Supporting Information

Sterically hindering the trajectory of nucleophilic attack towards *p*-benzynes by a properly oriented hydrogen atom: An approach to achieve regioselectivity

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Experimental Section

5.6.1 Chemical synthesis and characterization

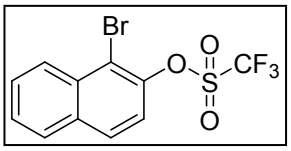
General experimental details

All reactions were performed under a nitrogen atmosphere unless otherwise stated. Glassware used in reactions was thoroughly oven-dried. All commercial grade reagents were used without further purification and solvents were dried prior to use following standard protocol. TLC was carried out on precoated plates (silica gel 60 F_{254}), and the spots were visualized by exposure to UV light and/or by staining with iodine. All crude products were purified by silica gel flash column chromatography (230–400 mesh) with petroleum ether and ethyl acetate as eluent and characterized by NMR and mass spectrometry unless otherwise mentioned. Melting points were determined in open capillary tubes and are reported as uncorrected. ^{1}H and ^{13}C NMR spectra for all the compounds were recorded at 400/500 MHz and 100/125 MHz (Bruker Ultrashield™ 400, Ascend™ 500), respectively. The spectra were recorded in deuterochloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6) as solvent at room temperature. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ_H = 7.26, δ_C = 77.16 ppm; ; DMSO-d_6: δ_H = 2.50, δ_C = 39.52 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as chemical shift. HRMS spectra using ESI were recorded on an ESI-FTMS mass spectrometer. Single crystal X-ray data was collected on a Bruker SMART APEXII CCD diffractometer using graphite-monochromated Mo-Kα radiation (0.71073 Å).

Experimental Procedure and Data analysis of the synthesized compounds

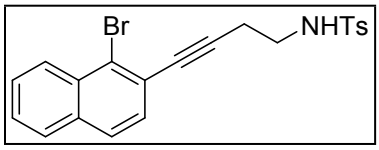
*(i) Synthesis of the arene triflate (**4**).* Triflate protection of commercially available 1-bromo-2-naphthol **3** (0.3 g, 1.345 mmol, 1 eq) was carried out by the reaction with trifluoromethanesulfonic anhydride (0.271 mL, 1.614 mmol, 1.2 eq) in presence of dry

triethylamine (0.394 mL, 2.825 mmol, 2.1 eq) in dichloromethane (7 mL) at 0 °C to room temperature for 30 min. The reaction was quenched by adding water. The mixture was extracted by dichloromethane and washed with 2(N) HCl, $NaHCO_3$, dried over Na_2SO_4 and subjected to column chromatography for further purification to afford the compounds **4.**

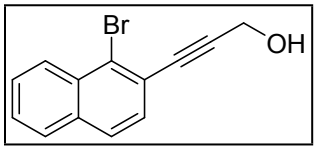


1-bromonaphthalen-2-yl trifluoromethanesulfonate[1] **(4)**. Yield: 0.43 g, 90%; State: White semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 9.2 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.0, 132.9, 132.5, 129.7, 128.7, 128.3, 127.7, 127.4, 119.7, 116.1. HRMS [ESI-TOF] calcd for $C_{10}H_8Br$ $(M-OTf+H)^+$ 206.9809, found 206.9812.

(ii) Chemoselective Sonogashira coupling of arene triflate[2] *with terminal alkyne for synthesis of* ***5a*** *&* ***5b***. A solution of the triflate **4** (0.132 g, 0.372 mmol, 1 eq) dissolved in dry DMF (7 mL) and triethylamine (0.103 mL, 0.743 mmol, 2 eq) was degassed with argon for 10 min. To this solution, $Pd(PPh_3)_4$ (0.021 g, 0.019 mmol, 0.05 eq), CuI (0.007 g, 0.037 mmol, 0.1 eq) and tosyl-protected homopropargyl amine (0.091 g, 0.409 mmol, 1.1 eq) (for **5a**) or propargyl alcohol (24 μL, 0.409 mmol, 1.1 eq) (for **5b**) were added and then heated at 60 °C for 3.5 h. Completion of the reaction was confirmed by TLC and the reaction was quenched by adding water. The organic layer was extracted with ethyl acetate, washed with aq. NH_4Cl solution, dried over anhydrous Na_2SO_4 and was subjected to column chromatography for further purification to afford the compounds **5a** and **5b**.

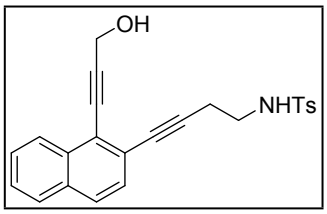


N-(4-(1-bromonaphthalen-2-yl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (5a). Yield: 138 mg, 87%; State: Brown viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 1H), 7.80 (t, *J* = 8.2 Hz, 3H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 1H), 3.27 (br t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.7, 137.1, 133.7, 132.2, 129.9, 129.0, 128.3, 128.1, 128.0, 127.7, 127.3, 127.2, 126.5, 123.1, 91.6, 83.2, 41.9, 21.6, 21.1. HRMS [ESI-TOF] calcd for $C_{21}H_{18}BrNO_2SH$ $(M+H)^+$ 428.0320, found 428.0321.



3-(1-bromonaphthalen-2-yl)prop-2-yn-1-ol (5b). Yield: 62 mg, 64%; State: Brown viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.52 – 7.49 (m, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 4.63 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 132.2, 129.1, 128.3, 128.0, 127.9, 127.6, 127.4, 126.5, 122.8, 92.8, 85.6, 51.9. MS (ESI) m/z for $C_{13}H_{10}BrO$ $(M+H)^+$ 261.1772.

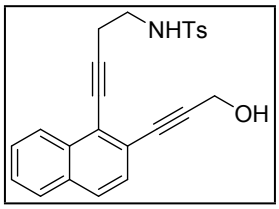
*Sonogashira coupling of bromo arene **5a** with terminal alkyne for synthesis of compounds* **6a**. To a degassed (argon) solution of **5a** (0.062 g, 0.145 mmol, 1 eq) in dry n-butylamine (5 mL), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol, 0.08 eq) and propargyl alcohol (10 µL, 0.174 mmol, 1.2 eq) were added and the reaction mixture was refluxed at 80 °C for 24-28 h. The reaction was monitored by TLC. After completion of the reaction, it was cooled to room temperature and quenched with water. The organic layer was extracted with EtOAc, washed with brine, dried over Na_2SO_4 and was subjected to column chromatography for further purification to afford the compound **6a**.



N-(4-(1-(3-hydroxyprop-1-yn-1-yl)naphthalen-2-yl)but-3-yn-1-yl)-4-methylbenzene sulfonamide (6a). Yield: 42 mg, 72%; State: Brown viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 3H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 4.77 (s, 2H), 3.25 – 3.24 (m, 2H), 2.64 (t, *J* = 5.8 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.3, 136.8, 133.3, 132.1, 129.9, 128.5, 128.3, 128.0, 127.6, 127.3, 127.2, 126.0, 124.0, 123.5, 97.6, 90.8, 83.3, 82.5, 52.4, 41.3, 21.6, 20.6. HRMS [ESI-TOF] calcd for $C_{24}H_{21}NO_3SH$ $(M+H)^+$ 404.1320, found 404.1322.

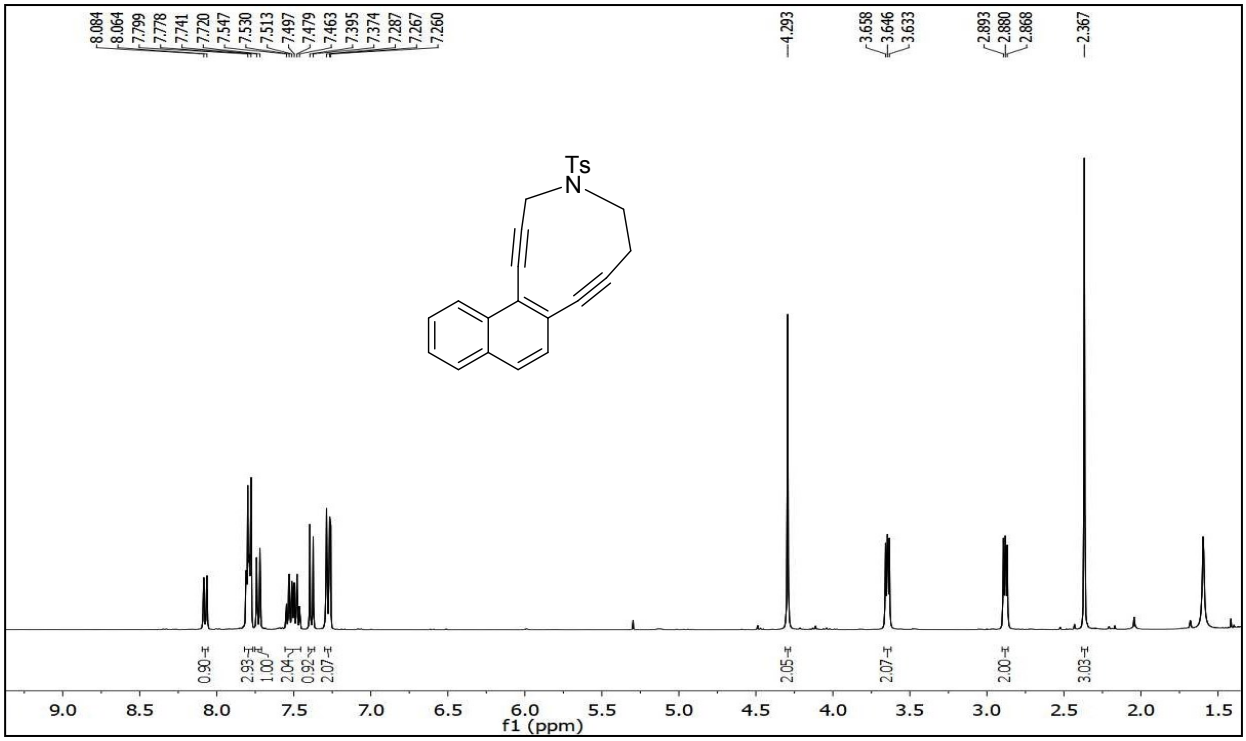
*Sonogashira coupling of bromo arene **5b** with terminal alkyne for synthesis of compounds **6b***. To a solution of **5b** (0.1 g, 0.383 mmol, 1 eq) in dry DMF (4ml) mixed with dry triethylamine (2ml) and degassed with argon for 15 min, $Pd(PPh_3)_4$ (0.022 g, 0.019 mmol, 0.05 eq), CuI (0.007 g, 0.038 mmol, 0.1 eq) and 1.1 eq of tosyl-protected homopropargyl amine were added and the reaction mixture was refluxed at 80 °C for 22 h. The reaction was monitored by TLC. After completion of the reaction, it was cooled to room temperature and quenched with water. The organic layer was extracted with EtOAc, washed with aq. NH_4Cl solution, dried over anhydrous

Na_2SO_4 and was subjected to column chromatography for further purification to afford the compound **6b**.

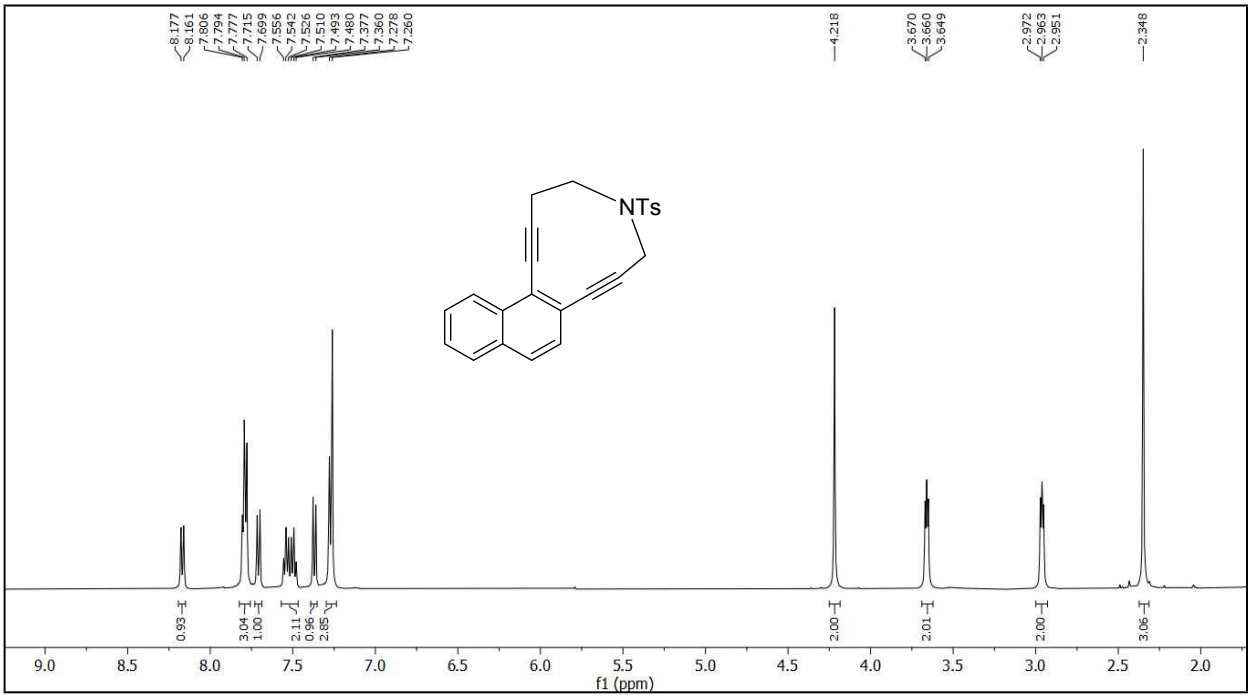


N-(4-(2-(3-hydroxyprop-1-yn-1-yl)naphthalen-1-yl)but-3-yn-1-yl)-4-methylbenzene sulfonamide (6b). Yield: 117 mg, 76%; State: Brown viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 − 7.73 (m, 2H), 7.54 – 7.49 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 2H), 3.29 (t, *J* = 6.0 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H). HRMS [ESI-TOF] calcd for $C_{24}H_{22}NO_3S$ $(M+H)^+$ 404.1320, found 404.1317.

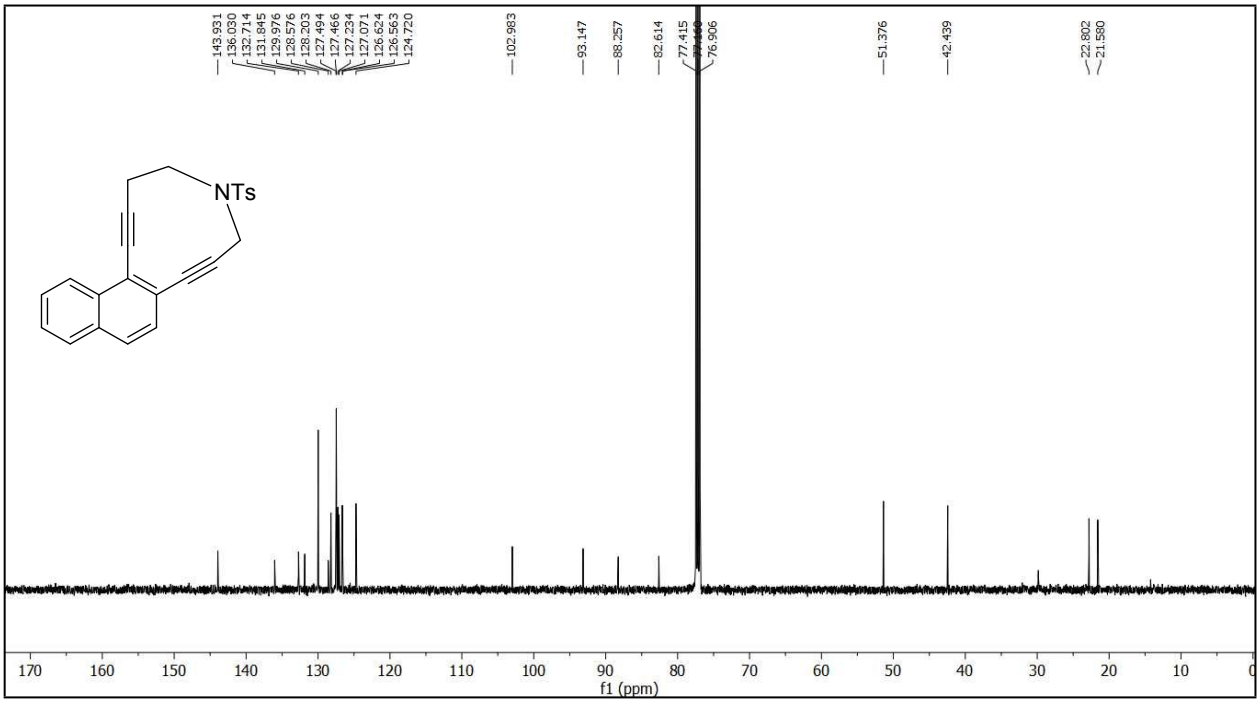
NMR Spectra of enediynes and final halogenated compounds



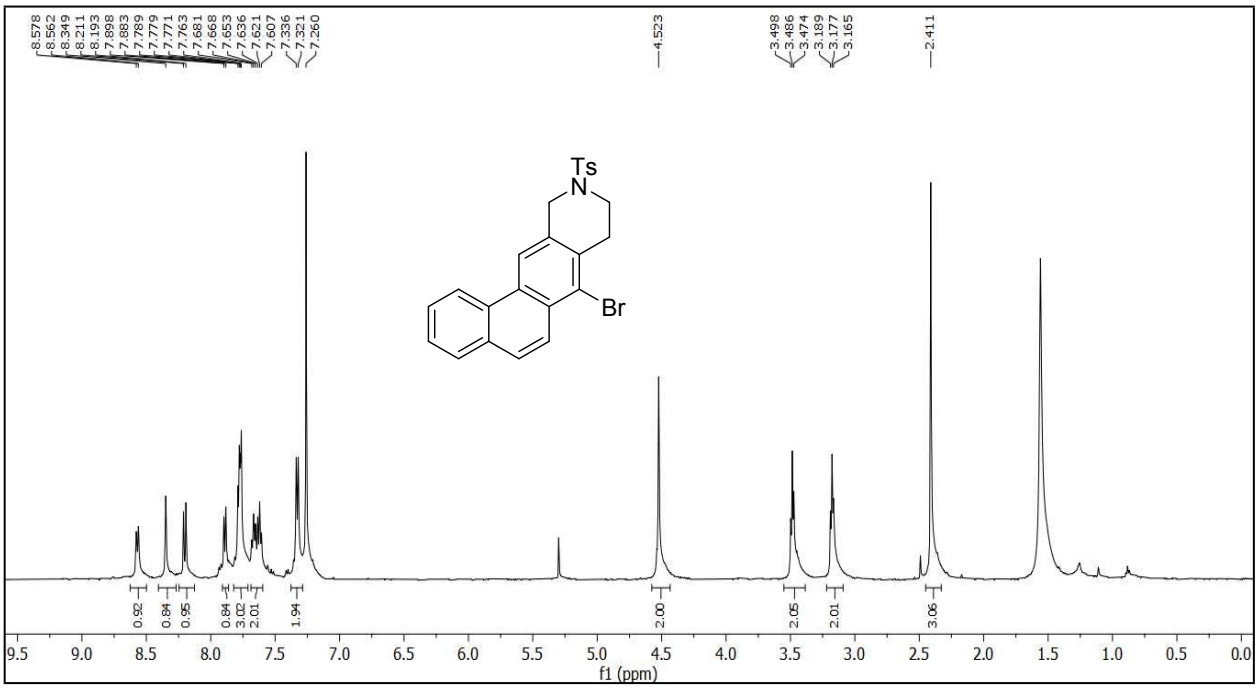
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **1a**



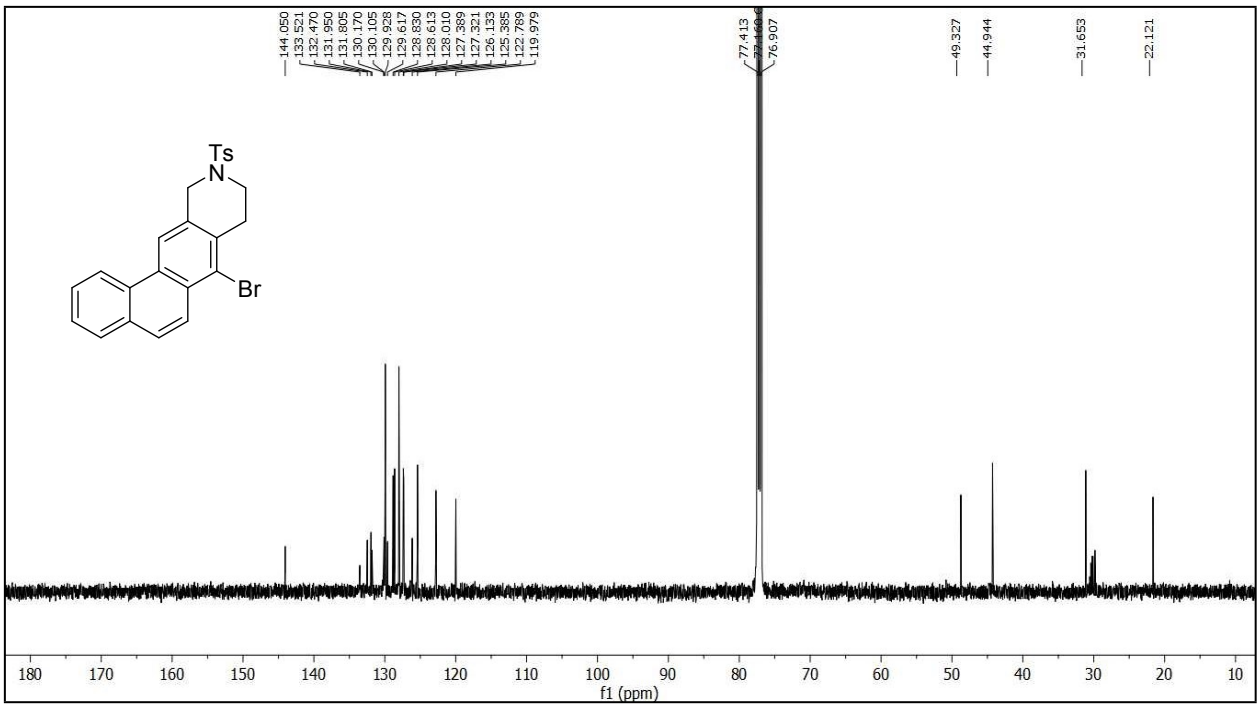
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **1b**



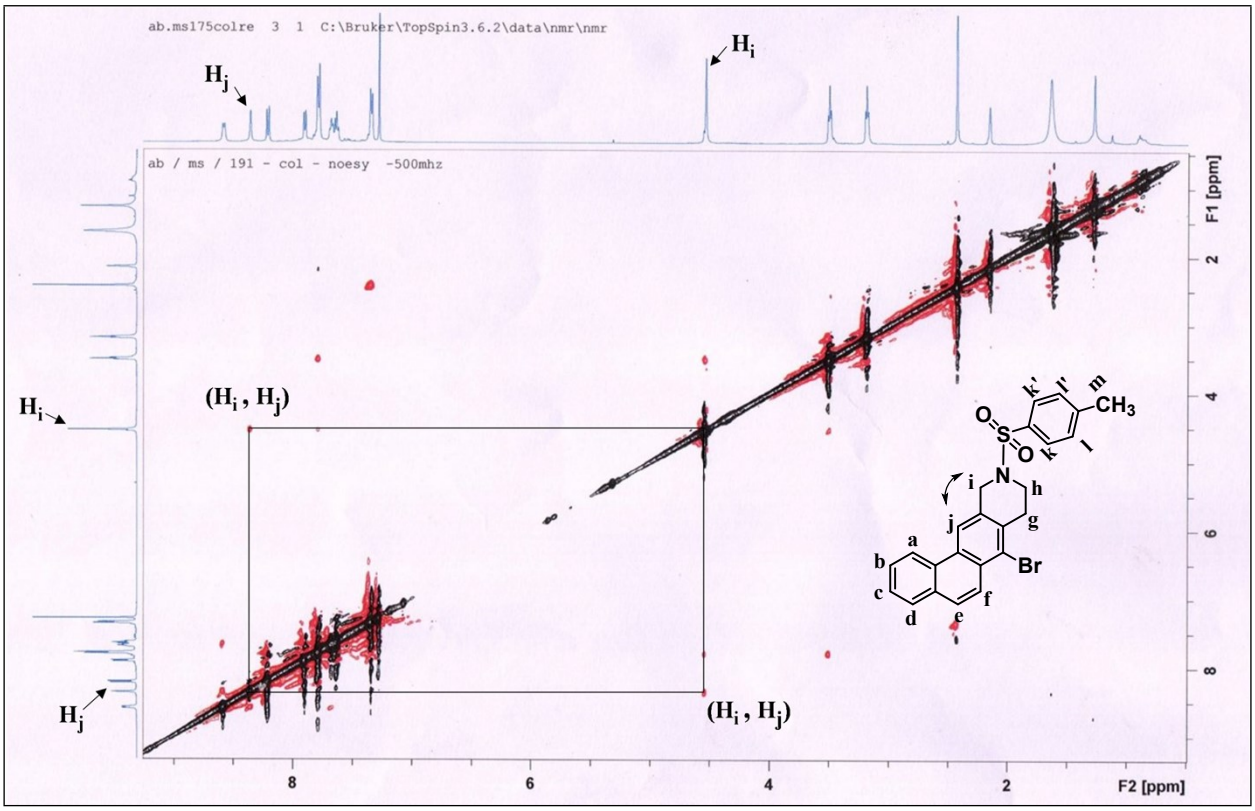
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **1b**



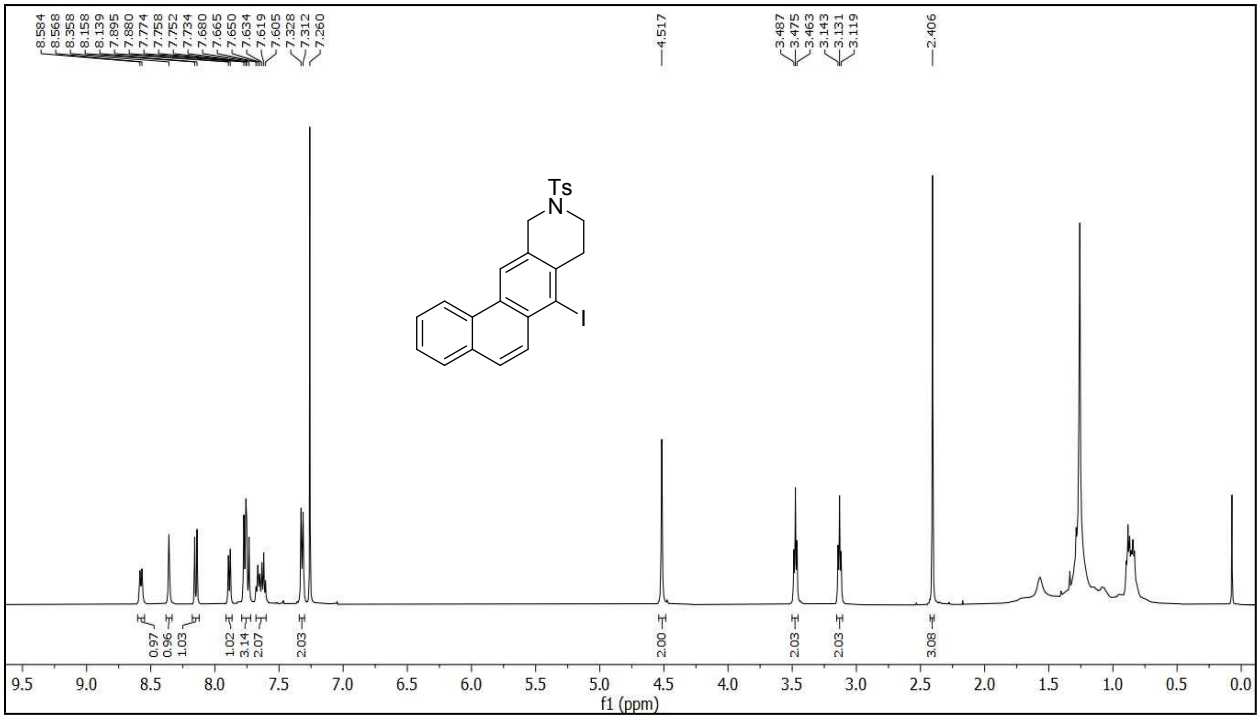
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **2.1a**



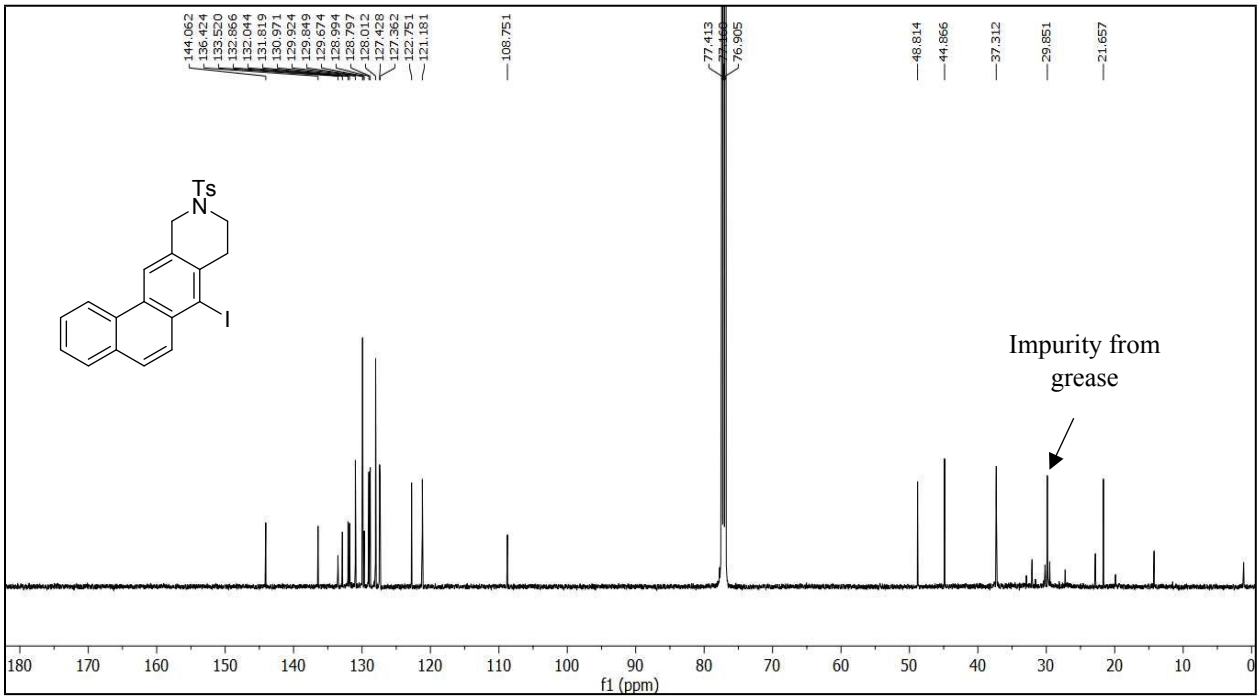
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **2.1a**



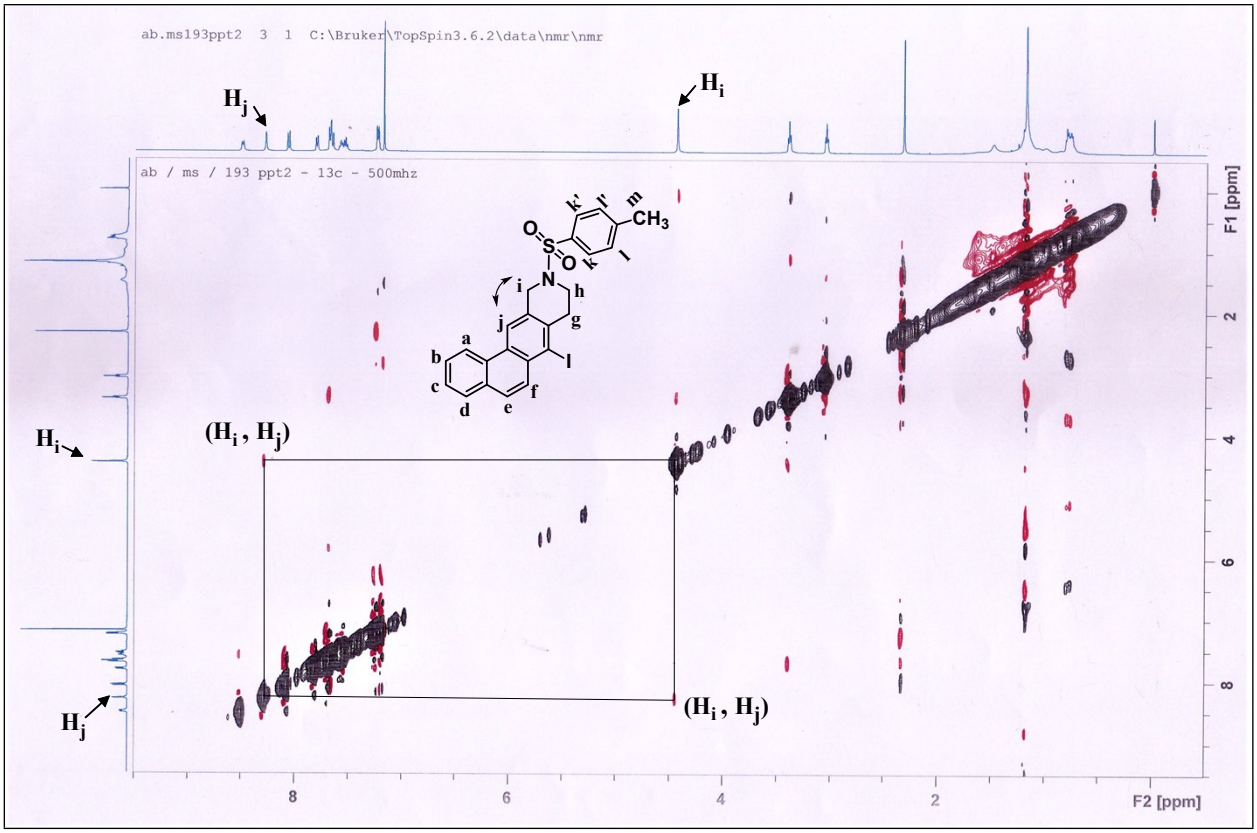
NOESY spectrum of compound **2.1a** in $CDCl_3$



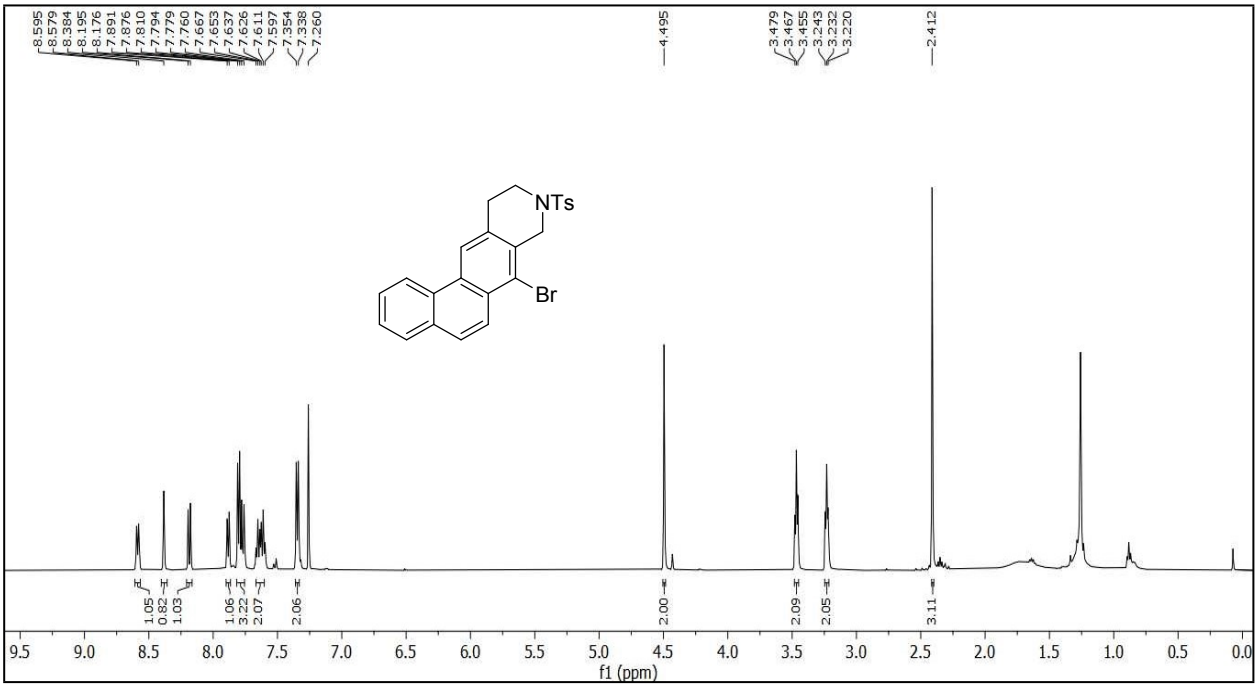
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **2.2a**



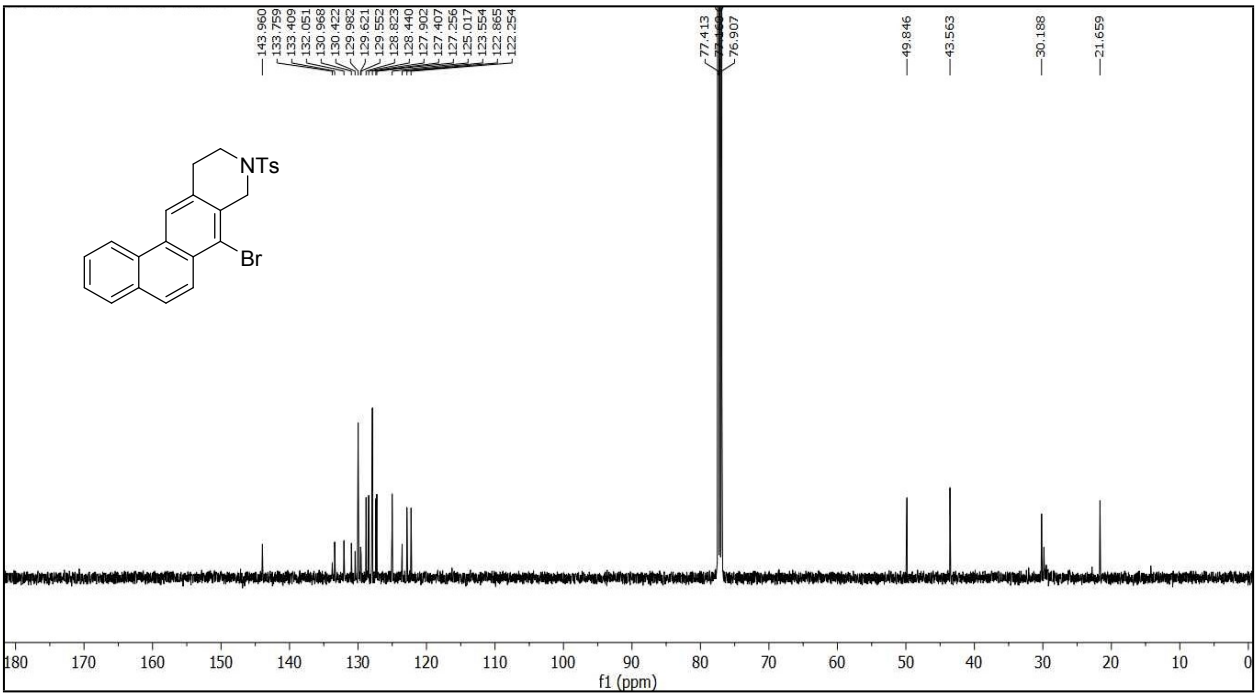
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **2.2a**



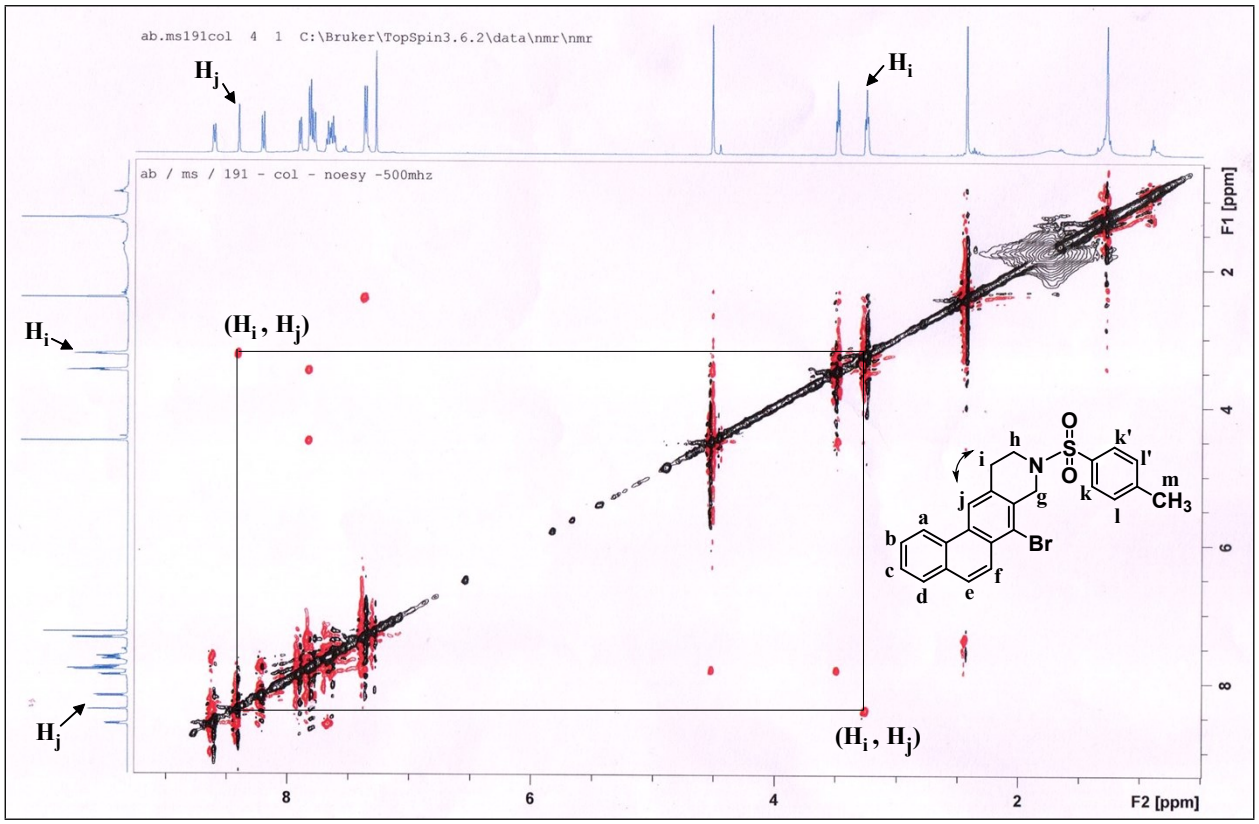
NOESY spectrum of compound **2.2a** in $CDCl_3$



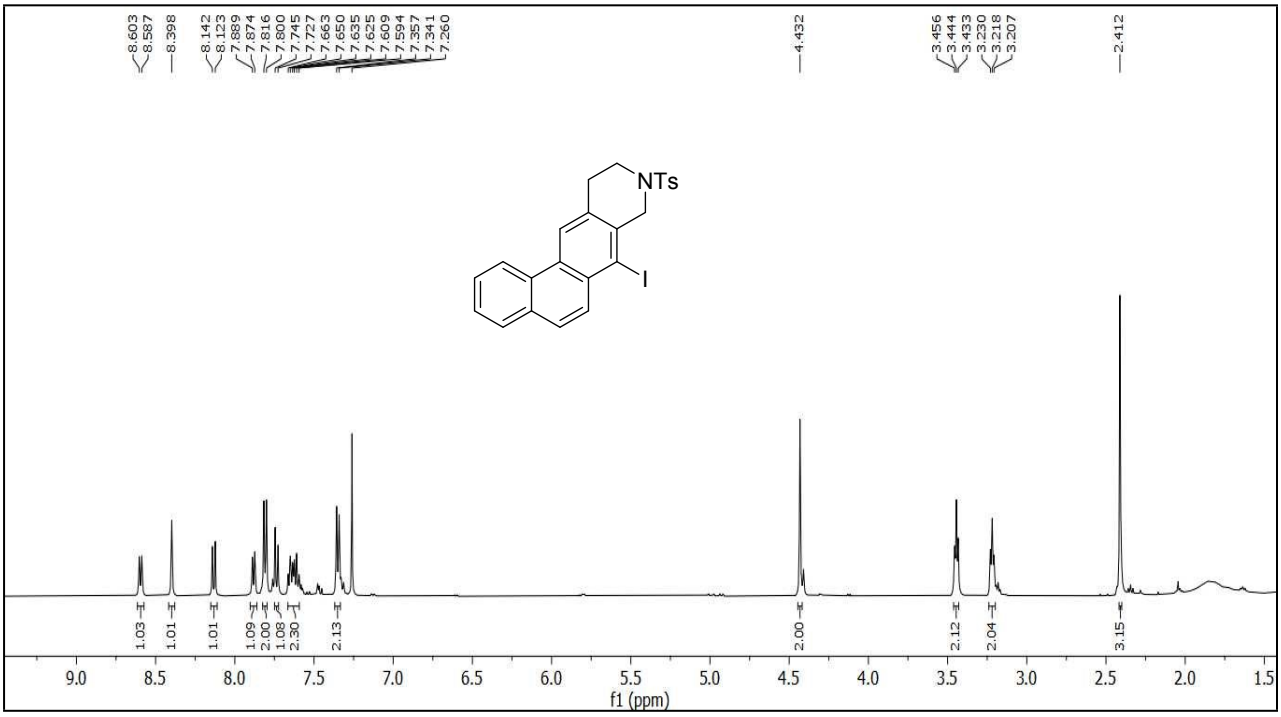
^1H NMR spectrum (500 MHz, $CDCl_3$) of the compound **2.1b**



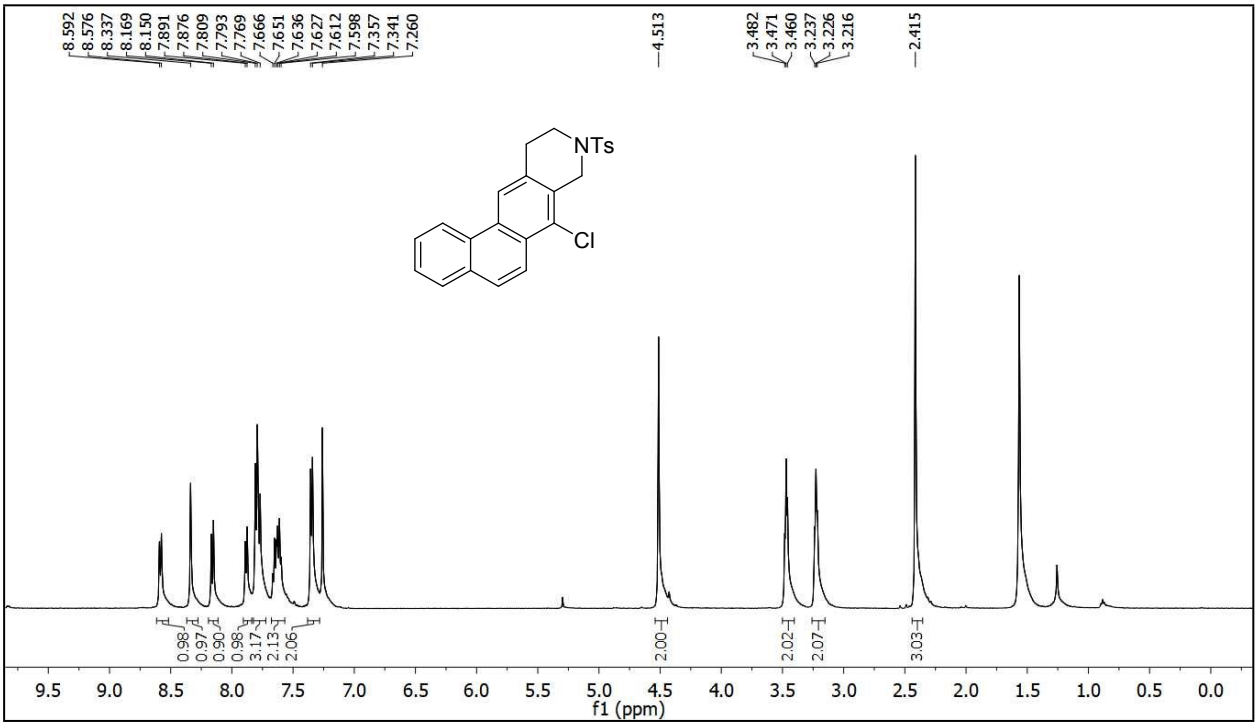
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **2.1b**



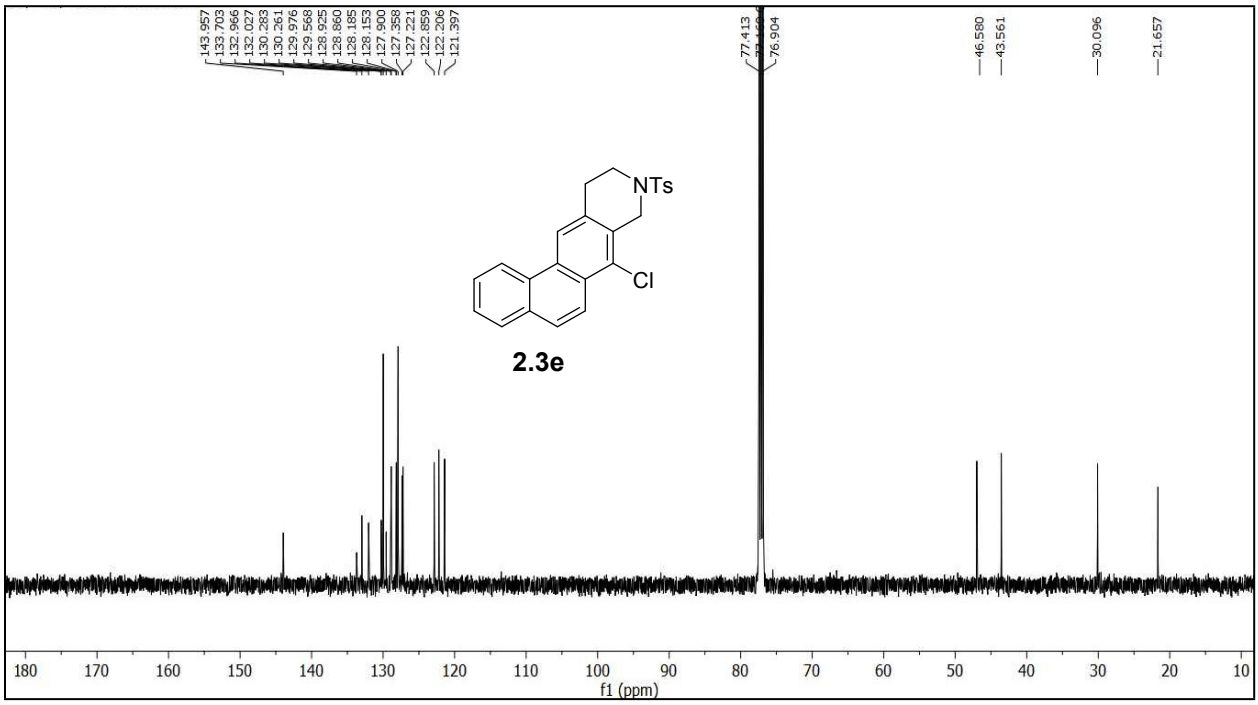
NOESY spectrum of compound **2.1b** in $CDCl_3$



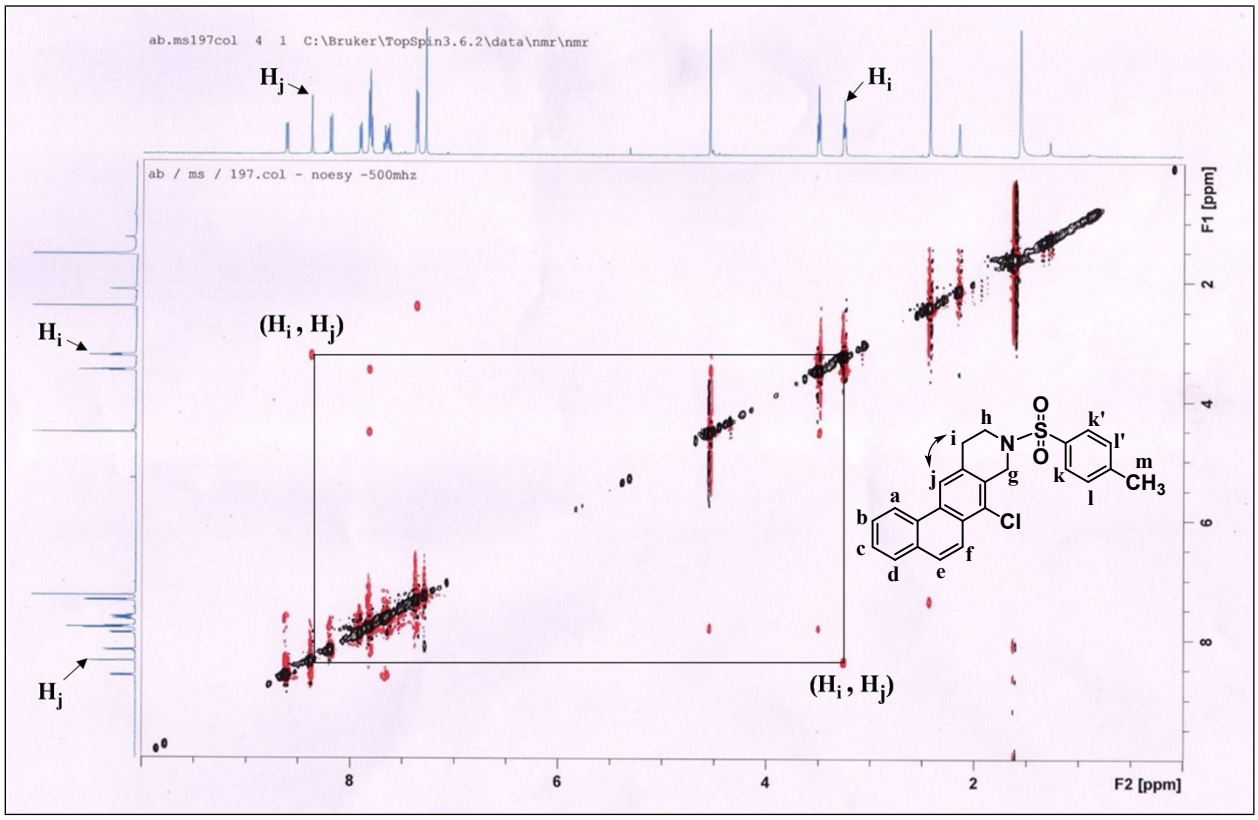
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **2.2b**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the compound **2.3b**

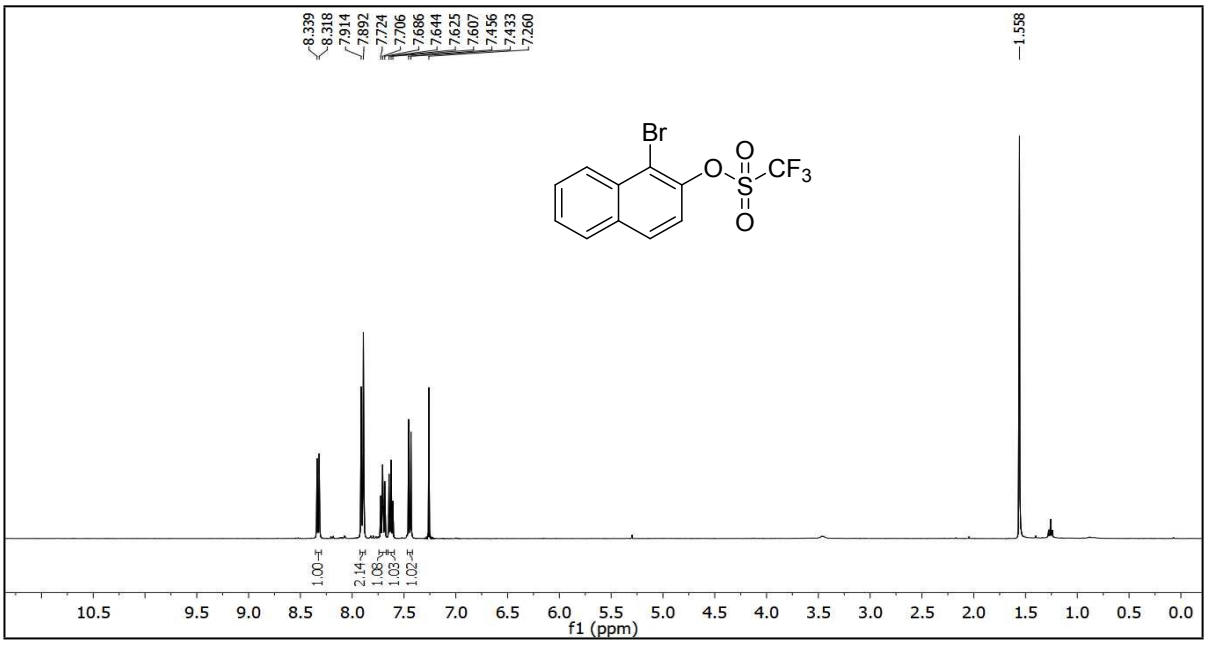


^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **2.3b**

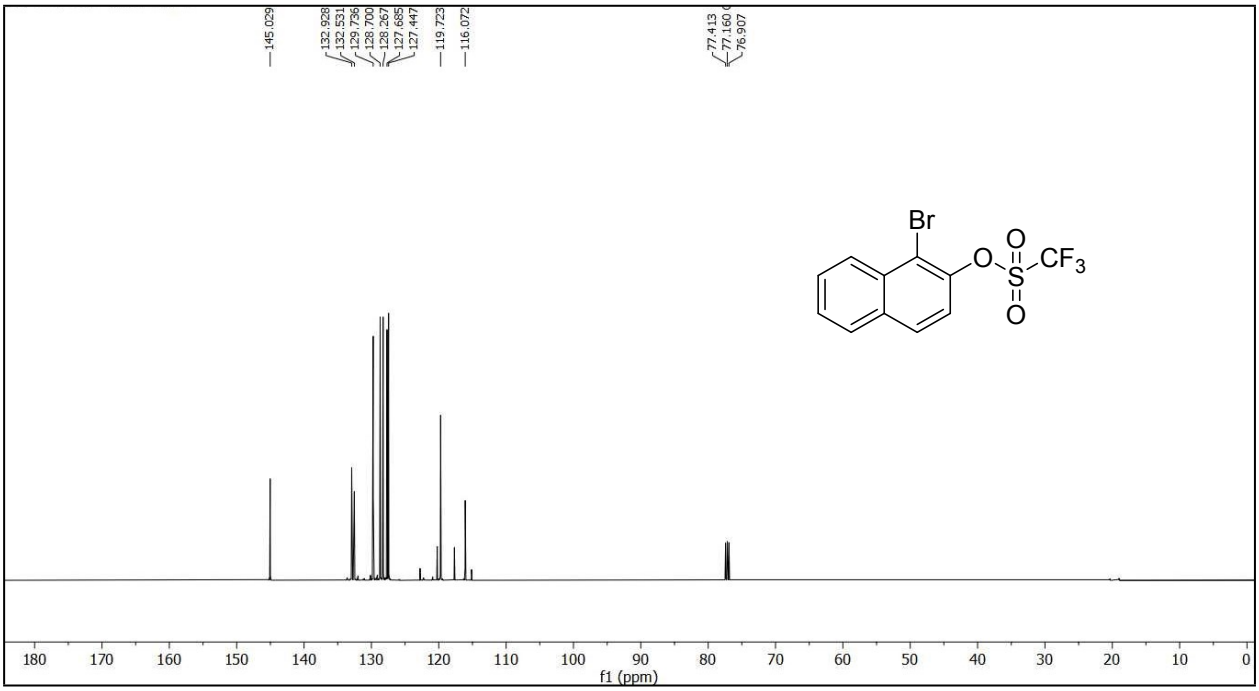


NOESY spectrum of compound **2.3b** in $CDCl_3$

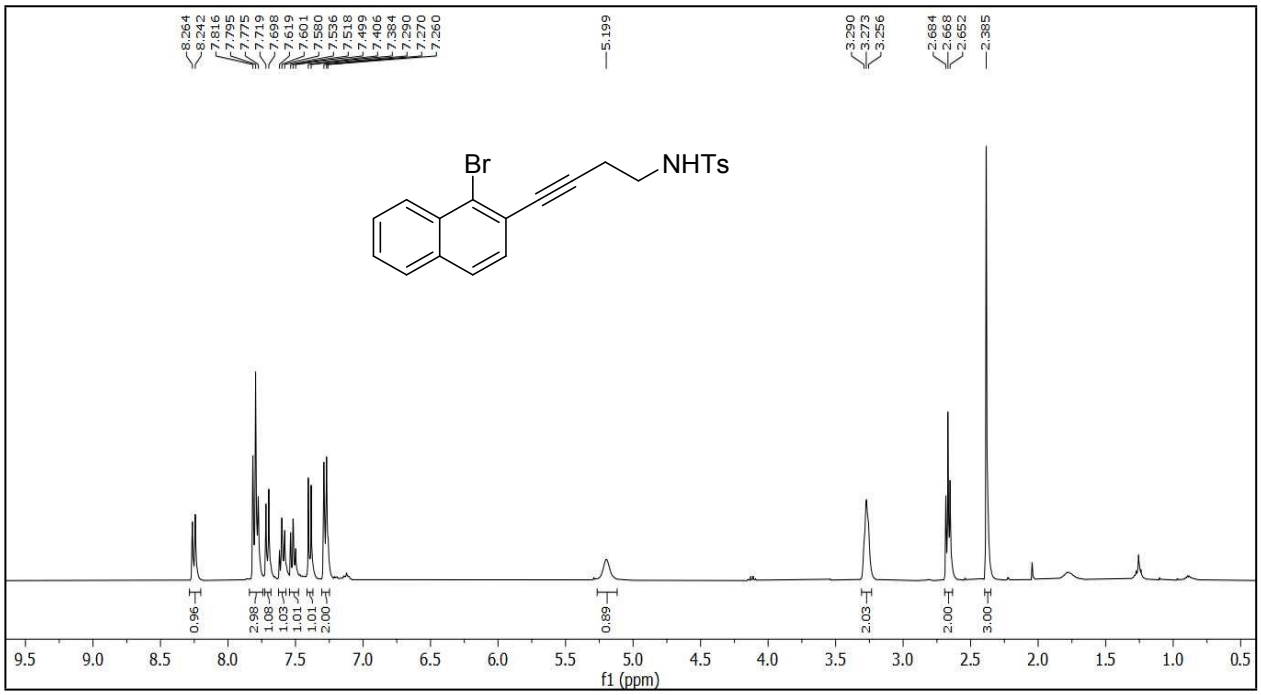
NMR Spectra of intermediated compounds



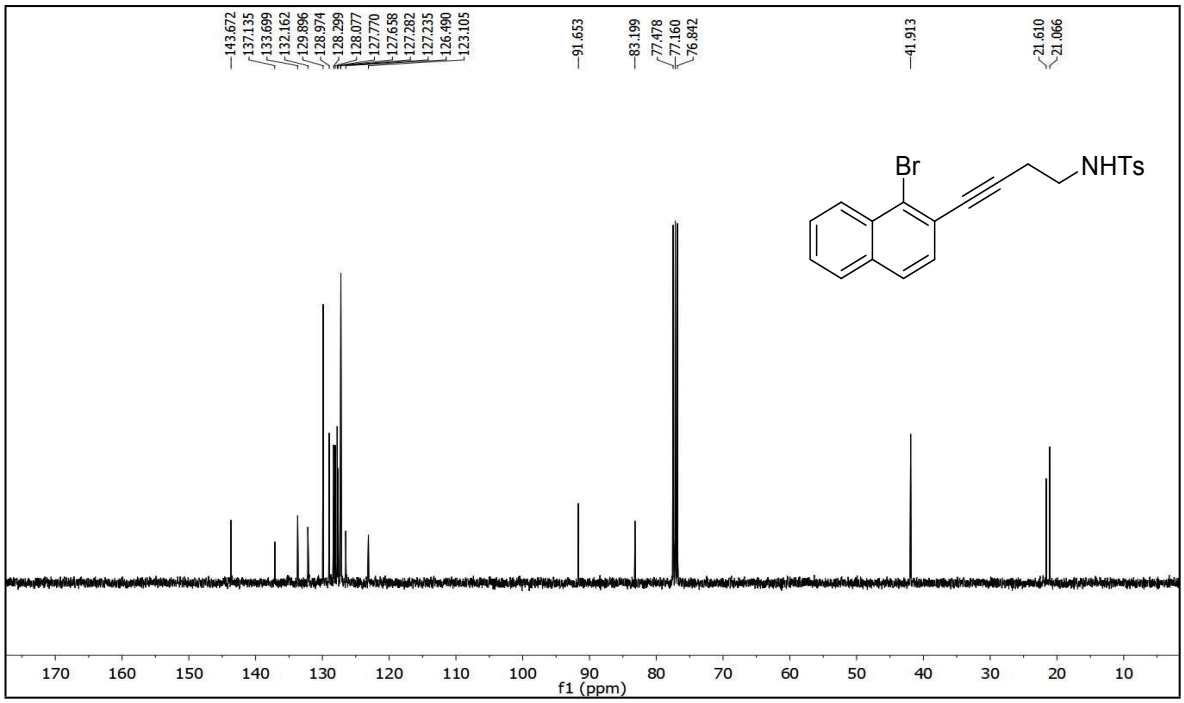
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **4**



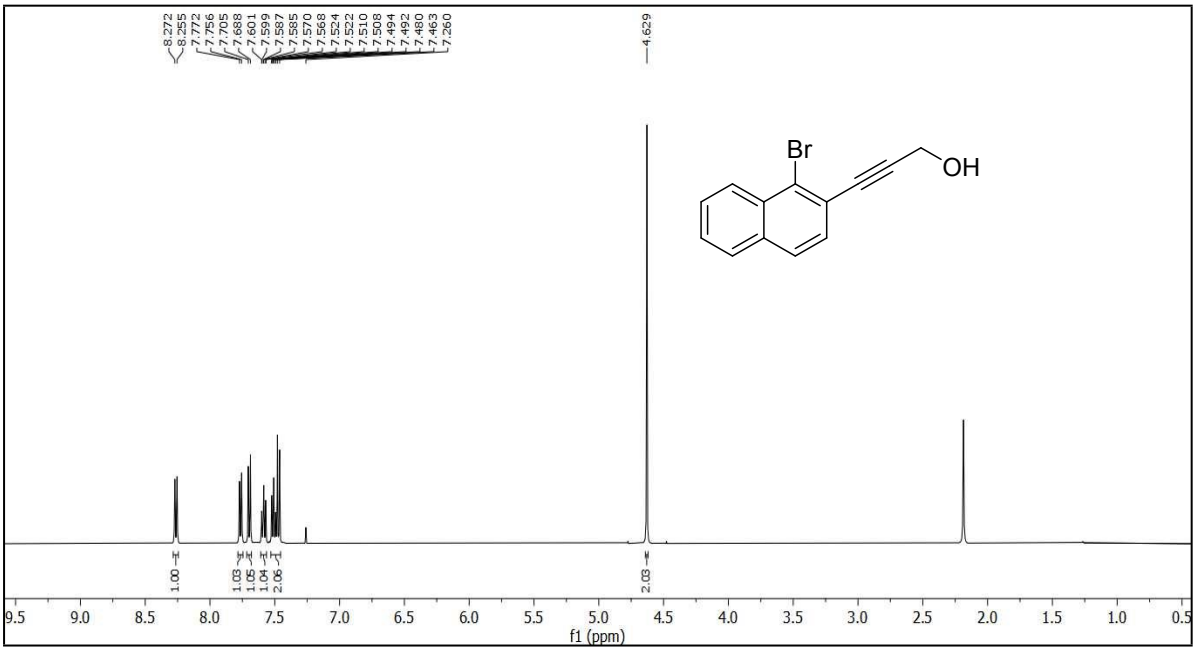
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **4**



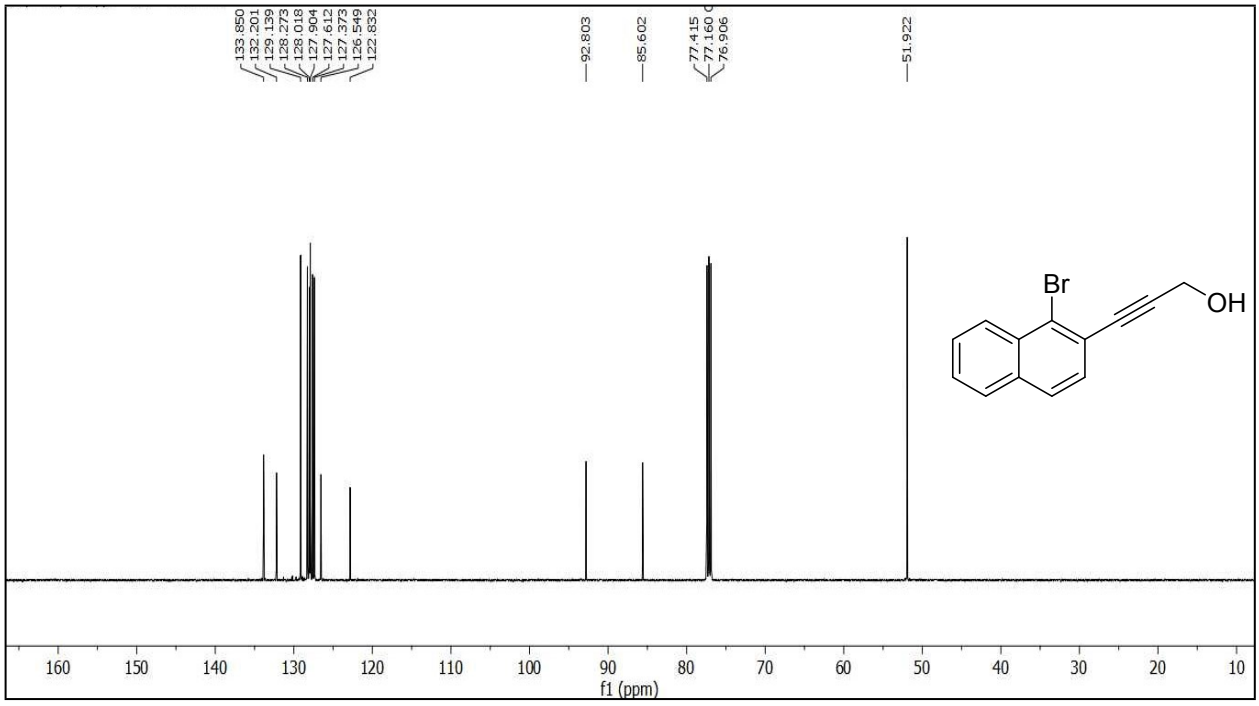
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **5a**



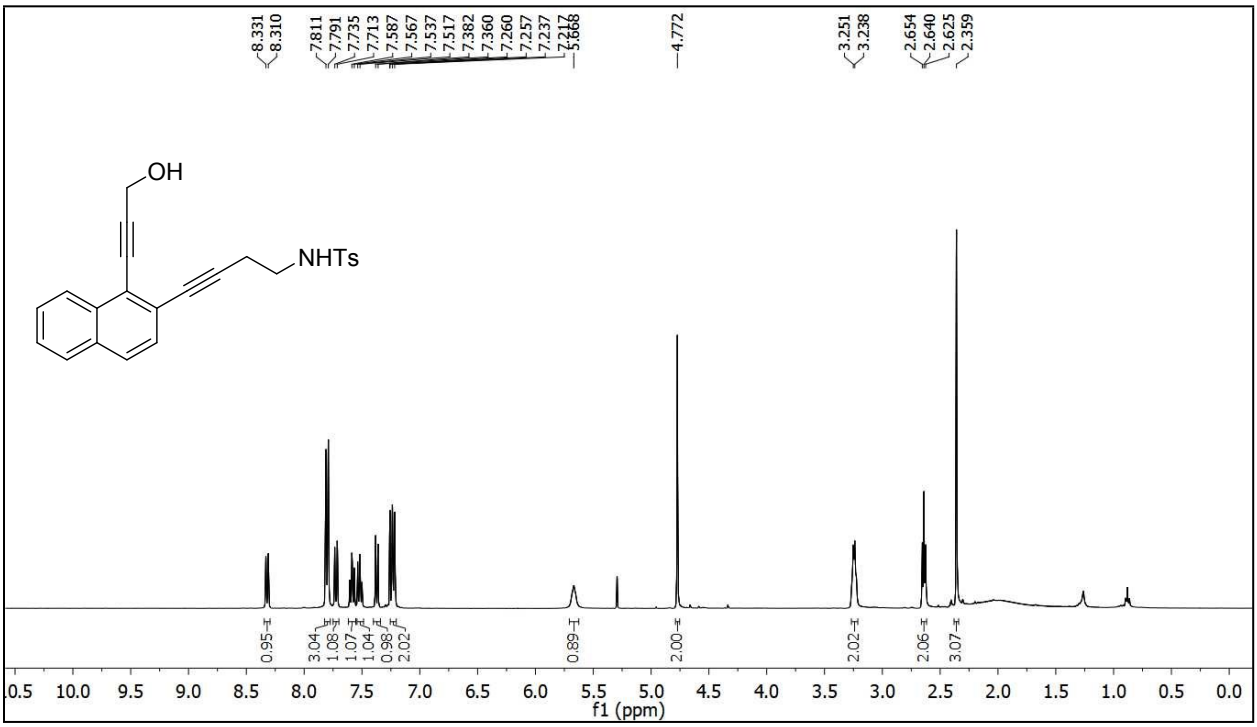
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the compound **5a**



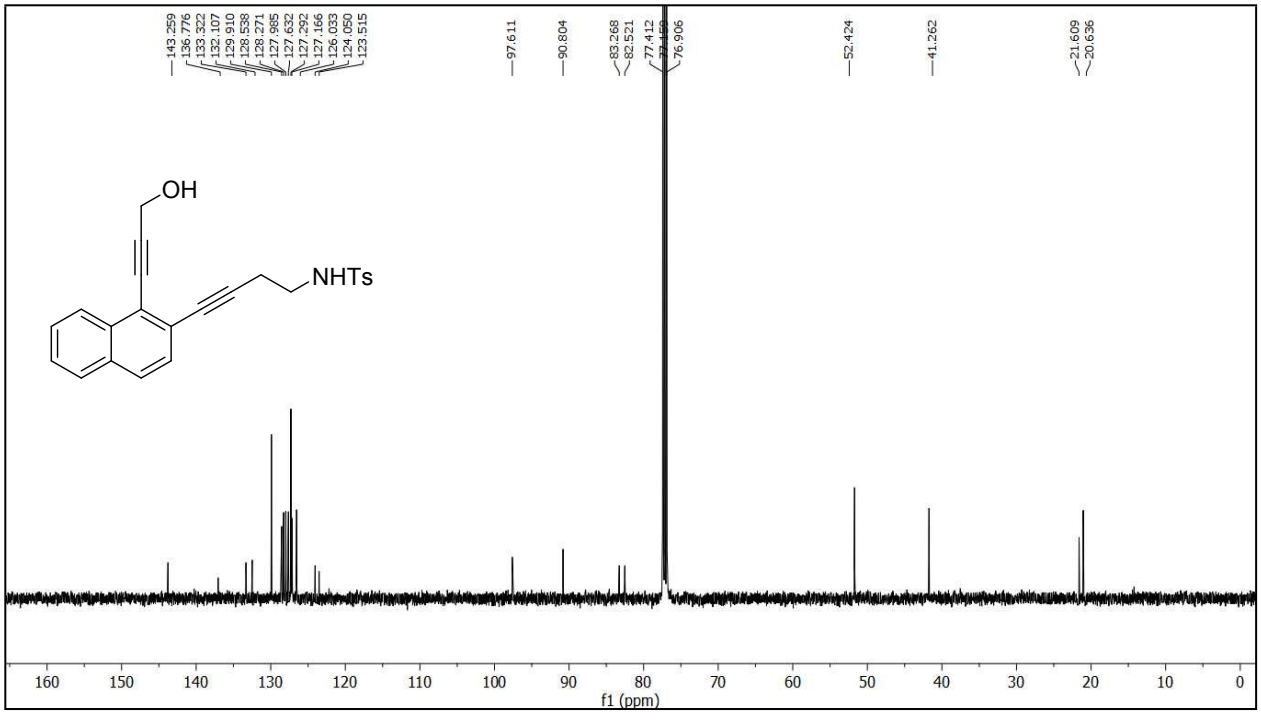
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **5b**



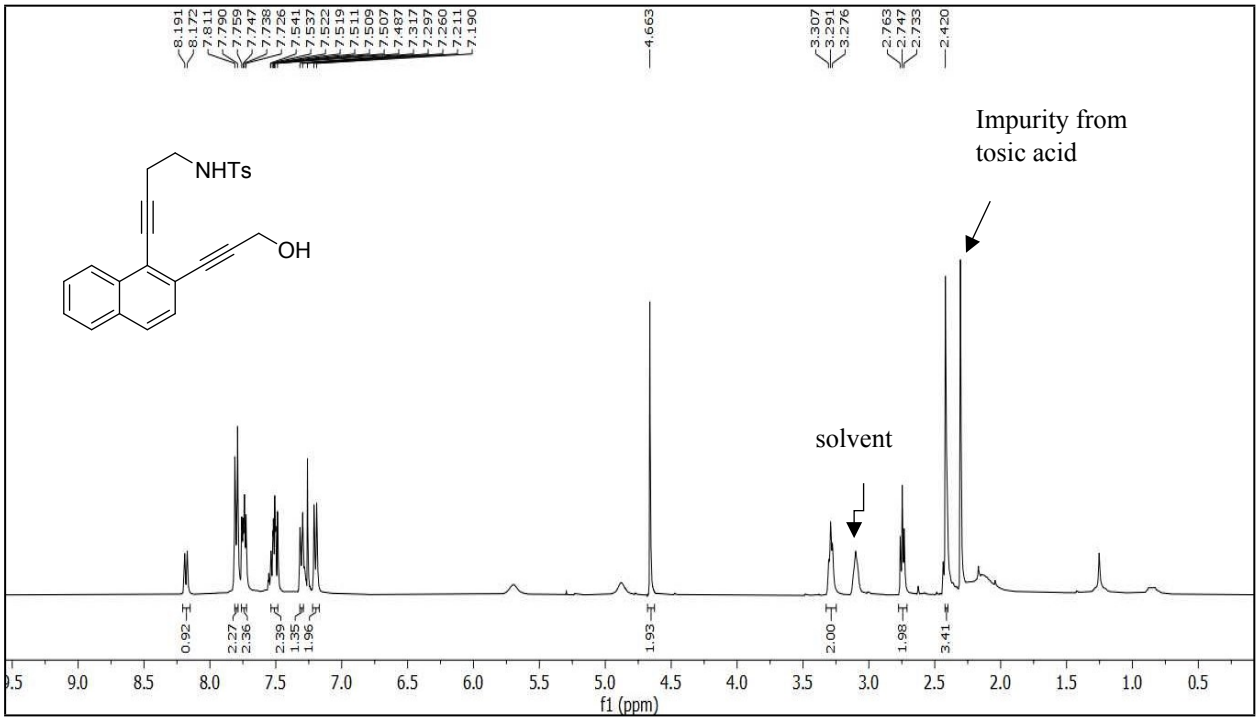
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **5b**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **6a**

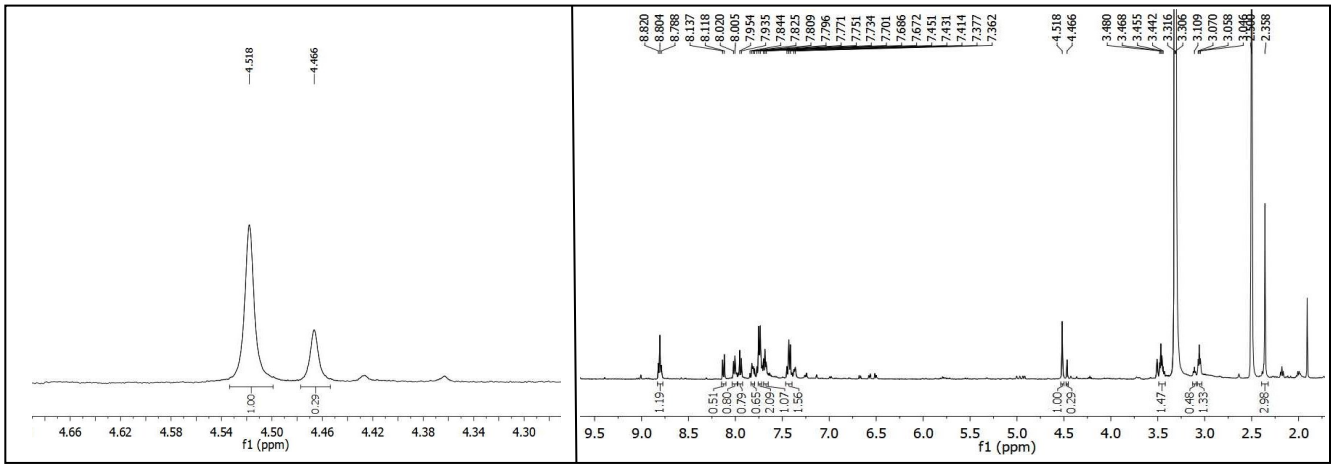


^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the compound **6a**

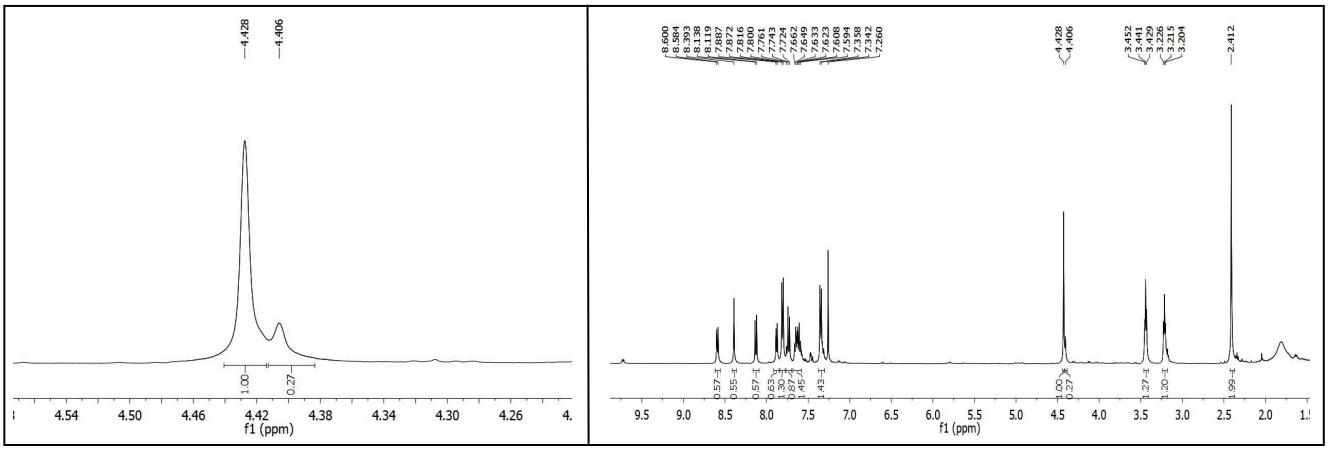


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **6b**

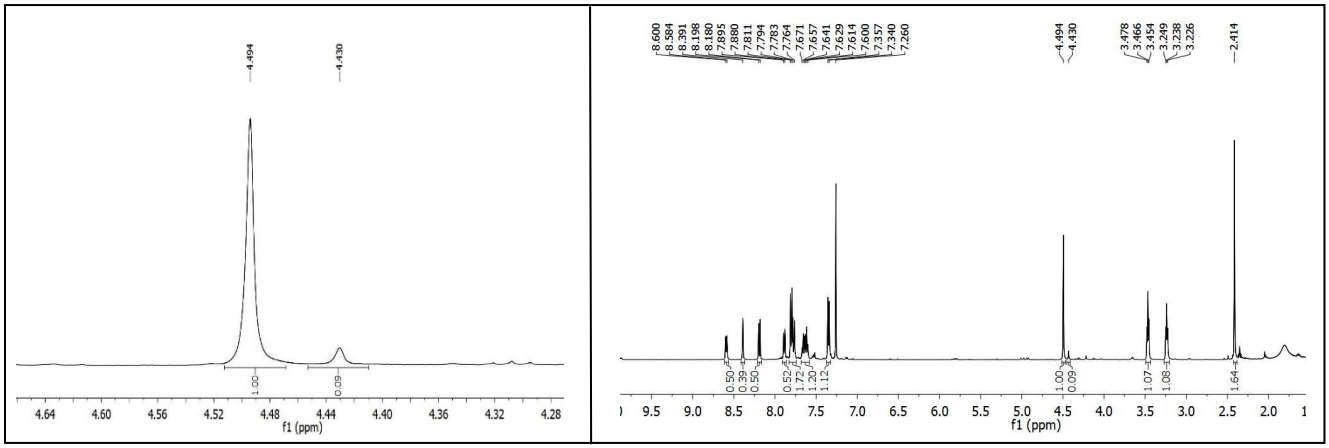
^{1}H NMR spectra of crude reaction mixture showing the ratio of the regioisomeric products.



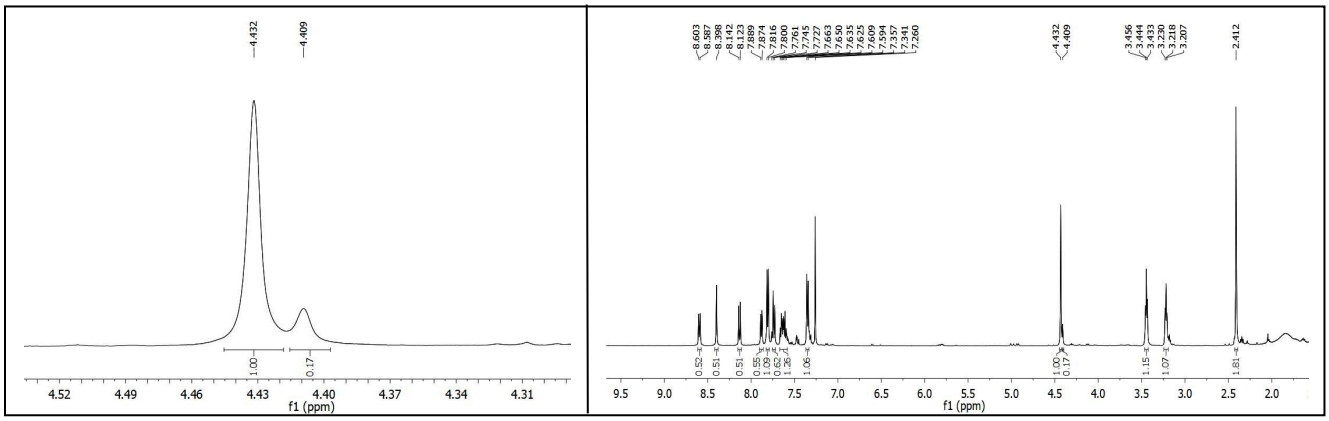
Crude NMR of compound **2.1a** + **2.1a'** in DMSO-d_6 (500 MHz)



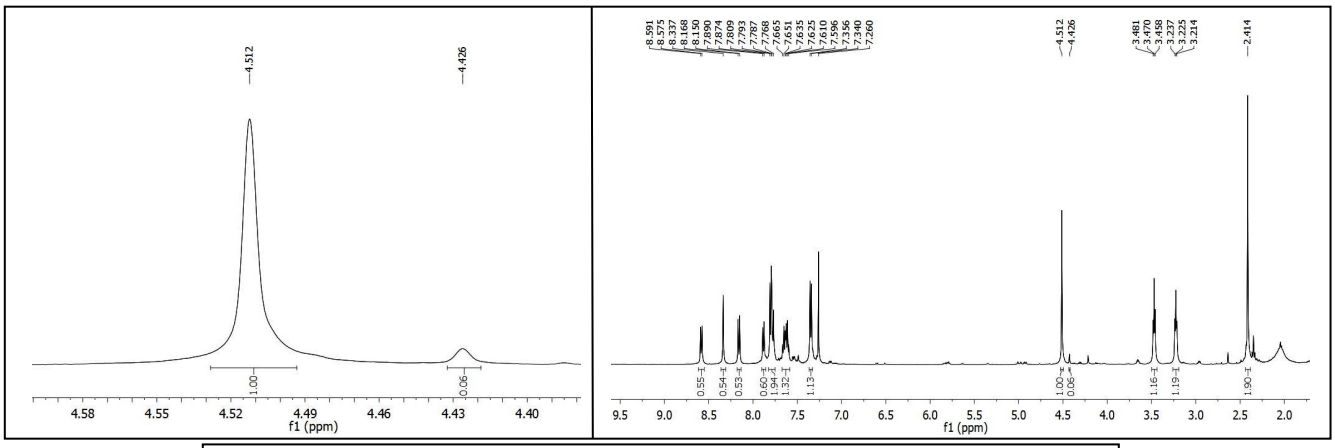
Crude NMR of compound **2.2a** + **2.2a'** in $CDCl_3$ (500 MHz)



Crude NMR of compound **2.1b** + **2.1b'** in $CDCl_3$ (500 MHz)



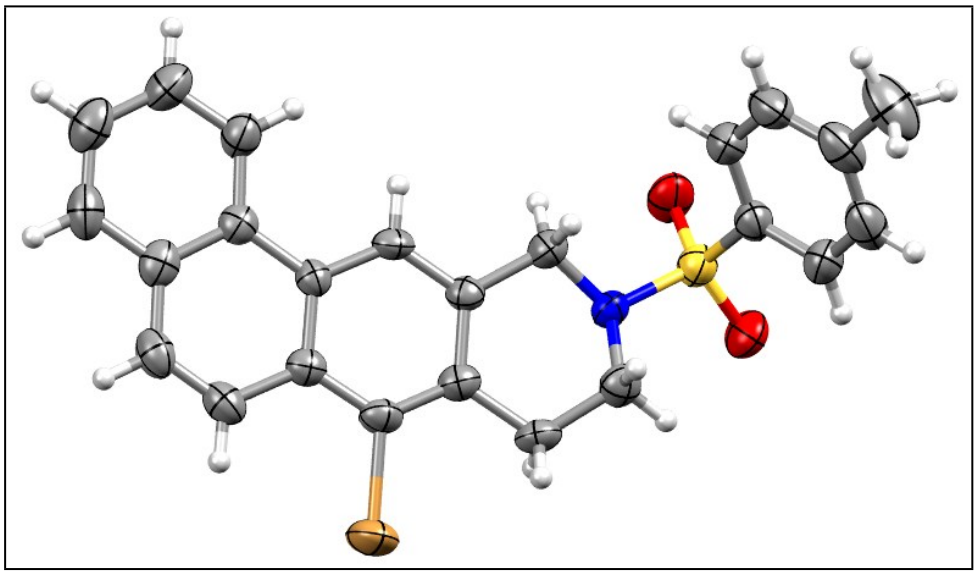
Crude NMR of compound **2.2b** + **2.2b'** in $CDCl_3$ (500 MHz)



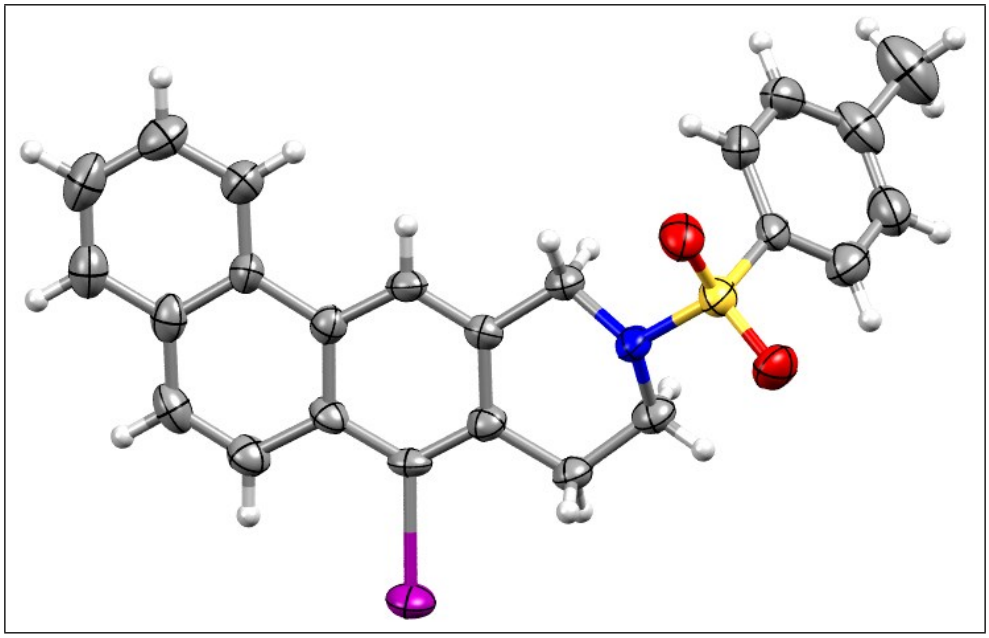
Crude NMR of compound **2.3b** + **2.3b'** in $CDCl_3$ (500 MHz)

ORTEP diagram of some halogenated products with 50% probability ellipsoids

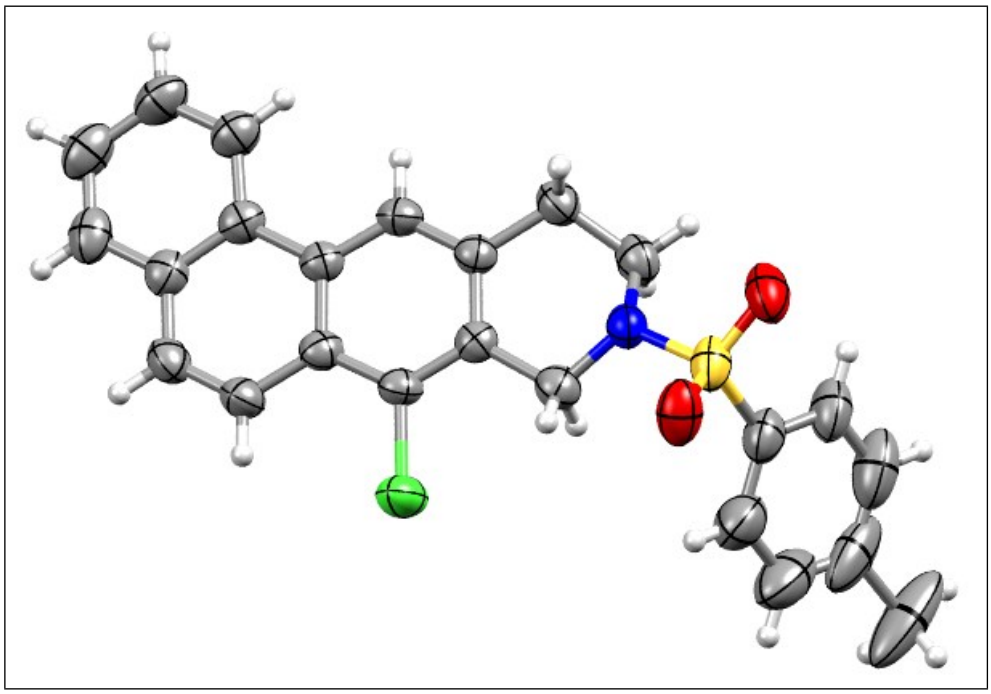
Sample preparation: In a 4/5 mg of respective compounds dissolved in distilled dichloromethane (~1 ml), 3-4 drops of HPLC grade hexane was added, swirled and then the solution was kept undisturbed until crystal growth occurred.



Compound 2.1a (CCDC: 2062240)



Compound 2.2a (CCDC: 2062241)



Compound 2.3b (CCDC: 2062245)

X-Ray Crystallographic Data

Table 1: Crystallographic data for Compound 2.1a (CCDC: 2062240)

Empirical formula	C24 H20 Br N O2 S
Formula weight	466.38
Temperature(K)	296(2)
Radiation	Mo-Kα
Wavelength(λ)	0.71073
Crystal system	monoclinic
Space group	P 21/c
a[Å]	16.51(5)
b[Å]	7.40(2)
c[Å]	16.74(5)
α[°]	90
β[°]	96.00(6)
γ[°]	90
Volume[$Å^3$]	2034(11)
Z	4
Density (calculated) [g/cm^3]	1.523
Absorption coefficient [$\mu(mm^{-1})$]	2.144
F(000)	952
R_{int}	0.1112
GOF	1.029
Final R indices[I>2σ(I)]	$R_1 = 0.0483$, $wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.1201$, $wR_2 = 0.1342$

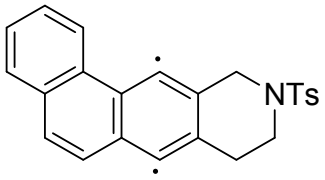
Table 2: Crystallographic data for Compound 2.2a (CCDC: 2062241)

Empirical formula	C24 H20 I N O2 S
Formula weight	513.37
Temperature(K)	296(2)
Radiation	Mo-Kα
Wavelength(λ)	0.71073
Crystal system	monoclinic
Space group	P 21/c
a[Å]	16.227(5)
b[Å]	7.418(2)
c[Å]	17.261(3)
α[°]	90
β[°]	96.413(18)
γ[°]	90
Volume[$Å^3$]	2064.8(10)
Z	4
Density (calculated) [g/cm^3]	1.651
Absorption coefficient [$\mu(mm^{-1})$]	1.673
F(000)	364
R_{int}	0.0956
GOF	0.967
Final R indices[I>2σ(I)]	$R_1 = 0.0567$, $wR_2 = 0.1456$
R indices (all data)	$R_1 = 0.1224$, $wR_2 = 0.1966$

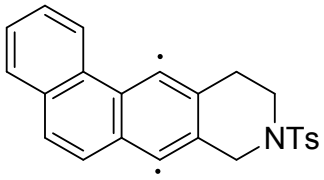
Table 3: Crystallographic data for Compound 2.3b (CCDC: 2062245)

Empirical formula	C24 H20 Cl N O2 S
Formula weight	421.92
Temperature(K)	296(2)
Radiation	Mo-Kα
Wavelength(λ)	0.71073
Crystal system	monoclinic
Space group	P 21/c
a[Å]	8.0989(18)
b[Å]	34.797(10)
c[Å]	7.6810(18)
α[°]	90
β[°]	107.300(16)
γ[°]	90
Volume[$Å^3$]	2066.7(9)
Z	4
Density (calculated) [g/cm^3]	1.356
Absorption coefficient [$\mu(mm^{-1})$]	0.306
F(000)	880
R_{int}	0.1011
GOF	1.005
Final R indices[$I>2\sigma(I)$]	$R_1 = 0.0686$, $wR_2 = 0.1659$
R indices (all data)	$R_1 = 0.1518$, $wR_2 = 0.2188$

Coordinates and energies of the geometry optimized diradicals



(E_1)



(E_2)

For *p*-benzyne E_1

TOTAL SCF ENERGY

Total Energy: -1520.30269459 Eh -41369.53951 eV

Components

Nuclear Repulsion: 2554.92220037 Eh 69522.96755 eV

Electronic Energy: -4075.22489497 Eh -110892.50706 eV

One Electron Energy: -7155.48581043 Eh -194710.66780 eV

Two Electron Energy: 3080.26091546 Eh 83818.16074 eV

Virial components

Potential Energy: -3035.63069473 Eh -82603.71070 eV

Kinetic Energy: 1515.32800013 Eh 41234.17119 eV

Virial Ratio: 2.00328292

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                    .--------------------.
---------------------|Geometry convergence|-------------------------
Item                 value                   Tolerance       Converged
---------------------------------------------------------------------
Energy change      -0.0000018576             0.0000050000      YES
RMS gradient        0.0000270685             0.0001000000      YES
MAX gradient        0.0002032672             0.0003000000      YES
RMS step            0.0003617529             0.0020000000      YES
MAX step            0.0014393394             0.0040000000      YES
.....................................................
Max(Bonds)      0.0001      Max(Angles)    0.03
Max(Dihed)        0.08      Max(Improp)    0.00
---------------------------------------------------------------------

          ************************HURRAY********************
          ***        THE OPTIMIZATION HAS CONVERGED     ***
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```

--- Optimized Parameters ---

CARTESIAN COORDINATES (Å)

C	-3.56984359455764	-1.09155719506711	-1.54014097548725
C	-4.09095381703151	-2.29656926020782	-2.06668916276223
C	-3.32811728305579	-3.42553868115112	-2.05784187557960
C	-2.01459909521009	-3.40441215070056	-1.51934291799843
C	-1.49568325931844	-2.20417097008289	-0.98933109101508
C	-2.31116698702916	-1.04324789462843	-1.01468813048402
C	-1.20599787918463	-4.57895052241876	-1.50504141415562
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C	0.55739755527303	-3.40270291157973	-0.38036817810816
C	-0.15747477098168	-2.18640305802333	-0.44454465702276
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C	1.85668054618371	-1.09068819522605	0.38237647223441
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C	4.11623983387664	-2.24313766203592	0.54855304247799
C	4.65047315312404	-0.82383627581621	0.63887251544378
N	3.77901127934618	-0.06478393774446	1.52165167105307
C	2.42367361722845	0.14875347186266	1.04126319794750
C	4.84459098488245	2.44982985361131	1.75905124422063
C	6.11671519728869	2.59051049508787	1.22096722587744
C	6.44244549662459	3.74618084237125	0.52764274641334
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C	4.24920121639378	4.61992459717908	0.93185058264927
C	3.91075347466885	3.47153603760798	1.62723509030025
C	5.88336914400912	6.04623910519208	-0.35627665628911
S	4.41058846761489	0.96593864445912	2.62304665169341
O	3.35603192844780	1.29612332607438	3.52775002167629
O	5.62531364709310	0.37396625835675	3.08870516607248
H	-4.17832260918838	-0.19672860620425	-1.55800622259435
H	-5.09209824168289	-2.31640769446503	-2.47632732186588
H	-3.71551856790287	-4.35306891698686	-2.45934967644386
H	-1.90560816573299	-0.12490071986796	-0.61970162588277
H	-1.60941537877011	-5.48824131174652	-1.93210331831008
H	0.61450201107332	-5.50372079542046	-0.90963513897086
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H	4.63234601357516	-2.79237093606409	-0.24245723948624
H	5.65530350351750	-0.83427792420423	1.04584385516944

H	4.68593156250778	-0.35830010952670	-0.35215389616884
H	1.79331267019569	0.43195750559946	1.87949762971056
H	2.37382579721165	0.95546538473843	0.30165788085231
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H	7.43629884233236	3.84981736669552	0.11195107679369
H	3.51770671705100	5.41155695945282	0.83200216934379
H	2.93478992940425	3.37223996078552	2.07960228835325
H	6.73009058565354	5.89118676831598	-1.02377539746797
H	5.04601102422496	6.41725100548091	-0.94736181611810
H	6.15843254569017	6.82878122723796	0.35477304142002

CARTESIAN COORDINATES (A.U.)

NO	LB	ZA	FRAG	MASS	X	Y	Z
0	C	6.0000	0	12.011	-6.746027	-2.062744	-2.910445
1	C	6.0000	0	12.011	-7.730782	-4.339887	-3.905477
2	C	6.0000	0	12.011	-6.289230	-6.473330	-3.888758
3	C	6.0000	0	12.011	-3.807041	-6.433407	-2.871142
4	C	6.0000	0	12.011	-2.826432	-4.165279	-1.869565
5	C	6.0000	0	12.011	-4.367473	-1.971453	-1.917483
6	C	6.0000	0	12.011	-2.279006	-8.652962	-2.844116
7	C	6.0000	0	12.011	0.061290	-8.682239	-1.787181
8	C	6.0000	0	12.011	1.053329	-6.430177	-0.718792
9	C	6.0000	0	12.011	-0.297584	-4.131703	-0.840068
10	C	6.0000	0	12.011	3.403697	-6.326715	0.577575

11 C	6.0000	0	12.011	4.977430	-4.233211	0.542507
12 C	6.0000	0	12.011	3.508618	-2.061102	0.722587
13 C	6.0000	0	12.011	1.003688	-1.836384	-0.292778
14 C	6.0000	0	12.011	7.778566	-4.238916	1.036615
15 C	6.0000	0	12.011	8.788121	-1.556825	1.207294
16 N	7.0000	0	14.007	7.141296	-0.122424	2.875505
17 C	6.0000	0	12.011	4.580079	0.281103	1.967702
18 C	6.0000	0	12.011	9.154950	4.629507	3.324125
19 C	6.0000	0	12.011	11.558917	4.895355	2.307294
20 C	6.0000	0	12.011	12.174458	7.079256	0.997100
21 C	6.0000	0	12.011	10.425582	9.024917	0.700116
22 C	6.0000	0	12.011	8.029827	8.730392	1.760942
23 C	6.0000	0	12.011	7.390253	6.560252	3.075029
24 C	6.0000	0	12.011	11.117956	11.425736	-0.673265
25 S	16.0000	0	32.060	8.334804	1.825360	4.956840
26 O	8.0000	0	15.999	6.341981	2.449318	6.666481
27 O	8.0000	0	15.999	10.630302	0.706694	5.836807
28 H	1.0000	0	1.008	-7.895885	-0.371763	-2.944205
29 H	1.0000	0	1.008	-9.622671	-4.377376	-4.679580
30 H	1.0000	0	1.008	-7.021313	-8.226108	-4.647497
31 H	1.0000	0	1.008	-3.601078	-0.236028	-1.171066
32 H	1.0000	0	1.008	-3.041354	-10.371273	-3.651146
33 H	1.0000	0	1.008	1.161241	-10.400525	-1.718961
34 H	1.0000	0	1.008	8.131547	-5.233172	2.806881
35 H	1.0000	0	1.008	8.753865	-5.276816	-0.458178

36 H	1.0000	0	1.008	10.686975	-1.576557	1.976358
37 H	1.0000	0	1.008	8.855127	-0.677089	-0.665474
38 H	1.0000	0	1.008	3.388870	0.816281	3.551736
39 H	1.0000	0	1.008	4.485881	1.805568	0.570051
40 H	1.0000	0	1.008	12.946683	3.421425	2.569962
41 H	1.0000	0	1.008	14.052568	7.275100	0.211557
42 H	1.0000	0	1.008	6.647502	10.226361	1.572256
43 H	1.0000	0	1.008	5.545949	6.372610	3.929879
44 H	1.0000	0	1.008	12.718028	11.132730	-1.934655
45 H	1.0000	0	1.008	9.535579	12.126847	-1.790254
46 H	1.0000	0	1.008	11.637751	12.904526	0.670424

INTERNAL COORDINATES (Å)

C	0	0	0	0.000000000000	0.00000000	0.00000000
C	1	0	0	1.414518622933	0.00000000	0.00000000
C	2	1	0	1.362560019039	119.81337365	0.00000000
C	3	2	1	1.419773745146	120.53665188	0.24065964
C	4	3	2	1.410944744890	119.69536659	0.00000000
C	1	2	3	1.364808148851	120.87867872	359.66905637
C	4	3	2	1.426036761871	121.07359239	180.04125891
C	7	4	3	1.358961118603	122.02256023	182.73181170
C	8	7	4	1.419673307278	119.42696330	358.66542018
C	9	8	7	1.412284106351	121.17705283	356.98000627

C	9	8	7	1.421459388634	123.23518725	175.52532414
C	11	9	8	1.386062699833	123.36978794	147.07233401
C	12	11	9	1.390829961429	108.89619425	40.34325937
C	10	9	8	1.425965684762	118.68047069	194.69885507
C	12	11	9	1.505184807854	125.99834526	202.95527285
C	15	12	11	1.519203499047	110.77875150	188.19933834
N	16	15	12	1.454271393846	108.23931533	47.77487213
C	17	16	15	1.453723319187	115.77015994	293.88732690
C	17	16	15	2.741368487794	107.36233228	177.20098750
C	19	17	16	1.388389522243	114.55307586	350.18803208
C	20	19	17	1.386496669062	119.57192848	140.16950130
C	21	20	19	1.393290564236	121.08445298	0.53253726
C	22	21	20	1.395236966232	118.39981480	0.16758008
C	23	22	21	1.384522578766	121.12140408	359.86550295
C	22	21	20	1.508804048204	121.01543919	178.54841663
S	17	16	15	1.635343905601	120.42231587	137.74617684
O	26	17	16	1.428145512870	106.68969388	193.76282723
O	26	17	16	1.429274787989	106.65505399	324.53055598
H	1	2	3	1.082258786865	119.41182789	179.49005823
H	2	1	3	1.081890541542	119.83280098	180.14093016
H	3	2	1	1.082405011096	120.47918872	180.09485563
H	6	1	2	1.078820573468	121.18383633	179.45630199
H	7	4	3	1.082560524178	118.46037311	1.11189889
H	8	7	4	1.080228149533	120.95722781	177.55494550
H	15	12	11	1.090539124291	108.59437568	308.90919551

H	15	12	11	1.092574960447	109.90338735	66.08520930
H	16	15	12	1.084167299106	109.83054653	167.18527413
H	16	15	12	1.095497407315	110.76949389	286.74896036
H	18	17	16	1.086368450785	108.92271858	162.21388419
H	18	17	16	1.095575164291	111.94179419	281.08870262
H	20	19	17	1.080268515960	119.99025864	319.00647422
H	21	20	19	1.082259010653	119.18468844	179.91861389
H	23	22	21	1.082467415310	119.68477429	179.30913693
H	24	23	22	1.080278035708	120.49122910	178.41156778
H	25	22	21	1.089280953834	111.35039639	22.02050817
H	25	22	21	1.090045924305	111.17696918	142.82905433
H	25	22	21	1.092530878434	110.53402334	262.27228716

INTERNAL COORDINATES (A.U.)

C	0	0	0	0.000000000000	0.00000000	0.00000000
C	1	0	0	2.673052808675	0.00000000	0.00000000
C	2	1	0	2.574865277014	119.81337365	0.00000000
C	3	2	1	2.682983550458	120.53665188	0.24065964
C	4	3	2	2.666299157937	119.69536659	0.00000000
C	1	2	3	2.579113626673	120.87867872	359.66905637
C	4	3	2	2.694818936841	121.07359239	180.04125891
C	7	4	3	2.568064340807	122.02256023	182.73181170
C	8	7	4	2.682793750393	119.42696330	358.66542018

C	9	8	7	2.668830184293	121.17705283	356.98000627
C	9	8	7	2.686168955009	123.23518725	175.52532414
C	11	9	8	2.619278907129	123.36978794	147.07233401
C	12	11	9	2.628287725952	108.89619425	40.34325937
C	10	9	8	2.694684620570	118.68047069	194.69885507
C	12	11	9	2.844387067783	125.99834526	202.95527285
C	15	12	11	2.870878554893	110.77875150	188.19933834
N	16	15	12	2.748174658765	108.23931533	47.77487213
C	17	16	15	2.747138947759	115.77015994	293.88732690
C	17	16	15	5.180435674092	107.36233228	177.20098750
C	19	17	16	2.623675964244	114.55307586	350.18803208
C	20	19	17	2.620098990121	119.57192848	140.16950130
C	21	20	19	2.632937591382	121.08445298	0.53253726
C	22	21	20	2.636615758101	118.39981480	0.16758008
C	23	22	21	2.616368500099	121.12140408	359.86550295
C	22	21	20	2.851226440857	121.01543919	178.54841663
S	17	16	15	3.090352116363	120.42231587	137.74617684
O	26	17	16	2.698803898714	106.68969388	193.76282723
O	26	17	16	2.700937919417	106.65505399	324.53055598
H	1	2	3	2.045172713205	119.41182789	179.49005823
H	2	1	3	2.044476830394	119.83280098	180.14093016
H	3	2	1	2.045449036955	120.47918872	180.09485563
H	6	1	2	2.038675431495	121.18383633	179.45630199
H	7	4	3	2.045742914090	118.46037311	1.11189889
H	8	7	4	2.041335364770	120.95722781	177.55494550

H	15	12	11	2.060820283237	108.59437568	308.90919551
H	15	12	11	2.064667456025	109.90338735	66.08520930
H	16	15	12	2.048779278664	109.83054653	167.18527413
H	16	15	12	2.070190080246	110.76949389	286.74896036
H	18	17	16	2.052938852517	108.92271858	162.21388419
H	18	17	16	2.070337019636	111.94179419	281.08870262
H	20	19	17	2.041411646261	119.99025864	319.00647422
H	21	20	19	2.045173136103	119.18468844	179.91861389
H	23	22	21	2.045566963829	119.68477429	179.30913693
H	24	23	22	2.041429635978	120.49122910	178.41156778
H	25	22	21	2.058442685644	111.35039639	22.02050817
H	25	22	21	2.059888270334	111.17696918	142.82905433
H	25	22	21	2.064584153093	110.53402334	262.27228716

For *p*-benzyne E_2

TOTAL SCF ENERGY

Total Energy: -1520.30407307 Eh -41369.57702 eV

Components

Nuclear Repulsion: 2523.00508519 Eh 68654.45869 eV

Electronic Energy: -4043.30915826 Eh -110024.03571 eV

One Electron Energy: -7091.25956849 Eh -192962.98291 eV

Two Electron Energy: 3047.95041022 Eh 82938.94720 eV

Virial components

Potential Energy: -3035.61764893 Eh -82603.35570 eV

Kinetic Energy: 1515.31357585 Eh 41233.77868 eV

Virial Ratio: 2.00329338

```
                    .--------------------.
----------------------|Geometry convergence|-------------------------
Item                 value                   Tolerance       Converged
-----------------------------------------------------------------------
Energy change      -0.0000046317             0.0000050000      YES
RMS gradient        0.0000347094             0.0001000000      YES
MAX gradient        0.0001732191             0.0003000000      YES
RMS step            0.0013291810             0.0020000000      YES
MAX step            0.0067830307             0.0040000000      NO
.......................................................
Max(Bonds)      0.0003      Max(Angles)    0.08
Max(Dihed)        0.39      Max(Improp)    0.00
-----------------------------------------------------------------------

The energies and gradients are converged
and the convergence on bond distances, angles, dihedrals and impropers
is acceptable.
Convergence will therefore be signaled now


                    ************************HURRAY********************
                    ***        THE OPTIMIZATION HAS CONVERGED     ***
                    **********************************************
```

--- Optimized Parameters ---

CARTESIAN COORDINATES (Å)

C	-3.78168809438171	-3.83642917073320	1.83678882945424
C	-3.59984540278451	-5.23027234588723	1.96971146162278
C	-2.34164227513923	-5.75670189005744	1.92134143047403
C	-1.21577631020811	-4.91416511082610	1.74528653897842
C	-1.39620892393400	-3.52337471525493	1.62606556172863
C	-2.71067929926508	-3.00244870312694	1.67340633992892
C	0.10745152062889	-5.44719933939063	1.66681549936245
C	1.20336515309653	-4.65502433498551	1.54224335227120
C	1.06460825330028	-3.23824310543034	1.49730302995577
C	-0.23947713487834	-2.66864886390544	1.46465248524280
C	2.22312564997659	-2.40104856432583	1.41593919822298
C	2.17812675780425	-1.19832255055768	0.74061354844628
C	0.90808844364887	-0.61893165419484	0.89209843995451
C	-0.28964446689197	-1.37606288552189	0.92226392176080
C	3.40377321798714	-0.38806602059358	0.39985479035863
C	2.15835222831425	1.54051169126439	1.24592004729683
C	0.80185698225641	0.87547156198667	1.09215336977381
N	3.04484532904966	1.01566361687806	0.21717145397129
C	3.27582232436981	3.11232530907444	-1.43474120038285
C	3.21064590459783	4.46356397046650	-1.14209524570825
C	2.51880922577809	5.31395034608899	-1.99665327486809

C	1.89998591948848	4.83002858840347	-3.14347600888385
C	1.98654213226198	3.46147590002000	-3.42205761519599
C	2.67195314302733	2.60608410847292	-2.58271161353184
C	1.17534782194304	5.75723879354772	-4.08745649549071
S	4.19367873648338	2.02713844433071	-0.38600312888013
O	4.75063294003769	2.82150039126173	0.66737784718647
O	5.05207582000253	1.21799407767515	-1.19392578368373
H	-4.78247380411879	-3.42528143552020	1.86221862976020
H	-4.45770695169245	-5.87540889939985	2.10416122495797
H	-2.18993102667742	-6.82421421198915	2.01604498248456
H	-2.84970329186579	-1.93700356253590	1.56694852915695
H	0.23319726554648	-6.52090523261757	1.72726534091406
H	2.19388271231038	-5.08331612761522	1.51085746868447
H	4.14210152257983	-0.52139388229937	1.19466867085887
H	3.84537490716777	-0.75703082793943	-0.52099826019108
H	2.05635793853740	2.61668881497957	1.13323823855565
H	2.57982236522961	1.36200925020101	2.23924466350122
H	0.16637771859103	1.08592539668303	1.95552915203338
H	0.28240988308069	1.27378532038614	0.21845141965404
H	3.69918324684503	4.84425635460007	-0.25729830150382
H	2.46756303765031	6.36918370580471	-1.76226452077910
H	1.51409842429289	3.06534271907873	-4.31170907020813
H	2.74166682863737	1.55236915439685	-2.81302139043820
H	0.87712007733416	6.67801344661280	-3.58783951413494
H	1.81957375320980	6.02724727132552	-4.92754394790276

H 0.28195979677162 5.28472520116911 -4.49584009476874

CARTESIAN COORDINATES (A.U.)

NO	LB	ZA	FRAG	MASS	X	Y	Z
0	C	6.0000	0	12.011	-7.146355	-7.249800	3.471028
1	C	6.0000	0	12.011	-6.802722	-9.883782	3.722215
2	C	6.0000	0	12.011	-4.425063	-10.878590	3.630809
3	C	6.0000	0	12.011	-2.297484	-9.286426	3.298114
4	C	6.0000	0	12.011	-2.638452	-6.658213	3.072819
5	C	6.0000	0	12.011	-5.122442	-5.673806	3.162280
6	C	6.0000	0	12.011	0.203054	-10.293715	3.149825
7	C	6.0000	0	12.011	2.274031	-8.796721	2.914418
8	C	6.0000	0	12.011	2.011818	-6.119393	2.829493
9	C	6.0000	0	12.011	-0.452546	-5.043016	2.767792
10	C	6.0000	0	12.011	4.201099	-4.537324	2.675737
11	C	6.0000	0	12.011	4.116063	-2.264501	1.399557
12	C	6.0000	0	12.011	1.716038	-1.169611	1.685822
13	C	6.0000	0	12.011	-0.547349	-2.600382	1.742826
14	C	6.0000	0	12.011	6.432199	-0.733339	0.755616
15	C	6.0000	0	12.011	4.078695	2.911145	2.354448
16	C	6.0000	0	12.011	1.515290	1.654401	2.063871
17	N	7.0000	0	14.007	5.753924	1.919326	0.410395
18	C	6.0000	0	12.011	6.190407	5.881442	-2.711268
19	C	6.0000	0	12.011	6.067241	8.434913	-2.158247

20 C	6.0000	0	12.011	4.759860	10.041911	-3.773128
21 C	6.0000	0	12.011	3.590453	9.127431	-5.940309
22 C	6.0000	0	12.011	3.754021	6.541241	-6.466752
23 C	6.0000	0	12.011	5.049260	4.924785	-4.880618
24 C	6.0000	0	12.011	2.221085	10.879605	-7.724173
25 S	16.0000	0	32.060	7.924904	3.830736	-0.729440
26 O	8.0000	0	15.999	8.977395	5.331863	1.261161
27 O	8.0000	0	15.999	9.547040	2.301675	-2.256193
28 H	1.0000	0	1.008	-9.037566	-6.472844	3.519083
29 H	1.0000	0	1.008	-8.423845	-11.102914	3.976288
30 H	1.0000	0	1.008	-4.138370	-12.895896	3.809773
31 H	1.0000	0	1.008	-5.385159	-3.660406	2.961104
32 H	1.0000	0	1.008	0.440679	-12.322725	3.264058
33 H	1.0000	0	1.008	4.145837	-9.606075	2.855107
34 H	1.0000	0	1.008	7.827437	-0.985292	2.257597
35 H	1.0000	0	1.008	7.266705	-1.430581	-0.984544
36 H	1.0000	0	1.008	3.885953	4.944825	2.141510
37 H	1.0000	0	1.008	4.875158	2.573824	4.231559
38 H	1.0000	0	1.008	0.314408	2.052102	3.695415
39 H	1.0000	0	1.008	0.533677	2.407105	0.412813
40 H	1.0000	0	1.008	6.990443	9.154318	-0.486223
41 H	1.0000	0	1.008	4.663018	12.036013	-3.330197
42 H	1.0000	0	1.008	2.861231	5.792658	-8.147949
43 H	1.0000	0	1.008	5.180999	2.933553	-5.315840
44 H	1.0000	0	1.008	1.657517	12.619617	-6.780034

45 H	1.0000	0	1.008	3.438496	11.389847	-9.311709
46 H	1.0000	0	1.008	0.532827	9.986683	-8.495907

INTERNAL COORDINATES (Å)

C	0	0	0	0.000000000000	0.00000000	0.00000000
C	1	0	0	1.411925631028	0.00000000	0.00000000
C	2	1	0	1.364750099947	119.74840719	0.00000000
C	3	2	1	1.417193607157	120.49690527	0.31150000
C	4	3	2	1.407503994284	119.74446472	0.31557050
C	1	2	3	1.367215088217	120.83281343	359.32685146
C	4	3	2	1.428710987282	121.38580984	181.18897520
C	7	4	3	1.357971335214	122.33282613	182.20240322
C	8	7	4	1.424268992231	120.30192920	0.58265912
C	9	8	7	1.423426274069	119.21134091	354.46468978
C	9	8	7	1.431669421051	120.30821348	177.67712829
C	11	9	8	1.380086771815	120.73324926	147.75431592
C	12	11	9	1.404150562641	109.65155823	34.31225475
C	10	9	8	1.402669107991	114.22928092	203.10827332
C	12	11	9	1.508257743531	123.52031979	191.44557770
C	15	12	11	2.446694065712	86.08266053	226.54585642
C	13	12	11	1.511472153521	119.06603790	140.56845029
N	16	15	12	1.455904937524	33.02414501	222.08820855
C	18	16	15	2.679208099702	101.89097124	176.90260241

C	19	18	16	1.384100986389	129.01799765	29.80151672
C	20	19	18	1.389987195339	119.38777055	221.63199585
C	21	20	19	1.390080909596	121.05110781	359.56847162
C	22	21	20	1.399298449305	118.50179235	0.05726445
C	23	22	21	1.380574185342	121.04084529	359.85899683
C	22	21	20	1.508614694358	121.07077084	181.38684789
S	18	16	15	1.645210959726	117.55568361	216.12799387
O	26	18	16	1.432068562719	110.05523198	39.61443422
O	26	18	16	1.429789905976	106.16885595	170.58549910
H	1	2	3	1.082248202460	119.46687847	179.16539338
H	2	1	3	1.081759838704	119.88798379	180.31096722
H	3	2	1	1.082389774134	120.43436185	180.36919429
H	6	1	2	1.079738062496	120.85255037	179.70231834
H	7	4	3	1.082732894512	118.32506542	1.09513763
H	8	7	4	1.079603616349	120.77536022	178.40427247
H	15	12	11	1.092993187859	108.60918884	326.70308991
H	15	12	11	1.085871733518	109.84848666	84.00426629
H	16	15	12	1.086856580592	142.41129699	208.81058569
H	16	15	12	1.093706537849	89.38449723	91.12276784
H	17	13	12	1.092493685327	109.62987274	230.13825101
H	17	13	12	1.091711608721	106.75305811	115.06210840
H	20	19	18	1.080028267492	119.73760131	41.84621161
H	21	20	19	1.082165284648	119.14218925	179.79631137
H	23	22	21	1.082406700666	119.64122758	180.18838043
H	24	23	22	1.080841244468	120.43196145	180.66574010

H	25	22	21	1.089212044297	111.34998064	337.82026604
H	25	22	21	1.092555973984	110.47484803	97.54088457
H	25	22	21	1.090040560099	111.20357878	216.94716532

INTERNAL COORDINATES (A.U.)

C	0	0	0	0.000000000000	0.00000000	0.00000000
C	1	0	0	2.668152764107	0.00000000	0.00000000
C	2	1	0	2.579003930141	119.74840719	0.00000000
C	3	2	1	2.678107796271	120.49690527	0.31150000
C	4	3	2	2.659797081597	119.74446472	0.31557050
C	1	2	3	2.583662082896	120.83281343	359.32685146
C	4	3	2	2.699872490488	121.38580984	181.18897520
C	7	4	3	2.566193921270	122.33282613	182.20240322
C	8	7	4	2.691478336353	120.30192920	0.58265912
C	9	8	7	2.689885829818	119.21134091	354.46468978
C	9	8	7	2.705463120095	120.30821348	177.67712829
C	11	9	8	2.607986039777	120.73324926	147.75431592
C	12	11	9	2.653460014184	109.65155823	34.31225475
C	10	9	8	2.650660470614	114.22928092	203.10827332
C	12	11	9	2.850194074640	123.52031979	191.44557770
C	15	12	11	4.623581717686	86.08266053	226.54585642
C	13	12	11	2.856268429202	119.06603790	140.56845029
N	16	15	12	2.751261608945	33.02414501	222.08820855

C	18	16	15	5.062969564219	101.89097124	176.90260241
C	19	18	16	2.615571805965	129.01799765	29.80151672
C	20	19	18	2.626695128848	119.38777055	221.63199585
C	21	20	19	2.626872223129	121.05110781	359.56847162
C	22	21	20	2.644290848807	118.50179235	0.05726445
C	23	22	21	2.608907117859	121.04084529	359.85899683
C	22	21	20	2.850868613946	121.07077084	181.38684789
S	18	16	15	3.108998146409	117.55568361	216.12799387
O	26	18	16	2.706217388537	110.05523198	39.61443422
O	26	18	16	2.701911351339	106.16885595	170.58549910
H	1	2	3	2.045152711578	119.46687847	179.16539338
H	2	1	3	2.044229837826	119.88798379	180.31096722
H	3	2	1	2.045420243270	120.43436185	180.36919429
H	6	1	2	2.040409234488	120.85255037	179.70231834
H	7	4	3	2.046068646816	118.32506542	1.09513763
H	8	7	4	2.040155168090	120.77536022	178.40427247
H	15	12	11	2.065457791295	108.60918884	326.70308991
H	15	12	11	2.052000192916	109.84848666	84.00426629
H	16	15	12	2.053861284169	142.41129699	208.81058569
H	16	15	12	2.066805827415	89.38449723	91.12276784
H	17	13	12	2.064513868306	109.62987274	230.13825101
H	17	13	12	2.063035957705	106.75305811	115.06210840
H	20	19	18	2.040957642452	119.73760131	41.84621161
H	21	20	19	2.044996019622	119.14218925	179.79631137
H	23	22	21	2.045452229781	119.64122758	180.18838043

H	24	23	22	2.042493946292	120.43196145	180.66574010
H	25	22	21	2.058312465489	111.34998064	337.82026604
H	25	22	21	2.064631576810	110.47484803	97.54088457
H	25	22	21	2.059878133454	111.20357878	216.94716532

References

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2. M. Satoh, Y. Shibata and K. Tanaka, *Chem. - A Eur. J.,* 2018, **24**, 5434.