Use of 2-bromophenylboronic esters as benzyne precursors in Pd–catalyzed synthesis of triphenylenes.

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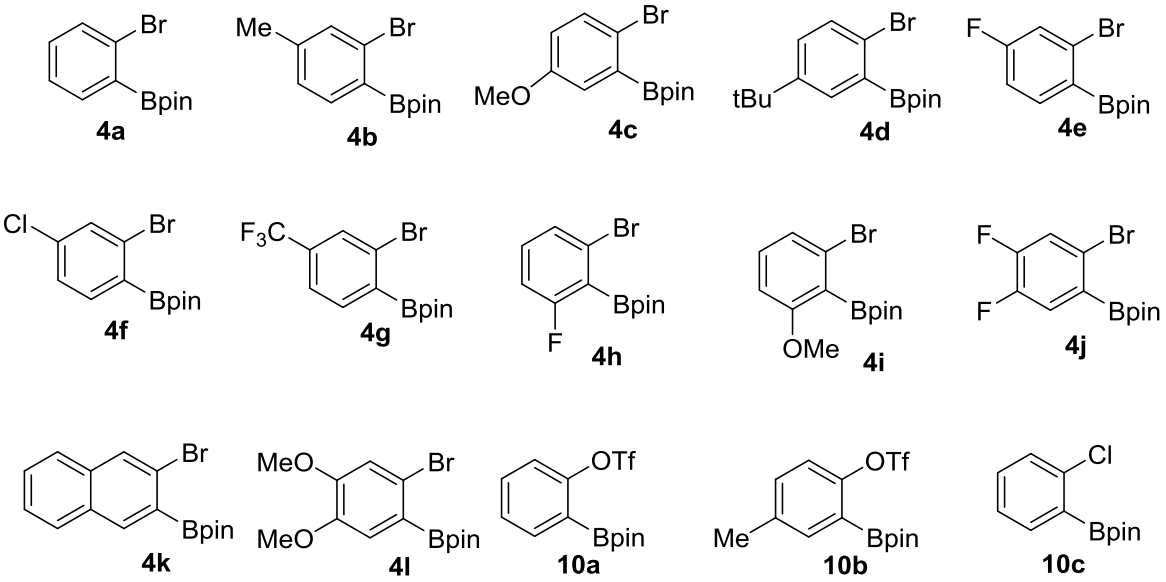
Supporting Information

General Remarks

Nuclear Magnetic Resonance (NMR) spectra were recorded on 500 or 400 MHz Bruker NMR spectrometers in $CDCl_3$ at 298 K (unless stated otherwise). All chemical shift values are reported in parts per million (ppm) relative to the $CDCl_3$ solvent signal (^{1}H NMR: δ = 7.26 ppm. ^{13}C NMR: δ = 77.16 ppm) with coupling constant (*J*) values reported in Hz. The notation of signals is: Proton: δ chemical shift in ppm (number of protons, multiplicity, *J* value(s), proton assignment). Carbon: δ chemical shift in ppm (carbon assignment). Fluorine: δ chemical shift in ppm (Fluorine assignment). Splitting patterns are assigned s = singlet, b = broad, d = doublet, td = triplet of doublet, dt = doublet of triplet, t = triplet, q = quartet. Catalytic reactions were carried out on a 0.50 mmol scale under N_2 using pre-dried glassware. All reactions were carried out in Schlenck glass tubes and heated in oil baths with a thermocouple temperature control. Toluene, THF and dichloromethane were freshly distilled over sodium or calcium hydride and stored under N_2. Other solvents, unless otherwise stated, were purchased in reagent grade or anhydrous quality and used as received. Reagents were either purchased directly from commercial suppliers or prepared according to literature procedures. Yields of triphenylene compounds refer to isolated compounds. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Silica gel (Sigma Aldrich, 40-63 μ, 60 Å). High Resolution Mass Spectrometry (HRMS) were recorded on Thermo Finnigan MAT95XP. Melting points were determined using a Buchi M565 melting point apparatus. The GCMS traces were recorded in an Agilent 7890 (GC) /5975C (MS) using the following parameters: Temperature gradient (50 deg C - 3.3 min hold, 25 °C / min to 300 °C – 20 min hold and 25 °C / min to 320 °C), injector temperature - 300 °C (back injector), column Agilent H5 -5 ms 30 m (length) × 0.25 mm (internal diameter) × 0.25 μm (film thickness) and carrier gas helium, column flow 1 ml / min.

Synthesis of starting materials



2-Bromophenyl pinacol ester derivatives were prepared from the corresponding boronic acids following procedure **A**. Triflate derivative **10a** was prepared from 2-bromo phenol (Aldrich) according to literature methods.[1] The parent boronic acids of compounds **4a** (Aldrich), **4h** (Alfa Aesar), **4j** (Aldrich) and **10c** (Frontier Scientific) were purchased from commercial sources. The precursors of compounds **4c** ((2-bromo 5-methoxyphenyl)boronic acid),[2] **4d** ((2-bromo 5-*tert*-butylphenyl)boronic acid)[3] and **4k** ((3-bromonaphthalen-2-yl)boronic acid)[4] were prepared following previously reported methods.

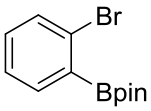
Esters **4b**, **4e**, **4f**, **4g**, **4i** and **4l** were synthesised from the parent boronic acid derivatives, accessed through procedure **B**. 2-Bromo-4-chloroiodobenzene (Alfa Aesar) and 2-bromo-4-(trifluoromethyl)iodobenzene (Fluorochem), precursor iodoarenes for **4f** and **4g** respectively, were purchased from commercial sources, while 2-bromo-4-methyl-iodobenzene,[5] 2-bromo-4-flouro-iodobenzene[5], 2-bromo 6-methoxy-iodobenzene[21] and 2-bromo 4,5-dimethoxy-iodobenzene[6] precursors for **4b**, **4e**, **4i** and **4l** respectively, were prepared following previously described methods.

Procedure A. Representative synthesis of pinacol esters from the corresponding boronic acids. *o*-Bromo-phenyl boronic acid (2 g, 10 mmol) was suspended in Et_2O (20 mL), and pinacol (1.42 g, 12 mmol) was added. The mixture was stirred for 15 h at room temperature. The solution was taken to dryness, and the oily crude was purified by column chromatography (silica, petroleum ether/EtOAc: 10/1) to give the pinacol ester **4a** (2.53 g, 8.94 mmol, 89%) as a colorless liquid.

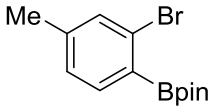
Procedure B. Representative synthesis of (2-bromophenyl)boronic acids from the corresponding 2-bromo iodobenzene derivatives: A 2 M solution of *i*-PrMgCl in THF (4.4 mL, 8.85 mmol, 1 eq) was added dropwise to a solution of 2-bromo-4-methyl-iodobenzene (2.63 g, 8.80 mmol, 1 eq) in 40 mL of a mixture of dry THF and Et_2O (1:1) at –78 ºC. The mixture was strirred at that temperature for 2 h and $B(OEt)_3$ (3.5 mL, 20 mmol, 2.3 eq) was added. The mixture was allowed to warm up to room temperature and stirred overnight. 40 mL of HCl (10% aq) was added, and the resulting mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with Et_2O (3 × 50 mL). The organic layer was dried over anhydrous Mg_2SO_4 and solvent was removed under reduced pressure. The crude was used without further purification for the pinacol esterification reaction.

Spectroscopic data for novel pinacol esters.

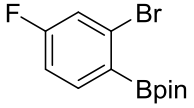
(2-Bromophenyl)boronic acid pinacol ester (**4a**). Prepared according to procedure **A**. Dense colorless liquid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.52 (dd, J = 7.2, 2.1 Hz, 1H), 7.44 (dd, J = 7.8, 1.4 Hz, 1H), 7.17 (td, J = 7.3, 1.4 Hz, 1H), 7.13 (td, J = 7.6, 2.1 Hz, 1H), 1.28 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 136.29 (CH), 132.53 (CH), 131.8 (CH), 127.9 (C_q), 126.2 (CH), 84.2 (C_q), 24.7 (CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{12}H_{16}O_2BBr$ $[M]^+$ 282.0421, found 282.0434.



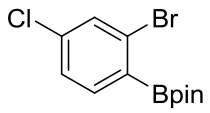
(2-Bromo-4-methylphenyl)boronic acid pinacol ester (**4b**). Prepared according to procedures **A** and **B** from 2-bromo-4-methyl-iodobenzene in 81% overall yield. Dense colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.5 Hz, 1H), 7.38 (s, 1H), 7.08 (br d, J = 7.5 Hz, 1H), 2.31 (s, 3H), 1.36 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 142.4 (C_q), 136.4 (CH), 133.3 (CH), 128.0 (C_q), 127.1 (CH), 84.0 (C_q), 24.7 (CH_3), 21.1 (CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{13}H_{18}O_2BBr$ $[M]^+$ 296.0567, found 296.0578.



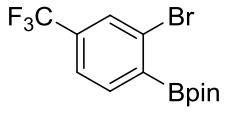
(2-Bromo-4-fluorophenyl)boronic acid pinacol ester (**4e**). Prepared according to procedures **A** and **B** from 2-bromo-4-fluoro-iodobenzene in 75% overall yield. White solid. Mp: 38–40 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, J = 8.3, 6.7 Hz, 1H), 7.29 (dd, J = 8.8, 2.5 Hz, 1H), 6.99 (td, J = 8.3, 2.5 Hz, 1H), 1.36 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 164.0 (d, J_{CF} = 254.6 Hz, C_q), 138.1 (d, J_{CF} = 8.5 Hz, CH), 128.7 (d, J_{CF} = 9.22 Hz, C_q), 120.3 (d, J_{CF} = 24.5 Hz, CH), 113.7 (d, J_{CF} = 20.1 Hz, CH), 84.3 (C_q), 24.8 (CH_3). The aromatic quaternary C–Bpin is not observed. ^{19}F-NMR (376 MHz, $CDCl_3$) δ = – 107.8 (s). HR-MS (EI) *m/z* calcd for $C_{12}H_{15}O_2BBrF$ $[M]^+$ 300.0327, found 300.0326.



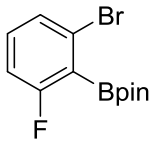
(2-Bromo-4-chlorophenyl)boronic acid pinacol ester (**4f**). Prepared according to procedures **A** and **B** from 2-bromo-4-cloro-iodobenzene in 68% overall yield. Pale orange solid. Mp: 34–36 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 5.5 Hz, 1H), 7.50 (s, 1H), 7.20 (dd, J = 8.0, 1.9 Hz, 1H), 1.30 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 137.3 (CH), 137.1 (C_q), 132.3 (CH), 128.4 (C_q), 126.6 (CH), 84.3 (C_q), 24.7 (CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{12}H_{15}O_2BBrCl$ $[M]^+$ 316.0032, found 316.0021.



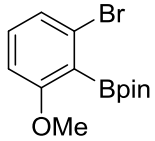
(2-Bromo-4-(trifluoromethyl)phenyl)boronic acid pinacol ester (**4g**). Prepared according to procedures **A** and **B** from 2-bromo-4-(trifluoromethyl)-iodobenzene in 44% overall yield. White solid. Mp: 32–34 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.52 (dd, J = 7.6, 1.0 Hz, 1H), 1.38 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 136.6 (CH), 133.5 (q, J_{CF} = 32.8 Hz, C_q), 129.2 (q, J_{CF} = 4.0 Hz, CH), 128.0 (s, C_q), 123.1 (q, J_{CF} = 272.0 Hz, CF_3), 122.9 (q, J_{CF} = 4.0 Hz, CH), 84.7 (C_q), 24.7 (CH_3). The aromatic quaternary C–Bpin is not observed. ^{19}F-NMR (376 MHz, $CDCl_3$) δ = – 63.1 (s). HR-MS (EI) *m/z* calcd for $C_{13}H_{15}O_2BBrF_3$ $[M]^+$ 350.0295, found 350.0285.



(2-Bromo-6-fluorophenyl)boronic acid pinacol ester (**4h**). Prepared according to procedure **A** from (2-Bromo-6-fluorophenyl)boronic acid in 83% yield. White solid. Mp: 64–66 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 (dd, J = 8.0, 0.8 Hz, 1H), 7.19 (td, J = 8.1, 6.2 Hz, 1H), 6.96 (td, J = 8.3, 0.8 Hz, 1H), 1.40 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 165.3 (d, J_{CF} = 248.5 Hz, C_q), 132.1 (d, J_{CF} = 8.8 Hz, CH), 127.8 (d, J_{CF} = 4.0 Hz, CH), 126.3 (d, J_{CF} = 10.5 Hz, C_q), 113.6 (d, J_{CF} = 24.0 Hz, CH), 84.8 (C_q), 24.2 (CH_3). The aromatic quaternary C–Bpin is not observed. ^{19}F-NMR (376 MHz, $CDCl_3$) δ = – 102.3 (s). HR-MS (EI) *m/z* calcd for $C_{12}H_{15}O_2BBrF$ $[M]^+$ 300.0327, found 300.0322.



(2-Bromo-6-fluorophenyl)boronic acid pinacol ester (**4i**). Prepared according to procedures **A** and **B** from 2-bromo-6-methoxy-iodobenzene in 81% overall yield. White solid. Mp: 82–84 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 3.76 (s, 3H, OMe), 1.40 (s, 12H, Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (s, C_q), 131.4 (s, CH), 126.1 (s, C_q), 124.1 (s, CH), 108.4 (s, CH), 84.4 (s, C_q), 55.9 (s, CH_3), 24.7 (s, CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{13}H_{18}O_3BBr$ $[M]^+$ 312.0527, found 312.0521.



(2-Bromo-4,5-difluorophenyl)boronic acid pinacol ester (**4j**). Prepared according to procedure **A** in 98% yield. Pale yellow solid. Mp: 56–58 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 10.5, 9.0 Hz, 1H), 7.36 (dd, J = 10.0, 7.0 Hz, 1H), 1.35 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 151.5 (dd, J_{CF} = 257.2, 14.0 Hz, C_q), 149.2 (dd, J_{CF} = 249.7, 12.0 Hz, C_q), 124.8 (dd, J_{CF} = 16.9, 1.0 Hz, CH), 122.1 (d, J_{CF} = 19.2 Hz, CH), 121.9 (dd, J_{CF} = 7.2, 3.7 Hz, C_q), 84.6 (C_q), 24.8 (CH_3). The aromatic quaternary C–Bpin is not observed. ^{19}F-NMR (376 MHz, $CDCl_3$) δ = – 131.7 (d, J = 21.1 Hz), – 140.5 (d, J = 20.6 Hz). HR-MS (EI) *m/z* calcd for $C_{12}H_{14}O_2BBrF_2$ $[M]^+$ 318.0233, found 318.0238.

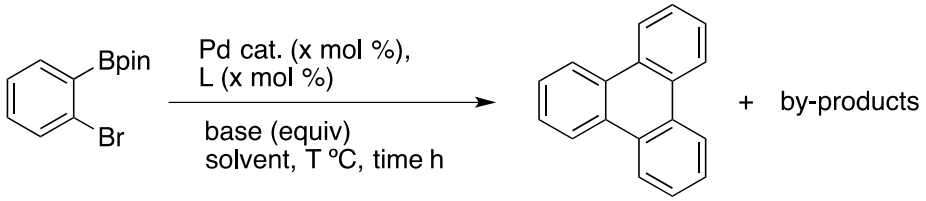
(3-Bromonaphthalen-2-yl)boronic acid pinacol ester (**4k**). Prepared according to procedure **A** from (3-bromonaphthalen-2-yl)boronic acid in 65% yield. Pale orange solid. Mp: 52–54 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1 H), 8.05 (s, 1 H), 7.83 (dd, J = 7.7, 1.1 Hz, 1H), 7.71 (dd, J = 7.8, 1.0 Hz, 1H), 7.45-7.53 (m, 2H), 1.43 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 137.6 (CH), 135.4 (C_q), 131.2 (C_q), 130.7 (CH), 128.2 (CH), 127.7 (CH), 126.6 (CH), 126.1 (CH), 123.8 (C_q), 84.3 (C_q), 24.8 (CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{16}H_{18}O_2BBr$ $[M]^+$ 332.0578, found 332.0578.

(2-Bromo-4,5-dimethoxyphenyl)boronic acid pinacol ester (**4l**). Prepared according to procedures **A** and **B** from 2-bromo-4,5-(dimethoxy)iodobenzene in 66% overall yield. Pale orange solid. Mp: 92–94 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.11 (s, 1H), 7.00 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 1.34 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 151.3 (C_q), 147.5 (C_q), 119.7 (C_q), 118.4 (CH), 116.0 (CH), 84.0 (C_q), 56.0 (OCH_3), 55.9 (OCH_3), 24.7 (CH_3). The aromatic quaternary C–Bpin is not observed. HR-MS (EI) *m/z* calcd for $C_{14}H_{20}O_4BBr$ $[M]^+$ 342.0633, found 342.0629.

Synthesis of (2-triflato-4-methylphenyl)boronic acid pinacol ester (**10b)**. Compound **10b** was prepared following a similar procedure than that reported for the synthesis of (2-hydroxyphenyl) boronic acid.[7] A solution of *n*-BuLi (1.6 M in hexane, 22 mL, 35 mmol) was slowly added to a cooled (–90 ºC) solution of 2-bromo-4-methyl phenol (3.09 g, 16.5 mmol) in dry ether (50 mL). The mixture was then allowed to warm up and stirred at rt for 2 h under a N_2 atmosphere. It was then cooled back to –90 ºC and trimethyl borate (3.2 mL, 28 mmol) was rapidly added. The mixture was stirred at –90 ºC for 0.5 h and then at rt for 15 h under N_2 atmosphere. A solution of HCl (aq) (25 mL, 2 M) at 0 ºC (cooled in an ice

bath) was then slowly added into the reaction mixture and stirred for 0.5 h. The ether layer was then separated and the aqueous layer was extracted with ether (3 × 100 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed to dryness. The crude was used without further purification for the pinacol esterification step following procedure **A**. The resulting crude mixture was purified by column chromatography (silica, petroleum ether/EtOAc: 9:1) to afford 2-hydroxy-4-methylphenyl boronic acid pinacol ester (1.87 g, 8 mmol, 50% yield from 2-bromo-4-methyl phenol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.42 (br s, 1H), 7.19 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 2.27 (s, 3H), 1.38 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 161.4 (C_q), 135.6 (CH), 134.6 (CH), 128.4 (C_q), 115.2 (CH), 84.4 (C_q), 24.8 (CH_3), 20.2 (CH_3). The (2-hydroxy 4-methylphenyl)boronic acid pinacol ester (1870 mg, 8 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under a N_2 atmosphere and pyridine (1.9 mL, 24 mmol) added. The mixture was cooled in an ice bath to 0 ºC and triflic anhydride (3.3 g, 11.7 mmol) was added dropwise and stirred at that temperature for 3 h. The reaction mixture was quenched with water (40 mL) and the organic phase was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layers were dried ($MgSO_4$) and the solvent was removed to dryness. The crude mixture was purified by column chromatography (silica, petroleum ether/EtOAc: 9:1) to afford the desired (2-triflato 4-methylphenyl) boronic acid pinacol ester **10b** (2.54 g, 6.9 mmol, 88% yield). White solid. Mp: 40–42 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 2.2 Hz, 1H), 7.29 (br dd, J = 8.3, 2.3 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H), 2.37 (s, 3H), 1.37 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 152.2 (C_q), 137.7 (C_q), 137.5 (CH), 133.4 (CH), 120.7, (CH), 118.9 (q , J_{CF} = 319.2 Hz, CF_3), 24.7 (CH_3), 20.6 (CH_3). The aromatic quaternary C–Bpin is not observed. ^{19}F-NMR (471 MHz, $CDCl_3$) δ = – 73.1 (s). HR-MS (EI) *m/z* calcd for $C_{14}H_{18}O_5BF_3S$ $[M]^+$ 366.0915, found 366.0907.

Optimization study: Representative procedure for the synthesis of triphenylene from (2-bromophenyl)boronic pinacol ester



To an oven dried 25 mL Schlenk tube containing a stir bar was added the pinacol ester of (2-bromo phenyl)boronic acid (**4a**) (141 mg, 0.50 mmol, 1.00 equiv), Pd catalyst (mol %) and ligand (mol %). A vacuum / N_2 cycle was applied three times to the tube to ensure the removal of air from the reaction vessel. Dry solvent (mL) was added and the mixture was stirred for 1 min before adding the base (equiv). The tube was sealed and heated with stirring in a preheated oil bath at different temperatures for stipulated time. After allotted time the mixture was cooled to room temperature,

diluted with EtOAc (5 mL) and filtered through celite pad. The pad was further washed with EtOAc (40 mL) and the combined organic solvent was evaporated *in vacuo* to afford a crude mixture. The NMR yields were determined by using 1,3,5-trimethoxy benzene as internal standard added to the crude reaction mixture. The reaction mixture could be purified by column chromatography (silica, pet.ether) to yield triphenylene **6a**.

Control experiments and screening of solvents

Table S1

entry	**Pd source (mol %)**	**ligand (mol %)**	**base (equiv)**	**solvent (mL)**	**T (ºC)**	**t (h)**	**yield** [a]
1	-	-	^{t}BuOK (2)	toluene (2)	100	16	-
2	$Pd(dba)_2$ (5)	PPh_3 (10)	-	toluene (2)	100	16	-
3	$Pd(dba)_2$ (5)	-	^{t}BuOK (2)	toluene (2)	100	16	33
4	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	toluene (2)	100	16	60[b]
5	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	toluene (5)	100	16	36
6	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	MeCN (2)	100	16	0
7	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	DMSO (2)	100	16	0
8	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	DCE (2)	100	16	2
9	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	HFIP (2)	100	16	0 [c]
10	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	THF (2)	100	16	58 [c]
11	$Pd(dba)_2$ (5)	PPh_3 (10)	^{t}BuOK (2)	1,4-dioxane (2)	100	16	57

Reactions carried out with 0.5 mmol of **4a** in a Schlenk tube under N_2 atmosphere. *a*: NMR yields. *b*: isolated yield. *c*: reaction carried out in a sealed microwave vial after purging with N_2.

Comments: toluene, THF and 1,4-dioxane afforded the best results.

Screening of temperature and bases

Table S2

entry	Pd source (mol %)	ligand (mol %)	base (equiv)	solvent (mL)	T (ºC)	t (h)	yield [a]
1	$Pd(dba)_2$ (5)	PPh_3 (10)	^tBuOK (2)	toluene (2)	RT	16	3
2	$Pd(dba)_2$ (5)	PPh_3 (10)	^tBuOK (2)	toluene (2)	50	16	7
3	$Pd(dba)_2$ (5)	PPh_3 (10)	K_2CO_3 (2)	toluene (2)	100	16	traces
4	$Pd(dba)_2$ (5)	PPh_3 (10)	NaOMe (2)	toluene (2)	100	16	traces
5	$Pd(dba)_2$ (5)	PPh_3 (10)	tBuOLi (2)	1,4-dioxane (2)	100	16	traces
6	$Pd(dba)_2$ (5)	PPh_3 (10)	Cs_2CO_3 (2)	1,4-dioxane (2)	100	16	34
7	$Pd(dba)_2$ (5)	PPh_3 (10)	CsF (2)	1,4-dioxane (2)	100	16	19
8	$Pd(dba)_2$ (5)	PPh_3 (10)	Cs_2CO_3 (2)	THF (2)	100	16	7
9	$Pd(dba)_2$ (5)	PPh_3 (10)	K_3PO_4 (2)	THF (2)	100	16	9

Reactions carried out with 0.5 mmol of **4a** in a Schlenk tube under N_2 atmosphere. *a*: NMR yields.

Comments: Lower temperatures lead to low product yield. Any other base different from ^tBuOK was less effective.

Screening of Pd catalyst

Table S3

entry	Pd source (mol %)	ligand (mol %)	base (equiv)	solvent (mL)	T (ºC)	t (h)	yield [a]
1	$Pd_2(dba)_3$ (2.5)	PPh_3 (10)	^tBuOK (2)	toluene (2)	100	16	21
2	$Pd(dmba)_2$ (5)	PPh_3 (10)	^tBuOK (2)	toluene (2)	100	16	32
3	$Pd(PPh_3)_4$ (5)	-	^tBuOK (2)	toluene (2)	100	16	35
4	$Pd(OAc)_2$ (5)	PPh_3 (20)	^tBuOK (2)	toluene (2)	100	16	20
5	$PdCl_2$ (5)	PPh_3 (20)	^tBuOK (2)	toluene (2)	100	16	traces
6	Herman-Beller cat.	-	^tBuOK (2)	toluene (2)	100	16	27
7	$Pd(dba)_2$ (10)	PPh_3 (20)	^tBuOK (2)	toluene (2)	100	16	38
8	$Pd(dba)_2$ (2.5)	PPh_3 (5)	^tBuOK (2)	toluene (2)	100	16	10

Reactions carried out with 0.5 mmol of **4a** in a Schlenk tube under N_2 atmosphere. *a*: NMR yields.

Comment: Other palladium sources different from $Pd(dba)_2$ were less effective.

Screening of ligands and stoichiometry of the base

Table S4

entry	Pd source (mol %)	ligand (mol %)	base (equiv)	solvent (mL)	T (ºC)	t (h)	yield [a]
1	$Pd(dba)_2$ (5)	PPh_3 (20)	^tBuOK (2)	toluene (2)	100	16	15
2	$Pd(dba)_2$ (5)	dppe (5)	^tBuOK (2)	toluene (2)	100	16	46
3	$Pd(dba)_2$ (5)	PPh_3 (10)	^tBuOK (1)	toluene (2)	100	16	73 [b]
4	$Pd(dba)_2$ (5)	P(*o*-Tol)$_3$ (10)	^tBuOK (1.1)	toluene (2)	100	16	38
5	$Pd(dba)_2$ (5)	dppb (5)	^tBuOK (1.1)	toluene (2)	100	16	50
6	$Pd(dba)_2$ (5)	DBBP (5)	^tBuOK (1.1)	toluene (2)	100	16	47
7	$Pd(dba)_2$ (5)	DPE (5)	^tBuOK (1.1)	toluene (2)	100	16	78 [b]
8	$Pd(dba)_2$ (5)	DPE (6)	^tBuOK (1.1)	toluene (2)	100	16	76 [b]
9	$Pd(dba)_2$ (5)	XantPhos (5)	^tBuOK (1.1)	toluene (2)	100	16	64
10	$Pd(dba)_2$ (5)	DPPF (5)	^tBuOK (1.1)	toluene (2)	100	16	54

Reactions carried out with 0.5 mmol of **4a** in a Schlenk tube under N_2 atmosphere. *a*: NMR yields. *b*: isolated yield.

Comment: Bulky phosphines such as P(*o*-Ttol)$_3$ or DBBP gave lower yields. Reducing equivalents of base from 2 to 1.1 equiv afforded better results. DPEphos showed the best results.

Miscellaneous screening

Table S5

entry	Pd source (mol %)	ligand (mol %)	base (equiv)	solvent (mL)	T (ºC)	t (h)	yield [a]
1	$Pd(dba)_2$ (5)	DPE (5)	^tBuOK (1.1)	1,4-dioxane (2)	100	16	73 [b]
2	$Pd(dba)_2$ (5)	DPE (5)	tBuONa (1.1)	toluene (2)	100	16	46
3	PdPEPPSI (5)	-	^tBuOK (1.1)	toluene (2)	100	16	35
4	$Pd(dba)_2$ (5)	DPE (5)	^tBuOK (1.1)	toluene (1)	100	16	67
5	$Pd(dba)_2$ (2.5)	DPE (2.5)	^tBuOK (1.1)	toluene (2)	100	16	75 [b]
6	$Pd(dba)_2$ (2.5)	DPE (2.5)	^tBuOK (1.1)	toluene (2)	100	7	73 [b]
7	$Pd(dba)_2$ (1)	DPE (1.1)	^tBuOK (1.1)	toluene (2)	100	7	60

Reactions carried out with 0.5 mmol of **4a** in a Schlenk tube under N_2 atmosphere. *a*: NMR yields. *b*: isolated yield.

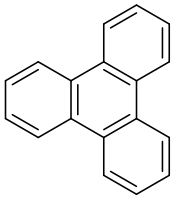
Comment: Lowering the Pd catalyst loading was tolerated, but slightly less effective.

Representative procedure C for the synthesis of triphenylene compounds 6a – 6l

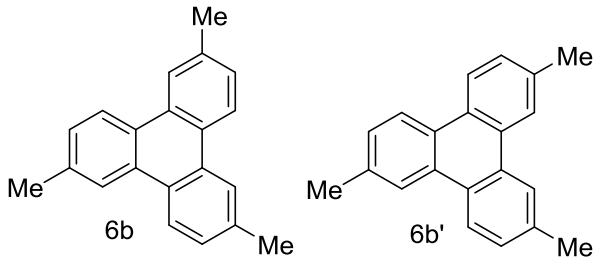
To an oven dried 25 mL Schlenck tube containing a stir bar was added the pinacol ester of 2-bromo phenylboronic acid (**4a**) (141 mg, 0.50 mmol, 1.00 equiv), $Pd(dba)_2$ (15 mg, 0.026 mmol, 5 mol %) and DPE phos (14 mg, 0.026 mmol, 5 mol %). A vacuum / N_2 cycle was applied three times to the tube in order to ensure the removal of air from the reaction vessel. Dry toluene distilled under N_2 (2 mL) was added and the mixture was stirred for 1 min before adding ^tBuOK (63 mg, 0.56 mmol, 1.1 equiv). The tube was sealed and heated with stirring in a preheated oil bath at 100 ºC for 16h. After that time the mixture was cooled to room temperature, diluted with EtOAc (5 mL) and filtered through celite pad. The pad was further washed with EtOAc (40 mL) and the combined organic solvent was evaporated *in vacuo* to afford a crude mixture that was latter purified by column chromatography (silica, petroleum ether) to yield triphenylene **6a** (29.8 mg, 0.129 mmol, 78% yield).

Spectroscopic data for triphenylenes 6a –6k.

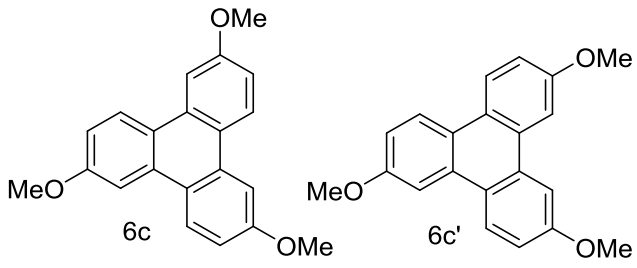
Triphenylene (6a). White solid. Mp: 196–198 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.69-8.65 (m, 6 H), 7.69-7.65 (m, 6 H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ 129.7 (C_q), 127.2 (CH), 123.25 (CH). HR-MS (EI) *m/z* calcd for $C_{18}H_{12}$ $[M]^+$ 228.0934, found 228.0927. The data are in agreement with those previously reported in the literature.[8]



2,6,10-Trimethyltriphenylene (6b) and 2,6,11-trimethyltriphenylene (6b'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give a mixture (1:3) of triphenylenes **6b** and **6b'** (30 mg, 0.111 mmol, 66% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 8.3 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 8.43 (br s, 2H), 8.39 (br s, 2H), 7.43-7.47 (m, 4H), 2.62 (s, 3H), 2.61 (s, 3H), 2.61 (s, 3H), 2.60 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 136.6 (C_q), 136.5 (C_q), 136.3 (C_q), 136.2 (C_q), 130.0 (C_q), 129.8 (C_q), 129.5 (C_q), 129.5 (C_q), 128.5 (CH), 128.4 (CH), 128.16 (CH), 128.1 (CH), 127.7 (C_q), 127.5 (C_q), 127.2 (C_q), 127.0 (C_q), 123.2 (CH), 123.19 (CH), 123.18 (CH), 123.13 (CH), 123.07 (CH), 123.02 (CH), 122.99 (CH), 122.95 (CH), 21.82 (br s, 2 CH_3), 21.80 (br s, 2 CH_3). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}$ $[M]^+$ 270.1403, found 270.1397. The data are in agreement with those previously reported in the literature.[9, 10, 11, 12, 13]

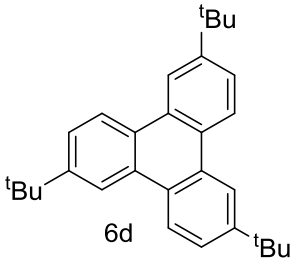


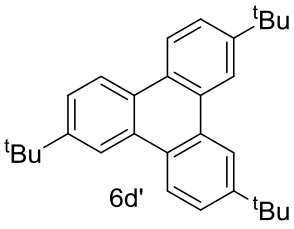
2,6,10-Trimethoxytriphenylene (6c) and 2,6,11-trimethyltriphenylene (6c'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet.ether/EtOAc: 15/1) to give a mixture (1:3) of triphenylenes **6c** and **6c'** (26 mg, 0.082 mmol, 49% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.40-8.47 (m, 4 H), 7.91-7.94 (m, 4 H), 7.23-7.27 (m, 2 H), 7.20 (t, *J* = 2.5 Hz, 1H), 7.18 (t, *J* = 2.5 Hz, 1H), 4.02 (s, 3H, OMe), 4.01 (s, 3H, OMe), 4.01 (s, 3H, OMe), 4.00 (s, 3H, OMe). ^{13}C-NMR (126 MHz, $CDCl_3$): 159.0 (C_q), 158.8 (C_q), 158.2 (C_q), 158.0 (C_q), 131.8 (C_q), 131.3 (C_q), 130.2 (C_q), 129.7 (C_q), 125.0 (CH), 124.9 (CH), 124.4 (CH), 124.35 (C_q), 124.3 (CH), 123.9 (C_q), 122.9 (C_q), 122.5 (C_q), 115.6 (CH), 115.4 (CH), 114.9 (CH), 114.7 (CH), 106.13 (CH), 106.11 (CH), 105.3 (CH), 105.2 (CH), 55.48 (OMe),



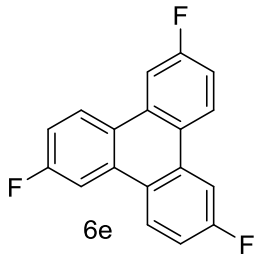
55.46 (OMe), 55.42 (OMe), 55.40 (OMe). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}O_3$ $[M]^+$ 318.1250, found 318.1242. The data are in agreement with those previously reported in the literature.[9,14]

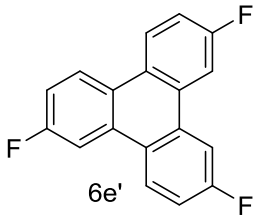
2,6,10-Tri-*tert*-butyltriphenylene (6d) and 2,6,11-trimethyltriphenylene (6d'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give a mixture (1:3) of triphenylenes **6d** and **6d'** (49 mg, 0.124 mmol, 74% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.71 (d, J = 2.1 Hz, 1H), 8.69 (d, J = 2.1 Hz, 1H), 8.67-8.64 (m, 4 H), 8.58 (d, J = 6.5 Hz, 1H), 8.56 (d, J = 6.5 Hz, 1H), 7.70–7.77 (m, 4 H), 1.56 (s, 9H), 1.55 (s, 9H), 1.54 (s, 9H), 1.53 (s, 9H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 149.5 (C_q), 149.4 (C_q), 149.3 (C_q), 149.2 (C_q), 129.7 (C_q), 129.5 (C_q), 129.3 (C_q), 129.1 (C_q), 127.9 (C_q), 127.6 (C_q), 127.5 (C_q), 127.2 (C_q), 124.9 (CH), 124.8 (CH), 124.7 (CH), 124.6 (CH), 123.0 (CH), 122.98 (CH), 122.9 (CH), 122.8 (CH), 119.1 (CH), 119.0 (CH), 118.9 (CH), 118.8 (CH), 35.01 (br s, C_q), 35.00 (br s, C_q), 31.50 (CH, ^{t}Bu) , 31.49 (CH, ^{t}Bu), 31.47 (CH, ^{t}Bu), 31.45 (CH, ^{t}Bu). HR-MS (EI) *m/z* calcd for $C_{30}H_{36}$ $[M]^+$ 396.2812, found 396.2815. The data are in agreement with those previously reported in the literature.[9, 11, 15]





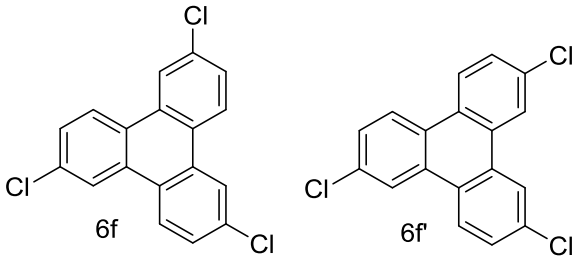
2,6,10-Trifluorotriphenylene (6e) and 2,6,11-trimethyltriphenylene (6e'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give a mixture (1:3) of triphenylenes **6e** and **6e'** (34 mg, 0.120 mmol, 72% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.51–8.47 (m, 2 H), 8.46–8.41 (m, 2 H), 8.13 (t, J = 2.3 Hz, 1H), 8.11 (t, J = 2.3 Hz, 1H), 8.08 (dd, J = 4.1, 2.7 Hz, 1H), 8.05 (dd, J = 4.1, 2.7 Hz, 1H), 7.42–7.34 (m, 4 H). ^{13}C-NMR (126 MHz, $CDCl_3$): 162.6 (d, J_{C-F} = 248.2 Hz, C_q), 162.4 (d, J_{C-F} = 247.2 Hz, C_q), 162.1 (d, J_{C-F} = 247.2 Hz, C_q), 161.9 (d, J_{C-F} = 246.5 Hz, C_q), 131.7 (d, J_{C-F} = 8.4 Hz, C_q), 131.4 (dd, J_{C-F} = 8.0, 3.6 Hz, C_q), 130.7 (d, J_{C-F} = 8.0 Hz, C_q), 130.3 (dd, J_{C-F} = 8.0, 3.6 Hz, C_q), 126.2 (d, J_{C-F} = 2.0 Hz, C_q), 125.91 (d, J_{C-F} = 8.0 Hz, CH), 125.87 (d, J_{C-F} = 8.0 Hz, CH), 125.5 (d, J_{C-F} = 8.3 Hz, CH), 125.4 (d, J_{C-F} = 8.3 Hz, CH), 125.3 (br s, C_q), 124.9 (br s, C_q), 116.3 (d, J_{C-F} = 22.3 Hz, CH), 116.2 (d, J_{C-F} = 22.8 Hz, CH), 115.5 (d, J_{C-F} = 23.0 Hz, CH), 115.4 (d, J_{C-F} = 23.0 Hz, CH), 109.1 (d, J_{C-F} = 8.0 Hz, CH), 108.9 (d, J_{C-F} = 8.0 Hz, CH), 108.8 (d, J_{C-F} = 6.9 Hz, CH), 108.6 (d, J_{C-F} = 6.3 Hz, CH). ^{19}F-NMR (471 MHz, $CDCl_3$) δ = –112.59 (s), –112.65 (s), –113.84 (d, J = 1.7 Hz), –113.89 (d, J = 1.7 Hz).



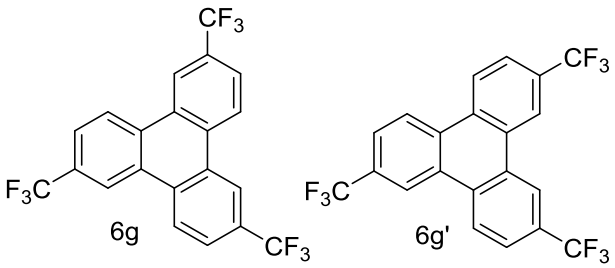


HR-MS (EI) *m/z* calcd for $C_{18}H_9F_3$ $[M]^+$ 282.0651, found 282.0640. The data are in agreement with those previously reported in the literature.[9]

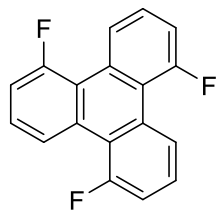
2,6,10-Triclorotriphenylene (6f) and 2,6,11-trimethyltriphenylene (6f'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give a mixture (1:3) of triphenylenes **6f** and **6f'** (27.5 mg, 0.083 mmol, 50% yield). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.42-8.35 (m, 8H), 7.61-7.53 (m, 4H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 134.3 (C_q), 134.27 (C_q), 133.9 (C_q), 133.86 (C_q), 130.7 (C_q), 130.3 (br s, 2 C_q), 129.8 (C_q), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.85 (CH), 127.76 (C_q), 127.3 (C_q), 127.28 (C_q), 126.8 (C_q), 124.93 (CH), 124.92 (CH), 124.8 (CH), 124.77 (CH) 123.1 (2 CH), 123.0 (2 CH). HR-MS (EI) *m/z* calcd for $C_{18}H_9Cl_3$ $[M]^+$ 329.9764, found 329.9776. The data are in agreement with those previously reported in the literature.[16]



2,6,10-Tri(triflouromehtyl)triphenylene (6g) and 2,6,11-trimethyltriphenylene (6g'). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give a mixture (1:3) of triphenylenes **6g** and **6g'** (43.5 mg, 0.101 mmol, 60% yield). ^{1}H-NMR (500 MHz, d_6-acetone): δ = 9.25 (br s, 2H), 9.15–9.12 (m, 4H), 9.05 (d, J = 8.2 Hz, 2H), 8.11–8.08 (br m, 4 H). ^{13}C-NMR (126 MHz, d_6-acetone): 132.2 (C_q), 131.9 (C_q), 131.8 (C_q), 131.5 (C_q), 130.2-129.2 (overlapped m, several C_q), 129.0 (CH), 125.6 (CH), 125.5 (CH), 125.4 (CH), 125.3 (CH), 124.7-124.6 (overlapped m, CH), 124.5-124.4 (overlapped m, CH), 124.42 (q, $J_{C\text{-}F}$ = 272.6 Hz, C_q), 124.39 (q, $J_{C\text{-}F}$ = 272.1 Hz, C_q), 124.36 (q, $J_{C\text{-}F}$ = 271.6 Hz, C_q). ^{19}F-NMR (471 MHz, d_6-acetone) δ = –114.88 (s), –114.84 (s), –114.78 (s), –114.74 (s). HR-MS (EI) *m/z* calcd for $C_{21}H_9F_9$ $[M]^+$ 432.0555, found 432.0573. The data are in agreement with those previously reported in the literature.[9]



1,5,9-Trifluorotriphenylene (6h). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet. ether) to give triphenylenes **6h** and **6h'** which could be separated by column chromatography. Triphenylene **6h**, R_f = 0.6, (1 mg, 0.003 mmol, 2% yield). White solid. Mp: 180–182 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.86 (dd, J = 8.5, 3.9 Hz, 3 H), 7.63–7.58 (m, 3 H), 7.40

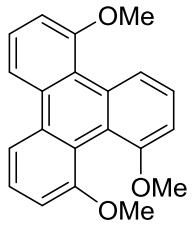


(ddd, J = 14.4, 7.7, 0.9 Hz, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 160.9 (d, $J_{C\text{-}F}$ = 251.8 Hz, C_q), 130.4 (dd, $J_{C\text{-}F}$ = 5.7, 2.8 Hz, C_q), 128.1 (dd, $J_{C\text{-}F}$ = 10.9, 2.4 Hz, CH), 124.0 (dd, $J_{C\text{-}F}$ = 29.9, 4.1 Hz, CH), 119.2 (m, C_q), 115.3 (dd, $J_{C\text{-}F}$ = 26.5, 2.5 Hz, CH). ^{19}F-NMR (376 MHz, $CDCl_3$) δ = –107.67 (s). IR (υ cm^{-1}, intensity): 2923 (w), 1607 (m), 1577 (br), 1491 (w), 1420 (s), 1294 (w), 1260 (w), 1228 (s), 1105 (w), 1057 (w), 871 (w), 799 (br), 736 (s). HR-MS (EI) *m/z* calcd for $C_{18}H_9F_3$ $[M]^+$ 282.0651, found 282.0639.

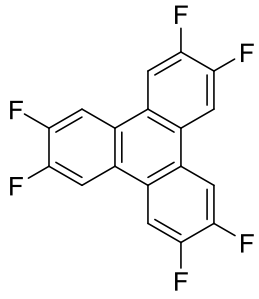
1,5,12-Trifluorotriphenylene (6h'). R_f = 0.4. (15 mg, 0.053 mmol, 32% yield). White solid. Mp: 136–138 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.80 (ddd, J = 8.5, 3.9, 1.0 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.65–7.60 (m, 2 H), 7.57 (td, J = 8.1, 5.2 Hz, 1H), 7.39–7.32 (m, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): 161.2 (d, $J_{C\text{-}F}$ = 252.5 Hz, C_q), 160.2 (dd, $J_{C\text{-}F}$ = 212.2, 42.7 Hz, C_q), 159.9 (dd, $J_{C\text{-}F}$ = 232.4, 21.0 Hz, C_q), 132.6 (m, 2 C_q), 130.55 (dd, $J_{C\text{-}F}$ = 5.1, 3.2 Hz, C_q), 128.8 (br d, $J_{C\text{-}F}$ = 8.6 Hz, CH), 128.7 (dd, $J_{C\text{-}F}$ = 8.5, 1.1 Hz, CH), 128.4 (d, $J_{C\text{-}F}$ = 10.5 Hz, CH), 122.7 (dd, $J_{C\text{-}F}$ = 27.0, 3.2 Hz, CH), 119.5 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 119.1 (dd, $J_{C\text{-}F}$ = 8.6, 2.3 Hz, C_q), 118.9 (d, $J_{C\text{-}F}$ = 2.7 Hz, CH), 115.7 (d, $J_{C\text{-}F}$ = 25.5 Hz, CH), 115.6 (partially overlapped d, $J_{C\text{-}F}$ = 8.4 Hz, C_q), 115.5 (d, $J_{C\text{-}F}$ = 8.9 Hz, C_q), 114.8 (m, CH), 114.6 (m, CH). ^{19}F-NMR (471 MHz, $CDCl_3$) δ = –102.63 (AB system, J_{AB} = 141.8 Hz), –108.10 (s). IR (υ cm^{-1}, intensity): 2925 (w), 2359 (br), 1608 (m), 1577 (br), 1547 (m), 1482 (w), 1442 (m),1424 (w), 1406 (m), 1278 (w), 1250 (m), 1232 (s), 1140 (w), 958 (m), 837 (w), 750 (s), 730 (s), 705 (m), 532 (m). HR-MS (EI) *m/z* calcd for $C_{18}H_9F_3$ $[M]^+$ 282.0651, found 282.0642.

1,5,9-Trimethoxytriphenylene (6i). The representative procedure **C** was followed. The crude was purified by column chromatography (silica, pet.ether/EtOAc: 20/1) to give triphenylenes **6i** and **6i'** which could be separated by column chromatography. Triphenylene **6i**, R_f = 0.22, (11.5 mg, 0.036 mmol, 21% yield). Colorless dense oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.00 (dd, J = 8.5, 1.0 Hz, 3H), 7.48 (t, J = 8.2 Hz, 3H), 7.14 (dd, J = 8.2, 1.0 Hz, 3H), 4.02 (s, 9H, OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (s, Cq), 131.7 (s, Cq), 126.3 (s, CH), 121.1 (s, Cq), 121.0 (s, CH), 110.0 (s, CH), 56.1 (s, CH_3). IR (υ cm^{-1}, intensity): 2940 (br), 2934 (w), 2833 (w), 1593 (m), 1575 (s), 1482 (m), 1461 (w), 1412 (s), 1284 (m), 1241 (vs), 1180 (w), 1123 (m), 1077 (s), 1011 (vs), 821 (m), 744 (s), 573 (m). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}O_3$ $[M]^+$ 318.1250, found 318.1241. The data are in agreement with those previously reported in the literature.[18]

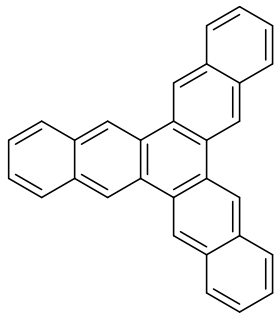
1,5,12-Trimethoxytriphenylene (6i'). R_f = 0.17. (13 mg, 0.041 mmol, 24% yield). Pale yellow solid. Mp: 184–186 ºC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.05 (dd, J = 8.5, 1 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.47-7.53 (m, 3 H), 7.13 (dd, J = 8.0, 1 Hz, 1H), 7.09 (dd, J = 8.0, 1 Hz, 1H), 7.05 (dd, J = 8.1, 0.8 Hz, 1H), 4.06 (s, 3H, OMe), 3.99 (br s, 6H, OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (s, Cq), 157.8 (s, Cq), 157.0 (s, Cq), 133.0 (s, Cq), 132.6 (s, Cq), 131.9 (s, Cq), 127.2 (s, CH), 127.0 (s, CH), 126.8 (s, CH), 121.1 (s, Cq), 118.8 (s, CH), 118.4 (s, Cq), 118.0 (s, Cq), 115.9 (s, CH), 115.0 (s, CH), 110.4 (s, CH), 108.6 (s, CH), 108.5 (s, CH), 56.0 (s, CH_3), 55.9 (s, CH_3), 55.8 (s, CH_3). IR (υ cm^{-1}, intensity): 2940 (br), 2933 (w), 2832 (w), 1573 (m), 1546 (w), 1478 (w), 1460 (m), 1426 (w), 1248 (vs), 1179 (w), 1151 (w), 1066 (w), 1019 (vs), 862 (w), 776 (s), 732 (m). HR-MS (EI) *m/z* calcd for $C_{21}H_{18}O_3$ $[M]^+$ 318.1250, found 318.1247. The data are in agreement with those previously reported in the literature.[18]



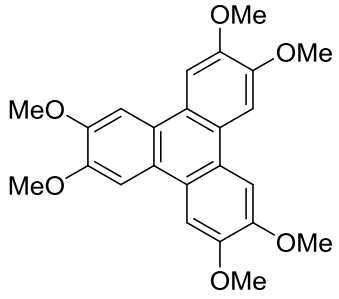
2,3,6,7,10,11-Hexafluorotriphenylene (6j). The representative procedure **C** was followed. The crude reaction mixture was taken to dryness, cold $CHCl_3$ (5 mL) was added and the resulting suspension was filtered. The solid was washed with cold $CHCl_3$ (2 mL) and loaded in a chromatography column for purification (silica, petroleum ether/EtOAc: 4/1) to yield the **6j** as a white solid (18.5 mg, 0.055 mmol, 33% yield). Mp: > 320 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.18 (t, J = 10.0 Hz, 6H). ^{19}F-NMR (471 MHz, $CDCl_3$) δ = –135.5 (s). The low solubility of the product in all common deuterated solvents prevented us from measuring the ^{13}C-NMR spectra. HR-MS (EI) *m/z* calcd for $C_{18}H_6F_6$ $[M]^+$ 336.0368, found 336.0363. The data are in agreement with those previously reported in the literature.[18]



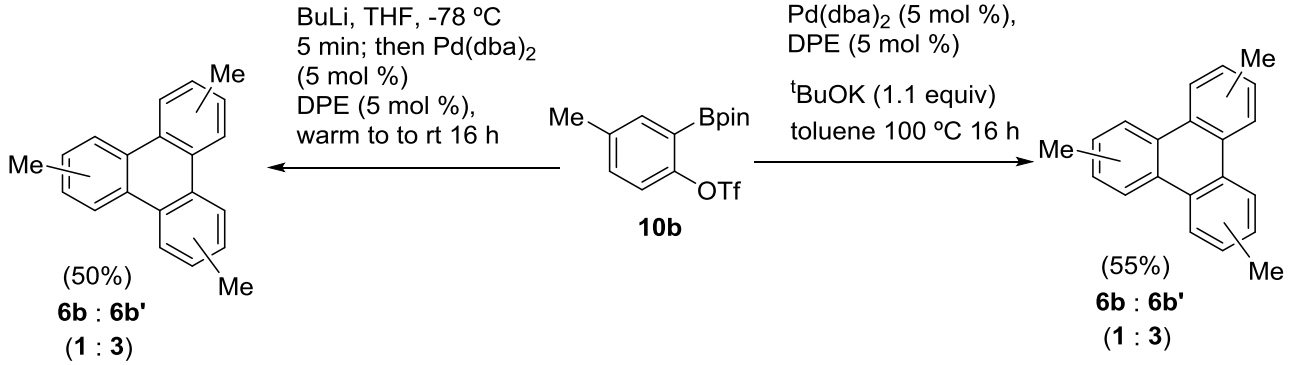
Trinaphthylene (6k). The representative procedure **C** was followed. The reaction mixture was cooled in an ice bath. The supension was filtered and the solid was washed with cold MeCN (3 x 5 mL) and cold CH_2Cl_2 (1 mL). The grey solid was dissolved in CH_2Cl_2 (150 mL) and filtered through a pad of Celite. The solvent from the filtrate was removed to dryness to afford trinaphthylene **6k** as a white solid (29.5 mg, 0.078 mmol, 47% yield). Mp: > 320 ºC ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.13 (s, 6H), 8.11–8.09 (m, 6H), 7.59–7.57 (m, 6 H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 132.8 (C_q), 129.0 (C_q), 128.1 (CH), 126.4 (CH), 122.7 (CH). HR-MS (EI) *m/z* calcd for $C_{30}H_{18}$ $[M]^+$ 378.1403, found 378.1409. The data are in agreement with those previously reported in the literature.[19]



2,3,6,7,10,11-Hexamethoxytriphenylene (6l, not in paper). The representative procedure **C** was followed. The reaction mixture was cooled in an ice bath. The supension was filtered and the solid was washed with cold MeCN (3 × 3 mL). The grey solid was dissolved in CH_2Cl_2 (200 mL) and filtered through a pad of Celite. The solvent from the filtrate was removed to dryness to afford triphenylene **6l** as a white solid (24.5 mg, 0.060 mmol, 36% yield). Mp: 324–326 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.73 (s, 6H), 4.11 (s, 18H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.7 (C_q), 123.2 (C_q), 104.3 (CH), 56.0 (OMe). HR-MS (EI) *m/z* calcd for $C_{24}H_{24}O_6$ $[M]^+$ 408.1567, found 408.1569. The data are in agreement with those previously reported in the literature.[17]



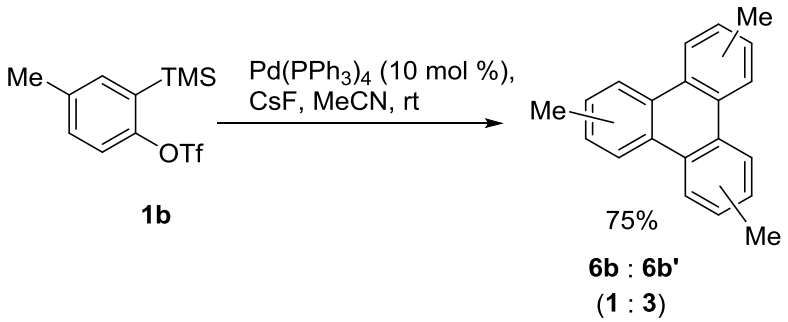
Cyclotrimerization of 2-triflato derivative **10b**:



a) When the substrate **10b** was submitted to the standard reaction conditions (procedure **C**) a 55% isolated yield of triphenylenes **6b**:**6b'** (1:3) was obtained.

b) To an oven dried 25 mL Schlenk tube containing a stir bar was added the pinacol ester **10b** (92 mg, 0.25 mmol, 1.00 equiv). Vacuum/N_2 cycle was applied three times to the tube in order to ensure the removal of air from the reaction vessel. Dry THF distilled under N_2 (2 mL) was added and the mixture was cooled to –78 ºC. Then, a 1.6 M solution of *n*-BuLi in hexane (170 μL, 0.27mmol, 1.1 equiv) was added. After 5 min $Pd(dba)_2$ (7.5 mg, 0.013 mmol, 5 mol%) and DPE phos (7 mg, 0.013 mmol, 5 mol%) were added. the tube was removed from the cooling bath and allowed to reach r.t and stirred for 16h. The reaction mixture was purified by column chromatrograpy using petroleum ether to afford a 50 % yield (11.5 mg, 0.042 mmol) of a mixture of triphenylenes **6b**:**6b'** (1:3).

Cyclotrimerization of the benzyne precursor 4-methyl 2-(trimethylsilyl)phenyl triflate.



1b

75%

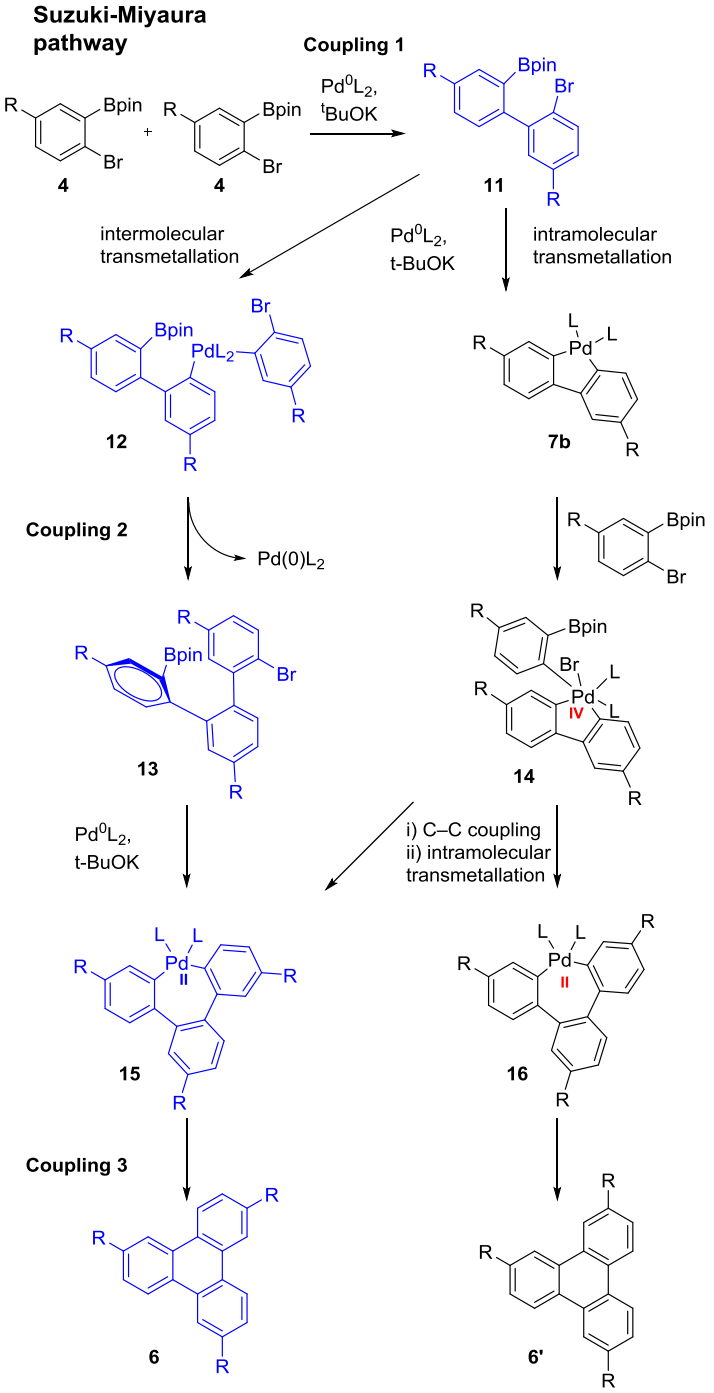
6b : **6b'**

(**1** : **3**)

To an oven dried 25 mL Schlenck tube containing a stir bar was added the benzyne precursor 4-methyl 2-(trimethylsylil) triflatobenzene (**1b**), prepared according to ref. 20, (156 mg, 0.50 mmol, 1.00 equiv), CsF (152 mg, 1 mmol, 2 equiv) and $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 10 mol%). Vacuum/N_2 cycle was applied three times to the tube in order to ensure the removal of air from the reaction vessel. Dry acetonitrile (3 mL) was added and the mixture was stirred at r.t. for 16 h. The usual purification procedure afforded a 75% isolated yield (34 mg, 0.126 mmol) of a mixture of triphenylenes **6b**:**6b'** (1:3).

Suzuki-Miyaura mechanism

An alternative Suzuki-Miyaura mechanism is set out in Scheme S1. Three successive Suzuki-Miyaura processes are not consistent with the isolation of triphenylene regio-isomers, as this pathway would yield the C_3-symmetric compound **6** exclusively.



An alternative inter / intra / inter-molecular process, *via* palladacycle **7b**, is possible, but unlikely. It would require a high energy Pd(IV) intermediate (**14**), and yield mixtures of palladacycles **15** and **16** according to the respective relative rates of reductive elimination. A consistent product ratio of 1:3 would not be expected to arise for a range of different R groups in this scenario.

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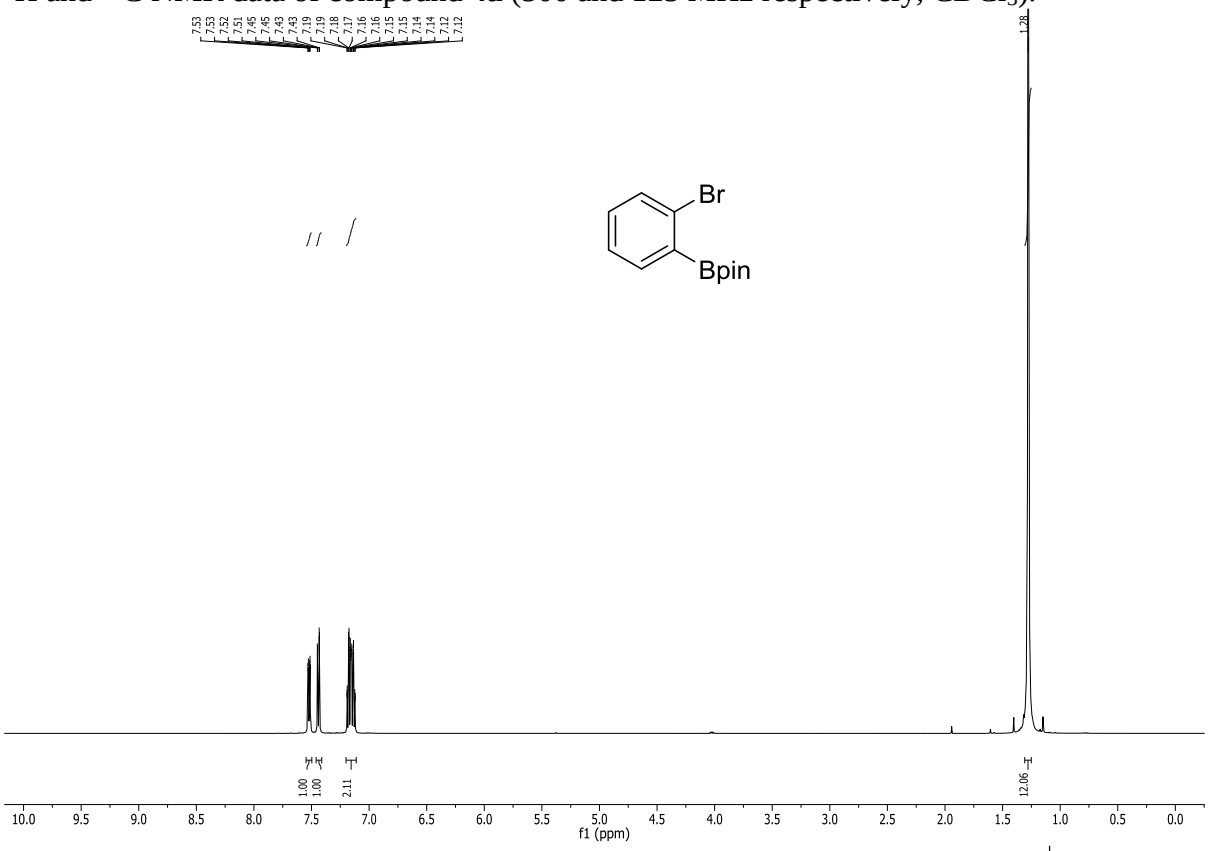
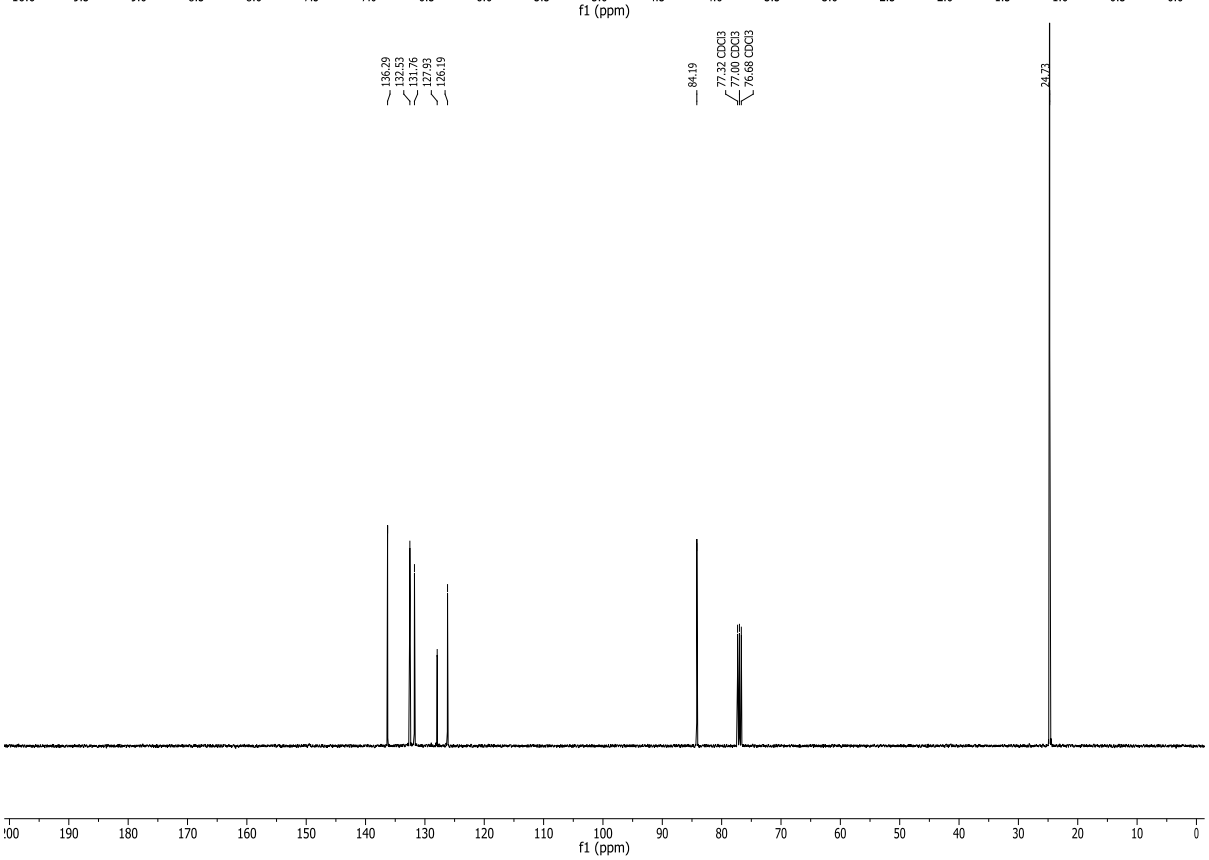
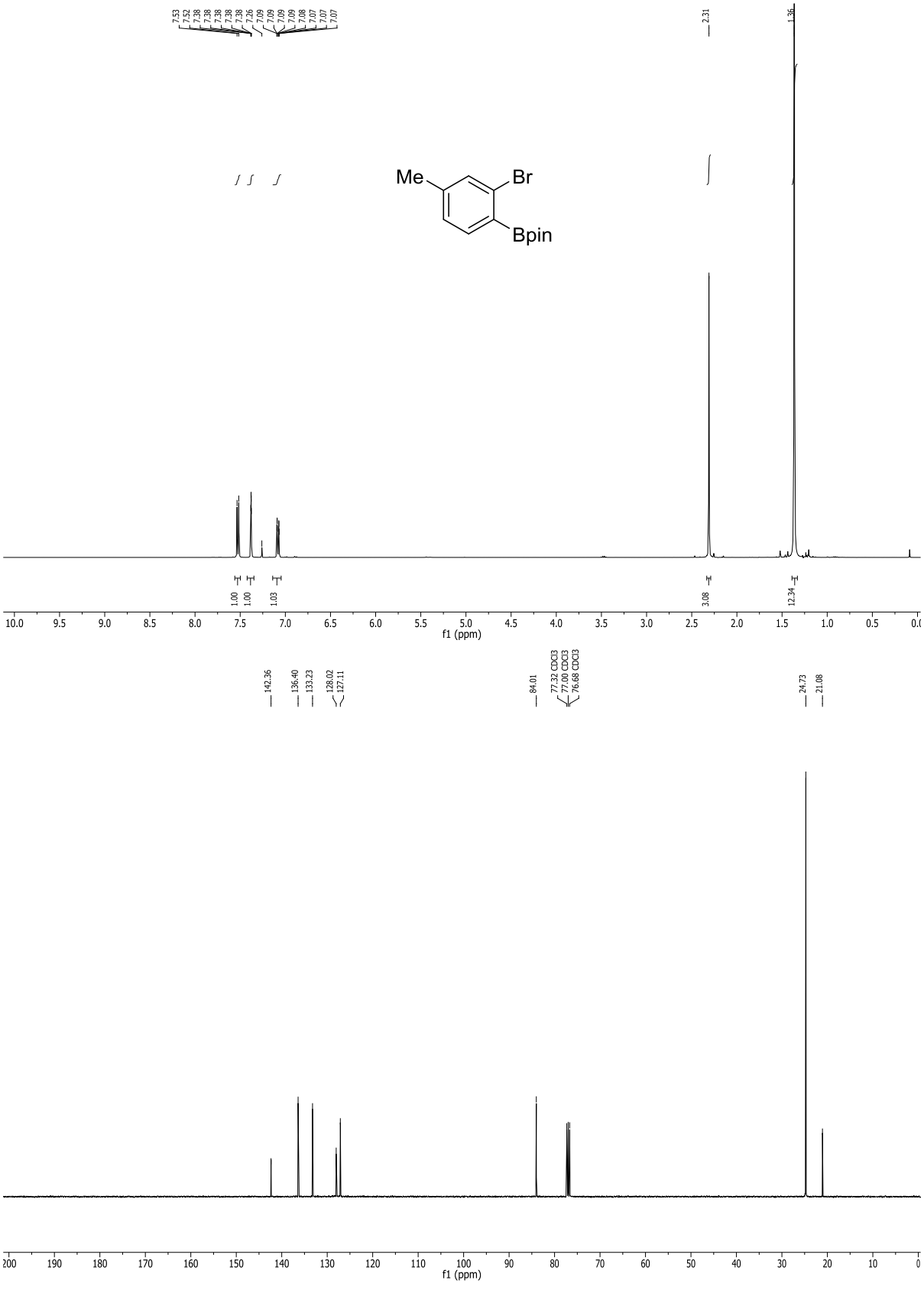
Spectroscopic Data

^{1}H and ^{13}C NMR data of compound **4a** (500 and 125 MHz respectively, $CDCl_3$).

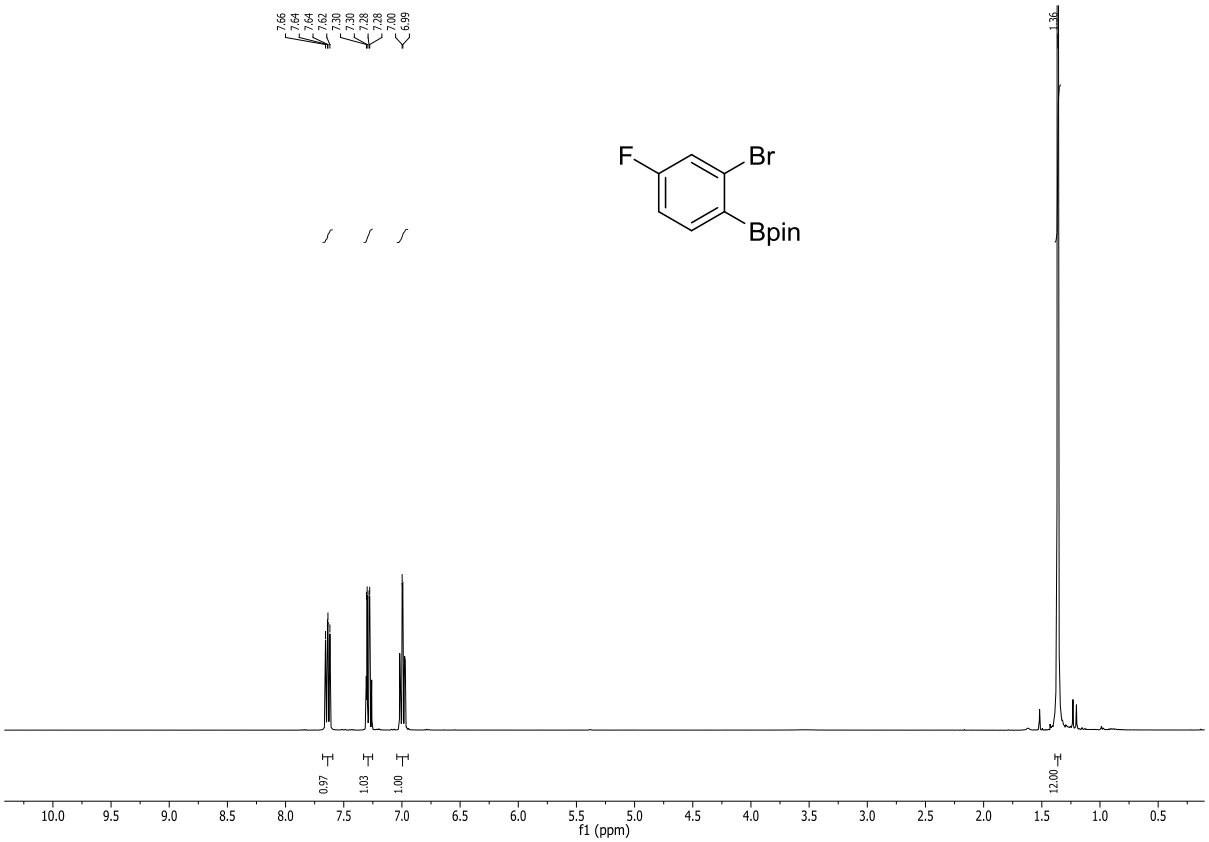


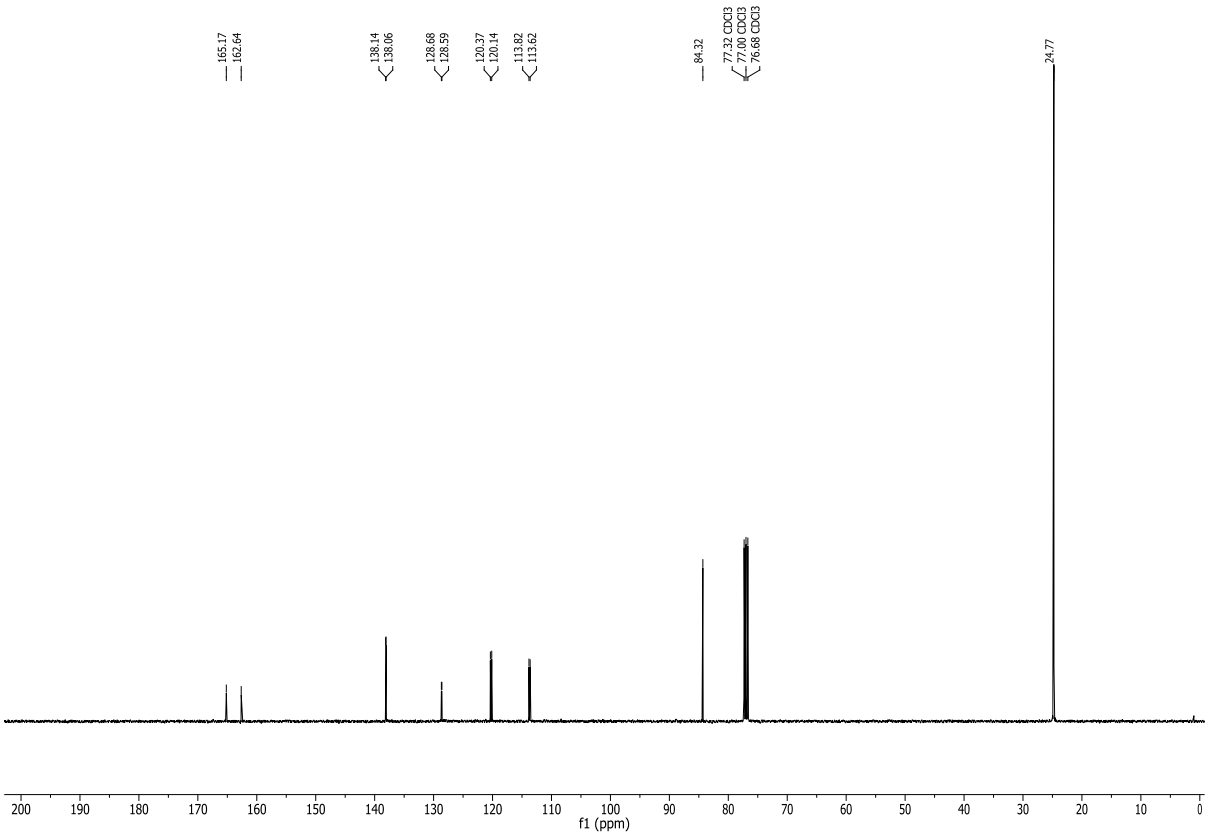


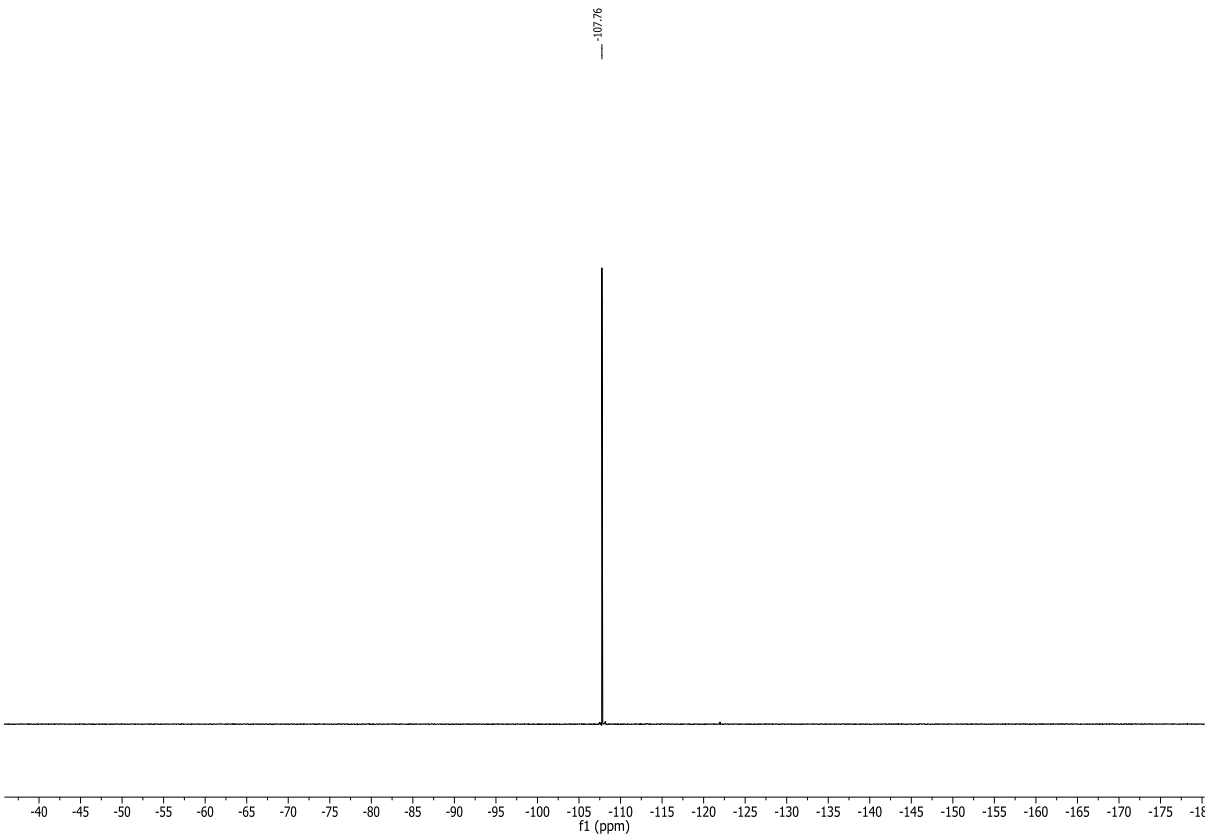
^{1}H and ^{13}C NMR data of compound **4b** (400 and 101 MHz respectively, $CDCl_3$).



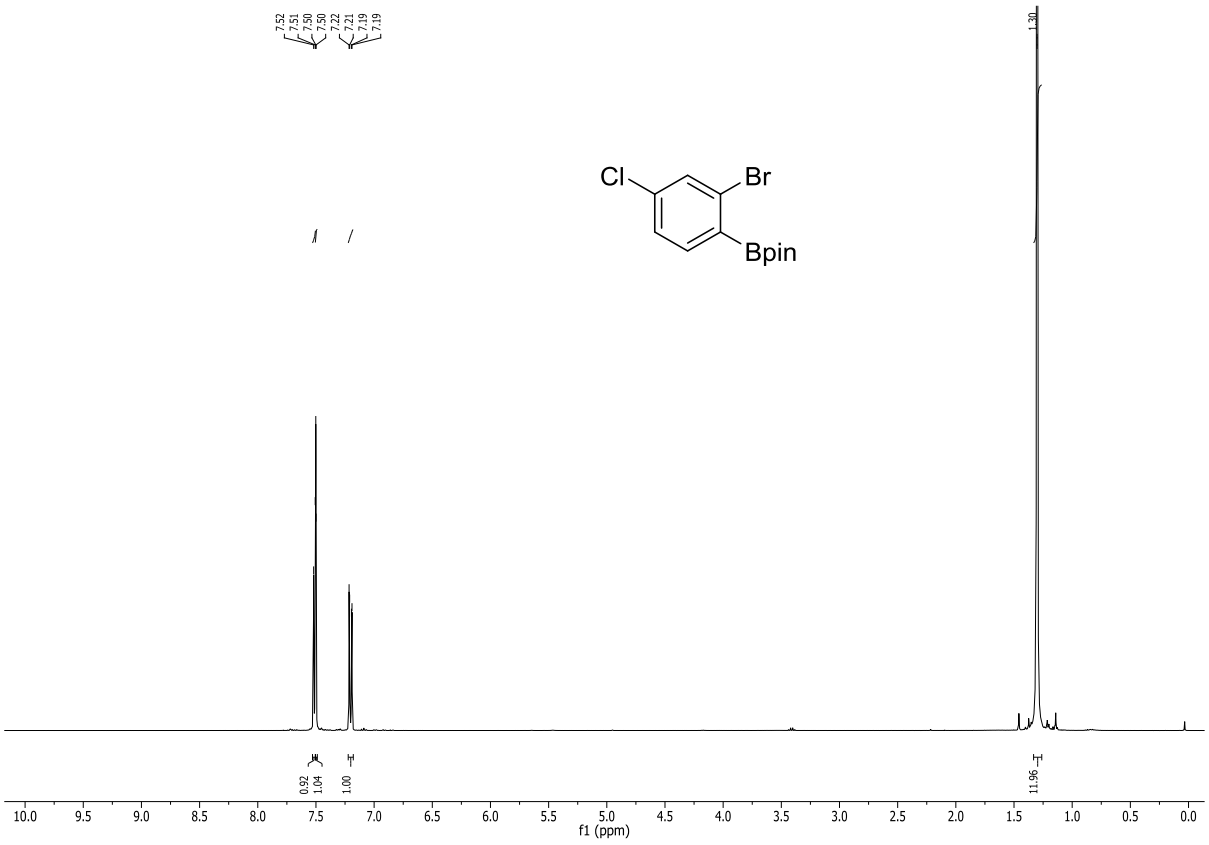
^{1}H, ^{13}C and ^{19}F NMR data of compound **4e** (400, 101 and 376 MHz respectively, $CDCl_3$).

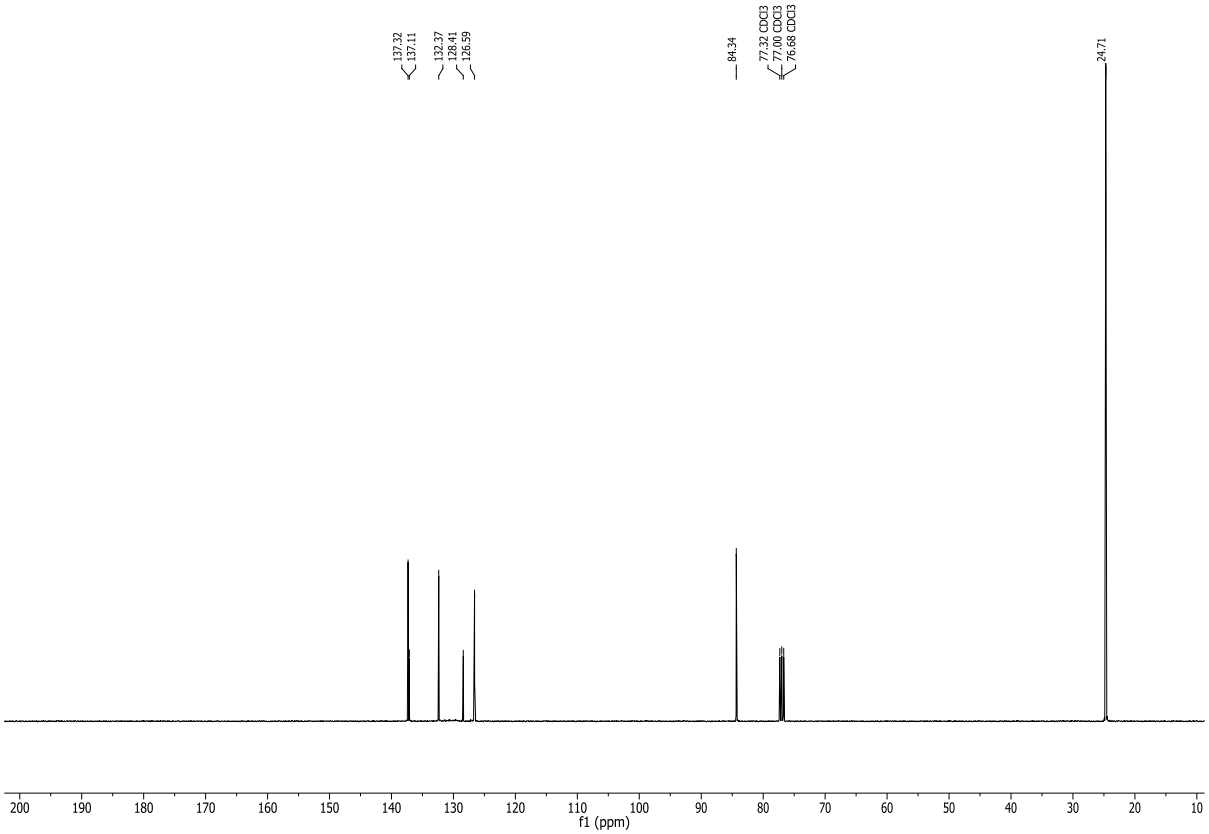




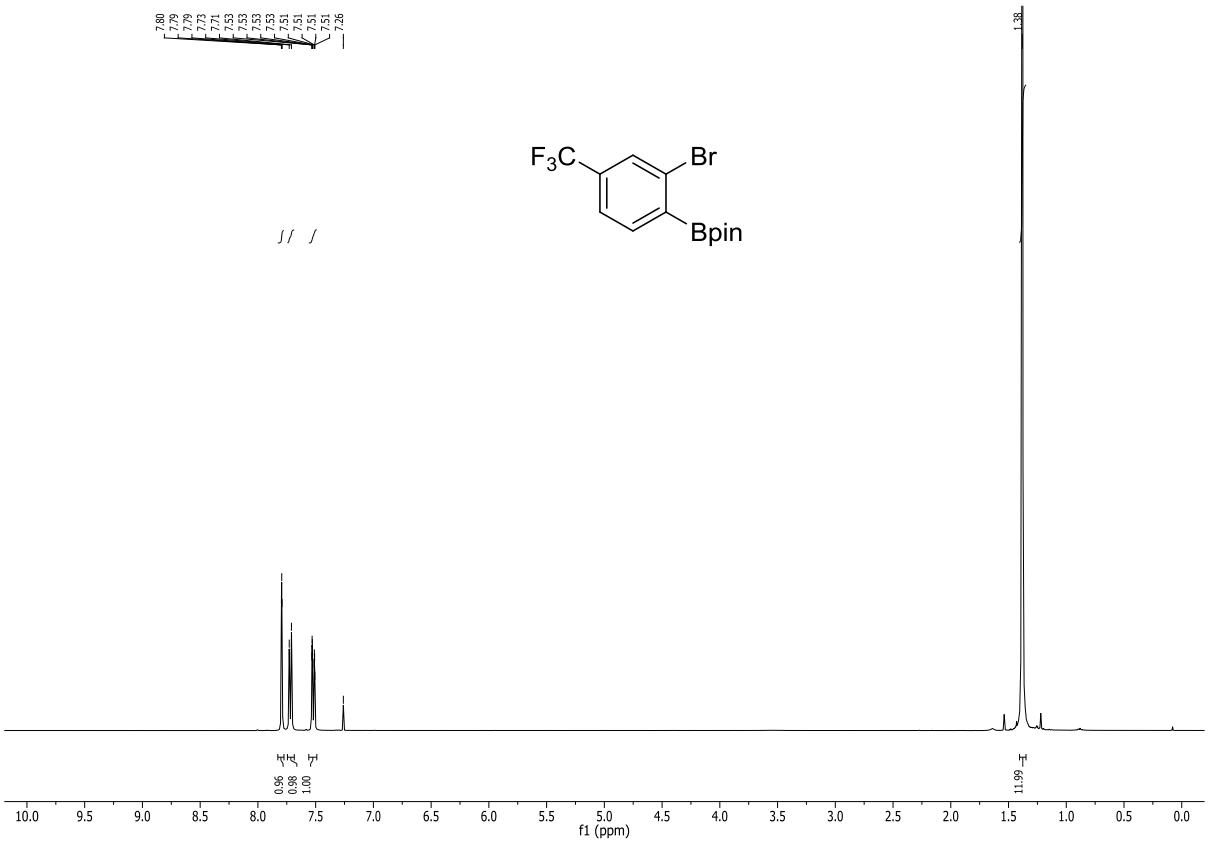


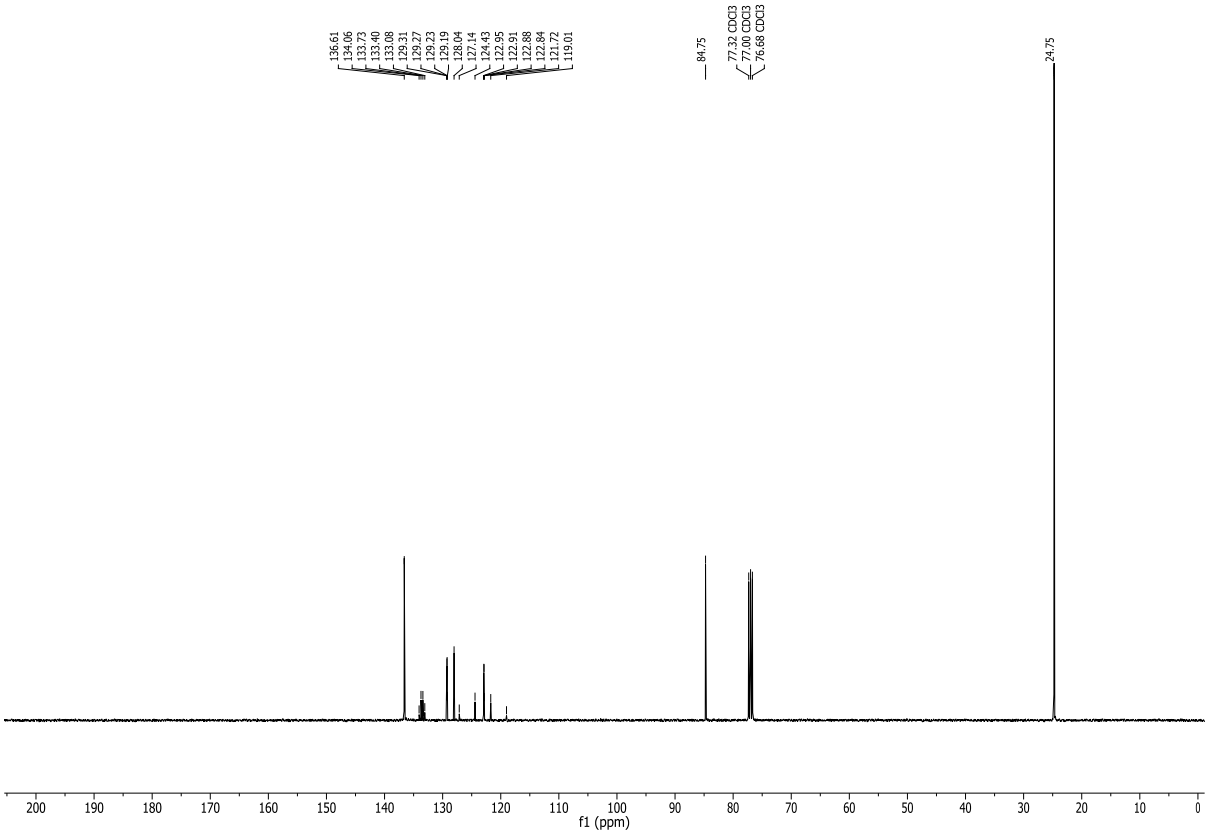
^{1}H and ^{13}C NMR data of compound **4f** (400 and 101 MHz respectively, $CDCl_3$).





^{1}H, ^{13}C and ^{19}F NMR data of compound **4g** (400, 101 and 376 MHz respectively, $CDCl_3$).




136.61
134.06
133.73
133.40
133.08
129.31
129.27
129.23
129.19
128.04
127.14
124.43
122.95
122.91
122.88
122.84
121.72
119.01
84.75
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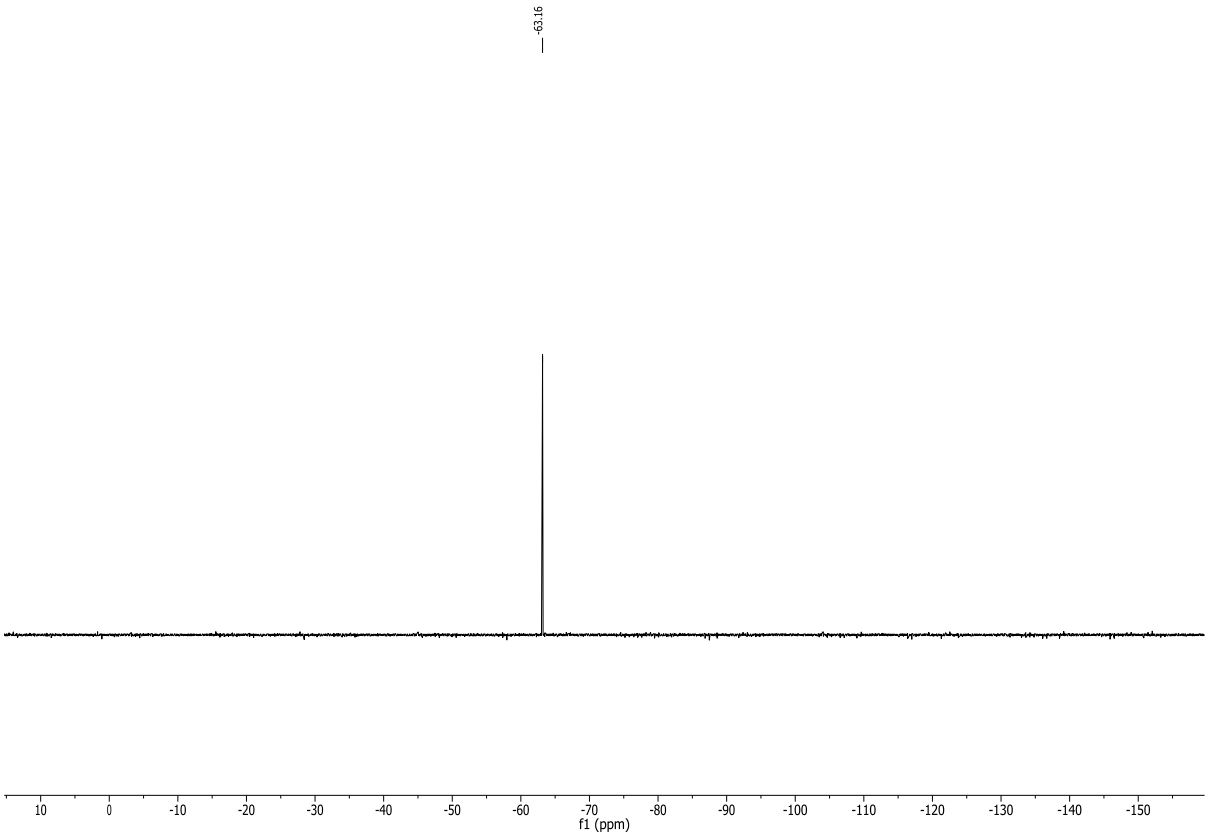
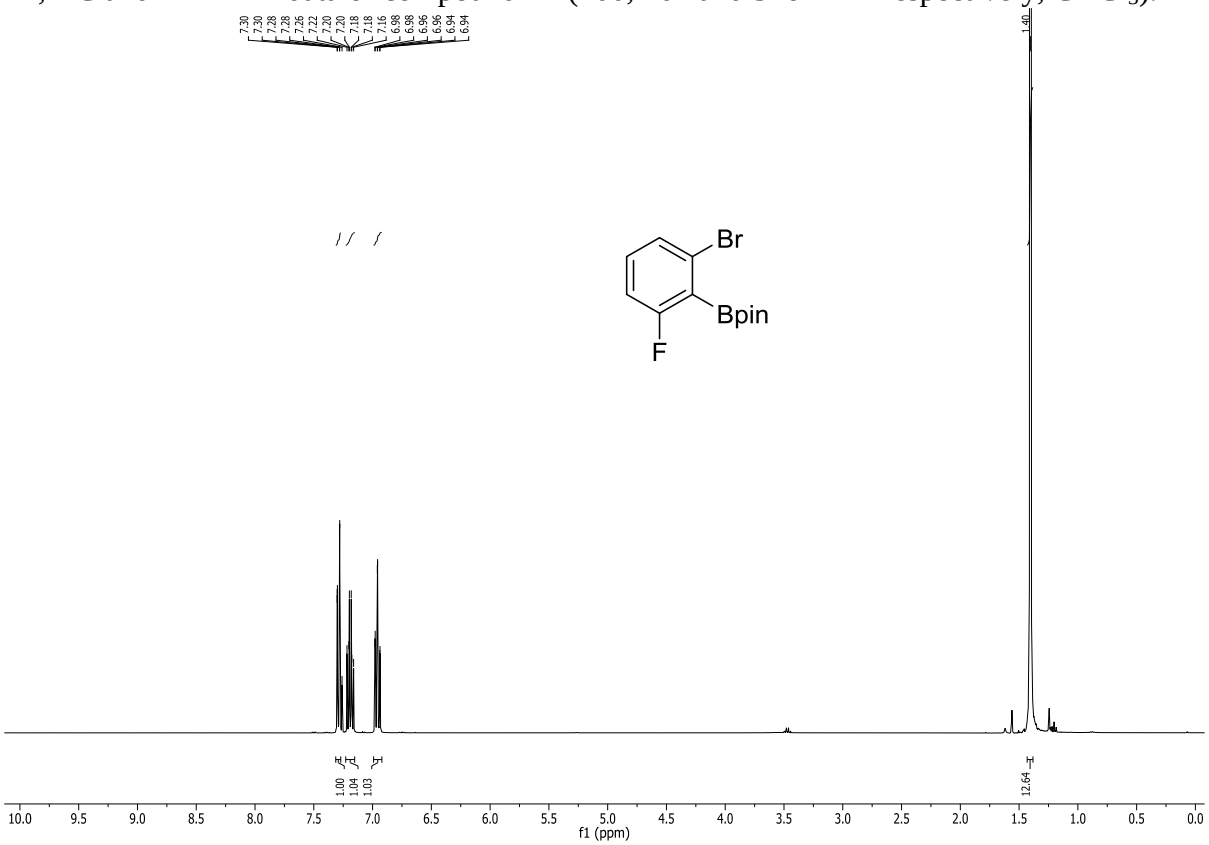
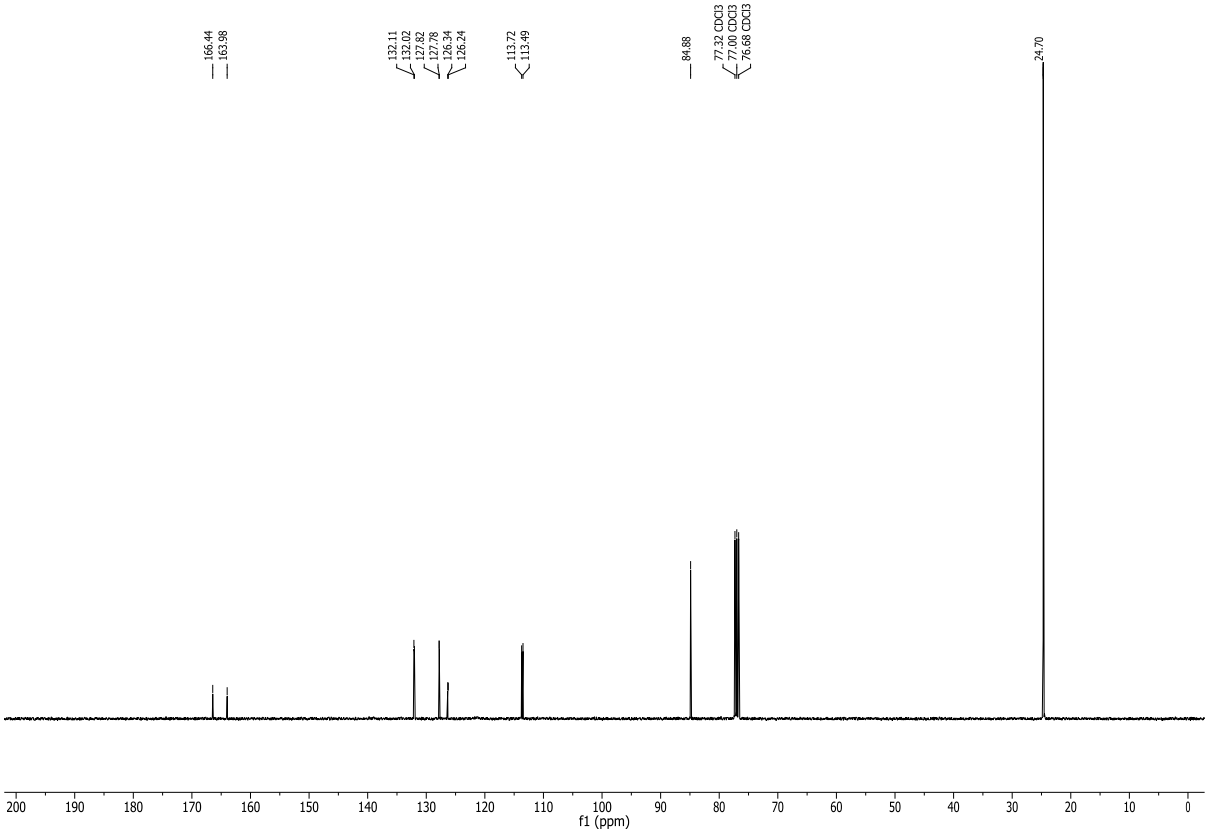
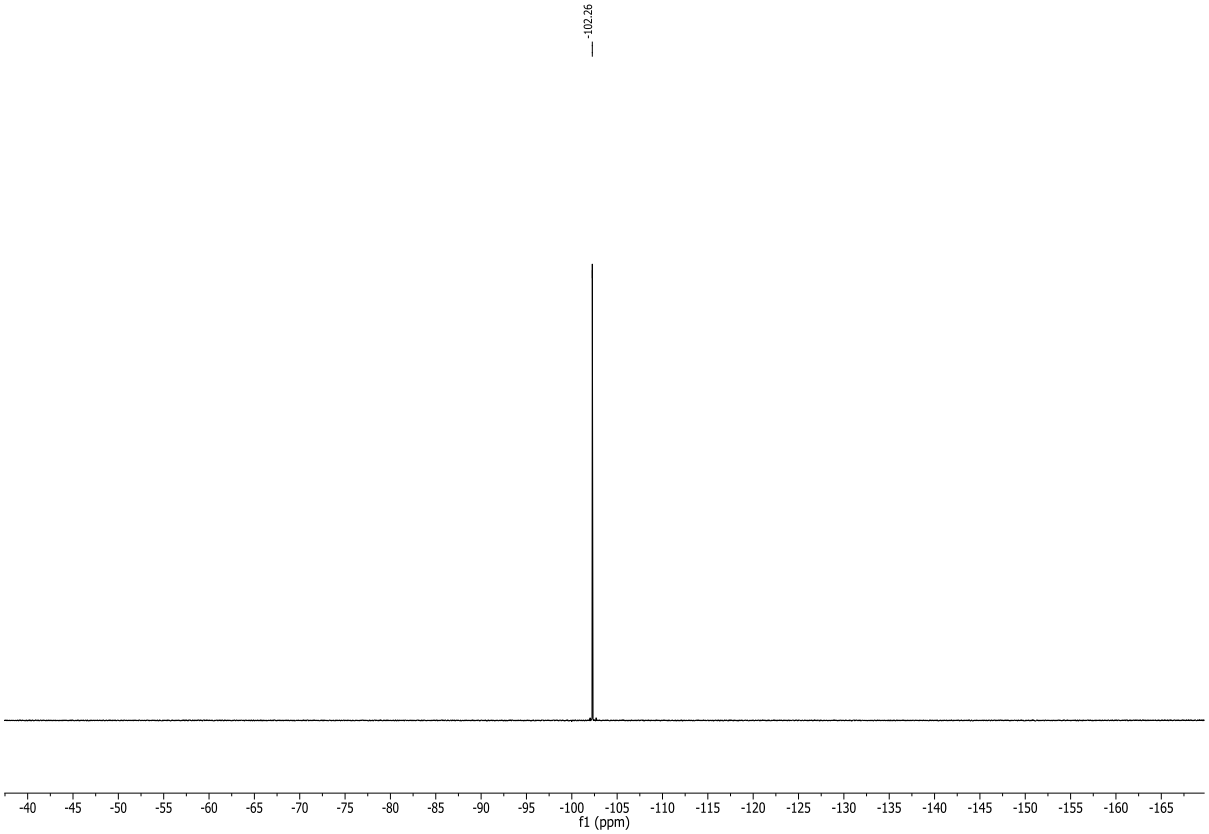
f1 (ppm)


-63.16
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

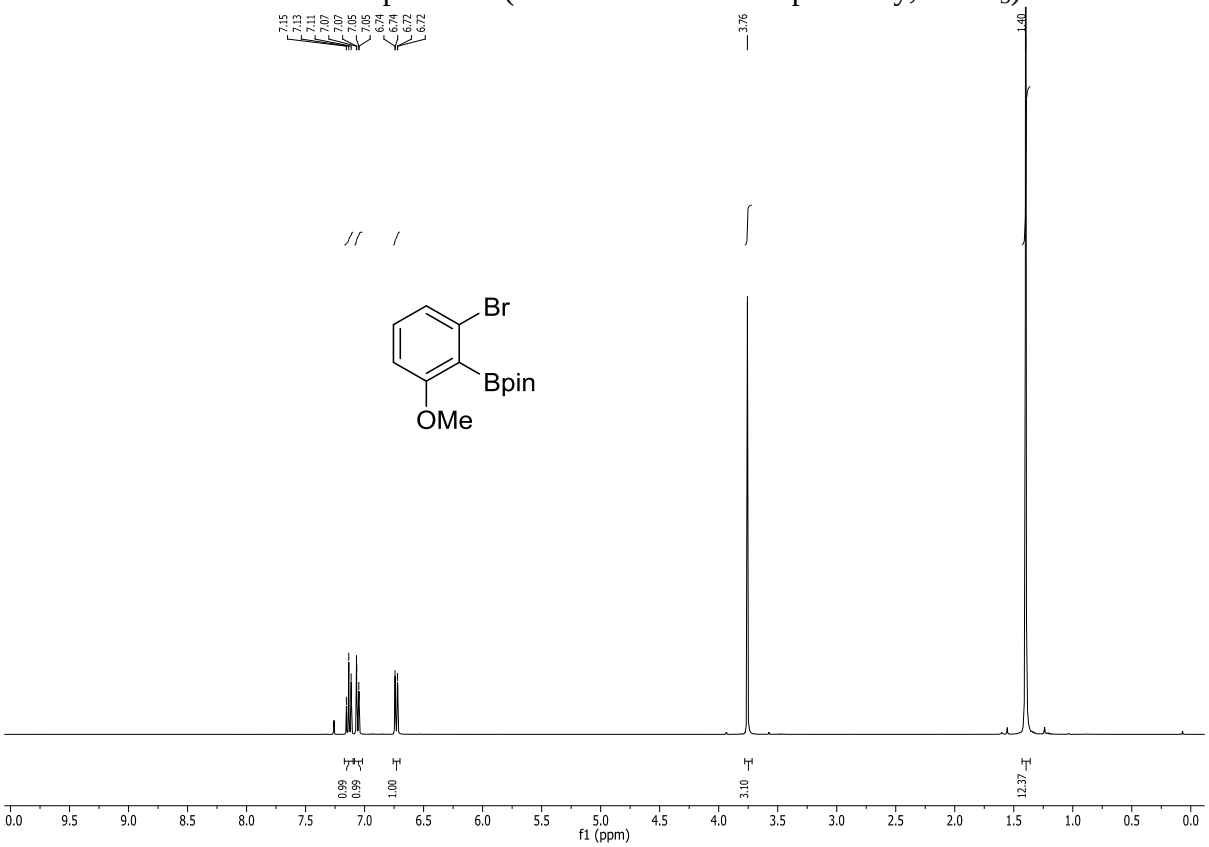
^{1}H, ^{13}C and ^{19}F NMR data of compound **4h** (400, 101 and 376 MHz respectively, $CDCl_3$).

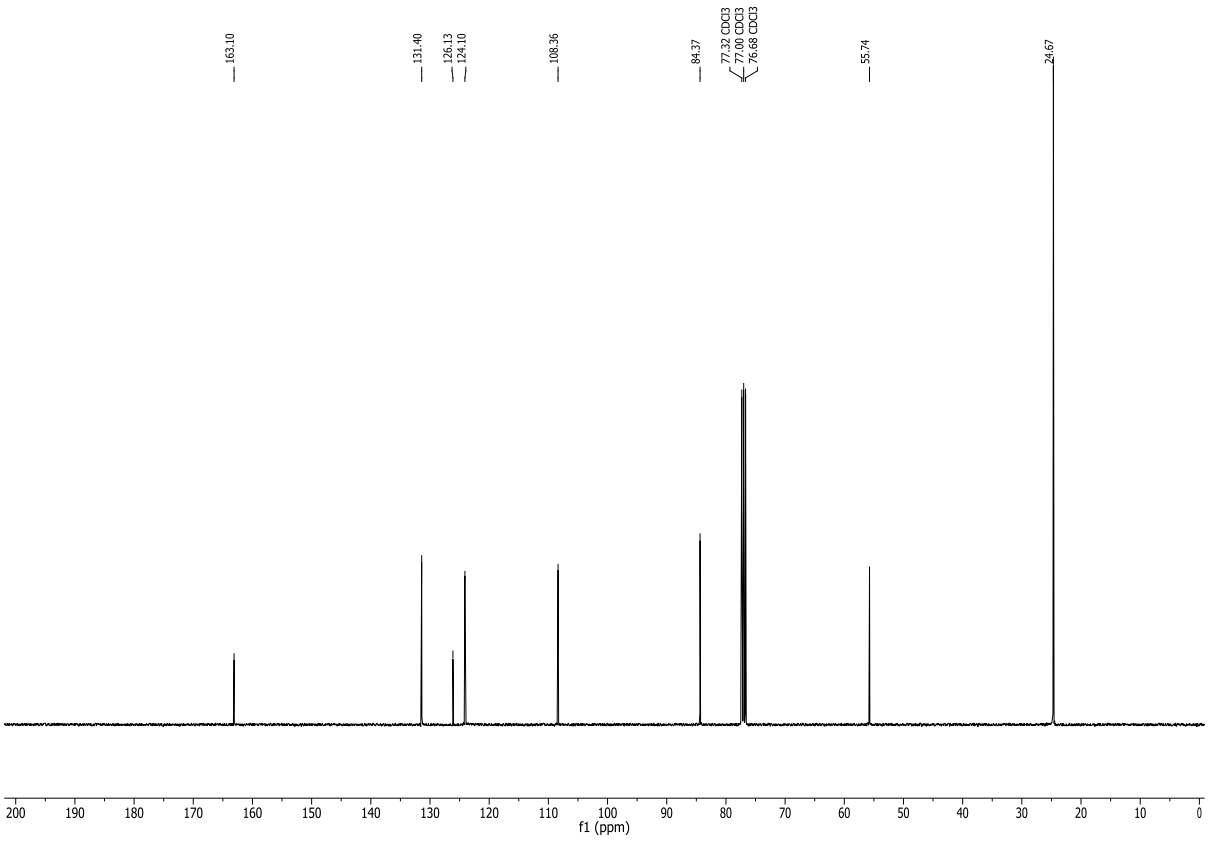




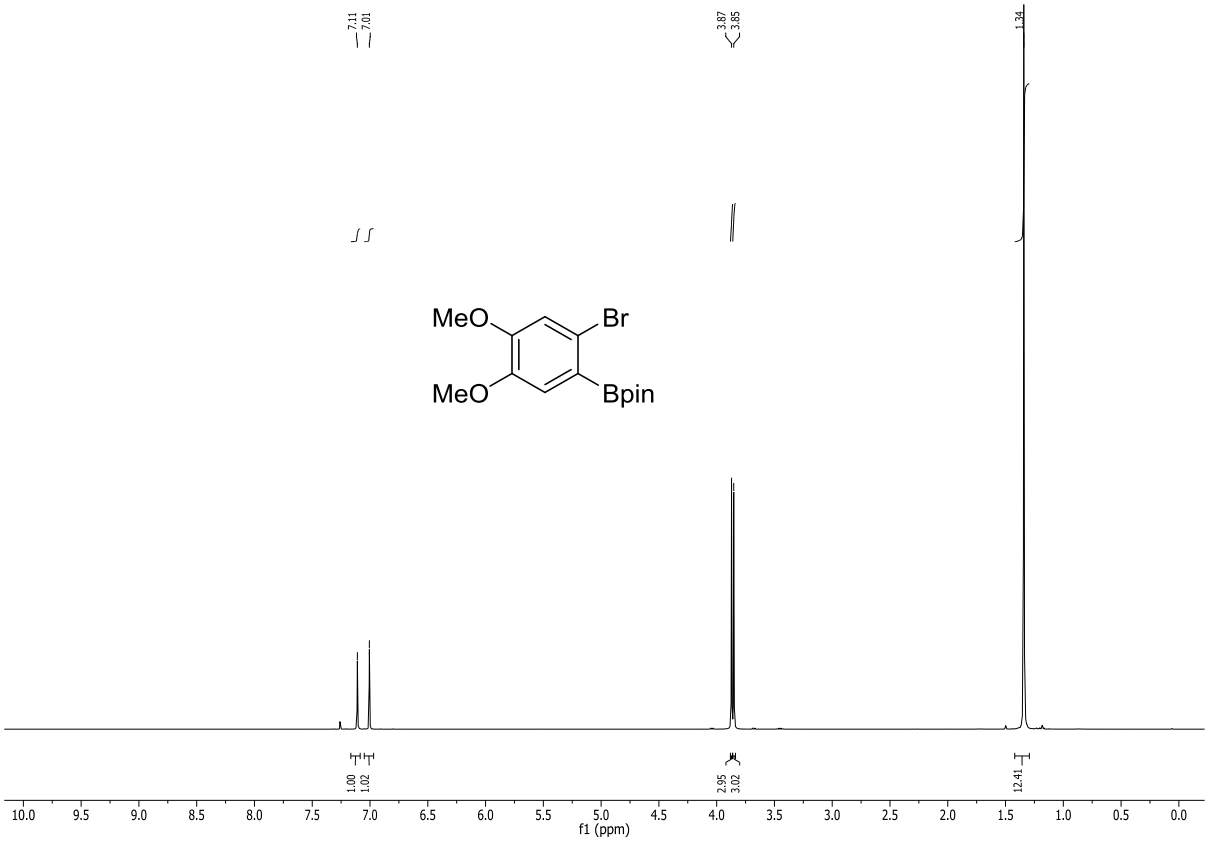


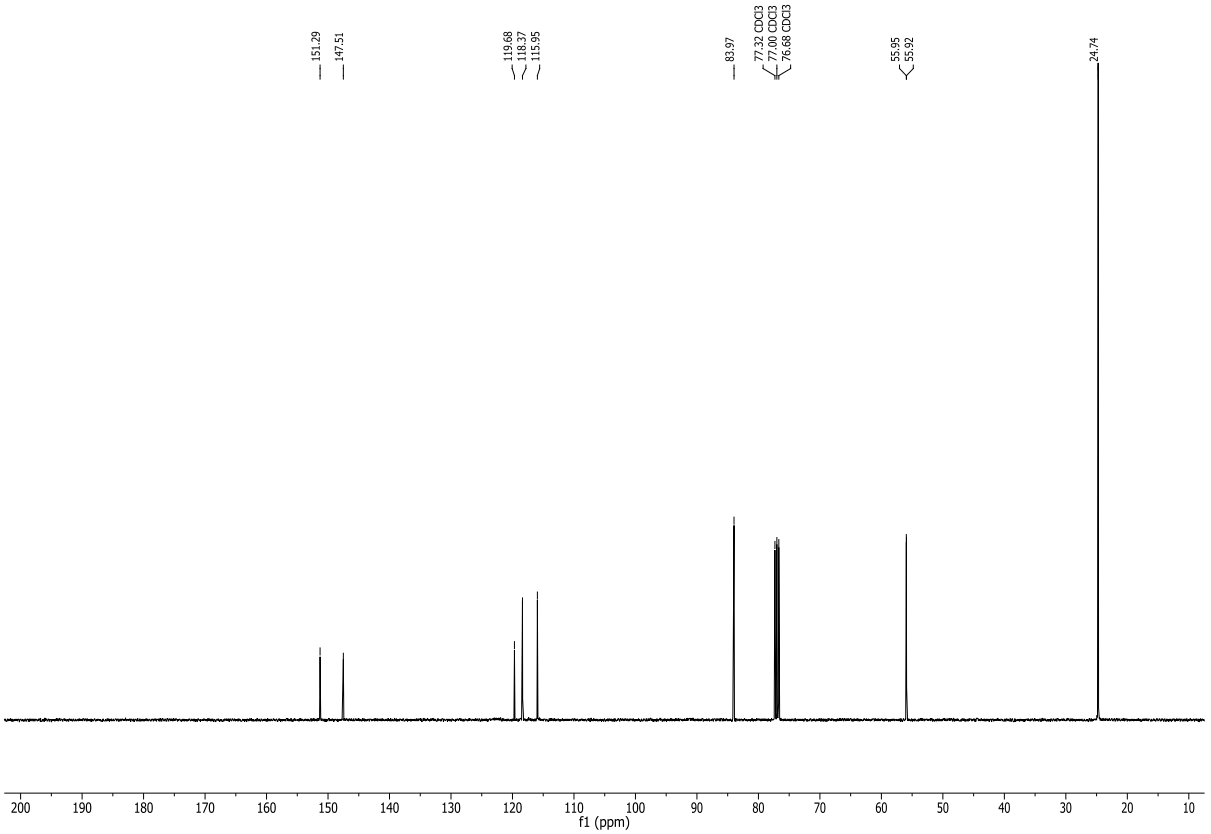
^{1}H and ^{13}C NMR data of compound **4i** (400 and 101 MHz respectively, $CDCl_3$).



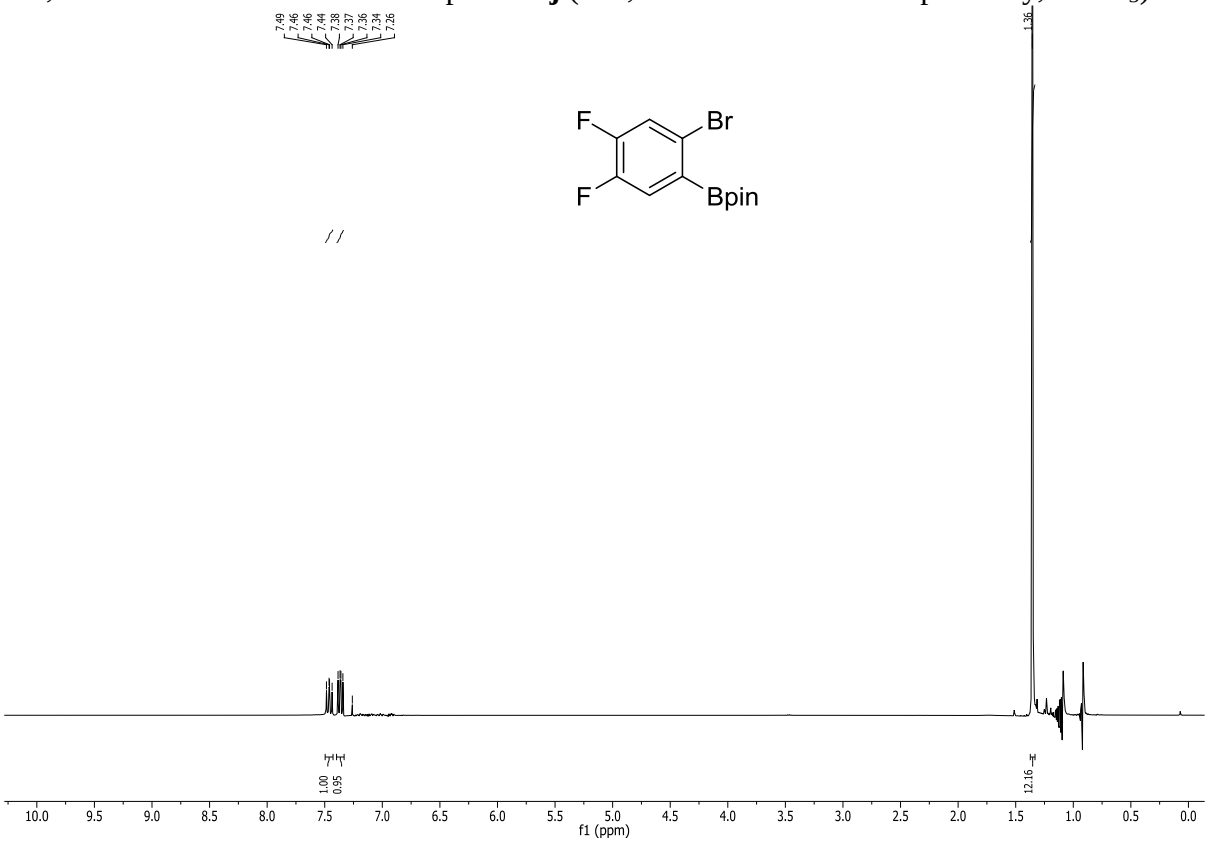


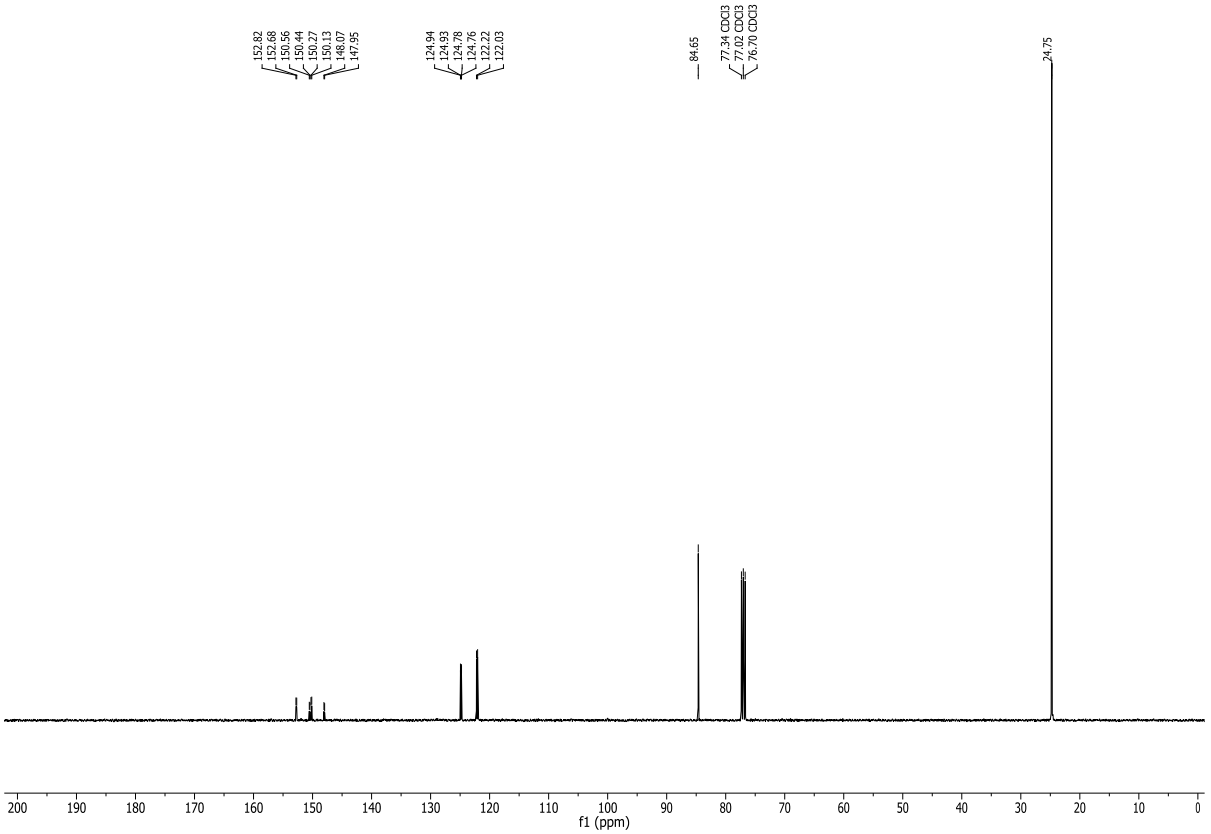
^{1}H and ^{13}C NMR data of compound **4l** (400 and 101 MHz respectively, $CDCl_3$).

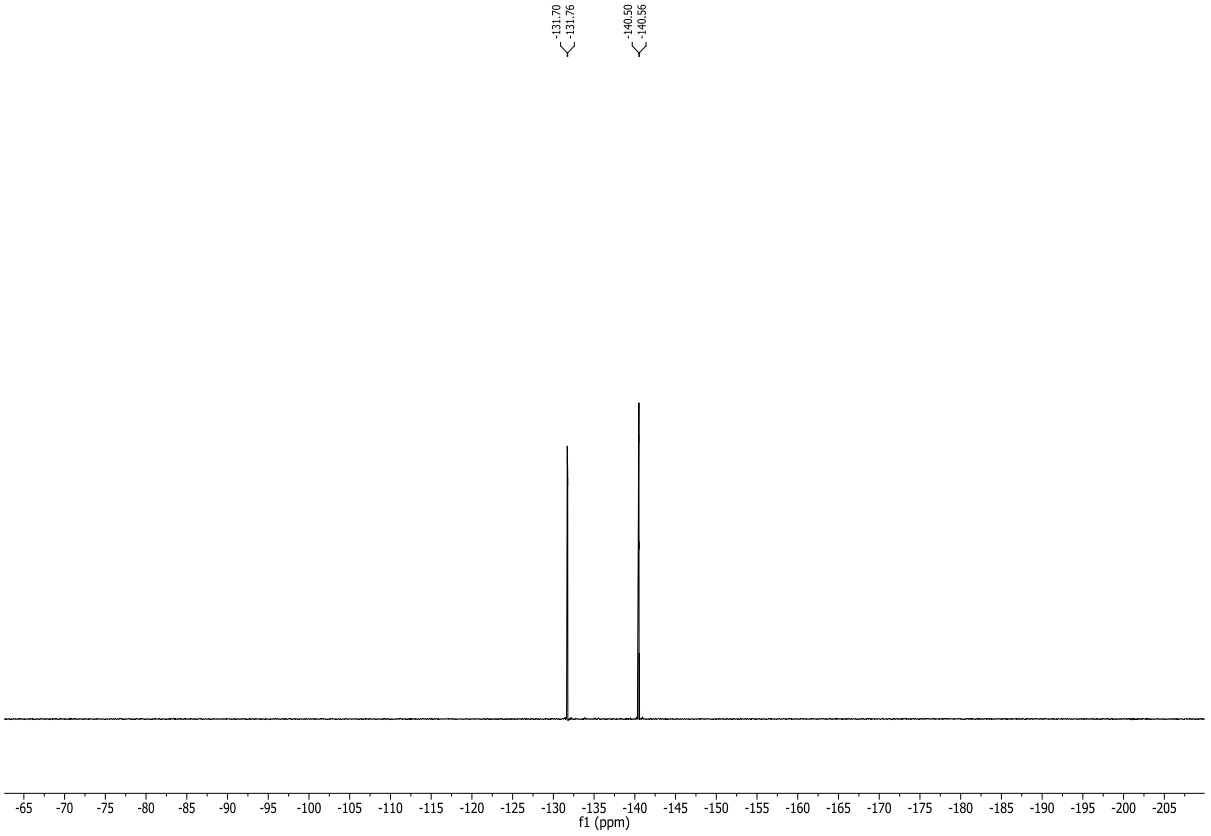




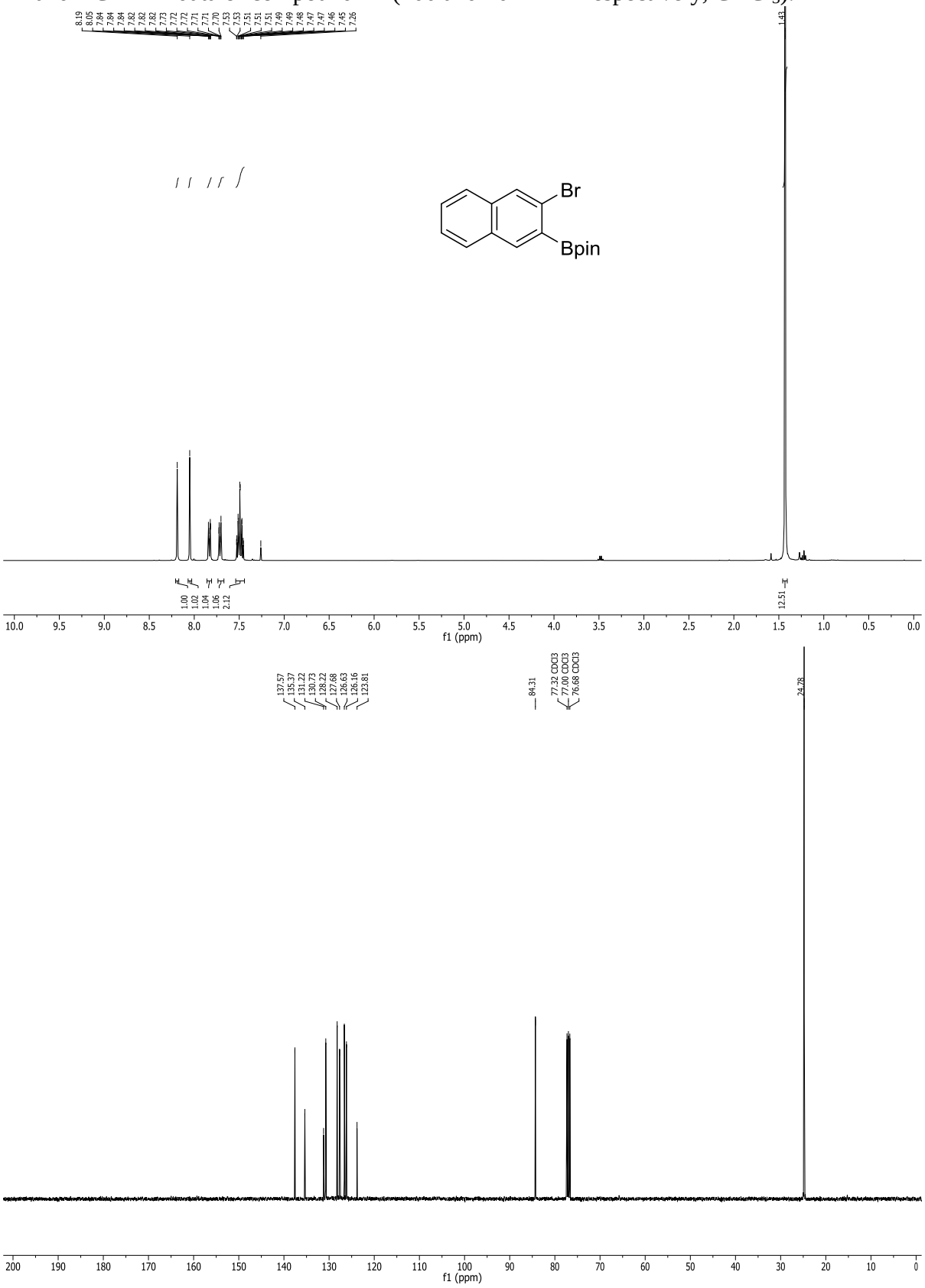
^{1}H, ^{13}C and ^{19}F NMR data of compound **4j** (400, 101 and 376 MHz respectively, $CDCl_3$).



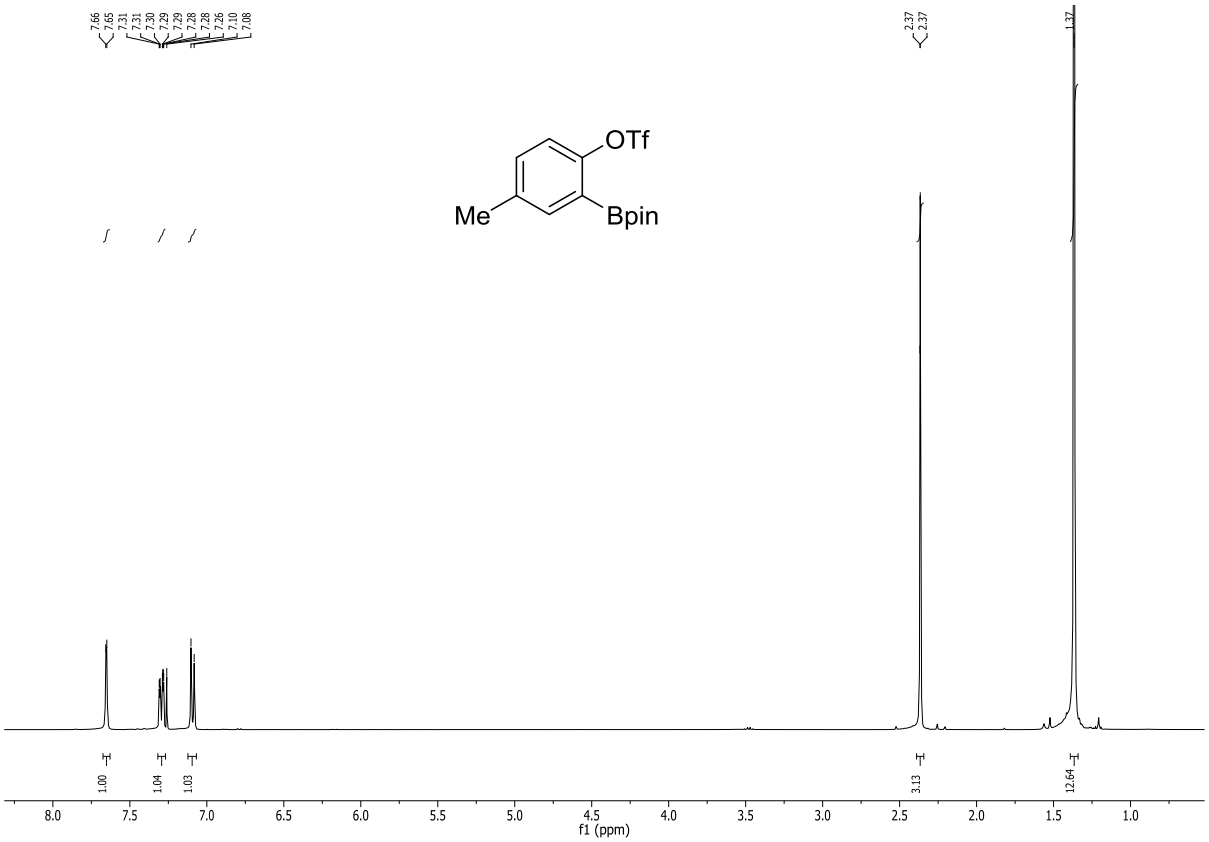

152.82
152.68
150.56
150.44
150.27
150.13
148.07
147.95
124.94
124.93
124.78
124.76
122.22
122.03
84.65
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
24.75
f1 (ppm)

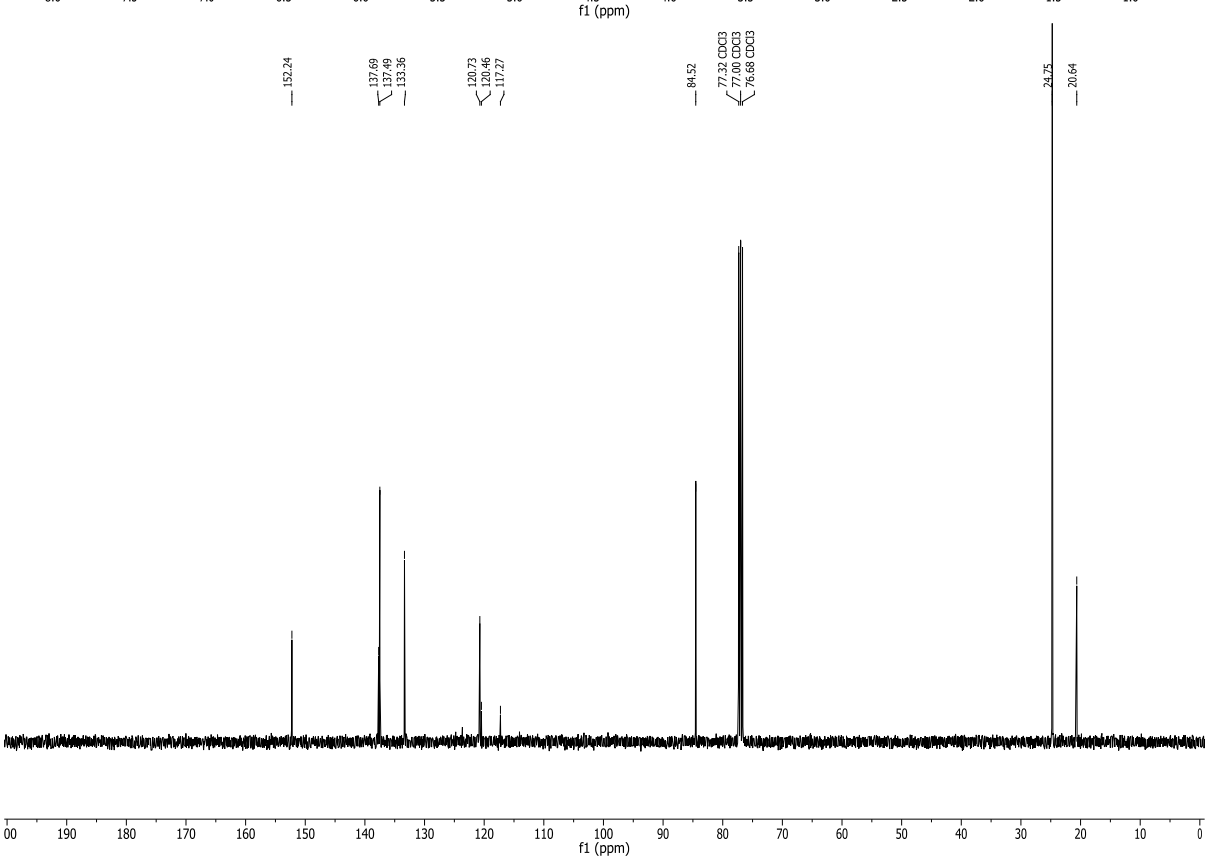

-131.70
-131.76
-140.50
-140.56
f1 (ppm)

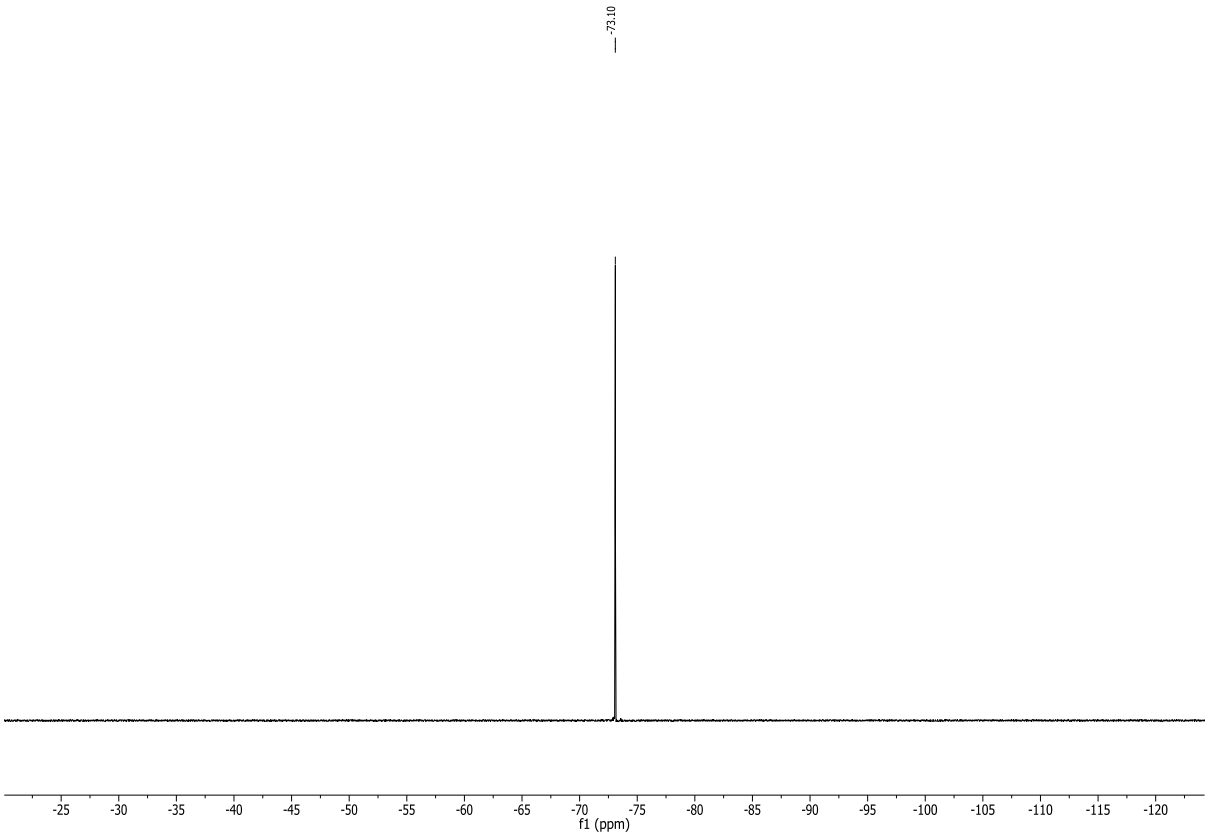
^{1}H and ^{13}C NMR data of compound **4k** (400 and 101 MHz respectively, $CDCl_3$).



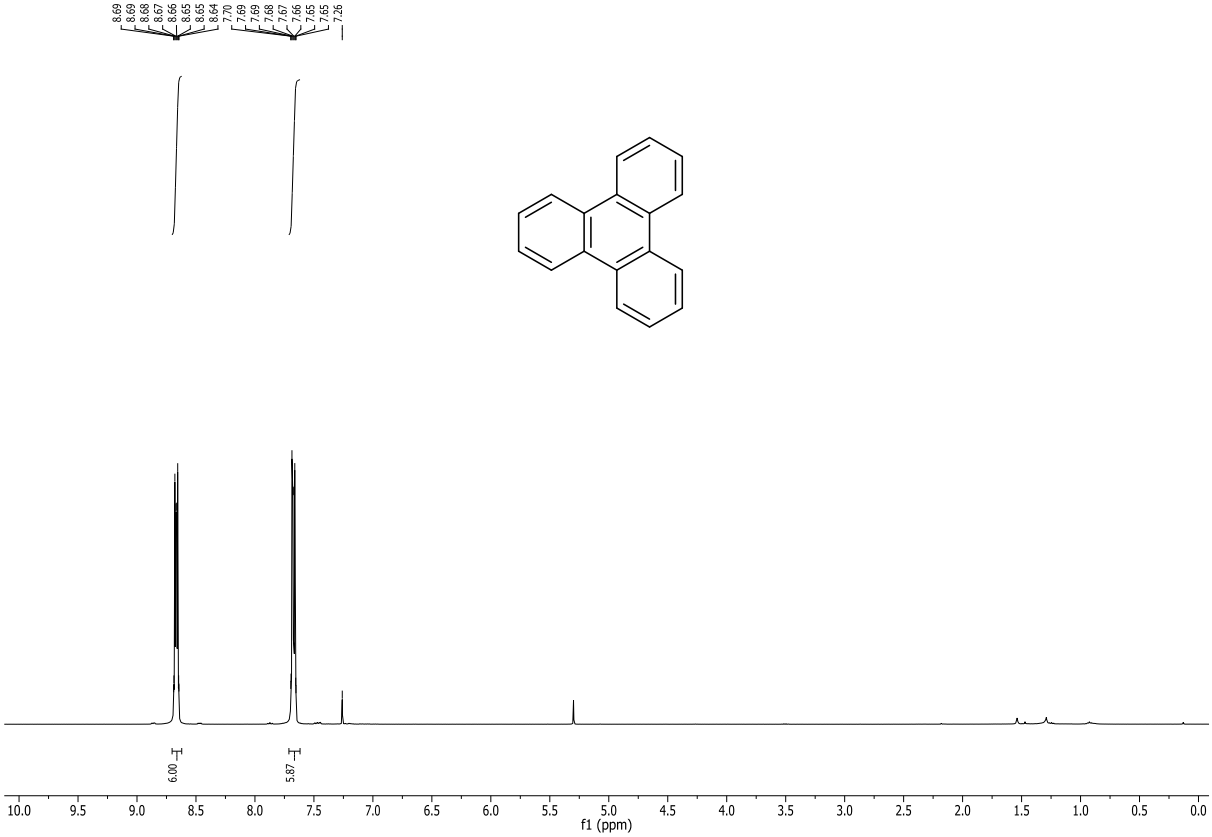
^{1}H, ^{13}C and ^{19}F NMR data of compound **10b** (500, 125 and 471 MHz respectively, $CDCl_3$).

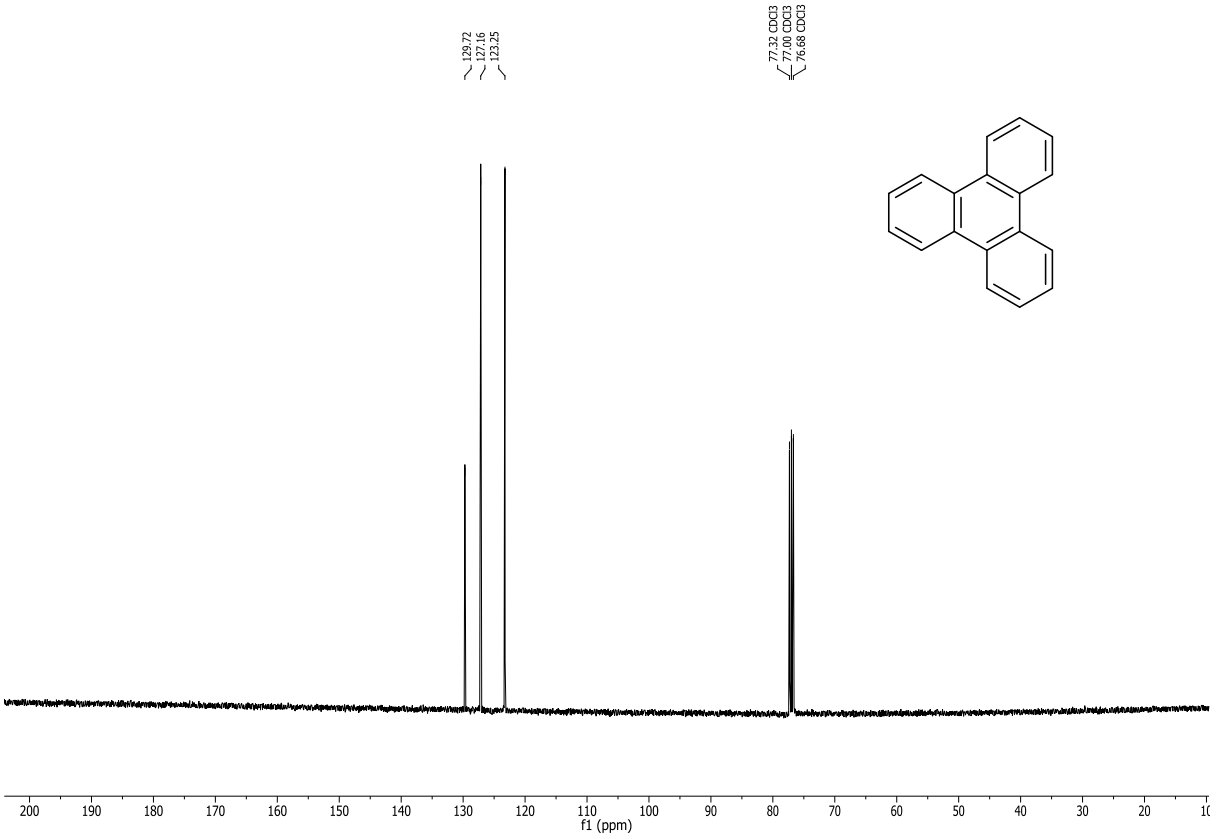




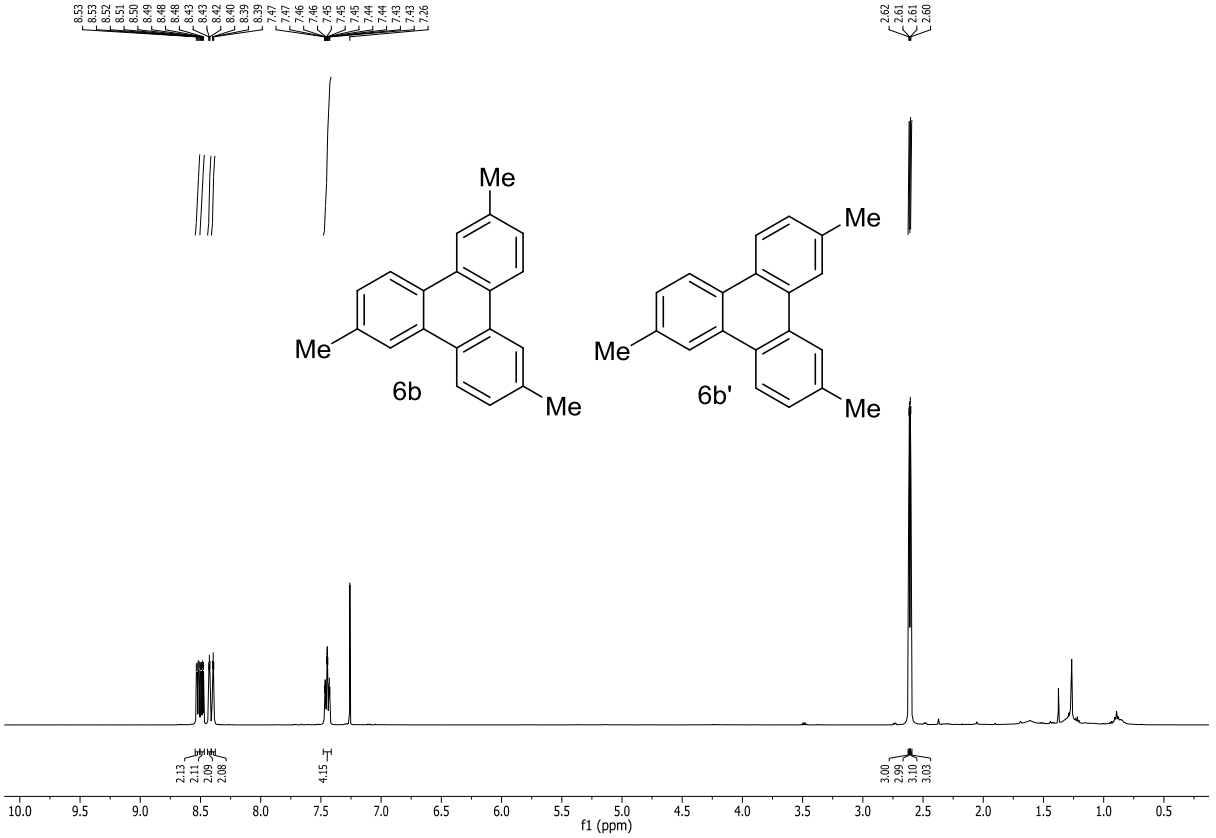


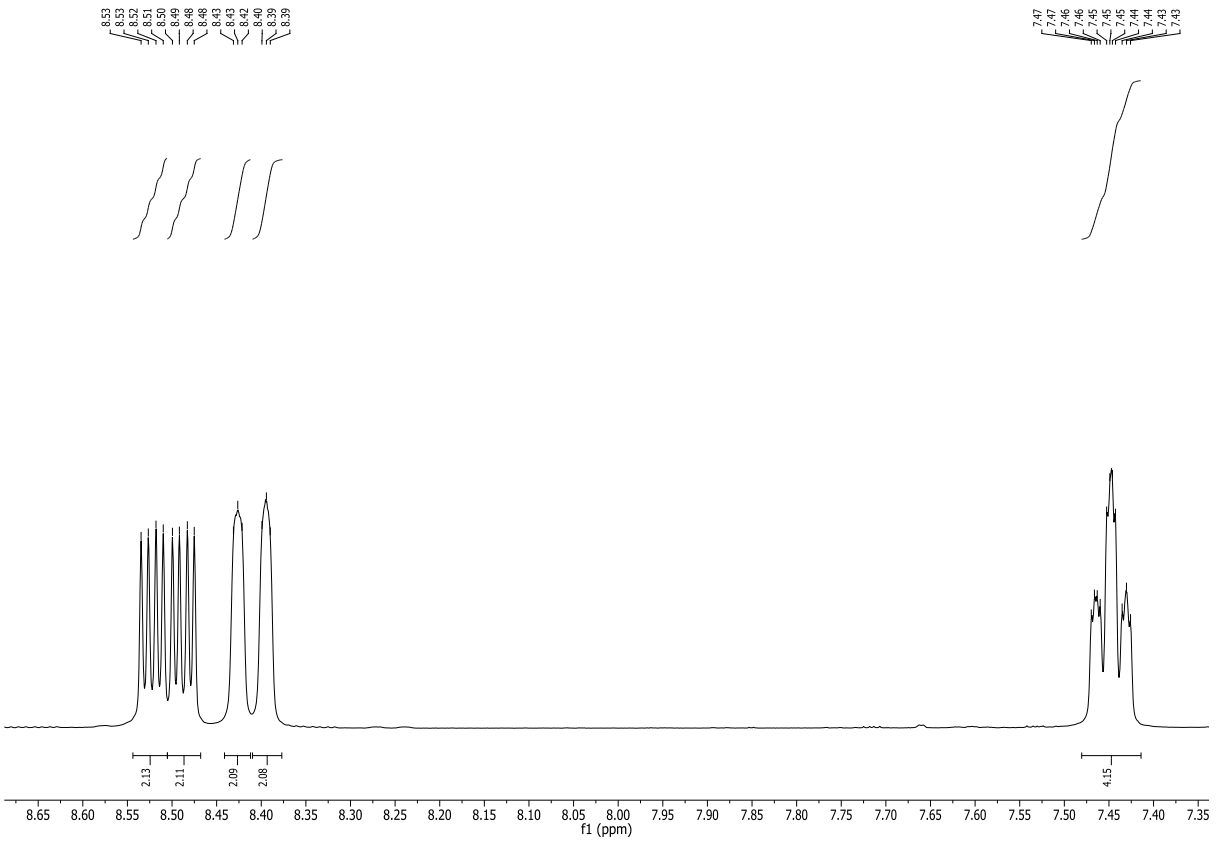
^{1}H and ^{13}C NMR data of compound **6a** (500 and 125 MHz respectively, $CDCl_3$).

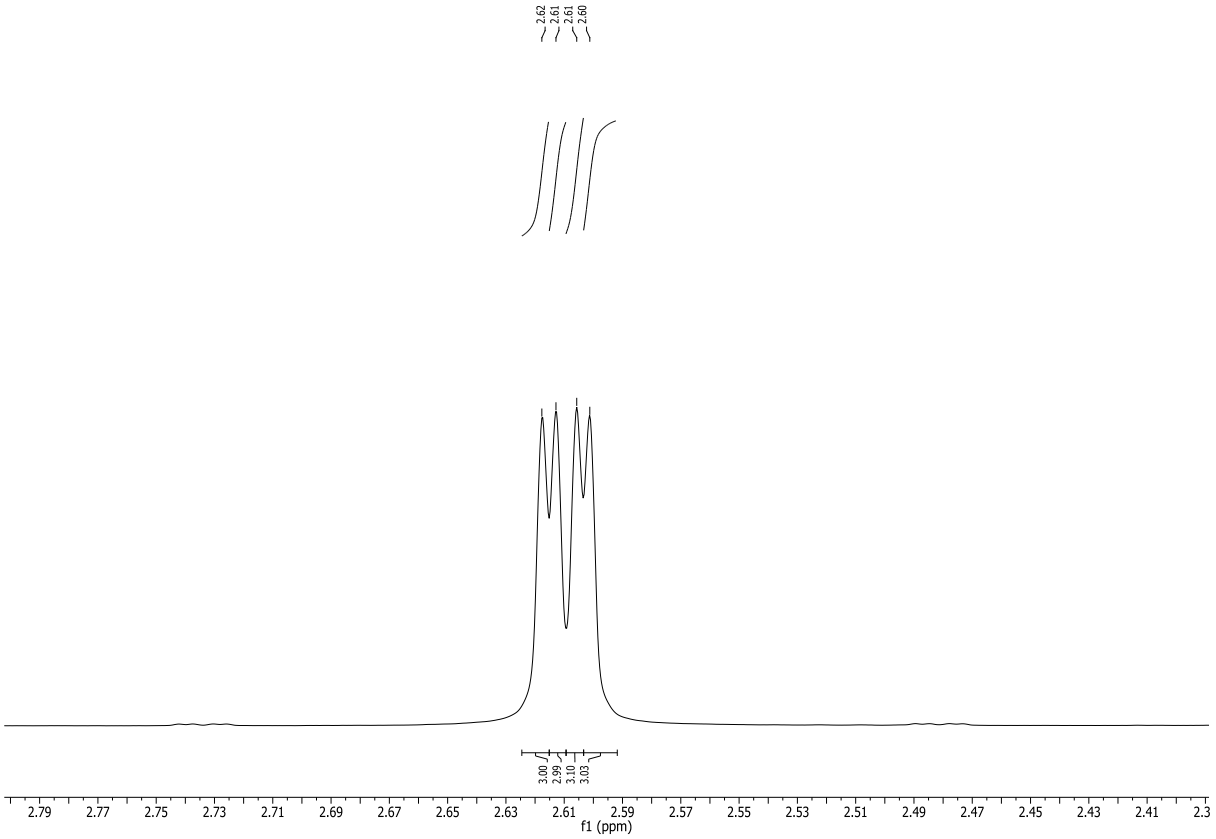


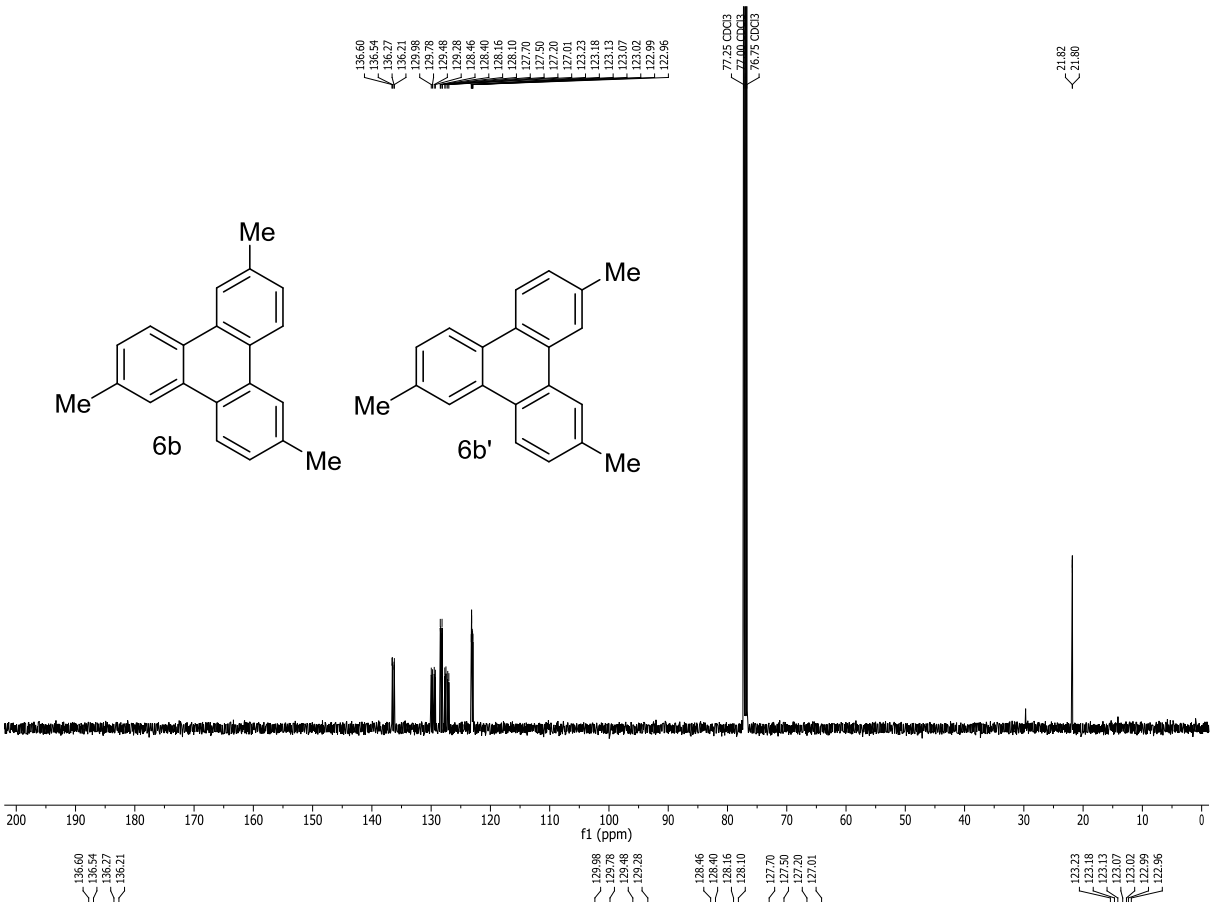


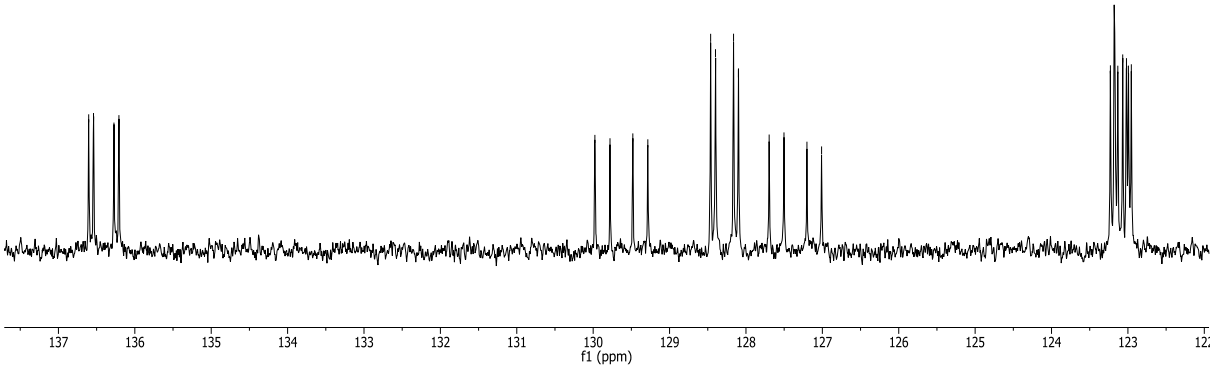
^{1}H and ^{13}C NMR data of the 1:3 mixture of compounds **6b:6b'** (500 and 125 MHz respectively, $CDCl_3$).



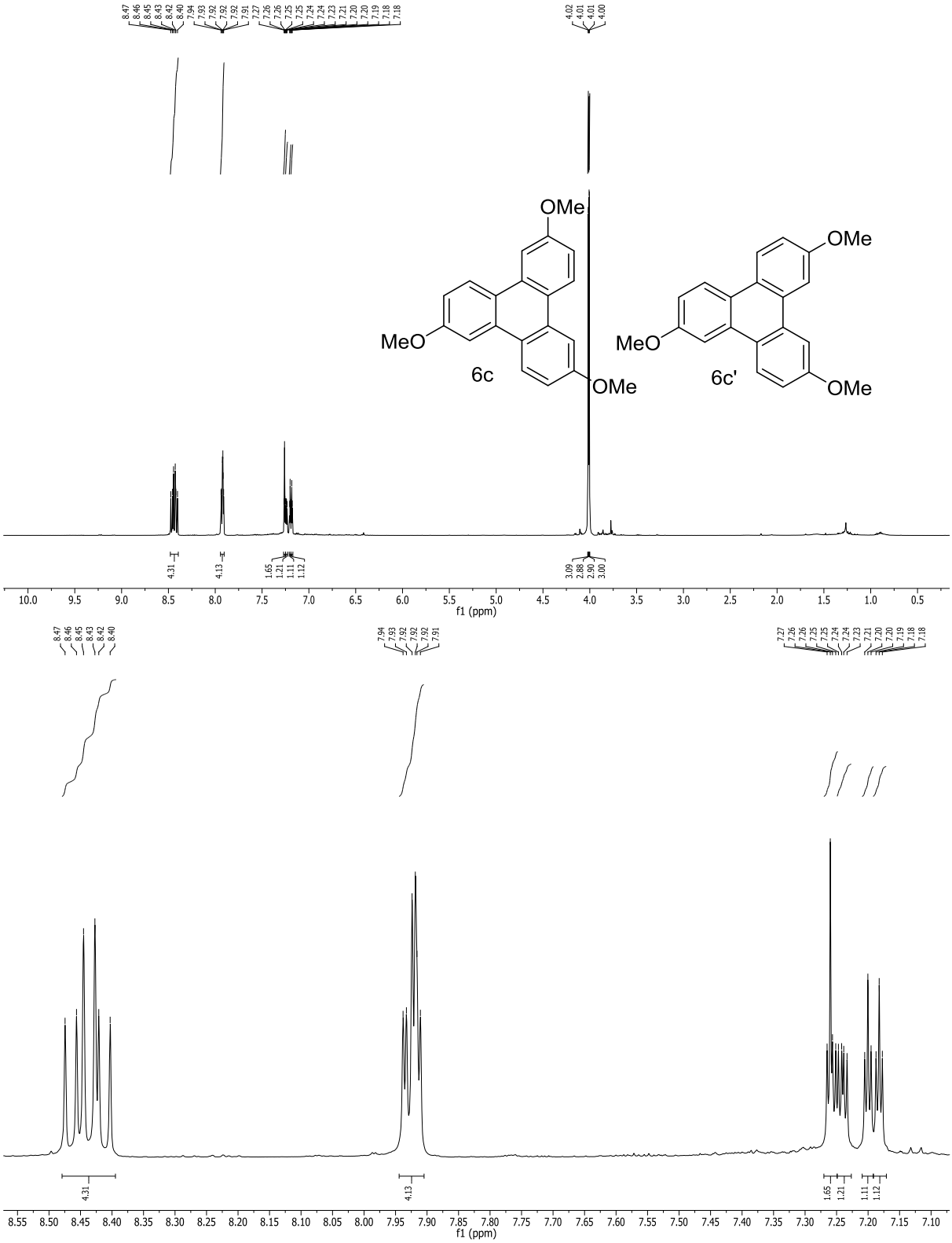

8.53
8.53
8.52
8.51
8.50
8.49
8.48
8.48
8.43
8.42
8.40
8.39
8.39
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
2.13
2.11
2.09
2.08
4.15
8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)

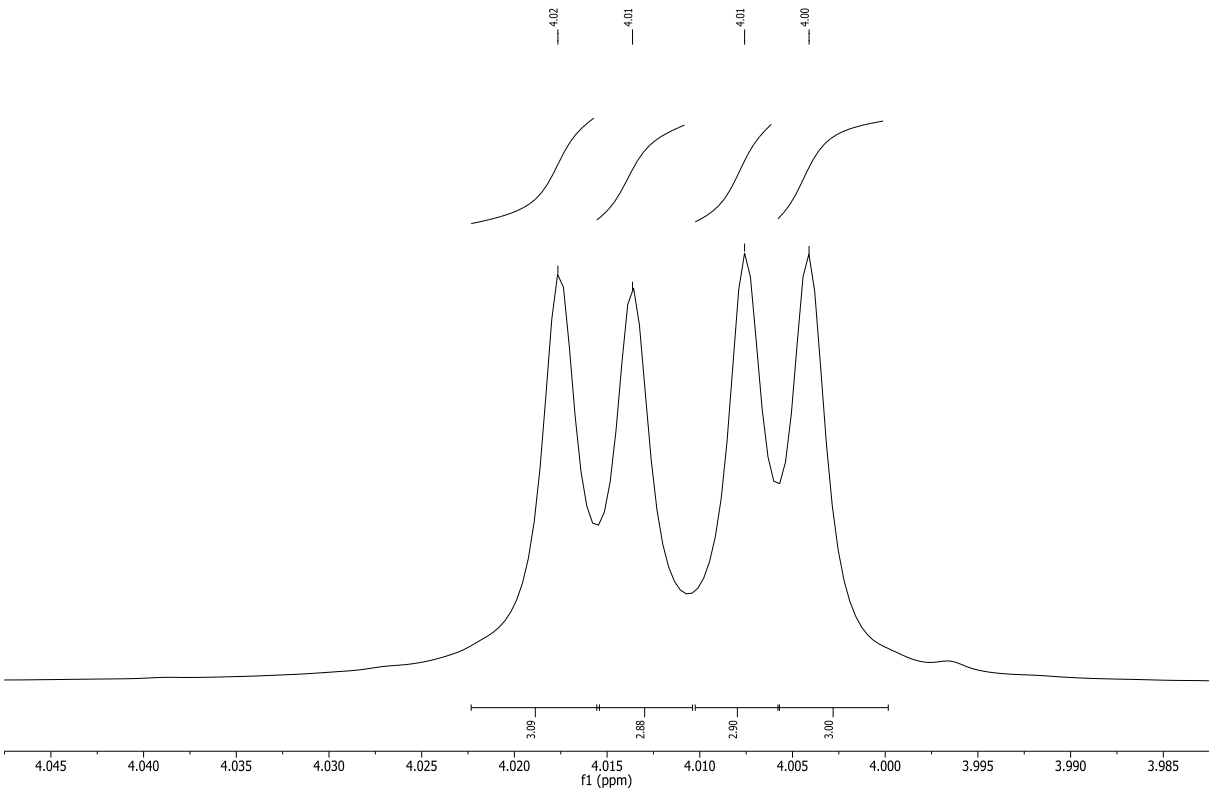

2.62
2.61
2.61
2.60
3.00
2.99
3.10
3.03
2.79 2.77 2.75 2.73 2.71 2.69 2.67 2.65 2.63 2.61 2.59 2.57 2.55 2.53 2.51 2.49 2.47 2.45 2.43 2.41 2.3
f1 (ppm)


136.60
136.54
136.27
136.21
129.98
129.78
129.48
129.28
128.46
128.40
128.16
128.10
127.70
127.50
127.20
127.01
123.23
123.18
123.13
123.07
123.02
122.99
122.96
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
21.82
21.80
Me
Me
Me
6b
Me
Me
Me
6b'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


137 136 135 134 133 132 131 130 129 128 127 126 125 124 123
f1 (ppm)

^{1}H and ^{13}C NMR data of the 1:3 mixture of compounds **6c:6c'** (500 and 125 MHz respectively, $CDCl_3$).




4.02
4.01
4.01
4.00
3.09
2.88
2.90
3.00
4.045
4.040
4.035
4.030
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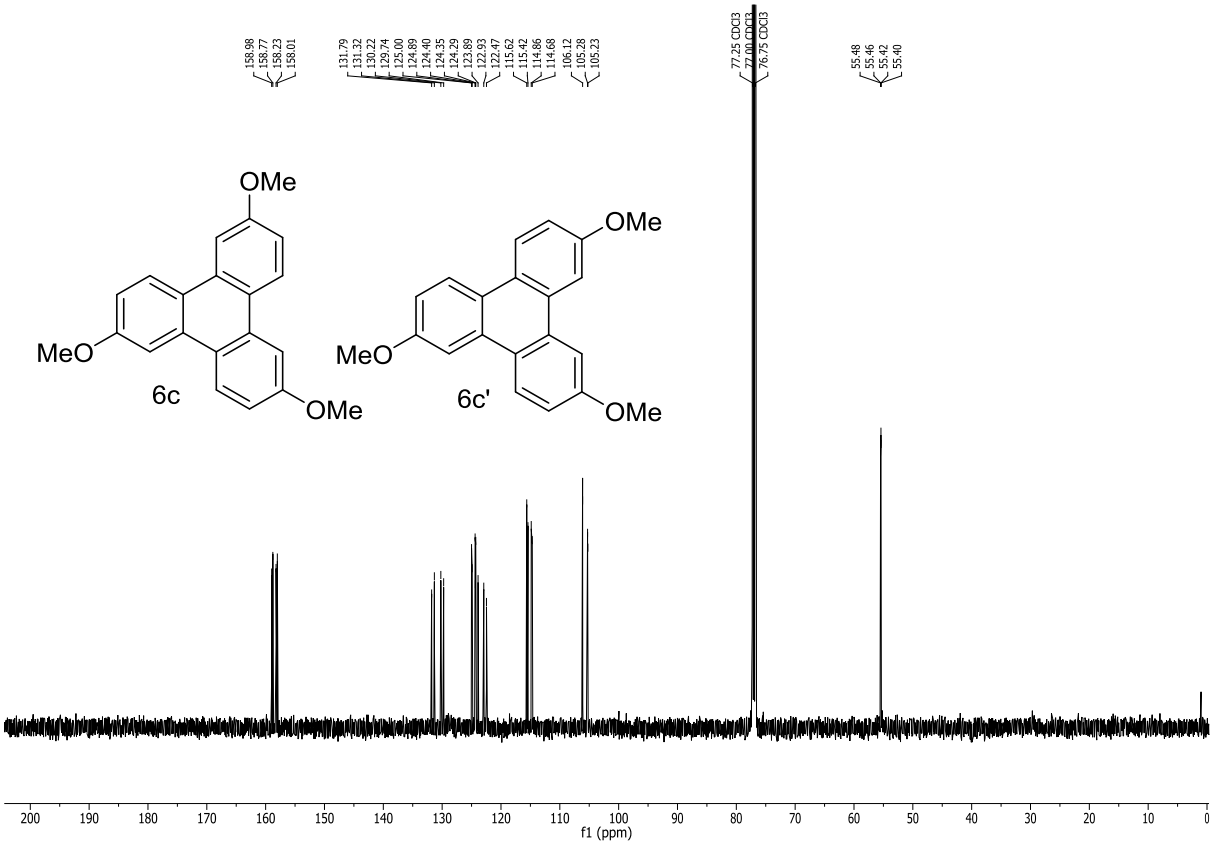
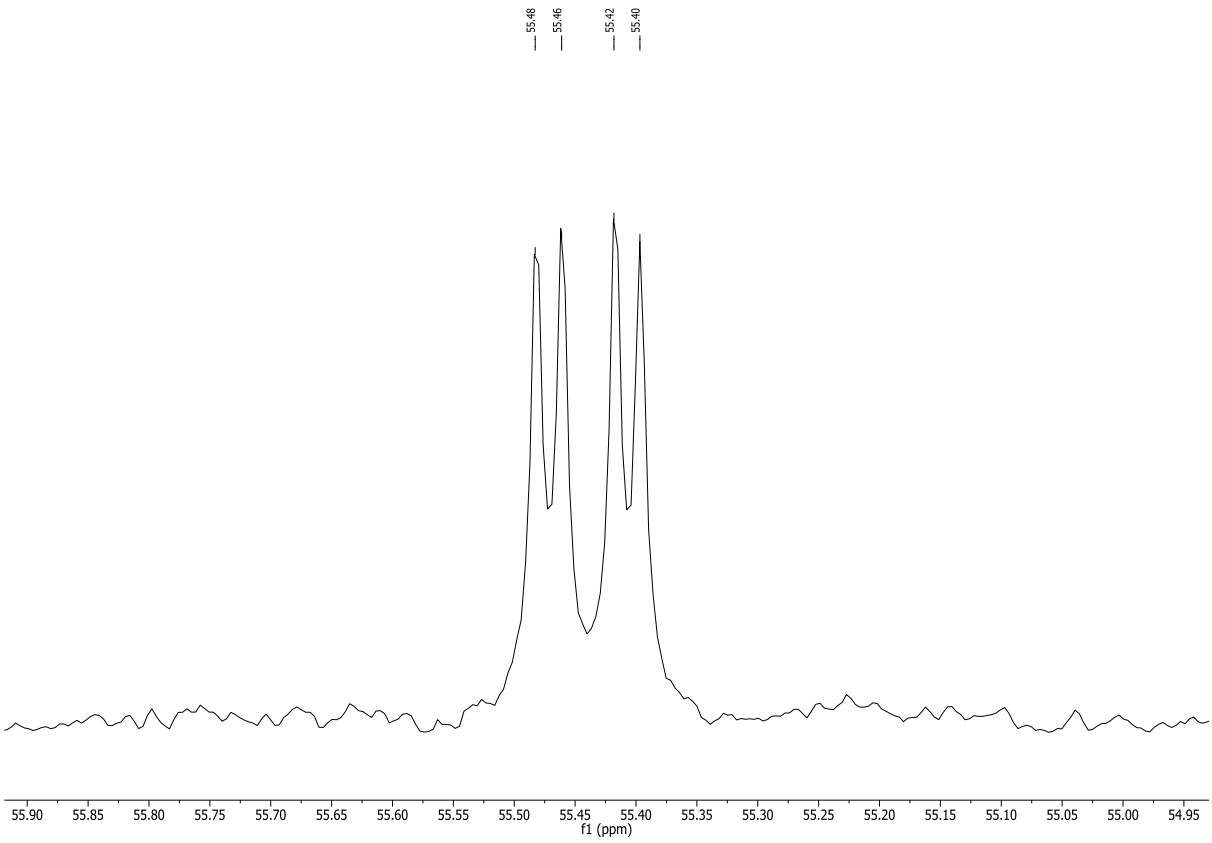
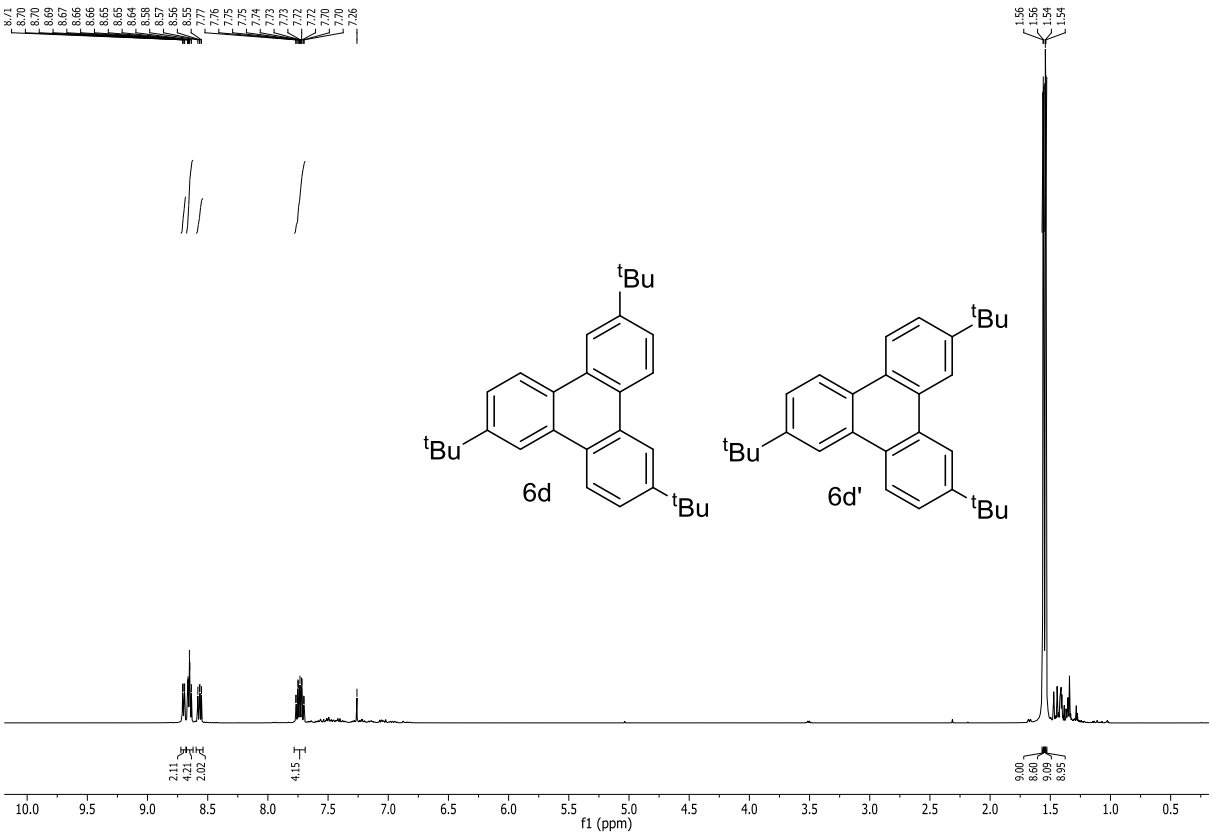
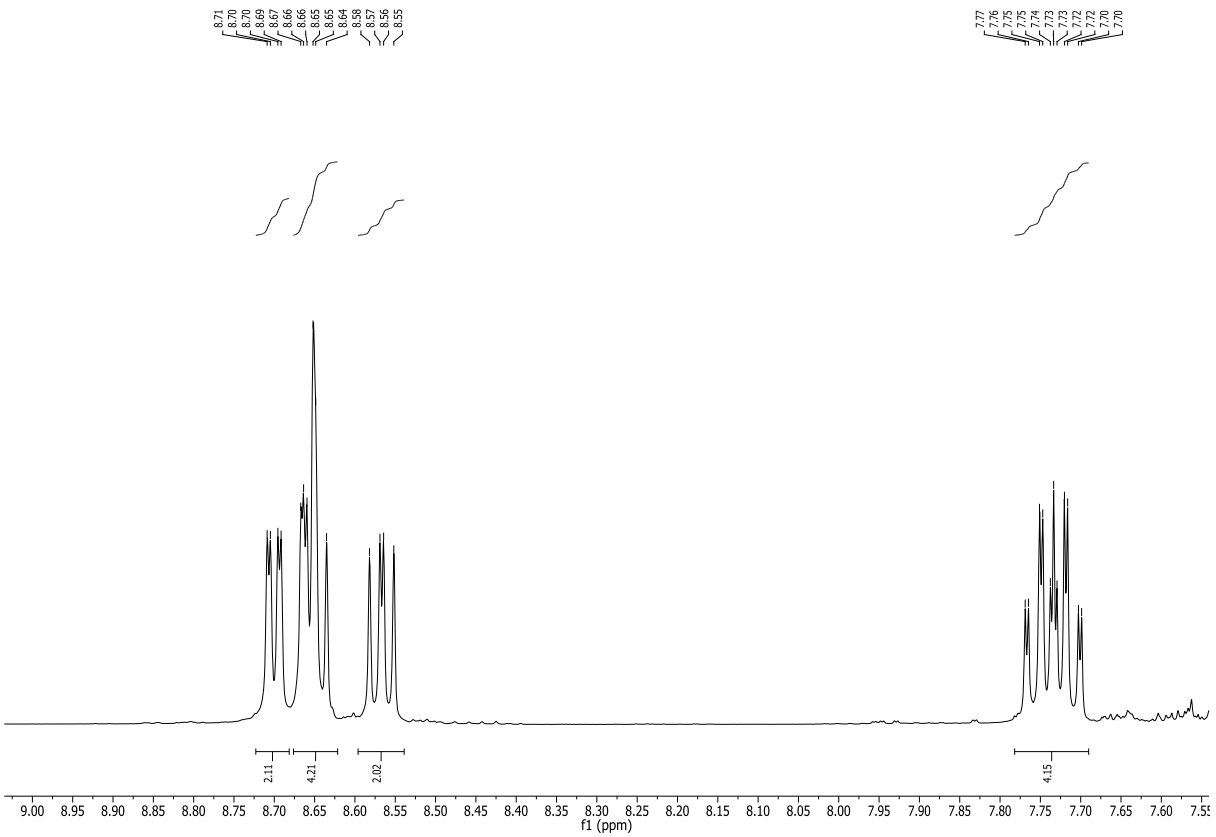
4.020
4.015
4.010
4.005
4.000
3.995
3.990
3.985
f1 (ppm)


158.98
158.77
158.23
158.01
131.79
131.32
130.22
130.24
125.00
124.89
124.40
124.35
124.29
123.89
122.93
122.47
115.62
115.42
114.86
114.68
106.12
105.28
105.23
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.48
55.46
55.42
55.40
OMe
MeO
OMe
6c
OMe
MeO
OMe
6c'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H and ^{13}C NMR data of the 1:3 mixture of compounds **6d:6d'** (500 and 125 MHz respectively, $CDCl_3$).




8.71
8.70
8.70
8.69
8.67
8.66
8.66
8.65
8.65
8.64
8.58
8.57
8.56
8.55
7.77
7.76
7.75
7.75
7.74
7.73
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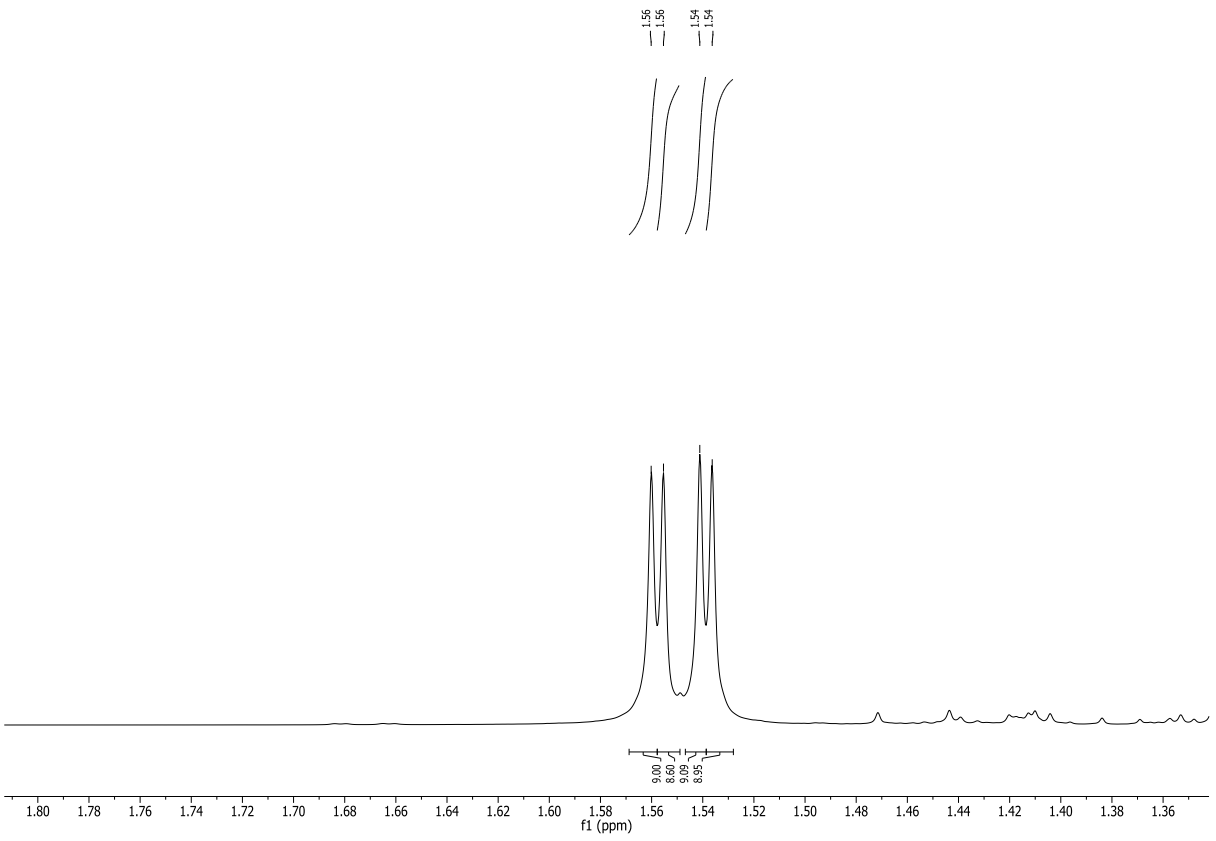
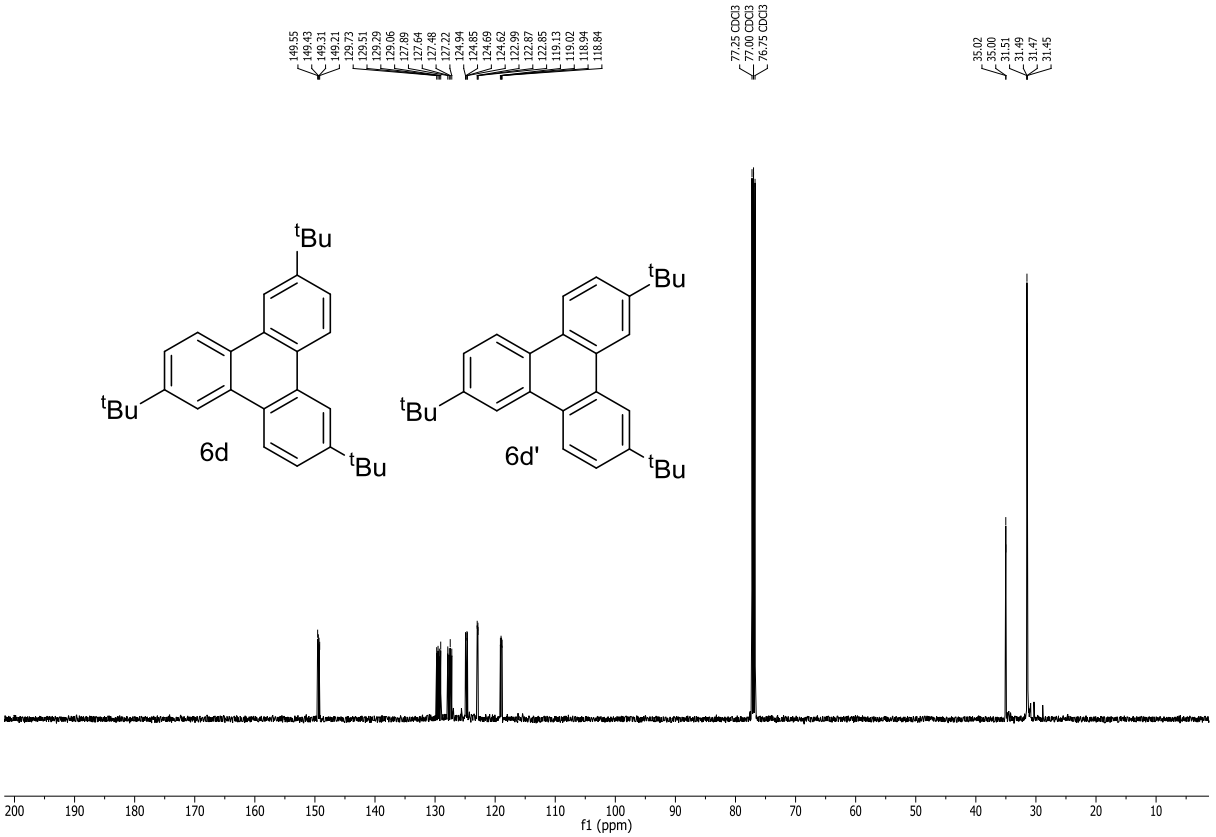
7.72
7.72
7.70
7.70
2.11
4.21
2.02
4.15
f1 (ppm)


1.56
1.56
1.54
1.54
9.00
8.60
9.09
8.95
f1 (ppm)


149.55
149.43
149.31
149.21
129.73
129.51
129.29
129.06
127.89
127.64
127.48
127.22
124.94
124.85
124.69
124.62
122.99
122.87
122.85
119.13
119.02
118.94
118.84
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
35.02
35.00
31.51
31.49
31.47
31.45
tBu
tBu
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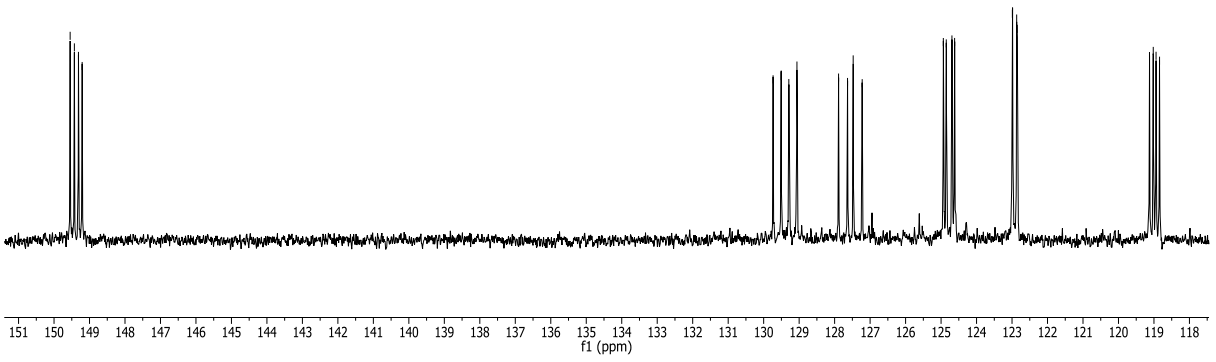
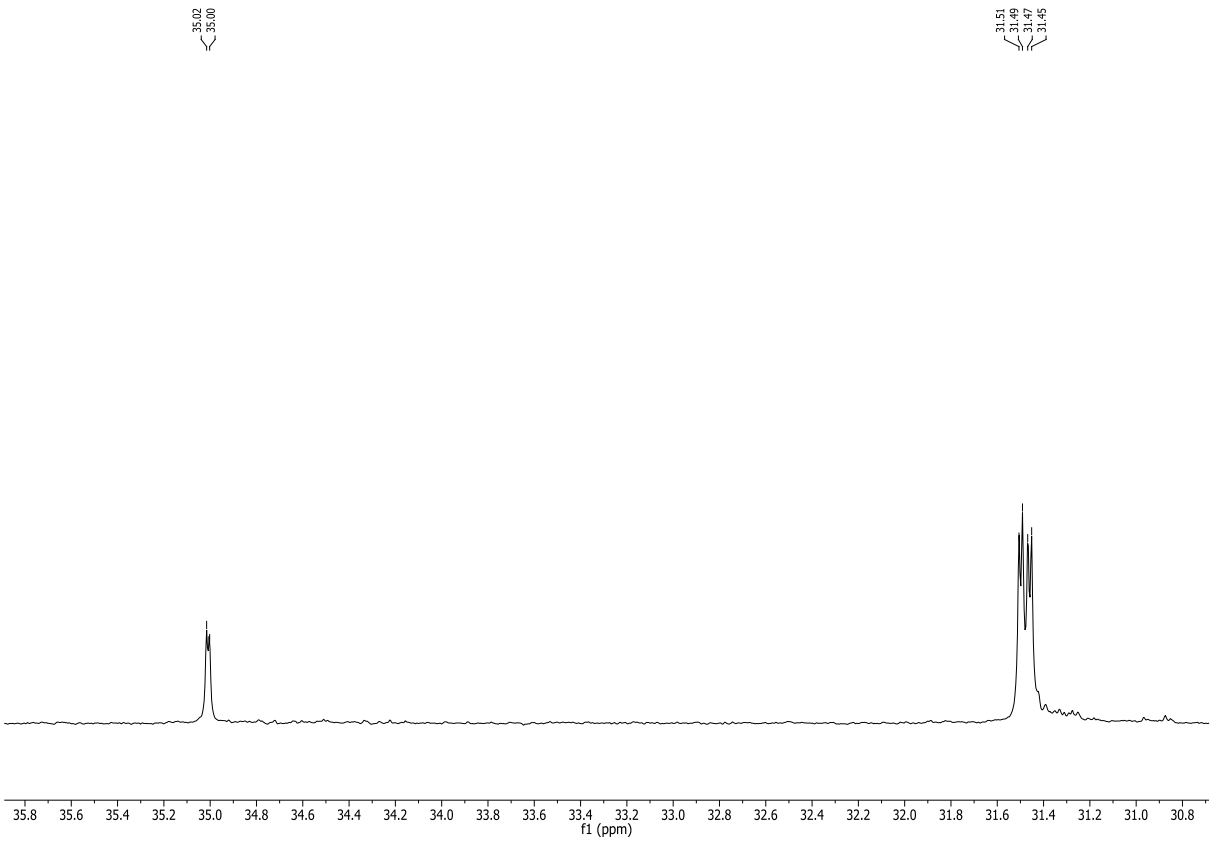
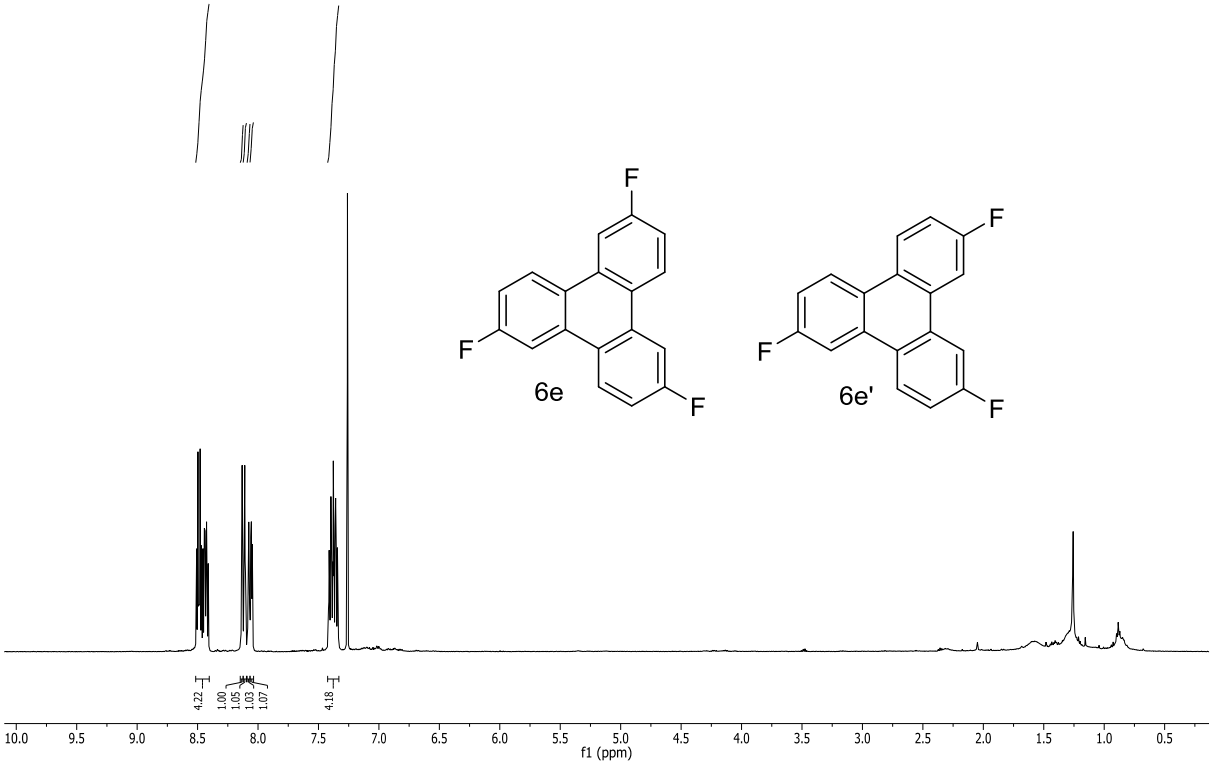
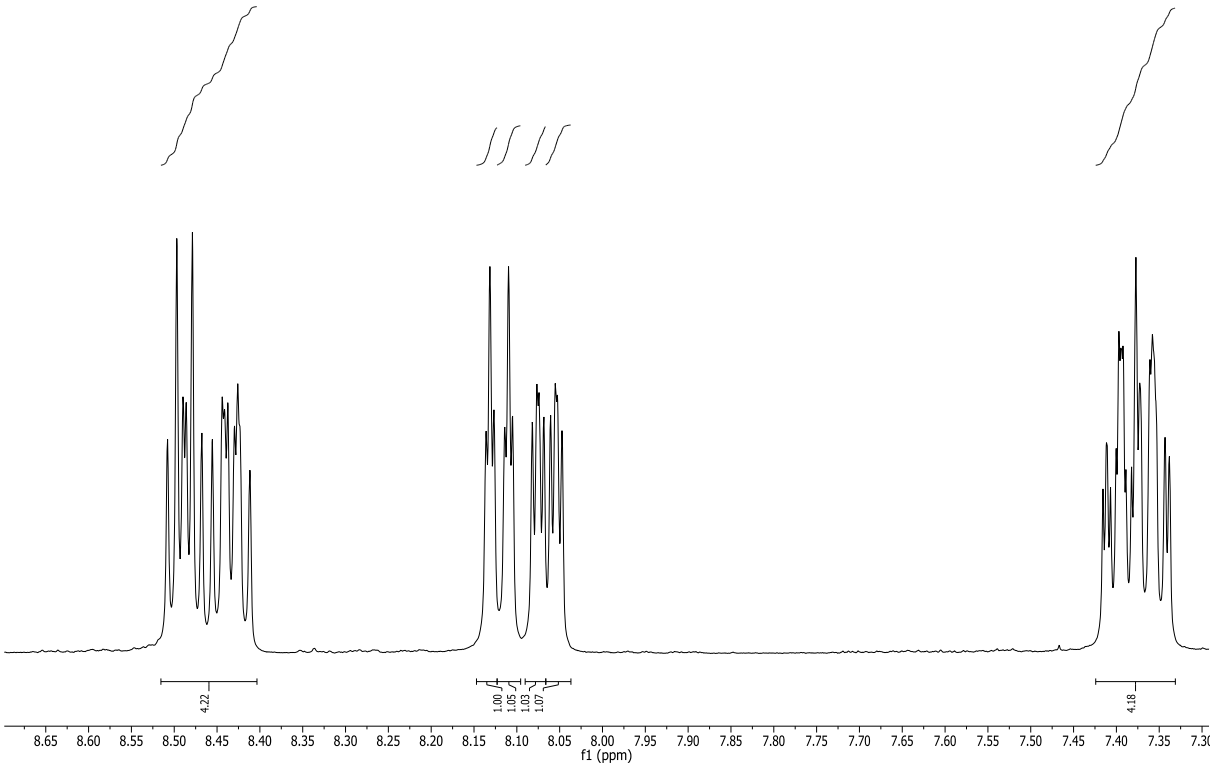
6d
tBu
tBu
tBu
6d'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

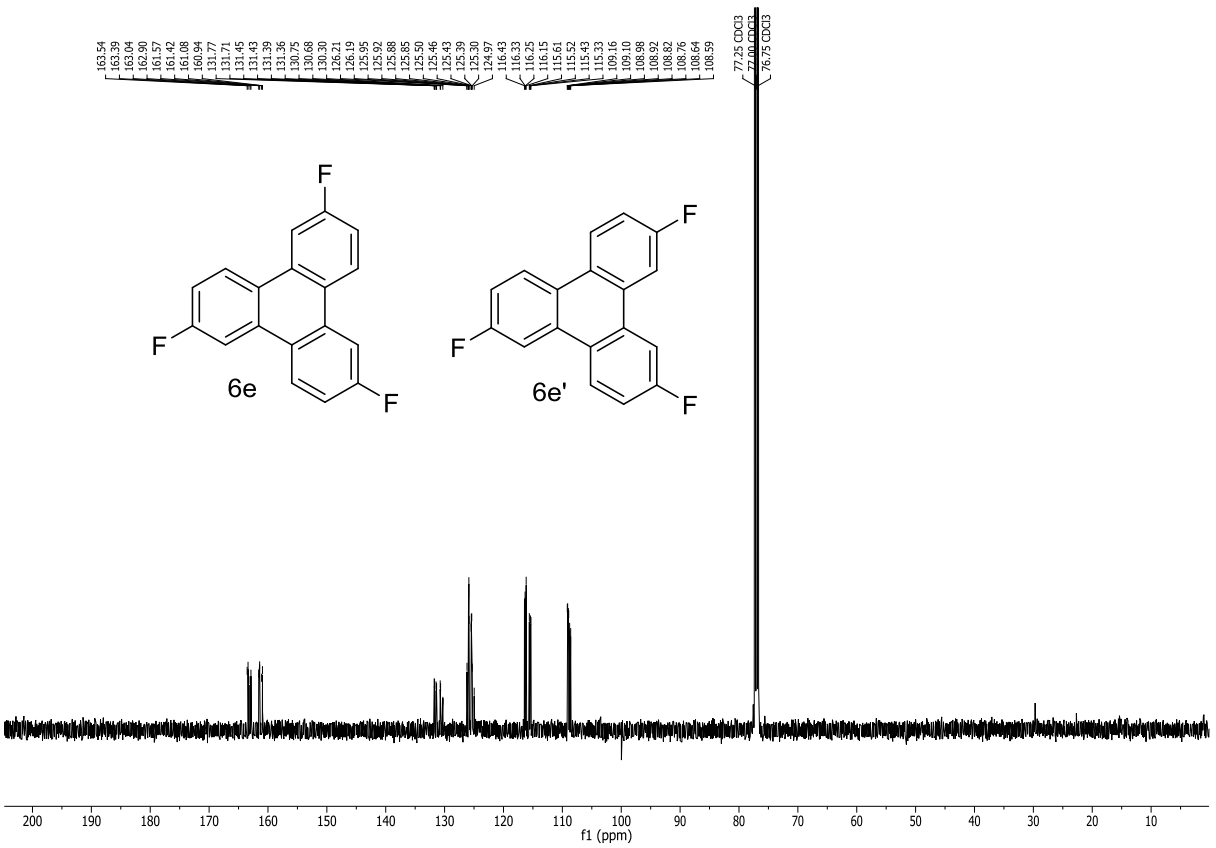

151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118
f1 (ppm)

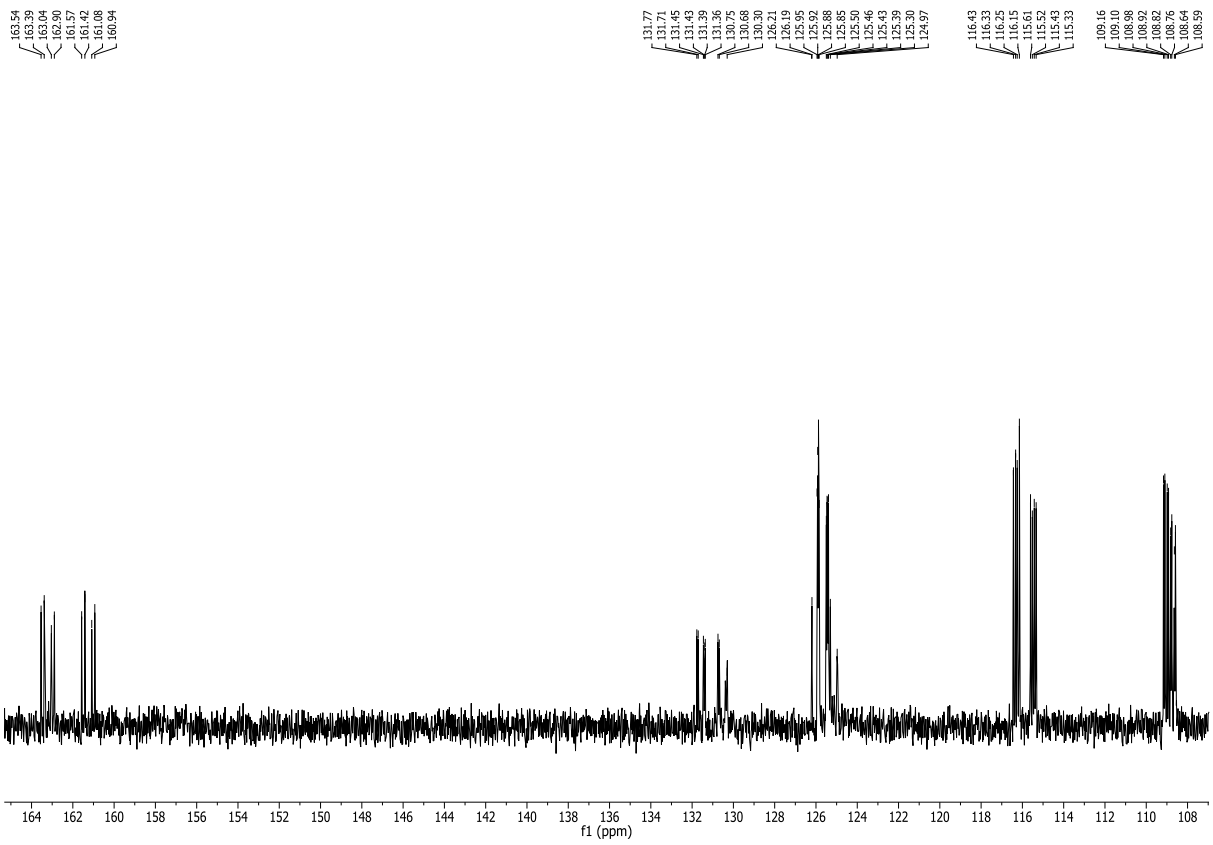


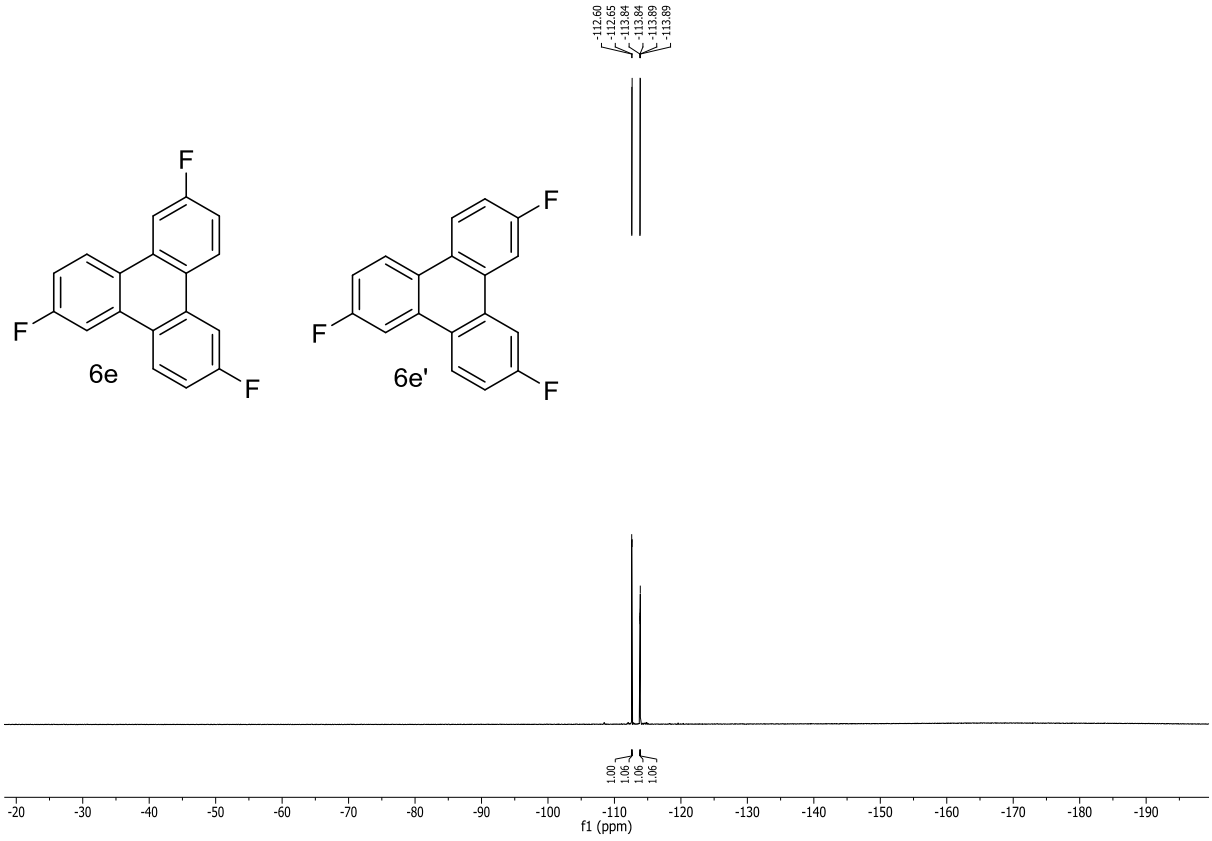
^{1}H, ^{13}C NMR and ^{19}F data of the 1:3 mixture of compounds **6e:6e'** (500 , 125 and 471 MHz respectively, $CDCl_3$).

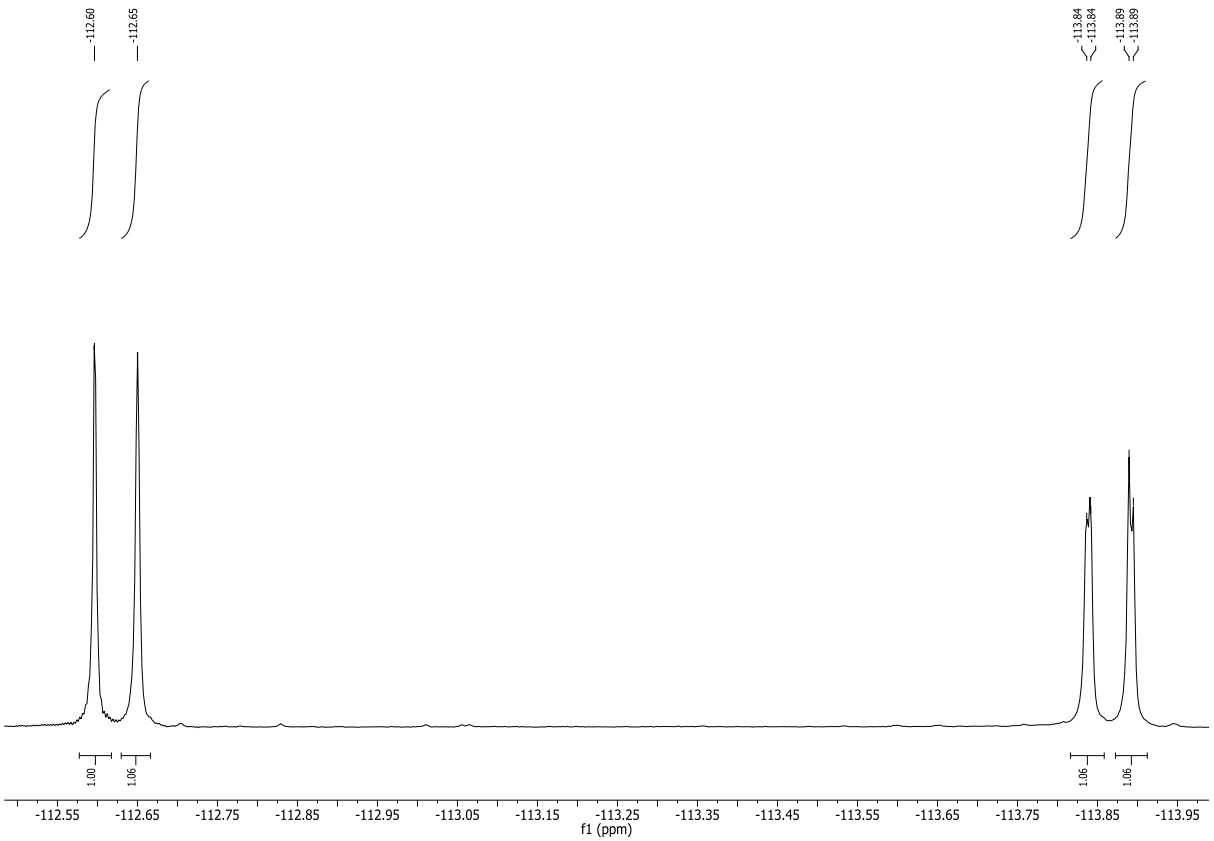



4.22
1.00
1.05
1.03
1.07
4.18
8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)

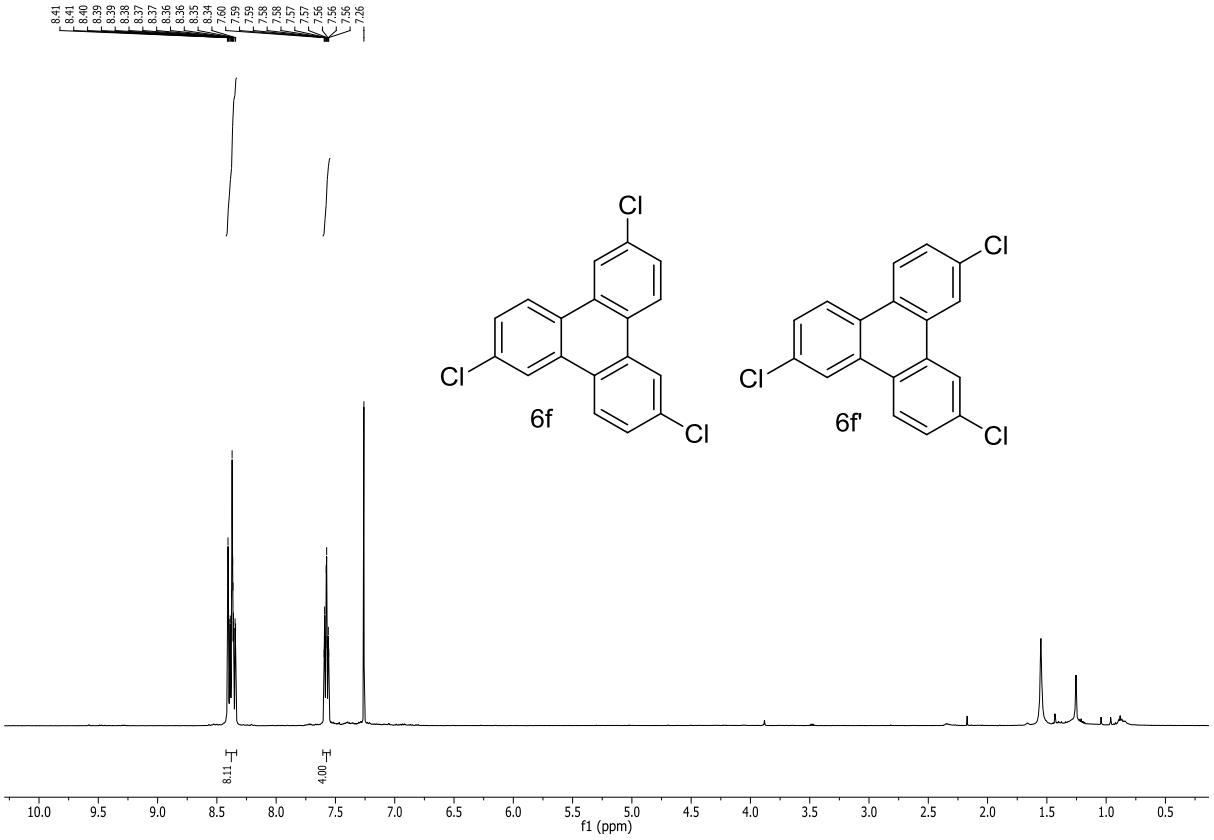

163.54
163.39
163.04
162.90
161.57
161.42
161.08
160.94
131.77
131.71
131.45
131.43
131.39
131.36
130.75
130.68
130.30
126.21
126.19
125.95
125.92
125.88
125.85
125.50
125.46
125.43
125.39
125.30
124.97
116.43
116.33
116.25
116.15
115.61
115.52
115.43
115.33
109.16
109.10
108.98
108.92
108.82
108.76
108.64
108.59
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
F
F
F
6e
F
F
F
6e'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

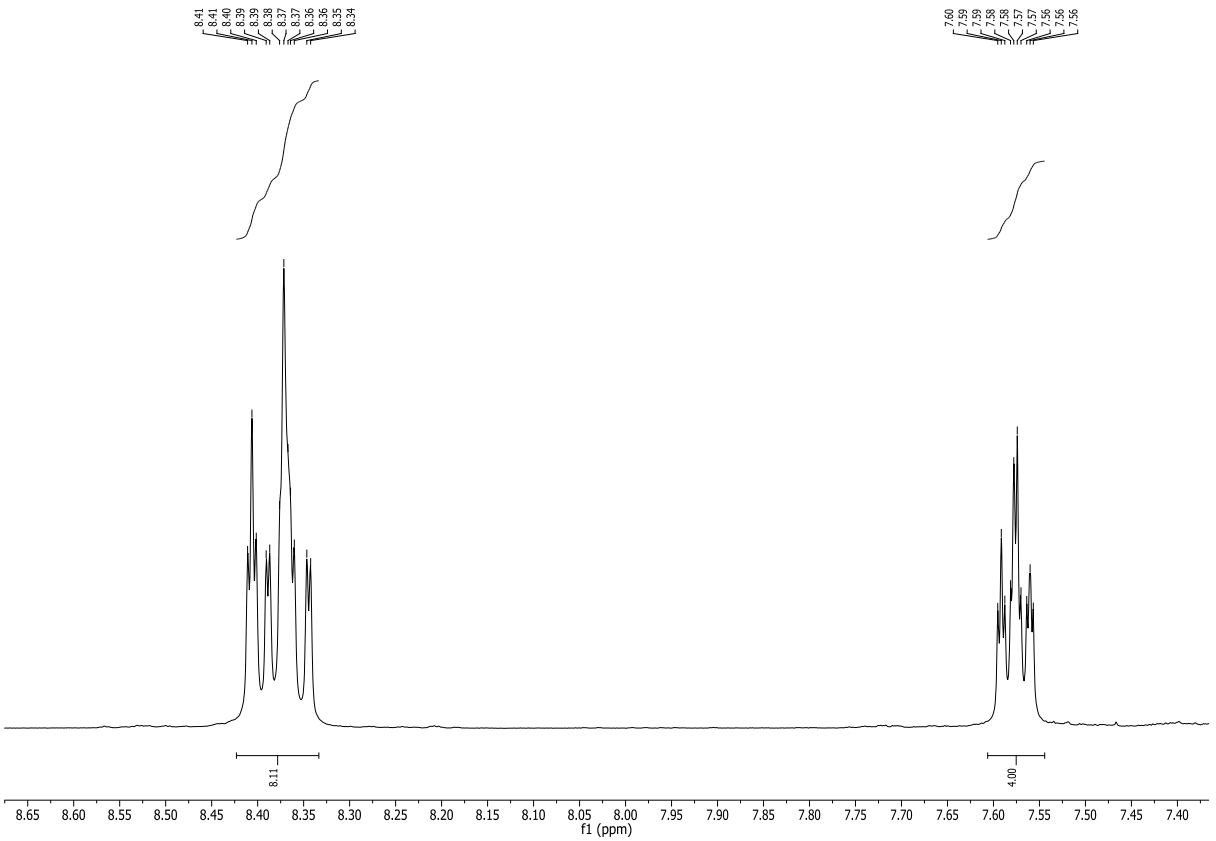

163.54
163.39
163.04
162.90
161.57
161.42
161.08
160.94
131.77
131.71
131.45
131.43
131.39
131.36
130.75
130.68
130.30
126.21
126.19
125.95
125.92
125.88
125.85
125.50
125.46
125.43
125.39
125.30
124.97
116.43
116.33
116.25
116.15
115.61
115.52
115.43
115.33
109.16
109.10
108.98
108.92
108.82
108.76
108.64
108.59
164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

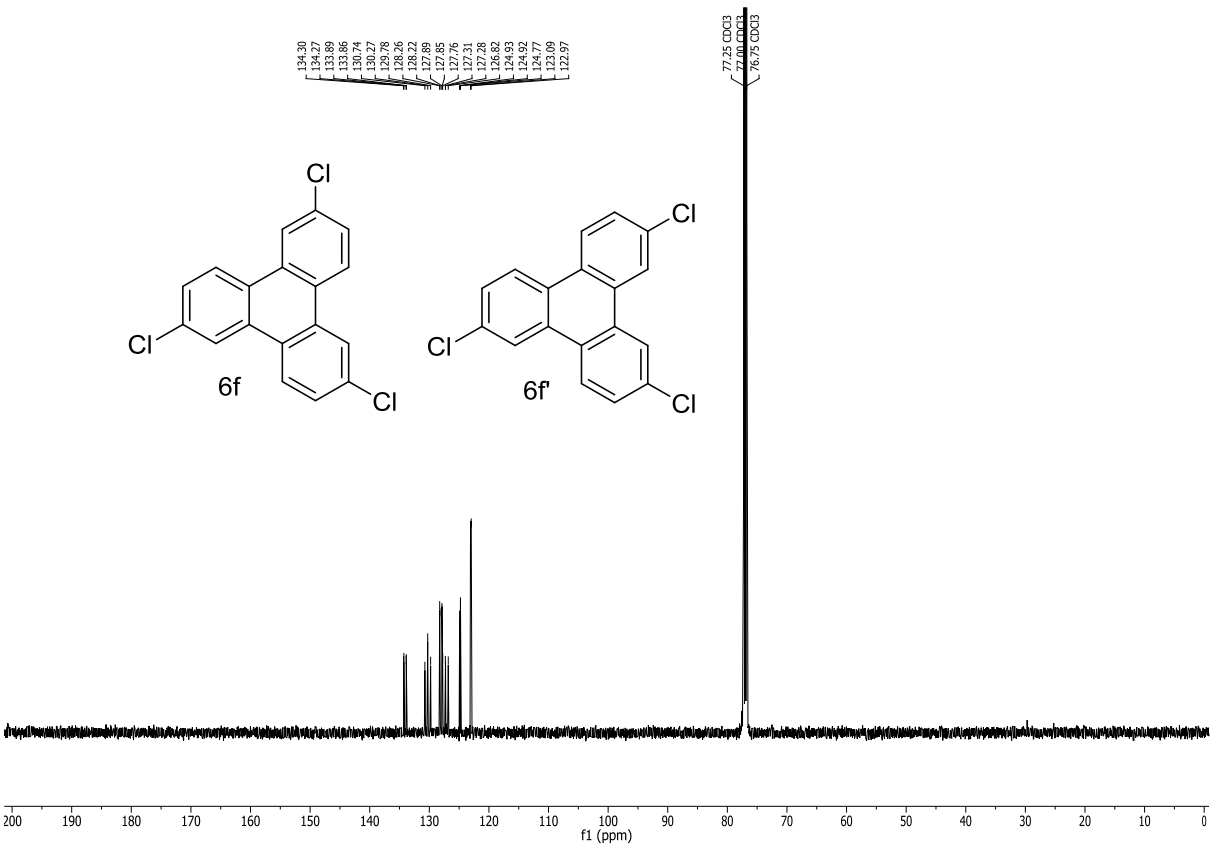

-112.60
-112.65
-113.84
-113.84
-113.89
-113.89
F
F
F
6e
F
F
F
6e'
1.00
1.06
1.06
1.06
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



^{1}H and ^{13}C NMR data of the 1:3 mixture of compounds **6f:6f'** (500 and 125 MHz respectively, $CDCl_3$).




8.41
8.41
8.40
8.39
8.39
8.38
8.37
8.37
8.36
8.36
8.35
8.34
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.56
8.11
4.00
8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
f1 (ppm)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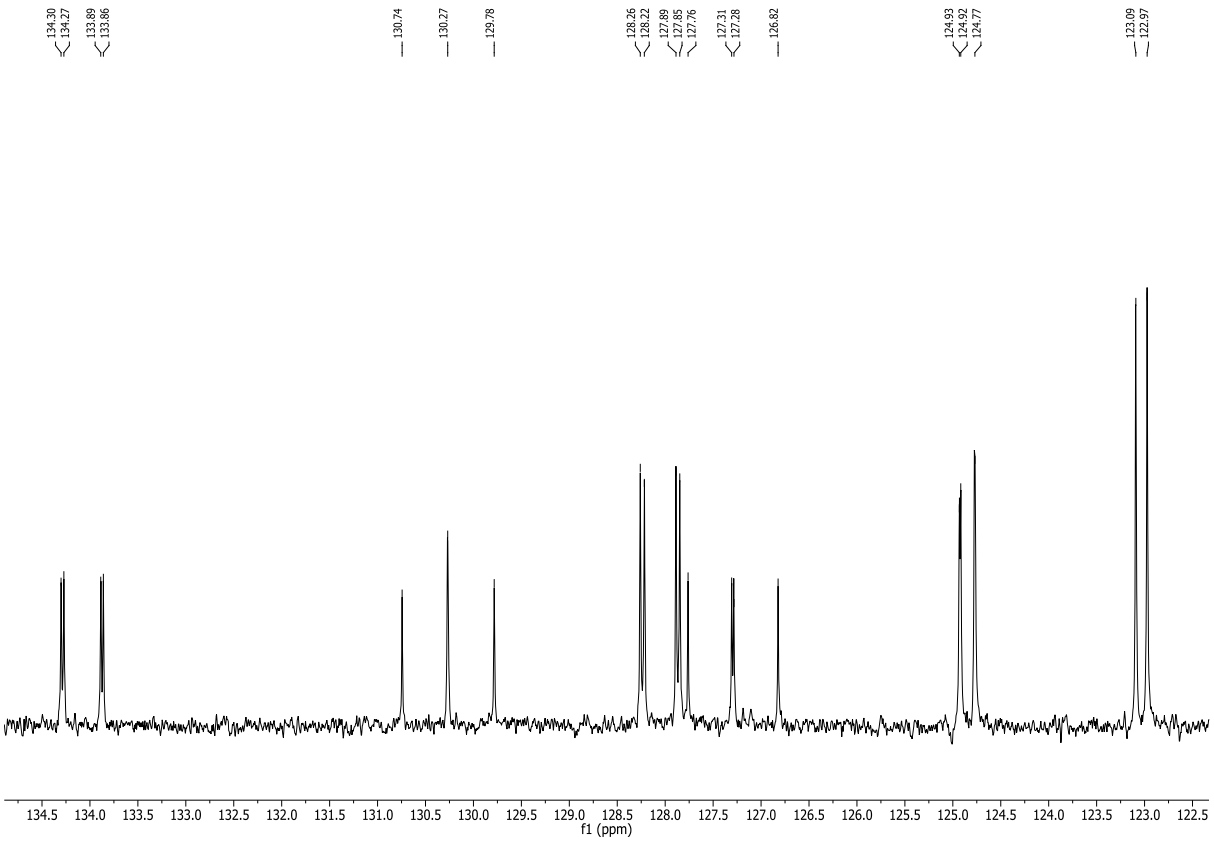
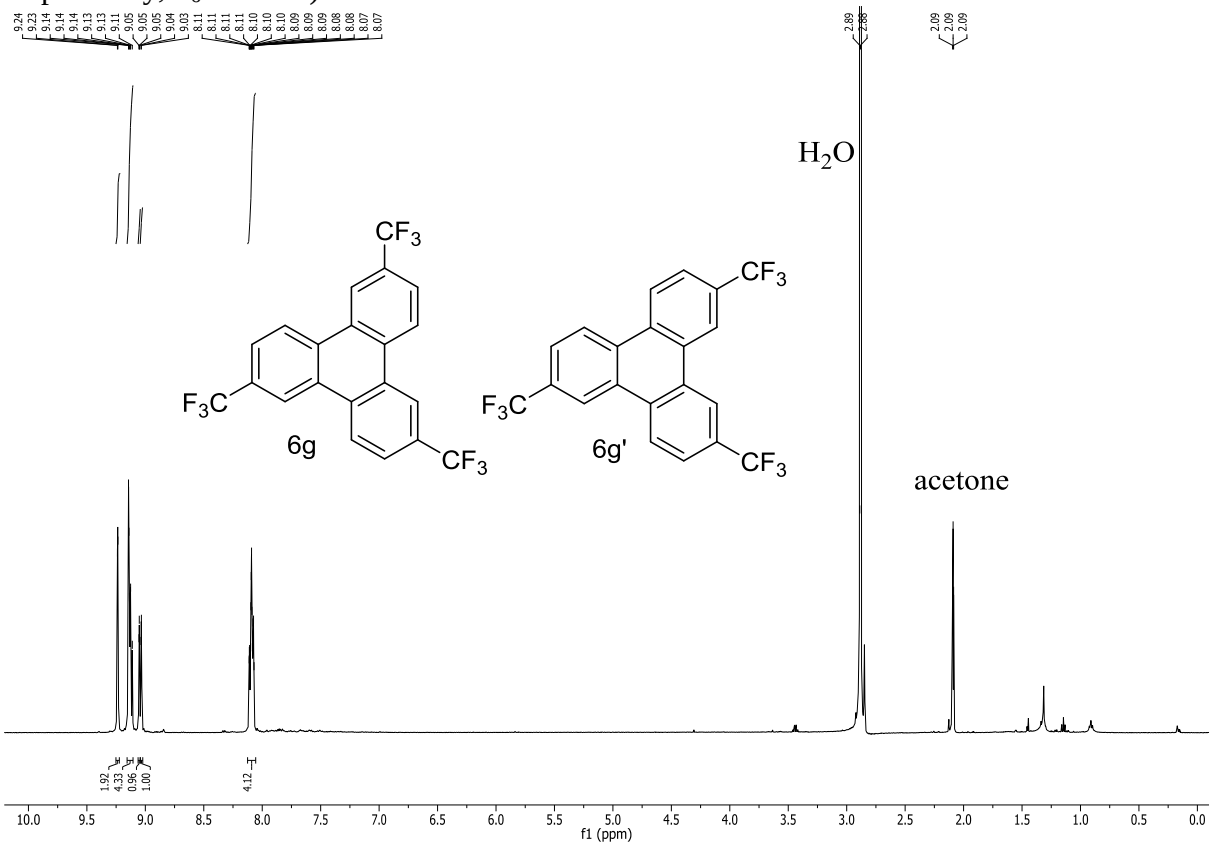
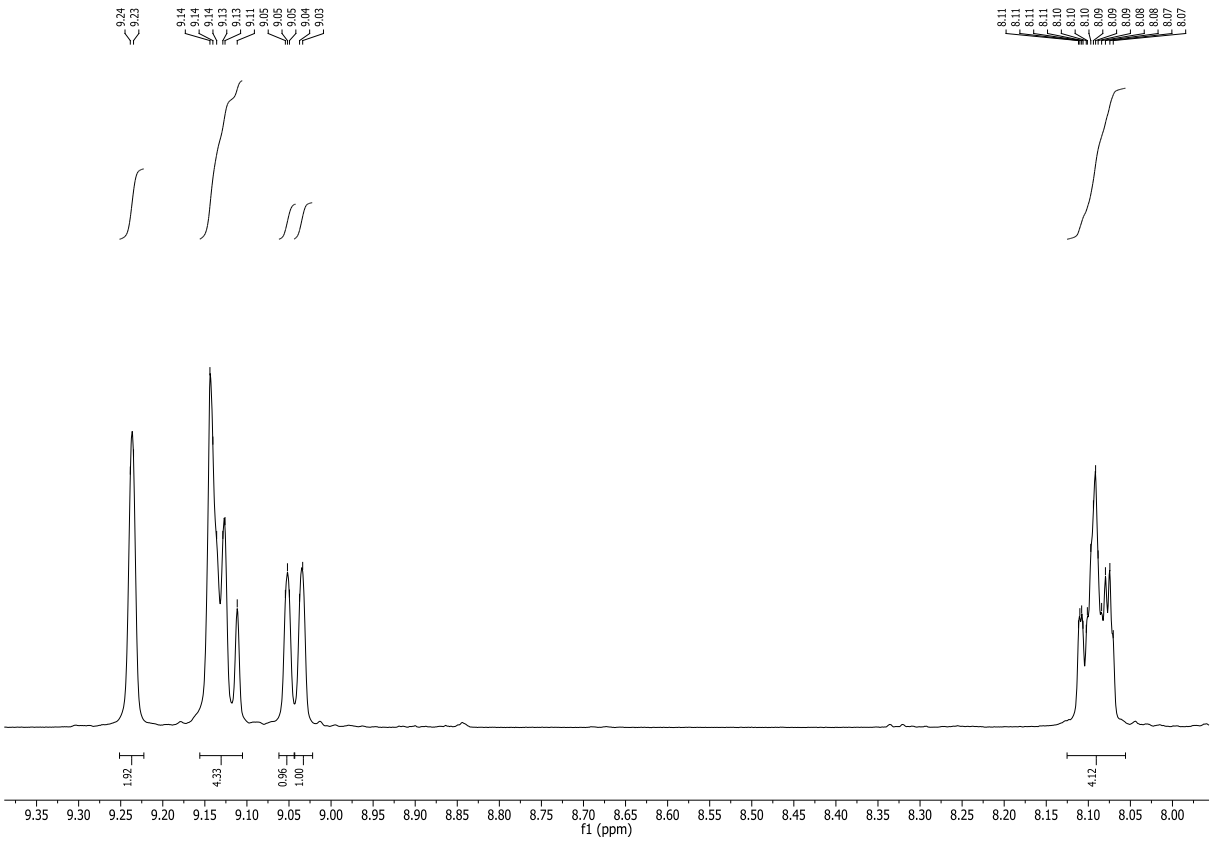
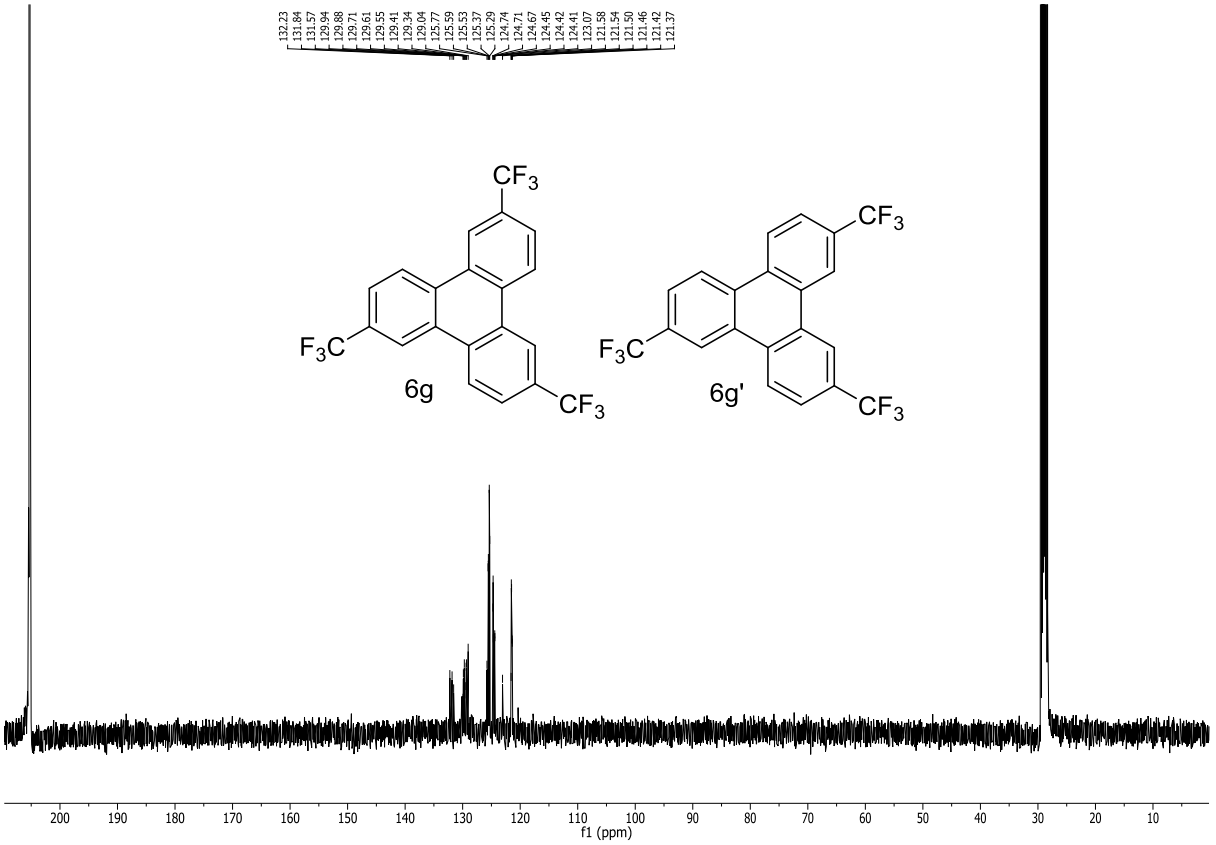
134.27
133.89
133.86
130.74
130.27
128.78
128.26
128.22
127.89
127.85
127.76
127.31
127.28
126.82
124.93
124.92
124.77
123.09
122.97
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
Cl
Cl
Cl
6f
Cl
Cl
Cl
6f'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H, ^{13}C NMR and ^{19}F data of the 1:3 mixture of compounds **6g:6g'** (500, 125 and 471 MHz respectively, d_6-acetone).




9.24
9.23
9.14
9.14
9.14
9.13
9.13
9.11
9.05
9.05
9.05
9.04
9.03
8.11
8.11
8.11
8.11
8.10
8.10
8.10
8.09
8.09
8.09
8.08
8.08
8.07
8.07
1.92
4.33
0.96
1.00
4.12
9.35 9.30 9.25 9.20 9.15 9.10 9.05 9.00 8.95 8.90 8.85 8.80 8.75 8.70 8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00
f1 (ppm)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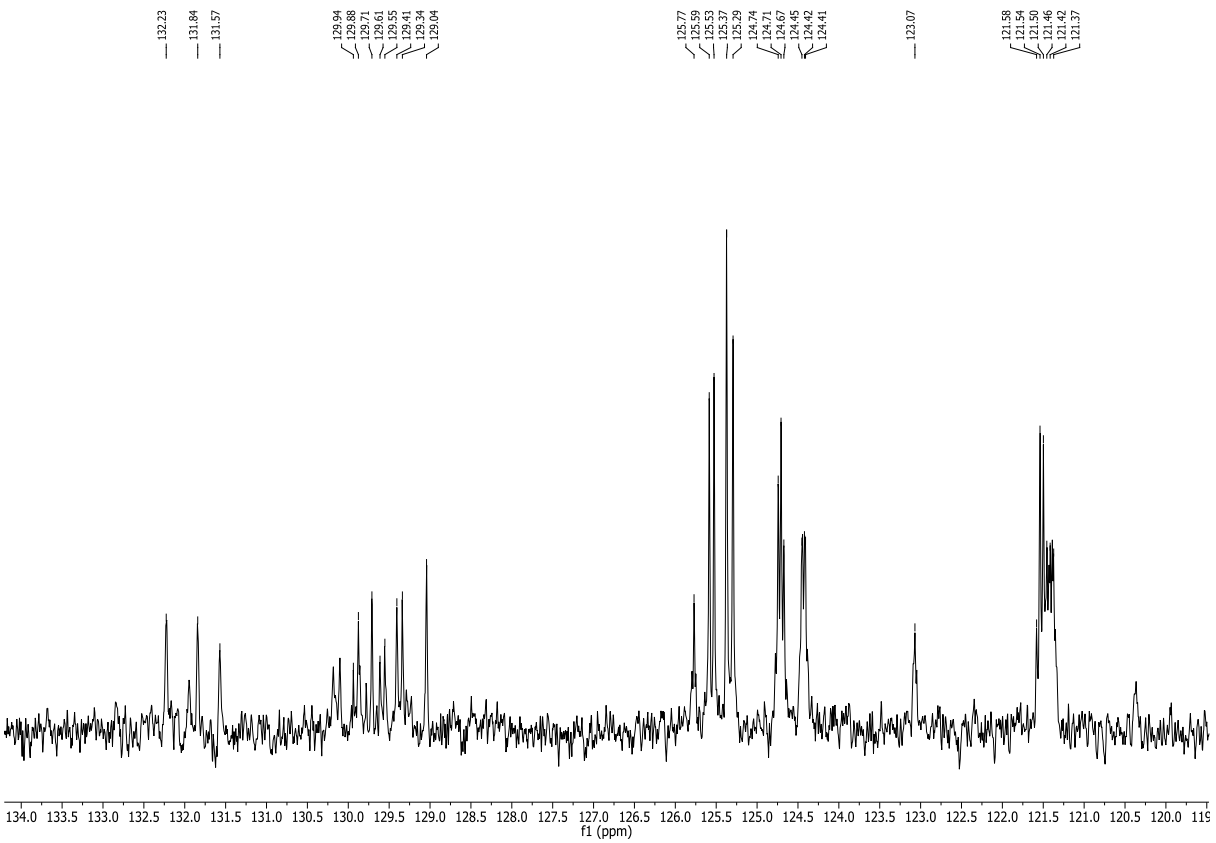
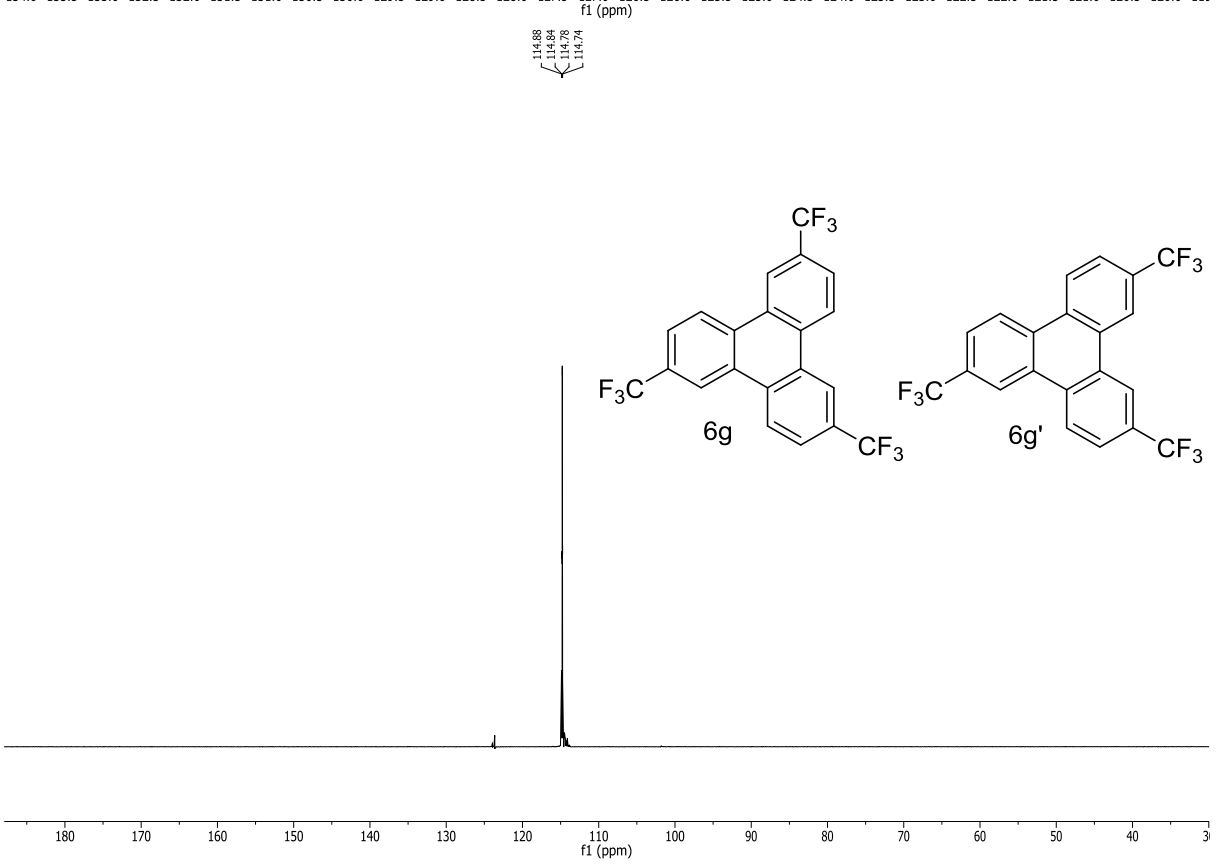
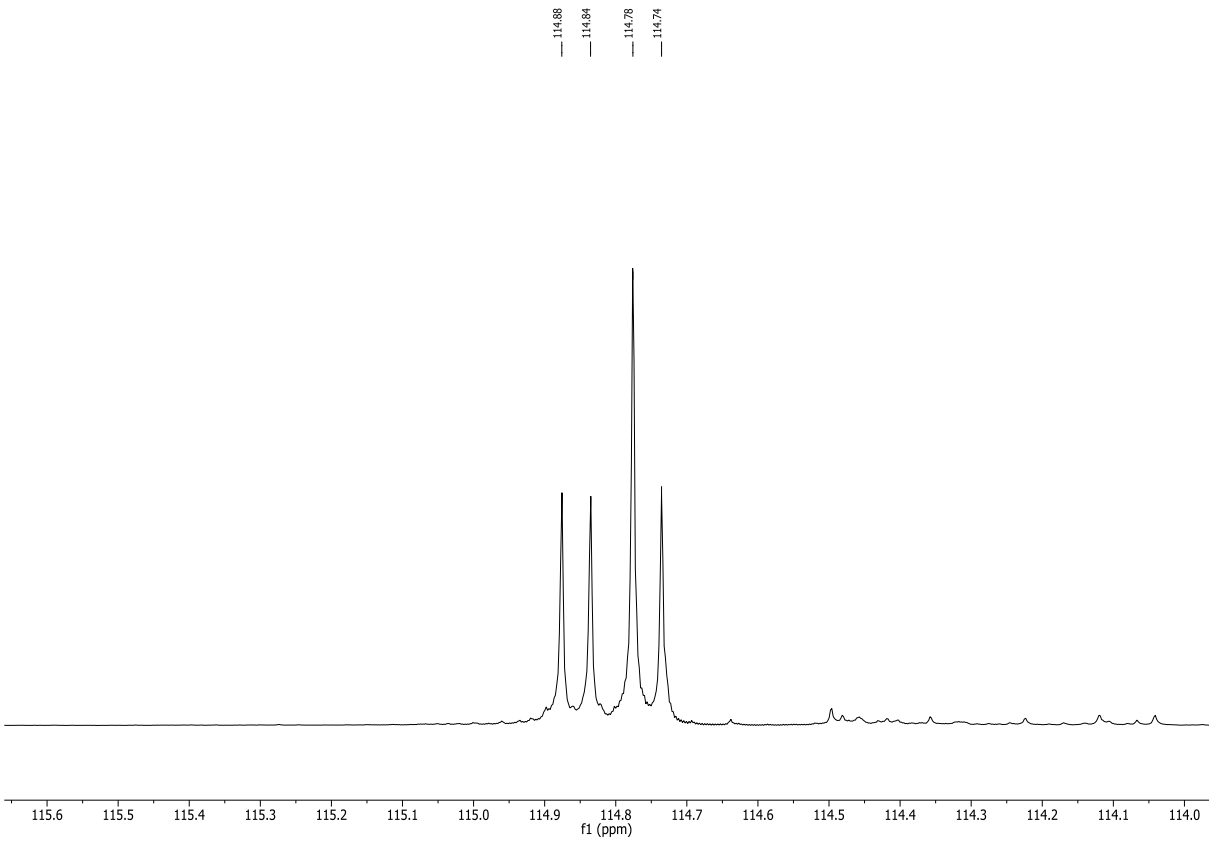
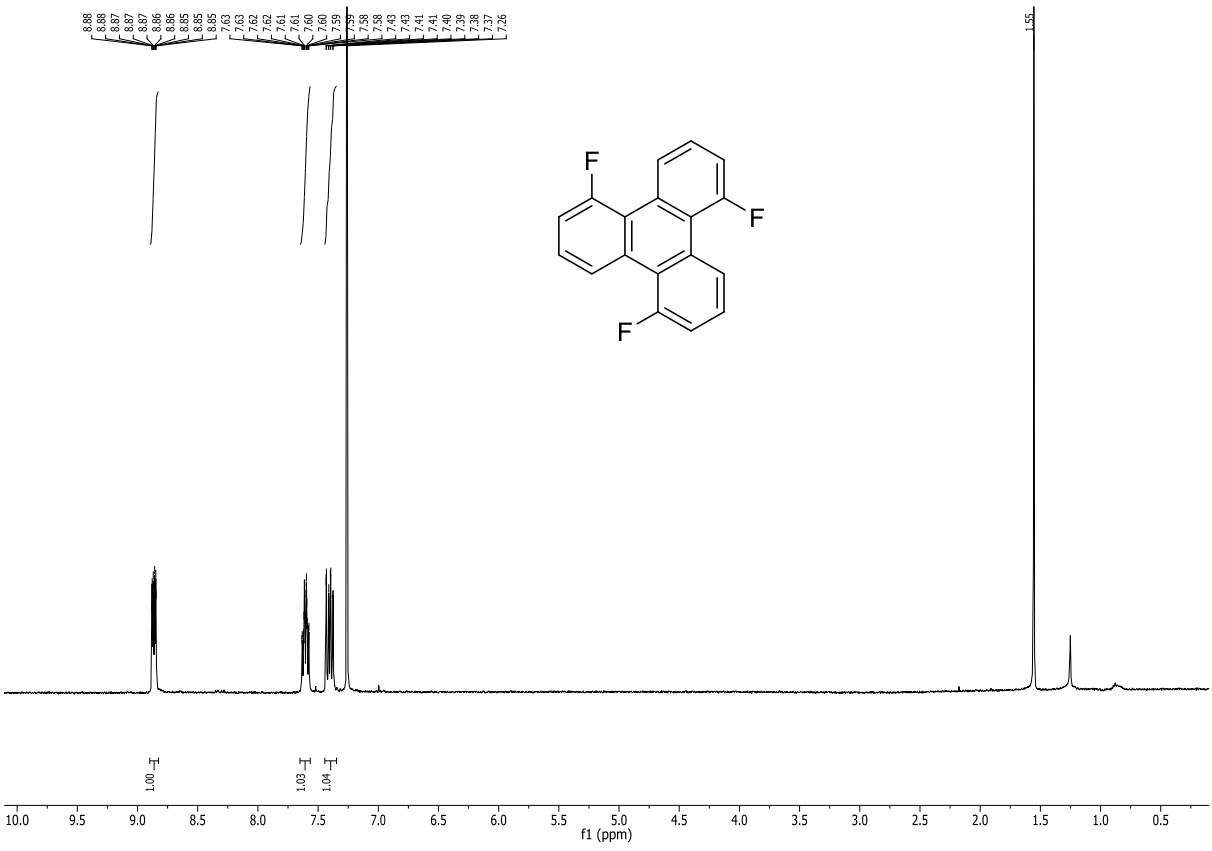
131.84
131.57
129.94
129.88
129.71
129.61
129.55
129.41
129.34
129.04
125.77
125.59
125.53
125.37
125.29
124.74
124.71
124.67
124.45
124.42
124.41
123.07
121.58
121.54
121.50
121.46
121.42
121.37
CF3
F3C
CF3
6g
CF3
F3C
CF3
6g'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

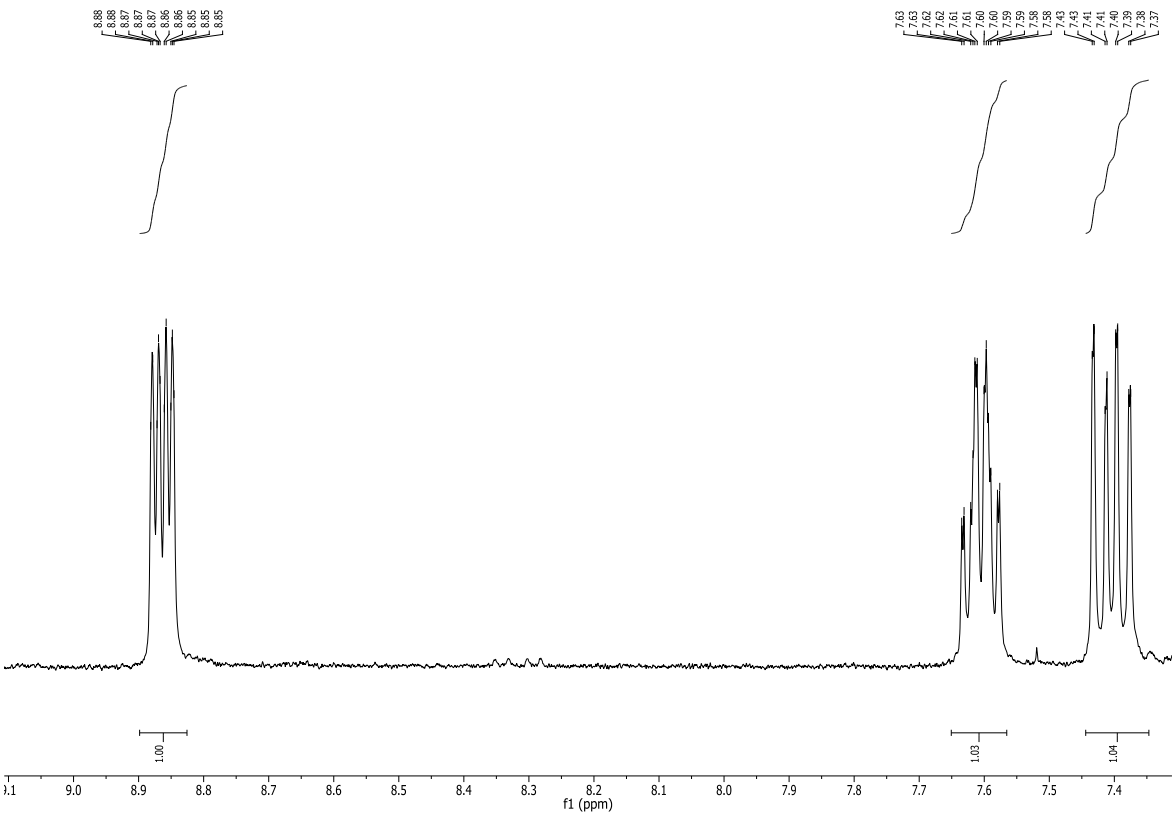

132.23
131.84
131.57
129.94
129.88
129.71
129.61
129.55
129.41
129.34
129.04
125.77
125.59
125.53
125.37
125.29
124.74
124.71
124.67
124.45
124.42
124.41
123.07
121.58
121.54
121.50
121.46
121.42
121.37
134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0 120.5 120.0
f1 (ppm)

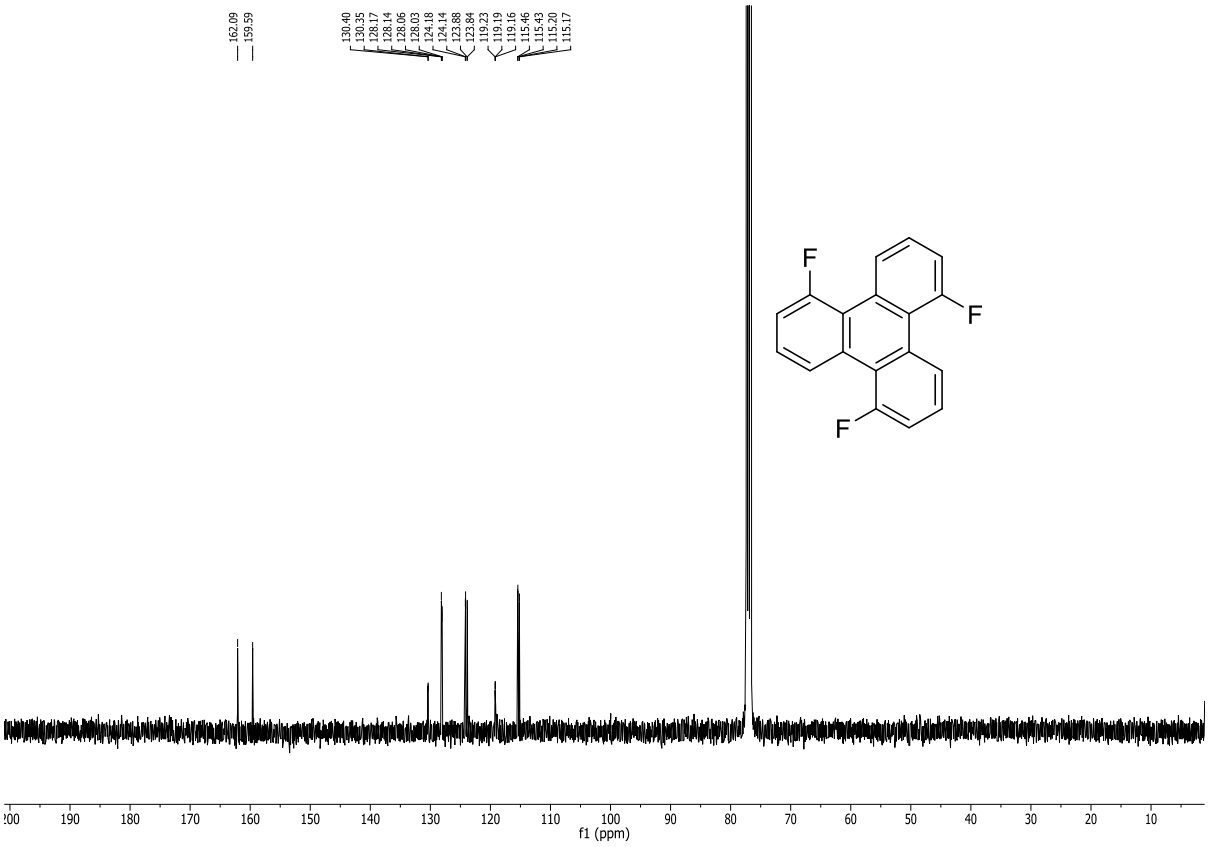

114.88
114.84
114.78
114.74
CF3
F3C
6g
CF3
CF3
F3C
6g'
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)

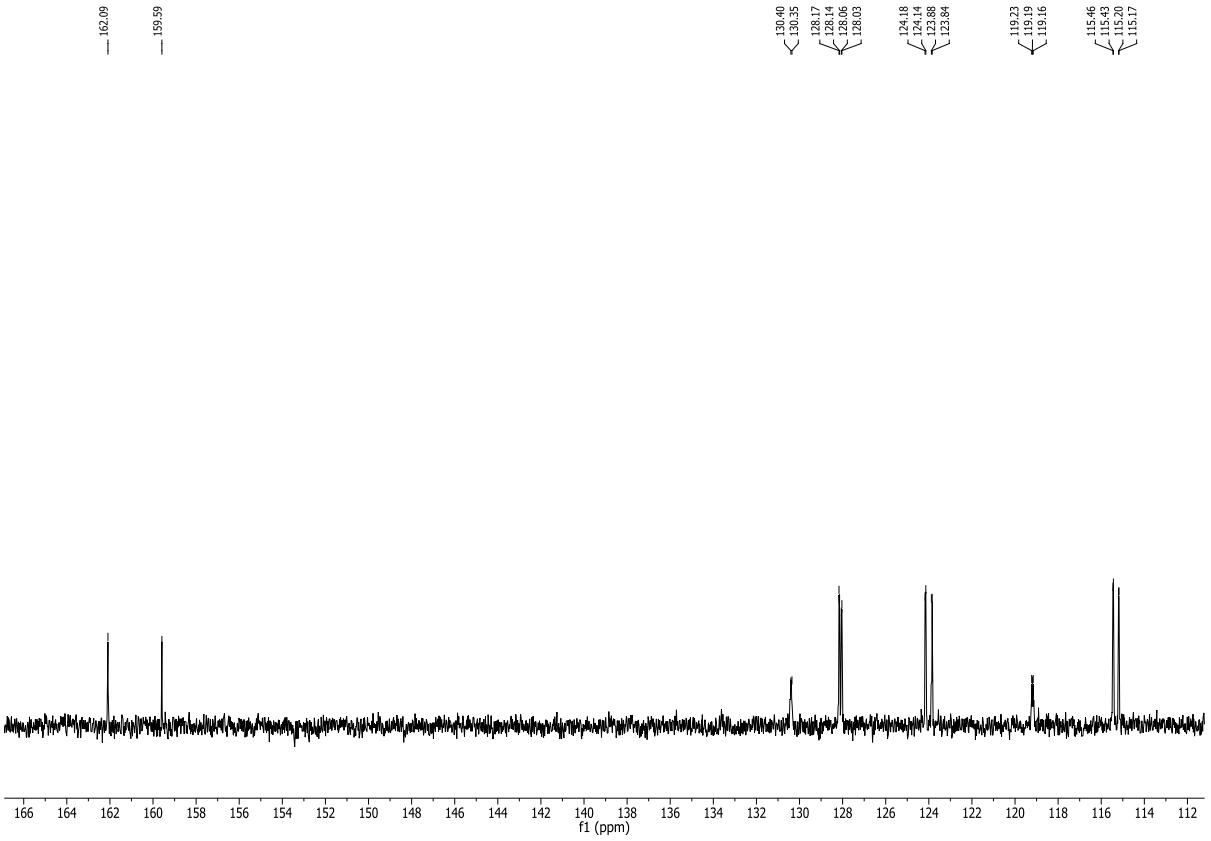


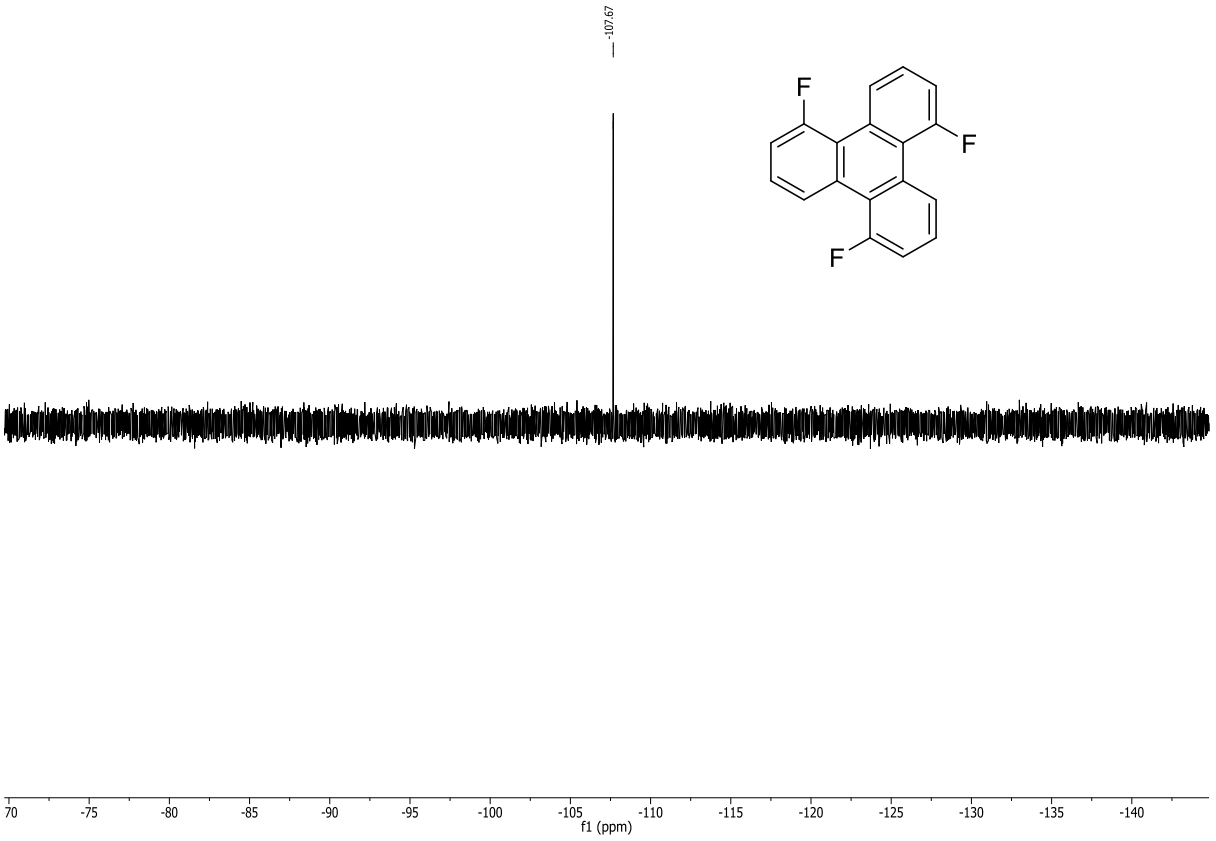
^{1}H, ^{13}C and ^{19}F NMR data of compound **6h** (500, 100 and 471 MHz respectively, $CDCl_3$).



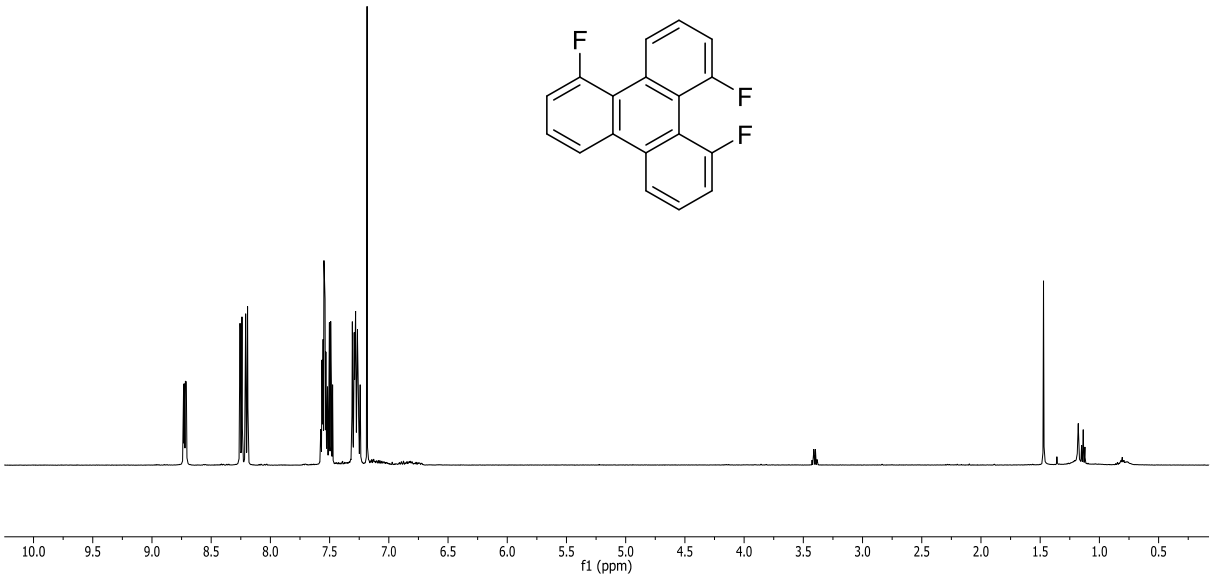

8.88
8.88
8.87
8.87
8.87
8.86
8.86
8.85
8.85
8.85
7.63
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.43
7.43
7.41
7.41
7.40
7.39
7.38
7.37
1.00
1.03
1.04
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)

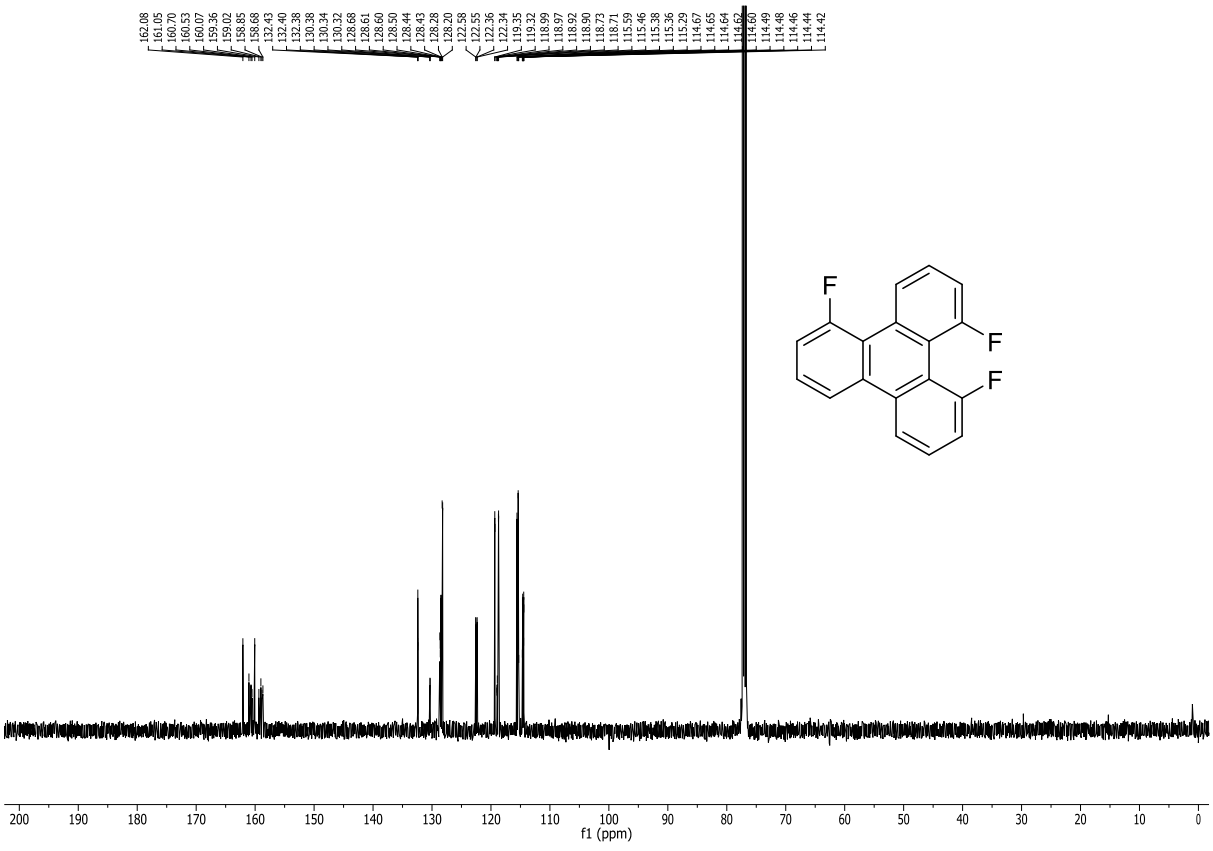

162.09
159.59
130.40
130.35
128.17
128.14
128.06
128.03
124.18
124.14
123.88
123.84
119.23
119.19
119.16
115.46
115.43
115.20
115.17
F
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

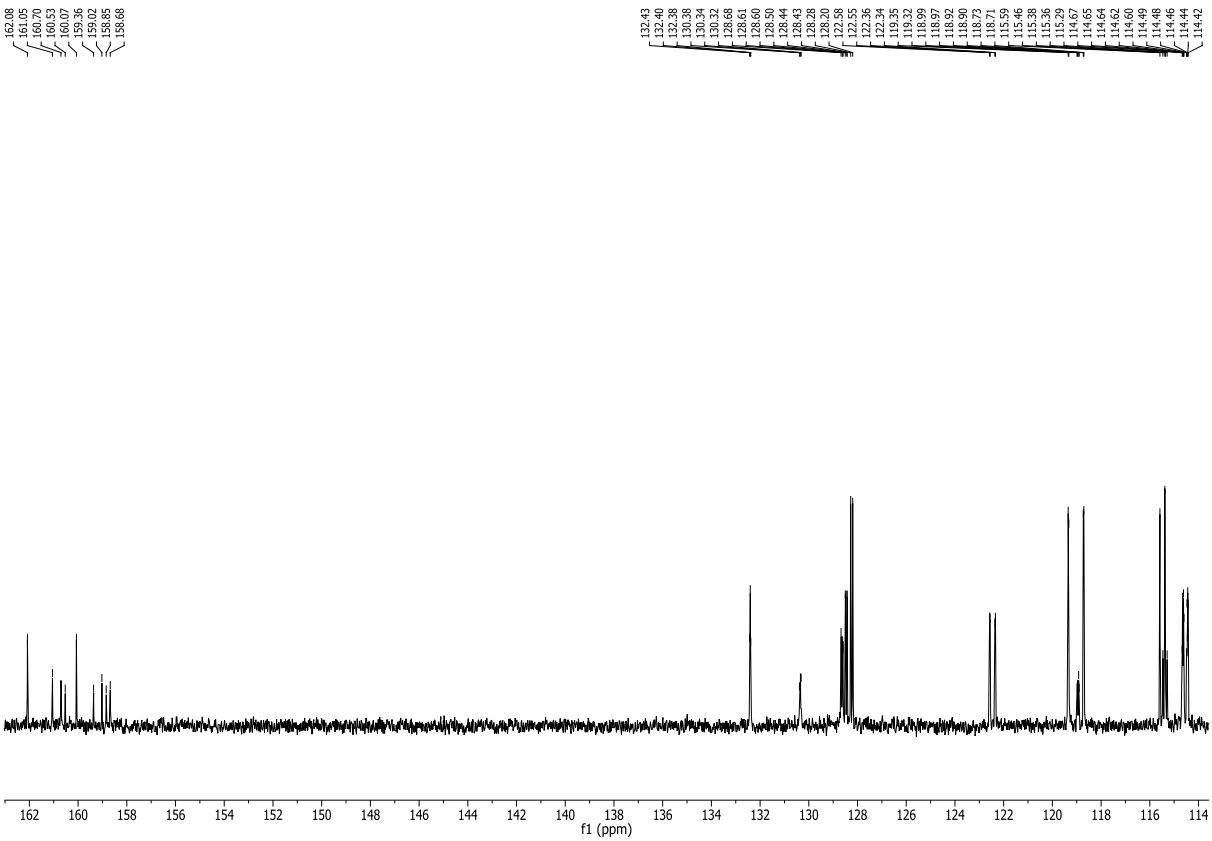

162.09
159.59
130.40
130.35
128.17
128.14
128.06
128.03
124.18
124.14
123.88
123.84
119.23
119.19
119.16
115.46
115.43
115.20
115.17
166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)

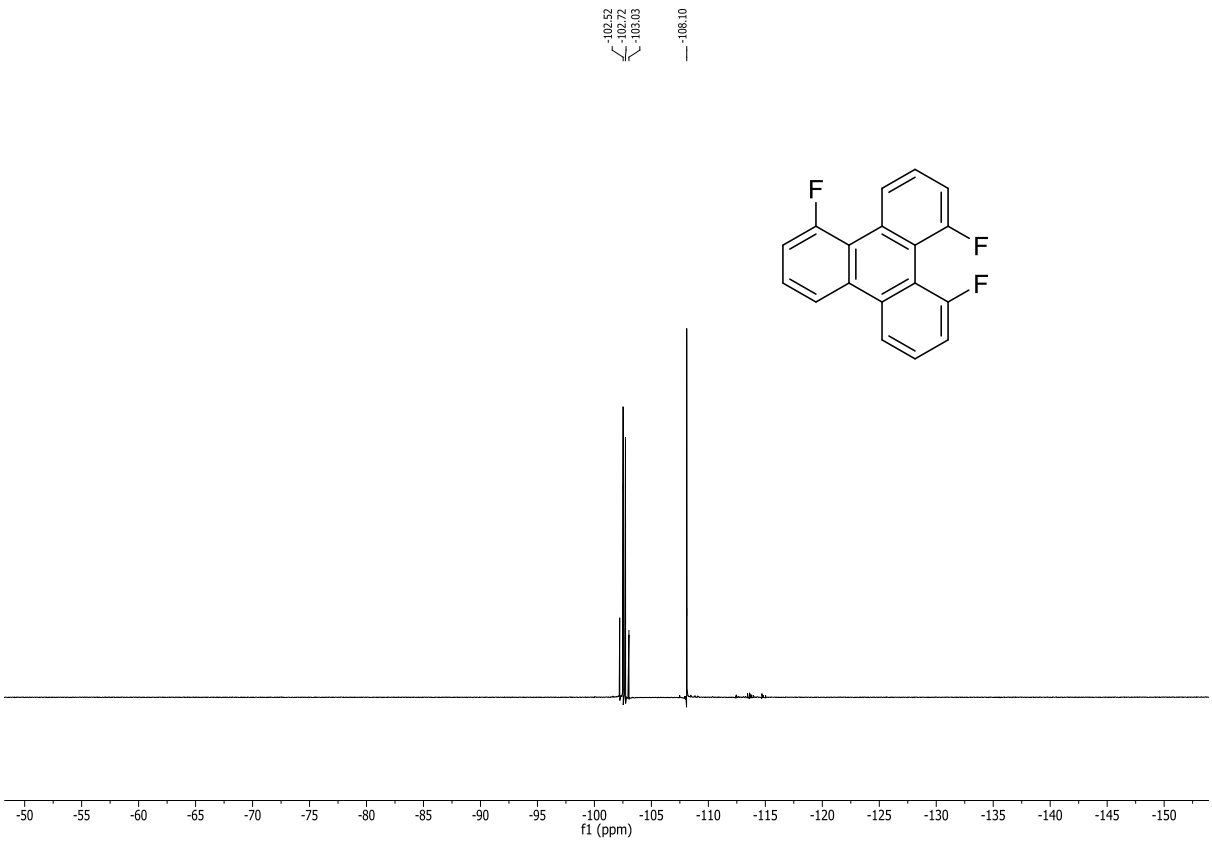

-107.67
F
F
F
70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)

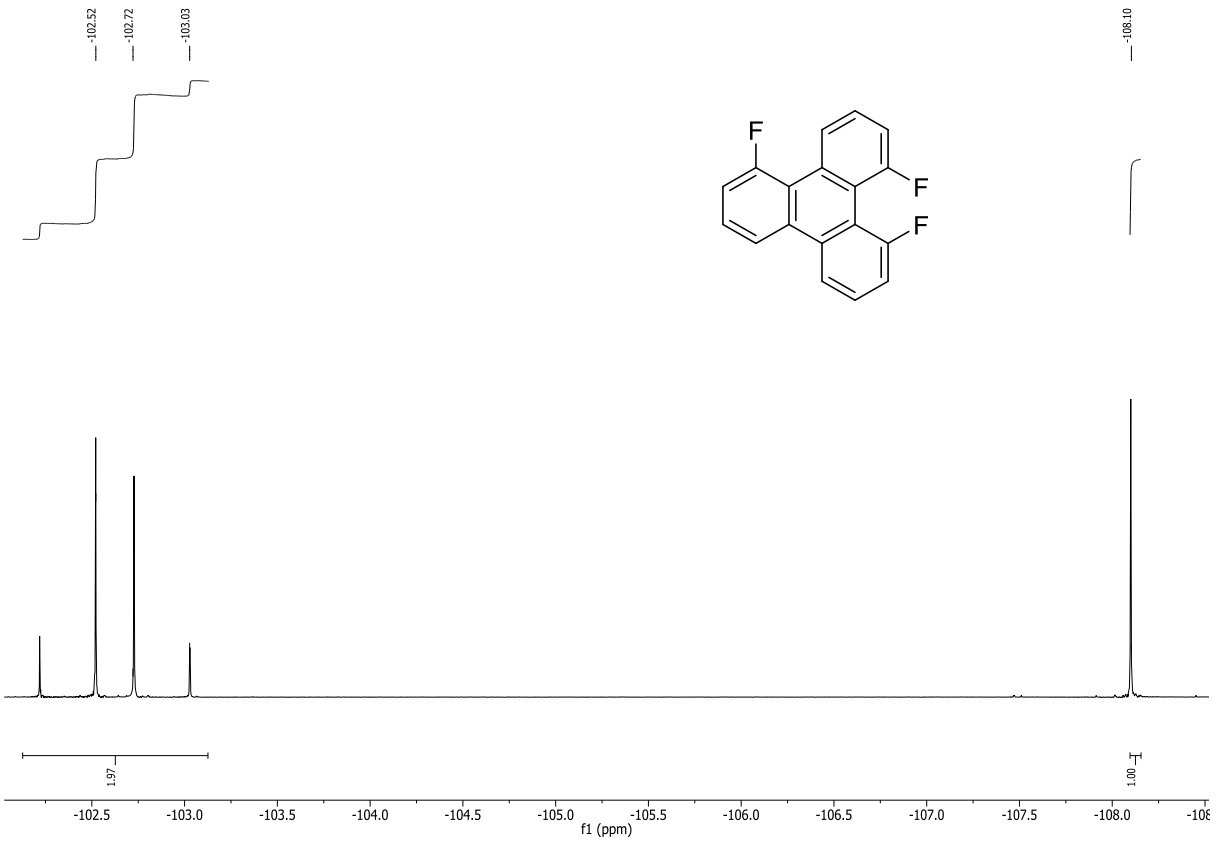
^{1}H, ^{13}C NMR and ^{19}F data of compound **6h'** (500 , 125 and 471 MHz respectively, $CDCl_3$).



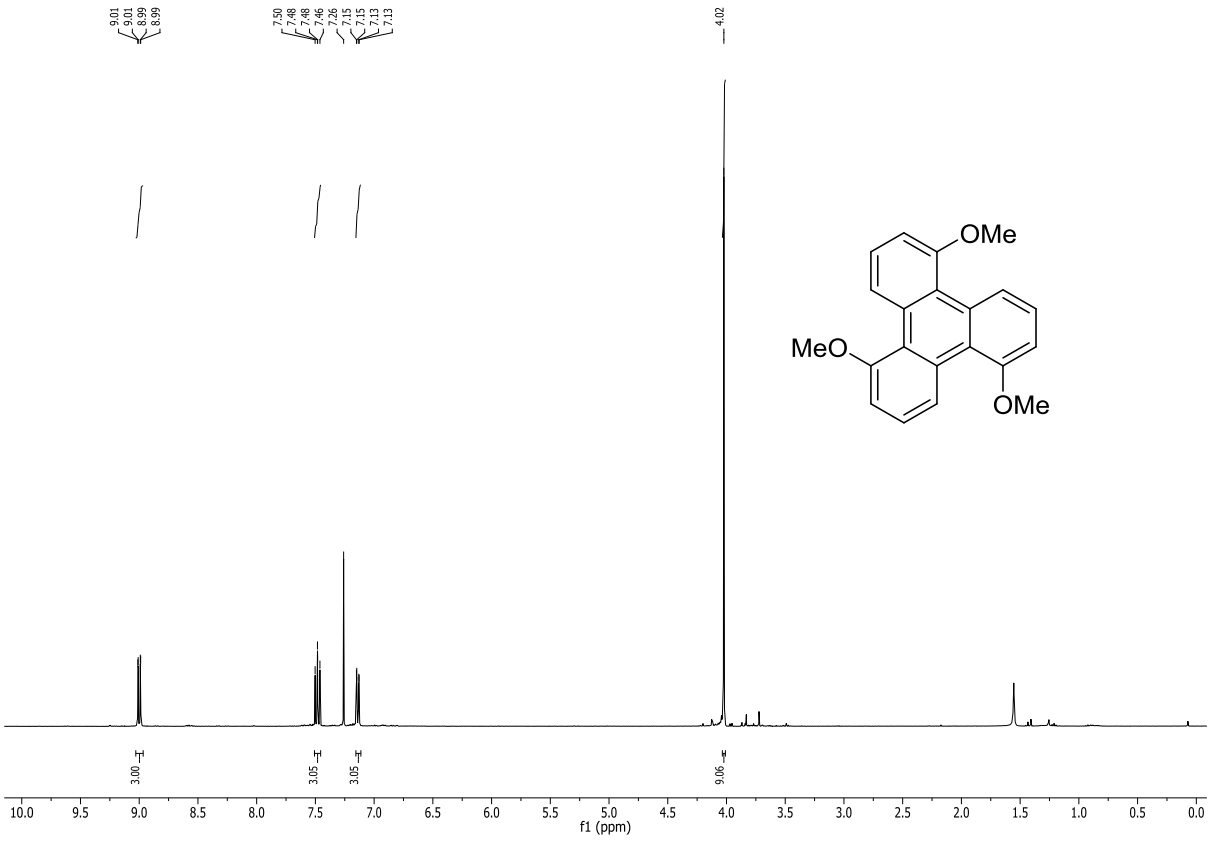


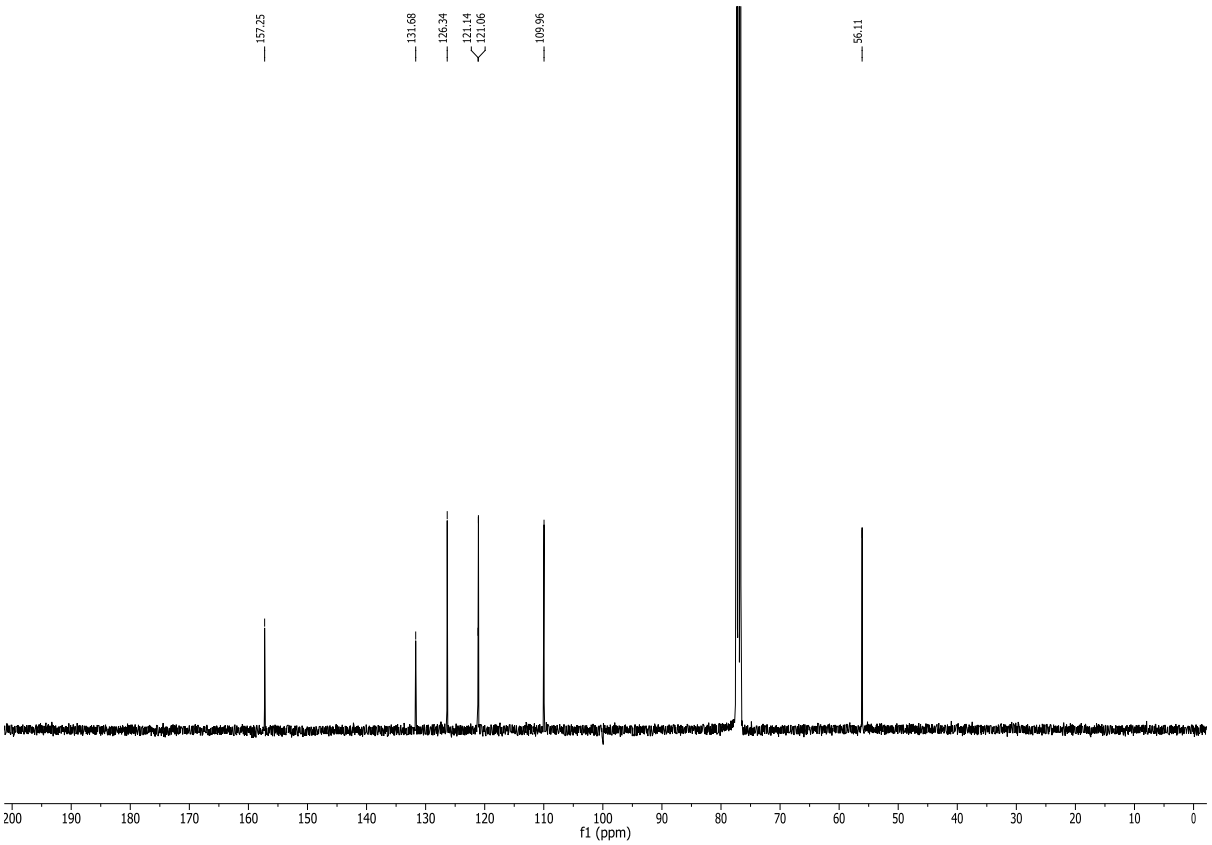

162.08
161.05
160.70
160.53
160.07
159.36
159.02
158.85
158.68
132.43
132.40
132.38
130.38
130.34
130.32
128.68
128.61
128.60
128.50
128.44
128.43
128.28
128.20
122.58
122.55
122.36
122.34
119.35
119.32
118.99
118.97
118.92
118.90
118.73
118.71
115.59
115.46
115.38
115.36
115.29
114.67
114.65
114.64
114.62
114.60
114.49
114.48
114.46
114.44
114.42
162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)


-102.52
-102.72
-103.03
-108.10
F
F
F
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

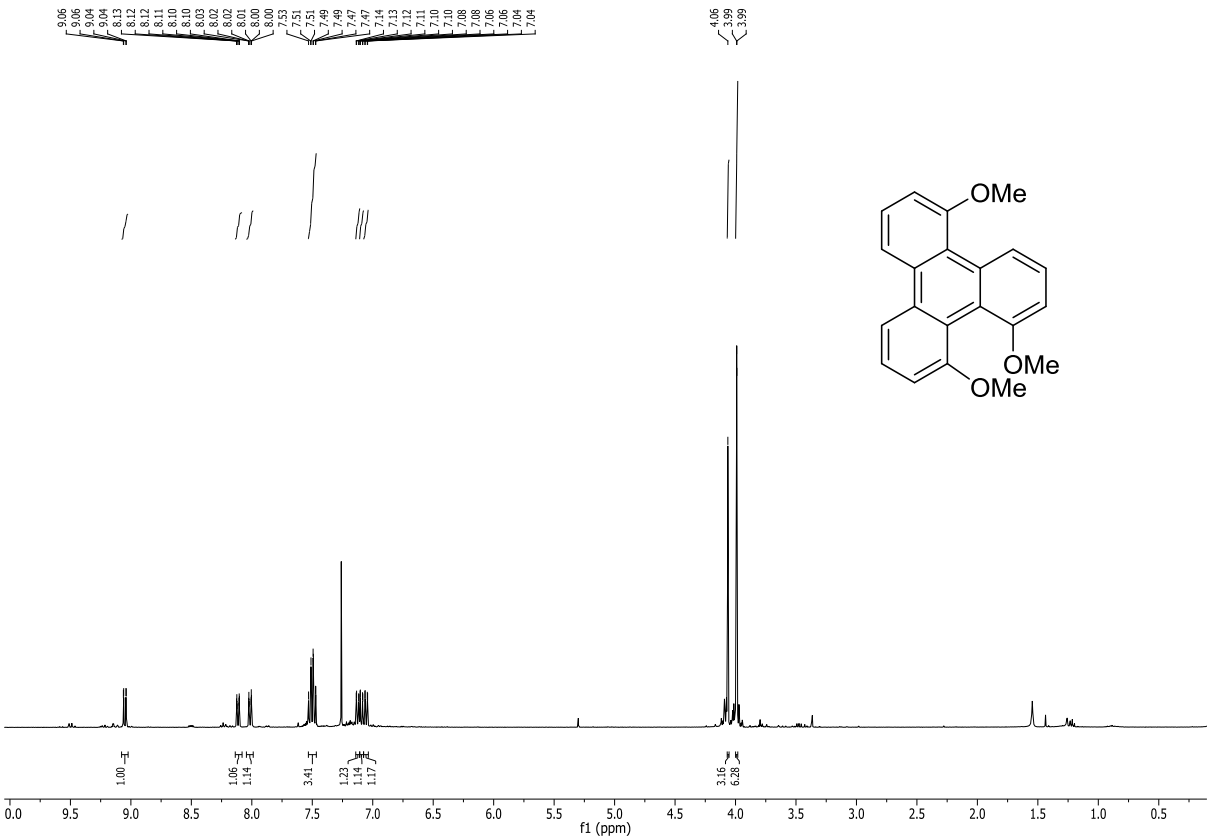


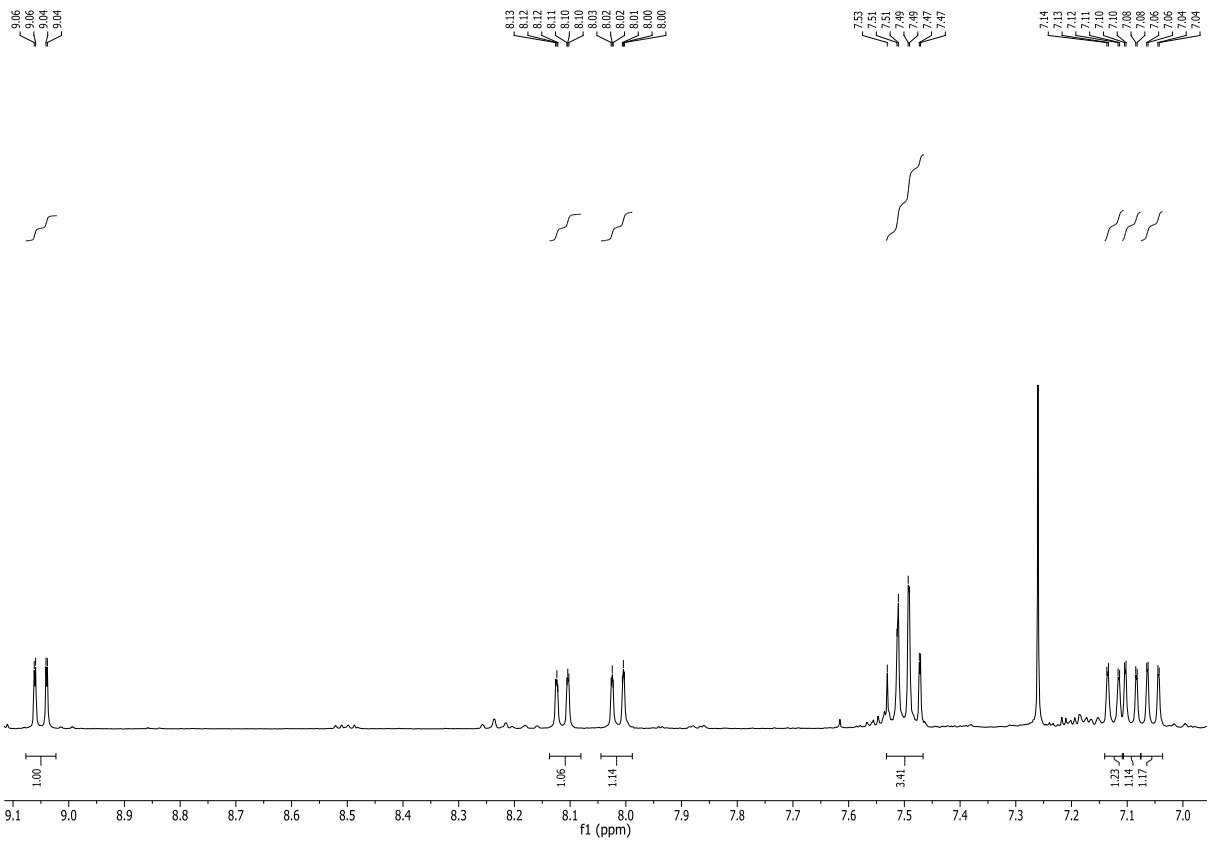
^{1}H and ^{13}C NMR data of compound **6i** (500 and 125 MHz respectively, $CDCl_3$).

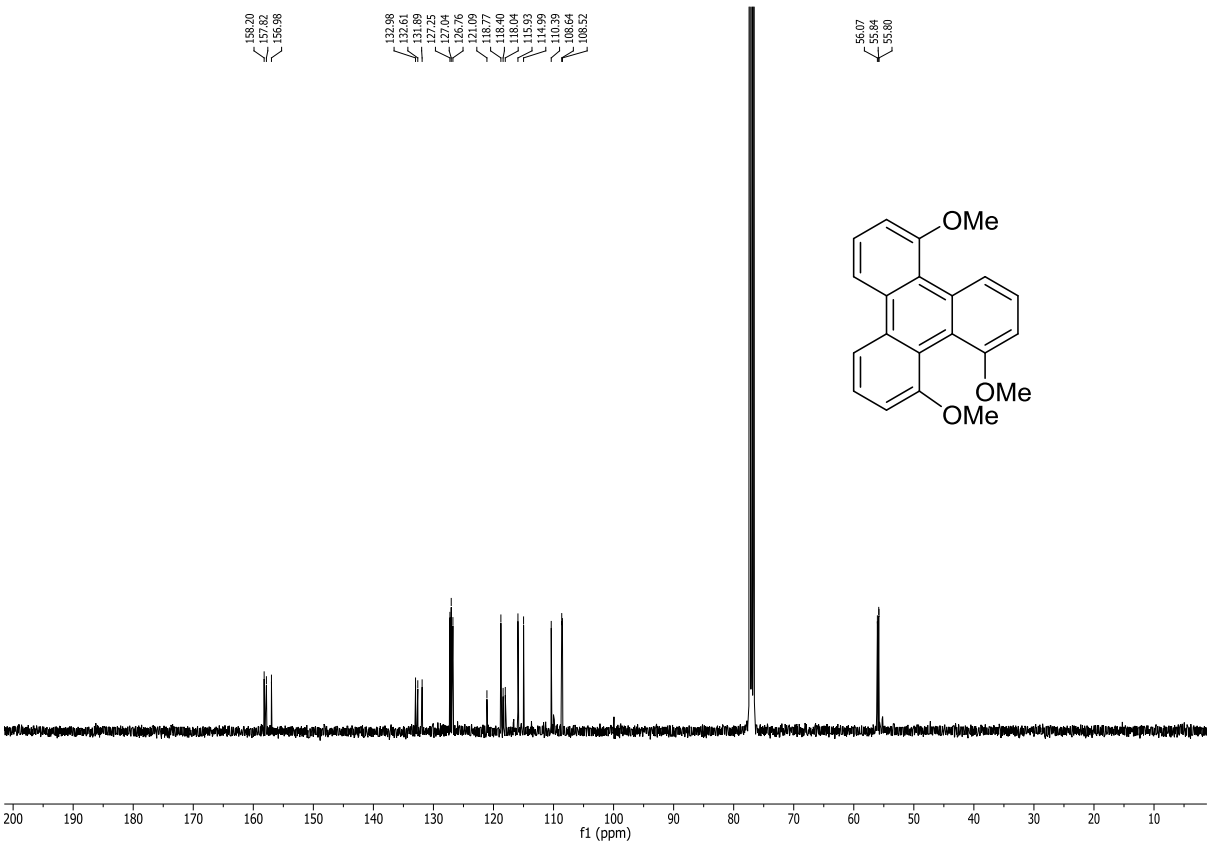


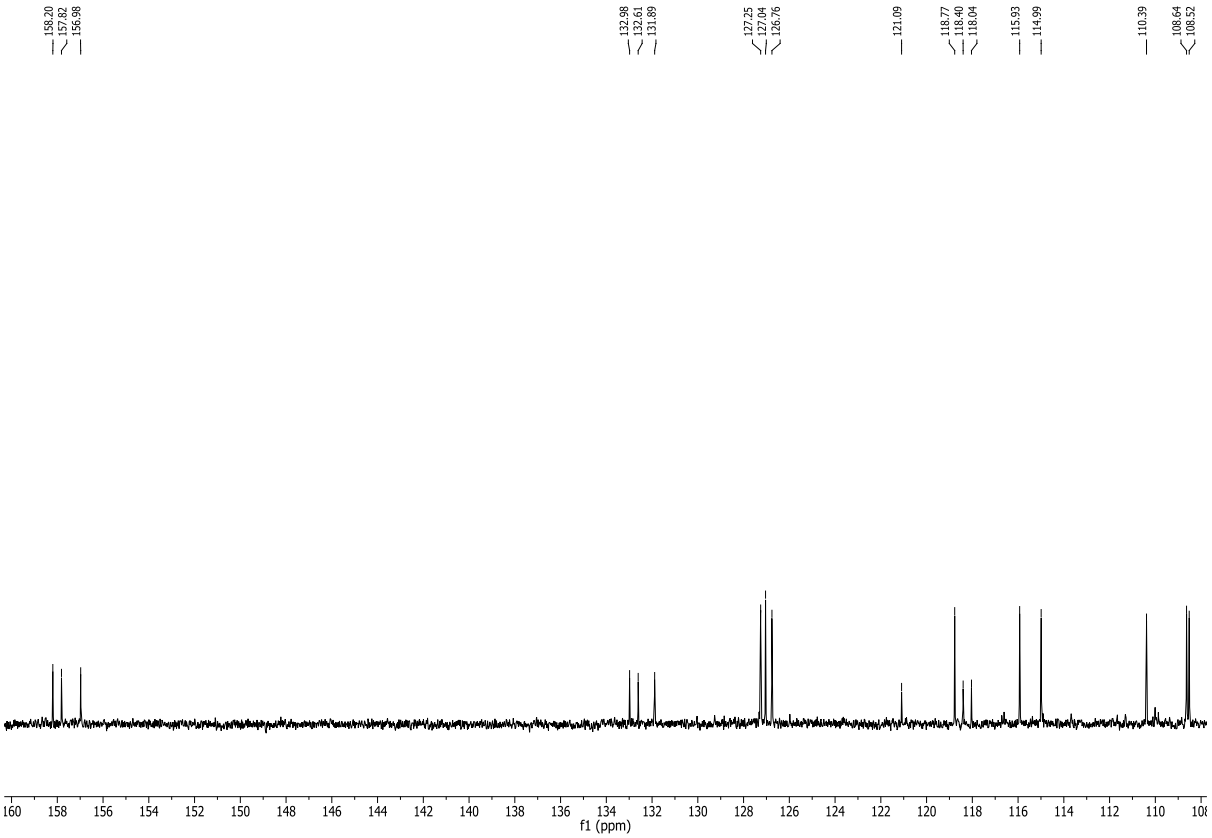


^{1}H and ^{13}C NMR data of compound **6i'** (500 and 125 MHz respectively, $CDCl_3$).

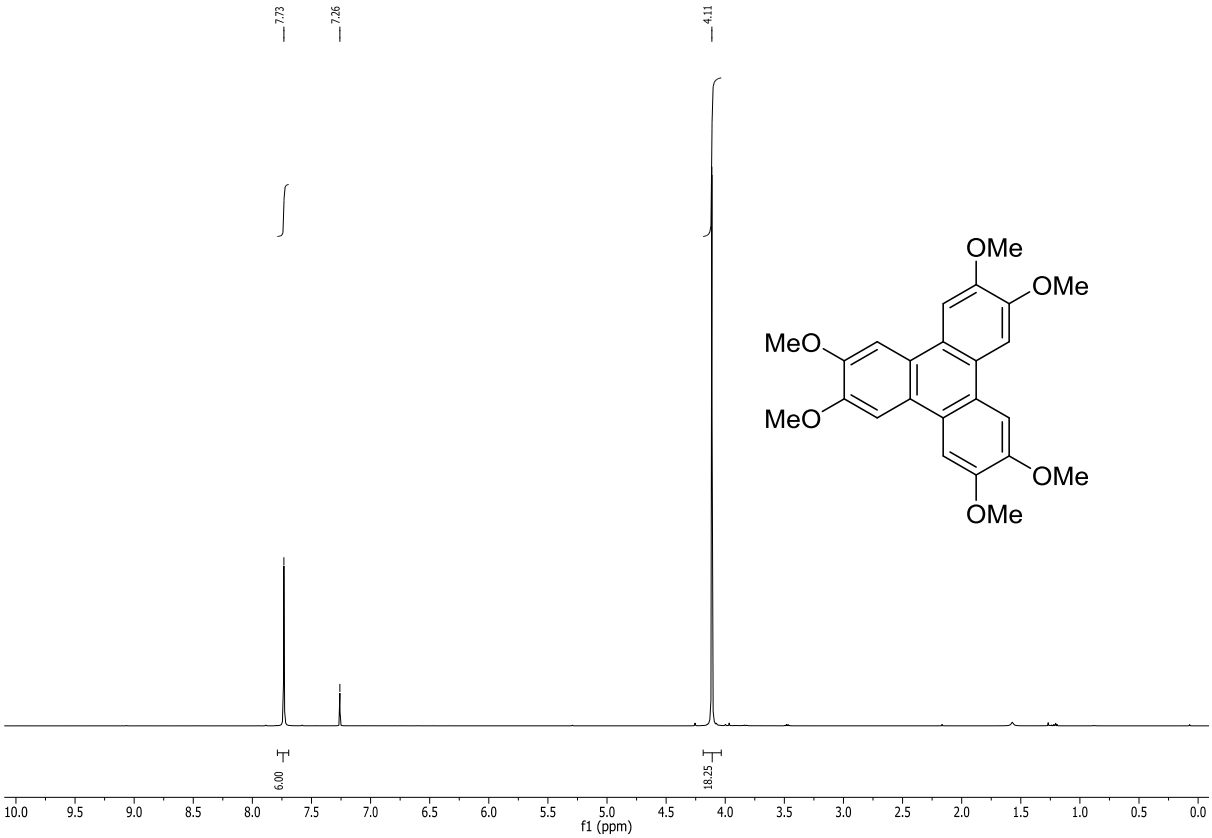


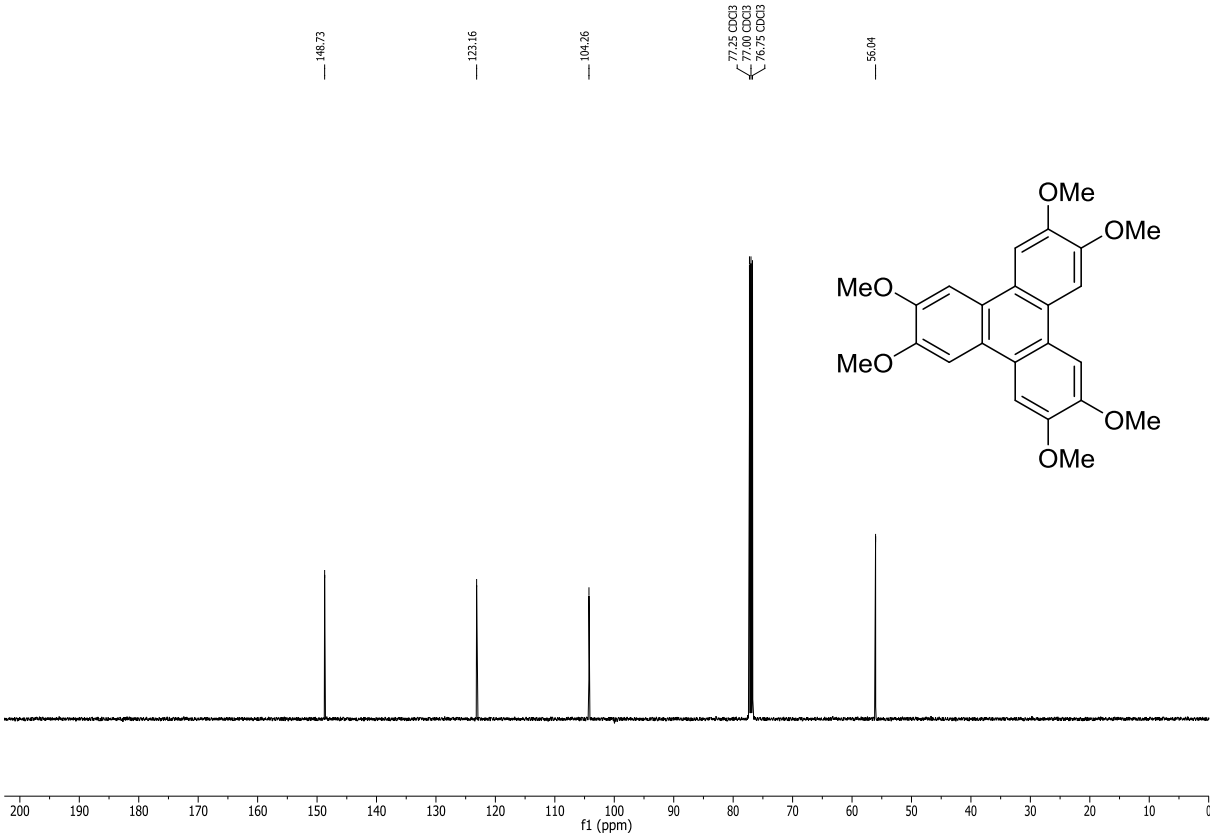

9.06
9.06
9.04
9.04
8.13
8.12
8.12
8.11
8.10
8.10
8.03
8.02
8.02
8.01
8.00
8.00
7.53
7.51
7.51
7.49
7.49
7.47
7.47
7.14
7.13
7.12
7.11
7.10
7.10
7.08
7.08
7.06
7.06
7.04
7.04
1.00
1.06
1.14
3.41
1.23
1.14
1.17
f1 (ppm)


158.20
157.82
156.98
132.98
132.61
131.89
127.25
127.04
126.76
121.09
118.77
118.40
118.04
115.93
114.99
110.39
108.64
108.52
56.07
55.84
55.80
OMe
OMe
OMe
f1 (ppm)

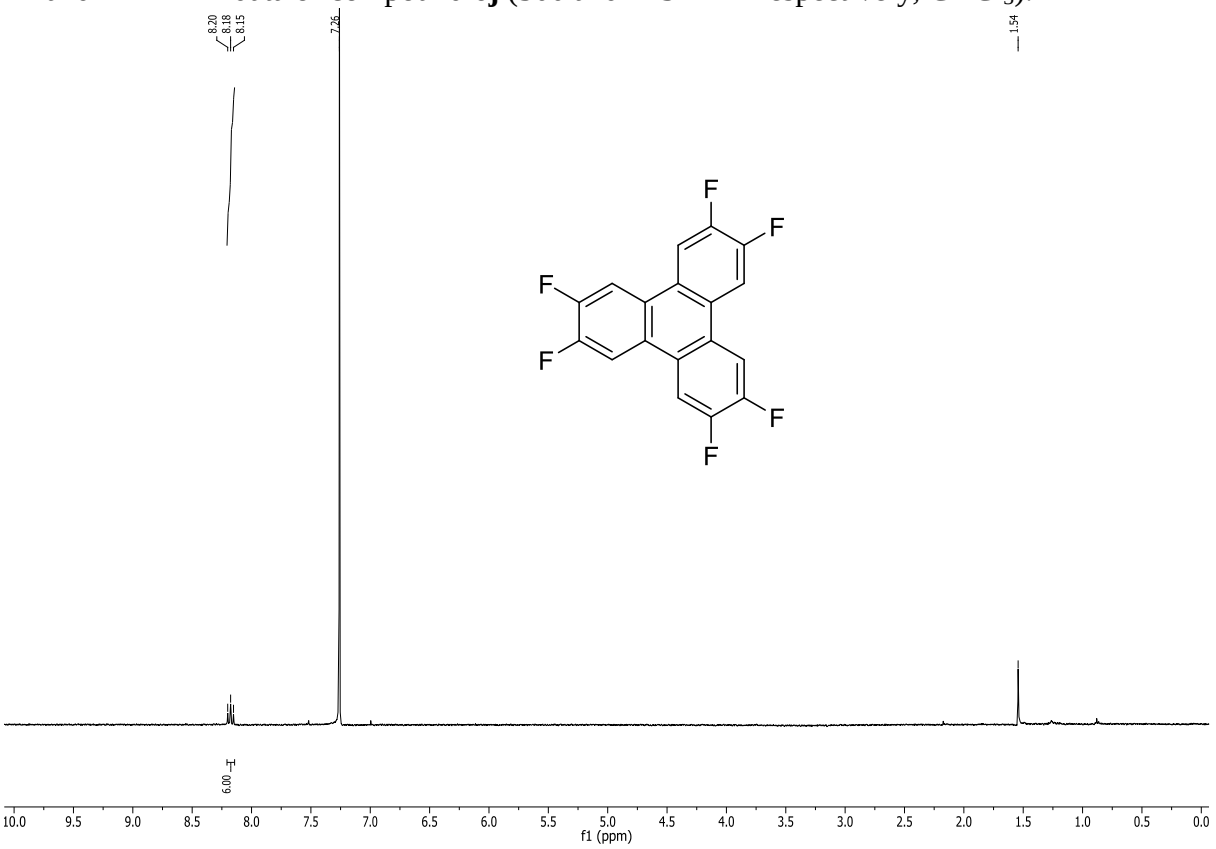


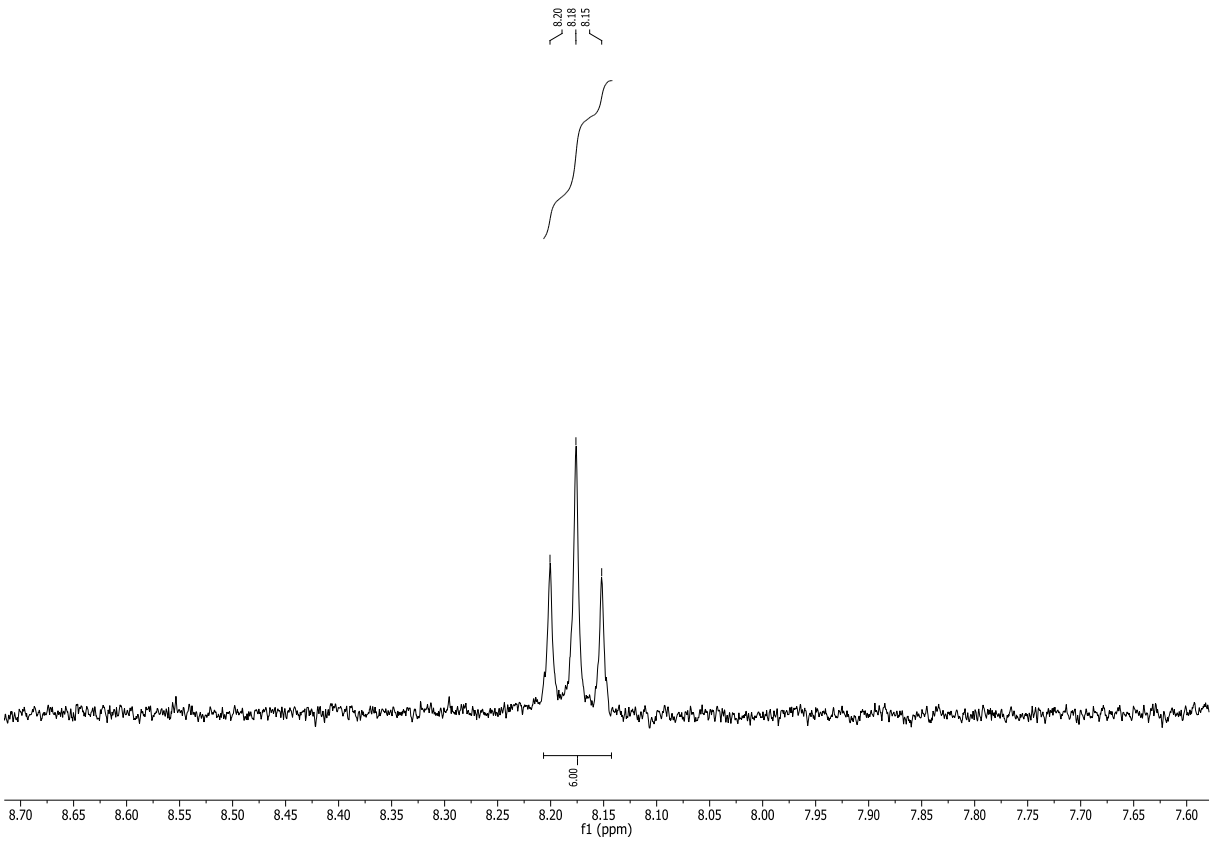
^{1}H and ^{13}C NMR data of compound **6l** (500 and 125 MHz respectively, $CDCl_3$).

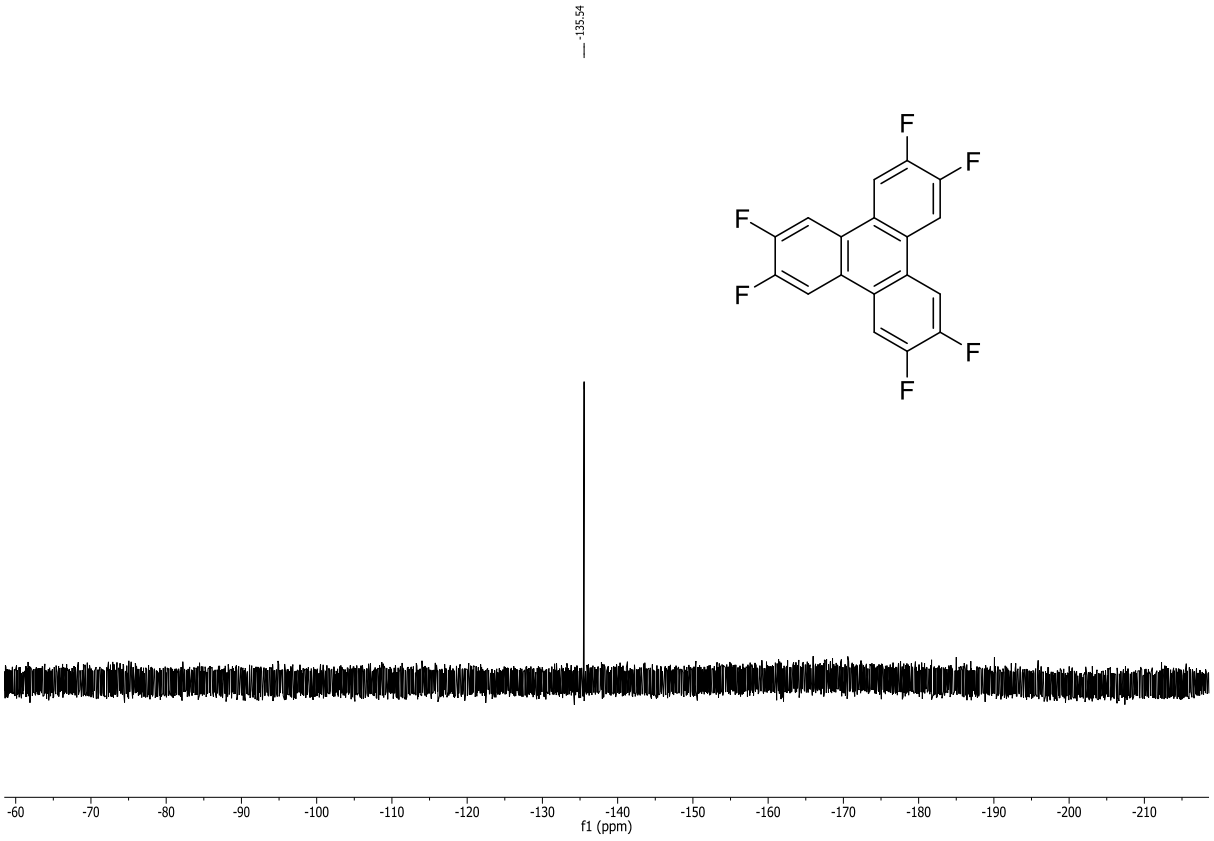




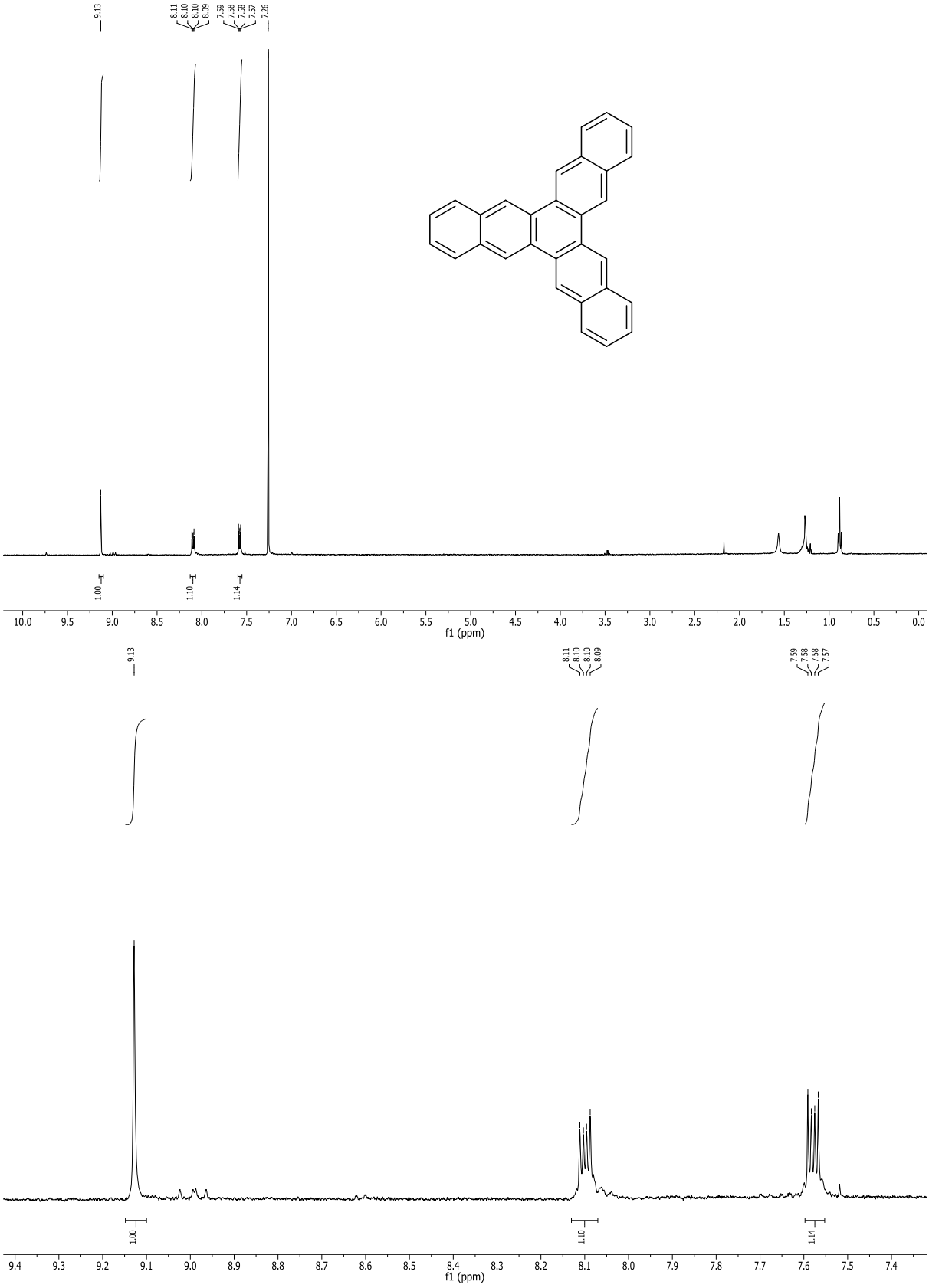
^{1}H and ^{19}F NMR data of compound **6j** (500 and 475 MHz respectively, $CDCl_3$).

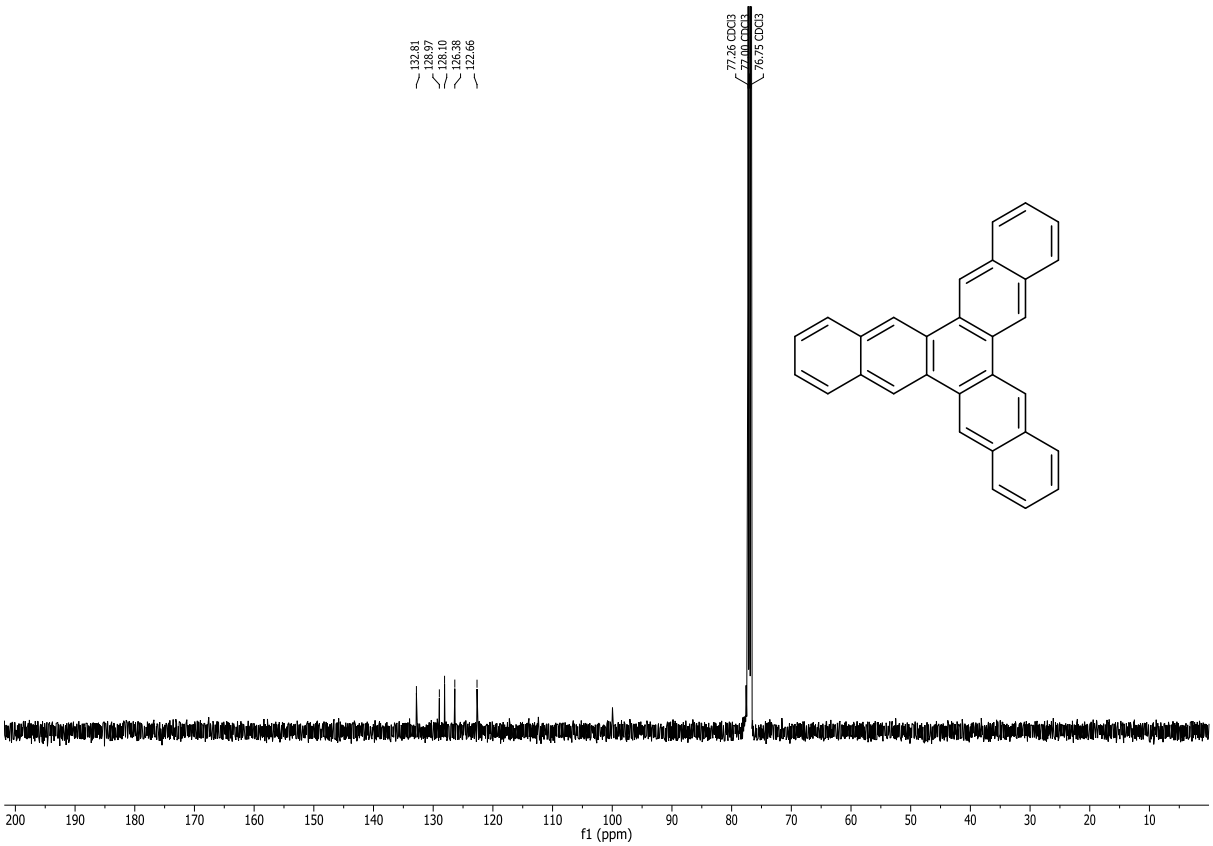


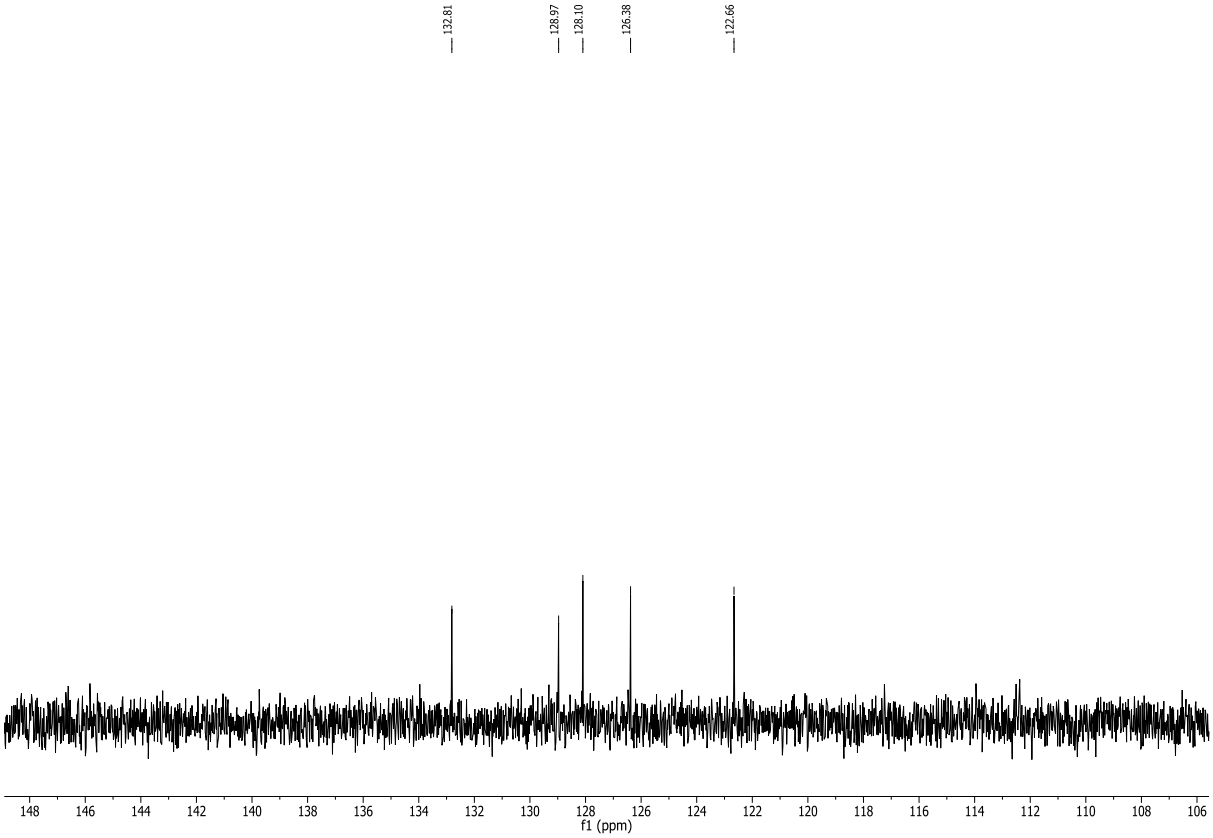

8.20
8.18
8.15
6.00
8.70 8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60
f1 (ppm)


-135.54
F
F
F
F
F
F
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H and ^{13}C NMR data of compound **6k** (500 and 125 MHz respectively, $CDCl_3$).



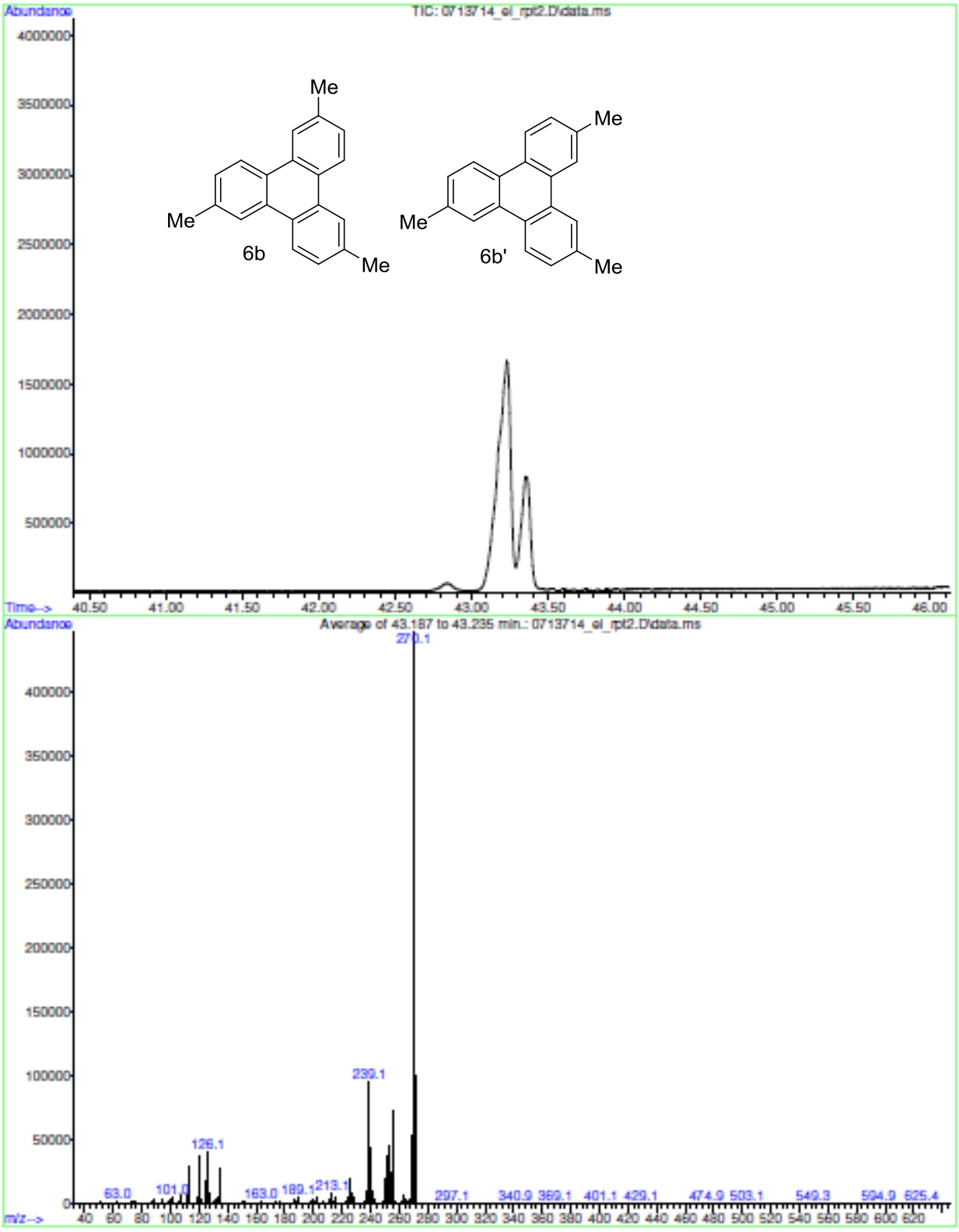

132.81
128.97
128.10
126.38
122.66
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
f1 (ppm)

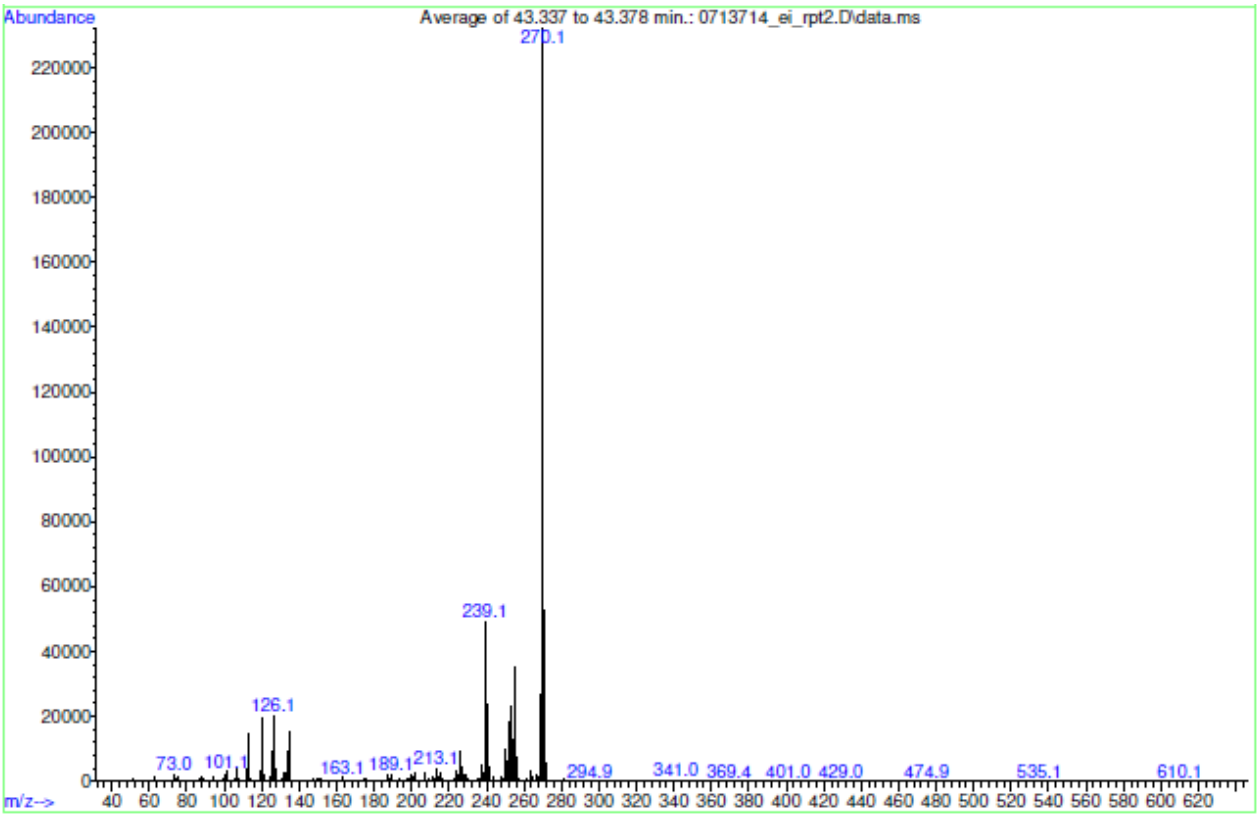

132.81
128.97
128.10
126.38
122.66
f1 (ppm)

GC-MS Data

GCMS traces of mixtures of compounds **6b / 6b´**, **6c / 6c´** and **6d / 6d´**

```
File       :U:\smsdata\current_data\msd2\data\0713714_gi_rpt2.D
Operator   :
Acquired   : 30 Jul 2013  15:56     using AcqMethod 50T300_JG_EI_10HOLD_20_SPLIT_B.M
Instrument :    MSD2
Sample Name: JAG291
Misc Info  :
Vial Number: 14
```

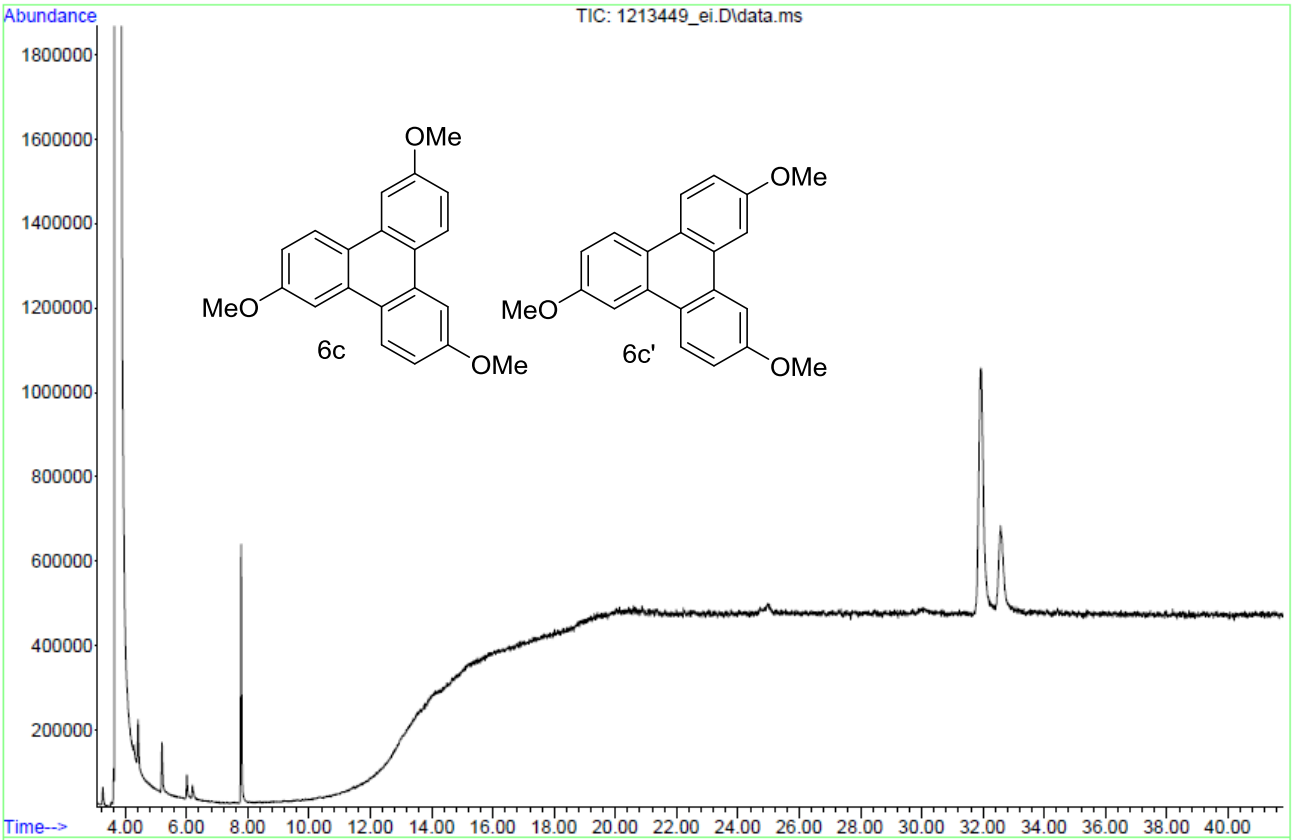


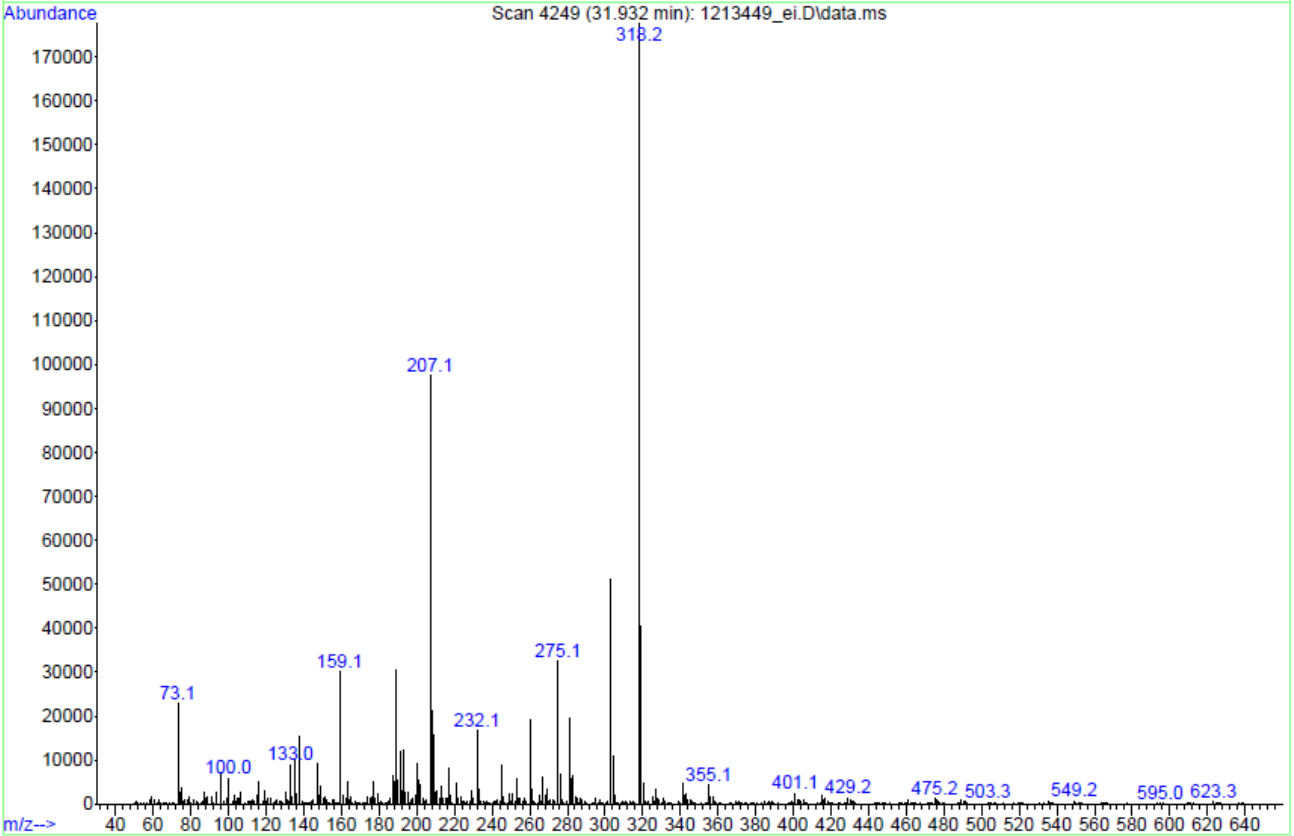


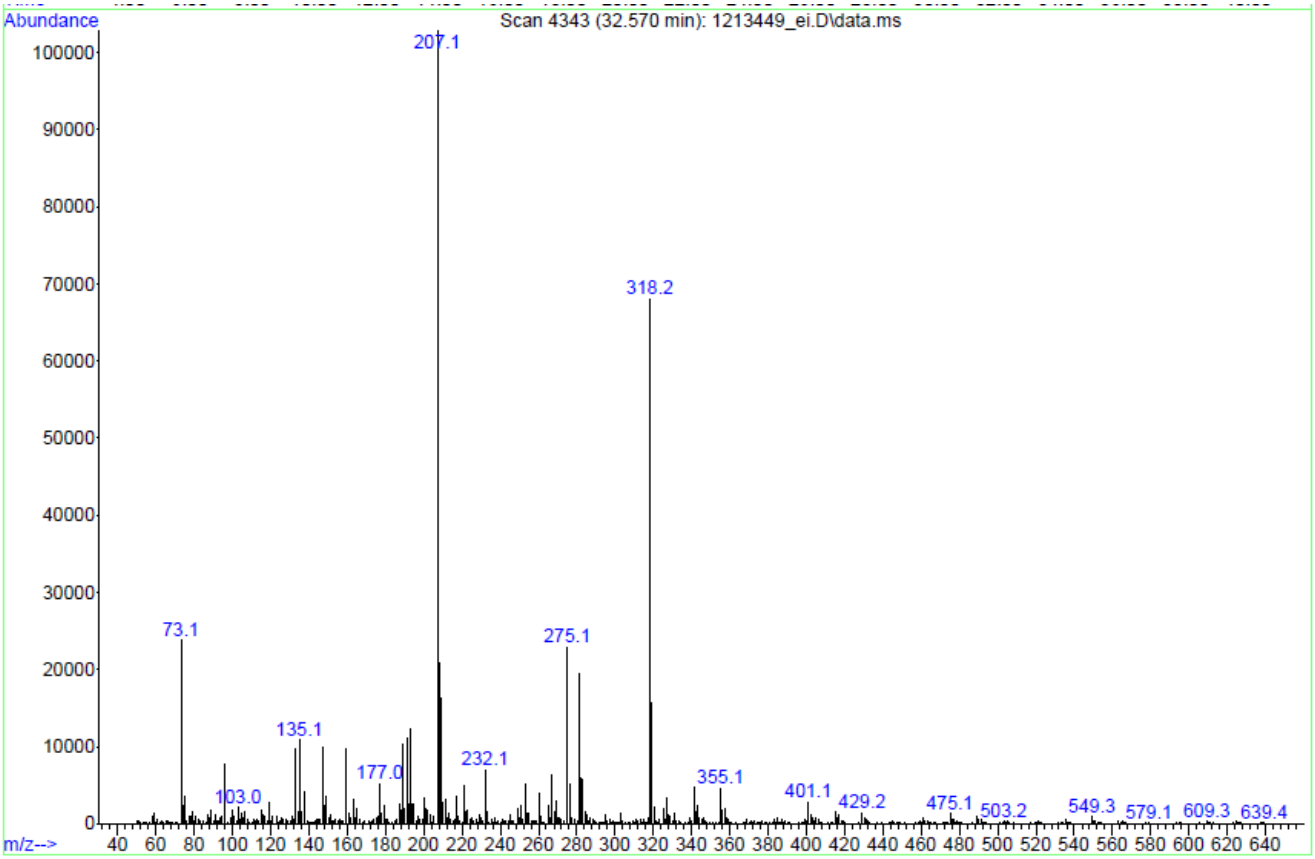
Method : C:\msdchem\1\METHODS\default.m
Title :

Signal : TIC: 0713714_ei_rpt2.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	43.230	5887	5913	5921	M	1642308	96389077	100.00%	74.190%
2	43.353	5922	5931	5942	M2	809687	33533166	34.79%	25.810%


Abundance
TIC: 1213449_ei.D\data.ms
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
OMe
MeO
6c
OMe
MeO
6c'
OMe
Time-->
4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00 36.00 38.00 40.00

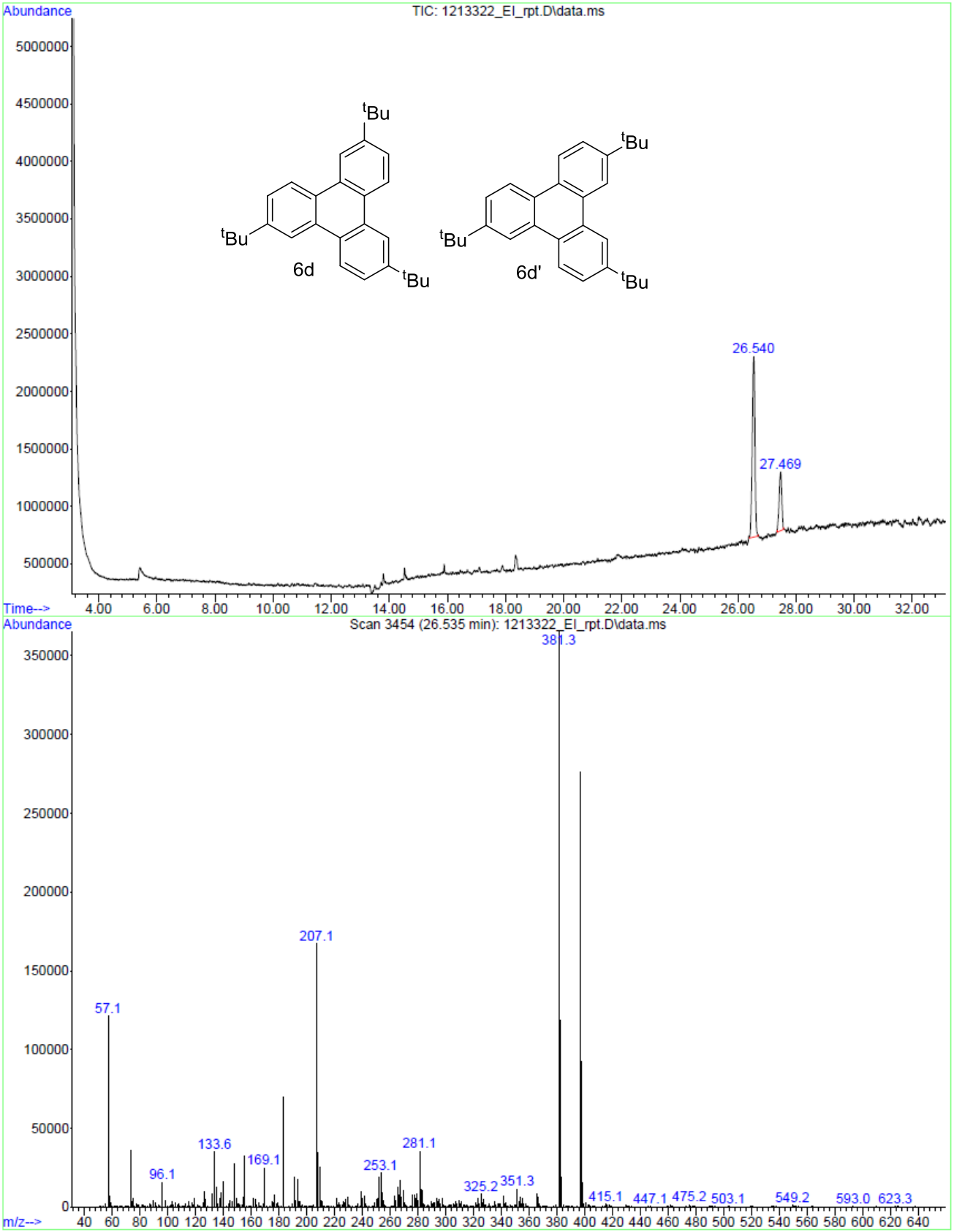

Abundance
Scan 4249 (31.932 min): 1213449_ei.D\data.ms
318.2
207.1
275.1
159.1
73.1
232.1
133.0
100.0
355.1
401.1
429.2
475.2
503.3
549.2
595.0
623.3
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640

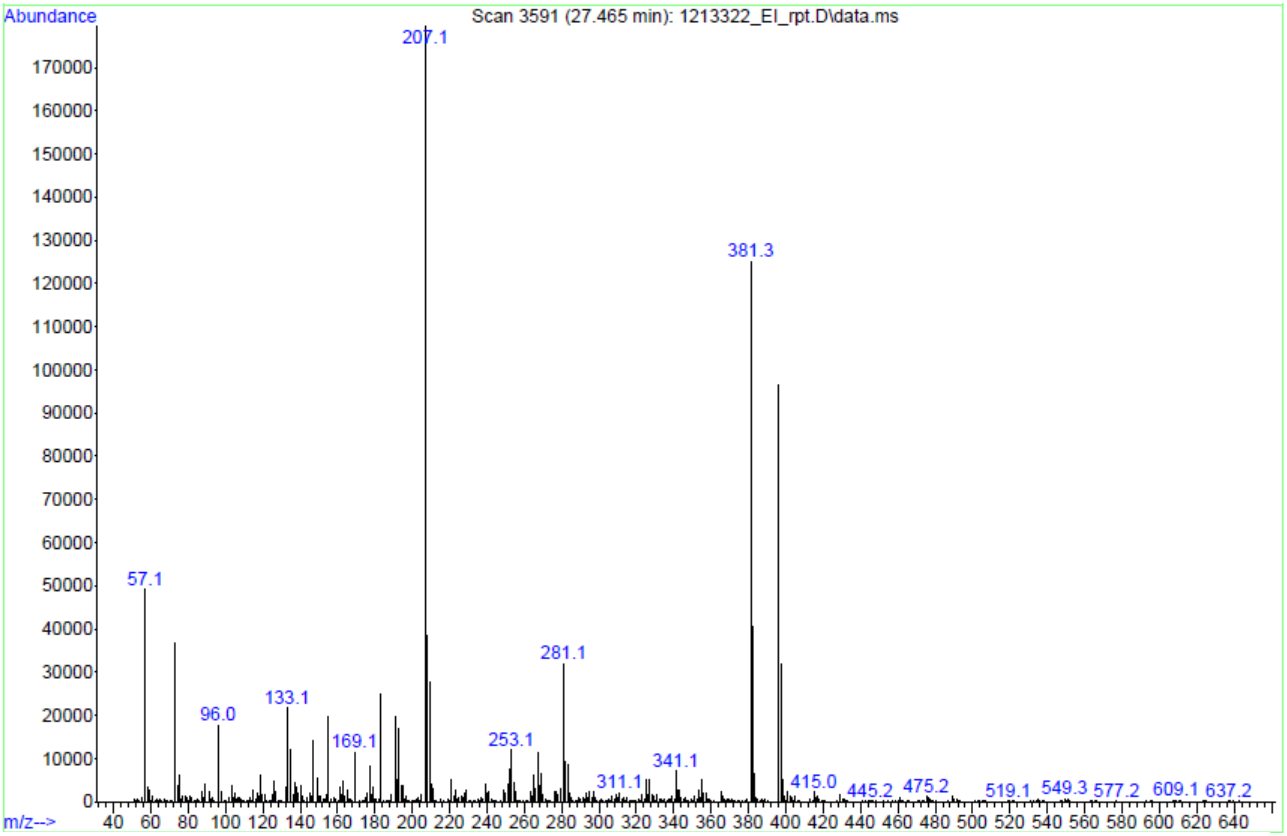


Method : C:\msdchem\1\METHODS\default.m
Title :

Signal : TIC: 1213449_ei.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	31.932	4215	4249	4302	M3	570189	59828219	100.00%	75.744%
2	32.571	4315	4343	4407	M2	191853	19158894	32.02%	24.256%


Abundance
TIC: 1213322_EI_rpt.D\data.ms
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
tBu
tBu
tBu
6d
tBu
tBu
tBu
6d'
26.540
27.469
Time-->
4.00 6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00
Abundance
Scan 3454 (26.535 min): 1213322_EI_rpt.D\data.ms
381.3
350000
300000
250000
200000
150000
100000
50000
0
207.1
57.1
133.6
169.1
96.1
253.1
281.1
325.2
351.3
415.1
447.1
475.2
503.1
549.2
593.0
623.3
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640




```
 Method     : C:\msdchem\1\METHODS\default.m
 Title      :

 Signal     : TIC: 1213322_EI_rpt.D\data.ms
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	26.540	3433	3455	3475	M2	1572583	99816772	100.00%	75.215%
2	27.469	3574	3592	3605	M2	513568	32891279	32.95%	24.785%