Electronic Supplementary Information

Contents

X-ray structures and refinement data

The solvents used for and the method of crystallization of **1** and **2** are given in their respective experimental sections. Data collection was performed using a Bruker D8 QUEST CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The space group for every structure was obtained by XPREP program. The structures were solved by SHELXT[1] which successfully located most of the nonhydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL Version 2018/3[2] to locate the remaining nonhydrogen atoms. Nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were fixed in calculated positions. The crystal structure was plotted using the ORTEP3 programme. The refinement data for the structure is summarized in Table S1. In the structure of dinuclear Mo complex **1**, two CH_2Cl_2 are present and disordered in the crystal lattice which was successfully solved by using EADP constraints and SADI restraints. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. This data can be obtained free of charge upon quoting the depository number CCDC 2386551-2386552 from web interface (at http://www.ccdc.cam.ac.uk).

Table S1. Crystallographic data for complexes **1** and **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{32}H_{40}Cl_4Mo_2N_8O_8$	$C_{20}H_{26}MoN_6O_4$
Formula weight	998.40	510.41
Wavelength (Å)	0.71073	0.71073
Temperature (K)	102(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C_2/c
a/Å	18.6388(7)	28.534 (3)
b/Å	13.4796(5)	9.0364 (8)
c/Å	16.9256(6)	18.5849 (16)
α/degree	90	90
β/degree	106.7300(10)	93.962 (5)
γ/degree	90	90

Volume (Å^3)	4072.4(3)	4780.5 (7)
Z	4	8
D_{calcd}, g cm^{-3}	1.628	1.418
μ/mm^{-1}	0.935	0.585
F(000)	2016	2096
Θ range (degree)	1.893 to 24.997	2.365 to 27.452
Data/restr/params.	7155 / 8 / 523	5446/0/280
GOF (F^2)	1.040	1.114
Limiting indices	$-22 \le h \le 22$, $-16 \le k \le 16$, $-20 \le l \le 19$	$-36 \le h \le 36$, $-11 \le k \le 11$ $-24 \le l \le 24$
R1, *wR2*	0.0374, 0.0933	0.0266, 0.0708
R indices (all data) *R1*, *wR2*	0.0439, 0.0971	0.0312, 0.0733
Largest different peak and hole (e Å^{-3})	1.835 and –0.951	0.309 to –0.475

NMR, ATR and HRMS data

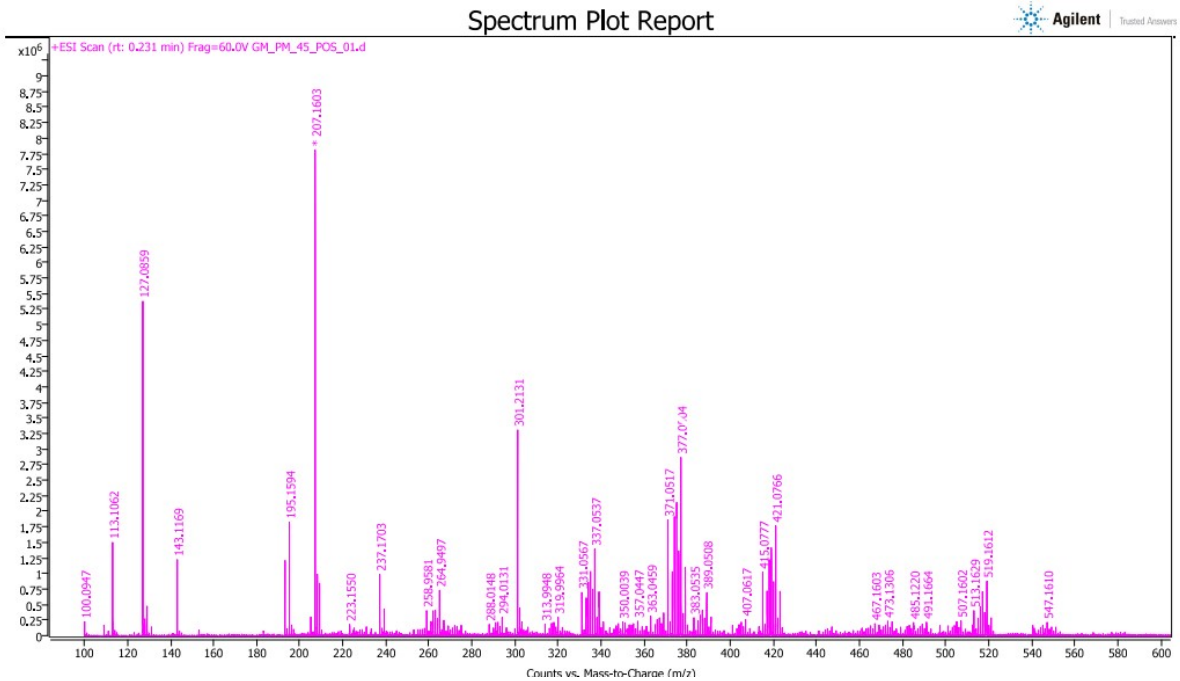


Figure S1. HRMS(ESI+) spectrum of the reaction mixture of ligand **L** and $Mo(CO)_6$ after 1h at 130 °C. A peak at *m/z* 415.0777 is due to the formation of $[Mo_2(CO)_8\{(C_4H_8N_2)CH_2pz^{Me2}CH_2\}_2\text{-}\kappa^2\text{-}N,N]^{2+}$ (complex $\mathbf{1}^{2+}$).

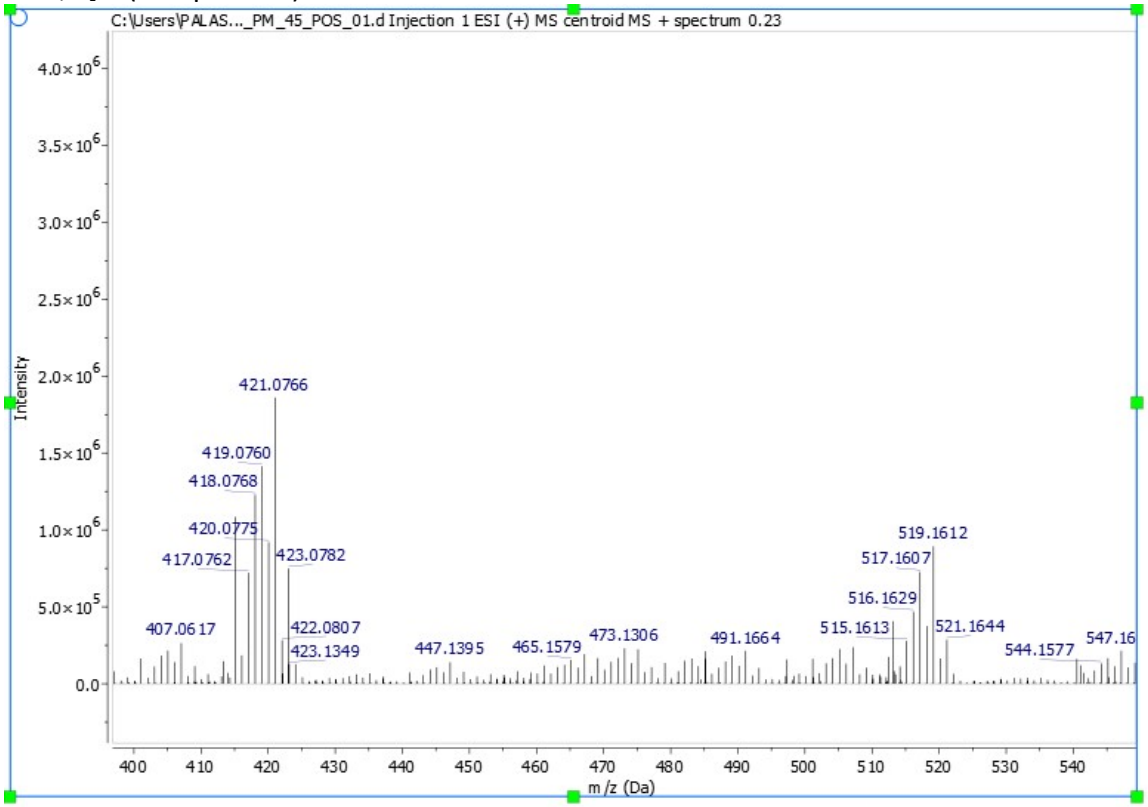


Figure S2. Partial HRMS(ESI+) spectrum of the reaction mixture of **L** and $Mo(CO)_6$ after 1h at 130 °C.

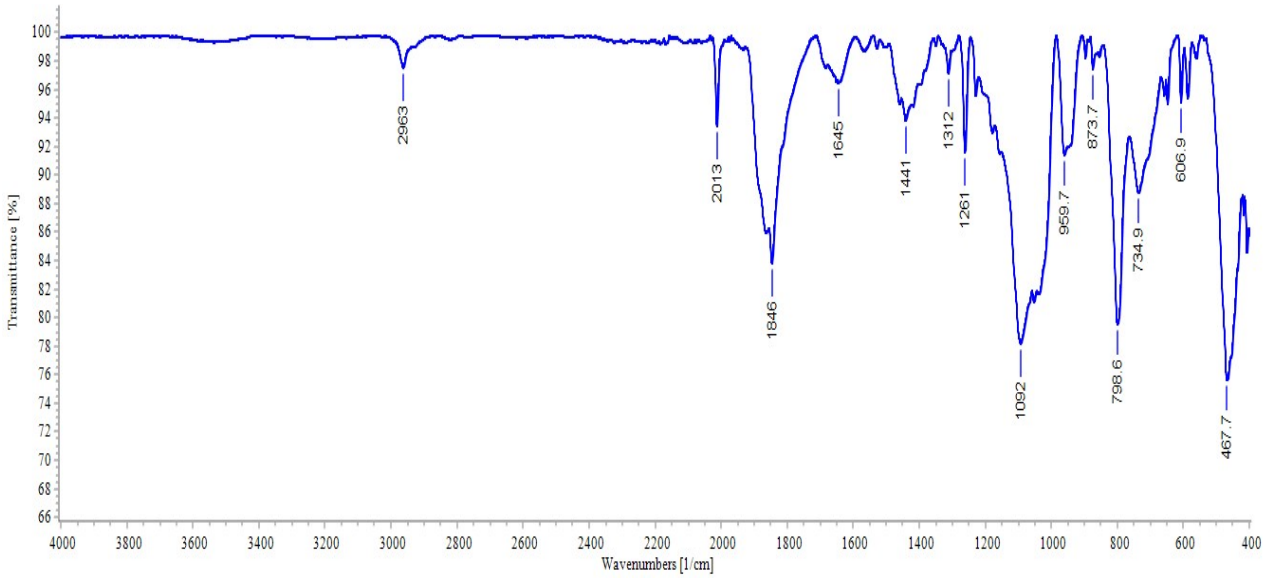


Figure S3. ATR-IR spectrum of $[Mo_2(CO)_8\{(NCH_2NCH_2Me_2Pz)(CH_2)_3$-$\kappa^2$-N,N$\}_2]$.

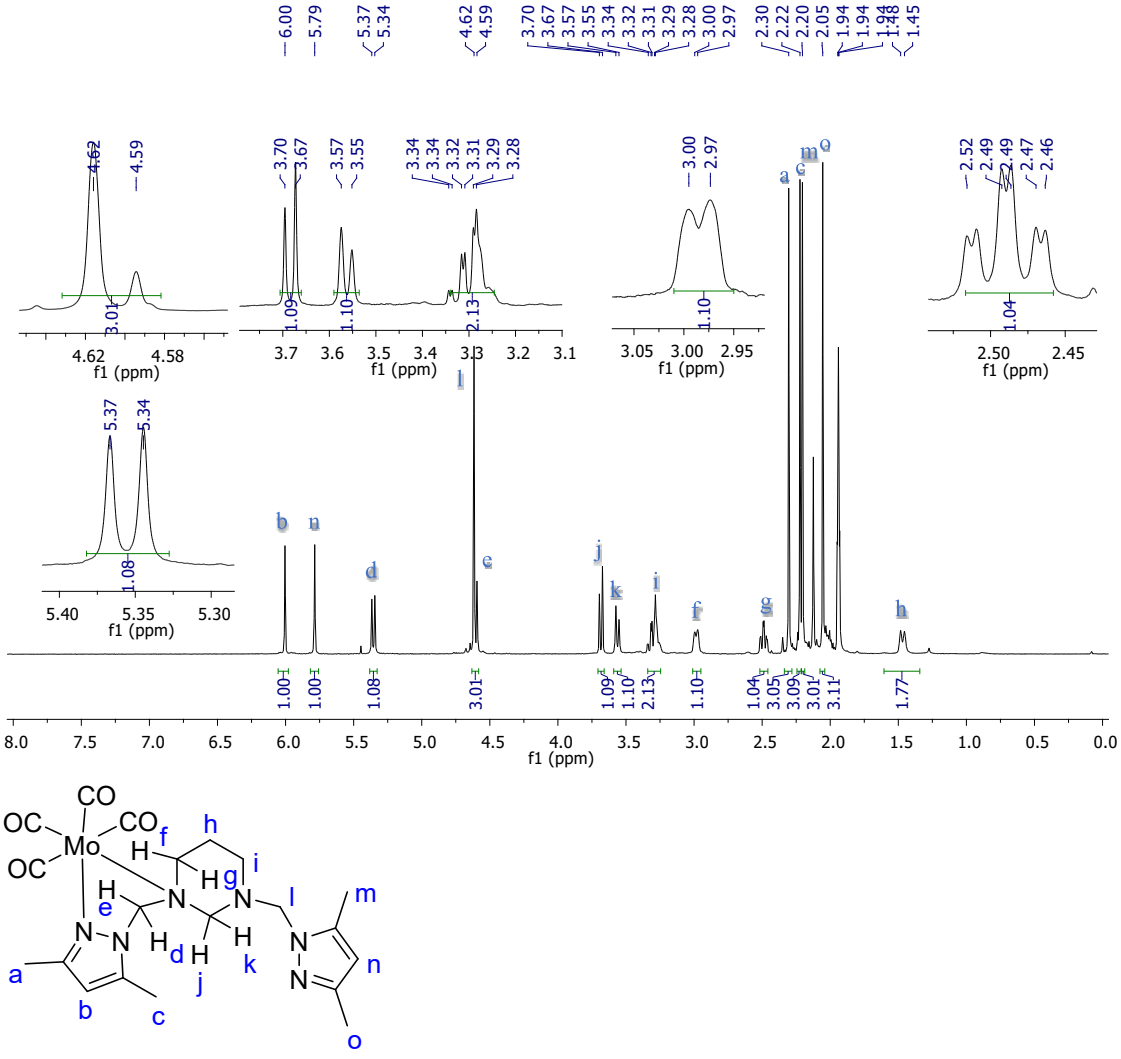


Figure S4. ^{1}H NMR (500 MHz, 25 °C) spectrum of $[Mo(CO)_4\{CH_2(NCH_2Me_2Pz)_2(CH_2)_3$-$\kappa^2$-N,N$\}]$, **2** in CD_3CN.

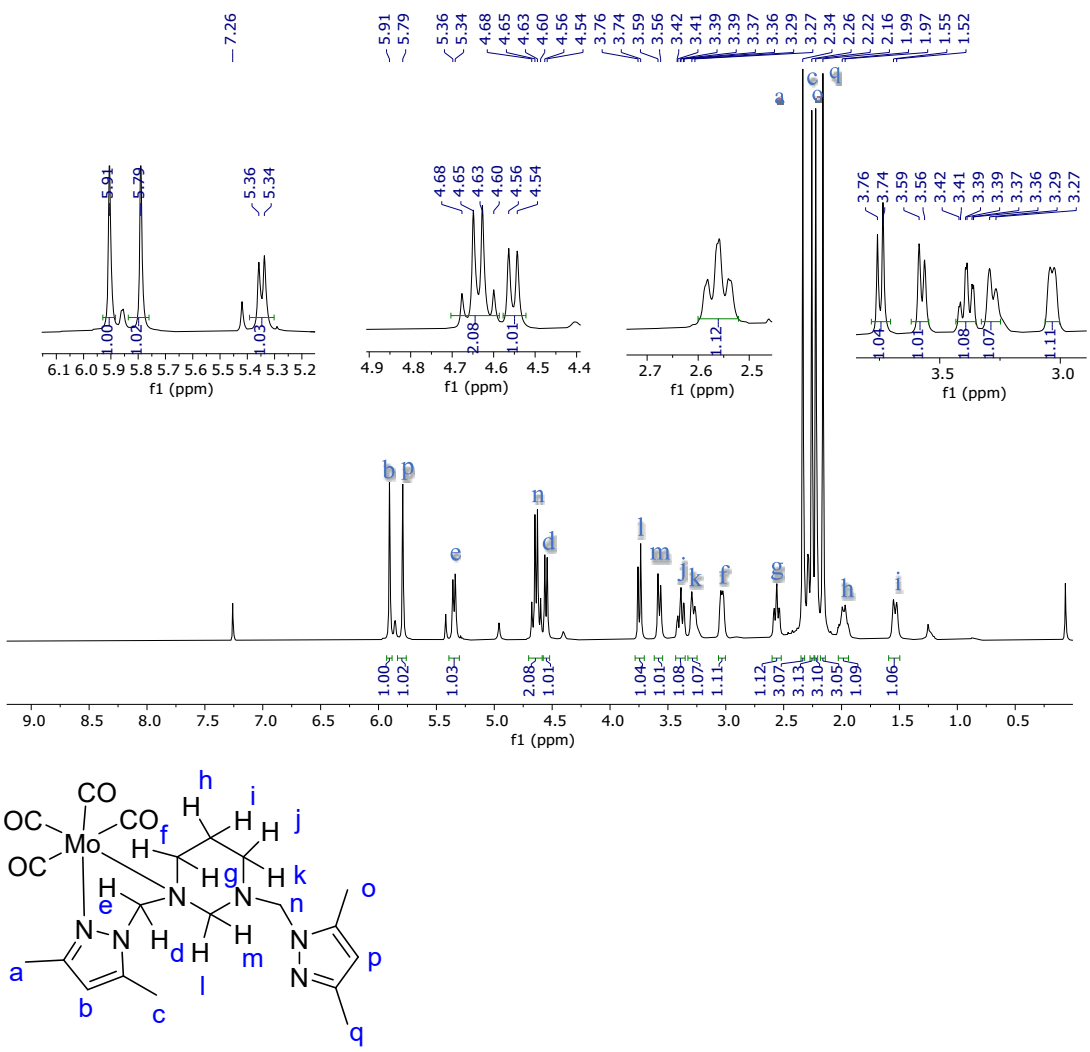


Figure S5. ^{1}H NMR (500 MHz, 25 °C) spectrum of [Mo(CO)$_4${CH$_2$(NCH$_2$Me$_2$Pz)$_2$(CH$_2$)$_3$-κ^2-N,N}], **2** in CDCl$_3$.

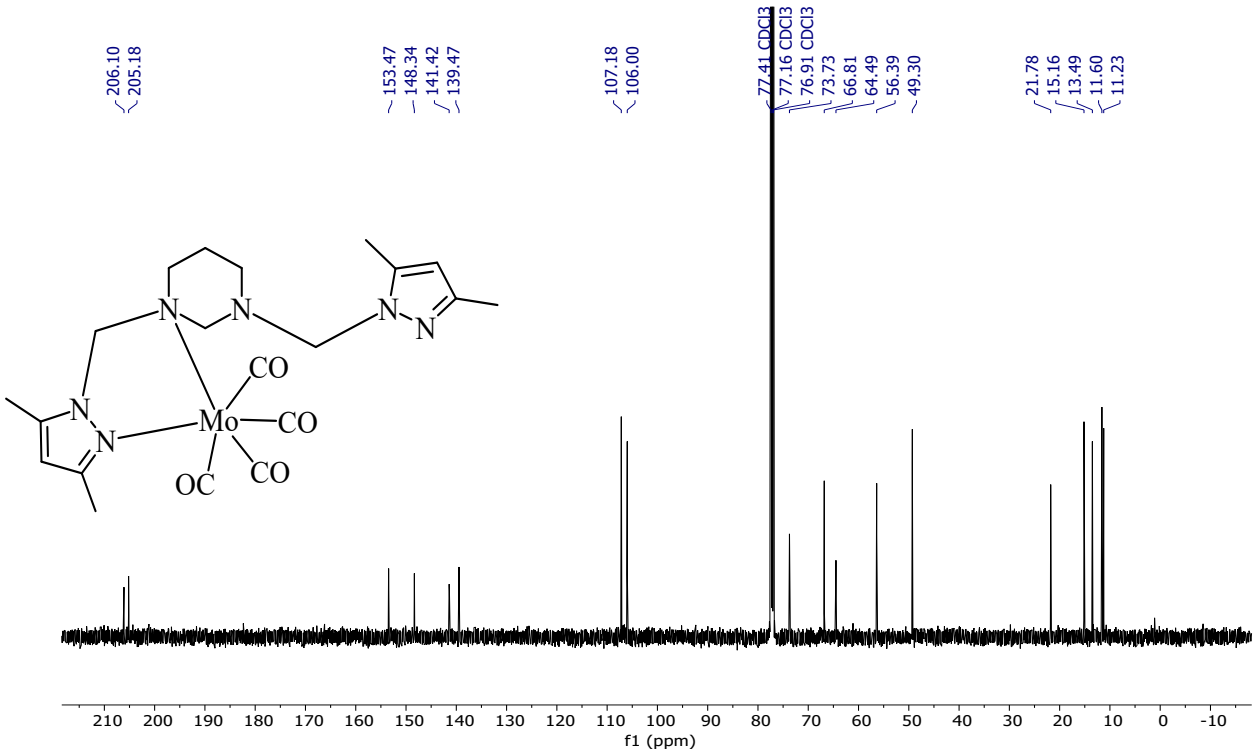


Figure S6. $^{13}C\{^{1}H\}$ NMR (125.76 MHz, 25 °C) spectrum of $[Mo(CO)_4\{CH_2(NCH_2Me_2Pz)_2(CH_2)_3$-$\kappa^2$-N,N$\}]$, **2** in $CDCl_3$.

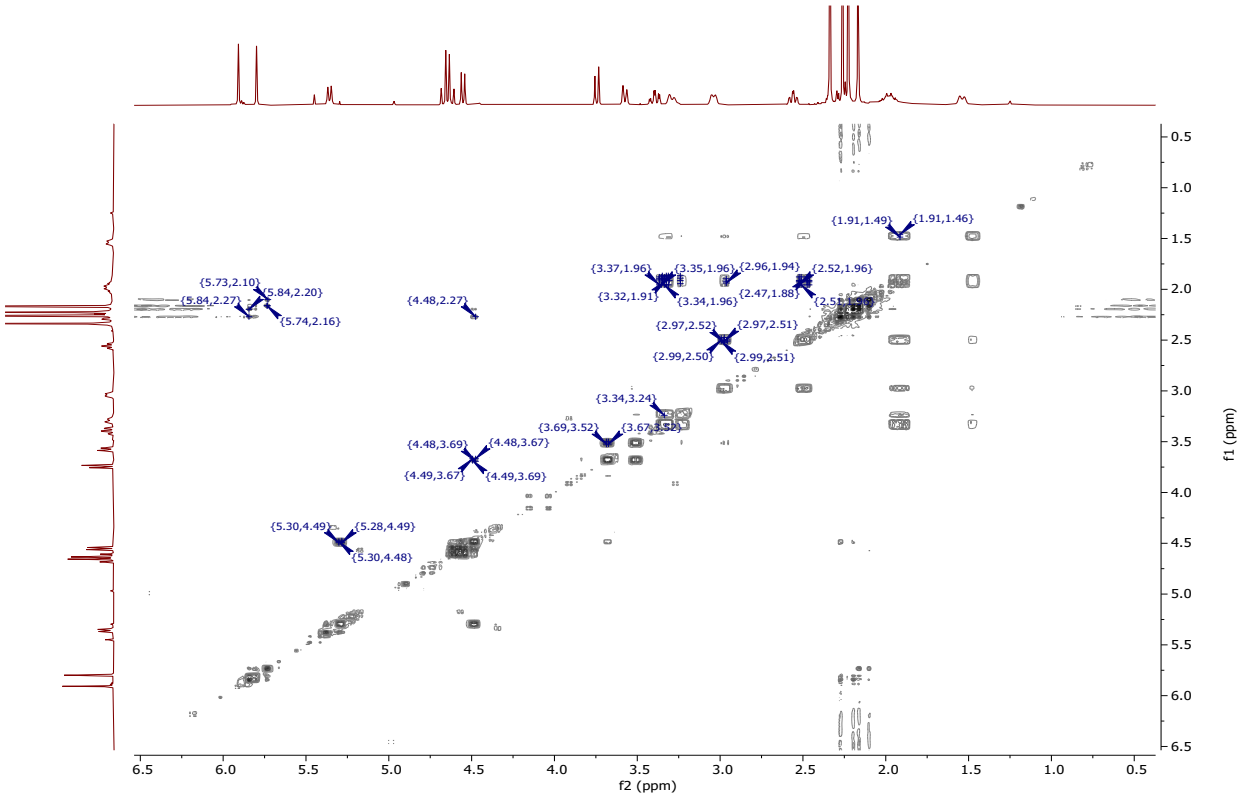


Figure S7. COSY NMR (500 MHz, 25 °C) spectrum of $[Mo(CO)_4\{CH_2(NCH_2Me_2Pz)_2(CH_2)_3$-$\kappa^2$-N,N$\}]$, **2** in $CDCl_3$.

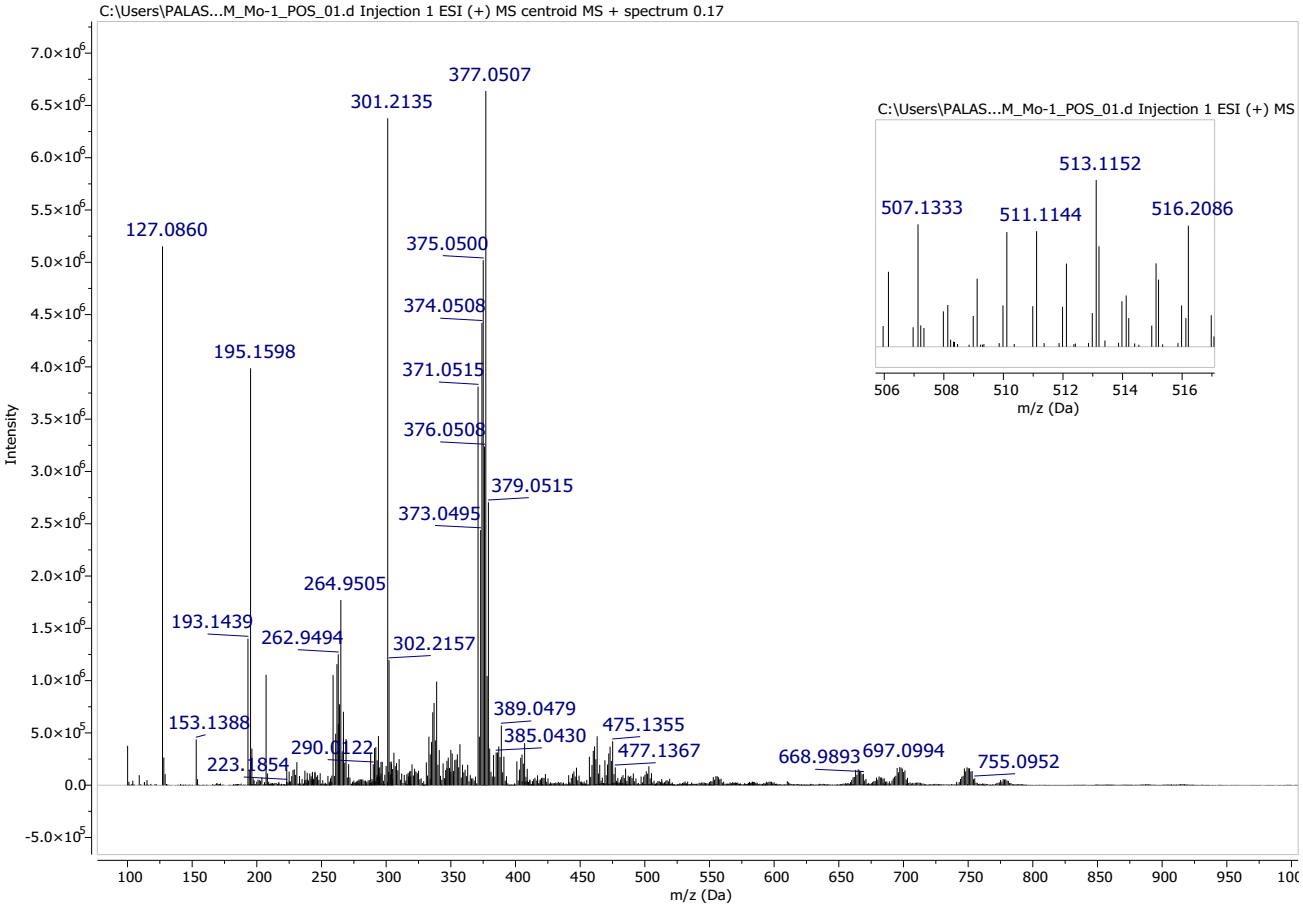


Figure S8. HRMS(ESI+) spectrum of $[Mo(CO)_4\{CH_2(NCH_2Me_2Pz)_2(CH_2)_3$-$\kappa^2$-N,N$\}]$, **2.**

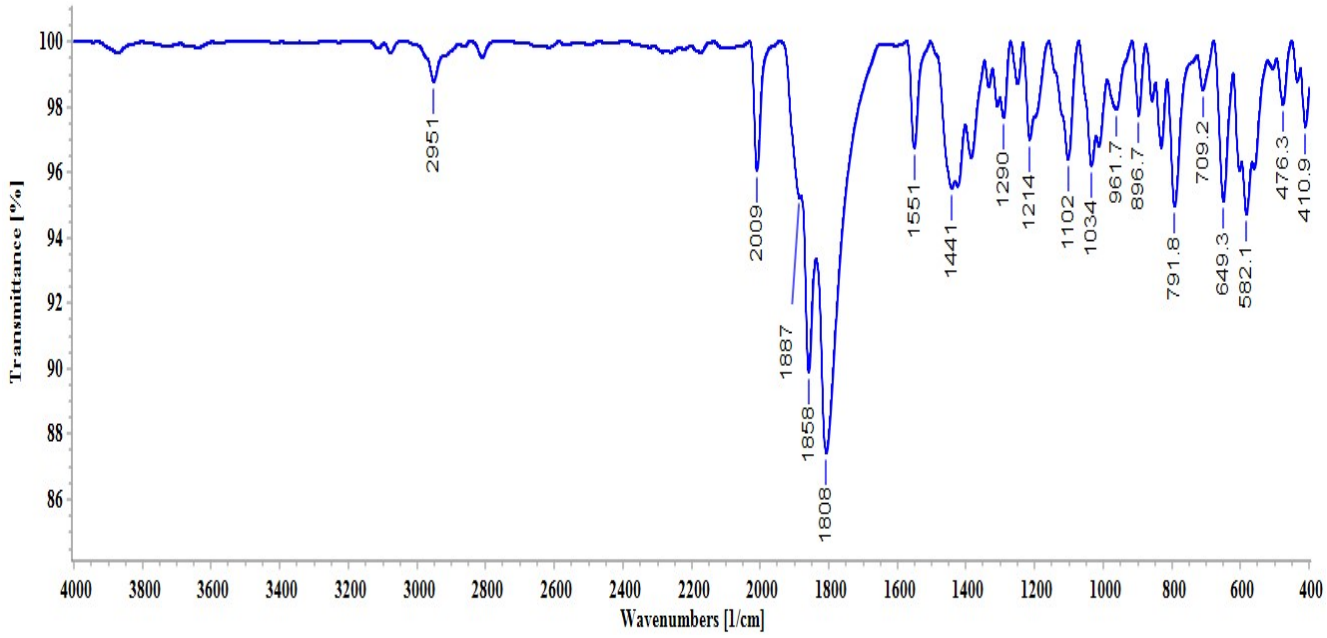


Figure S9. ATR-IR spectrum of $[Mo(CO)_4\{CH_2(NCH_2Me_2Pz)_2(CH_2)_3$-$\kappa^2$-N,N$\}]$, **2**.

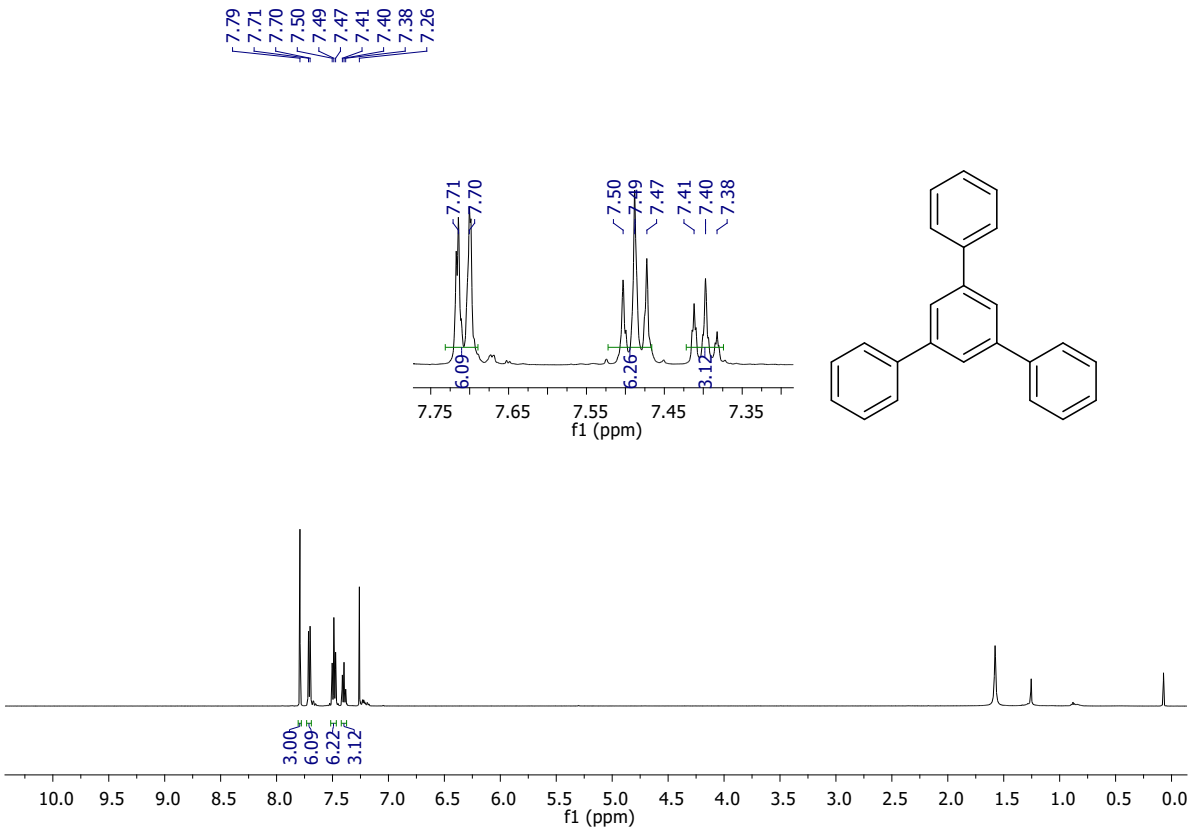


Figure S10. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-triphenylbenzene.

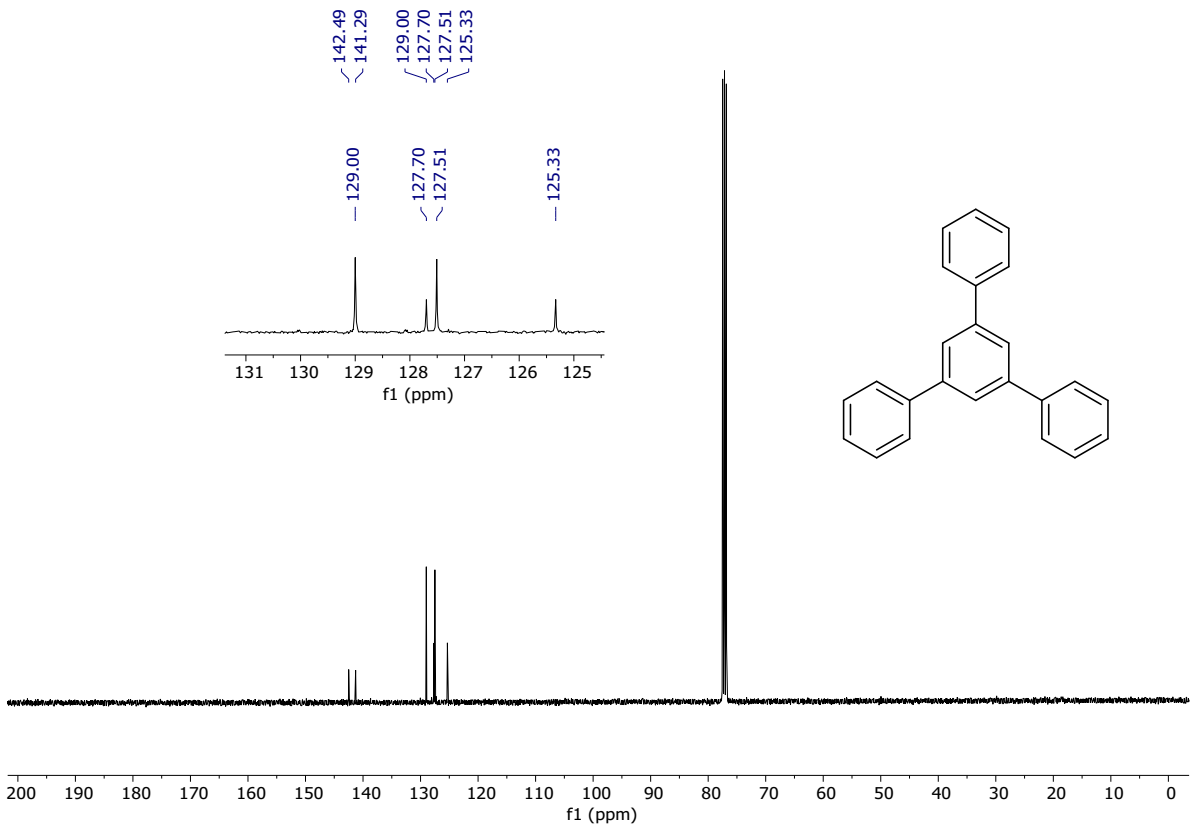


Figure S11. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 ℃) spectrum of the isolated 1,3,5-triphenylbenzene.

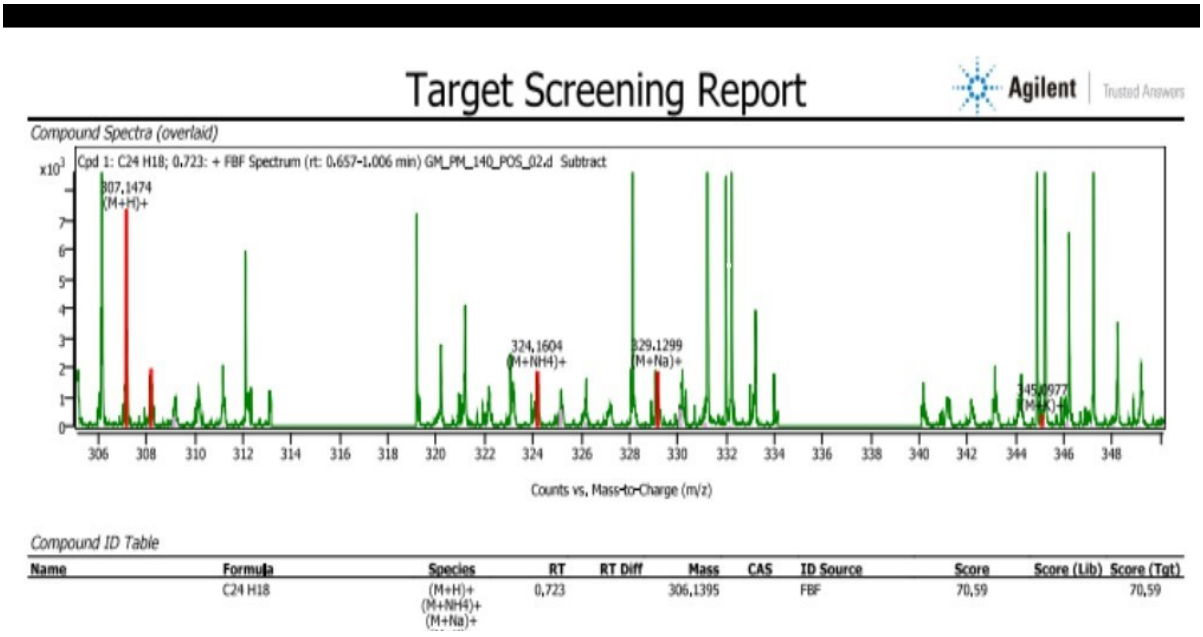


Figure S12. HRMS(ESI+) spectrum of the isolated 1,3,5-triphenylbenzene.

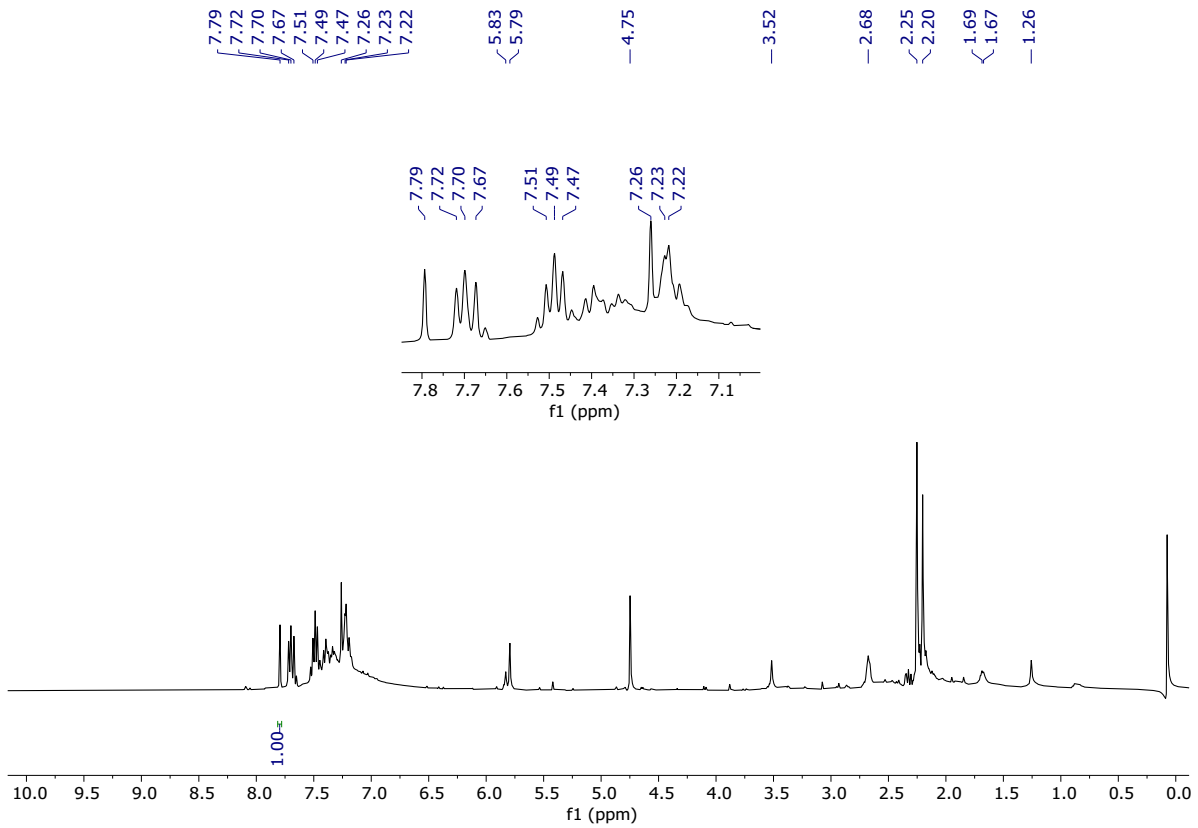


Figure S13. ^{1}H NMR spectrum (500 MHz, 25 ℃) of the reaction mixture of phenylacetylene and complex **2** (2.5 mol%) without any additional solvent at 80 °C for 8 h in $CDCl_3$. The peak due to the CH proton of PhCCH (3.02 ppm) is absent, suggesting full conversion of phenylacetylene and formation of the 1,3,5-triphenylbenzene (7.79 ppm).

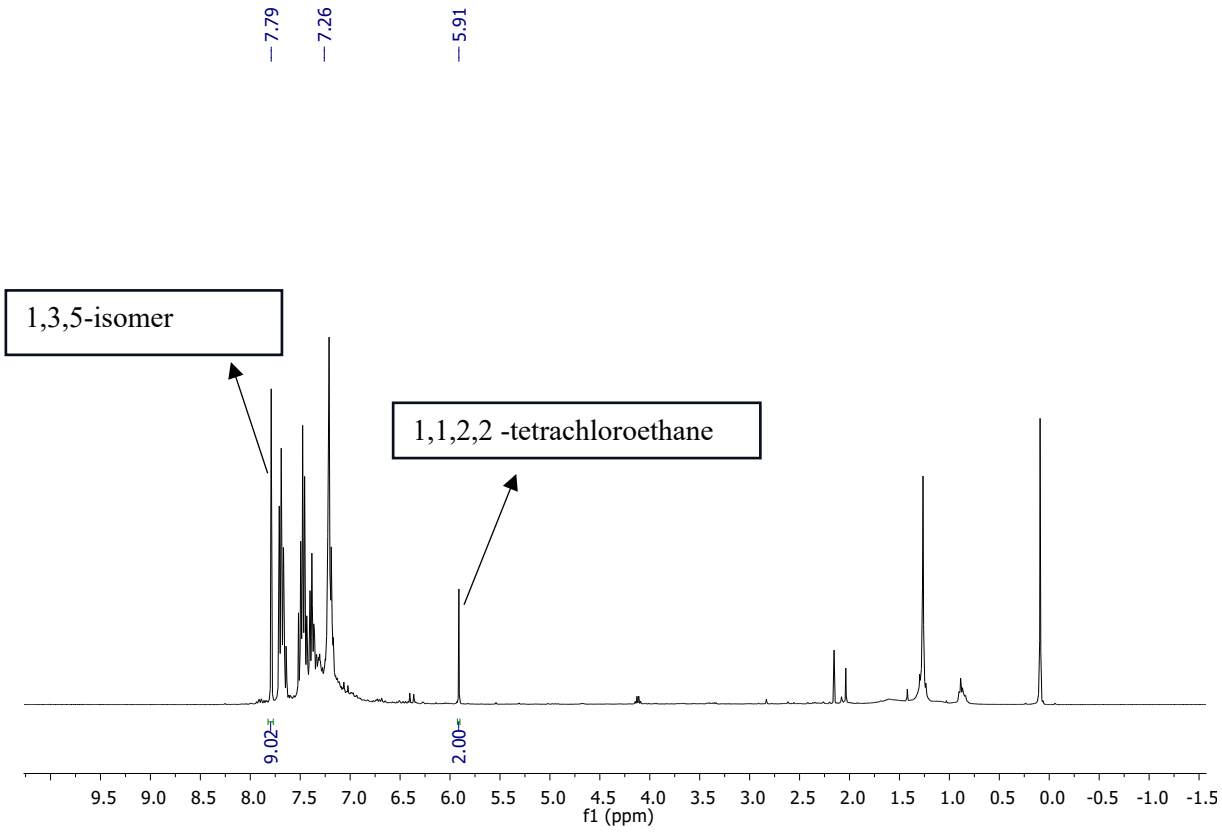


Figure S14. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of phenylacetylene (0.10 mL, 0.91 mmol) and complex **2** under neat condition after 8 h at 80 °C. $CDCl_3$ and 1,1,2,2- tetrachloroethane (0.01 mL, 0.09 mmol) as an internal standard were added. NMR yield for 1,3,5-isomer = 93%.

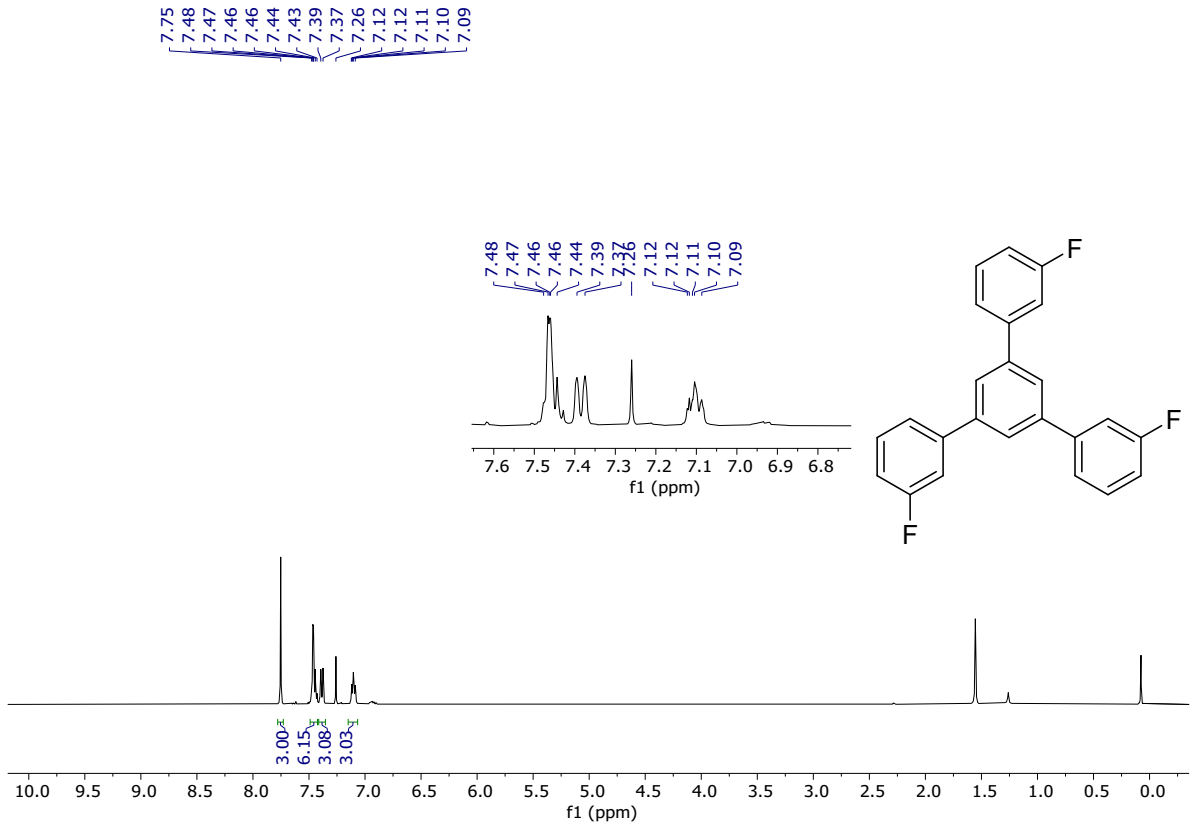


Figure S15. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 ℃) spectrum of the isolated 1,3,5-tris(3-fluorophenyl)benzene.

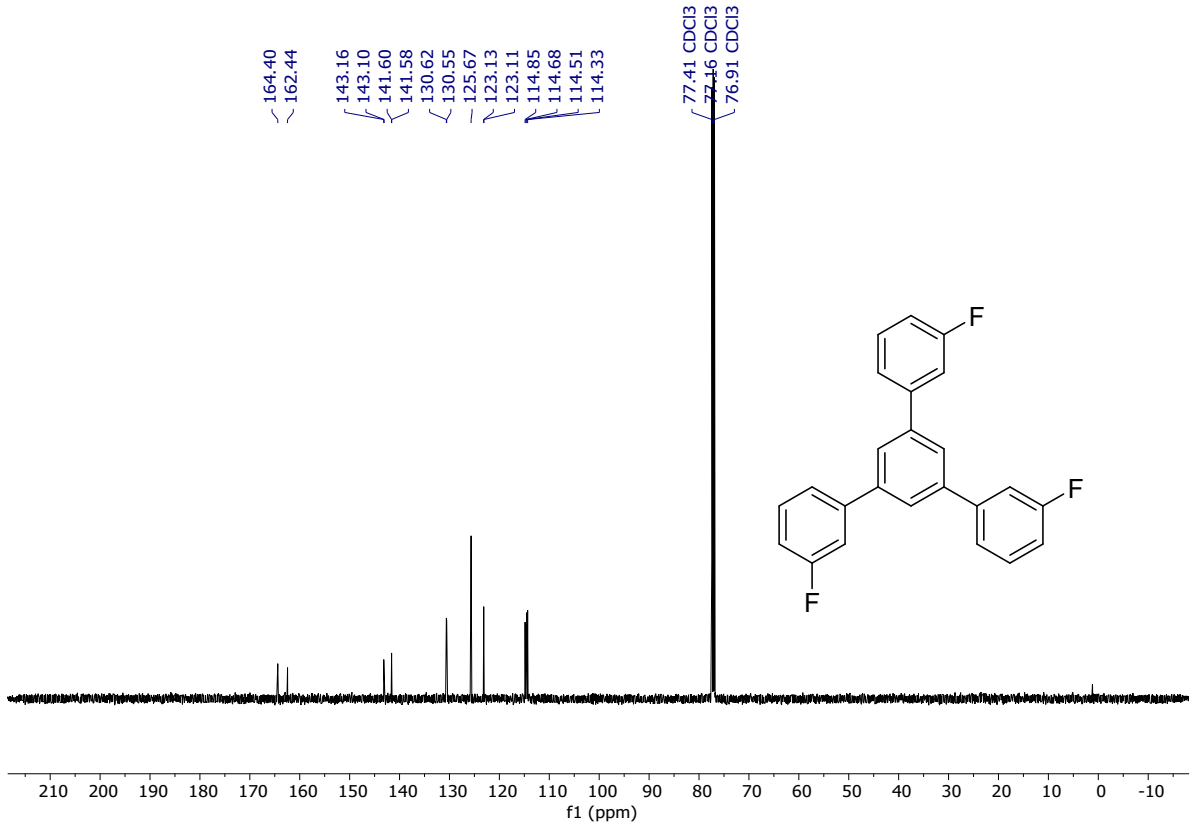


Figure S16. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 ℃) spectrum of the isolated 1,3,5-tris(3-fluorophenyl)benzene.

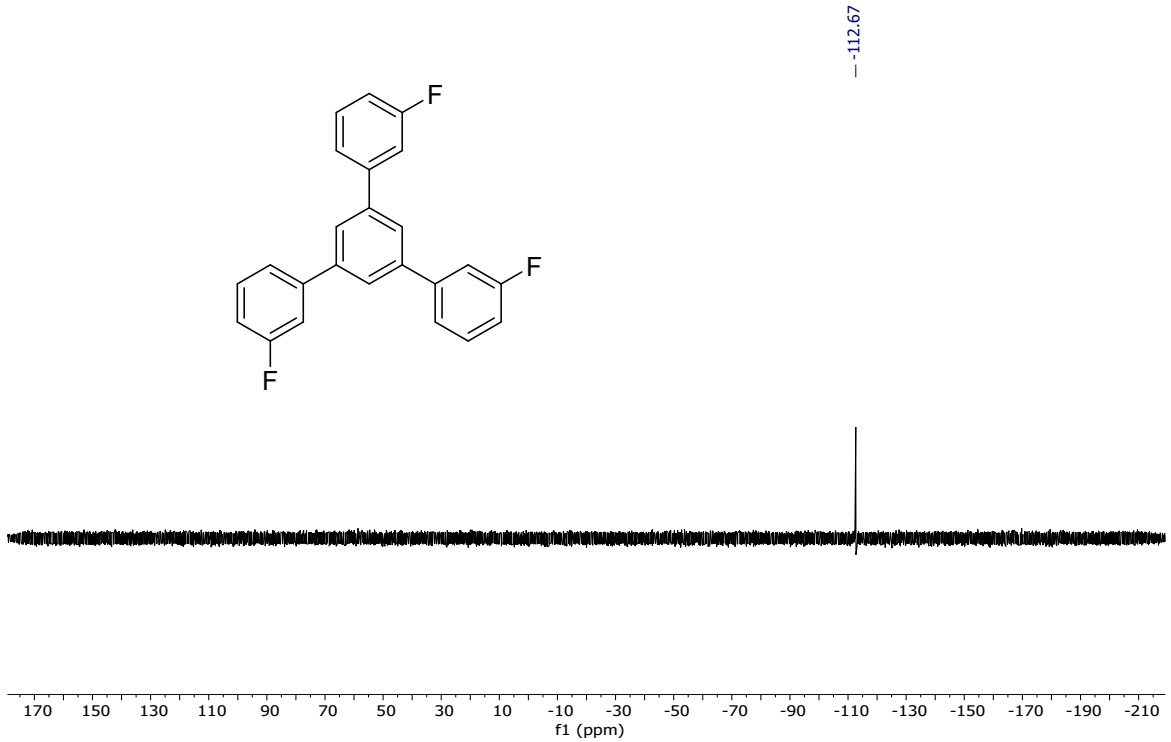


Figure S17. ^{19}F NMR spectrum ($CDCl_3$, 470.59 MHz, 25 °C) of the isolated 1,3,5-tris(3-fluorophenyl)benzene.

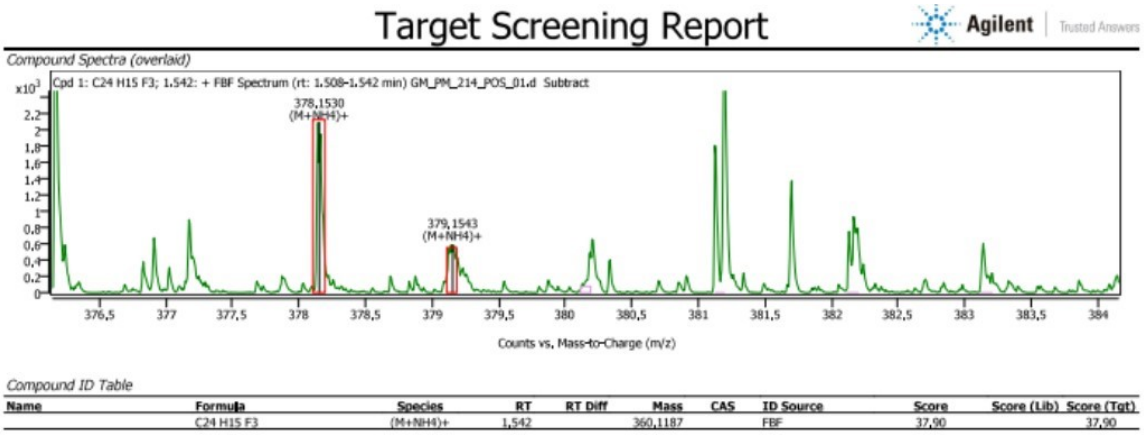


Figure S18. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(3-fluorophenyl)benzene.

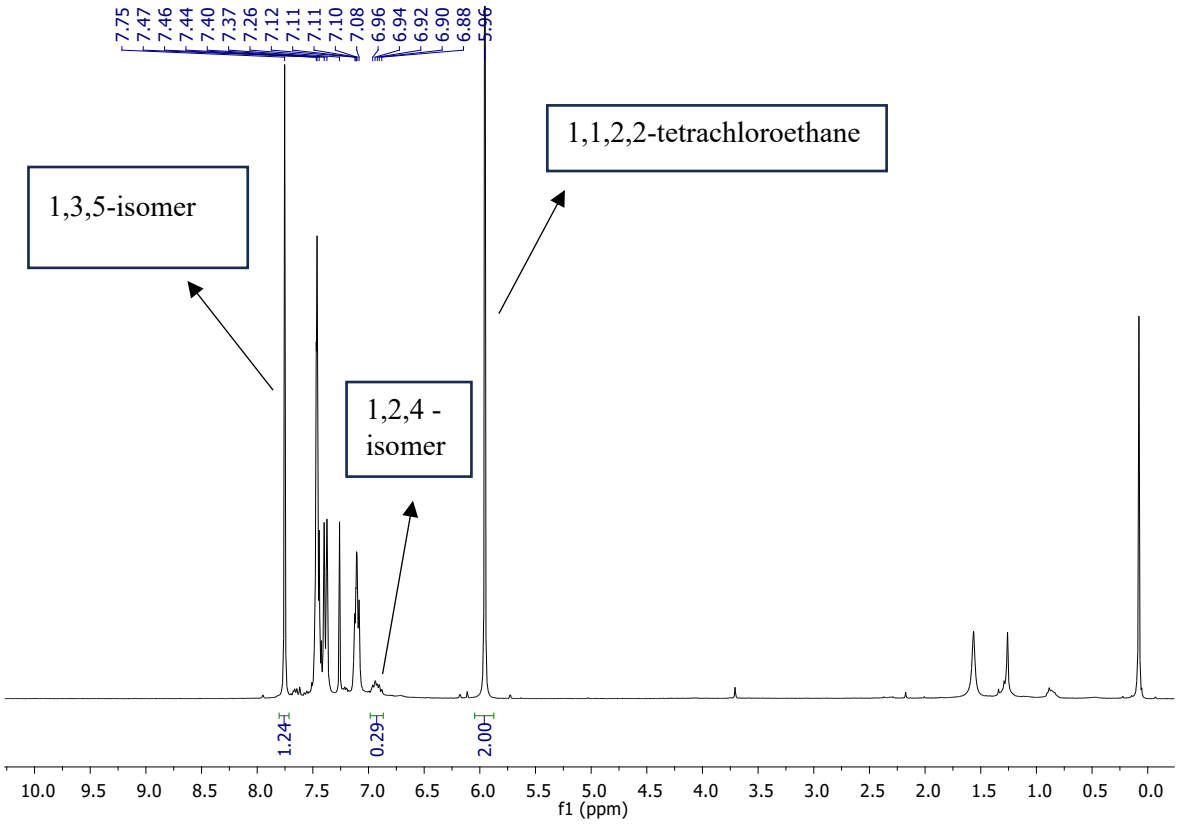


Figure S19. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 3-fluorophenylacetylene (0.03 mL, 0.26 mmol) and complex **2** in toluene after 24 h at 80℃. The reaction mixture was passed through a silica containing pipette and passed with EA/Hexane (1/5). Solvent was removed by rotary evaporator. $CDCl_3$ and 1,1,2,2 tetrachloroethane (0.02 mL, 0.19 mmol) as an internal standard were added. NMR yield for 1,3,5 isomer and 1,2,4 isomer respectively = 90% and 10%.

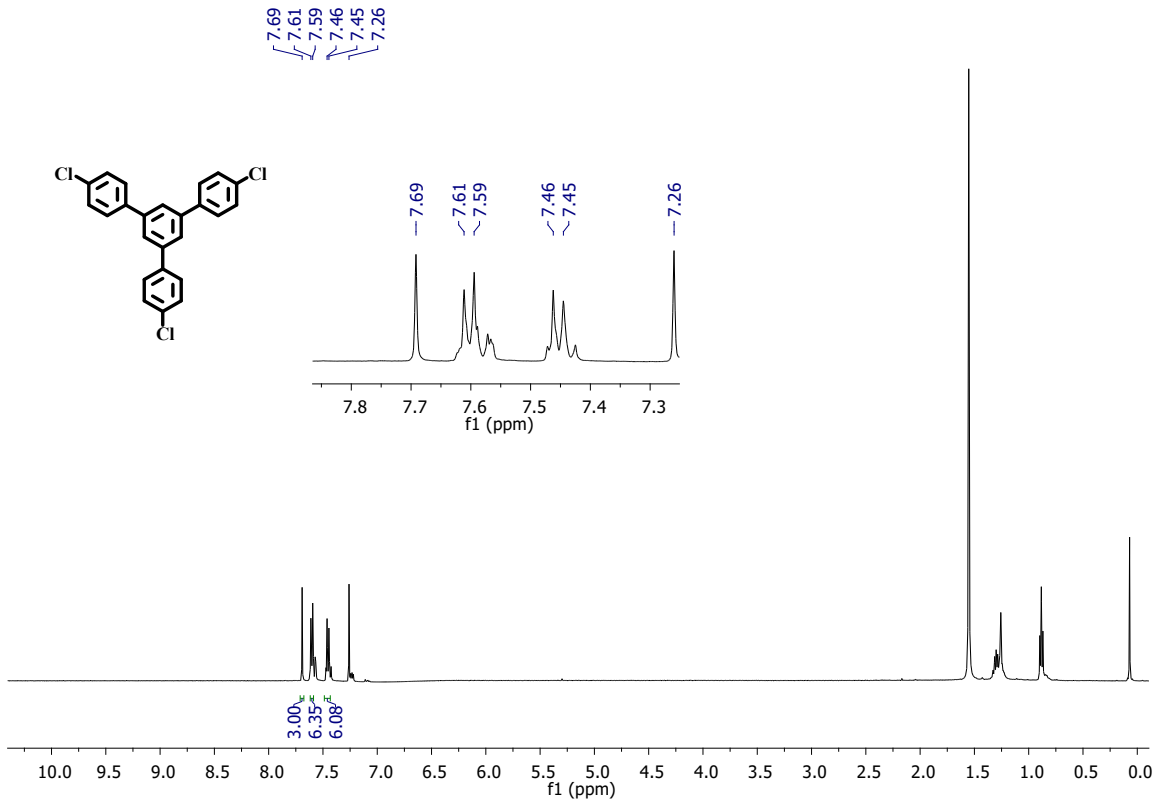


Figure S20. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-chlorophenyl)benzene.

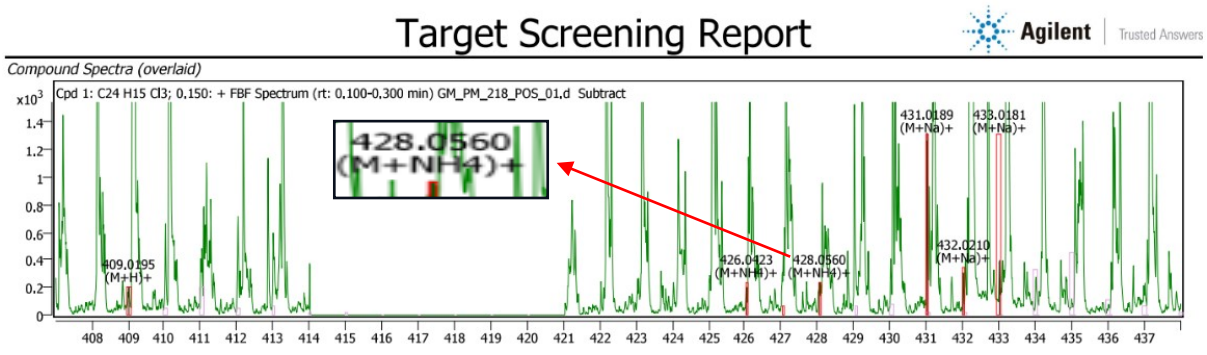


Figure S21. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(4-chlorophenyl)benzene.

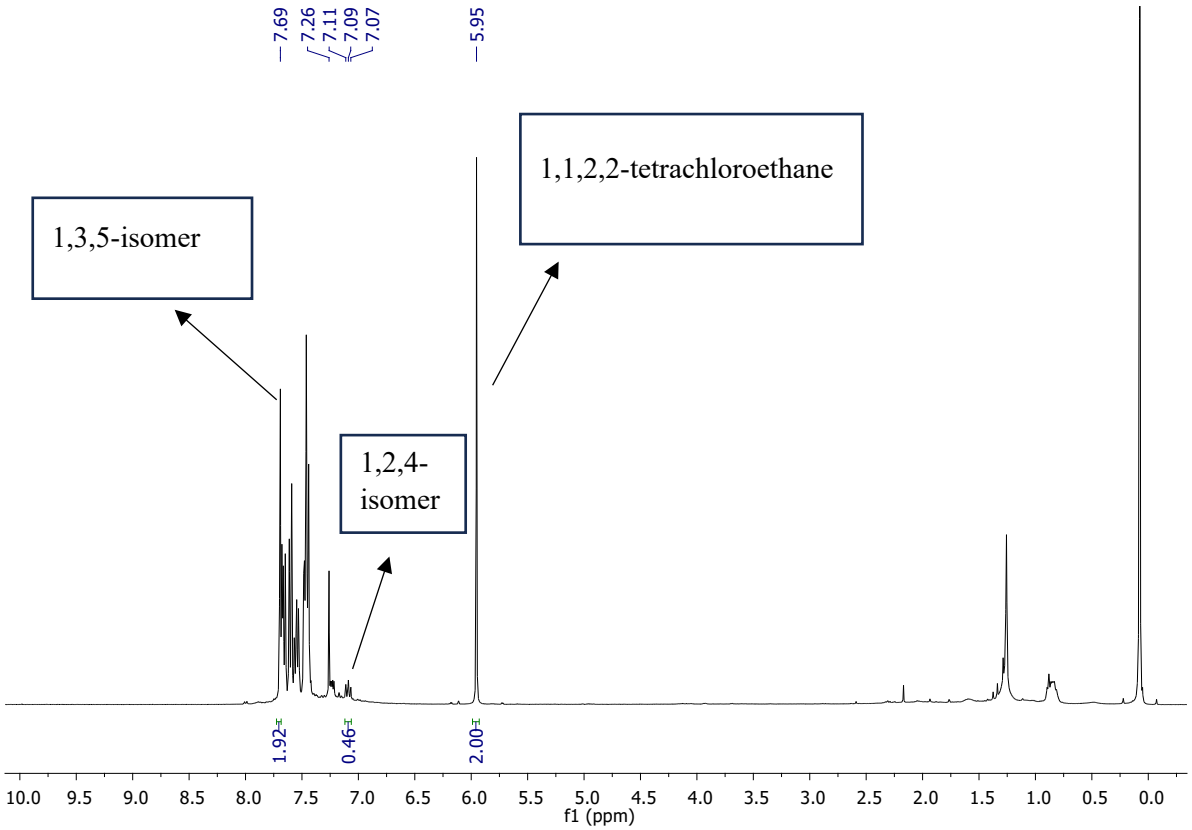


Figure S22. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 4-chloro ethynylbenzene (0.03 g, 0.22 mmol) catalyzed by complex **2** in toluene after 24 h at 80 °C. The solvent was removed. $CDCl_3$ and 1,1,2,2 tetrachloroethane (0.010 mL, 0.095 mmol) as an internal standard were added. NMR yield for 1,3,5 isomer and 1,2,4 isomer respectively = 83% and 15%.

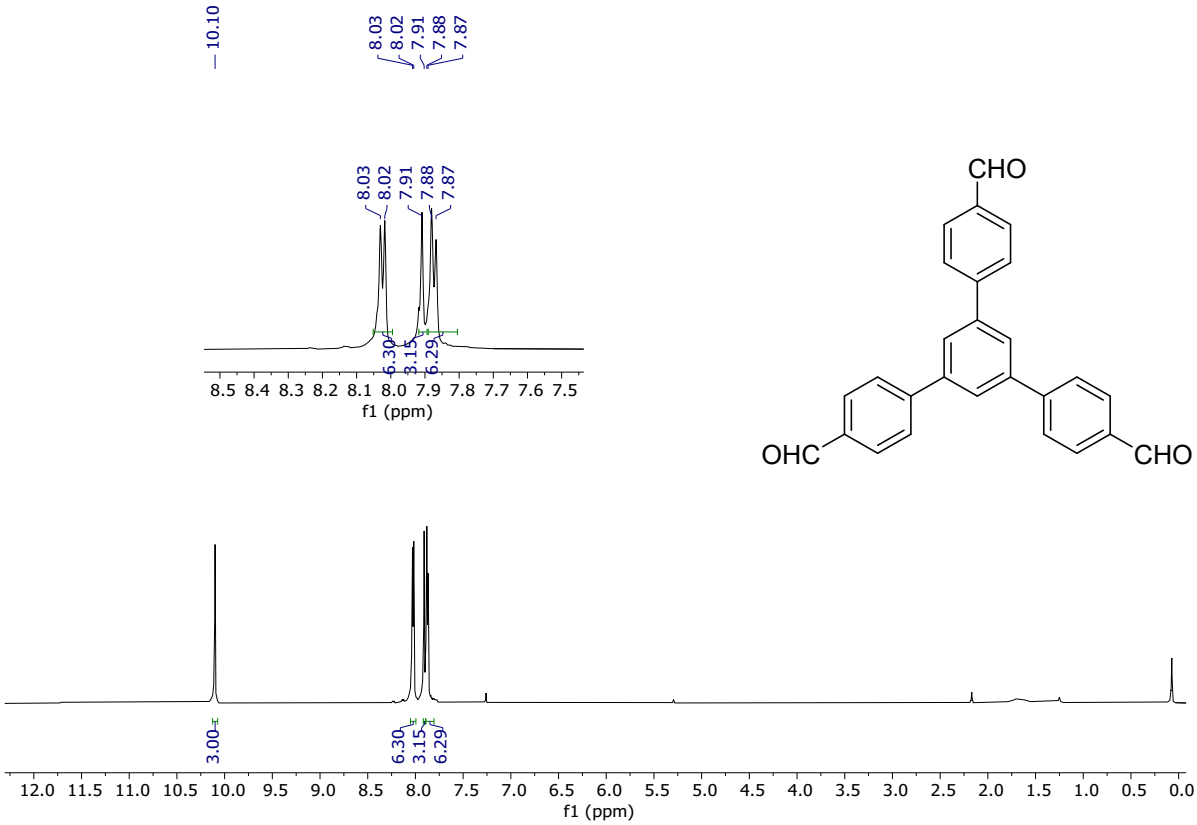


Figure S23. ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-formylphenyl)benzene.

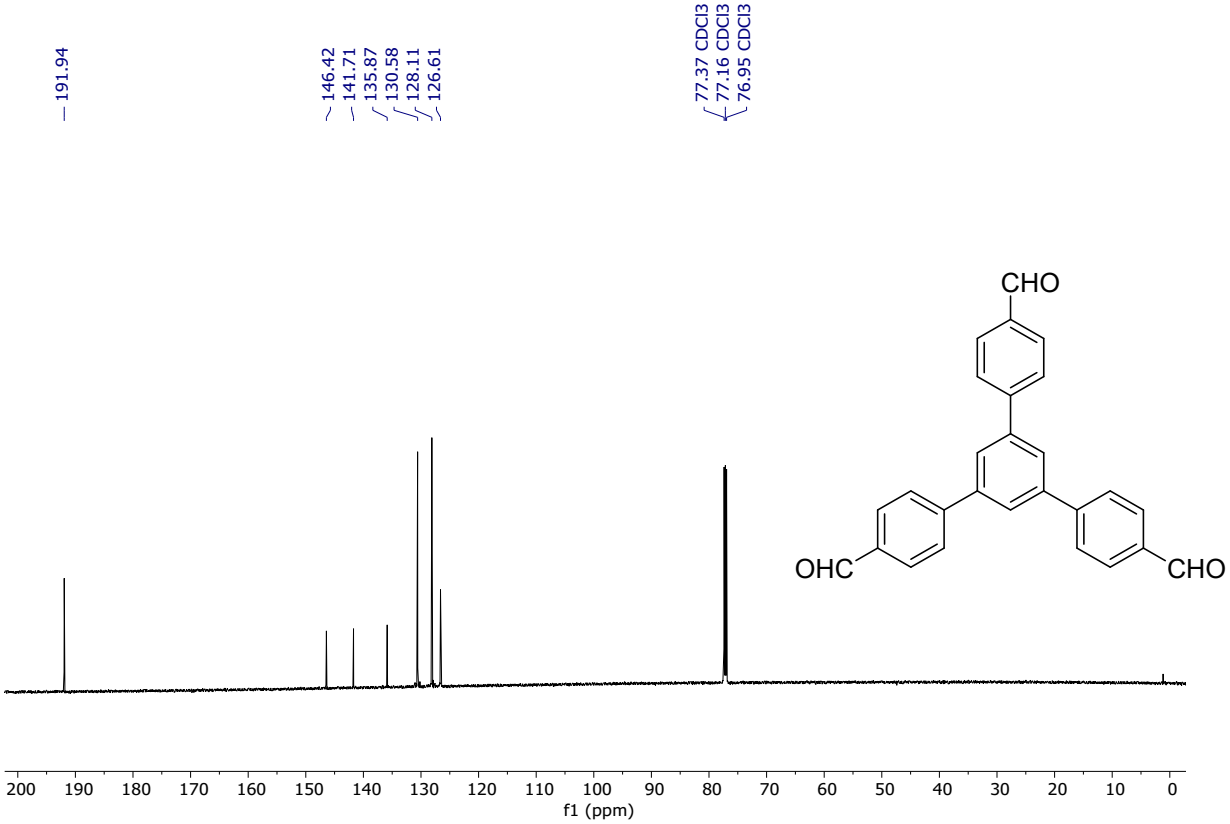


Figure S24. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-formylphenyl)benzene.

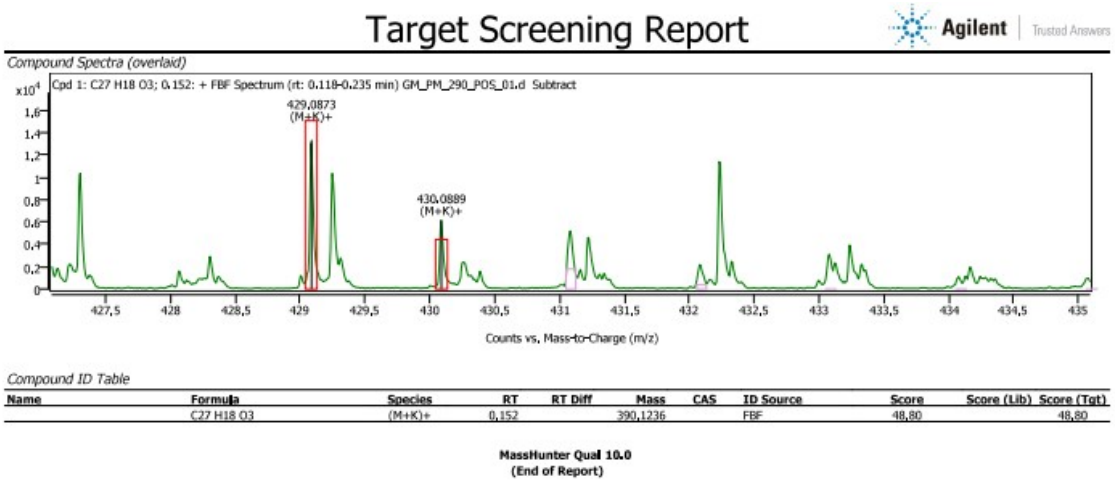


Figure S25. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(4-formylphenyl)benzene

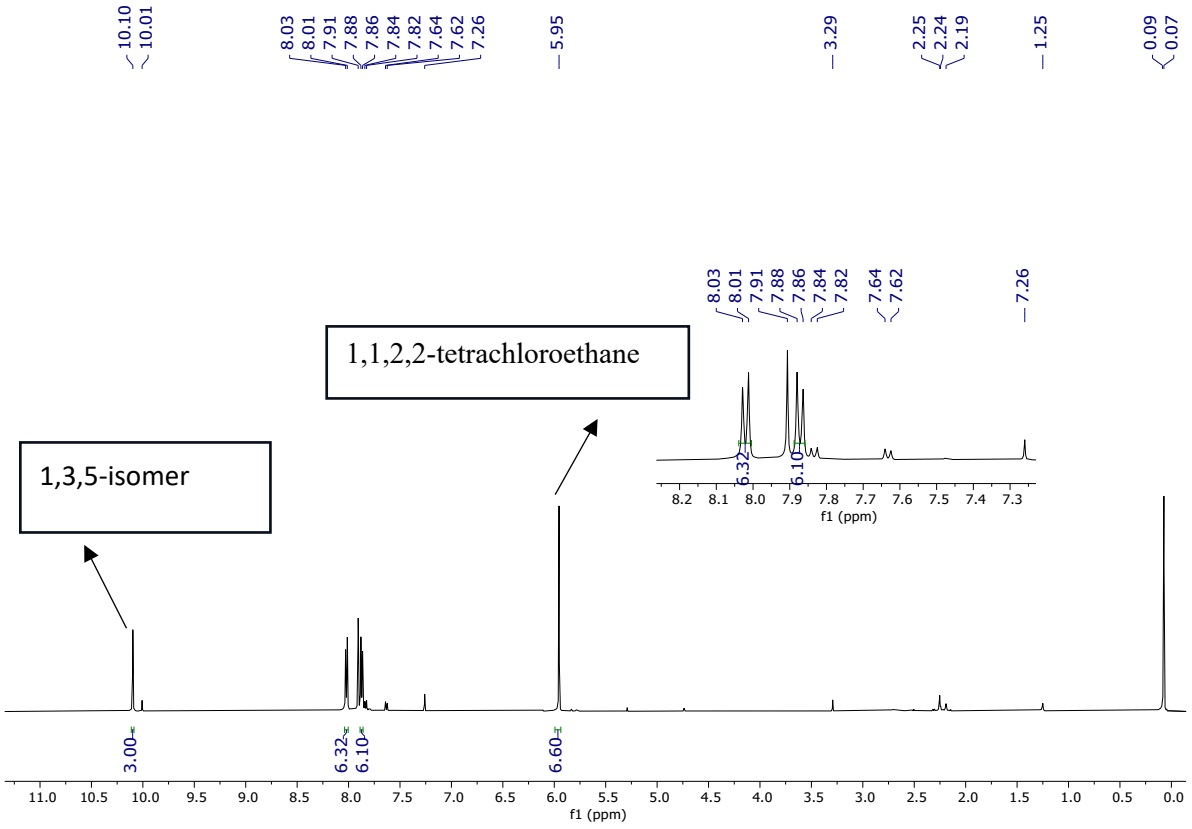


Figure S26. ^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 4-ethynylbenzaldehyde (0.025g, 0.192 mmol) and complex **2** in toluene after 24 h 84 °C. The solvent was removed by vacuum and 1,1,2,2 tetrachloroethane (0.020 mL, 0.190 mmol) was added as an internal standard. NMR yield for 1,3,5 isomer = 97%.

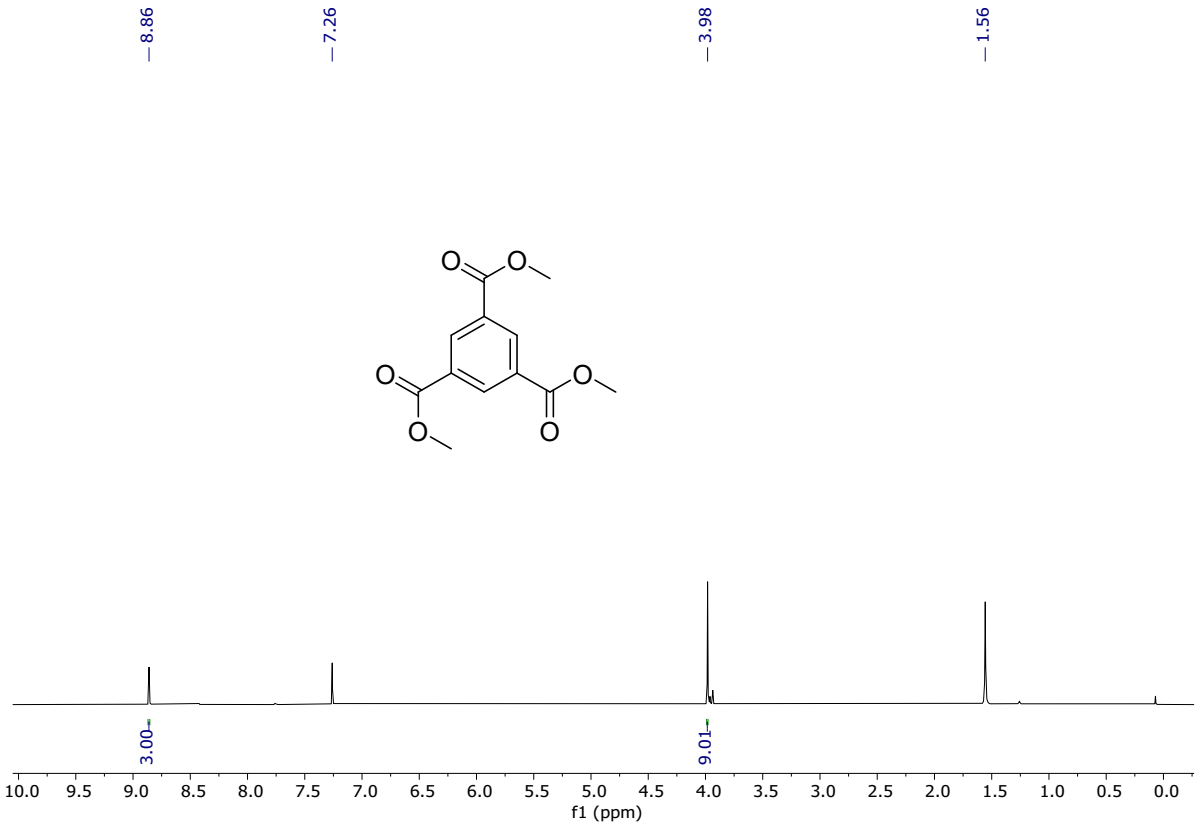


Figure S27. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated benzene-1,3,5-tricarboxylic acid trimethyl ester.

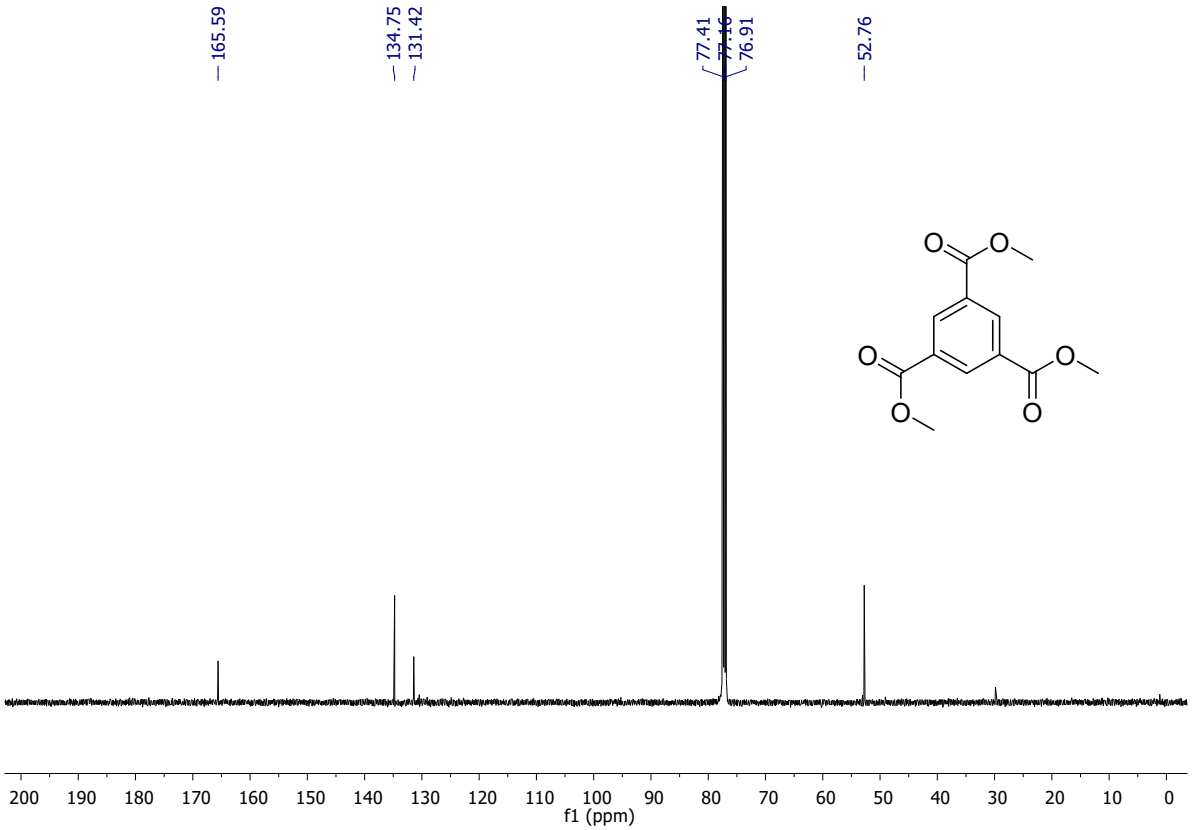


Figure S28. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 °C) spectrum of the isolated benzene-1,3,5-tricarboxylic acid trimethyl ester**.**

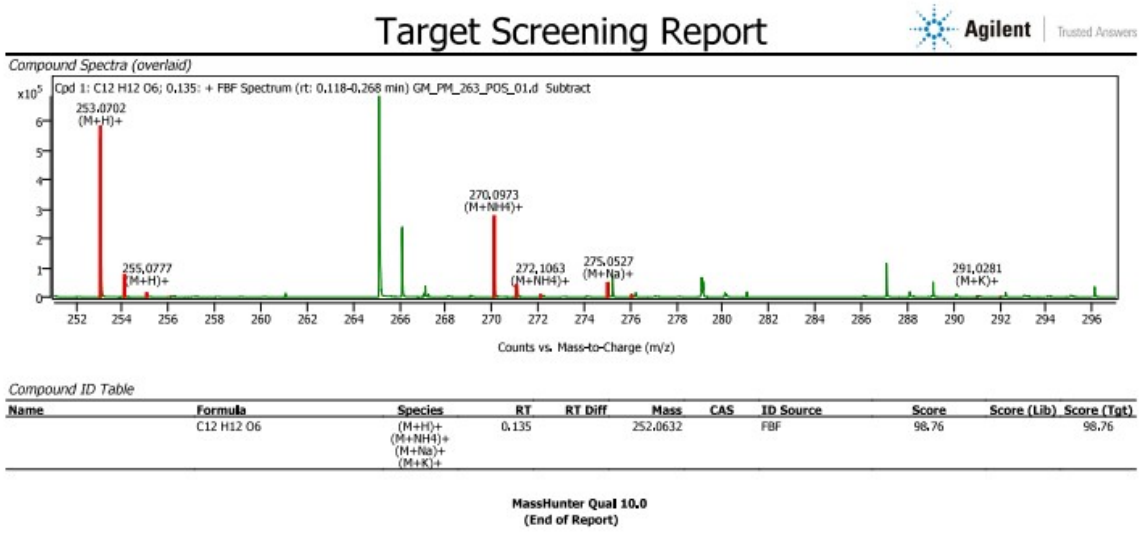


Figure S29. HRMS(ESI+) spectrum of the isolated benzene-1,3,5-tricarboxylic acid trimethyl ester**.**

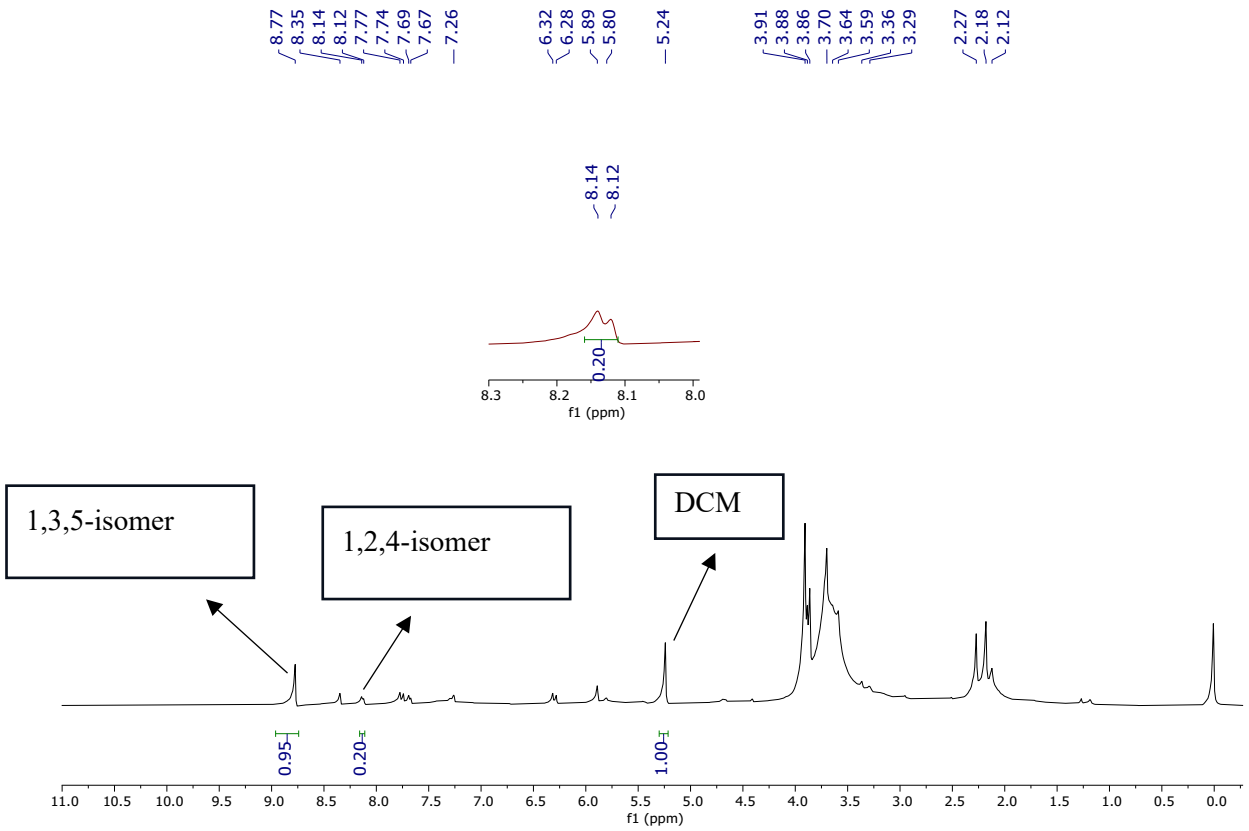


Figure S30. [1] H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of methyl propiolate (0.05 mL, 0.56 mmol) and complex **2** in toluene after 24 h at 85℃. The solvent was removed. $CDCl_3$ and dichloromethane (0.010 mL, 0.156 mmol) as an internal standard were added. The NMR yield for 1,3,5 isomer is 53% and that of the 1,2,4 isomer is 32%.

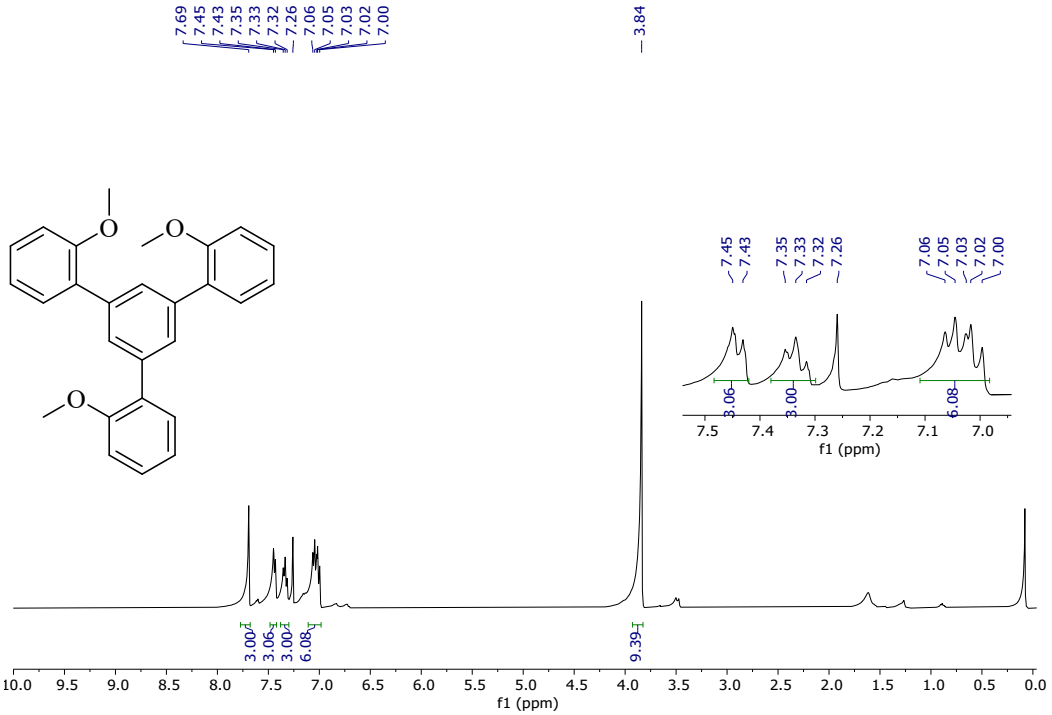


Figure S31. [1]H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-chlorophenyl)benzene.

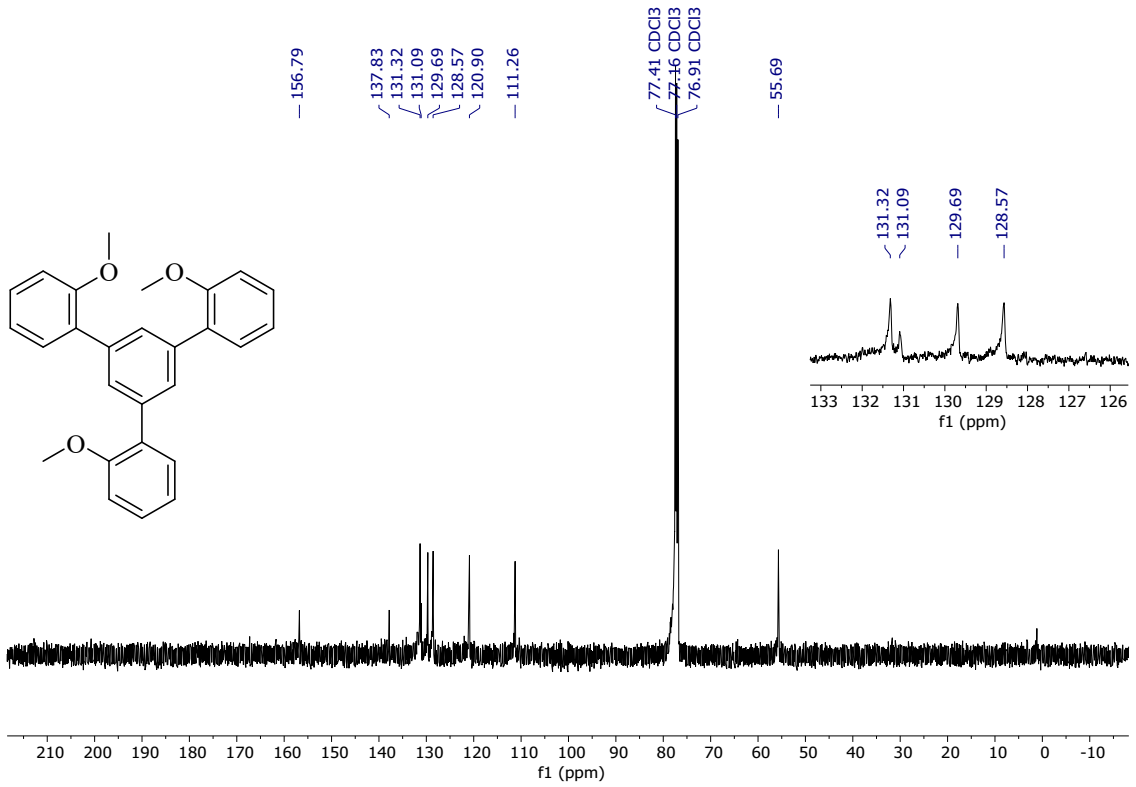
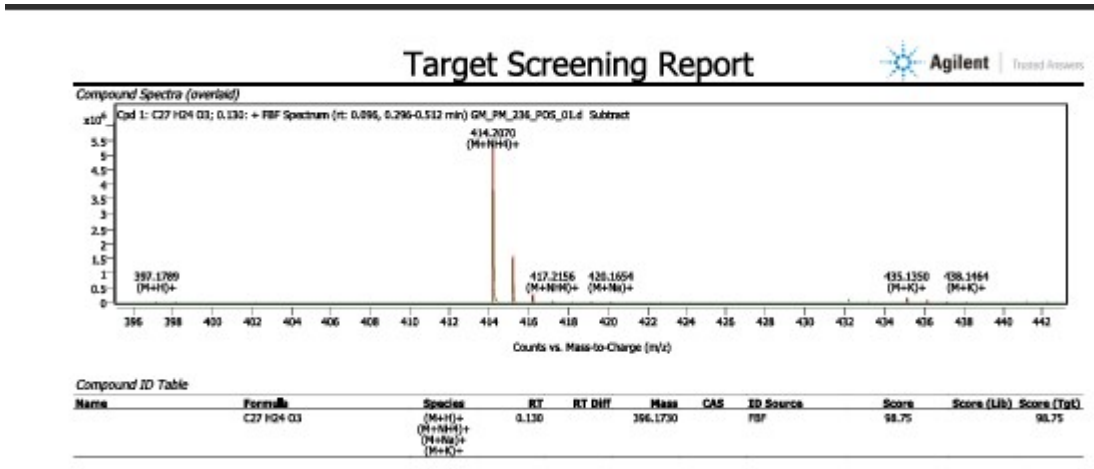


Figure S32. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 °C) spectrum of the isolated 1,3,5-Tris(2-methoxyphenyl)benzene.



.

Figure S33. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(2-methoxyphenyl)benzene.

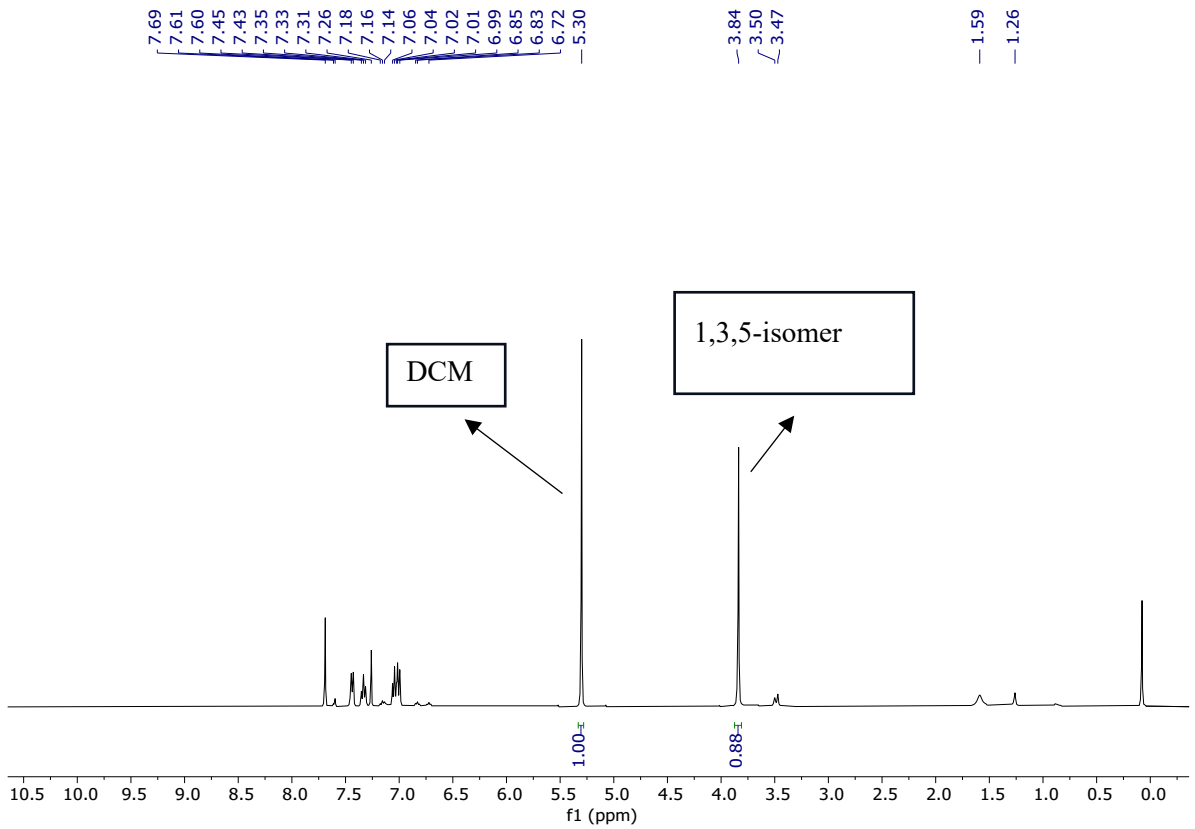


Figure S34. ^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 2-methoxyphenylacetylene (0.03 mL, 0.23 mmol) and complex **2** in toluene after 24 h 85 °C. The solvent was removed under vacuum, $CDCl_3$ followed by dichloromethane (0.020 mL, 0.313 mmol) (internal standard) were added. NMR yield for 1,3,5 isomer = 79%.

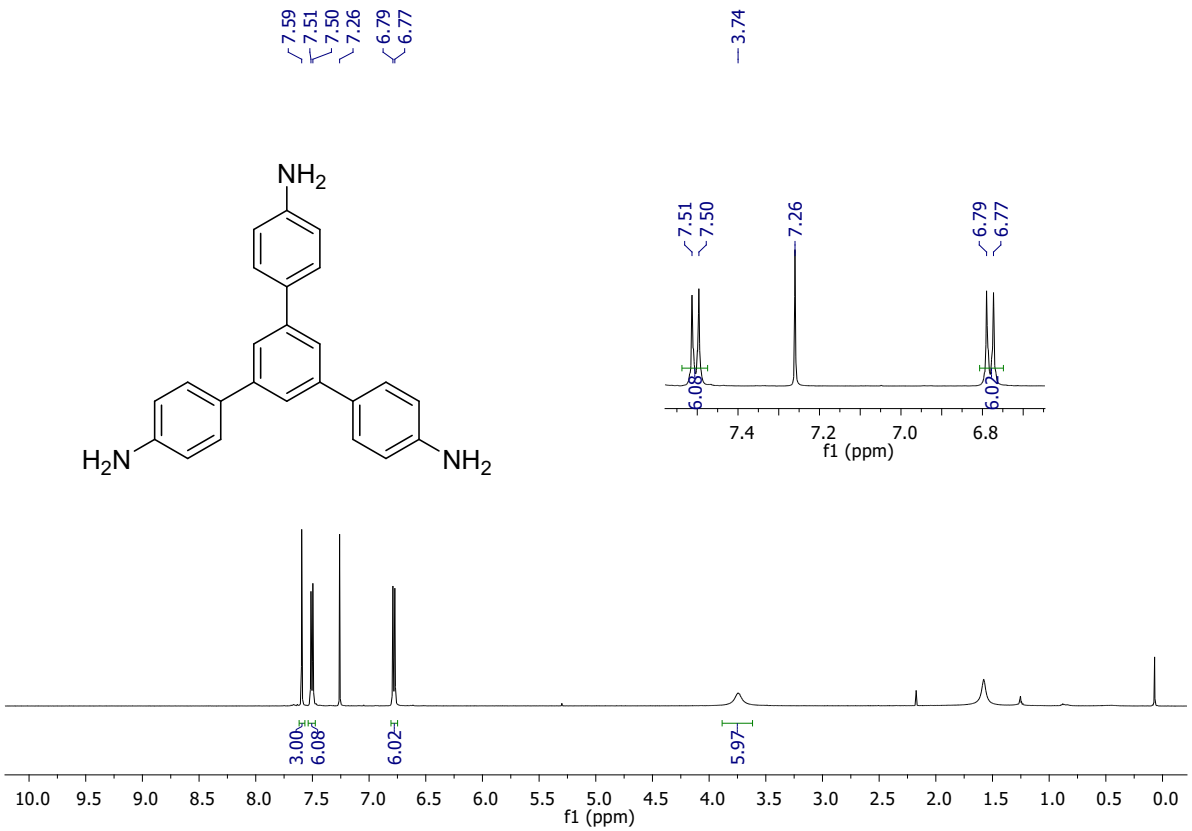


Figure S35. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-aminophenyl)benzene.

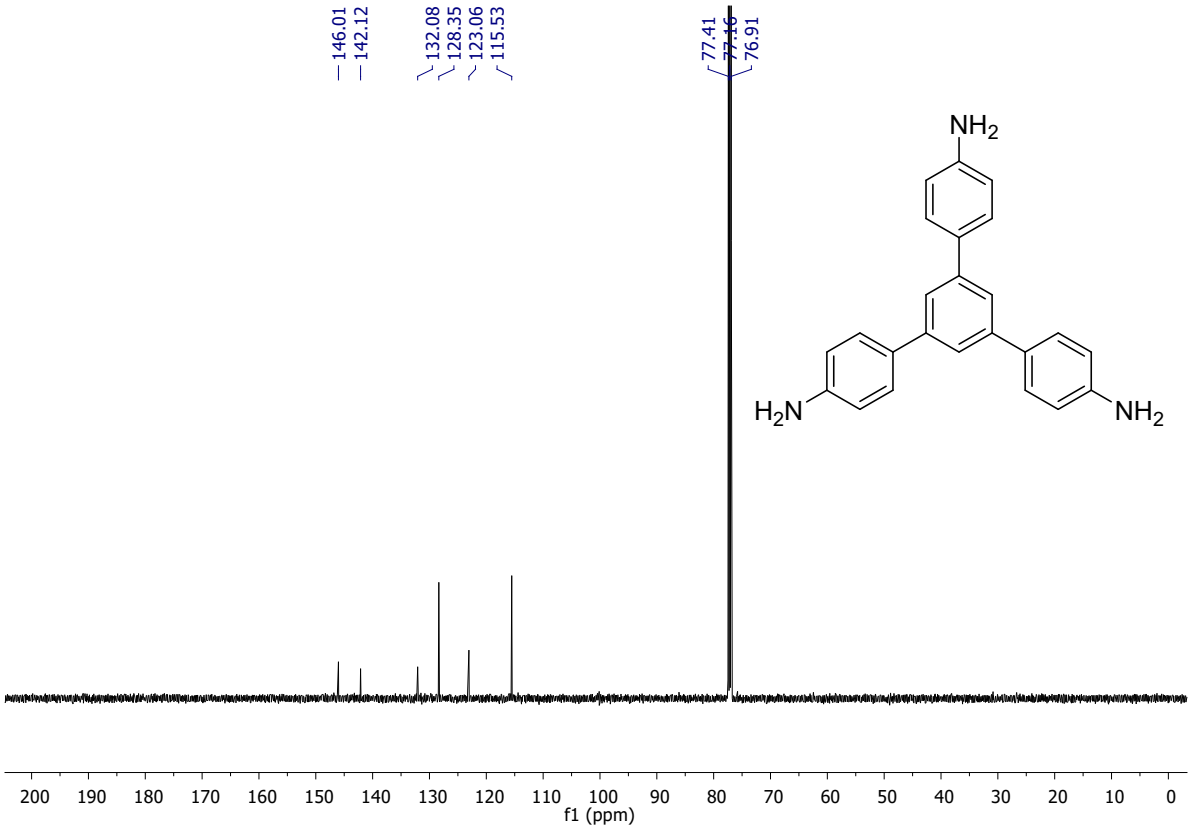


Figure S36. ^{13}C {^{1}H} NMR ($CDCl_3$, 125.76 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-aminophenyl)benzene.

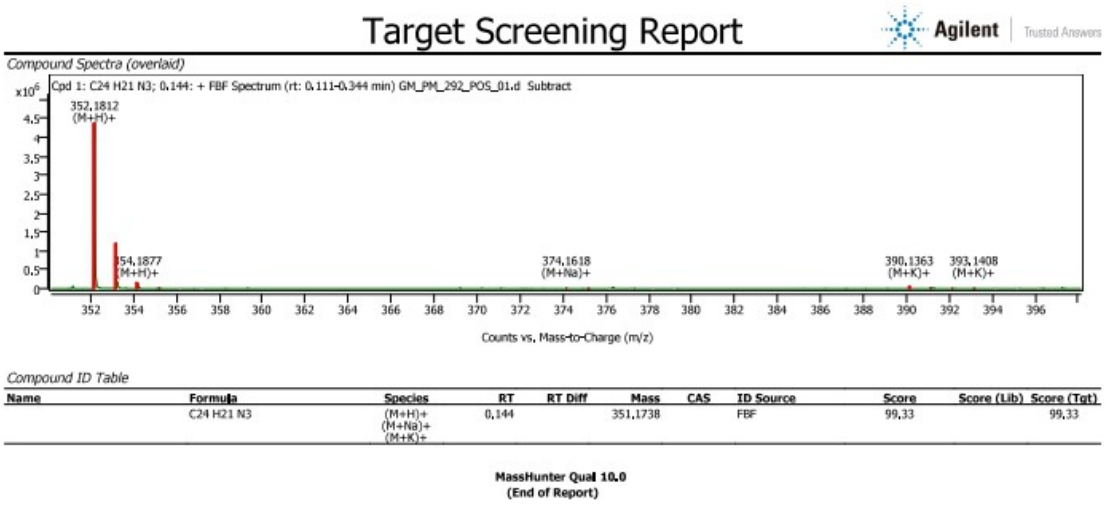


Figure S37. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(4-aminophenyl)benzene.

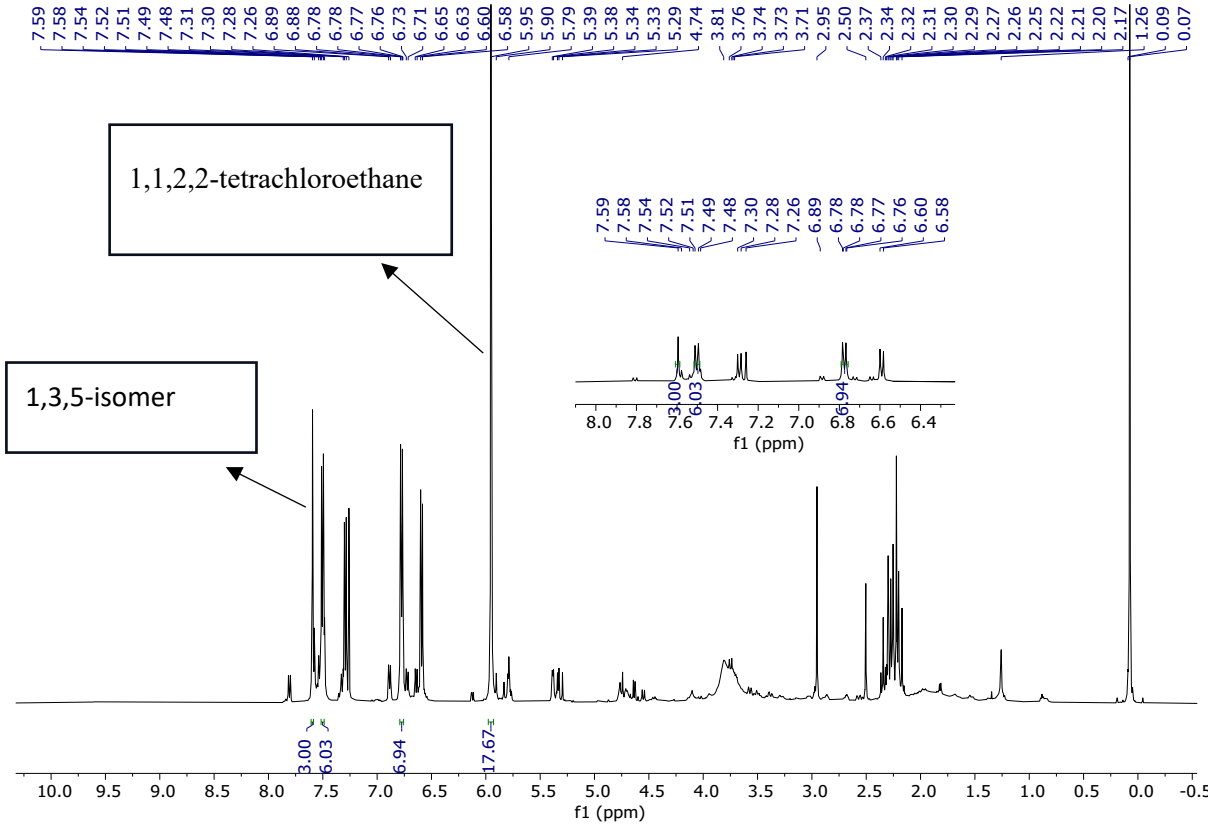


Figure S38. ^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 4-amino ethynylbenzene (0.05 g, 0.43 mmol) and complex **2** in toluene (1 mL) after 24 h at 85 °C. The solvent was removed under vacuum. $CDCl_3$ and 1,1,2,2-tetrachloroethane (0.10 mL, 0.95 mmol) as an internal standard were added. The NMR yield for the 1,3,5-isomer is 75%.

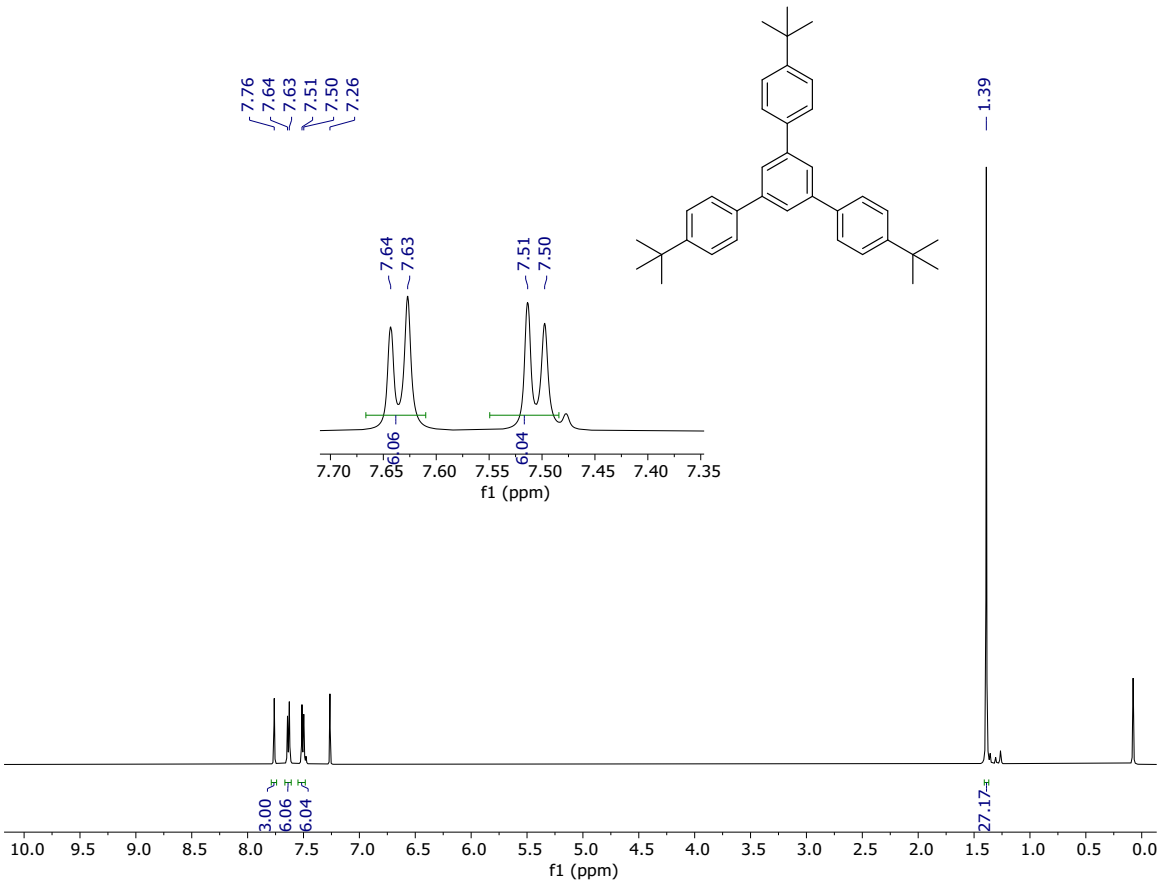


Figure S39. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-tert-butylphenyl)benzene.

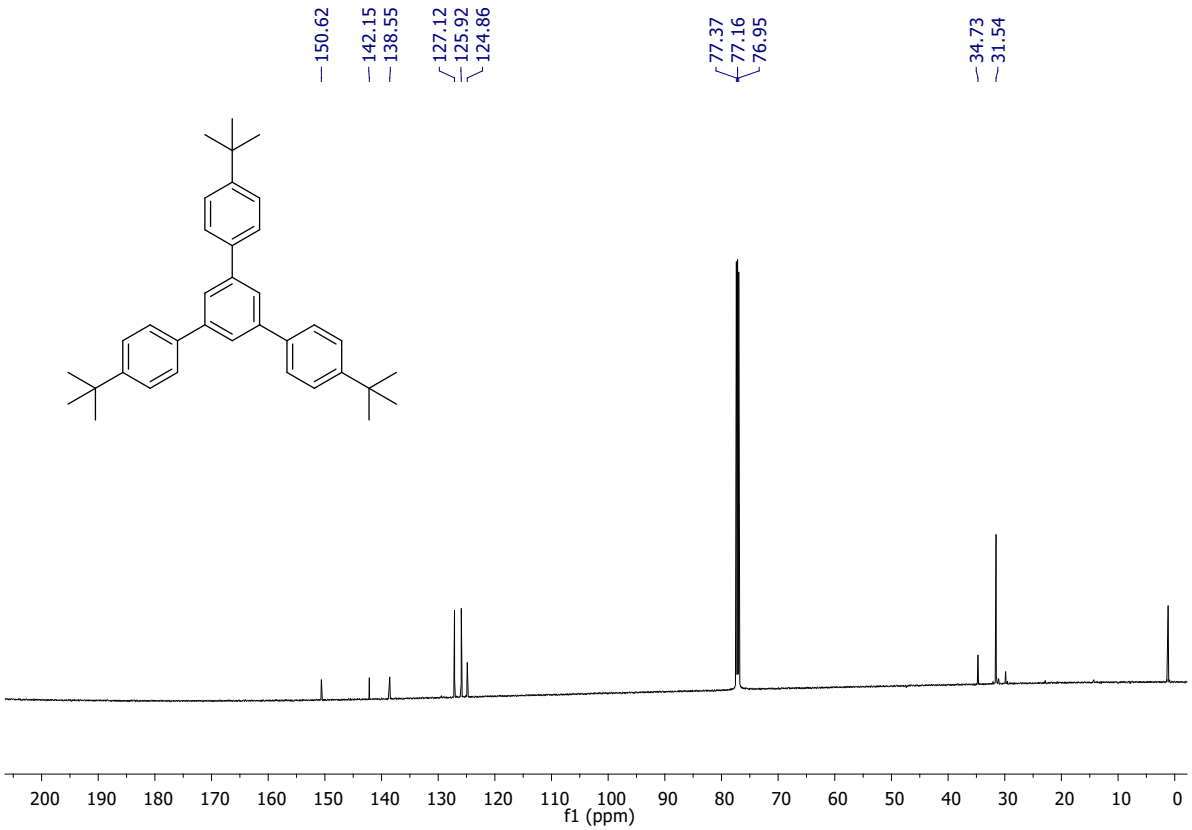


Figure S40. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150.90 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-tert-butylphenyl)benzene.

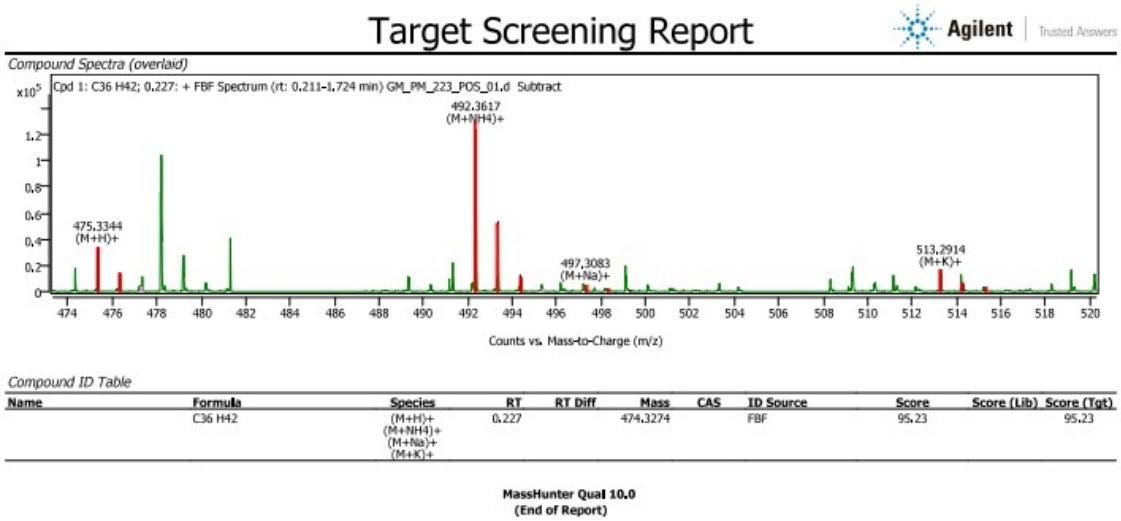


Figure S41. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(4-tert-butylphenyl)benzene.

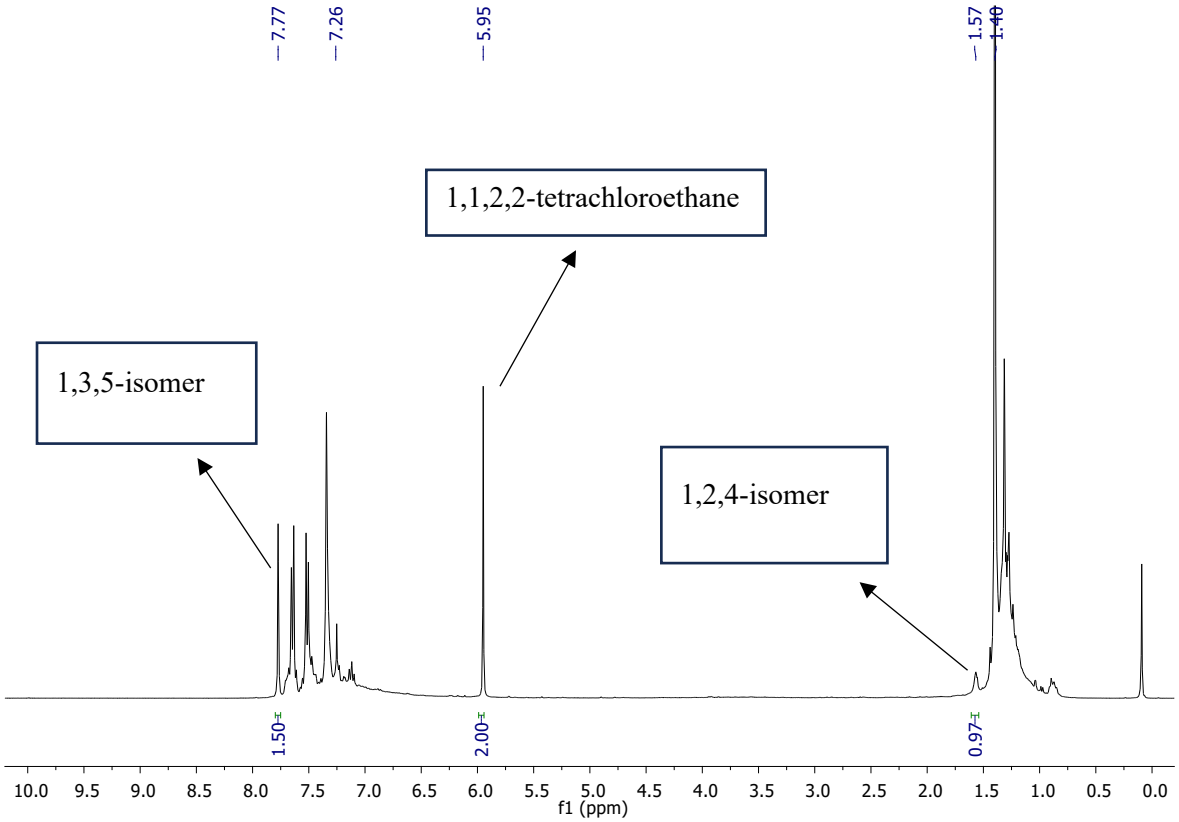


Figure S42. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 1-(tert-butyl)-4 ethynylbenzene (0.03 mL, 0.17 mmol) and complex **2** in toluene after 24 h at 80°C. The solvent was removed under vacuum. $CDCl_3$ and 1,1,2,2 tetrachloroethane (0.010 mL, 0.095 mmol) as an internal standard were added. The NMR yield for the 1,3,5-isomer is 86% and that of the 1,2,4-isomer is 9%.

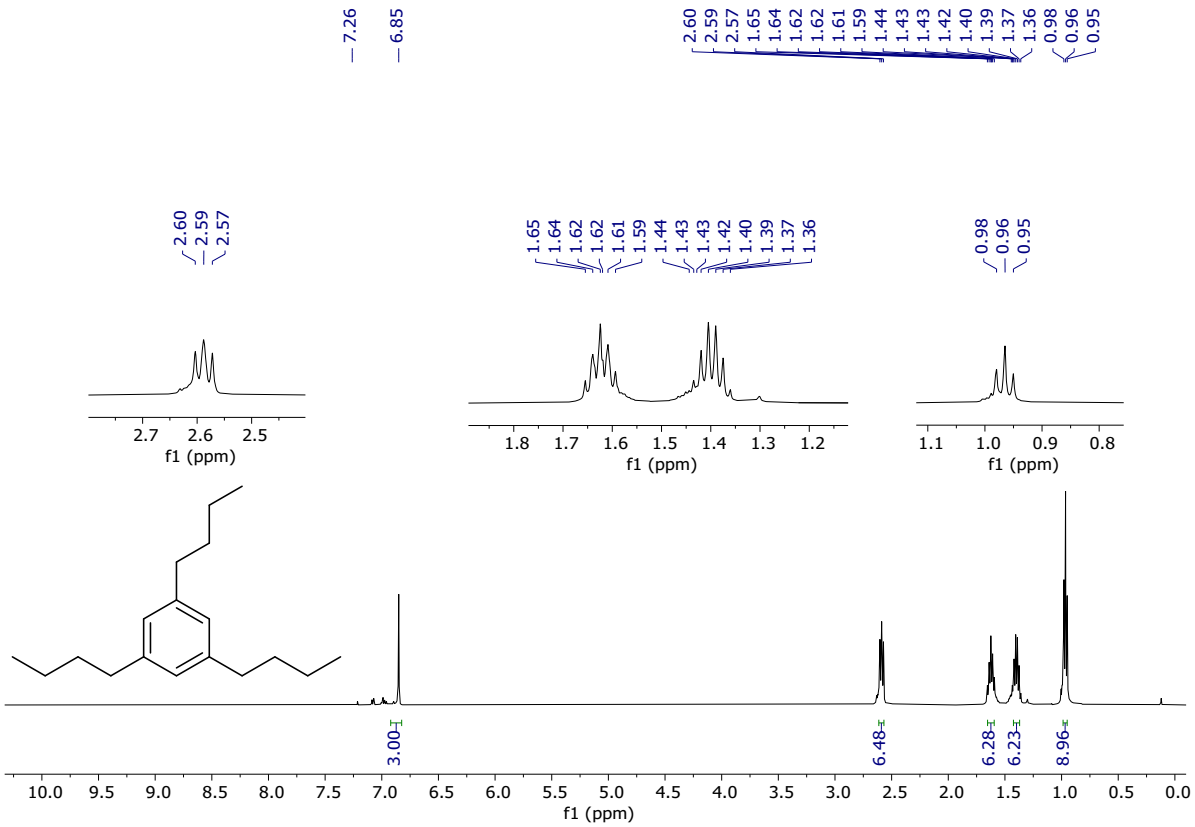


Figure S43. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tributylbenzene.

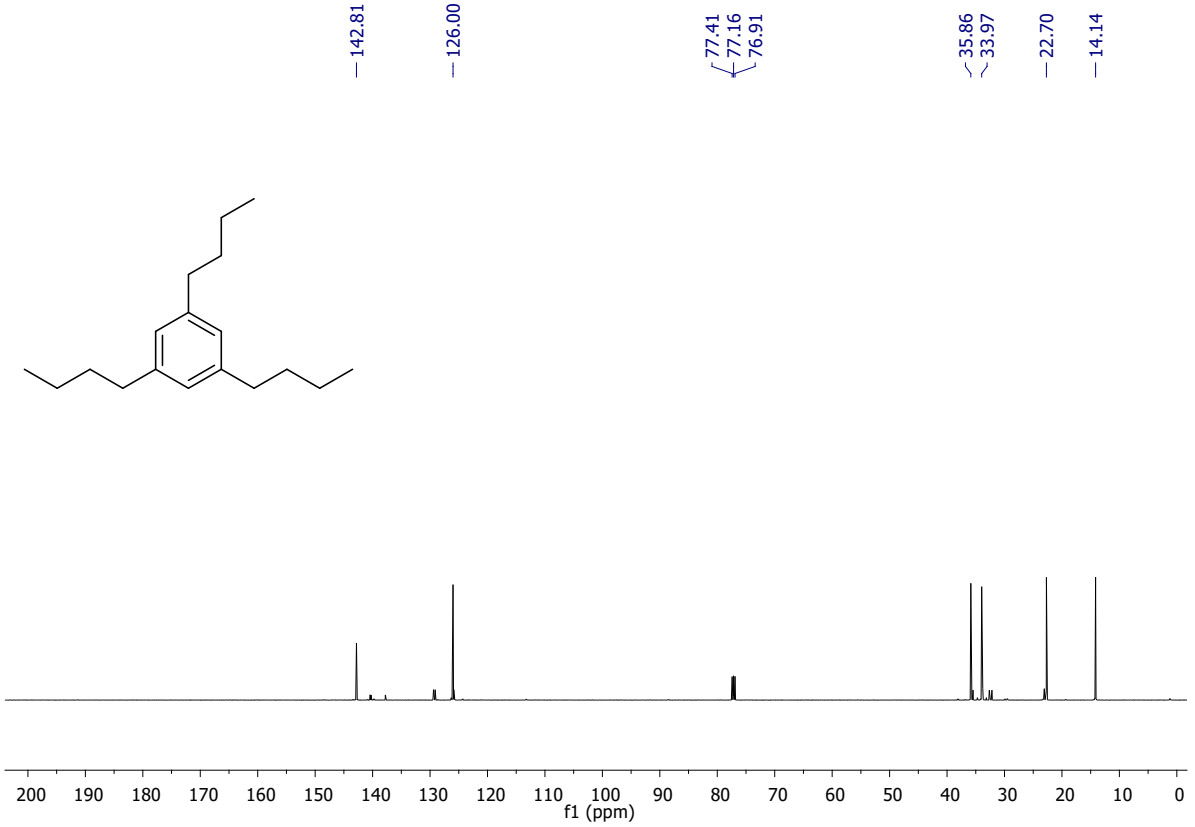


Figure S44. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 °C) spectrum of the isolated 1,3,5-tributylbenzene.

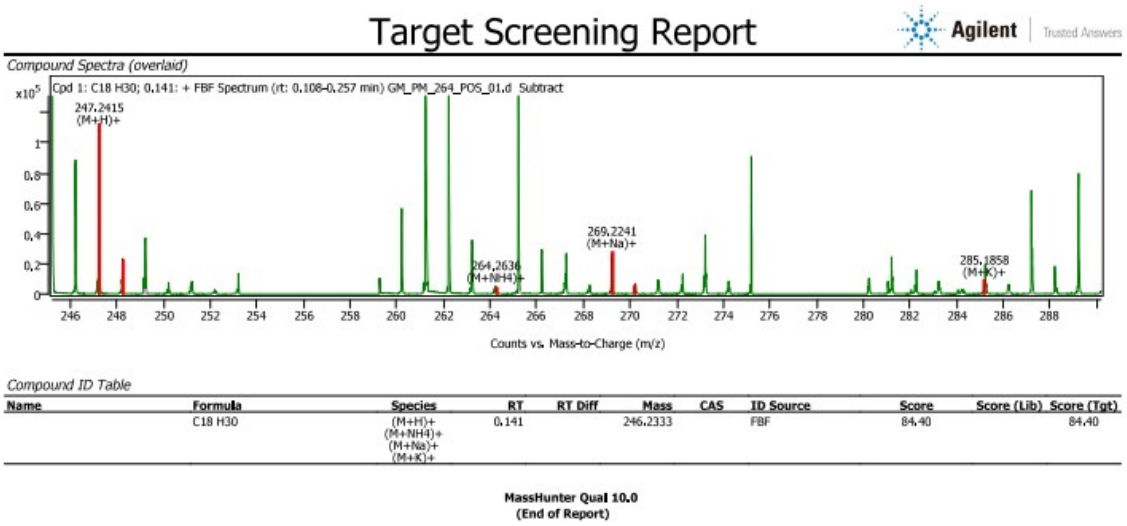


Figure S45. HRMS(ESI+) spectrum of the isolated 1,3,5-tributylbenzene.

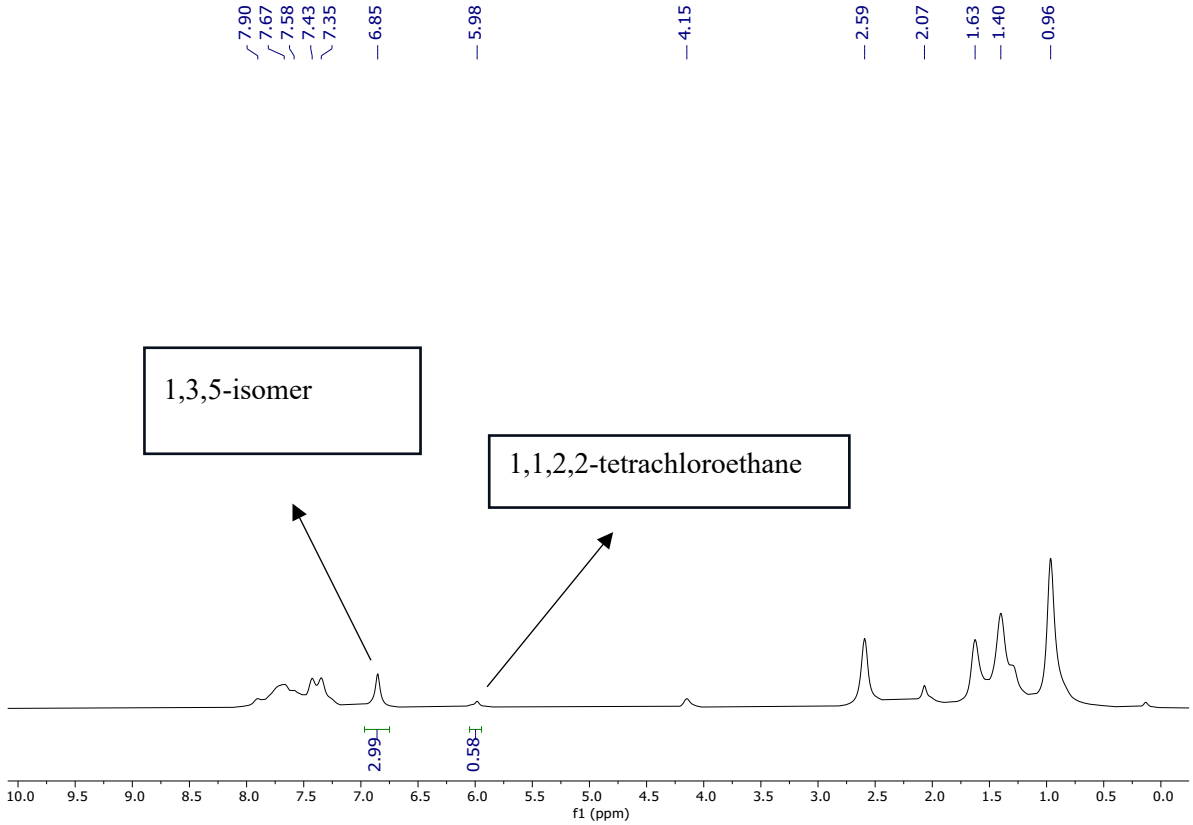


Figure S46. ^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 1-hexyne (0.3 mL, 2.6 mmol) and complex **2** in toluene after 24 h at 85 C°. The solvent was removed. $CDCl_3$ and 1,1,2,2-tetrachloroethane (0.025 mL, 0.236 mmol) as an internal standard were added. The NMR yield for the 1,3,5-isomer is 93%.

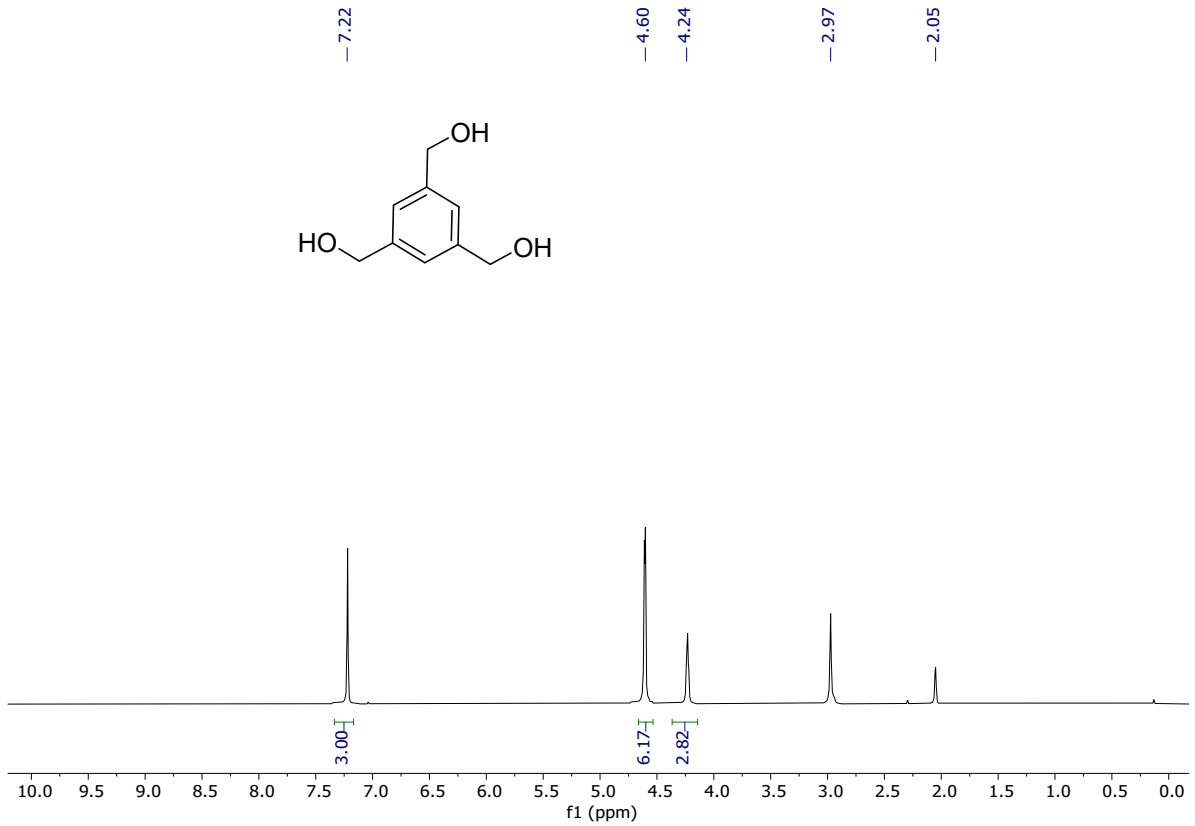


Figure S47. ^{1}H NMR (acetone-d_6, 600 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(hydroxymethyl)benzene.

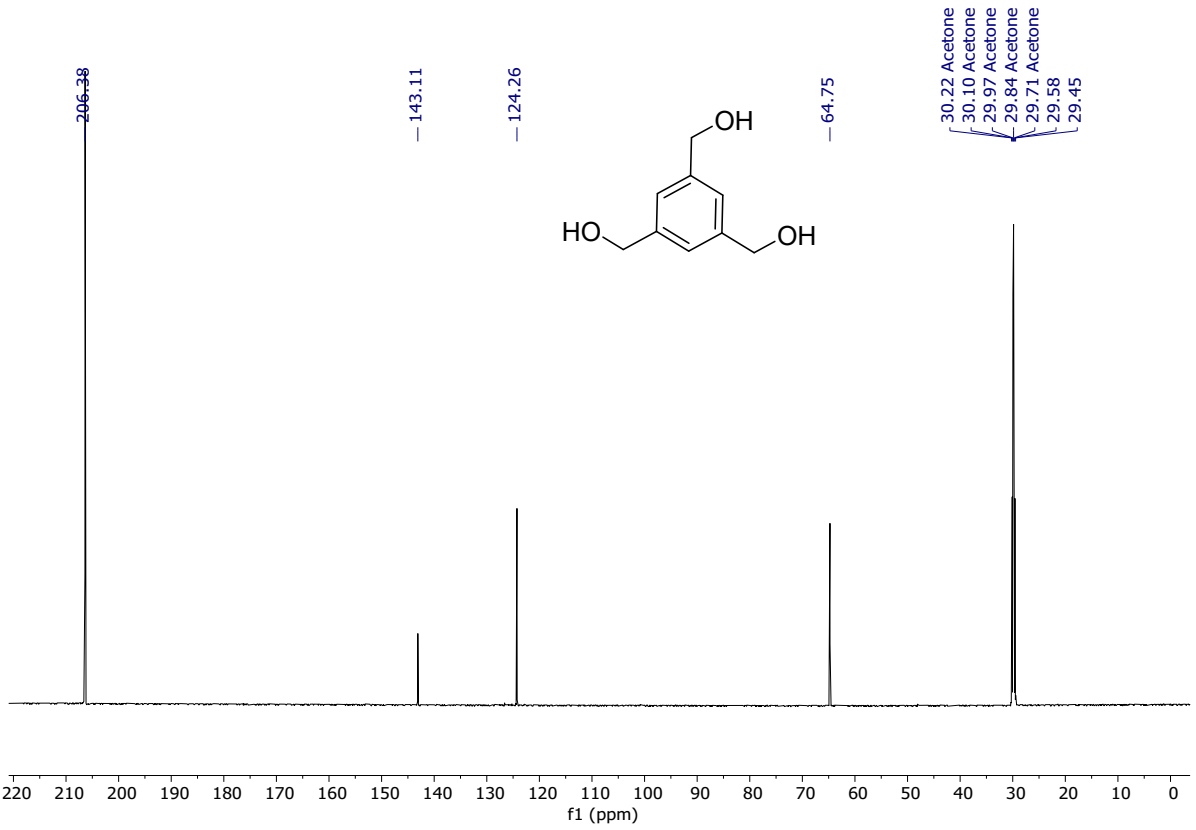


Figure S48. ^{13}C {^{1}H} NMR (acetone-d_6, 150.90 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(hydroxymethyl)benzene.

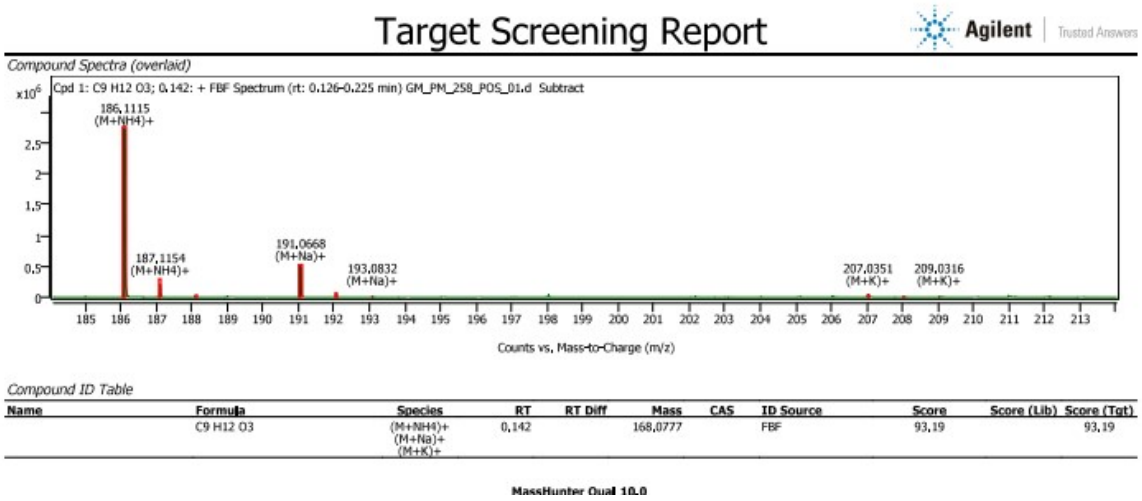


Figure S49. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(hydroxymethyl)benzene.

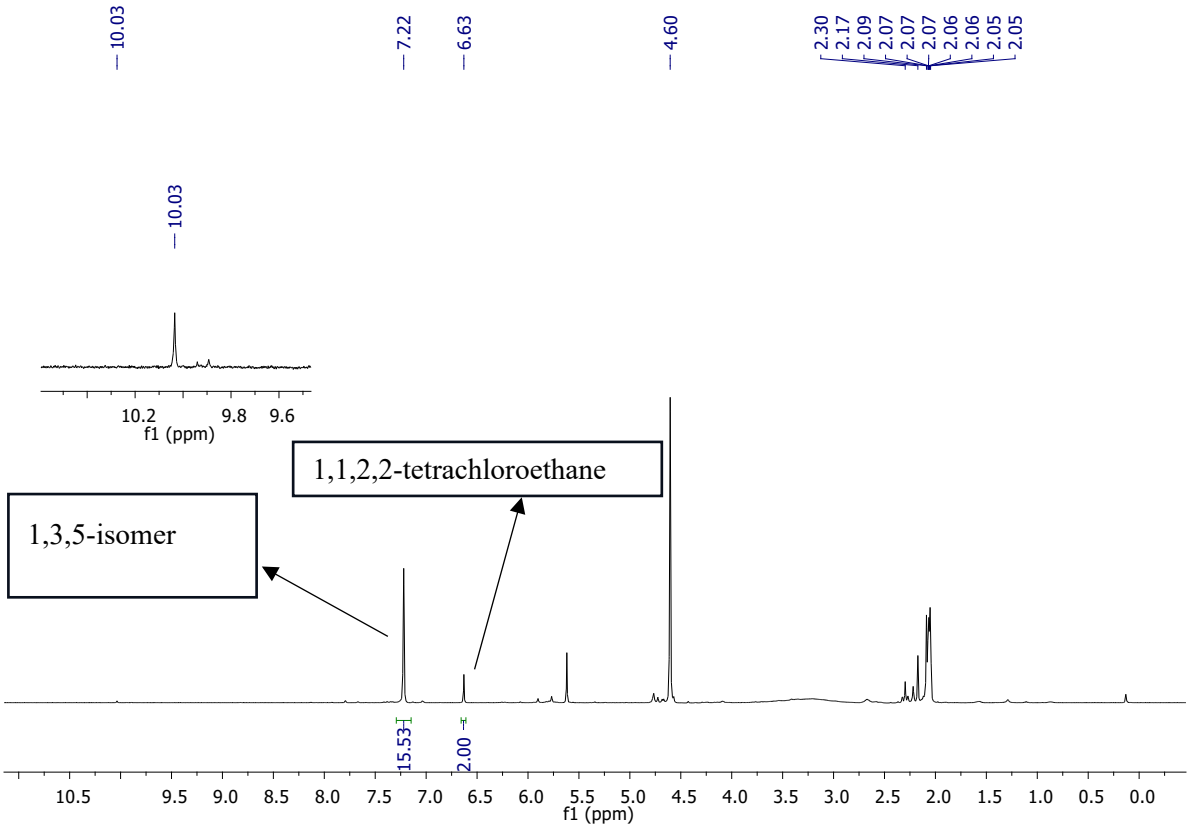


Figure S50. ^{1}H NMR spectrum (500 MHz, 25 °C, acetone-d_6) of the reaction mixture of propargyl alcohol (0.1 mL, 1.7 mmol) and complex **1** in CH_3CN after 24 h 86 °C. The solvent was removed, acetone-d_6 followed by 1,1,2,2-tetrachloroethane (0.010 mL, 0.095 mmol) (internal standard) were added. The NMR yield for the 1,3,5-isomer is 85%.

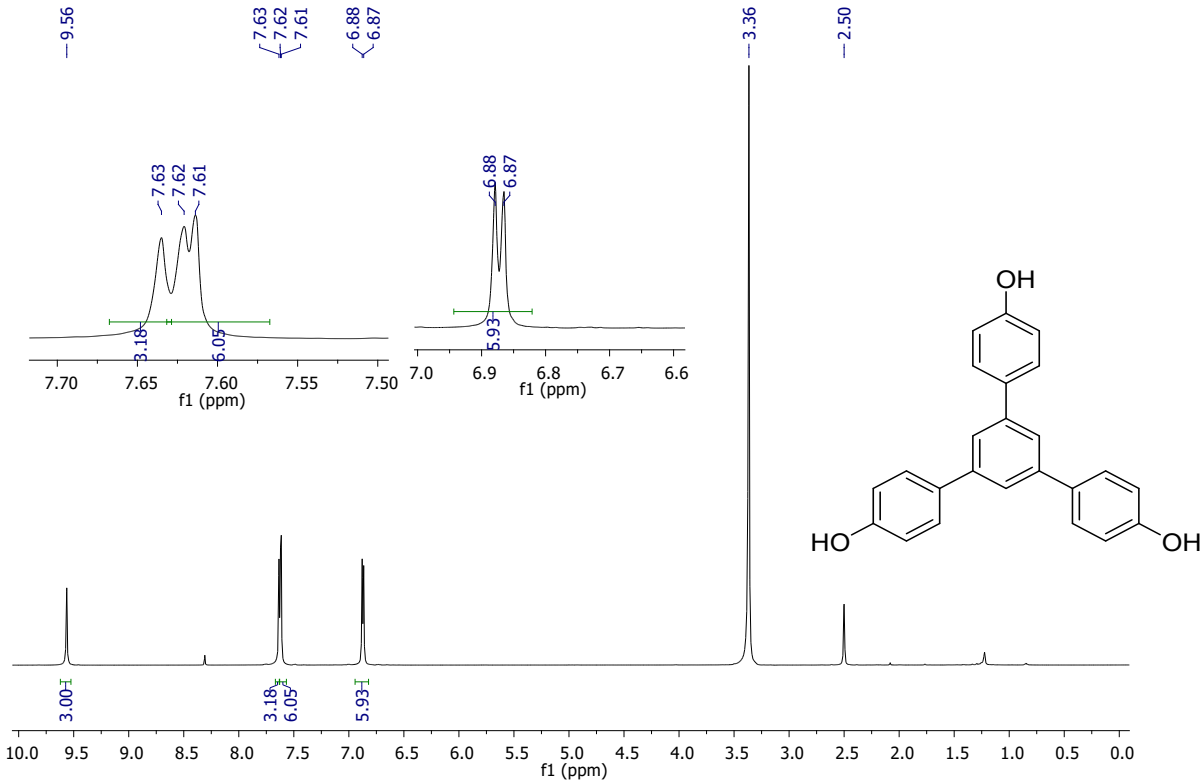


Figure S51. ^{1}H NMR (DMSO-d_6, 600 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-hydroxyphenyl)benzene.

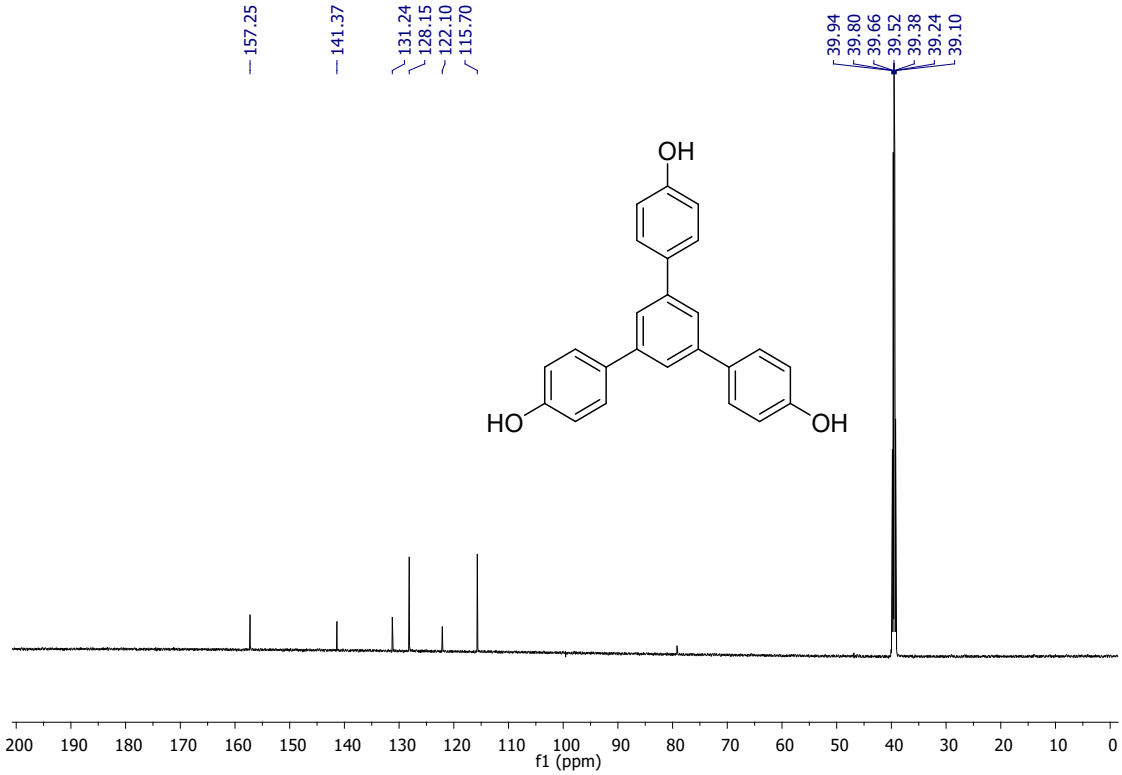


Figure S52. ^{13}C{^{1}H} NMR (DMSO-d_6, 150.90 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(4-hydroxyphenyl)benzene**.**

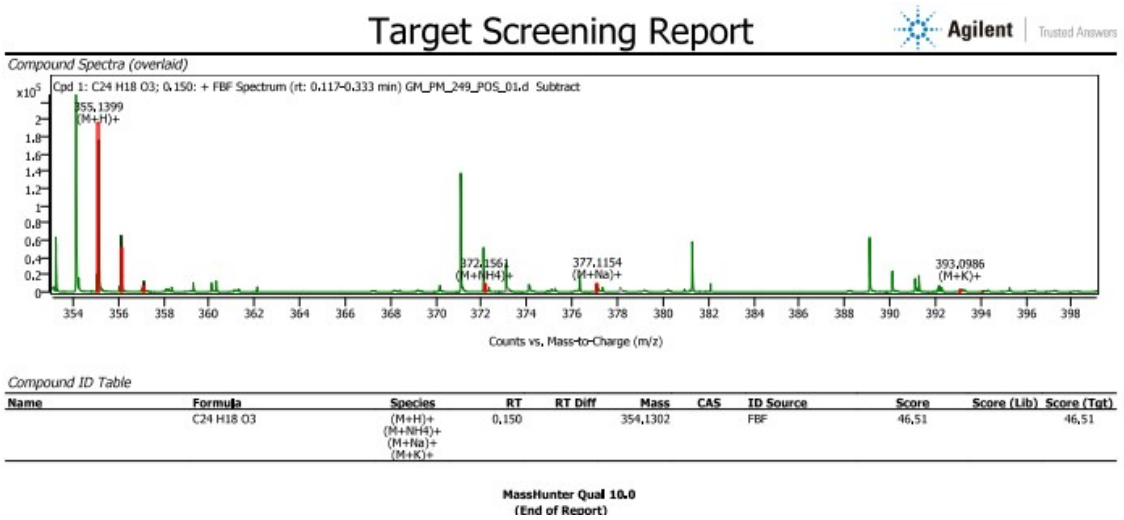


Figure S53. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(4-hydroxyphenyl)benzene.

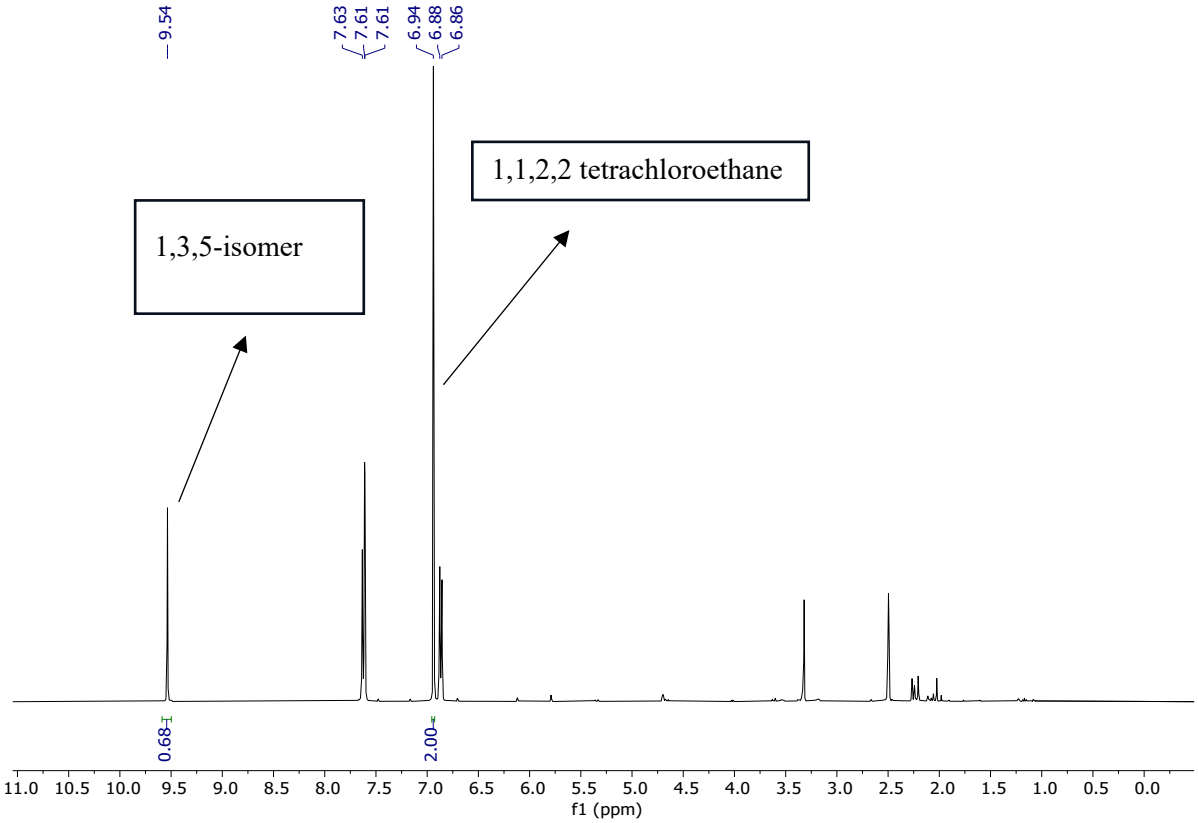


Figure S54. ^{1}H NMR spectrum (500 MHz, 25 °C, DMSO-d_6) of the reaction mixture of 4-ethynylphenol (0.020 g, 0.169 mmol) and complex **2** in toluene after 24 h at 80 °C. The solvent was removed under vacuum. DMSO-d_6 and 1,1,2,2-tetrachloroethane (0.020 mL, 0.189 mmol) as an internal standard were added. The NMR yield for the 1,3,5-isomer is 76.05%.

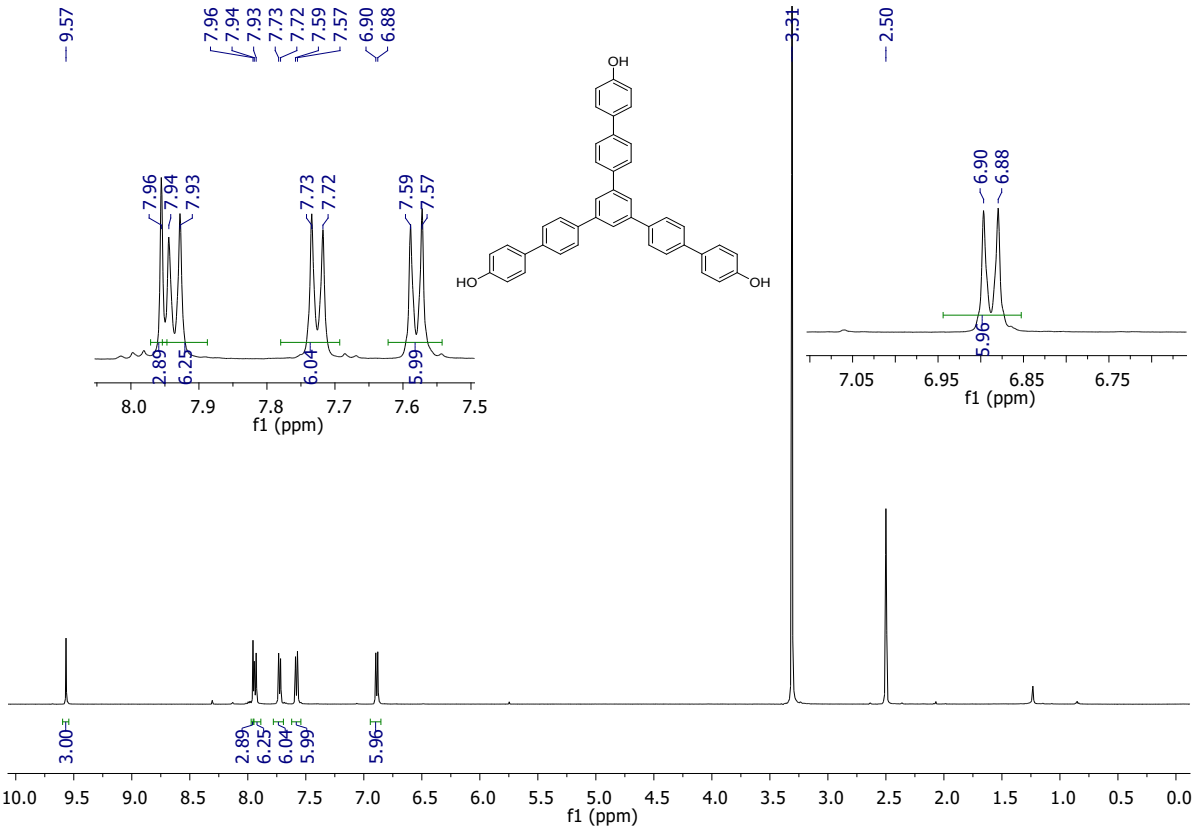


Figure S55. ^{1}H NMR (DMSO-d_6, 500 MHz, 25 °C) spectrum of the isolated compound **14**.

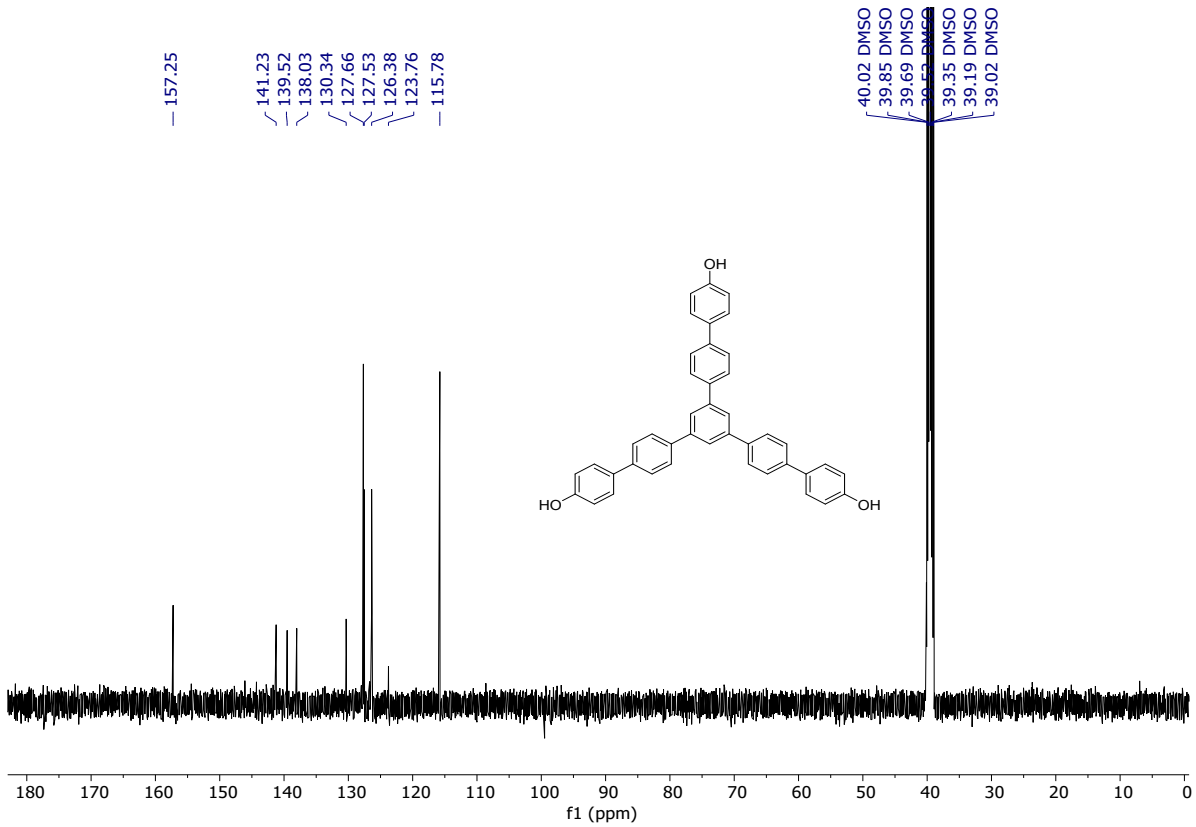


Figure S56. ^{13}C {^{1}H} NMR (DMSO-d_6, 125.76 MHz, 25 °C) spectrum of the isolated compound **14**.

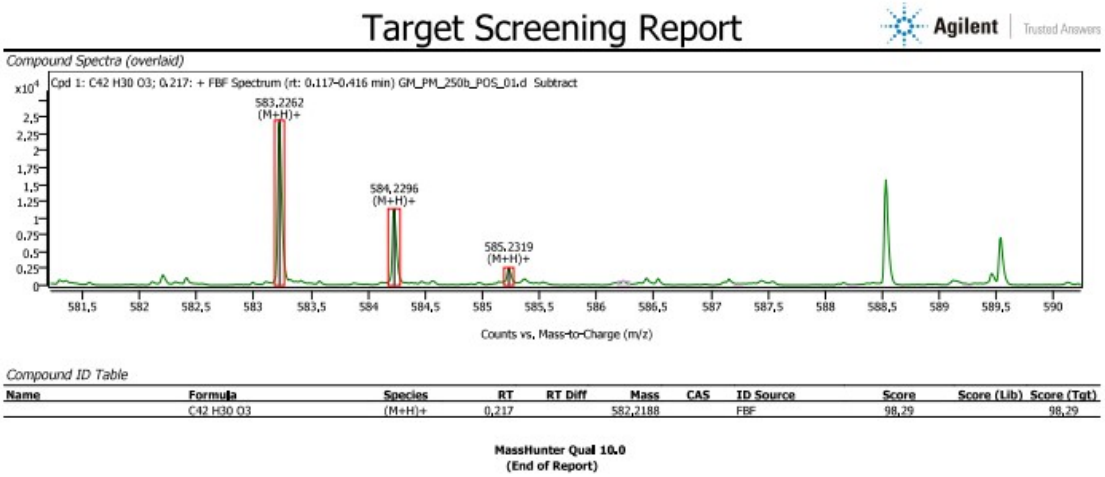


Figure S57. HRMS(ESI+) spectrum of the isolated compound **14**.

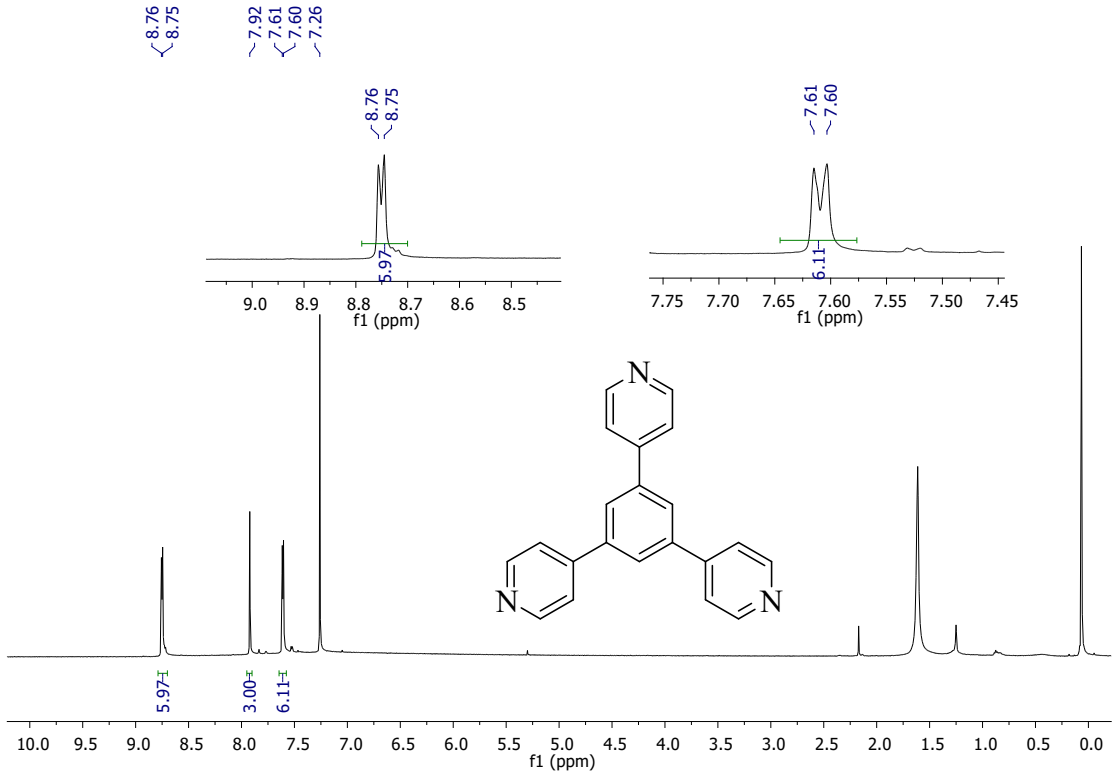


Figure S58. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(pyridine-4-yl)benzene.

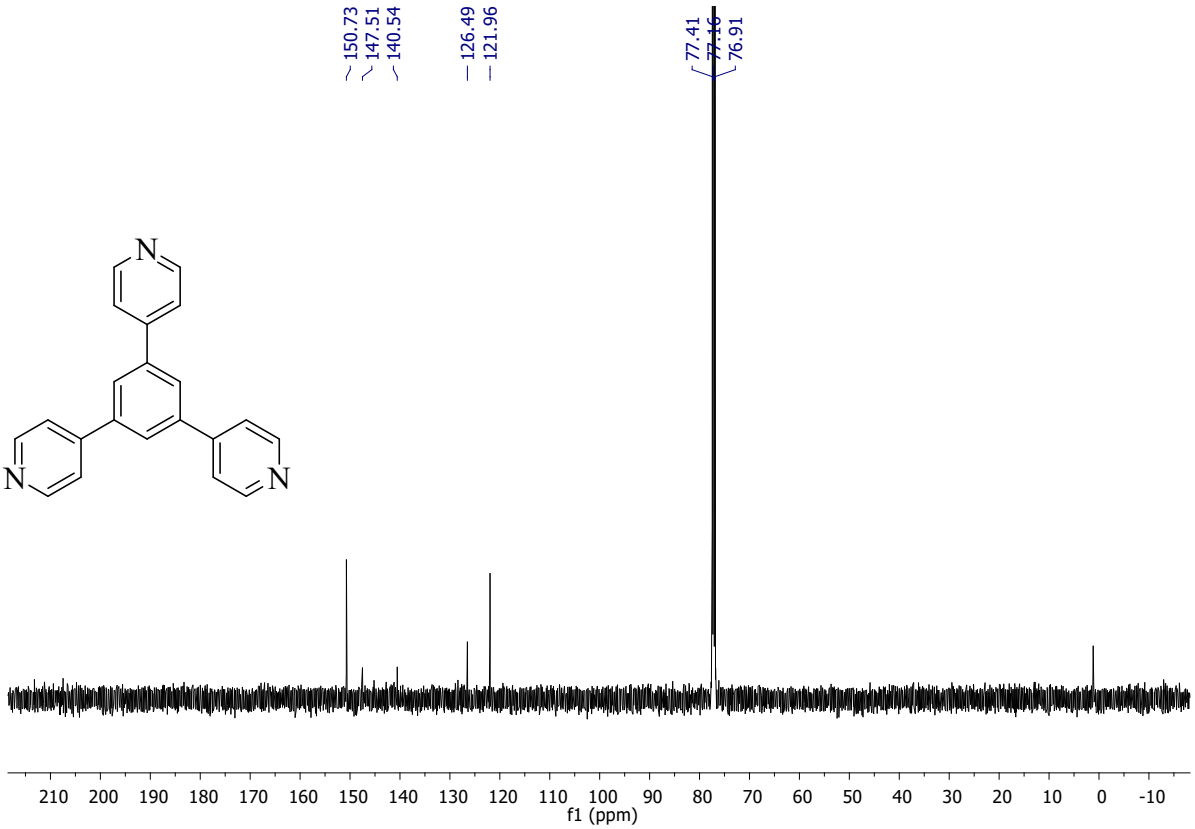


Figure S59. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.76 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(pyridine-4-yl)benzene.

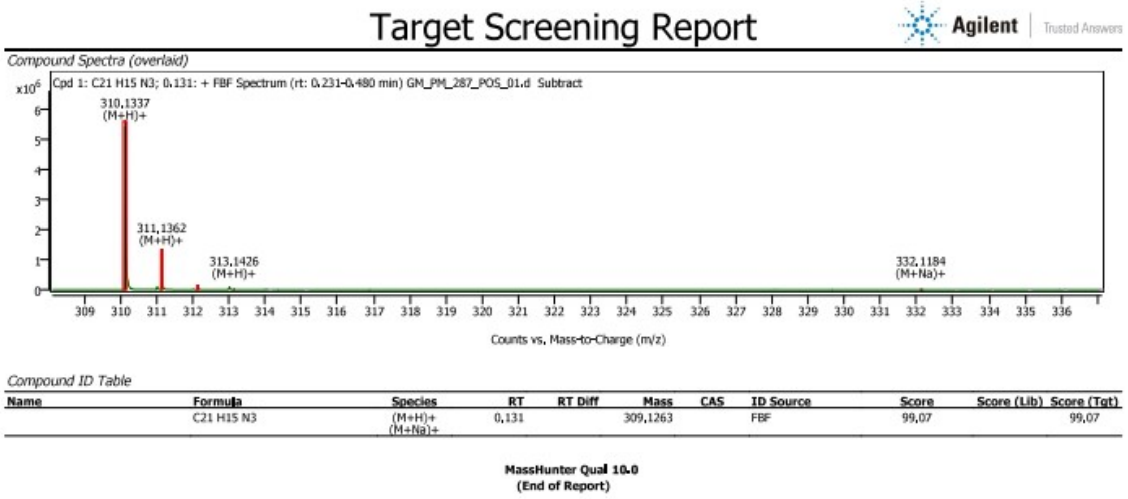


Figure S60. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(pyridine-4-yl)benzene.

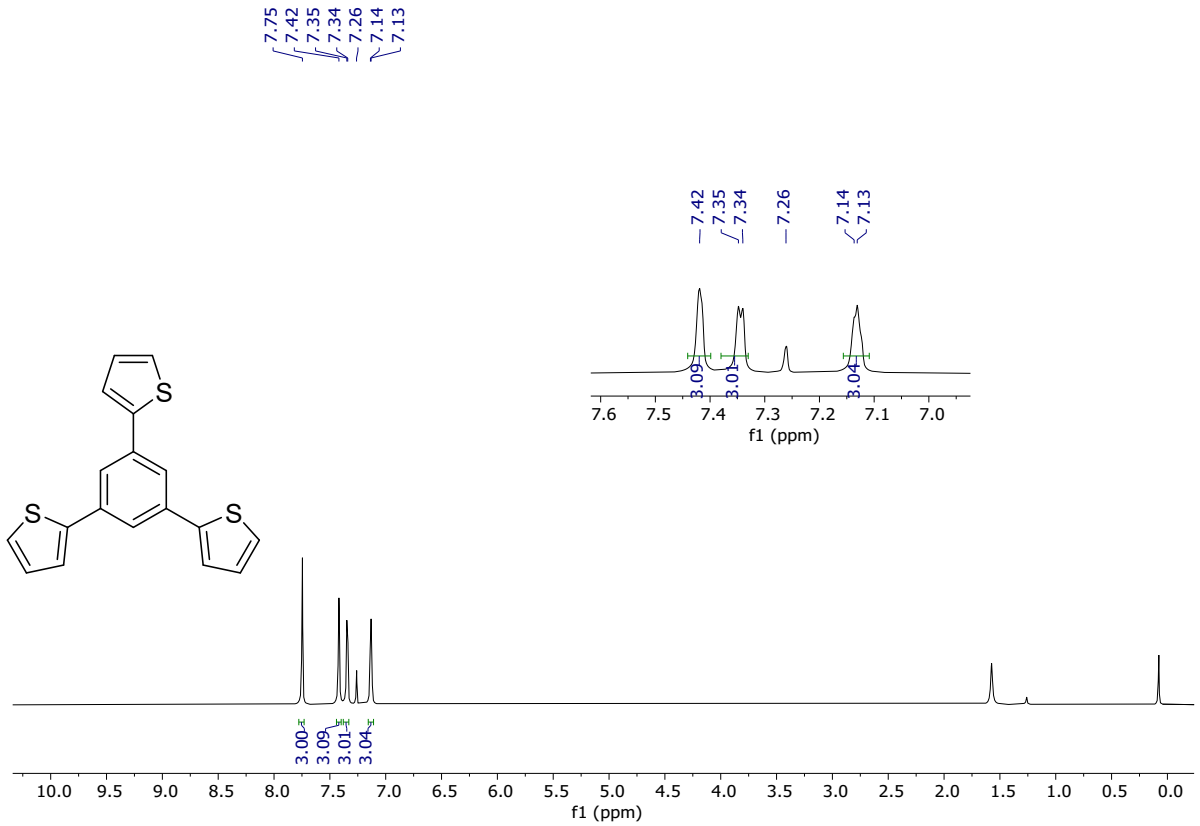


Figure S61. ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(2-thienyl)benzene.

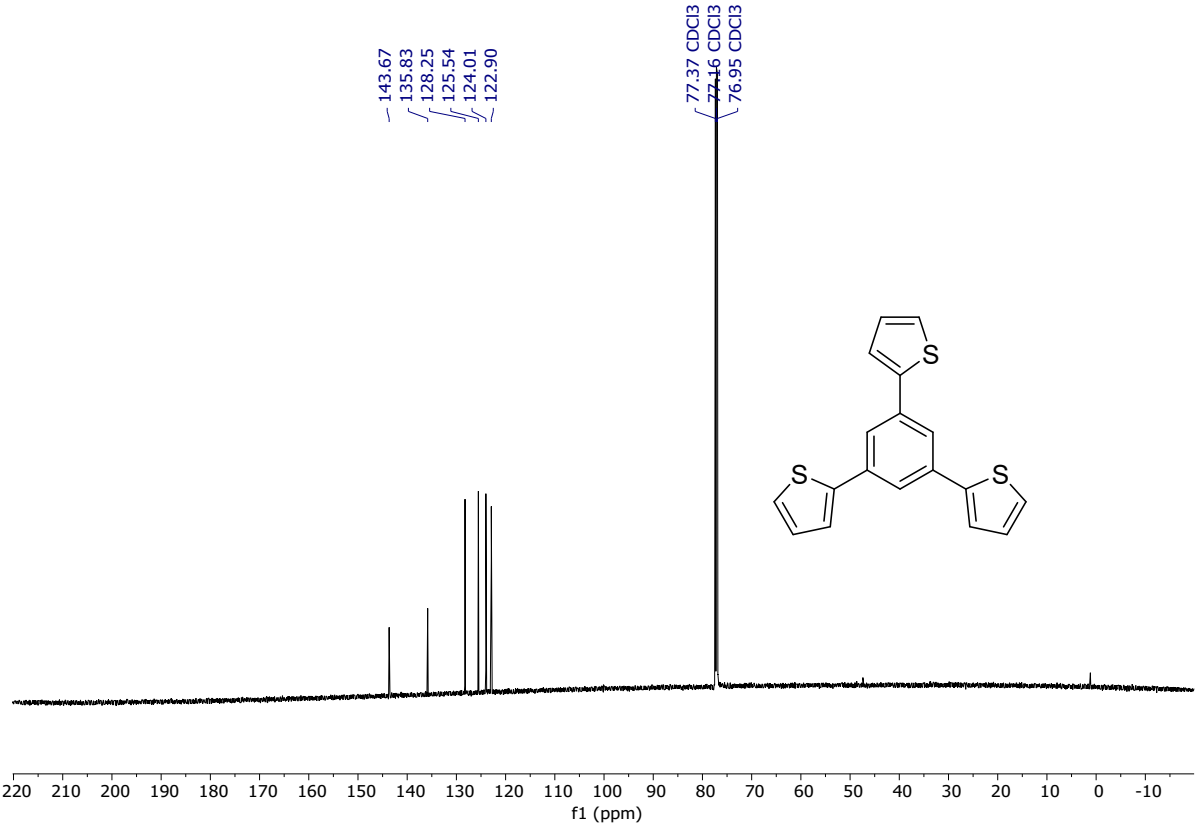


Figure S62. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$,150.90 MHz, 25 °C) spectrum of the isolated 1,3,5-tris(2-thienyl)benzene.

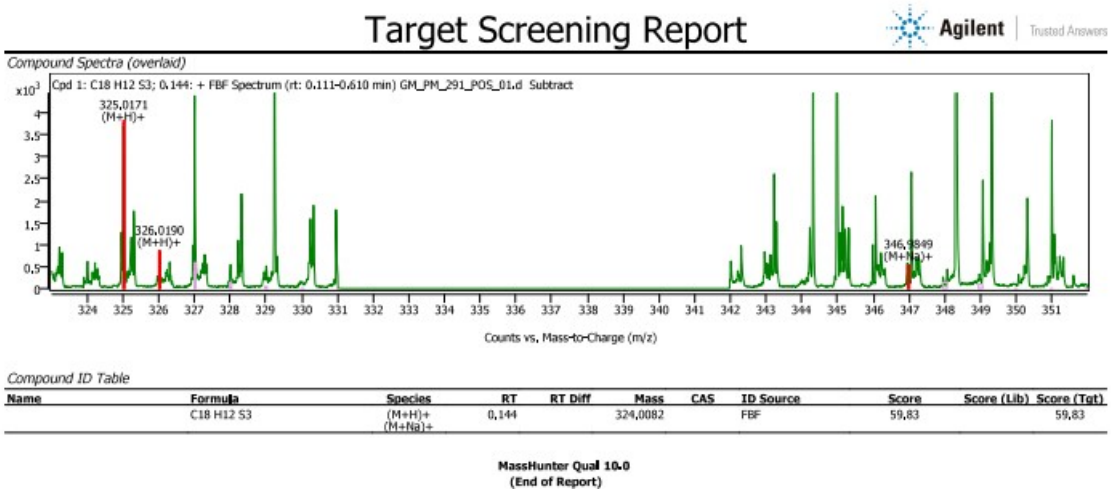


Figure S63. HRMS(ESI+) spectrum of the isolated 1,3,5-tris(2-thienyl)benzene.

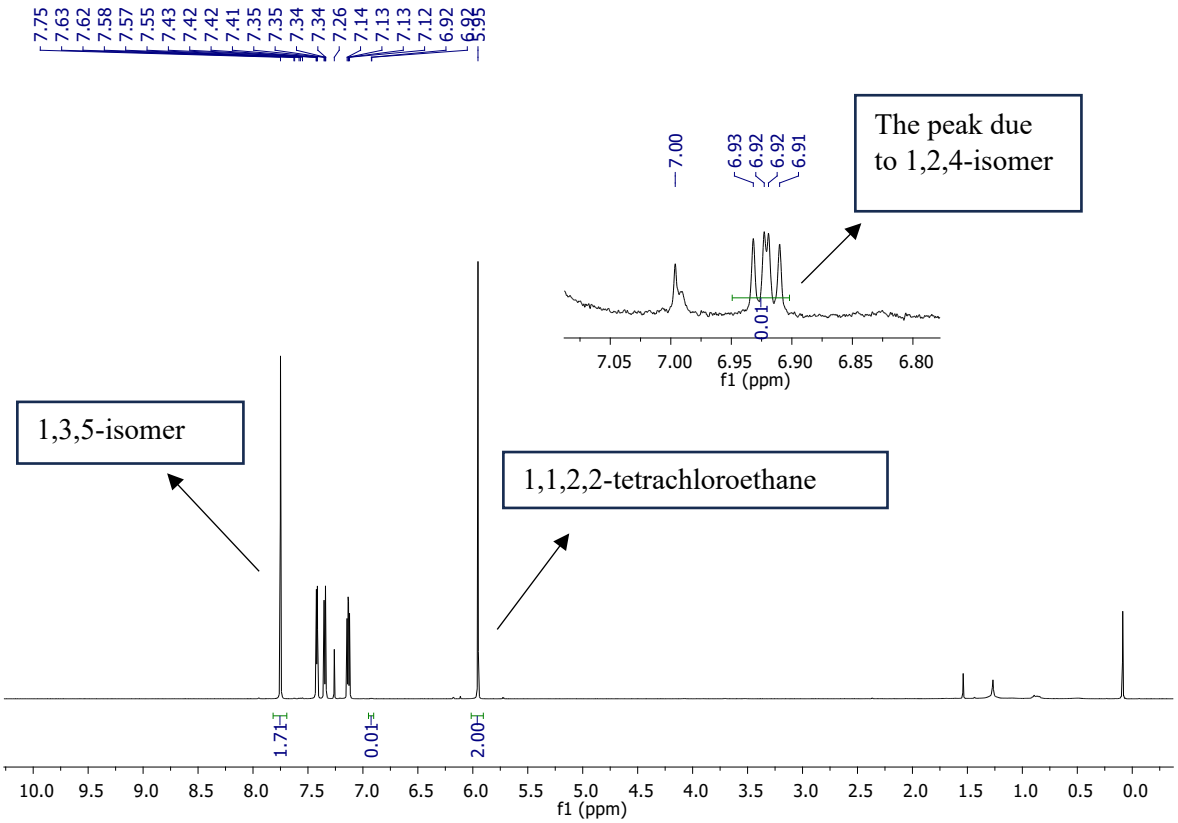


Figure S64. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 2-ethynylthiophene (0.020 mL, 0.203 mmol) and complex **2** in toluene after 24 h at 80 °C. The reaction mixture was passed through a flash silica gel column using DCM/pentane (*v*/*v* = 1/3). Solvent was removed by rotary evaporator. $CDCl_3$ and 1,1,2,2-tetrachloroethane (0.010 mL, 0.095 mmol) as an internal standard were added. The NMR yield for the 1,3,5-isomer is 79.61% and that of the 1,2,4-isomer is 1.4%.

Mechanistic Study.

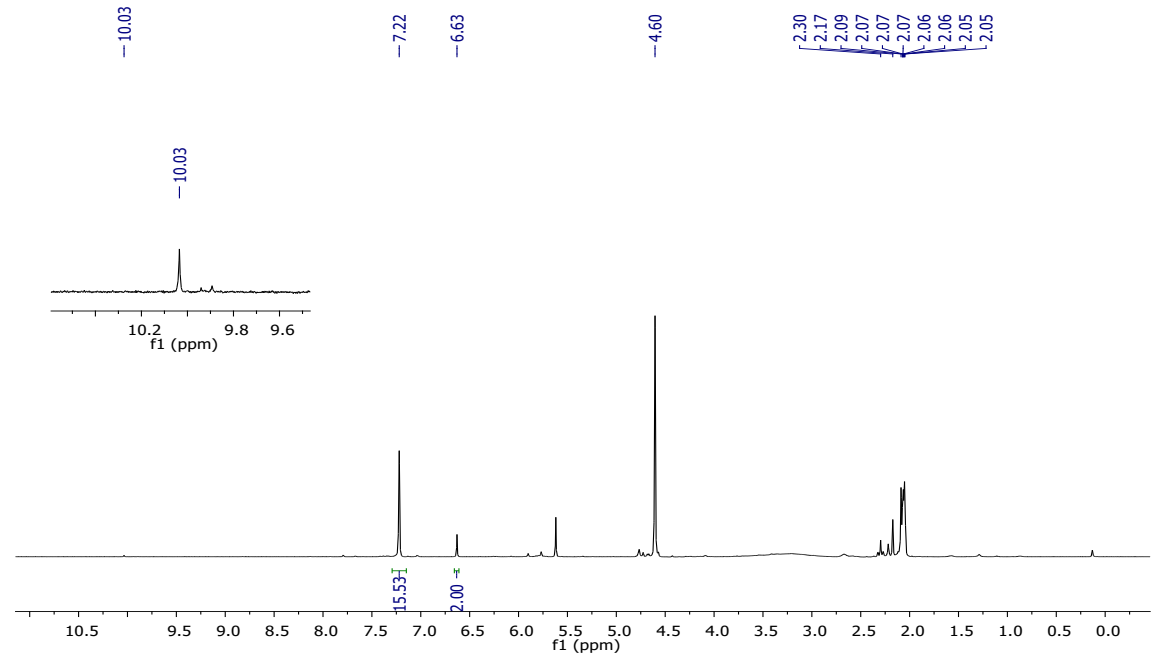


Figure S65. ^{1}H NMR spectrum (400 MHz, 25 °C, acetone-d_6) of the reaction mixture of propargyl alcohol in the presence of complex **2** (2.5 mol%) in CH_3CN at 80 °C for 24 h. The peak at δ 10.03 ppm is assigned to the η^2-coordination of alkyne to the molybdenum atom.

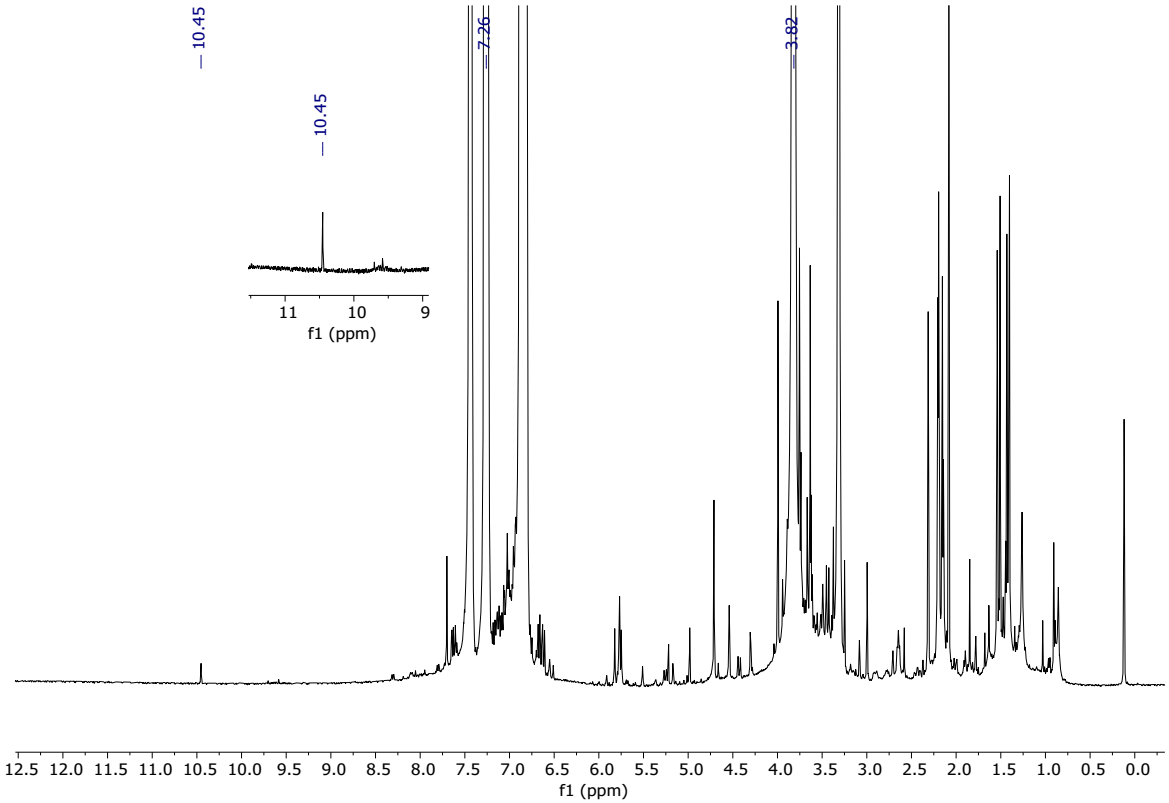


Figure S66. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 1-ethynyl -2-methoxybenzene in the presence of complex **2** under neat conditions at 80 °C for 3 h. The peak at δ 10.45 ppm is assigned to the η^2-coordination of alkyne to the molybdenum atom.

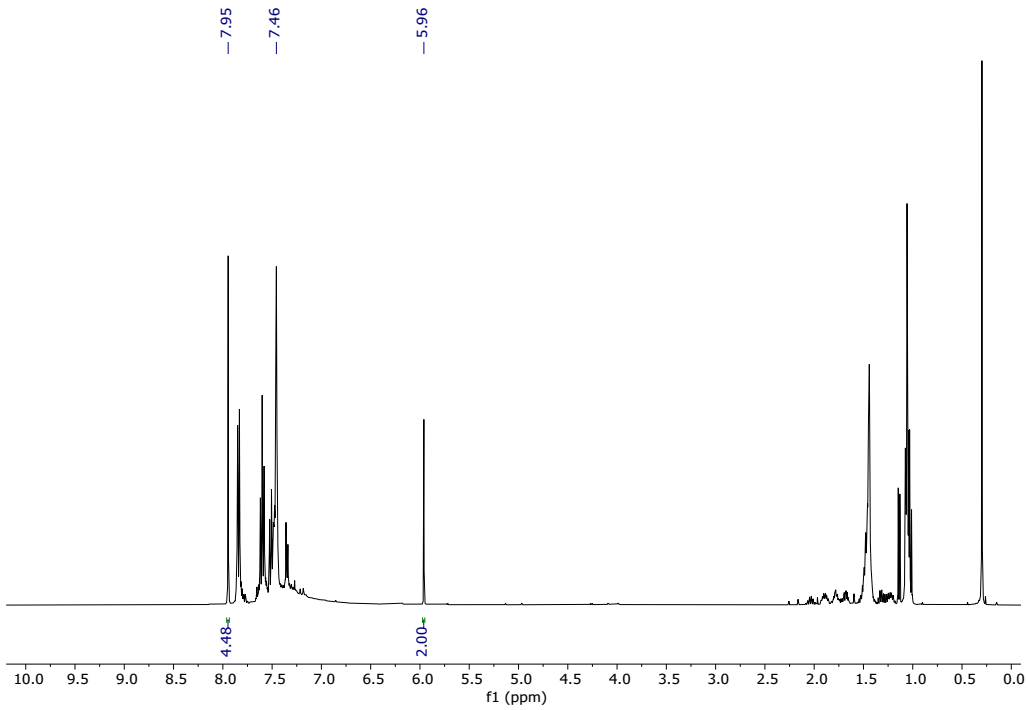


Figure S67. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of phenylacetylene (0.10 mL, 0.91 mmol), complex **2** (0.0116 g, 0.023 mmol) and mercury (0.091 g, 0.454 mmol) in toluene after 8 h at 80 °C. The solvent was removed by vacuum and 1,1,2,2 tetrachloroethane (0.020 mL, 0.189 mmol) was added as an internal standard. NMR yield for 1,3,5 isomer: 93%.

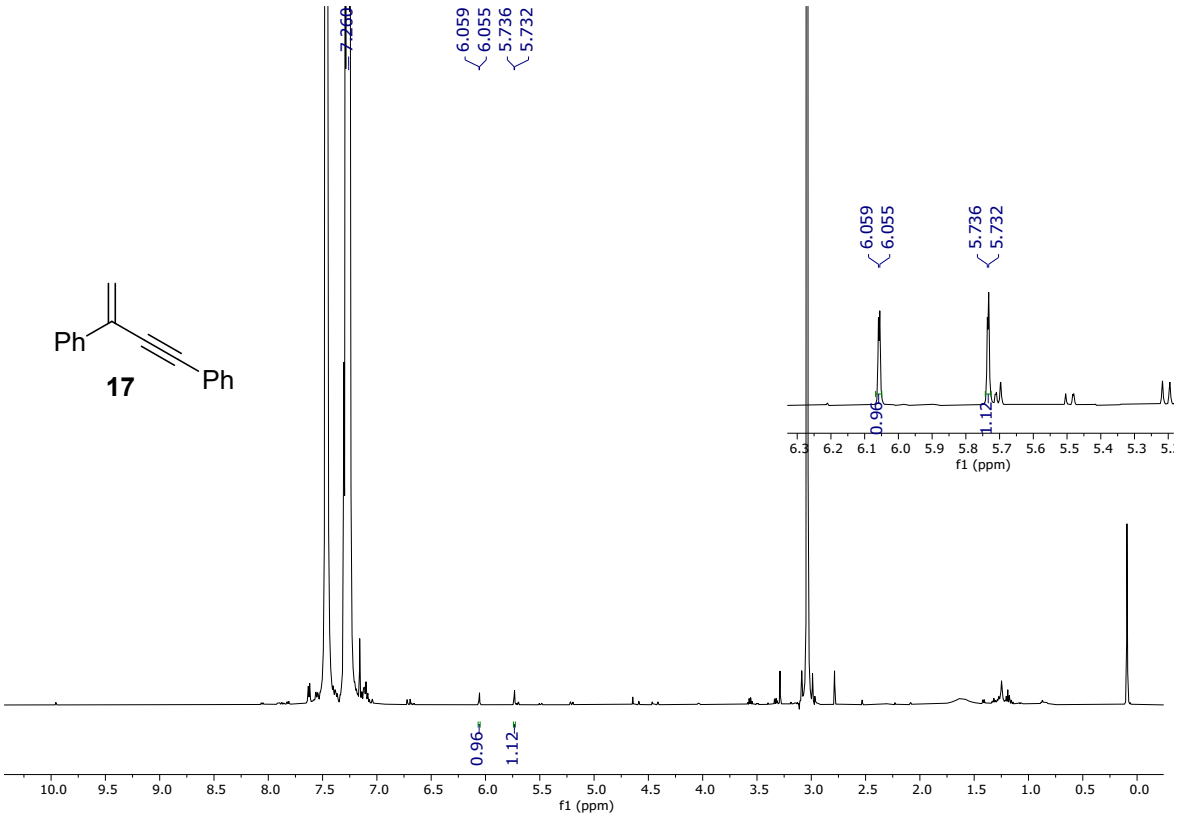


Figure S68. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of phenylacetylene (0.015 mL, 0.138 mmol) and complex **2** (0.030 g, 0.062 mmol) in toluene after 1 h at 80 °C. After 1 h, methanol (1 mL) was added, and the resulting solution was stirring at room temperature for 24 h. The solvent was removed under vacuum, $CDCl_3$ was added and then NMR was recorded. The two doublets (inlet spectrum) indicate the formation of gem-1,3-enynes **17**.

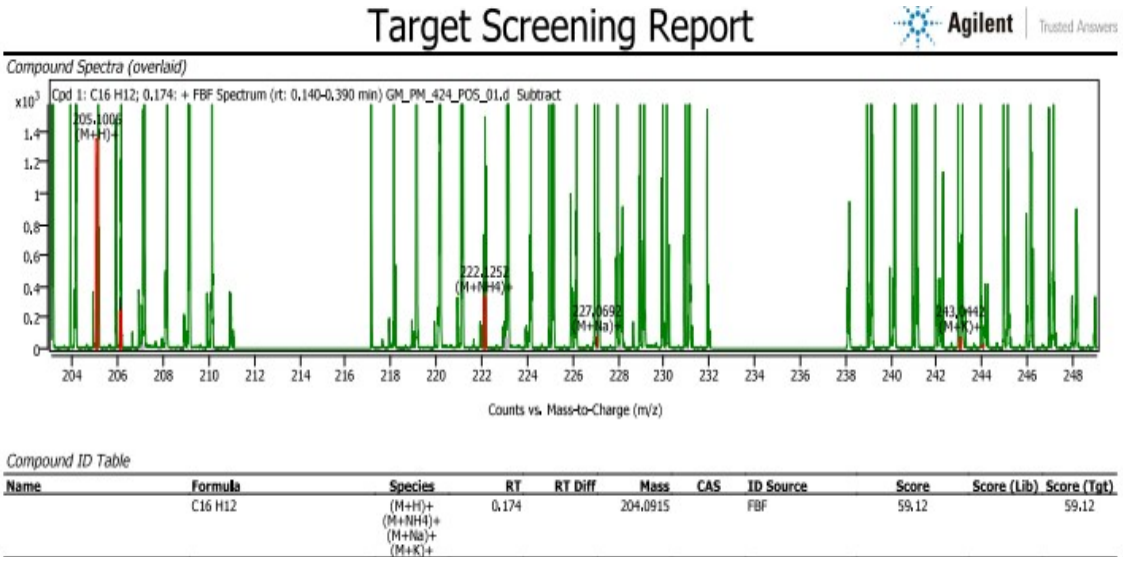


Figure S69. HRMS(ESI+) spectrum for the reaction mixture obtained of phenylacetylene (0.100 mL, 0.910 mmol) and complex **2** (0.465 g, 0.911 mmol) after 4 h at 80 °C. After 4 h, methanol (1 mL) was added, and the resulting solution was stirring at room temperature for 24 h. The solvent was removed under vacuum, and the residue was submitted for HRMS(ESI+); it shows 1,3-enynes **17** formation. [**17**+H]$^{+}$ $C_{16}H_{13}$: calc. 205.1012, found 205.1006.

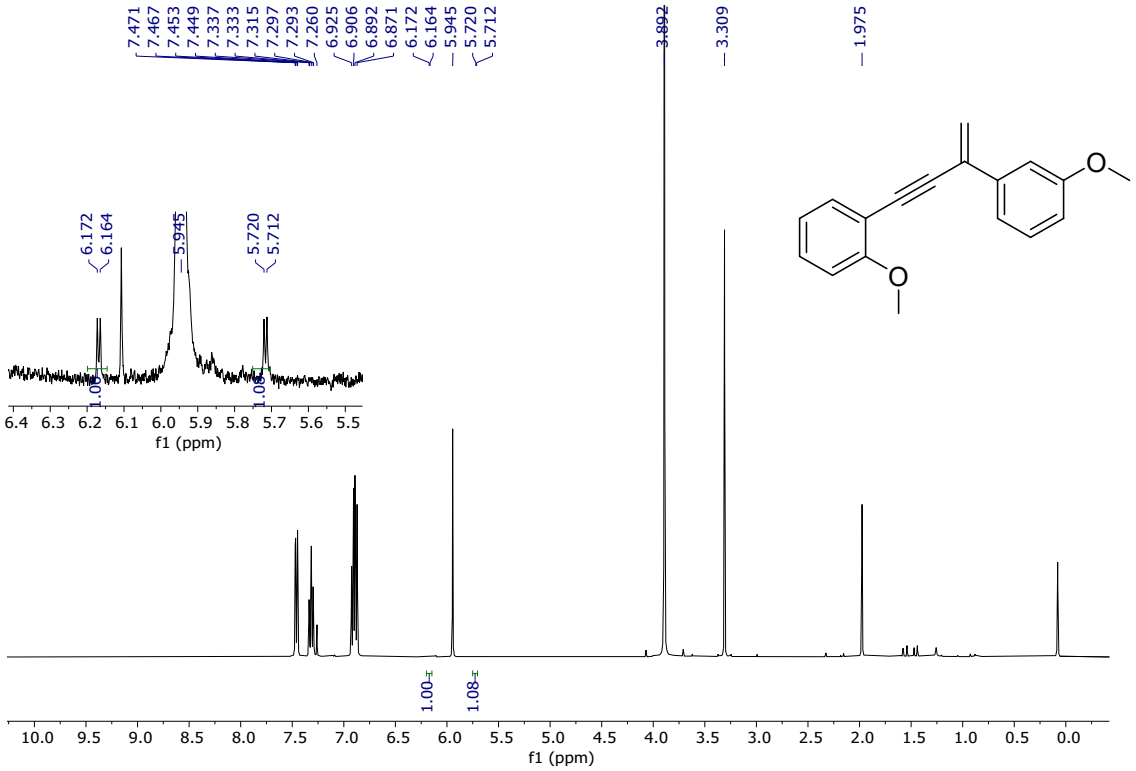


Figure S70. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of the reaction mixture of 1-ethynyl-2-methoxybenzene (0.40 mL, 3.09 mmol) and complex **2** (0.039 g, 0.076 mmol) in toluene after 1 h at 80 °C. The solvent was removed under vacuum, $CDCl_3$ was added and then NMR recorded. The two doublets (inlet spectrum) indicate the formation of gem-1,3-enynes **18**.

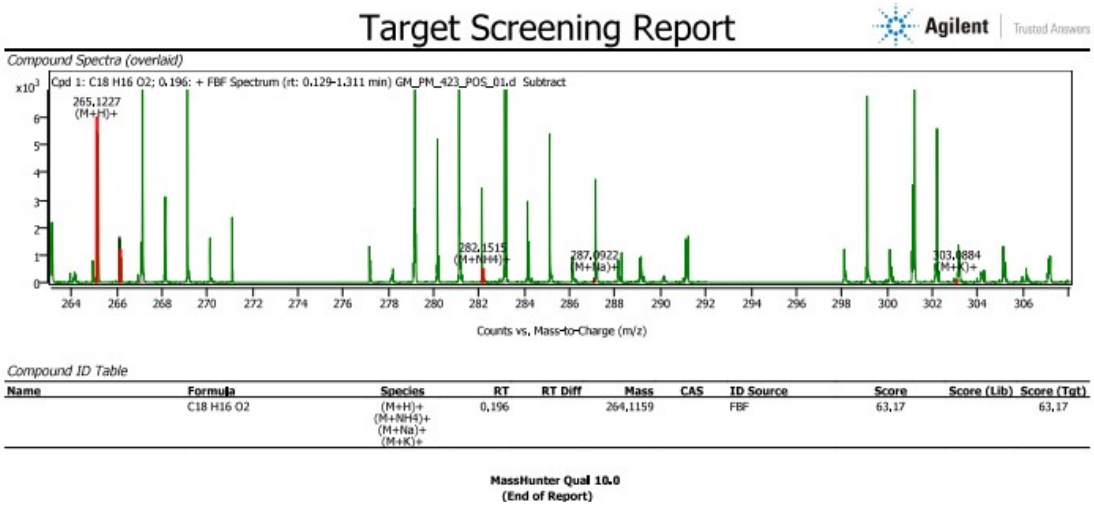


Figure S71. HRMS(ESI+) spectrum for the reaction mixture of 1-ethynyl-2-methoxybenzene (0.40 mL, 3.09 mmol) and complex **2** (0.039 g, 0.076 mmol) toluene after 1 h at 80 °C. The solvent was removed under vacuum, and the residue was submitted for HRMS(ESI+); it shows 1,3-enynes **18** formation. [**18**+H]$^{+}$ $C_{18}H_{17}O_2$: calc. 265.1223, found 265.1227.

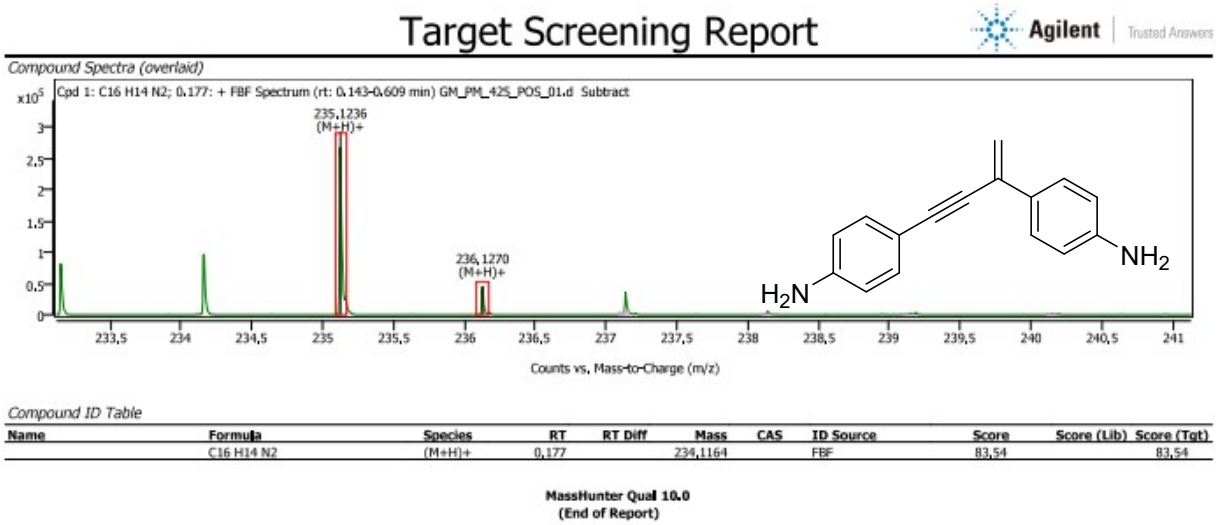


Figure S72. HRMS(ESI+) spectrum for the reaction mixture of 4-ethynylaniline (0.02 g, 0.17 mmol) and complex **2** (0.002 g, 0.004 mmol) toluene after 4 h at 80 °C. The solvent was removed under vacuum, and the residue was submitted for HRMS(ESI+); it shows 1,3-enynes formation. $[M+H]^+$ $C_{16}H_{15}N_2$: calc. 235.1230, found 235.1236.

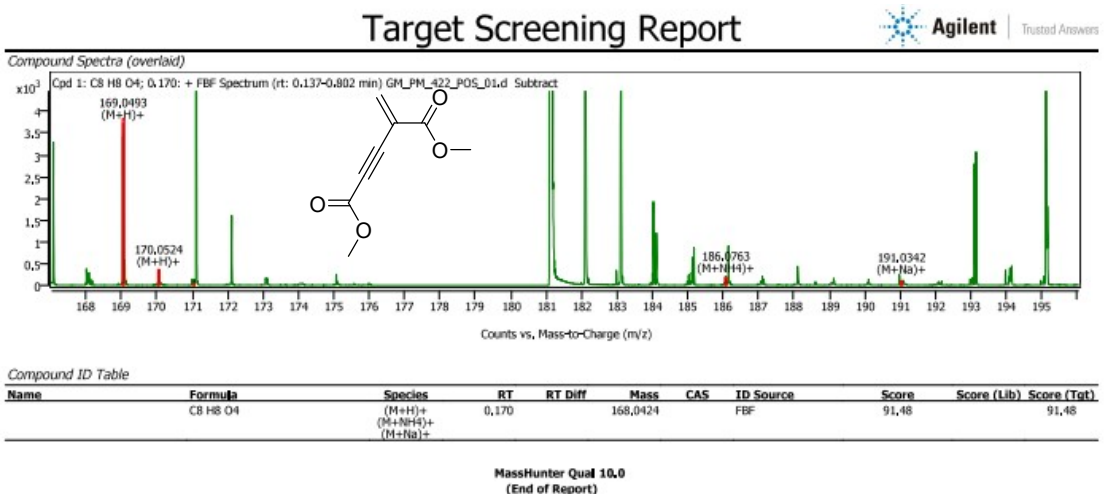


Figure S73. HRMS(ESI+) spectrum for the reaction mixture of methyl propiolate (0.05 mL g, 0.56 mmol) and complex **2** (0.007 g, 0.0.014 mmol) after 4 h at 80 °C without solvent. The residue was submitted for HRMS(ESI+); it shows 1,3-enynes formation. $[M+H]^+$ $C_8H_9O_4$: calc. 169.0495, found 169.0493.

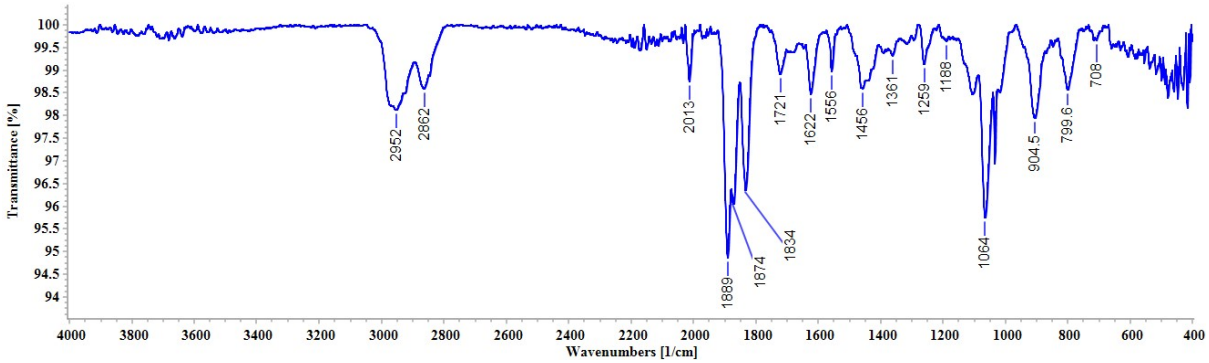


Figure S74. ATR-IR spectrum of the reaction mixture of complex **2** (0.050 g, 0.098 mmol) and phenylacetylene (0.021 mL, 0.191 mmol) after 4 h at 80 °C without solvent. The shifted carbonyl stretching frequencies compared with the spectrum of **2** indicate ligand bound Mo carbonyl acts as catalyst.

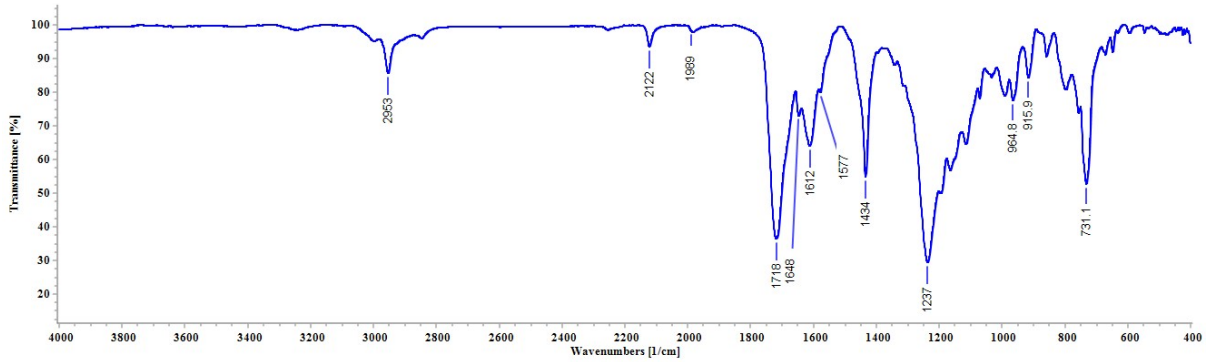


Figure S75. ATR-IR spectrum of the reaction mixture of complex **2** (0.050 g, 0.098 mmol) and methyl propiolate (0.035 mL, 0.393 mmol) after 1 h at 80 °C without solvent. The shifted carbonyl stretching frequencies compared with the spectrum of **2** indicate ligand bound Mo carbonyl acts as catalyst.

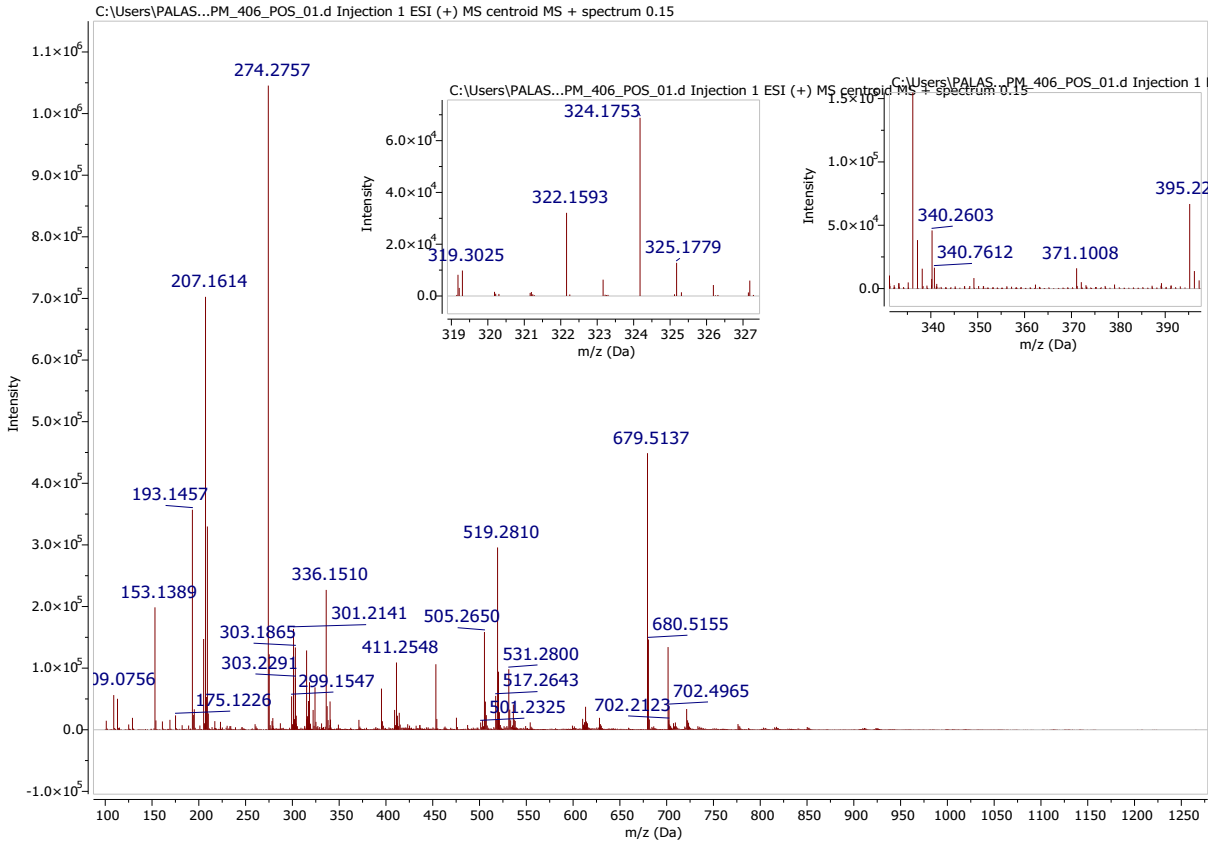


Figure S76. HRMS(ESI+) spectrum of the reaction mixture of phenylacetylene (0.028 mL, 0.255 mmol), gem-1,3-enyne **19** (0.062 g, 0.259 mmol) and complex **2** (0.003 g, 0.006 mmol) in toluene after 8 h at 80 °C. The solvent was removed, the residue was submitted for HRMS; it shows the formation of **3** [$M+NH_4]^+$ $C_{24}H_{22}N$ Calc: 324.1747; found 324.1753 and no formation of **20** (next inset).

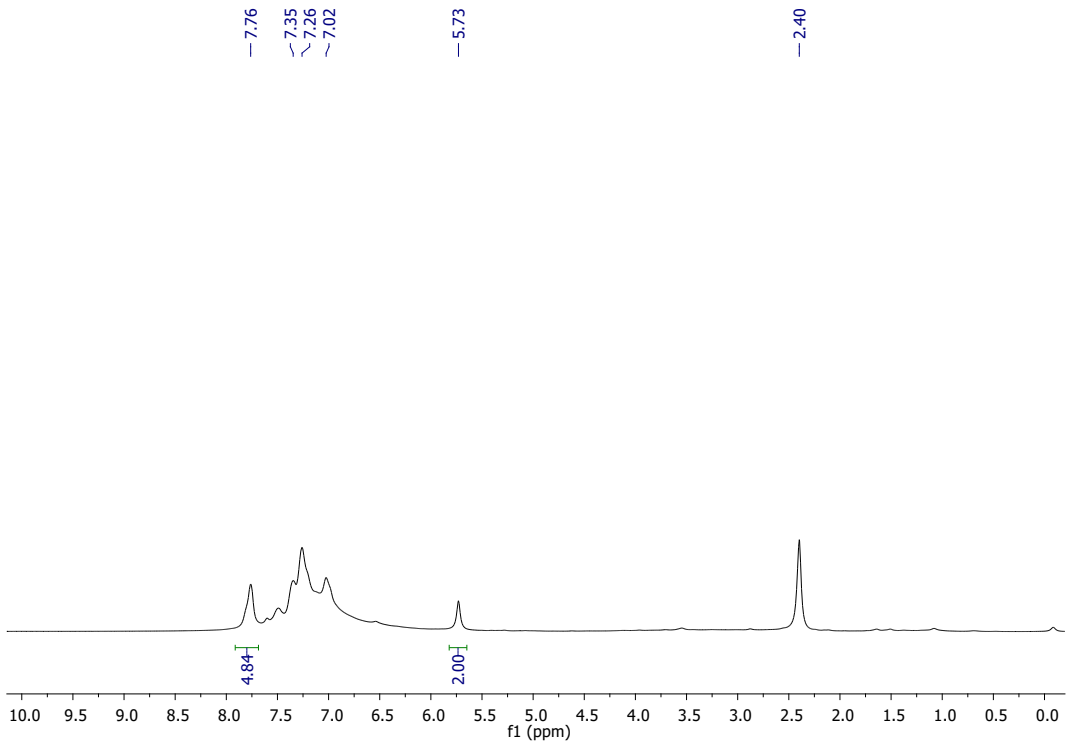


Figure S77. ^{1}H NMR spectrum (500 MHz, 25 ℃, $CDCl_3$) of the reaction mixture of phenylacetylene (0.250 mL, 2.276 mmol) and complex **1** (0.057 g, 0.057 mmol) without solvent after 24 h 80 °C. 1,1,2,2 Tetrachloroethane (0.020 mL, 0.189 mmol) was added as an internal standard. NMR yield for 1,3,5-isomer: 40.23 %. This lower yield compared with >90% (NMR yield) obtained with complex **2** can be due to the insolubility of complex **1**.

References

1 G. M. Sheldrick, *Acta Cryst. Sect. A*: *Found. Crystallogr.*, 2015, **71**, 3.
2 G. M. Sheldrick, *Acta Cryst. Sect. C*: *Struct. Chem.*, 2015, **71**, 3.