Supplementary Materials

Rhodium nanoparticles stabilized by PEG-tagged imidazolium salts as recyclable catalysts for the hydrosilylation of internal alkynes and the reduction of nitroarenes

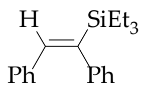
Guillem Fernández[1] and Roser Pleixats[1,]*

S1. Spectral data of the hydrosilylation products

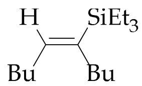
S2. Spectral data of the anilines

S3. Spectra collection

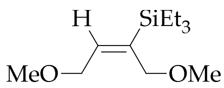
S1. Spectral data of the hydrosilylation products



(*E*)-(1,2-diphenylvinyl)triethylsilane **1** (Table 3, entry 1)[1]
[1]H NMR (360 MHz, $CDCl_3$, ppm): δ 7.27 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.11-7.02 (m, 3H), 7.01-6.91 (m, 4H), 6.77 (s, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H).

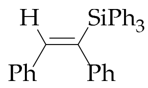


(E)-5-triethylsilyl-5-decene **2** (Table 3, entry 2)[1]
[1]H NMR (250 MHz, $CDCl_3$, ppm): δ 5.67 (t, *J* = 6.7 Hz, 1H), 2.14-2.02 (m, 4H), 1.37-1.21 (m, 8H), 0.97-0.84 (m, 15H), 0.57 (q, *J* = 7.5 Hz, 6H).

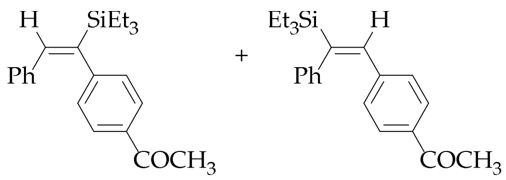


[1] Planellas, M., Guo, W., Alonso, F., Yus, M., Shafir, A., Pleixats, R., Parella, T. *Adv. Synth. Catal.* **2014**, *356*, 179.

(E)-(1,4-dimethoxybut-2-en-2-yl)triethylsilane **3** (Table 3, entry 3)[2]
^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 5.95 (t, *J* = 5.5 Hz, 1H), 4.09 (d, *J* = 5.5 Hz, 2H), 3.99 (s, 2H), 3.35 (s, 3H), 3.28 (s, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H).

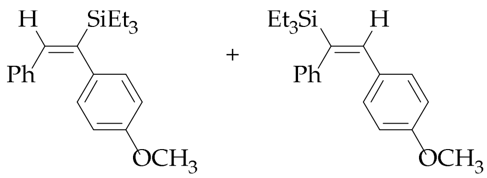


(E)-(1,2-diphenylvinyl)triphenylsilane **4** (Table 3, entry 4)[1]
^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 7.50-7.38 (m, 9H), 7.37-7.30 (m, 6H), 7.17-7.08 (m, 6H), 7.03 (s, 1H), 7.00-6.96 (m, 2H), 6.92-6.89 (m, 2H).



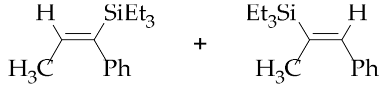
65:35

(E)-1-(4-(2-phenyl-1-(triethylsilyl)vinyl)phenyl)ethanone, (*E*)-**5a** (Table 4, entry 1)[2]
Selected spectroscopic data from the mixture: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ *(E)*-**5b**: 7.91 (d, *J* = 7.8 Hz, 2H, Ar**H**), 6.82 (s, 1H, =C**H**), 2.61 (s, 3H, $COCH_3$); *(E)*-**6b**: 7.68 (d, *J* = 8.1 Hz, 2H, Ar**H**), 2.50 (s, 3H $COCH_3$); 1.03-0.89 (two triplets overlapped from $SiCH_2CH_3$), 0.72-0.61 (two quartets overlapped from $SiCH_2CH_3$).



43:57

(E)-triethyl(2-*p*-methoxyphenyl-1-phenylvinyl)silane, (*E*)-**6b**[¡Error! Marcador no definido.] (Table 4, entry 4)[1]
Selected spectroscopic data from the mixture: ^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 6.77 (s, 1H, =C**H,** (*E*)-**5c**), 6.71 (s, 1H, =C**H,** (*E*)-**6c**), 3.83 (s, 3H, OCH_3, (*E*)-**5c**), 3.73 (s, 3H, OCH_3, (*E*)-**6c**), 1.00-0.94 (two triplets overlapped from $SiCH_2CH_3$), 0.69-0.61 (two quartets overlapped from $SiCH_2CH_3$) (for other signals see the spectrum).

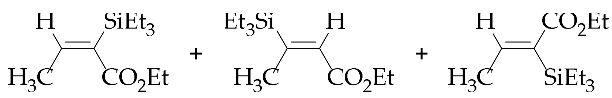


76:24

(E)-triethyl(1-phenyl-1-propenyl)silane, (*E*)-**7a** (Table 5, entry 1)[1]
Selected spectroscopic data from the mixture: ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ *(E)*-**7a**: 6.94

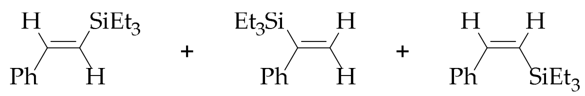
[2] Guo, W., Pleixats, R., Shafir, A., Parella, T. *Adv. Synth. Catal.* **2015**, *357*, 89.

(d, J = 7.0 Hz, 2H, Ar**H**), 6.07 (q, J = 6.5 Hz, 1H, =C**H**), 1.57 (d, J = 6.5 Hz, 3H, –**C**$\mathbf{H_3}$), 0.91 (t, J = 7.9 Hz, 9H $SiCH_2$**C**$\mathbf{H_3}$), 0.69 (q, J = 7.9 Hz, 6H SiC$\mathbf{H_2}$$CH_3$); *(E)*-**8a**: 6.72 (s, 1H =C**H**), 1.95 (s, 3H, –**C**$\mathbf{H_3}$), 0.99 (t, J = 7.8 Hz, 9H $SiCH_2$**C**$\mathbf{H_3}$), 0.69 (q, J = 7.8 Hz, 6H SiC$\mathbf{H_2}$$CH_3$) (for other signals see the spectrum).



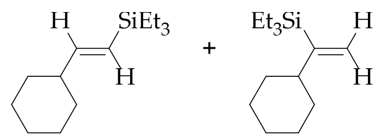
11:15:74

(Z)-ethyl 2-(triethylsilyl)-2-butenoate, (*Z*)-**7b** (Table 5, entry 4)[1]
Selected spectroscopic data from the mixture: ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ *(E)*-**7b**: 6.21 (q, *J* = 6.8 Hz, 1H, =C**H**), 4.16 (q, *J* = 7.1 Hz, 2H, COOC$\mathbf{H_2}$$CH_3$), 1.93 (d, *J* = 6.8 Hz, 3H, C$\mathbf{H_3}$CH), 1.29 (t, *J* = 7.1 Hz, 1H, $COOCH_2$C$\mathbf{H_3}$); *(E)*-**8b**: 6.00 (q, *J* = 1.8 Hz, 1H, =C**H**), 2.19 (d, *J* = 1.8 Hz, 3H, C$\mathbf{H_3}$CH); (*Z*)-**7b**: 7.26 (q, *J* = 7.2 Hz, 1H, =C**H**), 4.12 (q, *J* = 7.2 Hz, 2H, COOC$\mathbf{H_2}$$CH_3$), 1.89 (d, *J* = 7.2 Hz, 3H, C$\mathbf{H_3}$CH) (for other signals see the spectrum).



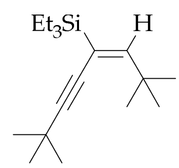
65:25:10

(E)-2-phenyl-1-(triethylsilyl)ethene, (*E*)-**7c** (Table 5, entry 7)[3]
Selected spectroscopic data from the mixture: *(E)*-**7c**: ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 6.99 (d, *J* = 19.3 Hz, 1H, =C**H**), 6.51 (d, *J* =19.3 Hz, 1H, =C**H**); **8c**: 5.96 (d, *J* = 2.6 Hz, 1H, =C**H**), 5.66 (d, *J* = 2.6 Hz, 1H, =C**H**); (*Z*)-**7c**: 5.85 (br s, 1H, =C**H**), 5.79 (br s, 1H, =C**H**) (for other signals see the spectrum).



80:20

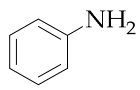
(E)-(2-cyclohexylvinyl)triethylsilane, *(E)*-**7d** (Table 5, entry 9)[2]
Selected spectroscopic data from the mixture: (*E*)-**7d**: ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 5.99 (dd, *J* = 18.9, 6.0 Hz, 1H, =C**H**), 5.49 (d, *J* = 18.9 Hz, 1H, =C**H**); **8d**: 5.68 (d, *J* = 2.3 Hz, 1H, =C**H**), 5.31 (d, *J* = 2.3 Hz, 1H, =C**H**) (for other signals see the spectrum).



[3] Yong, L., Kirels, K., Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833.

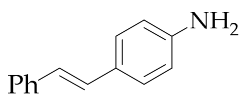
(E)-Triethyl(2,2,7,7-tetramethyloct-3-en-5-yn-4-yl)silane (E)-**9** (Table 5, entry 11)[2]
^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 5.86 (s, 1H), 1.24 (s, 9H), 1.20 (s, 9H), 0.95 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H).

S4. Spectral data of the anilines



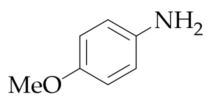
Aniline **10** (Table 7, entry 1)[4]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.23-7.15 (m, 2 H), 6.86-6.72 (m, 3 H), 3.65 (br s, 2H).



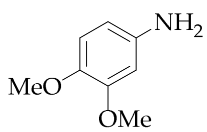
p-Aminostilbene **11** (Table 7, entry 3)[5]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.51-7.47 (m, 2H), 7.38-7.32 (m, 4H), 7.26-7.22 (m, 1H), 7.05 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 16.3 Hz, 1H), 6.68 (d, J = 8.47 Hz, 2H), 3.74 (br s, 2H); ^{13}C NMR (90 MHz, $CDCl_3$, ppm): δ 146.1, 137.9, 128.6, 128.5, 127.9, 127.7, 126.8, 126.0, 125.0, 115,1.



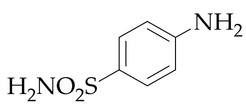
p-Methoxyaniline **12** (Table 7, entry 5)[4]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 6.75 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 3.75 (s, 3H), 3.42 (br s, 2 H).



3,4-Dimethoxyaniline **13** (Table 7, entry 6)[6]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 6.67 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 2.6 Hz, 1H), 6.20 (dd, J = 8.4, 2.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.48 (br s, 2H).



p-Aminobenzenesulfonamide **14** (Table 7, entry 9)[7]

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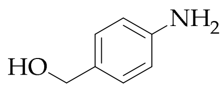
[4] K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki, H. Maheswaran. *Green Chem*. **2012**, *14*, 3164.

[5] Fernández, G.; Sort, J.; Pleixats, R. *ChemistrySelect* **2018**, *3*, 8597.

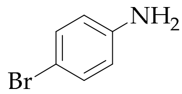
[6] A. V. Aksenov, N. A. Aksenov, O. N. Nadein, I. V. Aksenova. *Synlett* **2010**, 17, 2628.

^{1}H NMR (250 MHz, $(CD_3)_2CO$, ppm): δ 7.56 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 8.9 Hz, 2H), 6.15 (br s, 2H), 5.34 (br s, 2H).



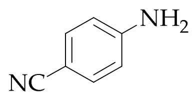
p-Aminobenzylalcohol **15** (Table 7, entry 12)[8]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.16 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 4.56 (s, 2H).



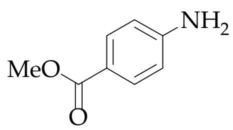
p-Bromoaniline **16** (Table 7, entry 13)[4]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.25 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 8.7 Hz, 2H), 3.69 (br s, 2H).



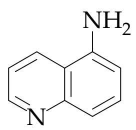
p-Aminobenzonitrile **17** (Table 7, entry 14)[4]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.39 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 4.2 (br s, 2 H).



Methyl *p*-aminobenzoate **18** (Table 7, entry 15)[7]

^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.85 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 4.06 (br s, 2H), 3.85 (s, 3H).



5-Quinolinamine **19** (Table 7, entry 16)[9]

^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 8.89 (dd, J = 4.2, 1.7 Hz, 1H), 8.18 (dd, J = 8.5, 1.7 Hz, 1H), 7.59-7.49 (m, 2H), 7.35 (dd, J = 8.5, 4.2 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 4.21 (br s, 2H).

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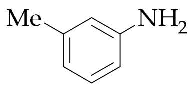
7 W. Guo, R. Pleixats, A. Shafir. *Chem. Asian J.* **2015**, *10*, 2437.

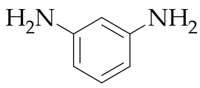
8 *Kim, J., Chang, S. Chem. Commun.* ***2008****, 3052.*

9 Rashidi, A., Afghan, A., Baradarani, M. M., Joule, J. A. *J. Heterocyclic Chem.* **2009**, *46*, 428.



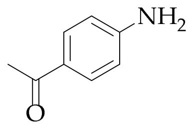
m-Toluidine **20** (Table 7, entry 17)[10]

[1]H NMR (360 MHz, $CDCl_3$, ppm): δ 7.06 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.5, 1.7 Hz, 1H), 6.54-6.50 (m, 2H), 3.58 (br s, 2H), 2.28 (s, 3H).



m-Phenylenediamine **21** (Table 7, entry 18)[4]

[1]H NMR (250 MHz, $CDCl_3$, ppm): δ 6.95 (t, *J* = 7.8 Hz, 1H), 6.12 (dd, *J* = 7.9, 2.2 Hz, 2 H), 6.01 (t, *J* = *2.2* Hz, 1H), 3.52 (br s, 4H).



p-Aminoacetophenone **22** (Table 7, entry 19)[11]

[1]H NMR (250 MHz, $CDCl_3$, ppm): δ 7.79 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 4.22 (br s, 2H), 2.49 (s, 3H). [13]C NMR (90 MHz, $CDCl_3$, ppm): δ 196.5, 151.1, 130.7, 127.7, 113.6, 26.0. IR (ATR): 3389, 3328, 3222, 1650 cm^{-1}.

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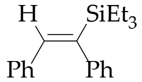
[10] Spectral Database for Organic Compounds (SDBS); [1]HNMR; No. 1156HSP-00-727

[11] C. Wang, Y. Pan, A. Wu. *Tetrahedron*, **2007**, *63*, 429.

S3. Spectra collection



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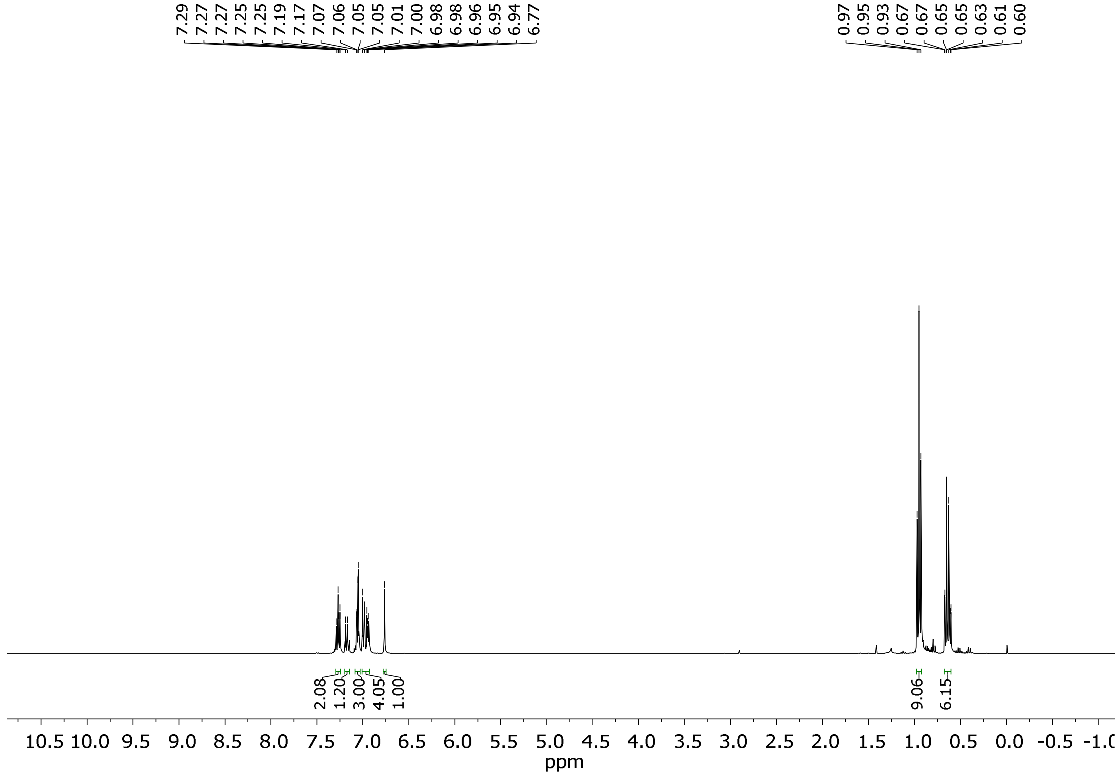
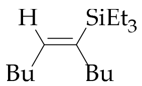
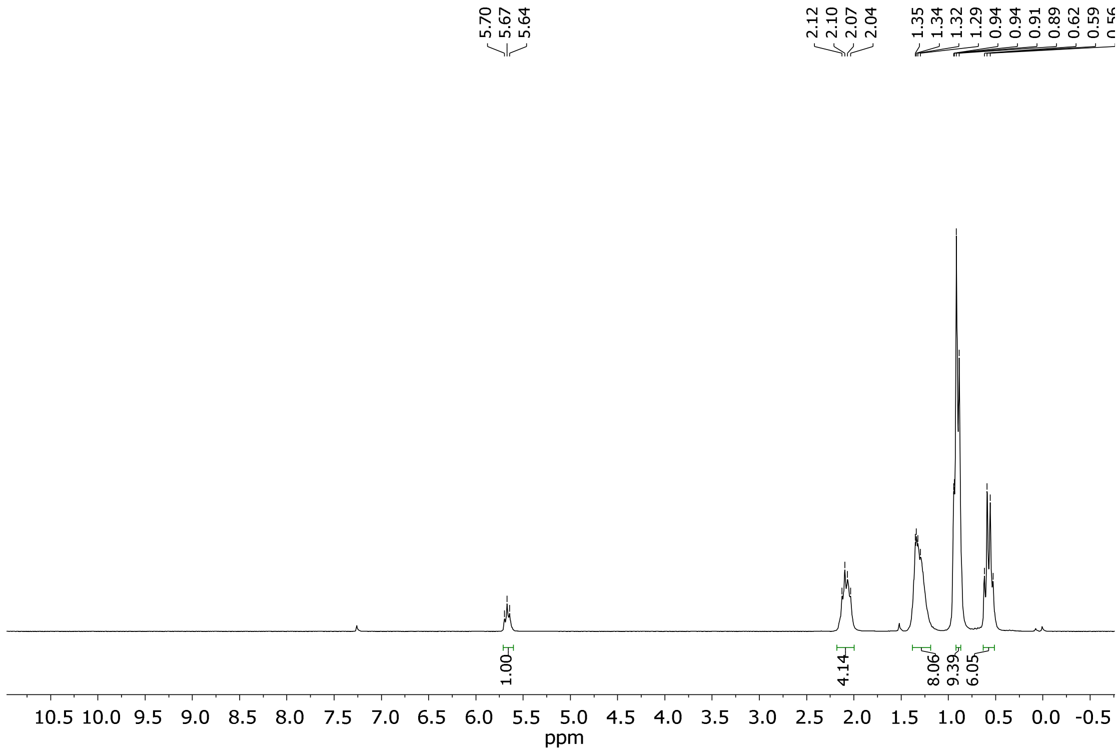
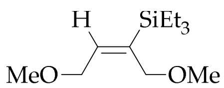


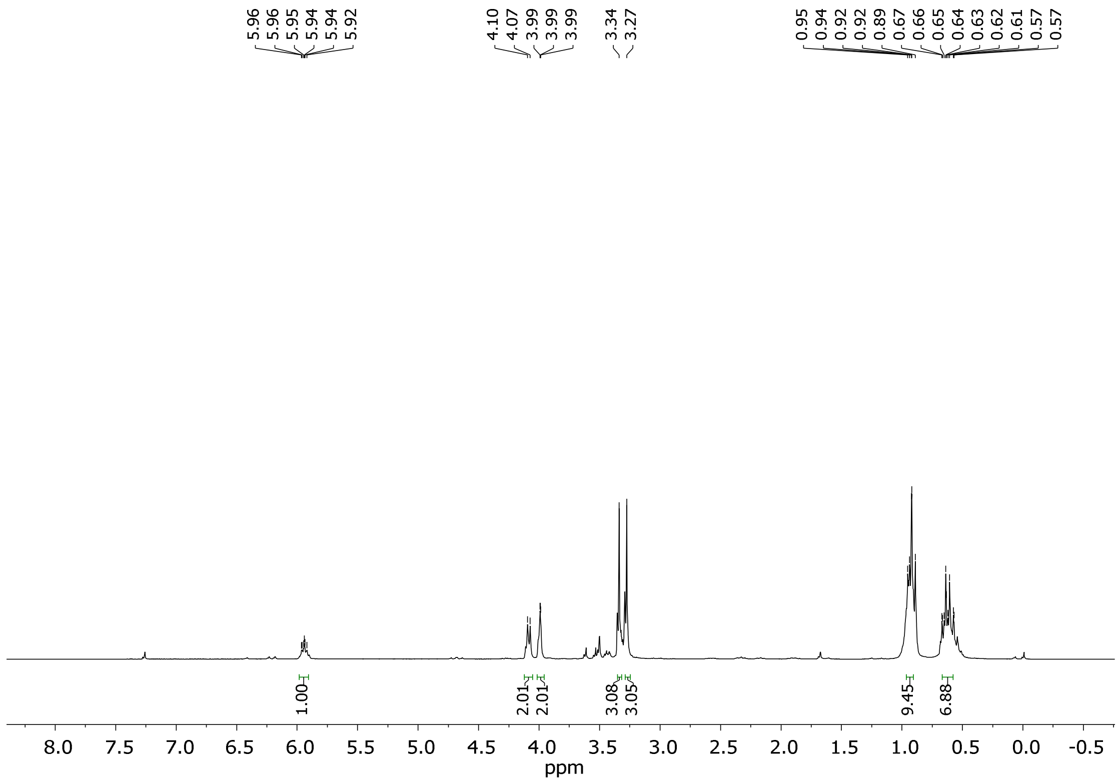


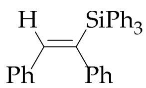
^{1}H NMR (250 MHz, $CDCl_3$)





^{1}H NMR (250 MHz, $CDCl_3$)





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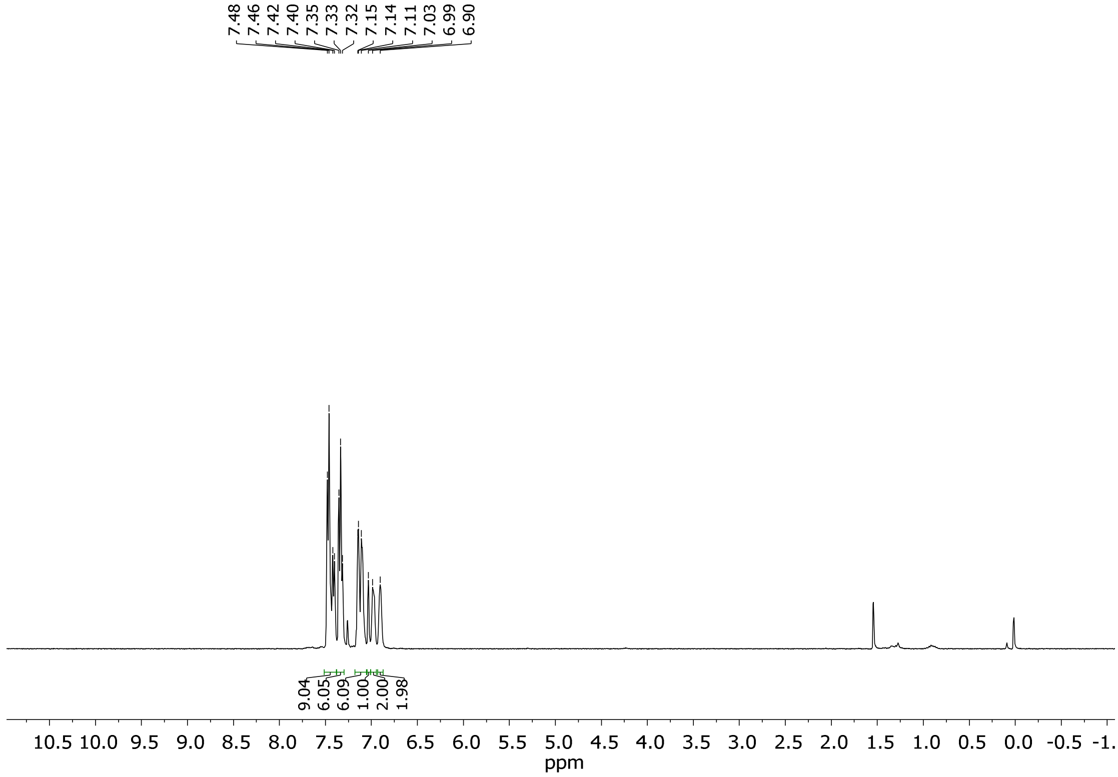

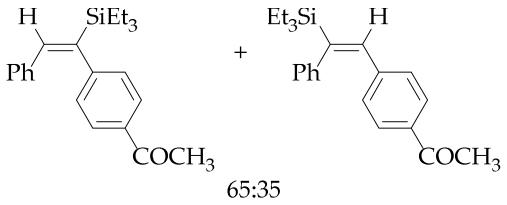

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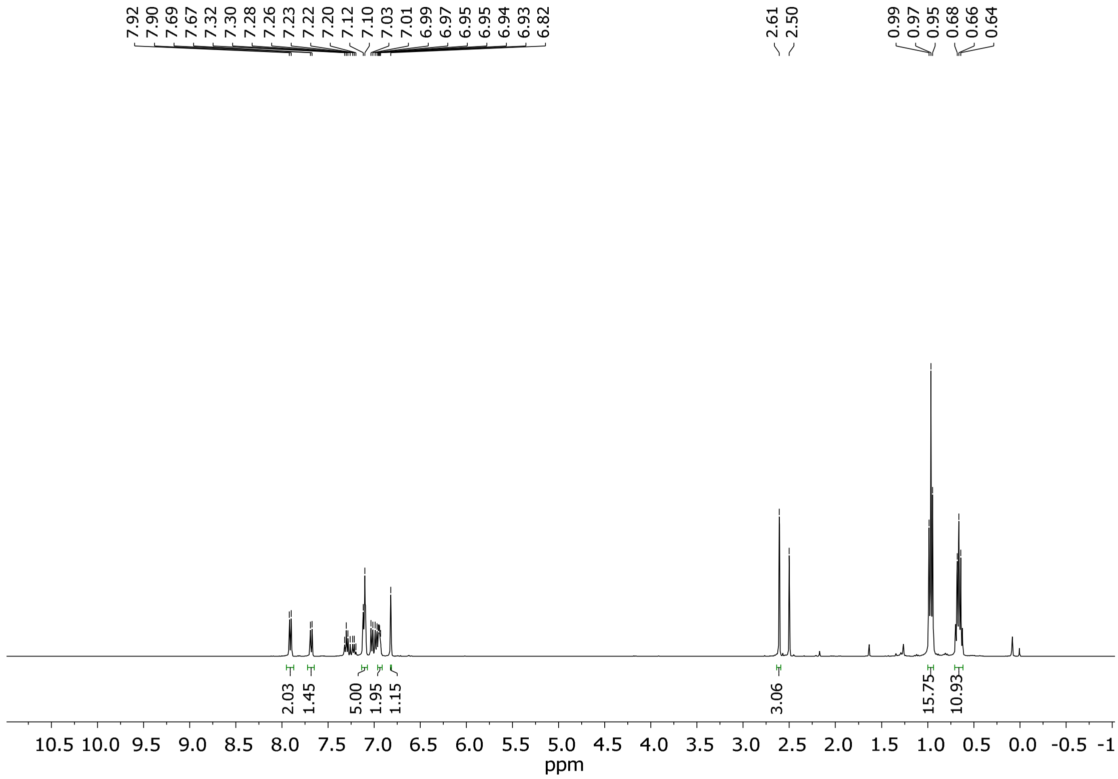

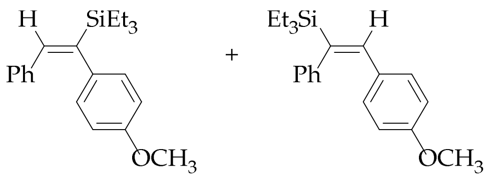

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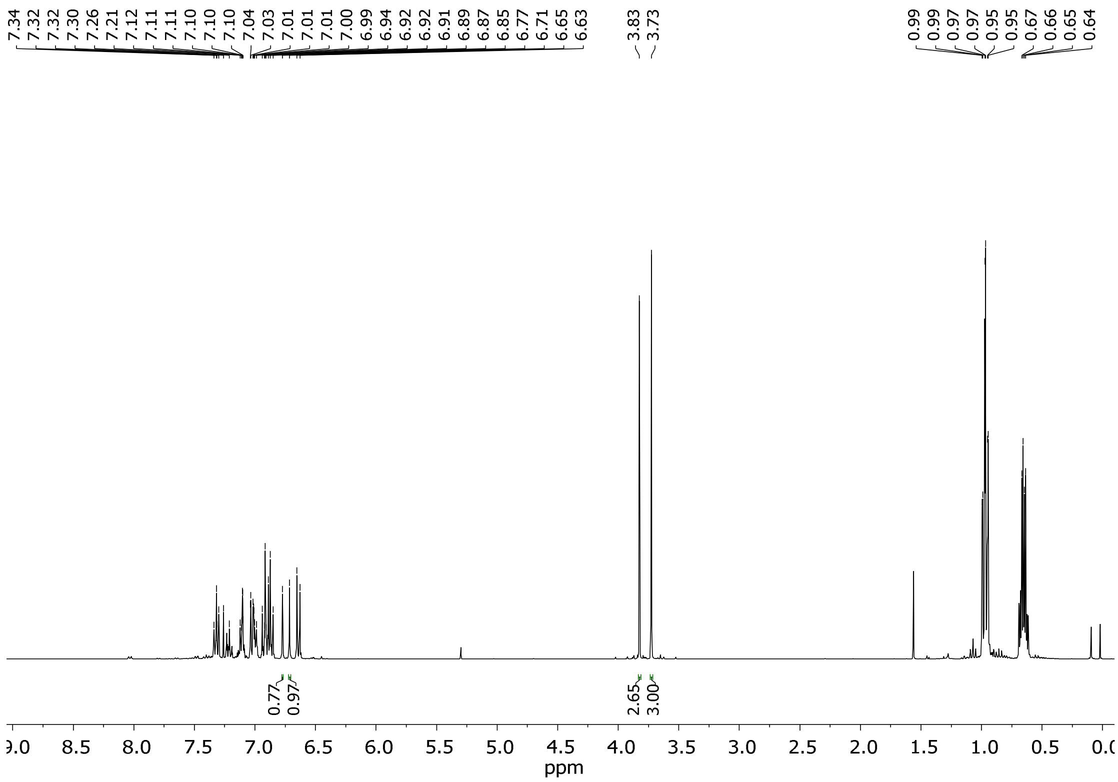
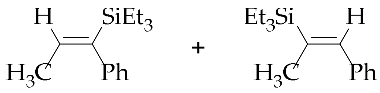
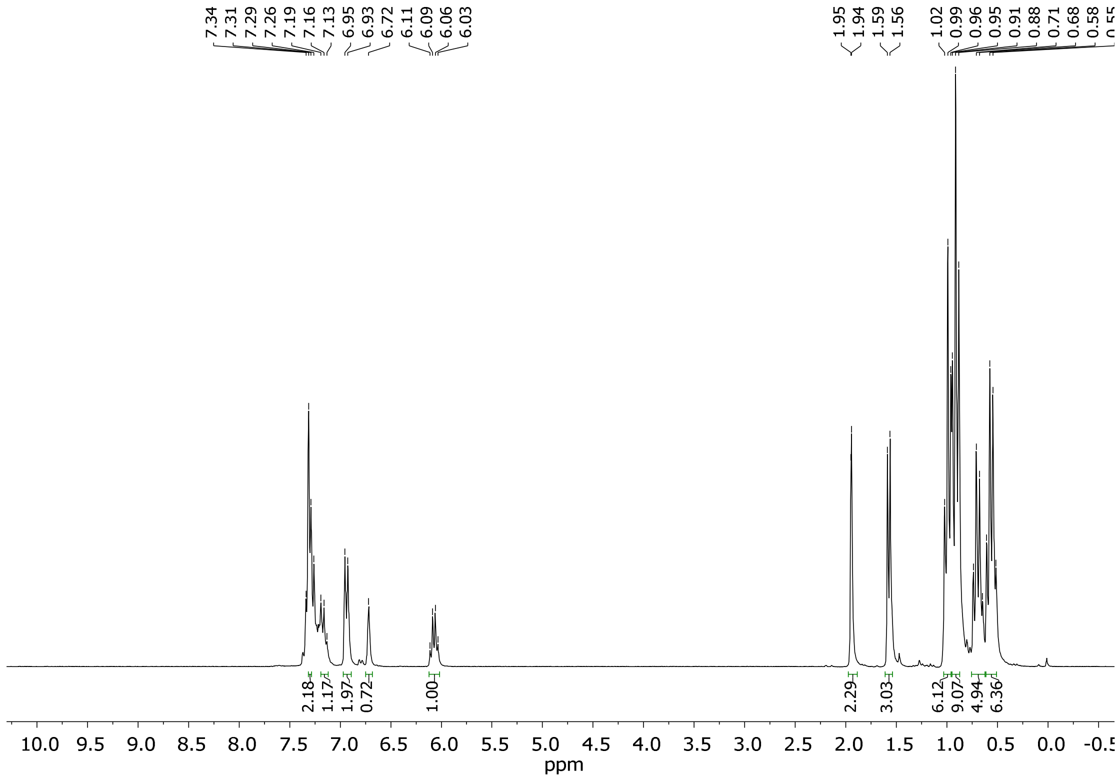
^1H NMR (360 MHz, $CDCl_3$)

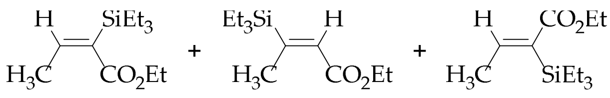




76:24

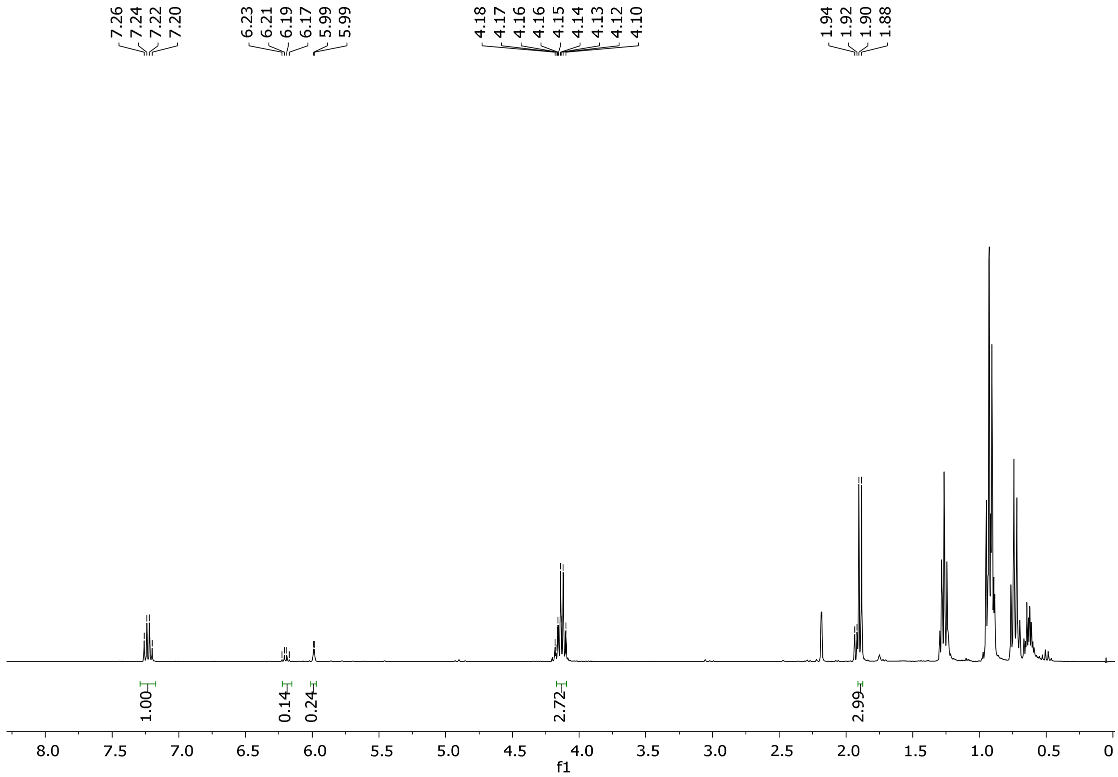
^{1}H NMR (250 MHz, $CDCl_3$)

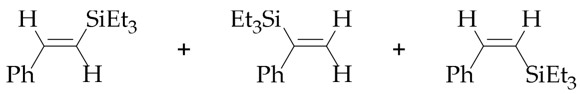




11:15:74

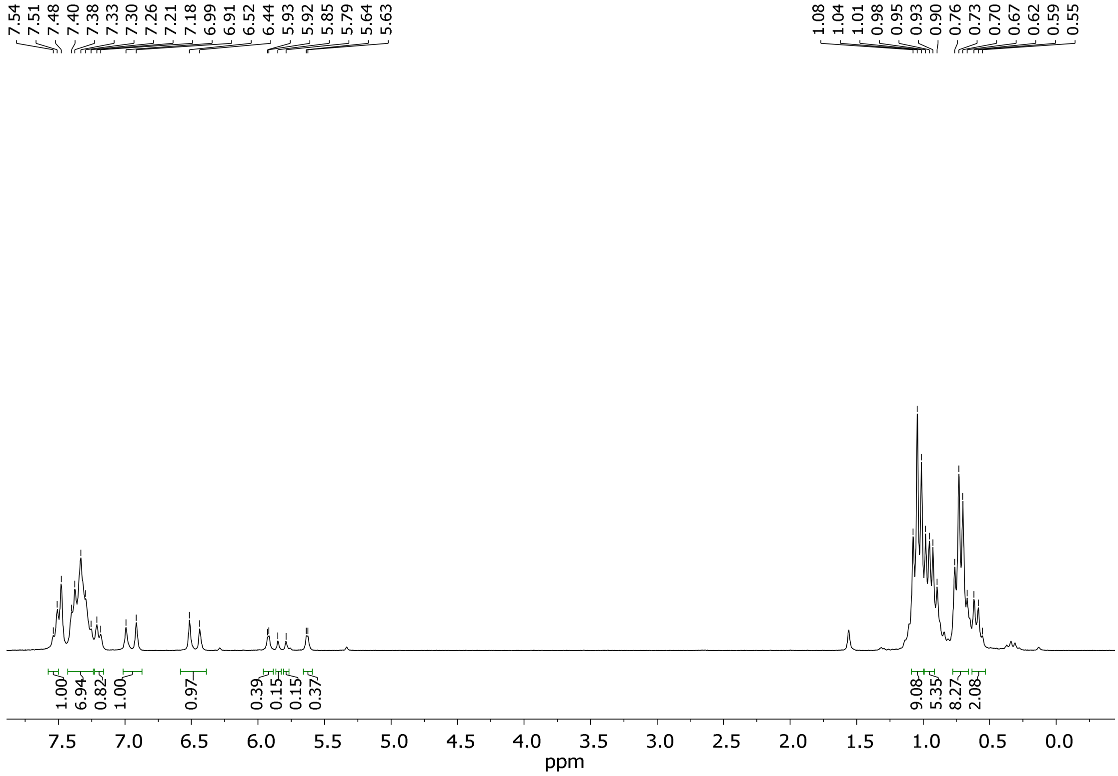
^{1}H NMR (250 MHz, $CDCl_3$)

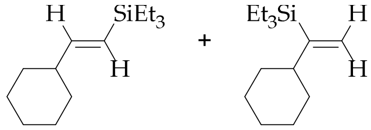




65:25:10

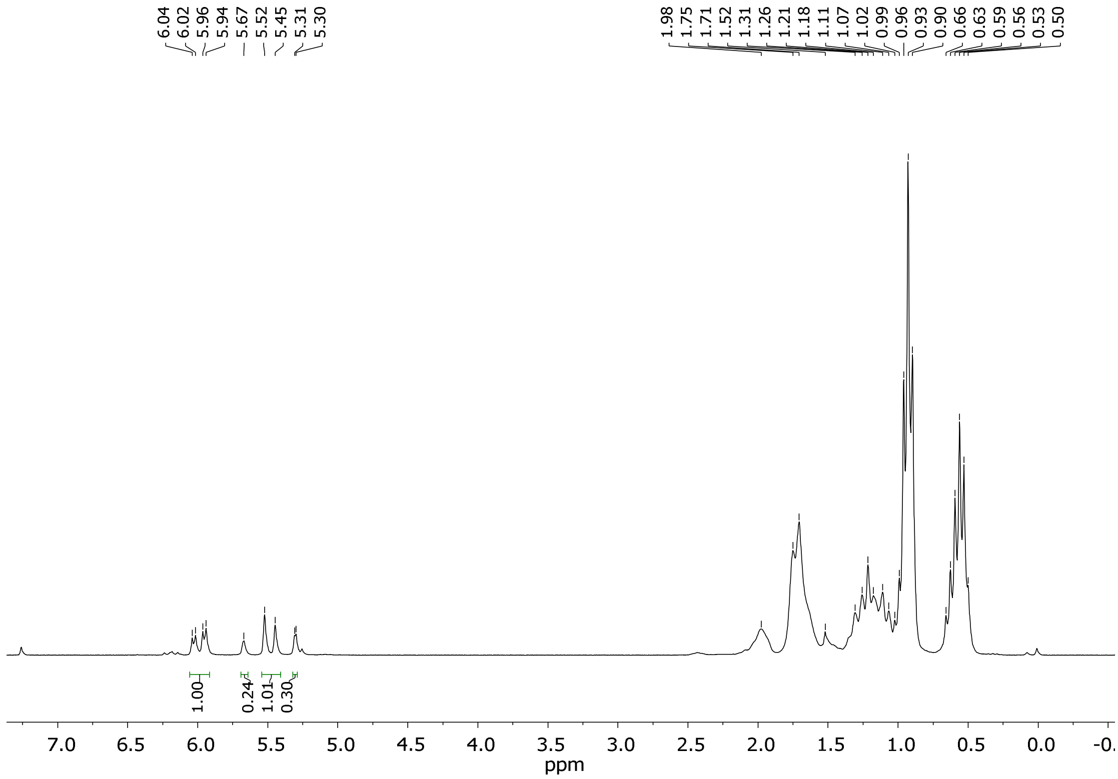
^{1}H NMR (250 MHz, $CDCl_3$)

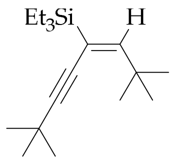




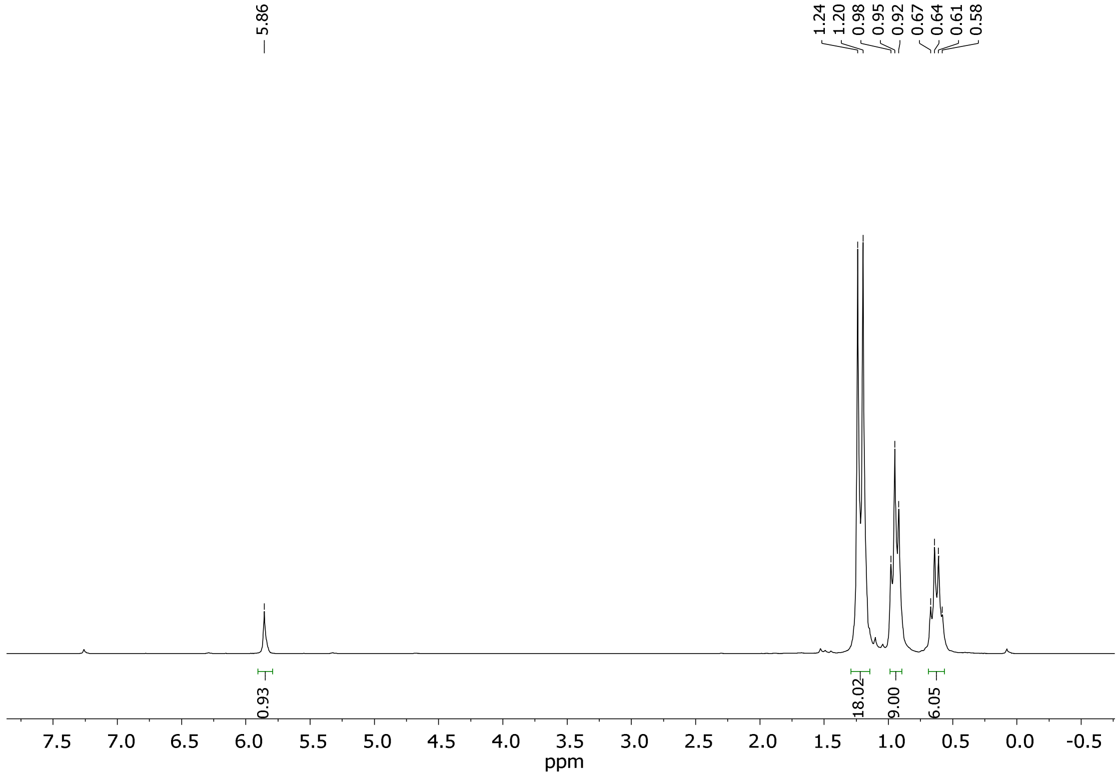
80:20

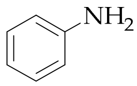
^{1}H NMR (250 MHz, $CDCl_3$)



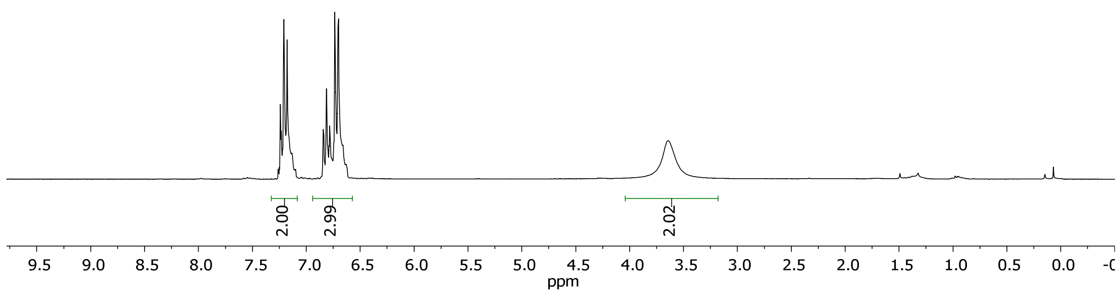


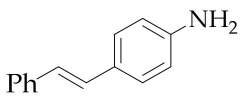
^1H NMR (250 MHz, $CDCl_3$)



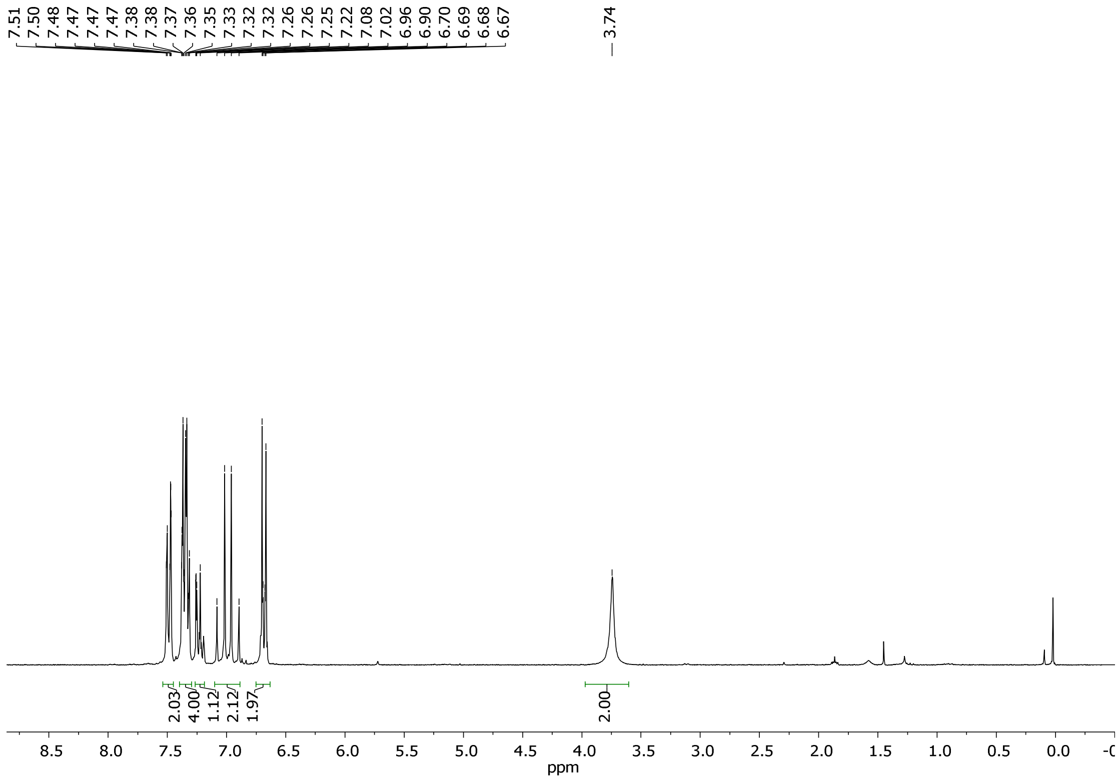


[1]H NMR (250 MHz, $CDCl_3$)

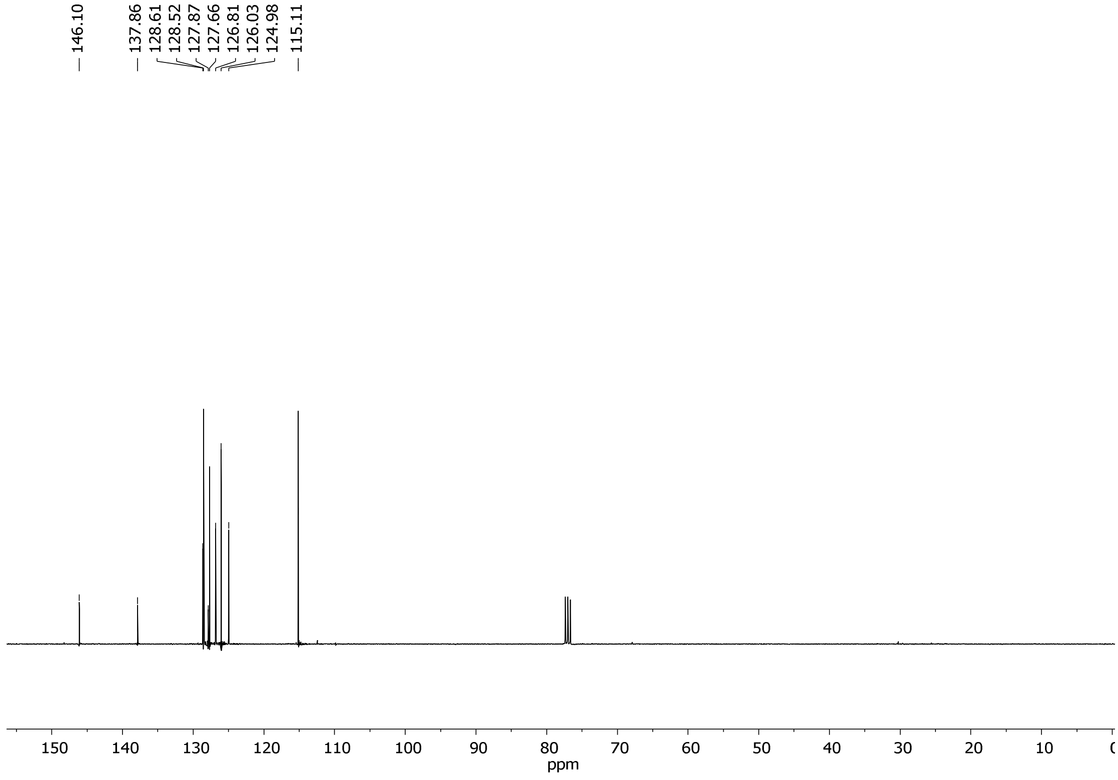


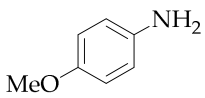


^{1}H NMR (250 MHz, $CDCl_3$)

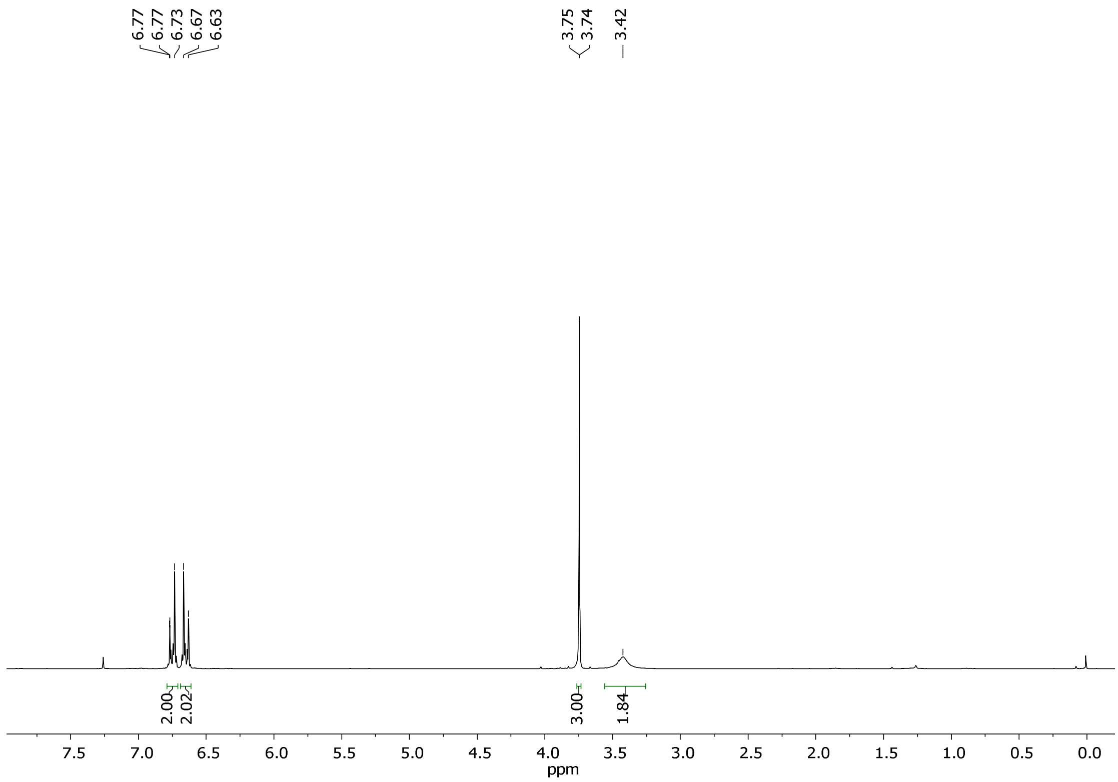


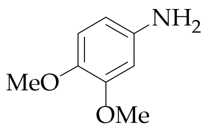
^{13}C NMR (90 MHz, $CDCl_3$)



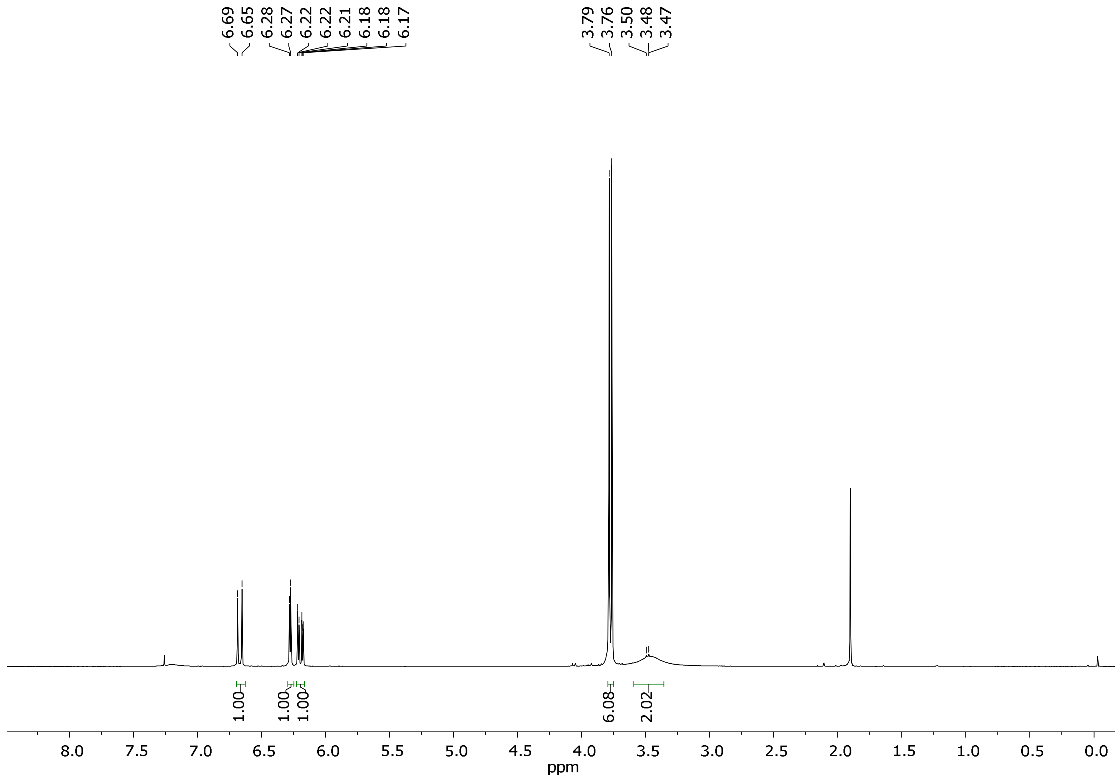


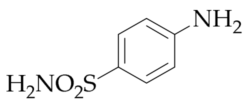
^{1}H NMR (250 MHz, $CDCl_3$)



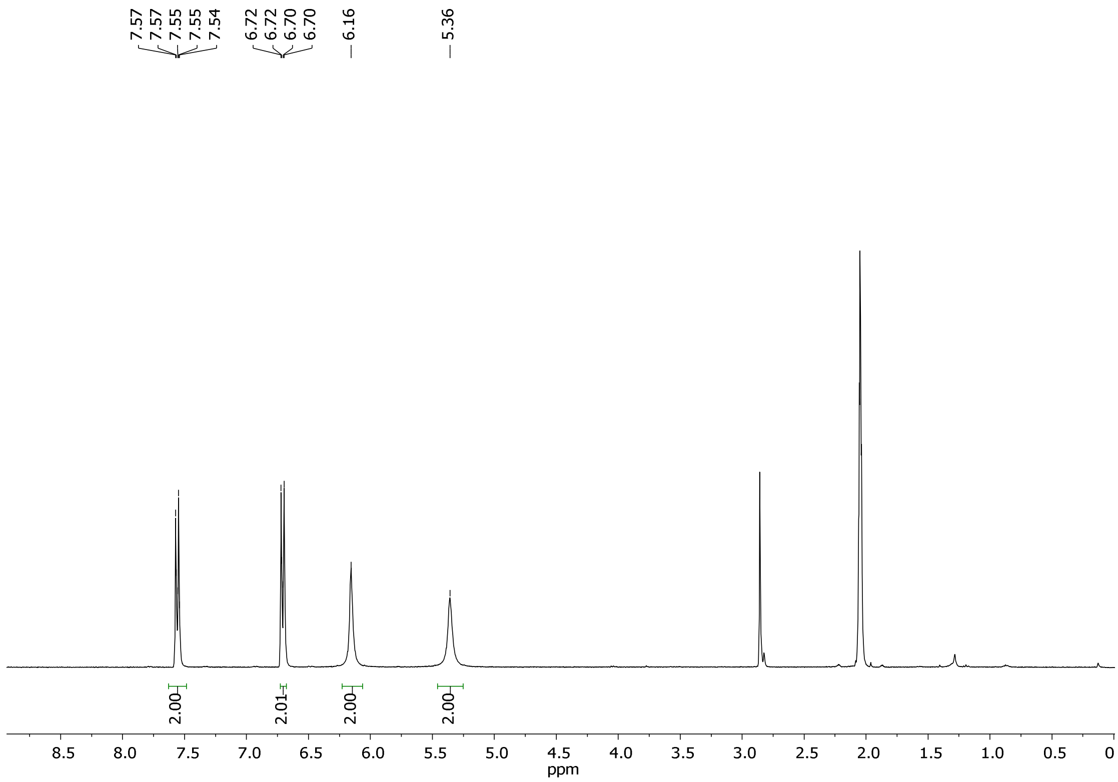


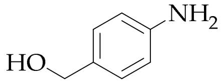
^1H NMR (250 MHz, $CDCl_3$)



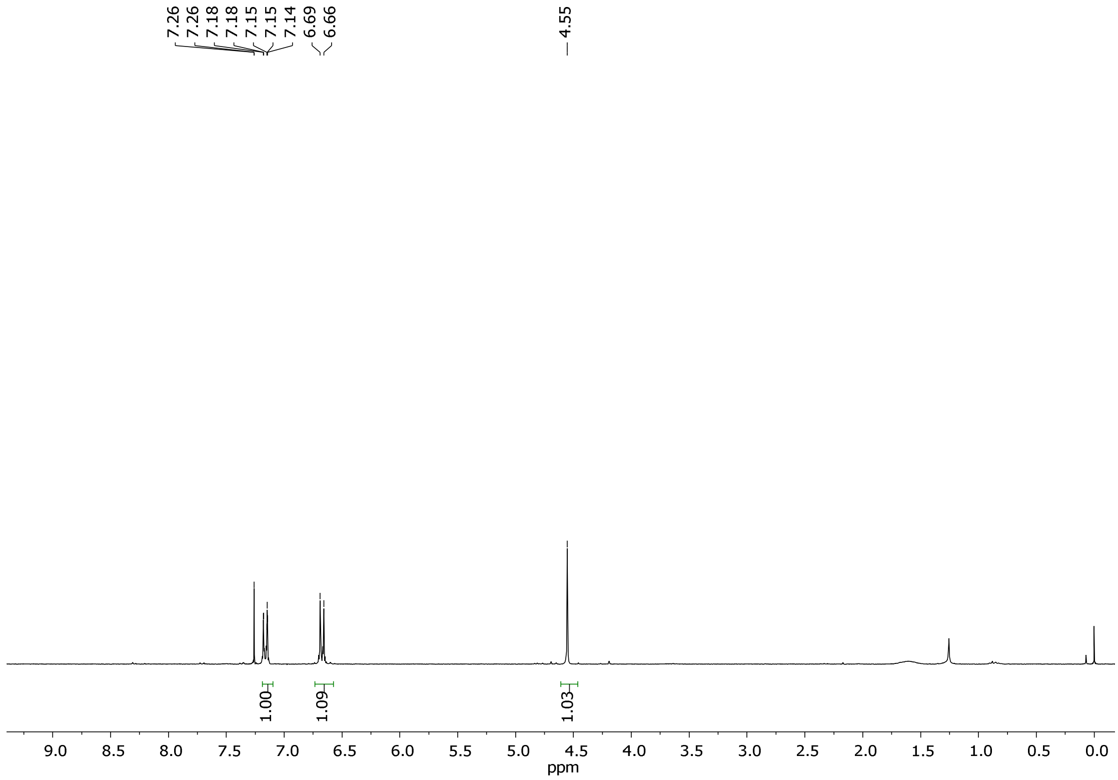


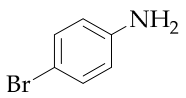
^1H NMR (250 MHz, $(CD_3)_2CO$)



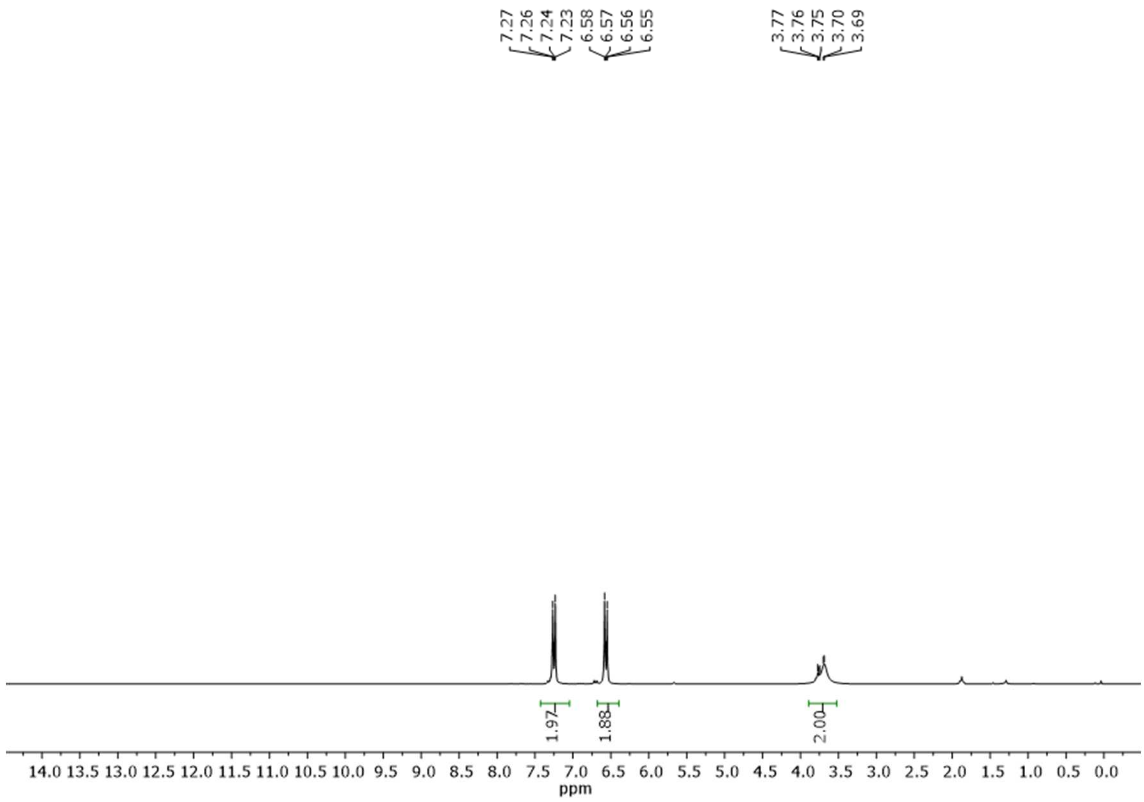


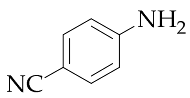
^{1}H NMR (250 MHz, $CDCl_3$)



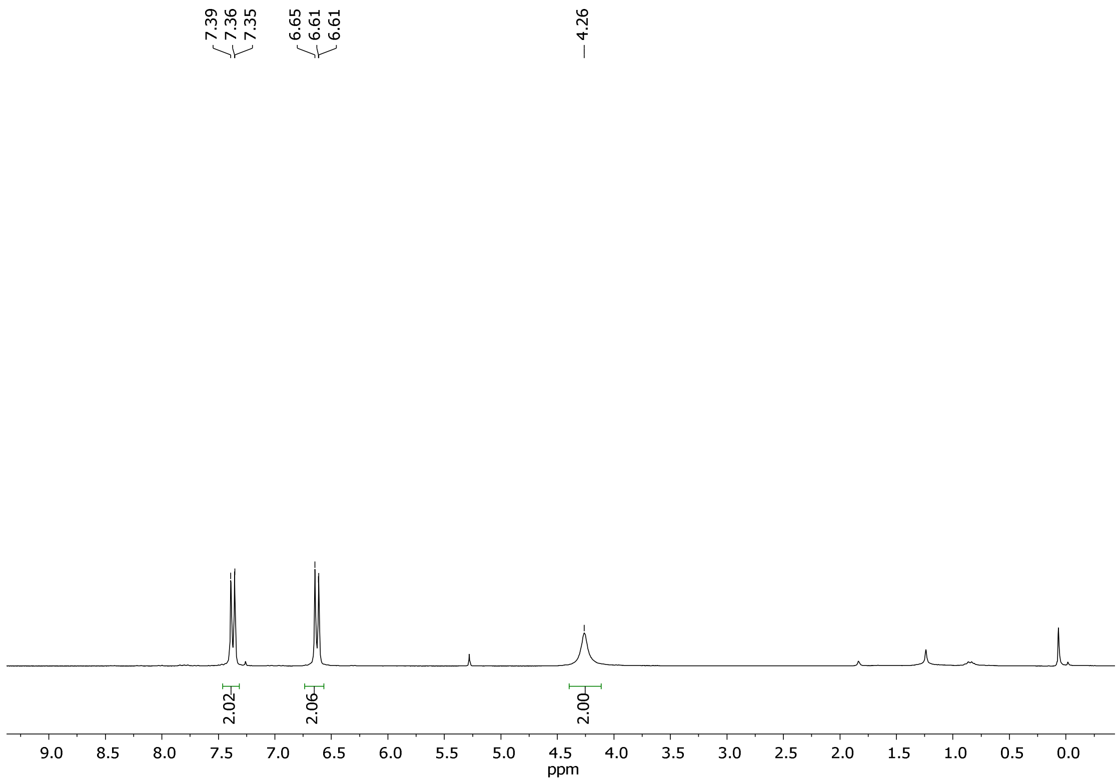


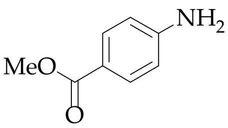
^1H NMR (250 MHz, $CDCl_3$)



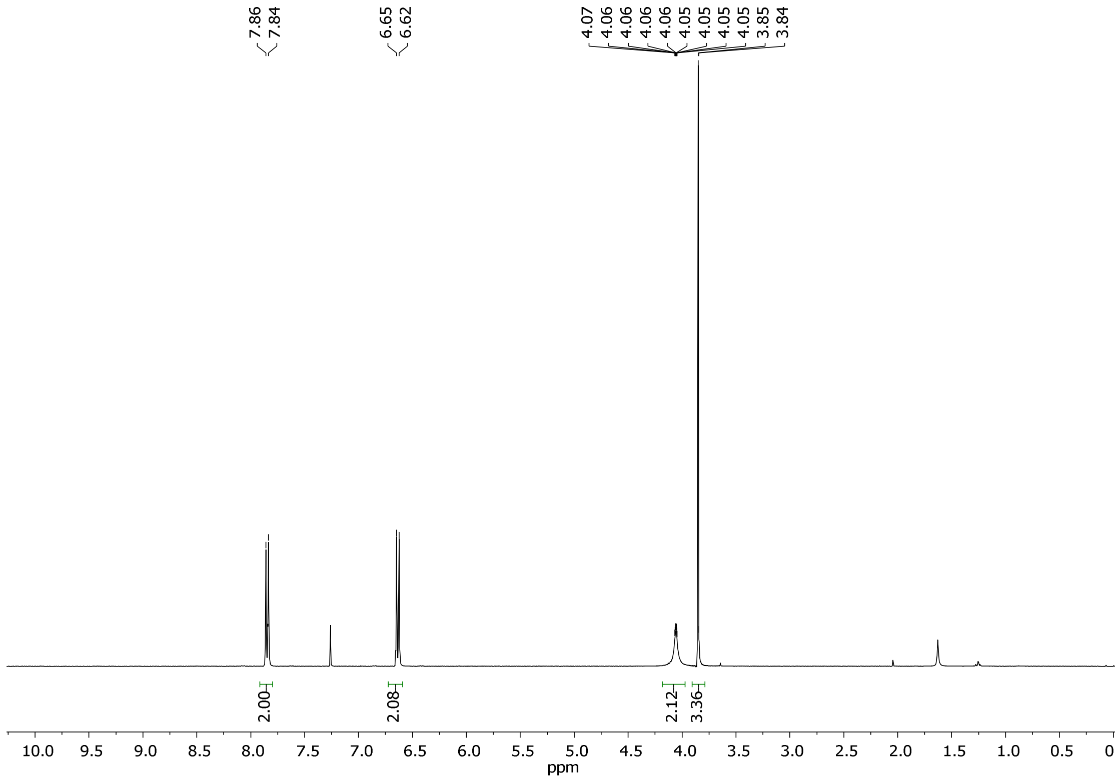


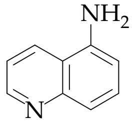
^1H NMR (250 MHz, $CDCl_3$)



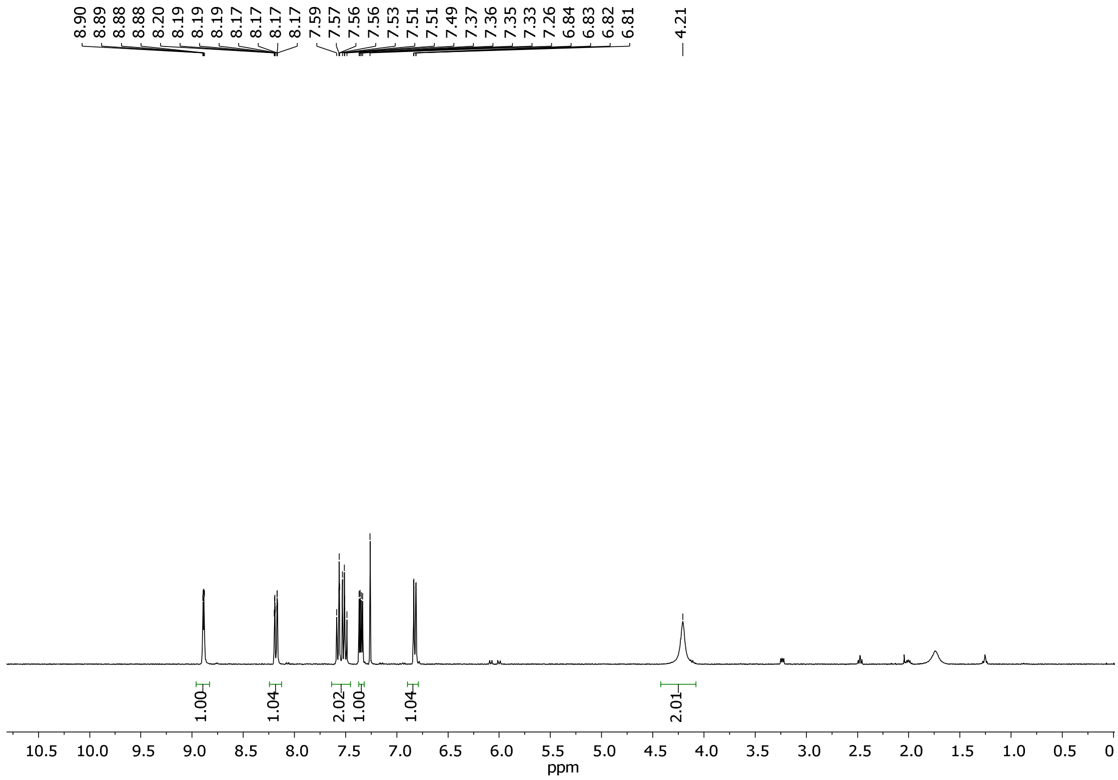


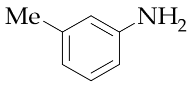
^{1}H NMR (360 MHz, $CDCl_3$)



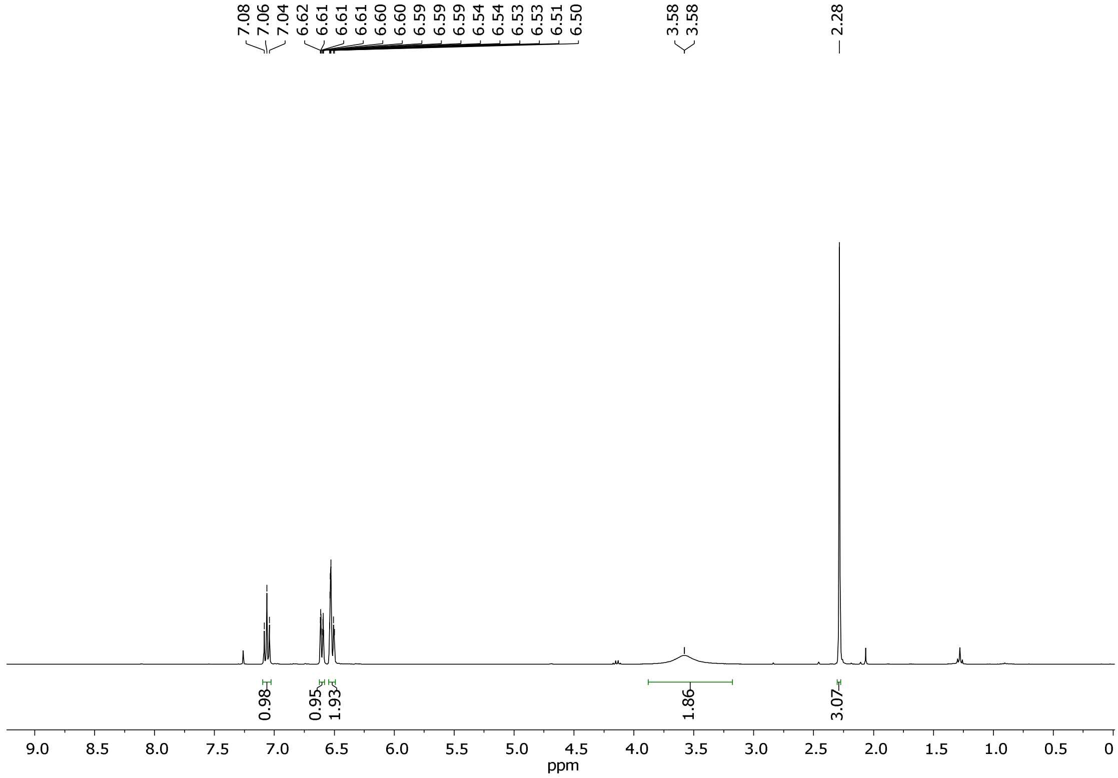


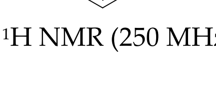
^1H NMR (360 MHz, $CDCl_3$)



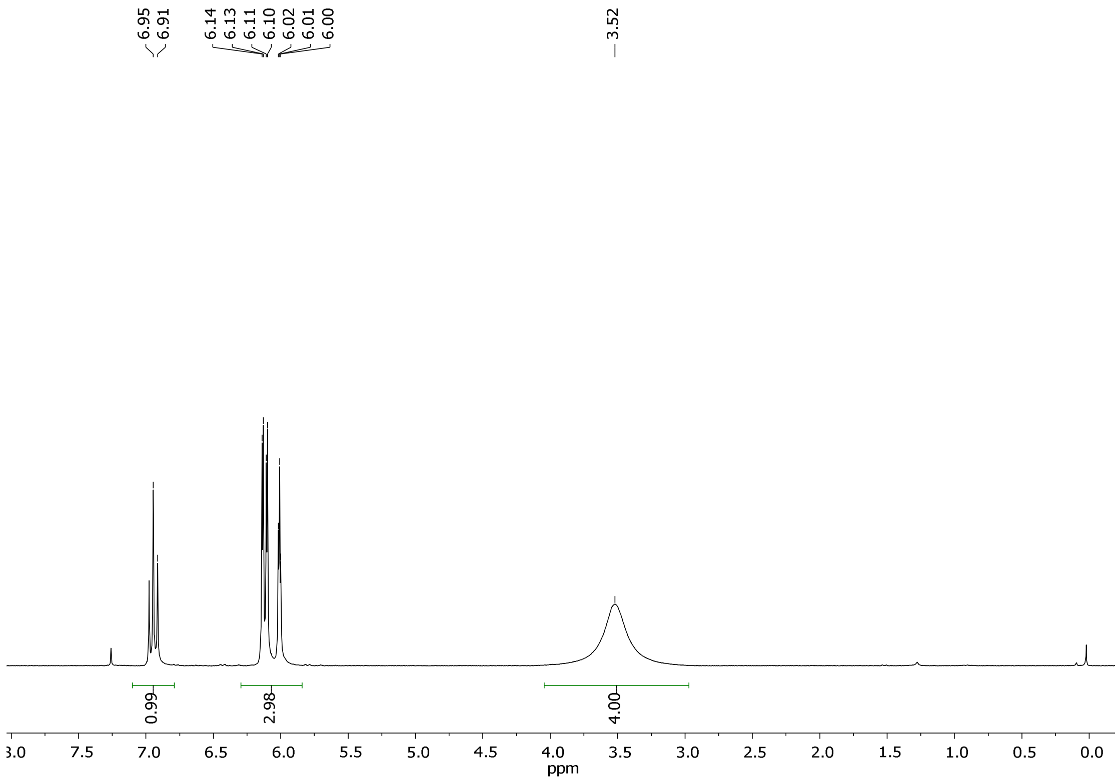


^{1}H NMR (360 MHz, $CDCl_3$)





^{1}H NMR (250 MHz, $CDCl_3$)


6.95
6.91
6.14
6.13
6.11
6.10
6.02
6.01
6.00
3.52
0.99
2.98
4.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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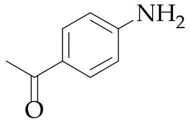
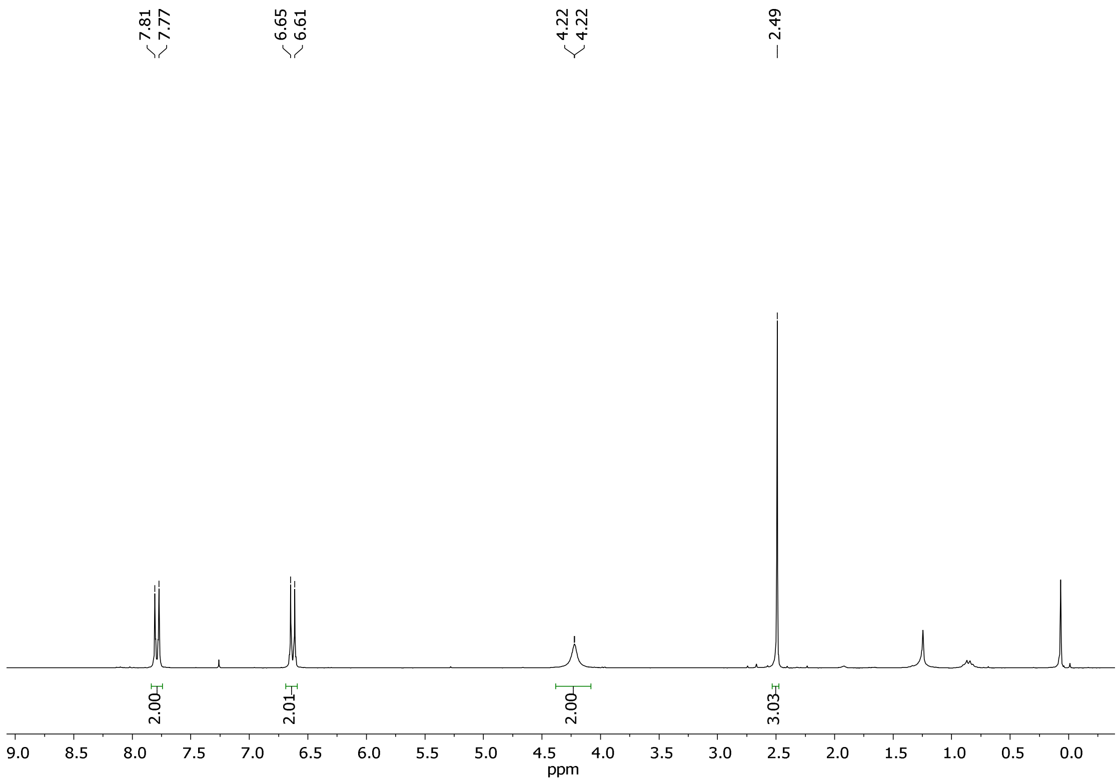
1.5
1.0
0.5
0.0
ppm



^{1}H NMR (250 MHz, $CDCl_3$)



^{13}C NMR (90 MHz, $CDCl_3$)