European Journal of Inorganic Chemistry

Supporting Information

Facile Synthesis of Triptycene-Azolium Salts and NHC-Metal Complexes

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Supporting Information

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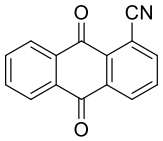
1. Synthesis

General Experimental

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. Tetrahydrofuran and toluene were dried with sodium, distilled under nitrogen, and stored over molecular sieves (4 Å). Cy/EA denotes “cyclohexane, ethyl acetate”. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC300 or DRX500 spectrometer. The chemical shifts are given in parts per million (ppm) on the δ scale and are referenced to the residual peak of chloroform (δ_H = 7.26 ppm, δ_C = 77.16 ppm) or [D_6] DMSO (δ_H = 2.50 ppm, δ_C = 39.52 ppm). Abbreviations for NMR: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, br. = broad. TLC was performed by using silica 60 F 254 (0.2 mm) on alumina plates. Preparative chromatography was carried out on Merck silica 60 (0.063–0.2 mm). Cyclic voltammetry was performed using standard electrochemical instrumentation consisting of an EG&G 273A-2 potentiostat-galvanostat. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as a counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of ferrocene (+0.46 V vs. Ag/AgCl). All cyclic voltammograms were recorded in dry methylene chloride under an atmosphere of nitrogen. Bu_4NPF_6 (0.1 mol L^{-1}) was used as supporting electrolyte.

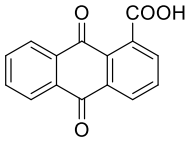
Educts



1-Cyanoanthroquinone was prepared according to the literature procedure.[1][2] Starting materials were 1-chloroanthraquinone (20.0 g, 71.7 mmol, 1.0 eq), CuCN (9.5 g, 106.3 mmol, 1.3 eq) in 100 mL DMAc. The title compound was obtained as a light brown solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.45 (d, J = 7.7 Hz, 1H), 8.33 (d, J = 7.5 Hz, 1H), 8.24 – 8.13 (m, 2H), 8.05 (t, J = 7.8 Hz, 1H), 8.00 – 7.90 (m, 2H). Spectra in accord with literature data.

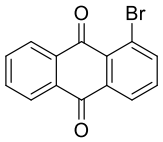
Yield: 95 % (18.4 g, 78.7 mmol).



Anthraquinone-1-carboxylic acid was prepared according to the literature procedure.[2] Starting materials were 1-cyanoanthroquinone (18.3 g, 78.5 mmol, 1.0 eq), NaOH (7.3 g, 235.5 mmol, 2.3 eq) in 120 mL EtOH and 120 mL H_2O. The title compound was obtained as a brown solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 13.29 (s, 1H), 8.25 (d, J = 7.8 Hz, 1H), 8.20 – 8.08 (m, 2H), 8.01 – 7.87 (m, 3H), 7.83 (d, J = 7.6 Hz, 1H). Spectra in accord with literature data.

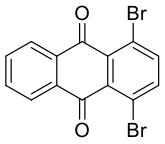
Yield: 88 % (17.5 g, 69.4 mmol).



1-Bromoanthraquinone was prepared according to the literature procedure.[3] Starting materials were 1-aminoanthraquionone (35 g, 156.8 mmol, 1.0 eq), $CuBr_2$ (52.5 g, 235.2 mmol, 1.5 eq) and *tert*-butyl nitrite (31.1 mL, 235.2 mmol, 1.5 eq) in 400 mL MeCN. The title compound was obtained as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 – 8.31 (m, 1H), 8.28 (dd, *J* = 7.4 Hz, 1.9 Hz, 1H), 8.23 (dd, *J* = 7.2 Hz, 1.9 Hz, 1H), 8.02 (dd, *J* = 8.0 Hz, 1.3 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 1H). Spectra in accord with literature data.

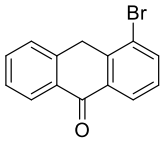
Yield: 94 % (42.1 g, 146.6 mmol).



1,4-Dibromoanthraquinone was prepared according to the literature procedure.[3] Starting materials were 1,4-diaminoanthraquionone (31.0 g, 117.1 mmol, 1.0 eq; 90% purity), $CuBr_2$ (60.2 g, 269.3 mmol, 2.3 eq) and *tert*-butyl nitrite (35.6 mL, 269.3 mmol, 2.3 eq) in 350 mL MeCN. The title compound was obtained as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 – 8.17 (m, 2H), 7.80 – 7.76 (m, 4H). Spectra in accord with literature data.

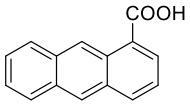
Yield: 79 % (33.8 g, 92.4 mmol).



Bromo-anthrone was prepared according to a modified literature procedure.[4] To a stirred suspension of 1-bromoanthraquinone (3.0 g, 10.45 mmol), in MeOH (120 mL) was added $NaBH_4$ (1.98 g, 52.2 mmol, 5 eq) in small portions over 3 h (approx. 0.3 g every 1 h). The mixture was further stirred for 1 h at r.t. to give a clear brown solution. After addition of conc. HCl (15 mL), the mixture was refluxed for 1 h. The formed solid was collected by filtration, washed with H_2O (300 mL), and air-dried. The solid was purfied by column chromatography (silica gel, Cy/DCM = 10:1 -> 1:1 v/v). The title compound was obtained as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (t, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 4.29 (s, 2H). Spectra in accord with literature data.

Yield: 70 % (1.97 g, 7.66 mmol).

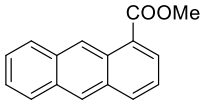


1-Anthracene carboxylic acid was prepared according to a modified literature procedure.[2][5] A mixture of anthraquinone-1-carboxylic acid (17.2 g, 68.2 mmol, 1.0 eq) and NaOH (0.83 g, 20.5 mmol, 0.3 eq) in 700 mL *i*PrOH was bubbled with N_2 for 15 min before the addition of $NaBH_4$ (25.8 g, 681.9 mmol, 10.0 eq) at 0 °C. After 1 h stirring at 0 °C, the mixture was refluxed for 100 h under N_2. Then the reaction mixture was poured carefully into water, conc. HCl added, stirred for 30 min. The precipate was filtered off, washed with water and dried under reduced pressure. The crude product was recrystallized in MeOH to obtain a yellow solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 13.19 (s, 1H), 9.56 (s, 1H), 8.65 (s, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.23 (dd, J = 7.0 Hz, 1.1 Hz, 1H), 8.17 – 8.02 (m, 2H), 7.65 – 7.47 (m, 3H). Spectra in accord with literature data.

^{13}C NMR (75 MHz, DMSO-d_6): δ 168.6, 133.5, 131.9, 131.5, 130.9, 130.5, 128.7, 128.2, 127.8, 127.5, 127.1, 126.2, 126.1, 124.7, 124.1. Spectra in accord with literature data.

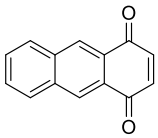
Yield: 71 % (10.8 g, 48.4 mmol).



1-Anthracenecarboxylic acid methyl ester was prepared according to a modified literature procedure.[6] 1-Anthracene carboxylic acid (15.0 g, 67.5 mmol, 1.0 eq) was suspended in 300 mL MeOH, then $SOCl_2$ (7.34 mL, 101.2 mmol, 1.5 eq) was added. The mixture was refluxed for 18 h. After this time the mixture was allowed to r.t. and water was added. The precipitate was filtered off, washed with sat. $NaHCO_3$-Solution, water and dried under reduce pressure. The title compound was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.46 (s, 1H), 8.24 (d, J = 7.0 Hz, 1H), 8.19 (d, J = 8.4, Hz 1H), 8.14 – 8.07 (m, 1H), 8.05 – 7.96 (m, 1H), 7.54 – 7.44 (m, 3H), 4.06 (s, 3H). Spectra in accord with literature data.

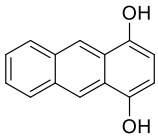
Yield: 77 % (12.4 g, 52.3 mmol).



1,4-Anthraquinone was prepared according to the literature procedure.[7] Quinizarin (60.0 g, 249.8 mmol, 1.0 eq) in 800 mL MeOH was added $NaBH_4$ (37.8 g, 999.1 mmol, 4 eq). The title compound was obtained as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.07 (dd, J = 6.2, 3.3 Hz, 2H), 7.70 (dd, J = 6.3, 3.3 Hz, 2H), 7.07 (s, 2H). Spectra in accord with literature data.

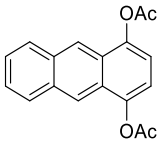
Yield: 94 % (49.0 g, 235.3 mmol).



1,4-Dihydroxyanthracene was prepared according to the literature procedure.[8] 1,4-anthraquinone (3.0 g, 14.41 mmol, 1.0 eq), sodium dithionite (12.54 g, 72.04 mmol, 5.0 eq) in 300 ml of dioxane and 100 ml water. The title compound was obtained as a green solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.53 (s, 2H), 8.67 (s, 2H), 8.10 – 8.03 (m, 2H), 7.49 – 7.42 (m, 2H), 6.62 (s, 2H). Spectra in accord with literature data.

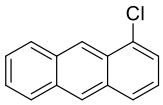
Yield: 68 % (2.05 g, 9.75 mmol).



1,4-Acetoxyanthracene was prepared according to a modified literature procedure.[9] 1,4-Anthraquinone (20.0 g, 96.1 mmol, 1.0 eq) disolved in 300 mL Ac_2O, zinc (13.82 g, 211.3 mmol, 2.2 eq), NaOAc (7.88 g, 96.1 mmol, 1.0 eq), reflux for 3h. After this time the mixture was allowed to r.t. and was poured into 1 L water. The precipitate was collected and dried. The title compound was obtained as a grey solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 2H), 8.02 (dd, J = 6.5, 3.3 Hz, 2H), 7.51 (dd, J = 6.6, 3.2 Hz, 2H), 7.24 (s, 2H), 2.54 (s, 6H). Spectra in accord with literature data.

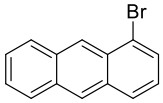
Yield: 97 % (27.3 g, 92.8 mmol).



1-Chloroanthracene was prepared according to a modified literature procedure. [5][10] A mixture of 1-chloroanthraquinone (5.0 g, 20.61 mmol) in 200 mL *i*PrOH was bubbled with N_2 for 15 min before the addition of $NaBH_4$ (7.80 g, 206.1 mmol) at 0 °C. After 1 h the mixture was refluxed for 2 days. Then the reaction mixture was poured carefully into water, conc. HCl added, stirred for 30 min and extracted with $CHCl_3$. The solvent was dried over $MgSO_4$, filtered, removed under reduced pressure and the resulting crude product was purified by column chromatography (silica gel, Cy/DCM = 1:0 -> 8:1 v/v). The title compound was obtained as a slightly yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (s, 1H), 8.44 (s, 1H), 8.13 – 8.06 (m, 1H), 8.04 – 7.99 (m, 1H), 7.97 – 7.90 (m, 1H), 7.58 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.36 (dd, *J* = 7.1, 1.1 Hz, 1H). Spectra in accord with literature data.

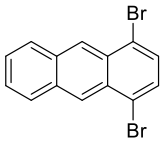
Yield: 50% (2.2 g, 10.3 mmol).



1-Bromoanthracene was prepared according to a modified literature procedure.[3] 1-Bromoanthraquinone (33.0 g, 120.8 mmol, 1.0 eq) was suspended in 300 mL of *i*PrOH, cooled with ice-water bath and $NaBH_4$ (22.9 g, 604.1 mmol, 5.0 equiv.) were added in three portion (one portion each 30 min). After 3 h of stirring in ice-water bath, the reaction mixture was quenched with 100 mL of water and stirred at room temperature overnight, then concentrated under reduced pressure to remove *i*PrOH, the residue was then extracted with toluene, dried over $MgSO_4$ and the solvent removed under reduced pressure. The greyish residue was dissolved in 300 mL of glacial acetic acid and solid $SnCl_2$ (2.4 eq.) was added into the solution in one portion. The reaction mixture was heated at 100 °C for 4 h, allowed to r.t. diluted with 100 mL of water and extracted with toluene. The solvent was dried over $MgSO_4$, filtered, removed under reduced pressure and the resulting crude product was purified by a silica filtration column with cyclohexane as eluent. The title compound was obtained as a slightly yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.43 (s, 1H), 8.14 – 8.07 (m, 1H), 8.05 – 8.00 (m, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.29 (dd, *J* = 8.6 Hz, 7.2, 1H). Spectra in accord with literature data.

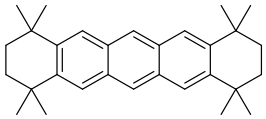
Yield: 63% (19.5 g, 75.8 mmol).



1,4-Dibromoanthracene was prepared according to the literature procedure.[3][11] Starting materials were 1,4-dibromoanthraquinone (30.0 g, 82.0 mmol, 1.0 eq), $NaBH_4$ (1.16 g, 184.4 mmol, 2.25 eq) in 600 mL *i*PrOH and $SnCl_2$ (46.3 g, 205.2 mmol, 2.5 eq) in 480 mL AcOH. The title compound was obtained as a yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 2H), 8.14 – 8.07 (m, 2H), 7.61 (s, 2H), 7.59 – 7.52 (m, 2H). Spectra in accord with literature data.

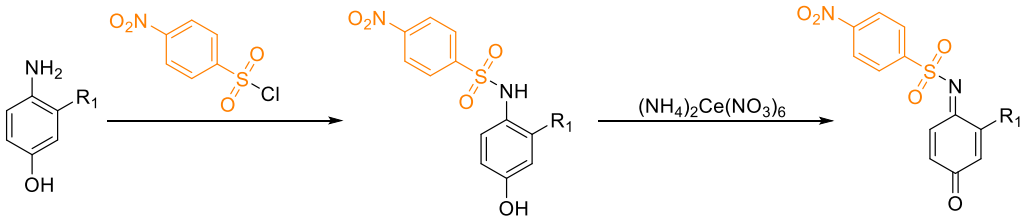
Yield: 48% (13.2 g, 39.3 mmol).



1,1,4,4,8,8,11,11-octamethyl-1,2,3,4,8,9,10,11-octahydropentacene was prepared according to a modified literature procedure.[12] Starting materials were anthracene (5.60 g, 31.2 mmol, 1.0 eq), 2,5-dichloro-2,5-dimethylhexane (17.3 g, 94.3 mmol, 3.0 eq) and $TiCl_4$ (10.7 mL, 97.4 mmol, 3.1 eq) in 200 mL dry DCM. The title compound was obtained as pale-yellow crystal needles.

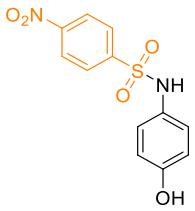
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 2H), 7.88 (s, 4H), 1.80 (s, 8H), 1.44 (s, 24H). Spectra in accord with literature data.

Yield: 30% (3.72 g, 9.33 mmol).



General procedure for nosyl-protection: Ar-NH_2 (1.0 eq) was dissolved in DCM (4 mL per 1 mmol) and pyridine (3.0 eq). The reaction mixture was cooled to 0 °C and *p*-nitrobenzenesulfonyl chloride (1.0 eq) was added in portions. After completion of the reaction (TLC control), water was added to the reaction mixture, the layers were separated and the aqueous phase extracted with ethyl acetate. The combined organic solutions were washed with 2M HCl (aq.) and H_2O. The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure.

General procedure for aminophenol oxidation Nosylated aminophenol (1.0 eq) was suspended in MeCN, H_2O and DCM (ratio 2 : 1 : 2; per 1 mmol aminophenol 3.5 ml: 1.75 mL: 3.5 mL are used). Then cerium(IV) ammonium nitrate (2.0 eq) was added portion wise (within ca. 10 min). The reaction was stirred vigorously at r.t. for 1 h. Next the layers were separated and the MeCN/H_2O layer extracted with DCM. The combined DCM layer were washed with H_2O, separated, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Next, the crude product was dissolved in DCM and filtered over a silica plug. After the solvent was removed under reduced pressure, the quinone monoamine **3a** or **3b** was obtained as an orange solid.

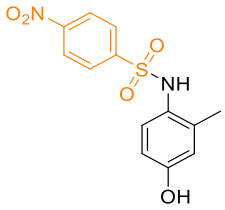


The procedure was modified in comparison to the literature known one and is therefore described here.[13] Nosyl-aminophenol (**2a**) was prepared according the general procedure. Starting materials were aminophenol (5.0 g, 45.8 mmol, 1.0 eq), nosyl chloride (10.2 g, 45.8 mmol, 1.0 eq), pyridine (11.1 mL, 137.5 mmol, 3 eq) in 200 mL DCM. The title compound was obtained as an orange/reddish solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.04 (s, 1H), 9.40 (bs, 1H), 8.35 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H). Spectra in accord with literature data.

^{13}C NMR (75 MHz, DMSO-d_6): δ 155.4, 149.7, 145.1, 128.3, 127.5, 124.7, 124.4, 115.8. Spectra in accord with literature data.

Yield: 74 % (9.9 g, 33.6 mmol).



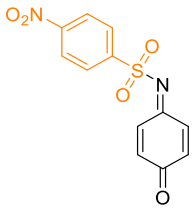
Nosyl-4-methyl-3-aminophenol (**2b**) was prepared according the general procedure. Starting materials used were 4-methyl-3-aminophenol (40.0 g, 321.6 mmol, 1.0 eq), nosyl chloride (73.5 g, 321.6 mmol, 1.0 eq), pyridine (78.0 mL, 964.6 mmol, 3.0 eq) in 1.5 L DCM. The title compound was obtained as an orange/reddish solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.62 (s, 1H), 9.42 (s, 1H), 8.38 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 8.3 Hz, 1H), 6.54 (s, 1H), 6.46 (d, J = 8.3 Hz, 1H), 1.91 (s, 3H). Spectra in accord with literature data.

HRMS (APCI): calcd. for $C_{13}H_{12}N_2O_5S$ [M] 308.04631. Found 308.04614 (Δ = 0.17 mmu).

R_f = 0.27 (Cy/EA = 3:2 v/v).

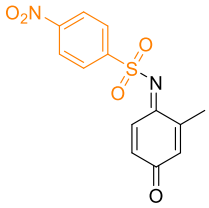
Yield: 86 % (85.0 g, 276 mmol).



The procedure was modified in comparison to the literature known one and is therefore described here. [13] Quinone monoimine (**3a**) was prepared according the general procedure. Starting materials were nosyl-aminophenol (5.0 g, 17.0 mmol, 1.0 eq) and Cerium Ammonium Nitrate (18.6 g, 34.0 mmol, 2.0 eq) in 60 ml MeCN: 20 mL H_2O: 60 mL DCM. The title compound was obtained as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H), 8.12 (dd, J = 10.5 Hz, 2.6 Hz, 1H), 6.99 (dd, J = 10.5, 2.6 Hz, 1H), 6.75 (d, J = 10.2 Hz, 2H). Spectra in accord with literature data.

Yield: 44 % (2.20 g, 7.9 mmol).



Methyl-quinone monoimine (**3b**) was prepared according the general procedure. Starting materials were nosyl-4-methyl-3-aminophenol (36.8 g, 119.4 mmol, 1.0 eq) and Cerium Ammonium Nitrate (130.9 g, 238.7 mmol, 2.0 eq) in 420 ml MeCN: 210 mL H_2O: 420 mL DCM. The title compound was obtained as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, J = 8.9 Hz, 2H; Ar**H**$_{Nosyl}$), 8.21 (d, J = 8.9 Hz, 2H; Ar**H**$_{Nosyl}$), 8.08 (d, J = 10.3 Hz, 1H),6.67 (dd, J = 10.3 Hz, 2.2 Hz, 1H), 6.62 – 6.57 (m, 1H; Ar**H**), 2.06 (d, J = 1.5 Hz, 3H; C**H$_3$**).

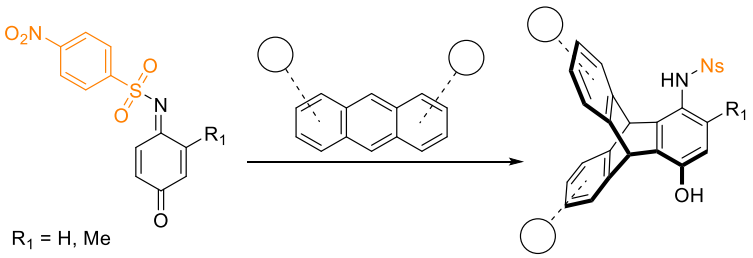
^{13}C NMR (75 MHz, $CDCl_3$): δ 185.9, 166.3, 150.7, 148.0, 145.8, 135.5, 134.0, 131.0, 128.8, 124.5, 17.8.

HRMS (ESI): calcd. for $C_{13}H_{11}N_2O_5S$ $[M+H]^+$ 307.03832. Found 307.03862 (Δ = 0.30 mmu).

R_f = 0.54 (DCM).

Yield: 75% (26.9 g, 87.8 mmol).

Nosylated aminophenols



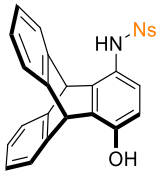
General procedure for quinone-imine/anthracene cycloaddition and aromatization to yield triptycenes 4: Anthracene 1.0 eq) and nosylated quinone-imine (1.0 – 1.3 eq **3a** or **3b**) were dissolved in $CHCl_3$ or DCE (approx. 5 mL per mmol). The reaction mixture was flushed with nitrogen and stirred under reflux for 1-3 days. The resulting precipitate was filtered off. If no precipitate had formed, the volatiles were evaporated under reduced pressure. Two methods were used to aromatize the Diels-Alder-adduct:

Method A**:** The crude Diels-Alder-adduct was suspended in AcOH, 4-5 drops of HBr (aq.) were added and refluxed until a clear yellow solution was obtained. After complete conversion (controlled by TLC). The reactions mixture was allowed to r.t. then water was added. The resulting precipitate was filtered off and washed several times with water, sat. aqueous $NaHCO_3$, dried and then triturated with pentane. The solid was purified by chromatography with Cy/EA through a silica gel column.

Method B: The crude Diels-Alder-adduct was suspended in EtOH/dioxane (approx. 10:1 v/v), 4-5 drops of HCl (37% aq.) were added and refluxed until a clear solution was obtained. After complete conversion (controlled by TLC) water is added to the reaction mixture. Either the resulting precipitate was filtered off, washed with water, dried and triturated with pentane or the mixture was extracted with EA dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The solid was purified by chromatography with Cy/EA through a silica gel column.

Before aromatization: After aromatization:

Aromatization progress (left: before and right: after) of nosylated aminophenol **4m.**



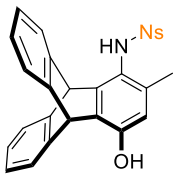
The nosylated aminophenol (**4a**) was prepared according the general procedure. Starting materials were anthracene (0.61 g, 3.42 mmol, 1.0 eq), quinone monoimine (1.0 g, 3.42 mmol, 1.0 eq), in 20 mL $CHCl_3$. It was not necessary to rearomatize the compound (rearomatized already before workup). The title compound was obtained as a yellow solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.17 (s, 1H; N**H**), 9.71 (s, 1H; O**H**), 8.29 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.79 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.34 (d, J = 7.2 Hz, 2H; Ar**H**), 7.10 (d, J = 6.0 Hz, 2H; Ar**H**), 6.93 (td, J = 7.4 Hz, 1.3 Hz, 2H; Ar**H**), 6.84 (td, J = 7.4 Hz, 1.3 Hz, 2H; Ar**H**), 6.51 (d, J = 8.6 Hz, 1H; ArC**H**), 6.43 (d, J = 8.6 Hz, 1H; ArC**H**), 5.79 (s, 1H; C**H**$_{\text{-bridge}}$), 5.70 (s, 1H; C**H**$_{\text{-bridge}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 150.9 (Ar**C**$_{\text{-OH}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 145.5, 145.2, 144.8, 143.4, 131.8, 128.2, 124.8, 124.6, 124.4, 123.8, 123.4, 121.9 (Ar**C**H), 113.1 (Ar**C**H), 48.1 (**C**H$_{\text{-bridge}}$), 46.2 (**C**H$_{\text{-bridge}}$).

HRMS (APCI): calcd. for $C_{26}H_{18}N_2O_5S$ $[M\text{-}H]^-$ 469.08637. Found 469.08736 (Δ = 1.01 mmu).

Yield: 72% (1.2 g, 2.50 mmol).



The nosylated aminophenol (**4b**) was prepared according the general procedure. Starting materials were anthracene (4.0 g, 22.44 mmol, 1.0 eq), methyl-quinone monoimine (6.87 g, 22.44 mmol, 1.0 eq), in 120 mL $CHCl_3$. Method A was used to rearomatize the compound. The title compound was obtained as a yellow solid.

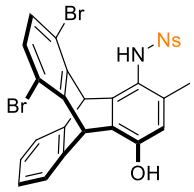
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.86 (s, 1H; N**H**), 9.67 (s, 1H; O**H**), 8.38 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.88 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.39 (dd, J = 6.0 Hz, 2.3 Hz, 2H; Ar**H**), 7.27 (bs, 2H; Ar**H**), 7.03 – 6.87 (m, 4H; Ar**H**), 6.29 (s, 1H; ArC**H**), 5.86 (s, 1H; C**H**$_{\text{-bridge}}$), 5.82 (s, 1H; C**H**$_{\text{-bridge}}$), 1.49 (s, 3H; ArC**H**$_{\textbf{3}\text{-ortho}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 151.0 (Ar**C**$_{\text{-OH}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 147.0, 146.7, 145.7, 145.2, 133.9, 129.8, 128.2, 124.8, 124.7, 124.6, 124.3, 123.3, 120.8, 114.4 (Ar**C**H), 49.9 (**C**H$_{\text{bridge}}$), 46.2 (**C**H$_{\text{bridge}}$), 17.5 (Ar**C**H$_{\text{3-ortho}}$).

HRMS (APCI): calcd. for $C_{27}H_{20}N_2O_5S$ $[M-H]^-$ 483.10202. Found 483.10237 (Δ = 0.35 mmu).

R_f = 0.11 (Cy/EA = 3:1 v/v).

Yield: 94 % (10.20 g, 21.05 mmol).



The nosylated aminophenol (**4c**) was prepared according the general procedure. Starting materials were 1,4-dibromoanthracene (7.67 g, 22.7 mmol, 1.0 eq), methyl-quinone imine (7.67 g, 25.0 mmol, 1.1 eq), in 250 mL DCE. Method B was used to rearomatize the compound. The title compound was obtained as a yellowish solid.

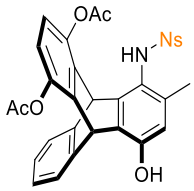
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.88 (s, 1H; N**H**), 9.86 (s, 1H; O**H**), 8.38 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.86 (d, J = 8.5 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.54 – 7.45 (m, 1H), 7.44 – 7.37 (m, 1H), 7.19 (s, 2H), 7.13 – 7.02 (m, 2H), 6.44 (s, 1H; ArC**H**), 6.31 (s, 1H, C**H**$_{\text{-bridge}}$), 6.23 (s, 1H; C**H**$_{\text{-bridge}}$), 1.39 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 151.3 (Ar**C**$_{\text{-OH}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 147.2, 145.8, 143.9, 134.3, 130.1, 128.5, 128.2, 125.4, 124.6, 123.7, 121.1, 117.1, 114.8 (Ar**C**H), 50.0 (**C**H$_{\text{bridge}}$), 46.4 (**C**H$_{\text{bridge}}$), 17.1 (Ar**C**H$_{3\ \text{ortho}}$).

HRMS (APCI): calcd. for $C_{27}H_{19}N_2O_5BrS$ $[M-H]^-$ 638.92304. Found 638.92248 (Δ = 0.56 mmu).

R_f = 0.44 (Cy/EA = 7:3 v/v).

Yield: 63% (9.58 g, 14.9 mmol).



The nosylated aminophenol (**4d**) was prepared according the general procedure. Starting materials were 1,4-acetoxyanthracene (12.0 g, 40.77 mmol, 1.0 eq), quinone monoimine (13.74 g, 44.85 mmol, 1.0 eq) and $Mg(ClO_4)_2$ (9.1 g, 40.77 mmol, 1.0 eq) in 300 mL $CHCl_3$. Method B (without acid) was used to rearomatize the compound. The title compound was obtained as a yellowish/brown solid.

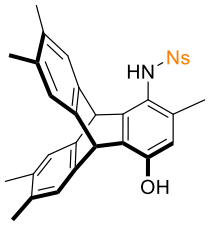
^{1}H NMR (500 MHz, DMSO-d_6): δ 9.79 (s, 1H; N**H**), 9.67 (s, 1H; O**H**), 8.36 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.89 (d, J = 9.1 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.42 – 7.36 (m, 1H), 7.36 – 7.30 (m, 1H), 7.05 – 7.00 (m, 2H), 6.86 – 6.79 (m, 2H), 6.25 (s, 1H; ArC**H**), 6.04 (s, 1H; C**H**$_{\text{-bridge}}$), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$), 2.48 (s, 3H; OCOC**H$_3$**), 2.44 (s, 3H; OC(O)C**H$_3$**), 1.35 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$).

^{13}C NMR (126 MHz, DMSO-d_6): δ 169.2 (O**C**OCH$_3$), 169.0 (O**C**OCH$_3$), 151.2 (Ar**C**$_{\text{-OH}}$), 149.7, 149.6, 147.1, 146.2, 143.1, 142.5, 133.8, 129.2, 128.8, 128.3, 128.2, 127.2, 125.0, 124.9, 124.6, 124.5, 124.1, 123.7, 121.2, 119.8, 119.7, 114.5 (Ar**C**H), 44.7 (**C**H$_{\text{-bridge}}$), 40.8 (**C**H$_{\text{-bridge}}$), 20.6 (OCO**C**H$_3$), 17.1 (Ar**C**H$_{3\text{-ortho}}$).

HRMS (ESI): calcd. for $C_{31}H_{28}N_3O_9S$ [M+NH$_4$] 618.15408 Found 618.15387 (Δ = 0.21 mmu).

R$_f$ = 0.34 (Cy/EA = 1:1 v/v).

Yield: 32% (8.0 g, 13.32 mmol).



The nosylated aminophenol (**4e**) was prepared according the general procedure. Starting materials were tetramethylanthracene (76.5 mg, 0.326 mmol, 1.0 eq), methyl-quinone monoimine (100 mg, 0.326 mmol, 1.0 eq) in 2 mL $CHCl_3$. Method B was used to rearomatize the compound. The title compound was obtained as a yellowish solid.

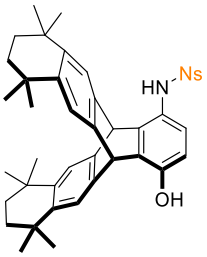
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.86 (s, 1H; N**H**), 9.54 (s, 1H; O**H**), 8.44 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.95 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.09 (s, 2H), 6.84 (bs, 2H), 6.29 (s, 1H; ArC**H**), 5.58 (s, 1H; C**H**$_{\text{-bridge}}$), 5.49 (s, 1H; C**H**$_{\text{-bridge}}$), 2.08 (s, 6H; ArC**H$_3$**), 2.04 (s, 6H; ArC**H$_3$**), 1.64 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$).

k**^{13}C NMR** (75 MHz, DMSO-d_6): δ 150.6 (Ar**C**$_{\text{-OH}}$), 149.5 (Ar**C**$_{\text{-NO2}}$), 147.4, 146.9, 143.4, 142.9, 134.0, 131.8, 131.4, 130.2, 128.3, 125.2, 124.7, 124.5, 120.5, 114.2 (Ar**C**H), 48.8 (**C**H$_{\text{-bridge}}$), 45.3 (**C**H$_{\text{-bridge}}$), 19.0 (Ar**C**H$_3$), 17.8 (Ar**C**H$_{3\text{-ortho}}$).

HRMS (APCI): calcd. for $C_{31}H_{29}N_2O_5S$ [M+H] 541.17917. Found 541.17901 (Δ = 0.16 mmu).

R$_f$ = 0.36 (Cy/EA = 4:1 v/v).

Yield: 77% (140 mg, 0.25 mmol).



The nosylated aminophenol (**4f**) was prepared according the general procedure. Starting materials were 1,1,4,4,8,8,11,11-octamethyl-1,2,3,4,8,9,10,11-octahydropentacene (640 mg, 1.61 mmol, 1.05 eq), quinone imine (446 mg, 1.51 mmol, 1.0 eq), 20 mL $CHCl_3$. Method B was used to rearomatize the compound. The title compound was obtained as a yellowish solid.

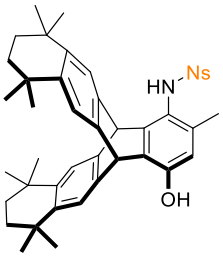
^{1}H NMR (300 MHz, DMSO-d_6): δ 10.08 (s, 1H; N**H**), 9.61 (s, 1H; O**H**), 8.41 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.01 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.27 (s, 2H), 7.24 (s, 2H), 6.36 (d, J = 8.6 Hz, 1H; ArC**H**), 6.31 (d, J = 8.6 Hz, 1H; ArC**H**), 5.73 (s, 1H; C**H**$_{\text{-bridge}}$), 5.66 (s, 1H; C**H**$_{\text{bridge}}$), 1.54 (s, 8H; C**H$_2$**$_{\text{-Cy}}$), 1.17 (s, 12H; C**H$_3$**$_{\text{-Cy}}$), 1.15 (s, 6H; C**H$_3$**$_{\text{-Cy}}$), 1.12 (s, 6H; C**H$_3$**$_{\text{-Cy}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 151.2 (Ar**C**$_{\text{-OH}}$), 150.0 (Ar**C**$_{\text{-NO2}}$), 146.9, 145.1, 142.9, 142.5, 141.0, 140.8, 132.9, 128.9, 125.1, 124.5, 122.3, 121.3, 113.3 (Ar**C**H), 48.5 (**C**H$_{\text{-bridge}}$), 46.2 (**C**H$_{\text{-bridge}}$), 35.2 (**C**(CH$_3$)$_{2\text{-Cy}}$), 34.3 (**C**H$_{2\text{-Cy}}$), 32.1 (**C**H$_{3\text{-Cy}}$).

HRMS (APCI): calcd. for $C_{42}H_{47}N_2O_5S$ [M+H] 691.32002. Found 691.31950 (Δ = 0.52 mmu).

R$_f$ = 0.24 (Cy/EA = 4:1 v/v).

Yield: 70% (0.74 g, 1.07 mmol).



The nosylated aminophenol (**4g**) was prepared according the general procedure. Starting materials were 1,1,4,4,8,8,11,11-octamethyl-1,2,3,4,8,9,10,11-octahydropentacene (1.96 g, 4.92 mmol, 1.0 eq), methyl-quinone imine (1.58 g, 5.16 mmol, 1.05 eq), 20 mL $CHCl_3$. Method B was used to rearomatize the compound. The title compound was obtained as a yellowish solid.

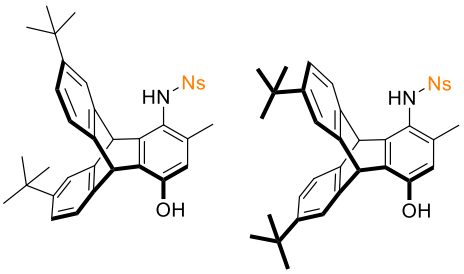
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.80 (s, 1H, N**H**), 9.53 (s, 1H, O**H**), 8.42 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.97 (d, J = 8.8 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.33 – 7.23 (m, 4H, H_{Ar}), 6.25 (s, 1H; ArC**H**), 5.76 (s, 1H; C**H**$_{\text{-bridge}}$), 5.65 (s, 1H; C**H**$_{\text{-bridge}}$), 1.57 (s, 8H; C**H$_2$**$_{\text{-Cy}}$), 1.41 (s, 3H, ArC**H$_3$**$_{\text{-ortho}}$), 1.24 – 1.14 (m, 24H, C**H$_3$**$_{\text{-Cy}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 150.7 (Ar**C**$_{\text{-OH}}$), 149.5 (Ar**C**$_{\text{-NO2}}$), 147.5, 142.7, 142.2, 140.4, 140.1, 133.5, 130.2, 128.1, 124.6, 122.0, 120.6, 114.1 (Ar**C**H), 49.4 (**C**H$_{\text{-bridge}}$), 45.6 (**C**H$_{\text{-bridge}}$), 34.7 (**C**$(CH_3)_{2\text{-Cy}}$), 33.8 (**C**$H_{2\text{-Cy}}$), 31.7 (**C**$H_{3\text{-Cy}}$), 17.3 (Ar**C**$H_{3\text{-ortho}}$).

HRMS (APCI): calcd. for $C_{43}H_{49}N_2O_5S$ [M+H] 705.33567. Found 705.33716 (Δ = 1.49 mmu).

R_f = 0.31 (Cy/EA = 3:1 v/v).

Yield: 91% (3.09 g, 4.47 mmol).



The nosylated aminophenol (**4h**) was prepared according the general procedure. Starting materials were 2,7-*tert*-butylanthracene (500 mg, 1.72 mmol 1.0 eq), methyl-quinone monoimine (528 mg, 1.72 mmol, 1.0 eq), in 20 mL $CHCl_3$. Method B was used to rearomatize the compound. Syn/anti-isomer (1:2 ratio) was obtained as a yellowish solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.82 (s, 1H; N**H** $_{\text{anti}}$), 9.81 (s, 1H; N**H** $_{\text{syn}}$), 9.58 (s, 1H; O**H** $_{\text{syn}}$), 9.55 (s, 1H; O**H** $_{\text{anti}}$), 8.43 – 8.35 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.99 – 7.85 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.41 (d, J = 2.0 Hz, 4H), 7.28 (d, J = 7.8, 2H), 7.15 (s, 2H), 7.01 – 6.91 (m, 4H), 6.28 (s, 1H; ArC**H** $_{\text{syn}}$), 6.25 (s, 1H; ArC**H** $_{\text{anti}}$), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$

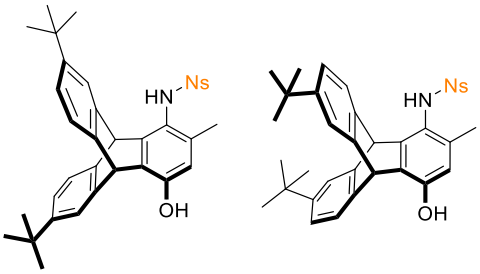
$_{anti}$), 5.76 (s, 1H; C**H**$_{\text{-bridge syn}}$), 5.74 (s, 1H$_A$; C**H**$_{\text{-bridge syn}}$), 5.73 (s, 1H; C**H**$_{\text{-bridge anti}}$), 1.53 (s, 3H; ArC**H**$_{\mathbf{3}\text{-ortho syn}}$), 1.43 (s, 3H; ArC**H**$_{\mathbf{3}\text{-ortho anti}}$), 1.22 (s, 36H; C(C**H**$_{\mathbf{3}}$)$_{3\ anti+syn}$). (Isomer anti:syn, 1:2 ratio)

^{13}C NMR (75 MHz, DMSO-*d*$_6$): *δ* 150.8 (Ar**C**$_{\text{-OH anti}}$), 150.8 (Ar**C**$_{\text{-OH syn}}$), 149.6 (Ar**C**$_{\text{-NO2 syn}}$), 149.5 (Ar**C**$_{\text{-NO2 anti}}$), 147.3, 147.3, 147.1, 147.0, 145.5, 145.1, 142.9, 142.4, 133.7, 133.5, 130.3, 130.1, 128.2, 124.6, 123.6, 122.5, 121.5, 121.1, 121.0, 120.7, 120.2, 114.3 (Ar**C**H $_{\text{syn}}$), 114.1 (Ar**C**H $_{\text{anti}}$), 50.6 (**C**H$_{\text{-bridge anti}}$), 48.9 (**C**H$_{\text{-bridge syn}}$), 46.8 (**C**H$_{\text{-bridge syn}}$), 45.3 (**C**H$_{\text{-bridge anti}}$), 34.2 (C(**C**H$_3$)$_3$), 31.3 (C(**C**H$_3$)$_3$), 17.5 (Ar**C**H$_{3\text{-ortho syn}}$), 17.3 (Ar**C**H$_{3\text{-ortho anti}}$). (Isomer anti:syn, 1:2 ratio)

HRMS (APCI): calcd. for $C_{35}H_{37}N_2O_5S$ [M+H] 597.24177. Found 597.24146 (Δ = 0.31 mmu).

R$_f$ = 0.39 (Cy/EA = 7:3 v/v).

Yield: 84% (0.86 g, 1.44 mmol).



The nosylated aminophenol (**4i**) was prepared according the general procedure. Starting materials were 2,6-*tert*-butylanthracene (1.0 g, 3.44 mmol, 1.0 eq). methyl-quinone monoimine (1.05 g, 3.44 mmol, 1.0 eq) in 30 mL $CHCl_3$. Method B was used to rearomatize the compound. The title compound was obtained as a yellowish solid. Isomer (1:1 ratio) was obtained as a yellowish solid.

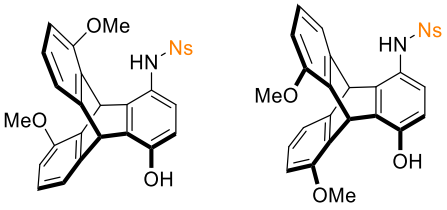
^{1}H NMR (300 MHz, DMSO-*d*$_6$): *δ* 9.82 (s, 1H; N**H**), 9.55 (s, 1H; O**H**), 8.38 (d, *J* = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.91 (d, *J* = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.42 – 7.37 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.11 (bs, 1H), 6.97 – 6.90 (m, 2H), 6.28 (s, 1H; ArC**H**), 5.78 (s, 1H; C**H**$_{\text{-bridge}}$), 5.74 (s, 1H; C**H**$_{\text{-bridge}}$), 1.51 (s, 3H; ArC**H**$_{\mathbf{3}\text{-ortho}}$), 1.22 (s, 9H; C(C**H**$_{\mathbf{3}}$)$_3$), 1.21 (s, 9H; C(C**H**$_{\mathbf{3}}$)$_3$). (Isomer 1:1 ratio)

^{13}C NMR (75 MHz, DMSO-*d*$_6$): *δ* 151.3 (Ar**C**$_{\text{-OH}}$), 150.1 (Ar**C**$_{\text{-NH2}}$), 147.6, 145.8, 142.8, 134.1, 130.6, 128.6, 125.1, 124.2, 123.1, 121.5, 121.4, 121.2, 120.6, 114.7 (Ar**C**H), 66.8 **C**(CH$_3$)$_3$, 50.2 (**C**H$_{\text{-bridge}}$), 46.5 (**C**H$_{\text{-bridge}}$), 34.7 (C(**C**H$_3$)$_3$), 31.7 (C(**C**H$_3$)$_3$), 17.9 (Ar**C**H$_{3\text{-ortho}}$).

HRMS (APCI): calcd. for $C_{35}H_{37}N_2O_5S$ [M+H] 597.24177. Found 597.24135 (Δ = 0.42 mmu).

R$_f$ = 0.47 (Cy/EA = 4:1 v/v).

Yield: 81% (1.66 g, 2.78 mmol).



The nosylated aminophenol (**4j**) was prepared according the general procedure. Starting materials were 1,8-dimethoxyanthracene (150 mg, 0.629 mmol, 1.0 eq), quinone monoimine (184 mg, 0.629 mmol, 1.0 eq) in 5 mL $CHCl_3$. Method B was used to rearomatize the compound. Syn/anti-isomer (1:1 ratio) was obtained as a yellowish solid.

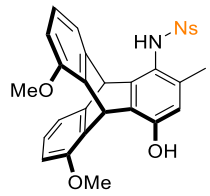
^{1}H NMR (500 MHz, DMSO-*d_6*): *δ* 10.16 (s, 1H; N**H**), 9.82 (s, 1H; N**H**), 9.68 (s, 1H; O**H**), 9.64 (s, 1H; O**H**), 8.33 (d, *J* = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.29 (d, *J* = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.88 (d, *J* = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.78 (d, *J* = 8.6 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.03 – 7.00 (m, 2H), 6.95 – 6.91 (m, 2H), 6.80 – 6.73 (m, 3H), 6.73 – 6.70 (m, 2H), 6.69 – 6.66 (m, 2H), 6.63 – 6.60 (m, 2H), 6.53 (s, 1H; C**H**$_{\text{-bridge}}$), 6.51 (d, *J* = 8.6 Hz, 1H; ArC**H**), 6.43 (d, *J* = 8.6 Hz, 1H; ArC**H**), 6.29 (d, *J* = 8.4 Hz, 1H; ArC**H**), 5.92 (d, *J* = 8.6 Hz, 1H; ArC**H**), 5.81 (s, 1H; C**H**$_{\text{-bridge}}$), 5.66 (s, 1H; C**H**$_{\text{-bridge}}$), 3.81 (s, 6H; COOC**H$_3$**), 3.76 (s, 6H; COOC**H$_3$**).

^{13}C NMR (126 MHz, DMSO-*d_6*): *δ* 154.5 (Ar**C**$_{\text{-OMe}}$), 153.7 (Ar**C**$_{\text{-OMe}}$), 151.3 (Ar**C**$_{\text{-OH}}$), 150.7 (Ar**C**$_{\text{-OH}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 149.5 (Ar**C**$_{\text{-NO2}}$), 148.0, 147.4, 146.4, 146.4, 145.5, 144.2, 133.0, 132.5, 132.5, 131.8, 128.4, 128.2, 125.7, 125.2, 124.7, 124.6, 124.3, 124.1, 121.9, 121.9, 116.7 (Ar**C**H), 116.3 (Ar**C**H), 112.9, 112.6, 108.8 (Ar**C**H), 108.5 (Ar**C**H), 55.7 (O**C**H$_3$), 55.5 (O**C**H$_3$), 48.4 (**C**H$_{\text{-bridge}}$), 46.8 (**C**H$_{\text{-bridge}}$), 35.7 (**C**H$_{\text{-bridge}}$), 33.0 (**C**H$_{\text{-bridge}}$).

HRMS (ESI): calcd. for $C_{28}H_{22}N_2O_7S$ [M+Na] 553.10399. Found 553.10402 (Δ = 0.03 mmu).

R_f = 0.13 (Cy/EA = 7:3 v/v).

Yield: 48% (160 mg, 0.302 mmol).



The nosylated aminophenol (**4k**) was prepared according the general procedure. Starting materials were 1,8-dimethoxyanthracene (1.0 g, 4.20 mmol, 1.0 eq), quinone monoimine (1.29 g, 4.20 mmol, 1.0 eq) in 30 mL $CHCl_3$. Method B was used to rearomatize the compound. Only Syn-Isomer was obtained.

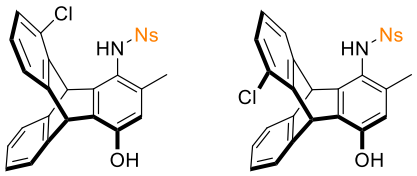
^{1}H NMR (500 MHz, DMSO-d_6): δ 9.80 (s, 1H; N**H**), 9.57 (s, 1H; O**H**), 8.38 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.01 – 6.75 (m, 4H), 6.68 – 6.64 (m, 2H), 6.54 (s, 1H; C**H**$_{\text{-bridge}}$), 6.26 (s, 1H; ArC**H**), 5.80 (s, 1H; C**H**$_{\text{-bridge}}$), 3.79 (s, 6H; OC**H$_3$**), 1.49 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 153.7 (Ar**C**$_{OCH3}$), 150.8 (Ar**C**$_{OH}$), 149.6, 147.8, 147.6, 147.0, 133.6, 132.9, 129.8, 128.2, 125.4, 124.7, 124.7, 120.7, 117.1, 114.1 (Ar**C**H), 108.5, 55.6 (O**C**H$_3$), 50.2 (**C**H$_{\text{-bridge}}$), 33.0 (**C**H$_{\text{-bridge}}$), 17.5 (Ar**C**H$_{3\text{-ortho}}$).

HRMS (ESI): calcd. for $C_{29}H_{25}N_2O_7S$ $[M+H]^+$ 545.13770. Found 545.13846 (Δ = 0.76 mmu).

R$_f$ = 0.16 (Cy/EA = 7:3 v/v).

Yield: 34% (0.78 g, 1.43 mmol).



The nosylated aminophenol (**4l**) was prepared according the general procedure. Starting materials were 1-chloroanthracene (1.04 g, 4.90 mmol, 1.0 eq), methyl-quinone imine (1.50 g, 4.90 mmol, 1.0 eq), in 30 mL $CHCl_3$. Method B was used to rearomatize the compound. Syn/anti-isomer (1:1 ratio) was obtained as a yellowish solid.

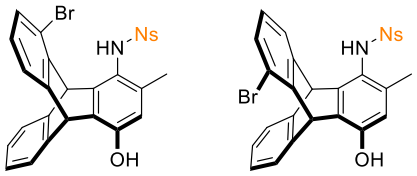
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.87 (s, 1H; N**H**), 9.84 (s, 1H; N**H**), 9.76 (s, 1H; O**H**), 9.73 (s, 1H; O**H**), 8.38 (d, J = 8.8 Hz, 4H; Ar**H**$_{\text{-Ns}}$), 7.87 (d, J = 8.6 Hz, 4H; Ar**H**$_{\text{-Ns}}$), 7.49 – 7.34 (m, 5H), 7.11 – 6.90 (m, 9H), 6.40 (s, 1H; C**H**$_{\text{-bridge anti}}$), 6.32 (s, 1H; ArC**H** $_{\text{syn}}$), 6.29 (s, 1H; ArC**H** $_{\text{anti}}$), 6.20 (s, 1H; C**H**$_{\text{-bridge syn}}$), 5.93 (s, 1H; C**H**$_{\text{-bridge syn}}$), 5.90 (s, 1H; C**H**$_{\text{-bridge anti}}$), 1.48 (s, 3H; ArC**H$_3$**$_{\text{-ortho syn}}$), 1.38 (s, 3H; ArC**H$_3$**$_{\text{-ortho anti}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 151.2 (Ar**C**$_{\text{-OH}}$), 151.1 (Ar**C**$_{\text{-OH}}$), 149.7 (Ar**C**$_{\text{-NO2}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 148.1, 146.7, 146.4, 146.0, 145.0, 142.7, 134.3, 133.8, 129.6, 128.7, 128.2, 128.1, 127.9, 126.7, 126.4, 125.2, 125.1, 124.9, 124.7, 124.6, 123.5, 122.2, 121.1, 120.8, 114.6 (Ar**C**H), 114.5 (Ar**C**H) 50.1 (**C**H$_{\text{-bridge anti}}$), 46.7 (**C**H$_{\text{-bridge anti}}$), 46.5 (**C**H$_{\text{-bridge anti}}$), 43.1 (**C**H$_{\text{-bridge syn}}$), 17.4 (Ar**C**H$_{3\text{-ortho syn}}$), 17.1 (Ar**C**H$_{3\text{-ortho anti}}$).

HRMS (APCI): calcd. for $C_{27}H_{19}N_2O_5SCl$ $[M-H]^-$ 517.06304. Found 517.06408 (Δ = 1.04 mmu).

R$_f$ = 0.11 (Cy/EA = 10:1 v/v).

Yield: 92% (2.37 g, 4.51 mmol).



The nosylated aminophenol (**4m**) was prepared according the general procedure. Starting materials were 1-bromoanthracene (14.3 g, 55.61 mmol, 1.0 eq), methyl-quinone imine (18.7 g, 61.18 mmol, 1.1 eq), in 300 mL $CHCl_3$. Method B was used to rearomatize the compound. Syn/anti-isomer (1:1 ratio) was obtained as a yellowish solid.

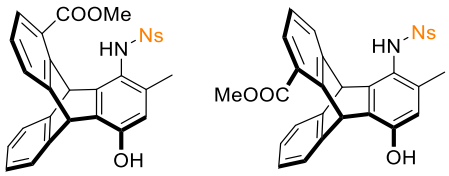
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.86 (s, 1H; N**H**), 9.82 (s, 1H; N**H**), 9.76 (s, 1H; O**H**), 9.72 (s, 1H; O**H**), 8.42 – 8.33 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.93 – 7.80 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.46 – 7.30 (m, 6H), 7.25 – 7.19 (m, 2H), 7.05 – 6.98 (m, 4H), 6.95 – 6.88 (m, 2H), 6.38 (s, 1H C**H**$_{\text{-bridge anti}}$), 6.32 (s, 1H ArC**H**$_{\text{syn}}$), 6.29 (s, 1H ArC**H**$_{\text{anti}}$), 6.17 (s, 1H C**H**$_{\text{-bridge syn}}$), 5.92 (s, 1H; C**H**$_{\text{-bridge syn}}$), 5.89 (s, 1H; C**H**$_{\text{-bridge anti}}$), 1.49 (s, 3H; ArC**H$_3$**$_{\text{-ortho syn}}$), 1.40 (s, 3H; ArC**H$_3$**$_{\text{-ortho anti}}$).

^{13}C NMR (75 MHz, DMSO-d_6): δ 151.2 (Ar**C**$_{\text{-OH}}$), 151.1 (Ar**C**$_{\text{-OH}}$), 149.7 (Ar**C**$_{\text{-NO2}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 148.1, 146.8, 146.4, 146.1, 145.0, 144.8, 144.1, 134.3, 133.9, 129.6, 128.7, 128.2, 127.0, 126.7, 125.1, 124.9, 124.7, 124.6, 123.8, 123.5, 122.8, 121.1, 120.8, 117.8, 114.6 (Ar**C**H), 114.5 (Ar**C**H), 50.3 (**C**H$_{\text{-bridge syn}}$), 49.3 (**C**H$_{\text{-bridge anti}}$), 46.6 (**C**H$_{\text{-bridge anti}}$), 45.7 (**C**H$_{\text{-bridge syn}}$), 17.4 (Ar**C**H$_{\text{3-ortho syn}}$), 17.1 (Ar**C**H$_{\text{3-ortho anti}}$).

HRMS (APCI): calcd. for $C_{27}H_{19}N_2O_5BrS$ $[M+H]^+$ 561.01253. Found 561.01311 (Δ = 0.58 mmu).

R_f = 0.38 (Cy/EA = 3:1 v/v).

Yield: 82% (26.80 g, 47.6 mmol).



The nosylated aminophenol (**4n)** was prepared according the general procedure. Starting materials were 1-anthracene carboxylic methylester (11.2 g, 47.4 mmol, 1.0 eq), methyl-quinone monoimine (14.66 g, 47.88 mmol, 1.0 eq), in 300 mL DCE. Method B was used to rearomatize the compound. Syn/anti-isomer (1:1 ratio) was obtained as a yellowish solid.

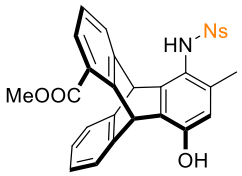
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.86 (s, 1H; O**H**$_{\text{syn}}$), 9.74 (s, 1H; O**H**$_{\text{anti}}$), 9.68 (s, 1H; N**H**$_{\text{syn}}$), 9.62 (s, 1H; N**H**$_{\text{anti}}$), 8.39 – 8.33 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.89 – 7.81 (m, 4H; Ar**H**$_{\text{-Ns}}$), 7.64 – 7.60 (m, 1H), 7.52 – 7.46 (m, 2H), 7.45 – 7.36 (m, 4H), 7.14 – 7.05 (m, 3H), 7.04 – 6.96 (m, 5H), 6.93 (s, 1H; C**H**$_{\text{-bridge syn}}$), 6.28 (s, 1H;

ArC**H** $_{syn}$), 6.27 (s, 1H; ArC**H** $_{anti}$), 5.94 (s, 1H; C**H**$_{-bridge\ anti}$), 5.91 (s, 1H; C**H**$_{-bridge\ syn}$), 4.00 (s, 3H; COOC**H$_3$** $_{anti}$), 3.94 (s, 3H; COOC**H$_3$** $_{syn}$), 1.48 (s, 3H; ArC**H$_3$**$_{-ortho\ syn}$), 1.34 (s, 3H; ArC**H$_3$**$_{-ortho\ anti}$).

^{13}C NMR (75 MHz, DMSO-*d_6*)**:** *δ* 166.8 (**C**OOMe), 151.4 (Ar**C**$_{-OH\ syn}$), 150.9 (Ar**C**$_{-OH\ anti}$), 149.6 (Ar**C**$_{-NO2\ syn}$), 149.5 (Ar**C**$_{-NO2\ anti}$), 147.2, 146.8, 146.6, 146.5, 145.2, 144.6, 134.2, 130.0, 129.0, 128.2, 128.2, 127.1, 125.8, 125.7, 125.3, 125.0, 124.8, 124.7, 124.5, 123.8, 123.4, 121.2, 120.6, 114.5 (Ar**C**H), 52.1 (COO**C**H$_3$), 50.0 (**C**H$_{-bridge\ syn}$), 46.9(**C**H$_{-bridge\ anti}$), 46.3(**C**H$_{-bridge\ anti}$), 42.9 (**C**H$_{-bridge\ syn}$), 17.4 (Ar**C**H$_{3-ortho\ syn}$), 17.1 (Ar**C**H$_{3-ortho\ anti}$).

R$_f$ = 0.18 (Cy/EA = 7:3 v/v).

Yield: 74% (18.97 g, 34.9 mmol).



The nosylated aminophenol (syn-**4n**) was prepared according the general procedure. Starting materials were 1-anthracene carboxylic ester (400 mg, 1.69 mmol, 1.0 eq), methyl-quinone monoimine (519 mg, 1.69 mmol, 1.0 eq) and $Mg(ClO_4)_2$ (378 mg, 1.0 eq) in 15 mL $CHCl_3$. It was not necessary to rearomatize the compound (rearomatized already before workup). The title compound was obtained as a yellowish solid. (Only syn-isomer formed)

^{1}H NMR (300 MHz, DMSO-*d_6*): *δ* 9.87 (s, 1H; O**H**), 9.66 (s, 1H; Ar**H**$_{-Ns}$), 8.36 (d, *J*=8.6, 2H; Ar**H**$_{-Ns}$), 7.85 (d, *J*=8.4, 2H), 7.55 – 7.45 (m, 2H), 7.39 (d, *J*=6.4, 1H), 7.34 – 7.19 (m, 1H), 7.14 – 7.03 (m, 1H), 7.03 – 6.95 (m, 2H), 6.92 (s, 1H C**H**$_{-bridge}$), 6.27 (s, 1H; ArC**H**), 5.93 (s, 1H; C**H**$_{-bridge}$), 3.93 (s, 3H; COOC**H$_3$**), 1.46 (s, 3H; ArC**H$_3$**$_{-ortho}$).

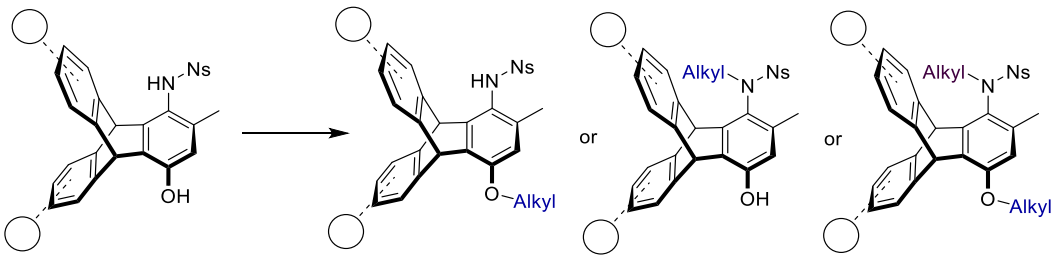
^{13}C NMR (75 MHz, DMSO-*d_6*): *δ* 166.9 (**C**OOCH$_3$), 151.5 (Ar**C**$_{-OH}$), 149.8 (Ar**C**$_{-NO2}$), 147.2, 146.9, 146.8, 145.4, 134.3, 129.2, 128.5, 128.3, 126.0, 125.5, 125.2, 125.0, 124.8, 124.5, 123.9, 120.8, 114.7 (Ar**C**H), 52.3 (COO**C**H$_3$), 50.1 (**C**H$_{-bridge}$), 43.1 (**C**H$_{-bridge}$) 17.5 (Ar**C**H$_{3-ortho}$).

HRMS (APCI): calcd. for $C_{29}H_{21}N_2O_7S$ [M-H] 541.10750. Found 541.10834 (Δ = 0.84 mmu).

R$_f$ = 0.18 (Cy/EA = 7:3 v/v).

Yield: 97% (0.89 g, 1.64 mmol).

N/O-Alkylated aminophenols (nosyl-protected)

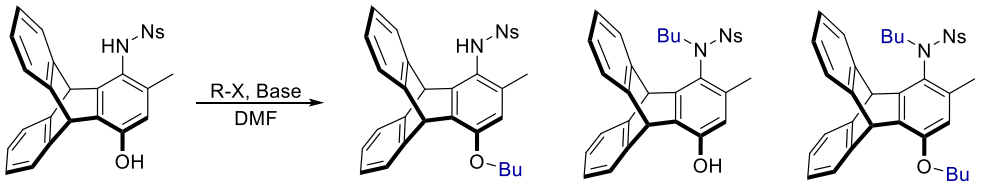


General procedure for O- or N-alkylation of 4 to triptycenes 5:

O-alkylation: To a solution of the nosylated aminophenol (1.0 eq) in dry DMF, NaH (2.5 eq, 60% dispersion in mineral oil) is added at 0 °C The reaction mixture was warmed up to r.t. and stirred for another 30 min. Then alkylhalide (1.0 eq) is added and stirred for 24 h at 50 °C.

N-alkylation: To a solution of the nosylated aminophenol (1.0 eq) in DMF or MeCN, K_2CO_3 (3.0 eq) is added at r.t. Then alkylhalide (1.0 – 4.0 eq) is added and stirred for 24 h at 50 °C.

Work up: The reaction mixture is poured into water, sat. aqueous NH_4Cl is added and extracted with EA. The organic phase is dried over $MgSO_4$, filtered and removed under reduced pressure. The crude product was purified by column chromatography.

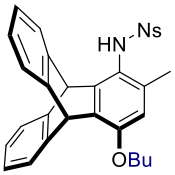


Edukt | O-Alkyl | N-Alkyl | N/O-Alkyl

Base	Butyl-X	T [°C] 24 h	Product	Ratio*
K_2CO_3 (3.0 eq)	X = I (1.05 eq)	RT	N-Butyl + N/O-Butyl	**10 : 1**
K_2CO_3 (3.0 eq)	X = Cl (1.05 eq)	60°C	Edukt + N-Butyl	**3 : 1**
NaH (2.5 eq)	X = Br, I (10 eq)	60°C	N/O-Butyl (only)	**1:0**
NaH (2.5 eq)	X = Cl (10 eq)	60°C	O-Butyl + N/O-Butyl	**1:1**
NaH (2.5 eq)	X = I (1.05 eq)	60°C	O-Butyl + N-Butyl + N/O-Butyl	**6:2:1**
NaH (2.5 eq)	X = Cl (1.05 eq)	60°C	O-Butyl (+ traces N/O)	**1:0**

*determined by NMR

	Solvent	Base	R-X
O-alkylation:	DMF (dry)	NaH (2.5 eq)	R-Cl (1.0 eq)
N-alkylation:	DMF or MeCN	K_2CO_3	R-Br / R-I (1.0 eq)
Double alkylation:	DMF or MeCN	NaH or K_2CO_3	R-X (X=Cl,Br,I | 2.0 eq)



The O-alkylated aminophenol (**5b**) was prepared according the general procedure. Starting materials were nosylated aminophenol (2.10 g, 4.33 mmol, 1.0 eq), NaH (433 mg, 10.8 mmol, 2.5 eq; 60% in mineral oil), butyl chloride (0.45 mL, 4.33 mmol, 1.0 eq), in 50 mL dry DMF. The crude product was purified by column chromatography (silica gel, Cy/EA = 8:1 v/v) to afford the title compound as a yellow solid.

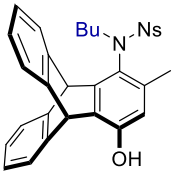
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.75 (d, *J* = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.51 – 7.41 (m, 2H), 7.44 – 7.35 (m, 2H), 7.06 – 6.94 (m, 4H), 6.24 (s, 1H; ArC**H**), 6.20 (s, 1H; N**H**), 6.14 (s, 1H; C**H**$_{\text{-bridge}}$), 5.88 (s, 1H; C**H**$_{\text{-bridge}}$), 3.91 (t, *J* = 6.4, 2H; OC**H$_2$**CH_2), 1.92 – 1.76 (m, 2H; OCH_2**CH_2**), 1.65 – 1.50 (m, 2H; C**H$_2$**CH_3), 1.44 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.05 (t, *J* = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5 (Ar**C**$_{\text{-OH}}$), 150.2 (Ar**C**$_{\text{-NO2}}$), 147.7, 145.7, 145.4, 133.9, 133.3, 128.7, 125.2, 125.2, 124.8, 124.2, 123.6, 120.8, 111.3 (Ar**C**H), 68.5 (O**C**H_2CH_2), 50.6 (**C**H$_{\text{-bridge}}$), 47.1 (**C**H$_{\text{-bridge}}$), 31.5 (OCH_2**CH_2**), 19.5 (**C**H_2CH_3), 17.9 (Ar**C**$H_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (APCI): calcd. for $C_{31}H_{28}N_2O_5S$ $[M\text{-}H]^-$ 539.16462. Found 539.16512 (Δ = 0.50 mmu).

R_f = 0.55 (Cy/EA = 7:3 v/v).

Yield: 73% (1.70 g, 3.14 mmol)



The N-alkylated aminotriptycene (**5ba**) was prepared according the general procedure. Starting materials used nosylated aminotriptycene (100 mg, 0.206 mmol, 1.0 eq), K_2CO_3 (86 mg, 0.619 mmol, 3.0 eq), butyl iodide (0.25 mL, 0.206 mmol, 1.0 eq), in 4 mL dry DMF. The crude product was purified by column chromatography (silica gel, Cy/EA = 8:3 v/v) to afford the title compound as a yellowish solid.

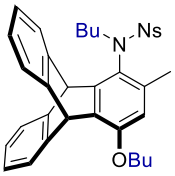
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.82 (s, 1H; O**H**), 8.39 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.00 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.48 – 7.37 (m, 3H), 7.31 (dd, J = 5.6, 3.0 Hz, 1H), 7.07 – 6.92 (m, 4H), 6.35 (s, 1H; ArC**H**), 5.84 (s, 1H; C**H**$_{\text{-bridge}}$), 5.76 (s, 1H; C**H**$_{\text{-bridge}}$), 3.98 – 3.77 (m, 1H; NC**H$_2$**CH$_2$), 3.23 – 3.06 (m, 1H; NC**H$_2$**CH$_2$), 1.94 – 1.56 (m, 1H; NCH$_2$C**H$_2$**), 1.43 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.31 – 1.22 (m, 2H; NCH$_2$C**H$_2$** + C**H$_2$**CH$_3$), 1.21 – 1.08 (m, 1H; C**H$_2$**CH$_3$), 0.82 (t, J = 7.0 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, DMSO-d_6) δ 151.6 (Ar**C**$_{\text{-OH}}$), 149.8 (Ar**C**$_{\text{-NO2}}$), 148.1, 146.1, 145.7, 145.3, 145.0, 144.9, 134.3, 130.0, 128.6, 125.0, 124.8, 124.6, 124.0, 123.5, 123.2, 115.0 (Ar**C**H), 51.4 (N**C**H$_2$CH$_2$), 50.5 (**C**H$_{\text{-bridge}}$), 46.2 (**C**H$_{\text{-bridge}}$), 31.6 (NCH$_2$**C**H$_2$), 19.4 (**C**H$_2$CH$_3$), 17.3 (Ar**C**H$_{3\text{-ortho}}$), 13.6 (CH$_2$**C**H$_3$).

HRMS (APCI): calcd. for $C_{31}H_{29}N_2O_5S$ $[M+H]^+$ 541.17917. Found 541.17856 (Δ = 0.61 mmu).

R$_f$ = 0.43 (Cy/EA = 7:3 v/v).

Yield: 90% (101 mg, 0.186 mmol).



The O/N-alkylated aminotriptycene (**5bb**) was prepared according the general procedure. Starting materials were nosylated aminophenol (50 mg, 0.103 mmol, 1.0 eq), NaH (10 mg, 0.258 mmol, 2.5 eq, 60% in mineral oil), butyl iodide (0.25 mL, 0.216 mmol, 2.1 eq), in 2 mL dry DMF. The title compound was obtained as a yellowish solid without further purification.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.39 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.02 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.52 – 7.28 (m, 5H), 7.13 – 6.89 (m, 5H), 6.57 (s, 1H; ArC**H**), 5.84 (s, 1H; C**H**$_{\text{-bridge}}$), 5.80 (s, 1H; C**H**$_{\text{-bridge}}$), 4.00 (t, J = 6.3 Hz, 2H; OC**H$_2$**CH$_2$), 3.94 – 3.80 (m, 1H; NC**H$_2$**CH$_2$), 3.24 – 3.11 (m, 1H; NC**H$_2$**CH$_2$), 1.82 – 1.72 (m, 3H; NCH$_2$C**H$_2$** + OCH$_2$C**H$_2$**), 1.59 – 1.53 (m, 2H; C**H$_2$**CH$_{3\text{-OBu}}$), 1.52 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.33 – 1.22 (m, 2H;

$NCH_2C\mathbf{H}_2$ + $C\mathbf{H}_2CH_{3\text{-}NBu}$), 1.20 – 1.09 (m, 1H; $C\mathbf{H}_2CH_{3\text{-}NBu}$), 1.00 (t, *J* = 7.4 Hz, 3H; $CH_2C\mathbf{H}_{3\text{-}OBu}$), 0.82 (t, *J* = 7.1 Hz, 3H; $CH_2C\mathbf{H}_{3\text{-}NBu}$).

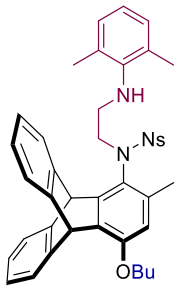
^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.28 (d, *J* = 8.8 Hz, 2H; Ar$\mathbf{H}_{\text{-Ns}}$), 7.91 (d, *J* = 8.9 Hz, 2H; Ar$\mathbf{H}_{\text{-Ns}}$), 7.57 – 7.47 (m, 1H), 7.47 – 7.34 (m, 3H), 7.08 – 6.89 (m, 4H), 6.33 (s, 1H; ArC**H**), 5.93 (s, 1H; C$\mathbf{H}_{\text{-bridge}}$), 5.89 (s, 1H; C$\mathbf{H}_{\text{-bridge}}$), 3.95 (t, *J* = 6.4 Hz, 2H; O$C\mathbf{H}_2CH_2$), 3.94 – 3.81 (m, 1H; N$C\mathbf{H}_2CH_2$), 3.21 – 3.04 (m, 1H; N$C\mathbf{H}_2CH_2$), 2.00 – 1.78 (m, 3H; $NCH_2C\mathbf{H}_2$ + $OCH_2C\mathbf{H}_2$), 1.69 – 1.48 (m, 3H; $NCH_2C\mathbf{H}_2$ + $C\mathbf{H}_2CH_{3\text{-}OBu}$), 1.49 (s, 3H; Ar$C\mathbf{H}_{3\text{-ortho}}$), 1.41 – 1.22 (m, 1H; $C\mathbf{H}_2CH_{3\text{-}NBu}$), 1.25 – 1.08 (m, 1H; $C\mathbf{H}_2CH_{3\text{-}NBu}$), 1.07 (t, *J* = 7.4 Hz, 3H; $CH_2C\mathbf{H}_{3\text{-OBu}}$), 0.90 (t, *J* = 7.3 Hz, 3H; $CH_2C\mathbf{H}_{3\text{-}NBu}$).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* 153.7 (Ar$\mathbf{C}_{\text{-OBu}}$), 150.0 (Ar$\mathbf{C}_{\text{-}NO2}$), 149.0, 146.7, 146.4, 145.5, 145.3, 145.2, 134.2, 133.4, 128.7, 125.6, 125.4, 125.3, 125.1, 125.0, 124.3, 124.2, 123.8, 123.5, 111.7 (Ar**C**H), 68.4 (O$\mathbf{C}H_2CH_2$), 52.6 (N$\mathbf{C}H_2CH_2$), 51.3 ($\mathbf{C}H_{\text{-bridge}}$), 47.2 ($\mathbf{C}H_{\text{-bridge}}$), 32.3 ($OCH_2\mathbf{C}H_2$), 31.6 ($NCH_2\mathbf{C}H_2$), 20.2 ($\mathbf{C}H_2CH_{3\text{-OBu}}$), 19.6 ($\mathbf{C}H_2CH_{3\text{-}NBu}$), 18.2 (Ar$\mathbf{C}H_{3\text{-ortho}}$), 14.1 ($CH_2\mathbf{C}H_{3\text{-OBu}}$), 13.8 ($CH_2\mathbf{C}H_{3\text{-}NBu}$).

HRMS (ESI): calcd. for $C_{35}H_{36}N_2O_5S$ $[M+NH_4]^+$ 614.26832. Found 614.26835 (Δ = 0.03 mmu).

R_f = 0.68 (Cy/EA = 3:1 v/v).

Yield: 99%. (61 mg, 0.102 mmol).



O-alkylated aminotriptycene (1.0 g, 1.8 mmol, 1.0 eq) and N-(2-iodoethyl)-2,4,6-dimethyl-anilinehydroiodide (0.75 g, 1.8 mmol 1.0 eq) were dissolved in dry DMF (30 mL). Subsequently, $NaHCO_3$ (466 mg, 5.55 mmol, 3.0 equiv) was added and the resulting reaction mixture was stirred for 60 hours at 50 °C. The reaction mixture was then poured into H_2O and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and the solvent evaporated. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 v/v) to afford the title compound (**5bc**) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.28 (d, *J* = 8.9 Hz, 2H; Ar$\mathbf{H}_{\text{-Ns}}$), 7.87 (d, *J* = 8.9 Hz, 2H; Ar$\mathbf{H}_{\text{-Ns}}$), 7.51 – 7.46 (m, 1H), 7.42 – 7.35 (m, 2H), 7.12 (d, *J* = 6.6 Hz, 1H), 7.03 – 6.93 (m, 6H), 6.87 – 6.81 (m, 2H), 6.32 (s, 1H; ArC**H**), 5.88 (s, 1H; C$\mathbf{H}_{\text{-bridge}}$), 5.86 (s, 1H; C$\mathbf{H}_{\text{-bridge}}$), 4.10 – 4.00 (m, 1H; N(Ns)$C\mathbf{H}_2CH_2$), 3.95 (t, *J* = 6.3,

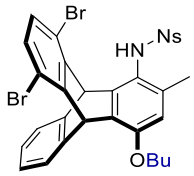
2H; OC**H₂**CH₂), 3.55 – 3.43 (m, 1H; N(Ns)C**H₂**CH₂), 3.36 – 3.20 (m, 2H; N(Ns)CH₂C**H₂**), 2.15 (s, 6H; ArC**H₃**), 1.91 – 1.80 (m, 2H; OCH₂C**H₂**), 1.63 – 1.55 (m, 2H; C**H₂**CH₃), 1.46 (s, 3H; ArC**H₃**$_{\text{-ortho}}$), 1.06 (t, *J* = 7.4 Hz, 3H; CH₂C**H₃**).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* 153.8 (Ar**C**$_{\text{-OBu}}$), 150.2 (Ar**C**$_{\text{-NO2}}$), 148.8, 146.2, 146.1, 145.2, 145.0, 134.0, 133.7, 129.1, 128.9, 125.5, 125.3, 125.2, 125.2, 125.1, 124.4, 124.1, 123.7, 123.5, 122.1, 111.9 (Ar**C**H), 68.4 (O**C**H₂CH₂), 52.8 (N(Ns)**C**H₂CH₂), 51.3 (N(Ns)CH₂**C**H₂), 47.6 (**C**H$_{\text{-bridge}}$), 47.1 (**C**H$_{\text{-bridge}}$), 31.5 (OCH₂**C**H₂), 19.6 (**C**H₂CH₃), 18.7, (Ar**C**H₃), 18.2 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH₂**C**H₃).

HRMS (ESI): calcd. for $C_{41}H_{42}N_3O_5S$ $[M+H]^+$ 688.28397. Found 688.28439 (Δ = 0.42 mmu).

R$_f$ = 0.30 (Cy/EA = 10:1 v/v).

Yield: 37% (0.47 g, 0.685 mmol).



The O-alkylated aminotriptycene (**5c**) was prepared according the general procedure. Starting materials were nosylated aminophenol (6.35 g, 9.90 mmol, 1.0 eq), NaH (1.0 g, 41.5 mmol 2.5 eq; 60% in mineral oil), butyl chloride (1.04 mL, 9.90 mmol 1.0 eq), in 120 mL dry DMF. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1) to afford the title compound as a yellow solid.

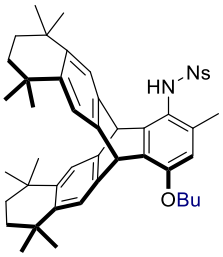
^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.26 – 8.22 (m, 2H; Ar**H**$_{\text{-Ns}}$), 7.85 – 7.81 (m, 2H; Ar**H**$_{\text{-Ns}}$), 7.52 – 7.48 (m, 1H), 7.47 – 7.44 (m, 1H), 7.09 – 7.06 (m, 2H), 7.01 (s, 2H), 6.53 (s, 1H; C**H**$_{\text{-bridge}}$), 6.37 (s, 1H; C**H**$_{\text{-bridge}}$), 6.33 (s, 1H; ArC**H**), 6.32 (s, 1H; N**H**), 4.00 – 3.91 (m, 2H; OC**H₂**CH₂), 1.92 – 1.81 (m, 2H; OCH₂C**H₂**), 1.70 – 1.59 (m, 2H; C**H₂**CH₃), 1.57 (s, 3H; ArC**H₃**$_{\text{-ortho}}$), 1.04 (t, *J* = 7.4 Hz, 3H; CH₂C**H₃**).

^{13}C NMR (126 MHz, $CDCl_3$): *δ* 154.0 (Ar**C**$_{\text{-OBu}}$), 150.3 (Ar**C**$_{\text{-NO2}}$), 148.0, 147.4, 146.9, 146.0, 144.0, 143.9, 134.6, 132.6, 130.2, 130.0, 128.9, 125.8, 125.7, 124.3, 124.2, 121.1, 118.5, 118.0, 111.7 (Ar**C**H), 68.4 (O**C**H₃CH₂), 50.5 (**C**H$_{\text{-bridge}}$), 47.0 (**C**H$_{\text{-bridge}}$), 31.5 (OCH₂**C**H₂), 19.5 (**C**H₂CH₃), 18.2 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH₂**C**H₃).

HRMS (APCI): calcd. for $C_{25}H_{23}Br_2NO$ $[M\text{-Ns}+H]^+$ 511.01409. Found 511.01404 (Δ = 0.05 mmu).

R$_f$ = 0.16 (Cy/EA = 10:1 v/v).

Yield: 62% (4.28 g, 6.13 mmol).



The O-alkylated aminotriptycene (**5g**) was prepared according the general procedure. Starting materials were nosylated aminophenol (2.99 g, 4.29 mmol, 1.0 eq), NaH (424 mg, 10.60 mmol, 2.5 eq, 60% in mineral oil), butyl chloride (0.44 mL, 4.29 mmol, 1.0 eq) in 50 mL dry DMF. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

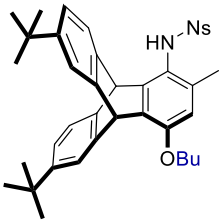
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.90 (s, 1H, N**H**), 8.41 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.97 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.29 – 7.27 (m, 4H), 6.46 (s, 1H; ArC**H**), 5.80 (s, 1H; C**H**$_{\text{-bridge}}$), 5.67 (s, 1H; C**H**$_{\text{-bridge}}$), 3.97 (t, J = 6.1 Hz, 2H; OC**H$_2$**CH$_2$), 1.72 (p, J = 6.3 Hz, 2H; OCH$_2$C**H$_2$**), 1.56 (s, 8H; C**H$_{2\text{-Cy}}$**), 1.52 – 1.55 (m, 2H; C**H$_2$**CH$_3$), 1.51 (s, 3H; ArC**H$_{3\text{-ortho}}$**), 1.17 (m, 24H; C**H$_{3\text{-Cy}}$**), 0.98 (t, J = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, DMSO-d_6): δ 152.1 (Ar**C**$_{\text{-OBu}}$), 149.6 (Ar**C**$_{\text{-NO2}}$), 147.4, 142.4, 142.1, 140.5, 140.3, 133.9, 128.1, 124.6, 122.0, 120.7, 111.7 (Ar**C**H), 68.1 (O**C**H$_2$CH$_2$), 49.4 (**C**H$_{\text{-bridge}}$), 45.6 (**C**H$_{\text{-bridge}}$), 34.7 (**C**(CH$_3$)$_{2\text{-Cy}}$), 33.8 (C(**C**H$_3$)$_{2\text{-Cy}}$), 31.6 (OCH$_2$**C**H$_2$), 30.6 (**C**H$_{2\text{-Cy}}$), 18.8 (CH$_2$**C**H$_3$), 17.6 (Ar**C**H$_{3\text{-ortho}}$), 13.6 (CH$_2$**C**H$_3$).

HRMS (APCI): calcd. for $C_{47}H_{56}N_2O_5S$ $[M+H]^+$ 761.39827. Found 761.39895 (Δ = 0.68 mmu).

R$_f$ = 0.50 (Cy/EA = 4:1 v/v).

Yield: 84%. (2.70 g, 3.55 mmol).



The O-alkylated aminotriptycene (**5h**) was prepared according the general procedure. Starting materials were nosylated aminophenol (250 mg, 0.419 mmol, 1.0 eq; syn/anti mixture), NaH (42 mg, 1.05 mmol, 2.5 eq, 60% in mineral oil), butyl chloride (0.44 mL, 0.419 mmol, 1.0 eq) in 10 mL dry DMF. Syn/anti-isomer (2:1 ratio) was separated by column chromatography (silica gel, Cy/EA 10:1 v/v)

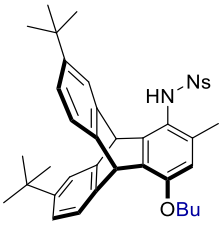
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.46 (s, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 6.54 (s, 1H; N**H**), 6.18 (s, 1H; ArC**H**), 6.02 (s, 1H; C**H**$_{\text{-bridge}}$), 5.84

(s, 1H; C**H**$_{\text{-bridge}}$), 3.92 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH$_2$), 1.91 – 1.79 (m, 2H; OCH$_2$C**H$_2$**), 1.65 – 1.57 (m, 2H; C**H$_2$**CH$_3$), 1.45 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.28 (s, 18H; C**H$_3$**$_{\text{-}t\text{Bu}}$), 1.07 (t, *J* = 7.4 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 153.4 (Ar**C**$_{\text{-OBu}}$), 150.0 (Ar**C**$_{\text{-NO2}}$), 148.3, 148.0, 145.8, 145.6, 142.5, 134.4, 133.3, 128.7, 124.2, 124.0, 121.8, 121.0, 120.7, 111.3 (Ar**C**H), 68.5 (O**C**H$_2$CH$_2$), 49.7 (**C**H$_{\text{-bridge}}$), 47.8 (**C**H$_{\text{-bridge}}$), 34.7, 31.7, 31.4, 19.5 (**C**H$_2$CH$_3$), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

R$_f$ = 0.06 (Cy/EA = 10:1 v/v).

Yield: 80% (146 mg, 0.224mmol).



Anti-isomer (**5h**) obtained after column chromatography from syn/anti mixture as a yellow solid.

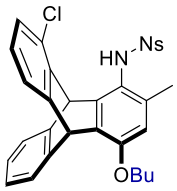
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.61 (s, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 1.5 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.19 (s, 1H; ArC**H**), 6.18 (s, 1H; C**H**$_{\text{-bridge}}$), 6.16 (s, 1H; N**H**), 5.82 (s, 1H; C**H**$_{\text{-bridge}}$), 3.88 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH$_2$), 1.84 – 1.79 (m, 2H; OCH$_2$C**H$_2$**), 1.58 – 1.54 (m, 2H; C**H$_2$**CH$_3$), 1.39 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.27 (s, 18H; C**H$_3$**$_{\text{-}t\text{Bu}}$), 1.04 (t, *J* = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (126 MHz, CDCl$_3$): δ 153.4 (Ar**C**$_{\text{-OBu}}$), 150.2 (Ar**C**$_{\text{-NO2}}$), 148.4, 148.0, 145.9, 145.3, 142.9, 134.5, 132.8, 128.9, 124.2, 122.8, 122.5, 121.6, 120.7, 111.1 (Ar**C**H), 68.3 (O**C**H$_2$CH$_2$), 51.2 (**C**H$_{\text{-bridge}}$), 46.2 (**C**H$_{\text{-bridge}}$), 34.7, 31.7, 31.5, 19.6 (**C**H$_2$CH$_3$), 17.9 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

HRMS (APCI): calcd. for C$_{39}$H$_{48}$N$_3$O$_5$S [M+NH$_4$]$^+$ 670.33092. Found 670.33085 (Δ = 0.07 mmu).

R$_f$ = 0.12 (Cy/EA = 10:1 v/v).

Yield: 80% (72 mg, 0.110 mmol).



The O-alkylated aminotriptycene (**5l**) was prepared according the general procedure. Starting materials were nosylated aminophenol (2.27 g, 4.37 mmol, 1.0 eq, syn/anti mixture), NaH (437 mg, 10.9 mmol, 2.5 eq; 60% in mineral oil), butyl chloride (0.46 mL, 4.37 mmol, 1.0 eq), in 50 mL dry DMF. Syn/anti-isomer (1:1 ratio) was separated by column chromatography (silica gel, Cy/EA 10:1 -> 4:1 v/v). The title compound was obtained as a yellow solid.

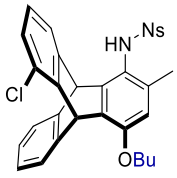
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.79 (d, J = 8.7 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.47 – 7.36 (m, 2H), 7.24 (s, 1H), 7.07 – 6.93 (m, 3H), 6.93 – 6.81 (m, 1H), 6.63 (s, 1H; N**H**), 6.53 (s, 1H; C**H**$_{\text{-bridge}}$), 6.28 (s, 1H; ArC**H**), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$), 3.93 (t, J = 6.3 Hz, 2H; OC**H$_2$**CH_2), 1.90 – 1.78 (m, 2H; OCH_3C**H$_2$**), 1.67 – 1.52 (m, 2H; C**H$_2$**CH_3), 1.54 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.05 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6 (Ar**C**$_{\text{-OBu}}$), 150.1 (Ar**C**$_{\text{-NO2}}$), 148.6, 146.9, 146.1, 145.1, 144.1, 143.0, 134.3, 133.4, 129.9, 128.8, 126.5, 125.7, 125.6, 125.5, 125.4, 124.2, 123.7, 122.1, 121.2, 111.6 (Ar**C**H), 68.5 (O**C**H_2CH_2), 47.4 (**C**H$_{\text{-bridge}}$), 47.2 (**C**H$_{\text{-bridge}}$), 31.4 (OCH_2**C**H_2), 19.5 (**C**H_2CH_3), 18.1 (Ar**C**H$_{\text{3-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (APCI): calcd. for $C_{31}H_{27}ClN_2O_5S$ $[M-H]^-$ 573.12564. Found 573.12584 (Δ = 0.19 mmu).

R$_f$ = 0.31 (Cy/EA = 4:1 v/v).

Yield: 76% (0.95 g, 3.3 mmol).



Syn-isomer (**5l**) obtained after column chromatography from syn/anti mixture as a yellow solid.

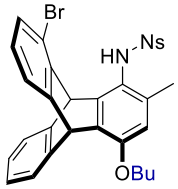
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.73 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.51 – 7.42 (m, 2H), 7.41 – 7.32 (m, 1H), 7.07 – 6.97 (m, 3H), 6.98 – 6.86 (m, 1H), 6.40 (s, 1H; C**H**$_{\text{-bridge}}$), 6.33 (s, 1H; N**H**), 6.25 (s, 1H; ArC**H**), 6.18 (s, 1H; C**H**$_{\text{-bridge}}$), 3.99 – 3.88 (m, 2H; OC**H$_2$**CH_2), 1.93 – 1.77 (m, 2H; OCH_2C**H$_2$**), 1.70 – 1.56 (m, 2H; C**H$_2$**CH_3), 1.43 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.05 (t, J = 7.3 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8 (Ar**C**$_{\text{-OBu}}$), 150.2 (Ar**C**$_{\text{-NO2}}$), 148.0, 147.6, 145.6, 145.2, 144.7, 143.2, 133.6, 133.0, 129.4, 128.8, 126.3, 125.8, 125.5, 124.9, 124.2, 124.1, 123.3, 120.8, 111.5 (Ar**C**H), 68.5

(O**C**H_2CH_2), 50.9 (**C**$H_{\text{-bridge}}$), 43.7 (**C**$H_{\text{-bridge}}$), 31.5 (OCH_2**C**H_2), 19.5 (**C**H_2CH_3), 17.9 (Ar**C**$H_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

R_f = 0.22 (Cy/EA = 4:1 v/v).

Yield: 76% (0.95 g, 3.3 mmol).



The O-alkylated aminotriptycene (**5m**) was prepared according the general procedure. Starting materials were nosylated aminophenol (12.0 g, 21.3 mmol, 1.0 eq, syn/anti mixture), NaH (2.13 g, 53.3 mmol, 2.5 eq; 60% in mineral oil), butyl chloride (2.24 mL, 21.30 mmol, 1.0 eq), in 350 mL dry DMF. Syn/anti-isomer (1:1 ratio) was separated by column chromatography (silica gel, Cy/EA 10:1 -> 4:1 v/v). The title compound was obtained as a yellow solid.

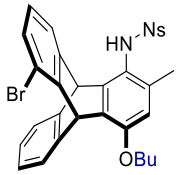
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.85 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.47 – 7.38 (m, 2H), 7.42 – 7.32 (m, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.15 (dd, J = 8.1 Hz, 1.0 Hz, 1H), 7.11 – 6.96 (m, 2H), 6.88 – 6.76 (m, 1H), 6.47 (s, 1H; C**H**$_{\text{-bridge}}$), 6.35 (s, 1H; N**H**), 6.32 (s, 1H; ArC**H**), 5.87 (s, 1H; C**H**$_{\text{-bridge}}$), 3.95 (t, J = 6.4 Hz, 2H; OC**H$_2$**CH_2), 1.93 – 1.77 (m, 2H; OCH_2C**H$_2$**), 1.62 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.60 – 1.53 (m, 2H; C**H$_2$**CH_3), 1.05 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7 (Ar**C**$_{\text{-OBu}}$), 150.3 (Ar**C**$_{\text{-NO2}}$), 148.7, 147.0, 146.2, 145.1, 144.9, 144.0, 134.5, 133.4, 128.9, 128.8, 126.8, 125.6, 125.4, 124.3, 123.7, 122.8, 121.2, 119.5, 111.7 (Ar**C**H), 68.5 (O**C**H_3CH_2), 49.9 (C**H**$_{\text{-bridge}}$), 47.6 (C**H**$_{\text{-bridge}}$), 31.5 (OCH_3C**H$_2$**), 19.5 (C**H$_2$**CH_3), 18.3 (Ar**C**$H_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (APCI): calcd. for $C_{31}H_{27}N_2O_5BrS$ $[M+H]^+$ 617.07513. Found 617.07480 (Δ = 0.33 mmu).

R_f = 0.40 (Cy/EA = 4:1 v/v).

Yield: 86% (5.7 g, 9.2 mmol).

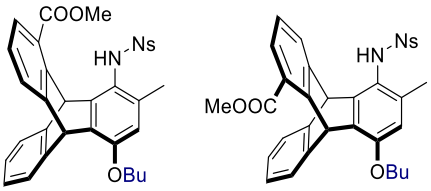


Syn-isomer (**5m**) was obtained after column chromatography from syn/anti mixture as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.72 (d, J = 8.9 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.50 – 7.43 (m, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.19 (dd, J = 8.1 Hz, 1.0 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.88 – 6.82 (m, 1H), 6.38 (s, 1H; C**H**$_{\text{-bridge}}$), 6.29 (s, 1H; N**H**) 6.25 (s, 1H; ArC**H**), 6.17 (s, 1H; C**H**$_{\text{-bridge}}$), 3.96 – 3.89 (m, 2H; OC**H$_2$**CH_2), 1.91 – 1.78 (m, 2H; OCH_3C**H$_2$**), 1.68 – 1.56 (m, 2H; C**H$_2$**CH_3), 1.43 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.06 (t, J = 7.3 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8 (Ar**C**$_{\text{-OBu}}$), 150.3 (Ar**C**$_{\text{-NO2}}$), 148.0, 147.5, 145.5, 145.3, 145.2, 144.7, 133.6, 133.0, 128.8, 128.8, 126.6, 125.5, 124.8, 124.2, 124.1, 124.0, 120.8, 119.0, 111.5 (Ar**C**H), 68.4 (O**C**H_3CH_2), 51.1 (C**H**$_{\text{-bridge}}$), 46.4 (C**H**$_{\text{-bridge}}$), 31.5 (OCH_3C**H$_2$**), 19.5 (C**H$_2$**CH_3), 17.9 (Ar**C**H_3), 14.1 (CH_2**C**H_3).

R_f = 0.27 (Cy/EA = 4:1 v/v). **Yield**: 86% (5.7 g, 9.2 mmol).



The O-alkylated aminotriptycene (**5n**) was prepared according the general procedure. Starting materials were nosylated aminophenol (2.0 g, 3.69 mmol, 1.0 eq), NaH (369 mg, 9.22 mmol, 2.5 eq, 60% in mineral oil), butyl chloride (0.38 mL, 3.69 mmol, 1.0 eq) in 8 mL dry DMF. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 8:1 v/v) to afford the title compound as a yellow solid. (Syn/anti-isomer 1:1 ratio).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.16 (d, J = 8.4 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.95 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.7 Hz, 2H;), 7.66 – 7.59 (m, 2H), 7.51 – 7.48 (m, 2H;), 7.47 – 7.44 (m, 2H), 7.39 (d, J = 7.1 Hz, 1H), 7.22 (s, 1H), 7.05 – 6.95 (m, 6H), 6.88 – 6.82 (m, 1H), 6.71 – 6.66 (m, 1H), 6.40 (s, 1H; C**H**$_{\text{-bridge}}$), 6.37 (s, 1H; C**H**$_{\text{-bridge}}$), 6.23 (s, 1H; ArC**H**), 6.21 (s, 1H; ArC**H**), 5.86 (s, 1H; C**H**$_{\text{-bridge}}$), 4.04 (s, 3H; COOC**H$_3$**), 4.01 (s, 3H; COOC**H$_3$**), 3.96 (t, J = 6.5 Hz, 2H; OC**H$_2$**CH_2), 3.91 (t, J = 6.4 Hz, 2H; OC**H$_2$**CH_2), 1.99 (s, 3H; ArC**H$_{3\text{-ortho}}$**), 1.88 – 1.78 (m, 4H; OCH_2C**H$_2$**), 1.68 – 1.46 (m, 4H; C**H$_2$**CH_3), 1.43 (s, 3H; ArC**H$_{3\text{-ortho}}$**), 1.10 – 1.01 (m, 6H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3 (COO**C**H_3), 167.7 (COO**C**H_3), 154.0 (Ar**C**$_{\text{-COOMe}}$), 153.5 (Ar**C**$_{\text{-OBu}}$), 150.2 (Ar**C**$_{\text{-NO2}}$), 147.8, 147.7, 147.3, 147.3, 147.2, 146.5, 145.6, 145.4, 145.2, 144.8, 143.6, 135.9, 133.5, 133.2, 132.8, 129.0, 128.8, 127.5, 126.9, 126.3, 126.2, 126.0, 125.9, 125.5, 125.4, 125.2, 125.2, 125.0, 124.9, 124.8, 124.7, 124.6, 124.4, 124.4, 124.3, 124.2, 123.6, 122.0, 120.7, 112.1 (Ar**C**H), 111.4 (Ar**C**H), 68.5 (O**C**H_2CH_2), 68.3 (O**C**H_2CH_2), 52.7 (COO**C**H_3), 52.0 (COO**C**H_3), 50.7 (**C**H$_{\text{-bridge}}$), 47.1 (**C**H$_{\text{-bridge}}$), 46.8 (**C**H$_{\text{-bridge}}$), 43.6 (**C**H$_{\text{-bridge}}$), 31.5 (OCH_2**C**H_2), 31.5 (OCH_2**C**H_2), 19.5 (**C**H_2CH_3), 19.4 (**C**H_2CH_3), 19.1 (Ar**C**H$_{3\text{-ortho}}$), 17.9 (Ar**C**H$_{3\text{-ortho}}$), 14.2 (CH_2**C**H_3), 14.1 (CH_2**C**H_3).

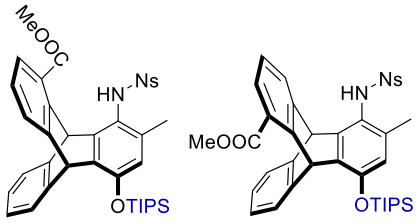
HRMS (APCI): calcd. for $C_{27}H_{27}NO_3$ $[M\text{-Ns+H}]^+$ 413.19855. Found 413.19917 (Δ = 0.63 mmu).
calcd. for $C_{33}H_{31}N_2O_7S$ $[M+H]^+$ 599.18465. Found 599.18409 (Δ = 0.56 mmu).

R$_f$ = 0.56 (Cy/EA = 7:3 v/v).

Yield: 58%* (1.33 g, 2.22 mmol).

*(Note: upscaling of O-alkylation lead to the formation of free carboxylic acid + undefined byproducts)

Silylated triptycene



Nosylated aminotriptycene (60 mg, 0.111 mmol 1.0 eq), imidazole (18.8 mg, 0.276 mmol, 2.5 eq) was dissolved 5 mL dry DCM and TIPSOTf (0.39 mL, 0.144 mmol, 1.3 eq) was slowly added. After stirring at r.t. for 24 h, the reaction mixture was treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. After removing the solvend under reduce pressure and chromatographic purification (silica gel, Cy/EA = 3:1 v/v), the title compound (**5na**) was obtained as a yellowish solid. Syn/anti-isomer (1:1 ratio).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, J = 8.5 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 8.15 (d, J = 8.4 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.91 (d, J = 8.4 Hz, 2H; Ar**H**$_{\text{-Ns}}$), 7.71 – 7.63 (m, 3H; Ar**H**$_{\text{-Ns}}$ + Ar**H**), 7.58 (d, J = 8.0 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.41 (d, J = 7.3 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.25 (s, 1H; N**H**), 7.16 (s, 1H; C**H**$_{\text{-bridge syn}}$), 7.07 – 6.96 (m, 6H), 6.84 (t, J = 7.7 Hz, 1H), 6.71 (bs, 1H), 6.67 (s, 1H; C**H**$_{\text{-bridge anti}}$), 6.36 (s, 1H; ArC**H**$_{\text{-anti}}$), 6.33 (bs, 1H; N**H**), 6.23 (s, 1H; C**H**$_{\text{-bridge syn}}$), 6.20 (s, 1H; ArC**H**$_{\text{- syn}}$), 5.83 (s, 1H; C**H**$_{\text{-bridge anti}}$), 4.04 (s, 3H; COOC**H$_3$** $_{\text{anti}}$), 3.96 (s, 3H; COOC**H$_3$** $_{\text{syn}}$), 1.96 (s, 3H; C**H$_3$**$_{\text{-ortho anti}}$), 1.39 (s, 3H; C**H$_3$**$_{\text{-ortho syn}}$), 1.36 – 1.28 (m, 6H; C**H**$(CH_3)_2$), 1.16 – 1.05 (m, 36H; C**H$_3$**$_{\text{-}i\text{Pr}}$).

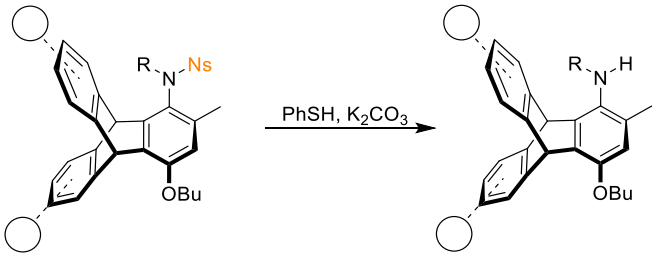
^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3 (**C**$OOCH_{3\ \text{anti}}$), 167.5 (**C**$OOCH_{3\ \text{syn}}$), 151.2, 150.5, 150.3, 147.7, 147.3, 147.1, 146.3, 145.3, 144.6, 143.5, 135.5, 134.9, 132.9, 129.0, 128.8, 127.5, 126.7, 126.4, 126.2, 125.9, 125.5, 125.3, 125.2, 125.0, 124.9, 124.8, 124.7, 124.7, 124.4, 124.2, 123.6, 122.5, 121.0, 118.6 (Ar**C**H$_{\text{anti}}$), 118.0 (Ar**C**H$_{\text{syn}}$), 52.7 (COO**C**$H_{3\ \text{anti}}$), 52.1 (COO**C**$H_{3\ \text{syn}}$), 50.7 (**C**H$_{\text{-bridge syn}}$), 47.9 (**C**H$_{\text{-bridge anti}}$), 46.8 (**C**H$_{\text{-bridge anti}}$), 44.2 (**C**H$_{\text{-bridge syn}}$), 18.9 (Ar**C**$H_{3\text{-ortho anti}}$), 18.2, 18.2, 17.8, 17.7 (Ar**C**$H_{3\text{-ortho syn}}$), 13.2, 13.1.

HRMS (ESI): calcd. for $C_{38}H_{43}N_2O_7SSi$ $[M+H]^+$ 699.25548. Found 699.25561 (Δ = 0.13 mmu).

R_f = 0.35; 0.42 (Cy/EA = 3:1 v/v).

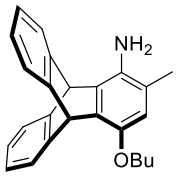
Yield: 86 % (67 mg, 95 µmol).

Denosylated aminotriptycene



General procedure for denosylation of 5 to triptycene 6: Alkylated aminotriptycene (1.0 eq), K_2CO_3 (6.0 eq) was charged in a Schlenk flask under N_2 in MeCN or THF. Then thiophenol (4.0 eq) was added and the reaction mixture was stirred at 50 °C until the triptycene is completely converted (controlled by TLC). The reaction mixture was allowed to r.t., H_2O was added and extracted with EA. The organic phase was dried and filtered over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography.

Primary amines



The aminotriptycene (**6b**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (300 mg, 0.555 mmol, 1.0 eq), PhSH (0.23 mL, 2.22 mmol, 4.0 eq), K_2CO_3 (460 mg, 3.33 mmol, 6.0 eq), in 15 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 8:1 -> 4:1 v/v) to afford the title compound as a beige solid.

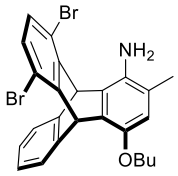
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.35 (m, 4H), 7.03 – 6.96 (m, 4H), 6.39 (s, 1H; ArC**H**), 5.85 (s, 1H; C**H**$_{\text{-bridge}}$), 5.49 (s, 1H; C**H**$_{\text{-bridge}}$), 3.93 (t, *J* = 6.3 Hz, 2H; OC**H$_2$**CH$_2$), 3.57 (bs, 2H; N**H$_2$**), 2.10 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.89 – 1.75 (m, 2H; OCH$_2$C**H$_2$**), 1.65 – 1.52 (m, 2H; C**H$_2$**CH$_3$), 1.05 (t, *J* = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2 (Ar**C**$_{\text{-OBu}}$), 146.0, 145.5, 133.2, 133.0, 132.3, 125.2, 125.0, 123.8, 123.5, 121.4, 113.7 (ArC**H**), 70.2 (O**C**H$_2$CH$_2$), 48.9 (C**H**$_{\text{-bridge}}$), 47.5 (C**H**$_{\text{-bridge}}$), 31.9 (OCH$_2$**C**H$_2$), 19.6 (**C**H$_2$CH$_3$), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

HRMS (ESI): calcd. for $C_{25}H_{25}NO$ $[M+H]^+$ 356.20089. Found 356.20089 (Δ = 0.01 mmu).

R_f = 0.34 (Cy/EA = 3:1 v/v).

Yield: 90% (178 mg, 0.50 mmol).



The aminotriptycene (**6c**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (4.08 g, 5.86 mmol, 1.0 eq), PhSH (2.4 mL, 23.5 mmol, 4.0 eq), K_2CO_3 (4.37 g, 31.6 mmol, 6.0 eq), in 250 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 v/v). The title compound was obtained as a yellow solid.

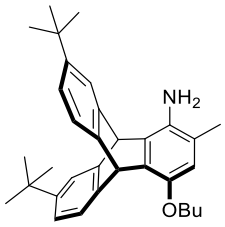
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.40 (m, 2H), 7.09 – 6.97 (m, 4H), 6.42 (s, 1H; ArC**H**), 6.33 (s, 1H; C**H**$_{\text{-bridge}}$), 5.99 (s, 1H; C**H**$_{\text{-bridge}}$), 3.94 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH$_2$), 3.66 (bs, 2H; N**H$_2$**), 2.12 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.94 – 1.75 (m, 2H; OCH$_2$C**H$_2$**), 1.73 – 1.51 (m, 2H; C**H$_2$**CH$_3$), 1.03 (t, *J* = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0 (Ar**C**$_{\text{-OBu}}$), 147.5, 144.6, 144.2, 133.7, 131.5, 131.0, 130.1, 129.6, 125.9, 125.6, 124.4, 124.2, 122.0, 118.3, 117.9, 114.0 (Ar**C**H), 70.1 (O**C**H$_2$CH$_2$), 48.6 (**C**H$_{\text{-bridge}}$), 47.4 (**C**H$_{\text{-bridge}}$), 31.9 (OCH$_2$**C**H$_2$), 19.5 (**C**H$_2$CH$_3$), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

HRMS (ESI): calcd. for $C_{25}H_{24}Br_2NO$ $[M+H]^+$ 512.02192. Found 512.02151 (Δ = 0.40 mmu).

R$_f$ = 0.20 (Cy/EA = 10:1 v/v).

Yield: 71% (2.13 g, 4.15 mmol).



The aminotriptycene (**6ha**) was prepared according the general procedure. Starting materials were (50 mg, 0.077 mmol, 1.0 eq), PhSH (30 µL, 0.307 mmol, 4.0 eq), K_2CO_3 (64 mg, 0.460 mmol, 6.0 eq) in 5 mL MeCN.

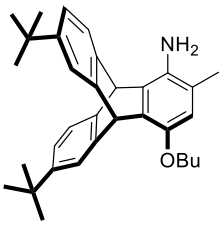
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (s, 2H), 7.31 – 7.26 (m, 5H), 6.99 – 6.94 (m, 2H), 6.35 (s, 1H; ArC**H**), 5.76 (s, 1H; C**H**$_{\text{-bridge}}$), 5.42 (s, 1H; C**H**$_{\text{-bridge}}$), 3.90 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH$_2$), 3.61 (bs, 2H; N**H$_2$**), 2.10 (s, 3H), 1.84 – 1.76 (m, 2H; OCH$_2$**CH$_2$**), 1.59 – 1.53 (m, 2H; C**H$_2$**CH$_3$), 1.25 (s, 18H; C**H$_3$**$_{\text{-}t\text{Bu}}$), 1.02 (t, *J* = 7.4 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.7, 145.5, 144.2, 143.2, 135.3, 133.6, 123.1, 121.8, 120.9, 113.5 (Ar**C**H), 70.1, 49.6 (**C**H$_{\text{-bridge}}$), 46.5 (**C**H$_{\text{-bridge}}$), 34.7 (**C**$(CH_3)_3$), 31.9, 31.7 (OCH_2**C**H_2), 29.9 (**C**H$_{3\text{-}t\text{Bu}}$), 19.6 (**C**H_2CH_3), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.2 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{33}H_{42}NO$ $[M+H]^+$ 468.32609. Found 468.32647 (Δ = 0.38 mmu).

R_f = 0.48 (Cy/EA = 10:3 v/v).

Yield: 70 % (25 mg, 53.5 µmol).



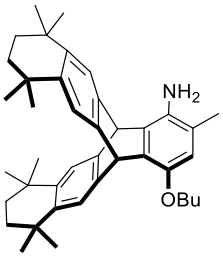
The aminotriptycene (**6hb**) was prepared according the general procedure. Starting materials were (100 mg, 0.153 mmol, 1.0 eq), PhSH (63 µL, 0.613 mmol, 4.0 eq), K_2CO_3 (127 mg, 0.919 mmol, 6.0 eq) in 5 mL MeCN.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.42 (m, 2H), 7.29 (s, 1H), 7.27 (s, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 1.9 Hz, 1H), 6.38 (s, 1H; ArC**H**), 5.78 (s, 1H; C**H**$_{\text{-bridge}}$), 5.48 (s, 1H; C**H**$_{\text{-bridge}}$), 4.01 – 3.91 (m, 2H; OC**H$_2$**CH_2), 2.11 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.87 – 1.76 (m, 2H; OCH_2**CH_2**), 1.62 – 1.53 (m, 2H; C**H$_2$**CH_3), 1.25 (s, 18H; C**H$_3$**$_{\text{-}t\text{Bu}}$), 1.04 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 147.0, 145.9, 142.7, 133.8, 133.3, 132.8, 122.8, 121.5, 121.2, 121.2, 114.0 (Ar**C**H), 70.6, 48.2 (**C**H$_{\text{-bridge}}$), 47.9 (**C**H$_{\text{-bridge}}$), 34.7 (**C**$(CH_3)_3$), 31.8, 31.7 (OCH_2**CH_2**), 19.6 (**CH_2**CH_3), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

R_f = 0.32 (Cy/EA = 10:3 v/v)

Yield: 73 % (52 mg, 0.11 mmol).



The aminotriptycene (**6g**) was prepared according the general procedure. Starting materials were (4.5 g, 5.91 mmol, 1.0 eq), PhSH (1.51 mL, 14.8 mmol, 2.5 eq), K_2CO_3 (4.10 g, 29.6 mmol, 5.0 eq) in 100 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 v/v) to afford the title compound as a yellow solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.31 – 7.22 (m, 4H), 6.35 (s, 1H; ArC**H**), 5.73 (s, 1H; C**H**$_{\text{-bridge}}$), 5.56 (s, 1H; C**H**$_{\text{-bridge}}$), 4.59 (bs, 2H; N**H$_2$**), 3.86 (t, *J* = 6.3 Hz, 2H; OC**H$_2$**CH$_2$), 1.98 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.74 – 1.63 (m, 2H; OCH$_2$C**H$_2$**), 1.55 (s, 8H; C**H$_2$**$_{\text{-Cy}}$), 1.52 – 1.45 (m, 2H; C**H$_2$**CH$_3$), 1.19 – 1.14 (m, 24H; C**H$_3$**$_{\text{-Cy}}$), 0.97 (t, *J* = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, DMSO): δ 144.7, 143.0, 142.8, 140.2, 140.0, 135.5, 132.8, 130.5, 120.8, 120.8, 119.7, 114.0 (Ar**C**H), 69.9 (O**C**H$_2$CH**$_2$**), 46.2 (**C**H$_{\text{-bridge}}$), 46.0 (**C**H$_{\text{-bridge}}$), 34.7 (**C**H$_{2\text{-Cy}}$), 33.8 (**C**(CH$_3$)$_2$), 31.8 (C(**CH$_3$**)$_{2\text{-Cy}}$), 31.7, 31.6, 30.9 (OCH$_2$**C**H**$_2$**), 18.8 (**C**H**$_2$**CH$_3$), 17.8 (Ar**C**H$_{3\text{-ortho}}$), 13.7 (CH$_2$**C**H$_3$).

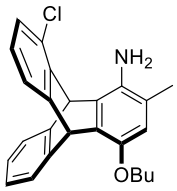
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 4H), 6.39 (s, 1H; ArCH), 5.70 (s, 1H; C**H**$_{\text{-bridge}}$), 5.34 (s, 1H; C**H**$_{\text{-bridge}}$), 3.94 (t, *J* = 6.5 Hz, 2H; OC**H$_2$**CH$_2$), 3.56 (bs, 2H; N**H$_2$**), 2.11 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.90 – 1.79 (m, 2H), 1.62 – 1.55 (m, 10H; C**H$_2$**$_{\text{-Cy}}$ + C**H$_2$**CH$_3$), 1.25 – 1.19 (m, 24H), 1.05 (t, *J* = 7.4 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.0 (Ar**C**$_{\text{-OBu}}$), 142.9, 142.5, 141.1, 140.8, 134.2, 133.2, 133.1, 121.7, 121.4, 121.0, 113.9, 70.5, 48.3 (**C**H$_{\text{-bridge}}$), 46.9 (**C**H$_{\text{-bridge}}$), 35.4 (**C**H$_{2\text{-Cy}}$), 34.3 (**C**(CH$_3$)$_2$), 32.1 (C(**CH$_3$**)$_{2\text{-Cy}}$), 32.0 (C(**CH$_3$**)$_{2\text{-Cy}}$), 31.8 (OCH$_2$**C**H**$_2$**), 19.6 (**C**H**$_2$**CH$_3$), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

HRMS (APCI): calcd. for $C_{41}H_{53}NO$ $[M+H]^+$ 576.41999. Found 576.42008 (Δ = 0.09 mmu).

R$_f$ = 0.50 (Cy/EA = 4:1 v/v).

Yield: 86% (2.93 g, 5.09 mmol).



The aminotriptycene (**6la**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (100 mg, 0.192 mmol, 1.0 eq), PhSH (78 µL, 0.770 mmol, 4.0 eq), K_2CO_3 (160 mg, 1.16 mmol, 6.0 eq), in 10 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

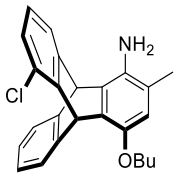
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.45 (m, 1H), 7.45 – 7.41 (m, 1H), 7.29 (d, J = 7.0 Hz, 1H), 7.04 – 7.00 (m, 3H), 6.91 (t, J = 7.7 Hz, 1H), 6.42 (s, 1H; ArC**H**), 6.03 (s, 1H; C**H**$_{\text{-bridge}}$), 5.88 (s, 1H; C**H**$_{\text{-bridge}}$), 3.95 (t, J = 6.5 Hz, 2H; OC**H$_2$**CH_2), 3.63 (bs, 2H; N**H$_2$**), 2.13 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.91 – 1.75 (m, 2H; OCH_2C**H$_2$**), 1.63 – 1.55 (m, 2H; C**H$_2$**CH_3), 1.06 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.6 (Ar**C**$_{\text{-OBu}}$), 147.1, 145.7, 144.4, 143.1, 133.6, 132.6, 131.1, 129.2, 126.3, 125.6, 125.4, 125.2, 124.1, 123.9, 122.3, 121.6, 113.8 (Ar**C**H), 70.1 (O**C**H_2CH_2), 47.7 (**C**H$_{\text{-bridge}}$), 45.2 (**C**H$_{\text{-bridge}}$), 31.8 (OCH_2**C**H_2), 19.6 (**C**H_2CH_3), 18.0 (Ar**C**$H_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{25}H_{25}ClNO$ $[M+H]^+$ 390.16192. Found 390.16232 (Δ = 0.4 mmu).

R$_f$ = 0.49 (Cy/EA = 7:3 v/v).

Yield: 77% (85 mg, 0.148 mmol).



The aminotriptycene (**6lb**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (100 mg, 0.192 mmol, 1.0 eq), PhSH (78 µL, 0.770 mmol, 4.0 eq), K_2CO_3 (160 mg, 1.16 mmol, 6.0 eq), in 10 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

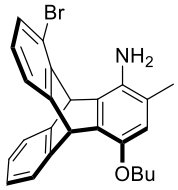
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.46 (m, 1H), 7.41 – 7.38 (m, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.04 – 6.99 (m, 3H), 6.92 – 6.87 (m, 1H), 6.42 (s, 1H; ArC**H**), 6.37 (s, 1H; C**H**$_{\text{-bridge}}$), 5.51 (s, 1H; C**H**$_{\text{-bridge}}$), 3.96 (t, J = 6.4 Hz, 2H; OC**H$_2$**CH_2), 3.51 (bs, 2H; N**H$_2$**), 2.12 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.88 – 1.79 (m, 2H; OCH_2C**H$_2$**), 1.68 – 1.58 (m, 2H; C**H$_2$**CH_3), 1.05 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.0 (Ar**C**$_{\text{-OBu}}$), 147.5, 145.3, 144.9, 143.5, 133.3, 132.0, 131.9, 129.7, 126.1, 125.9, 125.5, 125.2, 124.3, 123.6, 122.0, 121.7, 114.0 (Ar**C**H), 70.3 (O**C**H_2CH_2), 49.0 (**C**H$_{\text{-bridge}}$), 44.0 (**C**H$_{\text{-bridge}}$), 31.9 (OCH_2**C**H_2), 19.5 (**C**H_2CH_3), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{25}H_{25}ClNO$ $[M+H]^+$ 390.16192. Found 390.16158 (Δ = 0.34 mmu).

R_f = 0.25 (Cy/EA = 7:3 v/v).

Yield: 77% (86 mg, 0.149 mmol).



The aminotriptycene (**6ma**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (1.0 g, 1.61 mmol, 1.0 eq), PhSH (0.66 mL, 6.46 mmol, 4.0 eq), K_2CO_3 (1.34 g, 9.68 mmol, 6.0 eq), in 50 mL MeCN/THF (4:1). The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

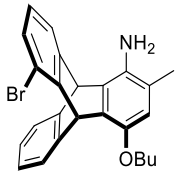
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 – 7.39 (m, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.88 – 6.80 (m, 1H), 6.40 (s, 1H; ArC**H**), 6.00 (s, 1H; C**H**$_{\text{-bridge}}$), 5.86 (s, 1H; C**H**$_{\text{-bridge}}$), 3.93 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH_2), 3.66 (bs, 2H; N**H$_2$**), 2.12 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.87 – 1.75 (m, 2H; OCH_2C**H$_2$**), 1.64 – 1.52 (m, 2H; C**H$_2$**CH_3), 1.04 (t, *J* = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7 (Ar**C**$_{\text{-OBu}}$), 147.1, 145.6, 145.2, 144.4, 133.7, 132.5, 131.2, 128.4, 126.6, 125.6, 125.2, 124.1, 123.9, 122.9, 121.6, 119.1, 113.8 (Ar**C**H), 70.1 (O**C**H_2CH_2), 47.9 (**C**H$_{\text{-bridge}}$), 47.9 (**C**H$_{\text{-bridge}}$), 31.8 (OCH_2**C**H_2), 19.6 (**C**H_2CH_3), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{25}H_{25}BrNO$ $[M+H]^+$ 434.1114. Found 434.1119 (Δ = 0.5 mmu).

R_f = 0.55 (Cy/EA = 4:1 v/v).

Yield: 90% (0.63 g, 1.45 mmol).



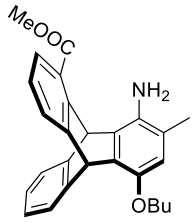
The aminotriptycene (**6mb**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (1.0 g, 1.61 mmol, 1.0 eq), PhSH (0.66 mL, 6.46 mmol, 4.0 eq), K_2CO_3 (1.34 g, 9.68 mmol, 6.0 eq), in 50 mL MeCN/THF (4:1). The crude product was purified by column chromatography (silica gel, Cy/EA = 8:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 1H), 7.41 – 7.36 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.85 – 6.77 (m, 1H), 6.41 (s, 1H; ArC**H**), 6.33 (s, 1H; C**H**$_{\text{-bridge}}$), 5.53 (s, 1H; C**H**$_{\text{-bridge}}$), 3.95 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH_2), 3.83 (s, 2H; N**H$_2$**), 2.13 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.90 – 1.78 (m, 2H; OCH_2**CH_2**), 1.68 – 1.53 (m, 2H; C**H$_2$**CH_3), 1.04 (t, *J* = 7.3 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0 (Ar**C**$_{\text{-OBu}}$), 147.7, 145.5, 145.2, 144.9, 132.8, 132.2, 131.9, 128.9, 126.4, 125.5, 125.3, 124.4, 123.6, 122.7, 122.0, 119.3, 113.9 (Ar**C**H), 70.2 (O**C**H_2CH_2), 49.2 (**C**H$_{\text{-bridge}}$), 46.7 (**C**H$_{\text{-bridge}}$), 31.9 (OCH_2**C**H_2), 19.5 (**C**H_2CH_3), 18.1 (Ar**C**H$_{3\text{-ortho}}$), 14.2 (CH_2**C**H_3).

R_f = 0.33 (Cy/EA = 7:3 v/v).

Yield: 77% (0.54 g, 1.24 mmol).



The aminotriptycene (**6n**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (70 mg, 1.0 eq), PhSH (4.0 eq), K_2CO_3 (6.0 eq), in 10 mL MeCN. Syn/anti-isomer (1:1 ratio) was separated by column chromatography (silica gel, Cy/EA 10:1 -> 7:3 v/v). The anti-isomer was obtained as a yellow solid.

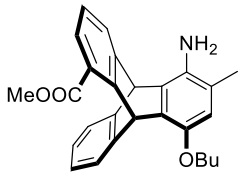
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.04 – 6.96 (m, 4H), 6.36 (s, 1H; ArC**H**), 5.85 (s, 1H; C**H**$_{\text{-bridge}}$), 3.96 (s, 3H; COOC**H$_3$**), 3.91 (t, *J* = 6.5 Hz, 2H; OC**H$_2$**CH_2), 2.10 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.83 – 1.73 (m, 2H; OCH_2C**H$_2$**), 1.62 – 1.51 (m, 2H; C**H$_2$**CH_3), 1.02 (t, *J* = 7.3 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0 (**C**$OOCH_3$), 148.2 (Ar**C**$_{\text{-OBu}}$), 148.1, 146.9, 145.7, 144.9, 144.8, 134.5, 127.9, 126.4, 125.6, 125.3, 125.2, 124.6, 124.6, 123.6, 121.3, 113.8 (Ar**C**H), 70.2 (O**C**H_2CH_2), 52.2 (COO**C**H_3), 47.6 (**C**H$_{\text{-bridge}}$), 44.8 (**C**H$_{\text{-bridge}}$), 31.9 (OCH_2**C**H_2), 19.6 (**C**H_2CH_3), 17.9 (Ar**C**H$_{\text{3-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{27}H_{28}NO_3$ $[M+H]^+$ 414.20637. Found 414.20647 (Δ = 0.09 mmu).

R_f = 0.45 (Cy/EA = 7:3 v/v).

Yield: 87 % (23 mg, 55 µmol).



Syn-isomer (**6n**) obtained after column chromatography from syn/anti mixture as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H), 7.48 (d, J = 6.6 Hz, 1H), 7.42 (d, J = 6.8 Hz, 1H), 7.16 (s, 1H; C**H**$_{\text{-bridge}}$), 7.06 – 6.91 (m, 3H), 6.40 (s, 1H; ArC**H**), 5.73 (s, 1H; C**H**$_{\text{-bridge}}$), 4.00 (s, 3H; COOC**H$_3$**), 3.92 (t, J = 6.7 Hz, 2H; OC**H$_2$**CH_2), 2.19 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.93 – 1.73 (m, 2H; OCH_2C**H$_2$**), 1.64 – 1.46 (m, 2H; C**H$_2$**CH_3), 1.02 (t, J = 7.3 Hz, 3H; CH_2C**H$_3$**).

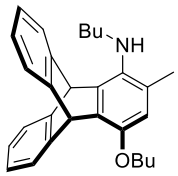
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7 (**C**$OOCH_3$), 148.7 (Ar**C**$_{\text{-OBu}}$), 147.8, 147.7, 147.4, 145.5, 145.4, 145.4, 132.1, 127.5, 126.9, 126.2, 125.5, 125.2, 124.6, 123.5, 120.6, 113.8 (Ar**C**H), 70.0 (O**C**H_2CH_2), 52.0 (COO**C**H_3), 49.0 (**C**H$_{\text{-bridge}}$), 44.0 (**C**H$_{\text{-bridge}}$), 31.9 (OCH_2**C**H_2), 19.4 (**C**H_2CH_3), 18.0 (Ar**C**H$_{\text{3-ortho}}$), 14.1 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{27}H_{28}NO_3$ $[M+H]^+$ 414.20637. Found 414.20667 (Δ = 0.30 mmu).

R_f = 0.30 (Cy/EA = 7:3 v/v).

Yield: 87 % (23 mg, 55 µmol).

Secondary amines



The aminotriptycene (**6bb**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (61.0 mg, 0.102 mmol, 1.0 eq), PhSH (42 µL, 0.409 mmol, 4.0 eq), K_2CO_3 (84.8 mg, 0.613 mmol 6.0 eq), in 5 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 v/v) to afford the title compound as a yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.42 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 6.99 – 6.94 (m, 4H), 6.46 (s, 1H; ArC**H**), 5.88 (s, 1H; C**H**$_{\text{-bridge}}$), 5.76 (s, 1H; C**H**$_{\text{-bridge}}$), 3.99 (bs, 1H; N**H**), 3.92 (t, *J* = 6.3, 2H; OC**H$_2$**CH$_2$), 2.87 (t, *J* = 6.5 Hz, 2H; NC**H$_2$**CH$_2$), 2.13 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.76 – 1.68 (m, 2H; OCH$_2$C**H$_2$**), 1.58 – 1.51 (m, 4H; NCH$_2$C**H$_2$** + C**H$_2$**CH$_{3\text{-OBu}}$), 1.43 – 1.37 (m, 2H; C**H$_2$**CH$_{3\text{-NBu}}$), 0.98 (t, *J* = 7.3, 3H; CH$_2$C**H$_3$**$_{\text{-OBu}}$), 0.92 (t, *J* = 7.3 Hz, 3H; CH$_2$C**H$_3$**$_{\text{-NBu}}$).

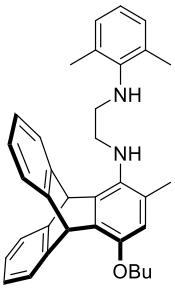
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.41 (m, 4H), 7.12 – 6.99 (m, 4H), 6.47 (s, 1H), 5.95 (s, 1H), 5.86 (s, 1H), 4.02 (t, *J* = 6.5 Hz, 2H; OCH$_2$C**H$_2$**), 3.10 (t, *J* = 7.3 Hz, 2H; NC**H$_2$**CH$_2$), 2.87 (s, 1H; N**H**), 2.26 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.95 – 1.86 (m, 2H; OCH$_2$C**H$_2$**), 1.81 – 1.73 (m, 2H; NCH$_2$C**H$_2$**), 1.72 – 1.63 (m, 2H; C**H$_2$**CH$_{3\text{-OBu}}$), 1.63 – 1.54 (m, 2H; C**H$_2$**CH$_{3\text{-NBu}}$), 1.20 – 1.03 (m, 6H; CH$_2$C**H$_3$**$_{\text{-NBu}}$ + CH$_2$C**H$_3$**$_{\text{-OBu}}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.6 (Ar**C**$_{\text{-OBu}}$), 146.2, 145.9, 140.7, 136.6, 132.6, 128.2, 125.0, 124.9, 123.7, 123.6, 112.2 (Ar**C**H), 69.0 (O**C**H$_2$CH$_2$), 51.4 (N**C**H$_2$CH$_2$), 49.9 (**C**H$_{\text{-bridge}}$), 47.3 (**C**H$_{\text{-bridge}}$), 33.5 (NCH$_2$**C**H$_2$), 31.8 (OCH$_2$**C**H$_2$), 20.7 (**C**H$_2$CH$_{3\text{-NBu}}$), 19.6 (**C**H$_2$CH$_{3\text{-OBu}}$), 18.0 (Ar**C**H$_{3\text{-ortho}}$), 14.2 (CH$_2$**C**H$_{3\text{-NBu}}$), 14.1 (CH$_2$**C**H$_{3\text{-OBu}}$)

HRMS (ESI): calcd. for $C_{29}H_{33}NO$ $[M+H]^+$ 412.26349. Found 412.26344 (Δ = 0.05 mmu).

R_f = 0.31 (Cy/EA = 10:1 v/v).

Yield: 92% (39 mg, 0.095 mmol).



The aminotriptycene (**9**) was prepared according the general procedure. Starting materials were nosylated aminotriptycene (100 mg, 0.145 mmol, 1.0 eq), PhSH (0.06 mL, 0.582 mmol, 4.0 eq), K_2CO_3 (120 mg, 0.872 mmol, 6.0 eq), in 5 mL MeCN. The crude product was purified by column chromatography (silica gel, Cy/EA = 10:1 -> 4:1 v/v) to afford the title compound as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.46 (m, 2H), 7.39 – 7.33 (m, 2H), 7.03 – 6.84 (m, 7H), 6.41 (s, 1H; ArC**H**), 6.24 (s, 1H; C**H**$_{\text{-bridge}}$), 5.86 (s, 1H; C**H**$_{\text{-bridge}}$), 3.96 (t, *J* = 6.4 Hz, 2H; OC**H$_2$**CH$_2$), 3.57 (t, *J* = 6.0 Hz, 2H; NC**H$_2$**CH$_2$N), 3.44 (t, *J* = 5.7 Hz, 2H; NCH$_2$C**H$_2$**N), 2.39 (s, 3H; ArC**H$_3$**), 2.28 (s, 6H; ArC**H$_3$**$_{\text{-ortho}}$ + ArC**H$_3$**), 1.89 – 1.76 (m, 2H; OCH$_2$C**H$_2$**), 1.65 – 1.51 (m, 2H; C**H$_2$**CH$_3$), 1.04 (t, *J* = 7.4 Hz, 3H; CH$_2$C**H$_3$**).

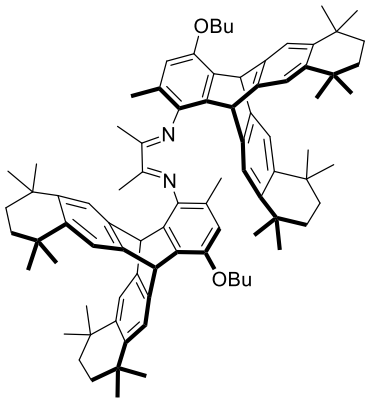
^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6 (Ar**C**$_{\text{-OBu}}$), 145.8, 145.3, 144.9, 141.6, 133.7, 129.8, 129.2, 125.3, 125.2, 124.2, 123.7, 122.8, 112.7 (Ar**C**H), 69.0 (O**C**H$_2$CH$_2$), 52.4 (N**C**H$_2$**C**H$_2$N), 49.4 (**C**H$_{\text{-bridge}}$), 47.2 (**C**H$_{\text{-bridge}}$), 31.6 (OCH$_2$**C**H$_2$), 29.8 (Ar**C**H$_3$), 19.6 (**C**H$_2$CH$_3$), 19.0 (Ar**C**H$_3$), 18.8 (Ar**C**H$_{\text{3-ortho}}$), 14.1 (CH$_2$**C**H$_3$).

HRMS (ESI): calcd. for $C_{35}H_{38}N_2O$ $[M+H]^+$ 503.30569. Found 503.30547 (Δ = 0.22 mmu).

R_f = 0.51 (Cy/EA = 3:1 v/v).

Yield: 86% (63 mg, 0.129 mmol).

Diimine



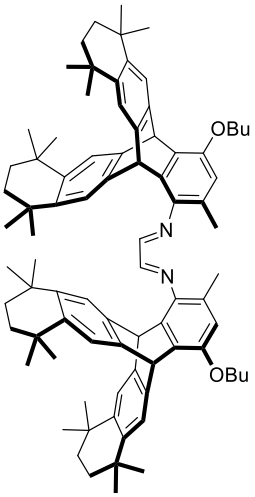
A mixture of aminotriptycene (150 mg, 0.26 mmol, 2.0 eq), butane-2,3-dione (11 µL, 0.13 mmol, 1.0 eq), and 1 mg of *p*-toluenesulfonic acid monohydrate in 6 mL EtOH was stirred under nitrogen in a Schlenk tube at 50 °C for 24 h. The cooled reaction mixture was filtered and residual solid was washed with cold pentane to give triptycendiimine (**11**) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.28 (m, 6H), 7.18 (s, 2H), 6.59 (s, 1H; ArC**H**), 6.54 (s, 1H; ArC**H**), 5.80 (s, 1H; C**H**$_{\text{-bridge}}$), 5.76 (s, 1H; C**H**$_{\text{-bridge}}$), 5.14 (s, 1H; C**H**$_{\text{-bridge}}$), 4.97 (s, 1H; C**H**$_{\text{-bridge}}$), 4.12 – 3.97 (m, 4H; OC**H$_2$**CH_2), 2.18 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 2.08 (s, 6H; C(C**H$_3$**)$_{\text{-backbone}}$), 1.97 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.93 – 1.79 (m, 4H; 2x OCH_2C**H$_2$**), 1.65 – 1.60 (m, 16H; 8x C**H$_2$**$C(CH_3)_2$), 1.53 – 1.47 (m, 4H; 2x C**H$_2$**CH_3), 1.30 – 1.17 (m, 48H; 8x CH_2C(C**H$_3$**)$_2$), 1.08 (t, *J* = 7.4 Hz, 6H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.8 (**C**$(CH_3)_{\text{-backbone}}$, assigned from HMBC-NMR), 150.6 (Ar**C**$_{\text{-OBu}}$), 143.6, 143.5, 143.3, 143.0, 142.7, 142.2, 142.1, 141.9, 141.8, 141.7, 139.2, 134.5, 132.8, 124.2, 122.3, 122.2, 122.1, 122.0, 121.9, 121.8, 112.5 (Ar**C**H), 69.6 (O**C**H_2CH_2), 49.8 (**C**H$_{\text{-bridge}}$), 49.5 (**C**H$_{\text{-bridge}}$), 47.0 (2x **C**H$_{\text{-bridge}}$), 35.7, 35.6, 34.7, 34.6, 32.6, 32.4, 32.3, 32.2, 32.0, 30.3, 20.1, 18.5 (Ar**C**$H_{3\text{-ortho}}$), 18.3 (Ar**C**$H_{3\text{-ortho}}$), 17.0 (C(**C**H_3)$_{\text{-backbone}}$), 16.8 (C(**C**H_3)$_{\text{-backbone}}$), 15.6, 14.4 (CH_2**C**H_3).

HRMS (APCI): calcd. for $C_{86}H_{108}N_2O_2$ $[M+H]^+$ 1201.84836. Found 1201.84826 (Δ = 0.10 mmu).

Yield: 74% (116 mg, 96.5 µmol).



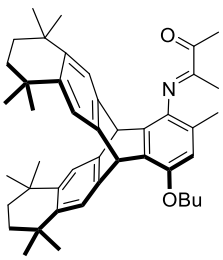
A mixture of aminotriptycene (25 mg, 43.4 µmol, 2.0 eq), glyoxal (2.5 µL, 21.7 µmol, 1.0 eq), and 1 mg of *p*-toluenesulfonic acid monohydrate in 1 mL EtOH was stirred under nitrogen in a Schlenk tube at 50 °C for 24 h. The cooled reaction mixture was filtered and residual solid was washed with cold pentane to give triptycendiimine as a red/orange solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.31 (s, 2H; C**H**$_{\text{-backbone}}$), 7.38 – 7.36 (m, 4H), 7.34 (s, 4H), 6.58 (s, 2H; ArC**H**), 5.79 (s, 2H; C**H**$_{\text{-bridge}}$), 5.57 (s, 2H; C**H**$_{\text{-bridge}}$), 4.06 (t, *J* = 6.4 Hz, 4H; OC**H$_2$**CH_2), 2.32 (s, 6H; ArC**H$_3$**$_{\text{-ortho}}$), 1.93 – 1.84 (m, 4H; 2x OCH_2C**H$_2$**), 1.66 – 1.60 (m, 16H; 8x C**H$_2$**$C(CH_3)_2$), 1.53 – 1.50 (m, 4H; 2x C**H$_2$**CH_3), 1.29 – 1.19 (m, 48H; 8x $CH_2C(C$**H$_3$**$)_2$), 1.08 (t, *J* = 7.4 Hz, 6H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 164.3 (**C**H$_{\text{-backbone}}$), 152.1 (Ar**C**$_{\text{-OBu}}$), 143.3, 143.0, 142.2, 142.1, 138.2, 133.1, 128.2, 122.1, 121.9, 112.5 (Ar**C**H), 69.5 (O**C**H_2CH_2), 49.4 (**C**H$_{\text{-bridge}}$), 46.9 (**C**H$_{\text{-bridge}}$), 35.7, 34.8, 32.4, 32.3, 32.3, 32.2, 32.0 (OCH_2**C**H_2), 20.1 (**C**H_2CH_3), 19.0 (Ar**C**$H_{3\text{-ortho}}$), 14.3 (CH_2**C**H_3).

HRMS (APCI): calcd. for $C_{84}H_{105}N_2O_2$ $[M+H]^+$ 1173.81706. Found 1173.81713 (Δ = 0.07 mmu).

Yield: 67% (17 mg, 14.5 µmol).



A mixture of aminotriptycene (200 mg, 0.35 mmol, 1.0 eq), butane-2,3-dione (0.15 mL, 1.74 mmol, 5 eq), and 1 mg of *p*-toluenesulfonic acid monohydrate in 4 mL EtOH was stirred under nitrogen in a

Schlenk tube at 50 °C for 24 h. The cooled reaction mixture was filtered and residual solid was washed with cold pentane to give triptycendiimine as a yellow solid.

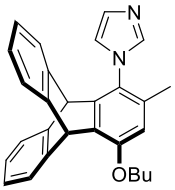
^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.34 – 7.30 (m, 2H), 7.21 – 7.07 (m, 2H), 6.51 (s, 1H), 5.73 (s, 1H), 4.85 (s, 1H), 4.04 – 3.88 (m, 2H), 2.67 (s, 3H), 1.93 (s, 3H), 1.90 – 1.81 (m, 2H), 1.74 (s, 3H), 1.64 – 1.58 (m, 10H), 1.24 – 1.16 (m, 24H), 1.06 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 200.7, 168.3, 151.0, 143.4, 143.2, 142.8, 142.4, 142.1, 142.0, 141.8, 137.8, 134.1, 132.8, 124.2, 122.4, 122.0, 112.4, 69.5, 49.2, 46.9, 35.7, 34.7, 34.7, 32.3, 32.2, 32.1, 32.0, 25.4, 20.0, 18.3, 15.4, 14.3.

HRMS (APCI): calcd. for $C_{45}H_{58}N_1O_2$ $[M+H]^+$ 644.44621. Found 644.44660 (Δ = 0.39 mmu).

Yield: 73% (163 mg, 0.25 mmol).

Imidazole



A mixture of 5 mL glacial acetic acid, paraformaldehyde (48.5 mg, 1.62 mmol, 1.5 eq.) and 39% aqueous glyoxal (184 µL, 1.62 mmol, 1.5 eq.) was heated to 70 °C. Then a solution of triptycenaminophenol (400 mg, 1.08 mmol 1.0 eq.), NH_4OAc (91 mg, 1.18 mmol, 1.1 eq) in 2 mL water and 5 mL glacial acetic acid was added after which the reaction mixture was heated at 70 °C for 12 h. After cooling to rt the resulting brown solution was added very slowly to a stirred solution of a sat. $NaHCO_3$, the precipitate was filtered and washed with water. The crude product (**7b**) was then purified by column chromatography (Cy/EA 1:1 v/v) to give a off white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 1H; NC**H**N), 7.42 (d, J = 7.1 Hz, 2H), 7.37 (s, 1H), 7.26 – 7.20 (m, 2H), 7.03 – 6.96 (m, 5H), 6.49 (s, 1H; ArC**H**), 5.91 (s, 1H; C**H**$_{\text{-bridge}}$), 4.92 (s, 1H; C**H**$_{\text{-bridge}}$), 4.02 (t, J = 6.4 Hz, 2H; OC**H$_2$**CH_2), 1.97 (s, 3H; ArC**H$_{3\text{-ortho}}$**), 1.91 – 1.84 (m, 2H; OCH_2C**H$_2$**), 1.64 – 1.56 (m, 2H; C**H$_2$**CH_3), 1.07 (t, J = 7.4 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.9 (Ar**C**$_{\text{-OBu}}$), 145.4, 145.4, 145.0, 145.0, 144.9, 138.4, 133.0, 132.6, 132.0, 131.7, 129.8, 125.5, 125.5, 125.4, 125.3, 123.9, 123.9, 123.8, 123.8, 121.2, 111.2 (Ar**C**H), 68.7 (O**C**H_2CH_2), 49.7 (**C**H$_{\text{-bridge}}$), 47.0 (**C**H$_{\text{-bridge}}$), 31.5 (OCH_2**C**H_2), 19.6 (**C**H_2CH_3), 17.6 (Ar**C**H$_{3\text{-ortho}}$), 14.1 (CH_2**C**H_3).

^{1}H NMR (500 MHz, MeOD-d_4): δ 7.69 (s, 1H; NC**H**N), 7.40 – 7.37 (m, 2H), 7.34 (s, 1H), 7.22 – 7.17 (m, 2H), 7.15 (s, 1H), 7.03 – 6.94 (m, 5H), 6.69 (s, 1H; ArC**H**), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$), 4.59 (s, 1H; C**H**$_{\text{-bridge}}$), 4.10 (t, J = 6.4 Hz, 2H; OC**H$_2$**CH_2), 1.99 (s, 3H; ArC**H$_{3\text{-ortho}}$**), 1.90 – 1.82 (m, 2H; OCH_2C**H$_2$**), 1.68 – 1.58 (m, 2H; C**H$_2$**CH_3), 1.07 (t, J = 7.5 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, MeOD-d_4): δ 155.2 (Ar**C**$_{\text{-OBu}}$), 146.7, 146.2, 146.2, 146.1, 139.8, 134.3, 133.9, 129.7, 127.1, 126.5, 126.3, 126.3, 125.9, 125.0, 124.7, 124.6, 124.5, 124.5, 123.0, 117.8, 112.5 (Ar**C**H), 69.7 (O**C**H_2CH_2), 51.0 (**C**H$_{\text{-bridge}}$), 48.3 (**C**H$_{\text{-bridge}}$), 32.5 (OCH_2**C**H_2), 20.5 (**C**H_2CH_3), 17.4 (Ar**C**H$_{3\text{-ortho}}$), 14.2 (CH_2**C**H_3).

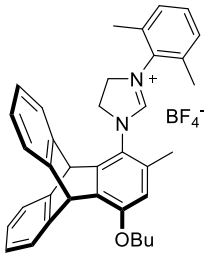
HRMS (ESI): calcd. for $C_{28}H_{27}N_2O$ $[M+H]^+$ 407.21179. Found 407.21235 (Δ = 0.56 mmu).

R_f = 0.28 (Cy/EA 1:1 v/v).

Yield: 68 % (310 mg, 0.73 mmol).

Azoliumsalts

The corresponding diamine (1.0 equiv) and NH_4Cl or NH_4BF_4 (1.1 equiv) were suspended in triethyl orthoformate and 1-2 drops of formic acid. The reaction mixture was stirred at 110 °C for 12 - 24 h. After this time the mixture was cooled to room temperature and poured into water. The aqueous phase was washed with Et_2O and extracted with DCM The combined organic layers were dried over $MgSO_4$. After drying under reduced pressure, the azolinium chloride was obtained as a white solid.



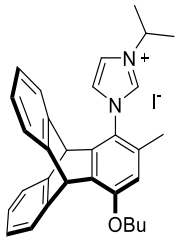
Starting materials used were triptycene-diamine (50 mg, 96.8 µmol, 1.0 eq), NH_4BF_4 (11.2 mg, 0.106 mmol, 1.1 eq) in 2 mL triethyl orthoformate. The crude product (**10**·HI) was then purified by column chromatography (DCM/MeOH) to give a off white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.24 (s, 1H; NC**H**N), 7.77 (d, J = 6.3 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.43 – 7.27 (m, 5H), 7.14 – 6.98 (m, 5H), 6.84 (s, 1H; ArC**H**), 5.95 (s, 1H; C**H**$_{\text{-bridge}}$), 5.92 (s, 1H; C**H**$_{\text{-bridge}}$), 4.80 – 4.46 (m, 4H; NC**H$_2$**C**H$_2$**N), 4.09 (t, J = 6.3 Hz, 2H; OC**H$_2$**CH$_2$), 2.64 (bs, 3H; ArC**H$_3$**), 2.42 (bs, 3H; ArC**H$_3$**), 2.29 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.85 – 1.72 (m, 2H; OCH$_2$C**H$_2$**), 1.62 – 1.43 (m, 2H; C**H$_2$**CH$_3$), 0.99 (t, J = 7.3 Hz, 3H; CH$_2$C**H$_3$**).

^{13}C NMR (126 MHz, DMSO-d_6): δ 160.6 (N**C**HN), 153.9 (Ar**C**$_{\text{-OBu}}$), 145.0, 144.7, 135.6, 133.4, 132.7, 130.0, 129.1, 125.5, 125.3, 125.2, 123.8, 122.5, 112.3 (Ar**C**H), 68.3 (O**C**H$_2$CH$_2$), 52.9 (N**C**H$_2$CH$_2$N), 51.4 (NCH$_2$**C**H$_2$N), 48.2 (**C**H$_{\text{-bridge}}$), 46.0 (**C**H$_{\text{-bridge}}$), 41.4 (ArC**H$_3$**), 30.6 (OCH$_2$**C**H$_2$), 18.7 (**C**H$_2$CH$_3$), 17.1 (ArC**H$_3$**$_{\text{-ortho}}$), 13.7 (CH$_2$**C**H$_3$), 11.0 (ArC**H$_3$**).

HRMS (ESI): calcd. for $C_{36}H_{37}N_2O$ $[M\text{-}BF_4]^+$ 513.29004. Found 513.29041 (Δ = 0.37 mmu).

Yield: 82% (49 mg, 81.6 µmol).



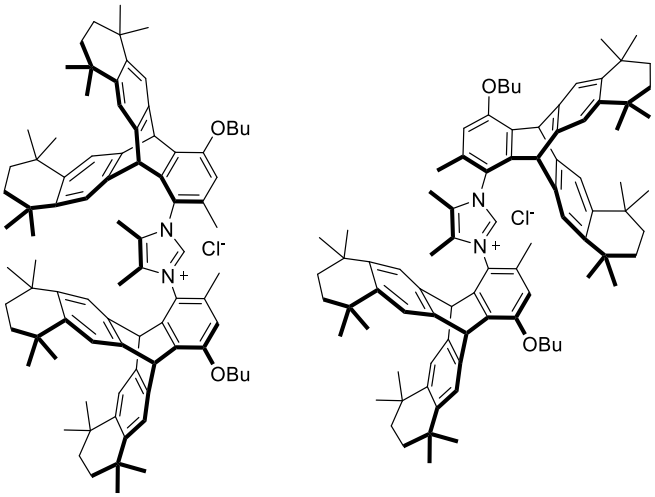
N-Triptycene(OBu) imidazole (200 mg, 0.492 mmol, 1.0 eq) was dissolved in 2 mL acetonitrile and excess (2 mL) of isopropyl iodide was added. The flask was sealed and the reaction mixture stirred at 80 °C for 24 h. After cooling to rt the content of the flask was poured into diethyl ether and the precipitate collected by filtration, washed with diethyl ether and dried in vacuo. The crude product (**8b**·HI) was then purified by column chromatography (DCM/MeOH) to give a off white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H; NC**H**N), 8.11 (s, 1H; C**H**$_{\text{-backbone}}$), 7.40 (t, J = 7.1 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.19 (s, 1H; C**H**$_{\text{-backbone}}$), 7.03 – 6.91 (m, 5H), 6.51 (s, 1H; ArC**H**), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$), 5.64 – 5.55 (m, 1H; C**H**$(CH_3)_2$), 5.02 (s, 1H; C**H**$_{\text{-bridge}}$), 4.01 (t, J = 6.5 Hz, 2H; OC**H$_2$**CH_2), 2.10 (s, 3H; ArC**H$_3$**$_{\text{-ortho}}$), 1.91 – 1.83 (m, 2H; OCH_2C**H$_2$**), 1.79 – 1.71 (m, 6H; ArC**H$_3$**), 1.64 – 1.53 (m, 2H; C**H$_2$**CH_3), 1.05 (t, J = 7.3 Hz, 3H; CH_2C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.3 (Ar**C**$_{\text{-OBu}}$), 145.1, 144.6, 144.2, 144.0, 143.5, 136.0, 133.8, 132.2, 126.0, 125.9, 125.7, 125.6, 124.2, 124.2, 124.1, 124.0, 123.7, 121.9, 121.8, 111.9 (Ar**C**H), 68.8 (O**C**H_2CH_2), 54.2 (**C**H$(CH_3)_2$), 49.5 (**C**H$_{\text{-bridge}}$), 46.8 (**C**H$_{\text{-bridge}}$), 31.3 (OCH_2**C**H_2), 23.7 (**C**$H_{3\text{-iPr}}$), 23.1 (**C**$H_{3\text{-iPr}}$), 19.5 (**C**H_2CH_3), 18.5 (ArC**H$_3$**$_{\text{-ortho}}$), 14.0 (CH_2**C**H_3).

HRMS (ESI): calcd. for $C_{31}H_{33}N_2O$ $[M\text{-}I]^+$ 449.25874. Found 449.25910 (Δ = 0.36 mmu).

Yield: 85 % (189 mg, 0.420 mmol).



A flame dried Schlenk flask containing triptycene-diimine (70 mg, 58.2 µmol, 1.0 eq), was evacuated and back-filled with nitrogen three times. Next, chloromethyl ethyl ether (2mL was added under a stream of nitrogen and the suspension was stirred overnight at 100 °C. After cooling to room temperature, diethyl ether was added, the resulting precipitate was collected by filtration. The crude product was then purified by column chromatography (DCM/MeOH). The corresponding imidazolium salt (**12**·HCl) was obtained as an off-white powder (Isomer 2:1 ratio).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00 (s, 1H; NC**H**N), 7.91 (s, 0.57H; NC**H**N), 7.44 (s, 2H), 7.41 – 7.31 (m, 7H), 7.12 (s, 2H), 6.92 (s, 0.71H), 6.73 (s, 0.74H; ArC**H**), 6.64 (s, 2H; ArC**H**), 5.84 (s, 2H; C**H**$_{\text{- bridge}}$), 5.82 (s, 0.74H; C**H**$_{\text{-bridge}}$), 5.19 (s, 2H; C**H**$_{\text{-b bridge}}$), 4.79 (s, 0.68H; C**H**$_{\text{- bridge}}$), 4.21 – 4.02 (m, 6H; OC**H$_2$**CH$_2$), 2.40 (s, 2.68H; C**H$_3$**$_{\text{-backbone}}$), 2.39 (s, 2.66H;ArC**H$_3$**$_{\text{-ortho}}$), 2.18 (s, 6H; C**H$_3$**$_{\text{-backbone}}$), 2.15 (s, 6H; ArC**H$_3$**$_{\text{-ortho}}$), 1.99 – 1.85 (m, 6H), 1.72 – 1.42 (m, 30.5H), 1.33 – 1.17 (m, 55H), 1.13 – 1.03 (m, 15.5H), 0.99 (s, 6H), 0.91 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.6 (Ar**C**$_{\text{-OBu}}$), 155.2 (Ar**C**$_{\text{-OBu}}$), 145.5, 144.7, 142.4, 142.3, 142.3, 142.2, 142.1, 141.9, 141.9, 141.8, 141.7, 141.6, 141.4, 140.8, 140.7, 140.6, 140.3, 137.1 (N**C**N), 135.1, 134.9, 133.0 (N**C**N), 131.6, 131.2, 130.2, 122.4, 122.3, 122.2, 122.2, 121.6, 120.9, 120.4, 119.3, 112.7 (Ar**C**H), 112.1 (Ar**C**H), 68.9 (O**C**H$_2$CH$_2$), 68.8 (O**C**H$_2$CH$_2$), 49.9 (**C**H$_{\text{-bridge}}$), 49.5 (**C**H$_{\text{-bridge}}$), 46.5 (**C**H$_{\text{-bridge}}$), 46.4 (**C**H$_{\text{-bridge}}$), 35.2, 35.2, 35.1, 35.0, 34.5, 34.4, 34.4, 34.2, 34.2, 32.5, 32.3, 32.2, 32.1, 32.0, 32.0, 31.9, 31.9, 31.9, 31.8, 31.3, 31.3, 19.6, 19.5, 19.1, 18.0, 14.1, 14.0, 9.8 (**C**H$_{3\text{-backbone}}$), 9.8 (**C**H$_{3\text{-backbone}}$).

HRMS (APCI): calcd. for $C_{87}H_{109}N_2O_2$ $[M\text{-}Cl]^+$ 1213.84836. Found 1213.84942 (Δ = 1.06 mmu).

Yield: 48% (35 mg, 28.0 µmol).

2. NMR-Spectra

Educts

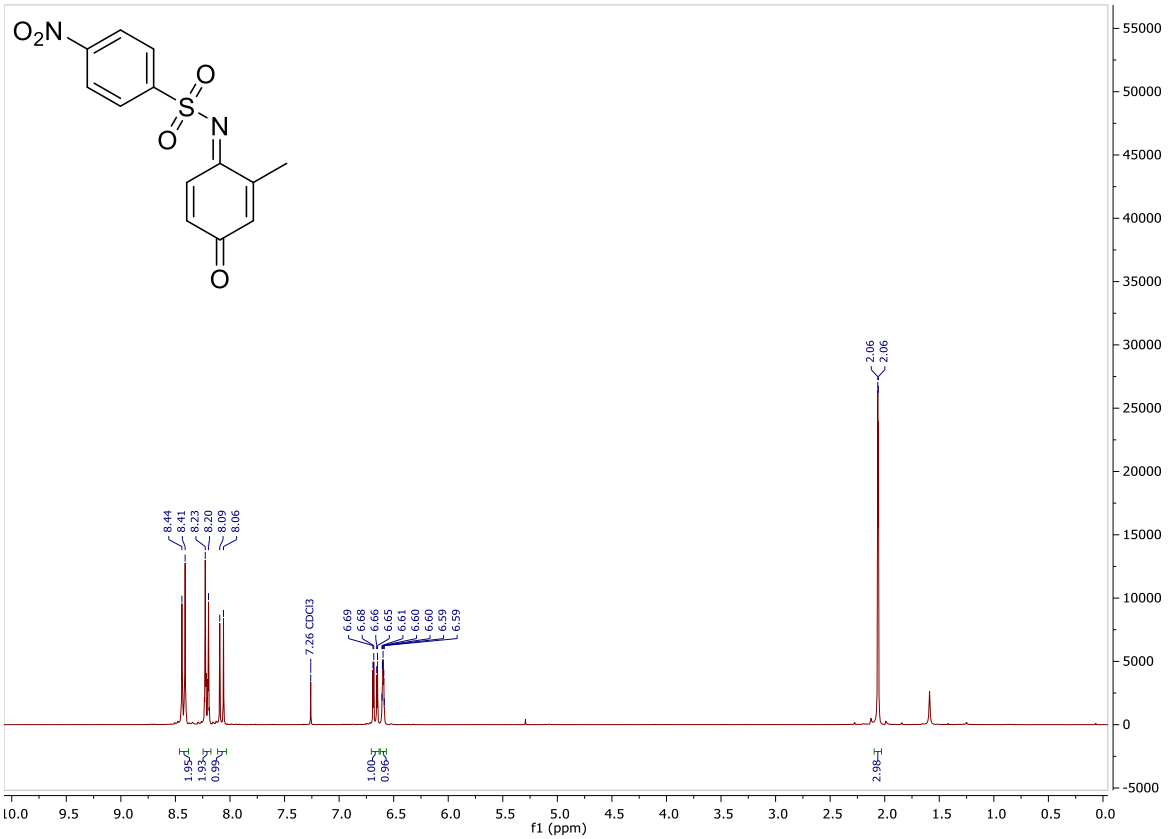


*Figure 1: ^{1}H-NMR of methyl-quinone monoamine (**3b**) in $CDCl_3$.*

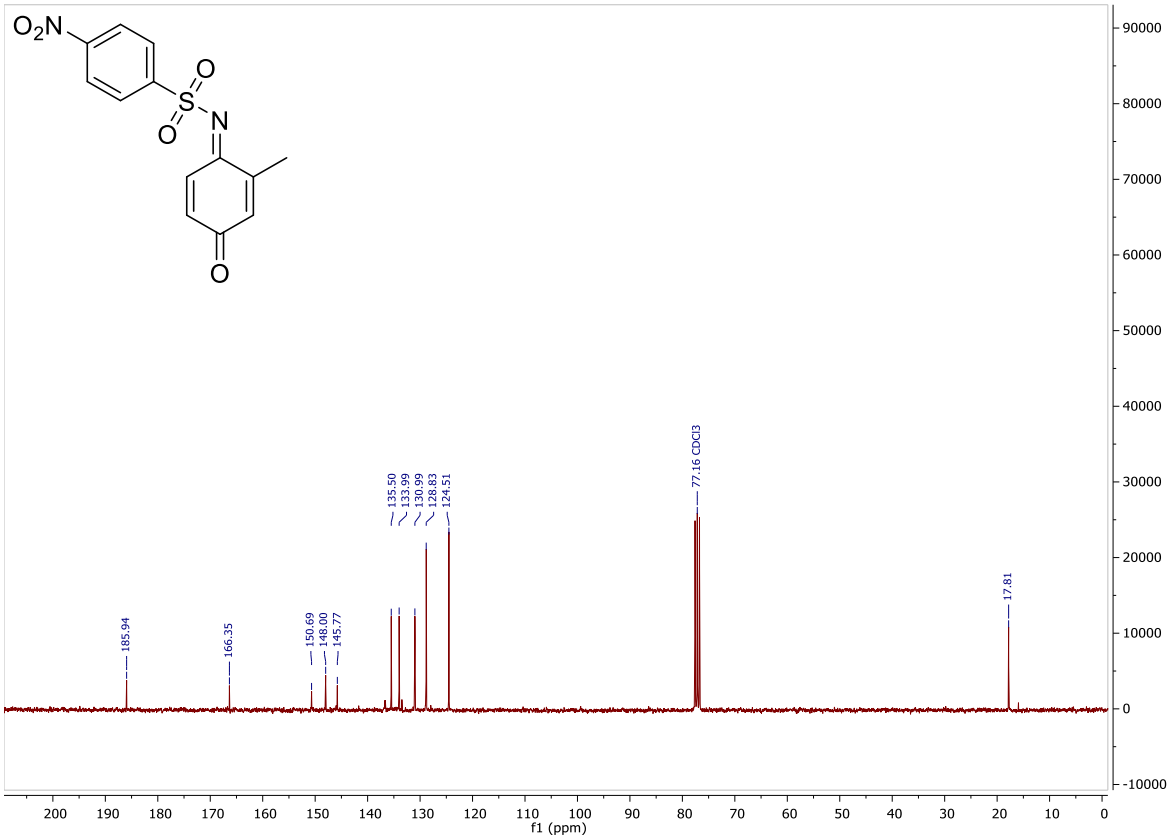


*Figure 2: ^{13}C-NMR of methyl-quinone monoamine (**3b**) in $CDCl_3$.*

Nosylated aminophenols

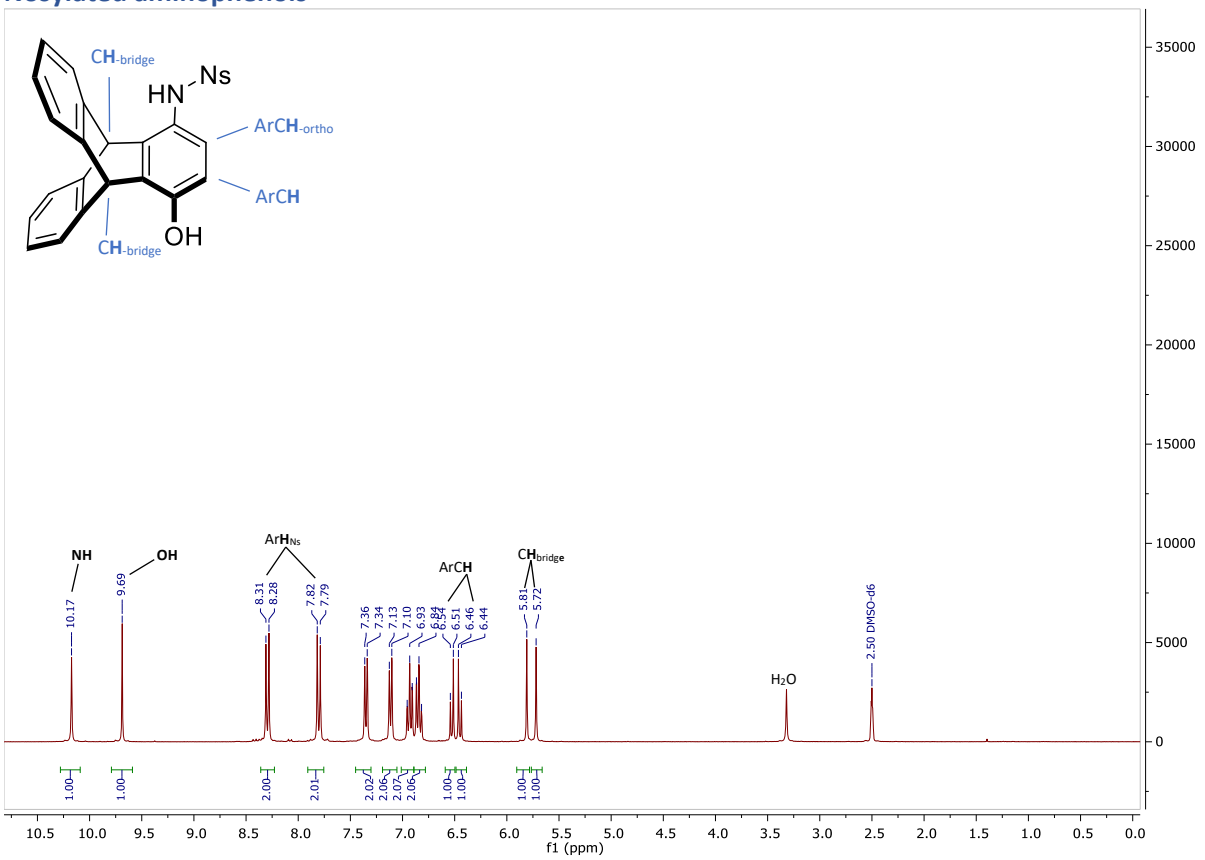


*Figure 3: ^{1}H-NMR of nosylated aminophenol (**4a**) in DMSO-d_6.*

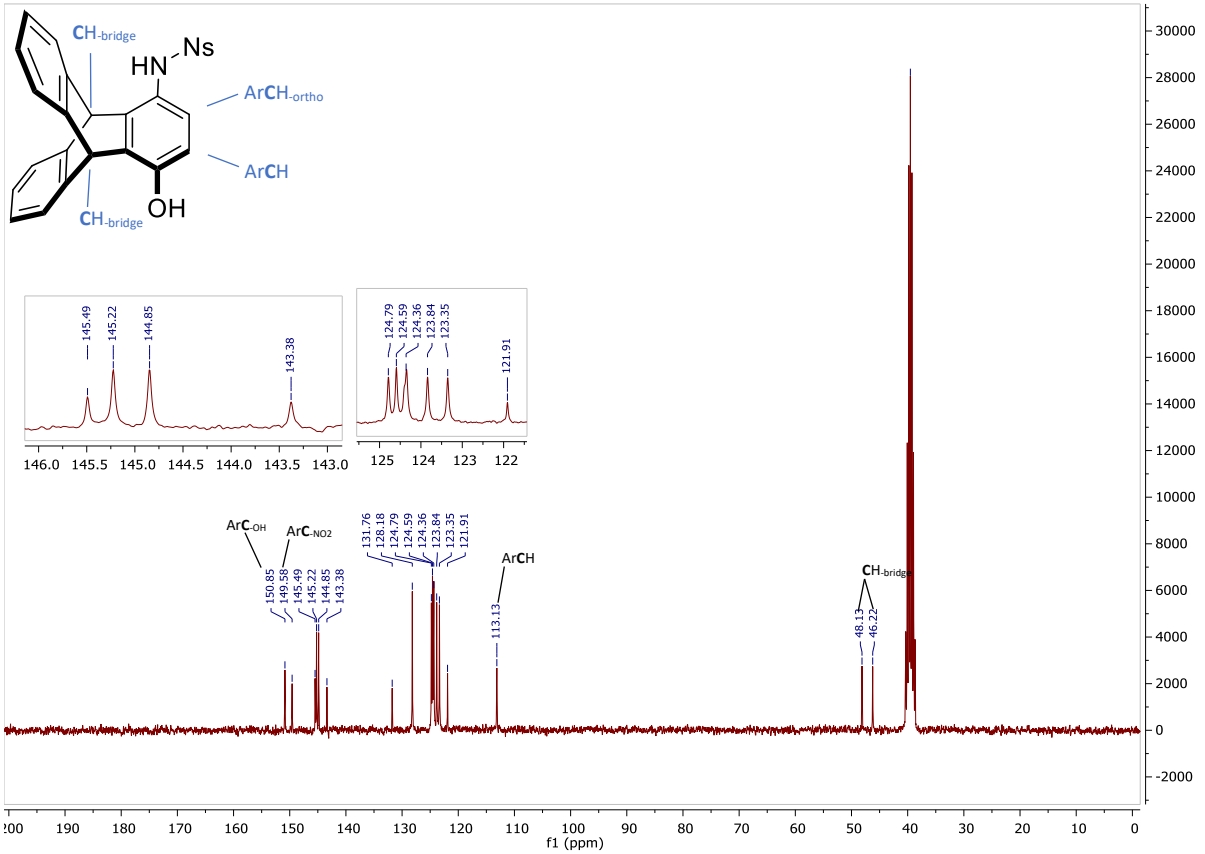


*Figure 4: ^{13}C-NMR of nosylated aminophenol (**4a**) in DMSO-d_6.*

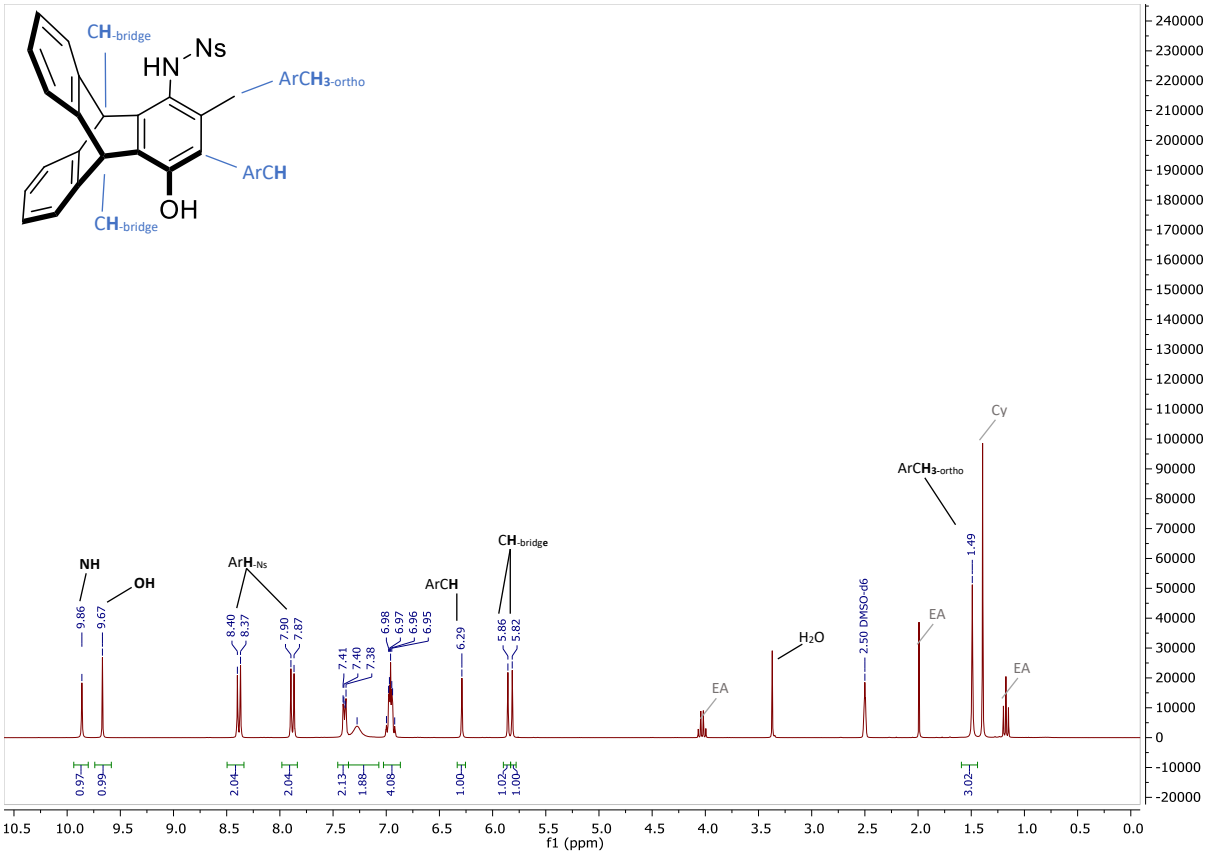


*Figure 5: [1]H-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

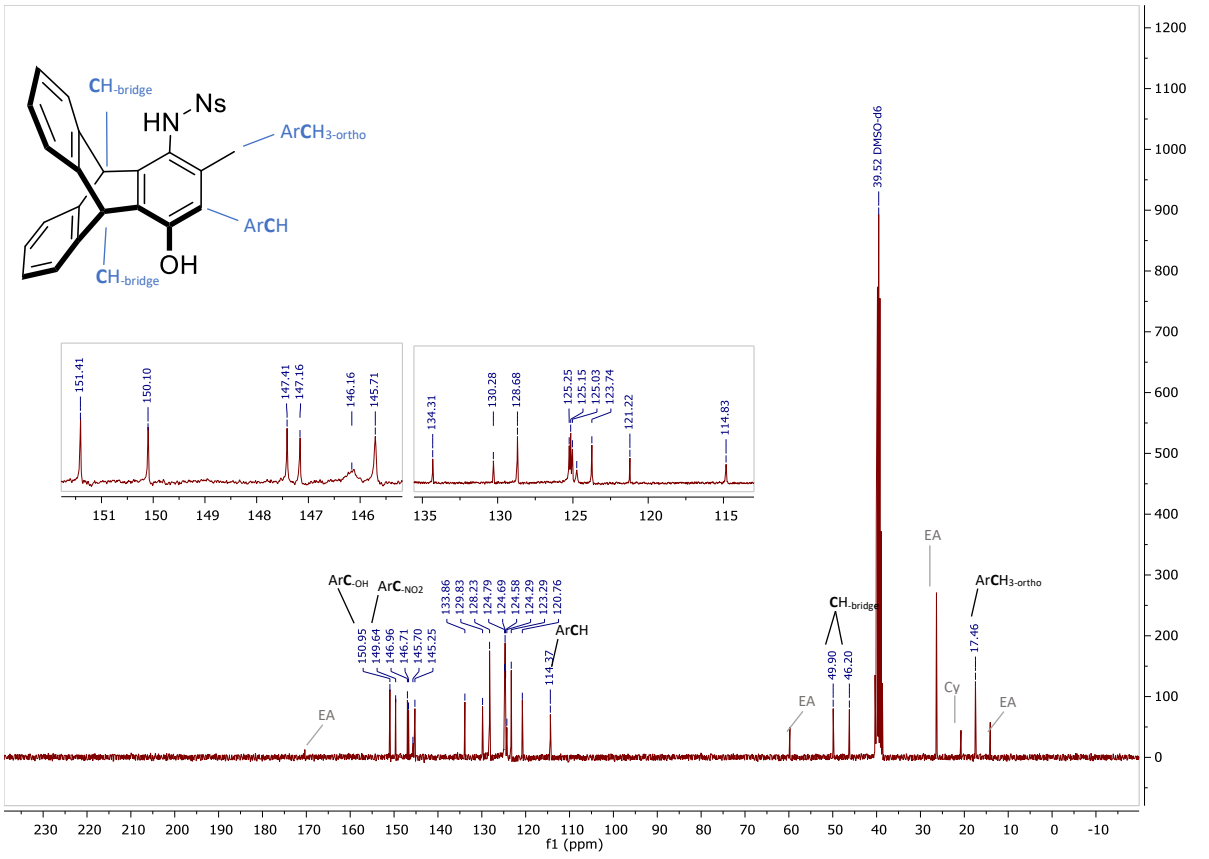


*Figure 6: [13]C-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

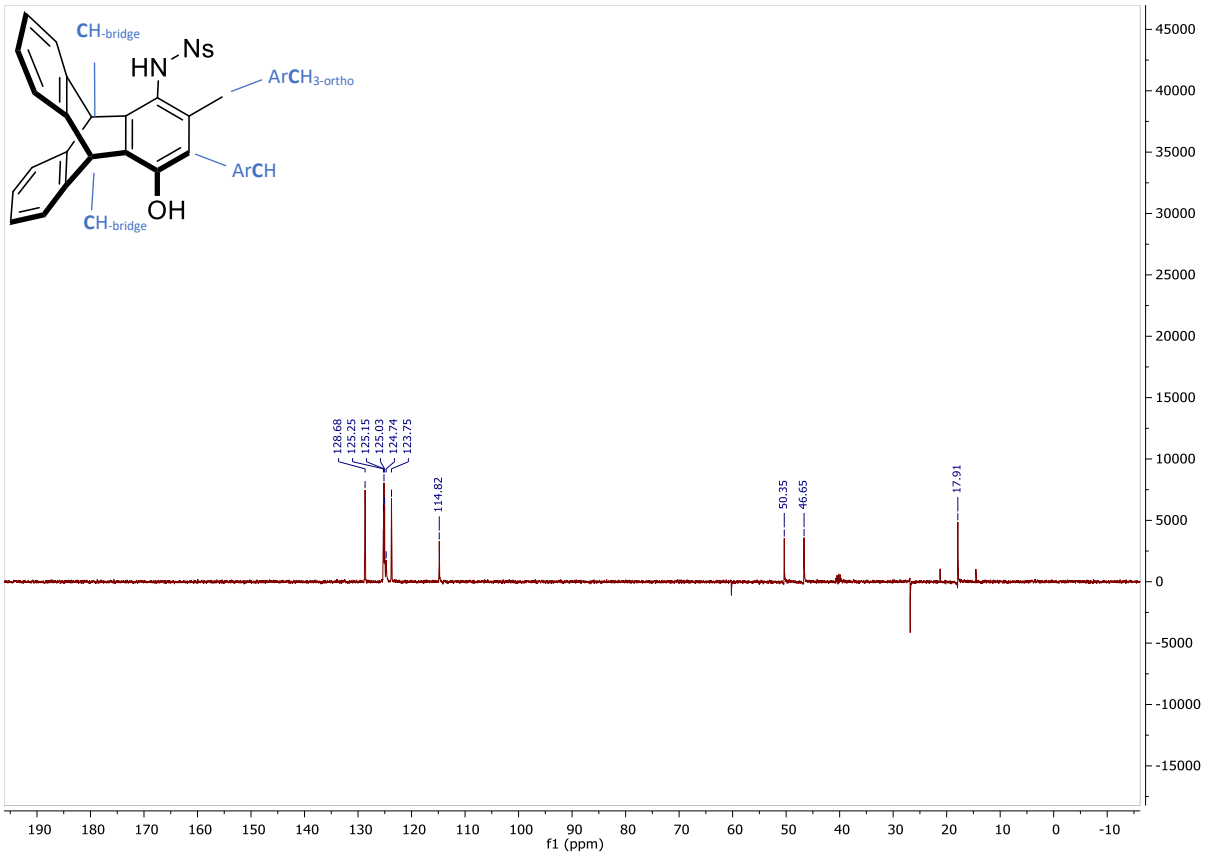


*Figure 7: ^{13}C-DEPT-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

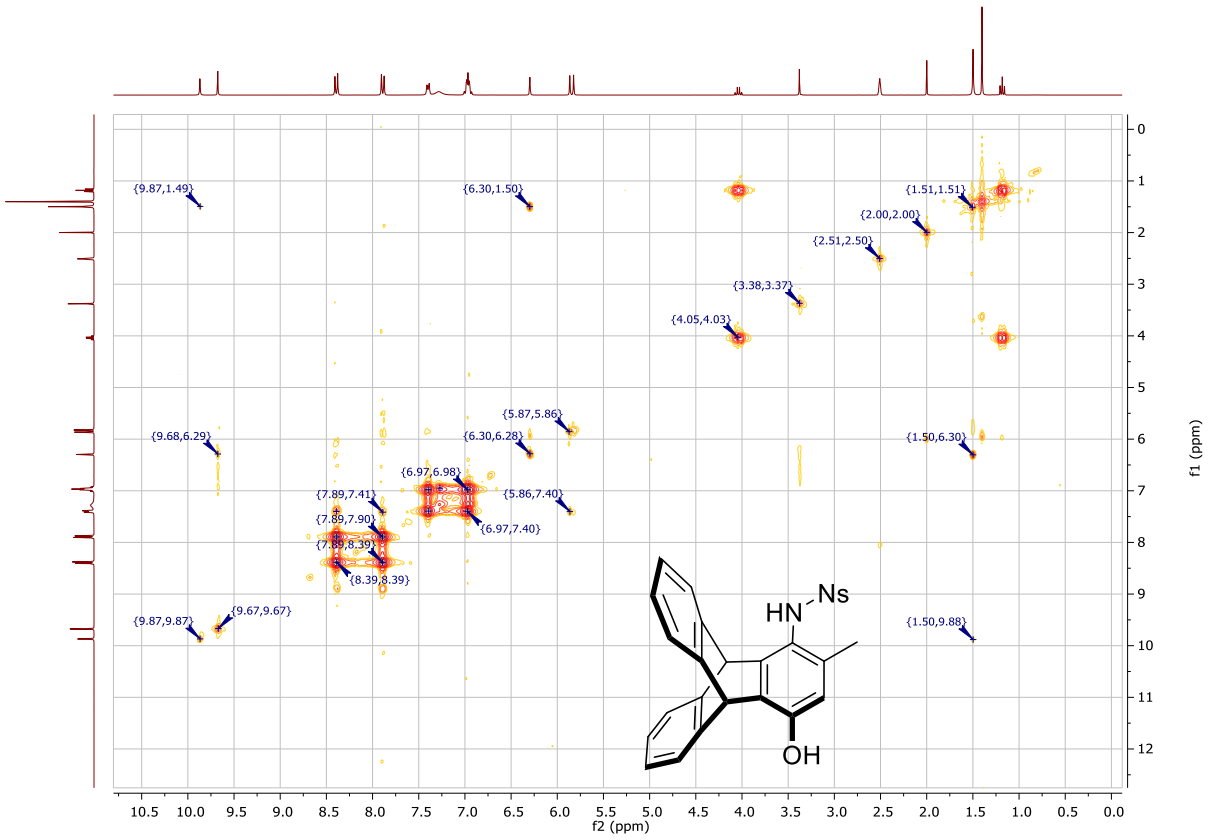


*Figure 8: COSY-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

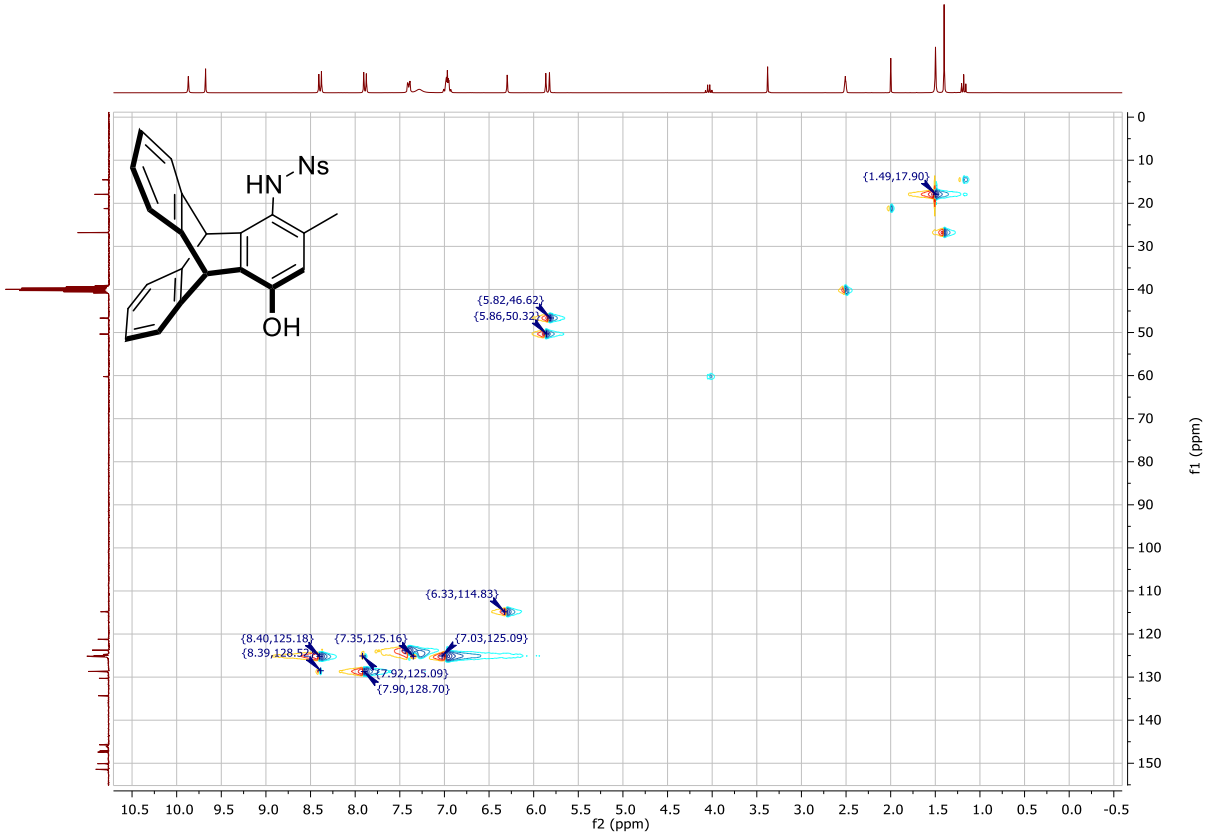


*Figure 9: HSQC-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

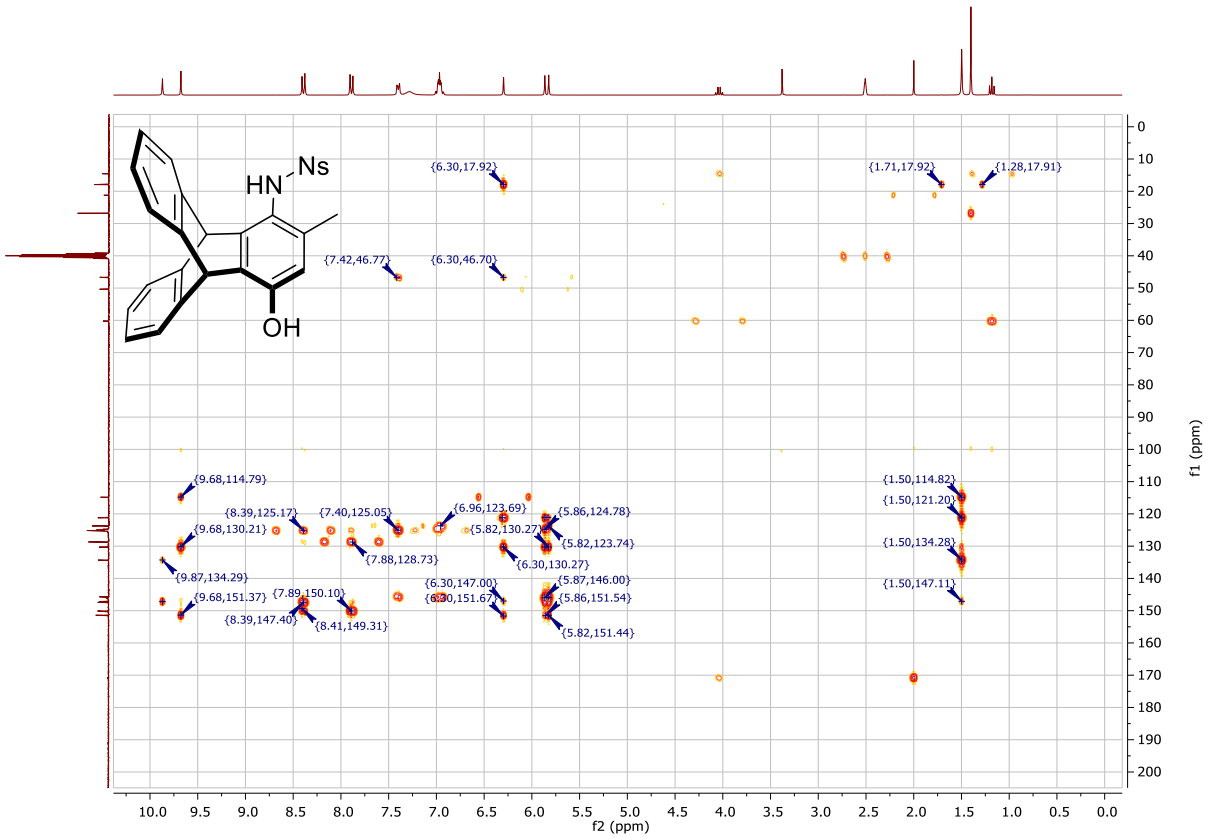


*Figure 10: HMBC-NMR of nosylated aminophenol (**4b**) in DMSO-d_6.*

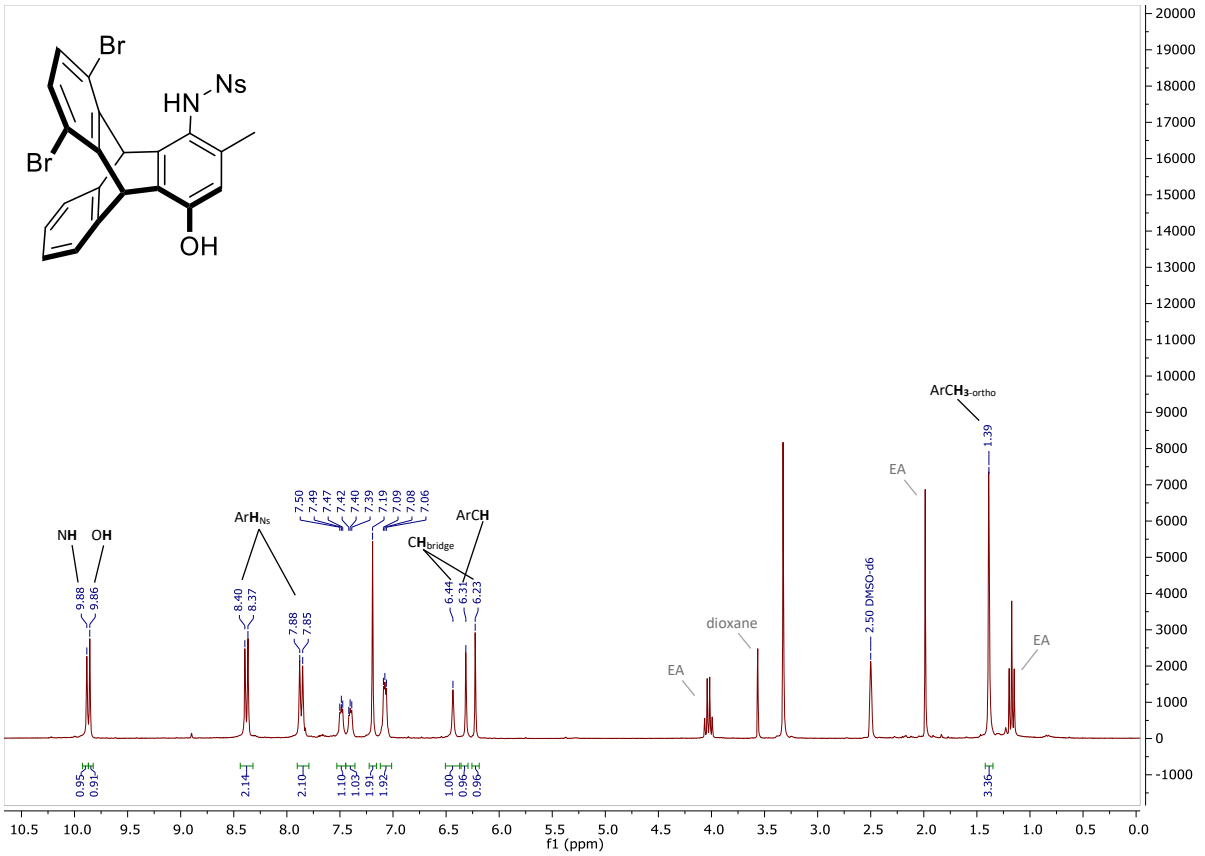


*Figure 11: ^{1}H-NMR of nosylated aminophenol (**4c**) in DMSO-d_6.*

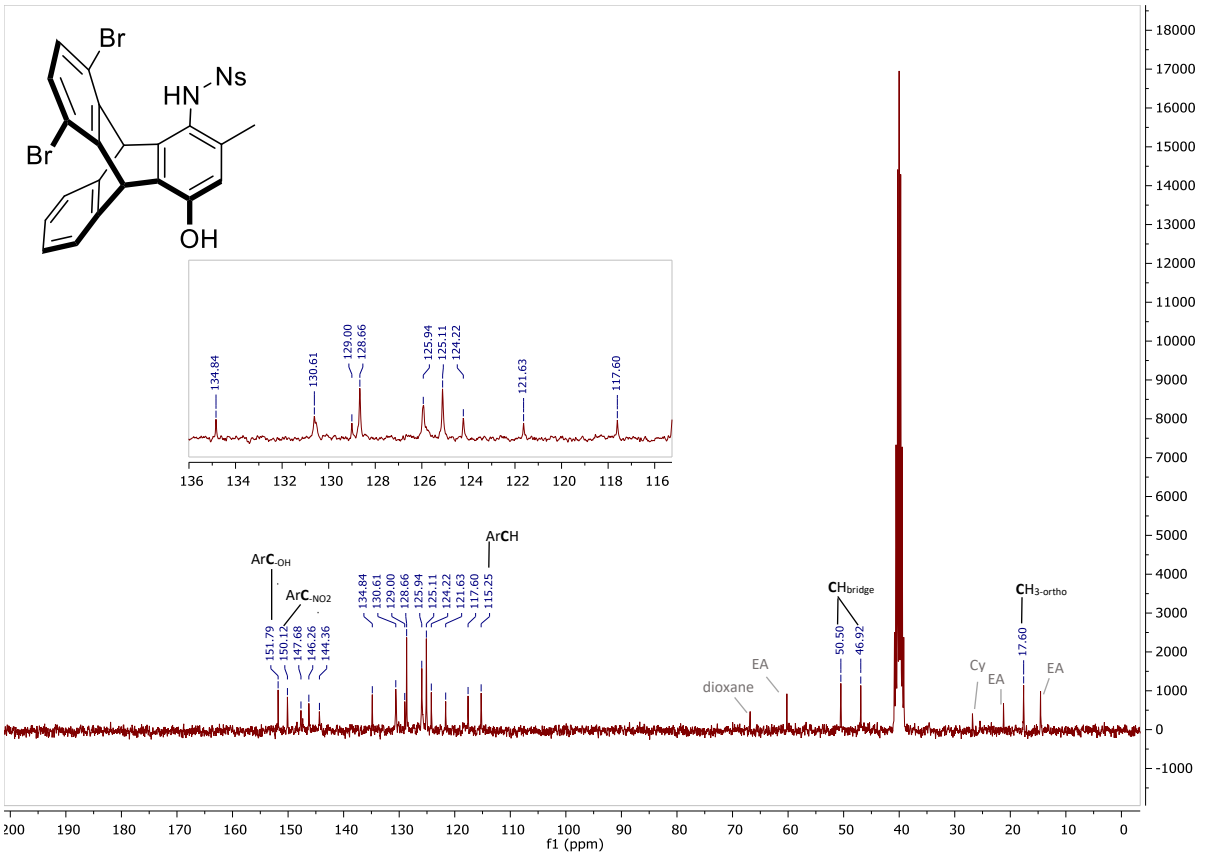


*Figure 12: ^{13}C-NMR of nosylated aminophenol (**4c**) in DMSO-d_6.*

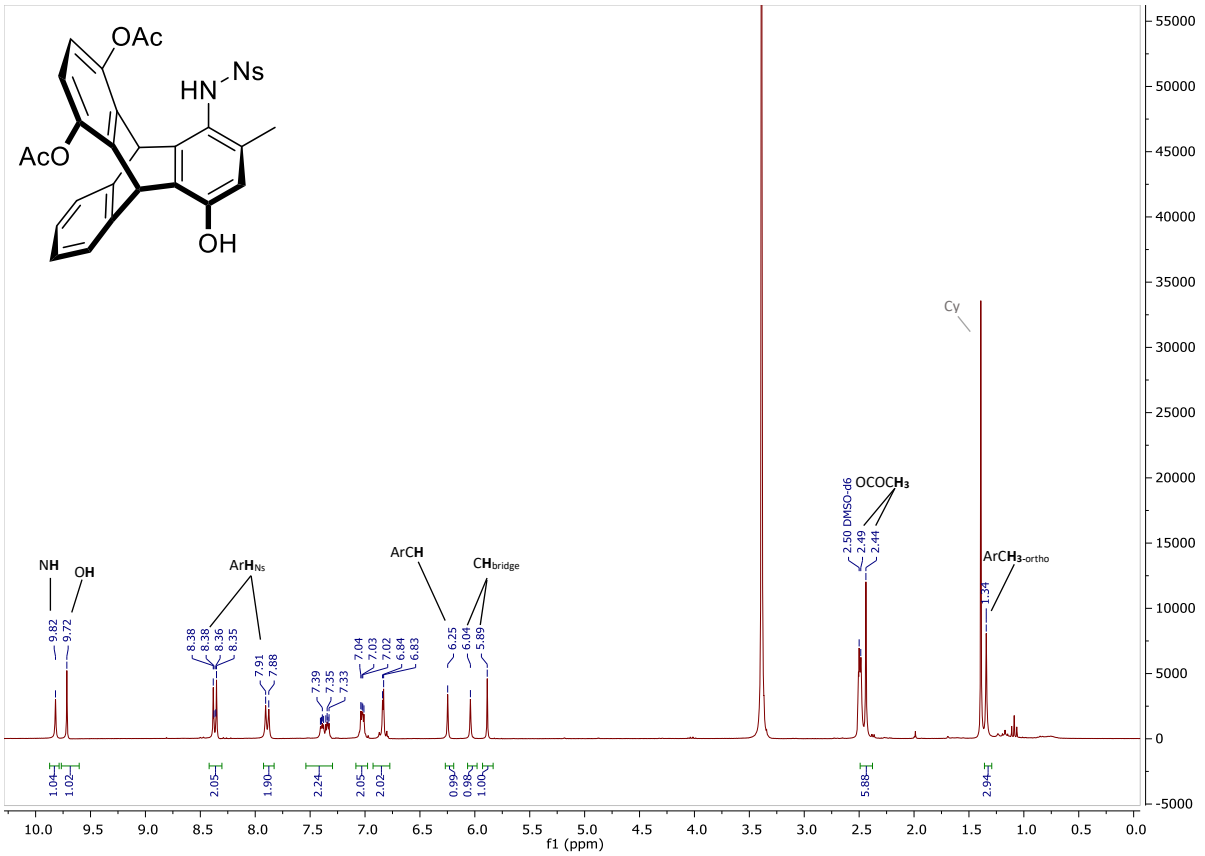


*Figure 13: [1]H-NMR of nosylated aminophenol (**4d**) in DMSO-d_6.*

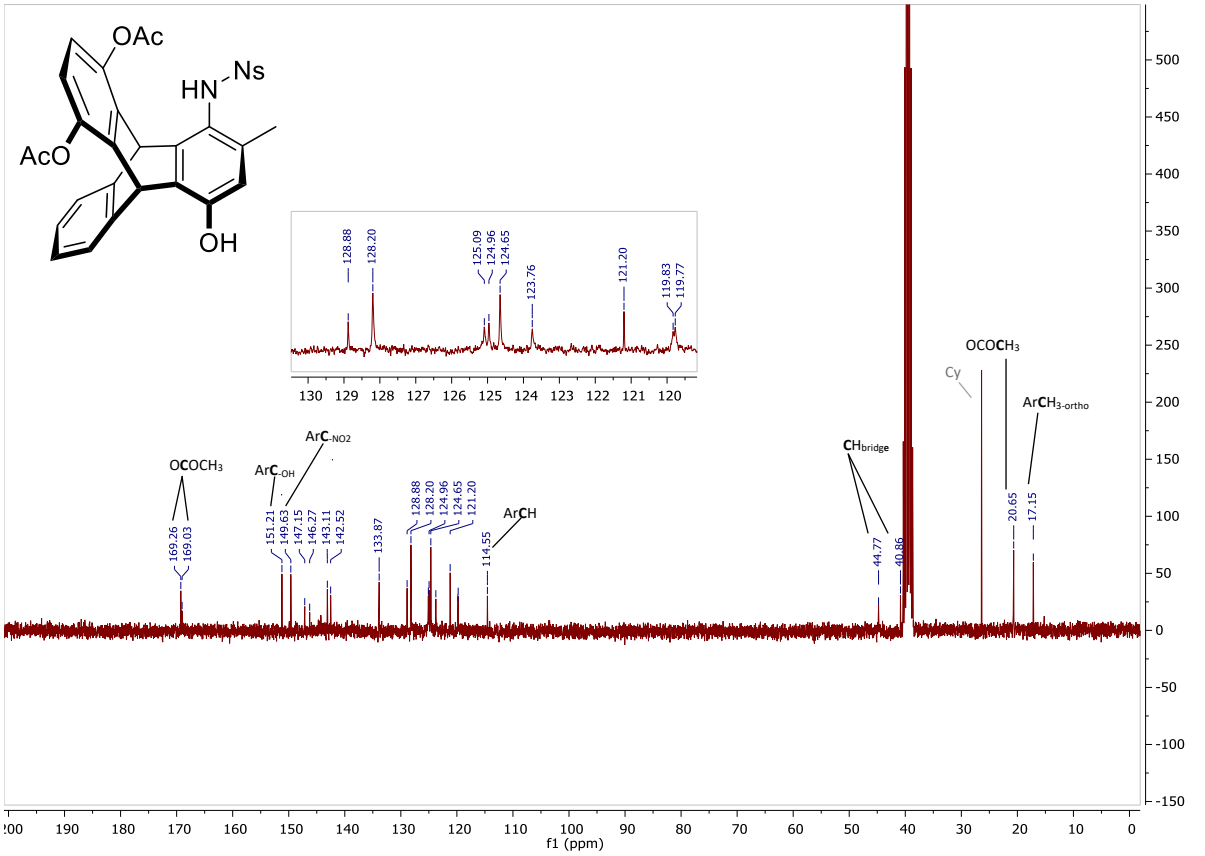


*Figure 14: [13]C-NMR of nosylated aminophenol (**4d**) in DMSO-d_6.*

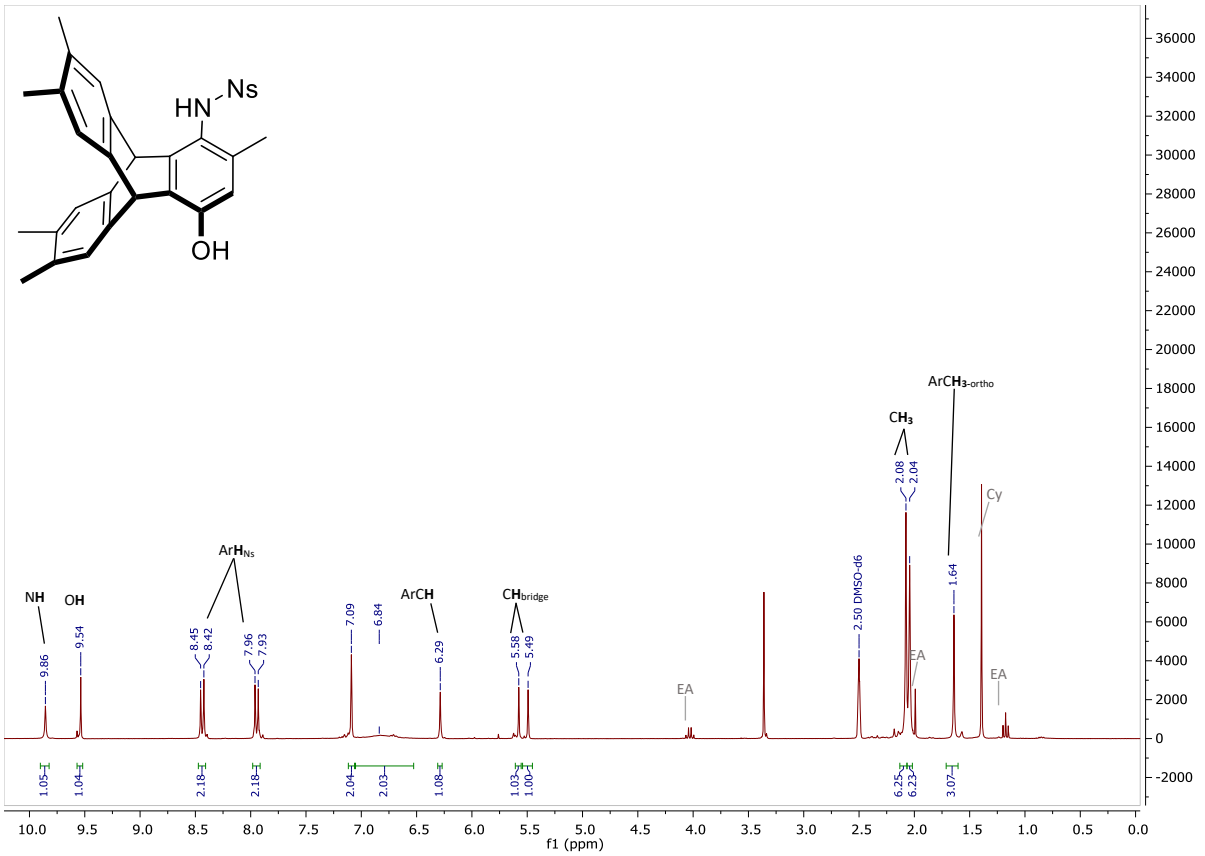


*Figure 15: ^{1}H-NMR of nosylated aminophenol (**4e**) in DMSO-d$_6$.*

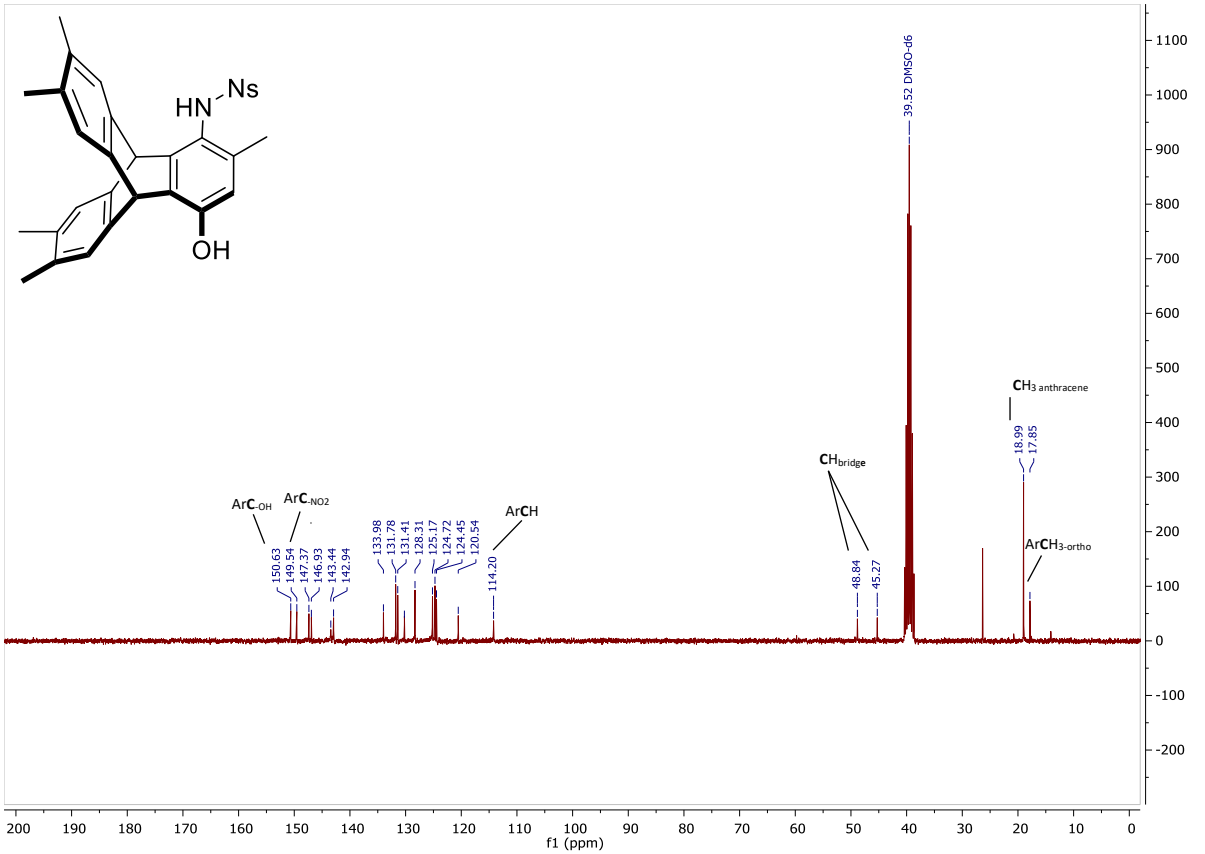


*Figure 16: ^{13}C-NMR of nosylated aminophenol (**4e**) in DMSO-d$_6$.*

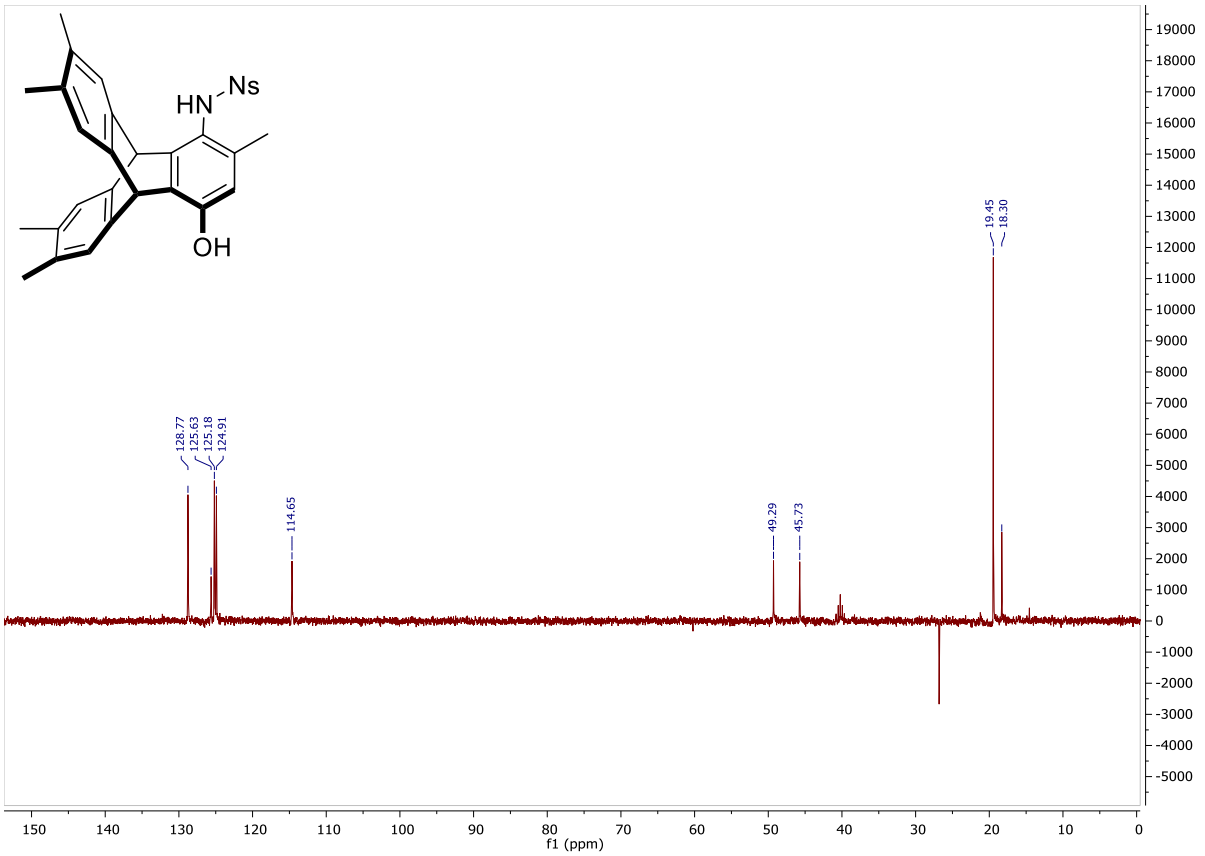


*Figure 17: DEPT-NMR of nosylated aminophenol (**4e**) in DMSO-d_6.*

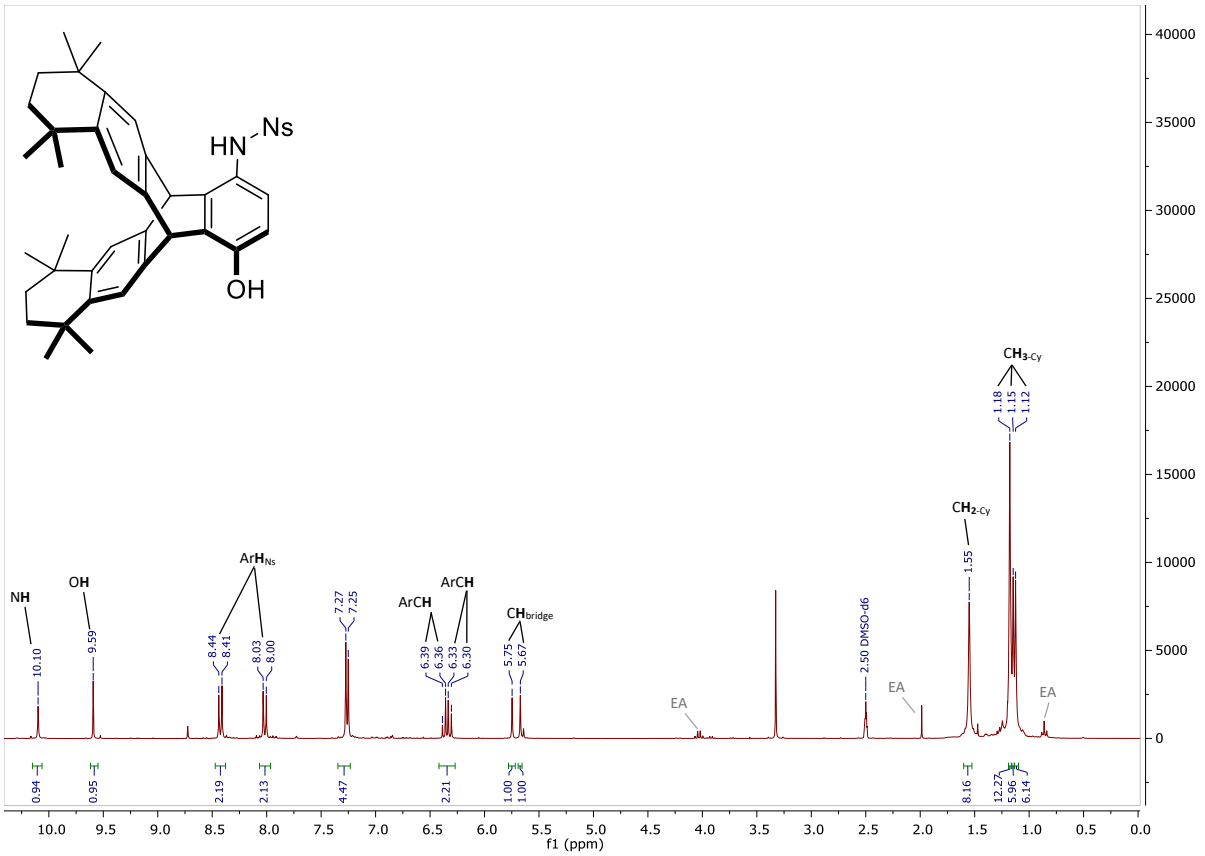


*Figure 18: ^{1}H-NMR of nosylated aminophenol (**4f**) in DMSO-d_6.*

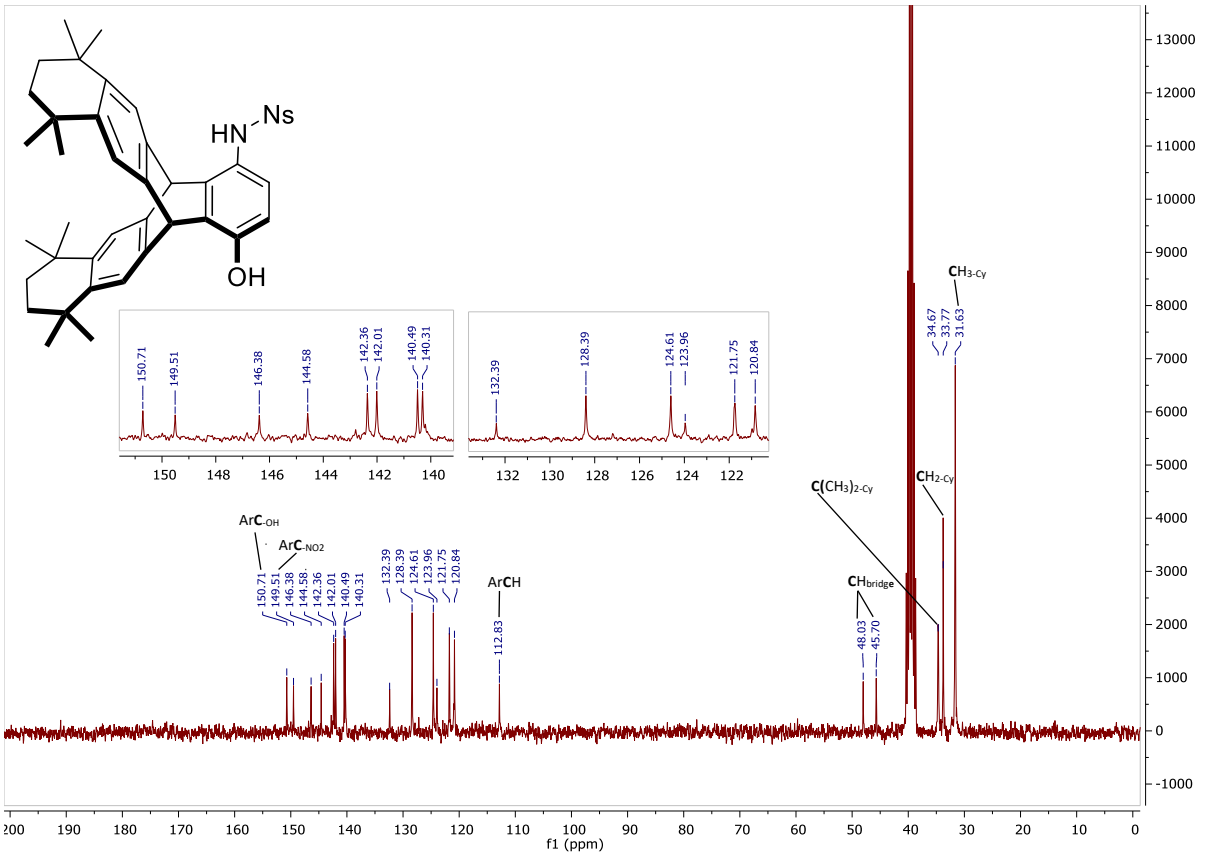


*Figure 19: ^{13}C-NMR of nosylated aminophenol (**4f**) in DMSO-d_6.*

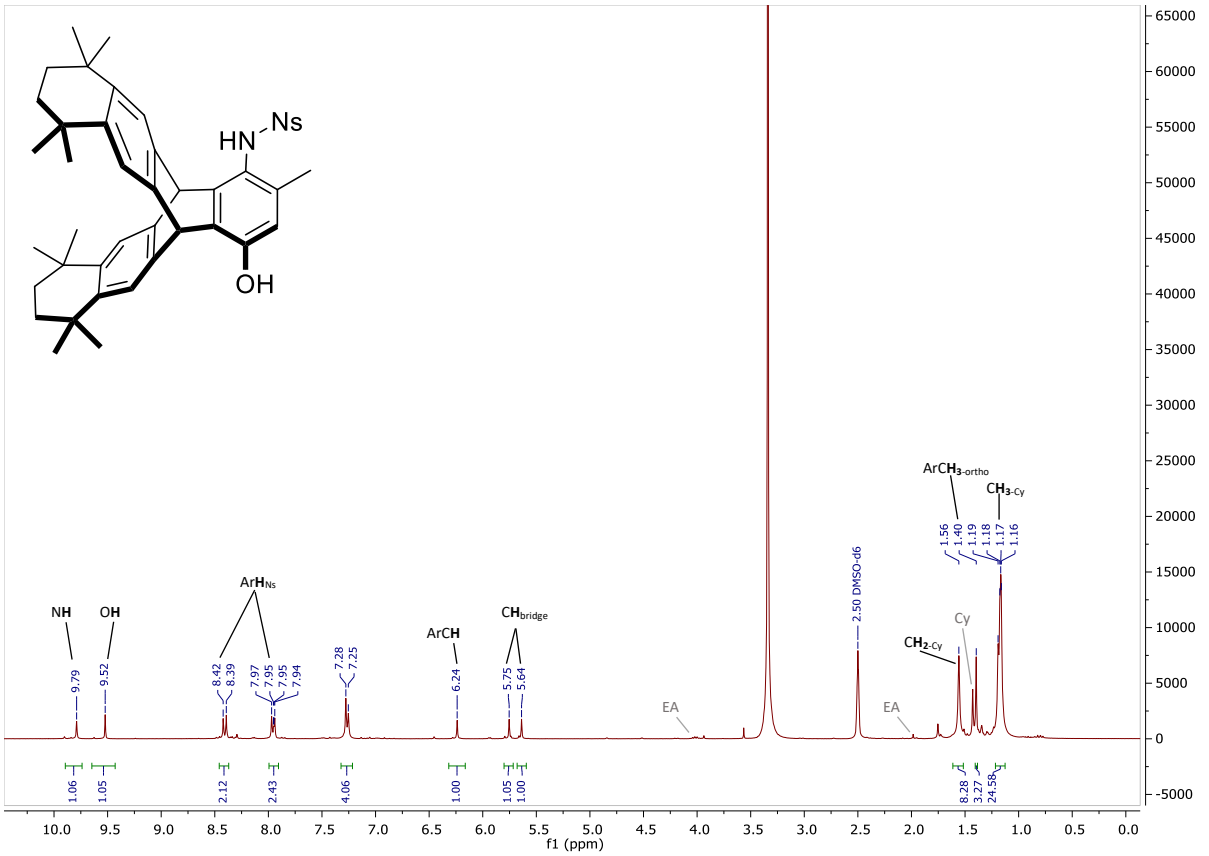


*Figure 20: ^{1}H-NMR of nosylated aminophenol (**4g**) in DMSO-d$_6$.*

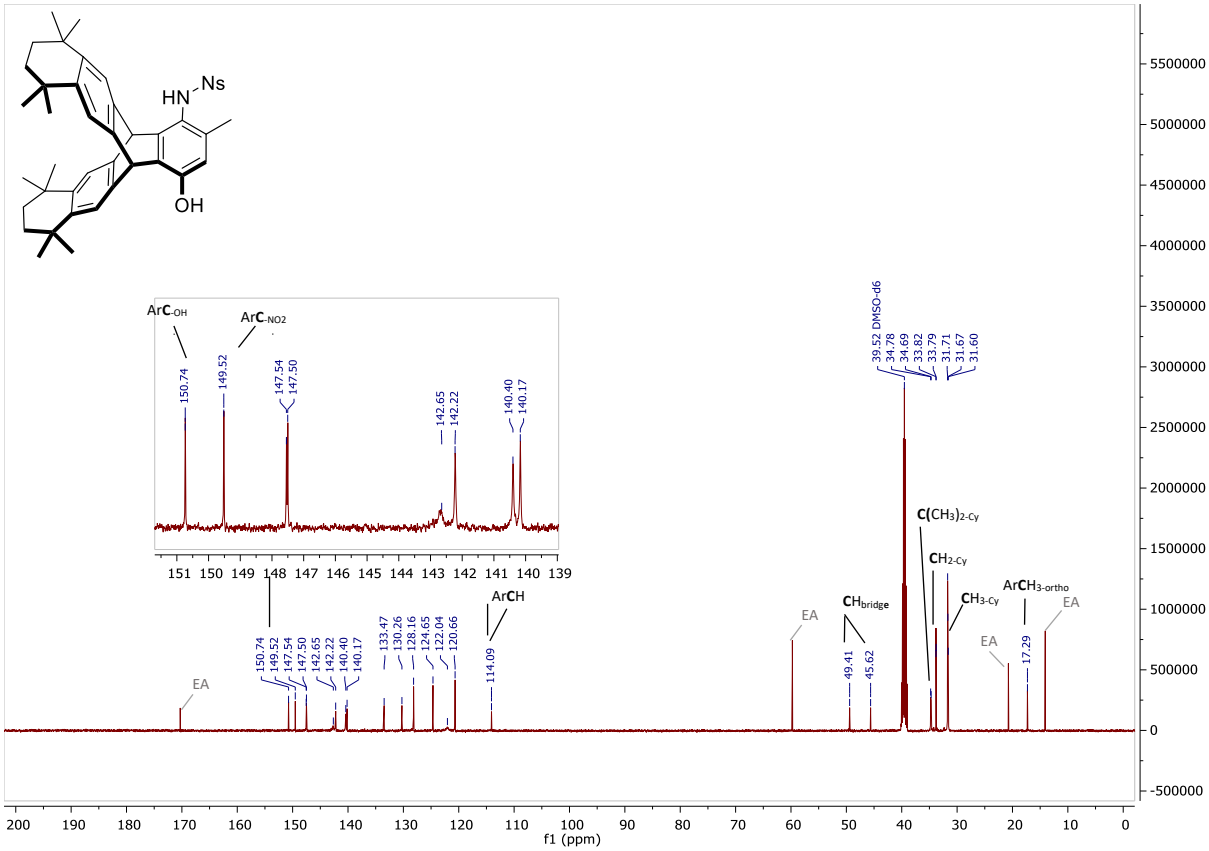


*Figure 21: ^{13}C-NMR of nosylated aminophenol (**4g**) in DMSO-d$_6$.*

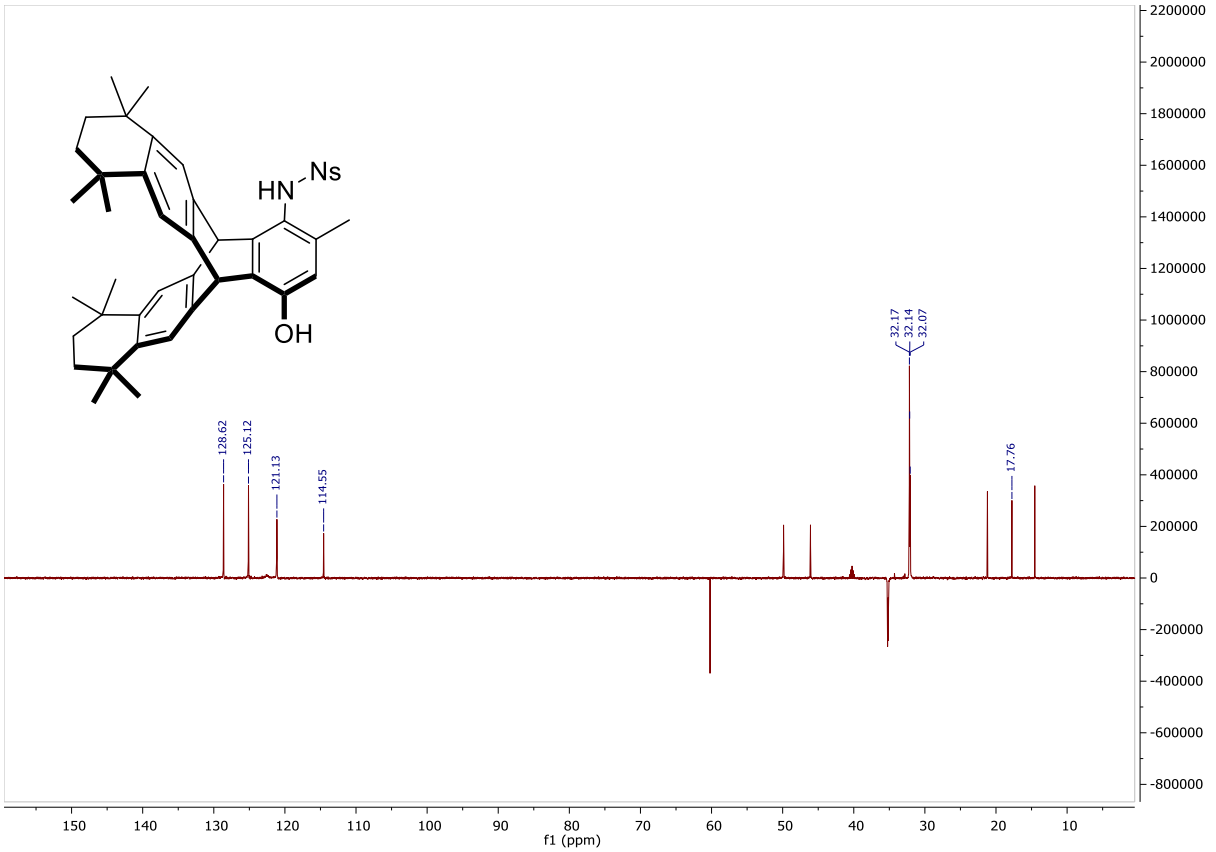


*Figure 22: DEPT-NMR of nosylated aminophenol (**4g**) in DMSO-d_6.*

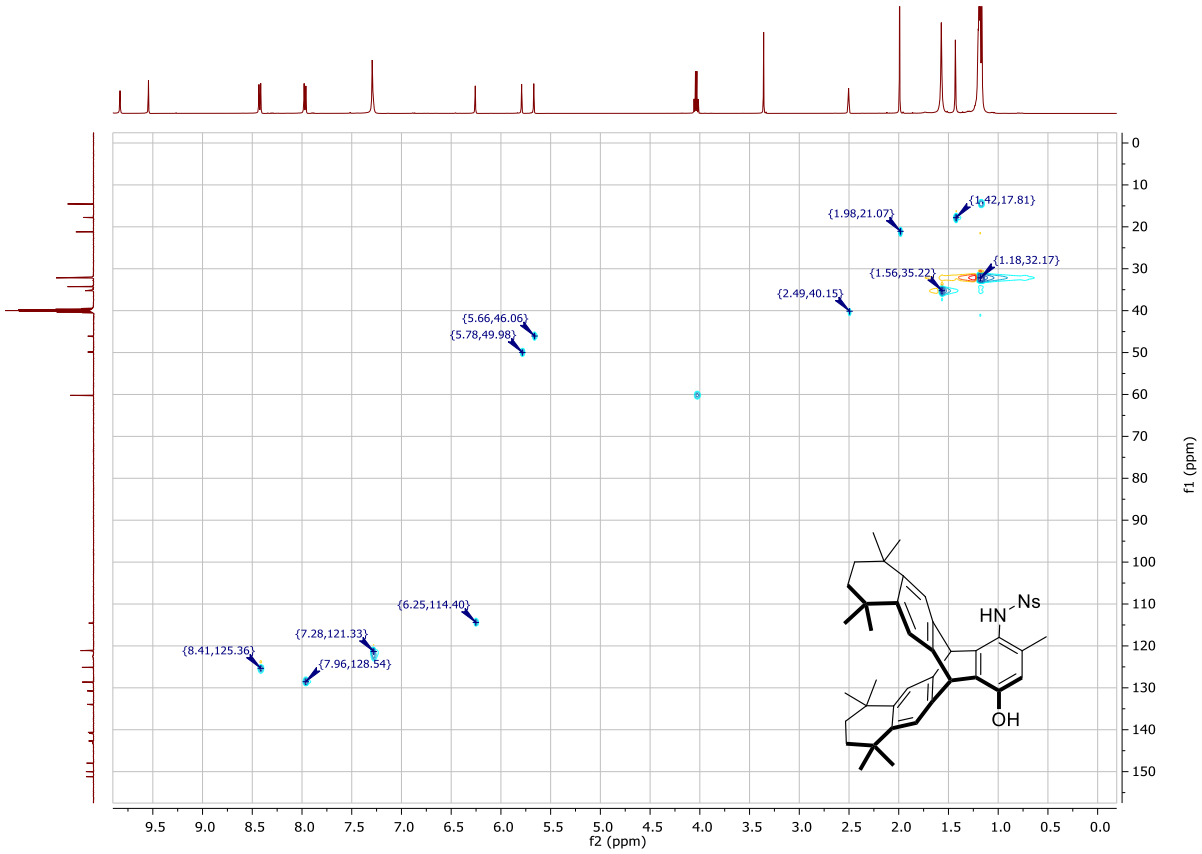


*Figure 23: HSQC-NMR of nosylated aminophenol (**4g**) in DMSO-d_6.*

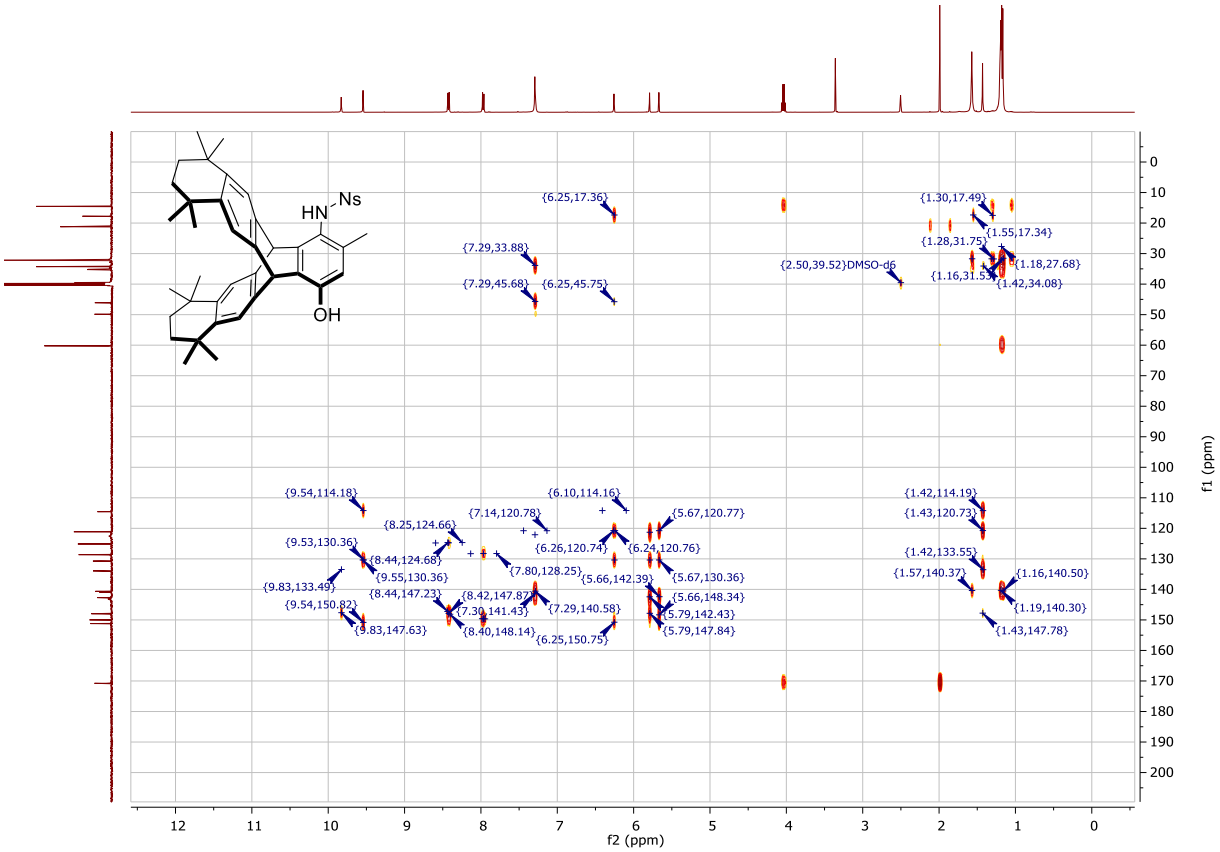


*Figure 24: HMBC-NMR of nosylated aminophenol (**4g**) in DMSO-d_6.*

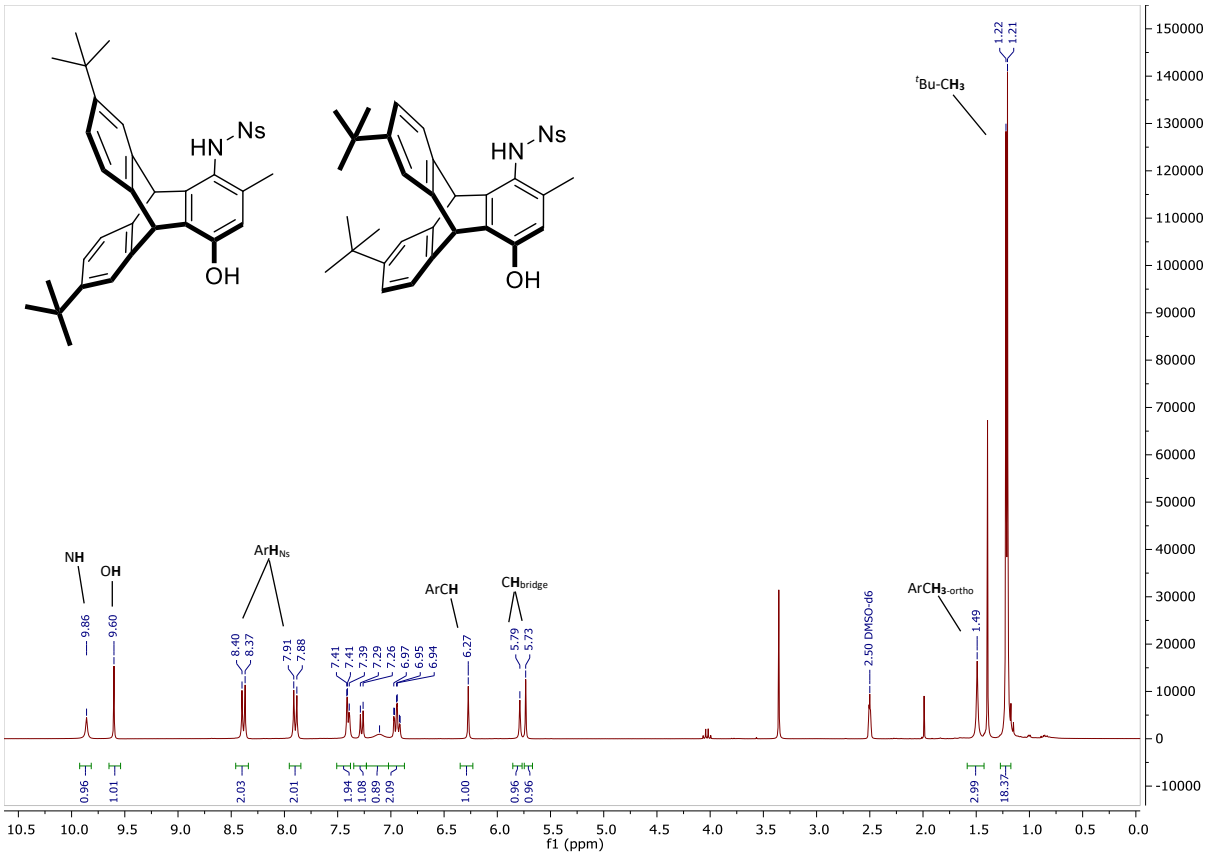


*Figure 25: [1]H-NMR of nosylated aminophenol (**4i**) in DMSO-d_6.*

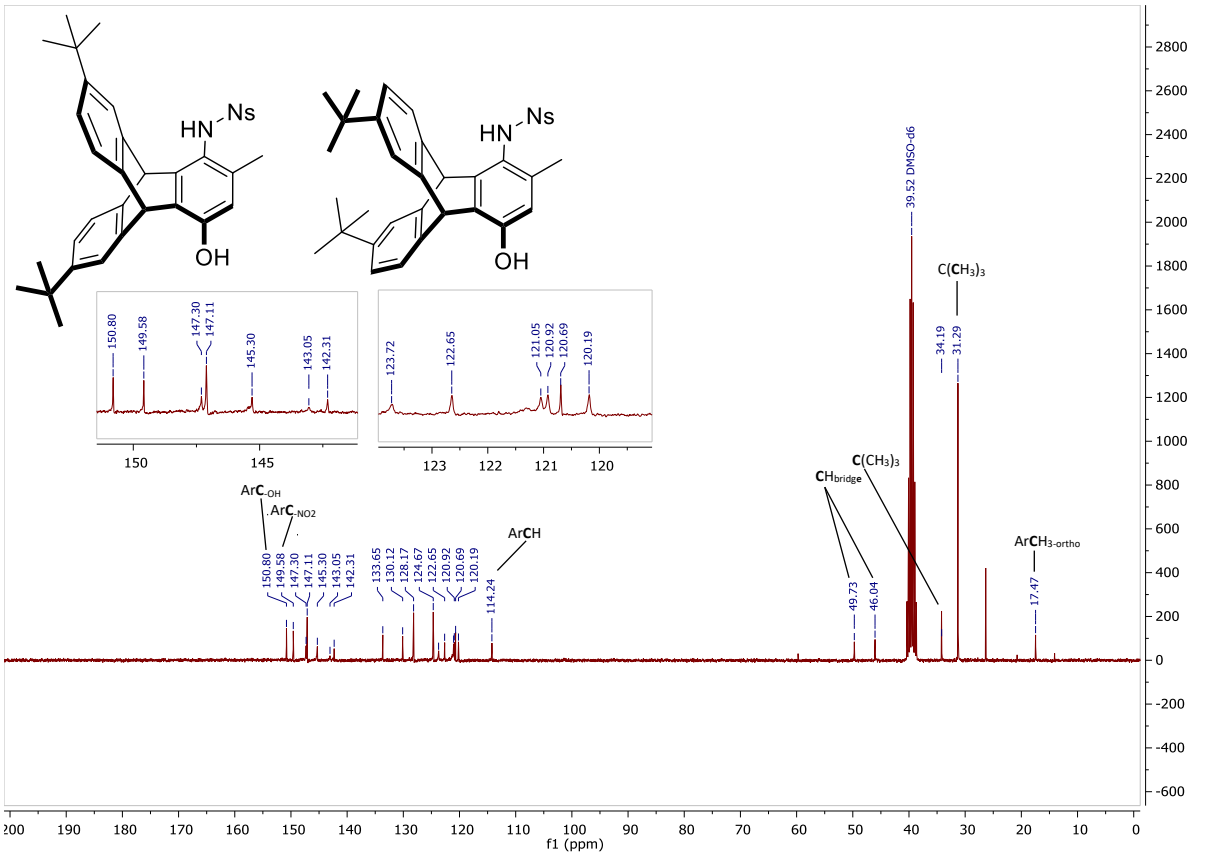


*Figure 26: [13]C-NMR of nosylated aminophenol (**4i**) in DMSO-d_6.*

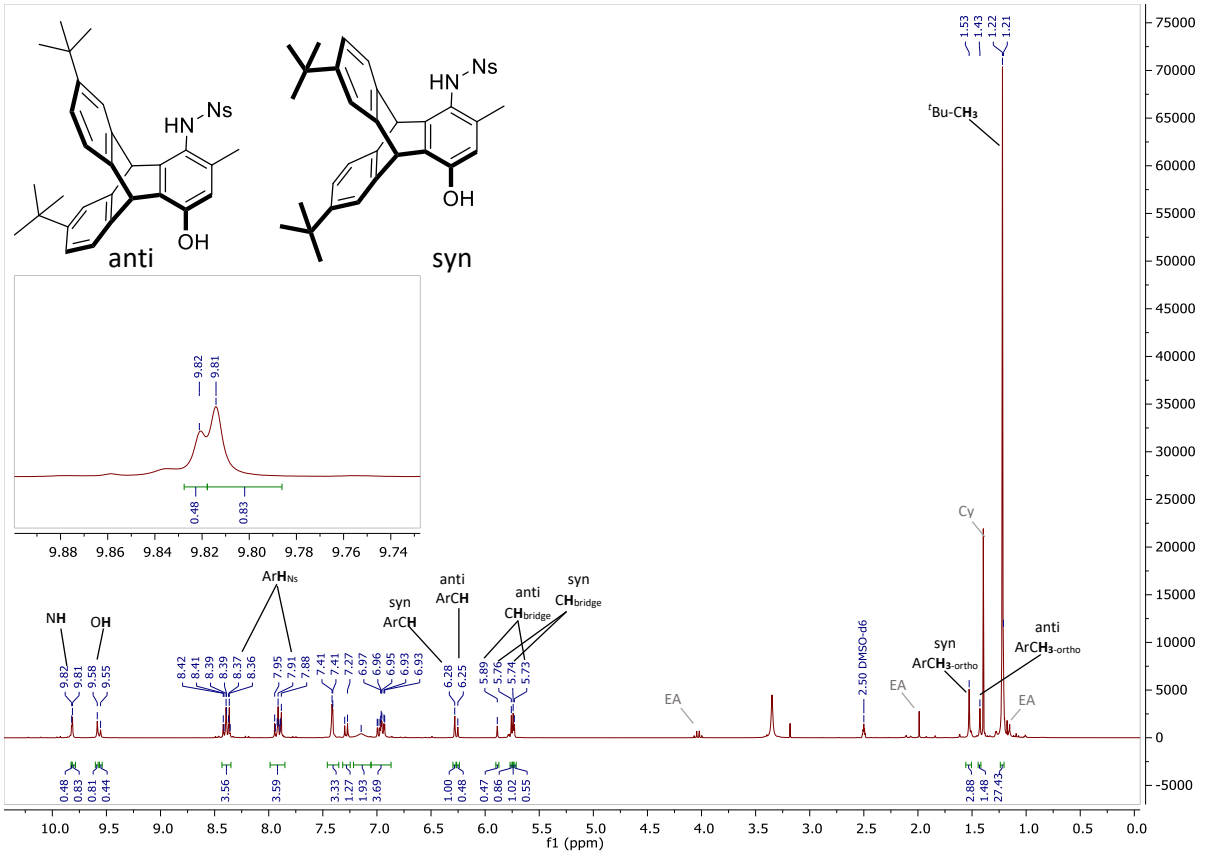


*Figure 27: [1]H-NMR of nosylated aminophenol (**4h**) in DMSO-d6.*

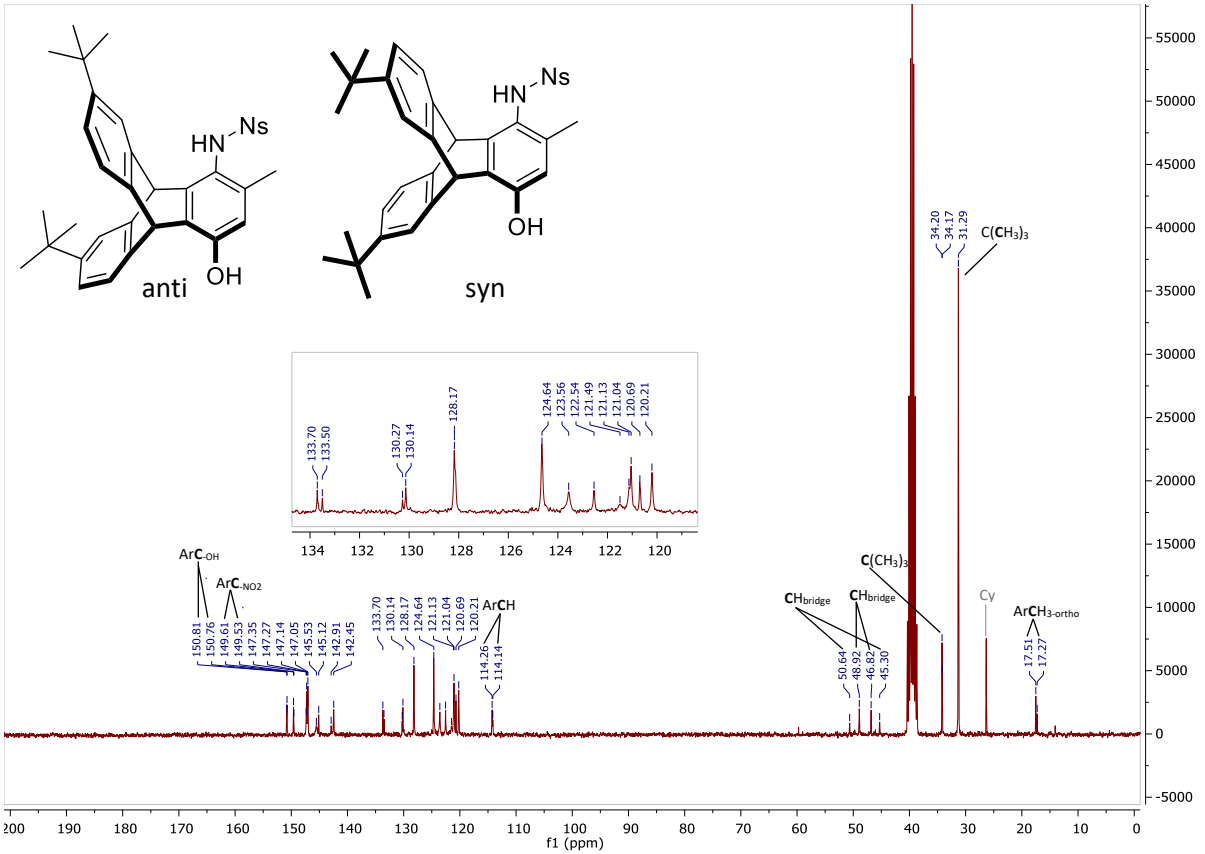


*Figure 28: [13]C-NMR of nosylated aminophenol (**4h**) in DMSO-d6.*

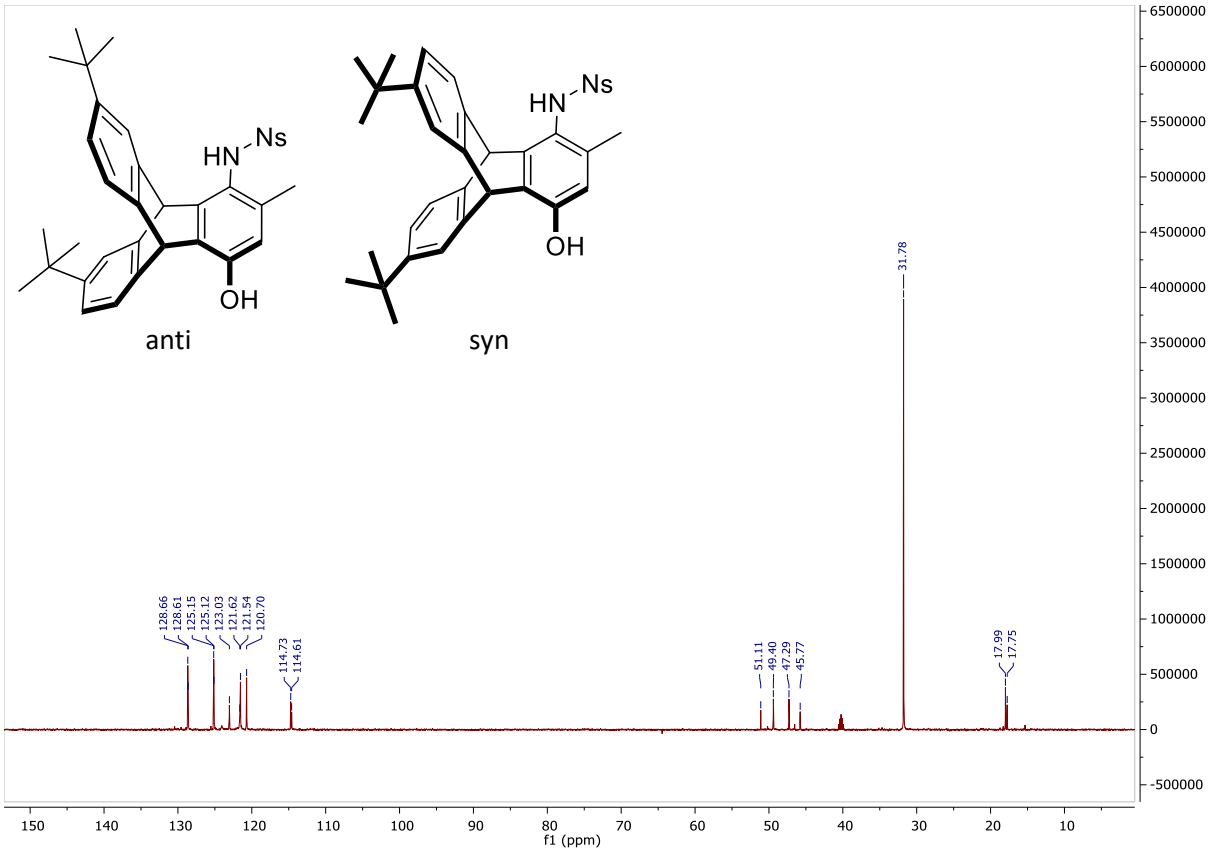


*Figure 29: ^{13}C-NMR of nosylated aminophenol (**4h**) in DMSO-d_6.*

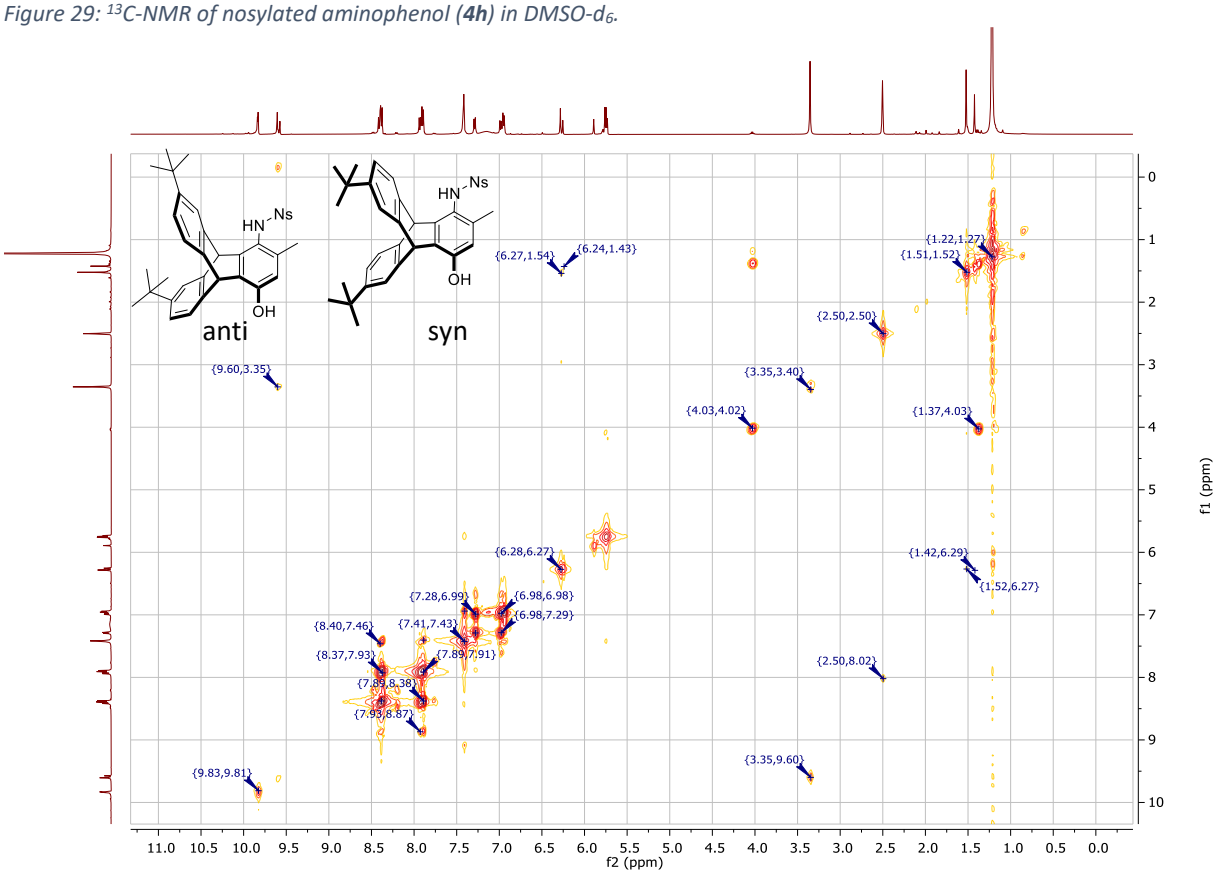


*Figure 30: COSY-NMR of nosylated aminophenol (**4h**) in DMSO-d_6.*

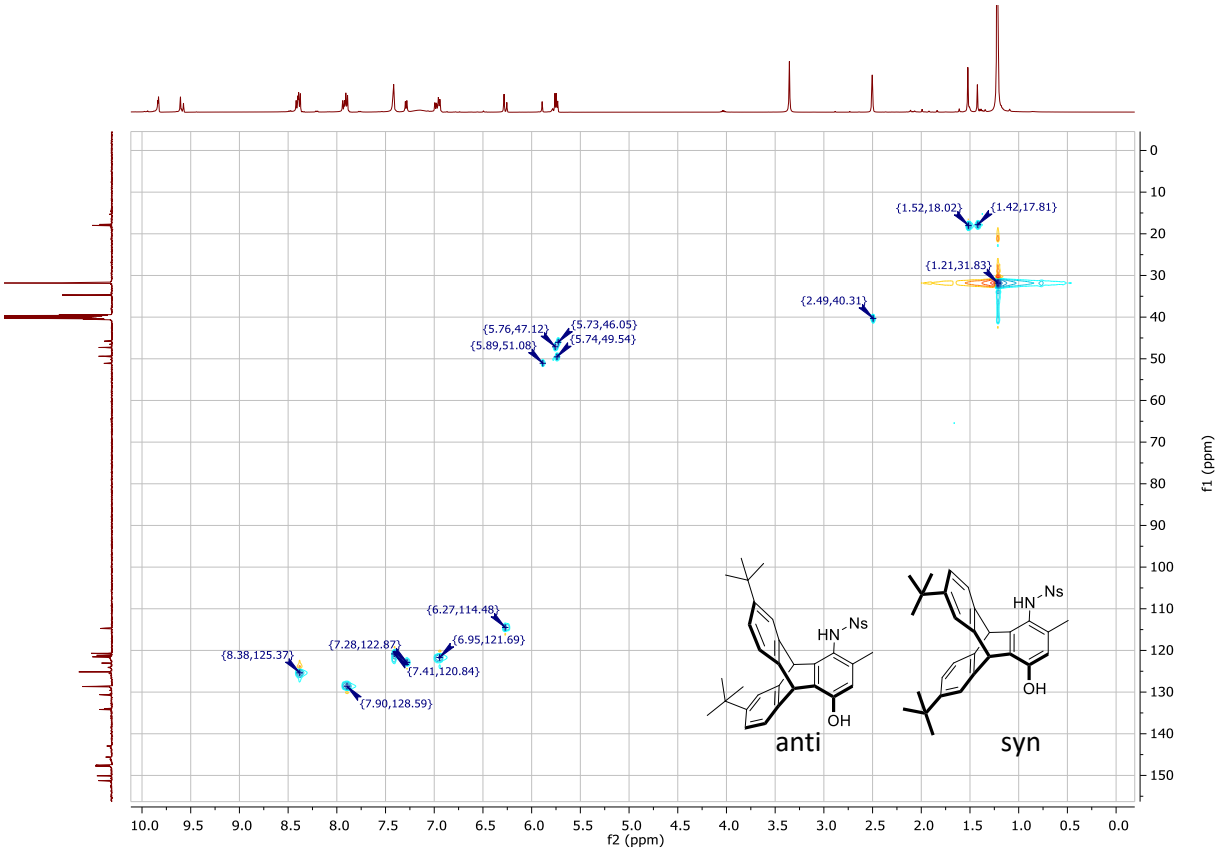


*Figure 31: HSQC-NMR of nosylated aminophenol (**4h**) in DMSO-d_6.*

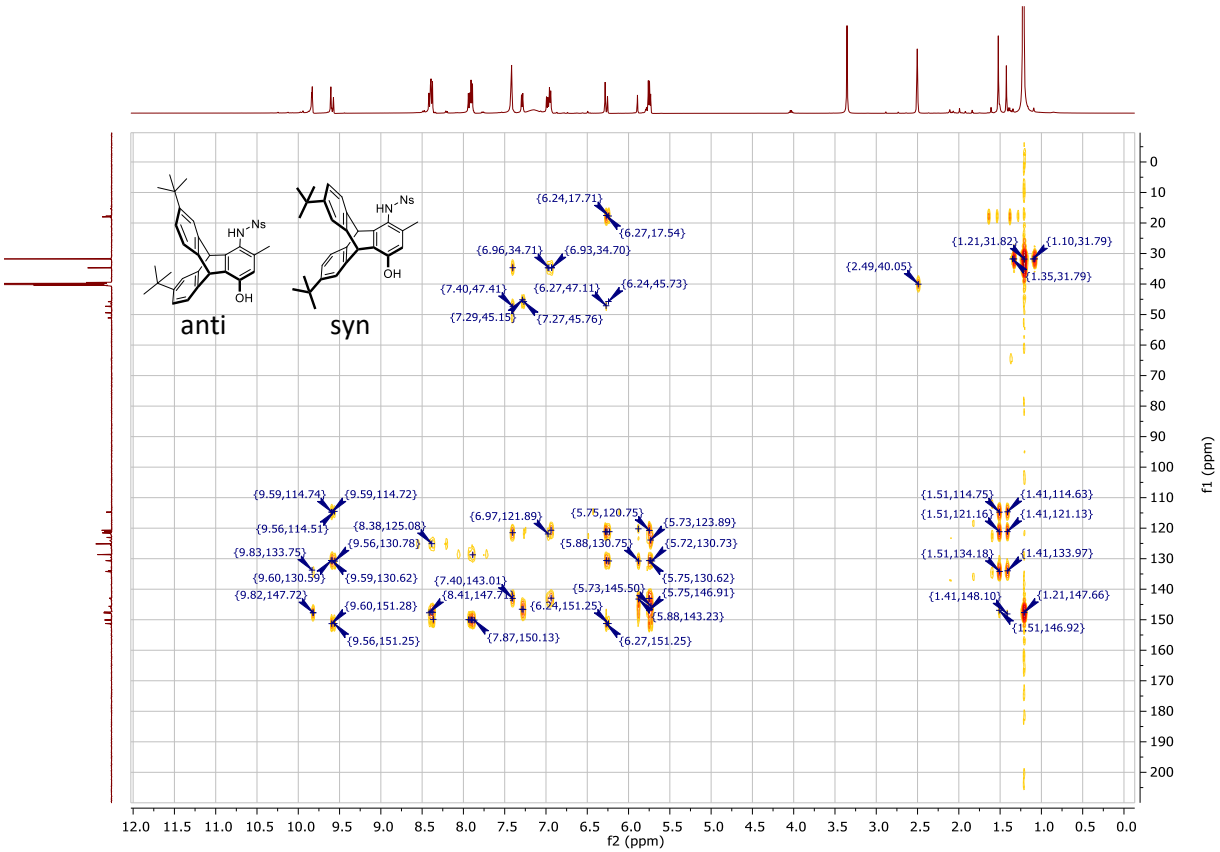


*Figure 32: HMBC-NMR of nosylated aminophenol (**4h**) in DMSO-d_6.*

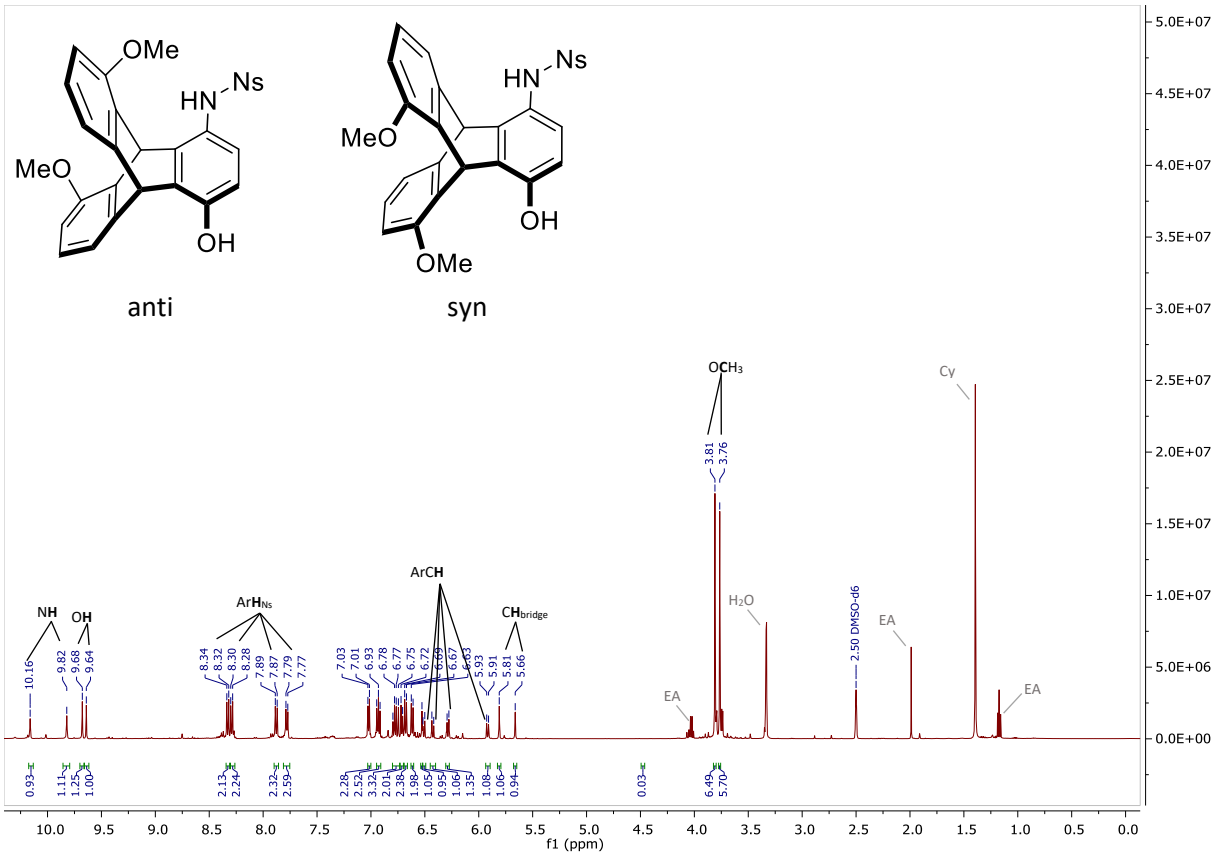


*Figure 33: [1]H-NMR of nosylated aminophenol (**4j**) in DMSO-d_6.*

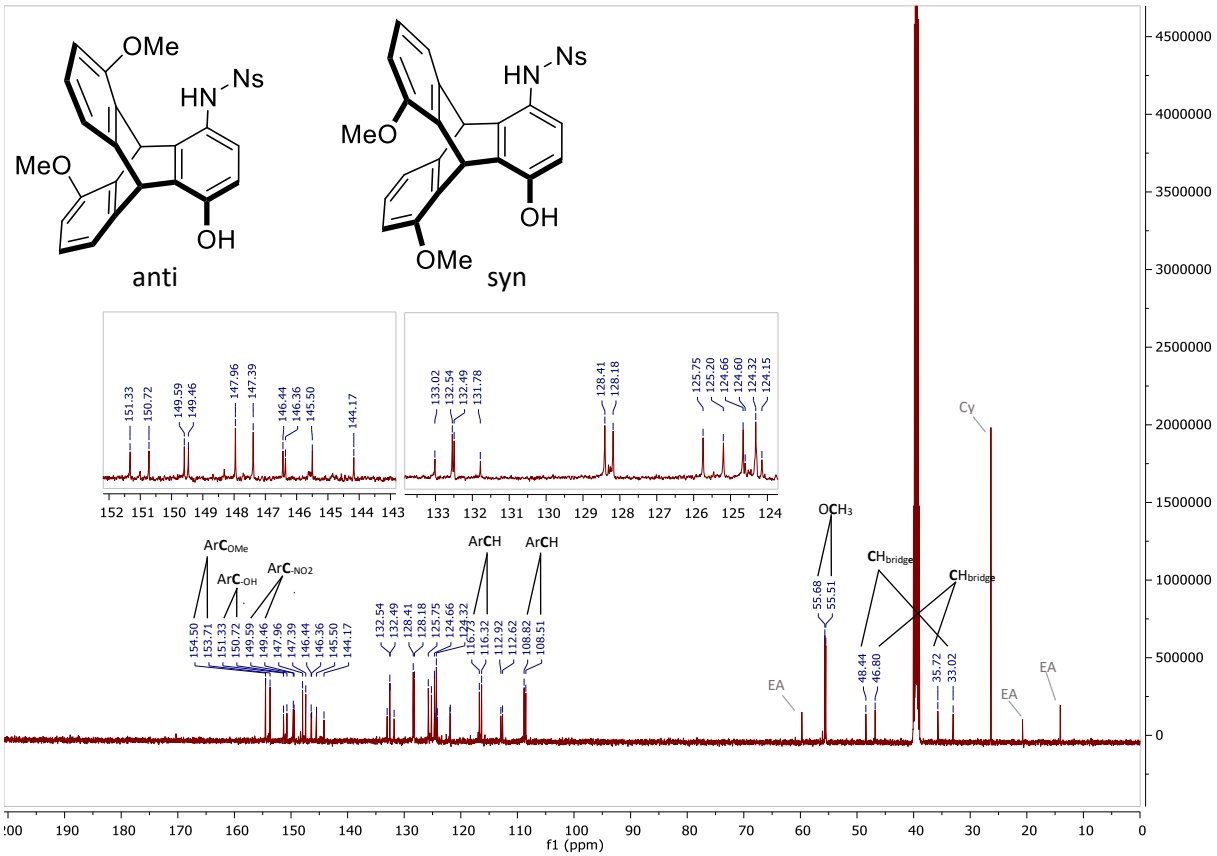


*Figure 34: [13]C-NMR of nosylated aminophenol (**4j**) in DMSO-d_6.*

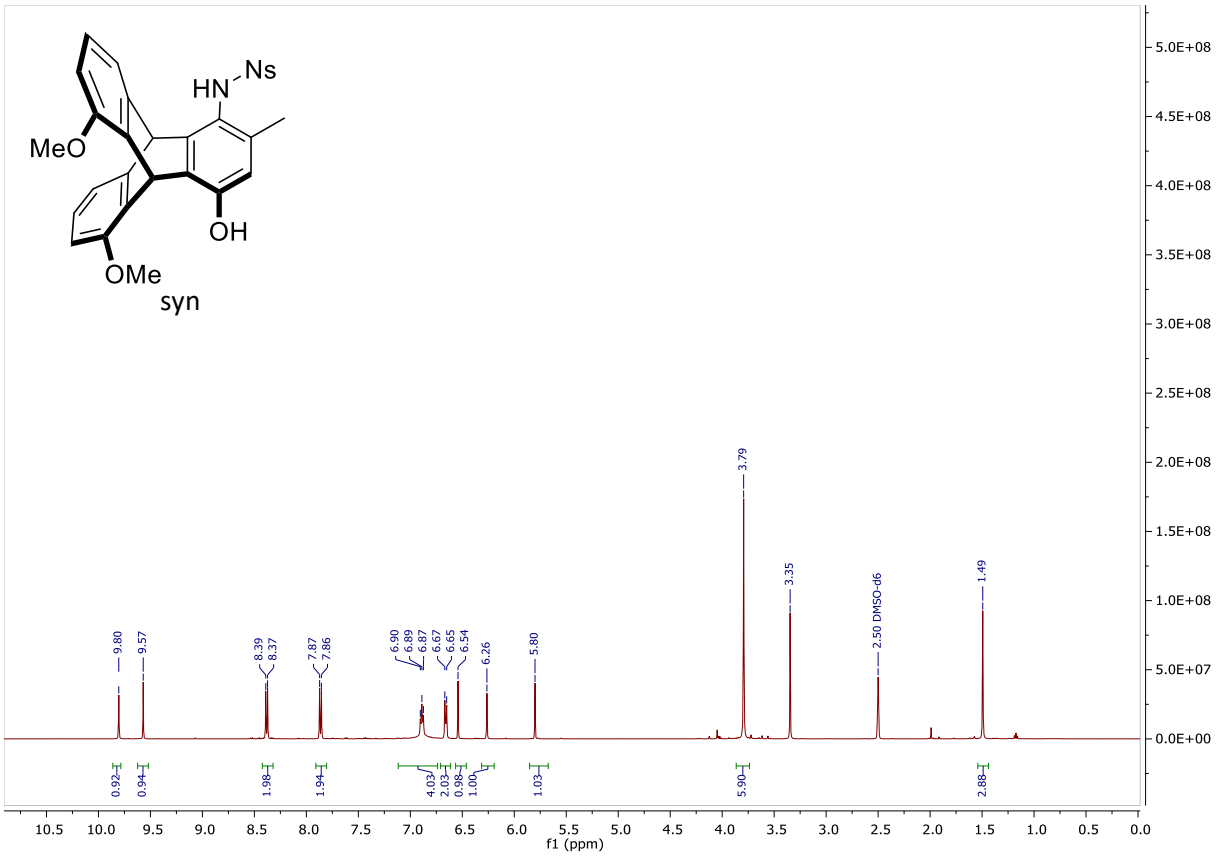


*Figure 35: [1]H-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

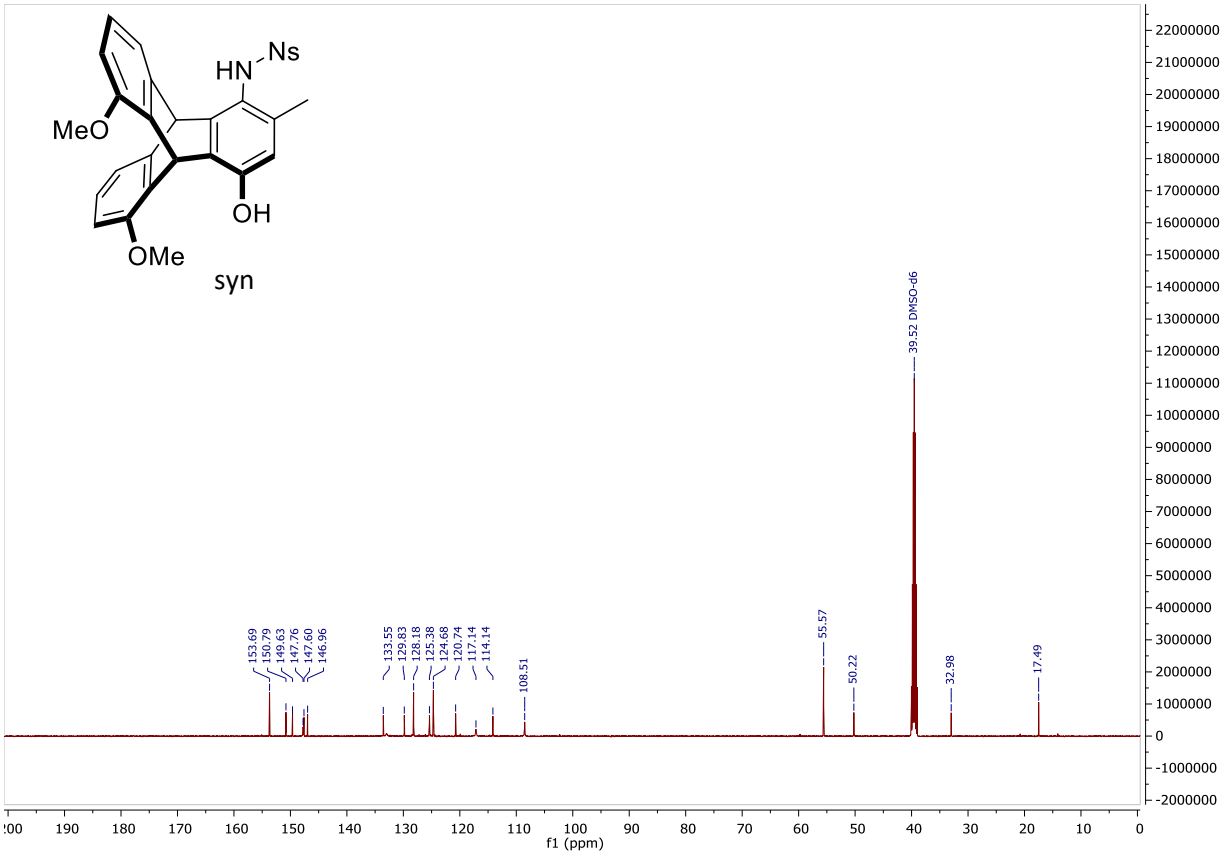


*Figure 36: [13]C-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

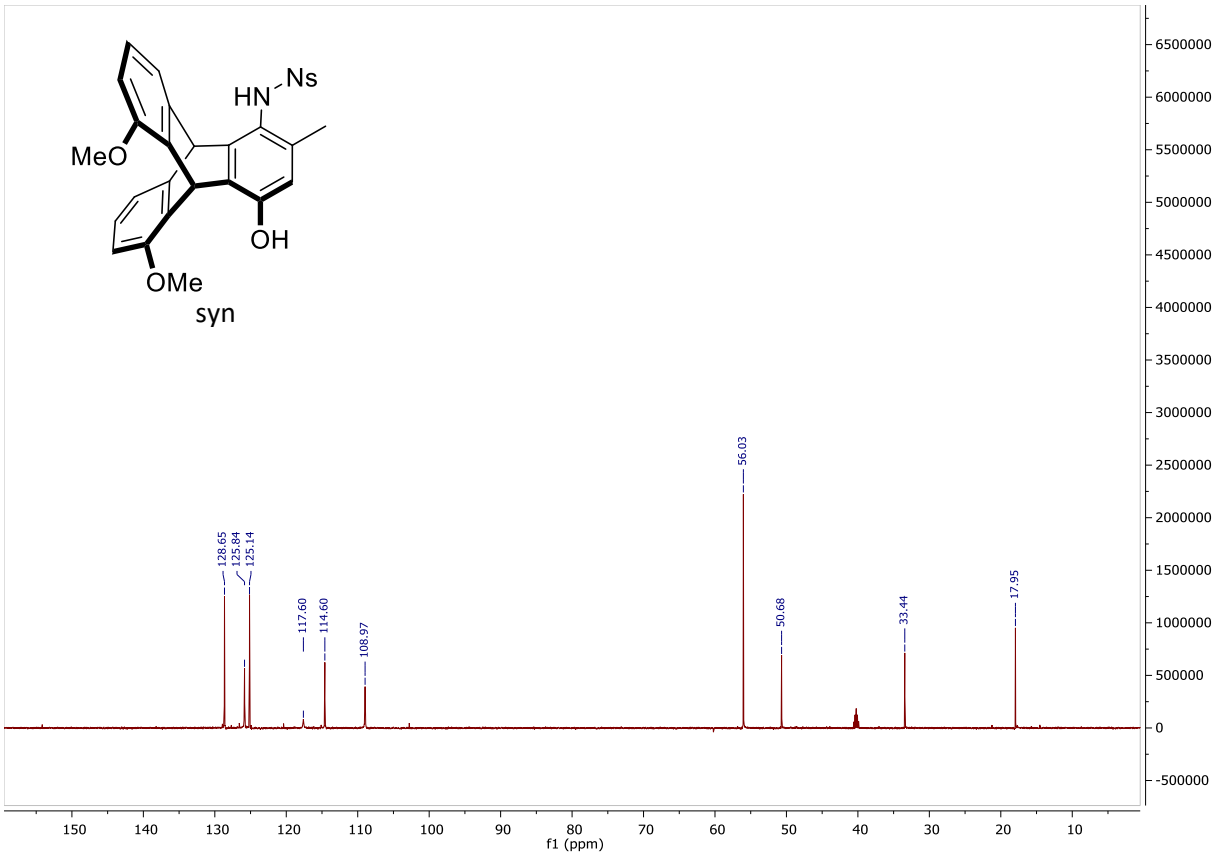


*Figure 37: DEPT-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

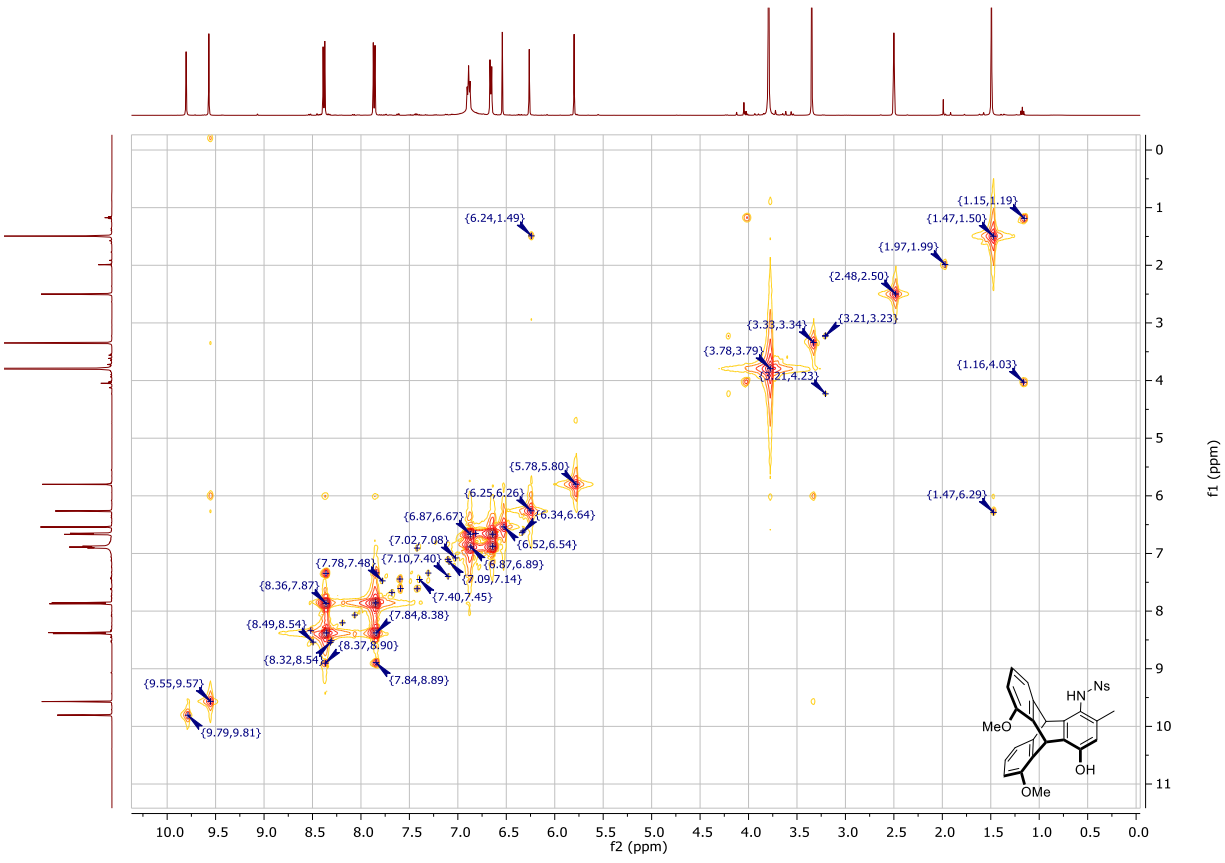


*Figure 38: ^{13}C-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

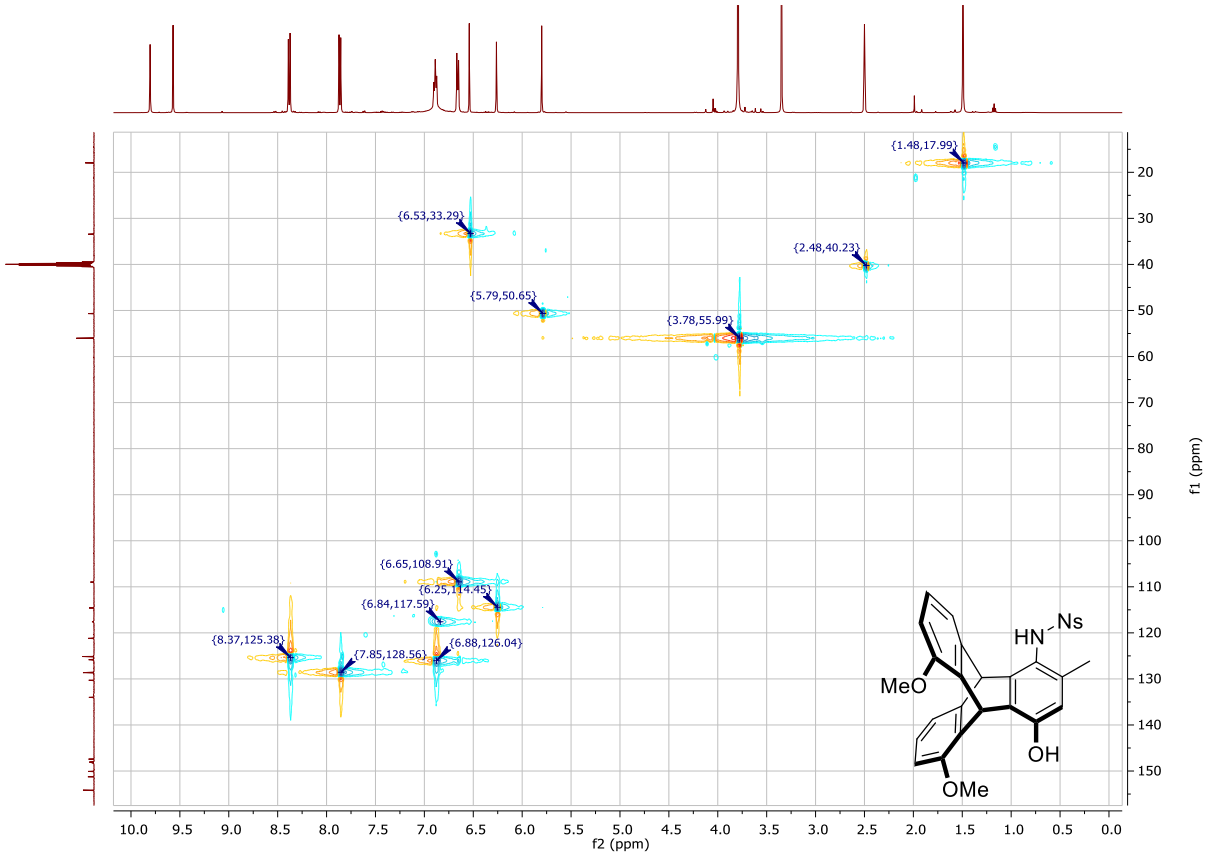


*Figure 39: ^{13}C-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

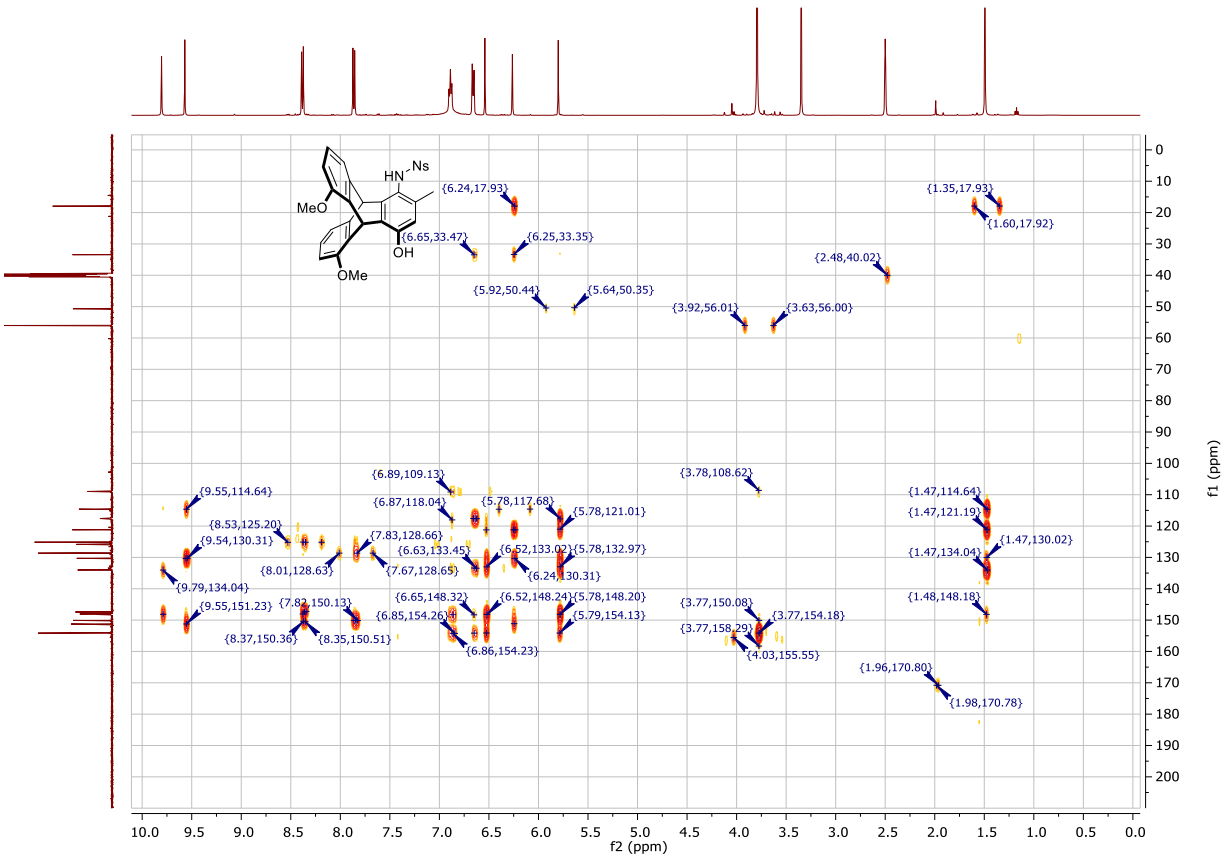


*Figure 40: ^{13}C-NMR of nosylated aminophenol (**4k**) in DMSO-d_6.*

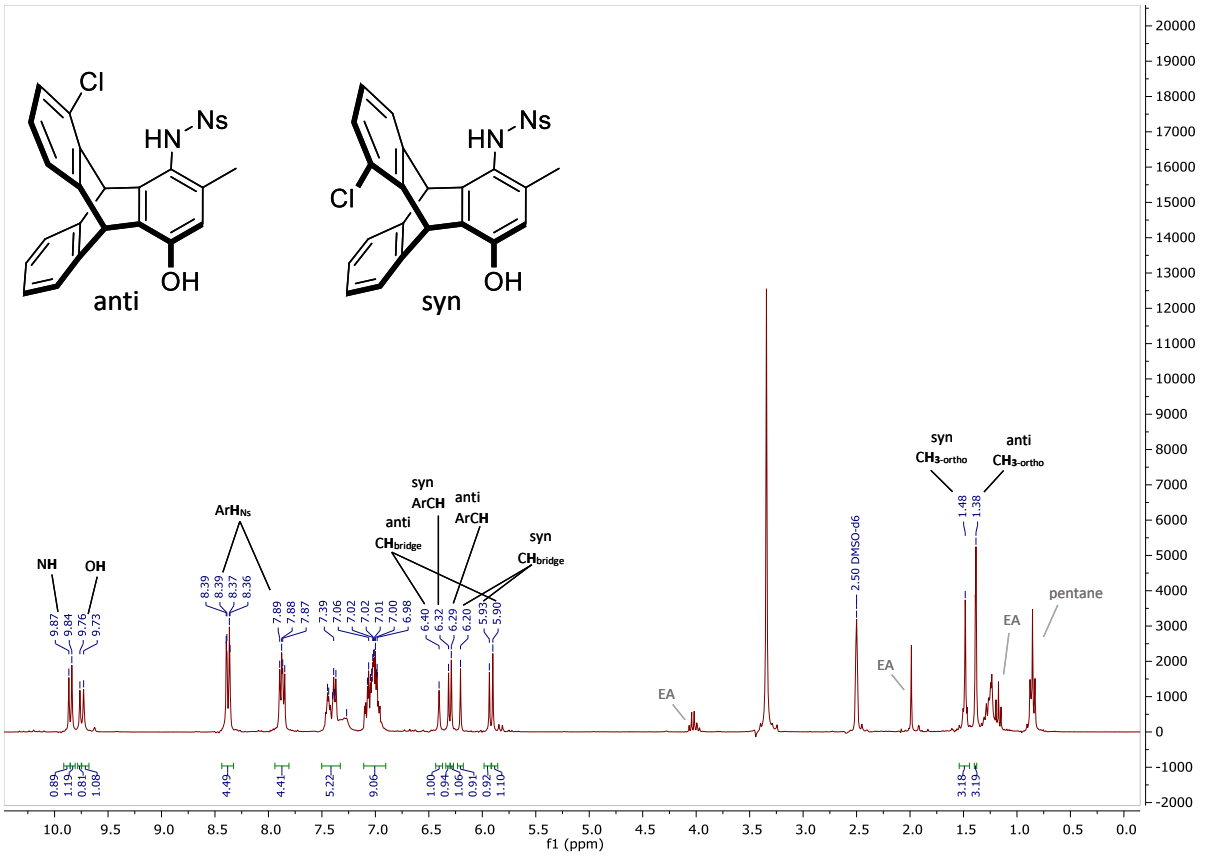


*Figure 41: [1]H-NMR of nosylated aminophenol (**4l**) in DMSO-d_6.*

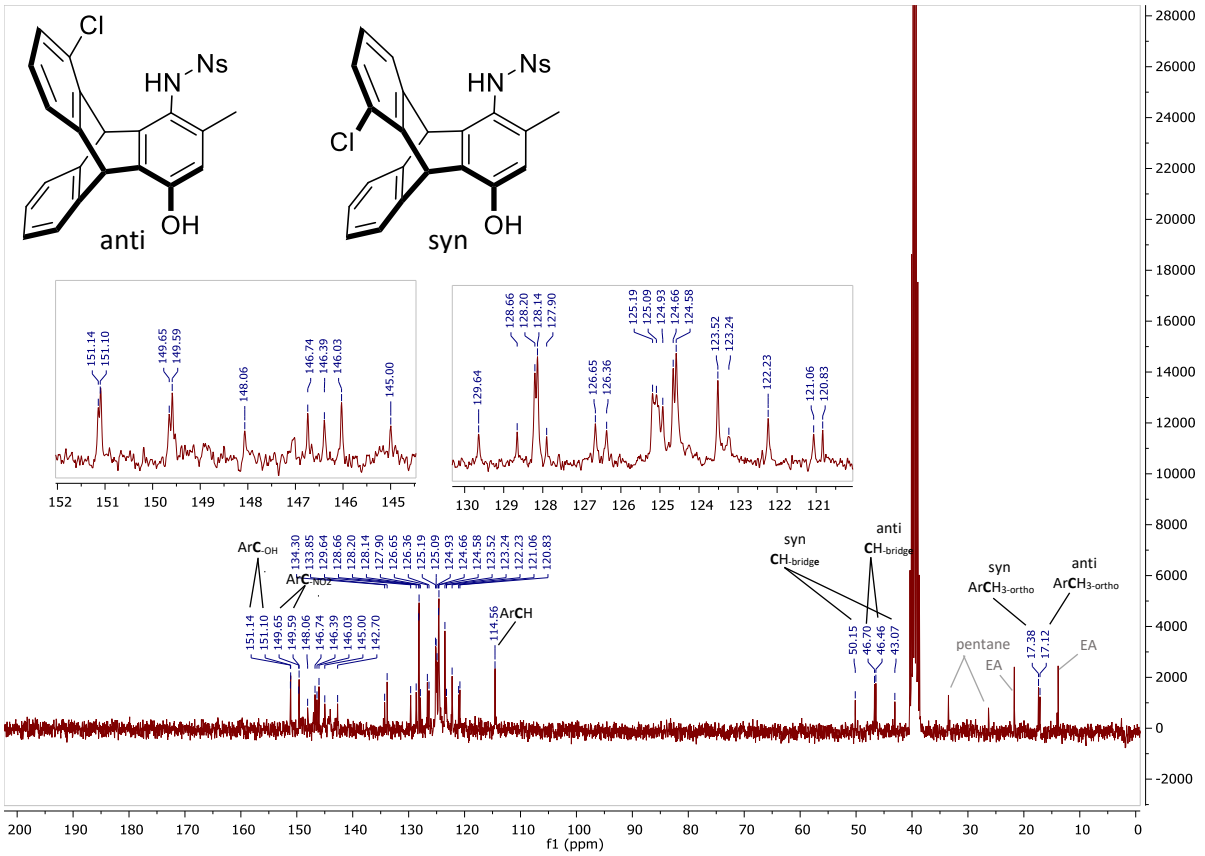


*Figure 42: [13]C-NMR of nosylated aminophenol (**4l**) in DMSO-d_6.*

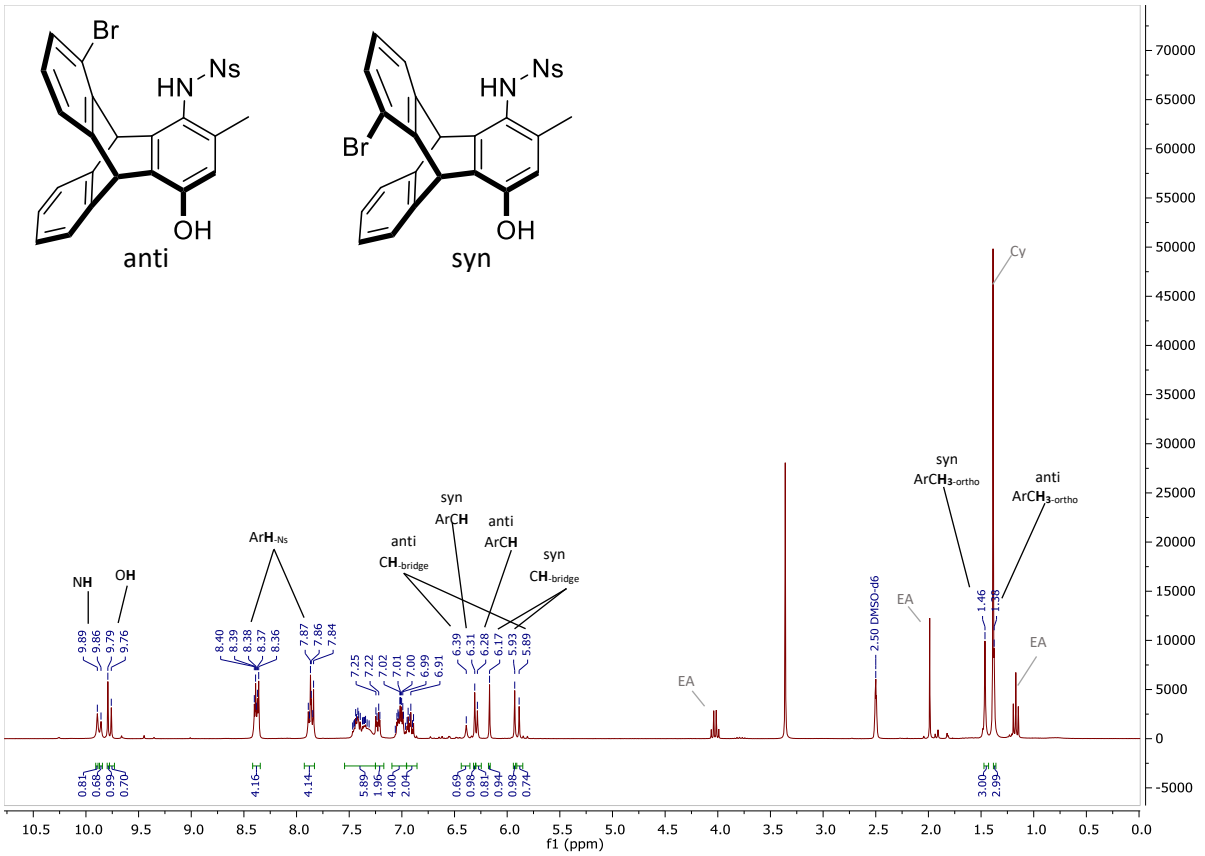


*Figure 43: [1]H-NMR of nosylated aminophenol (**4m**) in DMSO-d_6.*

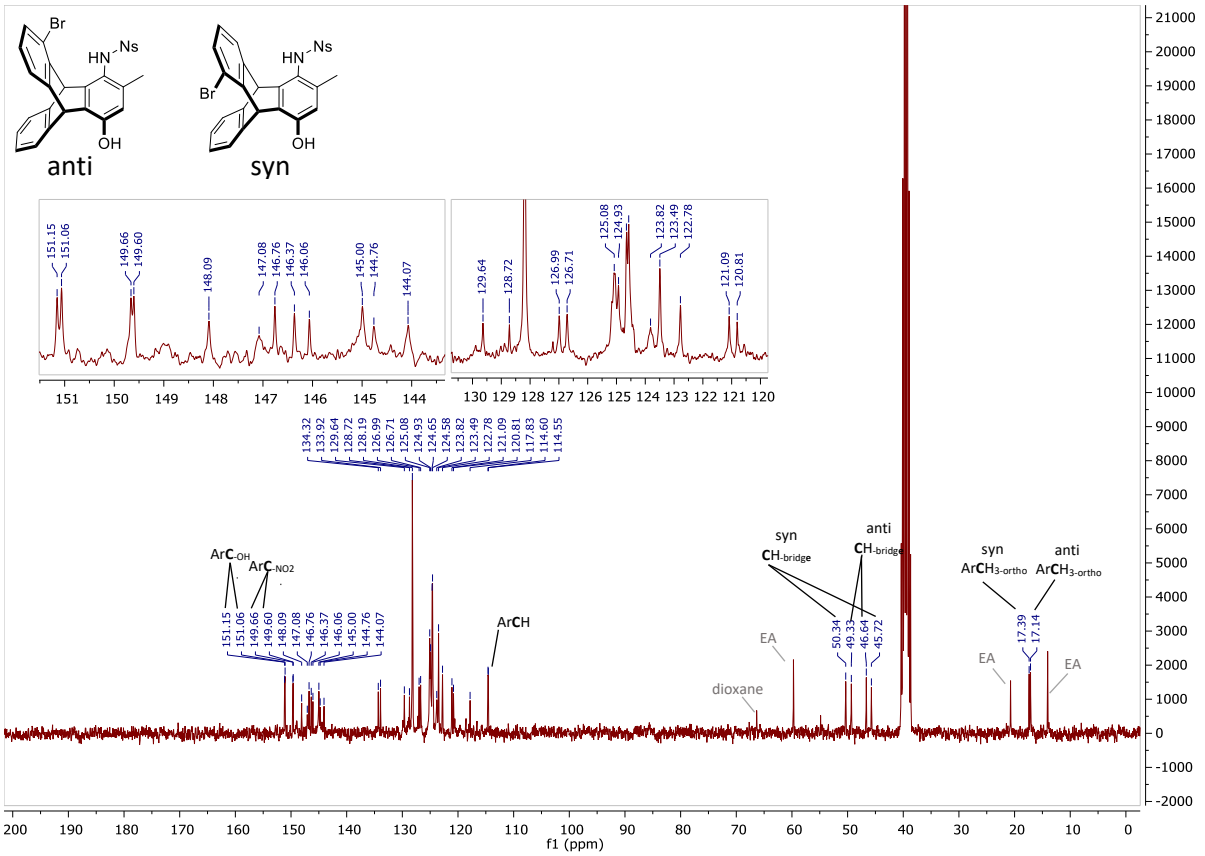


*Figure 44: [13]C-NMR of nosylated aminophenol (**4m**) in DMSO-d_6.*

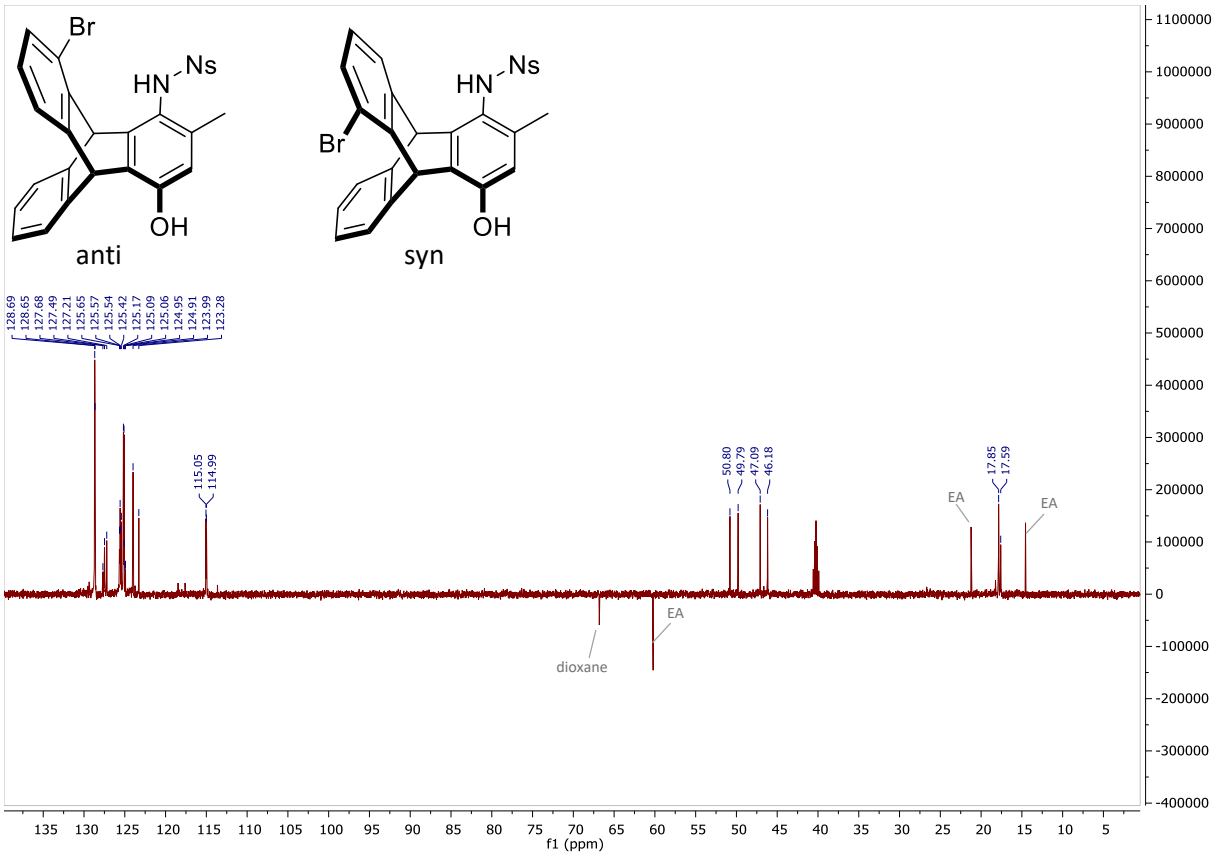


*Figure 45: DEPT-NMR of nosylated aminophenol (**4m**) in DMSO-d_6.*

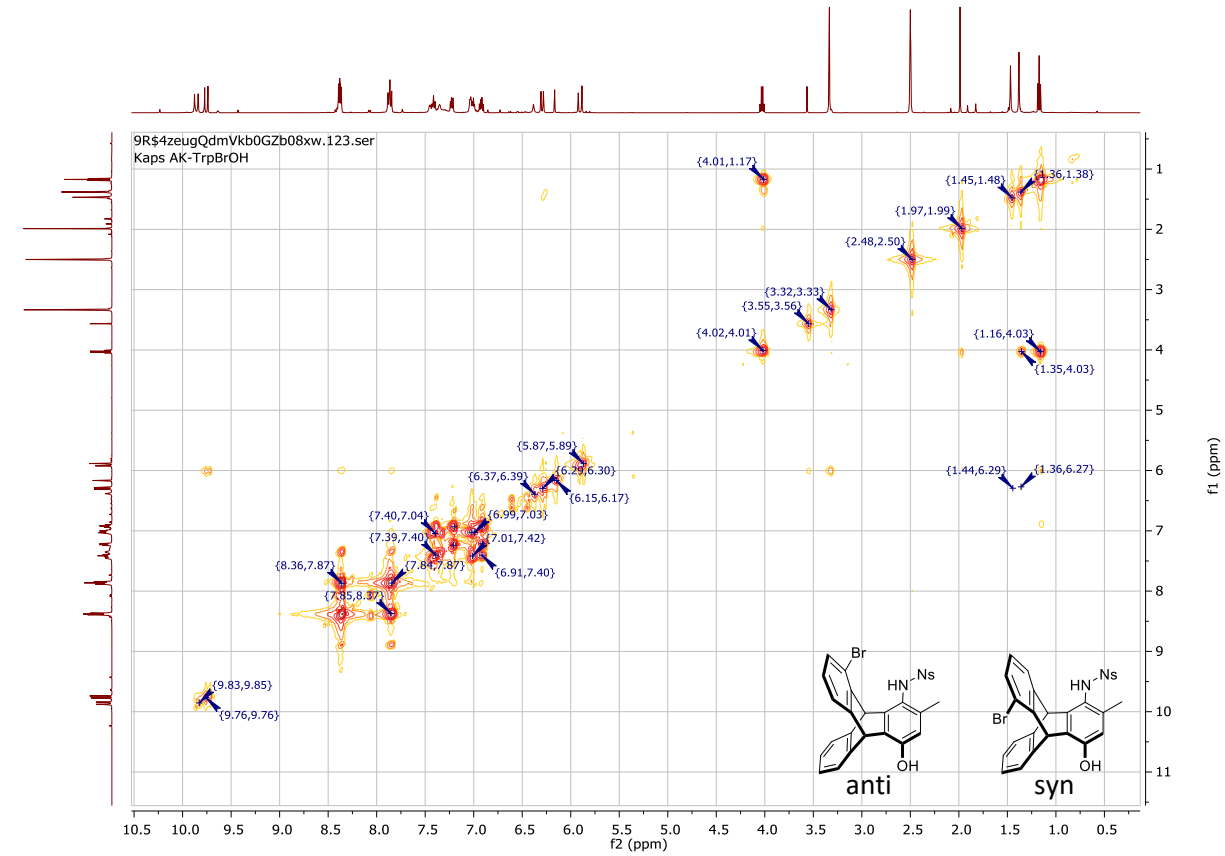


*Figure 46: COSY NMR of nosylated aminophenol (**4m**) in DMSO-d_6.*

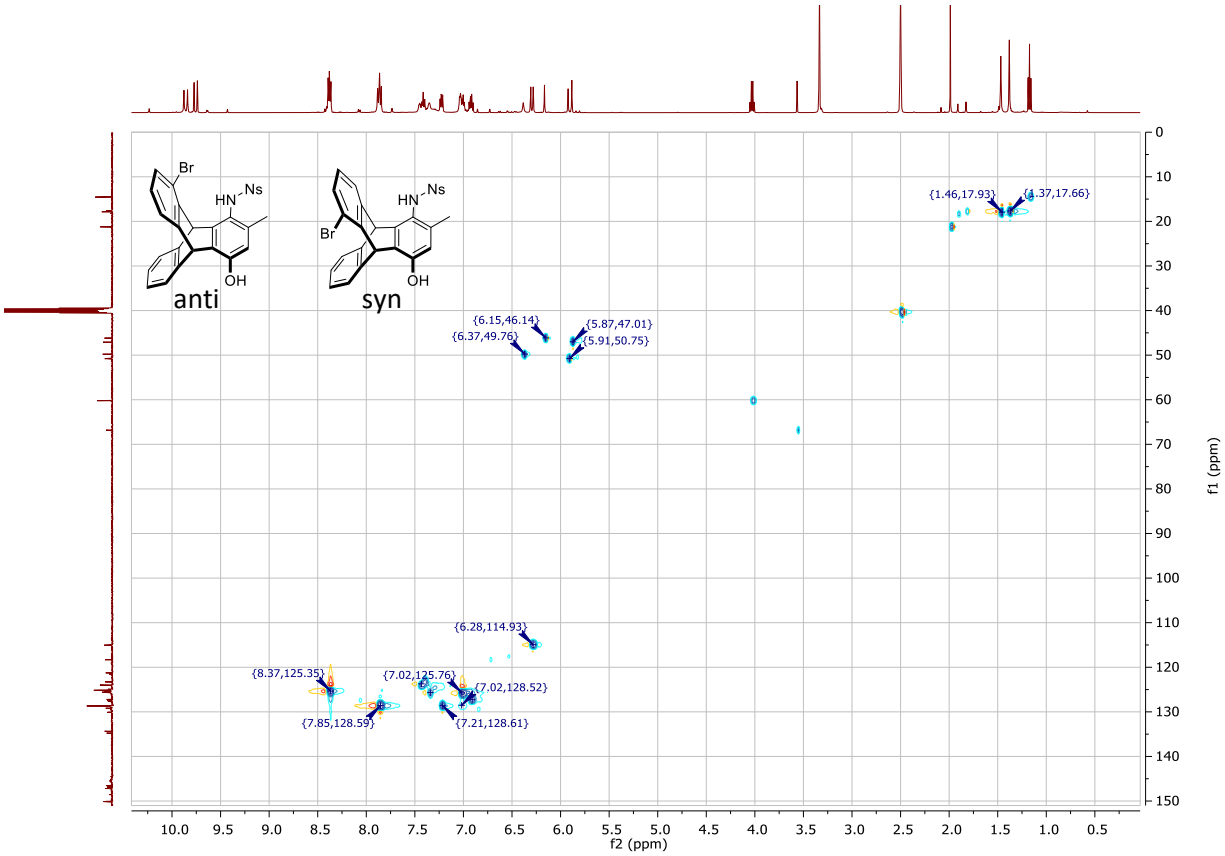


*Figure 47: HSQC of nosylated aminophenol (**4m**) in DMSO-d_6.*

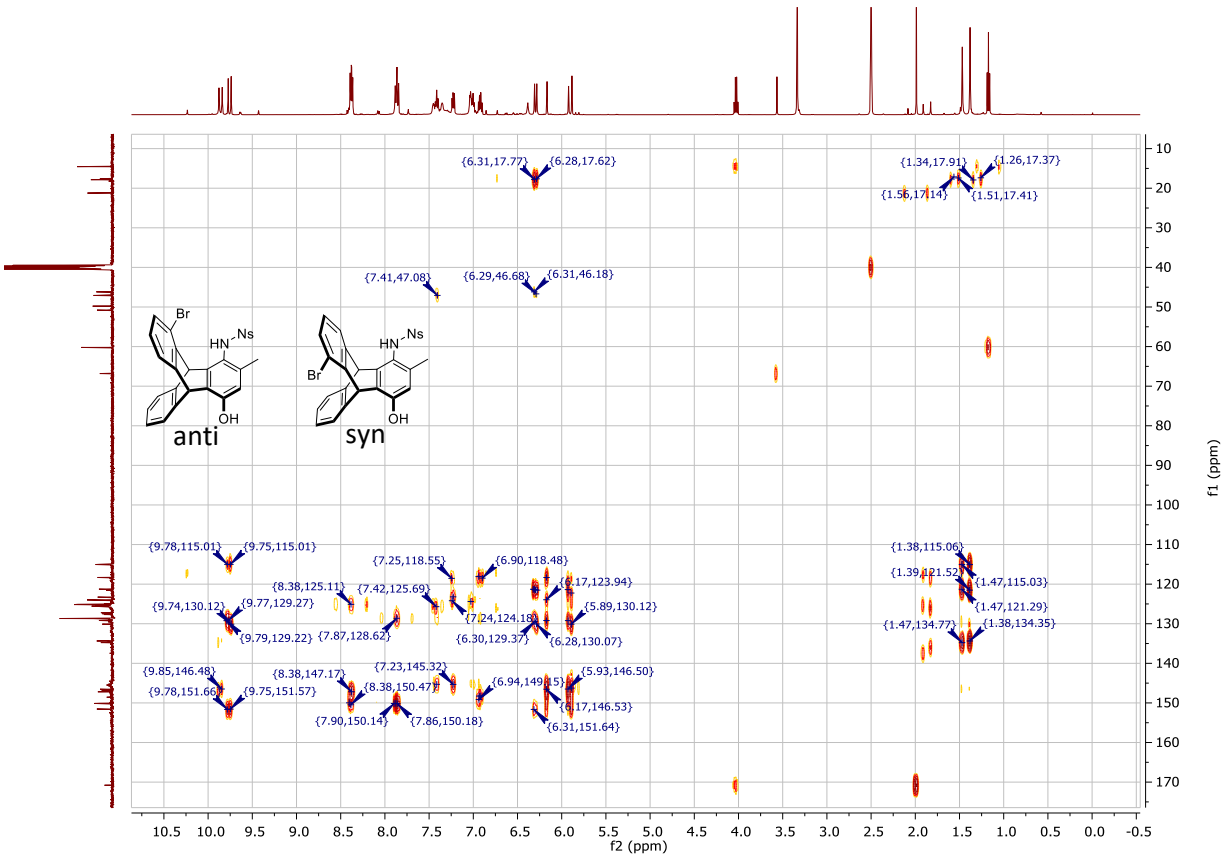


*Figure 48: HMBC of nosylated aminophenol (**4m**) in DMSO-d_6.*

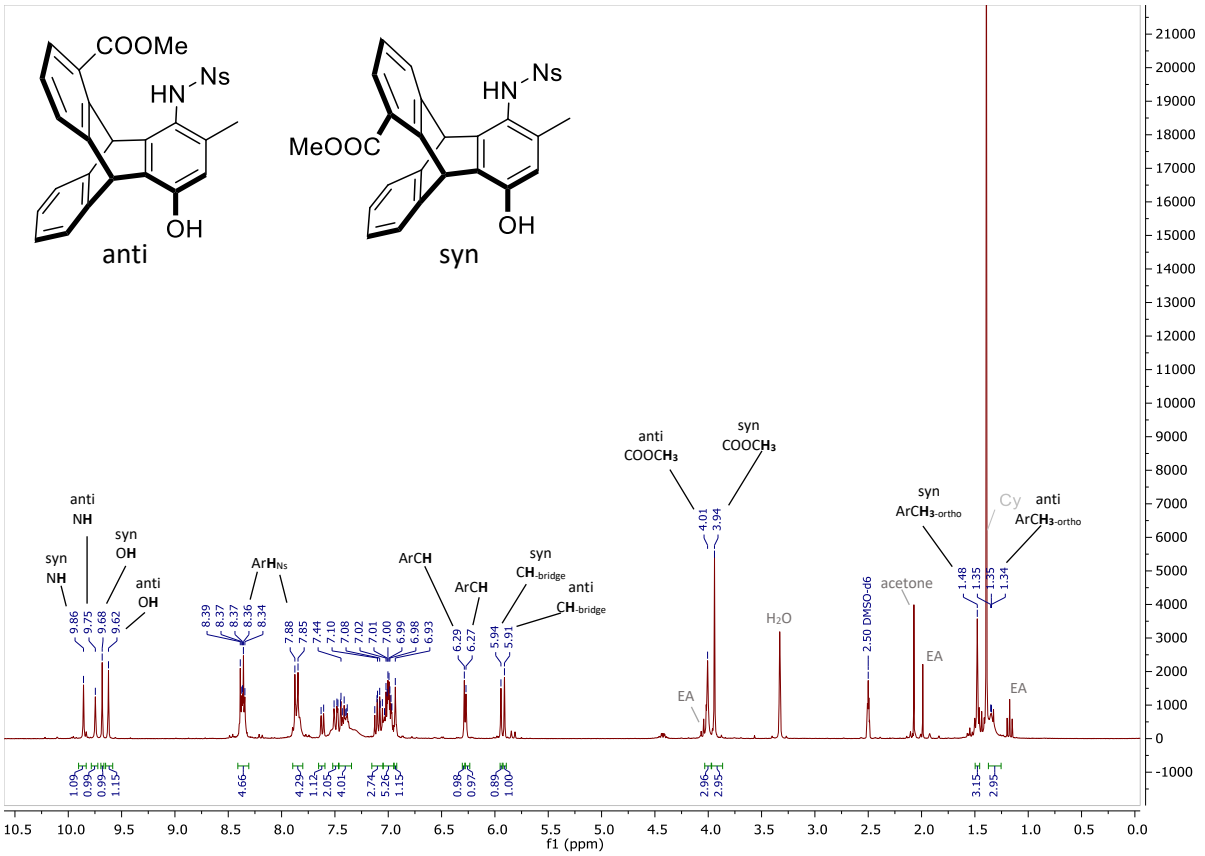


*Figure 49: ^{1}H-NMR of nosylated aminophenol (**4n**) in DMSO-d_6.*

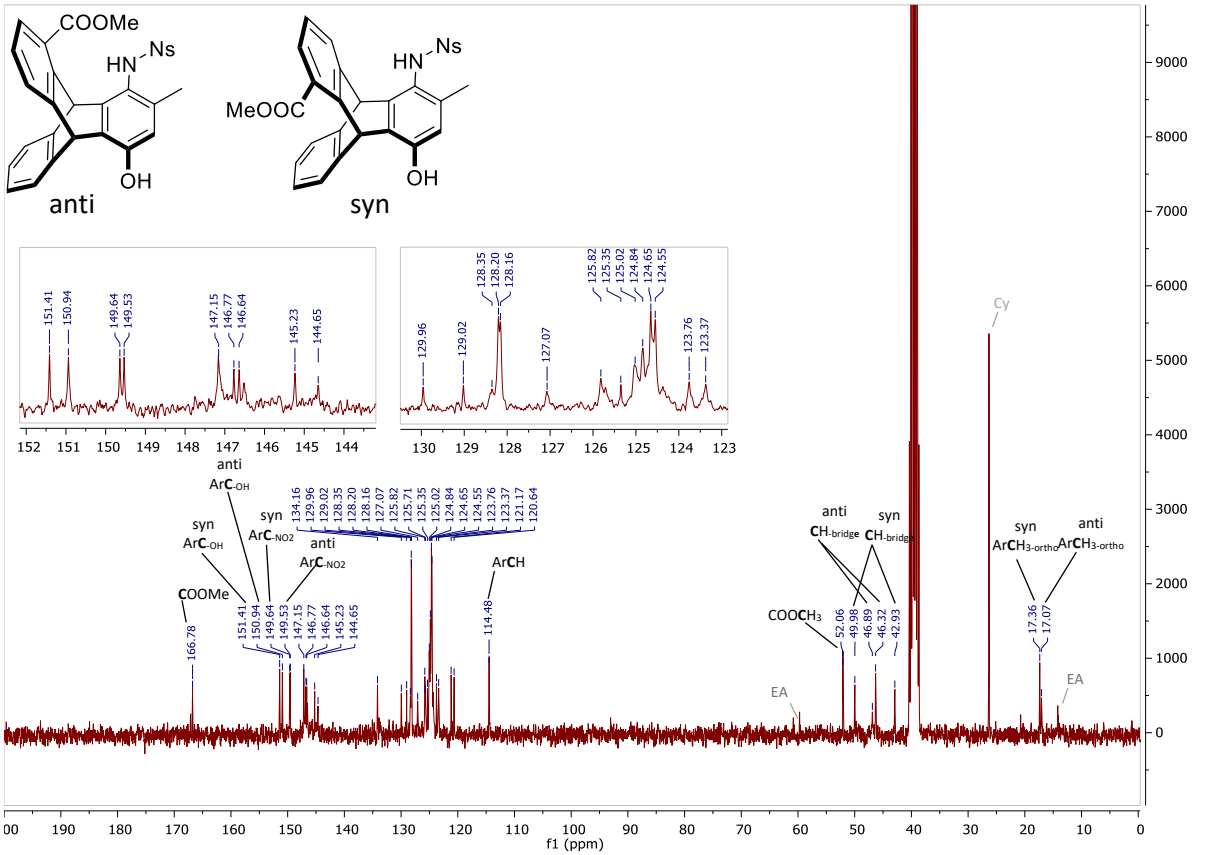


*Figure 50: ^{13}C-NMR of nosylated aminophenol (**4n**) in DMSO-d_6.*

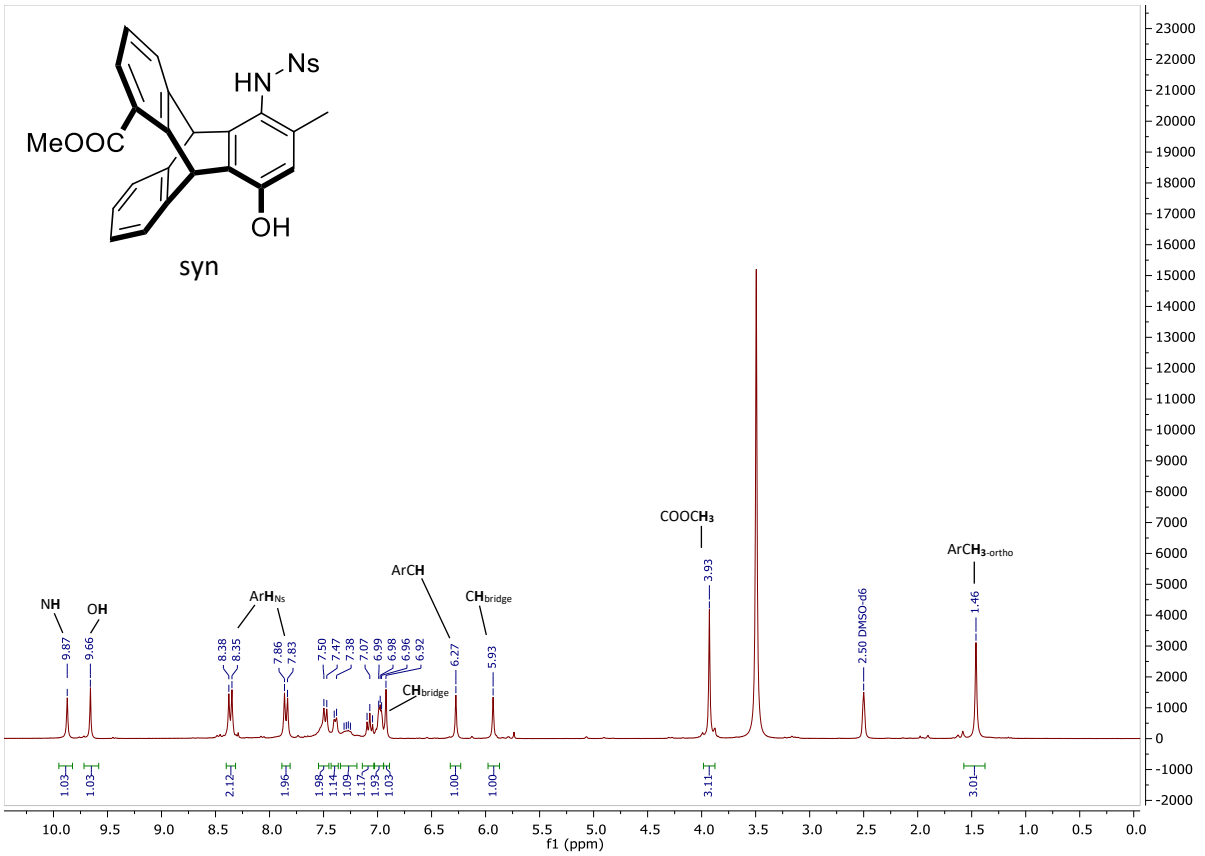


*Figure 51: [1]H-NMR of nosylated aminophenol (**4n**) in DMSO-d6.*

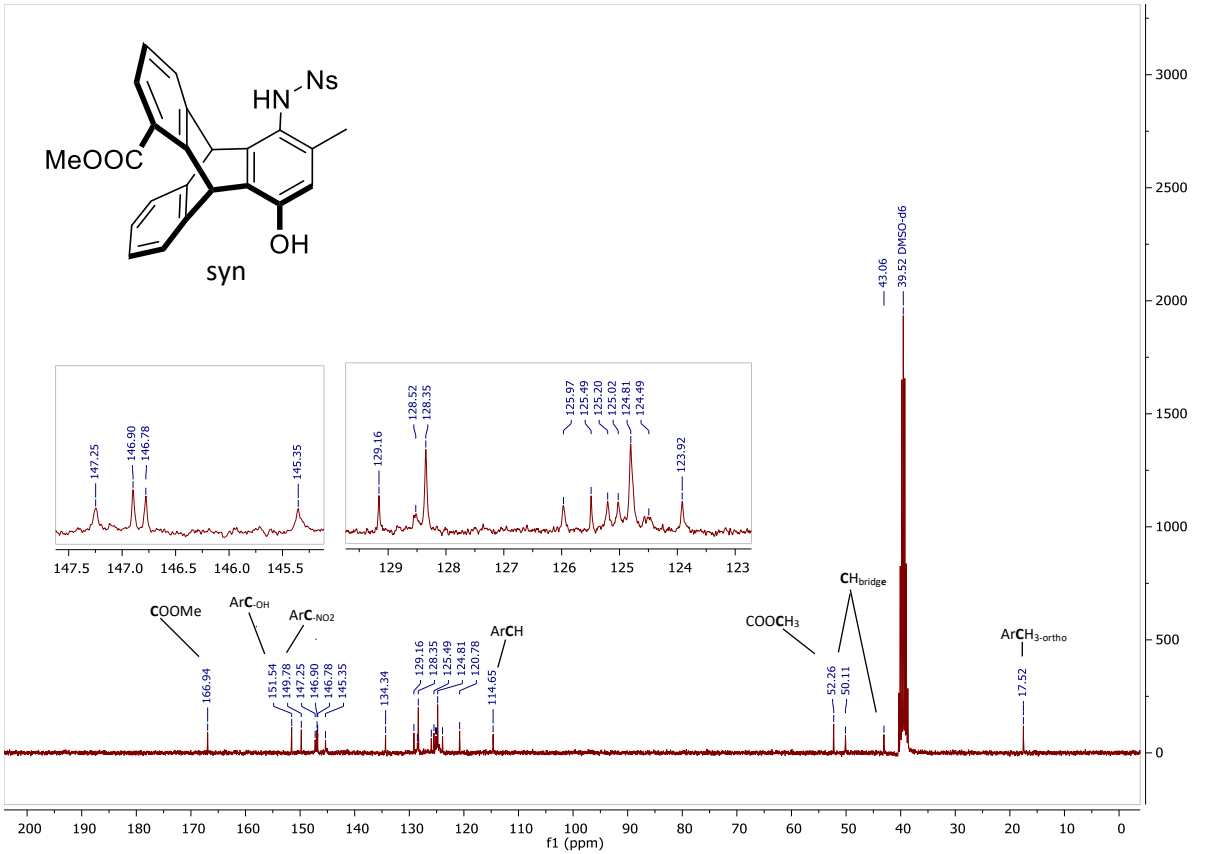


*Figure 52: [13]C-NMR of nosylated aminophenol (**4n**) in DMSO-d6.*

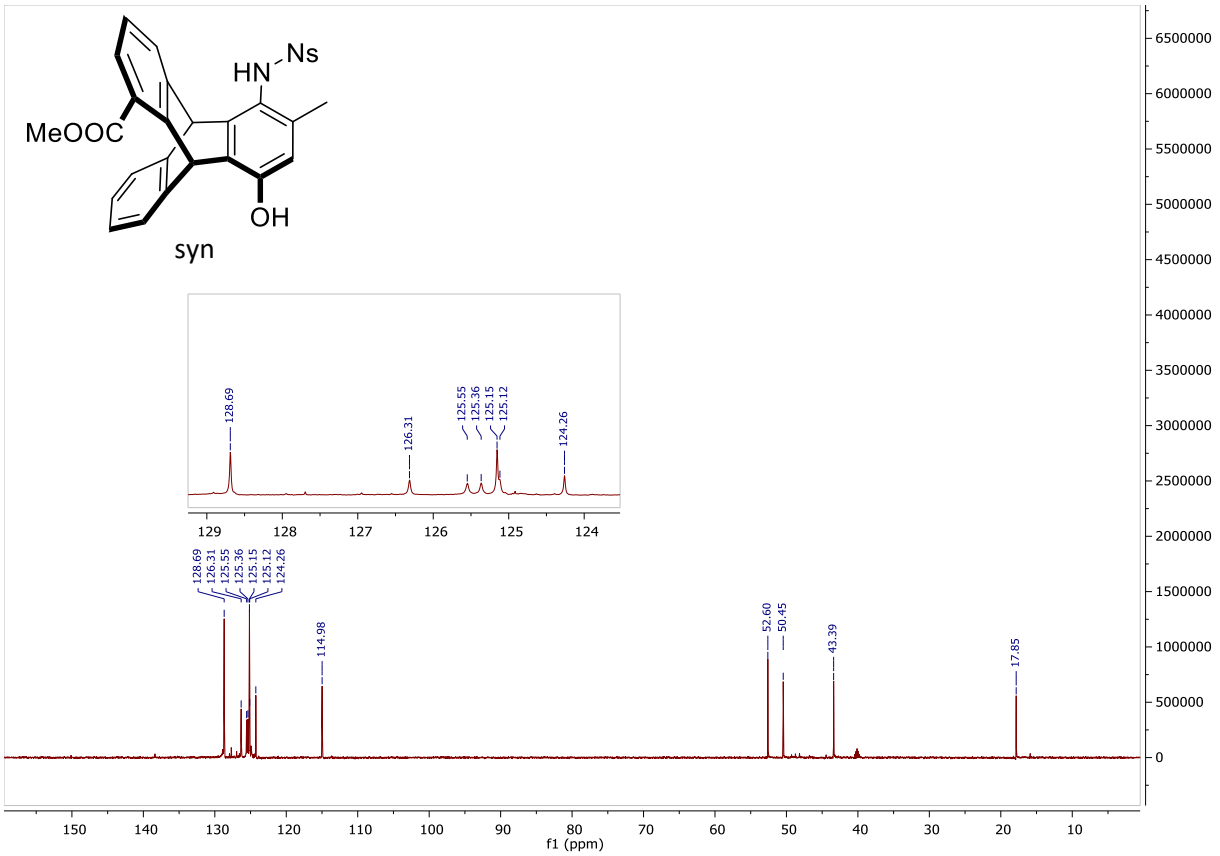


*Figure 53: DEPT-NMR of nosylated aminophenol (**4n**) in DMSO-d_6.*

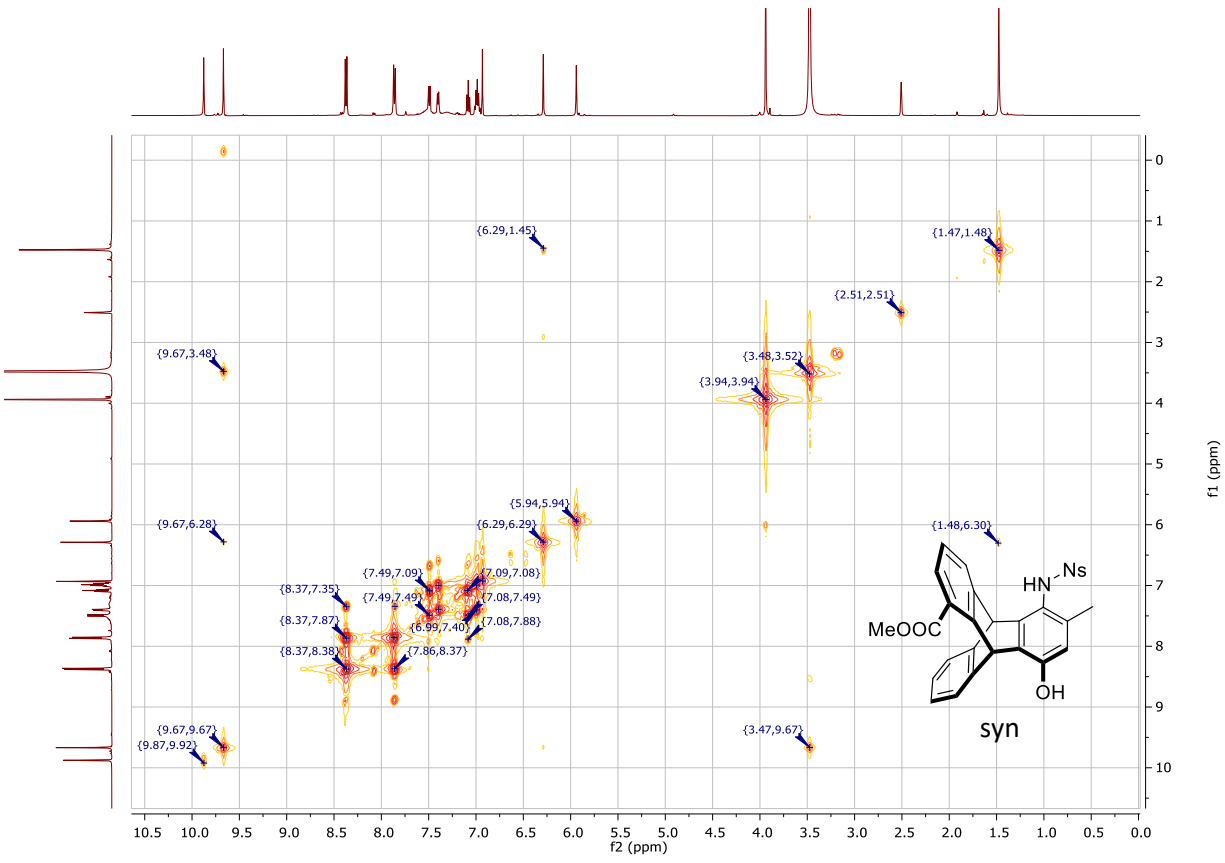


*Figure 54: COSY of nosylated aminophenol (**4n**) in DMSO-d_6.*

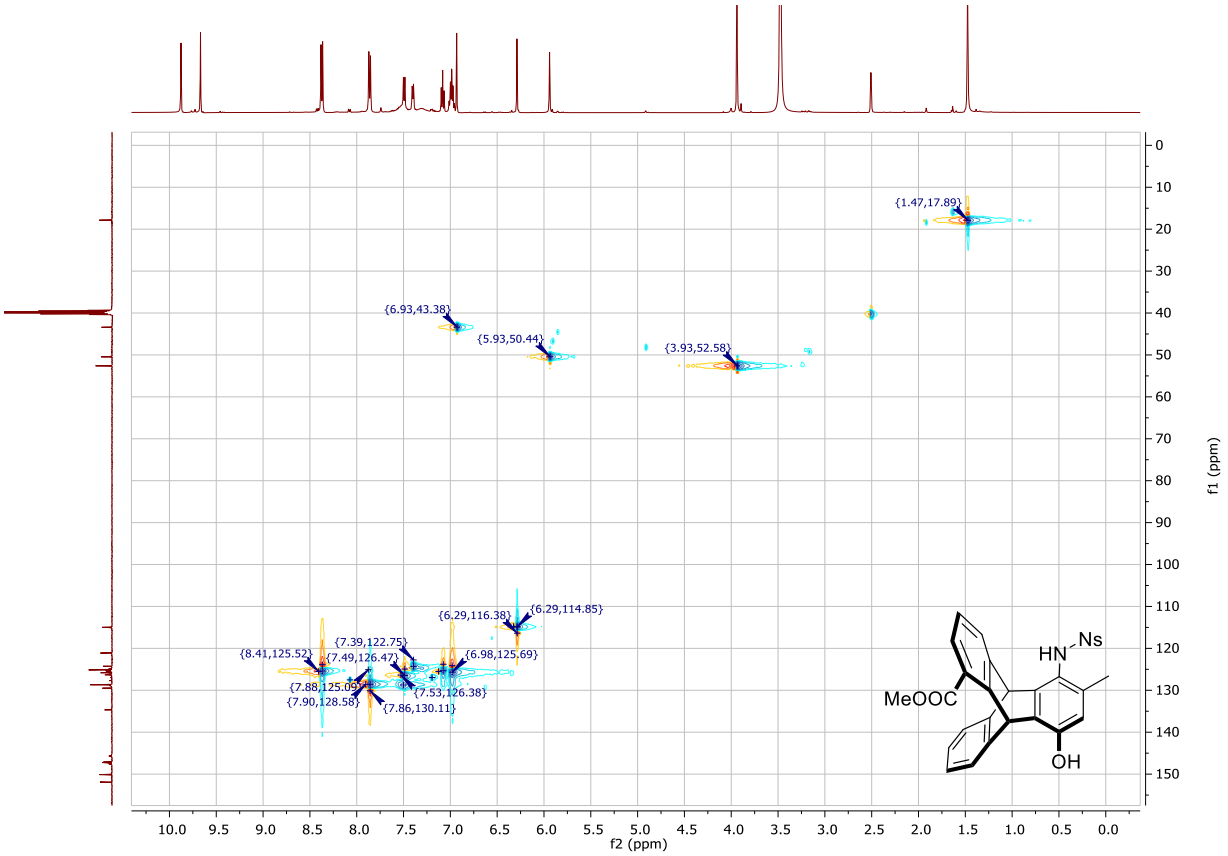


*Figure 55: HSQC of nosylated aminophenol (**4n**) in DMSO-d_6.*

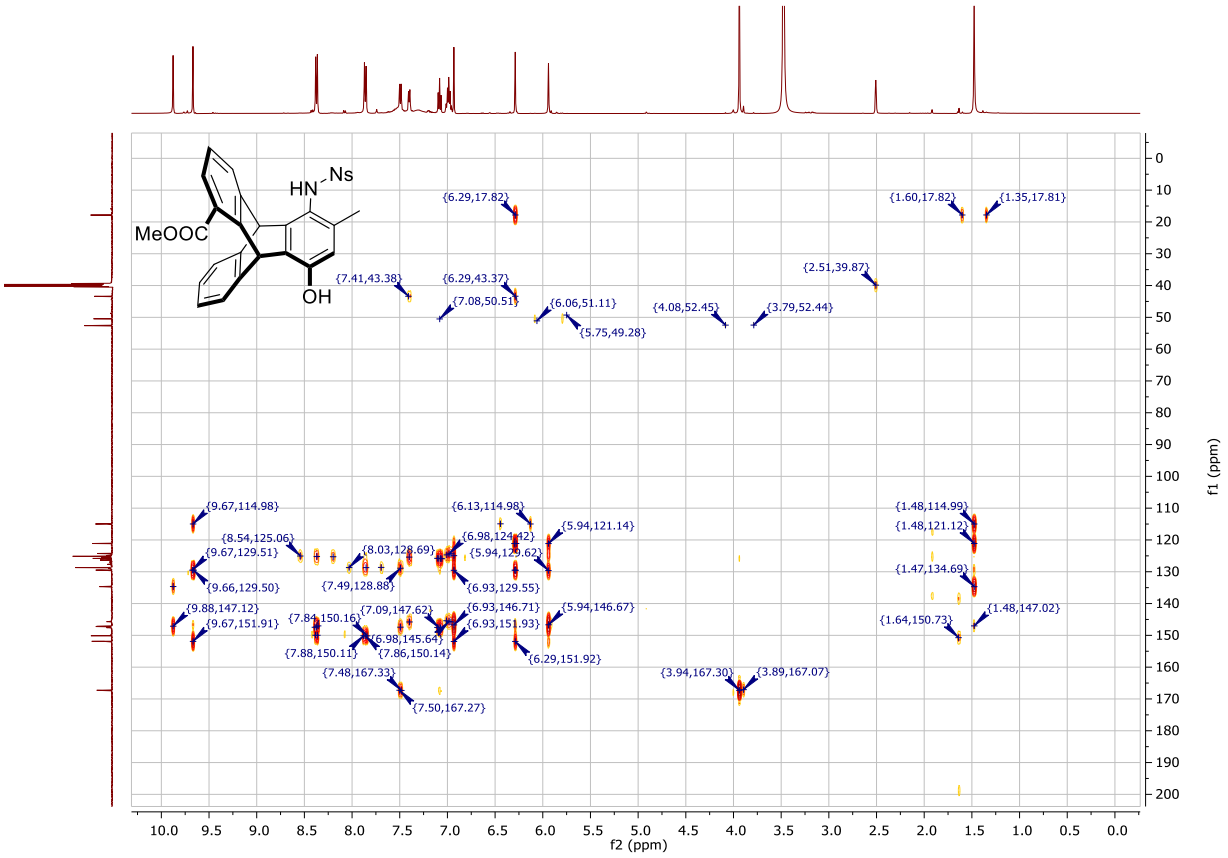


*Figure 56: HMBC of nosylated aminophenol (**4n**) in DMSO-d_6.*

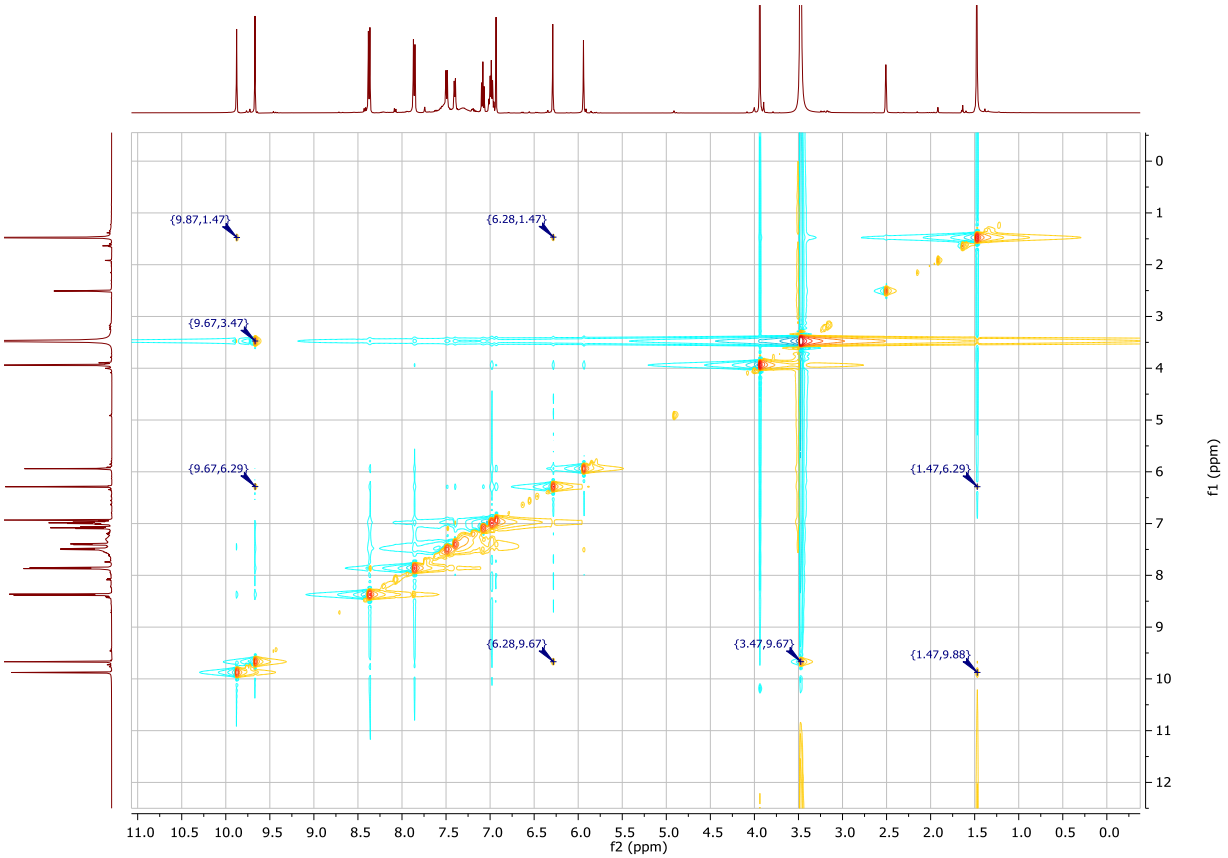


*Figure 57: NOESY of nosylated aminophenol (**4n**) in DMSO-d_6.*

N/O-Alkylated aminophenols (nosyl-protected)

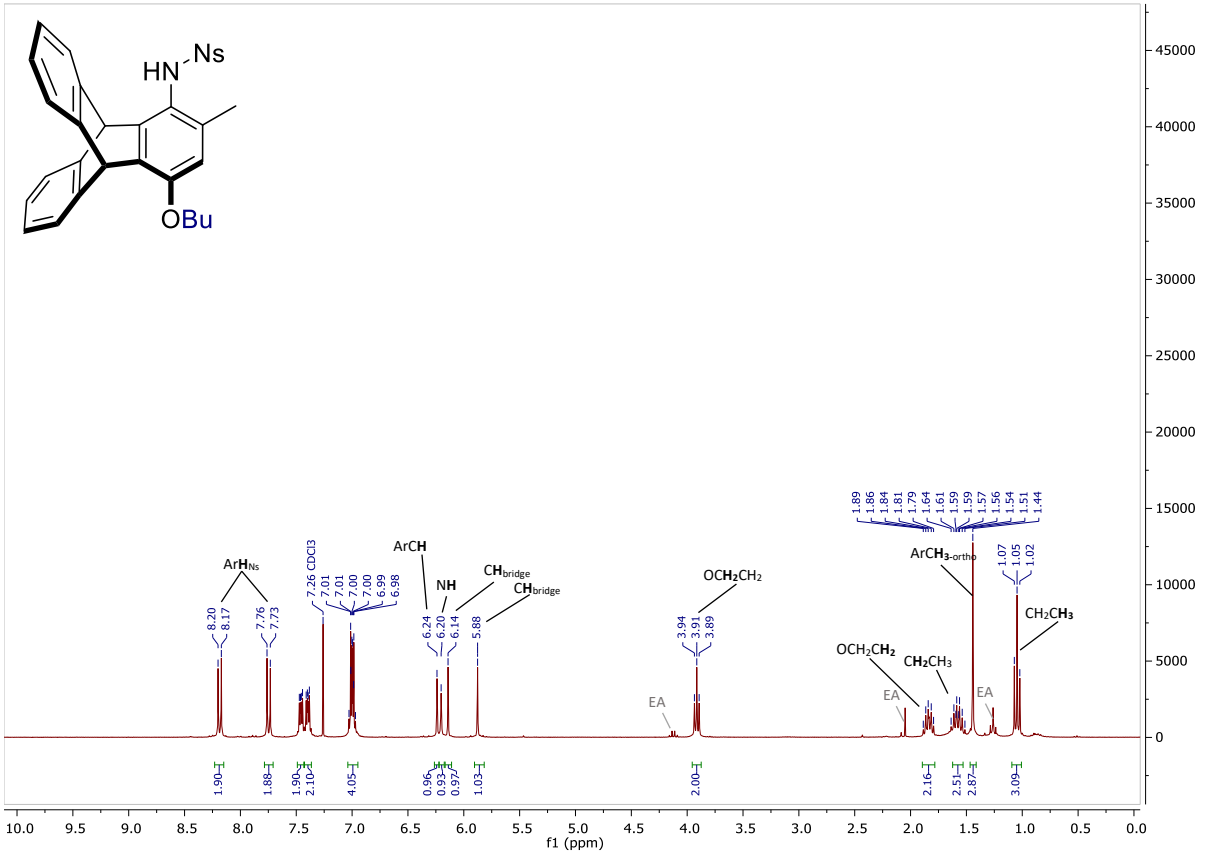


*Figure 58: ^{1}H-NMR of O-alkylated aminophenol (nosyl protected) (**5a**) in $CDCl_3$.*

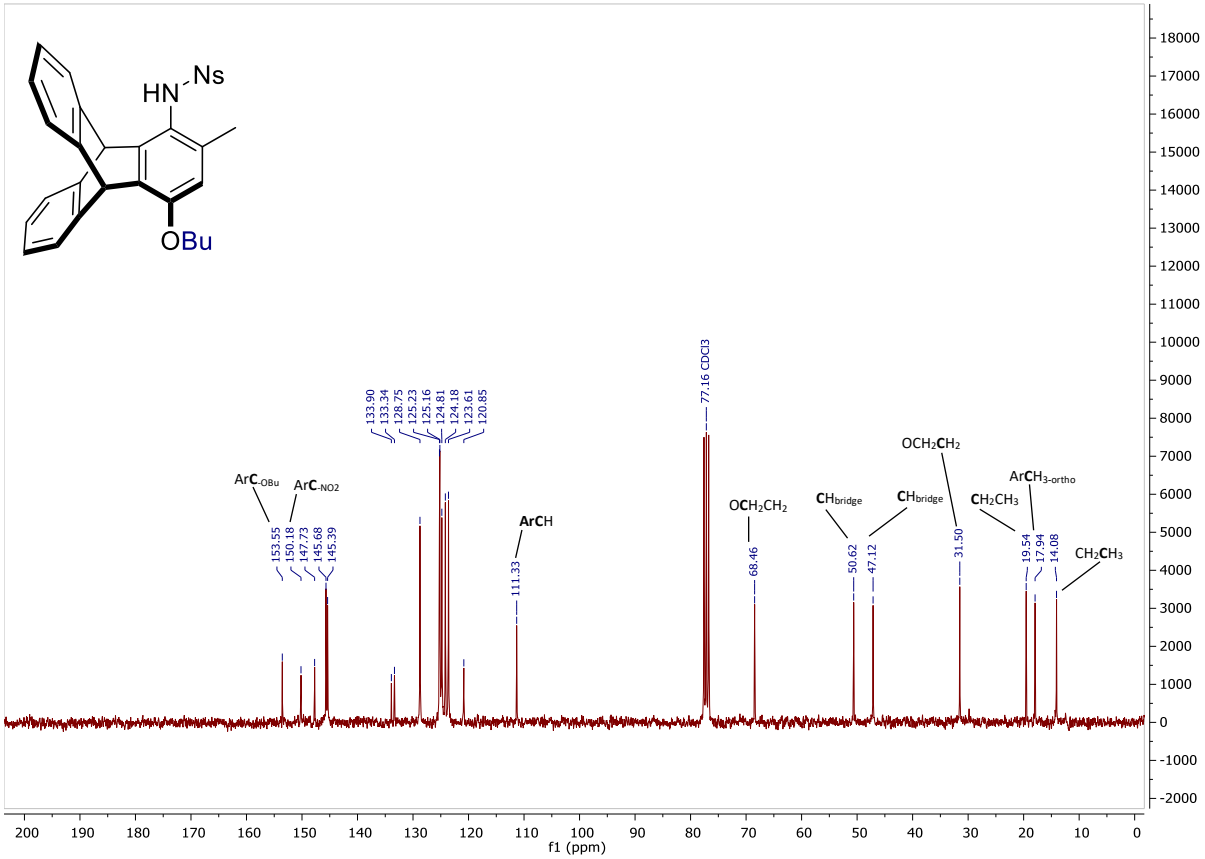


*Figure 59: ^{13}C-NMR of O-alkylated aminophenol (nosyl protected) (**5a**) in $CDCl_3$.*

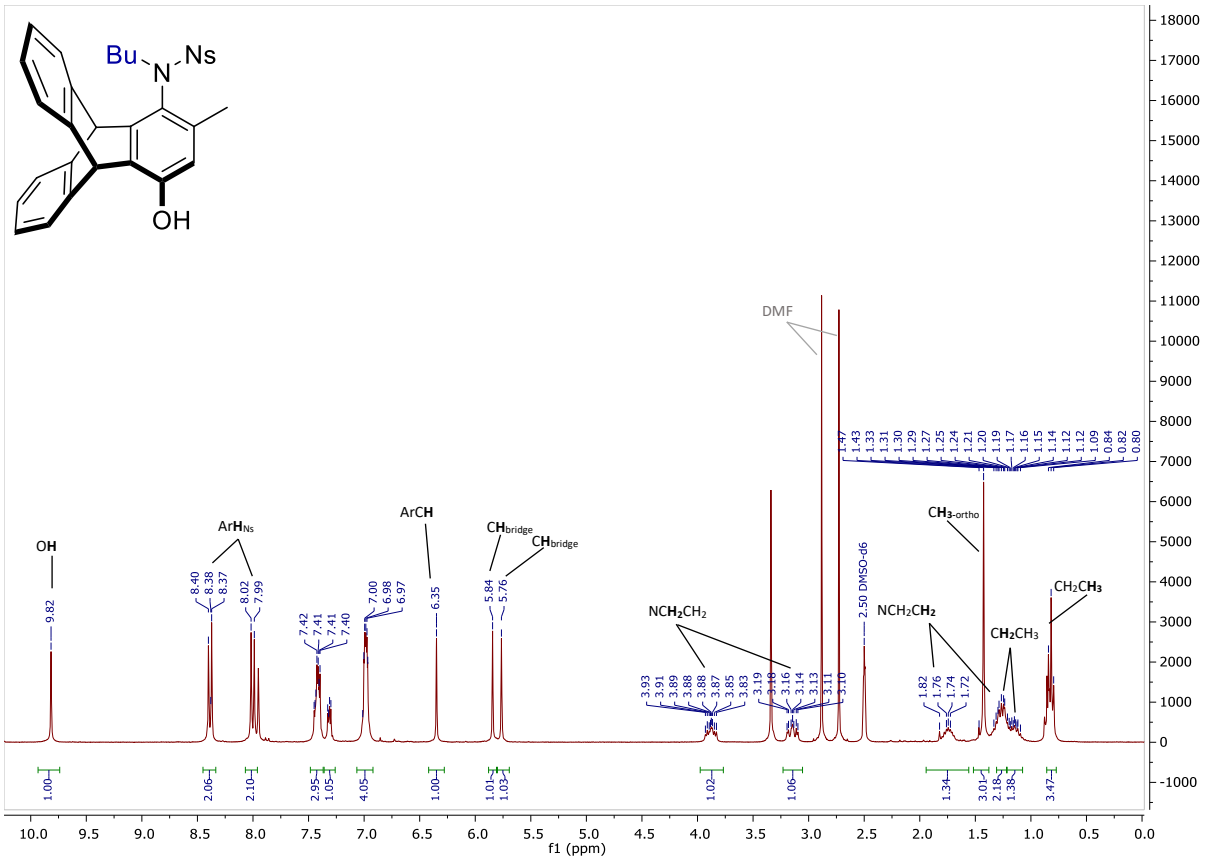


*Figure 60: ^{1}H-NMR of N-alkylated aminophenol (nosyl protected) (**5ba**) in $CDCl_3$.*

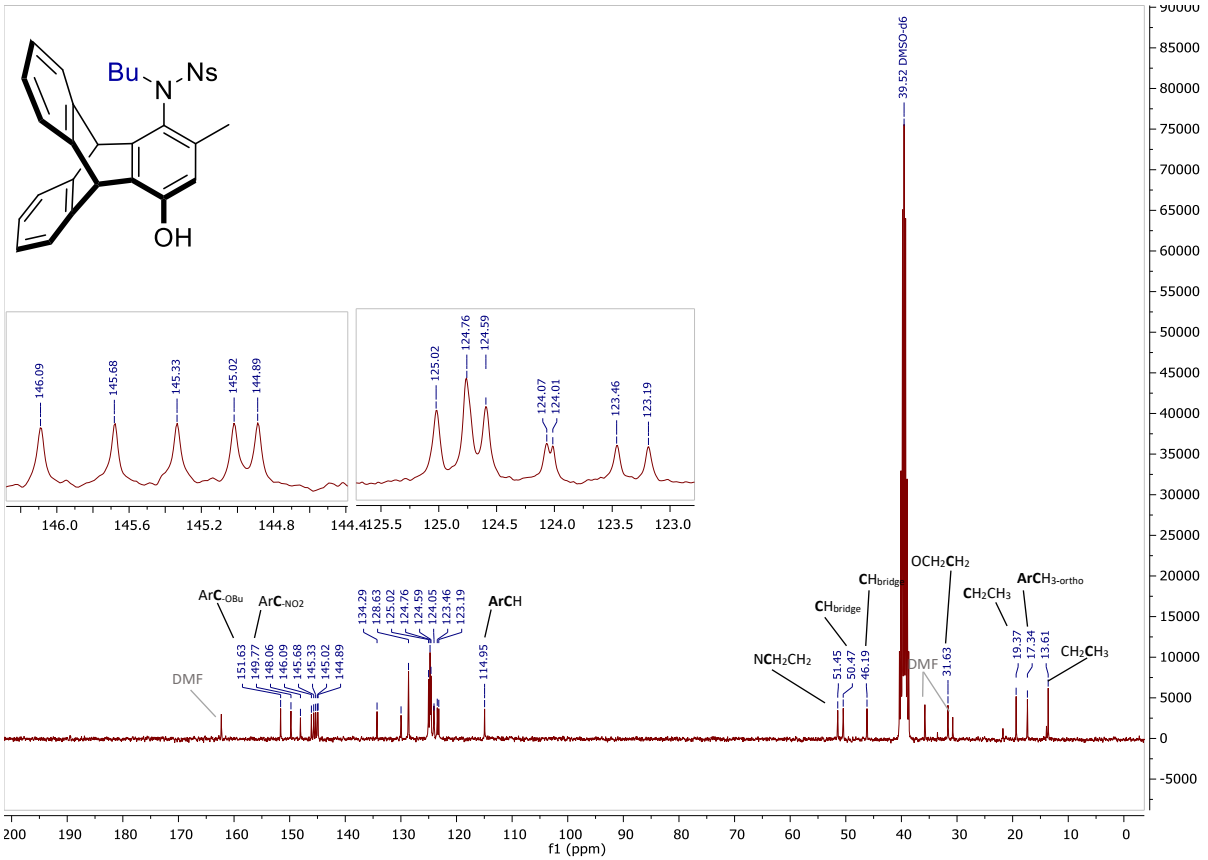


*Figure 61: ^{13}C{H}-NMR of N-alkylated aminophenol (nosyl protected) (**5ba**) in $CDCl_3$.*

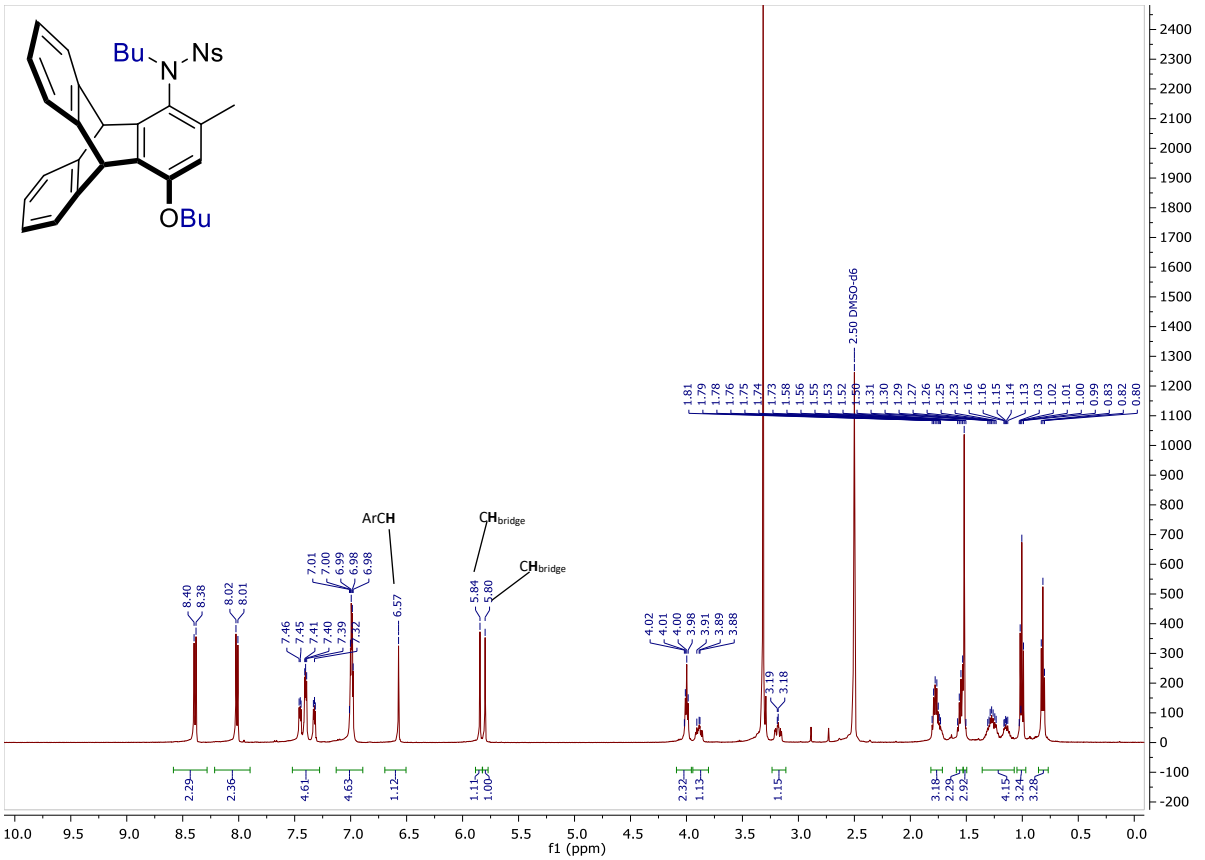


*Figure 62: ^{1}H-NMR of N/O-alkylated aminophenol (nosyl protected) (**5bb**) in DMSO-d_6.*

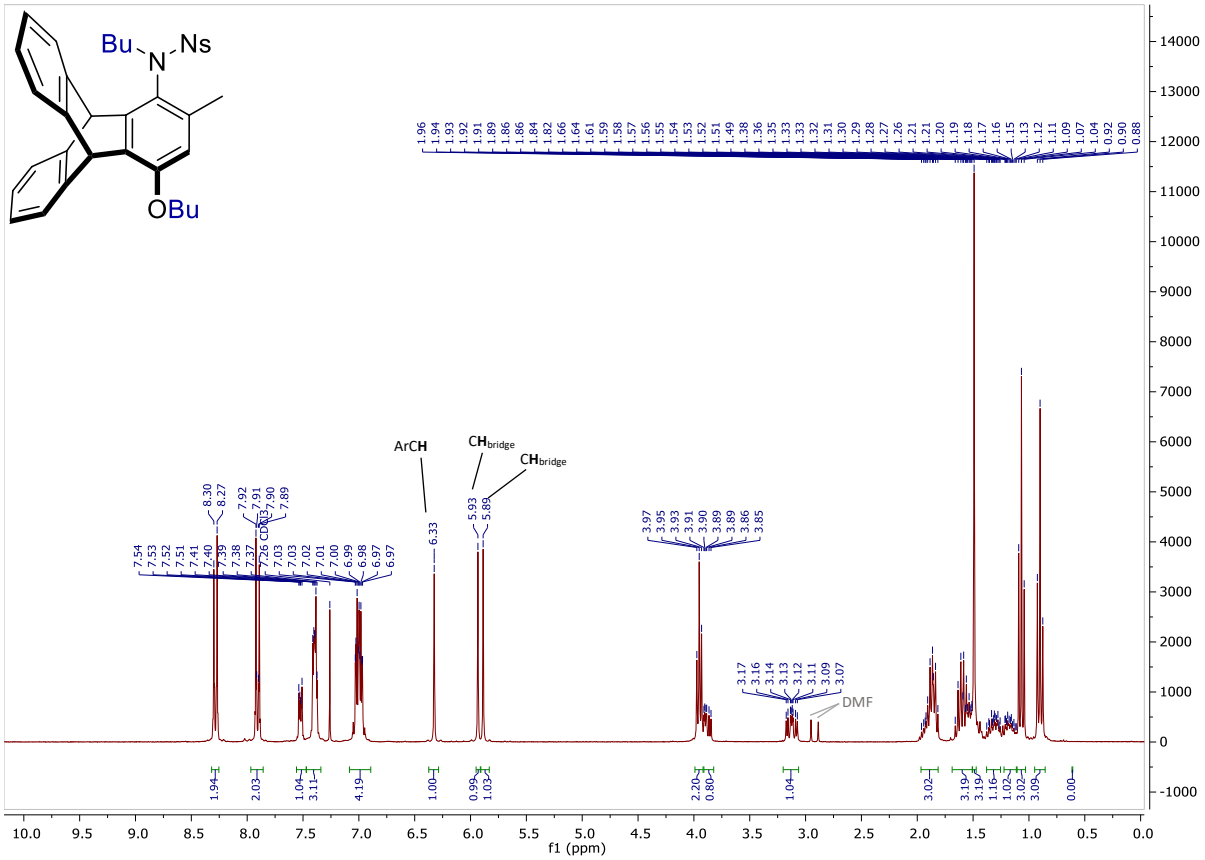


*Figure 63: ^{1}H-NMR of N/O-alkylated aminophenol (nosyl protected) (**5bb**) in $CDCl_3$.*

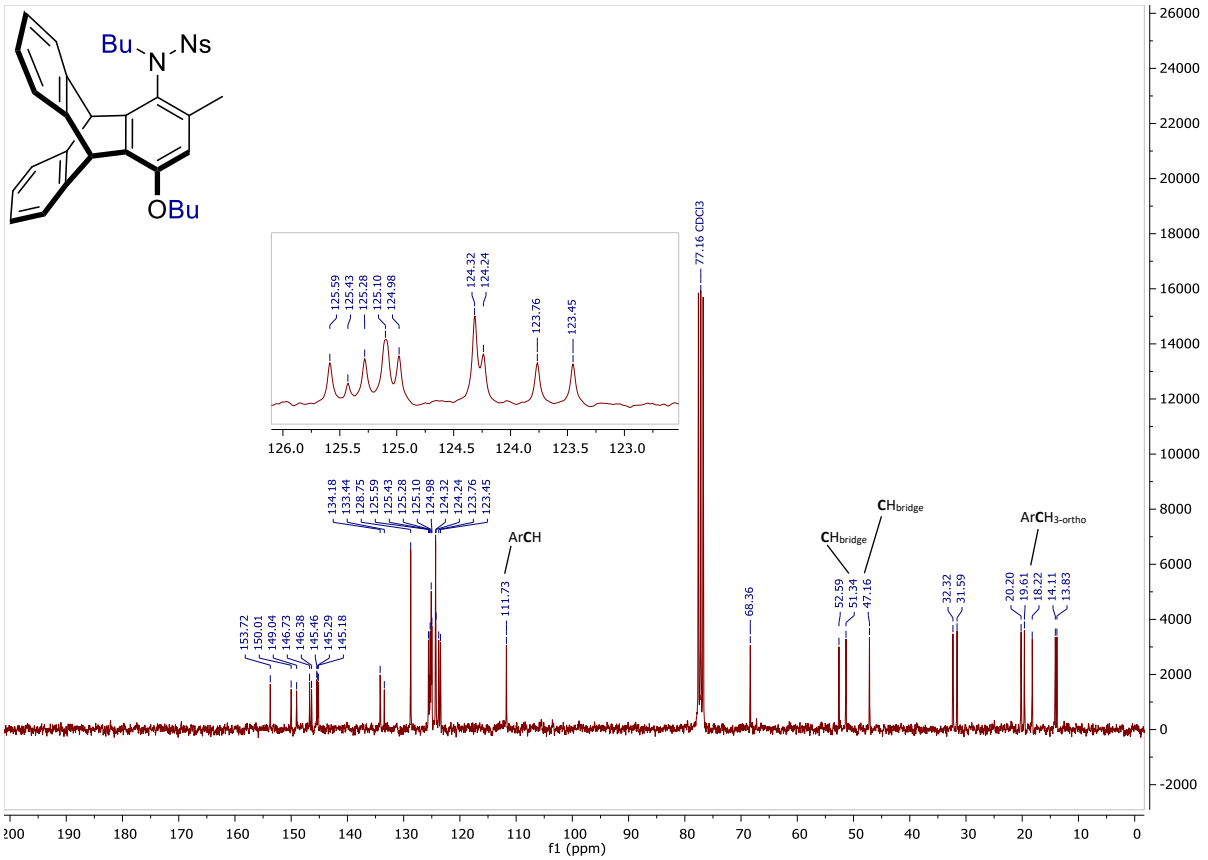


*Figure 64: ^{13}C-NMR of N/O-alkylated aminophenol (nosyl protected) (**5bb**) in $CDCl_3$.*

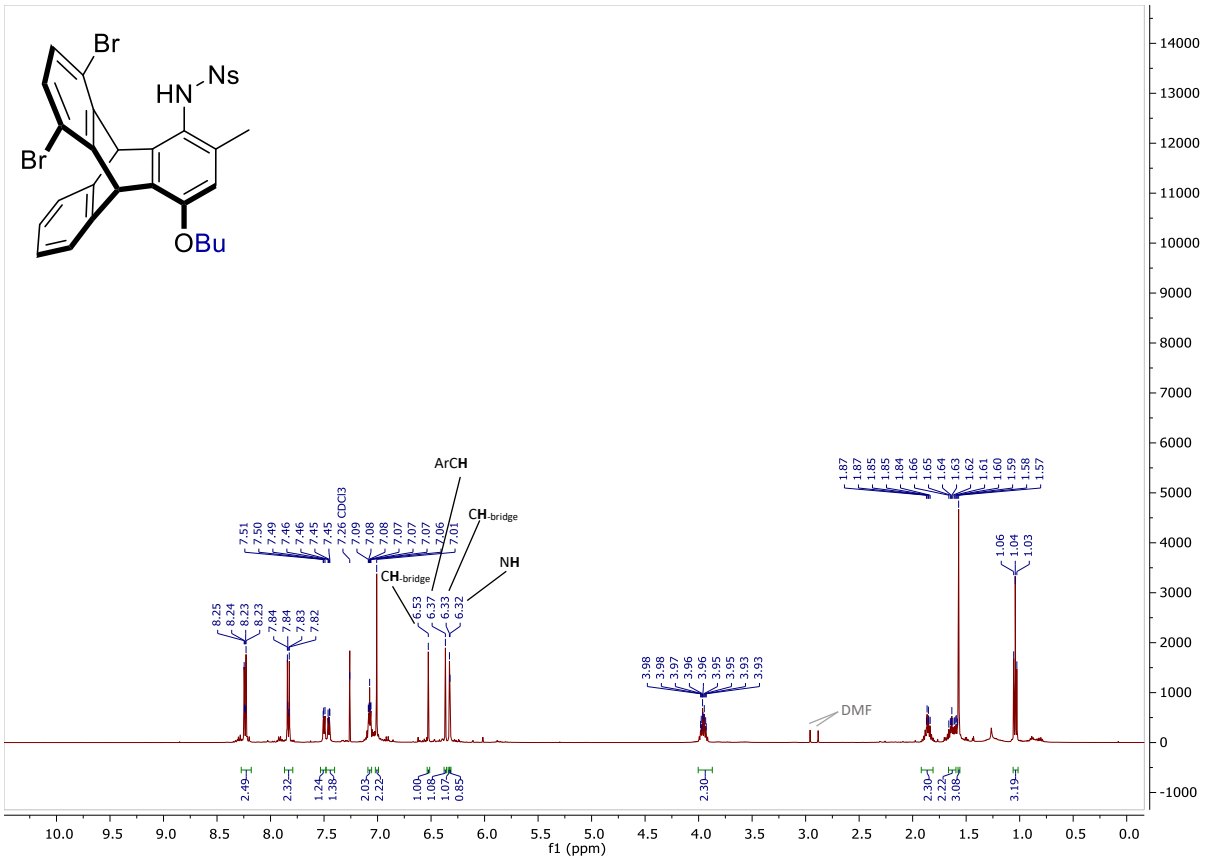


*Figure 65: [1]H-NMR of O-alkylated aminophenol (nosyl protected) (**5c**) in $CDCl_3$.*

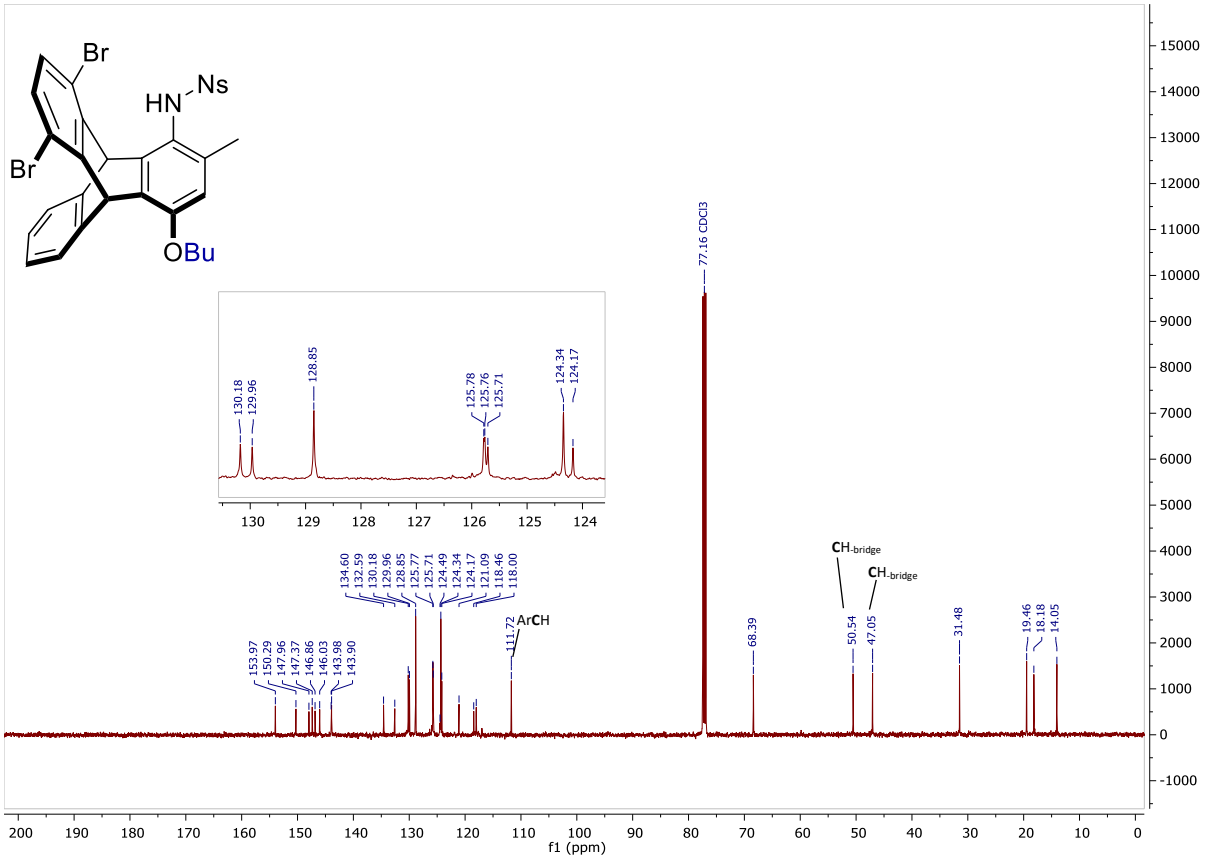


*Figure 66: [13]C-NMR of O-alkylated aminophenol (nosyl protected) (**5c**) in $CDCl_3$.*

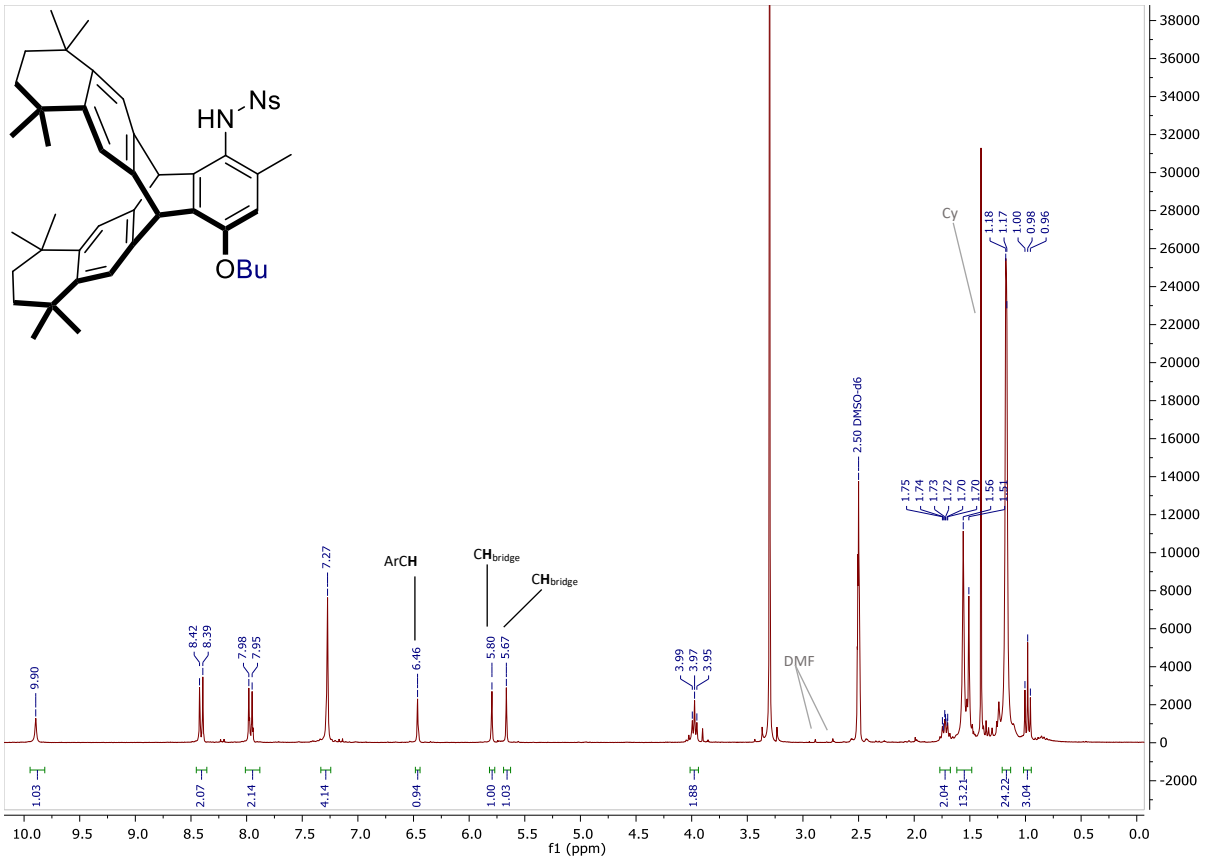


*Figure 67: ^{1}H-NMR of O-alkylated aminophenol (nosyl protected) (**5g**) in $CDCl_3$.*

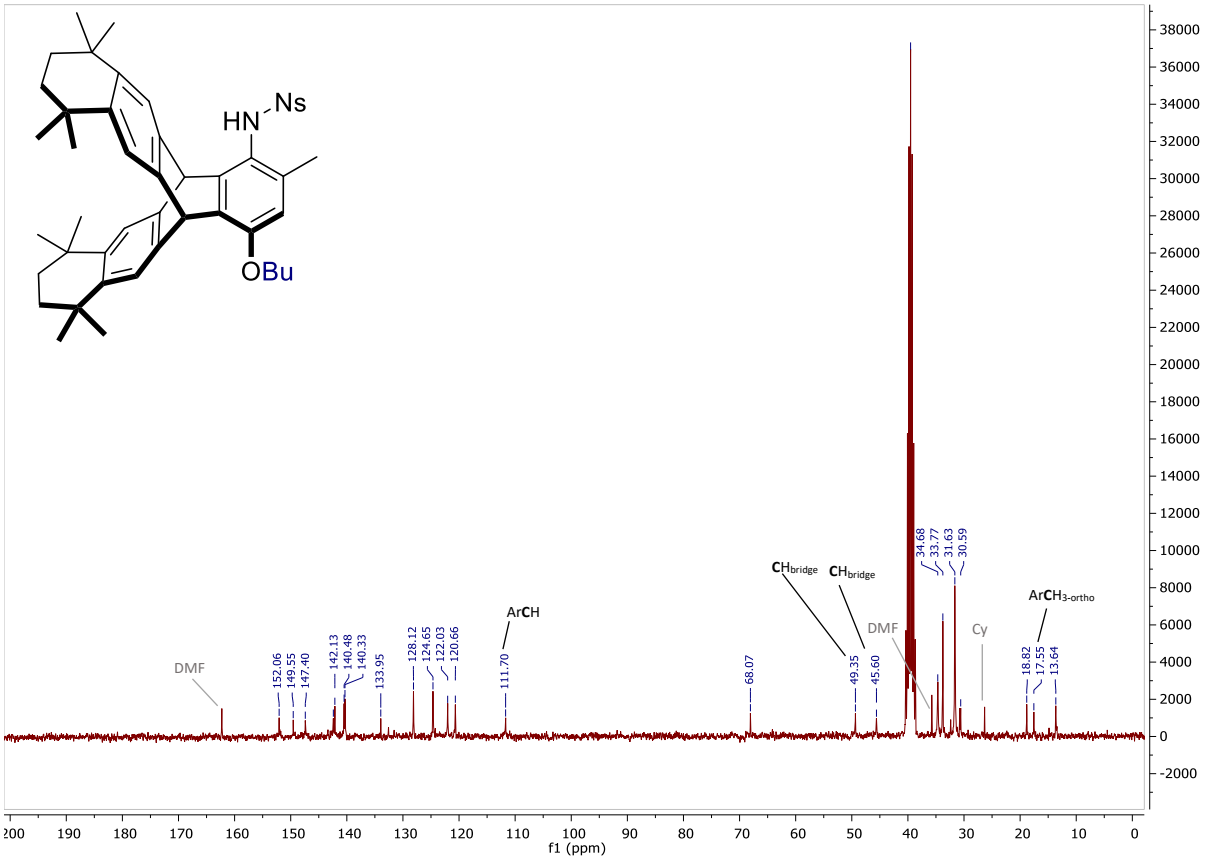


*Figure 68: ^{13}C-NMR of O-alkylated aminophenol (nosyl protected) (**5g**) in $CDCl_3$.*

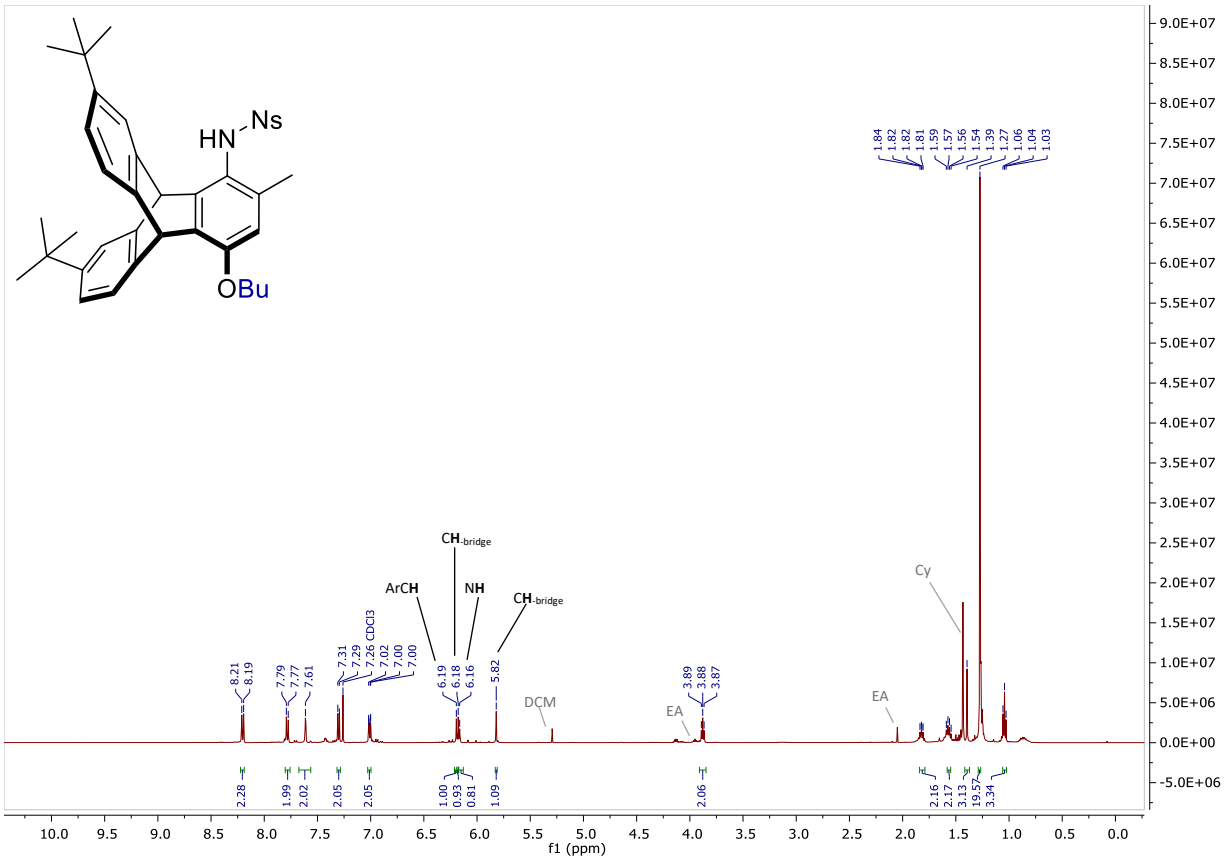


*Figure 69: [1]H-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

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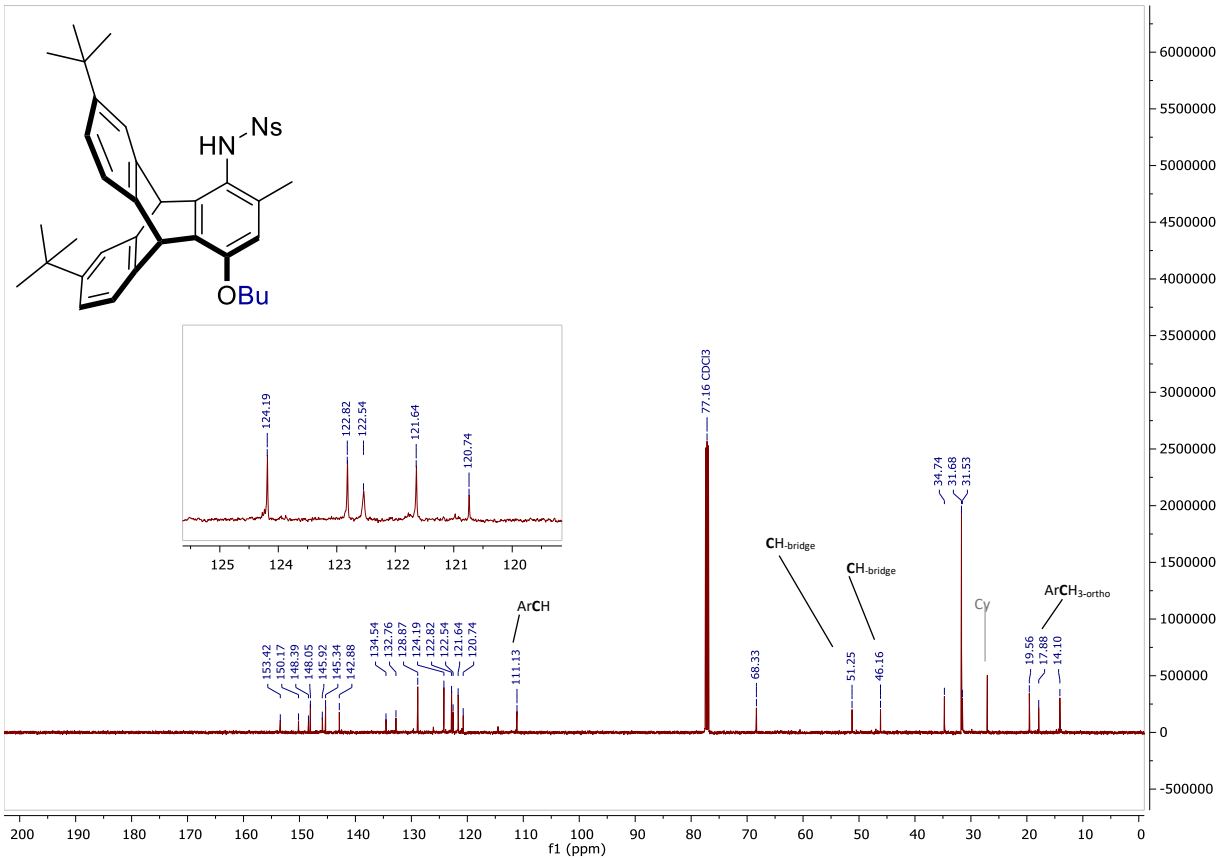


*Figure 70: [13]C-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

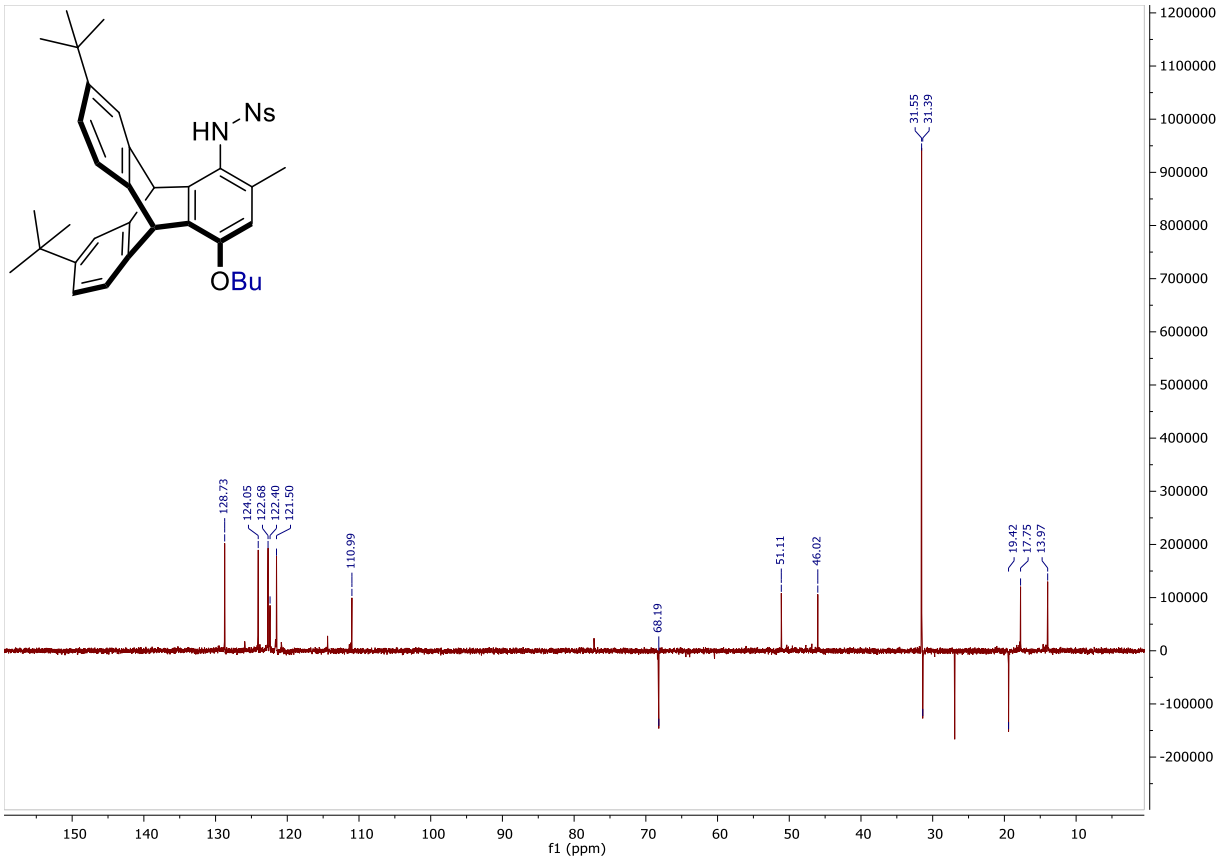


*Figure 71: DEPT-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

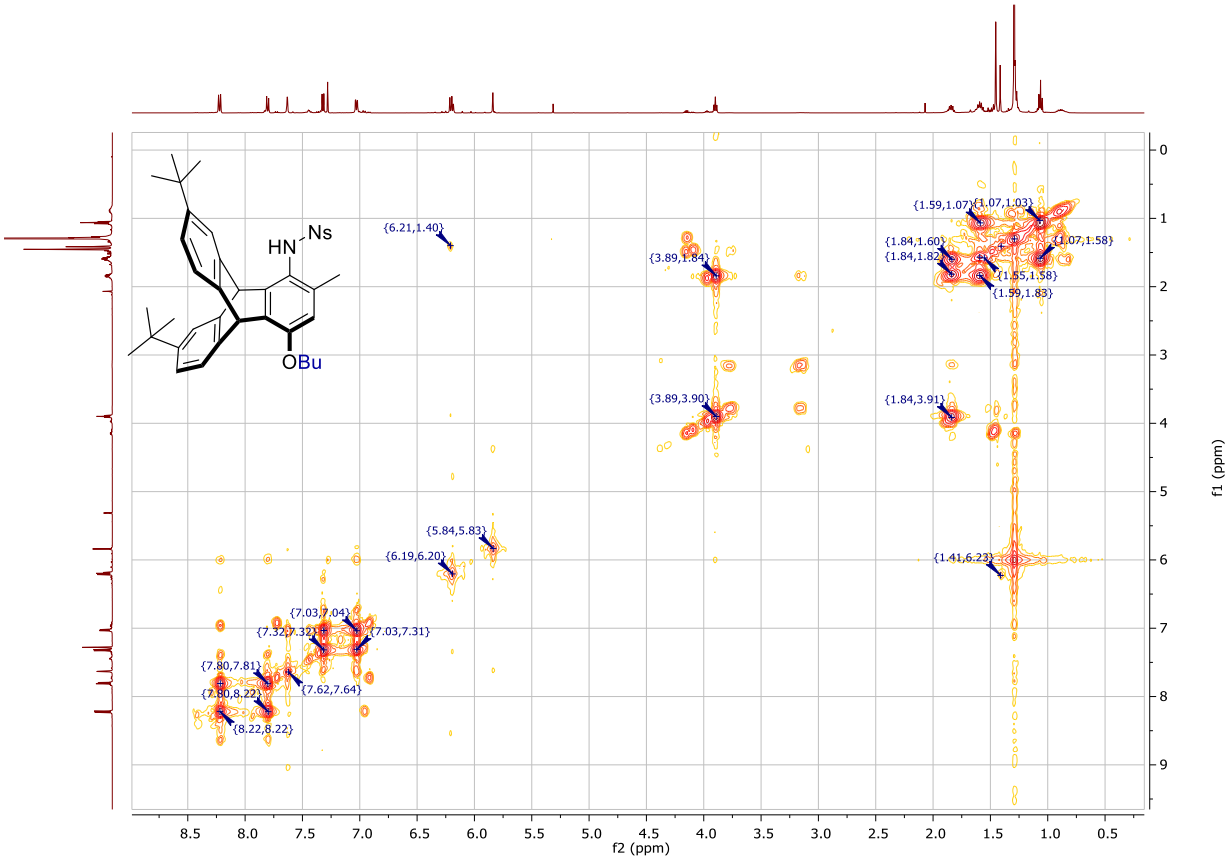


*Figure 72: COSY-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

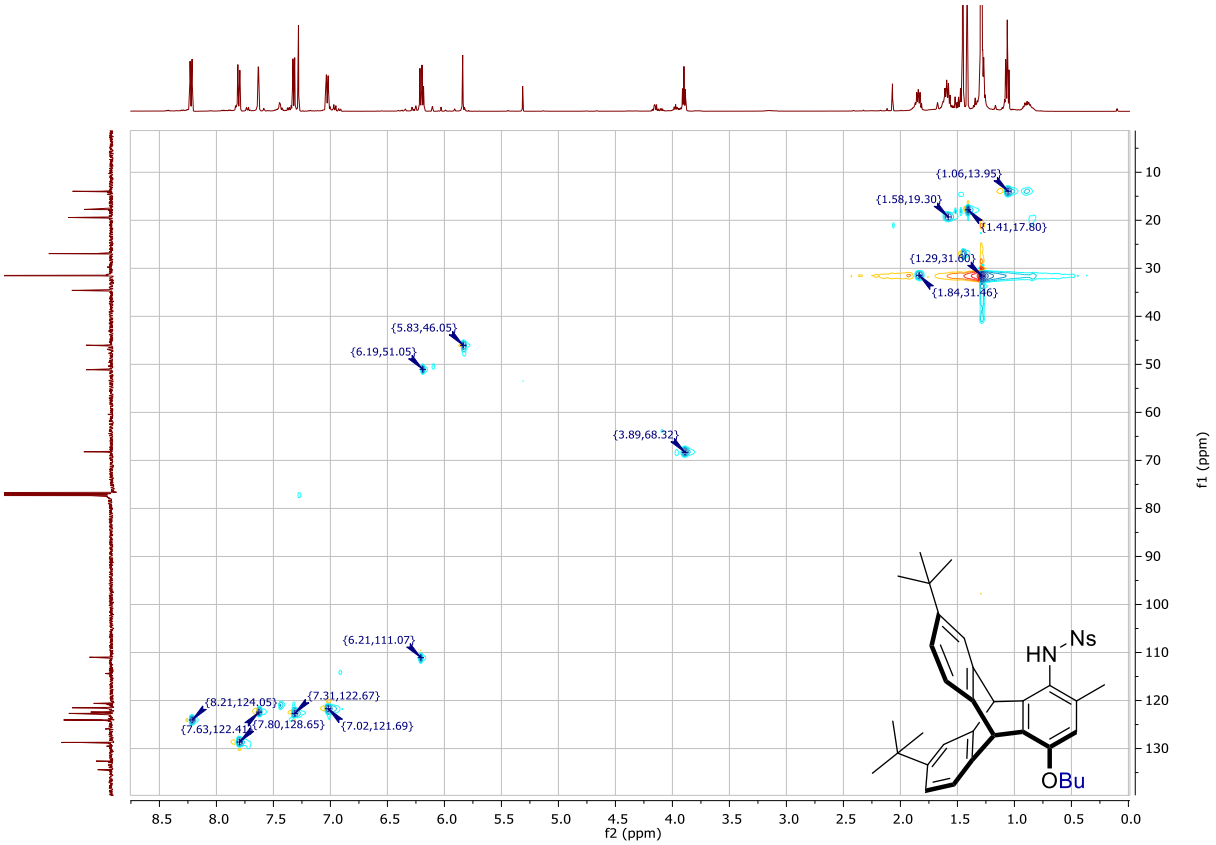


*Figure 73: HSQC-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

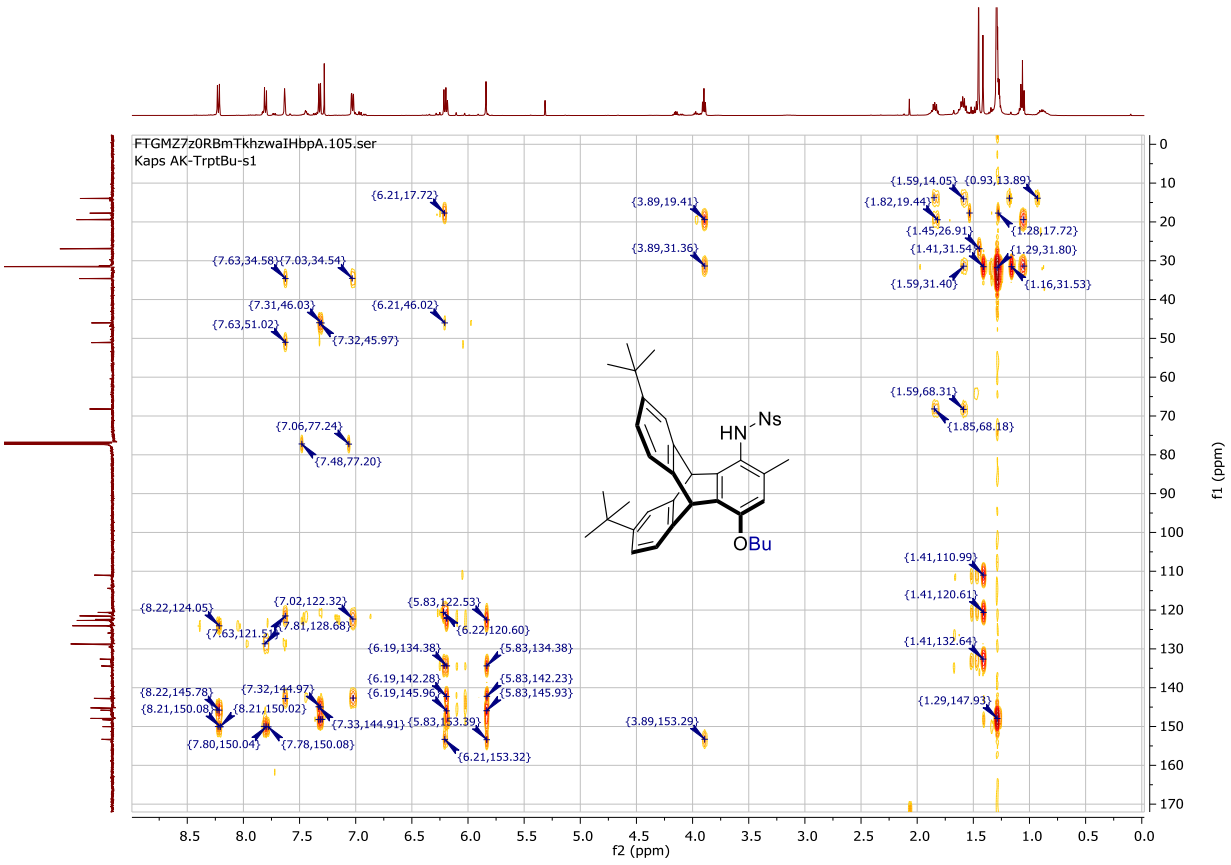


*Figure 74: HMBC NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

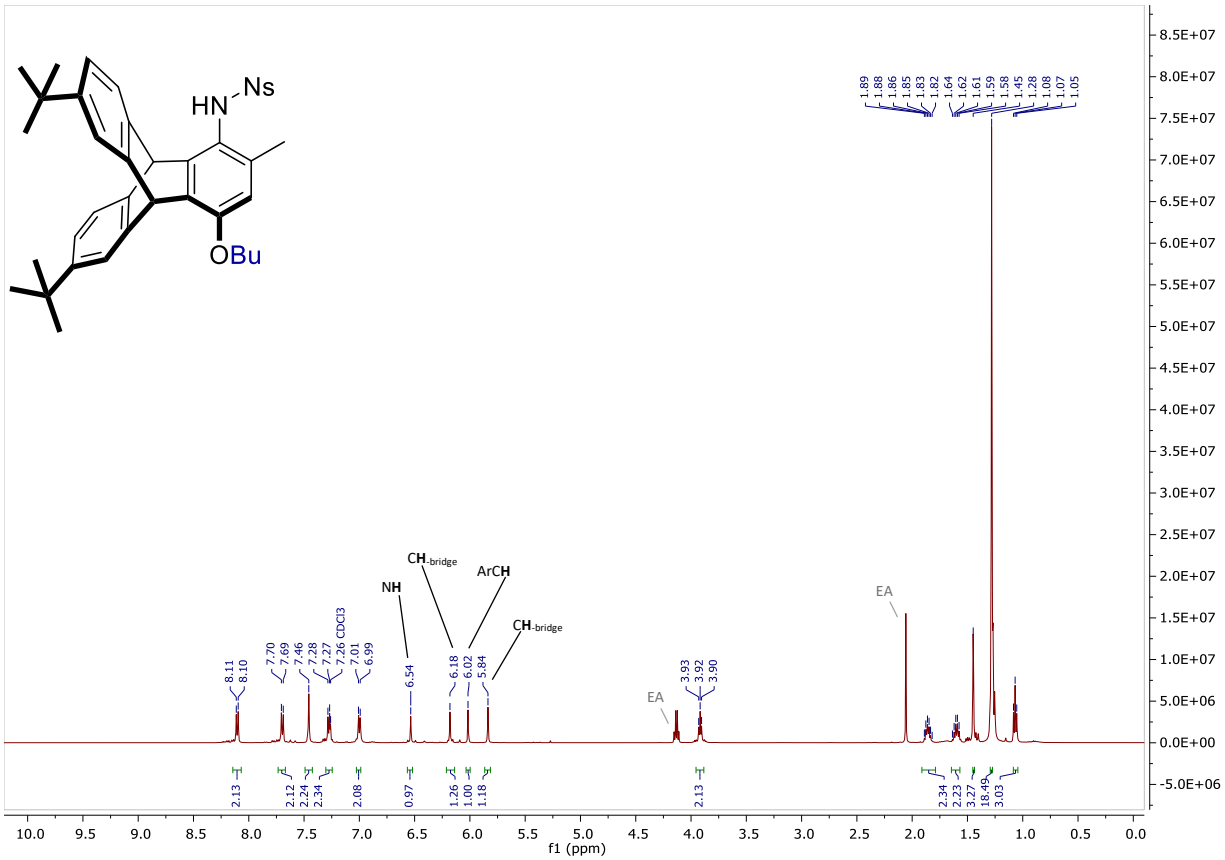


*Figure 75: ^{1}H-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

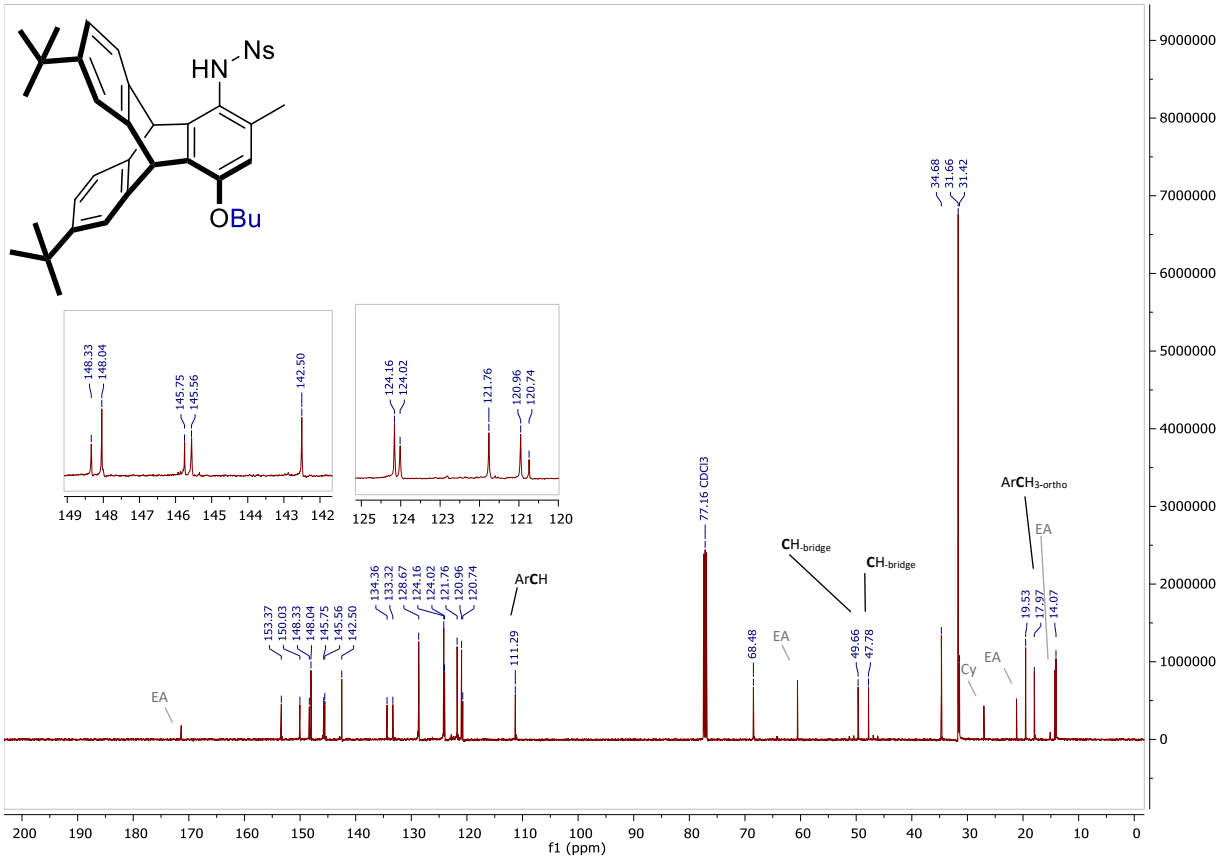


*Figure 76: ^{13}C-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

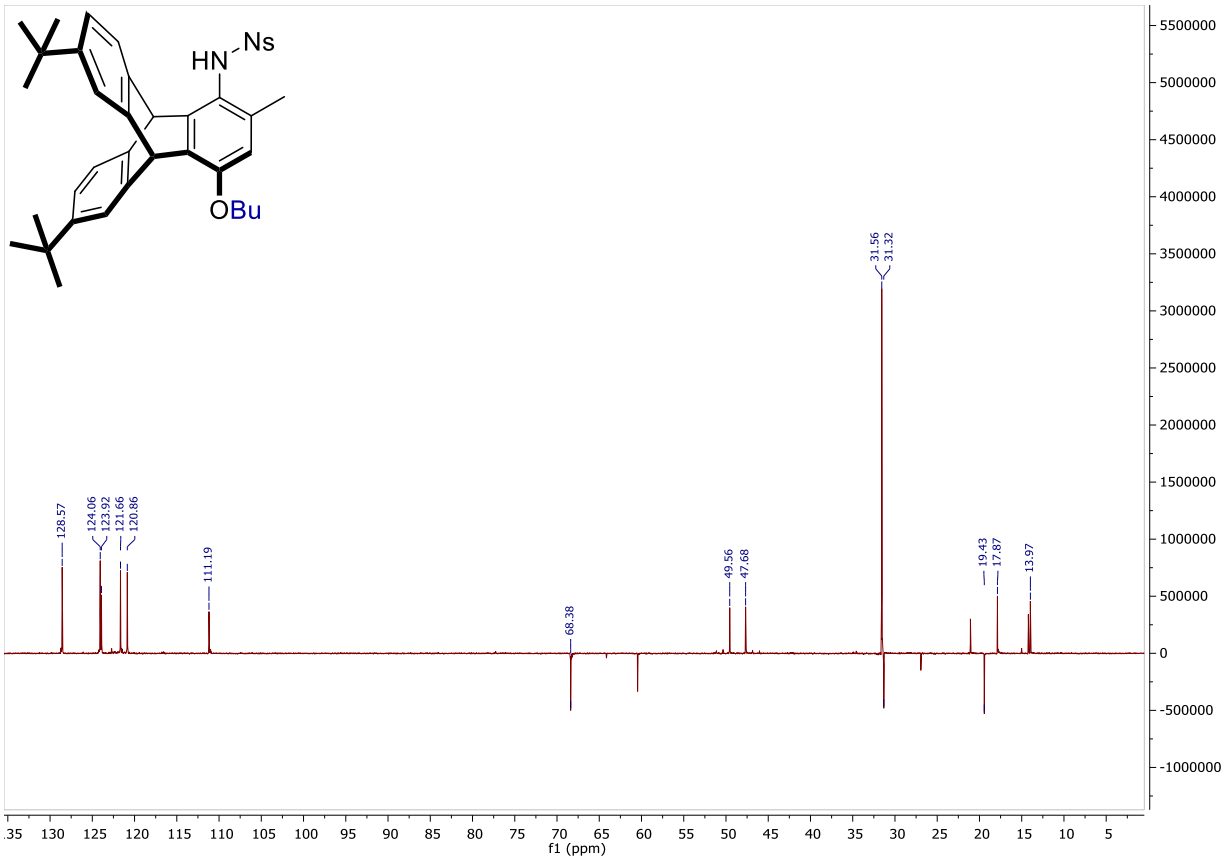


*Figure 77: DEPT-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

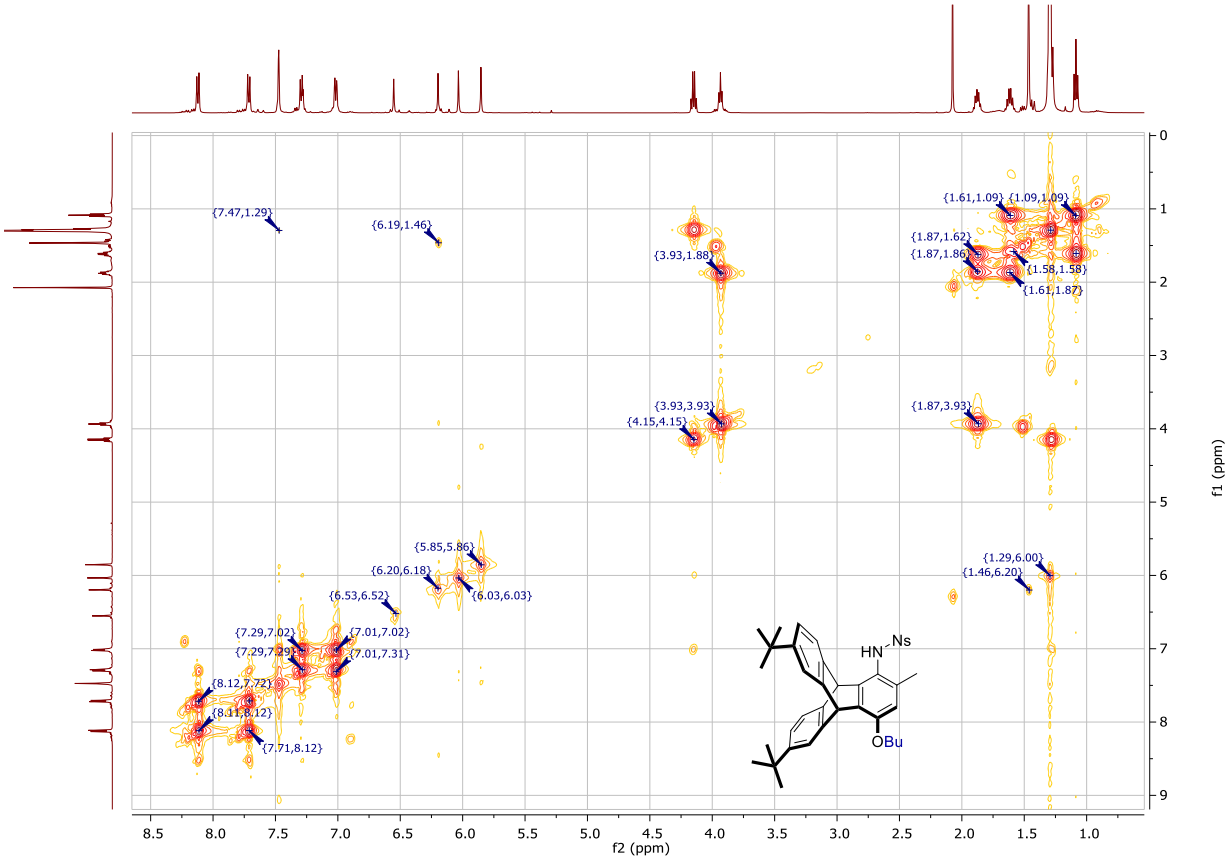


*Figure 78: COSY-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

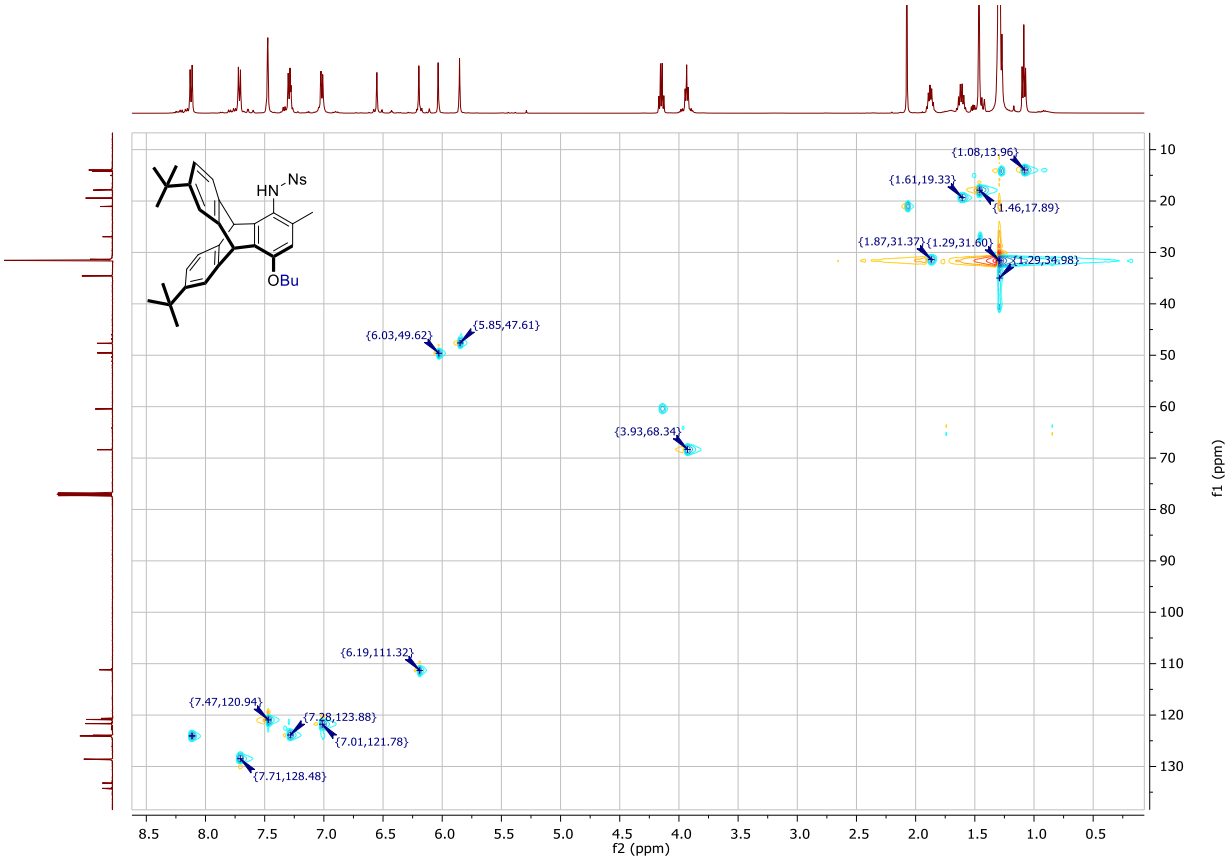


*Figure 79: HSQC NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

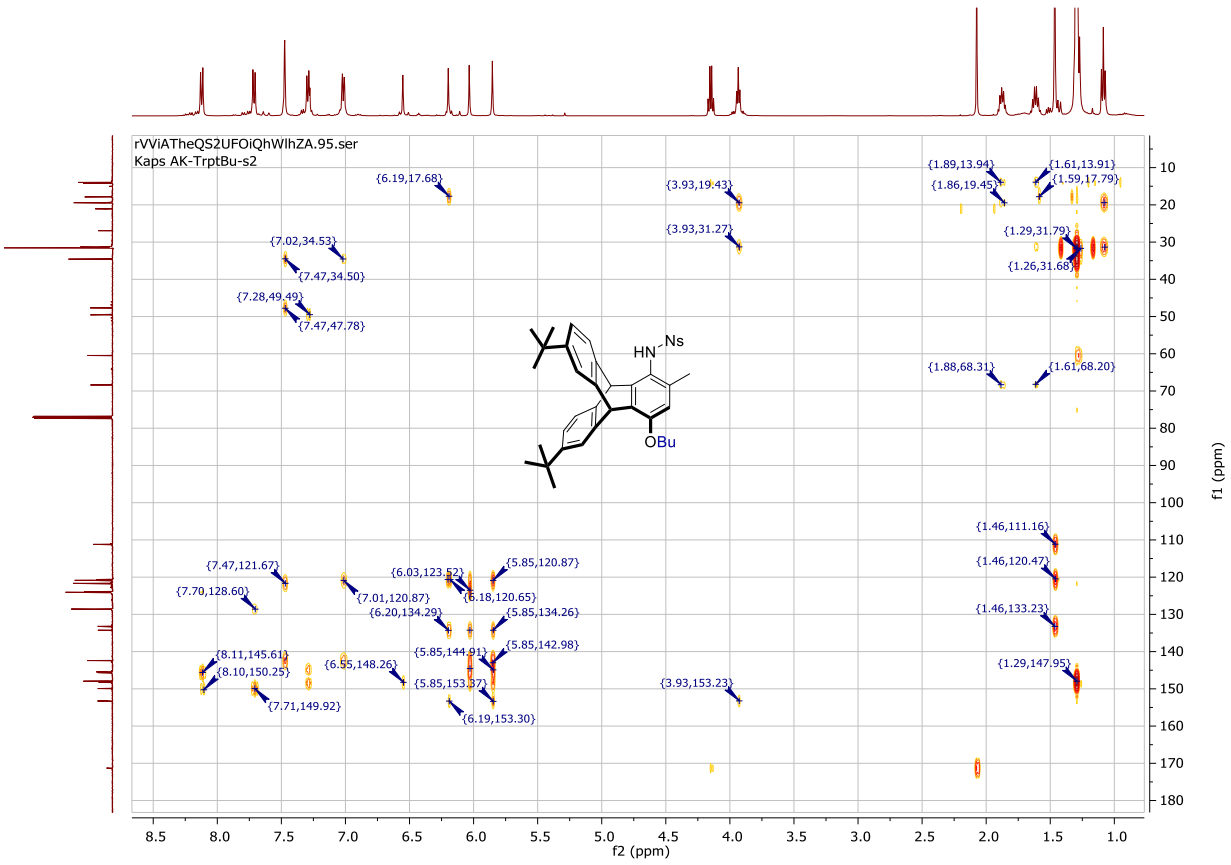


*Figure 80: HMBC-NMR of O-alkylated aminophenol (nosyl protected) (**5h**) in $CDCl_3$.*

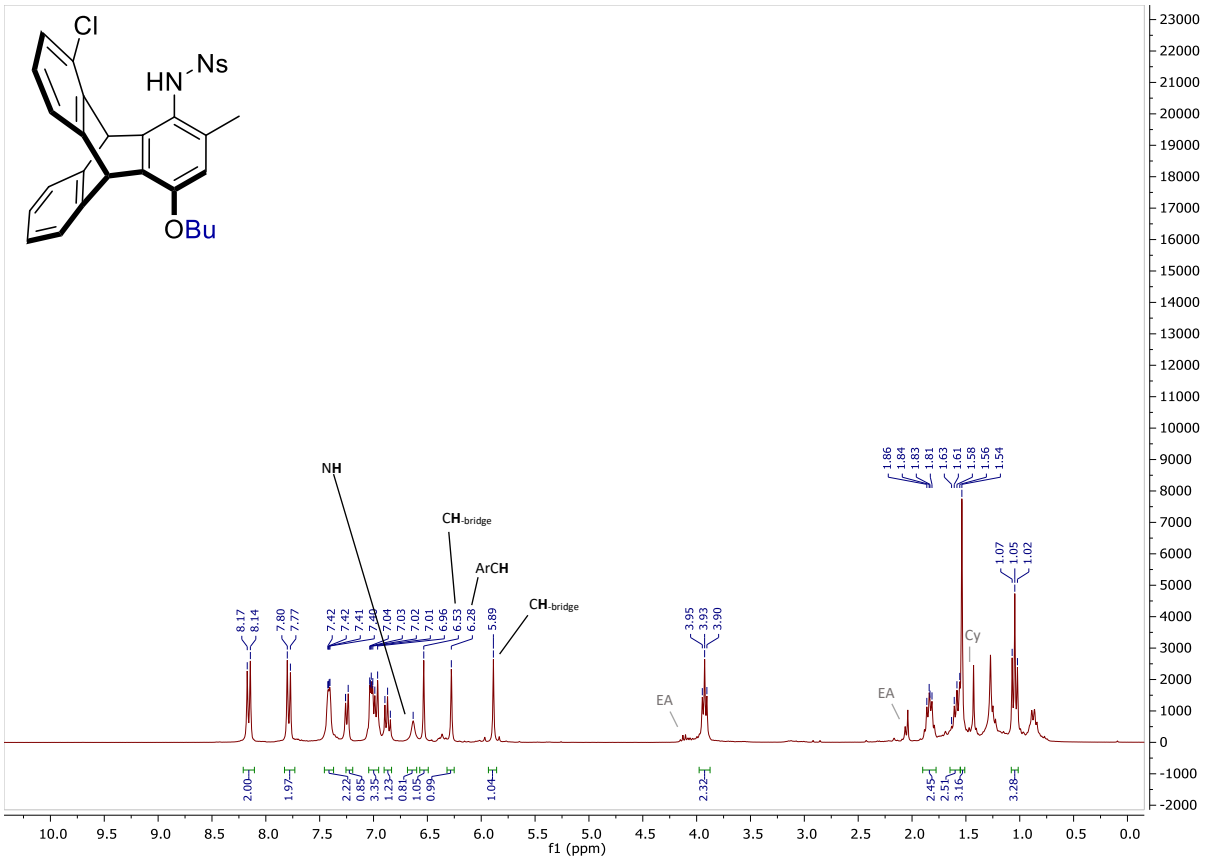


*Figure 81: ^{1}H-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

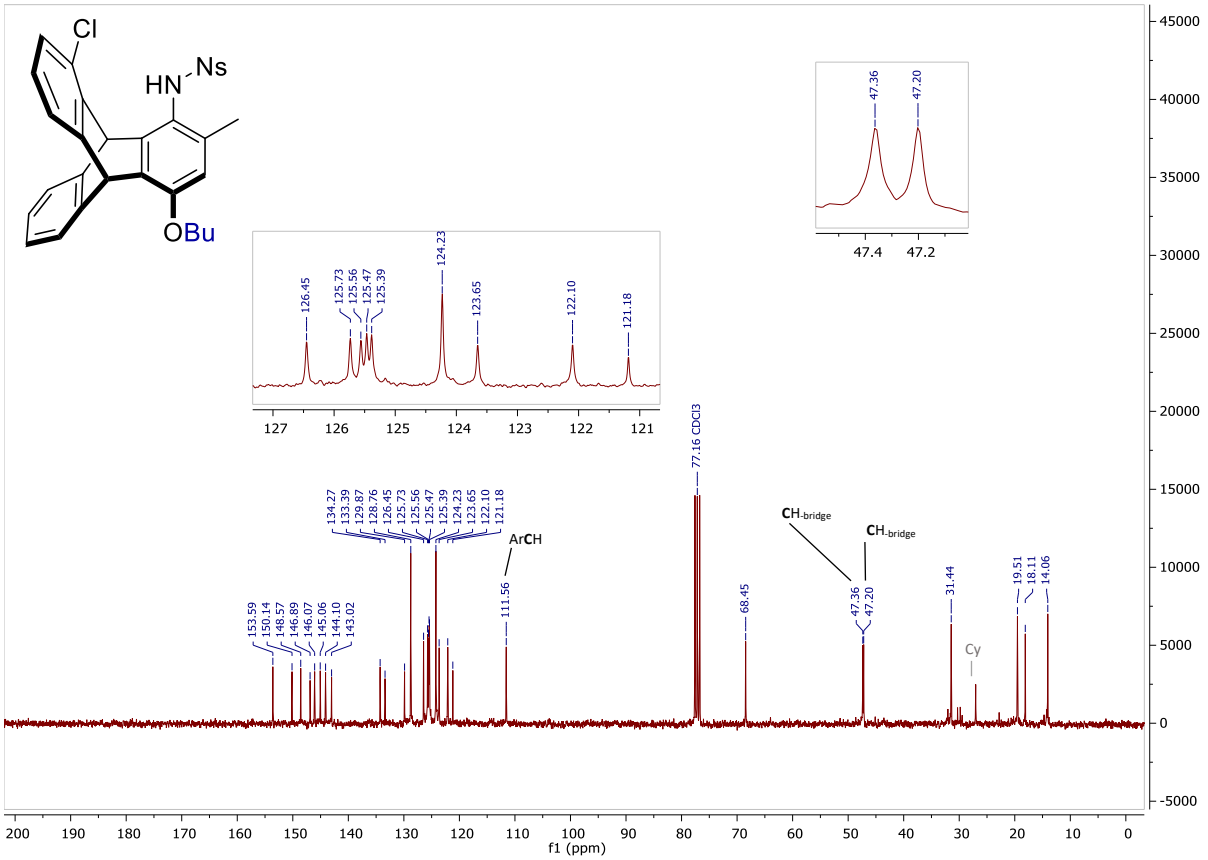


*Figure 82: ^{13}C-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

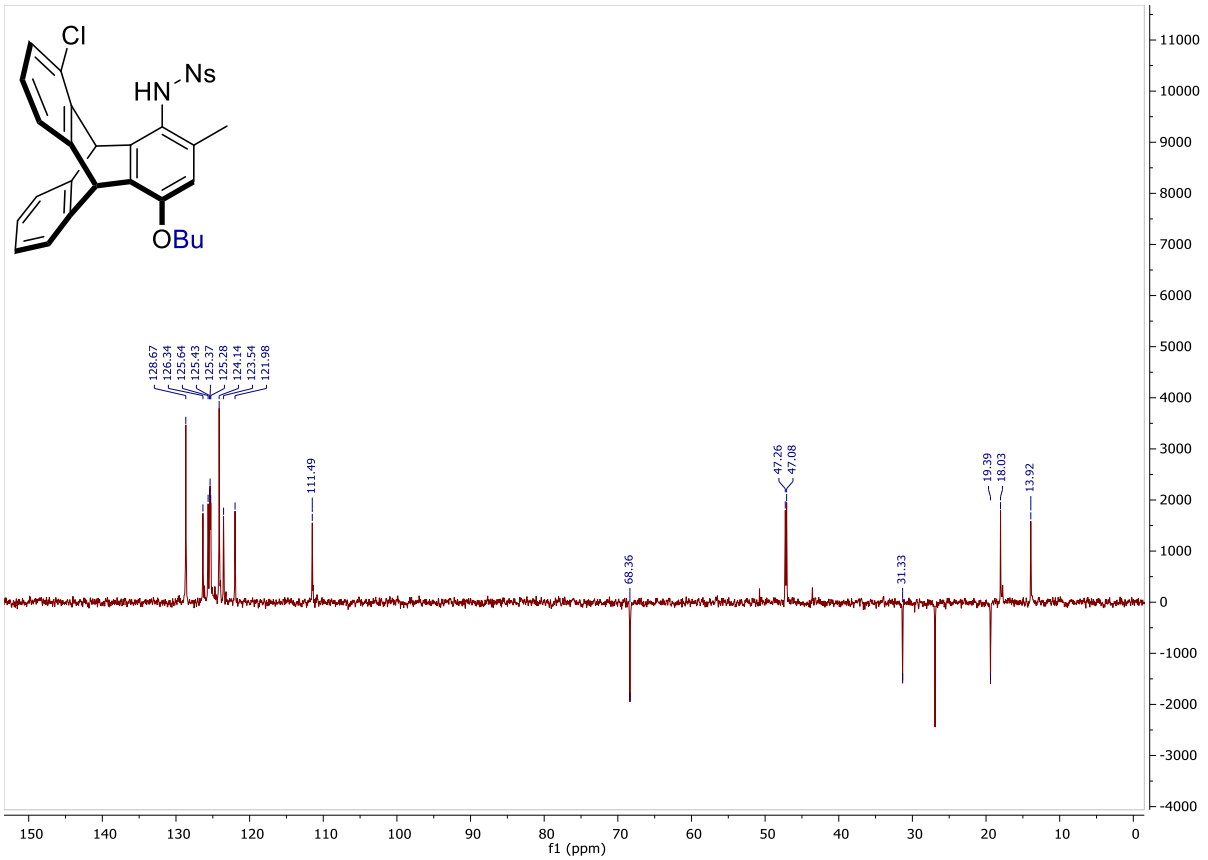


*Figure 83: DEPT-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

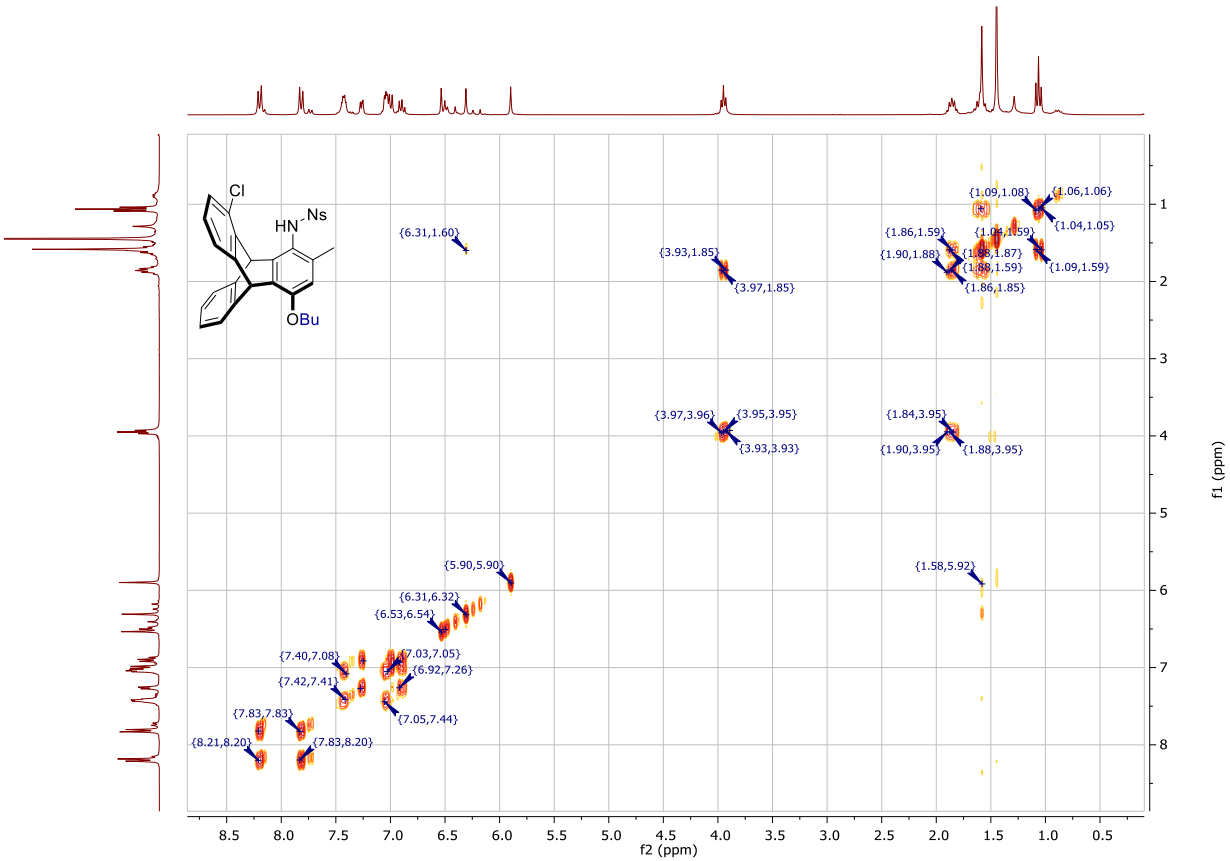


*Figure 84: COSY-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

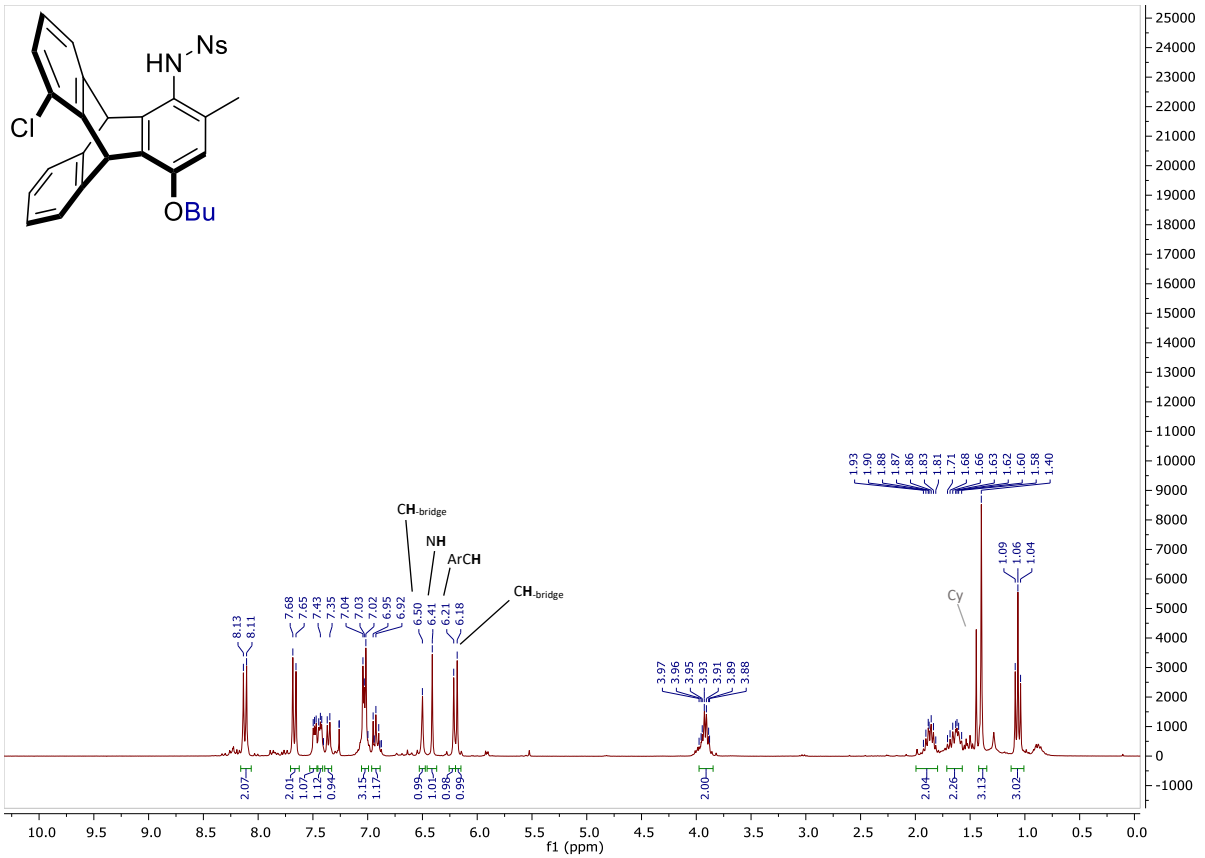


*Figure 85: [1]H-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

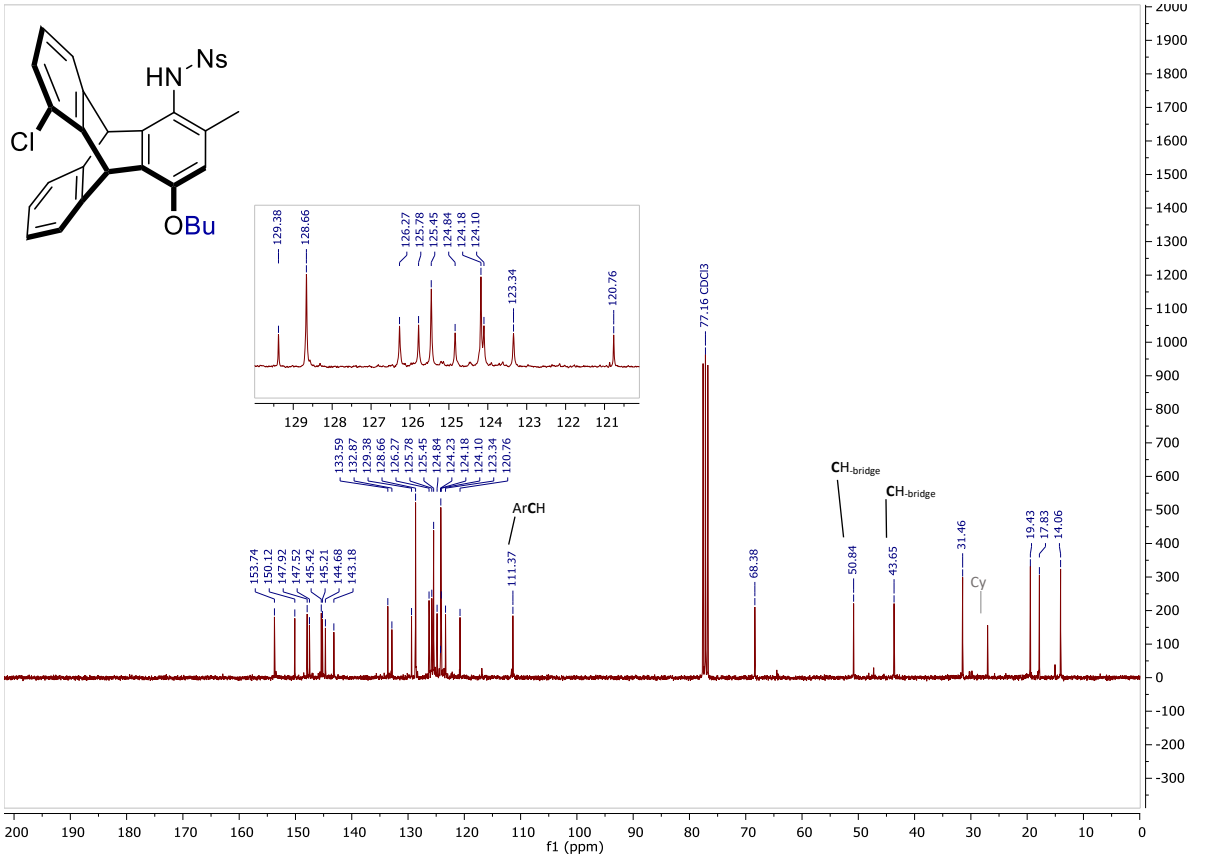


*Figure 86: [13]C-NMR of O-alkylated aminophenol (nosyl protected) (**5l**) in $CDCl_3$.*

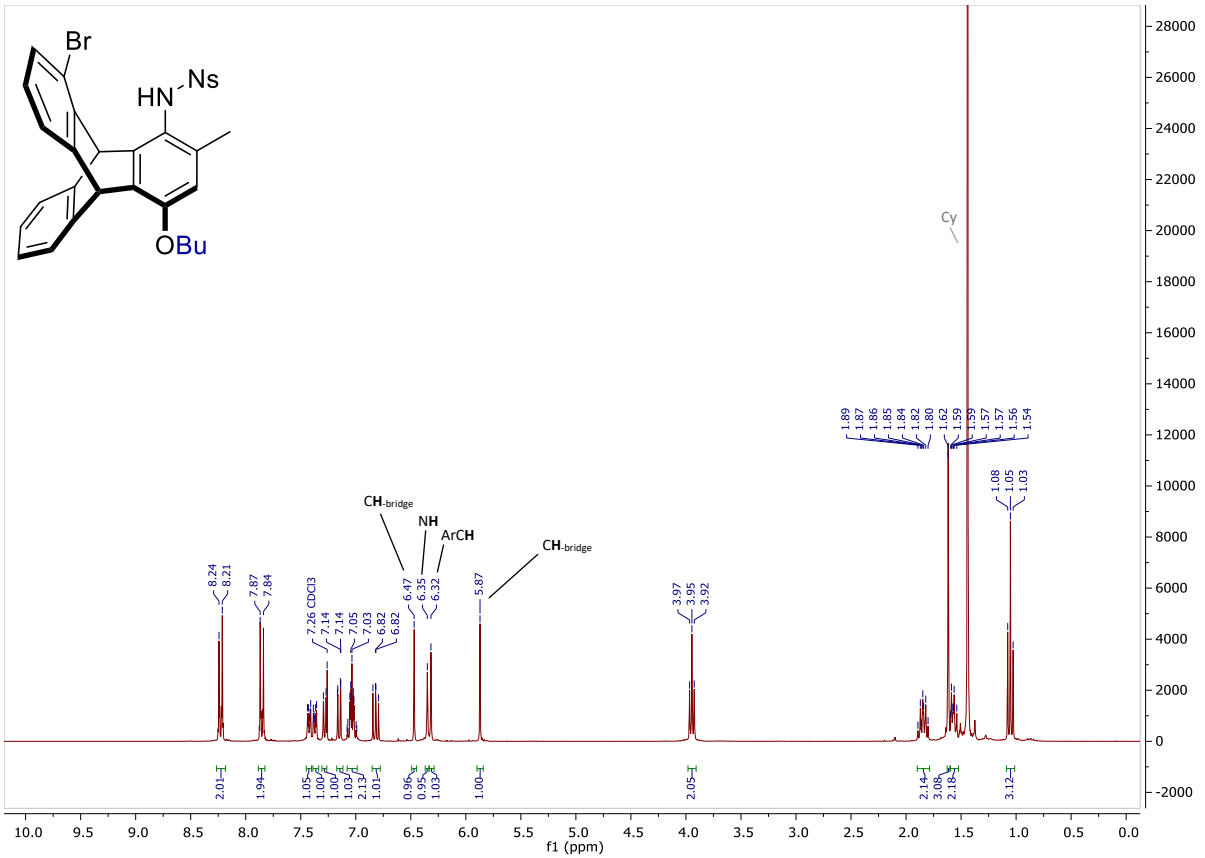


*Figure 87: [1]H-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

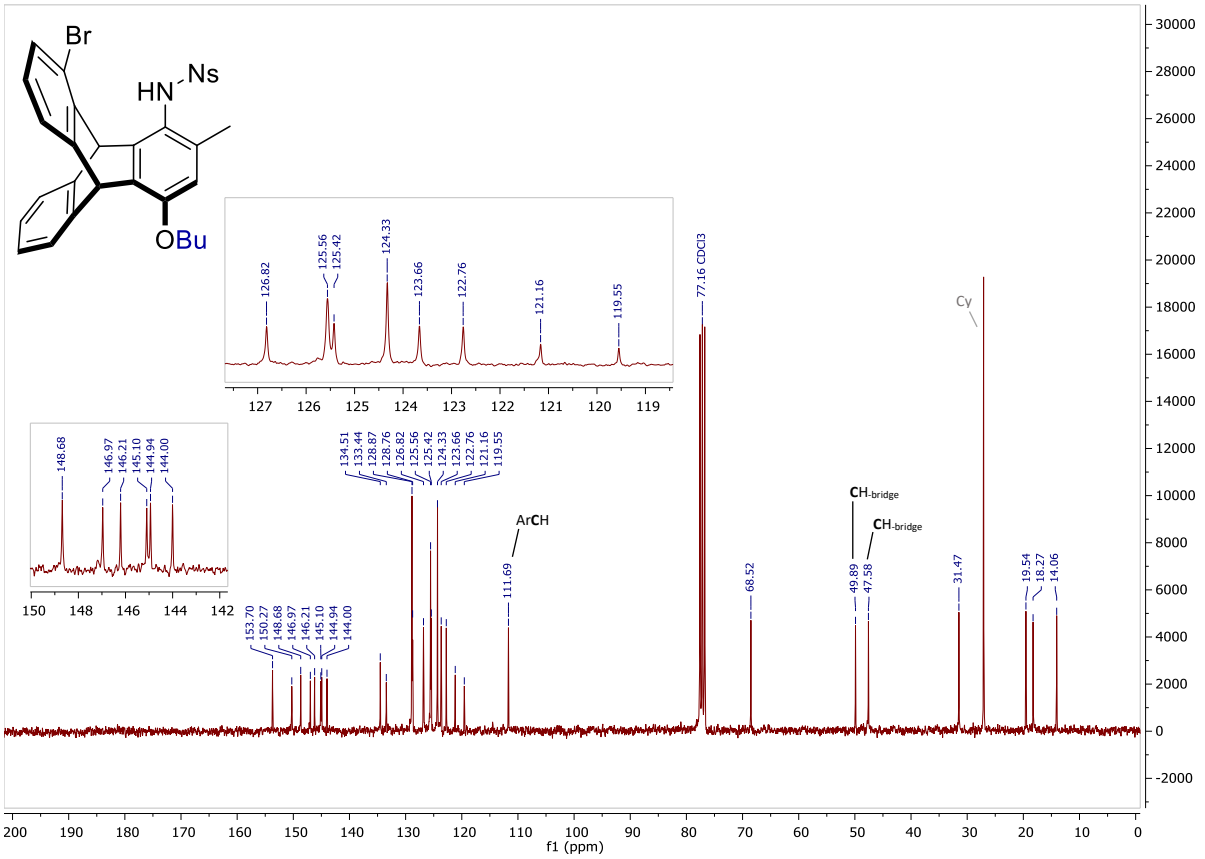


*Figure 88: [13]C-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

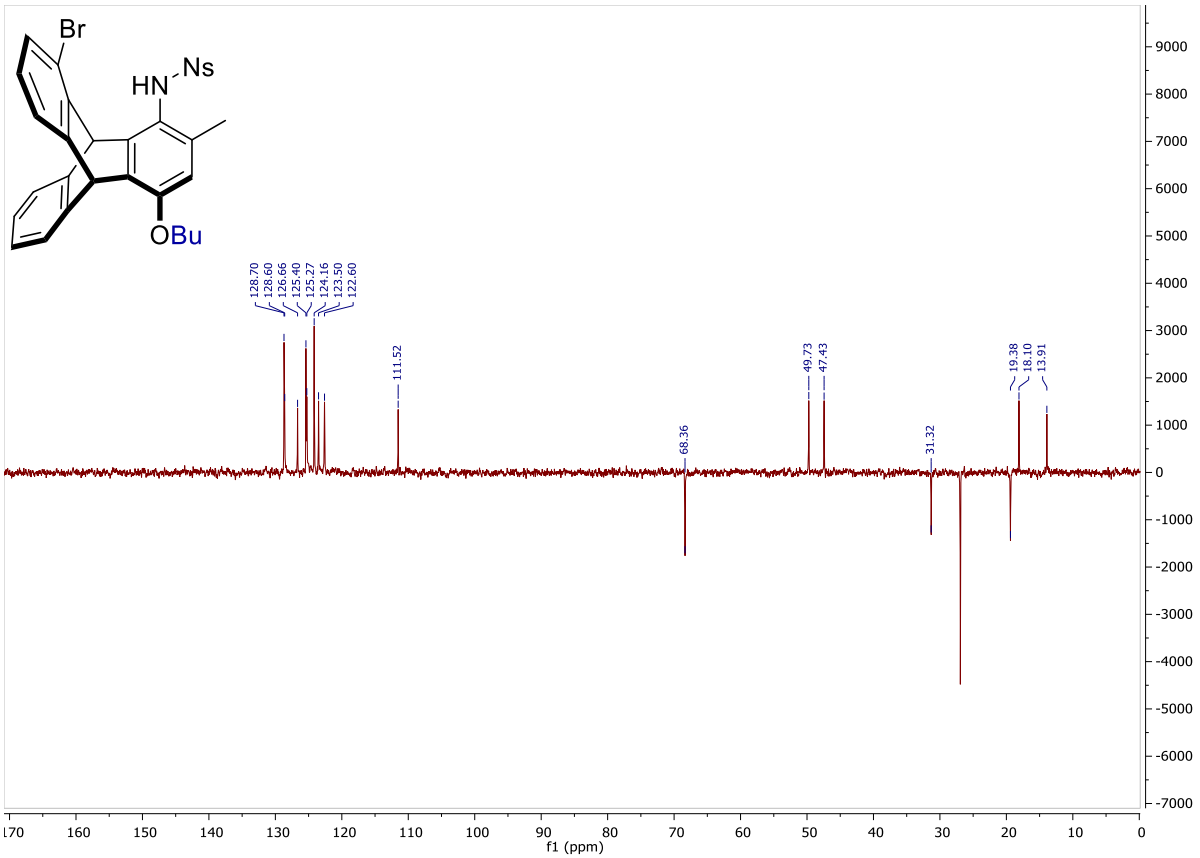


*Figure 89: DEPT-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

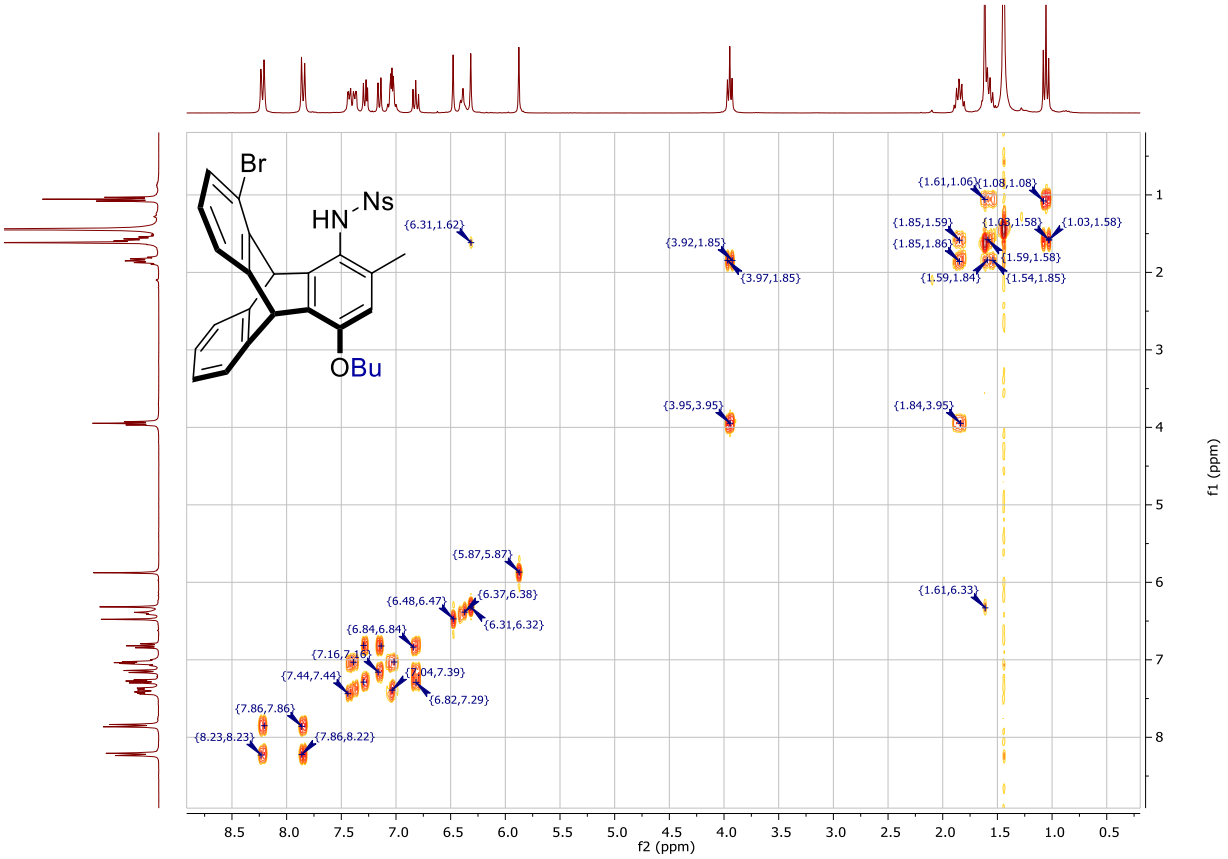


*Figure 90: COSY-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

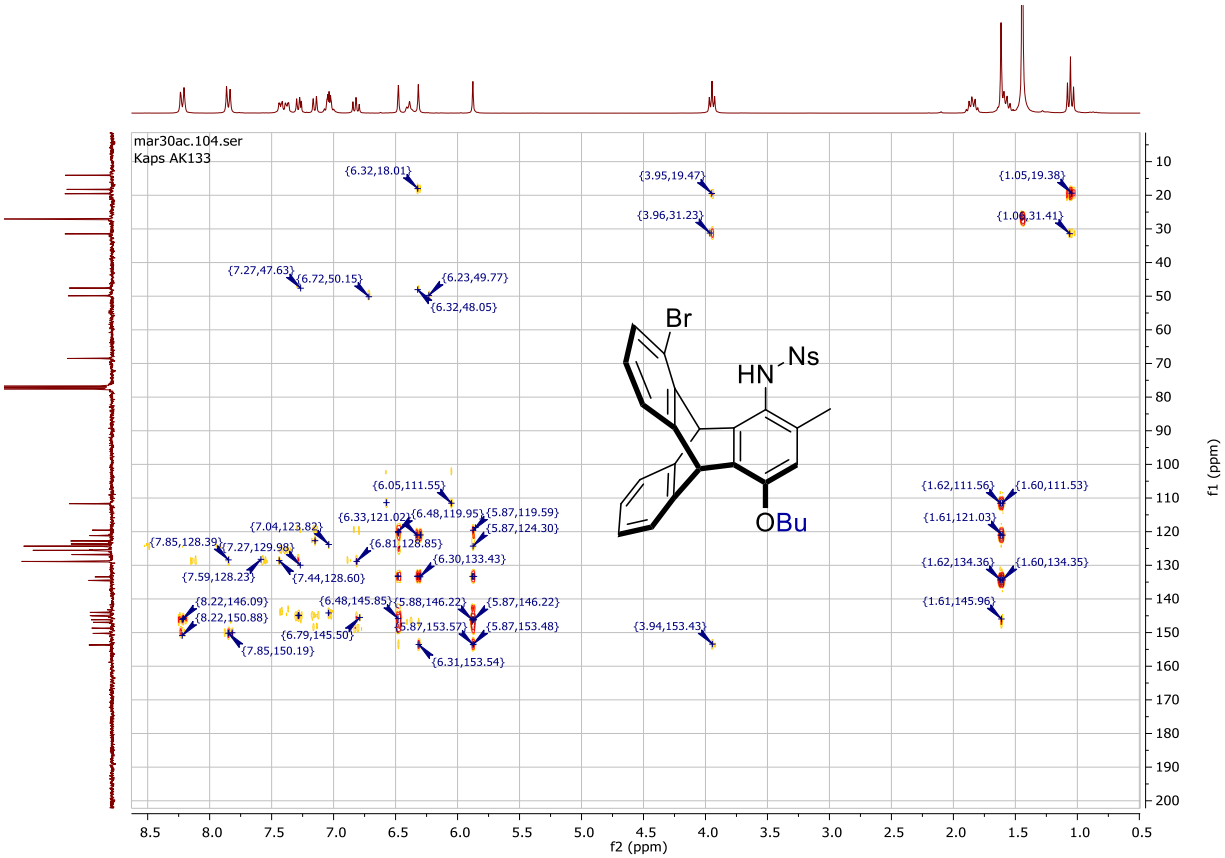


*Figure 91: HMBC-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

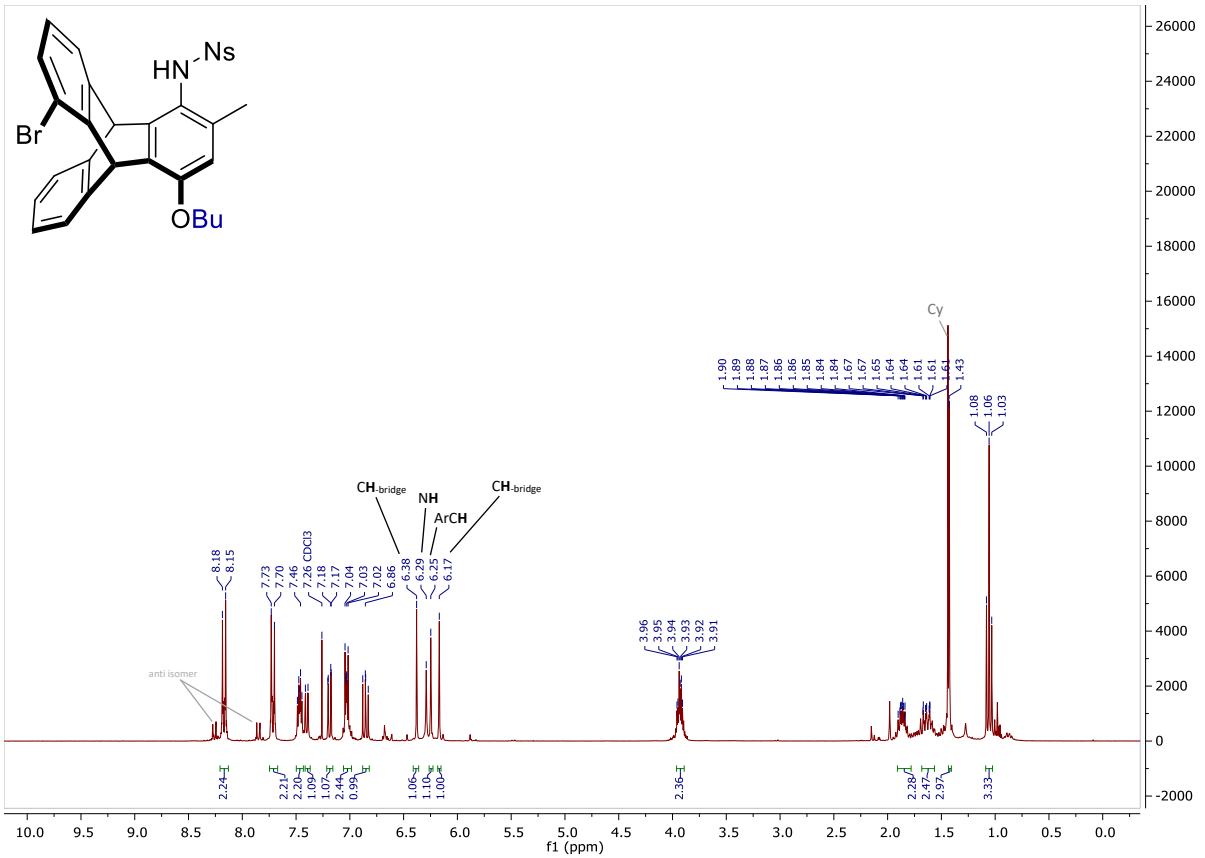


*Figure 92: [1]H-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

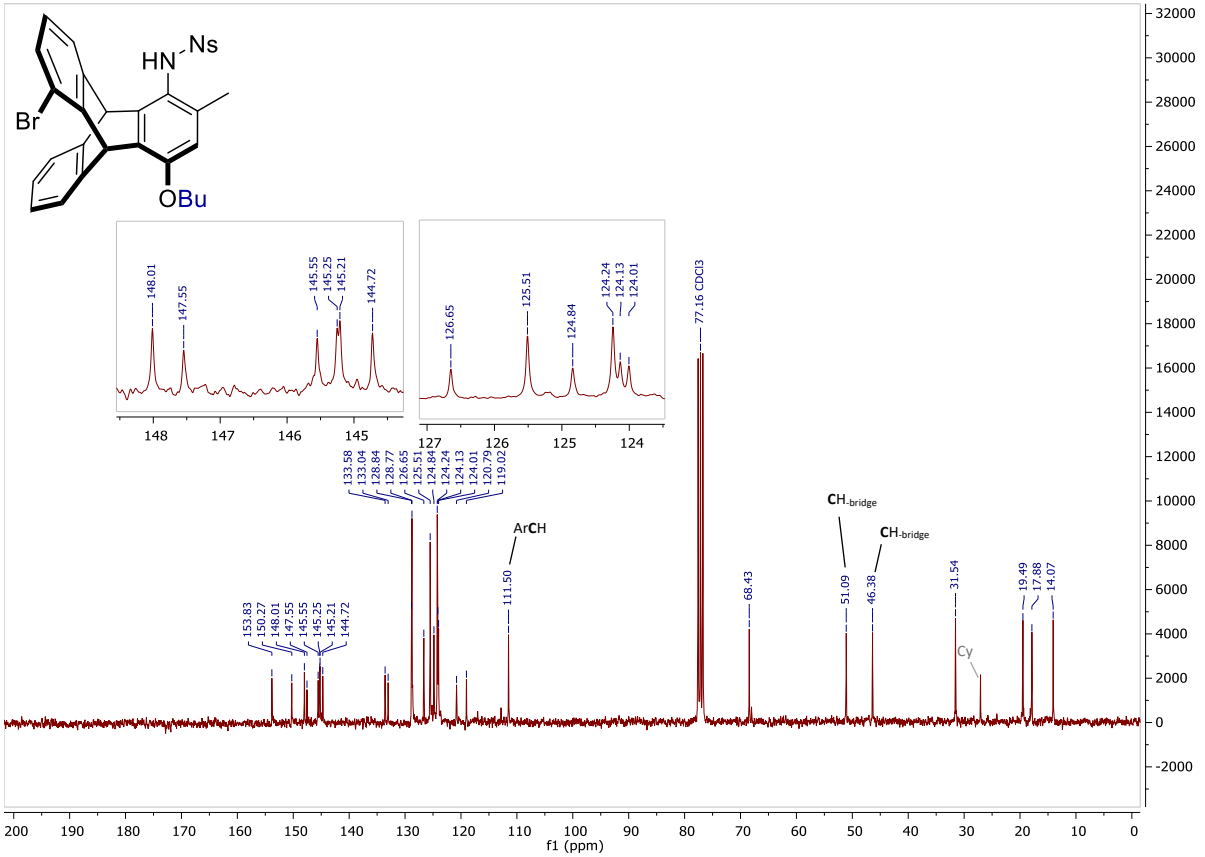


*Figure 93: [13]C-NMR of O-alkylated aminophenol (nosyl protected) (**5m**) in $CDCl_3$.*

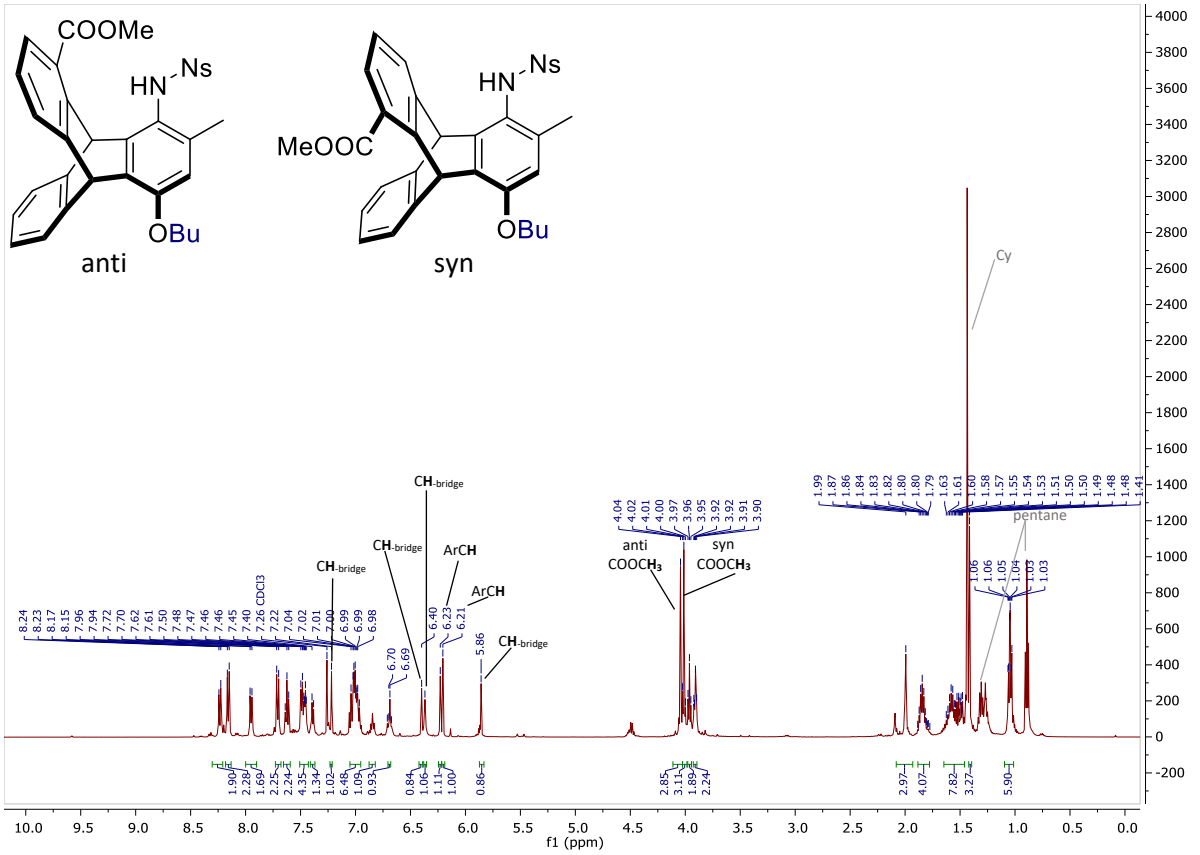


*Figure 94: ^{1}H-NMR of O-alkylated aminophenol (nosyl protected) (**5n**) in $CDCl_3$.*

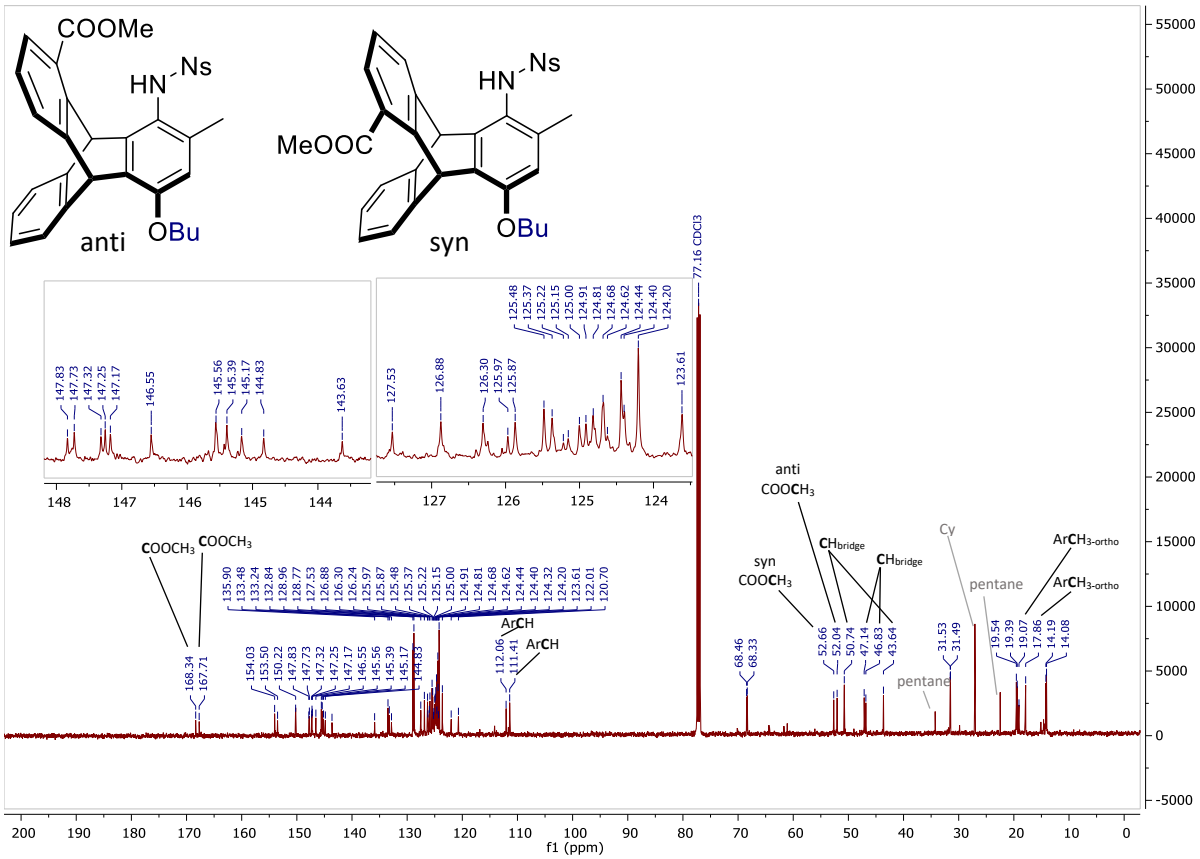


*Figure 95: ^{13}C-NMR of O-alkylated aminophenol (nosyl protected) (**5n**) in $CDCl_3$.*

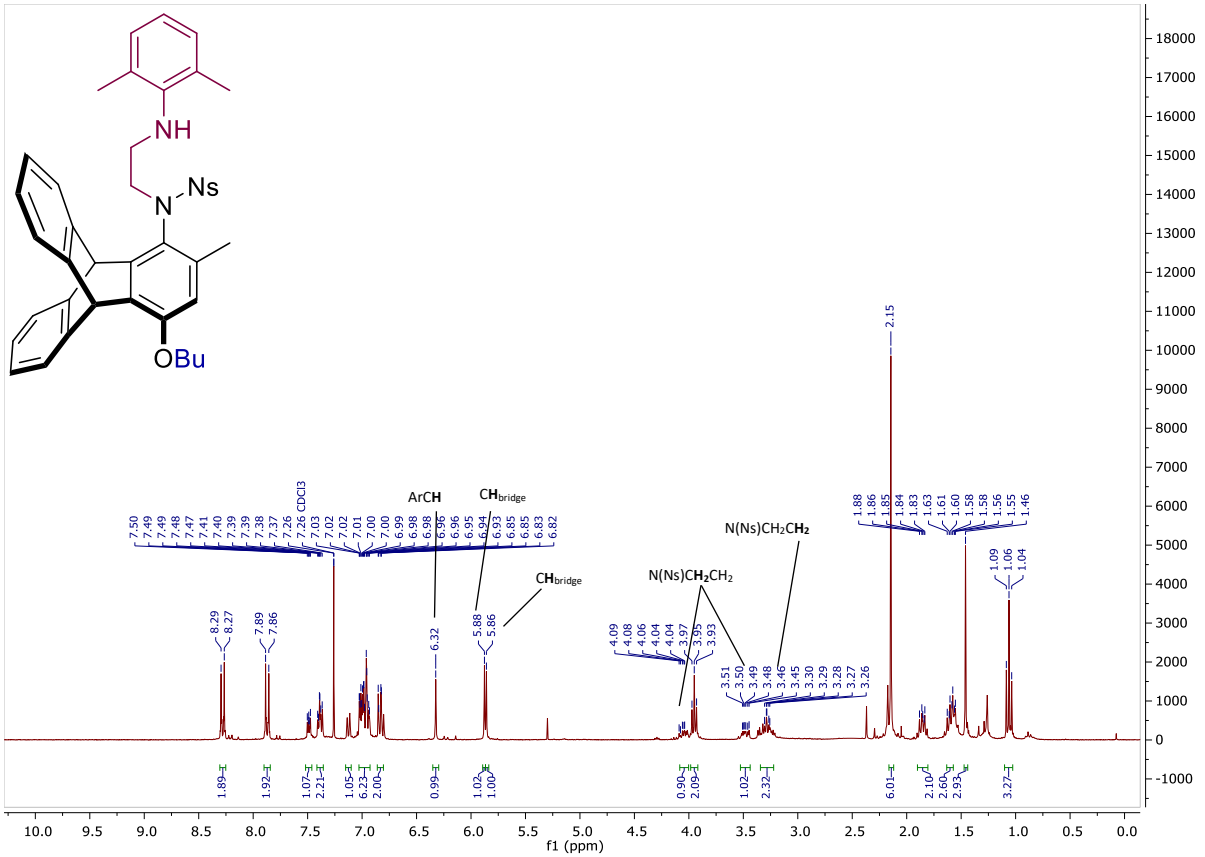


*Figure 96: [1]H-NMR of N/O-alkylated aminophenol (nosyl protected) (**5bc**) in $CDCl_3$.*

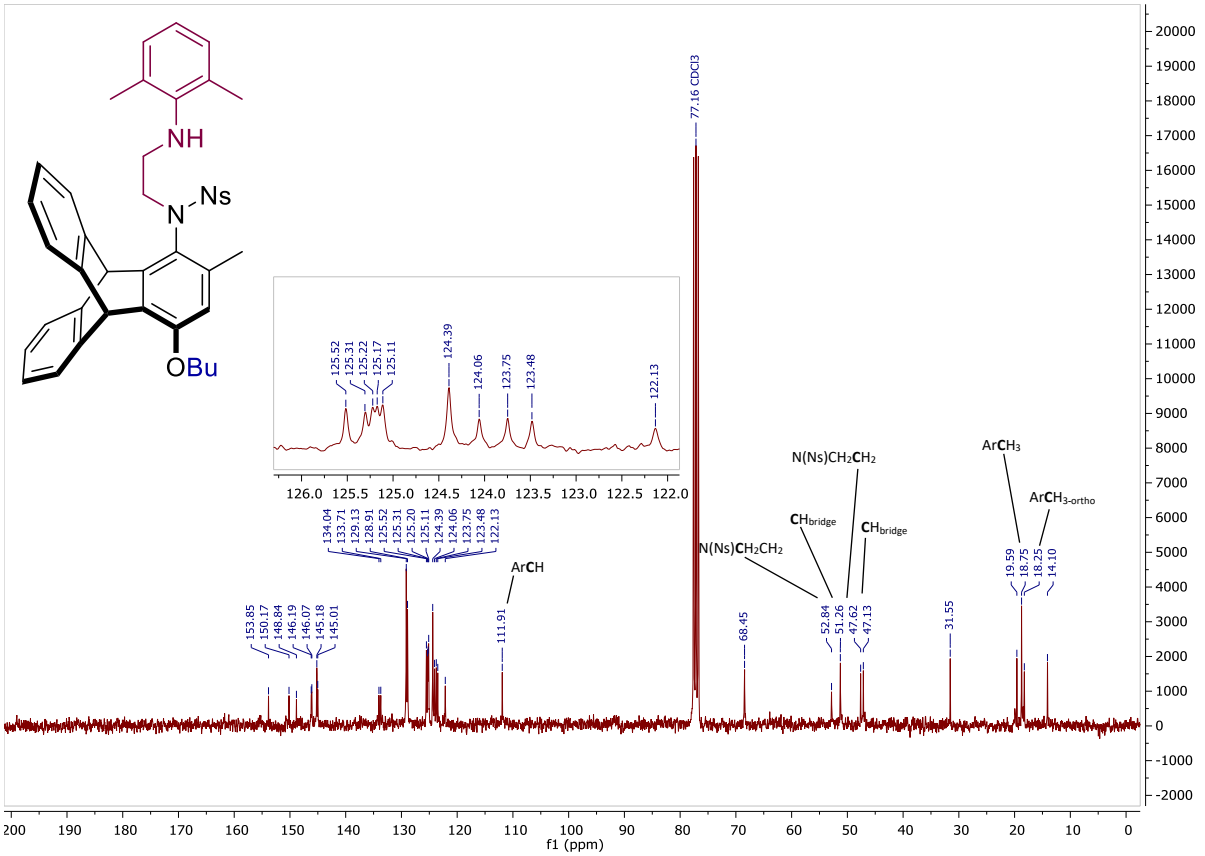


*Figure 97: [13]C-NMR of N/O-alkylated aminophenol (nosyl protected) (**5bc**) in $CDCl_3$.*

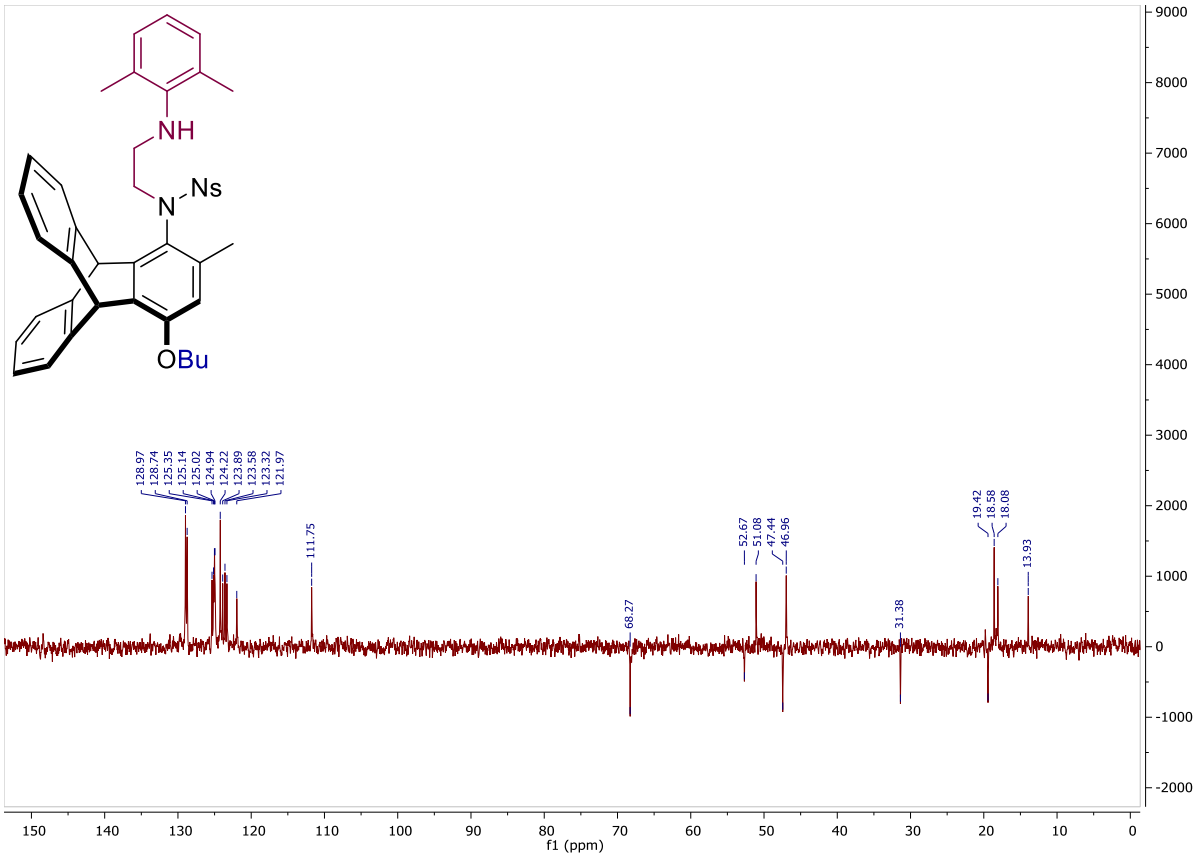


*Figure 98: DEPT of N/O-alkylated aminophenol (nosyl protected) (**5bc**) in $CDCl_3$.*

Silylated triptycene

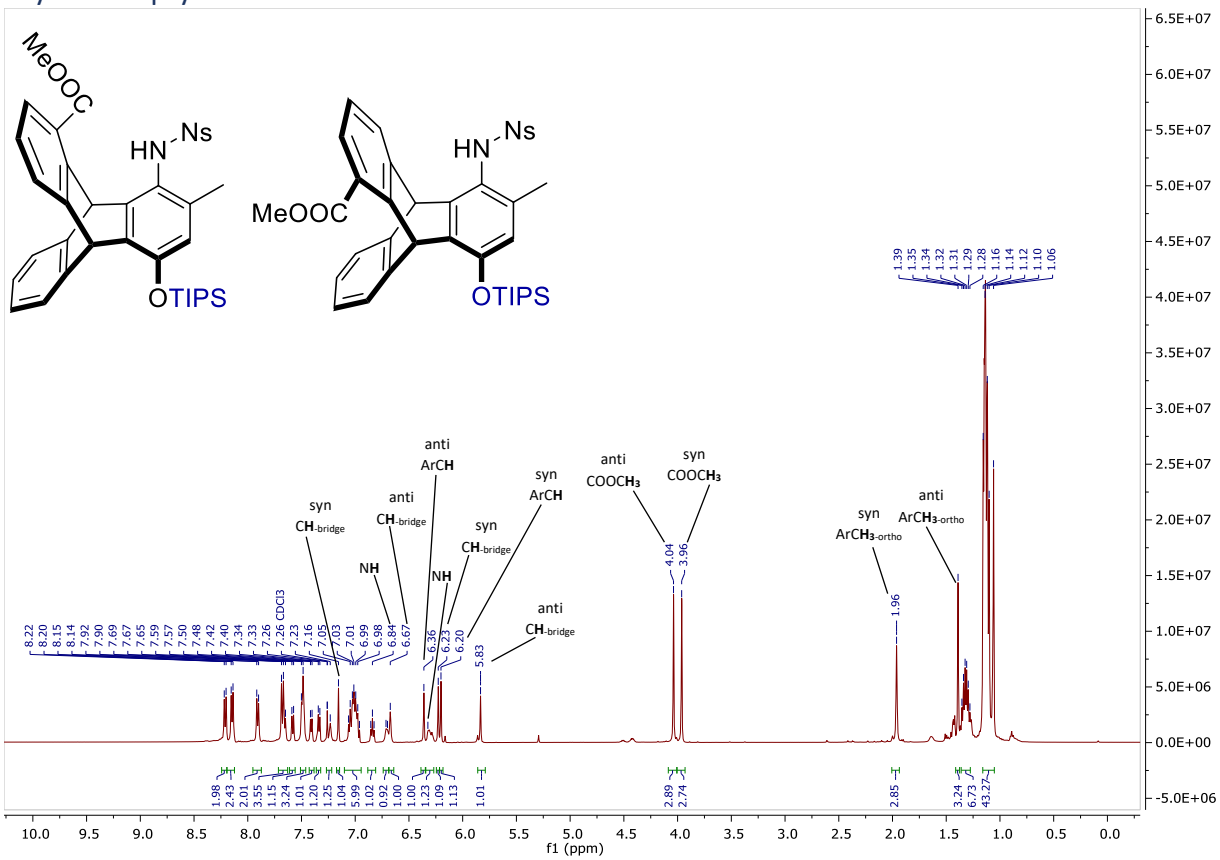


*Figure 99: ^{1}H-NMR of O-silylated aminophenol (nosyl protected) (**5na**) in $CDCl_3$.*

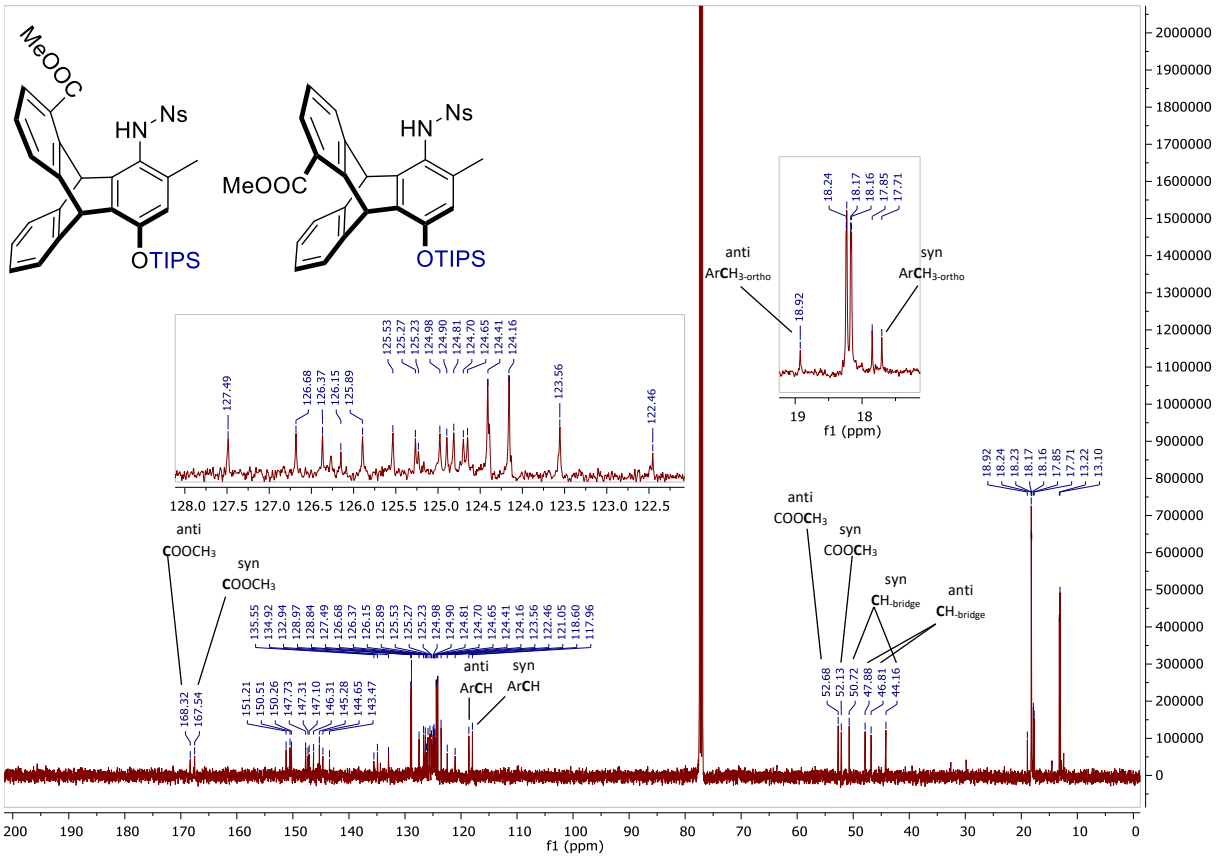


*Figure 100: ^{13}C-NMR of O-silylated aminophenol (nosyl protected) (**5na**) in $CDCl_3$.*

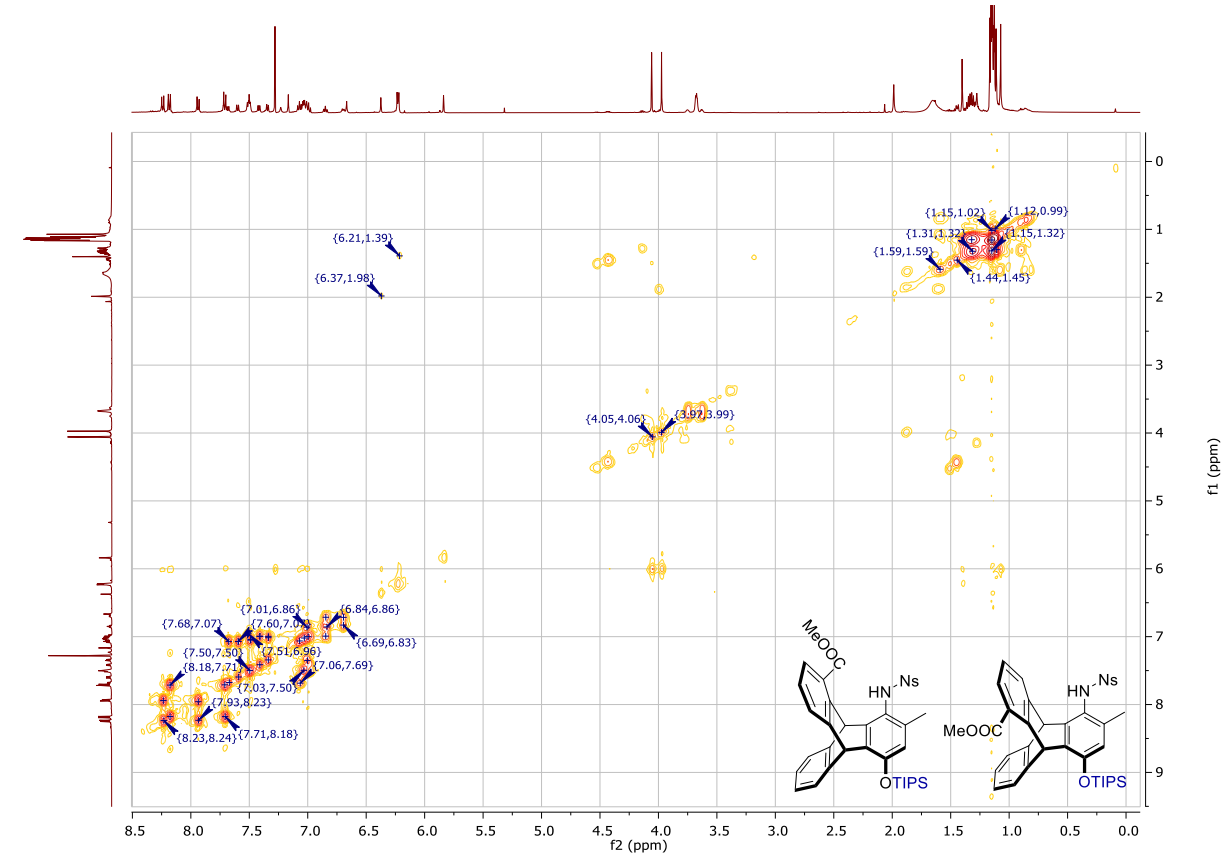


*Figure 101: COSY-NMR of O-silylated aminophenol (nosyl protected) (**5na**) in $CDCl_3$.*

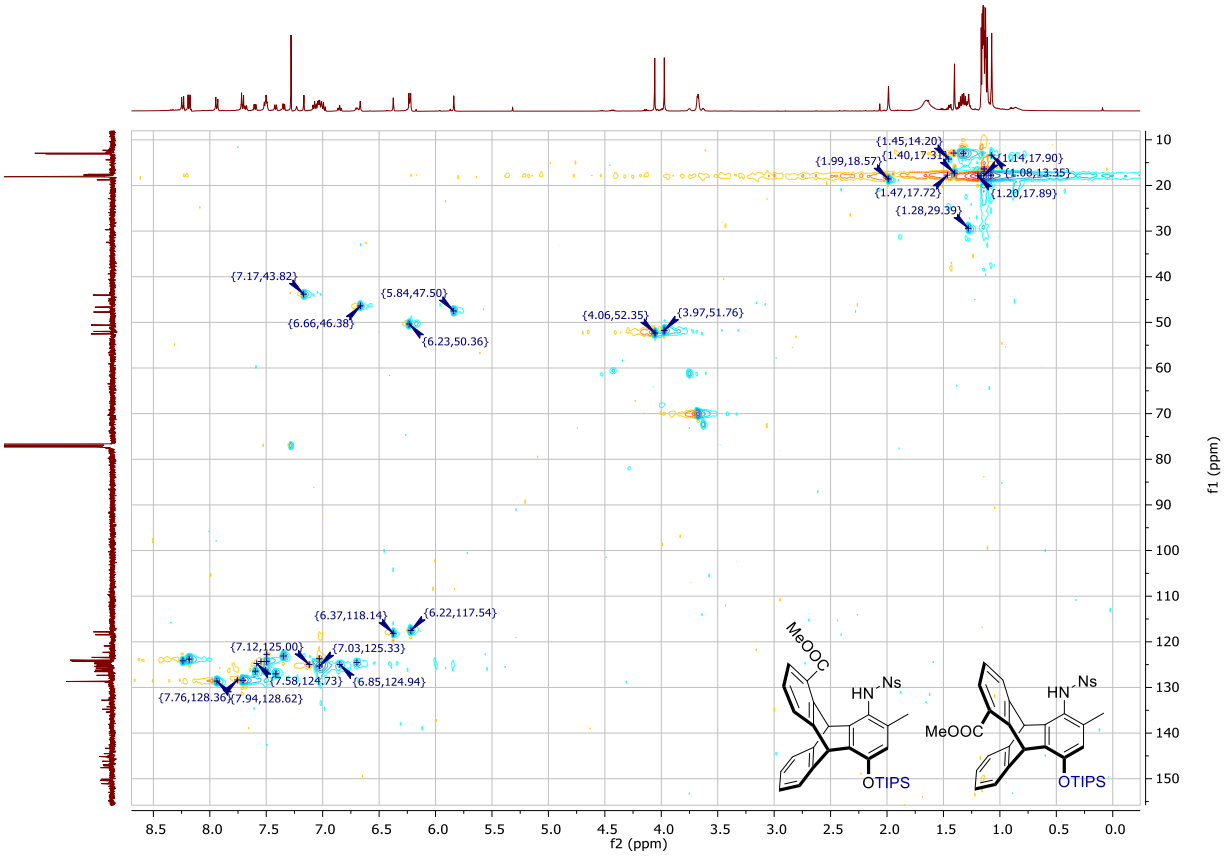


*Figure 102: HSQC-NMR of O-silylated aminophenol (nosyl protected) (**5na**) in $CDCl_3$.*

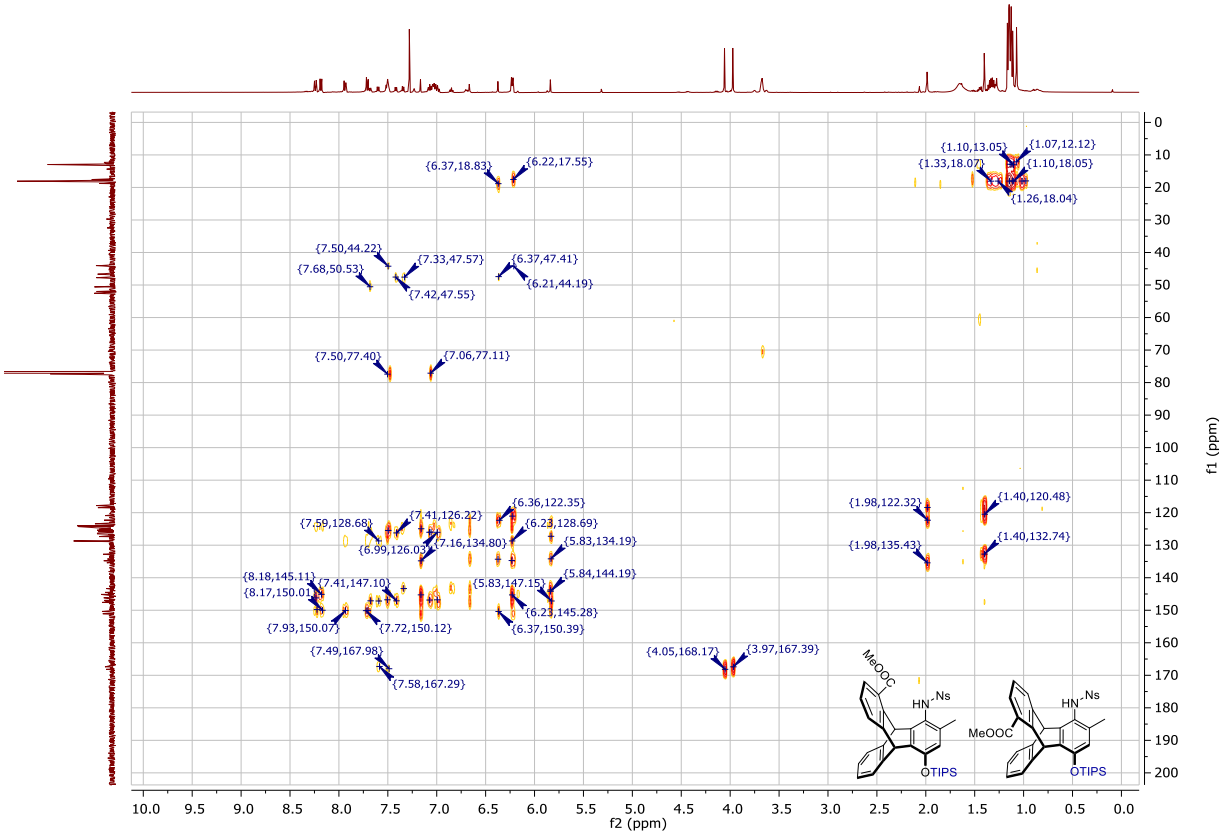


*Figure 103: HMBC-NMR of O-silylated aminophenol (nosyl protected) (**5na**) in $CDCl_3$.*

Denosylated aminotriptycene

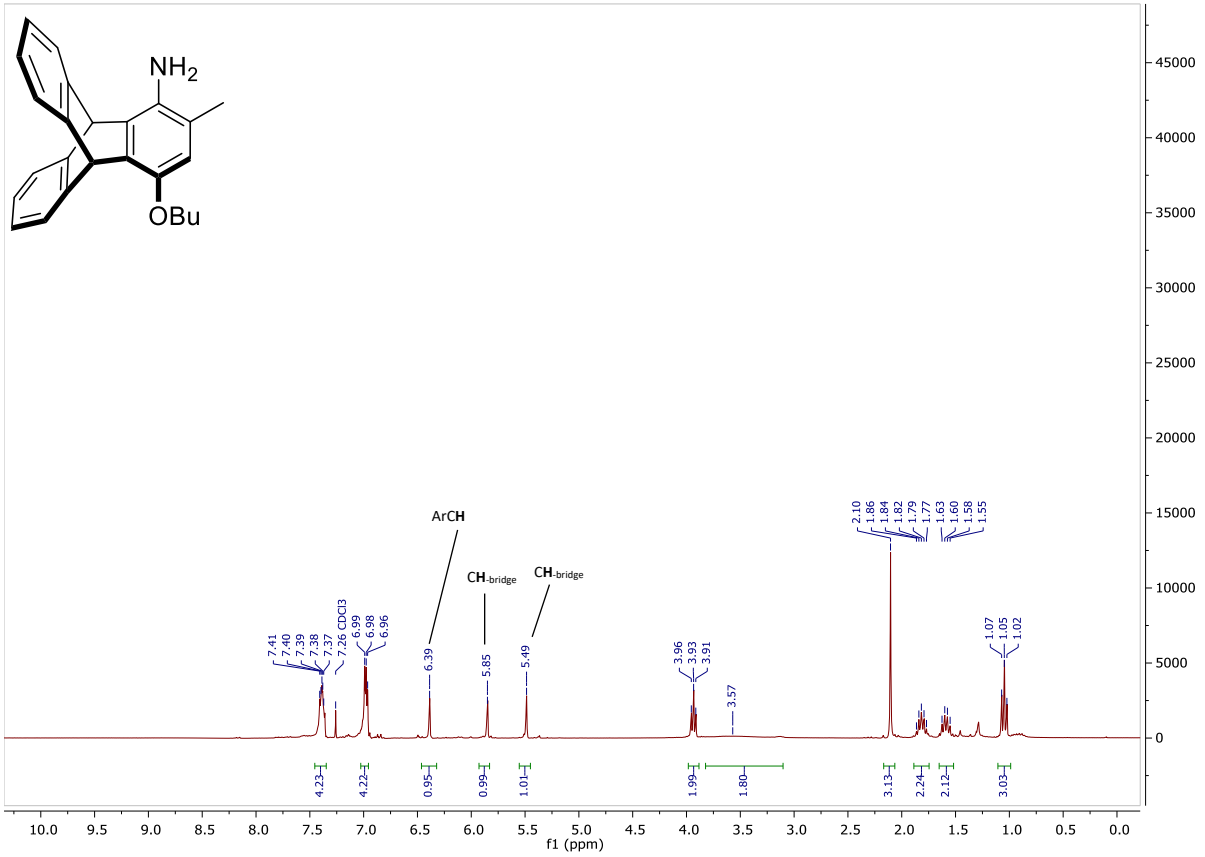


*Figure 104: ^{1}H-NMR of denosylated aminotriptycen (**6b**) in $CDCl_3$.*

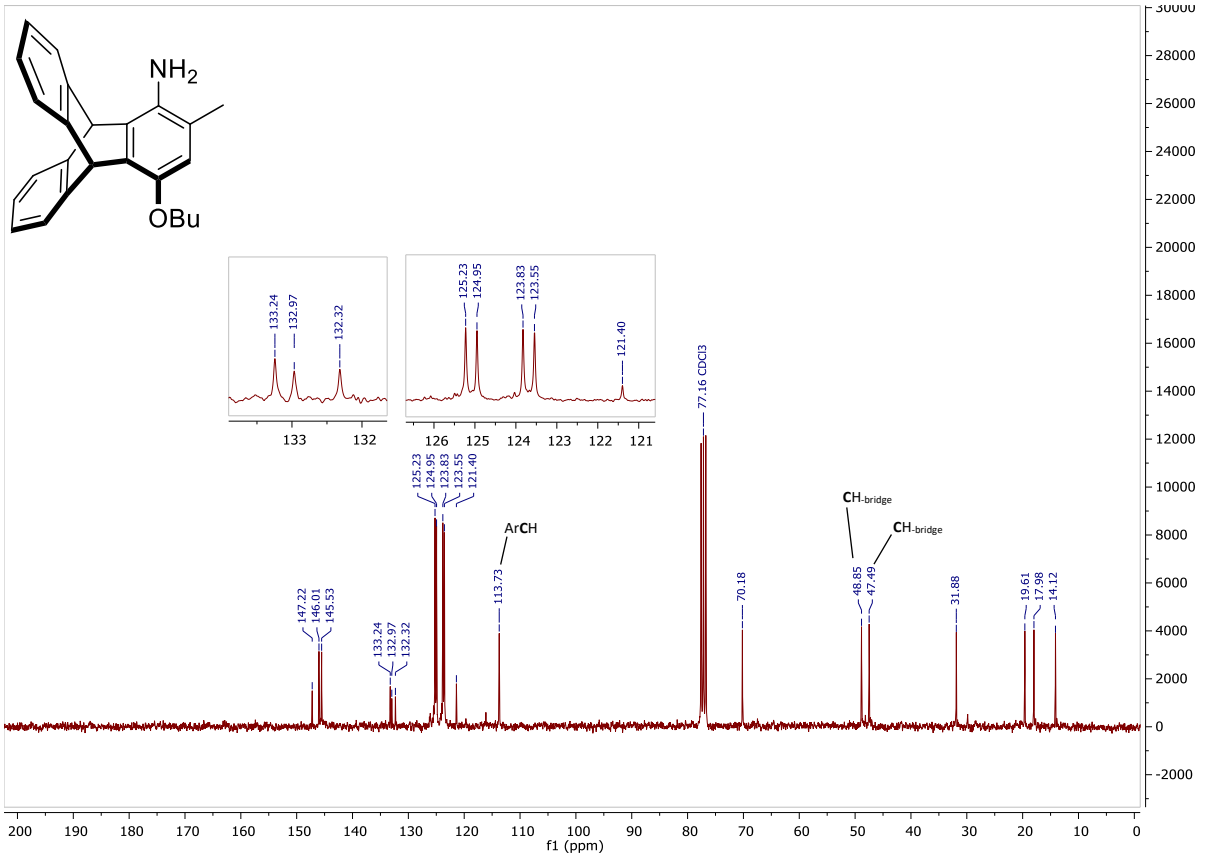


*Figure 105: ^{13}C-NMR of denosylated aminotriptycen (**6b**) in $CDCl_3$.*

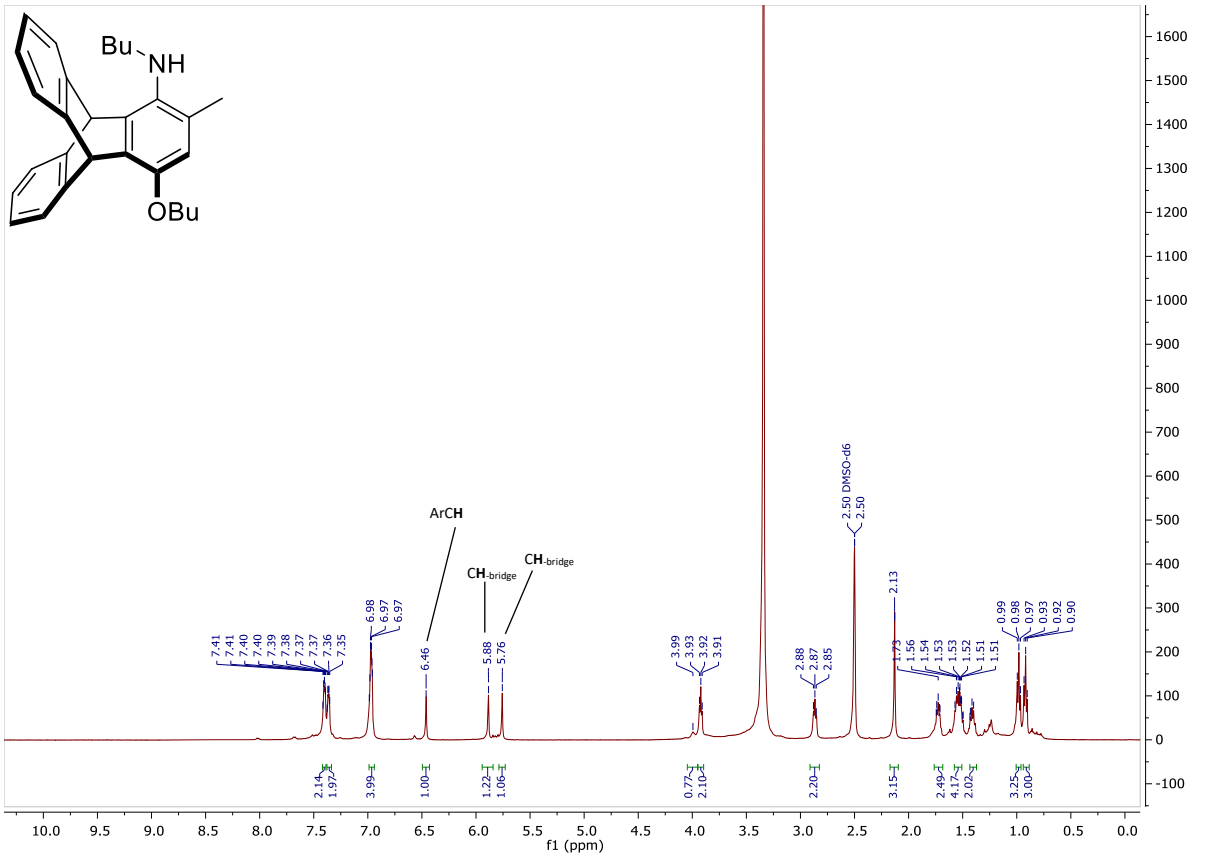


*Figure 106: ^{1}H-NMR of denosylated aminotriptycen (**6bb**) in DMSO-d_6.*

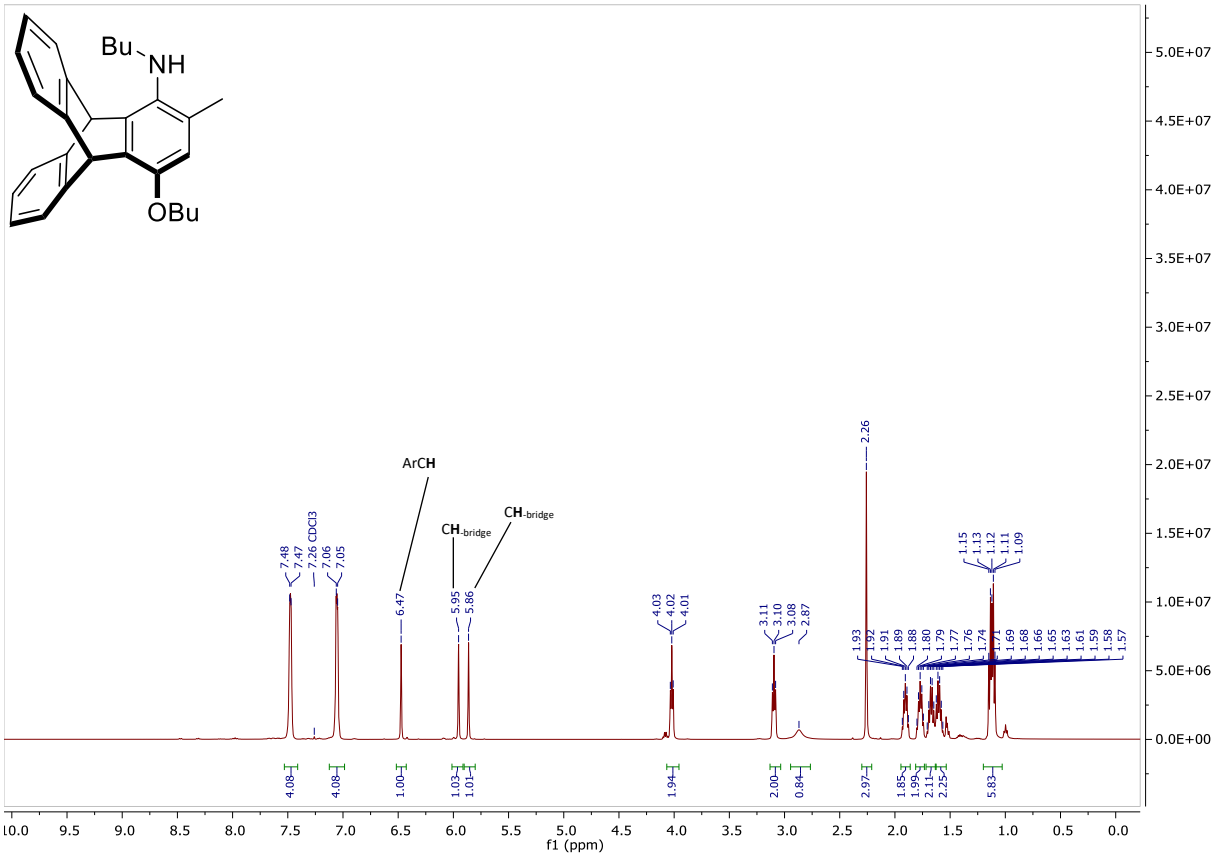


*Figure 107: ^{1}H-NMR of denosylated aminotriptycen (**6bb**) in $CDCl_3$.*

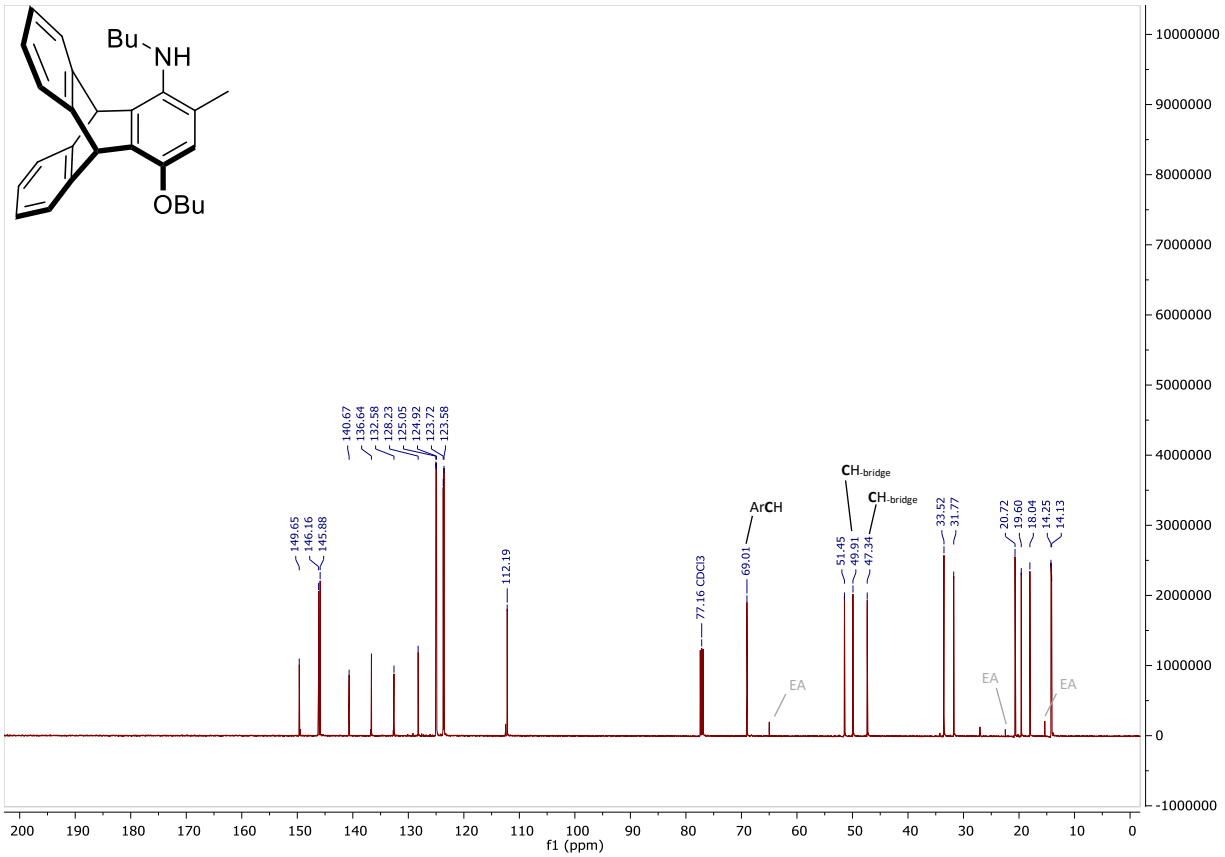


*Figure 108: ^{13}C-NMR of denosylated aminotriptycen (**6bb**) in $CDCl_3$.*

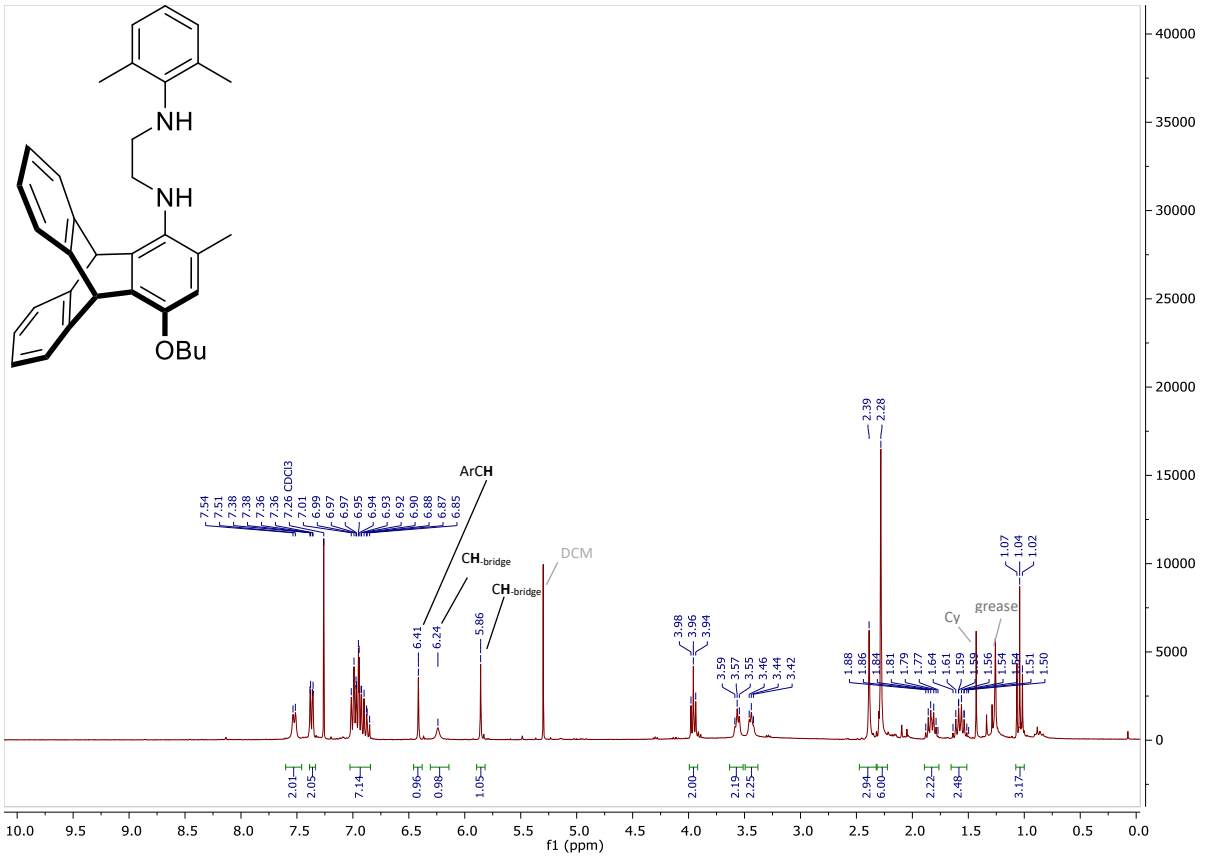


*Figure 109: ^{1}H-NMR of denosylated aminotriptycen (**9**) in $CDCl_3$.*

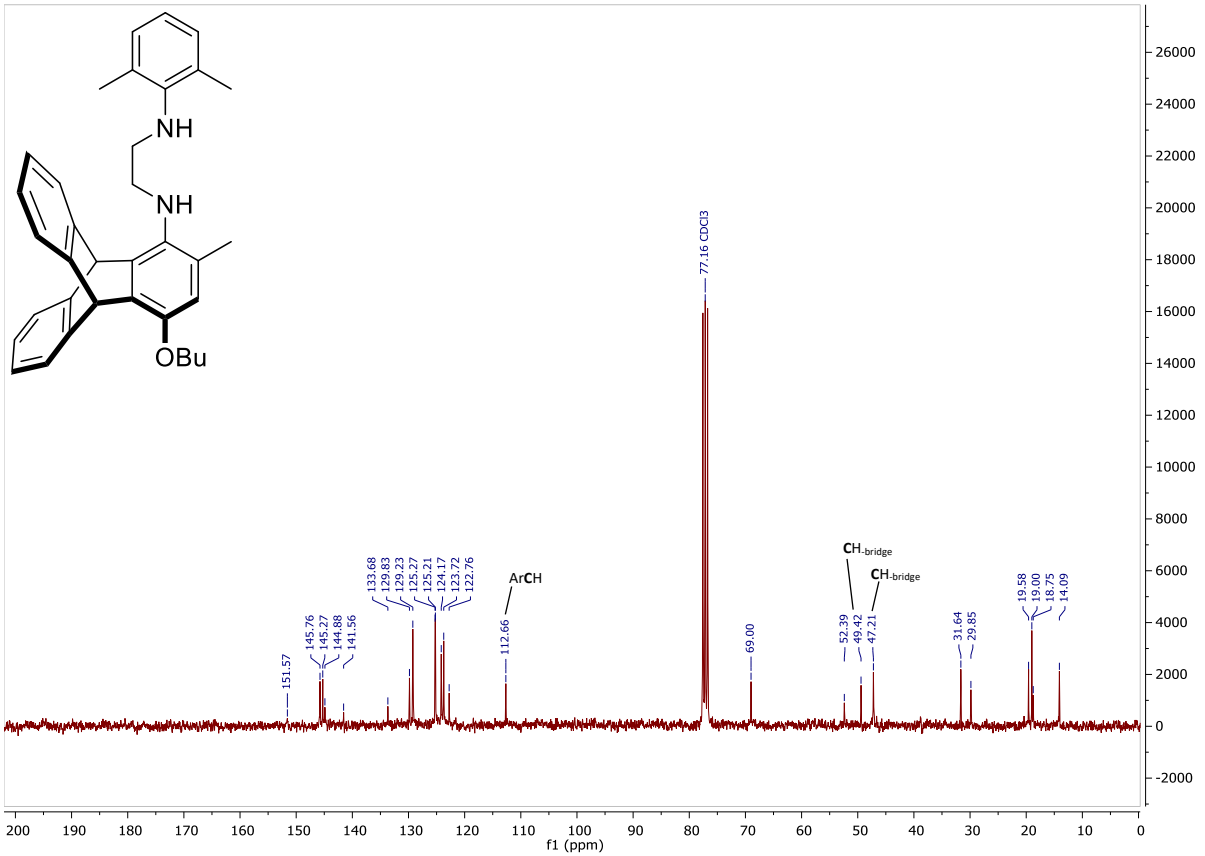


*Figure 110: ^{13}C-NMR of denosylated aminotriptycen (**9**) in $CDCl_3$.*

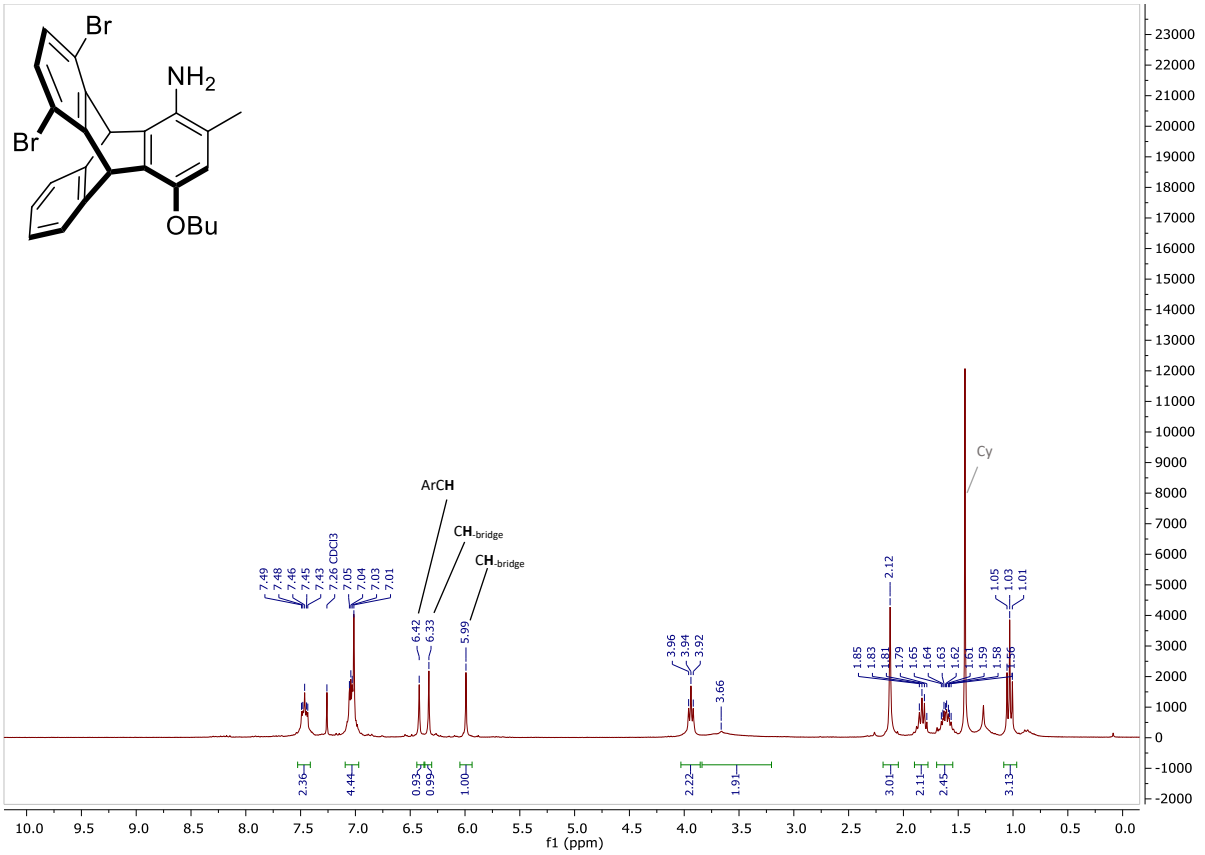


*Figure 111: [1]H-NMR of denosylated aminotriptycen (**6c**) in $CDCl_3$.*

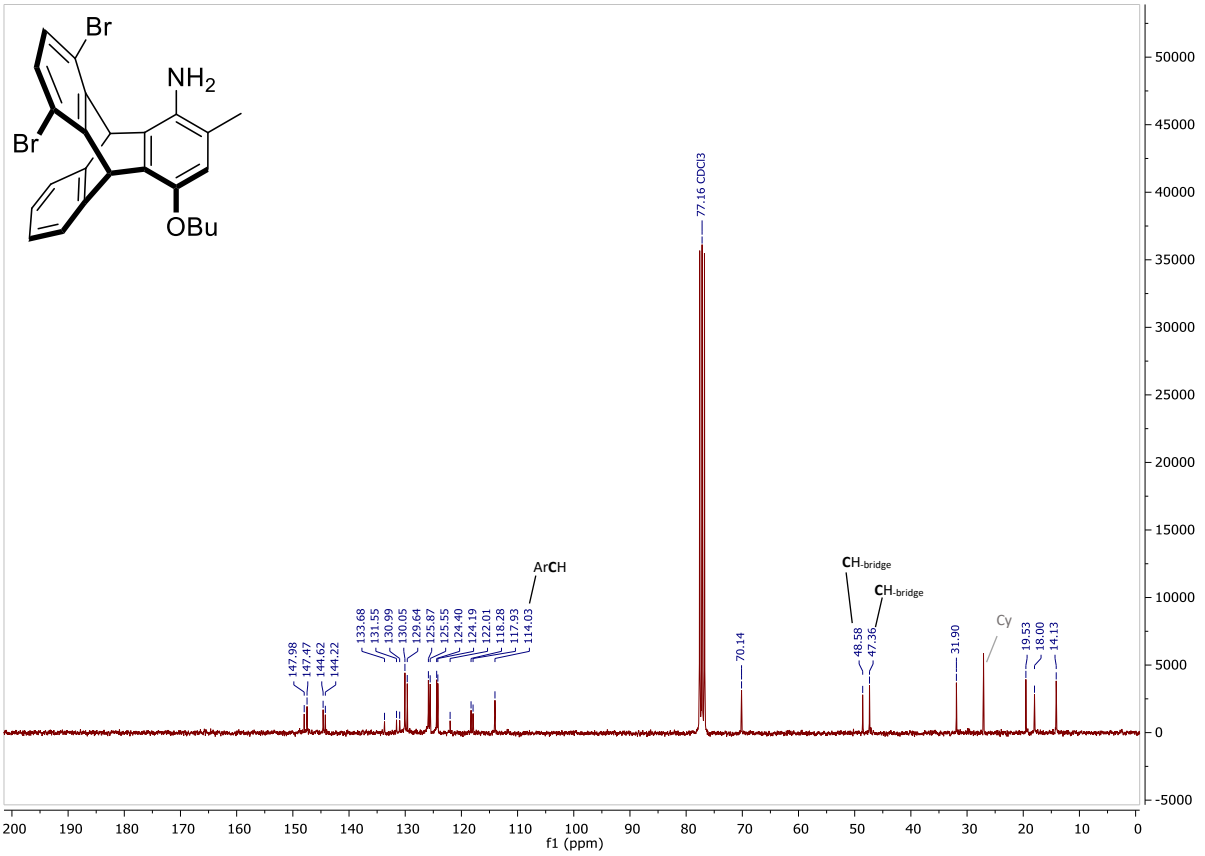


*Figure 112: [13]C-NMR of denosylated aminotriptycen (**6c**) in $CDCl_3$.*

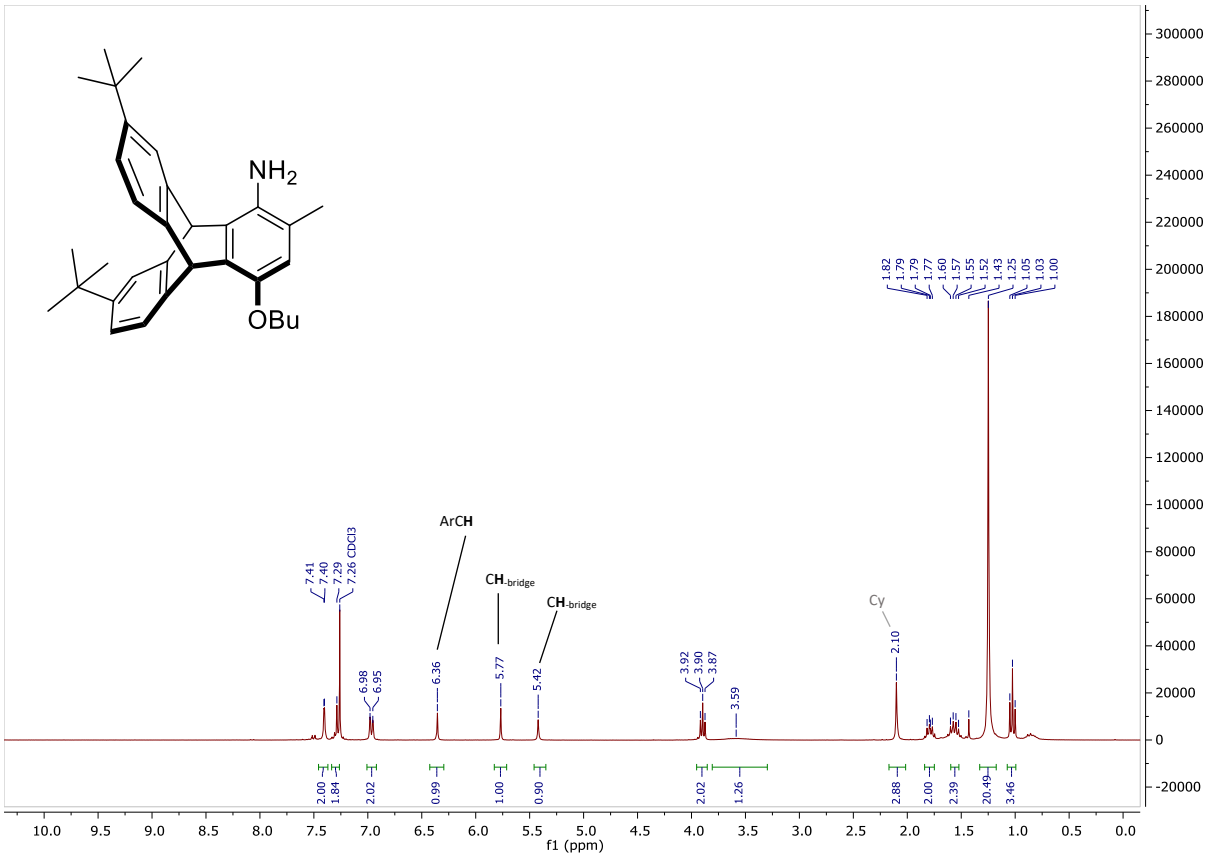


*Figure 113: [1]H-NMR of denosylated aminotriptycen (**6ha**) in $CDCl_3$.*

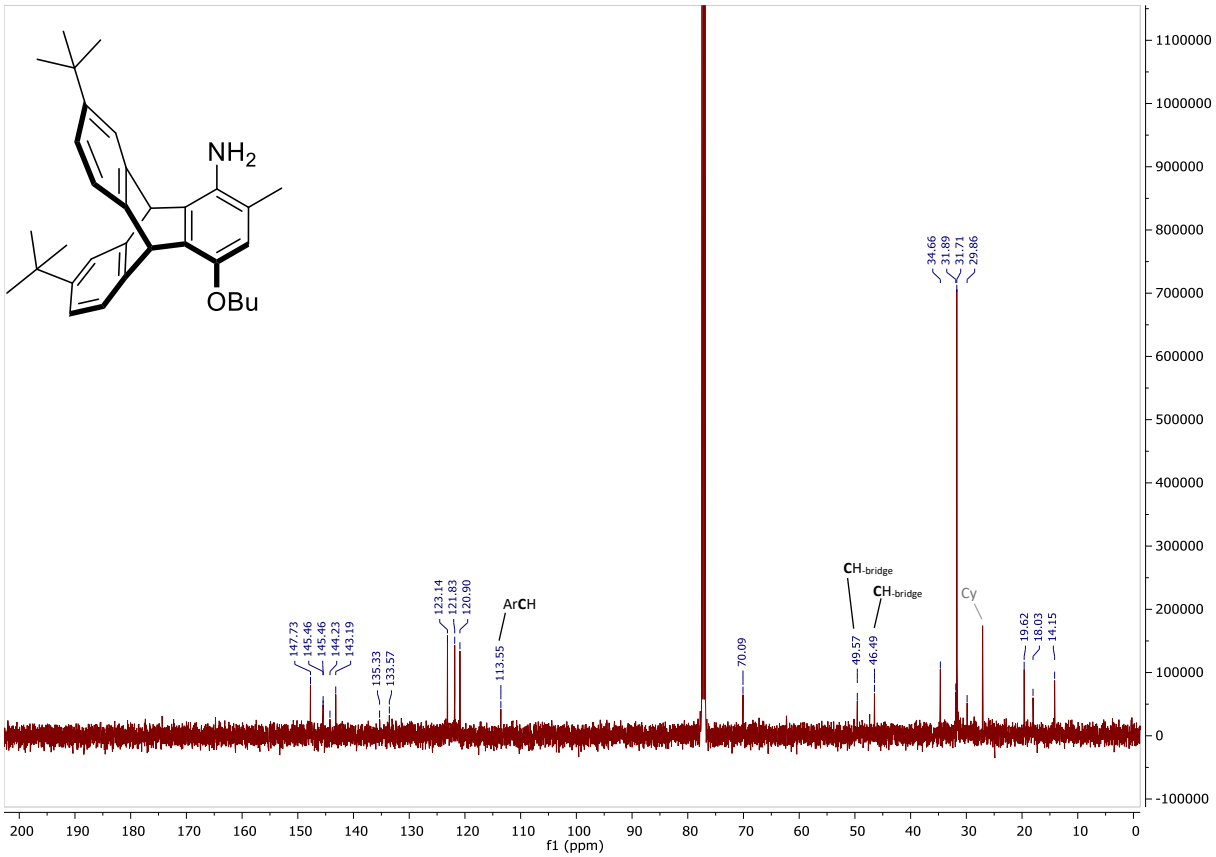


*Figure 114: [13]C-NMR of denosylated aminotriptycen (**6ha**) in $CDCl_3$.*

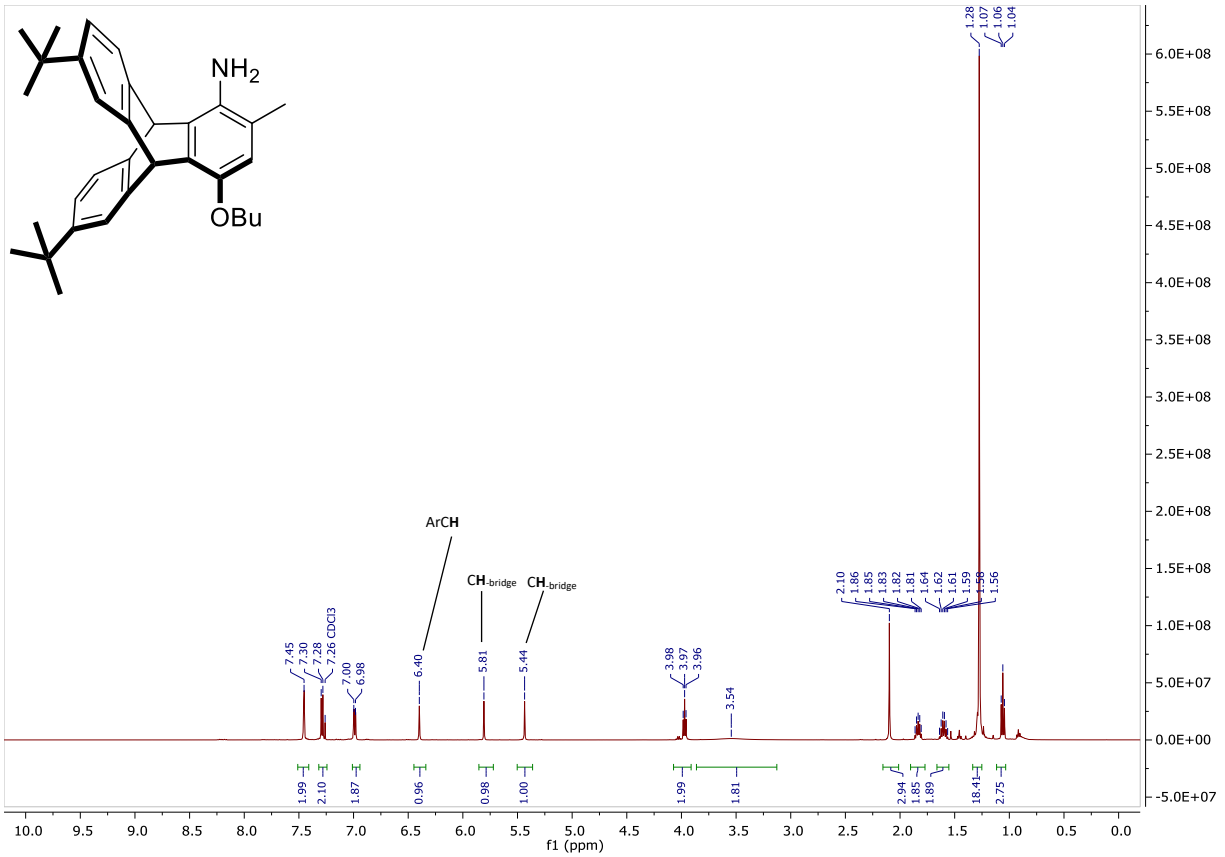


*Figure 115: ^{1}H-NMR of denosylated aminotriptycen (**6hb**) in $CDCl_3$.*

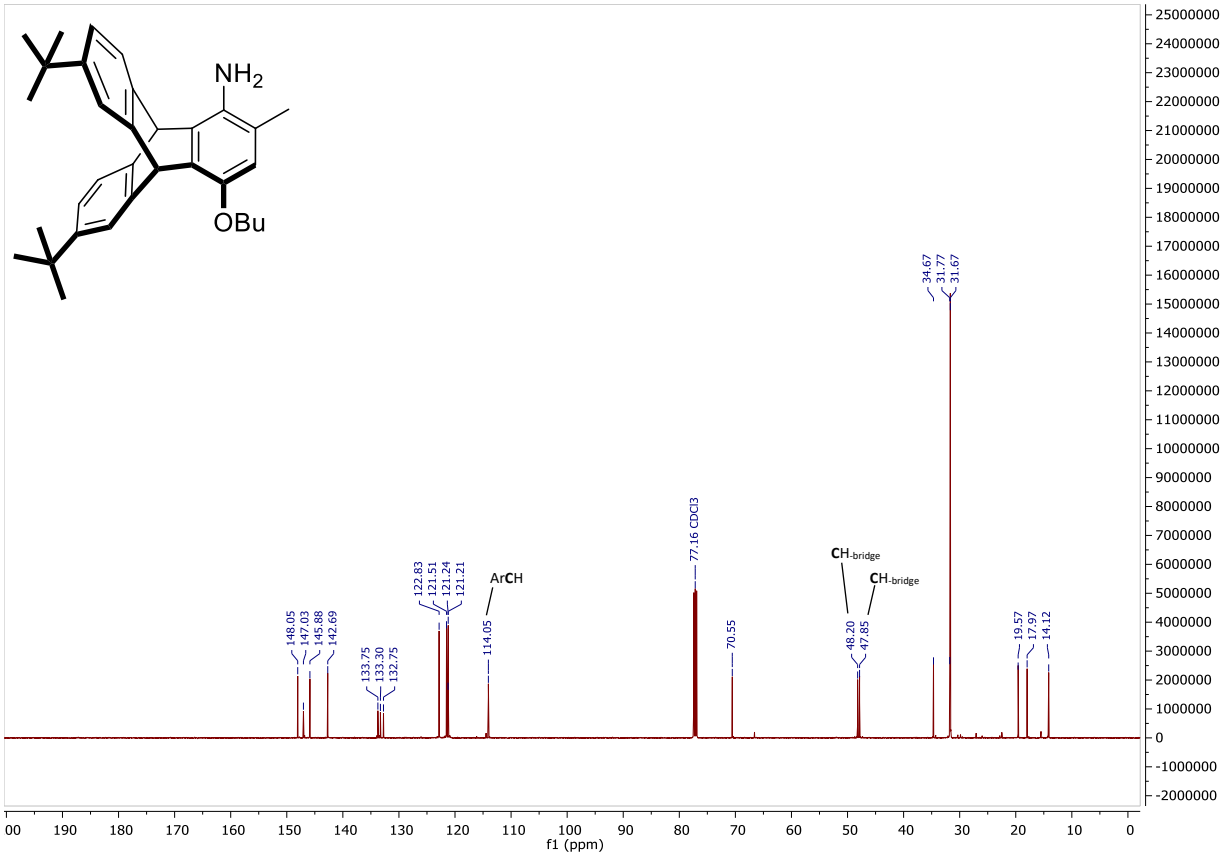


*Figure 116: ^{13}C-NMR of denosylated aminotriptycen (**6hb**) in $CDCl_3$.*

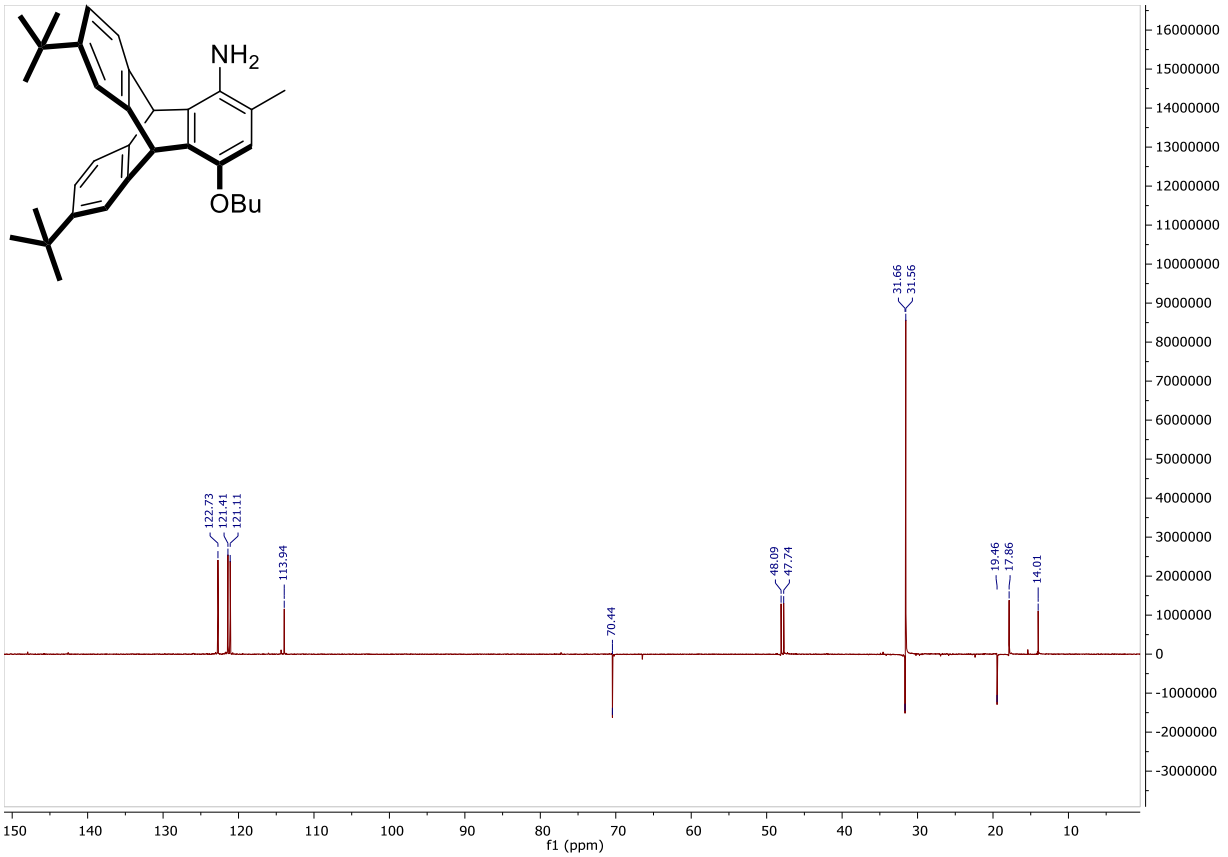


*Figure 117: DEPT-NMR of denosylated aminotriptycen (**6hb**) in $CDCl_3$.*

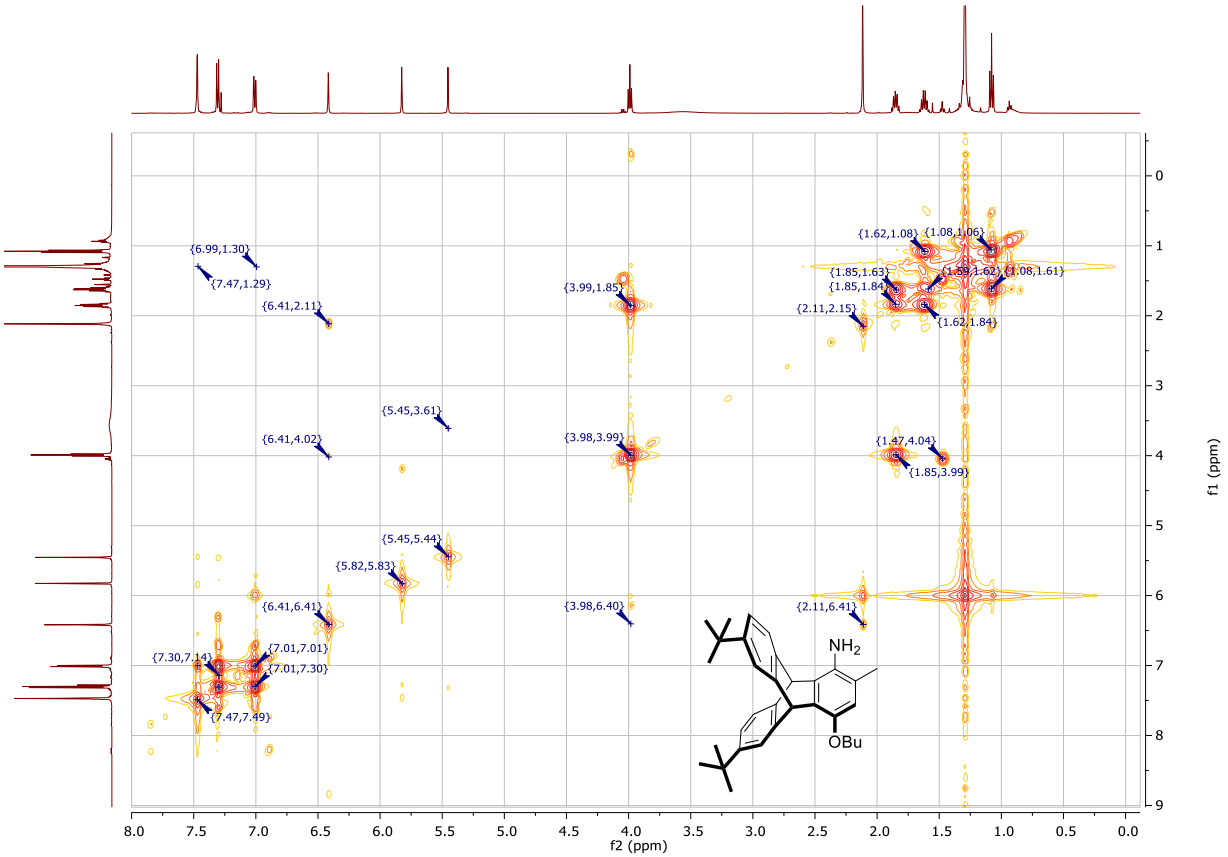


*Figure 118: COSY-NMR of denosylated aminotriptycen (**6hb**) in $CDCl_3$.*

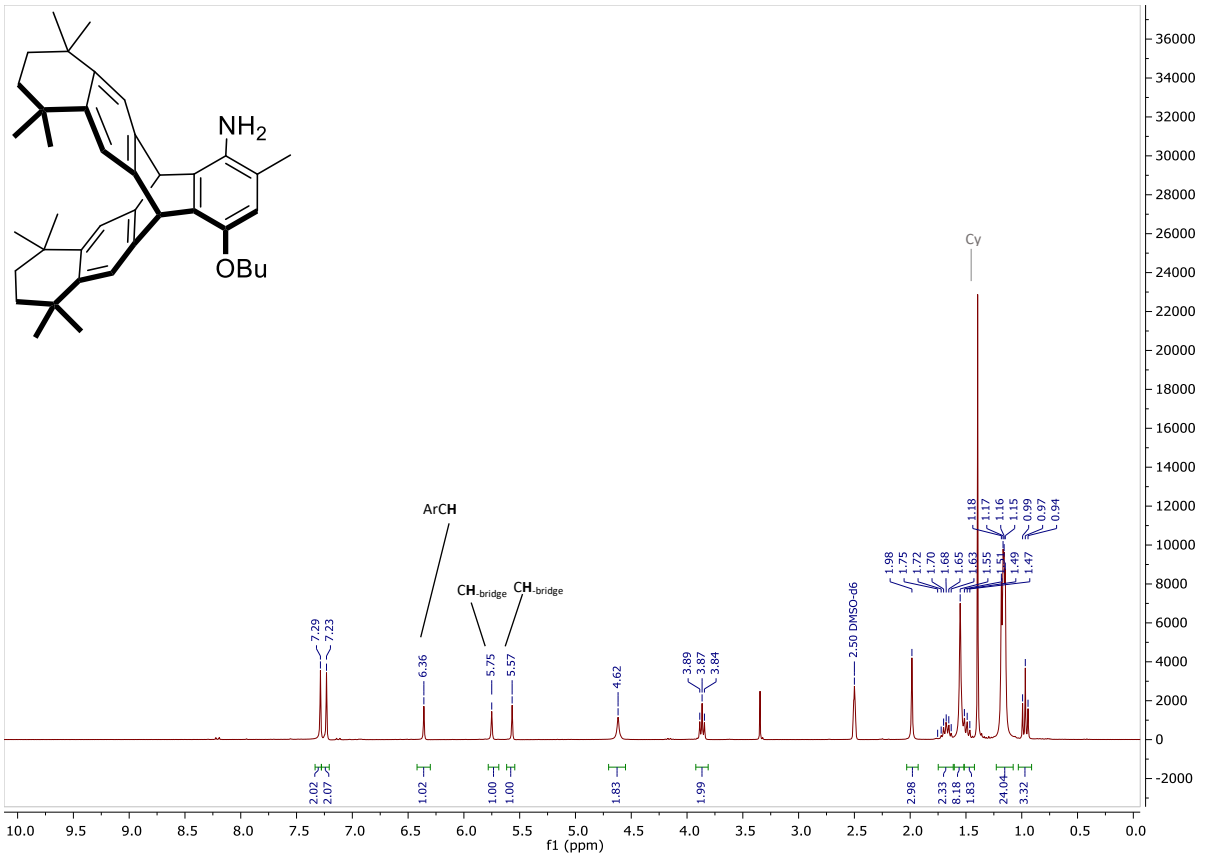


*Figure 119: ^{1}H-NMR of denosylated aminotriptycen (**6g**) in DMSO-d_6.*

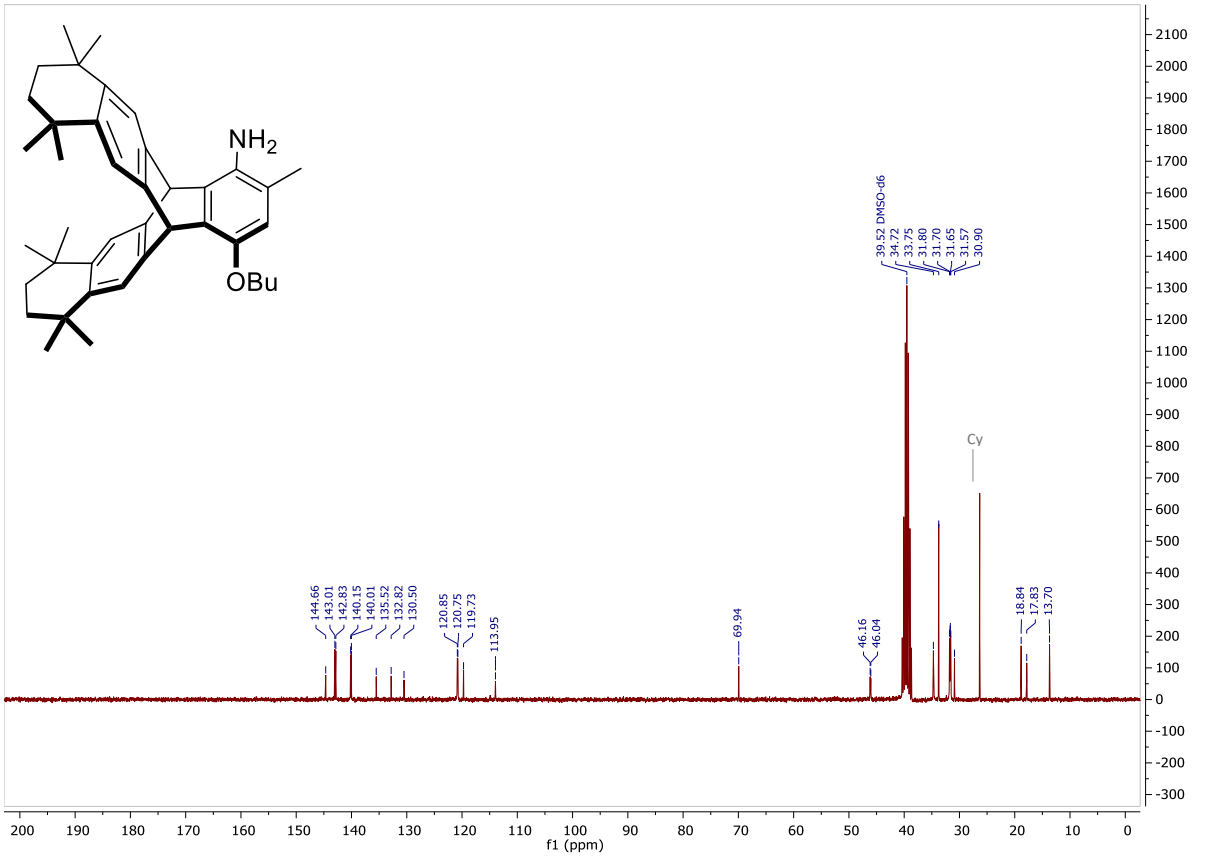


*Figure 120: ^{1}H-NMR of denosylated aminotriptycen (**6g**) in DMSO-d_6.*

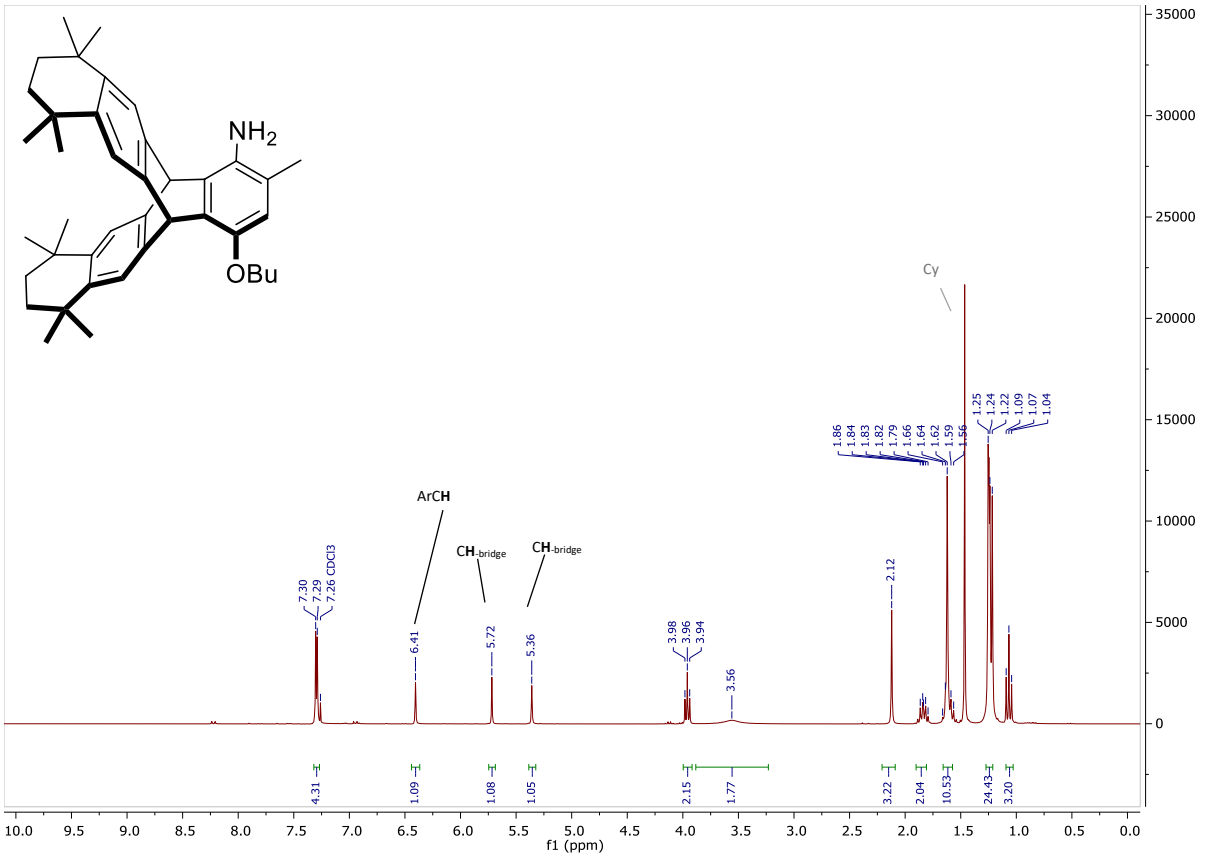


*Figure 121: ^{1}H-NMR of denosylated aminotriptycen (**6g**) in $CDCl_3$.*

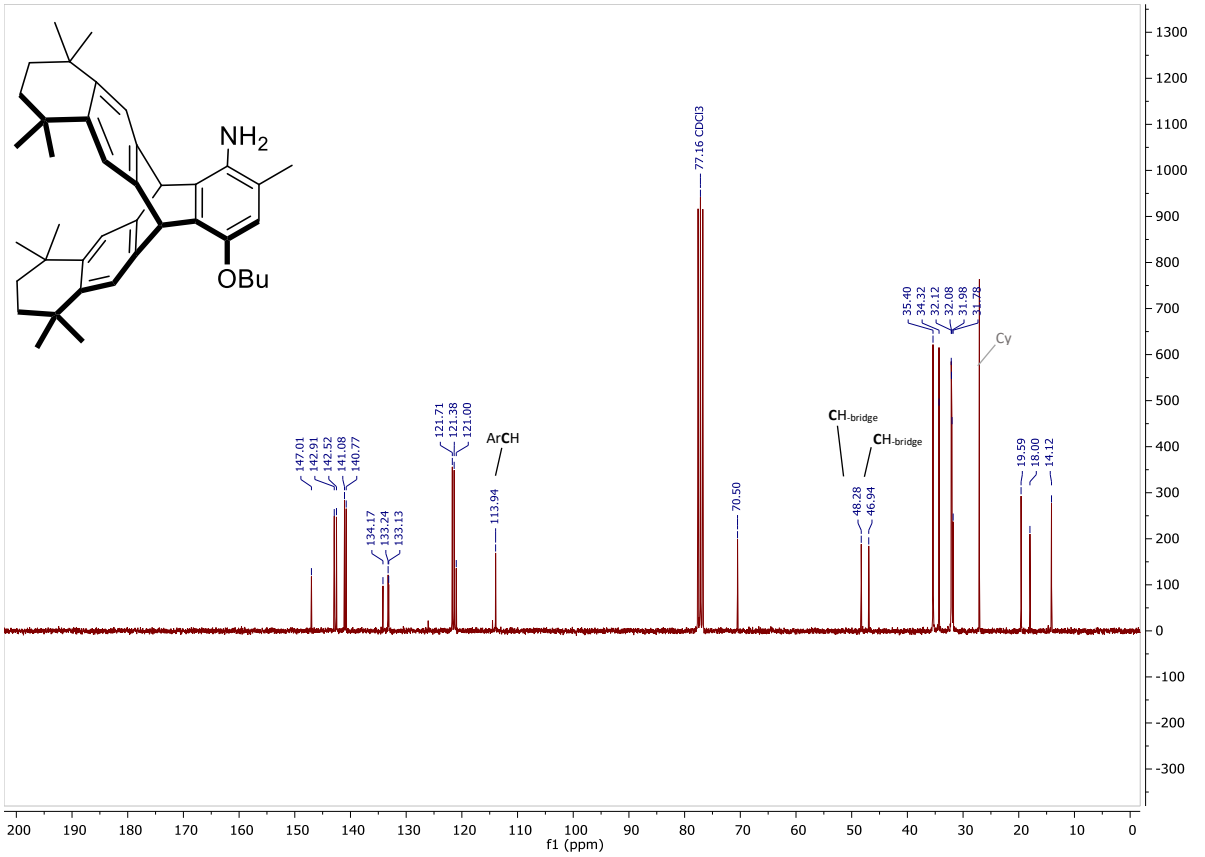


*Figure 122: ^{13}C-NMR of denosylated aminotriptycen (**6g**) in $CDCl_3$.*

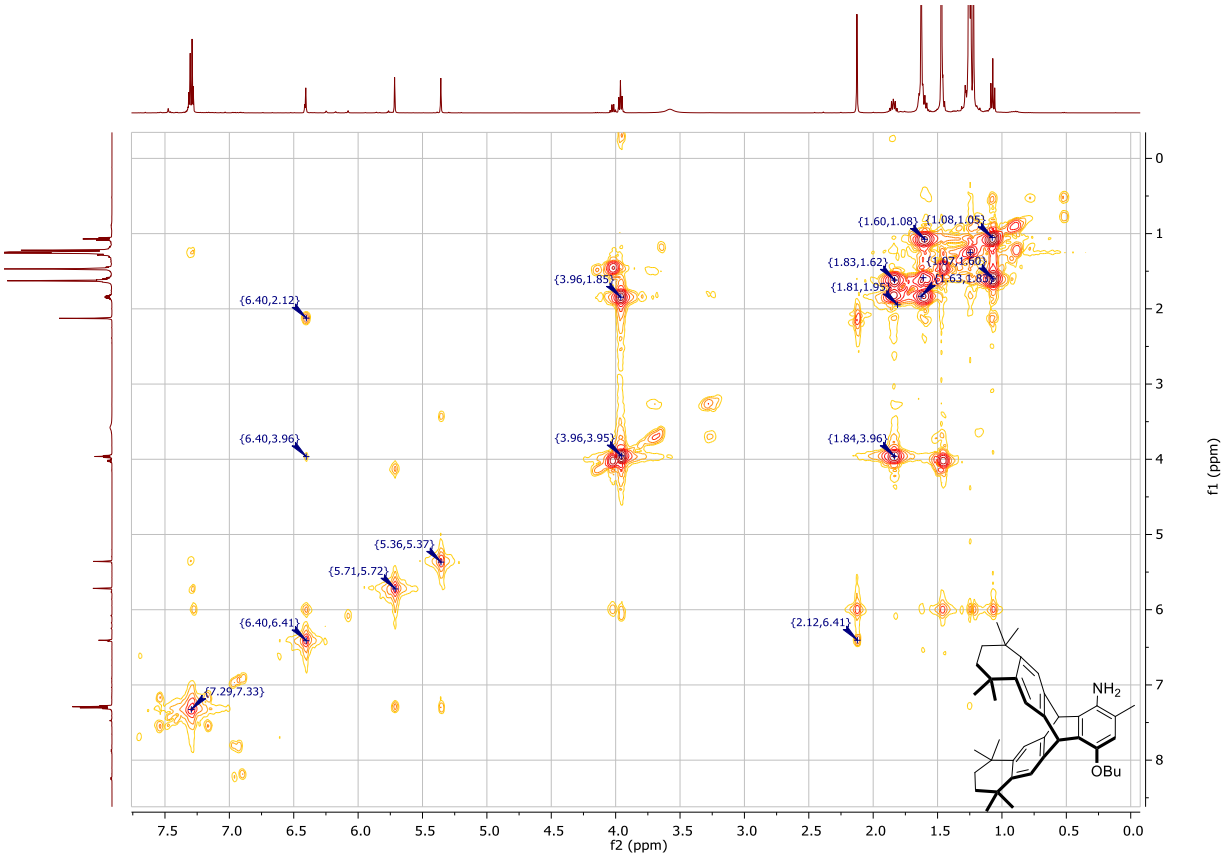


*Figure 123: COSY-NMR of denosylated aminotriptycen (**6g**) in $CDCl_3$.*

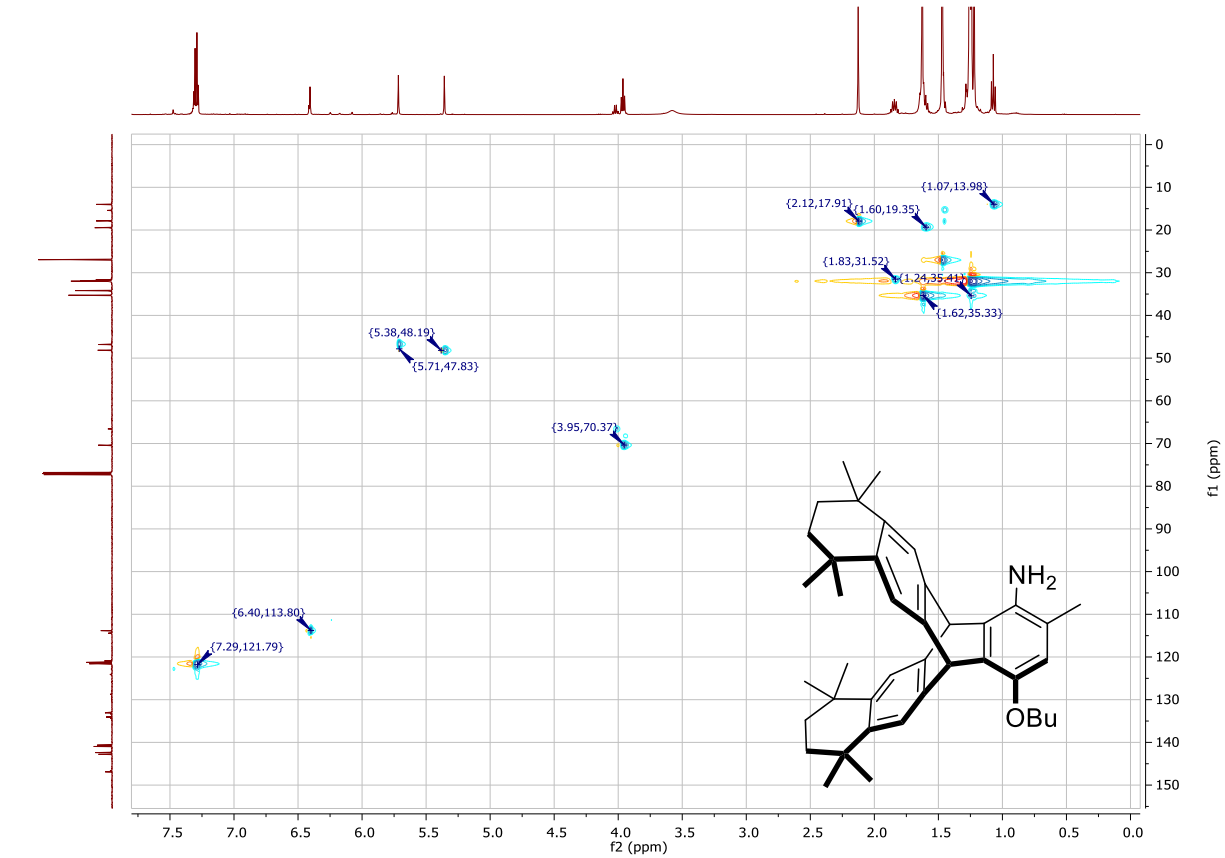


*Figure 124: HSQC-NMR of denosylated aminotriptycen (**6g**) in $CDCl_3$.*

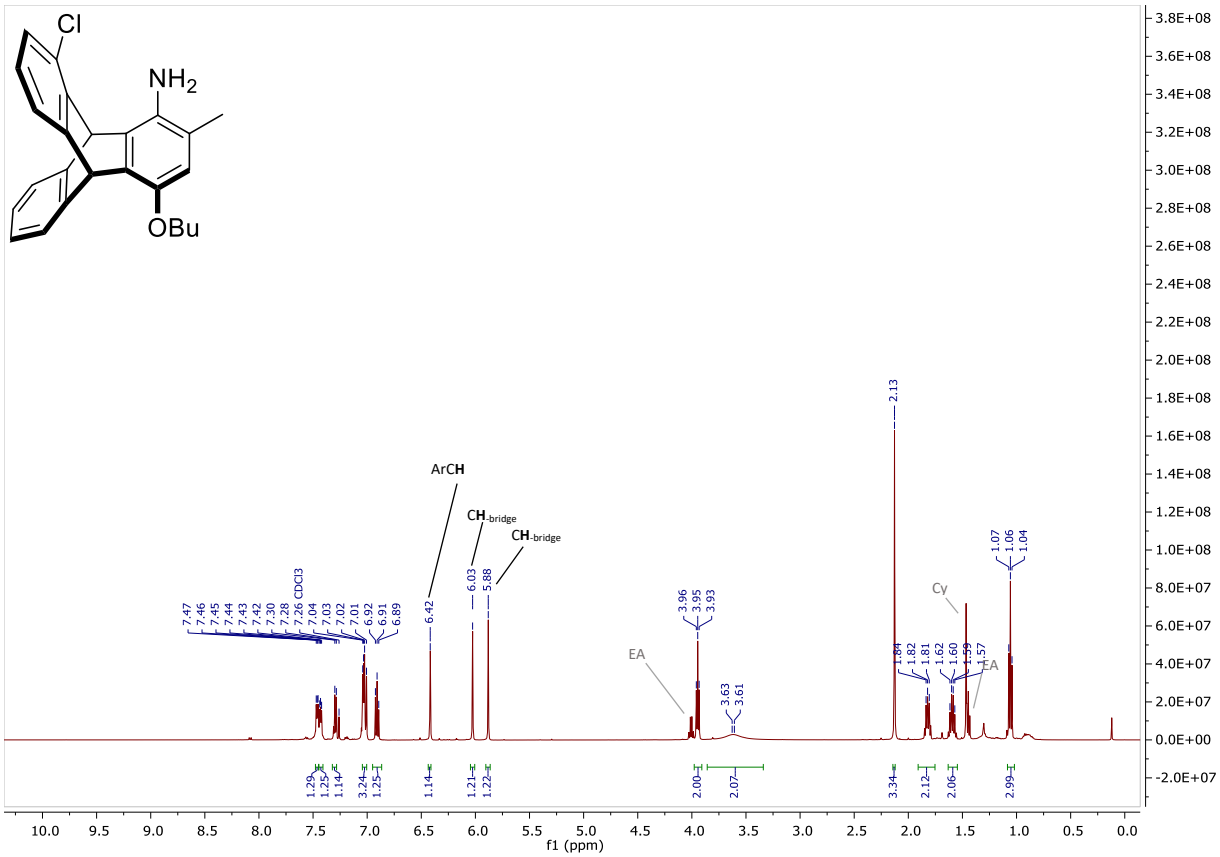


*Figure 125: ^{1}H-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

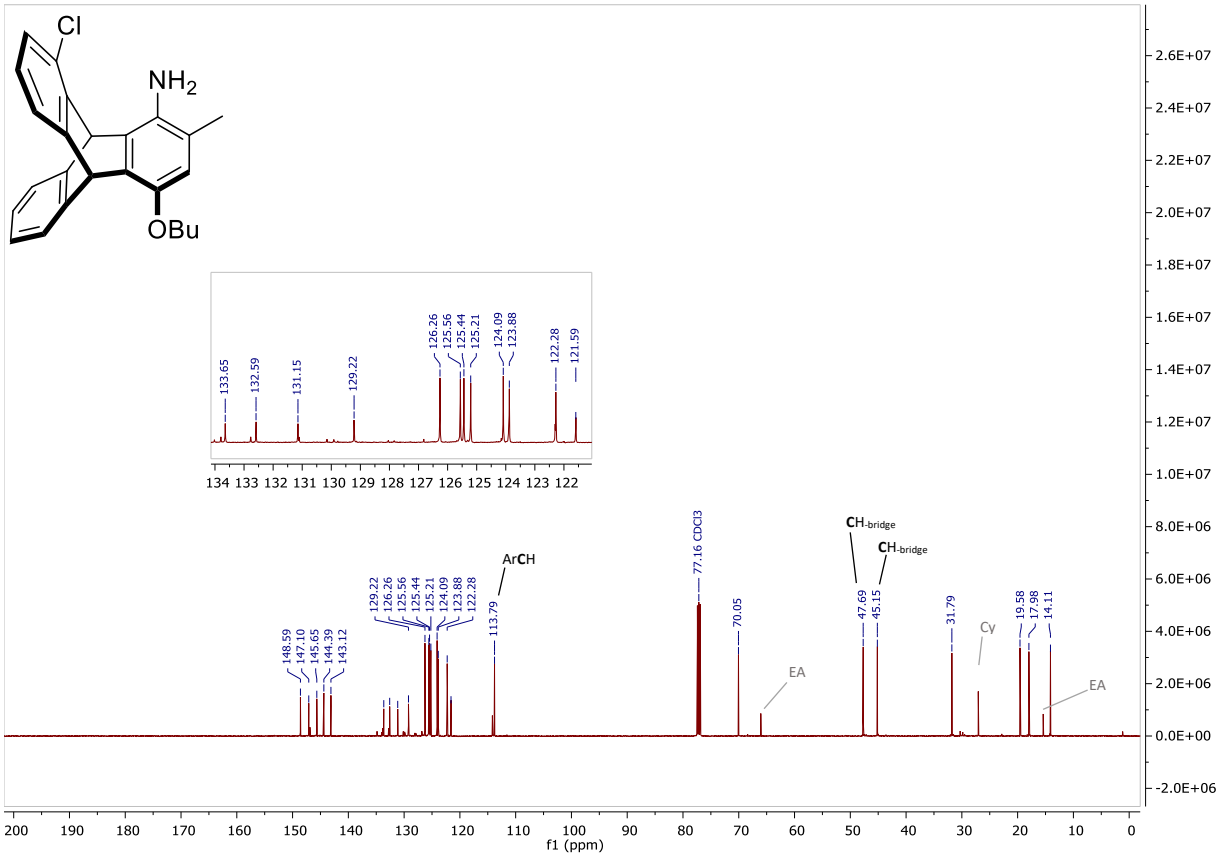


*Figure 126: ^{13}C-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

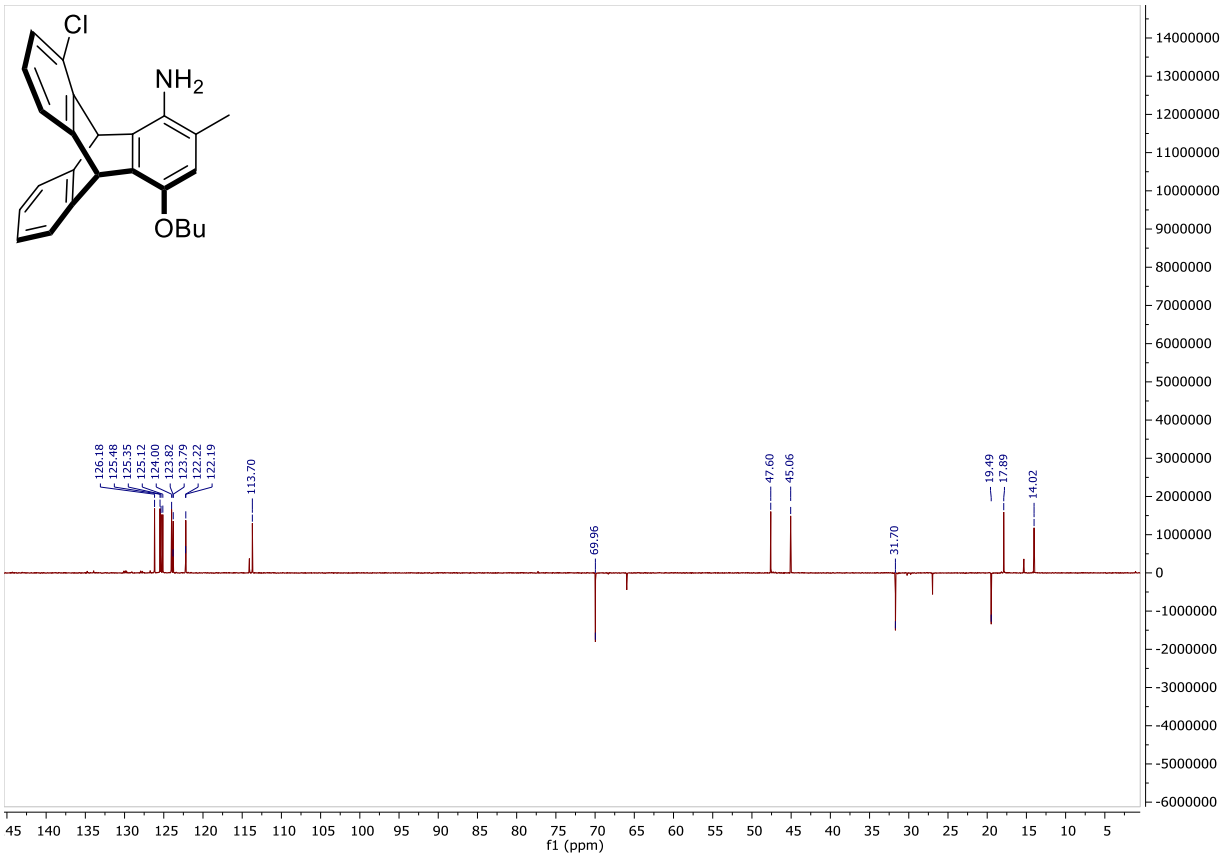


*Figure 127: DEPT-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

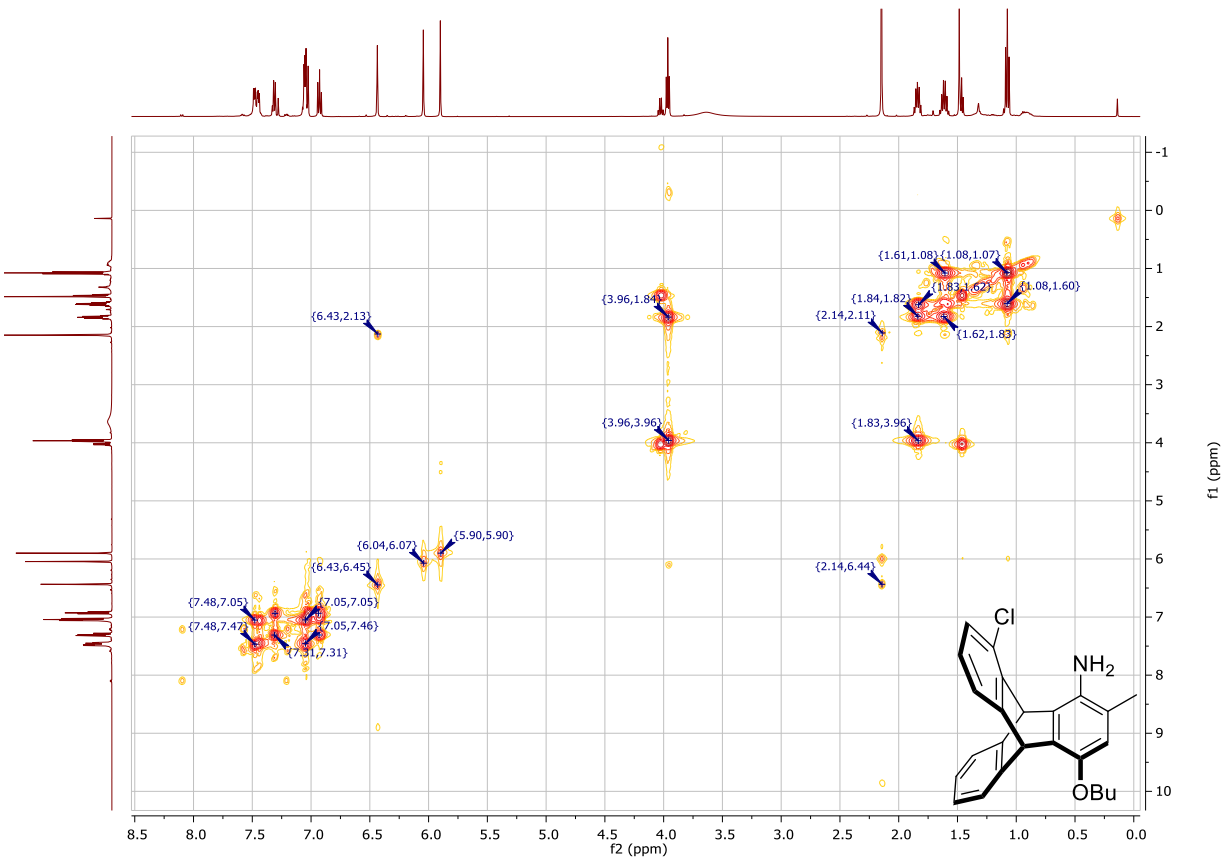


*Figure 128: COSY-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

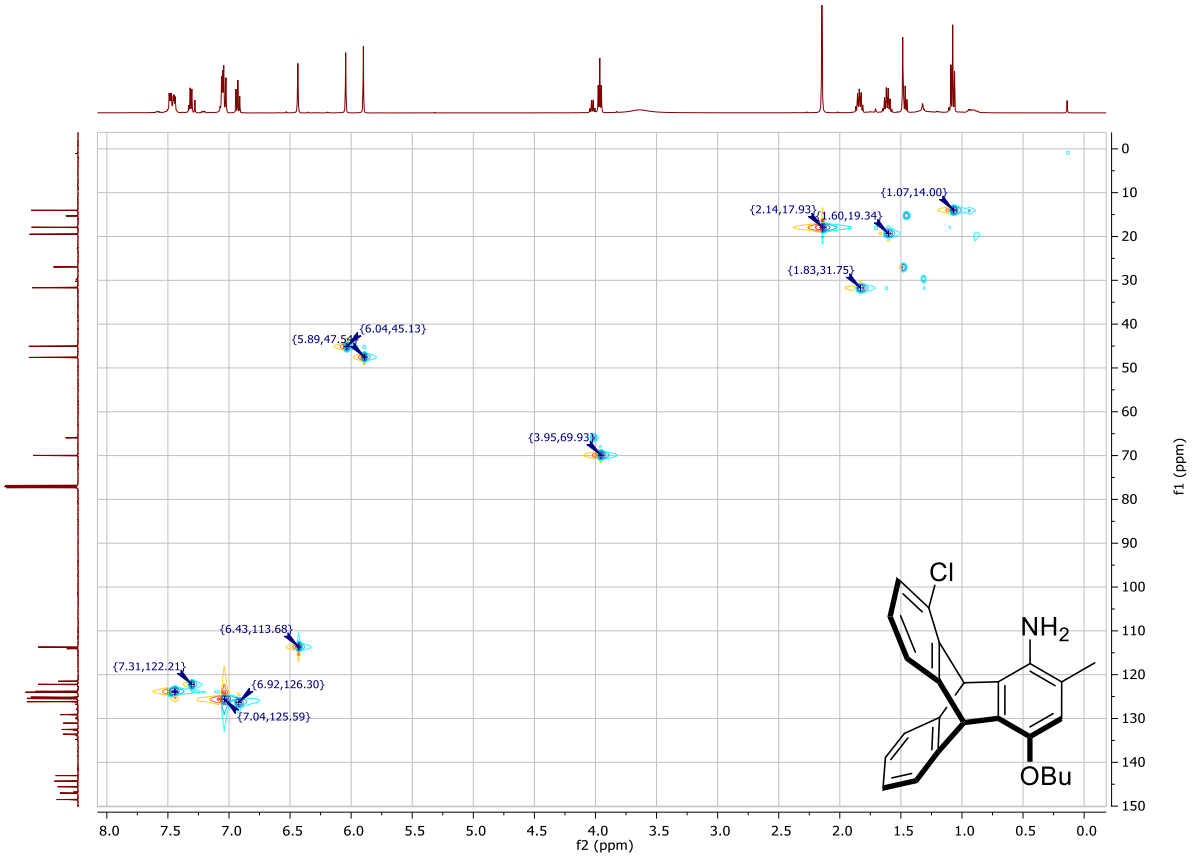


*Figure 129: HSQC-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

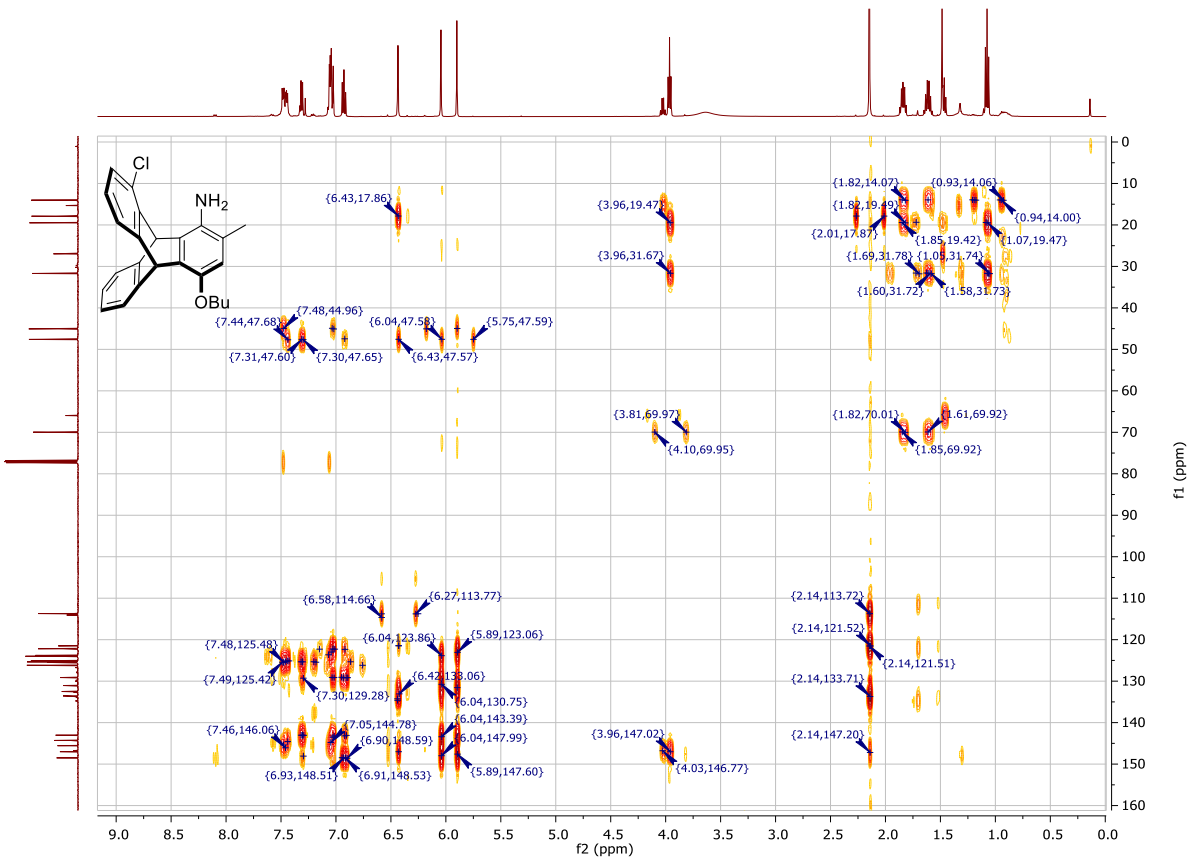


*Figure 130: HMBC-NMR of denosylated aminotriptycen (**6la**) in $CDCl_3$.*

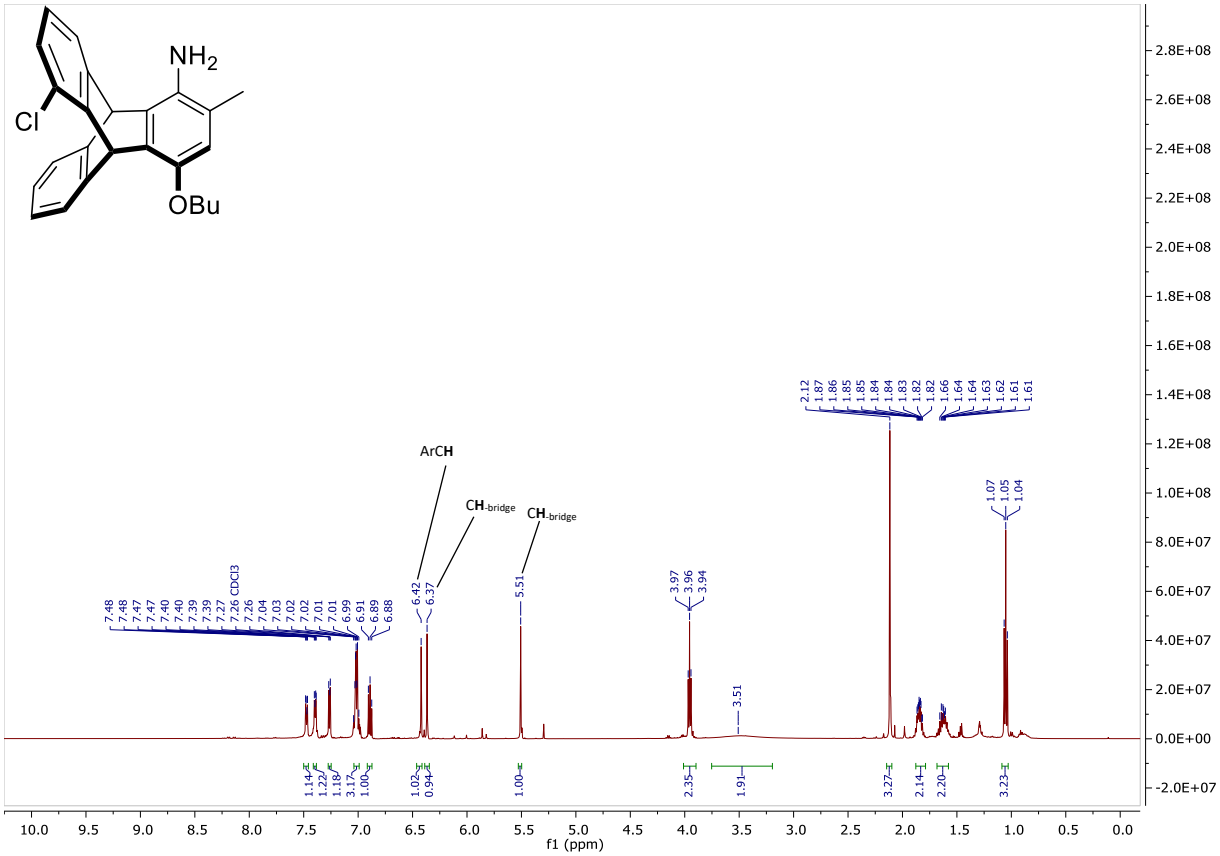


*Figure 131: ^{1}H-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

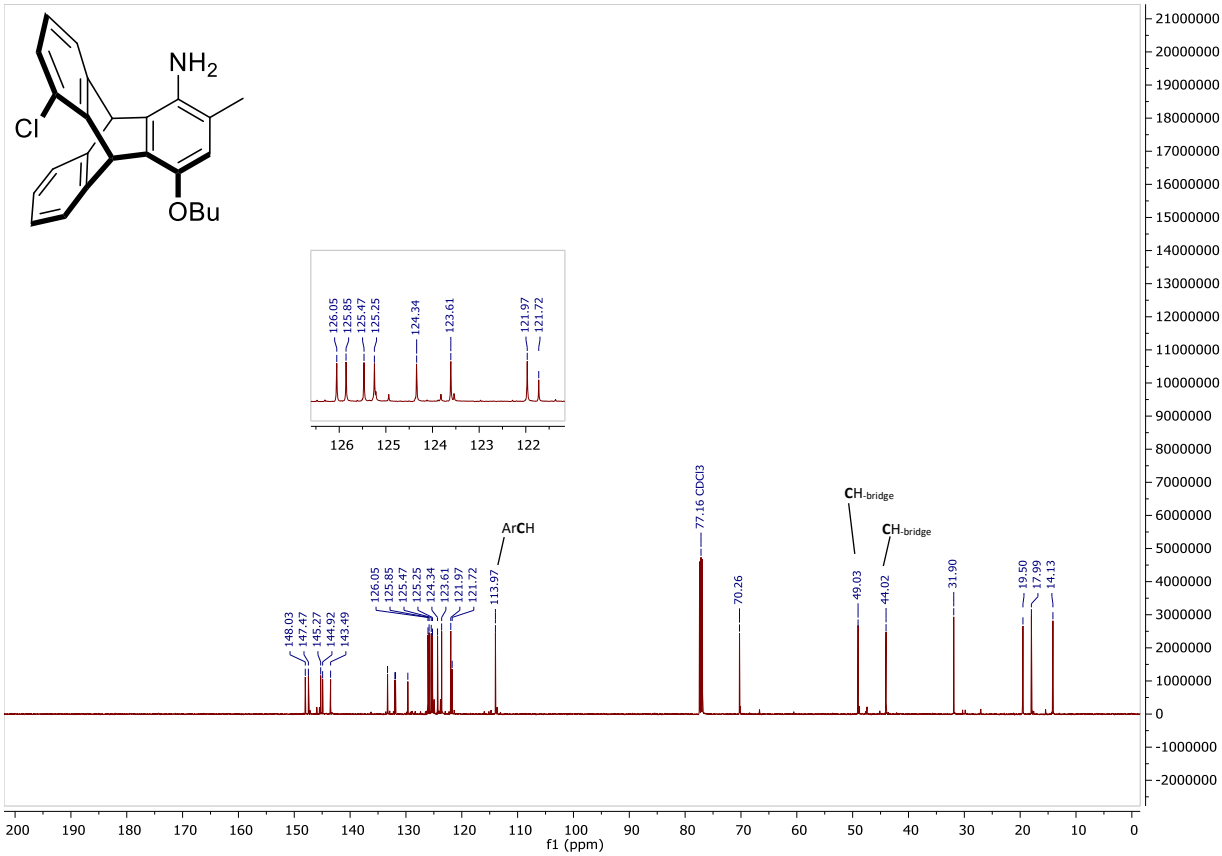


*Figure 132: ^{13}C-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

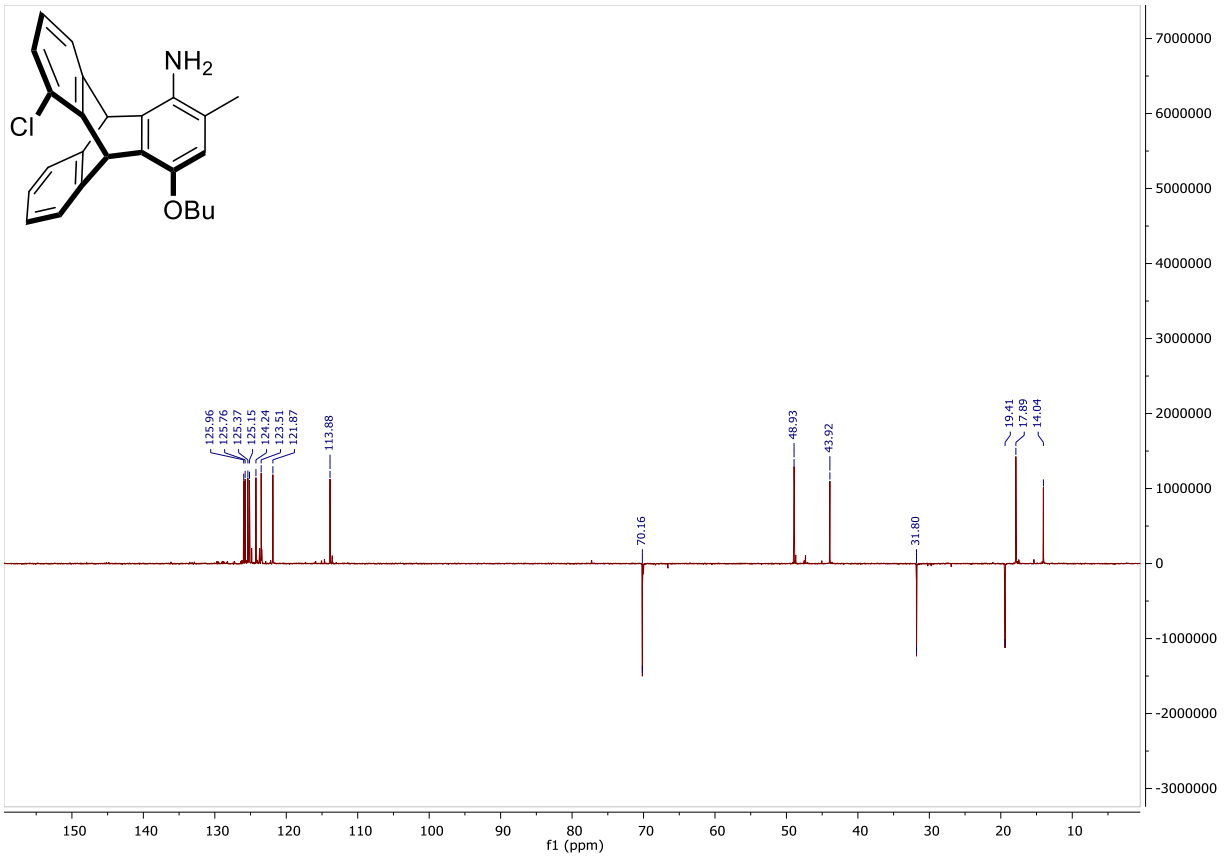


*Figure 133: DEPT-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

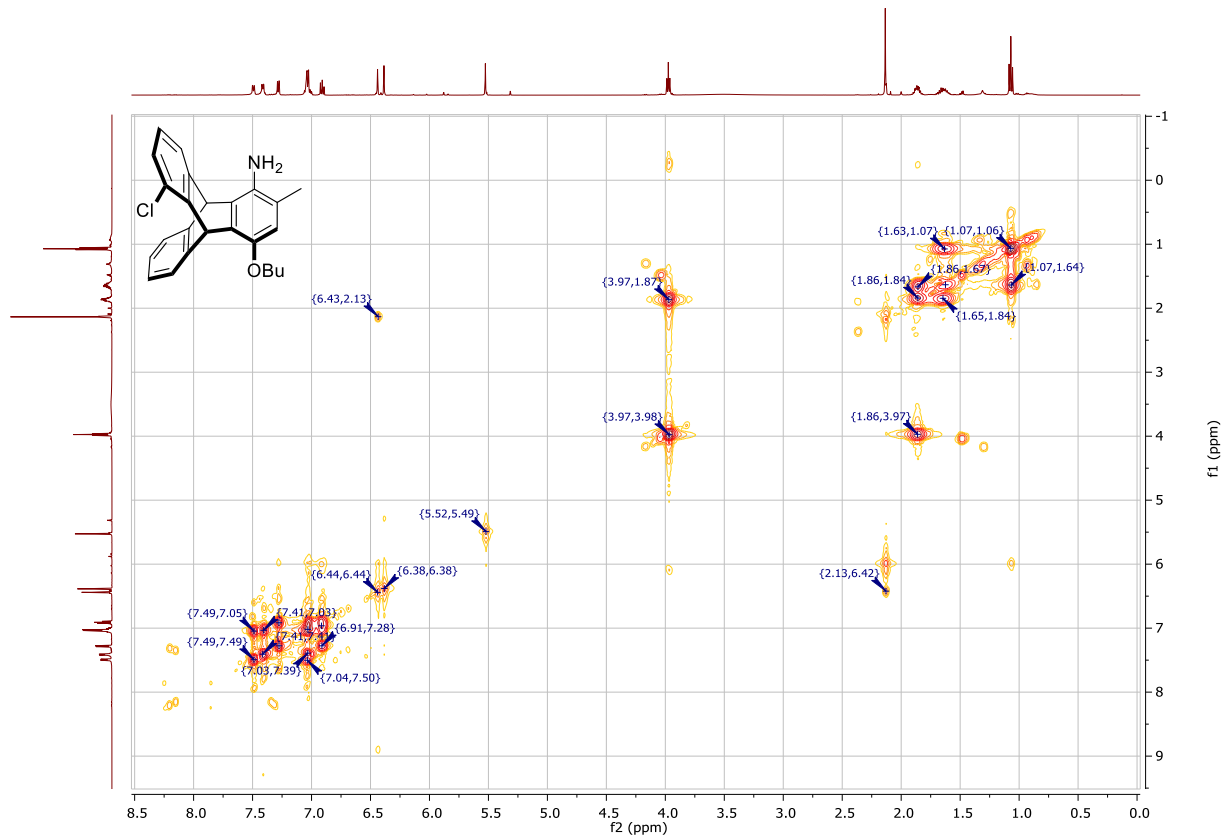


*Figure 134: COSY-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

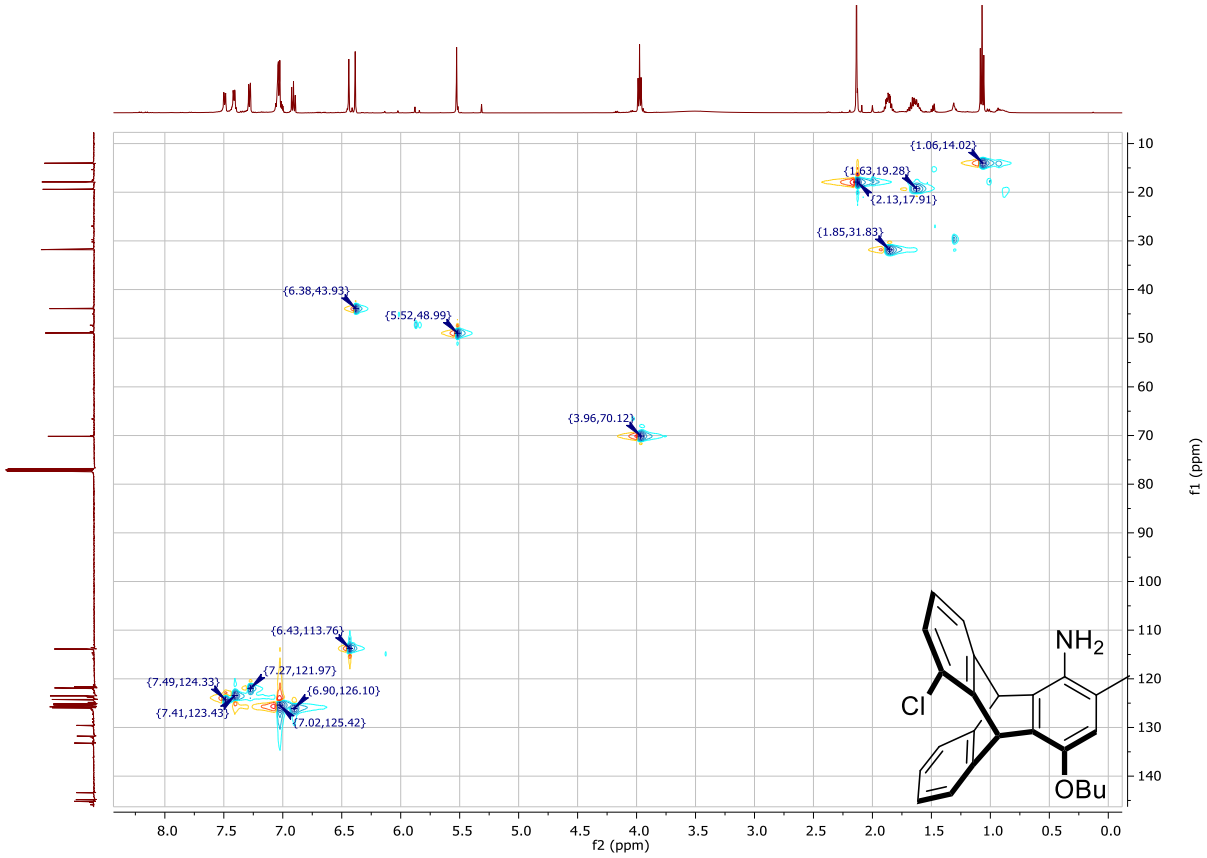


*Figure 135: HSQC-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

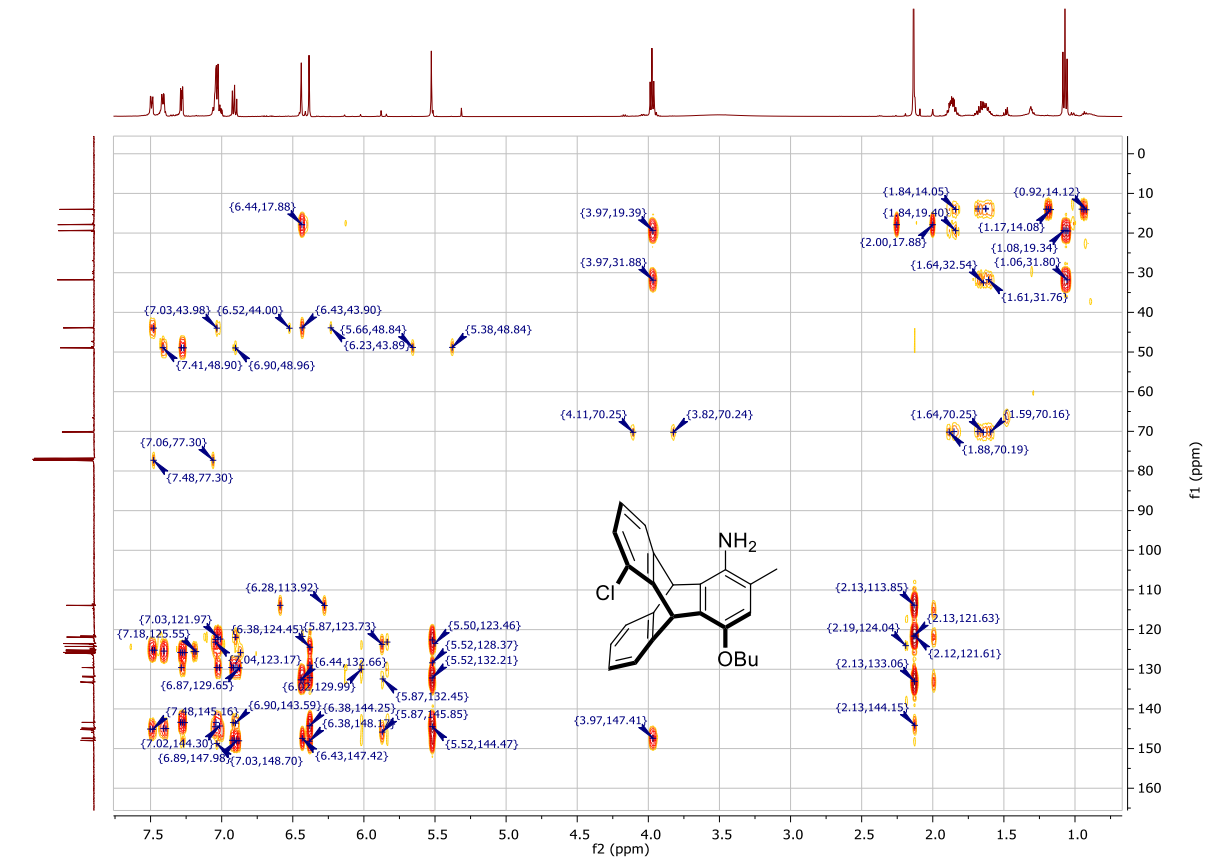


*Figure 136: HMBC-NMR of denosylated aminotriptycen (**6lb**) in $CDCl_3$.*

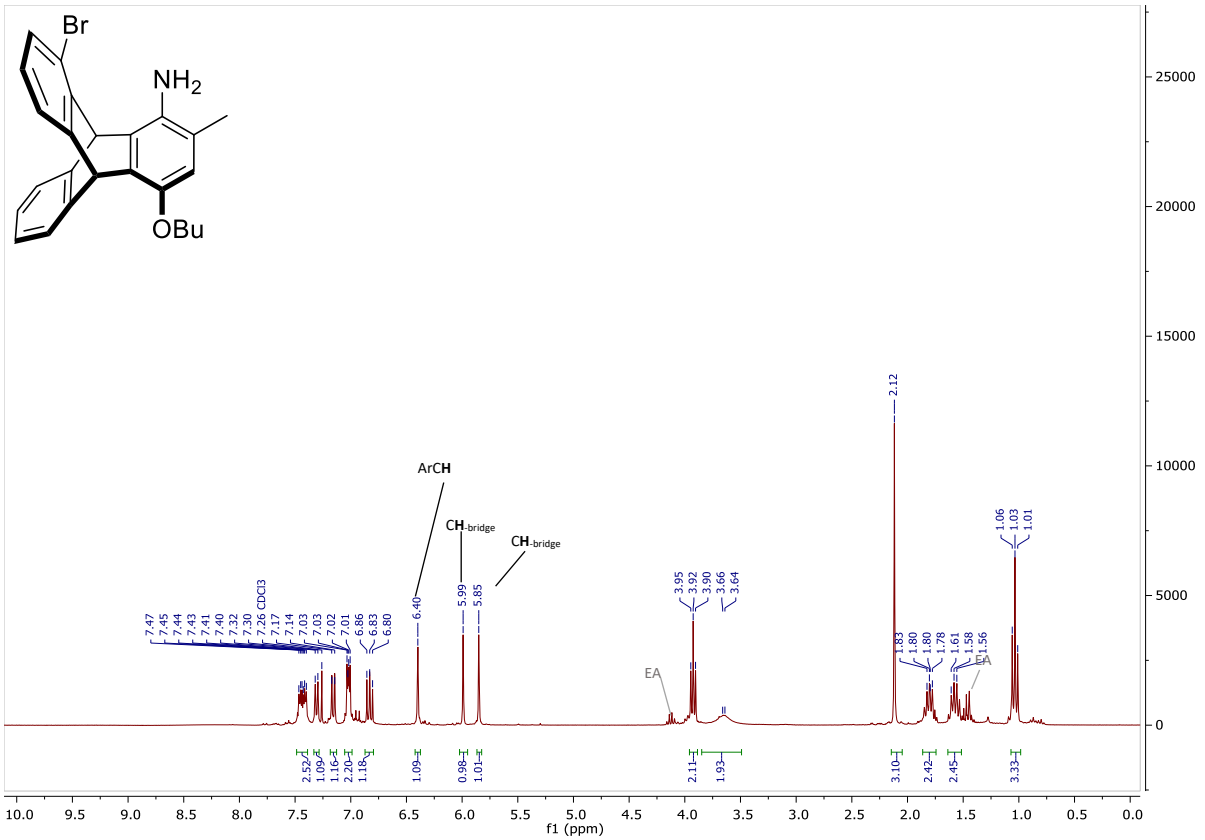


*Figure 137: ^{1}H-NMR of denosylated aminotriptycen (**6ma**) in $CDCl_3$.*

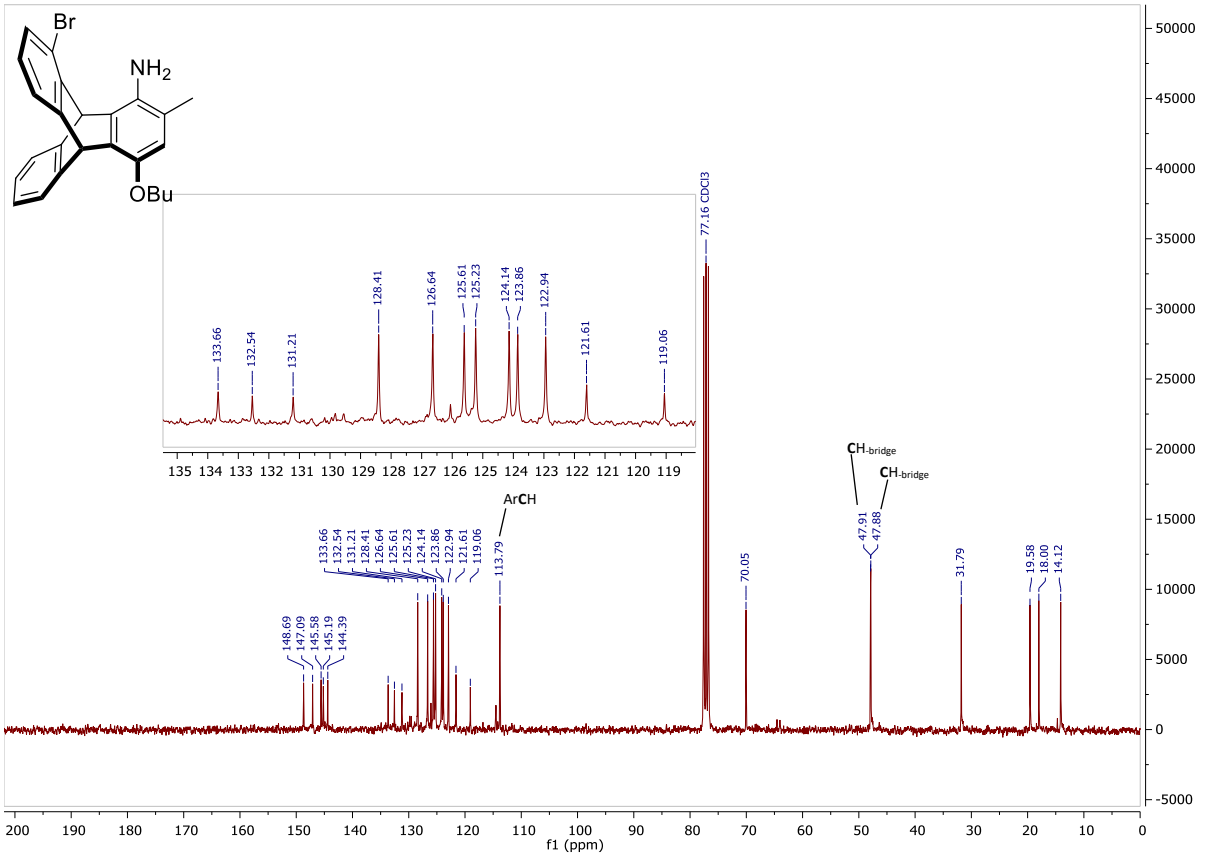


*Figure 138: ^{13}C-NMR of denosylated aminotriptycen (**6ma**) in $CDCl_3$.*

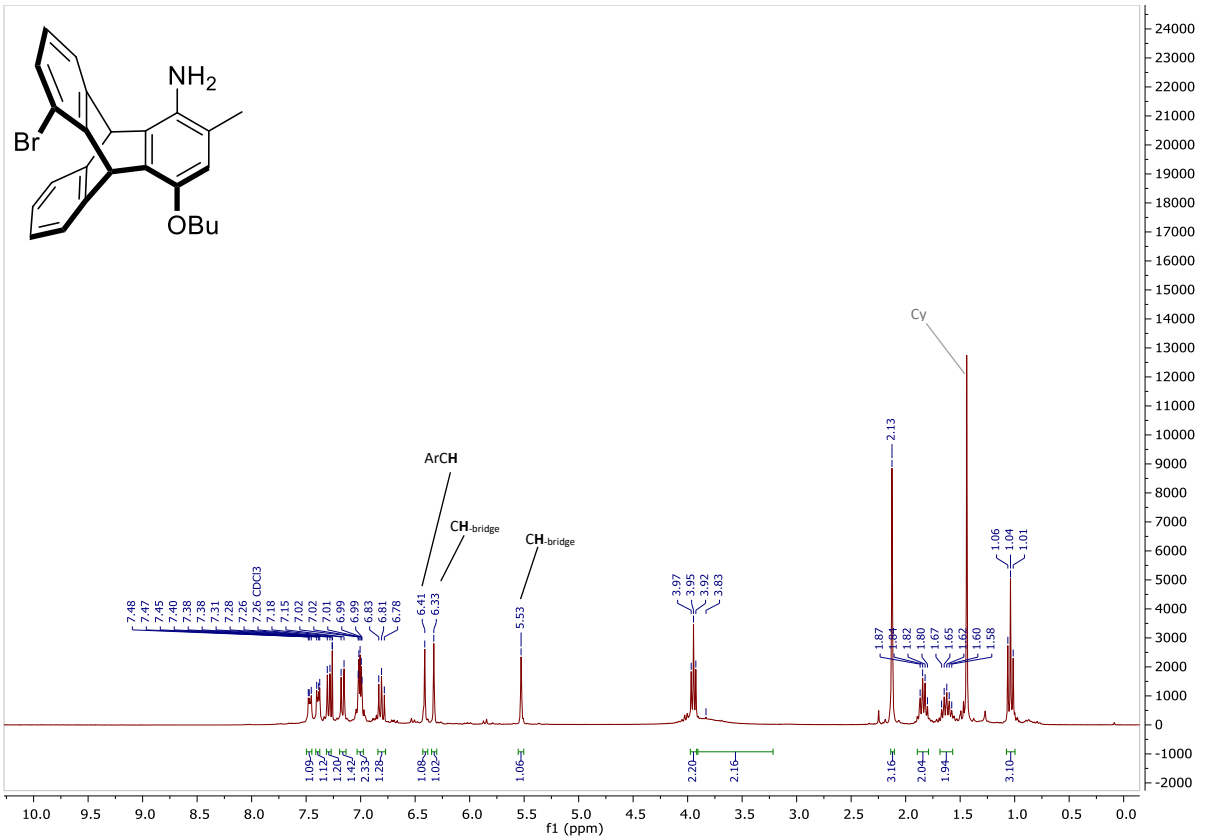


*Figure 139: ^{1}H-NMR of denosylated aminotriptycen (**6mb**) in $CDCl_3$.*

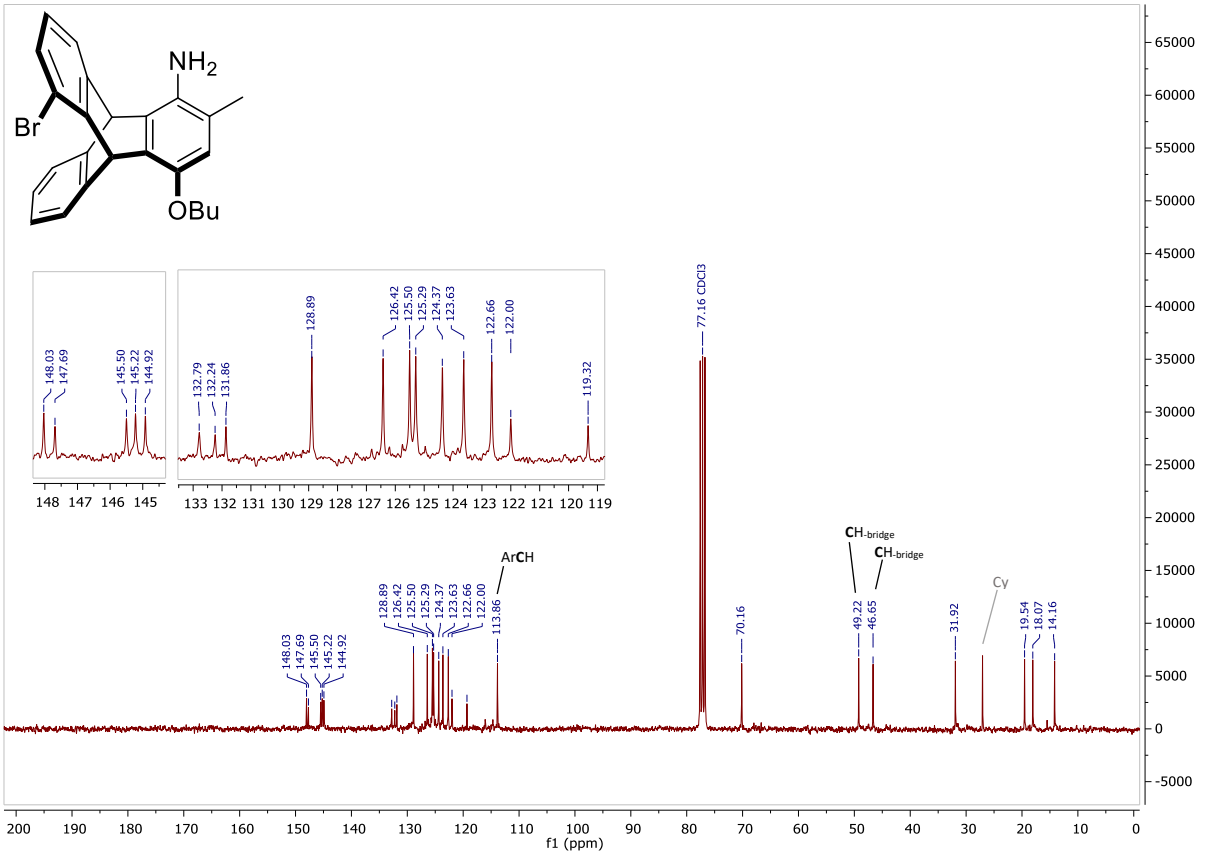


*Figure 140: ^{1}H-NMR of denosylated aminotriptycen (**6mb**) in $CDCl_3$.*

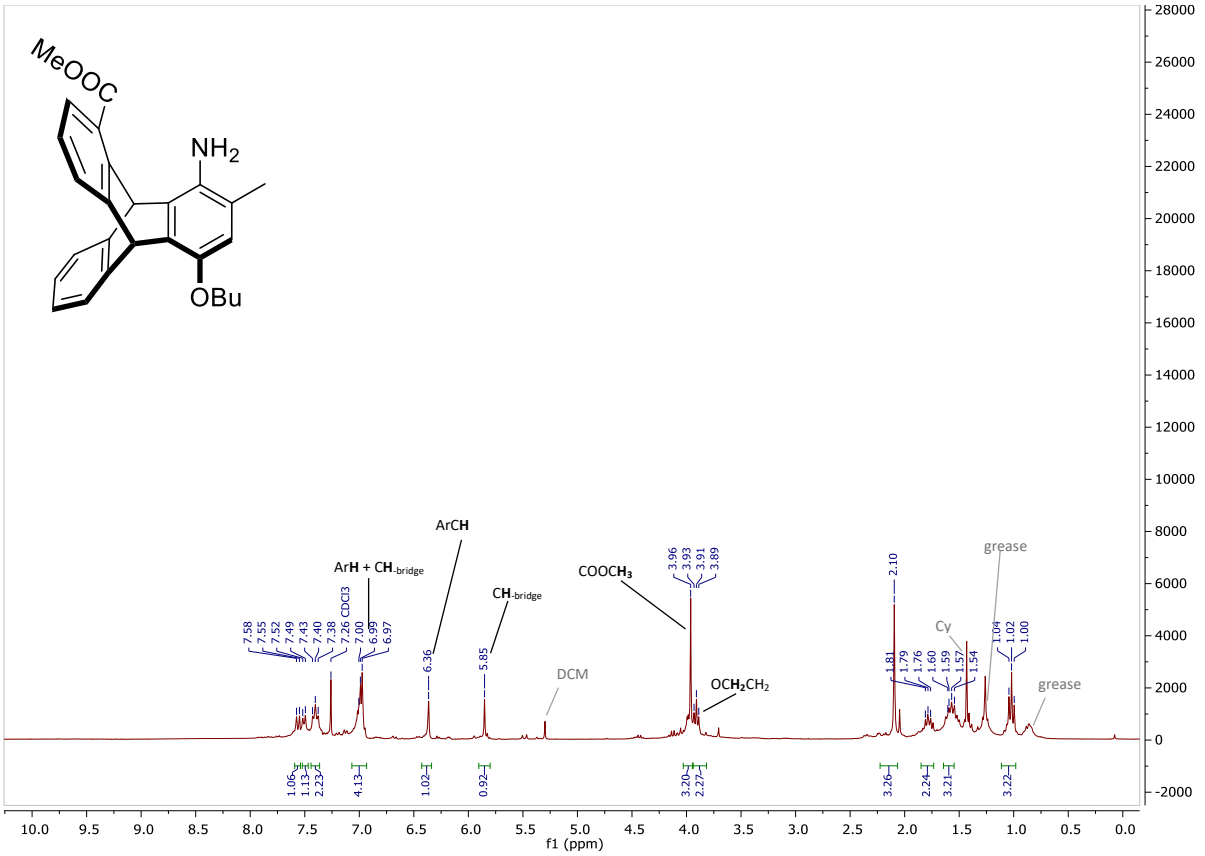


*Figure 141: [1]H-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

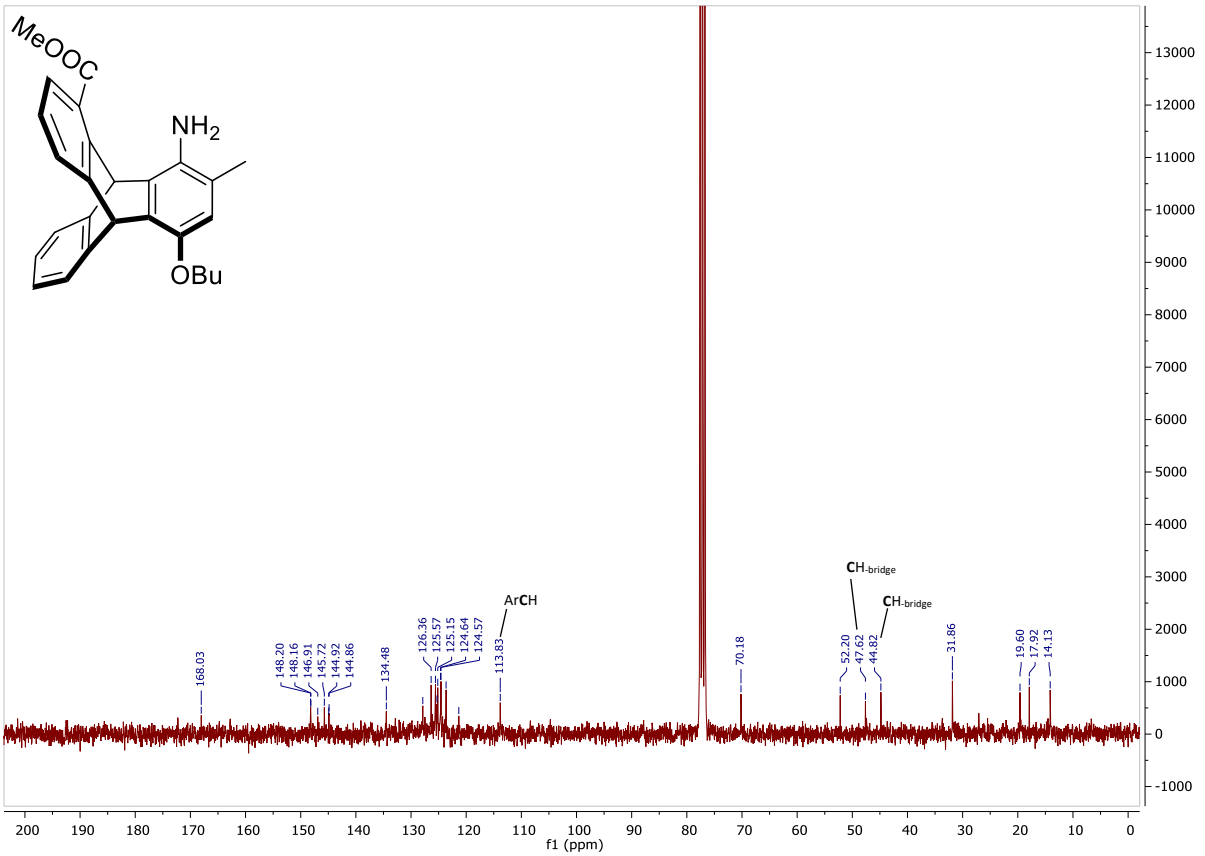


*Figure 142: [13]C-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

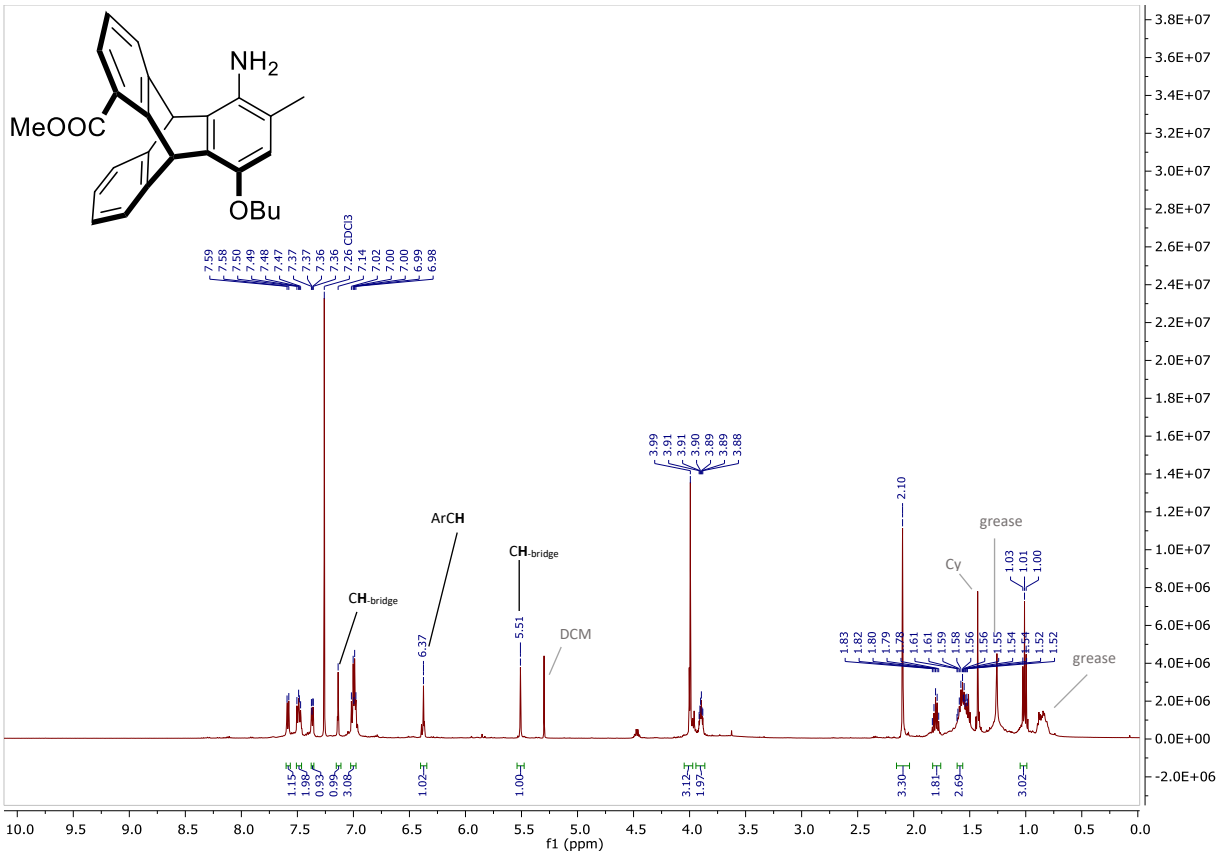


*Figure 143: ^{1}H-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

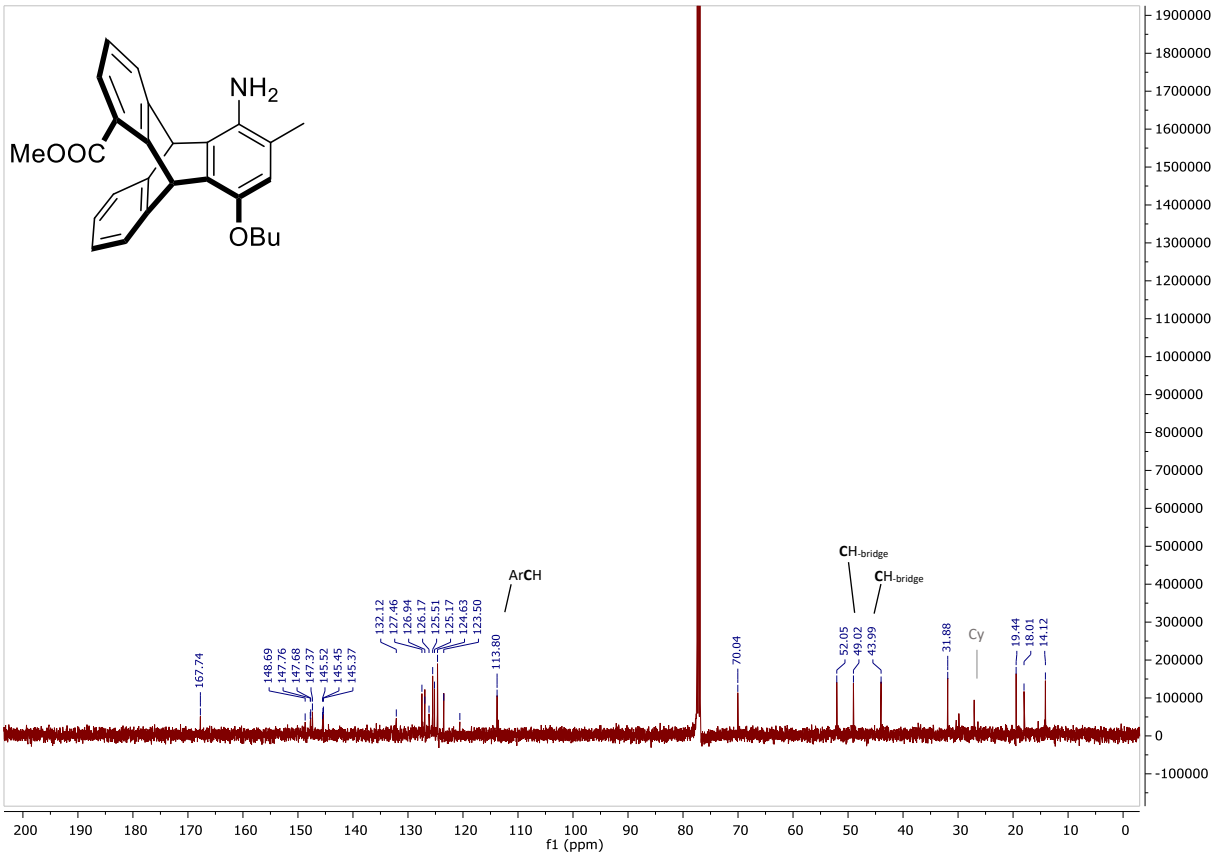


*Figure 144: ^{13}C-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

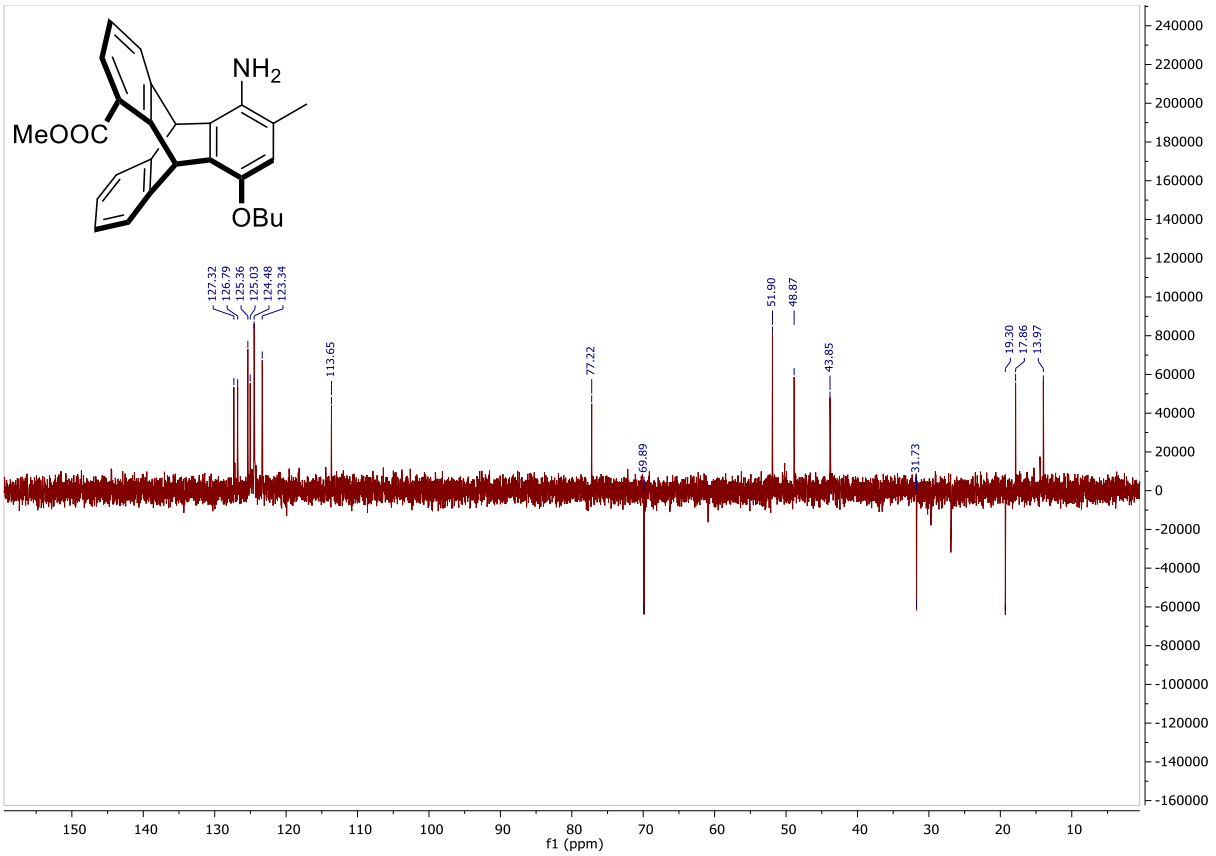


*Figure 145: DEPT-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

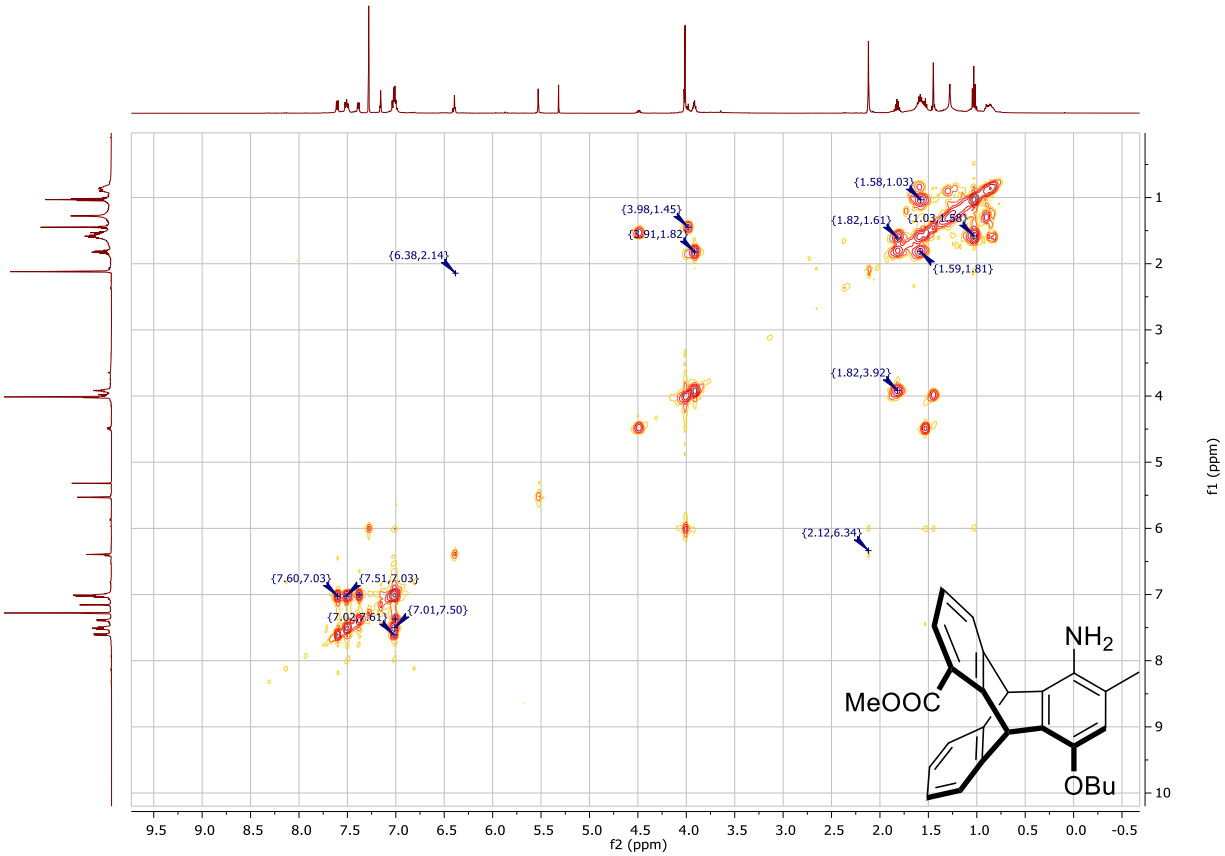


*Figure 146: COSY-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

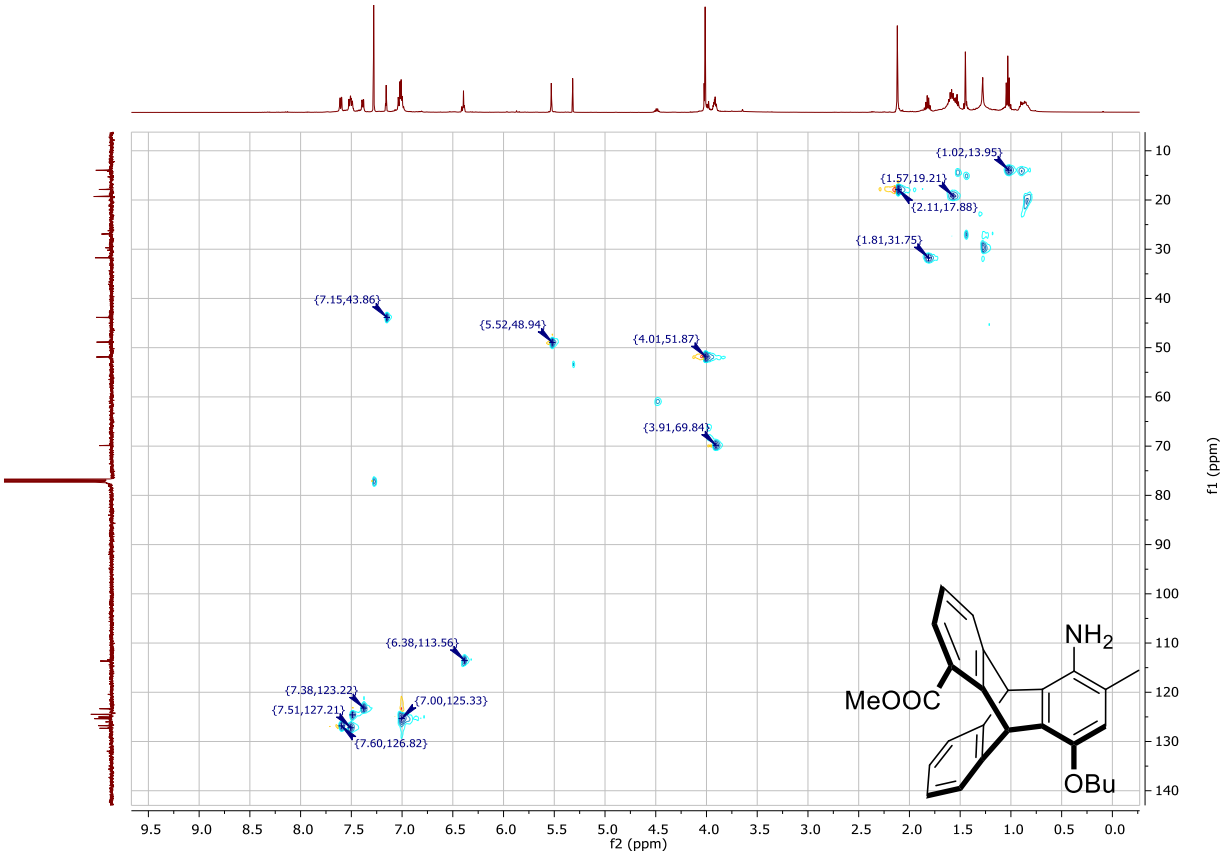


*Figure 147: ^{13}C-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

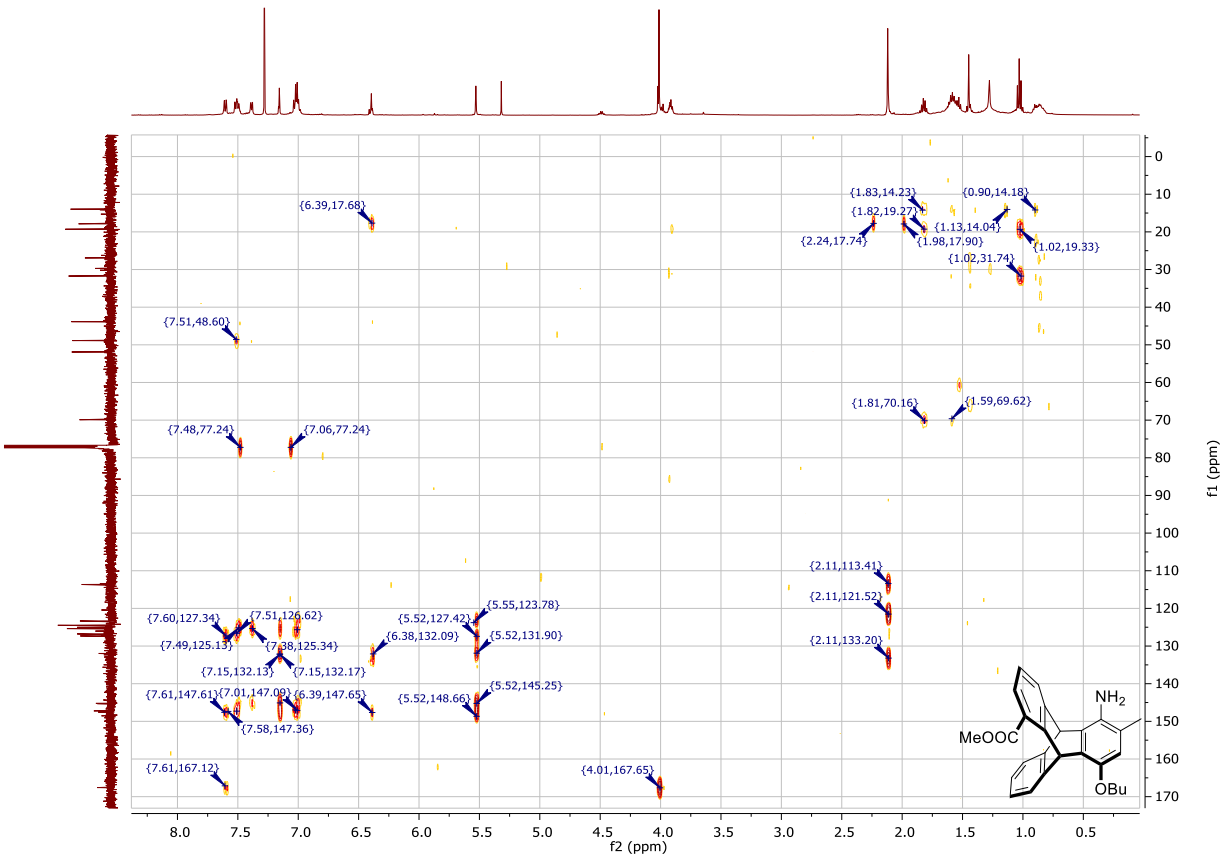


*Figure 148: HMBC-NMR of denosylated aminotriptycen (**6n**) in $CDCl_3$.*

Diimine

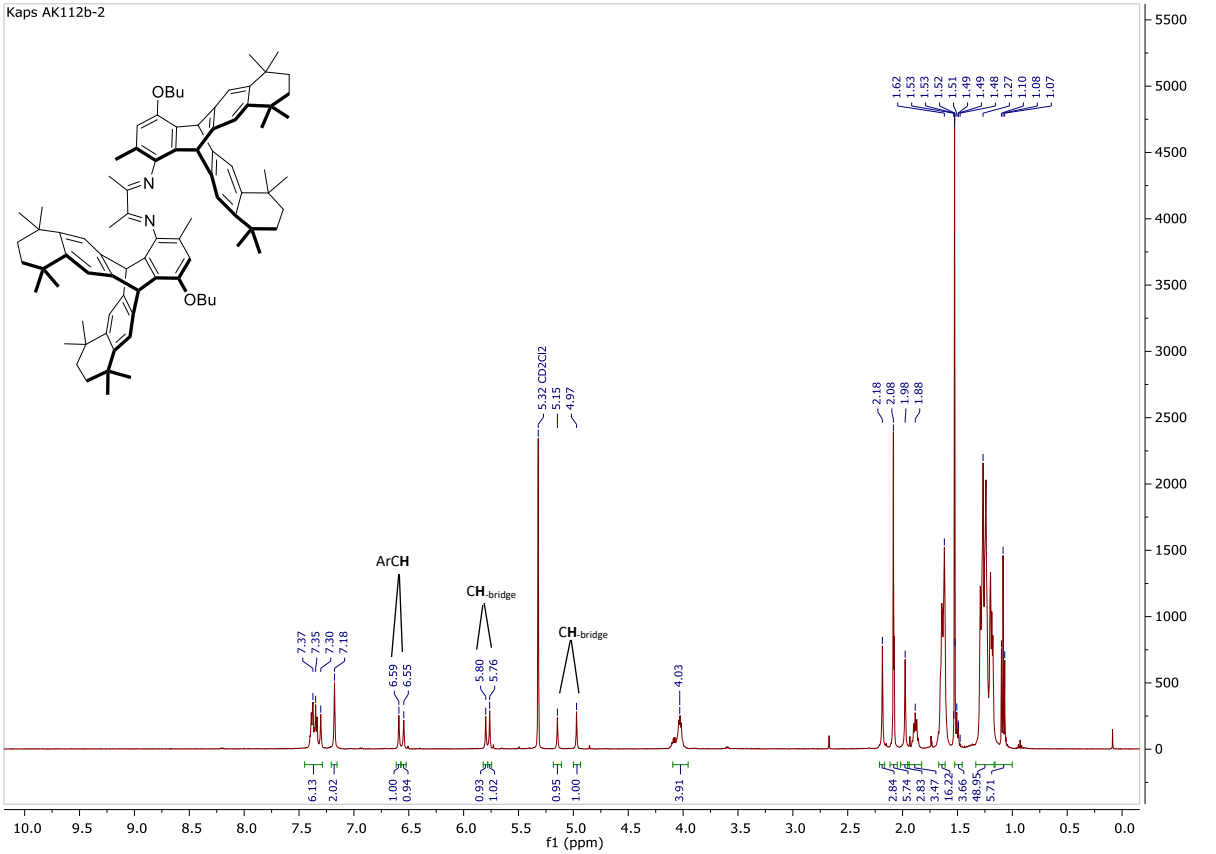


*Figure 149: ^{1}H-NMR of diimine (**11**) in CD_2Cl_2.*

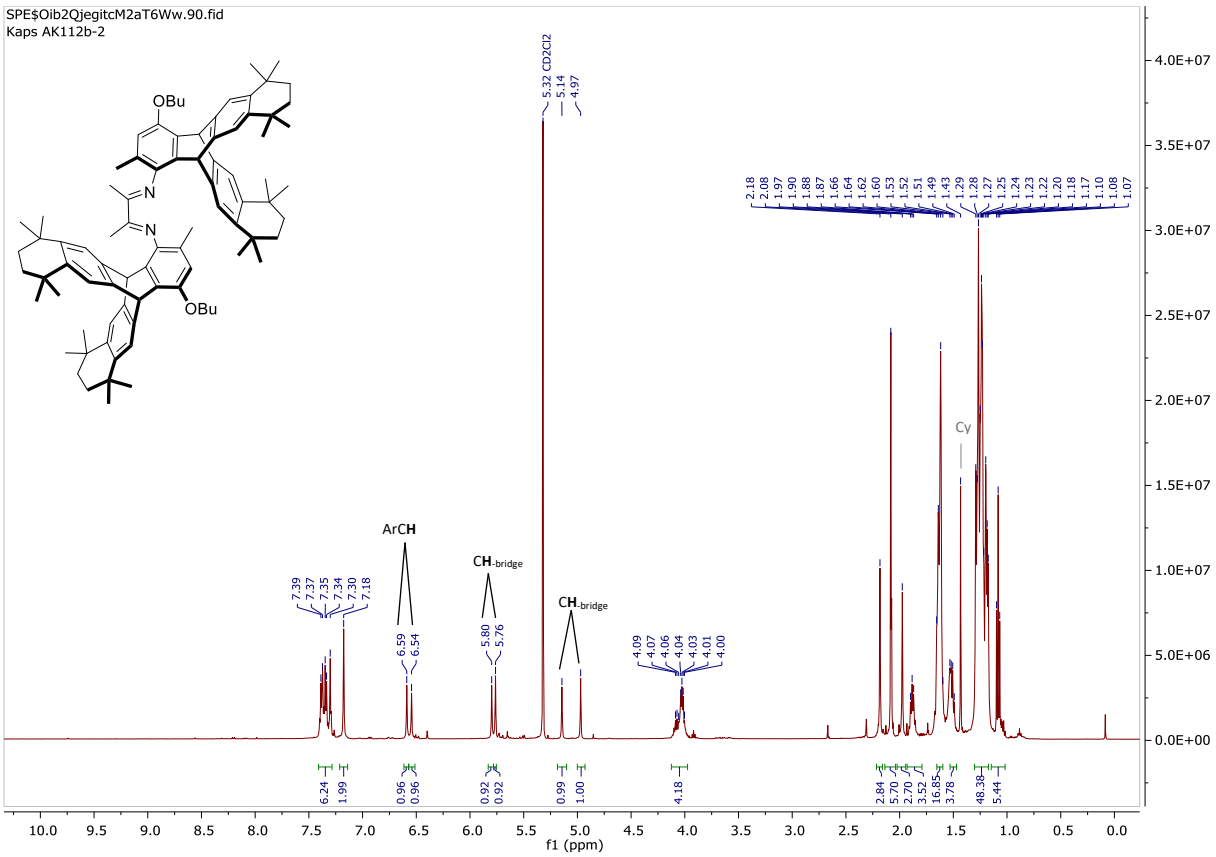


*Figure 150: ^{1}H-NMR of diimine (**11**) in CD_2Cl_2.*

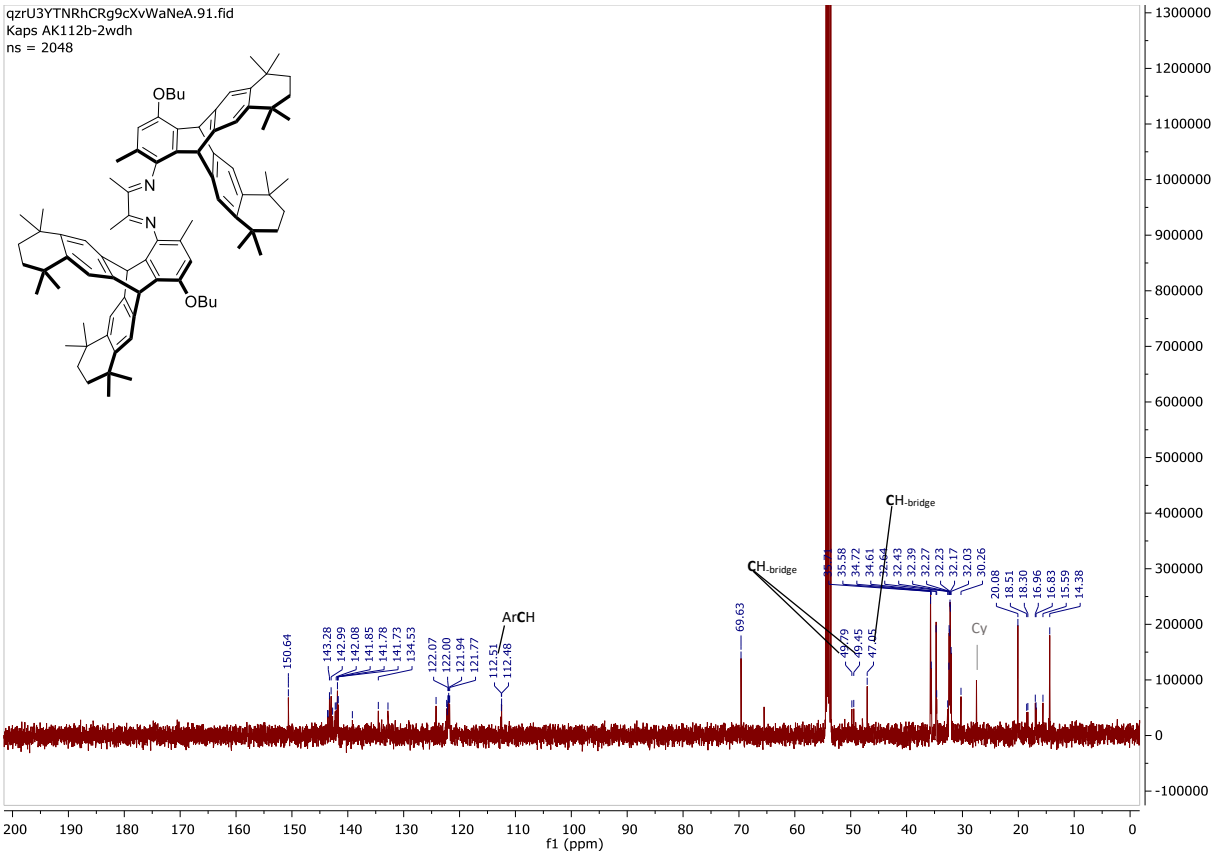


*Figure 151: ^{13}C-NMR of diimine (**11**) in CD_2Cl_2.*

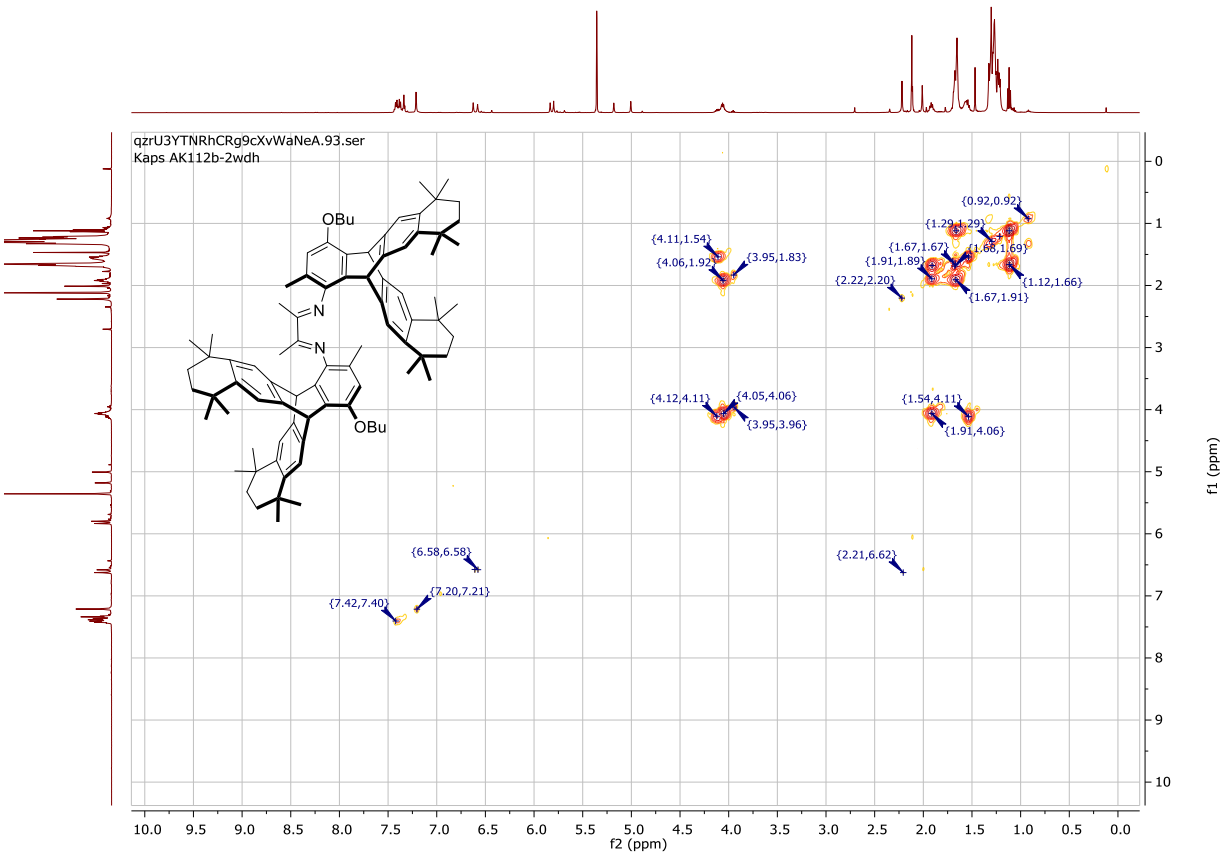


*Figure 152: COSY-NMR of diimine (**11**) in CD_2Cl_2.*

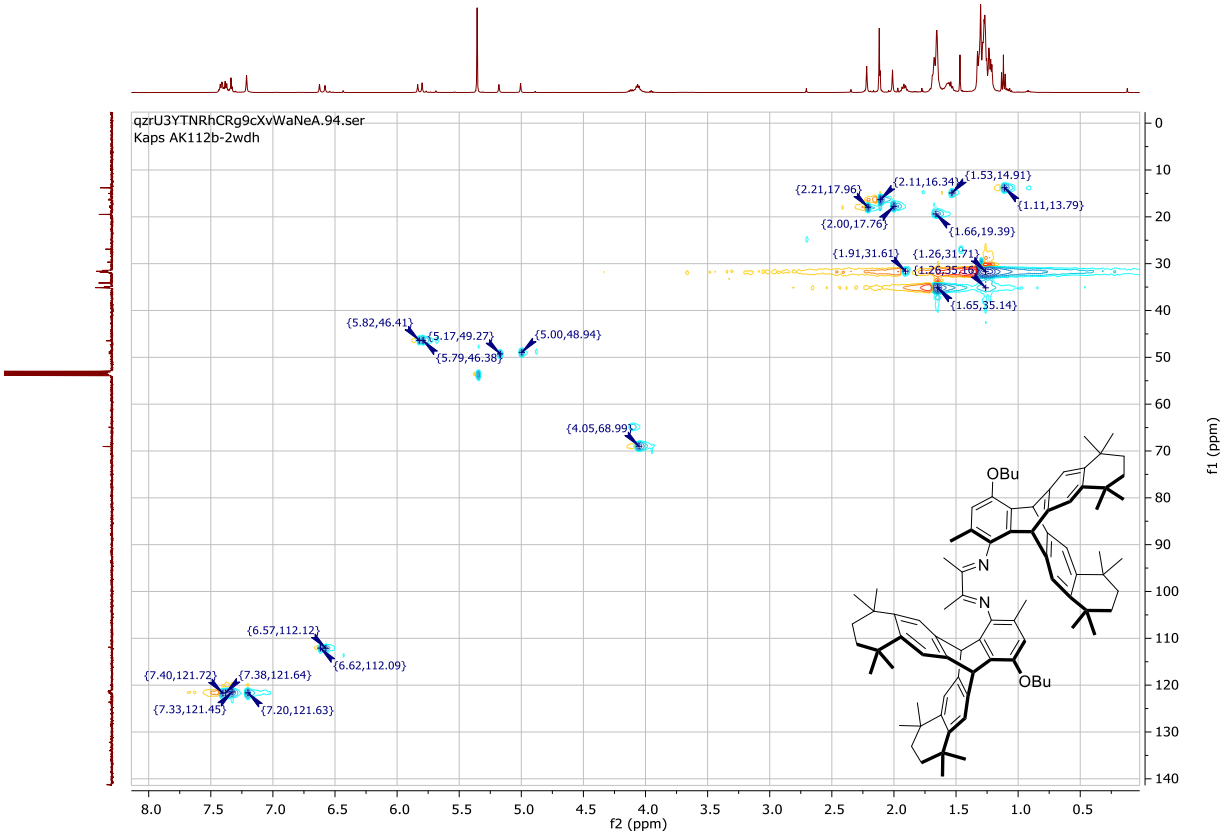


*Figure 153: HSQC-NMR of diimine (**11**) in CD_2Cl_2.*

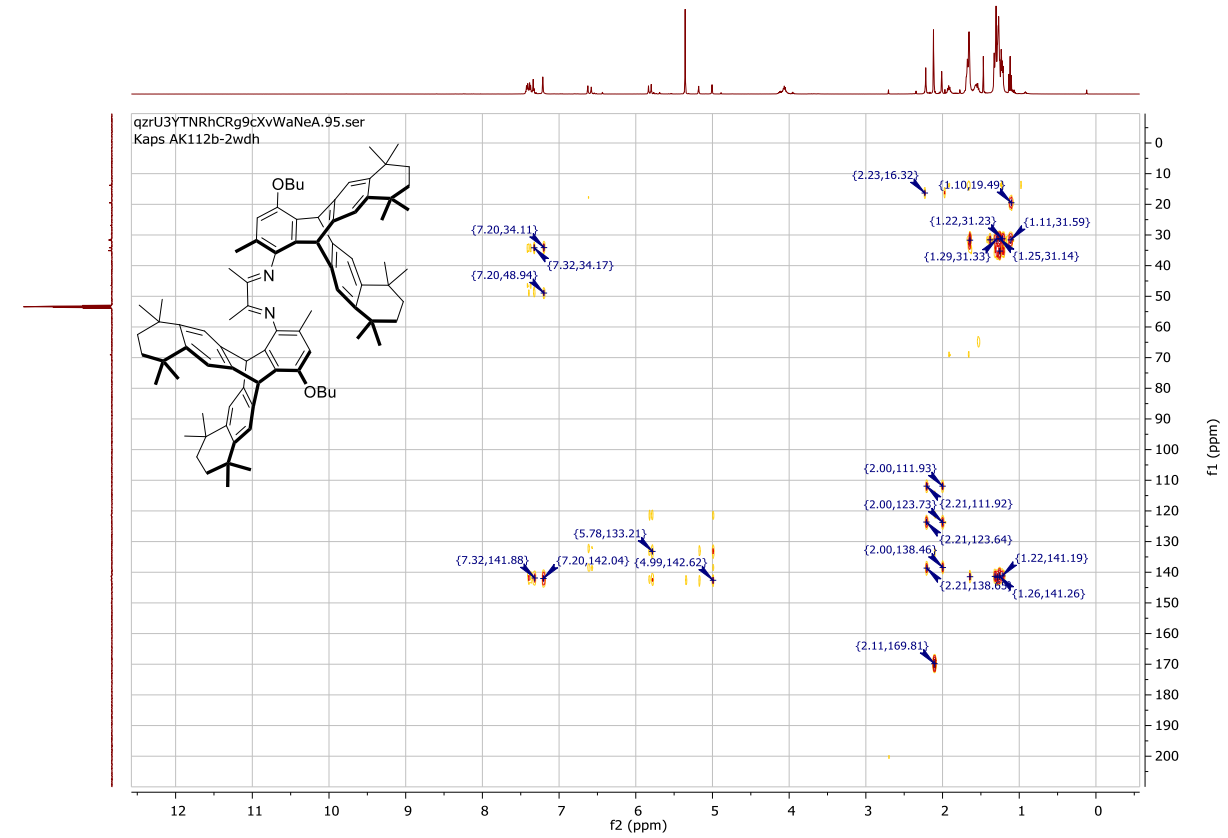


*Figure 154: HMBC-NMR of diimine (**11**) in CD_2Cl_2.*

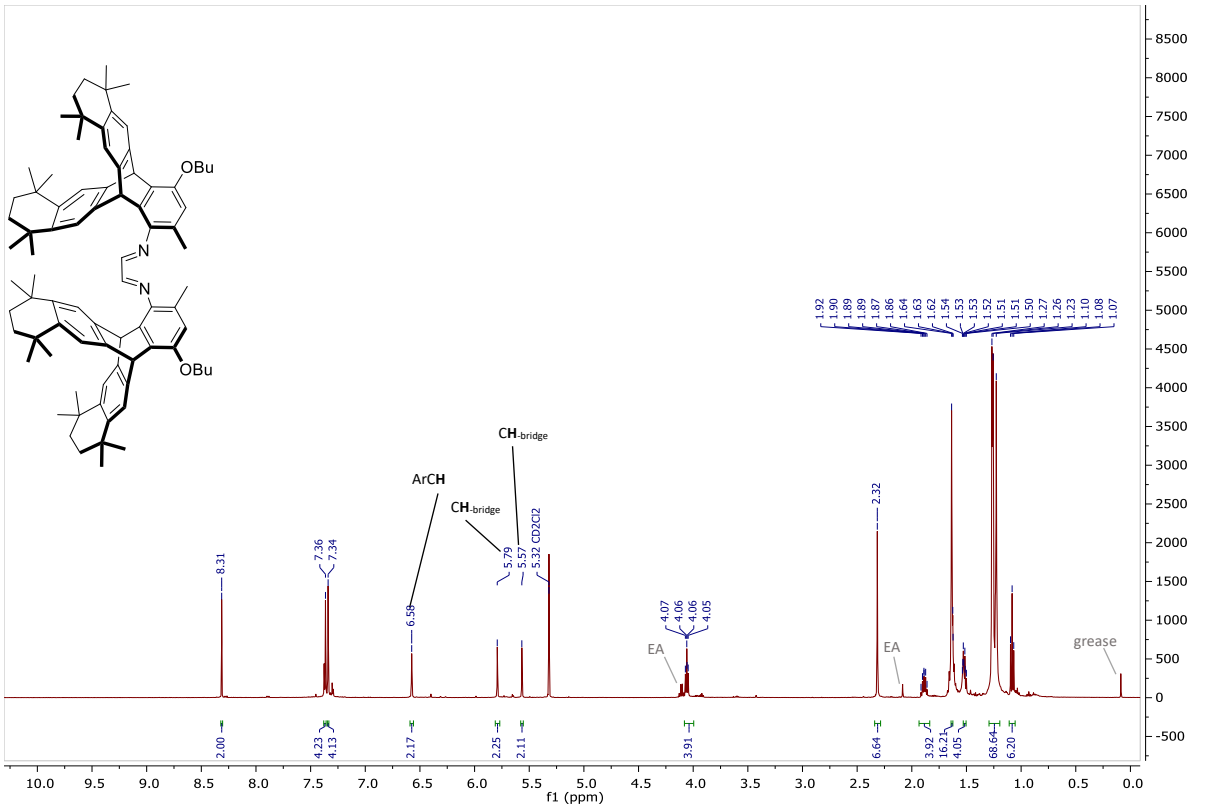


Figure 155: ^{1}H-NMR of diimine in CD_2Cl_2.

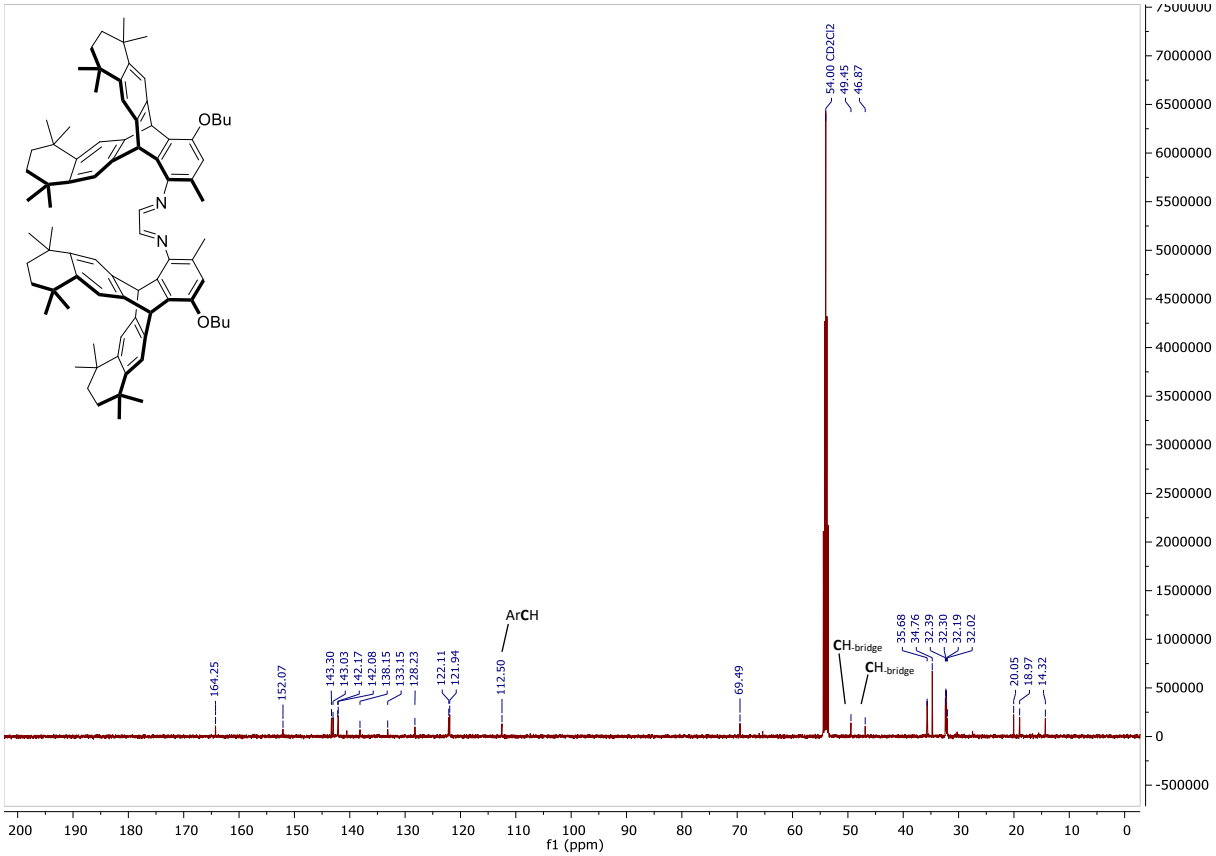


Figure 156: ^{13}C-NMR of diimine in CD_2Cl_2.

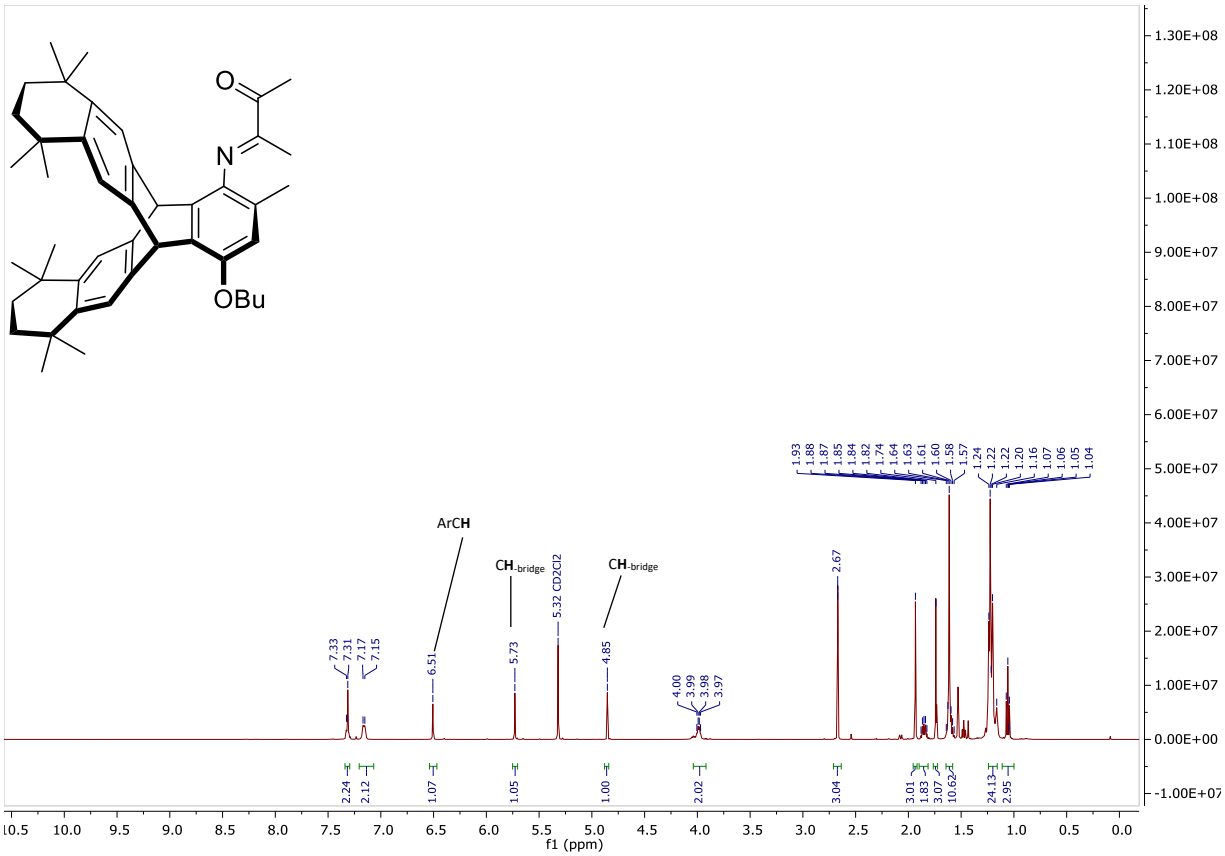


Figure 157: ^{1}H-NMR of diimine in CD_2Cl_2.

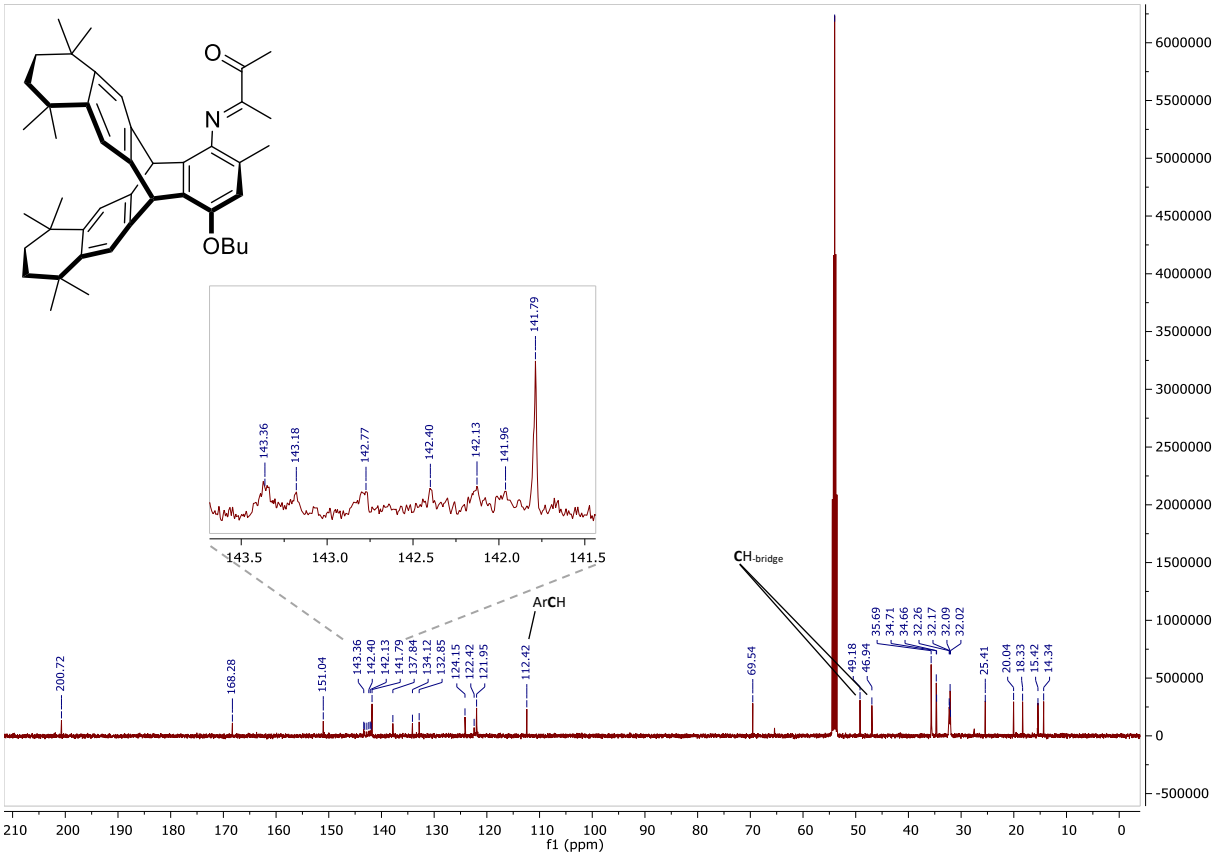


Figure 158: ^{13}C-NMR of diimine in CD_2Cl_2.

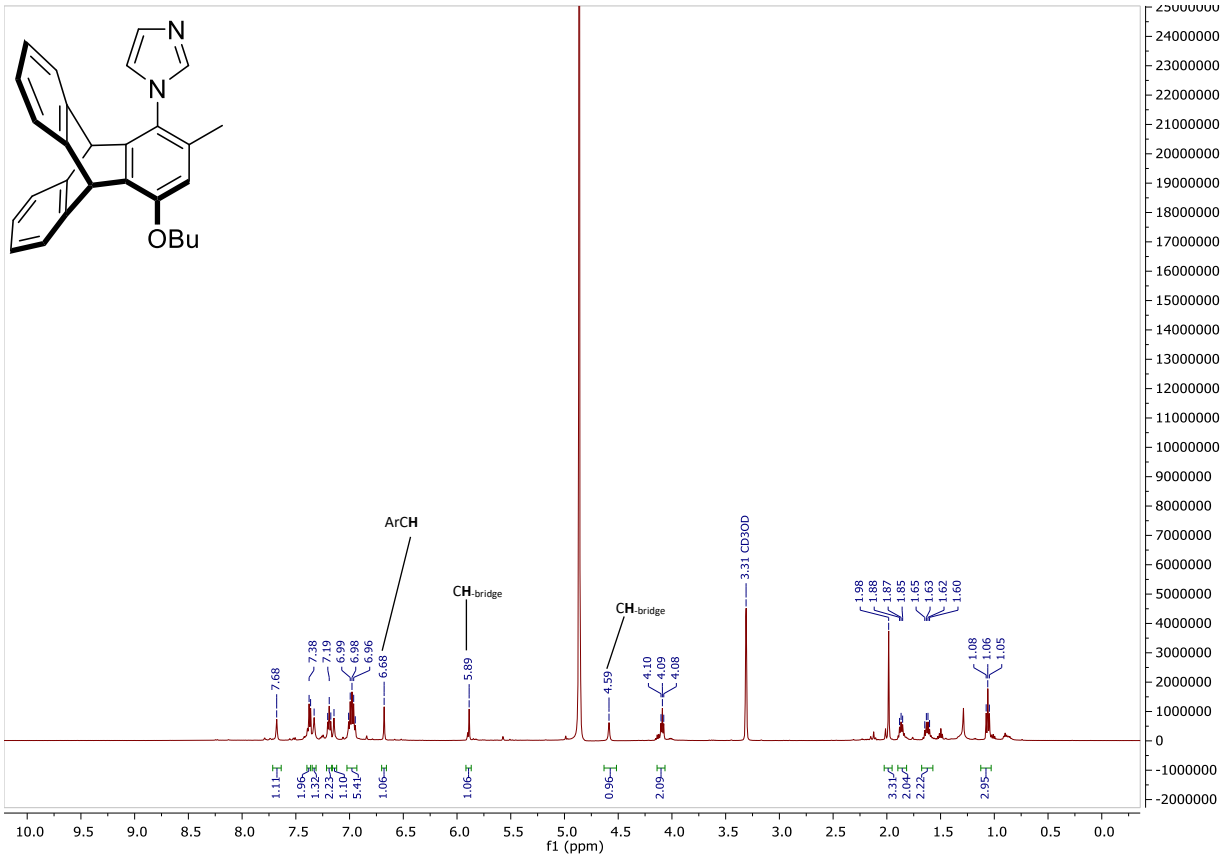


*Figure 159: ^{1}H-NMR of imidazole (**7b**) in MeOD-d_4.*

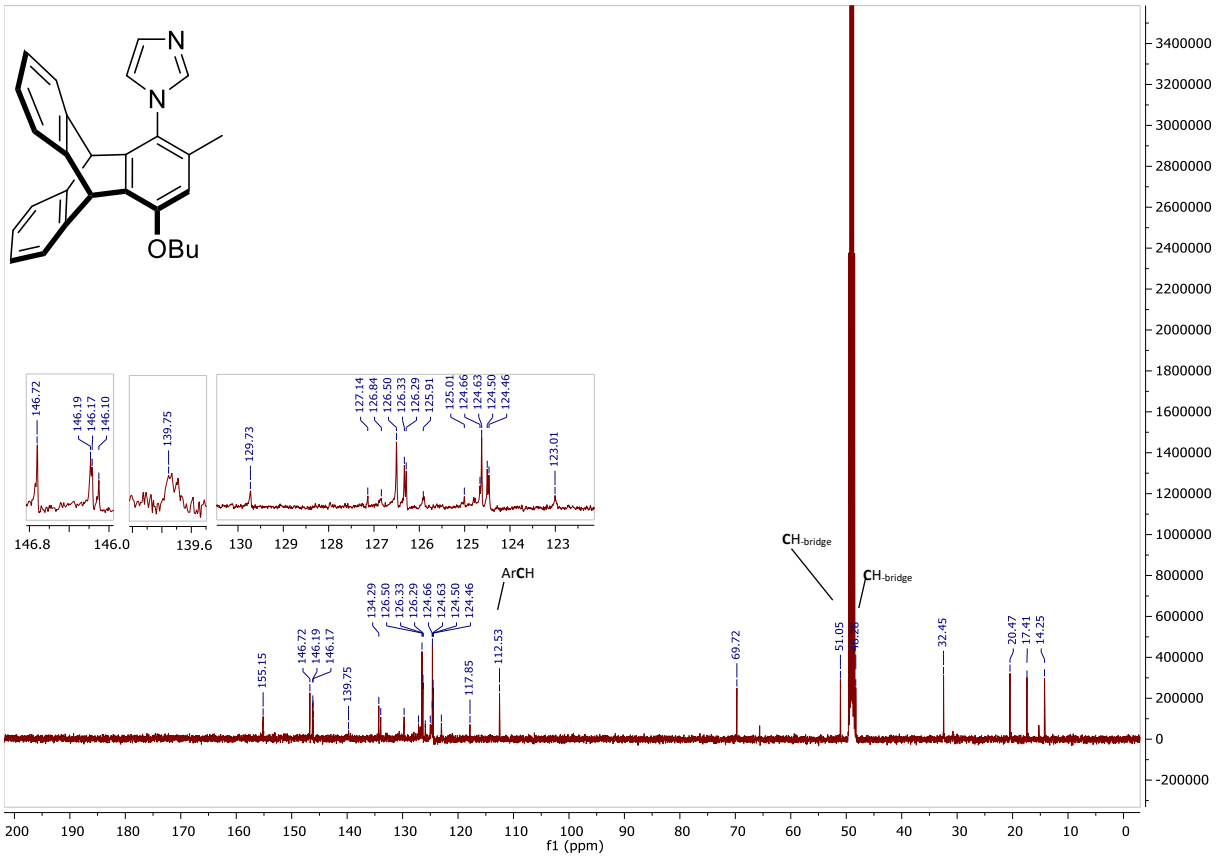


*Figure 160: ^{13}C-NMR of imidazole (**7b**) in MeOD-d_4.*

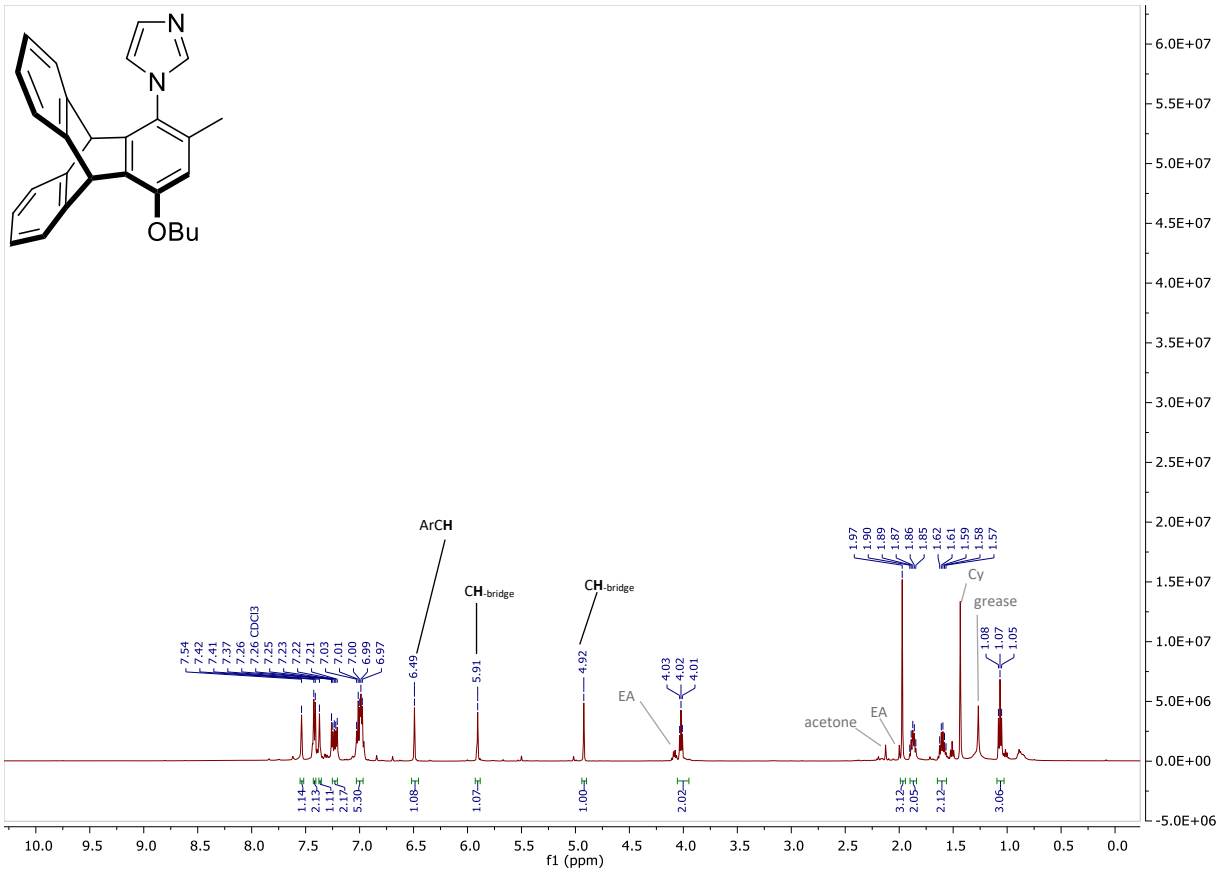


*Figure 161: ^{1}H-NMR of imidazole (**7b**) in $CDCl_3$.*

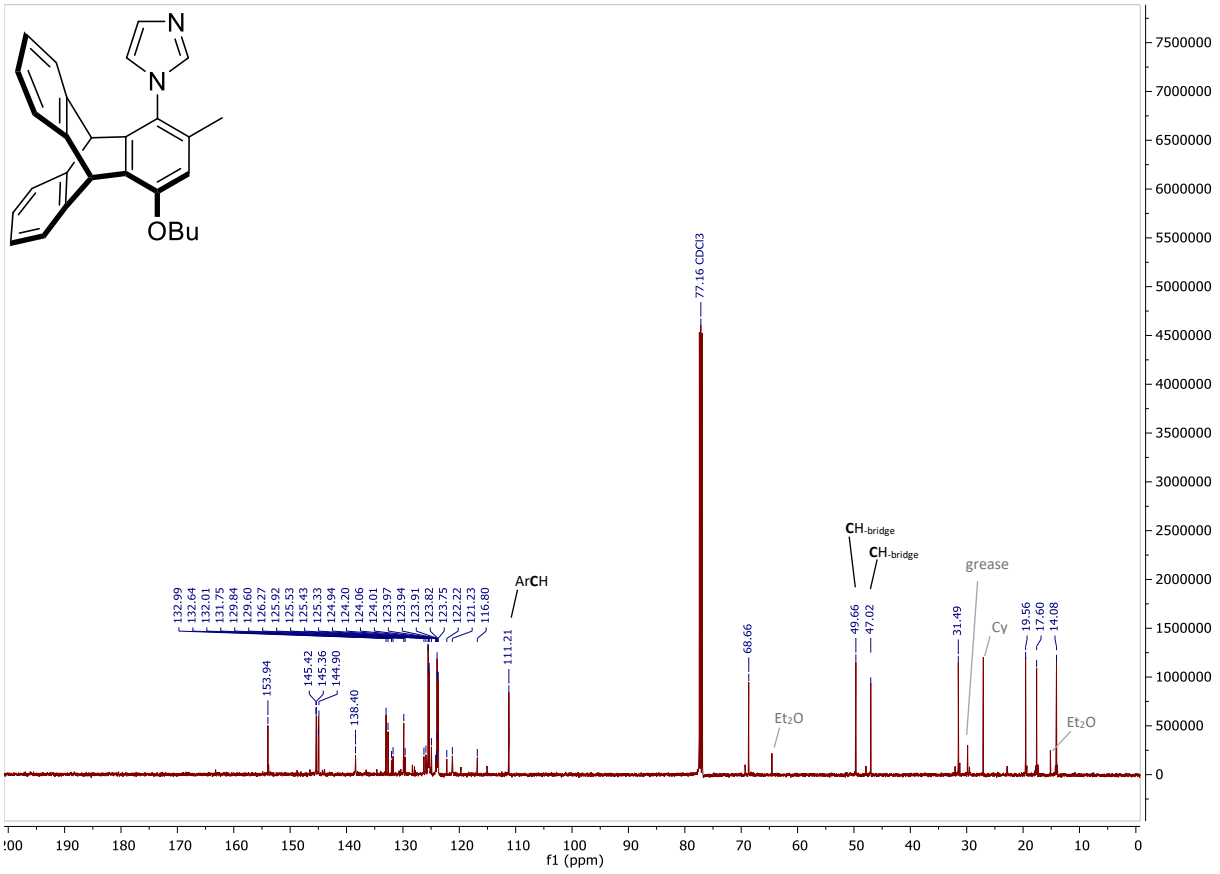


*Figure 162: ^{13}C-NMR of imidazole (**7b**) in $CDCl_3$.*

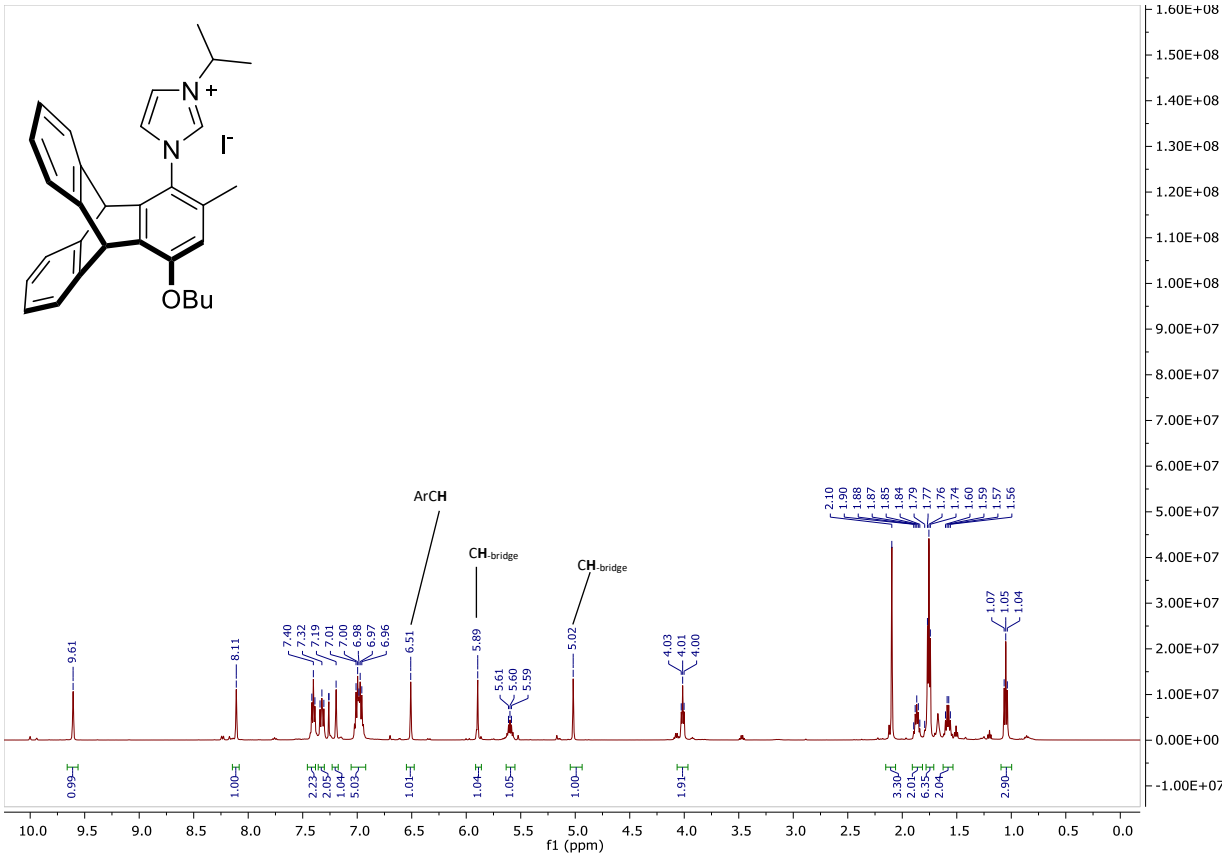


*Figure 163: ^{1}H-NMR of imidazolium salt (**8b**·HI) in $CDCl_3$.*

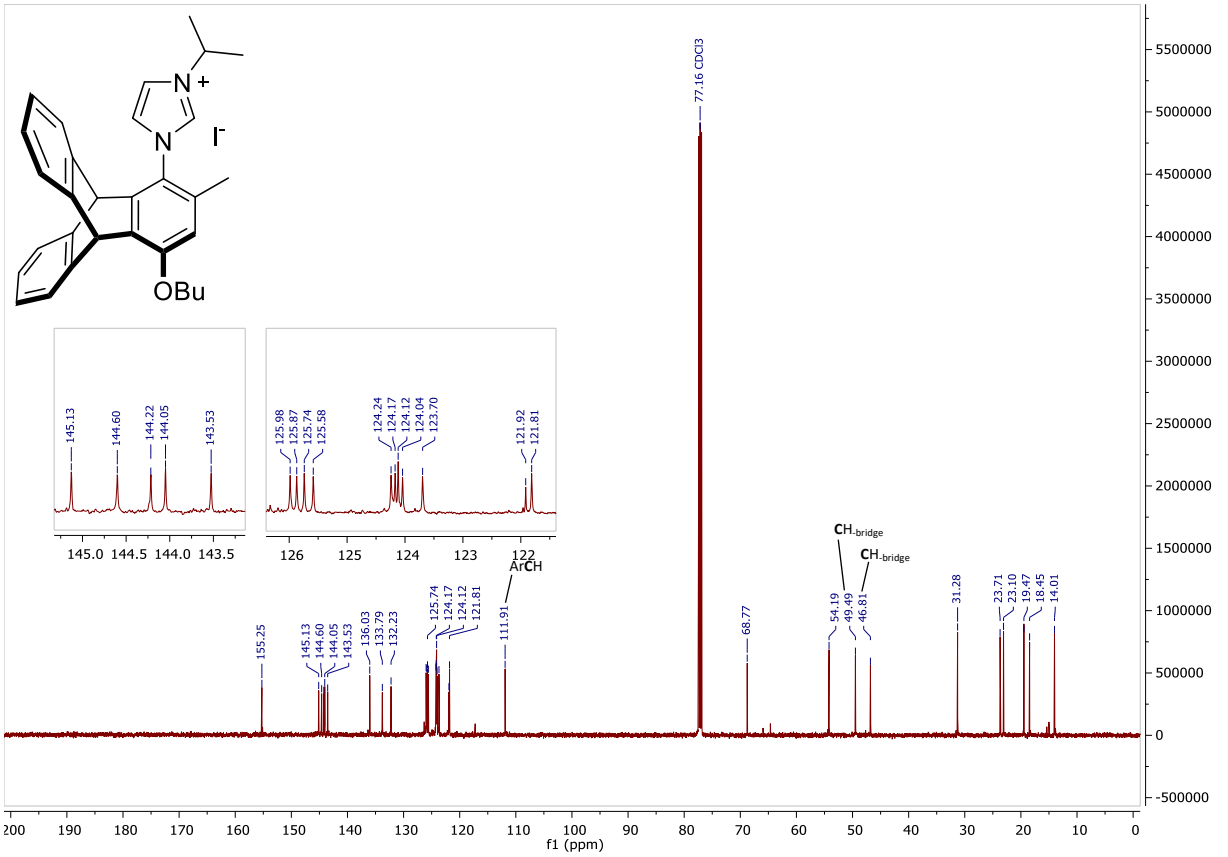


*Figure 164: ^{13}C-NMR of imidazolium salt (**8b**·HI) in $CDCl_3$.*

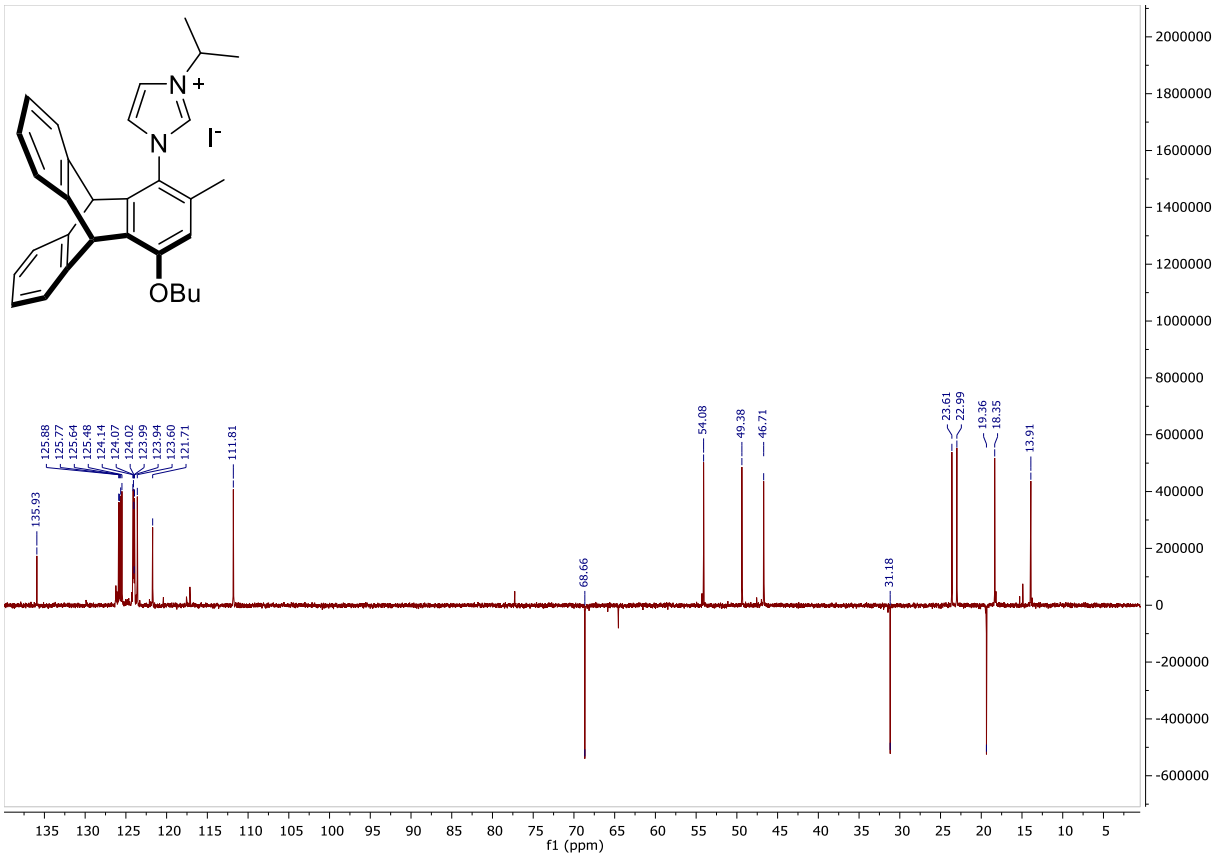


*Figure 165: DEPT-NMR of imidazolium salt (**8b**·HI) in $CDCl_3$.*

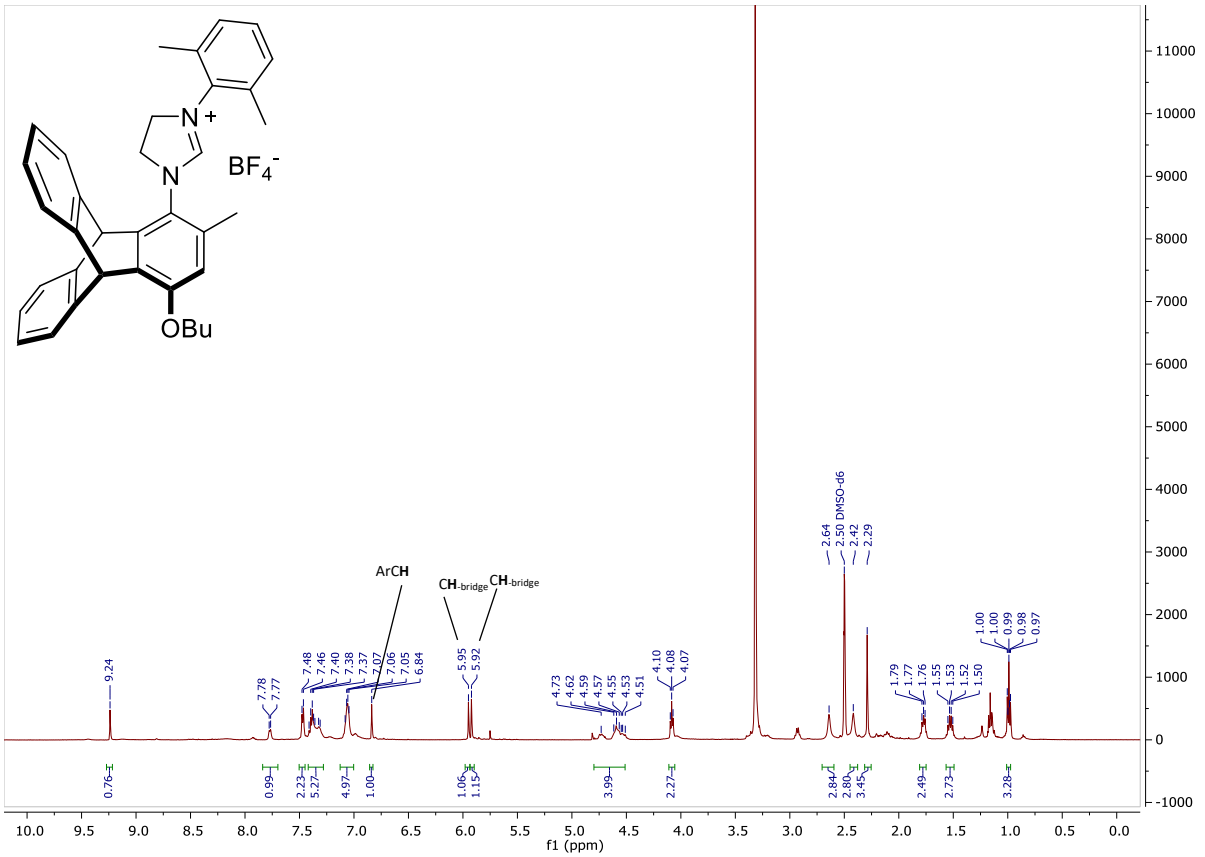


*Figure 166: ^{1}H-NMR of imidazolinium salt (**10**·HBF$_4$) in DMSO-d$_6$.*

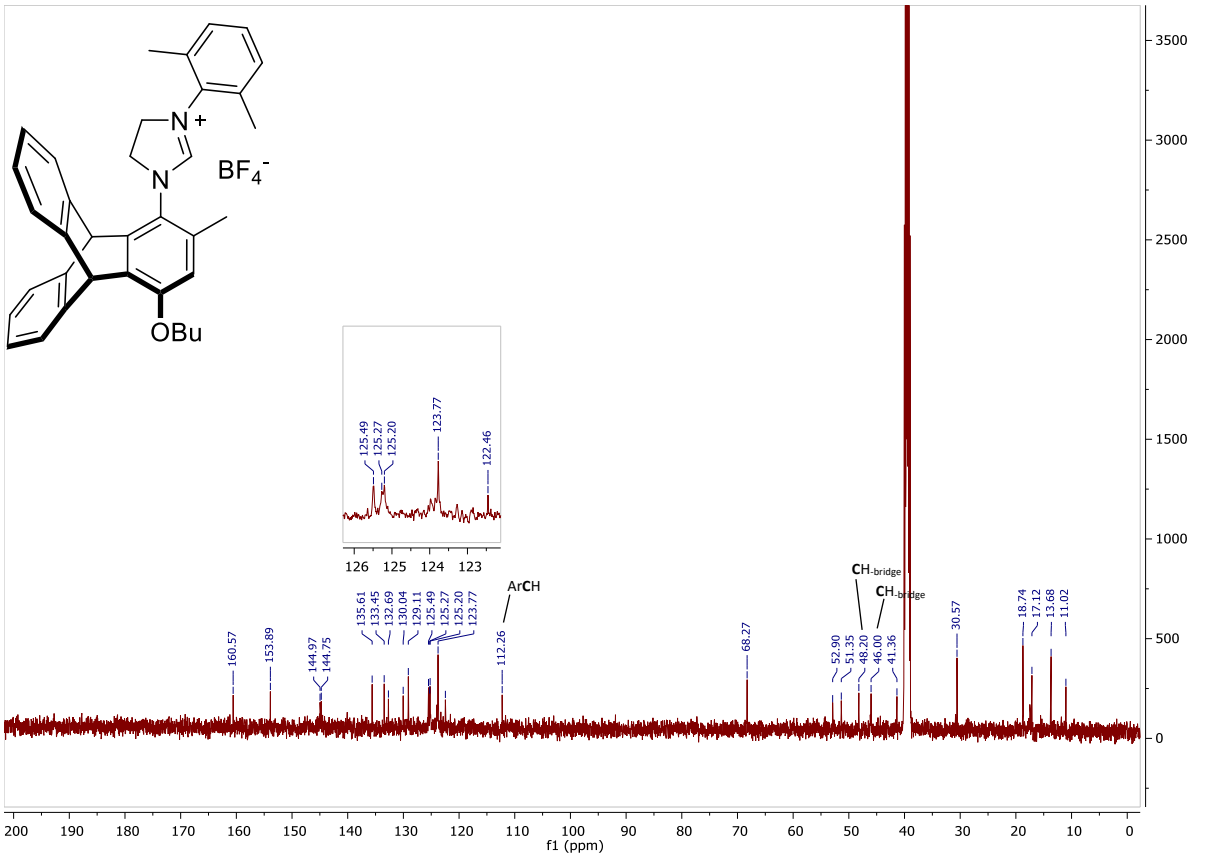


*Figure 167: ^{13}C-NMR of imidazolinium salt (**10**·HBF$_4$) in DMSO-d$_6$.*

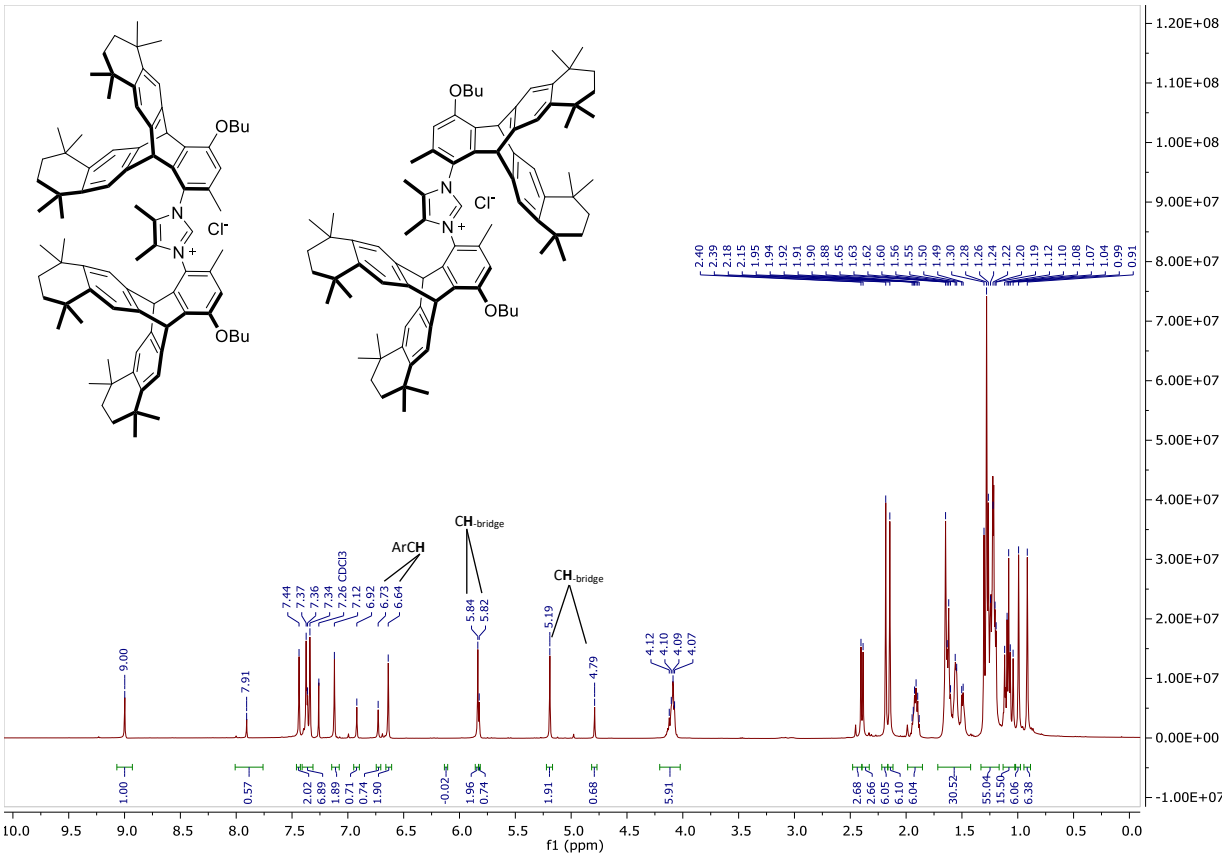


*Figure 168: ^{1}H-NMR of imidazolium salt (**12**·HCl) in CD_2Cl_2.*

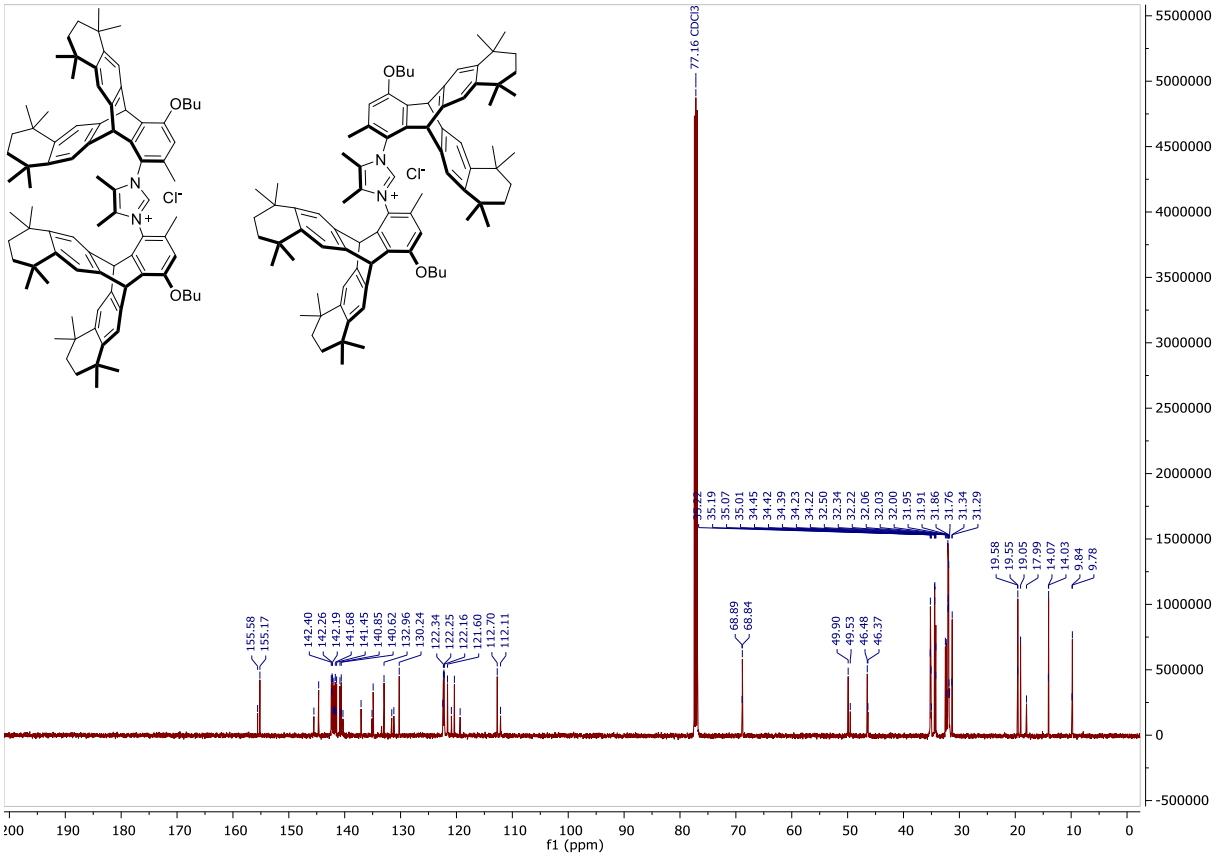


*Figure 169: ^{13}C-NMR of imidazolium salt (**12**·HCl) in $CDCl_3$.*

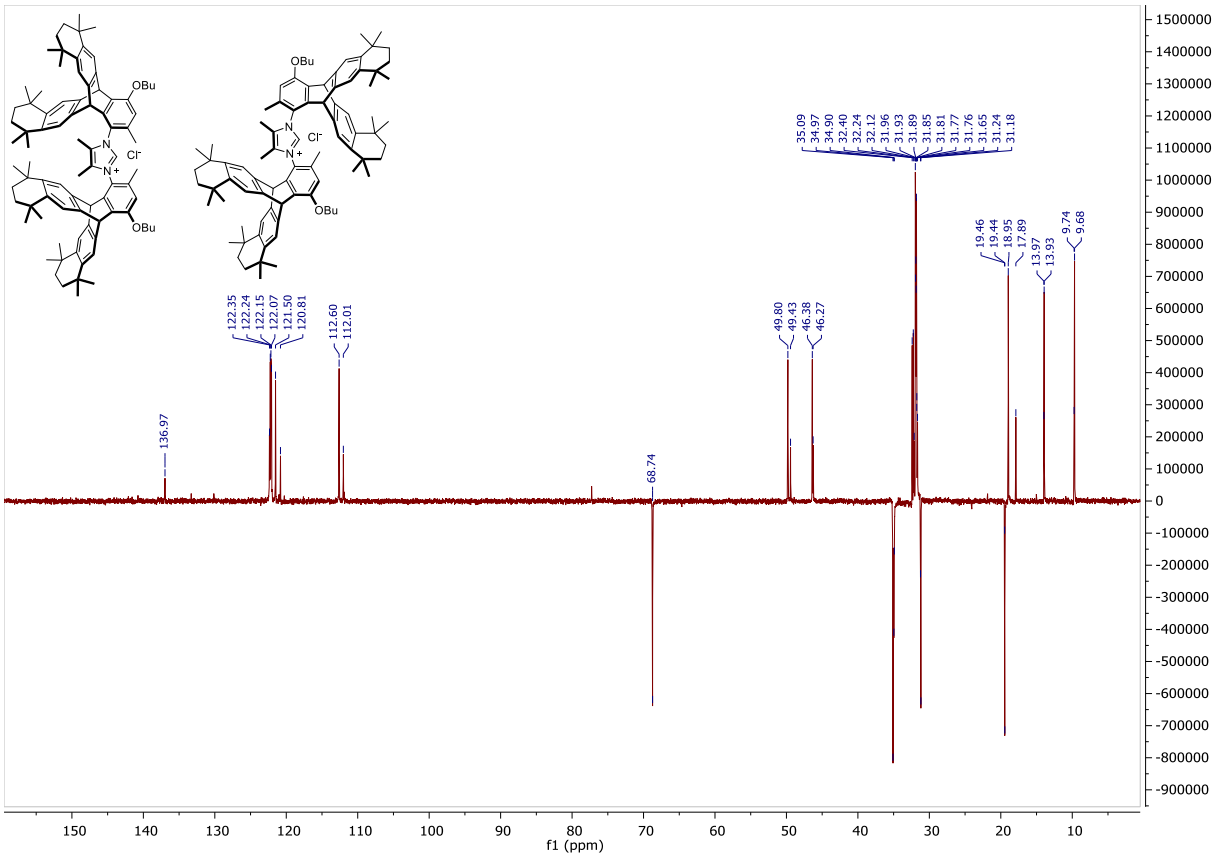


*Figure 170: DEPT-NMR of imidazolium salt (**12**·HCl) in $CDCl_3$.*

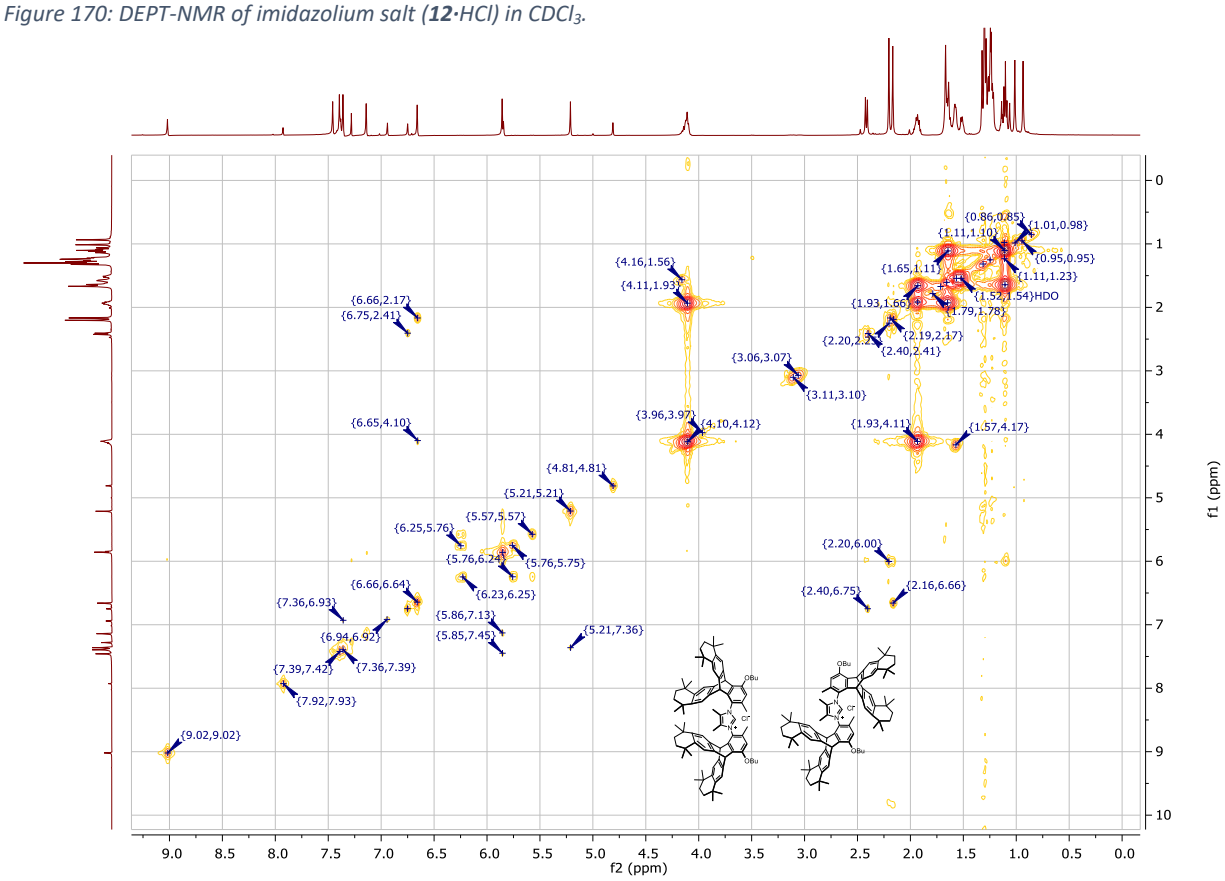


*Figure 171: COSY-NMR of imidazolium salt (**12**·HCl) in $CDCl_3$.*

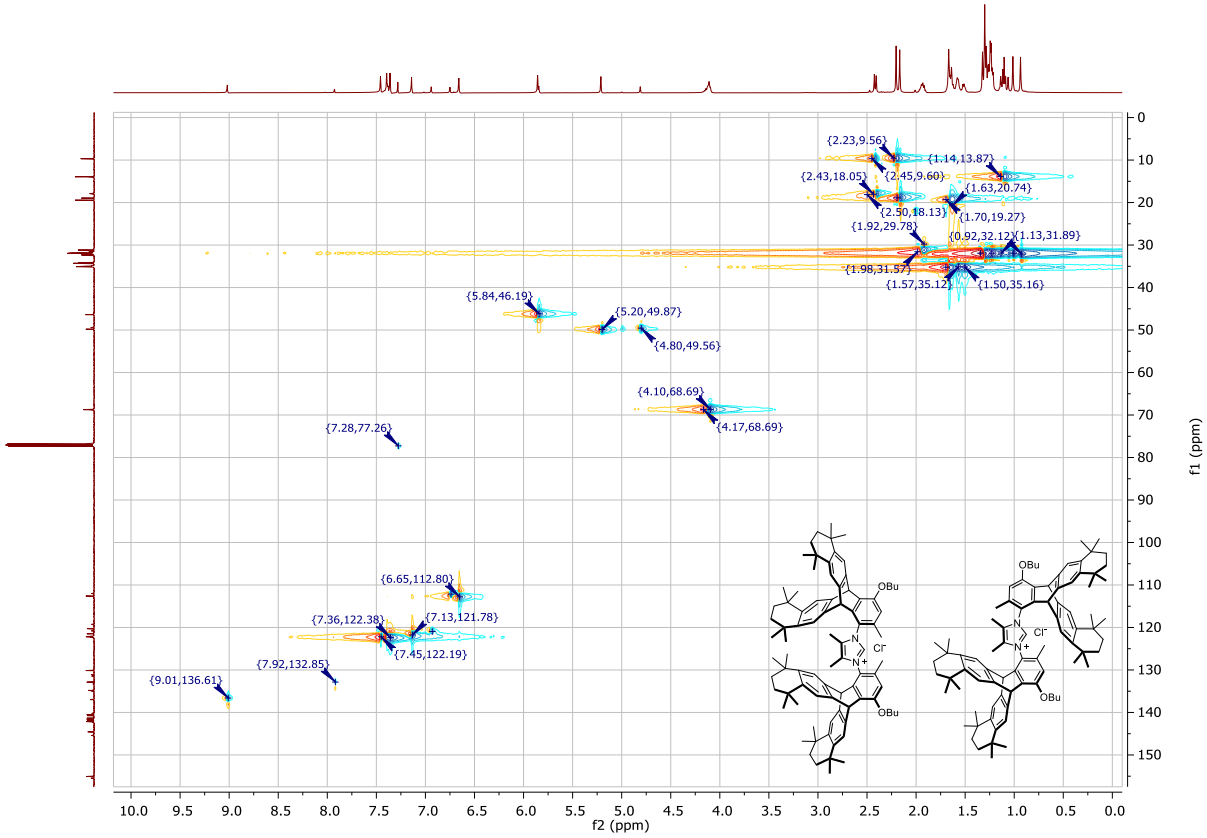


*Figure 172: HSQC-NMR of imidazolium salt (**12**·HCl) in $CDCl_3$.*

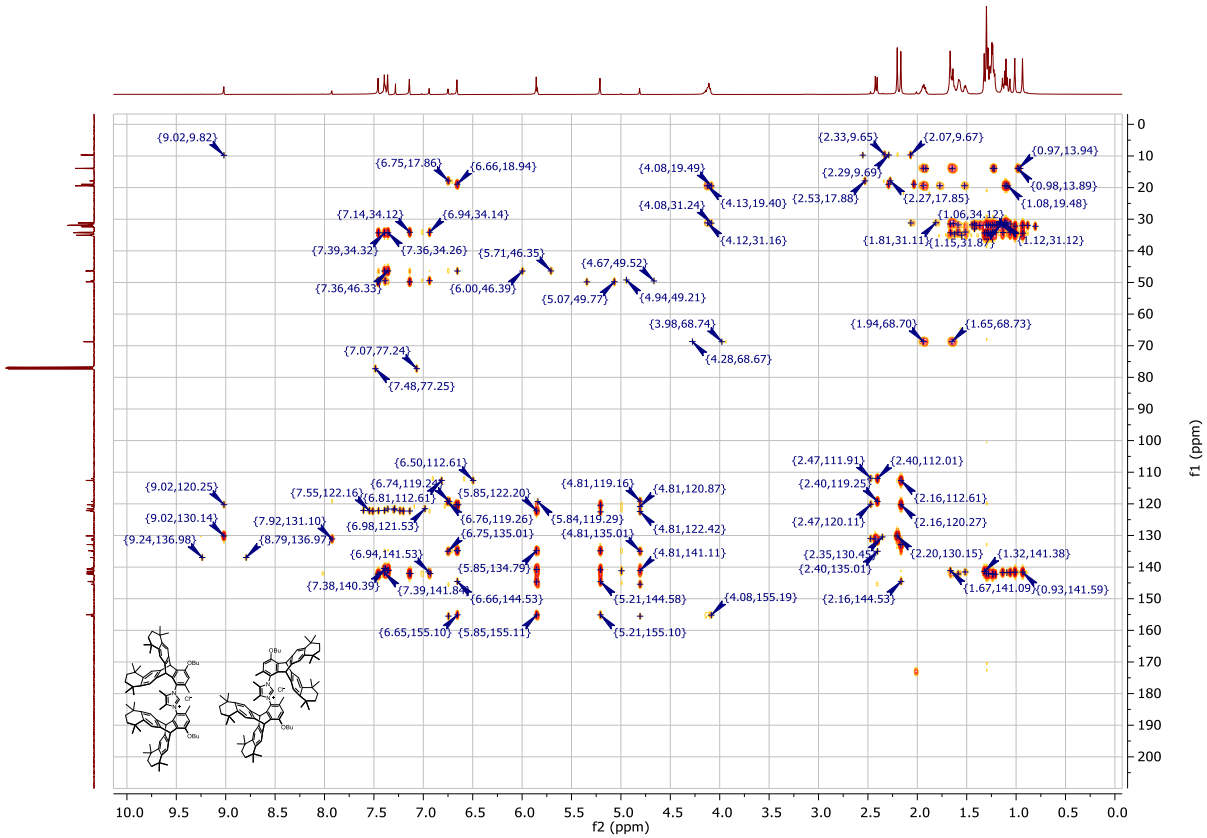


*Figure 173: HMBC-NMR of imidazolium salt (**12**·HCl) in $CDCl_3$.*

Metal complexes

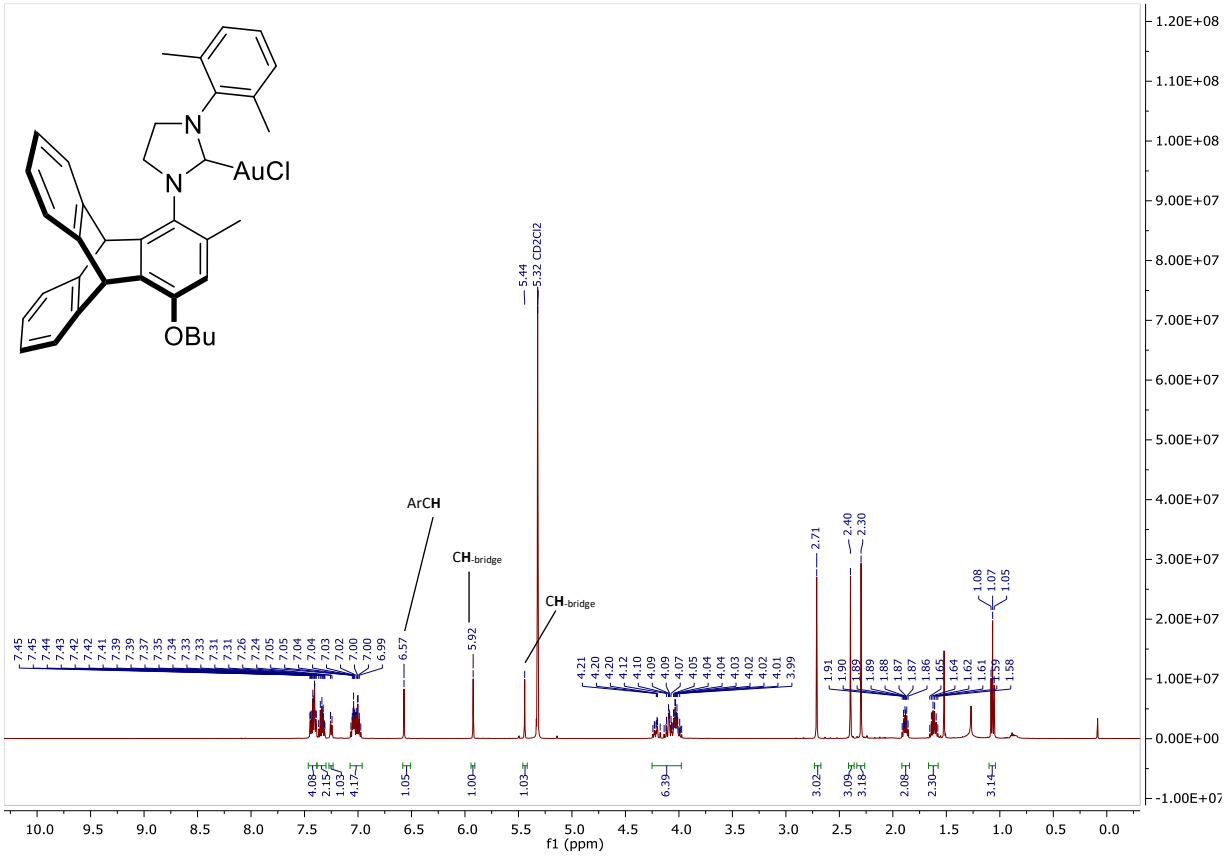


*Figure 174: ^{1}H-NMR of [AuCl(**10**)] complex in CD_2Cl_2.*

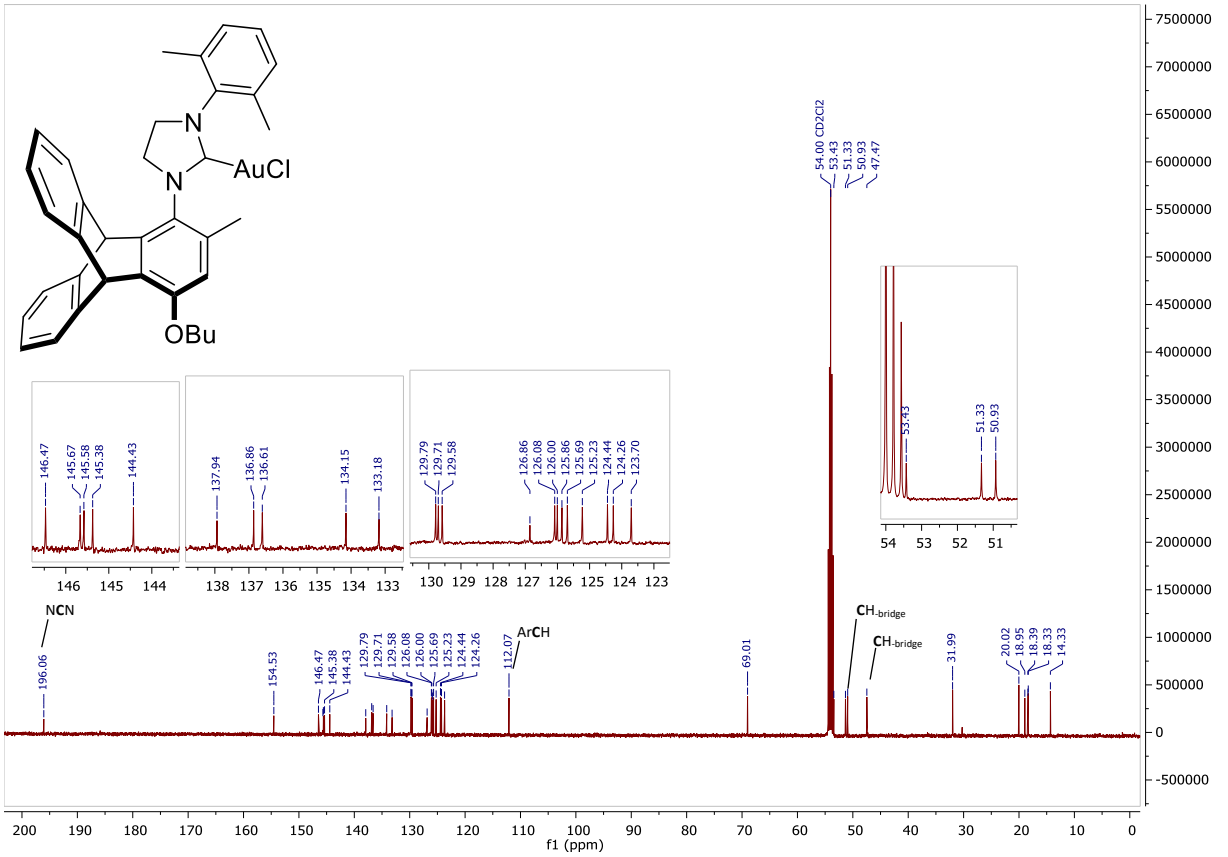


*Figure 175: ^{13}C-NMR of [AuCl(**10**)] complex in CD_2Cl_2.*

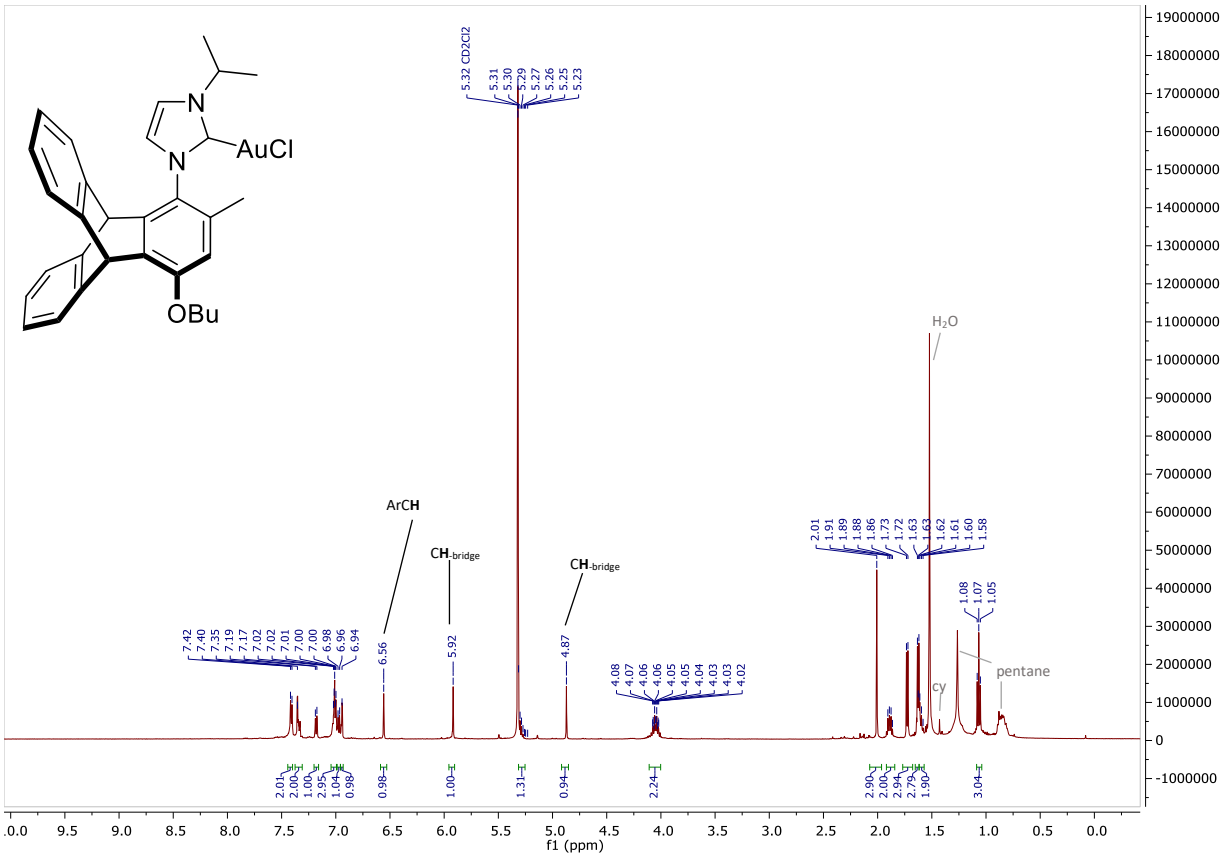


*Figure 176: ^{1}H-NMR of [AuCl(**8b**)]complex in CD_2Cl_2.*

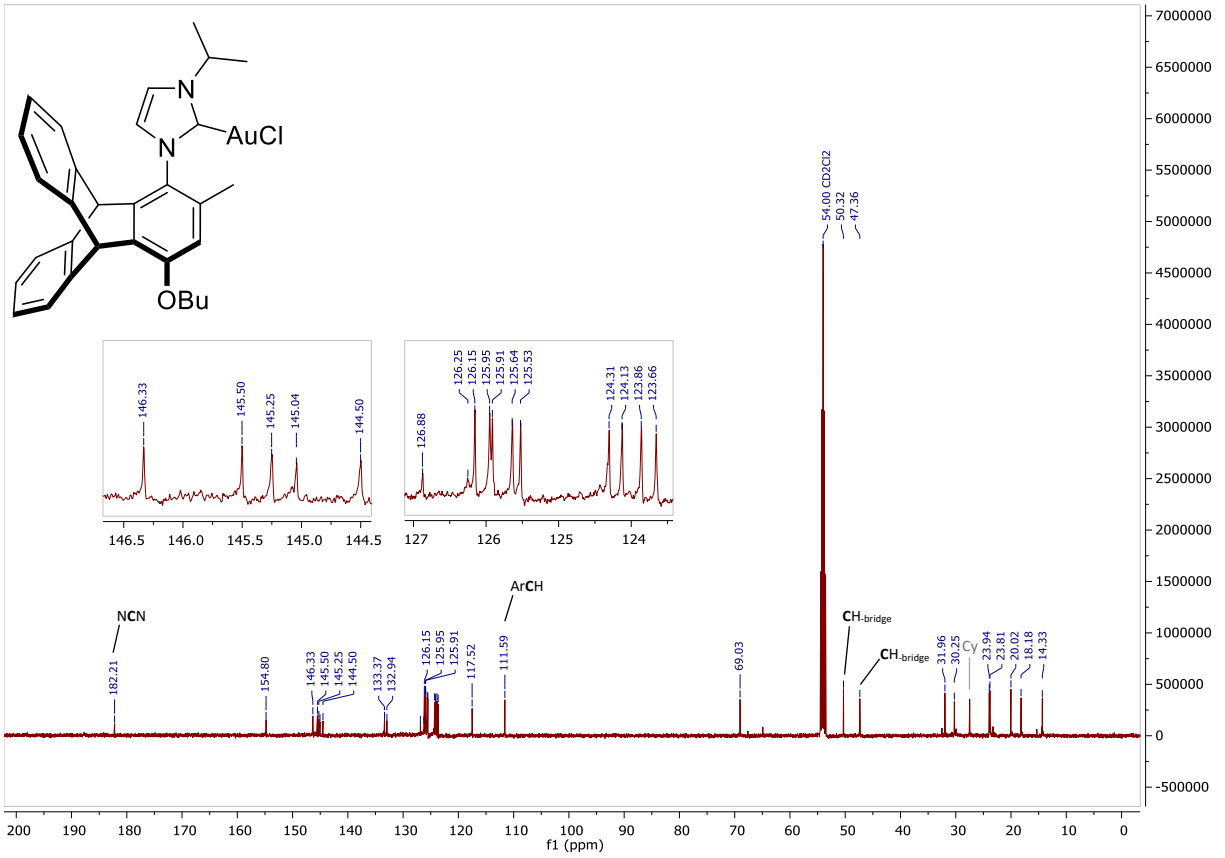


*Figure 177: ^{13}C-NMR of [AuCl(**8b**)]complex in CD_2Cl_2.*

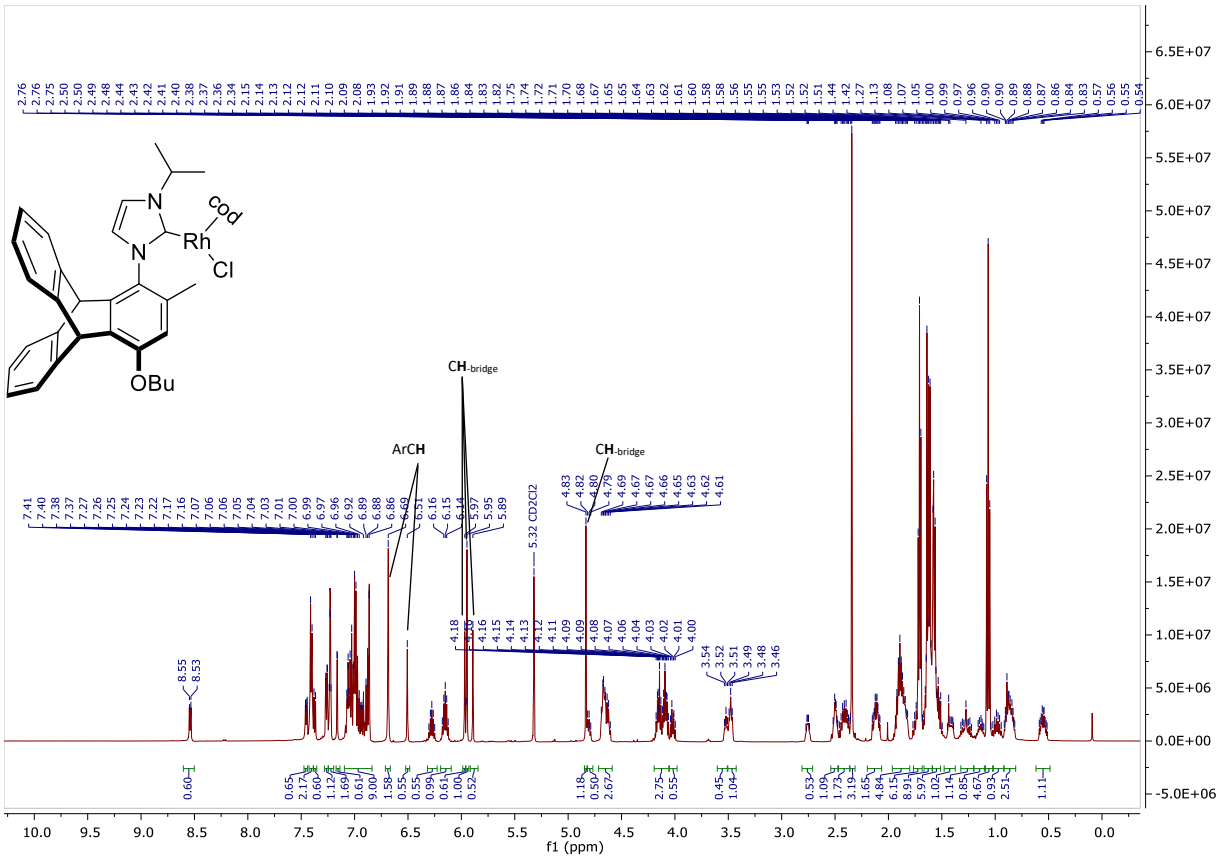


*Figure 178: ^{1}H-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

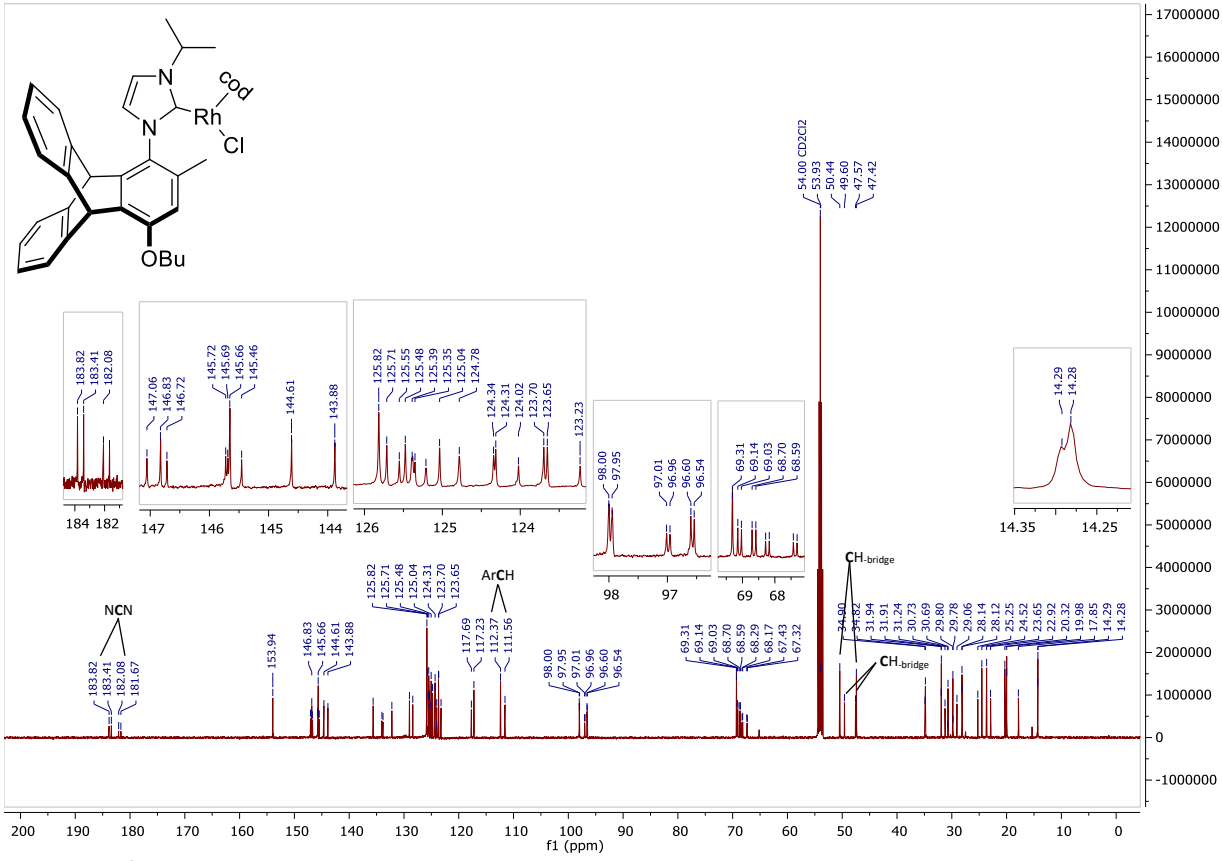


*Figure 179: ^{13}C-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

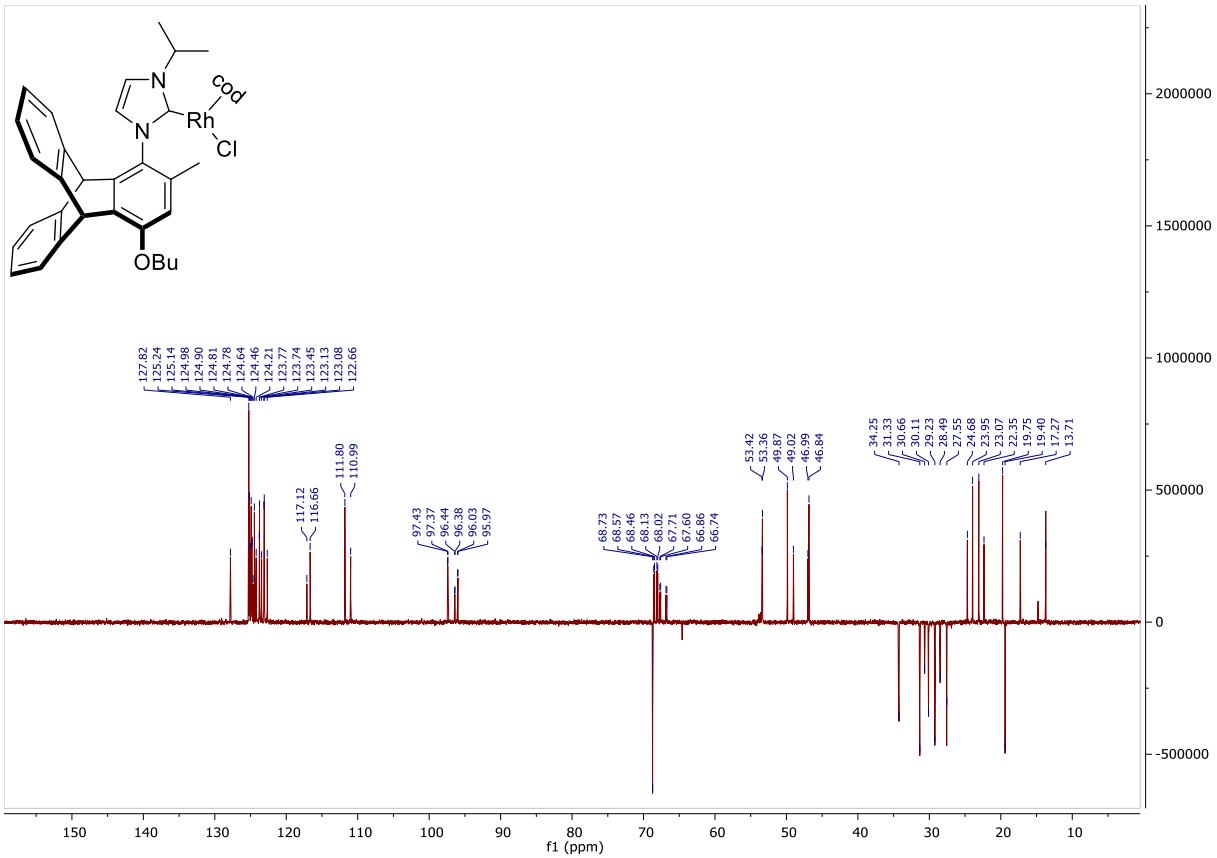


*Figure 180: ^{13}C-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

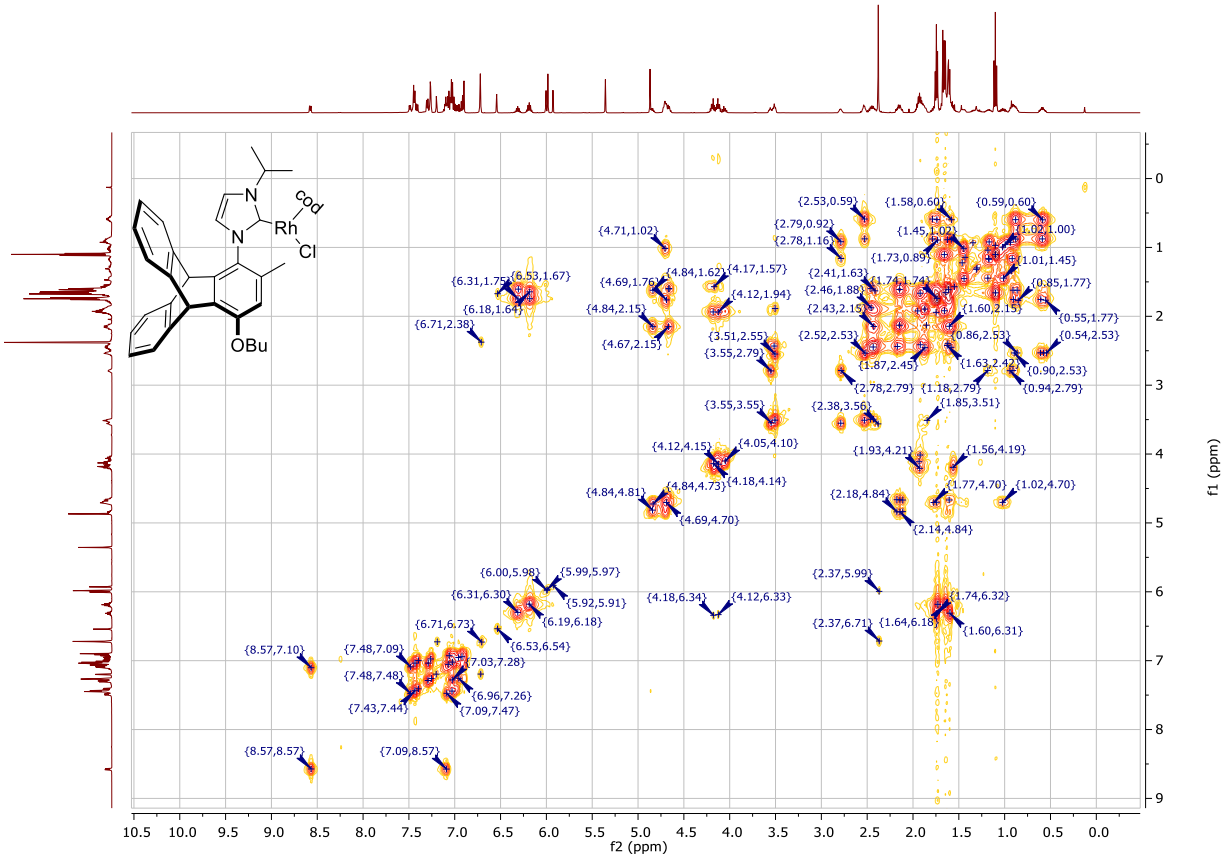


*Figure 181: DEPT-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

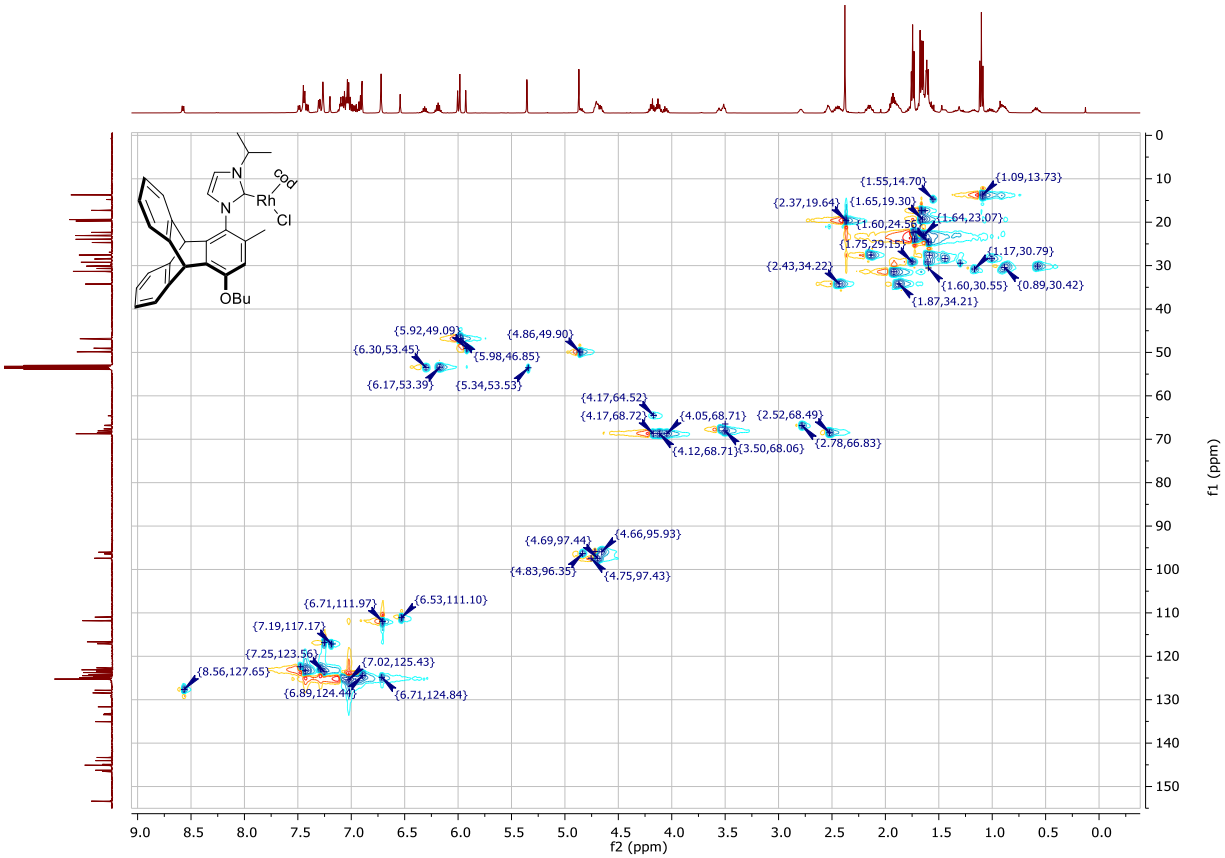


*Figure 182: HSQC-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

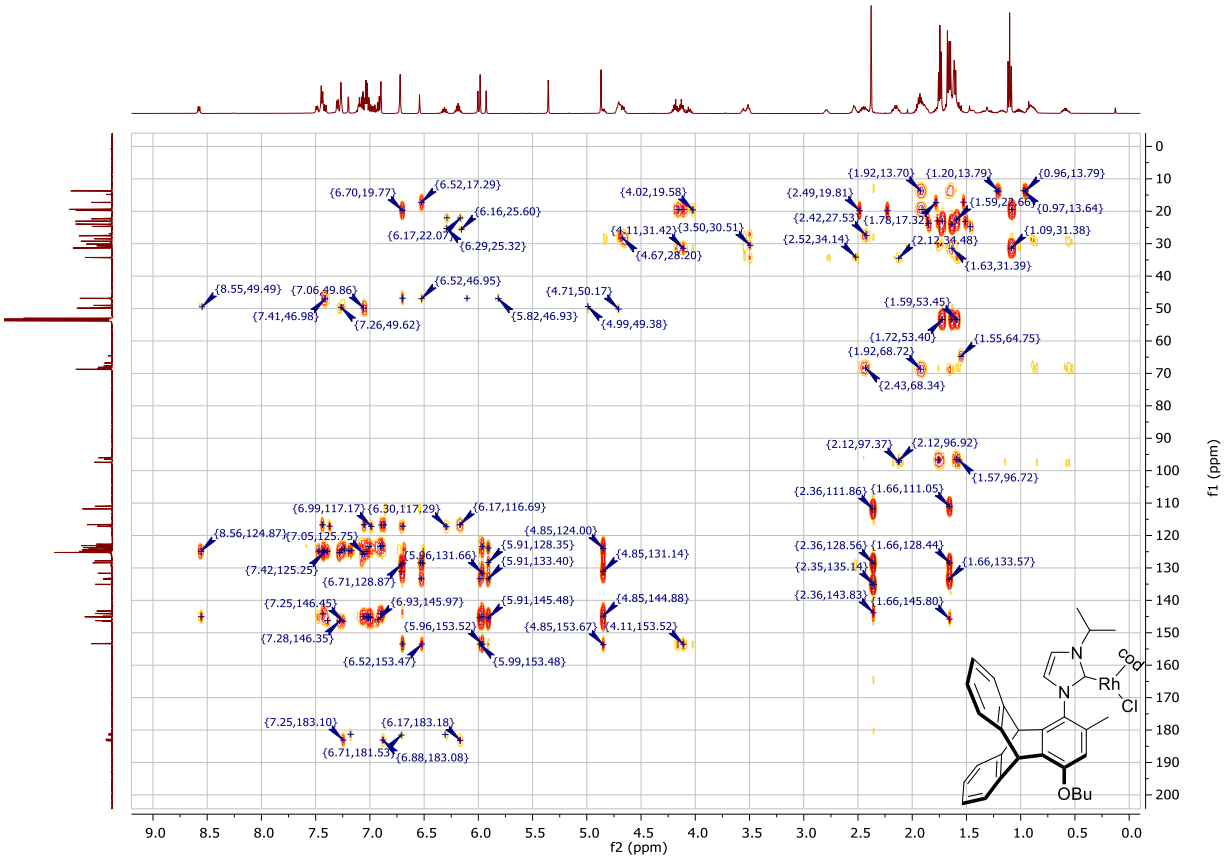


*Figure 183: HMBC-NMR of [RhCl(cod)(**8b**)]complex in CD_2Cl_2.*

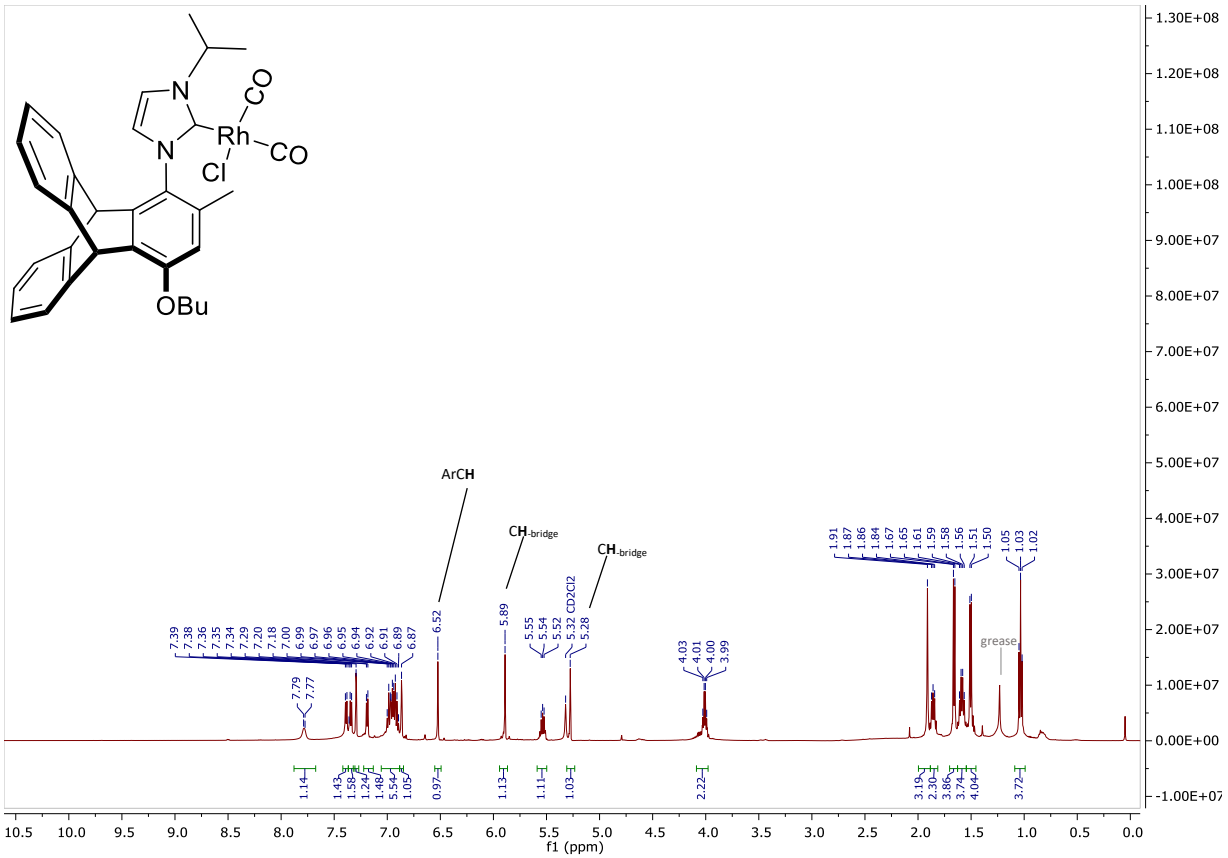


*Figure 184: ^{1}H-NMR of [RhCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

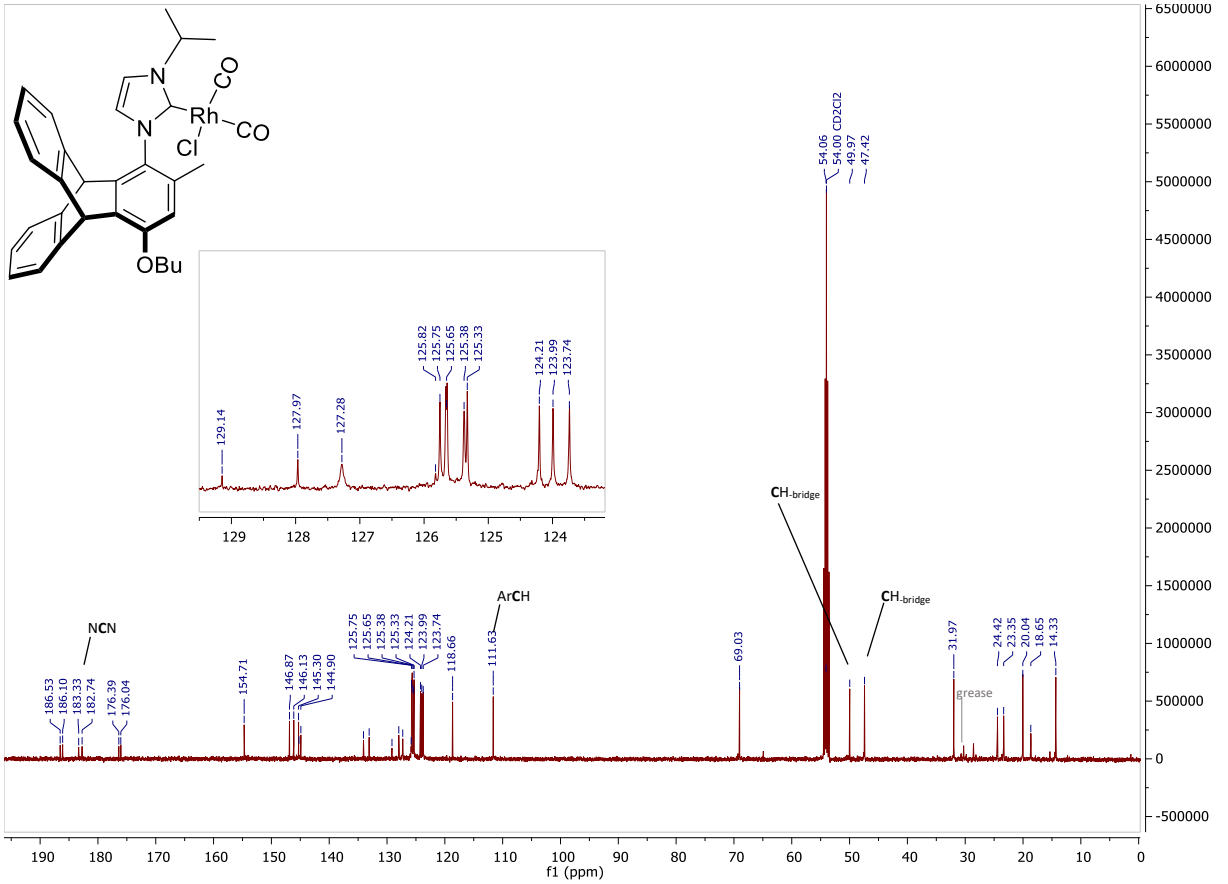


*Figure 185: ^{13}C-NMR of [RhCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

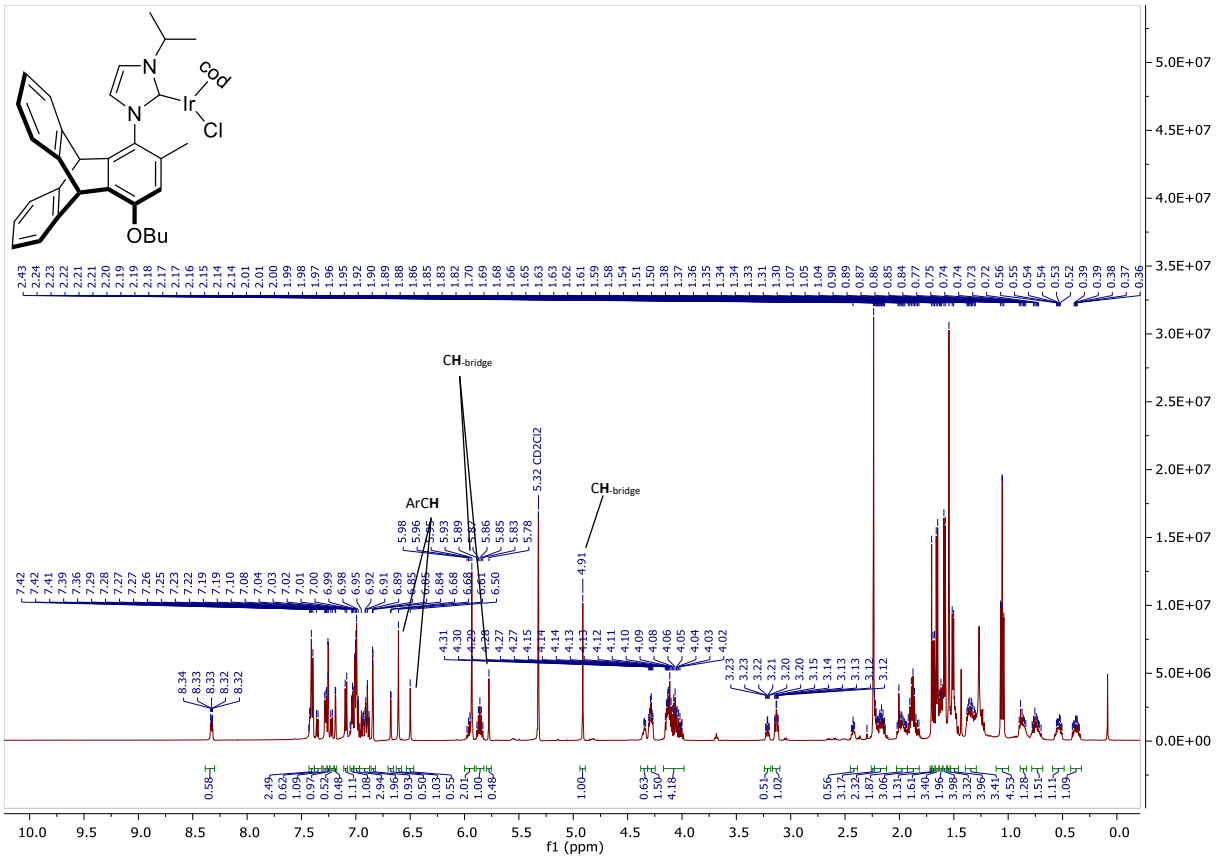


*Figure 186: [1]H-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

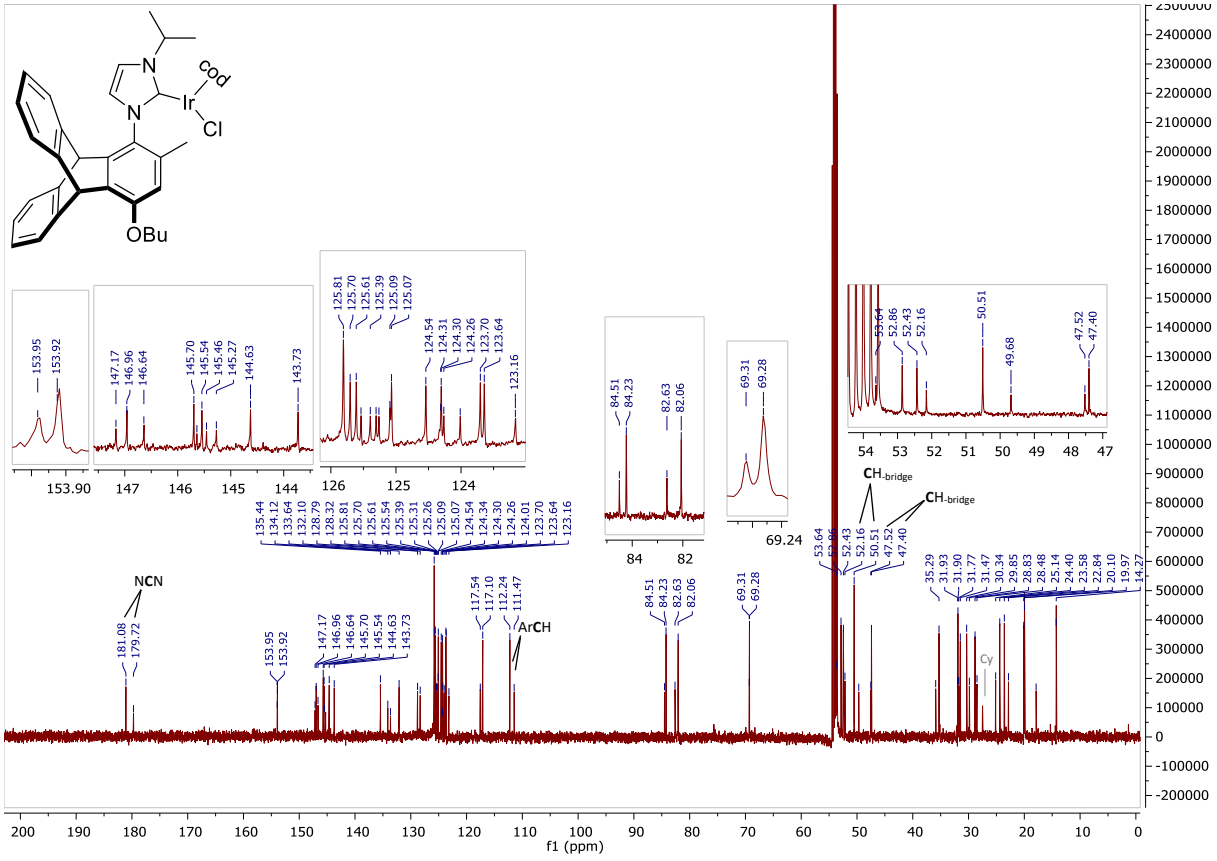


*Figure 187: [13]C-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

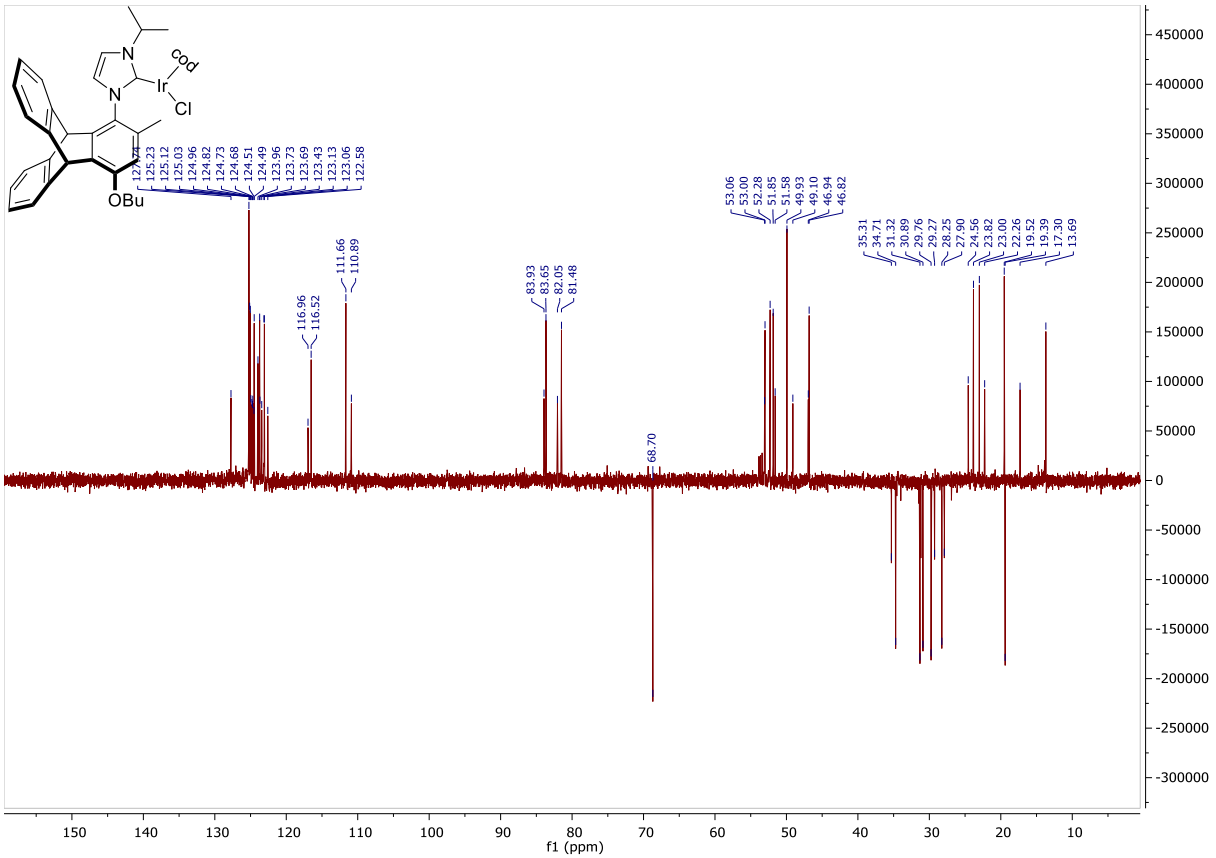


*Figure 188: DEPT-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

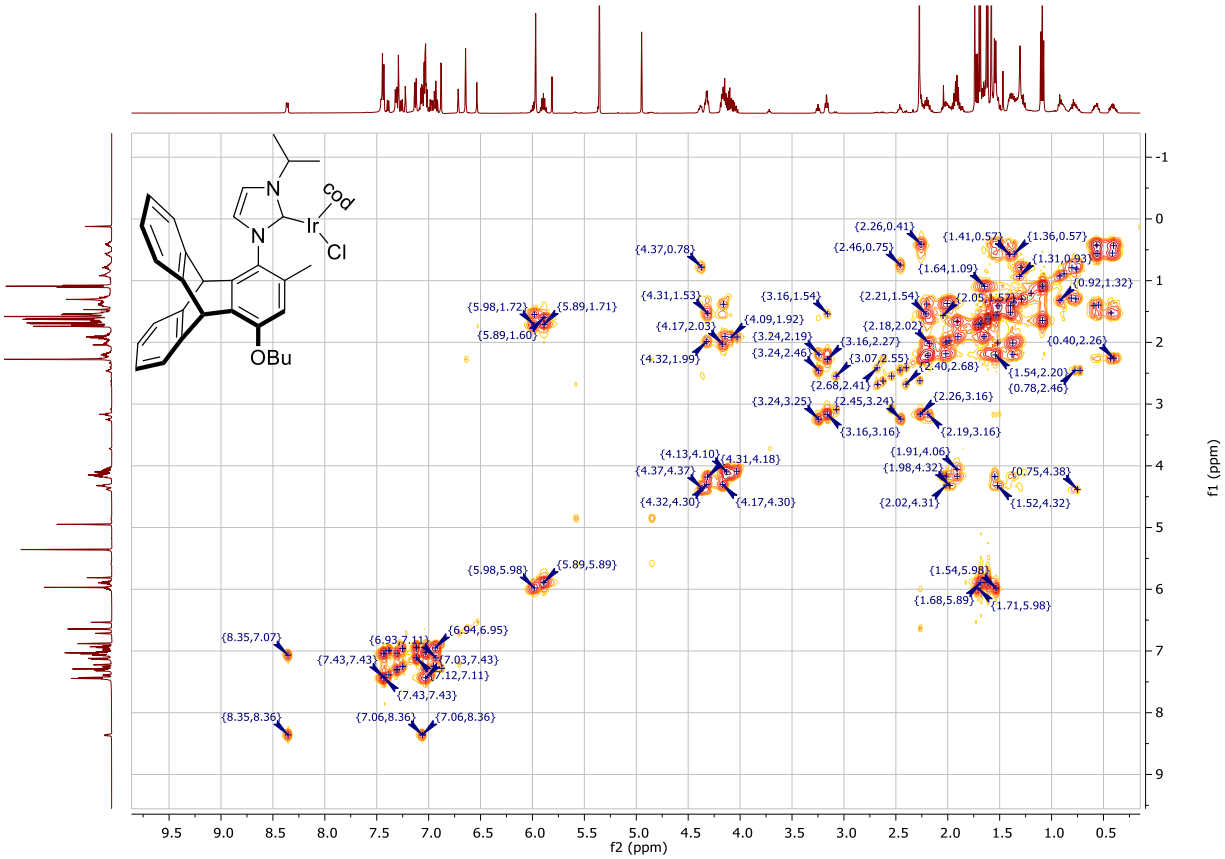


*Figure 189: COSY-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

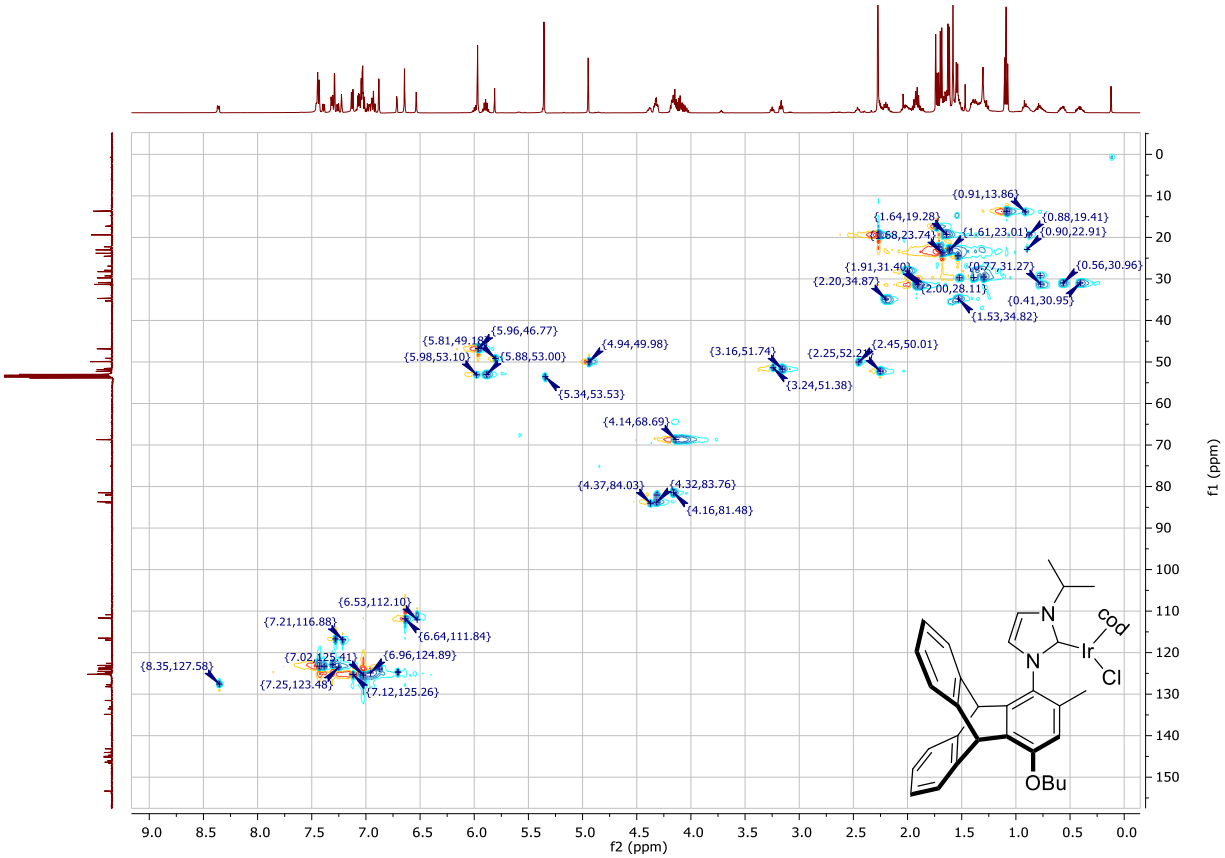


*Figure 190: HSQC-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

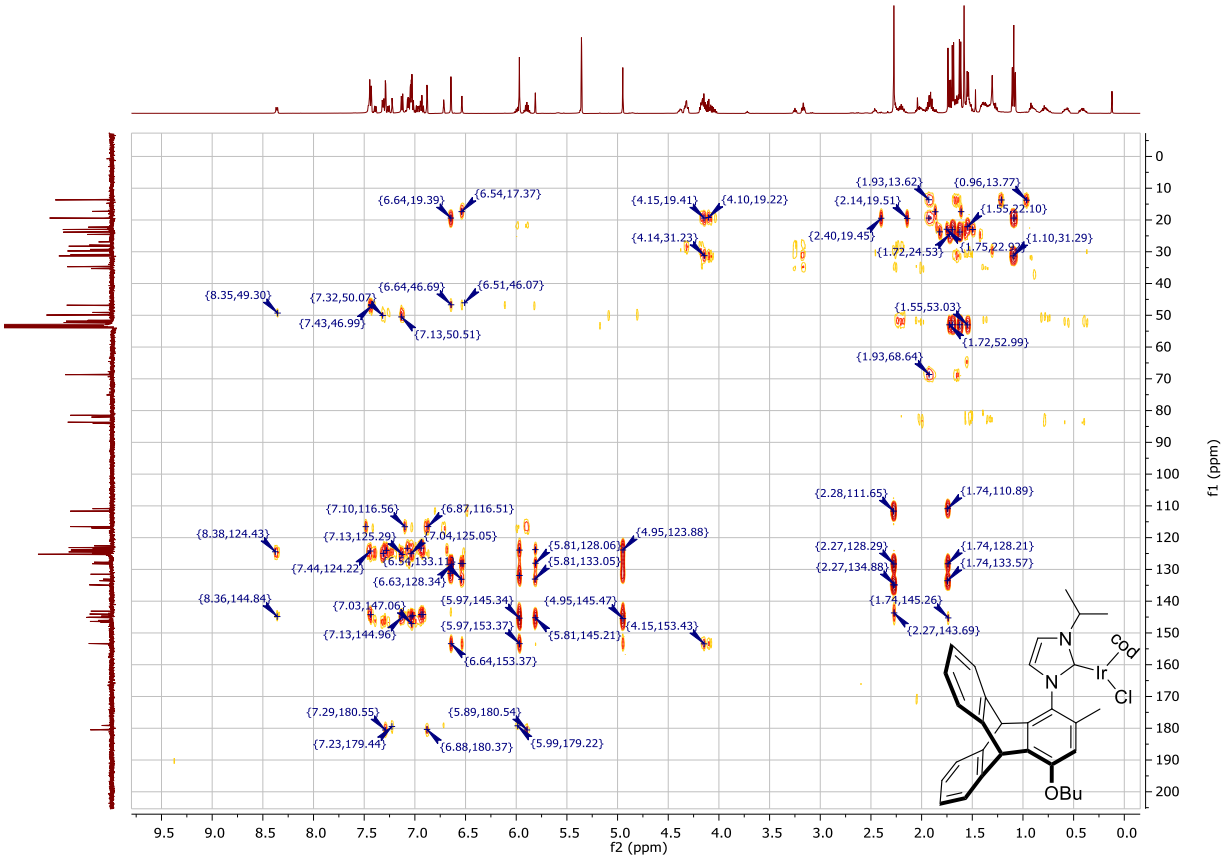


*Figure 191: HMBC-NMR of [IrCl(cod)(**8b**)] complex in CD_2Cl_2.*

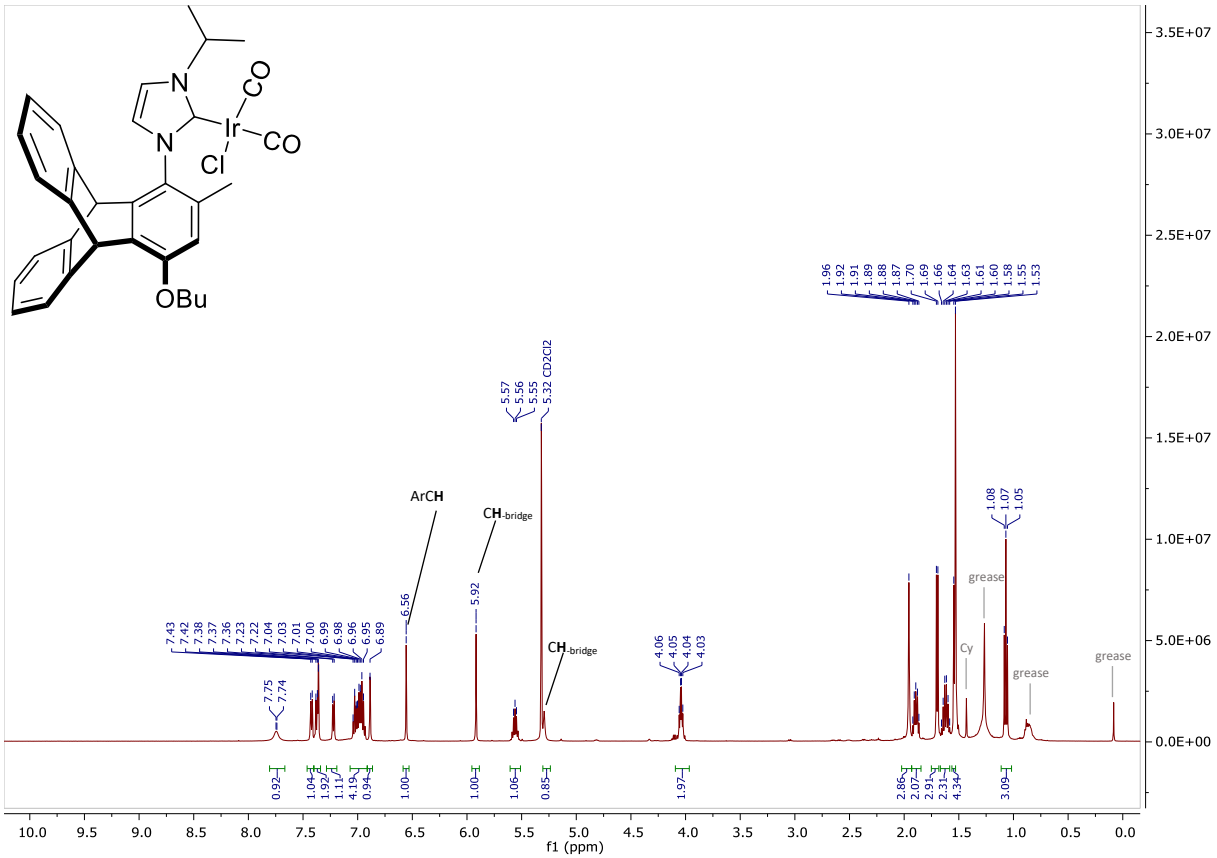


*Figure 192: ^{1}H-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

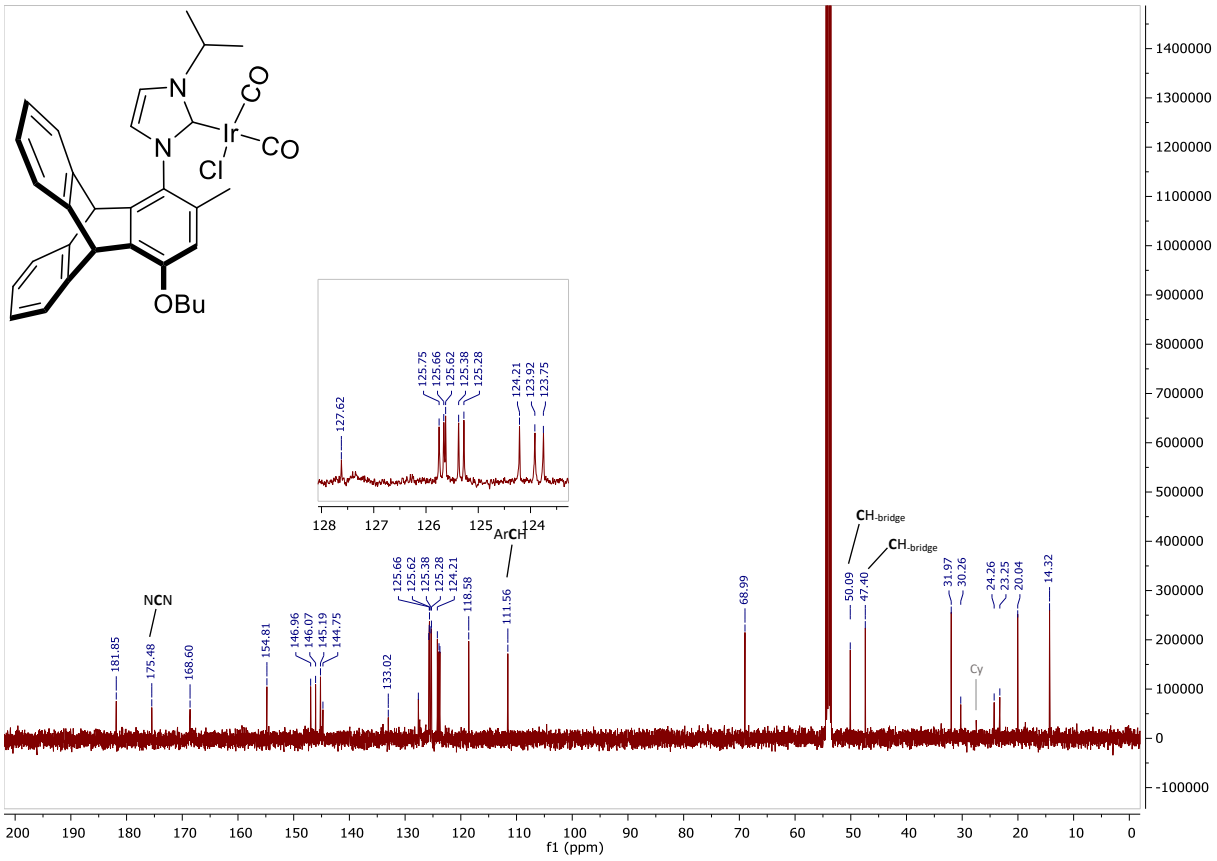


*Figure 193: ^{13}C-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

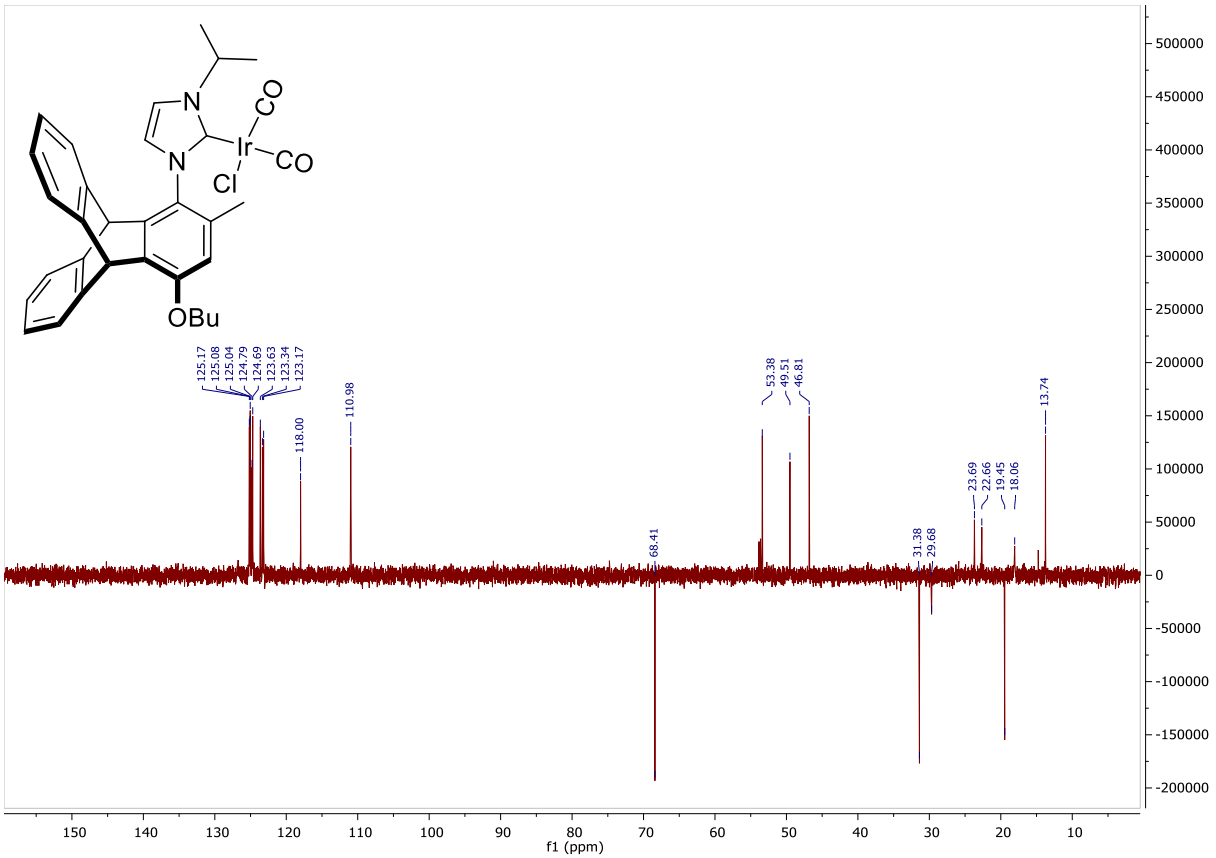


*Figure 194: DEPT-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

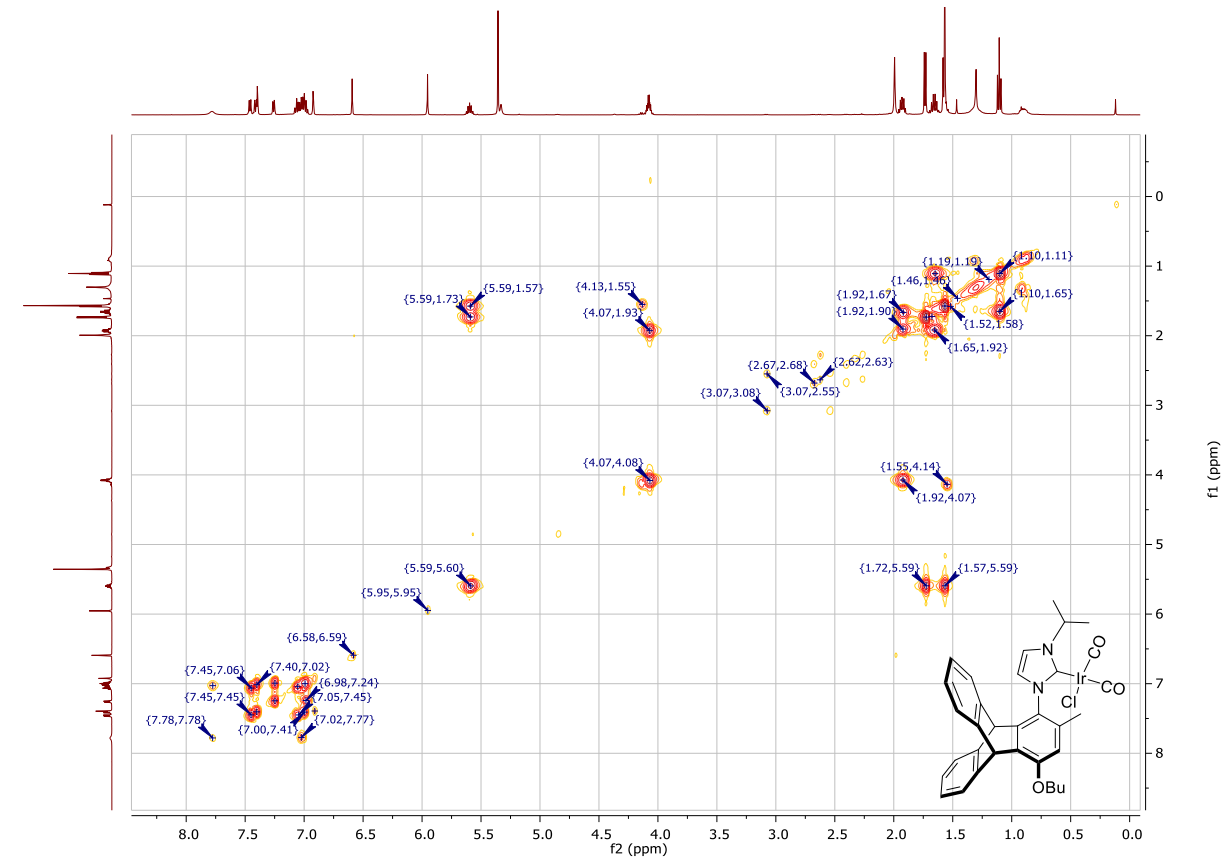


*Figure 195: COSY-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

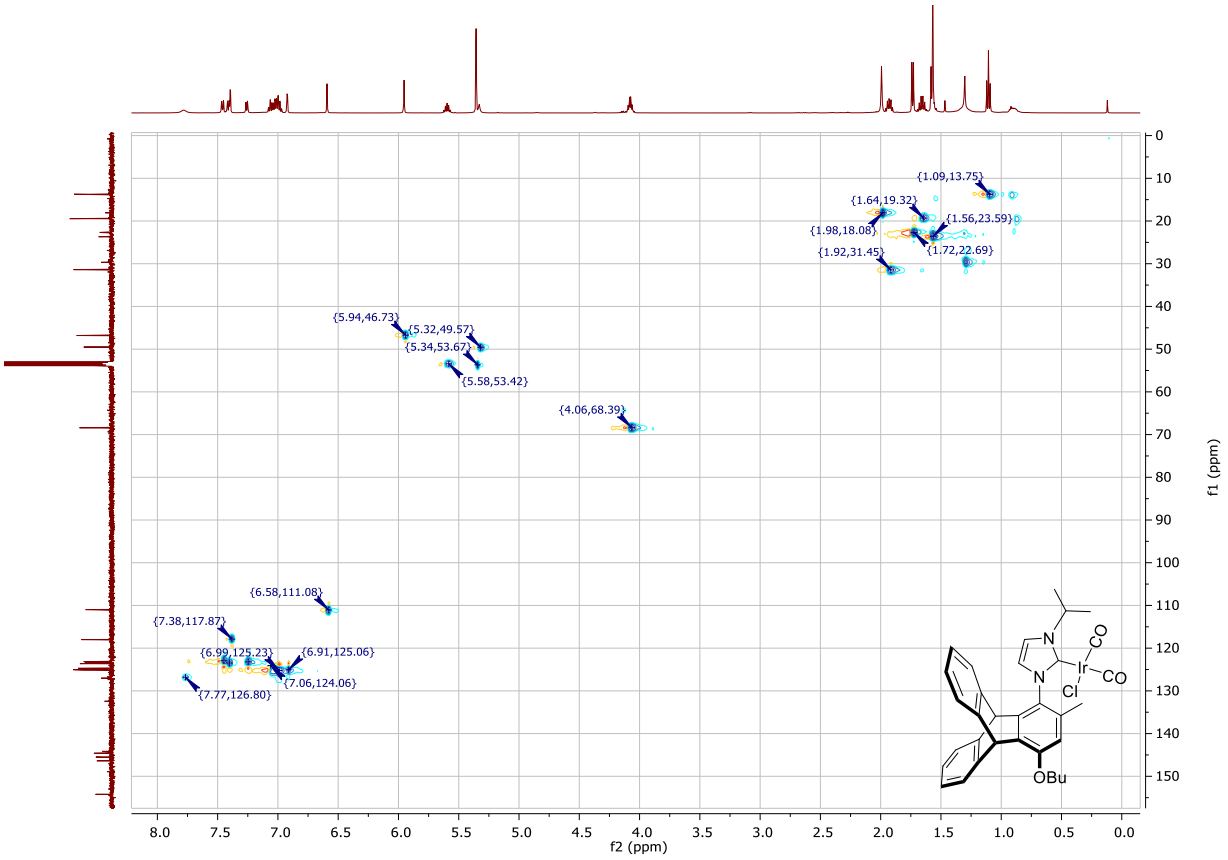


*Figure 196: HSQC-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

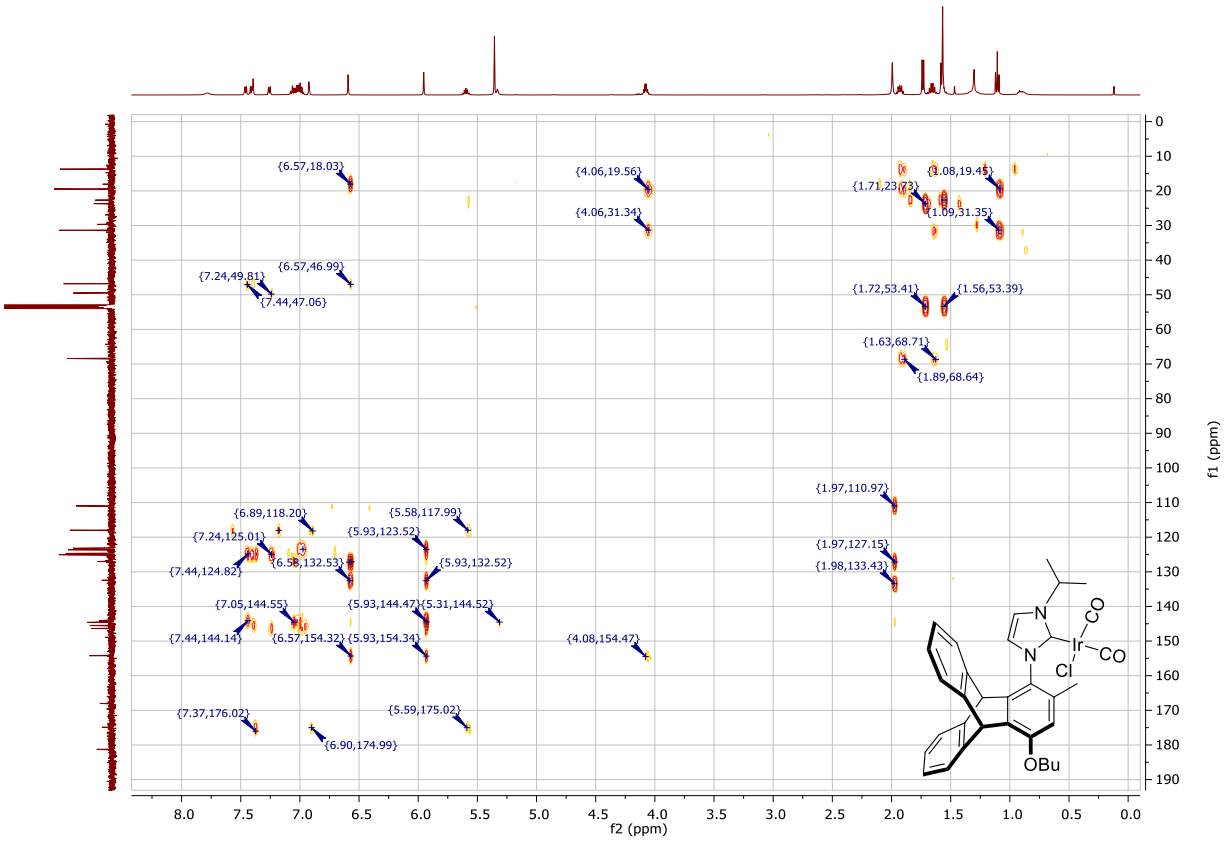


*Figure 197: HMBC-NMR of [IrCl(CO)$_2$(**8b**)] complex in CD_2Cl_2.*

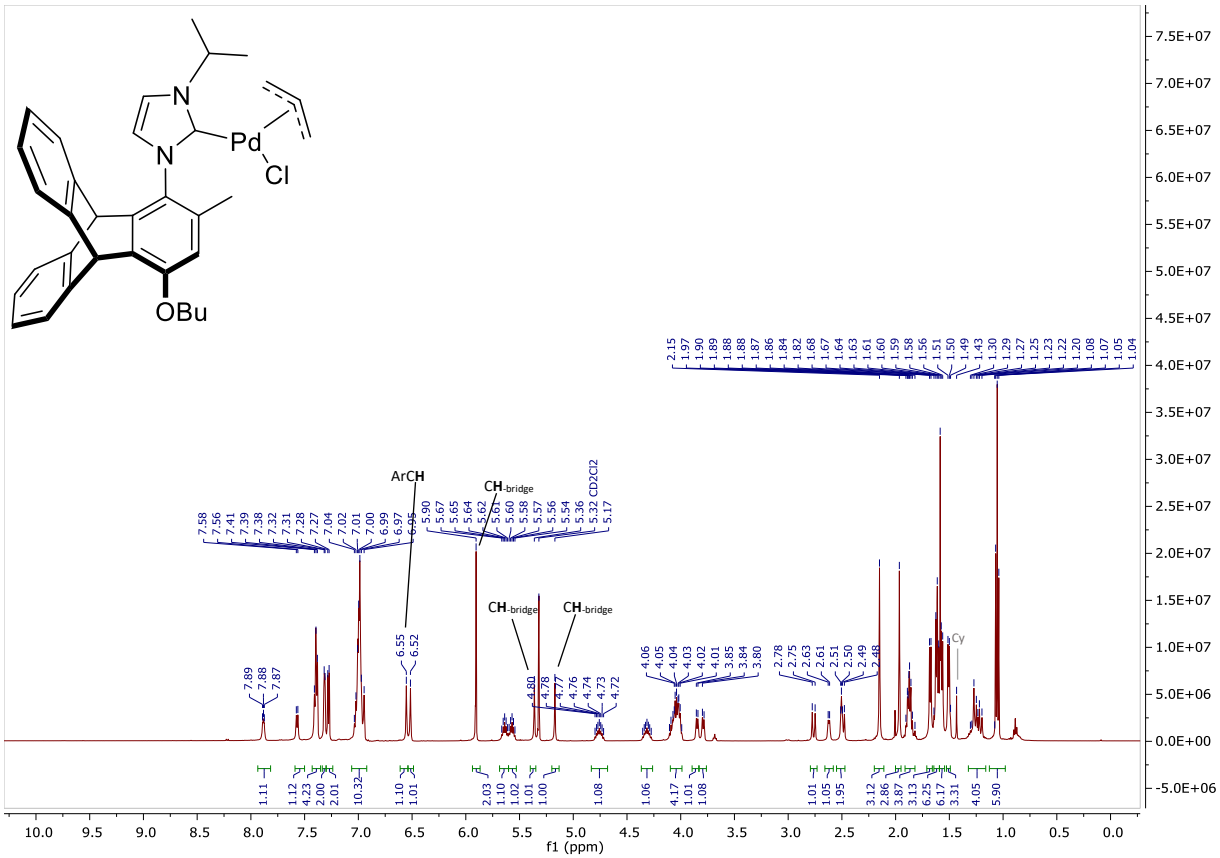


*Figure 198: ^{1}H-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

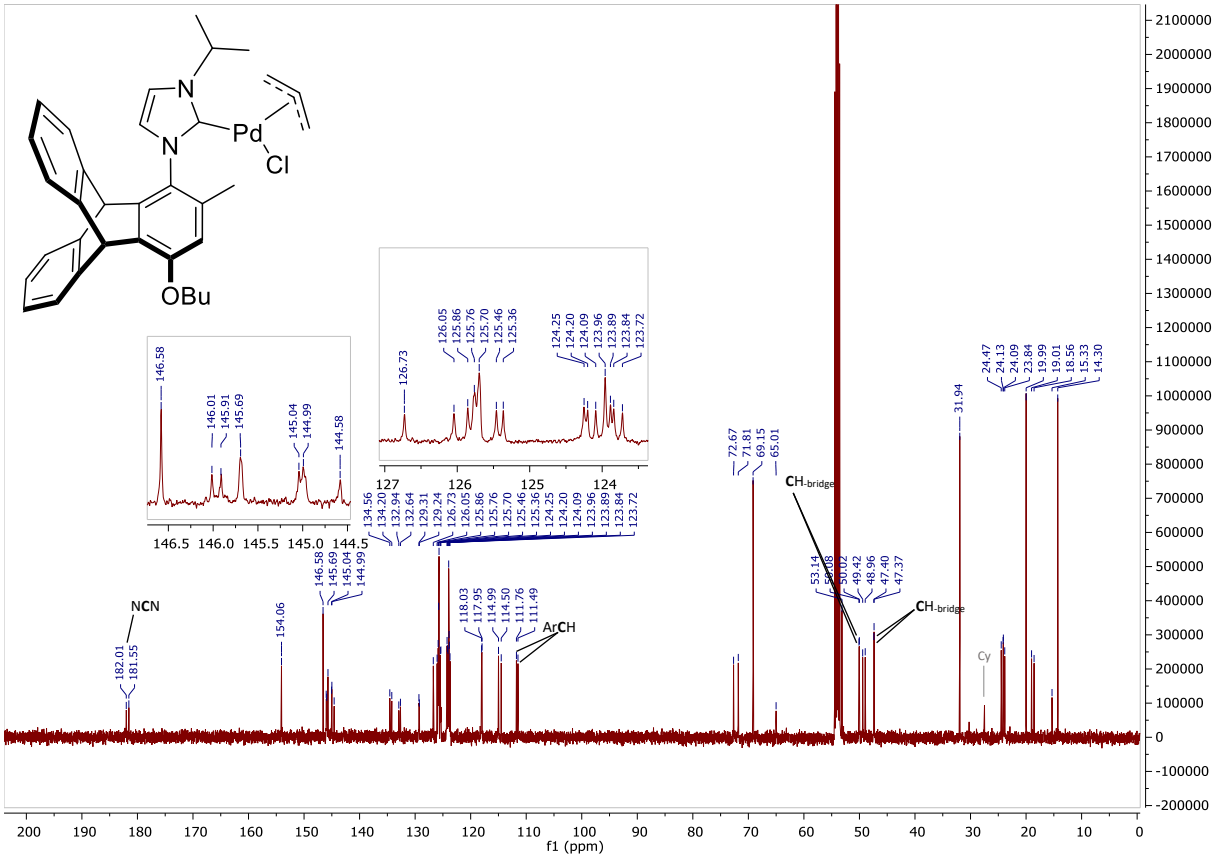


*Figure 199: ^{13}C-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

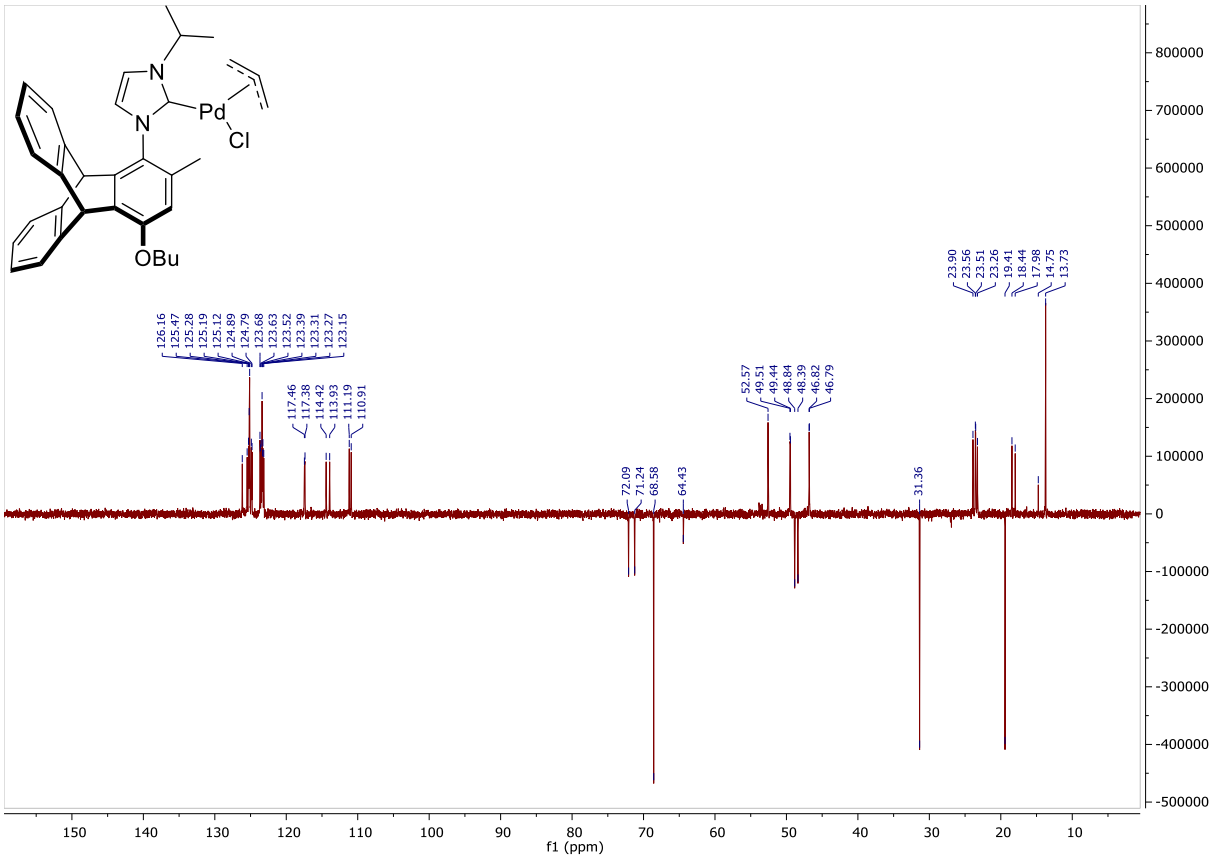


*Figure 200: DEPT-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

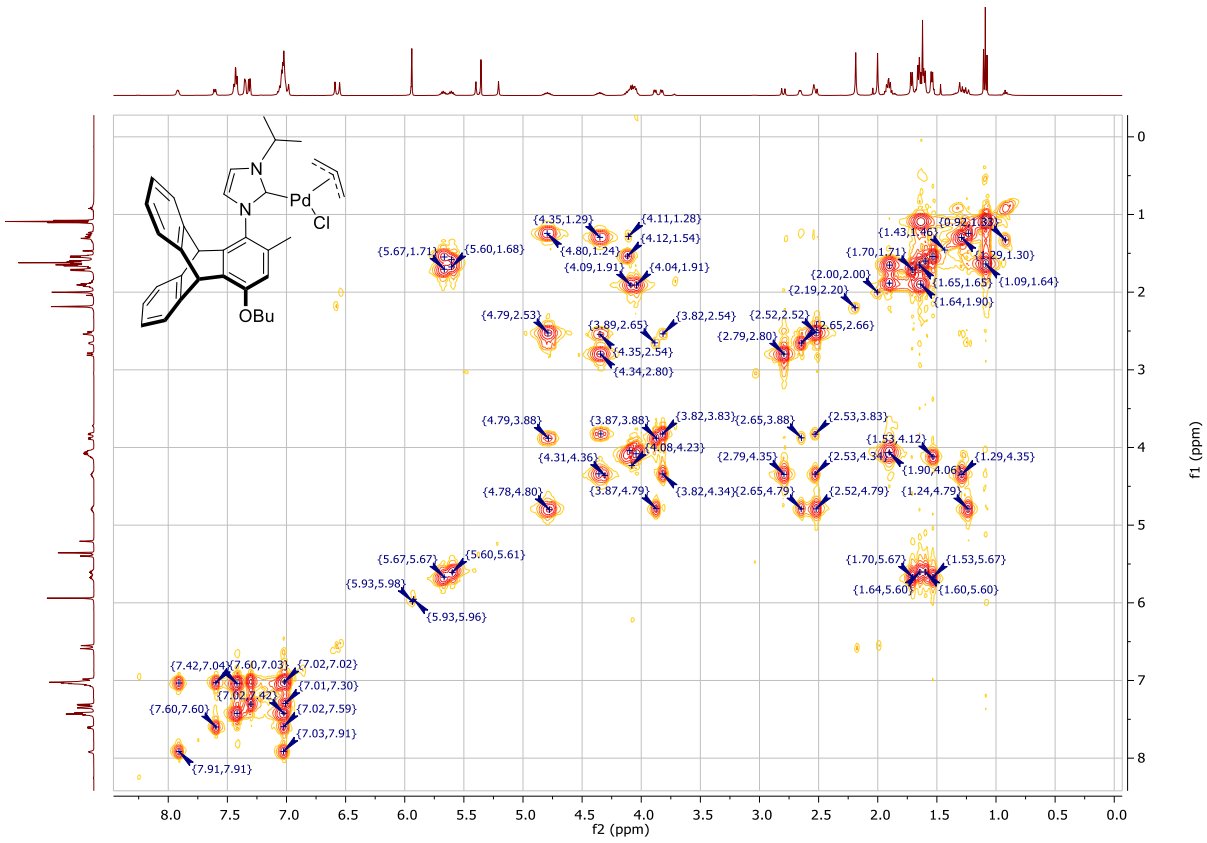


*Figure 201: COSY-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

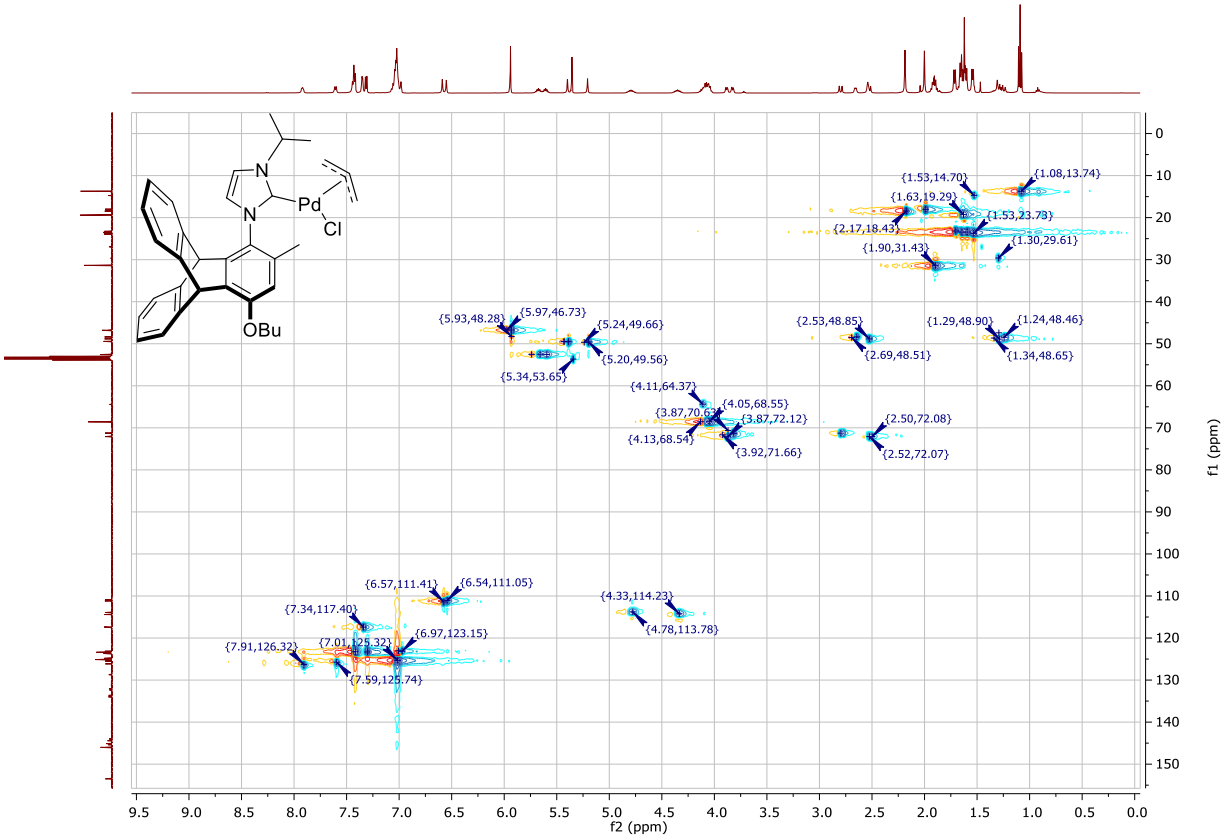


*Figure 202: HSQC-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

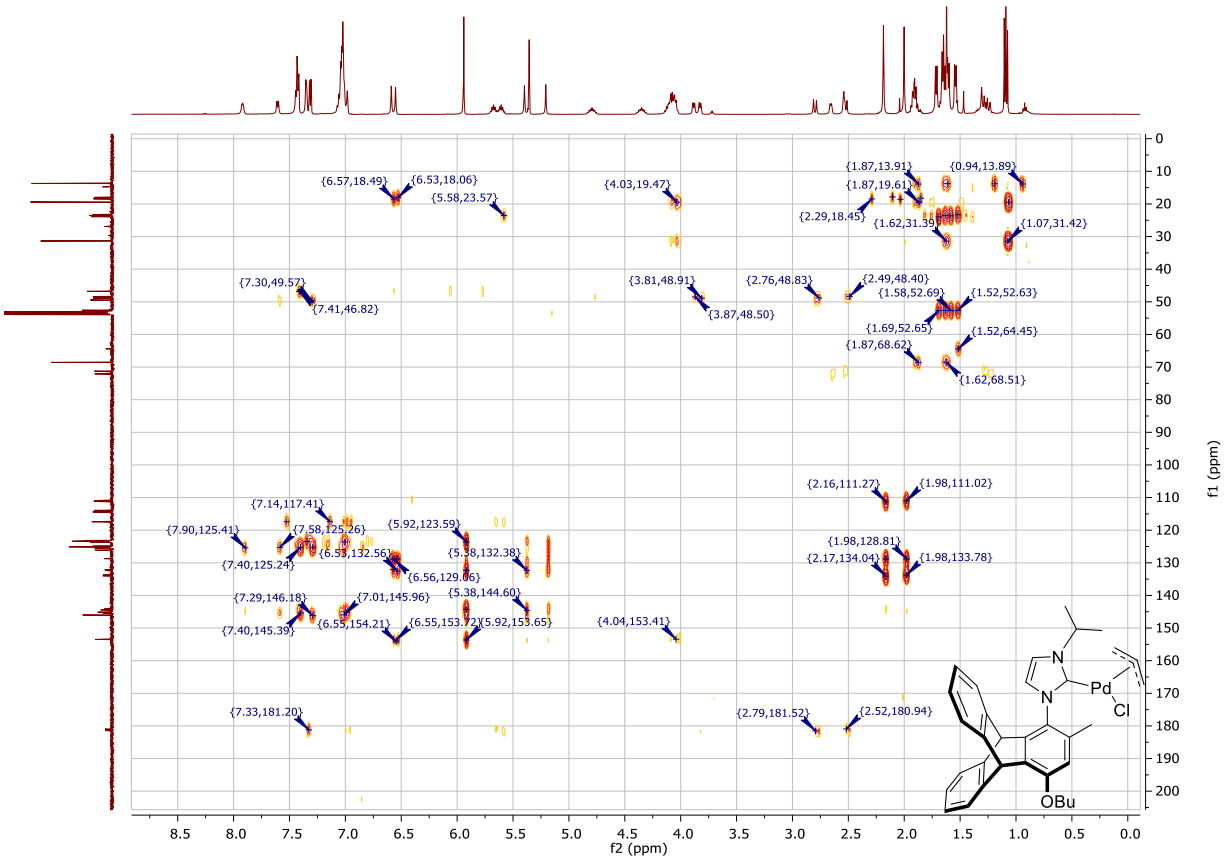


*Figure 203: HMBC-NMR of [PdCl(allyl)(**8b**)] complex in CD_2Cl_2.*

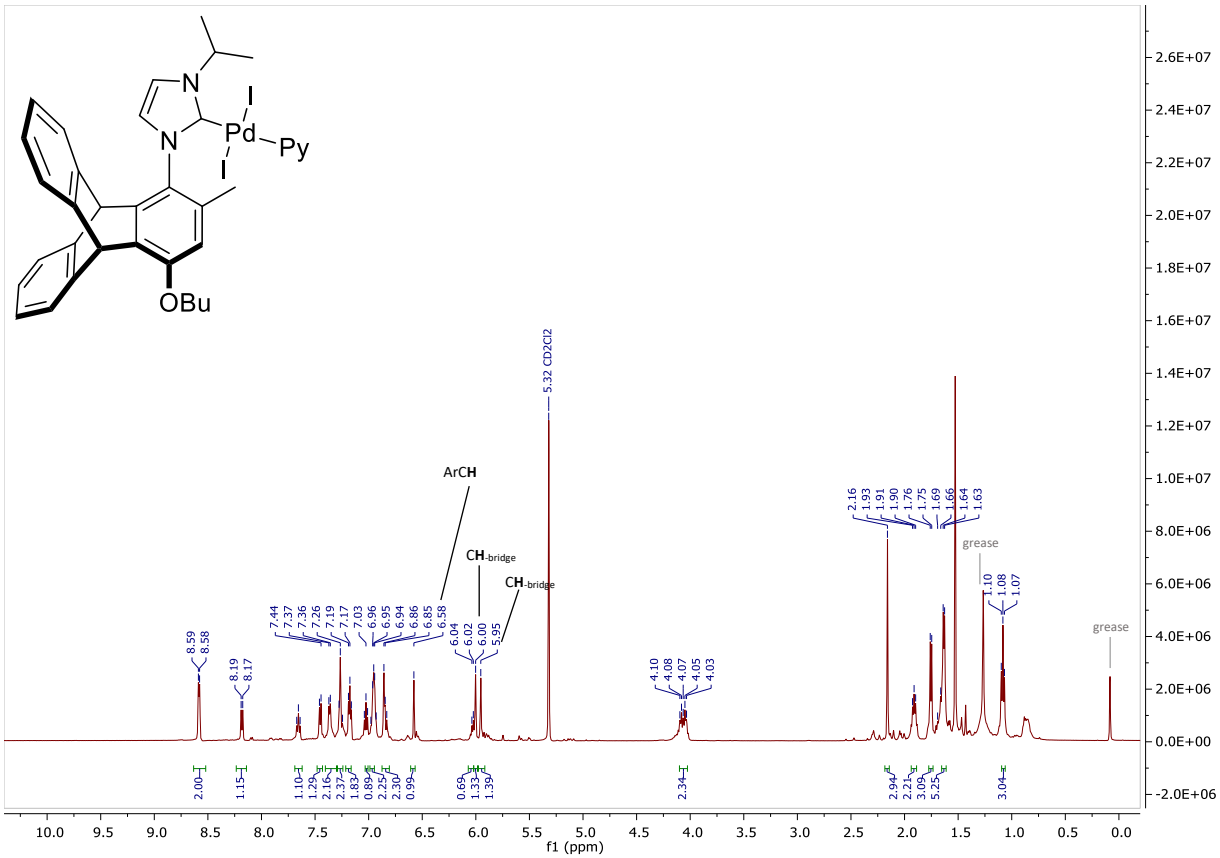


*Figure 204: ^{1}H-NMR of [PdI$_2$(**8b**)py] complex in CD_2Cl_2.*

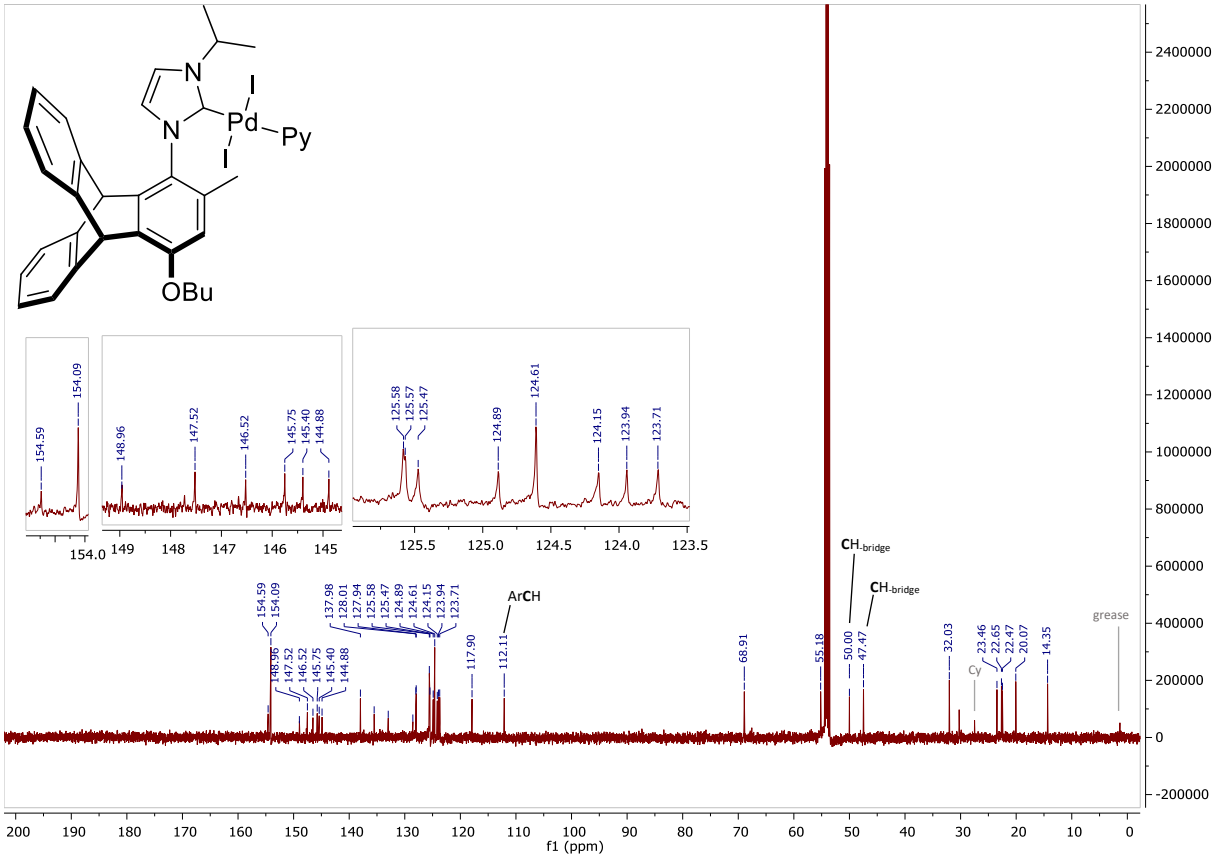


*Figure 205: ^{13}C-NMR of [PdI$_2$(**8b**)py] complex in CD_2Cl_2.*

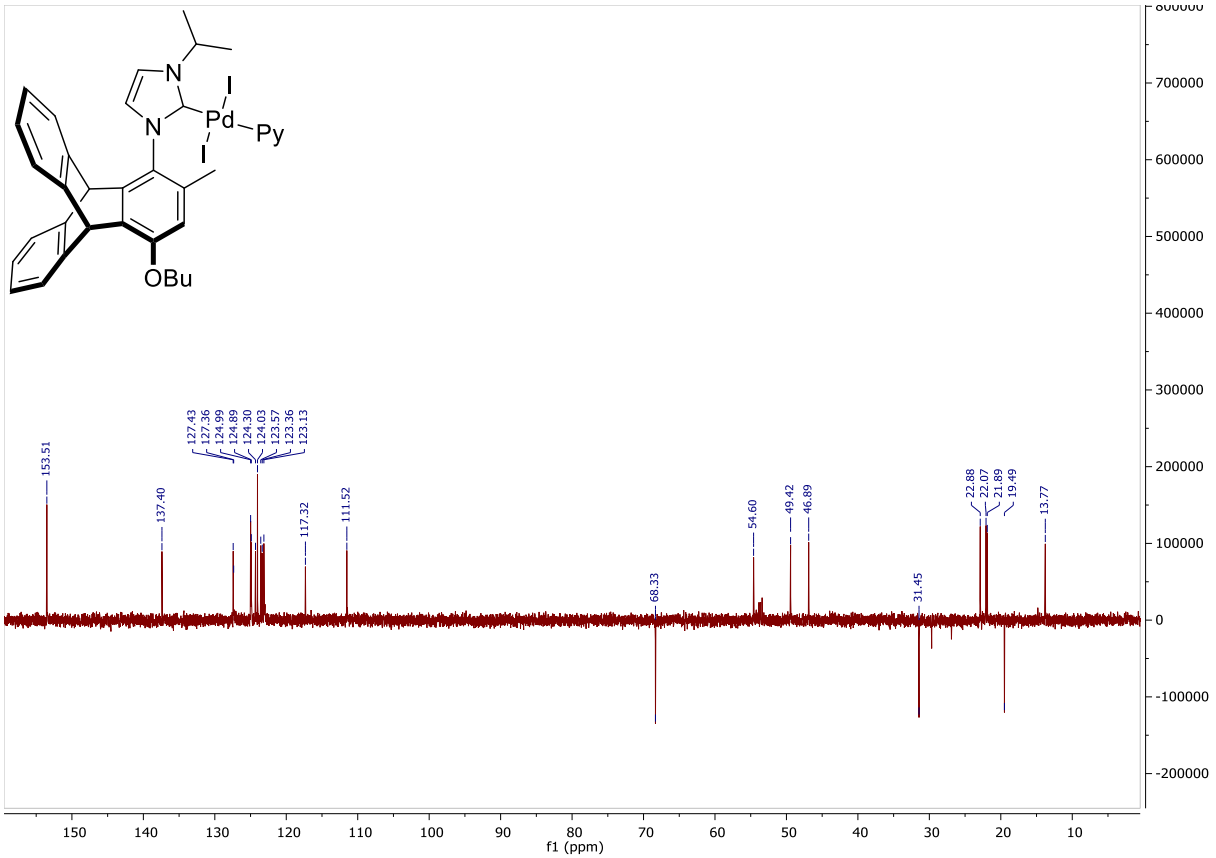


*Figure 206: DEPT-NMR of [PdI_2(**8b**)py] complex in CD_2Cl_2.*

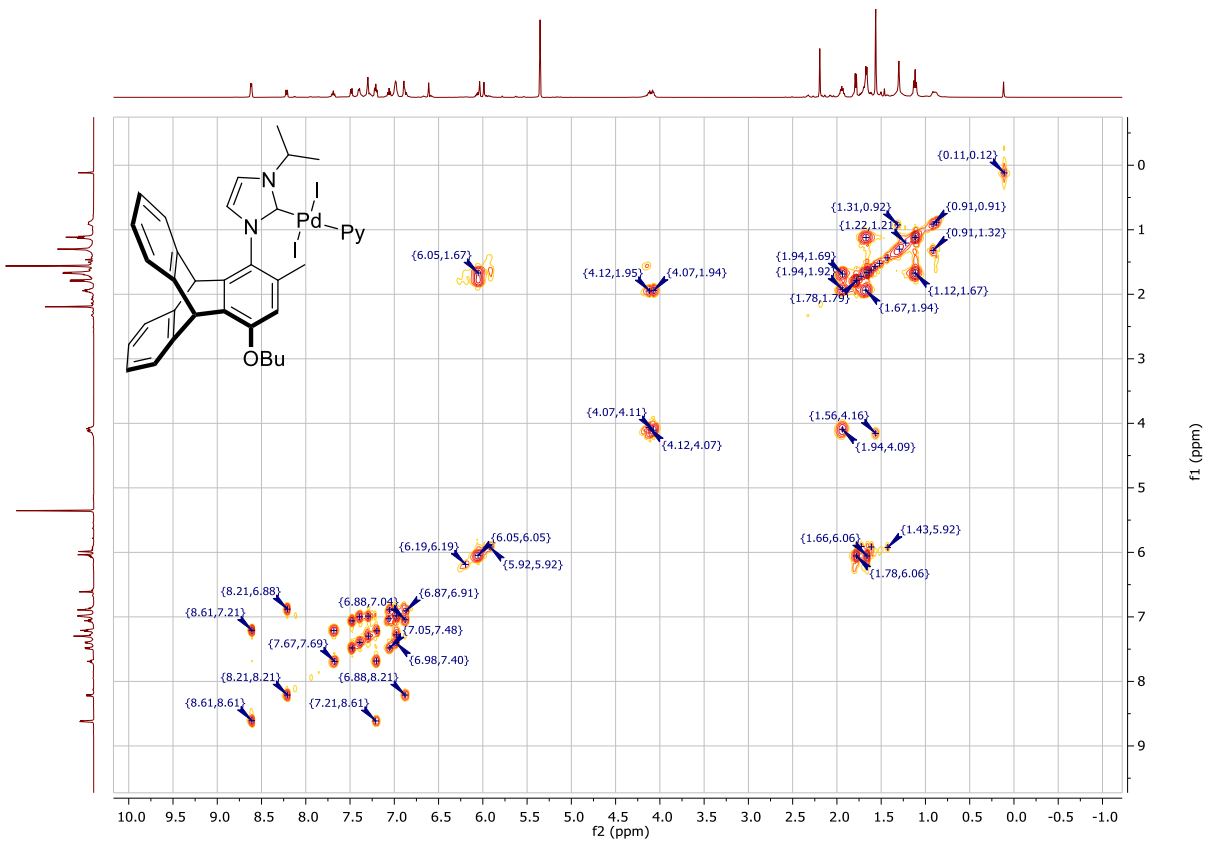


*Figure 207: COSY-NMR of [PdI_2(**8b**)py] complex in CD_2Cl_2.*

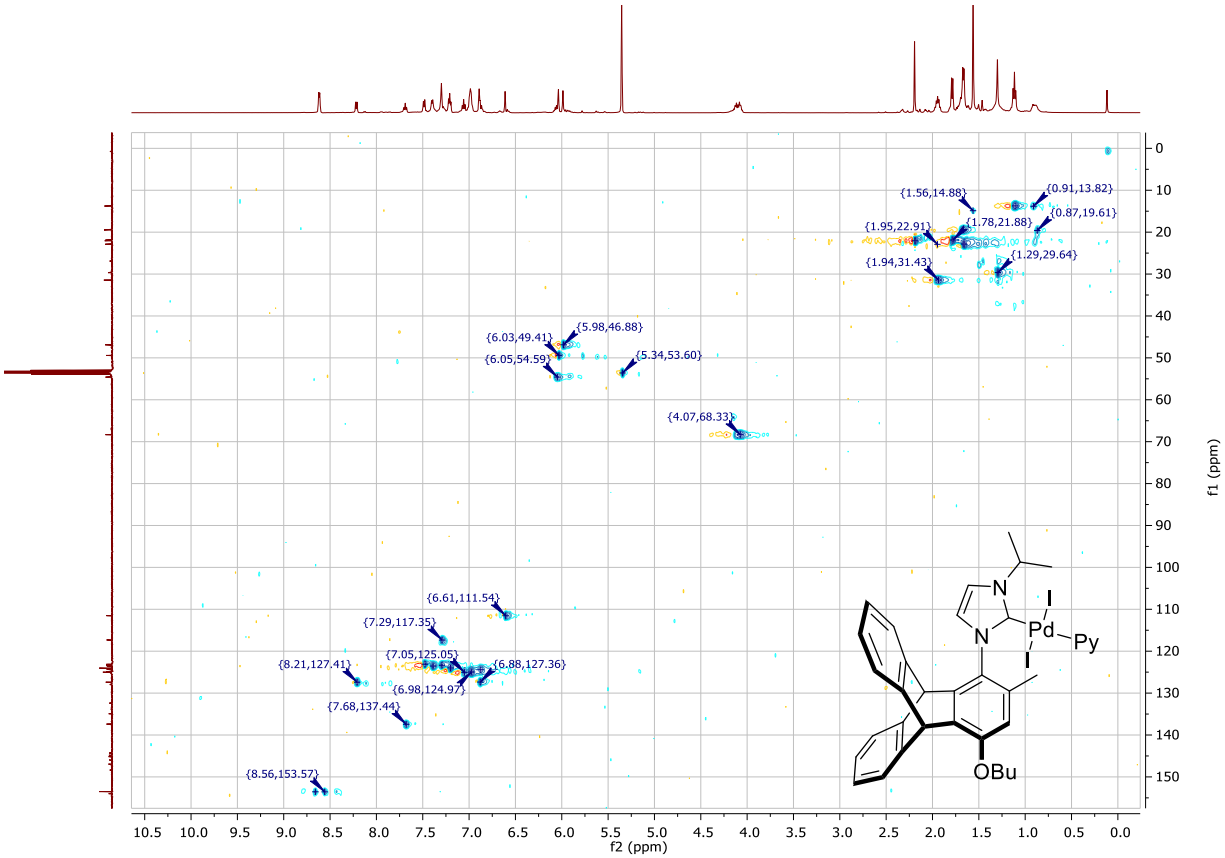


*Figure 208: HSQC-NMR of [PdI_2(**8b**)py] complex in CD_2Cl_2.*

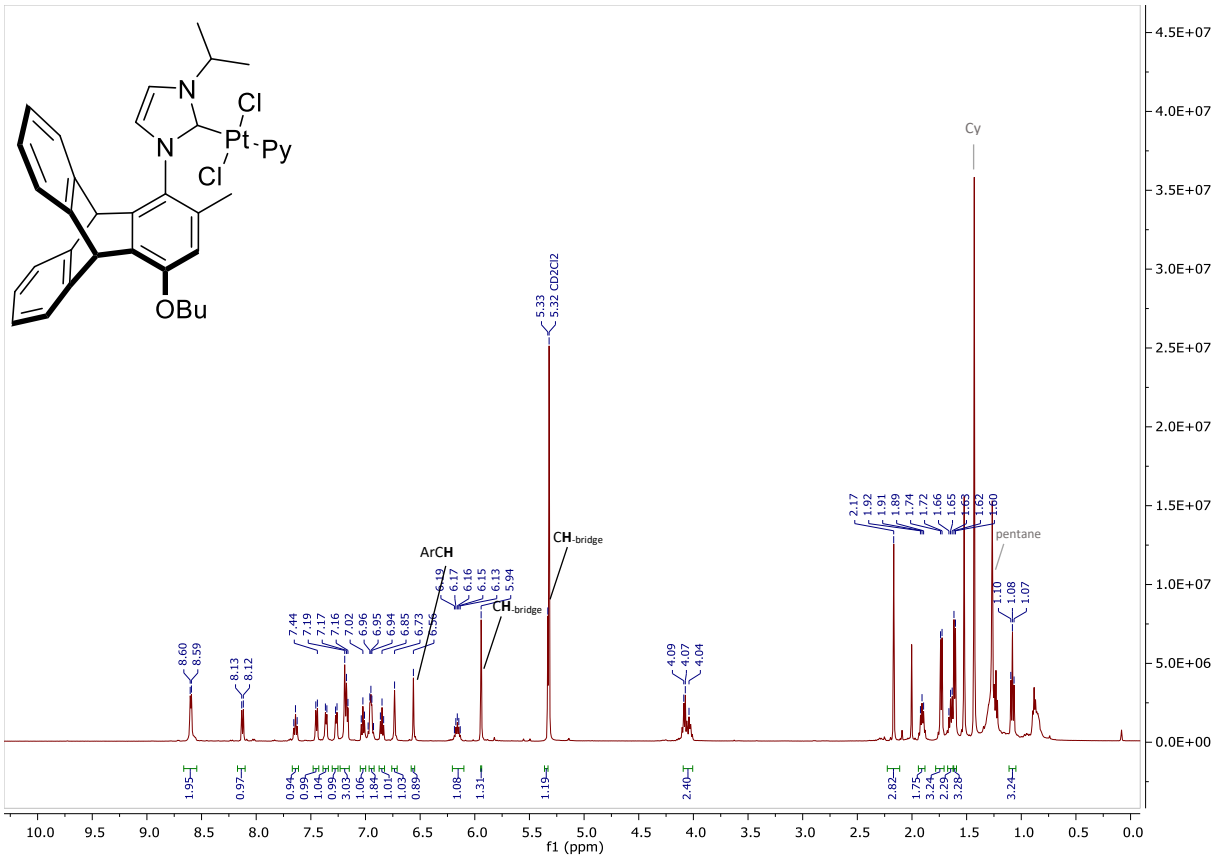


*Figure 209: ^{1}H-NMR of [$PtCl_2$(**8b**)py] complex in CD_2Cl_2.*

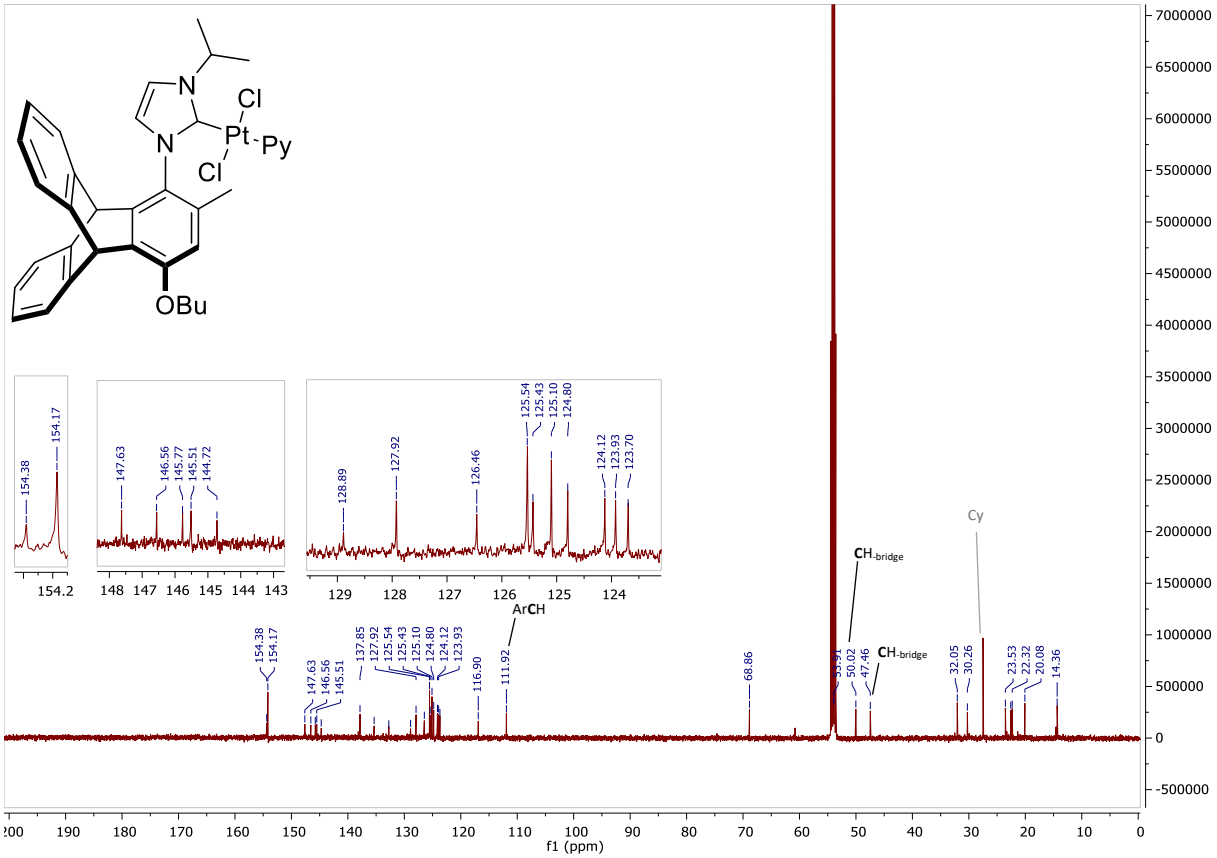


*Figure 210: ^{13}C-NMR of [$PtCl_2$(**8b**)py] complex in CD_2Cl_2.*

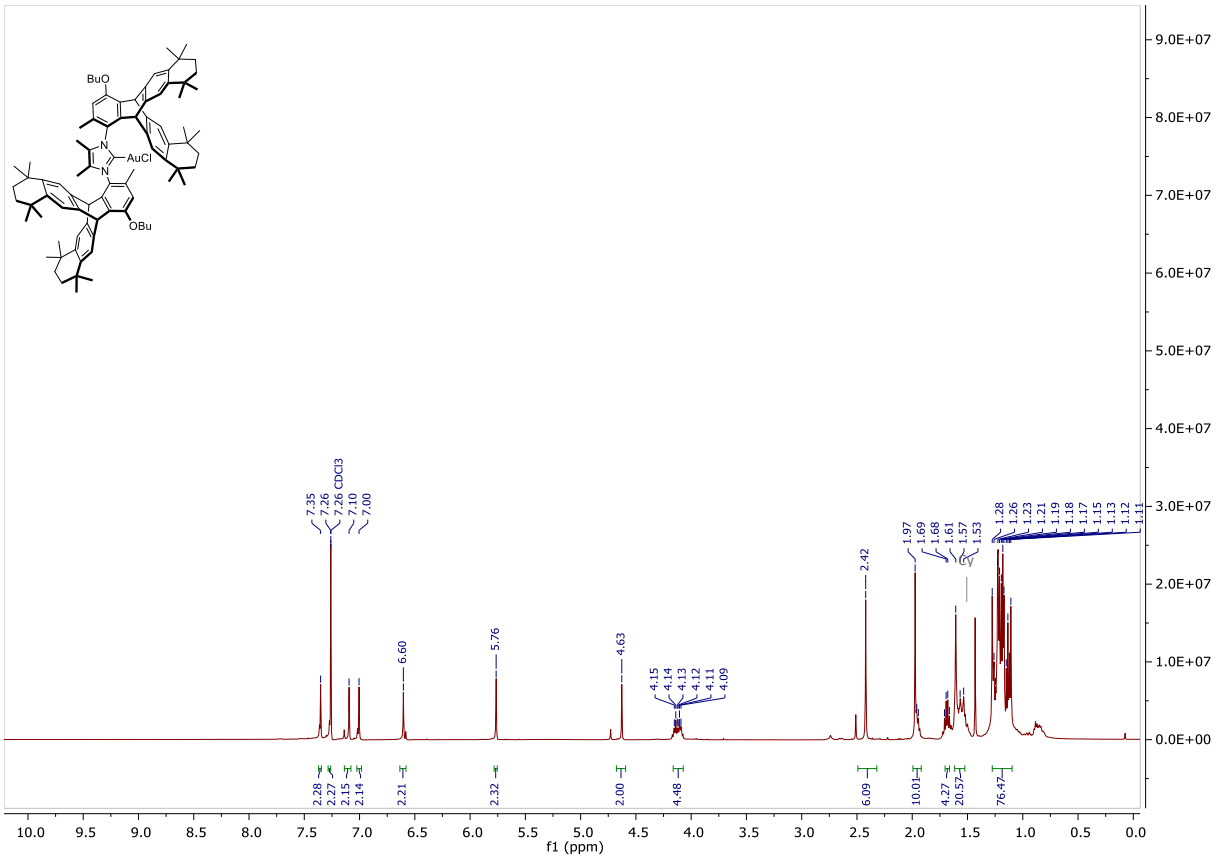


*Figure 211: ^{1}H-NMR of [AuCl(anti-**12**)] complex (isomer 1) in $CDCl_3$.*

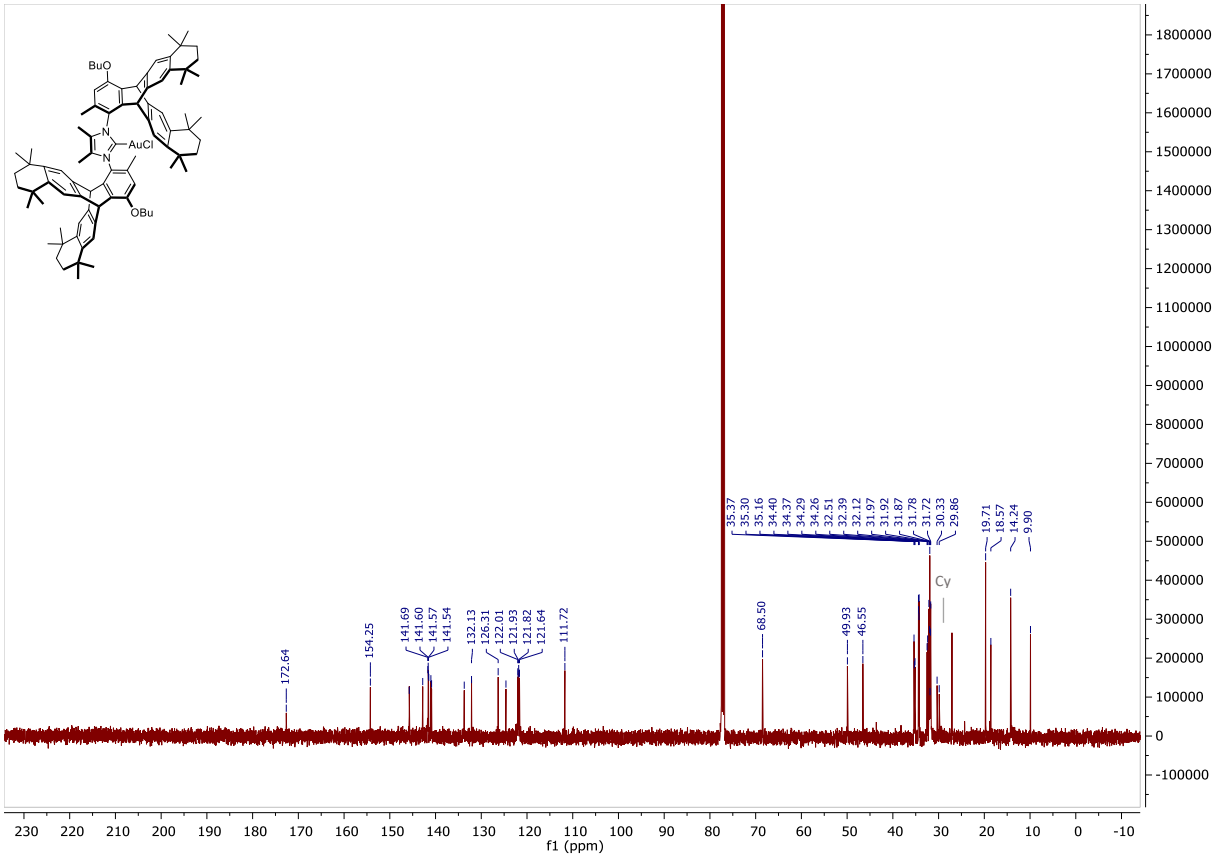


*Figure 212: ^{13}C-NMR of [AuCl(anti-**12**)] complex (isomer 1) in $CDCl_3$.*

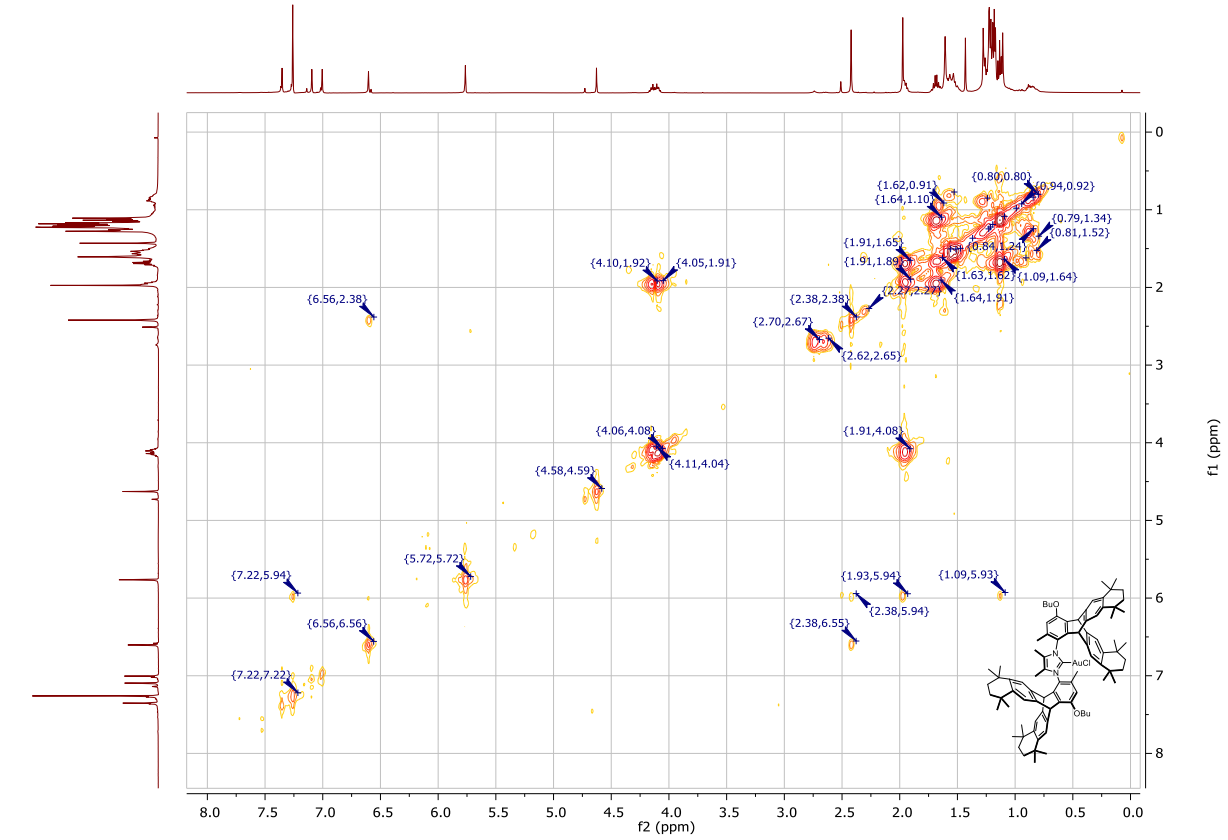


*Figure 213: COSY-NMR of [AuCl(anti-**12**)] complex in $CDCl_3$.*

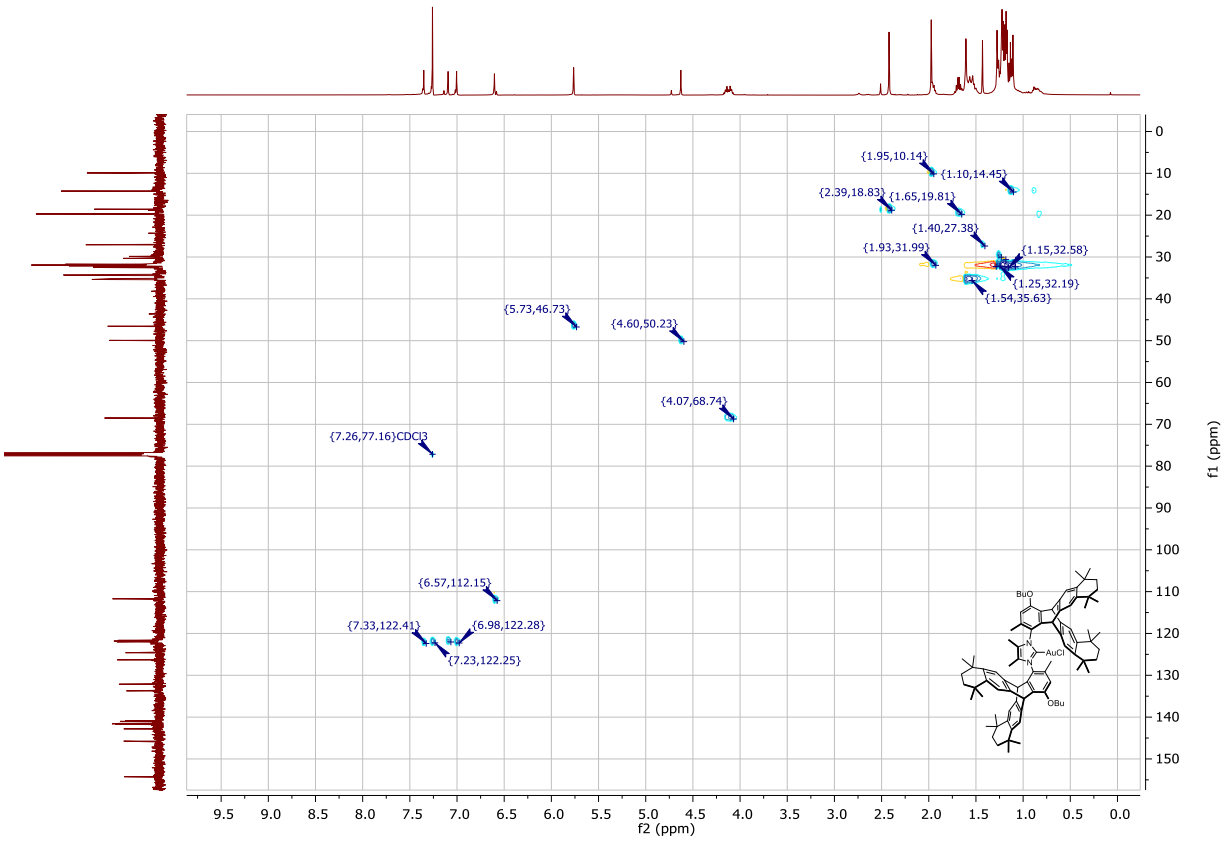


*Figure 214: HSQC-NMR of [AuCl(anti-**12**)] complex (isomer 1) in $CDCl_3$.*

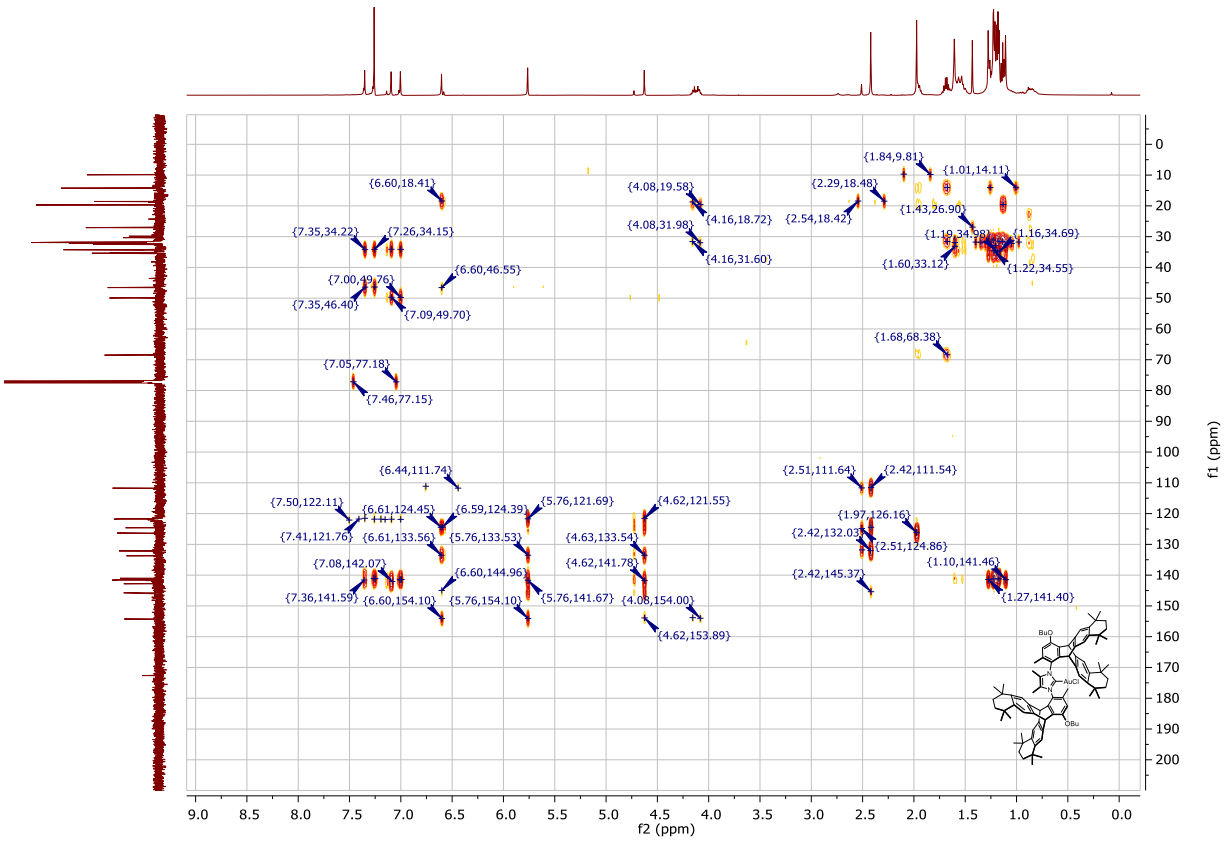


Figure 215: HMBC-NMR of [AuCl(NHC)] complex (isomer 1) in $CDCl_3$.

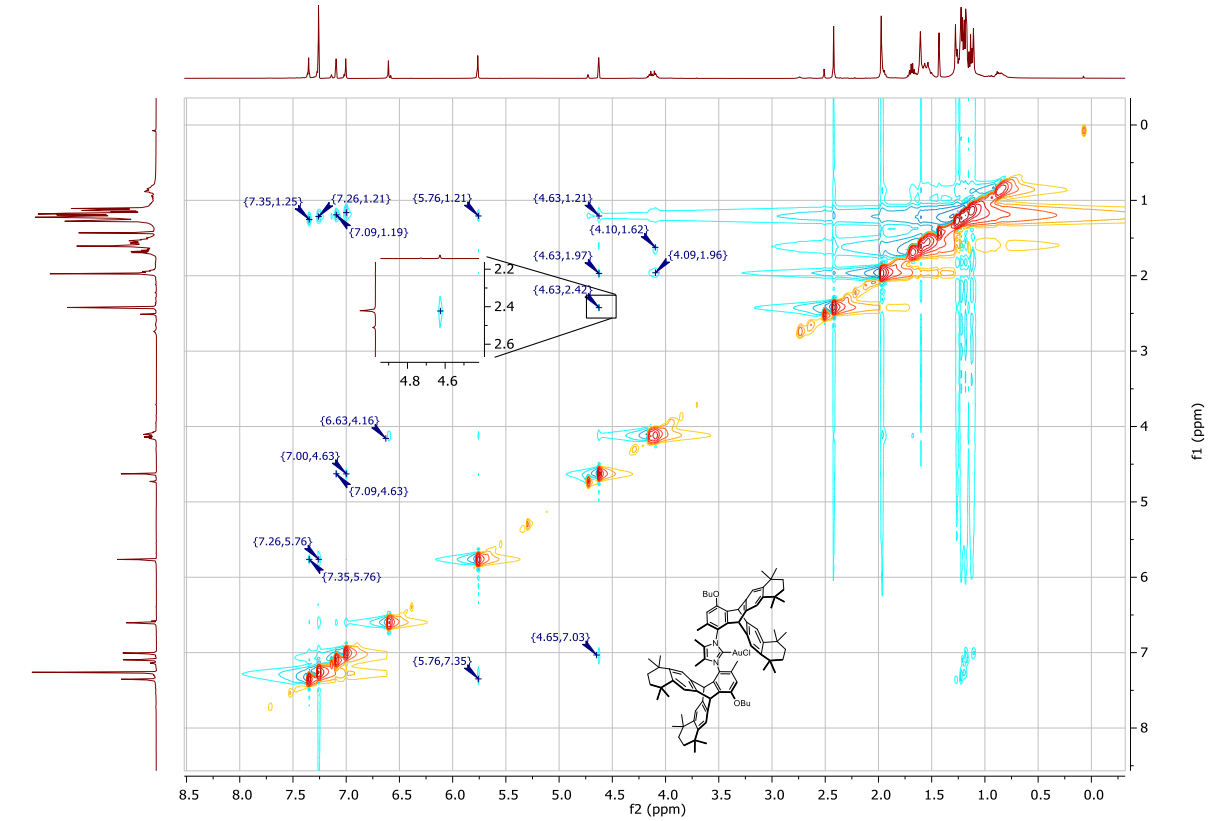


*Figure 216: HMBC-NMR of [AuCl(anti-**12**)] complex (isomer 1) in $CDCl_3$.*

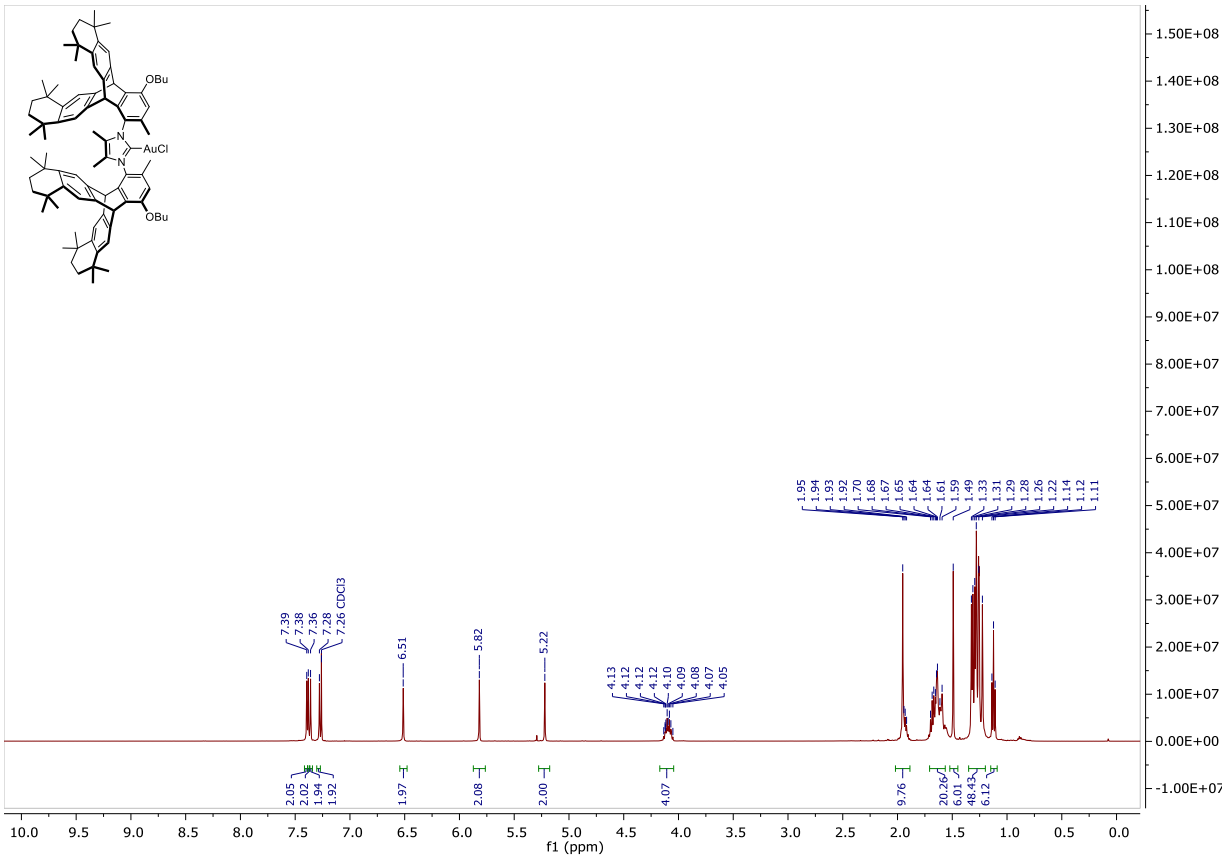


*Figure 217: [1]H-NMR of [AuCl(syn-**12**)]complex (isomer 2) in $CDCl_3$.*

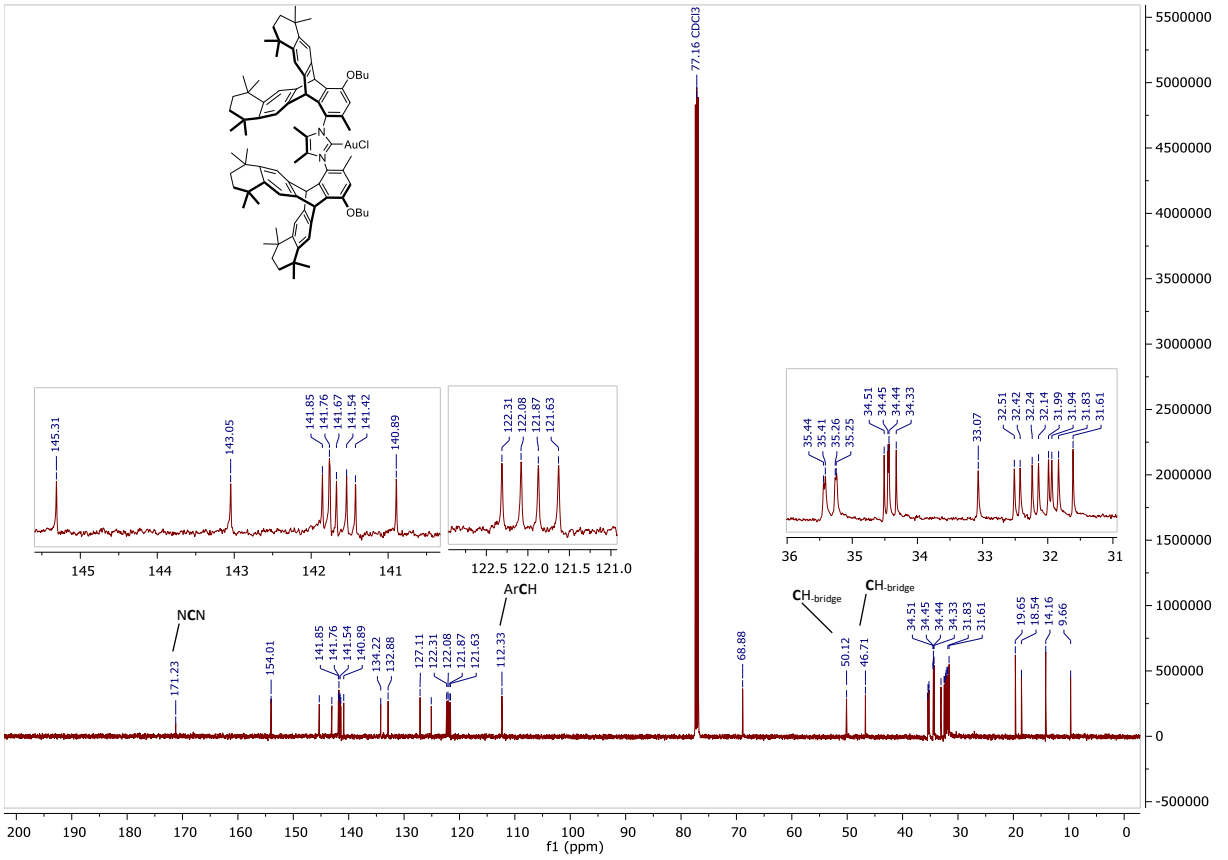


*Figure 218: [13]C-NMR of [AuCl(syn-**12**)] complex (isomer 2) in $CDCl_3$.*

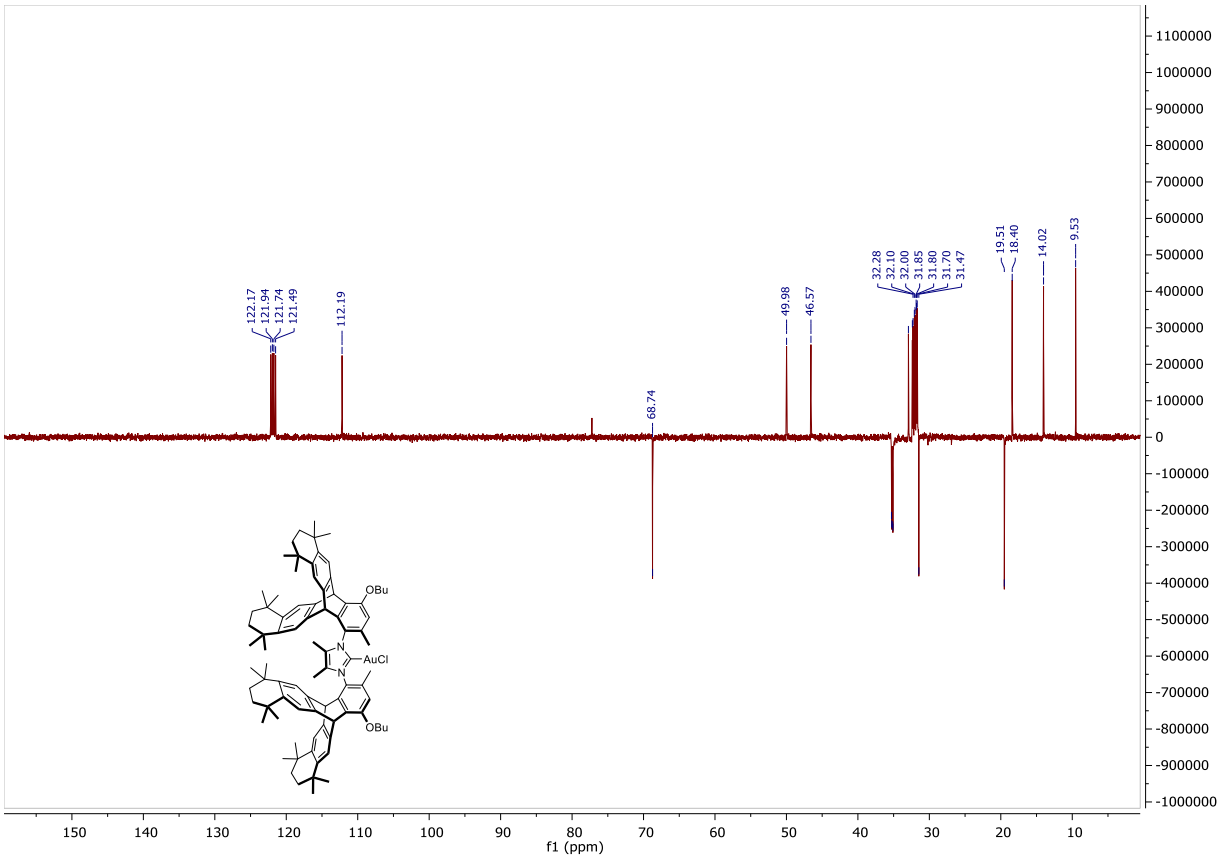


*Figure 219: DEPT-NMR of [AuCl(syn-**12**)] complex (isomer 2) in $CDCl_3$.*

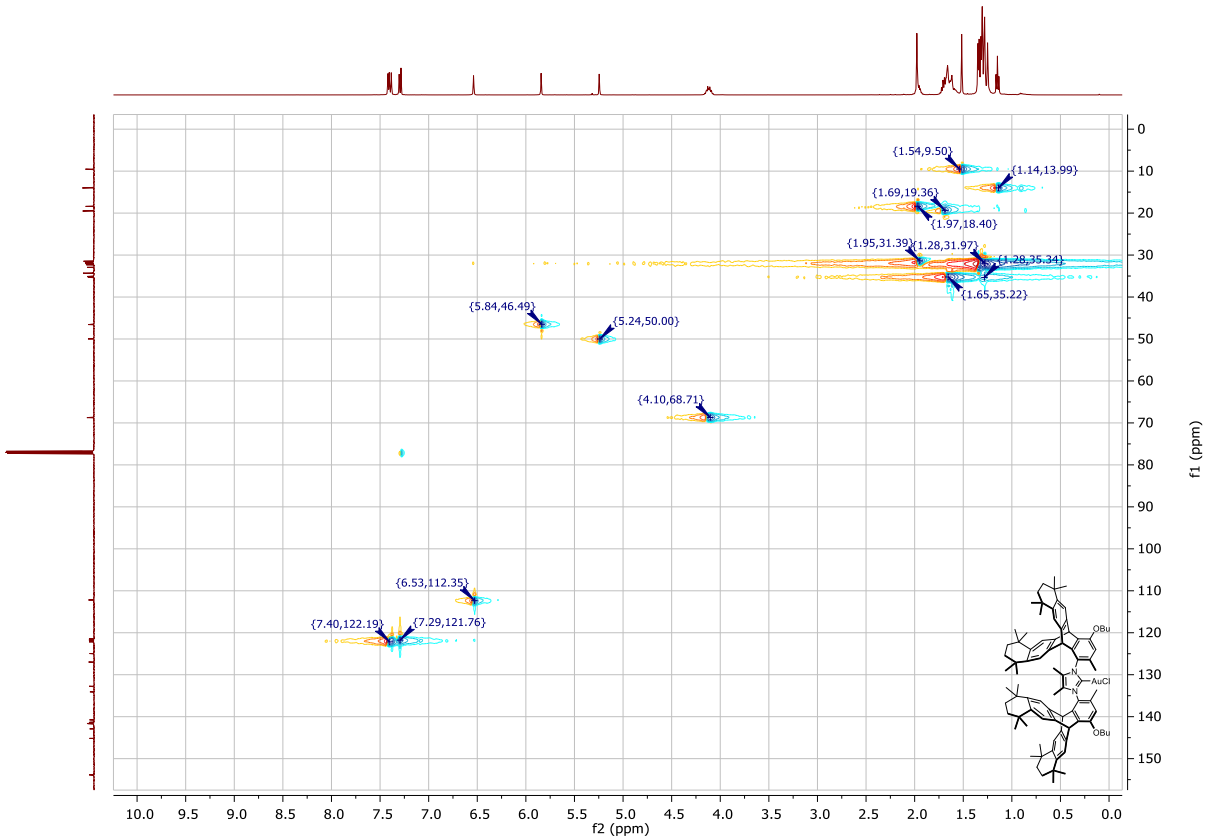


*Figure 220: HSQC-NMR of [AuCl(syn-**12**)] complex (isomer 2) in $CDCl_3$.*

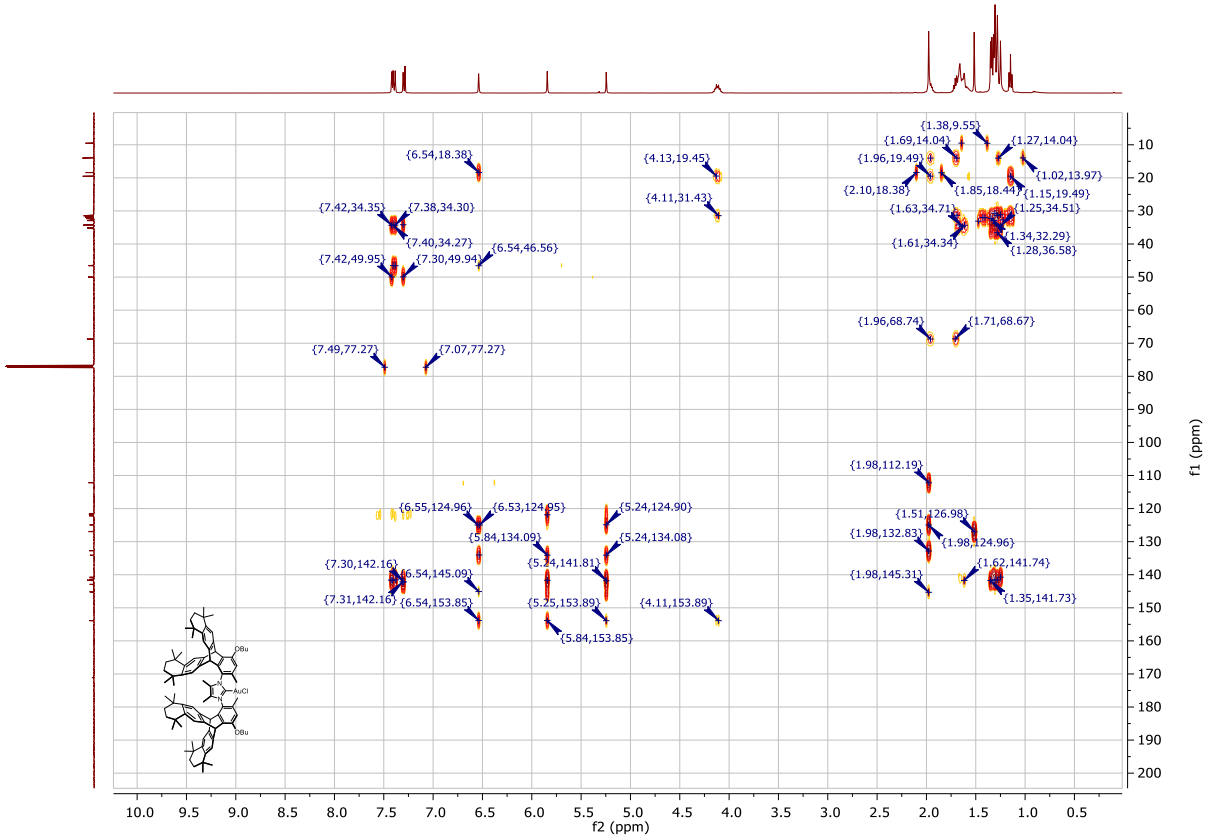


*Figure 221: HMBC-NMR of [AuCl(syn-**12**)] complex (isomer 2) in $CDCl_3$.*

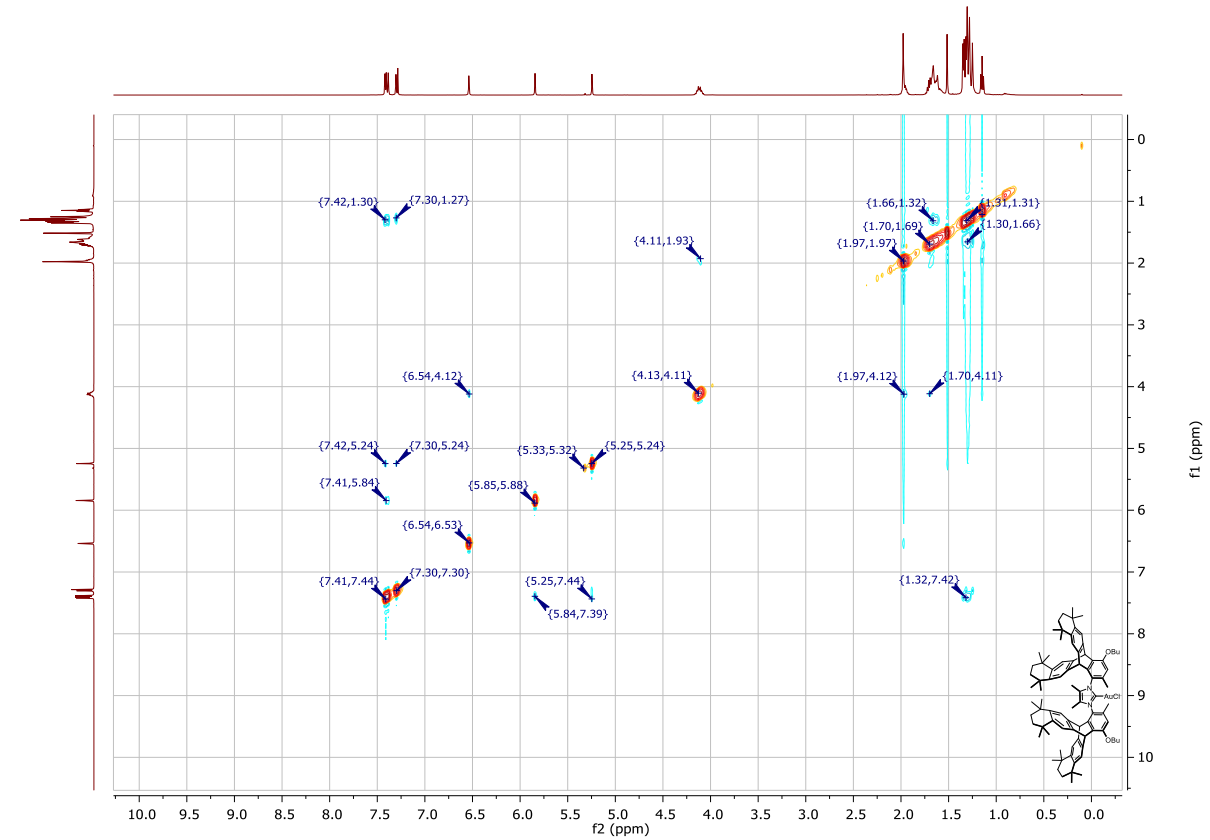


*Figure 222: NOSY-NMR of [AuCl(syn-**12**)] complex (isomer 2) in $CDCl_3$.*

#	Bridgehead resonance ^{1}H [ppm]				Bridgehead resonance ^{13}C [ppm]			
	N_side		O_ side		N_ side		O_ side	
4a	5.79		5.70		48.1		46.2	
4b	5.86		5.82		49.9		46.2	
4c	6.31		6.23		50.0		46.4	
4d	6.04		5.89		44.7		40.8	
4e	5.58		5.49		48.8		45.3	
4f	5.73		5.66		48.5		46.2	
4g	5.76		5.65		49.4		45.6	
4i	5.78		5.74		50.2		46.5	
	anti	**syn**	**syn**	**anti**	**syn**	**anti**	**anti**	**syn**
4h[a]	5.89	5.76	5.74	5.73	48.9	50.6	46.8	45.3
4j[a]	(overlap)	6.53	5.81	5.66	48.4	46.8	35.7	33.0
4k[b]	-	6.54	5.80	-	50.2	-	-	33.0
4l[a]	6.40	6.20	5.93	5.90	50.2	46.7	46.5	43.1
4m[a]	6.38	6.17	5.92	5.89	50.3	49.3	46.6	45.7
4n[a]	(overlap)	5.91	6.93	5.94	50.0	46.9	46.3	42.9
4n[b]	-	5.93	6.92	-	50.1	-	-	43.1

[a] isomers not separated, [b] only anti isomer formed [c] syn/anti-isomer separated,

Table 1. ^{1}H- and ^{13}C-NMR shifts for bridgehead CH-units in tripycenes **4** in $CDCl_3$.

#	bridgehead resonance ^{1}H [ppm]				bridgehead resonance ^{13}C [ppm]			
	N_ side		O_ side		N_ side		O_ side	
5b	6.14		5.88		50.6		47.1	
5ba	5.84[d]		5.76[d]		50.5[d]		46.2[d]	
5bb	5.93		5.89		51.3		47.2	
5bc	5.88		5.86		47.6		47.1	
5c	6.53		6.33		50.5		47.1	
5g	5.80[d]		5.67[d]		49.4[d]		45.6[d]	
	anti	**syn**	**syn**	**anti**	**syn**	**anti**	**anti**	**syn**
5h[c]	6.18	6.02	5.84	5.82	49.7	51.2	46.2	47.8
5l[c]	6.53	6.50	6.18	5.89	50.8	47.4	47.2	43.7
5m[c]	6.47	6.38	6.17	5.87	51.1	49.9	47.6	46.4
5n[a]	6.40	6.37	7.22	5.86	50.7	47.1	46.8	43.6
5na[c]	6.67	6.23	7.16	5.83	50.7	46.8	47.9	44.2

[a] isomers not separated, [b] only anti isomer formed [c] syn/anti-isomer separated, [d] measured in DMSO-d_6

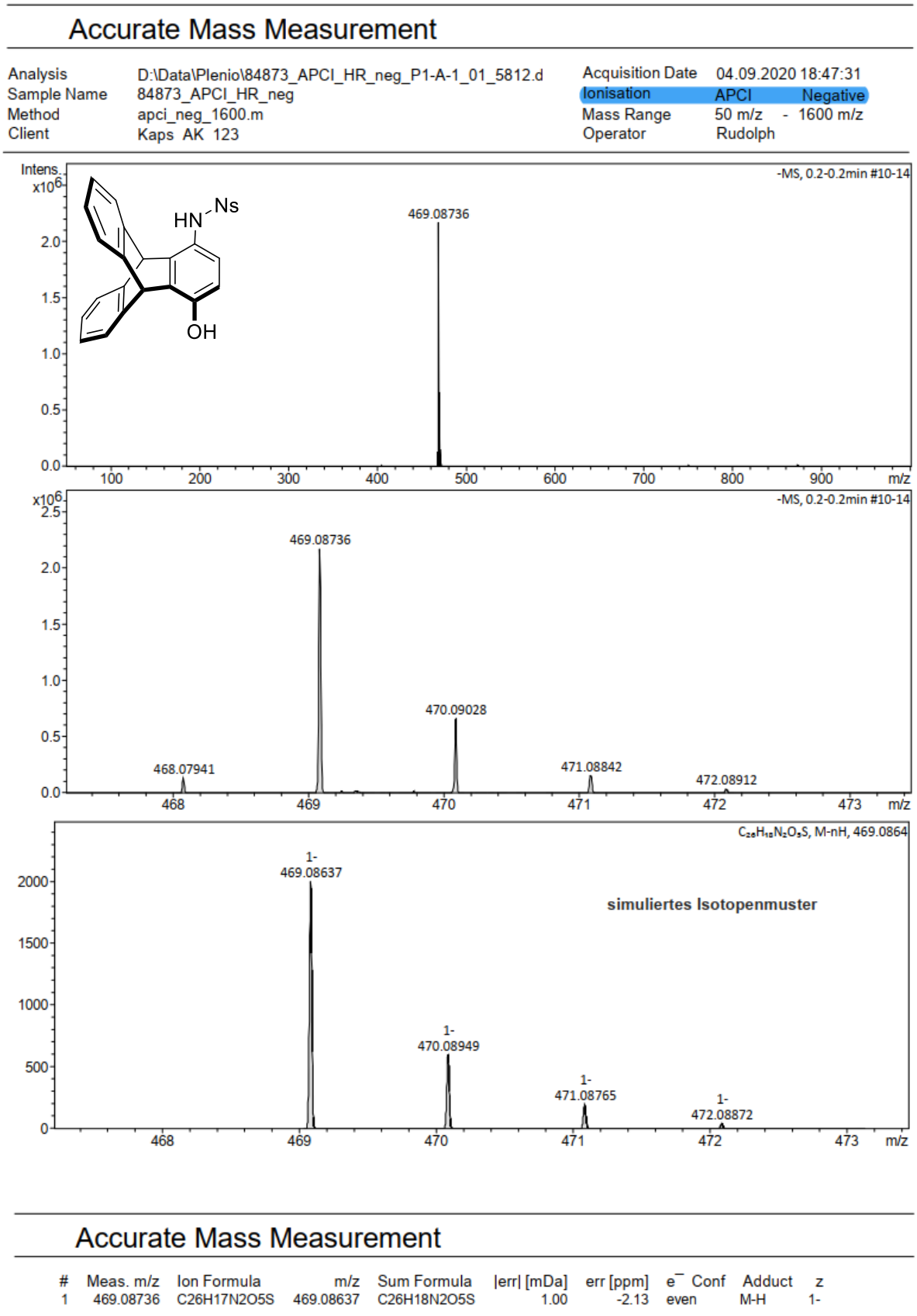
Table 2. ^{1}H- and ^{13}C-NMR shifts for bridgehead CH-units in tripycenes **5** in $CDCl_3$ (unless otherwise noted).

#	bridgehead resonance ^{1}H [ppm]				bridgehead resonance ^{13}C [ppm]			
	N_side		O_ side		N_ side		O_ side	
6b	5.49		5.85		48.9		47.5	
6bb	5.95		5.86		49.9		47.3	
6c	5.99		6.33		48.6		47.4	
6g	5.36		5.72		48.3		47.0	
9	6.24		5.86		49.4		47.2	
	anti	**syn**	**syn**	**anti**	**syn**	**anti**	**anti**	**syn**
6h[c]	5.42	5.44	5.81	5.77	48.2	49.6	46.5	47.9
6l[c]	6.03	5.51	6.37	5.88	49.0	45.2	47.7	44.0
6m[c]	5.99	5.53	6.33	5.85	49.2	47.9	47.9	46.7
6n[c]	6.69	5.51	7.14	5.85	49.0	44.8	47.6	44.0

[a] isomers not separated, [b] only anti isomer formed [c] syn/anti-isomer separated,

Table 3. ^{1}H- and ^{13}C-NMR shifts for bridgehead CH-units in tripycenes **6** in $CDCl_3$.

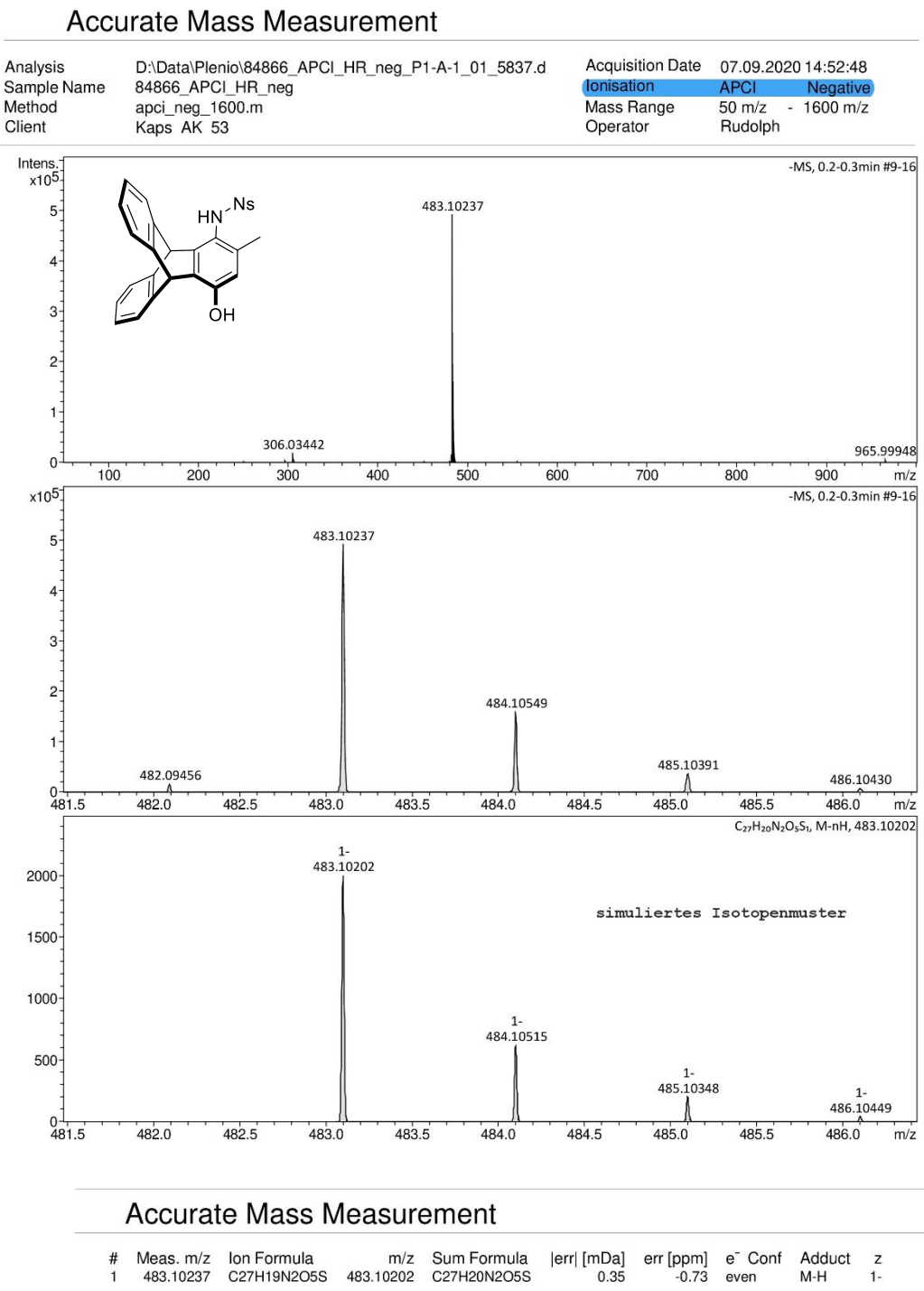
3. Mass spectrometry



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	469.08736	C26H17N2O5S	469.08637	C26H18N2O5S	1.00	-2.13	even	M-H	1-

Figure 223: HRMS (APCI, negative mode) of nosylated aminophenol (**4a**).



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	483.10237	C27H19N2O5S	483.10202	C27H20N2O5S	0.35	-0.73	even	M-H	1-

Figure 224: HRMS (APCI, negative mode) of nosylated aminophenol (**4b**).

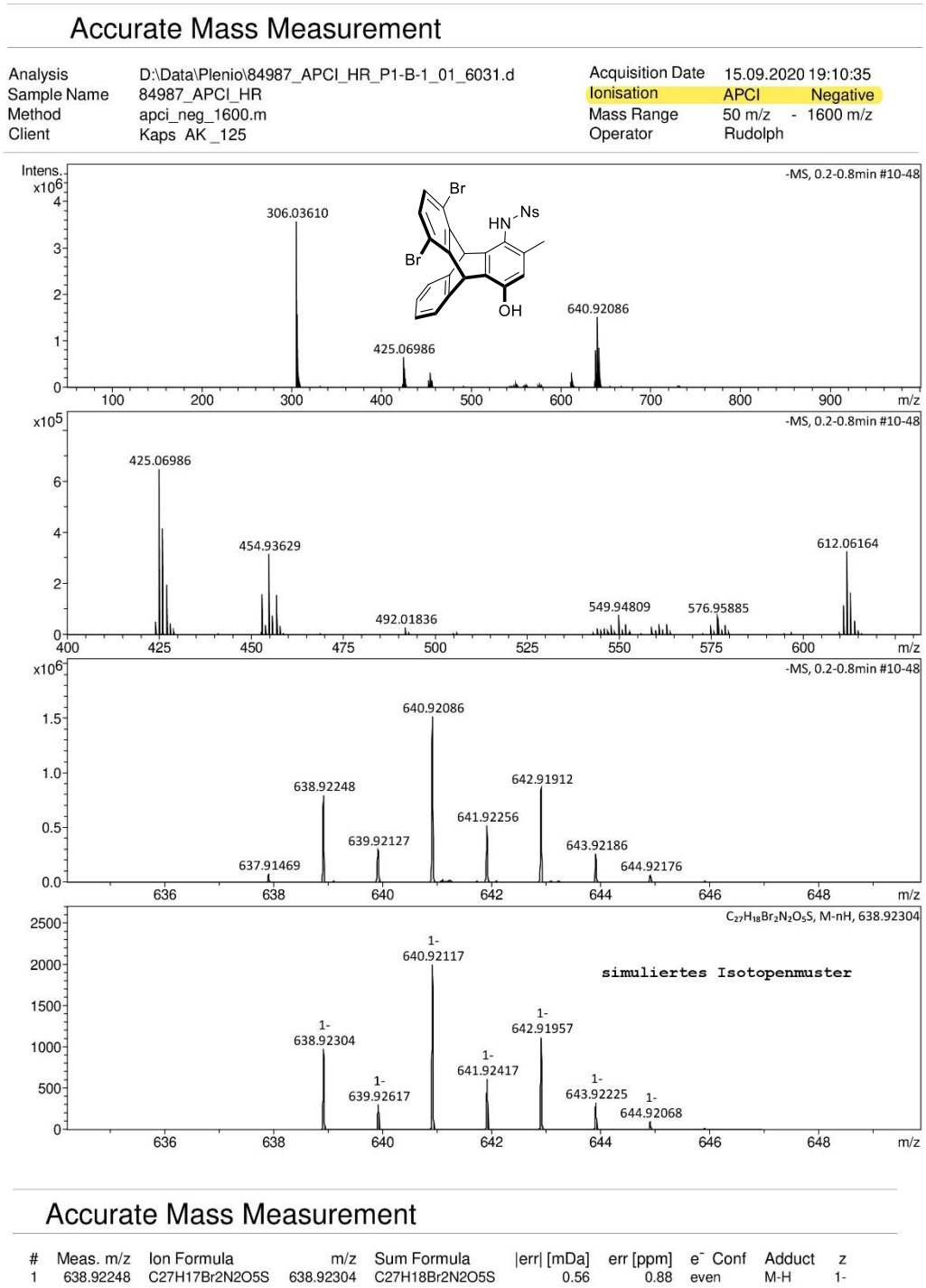
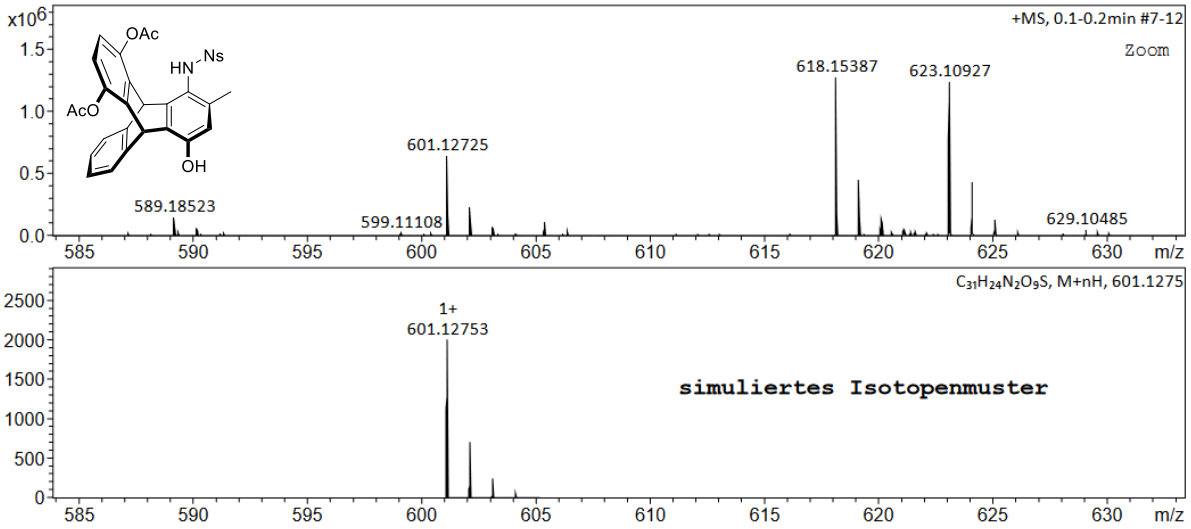


Figure 225: HRMS (APCI, negative mode) of nosylated aminophenol (**4c**).

Analysis	D:\Data\Plenio\87178_ESI_HR_P1-D-2_01_12597.d	Acquisition Date	18.10.2021 18:40:20
Sample Name	87178_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _320-4	Operator	Rudolph

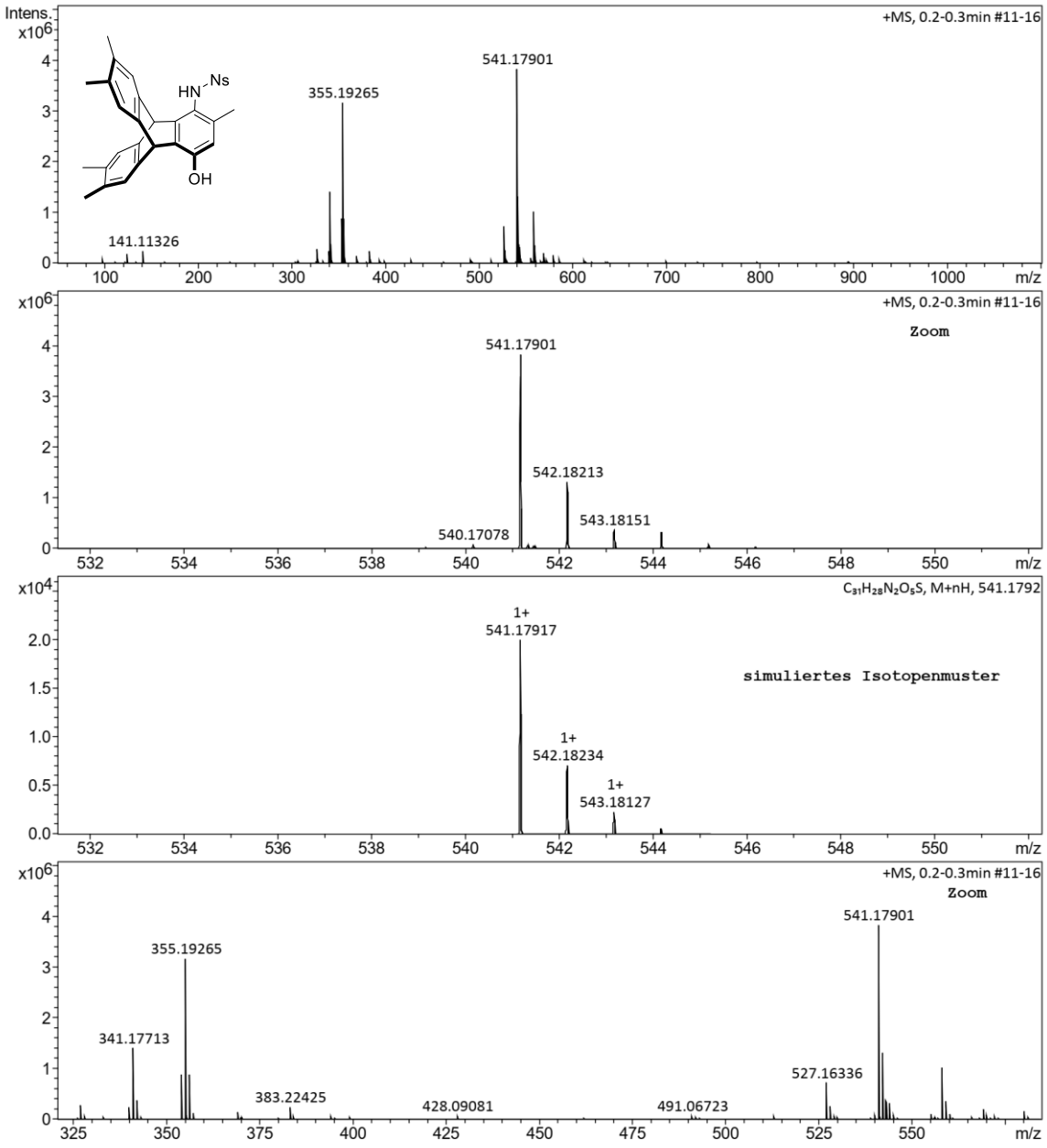


#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	601.12725	601.12753	C31H25N2O9S	M+H	C31H24N2O9S	0.28	0.46	8.7	even	1+
1	618.15387	618.15408	C31H28N3O9S	M+NH4	C31H24N2O9S	0.21	0.34	9.1	even	1+
1	623.10927	623.10947	C31H24N2NaO9S	M+Na	C31H24N2O9S	0.20	0.32	10.0	even	1+

Figure 226: HRMS (ESI, positive mode) of nosylated aminophenol (**4d**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86031_APCI_HR_P1-D-1_01_8936.d	Acquisition Date	16.03.2021 12:30:16
Sample Name	86031_APCI_HR	Ionisation	APCI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 95 B	Operator	Rudolph



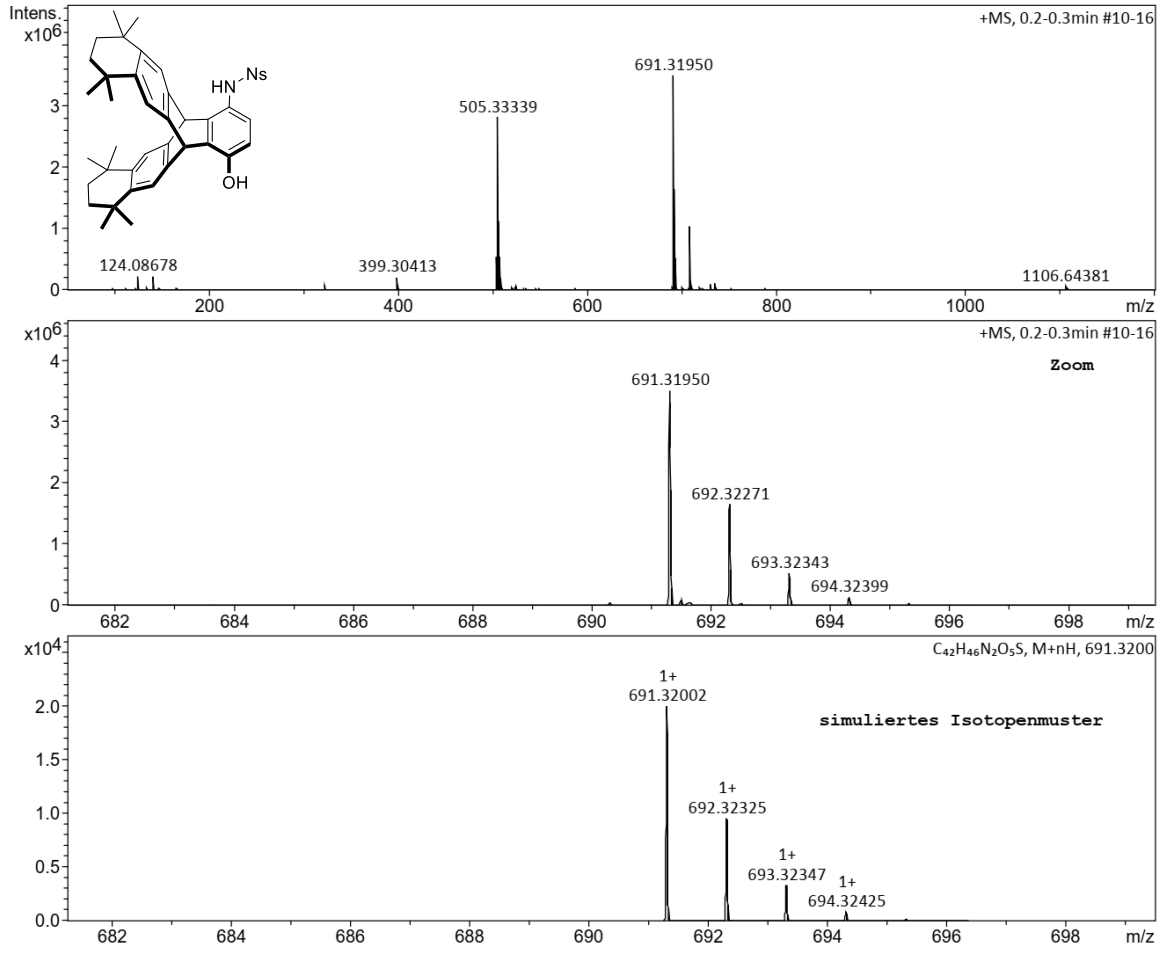
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	541.17901	C31H29N2O5S	541.17917	C31H28N2O5S	0.16	0.30	even	M+H

Figure 227: HRMS (APCI, positive mode) of nosylated aminophenol (**4e**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86032_APCI_HR_P1-D-2_01_8937.d	Acquisition Date	16.03.2021 12:34:09
Sample Name	86032_APCI_HR	Ionisation	APCI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 123	Operator	Rudolph



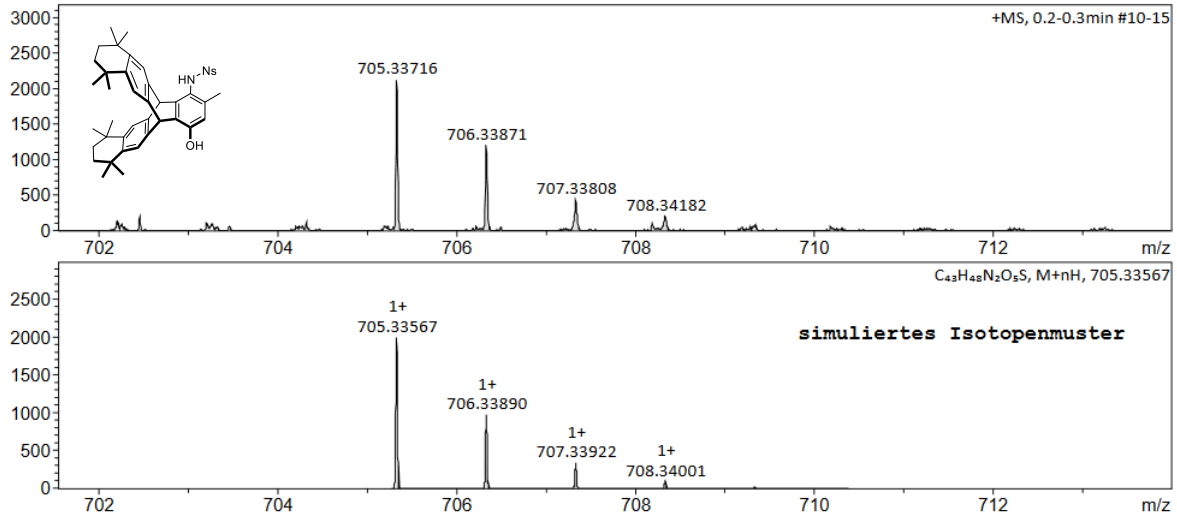
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	691.31950	C42H47N2O5S	691.32002	C42H46N2O5S	0.52	0.75	even	M+H

Figure 228: HRMS (APCI, negative mode) of nosylated aminophenol (**4f**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84988_APCI_HR_P1-B-1_01_6049.d	Acquisition Date	16.09.2020 16:18:15
Sample Name	84988_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _103_B	Operator	Rudolph



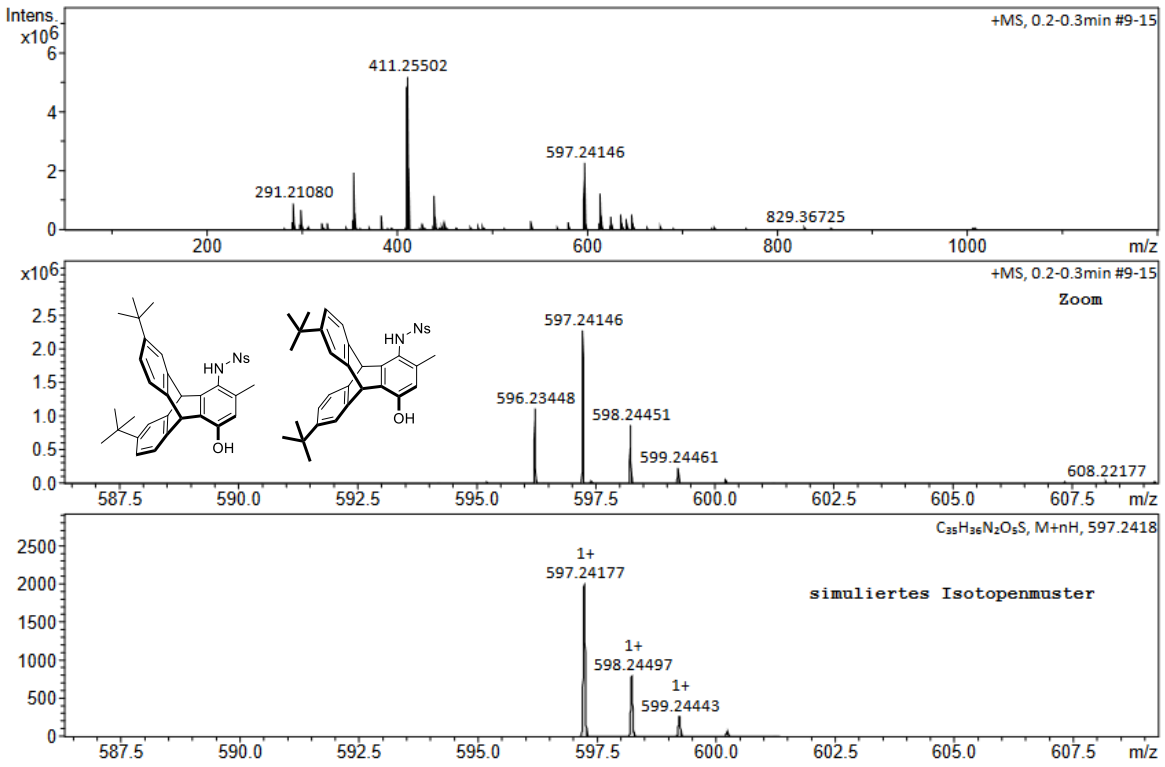
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e¯ Conf	Adduct	z
	705.33716	C43H49N2O5S	705.33567	C43H48N2O5S	1.49	-2.12	even	M+H	1+

Figure 229: HRMS (APCI, negative mode) of nosylated aminophenol (**4g**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86214_APCI_HR_P1-C-1_01_9633.d	Acquisition Date	20.04.2021 15:44:36
Sample Name	86214_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 93G	Operator	Rudolph



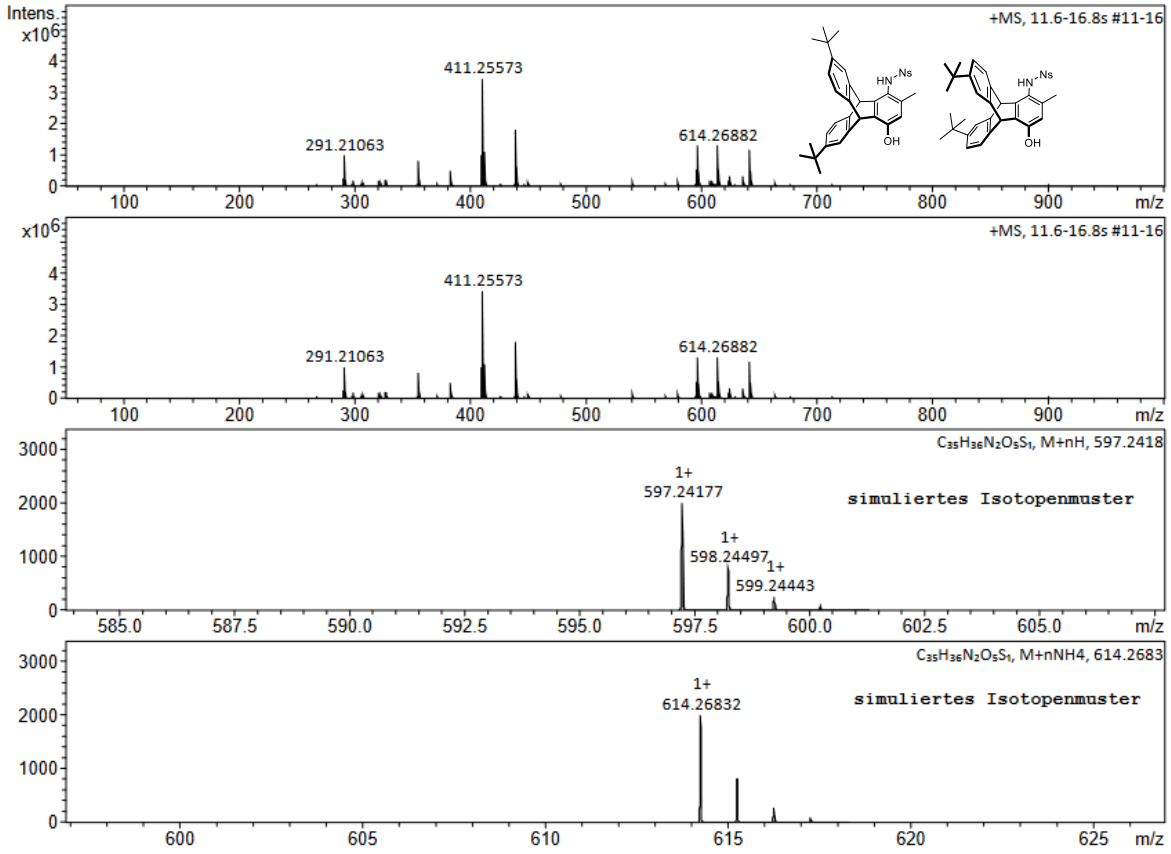
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e¯ Conf	Adduct	z
1	597.24146	C35H37N2O5S	597.24177	C35H36N2O5S	0.31	0.52	even	M+H	1+

Figure 230: HRMS (APCI, positive mode) of nosylated aminophenol (**4h**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85743_APCI_HR_P1-D-2_01_7562.d	Acquisition Date	19.01.2021 10:06:42
Sample Name	85743_ESI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 93E	Operator	Rudolph

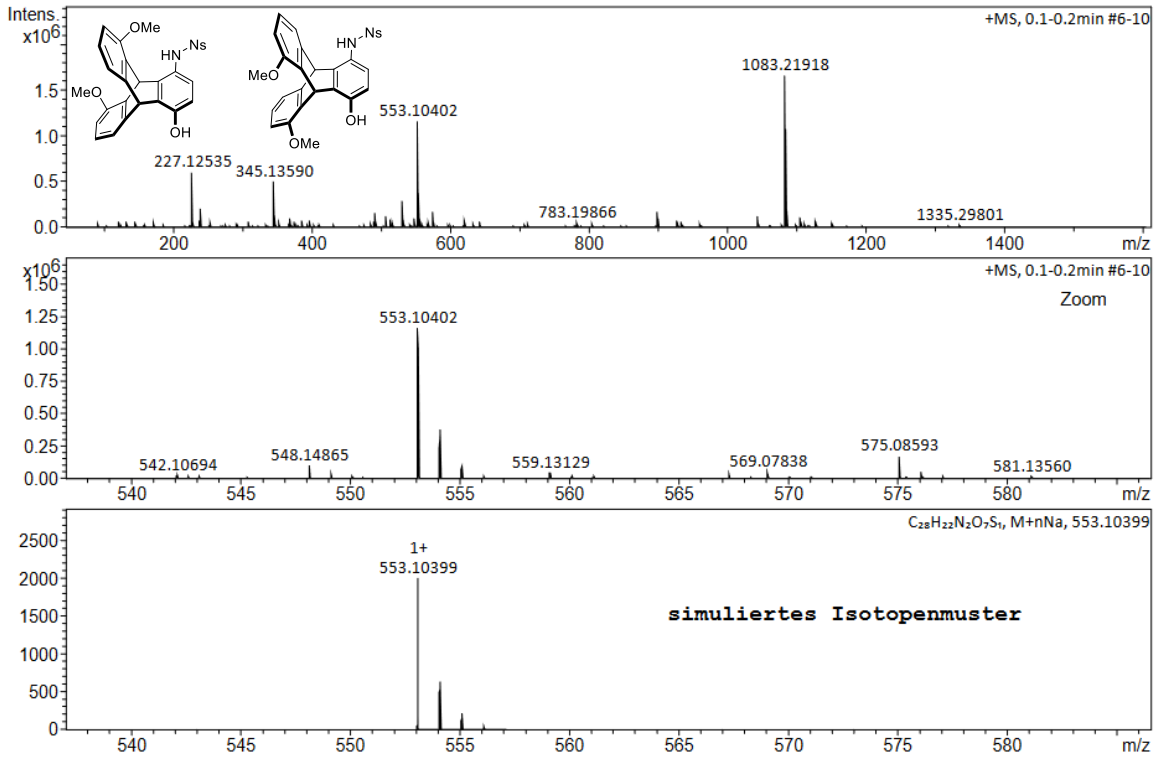


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e¯ Conf	Adduct
1	597.24135	C35H37N2O5S	597.24177	C35H36N2O5S	0.42	0.70	even	M+H
1	614.26882	C35H40N3O5S	614.26832	C35H36N2O5S	0.50	-0.81	even	M+NH4

Figure 231: HRMS (APCI, positive mode) of nosylated aminophenol (**4i**).

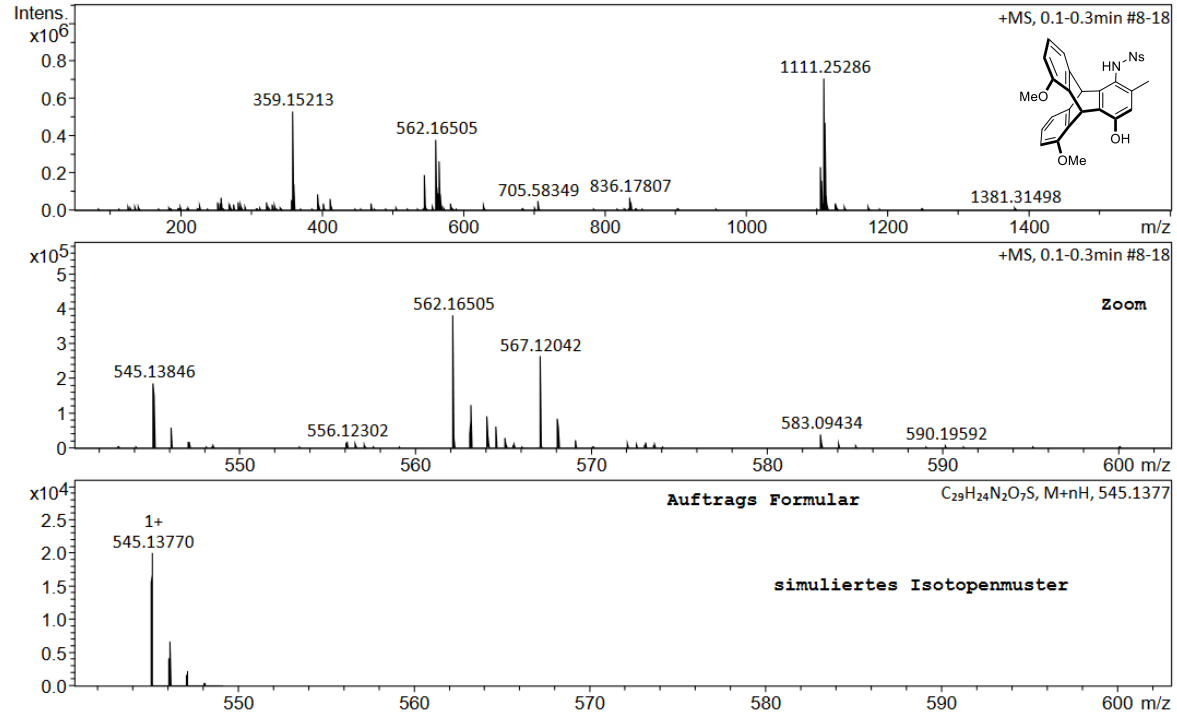
Analysis	D:\Data\Plenio\87177_ESI_HR_P1-D-1_01_12595.d	Acquisition Date	18.10.2021 18:27:21
Sample Name	87177_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _320-5	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	531.12202	531.12205	C28H23N2O7S	M+H	C28H22N2O7S	0.03	0.05	10.3	even	1+
1	553.10402	553.10399	C28H22N2NaO7S	M+Na	C28H22N2O7S	0.03	0.05	9.6	even	1+
1	1083.21918	1083.21876	C56H44N4NaO14S2	2M+Na	C28H22N2O7S	0.42	0.39	7.9	even	1+

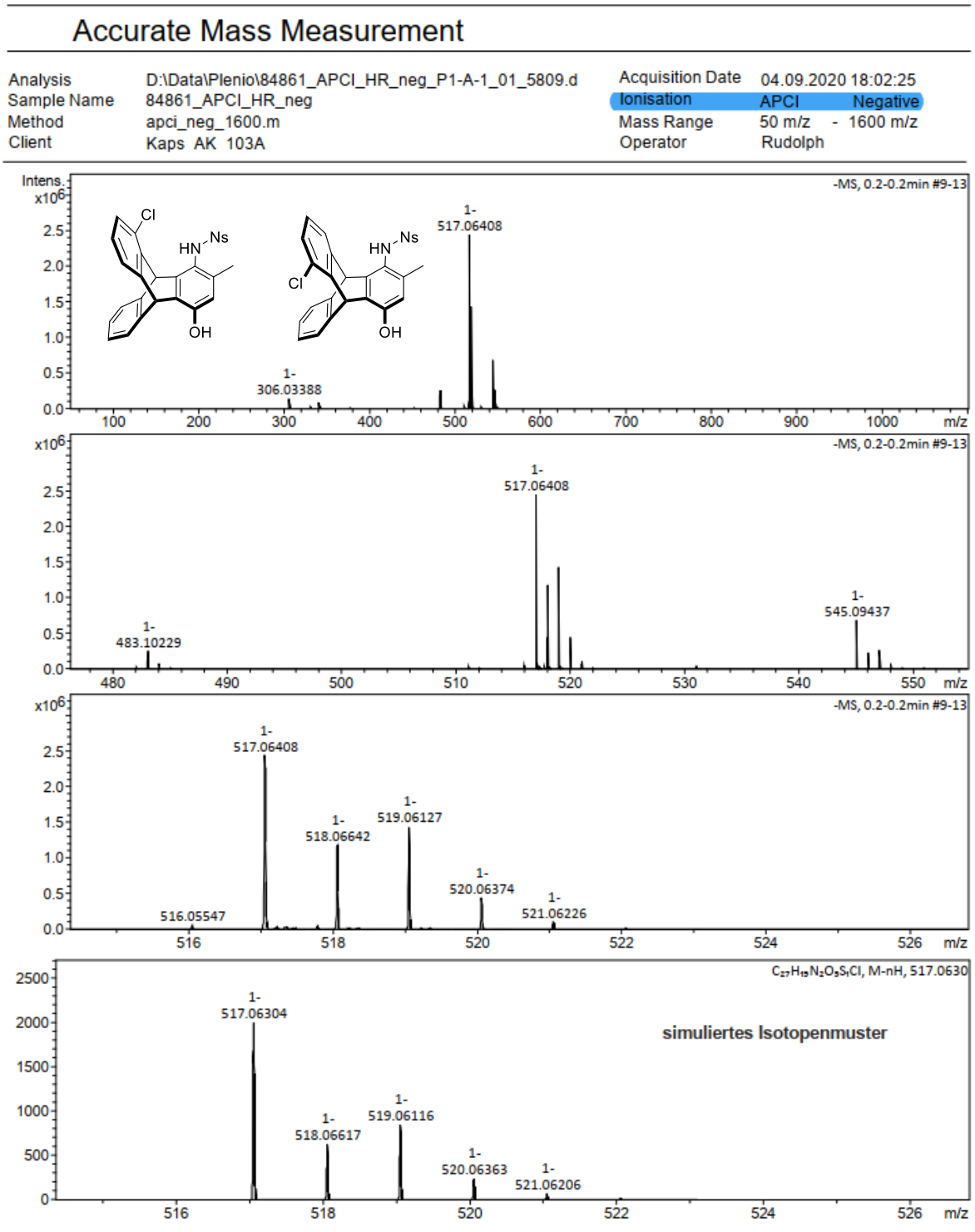
Figure 232: HRMS (ESI, positive mode) of nosylated aminophenol (**4j**).

Analysis	D:\Data\Plenio\87712_ESI_HR_P1-E-2_01_14689.d	Acquisition Date	17.01.2022 11:18:36
Sample Name	87712_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 320_6	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	545.13846	545.13770	C29H25N2O7S	M+H	C29H24N2O7S	0.77	1.41	8.6	even	1+
1	567.12042	567.11964	C29H24N2NaO7S	M+Na	C29H24N2O7S	0.78	1.38	9.8	even	1+
1	1111.25286	1111.25006	C58H48N4NaO14S2	2M+Na	C29H24N2O7S	2.80	2.52	9.4	even	1+

Figure 233: HRMS (ESI, positive mode) of nosylated aminophenol (**4k**).



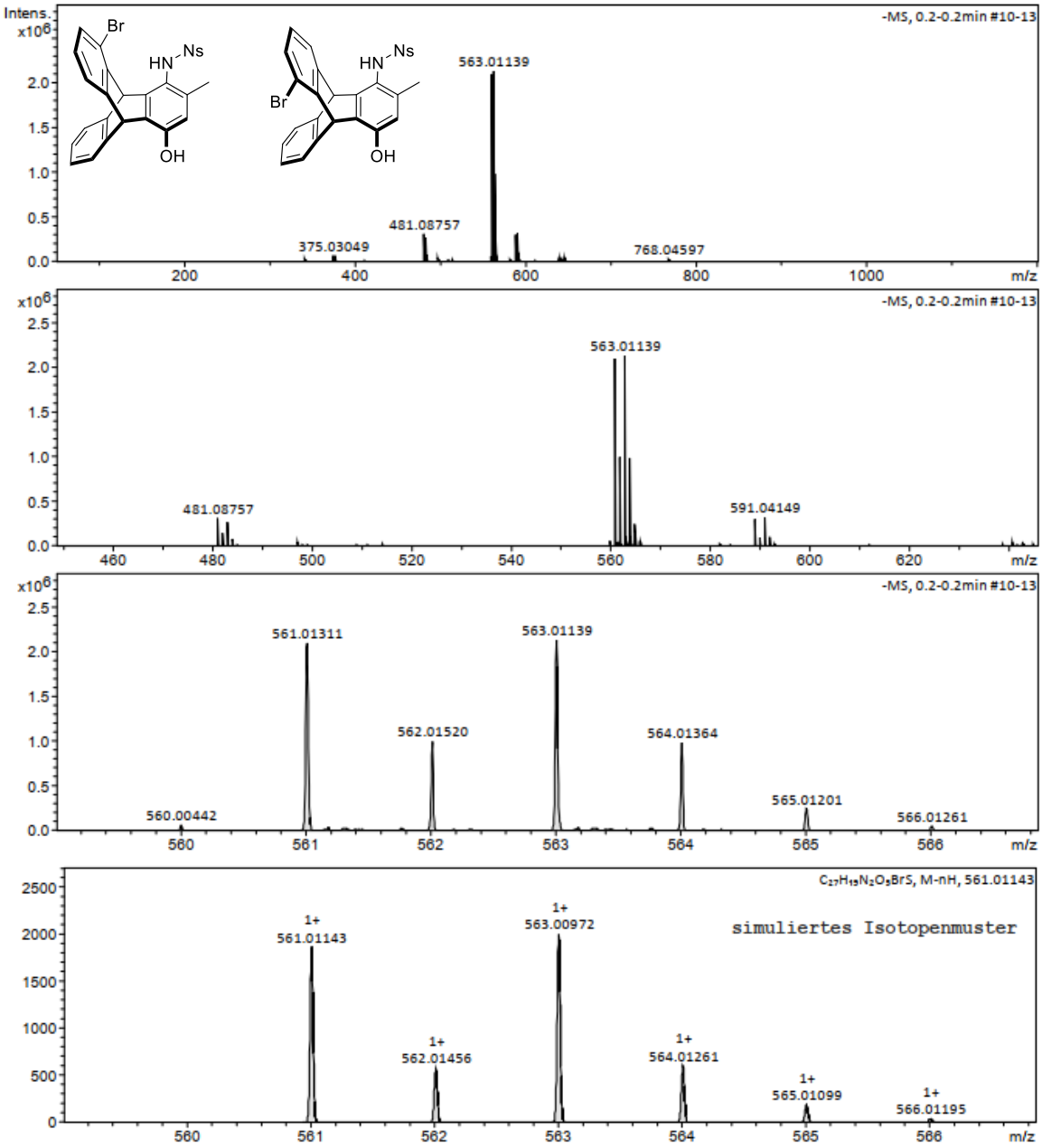
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	517.06408	C27H18ClN2O5S	517.06304	C27H19ClN2O5S	1.04	-2.00	even	M-H	1-

Figure 234: HRMS (APCI, negative mode) of nosylated aminophenol (**4l**).

Accurate Mass Measurement

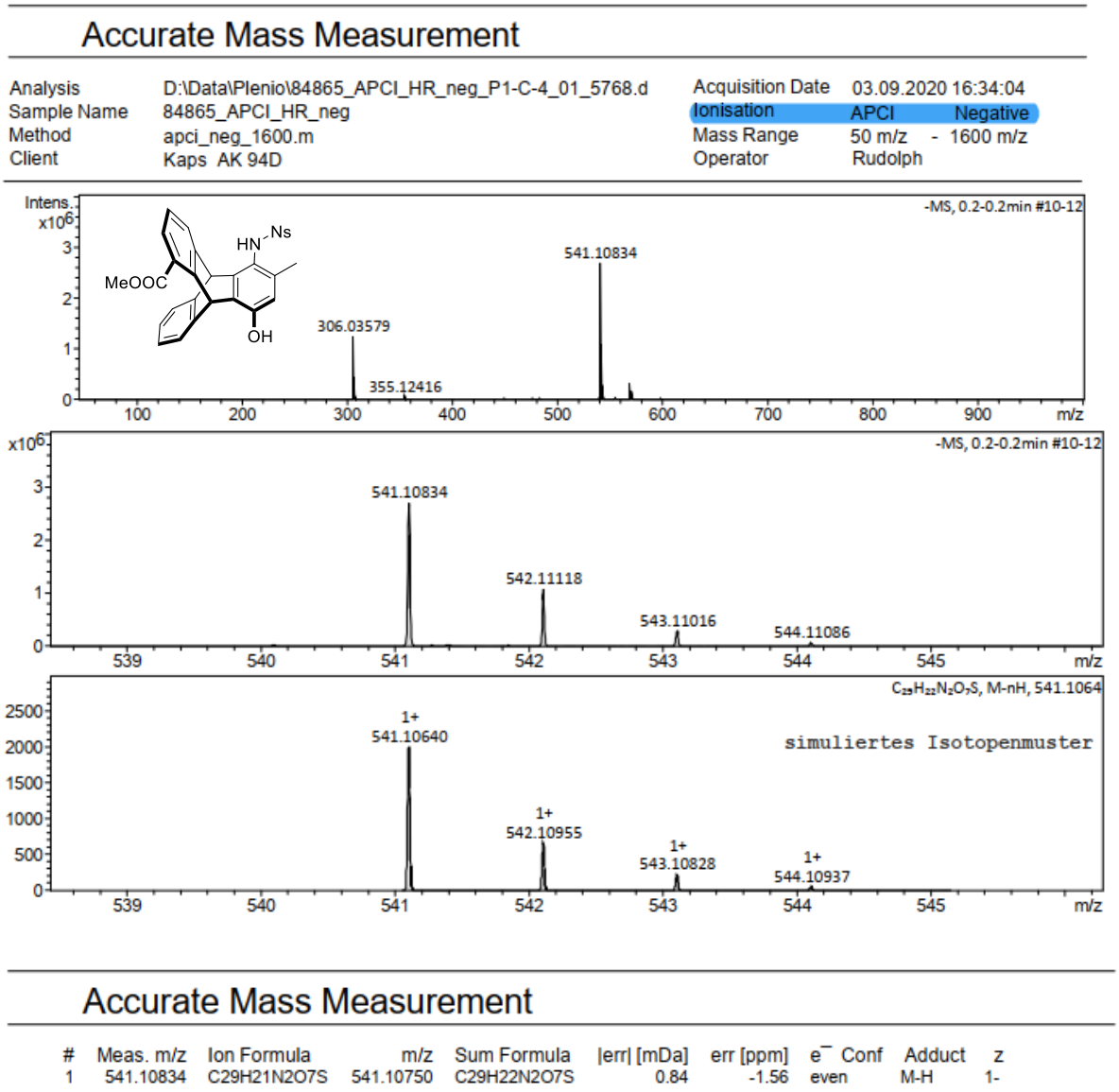
Analysis	D:\Data\Plenio\84863_APCI_HR_neg_P1-C-2_01_5760.d	Acquisition Date	03.09.2020 15:09:52
Sample Name	84863_APCI_HR_neg	Ionisation	APCI Negative
Method	apci_neg_1600.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 198-1	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	561.01311	C27H18BrN2O5S	561.01253	C27H19BrN2O5S	0.58	-1.04	even	M-H	1-

Figure 235: HRMS (APCI, negative mode) of nosylated aminophenol (**4m**).



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	541.10834	C29H21N2O7S	541.10750	C29H22N2O7S	0.84	-1.56	even	M-H	1-

Figure 236: HRMS (APCI, negative mode) of nosylated aminophenol (**4n**).

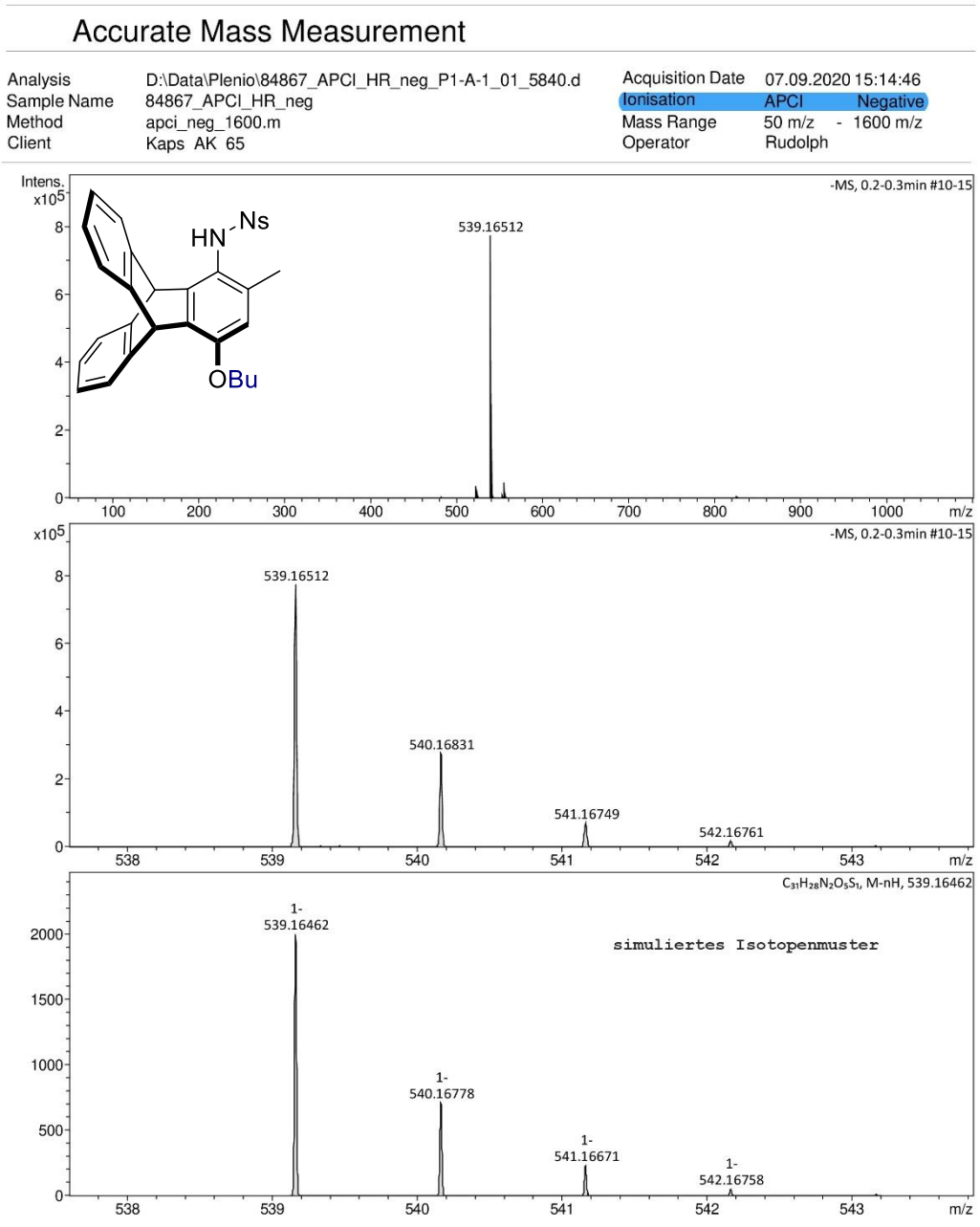
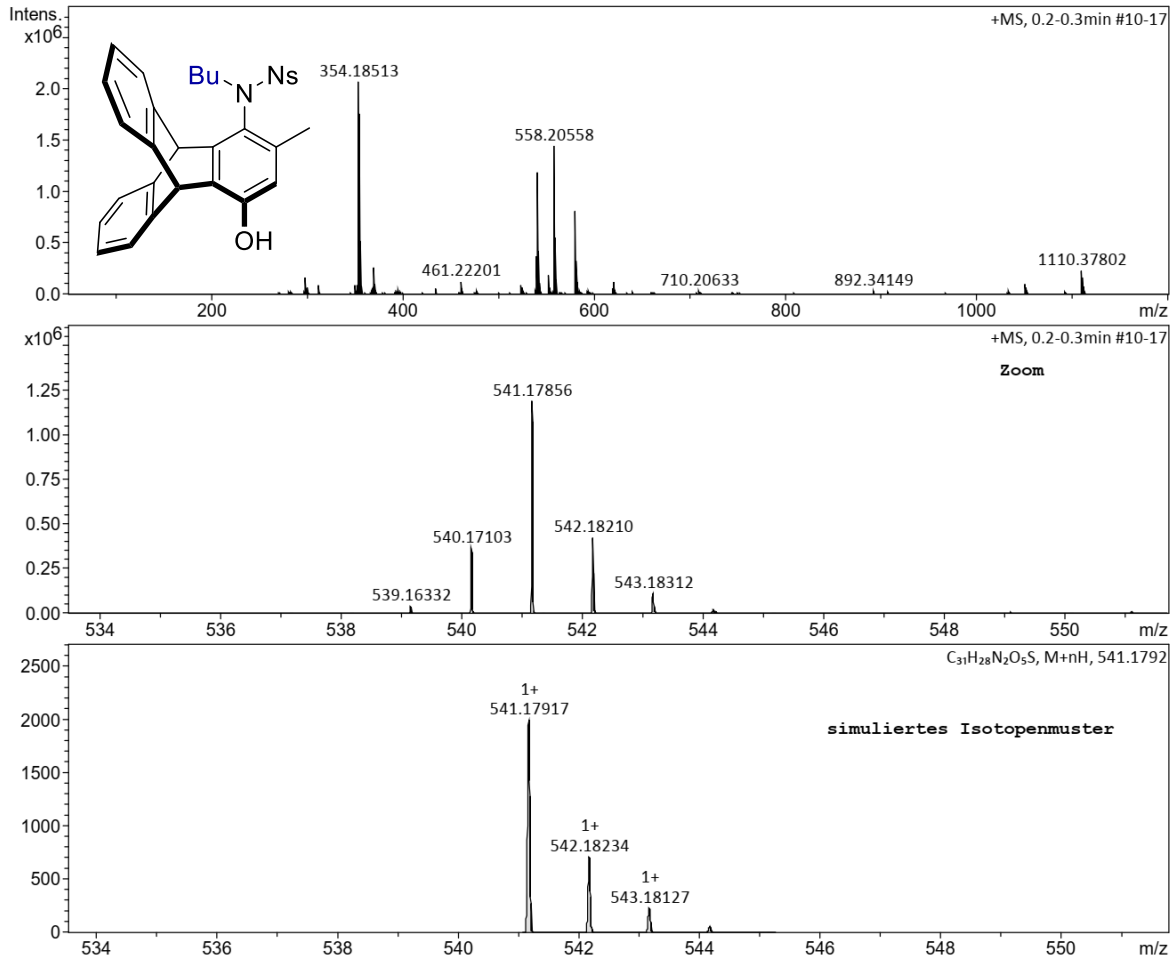


Figure 237: HRMS (APCI, negative mode) of *O-alkylated aminophenol (nosyl protected)* (**5b**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85881_APCI_HR_P1-C-2_01_8325.d	Acquisition Date	15.02.2021 14:32:17
Sample Name	85881_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 62 F	Operator	Rudolph



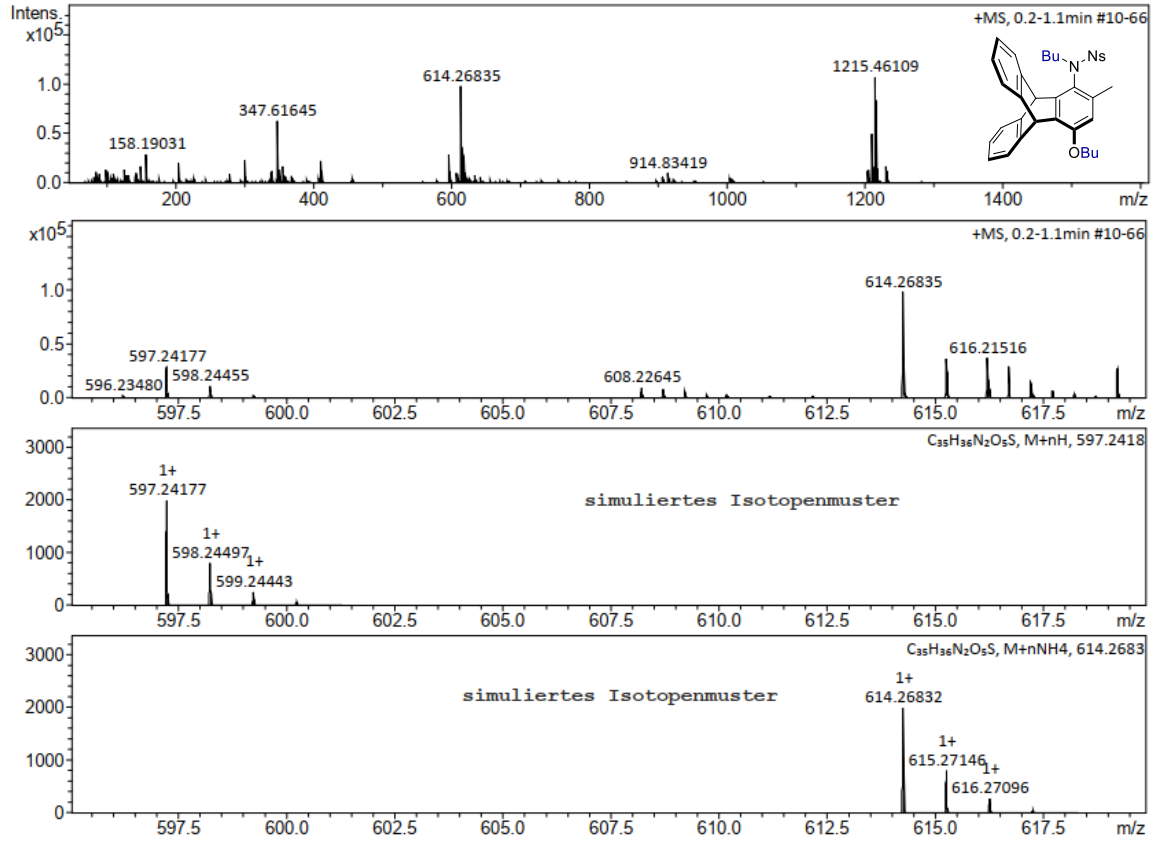
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	541.17856	C31H29N2O5S	541.17917	C31H28N2O5S	0.61	1.13	even	M+H
1	558.20558	C32H28N7OS	558.20706	C32H24N6OS	1.48	2.65	even	M+NH4
1	580.18995	C35H32O6S	580.19141	C35H31O6S	1.47	2.53	odd	M+H
2	541.17856	C32H25N6OS	541.18051	C32H24N6OS	1.95	3.60	even	M+H
2	558.20558	C31H32N3O5S	558.20572	C31H28N2O5S	0.14	0.25	even	M+NH4
2	580.18995	C33H30N3O5S	580.19007	C33H29N3O5S	0.12	0.21	even	M+H
3	580.18995	C34H26N7OS	580.19141	C34H25N7OS	1.46	2.52	even	M+H
4	580.18995	C32H24N10S	580.19006	C32H23N10S	0.12	0.20	odd	M+H
5	580.18995	C31H28N6O4S	580.18873	C31H27N6O4S	1.22	-2.10	odd	M+H

Figure 238: HRMS (APCI, negative mode) of *O-alkylated aminophenol (nosyl protected)* (**5ba**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84859_ESI_HR_P1-C-1_01_5646.d	Acquisition Date	31.08.2020 16:39:12
Sample Name	84859_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 62C	Operator	Rudolph



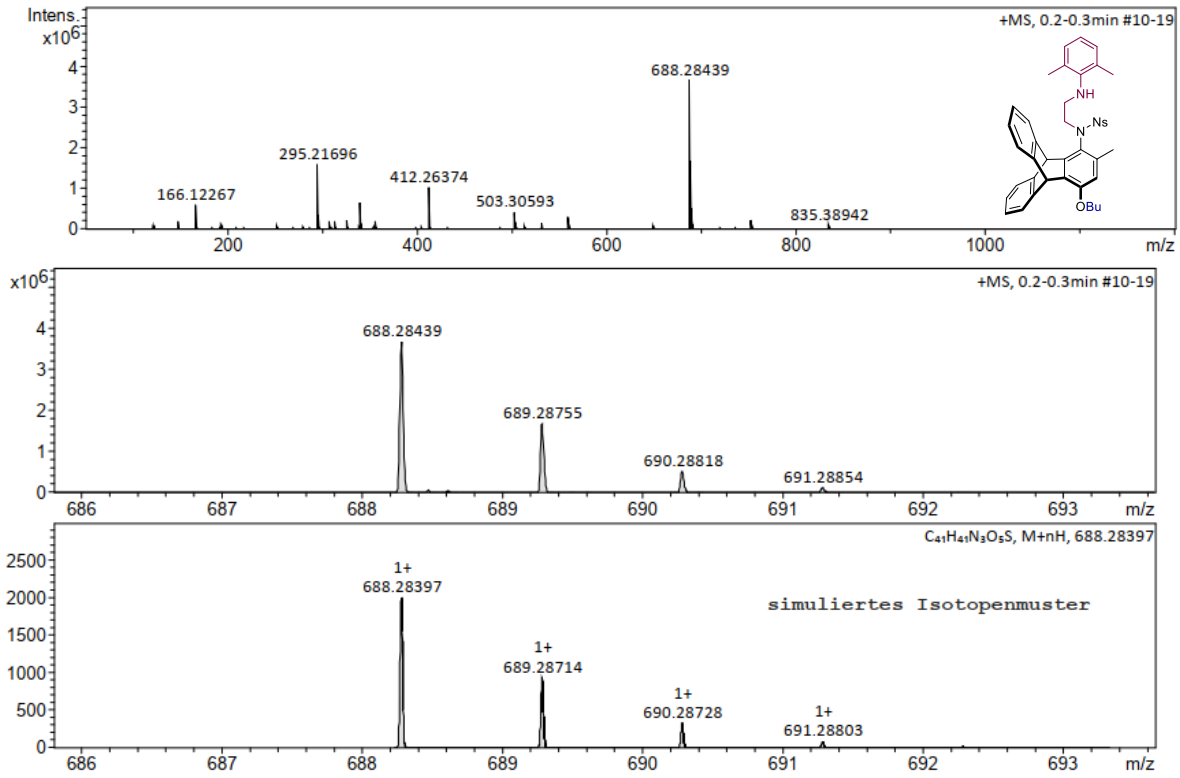
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	597.24177	C35H37N2O5S	597.24177	C35H36N2O5S	0.00	0.01	even	M+H
1	614.26835	C35H40N3O5S	614.26832	C35H36N2O5S	0.03	-0.05	even	M+NH4
1	1215.46109	C70H72N4NaO10S2	1215.45821	C35H36N2O5S	2.88	-2.37	even	2M+Na

Figure 239: HRMS (ESI, positive mode) of *O/N-alkylated aminophenol (nosyl protected)* (**5bb**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84857_ESI_HR_P1-C-2_01_5641.d	Acquisition Date	31.08.2020 15:41:00
Sample Name	84857_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 75	Operator	Rudolph



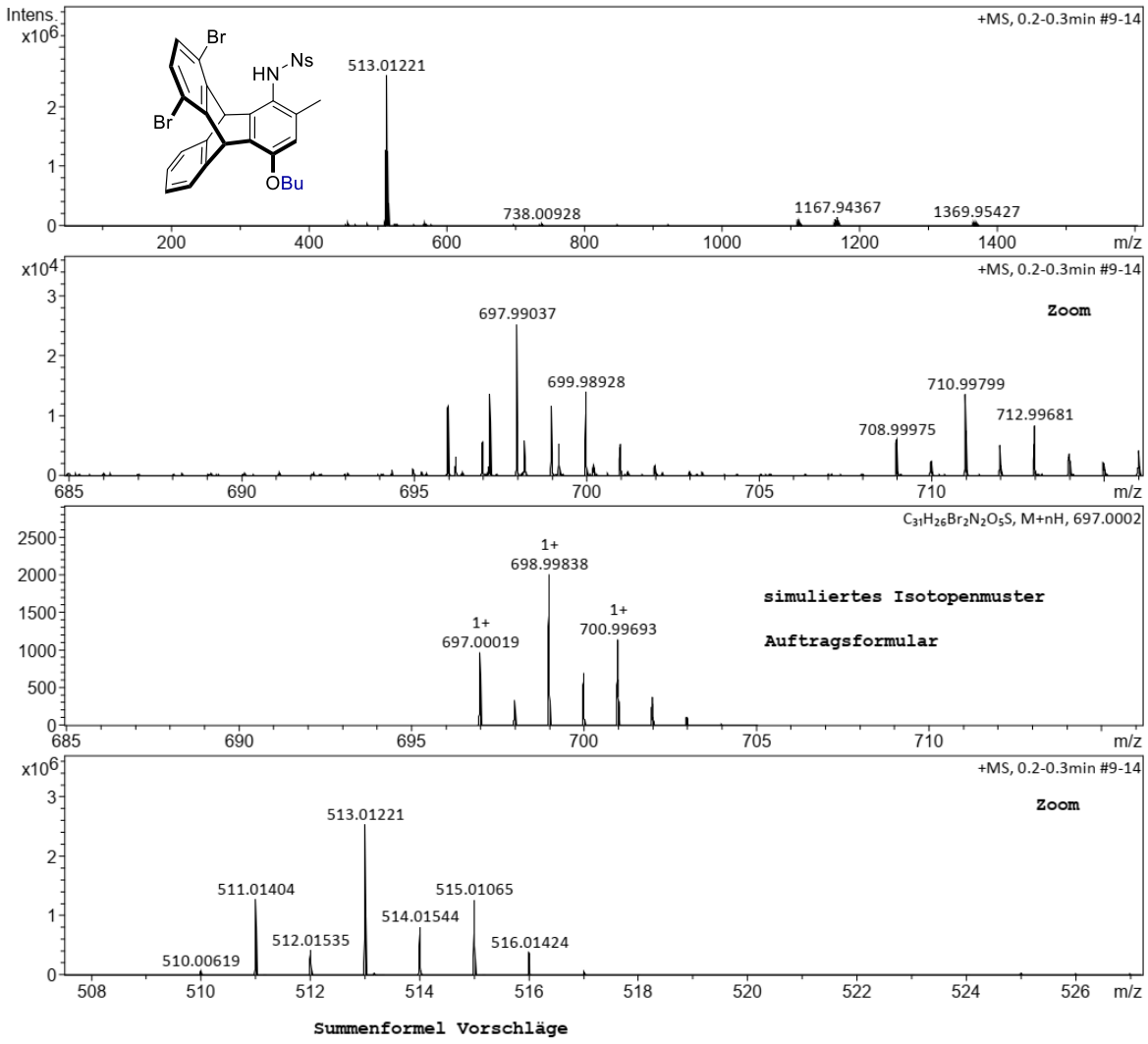
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e¯ Conf	Adduct
1	688.28439	C41H42N3O5S	688.28397	C41H41N3O5S	0.42	-0.61	even	M+H

Figure 240: HRMS (ESI, positive mode) of O/N-alkylated aminophenol (nosyl protected) (**5bc**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86217_APCI_HR_P1-C-3_01_9645.d	Acquisition Date	21.04.2021 08:55:59
Sample Name	86217_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 287_4_Br	Operator	Rudolph



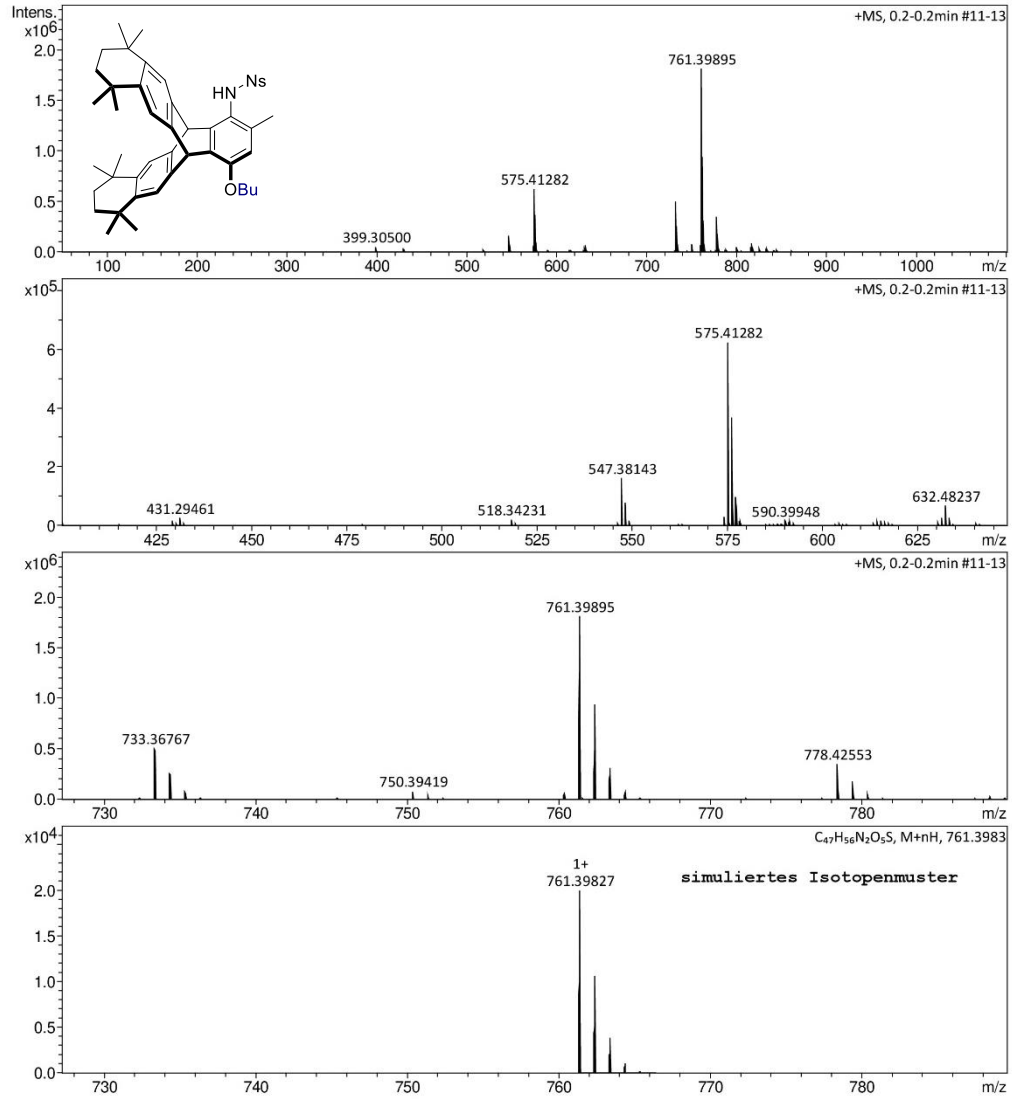
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	511.01404	C25H23Br2NO	511.01409	C25H22Br2NO	0.05	0.09	odd	M+H	1+

Figure 241: HRMS (APCI, positive mode) of O-alkylated aminophenol (nosyl protected) (**5c**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84989_APCI_HR_P1-B-1_01_6068.d	Acquisition Date	17.09.2020 13:26:04
Sample Name	84989_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK_109	Operator	Rudolph



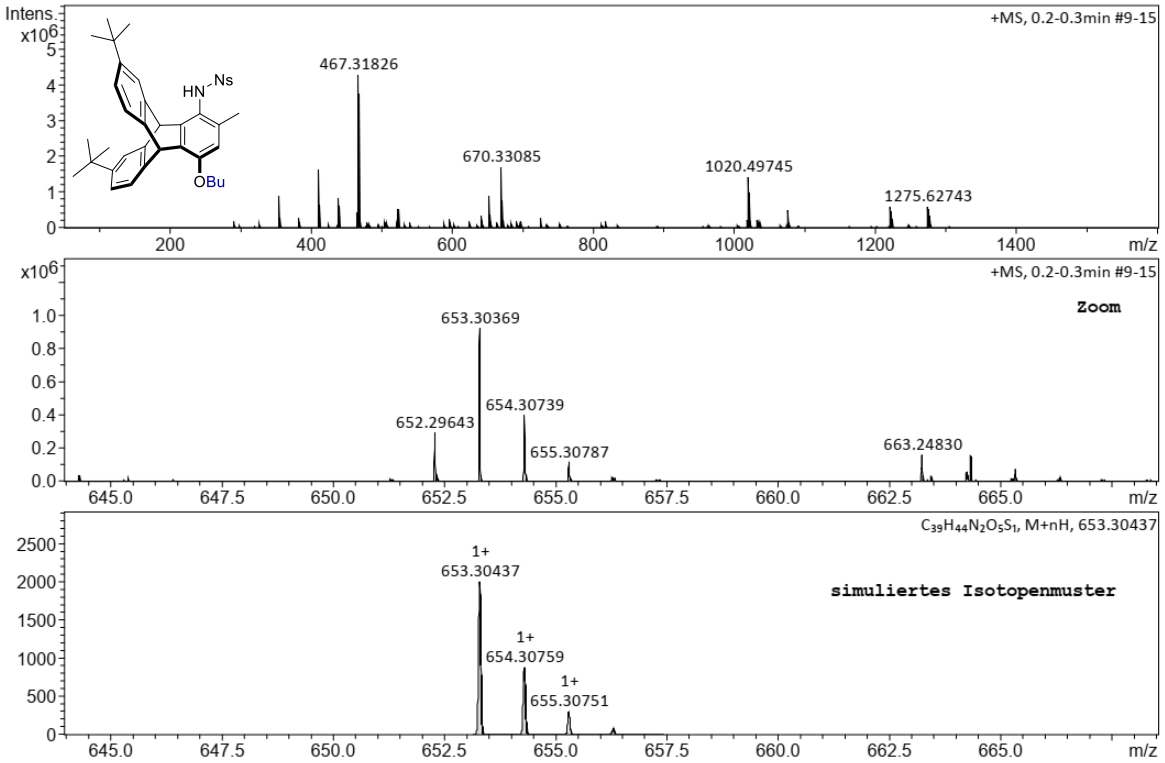
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	733.36767	C45H53N2O5S	733.36697	C45H53N2O5S	0.70	-0.96	even	M	1+
1	761.39895	C47H57N2O5S	761.39827	C47H56N2O5S	0.68	-0.90	even	M+H	1+
1	778.42553	C47H60N3O5S	778.42482	C47H56N2O5S	0.71	-0.91	even	M+NH4	1+

Figure 242: HRMS (APCI, positive mode) of *O-alkylated aminophenol (nosyl protected)* (**5g**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86215_APCI_HR_P1-C-1_01_9634.d	Acquisition Date	20.04.2021 15:58:48
Sample Name	86215_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 287_3tBu	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	653.30369	C39H45N2O5S	653.30437	C39H44N2O5S	0.68	1.05	even	M+H	1+
1	670.33085	C39H48N3O5S	670.33092	C39H44N2O5S	0.07	0.10	even	M+NH4	1+

Figure 243: HRMS (APCI, positive mode) of *O-alkylated aminophenol (nosyl protected)* (**5h**).

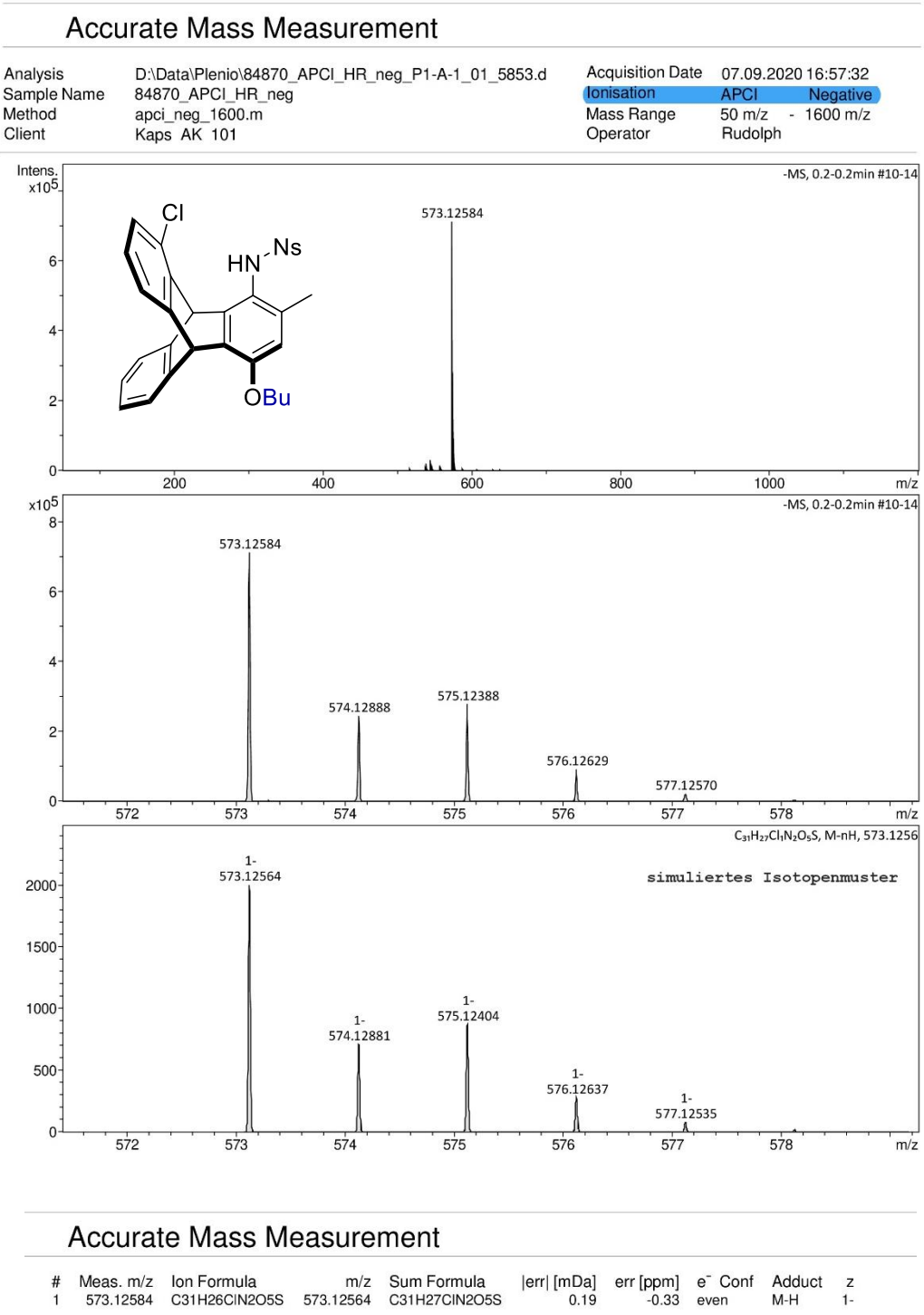
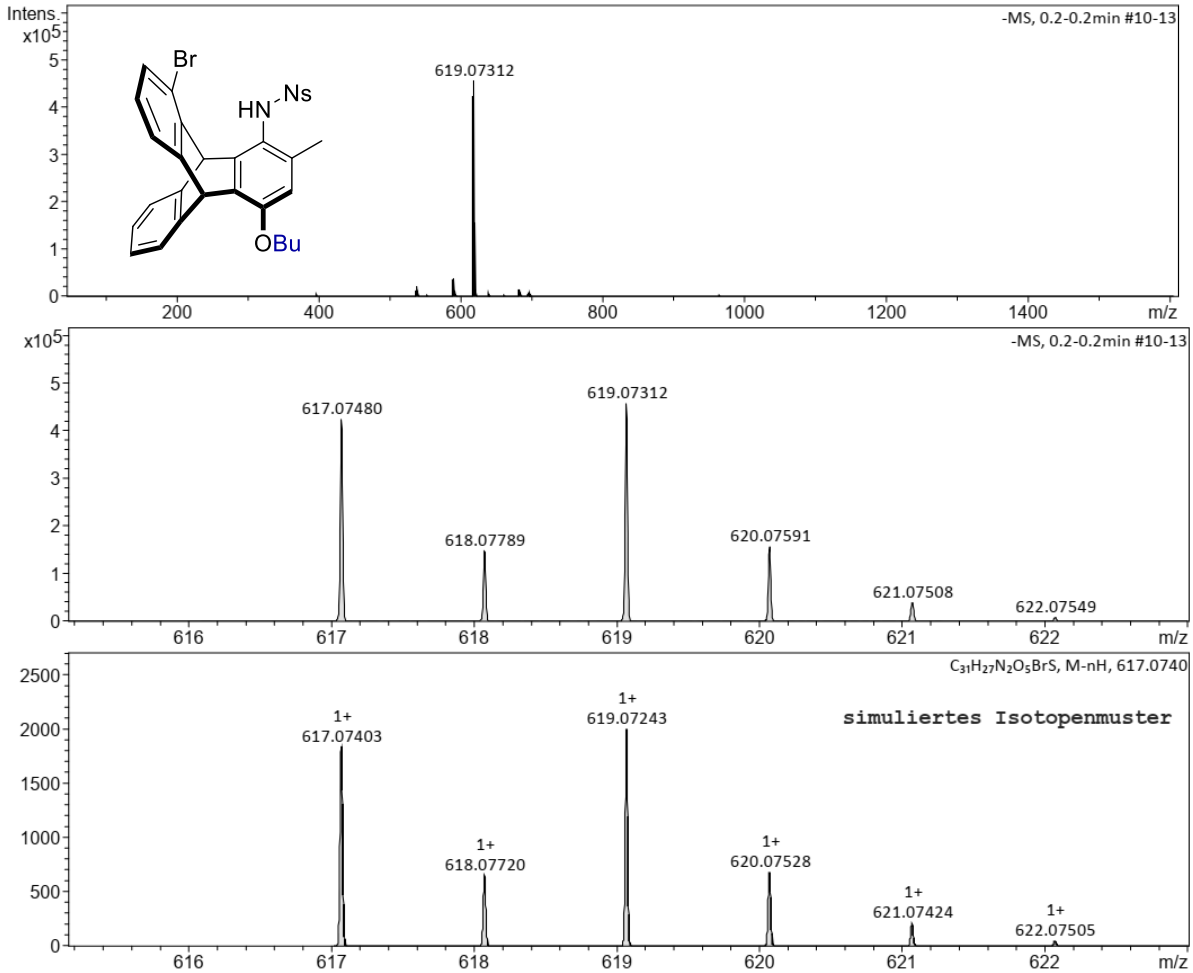


Figure 244: HRMS (APCI, negative mode) of O-alkylated aminophenol (nosyl protected) (**5l**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84864_APCI_HR_neg_P1-C-3_01_5765.d	Acquisition Date	03.09.2020 16:00:44
Sample Name	84864_APCI_HR_neg	Ionisation	APCI Negative
Method	apci_neg_1600.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 198-2	Operator	Rudolph



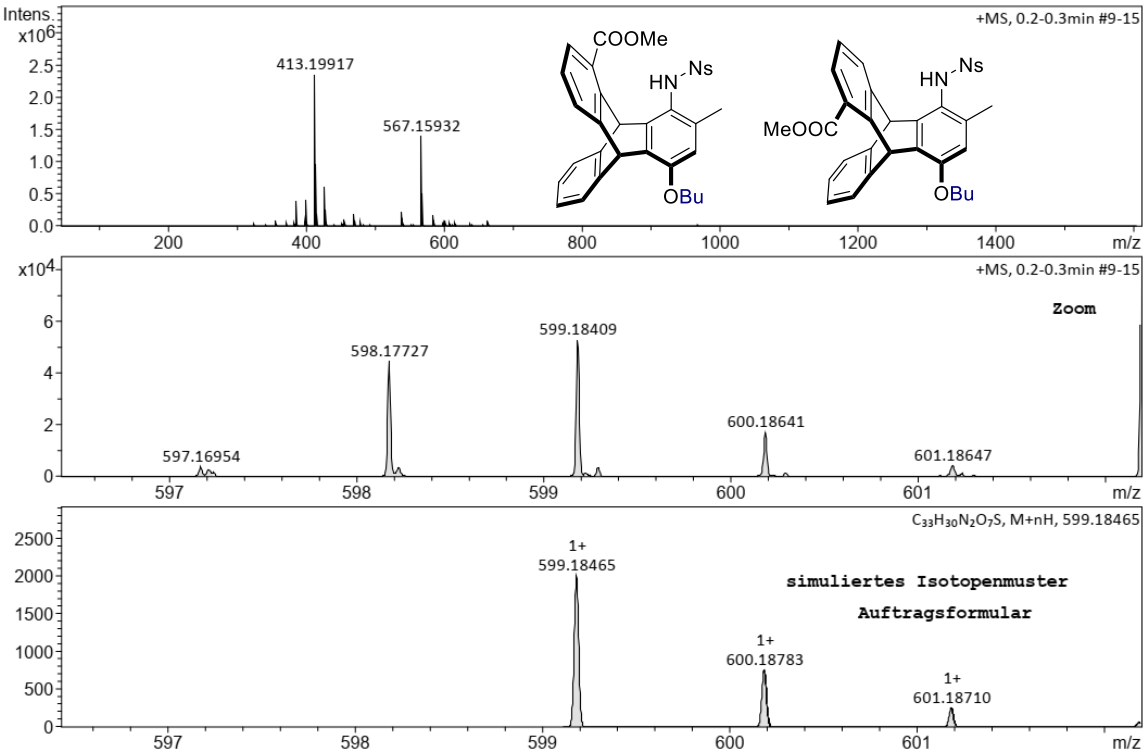
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	617.07480	C31H26BrN2O5S	617.07513	C31H27BrN2O5S	0.33	0.54	even	M-H	1-

Figure 245: HRMS (APCI, negative mode) of O-alkylated aminophenol (nosyl protected) (**5m**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86216_APCI_HR_P1-C-2_01_9644.d	Acquisition Date	21.04.2021 08:49:13
Sample Name	86216_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 287_2_cooMe	Operator	Rudolph

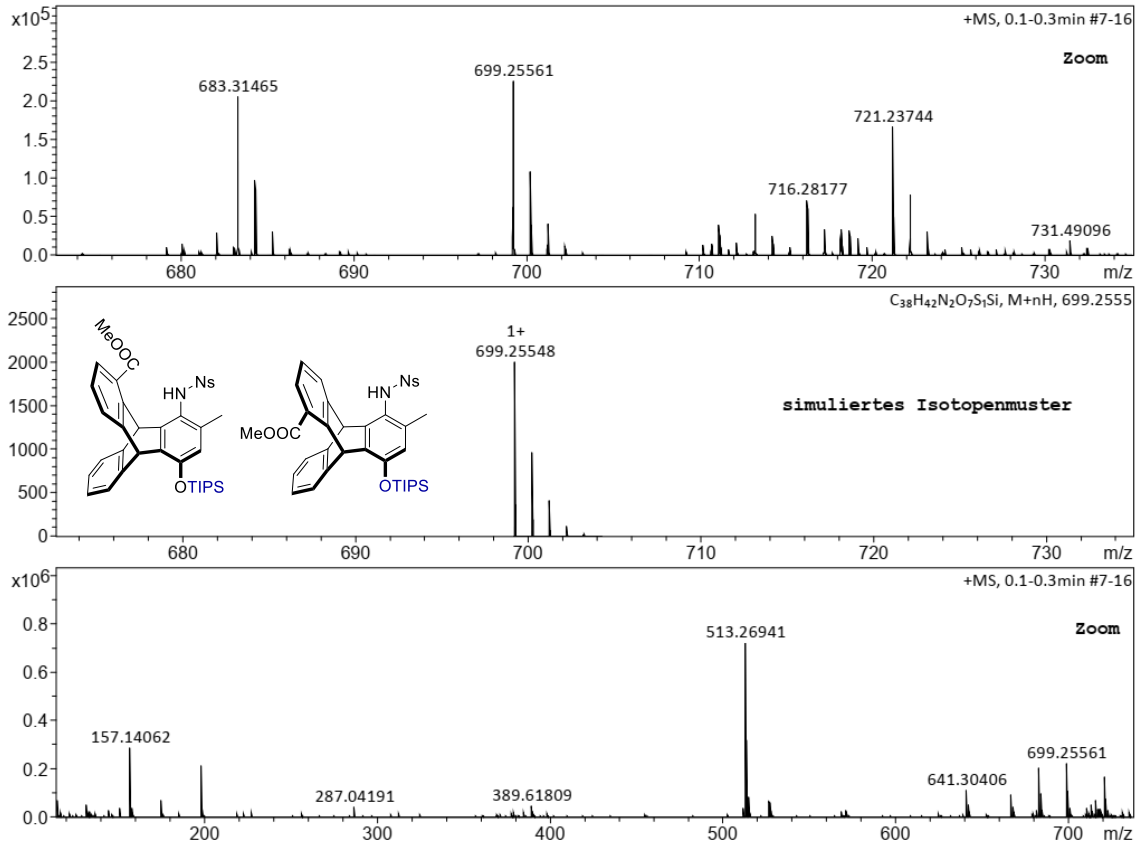


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	413.19917	C27H27NO3	413.19855	C27H27NO3	0.63	-1.52	odd	M	1+
1	413.19917	C27H27NO3	413.19855	C27H26NO3	0.63	-1.52	odd	M+H	1+
2	599.18409	C33H31N2O7S	599.18465	C33H31N2O7S	0.56	0.94	even	M	1+
2	599.18409	C33H31N2O7S	599.18465	C33H30N2O7S	0.56	0.94	even	M+H	1+

Figure 246: HRMS (ESI, positive mode) of O/N-alkylated aminophenol (nosyl protected) (**5n**).

Analysis	D:\Data\Plenio\88194_ESI_HR_P1-E-1_01_16216.d	Acquisition Date	08.03.2022 17:21:49
Sample Name	88194_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 344_1	Operator	Rudolph

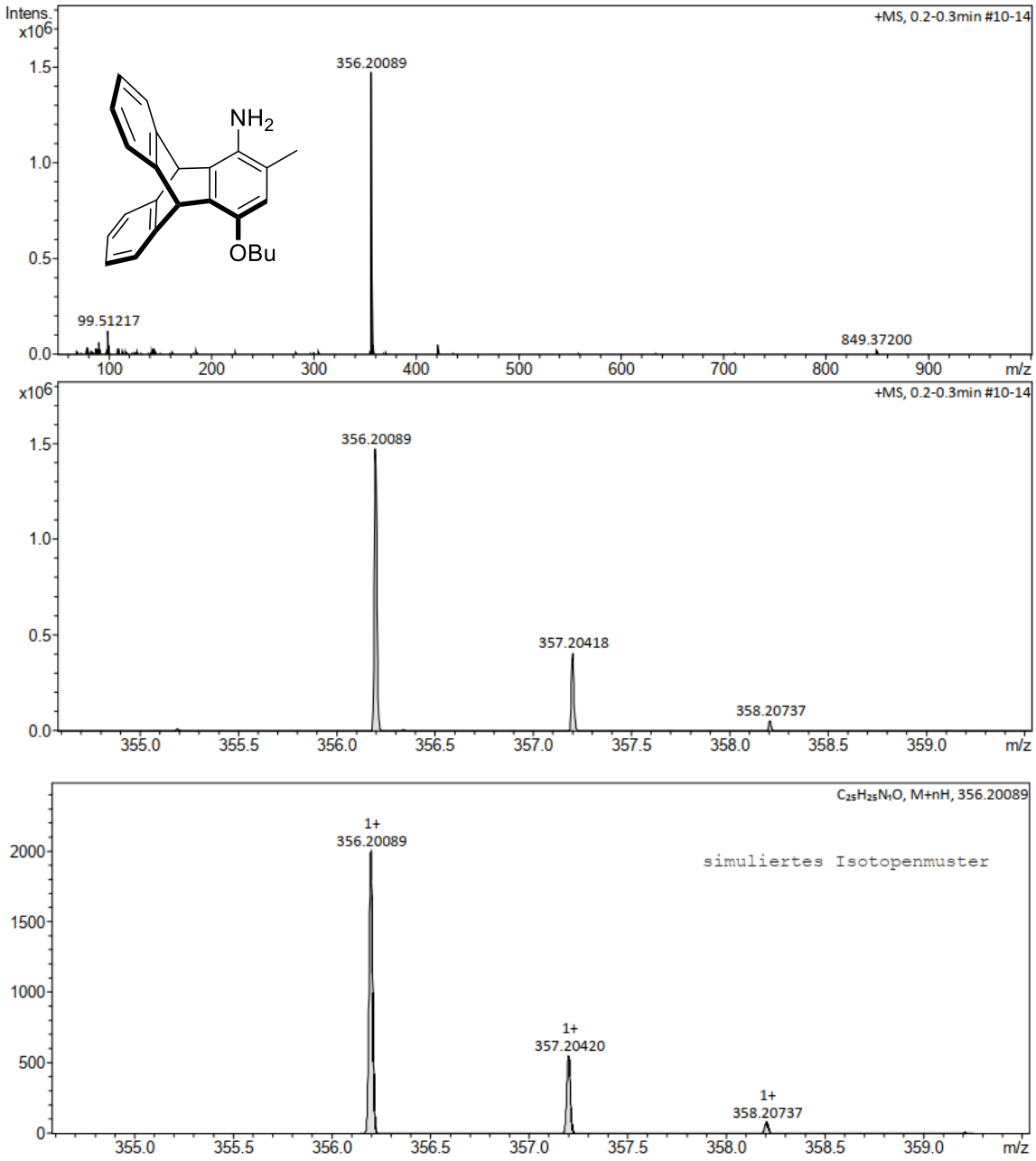


#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻	Conf	z
1	699.25561	699.25548	C38H43N2O7SSi	M+H	C38H42N2O7SSi	0.14	0.20	12.3	even		1+
1	721.23744	721.23742	C38H42N2NaO7SSi	M+Na	C38H42N2O7SSi	0.02	0.03	25.4	even		1+
1	1419.48902	1419.48562	C76H84N4NaO14S2Si2	2M+Na	C38H42N2O7SSi	3.40	2.39	17.0	even		1+

Figure 247: HRMS (ESI, positive mode) of O-silylated aminophenol (nosyl protected) (**5na**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84871_ESI_HR_P1-C-1_01_5695.d	Acquisition Date	01.09.2020 15:00:39
Sample Name	84871_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 91	Operator	Rudolph



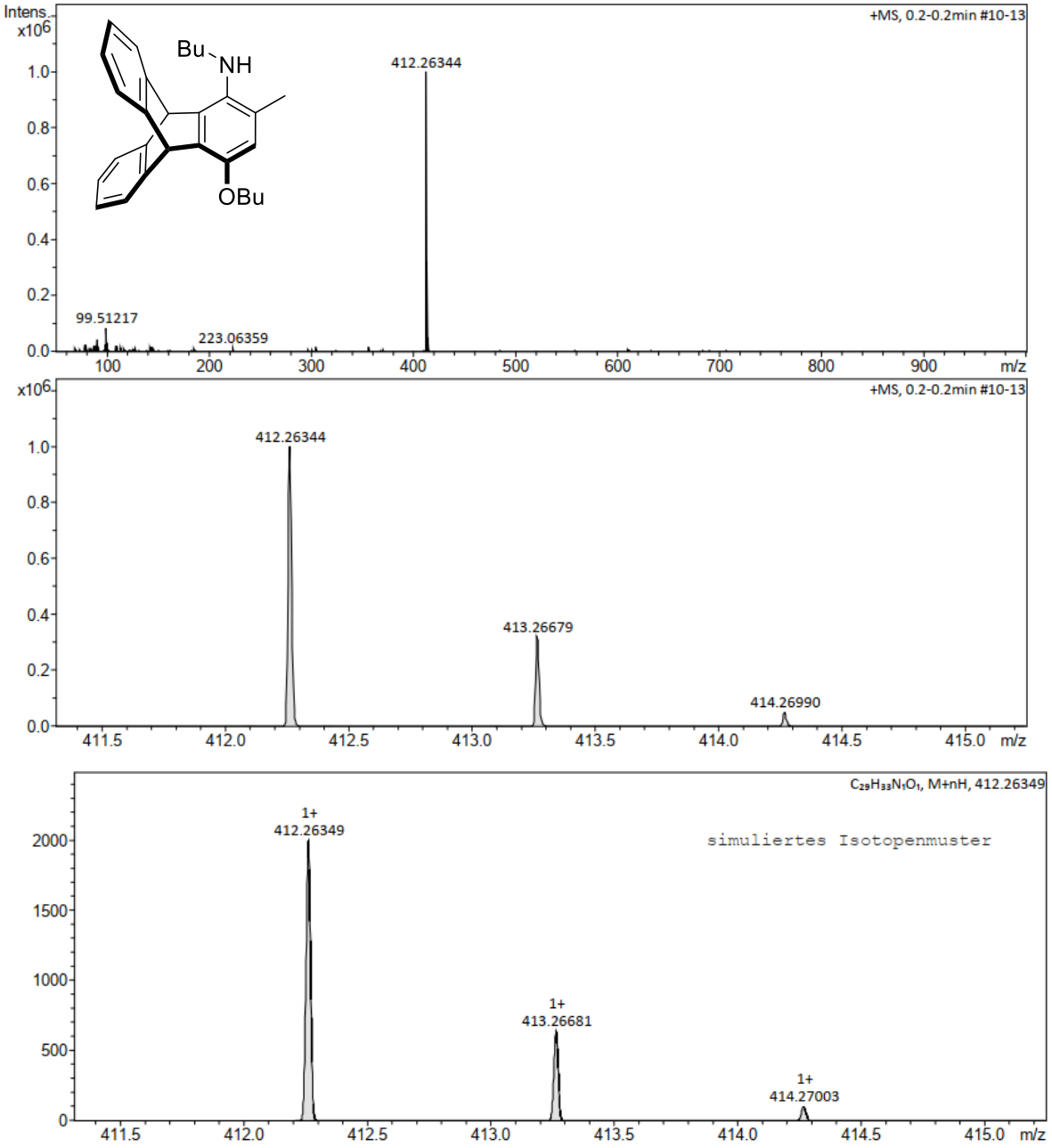
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	356.20089	C25H26NO	356.20089	C25H25NO	0.01	0.02	even	M+H

Figure 248: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6b**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84872_ESI_HR_P1-C-1_01_5697.d	Acquisition Date	01.09.2020 15:14:44
Sample Name	84872_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 63	Operator	Rudolph



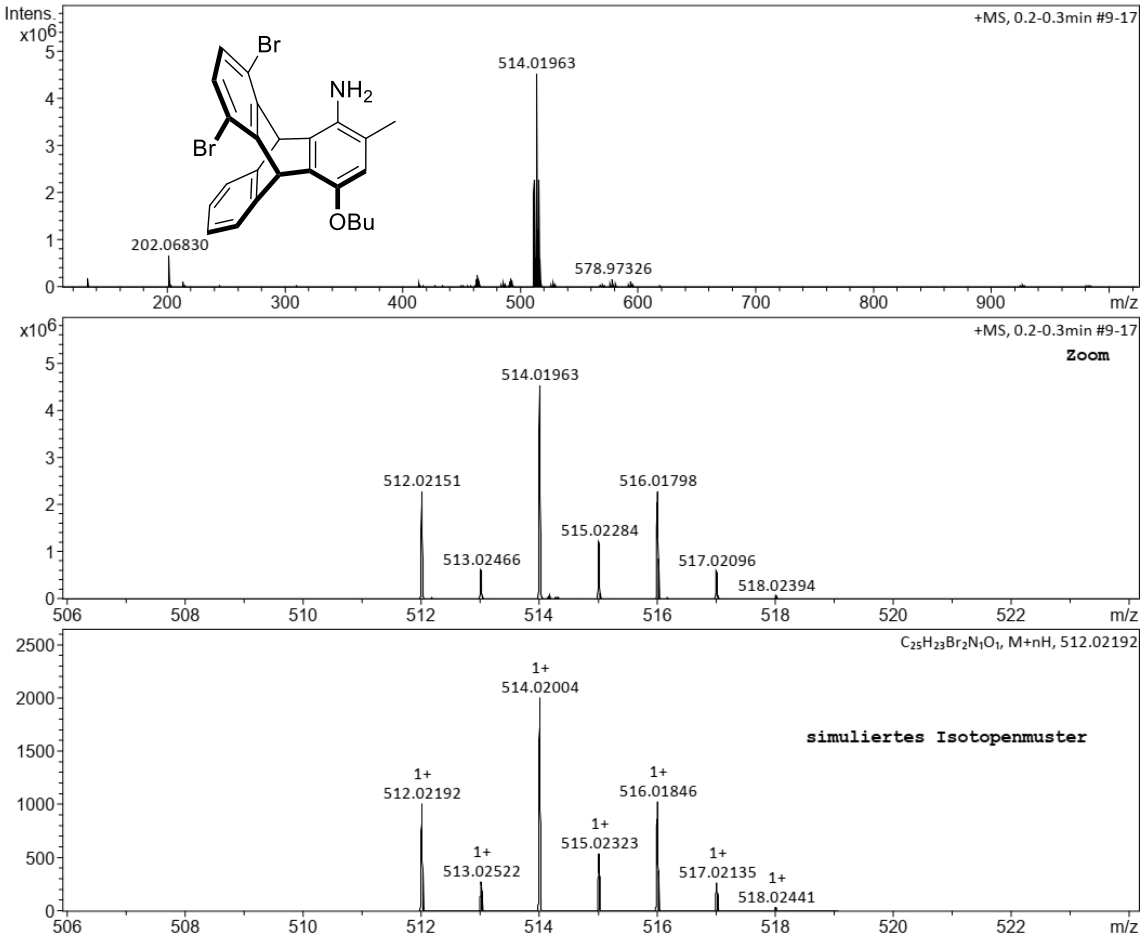
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	412.26344	C29H34NO	412.26349	C29H33NO	0.05	0.13	even	M+H

Figure 249: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6bb**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86731_ESI_HR_P1-D-1_01_11204.d	Acquisition Date	28.07.2021 11:42:04
Sample Name	86731_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 306-2	Operator	rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	512.02151	C25H24Br2NO	512.02192	C25H23Br2NO	0.40	0.79	even	M+H	1+

Figure 250: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6c**).

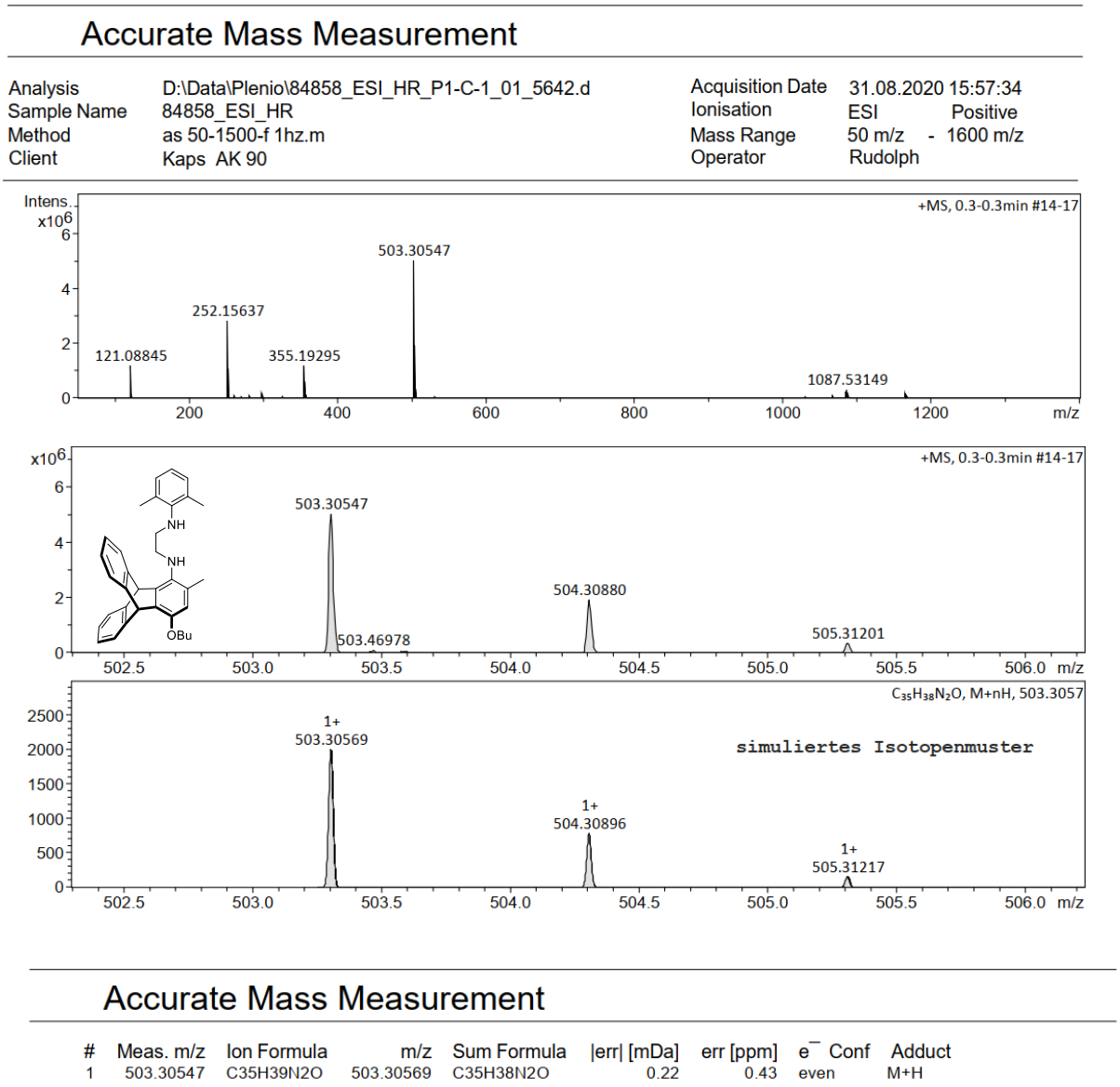
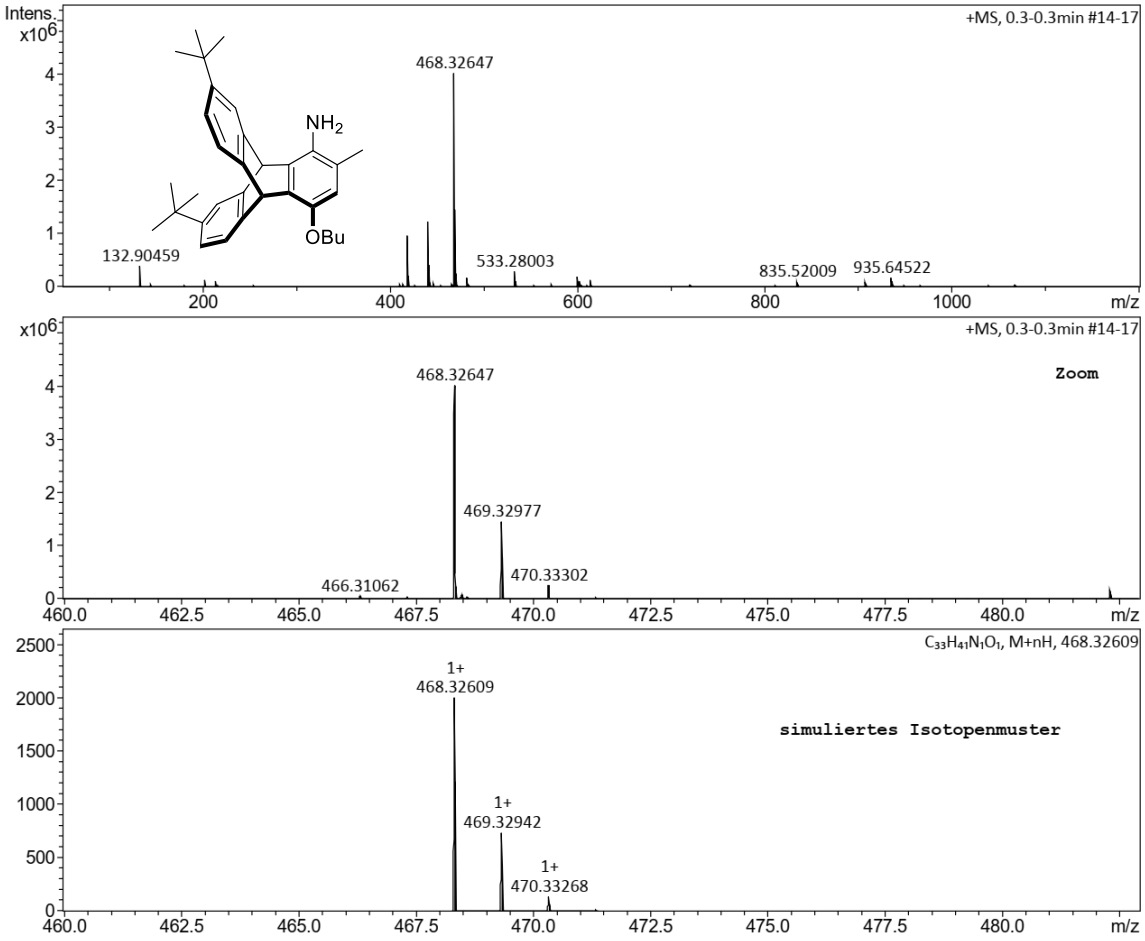


Figure 251: HRMS (ESI, positive mode) of denosylated aminotriptycene (**9**).

Accurate Mass Measurement

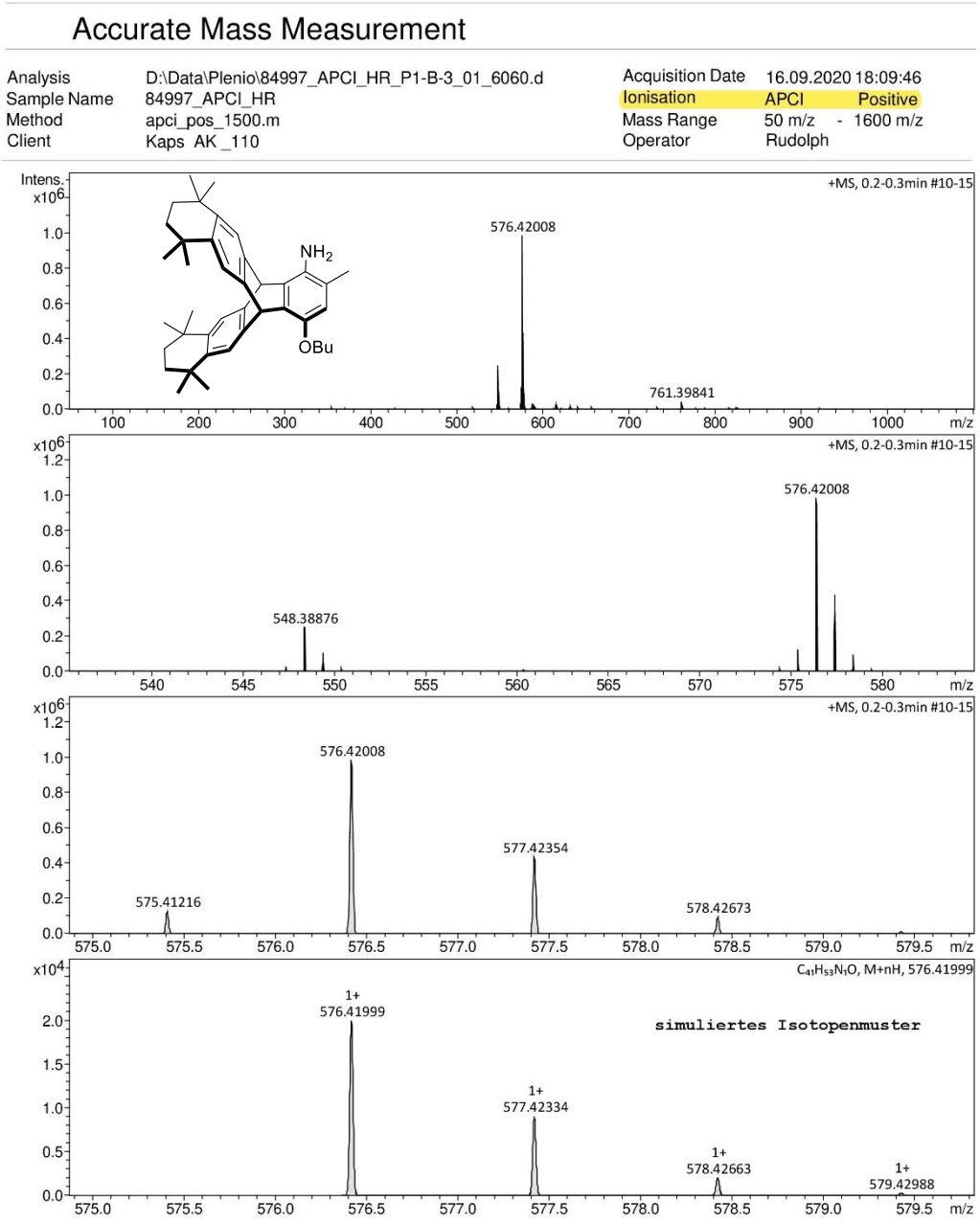
Analysis	D:\Data\Plenio\86732_ESI_HR_P1-D-2_01_11205.d	Acquisition Date	28.07.2021 11:58:46
Sample Name	86732_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 304-1	Operator	rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	468.32647	C33H42NO	468.32609	C33H41NO	0.38	-0.81	even	M+H	1+

Figure 252: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6ha**).

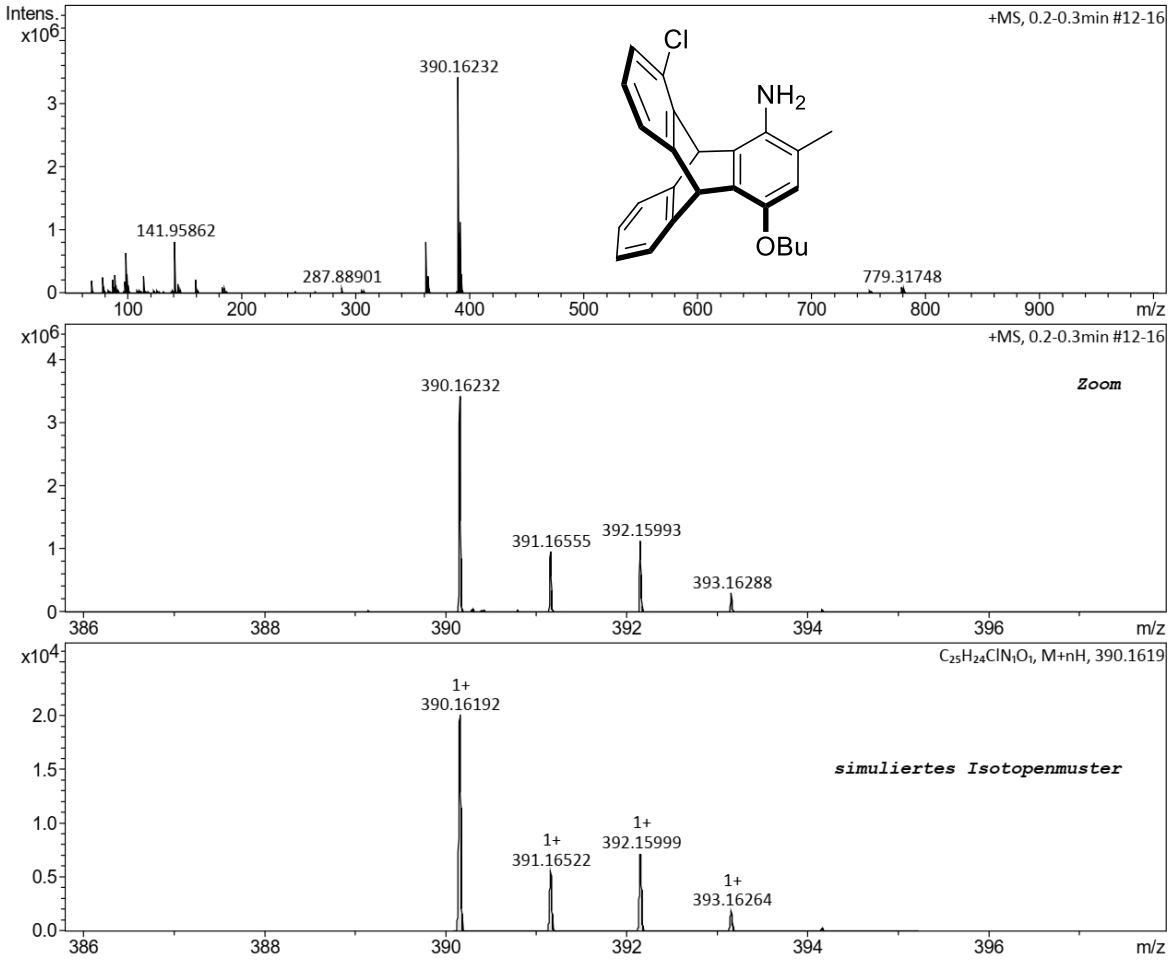


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	548.38876	C39H50NO	548.38869	C39H50NO	0.07	-0.12	even	M	1+
1	576.42008	C41H54NO	576.41999	C41H53NO	0.09	-0.15	even	M+H	1+

Figure 253: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6g**).

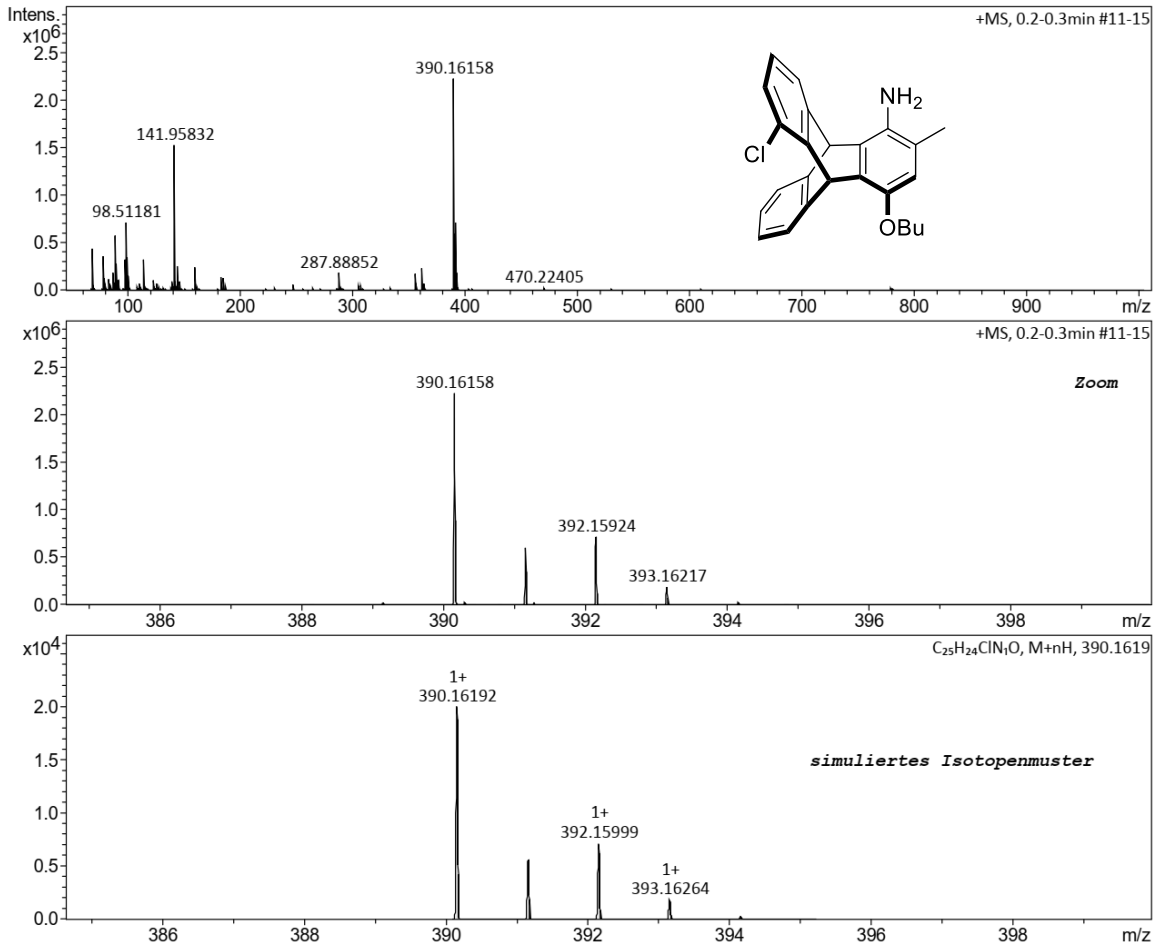
Analysis	D:\Data\Plenio\89644_ESI_HR_P1-E-1_01_20842.d	Acquisition Date	22.09.2022 11:37:36
Sample Name	89644_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Kaps AK TrpCl_NH2-1	Operator	rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	362.13091	362.13062	C23H21ClNO	M	C23H21ClNO	0.29	0.81	10.6	even	1+
1	390.16232	390.16192	C25H25ClNO	M+H	C25H24ClNO	0.40	1.02	14.0	even	1+

Figure 254: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6la**).

Analysis	D:\Data\Plenio\89645_ESI_HR_P1-E-2_01_20844.d	Acquisition Date	22.09.2022 12:04:33
Sample Name	89645_ESI_HR	Ionisation	ESI Positive
Method	as 50-1000 1hz.m	Mass Range	50 m/z - 1000 m/z
Client	Kaps AK TrpCl_NH2-2	Operator	rudolph

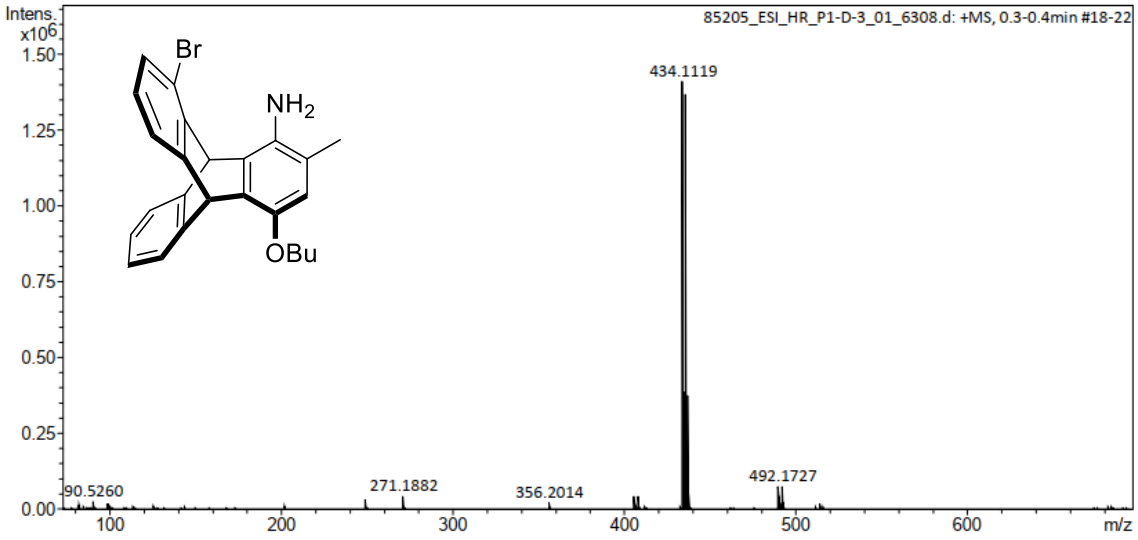


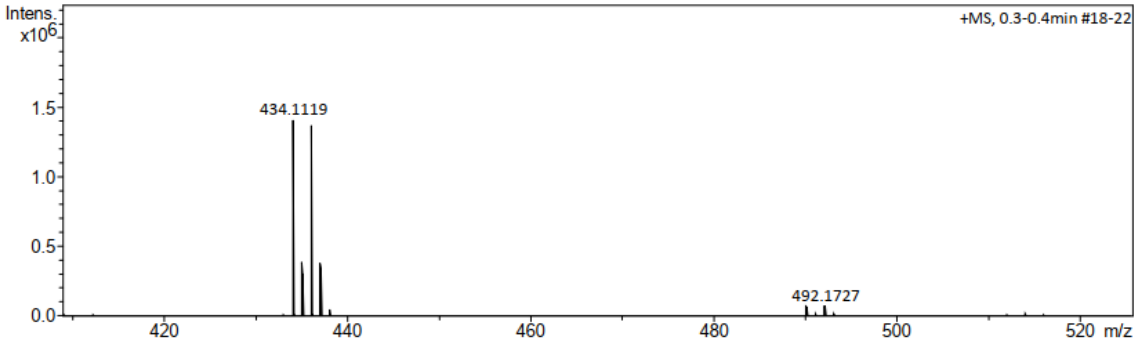
#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	390.16158	390.16192	C25H25ClNO	M+H	C25H24ClNO	0.34	0.87	17.1	even	1+
1	779.31581	779.31656	C50H49Cl2N2O2	2M+H	C25H24ClNO	0.75	0.96	52.1	even	1+

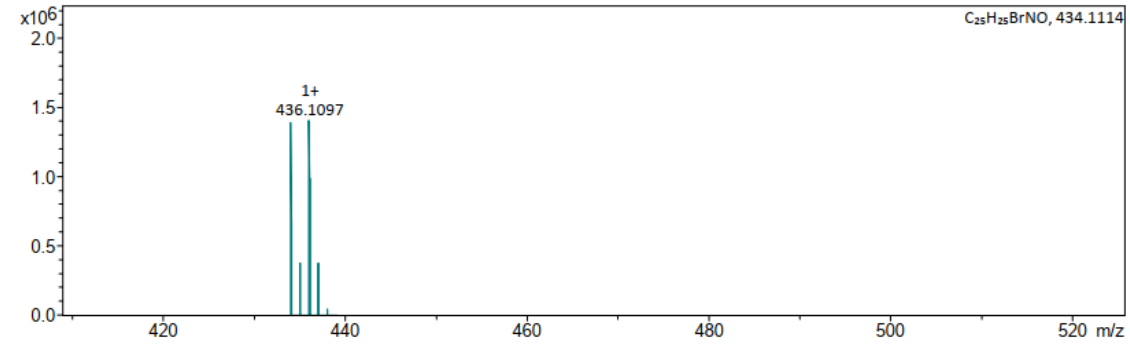
Figure 255: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6lb**).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\85205_ESI_HR_P1-D-3_01_6308.d	Acquisition Date	07.10.2020 14:55:22
Sample Name	85205_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _214A	Operator	1





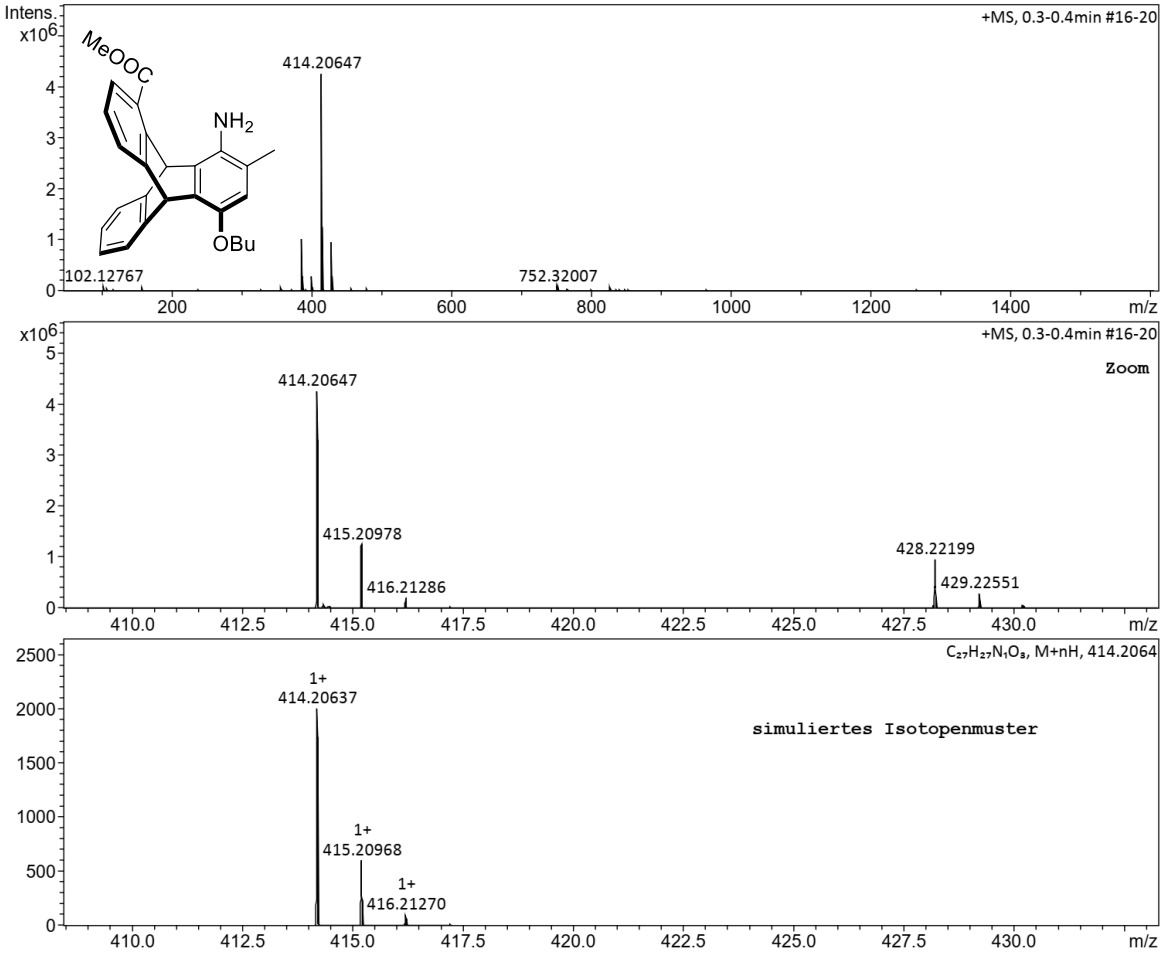


Accurate Mass Measurement

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
434.1119	1	C25H25BrNO	434.1114	-1.1	13.7	1	100.00	13.5	even	ok

Figure 256: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6ma**).

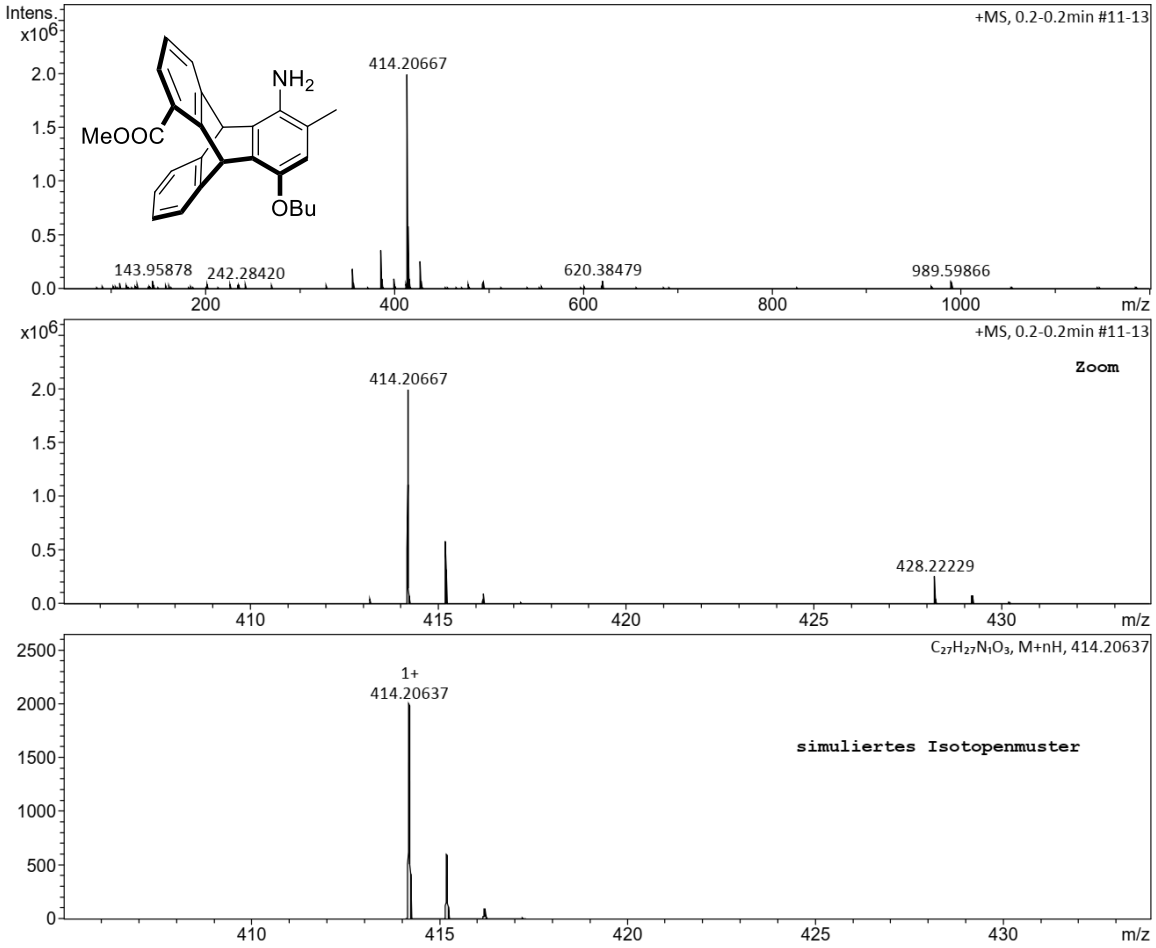
Analysis	D:\Data\Plenio\86749_ESI_HR_P1-D-1_01_11263.d	Acquisition Date	02.08.2021 16:02:00
Sample Name	86749_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 306-1Fr2	Operator	rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	414.20647	414.20637	C27H28NO3	M+H	C27H27NO3	0.09	0.23	3.9	even	1+
1	428.22199	428.22202	C28H30NO3	M+H	C28H29NO3	0.03	0.08	2.8	even	1+

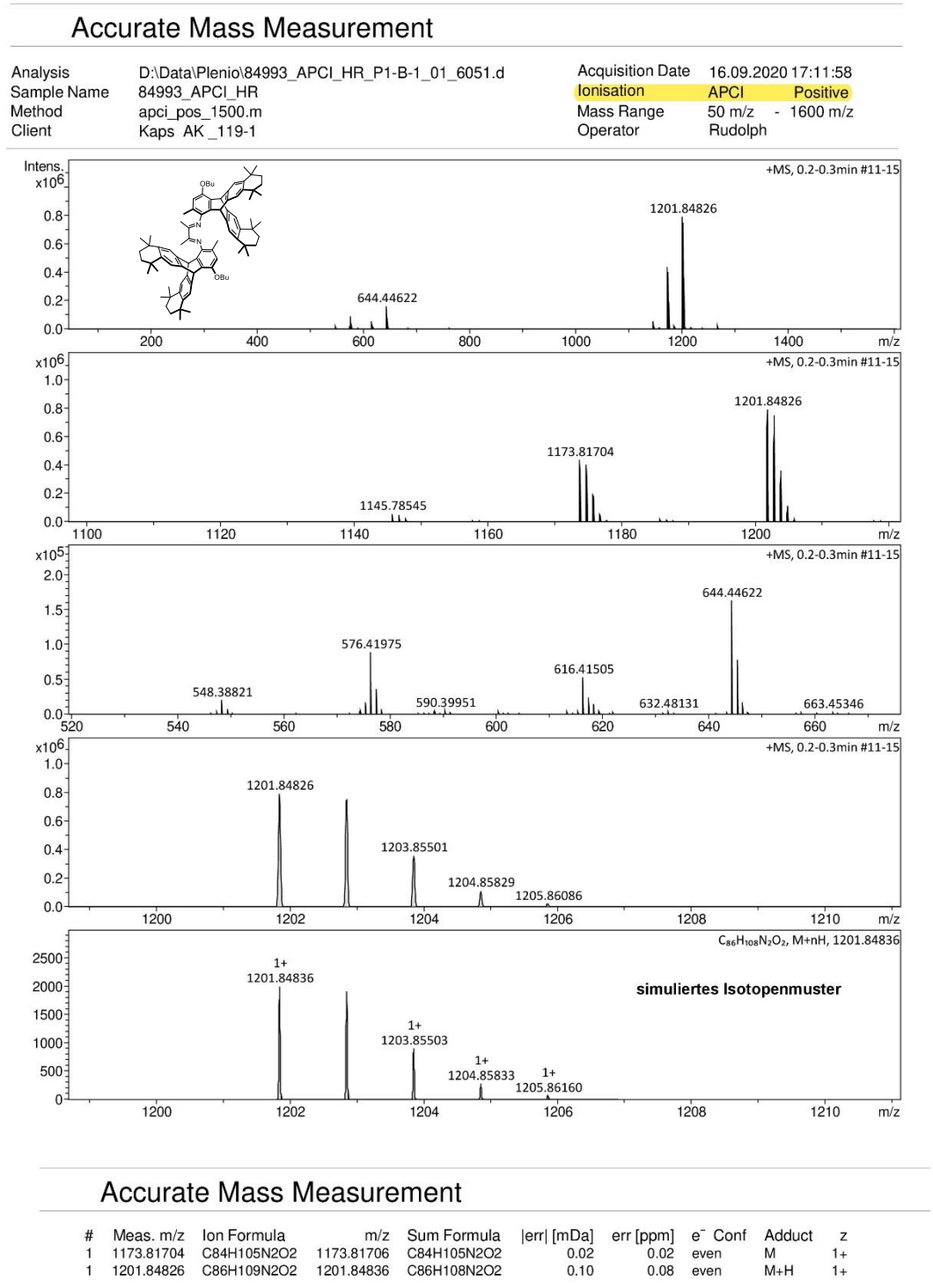
Figure 257: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6n**).

Analysis	D:\Data\Plenio\86968_ESI_HR_P1-D-1_01_12005.d	Acquisition Date	07.09.2021 18:29:07
Sample Name	86968_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 306-1s	Operator	rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	414.20667	414.20637	C27H28NO3	M+H	C27H27NO3	0.30	0.72	5.3	even	1+

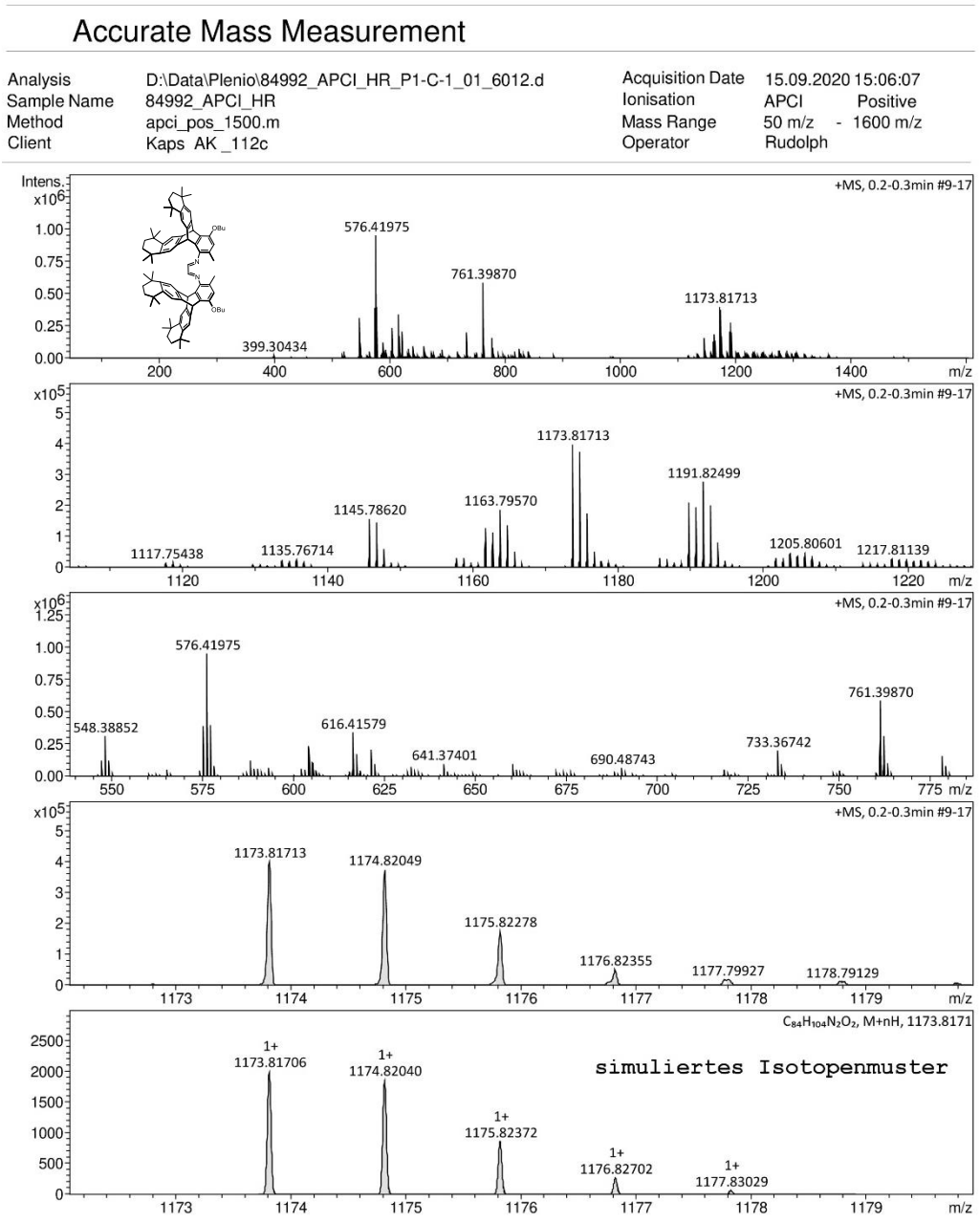
Figure 258: HRMS (ESI, positive mode) of denosylated aminotriptycene (**6n**).



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	1173.81704	C84H105N2O2	1173.81706	C84H105N2O2	0.02	0.02	even	M	1+
1	1201.84826	C86H109N2O2	1201.84836	C86H108N2O2	0.10	0.08	even	M+H	1+

Figure 259: HRMS (APCI, positive mode) of diamine (**11**).



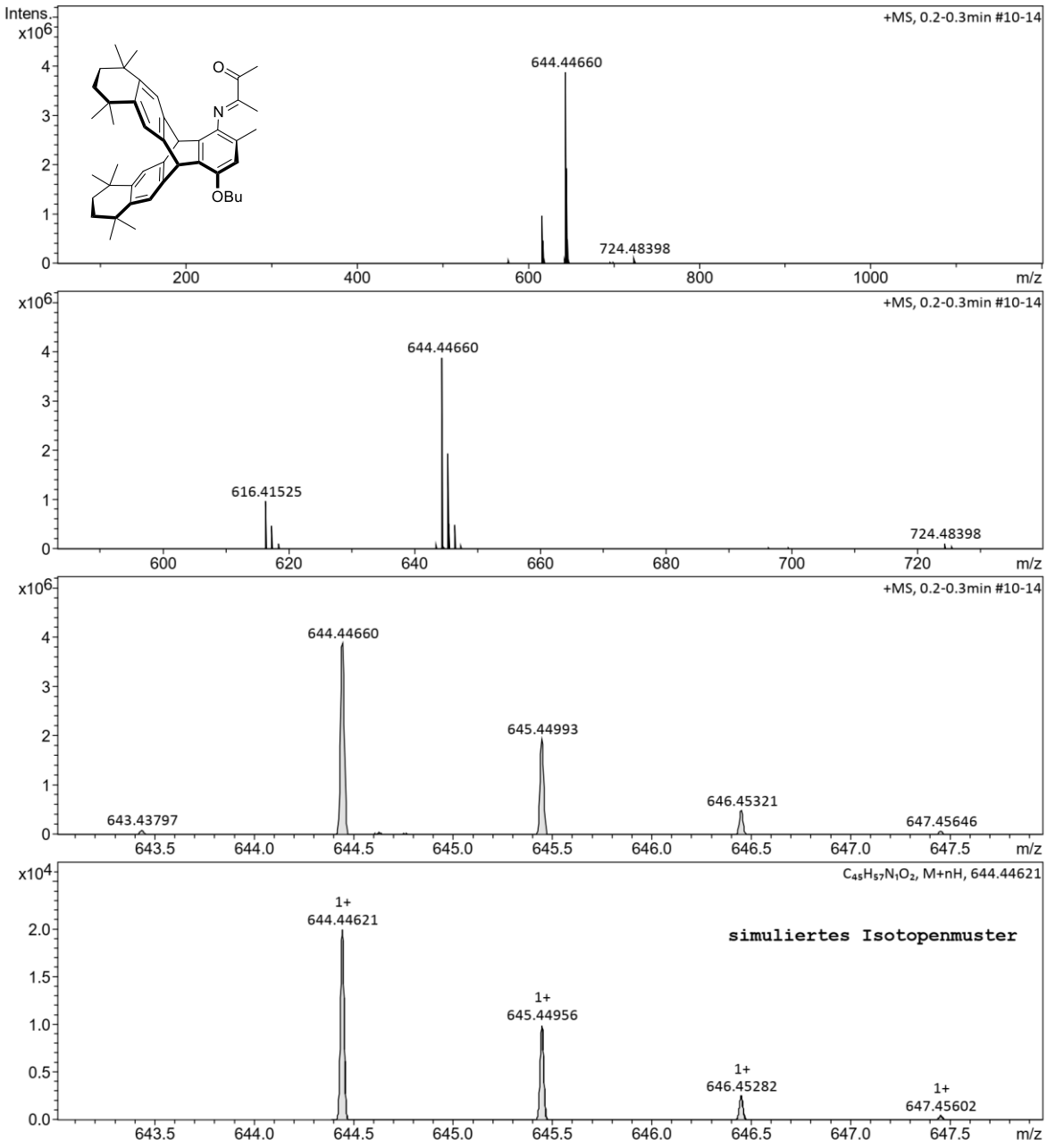
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	1145.78620	C82H101N2O2	1145.78576	C82H100N2O2	0.44	-0.38	even	M+H	1+
1	1173.81713	C84H105N2O2	1173.81706	C84H104N2O2	0.07	-0.06	even	M+H	1+

Figure 260: HRMS (APCI, positive mode) of diimine.

Accurate Mass Measurement

Analysis	D:\Data\Plenio\84991_APCI_HR_P1-B-1_01_6065.d	Acquisition Date	17.09.2020 11:20:42
Sample Name	84991_APCI_HR	Ionisation	APCI Positive
Method	apci_pos_1500.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _112_b	Operator	Rudolph

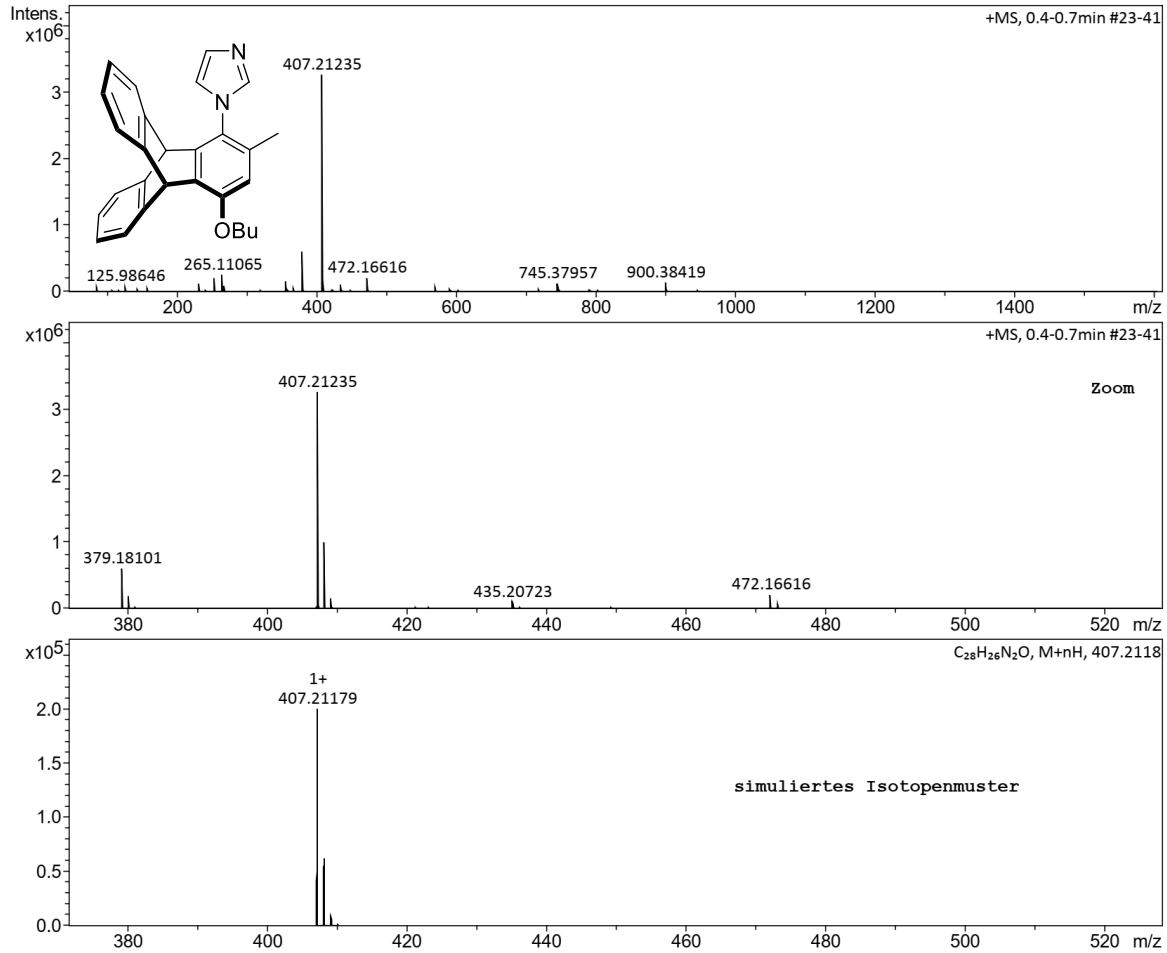


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e¯ Conf	Adduct	z
1	616.41525	C43H54NO2	616.41491	C43H54NO2	0.34	-0.56	even	M	1+
1	644.44660	C45H58NO2	644.44621	C45H57NO2	0.39	-0.60	even	M+H	1+

Figure 261: HRMS (APCI, positive mode) of monoimine.

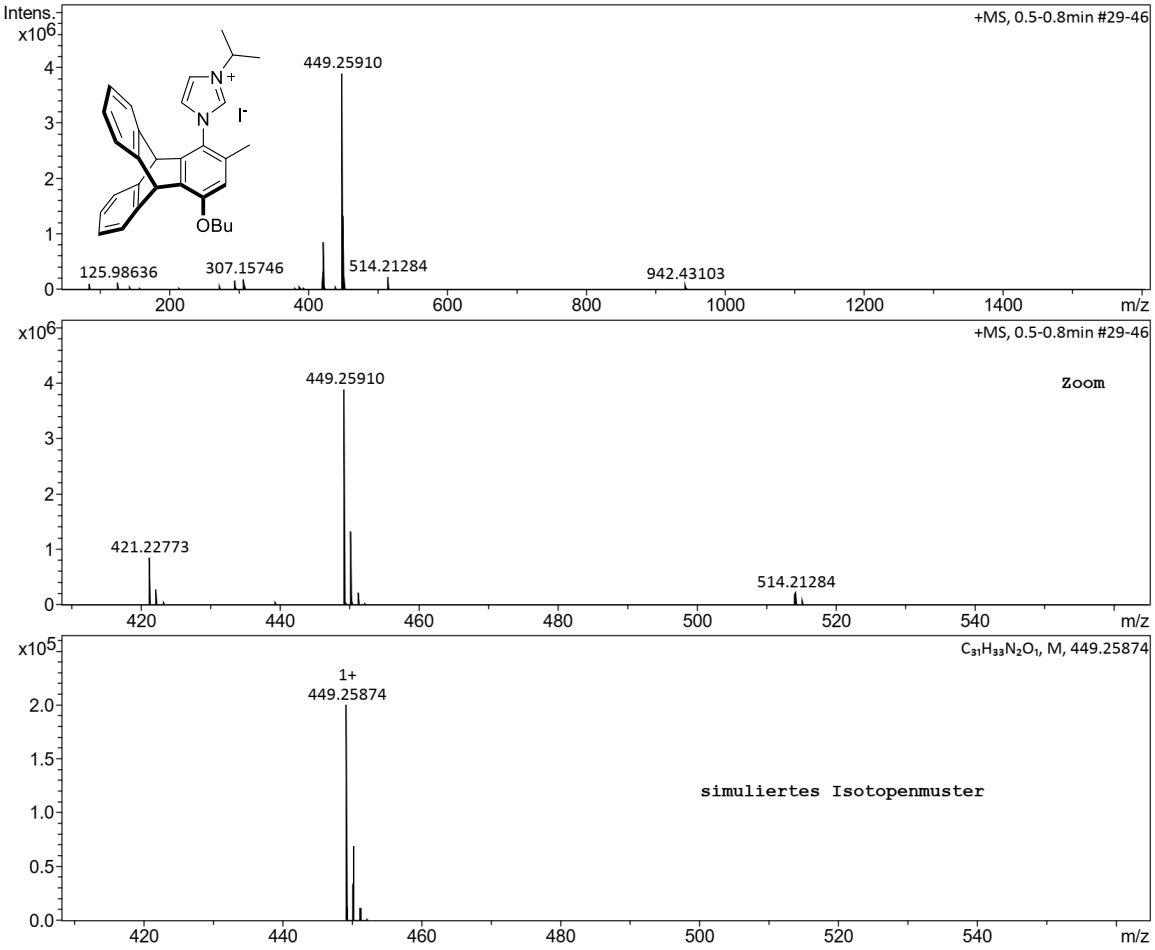
Analysis	D:\Data\Plenio\89089_ESI_HR_P1-D-3_01_18575.d	Acquisition Date	15.06.2022 09:54:27
Sample Name	89089_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 367. 1	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	407.21235	407.21179	C28H27N2O	M+H	C28H26N2O	0.56	1.37	3.7	even	1+

Figure 262: HRMS (ESI, positive mode) of imidazol (**7b**).

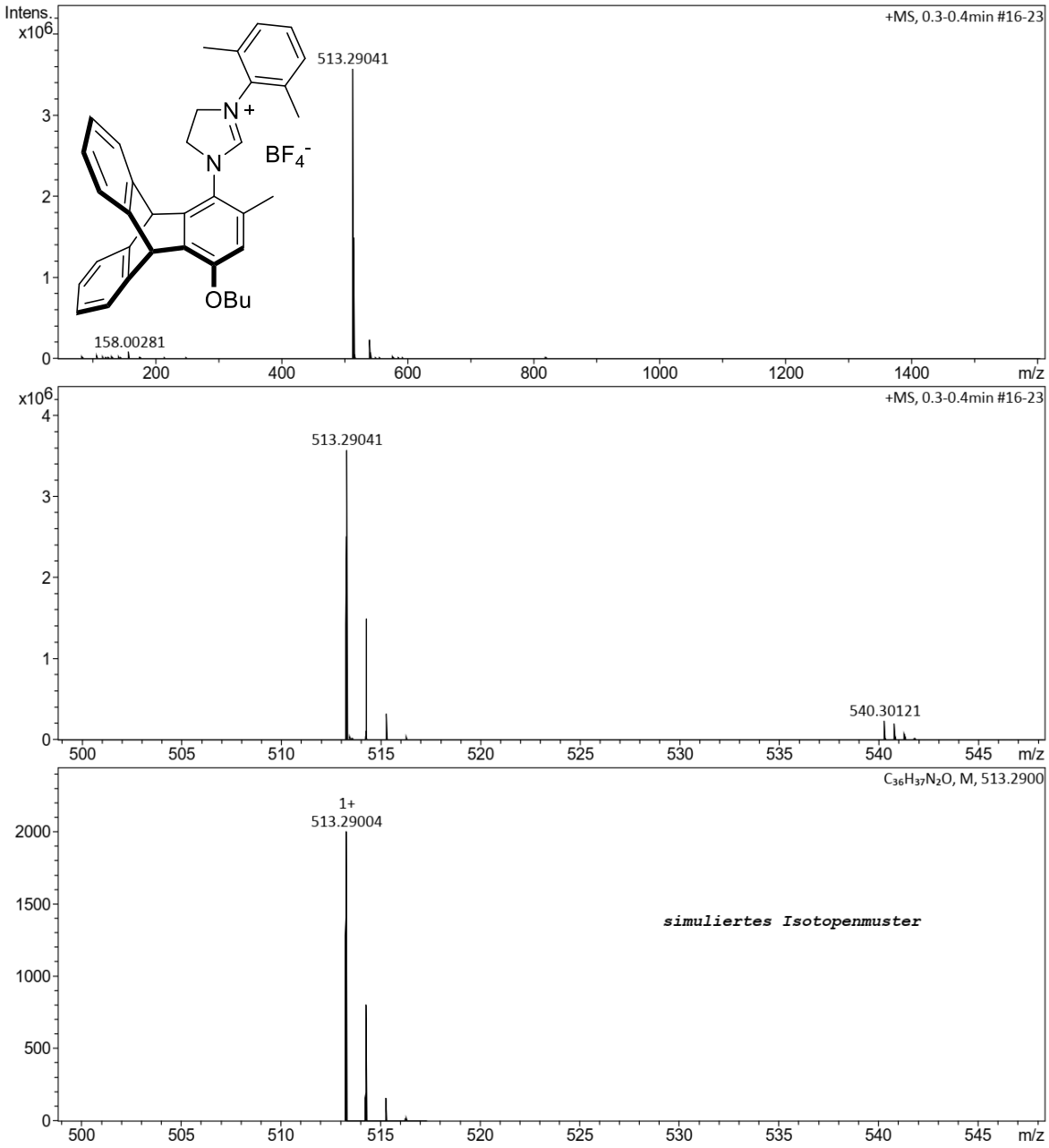
Analysis	D:\Data\Plenio\89088_ESI_HR_P1-D-2_01_18574.d	Acquisition Date	15.06.2022 09:49:34
Sample Name	89088_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 367. 1-2	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	421.22773	421.22744	C29H29N2O	M	C29H29N2O	0.29	0.68	1.1	even	1+
1	449.25910	449.25874	C31H33N2O	M	C31H33N2O	0.36	0.80	3.8	even	1+

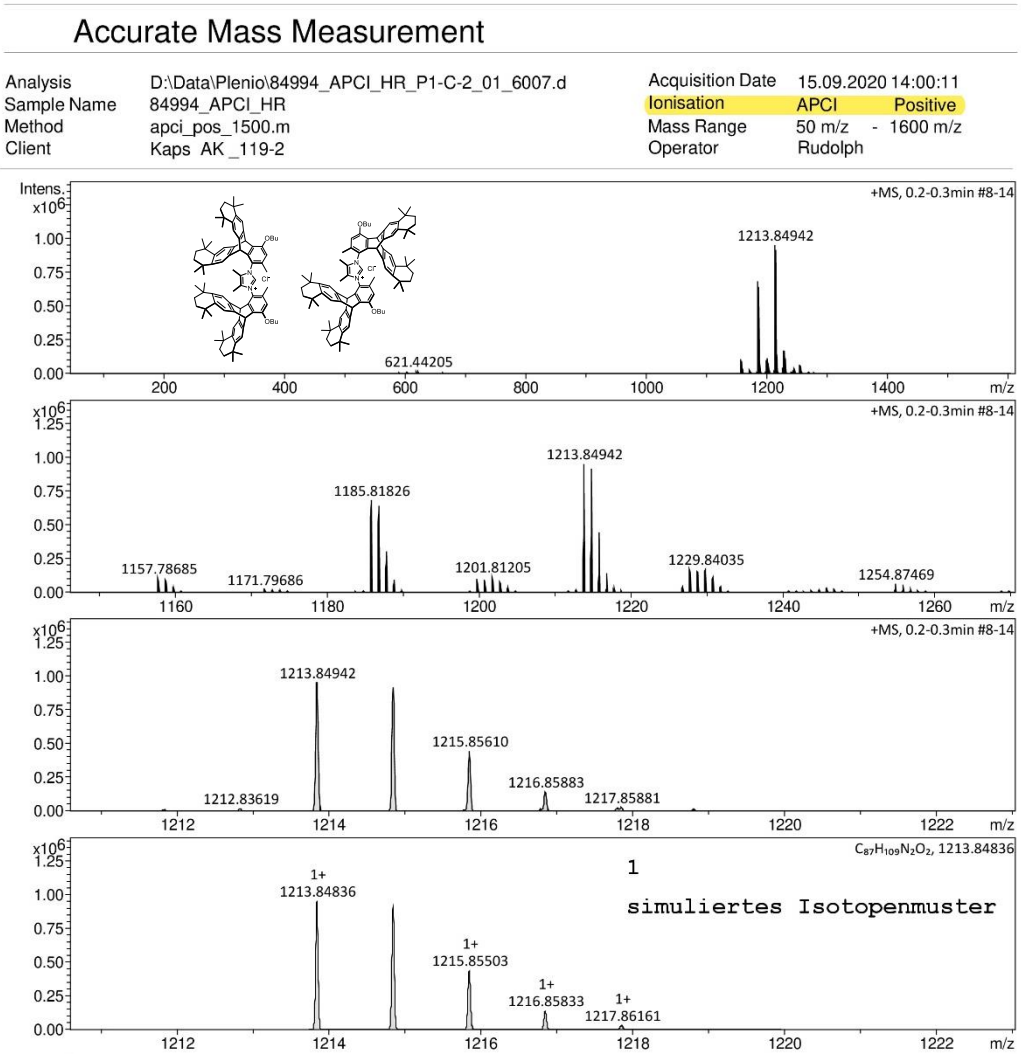
Figure 263: HRMS (ESI, positive mode) of imidazolium chloride (**8b**·HI).

Analysis	D:\Data\Plenio\90231_ESI_HR_P1-E-1_01_22240.d	Acquisition Date	17.11.2022 12:04:04
Sample Name	90160_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK_283	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	513.29041	513.29004	C36H37N2O	M	C36H37N2O	0.37	0.72	8.8	even	1+

Figure 264: HRMS (ESI, positive mode) of imidazolinium tetrafluoroborate (**10b**·HBF_4).



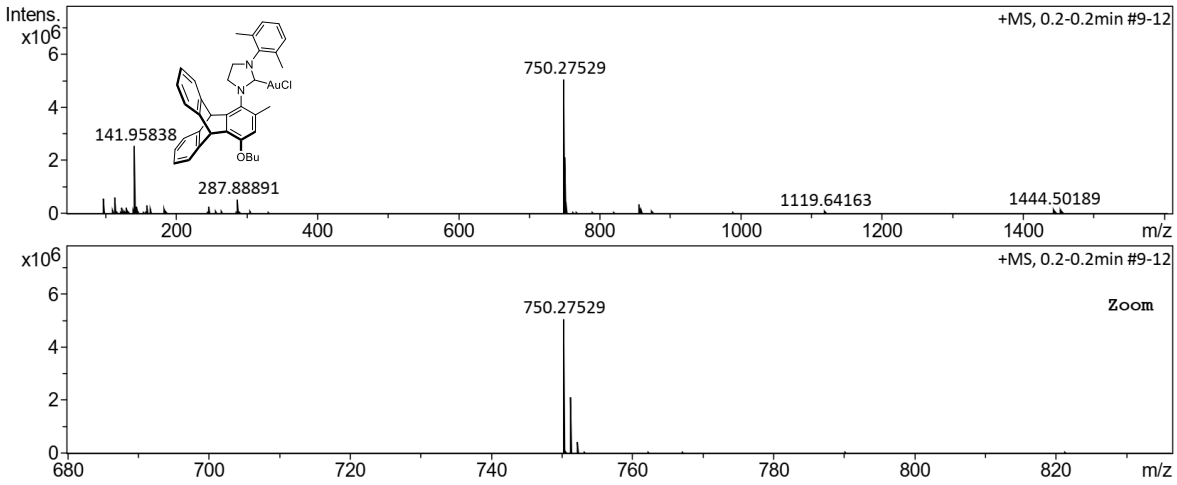
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	1185.81826	C85H105N2O2	1185.81706	C85H105N2O2	1.20	-1.01	even	M	1+
1	1213.84942	C87H109N2O2	1213.84836	C87H109N2O2	1.06	-0.88	even	M	1+

Figure 265: HRMS (APCI, positive mode) of imidazolium chloride (**12**·HCl).

Accurate Mass Measurement

Analysis	D:\Data\Plenio\87789_ESI_HR_P1-E-3_01_14876.d	Acquisition Date	20.01.2022 15:24:53
Sample Name	87789_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _331.2	Operator	Rudolph

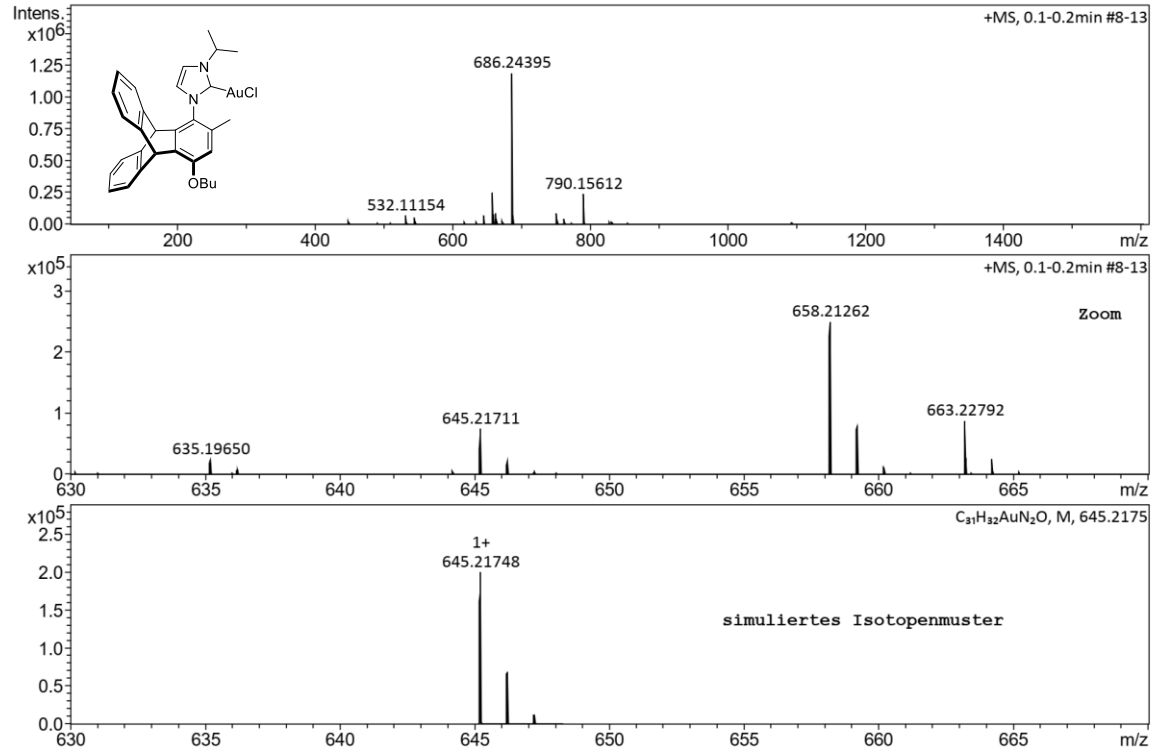


Accurate Mass Measurement

Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	|err| [mDa]	Score	Adduct	e¯ Conf
750.27529	C38H39AuN3O	750.27533	C38H38AuN3O	0.06	0.05	100.00	M+H	even

Figure 266: HRMS (ESI, positive mode) of *[AuCl(**10**)]* complex.

Analysis	D:\Data\Plenio\89113_APCI_HR_P1-E-1_01_18658.d		Acquisition Date	21.06.2022 12:32:44	
Sample Name	89113_APCI_HR		Ionisation	APCI	Positive
Method	apci_pos_1600.m		Mass Range	50 m/z	- 1600 m/z
Client	Kaps AK 369_Au		Operator	Rudolph	

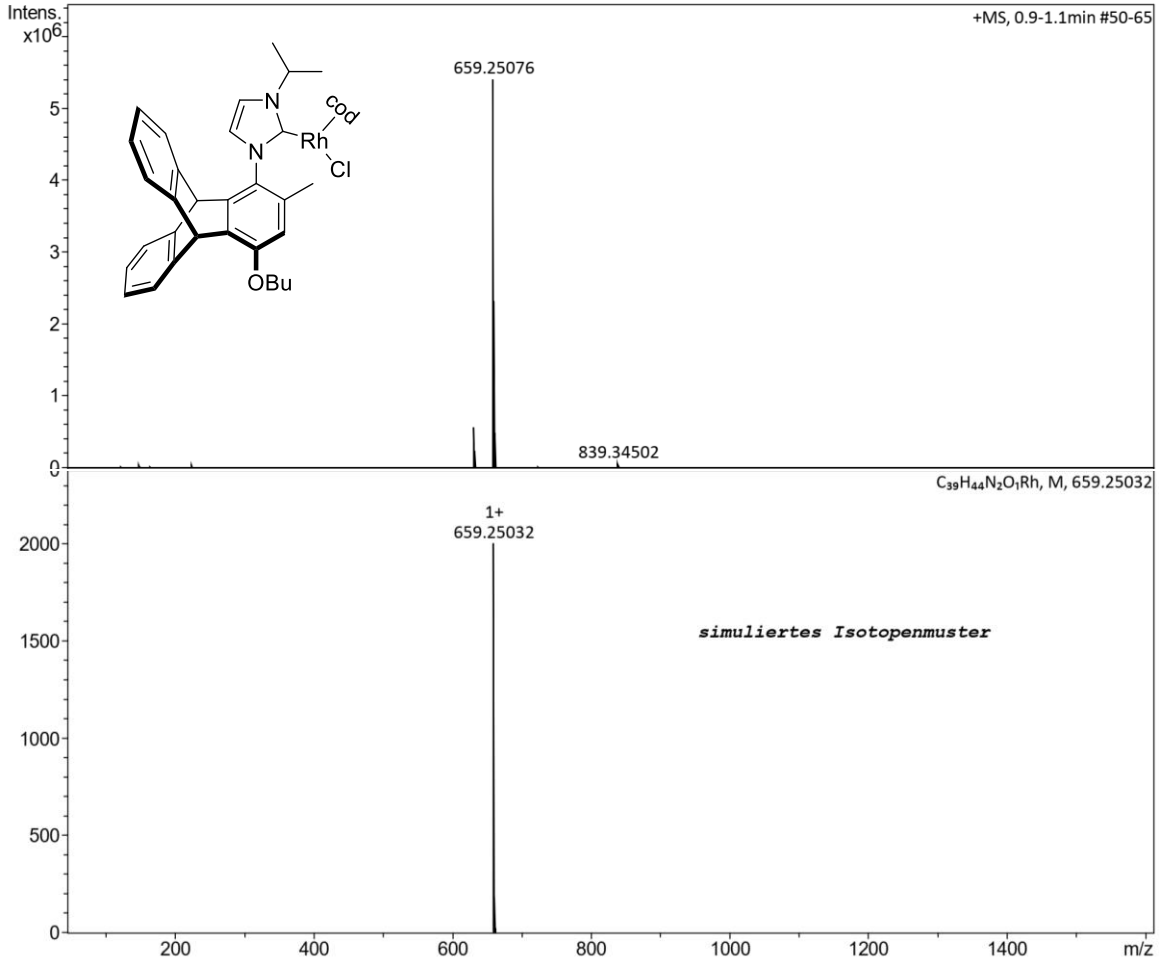


Summenformel Vorschläge

Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
686.24395	686.24403	C33H35AuN3O	M	C33H35AuN3O	0.09	0.13	3.1	even	1+
645.21711	645.21748	C31H32AuN2O	M	C31H32AuN2O	0.38	0.58	25.8	even	1+

Figure 267: HRMS (APCI, positive mode) of *[AuCl(**8b**)] complex.*

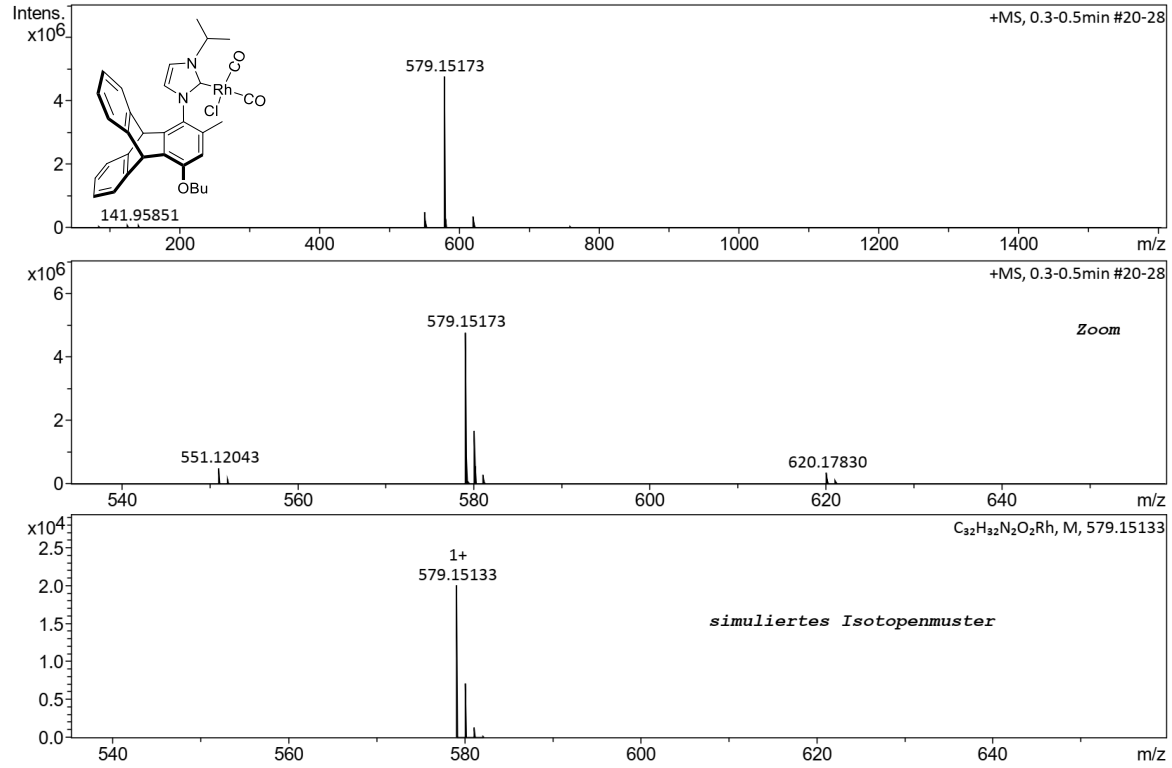
Analysis	D:\Data\Plenio\89517_ESI_HR_P1-E-1_01_20402.d	Acquisition Date	01.09.2022 17:40:51
Sample Name	89517_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _369_RClcod	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e¯ Conf	z
1	631.21934	631.21902	C37H40N2ORh	M	C37H40N2ORh	0.32	0.51	8.1	even	1+
1	659.25076	659.25032	C39H44N2ORh	M	C39H44N2ORh	0.44	0.67	3.3	even	1+

Figure 268: HRMS (ESI, positive mode) of *[RhCl(cod)(**8b**)] complex.*

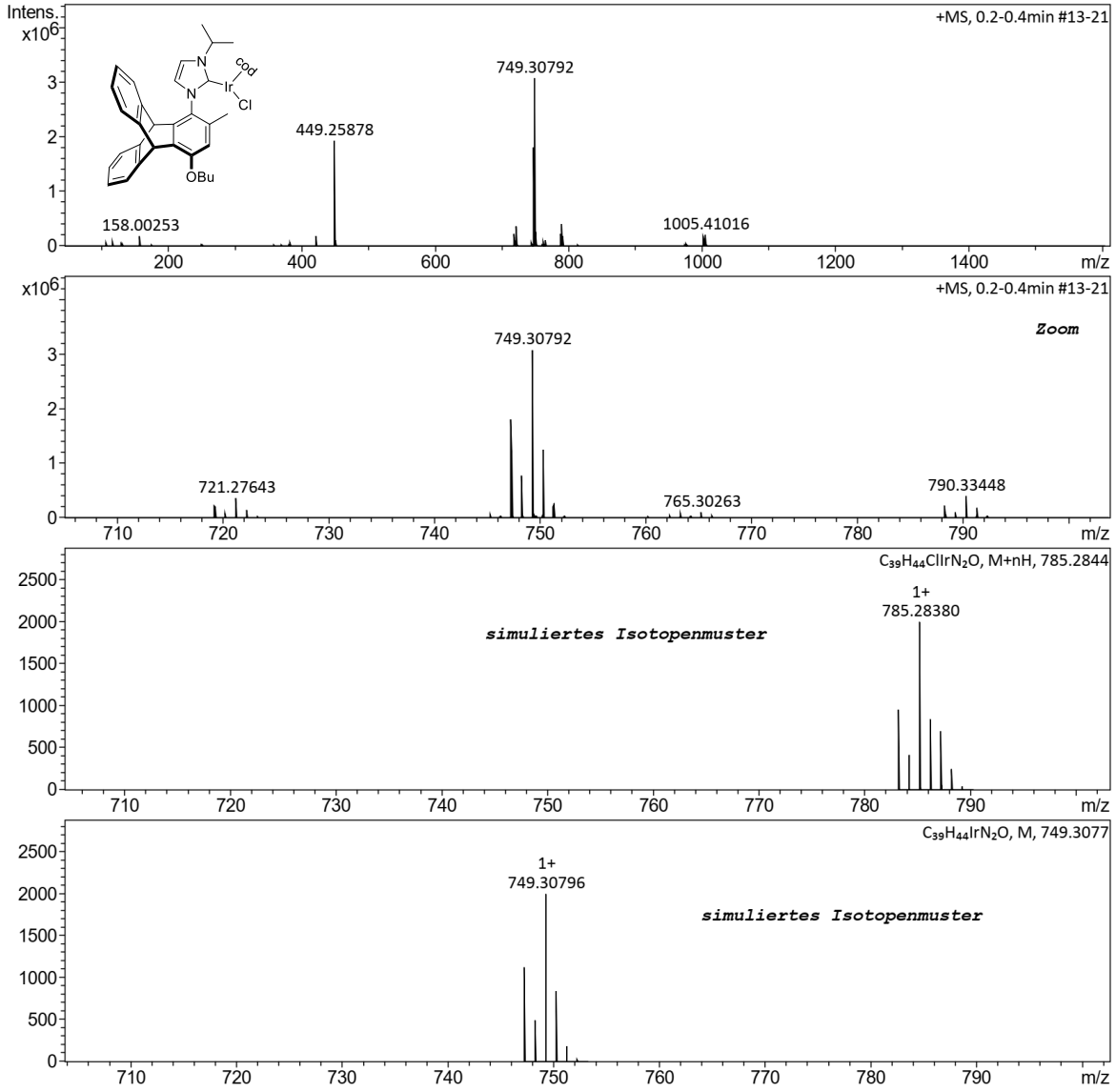
Analysis	D:\Data\Plenio\89740_ESI_HR_P1-E-2_01_20998.d	Acquisition Date	27.09.2022 11:19:58
Sample Name	89740_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 369.RhCO	Operator	rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	551.12043	551.12003	C30H28N2O2Rh	M	C30H28N2O2Rh	0.40	0.72	6.5	even	1+
1	579.15173	579.15133	C32H32N2O2Rh	M	C32H32N2O2Rh	0.40	0.68	3.5	even	1+
1	620.17830	620.17788	C34H35N3O2Rh	M	C34H35N3O2Rh	0.42	0.67	10.9	even	1+

Figure 269: HRMS (ESI, positive mode) of *[RhCl(CO)$_2$(**8b**)] complex.*

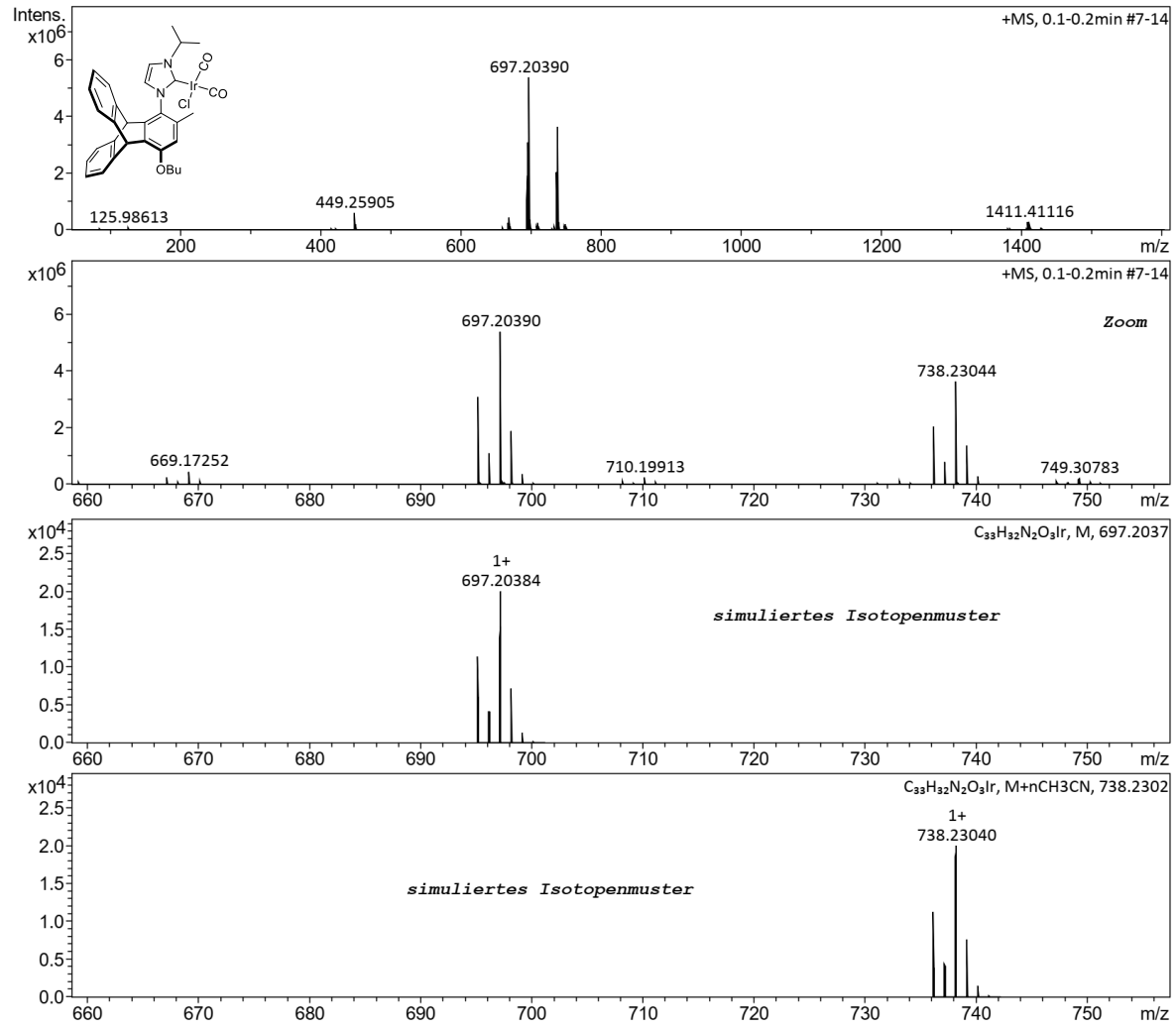
Analysis	D:\Data\Plenio\89505_ESI_HR_P1-E-1_01_20245.d	Acquisition Date	29.08.2022 18:03:38
Sample Name	89505_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _369_IrClcod	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e¯ Conf	z
1	721.27643	721.27644	C37H40IrN2O	M	C37H40IrN2O	0.21	0.29	16.6	even	1+
1	749.30792	749.30774	C39H44IrN2O	M	C39H44IrN2O	0.04	0.06	9.9	even	1+

Figure 270: HRMS (ESI, positive mode) of *[IrCl(cod)(**8b**)] complex.*

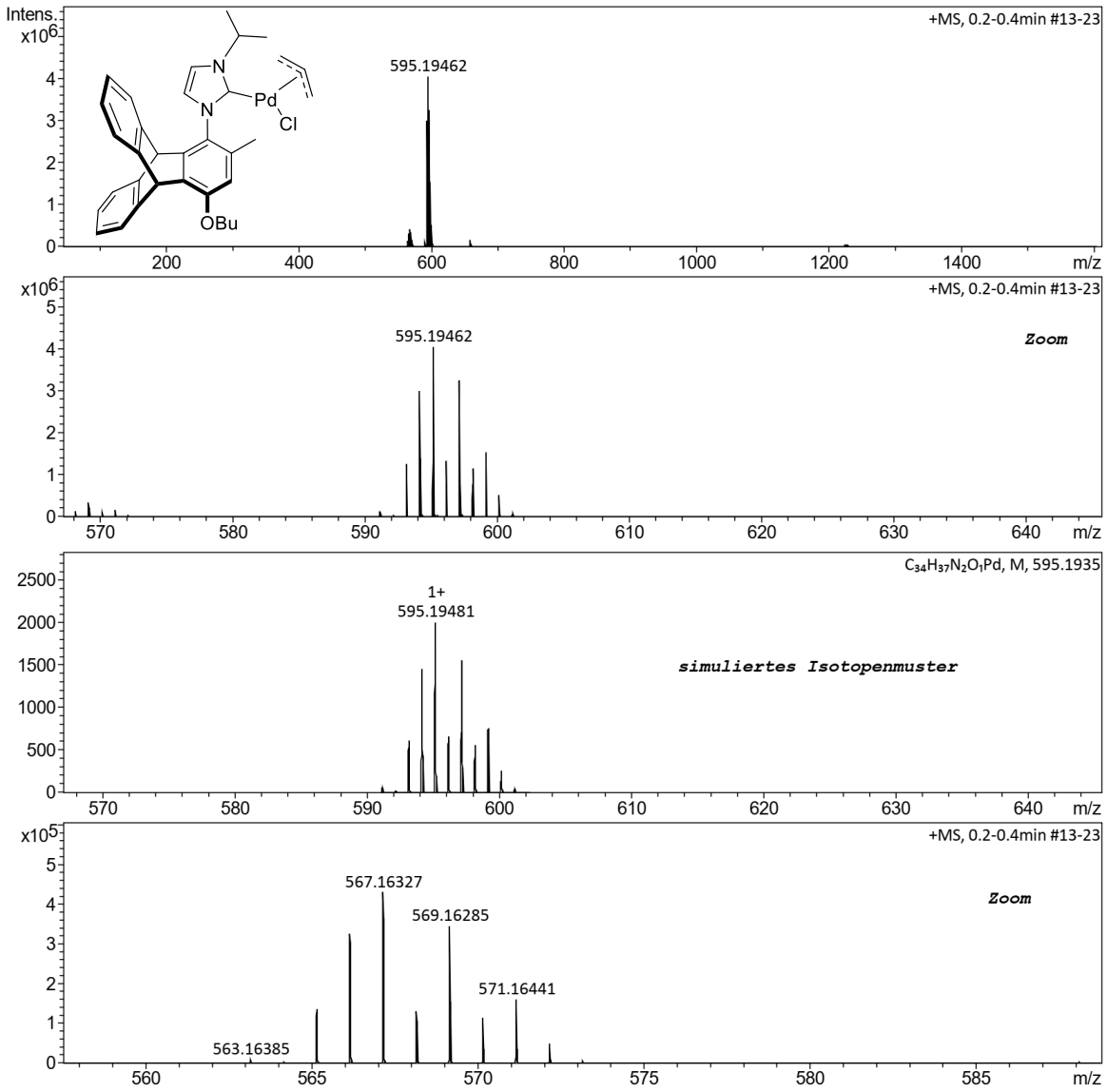
Analysis	D:\Data\Plenio\89739_ESI_HR_P1-E-1_01_20997.d	Acquisition Date	27.09.2022 11:14:53
Sample Name	89739_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 369.IrCO	Operator	rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	697.20390	697.20367	C33H32IrN2O3	M	C33H32IrN2O3	0.06	0.09	4.0	even	1+
1	738.23044	738.23022	C35H35IrN3O3	M	C35H35IrN3O3	0.04	0.05	1.7	even	1+

Figure 271: HRMS (ESI, positive mode) of *[IrCl(CO)$_2$(**8b**)] complex.*

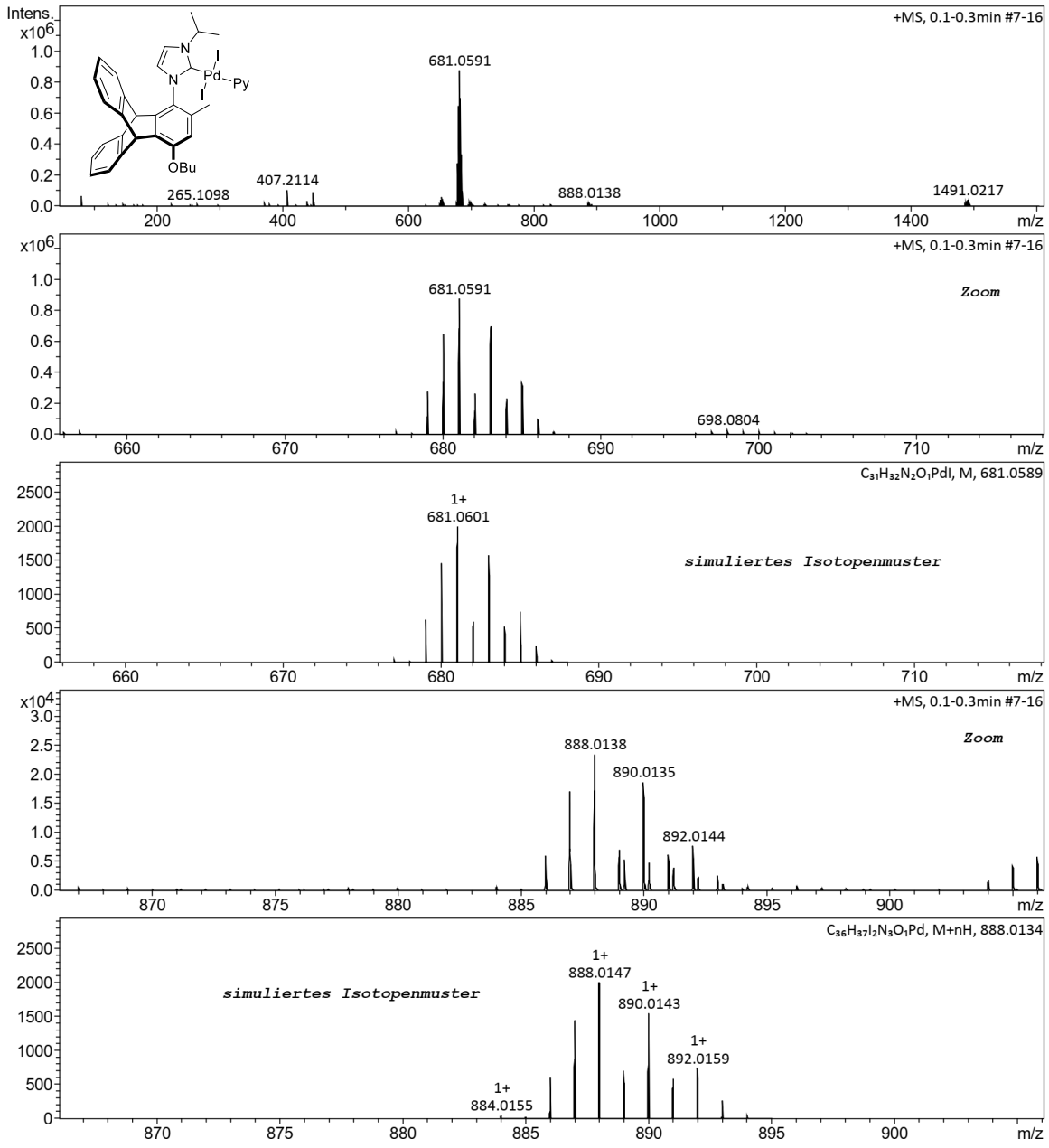
Analysis	D:\Data\Plenio\89561_ESI_HR_P1-E-2_01_20524.d	Acquisition Date	07.09.2022 15:37:40
Sample Name	89561_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _369_PdClAllyl	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	567.16327	567.16223	C32H33N2OPd	M	C32H33N2OPd	0.18	0.31	10.4	even	1+
1	595.19462	595.19353	C34H37N2OPd	M	C34H37N2OPd	0.19	0.32	7.7	even	1+

Figure 272: HRMS (ESI, positive mode) of *[Rh(allyl)Cl(**8b**)] complex.*

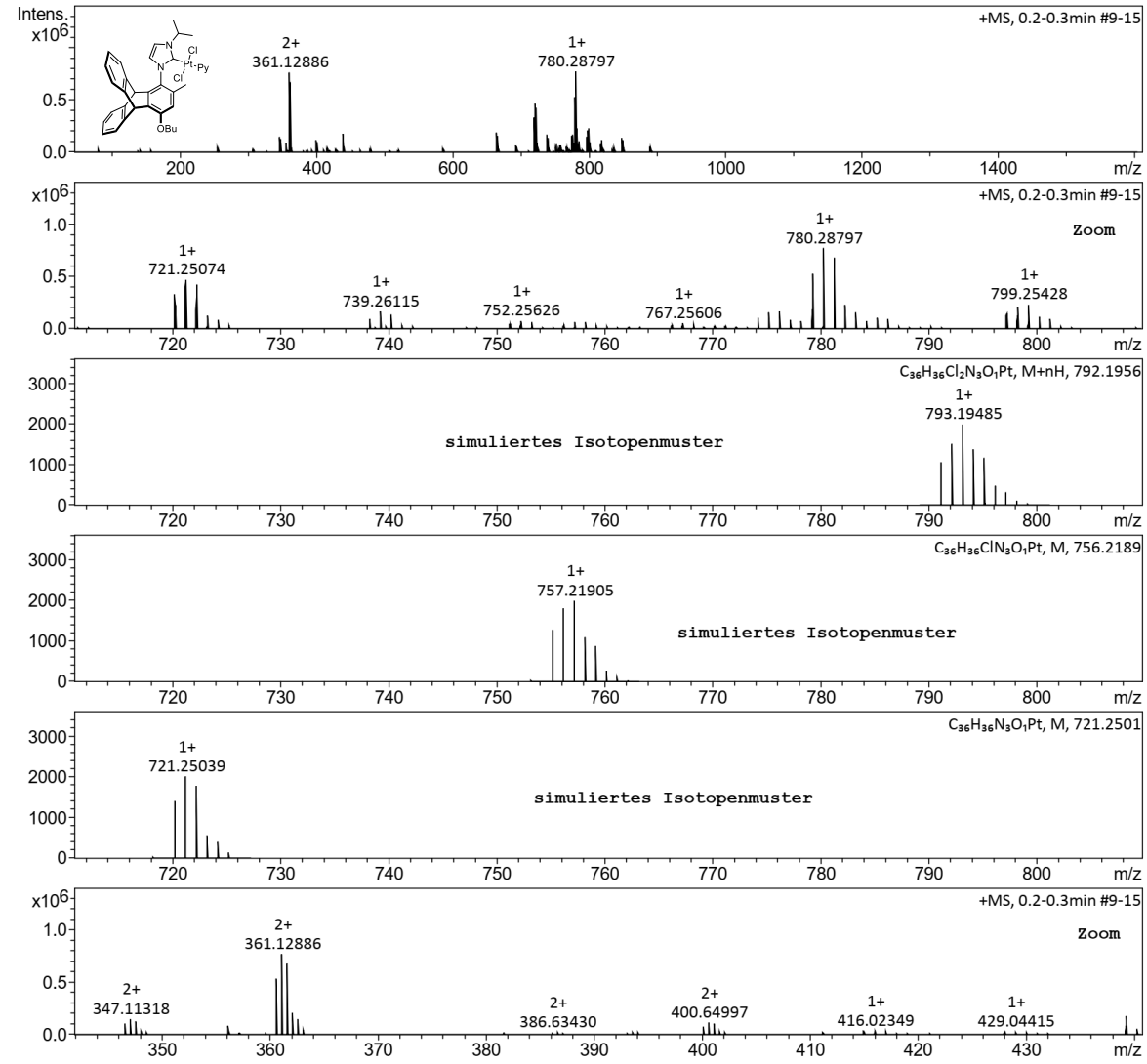
Analysis	D:\Data\Plenio\89397_ESI_HR_P1-E-1_01_19837.d	Acquisition Date	16.08.2022 10:06:39
Sample Name	89397_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK _369_Pdpy	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1	681.0591	681.0589	C31H32IN2OPd	M	C31H32IN2OPd	1.0	1.4	4.8	even	1+
1	888.0138	888.0134	C36H38I2N3OPd	M+H	C36H37I2N3OPd	1.0	1.1	31.3	even	1+

Figure 273: HRMS (ESI, positive mode) of *[PdI$_2$(**8b**)py] complex.*

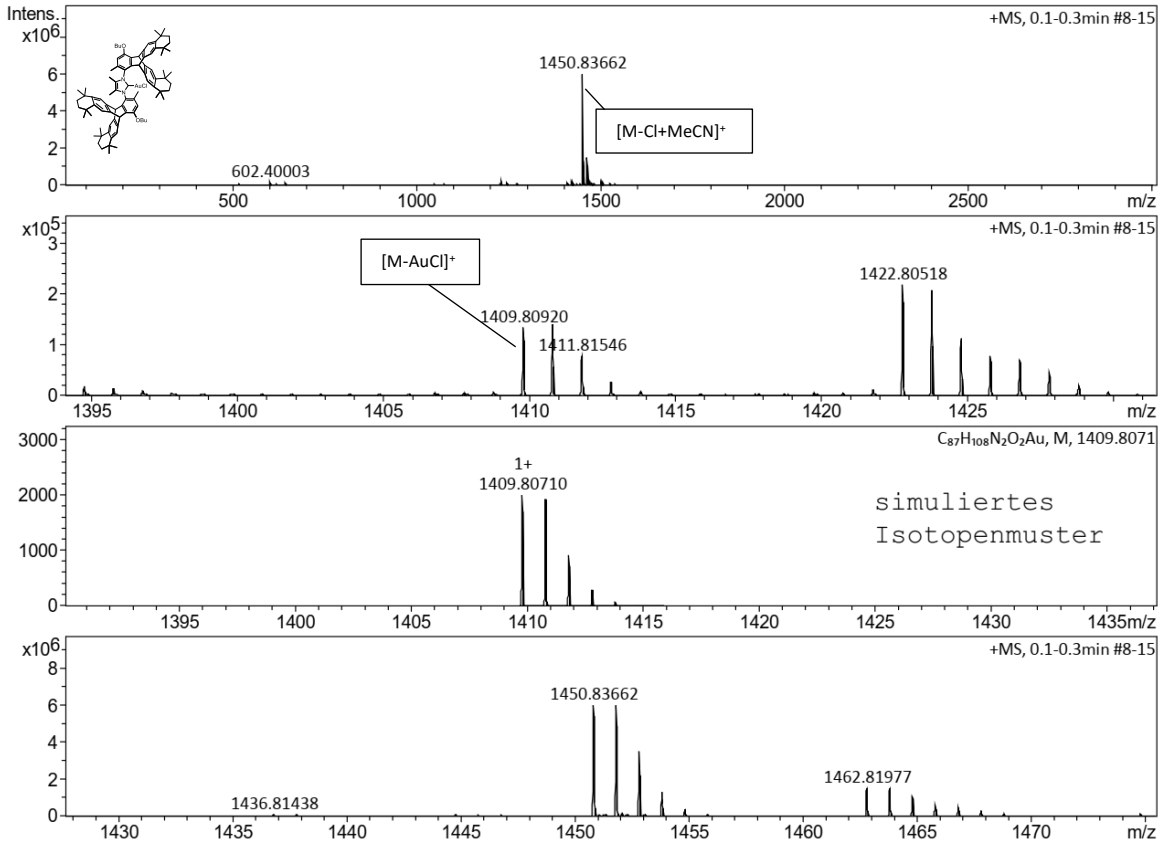
Analysis	D:\Data\Plenio\89248_ESI_HR_P1-E-1_01_19202.d	Acquisition Date	18.07.2022 19:01:55
Sample Name	89248_ESI_HR	Ionisation	ESI Positive
Method	as 50-1600 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 369.3_PtPy	Operator	Rudolph



#	Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e¯ Conf	z
1	361.12886	361.12868	C36H37N3OPt	M	C36H37N3OPt	0.03	0.08	3.8	even	2+
1	721.25074	721.25008	C36H36N3OPt	M	C36H36N3OPt	0.35	0.49	6.9	even	1+
1	739.26115	739.26064	C36H38N3O2Pt	M	C36H38N3O2Pt	0.19	0.25	49.4	even	1+
1	780.28797	780.28719	C38H41N4O2Pt	M	C38H41N4O2Pt	0.46	0.59	27.6	even	1+

Figure 274: HRMS (ESI, positive mode) of *[$PtCl_2$(**8b**)py] complex.*

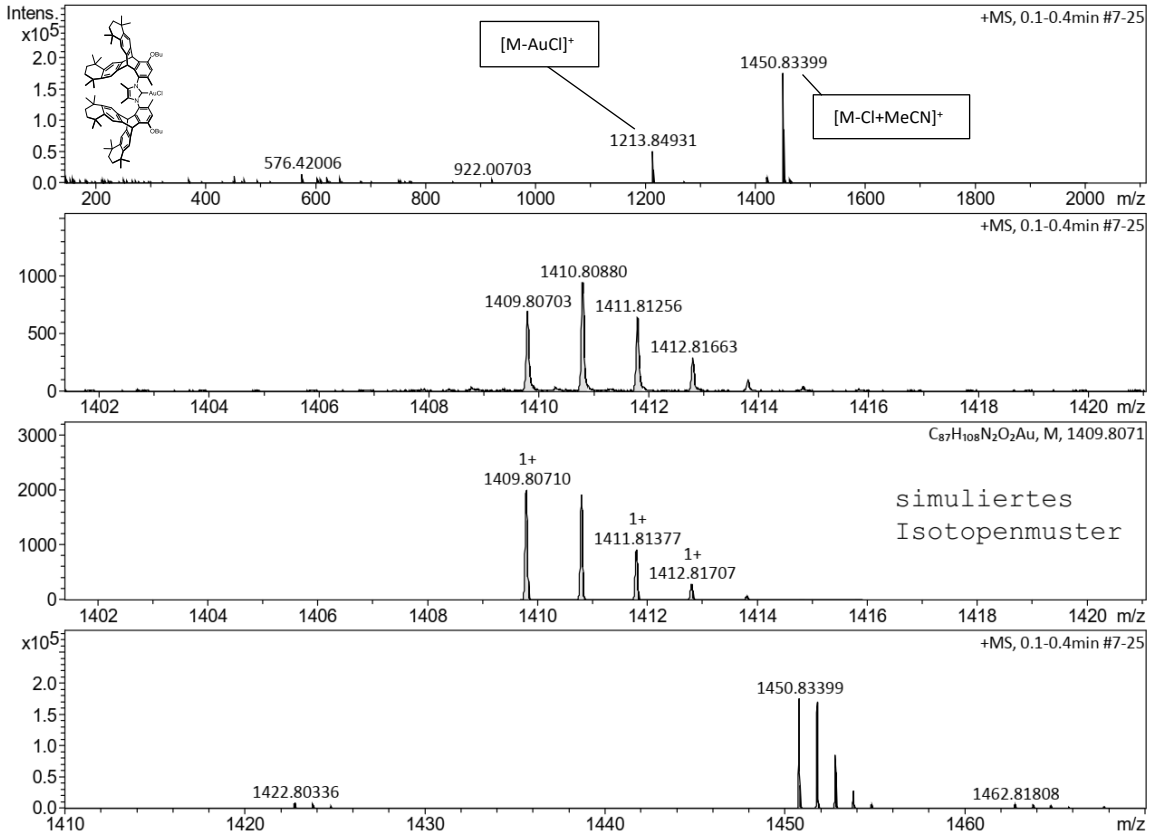
Analysis	D:\Data\Plenio\90672_APCI_HR_P1-E-5_01_23340.d	Acquisition Date	24.01.2023 17:39:01
Sample Name	90672_APCI_HR	Ionisation	APCI Positive
Method	apci_pos.m	Mass Range	50 m/z - 3000 m/z
Client	Kaps AK377 AuCl-Isomer 1	Operator	ms



Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e¯ Conf	z
1409.80920	1409.80710	C87H108AuN2O2	M	C87H108AuN2O2	2.10	1.49	57.0	even	1+
1450.83662	1450.83365	C89H111AuN3O2	M	C89H111AuN3O2	2.98	2.05	54.7	even	1+

Figure 275: HRMS (APCI, positive mode) of *[AuCl(anti-**12**)] complex* - Isomer 1.

Analysis	D:\Data\Plenio\90658_ESI_HR_P1-E-1_01_23348.d	Acquisition Date	24.01.2023 18:33:23
Sample Name	90658_ESI_HR	Ionisation	ESI Positive
Method	as 50-2000 1hz.m	Mass Range	50 m/z - 2000 m/z
Client	Kaps AK377.AuCl-Isomer2	Operator	ms



Meas. m/z	m/z	Ion Formula	Adduct	Sum Formula	|err| [mDa]	|err| [ppm]	mSigma	e⁻ Conf	z
1409.80703	1409.80710	C87H108AuN2O2	M	C87H108AuN2O2	0.08	0.05	174.9	even	1+
1450.83399	1450.83365	C89H111AuN3O2	M	C89H111AuN3O2	0.34	0.24	7.5	even	1+

Figure 276: HRMS (ESI, positive mode) of *[AuCl(syn-**12**)] complex* - Isomer 2.

4. IR spectroscopy

IR spectra of the metal carbonyls were recorded on a Fisher Scientific Nicolet 6700 FT-IR spectrometer in methylen chloride solution using the ATR method with germanium prism in the corresponding accessory.

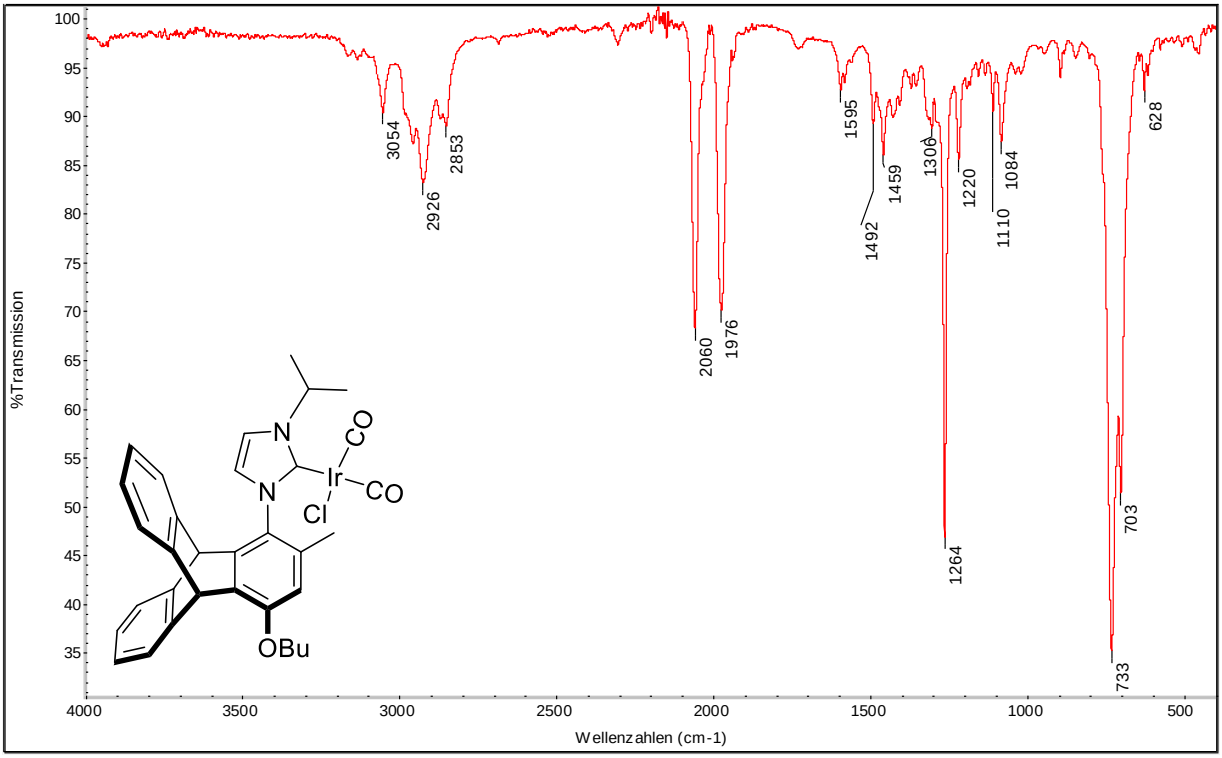


*Figure 277: IR spectrum of [IrCl(CO)$_2$(**8b**)] complex.*

IrCl(CO)$_2$-Complex	***ν*(CO) [cm^{-1}] measured**	***ν*(CO) [cm^{-1}] - corrected**	***ν*(CO) [cm^{-1}] *average***	***TEP***
IMes	2061 | 1974	2067 | 1980	2023.0	2050.7
[(**TrpNHC**)IrCl(CO)$_2$]	2060 | 1976	2066 | 1982	2023.5	2051.1

TEP = 0,8475 · *ν*(CO) + 336,2

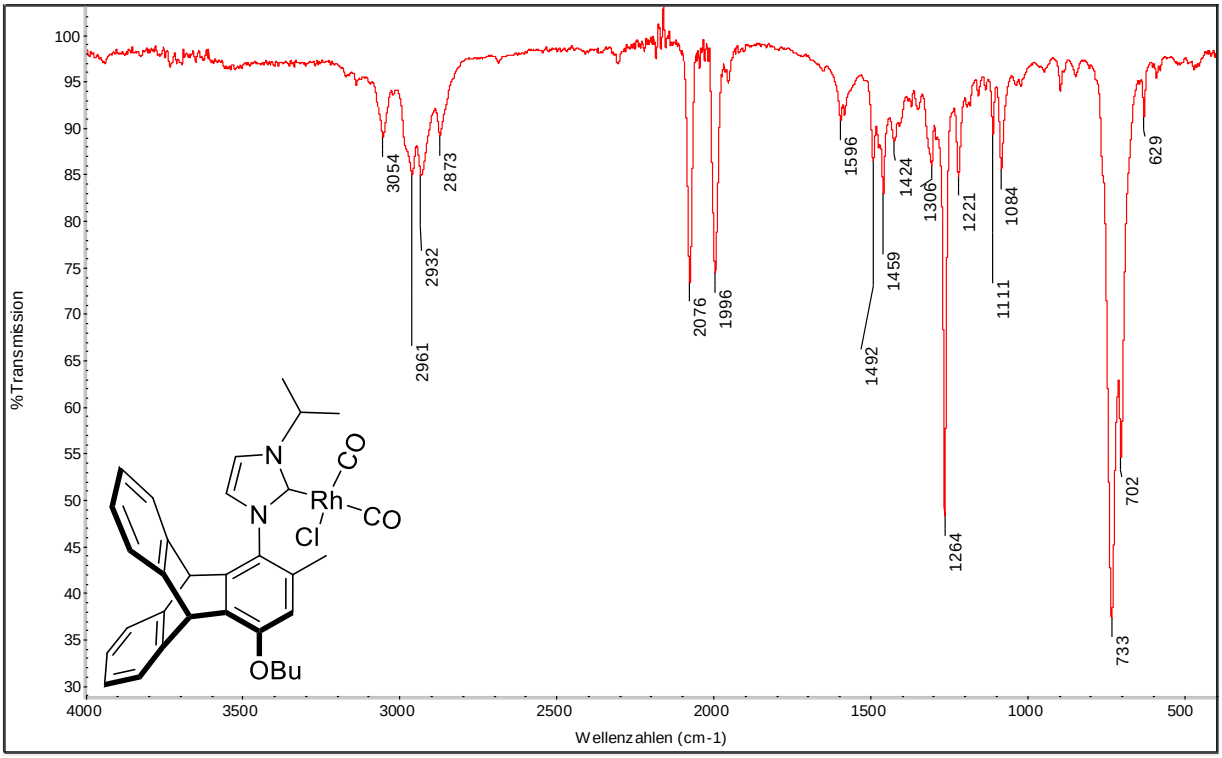


*Figure 278: IR spectrum of [RhCl(CO)$_2$(**8b**)] complex.*

RhCl(CO)$_2$-Complex	***v*(CO) [cm^{-1}] measured**	***v*(CO) [cm^{-1}] - corrected**	***v*(CO) [cm^{-1}] *average***	***TEP***
IMes	2081 | 1996	2087 | 2002	2044.0	2055.4
[(**TrpNHC**)RhCl(CO)$_2$]	2076 | 1996	2082 | 2002	2041.5	2054.4

TEP = 0,8001 · *v*(CO) + 420

5. Cyclic voltammetry

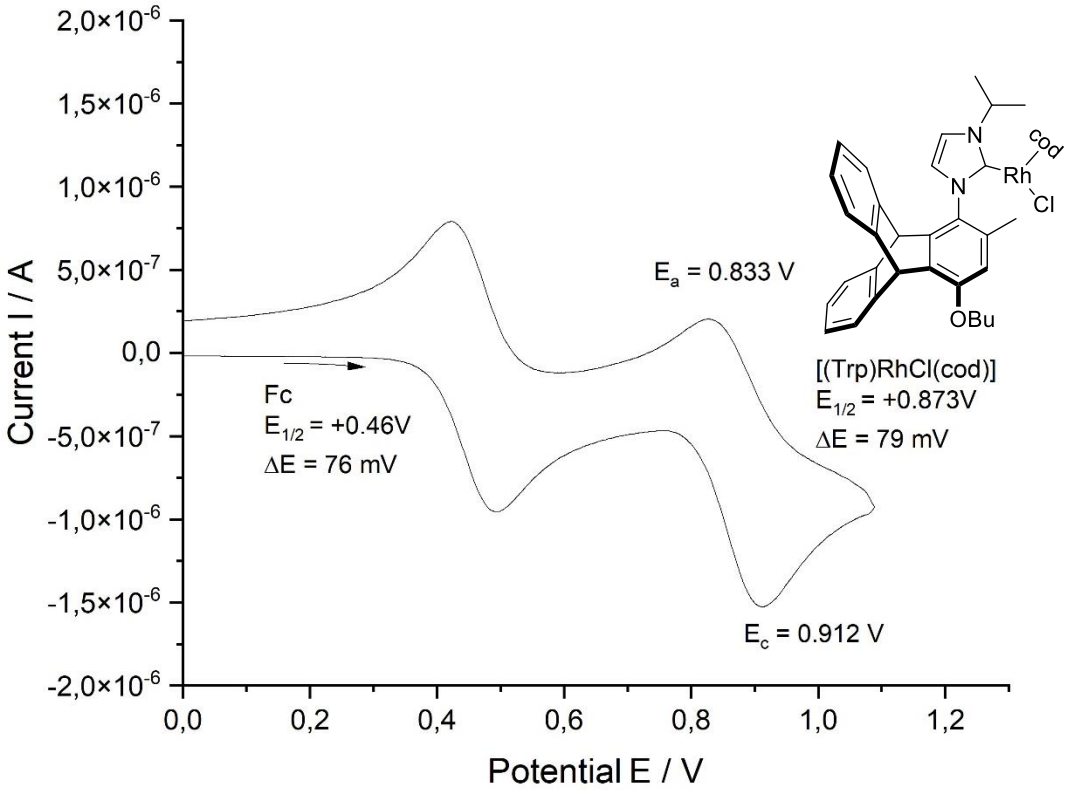


Figure 279: Cyclic voltammogram of [RhCl(cod)(**8b**)] complex was recorded in dry methylene chloride under an atmosphere of nitrogen, supporting electrolyte N*n*Bu$_4$PF$_6$ (c= *0.1 mol L^{-1}*) referenced vs Fc/Fc+.

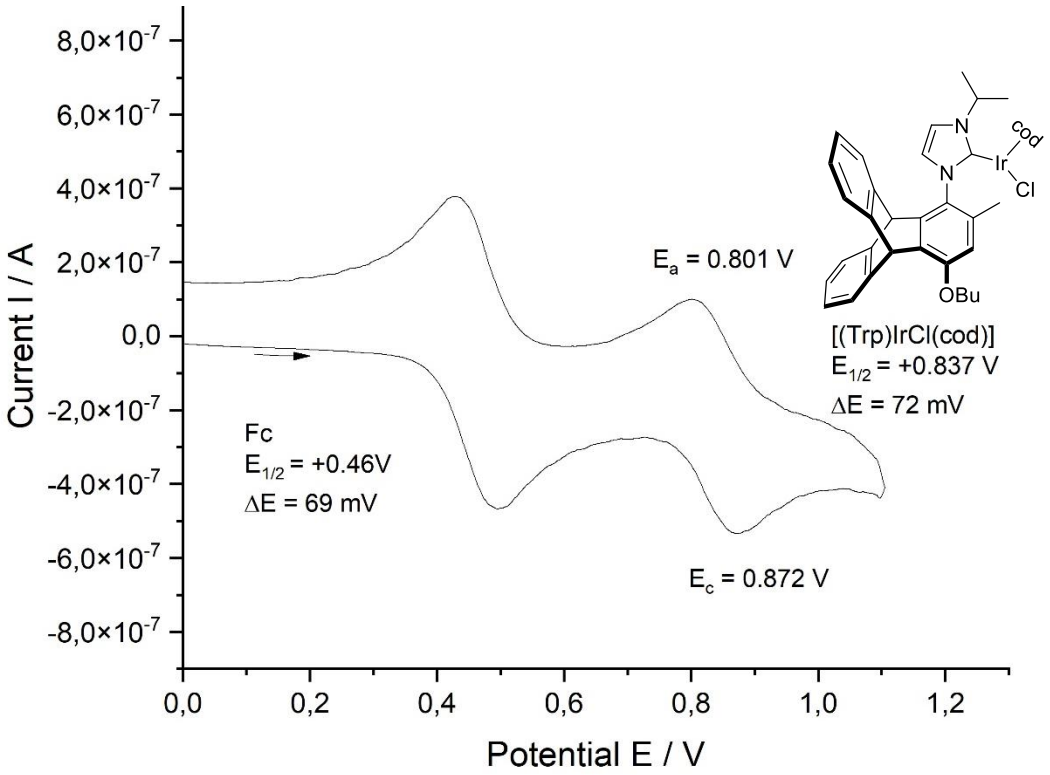


Figure 280: Cyclic voltammogram of [IrCl(cod)(**8b**)] complex was recorded in dry methylene chloride under an atmosphere of nitrogen, supporting electrolyte N*n*Bu$_4$PF$_6$ (c= *0.1 mol L^{-1}*) referenced vs Fc/Fc+.

6. Crystal data and structure refinement

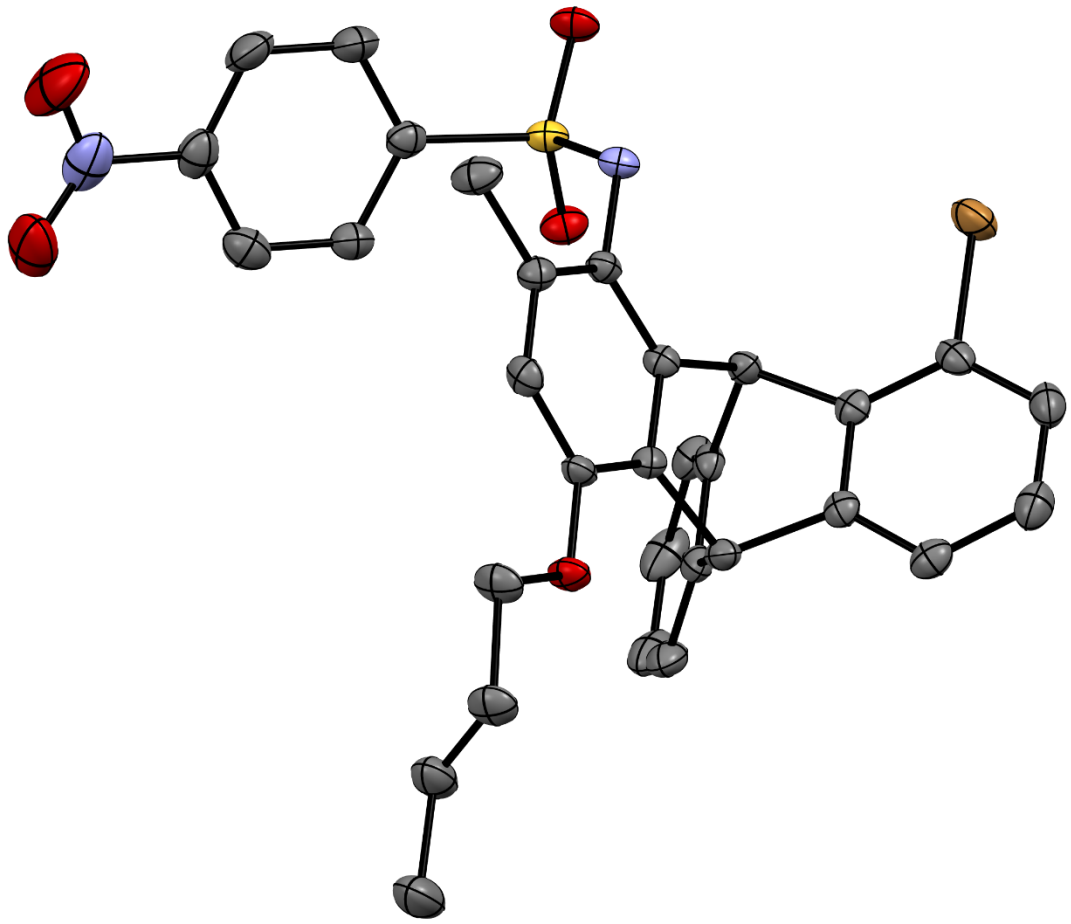


Table 4. Crystal data and structure refinement for compound **5m.**

Identification code	AK1	
Empirical formula	C33 H29 Br Cl3 N2 O7 S	
Formula weight	783.90	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3827(7) Å	α= 74.875(5)°.
	b = 12.8652(8) Å	β= 78.875(5)°.
	c = 13.5864(8) Å	γ = 89.499(5)°.
Volume	1717.36(19) $Å^3$	
Z	2	
Density (calculated)	1.516 Mg/m^3	

Absorption coefficient	1.541 mm^{-1}
F(000)	798
Crystal size	0.480 x 0.480 x 0.400 mm^3
Theta range for data collection	2.532 to 25.349°.
Index ranges	-12<=h<=12, -15<=k<=15, -15<=l<=16
Reflections collected	11291
Independent reflections	6310 [R(int) = 0.0196]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.79705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6310 / 34 / 434
Goodness-of-fit on F^2	1.139
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1148
R indices (all data)	R1 = 0.0535, wR2 = 0.1186
Largest diff. peak and hole	0.883 and -0.641 $e.Å^{-3}$

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AK1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	11316(1)	3863(1)	1974(1)	35(1)
S(1)	8193(1)	682(1)	4451(1)	21(1)
O(1)	7340(2)	1509(2)	4090(2)	27(1)
O(2)	8869(2)	749(2)	5262(2)	27(1)
O(3)	5955(3)	-4366(2)	5857(2)	67(1)
O(4)	4356(3)	-3635(2)	5162(2)	58(1)
O(5)	7898(2)	120(2)	-184(1)	24(1)
N(1)	9331(2)	600(2)	3463(2)	20(1)
N(2)	5401(4)	-3587(3)	5438(2)	46(1)
C(1)	7273(3)	-557(2)	4849(2)	23(1)
C(2)	6242(3)	-657(2)	4364(2)	26(1)
C(3)	5611(3)	-1648(3)	4566(2)	32(1)
C(4)	6027(3)	-2514(3)	5254(2)	31(1)
C(5)	7028(4)	-2425(3)	5764(2)	37(1)
C(6)	7659(3)	-1435(3)	5559(2)	34(1)
C(7)	8968(3)	439(2)	2530(2)	18(1)
C(8)	8974(3)	-583(2)	2352(2)	21(1)
C(9)	8623(3)	-698(2)	1442(2)	22(1)
C(10)	8281(3)	182(2)	711(2)	19(1)
C(11)	8332(3)	1199(2)	879(2)	19(1)
C(12)	8116(3)	2258(2)	116(2)	20(1)
C(13)	9386(3)	2944(2)	-94(2)	20(1)
C(14)	10156(3)	3418(2)	-1053(2)	25(1)
C(15)	11284(3)	4022(2)	-1104(2)	30(1)
C(16)	11633(3)	4159(2)	-208(2)	29(1)
C(17)	10835(3)	3672(2)	750(2)	22(1)
C(18)	9712(3)	3074(2)	827(2)	19(1)
C(19)	8722(3)	2507(2)	1802(2)	18(1)
C(20)	8676(3)	1331(2)	1780(2)	18(1)
C(21)	7406(3)	2968(2)	1619(2)	20(1)
C(22)	6590(3)	3512(2)	2225(2)	28(1)
C(23)	5451(3)	3925(3)	1913(3)	36(1)
C(24)	5122(3)	3778(3)	1028(3)	37(1)
C(25)	5927(3)	3226(3)	414(2)	29(1)

C(26)	7078(3)	2832(2)	705(2)	21(1)
C(27)	9357(3)	-1577(2)	3083(2)	30(1)
C(28)	7866(3)	-923(2)	-372(2)	28(1)
C(29)	7318(3)	-819(3)	-1352(2)	30(1)
C(30)	5884(3)	-521(3)	-1232(2)	34(1)
C(31)	5318(3)	-531(3)	-2184(3)	45(1)
O(6)	161(7)	6262(5)	5127(4)	188(3)
O(7)	1259(7)	4619(5)	5861(6)	189(3)
C(33)	240(12)	5266(8)	5368(9)	225(6)
Cl(1)	2788(1)	6033(1)	2370(1)	46(1)
Cl(2)	5251(1)	7098(1)	2280(1)	95(1)
Cl(3)	2783(2)	7821(2)	3328(3)	66(1)
Cl(3')	3091(8)	7978(6)	2753(9)	66(1)
C(32)	3664(3)	6731(3)	2997(3)	41(1)

Table 6. Bond lengths [Å] and angles [°] for AK1.

Br(1)-C(17)	1.899(3)
S(1)-O(1)	1.427(2)
S(1)-O(2)	1.4366(19)
S(1)-N(1)	1.634(2)
S(1)-C(1)	1.768(3)
O(3)-N(2)	1.216(4)
O(4)-N(2)	1.221(4)
O(5)-C(10)	1.372(3)
O(5)-C(28)	1.431(3)
N(1)-C(7)	1.453(3)
N(1)-H(1N)	0.835(17)
N(2)-C(4)	1.470(4)
C(1)-C(2)	1.383(4)
C(1)-C(6)	1.394(4)
C(2)-C(3)	1.375(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.381(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.376(4)
C(5)-C(6)	1.374(5)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(20)	1.397(4)
C(7)-C(8)	1.398(4)
C(8)-C(9)	1.397(4)
C(8)-C(27)	1.504(4)
C(9)-C(10)	1.391(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.390(4)
C(11)-C(20)	1.390(3)
C(11)-C(12)	1.526(4)
C(12)-C(26)	1.519(4)
C(12)-C(13)	1.530(4)
C(12)-H(12)	1.0000
C(13)-C(14)	1.378(4)
C(13)-C(18)	1.408(4)
C(14)-C(15)	1.392(4)

C(14)-H(14)	0.9500
C(15)-C(16)	1.387(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.394(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.374(4)
C(18)-C(19)	1.525(4)
C(19)-C(20)	1.523(4)
C(19)-C(21)	1.523(4)
C(19)-H(19)	1.0000
C(21)-C(22)	1.381(4)
C(21)-C(26)	1.402(4)
C(22)-C(23)	1.388(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.369(5)
C(23)-H(23)	0.9500
C(24)-C(25)	1.389(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.382(4)
C(25)-H(25)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.522(4)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.524(4)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.522(4)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
O(6)-C(33)	1.243(8)
O(7)-C(33)	1.493(8)
O(7)-H(7O)	0.8400
C(33)-C(33)#1	1.51(2)

Cl(1)-C(32)	1.752(3)
Cl(2)-C(32)	1.744(4)
Cl(3)-C(32)	1.776(4)
Cl(3')-C(32)	1.680(7)
C(32)-H(32)	1.0000

O(1)-S(1)-O(2)	119.98(12)
O(1)-S(1)-N(1)	108.28(12)
O(2)-S(1)-N(1)	106.08(12)
O(1)-S(1)-C(1)	107.51(13)
O(2)-S(1)-C(1)	108.35(13)
N(1)-S(1)-C(1)	105.83(13)
C(10)-O(5)-C(28)	117.1(2)
C(7)-N(1)-S(1)	120.14(18)
C(7)-N(1)-H(1N)	115(2)
S(1)-N(1)-H(1N)	112(2)
O(3)-N(2)-O(4)	124.4(3)
O(3)-N(2)-C(4)	117.9(3)
O(4)-N(2)-C(4)	117.7(3)
C(2)-C(1)-C(6)	121.2(3)
C(2)-C(1)-S(1)	118.1(2)
C(6)-C(1)-S(1)	120.4(2)
C(3)-C(2)-C(1)	119.4(3)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	118.6(3)
C(2)-C(3)-H(3)	120.7
C(4)-C(3)-H(3)	120.7
C(5)-C(4)-C(3)	122.8(3)
C(5)-C(4)-N(2)	118.1(3)
C(3)-C(4)-N(2)	119.1(3)
C(6)-C(5)-C(4)	118.5(3)
C(6)-C(5)-H(5)	120.8
C(4)-C(5)-H(5)	120.8
C(5)-C(6)-C(1)	119.5(3)
C(5)-C(6)-H(6)	120.2
C(1)-C(6)-H(6)	120.2
C(20)-C(7)-C(8)	119.7(2)
C(20)-C(7)-N(1)	119.2(2)

C(8)-C(7)-N(1)	121.0(2)
C(9)-C(8)-C(7)	118.9(2)
C(9)-C(8)-C(27)	117.5(2)
C(7)-C(8)-C(27)	123.5(2)
C(10)-C(9)-C(8)	121.5(2)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
O(5)-C(10)-C(11)	116.7(2)
O(5)-C(10)-C(9)	124.4(2)
C(11)-C(10)-C(9)	118.9(2)
C(20)-C(11)-C(10)	120.5(2)
C(20)-C(11)-C(12)	113.6(2)
C(10)-C(11)-C(12)	125.8(2)
C(26)-C(12)-C(11)	106.8(2)
C(26)-C(12)-C(13)	105.1(2)
C(11)-C(12)-C(13)	105.5(2)
C(26)-C(12)-H(12)	112.9
C(11)-C(12)-H(12)	112.9
C(13)-C(12)-H(12)	112.9
C(14)-C(13)-C(18)	121.2(3)
C(14)-C(13)-C(12)	126.6(2)
C(18)-C(13)-C(12)	112.2(2)
C(13)-C(14)-C(15)	119.0(3)
C(13)-C(14)-H(14)	120.5
C(15)-C(14)-H(14)	120.5
C(16)-C(15)-C(14)	121.0(3)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	118.7(3)
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	121.7(3)
C(18)-C(17)-Br(1)	119.7(2)
C(16)-C(17)-Br(1)	118.5(2)
C(17)-C(18)-C(13)	118.3(3)
C(17)-C(18)-C(19)	128.6(2)
C(13)-C(18)-C(19)	113.1(2)
C(20)-C(19)-C(21)	107.7(2)
C(20)-C(19)-C(18)	105.0(2)

C(21)-C(19)-C(18)	104.9(2)
C(20)-C(19)-H(19)	112.9
C(21)-C(19)-H(19)	112.9
C(18)-C(19)-H(19)	112.9
C(11)-C(20)-C(7)	120.4(2)
C(11)-C(20)-C(19)	112.6(2)
C(7)-C(20)-C(19)	127.0(2)
C(22)-C(21)-C(26)	120.2(3)
C(22)-C(21)-C(19)	126.8(3)
C(26)-C(21)-C(19)	113.0(2)
C(21)-C(22)-C(23)	119.1(3)
C(21)-C(22)-H(22)	120.5
C(23)-C(22)-H(22)	120.5
C(24)-C(23)-C(22)	120.7(3)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(23)-C(24)-C(25)	121.0(3)
C(23)-C(24)-H(24)	119.5
C(25)-C(24)-H(24)	119.5
C(26)-C(25)-C(24)	118.8(3)
C(26)-C(25)-H(25)	120.6
C(24)-C(25)-H(25)	120.6
C(25)-C(26)-C(21)	120.3(3)
C(25)-C(26)-C(12)	126.9(3)
C(21)-C(26)-C(12)	112.8(2)
C(8)-C(27)-H(27A)	109.5
C(8)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(8)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
O(5)-C(28)-C(29)	108.2(2)
O(5)-C(28)-H(28A)	110.1
C(29)-C(28)-H(28A)	110.1
O(5)-C(28)-H(28B)	110.1
C(29)-C(28)-H(28B)	110.1
H(28A)-C(28)-H(28B)	108.4
C(28)-C(29)-C(30)	113.3(3)
C(28)-C(29)-H(29A)	108.9

C(30)-C(29)-H(29A)	108.9
C(28)-C(29)-H(29B)	108.9
C(30)-C(29)-H(29B)	108.9
H(29A)-C(29)-H(29B)	107.7
C(31)-C(30)-C(29)	112.3(3)
C(31)-C(30)-H(30A)	109.1
C(29)-C(30)-H(30A)	109.1
C(31)-C(30)-H(30B)	109.1
C(29)-C(30)-H(30B)	109.1
H(30A)-C(30)-H(30B)	107.9
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(33)-O(7)-H(7O)	109.5
O(6)-C(33)-O(7)	128.1(9)
O(6)-C(33)-C(33)#1	113.3(12)
O(7)-C(33)-C(33)#1	110.8(11)
Cl(2)-C(32)-Cl(1)	110.8(2)
Cl(2)-C(32)-Cl(3)	113.8(2)
Cl(1)-C(32)-Cl(3)	111.9(2)
Cl(2)-C(32)-H(32)	106.6
Cl(1)-C(32)-H(32)	106.6
Cl(3)-C(32)-H(32)	106.6

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for AK1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	36(1)	34(1)	41(1)	-12(1)	-20(1)	-4(1)
S(1)	24(1)	23(1)	19(1)	-7(1)	-8(1)	4(1)
O(1)	29(1)	27(1)	26(1)	-8(1)	-8(1)	9(1)
O(2)	32(1)	31(1)	22(1)	-13(1)	-12(1)	4(1)
O(3)	122(3)	27(2)	52(2)	-1(1)	-27(2)	-6(2)
O(4)	74(2)	55(2)	47(2)	-17(1)	-10(1)	-28(2)
O(5)	33(1)	21(1)	23(1)	-9(1)	-14(1)	2(1)
N(1)	20(1)	23(1)	20(1)	-7(1)	-8(1)	4(1)
N(2)	77(2)	37(2)	25(2)	-12(1)	-3(2)	-15(2)
C(1)	24(2)	27(2)	18(1)	-6(1)	-3(1)	2(1)
C(2)	28(2)	29(2)	23(2)	-6(1)	-9(1)	3(1)
C(3)	32(2)	37(2)	32(2)	-15(2)	-10(1)	2(2)
C(4)	41(2)	28(2)	23(2)	-8(1)	0(1)	-5(2)
C(5)	53(2)	30(2)	24(2)	4(1)	-12(2)	0(2)
C(6)	41(2)	35(2)	28(2)	0(1)	-18(2)	-1(2)
C(7)	17(1)	21(2)	16(1)	-6(1)	-4(1)	1(1)
C(8)	21(2)	22(2)	22(2)	-5(1)	-6(1)	3(1)
C(9)	25(2)	16(2)	27(2)	-10(1)	-7(1)	1(1)
C(10)	18(1)	24(2)	17(1)	-7(1)	-6(1)	-1(1)
C(11)	18(1)	19(2)	20(1)	-3(1)	-6(1)	1(1)
C(12)	26(2)	17(2)	20(1)	-3(1)	-10(1)	0(1)
C(13)	22(2)	15(1)	23(2)	-5(1)	-5(1)	3(1)
C(14)	31(2)	20(2)	23(2)	-6(1)	-5(1)	6(1)
C(15)	27(2)	26(2)	32(2)	-1(1)	1(1)	1(1)
C(16)	23(2)	23(2)	38(2)	-2(1)	-6(1)	-3(1)
C(17)	21(2)	18(2)	30(2)	-8(1)	-10(1)	4(1)
C(18)	22(2)	14(1)	23(2)	-5(1)	-6(1)	4(1)
C(19)	22(2)	17(1)	18(1)	-6(1)	-6(1)	-1(1)
C(20)	18(1)	18(2)	20(1)	-7(1)	-5(1)	3(1)
C(21)	19(1)	14(1)	25(2)	-1(1)	-3(1)	0(1)
C(22)	33(2)	21(2)	25(2)	-2(1)	-3(1)	1(1)
C(23)	34(2)	27(2)	36(2)	1(1)	6(2)	13(2)
C(24)	28(2)	36(2)	37(2)	6(2)	-5(2)	9(2)
C(25)	27(2)	29(2)	27(2)	4(1)	-9(1)	2(1)

C(26)	22(2)	16(1)	24(2)	-1(1)	-5(1)	-1(1)
C(27)	42(2)	22(2)	28(2)	-7(1)	-15(1)	10(1)
C(28)	38(2)	24(2)	32(2)	-16(1)	-16(1)	4(1)
C(29)	40(2)	29(2)	28(2)	-16(1)	-14(1)	3(1)
C(30)	32(2)	46(2)	27(2)	-13(2)	-9(1)	-6(2)
C(31)	39(2)	63(3)	37(2)	-11(2)	-16(2)	-9(2)
O(6)	266(6)	155(4)	92(3)	14(3)	17(3)	151(4)
O(7)	227(6)	114(4)	193(5)	-20(4)	11(5)	50(4)
C(33)	229(7)	224(7)	219(7)	-61(5)	-37(5)	10(5)
Cl(1)	56(1)	46(1)	42(1)	-13(1)	-23(1)	-5(1)
Cl(2)	50(1)	148(1)	92(1)	-50(1)	1(1)	-32(1)
Cl(3)	59(1)	52(1)	108(2)	-49(1)	-34(1)	21(1)
Cl(3')	59(1)	52(1)	108(2)	-49(1)	-34(1)	21(1)
C(32)	45(2)	35(2)	49(2)	-16(2)	-19(2)	2(2)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for AK1.

	x	y	z	U(eq)
H(1N)	9950(20)	240(20)	3660(20)	24
H(2)	5973	-47	3896	31
H(3)	4903	-1734	4239	39
H(5)	7276	-3034	6245	45
H(6)	8353	-1350	5900	41
H(9)	8618	-1392	1320	26
H(12)	7880	2155	-532	24
H(14)	9920	3333	-1670	30
H(15)	11824	4346	-1762	37
H(16)	12400	4577	-248	34
H(19)	8954	2604	2454	22
H(22)	6806	3601	2848	33
H(23)	4893	4314	2317	43
H(24)	4332	4057	832	44
H(25)	5691	3122	-196	35
H(27A)	10025	-1942	2696	45
H(27B)	8583	-2064	3403	45
H(27C)	9715	-1372	3626	45
H(28A)	7303	-1435	226	34
H(28B)	8763	-1198	-463	34
H(29A)	7403	-1511	-1544	36
H(29B)	7851	-261	-1929	36
H(30A)	5361	-1037	-614	41
H(30B)	5810	207	-1115	41
H(31A)	4404	-317	-2080	68
H(31B)	5351	-1258	-2285	68
H(31C)	5835	-24	-2799	68
H(7O)	1956	4999	5729	227
H(32)	3757	6212	3667	49

Table 9. Torsion angles [°] for AK1.

O(1)-S(1)-N(1)-C(7)	-54.6(2)
O(2)-S(1)-N(1)-C(7)	175.4(2)
C(1)-S(1)-N(1)-C(7)	60.4(2)
O(1)-S(1)-C(1)-C(2)	28.9(3)
O(2)-S(1)-C(1)-C(2)	160.0(2)
N(1)-S(1)-C(1)-C(2)	-86.6(2)
O(1)-S(1)-C(1)-C(6)	-157.0(2)
O(2)-S(1)-C(1)-C(6)	-26.0(3)
N(1)-S(1)-C(1)-C(6)	87.4(3)
C(6)-C(1)-C(2)-C(3)	-1.8(5)
S(1)-C(1)-C(2)-C(3)	172.2(2)
C(1)-C(2)-C(3)-C(4)	0.3(4)
C(2)-C(3)-C(4)-C(5)	1.5(5)
C(2)-C(3)-C(4)-N(2)	-177.1(3)
O(3)-N(2)-C(4)-C(5)	-14.4(4)
O(4)-N(2)-C(4)-C(5)	165.4(3)
O(3)-N(2)-C(4)-C(3)	164.3(3)
O(4)-N(2)-C(4)-C(3)	-16.0(4)
C(3)-C(4)-C(5)-C(6)	-1.6(5)
N(2)-C(4)-C(5)-C(6)	177.0(3)
C(4)-C(5)-C(6)-C(1)	0.0(5)
C(2)-C(1)-C(6)-C(5)	1.7(5)
S(1)-C(1)-C(6)-C(5)	-172.2(3)
S(1)-N(1)-C(7)-C(20)	83.8(3)
S(1)-N(1)-C(7)-C(8)	-99.5(3)
C(20)-C(7)-C(8)-C(9)	-3.0(4)
N(1)-C(7)-C(8)-C(9)	-179.7(2)
C(20)-C(7)-C(8)-C(27)	176.1(3)
N(1)-C(7)-C(8)-C(27)	-0.6(4)
C(7)-C(8)-C(9)-C(10)	0.5(4)
C(27)-C(8)-C(9)-C(10)	-178.7(3)
C(28)-O(5)-C(10)-C(11)	178.9(2)
C(28)-O(5)-C(10)-C(9)	-0.6(4)
C(8)-C(9)-C(10)-O(5)	-178.4(2)
C(8)-C(9)-C(10)-C(11)	2.1(4)
O(5)-C(10)-C(11)-C(20)	178.3(2)
C(9)-C(10)-C(11)-C(20)	-2.2(4)

O(5)-C(10)-C(11)-C(12)	-5.6(4)
C(9)-C(10)-C(11)-C(12)	173.9(3)
C(20)-C(11)-C(12)-C(26)	-56.0(3)
C(10)-C(11)-C(12)-C(26)	127.6(3)
C(20)-C(11)-C(12)-C(13)	55.5(3)
C(10)-C(11)-C(12)-C(13)	-120.8(3)
C(26)-C(12)-C(13)-C(14)	-121.9(3)
C(11)-C(12)-C(13)-C(14)	125.4(3)
C(26)-C(12)-C(13)-C(18)	57.0(3)
C(11)-C(12)-C(13)-C(18)	-55.6(3)
C(18)-C(13)-C(14)-C(15)	0.9(4)
C(12)-C(13)-C(14)-C(15)	179.7(3)
C(13)-C(14)-C(15)-C(16)	-0.6(4)
C(14)-C(15)-C(16)-C(17)	0.5(4)
C(15)-C(16)-C(17)-C(18)	-0.8(4)
C(15)-C(16)-C(17)-Br(1)	-180.0(2)
C(16)-C(17)-C(18)-C(13)	1.1(4)
Br(1)-C(17)-C(18)-C(13)	-179.7(2)
C(16)-C(17)-C(18)-C(19)	-178.8(3)
Br(1)-C(17)-C(18)-C(19)	0.4(4)
C(14)-C(13)-C(18)-C(17)	-1.1(4)
C(12)-C(13)-C(18)-C(17)	179.8(2)
C(14)-C(13)-C(18)-C(19)	178.8(2)
C(12)-C(13)-C(18)-C(19)	-0.3(3)
C(17)-C(18)-C(19)-C(20)	-123.2(3)
C(13)-C(18)-C(19)-C(20)	56.9(3)
C(17)-C(18)-C(19)-C(21)	123.5(3)
C(13)-C(18)-C(19)-C(21)	-56.4(3)
C(10)-C(11)-C(20)-C(7)	-0.3(4)
C(12)-C(11)-C(20)-C(7)	-176.9(2)
C(10)-C(11)-C(20)-C(19)	178.0(2)
C(12)-C(11)-C(20)-C(19)	1.5(3)
C(8)-C(7)-C(20)-C(11)	3.0(4)
N(1)-C(7)-C(20)-C(11)	179.7(2)
C(8)-C(7)-C(20)-C(19)	-175.1(3)
N(1)-C(7)-C(20)-C(19)	1.6(4)
C(21)-C(19)-C(20)-C(11)	53.8(3)
C(18)-C(19)-C(20)-C(11)	-57.6(3)
C(21)-C(19)-C(20)-C(7)	-128.0(3)

C(18)-C(19)-C(20)-C(7)	120.6(3)
C(20)-C(19)-C(21)-C(22)	127.8(3)
C(18)-C(19)-C(21)-C(22)	-120.7(3)
C(20)-C(19)-C(21)-C(26)	-54.7(3)
C(18)-C(19)-C(21)-C(26)	56.8(3)
C(26)-C(21)-C(22)-C(23)	-0.4(4)
C(19)-C(21)-C(22)-C(23)	176.9(3)
C(21)-C(22)-C(23)-C(24)	1.4(5)
C(22)-C(23)-C(24)-C(25)	-0.9(5)
C(23)-C(24)-C(25)-C(26)	-0.5(5)
C(24)-C(25)-C(26)-C(21)	1.5(4)
C(24)-C(25)-C(26)-C(12)	-176.9(3)
C(22)-C(21)-C(26)-C(25)	-1.0(4)
C(19)-C(21)-C(26)-C(25)	-178.7(3)
C(22)-C(21)-C(26)-C(12)	177.6(3)
C(19)-C(21)-C(26)-C(12)	-0.1(3)
C(11)-C(12)-C(26)-C(25)	-126.8(3)
C(13)-C(12)-C(26)-C(25)	121.5(3)
C(11)-C(12)-C(26)-C(21)	54.8(3)
C(13)-C(12)-C(26)-C(21)	-57.0(3)
C(10)-O(5)-C(28)-C(29)	175.6(2)
O(5)-C(28)-C(29)-C(30)	-66.2(3)
C(28)-C(29)-C(30)-C(31)	-174.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 10. Hydrogen bonds for AK1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(2)#2	0.835(17)	2.23(2)	3.021(3)	159(3)
C(23)-H(23)...O(3)#3	0.95	2.49	3.288(4)	142.2
C(27)-H(27C)...O(2)#2	0.98	2.57	3.530(4)	167.1
C(32)-H(32)...O(3)#3	1.00	2.32	3.095(5)	133.1
C(32)-H(32)...O(4)#4	1.00	2.29	3.079(4)	134.8

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x+2,-y,-z+1 #3 -x+1,-y,-z+1

#4 x,y+1,z

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