, 116.16, 82.03, 80.33, 74.84, 74.84, 73.45, 55.33. Anal. Calcd for $C_{17}H_{11}ClO$: C, 76.55; H, 4.16. Found: C, 76.39; H, 4.13.

 **1-Methoxy-3-(octa-1,3-diyn-1-yl)benzene (Table 4, 3cm):**[12] Yield 78%. Oil. IR (KBr): ν_{max} = 3071, 2938, 2868, 2240, 2152, 1597, 1425, 1224, 1043, 781,

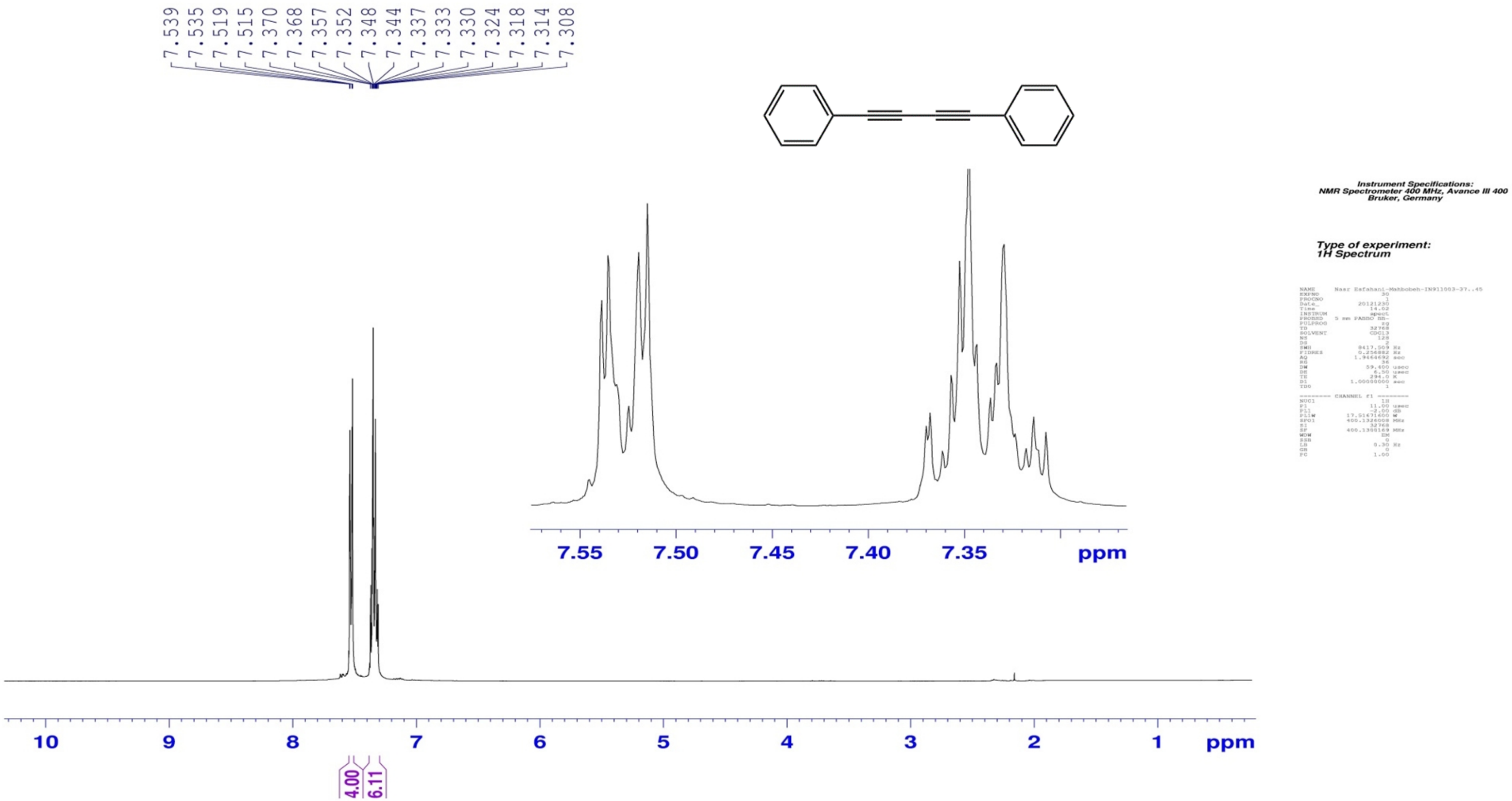
683 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, J = 8.0 Hz, 1H), 7.10 (dt, ^{1}J = 7.6, ^{2}J = 1.2 Hz, 1H), 7.02 (dd, ^{1}J = 4.0, ^{2}J = 1.6 Hz, 1H), 6.93 (ddd, ^{1}J = 8.4, ^{2}J = 2.8,^{2}J = 0.8 Hz, 1H), 3.81 (s, 3H), 2.40 (t, J = 7.6 Hz, 2H), 1.62-1.55(m, 2H), 1.53 (sex, J = 7.2, 2H), 0.97 (t, J = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.25, 129.42, 125.06, 123.09, 117.11, 115.67, 84.93, 74.60, 74.20, 55.27, 30.27, 21.96, 19.28, 13.54.



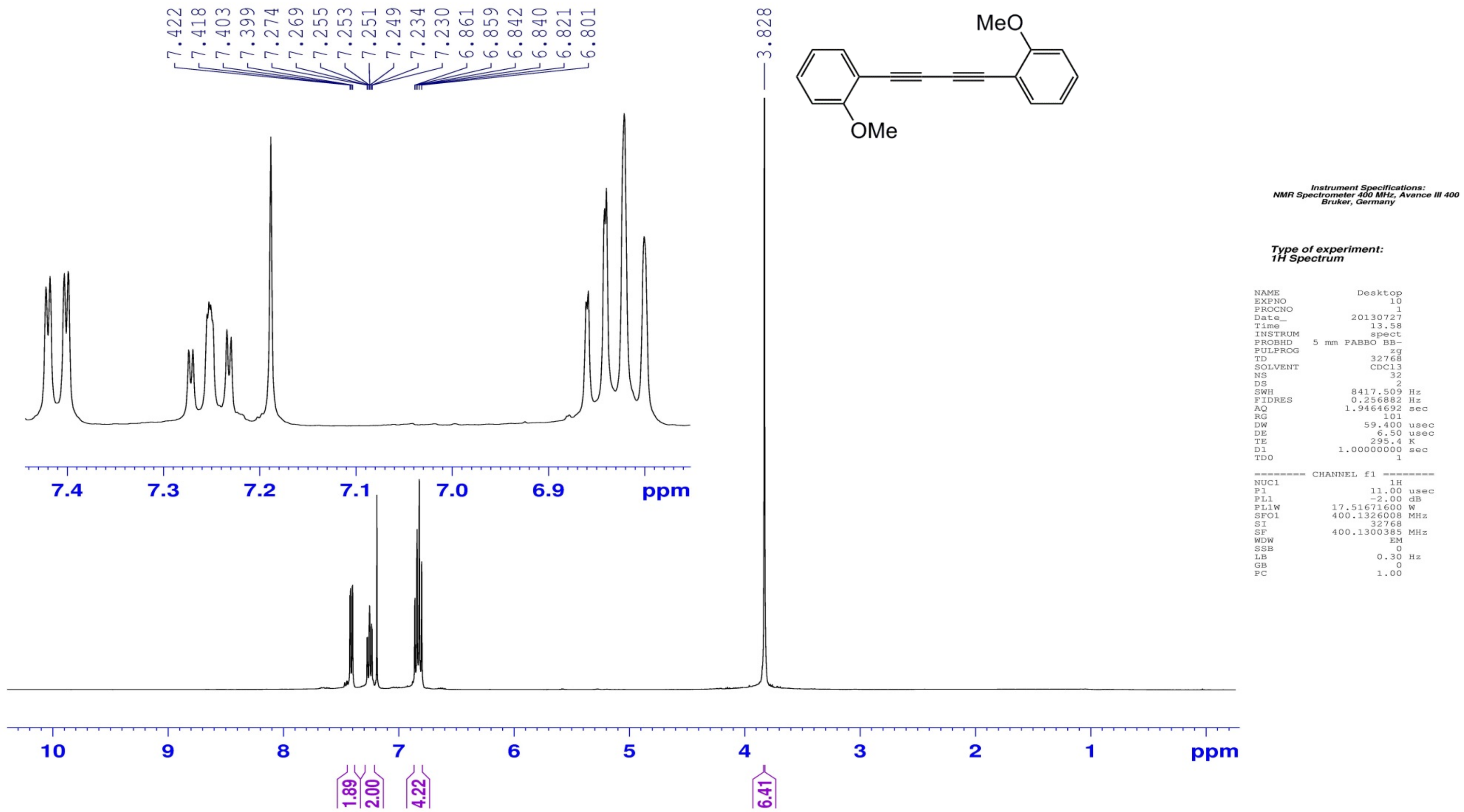
2-((4-Methoxyphenyl)buta-1,3-diyn-1-yl)thiophene (Table 4, 3dk): Yield 88%. Mp 74-75 °C. IR (KBr): v_{max} = 3092, 2926, 2199, 2137, 1597, 1504,1290, 1250, 832, 710, 466 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (dt, ^{1}J = 8.4, ^{2}J = 2.8 Hz, 2H), 7.17 (ddd, ^{1}J = 9.6, ^{2}J = 4.8, ^{2}J = 1.2 Hz, 1H), 7.10 (s, 1H), 6.84 (dd, ^{1}J = 5.2, ^{2}J = 3.6 Hz, 1H), 6.71(dt, ^{1}J = 6.8, ^{2}J = 2.4 Hz, 2H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.61, 134.13, 134.01, 130.88, 128.81, 128.43, 127.13, 114.19, 83.89, 78.21, 74.00, 68.16, 55.36. Anal. Calcd for $C_{15}H_{10}SO$: C, 75.60; H, 4.23; S, 13.46. Found: C, 75.47; H, 4.25; S, 13.22.

2. ¹H and ¹³C NMR spectra of the products:

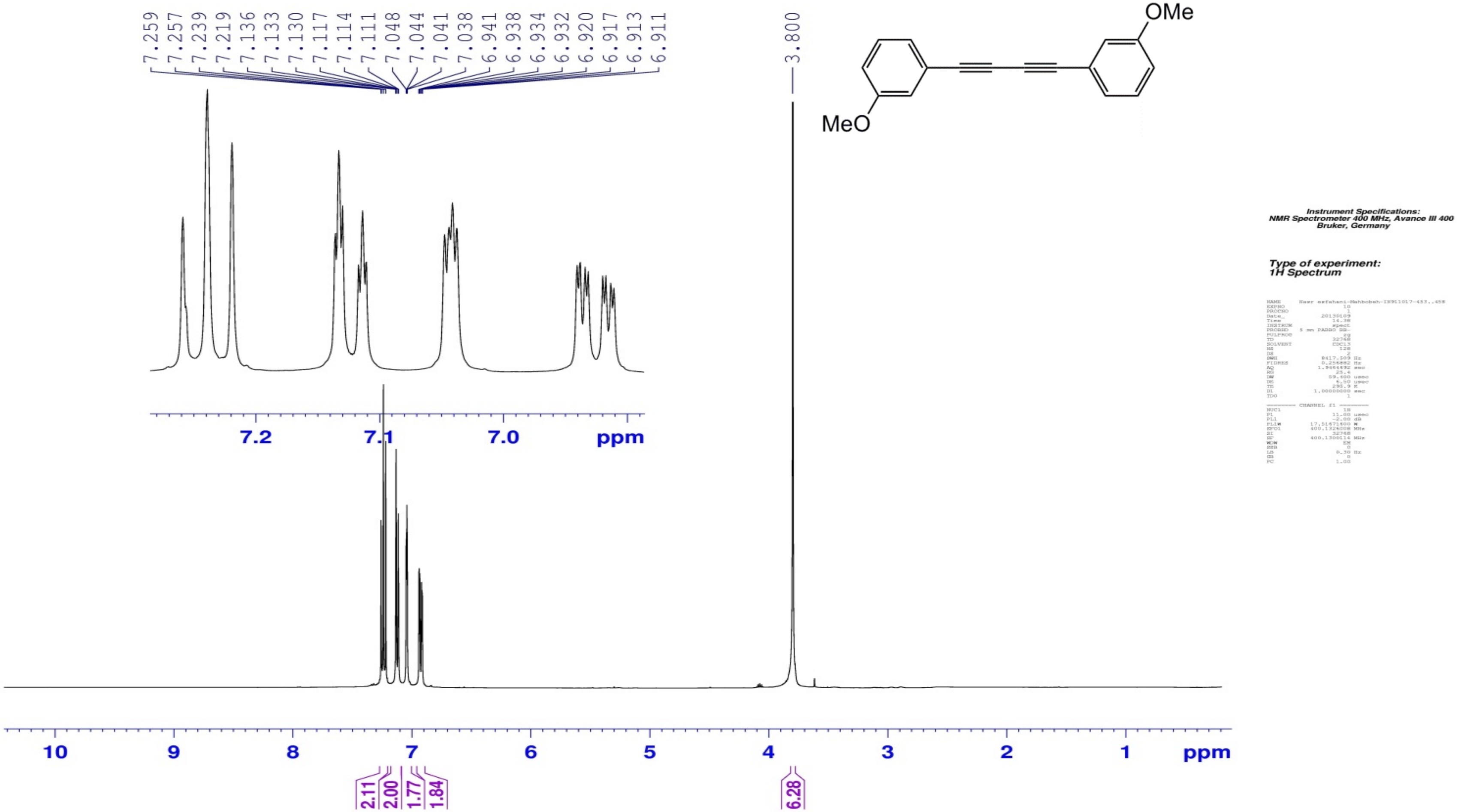
1,4-Diphenylbuta-1,3-diyne (Table 2, 2a): ¹H NMR (400 MHz, $CDCl_3$)



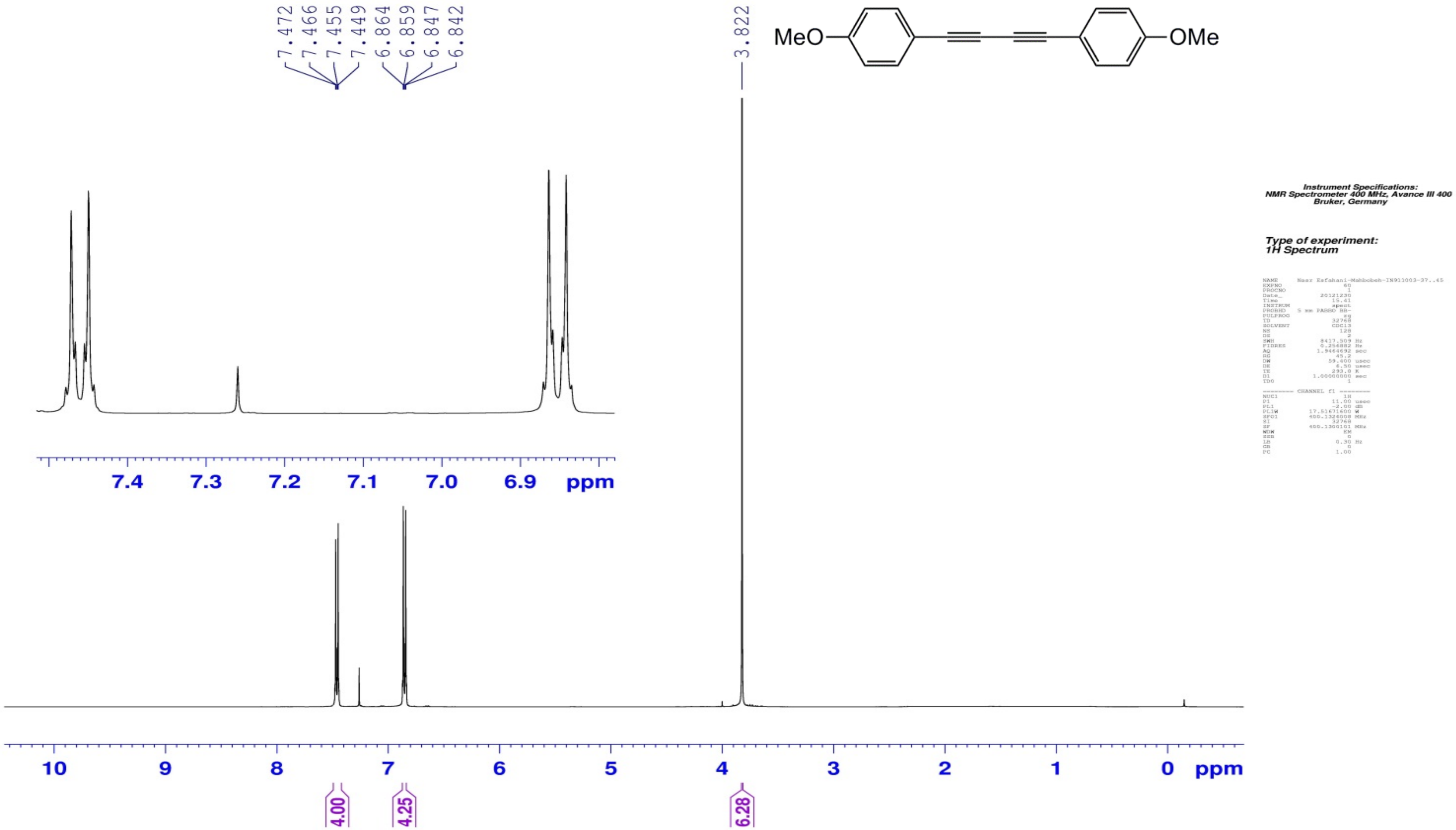
1,4-Bis(2-methoxyphenyl)buta-1,3-diyne (Table 2 , 2b): ^{1}H NMR (400 MHz, $CDCl_3$)



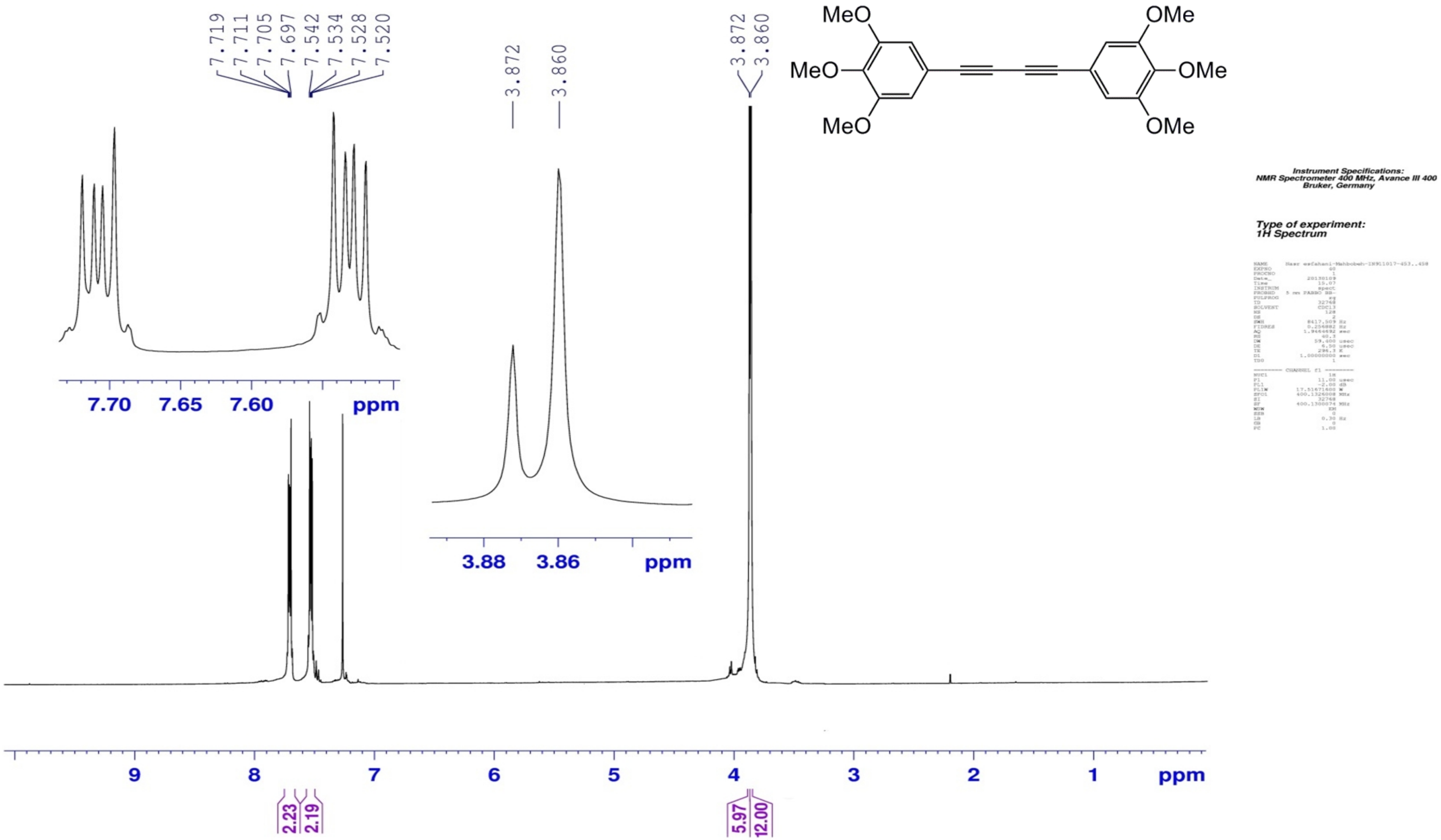
1,4-Bis(3-methoxyphenyl)buta-1,3-diyne (Table 2, 2c): ^{1}H NMR (400 MHz, $CDCl_3$)



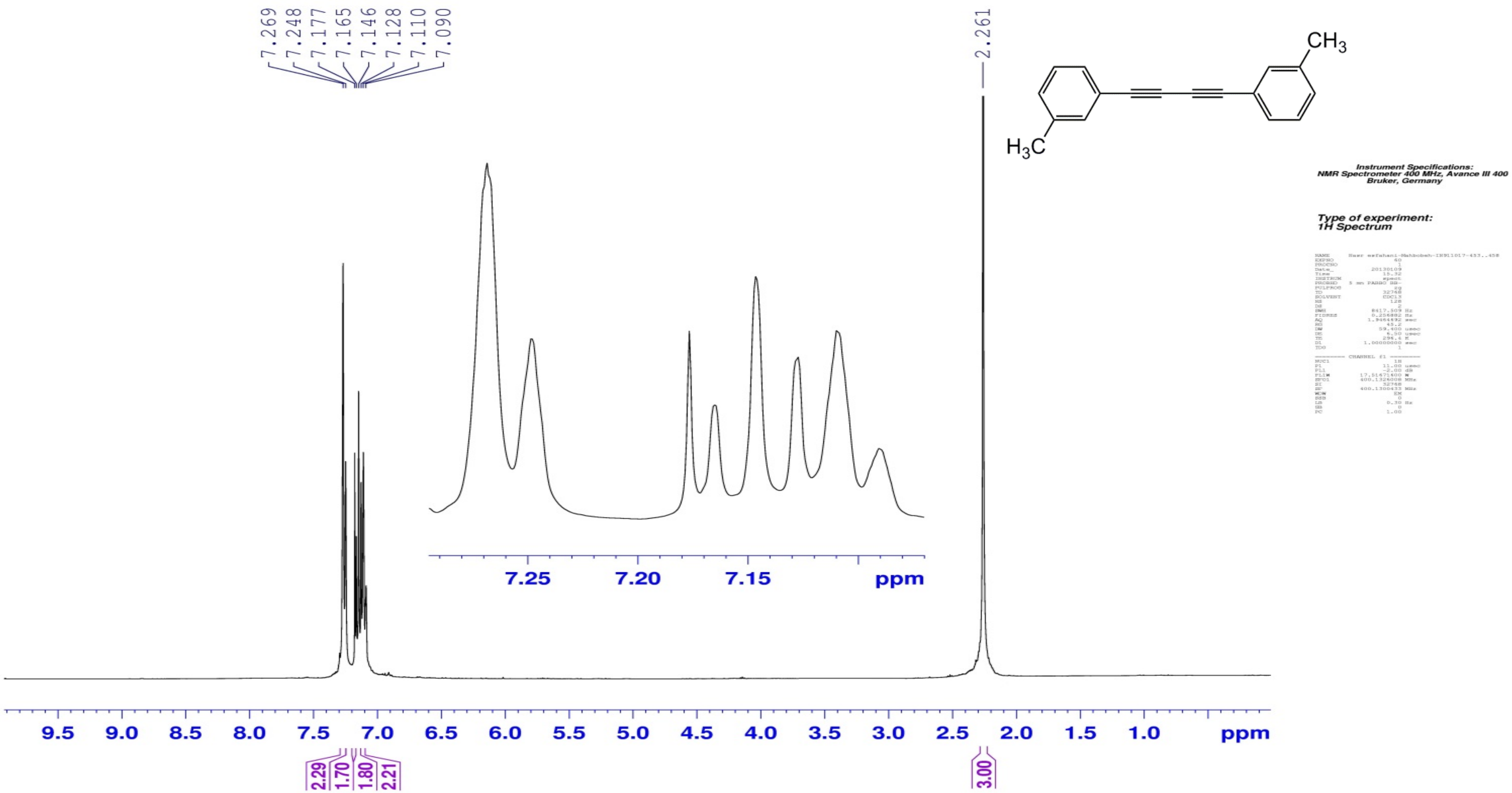
1,4-Bis(4-methoxyphenyl)buta-1,3-diyne) (Table 2, 2d): ^{1}H NMR (400 MHz, CDCl$_3$)



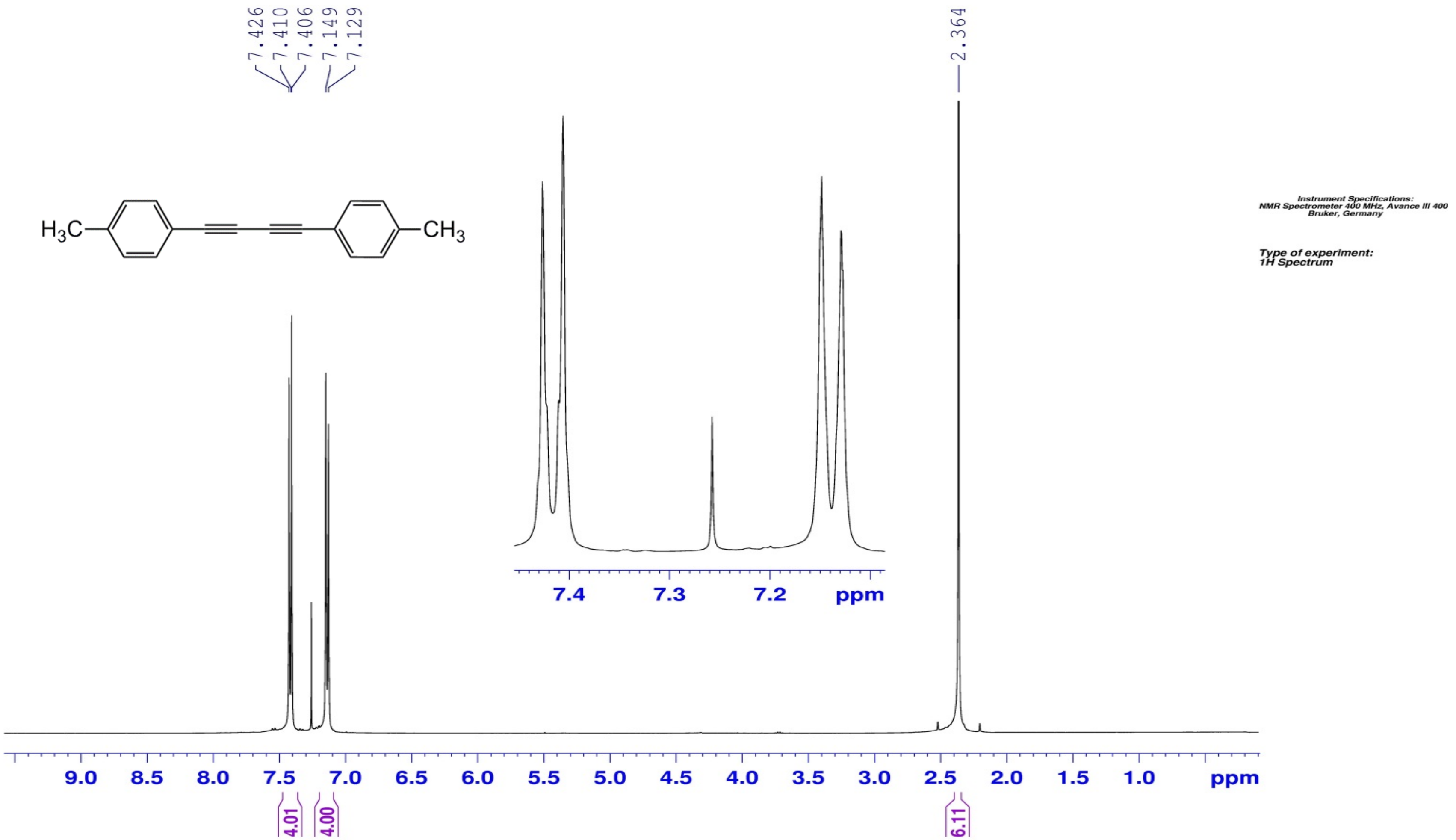
1,4-Bis(3,4,5-trimethoxyphenyl)buta-1,3-diyne (Table 2, 2e): ^{1}H NMR (400 MHz, $CDCl_3$)



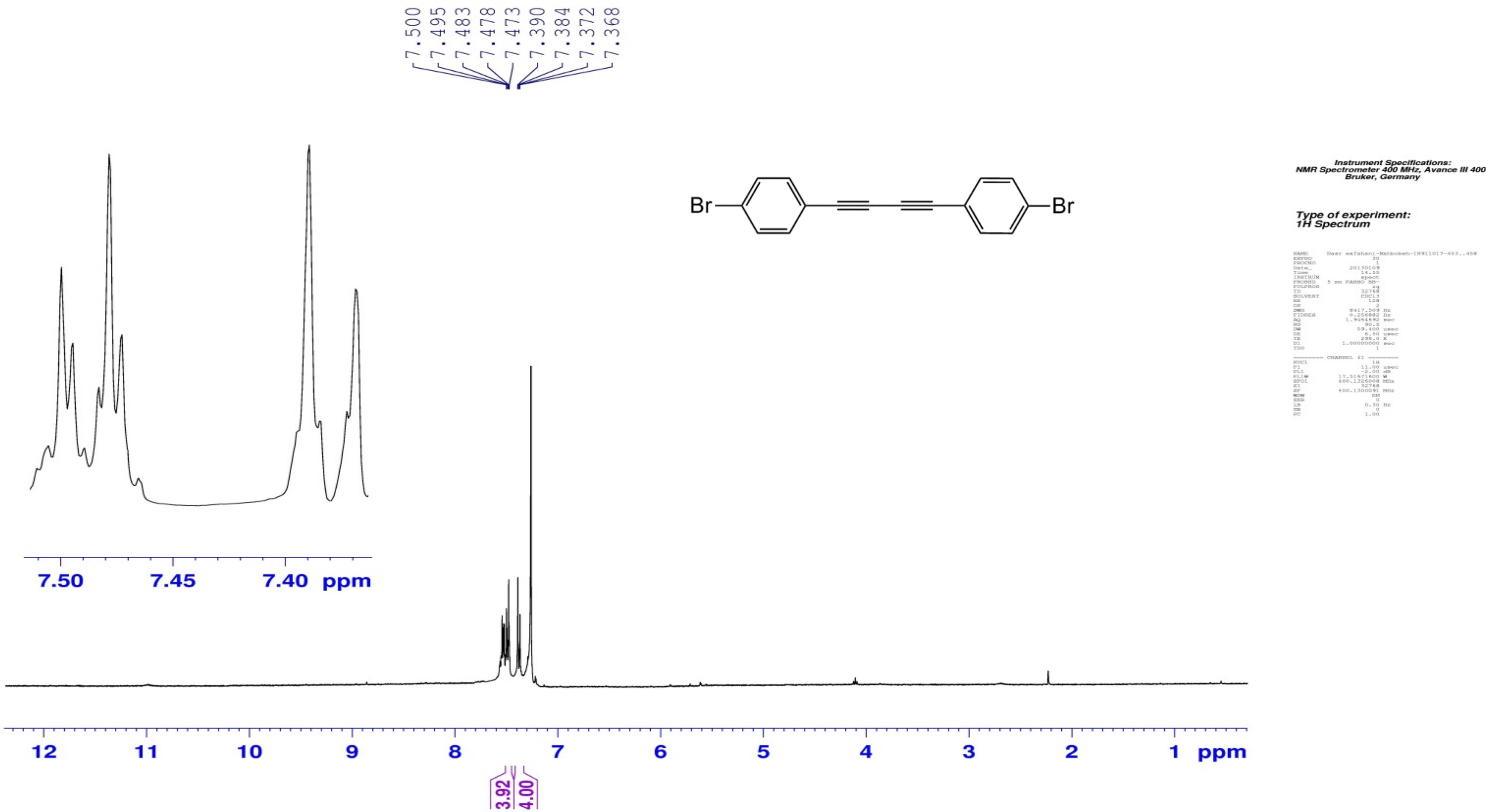
1,4-Di-*m*-tolylbuta-1,3-diyne (Table 2, 2f): ^{1}H NMR (400 MHz, $CDCl_3$)



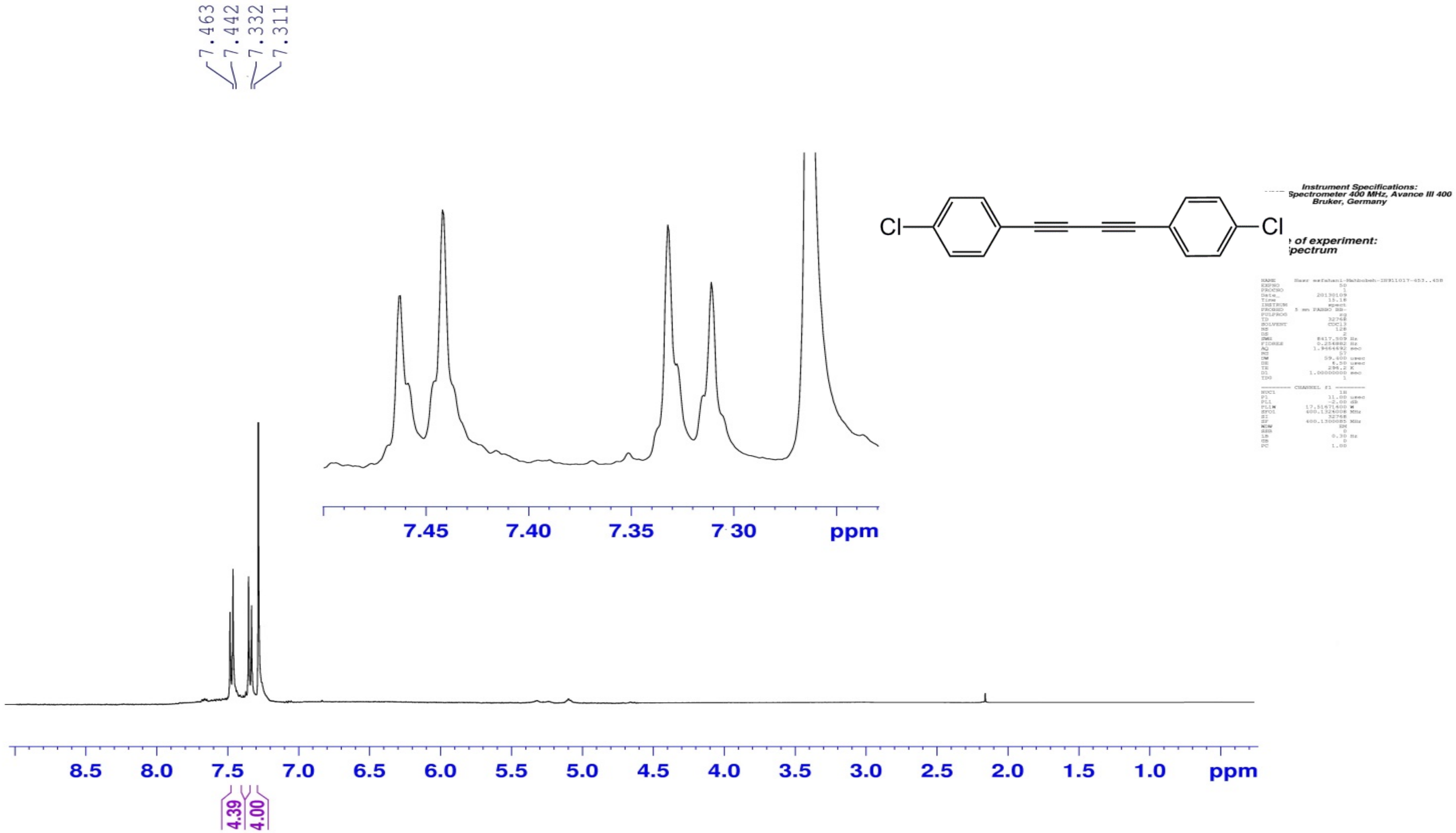
1,4-Di-*p*-tolylbuta-1,3-diyne (Table 2, 2g): ^{1}H NMR (400 MHz, $CDCl_3$)



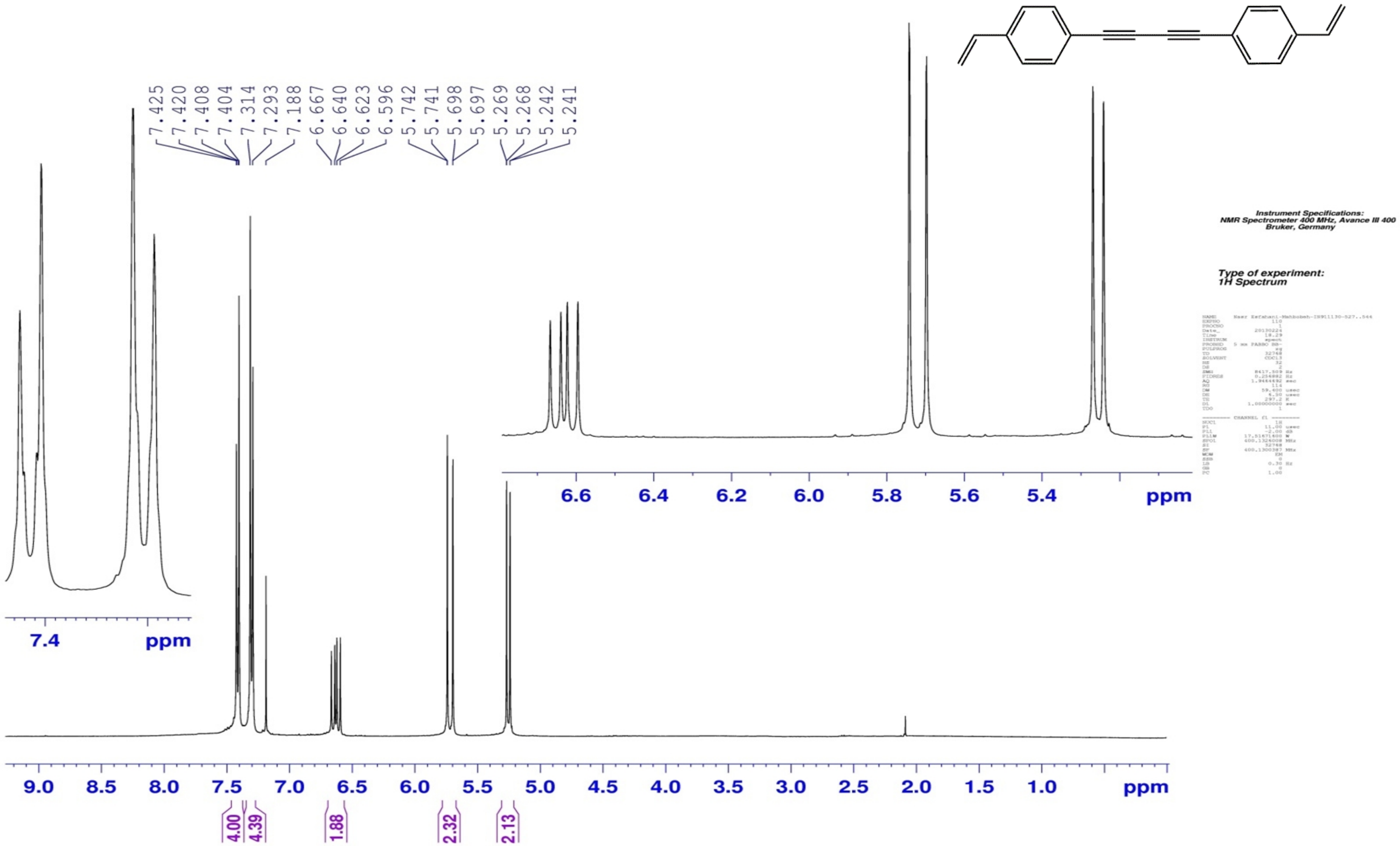
1,4-Bis(4-bromophenyl)buta-1,3-diyne (Table 2, 2h): ^{1}H NMR (400 MHz, $CDCl_3$)



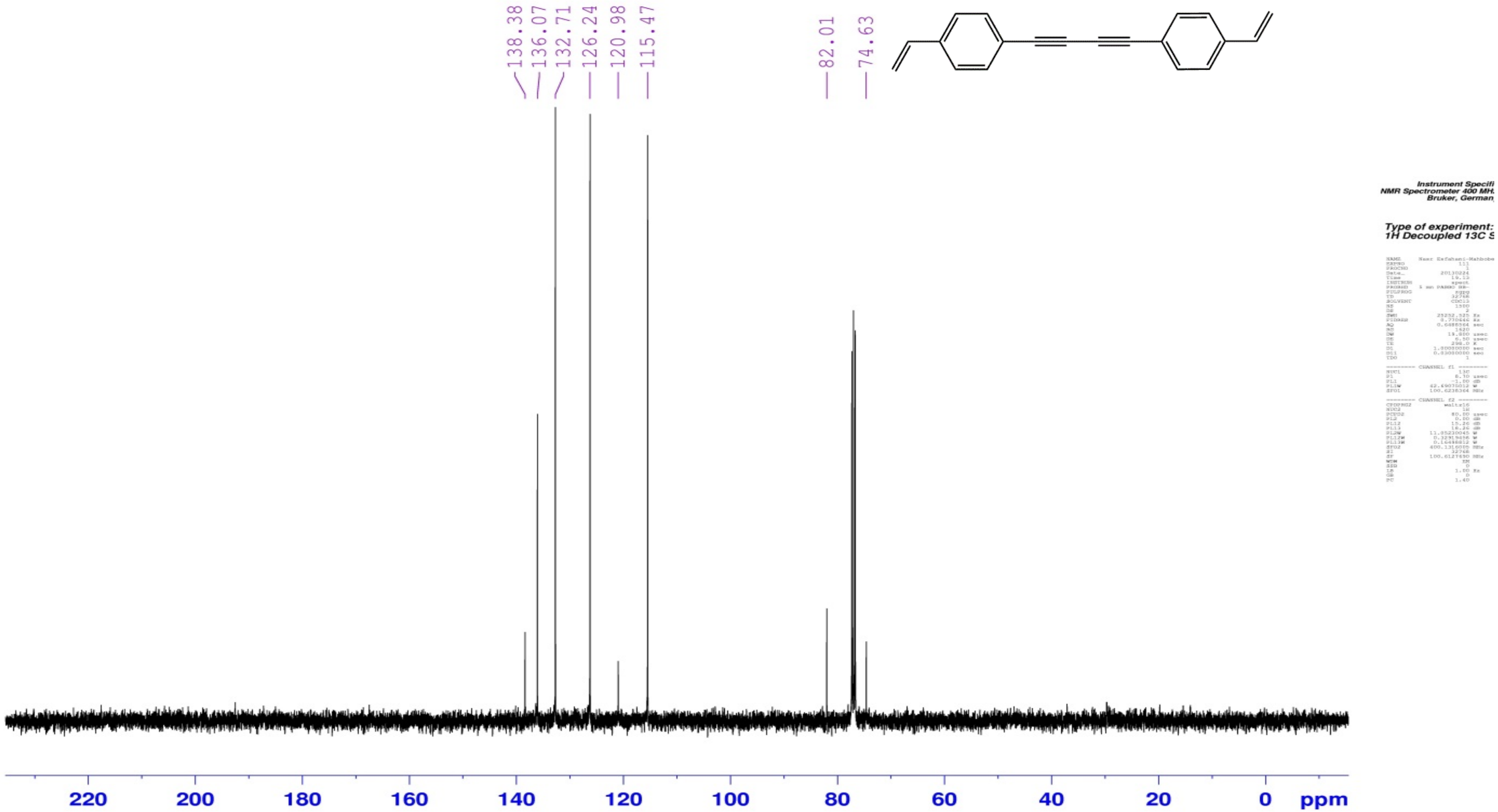
1,4-Bis(4-chlorophenyl)buta-1,3-diyne (Table 2, 2i): ^{1}H NMR (400 MHz, $CDCl_3$)



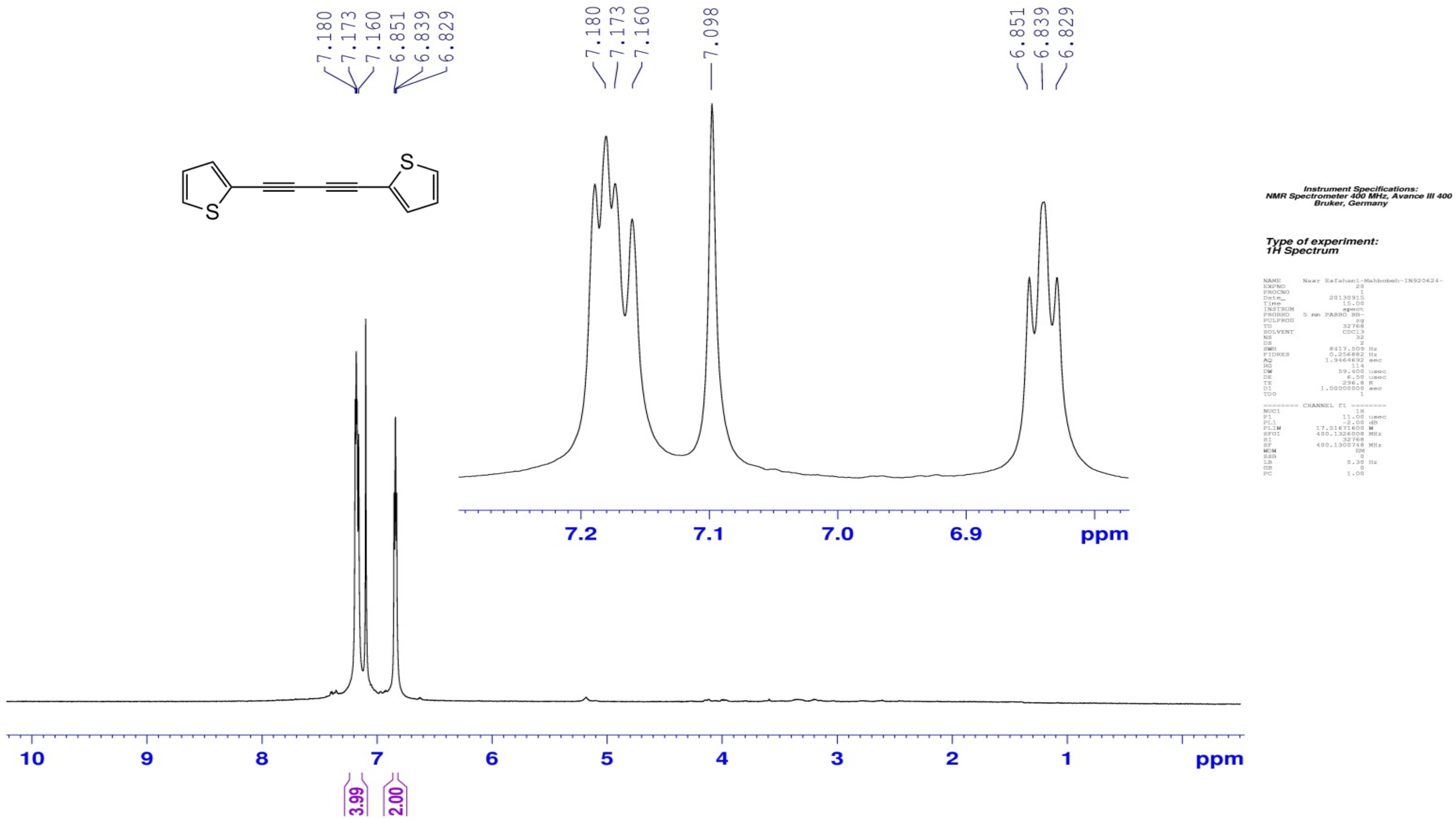
1,4-Bis(4-vinylphenyl)buta-1,3-diyne (Table 2, 2j): ^1H NMR (400 MHz, $CDCl_3$)



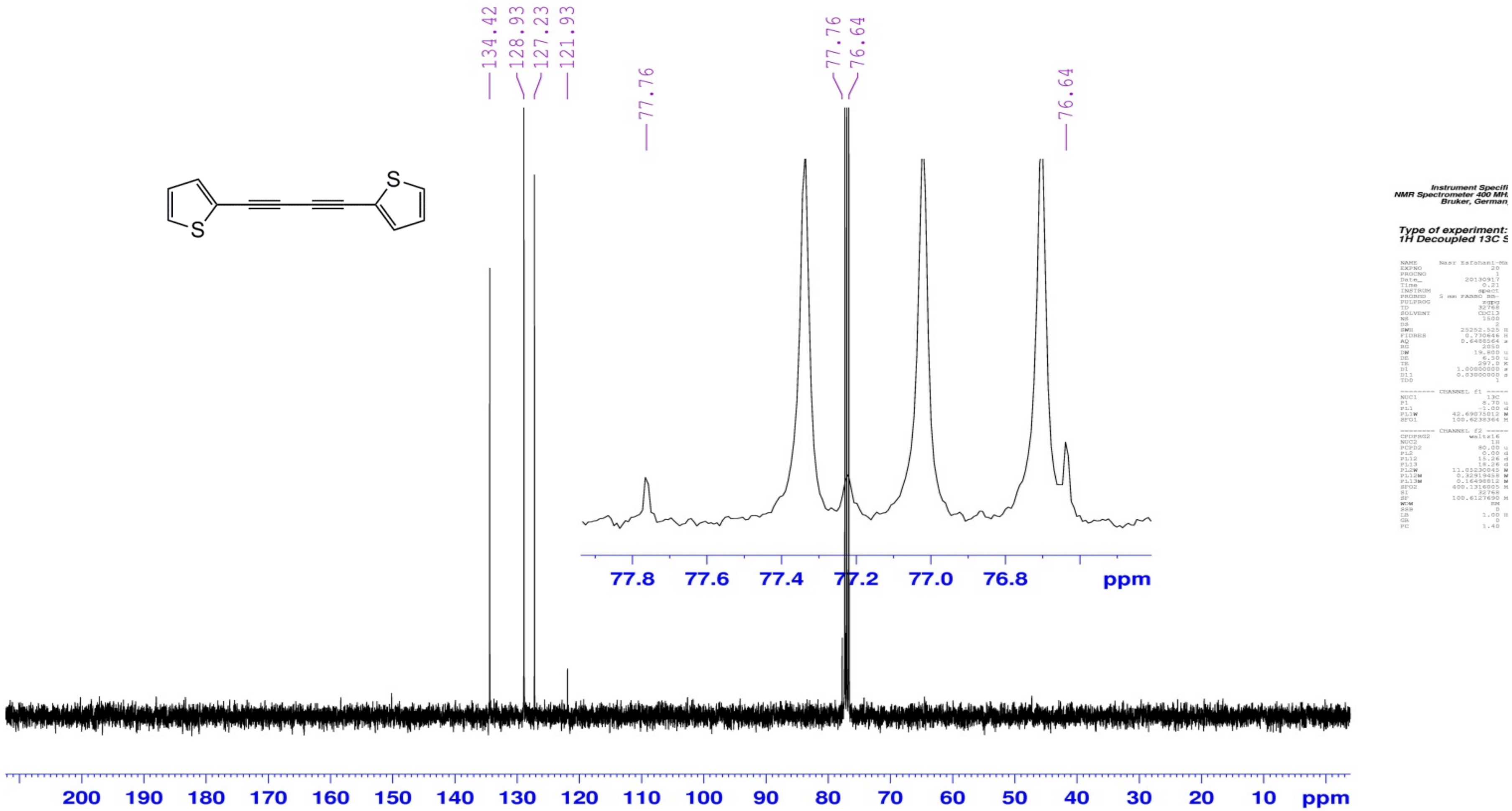
1,4-Bis(4-vinylphenyl)buta-1,3-diyne (Table 2, 2j): ^{13}C NMR (100 MHz, $CDCl_3$)



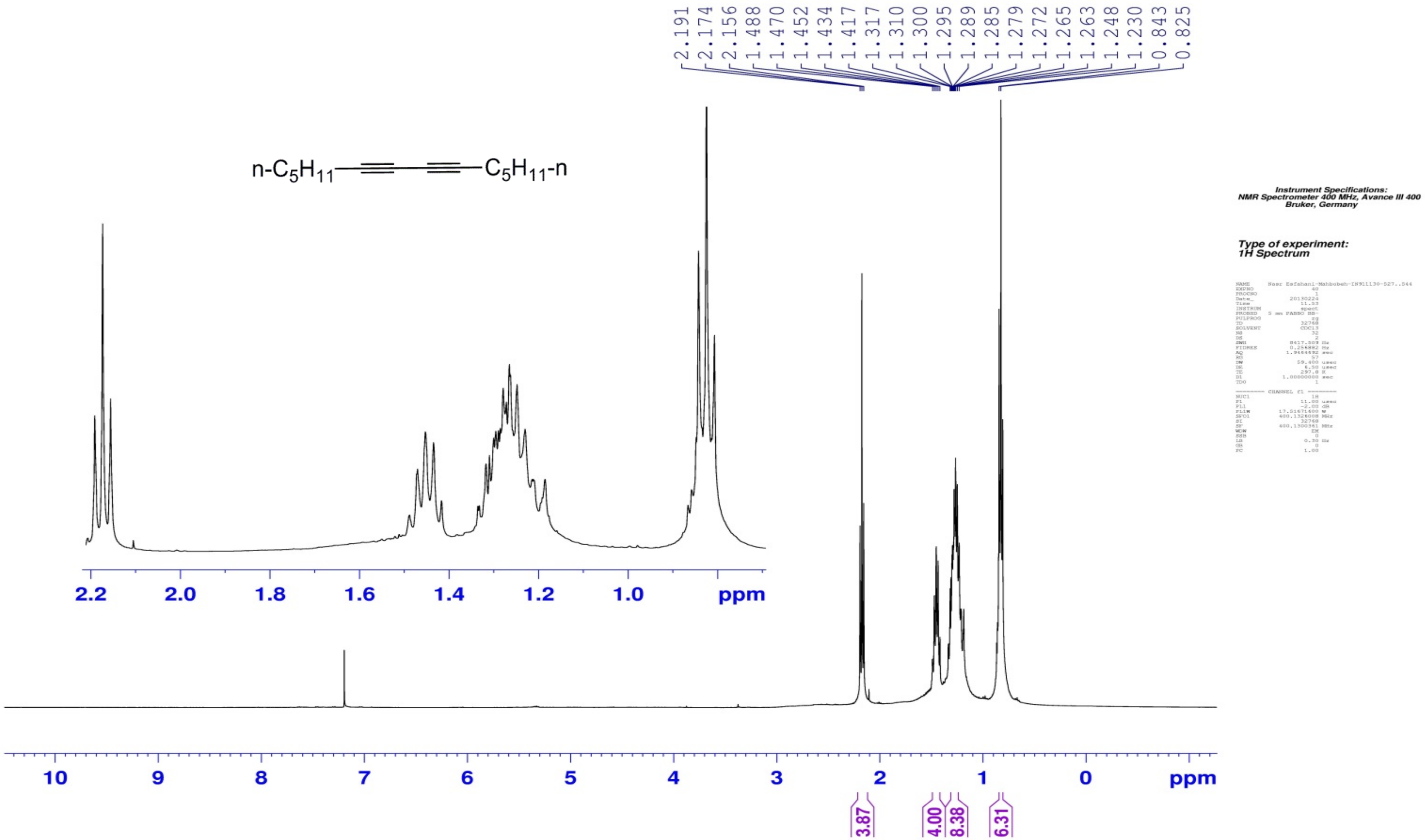
1,4-Di(thiophene-2-yl)buta-1,3-diyne (Table 2, 2k): ^{1}H NMR (400 MHz, $CDCl_3$)



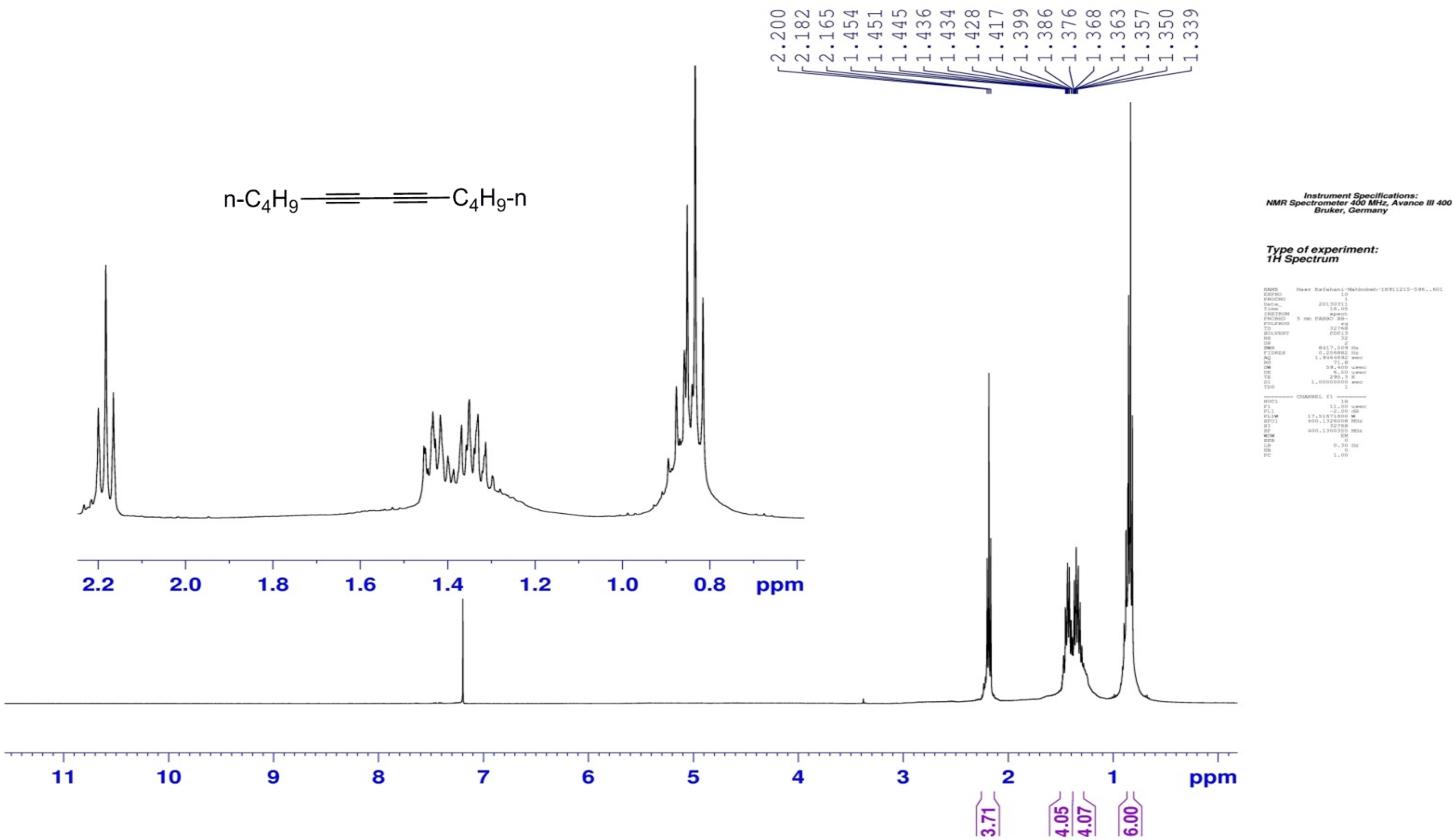
1,4-Di(thiophene-2-yl)buta-1,3-diyne (Table 2, 2k): ^{13}C NMR (100 MHz, $CDCl_3$)



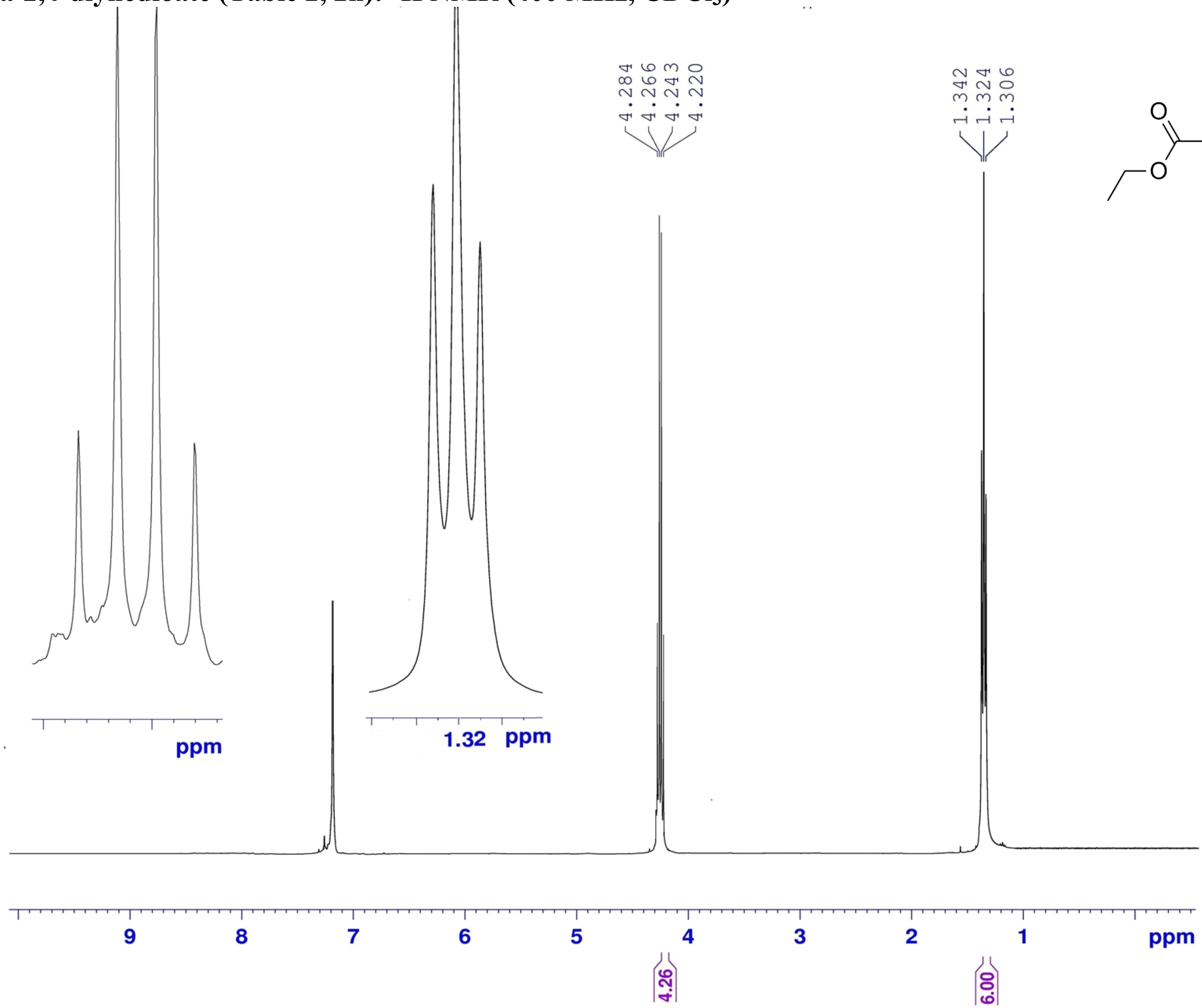
Tetradeca-6,8-diyne (Table 2, 3l): ^{1}H NMR (400 MHz, $CDCl_3$)

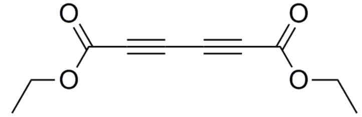


Dodeca-5,7-diyne (Table 2, 2m): ^{1}H NMR (400 MHz, $CDCl_3$)

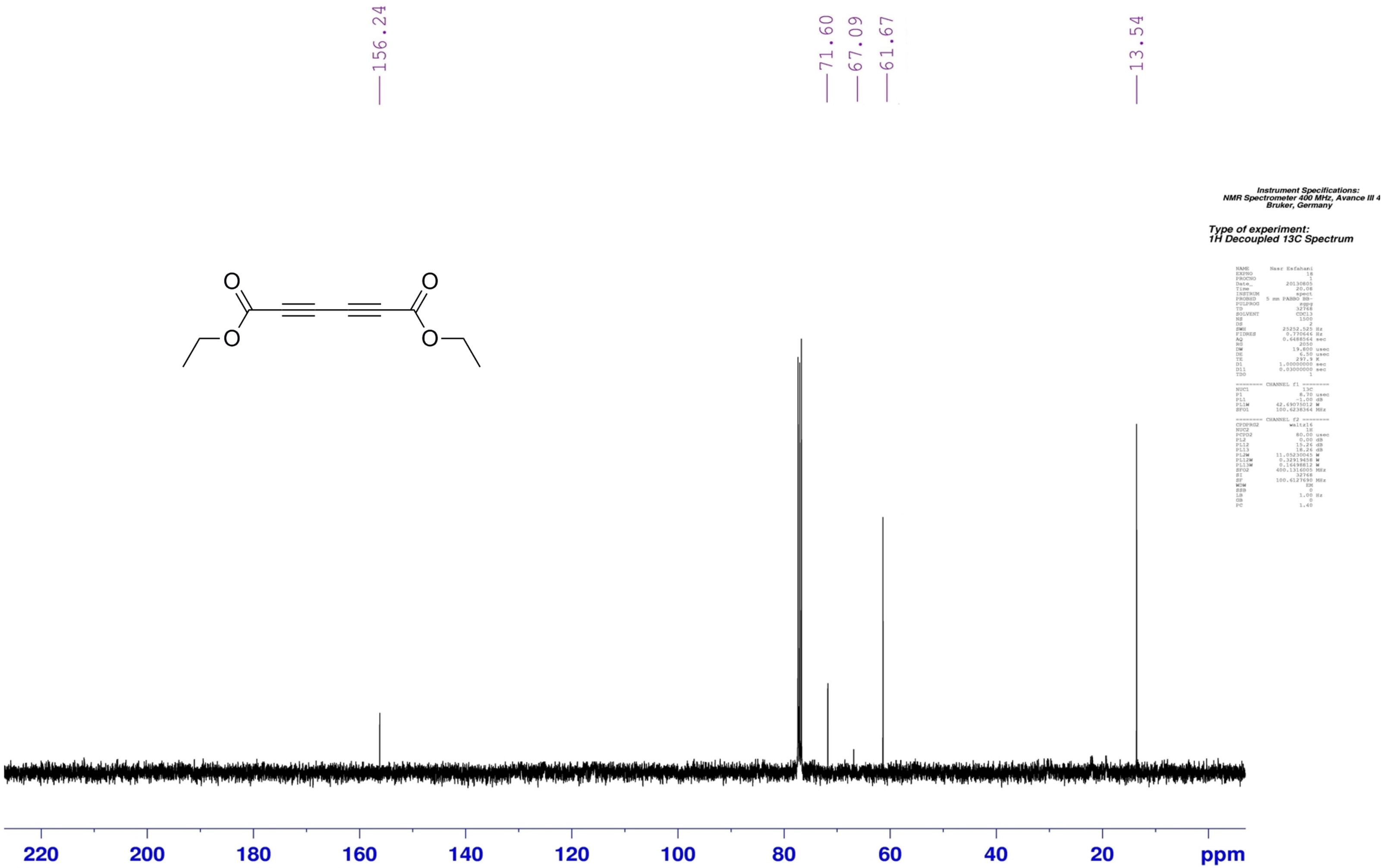


Diethyl hexa-2,4-diynedioate (Table 2, 2n): ^{1}H NMR (400 MHz, $CDCl_3$)

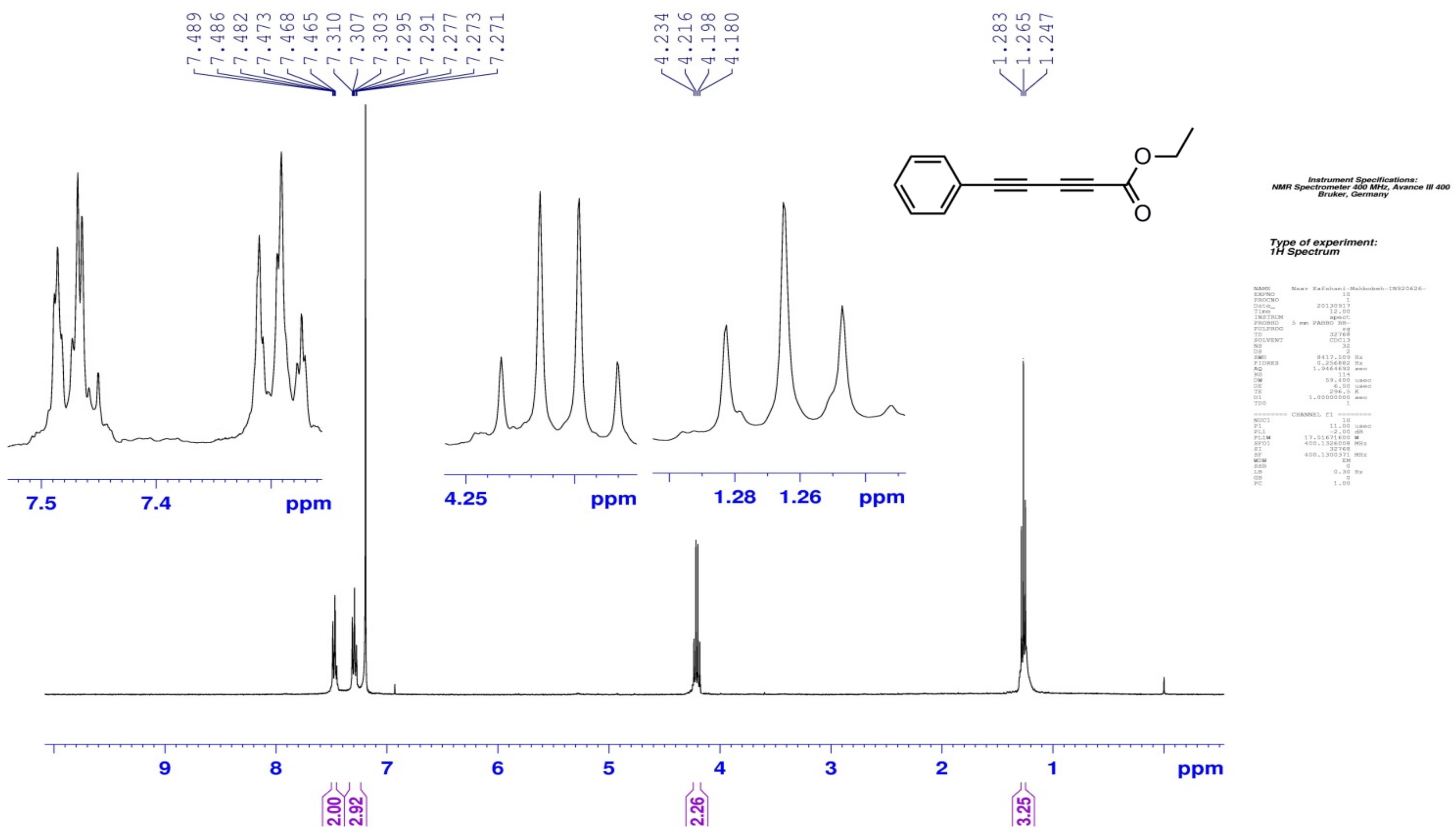




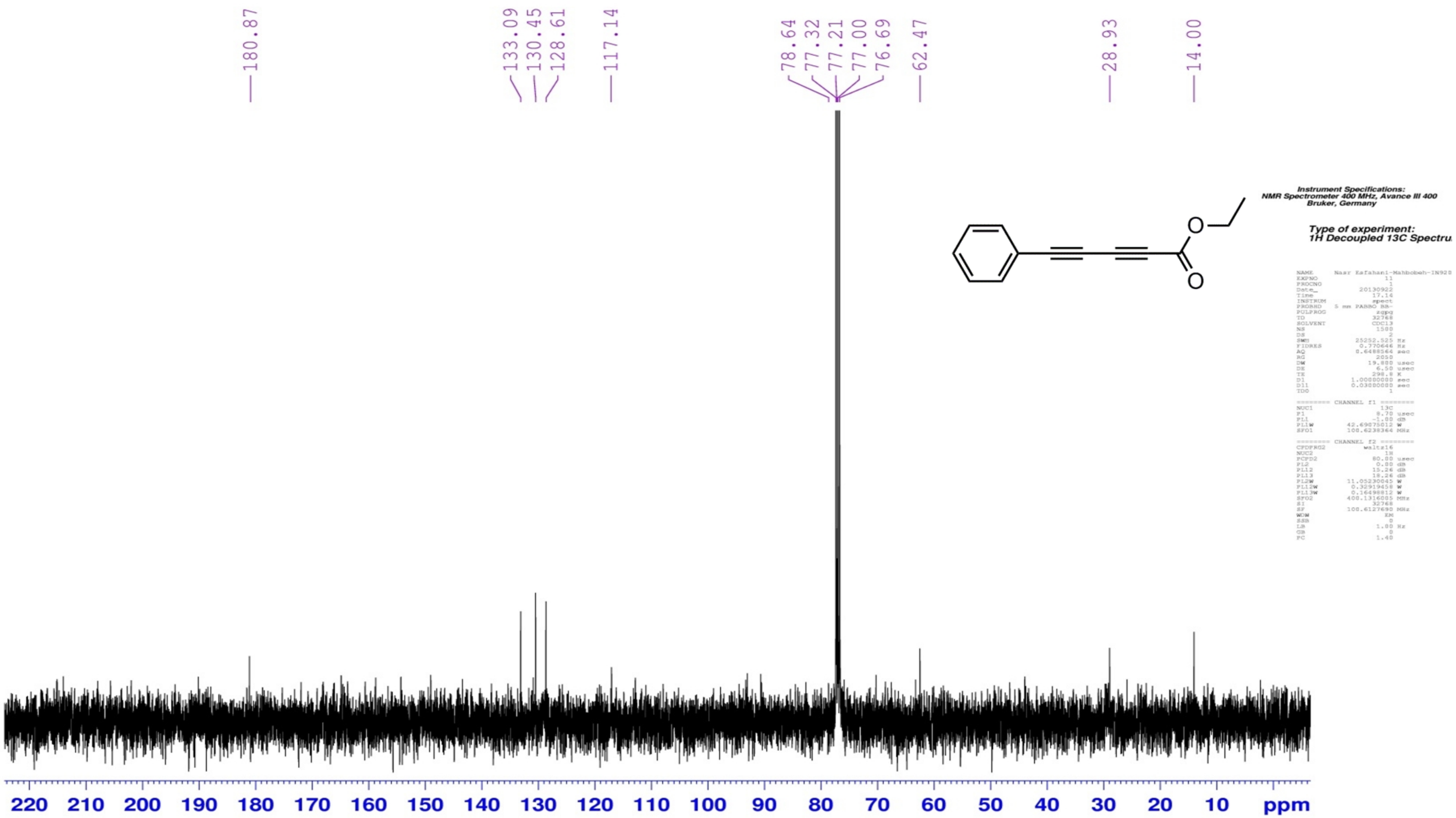
Diethyl hexa-2,4-diynedioate (Table 2, 2n): ^{13}C NMR (100 MHz, $CDCl_3$)



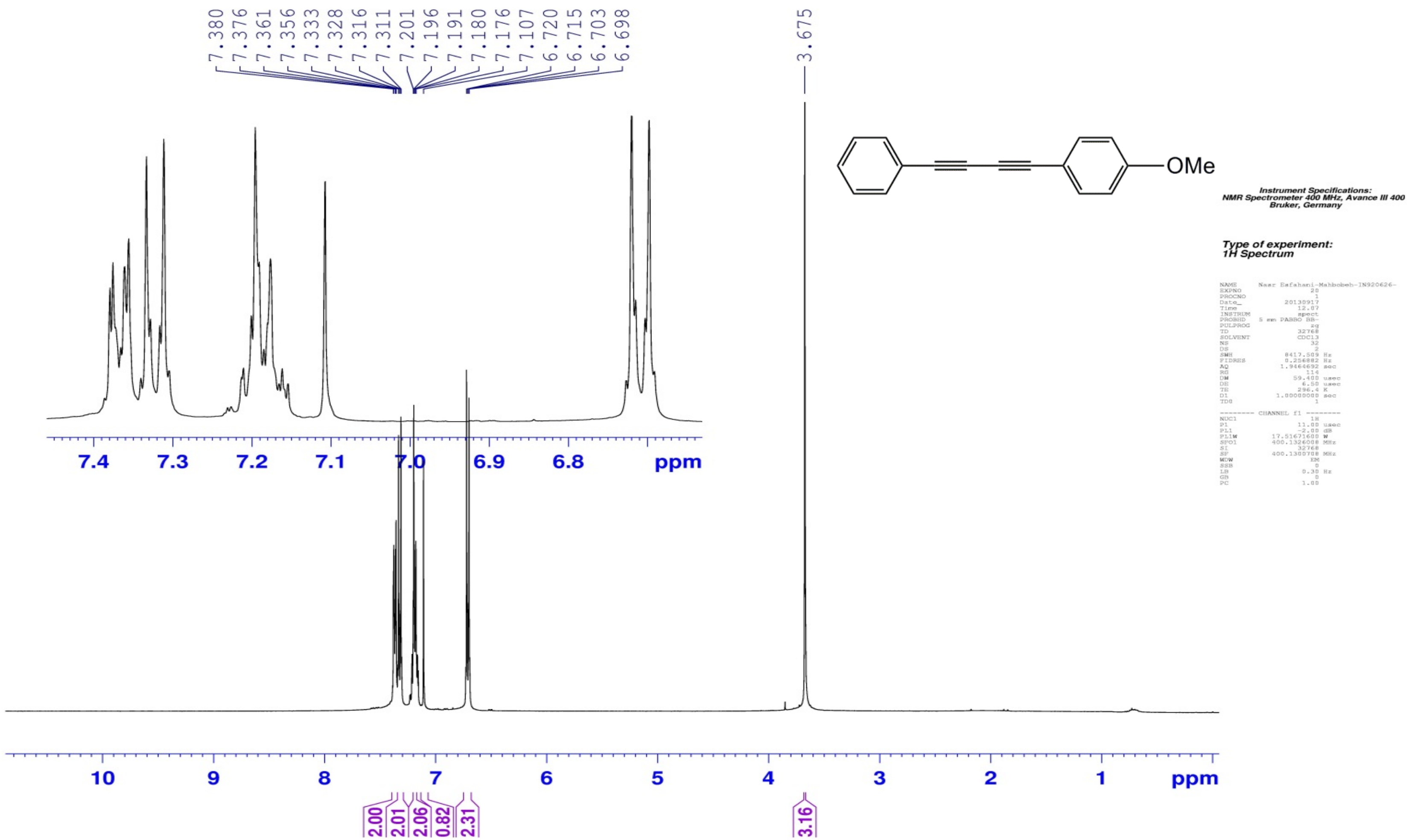
Ethyl 5-phenylpenta-2,4-diynoate (Table 4, 3an): ^{1}H NMR (400 MHz, $CDCl_3$)



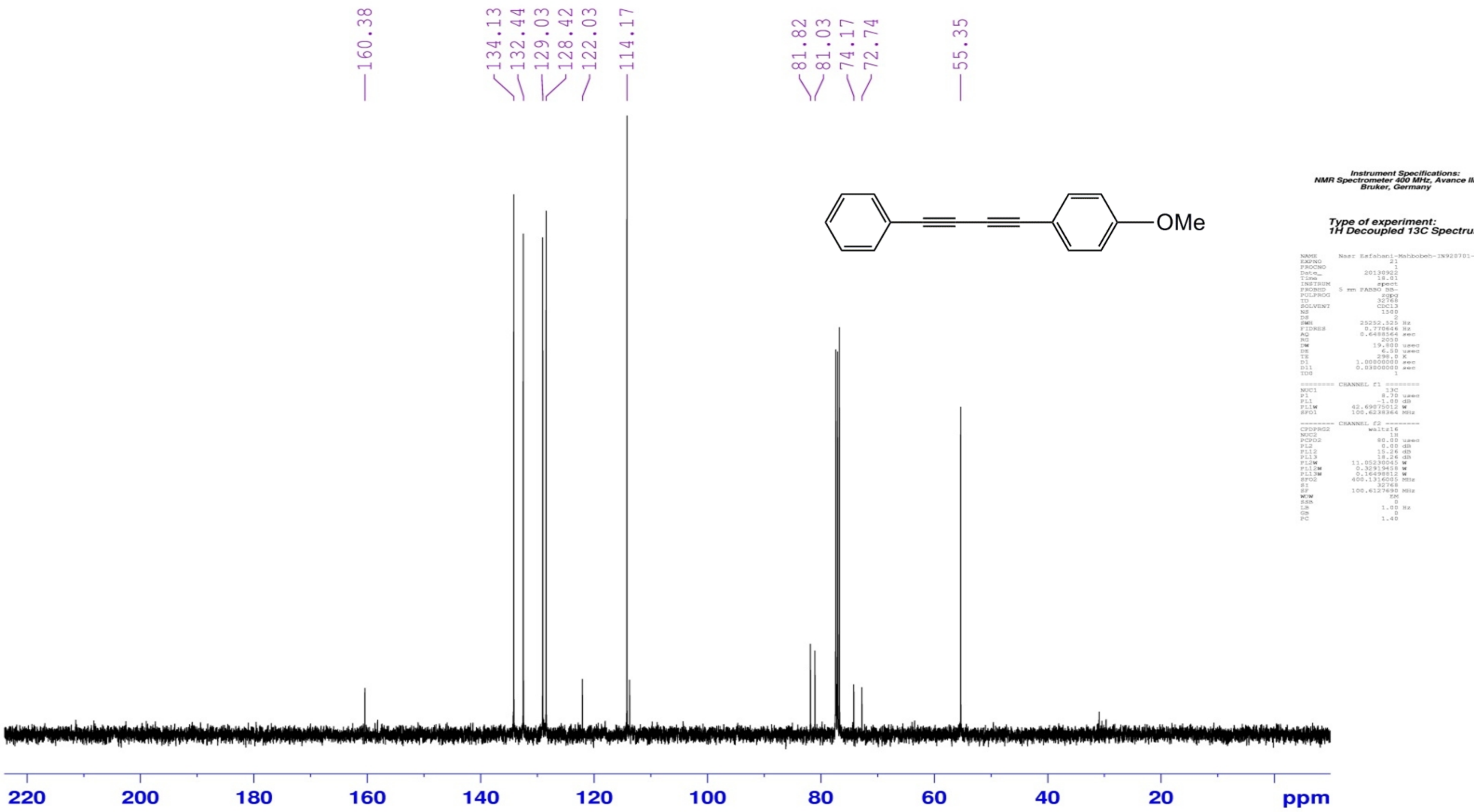
Ethyl 5-phenylpenta-2,4-diynoate (Table 4, 3an): ^{13}C NMR (100 MHz, $CDCl_3$)



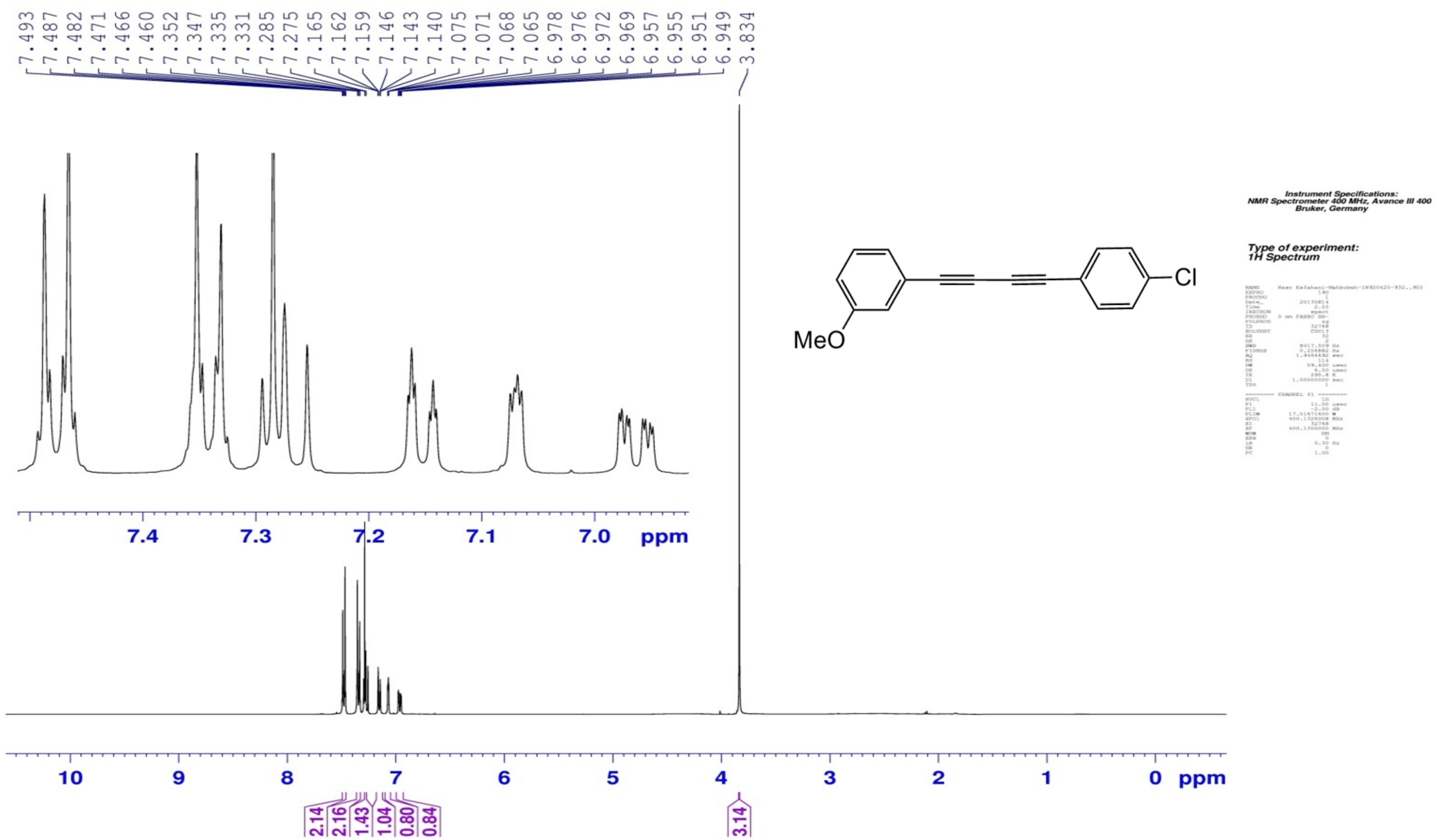
1-Methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (Table 4, 3ad): ^{1}H NMR (400 MHz, $CDCl_3$)



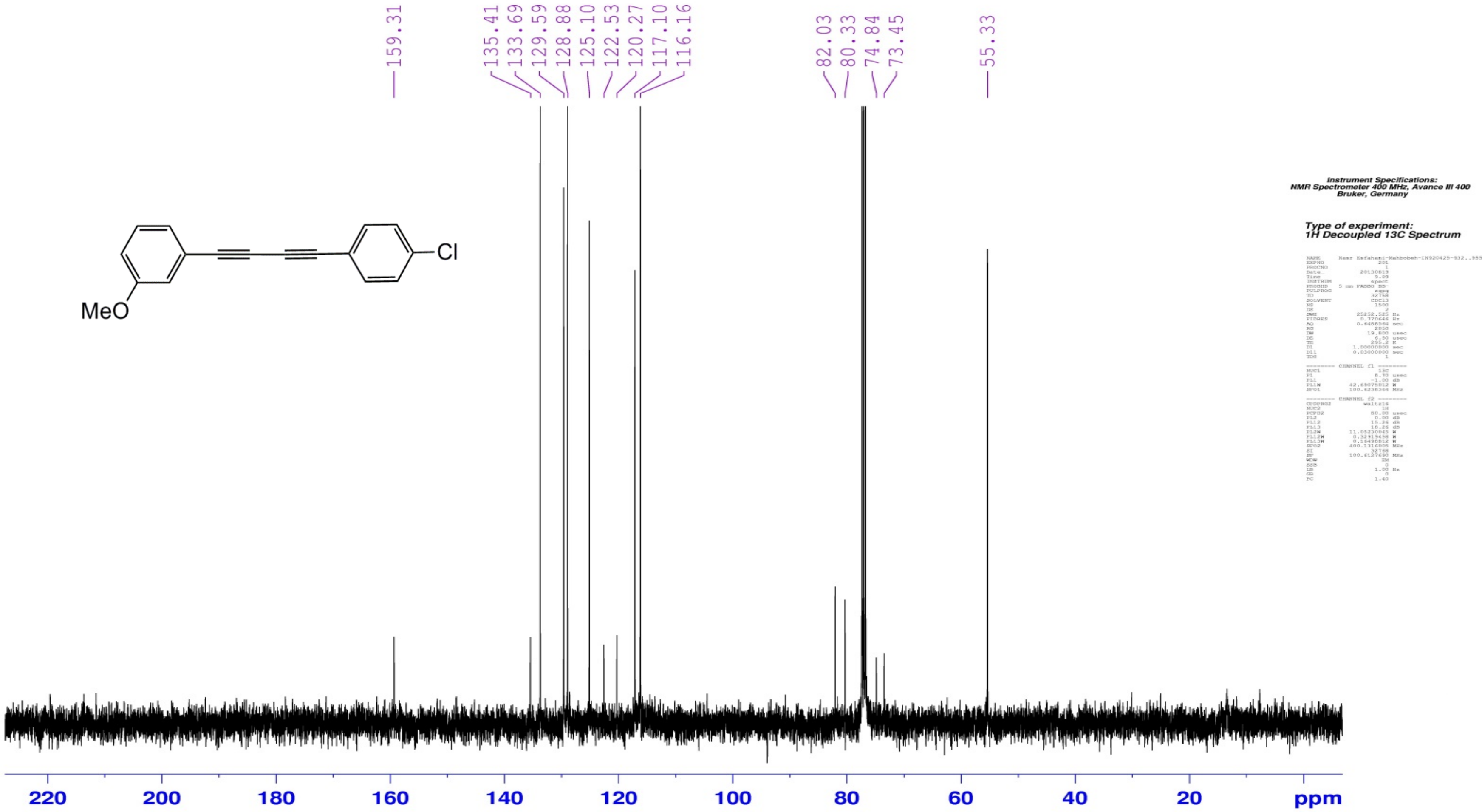
1-Methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (Table 4, 3ad): ^{13}C NMR (100 MHz, $CDCl_3$)



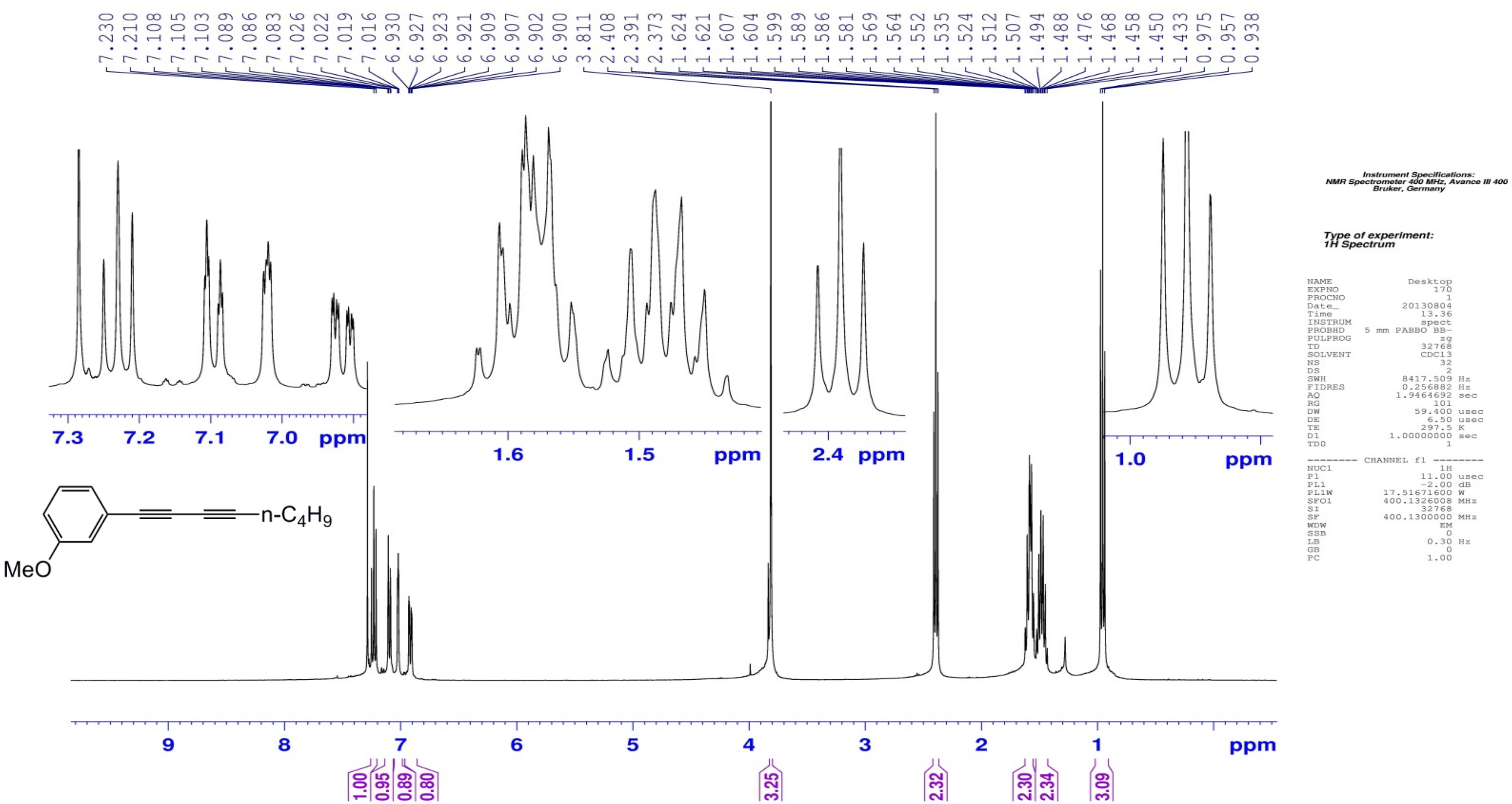
1-((4-Chlorophenyl)buta-1,3-diyn-1-yl)-3-methoxybenzene (Table 4, 3ci): ^{1}H NMR (400 MHz, $CDCl_3$)



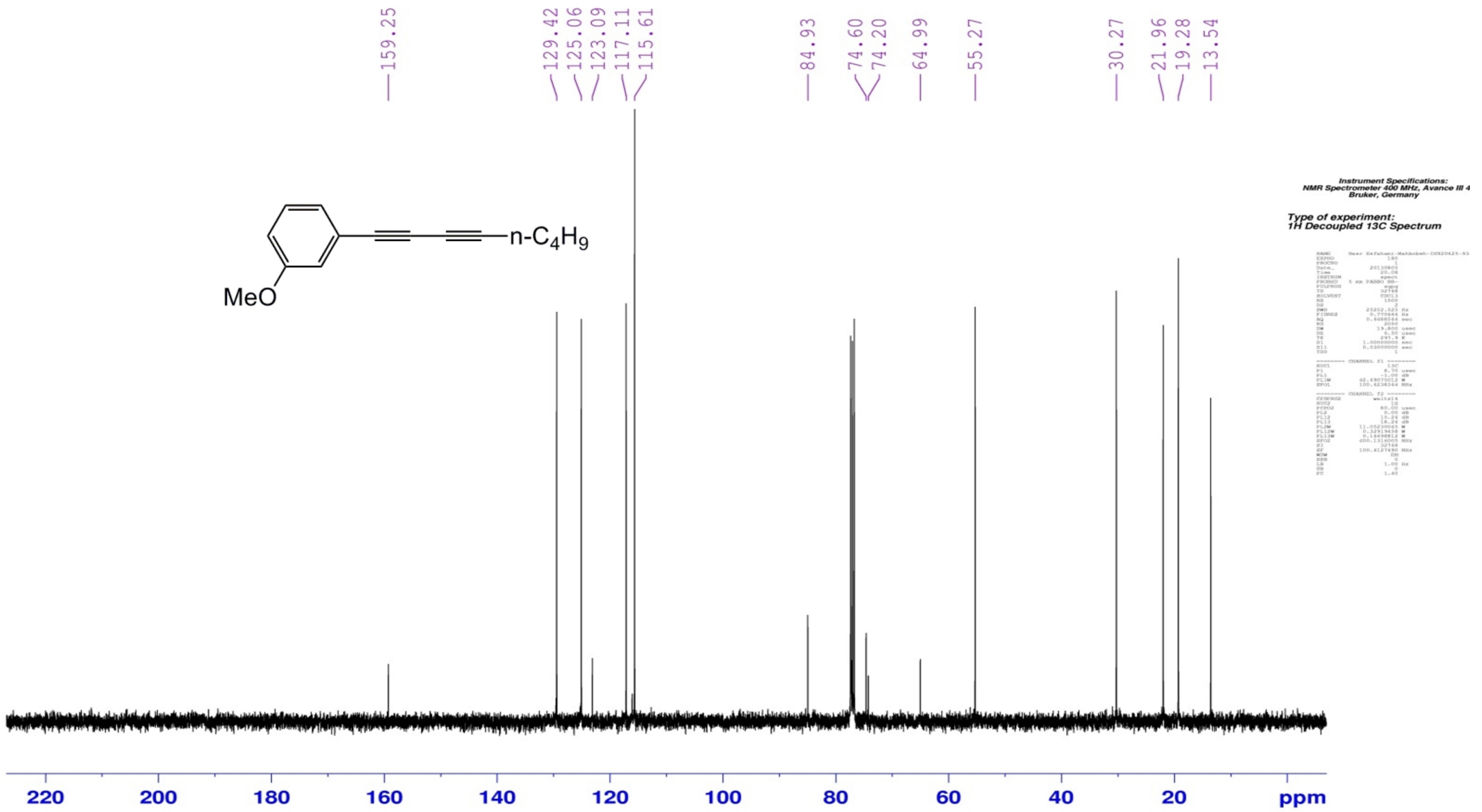
1-((4-Chlorophenyl)buta-1,3-diyn-1-yl)-3-methoxybenzene (Table4, 3ci): ^{13}C NMR (100 MHz, $CDCl_3$)



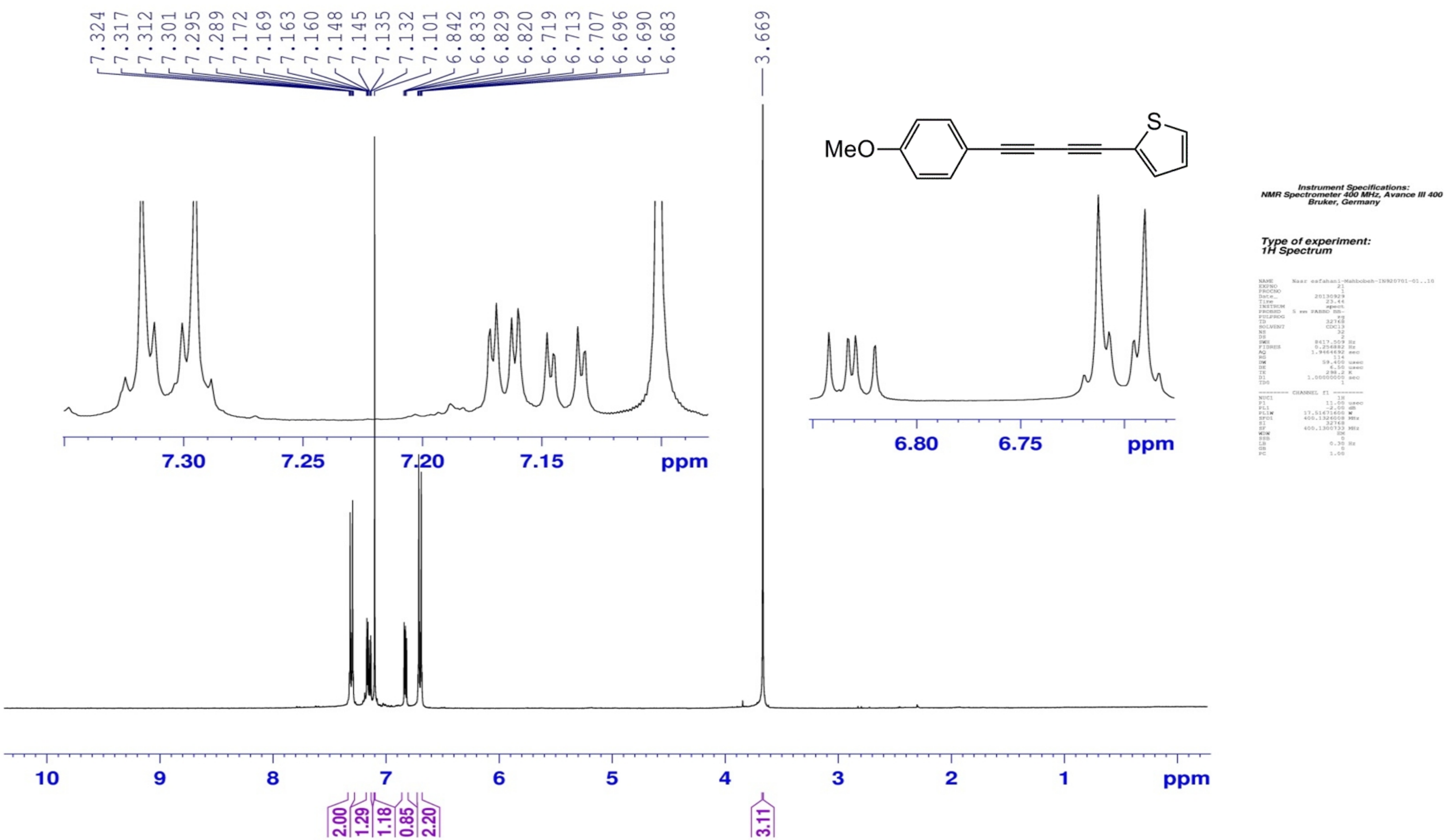
1-Methoxy-3-(octa-1,3-diyn-1-yl)benzene (Table 4, 3cm): ^{1}H NMR (400 MHz, $CDCl_3$)



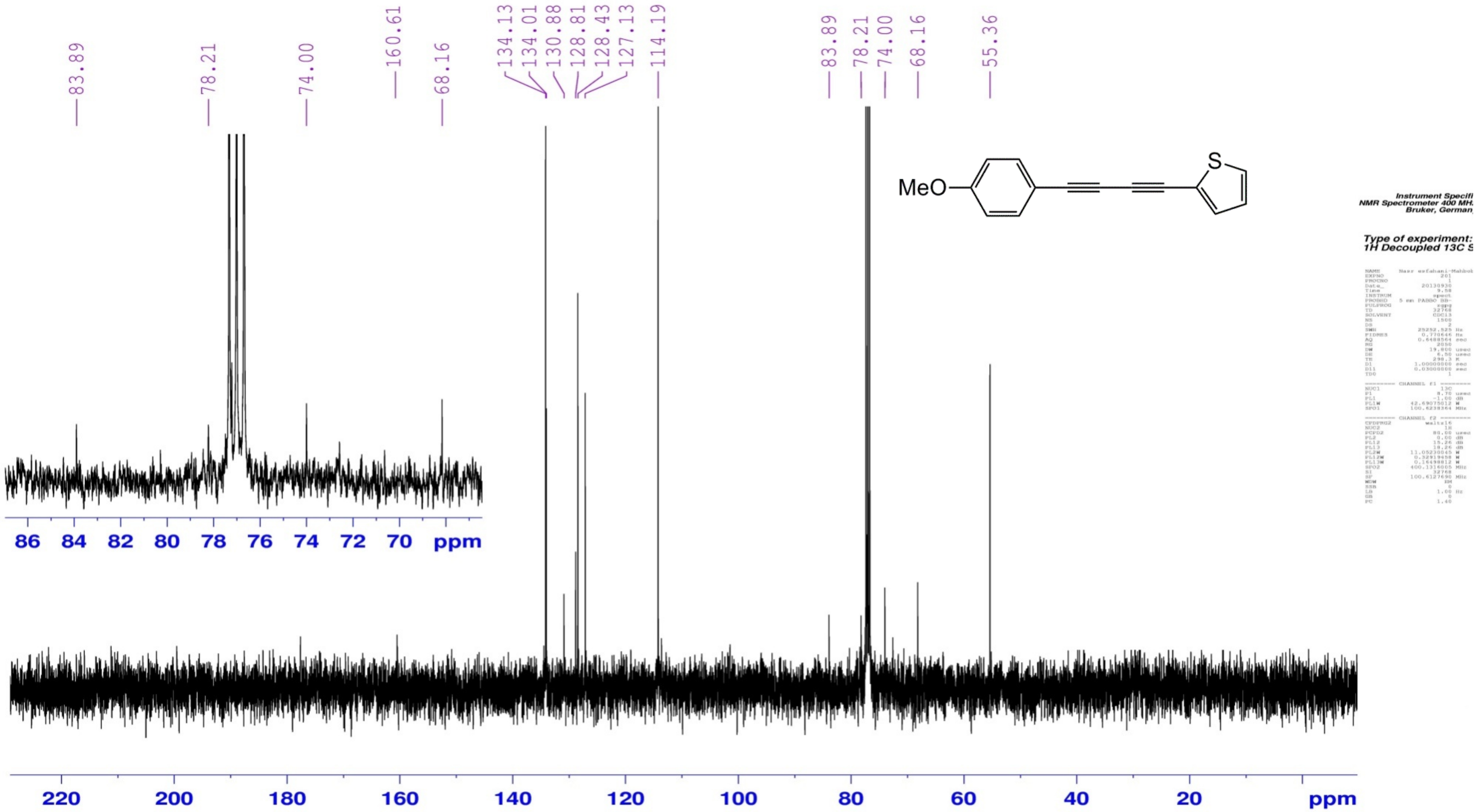
1-Methoxy-3-(octa-1,3-diyn-1-yl)benzene (Table 4, 3cm): ^{13}C NMR (100 MHz, CDCl$_3$)



2-((4-Methoxyphenyl)buta-1,3-diyn-1-yl)thiophene (Table 4, 3dk): ^{1}H NMR (400 MHz, $CDCl_3$)



2-((4-Methoxyphenyl)buta-1,3-diyn-1-yl)thiophene (Table 4, 3dk): ^{13}C NMR (100 MHz, CDCl$_3$)



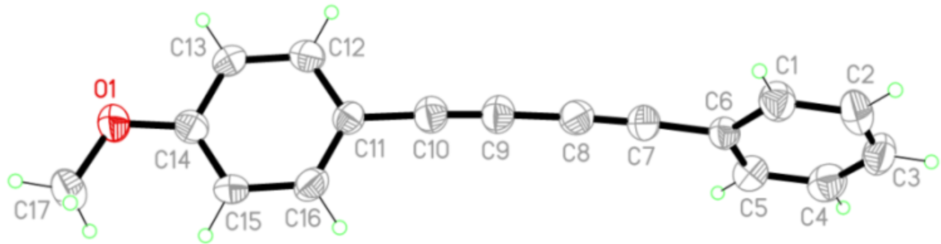


Figure 1 X-ray crystal structure of compound **3ad**. Thermal ellipsoids are drawn at the 30% probability level, while the hydrogen size is arbitrary.

Table 1 Crystal data and structure refinement for Compound **3ad**.

Empirical formula	$C_{17}H_{12}O$	
Temperature (K)	293(2)	
Formula weight	232.27	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.846(2) Å	α = 90°
	b = 9.3560(19) Å	β = 101.896(11)°
	c = 10.2300(15) Å	γ = 90°
Volume	1296.8(4) $Å^3$	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	488	
Theta range for data collection	2.65 to 25.00°	
Index ranges	-16<=h<=16, -11<=k<=11, -12<=l<=11	
Reflections collected	14290	
Independent reflections	2284 [R(int) = 0.1138]	
Completeness to theta = 25.00	100.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2284 / 0 / 165	
Goodness-of-fit on F^2	0.924	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.0806	
R indices (all data)	R1 = 0.1991, wR2 = 0.1092	
Largest diff. peak and hole	0.128 and -0.201 e.$Å^3$	

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