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Synthesis, Structure and Catalytic Properties of $[Ru(dppp)_2(CH_3CN)Cl][BPh_4]$ and Isolation of Catalytically Active $[Ru(dppp)_2Cl][BPh_4]$: Ruthenium Catalyzed Alkyne Homocoupling and Tandem Alkyne – Azide Cycloaddition

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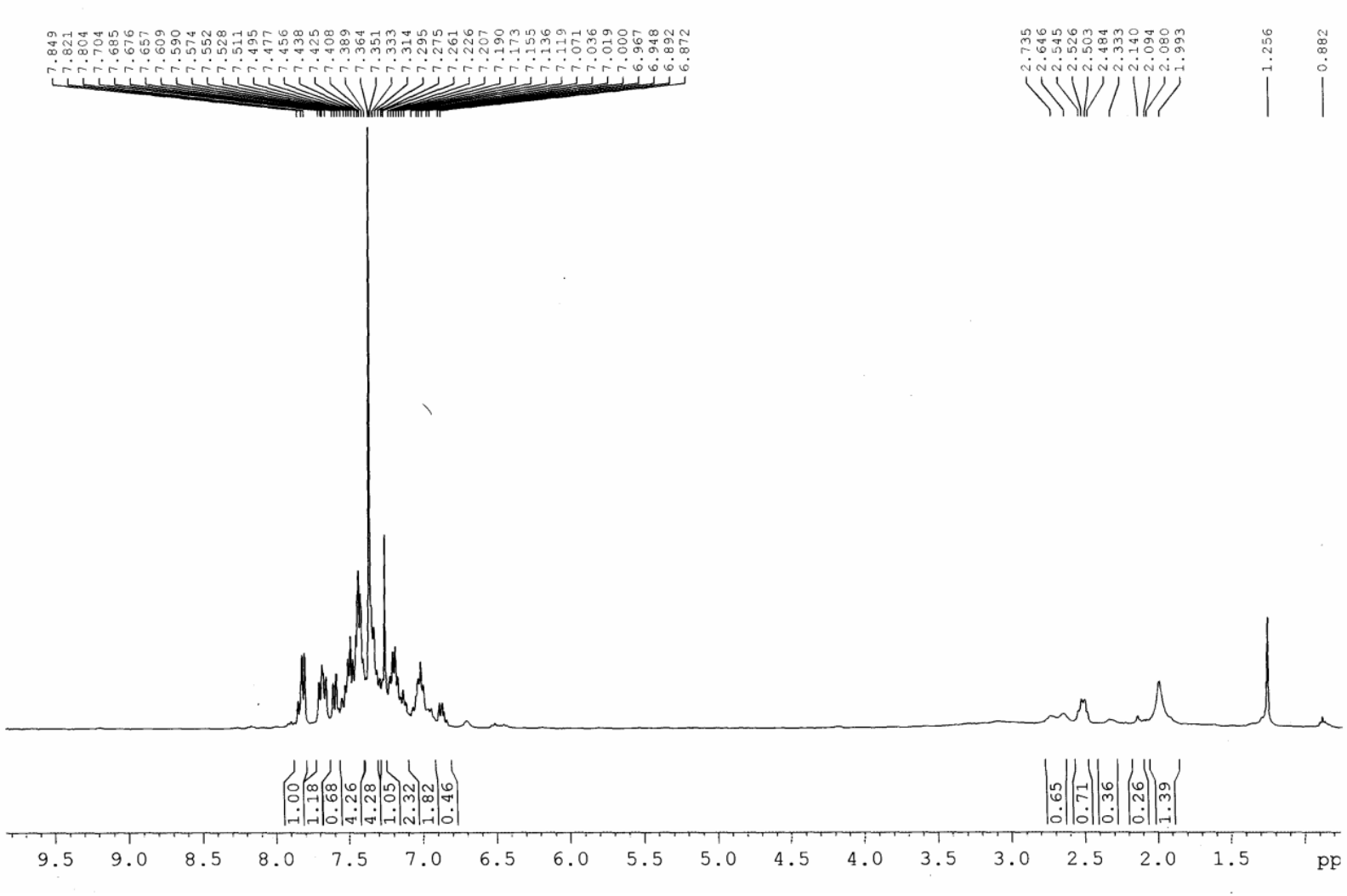


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**

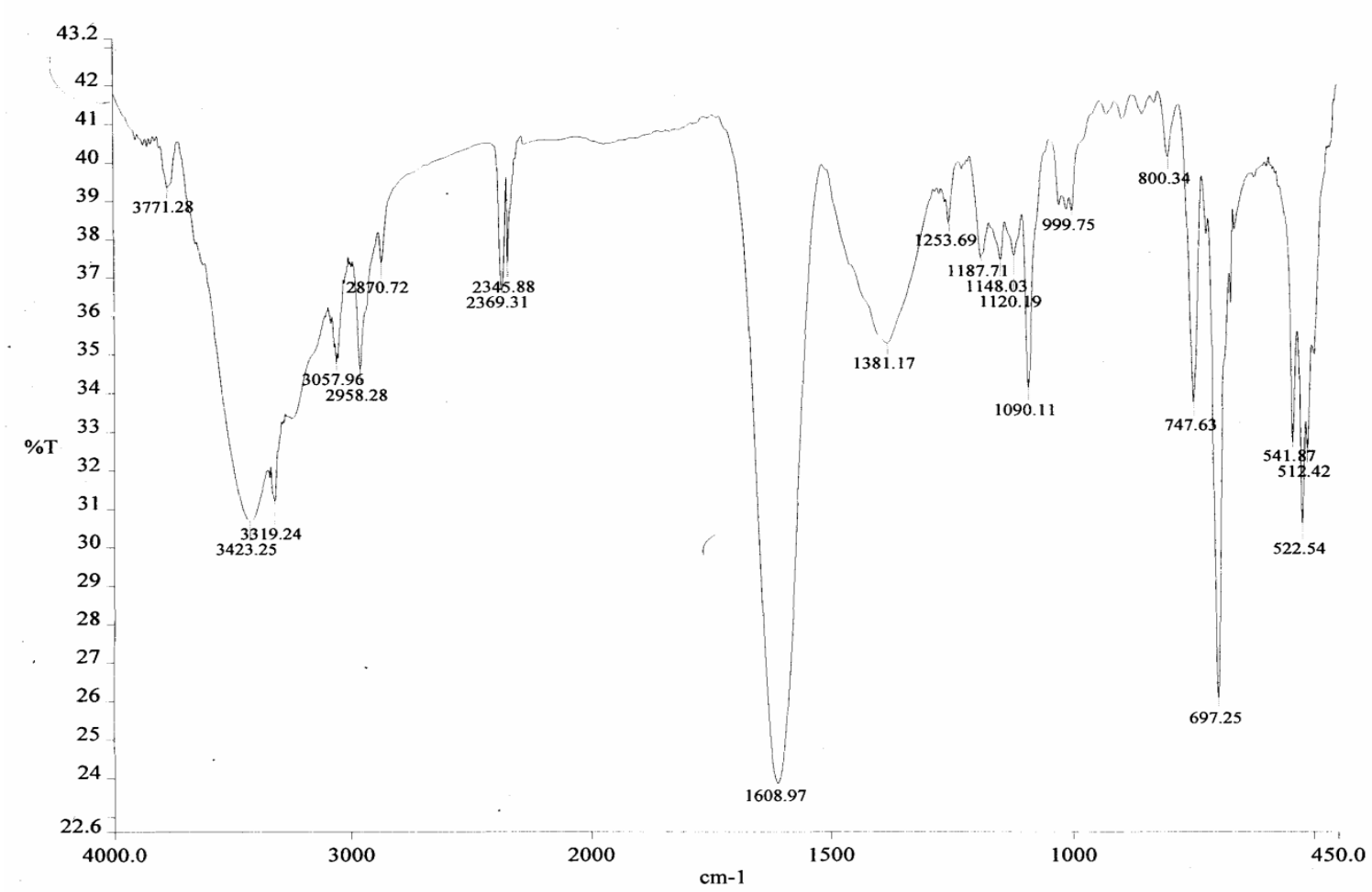


Figure S2 IR spectrum of **1**

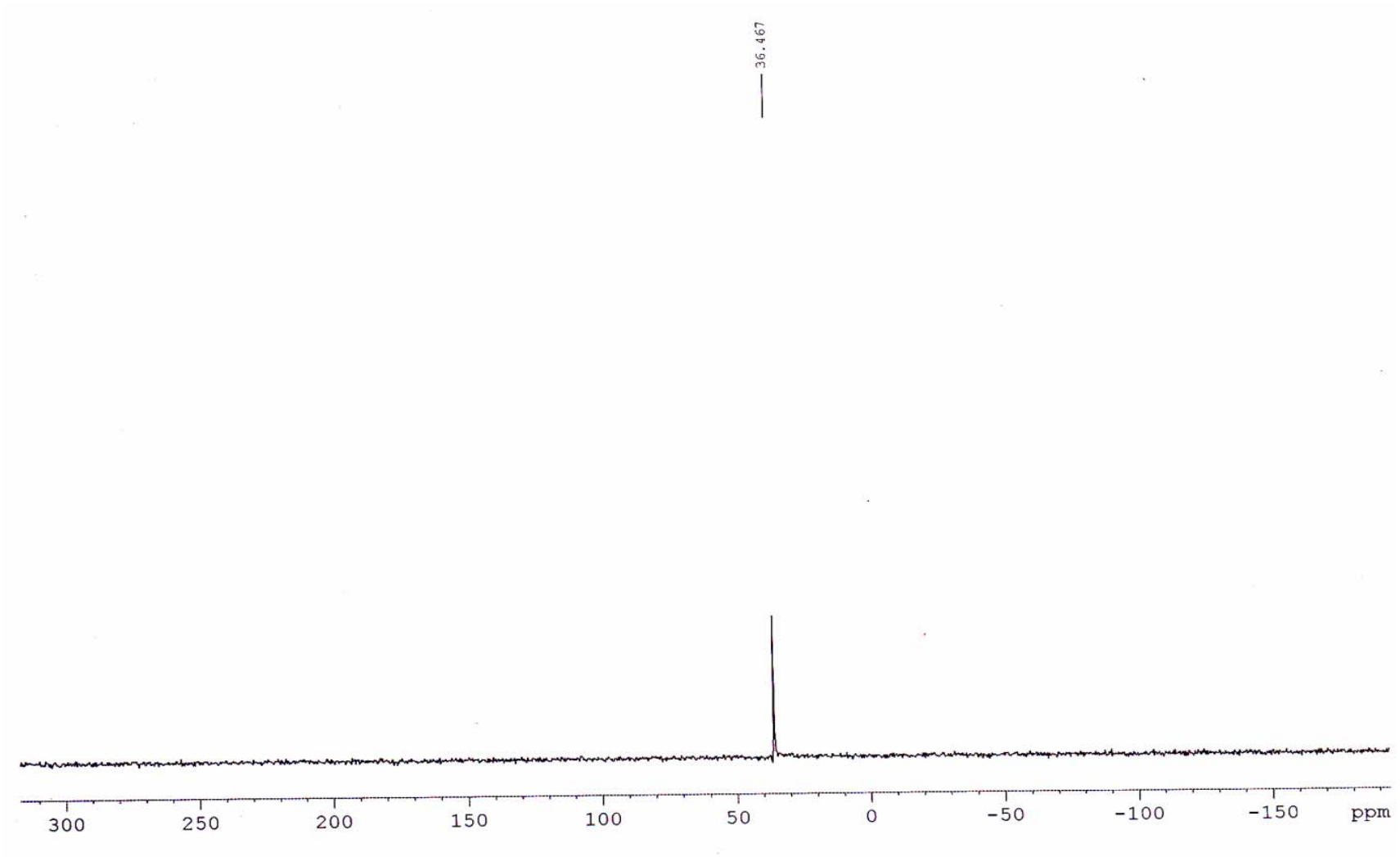


Figure S3 ^{31}P NMR (161.98 MHz, $CDCl_3$) spectrum of **1**

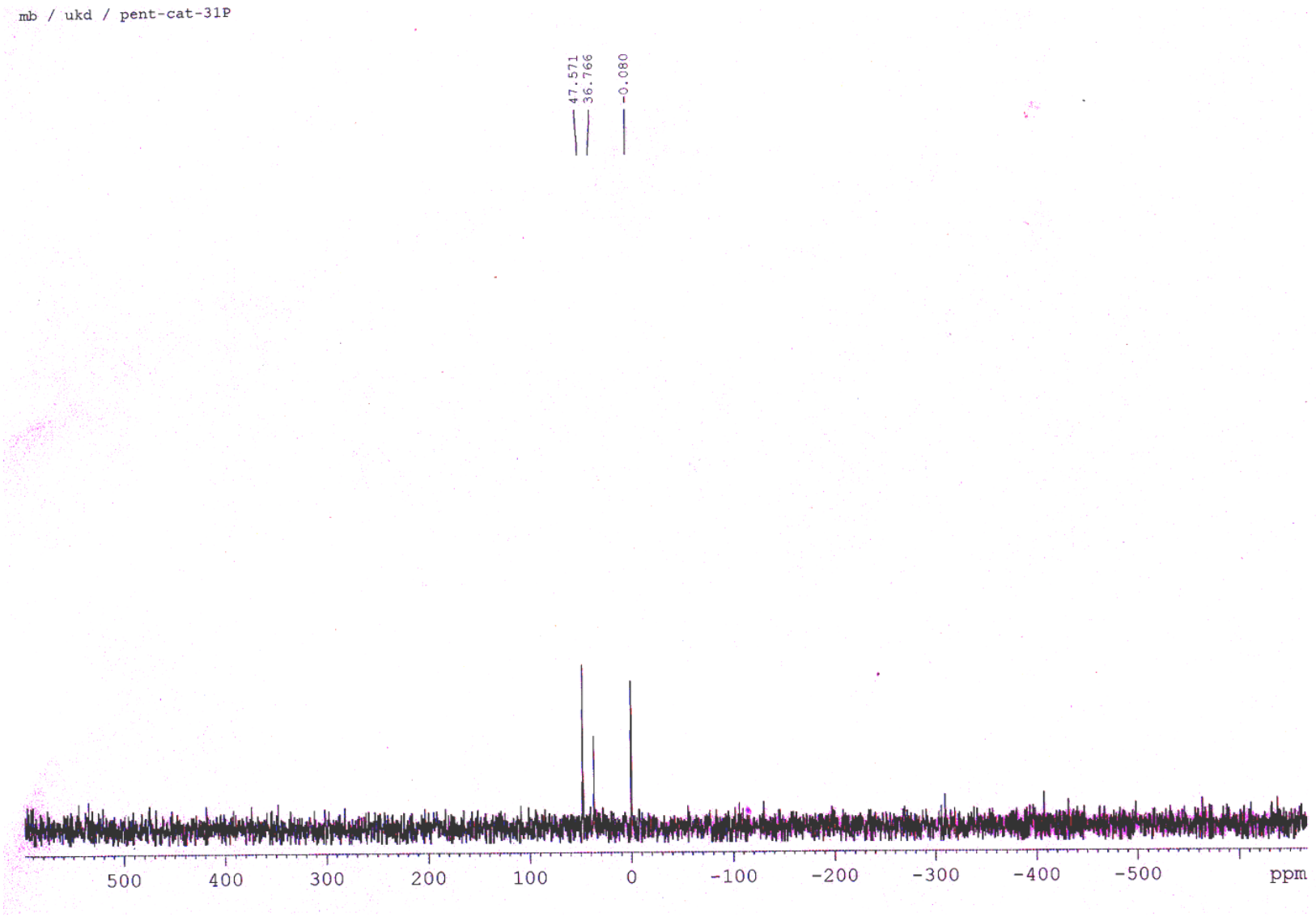


Figure S4 ^{31}P NMR(161.98 MHz) spectrum of **2** in

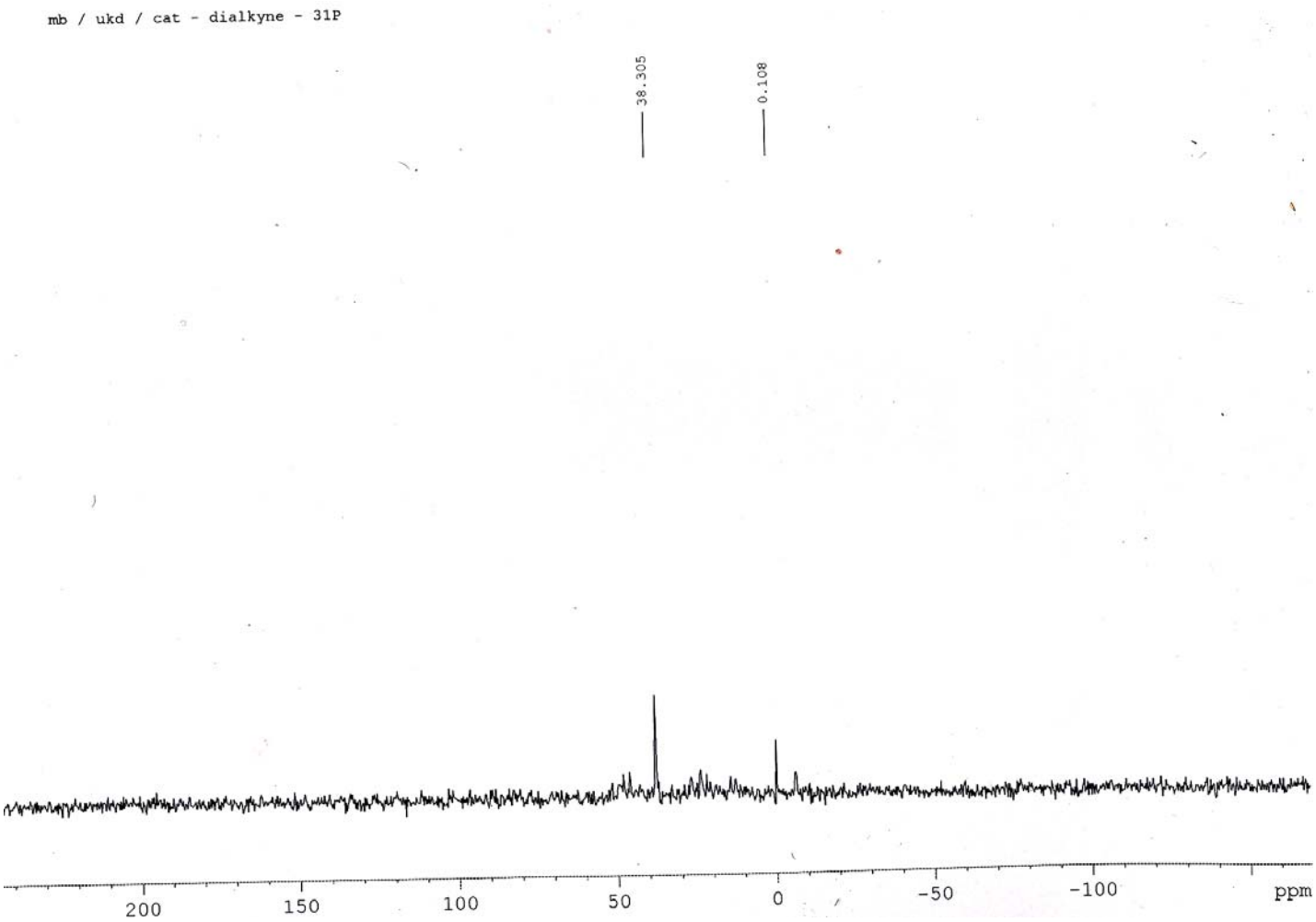


Figure S5 ^{31}P NMR(161.98 MHz) spectrum of *trans*-[Ru(dppp)$_2$(CCR)$_2$] in $CDCl_3$

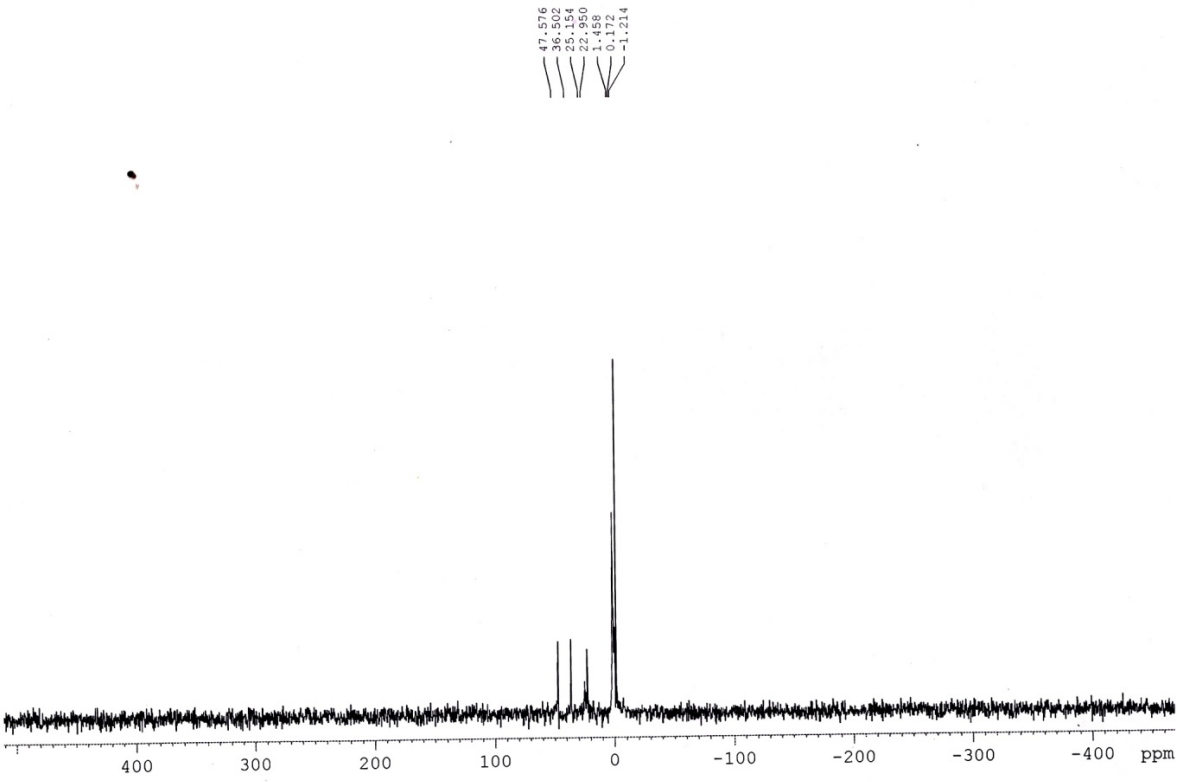


Figure S6 ^{31}P NMR (161.98 MHz) spectrum of reaction mixture of the reaction between **1**, phenyl acetylene and $Ag(NO_3)$ in $CDCl_3$

Table S1 Crystal data and structure refinement for **1**, **2** and **6**

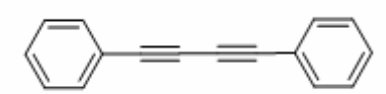
Compound	**1**	**2**	**6**
Empirical formula	$C_{80}H_{75}BClNP_4Ru$	$C_{78}H_{72}BClP_4Ru$	$C_{70}H_{62}P_4Ru$
Formula weight	1321.62	1280.57	1128.15
Temperature, K	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P21/a	P-1
A, b, c (Å)	12.620(5), 13.935(5), 19.343(5)	17.742(5), 19.095(5), 19.603(5)	12.454(4), 13.500(4), 20.224(7)
α, β, γ (°)	92.440(5), 96.936(5), 94.388(5)	90(0), 97.922(5), 90(0)	95.632(12), 91.802(11), 109.716(10)
V ($Å^3$)	3362(2)	6578(3)	3177.9(18)
Z	2	4	2
Dcalc. (Mg/m^3)	1.305	1.293	1.179
μ (Mo-Ka) (mm^{-1})	0.413	0.420	0.385
F(000)	1376	2664	1172
θ Range (°)	1.06 to 30.64	1.05 to 26.49	1.01 to 26.56
Reflections collected	49741	85071	41354
Unique reflections	18227	13498	12804
$R_{(int)}$	0.1009	0.2982	0.1359
Restraints	0	0	0
parameters	794	766	676
Goodness of fit (F2)	0.92	0.964	0.881
R1 [I>2σ(I)], wR2	0.0619, 0.1574	0.0732, 0.1274	0.0771, 0.1654

Table S2 Important bond distances [Å] and bond angles [°] of **1**, **2** and **6**

1		**2**		**6**	
N1-Ru1	2.003(4)	P1-Ru1	2.263(2)	P1-Ru1	2.394(2)
P1-Ru1	2.4025(15)	P2-Ru1	2.429(2)	P2-Ru1	2.3826(19)
P2-Ru1	2.4247(14)	P3-Ru1	2.280(2)	P3-Ru1	2.405(2)
P3-Ru1	2.4750(14)	P4-Ru1	2.416(2)	P4-Ru1 .	2.4096(19)
P4 Ru1	2.4428(15)	Cl1-Ru1	2.394(2)	C55-Ru1	2.041(7)
Cl1-Ru1	2.4222(13)			C63-Ru1	2.037(7)
N1 Ru1 P1	91.29(10)	P1 Ru1 P3	96.56(8)	C55 Ru1 C63	176.5(3)
N1 Ru1 Cl1	178.99(10)	P1 Ru1 Cl1	122.89(7)	C55 Ru1 P2	82.17(18)
P1 Ru1 Cl1	88.60(4)	P3 Ru1 Cl1	140.55(8)	C63 Ru1 P2	99.72(19)
N1 Ru1 P2	97.62(10)	P1 Ru1 P4	97.42(7)	C55 Ru1 P1	94.51(18)
P1 Ru1 P2	86.89(4)	P3 Ru1 P4	87.30(7)	C63 Ru1 P1	82.65(18)
Cl1 Ru1 P2	81.37(4)	Cl1 Ru1 P4	87.34(7)	P2 Ru1 P1	86.81(7)
N1 Ru1 P4	91.05(10)	P1 Ru1 P2	87.78(7)	C55 Ru1 P3	100.12(18)
P1 Ru1 P4	177.62(4)	P3 Ru1 P2	96.62(7)	C63 Ru1 P3	82.80(18)
Cl1 Ru1 P4	89.07(4)	Cl1 Ru1 P2	86.04(7)	P2 Ru1 P3	93.49(7)
P2 Ru1 P4	93.23(4)	P4 Ru1 P2	173.11(7)	P1 Ru1 P3	165.28(7)
N1 Ru1 P3	81.11(10)			C55 Ru1 P4	83.18(18)
P1 Ru1 P3	95.08(4)			C63 Ru1 P4	95.04(19)
Cl1 Ru1 P3	99.90(4)			P2 Ru1 P4	165.14(7)
P2 Ru1 P3	177.67(4)			P1 Ru1 P4	96.77(7)
P4 Ru1 P3	84.85(4)			P3 Ru1 P4	86.69(7)

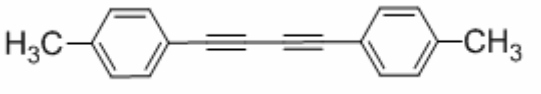
Characterization data of diynes:[4-6]

1,4-Diphenyl-1,3-butadiyne (4a):



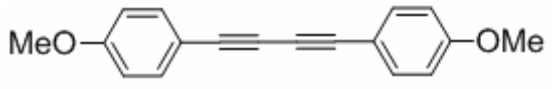
White Solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.31-7.42 (m, 6H), 7.51-7.56 (m, 4H).^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 74.0, 81.7, 121.9, 128.6, 129.4, 132.6.

1,4-Bis(4-methylphenyl)-1,3-butadiyne (4b):



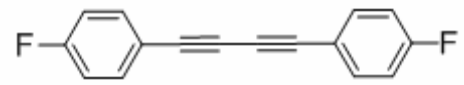
White Solid, 94% yield.^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.37 (s, 6H), 7.13 (d, *J* = 7.6 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 21.6, 73.6, 81.7, 118.9, 129.4, 132.6, 139.7.

1,4-Bis(4-methoxyphenyl)-1,3-butadiyne (4c):



White Solid, 98% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K, TMS): δ 3.81 (s, 6H), 6.82 (d, *J* = 9.0 Hz, 4H), 7.46 (d, *J* = 9.0 Hz, 4H). ^{13}C {1H} NMR (50 MHz, $CDCl_3$, 298 K, TMS): δ 55.5, 73.1, 81.4, 114.2, 114.3, 134.2, 160.4.

1,4-Bis(4-fluorophenyl)-1,3-butadiyne (4d):



White Solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.01-7.06 (m, 4H), 7.49-7.53 (m, 4H). ^{13}C {1H} NMR (50 MHz, $CDCl_3$, 298 K, TMS): δ 73.8, 80.6, 116.4 (^{2}J = 25 Hz), 118.0, 118.1, 134.6, 134.8, 160.8, 165.9 (^{1}J = 260 Hz).

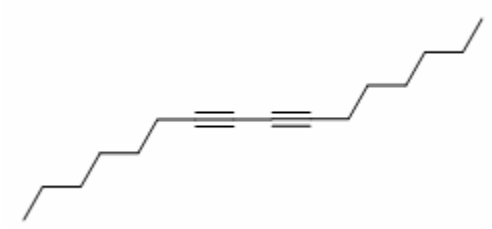
1,4-Bis(4-phenoxyphenyl)-1,3-butadiyne (4e):

White solid, 87% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K, TMS): δ 6.91-7.21 (m, 10H), 7.34-7.51 (m, 8H). ^{13}C {1H} NMR (50 MHz, $CDCl_3$, 298 K, TMS): δ 73.6, 81.2, 116.3, 118.3, 119.9, 124.3, 130.1, 134.3, 156.2, 158.7.

5, 7-Dodecadiyne (4f):

Colorless oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 0.87 (t, *J* = 7.2 Hz, 6H), 1.37-1.43 (m, 4H), 1.45-1.51 (m, 4H), 2.22 (t, *J* = 6.8 Hz, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 13.5, 18.9, 21.9, 30.4, 65.3, 77.5.

7, 9-Hexadecadiyne (4g):

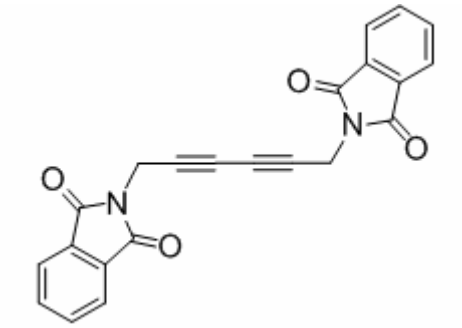


Colorless oil, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 0.86 (t, *J* = 6.8 Hz, 6H), 1.21-1.26 (m, 12H), 1.47-1.54 (m, 4H), 2.23 (t, *J* = 7.0 Hz, 4H). ^{13}C {1H} NMR (50 MHz, $CDCl_3$, 298 K, TMS): δ 13.9, 20.7, 24.4, 28.4, 31.2, 67.9, 77.5.

1,6-diphenoxyhexa-2,4-diyne (4h):

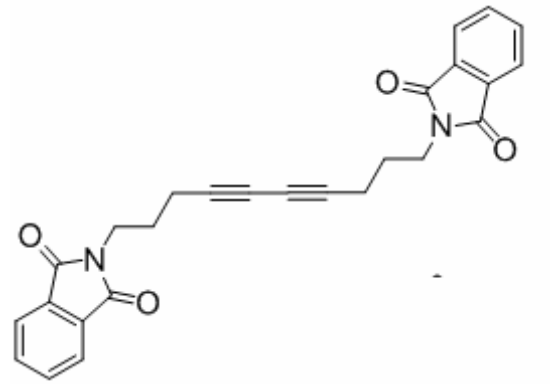
Crystalline solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 4.75 (s, 4H), 6.94-7.02 (m, 6H), 7.26-7.32 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 56.3, 71.2, 74.8, 115.0, 121.9, 129.7, 157.6.

2,2'-(hexa-2,4-diyne-1,6-diyl)diisoindoline-1,3-dione (4i):



White solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 4.56 (s, 4H), 7.71-7.75 (m, 4H), 7.85-7.88 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 27.8, 67.5, 72.3, 123.8, 132.1, 134.5,167.1.

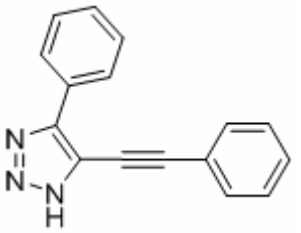
2,2'-(deca-4,6-diyne-1,10-diyl)diisoindoline-1,3-dione (4j):



White solid, 88% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K, TMS): δ 1.80-1.94 (m, 4H), 2.24 (t, *J* = 7.0 Hz, 4H), 3.71 (t, *J* = 7.0 Hz, 4H), 7.68-7.75 (m, 4H), 7.81-7.87 (m, 4H). ^{13}C {1H} NMR (50 MHz, $CDCl_3$, 298 K, TMS): δ 16.4, 27.4, 37.2, 69.2, 83.1, 123.3, 132.2, 134.1, 168.4.

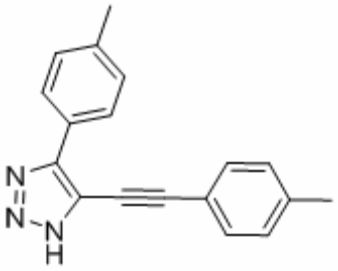
Characterization data of synthesized new trazoles

4-phenyl-5-(phenylethynyl)-1*H*-1,2,3-triazole (5a):



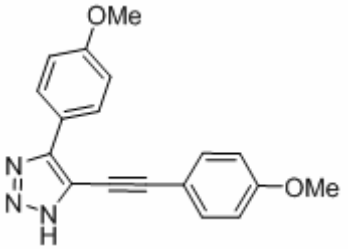
White solid, 85% yield**.** M.P: 96 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.35- 7.48 (m, 6H), 7.54 (d, *J* = 7.2 Hz, 2H), 8.14 (d, *J* = 7.6 Hz, 2H), 14.07 (s, 1H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 78.8, 96.0, 122.2, 127.0, 128.6, 129.0, 129.2, 129.5, 131.5. ESI-MS $[M+H]^+$ m/z calculated for $C_{16}H_{12}N_3$: 246.1031. Found: 246.1038. Elemental analysis calculated for $C_{16}H_{11}N_3$: C, 78.35; H, 4.52; N, 17.13. Found C, 78.85; H, 5.14; N, 17.45.

4-p-tolyl-5-(p-tolylethynyl)-1*H*-1,2,3-triazole (5b):



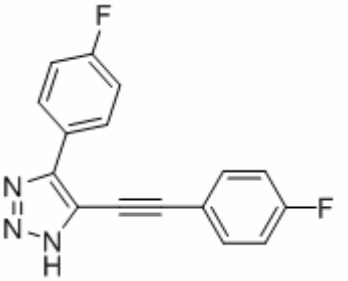
White solid, 85% yield. **.** M.P: 87 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 2.39(s, 3H), 2.41 (s, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 12.14(s, 1H).^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 78.5, 96.3, 114.2, 119.2, 126.9, 129.4, 129.6, 129.8, 131.8, 139.3, 139.6. ESI-MS $[M+H]^+$ m/z calculated for $C_{18}H_{16}N_3$: 274.1344. Found: 274.1339. Elemental analysis calculated for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37.Found. C, 79.51; H, 6.33; N, 15.46.

4-(4-methoxyphenyl)-5-((4-methoxyphenyl)ethynyl)-1*H*-1,2,3-triazole (5c):



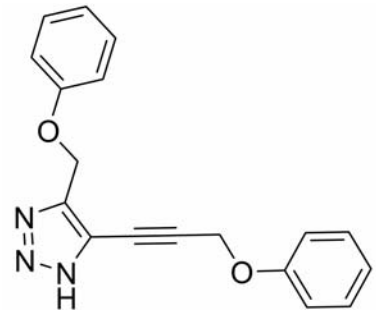
White solid, 78 % yield. **.** M.P: 92 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 3.830(s, 3H), 3.835 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 13.17(s, 1H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 55.43, 55.46, 77.8, 95.7, 114.2, 114.3, 121.6, 128.2, 133.3, 160.3. ESI-MS $[M+H]^+$ m/z calculated for $C_{18}H_{16}O_2N_3$: 306.1243. Found: 306.1252. Elemental analysis calculated for $C_{18}H_{15}O_2N_3$: C, 70.81; H, 4.95; N, 13.76. Found. C, 70.89; H, 5.11; N, 13.86.

4-(4-fluorophenyl)-5-((4-fluorophenyl)ethynyl)-1*H*-1,2,3-triazole (5d):



Semi solid, 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 7.06- 7.11 (m, 2H), 7.15-7.19 (m, 2H), 7.54-7.57 (m, 2H), 8.09- 8.13(m, 2H), 12.45 (s, 1H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 78.6, 94.8, 115.6, 115.9, 116.0, 116.2, 116.3, 118.2, 128.9, 129.6, 130.6, 133.9, 134.4, 164.7 (^{1}J = 250 Hz), 164.6 (^{1}J = 250 Hz). ESI-MS $[M+H]^+$ m/z calculated for $C_{16}H_{10}N_3F_2$: 282.0843. Found: 282.0816. Elemental analysis calculated for $C_{16}H_9N_3F_2$: C, 68.33; H, 3.23; N, 14.94. Found. C, 68.45; H, 4.21; N, 15.09.

4-(phenoxymethyl)-5-(3-phenoxyprop-1-ynyl)-1H-1,2,3-triazole (5e):



Colorless oil, 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 4.93 (s, 2H), 5.14(s, 2H), 6.94-7.01 (m, 6H), 7.24- 7.30 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$, 298 K, TMS): δ 56.4, 60.4, 75.3, 91.2, 115.1, 115.2, 121.8, 121.9, 129.7, 157.6, 158.2. ESI-MS $[M+H]^+$ m/z calculated for $C_{18}H_{16}N_3O_2$: 306.1243. Found: 306.1250 Elemental analysis calculated for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76. Found. C, 70.89; H, 4.97; N, 13.82.

Reference:

L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30* 565.

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2. T. Oishi, K. Yamaguchi, N. Mizuno, *ACS Catal*. **2011**, *1*, 1351–1354.
3. W. Yin, C. He, M.Chen, H. Zhang, A. Lei, *Org. Lett.* **2009**, *11*, 709–712.

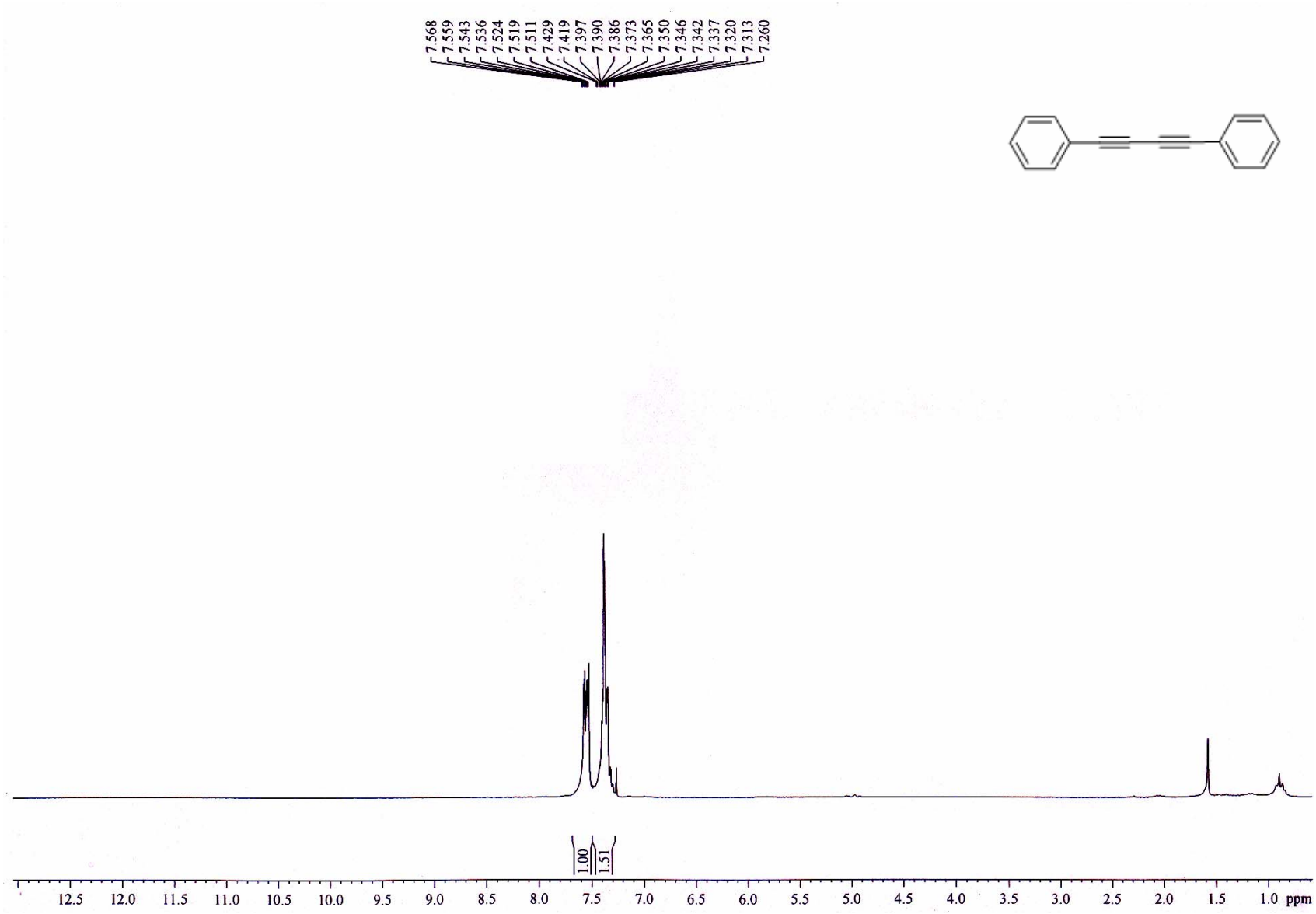

Figure S7 ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **4a**

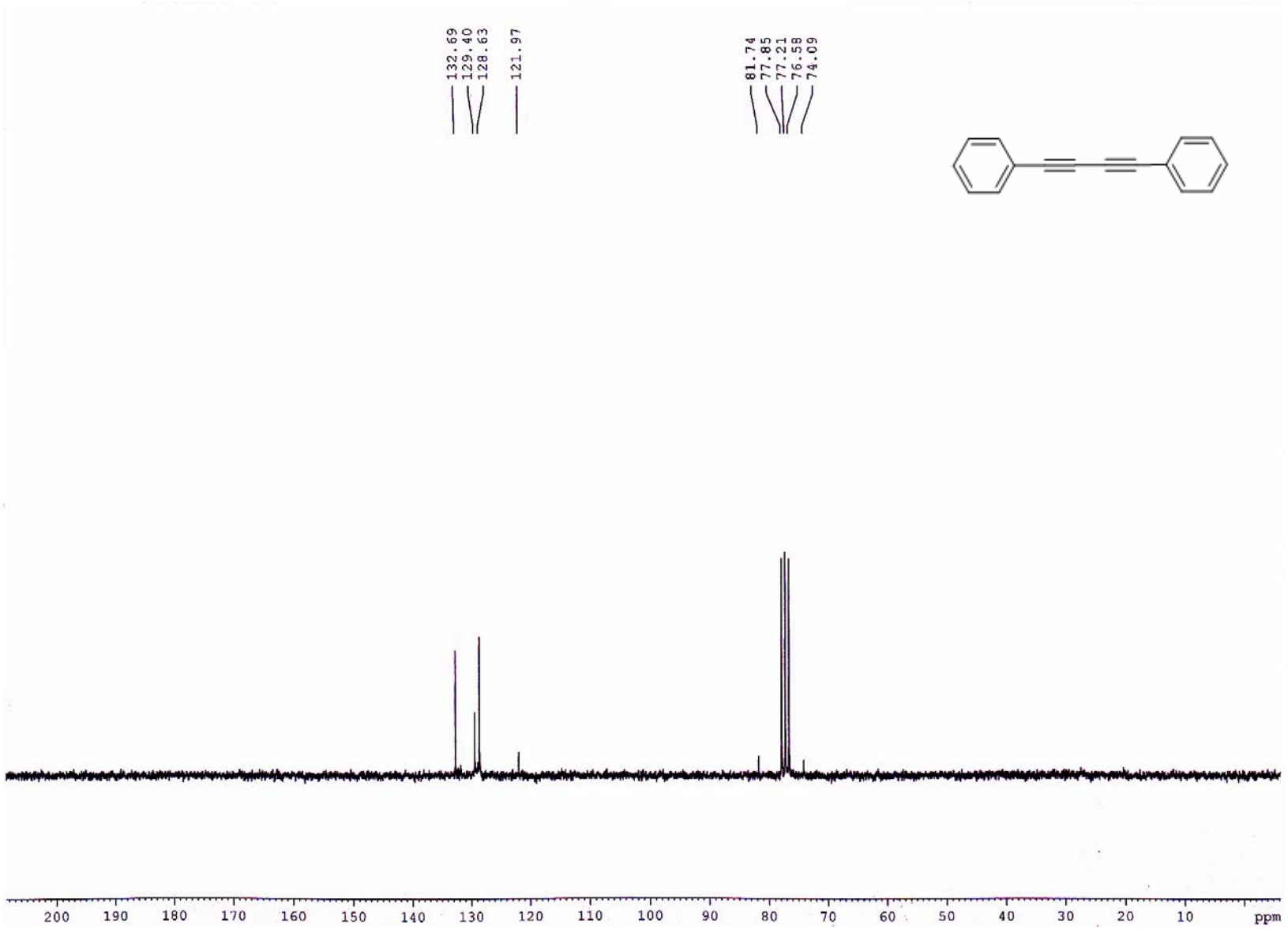

Figure S8 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**

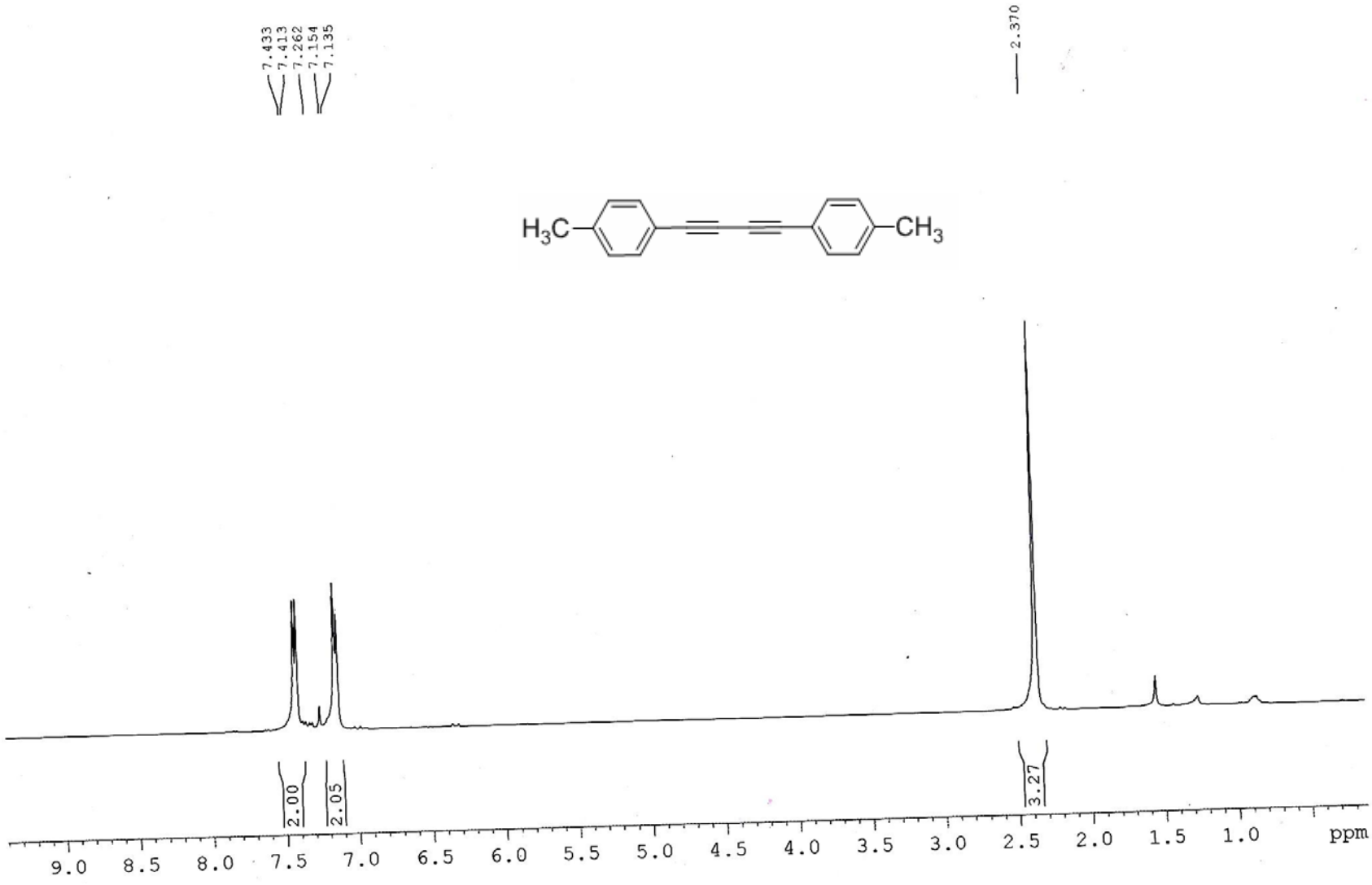

Figure S9 ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **4b**

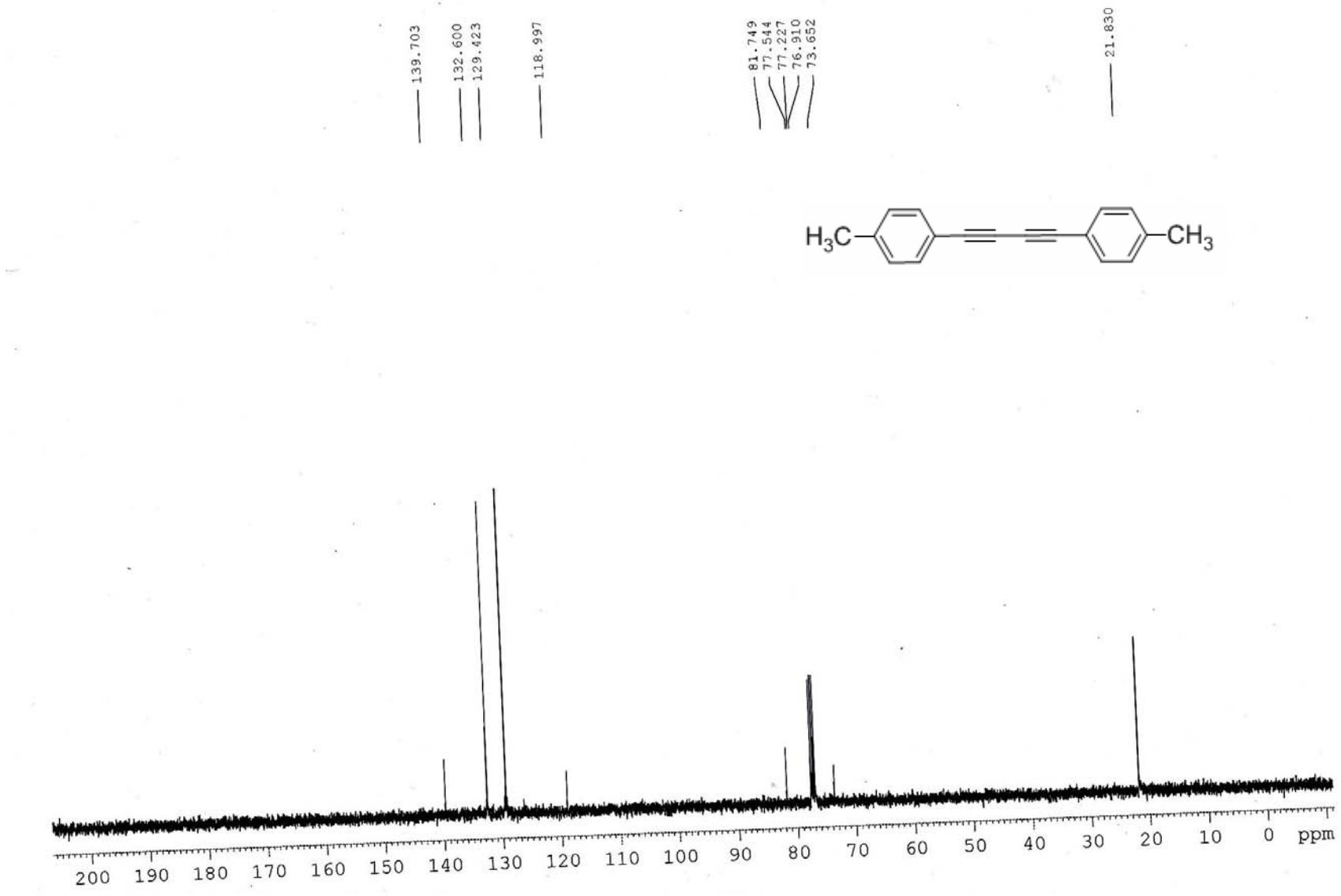

Figure S10 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**

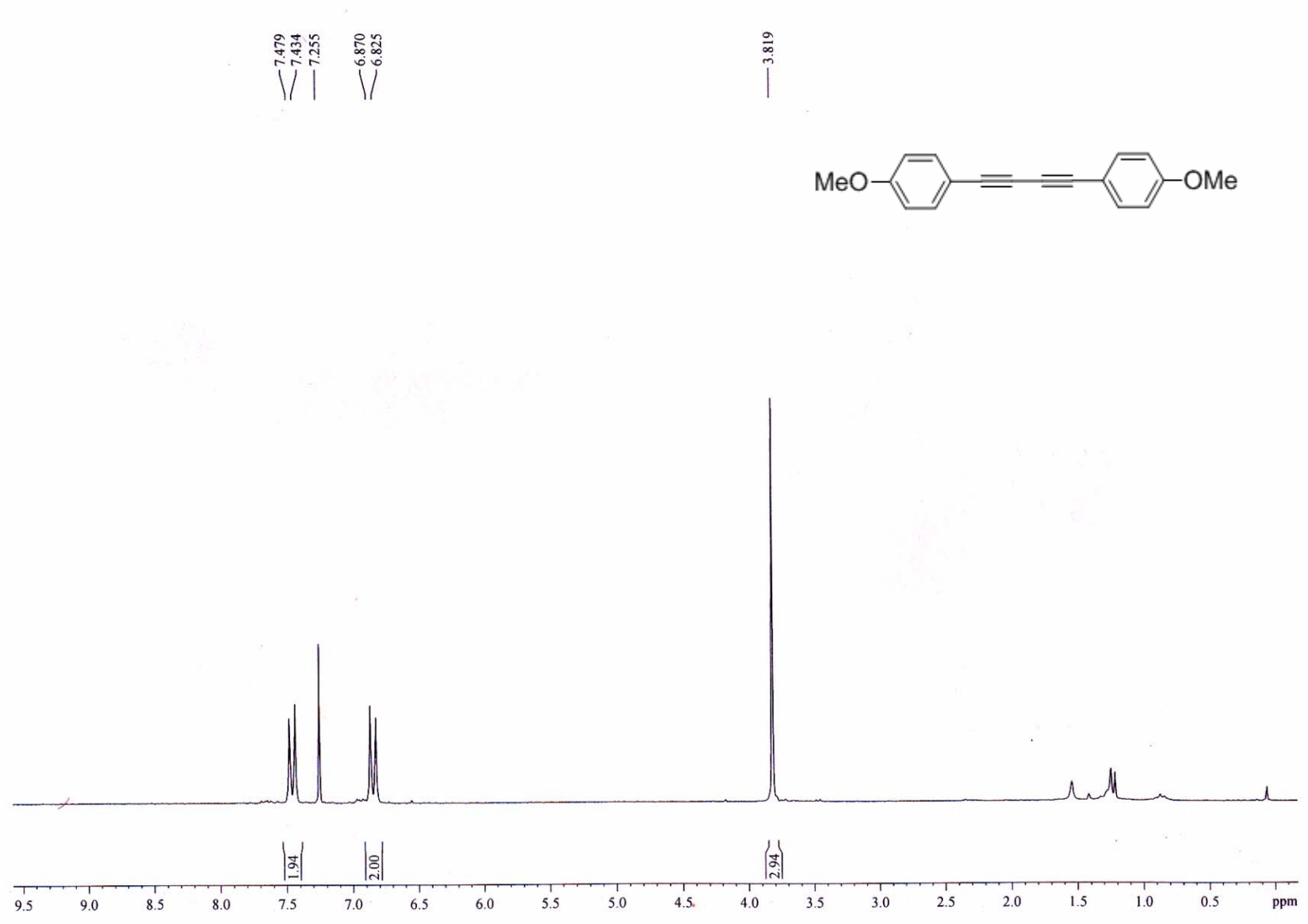

Figure S11 ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4c**

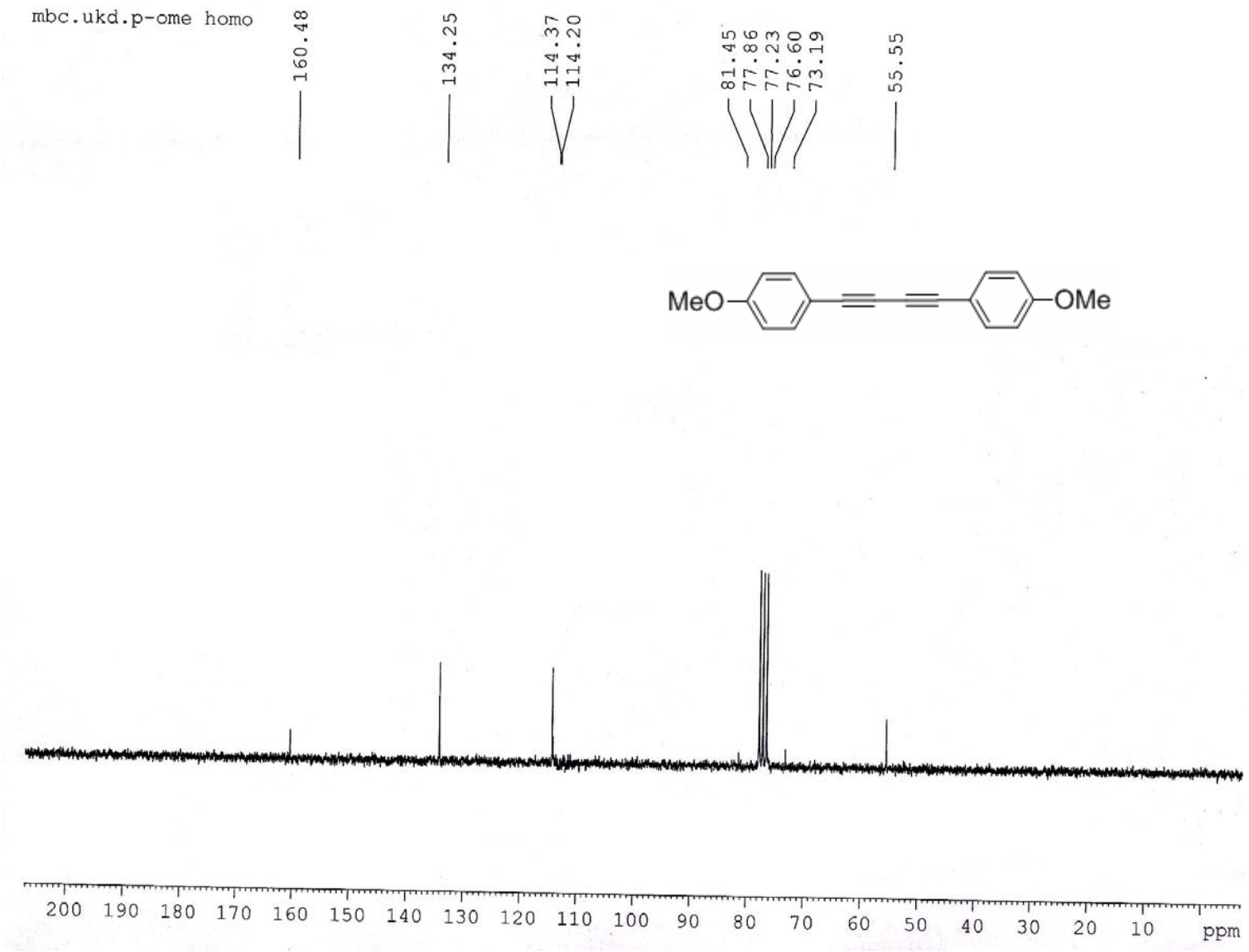

Figure S12 ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4c**

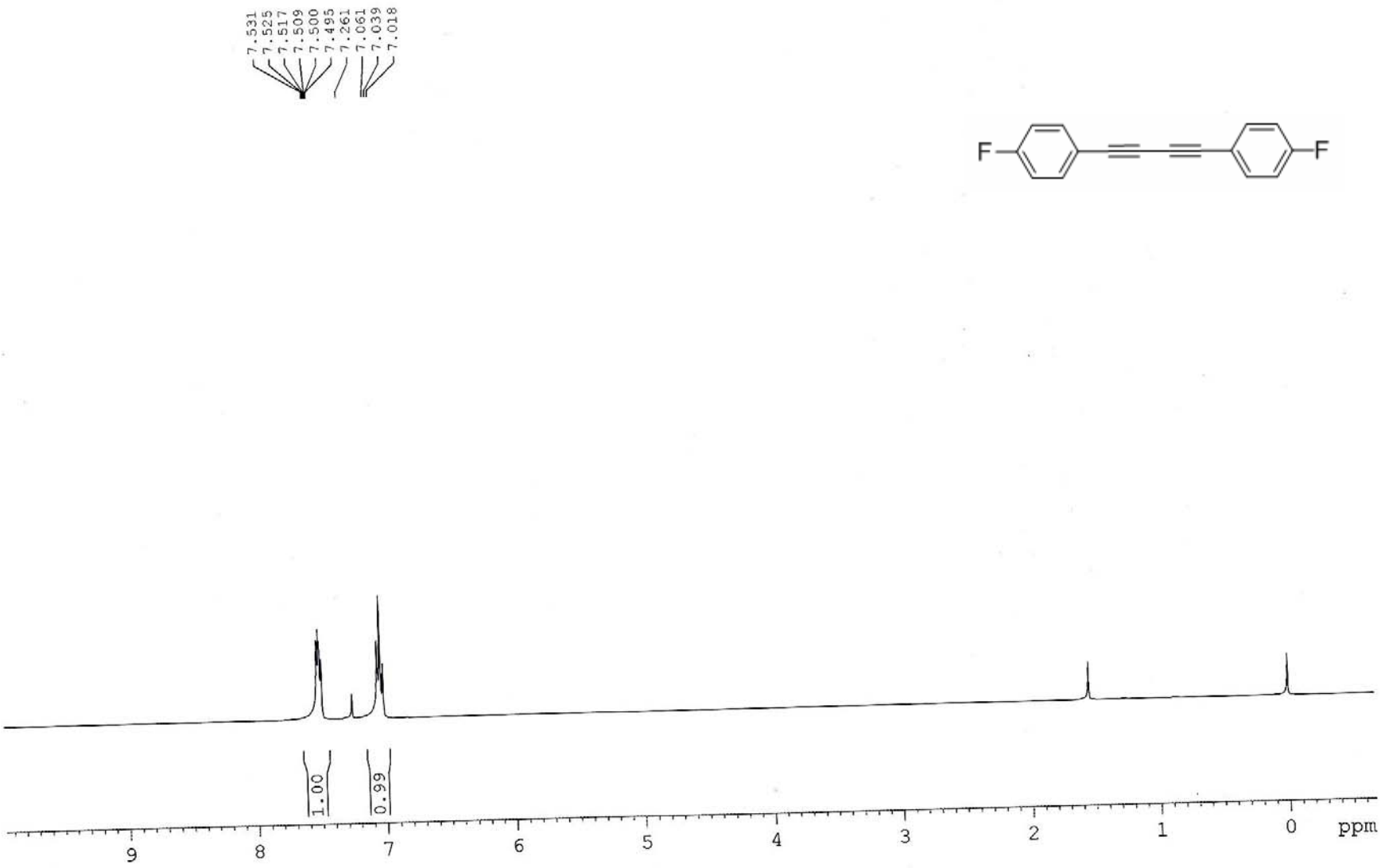

Figure S13 ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **4d**

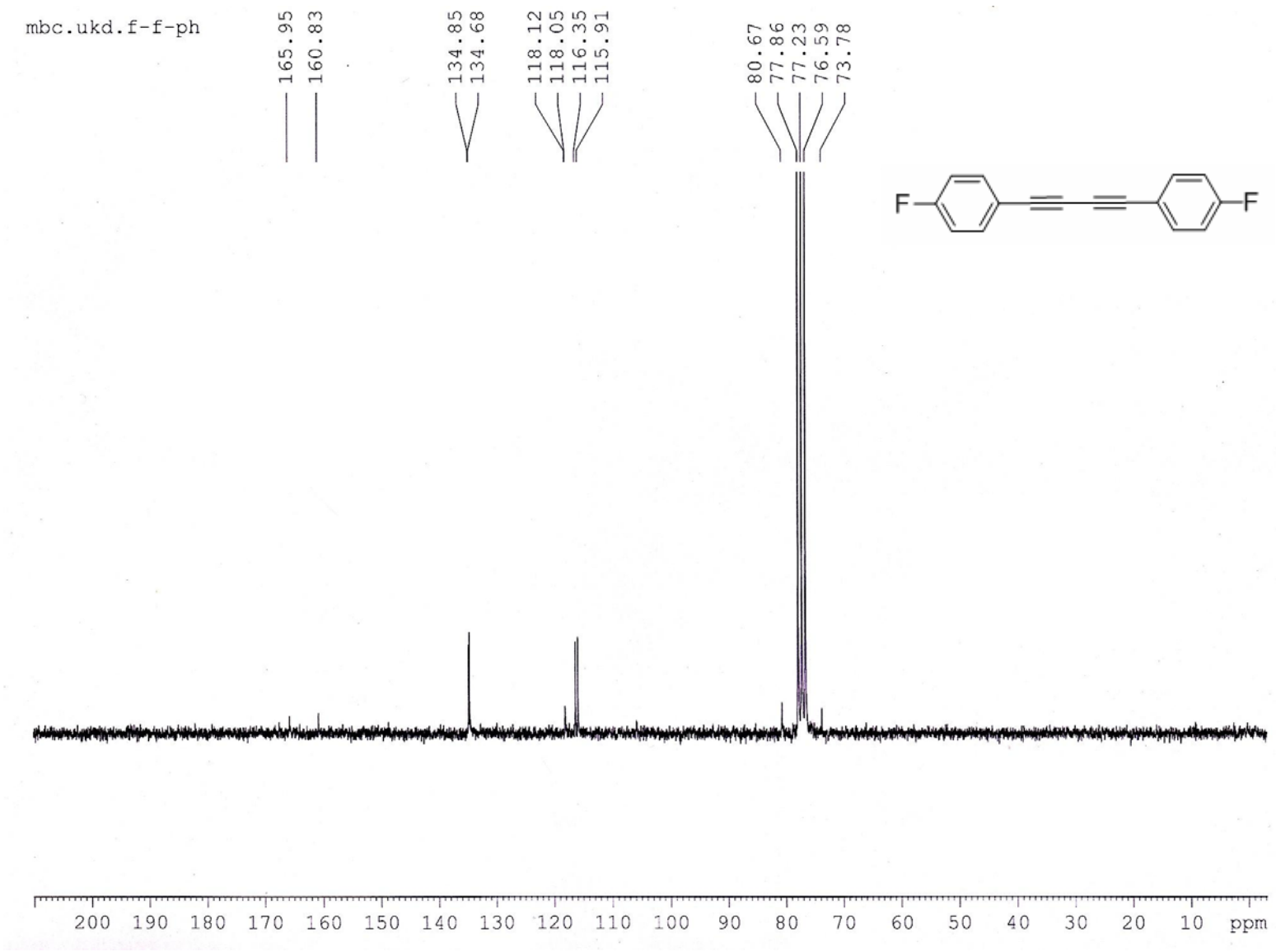

Figure S14 ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4d**

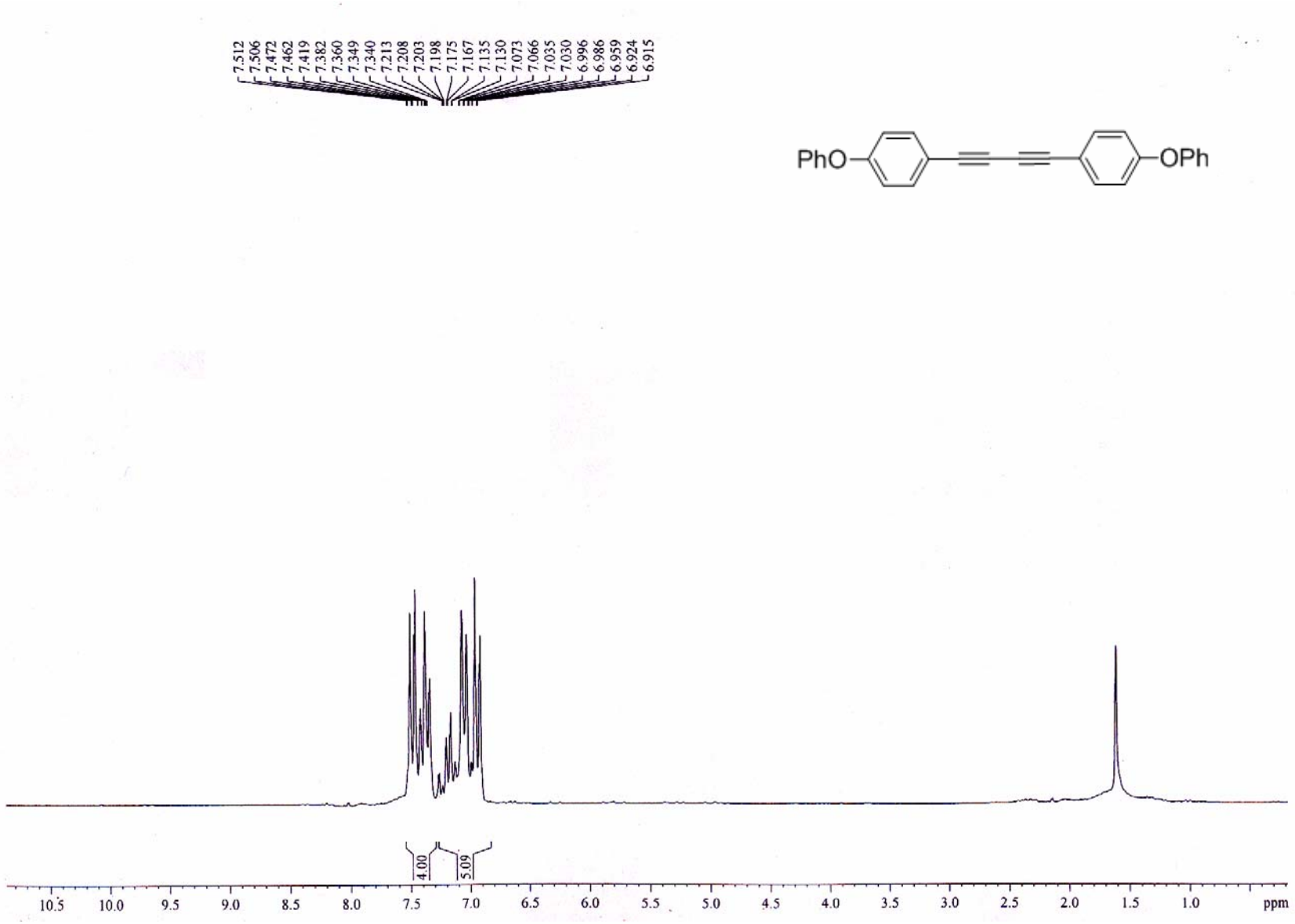

Figure S15 ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4e**

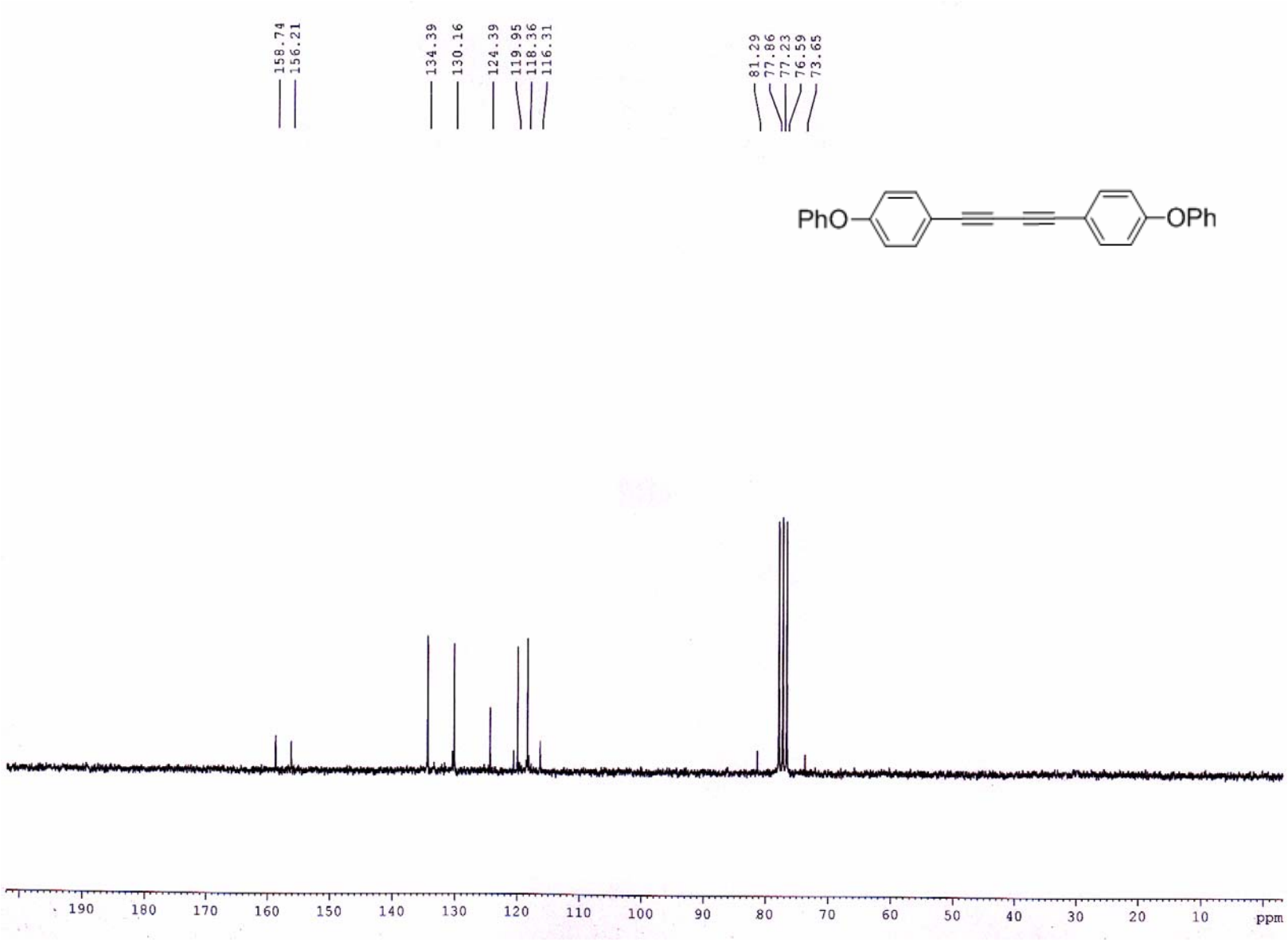

Figure S16 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4e**

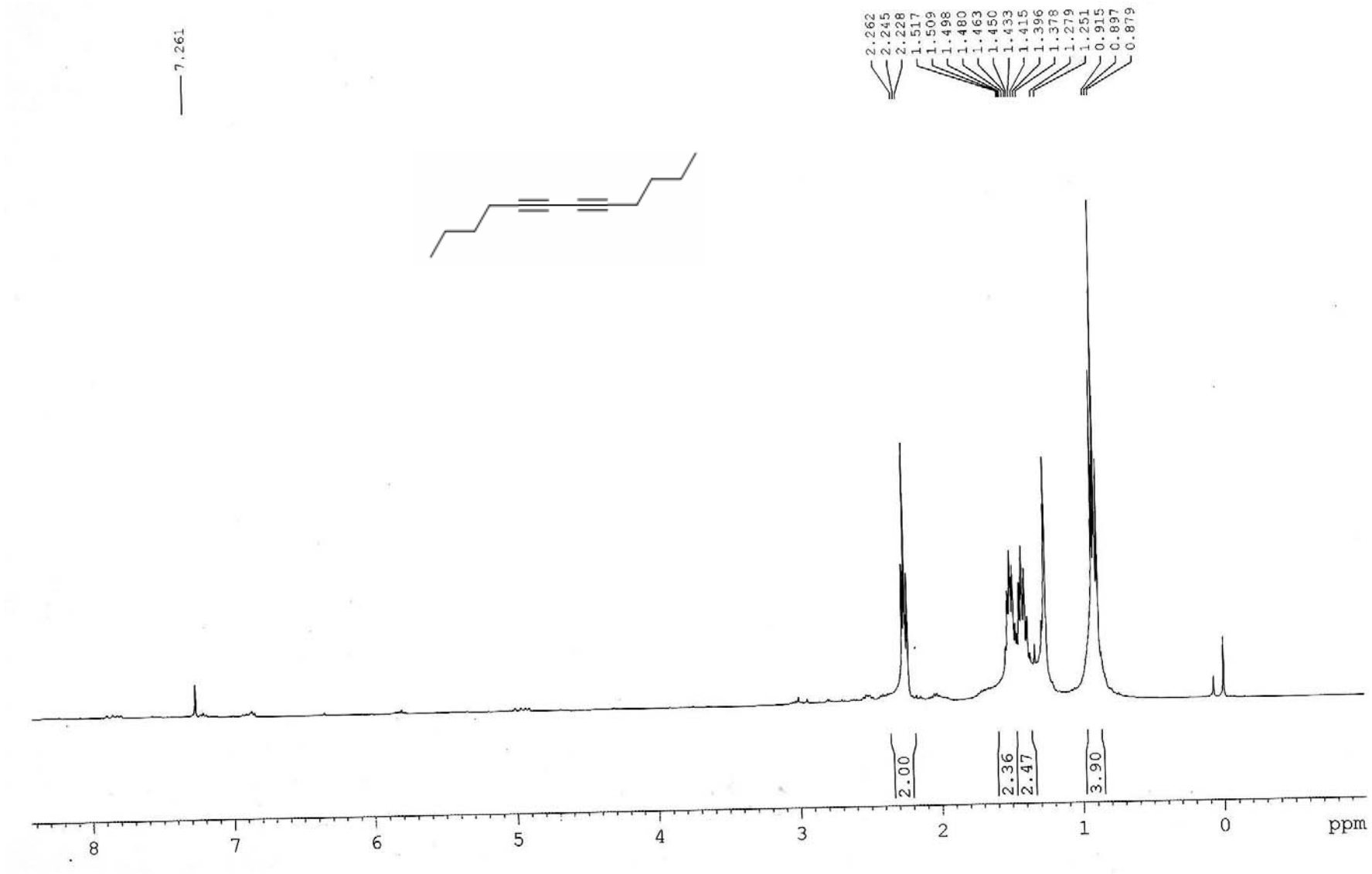

Figure S17 ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **4f**

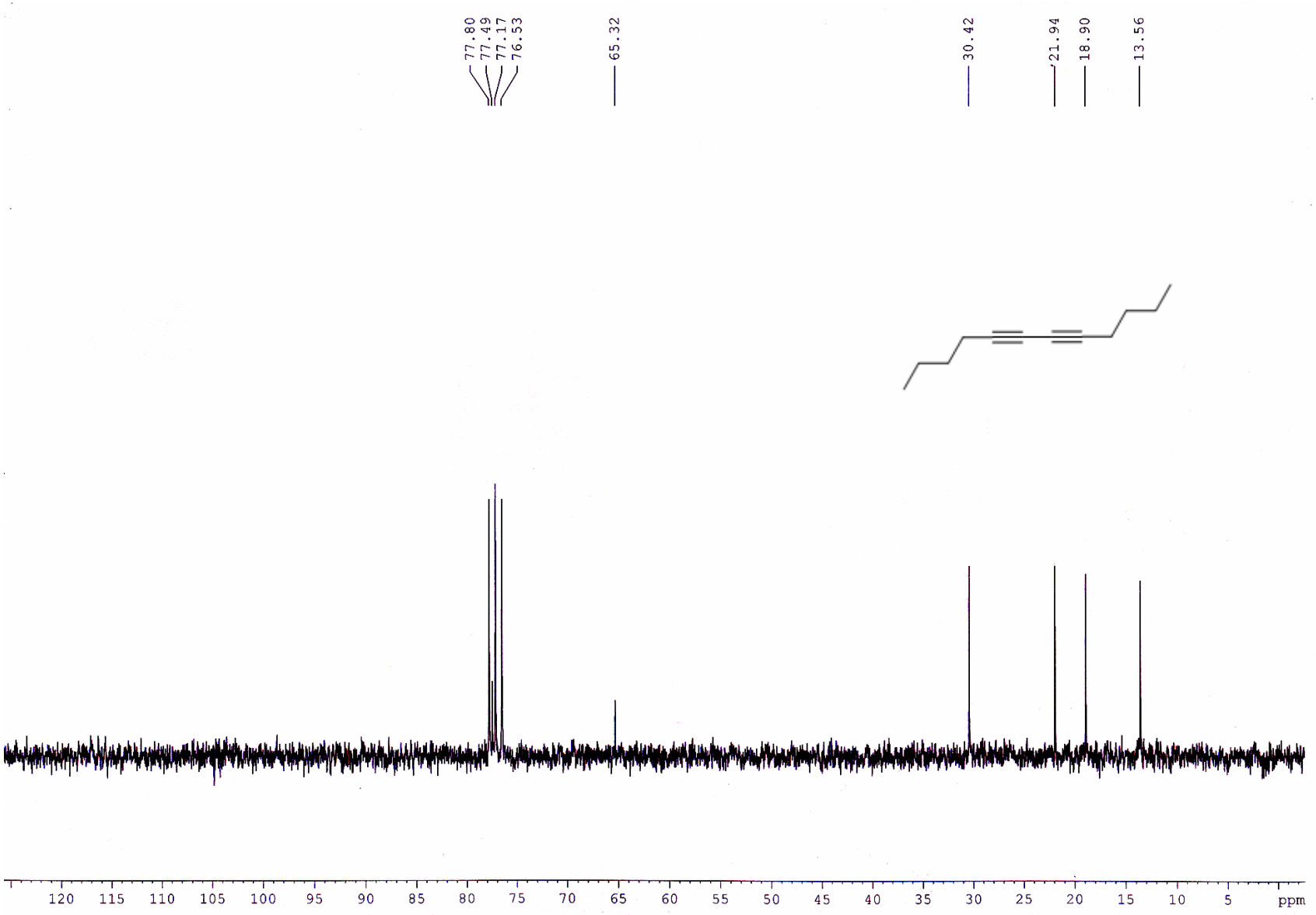

Figure S18 ^{13}C NMR (50MHz, $CDCl_3$) spectrum of **4f**

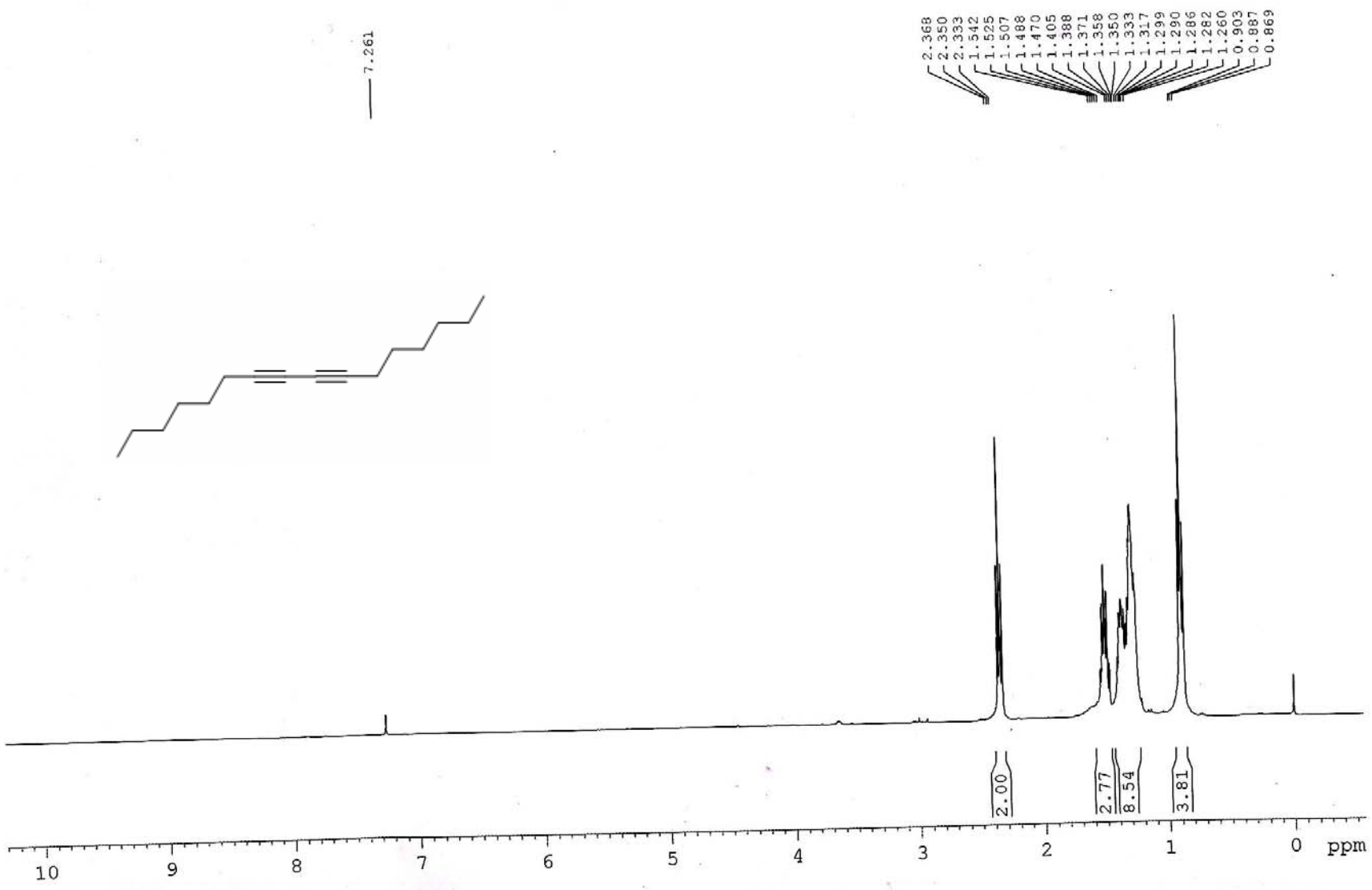

Figure S19 ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **4g**

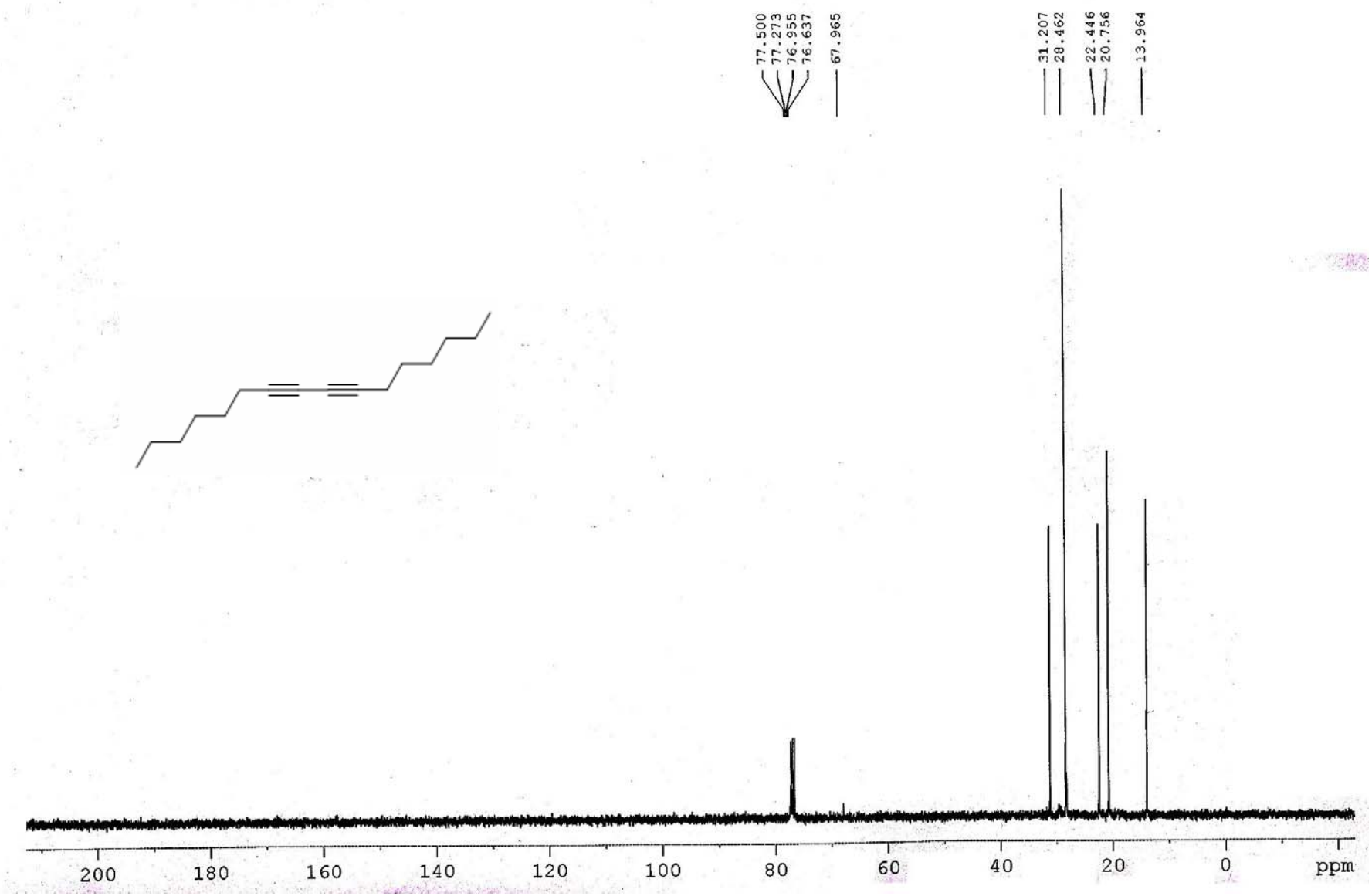

Figure S20 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4g**

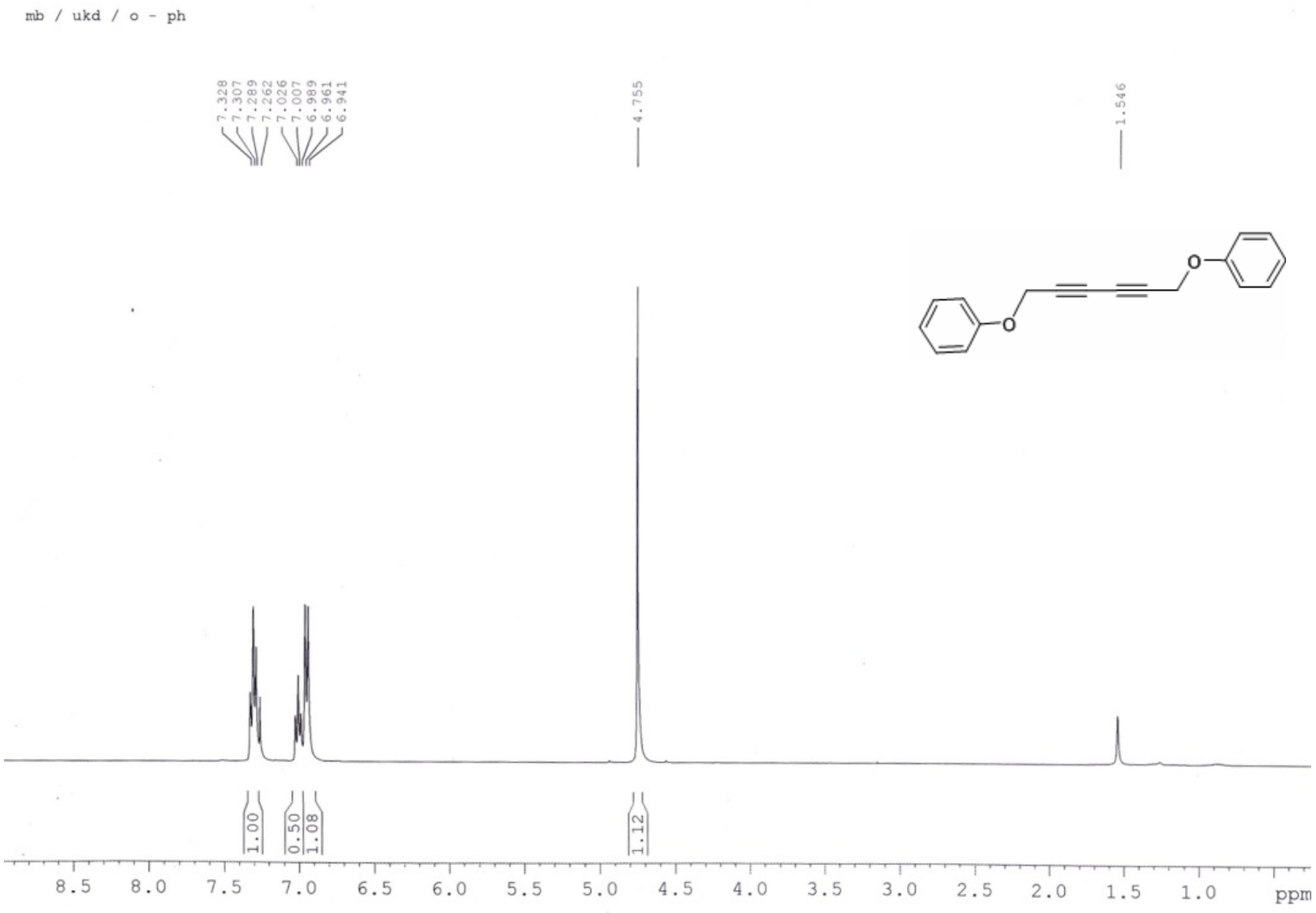

Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**

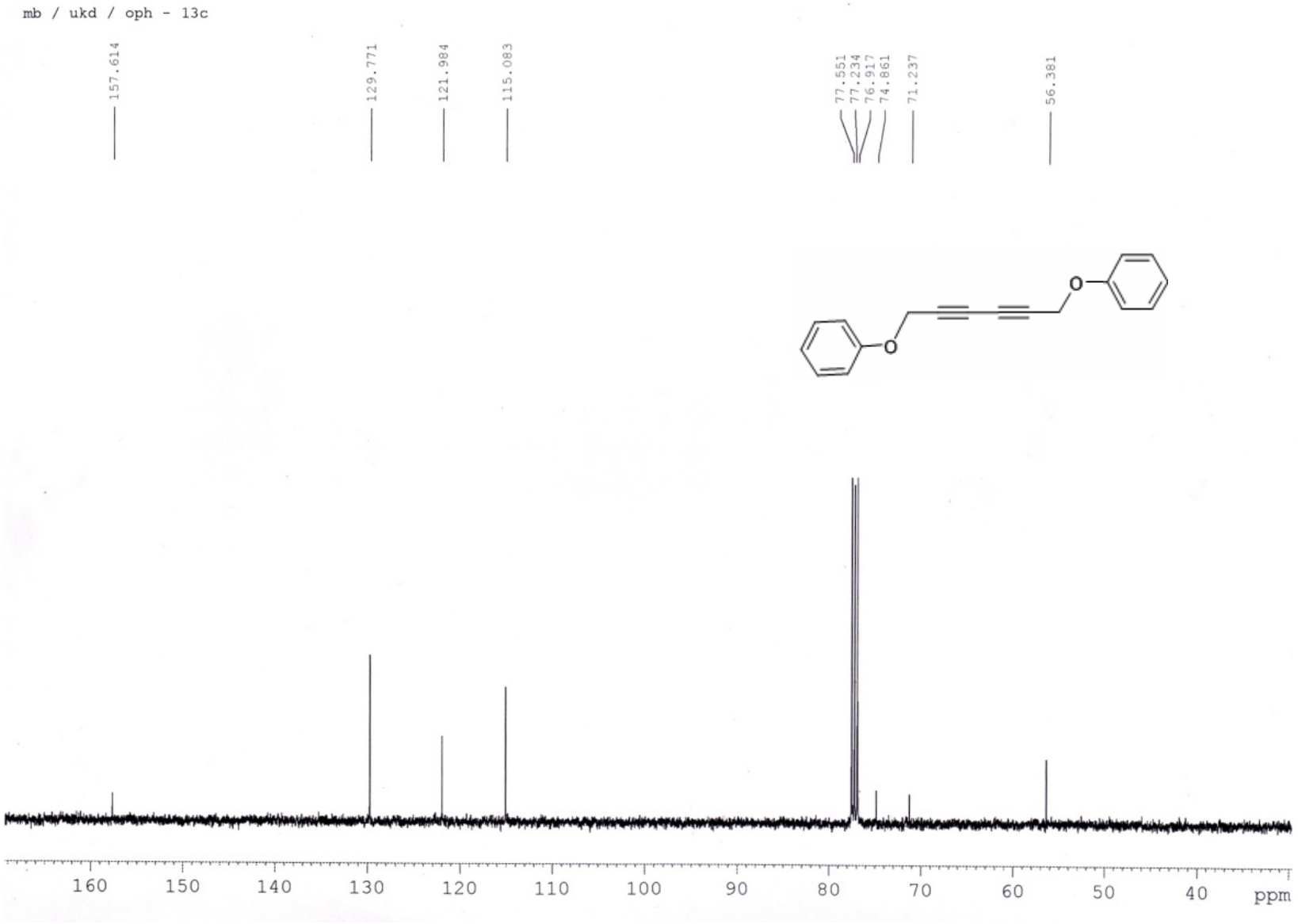

Figure S22 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4h**

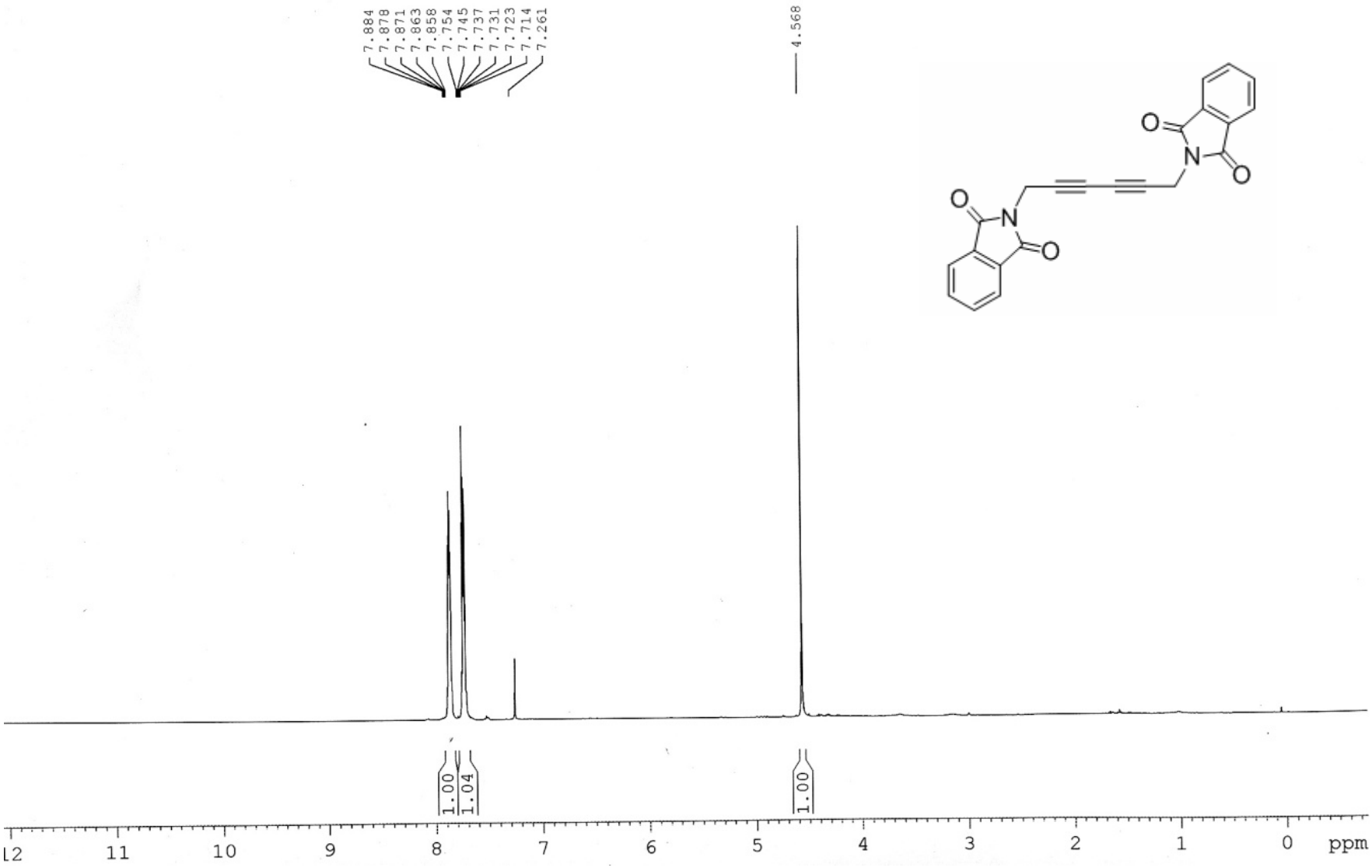

Figure S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**

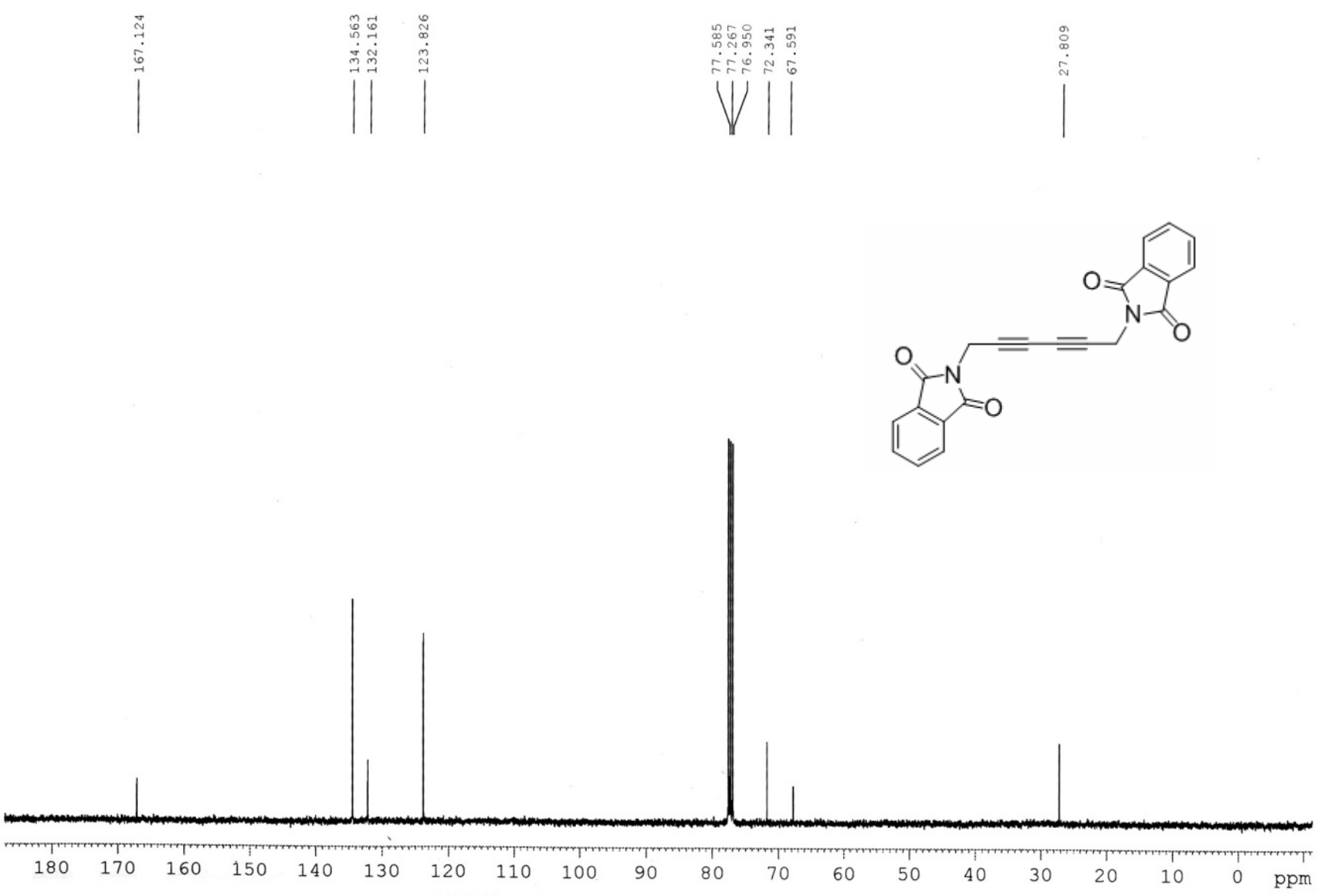

Figure S24 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4i**

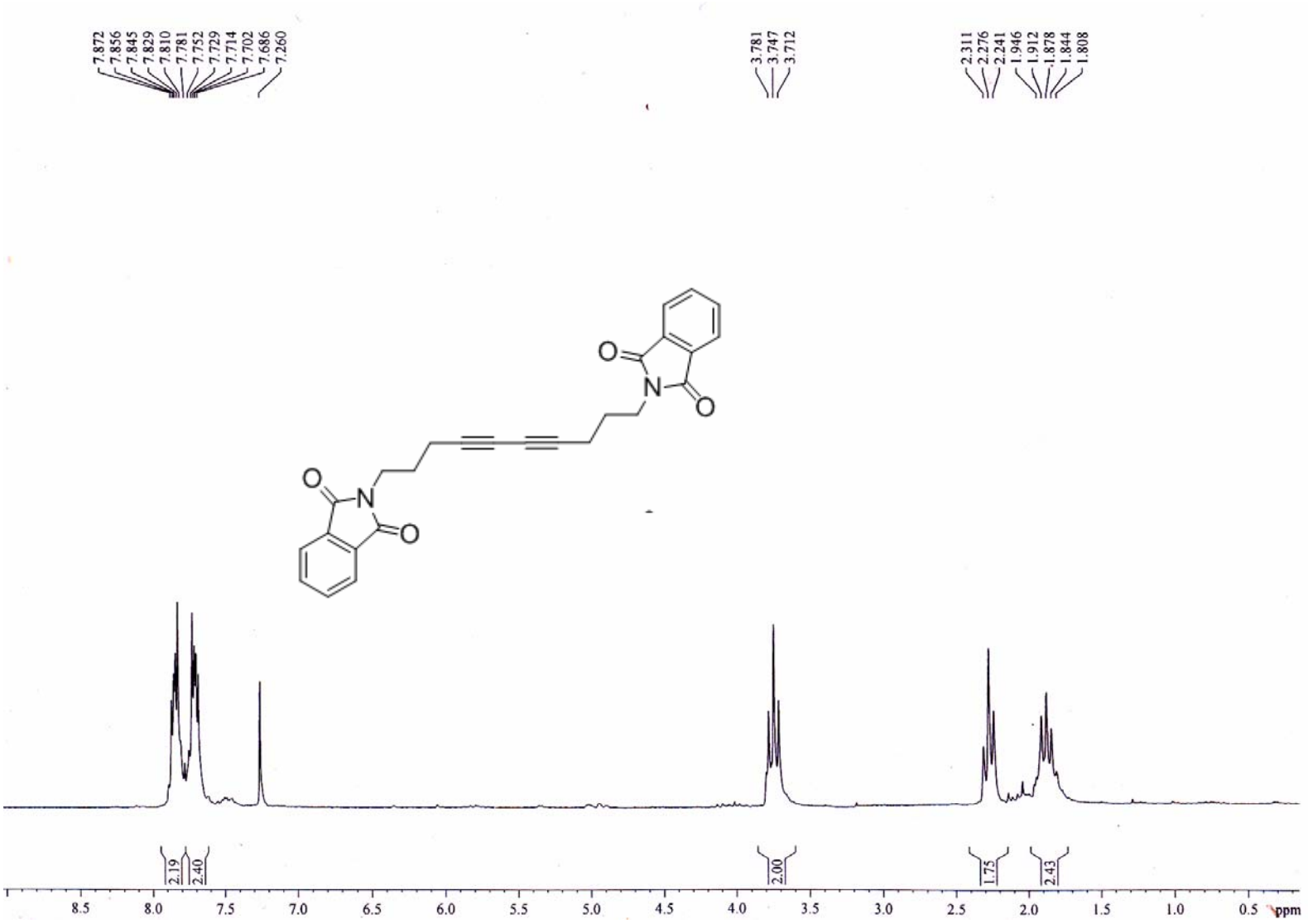

Figure S25 ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **4j**

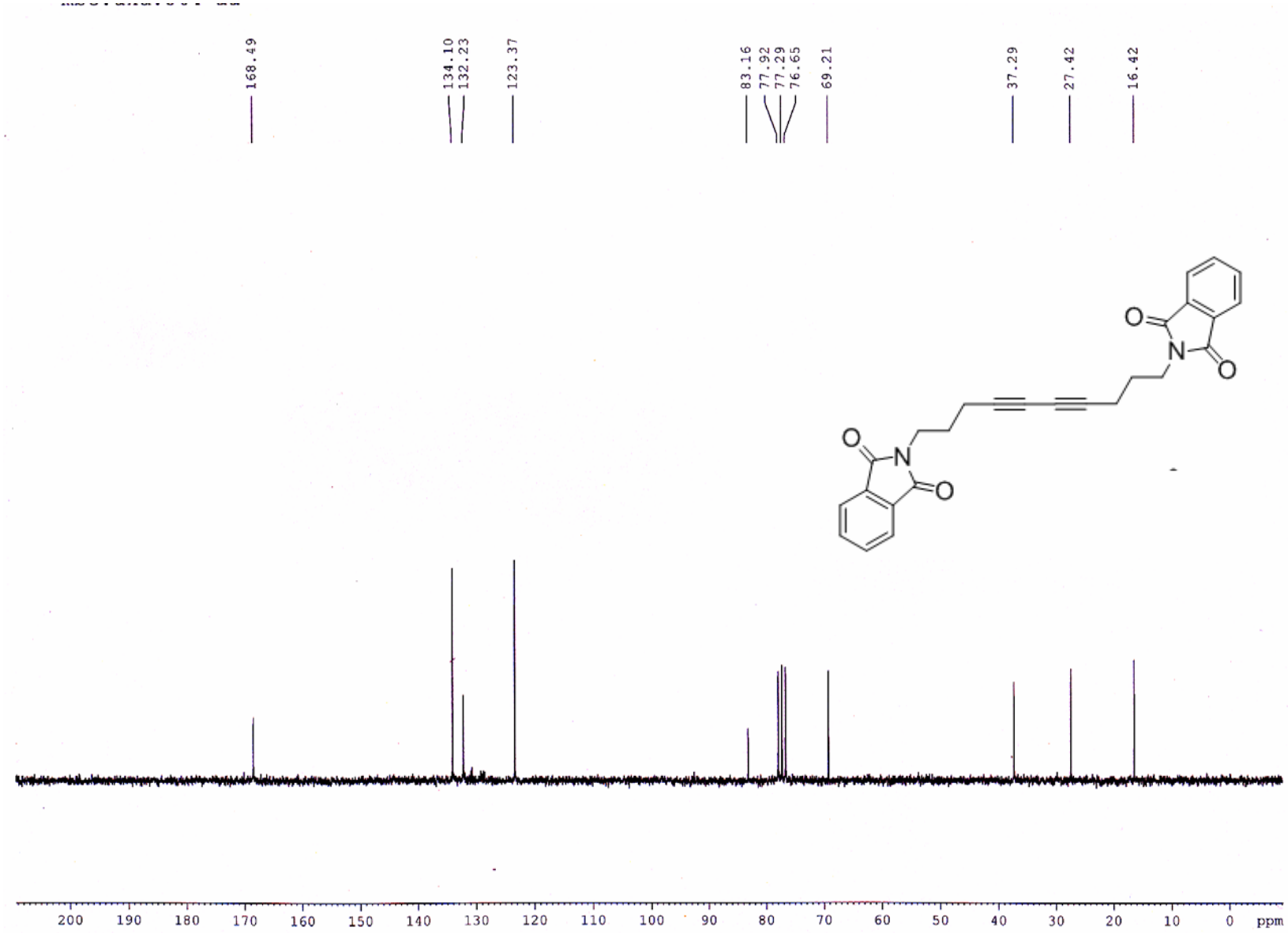

Figure S26 ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4j**

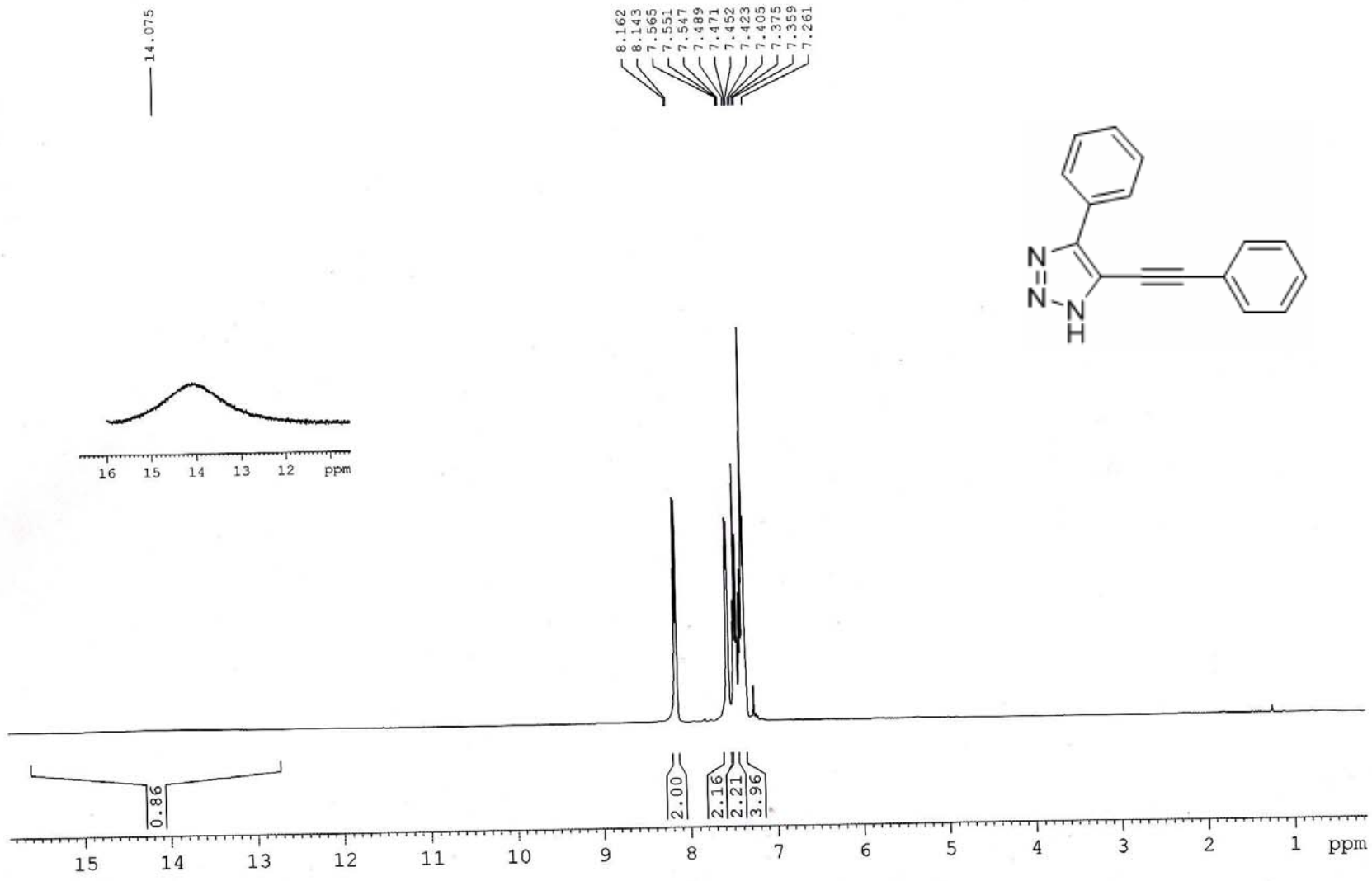

Figure S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**

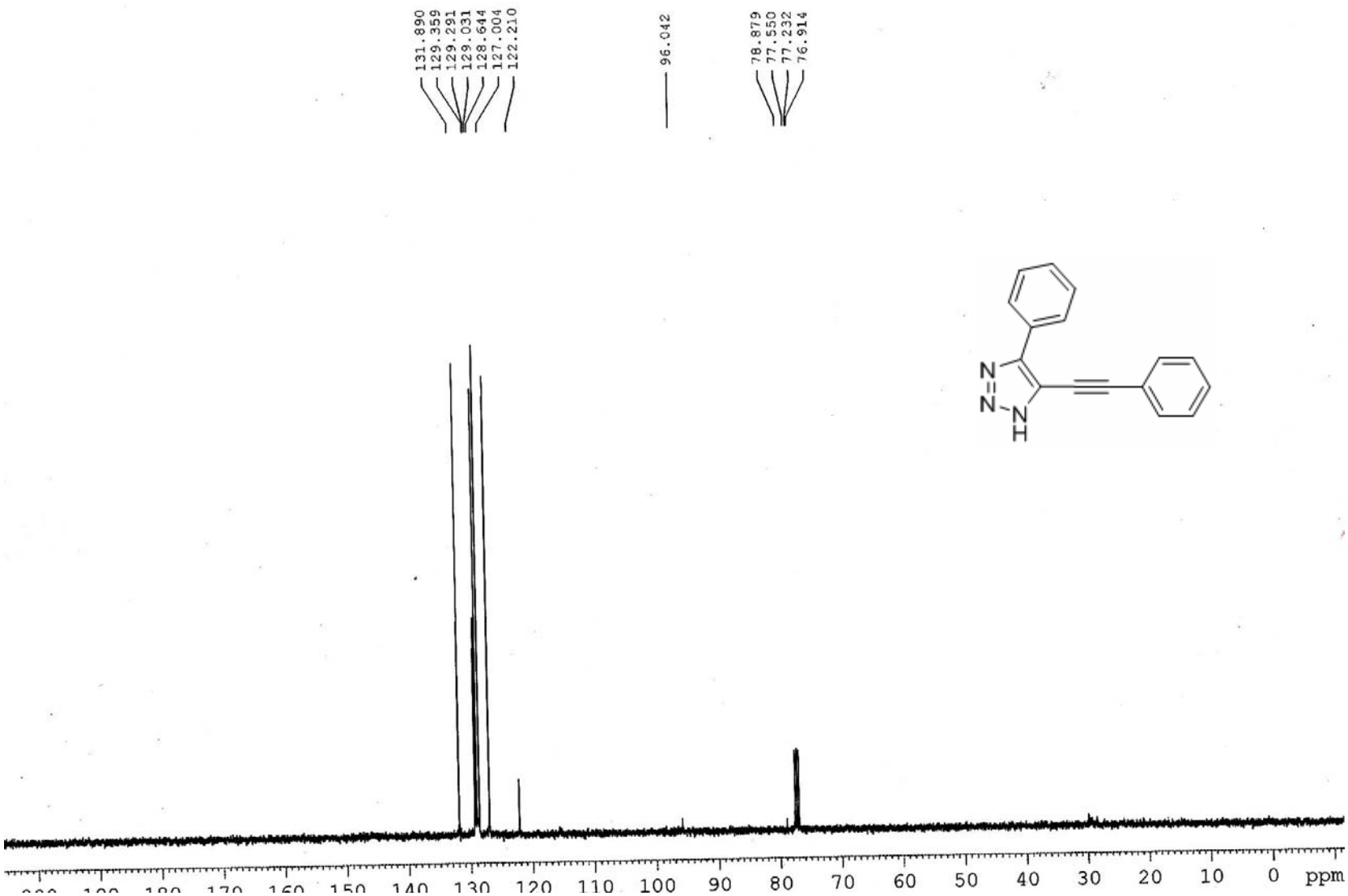

Figure S28 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5a**

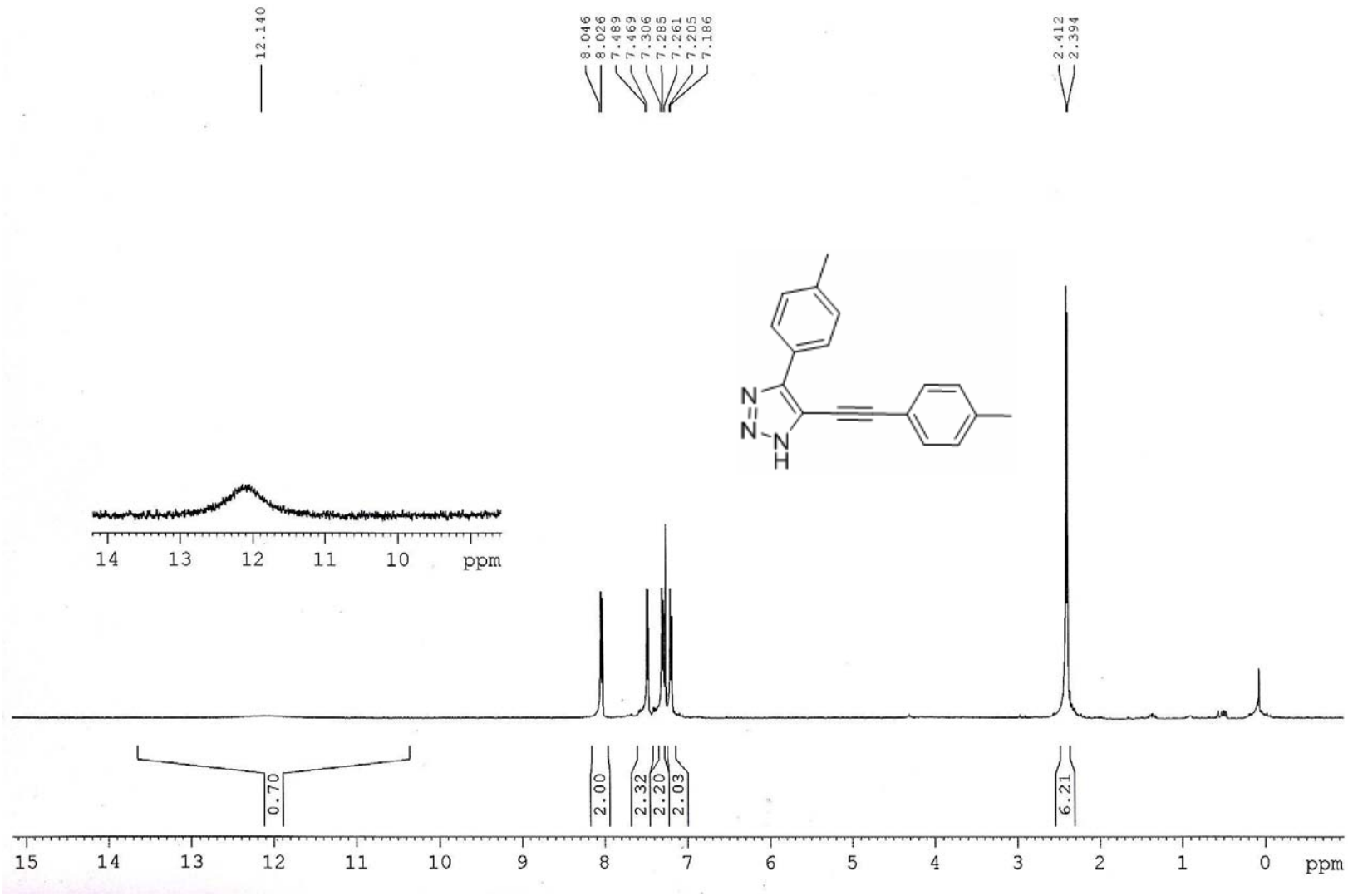

Figure S29 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

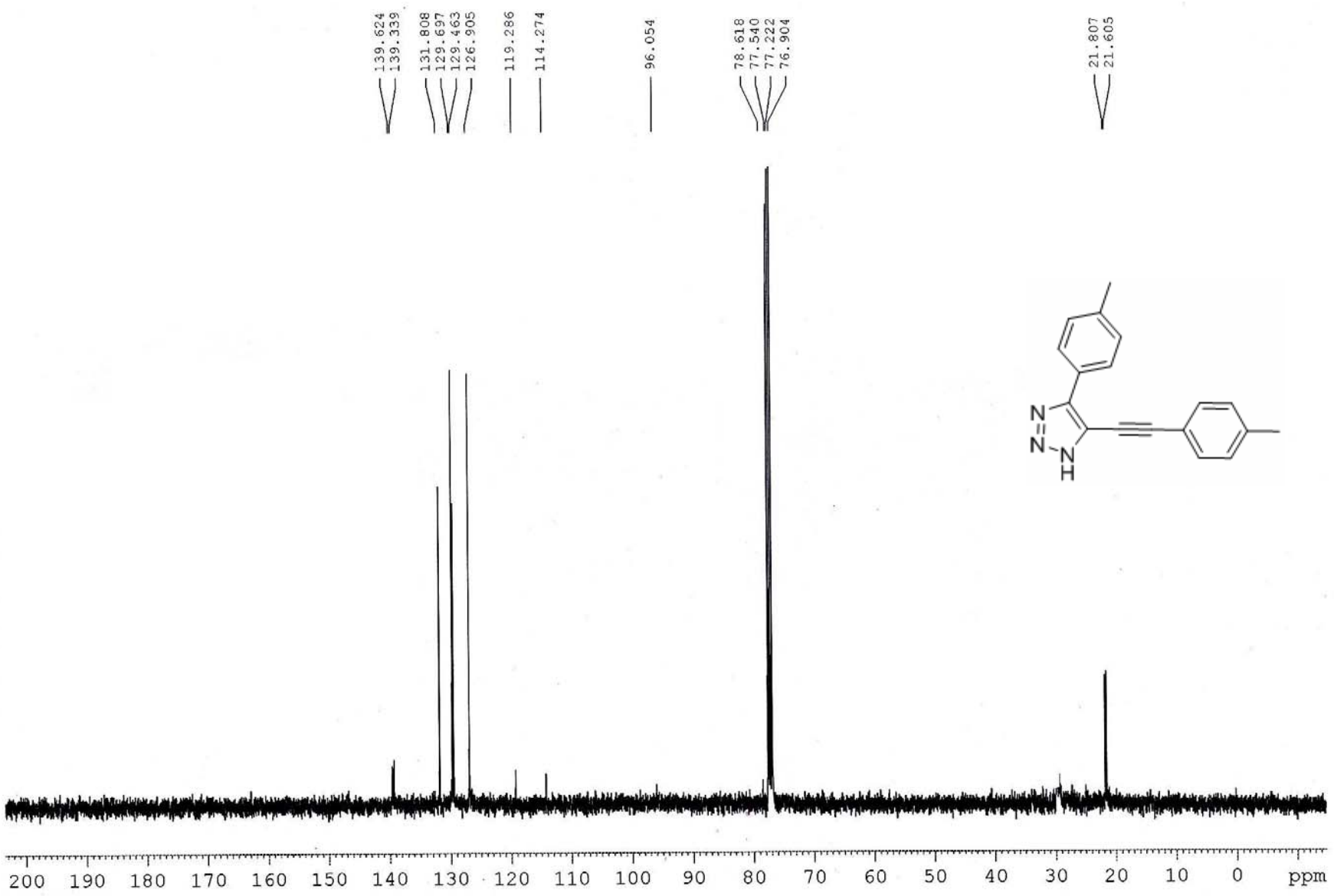

Figure S30 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5b**

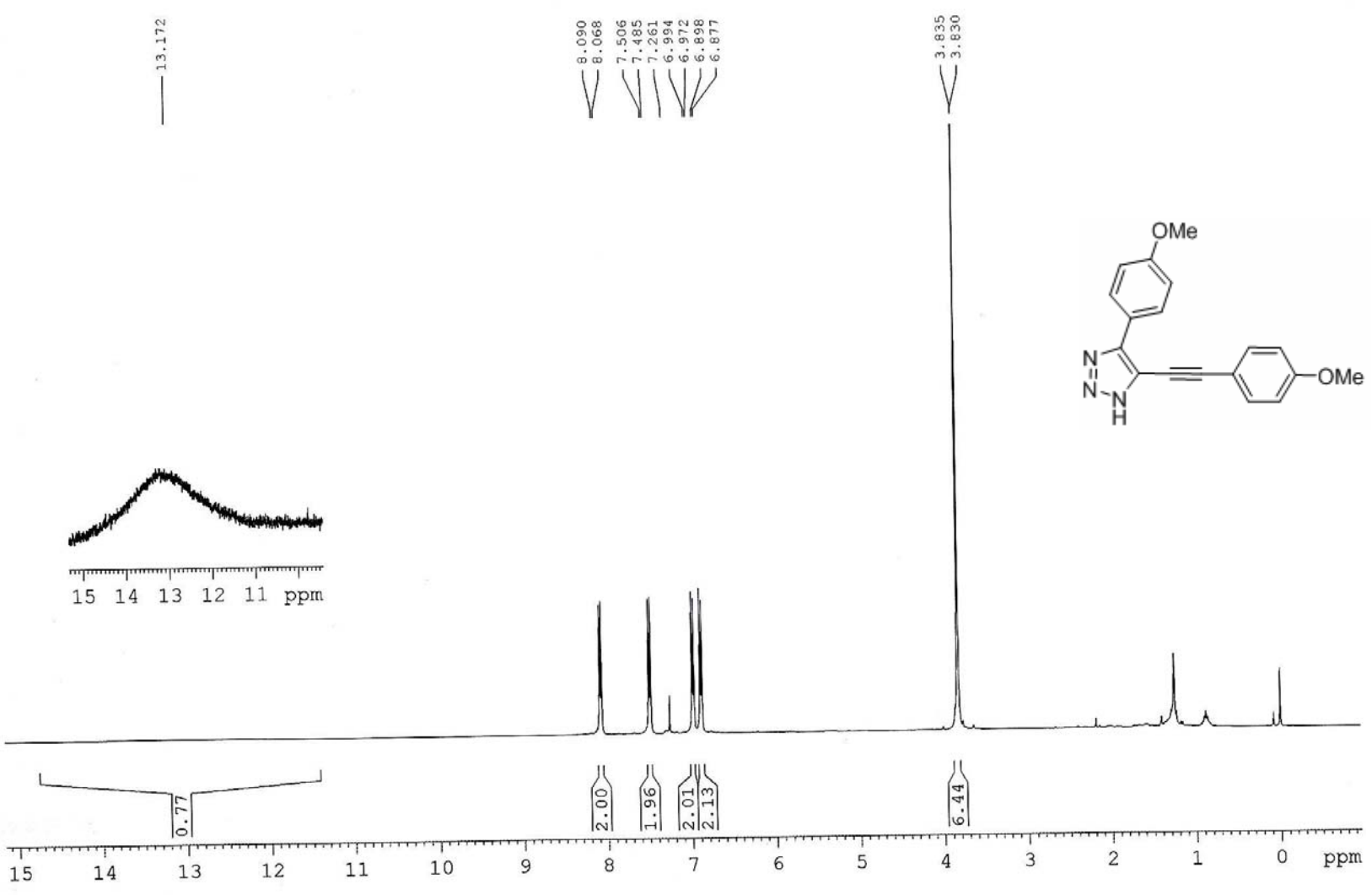

Figure S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5c**

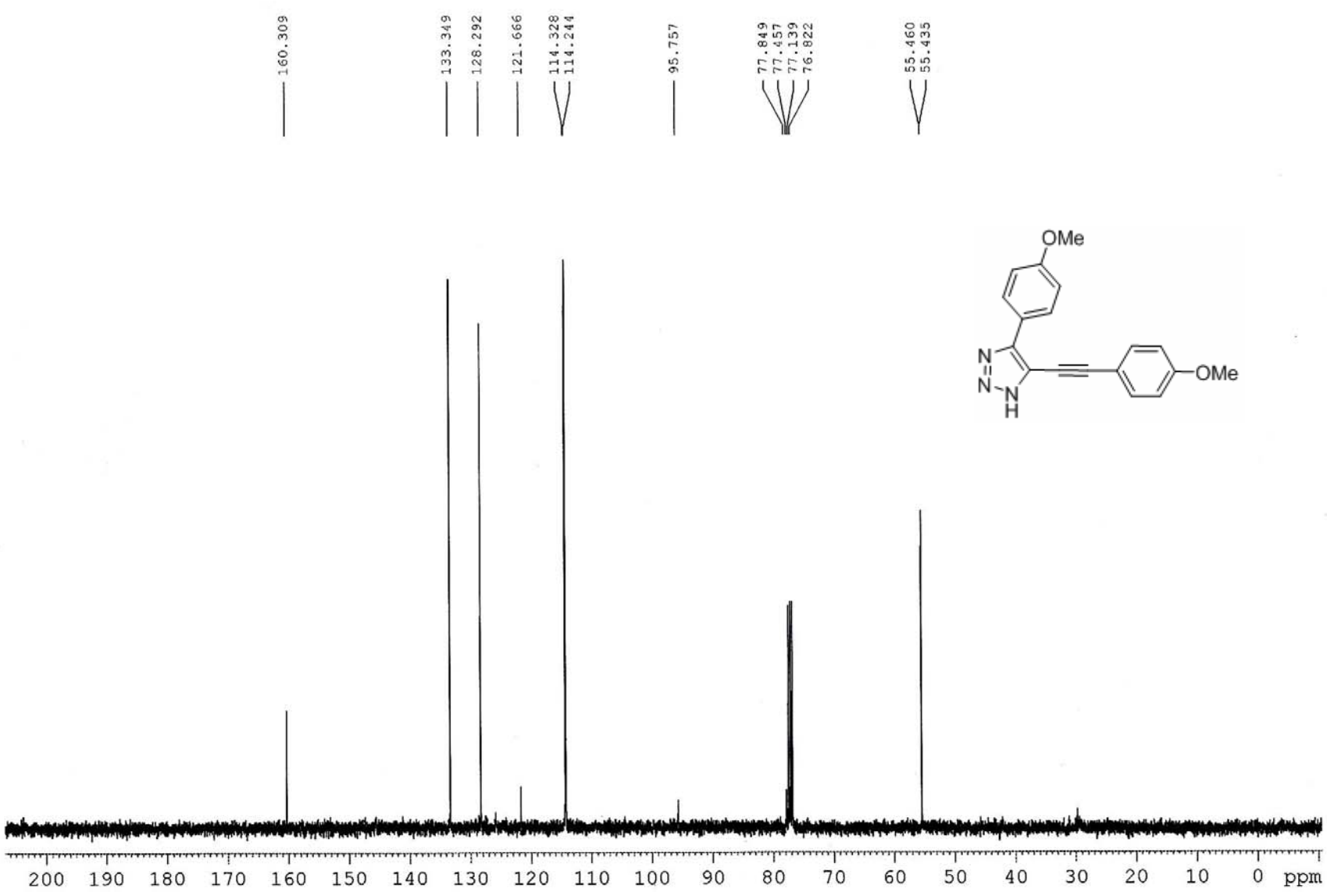

Figure S32 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5c**

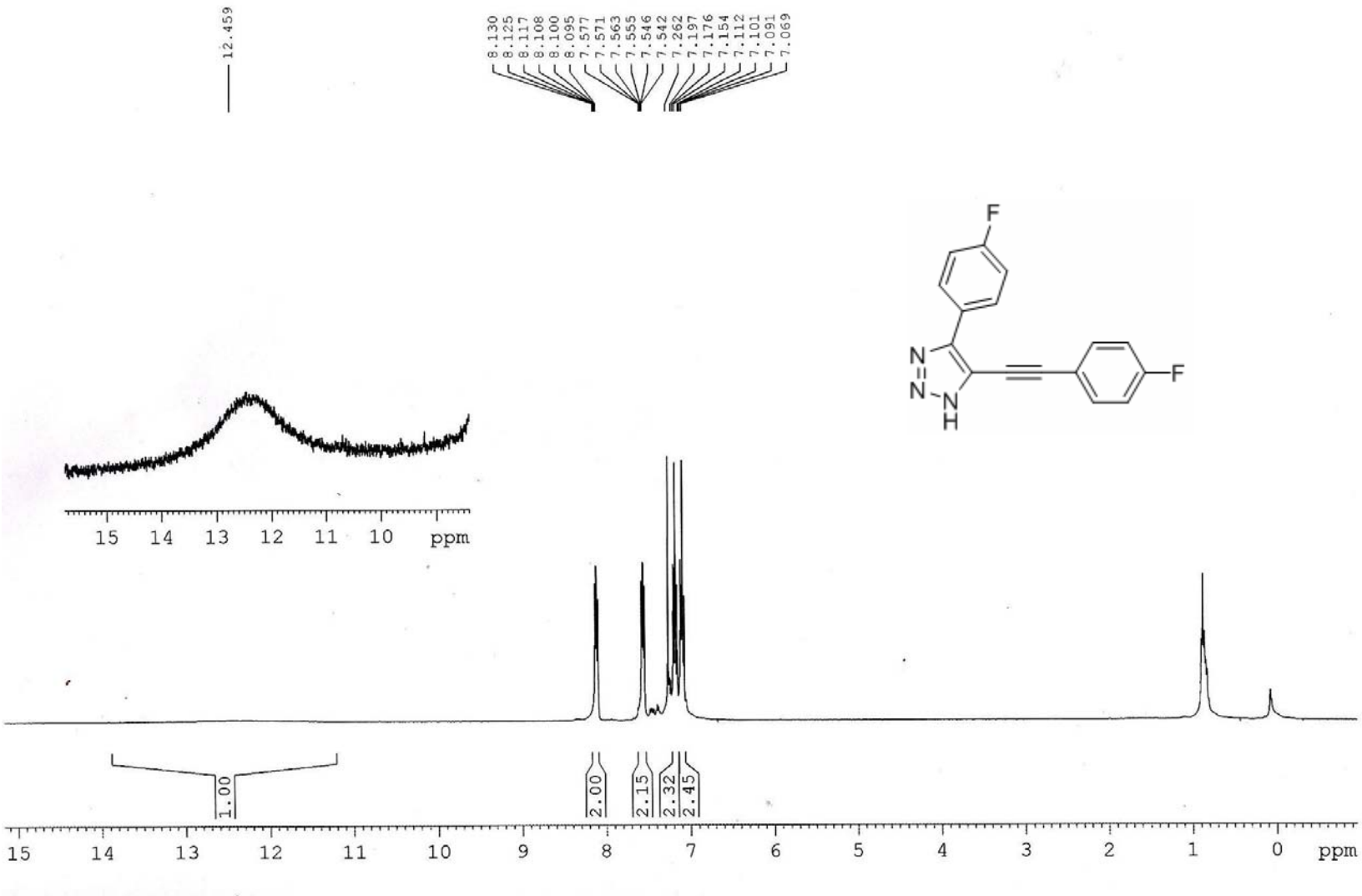

Figure S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**

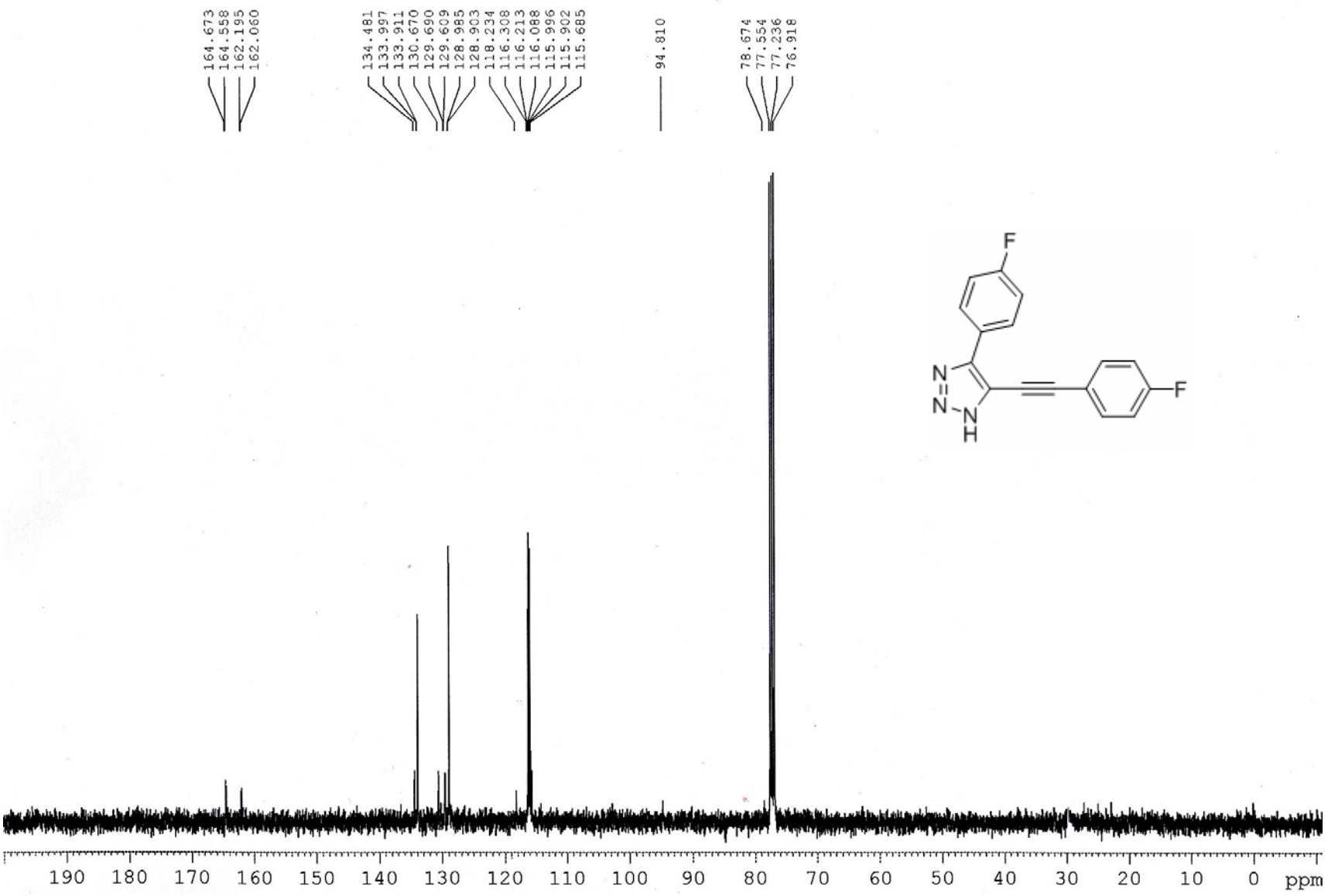

Figure S34 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5d**

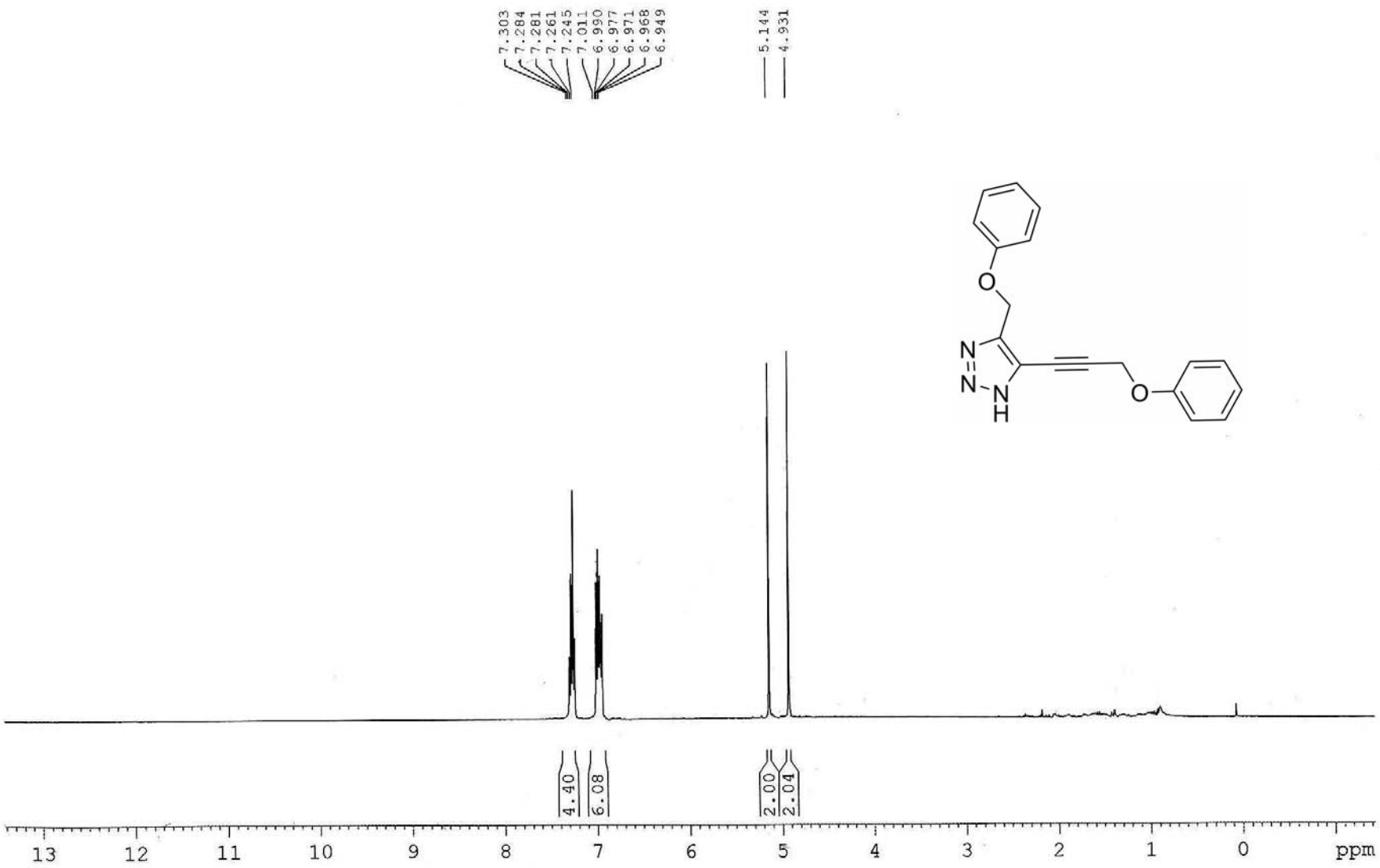

Figure S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**

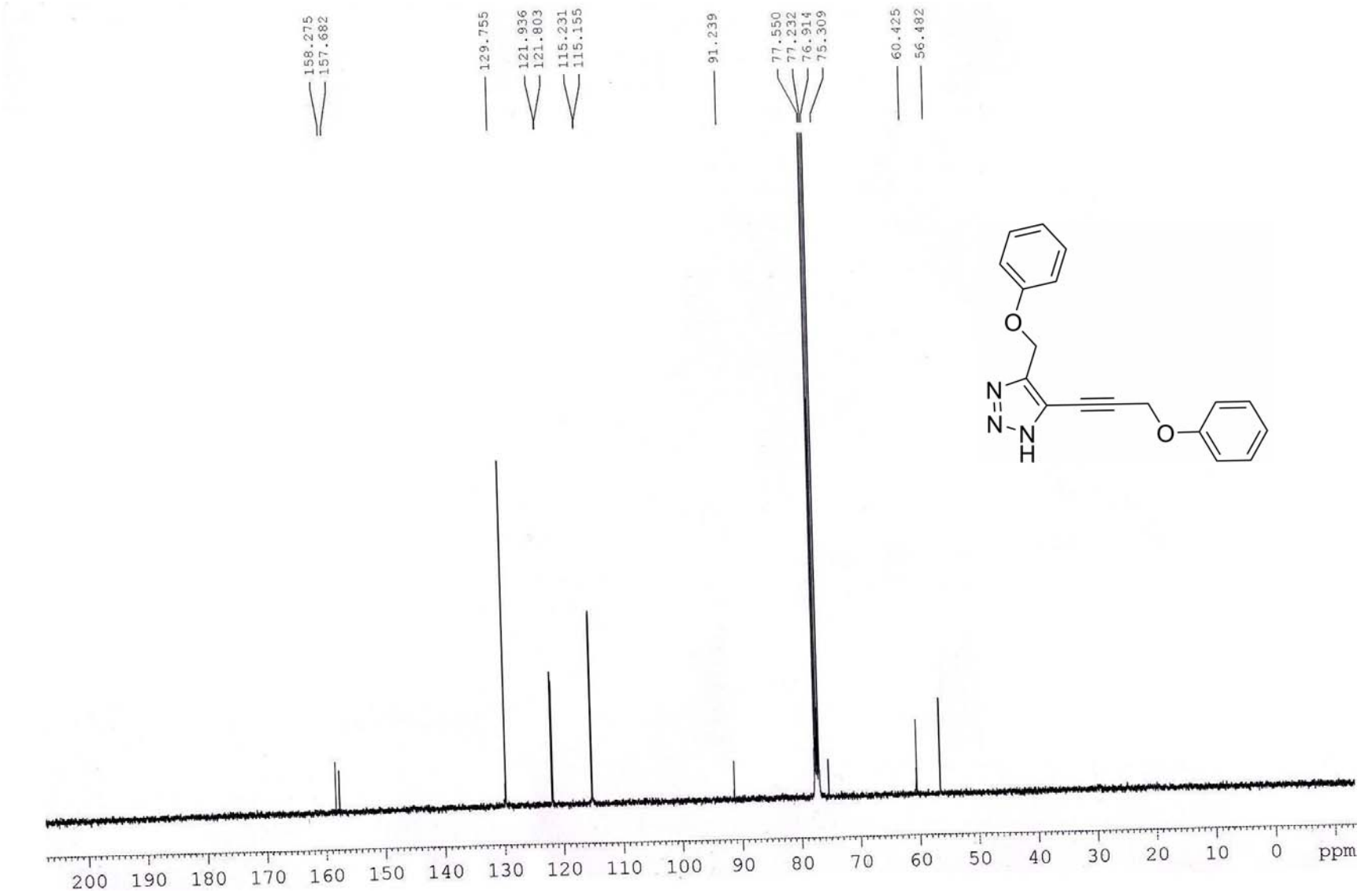

Figure S36 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5e**