Chemical Science

Electronic Supplementary Information

Pentalenes with novel topologies: exploiting the cascade carbopalladation reaction between alkynes and *gem*-dibromoolefins

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1ESI General remarks

Commercial reagents were purchased (ABCR, Aldrich, AlfaAesar, Acros, Fluka, and TCI Deutschland) as reagent–grade and used without further purification. Solvents for extraction or column chromatography were of technical quality and were distilled before use. Anhydrous solvents (CH_2Cl_2, THF, toluene) for reactions were purified by a solvent drying system from LC Technology Solutions Inc. SP-105 under nitrogen atmosphere. Organic solutions were concentrated by rotary evaporation at 40 °C. Thin layer chromatography was carried out on SiO_2–layered aluminium plates (60 F254, Merck). Flash column chromatography was performed using SiO_2-60 (230–400 mesh ASTM, 0.040–0.063 mm from Fluka) at 25 °C with a head pressure of 0.0–0.4 bar. Melting points (m.p.) were measured on a Büchi B-540 melting-point apparatus in open capillaries; "dec." refers to decomposition. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300, a Varian Mercury 300, a Bruker AV 400 or a Bruker DRX 400 spectrometer. All spectra were recorded at 25 °C. The residual solvent peak was used as the internal reference ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; CD_2Cl_2: $\delta_H = 5.32$ ppm, $\delta_C = 54.00$ ppm). The ^1H NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm), multiplicity, coupling constant (J in Hz), number of protons. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), combinations thereof or m (multiplet). Broad signals are described with br. (broad). ^{13}C NMR spectra are reported as follows: chemical shift δ *in* ppm relative to TMS ($\delta = 0$ ppm) (number of carbons if more than 1). Infrared (IR) spectra were recorded on an ATR-unit-upgraded (Golden Gate) Perkin-Elmer FT–IR Spectrum 1600 spectrometer. The spectra were measured between 4000−600 cm^{-1}. Selected absorption bands are reported in wave numbers (cm^{-1}) and their relative intensities described as s (strong), m (medium) or w (weak). When applicable, peak shape was characterized by br. (broad) or sh. (shoulder). UV/vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were measured in $CHCl_3$ in a quartz cuvette (1 cm) at 25 °C. High-resolution mass spectrometry (HR–MS) was performed by the MS service of the Laboratorium für Organische Chemie der ETH Zürich. High-resolution electron impact (HR-EI) spectra were measured at 70 eV on a Micromass (Waters) AutoSpec Ultima spectrometer. High–resolution electrospray ionization (HR–ESI) spectra were measured on a Bruker maXis spectrometer. High-resolution matrix-assisted laser desorption/ionization (HR-MALDI) spectra were measured on an Ionspec (Varian) Ultima FT-ICR or a Solarix (Bruker) FT-ICR mass spectrometer using 3-hydroxypicolinic acid (3-HPA) or [(2*E*)-3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. The most important signals are reported in *m*/*z* units with $[M]^+$ as the molecular ion. Nomenclature follows the suggestions proposed by the computer program ACD Name by ACD Labs.

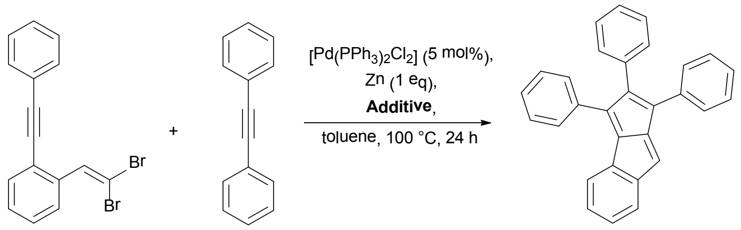
2ESI Optimisation studies

As model system for the optimisation studies, we chose the simple and easily accessible 1-(2,2-dibromovinyl)-2-(phenylethynyl)-benzene (**1**) and diphenylacetylene. *gem*-Dibromoolefin **1** and the product benzopentalene **2** have been characterised in our previous report.[1]

2.1ESI Screening of additives

In initial experiments, we examined the addition of various bases, as there is evidence that amine bases have an effect on regeneration of the active Pd^0 species,[2] furthermore, it is known from Suzuki-couplings that the ligand substitution on the organopalladium(II) halide by alkoxy, hydroxyl, or acetoxy groups is crucial to the transmetallation processes in the reaction mechanism. However, neither the use of NEt_3 nor of KOAc had an effect on the reaction (Table 1ESI, entries 1 and 2). Nevertheless, we found that the addition of 2 equivalents of anhydrous K_2CO_3 or Cs_2CO_3 to the reaction protocol enhanced the yield by about 25% (Table 1ESI, entries 3 and 5). Encouraged by this result, we decreased the equivalents of acetylene in the reaction mixture, but in both cases this had a negative effect on the conversion (Table 1SI, entries 4 and 6). Further attempts to vary the added equivalents of K_2CO_3 or the use of other carbonates, such as Ag_2CO_3 and $NaHCO_3$, only led to decreased yields (Table 1SI, entries 8, 11 and 12).

Table 1ESI Screening of additives for the carbopalladation cascade reaction.



1

2

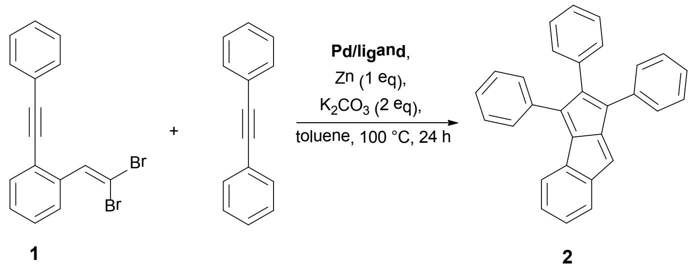
Entry	Acetylene	Additive[a]	Yield
1	20 eq	NEt_3 (2 eq)	29%
2	20 eq	KOAc (2 eq)	39%
3	20 eq	Cs_2CO_3 (2 eq)	62%
4	10 eq	Cs_2CO_3 (2 eq)	31%
5	**20 eq**	**K_2CO_3 (2 eq)**	**68%**
6	10 eq	K_2CO_3 (2 eq)	48%
7	20 eq	K_2CO_3 (5 eq)	53%
8	20 eq	K_2CO_3 (1 eq)	21%
9	20 eq	K_2CO_3 (2 eq), no Zn	35%
10	20 eq	no K_2CO_3, no Zn	recovery of **1**
11	20 eq	Ag_2CO_3 (2 eq)	29%
12	20 eq	$NaHCO_3$ (2 eq)	24%
13	20 eq.	NaI (2 eq)	13%
14	20 eq.	TBAI (2 eq)	18%

Surprisingly, we observed product formation with K_2CO_3 even when zinc dust was not present, whereas in the absence of both base and reducing agent, the product was not obtained (Table 1ESI, entries 9 and 10). This finding suggests that a Negishi-type termination of the catalytic cycle, as proposed in our previous report[1], can be excluded (for further discussion on the mechanism and for a revised catalytic cycle see Section 7.1ESI). Although the addition of Zn is not necessary for the reaction to proceed in the presence of K_2CO_3, higher yields were obtained when both Zn and K_2CO_3 were present in the reaction mixture (entries 5 and 10, Table 1ESI; for further discussion on the possible roles of Zn, see section 7.1ESI). The origin of the effect of the added carbonate remains unclear. Whether it plays a key role in the catalytic cycle or if it just affects the physical distribution in the heterogeneous and highly concentrated reaction mixture is unclear at this stage. In another attempt, we added 2 equivalents of sodium iodide or tetrabutylammonium iodide to the previously established reaction conditions, which showed no improvement of the yield (Table 1ESI, entries 13 and 14).

2.2ESI Screening of Pd/ligand systems

We carried out a second screening of the palladium sources (Table 2ESI), as recent reports indicated some potential for improvement.[3] However, all of the examined classes of ligands gave generally lower yields.

Table 2ESI Screening of Pd/ligand systems for the carbopalladation cascade reaction.



Pd source	Ligand[a]	Yield
1 equiv. $Pd(PPh_3)_4$[b]	-	Traces
$Pd(PPh_3)_4$[c]	-	22%
$Pd(OAc)_2$[c]	$P(tBu)_3$	17%
$Pd(OAc)_2$[c]	$P(o\text{-tol})_3$	Rsm
$Pd(OAc)_2$[c]	PCy_3	26%
$Pd(OAc)_2$[c]	Cyclohexyl JohnPhos	33%
$Pd(OAc)_2$[c]	JohnPhos	22%
$Pd(OAc)_2$[c]	SPhos	10%
$Pd(OAc)_2$[c]	Tetramethyl di^{t}Bu-XPhos	37%
$Pd(OAc)_2$[c]	di^{t}BuXPhos	23%
$Pd(OAc)_2$[c]	XPhos	9%
$Pd(OAc)_2$[c]	di^{t}BuDavePhos	5%

[a] 10 mol% ligand, [b] no Zn; [c] 5 mol% Pd source, 1 eq. Zn, 2 eq. K_2CO_3

The results show that sterically demanding ligands hinder the reaction and hence, less product formation was detected.

In summary, the best yield for the carbopalladation cascade reaction was obtained when 5 mol% [Pd(PPh$_3$)$_2$Cl$_2$], 1 eq. zinc dust, 2 eq. K$_2$CO$_3$ and 20 eq. acetylene were used.

3ESI Synthetic procedures and spectral data

3.1ESI General procedures

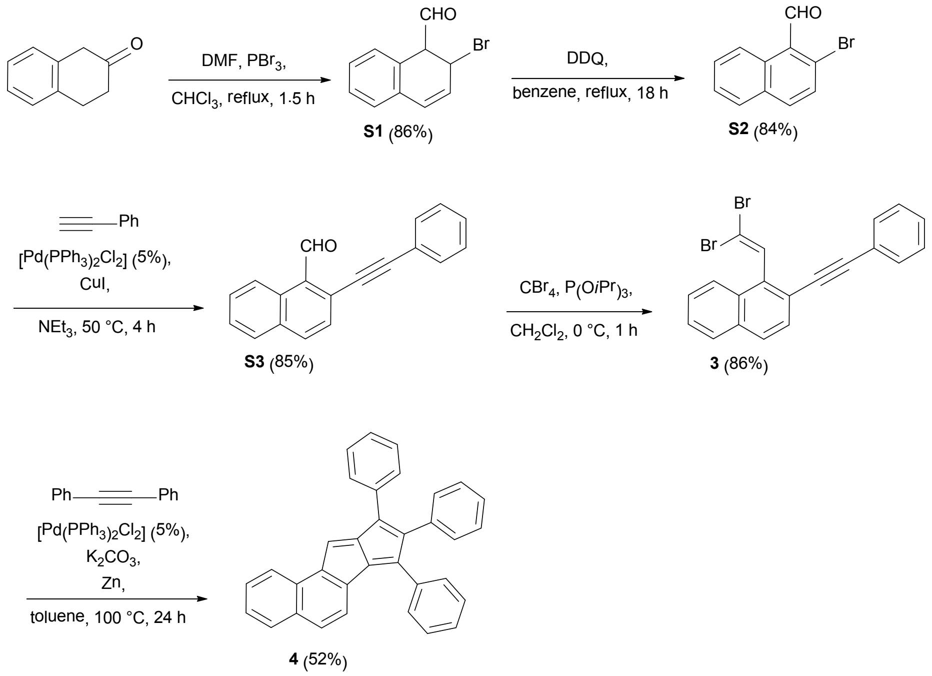
General procedure A for Ramirez *gem*-dibromoolefination

The aldehyde (1 equiv.) and CBr$_4$ (1.5 equiv.) were placed in a dry flask, which was subsequently purged with argon. Dry CH$_2$Cl$_2$ (0.1 M) was added to the mixture, and the flask was placed in an ice bath. Triisopropyl phosphite (3 equiv.) in CH$_2$Cl$_2$ was added to the solution, and the mixture was stirred for 1 h at 0 °C. The solvent was evaporated under vacuum and the remaining oil purified by column chromatography.

General procedure B for pentalene formation *via* intermolecular carbopalladation cascade reaction

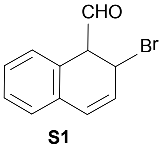
gem-Dibromoolefin (1 equiv.), alkyne (20 equiv.), [Pd(PPh$_3$)$_2$Cl$_2$] (0.05 equiv.), zinc dust (1 equiv.), and K$_2$CO$_3$ (2 equiv.) were placed in a dry Schlenk tube. The tube was evacuated and refilled with nitrogen five times. Dry toluene (enough to generate a 0.1 M solution) was added, the tube was sealed and the solution stirred at 100 °C for 24 h. After this time, the solvent was removed and the residue purified by column chromatography. The excess of the alkyne can be recovered pure after the chromatographic separation and/or by recrystallisation.

3.2ESI Synthesis of pentalene 4



Scheme 1ESI Synthetic route for the preparation of pentalene **4**.

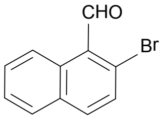
2-Bromo-3,4-dihydronaphthalene-1-carbaldehyde (S1)[4]



S1

Dry DMF (3.2 mL, 41.1 mmol) in dry $CHCl_3$ (60 mL) was cooled to 0 °C, PBr_3 (3.3 mL, 34.3 mmol) was added dropwise and the mixture was stirred for an additional 1 h at the temperature. A solution of β–tetralone (1.8 mL, 3.68 mmol) in 10 mL of $CHCl_3$ was added dropwise maintaining the temperature at 0 °C and the resulting mixture was subsequently heated to reflux for 1.5 h. The solution was cooled to 0 °C, carefully quenched with cold saturated $NaHCO_3$ solution and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the remaining oil was purified by column chromatography (SiO_2, pentanes/Et_2O, 3:1) to give **S1** (2.37 g, 86%; Lit. 84%) as a yellow oil, which solidified upon cooling. ^1H NMR (300 MHz, $CDCl_3$) δ_H 2.88–2.93 (m, 2 H), 3.00–3.06 (m, 2 H), 7.14–7.17 (m, 1 H), 7.21–7.29 (m, 2 H), 7.91–7.98 (m, 1 H), 10.32 (s, 1 H) ppm.

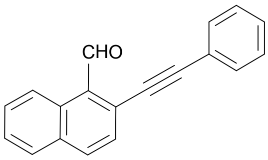
2-Bromo-1-naphthaldehyde (S2)[5]



S2

A mixture of **S1** (2.0 g, 8.44 mmol) and DDQ (2.87 g, 12.65 mmol) in dry benzene (40 mL) was heated to reflux under Ar for 18 h. The crude mixture was filtered through a pad of Celite®, and the filtrate was washed thoroughly with saturated Na_2CO_3 solution and water. The combined organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure, and the remaining oil was purified by column chromatography (SiO_2, hexanes/EtOAc, 3:1) to give product **S2** (1.66 g, 84%; Lit. 83%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.58 (ddd, J = 8.1, 6.9, 1.2 Hz, 1 H), 7.64–7.70 (m, 2 H), 7.83–7.89 (m, 2 H), 9.08–9.11 (m, 1 H), 10.76 (s, 1 H) ppm.

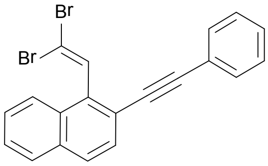
2-(Phenylethynyl)-1-naphthaldehyde (S3)



S3

$[Pd(PPh_3)_2Cl_2]$ (35 mg, 0.05 mmol) and CuI (5 mg, 0.026 mmol) were placed in a dry flask, which was evacuated under vacuum and refilled with N_2. Bromide **S2** (600 mg, 2.55 mmol) and phenylacetylene (0.34 mL, 3.06 mmol) were dissolved in triethylamine (10 mL), and the solution was degassed by bubbling Ar through for 15 min. The solution was transferred to the flask, and the suspension was stirred at 50 °C for 4 h. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2, pentanes/CH_2Cl_2, 10:1) to give compound **S3** (554 mg, 85%) as a pale yellow solid. m.p. 93 ºC; R_f = 0.26 (SiO_2, pentanes/CH_2Cl_2, 3:1); IR (ATR) ν_{max} (neat)/cm^{-1} 3053 (w), 2200 (w), 1682 (s), 1589 (m), 1501 (m), 1441 (w), 1428 (m), 1356 (m), 1297 (w), 1211 (m), 1170 (m), 1140 (m), 1059 (m), 1026 (w), 966 (w), 909 (w), 863 (m), 820 (s), 776 (m), 744 (s), 709 (m), 685 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39–7.43 (m, 3 H), 7.56–7.63 (m, 3 H), 7.66–7.71 (m, 2 H), 7.86 (d, 1 H, J = 8.1 Hz), 8.02 (d, 1 H, J = 8.5 Hz), 9.32 (d, 1 H, J = 8.6 Hz), 11.14 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 86.38, 98.87, 122.45, 125.77, 127.60, 128.39, 128.71, 129.38, 129.48, 129.81, 130.36, 130.46, 131.50, 131.89, 133.33, 134.58, 194.44 ppm; HRMS (EI) *m/z* (%): 256.0879 (100, $[M]^+$, calcd for $C_{19}H_{12}O^+$: 256.0883).

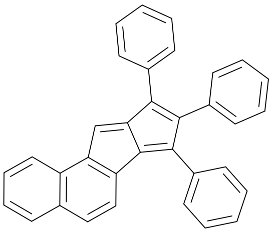
1-(2,2-Dibromovinyl)-2-(phenylethynyl)naphthalene (3)



3

Aldehyde **S3** (375 mg, 1.46 mmol) was treated according to general procedure A to give **3** (516 mg, 86%) as a pale yellow oil which solidified on standing. m.p. 105 ºC; R_f = 0.31 (SiO_2, pentanes/CH_2Cl_2, 9:1);; IR (ATR) ν_{max} (neat)/cm^{-1} 3060 (w), 3005 (w), 2208 (w), 1951 (w), 1596 (m), 1501 (m), 1489 (m), 1442 (m), 1261 (w), 1141 (w), 1071 (m), 1024 (w), 918 (w), 884 (m), 863 (m), 834 (m), 818 (s), 773 (s), 754 (s), 743 (s), 717 (m), 689 (s) 666 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.37–7.43 (m, 3 H), 7.53 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1 H), 7.58 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.61–7.64 (m, 3 H), 7.82–7.93 (m, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 88.66, 94.83, 95.20, 120.23, 123.33, 125.46, 126.99, 127.26, 128.38, 128.53, 128.60 (2), 128.67, 128.70, 130.36, 131.92, 133.02, 135.63, 136.73 ppm; HRMS (EI) *m/z* (%): 413.9255 (2, $[M]^+$, calcd for $C_{20}H_{12}{}^{81}Br_2{}^+$: 413.9259), 411.9294 (4, $[M]^+$, calcd for $C_{20}H_{12}{}^{79}Br^{81}Br^+$: 411.9280), 409.9308 (2, $[M]^+$, calcd for $C_{20}H_{12}{}^{79}Br_2{}^+$: 409.9300), 252.0935 (100, $[M - 2\,Br]^+$, calcd for $C_{20}H_{12}{}^+$: 252.0934).

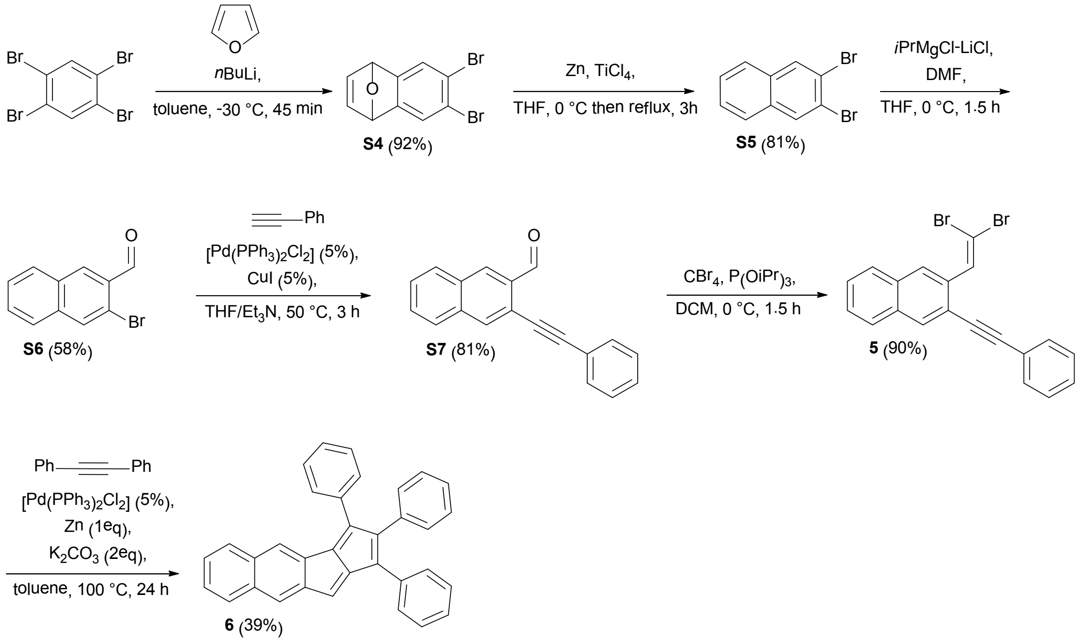
7,8,9-Triphenylpentaleno[2,1-*a*]naphthalene (4)



4

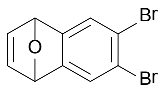
Compound **3** (50 mg, 0.12 mmol) was treated according to general procedure B to give **4** (27 mg, 52%) as a brown solid. m.p. > 213 ºC (dec.); R_f = 0.22 (SiO_2, pentanes/$CHCl_3$, 5:1); UV/Vis ($CHCl_3$) λ_{max}/nm 650 (ε/M^{-1} cm^{-1} 250), 460 (9900); IR (ATR) ν_{max} (neat)/cm^{-1} 3050 (w), 1567 (w), 1492 (w), 1440 (m), 1399 (w), 1302 (w), 1211 (w), 1144 (w), 1097 (w), 1027 (w), 991 (w), 864 (w), 815 (m), 799 (w), 766 (m), 775 (m), 746 (m), 704 (s), 668 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.60 (s, 1 H), 6.86 (t, J = 1.8 Hz, 1 H, arom.), 6.87 (t, J = 1.4 Hz, 1 H, arom.), 6.98 (d, J = 8.2 Hz, 1 H, naph.), 7.08–7.13 (m, 6 H, arom.), 7.15–7.24 (m, 7 H, arom.), 7.25–7.31 (m, 3 H, arom.), 7.49 ($d_{apparent}$, J = 9.1 Hz, 2 H, naph.) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 119.93, 123.08, 125.04, 126.81, 127.26, 127.41, 127.89 (2), 128.22, 128.29, 128.62, 128.82, 128.98, 129.43, 129.48, 130.96, 133.90, 134.25 (2), 134.61, 134.68, 134.81, 142.57, 144.79, 147.82, 154.51 ppm; HRMS (EI) m/z (%): 430.1718 (100, $[M]^+$, calcd for $C_{34}H_{22}^+$: 430.1716).

3.3ESI Synthesis of pentalene 6



Scheme 2ESI Synthetic route for the preparation of pentalene **6**.

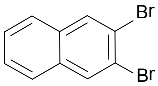
4,5-Dibromo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (S4)[6]



S4

1,2,4,5-Tetrabromobenzene (4.0 g, 10.2 mmol) and furan (5 mL, 68.8 mmol) were dissolved in toluene (100 mL) and cooled to –30 °C under Ar. *n*-Butyllithium (1.6 M solution in hexane, 6.9 mL, 11.0 mmol) was added dropwise in 30 min. Following an additional 15 min stirring at –30 °C, the mixture was warmed to 25 °C and MeOH (1 mL) was added. The solution was washed with water and brine, dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (SiO_2, heptane/EtOAc, 10:1). Compound **S4** was obtained as a white solid (2.78 g, 92%). m.p. 113-115 °C (lit.[6] 115-117 °C); R_f = 0.26 (SiO_2, cyclohexane/EtOAc, 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.66 (s, 2 H), 7.00 (t, J = 1.0 Hz, 2 H), 7.48 (s, 2 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 81.95 (2), 120.81 (2), 125.62 (2), 142.83 (2), 150.36 (2) ppm; HRMS (EI): *m/z* (%): 303.8746 (8, $[M]^+$, calcd for $C_{10}H_6{}^{81}Br_2O^+$: 303.8744), 301.8770 (19, $[M]^+$, calcd for $C_{10}H_6{}^{79}Br\,{}^{81}BrO^+$: 301.8765), 299.8782 (8, $[M]^+$, calcd for $C_{10}H_6{}^{79}Br_2O^+$: 299.8785), 192.9648 (100).

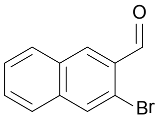
2,3-Dibromonaphthalene (S5)[6]



S5

$TiCl_4$ (4.0 mL, 36.5 mmol) was added dropwise to a stirred suspension of Zn-dust (4.0 g, 61.3 mmol) in THF (75 mL) at 0 °C under Ar carefully. (*Caution! Violent reaction!*) The resulting mixture was heated to reflux for 5 min then cooled to 0 °C again. Compound **S4** (1.9 g, 6.3 mmol) was added in THF solution (15 mL) and the mixture was heated at reflux for an additional 3 h. After cooling to 25 °C, it was poured on ice cold aqueous HCl (0.1 M, 300 mL), followed by extraction with CH_2Cl_2. The organic phase was washed with water and brine, dried, (Na_2SO_4) and filtered. After removal of the solvent under reduced pressure, purification by column chromatography (SiO_2, cyclohexane) gave **S5** as white crystals (1.46 g, 81%). R_f = 0.64 (SiO_2, cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49–7.53 (m, 2 H), 7.71–7.75 (m, 2 H), 8.14 (s, 2 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 122.09 (2), 127.00 (2), 127.32 (2), 132.38 (2), 133.18 (2) ppm; HRMS (EI): *m/z* (%): 287.8793 (48, $[M]^+$, calcd for $C_{10}H_6{}^{81}Br_2{}^+$: 287.8790), 285.8816 (100, $[M]^+$, calcd for $C_{10}H_6{}^{79}Br{}^{81}Br^+$: 285.8810), 283.8838 (51, $[M]^+$, calcd for $C_{10}H_6{}^{79}Br_2{}^+$: 283.8831), 126.0464 (62, $[M - 2\,Br]^+$, calcd for $C_{10}H_6{}^+$: 126.0464).

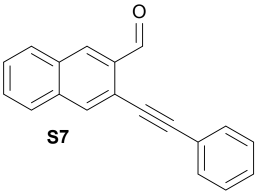
3-Bromonaphthalene-2-carbaldehyde (S6)[7]



S6

*i*PrMgCl·LiCl (1.3M in THF, 1.35 mL, 1.76 mmol) was added dropwise to a solution of compound **S5** (0.50 g, 1.75 mmol) in THF (10 mL) at 0 °C under Ar in 10 min. After stirring for 90 min at 0 °C, DMF (1 mL) was added and the mixture stirred for an additional 15 min at 0 °C. The mixture was treated with water (50 mL) and the aqueous mixture extracted with EtOAc. The organic phase was washed with water and brine, dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 20:1) giving **S6** as a white solid (240 mg, 58%). m.p. 123–125 °C; R_f = 0.51 (SiO_2, cyclohexane/EtOAc, 20 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.56 (ddd, J = 8.1, 6.9, 1.3 Hz, 1 H), 7.63 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H), 7.78 (d, J = 8.9 Hz, 1 H), 7.95 (d, J = 8.2 Hz, 1 H), 8.10 (s, 1 H), 8.43 (s, 1 H), 10.49 (s, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 120.63, 127.01, 127.55, 129.98, 130.13, 130.56, 131.60, 131.96, 132.59, 136.95, 192.08 ppm; HRMS (EI): *m/z* (%): 235.9669 (91, $[M]^+$, calcd for $C_{11}H_7{}^{81}BrO^+$: 235.9654), 233.9675 (91, $[M]^+$, calcd for $C_{11}H_7{}^{79}BrO^+$: 233.9675), 126.0471 (100, $[M - Br - CHO]^+$, calcd for $C_{10}H_6{}^+$: 126.0464).

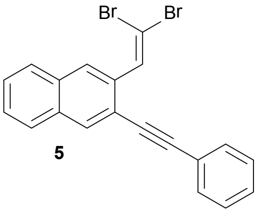
3-(Phenylethynyl)naphthalene-2-carbaldehyde (S7)



S7

$[Pd(PPh_3)_2Cl_2]$ (36 mg, 0.05 mmol) and CuI (8 mg 0.05 mmol) were placed in a dry Schlenk-tube and were purged with Ar. Phenylacetylene (0.13 mL, 1.18 mmol) and aryl bromide **S6** (240 mg, 1.02 mmol) were dissolved in a mixture of triethylamine (3 mL) and THF (5 mL) and purged with bubbling Ar for 10 min. The solution was then transferred to the Schlenk-tube and stirred for 3 h at 50 °C. The mixture was diluted with Et_2O (20 mL) and filtered through a pad of Celite®. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 20:1) to give **S7** (213 mg, 81%) as a brownish yellow solid. m.p. 89-91 °C; R_f = 0.35 (SiO_2, cyclohexane/EtOAc, 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 3063 (br., w), 2830 (w), 1697 (s), 1620 (m), 1585 (sh., m), 1489 (m), 1440 (m), 1398 (w), 1376 (w), 1335 (w), 1154 (m), 1070 (m), 1019 (w), 962 (w), 896 (s), 870 (m), 743 (s), 685 (s), 640 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38–7.41 (m, 3H), 7.54 (ddd, J = 8.1, 6.9, 1.3 Hz, 1 H), 7.59–7.63 (m, 3 H), 7.83 (d, J = 8.1 Hz, 1 H), 7.94 (d, J = 8.7 Hz, 1 H), 8.11 (s, 1 H), 8.44 (s, 1 H), 10.73 (s, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 85.72, 95.47, 121.14, 122.71, 127.71, 127.80, 128.62 (2), 128.99, 129.51, 129.77, 130.08, 131.77 (2), 132.01, 132.32, 133.48, 135.54, 191.90 ppm; HRMS (EI): *m/z* (%): 256.0889 (100, [*M*]$^+$, calcd for $C_{19}H_{12}O^+$: 256.0883).

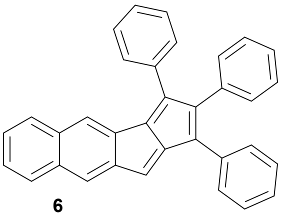
2-(2,2-Dibromoethenyl)-3-(phenylethynyl)naphthalene (5)



5

Aldehyde **S7** (210 mg, 0.82 mmol) was treated according to general procedure A to give **5** (309 mg, 91 %) as a light brown solid. m.p. 93–94 °C; R_f = 0.64 (SiO_2, cyclohexane/EtOAc, 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 3020 (w, sh), 1943 (w), 1596 (w), 1489 (w), 1441 (w), 1273 (w), 1140 (w), 1066 (w), 1025 (w), 953 (w, sh), 920 (w), 898 (s), 833 (w), 808 (m), 750 (s), 740 (s), 684 (s), 643 (w), 606 (w), 537 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38–7.43 (m, 3 H), 7.49–7.55 (m, 2 H), 7.59–7.62 (m, 2 H), 7.79–7.82 (m, 1 H), 7.84–7.87 (m, 1 H), 7.98 (d, J = 0.9 Hz, 1 H), 8.08 (s, 1 H), 8.23 (s, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 87.66, 91.57, 94.74, 120.32, 123.10, 127.35, 127.41, 127.67, 128.03, 128.37, 128.63 (2), 128.77, 131.80 (2), 132.14, 132.51, 132.62, 133.90, 136.01 ppm; HRMS (EI): *m/z* (%): 413.9259 (2, [*M*]$^+$, calcd for $C_{20}H_{12}{}^{81}Br_2{}^+$: 413.9260), 411.9280 (4, [*M*]$^+$, calcd for $C_{20}H_{12}{}^{79}Br{}^{81}Br^+$: 411.9280), 409.9297 (2, [*M*]$^+$, calcd for $C_{20}H_{12}{}^{79}Br_2{}^+$: 409.9301), 333.0092 (19, [*M* − Br]$^+$, calcd for $C_{20}H_{12}{}^{81}Br^+$: 333.0096), 331.0111 (19, [*M* − Br]$^+$, calcd for $C_{20}H_{12}{}^{79}Br^+$: 331.0117), 252.0935 (100, [*M* – 2 Br]$^+$, calcd for $C_{20}H_{12}{}^+$: 252.0934).

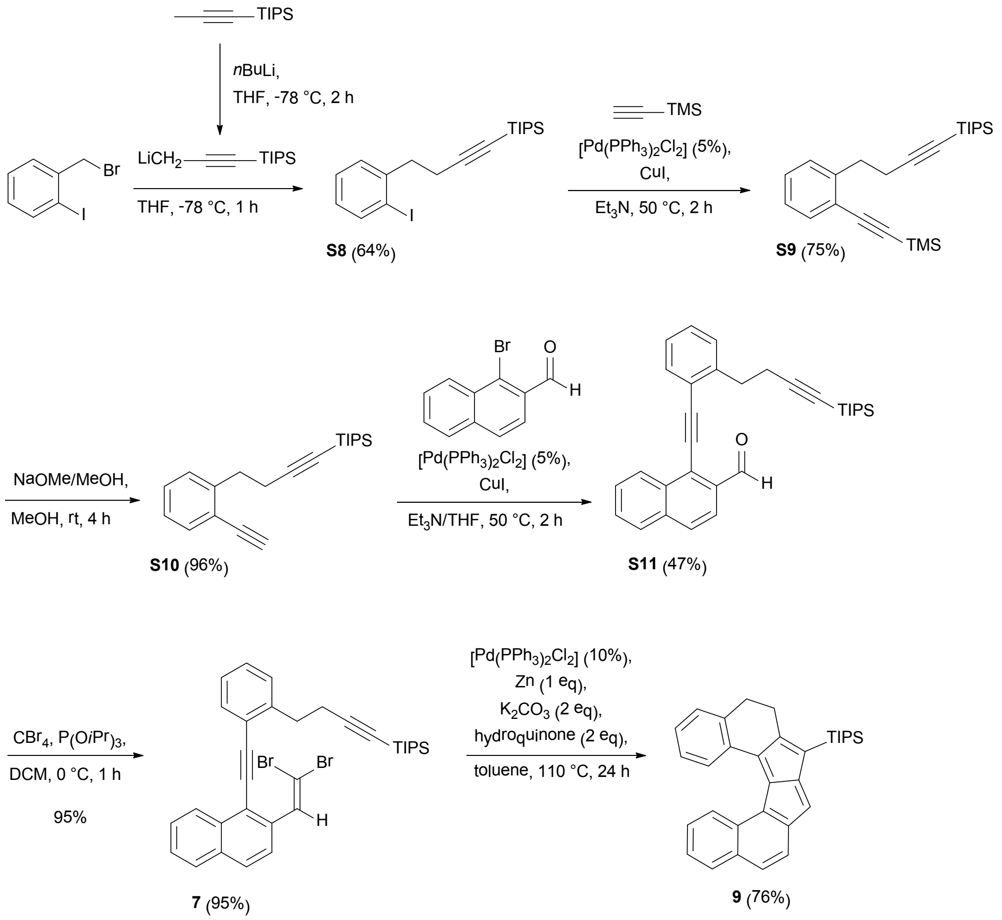
1,2,3-Triphenylpentaleno[1,2-*b*]naphthalene (6)



6

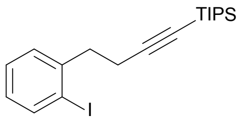
Compound **5** (50 mg, 0.12 mmol) was treated according to general procedure B to give **6** (20 mg, 39%) as a dark green solid. m.p. > 210 °C (dec.); $R_f = 0.43$ (SiO_2, cyclohexane/CH_2Cl_2, 5:1); UV/Vis ($CHCl_3$) λ_{max}/nm 566 (ε/M^{-1} cm^{-1} 789), 486 (7740), 456 (8980); IR (ATR) ν_{max} (neat)/cm^{-1} 3058 (w), 1564 (w), 1491 (w), 1439 (w), 1027 (w), 901 (w), 881 (m), 772 (m), 747 (m), 705 (s), 694 (s); ^1H NMR (400 MHz, CD_2Cl_2) δ_H 6.71 (s, 1 H), 6.95 (t, *J* = 1.8 Hz, 1 H), 6.97 (t, *J* = 1.4 Hz, 1 H), 7.14−7.25 (m, 13 H), 7.27 (s, 1 H), 7.29−7.32 (m, 3 H), 7.37−7.40 (m, 1 H), 7.47−7.49 (m, 1 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ_C 119.76, 124.18, 126.88, 127.33, 127.61, 127.90, 128.39 (3), 128.44, 128.68 (2), 129.08 (2), 129.27 (2), 129.47, 129.56 (2), 130.14 (2), 131.86, 133.90 (2), 134.47, 135.09, 135.17, 135.34, 135.73, 139.25, 141.40, 148.22, 150.97, 156.88 ppm; HRMS (EI): *m/z* (%): 430.1713 (100, $[M]^+$, calcd for $C_{34}H_{22}^+$: 430.1716).

3.4ESI Synthesis of pentalene 9



Scheme 3ESI Synthetic route for the preparation of pentalene **9**.

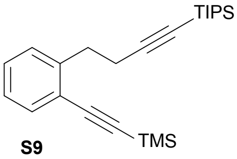
[4-(2-Iodophenyl)but-1-yn-1-yl][tri(propan-2-yl)]silane (S8)[8]



S8

n-Butyllithium (1.6 M solution in hexanes, 2.0 mL, 3.2 mmol) was added dropwise to a solution of 1-(triisopropylsilyl)-1-propyne (0.75 mL, 3.1 mmol) in THF (2 mL) at –78 °C under Ar. After stirring the mixture at –78 °C for 2 h, 2-iodobenzyl bromide (930 mg, 3.1 mmol) in THF (2 mL) was added dropwise. The solution was stirred at –78 °C for an additional 30 min then warmed to 25 °C. Water was added and the aqueous mixture extracted with EtOAc. The combined organic layers were washed with water and brine, dried (Na_2SO_4) and filtered. After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography (SiO_2, pentane/CH_2Cl_2, 20:1) to give **S8** (828 mg, 64%) as a yellow oil. $R_f = 0.75$ (SiO_2, pentane/CH_2Cl_2, 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2940 (s), 2863 (s), 2171 (m), 1562 (w), 1464 (s), 1435 (m, sh), 1040 (w, sh), 1011 (s), 994 (m, sh), 919 (w), 881 (s), 746 (s), 716 (w), 675 (s, sh), 659 (s); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 1.02–1.05 (m, 21 H), 2.57 (t, J = 7.2 Hz, 2 H), 2.95 (t, J = 7.2 Hz, 2 H), 6.91 (td, J = 7.6, 1.8 Hz, 1 H), 7.28 (td, J = 7.4, 1.3 Hz, 1H), 7.34 (dd, J = 7.6, 1.8 Hz, 1H), 7.82 ppm (dd, J = 7.9, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 11.43 (3), 18.77 (6), 20.61, 40.12, 81.54, 100.44, 107.51, 128.27, 128.30, 130.26, 139.53, 142.99 ppm; HRMS (MALDI): *m/z* (%): 435.0976 (100, $[M + Na]^+$, calcd for $C_{19}H_{29}INaSi^+$: 435.0975).

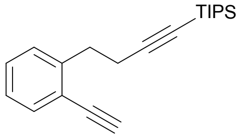
Trimethyl[(2-{4-[tri(propan-2-yl)silyl]but-3-yn-1-yl}phenyl)ethynyl]silane (S9)[8]



S9

[$Pd(PPh_3)_2Cl_2$] (126 mg, 0.175 mmol) and CuI (34 mg 0.175 mmol) were placed in a dry Schlenk-tube and was purged with Ar. Aryl iodide **S8** (720 mg, 1.75 mmol) was dissolved in triethylamine (3 mL) and purged with bubbling Ar for 10 min. The solution was transferred to the Schlenk-tube, TMS–acetylene (0.28 mL, 1.93 mmol) was added and the mixture stirred for 3 h at 50 °C. The mixture was diluted with cyclohexane and filtered through a pad of Celite®. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (SiO_2, heptane) to give **S9** (0.50 g, 75 %) as a pale yellow oil. $R_f = 0.38$ (SiO_2, heptane); IR (ATR) ν_{max} (neat)/cm^{-1} 2942 (m), 2864 (m), 2171 (m, sh), 2156 (m), 1481 (w, sh) 1463 (m), 1249 (m), 1099 (w), 1042 (w), 995 (w), 865 (s, sh), 840 (w), 755 (s), 675 (s, sh), 660 (s), 645 (m, sh); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 0.26 (s, 9 H), 1.01–1.06 (m, 21 H), 2.60 (t, J = 7.5 Hz, 2 H), 3.01 (t, J = 7.5 Hz, 2 H), 7.16 (td, J = 7.3, 1.9 Hz, 1 H), 7.22–7.29 (m, 2 H), 7.41 (ddd, J = 7.5, 1.4, 0.6 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 0.12 (3), 11.44 (3), 18.77 (6), 20.81, 34.54, 80.83, 98.61, 103.63, 108.35, 122.56, 126.31, 128.67, 129.29, 132.39, 143.18 ppm; HRMS (MALDI): *m/z*(%): 383.2585 (100, $[M + H]^+$, calcd for $C_{24}H_{39}Si_2^+$: 383.2585).

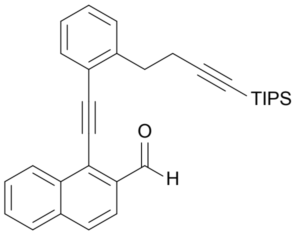
[4-(2-Ethynylphenyl)but-1-yn-1-yl][tri(propan-2-yl)]silane (S10)



S10

Sodium methoxide (25–50% in methanol, 10 mL) was added to a solution of **S9** (0.5 g, 1.31 mmol) in methanol (5 mL) and the solution stirred for 4 h at 25 °C. The mixture was treated with water and the aqueous solution extracted with pentane. The organic phase was washed with water and brine, dried (Na_2SO_4), and filtered. After the removal of the solvent *in vacuo*, the crude product was purified by column chromatography (SiO_2, heptane) to give **S10** (395 mg, 1.27 mmol, 96%) as a pale yellow oil. $R_f = 0.40$ (SiO_2, pentane); IR (ATR) ν_{max} (neat)/cm^{-1} 3303 (w), 2941 (s, sh), 2864 (s), 2171 (m), 1463 (m, sh), 1042 (s), 995 (m), 883 (s), 755 (s), 675 (s), 659 (s); ^{1}H NMR (300 MHz, CD_2Cl_2) δ_H 1.00–1.06 (m, 21 H), 2.61 (t, $J = 7.2$ Hz, 2 H), 3.02 (t, $J = 7.2$ Hz, 2 H), 3.33 (s, 1 H), 7.18 (td, $J = 7.4$, 1.8 Hz, 1H), 7.25–7.33 (m, 2 H), 7.46 ppm (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ_C 12.03 (3), 19.09 (6), 21.38, 34.37, 81.42 (2), 82.30, 108.35, 121.69, 126.53, 129.07, 129.71, 133.02, 143.30 ppm; HRMS (MALDI): *m/z* (%): 310.2111 (100, $[M]^+$, calcd for $C_{21}H_{30}Si^+$: 310.2111).

1-[(2-{4-[Tri(propan-2-yl)silyl]but-3-yn-1-yl}phenyl)ethynyl]naphthalene-2-carbaldehyde (S11)

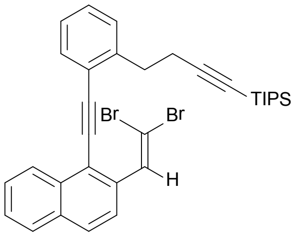


S11

$[Pd(PPh_3)_2Cl_2]$ (51 mg, 0.07 mmol) and CuI (20 mg, 0.10 mmol) were placed in a dry Schlenk-tube and was purged with Ar. Alkyne **S10** (210 mg, 0.68 mmol) and 1-bromo-2-naphthaldehyde (141 mg, 0.60 mmol) were dissolved in a mixture of triethylamine (5 mL) and THF (3 mL) and purged with bubbling Ar for 10 min. The solution was then transferred to the Schlenk-tube and the mixture stirred at 60 °C for 5 h. The mixture was diluted with pentane and filtered through a pad of Celite®.

After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, heptane/toluene, 2:3) to give **S11** (144 mg, 51 %) as a pale yellow oil that solidified to a waxy solid in the fridge. $R_f = 0.28$ (SiO_2, heptane/EtOAc, 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2941 (s), 2863 (s), 2170 (m), 1695 (s), 1590 (m), 1460 (m), 1222 (m), 995 (m), 882 (s), 817 (s), 754 (s), 675 (s, sh), 658 (s), 638 (m, sh); ^{1}H NMR (300 MHz, CD_2Cl_2) δ_H 0.96–1.02 (m, 21 H), 2.76 (t, J = 7.2 Hz, 2 H), 3.23 (t, J = 7.2 Hz, 2 H), 7.29–7.45 (m, 3 H), 7.67–7–75 (m, 3H), 7.90–7.99 (m, 3 H), 8.61–8.65 (m, 1 H), 10.87 (s, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 11.40 (3), 18.72 (6), 21.32, 34.35, 81.75, 86.87, 101.11, 107.50, 121.93, 122.29, 126.73, 127.30, 127.64, 127.97, 128.67, 129.06, 129.49, 129.55, 129.78, 132.93, 133.31, 134.35, 135.96, 142.73, 191.99 ppm; HRMS (MALDI): *m/z* (%): 464.2530 (100, $[M]^+$, calcd for $C_{32}H_{36}OSi^+$: 464.2530), 487.2428 (32, $[M + Na]$, calcd for $C_{32}H_{36}NaOSi$: 487.2428)

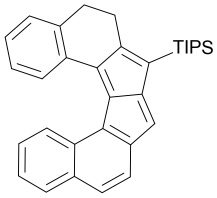
[4-(2-{[2-(2,2-Dibromoethenyl)naphthalen-1-yl]ethynyl}phenyl)but-1-yn-1-yl][tri(propan-2-yl)]silane (7)



7

Aldehyde **S11** (95 mg, 0.2 mmol) was treated according to general procedure A to give **7** (120 mg, 95%) as a pale brown solid. The product crystallises from hexane as pale brown needles. m.p. 86–87 °C; $R_f = 0.27$ (SiO_2, heptane); IR (ATR) ν_{max} (neat)/cm^{-1} 3056 (w), 2940 (s), 2862 (s), 2169 (m), 1595 (w), 1461 (m), 1382 (w), 1254 (w), 994 (m), 882 (s), 851 (s), 807 (m), 753 (s), 743 (s, sh), 673 (s); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 0.95–1.02 (m, 21 H), 2.80 (t, J = 7.0 Hz, 2 H), 3.23 (t, J = 7.0 Hz, 2 H), 7.30 (td, J = 7.4, 1.5 Hz, 1 H), 7.35 (td, J = 7.5, 1.6 Hz, 1 H), 7.44 (dd, J = 7.5, 1.1 Hz, 1 H), 7.59 (ddd, J = 8.1, 6.9, 1.4 Hz, 1 H), 7.64 (ddd, J = 8.3, 6.9, 1.5 Hz, 1 H), 7.70 (dd, J = 7.5, 1.4 Hz, 1 H), 7.86 (br s, 2 H), 7.87–7.89 (m, 1 H), 8.12 (s, 1 H), 8.47 ($d_{apparent}$, J = 8.2 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 11.44 (3), 18.76 (6), 21.18, 34.19, 81.58, 89.42, 92.05, 99.73, 107.86, 120.69, 122.54, 125.16, 126.54, 126.58, 127.17, 127.49, 128.22, 128.35, 128.93, 129.81, 132.73, 132.74, 133.22, 135.96, 136.84, 142.42 ppm; HRMS (MALDI): *m/z*: 641.0841 (100, [*M* + Na]$^+$, calcd for $C_{33}H_{36}Br_2NaSi^+$: 641.0845); elemental analysis calcd (%) for $C_{33}H_{36}Br_2Si$: C 63.87, H 5.85, Br 25.75; found C 63.85, H 5.92, Br 25.87.

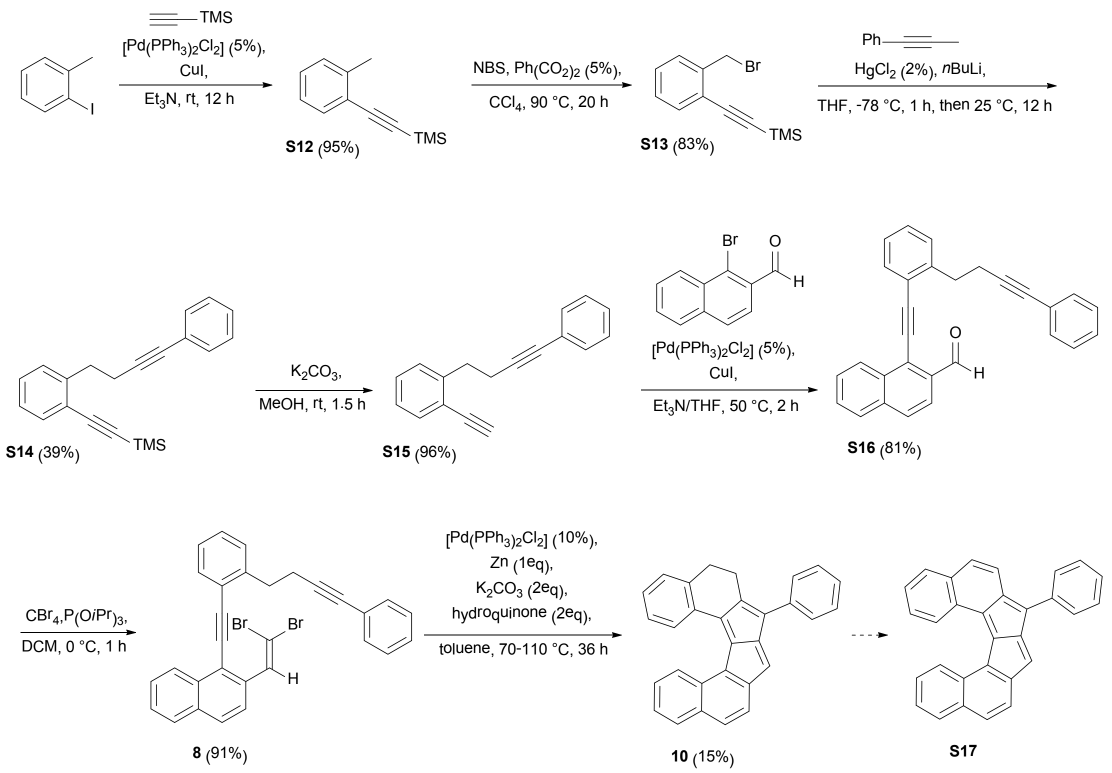
5,6-Dihydronaphtho[2',1':5,6]pentaleno[1,2-*a*]naphthalen-7-yl[tri(propan-2-yl)]silane (9)



9

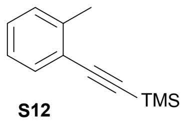
A mixture of *gem*-dibromoolefin **7**, (200 mg, 0.32 mmol), [Pd(PPh_3)$_2$$Cl_2$] (24 mg, 0.034 mmol), Zn-dust (20 mg, 0.32 mmol) and K_2CO_3 (90 mg, 0.65 mmol) in toluene (4 ml) was stirred at 110 °C for 5 h, followed by the addition of hydroquinone (70 mg, 0.64 mmol) and an additional 19 h stirring at the same temperature. After cooling to 25 °C, the solvent was evaporated under reduced pressure and the crude mixture purified by flash column chromatography (SiO_2, cyclohexane) to give the product as a green thick oil/waxy solid (112 mg, 76%). R_f = 0.29 (SiO_2; cyclohexane); UV/Vis ($CHCl_3$) λ_{max}/nm 638 (ε/M^{-1} cm^{-1} 271), 457 (5497), 438 (5817); IR (ATR) ν_{max} (neat)/cm^{-1} 3047 (w), 2941 (s, sh), 2862 (s), 1602 (w, sh), 1512 (w), 1457 (m), 1388 (w), 1296 (m), 1223 (m), 1013 (m), 994 (m), 882 (s), 850 (s), 808 (s), 742 (s), 727 (s), 689 (s), 644 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.15 (d, *J* = 7.0 Hz, 18 H), 1.23–1.32 (m, 3H), 2.43 (t, *J* = 6.0 Hz, 2 H), 2.79 (t, *J* = 6.0 Hz, 2 H), 5.81 (s, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 6.94 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1 H), 7.06 (ddd, *J* = 8.1, 6.7, 1.1 Hz, 1 H), 7.14–7.20 (m, 3 H), 7.28 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.42 (d, *J* = 8.3 Hz, 1 H), 7.46 (d, *J* = 8.6 Hz, 1 H), 7.65 (d, *J* = 7.7 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 12.44 (3), 19.00 (6), 27.60, 30.89, 122.18, 123.93, 125.18, 125.50, 125.86, 164.21, 125.98, 127.70, 127.97, 128.15, 129.09, 129.38, 129.61, 130.22, 130.74, 134.47, 134.50, 140.28, 141.46, 145.20, 149.71, 162.87 ppm; HRMS (MALDI): *m/z* (%): 460.2581 (100, [*M*]$^+$, calcd for $C_{33}H_{36}Si^+$: 460.2581).

3.5ESI Synthesis of pentalene 10



Scheme 4ESI Synthetic route for the preparation of pentalene **10**. (The preparation of **S17** was not attempted due to the low stability of the starting material **10**. For an optimised structure of **S17**, see section 6.3ESI.)

Trimethyl[(2-methylphenyl)ethynyl]silane (S12)[9]

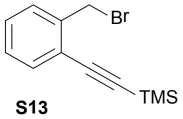


S12

[Pd(PPh$_3$)$_2$Cl$_2$] (461 mg, 0.69 mmol) and CuI (223 mg, 1.17 mmol) were placed in a dry Schlenk-tube and the mixture purged with Ar. 2-Iodotoluene (5.0 g, 22.9 mmol) was dissolved in triethylamine (30 mL) and purged with bubbling Ar for 10 min. The solution was transferred to the Schlenk-tube, cooled to 0 °C and TMS-acetylene (3.59 mL, 25.4 mmol) was added. The mixture was allowed to warm to 25 °C and stirred for 1 h. The mixture was diluted with cyclohexane (50 mL) and filtered through a plug of Celite®. After evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography (SiO$_2$, cyclohexane) to give **S12** (4.08 g, 95%) as a yellow liquid. R_f = 0.48 (SiO$_2$, cyclohexane); ^{1}H NMR (400 MHz,

$CDCl_3$) δ_H 0.26 (s, 9 H), 2.44 (s, 3 H), 7.09–7.13 (m, 1 H), 7.17–7.23 (m, 2H), 7.42 (d, J = 7.5 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 0.22 (3), 20.77, 98.34, 104.18, 123.05, 125.56, 128.59, 129.48, 132.23, 140.76 ppm; HRMS (EI): *m/z* (%): 188.1012 (30, $[M]^+$, calcd for $C_{12}H_{16}Si^+$: 188.1016), 173.0782 (100, $[M - CH_3]^+$, calcd for $C_{11}H_{13}Si^+$: 173.0781).

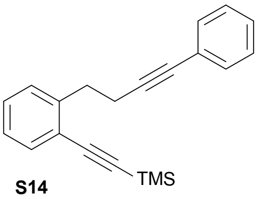
{[2-(Bromomethyl)phenyl]ethynyl}(trimethyl)silane (S13)[10]



S13

N-bromosuccinimide (2.14 g, 12 mmol) and benzoyl peroxide (128 mg, 0.53 mmol) was added to a solution of compound **S12** (2.0 g, 10.6 mmol) in CCl_4 (20 mL), and the mixture was refluxed for 20 h in a sealed Schlenk-tube (*note that the starting material **S12** is volatile*). The solid was filtered and the solvent removed under reduced pressure. Purification by column chromatography gave **S13** (2.35 g, 83%) as a colorless oil. R_f = 0.38 (SiO_2, cyclohexane); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.29 (s, 9 H), 4.67 (s, 2 H), 7.25 (td, J = 7.5, 1.4 Hz, 1 H), 7.30 (td, J = 7.5, 1.6 Hz, 1 H), 7.41 (dd, J = 7.6, 1.1 Hz, 1 H), 7.46 (dd, J = 7.5, 1.4 Hz, 1 H), ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 0.00 (3), 31.95, 100.89, 102.05, 123.17, 128.47, 129.11, 129.74, 132.80, 139.82 ppm; HRMS (EI): *m/z* (%): 268.0101 (14, $[M]^+$, calcd for $C_{12}H_{15}{}^{81}BrSi^+$: 268.0100), 266.0123 (14, $[M]^+$, calcd for $C_{12}H_{15}{}^{79}BrSi^+$: 266.0121), 187.0937 (100, $[M - Br]^+$, calcd for $C_{12}H_{15}Si^+$: 187.0938).

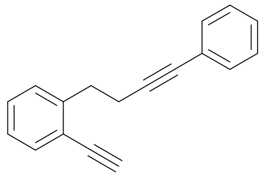
Trimethyl{[2-(4-phenylbut-3-yn-1-yl)phenyl]ethynyl}silane (S14)



S14

A solution of 1-phenyl-1-propyne (390 µL, 3.13 mmol) and $HgCl_2$ (16 mg, 0.063 mmol) in THF (10 mL) was cooled to −78 °C under Ar and treated dropwise with *n*-butyllithium (1.6 M in hexane, 2.0 mL, 3.13 mmol). The resulting mixture was stirred for 15 min at the same temperature, upon which its color turned to deep orange, followed by the dropwise addition of benzyl bromide **S13** (1.0 g, 3.76 mmol) in THF (2 mL). After additional stirring for 1 h at −78 °C, the mixture was warmed to 25 °C and treated with water. The aqueous mixture was extracted with EtOAc. The organic phase was washed with water and brine and dried (Na_2SO_4), filtered and the solvent evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane) to give **S14** as a colorless oil that solidifies to a waxy solid upon standing in the fridge (370 mg, 39%). R_f = 0.17 (SiO_2, cyclohexane); IR (ATR) ν_{max} (neat)/cm^{-1} 3063 (w, sh), 2958 (w, sh), 2155 (m), 1598 (w), 1490 (m, sh), 1443 (w), 1340 (w), 1249 (m), 1099 (w), 864 (s), 838 (s), 753 (s), 690 (s), 644 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.27 (s, 9 H), 2.75 (t, J = 7.5 Hz, 2 H), 3.09 (t, J = 7.5 Hz, 2 H), 7.17 (td, J = 7.4, 2.0 Hz, 1H), 7.25–7.30 (m, 5 H), 7.34–7.37 (m, 2 H), 7.46 (d, J = 7.1 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 0.13 (3), 20.43, 34.32, 81.35, 89.68, 98.71, 103.66, 122.73, 124.12, 126.42, 127.67, 128.30 (2), 128.70, 129.32, 131.67 (2), 132.48, 143.22 ppm; HRMS (EI): m/z (%): 302.1482 (75, $[M]^+$, calcd for $C_{21}H_{22}Si^+$: 302.1486), 115.0540 (52, $[M - C_{12}H_{15}Si]^+$, calcd for $C_9H_7^+$: 115.0542), 73.0467 (100, $[M - C_{18}H_{13}]^+$, calcd for $(CH_3)_3Si^+$: 73.0468).

1-Ethynyl-2-(4-phenylbut-3-yn-1-yl)benzene (S15)

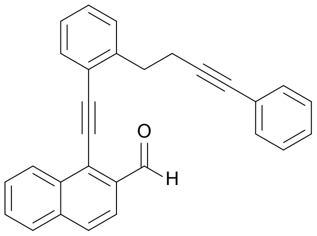


S15

K_2CO_3 (23 mg, 0.16 mmol) was added to a solution of **S14** (160 mg, 0.52 mmol) in MeOH (3 mL) and stirred at 25 °C for 1.5 h. The mixture was diluted with water and the aqueous mixture extracted with EtOAc. The organic phase was washed with water and brine, dried (Na_2SO_4), filtered and the solvent evaporated. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 20:1) to give **S15** as a pale yellow oil (115 mg, 96%). R_f = 0.33 (SiO_2, cyclohexane); IR (ATR) ν_{max} (neat)/cm^{-1} 3290 (m), 3062 (w, sh), 2931 (w, sh), 2103 (w), 1597 (w), 1489 (m, sh), 1442 (m), 1340 (w), 1096 (w), 1069 (w), 913 (w), 753 (s), 690 (s), 654 (m, sh); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 2.76 (t, J = 7.4 Hz, 2 H), 3.11 (t, J = 7.4 Hz, 2 H), 3.36 (s, 1H), 7.22 (ddd, J = 7.6, 6.5, 2.3 Hz, 1 H), 7.25–7.37 (m, 6H), 7.50 (d, J = 7.4 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 20.61, 33.91, 81.21, 81.49, 82.15, 89.56, 121.72, 124.01, 126.48, 127.72, 128.31 (2), 128.97, 129.36, 131.66 (2), 133.09, 143.23 ppm; HRMS (EI): m/z (%): 230.1082 (36, $[M]^+$, calcd for $C_{18}H_{14}^+$:

230.1090), 229.1010 (56, [*M* − H]$^+$, calcd for $C_{18}H_{13}^+$: 229.1012), 115.0550 (100, [*M* – C_9H_7]$^+$, calcd for $C_9H_7^+$: 115.0542)

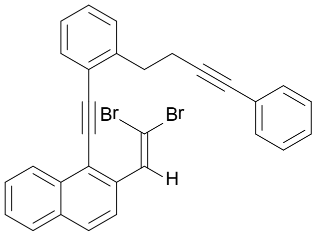
1-{[2-(4-Phenylbut-3-yn-1-yl)phenyl]ethynyl}naphthalene-2-carbaldehyde (S16)



S16

[$Pd(PPh_3)_2Cl_2$] (17 mg, 0.024 mmol), CuI (5 mg, 0.026 mmol) and 1-bromo-2-naphthaldehyde (118 mg, 0.50 mmol) were placed in a dry Schlenk-tube under Ar A solution of **S15** (110 mg, 0.48 mmol) in a mixture of THF (2 mL) and triethylamine (2 mL) was degassed with bubbling Ar for 10 min. The solution was transferred to the Schlenk-tube and the mixture stirred at 50 °C for 4 h. The suspension was diluted with EtOAc and filtered. After evaporation of the solvents under reduced pressure, the product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 20:1) to give **S16** as yellow needles (148 mg, 80%). m.p. 114–115 °C; R_f = 0.33 (SiO_2, cyclohexane/EtOAc 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 3059 (w, sh), 2837 (w), 2193 (w), 1678 (s), 1613 (w), 1590 (m), 1567 (w), 1487 (m), 1455 (m), 1428 (m), 1385 (m), 1332 (m), 1258 (m), 1222 (m), 1155 (w, sh), 1050 (w), 1028 (w), 945 (w), 906 (w), 860 (w), 817 (s), 756 (s), 744 (s), 738 (s), 688 (s), 654 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.89 (t, *J* = 7.5 Hz, 2 H), 3.32 (t, *J* = 7.5 Hz, 2 H), 7.24–7.27 (m, 3 H), 7.31–7.45 (m, 5 H), 7.64–7.68 (m, 2 H), 7.73 ($d_{apparent}$, *J* = 8.4 Hz, 1 H), 7.88–7.92 (m, 2 H), 8.01 (d, *J* = 8.6 Hz, 1 H), 8.63–8.68 (m, 1 H), 10.94 (d, *J* = 0.8 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 21.19, 34.53, 81.91, 86.93, 89.04, 101.03, 122.12, 122.31, 123.87, 126.89, 127.40, 127.61, 127.80, 128.02, 128.31 (2), 128.66, 129.10, 129.53, 129.63, 129.67, 131.72 (2), 133.01, 133.32, 134.39, 135.96, 142.85, 192.05 ppm; HRMS (MALDI): *m/z* (%): 384.1508 (100, [*M*]$^+$, calcd for $C_{29}H_{20}O^+$: 384.1509); elemental analysis calcd (%) for $C_{29}H_{20}O$: C 90.60, H 5.24, O 4.16; found C 90.53, H 5.35, O 4.12.

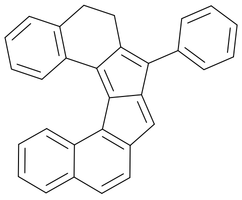
2-(2,2-Dibromoethenyl)-1-{[2-(4-phenylbut-3-yn-1-yl)phenyl]ethynyl}naphthalene (8)



8

Aldehyde **S16** (135 mg, 0.35 mmol) was treated according to general procedure A to give **8** (175 mg, 91 %) as pale brown solid. The product crystallises from hexane as pale brown needles. R_f = 0.54 (SiO_2, cyclohexane/EtOAc, 20:1); m.p. 96–98 °C; IR (ATR) ν_{max} (neat)/cm^{-1} 3024 (w, sh), 2954 (w), 2927 (w, sh), 2200 (w), 1588 (w), 1487 (m), 1443 (m), 1382 (w), 1263 (w), 1226 (w), 1161 (w, sh), 1103 (w), 1069 (w), 931 (w, sh), 912 (w), 867 (m), 832 (m), 813 (m), 754 (s), 743 (s), 716 (m), 688 (s), 667 (m), 627 (m); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 2.93 (t, J = 7.3 Hz, 2 H), 3.33 (t, J = 7.3 Hz, 2 H), 7.22–7.26 (m, 3 H), 7.31–7.36 (m, 3 H), 7.40 (td, J = 7.5, 1.5 Hz, 1 H), 7.45–7.47 (m, 1 H), 7.57 (ddd, J = 8.2, 6.9, 1.5 Hz, 1 H), 7.62 (ddd, J = 8.3, 6.9, 1.6 Hz, 1 H), 7.74 (dd, J = 7.6, 1.2 Hz, 1 H), 7.84–7.89 (m, 3 H), 8.15 (s, 1 H), 8.51 (d, J = 8.2 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ_C 21.35, 34.63, 82.07, 89.80, 89.91, 92.61, 100.03, 120.93, 123.11, 124.43, 125.71, 126.95, 127.19, 127.71, 128.05, 128.14, 128.73 (2), 128.78, 128.80, 129.55, 130.07, 132.01 (2), 133.15, 133.23, 133.62, 136.60, 137.42, 143.11 ppm; HRMS (EI): m/z (%): 461.0749 (3, $[M - Br]^+$, calcd for $C_{30}H_{20}{}^{81}Br^+$: 461.0722), 459.0734 (3, $[M - Br]^+$, calcd for $C_{30}H_{20}{}^{79}Br^+$: 459.0743), 380.1555 (100, $[M - 2\,Br]^+$, calcd for $C_{30}H_{20}{}^+$: 380.1560); elemental analysis calcd (%) for $C_{30}H_{20}Br_2$: C 66.69, H 3.73, Br 29.58; found C 66.66, H 3.91, Br 29.71.

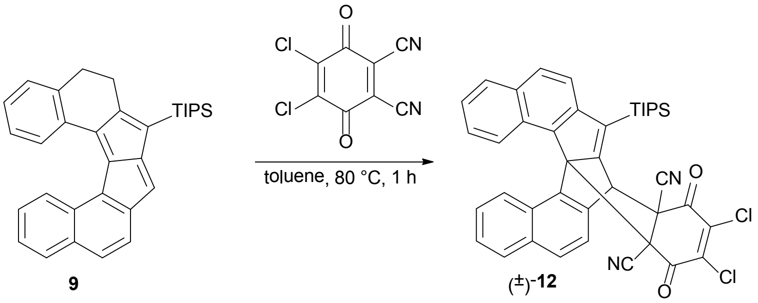
7-Phenyl-5,6-dihydronaphtho[2',1':5,6]pentaleno[1,2-*a*]naphthalene (10)



10

A mixture of *gem*-dibromoolefin **8** (60 mg, 0.11 mmol), [Pd(PPh_3)$_2$$Cl_2$] (7 mg, 0.01 mmol), Zn-dust (7 mg, 0.11 mmol), and K_2CO_3 (31 mg, 0.22 mmol) in toluene (2 ml) under Ar was stirred at 80 °C for 16 h, after which hydroquinone (24 mg, 0.22 mmol) was added and the mixture stirred for an additional 12 h at the same temperature. After further stirring for 9 h at 110 °C, the mixture was cooled to 25 °C, the solvent was evaporated under reduced pressure and the crude mixture purified by column chromatography (SiO_2, cyclohexane/$CHCl_3$ 5/1) to give **10** as dark brownish green solid (6 mg, 15%). m.p. > 105 °C (dec.); R_f = 0.32 (SiO_2, cyclohexane/$CHCl_3$ 5:1); UV/Vis ($CHCl_3$) λ_{max}/nm 684 (ε/M^{-1} cm^{-1} 412), 448 (7562); IR (ATR) ν_{max} (neat)/cm^{-1} = 3051 (w, br), 2940 (w, sh), 1594 (m), 1573 (w), 1492 (m), 1442 (w, sh), 1304 (m), 1264 (w), 1217 (m), 1156 (w), 1061 (w), 1028 (w), 944 (w), 863 (m), 810 (m), 781 (m), 768 (s), 746 (s), 728 (s), 696 (s), 670 (m); ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H 2.57 (t, *J* = 6.1 Hz, 2 H), δ 2.81 (t, *J* = 6.2 Hz, 2 H), 5.99 (s, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.98 ($t_{apparent}$, *J* = 8.0 Hz, 1 H), 7.12 ($t_{apparent}$, *J* = 6.0 Hz, 1 H), 7.18–7.29 (m, 4 H), 7.32–7.40 (m, 5 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.53 (d, *J* = 8.5 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ_C 25.97, 31.10, 122.90, 125.94, 126.10, 126.26, 126.32, 127.61, 127.69 (2), 128.22, 128.49, 128.73, 128.93 (2), 129.46, 129.51, 130.31, 130.70, 131.17, 131.64, 134.57, 135.09, 135.60, 141.03, 141.59, 142.17, 147.97, 148.52, 157.90 ppm; HRMS (MALDI): *m/z* (%): 380.1559 (100, [*M*]$^+$, calcd for $C_{30}H_{20}^+$: 380.1560).

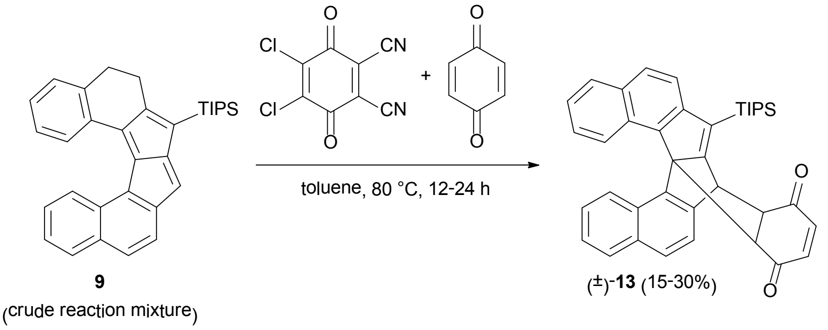
3.6ESI Synthesis of DDQ-adduct (±)-12



Scheme 5ESI Conditions for the preparation of DDQ-adduct (±)-**12**.

Compound **9** (30 mg, 0.065 mmol) was dissolved in toluene (2 mL), and 2,3-dichloro-5,6-dicyanobenzoquinone (15 mg, 0.066 mmol) was added to the solution. The mixture was stirred at 80 °C for 1 h and the solvent evaporated under reduced pressure. Purification was attempted in different ways: column chromatography (SiO_2, cyclohexane/Et_2O, 3:2) gave relatively clean solid (brownish orange) product, but decomposition is substantial; repeated precipitation from benzene/*n*-hexane mixtures gave rather clean product also, however, product is lost due to dissolution in the solvent mixture (note that although the compound is unstable as a solid in contact with air, during chromatographic separation in contact with silica or alumina stationary phases or in solution upon heating, it can be stored in solution ($CDCl_3$) at 25 °C for days without major decomposition). Due to the instability under ambient conditions and purification difficulties, an exact yield cannot be given (2–5 mg material was isolated in average). $R_f = 0.64$ (SiO_2, cyclohexane/Et_2O, 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.96 ($dd_{apparent}$, $J = 15.8, 7.5$ Hz, 18 H), 1.27–1.38 (m, 3 H), 4.72 (s, 1 H), 7.20 (ddd, $J = 8.4, 6.9, 1.3$ Hz, 1 H), 7.43 (ddd, $J = 8.1, 6.9, 1.0$ Hz, 1 H), 7.48 (d, $J = 8.5$ Hz, 1 H), 7.64 (ddd, $J = 8.0, 6.9, 0.9$ Hz, 1 H), 7.73 (d, $J = 8.3$ Hz, 1 H), 7.86 (ddd, $J = 8.4, 6.9, 1.3$ Hz, 1 H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1 H), 7.95 (d, $J = 8.3$ Hz, 1 H), 8.01 (d, $J = 8.3$ Hz, 1 H), 8.14 (d, $J = 9.1$ Hz, 1 H), 8.56 (d, $J = 8.5$ Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 12.56, 18.99, 19.06, 57.46, 59.70, 67.81, 80.40, 113.37, 114.24, 120.18, 123.31, 124.49, 125.80, 126.68, 126.92, 127.61, 127.68, 127.84, 128.71, 129.15, 129.82, 130.54, 131.56, 132.17, 132.24, 132.75, 133.43, 135.09, 142.81, 144.79, 145.66, 151.07, 169.03, 175.95, 178.67 ppm; HRMS (MALDI): *m/z* (%): 458.2424 (100, $[M - C_8Cl_2N_2O_2]^+$, calcd for $C_{33}H_{34}Si^+$: 458.2424)

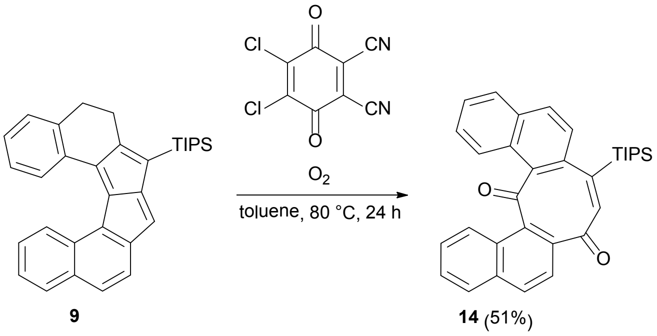
3.7ESI Synthesis of BQ-adduct (±)-13



Scheme 6ESI Conditions for the preparation of BQ-adduct (±)-**13**.

Monitoring the formation of compound **9** by ^{1}H NMR, 2,3-dichloro-5,6-dicyanobenzoquinone (4 eq.) was added to the crude reaction mixture. After an additional 12–24 h stirring at 80 °C, compound (±)-**13** was isolated by column chromatography (SiO_2, cyclohexane/EtOAc, 5:1) in varying yields of 15-30%. m.p. > 210 °C (dec.); $R_f = 0.59$ (SiO_2, cyclohexane/EtOAc, 5:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2940 (m, sh), 2862 (m), 1673 (s), 1627 (w), 1462 (m), 1367 (w), 1293 (w), 1220 (w), 1014 (w), 882 (m), 853 (m), 822 (s), 805 (m), 754 (s), 744 (s), 669 (m), 644 (m, sh); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.09 (dd$_{apparent}$, J = 11.0, 7.5 Hz, 18 H), 1.48–1.57 (m, 3 H), δ 3.52 (d, J = 8.9 Hz, 1 H), 4.29 (dd, J = 8.7, 4.0 Hz, 1 H), 4.46 (d, J = 4.2 Hz, 1 H), 6.04–6.11 (m, 2 H), 7.17 (ddd, J = 8.3, 6.8, 1.3 Hz, 1 H), 7.30 (d, J = 8.2 Hz, 1 H), 7.33–7.35 (m, 1 H), 7.49 (ddd, J = 8.0, 6.8, 1.0 Hz, 1 H), 7.55 (d, J = 8.5 Hz, 1 H), 7.66 (ddd, J = 8.5, 6.8, 1.4 Hz, 1 H), 7.70 (d, J = 8.2 Hz, 1 H), 7.75 (d, J = 8.2 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.91 (d$_{apparent}$, J = 8.1 Hz, 1 H), 8.39 (d, J = 8.6 Hz, 1 H), 8.69 (d, J = 8.7 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 12.45 (3), 18.93 (3), 18.97 (3), 48.48, 52.58, 59.25, 115.09, 120.59, 123.13, 124.88, 125.56, 125.72, 126.06, 126.37, 128.48, 128.76, 129.08, 129.12, 129.31, 130.16, 131.81, 132.58, 133.94, 134.38, 137.54, 139.96, 141.96, 145.75, 151.43, 178.70, 197.06, 198.45 ppm (one C is missing due to overlap); HRMS (MALDI): m/z (%): 458.2430 (100, $[M - C_6H_4O_2]$, calcd for $C_{33}H_{34}Si$: 458.2430).

3.8ESI Synthesis of ring-opened product 14



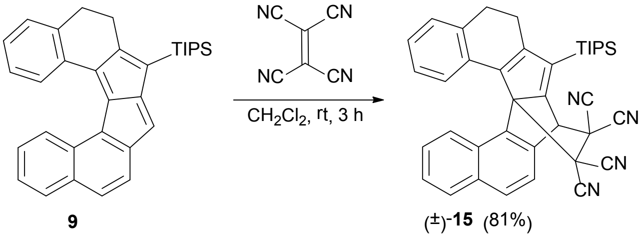
Scheme 7ESI Conditions for the preparation of ring-opened product **14**.

Compound **9** (30 mg, 0.065 mmol) was dissolved in toluene (2 mL), and 2,3-dichloro-5,6-dicyanobenzoquinone (15 mg, 0.066 mmol) was added to the solution. The reaction was heated up to 80 °C and stirred for 24 h under air. The solvent was evaporated under reduced pressure and the product purified by column chromatography (SiO_2, cyclohexane/EtOAc, 10:1) to give a brownish yellow solid (16 mg, 51%). m.p. > 130 °C (dec.); R_f = 0.52 (SiO_2, cyclohexane/EtOAc, 10:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2942 (m, sh), 2864 (m), 1667 (s), 1590 (w), 1458 (m), 1370 (w), 1241 (m), 1204 (m), 998 (m), 885 (m), 864 (m), 822 (s), 814 (s), 747 (s), 685 (m), 643 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.12 (d, J = 7.4 Hz, 9 H), 1.19 (d, J = 7.4 Hz, 9 H), 1.37 (hept, J = 7.3 Hz, 3 H), 6.56 (s, 1 H), 7.17 (ddd, J = 8.2, 6.9, 1.2 Hz, 1 H), 7.33 (ddd, J = 8.1, 6.9, 1.1 Hz, 1 H), 7.38 (d, J = 8.6 Hz, 1 H), 7.47 ($d_{apparent}$, J = 9.1 Hz, 1 H), 7.68 (d, J = 8.4 Hz, 1 H), 7.72 (ddd, J = 8.1, 6.9, 1.1 Hz, 1 H), 7.76 (d, J = 8.4 Hz, 2 H), 7.83 (ddd, J = 8.5, 6.9, 1.4 Hz, 1 H), 7.97 (d, J = 8.1 Hz, 1 H), 8.01 (d, J = 8.4 Hz, 1 H), 8.89 (d, J = 9.2 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 11.84 (3), 18.75 (3), 18.99 (3), 123.90, 123.96, 124.59, 126.13, 126.16, 127.24, 128.39, 128.59, 128.62, 128.94, 129.04, 129.31, 129.96, 132.30, 132.33, 135.07, 135.78, 136.66, 137.88, 140.35, 143.19, 144.10, 201.99, 203.94 ppm; HRMS (MALDI): m/z (%): 490.2324 (100, $[M]^+$, calcd for $C_{33}H_{34}O_2Si^+$: 490.2323).

Remark: The above reaction was repeated under inert conditions in a glove box: Compound **9** (20 mg, 0.043 mmol) was dissolved in toluene-d_8 (2 mL), and 2,3-dichloro-5,6-dicyanobenzoquinone (10 mg, 0.044 mmol) was added to the solution. The mixture was stirred at 80 °C in a glove box. Samples were taken after 1 h and 24 h. The ^{1}H NMR spectrum of the 1 h sample showed the formation of DDQ-adduct

(±)-**12** in 50% conversion and unreacted **9**. Complete decomposition was observed after 24 h reaction time (for ^{1}H NMR spectra, see Figure 38ESI).

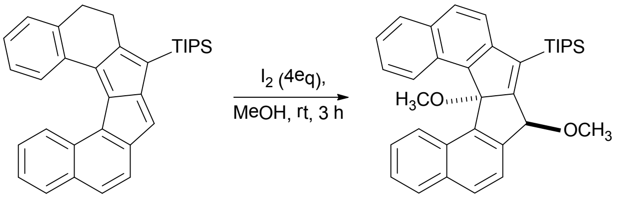
3.9ESI Synthesis of TCNE-adduct (±)-15



Scheme 8ESI Conditions for the preparation of TCNE-adduct (±)-**15**.

Compound **9** (25 mg, 0.054 mmol) was dissolved in CH_2Cl_2 (2 mL), and tetracyanoethylene (7 mg, 0.055 mmol) was added to the solution. The mixture was stirred at 25 °C for 3 h upon which its color changed from deep green to yellowish brown. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 5:1) to give (±)-**15** as a yellow solid (26 mg, 81%). m.p. > 150 °C (dec.); R_f = 0.41 (SiO_2, cyclohexane/EtOAc, 5:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2946 (m, sh), 2866 (m), 1619 (w), 1465 (m), 1379 (w), 1237 (w), 1071 (w), 1015 (m), 1003 (m), 920 (w), 884 (s), 858 (m), 817 (s), 805 (s), 749 (s), 738 (s), 711 (s), 691 (s), 671 (m), 643 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.10 (dd$_{apparent}$, J = 7.5, 2.4 Hz, 18 H), 1.30–1.41 (m, 3 H), 2.62–2.74 (m, 2 H), 2.83–2.91 (m, 2 H), 4.79 (s, 1 H), 7.29 (ddd, J = 8.4, 6.9, 1.3 Hz, 1 H), 7.32–7.34 (m, 2 H), 7.43–7.51 (m, 2 H), 7.58 (d, J = 8.3 Hz, 1 H), 7.91 (dd, J = 7.9, 3.7 Hz, 2 H), 8.01 (d, J = 8.3 Hz, 1 H), 8.18 (d$_{apparent}$, J = 9.3 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 12.52 (3), 18.92 (3), 19.01 (3), 26.57, 29.35, 48.01, 54.15, 56.98, 79.11, 109.46, 110.00, 111.55, 111.63, 119.94, 124.06, 125.06, 127.43, 127.70, 128.06, 128.30, 128.47, 128.58, 129.57, 129.76, 131.40, 132.12, 132.14, 133.16, 135.13, 135.14, 143.52, 157.36, 167.71 ppm; HRMS (MALDI): *m/z* (%): 460.2581 (100, $[M-C_6N_4]^+$, calcd for $C_{33}H_{36}Si^+$: 460.2581)

3.10ESI Synthesis of dimethoxy-derivative (±)-16



9

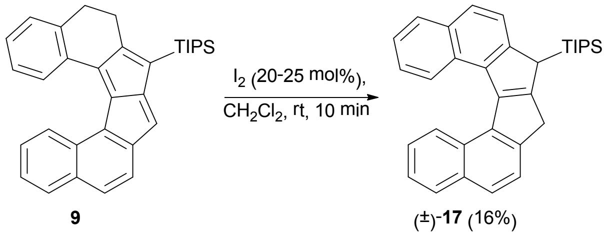
(±)-**16** (20%)

Scheme 9ESI Conditions for the preparation of compound (±)-**16**.

Compound **9** (30 mg, 0.065 mmol) was dissolved in methanol (6 mL), and iodine (66 mg, 0.26 mmol) was added to the solution. The mixture was stirred for 3 h at 25 °C. After dilution with water (20 ml), sat. $Na_2S_2O_3$ solution was added to the mixture. The aqueous solution was extracted with EtOAc until the aqueous phase became colourless. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and filtered. After the solvent was evaporated under reduced pressure, the product was purified by column chromatography (SiO_2, cyclohexane/EtOAc, 20:1) to give **16** as brown oil (7 mg, 20%). $R_f = 0.31$ (SiO_2, cyclohexane/EtOAc, 20:1); IR (ATR) ν_{max} (neat)/cm^{-1} 2942 (s, sh), 2865 (s), 2818 (w), 1698 (w, sh), 1590 (w, sh), 1513 (w), 1463 (m), 1182 (w), 1086 (s), 1009 (m), 881 (m), 816 (s), 769 (m), 742 (m), 663 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.11 (d, J = 7.5 Hz, 9 H), 1.20 (d, J = 7.5 Hz, 9 H), 1.61–1.71 (m, 3 H), 3.09 (s, 3 H), 3.73 (s, 3 H), 5.42 (s, 1 H), 7.17 (ddd, J = 8.4, 6.8, 1.3 Hz, 1 H), 7.35 (ddd, J = 8.1, 6.8, 1.1 Hz, 1 H), 7.53 (ddd, J = 8.1, 6.8, 1.1 Hz, 1 H), 7.57 (d, J = 8.3 Hz, 1 H), 7.66 (ddd, J = 8.4, 6.8, 1.3 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.1 Hz, 1 H), 7.86 (d, J = 8.3 Hz, 2 H), 7.93 (d, J = 8.2 Hz, 1 H), 8.68 (d, J = 8.6 Hz, 1 H), 8.98 (d, J = 8.5 Hz, 1 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 13.11 (3), 19.21 (6), 52.03, 57.37, 79.08, 99.84, 123.41, 123.57, 125.29, 125.60, 125.85, 125.99, 126.13, 126.52, 128.83, 128.87, 130.20, 130.34, 130.48, 131.35, 132.70, 133.67, 134.83, 136.59, 137.51, 146.92, 148.28, 165.53 ppm; HRMS (MALDI): m/z (%): 489.2608 (100, $[M - CH_3O]^+$, calcd for $C_{34}H_{37}OSi^+$: 489.2608), 543.2690 (5.5, $[M + Na]^+$, calcd for $C_{35}H_{40}O_2SiNa^+$: 543.2690).

Remark: The configuration at the CH_3O-substituted carbons was determined by 2D NMR techniques and confirmed by computation as well (for 2D NMR spectra, see Figures 41ESI and 42ESI, for computational results, see section 6.5ESI).

3.11ESI Synthesis of helicene (±)-17



Scheme 10ESI Conditions for the preparation of compound (±)-**17**.

Compound **9** (25 mg, 0.054 mmol) was dissolved in CH_2Cl_2 (2 mL), and a solution of iodine in CH_2Cl_2 (0.3 mL, c = 10 mg/mL) was added. After 5–10 min stirring at 25 °C, the color of the solution turned from green to orange-red. The solvent was removed under reduced pressure and the crude product purified by column chromatography (SiO_2, cyclohexane/$CHCl_3$, 10:1) to give (±)-**17** as pale brown crystals (4 mg, 16%). m.p. > 200 °C (dec.); R_f = 0.43 (SiO_2, cyclohexane/EtOAc, 10:1); IR (ATR) ν_{max} (neat)/cm^{-1} 3049 (w), 2943 (s), 2865 (s), 1479 (w), 1462 (m), 1358 (w), 1263 (w, sh), 1202 (w), 1013 (s), 972 (w), 881 (m), 803 (s), 778 (m), 740 (s), 707 (m), 674 (m), 655 (w), 620 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.97 (d, J = 7.5 Hz, 9 H), 1.05 (d, J = 7.5 Hz, 9 H), 1.34–1.41 (m, 3 H), 3.89 (s, 2 H), 4.28 (s, 1 H), 7.39 (t, J = 7.5 Hz, 2 H), 7.45–7.50 (m, 2 H), 7.68–7.77 (m, 4 H), 7.95 (d, J = 8.1 Hz, 2 H), 8.48 (dd, J = 8.3, 4.9 Hz, 2 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 12.49 (3), 18.84 (6), 37.71, 40.33, 123.09, 123.11, 123.67, 123.83, 124.10, 124.60, 124.91, 124.96, 127.59, 127.86, 127.99, 128.09, 128.86, 128.96, 132.88, 133.77, 135.96, 137.61, 144.96, 146.51, 148.14, 158.27 ppm; HRMS (MALDI): m/z (%): 460.2581 (100, $[M]^+$, calcd for $C_{33}H_{36}Si^+$: 460.2581).

4ESI X-Ray data

4.1ESI General information

X-ray intensity data were measured on a Bruker Kappa Apex-II Duo system equipped with a graphite monochromator with Mo-*K*α radiation (λ = 0.71073 Å) at 100 K. Collected data was processed with the Bruker SAINT[11] software package using a narrow-frame algorithm and corrected for absorption effects using the multi-scan method (SADABS). The structure was solved and refined using the OLEX2[12] and Bruker SHELXTL[13] Software Package. CCDC-952132 ((±)-**12**), CCDC-952133 ((±)-**13**), CCDC-952134 (**14**), CCDC-952131 ((±)-**15**), and CCDC-952135 ((±)-**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or *via* www.ccdc.cam.ac.uk/data_request/cif.

4.2ESI Crystal structure and data for DDQ-adduct (±)-12

Clear orange prism-like crystals were grown from *n*-hexane/EtOAc at 25 °C. Crystallographic data: $C_{90}H_{84}C_{14}N_4O_8Si_2$, m = 1547.59, monoclinic, space group P21/c, a = 20.094(7) Å, b = 17.545(6) Å, c = 24.430(8) Å, α = 90°, β = 112.452°, γ = 90°, V = 7960.(5) Å^3, Z = 4, D_c = 1.291 g/cm^3, μ(Mo-K_α) = 0.239 mm^{-1}, F(000) = 3248, T = 100.(2) K. Number of collected and independent reflections 9907 and 9907, respectively (R_{int} = 0.0000). Final $R_1(I > 2\sigma)$ = 0.2726, wR_2 (all data) = 0.4504 for 9907 independent reflections and 483 parameters with a goodness-of-fit on F^2 of 6.757.

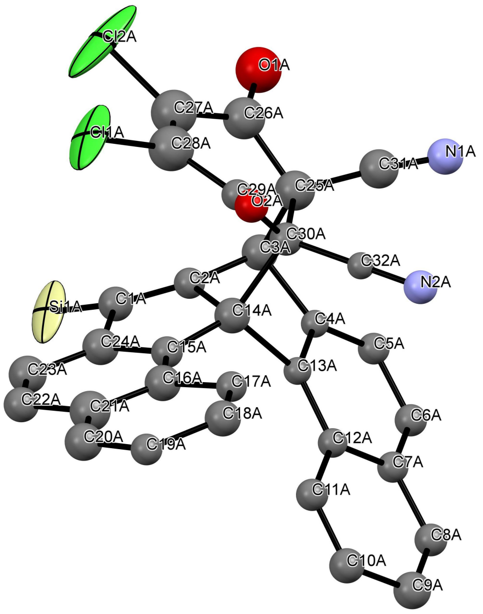


Figure 1SI ORTEP plot of (±)-**12**; arbitrary numbering. Atomic displacement parameters obtained at 100 K are drawn at the 50% probability level. H–atoms and disordered regions (CH and CH_3 groups of the TIPS group) are omitted for clarity.

4.3ESI Crystal structure and data for BQ-adduct (±)-13

Clear yellow plates were grown from acetonitrile/CH_2Cl_2 at 25 °C. Crystallographic data: $C_{39}H_{38}O_2Si$, $M_r = 566.78$, triclinic, space group P-1, $a = 14.7710(14)$ Å, $b = 14.8906(14)$ Å, $c = 15.1612(14)$ Å, $\alpha = 85.652(2)°$, $\beta = 86.843(2)°$, $\gamma = 66.337(2)°$, $V = 3044.4(5)$ Å^3, $Z = 4$, $D_c = 1.237$ g/cm^3, $\mu(\text{Mo-}K_\alpha) = 0.111$ mm^{-1}, F(000) = 1208, $T = 100(2)$ K. Number of collected and independent reflections 82196 and 14090, respectively ($R_{\text{int}} = 0.0438$). Final $R_1(I > 2\sigma) = 0.0890$, w$R_2$ (all data) = 0.2777 for 14090 independent reflections and 769 parameters with a goodness-of-fit on F^2 of 2.789.

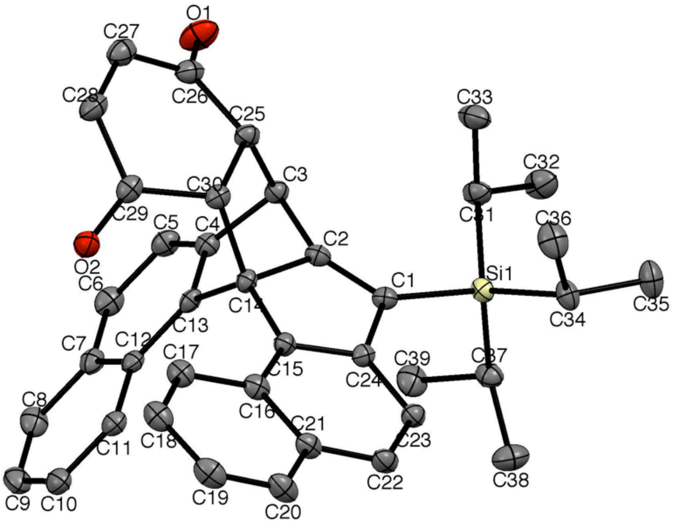


Figure 2ESI ORTEP plot of (±)-**13**; arbitrary numbering. Atomic displacement parameters obtained at 100 K are drawn at the 50% probability level. H–atoms are omitted for clarity.

4.4ESI Crystal structure and data for ring-opened compound 14

Clear pale yellow plates were grown from Et_2O at +3 °C. Crystallographic data: $C_{33}H_{34}O_2Si$, M_r = 490.69, monoclinic, space group C2/c, a = 38.218(8) Å, b = 19.296(4) Å, c = 8.514(18) Å, α = 90°, β = 90.665(4)°, γ = 90°, V = 6278.(2) Å^3, Z = 8, D_c = 1.038 g/cm^3, μ(Mo-K_α) = 0.099 mm^{-1}, F(000) = 2096, T = 100(2) K. Number of collected and independent reflections 42742 and 7289, respectively (R_{int} = 0.0494). Final $R_1(I > 2\sigma)$ = 0.0596, wR_2 (all data) = 0.1597 for 7289 independent reflections and 331 parameters with a goodness-of-fit on F^2 of 1.071.

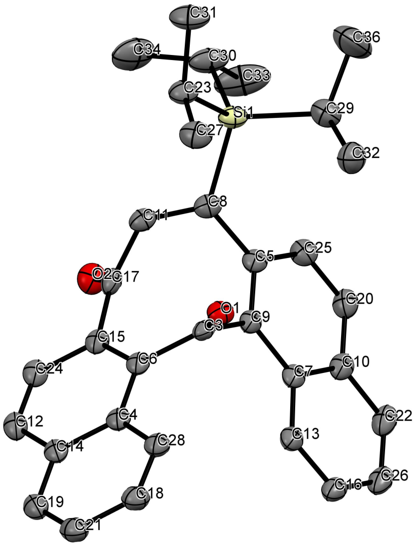


Figure 3ESI ORTEP plot of **14**; arbitrary numbering. Atomic displacement parameters obtained at 100 K are drawn at the 50% probability level. H–atoms are omitted for clarity.

4.5ESI Crystal structure and data for TCNE-adduct (±)-15

Clear colorless plates were grown from *n*-hexane/$CHCl_3$ at 25 °C. Crystallographic data: $C_{39}H_{36}N_4Si$, M_r = 588.81, triclinic, space group P-1, a = 8.265(2) Å, b = 11.375(3) Å, c = 17.895(4) Å, α = 105.856(9)°, β = 99.890(9)°, γ = 94.670(10)°, V = 1579.6(8) Å^3, Z = 2, D_c = 1.238 g/cm^3, μ(Mo-K_α) = 0.109 mm^{-1}, F(000) = 624, T = 100(2) K. Number of collected and independent reflections 23873 and 7321, respectively (R_{int} = 0.0681). Final $R_1(I > 2\sigma)$ = 0.0524, wR_2 (all data) = 0.1178 for 7321 independent reflections and 541 parameters with a goodness-of-fit on F^2 of 1.022.

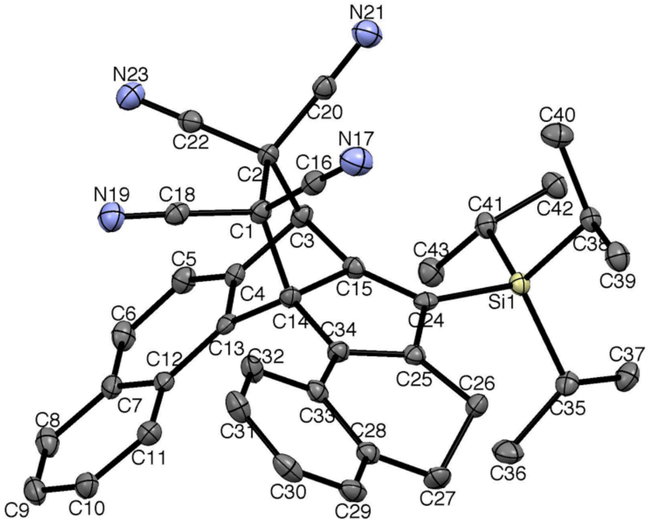


Figure 4ESI ORTEP plot of (±)-**15**; arbitrary numbering. Atomic displacement parameters obtained at 100 K are drawn at the 50% probability level. H–atoms are omitted for clarity.

4.6ESI Crystal structure and data for helicene (±)-17

Single crystals were grown from *n*-hexane/CH_2Cl_2 at 25 °C. Crystallographic data: $C_{33}H_{36}Si$, M_r = 460.71, monoclinic, space group P2$_1$/c, a = 8.8447(4) Å, b = 18.3363(9) Å, c = 17.4324(6) Å, α = 90°, β = 114.902(2)°, γ = 90°, V = 2564.3(2) Å^3, Z = 4, D_c = 1.193 g/cm^3, μ(Mo-K_α) = 0.111 mm^{-1}, F(000) = 992.0, T = 100.15 K. Number of collected and independent reflections 42779 and 5905, respectively (R_{int} = 0.0304). Final $R_1(I > 2\sigma)$ = 0.0478, wR_2 (all data) = 0.1196 for 5905 independent reflections and 313 parameters with a goodness-of-fit on F^2 of 1.064.

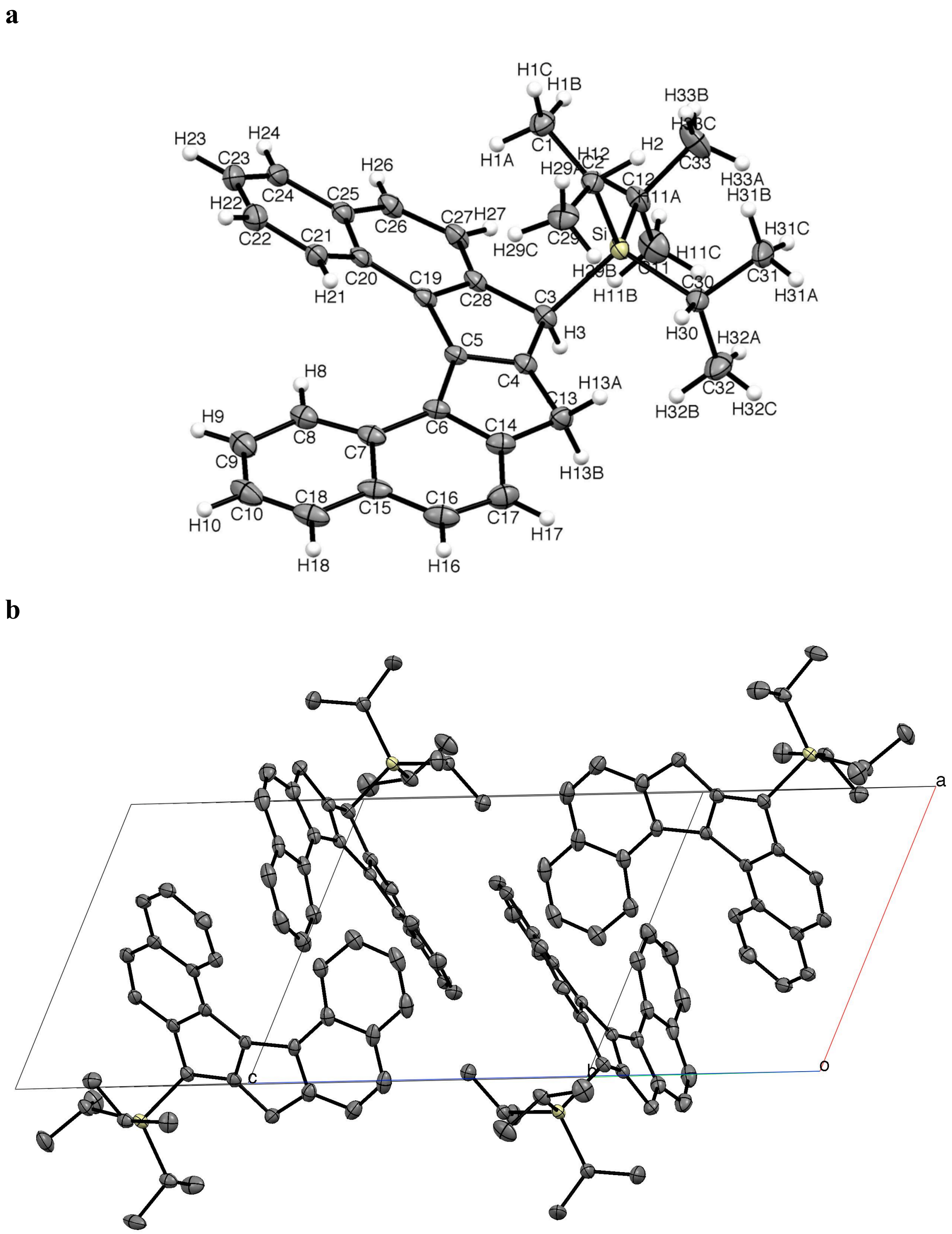


Figure 5ESI (a) ORTEP plot of (±)-**17** (the measured single crystal composed preferentially of diastereomer (*P*,*S*)-**17**); arbitrary numbering. Atomic displacement parameters obtained at 100 K are drawn at the 50% probability level. C8–C21 distance: 3.111Å; selected torsion angles [°]: C20-C19-C5-C6 18.12, C19-C5-C6-C7 9.74. (b) Crystal packing of (*P*,*S*)-**17**. H–atoms are omitted for clarity.

5ESI Electrochemical investigations

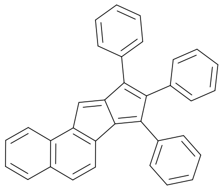
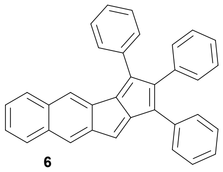
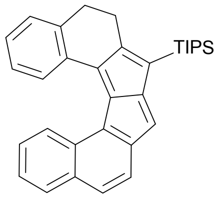
5.1ESI Methods

Electrochemical measurements were carried out in CH_2Cl_2 containing 0.1M Bu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a Pt wire and the pseudo-reference electrode a Pt wire. The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. All potentials are given *vs*. Fc^+/Fc used as internal reference and are uncorrected from ohmic drop.

5.2ESI Discussion

Investigations of the species were carried out by cyclic voltammetry and rotating disk voltammetry in CH_2Cl_2 and 0.1M Bu_4NPF_6. Two oxidations and two reduction of equal amplitude could be observed by RDV. By cyclic voltammetry, the species gave two oxidations steps, the first being reversible, whereas the second behave as irreversible electron transfer. The reduction shows two reductions whose characteristics depend on the structure. Species **4** show a first irreversible reduction peak at slow scan rates associated on the reverse scan with an oxidation peak at −1.08 V. This first reduction becomes reversible at scan rates higher than 2 V s^{-1}. The second reduction is of small amplitude and irreversible. On the reverse scan an oxidation peak is observed at −0.83 V. Compound **6** gave a first irreversible electron transfer followed by a second irreversible reduction of small amplitude. Compound **9** gave two steps of similar amplitudes (same peak currents), the first step being reversible at any scan rates and the second irreversible.

Table 3ESI Electrochemical data observed by cyclic voltammetry (CV) at a scan rate of v = 0.1 V s^{-1} and rotating disk voltammetry (RDV) in CH_2Cl_2 + 0.1M Bu_4NPF_6. All potentials are given versus ferrocene, used as internal standard.

Species	CV			RDV	
	E° a) $V/_{Fc+/Fc}$	ΔEp b) mV	Ep c) $V/_{Fc+/Fc}$	$E_{1/2}$ $V/_{Fc+/Fc}$	Slope (mV) d)
 **4**			+1.07	+1.10 **(1e$^-$)**	60
	+0.47	65		+0.50 **(1e$^-$)**	60
			−1.38 e)	−1.38 **(1e$^-$)**	60
			−1.98 f)	−2.02 **(1e$^-$)**	70
 **6**			+1.15	+1.18 **(1e$^-$)**	60
	+0.60	60		+0.63 **(1e$^-$)**	60
			−1.53	−1.51 **(1e$^-$)**	60
			−2.13 f)	−2.13 **(1e$^-$)**	65
 **9**			+1.03	+1.07 **(1e$^-$)**	60
	+0.43	60		+0.46 **(1e$^-$)**	60
	-1.53	70		−1.52 **(1e$^-$)**	70
			−2.12	−2.12 **(1e$^-$)**	70

a) $E^{o} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

b) $\Delta E_p = E_{pa} - E_{pc}$; c) E_p = irreversible peak potential

d) Logarithmic analysis of the wave obtained by plotting E versus $\log[I/(I_{lim} - I)]$.

e) Reversible electron transfer at scan rates higher than 2 V s^{-1}.

f) Small amplitude signal by CV.

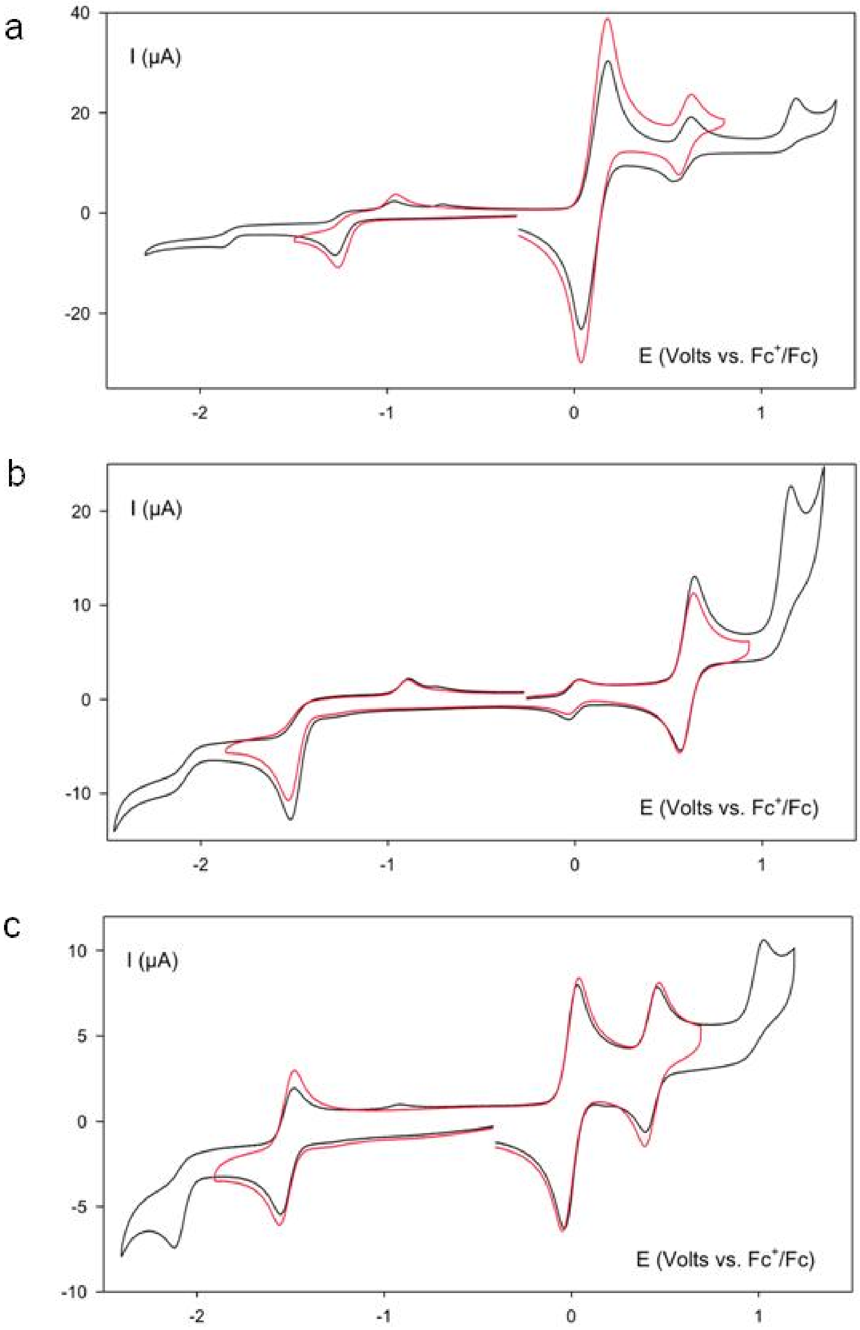


Figure 6ESI Cyclic voltammetry of compounds **4** (a), **6** (b) and **9** (c) on a glassy carbon working electrode at a scan rate of v = 0.1 V s^{-1} in CH_2Cl_2 + 0.1M Bu_4NPF_6 in the presence of ferrocene.

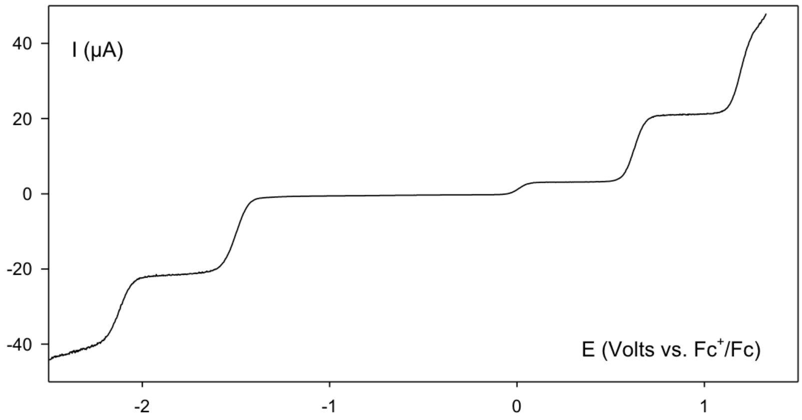


Figure 7ESI Rotating disk voltammetry (N = 1000 r.p.m.) of compound **6** on a glassy carbon working electrode at a scan rate of v = 0.02 V s^{-1} in CH_2Cl_2 + 0.1M Bu_4NPF_6 in the presence of ferrocene.

6ESI Computational studies

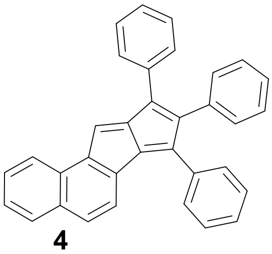
6.1ESI General computational methods

The molecular structures of **4**, **6**, **9**, **10**, **11**, (±)-**16**, (±)-**17**, **S17** and **18** were optimised at the B3LYP/6-31G(d) level of theory by using the software package Gaussian 09.[14] Unless otherwise stated, solvation in $CHCl_3$ was applied using the polarizable continuum model (PCM).[15] All structures are confirmed ground-state minima according to the analysis of their analytical frequencies computed at the same level, which show no imaginary frequencies. On these minima, the first ten vertical transition energies were calculated by time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/6-31G(d) level of theory in the gas phase.

The isosurfaces of the frontier orbitals (shown at 0.02 a.u.) were computed at the B3LYP/6-31G(d) level of theory in gas phase. All energies reported are zero-point corrected free enthalpies Δ*G* (sum of electronic and thermal free enthalpies) at 298 K.

6.2ESI Calculated optical and electronic properties of 4, 6 and 18

Table 3ESI Transition energies (*E*), oscillator strengths (*f*) and orbital assignments for **4**.

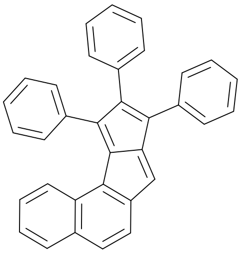


4

Exptl.: λ = 650 nm (in $CHCl_3$)

Excited state	**Δ*E* (eV)**	**λ (nm)**	***F***	Assignments
1	1.72	720	0.0004	H → L
2	2.99	414	0.277	H−1 → L
3	3.83	323	0.256	H−2 → L
4	4.06	306	0.096	H−3 → L+1 H → L+1 H−2 → L

Table 4ESI Transition energies (*E*), oscillator strengths (*f*) and orbital assignments for **18**.

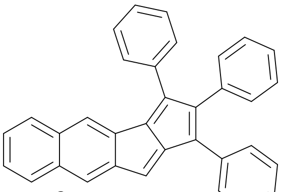


18

Exptl.: λ = 660 nm (in $CHCl_3$)

Excited state	**Δ*E* (eV)**	**λ (nm)**	***F***	Assignments
1	1.85	668	0.003	H → L
2	3.21	385	0.200	H−1 → L
3	3.69	336	0.114	H−2 → L
4	4.20	295	0.279	H−3 → L H → L+1

Table 5ESI Transition energies (*E*), oscillator strengths (*f*) and orbital assignments for **6**.

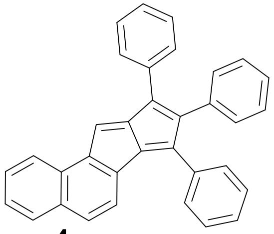
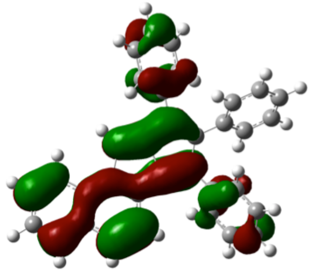
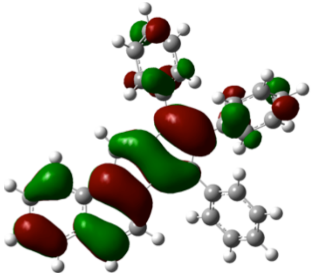
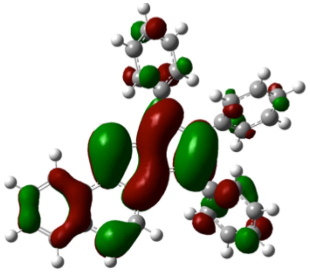
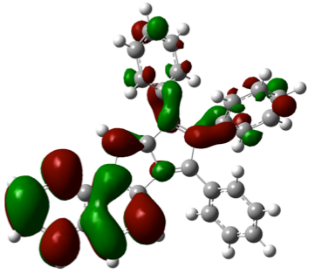
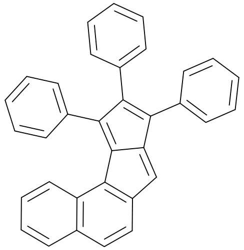
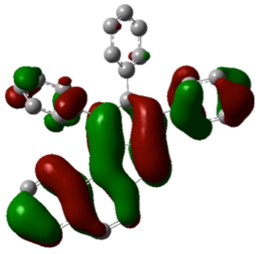
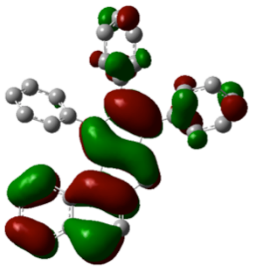
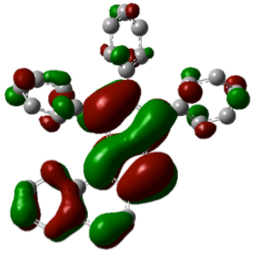
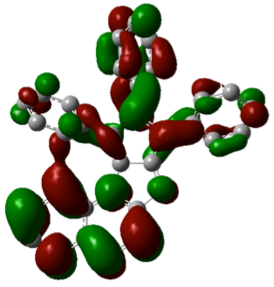
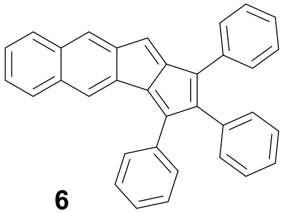
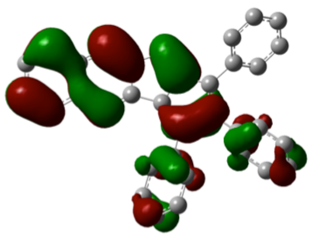
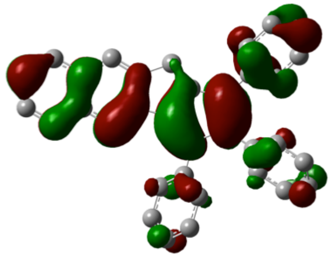
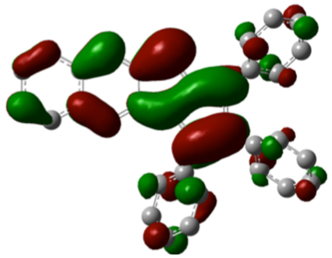
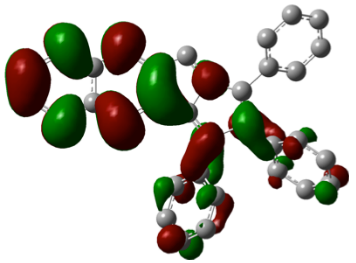


6

Exptl.: λ = 566 nm (in $CHCl_3$)

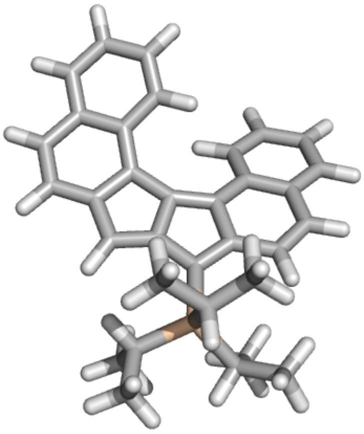
Excited state	ΔE (eV)	λ (nm)	*F*	Assignments
1	2.15	576	0.017	H → L
2	3.07	403	0.375	H−1 → L
3	3.91	317	0.055	H−2 → L
4	4.15	299	0.507	H−3 → L H → L+1 H−2 → L

Table 6ESI Depiction of calculated HOMOs and LUMOs over optimised ground-states of **4**, **6** and **18**.

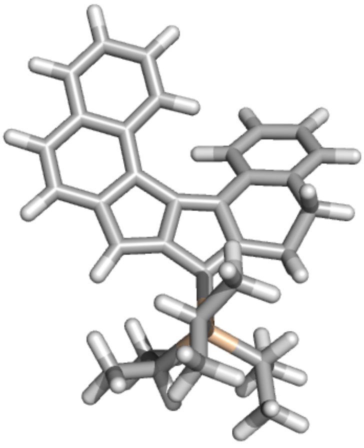
compound	HOMO–1	HOMO	LUMO	LUMO+1
 **4**				
 **18**				
 **6**				

6.3ESI Geometric analysis of helical pentalenes 11 and S17 and precursors 9 and 10

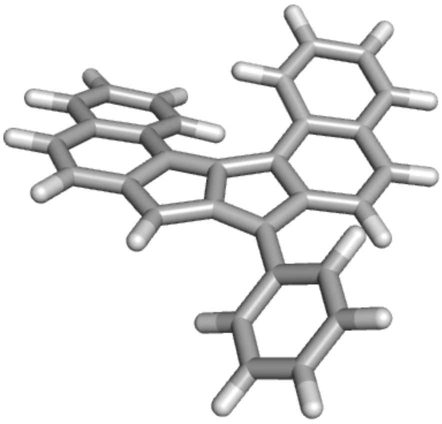
Table 7ESI Depictions of DFT-optimised geometries of **11**, **S17**, **9** and **10**. The structures show helical distortion of the scaffold. The torsion angle at the biaryl type bond to the phenyl substituent in compound **10** is 33°.



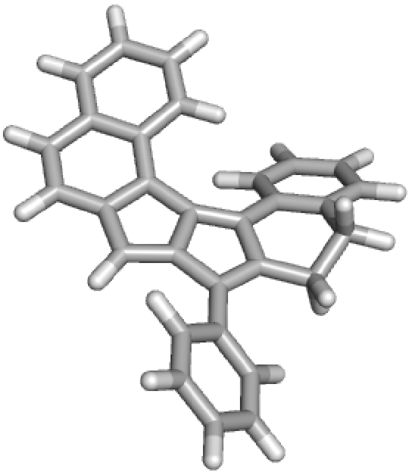
11



9



S17



10

In order to estimate the racemisation barrier ΔE_{rac} of the helically chiral pentalene **9**, we studied the isomerisation mechanism on an analogue TMS-substituted model compound with the help of computational methods. The racemisation can be rationalised by a change in the dihedral angel $\theta_{13,11,6,24}$ along the four inner carbon atoms in the helical scaffold (Fig. 8ESI a). That dihedral angle θ equals ≈ –35.4° in the DFT: B3LYP/6-31G(d)-optimized structure of the TMS-substituted analogue, and its energy is set as zero point. Conducting a relaxed scan along that dihedral coordinate gave the expected unsymmetrical potential energy surface with a maximum at –2.9° of 8.0 kcal mol^{-1} (Fig. 8ESI b). That energy maximum can be understood as an estimated racemisation energy barrier. However, no transition state was calculated for such an energy maximum, which should be even lower in energy when all coordinates are allowed to relax to an optimized saddle point. As a result, the mixture of stereo isomers of **9** cannot be separated at room temperature and isolation of a single *M* or *P* helical isomer is experimentally not possible.

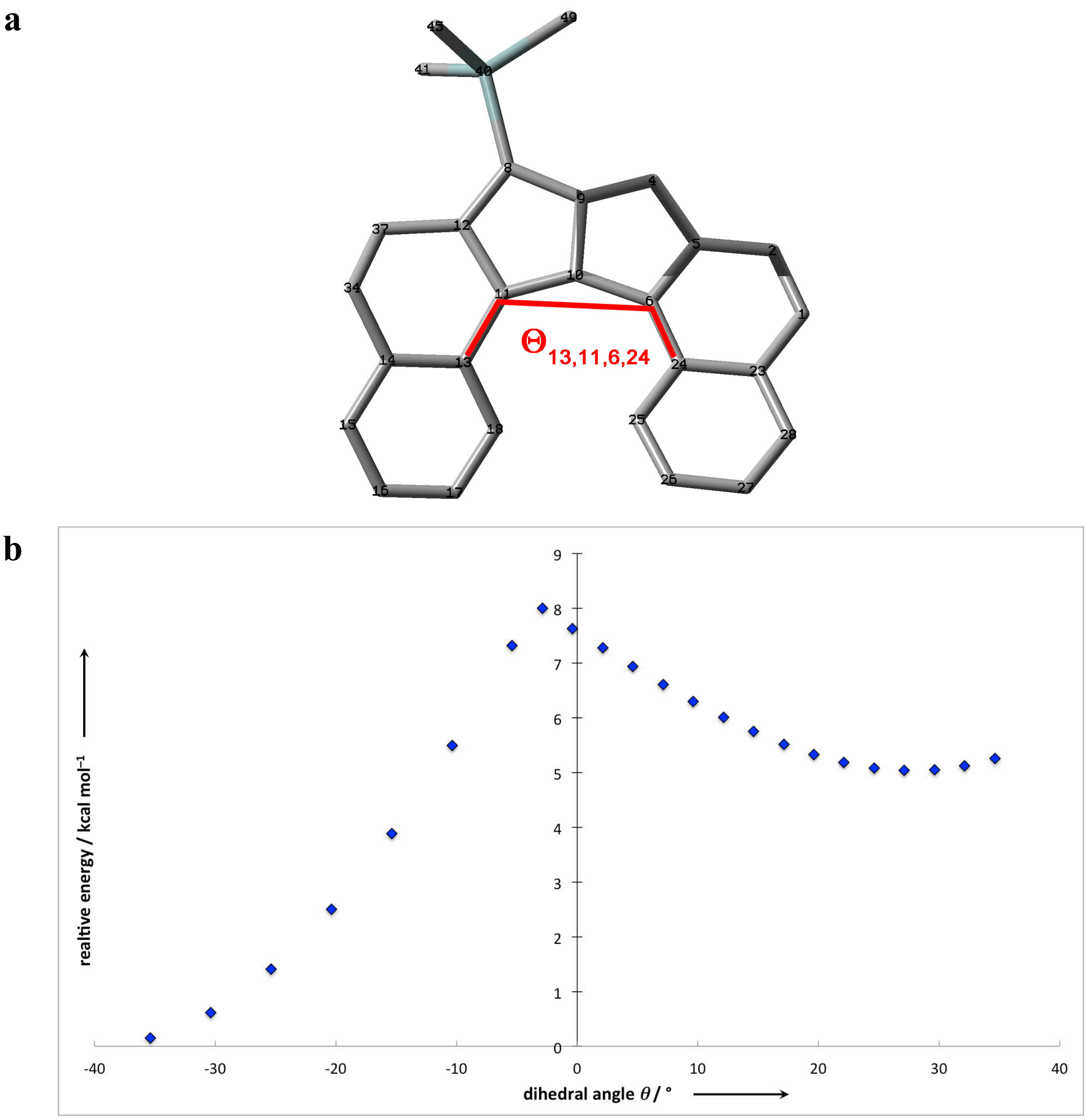


Figure 8ESI (a) Depiction of DFT-optimised geometries of the TMS-substituted analogue of **9** with the examined dihedral angle θ= –35.4° and (b) the potential energy surface along the dihedral angle θ having an energy maximum of 8.0 kcal mol^{-1} at –2.9°, which refers to an estimation of the helical racemization energy ΔE_{rac} for compound **9**.

6.4ESI Computed aromatic/antiaromaric character (NICS values) of 4, 6, 9, 10, 11 and 18

The nucleus-independent chemical shift (NICS) index is a theoretical evaluation of induced diatropic and paratropic ring currents, which are related to aromaticity (negative NICS values) and anti-aromaticity (positive NICS values), respectively.[16] NICS(1) and NICS(0) values of compound **4, 6, 18, 9, 10** and **11** were calculated at the GIAO-B3LYP/6-311+G(2d,p) level of theory (Figure 9SI).

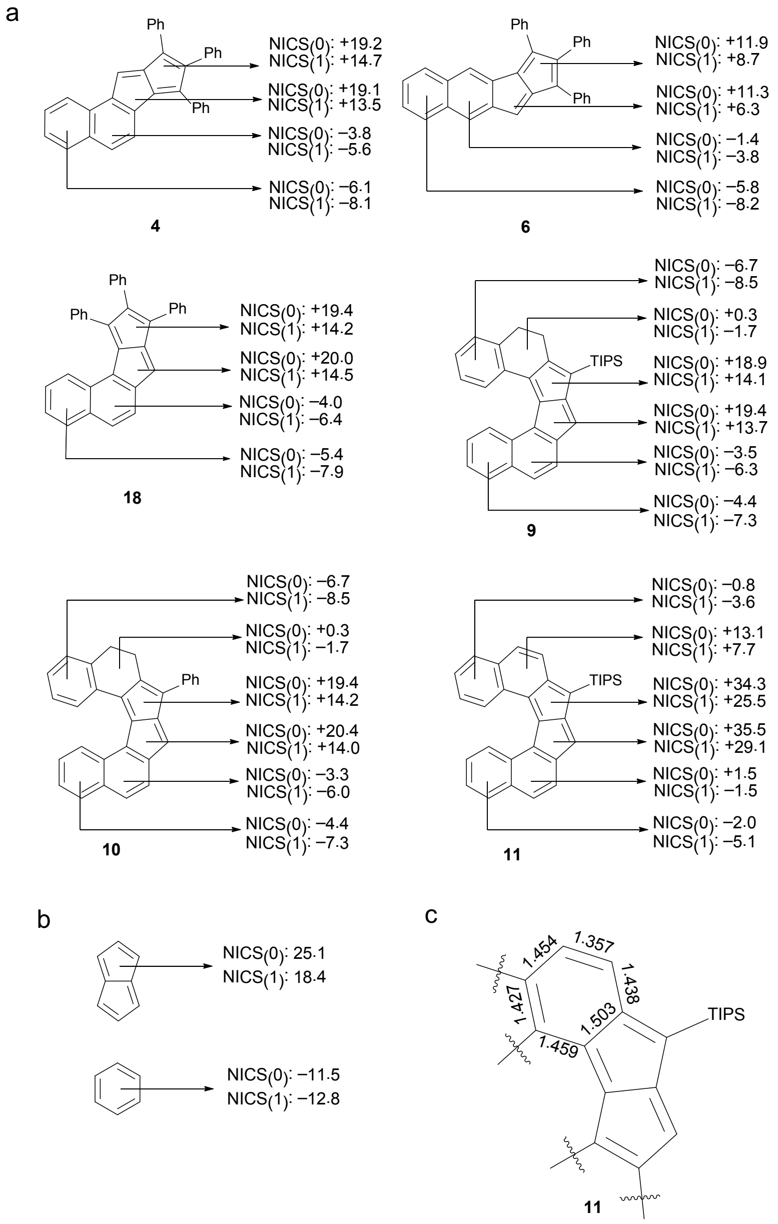


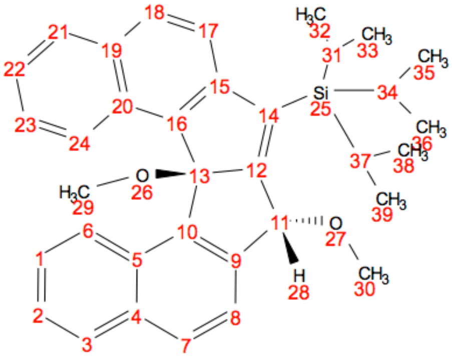
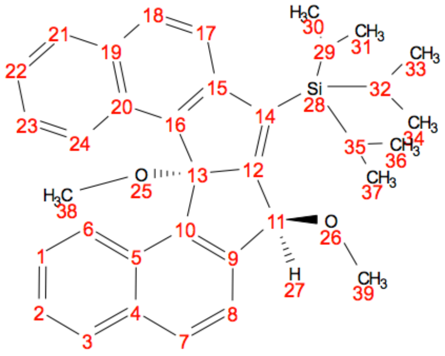
Figure 9ESI (a) Calculated NICS(0) and NICS(1) values of compounds **4**, **6**, **18**, **9**, **10** and **11**. (b) NICS values for pentalene and benzene. (c) Calculated bond-lengths (Å) of the antiaromatic six-membered ring of compound **11**.

6.5ESI Structure elucidation by theoretical NMR prediction of (±)-16

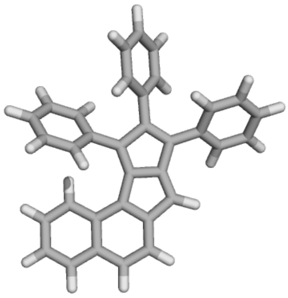
The ^1H NMR chemical shifts are predicted using the gauge-independent atomic orbital (GIAO) method at the mPW1PW91/6-311+G(2d,p))(GIAO, scrf=$CHCl_3$, smd)//B3LYP/6-31G*(scrf=$CHCl_3$) level of theory.[17] The effect of chloroform solvent on NMR chemical shifts is accounted for using the polarizable continuum solvation model PCM[15] including the radii and non-electrostatic terms for the SMD solvation model by Truhlar and coworkers.[18] The obtained isotropic shieldings were scaled using the method of Tantillo and coworkers,[19] with the scaling factors of the mPW1PW91/6-311+G(2d,p))(GIAO, scrf=$CHCl_3$, smd)//B3LYP/6-31+G(d,p)(gas phase) method (^1H: slope: –1.0936, intercept: 31.8018; ^{13}C: slope: –1.0533, intercept: 186.5242).

In order to support the structure elucidation of (±)-**16**, we turned to computational methods and predicted the NMR chemical shifts of selected nuclei (^1H and ^{13}C). Except for the methoxy protons, both isomers (±)-**16**-*trans*-***a*** and (±)-**16**-*trans*-***b*** show similar predicted chemical shifts on all selected nuclei (shifts within the root-mean-square deviation (RMSD), see Table 8ESI). Only the predicted chemical shift of the C(30)–*H* proton of the isomer (±)-**16**-*trans*-***a*** is not within the RMSD-range. Furthermore, the overall RMSD of the ^1H and ^{13}C chemical shifts of (±)-**16**-*trans*-***a*** is higher than the RMSD of (±)-**16**-*trans*-***b*** (^1H: RMDS((±)-**16**-*trans*-***a***) = 0.48 ppm, RMDS((±)-**16**-*trans*-***b***) = 0.27 ppm; ^{13}C: RMDS((±)-**16**-*trans*-***a***) = 4.48 ppm, RMDS((±)-**16**-*trans*-***b***) = 2.17 ppm), which leads, together with the experimental 2D NMR spectra, to the conclusion that (±)-**16**-*trans*-***b*** is the isolated product of the reaction of **9** with iodine in MeOH solution (Table 8ESI and Figures 42ESI and 43ESI for 2D NMR spectra).

Table 8ESI Comparison of selected experimental and calculated (DFT: mPW1PW91/6-311+G(2d,p)) chemical shifts δ of the ^{1}H and ^{13}C NMR spectra of two possible stereoisomers of **(±)-16**. The root-mean-square deviation (RMDS) is given for every list of selected peaks. Deviations of predicted chemical shift higher than the RMSD are highlighted in red (arbitrary numbering).

Exp. chemical shifts δ / ppm	 (±)-**16**-*trans*-***a***		 (±)-**16**-*trans*-***b***	
^{1}H	calculated δ / ppm	Atom No.	calculated δ / ppm	Atom No.
3.09	2.97	C(29)–H	2.93	C(38)–H
3.73	2.97	C(30)–H	3.80	C(39)–H
5.42	5.92	C(11)–H	5.79	C(11)–H
8.68	8.42	C(24)–H	8.23	C(6)–H
8.98	8.80	C(6)–H	8.69	C(24)–H
	RMSD(^{1}H)=0.48		RMSD(^{1}H)=0.27	
^{13}C				
52.0	48.2	C(30)	50.9	C(38)
57.4	54.4	C(29)	58.1	C(39)
79.1	78.5	C(11)	80.7	C(11)
99.8	101.3	C(13)	96.3	C(13)
125.9	125.8	C(24)	123.9	C(24)
126.6	126.9	C(6)	124.5	C(6)
165.5	172.3	C(12)	169.6	C(12)
	RMSD(^{13}C)=4.48		RMSD(^{13}C)=2.17	

6.6ESI Cartesian Coordinates of Calculated Molecular Geometries

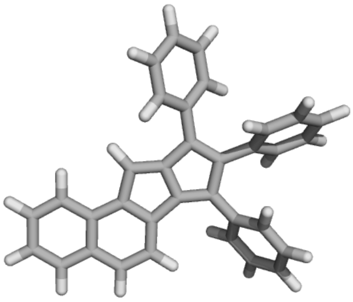


18

B3LYP/6-31G* (gas phase)

Atom type, (x,y,z) coordinates:

C	-3.80144300	0.59319500	-0.44465100
C	-5.11150400	0.98793800	-0.57668800
C	-6.16815900	0.05725400	-0.40605800
C	-5.88399400	-1.25823600	-0.13060400
H	-3.00597200	1.31155200	-0.59327700
H	-5.34002400	2.02258000	-0.81823800
H	-7.19925000	0.38574300	-0.50565100
H	-6.68696700	-1.98312500	-0.01706200
C	-4.54120300	-1.71277500	-0.00207400
C	-3.46416700	-0.75592600	-0.13432400
C	-2.95297300	-3.53472300	0.30335500
C	-4.25695400	-3.08088300	0.22824800
H	-2.74191200	-4.59074900	0.45216100
H	-5.08681000	-3.77655900	0.32425700
C	-2.13664700	-1.23038500	0.01450600
C	-1.90171700	-2.61305300	0.18714300
C	-0.44954900	-2.86585100	0.19714100
C	1.37055200	0.26065900	-0.02676700
C	0.18536100	-1.67893100	0.02758100
C	-0.79628200	-0.59850800	-0.02075300
C	-0.10572000	0.58485000	-0.00016200
H	-0.00103500	-3.84487100	0.32914700
C	1.53537500	-1.10497800	0.00205100
C	-1.59595500	4.59618800	0.31498300
C	-1.90354300	3.65090300	1.29545800
C	-1.42438200	2.34601500	1.18499300
C	-0.62176400	1.96587200	0.09498500
C	-0.30563600	2.93090900	-0.87660900
C	-0.79908100	4.23074000	-0.77224300
H	-1.97234200	5.61223100	0.39863200
H	-2.51956300	3.92747700	2.14696500
H	-1.66800800	1.60883200	1.94456000
H	0.32090900	2.65471400	-1.71913200
H	-0.55533100	4.96088100	-1.53933200
C	4.49339000	3.20406700	-0.27667700
C	3.53886000	3.28316000	0.73900900
C	2.51933000	2.33518200	0.82193900
C	2.43788500	1.28144000	-0.10609800
C	3.40510600	1.21734300	-1.12579700
C	4.42118200	2.16748800	-1.20990500
H	5.28536700	3.94543800	-0.34209700
H	3.58631000	4.08545900	1.47078000
H	1.78318300	2.40431200	1.61699200
H	3.35050200	0.41487300	-1.85539700
H	5.15614400	2.09965600	-2.00786400
C	5.08317900	-3.51491100	0.17525200
C	3.98549000	-3.92173300	-0.58474900
C	2.83937800	-3.13014900	-0.64139500
C	2.76686100	-1.90840700	0.05488900
C	3.88100100	-1.51397400	0.81951600
C	5.02338800	-2.30834200	0.87747100
H	5.97617500	-4.13239100	0.22256500
H	4.02111500	-4.85666300	-1.13815700
H	1.99529800	-3.44456000	-1.24837400
H	3.83916400	-0.58654000	1.38074600
H	5.86905400	-1.98692500	1.47998300

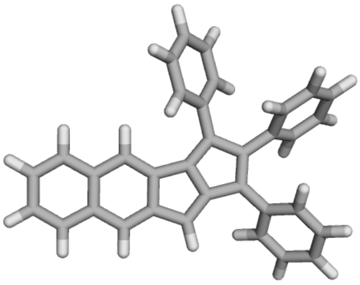


4

B3LYP/6-31G* (gas phase)

Atom type, (x,y,z) coordinates:

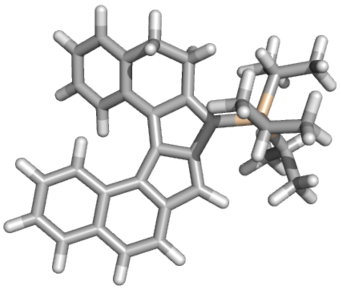
C	-4.90722900	1.83022200	-0.04148700
C	-6.28379900	1.86194300	-0.02801300
C	-7.03342400	0.65644600	0.02298700
C	-6.38531400	-0.55772300	0.05876200
H	-4.34588900	2.75976500	-0.08258300
H	-6.80401700	2.81609600	-0.05725500
H	-8.11946400	0.69763400	0.03357000
H	-6.95527300	-1.48372700	0.09838400
C	-4.20273200	0.59157600	-0.00589200
C	-4.96342300	-0.63391900	0.04563800
C	-4.28321000	-1.87769900	0.08672700
C	-2.89750500	-1.95441400	0.06710300
H	-4.87293000	-2.79049900	0.13569800
H	-2.40467800	-2.92112700	0.10318400
C	-1.76377600	1.54874200	-0.03595100
C	-2.79135500	0.48747800	-0.01666700
C	-2.14596700	-0.76926000	0.01131000
H	-1.97231100	2.61275000	-0.05819000
C	1.55725500	0.05029400	0.00954100
C	0.89893700	1.26114800	-0.00625700
C	-0.53869700	0.95268000	-0.01289000
C	-0.70086000	-0.49101800	-0.01173800
C	0.53932400	-1.06861800	0.00133900
C	2.43388500	5.27080800	-0.20038300
C	3.00957200	4.26208800	-0.98000000
C	2.52349400	2.95638500	-0.91610100
C	1.44794100	2.62709000	-0.06903100
C	0.87275000	3.65498600	0.70380400
C	1.36290000	4.96067100	0.64230900
H	2.81458700	6.28770100	-0.25171200
H	3.83751700	4.49392800	-1.64555300
H	2.96921800	2.18411500	-1.53525200
H	0.05097100	3.41938100	1.37486900
H	0.90898000	5.73523100	1.25583200
C	5.81592200	-0.55884100	0.06954500
C	5.02964600	-1.18520700	-0.90190400
C	3.64669600	-0.99440600	-0.91805600
C	3.02024700	-0.16508500	0.03118200
C	3.82452800	0.45559000	1.00534500
C	5.20648800	0.26135100	1.02436400
H	6.89228400	-0.71054400	0.08442900
H	5.49240900	-1.82532900	-1.64912500
H	3.04573800	-1.48425700	-1.67936800
H	3.35671900	1.09150300	1.75185700
H	5.80749600	0.74966400	1.78766800
C	1.38705100	-5.27574600	0.09627200
C	0.48362100	-4.75755500	-0.83666700
C	0.21581700	-3.38814600	-0.86725000
C	0.85284700	-2.50796700	0.02795900
C	1.77203000	-3.04122000	0.95142000
C	2.02729500	-4.41238500	0.99064000
H	1.59395700	-6.34256200	0.12306800
H	-0.01109100	-5.41910300	-1.54362400
H	-0.47647900	-2.98644500	-1.60233600
H	2.27545200	-2.37928000	1.64931800
H	2.73108100	-4.80661500	1.71936300



6

B3LYP/6-31G* (gas phase)
Atom type, (x,y,z) coordinates:

C	6.03706100	-1.98944000	0.01145000
C	7.14227200	-1.15930600	0.04973400
C	6.97261100	0.23978200	0.07913500
C	5.70244000	0.78734500	0.06841300
H	6.16353000	-3.06959800	-0.01055500
H	8.14239300	-1.58389200	0.05777400
H	7.84338900	0.88914600	0.11020400
H	5.57186100	1.86683900	0.09138100
C	4.72637800	-1.45845100	0.00083500
C	4.55265600	-0.03508500	0.02853300
C	3.23135300	0.52212700	0.01244200
C	3.56980800	-2.30138600	-0.03216800
H	3.12248200	1.60271500	0.03237400
H	3.70436700	-3.38098200	-0.04579000
C	0.99599400	-2.37869600	-0.04873800
C	2.31918800	-1.74447700	-0.04009400
C	2.13801500	-0.30108000	-0.02134700
H	0.83444400	-3.45131100	-0.06099500
C	-1.60969500	0.15434100	0.00081200
C	-1.39854600	-1.21134800	-0.00966600
C	0.05039200	-1.39892600	-0.02578500
C	0.68962100	-0.08567600	-0.03658300
C	-0.28897600	0.87174500	-0.01639300
C	-4.17595900	-4.48227900	-0.18491900
C	-4.39895700	-3.33443100	-0.94963000
C	-3.50904700	-2.26439500	-0.89212000
C	-2.37237400	-2.31535000	-0.06401700
C	-2.15859300	-3.48043300	0.69663400
C	-3.05099700	-4.55001600	0.63844900
H	-4.87158900	-5.31583900	-0.23221900
H	-5.26712100	-3.27452000	-1.60096100
H	-3.68256900	-1.38414600	-1.50227800
H	-1.29628000	-3.53248400	1.35535700
H	-2.86868700	-5.43590300	1.24152700
C	-5.42560400	2.12822100	0.07803100
C	-4.47901900	2.46950000	-0.88982300
C	-3.23701600	1.83607100	-0.91209200
C	-2.92022300	0.83863800	0.02764600
C	-3.88306500	0.50679500	0.99780300
C	-5.12161100	1.14561000	1.02291000
H	-6.39161100	2.62578000	0.09766700
H	-4.70622000	3.23251200	-1.62978200
H	-2.50640000	2.10709500	-1.66832000
H	-3.64937000	-0.25503000	1.73529100
H	-5.84990000	0.87665000	1.78360500
C	0.33455300	5.11570300	0.11163400
C	1.03638000	4.32519500	-0.80094300
C	0.82185600	2.94840800	-0.84500100
C	-0.10114800	2.33260600	0.02028500
C	-0.80924700	3.14355500	0.92617500
C	-0.58694300	4.51854200	0.97439200
H	0.50195900	6.18884900	0.14784200
H	1.74816600	4.78144000	-1.48412000
H	1.35682200	2.33766500	-1.56658100
H	-1.52459000	2.68893200	1.60358800
H	-1.13642400	5.12561000	1.68902600

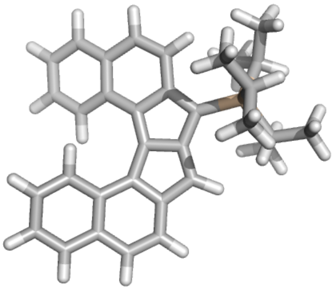


9

B3LYP/6-31G* (PCM in chloroform)
Atom type, (x,y,z) coordinates:

C	-3.45768700	-3.76743700	-0.31855600
C	-2.08053800	-3.73880700	-0.45521400
H	-1.52660400	-4.65073600	-0.66300900
C	0.04488400	-2.25314700	-0.35590100
C	-1.40595100	-2.51603200	-0.32153400
C	-2.09541300	-1.30625400	-0.08497000
H	0.78586200	-3.02614000	-0.51750500
C	1.34163300	0.07392000	-0.07363600
C	0.24727900	-0.92495200	-0.15563000
C	-1.05749900	-0.25490600	-0.06047600
C	-0.80850900	1.09281200	-0.06186600
C	0.68875200	1.27629300	0.02437900
C	-1.64994300	2.27809000	-0.21874000
C	-1.17396600	3.50392300	0.30865600
C	-1.93342600	4.66333200	0.13773300
C	-3.14194200	4.63313700	-0.56096900
C	-3.59437900	3.43349500	-1.11800800
C	-2.85080000	2.26829300	-0.95306100
H	-1.56878900	5.60218500	0.54797600
H	-3.71770300	5.54590100	-0.68796700
H	-4.51755200	3.40920700	-1.69021100
H	-3.18359400	1.34411900	-1.41379400
C	-4.18161300	-2.59572200	0.01265700
C	-3.49165500	-1.33361800	0.16777400
C	-4.24464400	-0.21350200	0.62516400
C	-5.59765200	-0.30689900	0.85451600
C	-6.28434000	-1.53030100	0.64061700
C	-5.58747400	-2.64401200	0.23679800
H	-3.73116600	0.72073000	0.81605800
H	-6.14566600	0.56176100	1.20976500
H	-7.35539600	-1.58646300	0.81453500
H	-6.09951900	-3.59358500	0.09866700
H	-4.00086300	-4.70240700	-0.43045500
C	0.16278300	3.51762300	1.01037900
H	0.52080900	4.54652500	1.12230700
H	0.06575600	3.10277700	2.02387300
C	1.19527000	2.67892300	0.22463500
H	2.15114300	2.68344000	0.75243000
H	1.36581300	3.16908600	-0.74519800
Si	3.19074600	-0.37142700	0.04448300
C	4.29315900	1.18289000	-0.26414400
H	4.00382000	1.92605400	0.49184100
C	3.39537400	-1.09807800	1.82217100
H	2.76170700	-1.99916800	1.79510800
C	3.69401800	-1.66915800	-1.30337500
H	4.73764800	-1.39664100	-1.52575500
C	2.90881700	-1.52093100	-2.62416800
H	2.93185900	-0.49715000	-3.01175400
H	3.33198400	-2.17638000	-3.39818800
H	1.85624500	-1.79627600	-2.49966900
C	3.72425100	-3.14751600	-0.86807300
H	4.09553600	-3.77822700	-1.68776400
H	4.37574800	-3.31587000	-0.00552700
H	2.73201000	-3.52726100	-0.60116800
C	4.05730600	1.80950500	-1.65495200
H	4.57975200	2.77218500	-1.74049200
H	4.45065300	1.16091500	-2.44708400
H	2.99831000	1.98320500	-1.86997600
C	5.80452700	0.93233700	-0.07753200
H	6.37074900	1.84678300	-0.30274000
H	6.05945300	0.63488300	0.94305900
H	6.17772600	0.15280300	-0.75358500
C	2.81364300	-0.16859600	2.90663000
H	3.38734600	0.76486600	2.98076400
H	1.77061900	0.09669500	2.70703900
H	2.85394400	-0.64949700	3.89386400
C	4.81128400	-1.54625100	2.23882200
H	5.44874000	-0.68408100	2.46439500

H	4.76616300	-2.15513400	3.15226900
H	5.32371500	-2.13985300	1.47437100

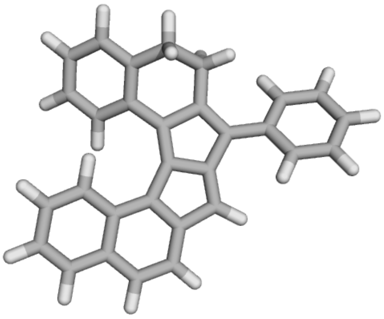


11

B3LYP/6-31G* (PCM in chloroform)
Atom type, (x,y,z) coordinates:

C	-3.59850900	-3.62162400	-0.56524800
C	-2.22400600	-3.63785900	-0.72851500
H	-1.71230800	-4.54908300	-1.02744400
C	-0.04119700	-2.25864400	-0.51281200
C	-1.49615700	-2.45981500	-0.50228600
C	-2.12801600	-1.24283200	-0.15545300
H	0.66768900	-3.04004200	-0.75991700
C	1.35944800	-0.03450100	-0.04232200
C	0.22314100	-0.95981600	-0.18404600
C	-1.04762200	-0.23885600	-0.06359900
C	-0.73597900	1.10434500	-0.05370500
C	0.75765900	1.20865200	0.07501000
C	1.33252600	2.49845700	0.34629500
C	0.55433200	3.60957800	0.37972100
H	2.39541000	2.57499200	0.54727000
H	0.99223400	4.57868800	0.60508700
C	-1.50434600	2.33087400	-0.23500100
C	-0.85821200	3.57427000	0.03645100
C	-1.58398700	4.76842600	-0.10541600
C	-2.90007400	4.76123800	-0.56010900
C	-3.50850300	3.54976200	-0.90468600
C	-2.81389300	2.35295800	-0.74615600
H	-1.09279000	5.71153300	0.12162800
H	-3.44141300	5.69671700	-0.67077600
H	-4.51897600	3.53752100	-1.30298200
H	-3.28124600	1.42304900	-1.04753000
C	-4.25957700	-2.45882700	-0.09851900
C	-3.51137000	-1.24610000	0.15690200
C	-4.19264800	-0.15836700	0.77822400
C	-5.53754100	-0.22298200	1.05648100
C	-6.28669400	-1.38379400	0.72935500
C	-5.65752600	-2.47259700	0.17490500
H	-3.62606800	0.72041700	1.06266000
H	-6.03038700	0.61603600	1.54005500
H	-7.35180500	-1.41589000	0.94142000
H	-6.21696000	-3.37921600	-0.04348100
H	-4.18511300	-4.51757500	-0.75071900
Si	3.19342800	-0.50349500	0.10381100
C	3.46559500	-2.23038900	-0.70736500
H	2.75324700	-2.91208500	-0.22150100
C	3.62154100	-0.66294200	1.97837000
H	4.71173500	-0.81170800	2.02572700
C	4.38731800	0.70384000	-0.83013800
H	5.14299300	0.00262300	-1.21868100
C	3.18124400	-2.25125800	-2.22192300
H	3.90325500	-1.63372300	-2.76983900
H	3.26431800	-3.27149300	-2.62183800
H	2.17933600	-1.88010600	-2.46373000
C	4.87681400	-2.78799500	-0.42932100
H	5.09185300	-2.86965400	0.64176300
H	4.98939400	-3.79065700	-0.86425200
H	5.65701500	-2.15812600	-0.87510800
C	3.75784600	1.39093400	-2.05914100
H	3.01502100	2.14143700	-1.76855700
H	4.53046900	1.90509000	-2.64764000
H	3.25695400	0.67876700	-2.72346300
C	5.16594200	1.72524000	0.02030000
H	5.92506900	2.23045600	-0.59284400
H	4.51785900	2.51021400	0.42804800
H	5.68513500	1.25543800	0.86307500
C	3.28078300	0.58795200	2.81010700
H	3.55678900	0.43720300	3.86303300
H	3.80610100	1.48217100	2.46054300
H	2.20570400	0.80111600	2.78196000
C	2.95111300	-1.89987300	2.61068800
H	1.85739000	-1.83120800	2.55698900

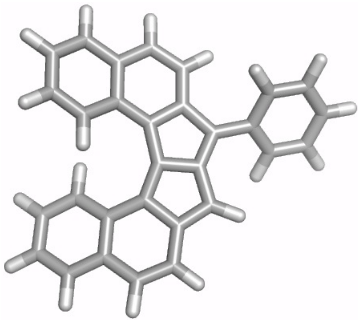
H	3.24789600	-2.83426900	2.12264000
H	3.21953700	-1.98442900	3.67277800



10

B3LYP/6-31G* (PCM in chloroform)
Atom type, (x,y,z) coordinates:

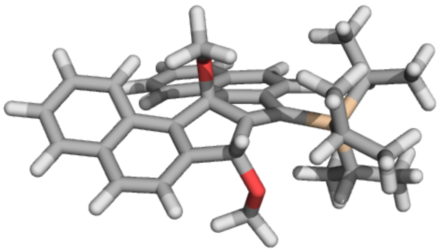
C	-2.96706600	-3.62412400	-0.44925100
C	-1.59192400	-3.72304900	-0.57027400
H	-1.12549400	-4.67375800	-0.81558000
C	0.66579500	-2.45462900	-0.38234800
C	-0.80346900	-2.57905800	-0.37303400
C	-1.37812800	-1.31852200	-0.08751800
H	1.34462600	-3.27341600	-0.59504700
C	2.14586600	-0.26548500	-0.01826600
C	0.97925900	-1.16400900	-0.10062000
C	-0.24869100	-0.37103900	-0.00525500
C	0.13337900	0.95159400	-0.01023300
C	1.63111100	1.00057700	0.06014300
C	-0.58352000	2.21676900	-0.16649500
C	0.03176300	3.39384600	0.33083600
C	-0.60738000	4.62320700	0.15479100
C	-1.82689200	4.71033400	-0.51949700
C	-2.41503500	3.55715500	-1.04656600
C	-1.79447700	2.32296100	-0.87554200
H	-0.13800200	5.52482500	0.54130500
H	-2.30568400	5.67692900	-0.65061100
H	-3.34758300	3.62147200	-1.60008900
H	-2.23216500	1.43276900	-1.31439900
C	-3.57957300	-2.40371200	-0.07034400
C	-2.77406000	-1.22285900	0.15003400
C	-3.42029400	-0.05669300	0.65306700
C	-4.77891400	-0.02835700	0.86622000
C	-5.57719300	-1.16837300	0.58864900
C	-4.98624500	-2.32501400	0.13870900
H	-2.82029600	0.81310500	0.89222600
H	-5.24528500	0.87171400	1.25783000
H	-6.65083900	-1.12840100	0.75063100
H	-5.58609200	-3.21278500	-0.04813800
C	6.23503200	-1.56823400	0.08443200
C	5.22310300	-2.36180100	0.63101100
C	3.89704300	-1.93564400	0.59255800
C	3.54669900	-0.70106800	0.00862500
C	4.57857600	0.08237500	-0.54530700
C	5.90493800	-0.34533400	-0.50461200
H	7.26890900	-1.90108800	0.11371600
H	5.46769500	-3.31445800	1.09355300
H	3.12130500	-2.54990000	1.03944100
H	4.33466100	1.01751000	-1.03883800
H	6.68179800	0.27462600	-0.94443900
H	-3.59617900	-4.49594100	-0.60981400
C	1.37607200	3.28768700	1.01472700
H	1.83575500	4.27812900	1.09711000
H	1.25046800	2.90936100	2.03920100
C	2.30731700	2.32707300	0.24308700
H	3.25914300	2.20778300	0.77239600
H	2.54471600	2.78208000	-0.73081700



S17

B3LYP/6-31G* (PCM in chloroform)
Atom type, (x,y,z) coordinates:

C	-1.51171400	3.48757000	0.46223000
C	-2.21673300	2.29726200	0.42772300
H	-3.28034400	2.28901400	0.64295000
C	-2.08052500	-0.27339300	-0.02450400
C	-1.54085600	1.10223100	0.13097500
C	-0.13549500	1.07331600	-0.04509200
C	-0.13591400	3.52455700	0.12998300
C	0.57083600	2.29909600	-0.16929800
C	1.90911300	2.39912700	-0.64972500
C	2.54272400	3.61529000	-0.75328300
C	1.87380300	4.80957900	-0.37800900
C	0.56642700	4.76059200	0.04352600
H	2.41768900	1.49913800	-0.97418300
H	3.55845100	3.66496000	-1.13590100
H	2.39052900	5.76268700	-0.44956600
H	0.03469500	5.67507700	0.29565200
H	-2.01842800	4.41765400	0.70544300
C	-6.17808300	-1.49389700	0.21101700
C	-5.84418800	-0.28733800	-0.40906600
C	-4.51466600	0.12530400	-0.47416000
C	-3.48732000	-0.67136200	0.07028700
C	-3.83964800	-1.88903400	0.68726400
C	-5.17059500	-2.29252400	0.75914600
H	-7.21615400	-1.80921900	0.26777400
H	-6.62071400	0.33334600	-0.84734000
H	-4.26421300	1.04877500	-0.98549800
H	-3.06160800	-2.49941000	1.13495200
H	-5.42311300	-3.22863000	1.24938600
C	0.24124200	-0.34579300	-0.18362400
C	-1.00275900	-1.09739200	-0.26165200
C	-0.70875800	-2.49545900	-0.48799600
C	1.27221200	-1.27656500	-0.17286400
C	0.65941700	-2.61368000	-0.45964200
C	1.49534900	-3.75419600	-0.69675000
C	2.84311500	-3.63861000	-0.58862200
H	1.03593300	-4.70038400	-0.97147400
H	3.48832800	-4.49183300	-0.78168900
C	2.69423500	-1.24054200	0.13864100
C	3.47280700	-2.41145900	-0.12626300
C	4.85253400	-2.38750900	0.14062300
C	5.45974500	-1.27193300	0.70960800
C	4.68420900	-0.15762700	1.04934500
C	3.32084800	-0.14991200	0.77024400
H	5.44381200	-3.27257300	-0.08174600
H	6.52687600	-1.27933600	0.91378600
H	5.13944100	0.69902400	1.53806000
H	2.72261300	0.70222000	1.06939200
H	-1.42196000	-3.28469500	-0.69038500



(±)-16-*trans*-*a*

B3LYP/6-31G* (PCM in chloroform)
Atom type, (x,y,z) coordinates:

C	-1.78109800	4.90804500	-0.50442600
C	-3.14157600	4.80910700	-0.67207300
C	-3.75900100	3.53416000	-0.63143900
C	-3.01899300	2.40058000	-0.38698100
H	-1.28618000	5.87456300	-0.56551700
H	-3.73963900	5.69687800	-0.85819300
H	-4.82788500	3.44822600	-0.80867000
H	-3.50940000	1.43876100	-0.40772100
C	-1.61277600	2.45946200	-0.15825800
C	-0.98129900	3.75549800	-0.26694500
C	0.42631200	3.86101900	-0.16764400
C	1.21366300	2.73977400	-0.02082000
H	0.88349700	4.84473500	-0.24204200
H	2.29217800	2.84206800	0.00631400
C	1.29236300	0.12779800	0.12403500
C	0.61243700	1.46780400	0.09039000
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C	3.31055200	1.34221000	2.49683400
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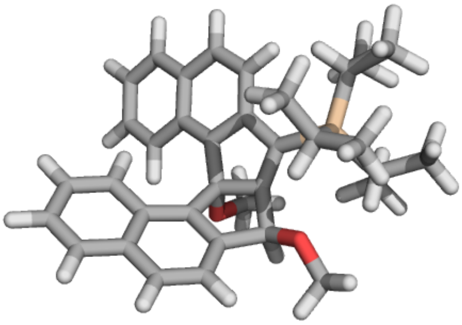

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H	1.46520700	0.65133100	4.17810500
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C	-2.09445600	-3.56401300	1.79165800
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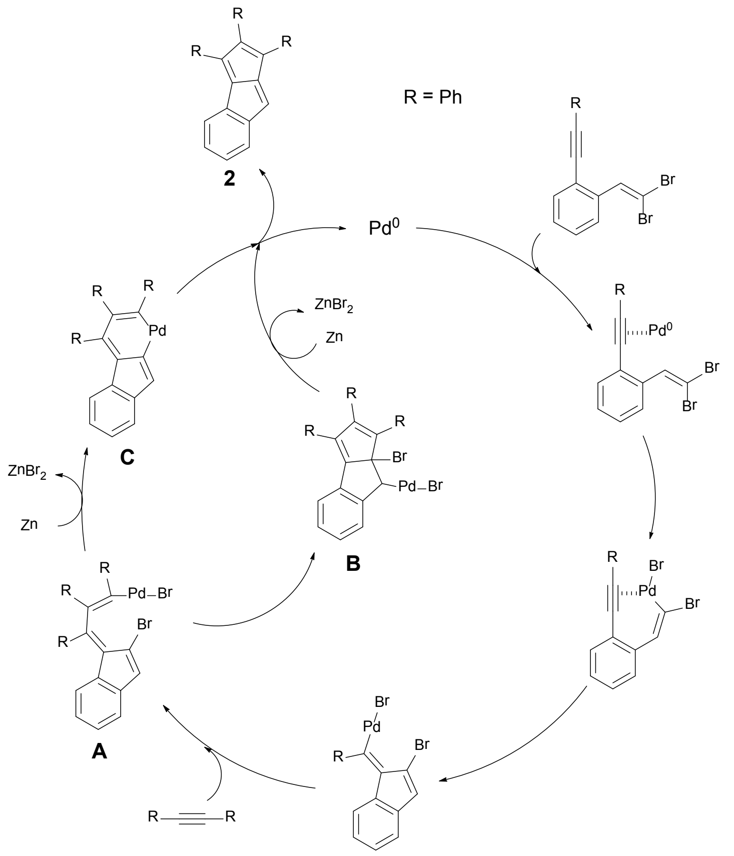
H	-1.35109200	-4.34053800	2.01398500
H	-2.38969400	-3.08049300	2.73336600

7ESI Mechanistic considerations

7.1ESI Carbopalladation cascade reaction

Our optimisation studies (section 2ESI) showed that the cascade carbopalladation reaction between alkynes and *gem*-dibromoolefins proceeds without the addition of Zn in the presence of K_2CO_3 (Table 1ESI). This suggests that a Negishi-type sequence from species **A** to pentalene **2** (that involves oxidative addition of Zn to the CBr bond in **A**) (Scheme 11ESI) as we proposed in our previous report[1] can be excluded from the mechanism. Accordingly, the modified catalytic cycle (Scheme 11ESI) contains two possible termination steps: (1) intramolecular carbopalladation at fulvene **A** leading to species **B**, followed by Zn assisted reductive elimination and (2) two-electron reduction of the Pd(II)-centre in **A** by Zn, a second oxidative addition, leading to the formation of palladacycle **C** and reductive elimination.

It should be noted, that although the reaction works in the presence of K_2CO_3 without the addition of Zn, we obtained higher yields when both K_2CO_3 and Zn were present in the reaction mixture (entry 5 vs. 10, Table 1ESI). This could be explained by the contribution of Zn to the reduction of Pd(II) to Pd(0) to initiate the catalytic cycle, furthermore, metal cations (such as Li^+ or Zn^{2+}) have been described to activate Pd(0)-species towards oxidative addition[20] that could lead to higher conversions as well.



Scheme 11ESI Proposed catalytic cycle for the cascade carbopalladation reaction between alkynes and *gem*-dibromoolefins with two possible termination steps.

7.2ESI Pentalene reactions

Examination of the HOMOs and LUMOs of compounds **9** and **11** (Figure 10SI) gives further insights regarding to their reactivity. Based on the structure of products (±)-**12**, (±)-**13**, and (±)-**15**, a Diels-Alder type reaction could be suggested for their formation. The orbital symmetry, that is necessary for the reaction to proceed, however, does not support such reactivity (Figures 10SI and 11SI) as the symmetry of the HOMO of the "diene" **11** and the LUMO of the "dienophile" (BQ is used here as example) do not match.

Alternatively, a stepwise, formal [6+2], addition of BQ to **11** is suggested, driven by the formation of an aromatic naphthyl ring system (Scheme 12SI).

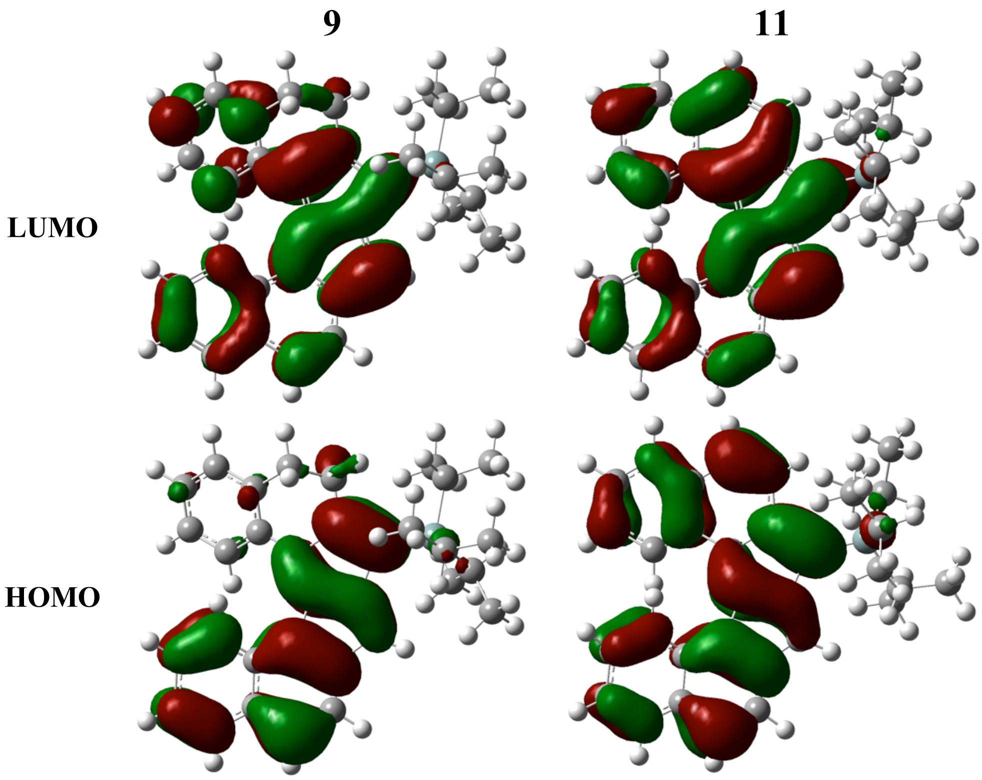
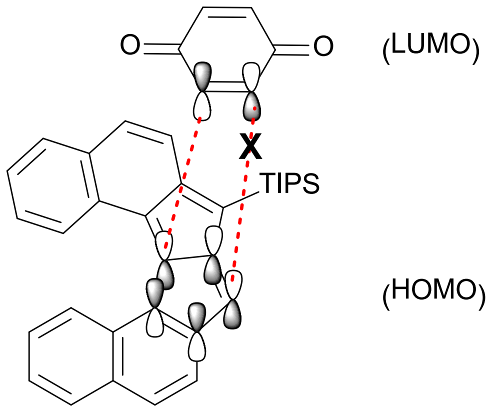
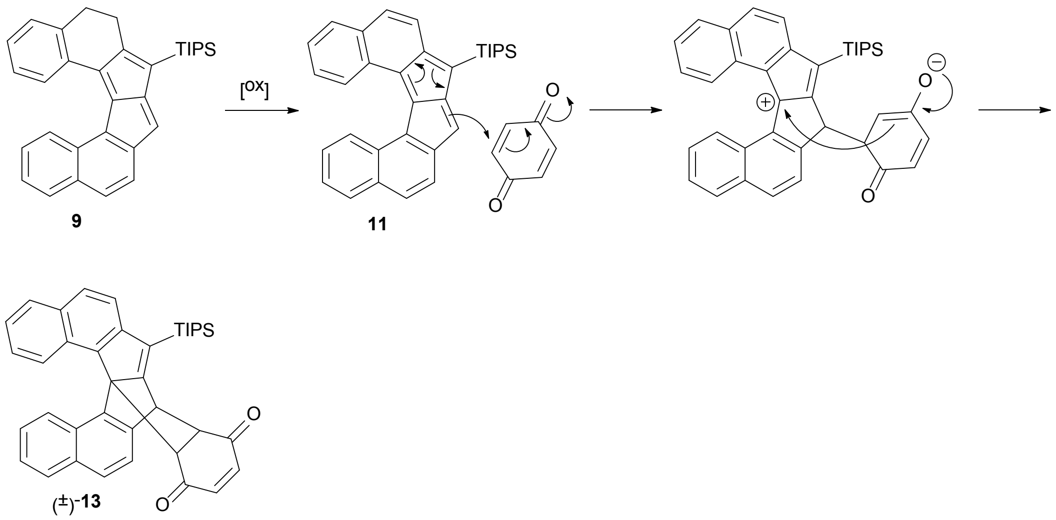


Figure 10SI Depiction of calculated HOMOs and LUMOs over optimised ground-states of compounds **9** and **11**.



11

Figure 11ESI Schematic representation of interactions between the HOMO of compound **11** and the LUMO of BQ. Based on the orbital symmetry, a Diels-Alder type reaction can be excluded.



Scheme 12ESI A stepwise, formal [6+2], addition of BQ to compound **11**. The formation of the aromatic naphthyl ring system is a strong driving force for the reaction.

8ESI ^{1}H and ^{13}C NMR spectra

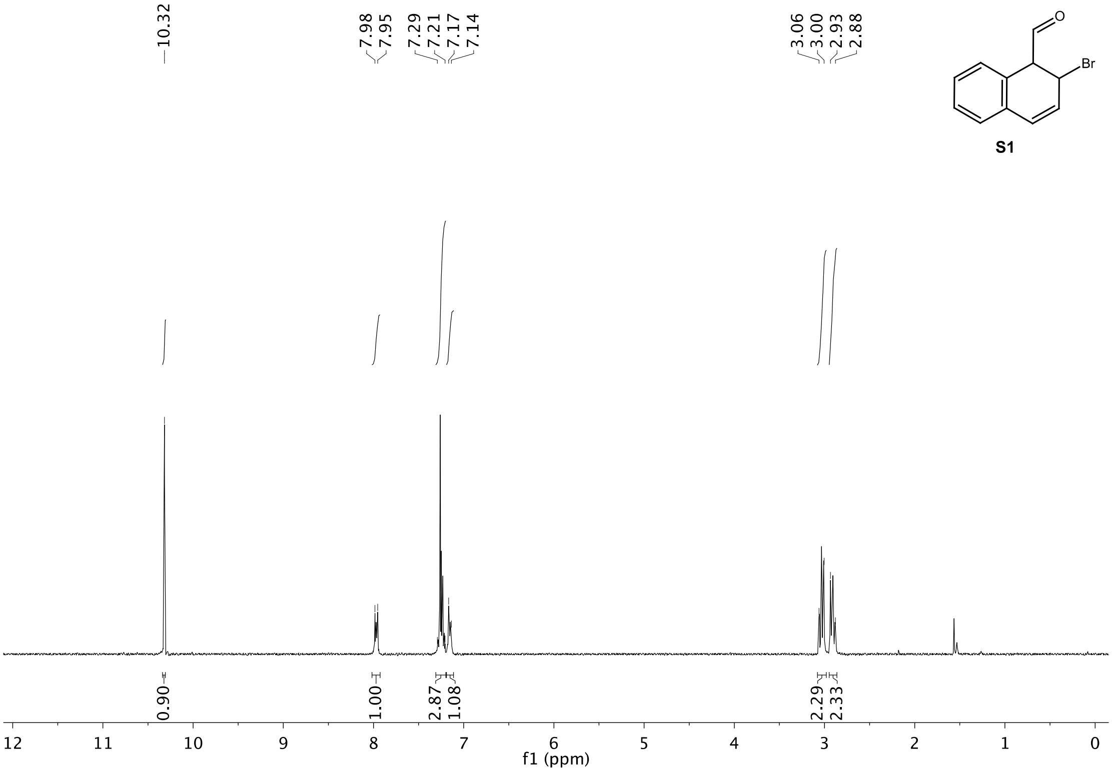


Figure 12ESI 300 MHz ^{1}H NMR spectrum of **S1** recorded at 25°C in CDCl$_3$.

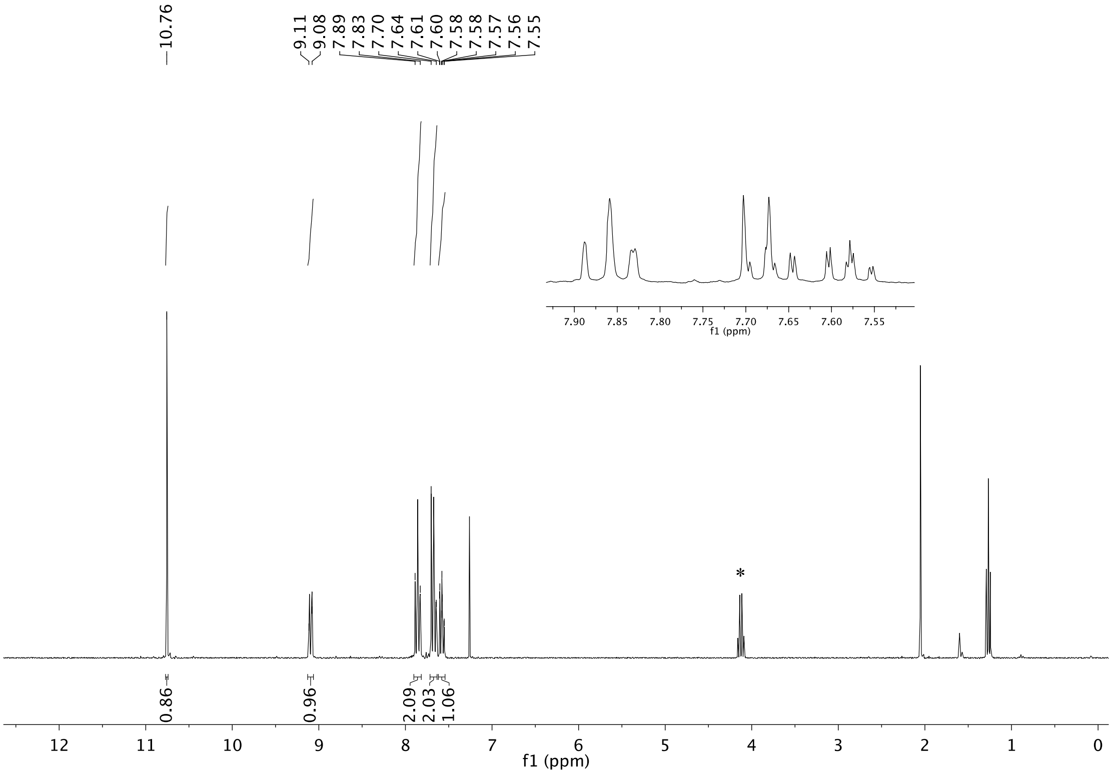
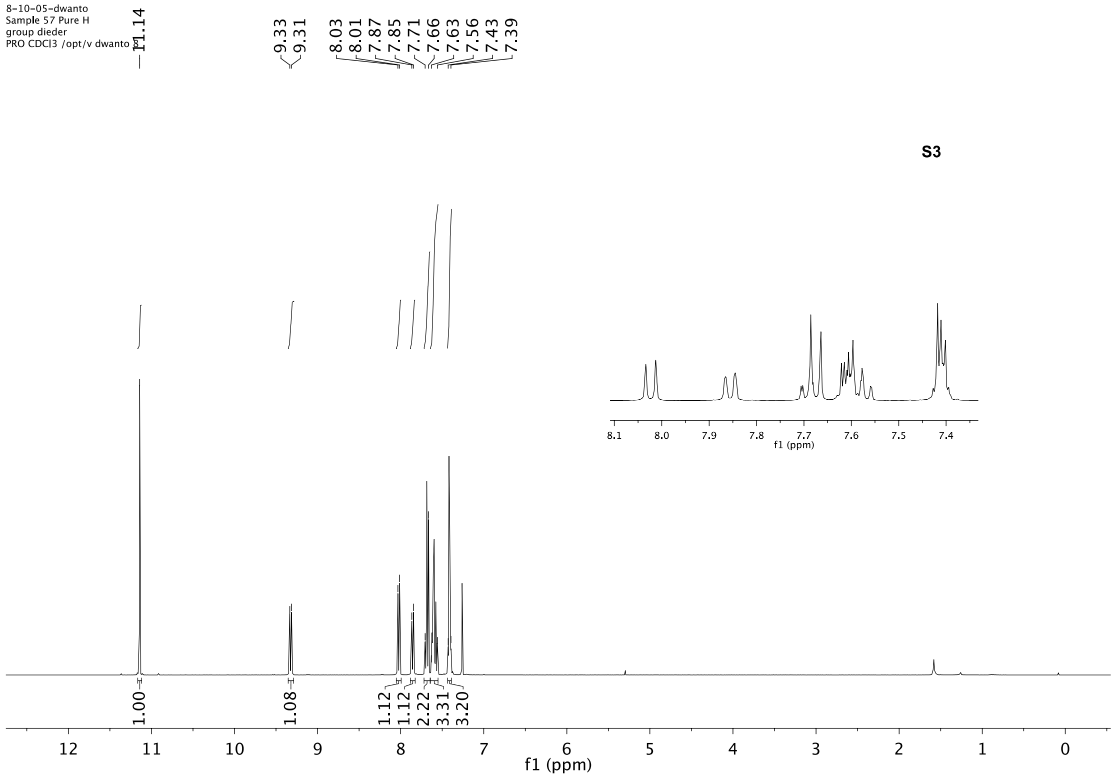


Figure 13ESI 300 MHz ^{1}H NMR spectrum of **S2** recorded at 25 °C in CDCl$_3$.



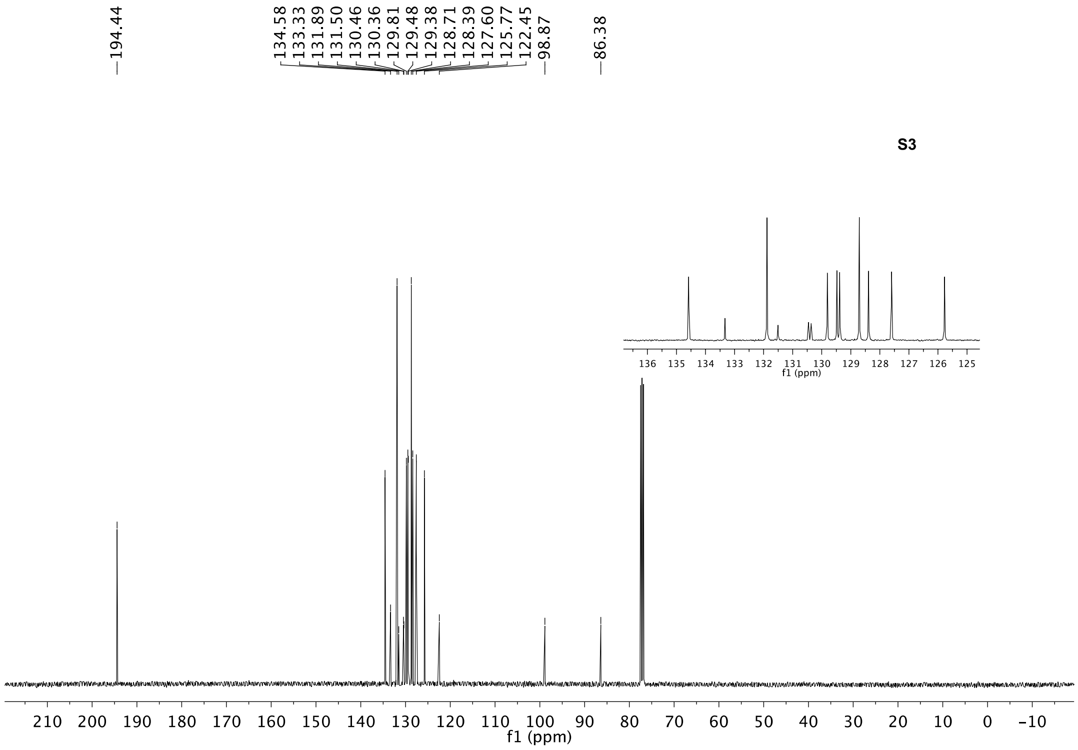


Figure 14ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S3** recorded at 25 °C in $CDCl_3$.

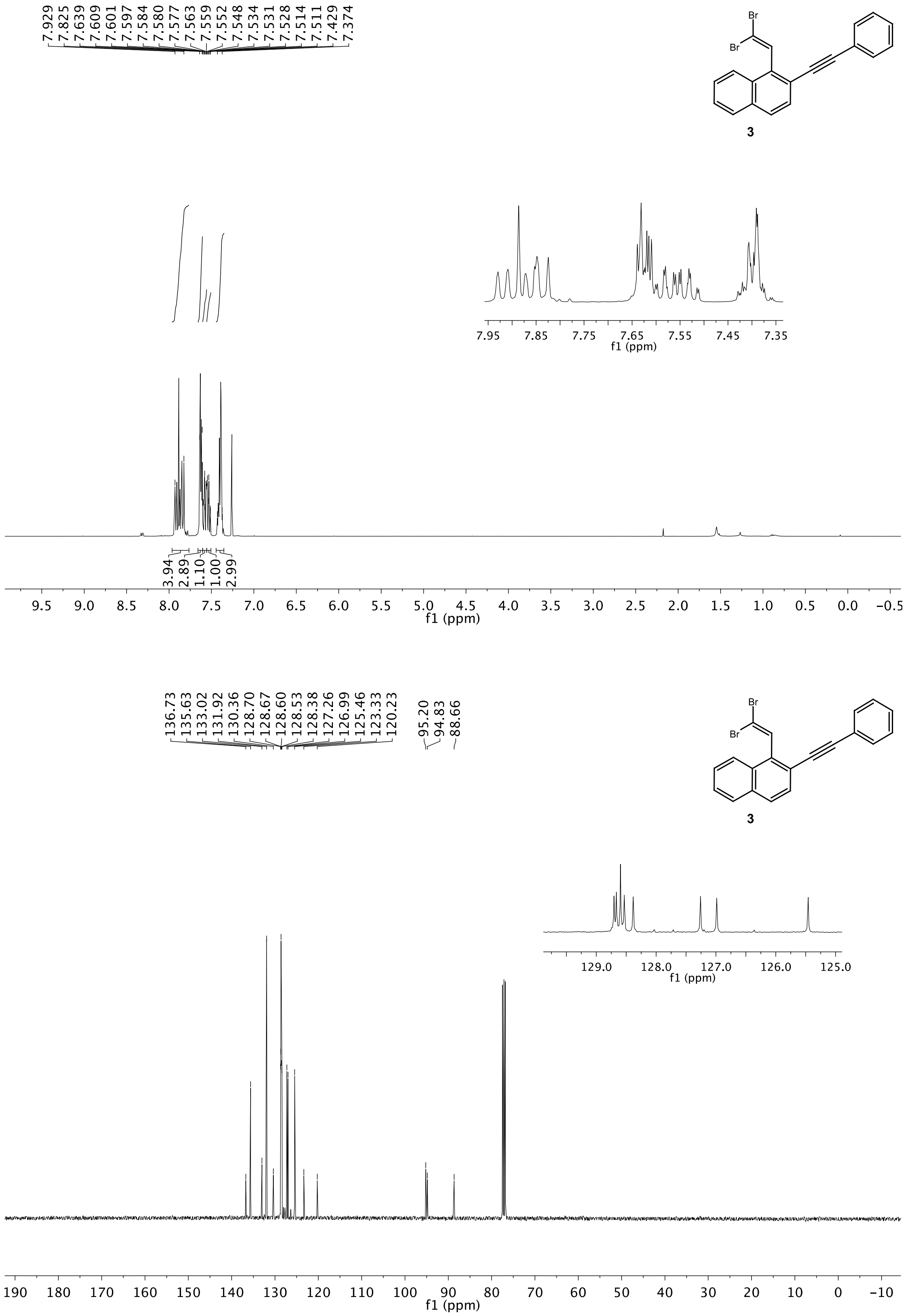


Figure 15SEI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **3** recorded at 25 °C in $CDCl_3$.

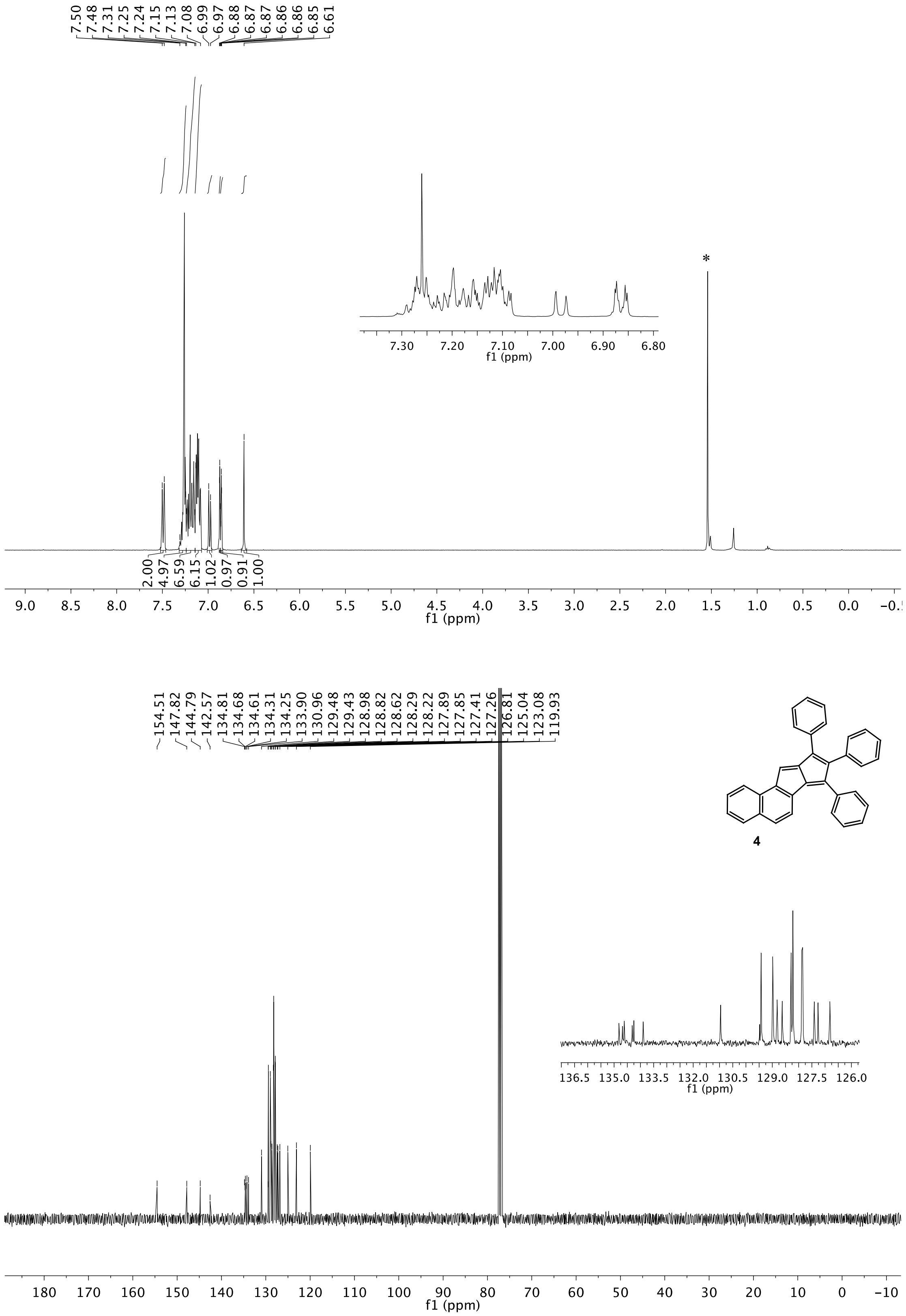


Figure 16ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **4** recorded at 25 °C in $CDCl_3$.

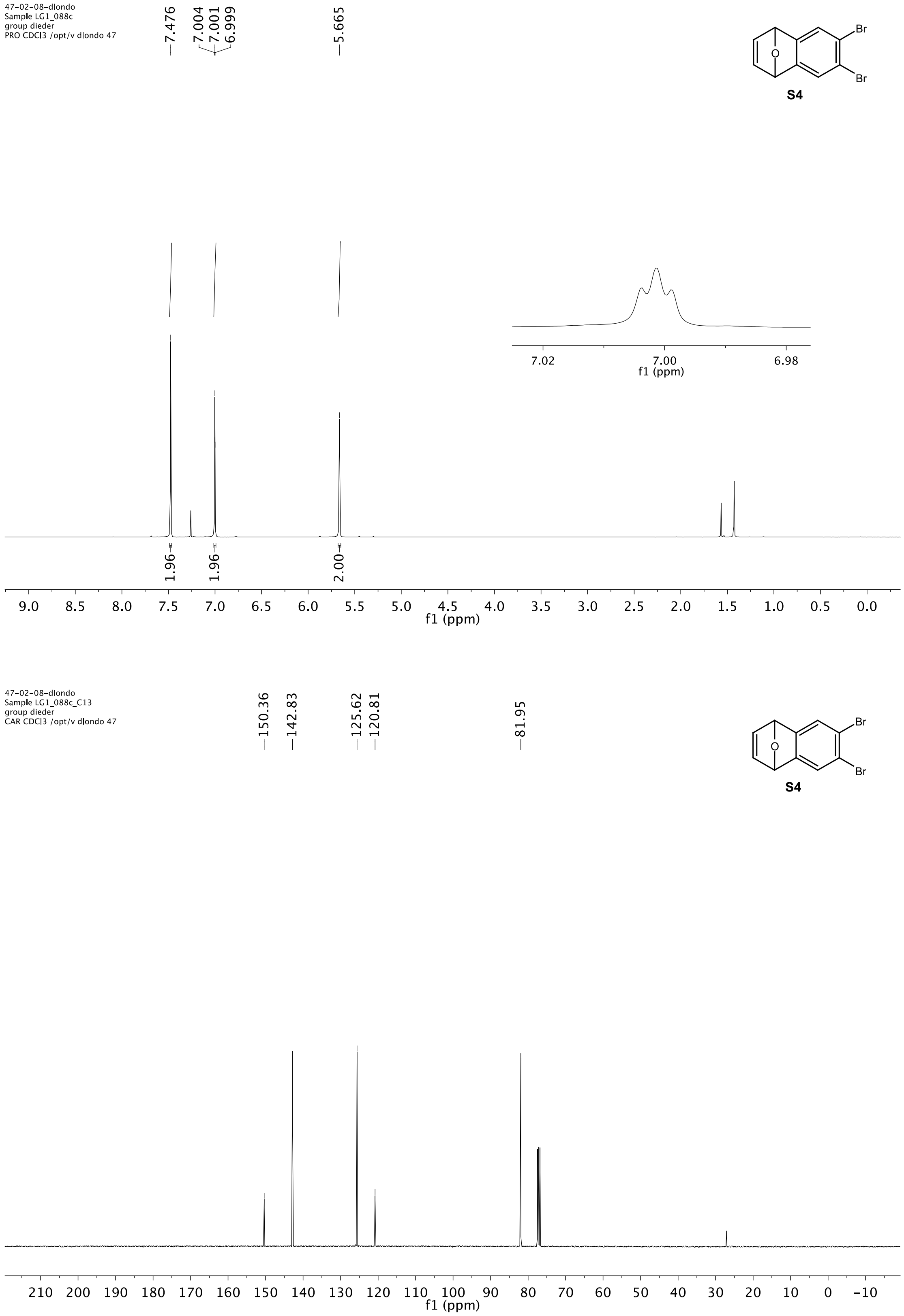


Figure 17ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S4** recorded at 25 °C in $CDCl_3$.

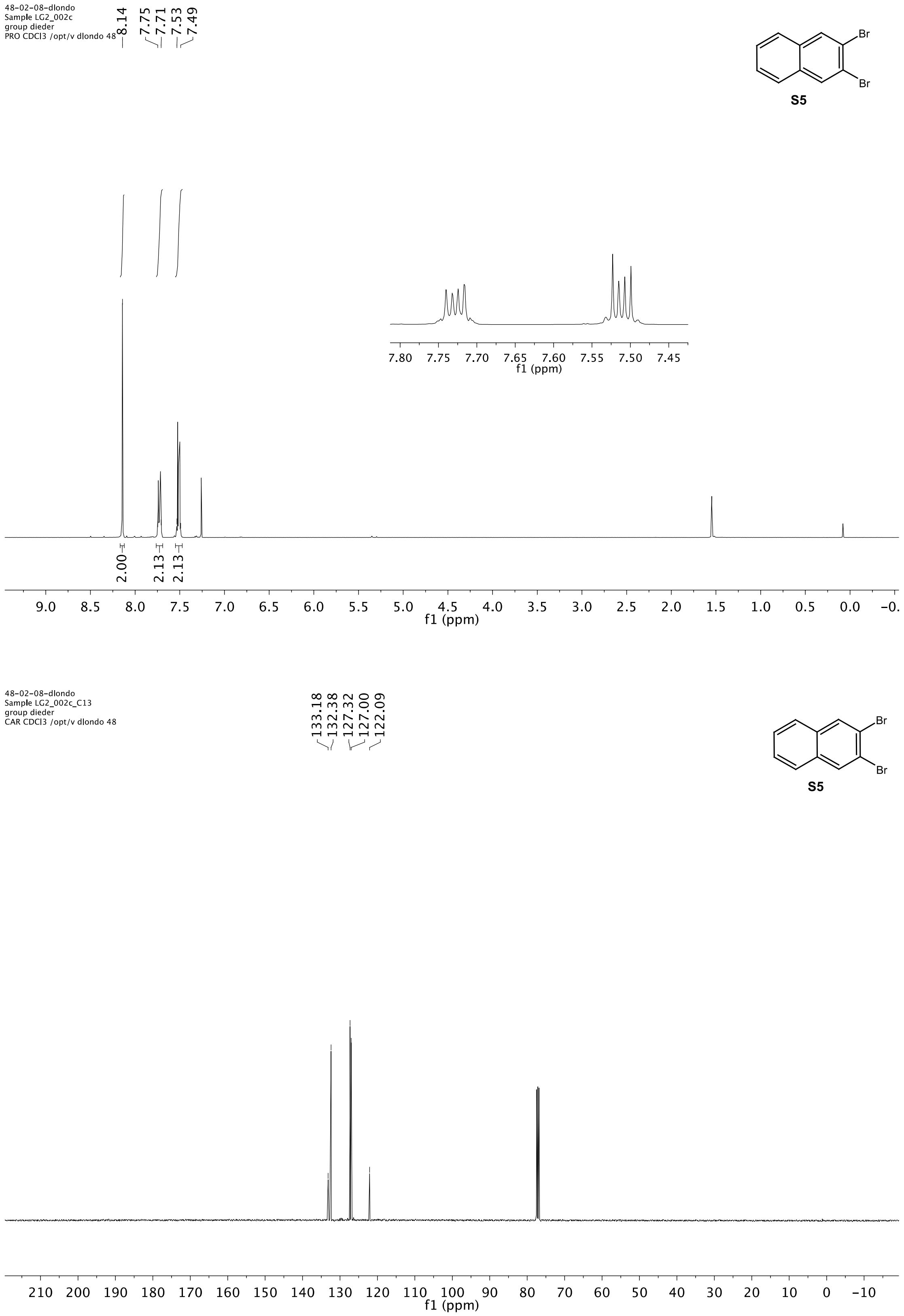
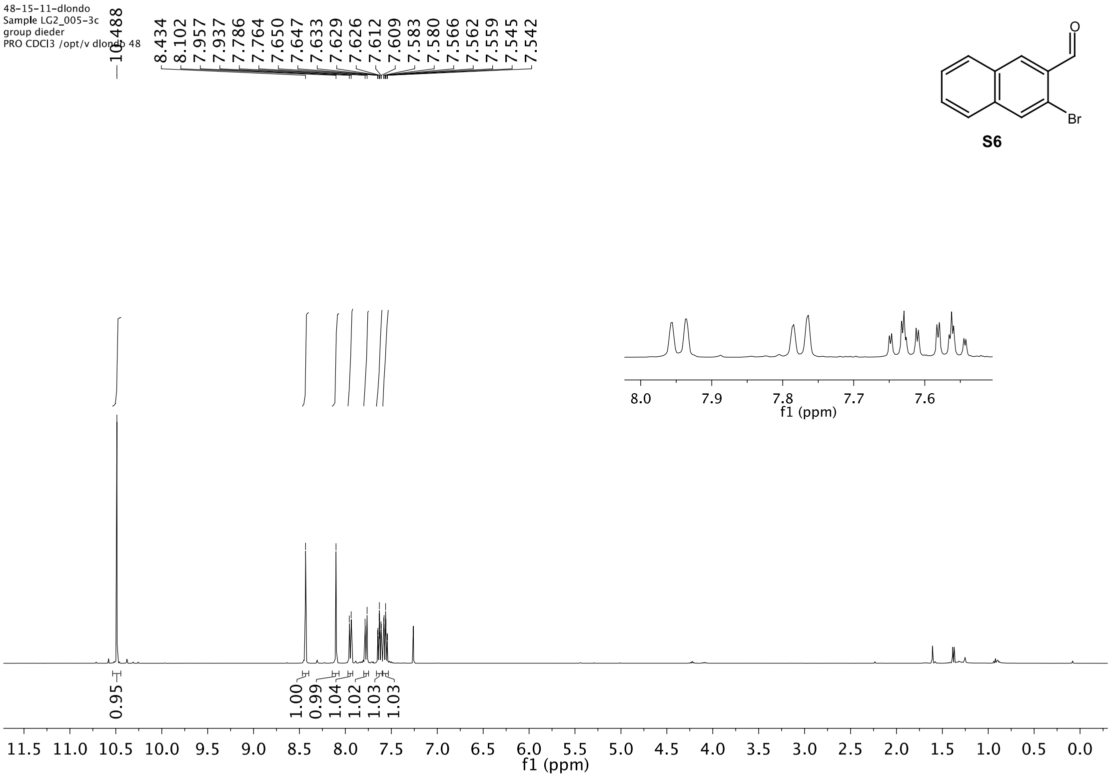


Figure 18ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S5** recorded at 25 °C in $CDCl_3$.



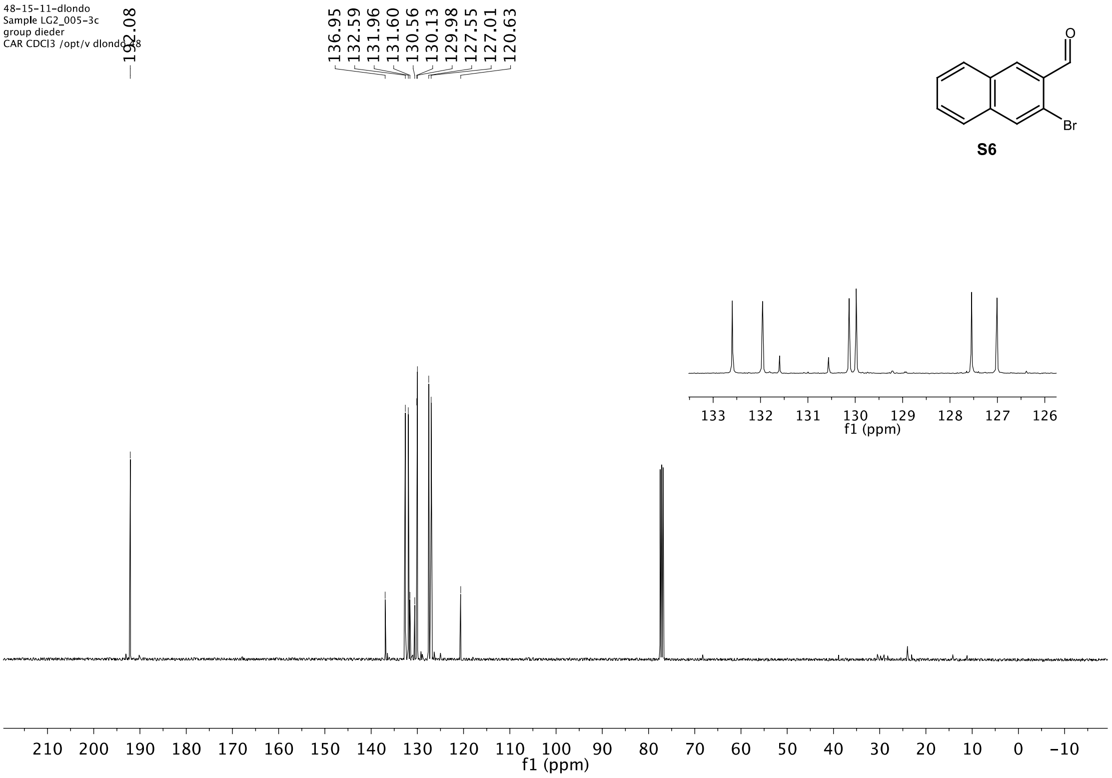


Figure 19ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S6** recorded at 25 °C in $CDCl_3$.

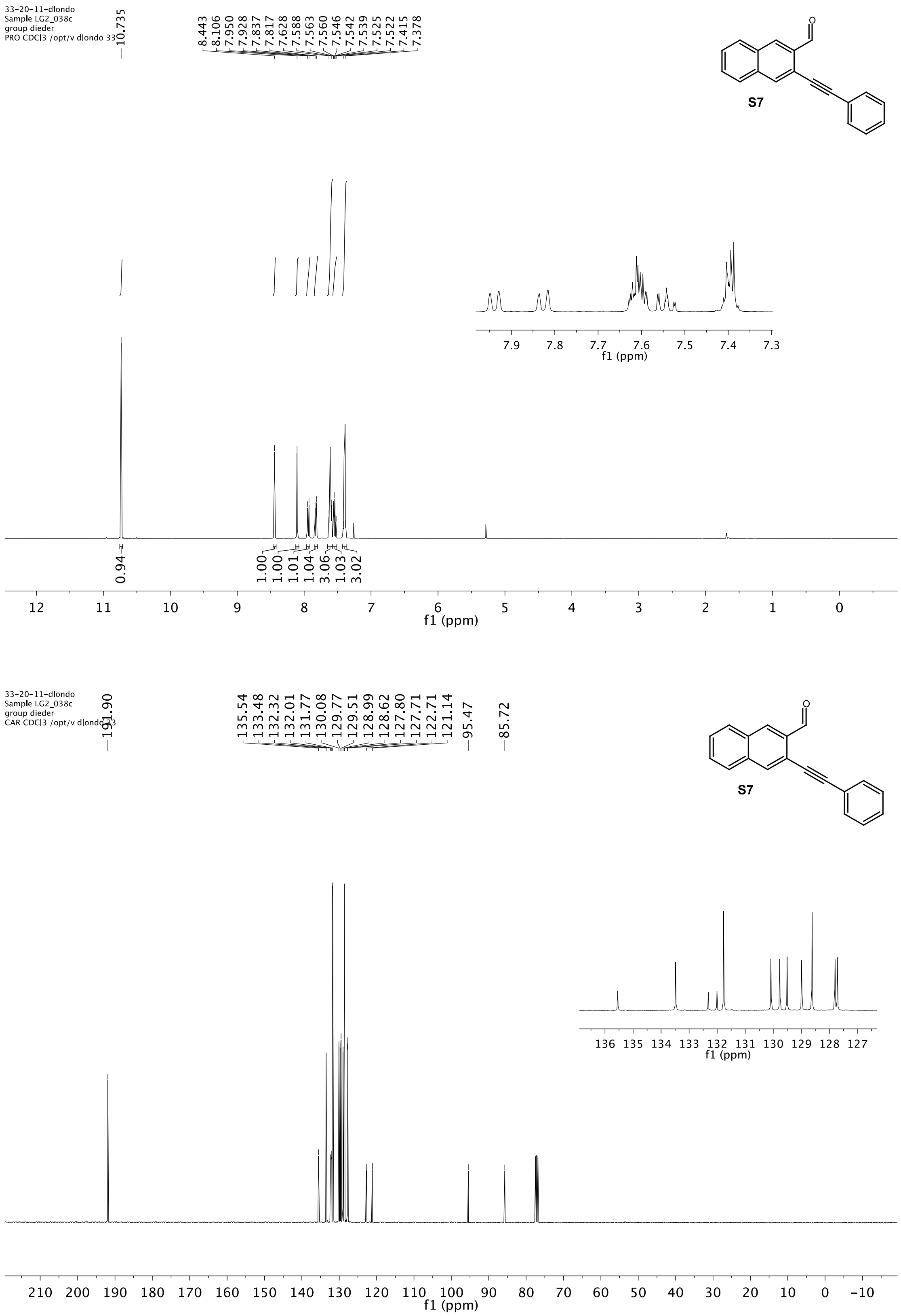


Figure 20ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S7** recorded at 25 °C in $CDCl_3$.

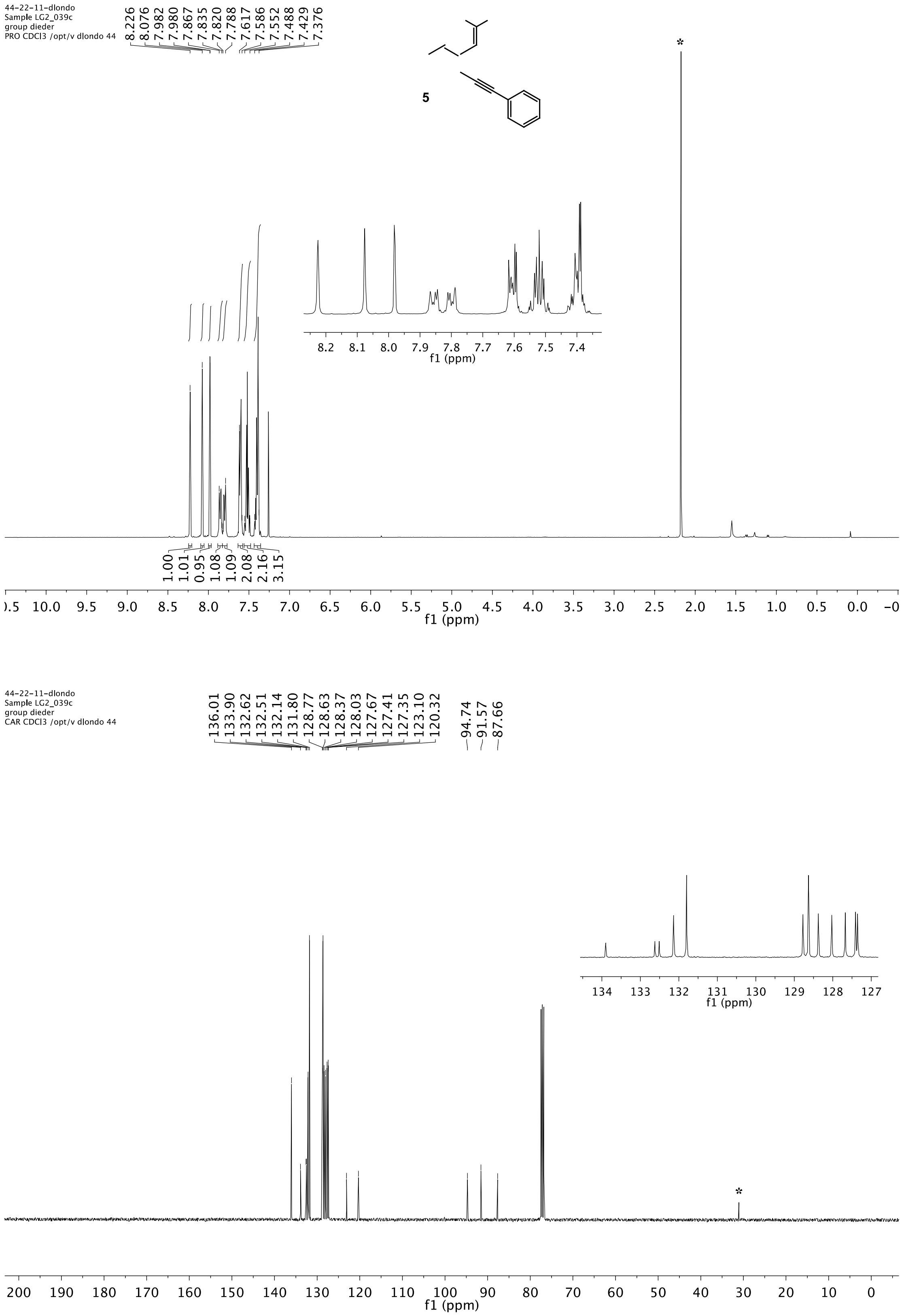
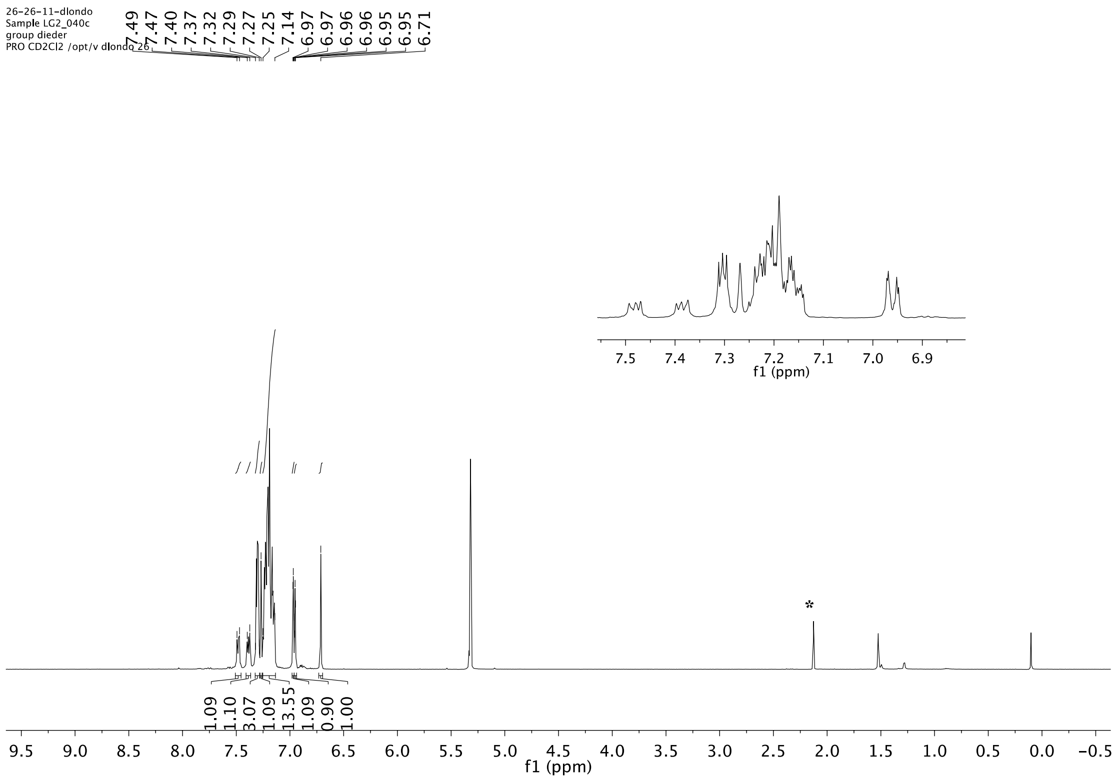


Figure 21ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **5** recorded at 25 °C in $CDCl_3$.



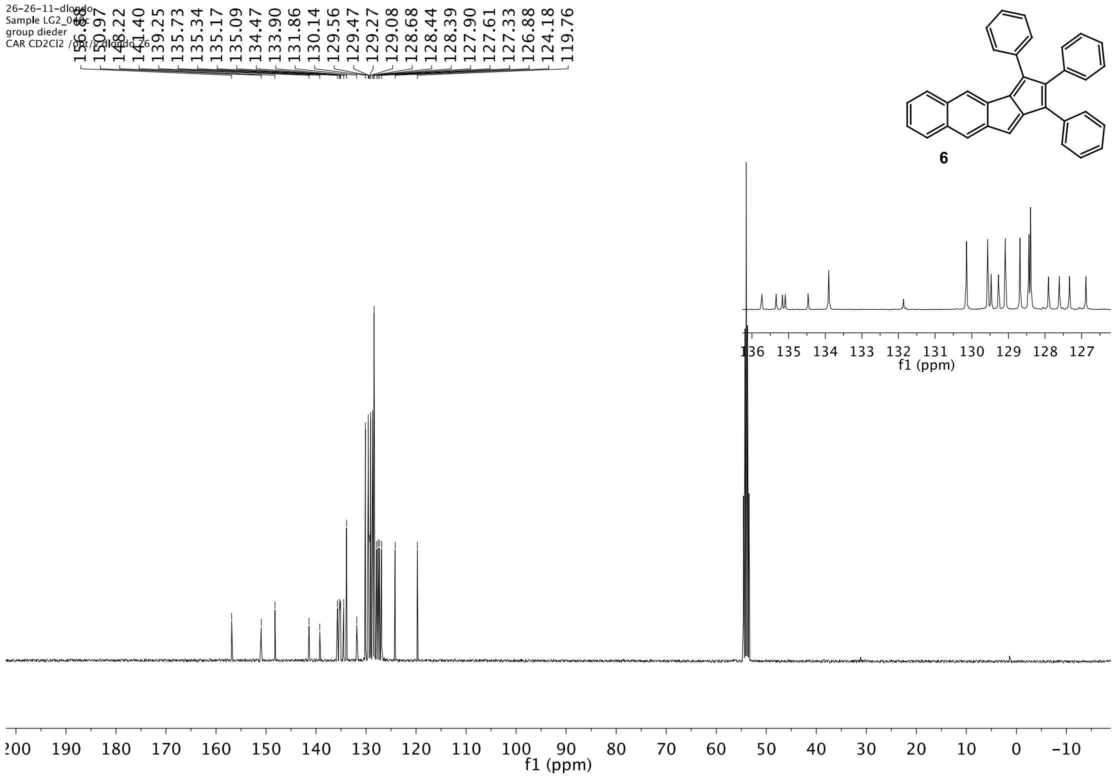
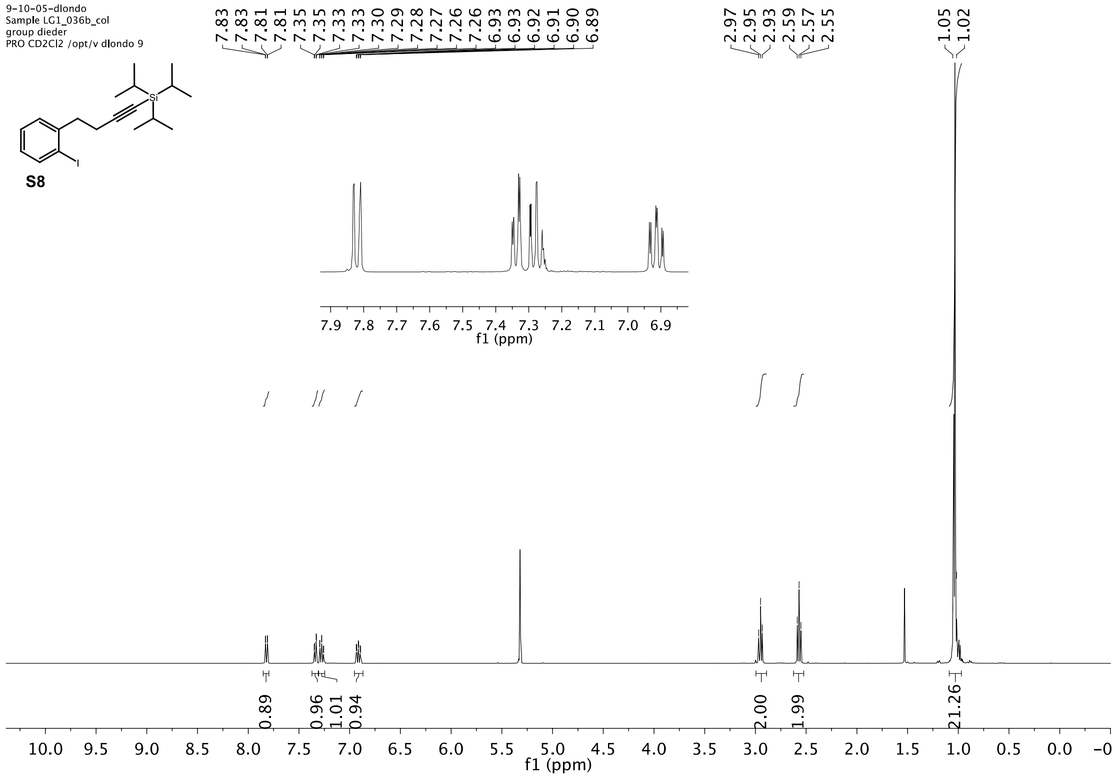


Figure 22ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **6** recorded at 25 °C in CD_2Cl_2.



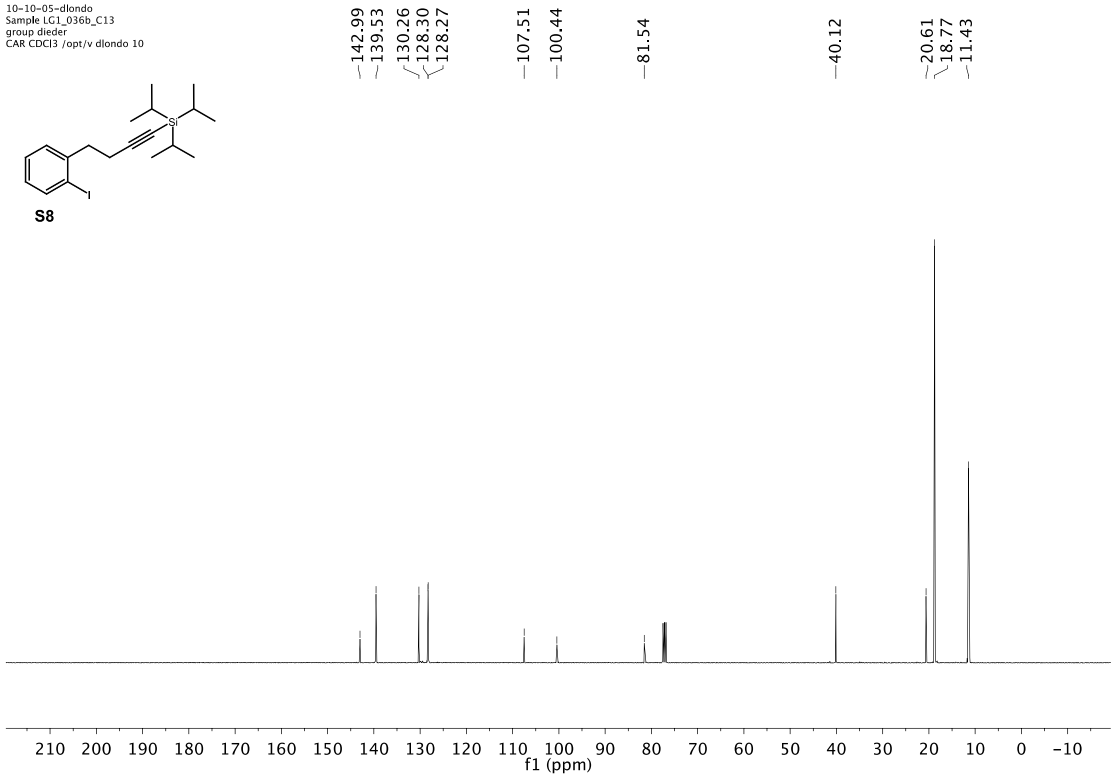
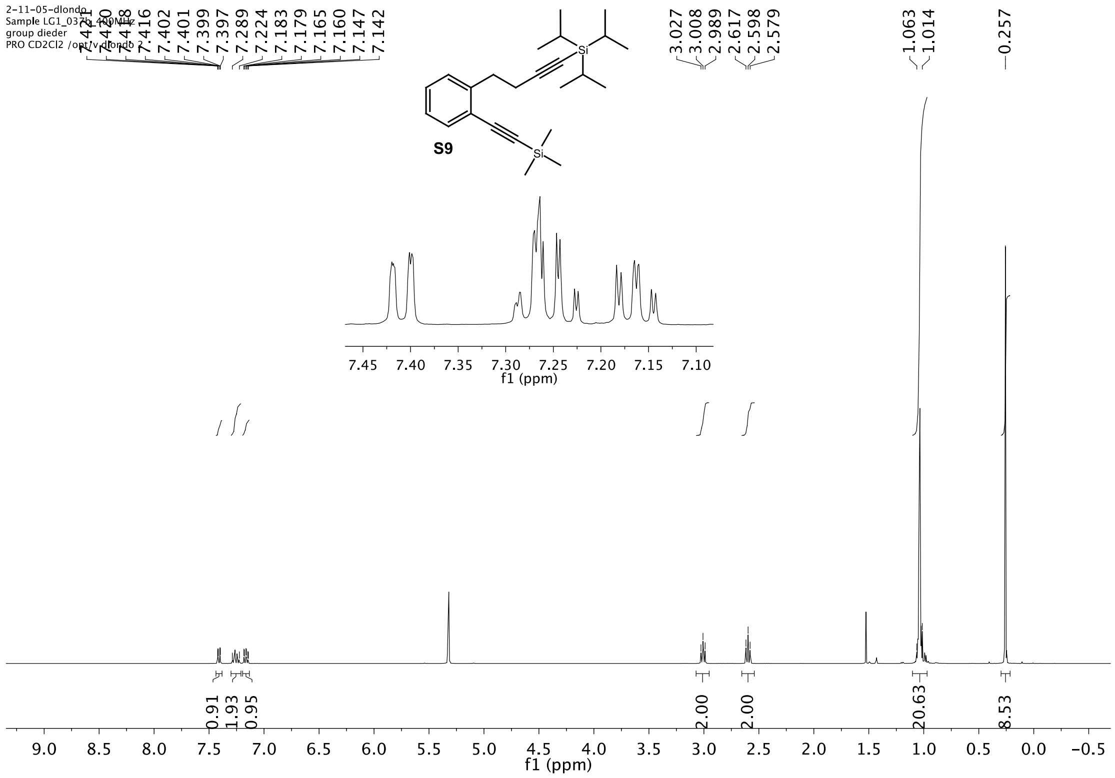


Figure 23ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S8** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.



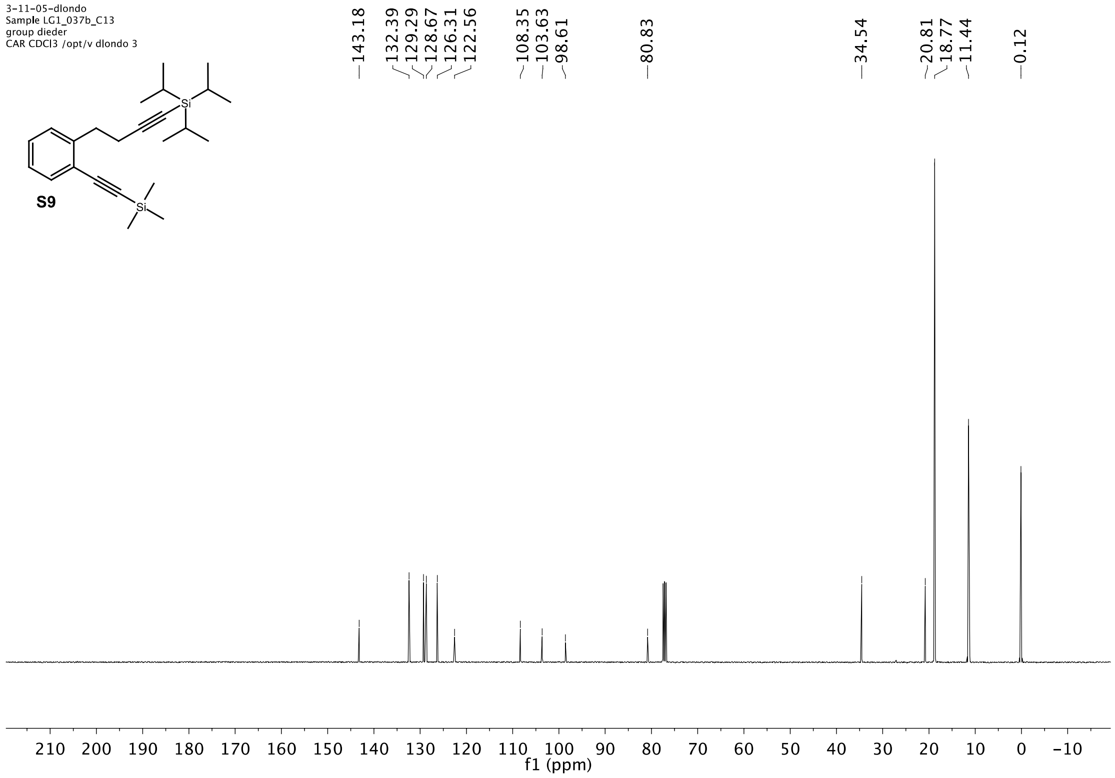


Figure 24ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S9** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.

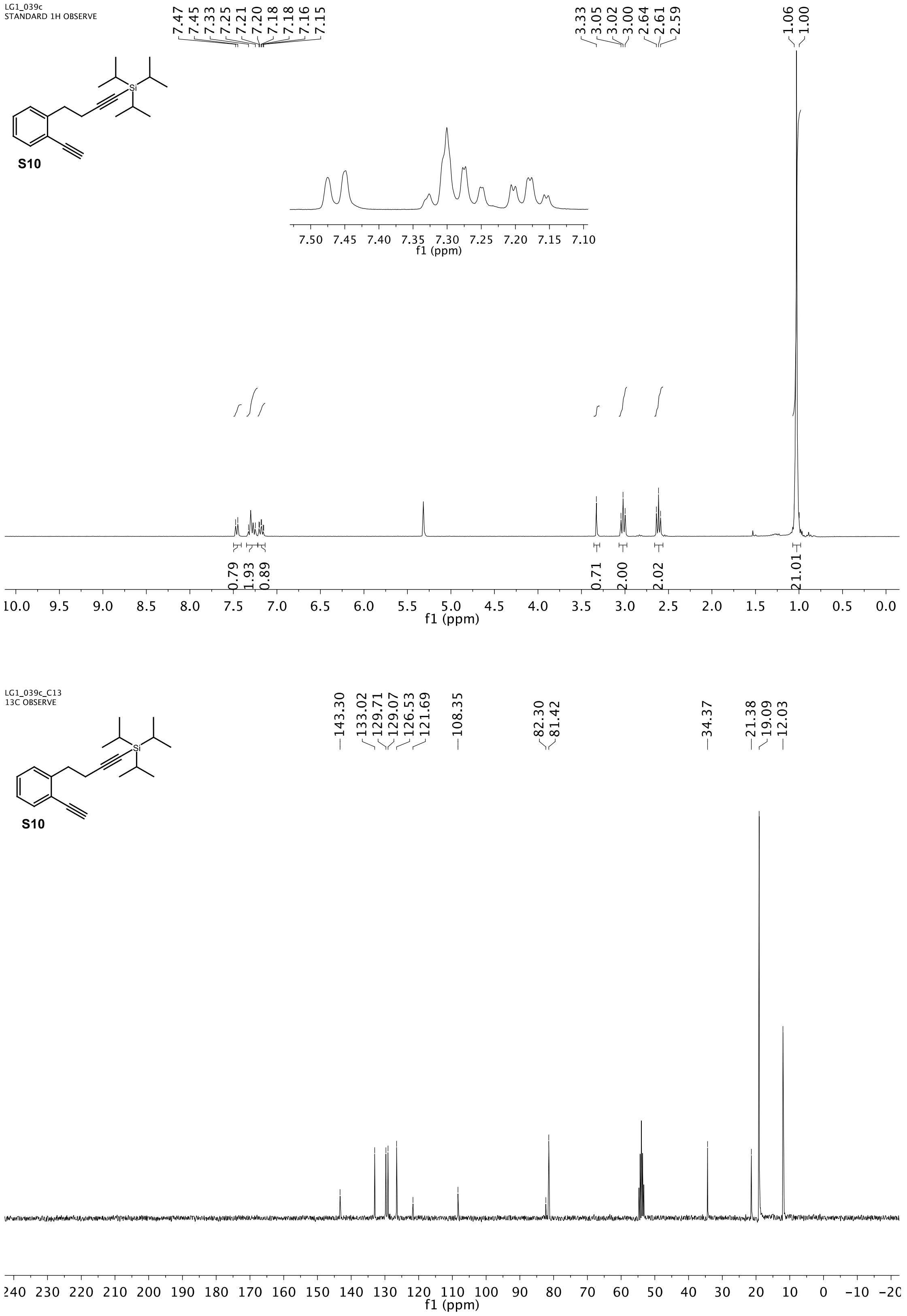


Figure 25ESI 300 MHz ^{1}H NMR (top) and 75 MHz ^{13}C NMR (bottom) spectra of **S10** recorded at 25 °C in CD_2Cl_2.

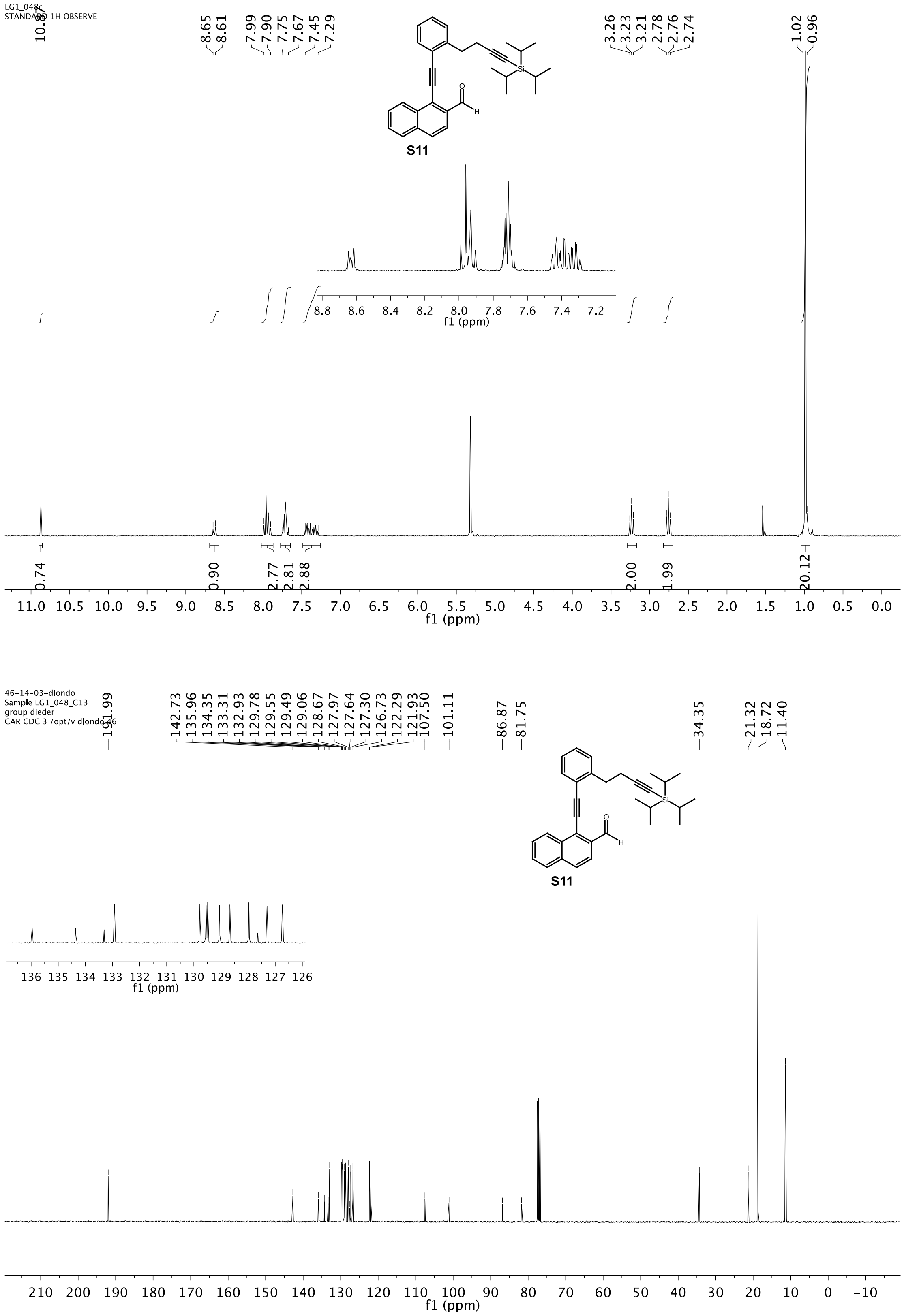


Figure 26ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S11** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.

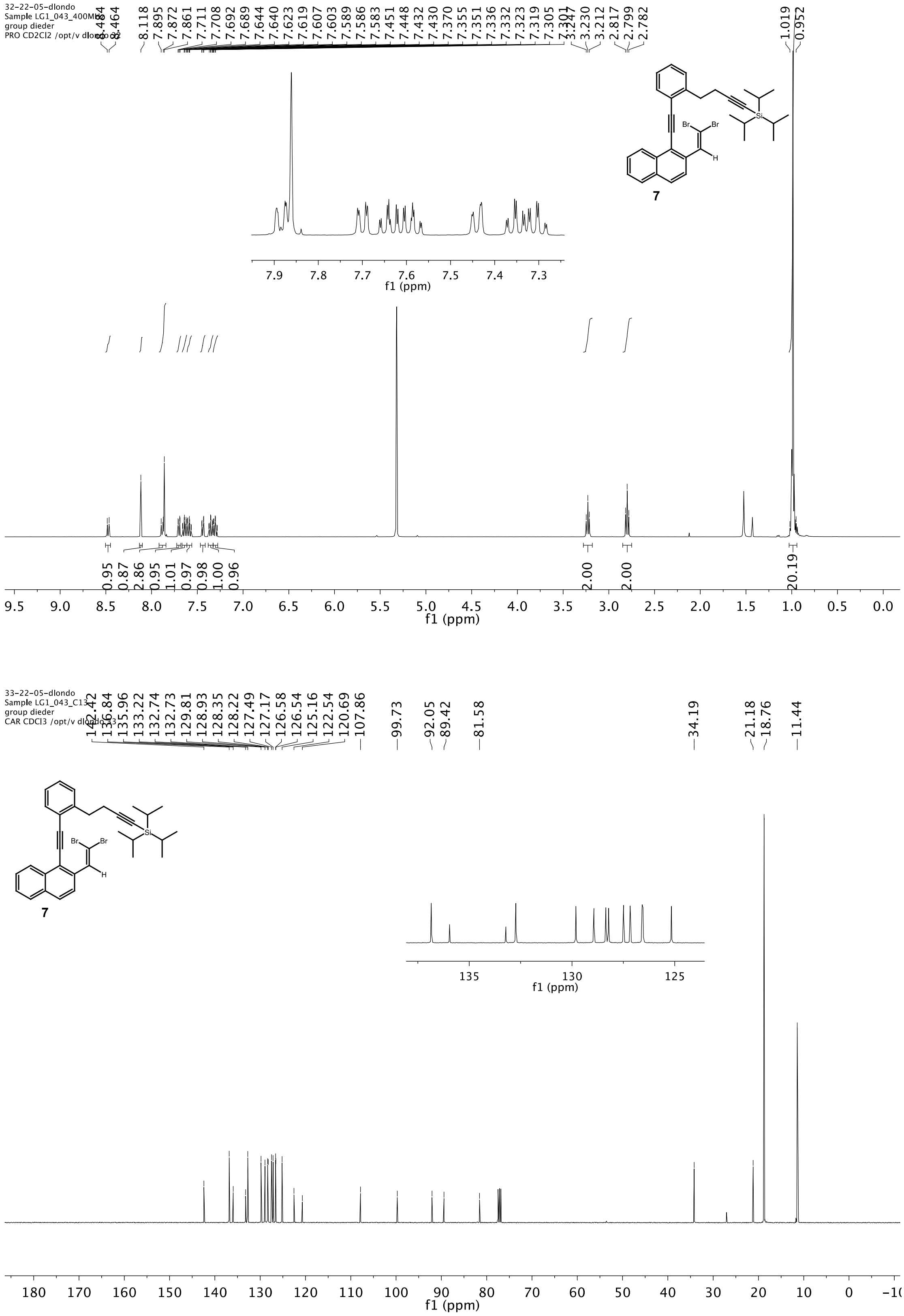


Figure 27ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **7** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.

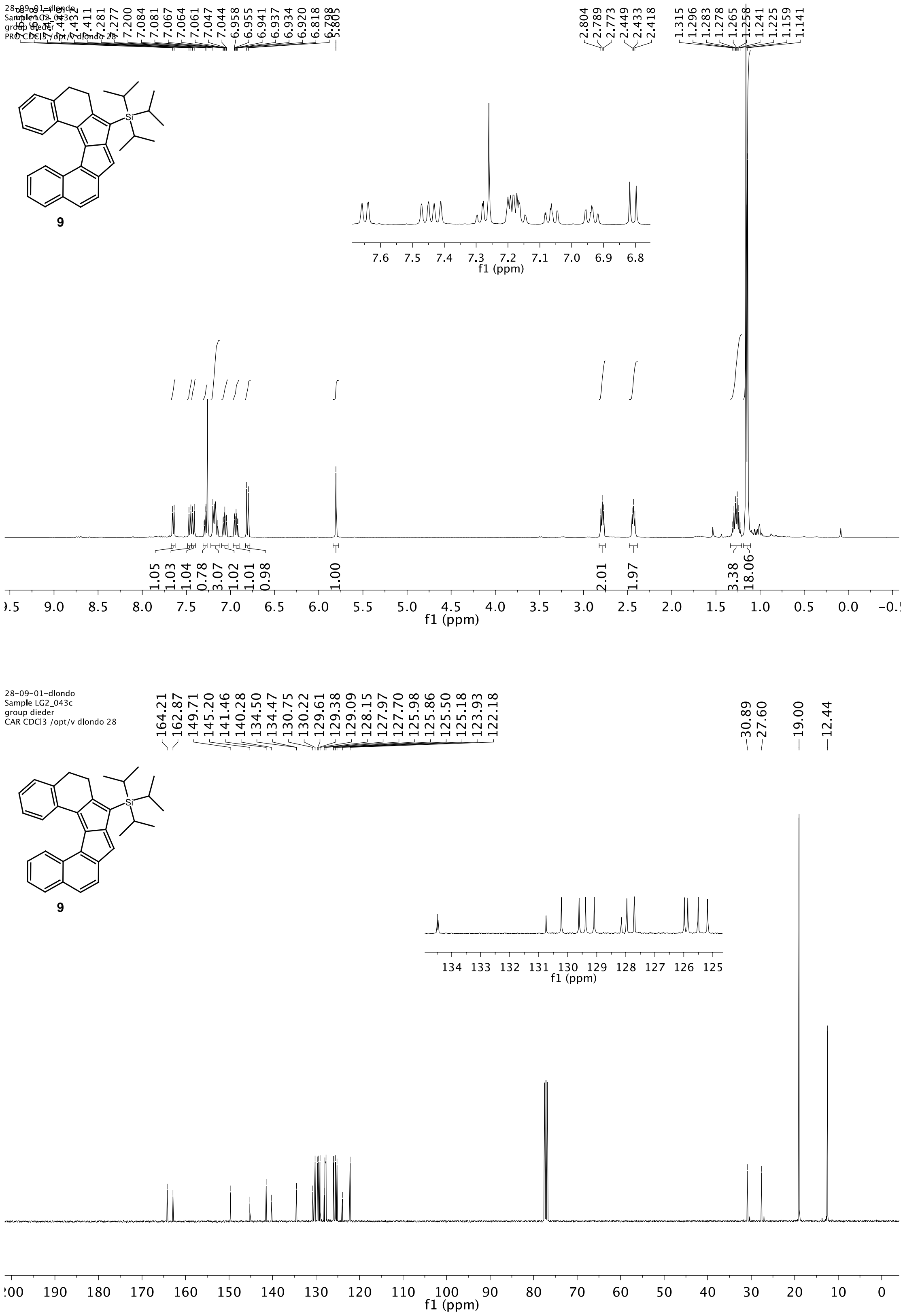


Figure 28ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **9** recorded at 25 °C in $CDCl_3$.

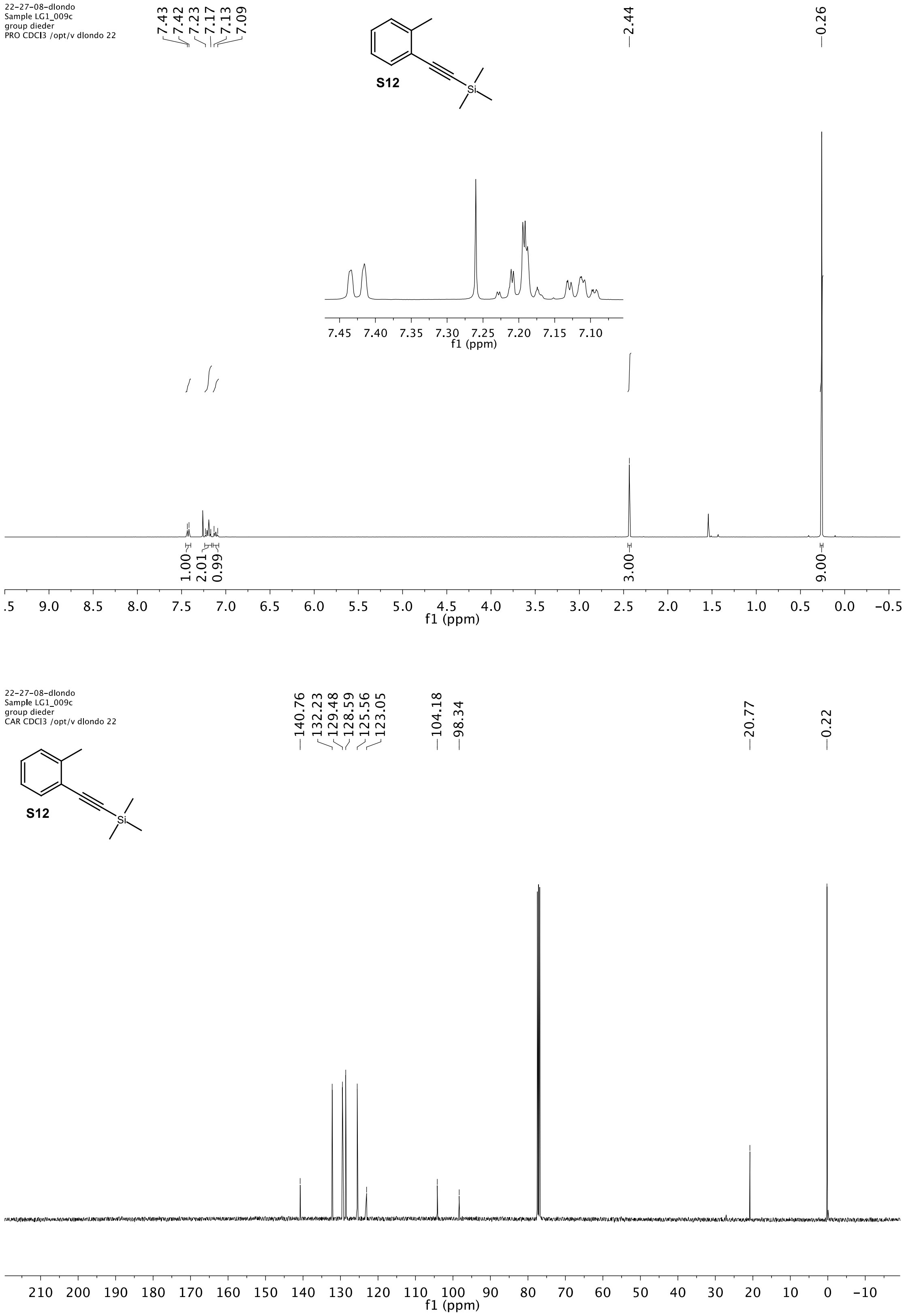
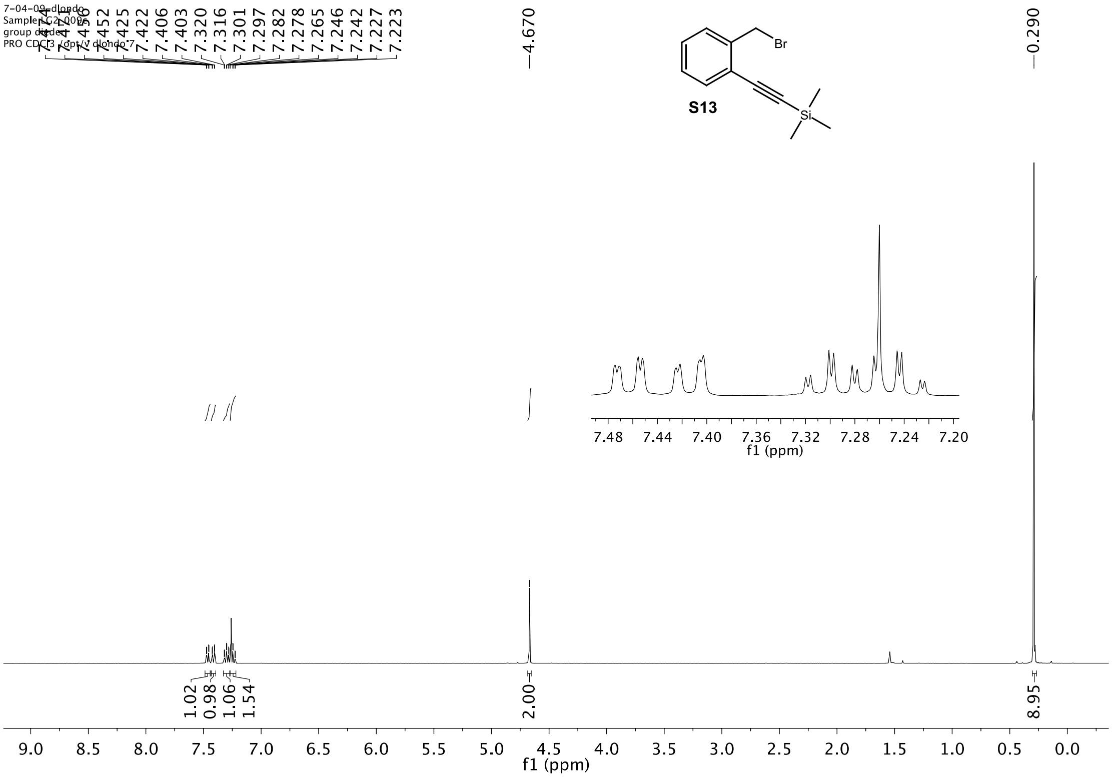


Figure 29ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S12** recorded at 25 °C in $CDCl_3$.



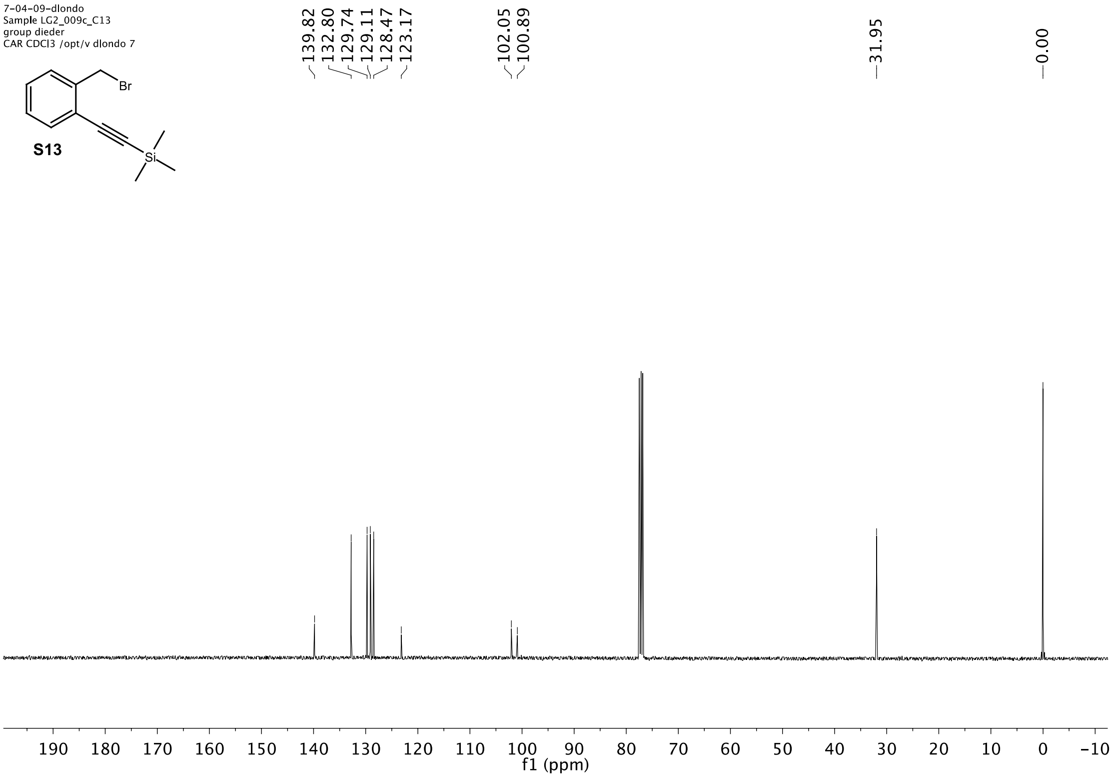


Figure 30ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S13** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.

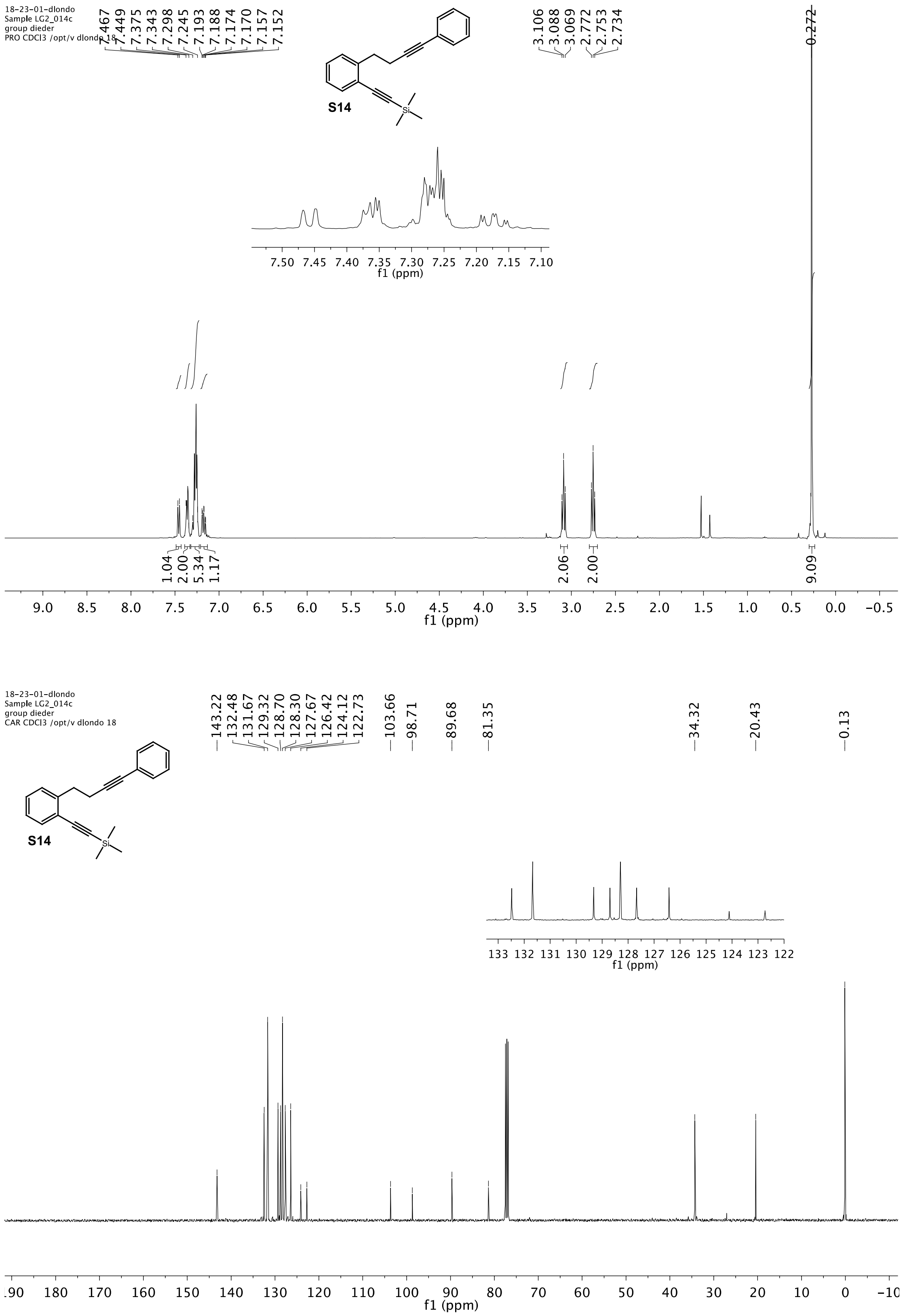


Figure 31ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S14** recorded at 25 °C in $CDCl_3$.

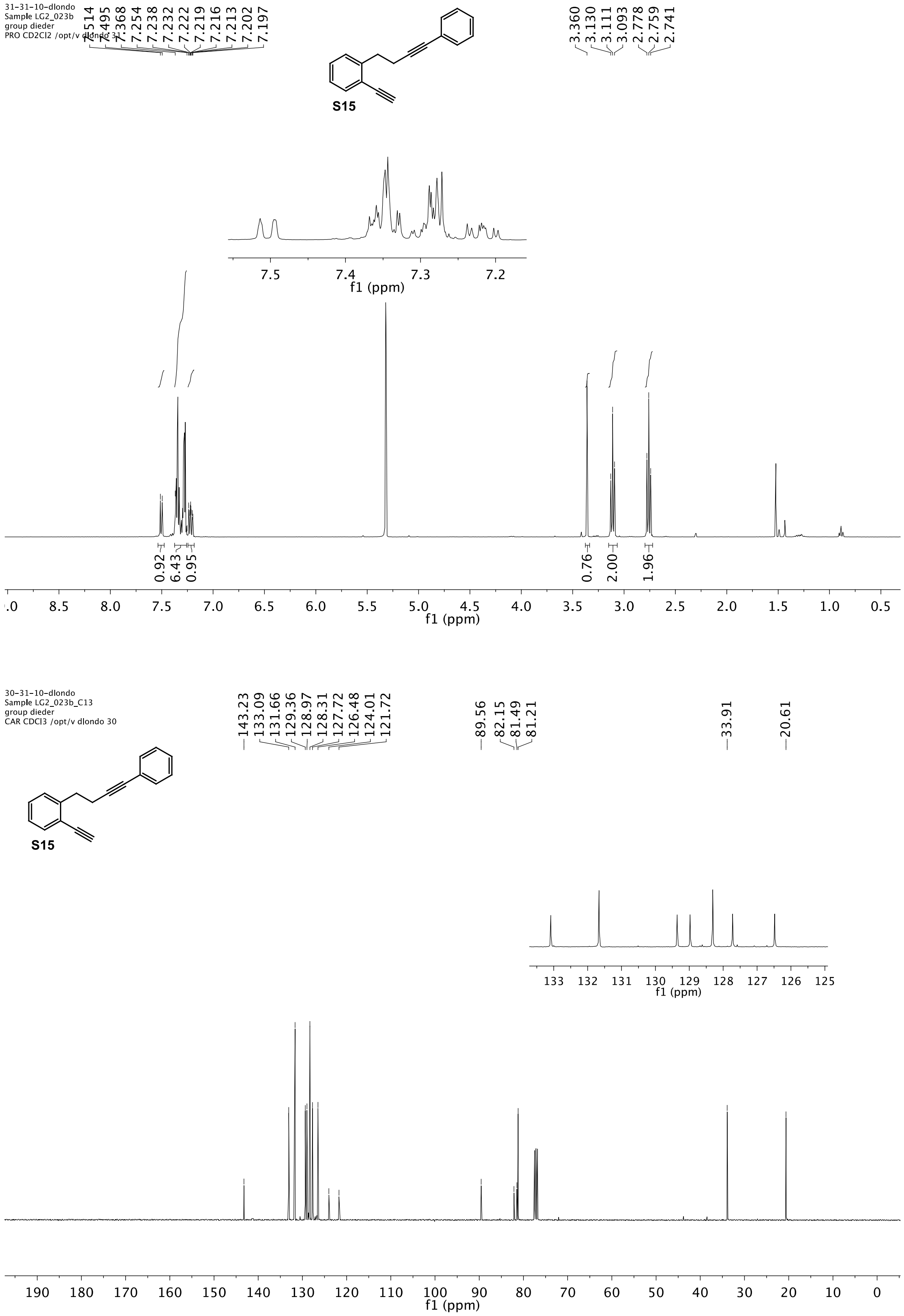


Figure 32ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S15** recorded at 25 °C in CD_2Cl_2 and $CDCl_3$, respectively.

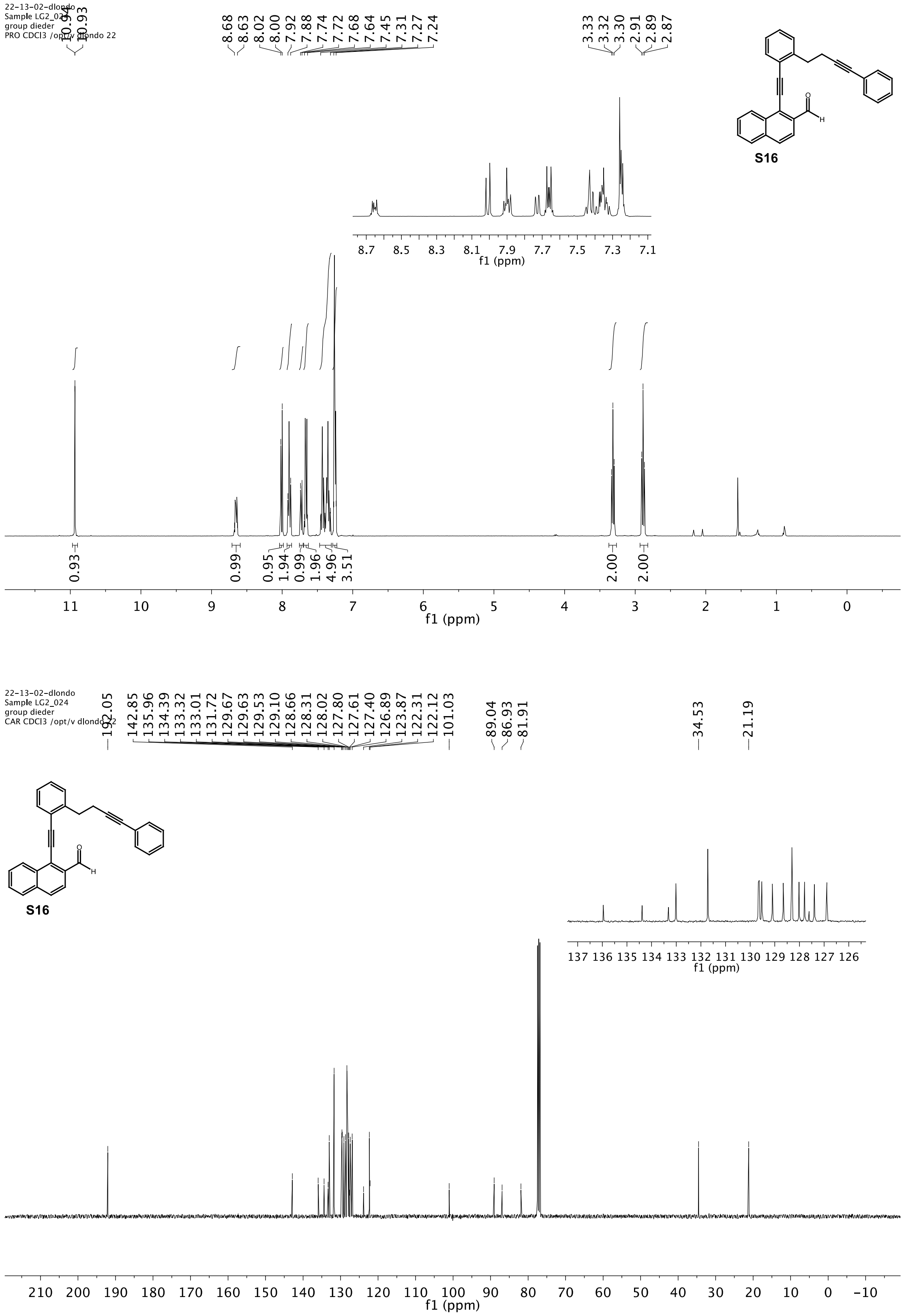


Figure 33ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **S16** recorded at 25 °C in $CDCl_3$.

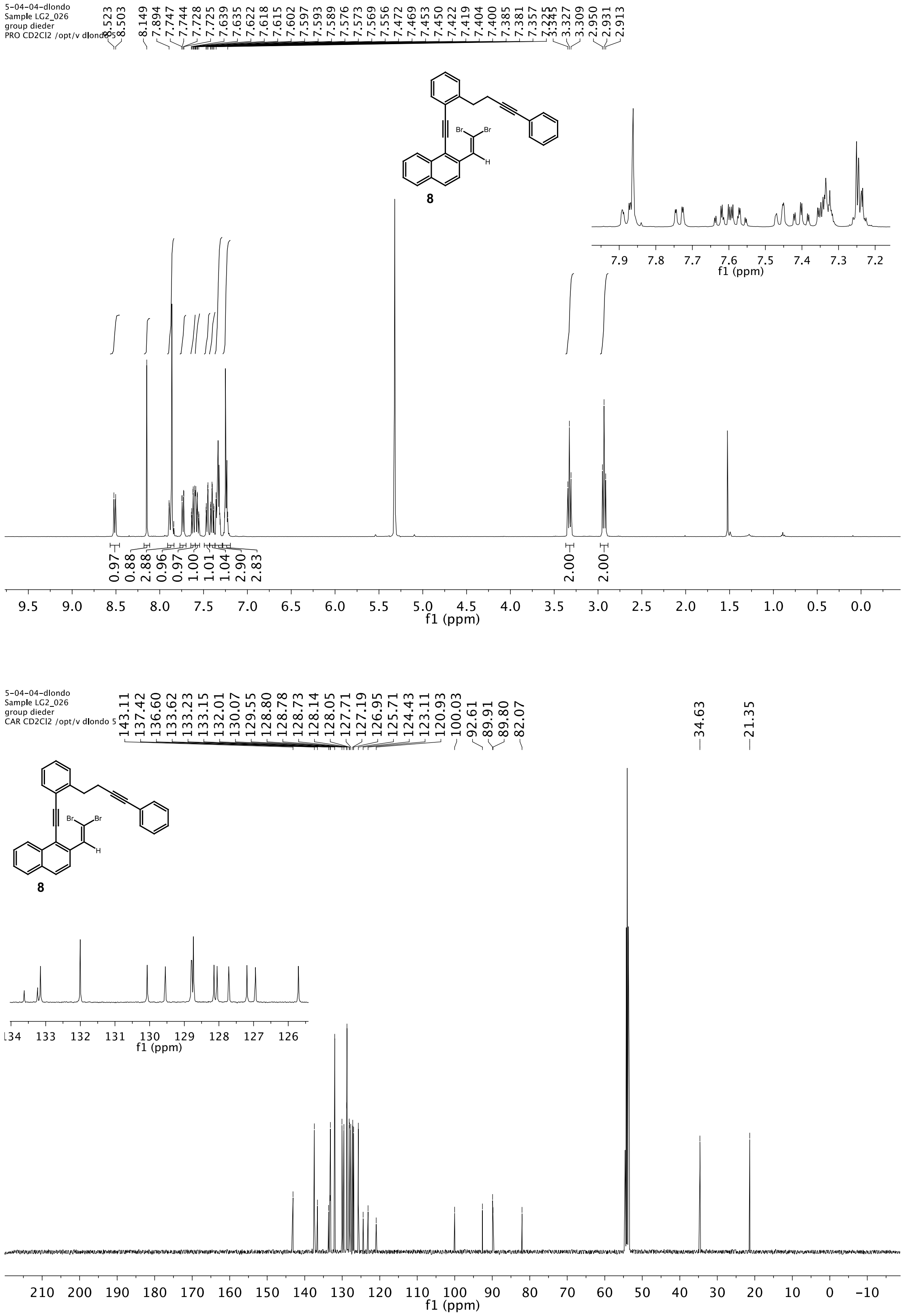


Figure 34ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **8** recorded at 25 °C in CD_2Cl_2.

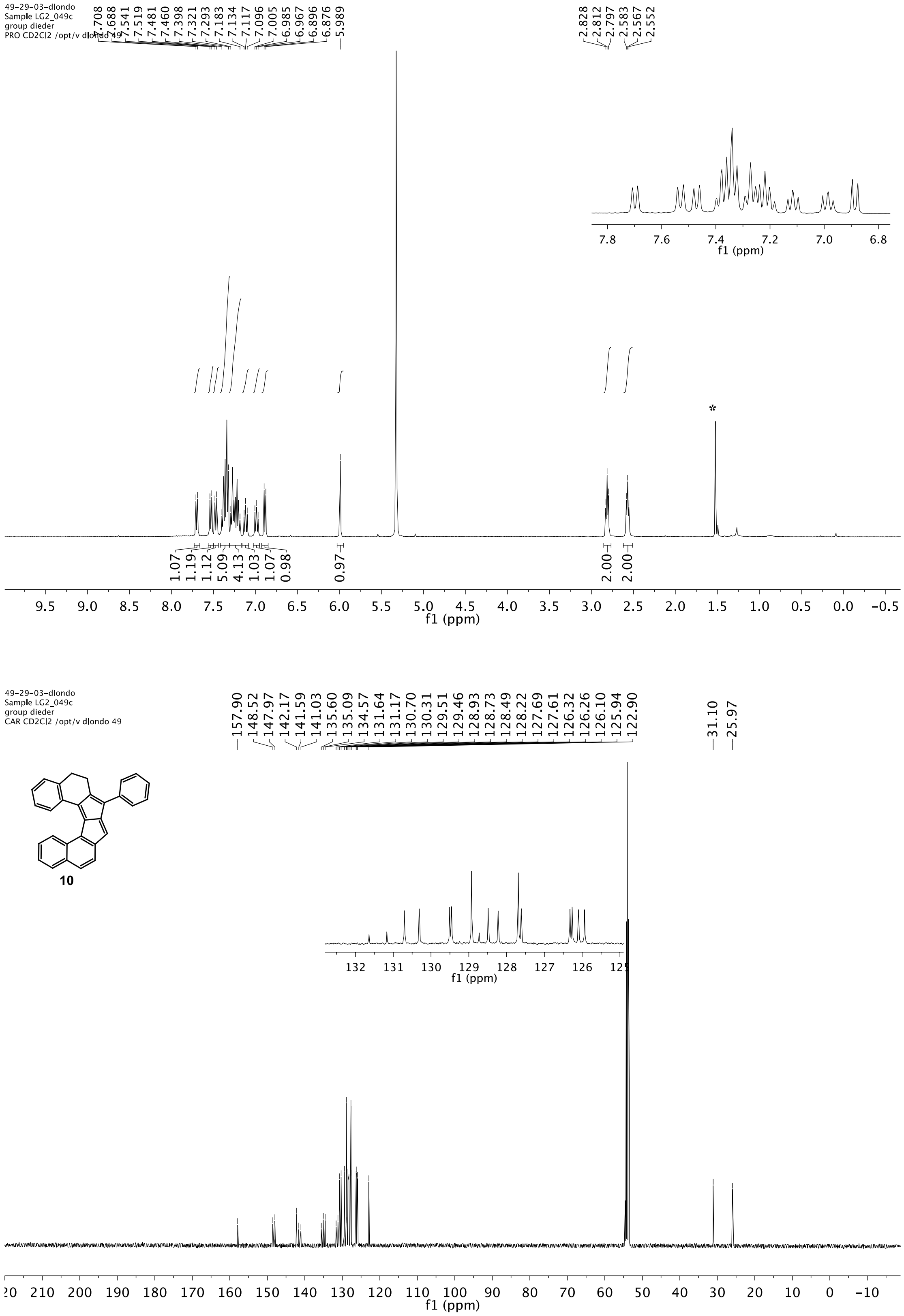


Figure 35ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **10** recorded at 25 °C in CD_2Cl_2.

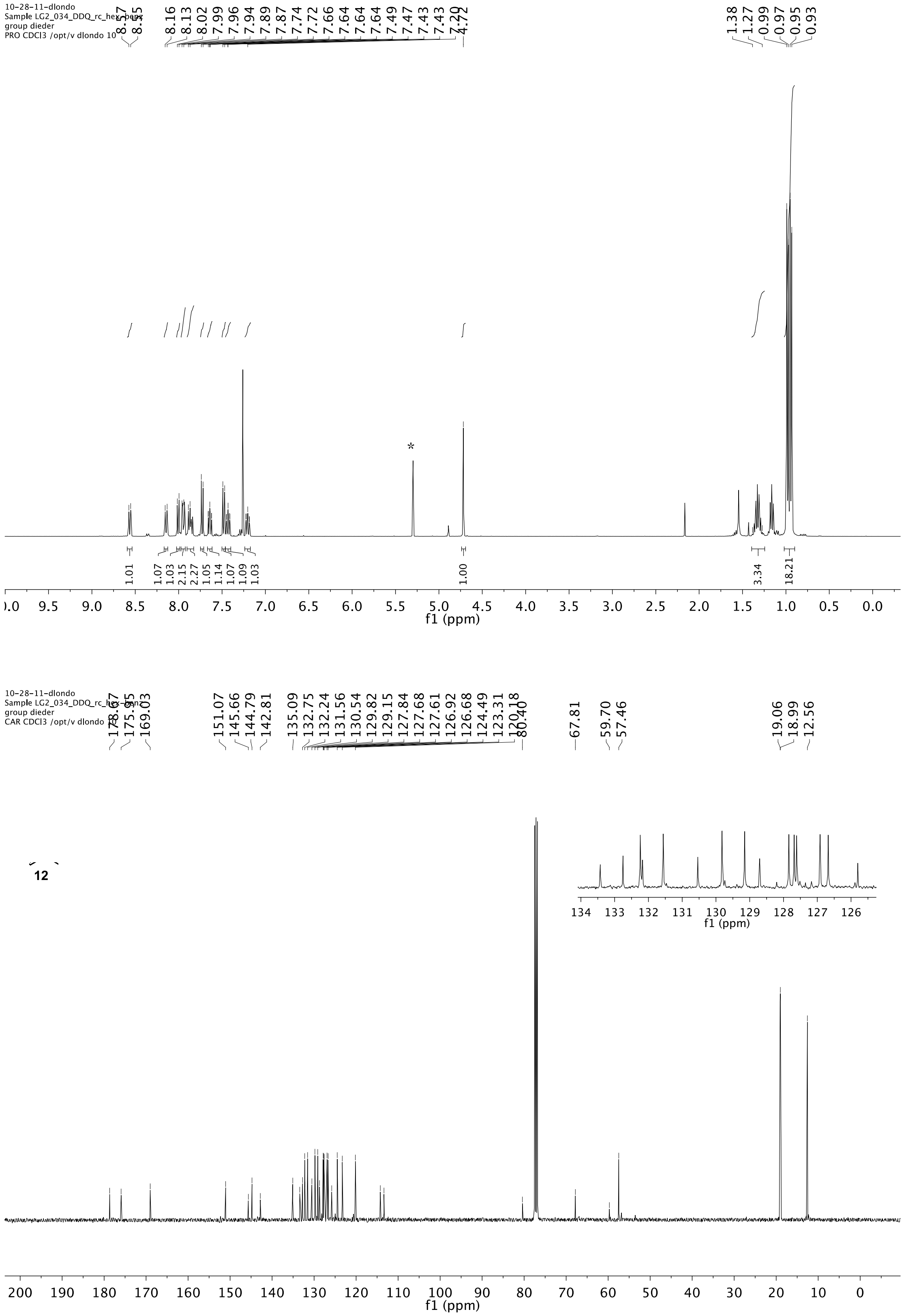
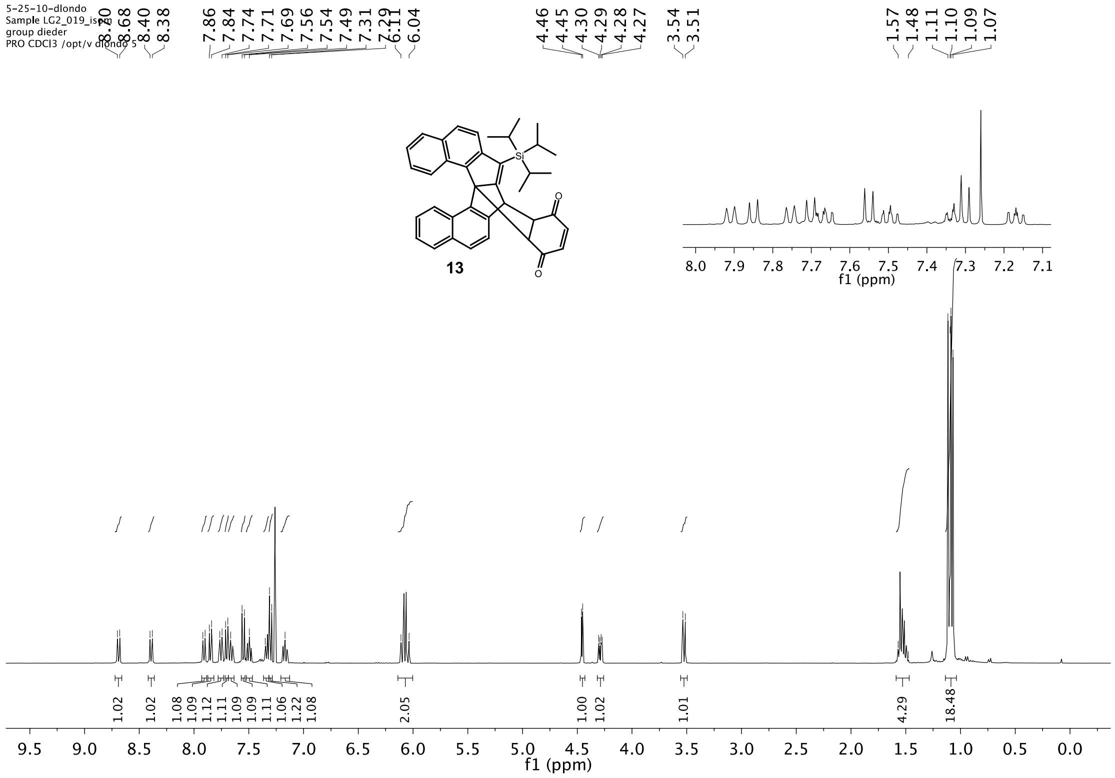


Figure 36ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of (±)-**12** recorded at 25 °C in $CDCl_3$.



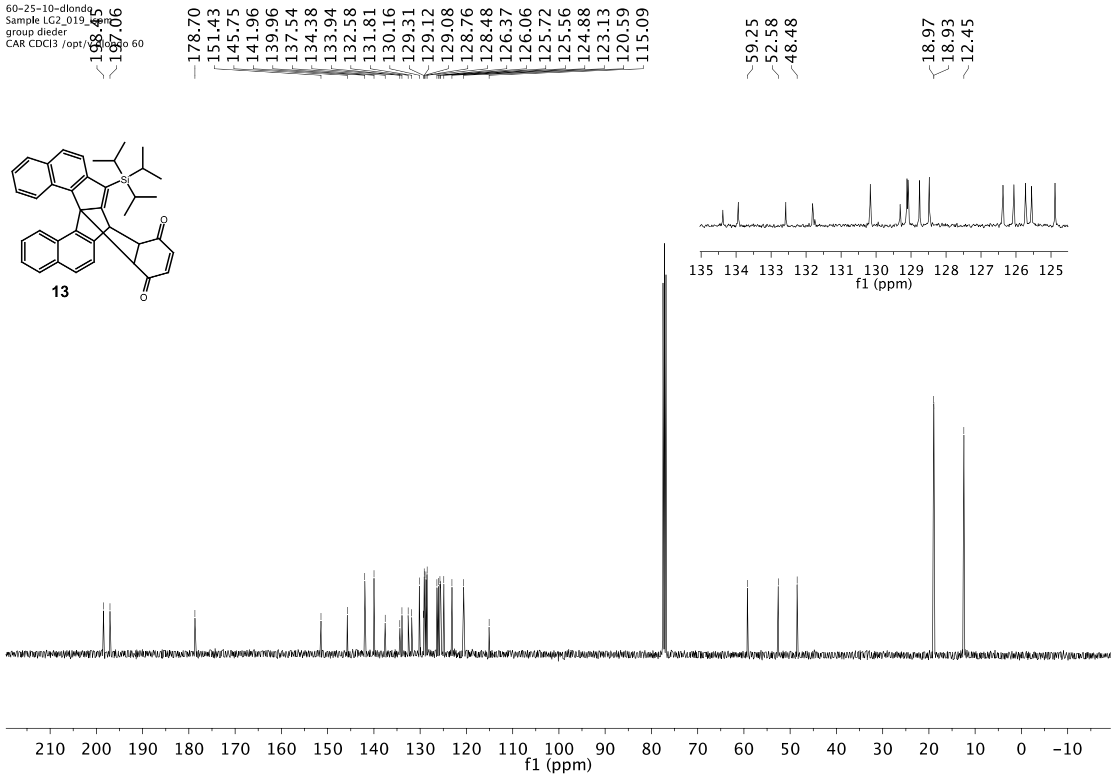


Figure 37ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of (±)-**13** recorded at 25 °C in CDCl$_3$.

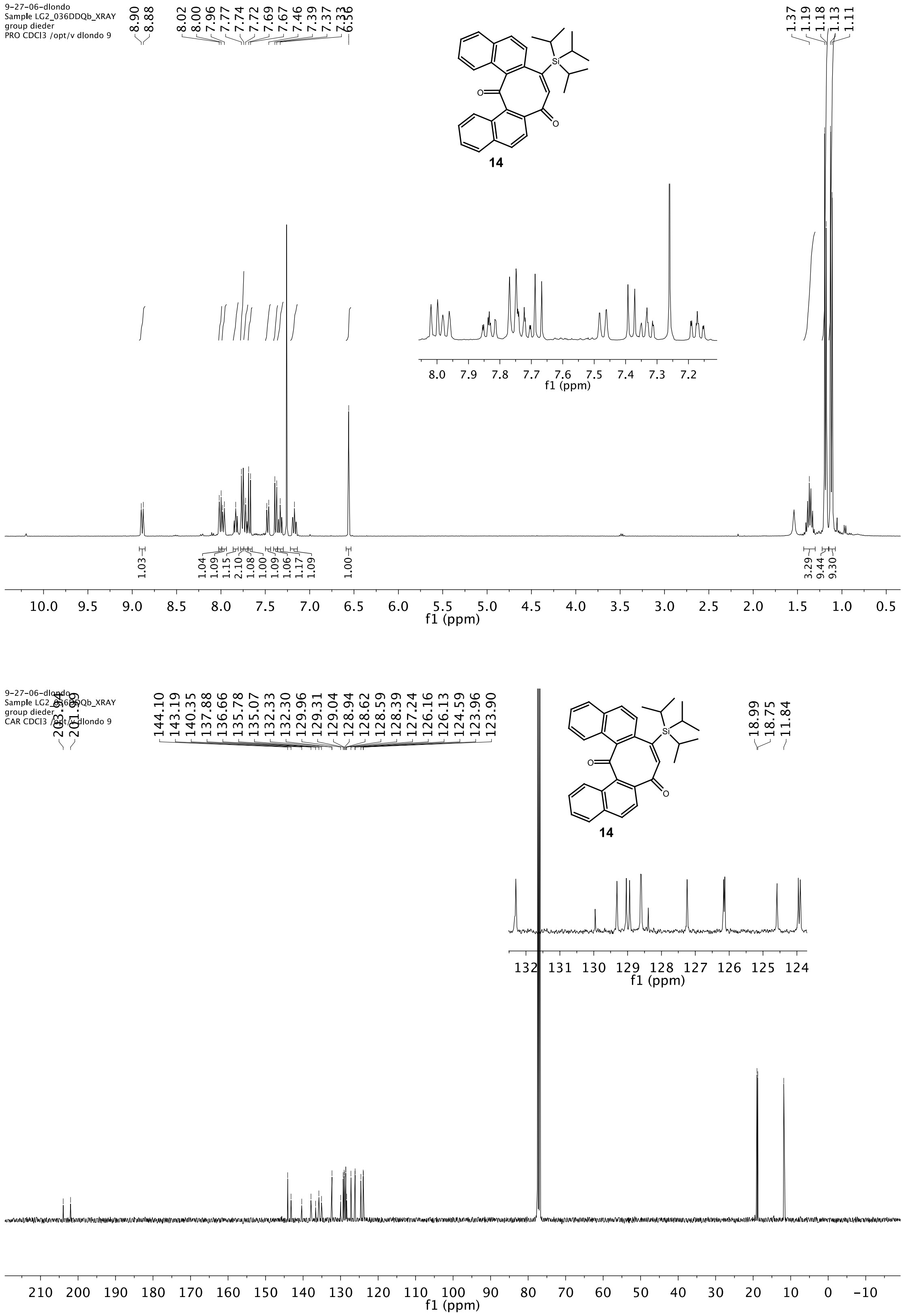


Figure 38ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **14** recorded at 25 °C in $CDCl_3$.

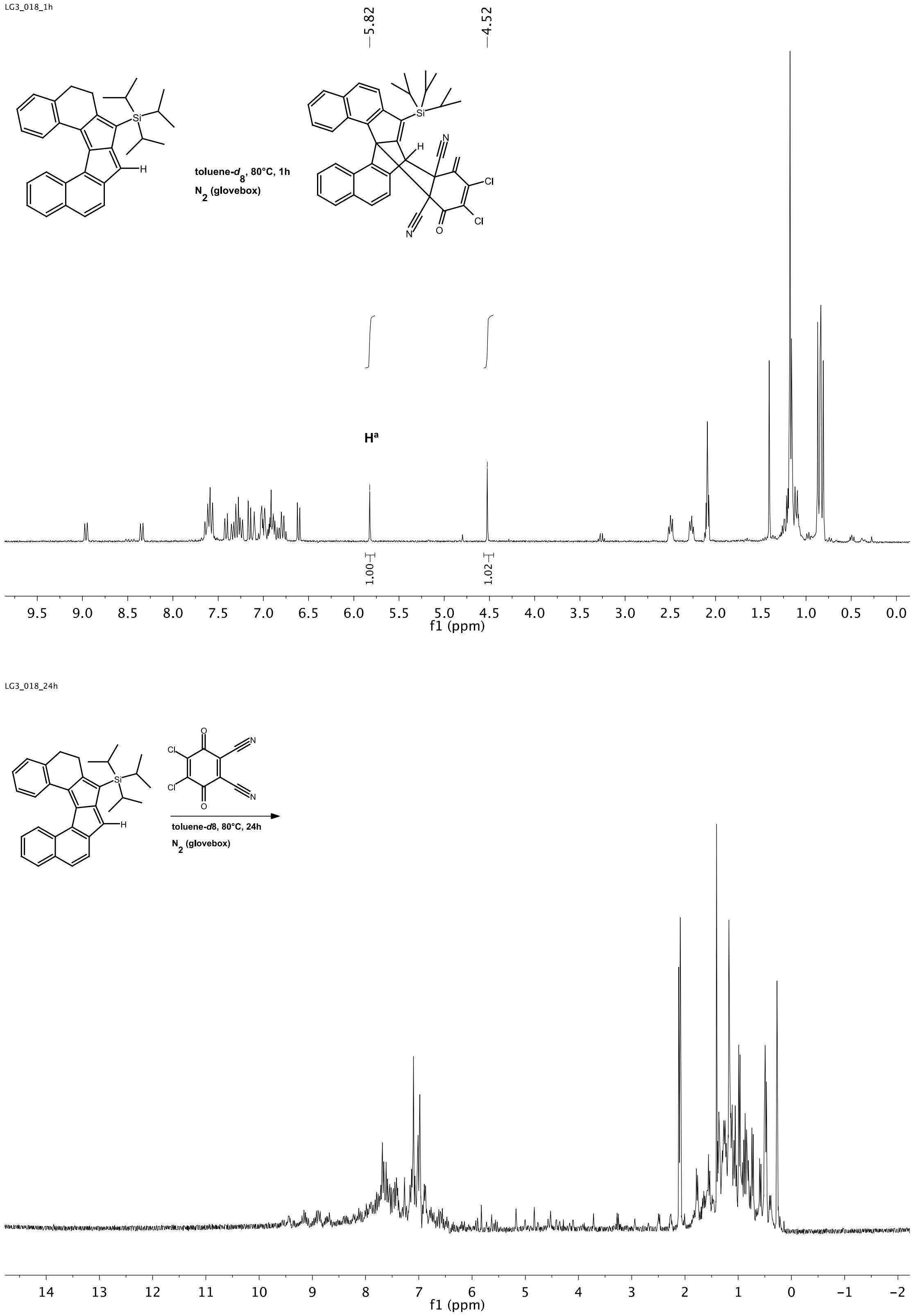
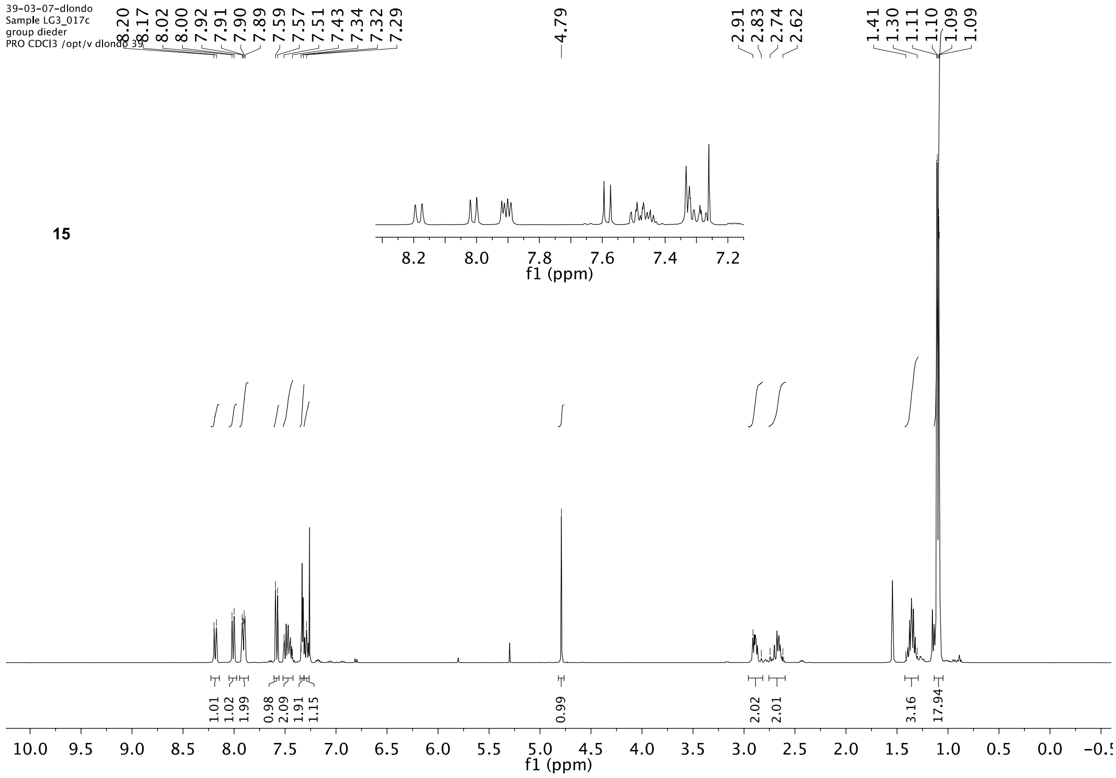


Figure 39ESI 300 MHz ^{1}H NMR spectra of crude samples of the reaction between **9** and DDQ after 1 h reaction (top) and after 24 h reaction (bottom). Spectra were recorded at 25 °C in toluene-d_8.



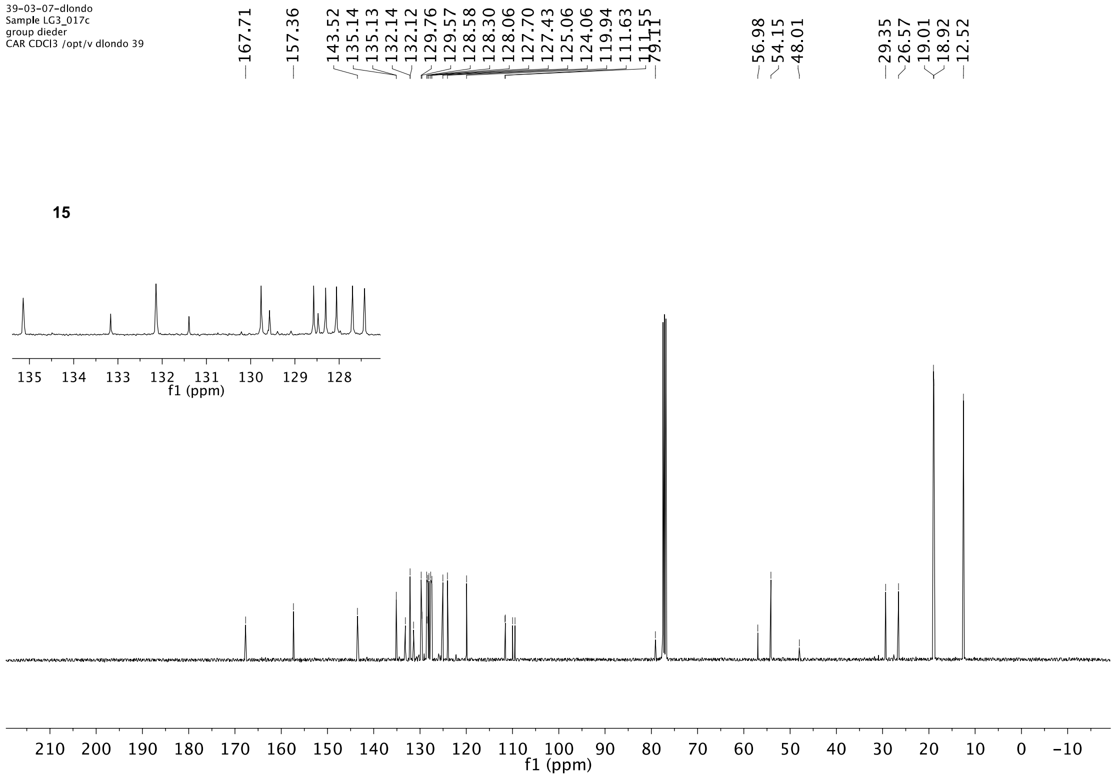


Figure 40ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of (±)-**15** recorded at 25 °C in $CDCl_3$.

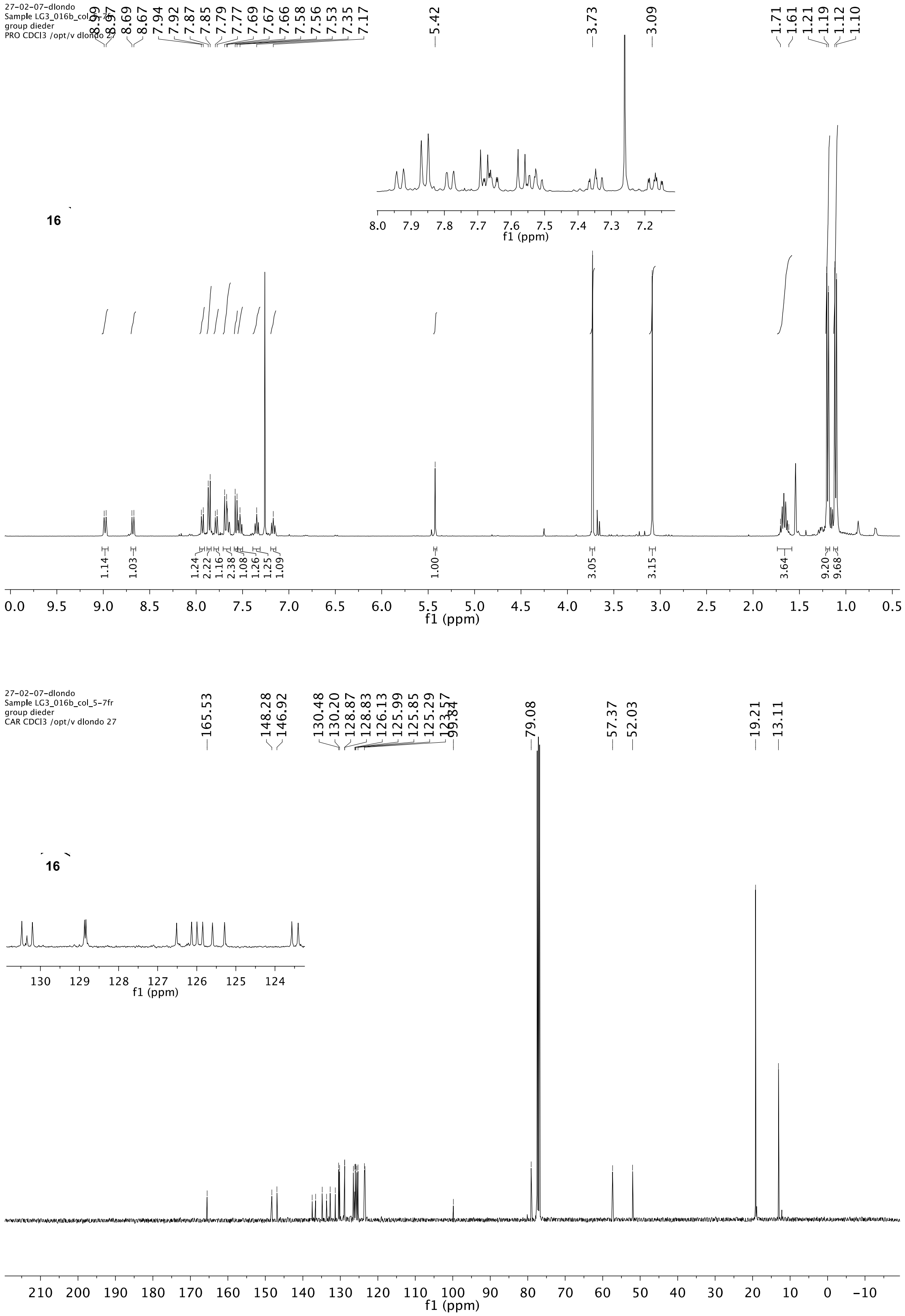


Figure 41ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of (±)-**16** recorded at 25 °C in $CDCl_3$.

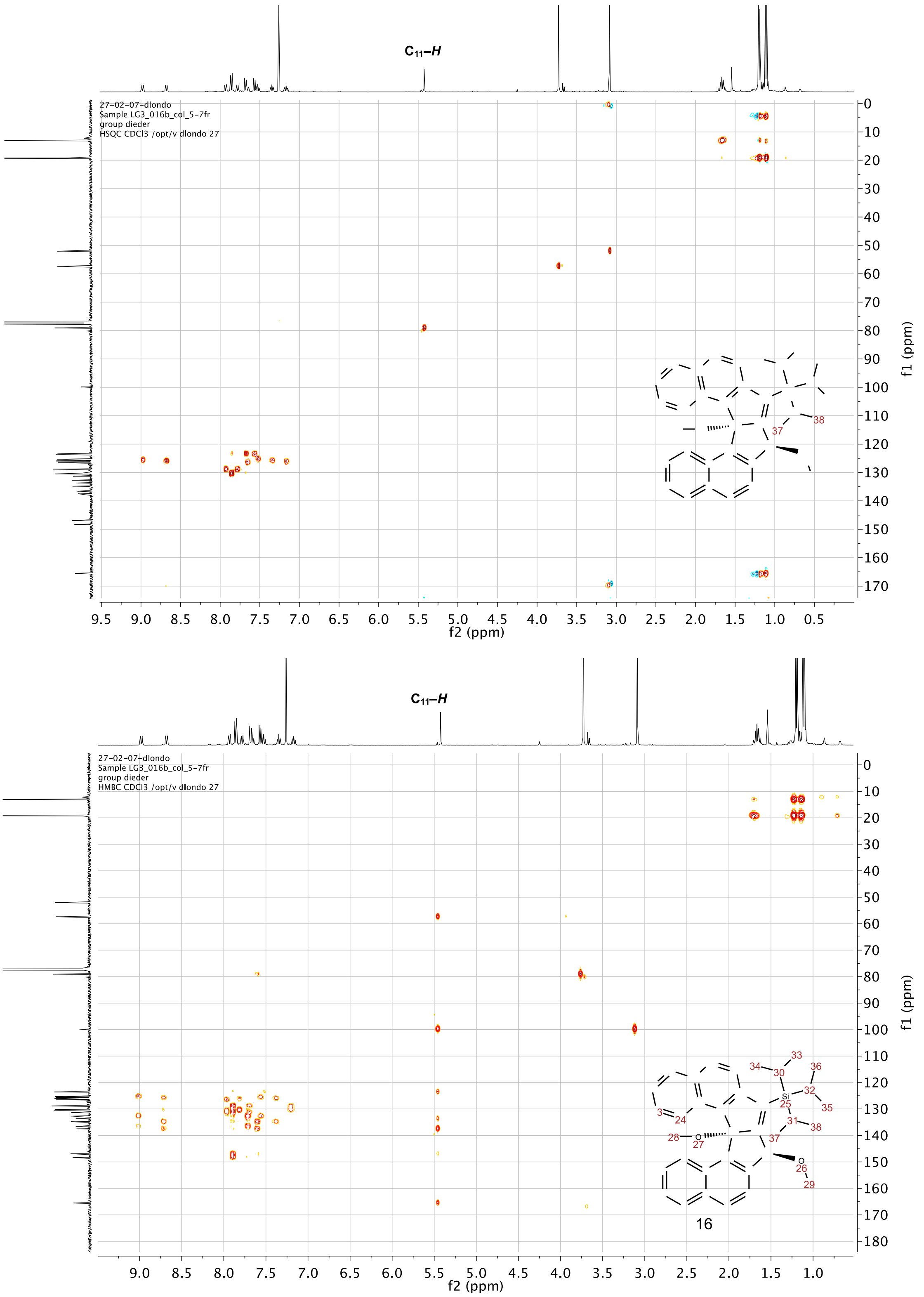
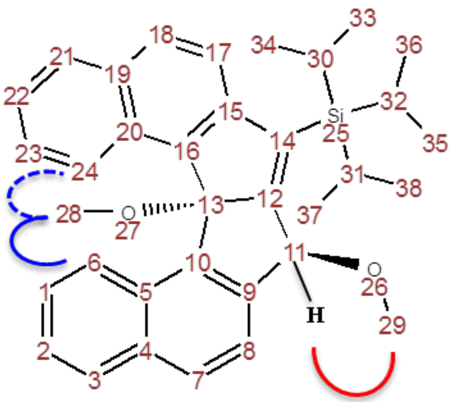


Figure 42ESI 400 MHz HSQC (top) and HMBC (bottom) spectra of (±)-**16** recorded at 25 °C in $CDCl_3$. (Arbitrary numbering.)



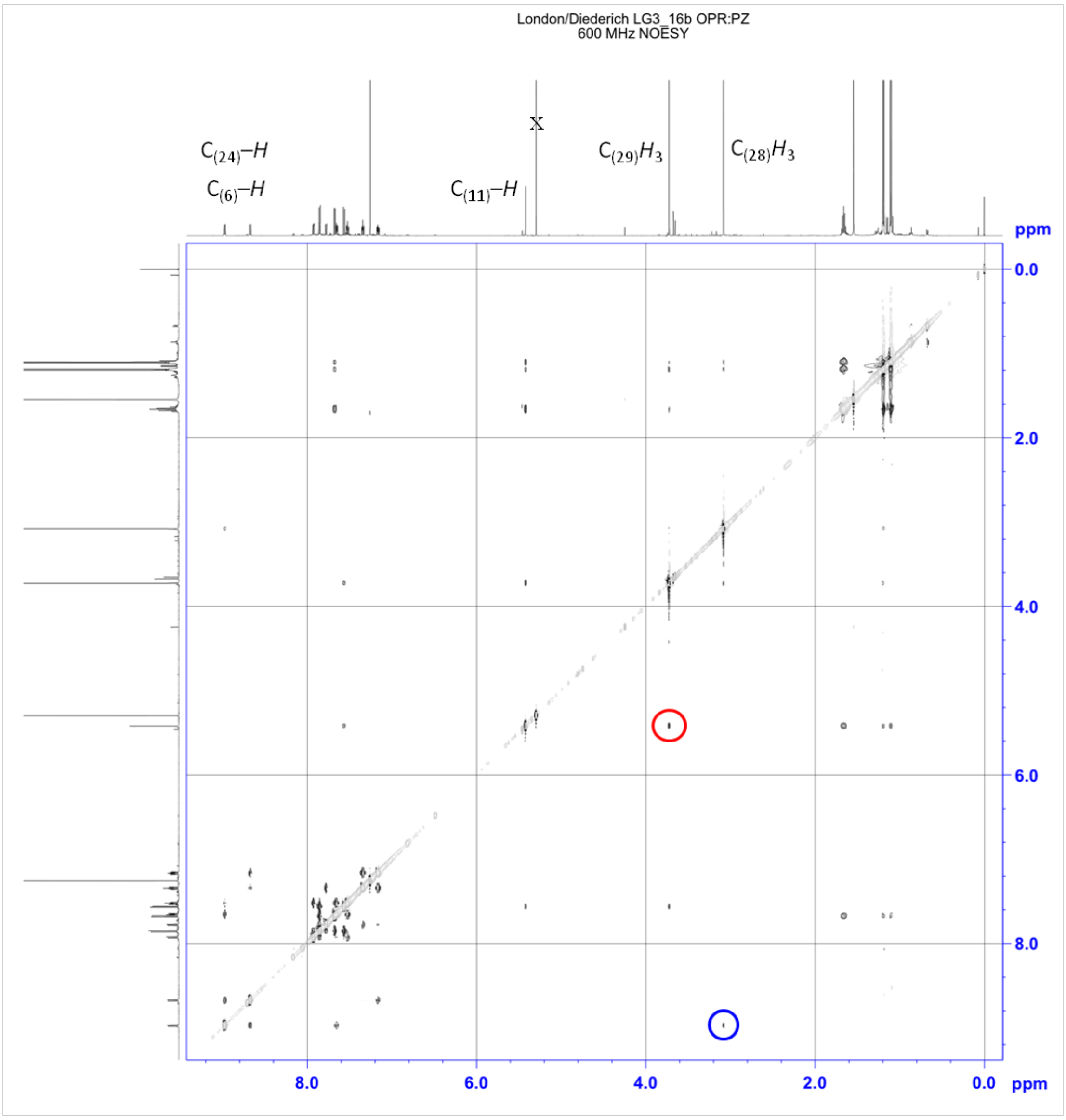
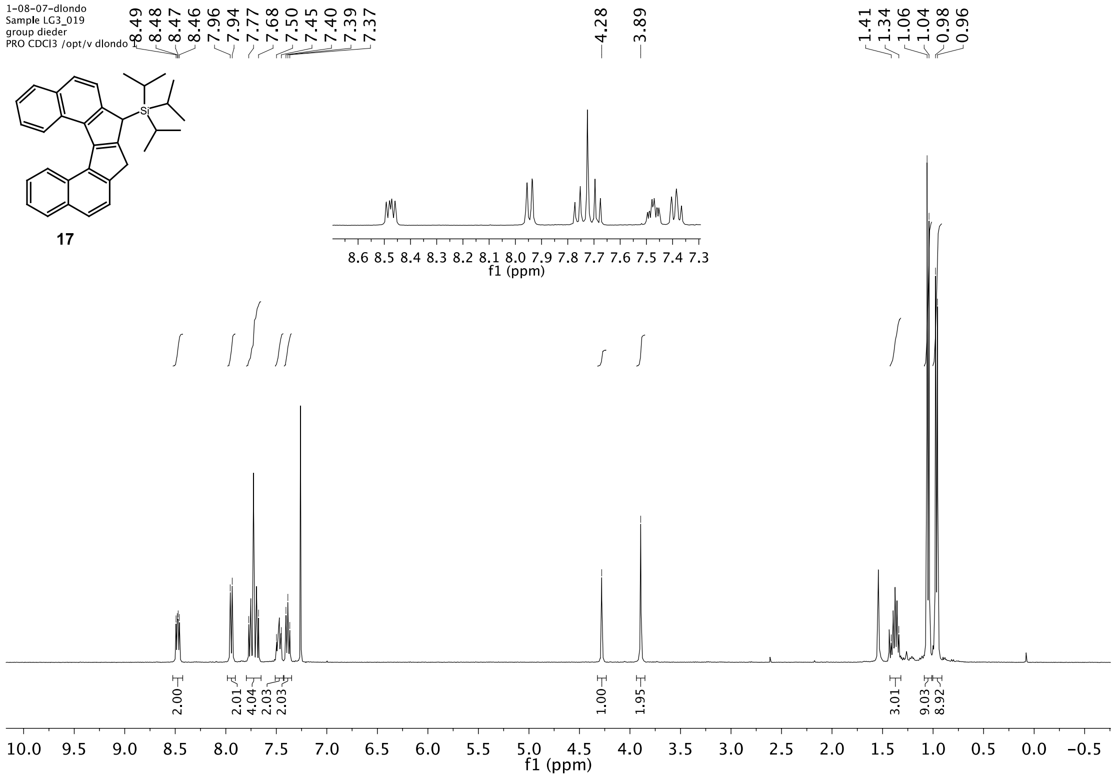


Figure 43ESI 600 MHz NOESY spectrum of (±)-**16** recorded at 25 °C in $CDCl_3$. (Arbitrary numbering. The solid and dashed blue lines in the structure indicate that the protons of C(29)–H_3 group couple either with C(24)*H* or C(6)*H* proton.)



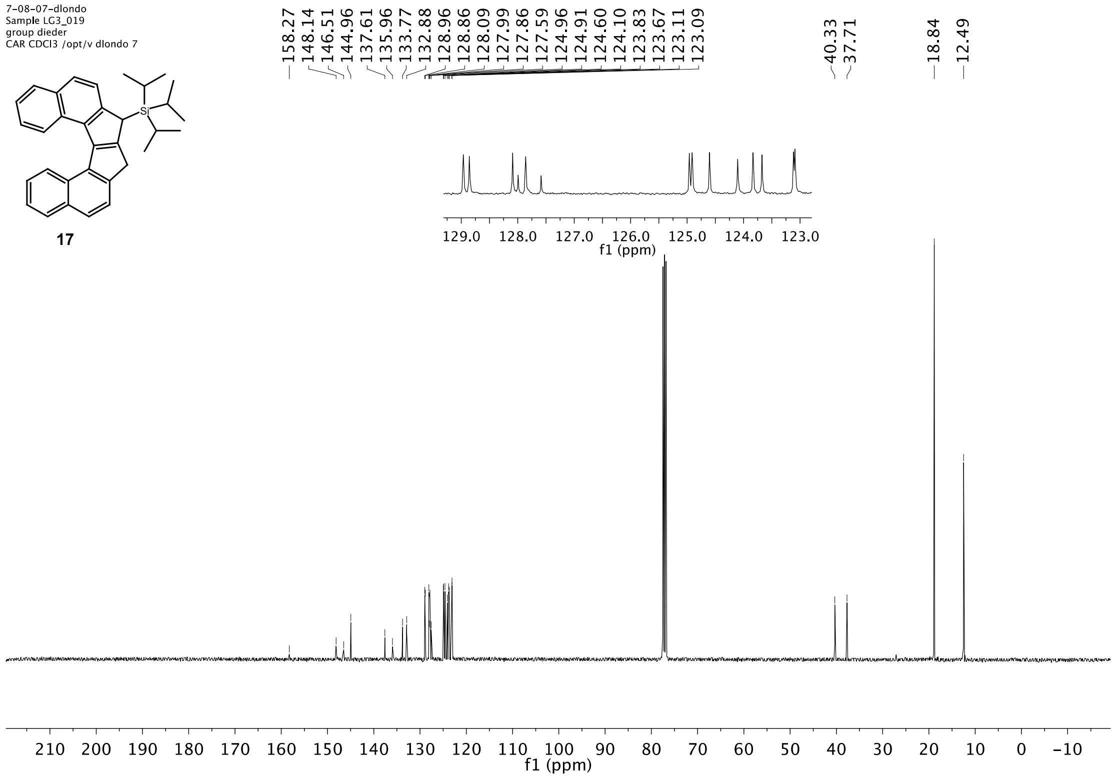


Figure 44ESI 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of (±)-**17** recorded at 25 °C in $CDCl_3$.

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