Electronic Supplementary Material (ESI) for Chemical Science.

Studying the reactivity of alkyl substituted BODIPY. First enantioselective addition of BODIPY to MBH carbonates.

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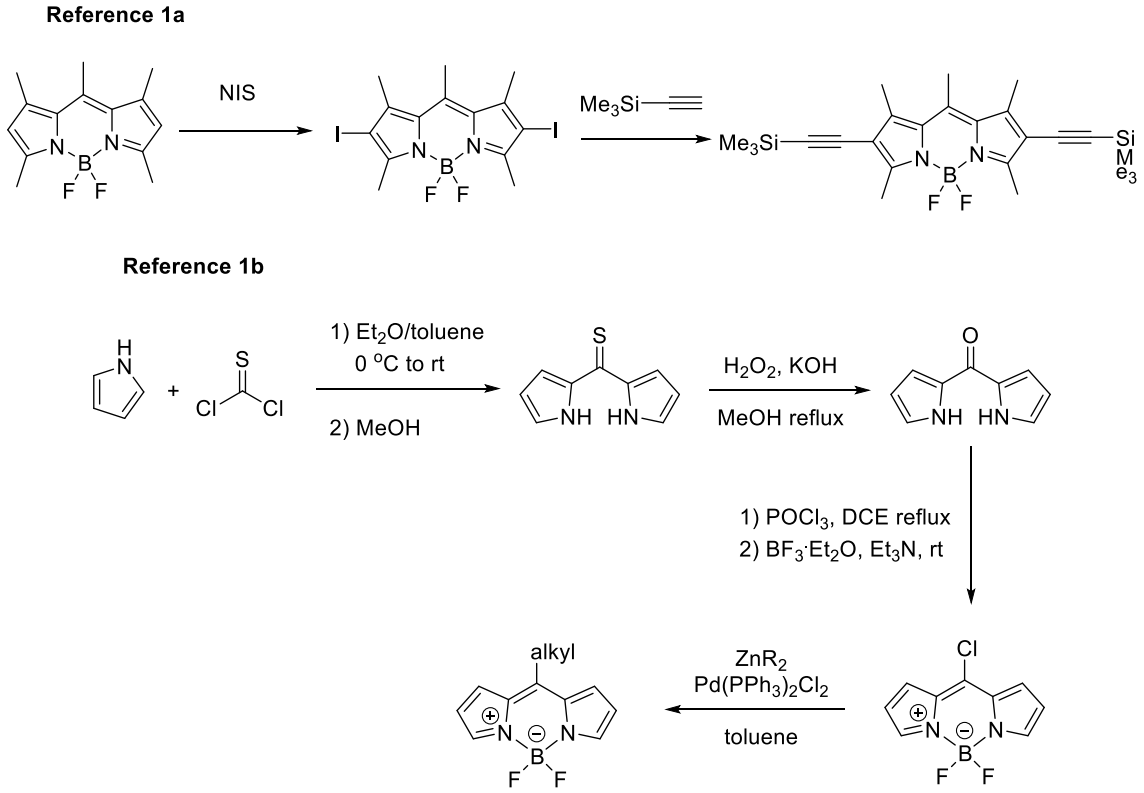
General information

Thin layer chromatography (TLC) was performed on Mark TLC Silicagel 60 F254. Product marks were visualized by UV-light at 254 nm and potassium permanganate stain. Flash column chromatography was effectuated using silica gel (Geduran Si60, 40-63µm). ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, 2D-NMR were recorded with a Bruker DPX400 NMR. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR; $CDCl_3$, 77.15 ppm for ^{13}C NMR). Optical rotations were performed on an Optical Activity PolAAr 2001 machine. High resolution mass spectrometer equipped with a Time of Flight (TOF) analyzer. The HPLC analysis were performed on an Agilent 1220 Infinity LC system HPLC. All analytical grade solvents and commercially available reagents were purchased from Sigma-Aldrich, Alfa-Aesar and Fluorochem and used as received without further purification.

Synthesis of the starting materials

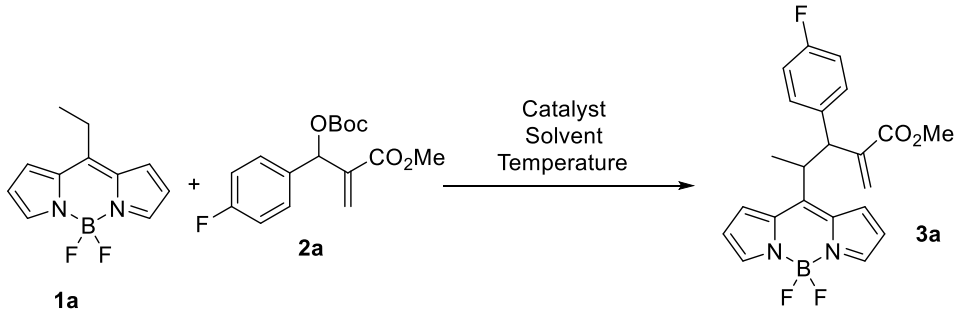
Bodipys were synthesised using modified general procedures reported in the literature.[1]



Scheme S1: Compound 1 general Synthesis

1 [1] a) M. Morisue, M. Kawanishi and S. Nakano, J. Polymer Sci. A, 2019, **57**, 2457-2465; b) E. Palao, G. Duran-Sampedro, S. de la Moya, M. Madrid, C. García-López, A. R. Agarrabeitia, B. Verbelen, W. Dehaen, N. Boens and M. J. Ortiz,*J. Org. Chem.* 2016, **81**, 3700.

Table S1: Optimization table



HPLC separation: **IE 90:10** (23 min and 25 min)

Entry	Ratio	Catalyst	Solvent	temperature	conversion	ee
1	1:1	DABCO 40%	$CHCl_3$	rt	1 d: full	Rac
2	1:1	$(DHQD)_2PHAL$ 20%	$CHCl_3$	rt	1 d: no conv 4 d: 23%	11
3	1:1	β-isocupreidine 20%	$CHCl_3$	rt	1 d: full	13
4	1:2	Quinine 20%	$CHCl_3$	rt	1 d: 12% 3 d: 40% 7 d: 65% 11 d: 79%	+88
5	1:1	Quinidine 20%	$CHCl_3$	rt	1 d: 13% 6 d: 70% 10 d: 86%	-90
6	1:1	Cinchonine 20%	$CHCl_3$	rt	1 d: 21% 6 d: 91%	-89-88
7	1:1	Cinchonidine aldehyde 20%	$CHCl_3$	rt	1 d: 13% 6 d: 77% 10 d: >90%	+71
8	1:1	Cinchonine 20%	Toluene	rt	0	-
9	1:1	Cinchonine 20%	trifluorotoluene	rt	0	-
10	1:1	Cinchonine 20%	ACN	rt	Traces	-
11	1:1	Cinchonine 20%	THF	rt	5 d: 45%	-48
12	1:1	Cinchonine 20%	DCE	rt	1 d: 0% 4 d: 23%	-77
13	1:2	Cinchonine 20%	$CHCl_3$	rt	1 d: 22% 4 d: full	-88
14	1:2	Quinidine 20%	$CHCl_3$	rt	1 d: 0 4 d: 34%	-89
15	1:2	Cinchonidine 20%	$CHCl_3$	rt	1 d: 25% 3 d: 90% 4 d: full	+79
16	1:2	Cinchonine 20%	$CHCl_3$	4	1 d: 0	-
17	1:2	Cinchonidine 20%	$CHCl_3$	4	1 d: 26%	+76

General procedure for the stereoselective reaction

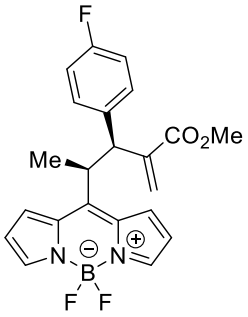
In a closed vial were added: the organic catalyst quinine, cinchonine or cinchonidine (20 mol%), the bodipy (0.05 mmol, 1 equiv) the Morita-Baylis-Hillman carbonate (2 equiv), and chloroform (1 ml) and stirred at rt for 2-10 days, monitored by ^{1}H-NMR. The crude was purified by flash column chromatography (*n*-hexane/EtOAc) to obtain the desired product.

Scale up Reaction (1g scale)

In a round bottom flask 1g of **1a** (4.5 mmols) were added in 100 mL of $CHCl_3$. Next, 2.97g of **2b** (2 equiv., 9 mmols) and 0.295g of quinine (0.2 equiv, 0.9 mmols) were added and the reaction was stirred for 7 days until completion of **1a** (NMR monitored). The crude reaction was purified by flash chromatography achieving 1.85 g of **3b** (95% yield, 88% ee).

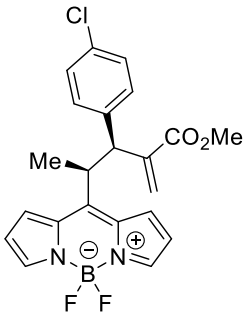
Final products characterization

methyl (3*S*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-3-(4-fluorophenyl)-2-methylenepentanoate, 3a



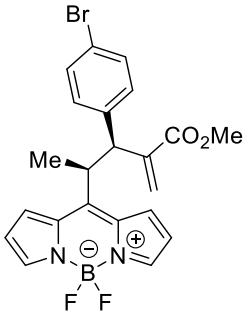
Following the general procedure the product was obtained after 4 days in 87% yield with quinine and >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (s, 2H), 7.68 – 7.57 (bs, 1H), 7.38 – 7.22 (bs, 1H), 7.01 – 6.94 (m, 2H), 6.76 – 6.68 (m, 2H), 6.62 – 6.53 (bs, 1H), 6.51 (s, 1H), 6.46 – 6.37 (bs, 1H), 5.93 (s, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.77 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.3, 162.9, 160.5, 153.7, 144.9 (bs), 142.1 (bs), 141.6, 136.1 (bs), 135.5, 135.4, 133.1 (bs), 129.8, 129.7, 128.8, 126.0, 118.0, 115.4, 115.2, 53.5, 52.5, 41.4, 21.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115,4 (s, 1F), -145.9 (dq, *J* = 57.5, 28.0 Hz, 1F), -146.7 (dq, *J* = 57.5, 28.0 Hz, 1F). **$[\alpha]_D^{25}$** = +479.4° (c = 0.25, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -432.7° (c = 0.6, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BF_3N_2O_2$ $[M+H]^+$: 413.1643, found: 413.1645. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 23.6, 25.8, 86% ee quinine and 83% ee cinchonine.

methyl (3*S*,4*S*)-3-(4-chlorophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenepentanoate, 3b



Following the general procedure the product was obtained after 6 days in >99% yield with quinine and 89% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 2H), 7.70 - 7.55 (bs, 1H), 7.36 - 7.25 (bs, 1H), 7.04 - 6.94 (m, 4H), 6.62 - 6.51 (bs, 1H), 6.50 (s, 1H), 6.49 - 6.40 (bs, 1H), 5.92 (s, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.04 - 3.96 (m, 1H), 3.79 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 153.5, 145.0 (bs), 142.3 (bs), 141.5, 138.3, 133.0 (bs), 129.6, 128.8 (bs), 128.6, 126.3, 118.1 (bs), 53.6, 52.5, 41.2, 22.0. **^{19}F NMR (376 MHz, $CDCl_3$)** -145.7 (dq, *J* = 55.0, 27.7 Hz, 1F), -146.9 (dq, *J* = 55.0, 27.7 Hz, 1F). **$[\alpha]_D^{25}$** = +449.2° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -394.7° (c = 0.3, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BClF_2N_2O_2$ $[M+H]^+$: 429.1347, found: 429.1343. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 24.6, 26.5, 89% ee quinine and 92% ee cinchonine.

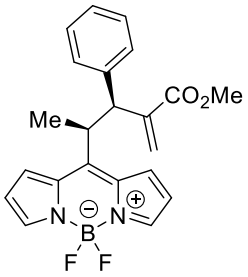
methyl (3*S*,4*S*)-3-(4-bromophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenepentanoate, 3c



Following the general procedure the product was obtained after 7 days and 97% yield with quinine and 3 days and 93% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 2H), 7.67 - 7.56 (bs, 1H), 7.36 - 7.26 (bs, 1H), 7.18 - 7.15 (m, 2H), 6.93 - 6.89 (m, 2H), 6.62 - 6.49 (bs, 1H), 6.50 (s, 1H), 6.50 - 6.39 (bs, 1H), 5.92 (s, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.06 - 3.96 (m, 1H), 3.77 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 153.4, 145.0 (bs), 142.2 (bs), 141.4, 138.9, 136.0 (bs), 133.2 (bs), 131.6, 129.9, 128.8 (bs), 126.3, 121.2, 118.1 (bs), 54.0, 52.5, 41.4, 22.0. **^{19}F NMR (376**

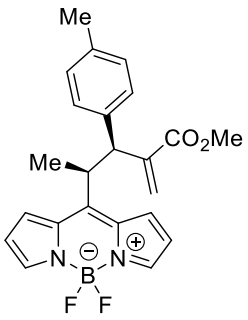
MHz, $CDCl_3$) δ -145.7 (dq, *J* = 57.7, 29.7 Hz, 1F), -146.9 (dq, *J* = 57.7, 29.7 Hz, 1F). **$[\alpha]_D^{25}$** = +97.4° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -375.3° (c = 0.5, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BBrF_2N_2O_2$ $[M+H]^+$: 473.0842, found: 473.0846. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 26.2, 28.2, 91% ee quinine and 90% ee cinchonine.

methyl (3*S*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylene-3-phenylpentanoate, 3d



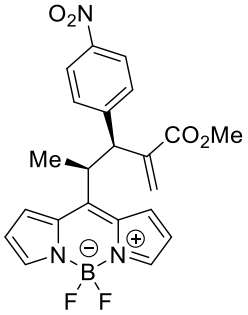
Following the general procedure the product was obtained after 8 days in >99% yield with quinine and >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (s, 2H), 7.70 - 7.60 (bs, 1H), 7.35 - 7.20 (bs, 1H), 7.05 - 6.95 (m, 5H), 6.65 - 6.55 (bs, 1H), 6.51 (s, 1H), 6.48 - 6.26 (bs, 1H), 5.95 (s, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.01 (dq, *J* = 11.9, 7.0 Hz, 1H), 3.77 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.4, 154.0, 144.6 (bs), 142.0 (bs), 141.7, 139.7, 136.1 (bs) 133.3 (bs), 128.9 (bs), 128.4, 128.3, 127.2, 126.0, 117.9 (bs), 54.0, 52.4, 41.6, 21.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.9 (dq, *J* = 56.4, 28.1 Hz, 1F), -146.8 (dq, *J* = 56.4, 28.1 Hz, 1F). **$[\alpha]_D^{25}$** = +449.2° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -394.7° (c = 0.3, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{22}BF_2N_2O_2$ $[M+H]^+$: 395.1737, found: 395.1739. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 24.9, 26.4, 86% ee quinine and 83% ee cinchonine.

methyl (3*S*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylene-3-(*p*-tolyl)pentanoate, 3e



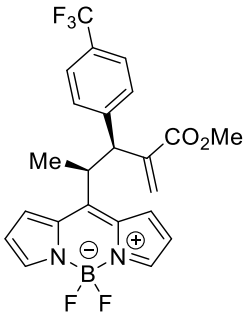
Following the general procedure the product was obtained after 6 days in >99% yield with quinine and >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (s, 2H), 7.72 - 7.60 (bs, 1H), 7.45 - 7.25 (bs, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.63 - 6.52 (bs, 1H), 6.47 (s, 1H), 6.45 - 6.34 (bs, 1H), 5.92 (s, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.08 - 3.98 (m, 1H), 3.76 (s, 3H), 2.13 (s, 3H), 1.57 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.5, 154.3, 144.4 (bs), 142.2, 141.9 (bs), 137.8, 136.7, 129.1, 128.9 (bs), 128.1, 125.8, 117.9 (bs), 53.5, 52.4, 41.6, 22.2, 21.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.4 (m, 1F), -147.1 (m, 1F). **$[\alpha]_D^{25}$** = +446.9° (c = 0.4, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -392.6° (c = 0.4, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{23}H_{24}BF_2N_2O_2$ $[M+H]^+$: 409.1893, found: 409.1899. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 23.4, 24.9, 86% ee quinine and 88% ee cinchonine.

methyl (3*S*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylene-3-(4-nitrophenyl)pentanoate, 3f



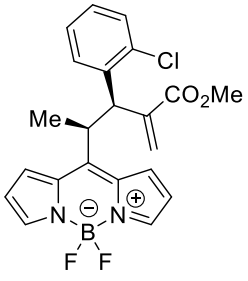
Following the general procedure the product was obtained after 2 days in >99% yield with quinine and >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 - 7.87 (m, 2H), 7.75 (bs, 2H), 7.70 - 7.65 (bs, 1H), 7.45 - 7.25 (bs, 1H), 7.24 - 7.19 (m, 2H), 6.65 - 6.56 (bs, 1H), 6.57 (s, 1H), 6.53 - 6.40 (bs, 1H), 6.00 (s, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.07 (dq, *J* = 12.0, 7.0 Hz, 1H), 3.78 (s, 3H), 1.62 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 152.4, 147.3, 146.9, 145.5 (bs), 142.6 (bs), 140.6, 135.9 (bs), 133.0 (bs), 129.2, 128.7 (bs), 127.2, 123.6, 118.4 (bs), 52.4, 52.6, 40.7, 21.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.4 (m, 2F). **$[\alpha]_D^{25}$** = +512.2° (c = 0.4, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -24.8° (c = 0.25, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BF_2N_3O_4$ $[M+H]^+$: 440.1588, found: 440.1594. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 67.8, 75.5, 89% ee quinine and 87% ee cinchonine.

methyl (3*S*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylene-3-(4-trifluoromethyl)phenyl)pentanoate, 3g



Following the general procedure the product was obtained after 9 days in >99% yield with cinchonine and 48% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 2H), 7.70 - 7.55 (bs, 1H), 7.35 - 7.27 (bs, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.64 - 6.52 (bs, 1H), 6.55 (s, 1H), 6.53 - 6.38 (bs, 1H), 5.96 (s, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.04 (dq, *J* = 12.0, 7.0 Hz, 1H), 3.79 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 153.0, 145.1 (bs), 143.8, 142.4 (bs), 141.0, 136.0 (bs), 133.0 (bs), 129.5, 129.2, 128.9, 128.8 (bs), 128.6, 126.8, 125.4 (q), 122.6, 118.2 (bs), 53.9, 52.6, 41.0, 21.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.7 (s, 3F), -146.7 (dq, *J* = 58.4, 29.1 Hz, 1F), -147.9 (dq, *J* = 58.4, 29.1 Hz, 1F). **$[\alpha]_D^{25}$** = -353.3° (c = 0.4, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +245.5° (c = 0.2, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{23}H_{21}BF_5N_2O_2$ $[M+H]^+$: 463.1611, found: 463.1619. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 17.3, 19.0, 77% ee cinchonine and 37% ee cinchonidine.

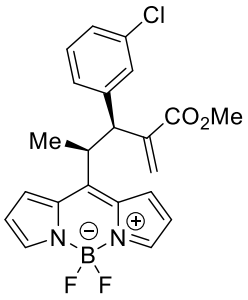
methyl (3*R*,4*S*)-3-(2-chlorophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenepentanoate, 3h



Following the general procedure the product was obtained after 6 days in >99% yield with quinine and >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (s, 2H), 7.70 - 7.54 (bs, 2H), 7.47 - 7.45 (m, 1H), 7.17 - 7.13 (m, 1H), 7.03 - 6.69 (m, 2H), 6.53 - 6.51 (m, 2H), 6.44 (s, 1H), 5.90 (s, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 4.29 (dq, *J* = 12.0, 7.0 Hz, 1H), 3.81 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 153.8 (bs), 143.5 (bs), 143.2, 140.6 (bs), 137.1, 134.2, 130.1, 129.4 (bs),

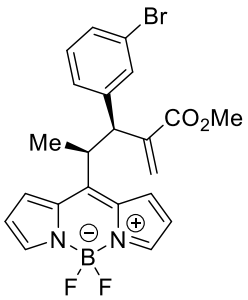
128.9, 128.4, 126.7, 118.1 (bs), 52.4, 49.6, 40.6, 22.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.2 (m, 2F). **$[\alpha]_D^{25}$** = -16.3° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = +93.9° (c = 0.4, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BClF_2N_2O_2$ $[M+H]^+$: 429.1347, found: 429.1343. The enantiomeric excess was determined by **HPLC** using a Chiralpak OZH column, hexane/iPrOH = 95:5, flow rate 1.0 mL/min, λ = 210 nm: t_r = 14.1, 15.8, 84% ee quinine and 89% ee cinchonine.

methyl (3*S*,4*S*)-3-(3-chlorophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenepentanoate, 3i



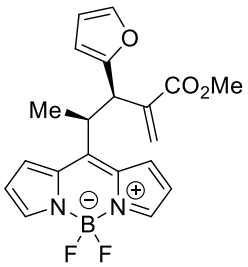
Following the general procedure the product was obtained after 6 days in 98% yield with quinine and 93% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 2H), 7.70 - 7.55 (bs, 1H), 7.40 - 7.25 (bs, 1H), 7.06 - 7.03 (m, 1H), 7.00 - 6.92 (m, 2H), 6.86 - 6.82 (m, 1H), 6.64 - 6.55 (bs, 1H), 6.54 (s, 1H), 6.52 - 6.38 (bs, 1H), 5.95 (s, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.99 (dq, *J* = 12.0, 7.0 Hz, 1H), 3.77 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 153.2, 145.0 (bs), 142.2 (bs), 141.8, 141.2, 136.1 (bs), 134.2, 133.1 (bs), 129.6, 128.8 (bs), 128.2, 127.4, 126.9, 126.5, 118.1 (bs), 52.7, 52.5, 41.2, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.8 (dq, *J* = 58.1, 29.0 Hz, 1F), -146.9 (dq, *J* = 58.1, 29.0 Hz, 1F). **$[\alpha]_D^{25}$** = +511.5° (c = 0.4, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -513.3° (c = 0.3, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BClF_2N_2O_2$ $[M+H]^+$: 429.1347, found: 429.1353. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 21.7, 23.3, 93% ee quinine and 87% ee cinchonine.

methyl (3*S*,4*S*)-3-(3-bromophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenepentanoate, 3j



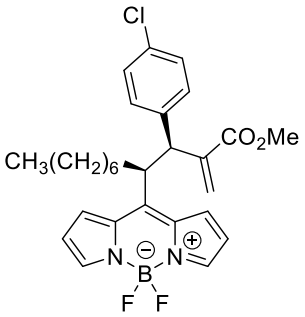
Following the general procedure the product was obtained after 8 days in 89% yield with quinine and 85% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 2H), 7.70 - 7.53 (bs, 1H), 7.40 - 7.23 (bs, 1H), 7.22 - 7.19 (m, 1H), 7.16 - 7.10 (m, 1H), 6.92 - 6.85 (m, 2H), 6.63 - 6.53 (bs, 1H), 6.55 (s, 1H), 6.54 - 6.40 (bs, 1H), 5.95 (s, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.96 (dq, *J* = 12.0, 7.0 Hz, 1H), 3.79 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 153.1, 145.1 (bs), 142.3 (bs), 142.0, 141.0, 133.2, 131.1, 130.3, 129.9, 128.9 (bs), 127.4, 126.5, 122.4, 118.1 (bs), 55.7, 52.5, 41.2, 21.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.9 (dq, *J* = 58.7, 28.6 Hz, 1F), -147.0 (dq, *J* = 58.7, 28.6 Hz, 1F). **$[\alpha]_D^{25}$** = +394.0° (c = 0.4, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -411.5° (c = 0.4, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{21}BBrF_2N_2O_2$ $[M+H]^+$: 473.0842, found: 473.0847. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 23.2, 25.1, 89% ee quinine and 85% ee cinchonine.

methyl (3*R*,4*S*)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-3-(furan-2-yl)-2-methylenepentanoate, 3k



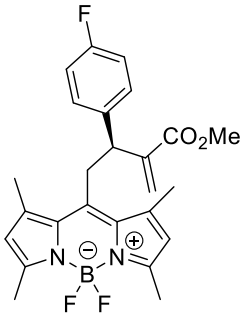
Following the general procedure the product was obtained after 3 days in >99% yield with quinine and 99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (s, 2H), 7.75 - 7.64 (bs, 1H), 7.44 - 7.32 (bs, 1H), 7.12 (dd, *J* = 1.8, 0,6 Hz, 1H), 6.65 - 6.50 (bs, 1H), 6.53 (s, 1H), 6.50 - 6.40 (bs, 1H), 6.09 (s, 1H), 6.04 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.82 (d, *J* = 3.2 Hz, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 3.94 (dq, *J* = 11.6, 7.2 Hz, 1H), 3.84 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.6, 154.0, 152.9, 144.7 (bs), 142.1 (bs), 142.0, 139.8, 135.7, 133.0, 128.8 (bs), 128.0, 118.0 (bs), 110.4, 107.9, 52.6, 46.3, 42.2, 21.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.5 (dq, *J* = 59.7, 29.3 Hz, 1F), -146.9 (dq, *J* = 59.7, 29.3 Hz, 1F). **$[\alpha]_D^{25}$** = +33.3° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -7.5° (c = 0.3, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{22}H_{20}BF_2N_2O_3$ $[M+H]^+$: 385.1530, found: 385.1536. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 21.0, 22.3, 94% ee quinine and 86% ee cinchonine.

methyl (3*S*,4*S*)-3-(4-chlorophenyl)-4-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methyleneoctanoate, 3l



Following the general procedure the product was obtained after 10 days in >99% yield with quinine and 6 days in >99% yield with cinchonine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (bs, 1H), 7.73 (bs, 1H), 7.62 (d, *J* = 4.1 Hz, 1H), 7.29 (d, *J* = 4.1 Hz, 1H), 7.01 - 6.59 (m, 2H), 6.95 - 6.89 (m, 2H), 6.57 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.48 (s, 1H), 6.44 (dd, *J* = 4.1, 1.7 Hz, 1H), 5.91 (s, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 3.98 - 3.79 (m, 1H), 3.77 (s, 3H), 2.05 - 1.90 (m, 2H), 1.28 - 1.10 (m, 10H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 152.5, 145.0 (bs), 142.3 (bs), 141.8, 138.2, 137.6 (bs), 133.1 (bs), 132.9, 129.7, 129.4 (bs), 128.7, 128.5 (bs), 128.1, 125.9, 124.4, 118.3 (bs), 117.9 (bs), 53.5, 52.5, 47.3, 35.9, 31.8, 29.6, 29.0, 28.6, 22.7, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.8 (dq, *J* = 57.7, 28.7 Hz, 1F), -147.0 (dq, *J* = 57.7, 28.7 Hz, 1F). **$[\alpha]_D^{25}$** = +200.4° (c = 0.3, $CHCl_3$) quinine, **$[\alpha]_D^{25}$** = -82.5° (c = 0.1, $CHCl_3$) cinchonine. **HRMS (ESI+):** Exact mass calculated for $C_{28}H_{32}BClF_2N_2O_2$ $[M+H]^+$: 512.2213, found: 512.2221. The enantiomeric excess was determined by **HPLC** using a Chiralpak ID column, hexane/iPrOH = 95:5, flow rate 1.0 mL/min, λ = 210 nm: t_r = 20.2, 23.9, 92% ee quinine and 94% ee cinchonine.

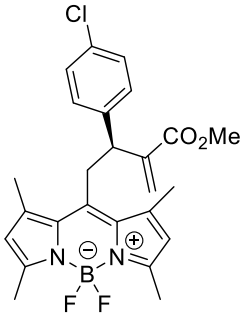
methyl (*S*)-4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-3-(4-fluorophenyl)-2-methylenebutanoate, 3m



Following the general procedure the product was obtained after 8 days in 81% yield with cinchonine and 9 days in >99% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.04 - 6.97 (m, 2H), 6.88 - 6.80 (m, 2H), 6.48 (s, 1H), 6.08 (bs, 1H), 5.81 (bs, 1H), 5.78 (d, *J* = 0.9 Hz, 1H), 4.19 (dd, *J* =

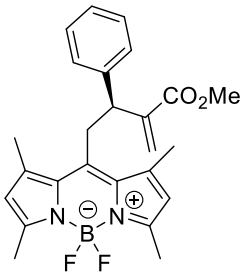
9.5, 4.9 Hz, 1H), 3.48 - 3.37 (m, 2H), 3.60 (s, 3H), 2.54 (s, 3H), 2.47 (s, 3H), 2.35 (s, 3H), 1.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 163.2, 160.7, 155.2, 153.1, 143.4, 142.8, 141.5 (bs), 139.4 (bs), 135.2, 132.9 (bs), 131.6 (bs), 129.4, 129.3, 125.0, 122.2 (bs), 121.6 (bs), 115.0, 114.8, 52.2, 48.4, 32.3, 16.7, 16.5, 14.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115,7 (s, 1F), -146.1 (dq, *J* = 63.9, 31.6 Hz, 1F), -147.6 (dq, *J* = 63.9, 31.6 Hz, 1F). **$[\alpha]_D^{25}$** = -475.3° (c = 0.3, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +870.2° (c = 0.3, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{27}BF_3N_2O_2$ $[M+H]^+$: 455.2112, found: 455.2115. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 11.0, 16.8, 88% ee cinchonine and 85% ee cinchonidine.

methyl (*S*)-4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-3-(4-chlorophenyl)-2-methylenebutanoate, 3n



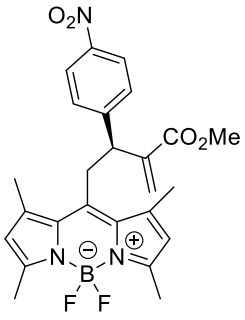
Following the general procedure the product was obtained after 3 days in 98% yield with cinchonine and 5 days in 98% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H), 6.07 (bs, 1H), 5.83 (bs, 1H), 5.77 (d, *J* = 0.9 Hz, 1H), 4.18 (dd, *J* = 9.2, 5.0 Hz, 1H), 3.59 (s, 3H), 3.46 (dd, *J* = 12.7, 5.0 Hz, 1H), 3.40 (dd, *J* = 12.7, 9.2 Hz, 1H), 2.54 (s, 3H), 2.47 (s, 3H), 2.35 (s, 3H), 1.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 155.4 (bs), 153.4 (bs), 143.4, 142.7, 141.5 (bs), 139.5 (bs), 138.3, 133.1, 131.7, 129.3, 128.4, 125.4, 122.4 (bs), 121.8 (bs), 52.3, 48.7, 32.2, 16.8, 16.7, 14.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.1 (dq, *J* = 63.8, 31.5 Hz, 1F), -147.5 (dq, *J* = 63.8, 31.5 Hz, 1F). **$[\alpha]_D^{25}$** = -784.2° (c = 0.3, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +834.6° (c = 0.25, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{27}BClF_2N_2O_2$ $[M+H]^+$: 471.1817, found: 471.1823. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 11.7, 18.7, 90% ee cinchonine and 92% ee cinchonidine.

methyl (*S*)-4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-3-phenylbutanoate, 3o



Following the general procedure the product was obtained after 6 days in 96% yield with cinchonine and 5 days in 99% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 - 7.12 (m, 3H), 7.08 - 7.05 (m, 2H), 6.44 (s, 1H), 6.07 (bs, 1H), 5.83 (bs, 1H), 5.73 (s, 1H), 4.24 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.58 (s, 3H), 3.53 - 3.37 (m, 2H), 2.54 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H), 1.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 155.0 (bs), 153.2 (bs), 143.9, 143.1, 141.7 (bs), 139.8, 139.7 (bs), 133.1, 131.8, 128.3, 128.0, 127.3, 125.2, 122.1, 121.7, 52.2, 49.1, 32.4, 16.8, 16.7, 14.6 (bs). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.2 (dq, *J* = 67.0, 33.2 Hz, 1F), -147.3 (dq, *J* = 67.0, 33.2 Hz, 1F). **$[\alpha]_D^{25}$** = -572.9° (c = 0.3, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +637.9° (c = 0.35, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{22}BF_2N_2O_2$ $[M+H]^+$: 437.2206, found: 437.2209. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 12.4, 19.8, 87% ee cinchonine and 90% ee cinchonidine.

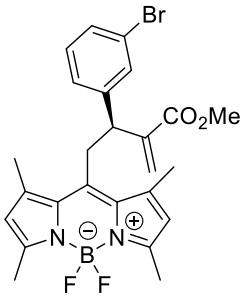
methyl (*S*)-4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylene-3-(4-nitrophenyl)butanoate, 3p



Following the general procedure the product was obtained after 12 days in 71% yield with cinchonine and 71% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.59 (s, 1H), 6.10 (bs, 1H), 5.90 (d, *J* = 1.1Hz, 1H), 5.76 (bs, 1H), 4.27 (dd, *J* = 10.1, 4.5 Hz, 1H), 3.61 (s, 3H), 3.51 (dd, *J* = 12.7, 4.5 Hz, 1H), 3.45 (dd, *J* = 12.7, 10.1 Hz, 1H), 2.55 (s, 3H), 2.45 (s, 3H), 2.35 (s, 3H), 1.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.2, 155.8 (bs), 153.9 (bs), 147.2, 142.5, 141.8, 140.9 (bs), 139.5 (bs), 132.9 (bs), 131.7 (bs), 128.8, 127.5, 126.2, 123.4, 1226 (bs),

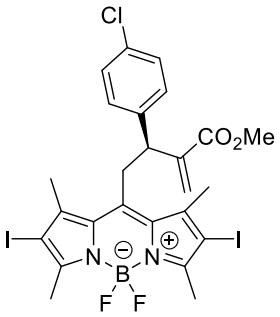
122.0 (bs), 52.5, 49.3, 31.8, 16.9, 16.5, 14.7 (bs). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.8 (dq, *J* = 67.8, 33.6 Hz, 1F), -147.8 (dq, *J* = 67.8, 33.6 Hz, 1F). **$[\alpha]_D^{25}$** = -471.8° (c = 0.2, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +829.7° (c = 0.2, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{27}BF_2N_3O_4$ $[M+H]^+$: 482.2057, found: 482.2061. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 31.3, 40.9, 71% ee cinchonine and 70% ee cinchonidine.

methyl (*S*)-3-(3-bromophenyl)-4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenebutanoate, 3q



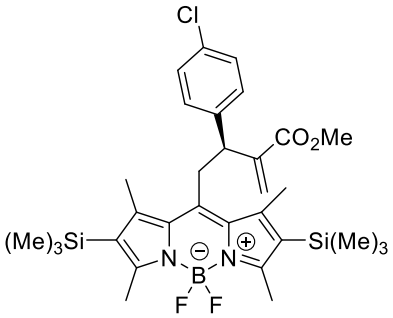
Following the general procedure the product was obtained after 10 days in >99% yield with cinchonine and 4 days in 98% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (dd, *J* = 1.8, 1.3 Hz, 1H), 7.21 (t, *J* = 1.8 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.96 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.50 (s, 1H), 6.07 (bs, 1H), 5.82 (bs, 1H), 5.79 (d, *J* = 1.0 Hz, 1H), 4.16 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.61 (s, 3H), 3.46 (dd, *J* = 12.7, 5.0 Hz, 1H), 3.39 (dd, *J* = 12.7, 9.5 Hz, 1H), 2.54 (s, 3H), 2.47 (s, 3H), 2.34 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 155.4 (bs), 153.4 (bs), 143.2, 142.3, 142.0, 141.5 (bs), 139.5 (bs), 133.1 (bs), 131.7 (bs), 130.5, 130.4, 129.8, 127.1, 125.8, 122.4 (bs), 122.3, 121.8 (bs), 52.4, 48.9, 32.2, 16.7, 14.7 (bs). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.1 (dq, *J* = 64.3, 31.5 Hz, 1F), -147.4 (dq, *J* = 64.3, 31.5 Hz, 1F). **$[\alpha]_D^{25}$** = -587.0° (c = 0.3, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +603.7° (c = 0.3, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{27}BBrF_2N_2O_2$ $[M+H]^+$: 515.1312, found: 515.1319. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 90:10, flow rate 1.0 mL/min, λ = 210 nm: t_r = 12.5, 16.2, 84% ee cinchonine and 86% ee cinchonidine.

methyl (*S*)-3-(4-chlorophenyl)-4-(5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenebutanoate, 3r



Following the general procedure the product was obtained after 8 days in 58% yield with cinchonine and 5 days in 99% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13 (m, 2H), 6.95 (m, 2H), 6.48 (s, 1H), 5.77 (bs, 1H), 4.09 (dd, *J* = 11.3, 7.2 Hz, 1H), 3.59 (s, 3H), 3.58-3.42 (m, 2H), 2.63 (s, 3H), 2.57 (s, 3H), 2.41 (bs, 3H), 2.01 (bs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 156.6, 155.0, 143.4, 143.3 (bs), 142.1, 141.5 (bs), 137.8, 133.4, 133.1 (bs), 131.7 (bs), 129.1, 128.6, 128.4, 125.6, 52.4, 49.0, 33.1, 19.7, 19.3, 16.3 (bs). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -145.6 (m, 1F), -146.3 (m, 1F). **$[\alpha]_D^{25}$** = -168.5° (c = 0.5, $CHCl_3$) cinchonine, **$[\alpha]_D^{25}$** = +235.3° (c = 0.5, $CHCl_3$) cinchonidine. **HRMS (ESI+):** Exact mass calculated for $C_{25}H_{25}BClF_2I_2N_2O_2$ $[M+H]^+$: 722.9750, found: 722.9756. The enantiomeric excess was determined by **HPLC** using a Chiralpak IE column, hexane/iPrOH = 95:5, flow rate 1.0 mL/min, λ = 210 nm: t_r = 14.7, 19.1, 85% ee cinchonine and 87% ee cinchonidine.

methyl (*S*)-3-(4-chlorophenyl)-4-(5,5-difluoro-1,3,7,9-tetramethyl-2,8-bis(trimethylsilyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)-2-methylenebutanoate, 3s

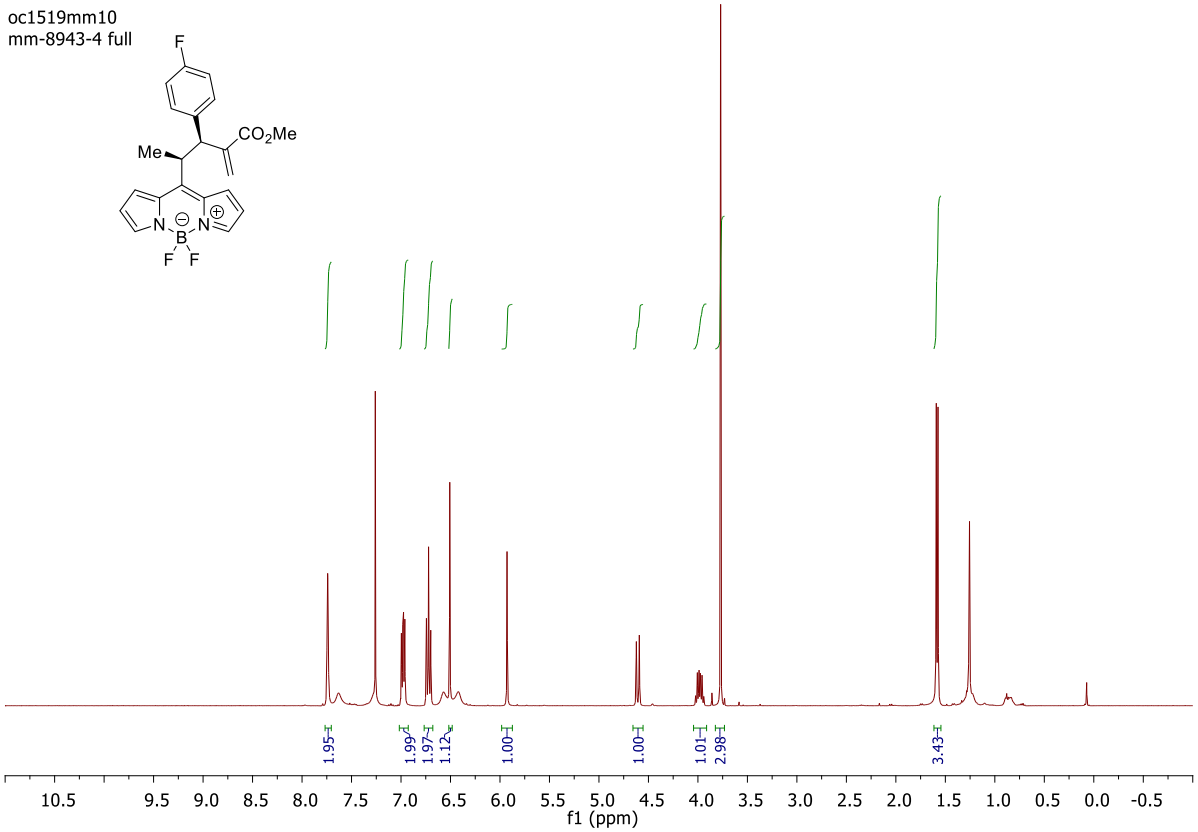


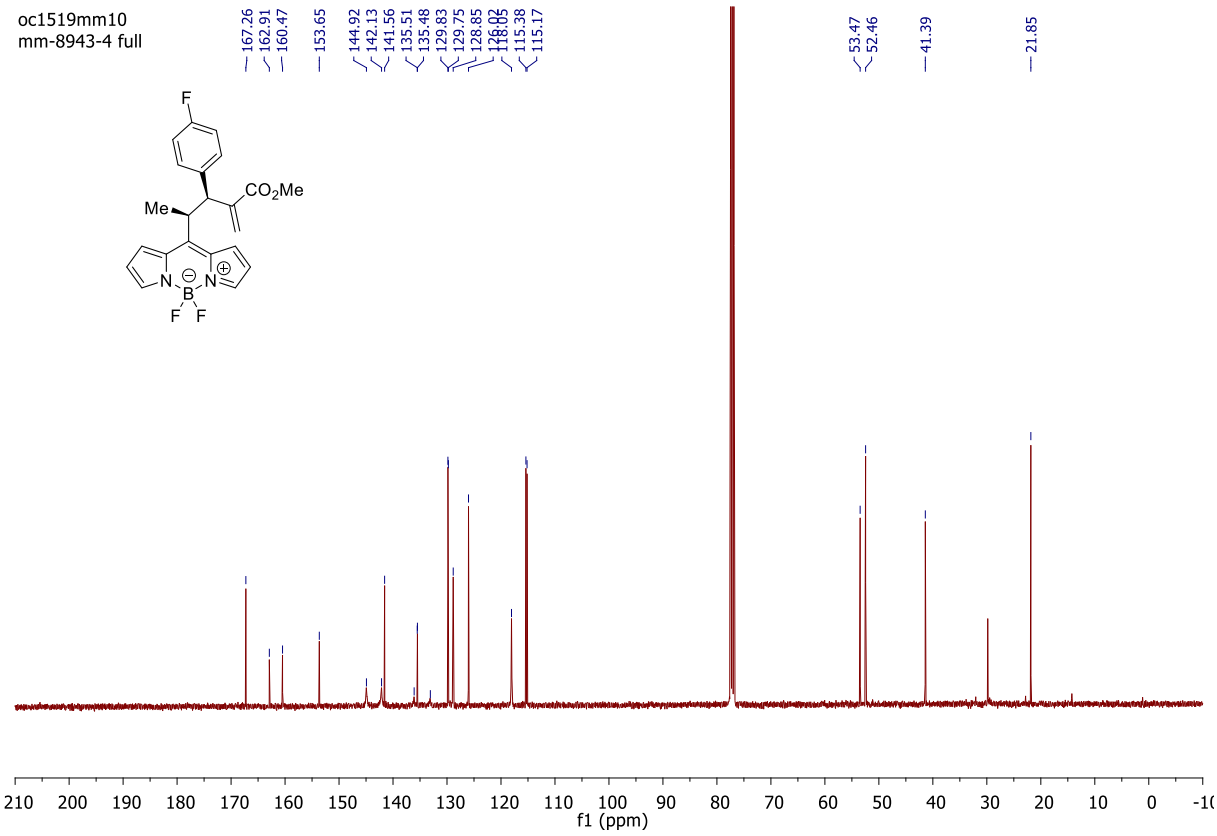
Following the general procedure the product was obtained after 3 days in 56% yield with cinchonine and 3 days in 68% yield with cinchonidine as a red foam. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 (m, 2H), 6.97 (m, 2H), 6.45 (s, 1H), 5.73 (d, *J* = 0.9 Hz, 1H), 4.13 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.58 (s, 3H), 3.57-3.45 (m, 2H), 2.62 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H), 2.08 (s, 3H), 0.26 (s, 9H), 0.23 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 158.6, 157.2, 144.8, 142.7, 142.4, 141.3, 138.2, 133.4, 132.6, 129.1, 128.6, 125.7, 52.3, 48.9, 32.6, 15.6, 15.5, 13.7 (bs), 0.28, 0.22. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -146.3 (dq, *J* = 65.3, 32.2 Hz,

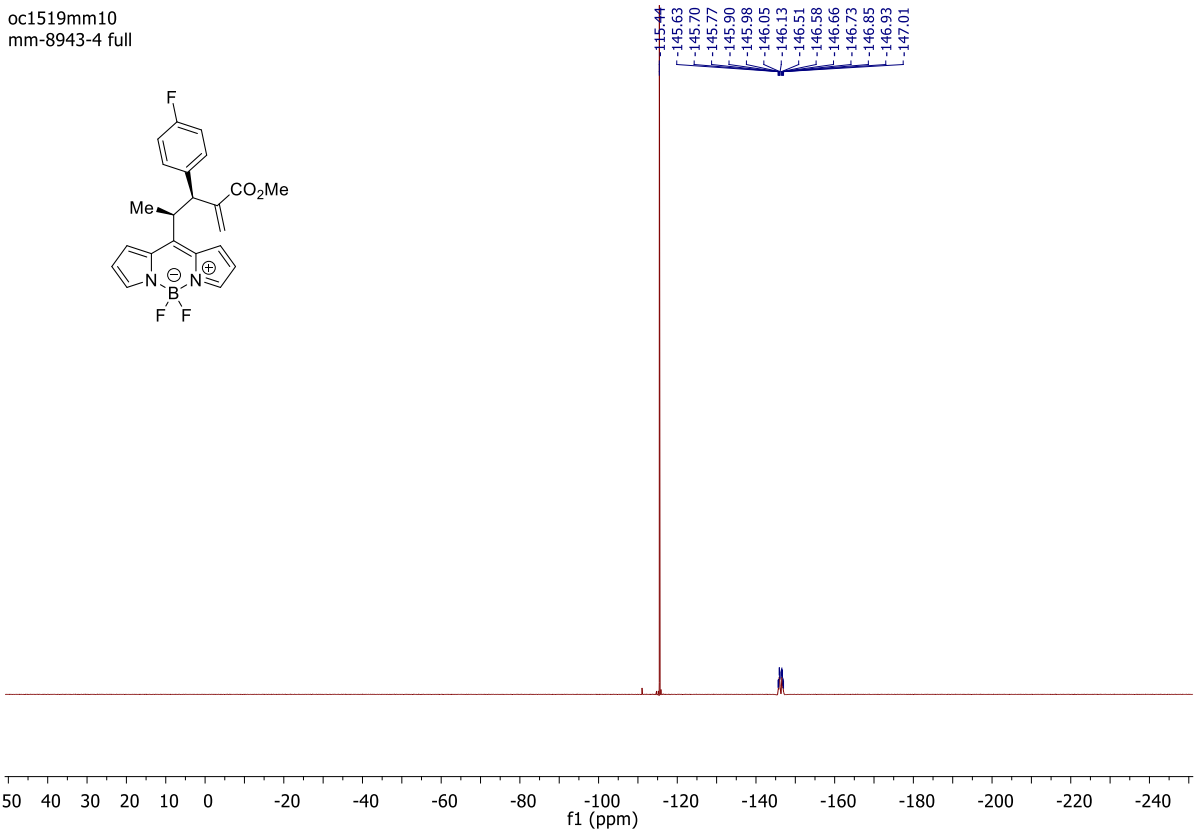
1F), -147.7 (dq, *J* = 65.3, 32.2 Hz, 1F). **HRMS (ESI+):** Exact mass calculated for $C_{31}H_{43}BClF_2N_2O_2Si_2$ $[M+H]^+$: 615.2607, found: 615.2613.

NMR spectra

3a



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F
CO2Me
Me
N
B
N
F
F
-115.44
-145.63
-145.70
-145.77
-145.90
-145.98
-146.05
-146.13
-146.51
-146.58
-146.66
-146.73
-146.85
-146.93
-147.01
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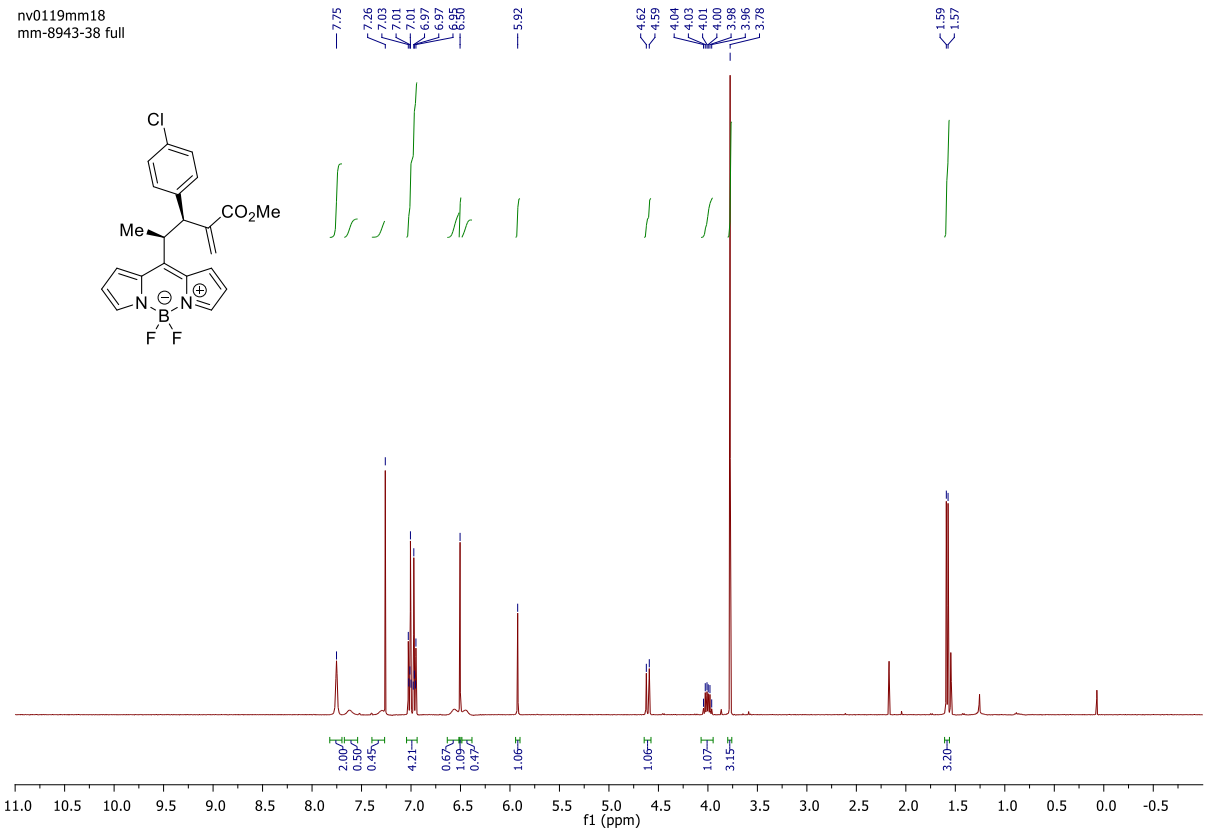
f1 (ppm)

3b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Cl
CO2Me
Me
N
B
N
F
F
7.75
7.26
7.03
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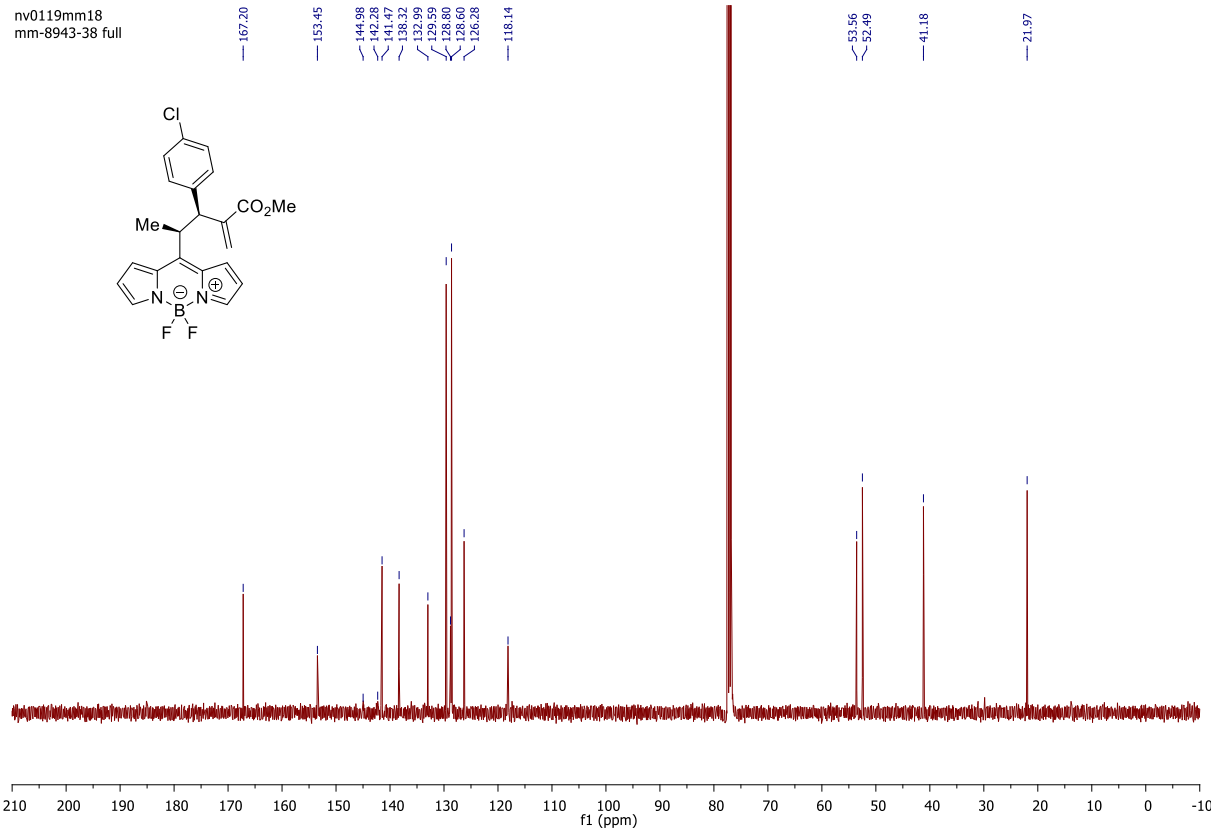
7.01
6.97
6.97
6.95
6.50
5.92
4.62
4.59
4.04
4.03
4.01
4.00
3.98
3.96
3.78
1.59
1.57
2.00
0.50
0.45
4.21
0.67
1.09
0.47
1.06
1.06
1.07
3.15
3.20
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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144.98
142.28
141.47
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132.99
129.59
128.80
128.60
126.28
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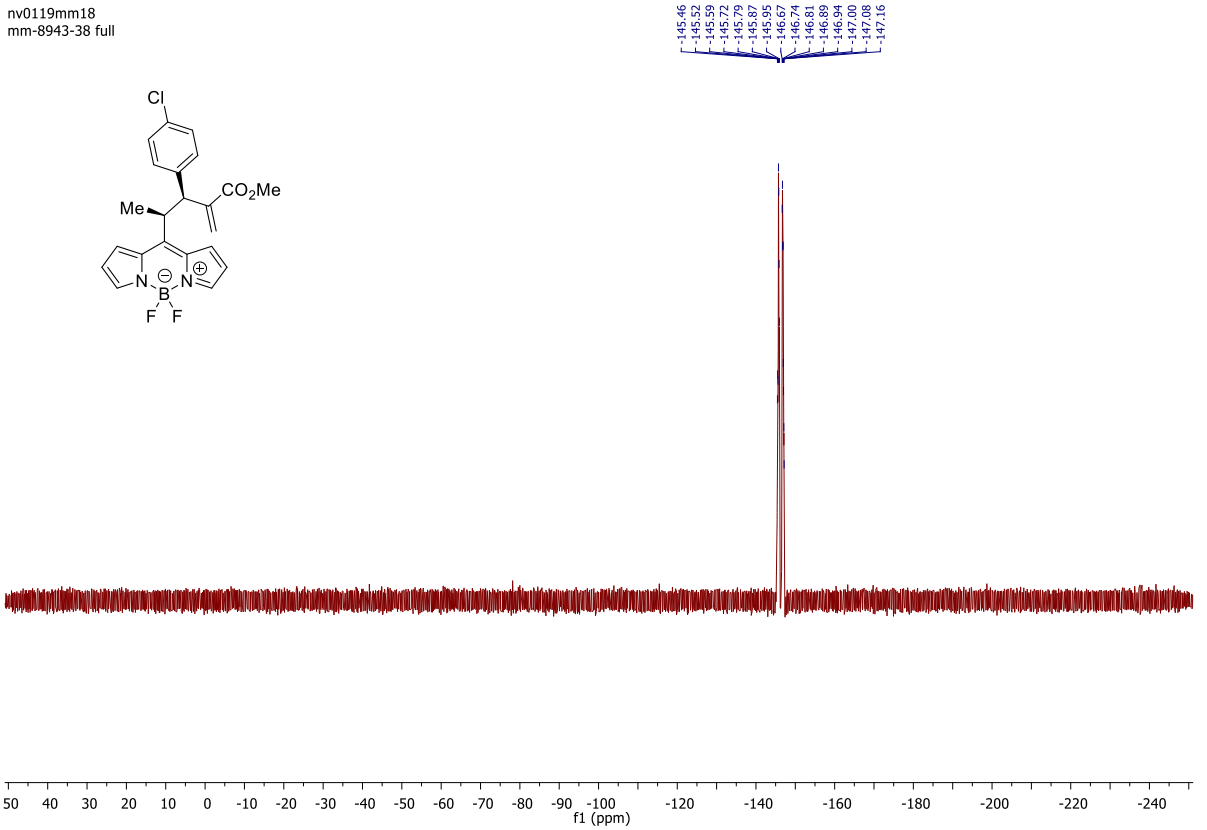
53.56
52.49
41.18
21.97
Cl
CO2Me
Me
N
B
F
F
f1 (ppm)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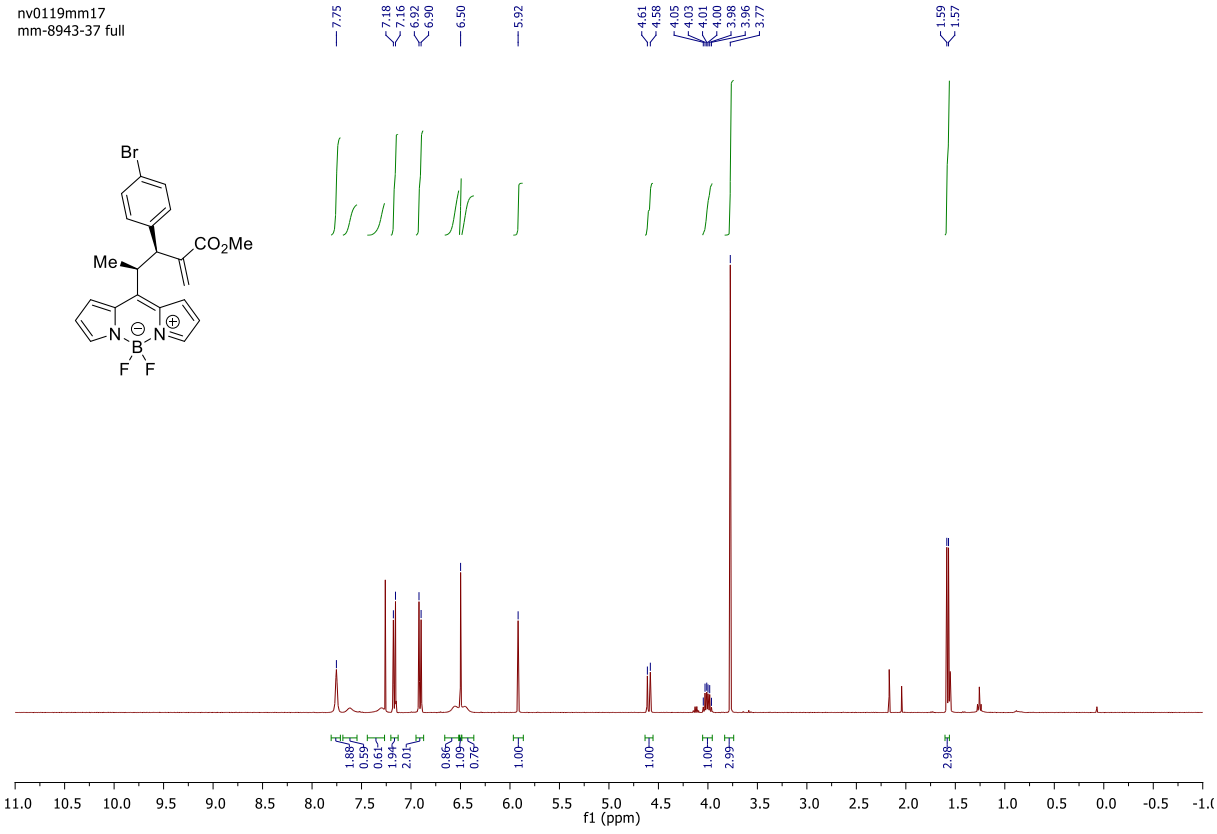
145.52
145.59
145.72
145.79
145.87
145.95
146.67
146.74
146.81
146.89
146.94
147.00
147.08
147.16
Cl
CO2Me
Me
N
B
F
F
f1 (ppm)

3c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mm-8943-37 full
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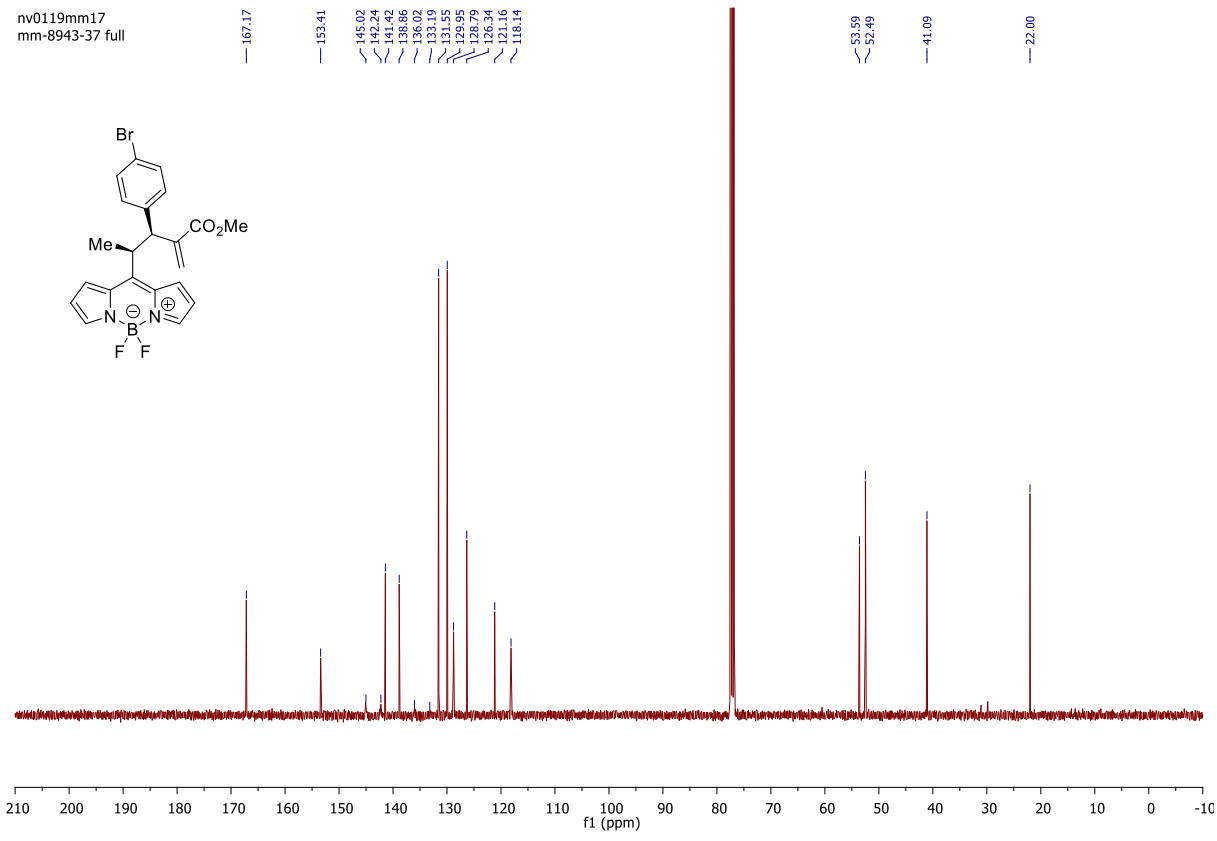
CO2Me
Me
N
B
F
F
f1 (ppm)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mm-8943-37 full
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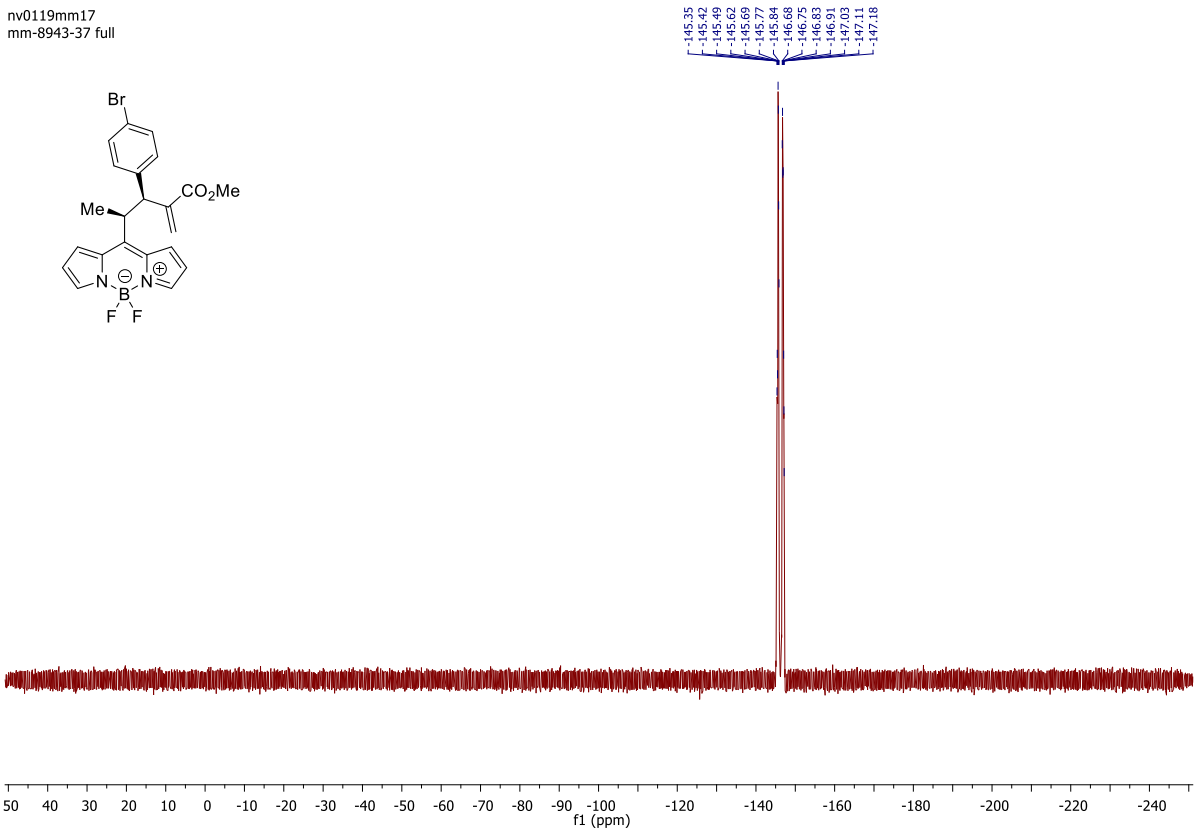
CO2Me
Me
N
B
F
F
f1 (ppm)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-146.68
-146.75
-146.83
-146.91
-147.03
-147.11
-147.18
Br
CO2Me
Me
N
B
N
F
F
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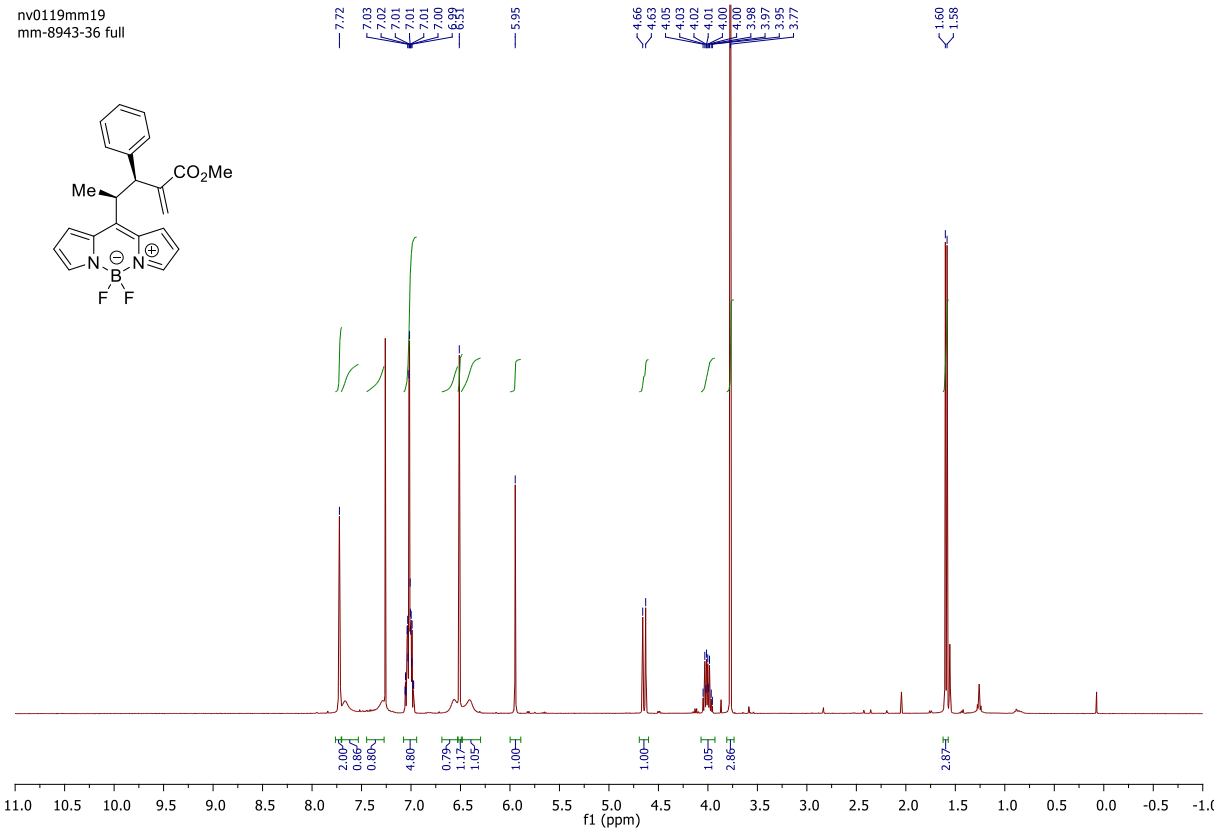
f1 (ppm)

3d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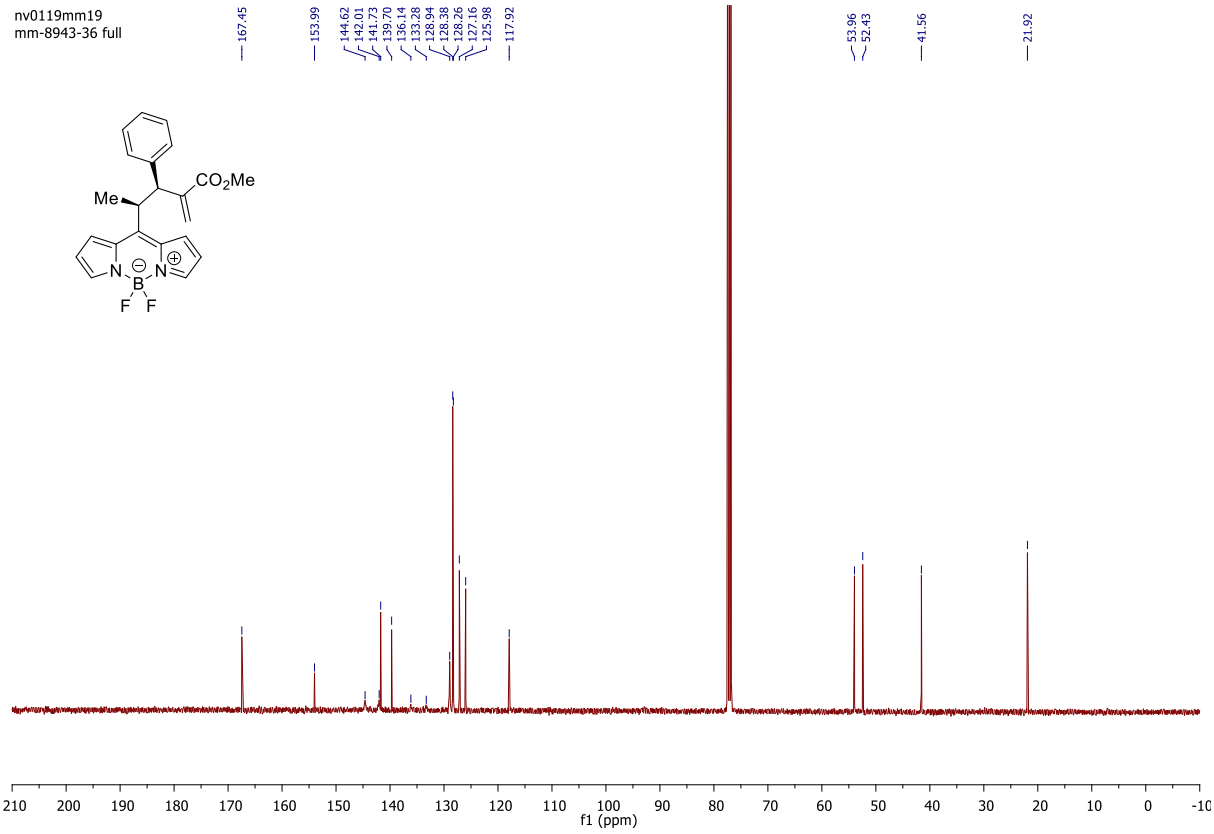
7.03
7.02
7.01
7.01
7.01
7.00
6.99
6.51
5.95
4.66
4.63
4.05
4.03
4.02
4.01
4.00
4.00
3.98
3.97
3.95
3.77
1.60
1.58
CO2Me
Me
N
B
N
F
F
2.00
0.86
0.80
4.80
0.79
1.17
1.05
1.00
1.00
1.05
2.86
2.87
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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141.73
139.70
136.14
133.28
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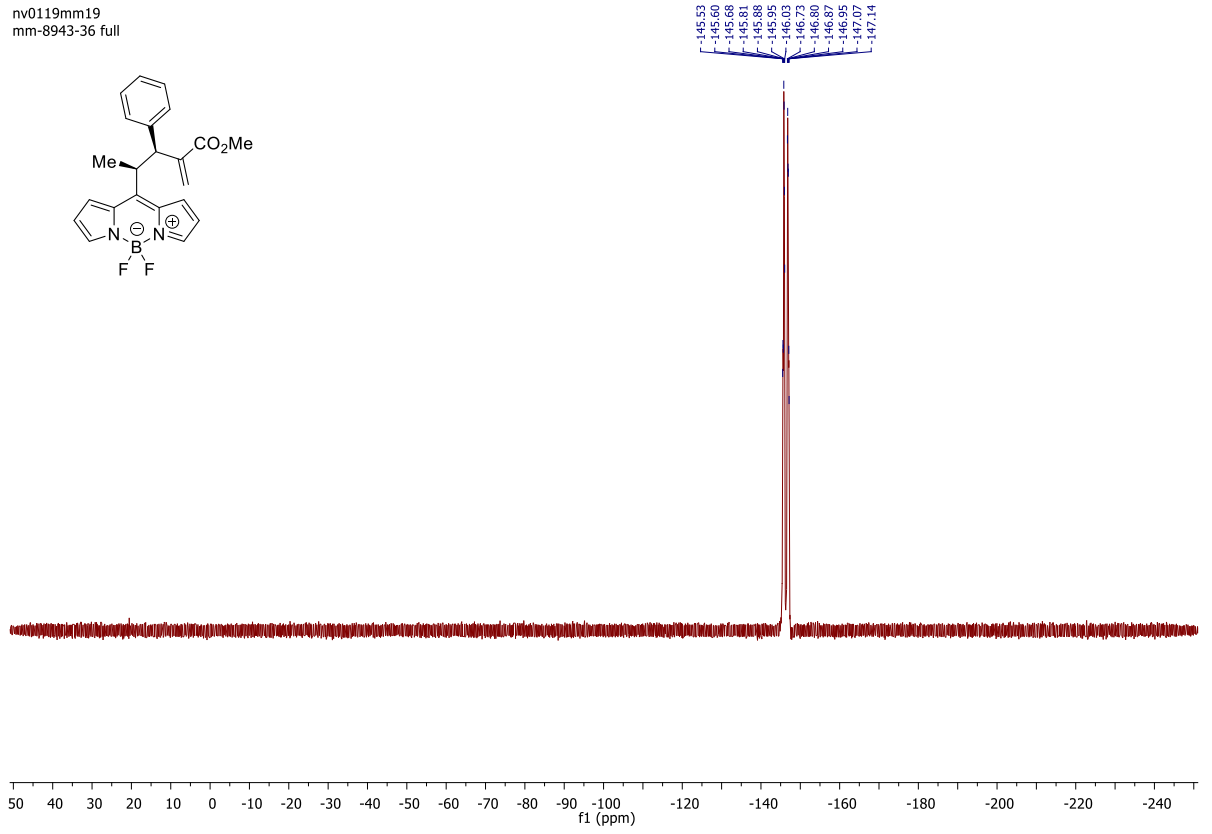
128.38
128.26
127.16
125.98
117.92
53.96
52.43
41.56
21.92
CO2Me
Me
N
B
N
F
F
f1 (ppm)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146.03
146.73
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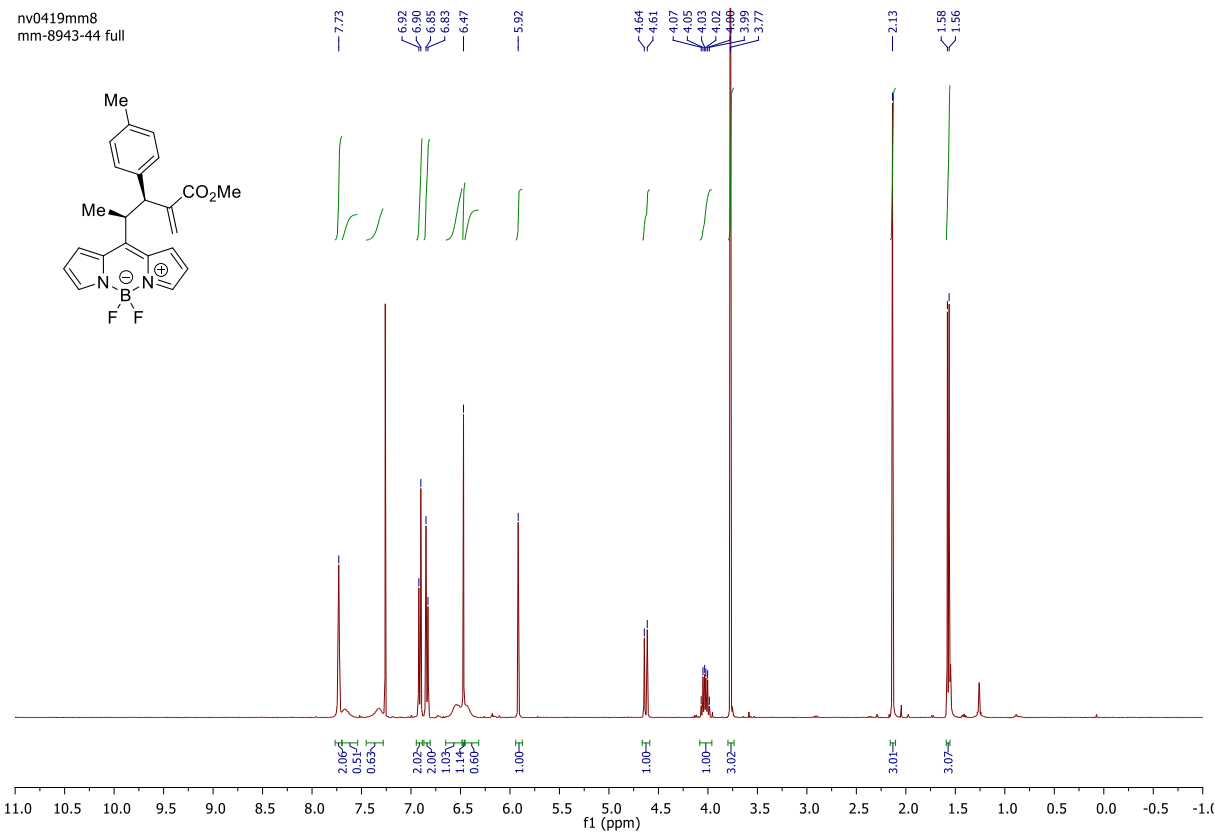
146.95
147.07
147.14
CO2Me
Me
N
B
N
F
F
f1 (ppm)

3e


nv0419mm8
mm-8943-44 full
Me
CO2Me
Me
N
B
N
F F
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6.92
6.90
6.85
6.83
6.47
5.92
4.64
4.61
4.07
4.05
4.03
4.02
4.00
3.99
3.77
2.13
1.58
1.56
2.06
0.51
0.63
2.02
2.00
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1.14
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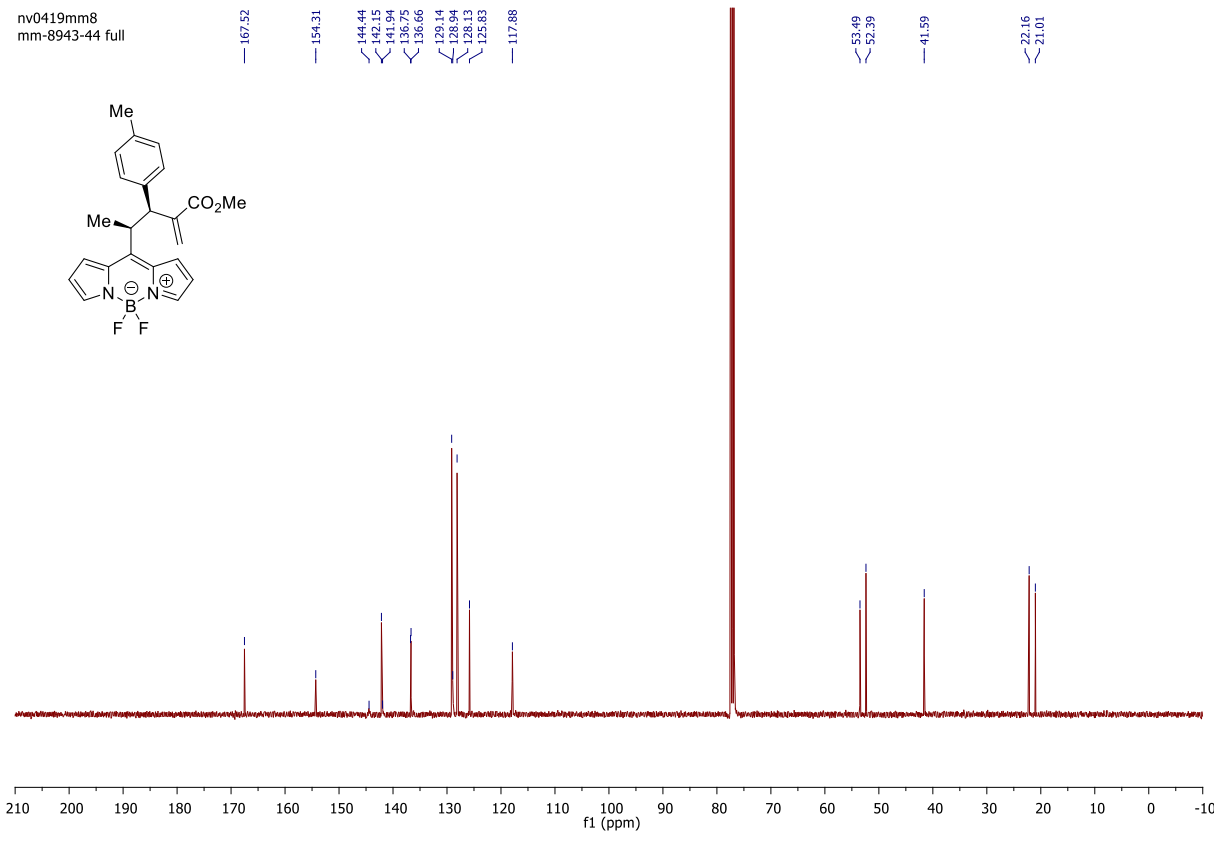
1.00
1.00
1.00
3.02
3.01
3.07
f1 (ppm)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CO2Me
Me
N
B
N
F F
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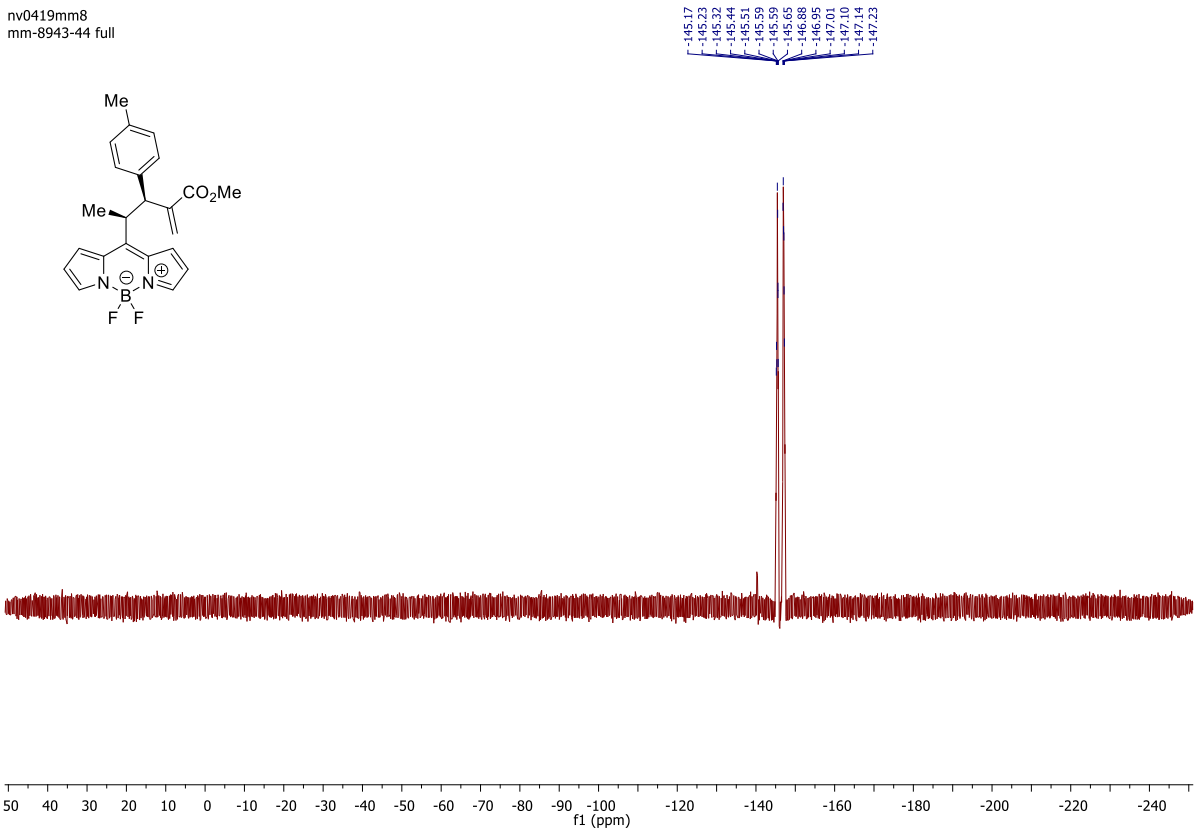
144.44
142.15
141.94
136.75
136.66
129.14
128.94
128.13
125.83
117.88
53.49
52.39
41.59
22.16
21.01
f1 (ppm)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-146.88
-146.95
-147.01
-147.10
-147.14
-147.23
Me
CO2Me
Me
N
B
N
F
F
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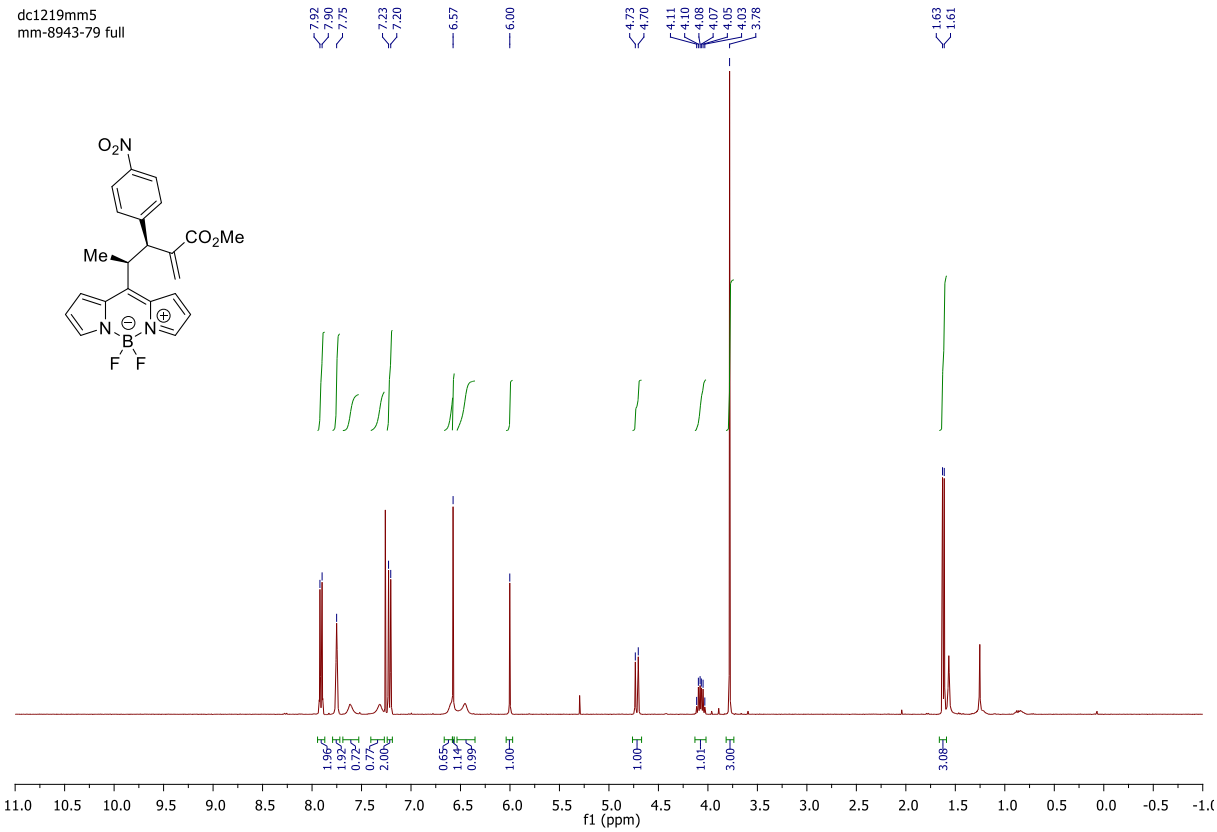
f1 (ppm)

3f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6.00
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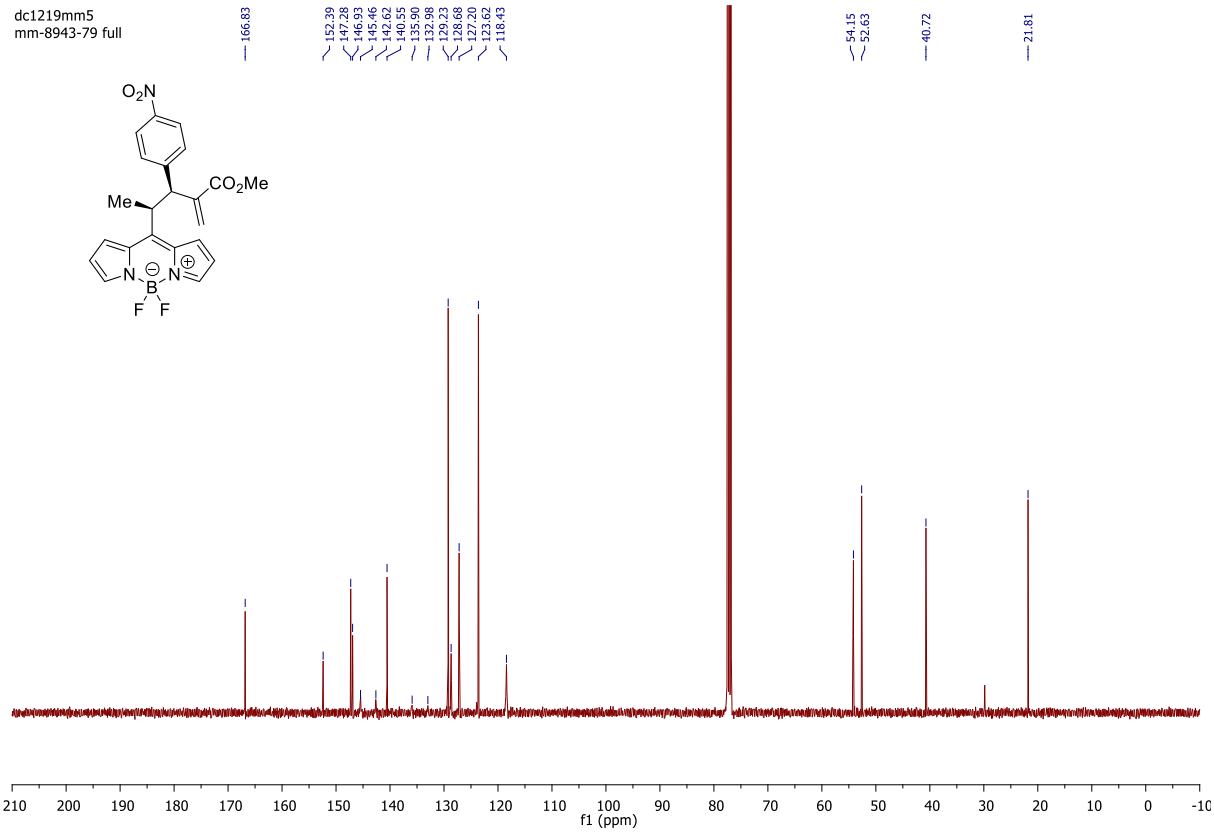
4.05
4.03
3.78
1.63
1.61
O2N
CO2Me
Me
N
B
N
F
F
1.96
1.92
0.72
0.77
2.00
0.65
1.14
0.99
1.00
1.00
1.01
3.00
3.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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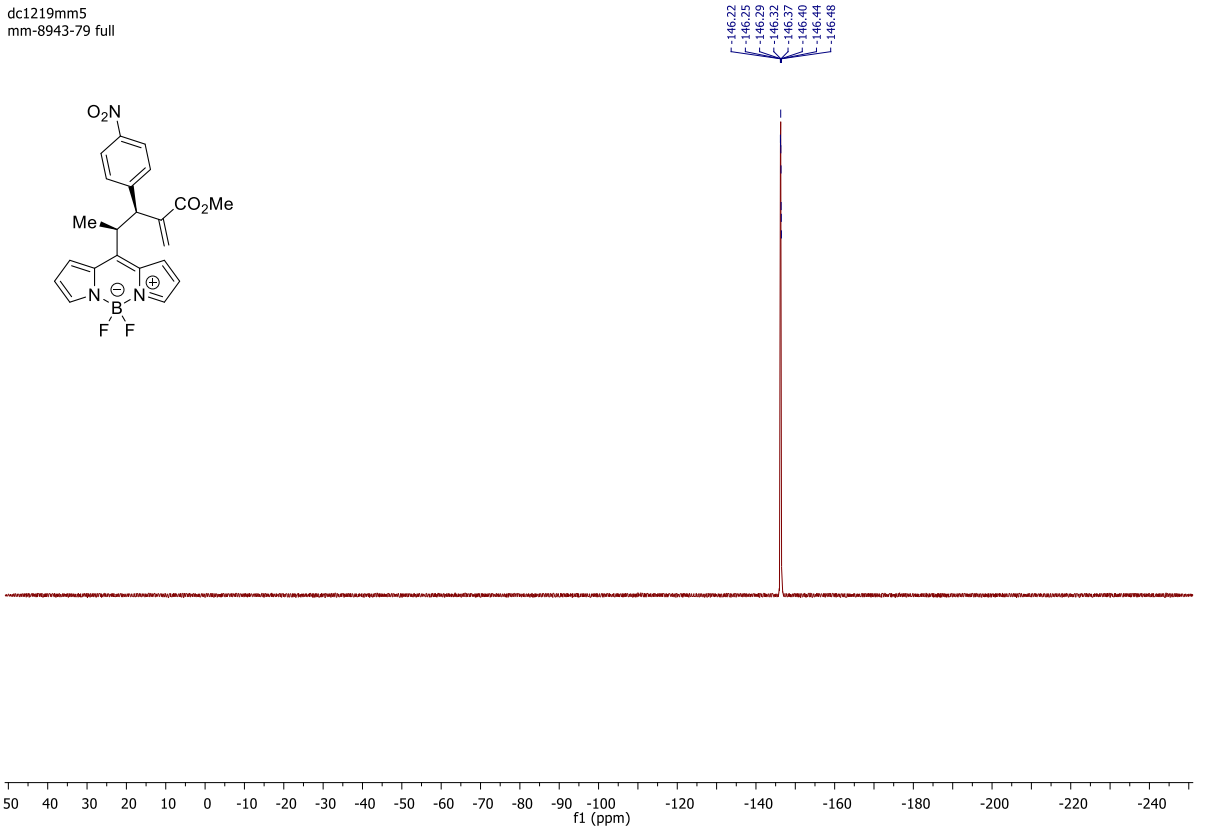
140.55
135.90
132.98
129.23
128.68
127.20
123.62
118.43
54.15
52.63
40.72
21.81
O2N
CO2Me
Me
N
B
F F
f1 (ppm)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-146.48
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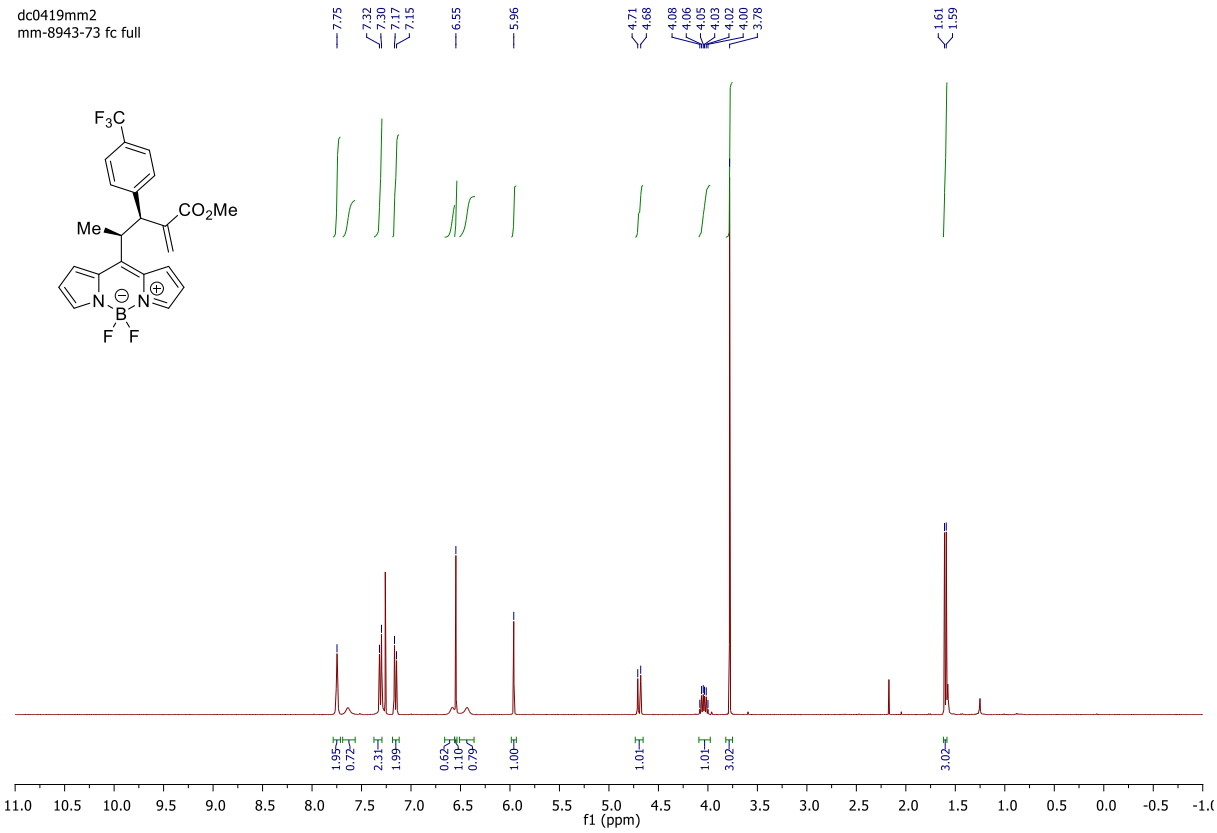
CO2Me
Me
N
B
F F
f1 (ppm)

3g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mm-8943-73 fc full
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7.32
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7.15
6.55
5.96
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1.61
1.59
F3C
CO2Me
Me
N
B
N
F
F
1.95
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2.31
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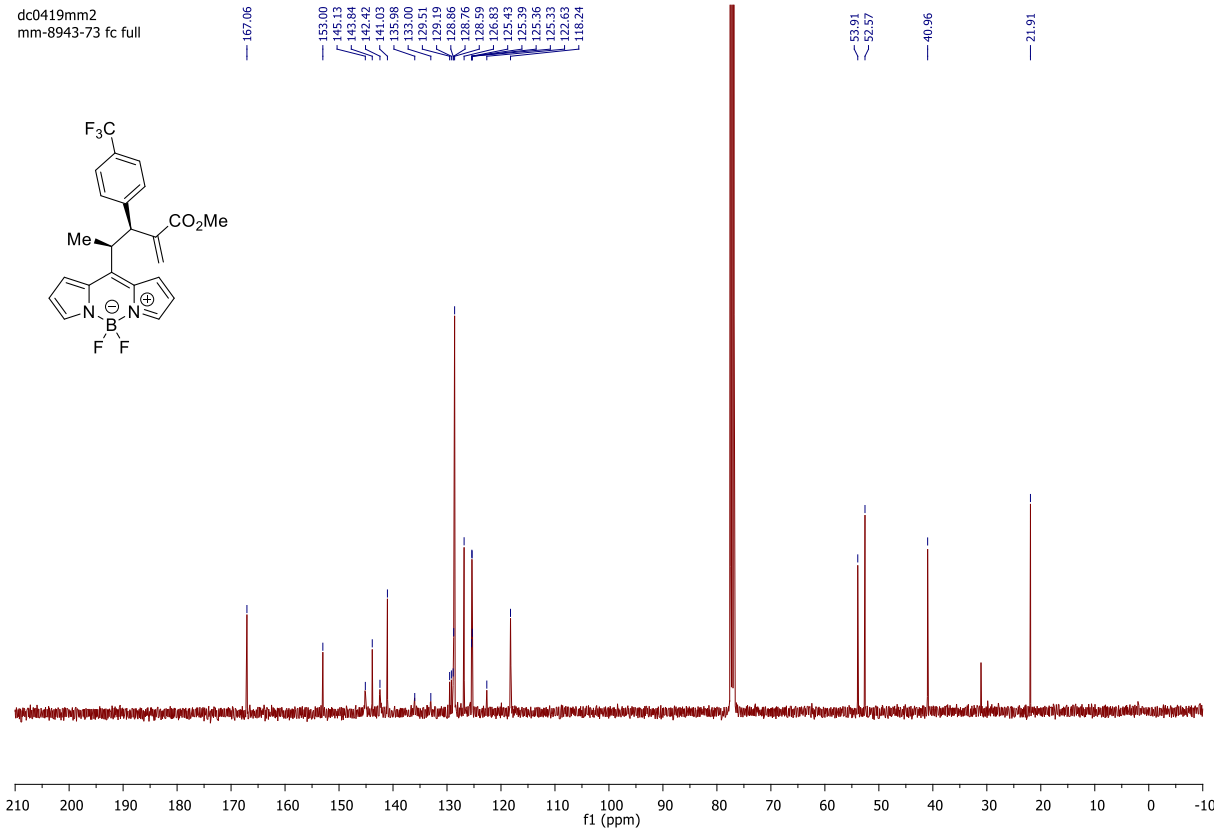
0.62
1.10
0.79
1.00
1.01
1.01
3.02
3.02
f1 (ppm)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133.00
129.51
129.19
128.86
128.76
128.59
126.83
125.43
125.39
125.36
125.33
122.63
118.24
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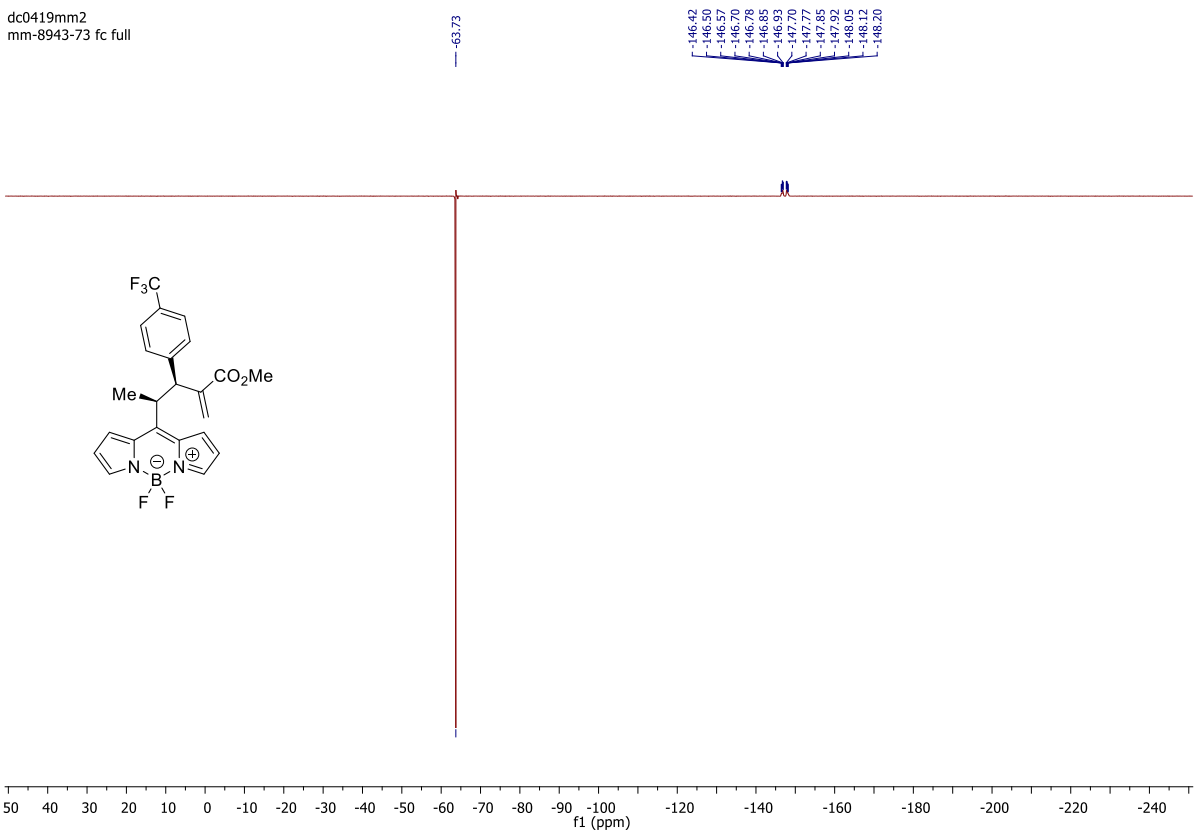
52.57
40.96
21.91
F3C
CO2Me
Me
N
B
N
F
F
f1 (ppm)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-147.77
-147.85
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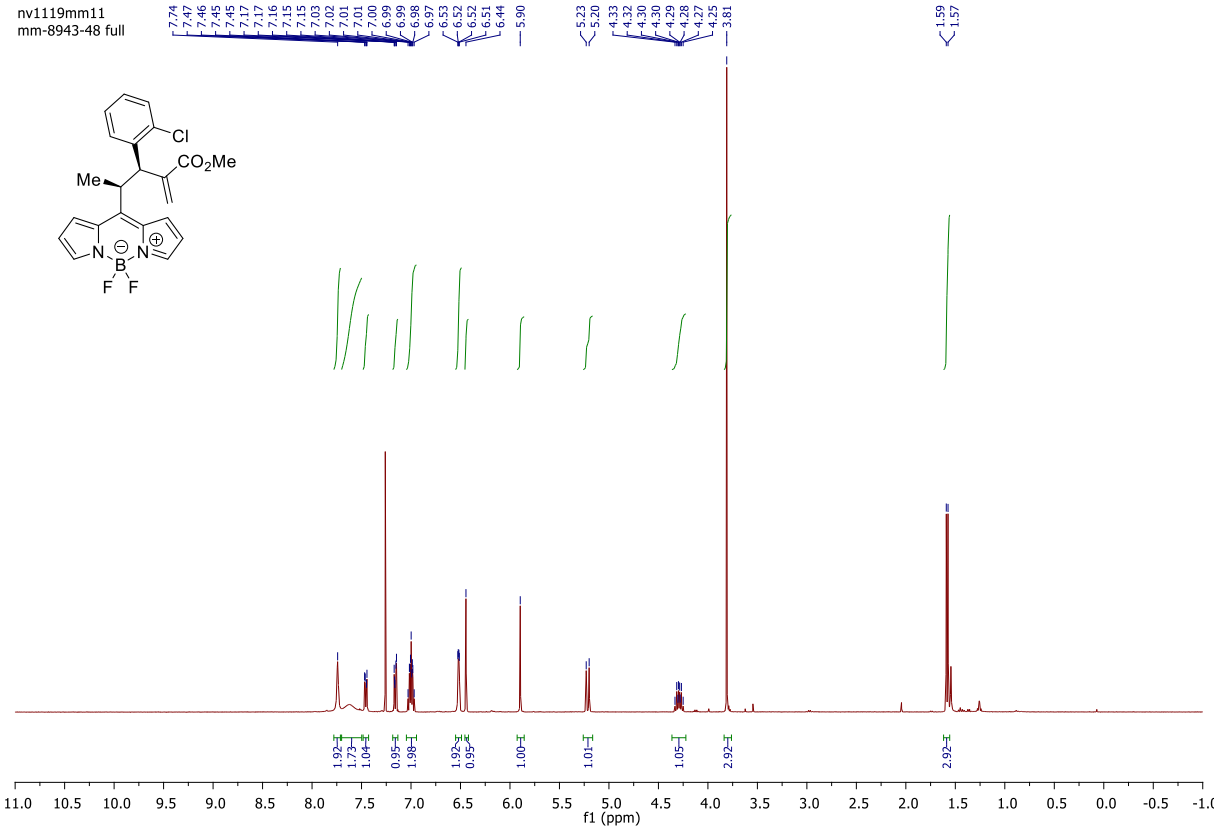
-148.20
F3C
CO2Me
Me
N
B
N
F
F
f1 (ppm)

3h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7.00
6.99
6.99
6.98
6.97
6.53
6.52
6.52
6.51
6.44
5.90
5.23
5.20
4.33
4.32
4.30
4.30
4.29
4.28
4.27
4.25
3.81
1.59
1.57
Cl
CO2Me
Me
N
B
N
F
F
1.92
1.73
1.04
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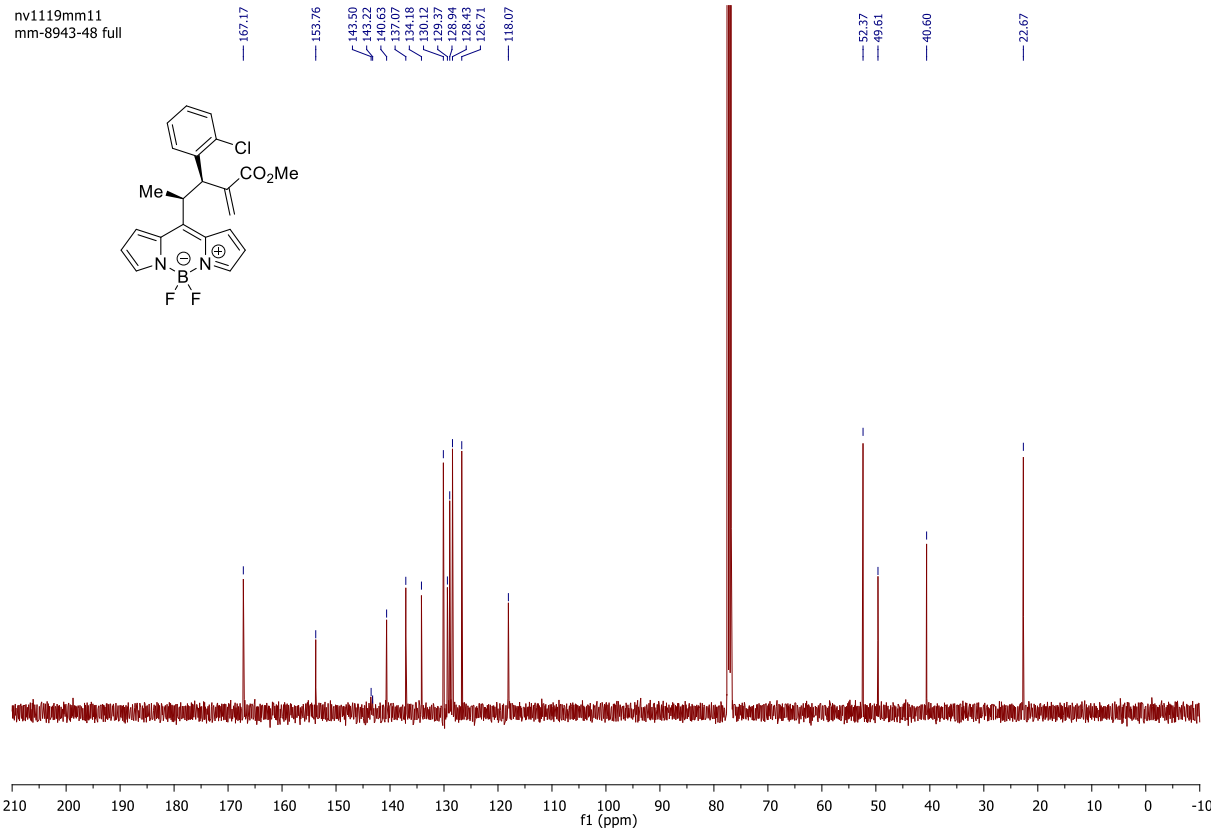
1.98
1.92
0.95
1.00
1.01
1.05
2.92
2.92
f1 (ppm)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140.63
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134.18
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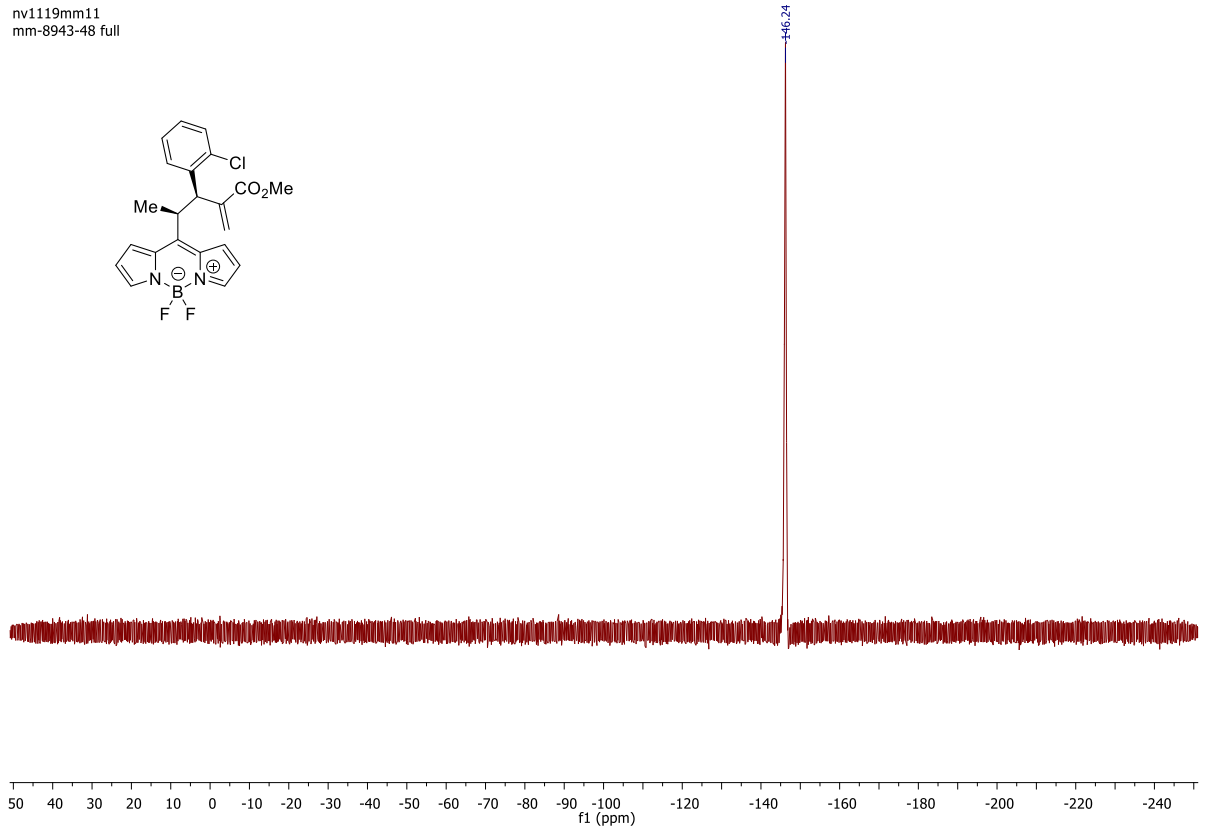
128.94
128.43
126.71
118.07
52.37
49.61
40.60
22.67
Cl
CO2Me
Me
N
B
N
F
F
f1 (ppm)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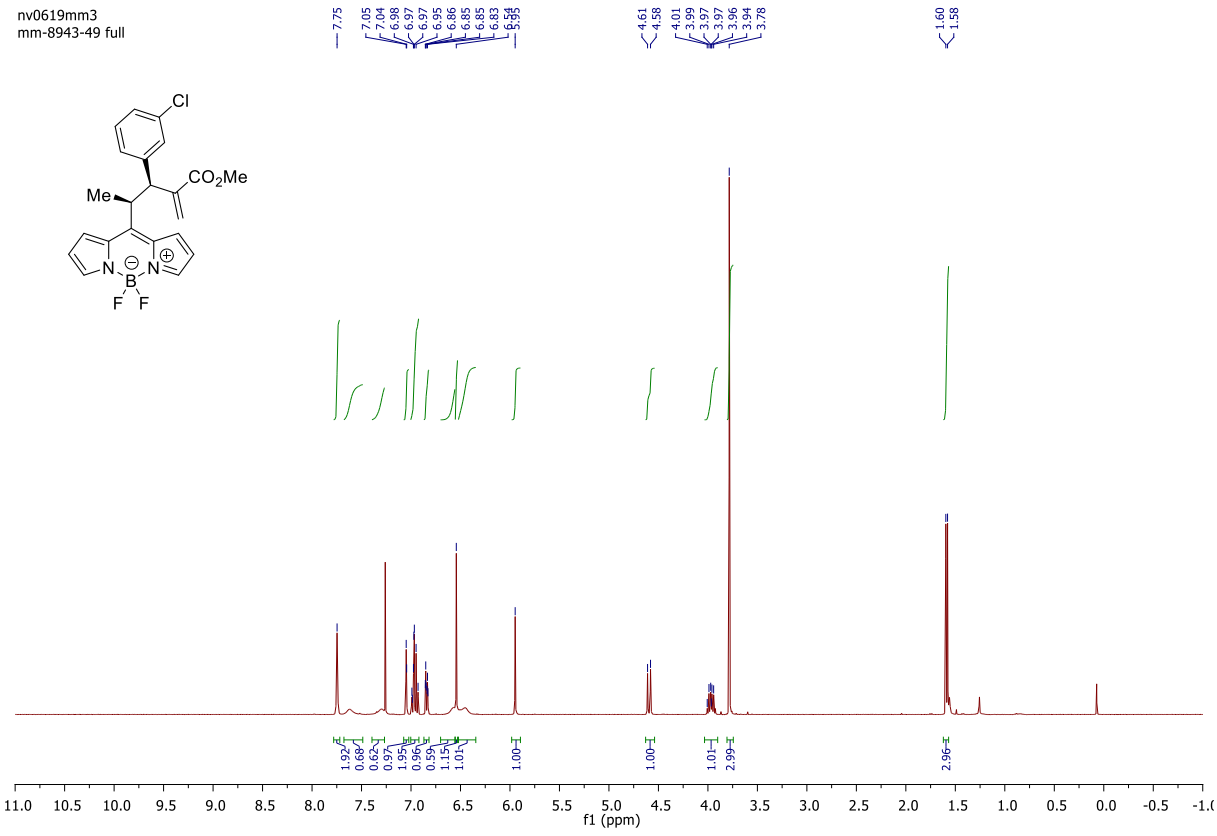
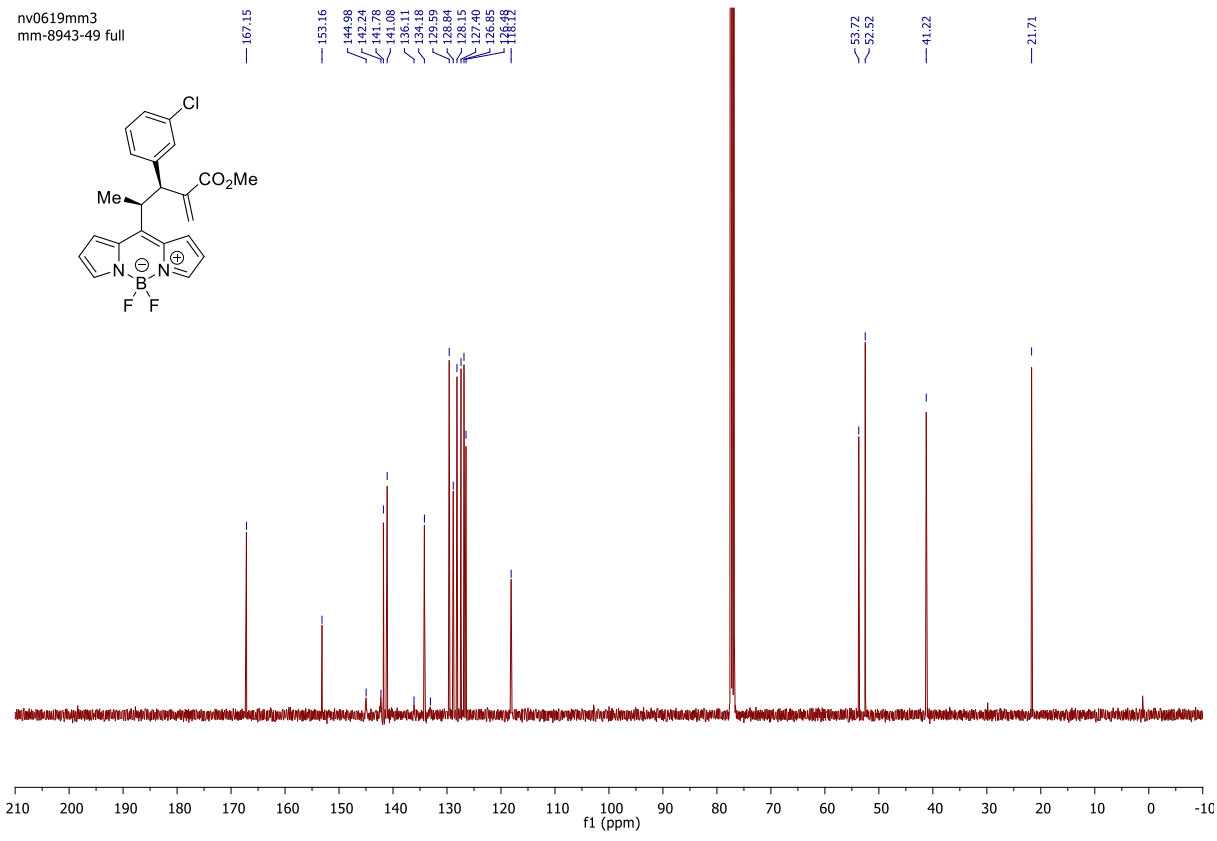
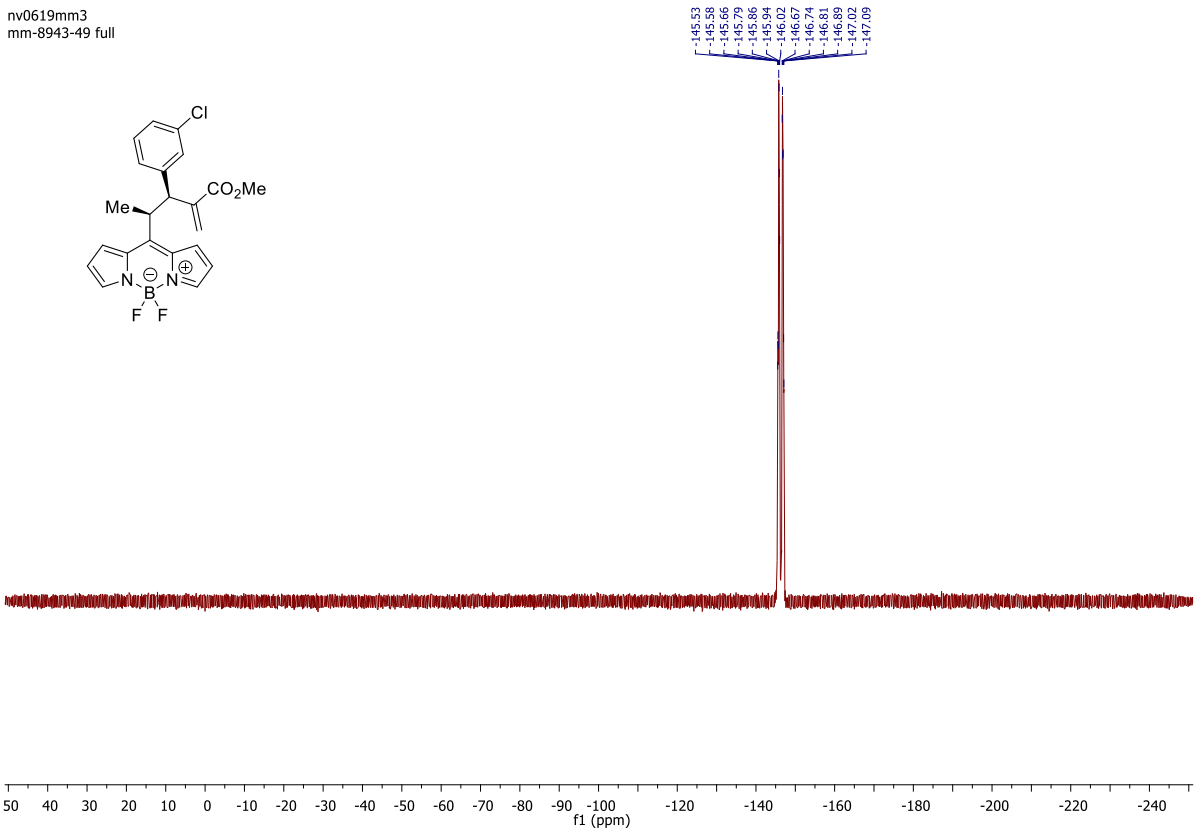
mm-8943-48 full
146.24
Cl
CO2Me
Me
N
B
N
F
F
f1 (ppm)

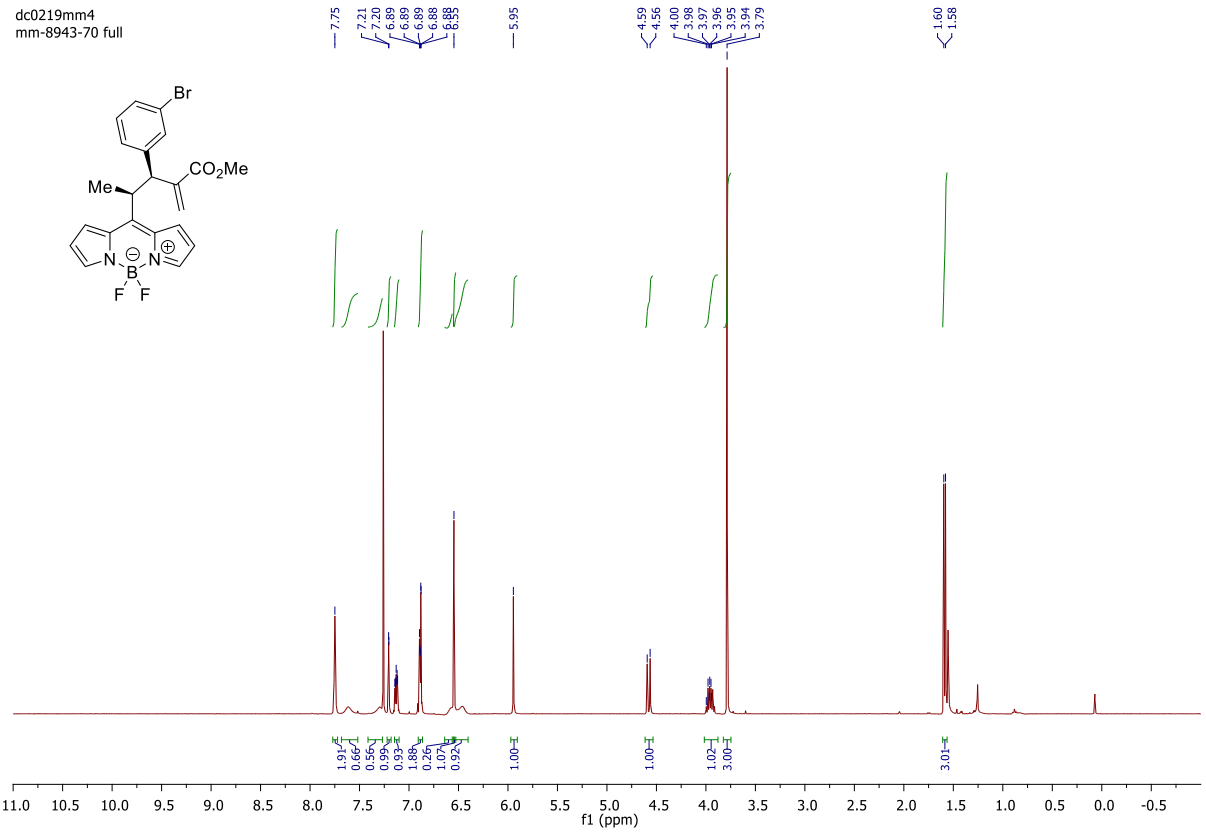
3i

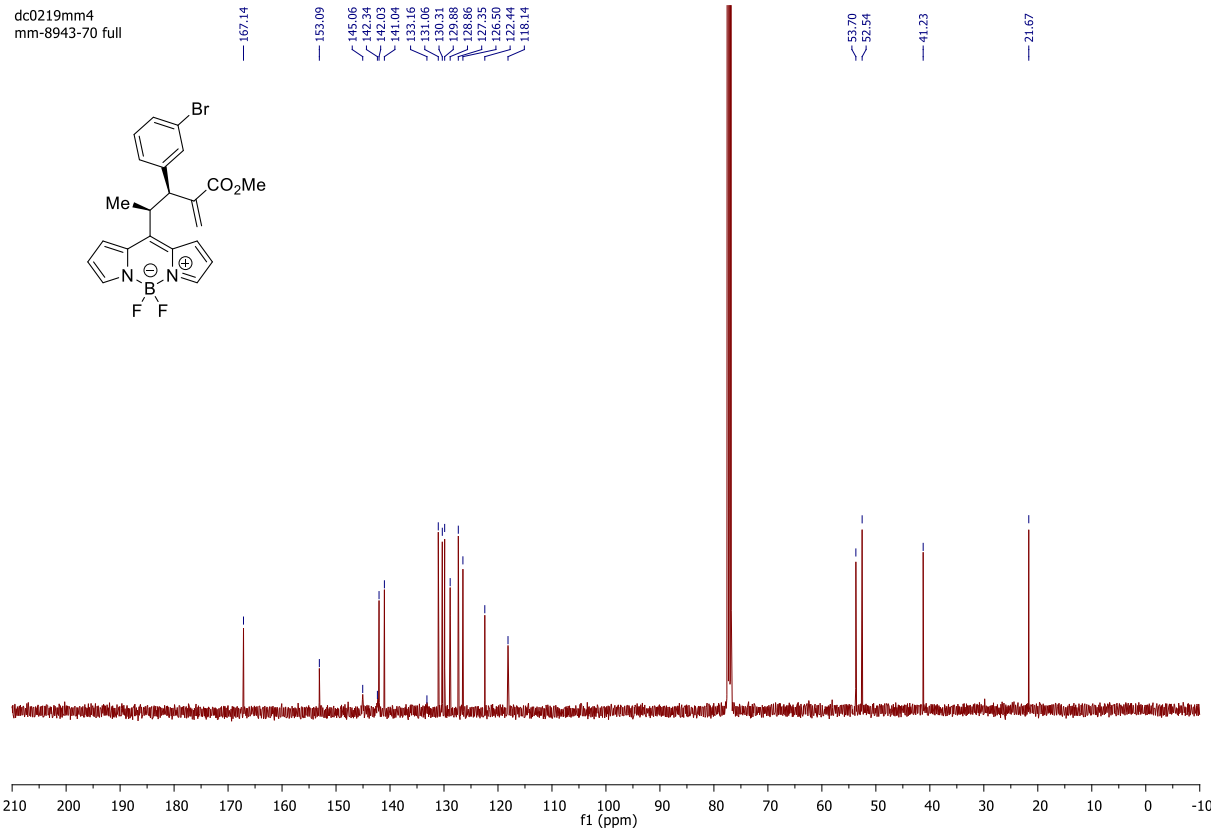

nv0619mm3
mm-8943-49 full
Cl
CO2Me
Me
N
B
N
F
F
f1 (ppm)

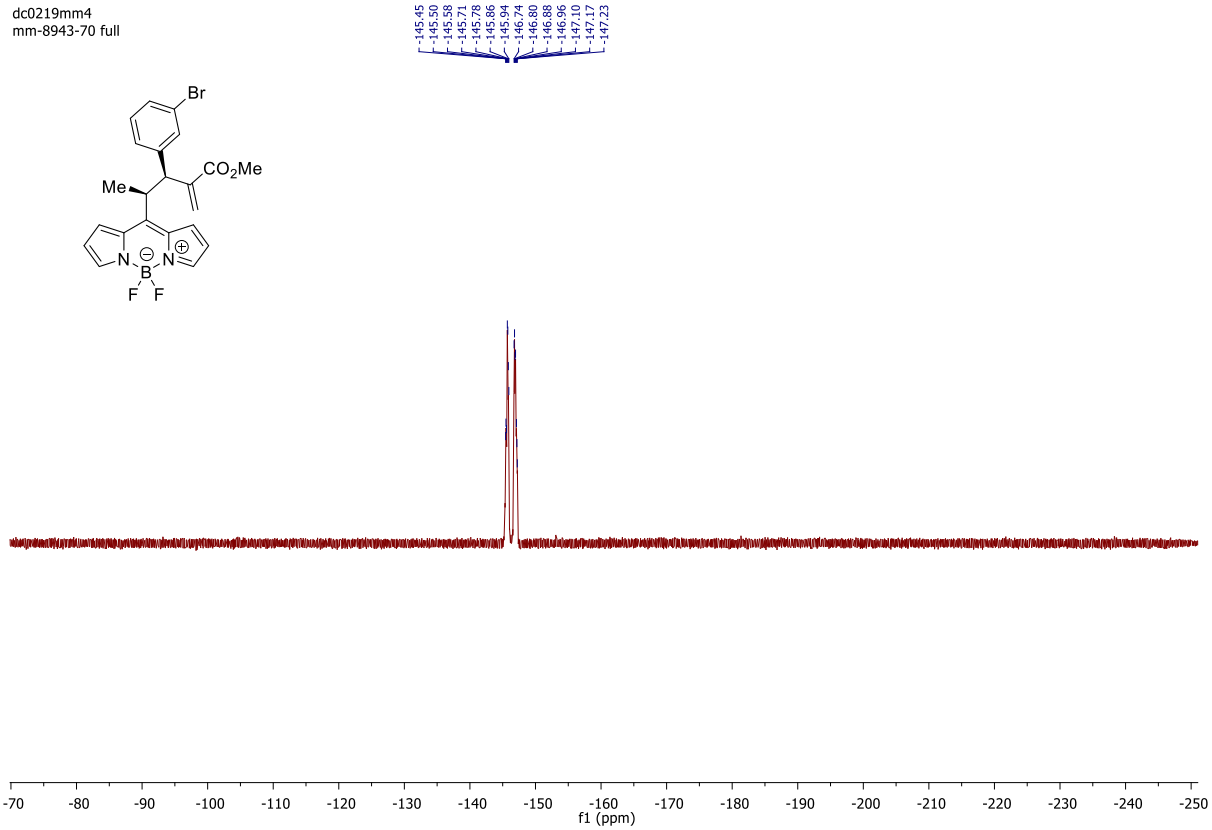

nv0619mm3
mm-8943-49 full
Cl
CO2Me
Me
N
B
N
F
F
f1 (ppm)


nv0619mm3
mm-8943-49 full
-145.53
-145.58
-145.66
-145.79
-145.86
-145.94
-146.02
-146.67
-146.74
-146.81
-146.89
-147.02
-147.09
Cl
CO2Me
Me
N
B
N
F
F
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

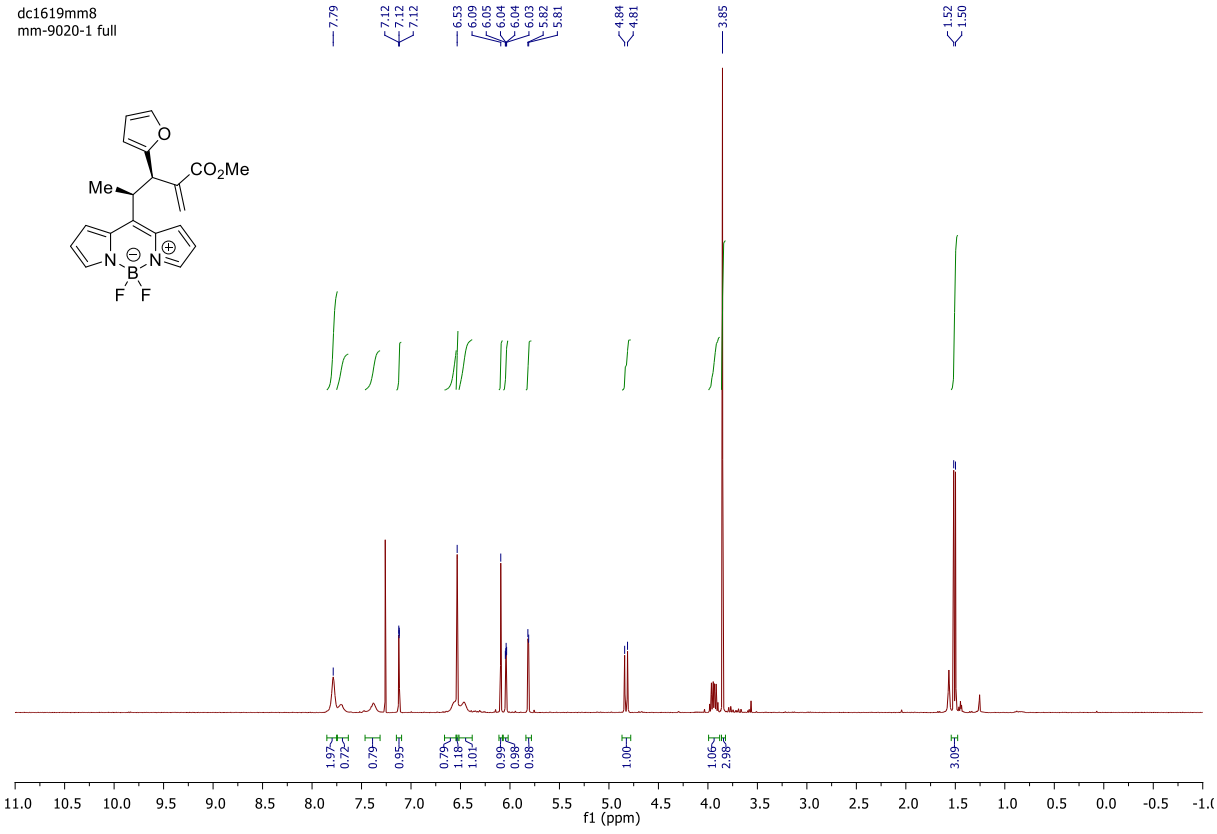
3j

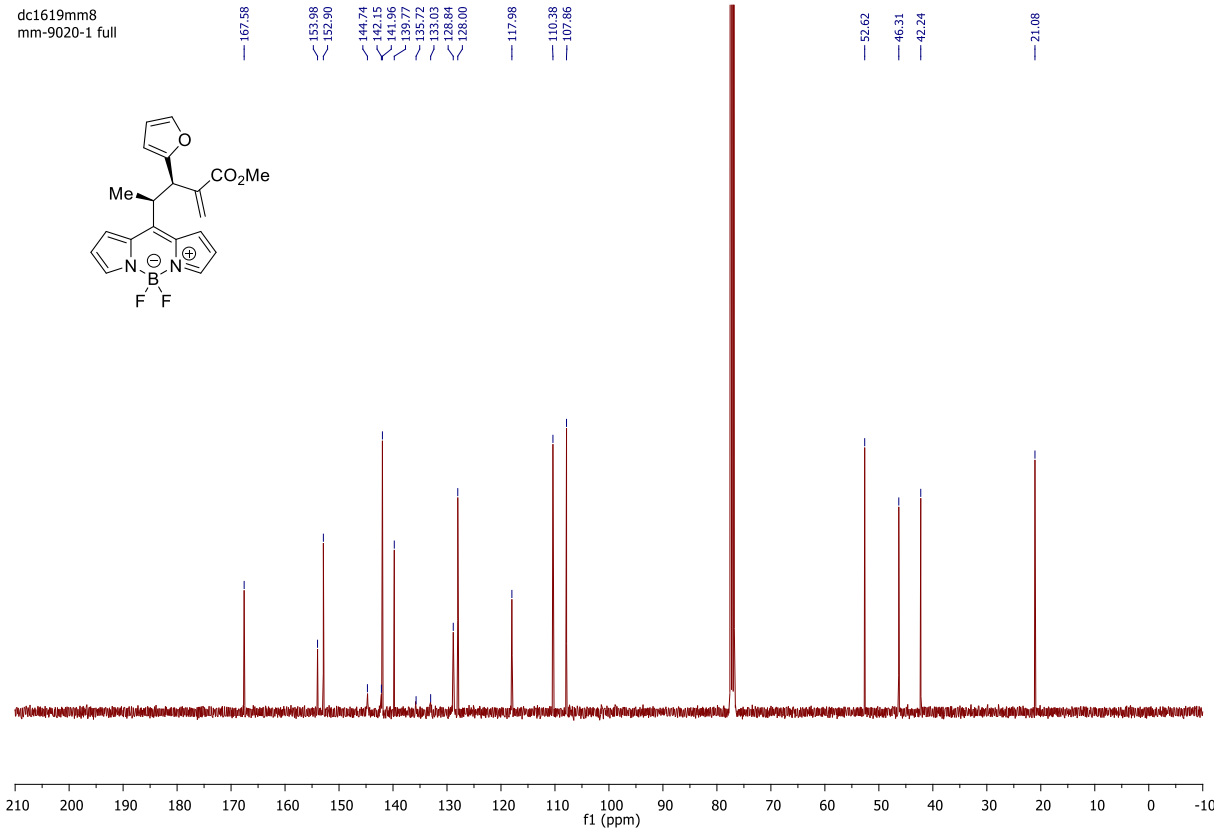

dc0219mm4
mm-8943-70 full
7.75
7.21
7.20
6.89
6.89
6.89
6.88
6.88
6.85
5.95
4.59
4.56
4.00
3.98
3.97
3.96
3.95
3.94
3.79
1.60
1.58
Br
CO2Me
Me
N
B
N
F
F
1.91
0.66
0.56
0.99
0.93
1.88
0.26
1.07
0.92
1.00
1.00
1.02
3.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

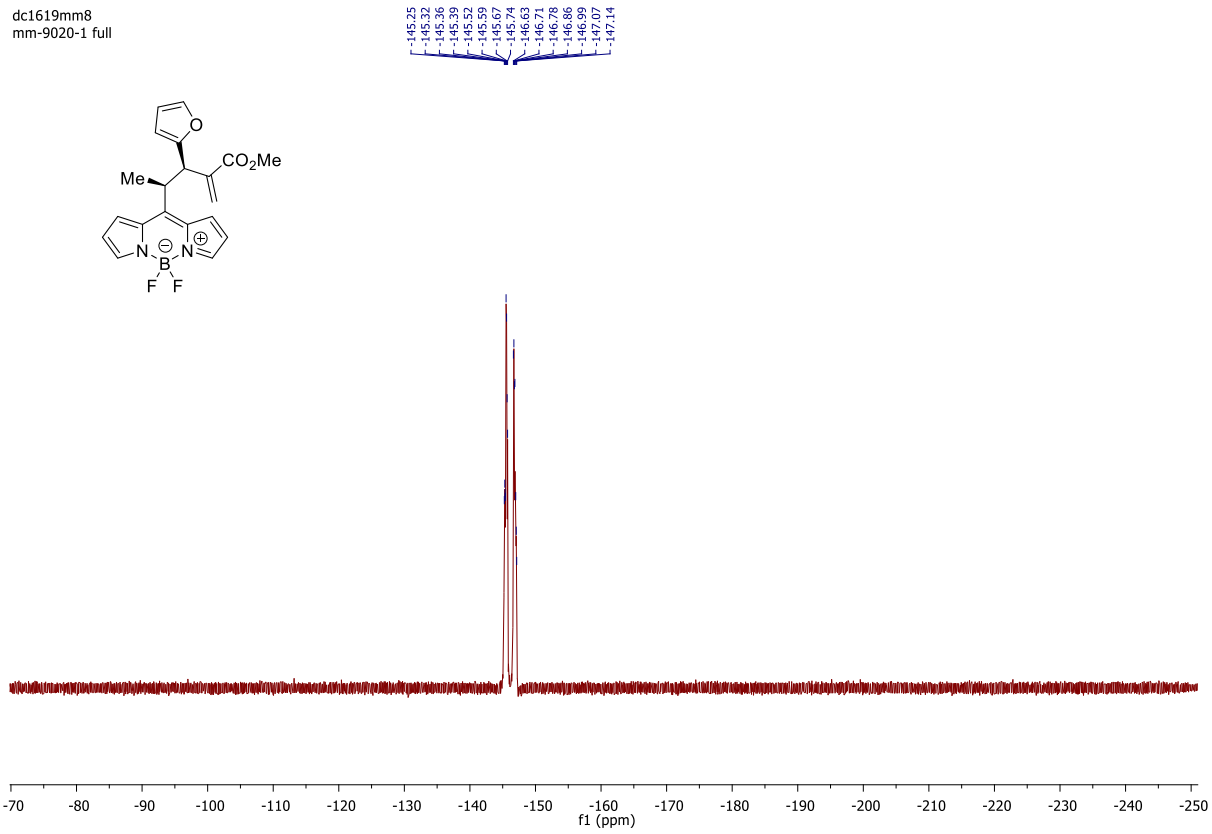

dc0219mm4
mm-8943-70 full
167.14
153.09
145.06
142.34
142.03
141.04
133.16
131.06
130.31
129.88
128.86
127.35
126.50
122.44
118.14
53.70
52.54
41.23
21.67
Br
CO2Me
Me
N
B
F
F
f1 (ppm)


dc0219mm4
mm-8943-70 full
-145.45
-145.50
-145.58
-145.71
-145.78
-145.86
-145.94
-146.74
-146.80
-146.88
-146.96
-147.10
-147.17
-147.23
Br
CO2Me
Me
N
B
F
F
f1 (ppm)

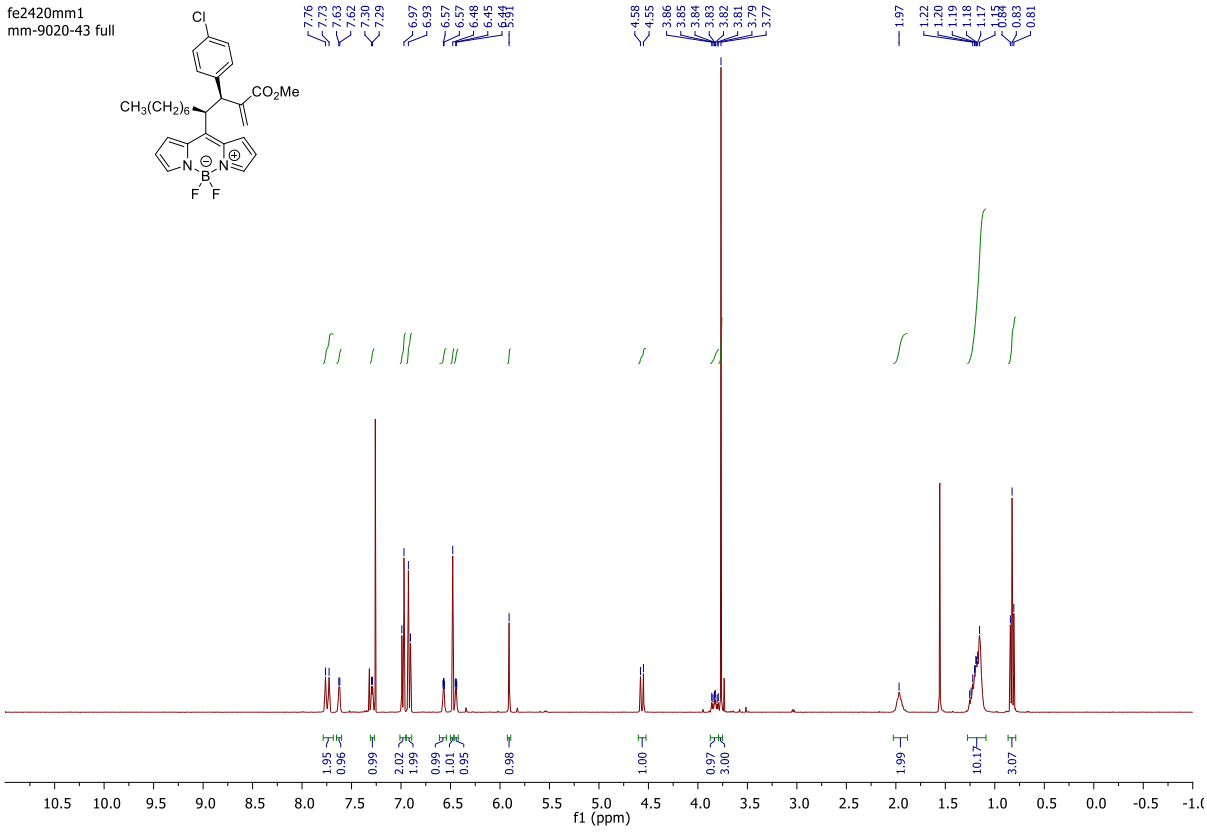
3k

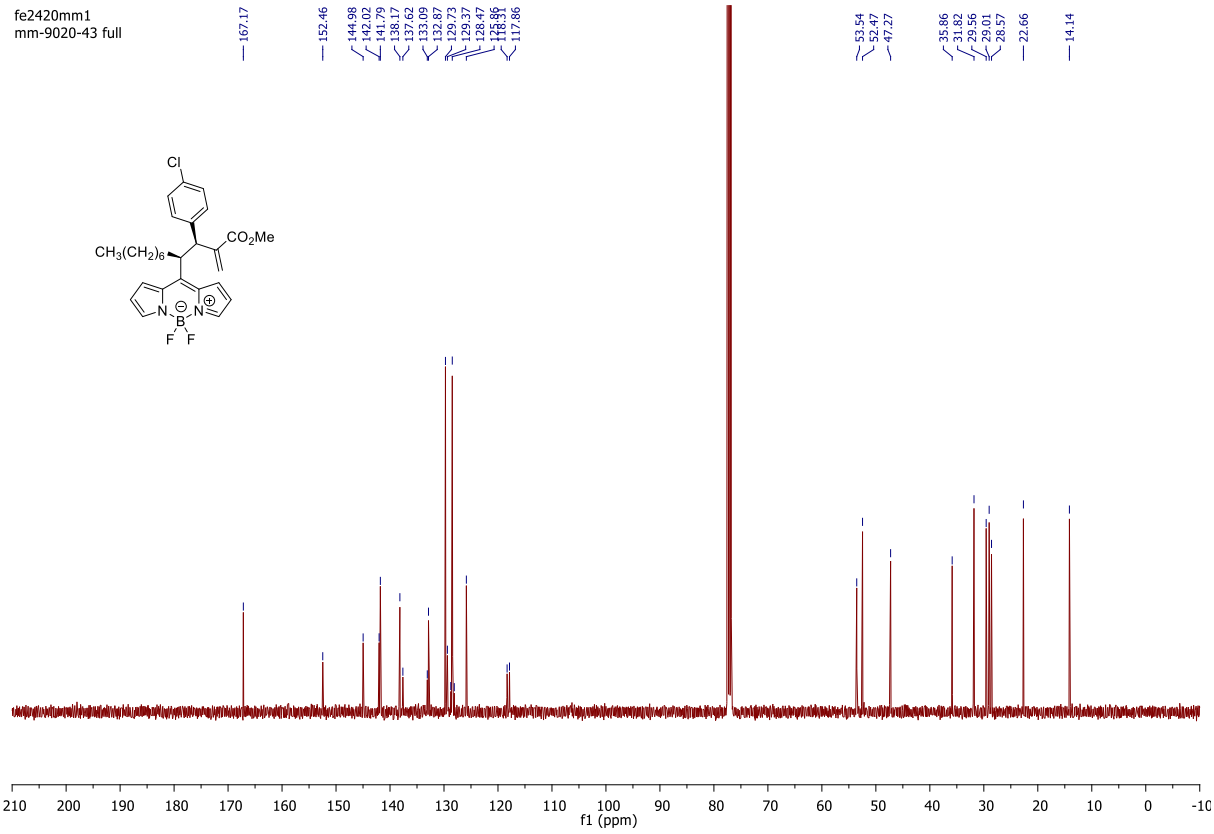

dc1619mm8
mm-9020-1 full
7.79
7.12
7.12
7.12
6.53
6.09
6.05
6.04
6.04
6.03
5.82
5.81
4.84
4.81
3.85
1.52
1.50
O
CO2Me
Me
N
B
N
F F
1.97
0.72
0.79
0.95
0.79
1.18
1.01
0.99
0.98
0.98
1.00
1.06
2.98
3.09
f1 (ppm)

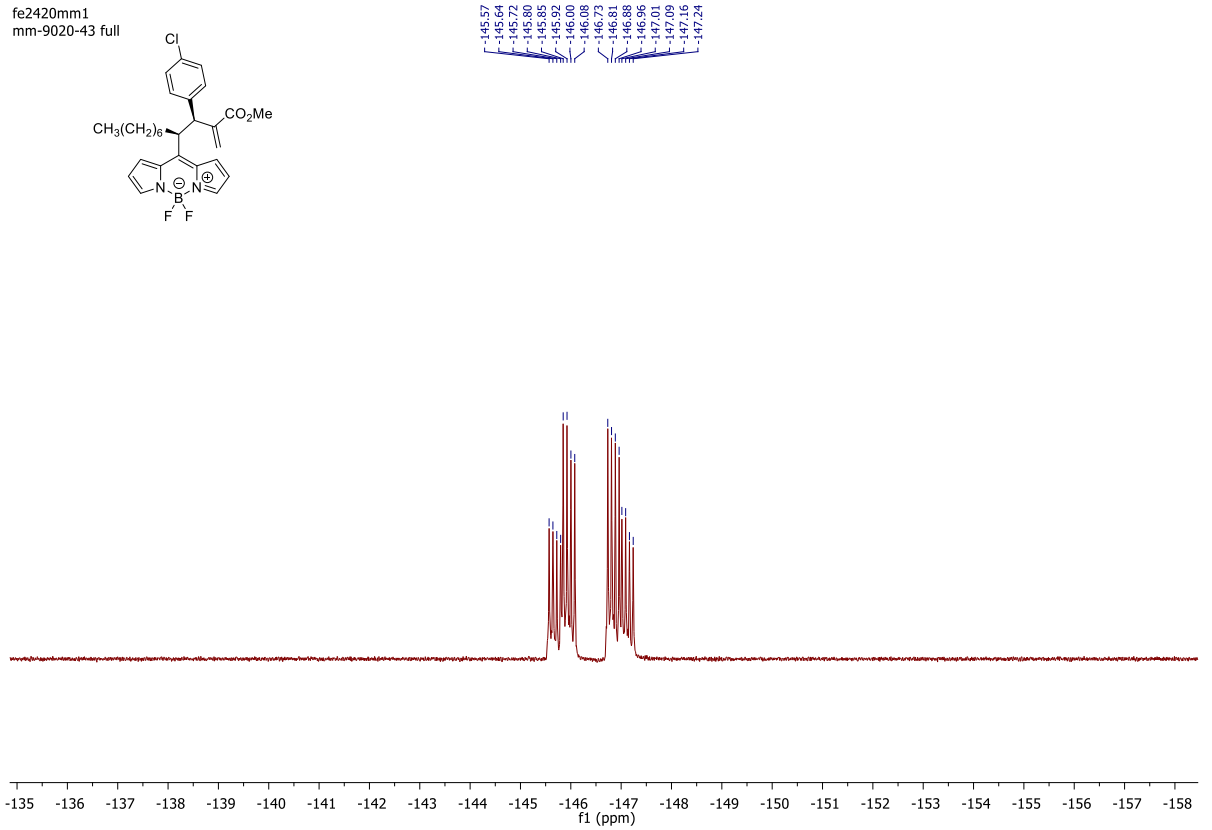

dc1619mm8
mm-9020-1 full
167.58
153.98
152.90
144.74
142.15
141.96
139.77
135.72
133.03
128.84
128.00
117.98
110.38
107.86
52.62
46.31
42.24
21.08
O
CO2Me
Me
N
B
N
F F
f1 (ppm)


dc1619mm8
mm-9020-1 full
-145.25
-145.32
-145.36
-145.39
-145.52
-145.59
-145.67
-145.74
-146.63
-146.71
-146.78
-146.86
-146.99
-147.07
-147.14
Me
CO2Me
O
N
B
F F
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

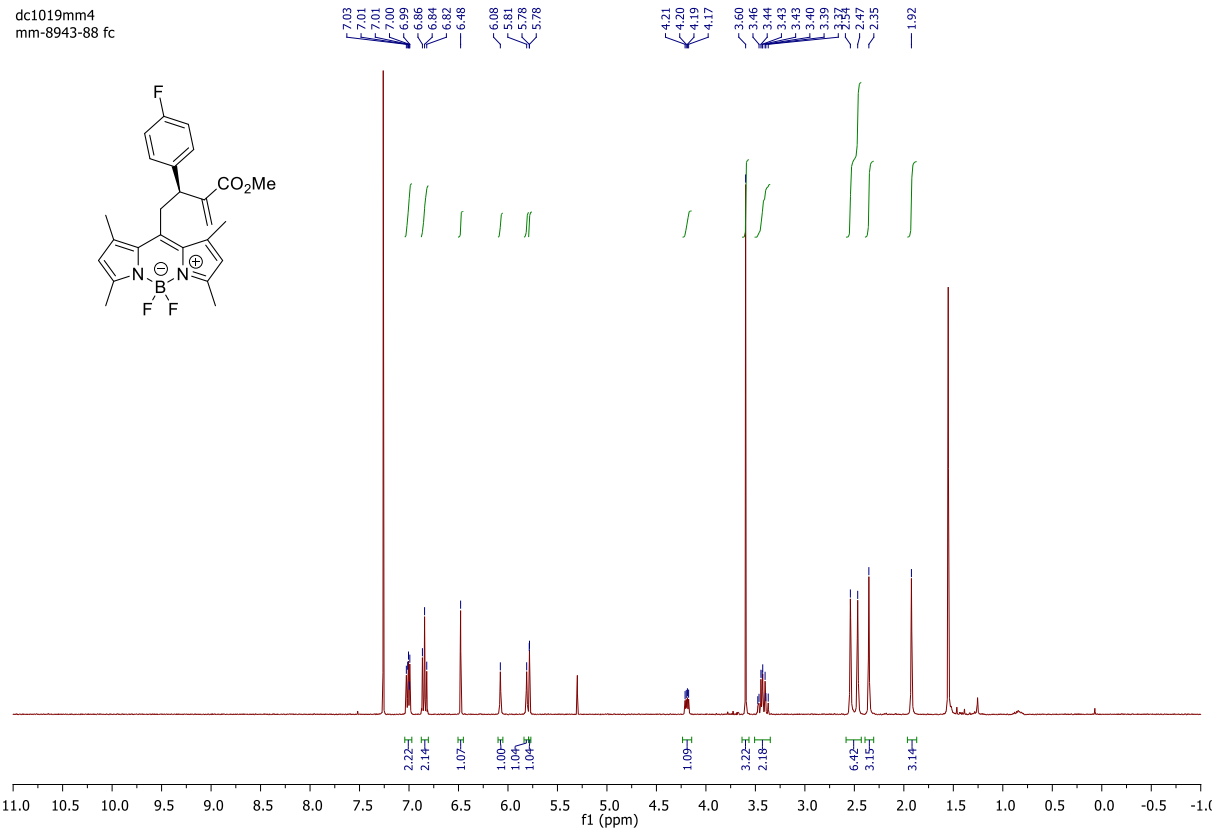
3l

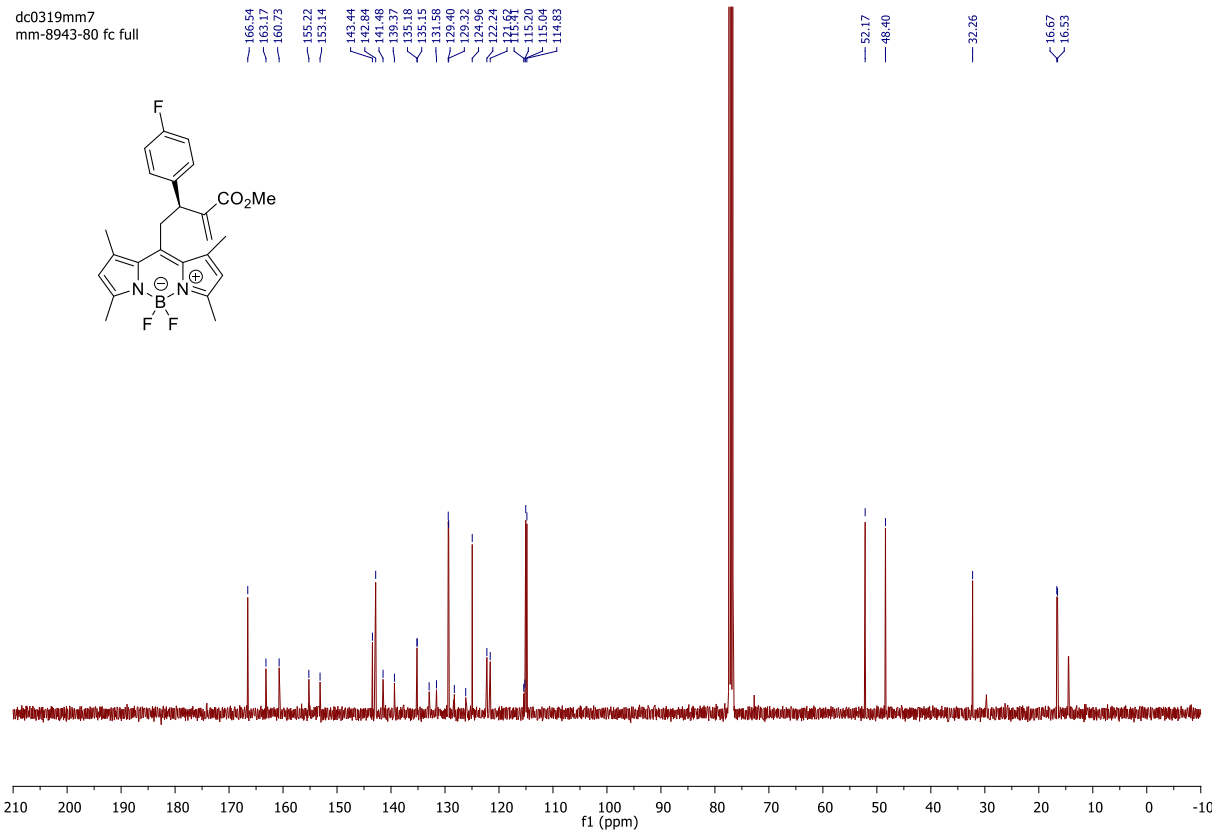

fe2420mm1
mm-9020-43 full
Cl
CO2Me
CH3(CH2)6
7.76
7.73
7.63
7.62
7.30
7.29
6.97
6.93
6.57
6.57
6.48
6.45
6.44
5.91
4.58
4.55
3.86
3.85
3.84
3.83
3.82
3.81
3.79
3.77
1.97
1.22
1.20
1.19
1.18
1.17
0.84
0.83
0.81
1.95
0.96
0.99
2.02
1.99
0.99
1.01
0.95
0.98
1.00
0.97
3.00
1.99
10.17
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

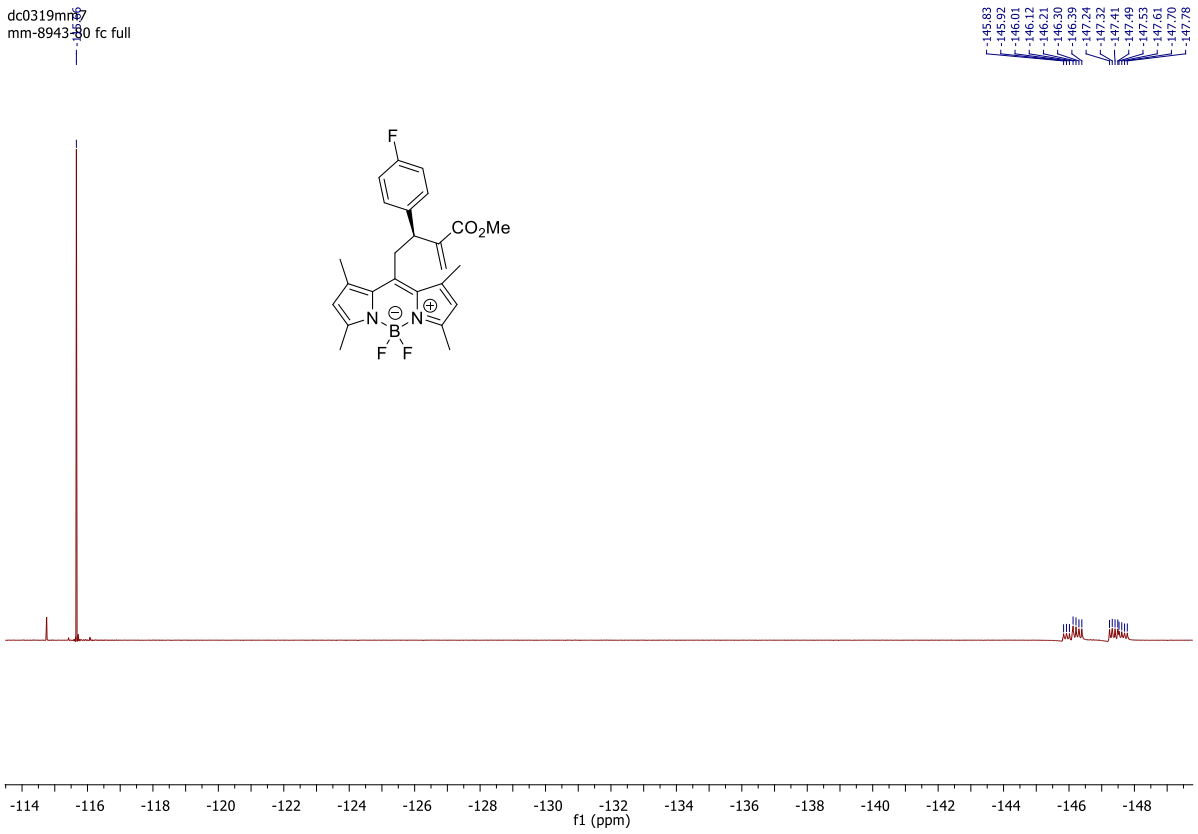

fe2420mm1
mm-9020-43 full
167.17
152.46
144.98
142.02
141.79
138.17
137.62
133.09
132.87
129.73
129.37
128.47
125.86
118.31
117.86
53.54
52.47
47.27
35.86
31.82
29.56
29.01
28.57
22.66
14.14
Cl
CO2Me
CH3(CH2)6
N
B
F F
f1 (ppm)


fe2420mm1
mm-9020-43 full
-145.57
-145.64
-145.72
-145.80
-145.85
-145.92
-146.00
-146.08
-146.73
-146.81
-146.88
-146.96
-147.01
-147.09
-147.16
-147.24
Cl
CO2Me
CH3(CH2)6
N
B
F F
f1 (ppm)

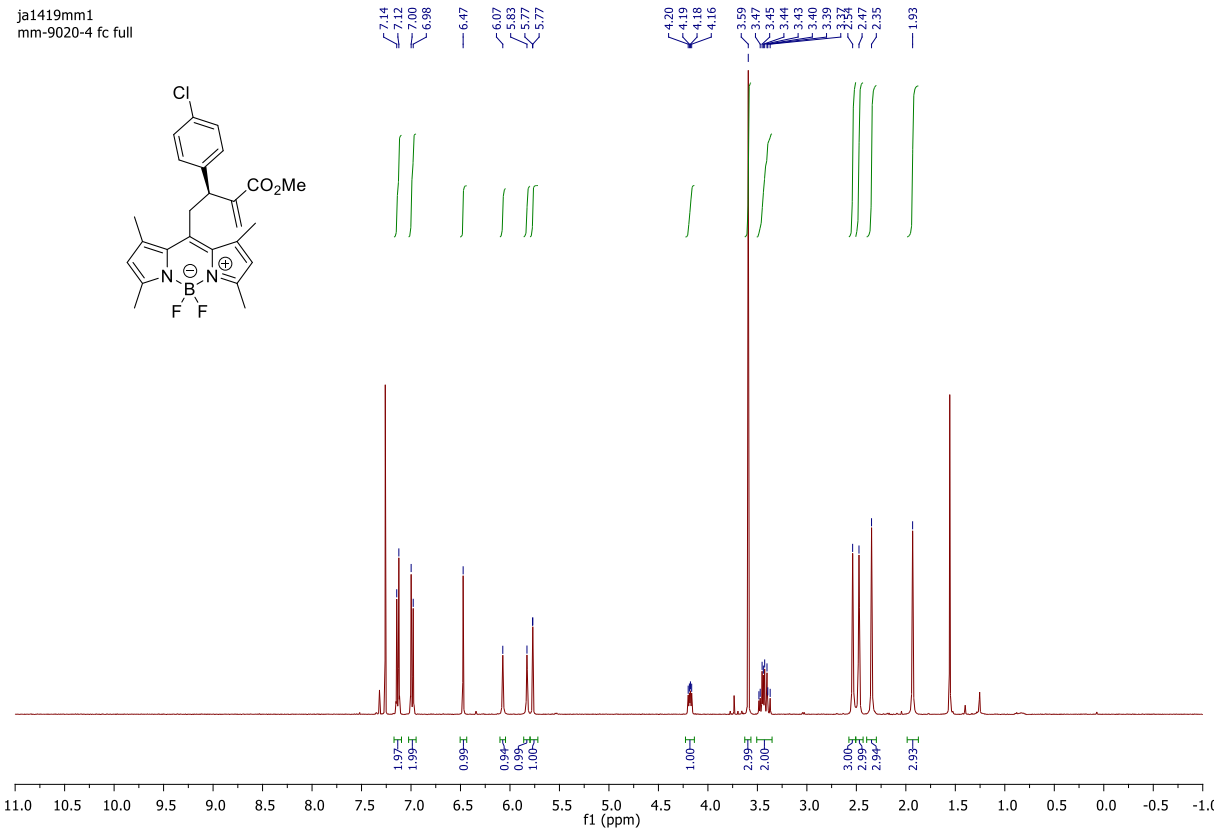
3m

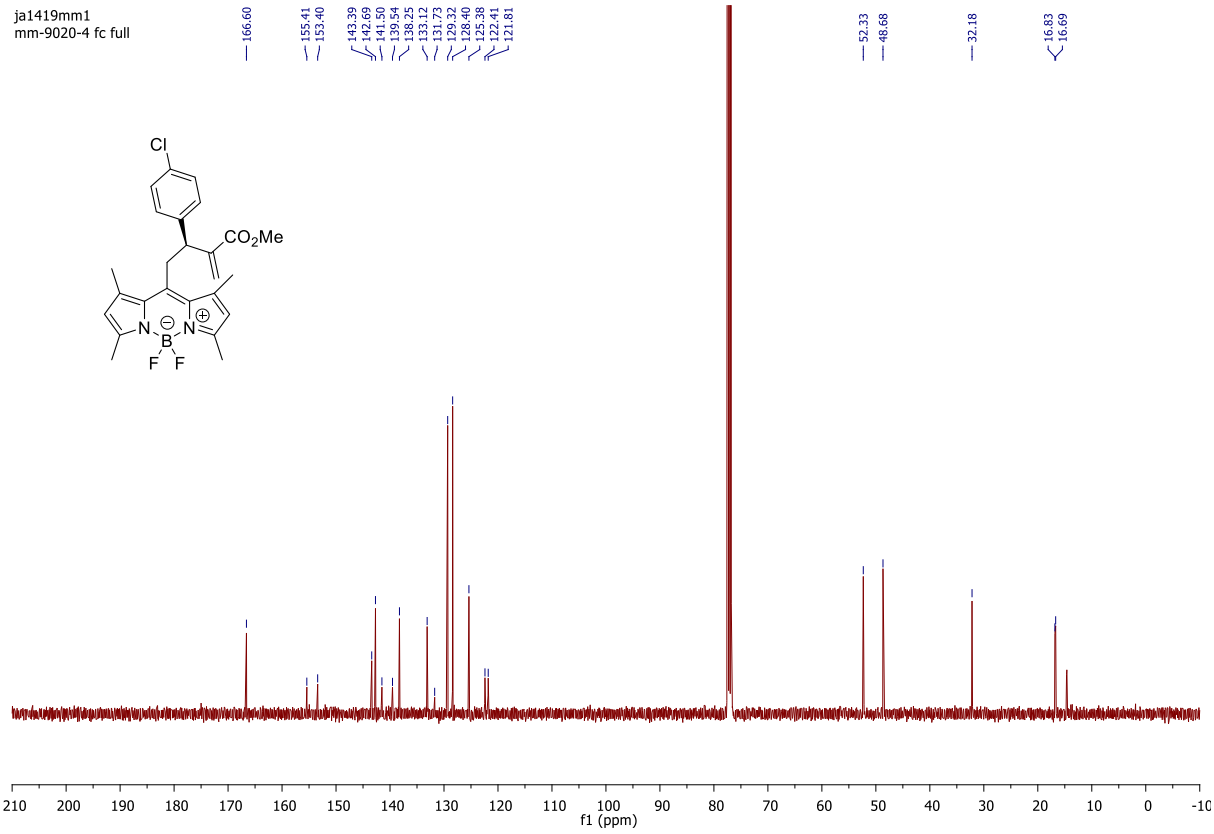

dc1019mm4
mm-8943-88 fc
F
CO2Me
N
B
F F
7.03
7.01
7.01
7.00
6.99
6.86
6.84
6.82
6.48
6.08
5.81
5.78
5.78
4.21
4.20
4.19
4.17
3.60
3.46
3.44
3.43
3.43
3.40
3.39
2.47
2.35
1.92
2.22
2.14
1.07
1.00
1.04
1.04
1.09
3.22
2.18
6.42
3.15
3.14
f1 (ppm)

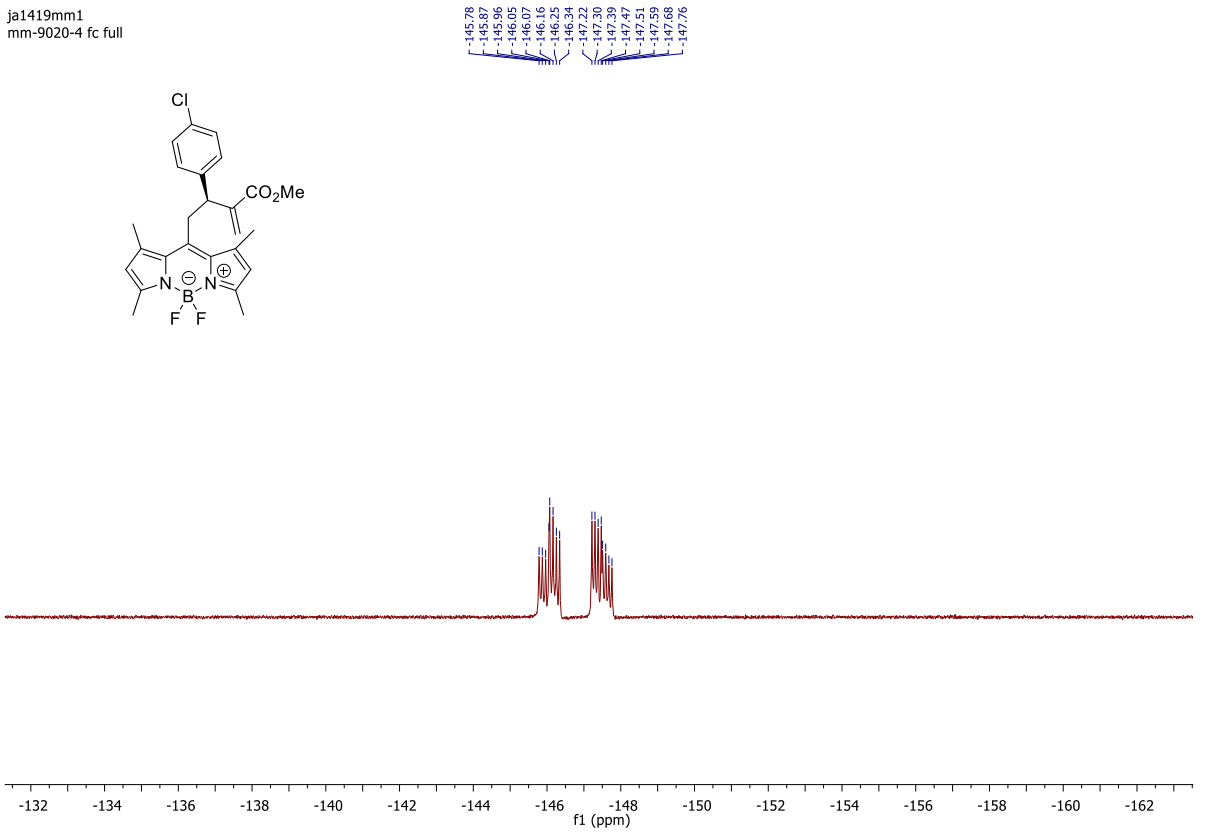

dc0319mm7
mm-8943-80 fc full
F
CO2Me
N
B
F F
166.54
163.17
160.73
155.22
153.14
143.44
142.84
141.48
139.37
135.18
135.15
131.58
129.40
129.32
124.96
122.24
115.20
115.04
114.83
52.17
48.40
32.26
16.67
16.53
f1 (ppm)


dc0319mm7
mm-8943-30 fc full
-145.83
-145.92
-146.01
-146.12
-146.21
-146.30
-146.39
-147.24
-147.32
-147.41
-147.49
-147.53
-147.61
-147.70
-147.78
F
CO2Me
N
B
N
F
F
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
f1 (ppm)

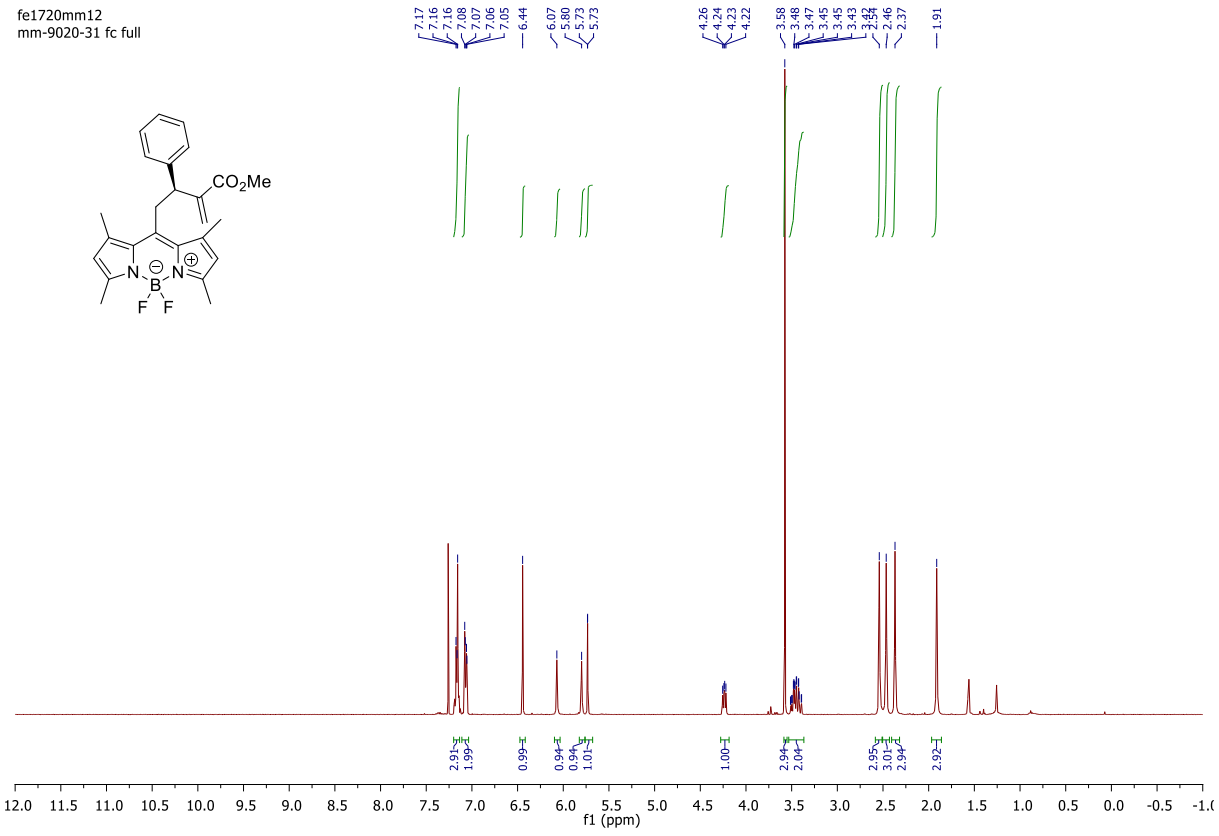
3n

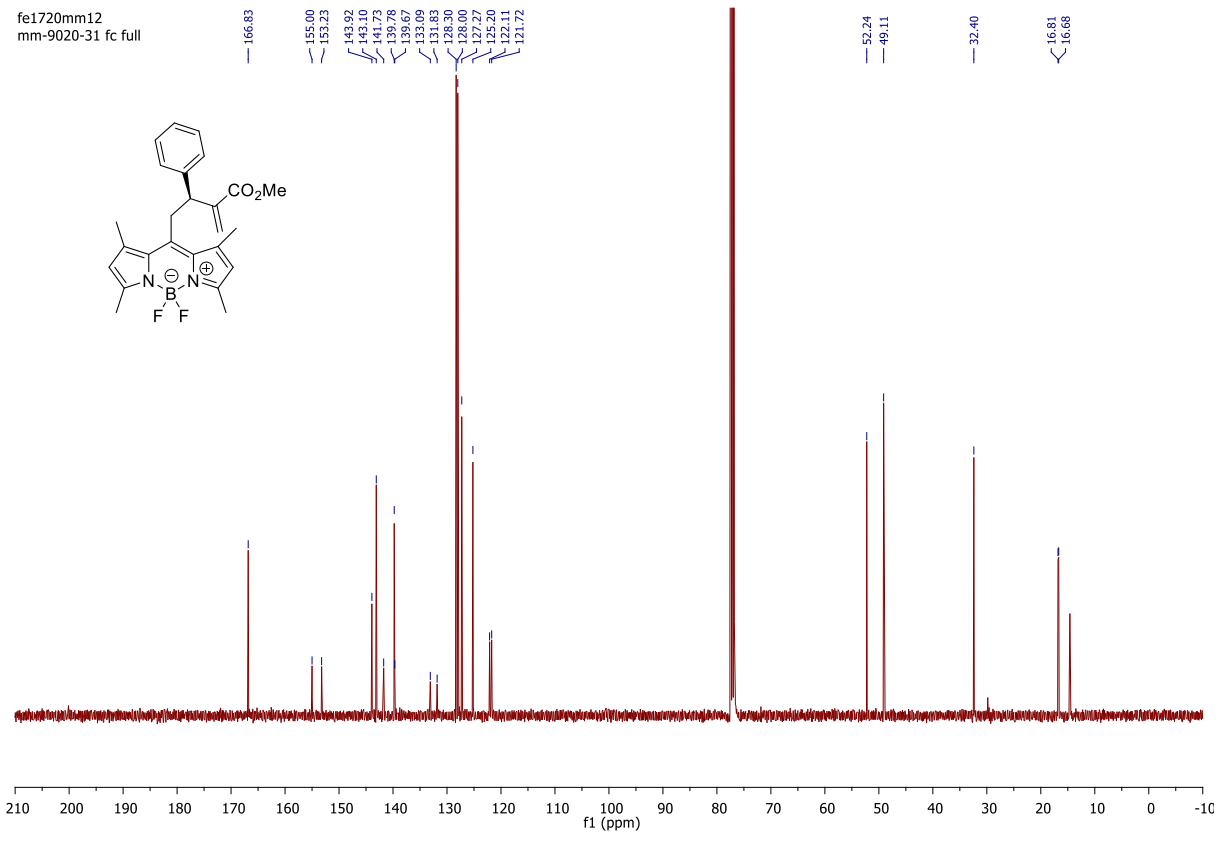

ja1419mm1
mm-9020-4 fc full
7.14
7.12
7.00
6.98
6.47
6.07
5.83
5.77
5.77
4.20
4.19
4.18
4.16
3.59
3.47
3.45
3.44
3.43
3.40
3.39
2.47
2.35
1.93
Cl
CO2Me
N
B
N
F
F
1.97
1.99
0.99
0.94
0.99
1.00
1.00
2.99
2.00
3.00
2.99
2.94
2.93
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

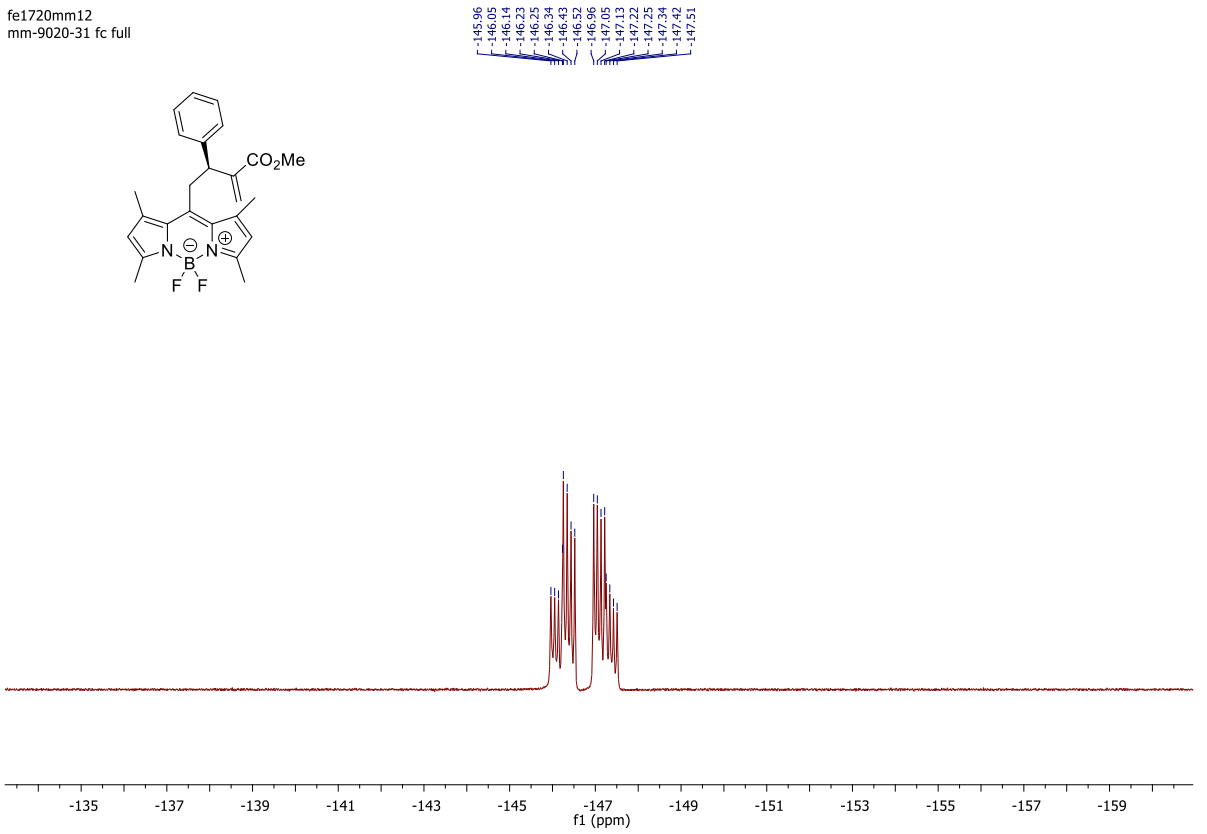

ja1419mm1
mm-9020-4 fc full
166.60
155.41
153.40
143.39
142.69
141.50
139.54
138.25
133.12
131.73
129.32
128.40
125.38
122.41
121.81
52.33
48.68
32.18
16.83
16.69
Cl
CO2Me
N
B
N
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ja1419mm1
mm-9020-4 fc full
-145.78
-145.87
-145.96
-146.05
-146.07
-146.16
-146.25
-146.34
-147.22
-147.30
-147.39
-147.47
-147.51
-147.59
-147.68
-147.76
Cl
CO2Me
N
B
N
F
F
-132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162
f1 (ppm)

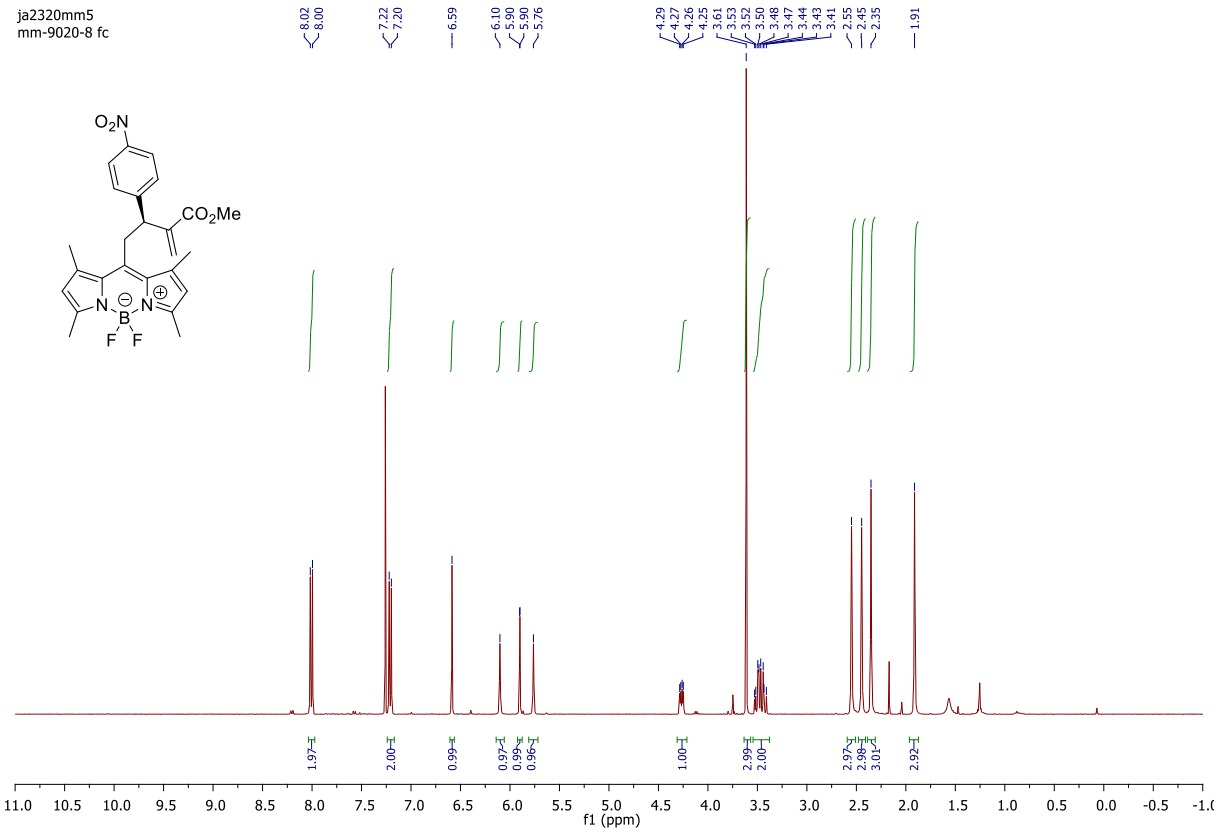
3o

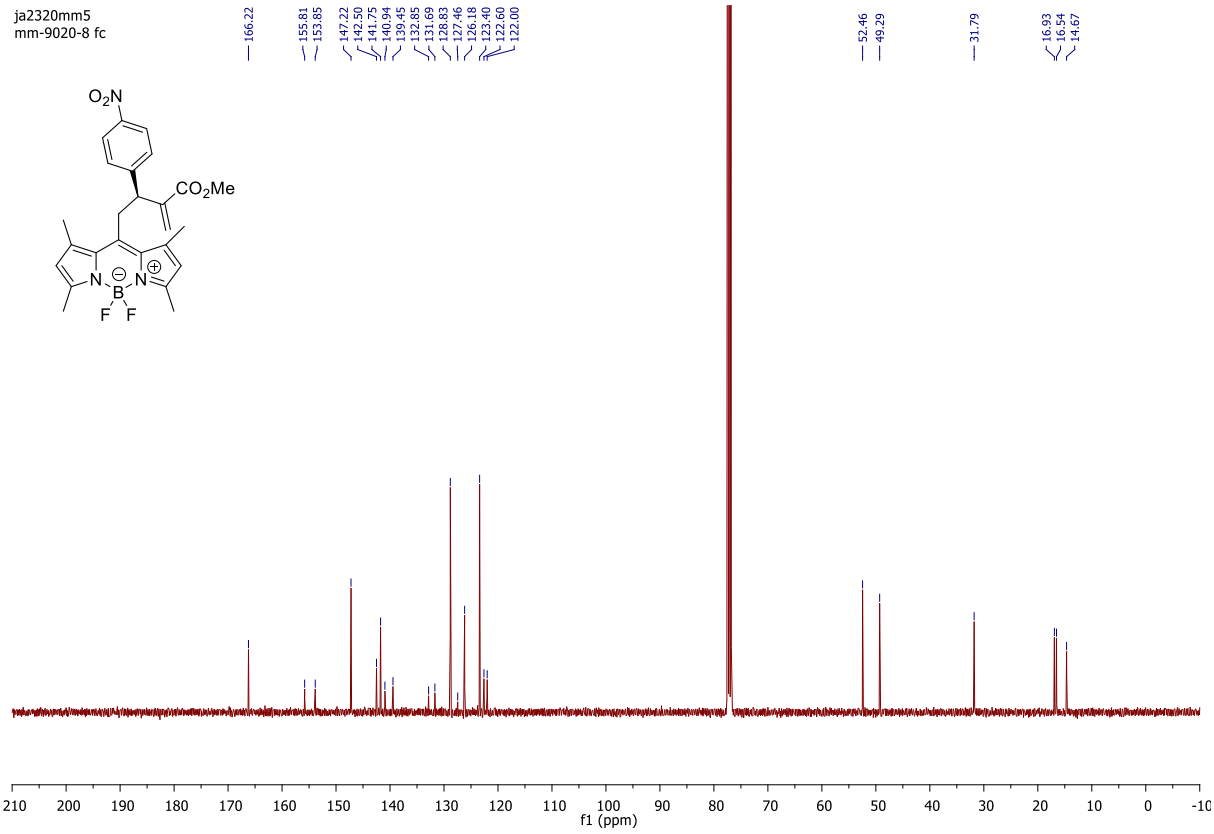

fe1720mm12
mm-9020-31 fc full
CO2Me
N
B
F F
f1 (ppm)

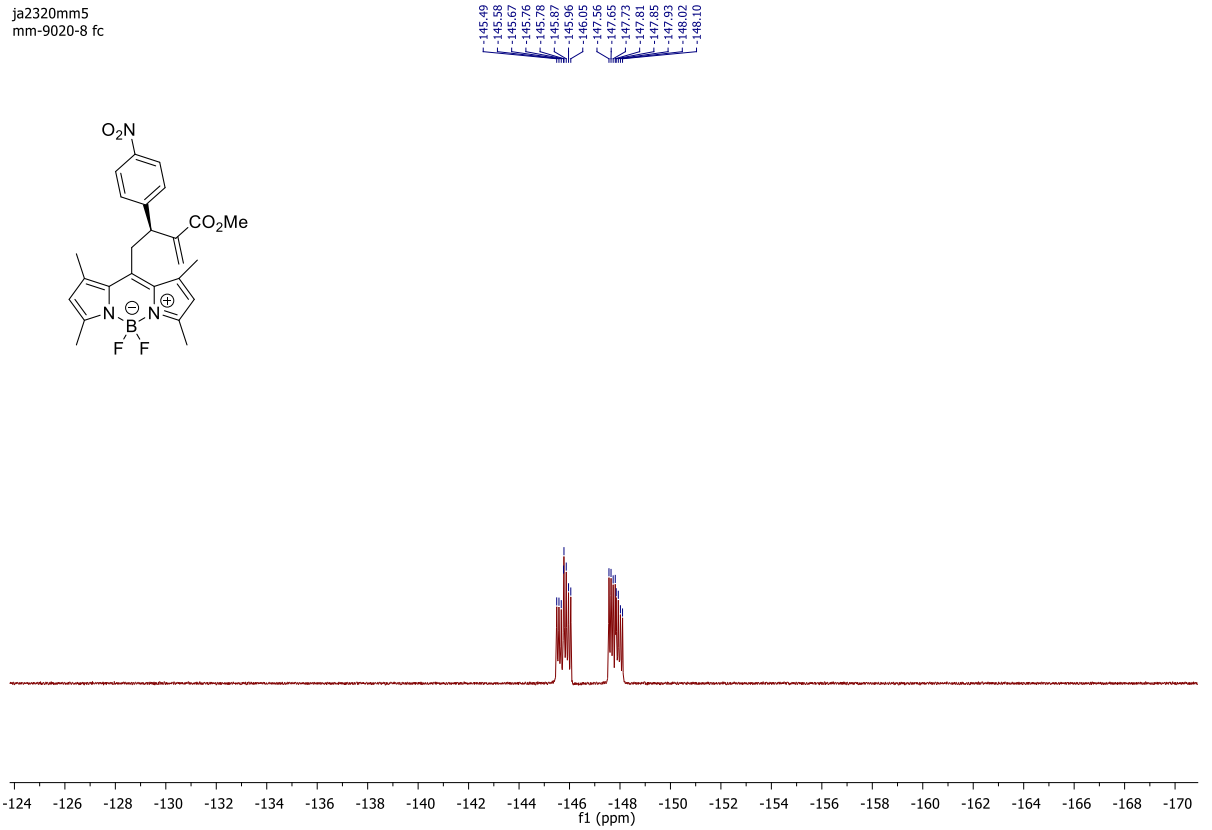

fe1720mm12
mm-9020-31 fc full
CO2Me
N
B
F F
f1 (ppm)


fe1720mm12
mm-9020-31 fc full
-145.96
-146.05
-146.14
-146.23
-146.25
-146.34
-146.43
-146.52
-146.96
-147.05
-147.13
-147.22
-147.25
-147.34
-147.42
-147.51
CO2Me
N
B
N
F
F
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
-157
-159
f1 (ppm)

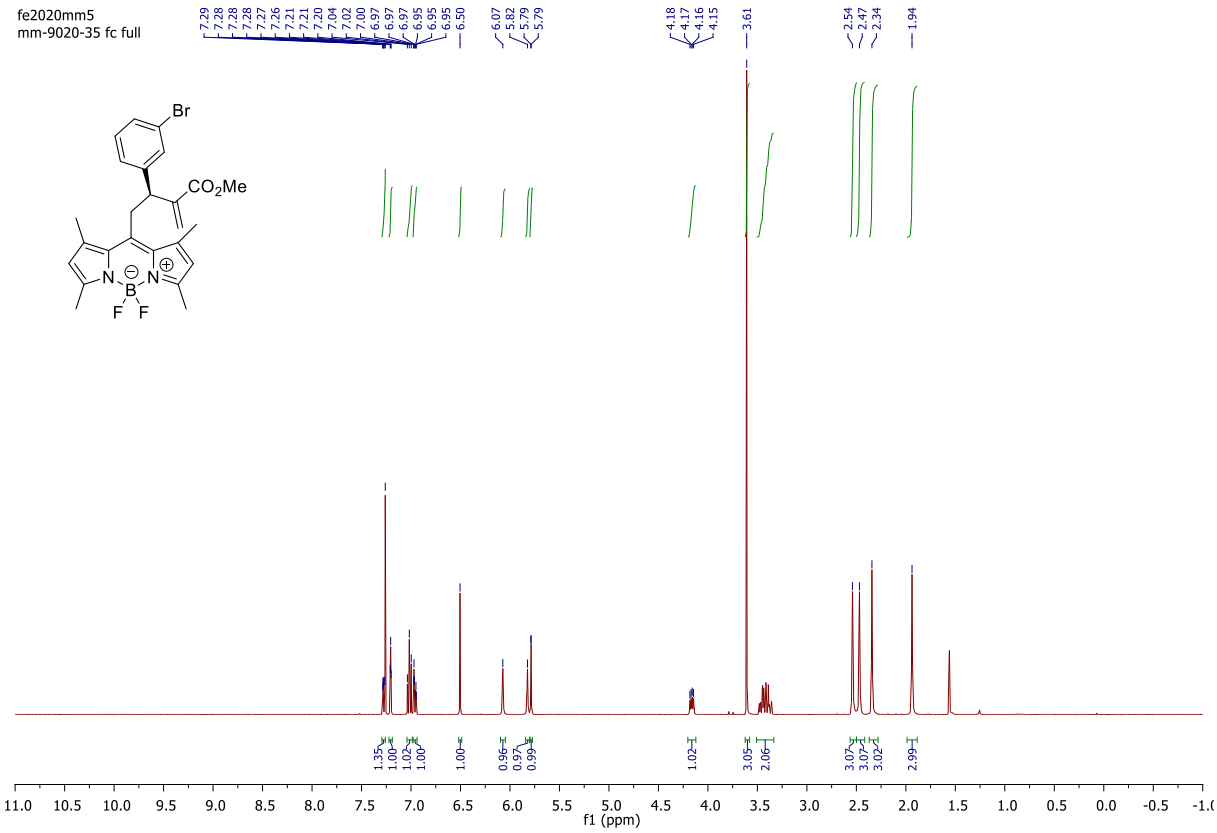
3p

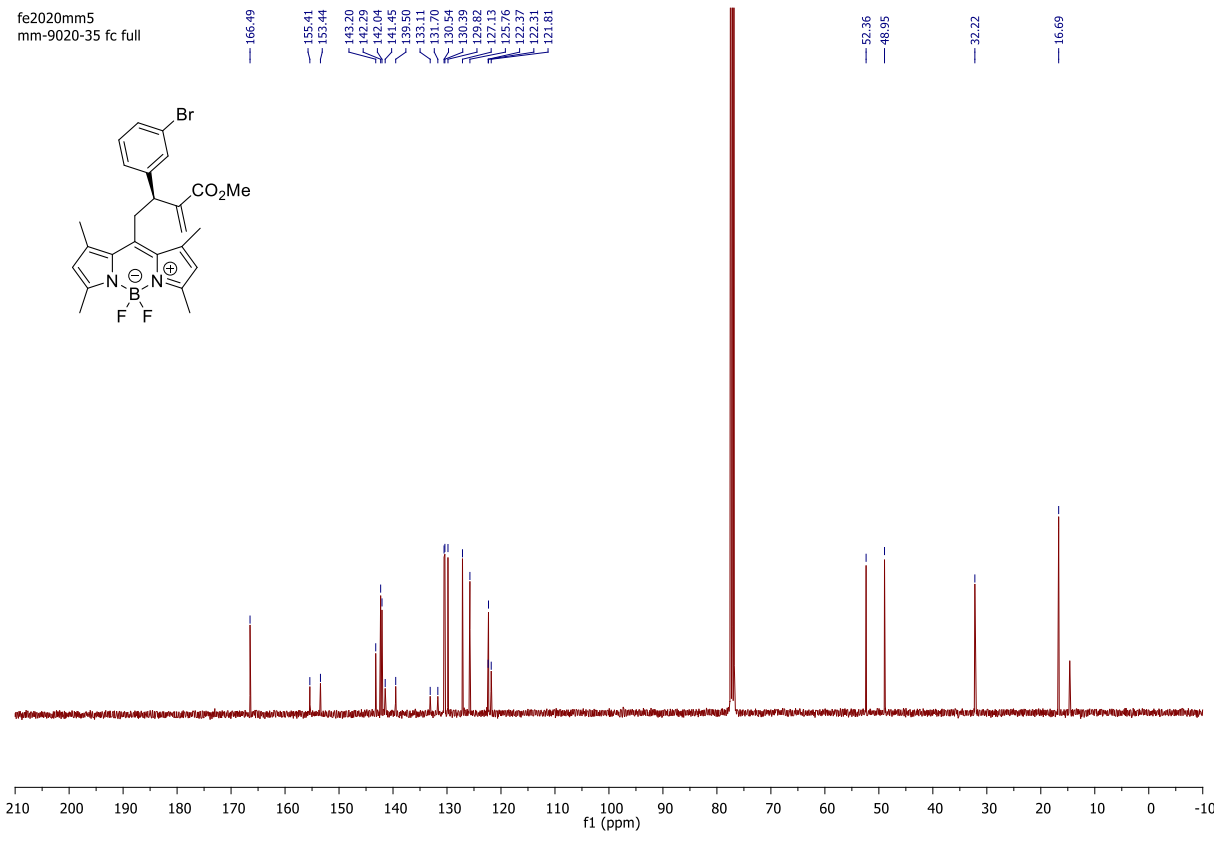

ja2320mm5
mm-9020-8 fc
8.02
8.00
7.22
7.20
6.59
6.10
5.90
5.90
5.76
4.29
4.27
4.26
4.25
3.61
3.53
3.52
3.50
3.48
3.47
3.44
3.43
3.41
2.55
2.45
2.35
1.91
O2N
CO2Me
N
B
N
F
F
1.97
2.00
0.99
0.97
0.99
0.96
1.00
2.99
2.00
2.97
2.98
3.01
2.92
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

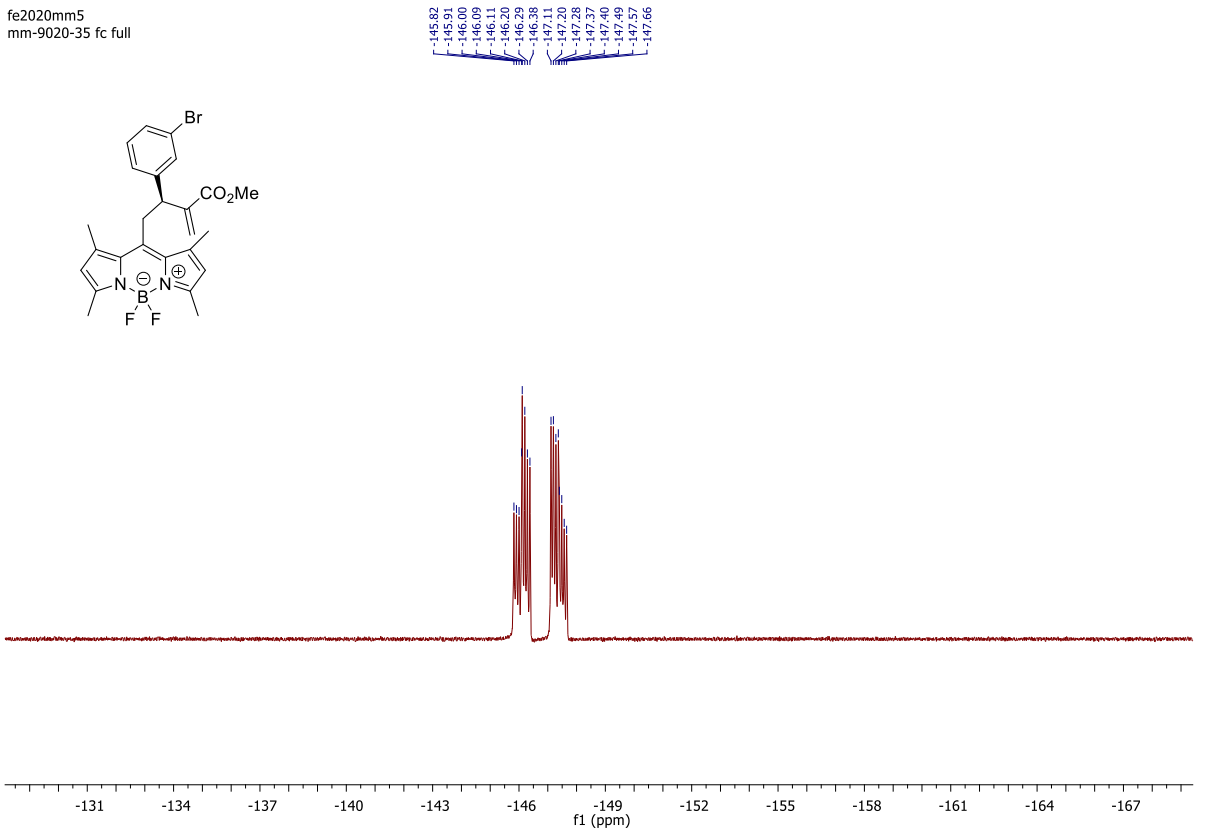

ja2320mm5
mm-9020-8 fc
166.22
155.81
153.85
147.22
142.50
141.75
140.94
139.45
132.85
131.69
128.83
127.46
126.18
123.40
122.60
122.00
52.46
49.29
31.79
16.93
16.54
14.67
O2N
CO2Me
N
B
F F
f1 (ppm)


ja2320mm5
mm-9020-8 fc
-145.49
-145.58
-145.67
-145.76
-145.78
-145.87
-145.96
-146.05
-147.56
-147.65
-147.73
-147.81
-147.85
-147.93
-148.02
-148.10
O2N
CO2Me
N
B
F F
f1 (ppm)

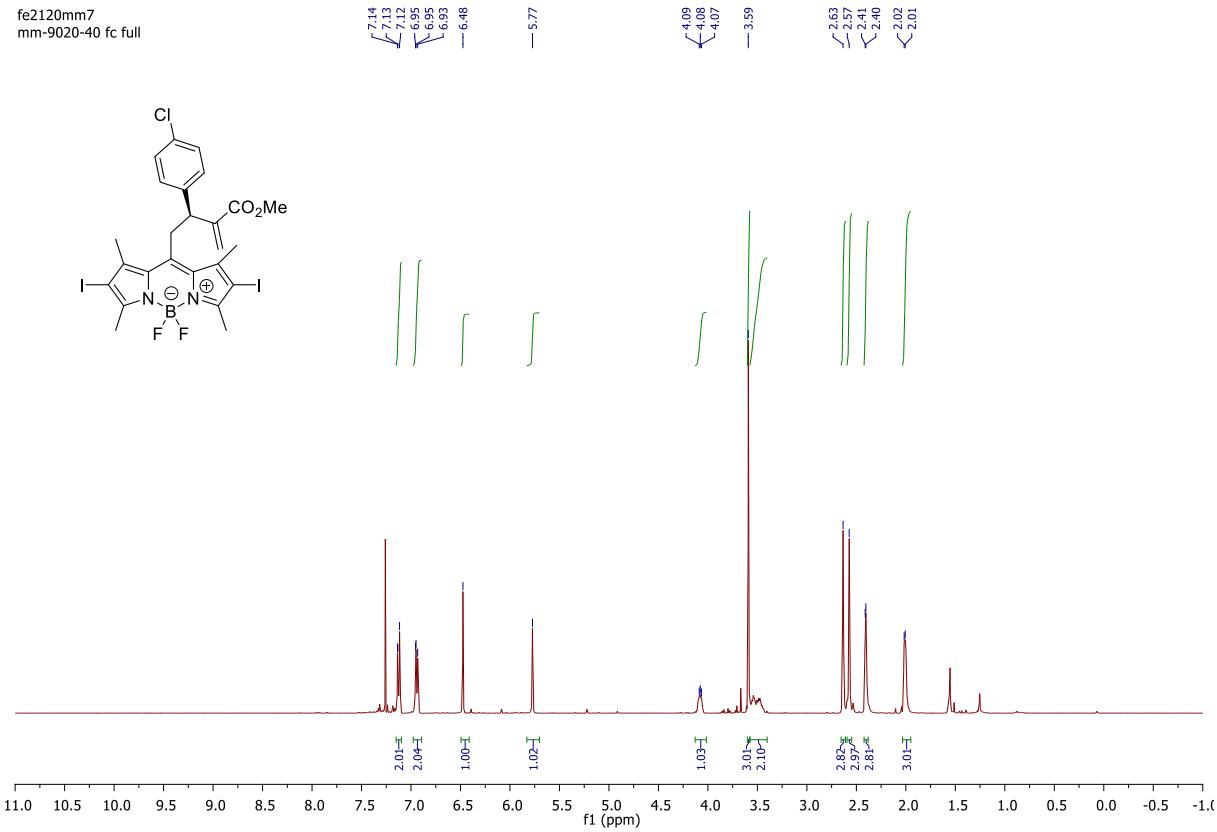
3q

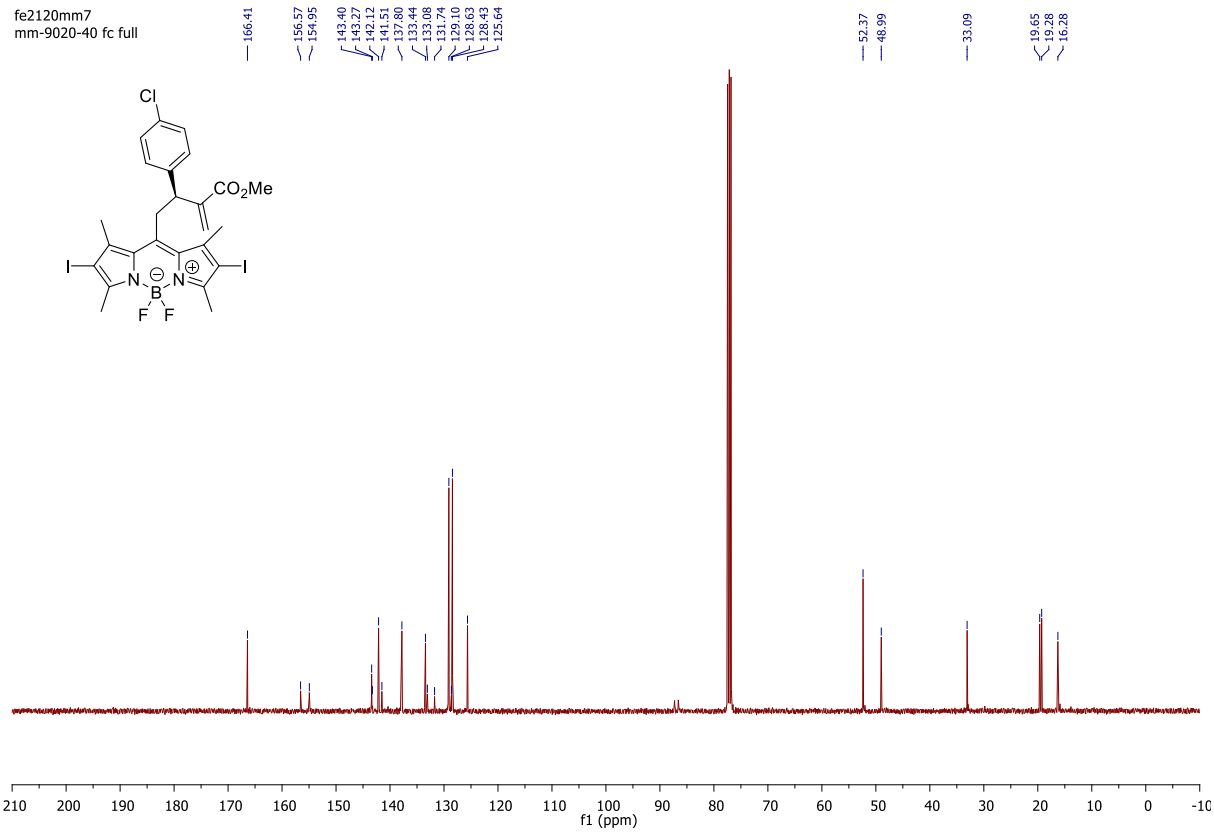

fe2020mm5
mm-9020-35 fc full
Br
CO2Me
N
B
F F
f1 (ppm)


fe2020mm5
mm-9020-35 fc full
Br
CO2Me
N
B
F F
f1 (ppm)


fe2020mm5
mm-9020-35 fc full
-145.82
-145.91
-146.00
-146.09
-146.11
-146.20
-146.29
-146.38
-147.11
-147.20
-147.28
-147.37
-147.40
-147.49
-147.57
-147.66
Br
CO2Me
N
B
N
F
F
-131
-134
-137
-140
-143
-146
-149
-152
-155
-158
-161
-164
-167
f1 (ppm)

3r


fe2120mm7
mm-9020-40 fc full
7.14
7.13
7.12
6.95
6.95
6.93
6.48
5.77
4.09
4.08
4.07
3.59
2.63
2.57
2.41
2.40
2.02
2.01
Cl
CO2Me
I
I
N
B
N
F
F
2.01
2.04
1.00
1.02
1.03
3.01
2.10
2.82
2.97
2.81
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


fe2120mm7
mm-9020-40 fc full
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154.95
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142.12
141.51
137.80
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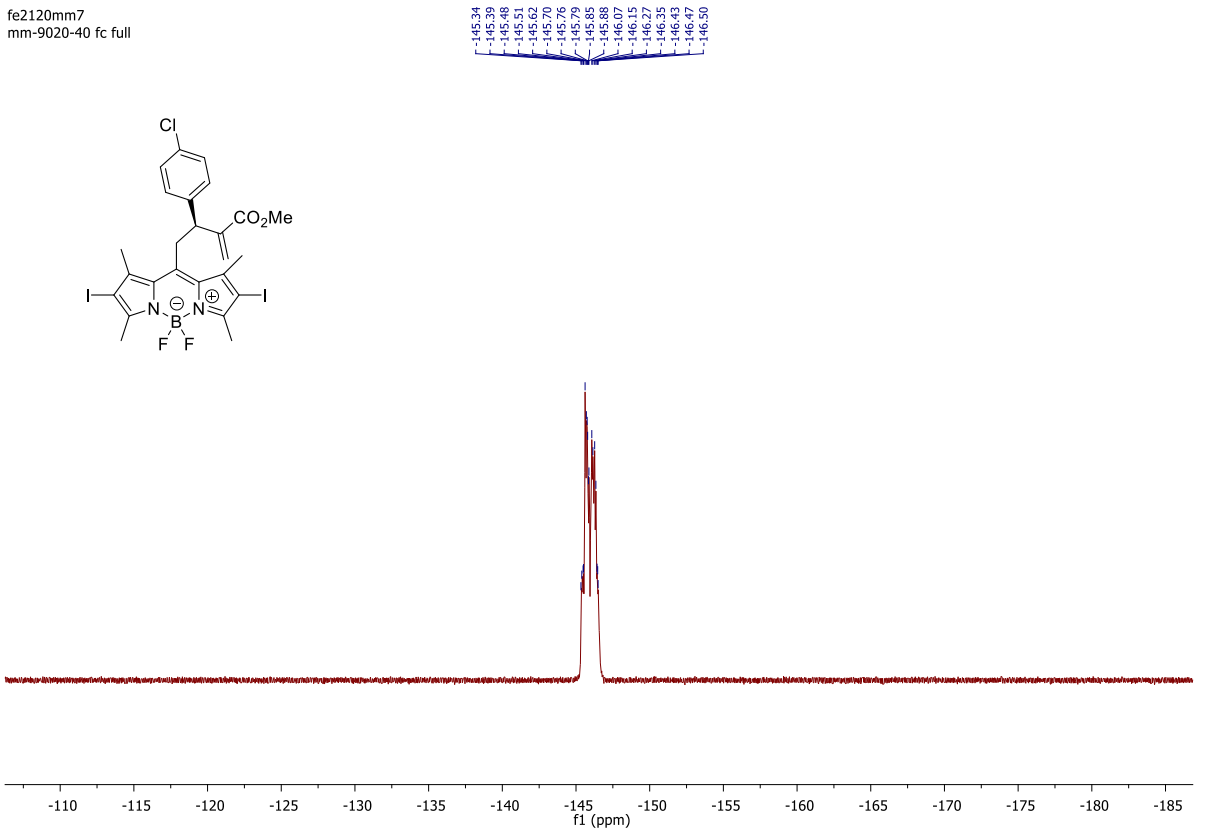
133.08
131.74
129.10
128.63
128.43
125.64
52.37
48.99
33.09
19.65
19.28
16.28
Cl
CO2Me
I
I
N
B
N
F
F
f1 (ppm)


fe2120mm7
mm-9020-40 fc full
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-145.51
-145.62
-145.70
-145.76
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-145.85
-145.88
-146.07
-146.15
-146.27
-146.35
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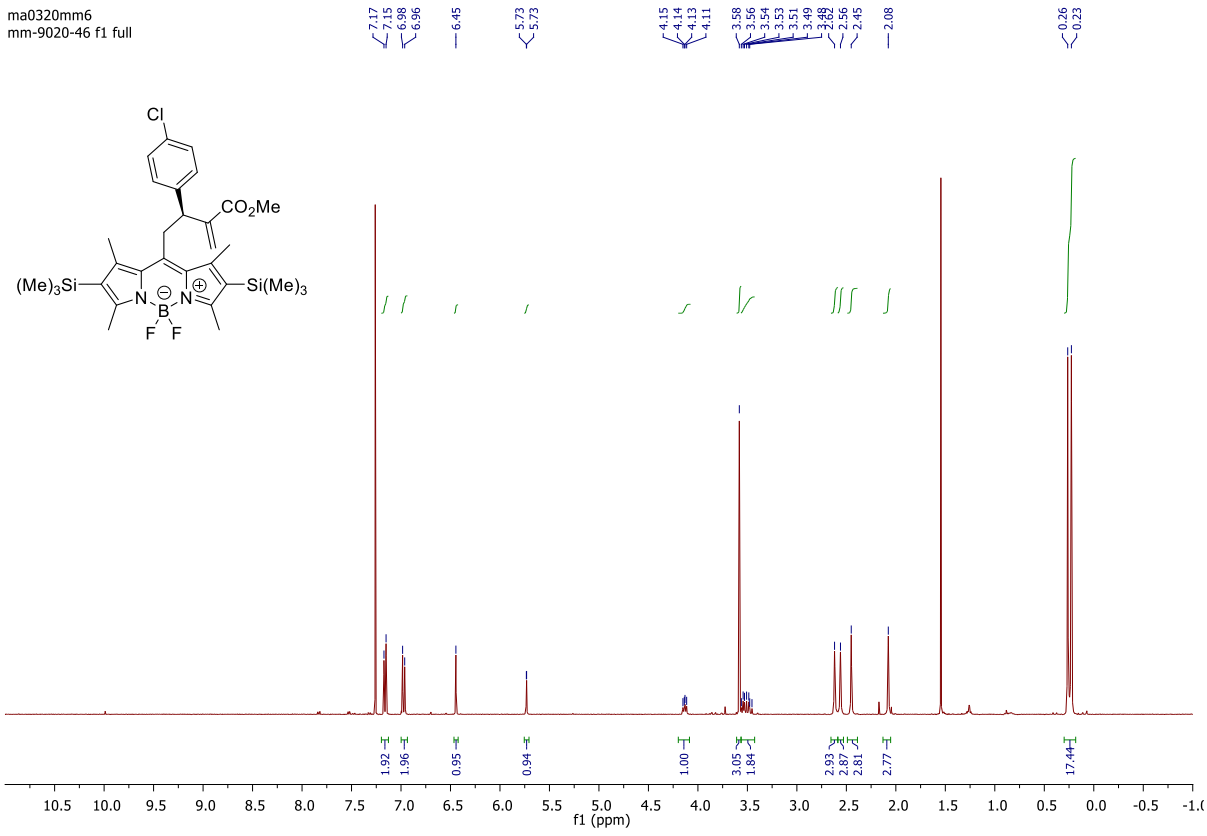
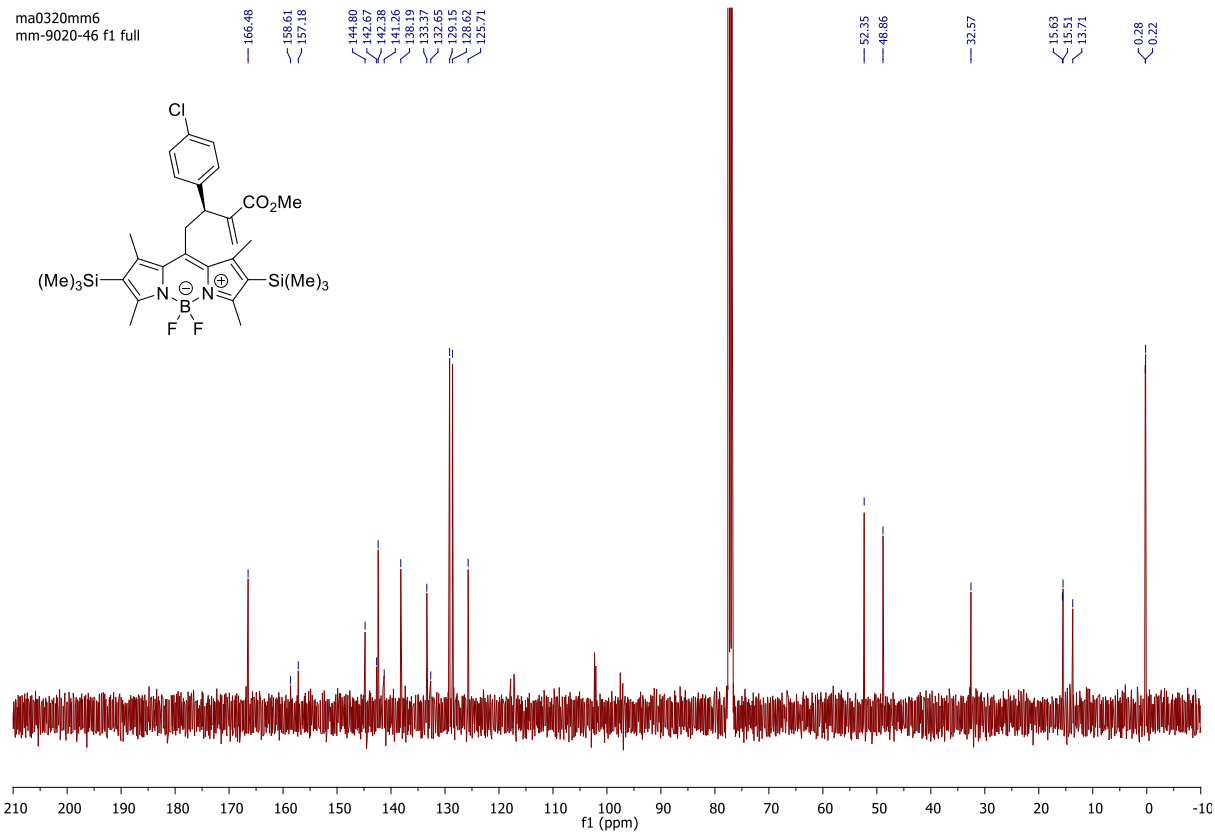
CO2Me
I
I
N
B
N
F
F
f1 (ppm)

3s


ma0320mm6
mm-9020-46 f1 full
Cl
CO2Me
(Me)3Si
Si(Me)3
N
B
N
F
F
f1 (ppm)


ma0320mm6
mm-9020-46 f1 full
Cl
CO2Me
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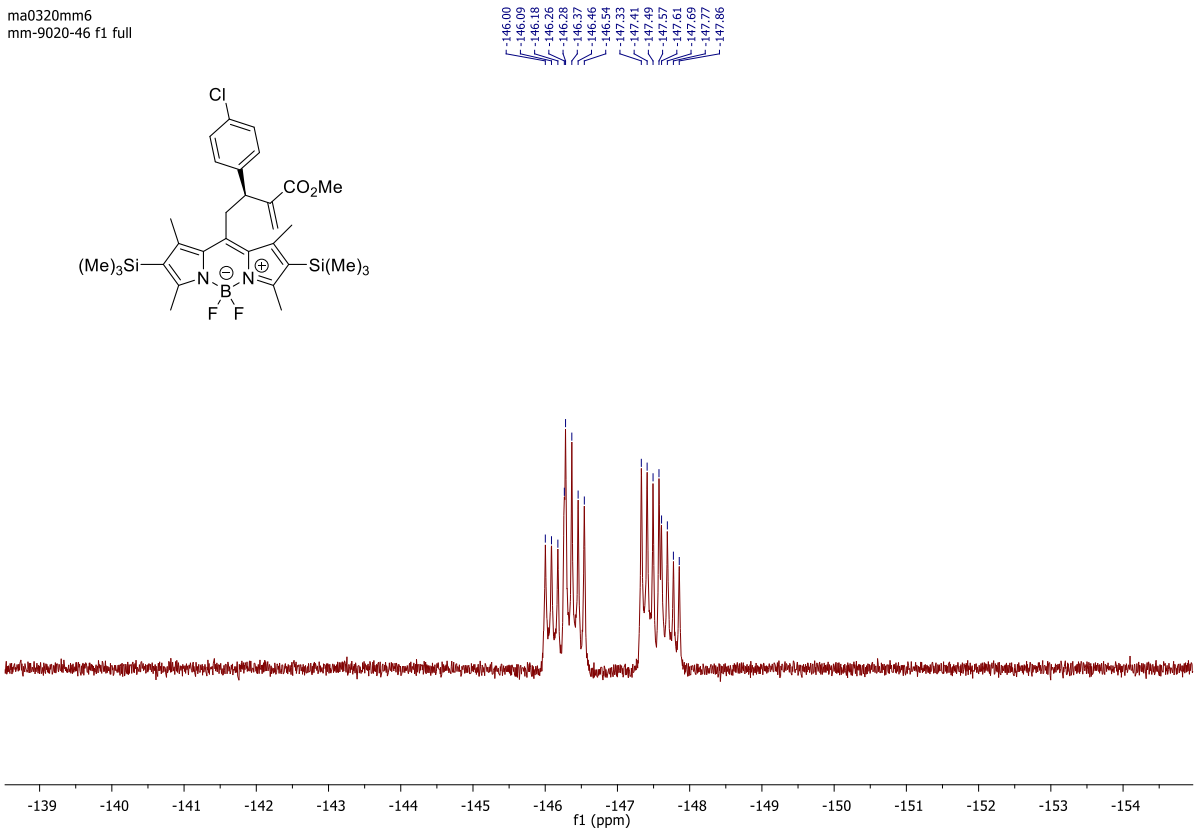
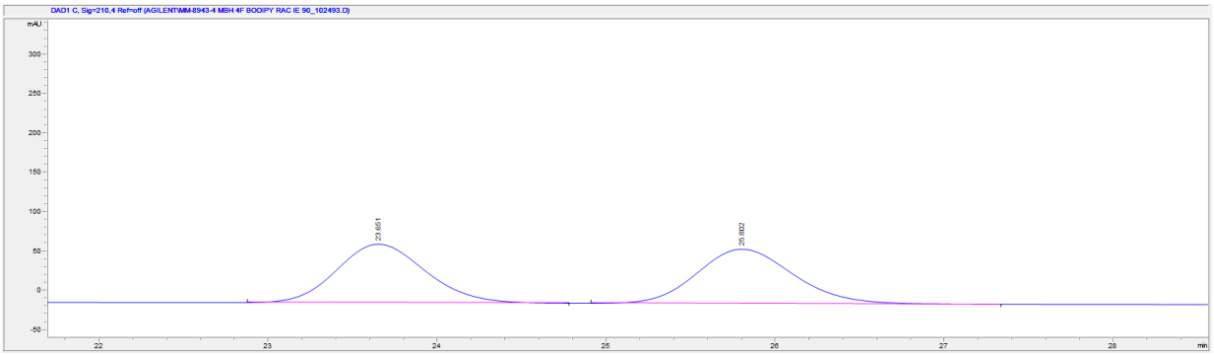
Si(Me)3
N
B
N
F
F
f1 (ppm)

ma0320mm6
mm-9020-46 f1 full



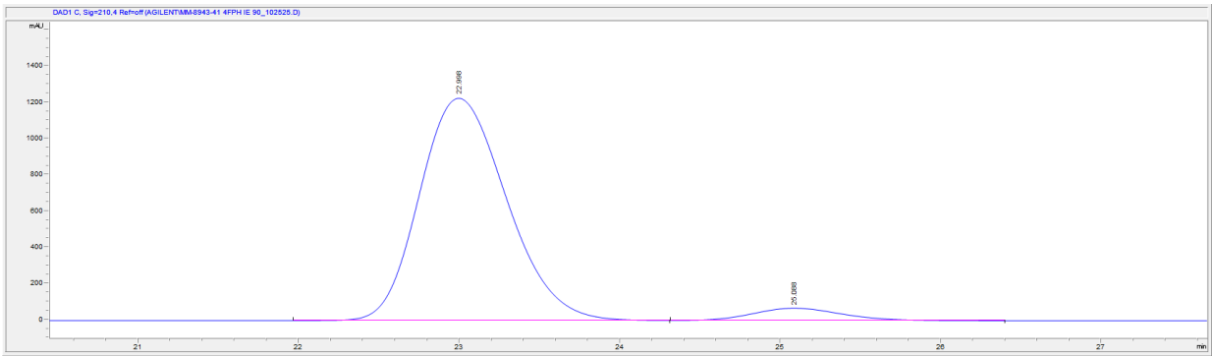
HPLC traces

3a racemic



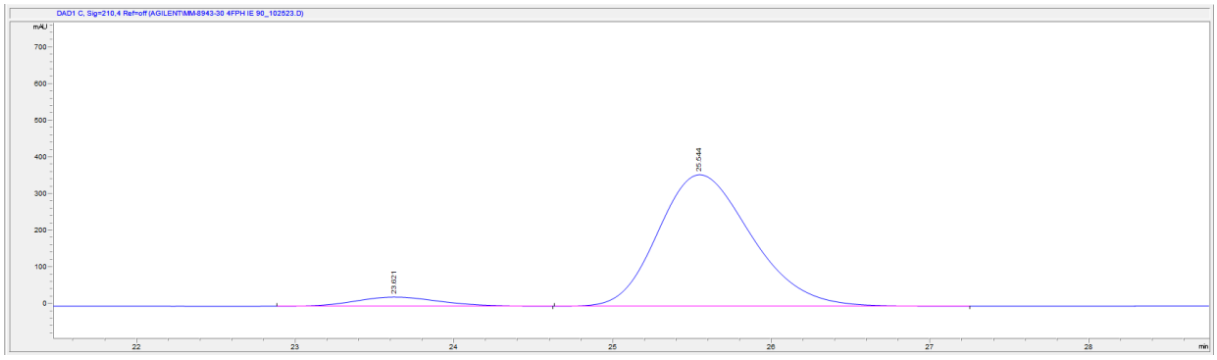
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.651	BB	0.5614	2728.31079	74.46984	49.8298
2	25.802	BB	0.5976	2746.94971	69.12315	50.1702

3a quinine



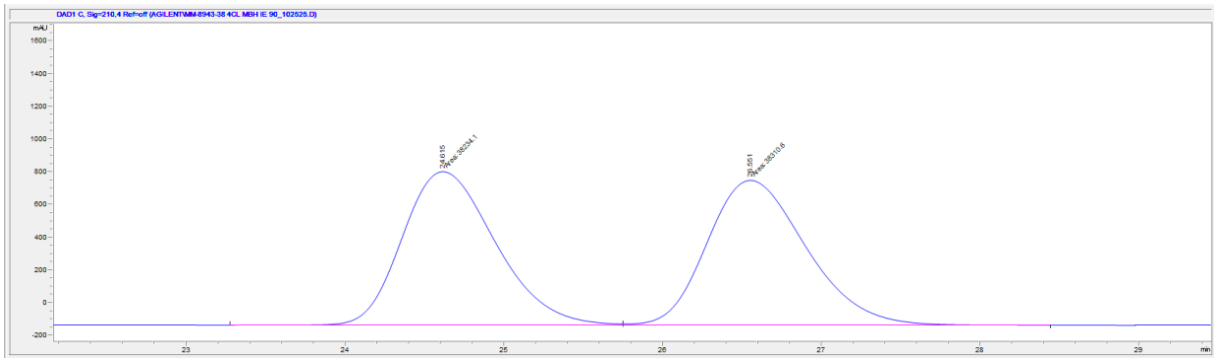
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.998	BB	0.5913	4.62685e4	1228.77905	94.6683
2	25.088	BB	0.5849	2605.83350	68.02283	5.3317

3a cinchonine



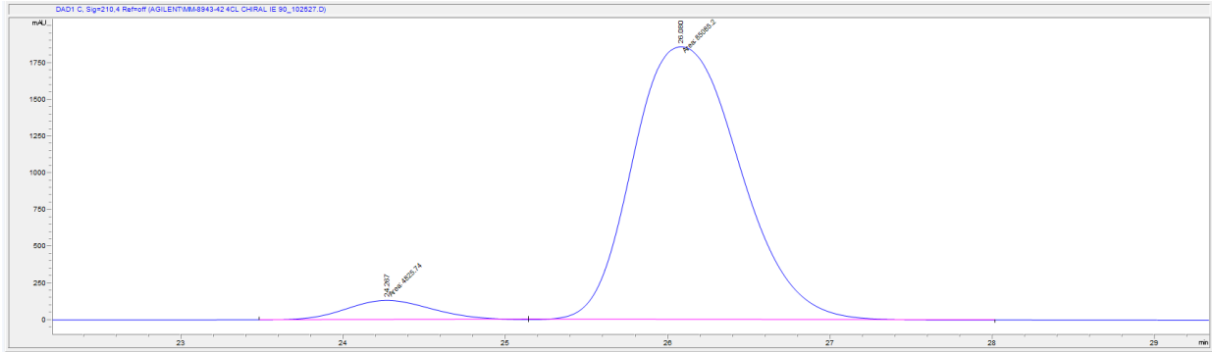
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.621	BB	0.5682	925.71619	24.98757	5.9353
2	25.544	BB	0.6346	1.46711e4	359.13065	94.0647

3b racemic



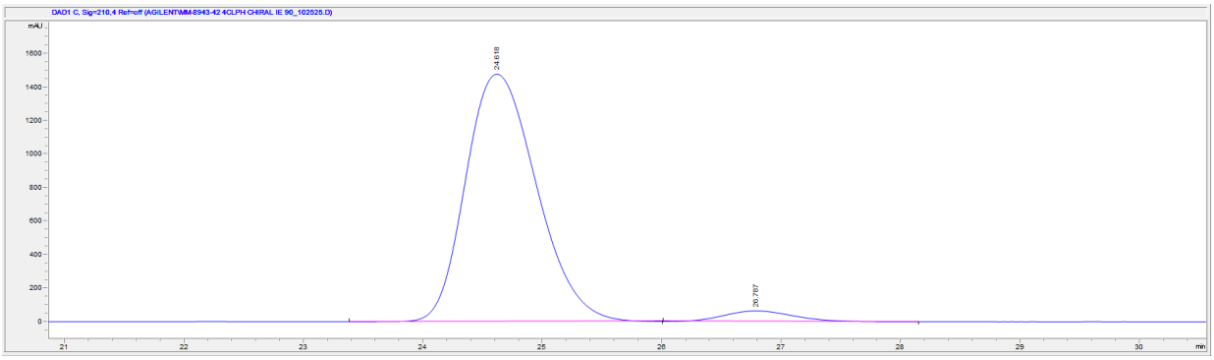
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.615	MM	0.6789	3.82341e4	938.56268	49.9500
2	26.551	MM	0.7213	3.83106e4	885.18628	50.0500

3b quinine



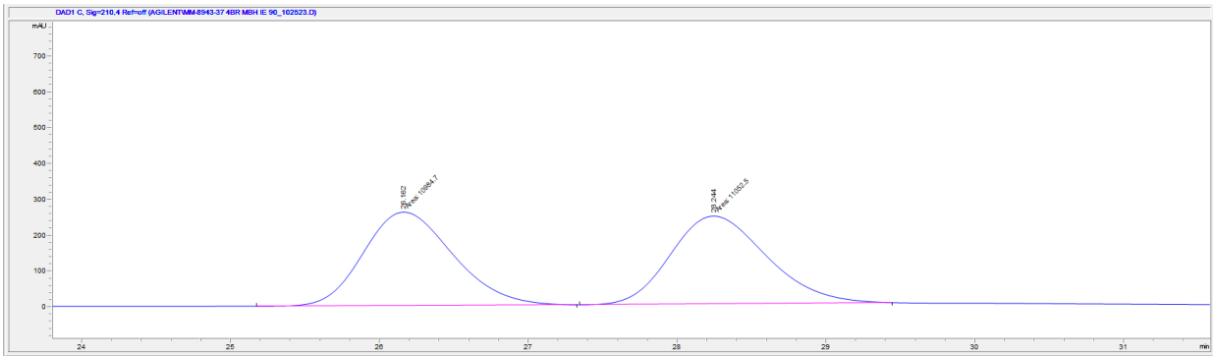
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.267	MM	0.6157	4825.74414	130.62802	5.3672
2	26.080	MM	0.7645	8.50852e4	1854.95557	94.6328

3b cinchonine



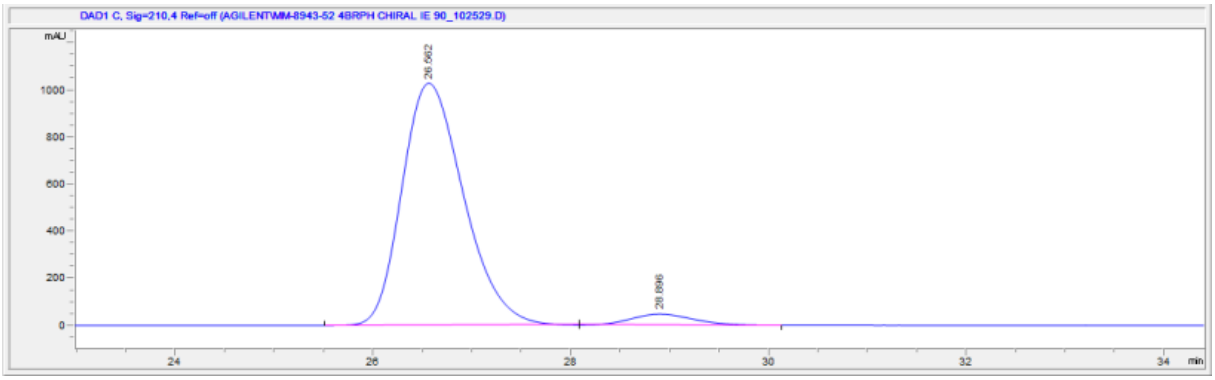
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.618	BB	0.6526	6.09378e4	1479.16125	95.8822
2	26.787	BB	0.6312	2617.05151	63.98225	4.1178

3c racemic



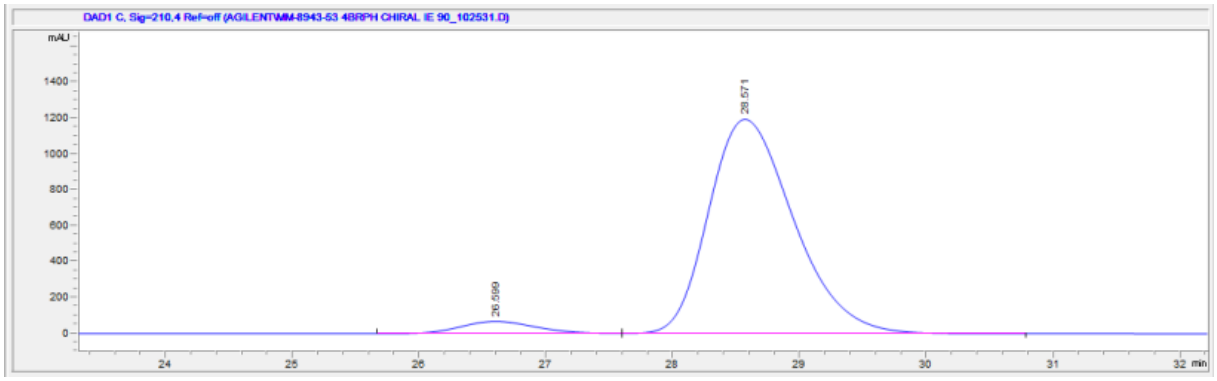
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.162	MM	0.7013	1.09847e4	261.06619	49.8461
2	28.244	MM	0.7504	1.10525e4	245.47301	50.1539

3c quinine



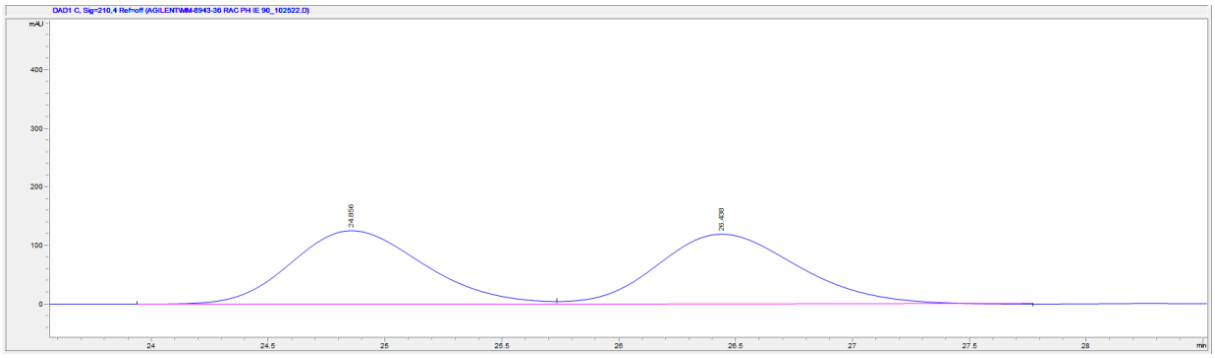
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.562	BB	0.6737	4.43787e4	1023.92645	95.6358
2	28.896	BB	0.6665	2025.15247	46.10466	4.3642

3c cinchonine



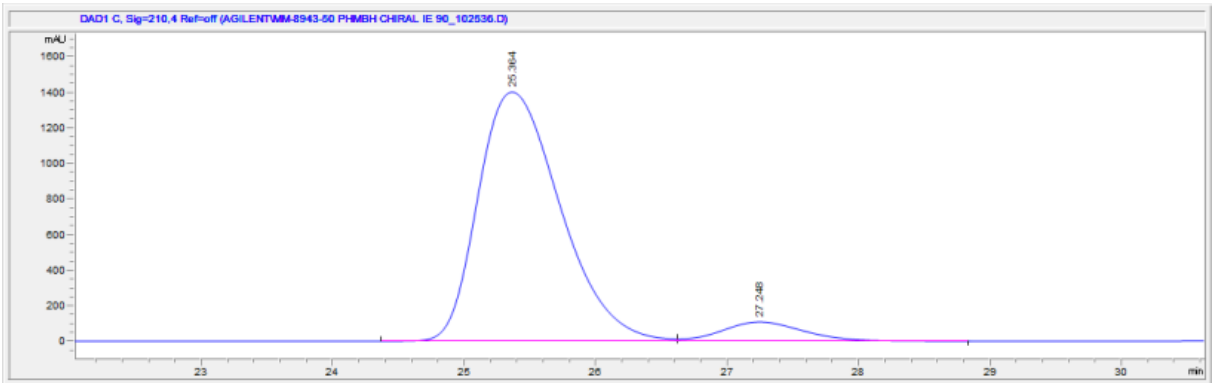
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.599	BV	0.6422	2827.30933	67.84736	4.8299
2	28.571	VB	0.7262	5.57107e4	1194.40967	95.1701

3d racemic



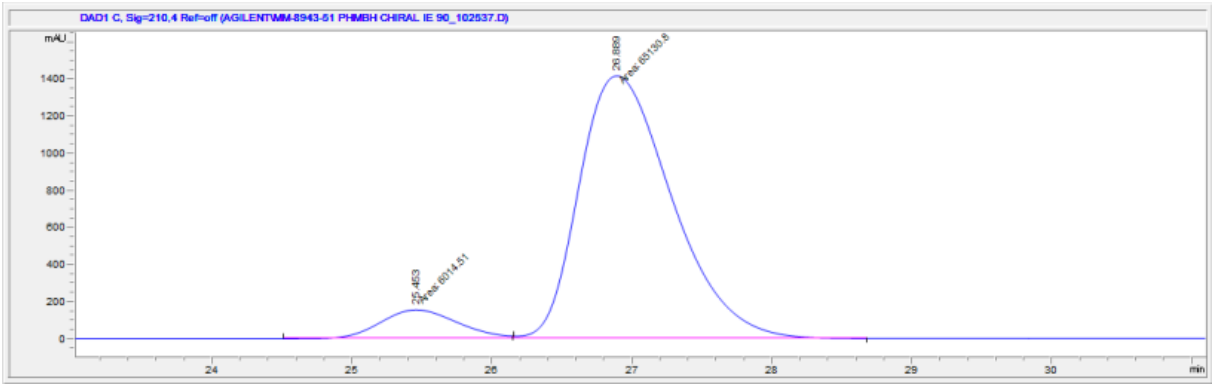
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.856	BV	0.6061	4936.85352	125.17850	49.7015
2	26.438	VB	0.6489	4996.16211	119.21275	50.2985

3d quinine



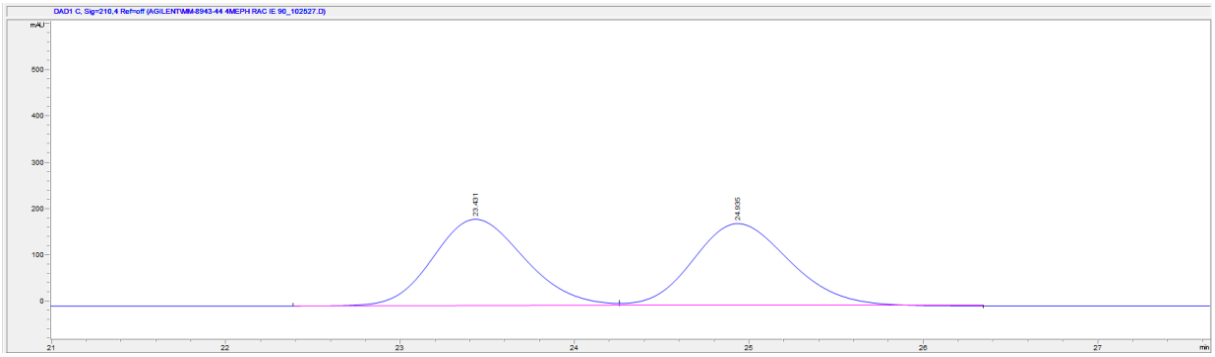
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.364	BV	0.6813	6.09879e4	1402.55688	92.9027
2	27.248	VB	0.6645	4659.17188	107.74294	7.0973

3d cinchonine



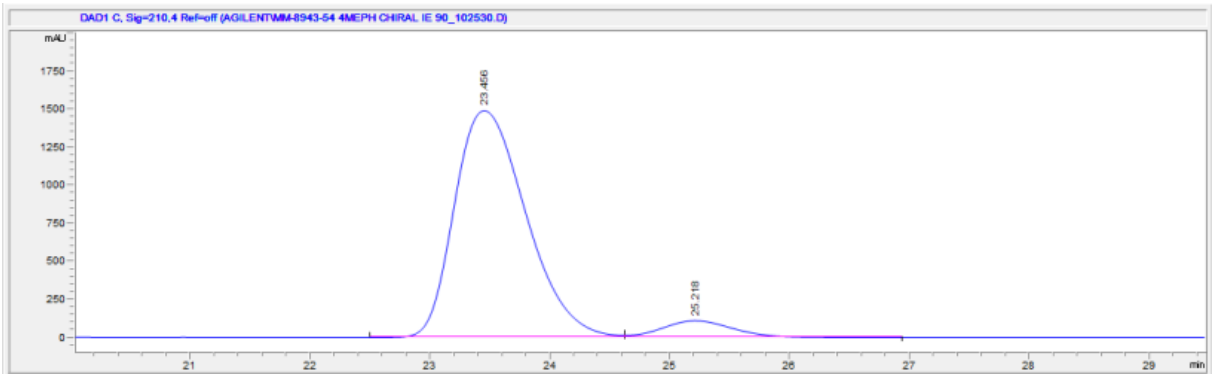
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.453	MM	0.6454	6014.50537	155.32388	8.4538
2	26.889	MM	0.7677	6.51308e4	1414.06580	91.5462

3e racemic



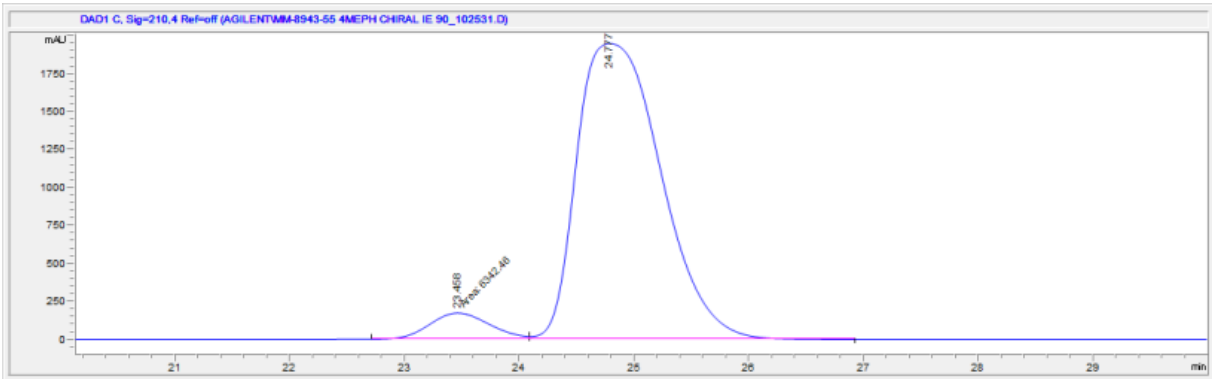
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.431	BV	0.5707	6879.28760	187.20409	49.9593
2	24.935	VB	0.6003	6890.50244	177.75215	50.0407

3e quinine



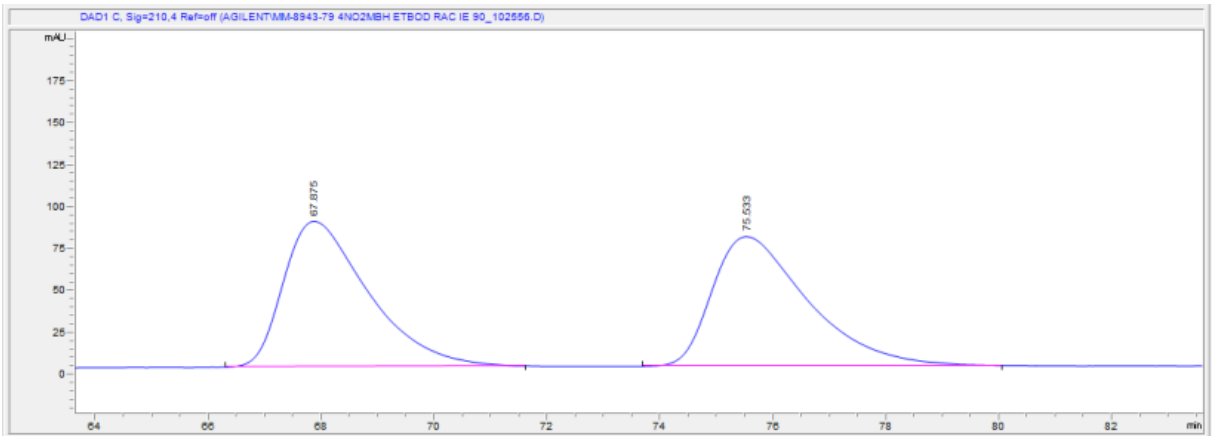
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.456	BV	0.6531	6.20796e4	1492.88257	93.1489
2	25.218	VB	0.6369	4565.97168	110.30869	6.8511

3e cinchonine



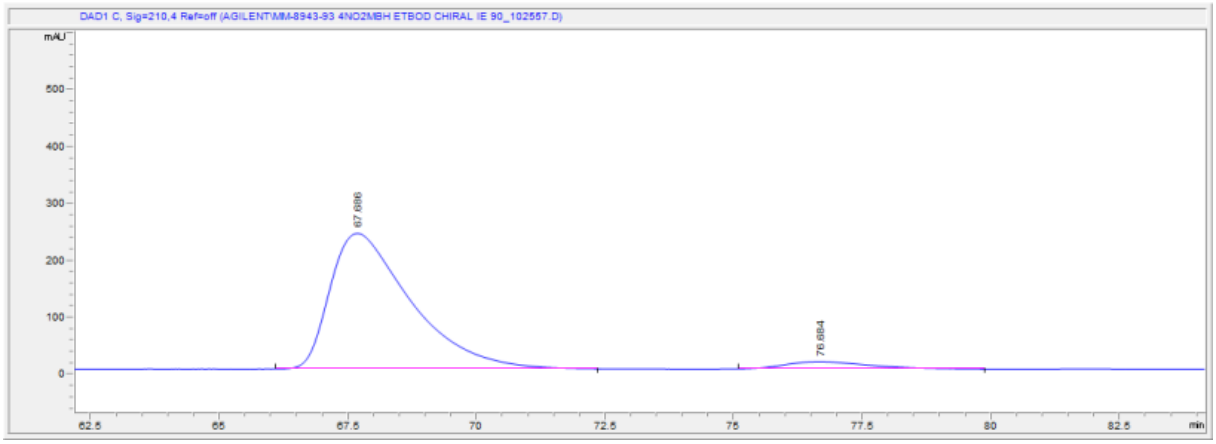
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.458	MM	0.6121	6342.46338	172.69540	6.0268
2	24.777	VB	0.6068	9.88957e4	1946.25940	93.9732

3f racemic



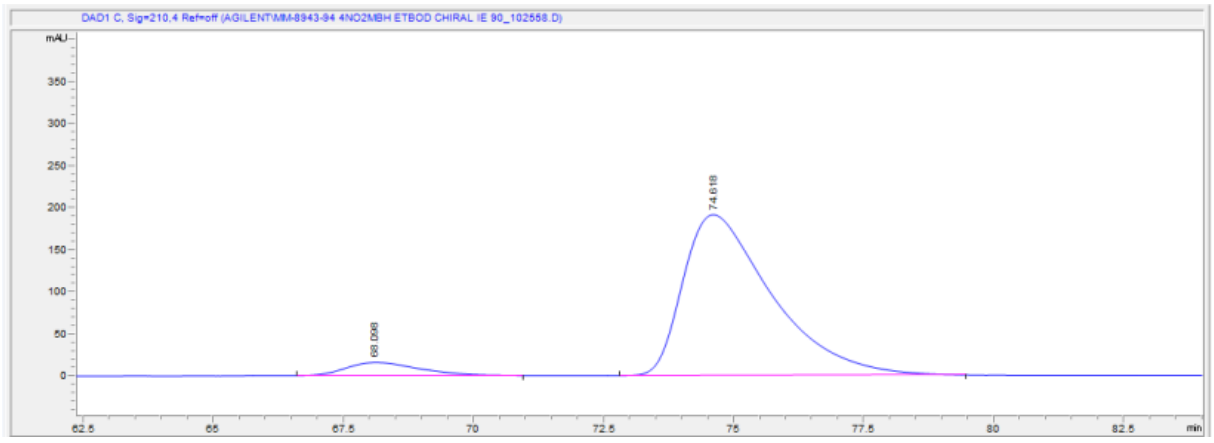
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.875	BB	1.2968	9088.78711	86.99923	49.8857
2	75.533	BB	1.3911	9130.45410	77.46476	50.1143

3f quinine



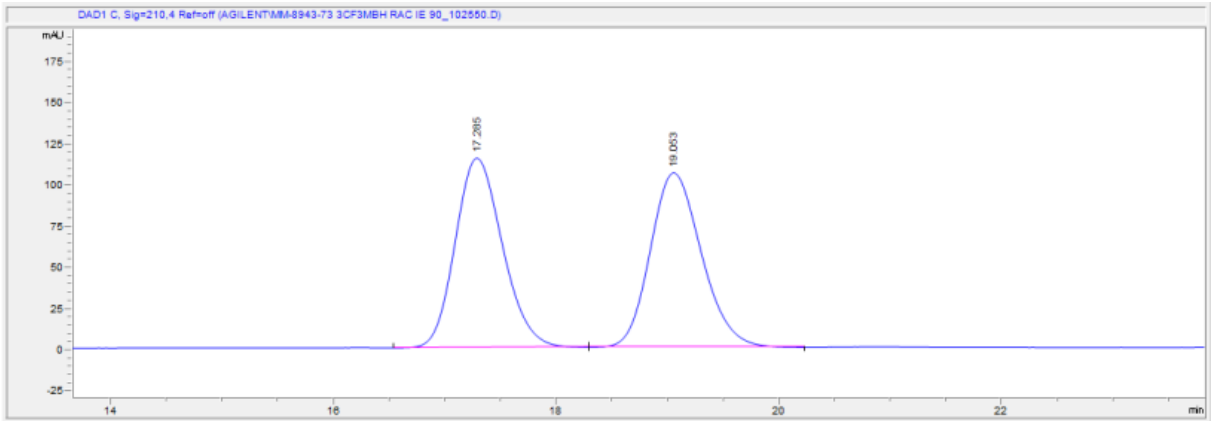
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.686	BB	1.5331	2.60653e4	238.85634	94.8079
2	76.684	BB	1.3208	1427.43689	12.72439	5.1921

3f cinchonine



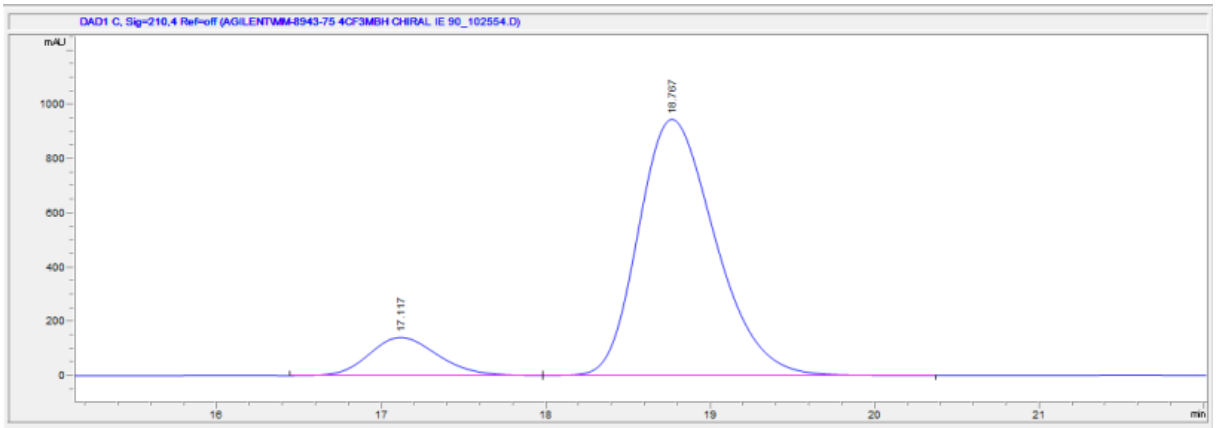
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.098	BB	1.1679	1525.76160	15.42610	6.3191
2	74.618	BB	1.6397	2.26196e4	190.44102	93.6809

3g racemic



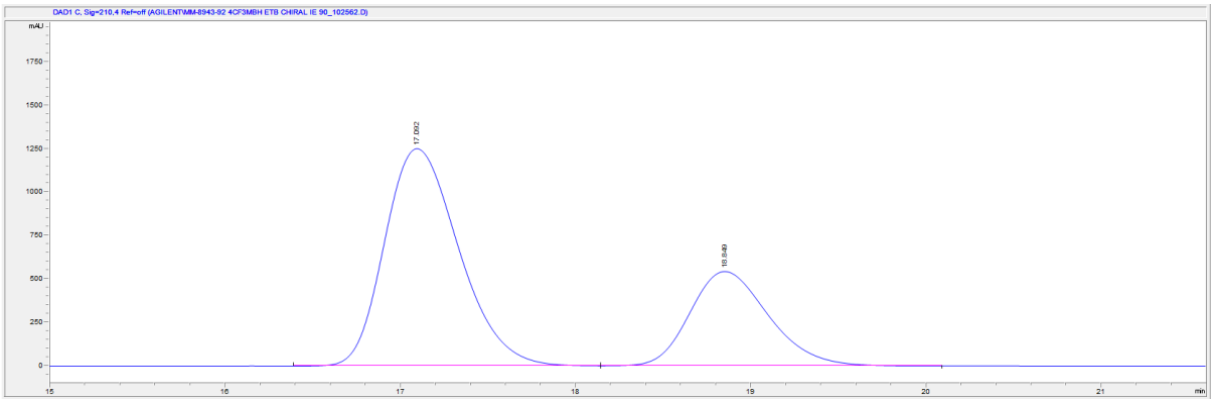
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.285	BB	0.4560	3395.69165	115.17260	50.0560
2	19.053	BB	0.4969	3388.08838	106.01086	49.9440

3g cinchonine



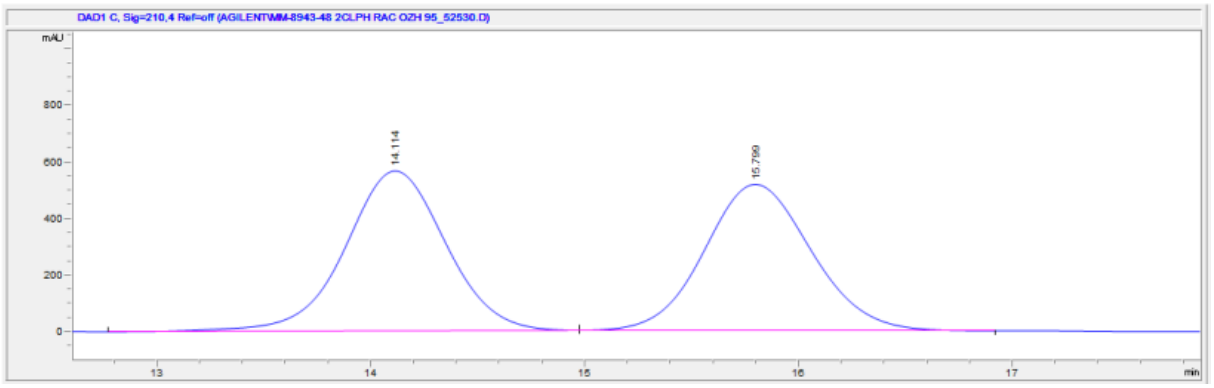
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.117	BB	0.4462	4044.51733	140.33115	11.7041
2	18.767	BB	0.5033	3.05120e4	943.36212	88.2959

3g cinchonidine



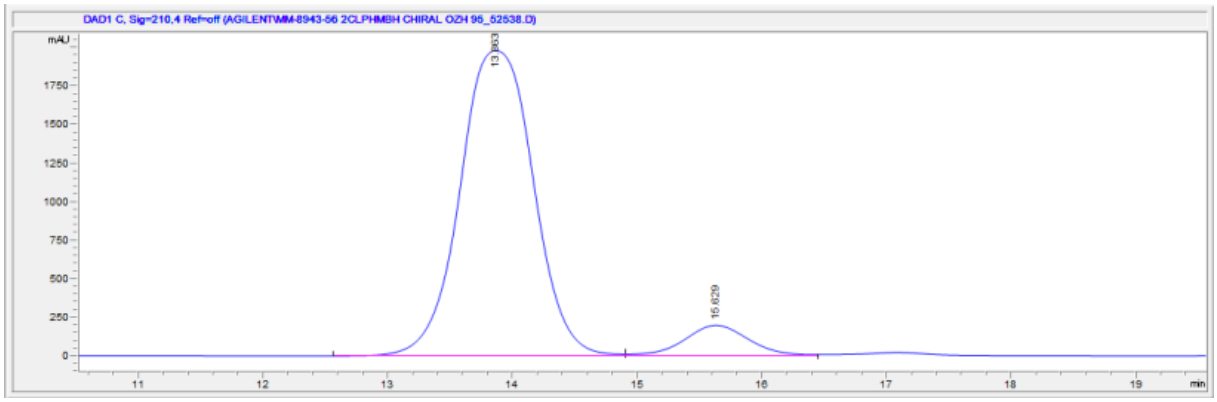
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.092	BV	0.4614	3.67415e4	1248.10413	68.4555
2	18.849	VB	0.4841	1.69306e4	542.54004	31.5445

3h racemic



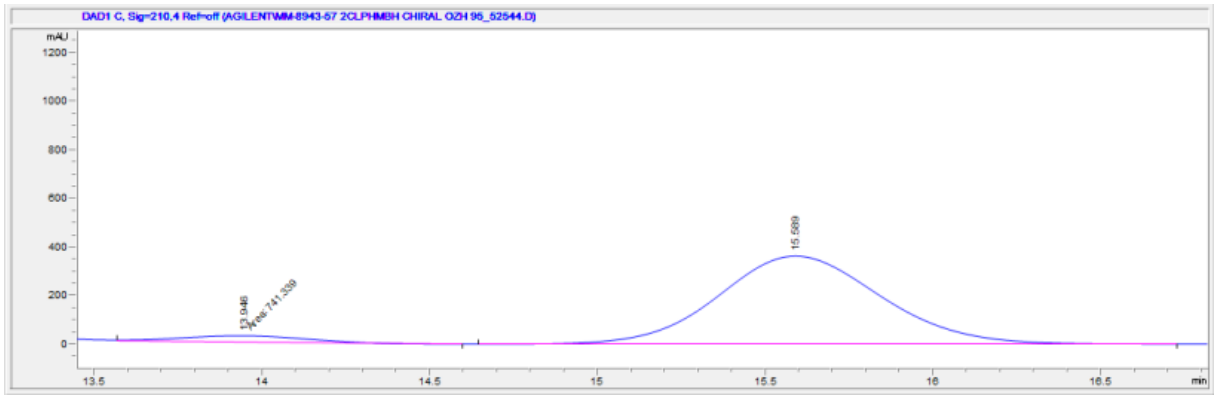
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.114	BV	0.5067	1.86873e4	566.66266	50.7698
2	15.799	VB	0.5402	1.81205e4	517.89227	49.2302

3h quinine



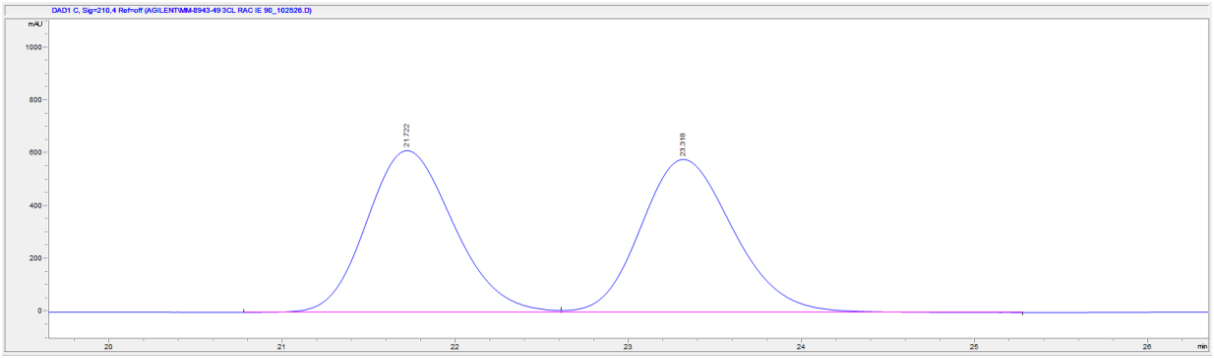
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.863	BV	0.6425	8.11509e4	1986.81567	91.8676
2	15.629	VV	0.5547	7183.68799	198.27872	8.1324

3h cinchonine



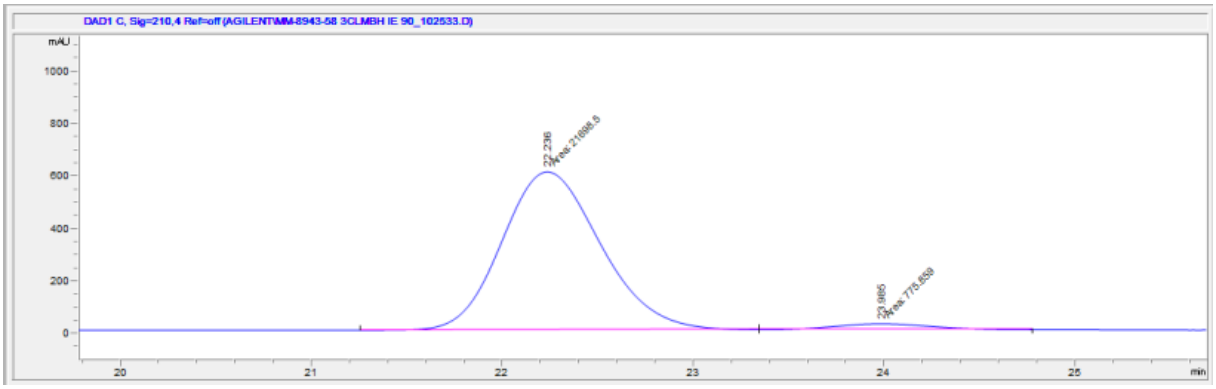
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.946	MM	0.4482	741.33929	27.56478	5.7083
2	15.589	BB	0.5210	1.22458e4	361.73288	94.2917

3i racemic



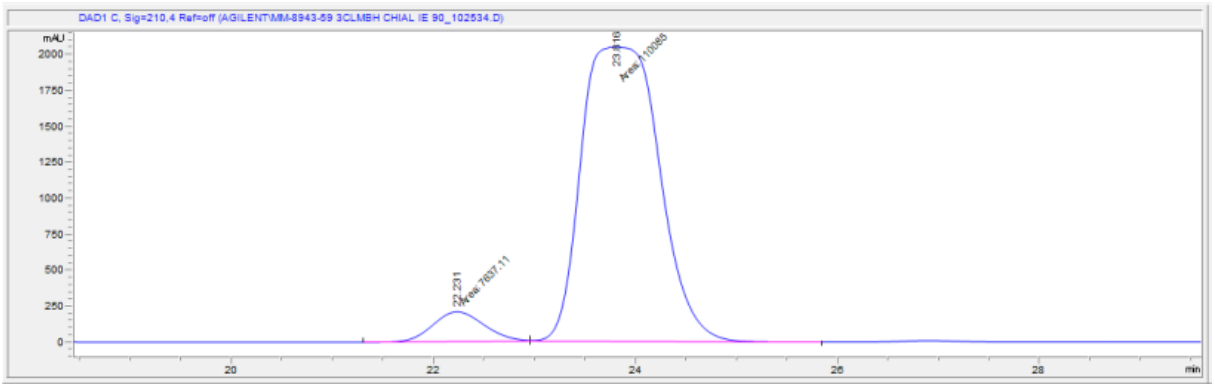
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.722	BV	0.5459	2.13964e4	612.02673	49.8883
2	23.318	VB	0.5772	2.14922e4	578.85095	50.1117

3i quinine



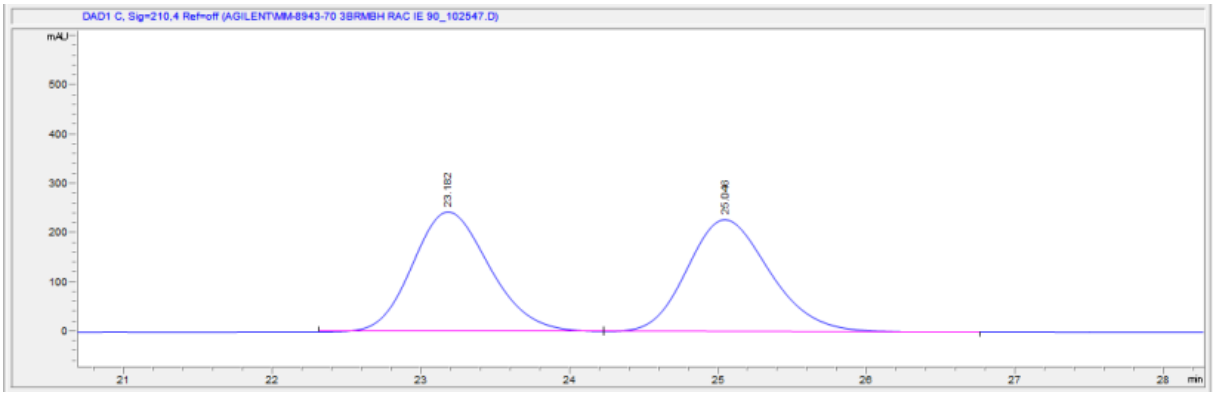
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.236	MM	0.5993	2.16985e4	603.39240	96.5478
2	23.985	MM	0.5867	775.85919	22.03879	3.4522

3i cinchonine



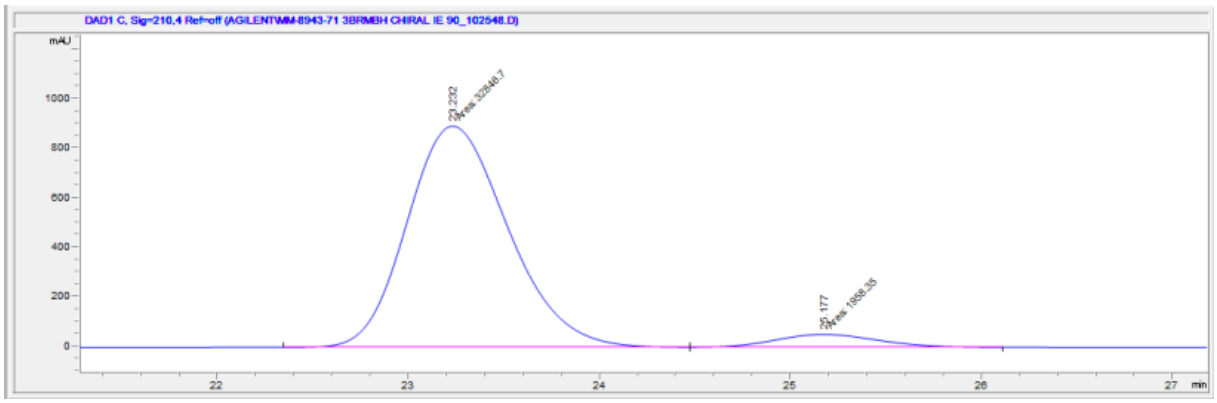
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.231	MM	0.6049	7637.11230	210.43970	6.4874
2	23.816	MM	0.8954	1.10085e5	2049.02905	93.5126

3j racemic



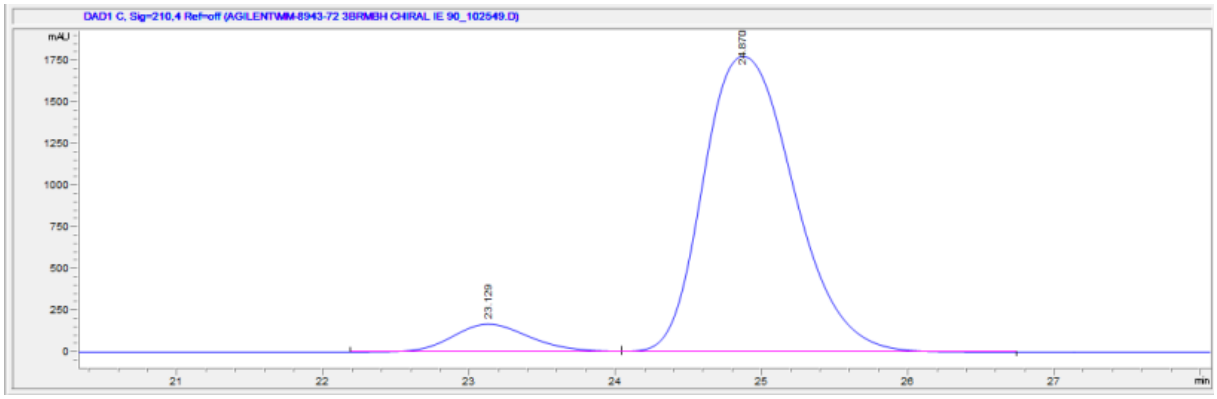
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.182	BV	0.5616	8831.56445	243.24799	49.9717
2	25.046	VB	0.6015	8841.56836	227.45883	50.0283

3j quinine



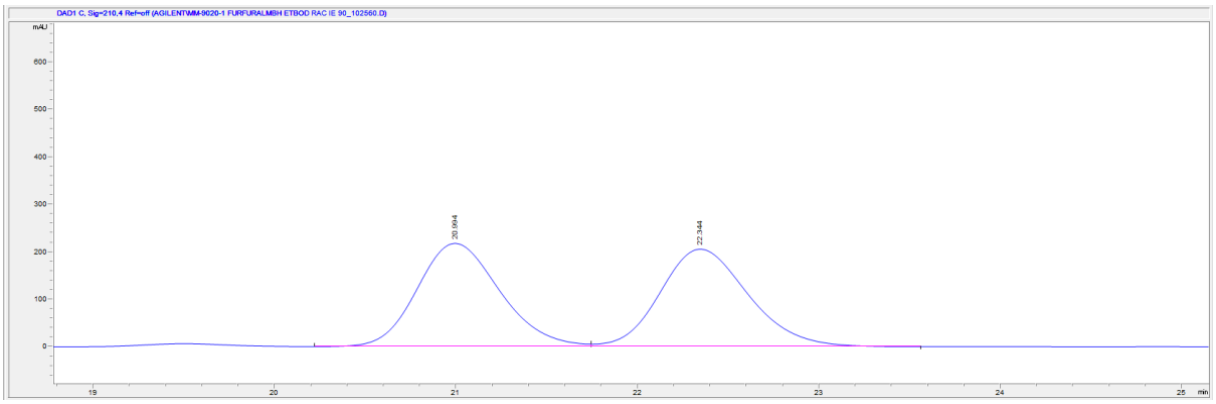
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.232	MM	0.6132	3.28467e4	892.81555	94.3734
2	25.177	MM	0.6269	1958.34741	52.06397	5.6266

3j cinchonine



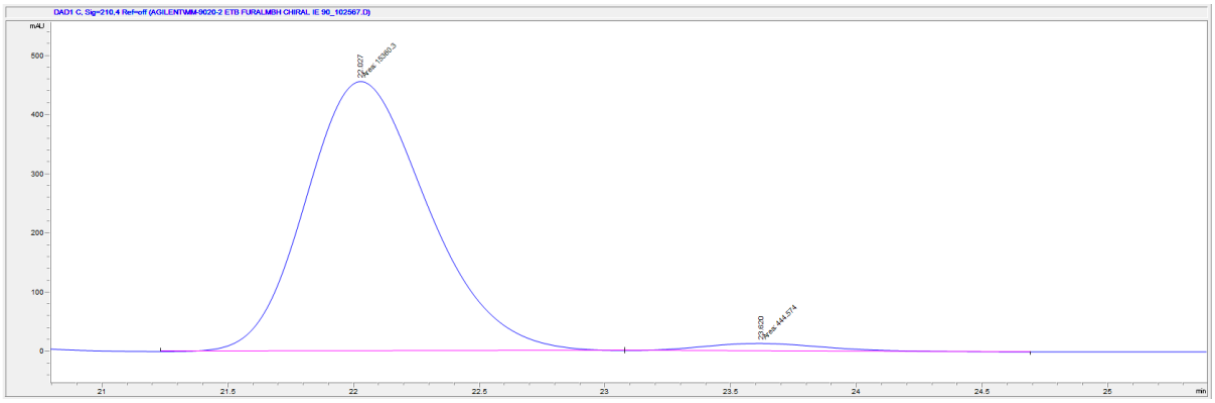
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.129	BV	0.5789	6265.60840	167.32080	7.5651
2	24.870	VB	0.6850	7.65574e4	1775.59546	92.4349

3k racemic



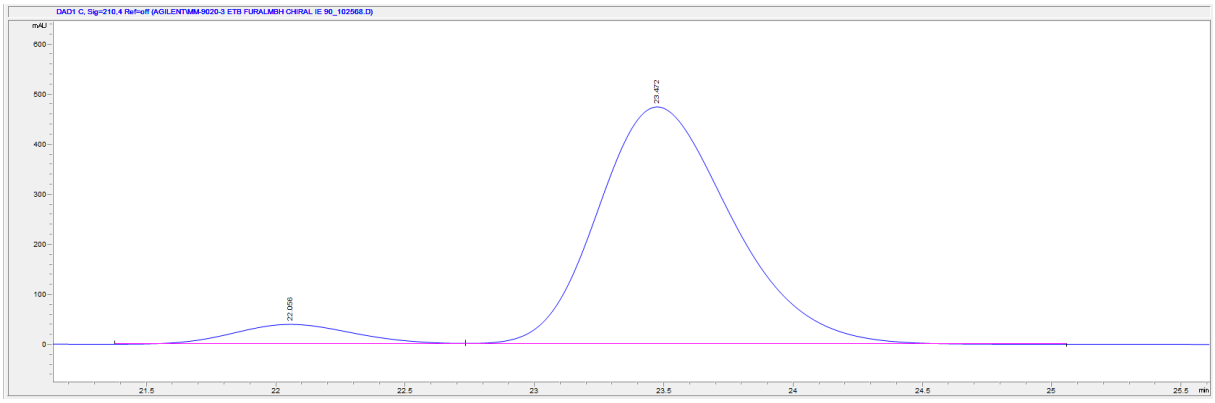
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.994	BV	0.4920	6921.49316	218.24988	49.9204
2	22.344	VB	0.5231	6943.57959	206.07634	50.0796

3k quinine



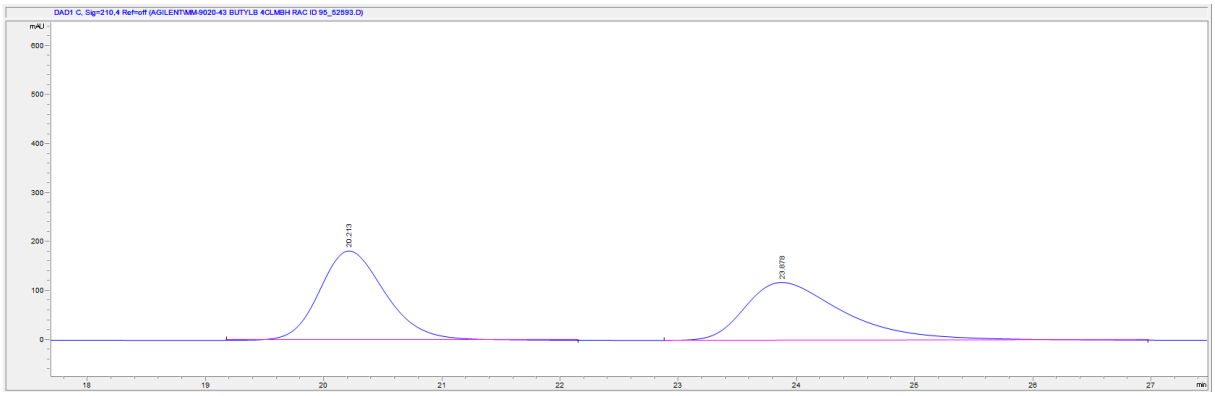
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.027	MM	0.5621	1.53603e4	455.41031	97.1871
2	23.620	MM	0.5714	444.57407	12.96646	2.8129

3k cinchonine



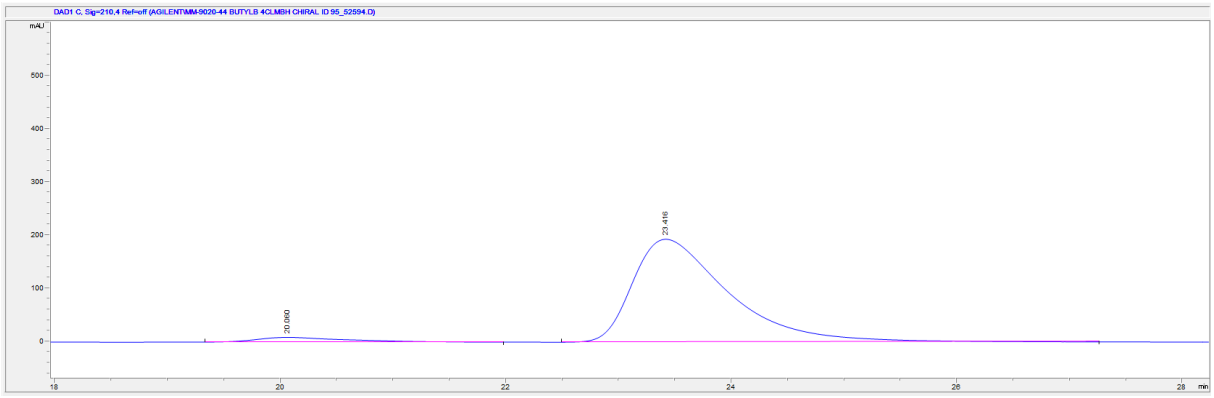
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.056	BV	0.5039	1295.22485	39.56888	7.0698
2	23.472	VB	0.5557	1.70254e4	473.25195	92.9302

3l racemic



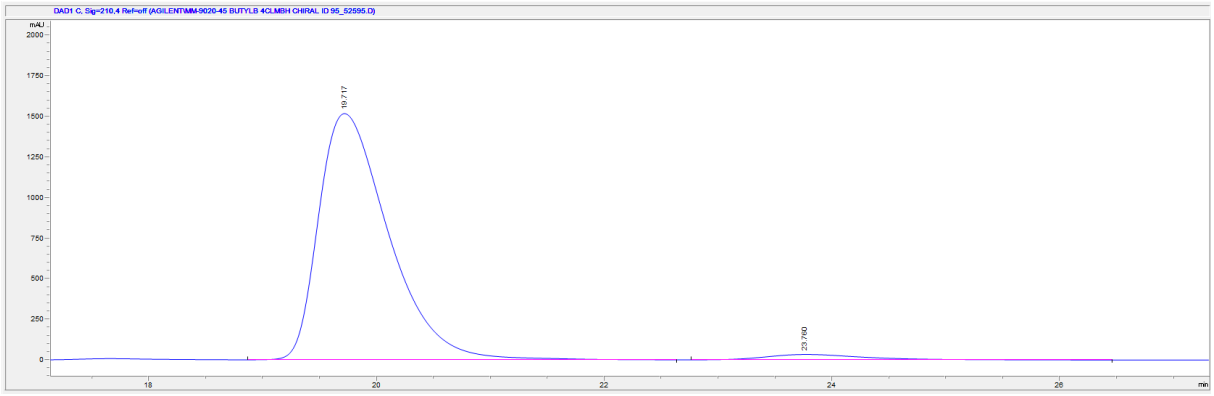
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.213	BB	0.5970	7116.46582	182.46945	50.6609
2	23.878	BB	0.8655	6930.77979	118.29440	49.3391

3l quinine



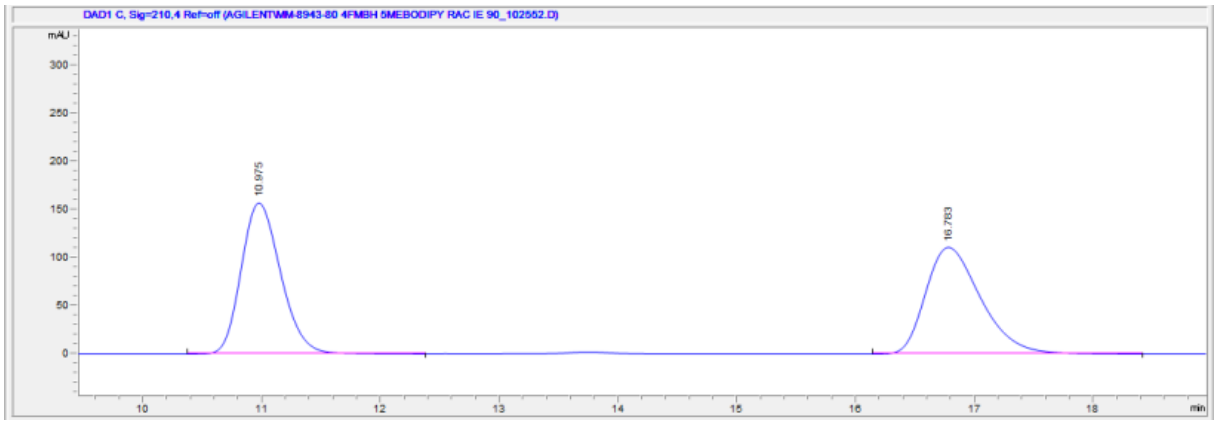
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.060	BB	0.6667	496.75235	8.98897	4.1589
2	23.416	BB	0.8702	1.14475e4	194.05899	95.8411

3l cinchonine



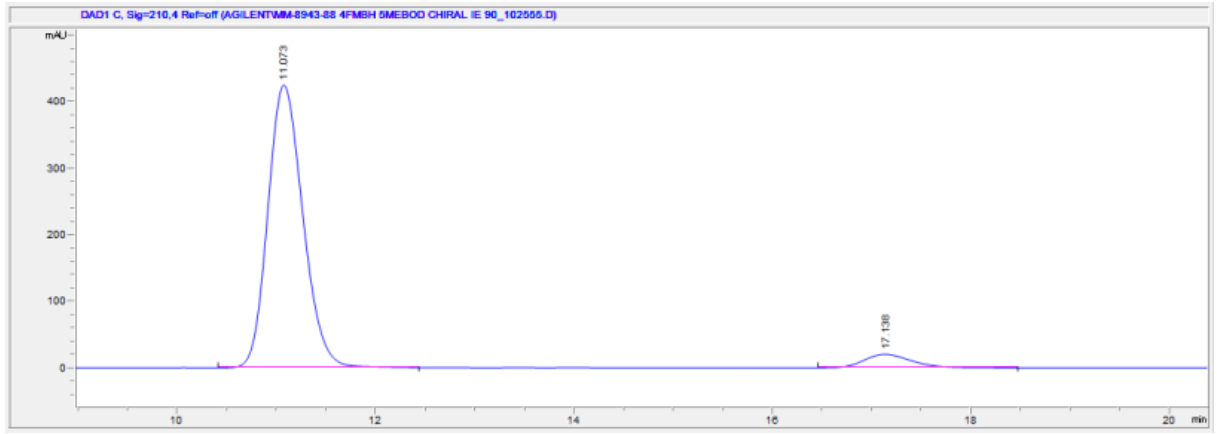
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.717	BB	0.6562	6.46285e4	1519.69202	96.9816
2	23.760	BB	0.8430	2011.48218	33.38048	3.0184

3m racemic



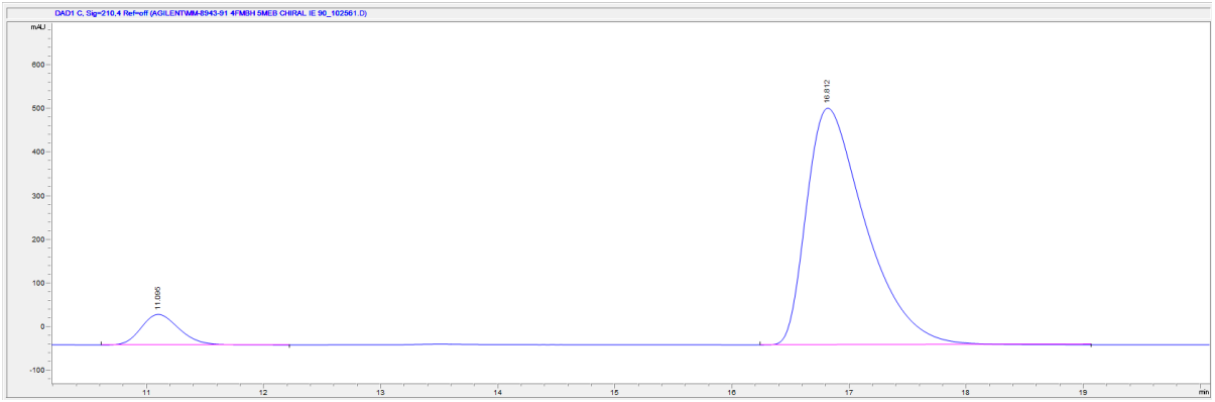
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.975	BB	0.3601	3652.19556	157.73555	50.2874
2	16.783	BB	0.5001	3610.45288	111.40118	49.7126

3m cinchonine



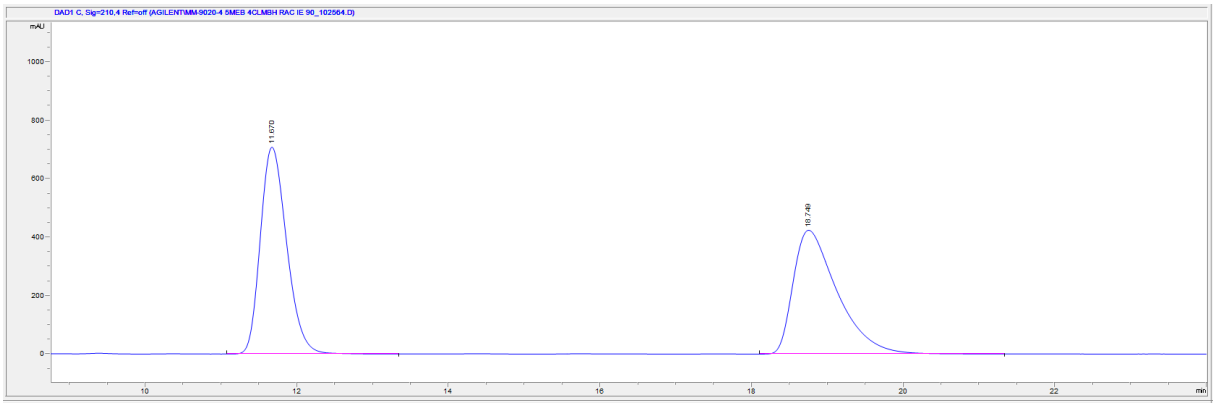
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.073	BB	0.3823	1.04135e4	424.32004	93.9802
2	17.138	BB	0.5024	667.02216	20.03463	6.0198

3m cinchonidine



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.095	BB	0.3518	1582.48059	69.99358	7.6732
2	16.812	BB	0.5326	1.90410e4	543.66583	92.3268

3n racemic

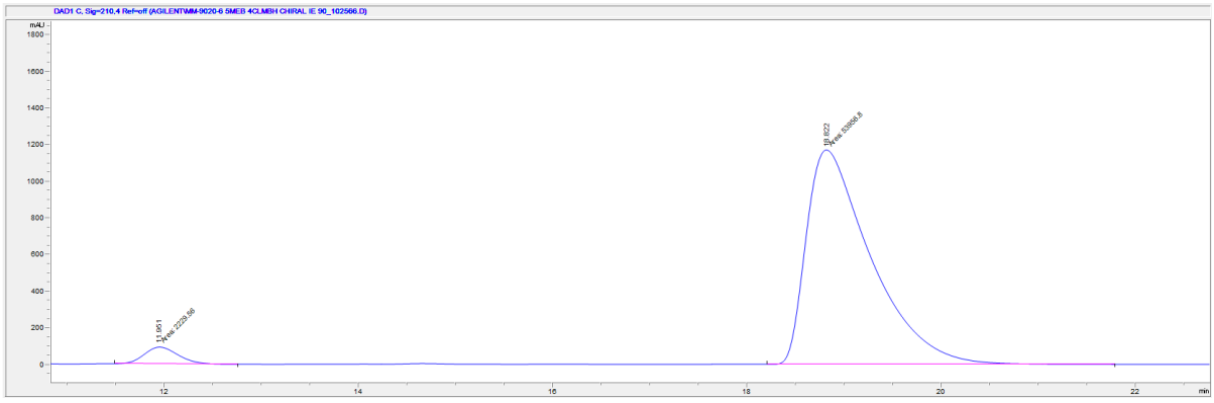


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.670	BB	0.3755	1.70526e4	706.85925	49.9732
2	18.749	BB	0.6026	1.70708e4	423.21832	50.0268

3n cinchonine

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.514	MM	0.5123	6.25799e4	2035.77698	94.9849
2	18.940	MM	0.6057	3304.12622	90.91669	5.0151

3n cinchonidine

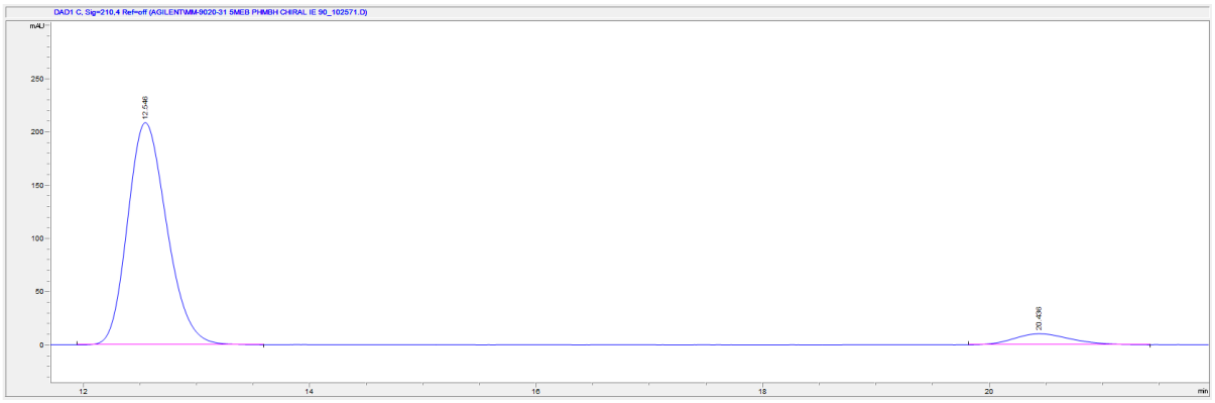


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.951	MM	0.4062	2229.55688	91.47264	3.9681
2	18.822	MM	0.7690	5.39568e4	1169.36951	96.0319

3o racemic

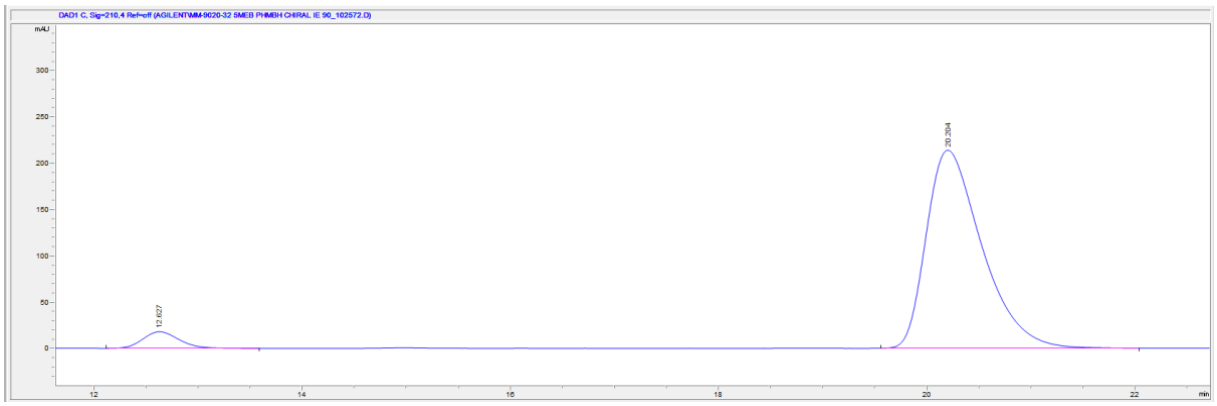
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.386	BB	0.3732	1.34291e4	561.16174	49.9785
2	19.758	BB	0.5674	1.34406e4	360.15982	50.0215

3o cinchonine



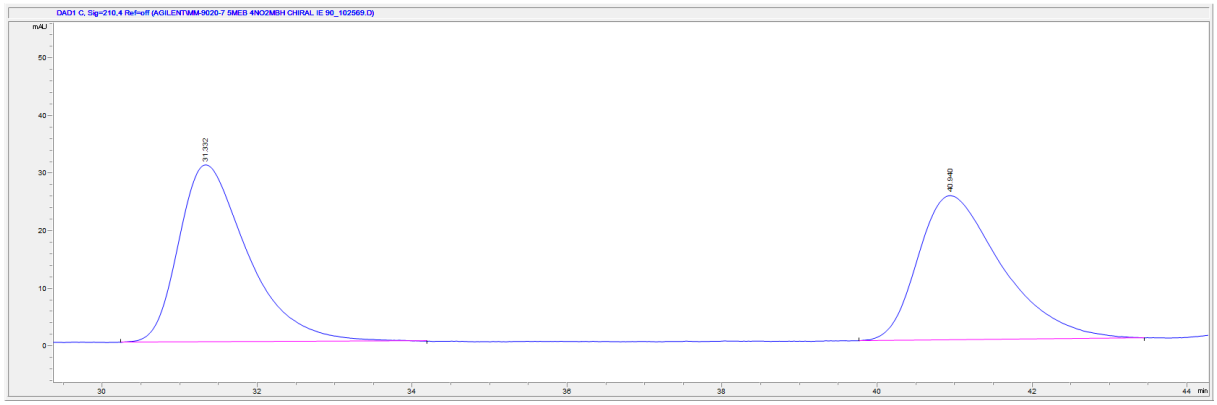
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.546	BB	0.3739	4992.85742	208.11278	93.2590
2	20.436	BB	0.4870	360.89615	10.29441	6.7410

3o cinchonidine



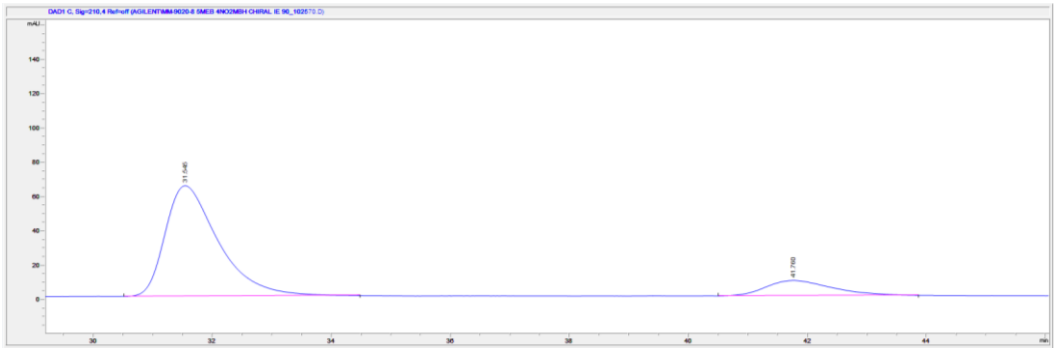
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.627	BB	0.3727	432.08942	17.83053	5.1797
2	20.204	BB	0.5626	7909.87305	213.33762	94.8203

3p racemic



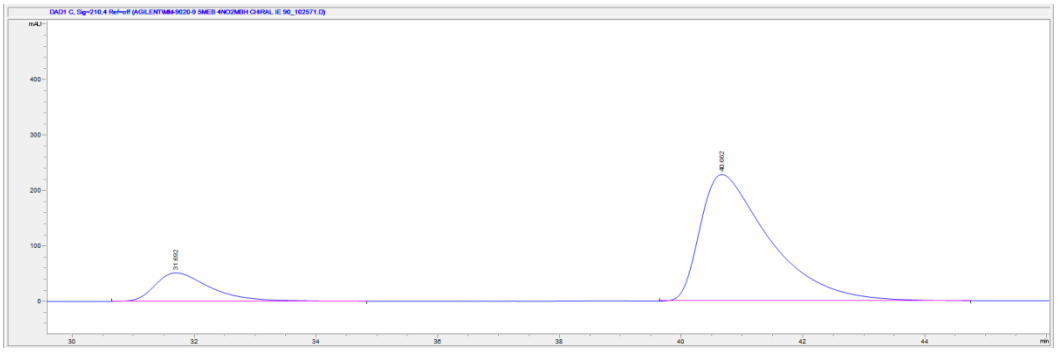
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.332	BB	0.9037	1904.46606	30.70138	50.3587
2	40.940	BB	0.9542	1877.33350	24.99619	49.6413

3p cinchonine



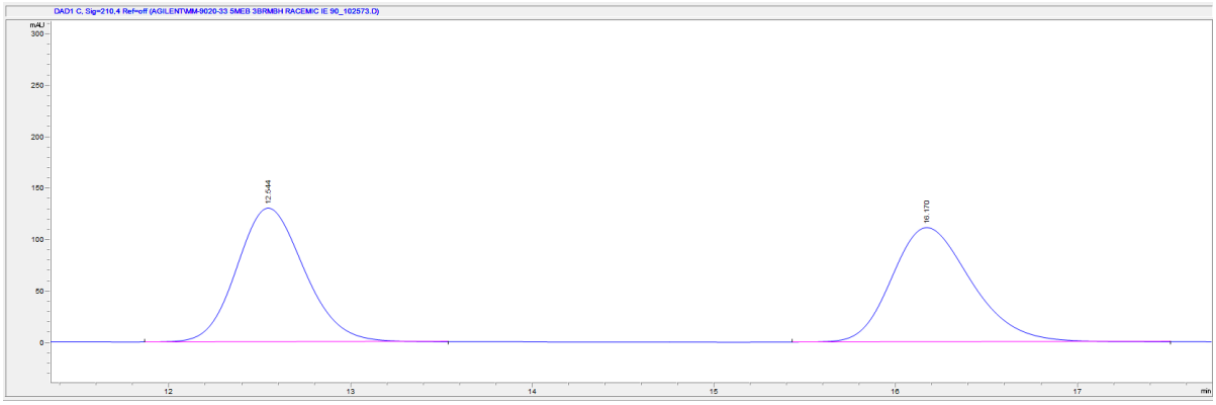
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.545	BB	0.9013	4011.50635	64.52317	85.4477
2	41.760	BB	0.9143	683.18774	8.83391	14.5523

3p cinchonidine



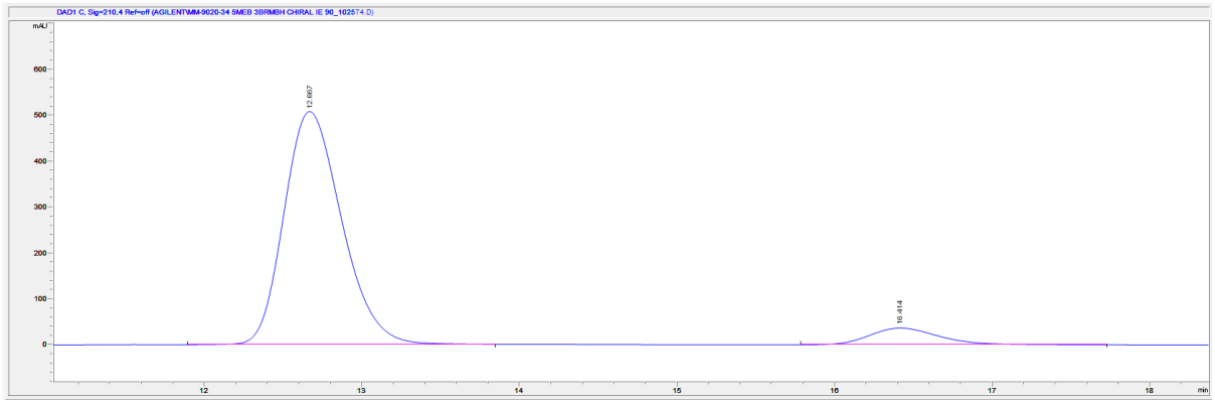
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.692	BB	0.8888	3216.29956	51.34625	15.1554
2	40.662	BB	1.1209	1.80059e4	228.11966	84.8446

3q racemic



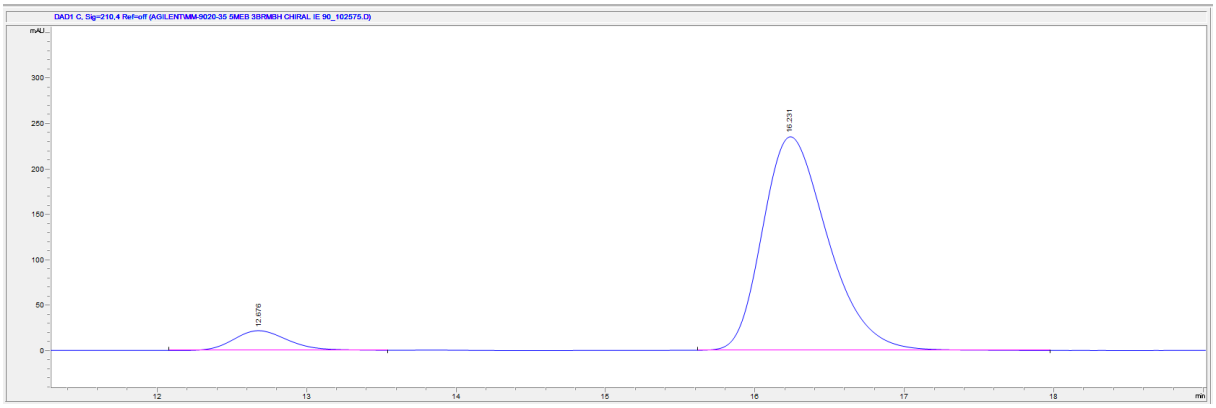
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.544	BB	0.4043	3367.25659	129.96225	49.9195
2	16.170	BB	0.4709	3378.11792	111.04742	50.0805

3q cinchonine



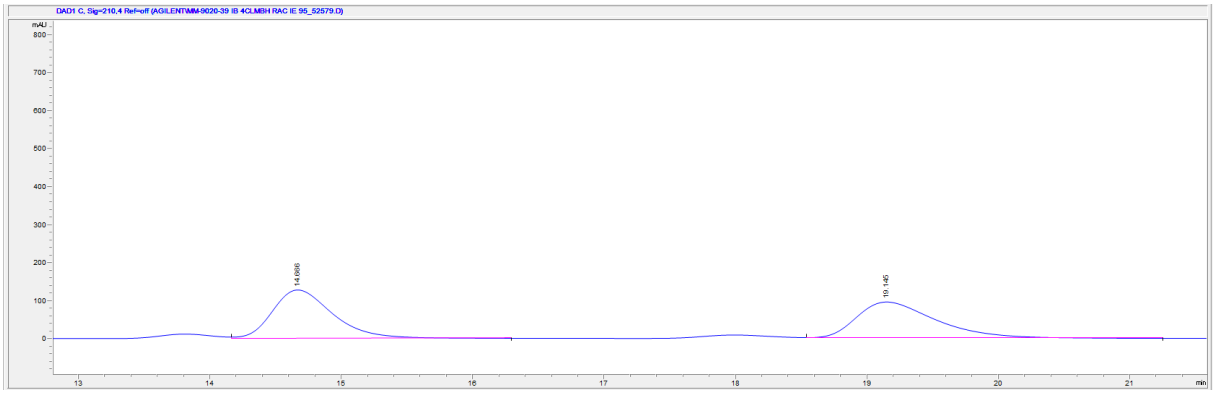
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.667	BB	0.3959	1.28446e4	506.36914	92.0877
2	16.414	BB	0.4665	1103.62000	36.12130	7.9123

3q cinchonidine



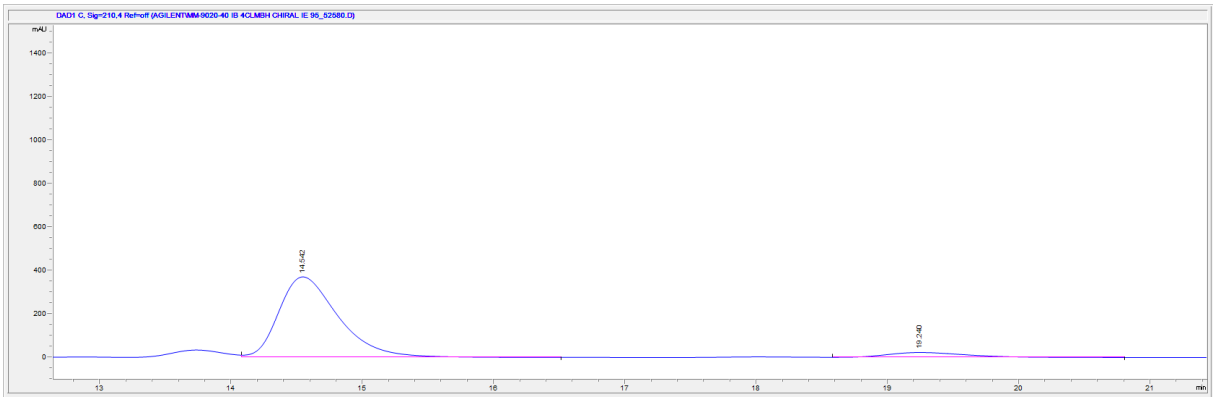
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.676	BB	0.3850	550.74200	21.77747	7.1688
2	16.231	BB	0.4670	7131.70605	235.67038	92.8312

3r racemic



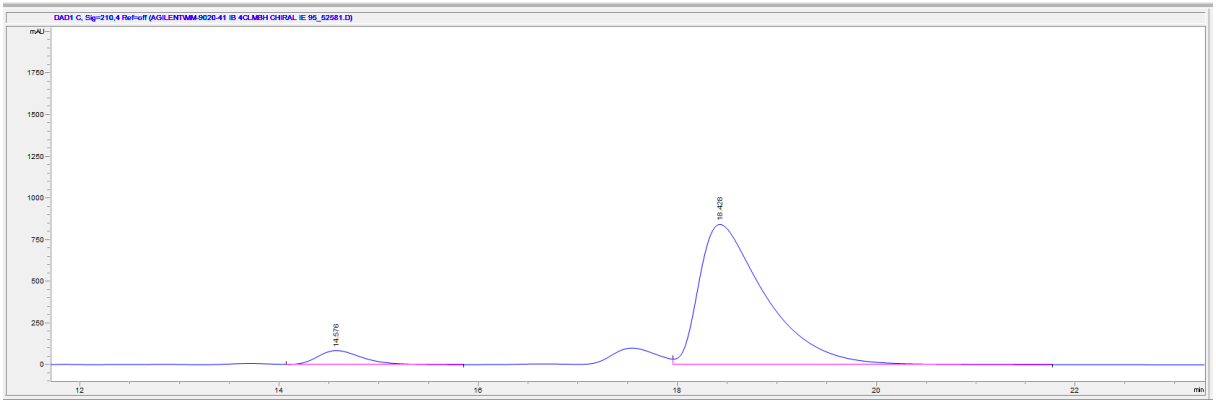
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.666	VB	0.4867	4073.21338	127.51538	50.0327
2	19.145	VB	0.6303	4067.88428	95.62227	49.9673

3r cinchonine



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.542	VB	0.4824	1.17115e4	370.86243	92.5860
2	19.240	BB	0.6064	937.82837	22.40251	7.4140

3r cinchonidine



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.576	VB	0.4762	2663.45483	84.86239	6.3819
2	18.428	VB	0.6849	3.90709e4	842.71863	93.6181

Crystal of racemic 3d

Table S2 Crystal data and structure refinement for 2019-mm04.

Identification code	2019-mm04
Empirical formula	$C_{22}H_{21}BF_2N_2O_2$
Formula weight	394.22
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	12.6493(2)
b/Å	9.2440(2)
c/Å	18.0005(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2104.80(7)
Z	4
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.091
F(000)	824.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.318 to 61.47
Index ranges	-17 ≤ h ≤ 18, -13 ≤ k ≤ 11, -25 ≤ l ≤ 25
Reflections collected	28599
Independent reflections	6184 [R_{int} = 0.0266, R_{sigma} = 0.0208]
Data/restraints/parameters	6184/1/272
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1535
Final R indexes [all data]	R_1 = 0.0724, wR_2 = 0.1622
Largest diff. peak/hole / e Å^{-3}	0.33/-0.17
Flack parameter	0.1(2)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2019-mm04. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	8205.9(16)	4162(3)	6238.4(13)	70.5(6)
F1	5489(2)	8940(4)	2500.3(15)	111.4(9)
O1	7264.3(16)	3224(2)	7155.0(11)	64.2(5)
F2	6244(2)	10046(3)	3489.0(19)	110.9(9)
C15	7367(2)	3939(3)	6520.1(14)	45.6(5)
C10	5560(2)	5227(3)	4943.3(14)	48.2(5)
C9	5645(2)	6380(3)	4345.6(13)	46.4(5)
N1	4830(2)	8421(3)	3727.3(15)	63.5(6)
C8	6517(2)	6454(3)	3859.7(15)	54.5(6)
N2	6560(2)	7519(3)	3313.5(13)	63.0(6)
C12	6474.5(19)	5369(3)	5515.3(13)	44.5(5)

C4	4815(2)	7349(3)	4273.9(14)	50.0(5)
C13	6338(2)	4381(3)	6187.0(13)	48.5(5)
C11	5482(3)	3709(3)	4610.3(19)	64.3(7)
C7	7426(3)	5594(4)	3772.7(19)	68.7(8)
C3	3844(2)	7482(4)	4659.2(19)	62.9(7)
C16	6611(2)	6933(3)	5782.7(14)	49.8(5)
C1	3924(3)	9151(4)	3776(3)	85.4(11)
C5	7451(3)	7304(5)	2918(2)	82.1(11)
C2	3294(3)	8609(5)	4339(3)	84.0(11)
C00L	8236(3)	2741(5)	7503(2)	88.2(12)
C14	5443(3)	3923(4)	6476(2)	75.0(9)
C6	8001(3)	6137(5)	3185(2)	85.4(11)
C17	7558(3)	7626(4)	5655(2)	72.6(8)
C21	5806(3)	7649(4)	6142.5(19)	75.3(9)
B1	5796(3)	8785(4)	3233(2)	70.5(10)
C18	7696(5)	9044(6)	5887(3)	117(2)
C20	5930(5)	9043(5)	6358(3)	107.3(17)
C19	6849(7)	9768(5)	6248(3)	129(3)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2019-mm04. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	52.7(10)	90.3(17)	68.3(12)	19.7(11)	0.9(10)	6.5(10)
F1	124.4(19)	141(2)	68.5(12)	47.0(13)	-28.4(13)	-1.5(17)
O1	70.8(12)	69.0(12)	53(1)	21.0(9)	-3.1(9)	12(1)
F2	119.3(19)	68.1(13)	145(2)	22.2(14)	-18.0(17)	-40.9(13)
C15	52.2(12)	40.7(10)	44(1)	2.8(8)	-2.0(9)	4.6(9)
C10	50.2(12)	45.0(12)	49.4(12)	7.7(9)	-4.2(10)	-1.4(9)
C9	54.5(12)	43.6(11)	41(1)	4.0(9)	-8.3(9)	-6.0(9)
N1	67.9(14)	52.0(12)	70.5(15)	13.3(11)	-23.9(12)	-6.5(10)
C8	58.2(14)	61.5(15)	43.8(12)	6.5(10)	-7.4(10)	-5.2(12)
N2	68.1(14)	73.4(15)	47.6(12)	13.3(10)	-6.9(10)	-19.2(12)
C12	44.8(10)	45.5(11)	43.3(10)	7.4(9)	-2.5(9)	1.4(9)
C4	51.8(12)	44.9(11)	53.3(12)	3.9(10)	-13.2(10)	-8.2(9)
C13	52.1(12)	46.0(12)	47.4(12)	12.0(9)	-2.7(10)	0.7(10)
C11	72.3(17)	48.2(14)	72.3(18)	2.9(12)	-10.2(14)	-10.0(12)
C7	65.8(16)	84(2)	56.1(15)	-5.2(15)	2.6(13)	8.4(15)
C3	55.4(15)	65.5(18)	67.7(17)	-2.2(12)	-7.0(13)	-1.5(12)
C16	57.4(13)	45.4(12)	46.4(11)	10.8(9)	-13.3(10)	-2.2(10)
C1	84(2)	61.3(18)	111(3)	16.8(19)	-35(2)	7.7(17)
C5	78(2)	116(3)	53.1(15)	13.0(18)	5.7(15)	-26(2)
C2	65.2(19)	80(2)	107(3)	-6(2)	-19.4(19)	18.3(17)
C00L	96(3)	97(3)	71(2)	24.0(18)	-18.6(19)	30(2)
C14	54.7(16)	88(2)	82(2)	37.3(19)	1.3(14)	-0.7(15)
C6	73.2(19)	122(3)	60.9(17)	-6.5(19)	11.1(17)	-4(2)

C17	80.0(19)	64.0(18)	73.8(19)	14.0(14)	-10.0(16)	-21.3(15)
C21	81(2)	76(2)	68.9(19)	-14.5(15)	-15.4(16)	18.5(17)
B1	85(2)	63.5(19)	63.5(18)	24.1(15)	-20.4(18)	-18.8(17)
C18	154(5)	81(3)	116(4)	28(3)	-44(4)	-61(3)
C20	152(4)	78(3)	92(3)	-29(2)	-38(3)	35(3)
C19	224(7)	47(2)	116(4)	-9(2)	-78(5)	2(3)

Table S5 Bond Lengths for 2019-mm04.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C15	1.194(3)	N2	C5	1.348(5)
F1	B1	1.383(4)	N2	B1	1.525(5)
O1	C15	1.326(3)	C12	C13	1.525(3)
O1	C00L	1.451(4)	C12	C16	1.534(4)
F2	B1	1.375(5)	C4	C3	1.415(4)
C15	C13	1.490(3)	C13	C14	1.316(4)
C10	C9	1.518(3)	C7	C6	1.379(6)
C10	C12	1.554(3)	C3	C2	1.380(5)
C10	C11	1.529(4)	C16	C17	1.378(4)
C9	C8	1.409(4)	C16	C21	1.376(4)
C9	C4	1.387(4)	C1	C2	1.383(7)
N1	C4	1.396(3)	C5	C6	1.371(7)
N1	C1	1.333(5)	C17	C18	1.387(7)
N1	B1	1.548(5)	C21	C20	1.355(6)
C8	N2	1.393(4)	C18	C19	1.420(10)
C8	C7	1.407(5)	C20	C19	1.357(10)

Table S6 Bond Angles for 2019-mm04.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C15	O1	C00L	116.3(2)	N1	C4	C3	107.2(2)
O2	C15	O1	122.6(2)	C15	C13	C12	112.6(2)
O2	C15	C13	123.9(2)	C14	C13	C15	120.3(2)
O1	C15	C13	113.4(2)	C14	C13	C12	127.1(2)
C9	C10	C12	110.94(19)	C6	C7	C8	108.1(3)
C9	C10	C11	111.8(2)	C2	C3	C4	107.3(3)
C11	C10	C12	112.7(2)	C17	C16	C12	118.9(3)
C8	C9	C10	122.0(2)	C21	C16	C12	121.2(3)
C4	C9	C10	117.7(2)	C21	C16	C17	119.9(3)
C4	C9	C8	120.2(2)	N1	C1	C2	111.1(3)
C4	N1	B1	124.8(3)	N2	C5	C6	110.8(3)
C1	N1	C4	107.5(3)	C3	C2	C1	106.8(3)
C1	N1	B1	127.3(3)	C5	C6	C7	106.7(4)
N2	C8	C9	120.2(3)	C16	C17	C18	119.9(5)
N2	C8	C7	106.8(3)	C20	C21	C16	120.4(5)

C7	C8	C9	132.9(3)	F1	B1	N1	110.5(3)
C8	N2	B1	125.8(3)	F1	B1	N2	110.3(4)
C5	N2	C8	107.6(3)	F2	B1	F1	110.3(3)
C5	N2	B1	126.4(3)	F2	B1	N1	108.5(4)
C13	C12	C10	112.98(19)	F2	B1	N2	110.9(3)
C13	C12	C16	109.2(2)	N2	B1	N1	106.2(2)
C16	C12	C10	111.80(18)	C17	C18	C19	119.3(5)
C9	C4	N1	120.9(3)	C21	C20	C19	121.8(5)
C9	C4	C3	131.9(2)	C20	C19	C18	118.7(4)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2019-mm04.

Atom	*x*	*y*	*z*	U(eq)
H10	4885.95	5408.75	5217.93	58
H12	7143.34	5080.32	5259.02	53
H11A	4903.58	3680.74	4248.69	96
H11B	5345.04	3007.53	5006.75	96
H11C	6148.67	3466.96	4361.9	96
H7	7611.53	4780.16	4067.65	82
H3	3614.39	6901.48	5063.81	75
H1	3735.89	9940.56	3464.68	103
H5	7667.93	7882.91	2509.14	99
H2	2613.06	8947.55	4477.63	101
H00A	8608.99	2080.24	7167.79	132
H00B	8069.72	2237.23	7967.98	132
H00C	8686.19	3578.56	7609.85	132
H6	8652.72	5773.71	3000.4	102
H17	8116.04	7132.6	5408.72	87
H21	5158.93	7162.23	6240.4	90
H18	8348.67	9525.72	5805.63	140
H20	5356.96	9526.94	6592.61	129
H19	6925.51	10740.46	6409.95	155
H14A	5420(30)	3260(50)	6850(30)	88(12)
H14B	4730(30)	4150(40)	6310(20)	77(11)

Experimental

A suitable crystal was selected and **mounted** on a **XtaLAB AFC12 (RCD3): Kappa single** diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [S1], the structure was solved with the ShelXT [S2] structure solution program using Intrinsic Phasing and refined with the ShelXL [S3] refinement package using Least Squares minimisation.

Crystal structure determination of [2019-mm04]

Crystal Data for $C_{22}H_{21}BF_2N_2O_2$ (*M* =394.22 g/mol): orthorhombic, space group $Pca2_1$ (no. 29), *a* = 12.6493(2) Å, *b* = 9.2440(2) Å, *c* = 18.0005(3) Å, *V* = 2104.80(7) Å^3, *Z* = 4, *T* = 100(2) K, μ(MoKα) = 0.091 mm^{-1}, *Dcalc* = 1.244 g/cm^3, 28599 reflections measured (6.318° ≤ 2Θ ≤ 61.47°), 6184 unique (R_{int}

= 0.0266, R_{sigma} = 0.0208) which were used in all calculations. The final R_1 was 0.0612 (I > 2σ(I)) and wR_2 was 0.1622 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

C10(H10), C12(H12)

2.b Aromatic/amide H refined with riding coordinates:

C7(H7), C3(H3), C1(H1), C5(H5), C2(H2), C6(H6), C17(H17), C21(H21), C18(H18), C20(H20), C19(H19)

2.c Idealised Me refined as rotating group:

C11(H11A,H11B,H11C), C00L(H00A,H00B,H00C)

Photophysical properties

Absorption spectra were recorded on a Perkin–Elmer Lambda 650 UV/Vis spectrophotometer with a temperature-controlled cell.

Steady-state fluorescence emission spectra were performed on a JASCO FP-6500 spectrofluorometer equipped with a 450 W xenon lamp for excitation.

Fluorescence-decay traces of solutions were recorded by the single-photon timing method on a FluoTime 200 fluorometer (PicoQuant, Inc.). The excitation was achieved with an LDH-505 laser head (PicoQuant, Inc.), and the observation was performed through a monochromator at corresponded emission wavelengths. The pulse repetition rate was 20 MHz. Fluorescence-decay histograms were collected in 1320 channels using cuvettes 10×10 mm. The time increment per channel was 36 ps. Histograms of the instrument-response functions (using a LUDOX scatterer) and sample decays were re-corded until they typically reached 2×10^4 counts in the maximum l. Three fluorescence decays were recorded for all of the samples. The fluorescence-decay traces were individually analyzed by using an iterative deconvolution method with exponential models that employed FluoFit software (PicoQuant, Inc.).

Quantum yield and data analysis

The relative fluorescence quantum yield values were determined using the Knowing formula:

$$\emptyset = \emptyset_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2} \quad \text{[Eq. S1]}$$

where Φ and Φ_R denote the fluorescence quantum yield of the sample and the reference, respectively, I and I_R the integrated fluorescence spectra of the sample and the reference, OD and OD_R the absorption at the excitation wavelength of the sample and the reference and n and n_R the refractive index of the solvent where the sample and reference are dissolved. As references, we have used Fluorescein in 0,1 M NaOH (Φ = 0.95) [S4]. The dyes and reference were excited at the maximum of each dye (see table).

Data graphical representation and quantum yield calculation was realized using Originpro 8.5 software (OriginLab, corp). Fluorescence decay curves were analyzed individually and globally through an iterative deconvolution method with exponential models using the software FluoFit (PicoQuant, Inc.).

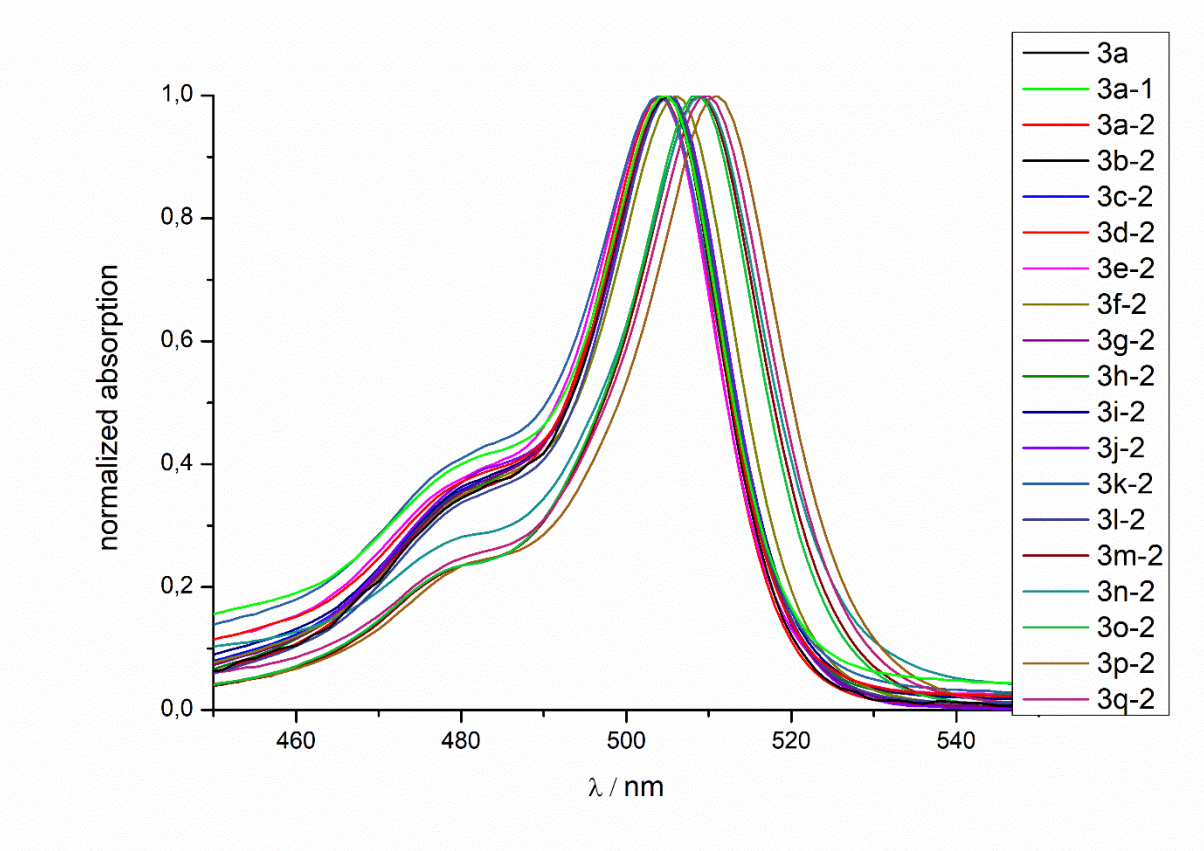


Figure S1. Absorbance spectra of compounds **3a-s** (1×10^{-6} M in chloroform).

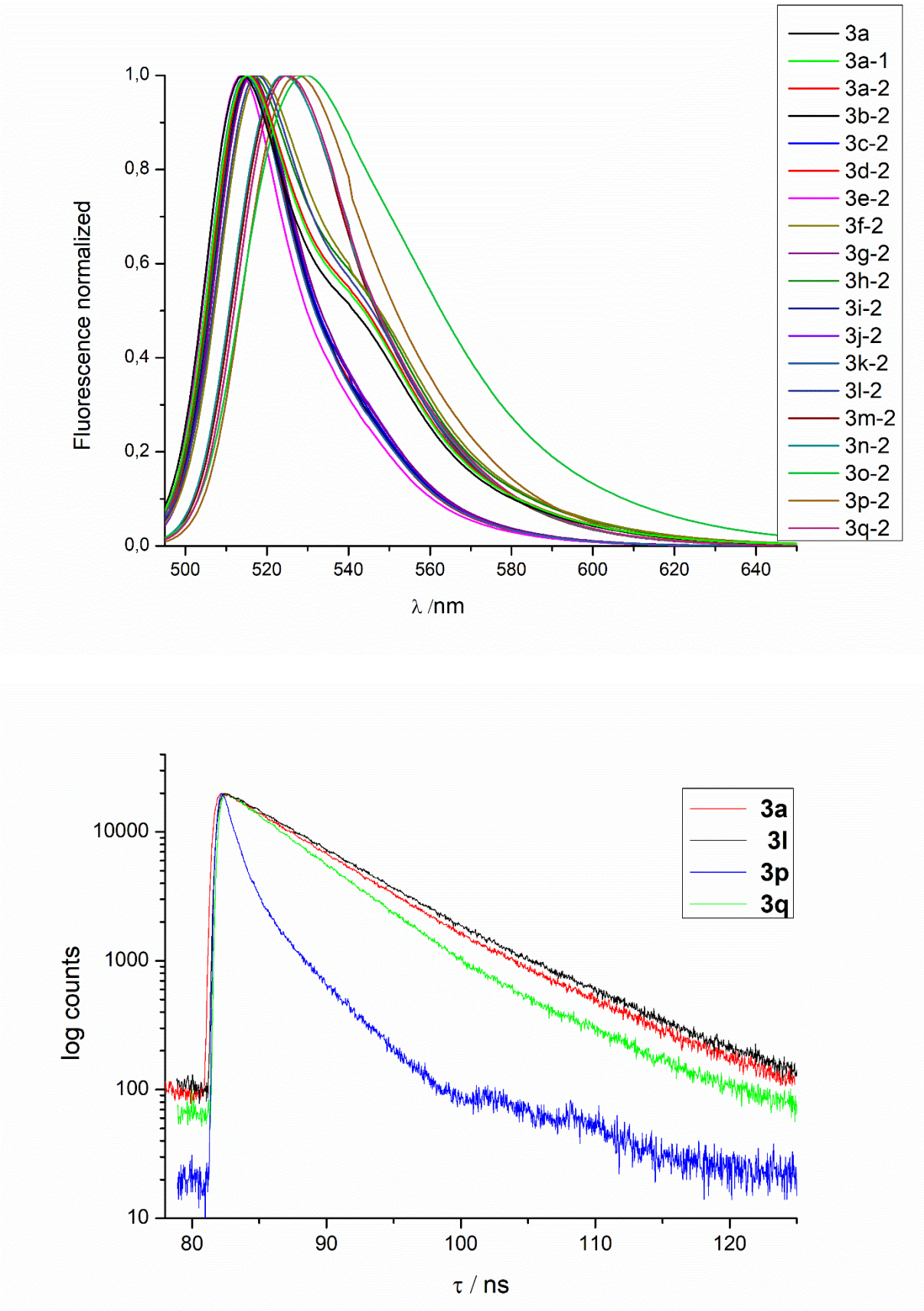


Figure S2. A) Fluorescence spectra of compounds **3a-s** (1×10^{-6} M in chloroform).

b) Fluorescence decay profiles of selected compound **3a**, **3l**, **3p** and **3q**. For clarity we selected a representative decay for the similar fluorescence lifetime

Table S8: Maximum absorption and molar extinction coefficient at this maximum

Compound	**Catalyst**	λ_{abs}^{max} / nm	ε_{max}/ $M^{-1}cm^{-1}$
3a	-	505	95100
3a	II	505	89416
3a	I	505	74767
3b	II	505	94023
3c	II	505	38116
3d	II	504	41578
3e	II	504	68124
3f	II	506	53860
3g	II	505	82534
3h	II	505	90506
3i	II	505	65809
3j	II	505	98484
3k	II	504	69203
3l	II	505	14898
3m	II	509	90854
3n	II	509	67147
3o	II	509	73151
3p	II	511	14499
3q	II	510	80329

Electronic circular dichroism measurements

Electronic circular dichroism (ECD) was recorded in an Olis DSM172 spectrophotometer equipped with a xenon lamp of 150 W. The spectra were recorded at 1×10^{-6} M concentrations in HPLC grade solvents and room temperature. For ECD measurements a fixed slitwidth of 1mm and 0.1 s of integration time were selected, the ECD spectra showed in Figure S4 are an average spectra calculated after 50 scans (each one).

Theoretical calculations

All the calculations were performed by using the Gaussian 09 suite.[S5] Geometry optimizations of seven conformations of compound **3a** were carried out at DFT-CAMB3LYP/6-31G(d,p) level of theory. Harmonic frequencies were calculated in order to corroborate that found geometries were true minima. Electronic transitions were studied by TD-DFT method at the same level of theory. Figure S3 shows the conformation of the six calculated geometries.

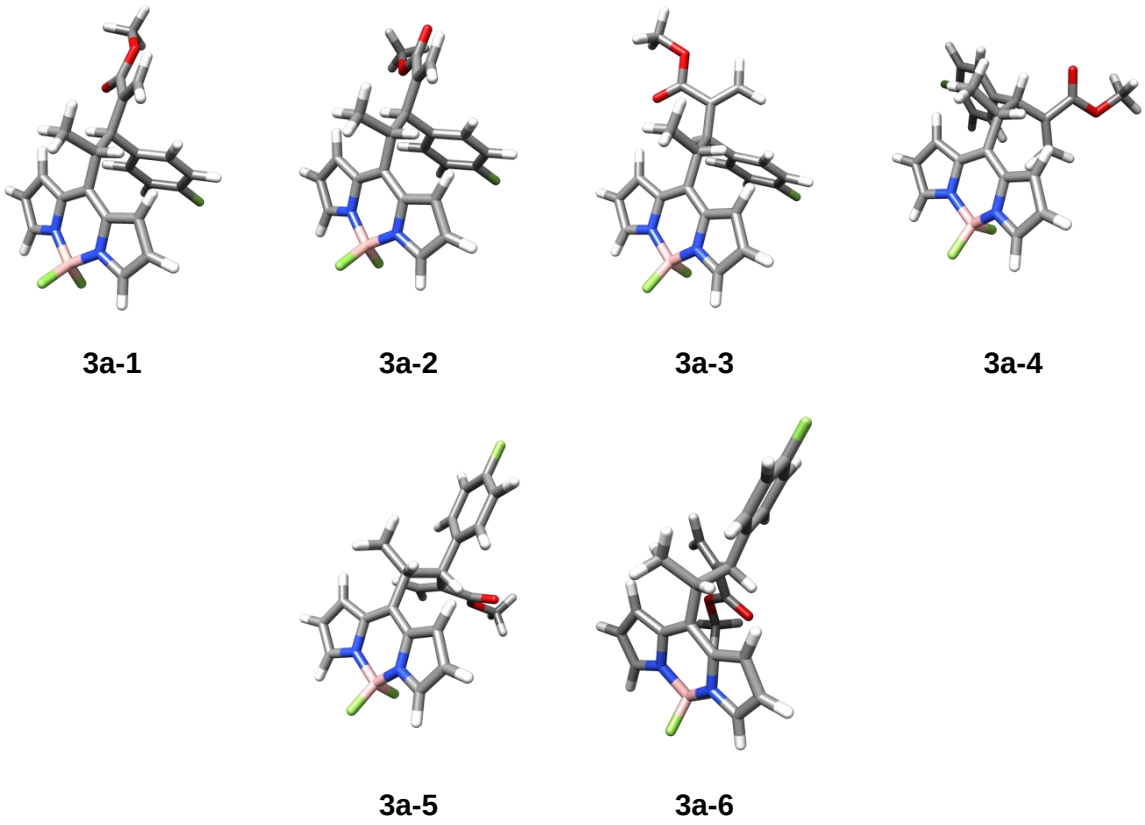


Figure S3. Calculated geometries for the 7 less energetic conformations of compound **3a**.

According to the calculated relative energies of the optimized conformers of compound **3a**, the corresponding Boltzmann distribution was determined using the equation S2:

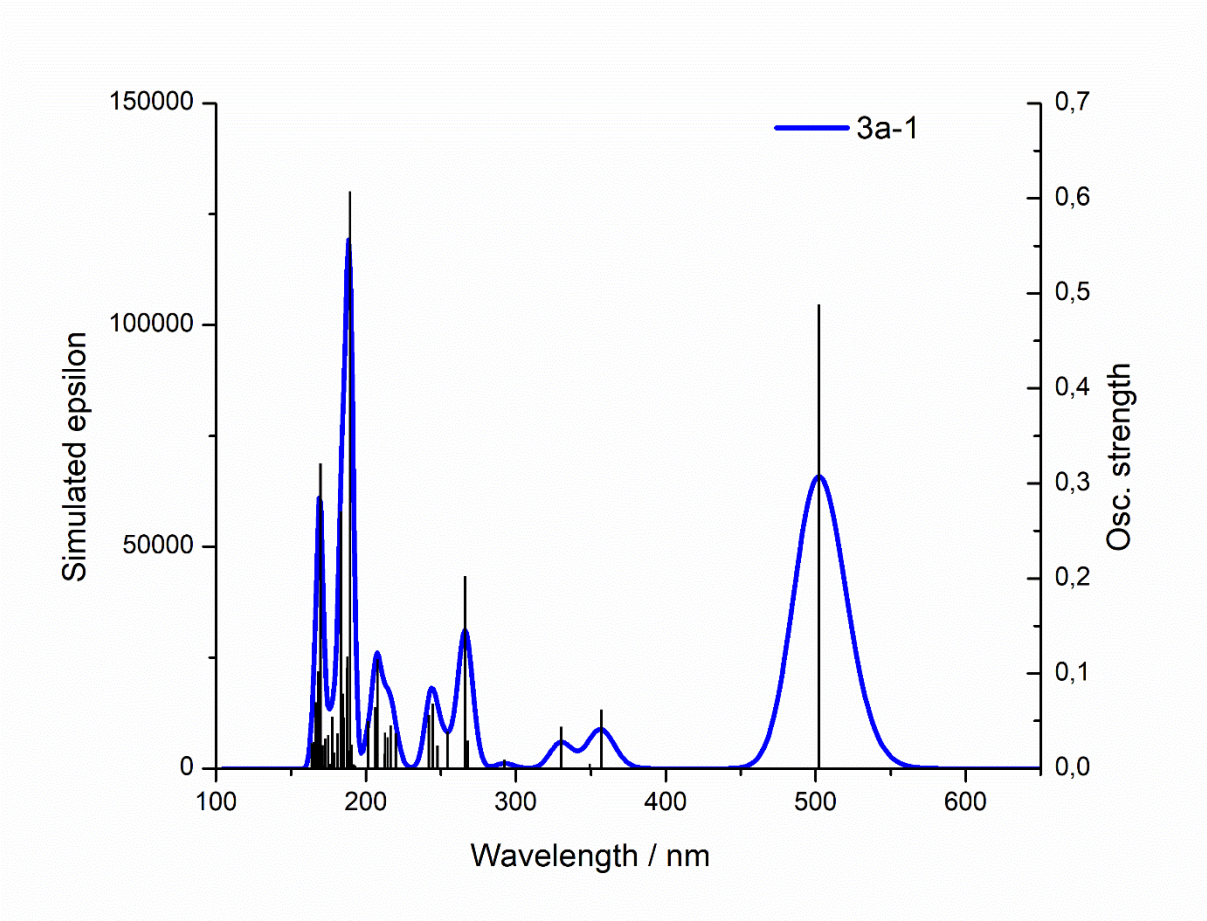
$$\frac{N_i}{N} = \frac{e^{\frac{-E_i}{RT}}}{\sum_i e^{\frac{-E_i}{RT}}} \qquad \text{[Eq. S2]}$$

Where N is the number of molecules of the system, N_i is the number of molecules for each conformer, E_i is the relative energy for each conformer, R is the Boltzmann constant in kcal mol^{-1} K^{-1}, and T is the assumed constant temperature (298.15 K).

Simulated UV-Vis and ECD spectra were calculated for the four less energetic conformations. Boltzmann weighted spectra were obtained using SpecDis version 1.71[S6] and corrected with a UV shift of -0.55 eV to better fit the experimental ones.

Table S9. Calculated energies (a.u.), relative energies (kcal mol^{-1}) and Boltzmann distribution of the optimized conformers of compound **3a**.

Compound	**Calculated energy (a.u.)**	**Relative energy (kcal mol^{-1})**	**Boltzmann distribution at 298.15 K**
3a-1	-1433.905029	0.00	61.91
3a-2	-1433.903907	0.70	18.86
3a-3	-1433.903925	0.69	19.22
3a-4	-1433.896484	5.36	0.01
3a-5	-1433.894261	6.76	0.00
3a-6	-1433.894773	6.44	0.00


3a-1
Simulated epsilon
Osc. strength
Wavelength / nm
150000
100000
50000
0
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
100
200
300
400
500
600

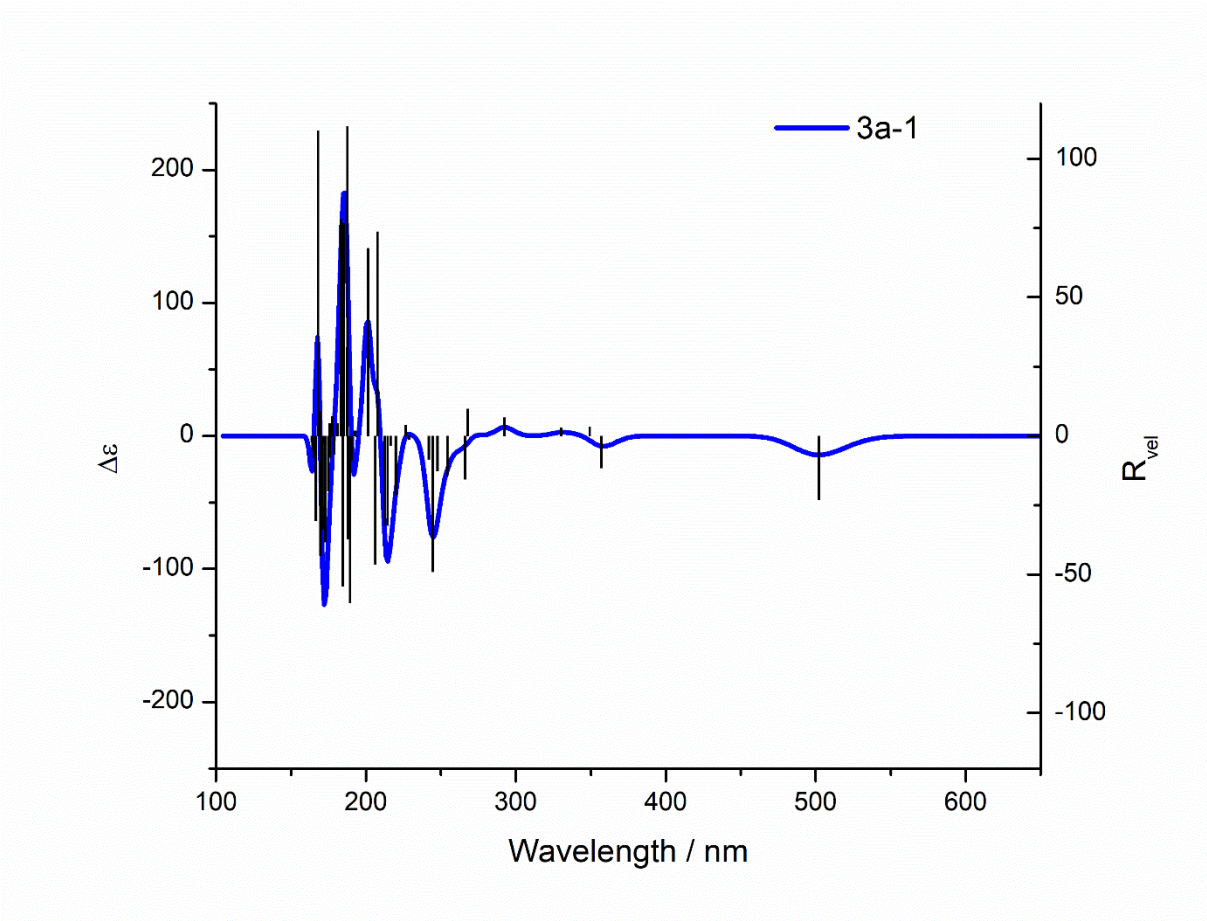
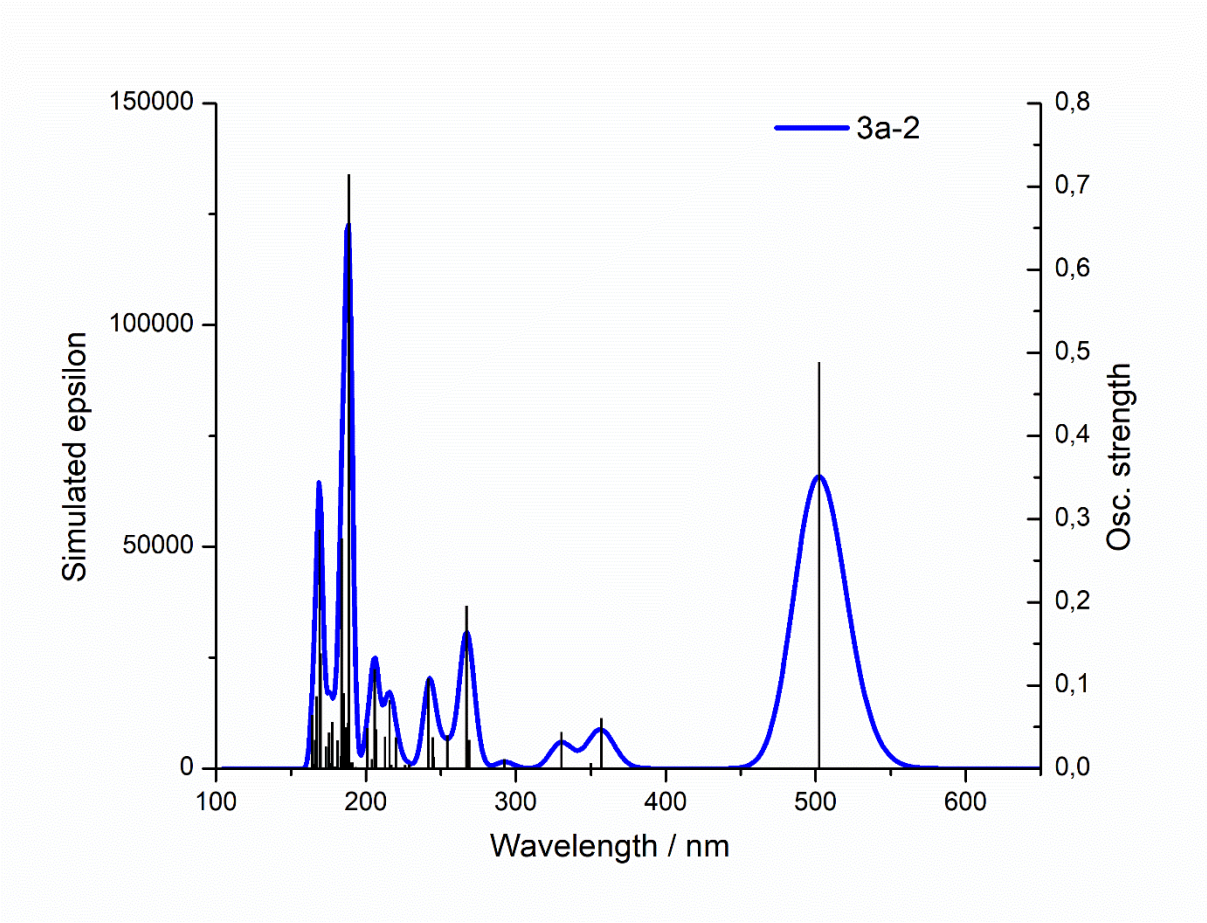


Figure S4. Top: Calculated electronic transitions and simulated UV-Vis spectrum of conformer (R,R)-**3a-1**. Bottom: Calculated electronic transitions and simulated ECD spectrum of conformer (R,R)-**3a-1**.


3a-2
Simulated epsilon
Osc. strength
Wavelength / nm
150000
100000
50000
0
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
100
200
300
400
500
600

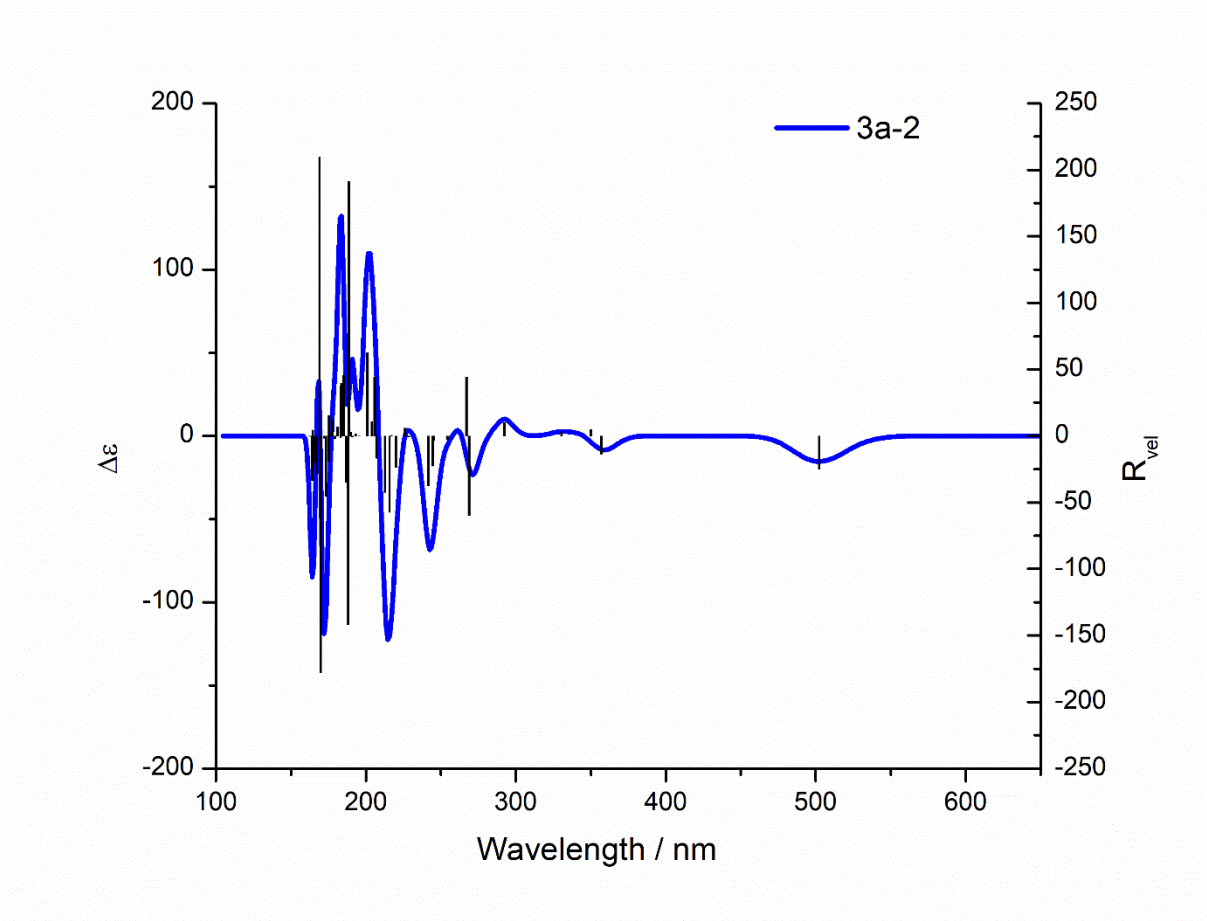
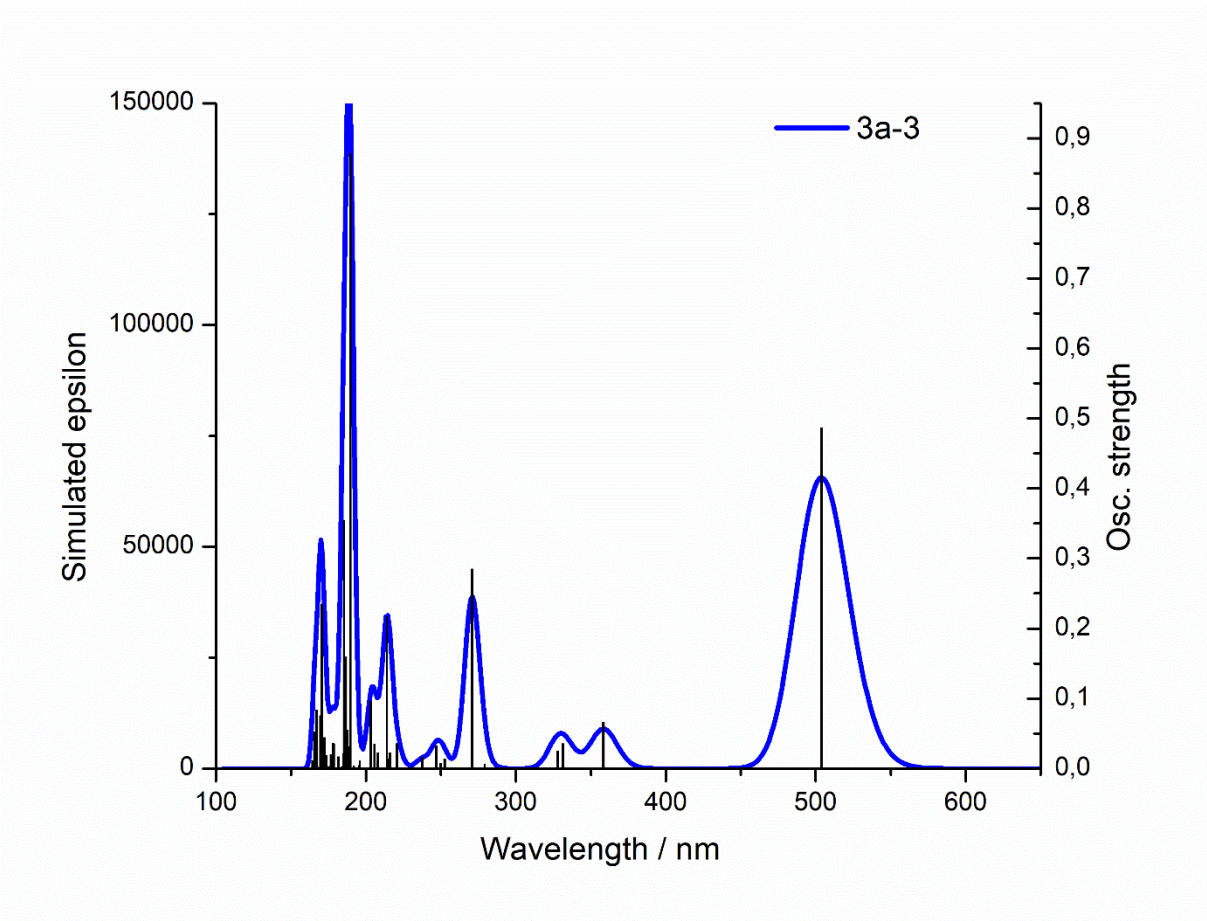


Figure S5. Top: Calculated electronic transitions and simulated UV-Vis spectrum of conformer (R,R)-**3a-2**. Bottom: Calculated electronic transitions and simulated ECD spectrum of conformer (R,R)-**3a-2**.


3a-3
Simulated epsilon
Osc. strength
Wavelength / nm
150000
100000
50000
0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
100
200
300
400
500
600

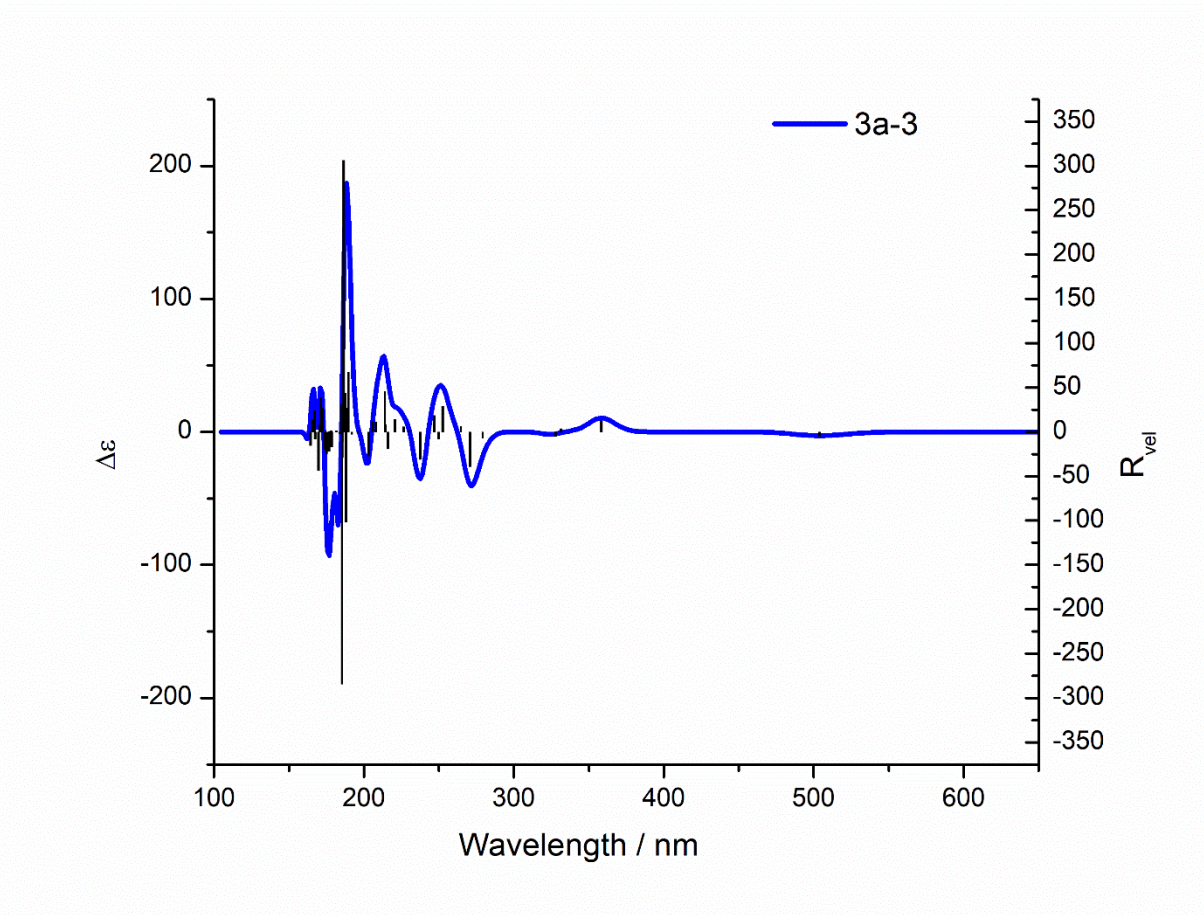
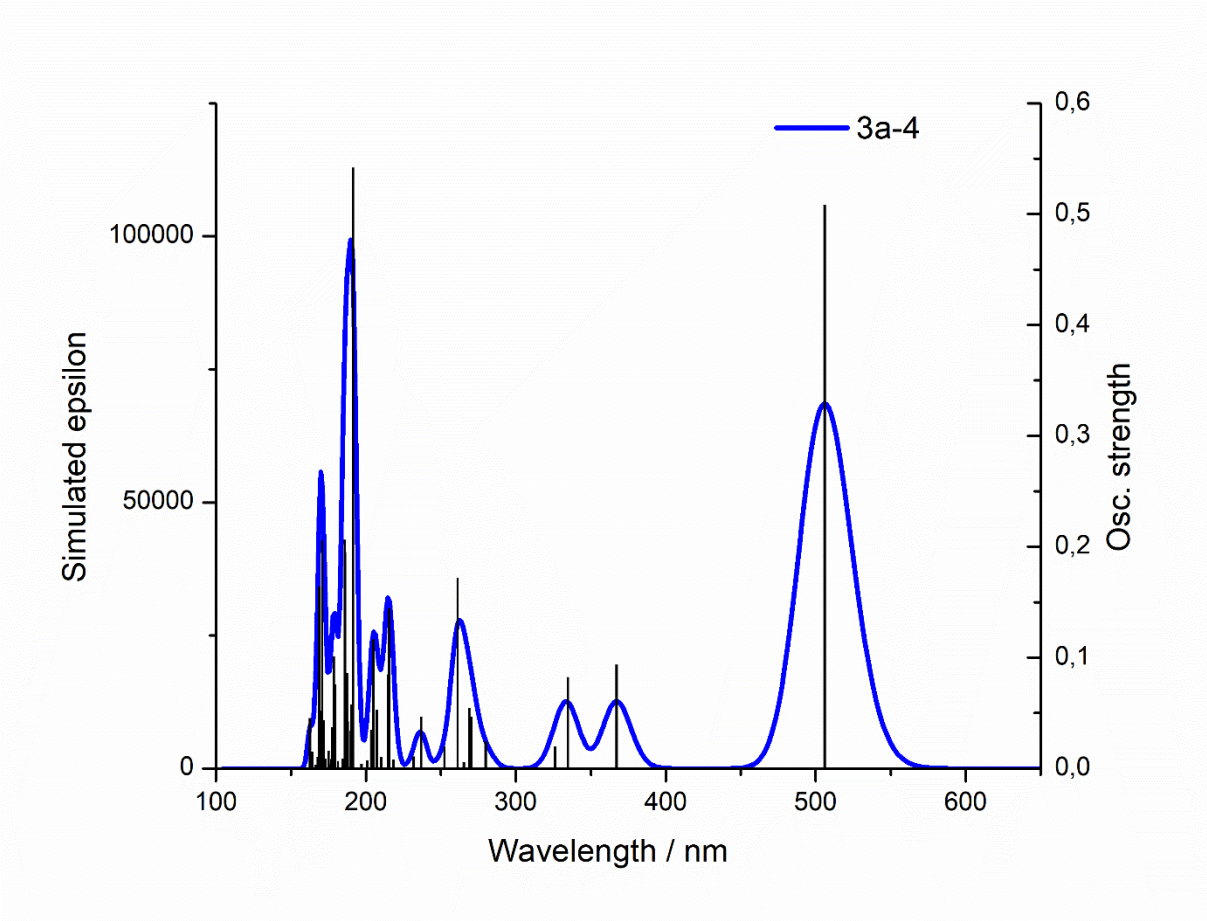


Figure S6. Top: Calculated electronic transitions and simulated UV-Vis spectrum of conformer (R,R)-**3a-3**. Bottom: Calculated electronic transitions and simulated ECD spectrum of conformer (R,R)-**3a-3**.


3a-4
Simulated epsilon
Osc. strength
Wavelength / nm
0
50000
100000
0,0
0,1
0,2
0,3
0,4
0,5
0,6
100
200
300
400
500
600

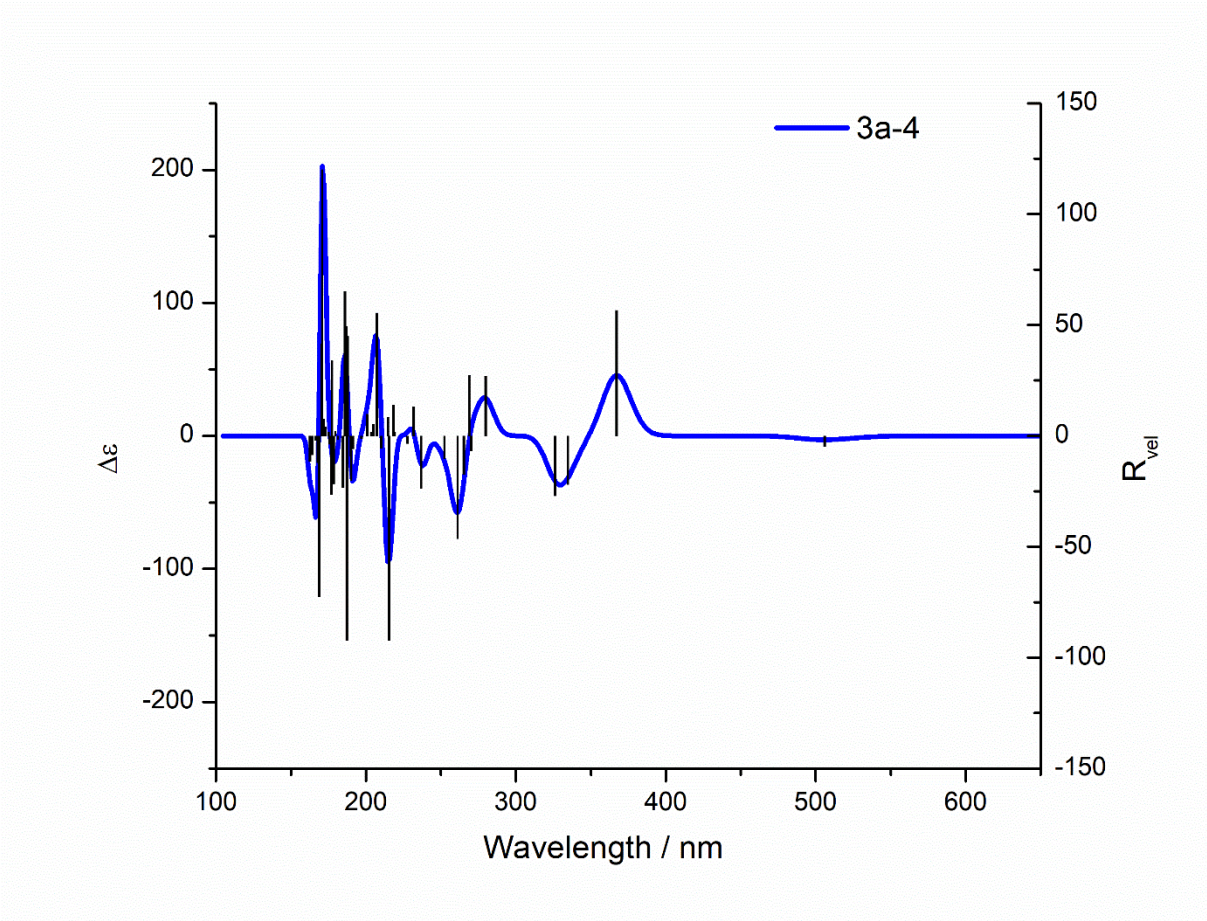
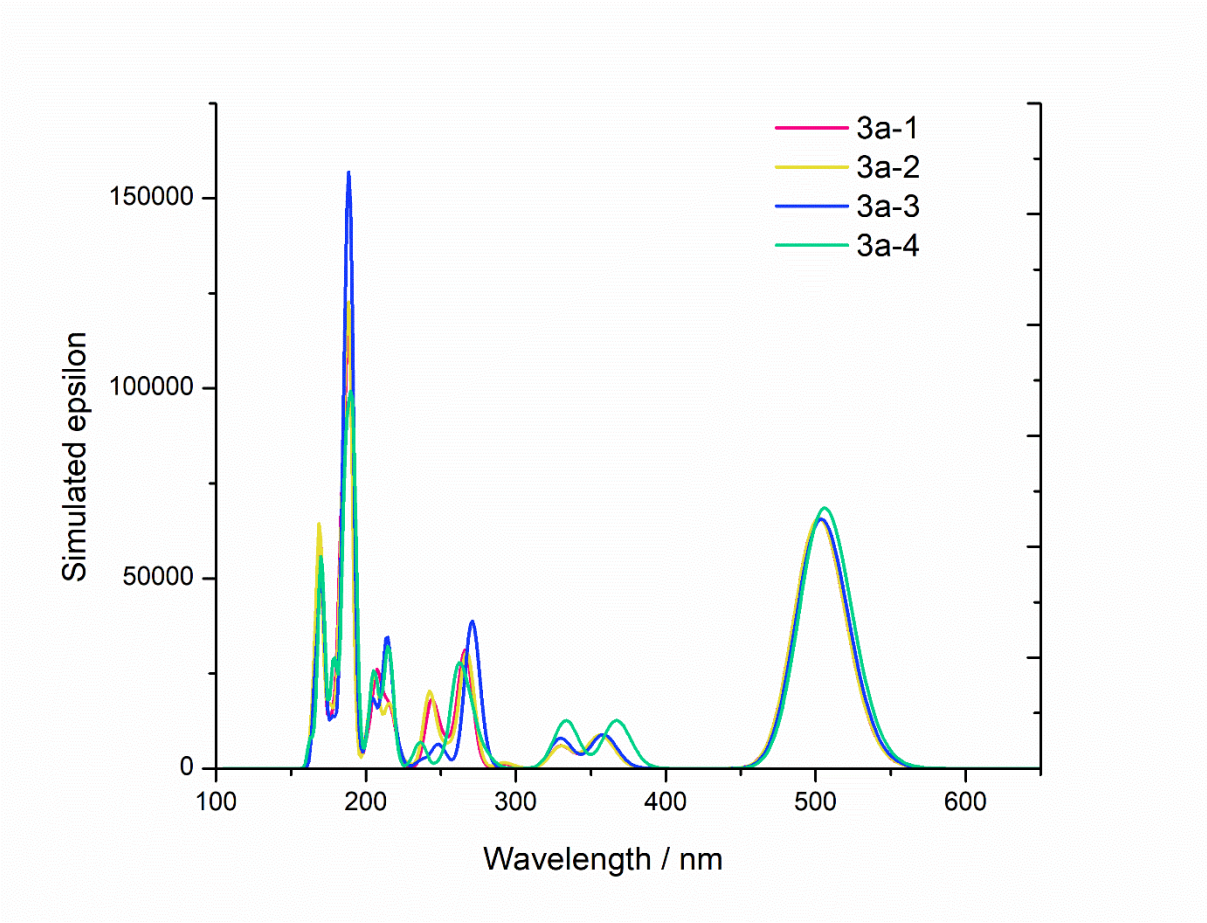


Figure S7. Top: Calculated electronic transitions and simulated UV-Vis spectrum of conformer (R,R)-**3a-4**. Bottom: Calculated electronic transitions and simulated ECD spectrum of conformer (R,R)-**3a-4**.


3a-1
3a-2
3a-3
3a-4
Simulated epsilon
150000
100000
50000
0
100
200
300
400
500
600
Wavelength / nm

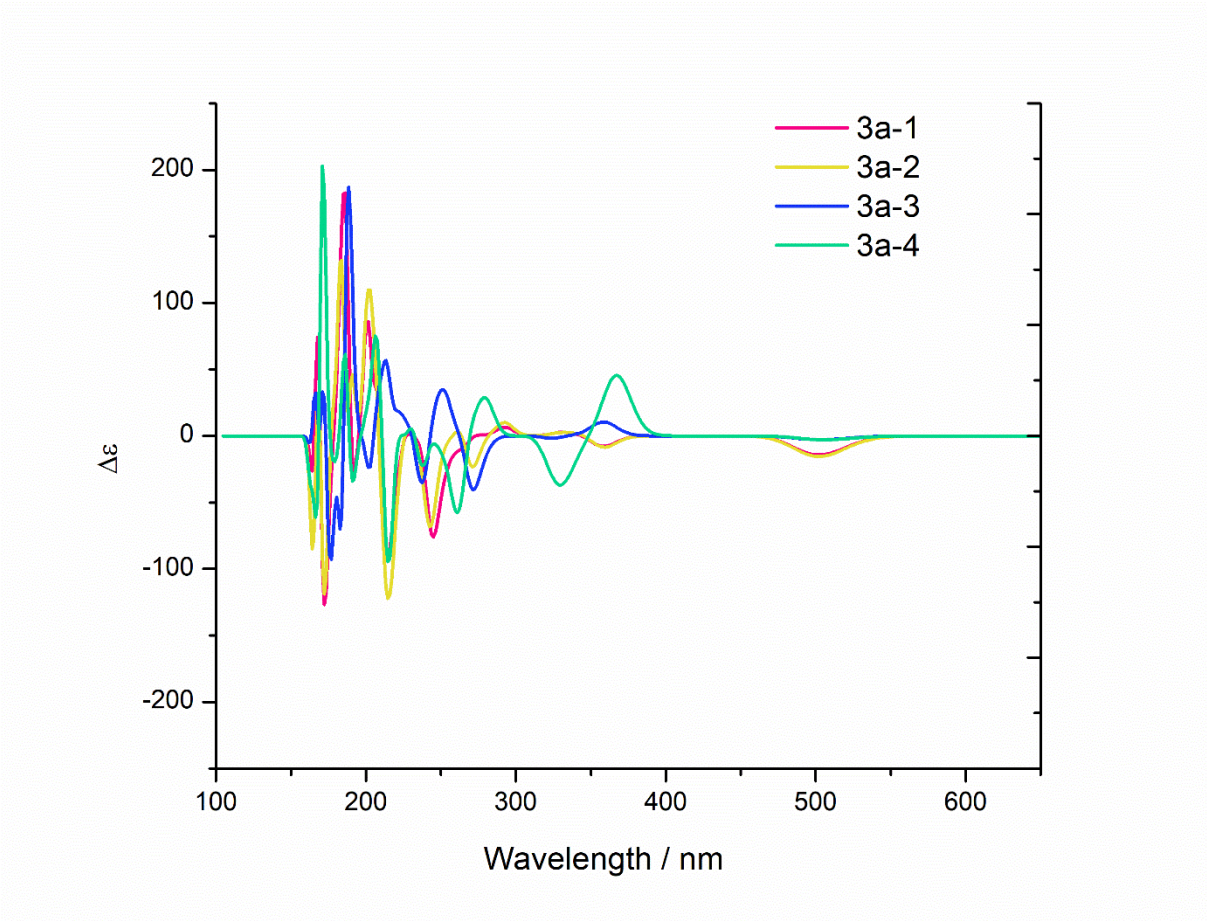


Figure S8. Top: Overlapped simulated UV-Vis spectra of conformers (R,R)-**3a-1** to **3a-4**. Bottom: Overlapped simulated ECD spectra of conformer (R,R)-**3a-4** to **3a-4**.

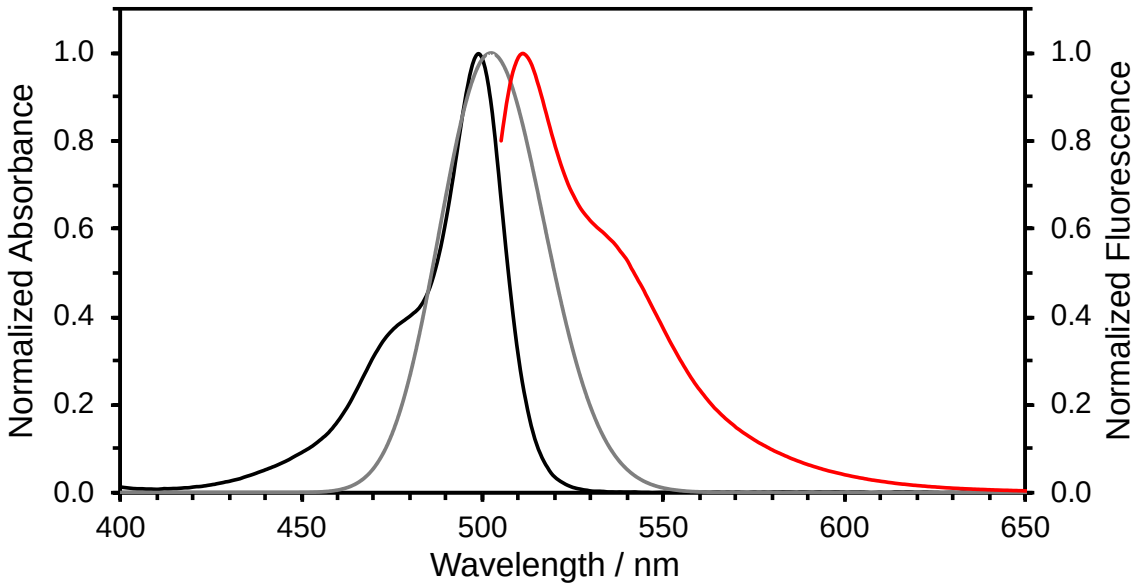


Figure S9. Experimental absorbance (black) and fluorescence (red) of compound **3a**, and simulated Boltzmann weighted (CAM-B3LYP/6-31G(d,p)) UV-vis spectrum of compounds **3a** (gray).

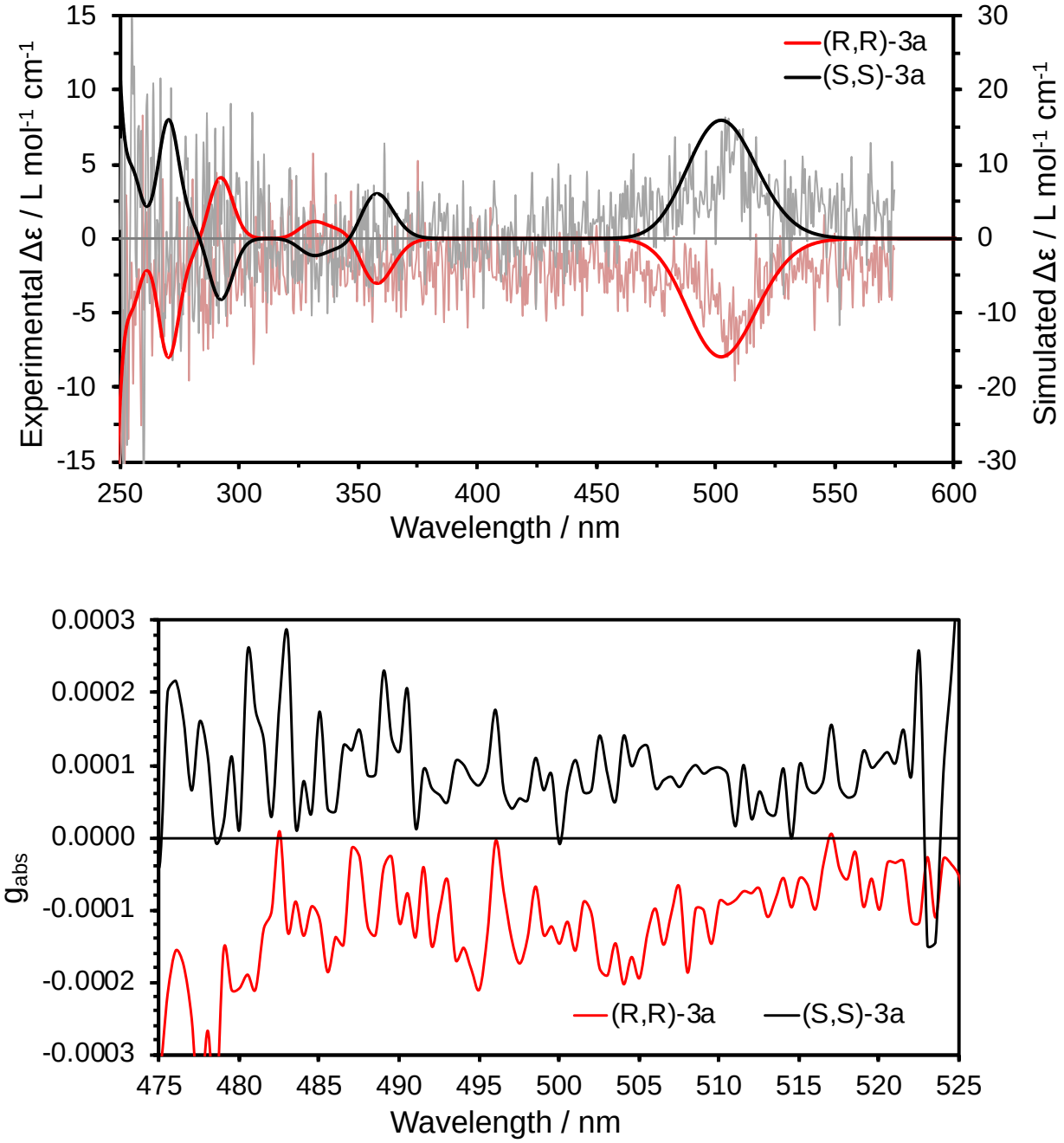


Figure S10. Top: Experimental ECD spectra of compounds (*S,S*)- (gray) and (*R,R*)-**3a** (pale red) measured at 1×10^{-6} M in $CHCl_3$ and simulated Boltzmann weighted (CAM-B3LYP/6-31G(d,p)) ECD spectra of compounds (*S,S*)- (black) and (*R,R*)-**3a** (red). Bottom: Partial experimental g_{abs} spectra of compounds (*S,S*)- (black) and (*R,R*)-**3a** (red) measured at 1×10^{-6} M in $CHCl_3$.

Table S10 Geometries

(*R,R*)-3a-1

C	1.85753900	0.04777300	1.33243700
N	3.14346000	0.30146100	0.86531900
B	3.83125600	-0.41107400	-0.32595000
N	2.71111600	-1.23384700	-1.01158000
C	1.43472300	-1.46984300	-0.50721800
C	0.99865600	-0.83610900	0.66809600
C	2.84746000	-1.91471100	-2.15067300
C	1.67282300	-2.62386400	-2.43546300
C	0.78786100	-2.35085600	-1.40726500
C	1.66142200	0.85270600	2.48182200
C	2.82151900	1.57623700	2.68581000
C	3.70982800	1.20513600	1.66496200
C	-0.37843300	-1.09235600	1.25239300
F	4.35771000	0.51601200	-1.20590600
F	4.82707000	-1.25718800	0.13706700
C	-0.51722200	-2.56546700	1.67181000
C	-1.51638000	-0.61349900	0.30939500
C	-2.89928300	-0.72078800	0.92620700
C	-1.29085800	0.80826500	-0.19829800
C	-3.19377900	-0.65538400	2.22335300
C	-0.94340100	1.03388600	-1.52996900
C	-0.71568800	2.31933100	-2.00696700
C	-0.84134500	3.38063900	-1.12980100
C	-1.18991800	3.19965500	0.19735000
C	-1.41644700	1.90756300	0.65246100
F	-0.62543000	4.63045500	-1.58089100
C	-3.99128500	-0.87969200	-0.08522800
O	-3.78829200	-1.07856500	-1.26476400
O	-5.21871400	-0.78767100	0.43665500
C	-6.29798200	-0.95529200	-0.48902100
H	3.77091800	-1.87200900	-2.71102400
H	1.50462100	-3.25469400	-3.29535600
H	-0.21476100	-2.73764600	-1.31521700
H	0.76560800	0.90248700	3.08189500
H	3.01949500	2.29437500	3.46731800
H	4.71826200	1.54932100	1.48191800
H	-0.44084300	-0.49287300	2.16133300
H	-0.52854900	-3.23649100	0.81218300
H	0.31842300	-2.85697100	2.31220800
H	-1.44111700	-2.71736200	2.23006700
H	-1.53088500	-1.25792500	-0.56953500
H	-4.22041300	-0.70560300	2.56299200
H	-2.42841500	-0.55626800	2.98505800
H	-0.84868700	0.19255000	-2.20809000
H	-0.44639700	2.50326700	-3.04040900
H	-1.28518200	4.05914500	0.85054900
H	-1.71131300	1.75954300	1.68640600

H	-7.20860000	-0.83938900	0.09499700
H	-6.24746400	-0.19898500	-1.27363100
H	-6.25999300	-1.94601000	-0.94481600

(*R,R*)-3a-2

C	1.84797300	0.18665200	1.28523500
N	3.10312200	0.41767900	0.72994800
B	3.74690700	-0.39300900	-0.42284400
N	2.61402500	-1.30052900	-0.96596300
C	1.36928700	-1.50796200	-0.37793500
C	0.97812600	-0.77205600	0.75413600
C	2.70981900	-2.08504600	-2.04103100
C	1.53783800	-2.83630200	-2.19857800
C	0.69810600	-2.48061700	-1.15728600
C	1.69012900	1.09659200	2.36029000
C	2.84129900	1.85759600	2.43351100
C	3.68679900	1.40479600	1.40864400
C	-0.36204000	-0.99795800	1.43016600
F	4.20272300	0.45516200	-1.41464000
F	4.78640700	-1.16949000	0.06428200
C	-0.45080400	-2.43376500	1.97462500
C	-1.55449500	-0.60874400	0.51028500
C	-2.90234800	-0.68326900	1.20722800
C	-1.37098600	0.77453500	-0.10961400
C	-3.12329900	-0.56050400	2.51477300
C	-1.03675800	0.90541100	-1.45750100
C	-0.84018600	2.15484400	-2.03307200
C	-0.98410600	3.27751100	-1.23858000
C	-1.32041200	3.19083700	0.10093400
C	-1.51521100	1.93268400	0.65569300
F	-0.79891700	4.49302600	-1.78610500
C	-4.12054800	-0.84881300	0.34780600
O	-5.26152500	-0.81436200	0.75467300
O	-3.81408400	-1.05162800	-0.93970900
C	-4.92878500	-1.20866300	-1.82452000
H	3.60428900	-2.08160900	-2.64804900
H	1.34175800	-3.54973300	-2.98488200
H	-0.29029400	-2.87348500	-0.97851900
H	0.82379900	1.18837900	2.99736000
H	3.06083300	2.65228300	3.13059100
H	4.67665100	1.74811700	1.14172000
H	-0.38877500	-0.32697100	2.28946300
H	-0.49090900	-3.17423800	1.17530100
H	0.42241700	-2.65729000	2.59186600
H	-1.34119300	-2.55551600	2.59112600
H	-1.58795600	-1.31992000	-0.31461700

H	-4.13898200	-0.58624000	2.89130300
H	-2.32460000	-0.43667500	3.23629000
H	-0.92597500	0.01699300	-2.07028100
H	-0.58054000	2.26492700	-3.07942200
H	-1.43149000	4.09542700	0.68730100
H	-1.80071800	1.85811300	1.70017700
H	-5.55685300	-0.31691300	-1.80528100
H	-4.50253700	-1.35426100	-2.81484100
H	-5.52693300	-2.07330400	-1.53307400

(R,R)-3a-3

C	1.81478500	-0.22342000	1.34353400
N	3.12632800	-0.40082400	0.91765000
B	3.55323800	-1.03250200	-0.43140900
N	2.28486400	-1.74808000	-0.96217200
C	0.98364700	-1.55134800	-0.50469100
C	0.73623700	-0.76809600	0.63249800
C	2.24315500	-2.58531100	-1.99892400
C	0.91972900	-2.96851500	-2.26063300
C	0.12605800	-2.32264200	-1.32942100
C	1.86039600	0.48575600	2.56725200
C	3.19208400	0.72078000	2.86142300
C	3.93865600	0.15954400	1.81524000
C	-0.67141800	-0.55077400	1.15125200
F	3.95073000	-0.04372000	-1.31733700
F	4.57367800	-1.94473500	-0.23516700
C	-1.24178000	-1.86210500	1.71775100
C	-1.56656900	0.15301600	0.08279900
C	-3.03267900	0.14885900	0.49016700
C	-1.05099800	1.53548700	-0.28313000
C	-3.64792100	1.10914000	1.17751500
C	-0.96435500	1.88756300	-1.63174900
C	-0.52373400	3.14297200	-2.02958600
C	-0.16334000	4.05448900	-1.05388700
C	-0.22773400	3.74780400	0.29284200
C	-0.67059700	2.48500000	0.66839100
F	0.26683000	5.27433700	-1.42539400
C	-3.79988700	-1.04551400	0.01907200
O	-3.33980600	-1.89701300	-0.71732600
O	-5.05249500	-1.09266900	0.47905600
C	-5.83654600	-2.20632700	0.03529400
H	3.15089800	-2.87498400	-2.50965200
H	0.59830600	-3.64523600	-3.03821600
H	-0.94794100	-2.40133600	-1.23840300
H	1.01238200	0.76954300	3.17223100

H	3.59437600	1.22822400	3.72539600
H	5.01062700	0.14046600	1.67647400
H	-0.60424700	0.13446100	1.99711400
H	-1.43124400	-2.60676400	0.94630700
H	-0.53899500	-2.28571900	2.43891400
H	-2.17793900	-1.66598600	2.24515400
H	-1.52144600	-0.44455500	-0.82535200
H	-4.69800900	1.03020100	1.42861200
H	-3.12398900	2.00400300	1.49184100
H	-1.24502700	1.16312800	-2.38996300
H	-0.45205800	3.41594800	-3.07586000
H	0.07023400	4.48648000	1.02763600
H	-0.70968300	2.25086800	1.72663300
H	-5.93385700	-2.19518800	-1.05127000
H	-5.37303300	-3.14454700	0.34354300
H	-6.80977300	-2.08779400	0.50675700

(R,R)-3a-4

C	2.17394800	1.01256600	0.72193100
N	3.32684600	0.68194200	0.02081800
B	3.46413500	-0.58459500	-0.85251100
N	2.47279700	-1.59665300	-0.22982200
C	1.31761000	-1.24159900	0.46874300
C	1.13452200	0.07921900	0.90594300
C	2.45706500	-2.91151900	-0.43663700
C	1.29846100	-3.47557700	0.11914000
C	0.57996700	-2.43576900	0.67746600
C	2.34503900	2.32952400	1.21129100
C	3.59650000	2.76441500	0.80689600
C	4.16556700	1.71907500	0.06759400
C	-0.10983900	0.55231900	1.62798000
F	3.07103600	-0.29367700	-2.15437400
F	4.75276000	-1.07458700	-0.81948300
C	-0.35585600	-0.21581200	2.93511300
C	-1.42039700	0.69908800	0.77010800
C	-1.30929700	1.74962100	-0.32114900
C	-2.07902600	-0.58895600	0.29228400
C	-0.39362800	1.79788800	-1.28976000
C	-2.95275000	-1.25812200	1.15524500
C	-3.57108300	-2.44710300	0.78885100
C	-3.31944500	-2.95822600	-0.47183700
C	-2.48253800	-2.31700600	-1.36651800
C	-1.86837000	-1.13380800	-0.97568000
F	-3.91723100	-4.10545400	-0.84223800
C	-2.36724300	2.80893200	-0.25771000

O	-3.18294800	2.89882700	0.63723800
O	-2.33016000	3.66054600	-1.28796100
C	-3.31192300	4.70163700	-1.26717600
H	3.26274500	-3.39290300	-0.97329200
H	1.03478600	-4.52248200	0.10955100
H	-0.36656900	-2.51829500	1.18540200
H	1.64302800	2.88655300	1.81315900
H	4.05948900	3.71629100	1.01994800
H	5.12503900	1.67353000	-0.42832800
H	0.09559000	1.57918100	1.92937000
H	-0.68457600	-1.24142800	2.77704600
H	0.55723100	-0.24300100	3.53417400
H	-1.12512200	0.29712100	3.51827300
H	-2.12077600	1.12601500	1.49152800
H	-0.41256000	2.59270500	-2.02480800
H	0.39621000	1.06347200	-1.38832300
H	-3.16271400	-0.83908900	2.13401000
H	-4.24925300	-2.96560900	1.45647000
H	-2.31899500	-2.74188100	-2.34995600
H	-1.22083700	-0.62907500	-1.68163400
H	-4.31730800	4.27792900	-1.27151400
H	-3.19067700	5.32401600	-0.37911400
H	-3.14083300	5.28665000	-2.16844100

(R,R)-3a-5

C	1.69109500	-0.73604100	1.24406900
N	2.98656100	-0.30473000	1.49813900
B	3.99565400	0.13151200	0.41507600
N	3.46067300	-0.50063300	-0.89527000
C	2.14815700	-0.91579800	-1.12841700
C	1.23279700	-0.98686600	-0.06527000
C	4.14726800	-0.59283400	-2.03188200
C	3.32238200	-1.07503100	-3.05828800
C	2.07417300	-1.27446200	-2.50113700
C	1.06338800	-0.93153900	2.49727500
C	1.98527900	-0.61593700	3.48074800
C	3.15883900	-0.23056800	2.81957700
C	-0.24239900	-1.33651400	-0.20536700
F	4.01658300	1.51302600	0.30119300
F	5.25792600	-0.35341500	0.69980500
C	-0.66873300	-2.15360400	-1.42836900
C	-1.14003800	-0.08023700	0.08778600
C	-0.90597200	1.17275800	-0.73192000
C	-2.61601100	-0.46491600	0.10323200
C	-0.37547200	1.26748900	-1.94936900

C	-3.17586600	-0.98528800	1.27179600
C	-4.50615400	-1.37933700	1.32379600
C	-5.27936100	-1.24082500	0.18441200
C	-4.76642300	-0.72380800	-0.99101800
C	-3.43140900	-0.33772400	-1.02156100
F	-6.57163000	-1.61495600	0.22433000
C	-1.34936000	2.41670400	-0.02213500
O	-1.70129000	2.43943200	1.13855900
O	-1.31776900	3.50960300	-0.79251500
C	-1.69759600	4.72978900	-0.14808400
H	5.19016400	-0.31048300	-2.06839000
H	3.62105500	-1.26309100	-4.07862200
H	1.21372300	-1.66474700	-3.01623900
H	0.05952100	-1.29462400	2.65995400
H	1.84620100	-0.66557500	4.55025000
H	4.10420900	0.08981500	3.23435400
H	-0.44693600	-1.99175300	0.64608200
H	-0.74548500	-1.57194700	-2.34688600
H	0.01770700	-2.98513800	-1.59691600
H	-1.65688100	-2.57412000	-1.23960600
H	-0.90066900	0.21656300	1.11000100
H	-0.26450600	2.23301300	-2.42620300
H	-0.02080800	0.40718200	-2.49789800
H	-2.56592300	-1.07557400	2.16572200
H	-4.94767600	-1.77828000	2.22953600
H	-5.40659500	-0.62513700	-1.85993300
H	-3.02297300	0.07696000	-1.93663800
H	-2.72322100	4.66403000	0.21826500
H	-1.03202700	4.94221100	0.68998600
H	-1.61272700	5.50403100	-0.90782900

(R,R)-3a-6

C	1.23778200	1.73530400	0.10416900
N	2.55136700	1.85392300	-0.33179300
B	3.62322900	0.75101600	-0.21178000
N	3.07466400	-0.22598500	0.85716700
C	1.73969200	-0.33941800	1.25123100
C	0.80341400	0.62852200	0.85625000
C	3.76593900	-1.22365900	1.40455400
C	2.92100200	-2.03217900	2.17848700
C	1.65523300	-1.48812100	2.08079700
C	0.54900900	2.89728200	-0.31466400
C	1.45481600	3.69679100	-0.99160900
C	2.67771600	3.01372100	-0.98138700
C	-0.68438700	0.54668400	1.15759100

F	3.76925900	0.07690800	-1.42219900
F	4.83392000	1.28099800	0.18958700
C	-1.07032900	-0.08199800	2.49906600
C	-1.43155000	-0.08433300	-0.07543100
C	-0.93666000	-1.49559000	-0.33426300
C	-2.95280900	0.06309400	-0.02013400
C	-1.42344300	-2.60348200	0.22254900
C	-3.58217200	1.06366300	0.72465700
C	-4.95951600	1.25137600	0.68166300
C	-5.71692800	0.42945300	-0.12949000
C	-5.13706300	-0.56300000	-0.89829500
C	-3.76098200	-0.73508200	-0.83742900
F	-7.05112500	0.60032000	-0.17551300
C	0.19405900	-1.57996100	-1.31272600
O	0.44909300	-0.70064400	-2.10937100
O	0.89550300	-2.71169000	-1.22523200
C	2.01334700	-2.80730000	-2.12232000
H	4.82631000	-1.32448400	1.21915500
H	3.21721900	-2.90384100	2.74251100
H	0.76966800	-1.86118900	2.56357700
H	-0.48961500	3.12789100	-0.12885300
H	1.27177200	4.66290100	-1.43751200
H	3.62682000	3.30517600	-1.40893700
H	-1.01197600	1.58607800	1.19712600
H	-1.07965400	-1.17067800	2.46157100
H	-0.38864300	0.23185600	3.29184700
H	-2.07584600	0.23343400	2.77877100
H	-1.10069800	0.49897000	-0.94000000
H	-0.98911400	-3.57240000	0.00863100
H	-2.28159200	-2.57345000	0.88491800
H	-3.00697300	1.72880600	1.35699500
H	-5.44182800	2.02543400	1.26697500
H	-5.75687200	-1.18518500	-1.53341700
H	-3.30904000	-1.50929400	-1.44530300
H	2.50648300	-3.74517800	-1.87443400
H	1.66859100	-2.82139100	-3.15770300
H	2.68434200	-1.96006800	-1.97428400

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