Supporting Information

Efficient (Z)-selective semihydrogenation of alkynes catalyzed by air-stable imidazolyl amino molybdenum cluster sulfides

*María Gutiérrez-Blanco,[a] Eva Guillamón,[a] Vicent S. Safont,[a] Andrés G. Algarra,[b] M. Jesús Fernández-Trujillo,[b] Kathrin Junge,[c] Manuel G. Basallote, *[b] Rosa Llusar,*[a] and Matthias Beller*[c]*

[a] Departament de Química Física i Analítica, Universitat Jaume I. Av. Sos Baynat s/n, 12071 Castelló, Spain

[b] Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Instituto de Biomoléculas (INBIO), Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 Cádiz, Spain.

[c] Leibniz-Institute for Catalysis, Albert-Einstein-Street 29a, 18059 Rostock, Germany

Table of contents

1. Catalysts characterization

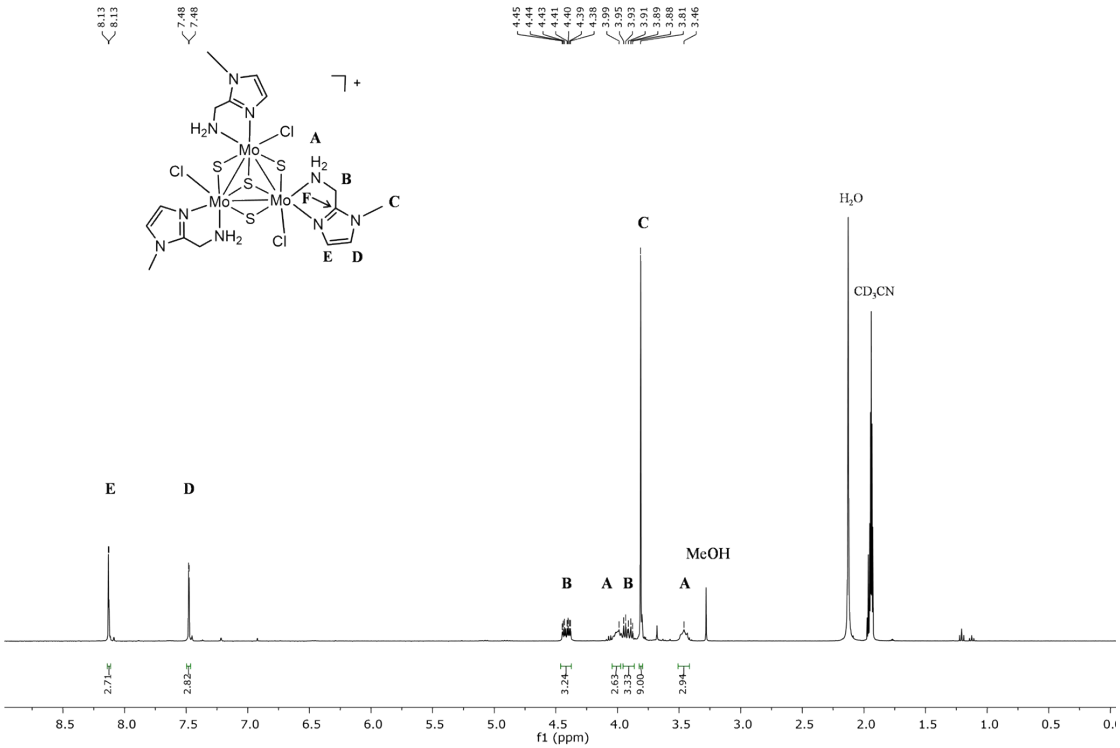


Figure SI1. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of the [**1**]BF_4 complex

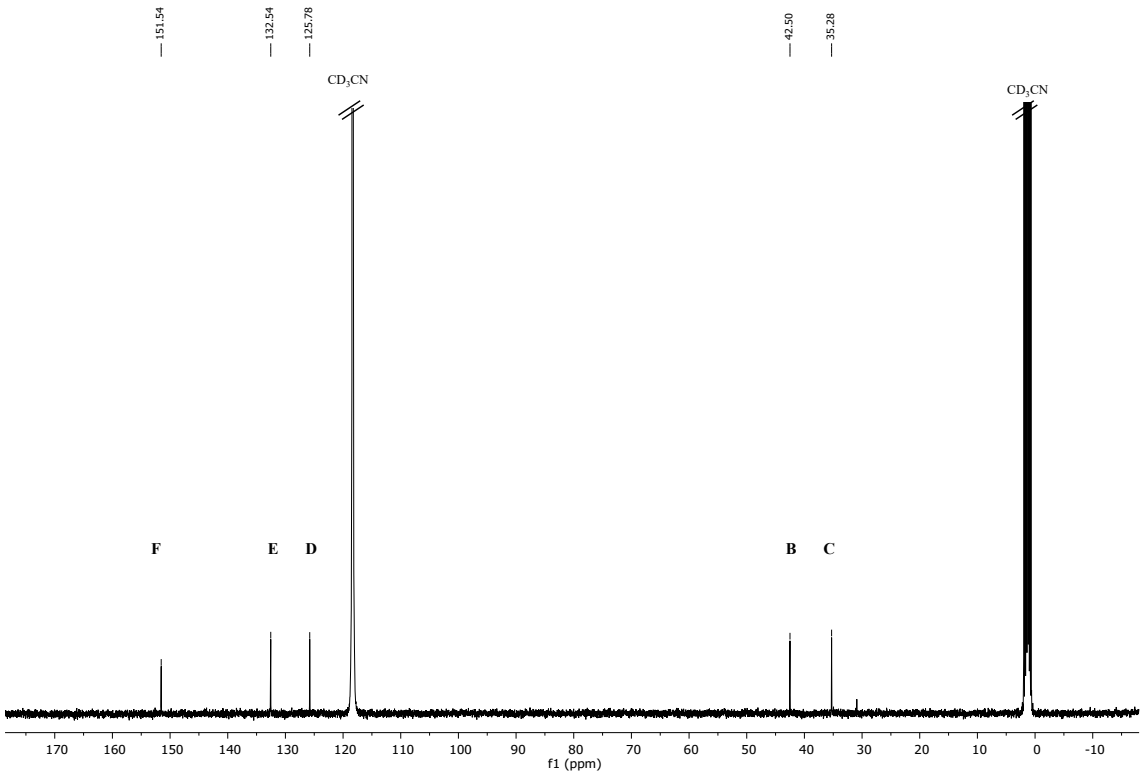


Figure SI2. ^{13}C NMR (101MHz, CD_3CN, 298 K) spectrum of the [**1**]BF_4 complex.

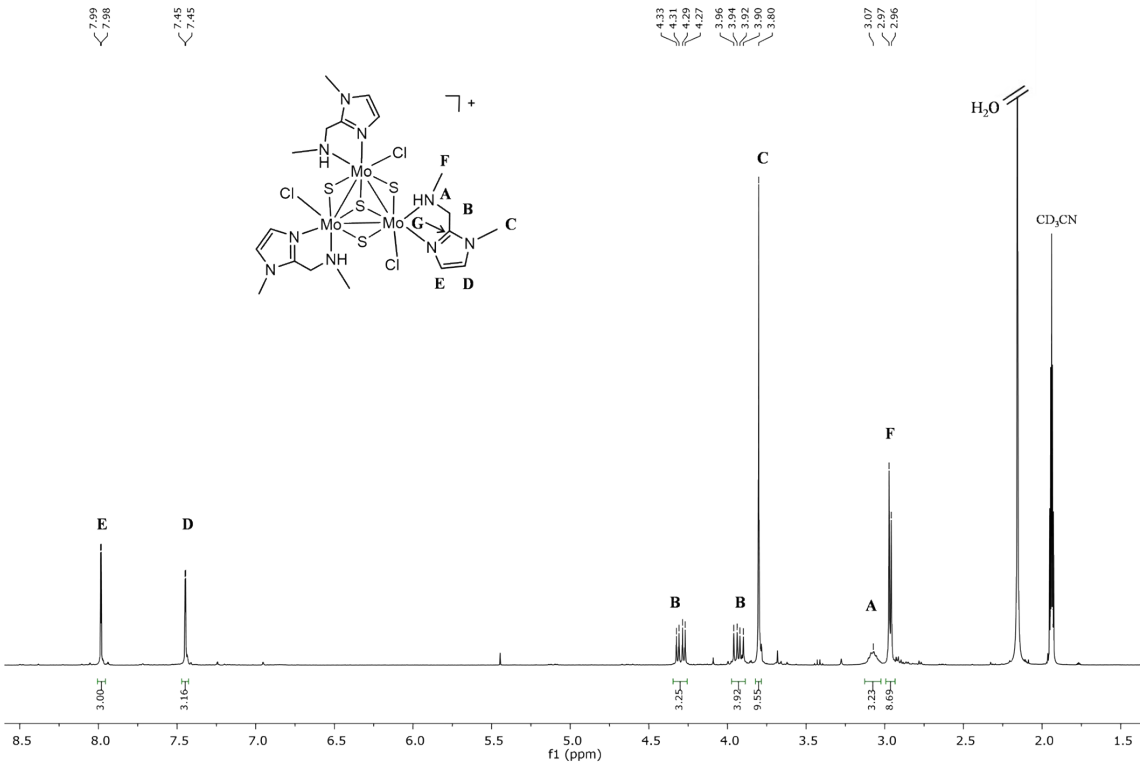


Figure SI3. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of the [**2**]BF_4 complex.

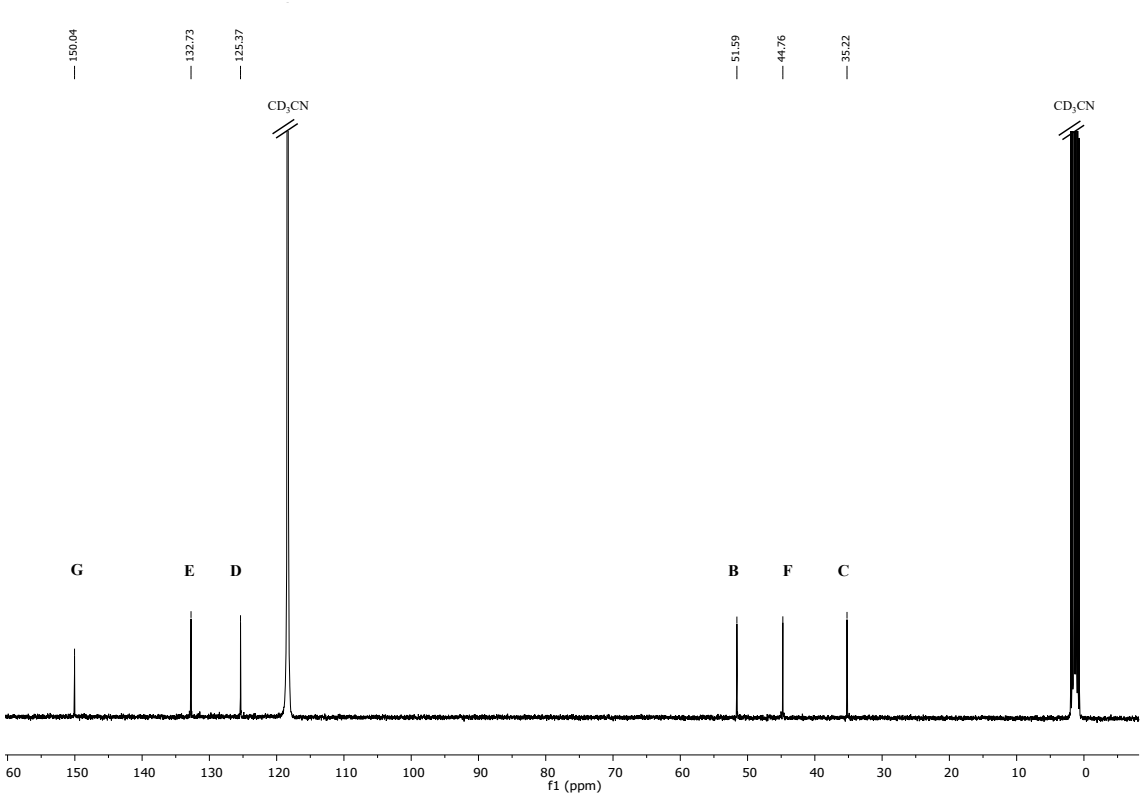


Figure SI4. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of the [**2**]BF_4 complex.

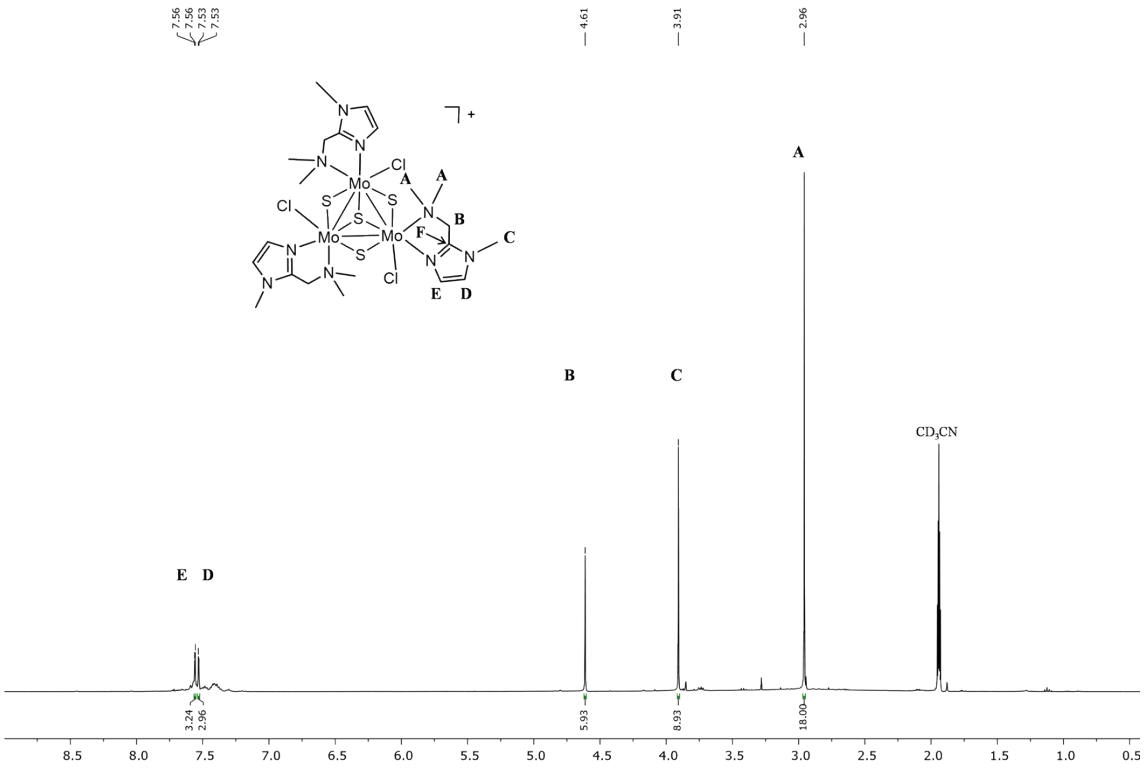


Figure SI5. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of the [**3**]BF_4 complex.

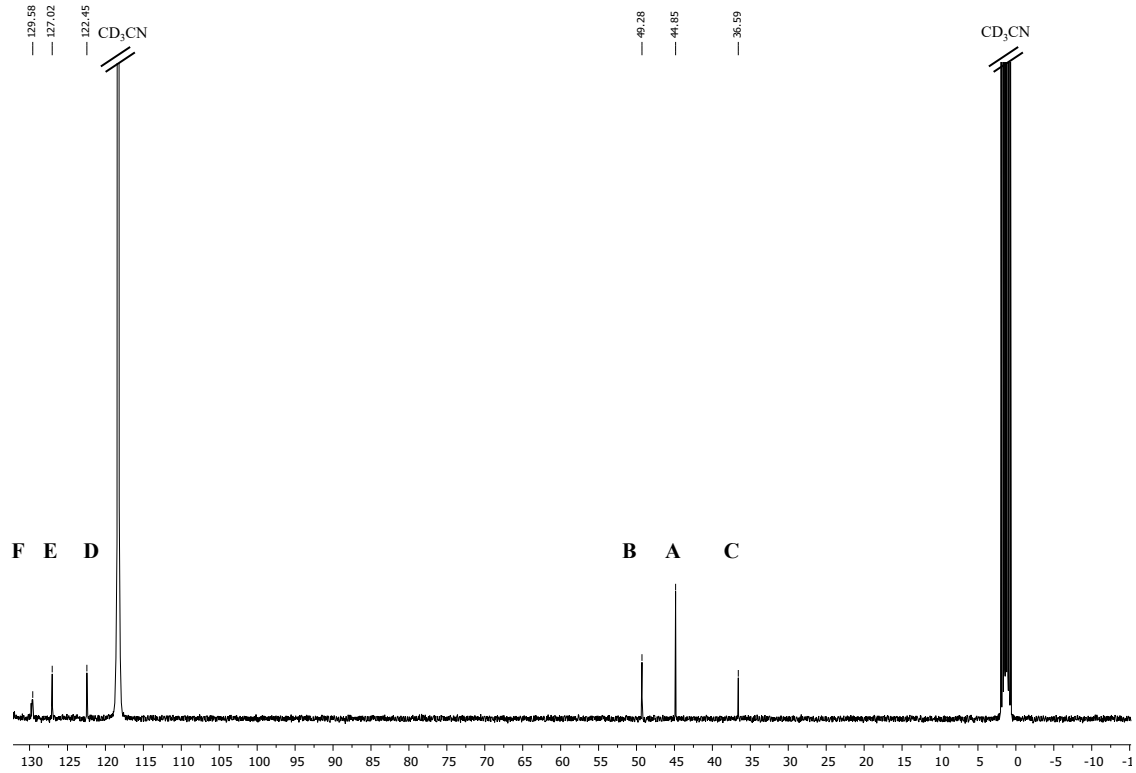


Figure SI6. ^{13}C NMR (101 MHz, CD_3CN, 298 K) spectrum of the [**3**]BF_4 complex.

2. Mo_3S_4 cluster reactivity towards diphenylacetylene (dpa)

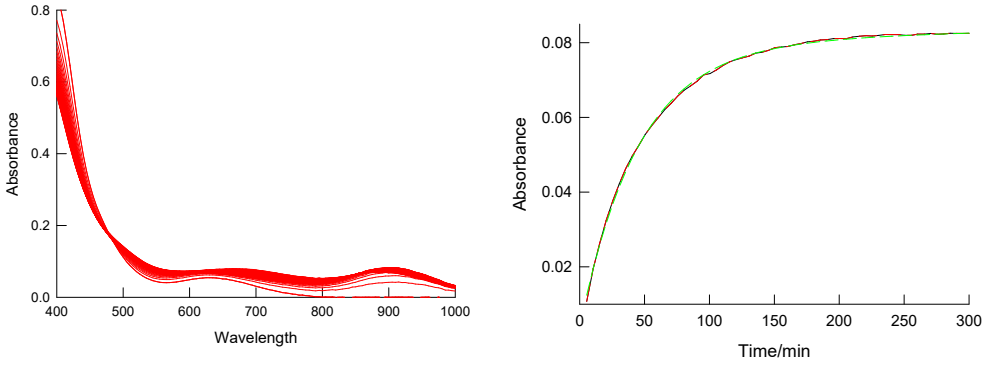


Figure SI7. Left: typical spectral changes in UV-Vis spectrum of $[Mo_3S_4Cl_3(ImNH_2)_3]^+$ (**1**$^+$) upon reaction with an excess of dpa ([**1**$^+$]= 2.5×10^{-4} M, [dpa]= 0.042 M, acetonitrile solution at 25.0ºC). Right: trace at 900 nm: red (experimental) and green (fit to a single exponential).

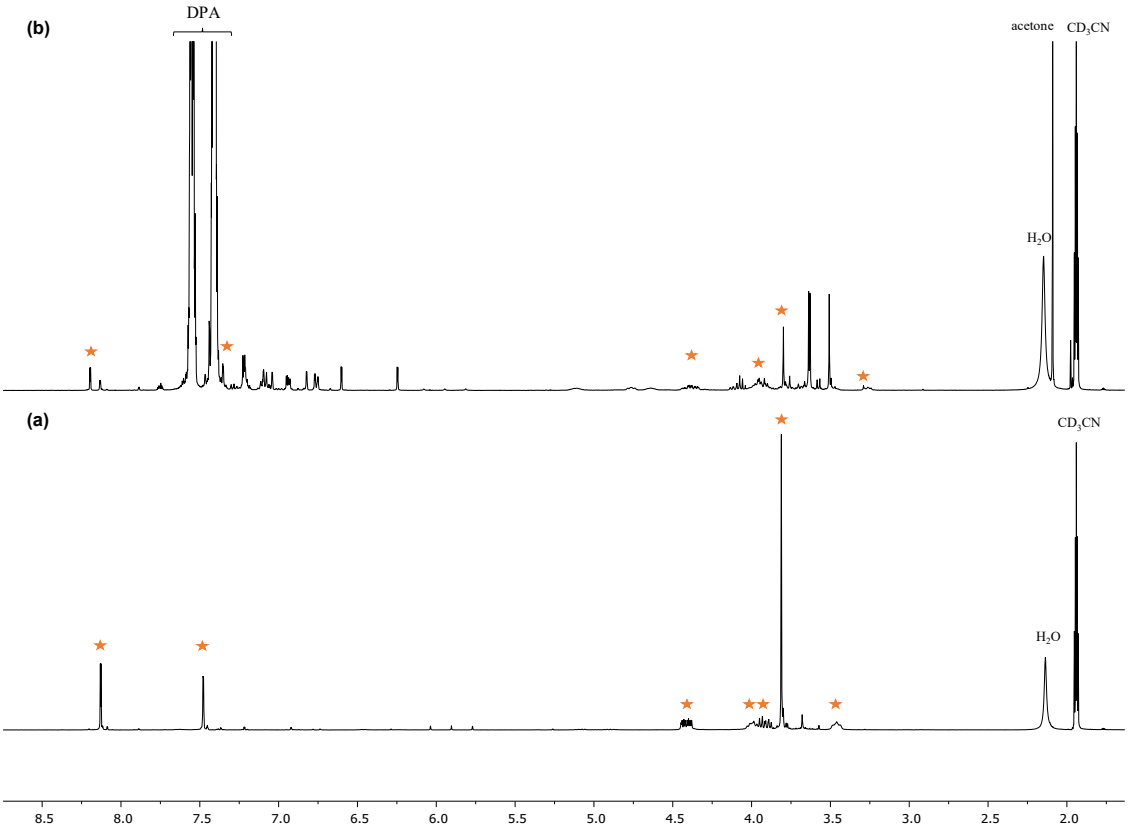


Figure SI8. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectra of complex **1**$^+$ (a) and complex **1**$^+$ with an excess of diphenylacetylene (20 equiv.) after 18 h of reaction (b). Signals marked with a star in both spectra correspond to the **1**$^+$ cluster.

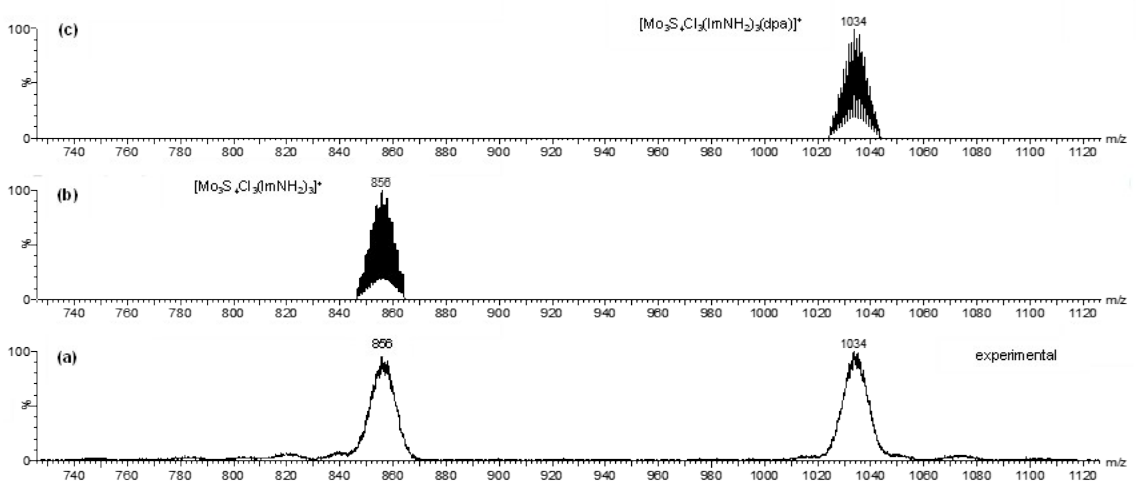
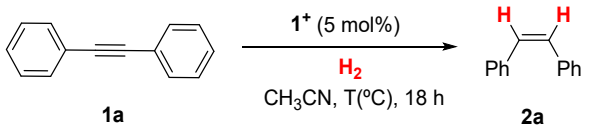


Figure SI9. ESI-MS spectrum of a solution 1 M of $[Mo_3S_4Cl_3(ImNH_2)_3]^+$ ($\mathbf{1}^+$) in acetonitrile after addition of a 20 molar excess of dpa (a) together with the simulated spectra of $\mathbf{1}^+$(b) and [**1** + dpa]$^+$ (c). The experiment was recorded at 20 V.

3. Conditions optimization for the semihydrogenation of diphenylacetylene (1a) to cis-stilbene (2a)

Table SI1. Influence of the pressure and temperature on the catalytic reduction of **1a** to **2a**.[a]

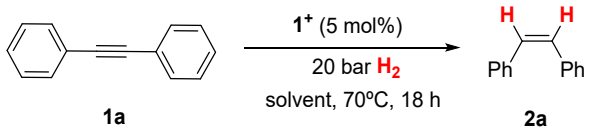


1a **2a**

Entry	T (ºC)	H_2 (bar)	Conversion[b] (%)	Yield 2a [b] (%)
1	150	-	0	0
2	150	50	>99	99
3	100	50	>99	99
4	100	30	>99	99
5	100	20	>99	99
6	70	20	>99	99
7	70	10	16	16
8	60	20	80	79
9	50	20	42	42

[a] Reaction conditions: diphenylacetylene (0.1 mmol), catalyst (5 mol%),18 h. [b] Determined by GC analysis using n-hexadecane as an internal standard.

Table SI2. Influence of the solvent on the catalytic reduction of **1a** to **2a**.[a]



1a **2a**

Entry	Solvent	Conversion[b] (%)	Yield 2a [b] (%)
1	CH_3CN	>99	99
2	CH_3OH	>99	99
3	2-Fluoroethanol	n.r	-
4	Hexafluoroisopropanol	n.r	-
5	THF	90	90

[a] Reaction conditions: diphenylacetylene (0.1 mmol), H_2 (20 bar), catalyst (5 mol%), 18 h, 70 ℃. [b] Determined by GC analysis using n-hexadecane as an internal standard.

4. Cluster monitoring during catalysis

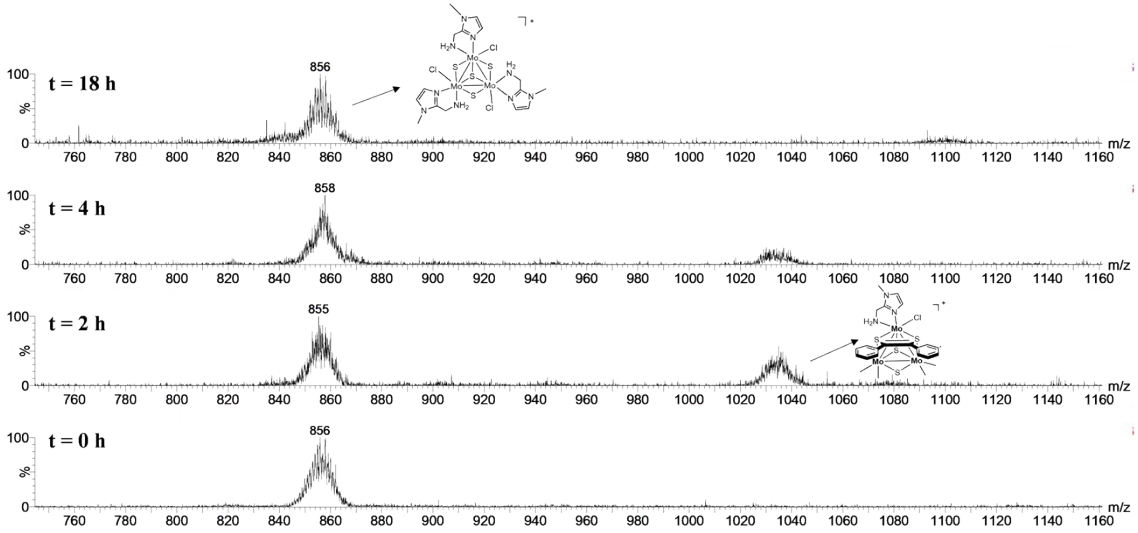


Figure SI10. ESI-MS spectra for the dpa semihydrogenation reaction monitoring at t= 0 (a), t= 2h (b), t= 4 h (c) and t = 18 h (d). All the experiments were recorded at 20 V.

5. Mechanism control experiments

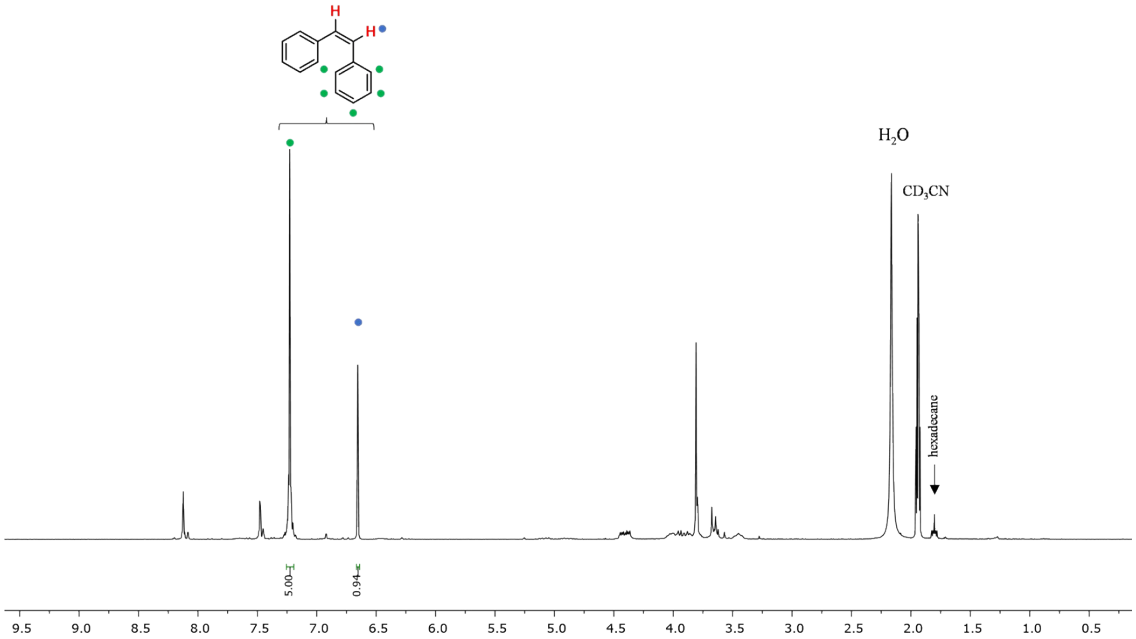


Figure SI11. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of the catalytic reaction mixture (diphenylacetylene and the $[Mo_3S_4Cl_3(ImND_2)_3)]^+$ complex) at 70ºC and 20 bar H_2 after 18 hours of reaction.

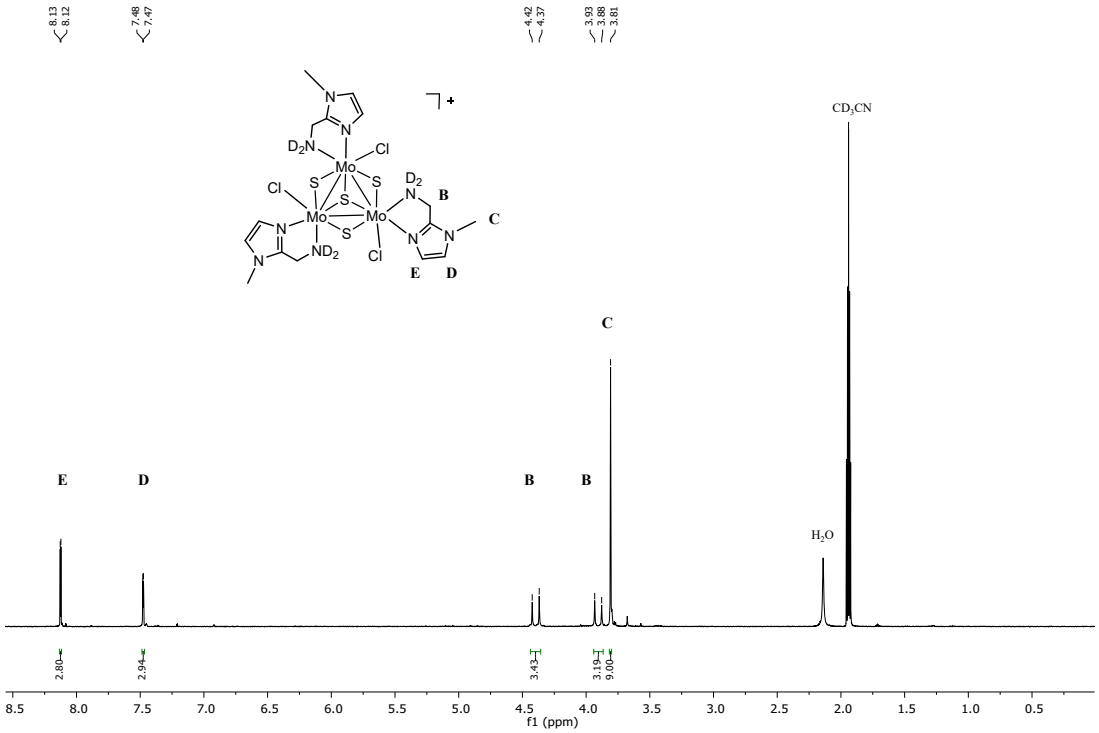


Figure SI12. ^{1}H NMR (300 MHz, CD_3CN, 298 K) spectrum of the$[Mo_3S_4Cl_3(ImND_2)_3]PF_6$ complex.

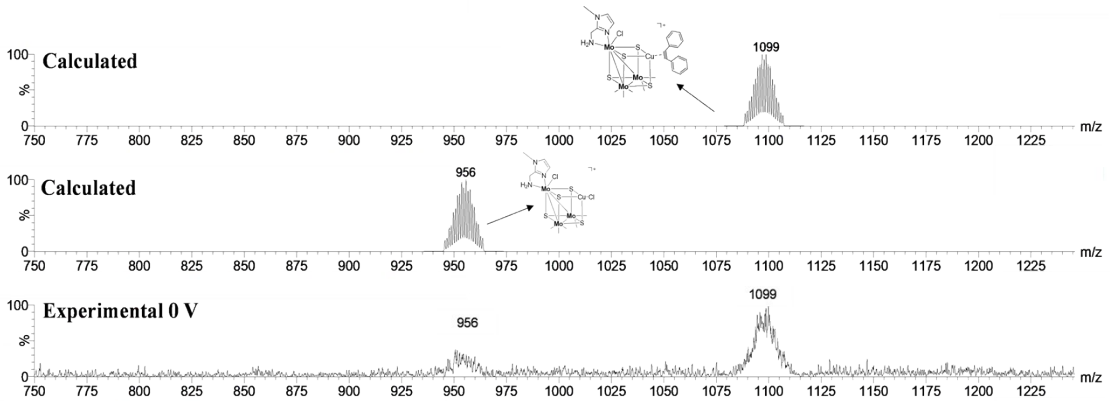
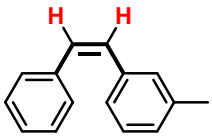
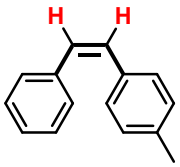


Figure SI13. ESI spectrum of the catalytic reaction mixture (diphenylacetylene, the $[Mo_3S_4Cl_3(ImNH_2)_3)]^+$ complex and CuCl) at 70ºC and 20 bar H_2 after 18 hours of reaction. The experiment was recorded at 0 V.

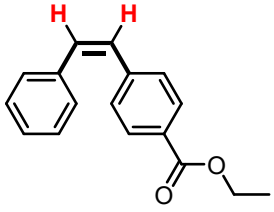
6. Characterization data of isolated alkenes prepared from diphenylacetylene derivatives



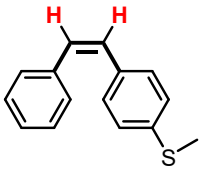
***(Z)*-1-methyl-2-styrylbenzene**[1] 51 mg. 90 %. colorless oil (pentane) **^{1}H NMR (300 MHz. $CDCl_3$)** δ 7.28 – 7.19 (m, 5H), 7.14 – 7.01 (m, 4H), 6.58 (s, 2H), 2.27 (s,3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.91, 137.49, 137.35, 130.52, 130.22, 129.74, 129.02, 128.29, 128.21, 127.98, 127.18, 126.01, 21.47.



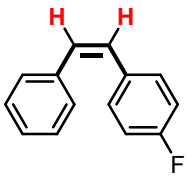
***(Z)*-1-methyl-4-styrylbenzene**[1] 26.6 mg. yield 46 %. colorless oil (pentane) **^{1}H NMR (300 MHz. $CDCl_3$)** δ 7.30 – 7.19 (m, 5H), 7.18 – 7.14 (m, 2H), 7.04 (d, 2H), 6.55 (s, 2H), 2.32 (s,3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 137.62, 136.99, 134.39, 130.33, 129.68, 129.04, 128.97, 128.92, 128.32, 127.10, 21.37.



Ethyl-*(Z)*-4-styrylbenzoate[1] 62 mg. 81 %. colorless liquid (pentane) **^{1}H NMR (300 MHz, CDCl3)** δ 7.89 (m, 2H), 7.29 (m, 2H), 7.23 (m, 5 H), 6.66 (q, 2H), 4.36 (q, 2 H), 1.38 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 166.57, 142.10, 136.82, 132.29, 129.61, 129.39, 128.99, 128.95, 128.47, 127.62, 61.02, 14.46.

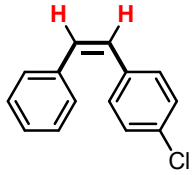


***(Z)*-methyl(4-styrylphenyl)sulfane**[1] 60 mg. 89 %. white solid (pentane) **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.43-7.32 (m, 4 H), 7.24 – 7.29 (m, 2 H), 7.16 – 7.14 (m, 3H), 6.97 (s, 2H), 2.41 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 137.98. 137.44. 134.40. 128.81. 128.19. 128.15. 127.68. 127.02. 126.81. 126.56. 15.93.

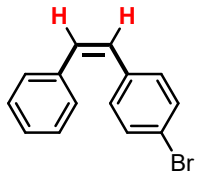


***(Z)*-1-fluoro-4-styrylbenzene**[1] 50 mg. 86 %. colorless liquid (pentane) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.21 (m, 6H), 6.94 (t, J = 8.8 Hz, 1H),

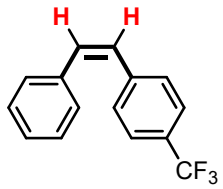
6.63 (d, *J* = 12.2 Hz, 1H), 6.58 (d, *J* = 12.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.21, 160.76, 137.20, 133.33, 130.71, 130.63, 130.41, 129.23, 128.97, 128.45, 127.34, 115.39, 115.18.



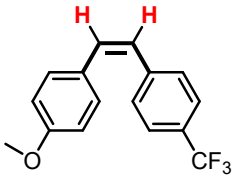
***(Z)*-1-chloro-4-styrylbenzene**[1] 41.4 mg. 65 %. colorless liquid (pentane) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25-7.14 (m, 9 H), 6.63 (d, 12.2 Hz, 1H), 6.53 (d, 12.2 Hz. 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.72, 135.50, 132.60, 130.80, 130.05, 128.76, 128.64, 128.24, 128.17, 127.15.



***(Z)*-1-bromo-4-styrylbenzene**[1] 53.9 mg. 70 %. colorless liquid (pentane) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.32 (m, 2H), 7.25 – 7.19 (m, 5H), 7.14 – 7.08 (m, 2H), 6.64 (d, *J* = 12.2 Hz, 1H), 6.51 (d, *J* = 12.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.01, 136.28, 131.52, 131.20, 130.69, 129.10, 128.94, 128.50, 127.49, 121.09.



(*Z*)-1-styryl-4-(trifluoromethyl)benzene[1] 58 mg. 78 %. colorless liquid (pentane) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.2 Hz, 3H), 7.34 (d, *J* = 8.1 Hz, 3H), 7.28 – 7.19 (m, 5H), 6.73 (d, *J* = 12.2 Hz, 1H), 6.60 (d, *J* = 12.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.08, 136.72, 132.49, 129.29, 128.97, 128.90, 128.57, 127.72, 125.36, 125.32, 125.28, 125.24.



(*Z*)-1-methoxy-4-(4-(trifluoromethyl)styryl)benzene[2] 45 mg. 55 %. colorless liquid (pentane) **^{1}H NMR (400 MHz. $CDCl_3$)** δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.78 (d, 2H), 6.65 (d, *J* = 12.2 Hz, 1H), 6.50 (d, *J* = 12.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.23, 141.51, 131.98, 130.32, 129.22, 129.09, 128.77, 127.37, 125.3, 123.02, (q, J = 3.8 Hz), 113.96, 55.36.

7. ^{1}H NMR and ^{13}C NMR spectra of isolated products

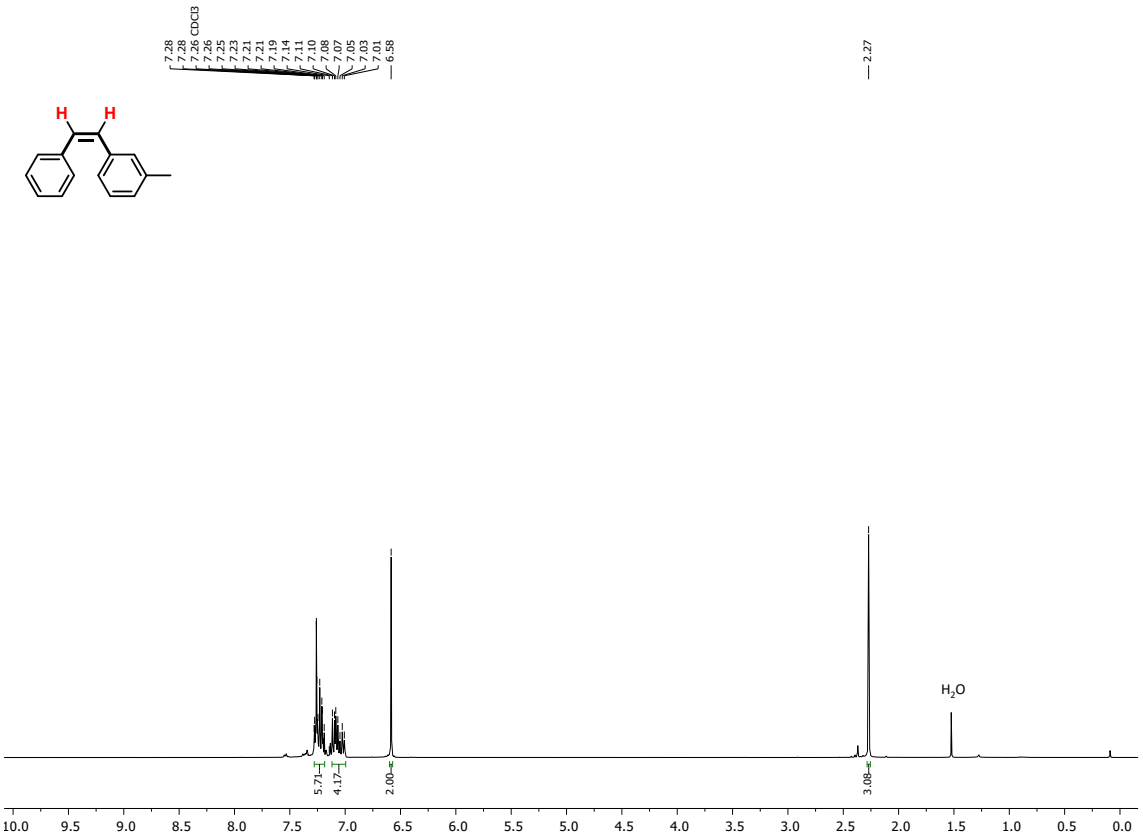


Figure SI14. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-methyl-2-styrylbenzene.

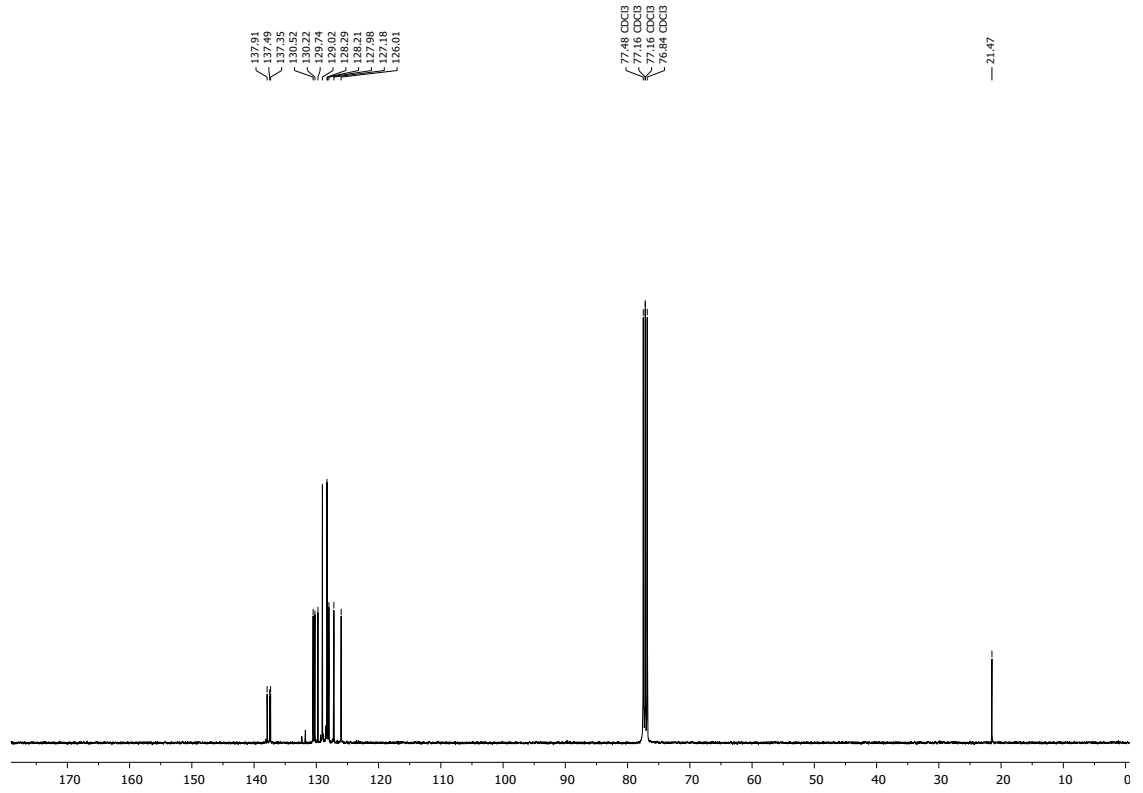


Figure SI15. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-methyl-2-styrylbenzene**.**

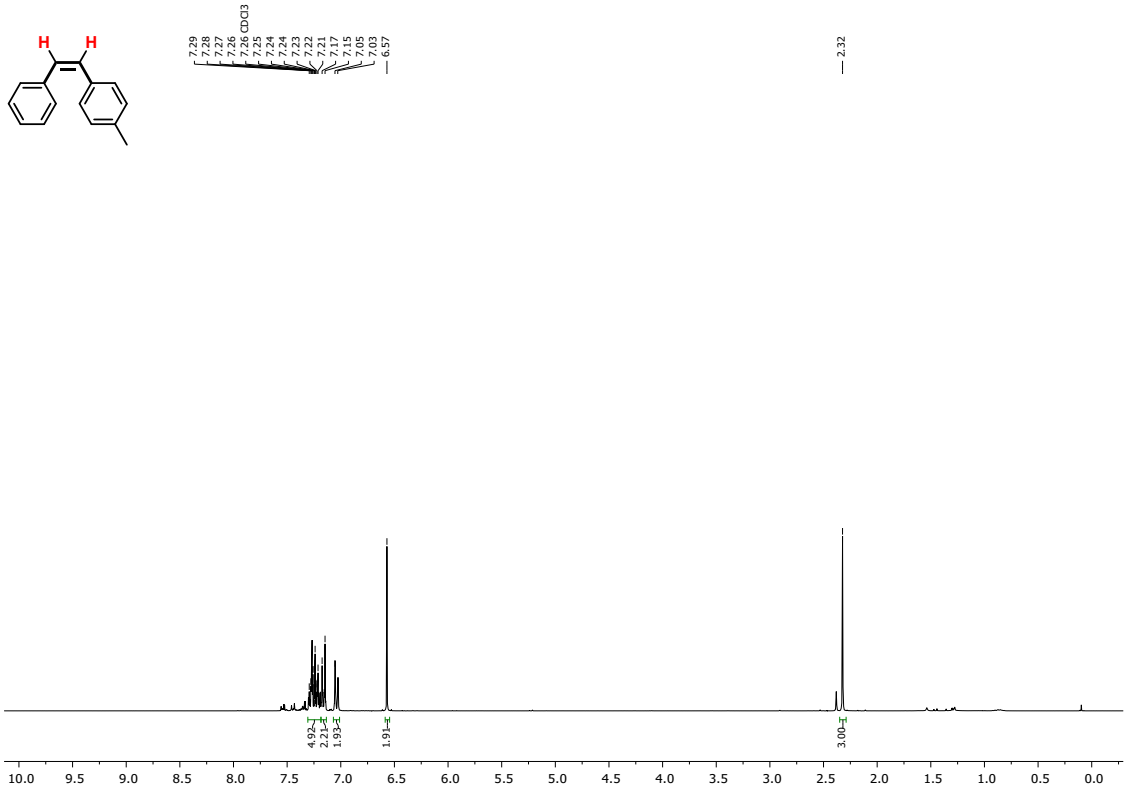


Figure SI16. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-methyl-4-styrylbenzene.

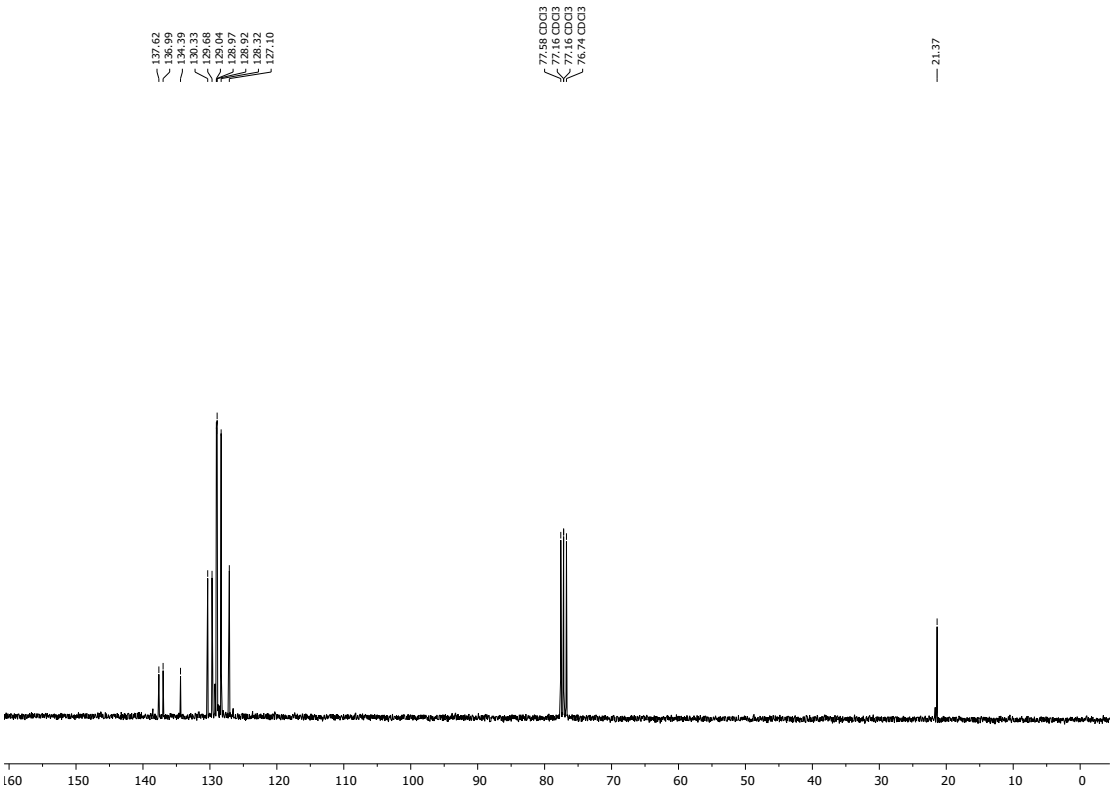


Figure SI17. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-methyl-4-styrylbenzene.

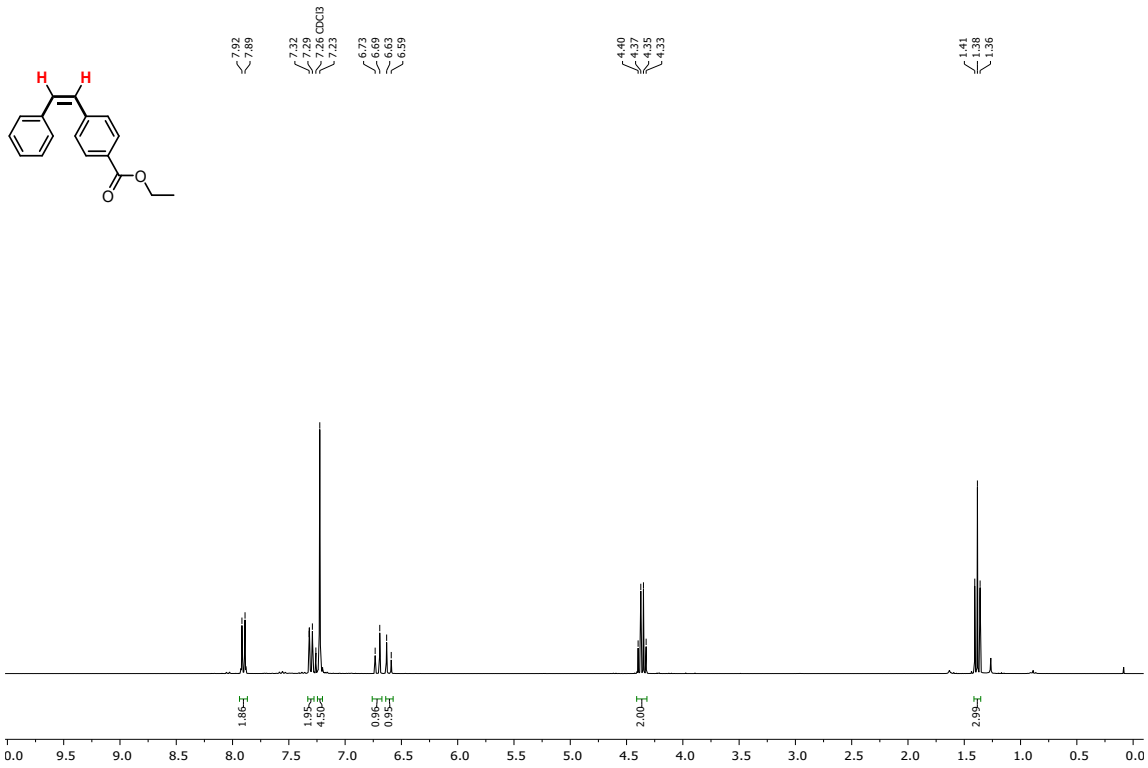


Figure SI18. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of ethyl-*(Z)*-4-styrylbenzoate.

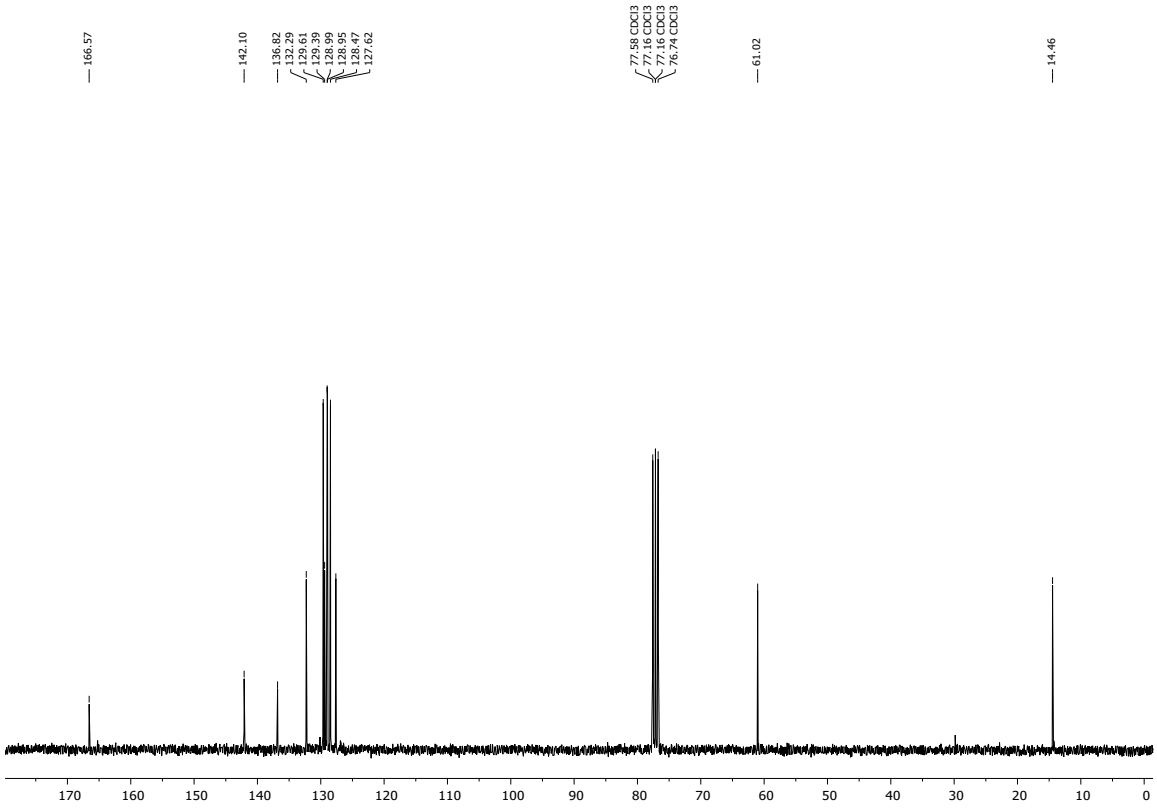


Figure SI19. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of ethyl-*(Z)*-4-styrylbenzoate.

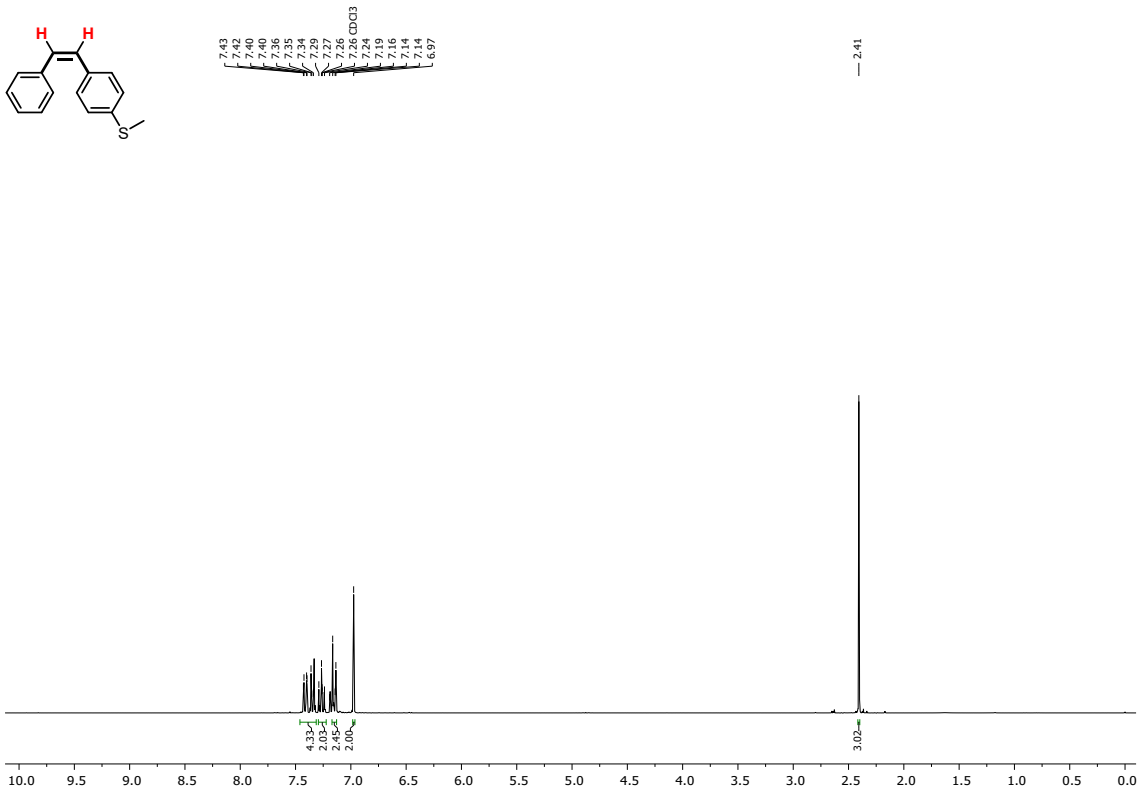


Figure SI20. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-methyl(4-styrylphenyl)sulfane.

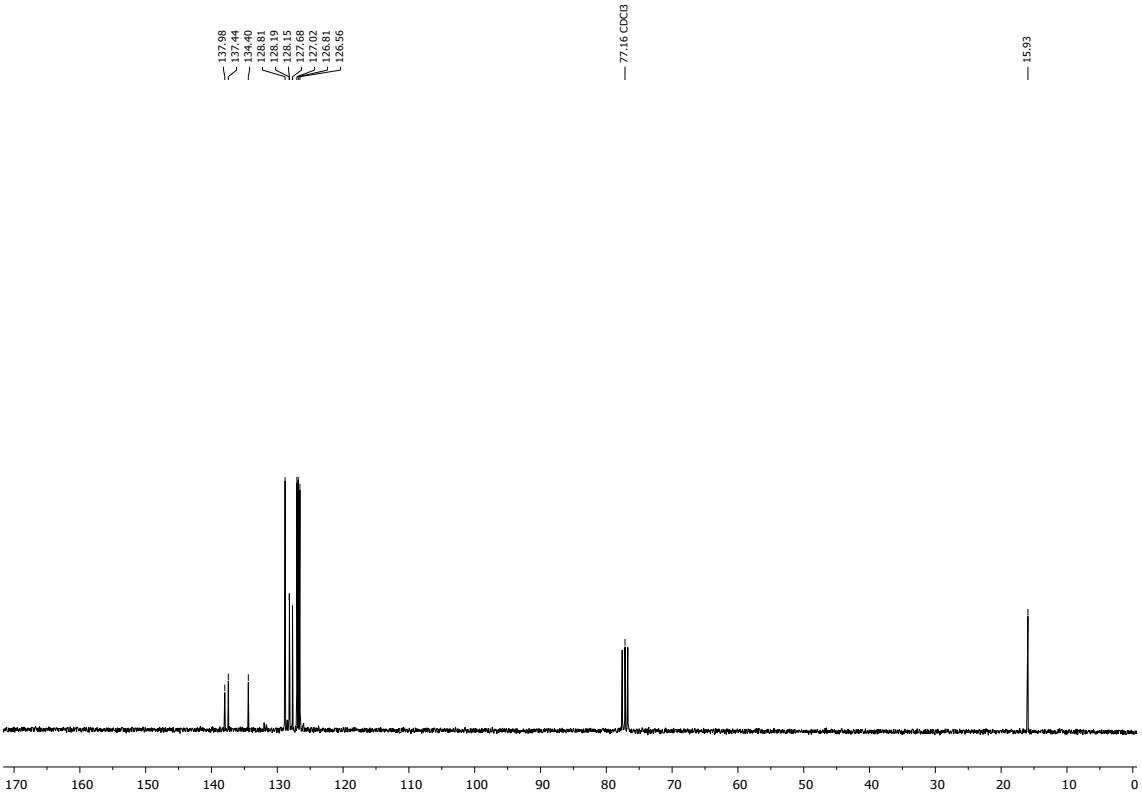


Figure SI21. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) spectrum of (Z)-methyl(4-styrylphenyl)sulfane.

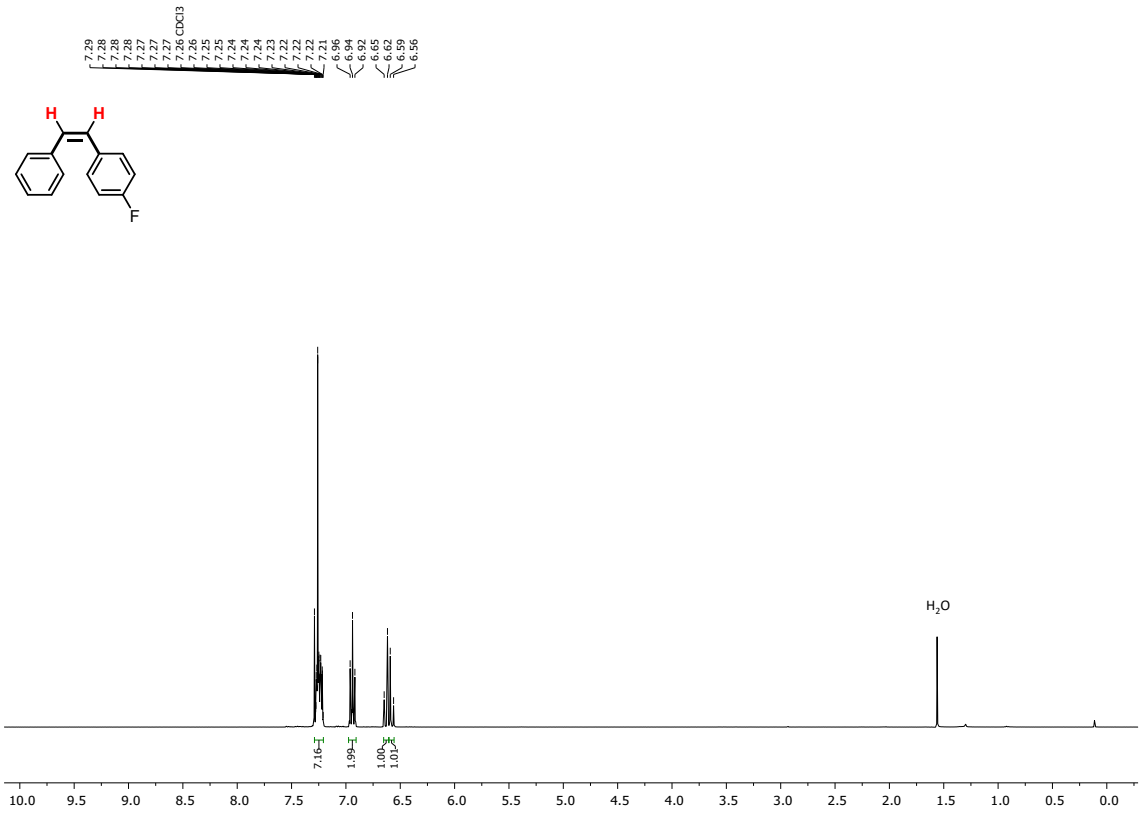


Figure SI22. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-fluoro-4-styrylbenzene.

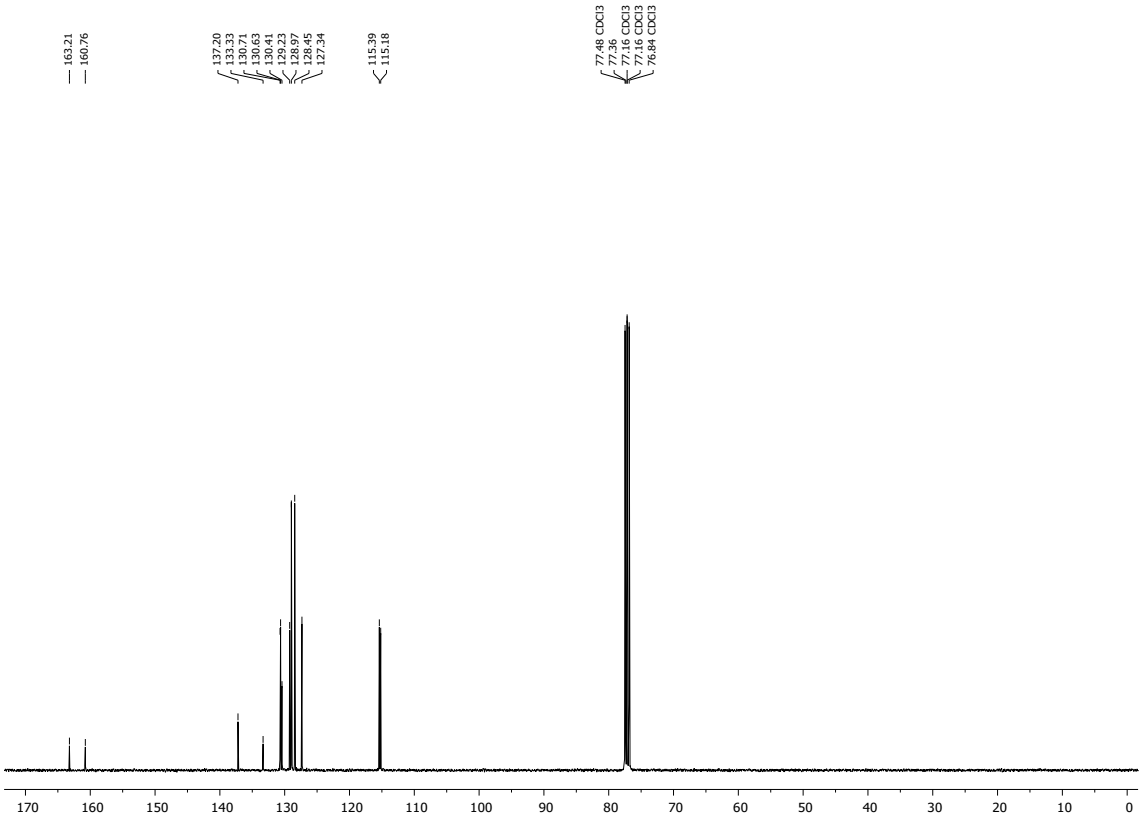


Figure SI23. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-fluoro-4-styrylbenzene.

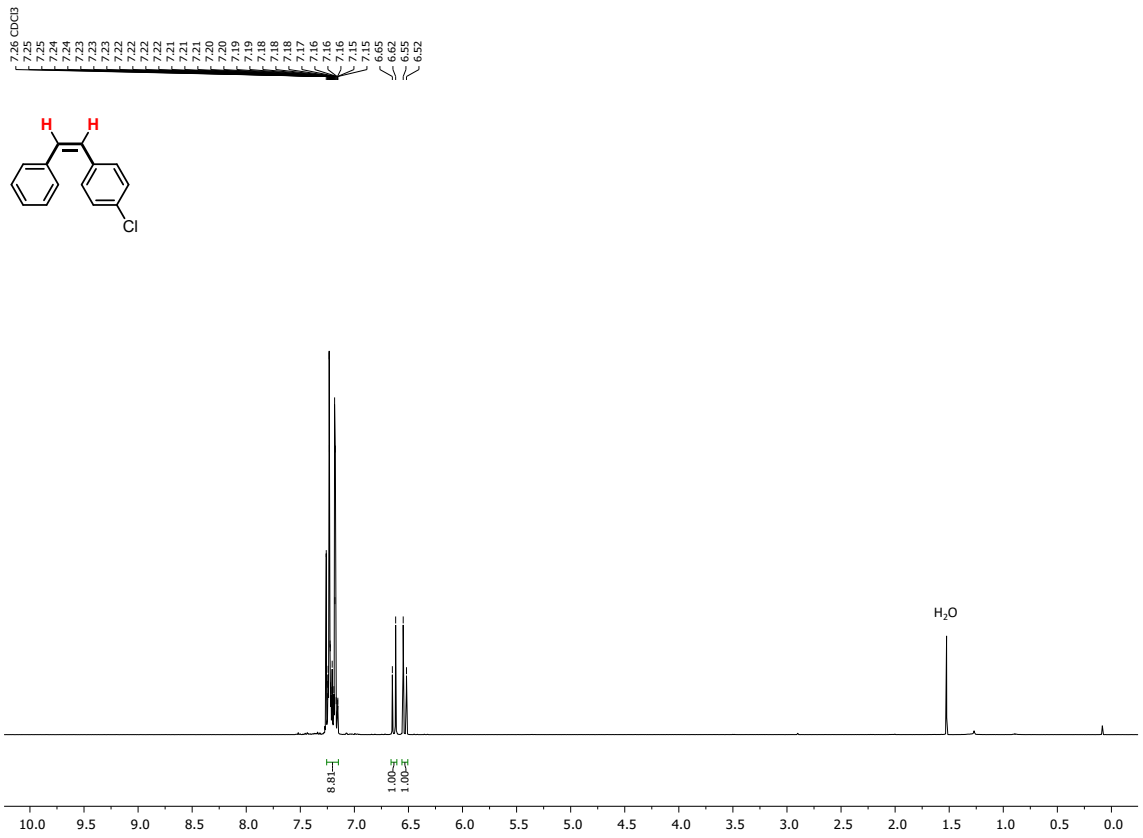


Figure SI24. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-chloro-4-styrylbenzene

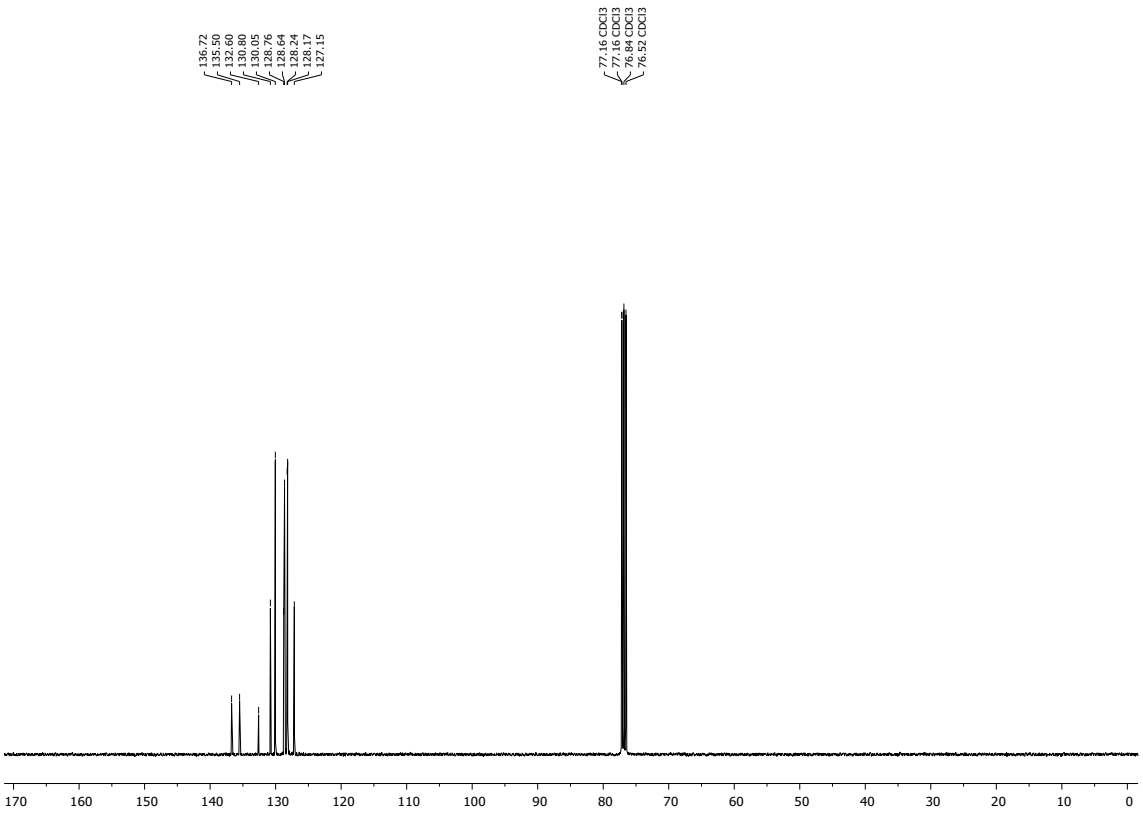


Figure SI25. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-chloro-4-styrylbenzene.

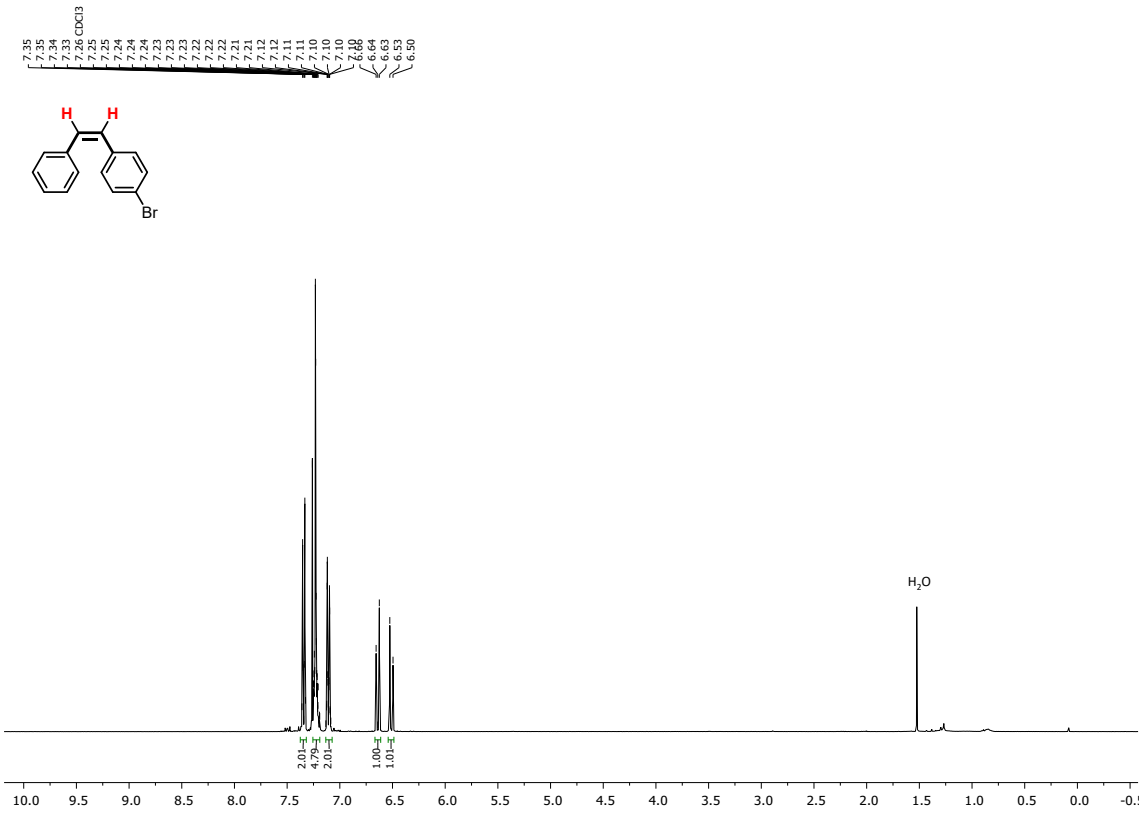


Figure SI26. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-bromo-4-styrylbenzene.

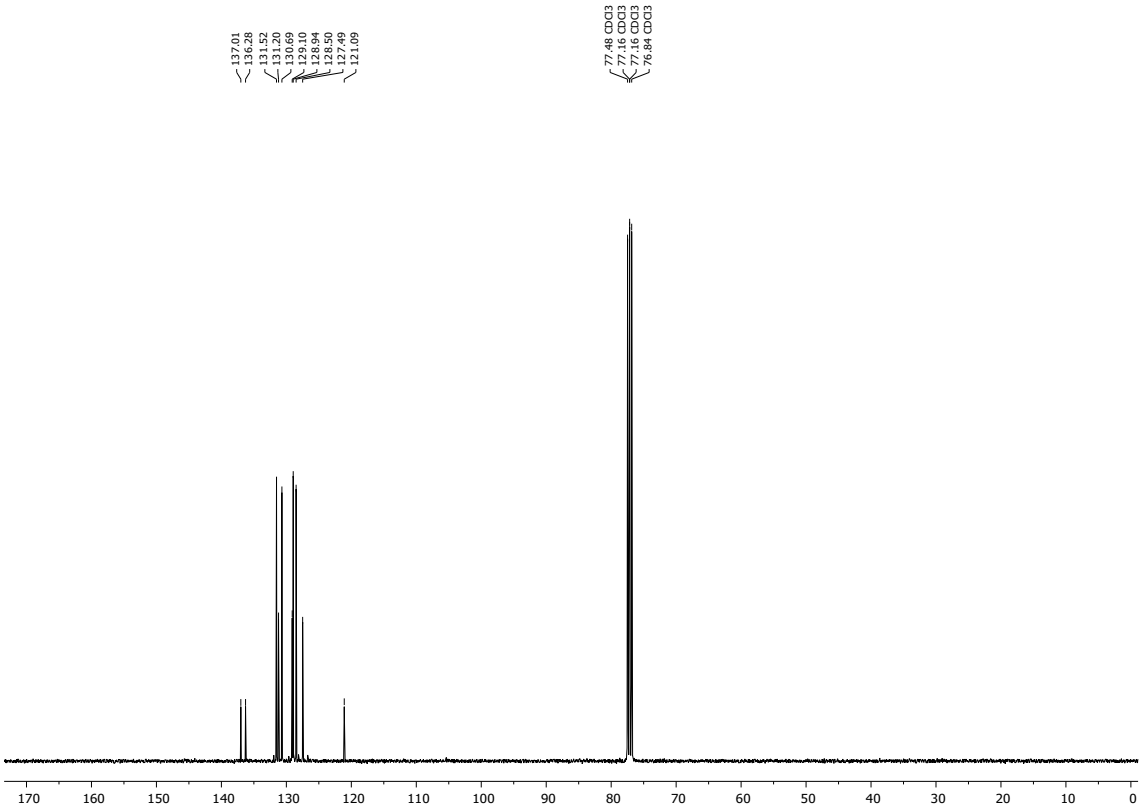


Figure SI27. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of *(Z)*-1-bromo-4-styrylbenzene.

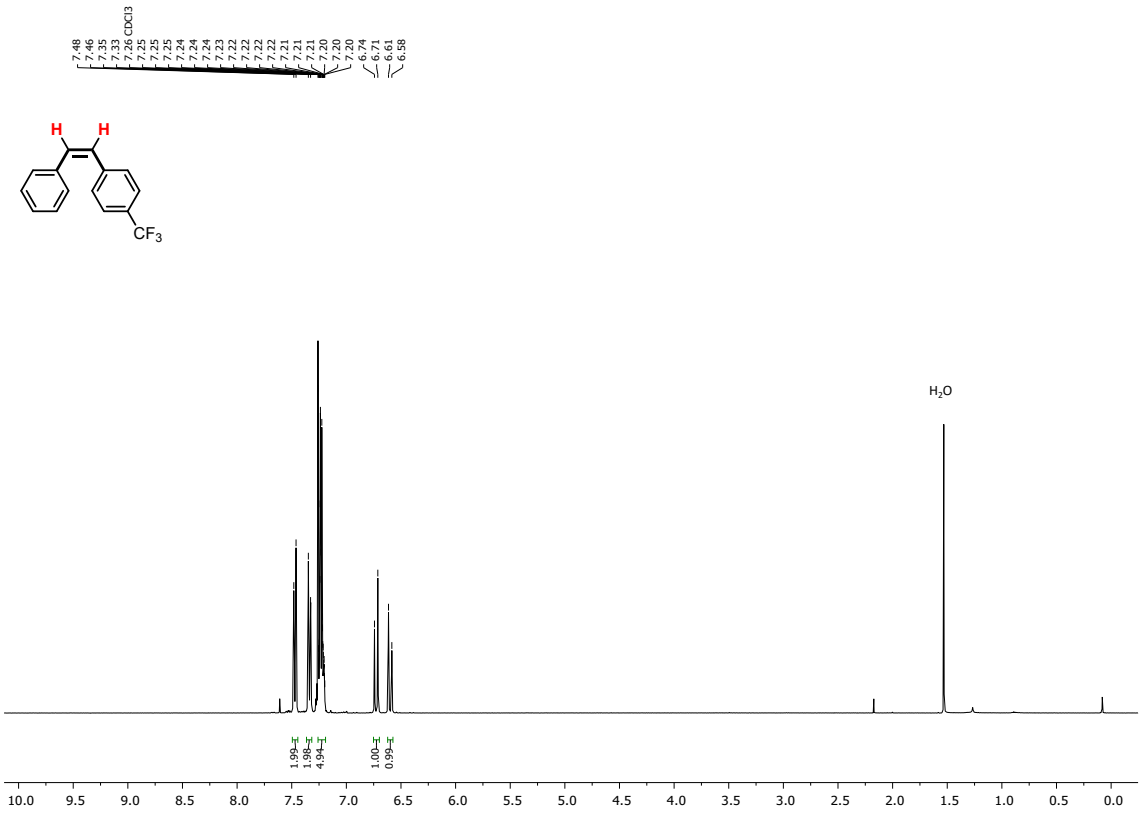


Figure SI28. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of (*Z*)-1-styryl-4-(trifluoromethyl)benzene.

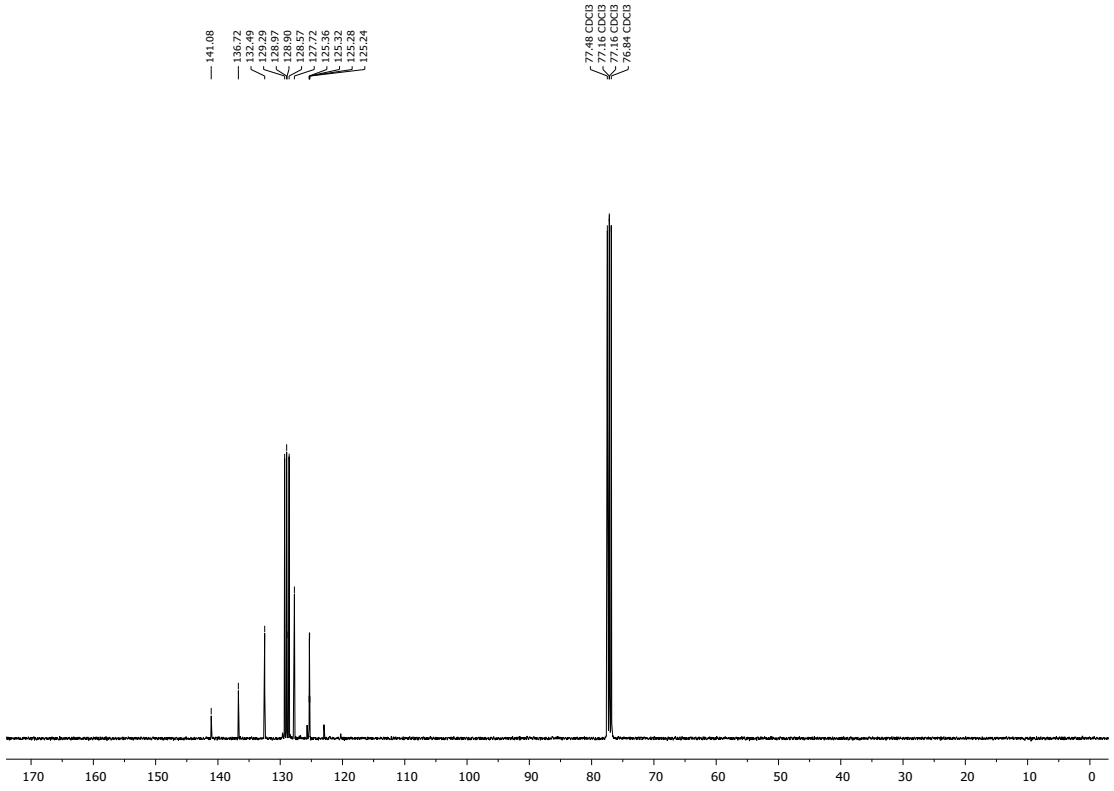


Figure SI29. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of (*Z*)-1-styryl-4-(trifluoromethyl)benzene.

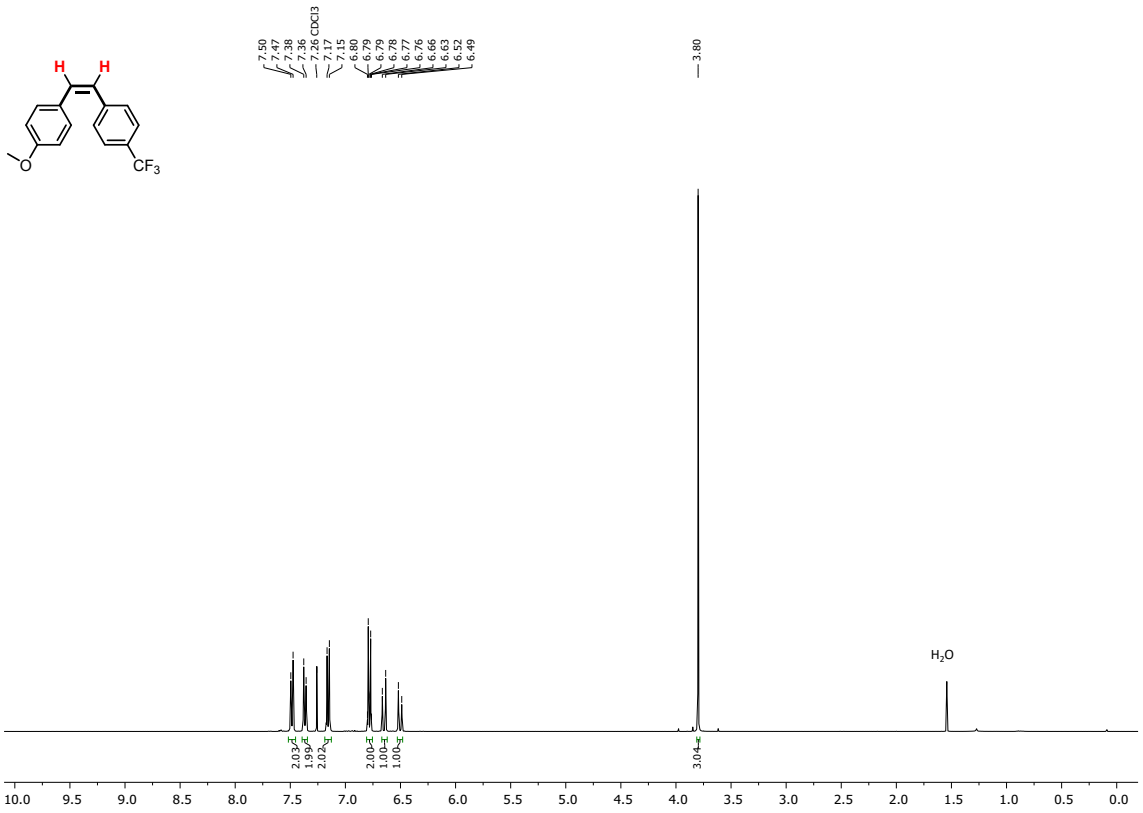


Figure SI30. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of (*Z*)-1-methoxy-4-(4-(trifluoromethyl)styryl)benzene.

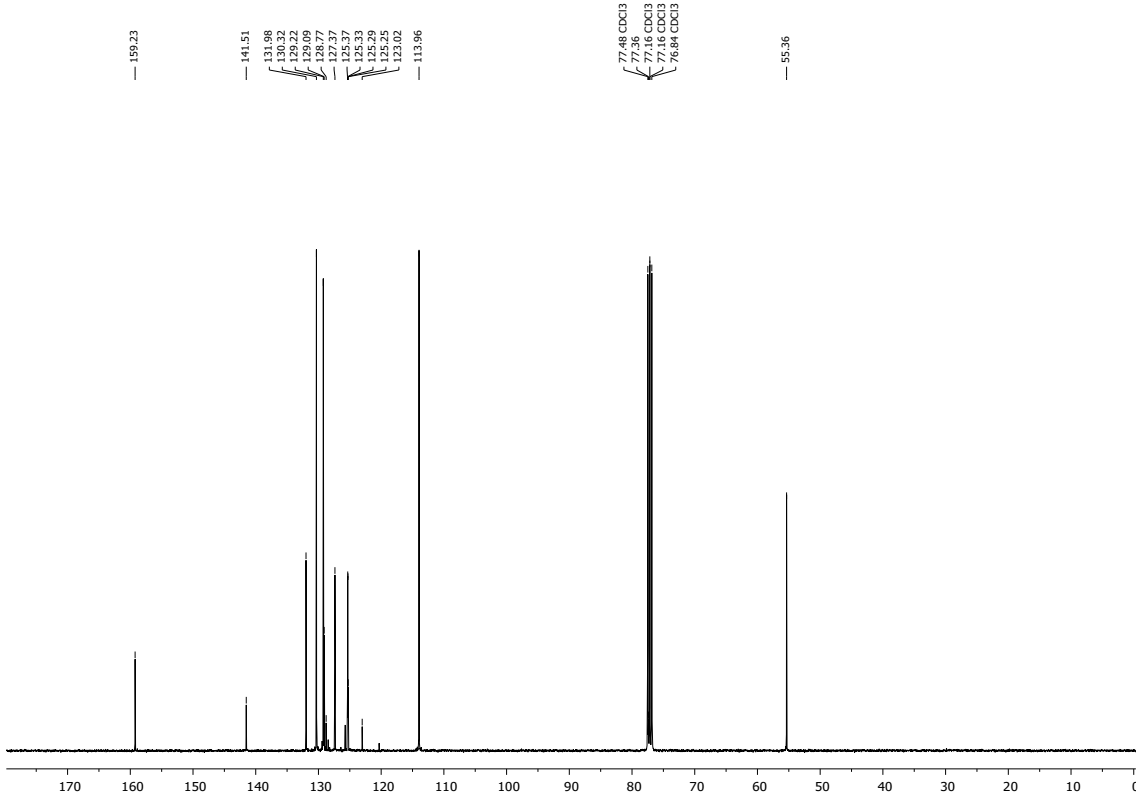
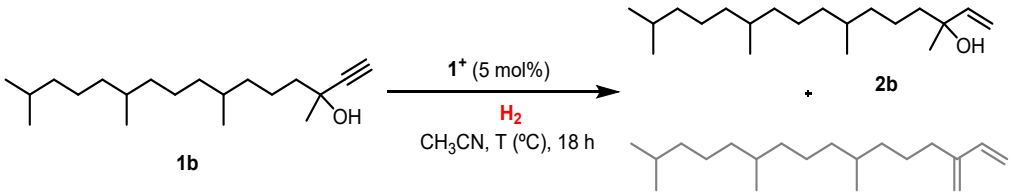


Figure SI31. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of (*Z*)-1-methoxy-4-(4-(trifluoromethyl)styryl)benzene.

8. Conditions optimization for the semihydrogenation of 3,7,11,15- tetramethylhexadec-1-yn-3-ol (2a) and reaction monitoring

Table SI3. Optimization of the pressure and temperature on the catalytic reduction of **1b** to **2b**.[a]



Entry	T (ºC)	H_2 (bar)	Conversion[b] (%)	Yield 2b [b] (%)
1	60	20	n.r	n.r
2	100	20	22	22
3	120	20	>99	90
4	120	40	>99	82

[a] Reaction conditions: 3,7,11,15- tetramethylhexadec-1-yn-3-ol (0.1 mmol), catalyst (5 mol%), 18 h. [b] Determined by GC analysis using n-hexadecane as an internal standard.

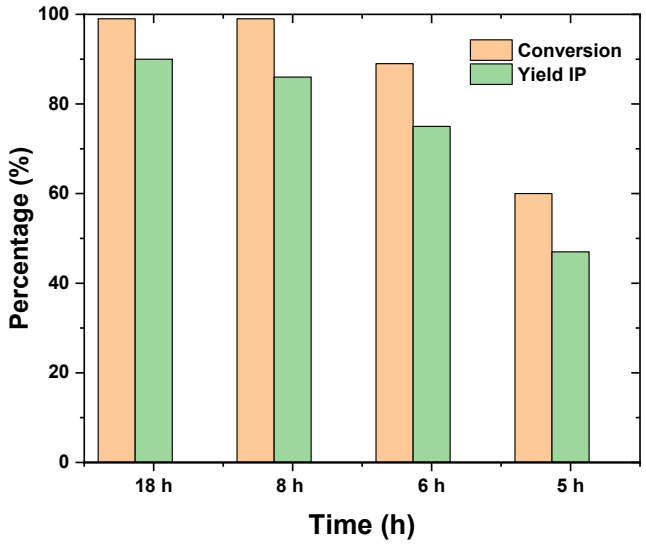


Figure SI32 Influence of the time on the catalytic reduction of **1b** to **2b**.Reaction conditions: 3,7,11,15- tetramethylhexadec-1-yn-3-ol (0.1 mmol), catalyst (5 mol%), 120 ºC, 20 bar H_2, 18 h. Conversion and yield determined by GC analysis using n-hexadecane as an internal standard.

9. References

[1] Huang, Z.; Wang, Y.; Leng, X.; Huang, Z. An Amine-Assisted Ionic Monohydride Mechanism Enables Selective Alkyne Cis-Semihydrogenation with Ethanol: From Elementary Steps to Catalysis. *J. Am. Chem. Soc.* **2021**, *143* (12), 4824–4836.

[2] Armstrong, M. K.; Goodstein, M. B.; Lalic, G. Diastereodivergent Reductive Cross Coupling of Alkynes through Tandem Catalysis: Z - and E -Selective Hydroarylation of Terminal Alkynes. *J. Am. Chem. Soc.* **2018**, *140* (32), 10233–10241.