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Aza-Favorsky reaction with regioisomeric C- and N-linked 1,4-bis(imino)benzenes: synthetic and reactivity dissimilarities

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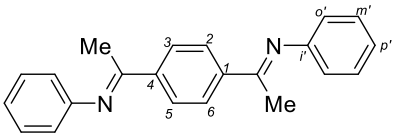
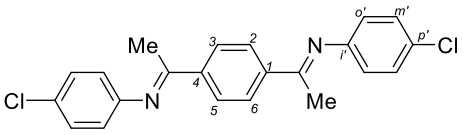
General information

The NMR spectra were recorded on a Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 40.5 MHz for ^{15}N) in $CDCl_3$. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), ddd (doublet of doublets of doublets), m (multiplet). Melting points (uncorrected) were measured on a SMP50 Stuart apparatus. Mass spectra of positive electron ionization ions (70 eV) were registered on a Shimadzu GCMS-QP5050A with a DI-50 direct sample injection system (quadrupole mass analyzer, range of detected masses 34 - 650 Da). Bisimines **1a** and **1b** were synthesized by the condensation of 1,4-diacetylbenzene with aniline and 4-chloroaniline, respectively, according to the literature procedure.[S1] Bisimine **1c** was prepared from 1,4-diaminobenzene and acetophenone by the published procedure.[S2] Spectral data for the imine **1c** correspond to literature data.[S3]

***(1E,1'E)-1,1'-(1,4-Phenylene)bis(N-phenylethan-1-imine)* (*1a*).** Yellow powder. M.p. = 195-198 °C. Elemental analysis calcd (%) for $C_{22}H_{20}N_2$ (312.42): C, 84.58; H, 6.45; N, 8.97; found: C, 84.56; H, 6.49; N, 8.95. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.06 (s, 4H, H*2,3,5,6*), 7.43 – 7.35 (m, 4H, H*m′*), 7.19 – 7.09 (m, 2H, H*p′*), 6.90 – 6.75 (m, 4H, H*o′*), 2.28 (s, 6H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.0 (C=N), 151.6 (C*i′*), 141.2 (C*1,4*), 129.0 (C*2,3,5,6*), 127.3 (C*m′*), 123.4 (C*p′*), 119.4 (C*o′*), 17.5 (Me) ppm. MS (EI), m/z (%): 312.10 $[M]^{+\cdot}$. Calc. for $C_{22}H_{20}N_2$ m/z 312.16.



(1E,1'E)-1,1'-(1,4-Phenylene)bis(N-(4-chlorophenyl)ethan-1-imine) (*1b*). Light yellow powder. M.p. = 261-262 °C. Elemental analysis calcd (%) for $C_{22}H_{18}Cl_2N_2$ (381.30): C, 69.30; H, 4.76; Cl, 18.59; N, 7.35; found: C, 69.38; H, 4.67; Cl, 18.26; N, 7.40. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.04 (s, 4H, H*2,3,5,6*), 7.39 – 7.31 (m, 4H, H*o′*), 6.93 – 6.71 (m, 4H, H*m′*). 2.28 (s, 6H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.6 (C=N), 149.9 (C*i′*), 140.9 (C*1,4*), 129.0 (C*2,3,5,6*), 128.7 (C*p′*), 127.2 (C*m′*), 120.7 (C*o′*), 17.5 (Me) ppm. MS (EI), m/z (%): 380.10 $[M]^{+\cdot}$. Calc. for $C_{22}H_{18}Cl_2N_2$ m/z 380.08.



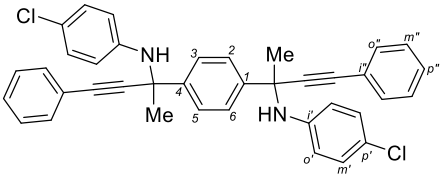
***(1E,1'E)-N,N'-(1,4-Phenylene)bis(1-phenylethan-1-imine)* (*1c*).** Light yellow solid. M.p. = 210-211 °C. Elemental analysis calcd (%) for $C_{22}H_{20}N_2$ (312.42): C, 84.58; H, 6.45; N, 8.97; found: C, 84.61; H, 6.47; N, 8.92. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.29 – 7.96 (m, 4H, H*o'*), 7.62 – 7.35 (m, 6H, H*m'*,*p'*), 6.84 (s, 4H, H*2*,*3*,*5*,*6*), 2.31 (s, 6H, Me) ppm.^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.8 (C=N), 147.4 (C*1*,*4*), 139.8 (C*i'*), 130.5 (C*p'*), 128.5, 127.2 (C*o'*,*m'*), 120.3 (C*2*,*3*,*5*,*6*), 17.5 (Me) ppm. MS (EI), m/z (%): 312.15 $[M]^{+\cdot}$. Calc. for $C_{22}H_{20}N_2$ m/z 312.16.

N,N'-[1,4-Phenylenebis(but-3-yne-2,2-diyl)]dianiline (3aa) was prepared from bisimine **1a** (0.5 mmol, 0.16 g). **3aa** was isolated as two diastereomers. Light yellow powder (0.23 g, 62% yield). M.p. = 220-222 °C. Elemental analysis calcd (%) for $C_{26}H_{24}N_2$ (364.49): C, 85.68; H, 6.64; N, 7.69; found: C, 85.61; H, 6.73; N, 7.58. MS (EI), m/z (%): 364.10 $[M]^{+\cdot}$. Calc. for $C_{26}H_{24}N_2$ m/z: 364.19. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54 (s, 4H, H*2*,*3*,*5*,*6*), 6.94 – 6.82 (m, 4H, H*m'*), 6.53 – 6.39 (m, 2H, H*p'*, H*o'*, NH), 3.41, 3.40 (s, 2H, ≡CH), 1.70 (s, , 6H, Me).^{13}C NMR (100.6 MHz, DMSO-d_6): δ 145.8, 145.7 [C*i'*], 143.3 (C*1*,*4*), 127.9, 127.8 [C*m'*], 125.3 (C*2*,*3*,*5*,*6*), 116.5, 116.4 (C*p'*), 114.9 (C*o'*), 86.4, 86.3 [C≡CH], 74.4, 74.3 [C≡CH], 54.1 (C-N), 35.0 (Me). ^{15}N NMR (40.5 MHz, DMSO-d_6): δ -295.4 ppm.

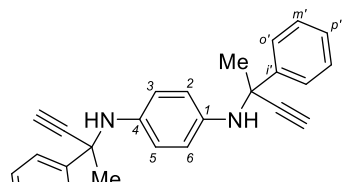
***N,N'-[1,4-Phenylenebis(but-3-yne-2,2-diyl)]bis(4-chloroaniline)* (*3ba*)** was prepared from bisimine **1b** (0.5 mmol, 0.19 g). **3ba** was isolated as two diastereomers. Beige powder (0.18 g, 82% yield). M.p. = 174-175 °C. Elemental analysis calcd (%) for $C_{26}H_{22}Cl_2N_2$ (433.38): C, 72.06; H, 5.12; Cl, 16.36; N, 6.46; found: C, 72.10; H, 5.09; Cl, 16.24; N, 6.37. MS (EI), m/z (%): 432.15 $[M]^{+\cdot}$. Calc. for $C_{26}H_{22}Cl_2N_2$ m/z: 432.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 4H, H*2*,*3*,*5*,*6*), 7.01 – 6.99 (m, 4H, H*m'*), 6.45 – 6.42 (m, 4H, H*o'*), 4.27, 4.25 [br. s, 2H, NH], 2.49 (s, 2H, ≡CH), 1.80 (s, 6H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.6 (C*i'*), 142.9 (C*1*,*4*), 128.6 (C*m'*), 126.0 (C*2*,*3*,*5*,*6*), 123.6, 123.5 [C*p'*], 117.2, 117.1 [C*o'*], 85.7, 85.6 [C≡CH], 72.9, 72.8 [C≡CH], 55.4, 55.3 [C-N], 35.6 (Me) ppm. ^{15}N NMR: δ -295.2 (NH) ppm.

***N,N'-[1,4-Phenylenebis(4-phenylbut-3-yne-2,2-diyl)]dianiline* (*3ab*)** was prepared from bisimine **1a** (1.0 mmol, 0.31 g). **3ab** was isolated as two diastereomers. Yellow solid (0.32 g, 62% yield). M.p. = 195-197 °C. Elemental analysis calcd (%) for $C_{38}H_{32}N_2$ (516.69): C, 88.34; H, 6.24; N, 5.42; found: C, 88.46; H, 6.31; N, 5.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77, 7.76 [s, 4H, H*2*,*3*,*5*,*6*], 7.48 – 7.35 (m, 4H, H*o''*), 7.30 – 7.27 (m, 6H, H*m'*, H*p'*), 7.12 – 7.08 (m, 4H, H*m'*), 6.77 – 6.72 (m, 2H, H*p'*), 6.65 – 6.63 (m, 4H, H*o'*), 4.36 (br. s, 2H, NH), 1.92 (s, 6H, Me). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3 (C*i'*), 143.8 (C*1*,*4*), 131.9, 131.8 [C*o''*], 128.6, 128.5 [C*m'*], 128.3 (C*m''*), 128.2 (C*p''*), 126.2, 126.1 (C*2*,*3*,*5*,*6*), 123.2, 123.2 [C*i''*], 118.6, 118.5 (C*p'*), 116.4, 116.3 [C*o'*], 92.0, 91.8 [C≡C-Ph], 84.8, 84.7 [C≡C-Ph], 56.0, 55.9 [C-N], 35.5, 35.5 [Me]. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ -293.2, -293.8 [NH] ppm. MS (EI), m/z (%): 516.30 $[M]^{+\cdot}$. Calc. for $C_{38}H_{32}N_2$ m/z: 516.26.

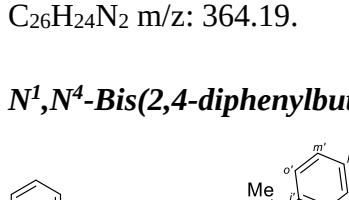
N,N'-[1,4-Phenylenebis(4-phenylbut-3-yne-2,2-diyl)]bis(4-chloroaniline) (3bb) was prepared from bisimine **1b** (1 mmol, 0.38 g). **3bb** was isolated as a mixture of two diastereomers in a 1:1 molar ratio as a beige powder (0.21 g, 73% yield). M.p. = 194-195 °C. Elemental analysis calcd (%) for $C_{38}H_{30}Cl_2N_2$ (585.57): C, 77.94; H, 5.16; Cl, 12.11; N, 4.78; found (%): C, 78.00; H, 5.21; Cl, 12.01; N, 4.69. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.69 (s, 4H, H*2,3,5,6*), 7.41 – 7.33 (m, 4H, H*o''*), 7.32 – 7.25 (m, 6H, H*m'',p''*), 7.05 – 6.95 (m, 4H, H*m'*), 6.60 – 6.38 (m, 4H, H*o'*), 4.34 (br. s, 2H, NH), 1.87 (s, 6H, Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 143.7 (C*i'*), 143.4 (C*1,4*), 131.7, 131.6 8 (C*o''*), 128.9 (C*m'*), 128.5, 128.3 (C*m''*), 128.2 (C*p''*), 126.0, 125.9 (C*2,3,5,6*), 123.2 (C*p'*), 122.8 (C*i''*), 117.1, 117.0 (C*o'*), 91.2 (C≡C-Ph), 84.8, 84.7 (C≡C-Ph), 55.8, 55.7 (C-N), 35.3 (Me) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ -293.2 ppm. MS (EI), m/z (%): 584.10 $[M]^{+\cdot}$. Calc. for $C_{38}H_{30}Cl_2N_2$ m/z: 584.18.



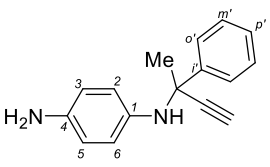
N^1,N^4-Bis(2-phenylbut-3-yn-2-yl)benzene-1,4-diamine (4ca) was prepared from bisimine **1c** (1 mmol, 0.31 g). **4ca** was isolated as a beige powder (0.15 g, 42% yield). M.p. = 184-185 °C. Elemental analysis calcd (%) for $C_{26}H_{24}N_2$ (364.49): C, 85.68; H, 6.64; N, 7.69; found (%): C, 85.71; H, 6.68; N, 7.57. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.71-7.68 (m, 4H, H*o'*), 7.34-7.30 (m, 4H, H*m'*), 7.25-7.23 (m, 2H, H*p'*), 6.35 (s, 4H, H*2,3,5,6*), 3.79 (br. s, 2H, NH), 2.46 (s, 2H, ≡CH), 1.74 (s, 6H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6 (C*i'*), 138.1 (C*1,4*), 128.6 (C*m'*), 127.3 (C*p'*), 125.9 (C*o'*), 117.6 (C*2,3,5,6*), 86.8 (C≡CH), 72.6 (C≡CH), 56.1 (C-N), 35.6 (Me) ppm. ^{15}N NMR (41 MHz, $CDCl_3$) δ: -297.9 (NH) ppm. MS (EI), m/z (%): 364.15 $[M]^{+\cdot}$. Calc. for $C_{26}H_{24}N_2$ m/z: 364.19.



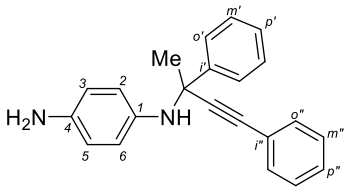
N^1,N^4-Bis(2,4-diphenylbut-3-yn-2-yl)benzene-1,4-diamine (4cb) was prepared from bisimine **1c** (1 mmol, 0.31 g). **4cb** was isolated as a light brown solid (0.20 g, 38% yield). M.p. = 212-213 °C. Elemental analysis calcd (%) for $C_{38}H_{32}N_2$ (516.69): C, 88.34; H, 6.24; N, 5.42; found (%):C, 88.20; H, 6.48; N, 5.06. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ 7.63-7.61 (m, 4H, H*o'*), 7.31- 7.18 (m, 17H, *Ar*), 6.30 (s, 4H, H*2,3,5,6*), 5.73 (s, 2H, NH), 1.71 (s, 6H, Me) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 145.6 (C*1,4*), 137.6 (C*i'*), 131.1 (C*o''*), 128.5 (C*o'*), 128.3 (C*m'*), 128.2 (C*p''*), 126.8 (C*p'*), 125.4 (C*m''*), 122.5 (C*i''*), 116.1 (C*2,3,5,6*), 93.3 (C≡C-Ph), 83.5 (C≡C-Ph), 55.4 (C-N), 35.0 (Me) ppm. MS (EI), m/z (%): 516.25 $[M]^{+\cdot}$. Calc. for $C_{38}H_{32}N_2$ m/z: 516.26.



N^1-(2-Phenylbut-3-yn-2-yl)benzene-1,4-diamine (5ca) ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.78 – 7.65 (m, 2H, H*o'*), 7.41 – 7.30 (m, 2H, H*m'*), 7.31 – 7.06 (m, 1H, H*p'*), 6.75 – 5.97 (s, 4H, H*2,3,5,6*), 2.48 (s, 1H, ≡CH), 1.77 (s, 3H, Me) ppm.



N*^{1}*-(2,4-Diphenylbut-3-yn-2-yl)benzene-1,4-diamine (5cb) was prepared from bisimine **1c** (1 mmol, 0.31 g). **5cb** was isolated as a brown oil (0.10 g, 32% yield). Elemental analysis calcd (%) for $C_{22}H_{20}N_2$ (312.42): C, 84.34; H, 6.44; N, 8.62; found (%): C, 84.58; H, 6.45; N, 8.97. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.75-7.73 (m, 2H, H*o′*), 7.36-7.31 (m, 4H), 7.26-7.23 (m, 4H) [*Ph*], 6.51-6.46 (m, 4H, H*2,3,5,6*), 3.53 (br. s, 3H, NH, NH_2), 1.82 (s, 3H, Me) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.1 (C*4*), 139.0 (C*1*), 138.0 (C*i′*), 131.8 (C*o″*), 128.5 (C*o′*), 128.3 (C*m′*), 128.1 (C*p″*), 127.2 (C*p′*), 126.0 (C*m″*), 123.3 (C*i″*), 119.1 (C*2,6*), 116.1 (C*3,5*), 92.5 (C≡C-Ph), 84.9 (C≡C-Ph), 56.9 (C-N), 35.1 (Me) ppm. ^{15}N NMR (41 MHz, $CDCl_3$) δ: -296.0 (NH) ppm. MS (EI), m/z (%): 312.16 $[M]^{+\cdot}$. Calc. for $C_{22}H_{20}N_2$ m/z: 312.20.



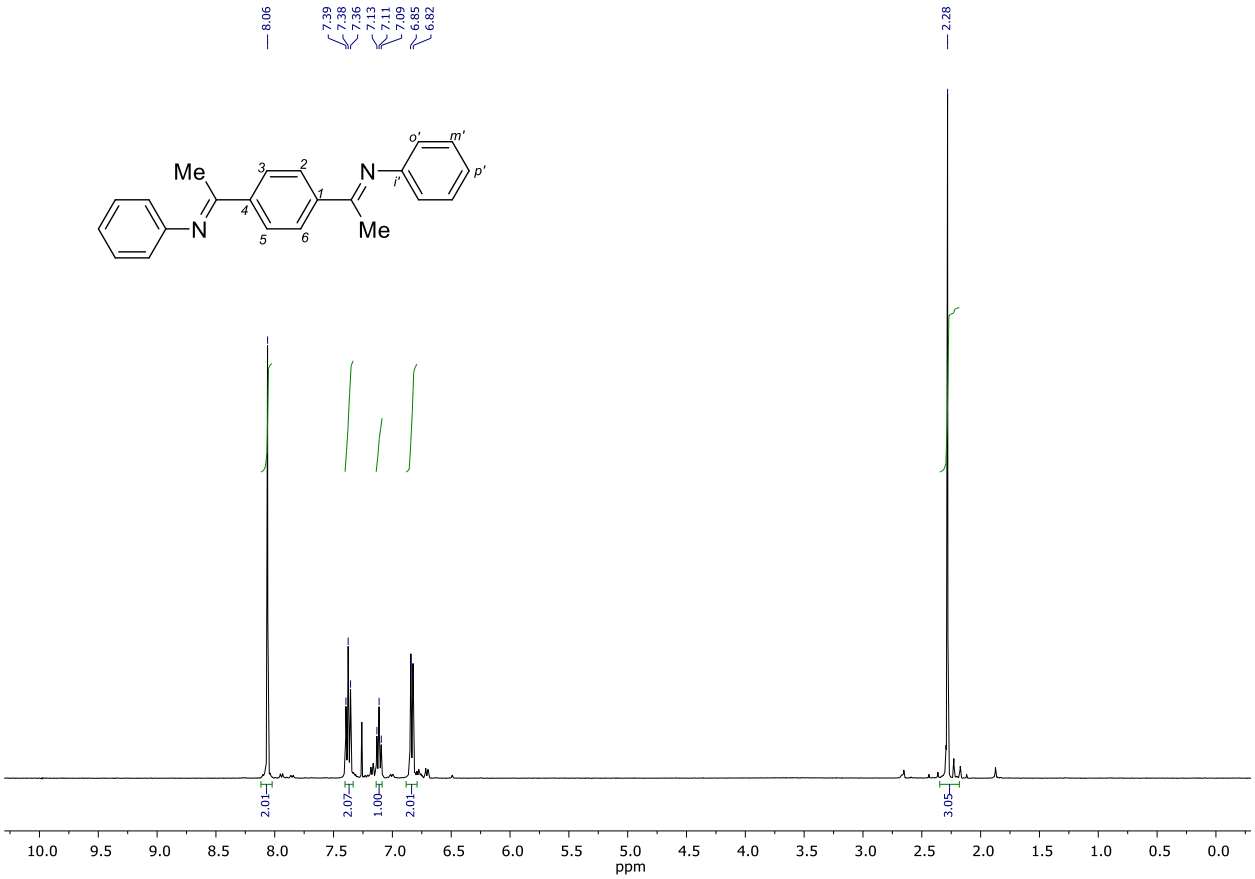
References

S1 C. Pozo-Gonzalo, J. A.Pomposo, J. Rodríguez, E. Yu. Schmidt, A. M. Vasil'tsov, N. V. Zorina, A. V. Ivanov, B. A. Trofimov, A. I. Mikhaleva and A. B. Zaitsev, *Synth. Met.*, 2007, **157**, 60.

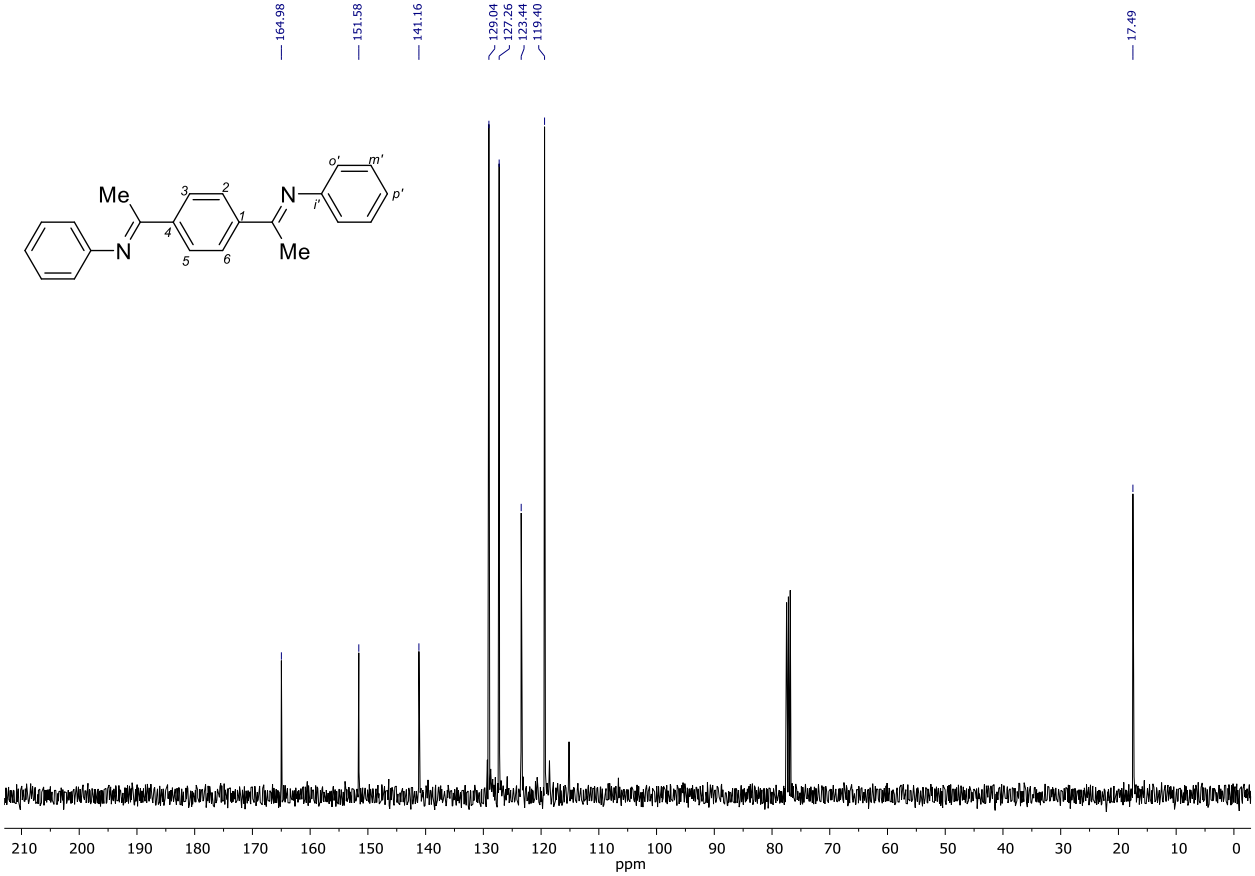
S2 D. Y. Curtin, E. J. Grubbs and C. G. McCarty, *J. Am. Chem. Soc.*, 1966, **88**, 2775.

S3 Y. Wei, I. Deb and N. Yoshikai, *J. Am. Chem. Soc.*, 2012, **134**, 9098.

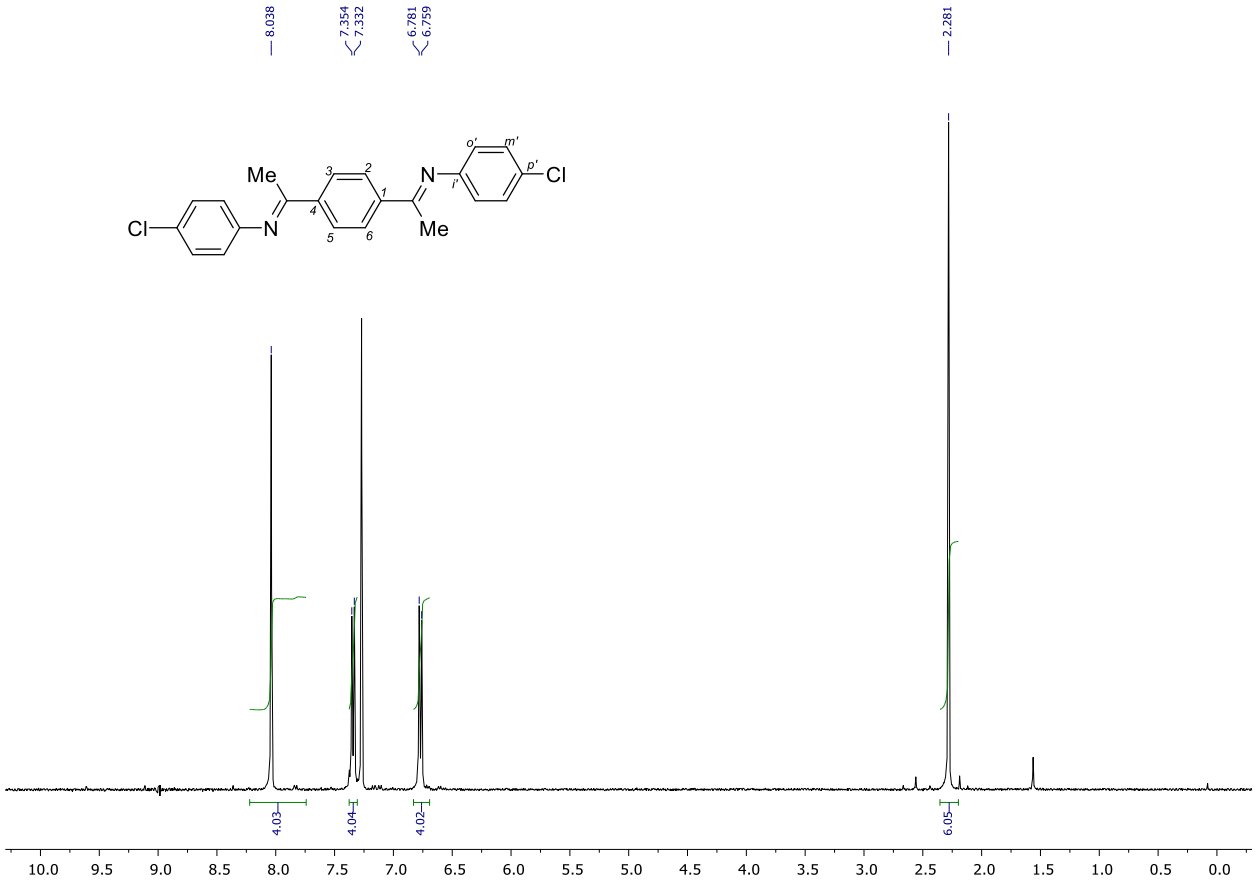
NMR Spectra



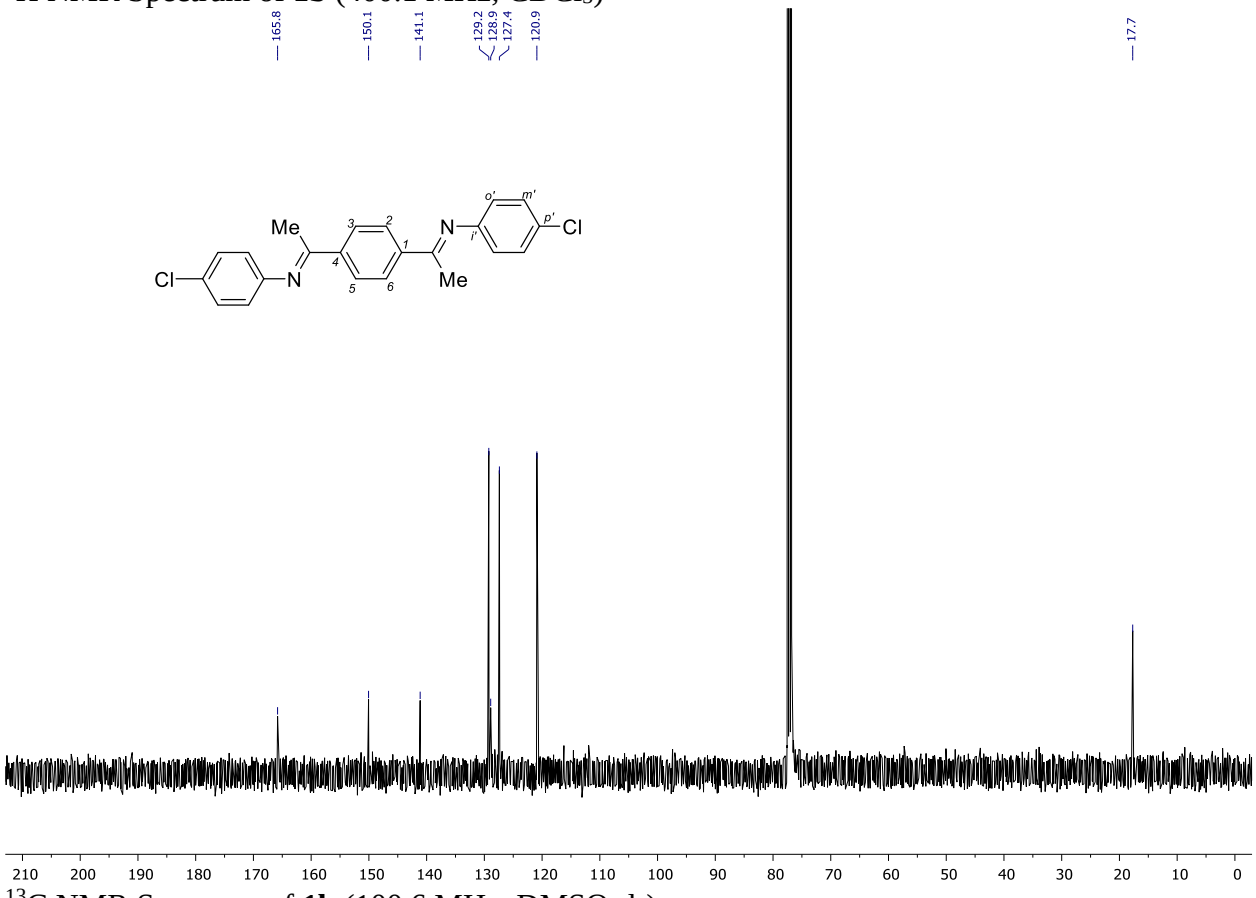
^{1}H NMR Spectrum of **1a** (400.1 MHz, $CDCl_3$)



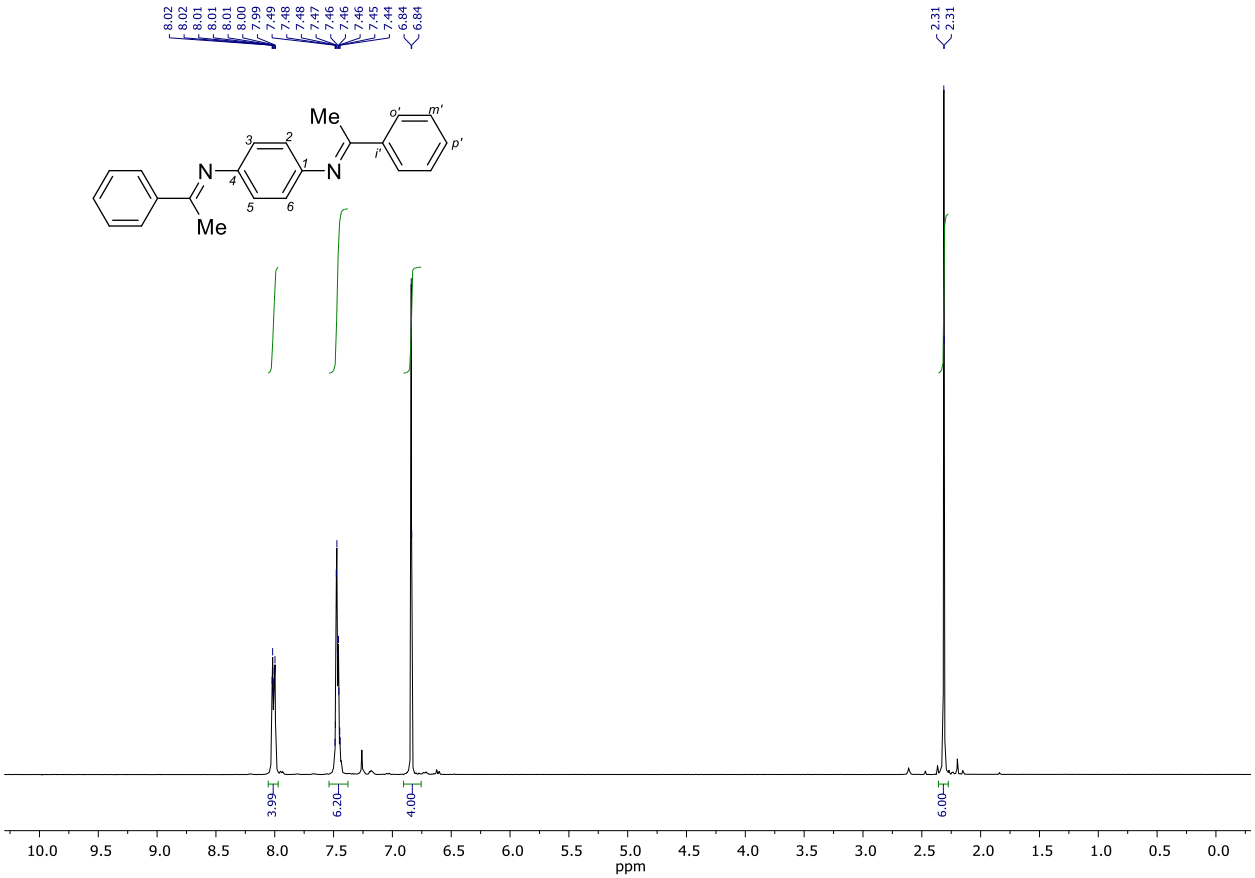
^{13}C NMR Spectrum of **1a** (100.6 MHz, $CDCl_3$)



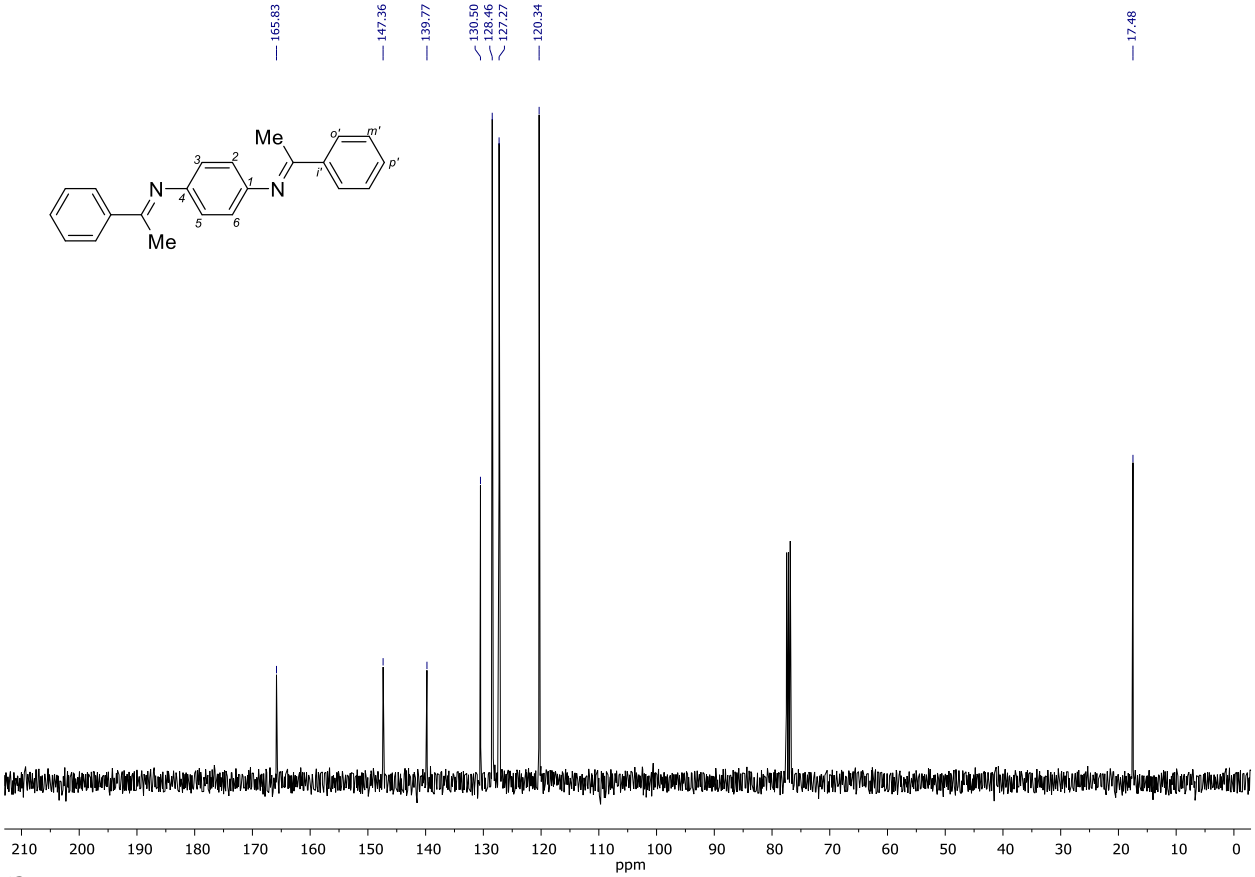
^{1}H NMR Spectrum of **1b** (400.1 MHz, $CDCl_3$)



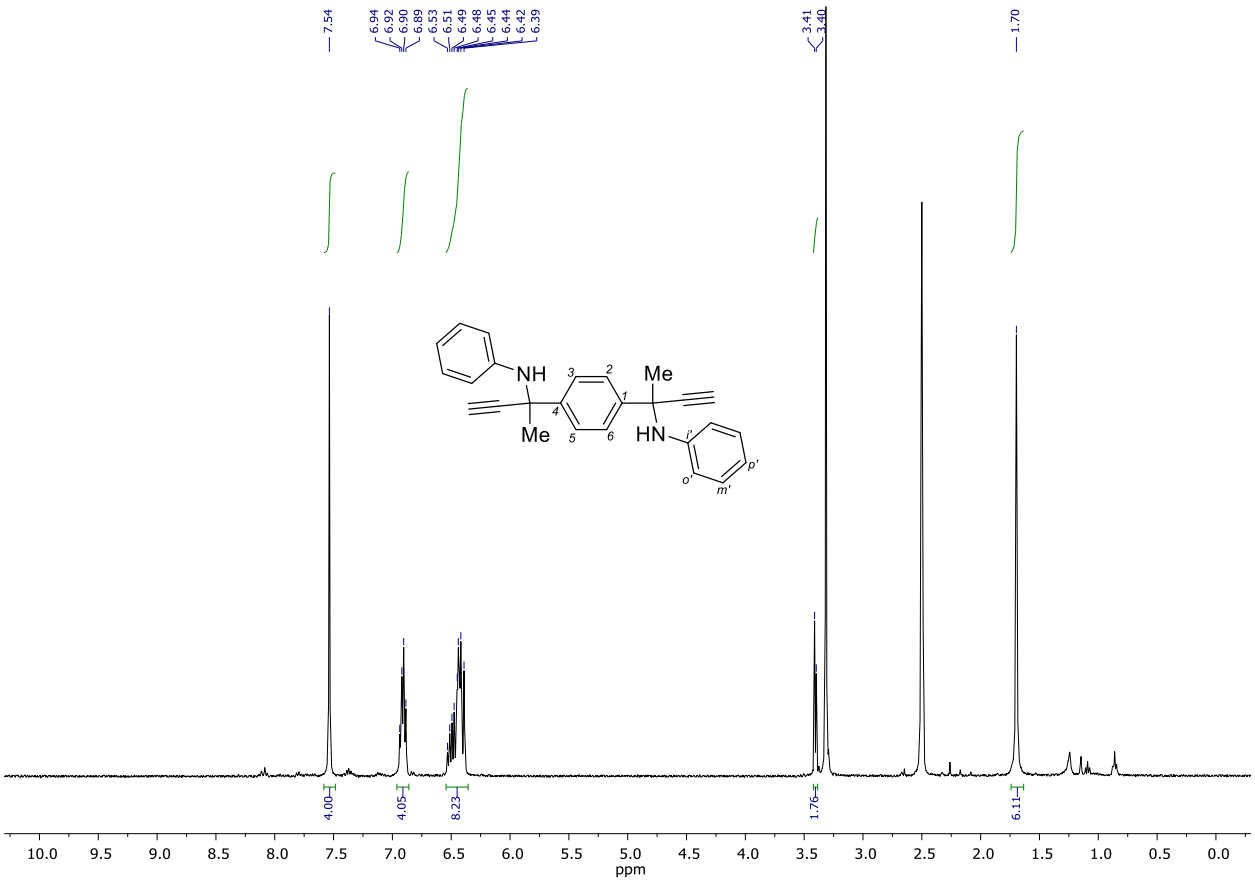
^{13}C NMR Spectrum of **1b** (100.6 MHz, DMSO-d_6)



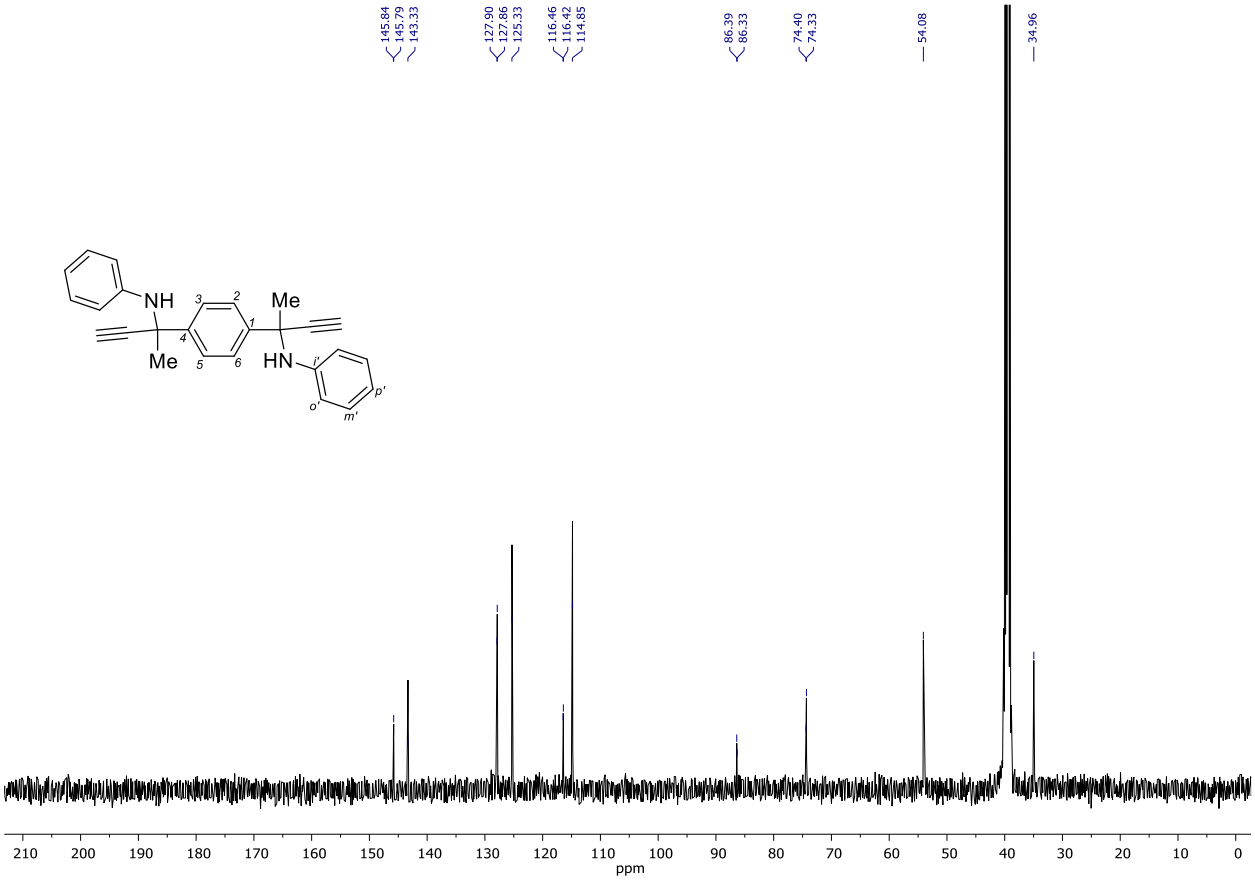
^{1}H NMR Spectrum of **1c** (400.1 MHz, $CDCl_3$)



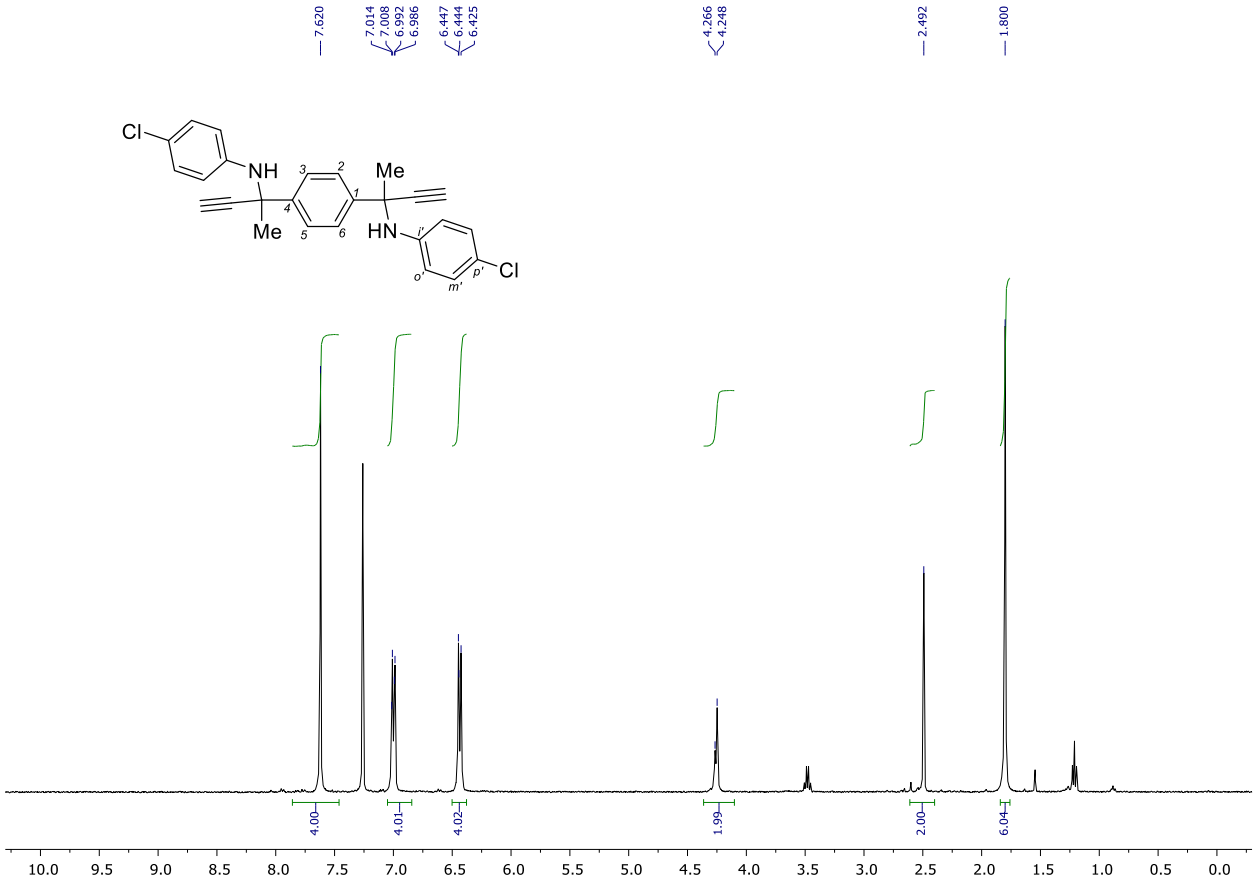
^{13}C NMR Spectrum of **1c** (100.6 MHz, $CDCl_3$)



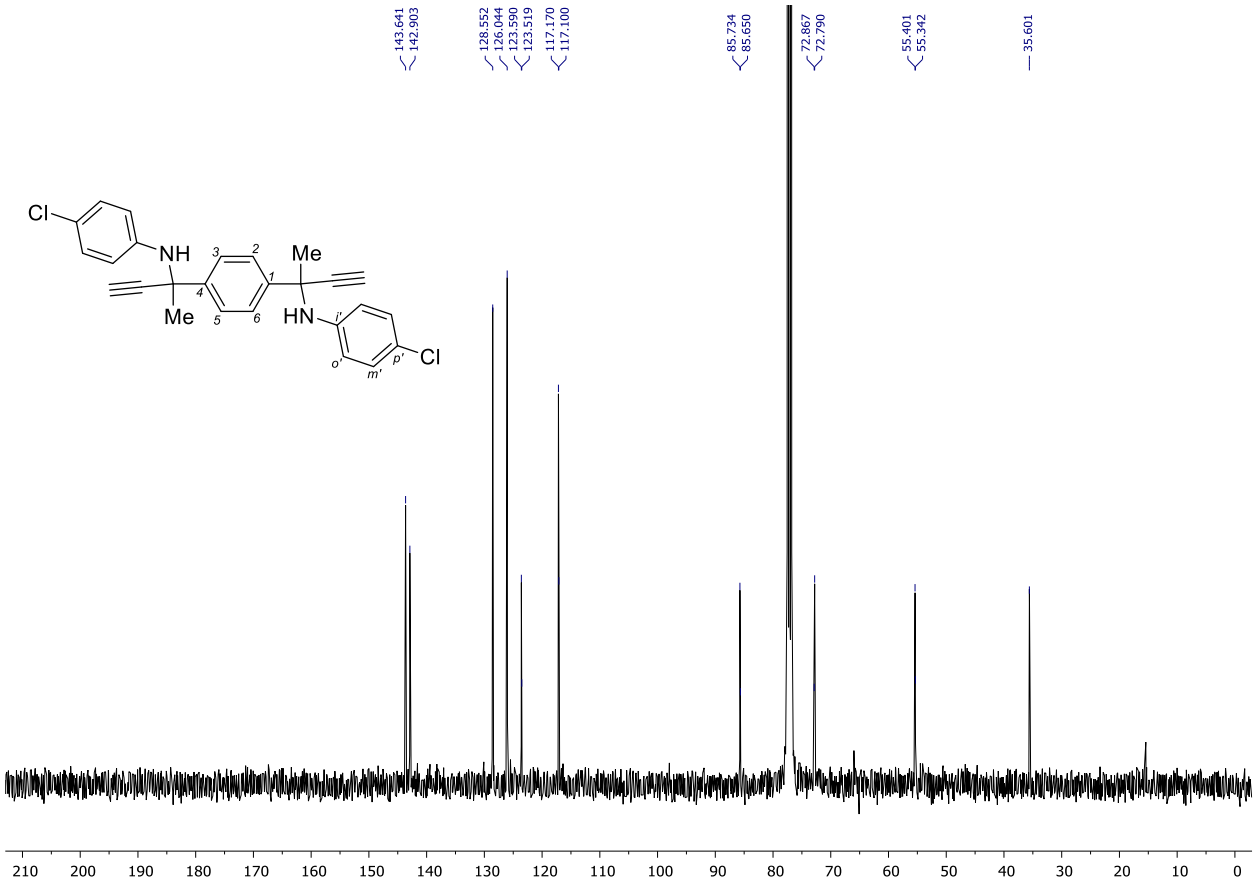
^{1}H NMR Spectrum of **3aa** (400.1 MHz, DMSO-d_6)



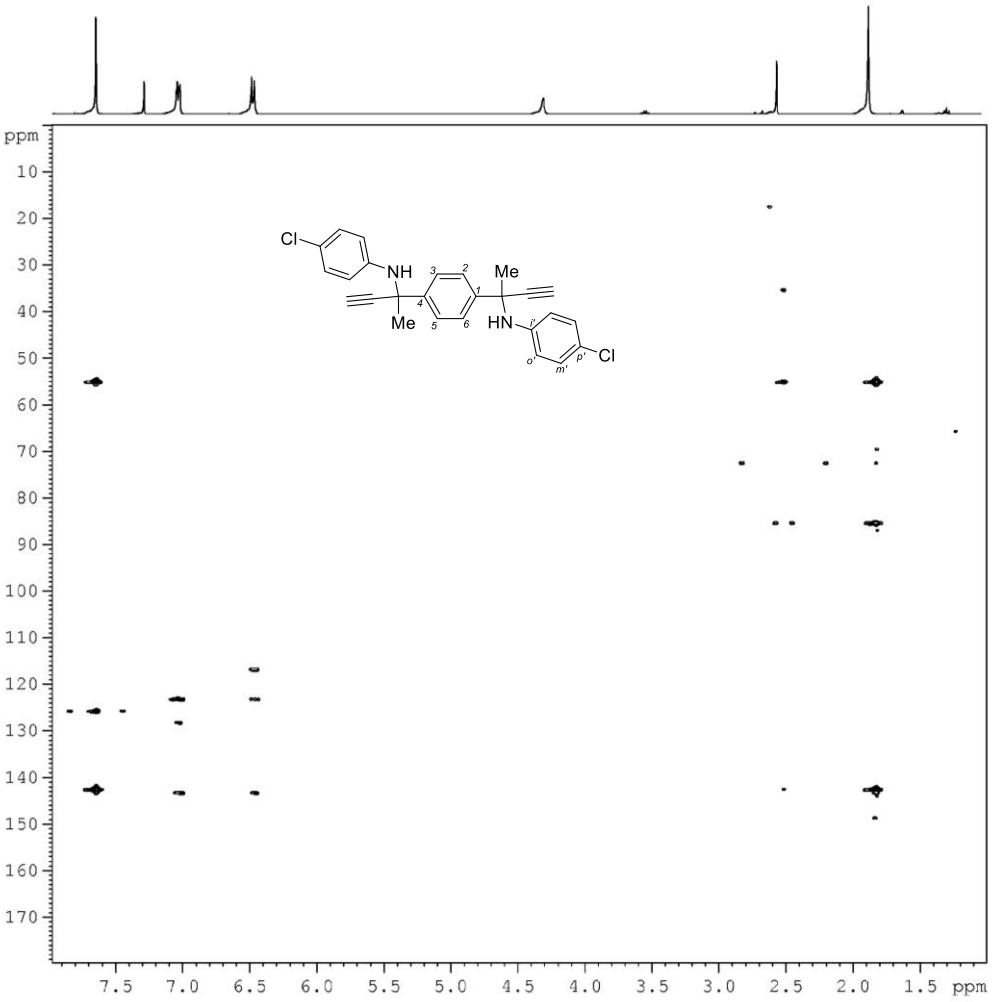
^{13}C NMR Spectrum of **3aa** (100.6 MHz, DMSO-d_6)



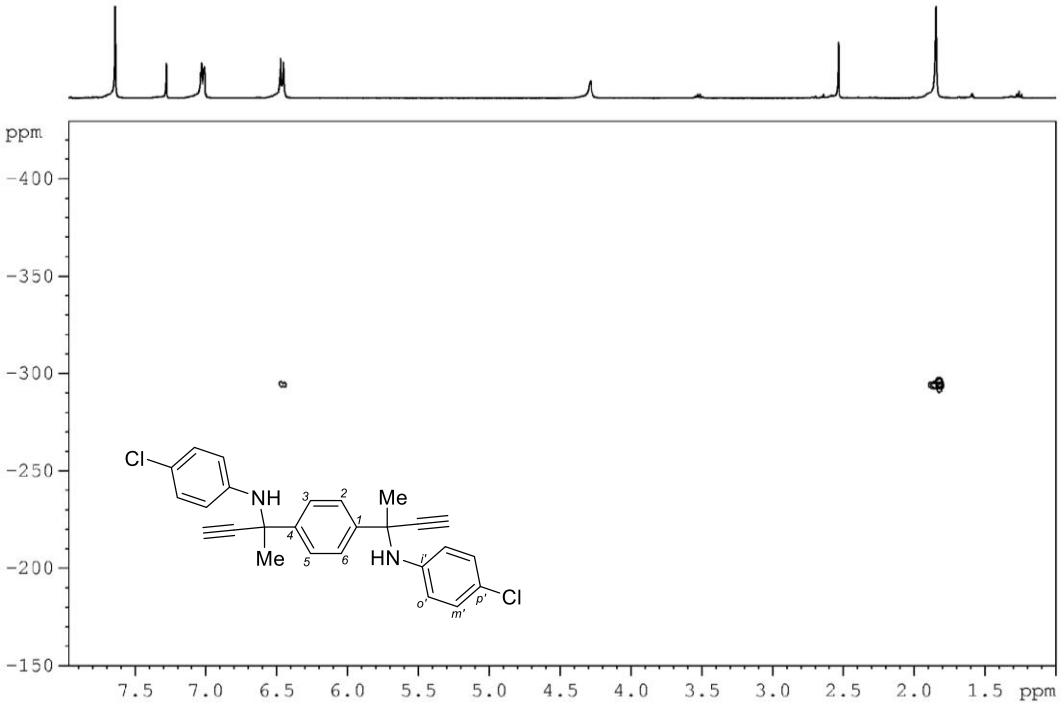
^{1}H NMR Spectrum of **3ba** (400.1 MHz, $CDCl_3$)



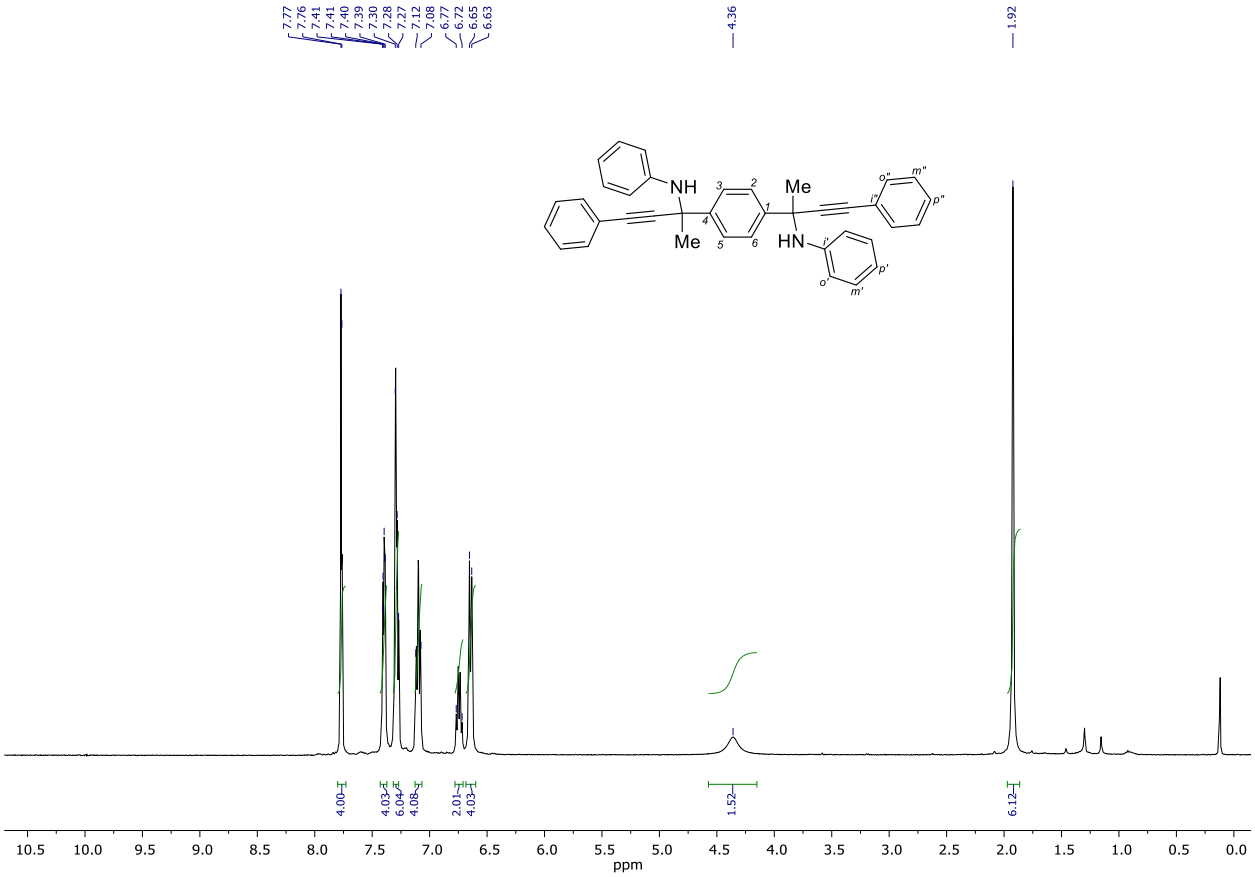
^{13}C NMR Spectrum of **3ba** (100.6 MHz, $CDCl_3$)



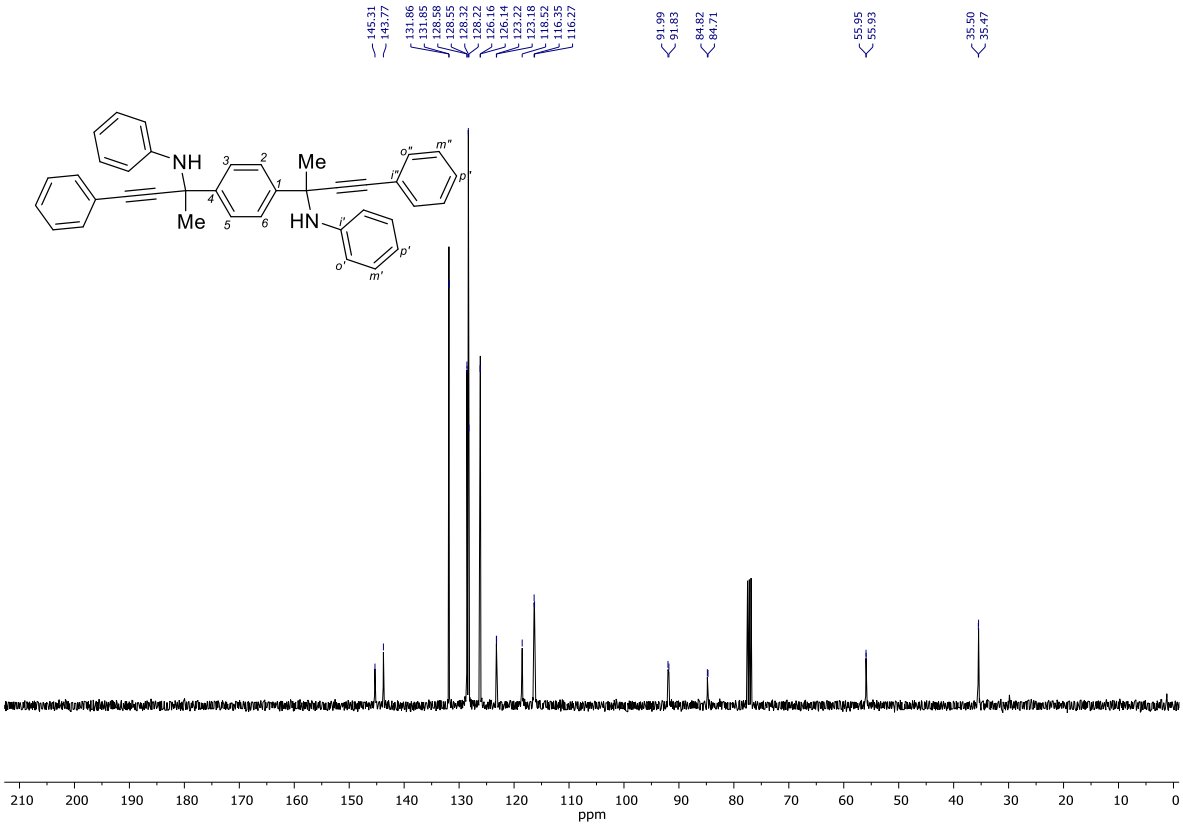
2D ^{1}H-^{13}C HMBC spectrum of **3ba**



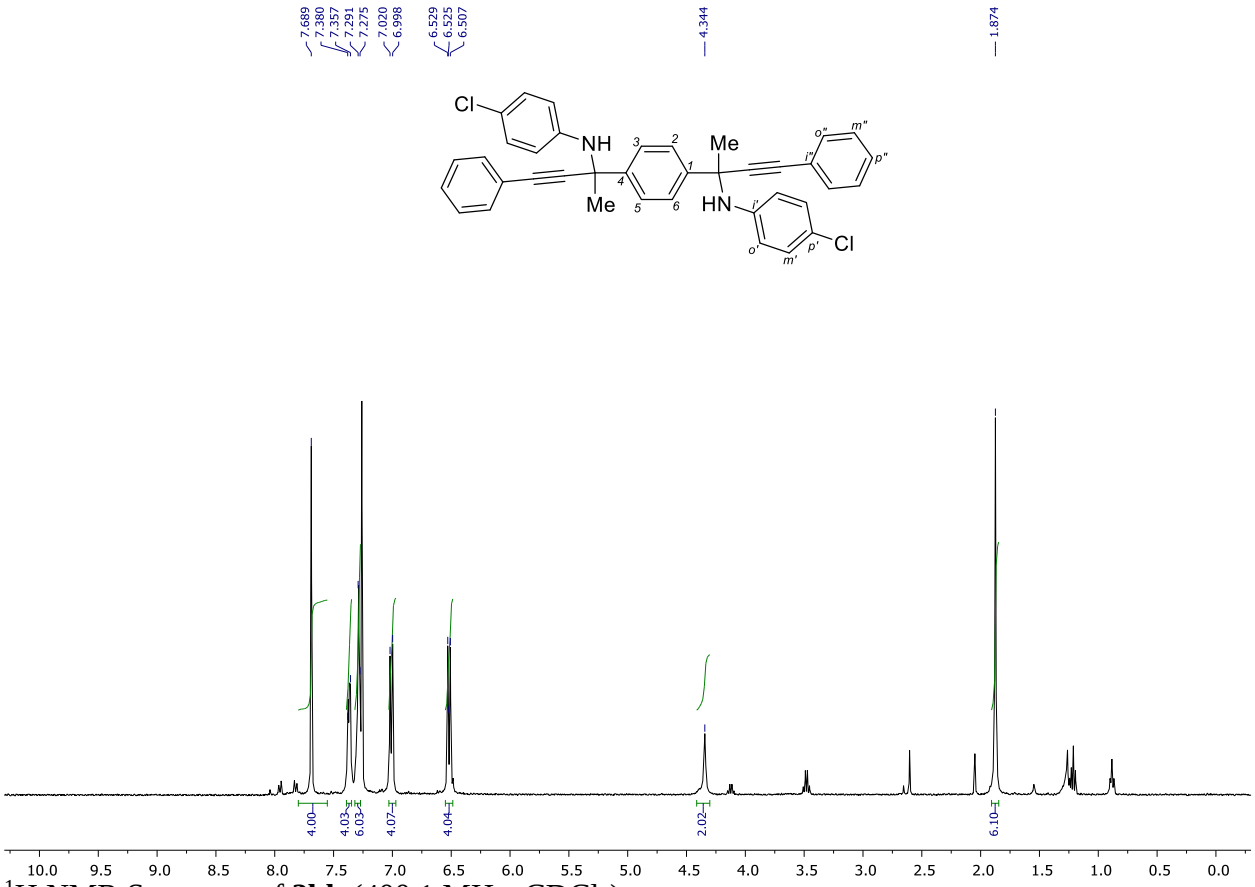
2D ^{1}H-^{15}N HMBC spectrum of **3ba**



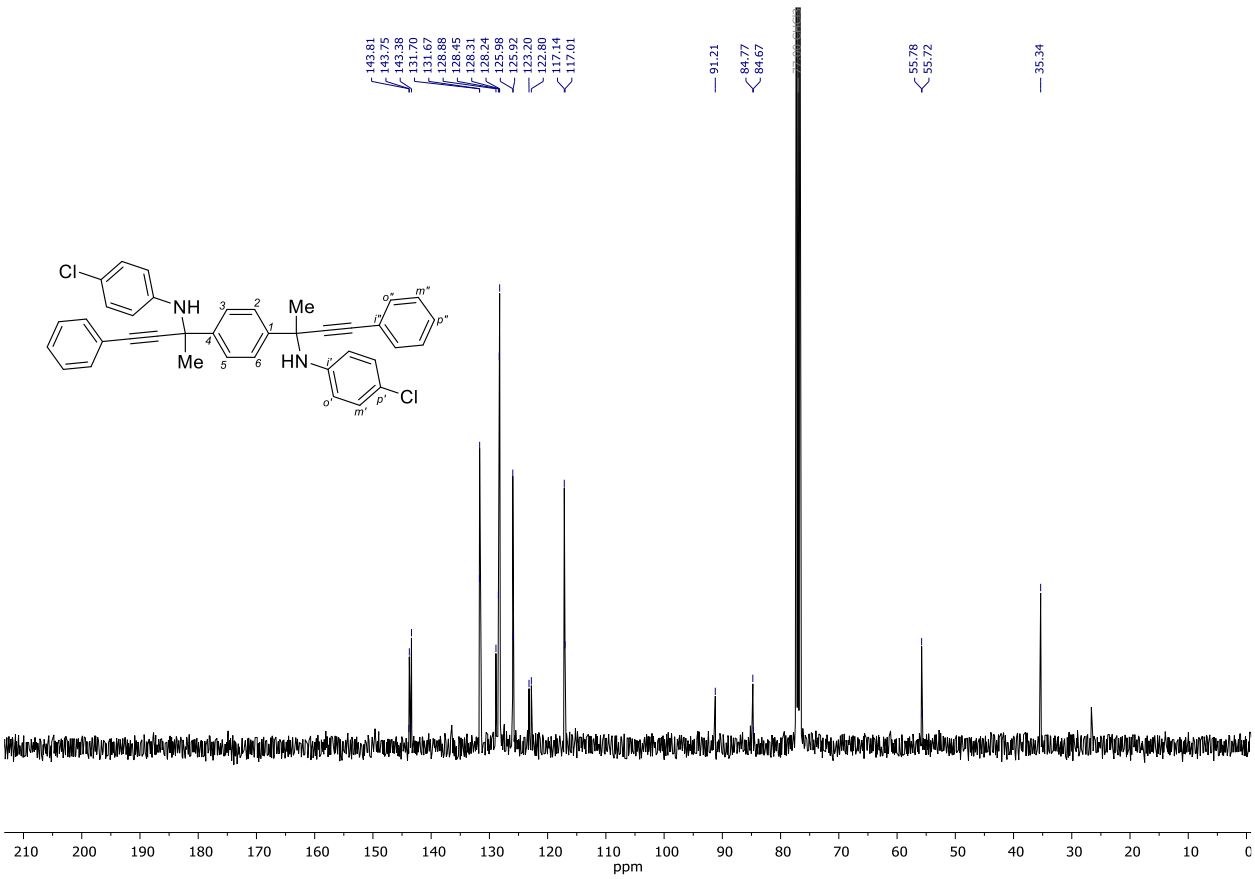
^{1}H NMR Spectrum of **3ab** (400.1 MHz, $CDCl_3$)



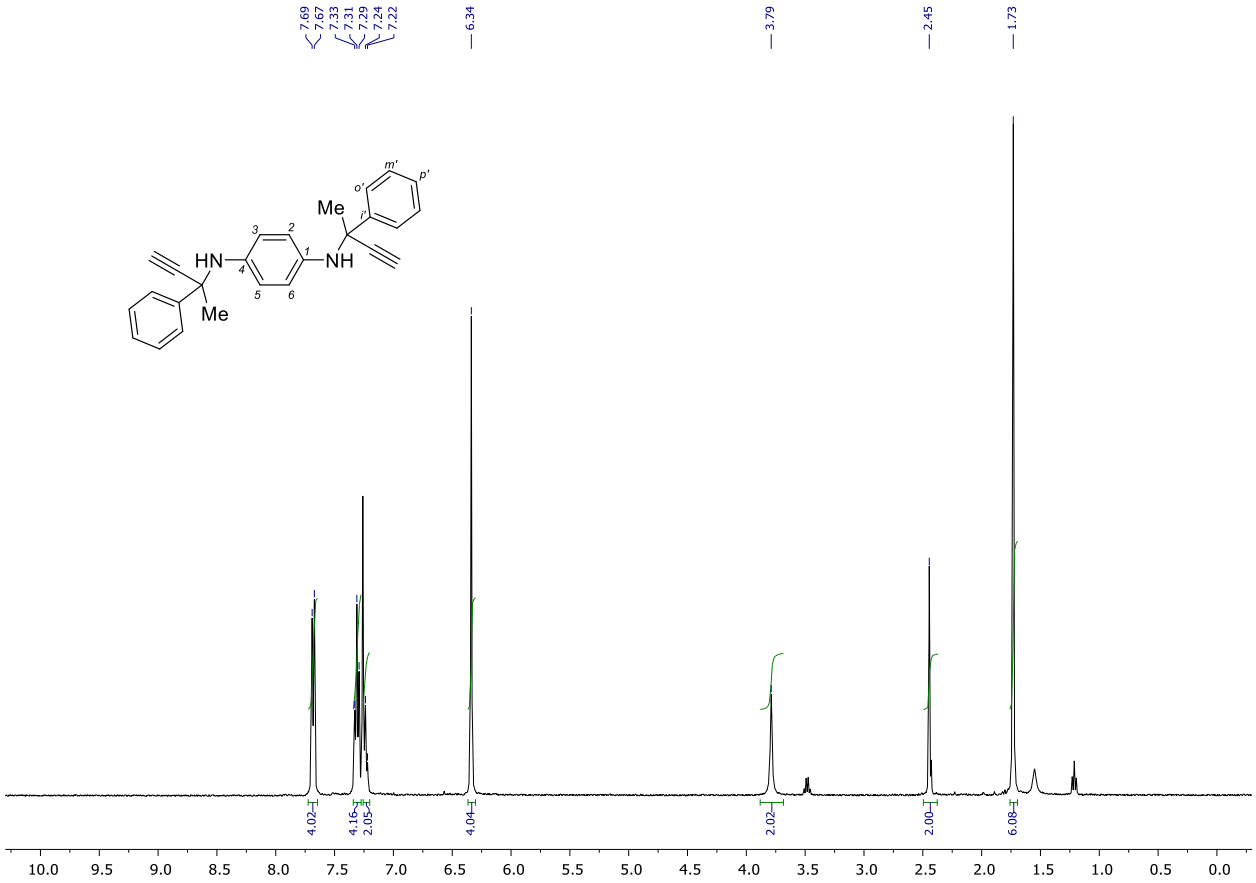
^{13}C NMR Spectrum of **3ab** (100.6 MHz, $CDCl_3$)



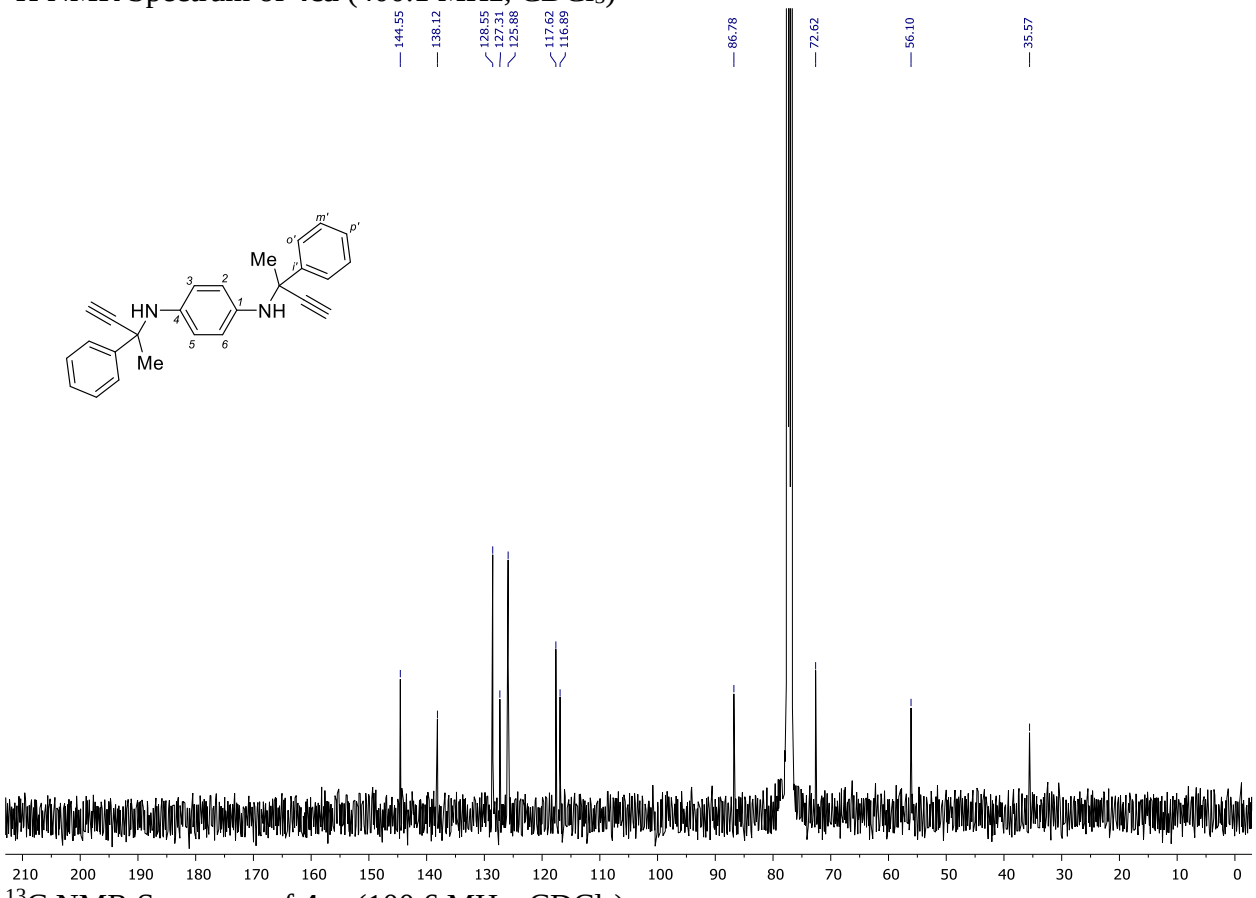
^{1}H NMR Spectrum of **3bb** (400.1 MHz, $CDCl_3$)



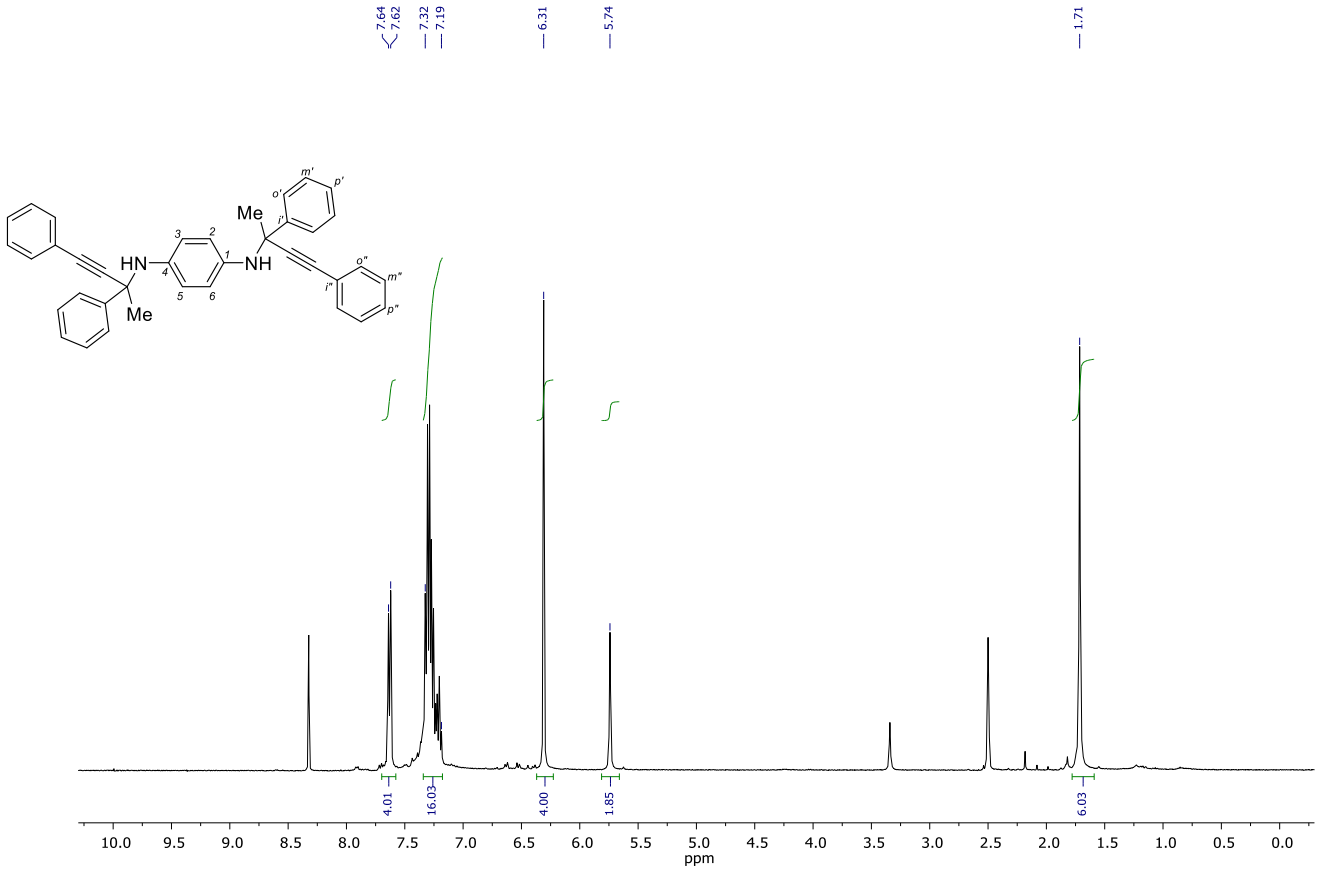
^{13}C NMR Spectrum of **3bb** (100.6 MHz, $CDCl_3$)



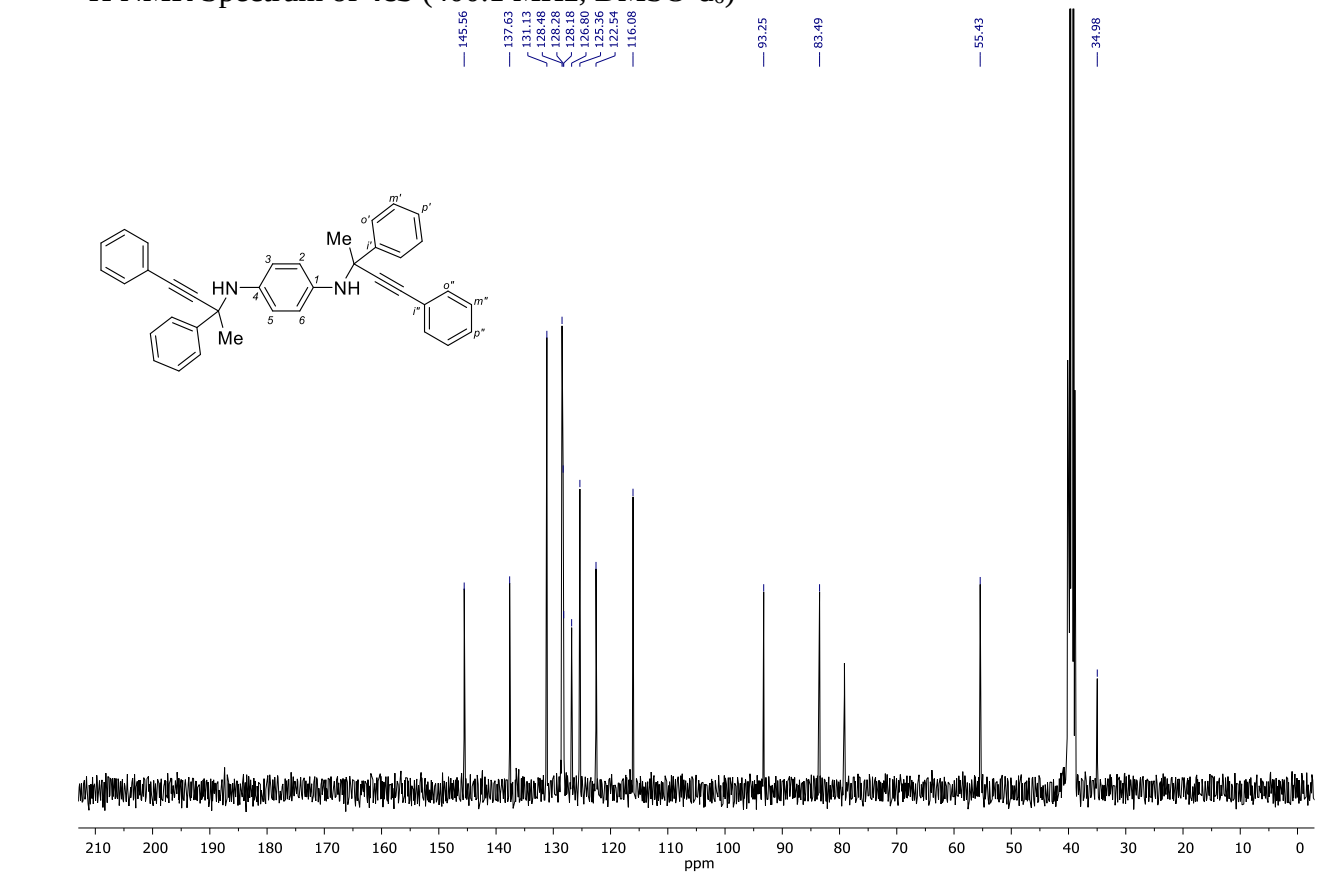
^{1}H NMR Spectrum of **4ca** (400.1 MHz, $CDCl_3$)



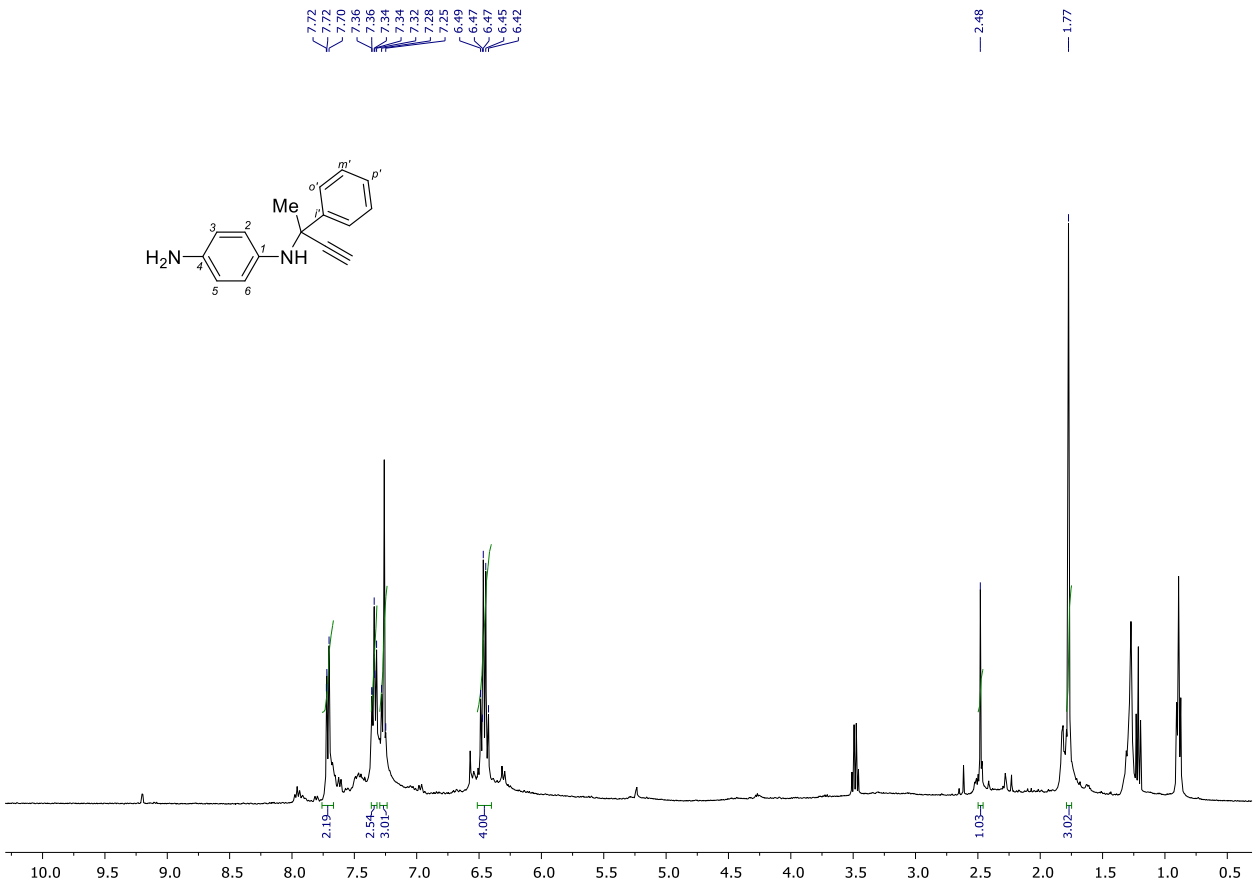
^{13}C NMR Spectrum of **4ca** (100.6 MHz, $CDCl_3$)



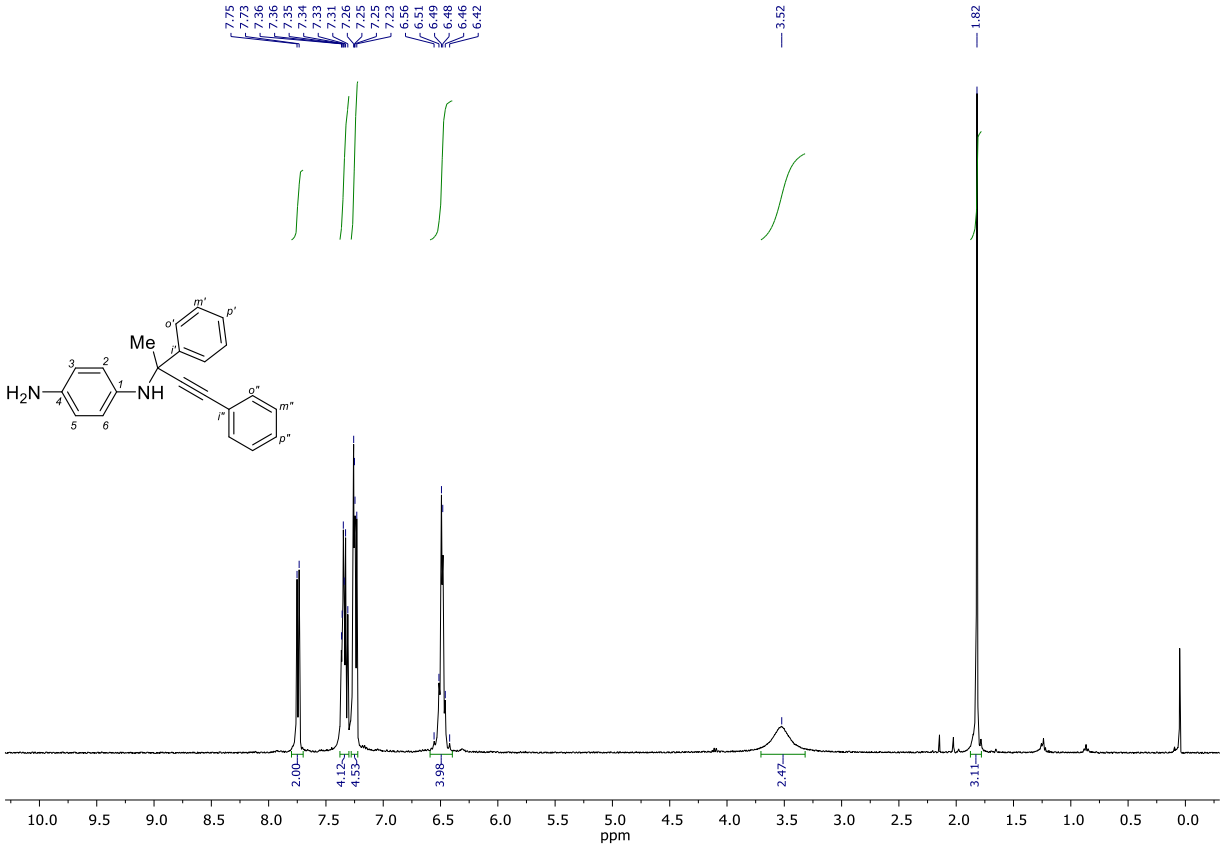
^{1}H NMR Spectrum of **4cb** (400.1 MHz, DMSO-d_6)



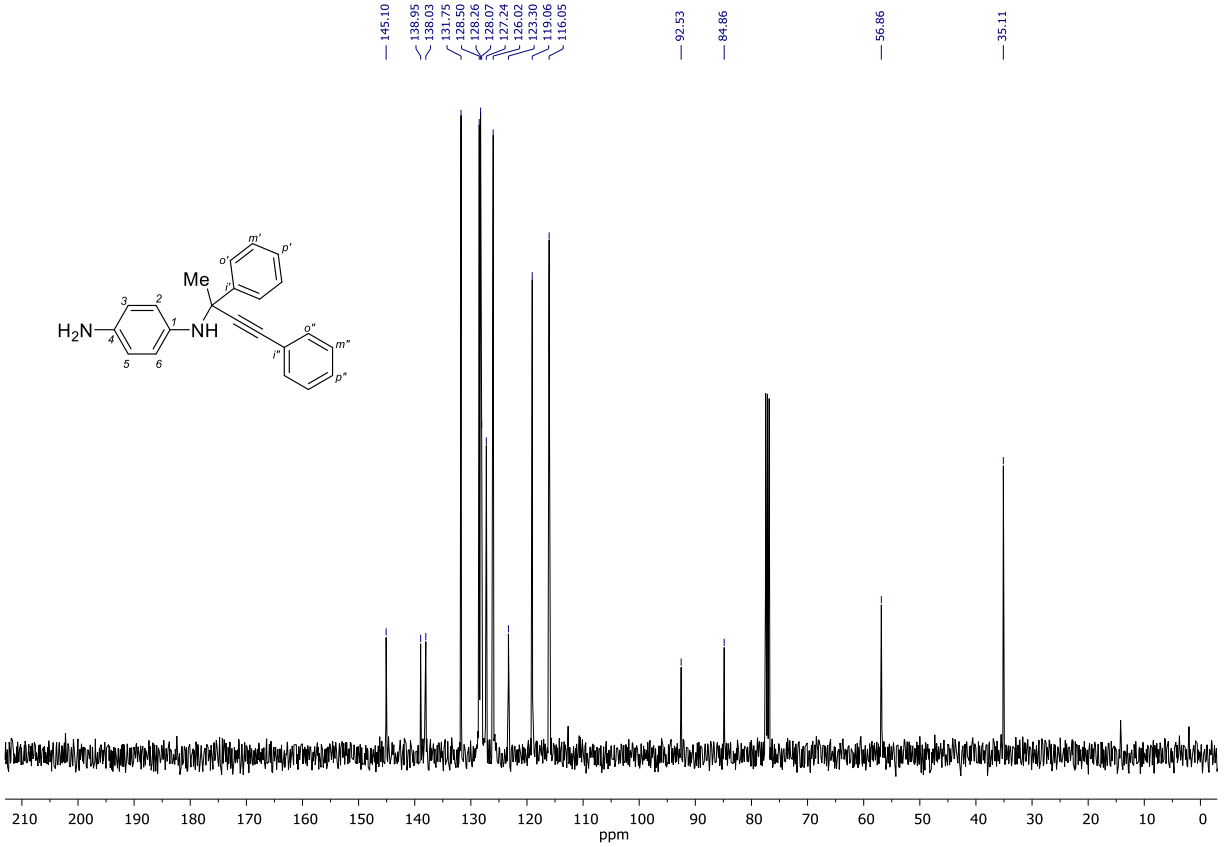
^{13}C NMR Spectrum of **4cb** (100.6 MHz, DMSO-d_6)



^{1}H NMR Spectrum of **5ca** before chromatographic purification (400.1 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **5cb** (400.1 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **5cb** (100.6 MHz, $CDCl_3$)