Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Axially Chiral BODIPYs

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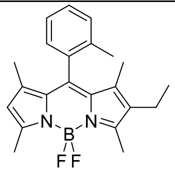
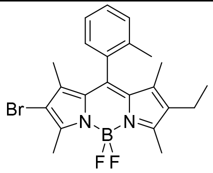
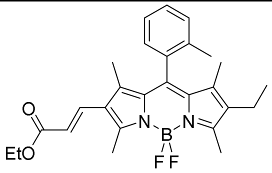
Experimental procedures:

^{1}H and ^{13}C NMR Spectra:

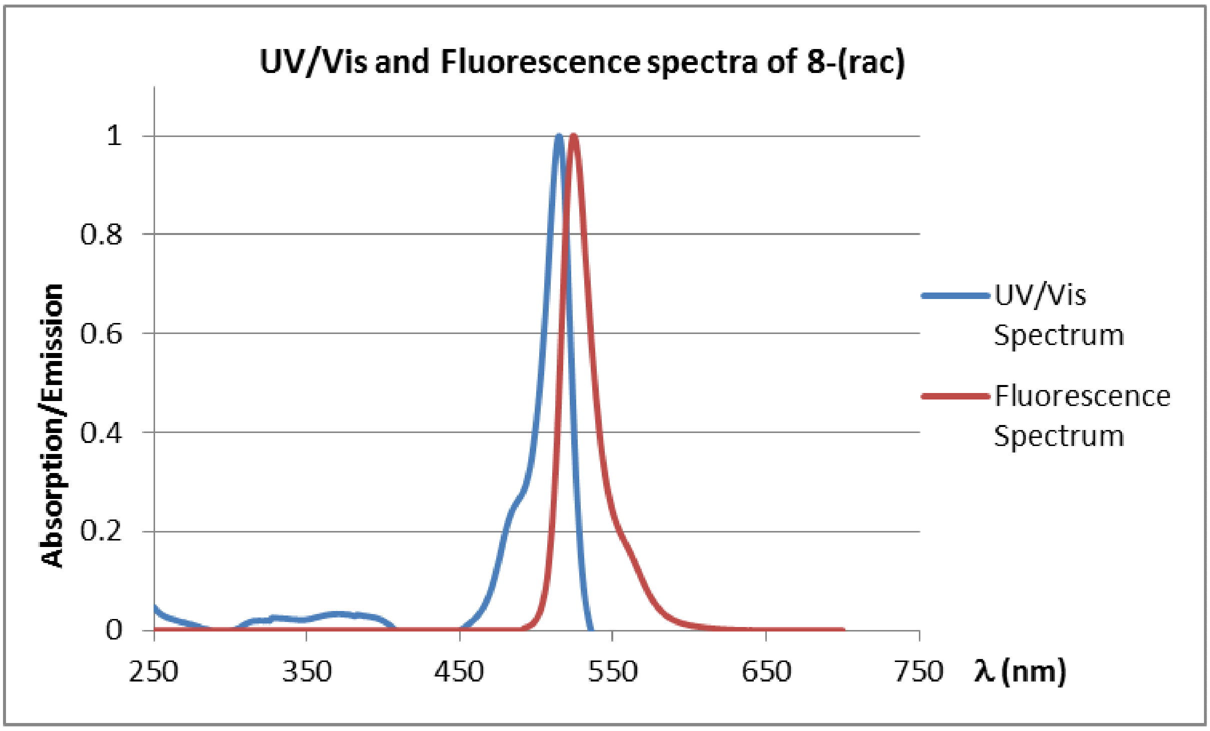
General experimental information

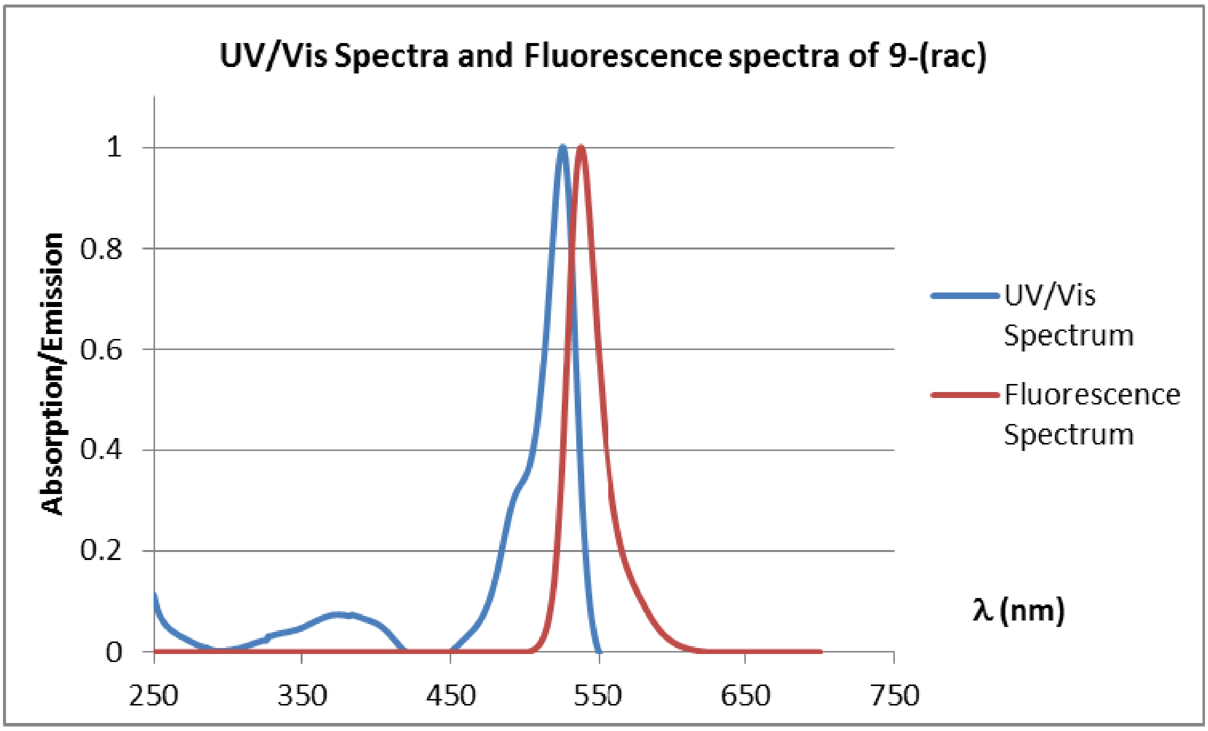
^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Jeol Lambda/Eclipse 500, Jeol ECS-400 or Bruker Avance 300 MHz NMR spectrometer. HRMS data were provided by the EPSRC National Mass Spectrometry Service (University of Swansea). X-ray diffraction data was obtained on an Oxford Diffraction Gemini. IR spectra were obtained as neat samples using a Varian 800 FT-IR Scimitar Series spectrometer scanning from 4000-600 cm^{-1}. THF and Et$_2$O were distilled from sodium/benzophenone, DCM was distilled from CaH$_2$ and used directly. ECD Spectra were measured in hexane using an Applied Photophysics Chirascan-plus.

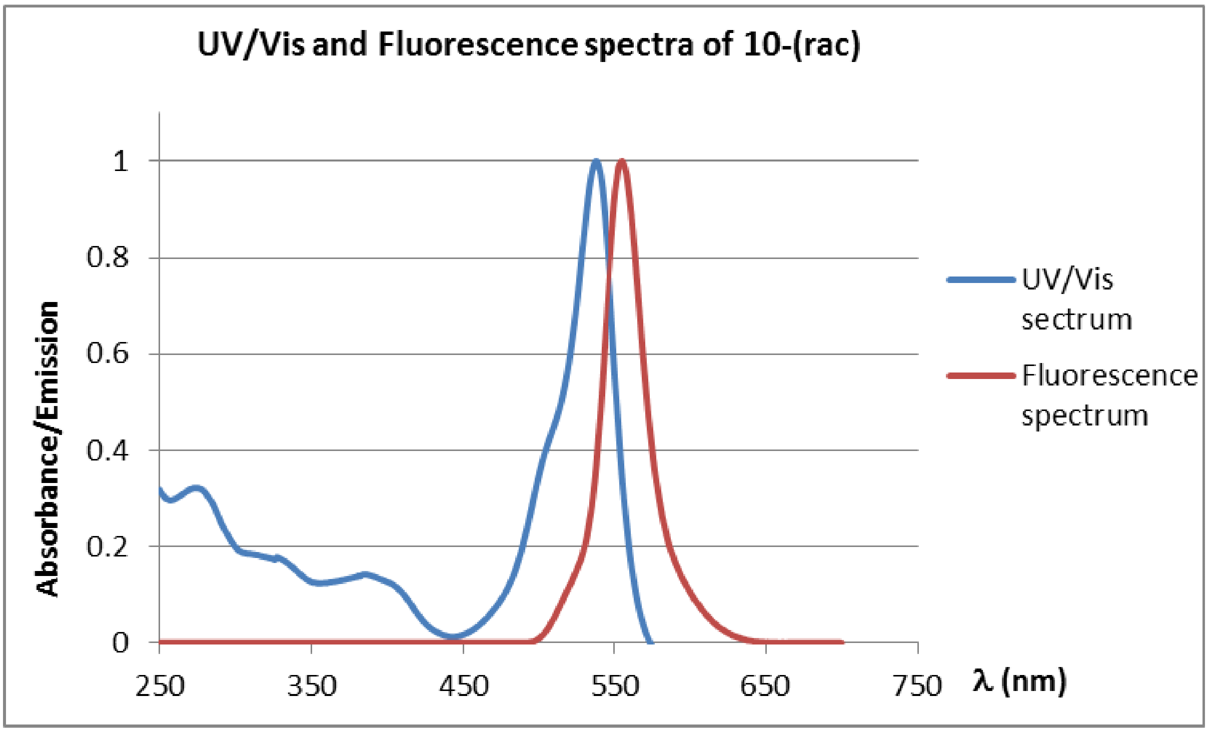
UV/Vis absorbtion spectra, fluorescence spectra and quantum yields[a]

Compound[c]	Number	UV/Vis Absorption		Fluorescence	
		$\lambda_{(max)}$/nm	ε	$\lambda_{(max)}$/nm	Φ_F[b]
	8	515	81600	525	0.85
	9	526	98900	540	0.15
	10	538	95600	555	0.23

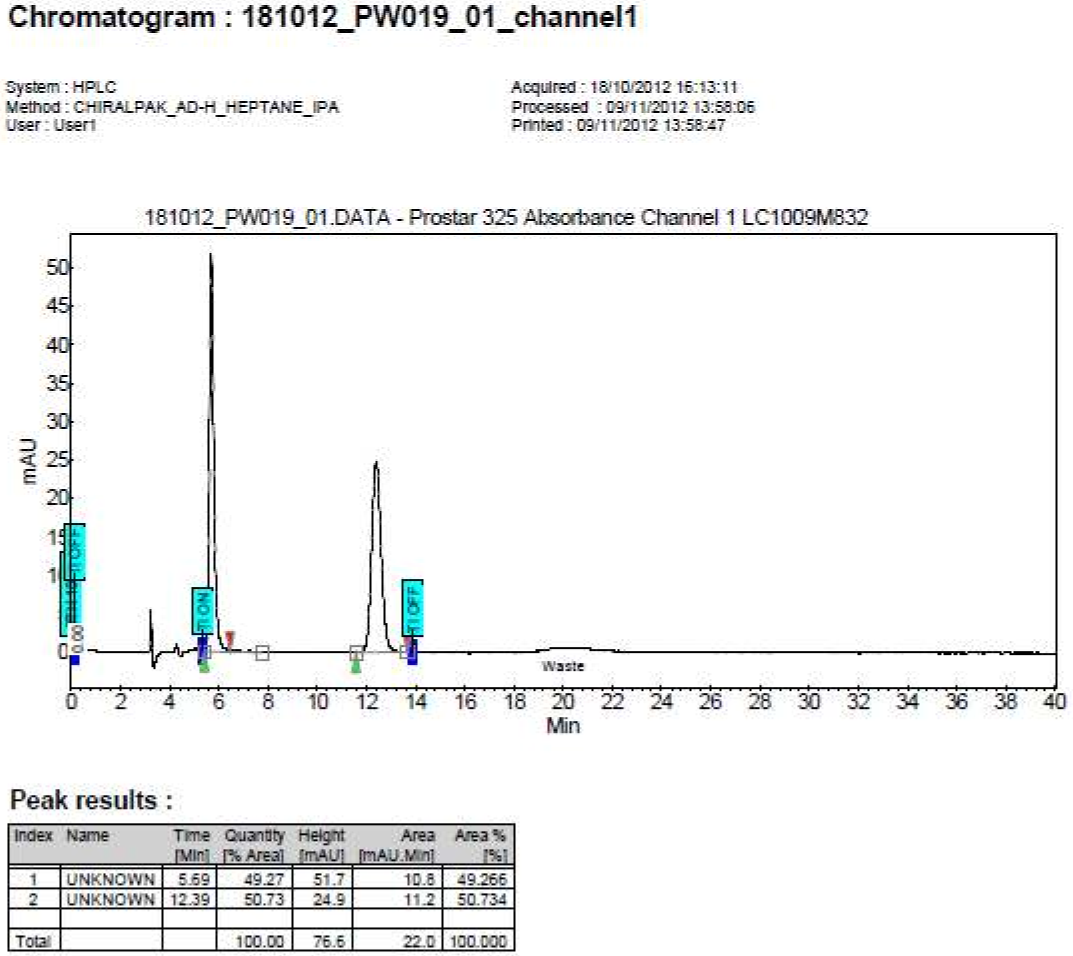
[a] all spectra were recorded in spectroscopic grade $CHCl_3$, [b] Rhodamine B was used as a standard (φfl = 0.7 in MeOH)




UV/Vis Spectra and Fluorescence spectra of 9-(rac)
Absorption/Emission
1
0.8
0.6
0.4
0.2
0
250
350
450
550
650
750
λ (nm)
UV/Vis Spectrum
Fluorescence Spectrum


UV/Vis and Fluorescence spectra of 10-(rac)
Absorbance/Emission
1
0.8
0.6
0.4
0.2
0
250
350
450
550
650
750
λ (nm)
UV/Vis sectrum
Fluorescence spectrum

Chiral HPLC separation of Compound 10



Chromatogram : 181012_PW019_01_channel1

System : HPLC
Method : CHIRALPAK_AD-H_HEPTANE_IPA
User : User1

Acquired : 18/10/2012 16:13:11
Processed : 09/11/2012 13:58:06
Printed : 09/11/2012 13:58:47

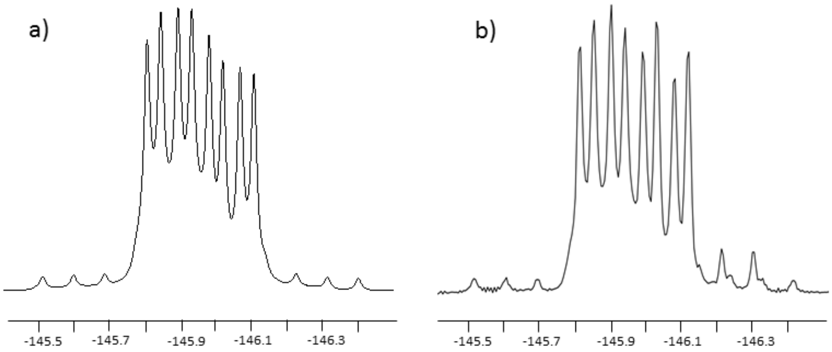
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.69	49.27	51.7	10.8	49.266
2	UNKNOWN	12.39	50.73	24.9	11.2	50.734
Total			100.00	76.6	22.0	100.000

Simulated and experimental ^{19}F NMRspectra for 8-(*rac*), 9-(*rac*) and 10-(*rac*)

NMR spectra were recorded on a Jeol ECS 400 Spectrometer operating at 128.27 (^{11}B) and 376.17 (^{19}F) MHz; chemical shifts are quoted in ppm relative to $BF_3(OEt_2)$ (^{11}B) and $CFCl_3$ (^{19}F). ^{19}F NMR spectra were simulated using gNMR and anisotope shift of 0.07 ppm for ^{10}B/^{11}B was estimated. For **9**-(*rac*) a ^{19}F{^{11}B} NMR spectrum was obtained, which clearly shows the AB nature of the $^{2}J_{FF}$ coupling.

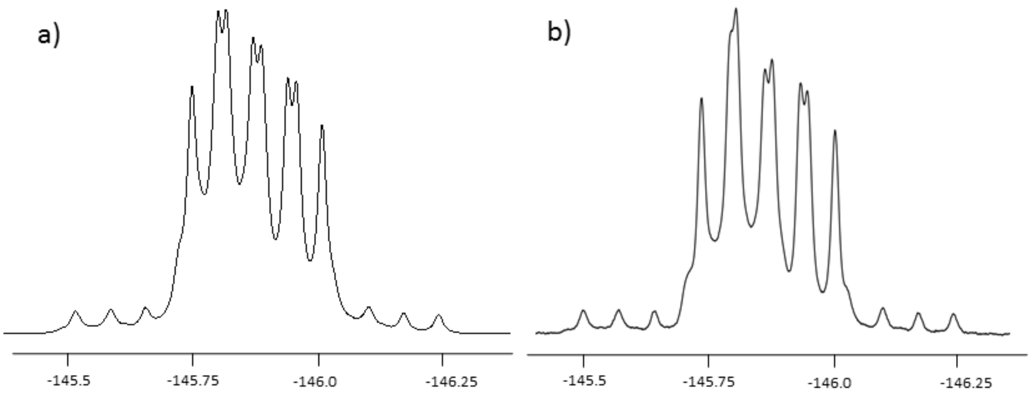
8-(*rac*)



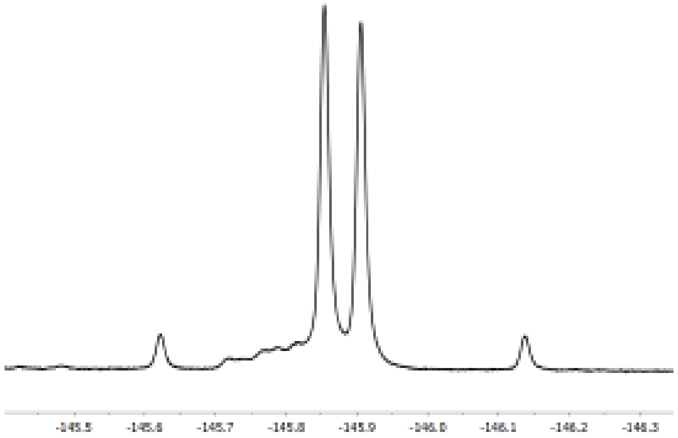
(a) simulated and (b) experimental ^{19}F NMR spectra of 8-(*rac*)

^{11}B{^{1}H} NMR ($CDCl_3$, 21 ºC): δ -0.13 (dd, $^{1}J_{BF}$ = 33 Hz). ^{19}F NMR ($CDCl_3$, 21 ºC): δ -146.04 (m, $^{2}J_{FF}$ = 111 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz), -145.88 (m, $^{2}J_{FF}$ = 111 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz).

9-(*rac*)



(a) simulated and (b) experimental ^{19}F NMR spectra of 9-(*rac*)

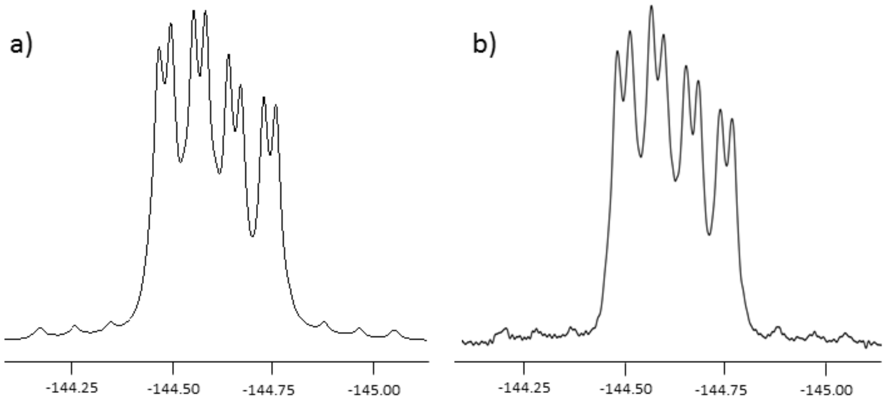


$^{19}F\{^{11}B\}$ NMR spectrum of 9-(*rac*)

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 21 ºC): δ -0.30 (dd, $^{1}J_{BF}$ = 33 Hz).

^{19}F NMR ($CDCl_3$, 21 ºC): δ -145.80 (m, $^{2}J_{FF}$ = 110 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz), -145.96 (m, $^{2}J_{FF}$ = 110 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz).

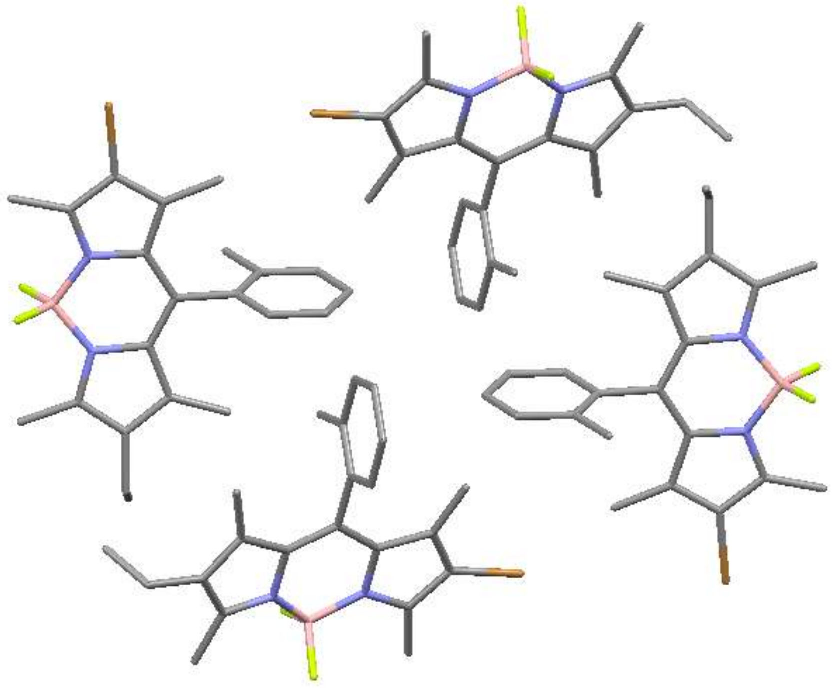
10-(*rac*)

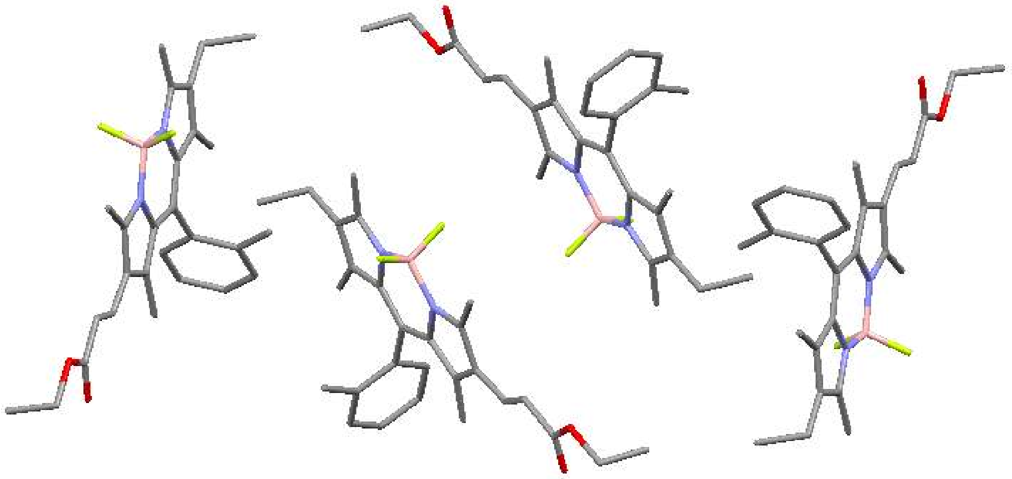


(a) simulated and (b) experimental ^{19}F NMR spectra of 10-(*rac*)

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$, 21 ºC): δ -0.18 (dd, $^{1}J_{BF}$ = 33 Hz). ^{19}F NMR ($CDCl_3$, 21 ºC): δ -144.55 (m, $^{2}J_{FF}$ = 111 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz), -144.69 (m, $^{2}J_{FF}$ = 111 Hz, $^{1}J_{10BF}$ = 10 Hz, $^{1}J_{11BF}$ = 33 Hz).

Crystal packing diagrams of 9-(*rac*) and 10-(*rac*)

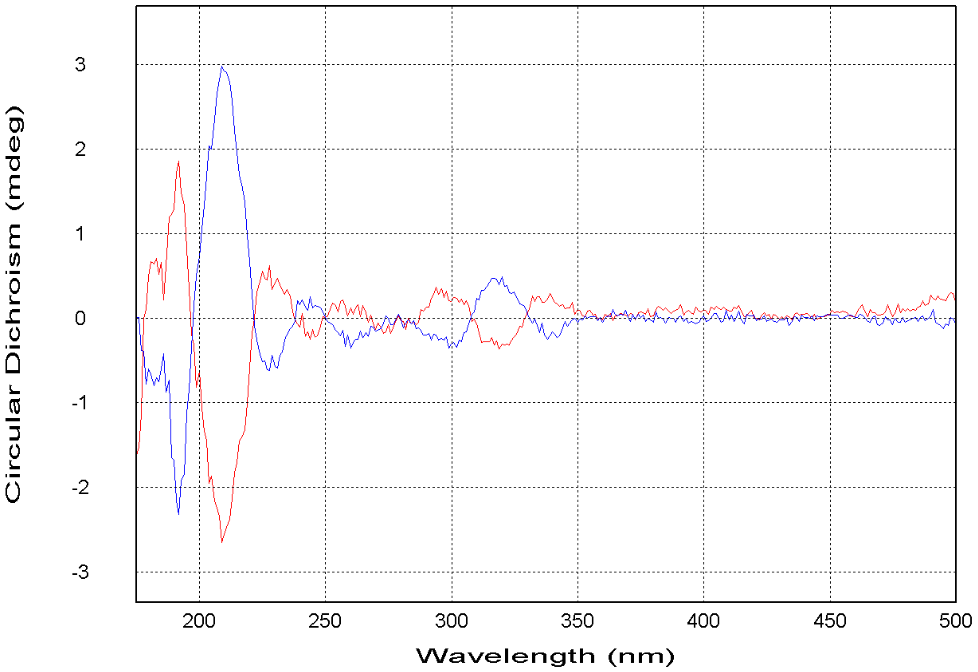




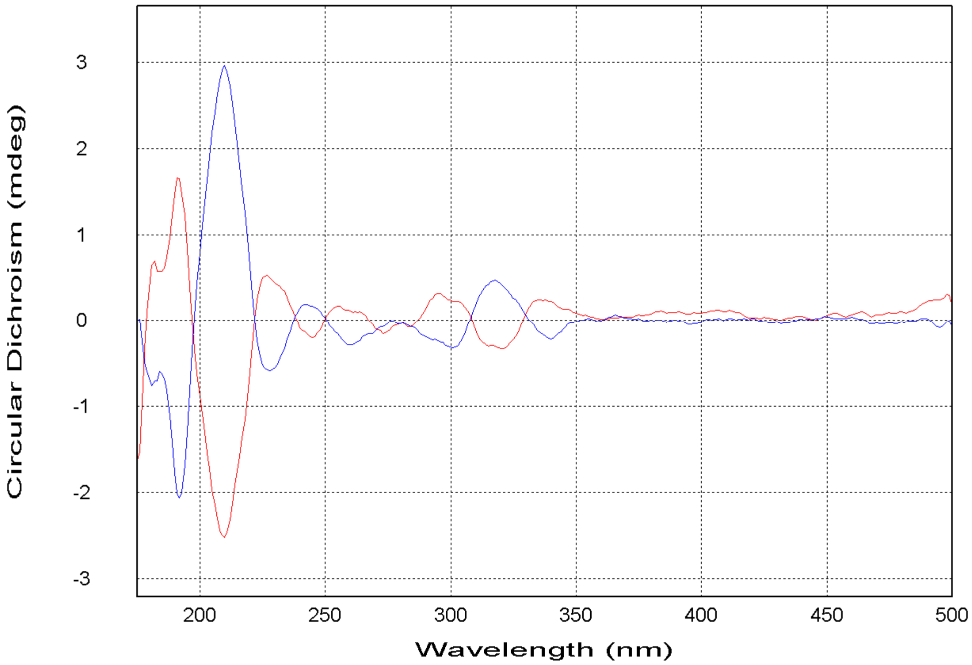
Crystal packing diagram of **9-(*rac*)** [top] and **10-(*rac*)** [bottom]

ECD spectra of 10-(+) and 10-(-)

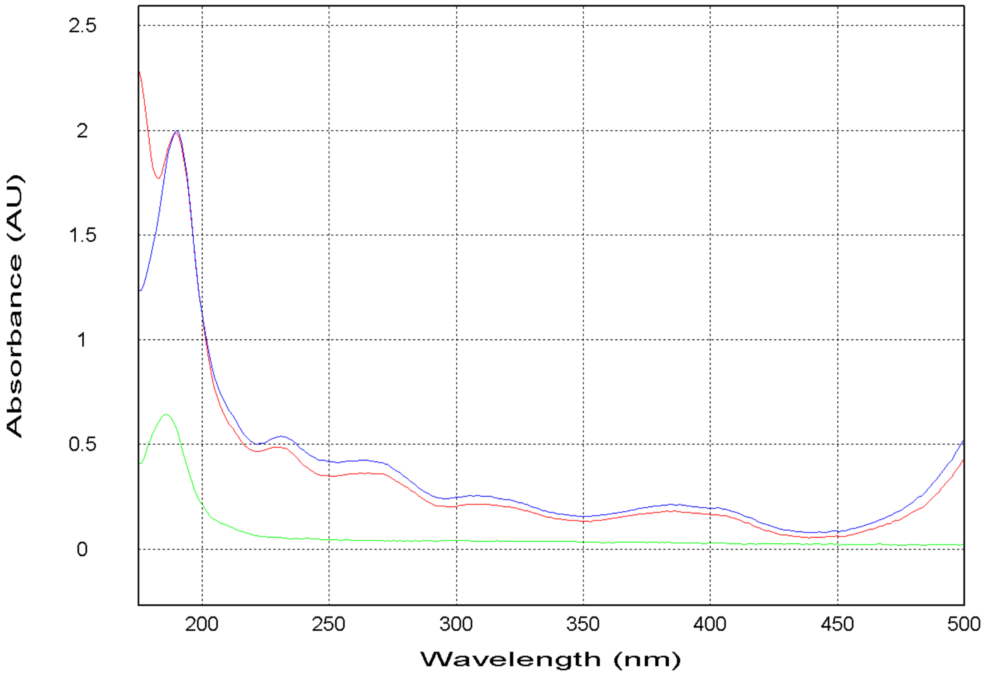
Spectrometer	**Applied Photophysics Chirascan-plus**
Lamp	150 watt xenon arc ~ 500 hours use
Detector	Avalanche photodiode (APD)
Wavelength range	175 - 500nm
Wavelength increment	1.0 nm
Bandwidth	1 nm
Time per point	0.5 seconds
Pathlength	0.5 mm
Repeats	4 for each sample
Total scan time per spectrum.	~ 3.5 minutes
Smoothing	**NO SMOOTHING** was applied to the data



Baseline corrected CD spectra of compound **10-(+)** [Red] and **10-(-)** [Blue] in Hexane, no smoothing.



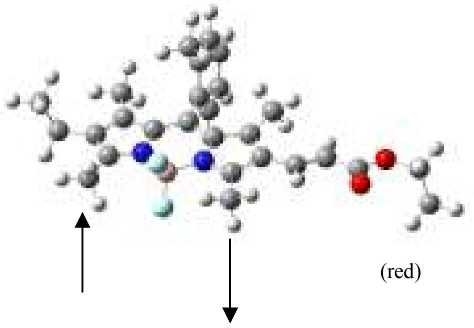
ECD spectra for **10-(+)** [red] and **10-(-)** [blue] after 5-point Savitzky-Golay smoothing.



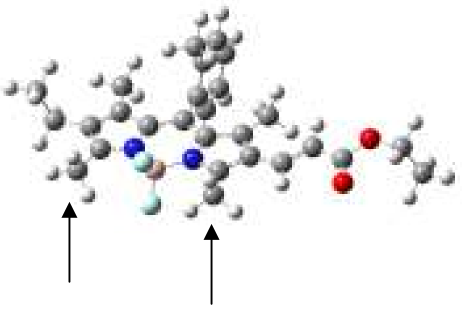
Absorbance spectra (sample + solvent) for the compound **10-(+)** [Red], **10-(-)** [Blue] and hexane [Green].

Computational Studies: VCD

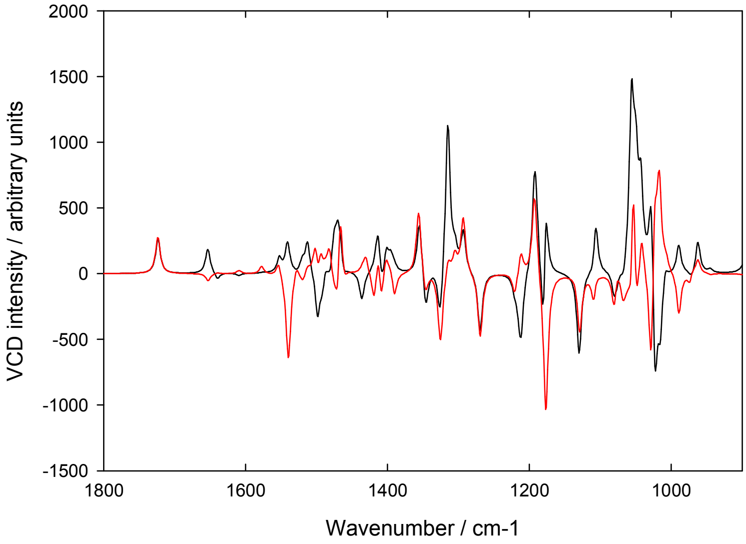
To be able to calculate Boltzmann weighted VCD spectra, and to be able to rationalize why samples **10-(+)** and **10-(-)** did not yield significant VCD signals, a conformational search was initiated. In the first phase, conformer libraries were generated using different search engines and force fields, and DFT geometry optimizations and frequency calculations were initiated at the B3LYP/6-311++G(2d,p) level. During analysis, it was observed that, apart from the conformations generated through changes due to the relative orientation of the ethyl and ester substituents with respect to the framework (orientation of the substituent) and the orientation of the ethyl group with respect to the other parts of the ester substituent (orientation in the substituent), different conformations could be obtained by slightly changing the orientation of the F proximal methyl groups. Typical examples of such conformations and the corresponding VCD spectra are given below. It can be seen that the subtle change in one single methyl group immediately affects the VCD spectrum, and that most of the signals related to the first conformation are almost completely cancelled by those of the second set. Manual inspection of the conformations generated and correction for missing conformations finally lead to 18 important conformations with Boltzmann populations varying between 6.9 and 4.1%. Combination of the different conformations generated by changing the relative orientation of and in the ester and ethyl groups and those obtained by changing the relative orientation of the methyl groups towards the BF_2 subunit generated by slightly adopting the orientation finally lead to a Boltzmann weighted spectrum in which most, if not all, of the VCD signals were largely wiped out. This result, obviously, is in line with the lack of data that could be obtained experimentally.



(red)



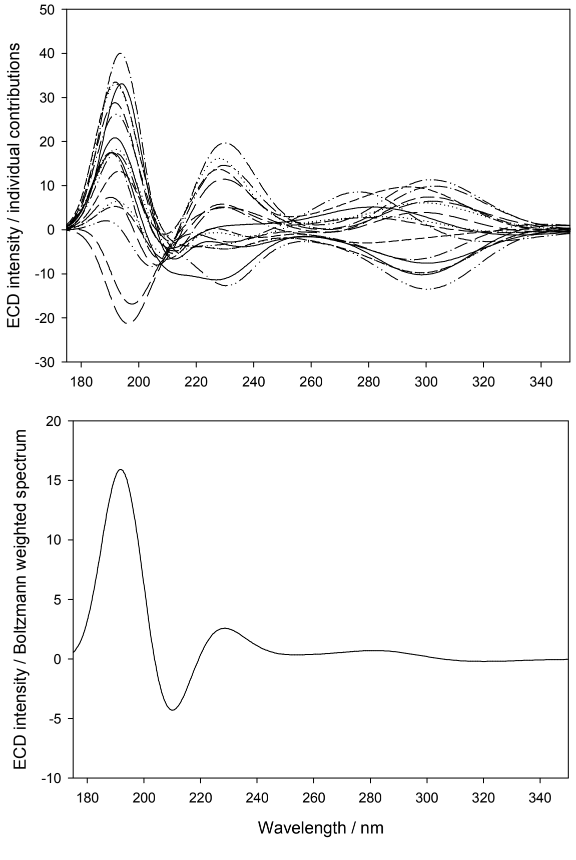
(black)


2000
1500
1000
500
0
-500
-1000
-1500
VCD intensity / arbitrary units
1800
1600
1400
1200
1000
Wavenumber / cm-1

Computational Studies: ECD

Boltzmann weighted ECD spectra were obtained from TD-DFT calculations at the cam-B3LYP/6-311++G(2d,p) level. The individual ECD spectra obtained for the same conformations as those used for the VCD studies, and the Boltzmann weighted spectra are shown below. A blue shift of 10 nm was used throughout to correct for the fact that TD-DFT calculations typically underestimate the transition energies involved [J. Autschbach, *Comprehensive Chiroptical Spectroscopy, Volume 1: Instrumentation, Methodology and Theoretical Simulations*, ed. N. Berova, P.L. Polavarapu, K. Nakanishi and R.W. Woody, John Wiley & Sons, 2012, ch. 21, pp. 593].

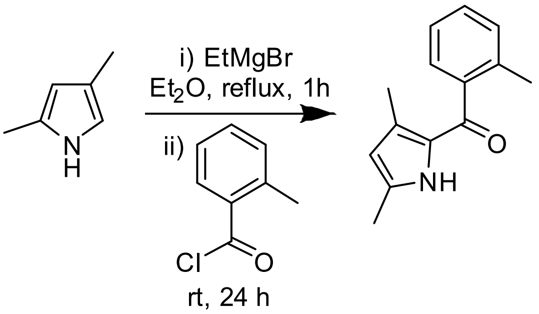
Stereochemical model of ***(R)*-10** used for computation studies.



Individual conformation contributions to calculated ECD of ***(R)*-10** [top], Boltzmann weighted ECD of ***(R)*-10** [bottom]

Experimental procedures:

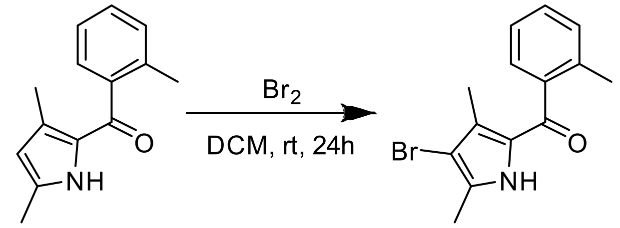
6 - (3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone



To a 100 mL round bottomed flask, under an atmosphere of nitrogen, was added 2,4-dimethylpyrrole (2.2 mL, 21.0 mmol) and diethylether (40 mL). Ethyl magnesium bromide (3M in Et_2O, 3.1 mL, 23.0 mmol) was added dropwise to the reaction. The reaction mixture was then heated at reflux for 1 hour, cooled to room temperature and added via cannula to a mixture of diethylether (10 mL) and 2-methylbenzoyl chloride (3.6 mL, 27.0 mmol). The reaction mixture was then stirred at room temperature for 24 hours. The reaction mixture was then washed with water (3 x 100 mL) and the combined aqueous layers extracted with diethylether (100 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was purified via column chromatography (silica, 50% DCM : 50% Petrol gradient to DCM 100%) to give (3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (2.7g, 12.6 mmol, 60%) as a light pink solid.

Mp: 121 ^{o}C; R_f: 0.3 (1 : 1, DCM : Petrol); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ_H 9.43 (br s, 1H), 7.40 – 7.30 (m, 1H), 7.30 – 7.24 (m, 3H), 5.86 (d, J = 2.7 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.68 (s, 3H); ^{13}C{^{1}H} NMR (100.53 MHz, $CDCl_3$): δ_C 186.7, 140.6, 136.4, 134.8, 131.8, 130.7, 129.3, 128.5, 126.7, 125.8, 113.1, 19.1, 13.3, 13.0; IR(neat): υ_{max}/cm^{-1} 3000, 2968, 2816, 1674.

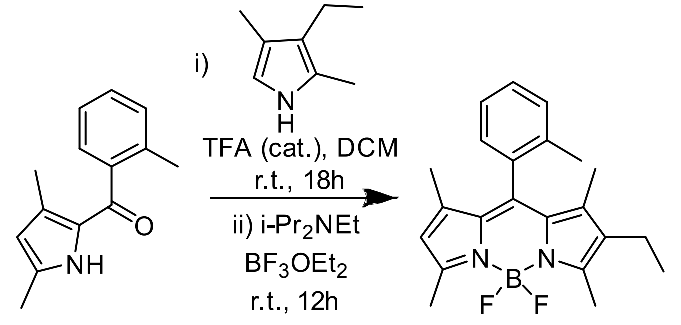
7 (4-bromo-3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone



To a round bottomed flask, under an atmosphere of nitrogen, was placed (3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (0.71 g, 3.3 mmol). To this was added as solution of bromine (0.60 g, 3.7 mmol) in DCM (100 mL) over 10 minutes. The reaction mixture was then stirred at room temperature for 24 hours, after which the reaction mixture was washed with water (3 x 100 mL). The combined aqueous layers were extracted with DCM (100 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to give (4-bromo-3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (1.03 g, 3.3 mmol, 100%) as a purple/brown solid with no further purification required.

Mp: 114 – 116°C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ_H 10.99 (br s, 1H), 7.36 (ddd, *J* = 8.0, 5.6, 3.0 Hz, 1H), 7.30 – 7.20 (m, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 1.62 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100.53 MHz, $CDCl_3$): δ_C 186.8, 140.0, 135.9, 135.0, 130.8, 130.2, 129.8, 127.6, 127.0, 126.0, 102.7, 19.3, 12.5, 12.3; IR(neat): υ_{max}/cm^{-1} 3245, 2921, 2877, 1592 (C=O); MS (p APCI): 292.0 (100%, $[M+H]^+$), 294.0 (98%, $[M+H]^+$); HRMS (p APCI): calcd for $C_{14}H_{15}ONBr$ $[M+H]^+$: 292.0332; observed: 292.0332.

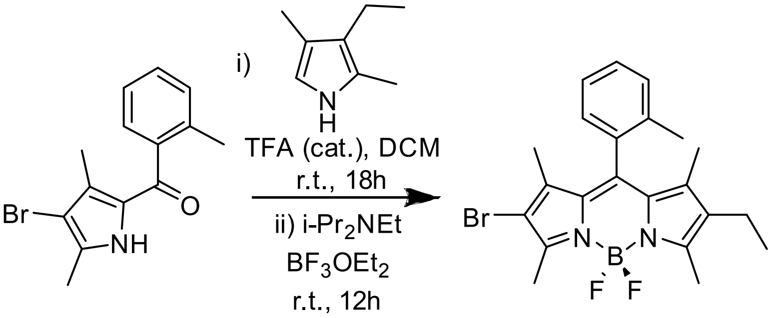
8-(*rac*) - 2-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine



Into a 500 mL round bottom flask, under an atmosphere of nitrogen, was placed (3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (1.35 g, 6.3 mmol) and DCM (150 mL). To this were added 2,4-dimethyl-3-ethylpyrrole (1.02 mL, 7.6 mmol) and catalytic TFA (2 drops) and the reaction mixture stirred at room temperature for 18 hours. After which *N*,*N*-diisopropylethylamine (6.2 mL, 38.0 mmol) and $BF_3.Et_2O$ (6.2 mL, 50.4 mmol) were added and the reaction mixture stirred for 12 hours. The reaction mixture was washed with water (3 x 100 mL) and brine (200 mL). The combined aqueous layers were extracted with DCM (100 mL) and the combined organic layers were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was purified via column chromatography (silica, toluene: petrol [1:1]) to give 2-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-5λ^4,6λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (0.59 g, 1.6 mmol, 26%) as a red solid.

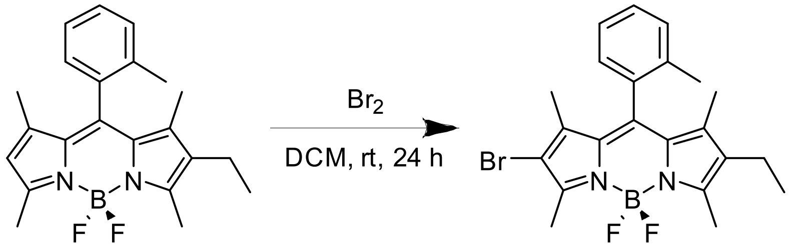
Mp: 141; R*f*: 0.4 (1 : 1, DCM : Petrol); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ_H 7.38 – 7.32 (m, 1H), 7.31 – 7.26 (m, 2H), 7.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.92 (s, 1H), 2.55 (s, 3H), 2.54 (s, 3H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.18 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.53 MHz): δ_C 155.4, 153.8, 141.6, 140.6, 139.1, 135.6, 134.9, 133.4, 130.9, 130.7, 130.5, 129.2, 128.1, 126.9, 120.5, 53.5, 29.8, 19.4, 17.2, 14.7, 14.6, 13.7, 12.7, 11.1, 9.5; $^{11}B\{^1H\}$ NMR ($CDCl_3$, 128.27 MHz): δ_B -0.13 (dd, $^1J_{BF}$ = 33 Hz); ^{19}F NMR ($CDCl_3$, 376.17 MHz): δF -146.04 (m, $^2J_{FF}$ = 111 Hz, $^1J_{11BF}$ = 33 Hz), -145.88 (m, $^2J_{FF}$ = 111 Hz, $^1J_{11BF}$ = 33 Hz); IR(neat): υ_{max}/cm^{-1} 2961, 2855, 1540, 1514, 1193; MS (p NSI): 347.2 (34%), 367.2 (100%, $[M+H]^+$), 389.2 (17%), 750.5 (7%), 755.4 (6%); HRMS (p NSI): calcd for $C_{22}H_{26}BF_2N_2$ $[M+H]^+$: 367.2152; observed: 367.2154.

9-(*rac*) - 2-bromo-8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ium-5-uide



Route A:

Into a 500 mL round bottom flask, under a nitrogen atmosphere, was added (4-bromo-3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (1.0 g, 3.5 mmol), DCM (150 mL), 2,4-dimethyl-3-ethylpyrrole (0.6 g, 3.6 mmol) and catalytic TFA (2 drops) and the reaction mixture stirred at room temperature for 18 hours. After this time *N*,*N*-diisopropylethylamine (3.5 mL, 28.0 mmol) and $BF_3.Et_2O$ (3.5 mL, 21.0 mmol) were added and the reaction mixture stirred for 12 hours. The reaction mixture was washed with water (3 x 100 mL) and brine (200 mL). The combined aqueous layers were extracted with DCM (100 mL). The organic portions were combined, dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified via column chromatography (silica, DCM: petrol [1:2]) to give 2-bromo-8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ium-5-uide as red/ green solid (0.7 g, 1.6 mmol, 47%).



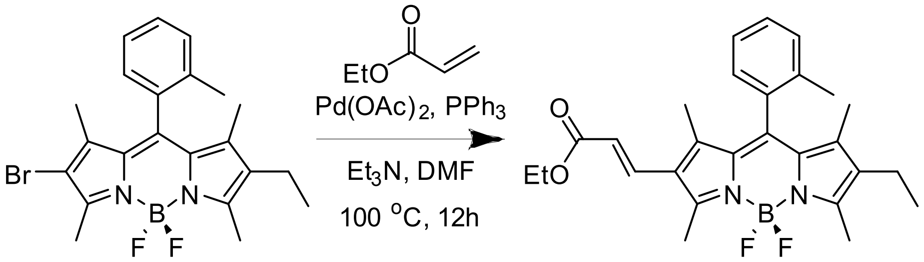
Route B:

8-Ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ium-5-uide (0.3 g, 0.8 mmol) was dissolved in DCM (100 mL) containing bromine (0.6 mL, 0.91 mmol, 1.2 eq.). The reaction mixture was then stirred at room temperature for 24 hours. The reaction mixture was washed with water (3 x 100 mL), the combined aqueous layers were extracted with DCM (100 mL). The combined organic portions were dried over $MgSO_4$, filter and the solvent removed under reduced pressure to give 2-bromo-8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-dipyrrolo[1,2-*c*:2',1'-

f][1,3,2]diazaborinin-4-ium-5-uide (0.2 g, 0.4mmol, 54%) as a purple/brown solid with no further purification required.

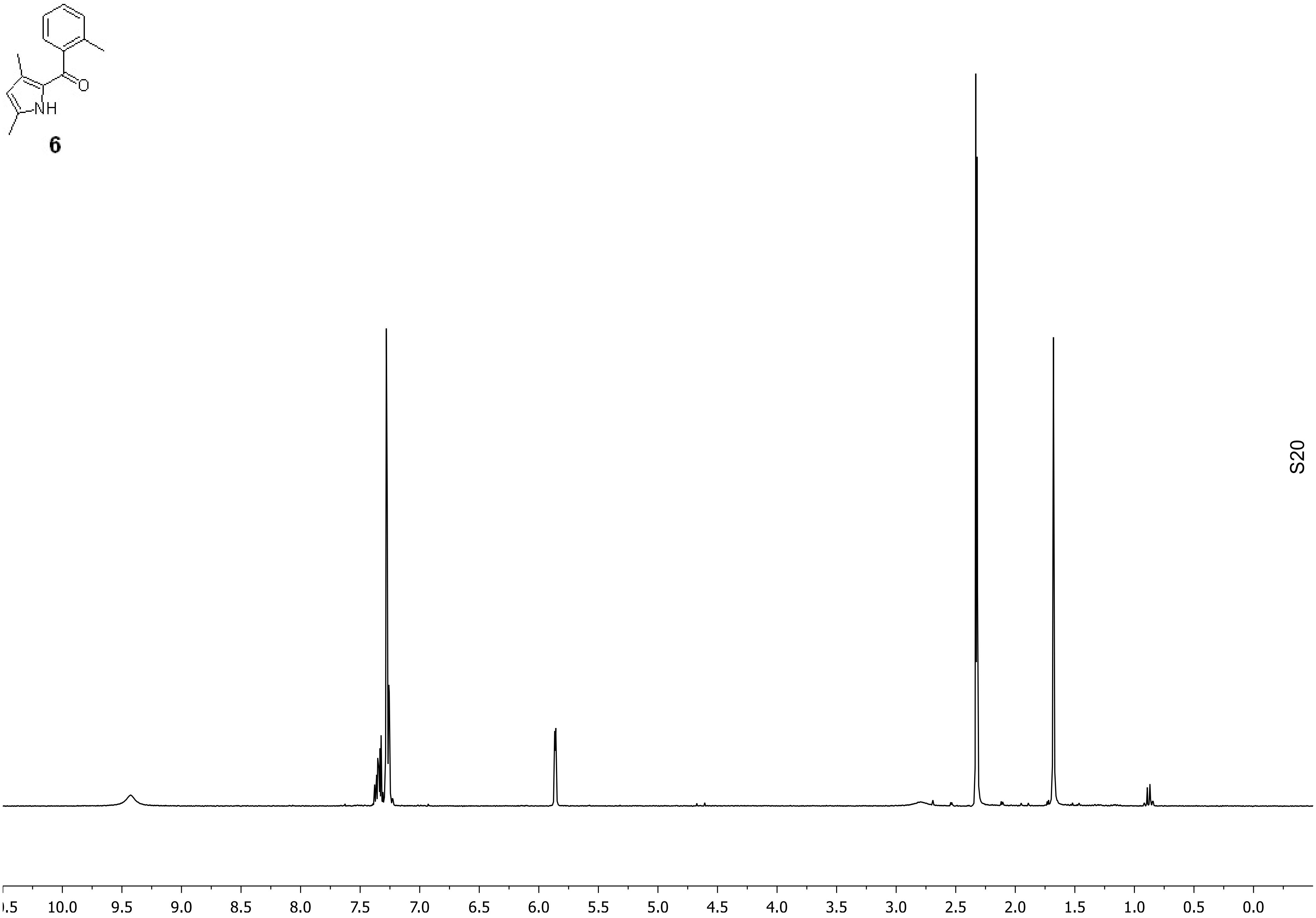
Mp: 114 – 116^{o}C; R$_{f}$: 0.17 (1 : 2, DCM : Petrol); ^{1}H NMR (CDCl$_3$, 500.16 MHz): δ_H 7.40 – 7.36 (m, 1H), 7.33 – 7.28 (m, 2H), 7.14 – 7.11 (m, 1H), 2.57 (s, 3H), 2.56 (s, 3H), 2.31 (q, *J* = 7.6 Hz, 2H), 2.17 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100.53 MHz): δ_C 189.8, 158.2, 149.8, 140.6, 137.2, 135.6, 134.6, 134.5, 131.6, 130.8, 129.4, 128.9, 128.0, 127.0, 100.0, 19.4, 17.2, 14.5, 13.5 (t, *J* = 2.5 Hz), 13.0 (t, *J* = 2.5 Hz), 12.7, 11.3. ^{11}B{^{1}H} NMR (CDCl$_3$, 128.27 MHz): δ_B -0.30 (dd, $^{1}J_{BF}$ = 33 Hz); ^{19}F NMR (470.62 MHz, CDCl$_3$): δ_F -145.80 (m, $^{2}J_{FF}$ = 110 Hz, $^{1}J_{11BF}$ = 33 Hz), -145.96 (m, $^{2}J_{FF}$ = 110 Hz, $^{1}J_{11BF}$ = 33 Hz); IR(neat): υ_{max}/cm^{-1} 2926, 2869, 1543, 1193; MS (p APCI): 292.0 (100%), 294.0 (98%), 320.0 (100%), 322.0 (99%), 340.0 (44%), 342.0 (43%), 425.1 (73%), 427.1 (72%), 444.1 (16%, [M]$^{+}$), 446.1 (16%, [M]$^{+}$), 631.0 (21%); HRMS (p APCI): calcd for $C_{22}H_{24}BBrF_2N_2$ [M]$^{+}$: 444.1178; observed: 444.1171.

10-(*rac*) - ethyl (*E*)-3-(8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate



To a dry schlenk flask, under a nitrogen atmosphere, was added (4-bromo-3,5-dimethyl-1*H*-pyrrol-2-yl)(*o*-tolyl)methanone (0.3 g, 0.6 mmol), palladium acetate (0.017 g, 0.08 mmol, 0.13 eq), triphenylphosphine (0.02 g, 0.08 mmol, 0.13 eq) and DMF (5 mL). After which ethyl acrylate (0.2 mL, 1.5 mmol, 2.3 eq) and triethylamine (0.4 mL, 2.8 mmol, 4.5 eq) were added in DMF (6 mL) and the reaction stirred at 100 °C. After 12 hours the reaction mixture was allowed to cool to room temperature, dissolved in DCM (100 mL) and washed with water (3 x 100 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (DCM 100% gradient to DCM: EtOAc; 99:1) to give ethyl (*E*)-3-(8-ethyl-5,5-difluoro-1,3,7,9-tetramethyl-10-(*o*-tolyl)-5H-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-2-yl)acrylate (0.06 g, 0.3 mmol, 46 %) as a red solid.

Mp: 160 °C; R*f*: 0.10 (DCM); ^{1}H NMR ($CDCl_3$, 399.78 MHz): δ_H 7.60 (d, *J* = 16.2 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.01 (d, *J* = 16.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 2.57 (s, 3H), 2.32 (q, *J* = 7.5 Hz, 2H), 2.17 (s, 3H), 1.42 (s, 3H), 1.33 – 1.25 (m, 6H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101.53 MHz): δ_C 167.8, 158.8, 141.1, 140.8, 138.9, 136.2, 135.7, 135.1, 135.1, 134.6, 132.3, 130.8, 129.7, 129.5, 128.1, 127.1, 124.3, 116.9, 60.4, 19.4, 17.2, 14.5, 14.5, 14.1, 13.1, 11.9, 11.4; ^{11}B {^{1}H} NMR ($CDCl_3$, 128.27 MHz): δ_B -0.18 (dd, $^1J_{BF}$ = 33 Hz); ^{19}F NMR ($CDCl_3$, 376.17 MHz): δ_F -144.55 (m, $^2J_{FF}$ = 111 Hz, $^1J_{11BF}$ = 33 Hz),, -144.69 (m, $^2J_{FF}$ = 111 Hz, $^1J_{11BF}$ = 33 Hz),; IR(neat): υ_{max}/cm^{-1} 2969, 2890, 1700, 1528, 1072; MS (p APCI): 445.2 (73%), 464.2 (100%, [M]$^+$); HRMS (p APCI): calcd for $C_{27}H_{31}BF_2N_2O_2$ [M]$^+$: 464.2442; observed: 464.2441.



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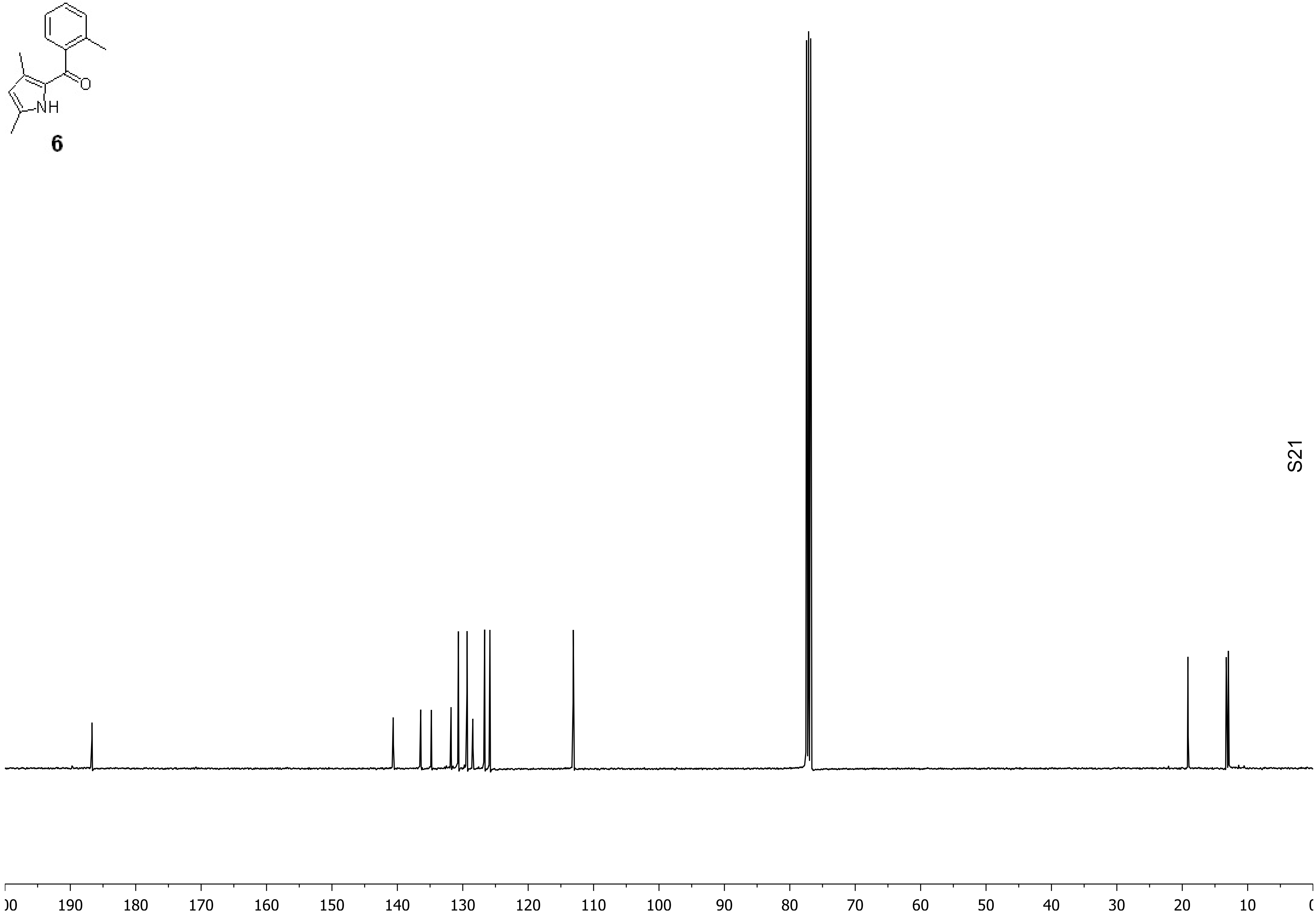
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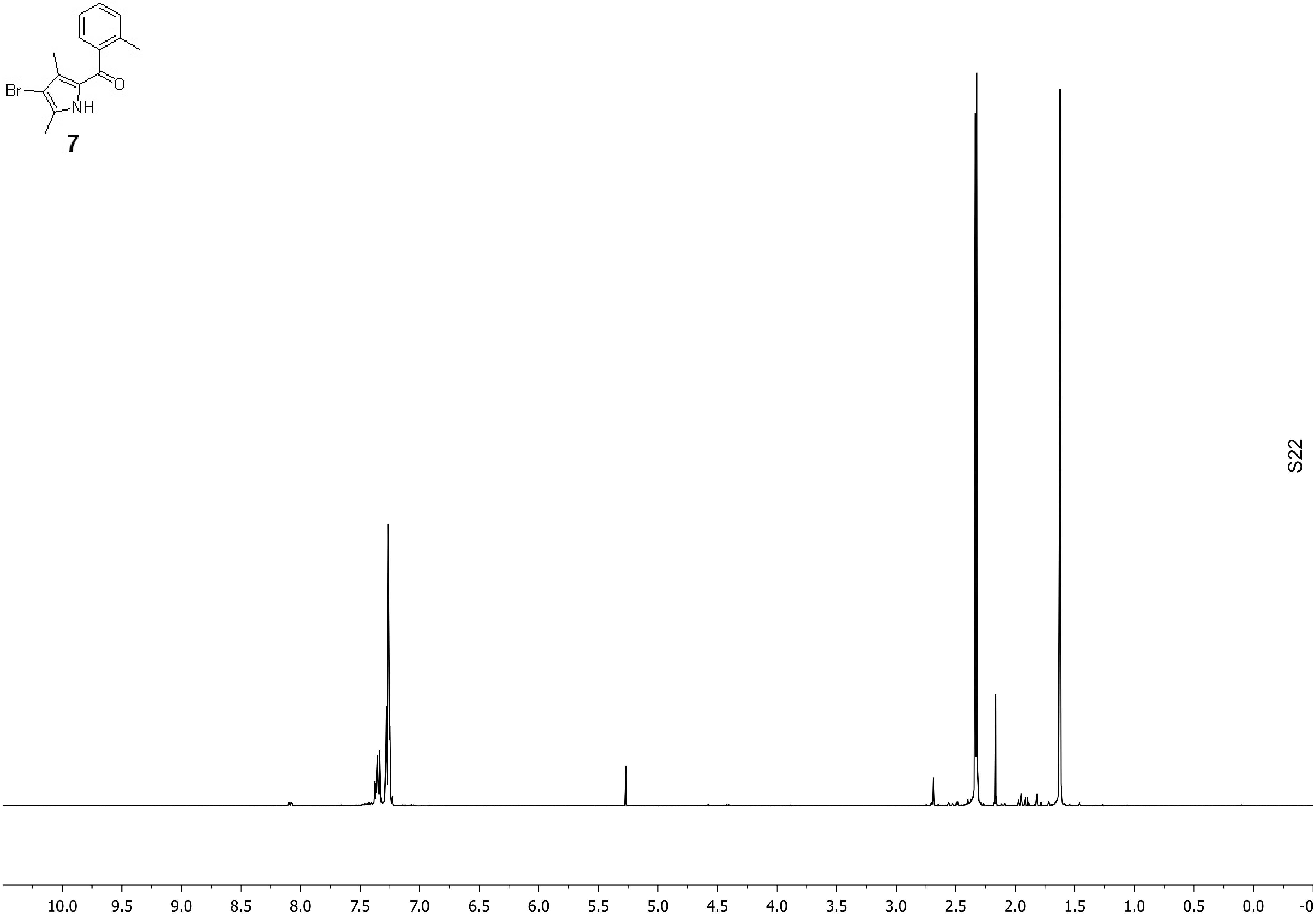
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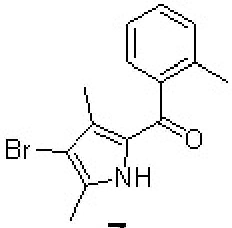
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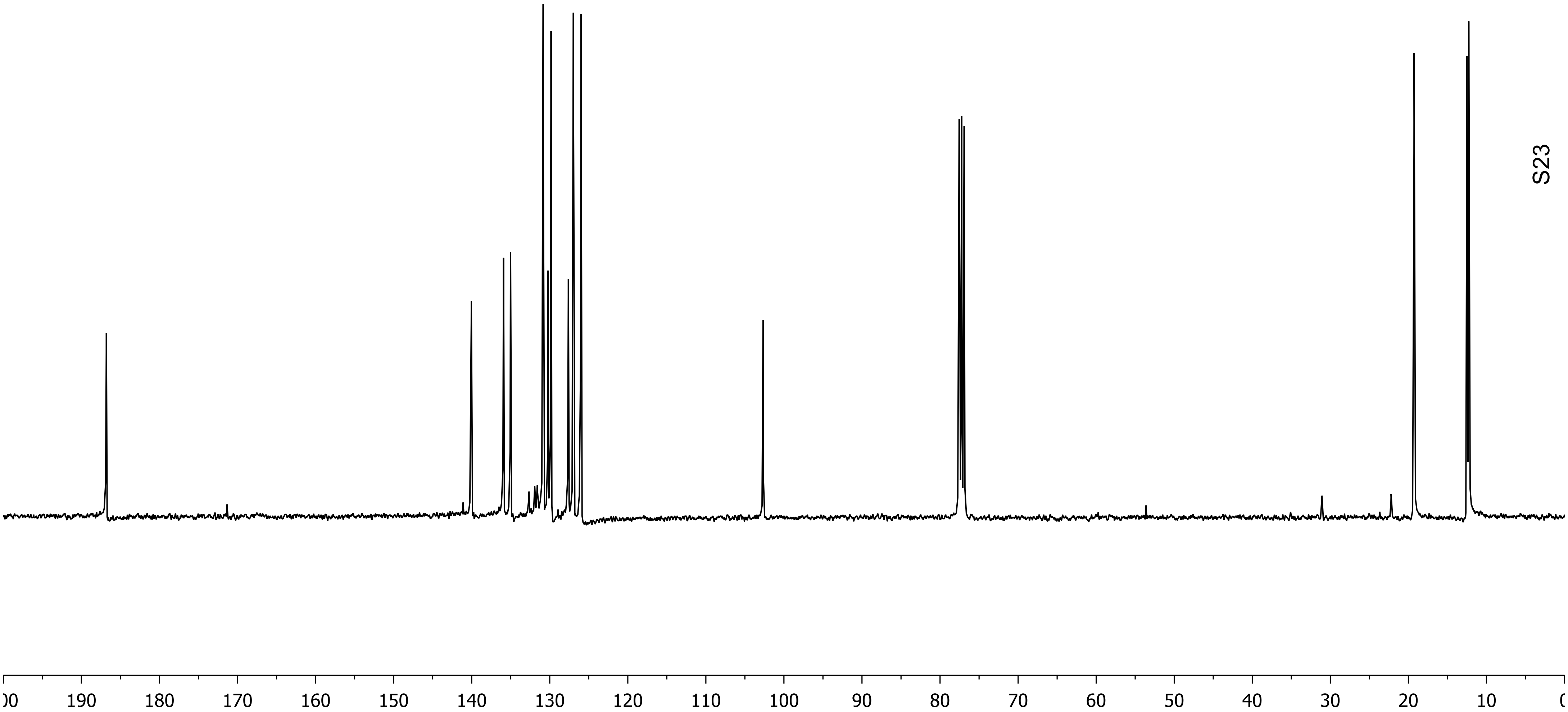
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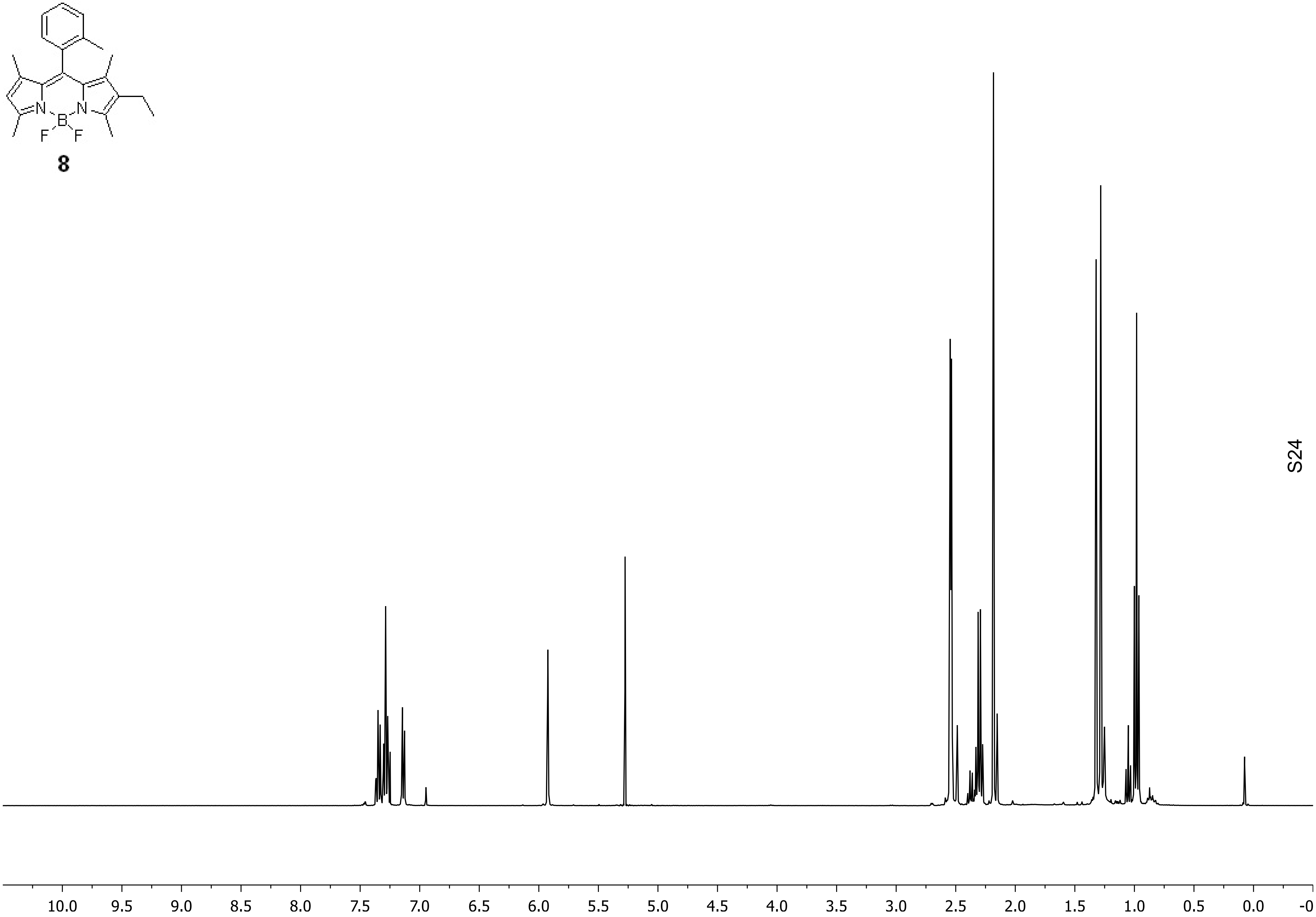

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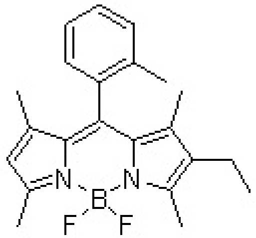

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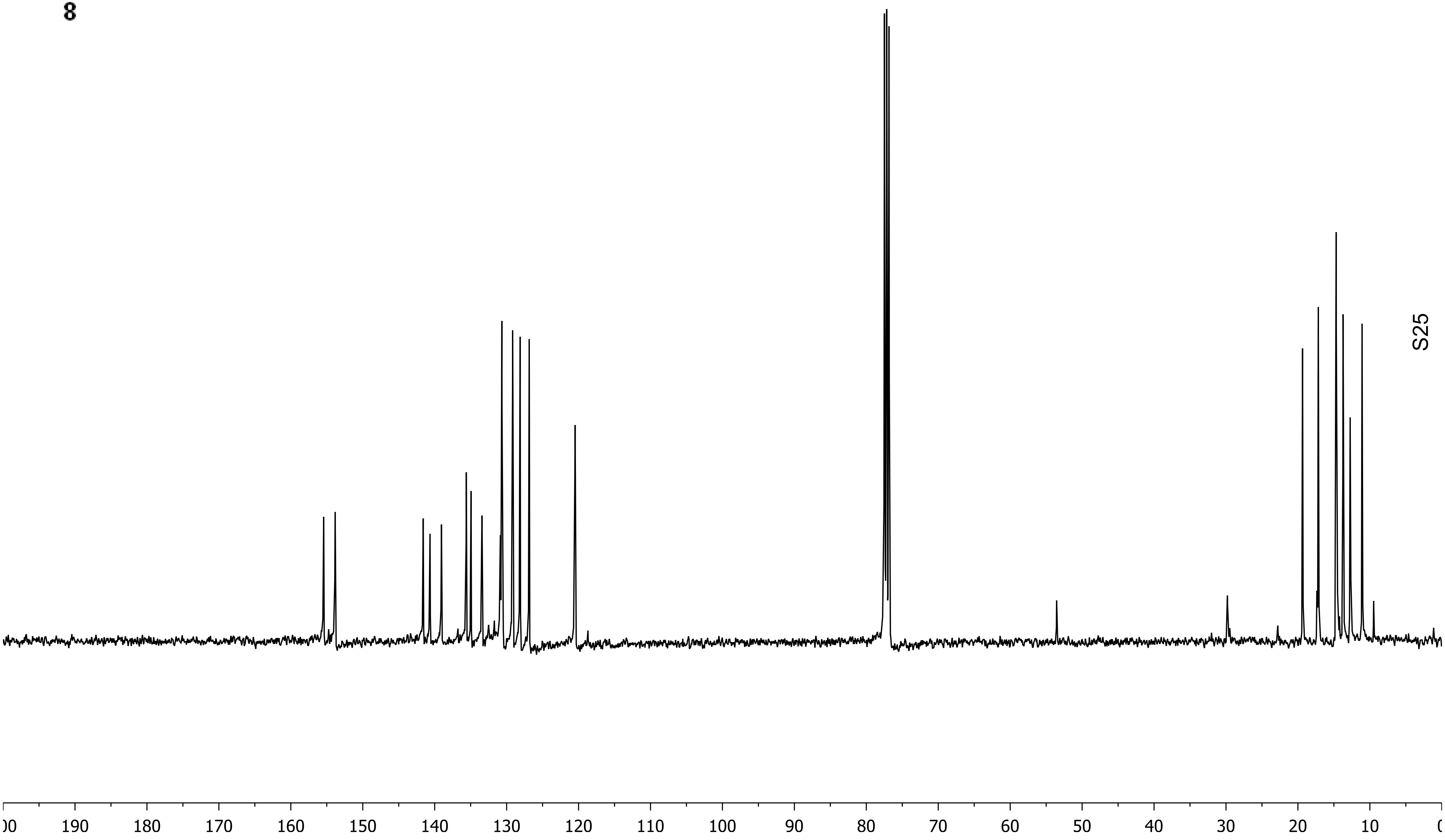

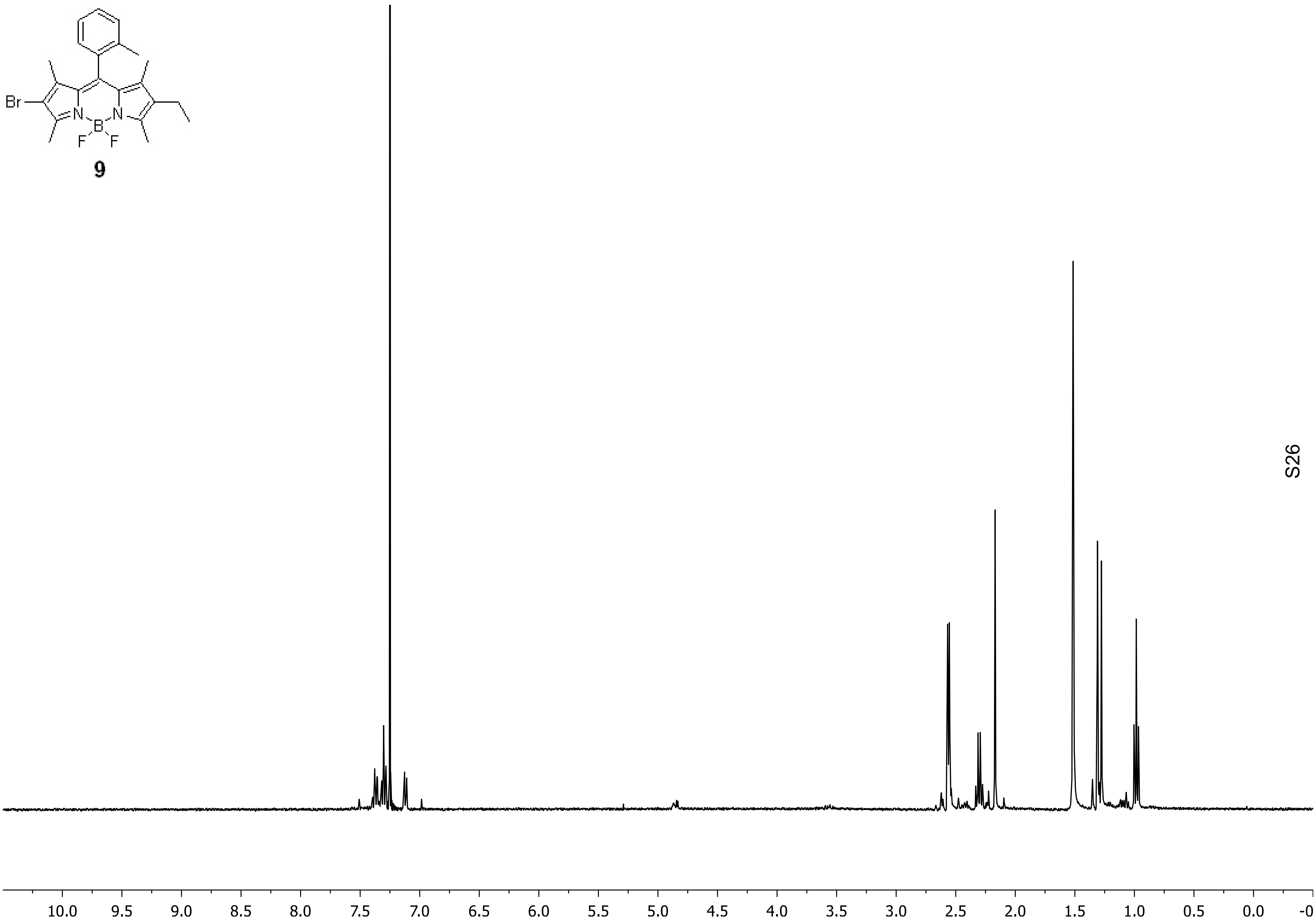

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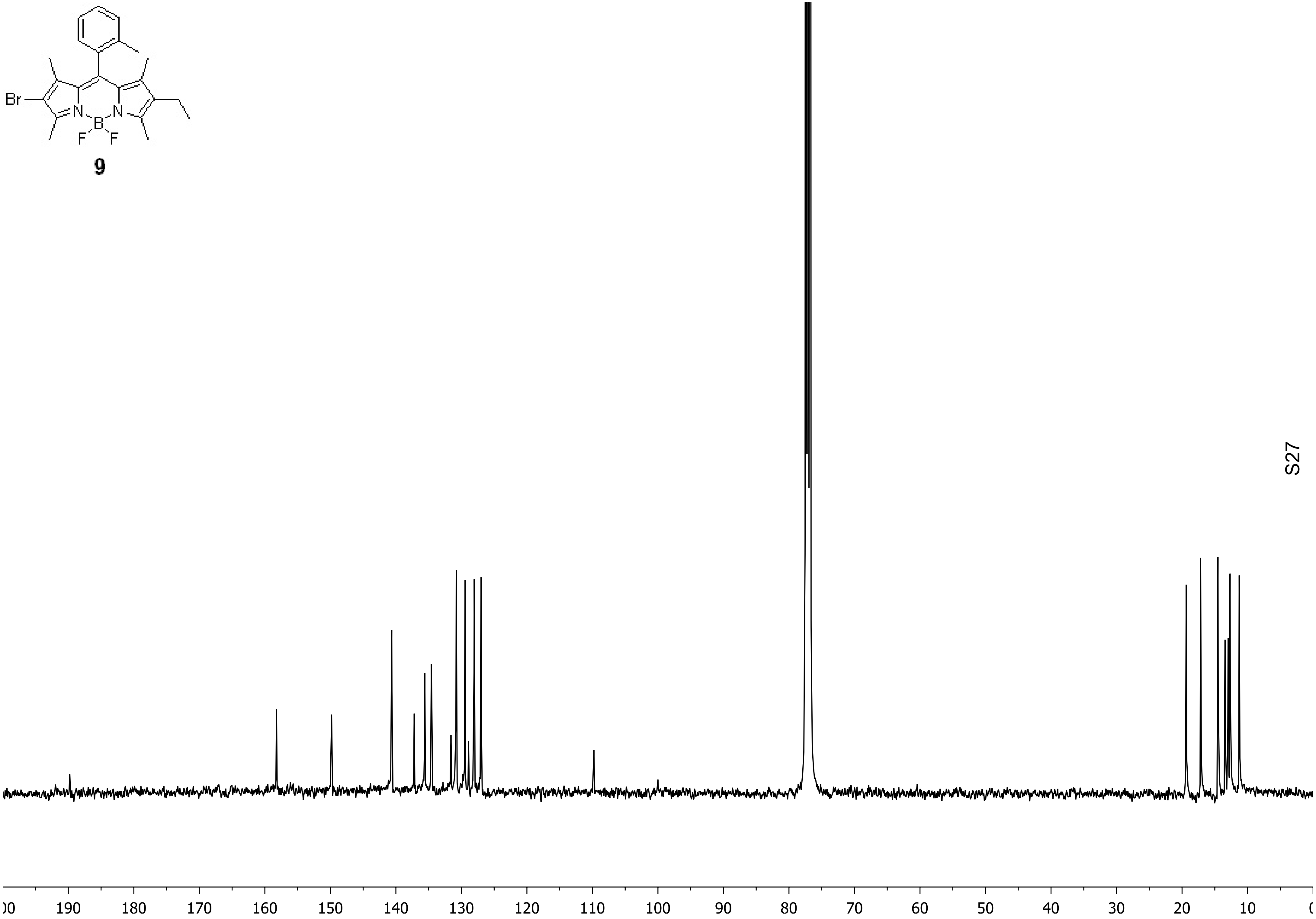

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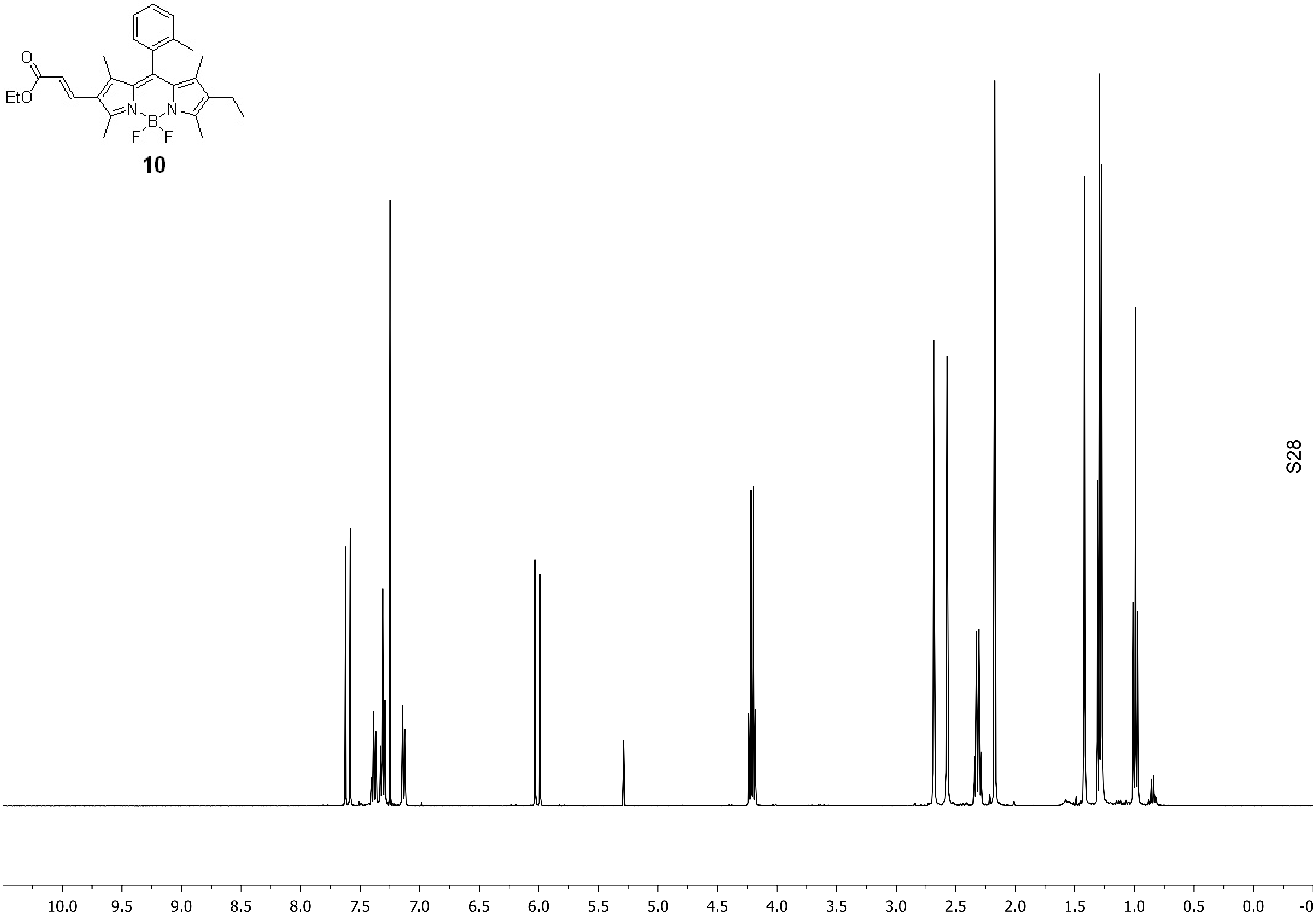

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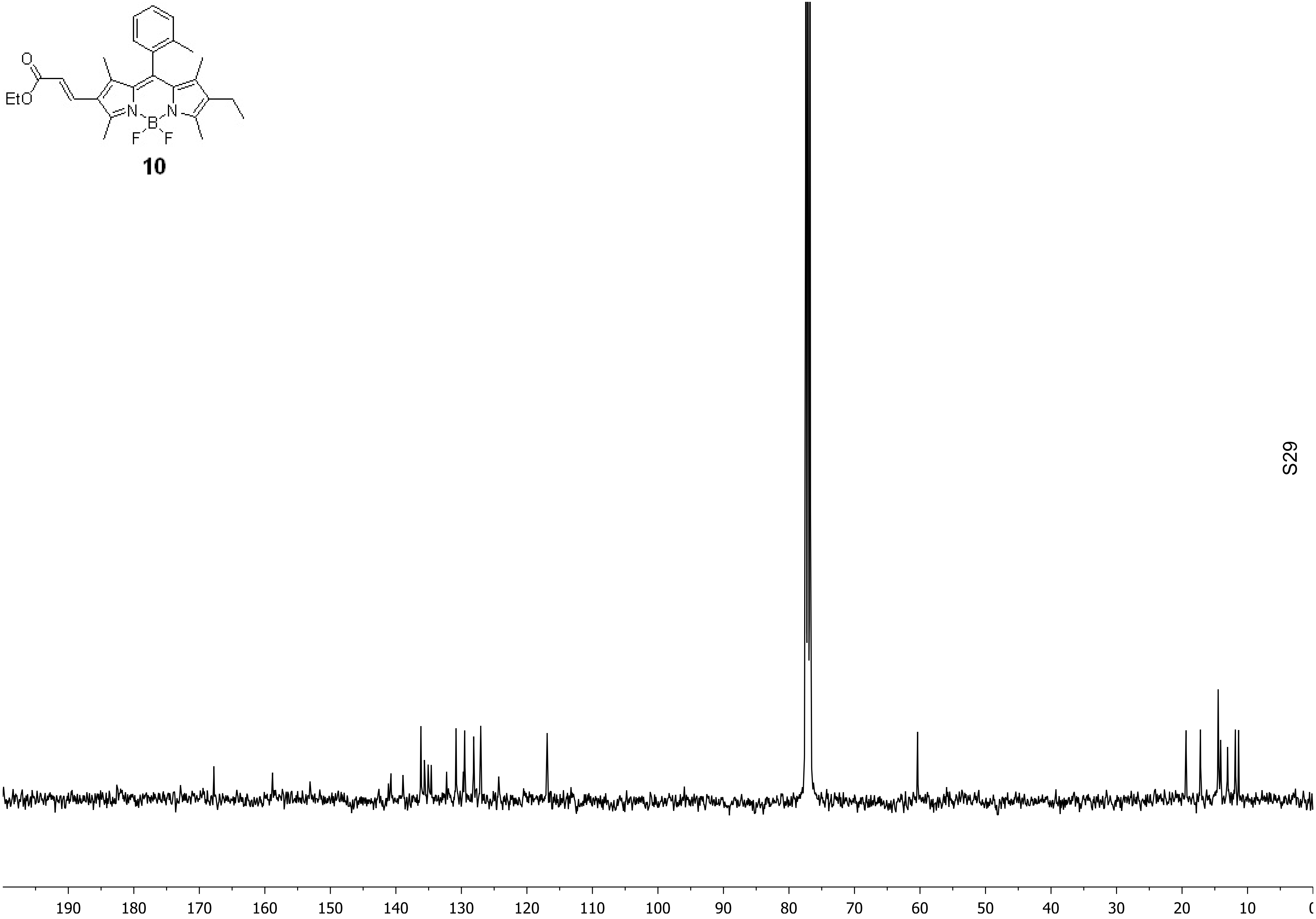

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