Supporting Information

for

Asymmetric Borylation of α, β-unsaturated Esters Catalyzed by Novel Ring Expanded N-heterocyclic Carbenes Based on Chiral 3,4-Dihydro-quinazolinium Compounds

Liliang Huang,[†] Yong Cao,[†] Manping Zhao,[†] Zhongfeng Tang,[‡] Zhihua Sun*,[†]

[†]*College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, 333 Longteng Road, Shanghai, China*

[‡]*Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences, Shanghai 201800, China*

E-mail: sungaris@gmail.com

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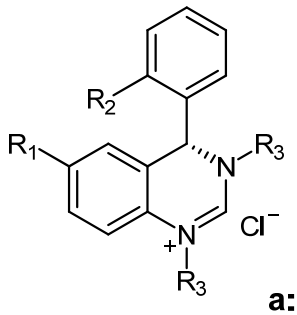
General Methods

All commercially available reagents were used without purification unless otherwise noted. Column chromatography was performed using silica gel from Merck (300-400 mesh). Visualization of the compounds was accomplished with UV light (254 nm) and iodine. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 and 3.33 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.00 ppm) or DMSO-d_6 (40.0 ppm). Data are represented as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), and integration. Products were identified by comparison to spectral data reported in the literature. Mass spectra (both at low resolution and at high resolution) were recorded on a time-of-flight mass spectrometer with an ESI source. High performance liquid chromatography (HPLC) was performed using a chromatograph equipped with a Chiralpak column (250 mm × 4.6 mm) with hexane/i-PrOH as the eluent.

Compound characterizations

Table S1 12 Examples of Chiral 3,4-dihydro-quinazoliniums (RE-NHC precursors)



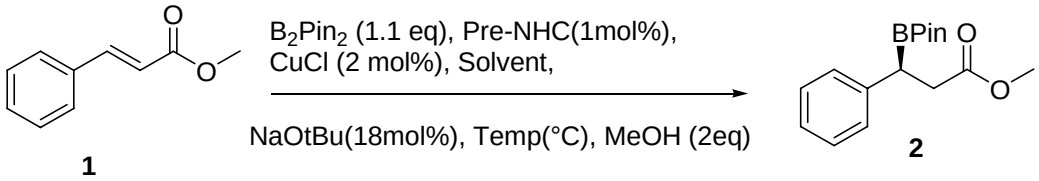
5a, 5b, or 5c

a: R_1=R_2=H;
b: R_1=Cl, R_2=H;
c: R_1=Cl, R_2=F

Compound	Structure of R_3	Last-Step Yield[a]	Overall Yield[a]
5a1	Ph-	96%	62%
5a2	4-Ph-Ph-	93%	59%
5a3	3,5-diMe-Ph-	91%	57%
5a4	2-naphthyl-	92%	60%
5b1	Ph-	94%	60%
5b2	4-Ph-Ph-	91%	57%
5b3	3,5-diMe-Ph-	94%	58%
5b4	2-naphthyl-	89%	58%
5c1	Ph-	95%	57%
5c2	4-Ph-Ph-	91%	55%
5c3	3,5-diMe-Ph-	92%	54%
5c4	2-naphthyl-	90%	56%

[a] Isolated yields.

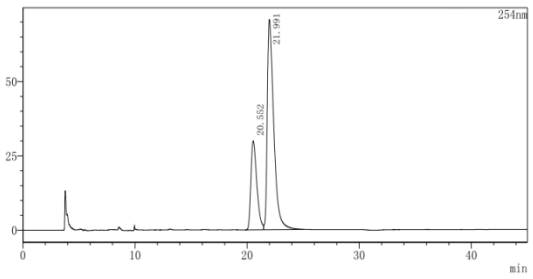
Table S2 Screening Catalysts and Temperature for β-borylated Ester Synthesis

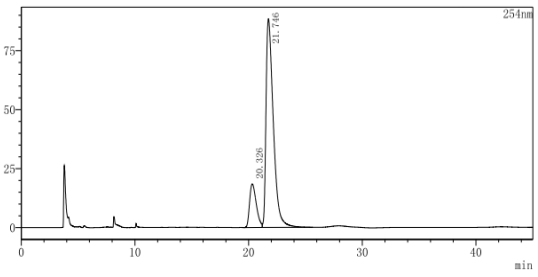


1 **2**

Entry	Pre-NHC	Temp.(°C)	Yield (%)	ee (%)
1[a]	**-**	**rt**	-	-
2[b]	**5a1**	**rt**	-	-
3	**5a1**	**rt**	91	44
4	**5a2**	**rt**	95	68
5	**5a3**	**rt**	93	61
6	**5a4**	**rt**	92	59
7	**5b1**	**rt**	93	48
8	**5b2**	**rt**	92	58
9	**5b3**	**rt**	90	41
10	**5b4**	**rt**	91	64
11	**5c1**	**rt**	92	65
12	**5c2**	**rt**	96	72
13	**5c3**	**rt**	93	48
14	**5c4**	**rt**	94	66
15	**5c2**	**0**	91	72
16	**5c2**	**-55**	93	91
17	**5c2**	**-78**	68	59

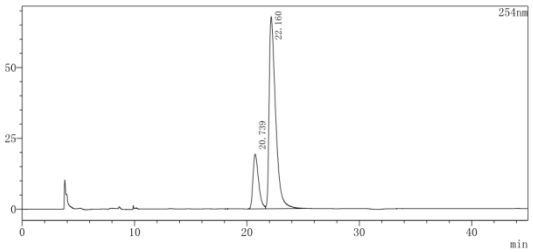
[a] Only 2 mol% CuCl used; [b] only 1 mol% pre-NHC used without adding CuCl.

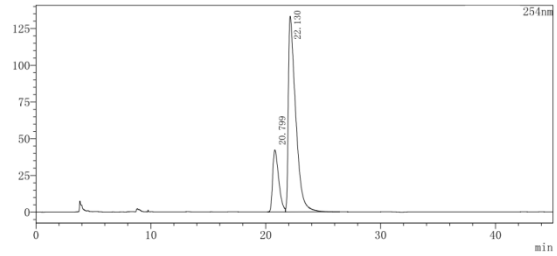




5a1 **5a2**

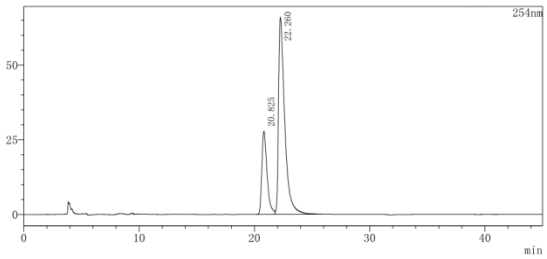
	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5a1	1	20.552	27.832	**5a2**	1	20.326	16.094
	2	21.991	72.168		2	21.746	83.906

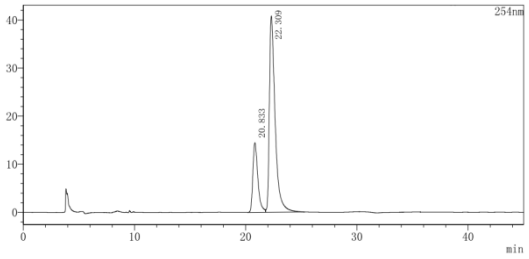




5a3 **5a4**

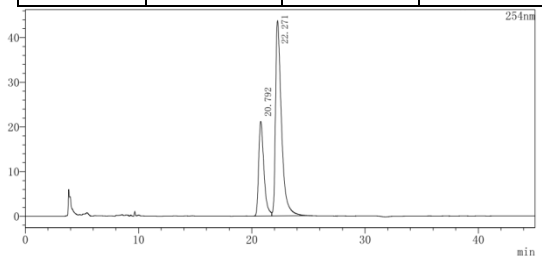
	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5a3	1	20.739	19.585	**5a4**	1	20.799	20.468
	2	22.160	80.415		2	22.130	79.532

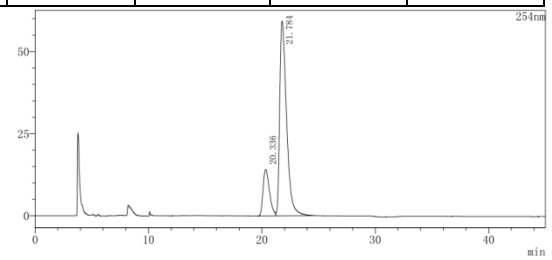




5b1 **5b2**

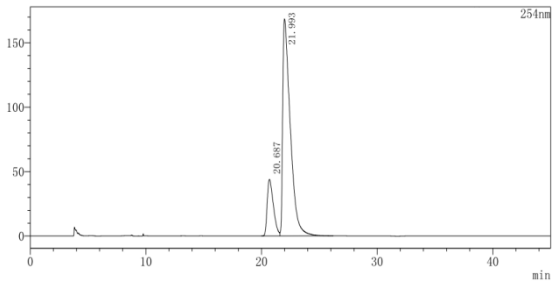
	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5b1	1	20.825	26.062	**5b2**	1	20.833	23.400
	2	22.260	73.938		2	22.309	76.600

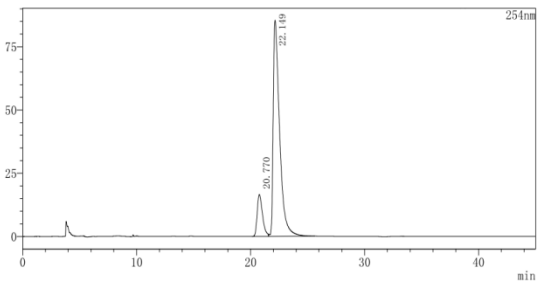




5b3 **5b4**

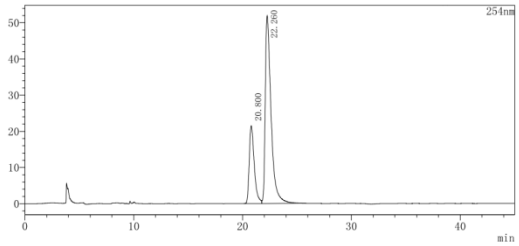
	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5b3	1	20.792	29.688	**5b4**	1	20.336	18.242
	2	22.271	70.312		2	21.784	81.758

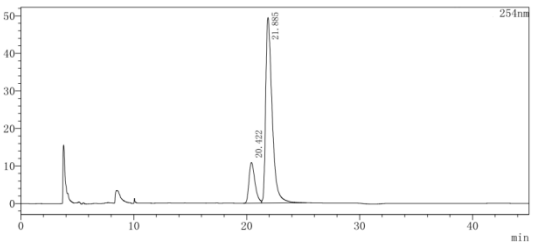




5c1 **5c2**

	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5c1	1	20.687	17.482	**5c2**	1	20.770	13.811
	2	21.993	82.518		2	22.149	86.189

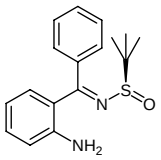




5c3 **5c4**

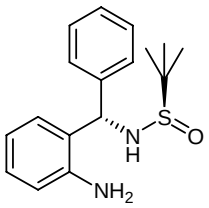
	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
5c3	1	20.800	26.242	**5c4**	1	20.422	16.825
	2	22.260	73.758		2	21.885	83.175

Representative procedure for synthesis of RE-NHC precursors



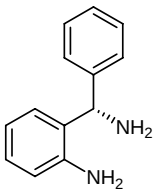
1a

2-Aminobenzophenone (**a**) (4.0 g, 20.3 mmol) and R-(+)-tert-butylsulfinamide (3.44 g, 22.5 mmol) were dissolved in tetraisopropyl titanate (10 mL). The mixture was heated in a microwave at 122 ℃ for 40 minutes. The mixture was cooled to rt and quenched with saturated $NaHCO_3$ solution, then suction filtered through Celite, and washed with EtOAc. The combined organic layer was dried with Na_2SO_4. The crude product was purified by silica gel chromatography (hexane:EtOAc = 4:1) to give the desired product **1a** (5.4 g, 18.0 mmol) as a yellow solid in 89% yield. mp 140-142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49(s, 3H), 7.24-7.26 (m, 2H), 6.73-6.91 (m, 4H), 6.51 (s, 4H), 1.28 (s, 9H); MS (ESI-TOF) m/z: 301.2 $[M+H]^+$.



2a

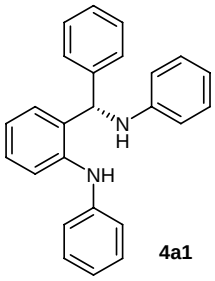
A flame dried 250 ml three-necked flask was charged with compound **1a** (4.0 g, 13.3 mmol) and THF (100 mL). Before the addition of DIBAL-H, the mixture was cooled to -78℃. Then, 1.5 M DIBAL-H solution (10 mL, 15 mmol) in toluene was slowly added by a constant pressure drop funnel in 0.5 h. The reaction mixture was stirred for 2 h at -78℃. The reaction mixture was quenched with saturated NaCl solution, suction filtered through Celite and washed with EtOAc. The filtrate was extracted with EtOAc and dried with Na_2SO_4. The crude product was purified by silica gel chromatography (hexane : EtOAc = 4 : 1) to give 3.2 g the desired product **2a** as a yellow solid in 80% yield and 98% ee. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (250 mm × 4.6 mm) with hexane/iPrOH=90/10 as eluents. mp154.0-156.0℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.43 (m, 4H), 7.33-7.36 (m,1H), 7.10-7.15 (m, 1H), 6.62-6.75 (m, 3H),5.70 (d, J = 2.4 Hz, 1H), 4.38 (s, 2H), 3.74 (d, J = 1.6 Hz, 1H),1.29(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ144.3, 140.5, 129.1, 129.0, 128.5, 128.3, 127.6, 126.1, 111.9, 116.7, 57.4, 55.8, 22.7; MS (ESI-TOF) m/z: 303.1 $[M+H]^+$.



3a

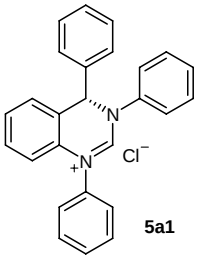
Compound **2a** (5 mmol) was dissolved in a mixed solvent of anhydrous methanol and 1, 4-dioxane (24 mL). Then a solution of 2.2 M HCl in dioxane (10 ml) was added to the mixture. The solution was stirred for 2 h. The reaction solution gradually turned into deep yellow. After most solvent was evaporated under reduced pressure, the resulting solution was treated with water (100 mL) and washed with ethyl acetate (100 mL). For the aqueous part, pH was adjusted to 8 with aqueous ammonia and it was then extracted with ethyl acetate. The combined organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. This afforded 623 mg (96%) of the desired product **3a** as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.38-7.43 (m, 4H), 7.31-7.33 (m, 1H), 7.12 (td, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 2H), 7.02 (d, J = 3.6Hz, 1H),

6.68-6.76 (m, 2H), 5.25 (s, 1H), 4.46 (brs, 2H), 1.83 (brs, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 145.6, 144.0, 128.7, 128.6, 128.4, 128.2, 127.1, 127.0, 118.0, 116.6, 57.8; MS(ESI-TOF) m/z: 199.1 $[M+H]^+$.



4a1

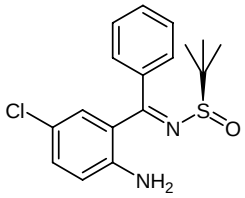
Compound **3a** (0.5 mmol), bromobenzene (1.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), BINAP (0.006 mmol) and sodium tert-butoxide (1.2 mmol) were dissolved in toluene (5 mL). The mixture was allowed to react at 110 ℃ for 4 h. The reaction mixture was cooled to rt and quenched with saturated $NaHCO_3$ solution, then suction filtered through Celite, and washed with EtOAc. The combined organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (hexane : EtOAc = 50 : 1) to give the desired product **4a1** (160 mg) as a yellow solid in 94% yield. mp 63.6-64.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.42 (m, 6H), 7.25-7.28 (m, 2H), 7.11-7.19 (m, 3H), 6.93-6.96 (m, 4H), 6.81(t, *J* = 3.6Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 5.83 (1H, s), 4.35(s,1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 146.9, 143.6, 141.8, 140.8, 132.1, 129.4, 129.1, 128.9, 127.9, 127.7, 121.7, 120.7, 119.2, 118.4, 117.8, 114.0, 58.9; MS(ESI-TOF) m/z: 338.2 $[M+H]^+$.



5a1

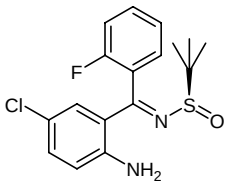
Compound **4a1** (0.5 mmol) was dissolved in trimethyl orthoformate (5 mL). Then, formic acid (0.1 mL) and concentrated hydrochloric acid (0.1 mL) were added. The mixture was reacted at room temperature for 12 h. Then most solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (dichloromethane: methanol = 10 : 1) to give the desired product **5a1** (170 mg) as a yellow solid in 96% yield. mp186.5-187.4℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.95 (d, *J* = 5.2 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 3H), 7.48-7.58 (m, 3H), 7.43 (d, *J* =

6.8 Hz, 2H), 7.28-7.32 (m, 5H), 7.19-7.27 (m,2H), 7.04 (d, J = 2.4 Hz, 1H), 6.86 (s, 1H), 6.65 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 151.3, 143.8, 142.5, 139.4, 139.2, 139.0, 138.6, 135.4, 132.1, 129.5, 129.4, 129.1, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 127.1, 125.9, 122.9, 117.2, 65.5; MS(ESI-TOF) m/z: 361.2 $[M]^+$; $[\alpha]_D^{25}$ = -31.2° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{26}H_{21}N_2^+[M]^+$ 361.1699, Found 361.1692.



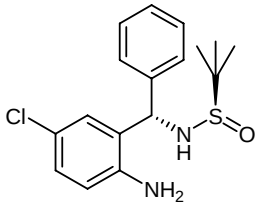
1b

Compound **1b** was prepared according to the general procedure of **1a**. Yellow solid 4.8 g (yield 88%)， mp 138.0-139.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50(s, 3H), 7.15-7.26 (m, 3H), 6.84 (s, 1H), 6.71 (d, J = 8.8 Hz, 1H), 1.27 (s, 9H); MS (ESI-TOF) m/z: 335.2 $[M+H]^+$.



1c

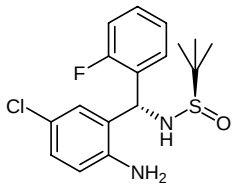
Compound **1c** was prepared according to the general procedure of **1a**. Yellow solid 5.6 g (yield 86%)，mp 136-138℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.53 (m, 1H), 7.15-7.30 (m, 4H), 6.84 (s, 1H), 6.71(d, J = 8.8 Hz, 1H), 1.27 (s, 9H); MS (ESI-TOF) m/z: 353.1 $[M+H]^+$.



2b

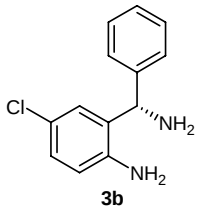
Compound **2b** was prepared according to the general procedure of **2a**. Yellow solid 3.6 g (yield 80%), 97% ee. Enantiomeric excess were determined by High performance liquid chromatography (HPLC) with a Chiralcel OD-H column (250 mm × 4.6 mm) with hexane/*i*-PrOH = 90/10 as the eluent. mp 151.1-152.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.43 (m, 5H), 7.07 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H),

6.65-6.69 (m, 2H), 5.63 (d, J = 2.4 Hz, 1H), 4.39 (brs, 2H), 3.69 (d, J = 2.0 Hz, 1H), 1.29(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 139.7, 129.1, 128.9, 128.6, 128.1, 127.9, 127.5, 122.6, 117.8, 57.1, 55.8, 22.6； MS (ESI-TOF) m/z: 337.2$[M+H]^+$.



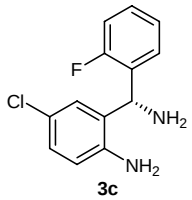
2c

Compound **2c** was prepared according to the general procedure of **2a**. Yellow solid 3.4 g (yield 81%), 99% ee. Enantiomeric excess were determined by High performance liquid chromatography (HPLC) with a Chiralcel OD-H column (250 mm × 4.6 mm) with hexane/i-PrOH = 90/10 as the eluent. mp144.0-145.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.34-7.39 (m, 1H), 7.12-7.26 (m, 1H), 7.07 (t, J = 2.4 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 5.88 (d, J = 2.8 Hz, 1H), 4.49 (brs, 2H), 3.61 (brs, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7,159.2, 143.1, 129.7, 129.3, 127.8, 127.3, 125.8, 124.2, 122.5, 117.9, 115.9, 115.7, 55.9, 51.2, 22.6； MS (ESI-TOF) m/z: 337.2$[M+H]^+$.



3b

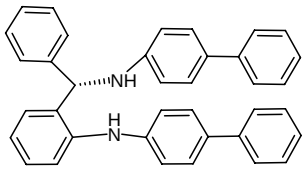
Compound **3b** was prepared according to the general procedure of **3a**. Yellow oil (yield 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.42 (m, 4H), 7.30-7.33 (m, 1H), 7.03-7.07 (m, 2H), 6.58 (d, J = 8.0 Hz, 1H), 5.17 (s, 1H), 4.39 (brs, 2H), 1.91(brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.2, 130.2, 128.7, 128.1, 127.8, 127.4, 126.9, 122.6, 117.6, 57.5; MS(ESI-TOF) m/z: 233.2 $[M+H]^+$.



3c

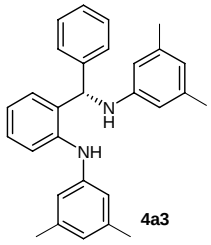
Compound **3c** was prepared according to the general procedure of **3a**.Yellow oil (yield 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 1.6 Hz, 1H), 7.29-7.38 (m, 1H), 7.19 (dd, J_1= 0.8 Hz, J_2= 7.6 Hz, 1H), 7.00-7.16 (m, 3H), 6.60 (d, J = 8.4 Hz, 1H), 5.45 (s, 1H), 4.53 (brs, 2H), 1.82(brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 161.8,

159.4, 144.3, 130.2, 130.1, 129.2, 129.1, 128.4,128.3, 128.0, 127.8, 124.5, 122.6, 117.5, 115.8, 115.6, 51.4; MS(ESI-TOF) m/z: 251.2 $[M+H]^+$.



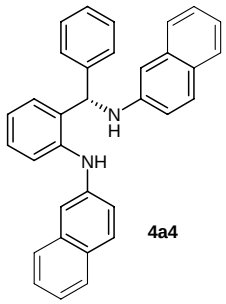
4a2

Compound **4a2** was prepared according to the general procedure of **4a1**.Yellow solid (yield 93%), mp 72.4-73.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.48-7.54 (m, 4H), 7.38-7.46 (m, 10H), 7.26-7.36 (m, 5H), 7.16 (d, *J* = 6.8 Hz, 1H), 6.96-7.03 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 5.83 (d, *J* = 5.6 Hz, 1H), 4.38 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 143.0, 141.4, 141.0, 140.9, 133.5, 132.3, 131.3, 129.0, 128.9, 128.7, 128.4, 128.0, 127.9, 127.8, 127.7, 126.5, 126.3, 126.2, 122.1, 119.7, 117.7, 114.2, 58.9; MS(ESI-TOF) m/z: 503.1 $[M+H]^+$.



4a3

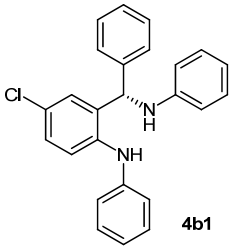
Compound **4a3** was prepared according to the general procedure of **4a1**. Yellow solid (yield 91%). mp 136.7-137.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.34-7.40 (m, 6H), 7.21-7.27 (m, 1H), 7.07 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 6.92-6.98 (m, 3H), 6.91-6.95 (m, 1H), 6.58 (s, 3H), 6.41 (s, 1H), 6.28 (s, 2H), 6.04 (s, 1H), 5.76 (d, *J* = 4.4 Hz, 1H), 4.18 (brs, 1H), 2.27 (s, 6H), 2.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 143.7, 141.8, 141.1, 139.1, 138.9, 132.7, 128.9, 128.8, 128.2, 127.8, 127.5, 122.4, 121.6, 120.3, 119.7, 115.4, 111.8, 58.6, 21.5, 21.4; MS(ESI-TOF) m/z: 407.1 $[M+H]^+$.



4a4

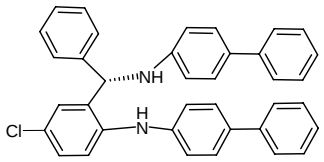
Compound **4a4** was prepared according to the general procedure of **4a1**. Yellow solid

(yield 95%). mp 166.1-167.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.74 (m, 5H), 7.49 (t, *J* = 4.8 Hz, 2H), 7.40-7.43 (m, 5H), 7.28-7.33 (m, 4H), 7.20-7.21 (m, 2H), 7.11 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 6.97-7.01 (m, 2H), 6.80 (d, *J* = 2.0 Hz, 1H), 6.29 (s, 1H), 5.96 (s, 1H), 4.50 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.4, 132.7, 129.2, 129.1, 129.0, 128.9, 128.5,127.9, 127.7, 127.6, 126.5, 126.4,126.3, 126.2, 123.3, 122.4, 120.3, 119.9, 117.9, 111.2, 106.7, 58.7; MS(ESI-TOF) m/z: 451.1$[M+H]^+$.



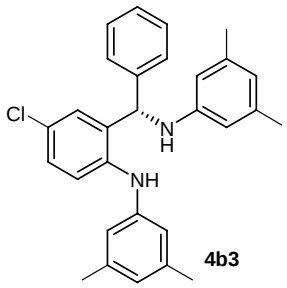
4b1

Compound **4b1** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 93%). mp 60.6-61.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.43 (m, 5H), 7.20-7.31 (m, 2H), 7.15-7.19 (m, 4H), 6.91-6.96 (m, 3H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 6.03 (s, 1H), 5.70 (d, *J* = 6.4 Hz, 1H), 4.22 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 146.5, 143.1, 140.3, 140.0, 133.8, 129.4, 129.3, 129.1, 128.7, 128.2, 127.8, 126.7, 121.1, 120.4, 118.6, 117.9, 113.9, 58.90; MS(ESI-TOF) m/z: 385.2$[M+H]^+$.



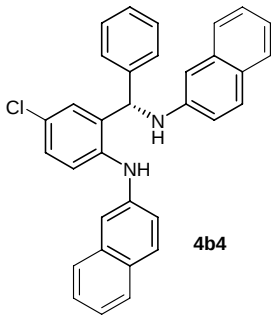
4b2

Compound **4b2** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 92%).mp 105.1- 106.2℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.61 (m, 6H), 7.38-7.46 (m, 12H), 7.30-7.33 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 5.76 (d, *J* = 5.6 Hz, 1H), 4.32 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 142.6, 140.9, 140.7, 140.0, 139.9, 134.1, 133.9, 129.2, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8, 126.7, 126.5, 126.4, 126.3, 120.9, 117.9, 114.2, 58.9; MS(ESI-TOF) m/z: 538.1 $[M+H]^+$.



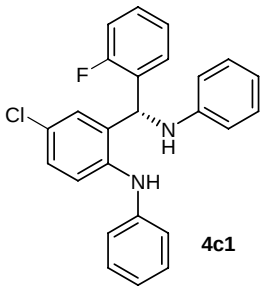
4b3

Compound **4b3** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 90%). mp 149.5-151.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.43 (m, 6H), 7.15-7.21 (m, 4H), 6.61 (s, 1H), 6.55 (s, 2H), 6.45 (s, 1H), 6.28 (s, 2H), 5.90 (s, 1H), 5.70 (d, J = 2.8 Hz, 1H), 4.13 (brs, 1H), 2.29 (s, 6H), 2.23(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 143.3, 140.4, 140.3, 139.2, 138.9, 134.4, 129.0, 128.6, 128.2, 127.8, 126.7, 122.8, 121.1, 121.0, 120.5, 115.6, 111.8, 58.6, 21.5; MS (ESI-TOF) m/z: 442.2 $[M+H]^+$.



4b4

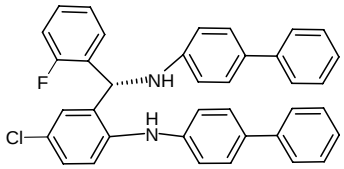
Compound **4b4** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 95%). mp 168.2-169.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.73(m, 5H), 7.41-7.52 (m, 5H), 7.31-7.37 (m, 4H), 7.25-7.27 (m, 3H), 7.15-7.23 (m, 3H), 7.02 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 6.88 (s, 1H), 6.61 (s, 1H), 6.22 (d, J = 6.8 Hz, 1H), 4.45 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 141.2, 141.0, 134.7, 134.6, 132.7, 129.8, 129.7, 129.3, 129.2, 128.8, 128.7, 128.3, 128.2, 127.8, 127.6, 126.9, 126.6, 126.5, 126.4, 126.3, 124.7, 123.6, 122.8, 120.8, 120.0, 117.8, 116.2, 116.0, 112.0, 111.6, 107.3, 52.8; MS(ESI-TOF) m/z: 486.2 $[M+H]^+$.



4c1

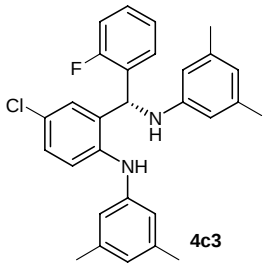
Compound **4c1** was prepared according to the general procedure of **4a1**. Pale yellow

solid (yield 89%). mp 71.3- 72.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.29-7.36 (m, 4H), 7.14-7.25 (m, 5H), 6.98-6.99 (m, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 2H), 6.54 (s, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 4.27 (d, *J*= 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.7, 146.2, 143.1, 140.8, 132.1, 129.8, 129.7, 129.5, 129.1, 129.0, 128.6, 128.3, 126.3, 124.8, 124.7, 121.3, 119.8, 119.2, 118.2, 116.2, 115.9, 114.3, 52.9; MS(ESI-TOF) m/z: 403.2 $[M+H]^+$.



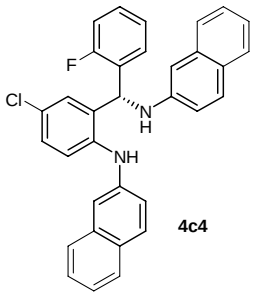
4c2

Compound **4c2** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 91%). mp 79.4-80.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.62 (d, *J* = 8.0 Hz, 2H), 7.50-7.57 (m, 4H), 7.39-7.49 (m, 8H), 7.12-7.46 (m, 5H), 7.06 (d, *J* = 2.0 Hz, 3H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.53 (s, 1H), 6.09 (d, *J* = 6.8 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.5, 140.9, 140.8, 140.5, 134.0, 132.4, 132.1, 129.8, 129.7, 129.0, 128.8, 128.7, 128.3, 128.1, 126.8, 126.7, 126.6, 126.5, 126.4, 124.8, 120.4, 118.2, 116.2, 115.9, 114.5, 52.9; MS(ESI-TOF) m/z: 555.2 $[M+H]^+$.



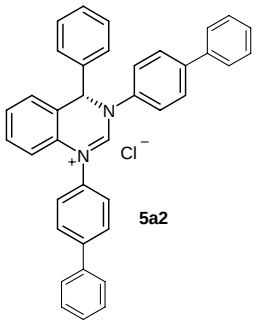
4c3

Compound **4c3** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 88%). mp 144.1-145.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.31-7.39 (m, 3H), 7.10-7.20 (m, 3H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.61 (s, 3H), 6.45 (s, 1H), 6.38 (s, 1H), 6.31 (s, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 1H), 2.28 (s, 6H), 2.21(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.0, 140.9, 139.2, 139.0, 132.4, 129.6, 129.5, 128.4, 128.1, 127.1, 126.9, 125.9, 124.6, 122.9, 121.1, 120.2, 116.1, 115.9, 115.8, 112.2, 52.8, 21.4; MS (ESI-TOF) m/z: 459.2 $[M+H]^+$.



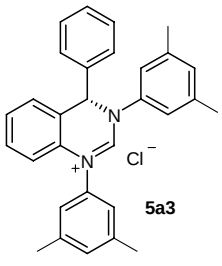
4c4

Compound **4c4** was prepared according to the general procedure of **4a1**. Pale yellow solid (yield 93%). mp 178.3-179.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.82 (m, 5H), 7.54 (d, *J* = 5.2 Hz, 1H), 7.40-7.50 (m, 3H), 7.19-7.38 (m, 6H), 7.11-7.18 (m, 4H), 7.03 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz,1H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.62 (s, 1H), 6.24 (d, *J* = 7.6 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 159.7, 143.7, 140.9, 140.6, 134.8, 134.6, 132.8, 129.8, 129.7, 129.3, 128.9, 128.7, 128.3, 127.7, 127.6, 127.0 , 126.6, 126.5, 126.4, 124.8, 123.6, 122.9, 120.9, 117.9, 116.2, 116.0 , 112.0, 107.3, 52.8; MS (ESI-TOF) m/z: 504.1 $[M+H]^+$.



5a2

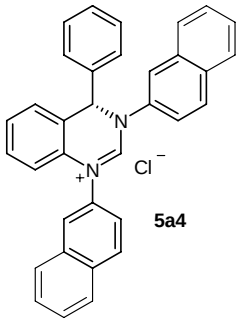
Compound **5a2** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 93%).mp 103.2-104.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 1.2 Hz, 2H), 7.33-7.54 (m, 16H), 7.22-7.31 (m, 2H), 7.10 (d, *J* = 1.6 Hz, 1H), 6.92 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 143.8, 142.5, 139.4, 139.2, 138.9, 138.5, 135.4, 132.1, 129.5, 129.4, 129.2, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 127.3, 127.1, 125.8, 122.9, 117.2, 65.5; MS(ESI-TOF) m/z: 513.2 $[M]^+$; $[\alpha]_D^{25}$ = -40.5° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{38}H_{29}N_2^+[M]^+$ 513.2325, Found 513.2328.



5a3

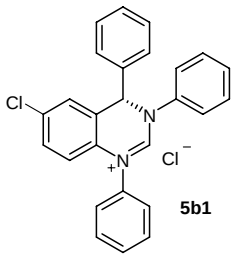
Compound **5a3** was prepared according to the general procedure of **5a1**. Pale yellow

solid (yield 91%). mp 119.4- 121.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.52 (s, 2H), 7.44 (d, *J* = 1.2 Hz, 2H), 7.29-7.43 (m, 4H), 7.20-7.25 (m, 3H), 7.08 (t, *J* = 4.0 Hz, 1H), 6.93 (s, 1H), 6.87 (s, 1H), 6.75-6.77 (m, 3H), 2.43 (s, 6H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 140.8, 139.9, 139.2, 136.2, 132.5, 132.1, 131.4, 129.3, 129.2, 128.7, 128.6, 128.4, 125.3, 122.8, 117.2, 65.3, 21.2; MS (ESI-TOF) m/z: 417.2 $[M]^+$; $[\alpha]_D^{25}$ = -36.2° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{30}H_{29}N_2^+$ $[M]^+$ 417.2325, Found 417.2327.



5a4

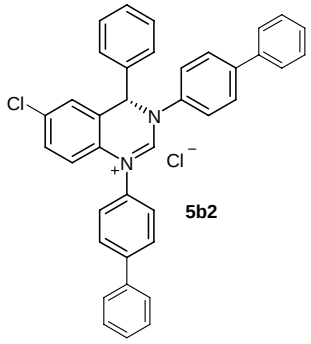
Compound **5a4** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 92%).mp 186.3-187.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.67 (s, 1H), 8.45 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.91 (dd, J_1= 13.2, J_2 = 8.4Hz, 2H), 7.70 (t, *J* = 8.8 Hz, 2H), 7.52-7.54 (m, 5H), 7.45-7.47 (m, 2H), 7.14-7.34 (m, 6H), 7.07 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 136.8, 133.7, 133.6, 133.0, 132.1, 130.6, 130.0, 127.9, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.1, 127.9, 127.8, 127.6, 127.5, 127.2, 125.2, 124.4, 123.0, 121.9, 65.4; MS(ESI-TOF) m/z: 461.2 $[M]^+$; $[\alpha]_D^{25}$ = -38.7° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{34}H_{25}N_2^+[M]^+$ 461.2012, Found 461.2001.



5b1

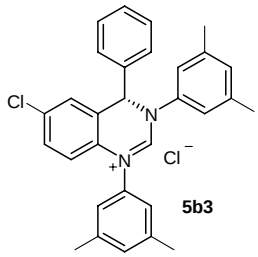
Compound **5b1** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 94%). mp 211.0-212.3 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 7.86 (d, *J* = 6.8 Hz, 2H), 7.67-7.74 (m, 6H), 7.33-7.49 (m, 7H), 7.15 (s, 1H), 6.69 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100MHz, DMSO-d_6) δ 153.0, 140.0, 139.9, 136.8, 132.7, 131.1, 131.0, 129.8, 129.6, 128.4, 128.3, 125.6, 124.8, 119.0, 62.8; MS(ESI-TOF) m/z: 395.1 $[M]^+$; $[\alpha]_D^{25}$ = -32.8° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for

$C_{26}H_{20}ClN_2^+[M]^+$ 395.1315, Found 395.1308.



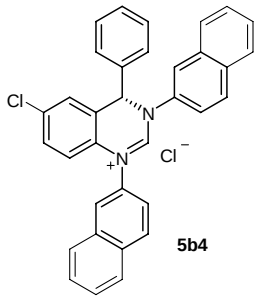
5b2

Compound **5b2** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 91%).mp 164.1-165.3 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.73-7.80 (m, 5H), 7.64-7.67 (m, 4H), 7.52-7.56 (m, 3H), 7.36-7.48 (m, 10H), 7.06 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.7, 142.8, 141.3, 139.9, 139.0, 138.9, 138.7, 135.8, 132.9, 130.8, 129.9, 129.7, 129.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.2, 127.0, 126.9, 125.8, 125.5, 125.1, 119.1, 62.9; MS (ESI-TOF) m/z: 547.2 $[M]^+$; $[\alpha]_D^{25}$ = -41.6° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{38}H_{28}ClN_2^+[M]^+$547.1936, Found 547.1935.



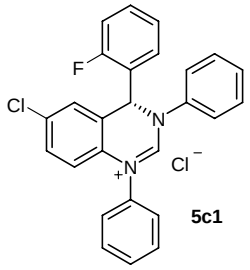
5b3

Compound **5b3** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 94%).mp 116.3-117.2 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.36-7.46 (m, 10H), 7.15 (s, 1H), 7.04 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 2.41 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (100MHz, DMSO-d_6) δ 152.6, 140.5, 140.1, 139.7, 139.5, 136.6, 132.6, 132.3, 131.0, 130.9, 129.8, 129.6, 128.2, 127.9, 125.6, 125.5, 121.9, 119.1, 62.4, 21.2; MS (ESI-TOF) m/z: 451.2 $[M]^+$; $[\alpha]_D^{25}$ = -35.8° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{30}H_{28}ClN_2^+[M]^+$ 451.1936, Found 451.1916.



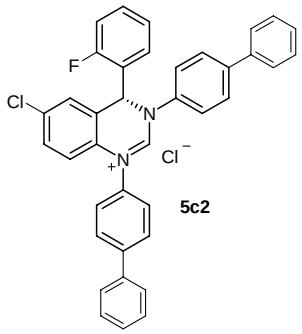
5b4

Compound **5b4** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 89%). mp 179.3-181.1 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (s, 1H), 8.49 (d, *J* = 1.2 Hz, 1H), 8.31 (t, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 1.6 Hz, 2H), 8.14 (d, *J* = 6.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.97 (t, *J* = 5.6 Hz, 1H), 7.91 (d, *J* = 5.6 Hz, 1H), 7.81-7.88 (m, 4H), 7.59-7.77 (m, 2H), 7.19-7.46 (m, 9H), 6.84 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.3, 136.8, 134.1, 133.8, 133.6, 132.9, 132.8, 131.6, 131.5, 131.0, 130.2, 128.8, 128.5, 128.3, 128.2, 128.1, 127.9, 125.1, 124.1, 124.0, 121.7, 119.2, 117.1, 116.8, 58.99; MS(ESI-TOF) m/z: 495.1 $[M]^+$; $[\alpha]_D^{25}$ = -39.5° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{34}H_{24}ClN_2^+[M]^+$ 495.1623, Found 495.1611.



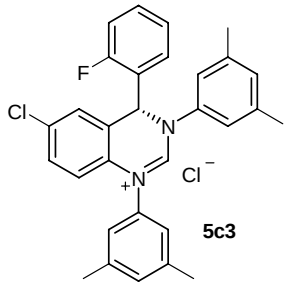
5c1

Compound **5c1** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 95%). mp 208.2-209.1 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (s, 1H), 7.71 (s, 5H), 7.55-7.57 (m, 2H), 7.41-7.47 (m, 5H), 7.16-7.27 (m, 5H), 6.69 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.6, 159.7, 152.7, 139.3, 136.4, 132.9, 131.4, 131.3,131.1, 130.3, 130.1, 128.1, 126.5, 126.3, 125.8, 124.8, 123.9, 118.9, 117.1, 116.8, 59.4; MS(ESI-TOF) m/z:413.1 $[M]^+$; $[\alpha]_D^{25}$ = -33.2° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) calcd for $C_{26}H_{19}ClFN_2^+[M]^+$413.1215, Found 413.1210.



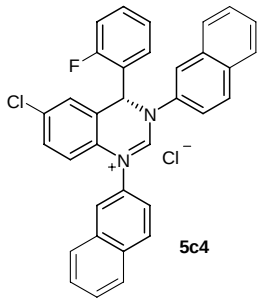
5c2

Compound **5c2** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 91%). mp 111.6-112.3 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.81-7.84 (m, 6H), 7.68-7.70 (m, 2H), 7.54-7.58 (m, 3H), 7.28-7.50 (m, 10H), 6.85 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 159.7, 152.9, 142.9, 142.6, 139.1, 138.8, 135.9, 132.9, 131.5, 131.3, 130.2, 129.7, 129.5, 129.4, 129.2, 128.8, 128.2, 127.5, 125.9, 125.2, 124.1, 119.1, 117.1, 116.9, 58.9; MS (ESI-TOF) m/z: 565.2 [M]+; $[\alpha]_D^{25}$ = -46.5° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) m/z: calcd for $C_{38}H_{27}ClFN_2^+[M]^+$ 565.1841, Found 565.1841.



5c3

Compound **5c3** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 92%). mp 139.7-140.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.75 (t, *J* = 3.6 Hz, 1H), 7.45 (dd, J_1= 2.0 Hz, J_2= 8.4 Hz, 2H), 7.23-7.37 (m, 9H), 7.05 (s, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 2.41 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2, 159.8, 152.5, 140.6, 139.7, 139.3, 136.5, 132.6, 132.4, 131.5, 131.3, 130.1, 128.1, 126.8, 126.7, 125.8, 125.5, 124.0, 122.0, 119.0, 117.1, 116.8, 58.8, 21.2, 21.1; MS(ESI-TOF) m/z: 469.2 $[M]^+$; $[\alpha]_D^{25}$ = -36.0° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) m/z: calcd for $C_{30}H_{27}ClFN_2^+[M]^+$ 469.1841, Found 469.1843.



5c4

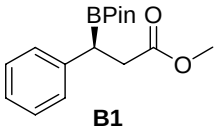
Compound **5c4** was prepared according to the general procedure of **5a1**. Pale yellow solid (yield 90%). mp 220.0-221.2 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 8.46 (d, *J* = 1.6 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.15-8.17 (m, 2H), 8.07 (d, *J* = 9.2 Hz, 1H), 7.60-7.98 (m, 6H), 7.20-7.59 (m, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 153.3, 136.9, 134.1, 133.8, 133.6, 132.9, 132.8, 131.6, 131.4, 131.0, 130.3, 130.2, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 125.8, 125.0, 124.1, 121.7, 119.3, 117.1, 116.8, 59.1; MS(ESI-TOF) m/z: 513.1 $[M]^+$; $[\alpha]_D^{25}$ = -40.2° (*c* 1.00, $CHCl_3$); HRMS (ESI-TOF) m/z: calcd for $C_{34}H_{23}ClFN_2^+[M]^+$ 513.1528, Found 513.1520.

Representative Procedure for NHC–Cu-Catalyzed Enantioselective Boron Conjugate Additions (B1-6):

Typical reaction condition for β-borylation reactions: **5c2** (6.1 mg, 0.01 mmol), NaO^{t}Bu (2 mg, 0.02 mmol), and CuCl (2 mg, 0.02 mmol) were placed and THF (2.0 mL) was added in the glovebox. The solution was allowed to stir for 20 minutes at 22 ℃ under dry N_2 atmosphere. And then the reaction mixture was cooled to -55 ℃ and MeOH (45 μL, 1 mmol) was added. After 5 min, α, β-unsaturated ester (1 mmol) and bis(pinacolato) diboron (1.1 mmol) were added to the reaction mixture. NaO^{t}Bu (16 mg, 0.16 mmol) was added to the reaction mixture. The solution was stirred for 10 hour at -55℃. After completion of the reaction, the solution was quenched with saturated aqueous NaCl solution. The mixture is extracted twice with ethyl acetate and the combined organic phase is washed with brine, dried with anhydrous sodium sulfate. The organic layer was evaporated under reduced pressure. The resulting residue was purified by column chromatography (petroleum ether : EtOAc = 20 : 1) to afford the desired products.

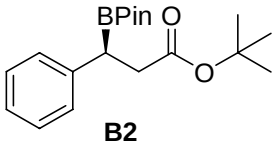
For the determination of enantioselectivity, the resulting boronate was dissolved in EtOAc (2 mL) and oxidized by treatment of H_2O_2 (5 eq.) and 1 M NaOH solution (5 eq.) for 30 min. After phase separation, the organic layer was evaporated under

reduced pressure. The crude alcohol product was determined without purification.



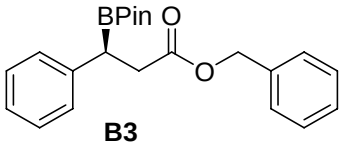
B1

Prepared according to the general procedure using methyl cinnamate (-55 ºC, 10 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (94% yield, 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.30 (m, 4H), 7.18 (t, J = 6.0 Hz, 1H), 3.68 (s, 3H), 2.91 (q, J = 8.0 Hz, 1H), 2.66-2.78 (m, 2H), 1.24 (s, 6H), 1.20 (s, 6H). MS $[M+H]^+$ 291.1; $[\alpha]_D^{25}$ = +16.1° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (93% ee; chiralpak AD–H column (25 cm × 0.46 cm), 96/4 hexane/*i*-PrOH, 0.8 mL/min, 254 nm).



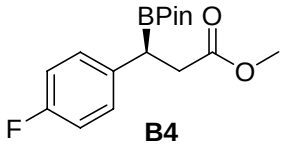
B2

Prepared according to the general procedure using tert-butyl cinnamate (-55 ºC, 9 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (90% yield, 90% ee) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.28 (m, 4H), 7.13-7.17 (m, 1H), 2.82 (dd, J_1= 12, J_2 = 16 Hz, 1H), 2.72 (m, 1H), 2.59 (dd, J_1 = 4.0, J_2 =16.0 Hz, 1H), 1.43 (s, 9H), 1.19 (s, 6H). EMS $[M+H]^+$ 333.2; $[\alpha]_D^{25}$ = +14.3° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (90% ee; chiralpak AS–H column (25 cm × 0.46 cm), 99/1 hexane/*i*-PrOH, 0.4 mL/min, 220 nm).



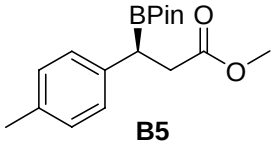
B3

Prepared according to the general procedure using Benzyl cinnamate (-55 ºC, 11 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (89% yield, 91% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.39 (m, 10H), 5.16 (dd, J_1 = 12.4, J_2 =29.2 Hz, 2H), 2.74-3.03 (m, 3H), 1.24 (s, 6H), 1.19 (s, 6H). EMS $[M+H]^+$ 367.2; $[\alpha]_D^{25}$ = +16.8° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (91% ee; chiralpak AS–H column (25 cm × 0.46 cm), 98/2 hexane/*i*-PrOH, 0.7 mL/min, 220 nm).



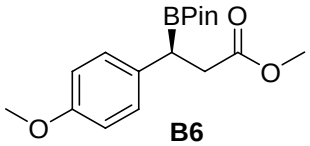
B4

Prepared according to the general procedure using methyl p-fluorocinnamate (-55 ºC, 10 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (94% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.21 (m, 2H), 6.97 (t, *J* = 4.0 Hz, 2H), 3.67 (s, 3H), 2.63-2.90 (m, 3H), 1.22 (s, 12H). EMS $[M+H]^+$ 309.2; $[\alpha]_D^{25}$ = +13.5° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (92% ee; chiralpak AS–H column (25 cm × 0.46 cm), 97/3 hexane/i-PrOH, 0.7 mL/min, 254 nm).



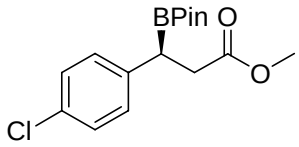
B5

Prepared according to the general procedure using 4-methyl cinnamic acid methyl ester (-55 ºC, 8 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (93% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (q, J = 8.0 Hz, 4H), 3.67 (s, 3H), 2.90 (m, 1H), 2.63-2.74 (m, 2H), 2.32 (s, 3H), 1.25 (s, 6H), 1.20 (s, 6H). EMS $[M+H]^+$ 305.1; $[\alpha]_D^{25}$ = +14.8° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (92% ee; chiralpak AS–H column (25 cm × 0.46 cm), 98/2 hexane/*i*-PrOH, 0.5 mL/min, 220 nm).



B6

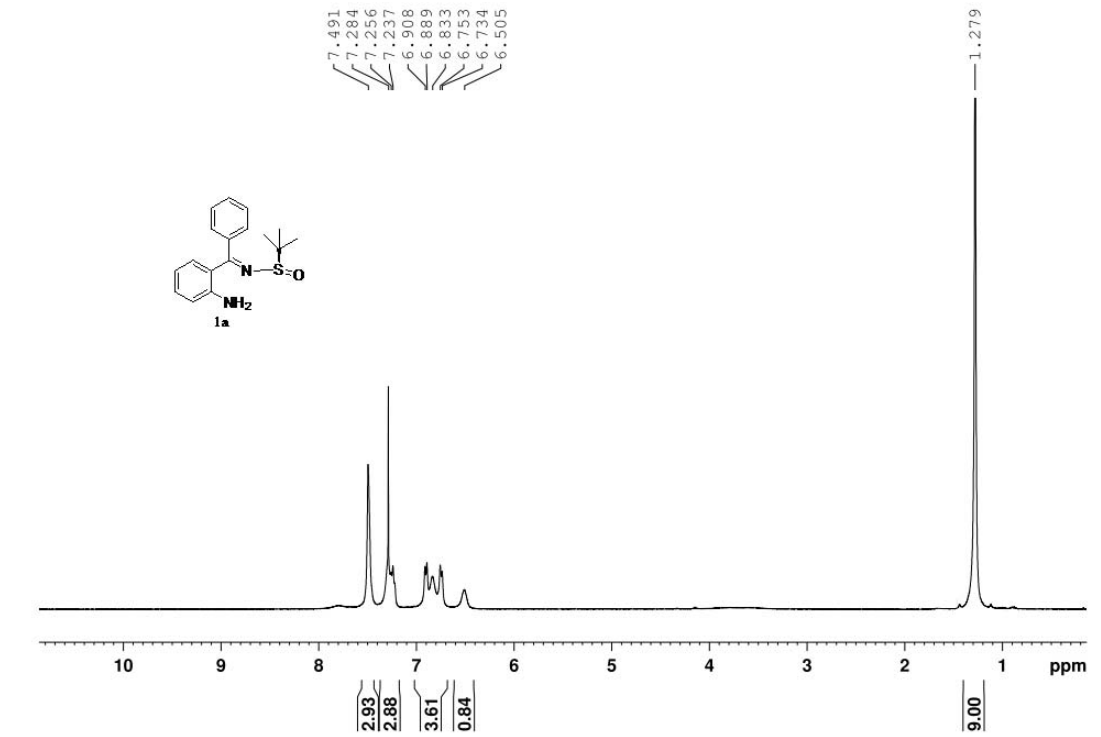
Prepared according to the general procedure using methyl p-methoxycinnamate (-55 ºC, 12 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (87% yield, 88% ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.67 (s, 3H), 2.84-2.87 (m, 1H), 2.63-2.72 (m, 2H), 1.22 (s, 12H). EMS $[M+H]^+$ 309.2; $[\alpha]_D^{25}$ = +15.6° (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis in comparison with authentic racemic material (88% ee; chiralpak AS–H column (25 cm × 0.46 cm), 92/8 hexane/*i*-PrOH, 0.8 mL/min, 220 nm).

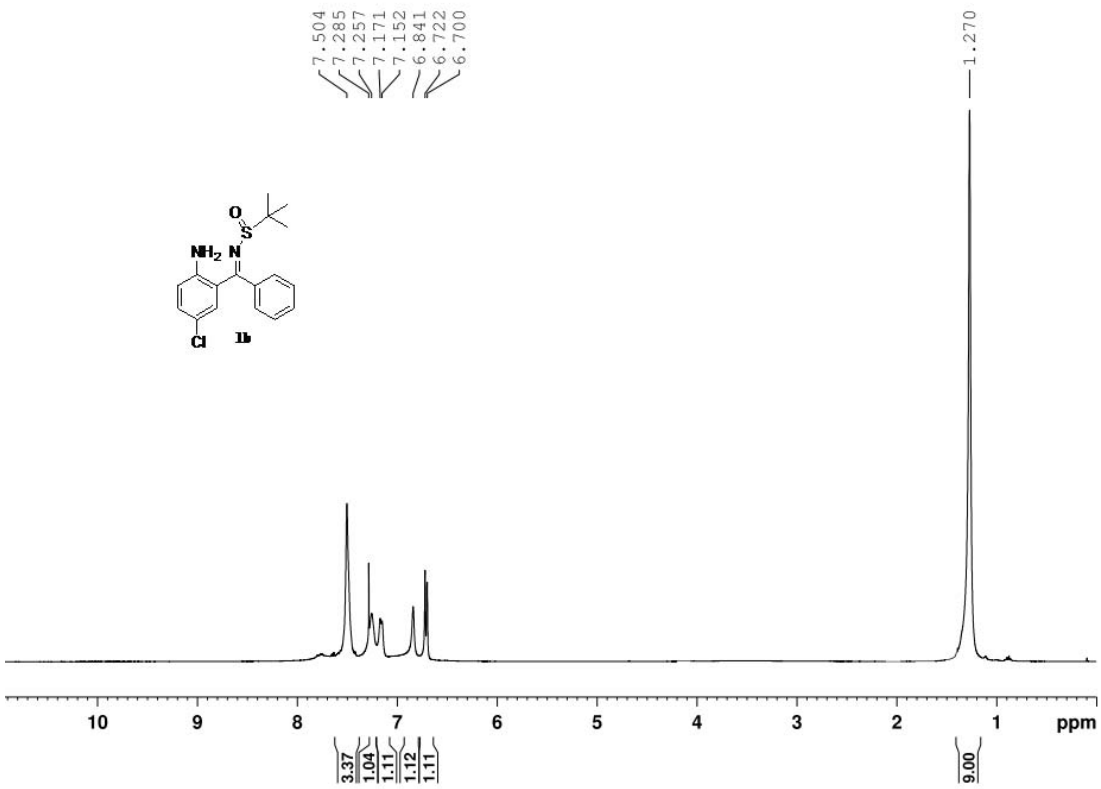


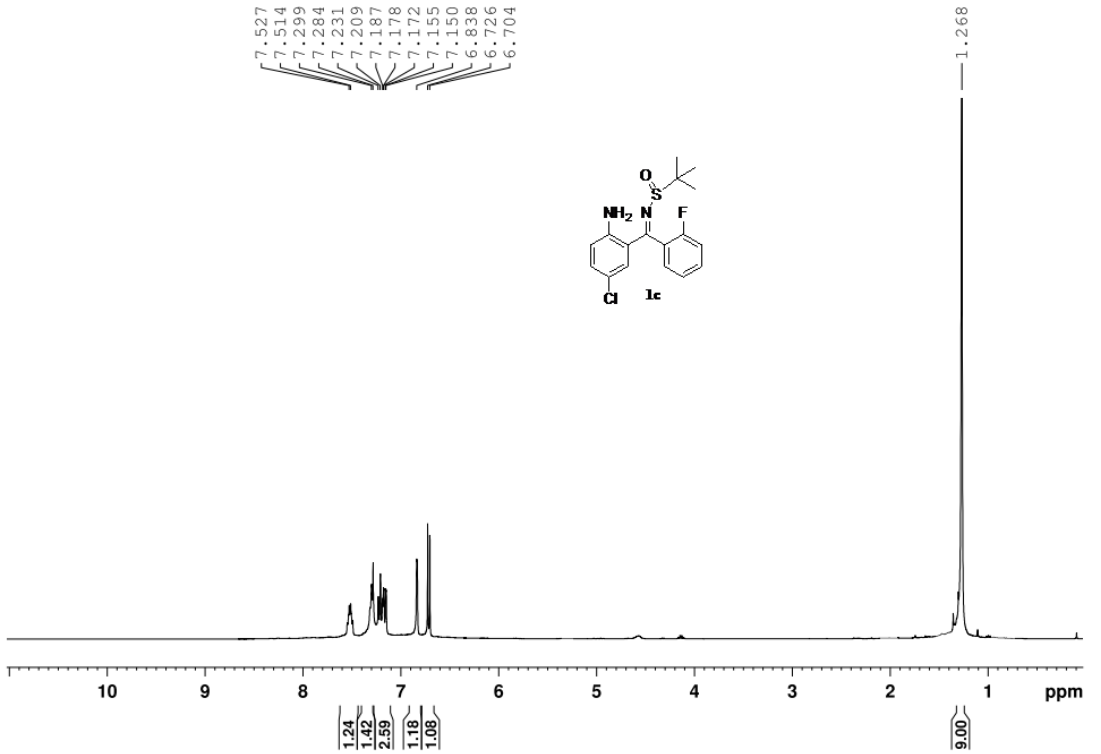
B7

Prepared according to the general procedure using methyl cinnamate (-55 ºC, 10 h, 1 mol% of catalyst) in THF to afford the desired compound as a colorless oil (89% yield, 82% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 8.0 Hz, 1H), 3.65 (m, 4H), 3.03 (dd, J_1= 8.0 Hz, J_2 = 16.0 Hz, 1H), 2.64 (dd, J_1= 8.0 Hz, J_2 = 16.0 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), EMS $[M+H]^+$ 325.2;

NMR spectra of RE-NHC precursors and intermediates



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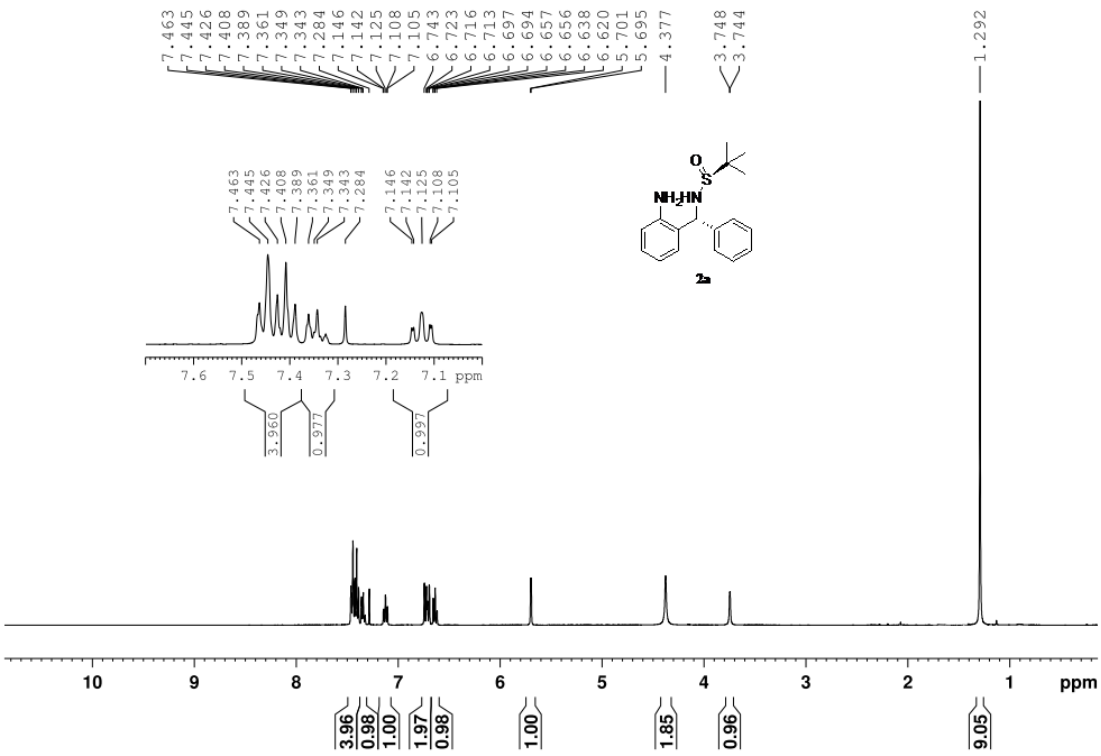
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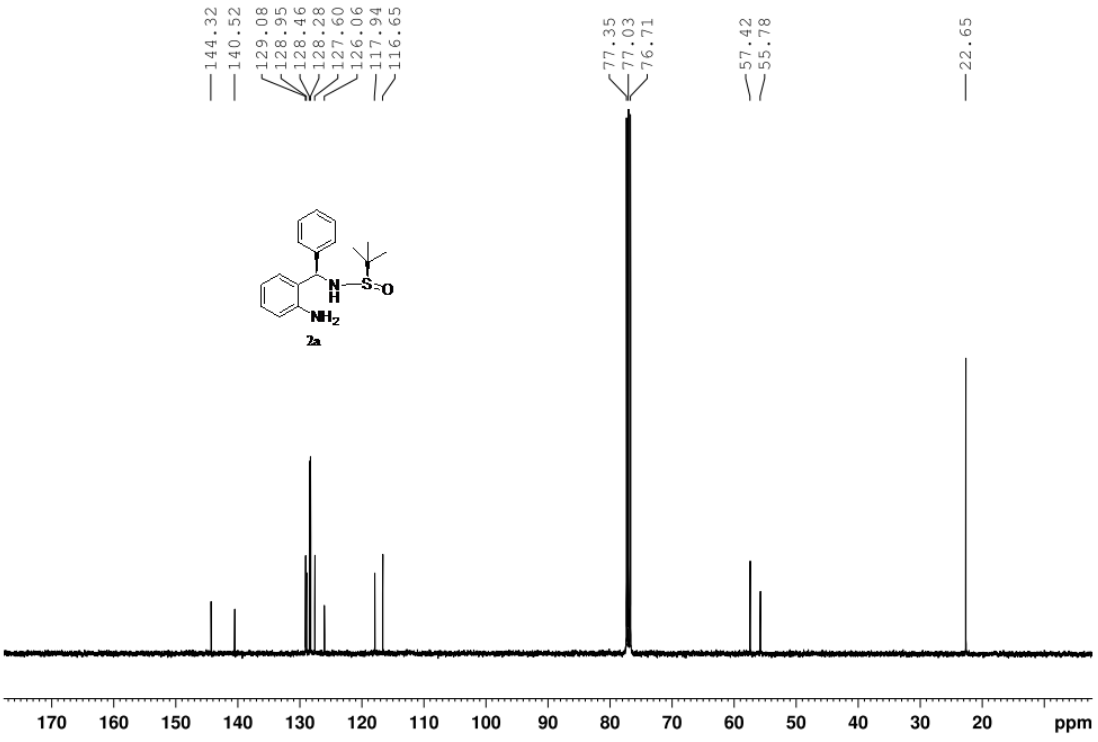
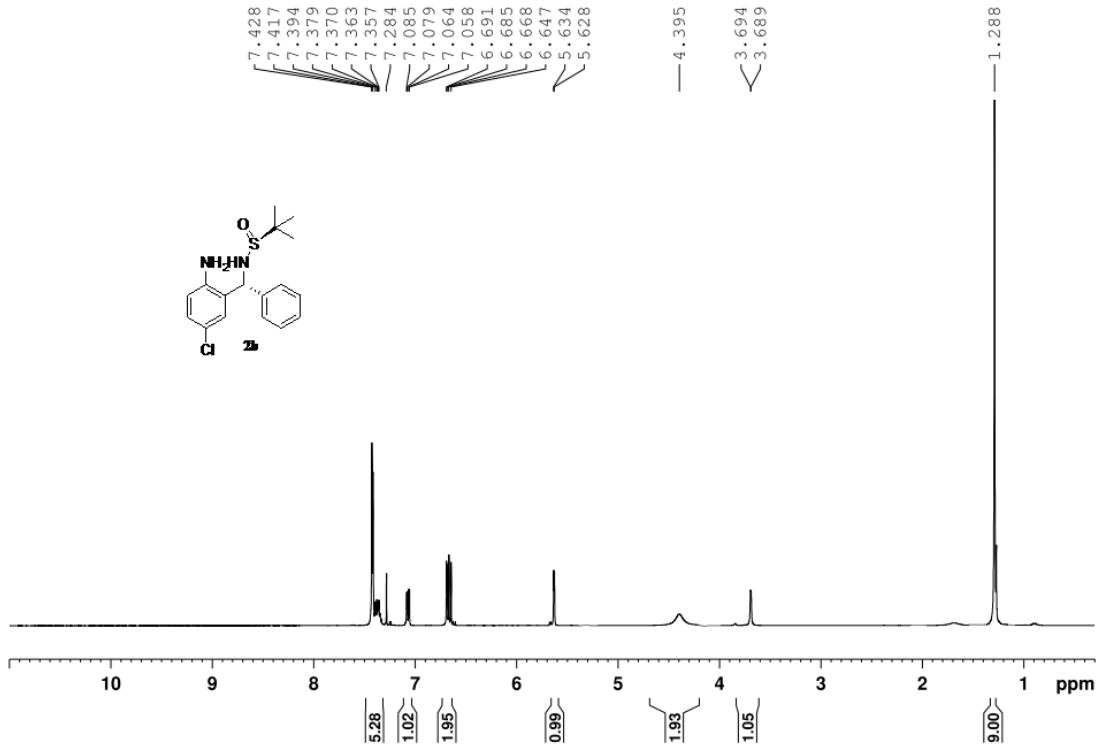
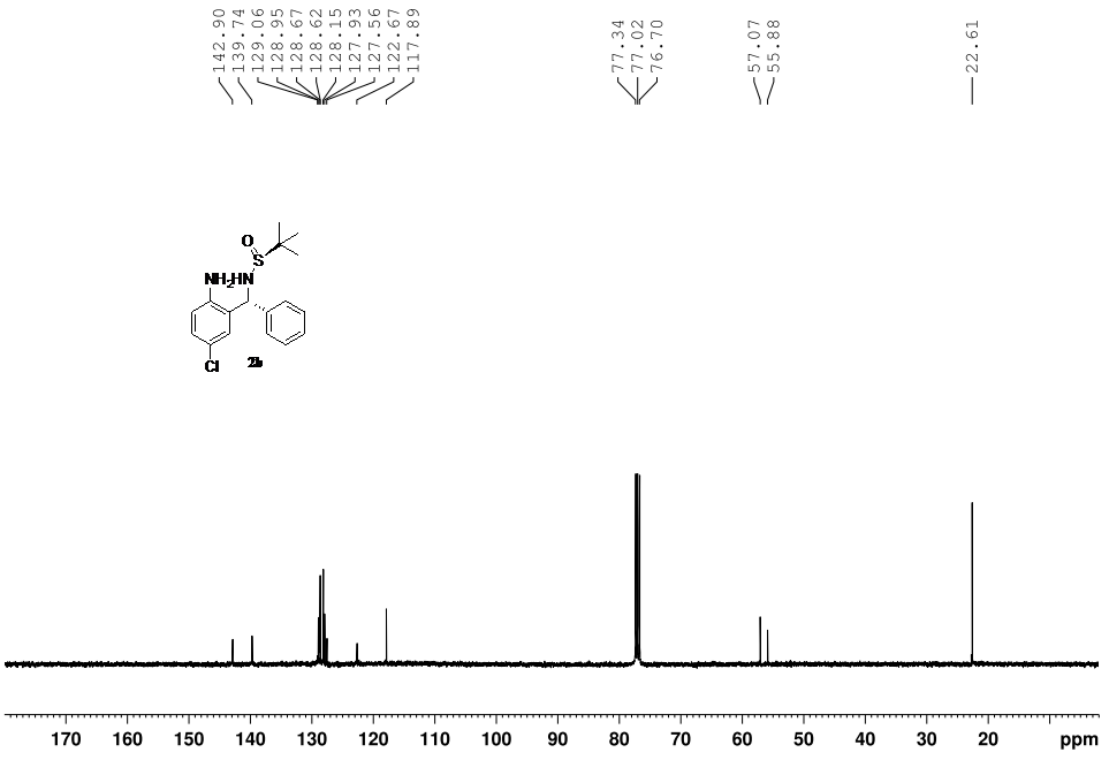
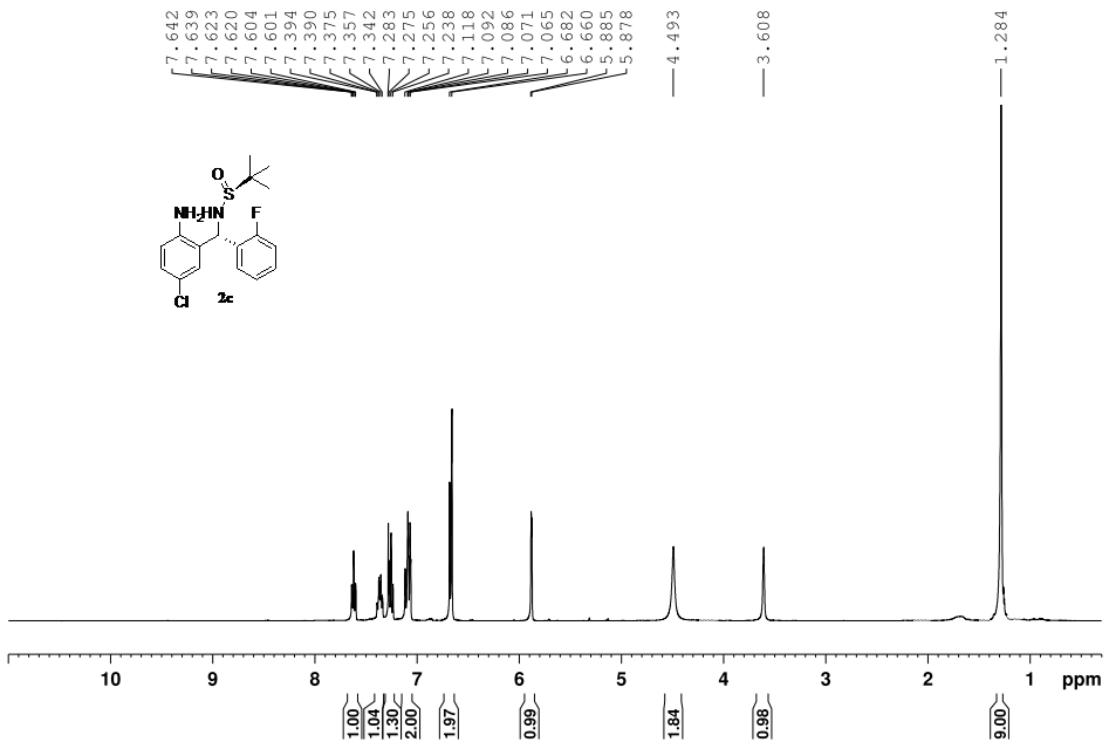
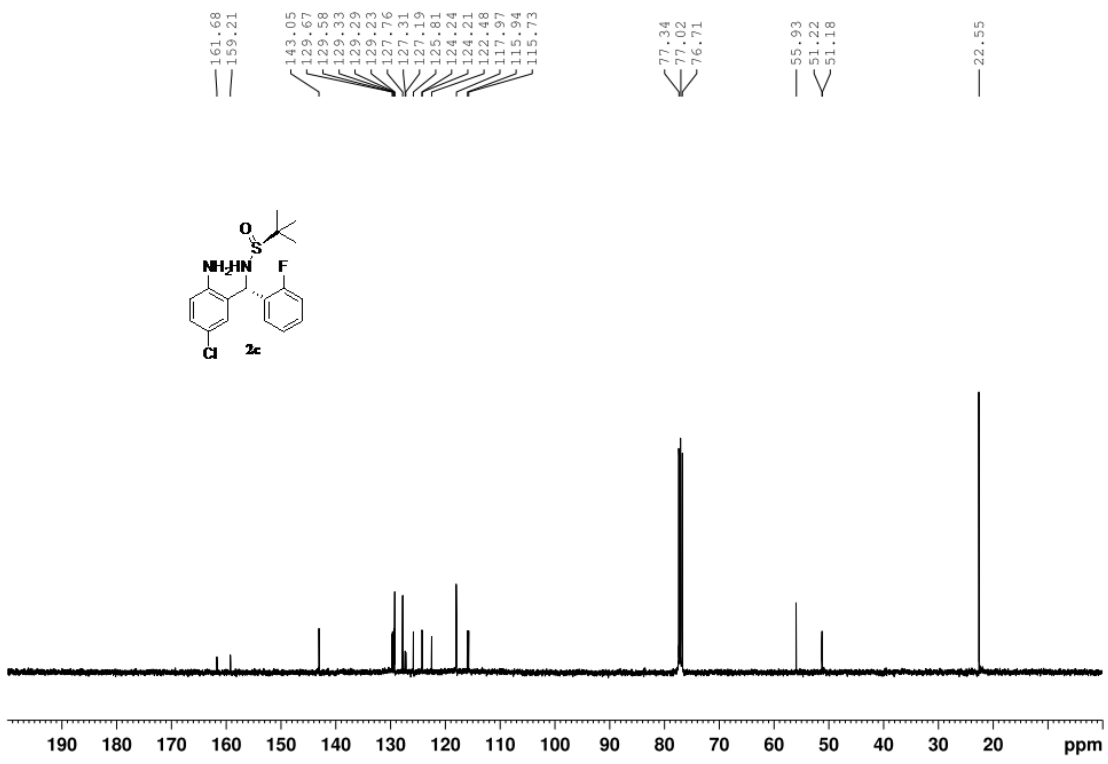
1.00
1.85
0.96
9.05


144.32
140.52
129.08
128.95
128.46
128.28
127.60
126.06
117.94
116.65
77.35
77.03
76.71
57.42
55.78
22.65
2a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

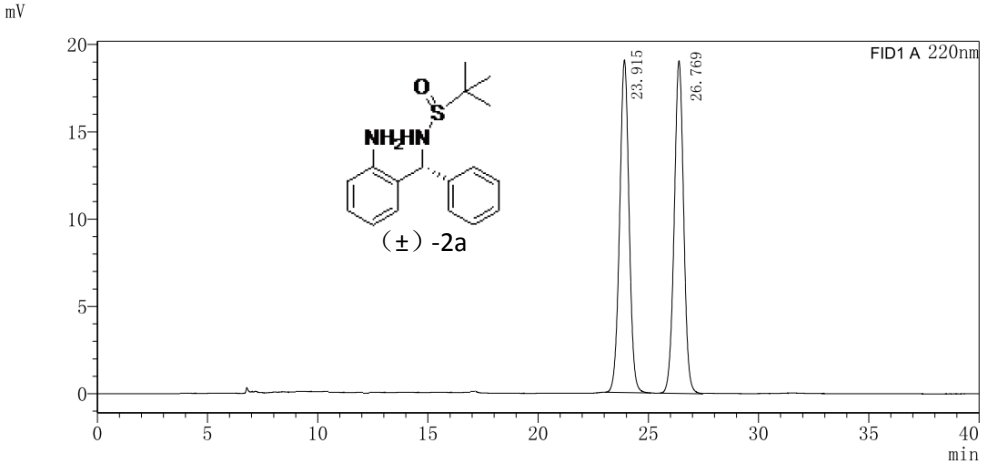

7.428
7.417
7.394
7.379
7.370
7.363
7.357
7.284
7.085
7.079
7.064
7.058
6.691
6.685
6.668
6.647
5.634
5.628
4.395
3.694
3.689
1.288
2b
10
9
8
7
6
5
4
3
2
1
ppm
5.28
1.02
1.95
0.99
1.93
1.05
9.00

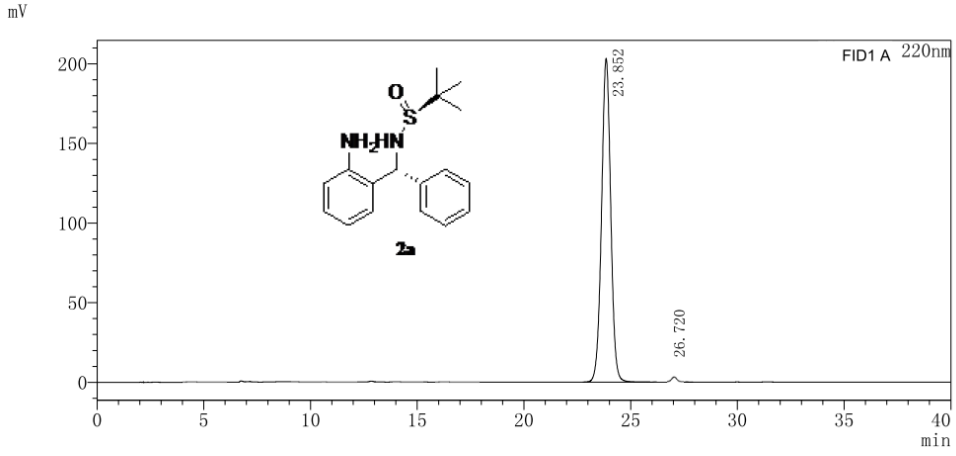

142.90
139.74
129.06
128.95
128.67
128.62
128.15
127.93
127.56
122.67
117.89
77.34
77.02
76.70
57.07
55.88
22.61
O
S
NH2HN
Cl
2b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

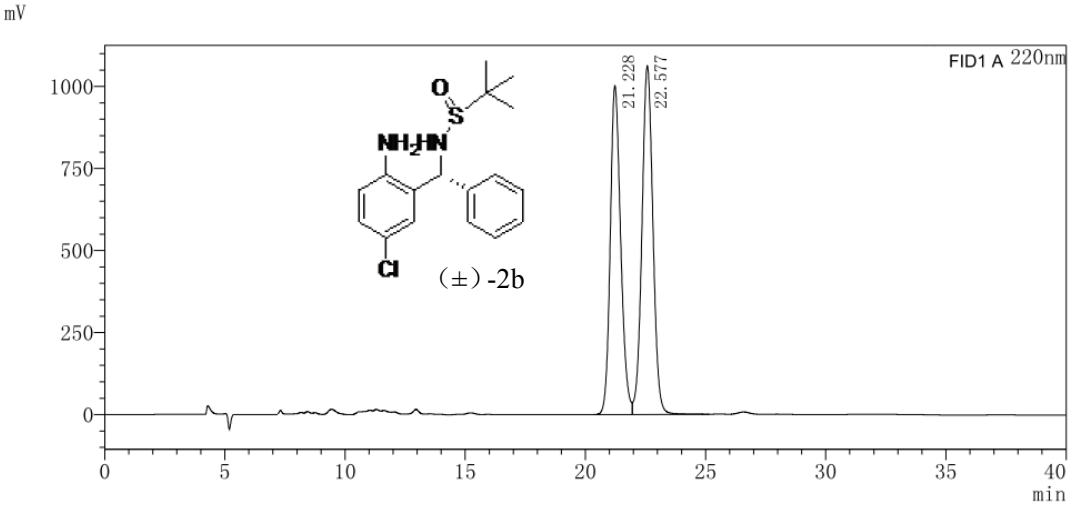

7.642
7.639
7.623
7.620
7.604
7.601
7.394
7.390
7.375
7.357
7.342
7.283
7.275
7.256
7.238
7.118
7.092
7.086
7.071
7.065
6.682
6.660
5.885
5.878
4.493
3.608
1.284
O
S
NH2HN
F
Cl
2c
10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.04
1.30
2.00
1.97
0.99
1.84
0.98
9.00

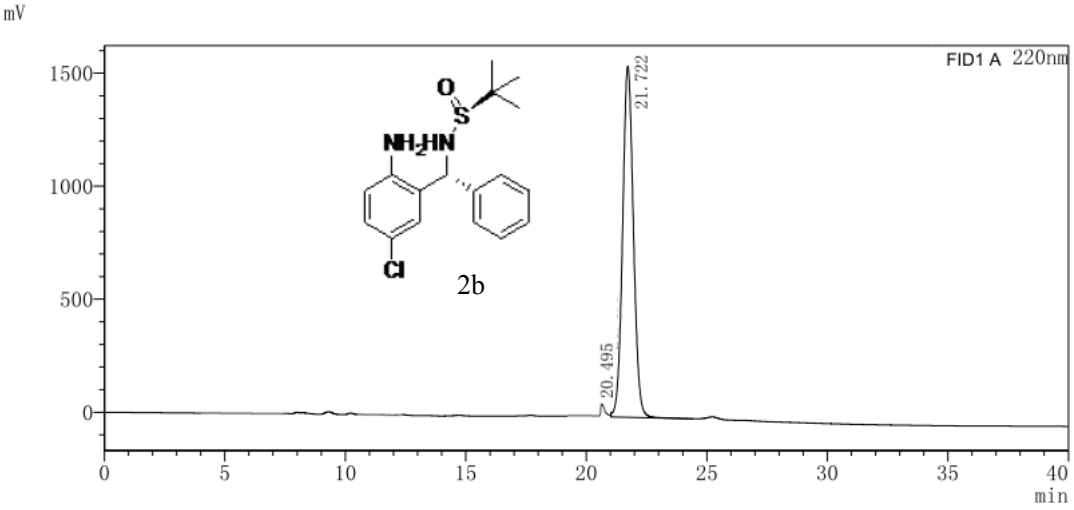


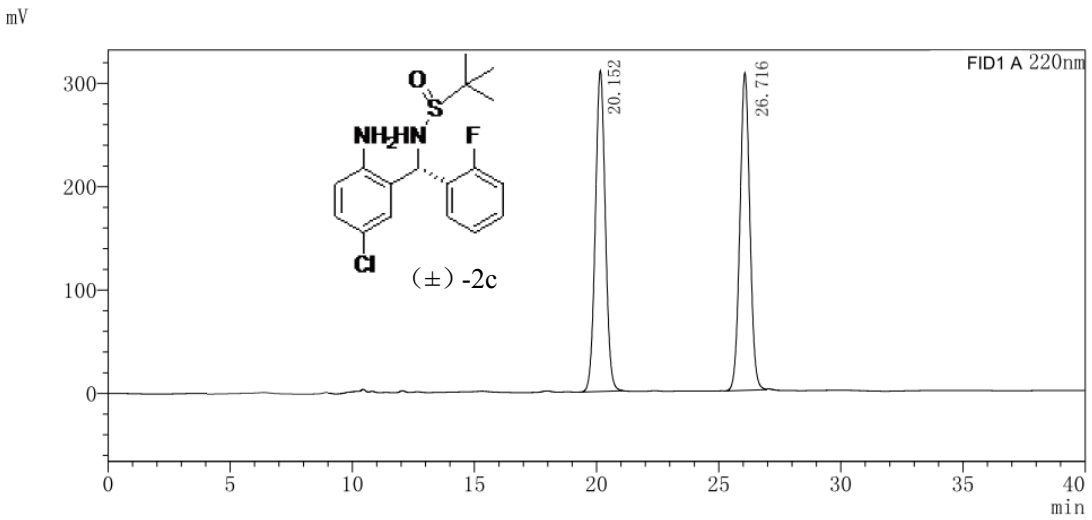
Optical purity of **2**

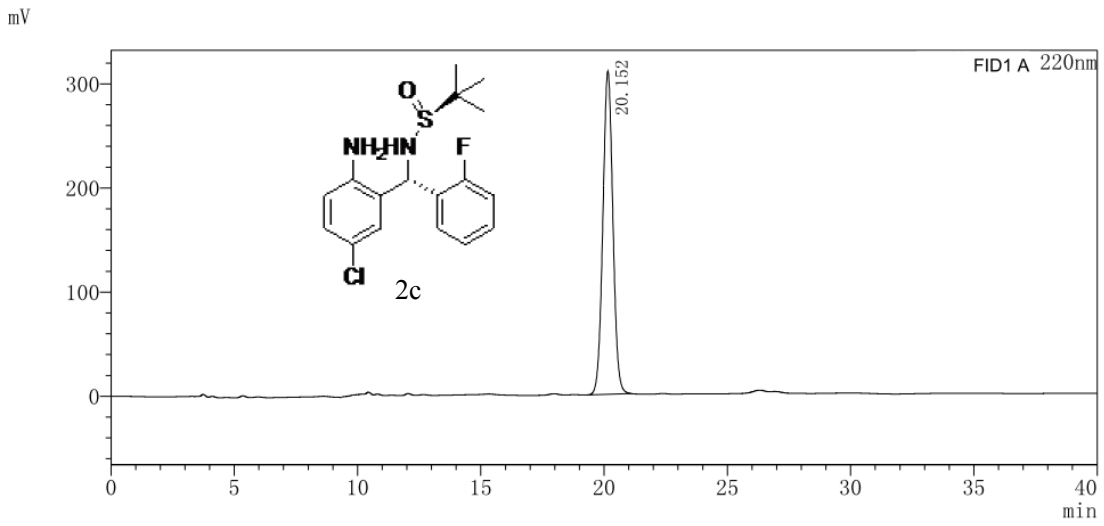


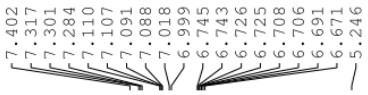


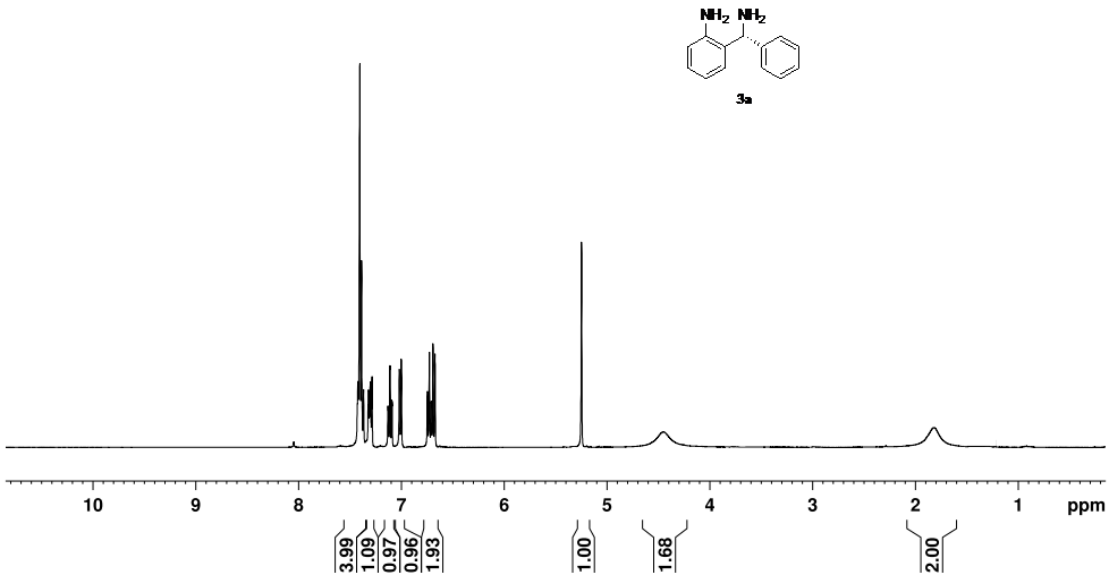

mV
FID1 A 220nm
21.228
22.577
(±)-2b
min

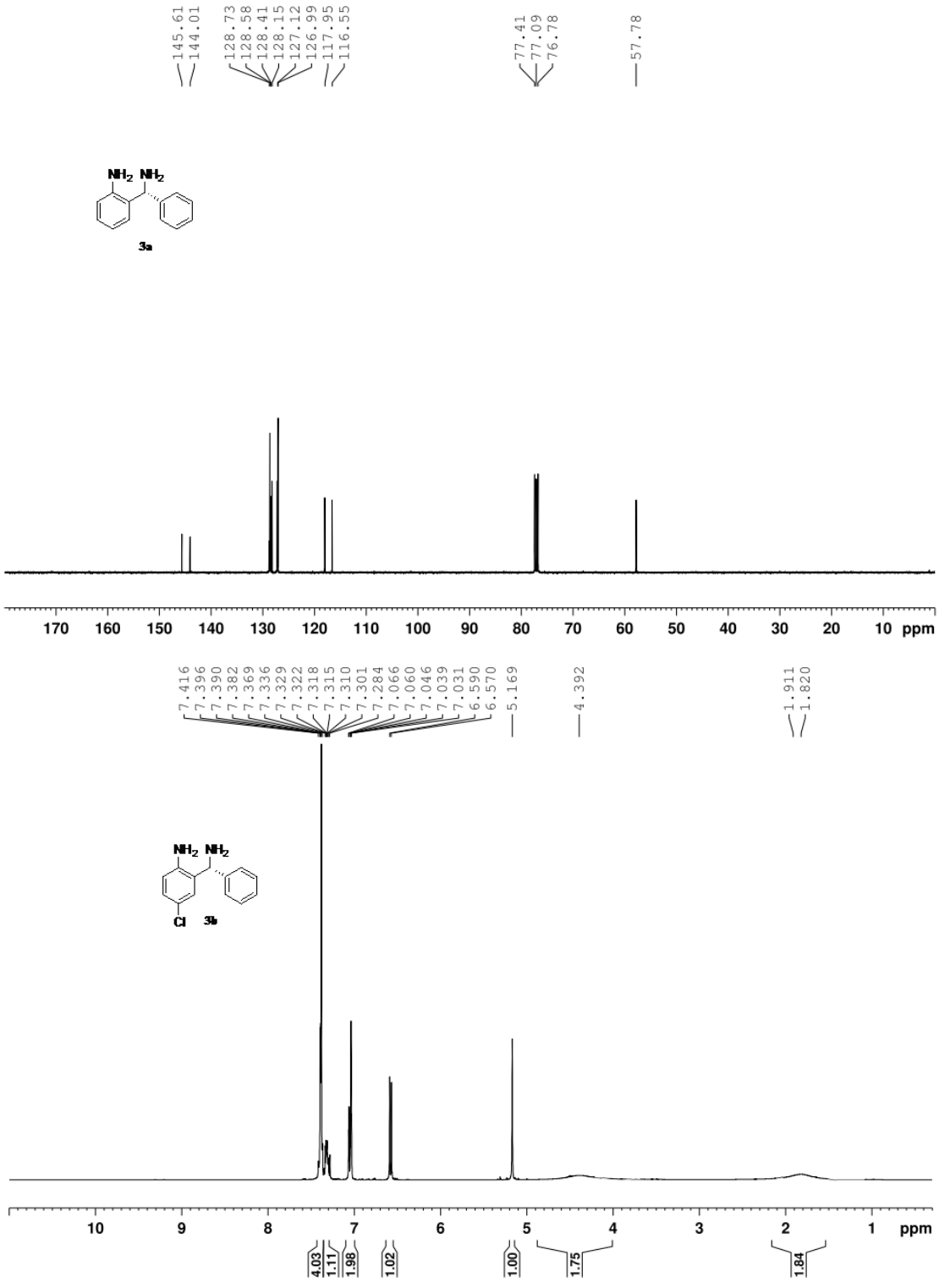

mV
FID1 A 220nm
21.722
20.495
2b
min

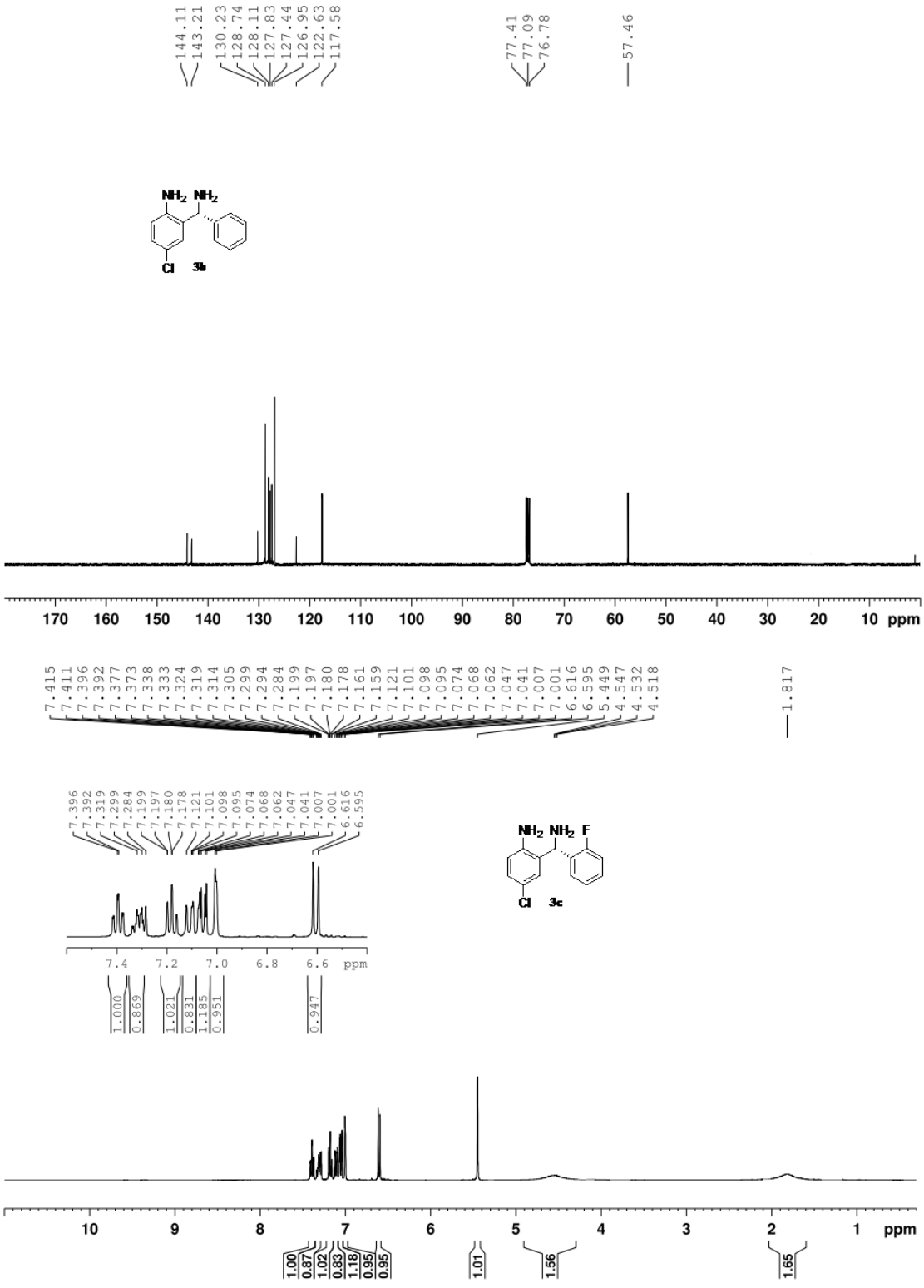

mV
FID1 A 220nm
20.152
26.716
(±)-2c
min

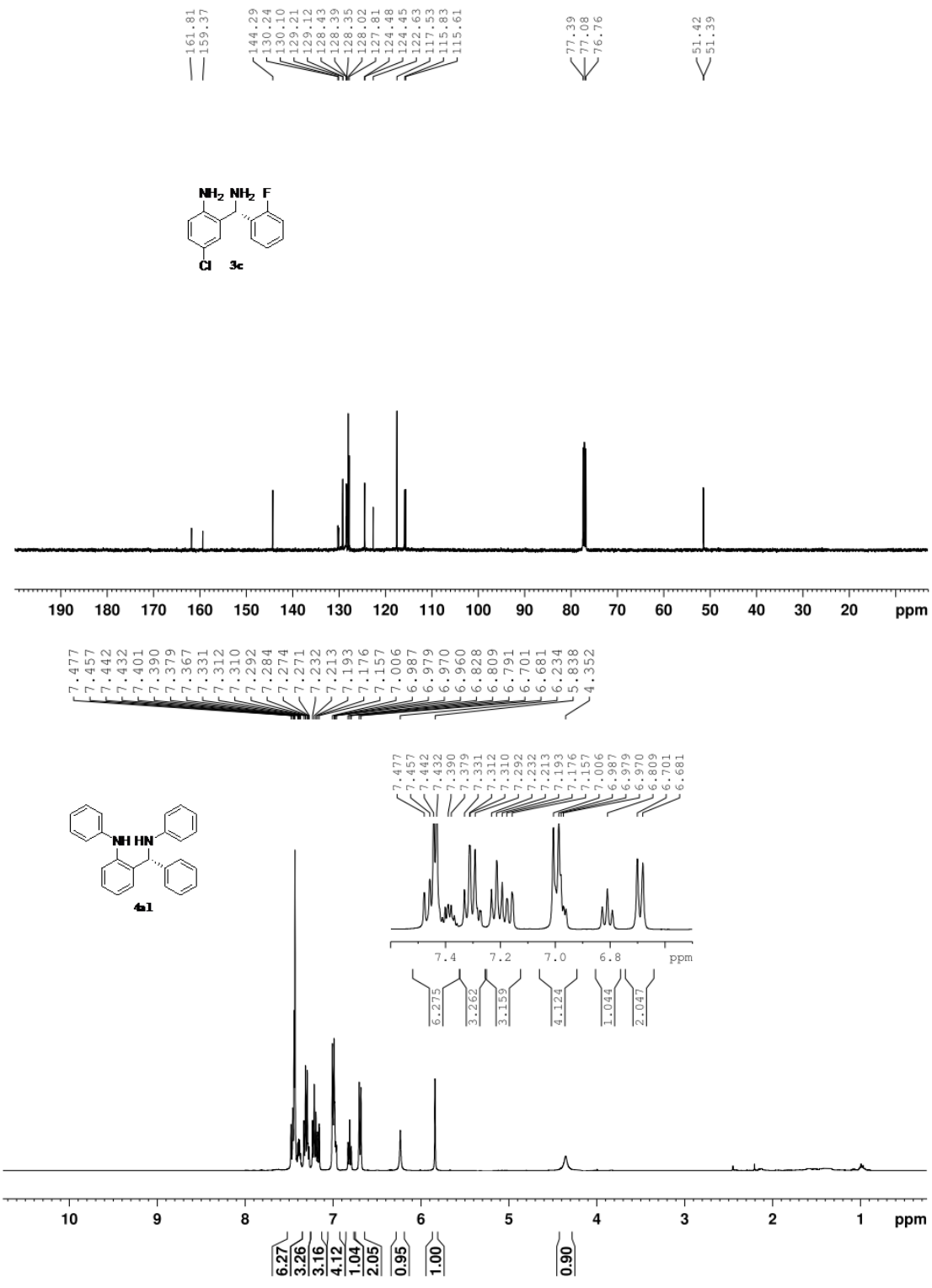

mV
FID1 A 220nm
20.152
2c
min

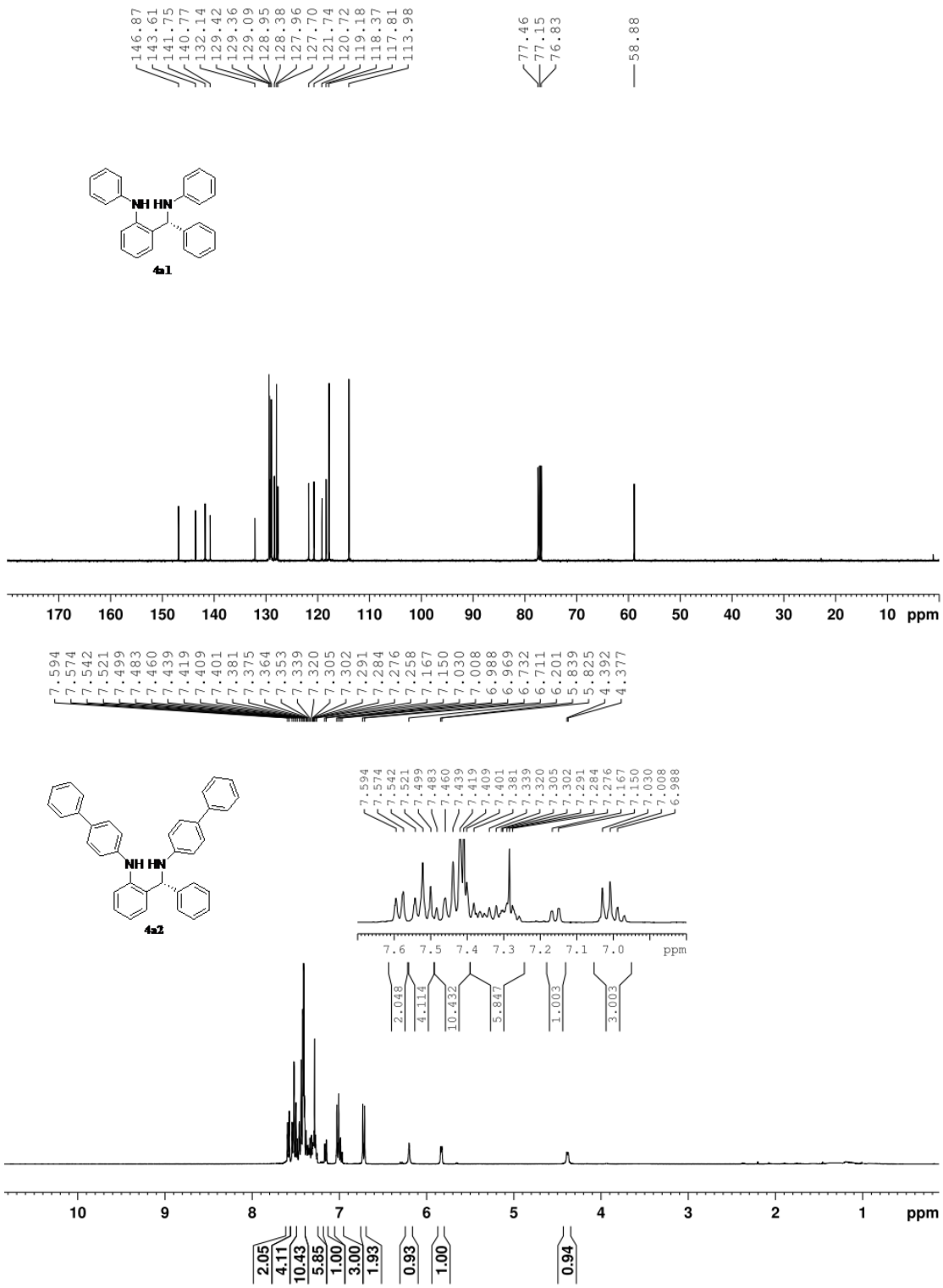

7.402
7.317
7.301
7.284
7.110
7.107
7.091
7.088
7.018
6.999
6.745
6.743
6.726
6.725
6.708
6.706
6.691
6.671
5.246
4.449
1.818

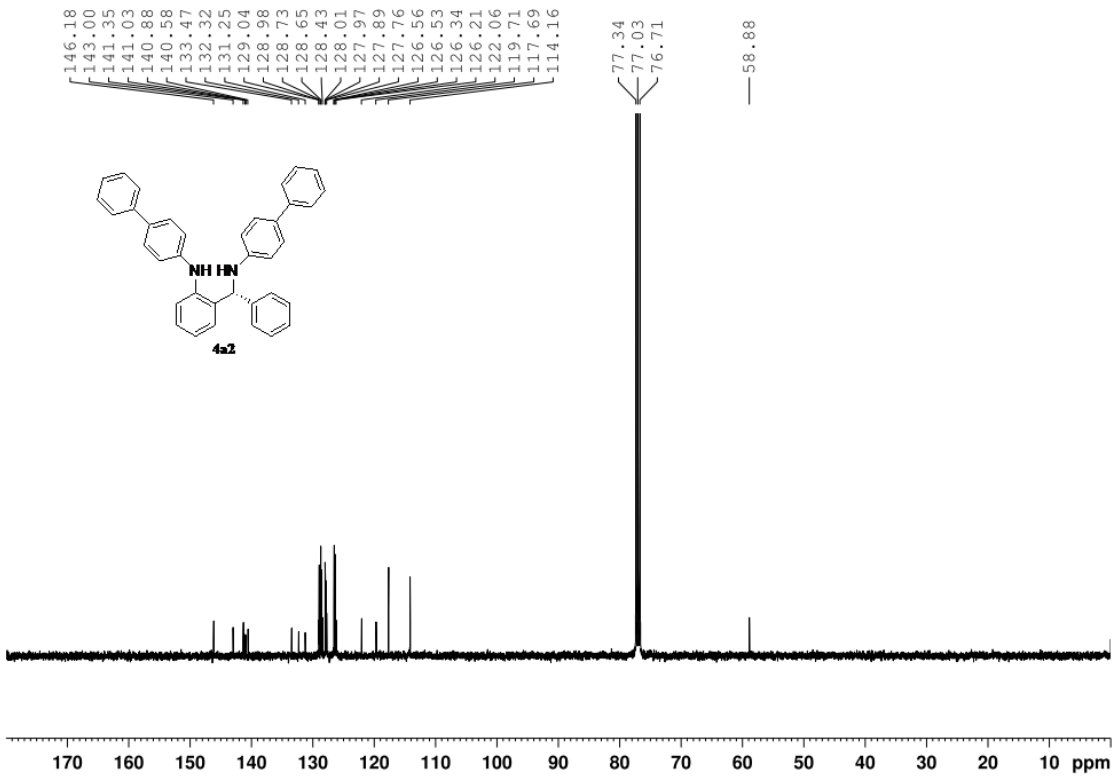

3a
ppm
3.99
1.09
0.97
0.96
1.93
1.00
1.68
2.00

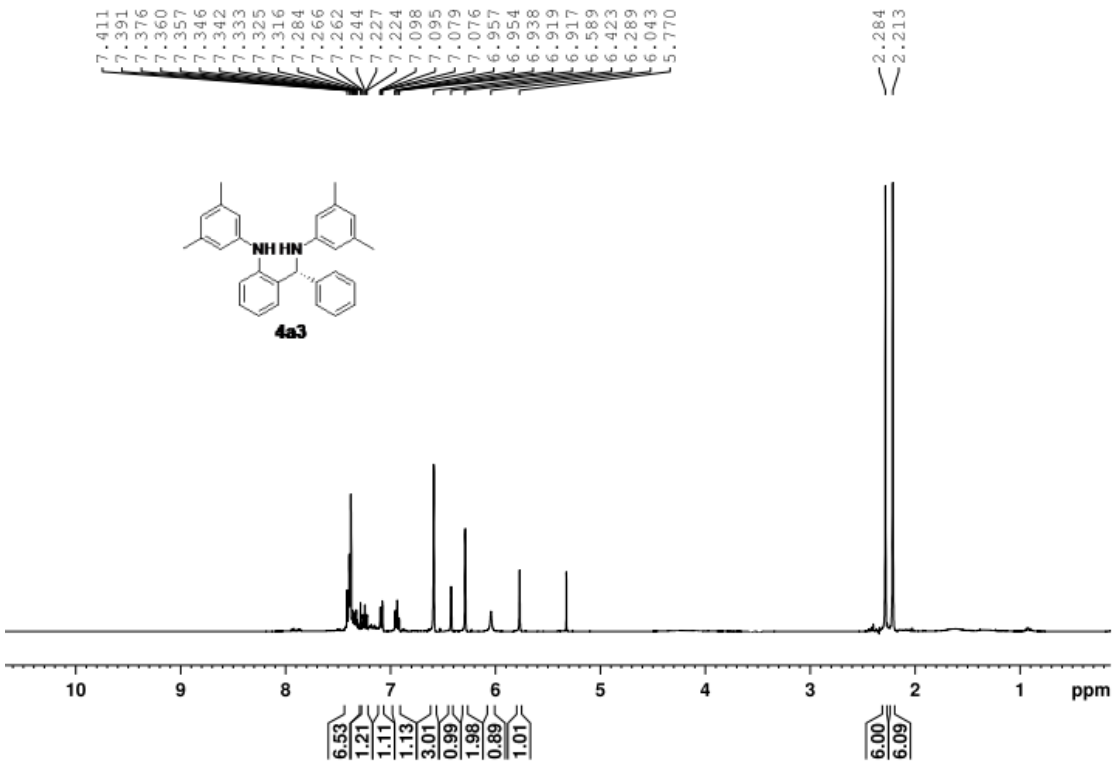

145.61
144.01
128.73
128.58
128.41
128.15
127.12
126.99
117.95
116.55
77.41
77.09
76.78
57.78
NH2 NH2
3a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.416
7.396
7.390
7.382
7.369
7.336
7.329
7.322
7.318
7.315
7.310
7.301
7.284
7.066
7.060
7.046
7.039
7.031
6.590
6.570
5.169
4.392
1.911
1.820
NH2 NH2
Cl
3b
10 9 8 7 6 5 4 3 2 1 ppm
4.03
1.11
1.98
1.02
1.00
1.75
1.84

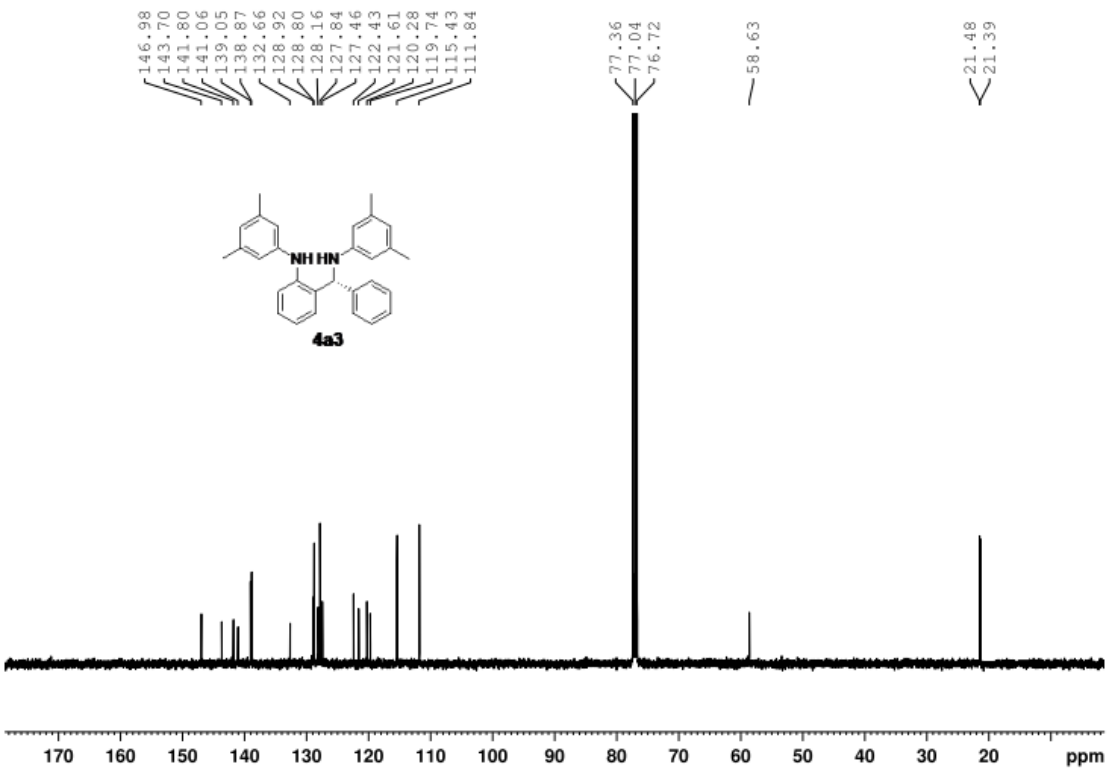

144.11
143.21
130.23
128.74
128.11
127.83
127.44
126.95
122.63
117.58
77.41
77.09
76.78
57.46
NH2 NH2
Cl 3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.415
7.411
7.396
7.392
7.377
7.373
7.338
7.333
7.324
7.319
7.314
7.305
7.299
7.294
7.284
7.199
7.197
7.180
7.178
7.161
7.159
7.121
7.101
7.098
7.095
7.074
7.068
7.062
7.047
7.041
7.007
7.001
6.616
6.595
5.449
4.547
4.532
4.518
1.817
7.4 7.2 7.0 6.8 6.6 ppm
1.000
0.869
1.021
0.831
1.185
0.951
0.947
NH2 NH2 F
Cl 3c
10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.87
1.02
0.83
1.18
0.95
0.95
1.01
1.56
1.65

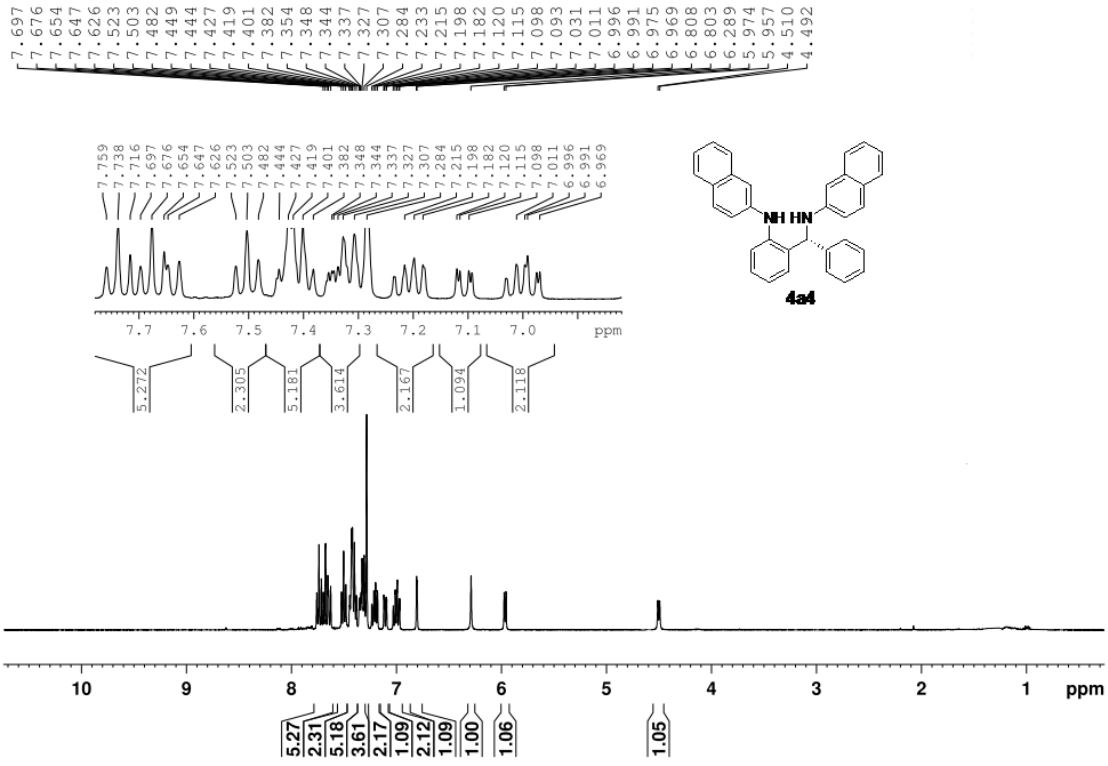

161.81
159.37
144.29
130.24
130.10
129.21
129.12
128.43
128.39
128.35
128.02
127.81
124.48
124.45
122.63
117.53
115.83
115.61
77.39
77.08
76.76
51.42
51.39
NH2 NH2 F
Cl 3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
7.477
7.457
7.442
7.432
7.401
7.390
7.379
7.367
7.331
7.312
7.310
7.292
7.284
7.274
7.271
7.232
7.213
7.193
7.176
7.157
7.006
6.987
6.979
6.970
6.960
6.828
6.809
6.791
6.701
6.681
6.234
5.838
4.352
NH HN
4a1
7.4 7.2 7.0 6.8 ppm
6.275
3.262
3.159
4.124
1.044
2.047
10 9 8 7 6 5 4 3 2 1 ppm
6.27
3.26
3.16
4.12
1.04
2.05
0.95
1.00
0.90

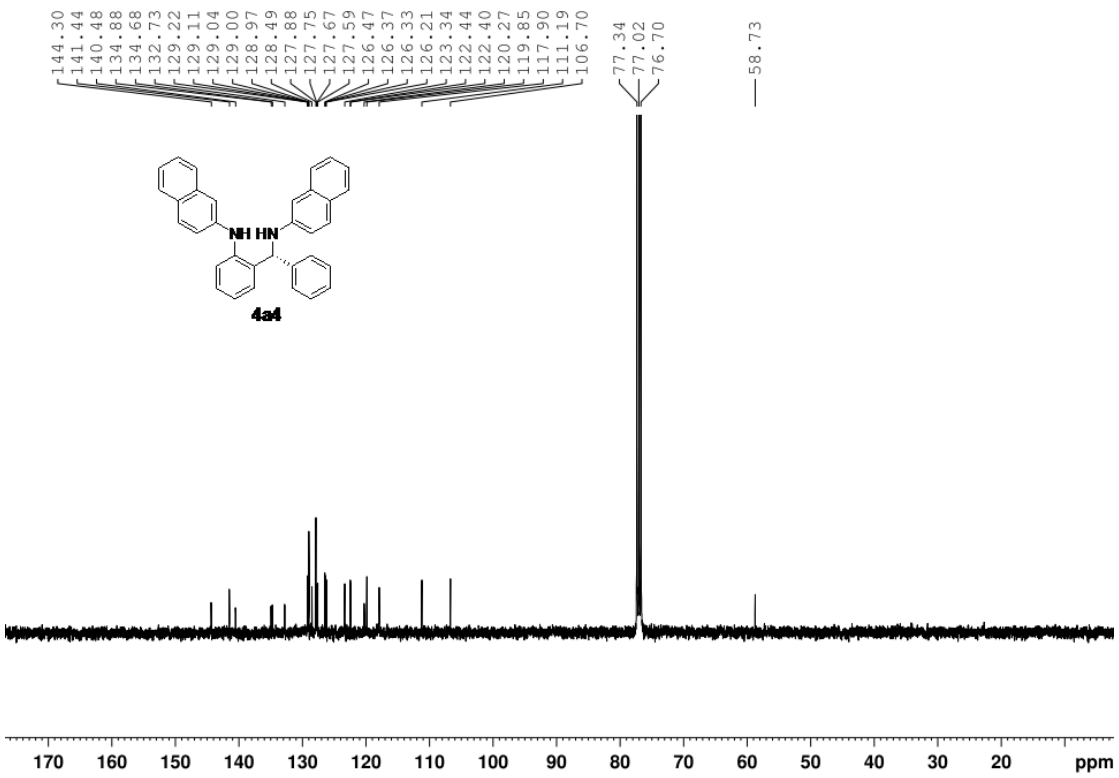

146.87
143.61
141.75
140.77
132.14
129.42
129.36
129.09
128.95
128.38
127.96
127.70
121.74
120.72
119.18
118.37
117.81
113.98
77.46
77.15
76.83
58.88
NH HN
4a1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.594
7.574
7.542
7.521
7.499
7.483
7.460
7.439
7.419
7.409
7.401
7.381
7.375
7.364
7.353
7.339
7.320
7.305
7.302
7.291
7.284
7.276
7.258
7.167
7.150
7.030
7.008
6.988
6.969
6.732
6.711
6.201
5.839
5.825
4.392
4.377
NH HN
4a2
7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
2.048
4.114
10.432
5.847
1.003
3.003
10 9 8 7 6 5 4 3 2 1 ppm
2.05
4.11
10.43
5.85
1.00
3.00
1.93
0.93
1.00
0.94

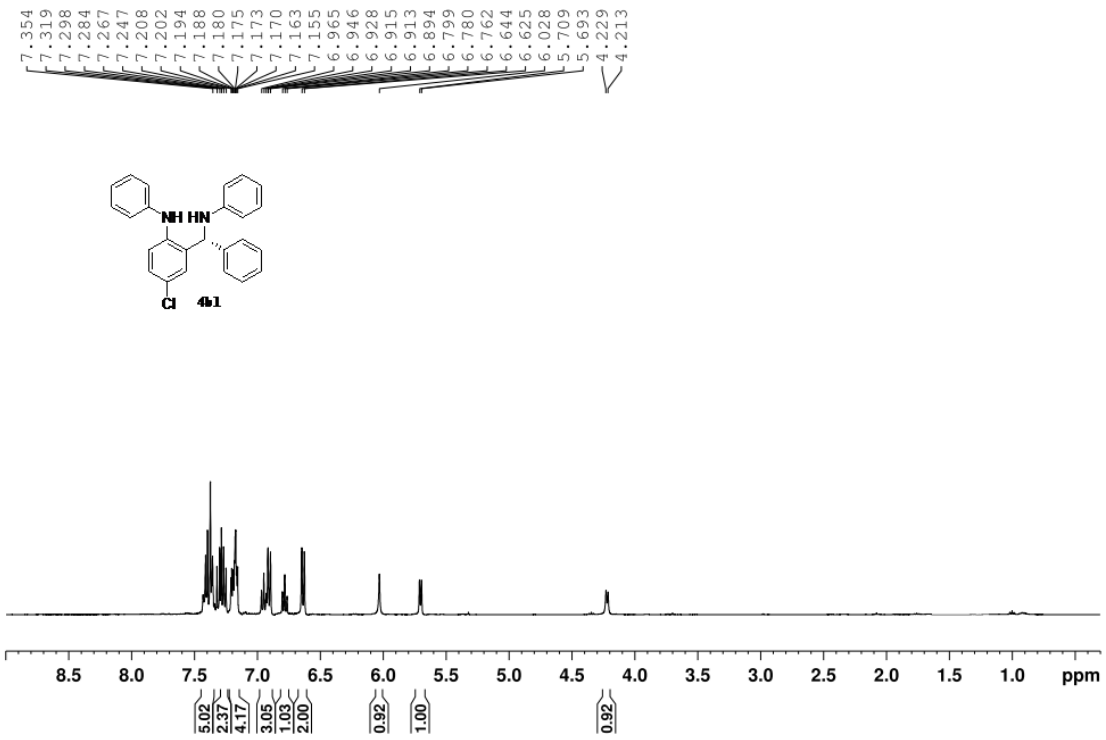

146.18
143.00
141.35
141.03
140.88
140.58
133.47
132.32
131.25
129.04
128.98
128.73
128.65
128.43
128.01
127.97
127.89
127.76
126.56
126.53
126.34
126.21
122.06
119.71
117.69
114.16
77.34
77.03
76.71
58.88
NH HN
4a2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

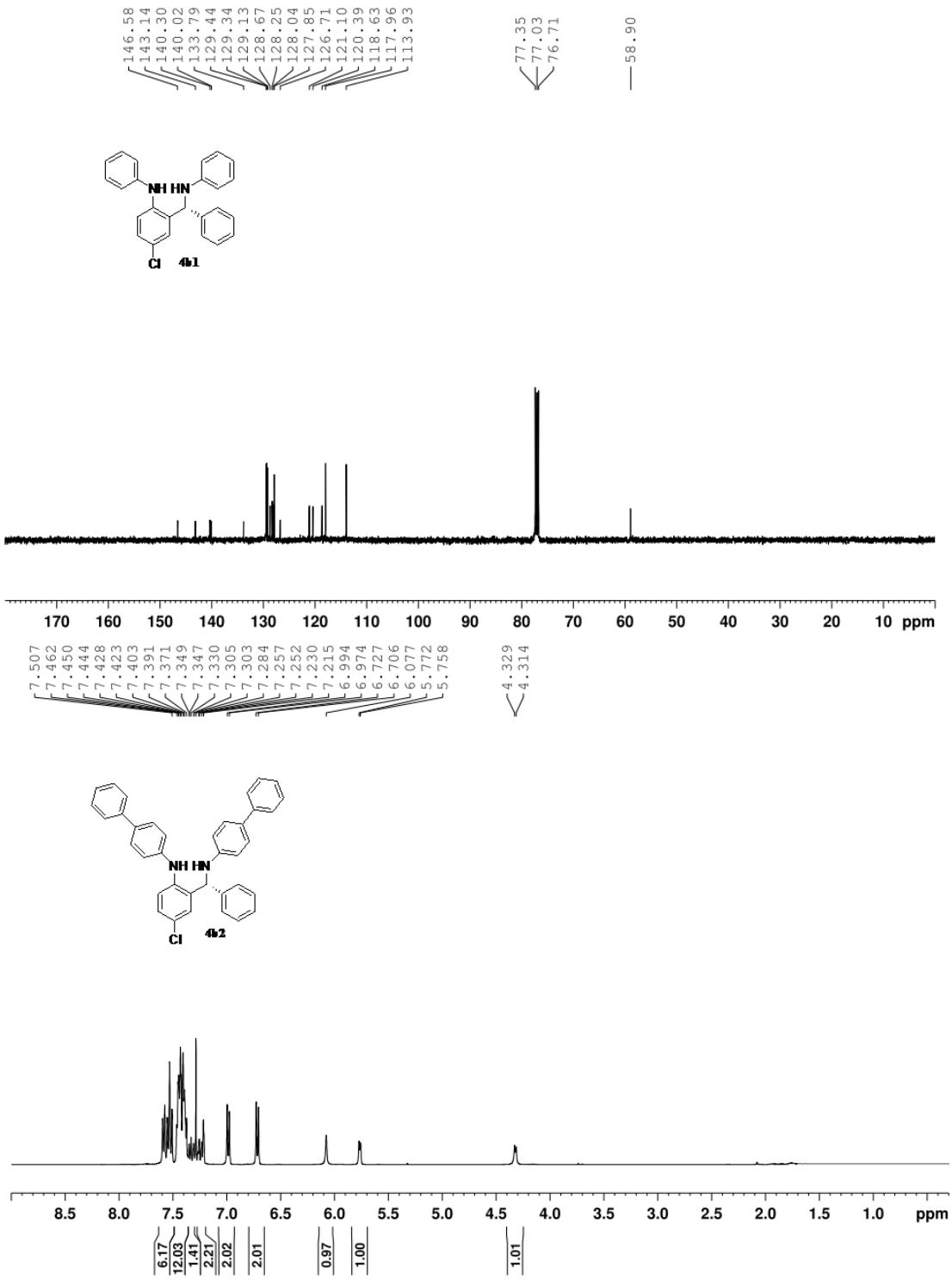

7.411
7.391
7.376
7.360
7.357
7.346
7.342
7.333
7.325
7.316
7.284
7.266
7.262
7.244
7.227
7.224
7.098
7.095
7.079
7.076
6.957
6.954
6.938
6.919
6.917
6.589
6.423
6.289
6.043
5.770
2.284
2.213
NH HN
4a3
10 9 8 7 6 5 4 3 2 1 ppm
6.53
1.21
1.11
1.13
3.01
0.99
1.98
0.89
1.01
6.00
6.09

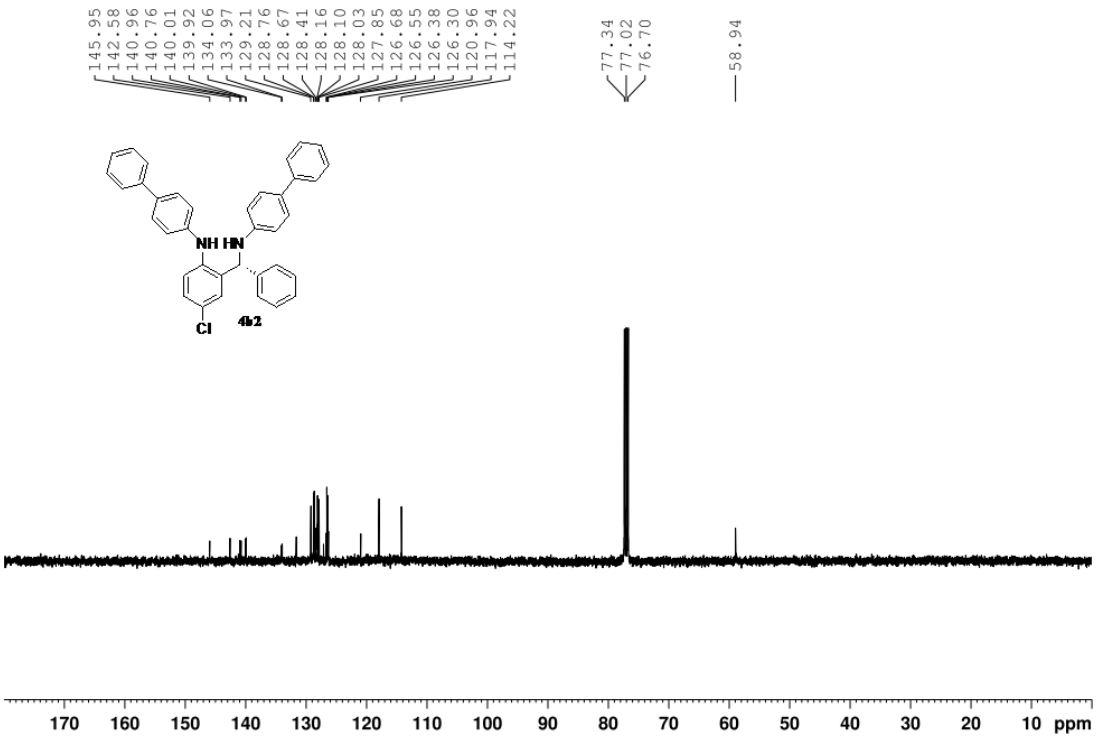

146.98
143.70
141.80
141.06
139.05
138.87
132.66
128.92
128.80
128.16
127.84
127.46
122.43
121.61
120.28
119.74
115.43
111.84
77.36
77.04
76.72
58.63
21.48
21.39
NH HN
4a3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

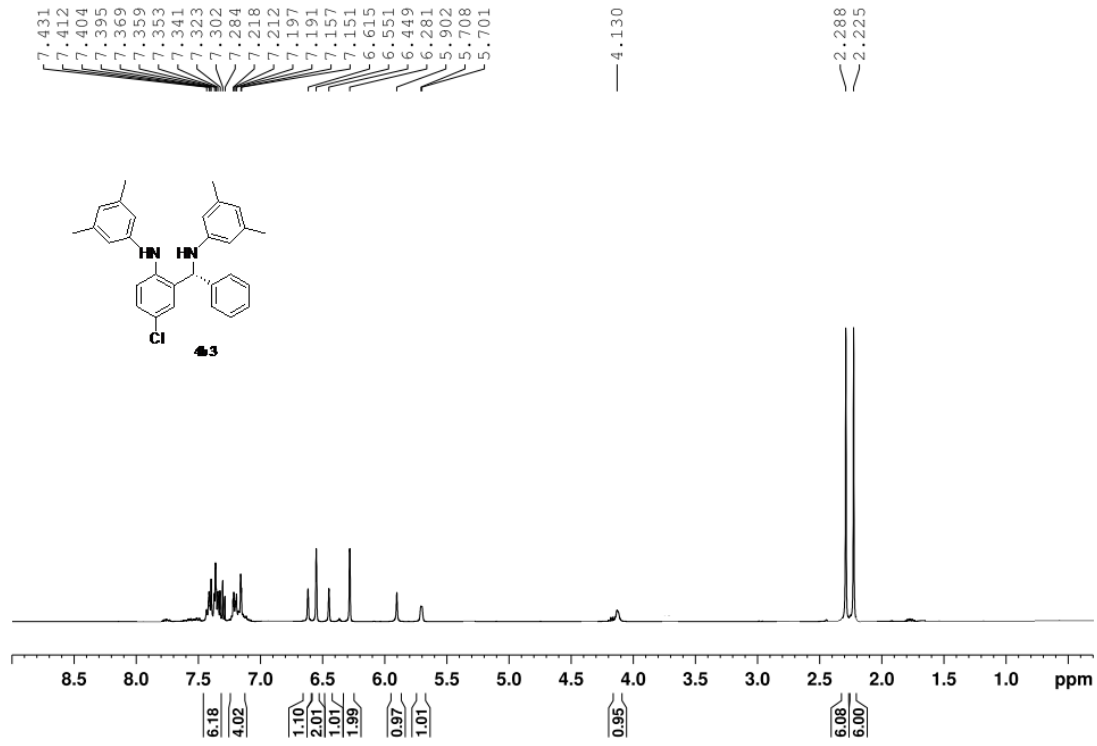

7.697
7.676
7.654
7.647
7.626
7.523
7.503
7.482
7.449
7.444
7.427
7.419
7.401
7.382
7.354
7.348
7.344
7.337
7.327
7.307
7.284
7.233
7.215
7.198
7.182
7.120
7.115
7.098
7.093
7.031
7.011
6.996
6.991
6.975
6.969
6.808
6.803
6.289
5.974
5.957
4.510
4.492
NH HN
4a4
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
5.272
2.305
5.181
3.614
2.167
1.094
2.118
10 9 8 7 6 5 4 3 2 1 ppm
5.27
2.31
5.18
3.61
2.17
1.09
2.12
1.09
1.00
1.06
1.05


144.30
141.44
140.48
134.88
134.68
132.73
129.22
129.11
129.04
129.00
128.97
128.49
127.88
127.75
127.67
127.59
126.47
126.37
126.33
126.21
123.34
122.44
122.40
120.27
119.85
117.90
111.19
106.70
77.34
77.02
76.70
58.73
NH HN
4a4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.354
7.319
7.298
7.284
7.267
7.247
7.208
7.202
7.194
7.188
7.180
7.175
7.173
7.170
7.163
7.155
6.965
6.946
6.928
6.915
6.913
6.894
6.799
6.780
6.762
6.644
6.625
6.028
5.709
5.693
4.229
4.213
NH HN
Cl
4b1
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
ppm
5.02
2.37
4.17
3.05
1.03
2.00
0.92
1.00
0.92


146.58
143.14
140.30
140.02
133.79
129.44
129.34
129.13
128.67
128.25
128.04
127.85
126.71
121.10
120.39
118.63
117.96
113.93
77.35
77.03
76.71
58.90
NH HN
Cl
4b1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.507
7.462
7.450
7.444
7.428
7.423
7.403
7.391
7.371
7.349
7.347
7.330
7.305
7.303
7.284
7.257
7.252
7.230
7.215
6.994
6.974
6.727
6.706
6.077
5.772
5.758
4.329
4.314
NH HN
Cl
4b2
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 ppm
6.17
12.03
1.41
2.21
2.02
2.01
0.97
1.00
1.01


145.95
142.58
140.96
140.76
140.01
139.92
134.06
133.97
129.21
128.76
128.67
128.41
128.16
128.10
128.03
127.85
126.68
126.55
126.38
126.30
120.96
117.94
114.22
77.34
77.02
76.70
58.94
NH HN
Cl
4b2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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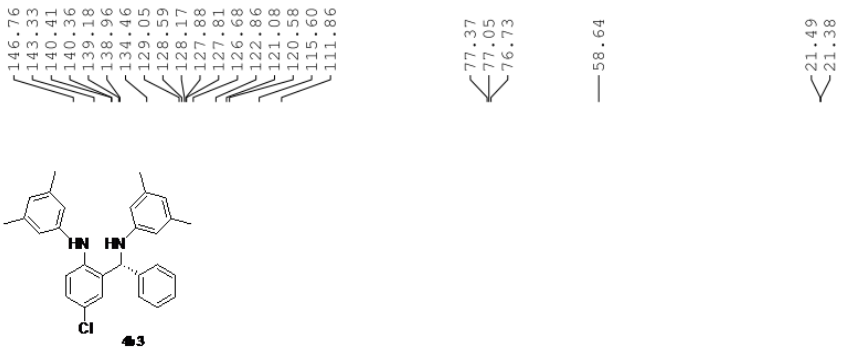
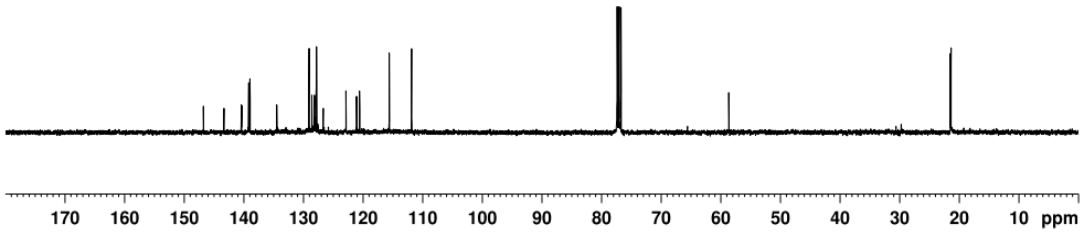
7.412
7.404
7.395
7.369
7.359
7.353
7.341
7.323
7.302
7.284
7.218
7.212
7.197
7.191
7.157
7.151
6.615
6.551
6.449
6.281
5.902
5.708
5.701
4.130
2.288
2.225
HN HN
Cl
4b3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.18
4.02
1.10
2.01
1.01
1.99
0.97
1.01
0.95
6.08
6.00


146.76
143.33
140.41
140.36
139.18
138.96
134.46
129.05
128.59
128.17
127.88
127.81
126.68
122.86
121.08
120.58
115.60
111.86
77.37
77.05
76.73
58.64
21.49
21.38
HN
HN
Cl
4a3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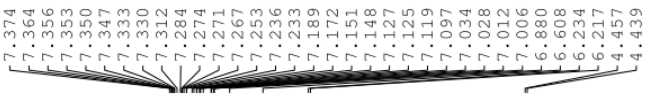
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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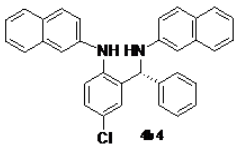
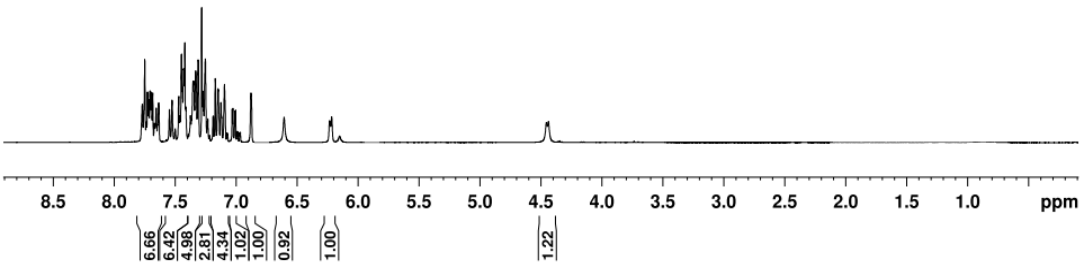
7.364
7.356
7.353
7.350
7.347
7.333
7.330
7.312
7.284
7.274
7.271
7.267
7.253
7.236
7.233
7.189
7.172
7.151
7.148
7.127
7.125
7.119
7.097
7.034
7.028
7.012
7.006
6.880
6.608
6.234
6.217
4.457
4.439


NH HN
Cl
4a4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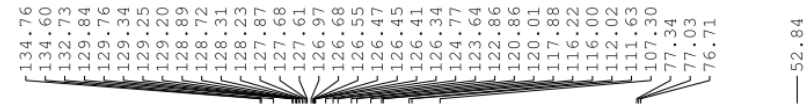
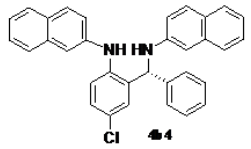
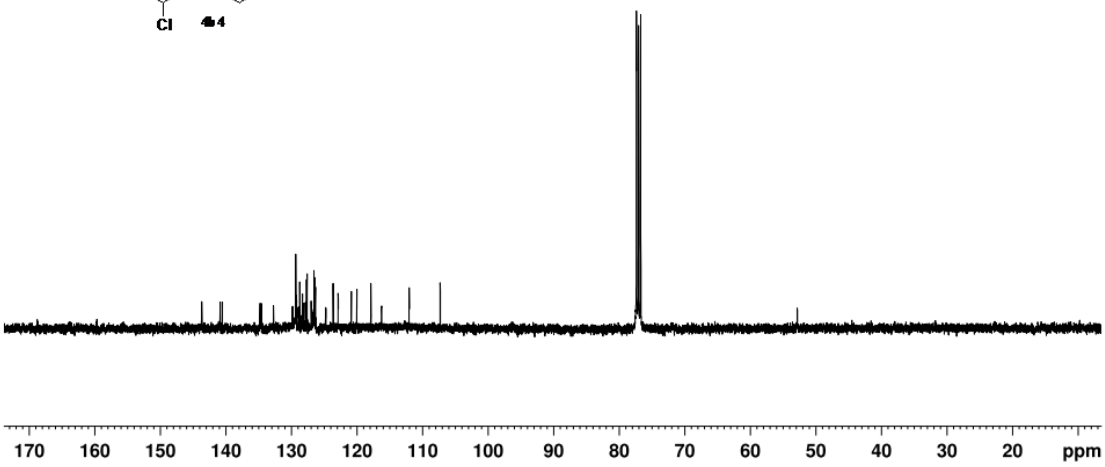
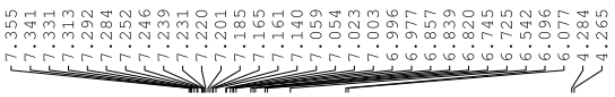
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.66
6.42
4.98
2.81
4.34
1.02
1.00
0.92
1.00
1.22

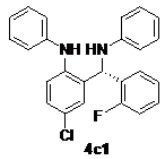

134.76
134.60
132.73
129.84
129.76
129.34
129.25
129.20
128.89
128.72
128.31
128.23
127.87
127.68
127.61
126.97
126.68
126.55
126.47
126.45
126.41
126.34
124.77
123.64
122.86
120.86
120.01
117.88
116.22
116.00
112.02
111.63
107.30
77.34
77.03
76.71
52.84


NH HN
Cl

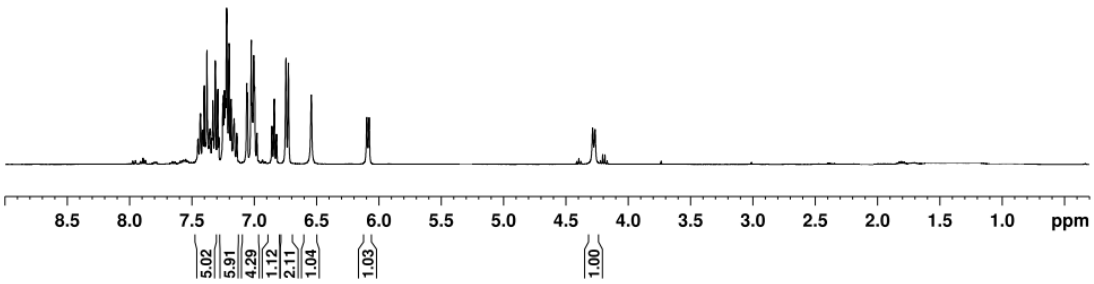
4s4


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.355
7.341
7.331
7.313
7.292
7.284
7.252
7.246
7.239
7.231
7.220
7.201
7.185
7.165
7.161
7.140
7.059
7.054
7.023
7.003
6.996
6.977
6.857
6.839
6.820
6.745
6.725
6.542
6.096
6.077
4.284
4.265


NH HN
F
Cl

4c1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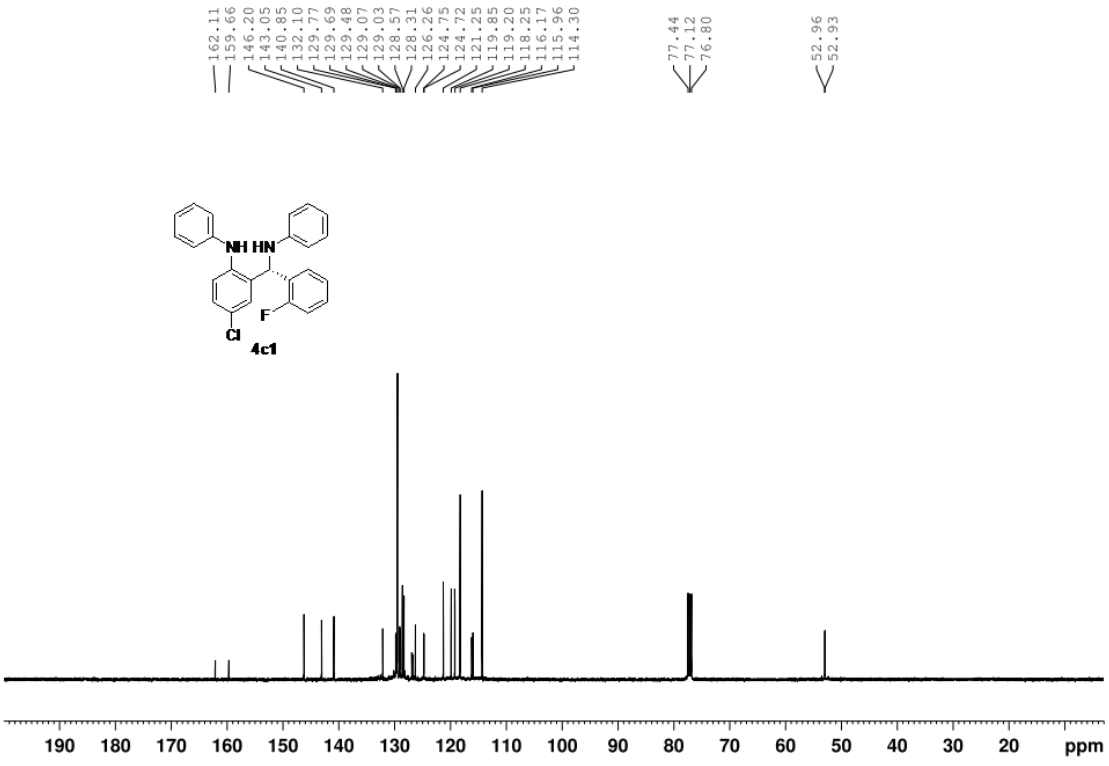
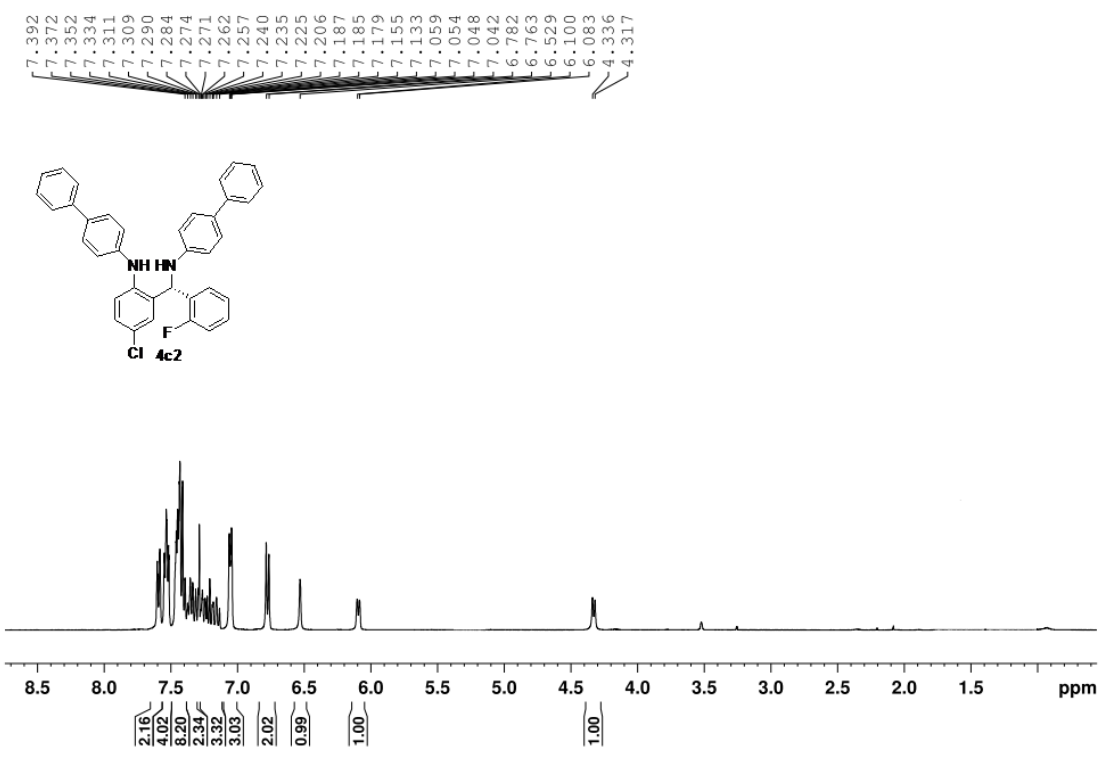
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.02
5.91
4.29
1.12
2.11
1.04
1.03
1.00


162.11
159.66
146.20
143.05
140.85
132.10
129.77
129.69
129.48
129.07
129.03
128.57
128.31
126.26
124.75
124.72
121.25
119.85
119.20
118.25
116.17
115.96
114.30
77.44
77.12
76.80
52.96
52.93
NH HN
F
Cl
4c1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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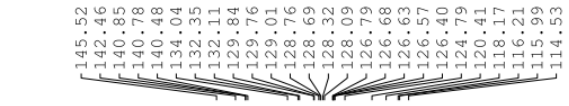
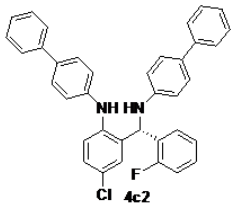
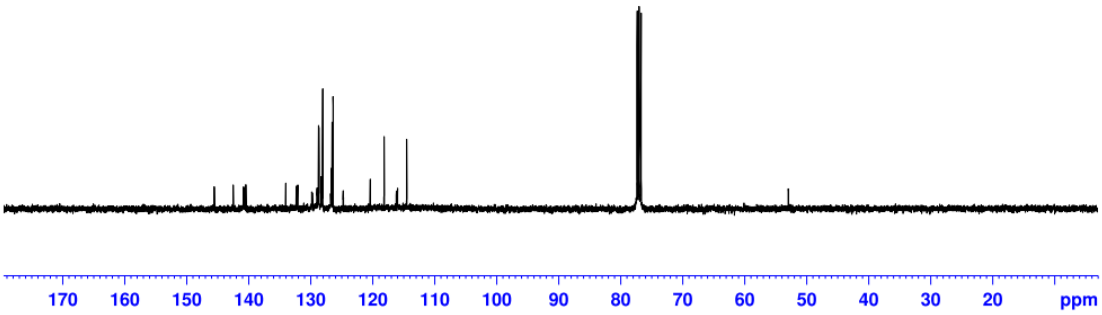
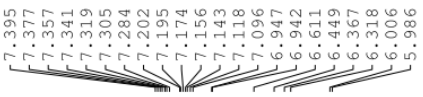
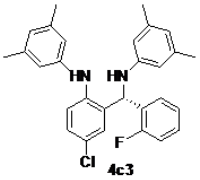
7.352
7.334
7.311
7.309
7.290
7.284
7.274
7.271
7.262
7.257
7.240
7.235
7.225
7.206
7.187
7.185
7.179
7.155
7.133
7.059
7.054
7.048
7.042
6.782
6.763
6.529
6.100
6.083
4.336
4.317
NH HN
F
Cl
4c2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
2.16
4.02
8.20
2.34
3.32
3.03
2.02
0.99
1.00
1.00

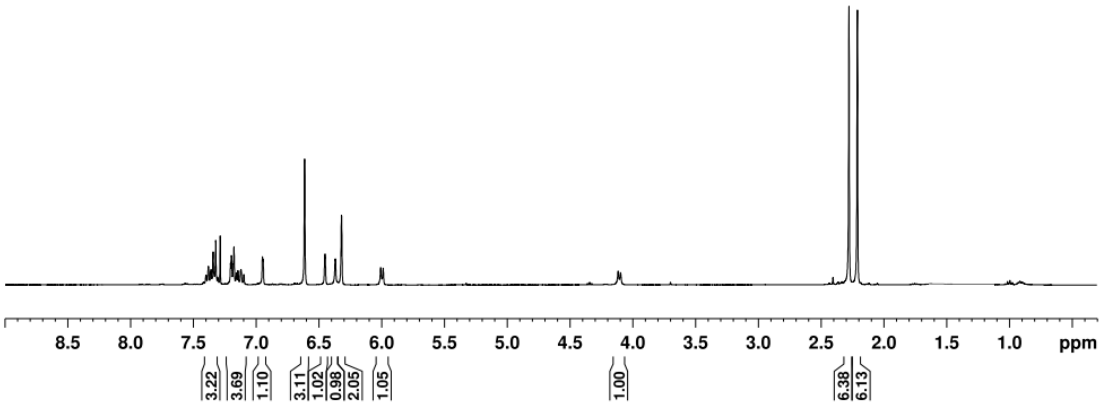

145.52
142.46
140.85
140.78
140.48
134.04
132.35
132.11
129.84
129.76
129.01
128.76
128.69
128.32
128.09
126.79
126.68
126.63
126.57
126.40
124.79
120.41
118.17
116.21
115.99
114.53
77.35
77.03
76.72
52.97

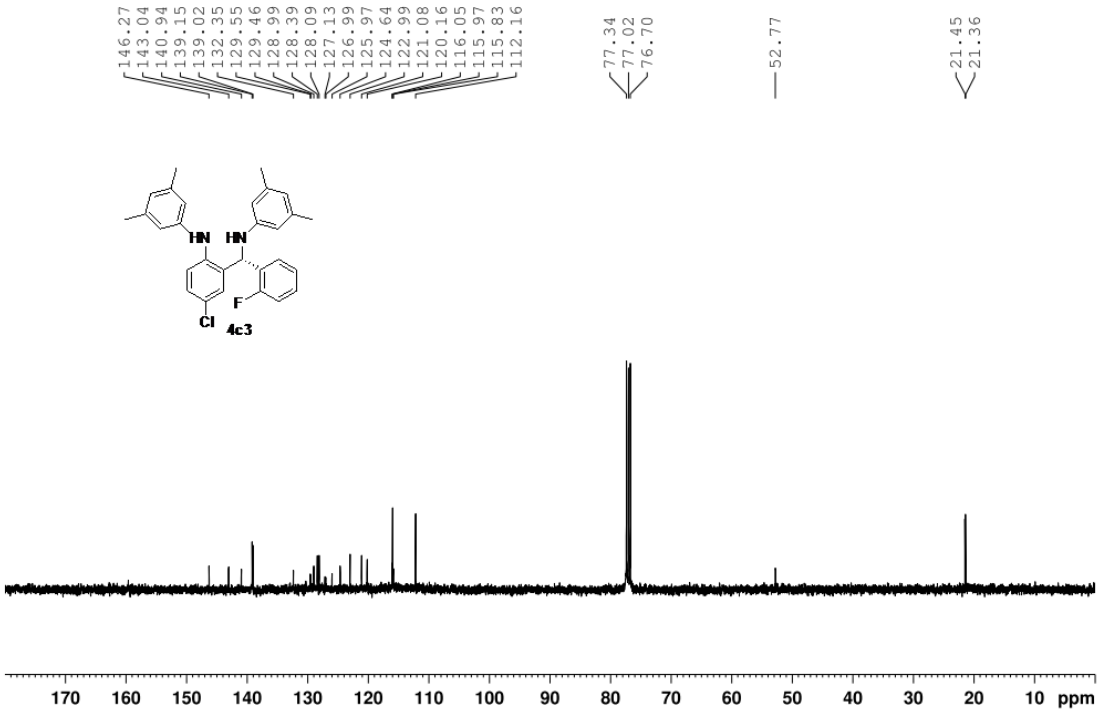

NH HN
F
Cl
4c2

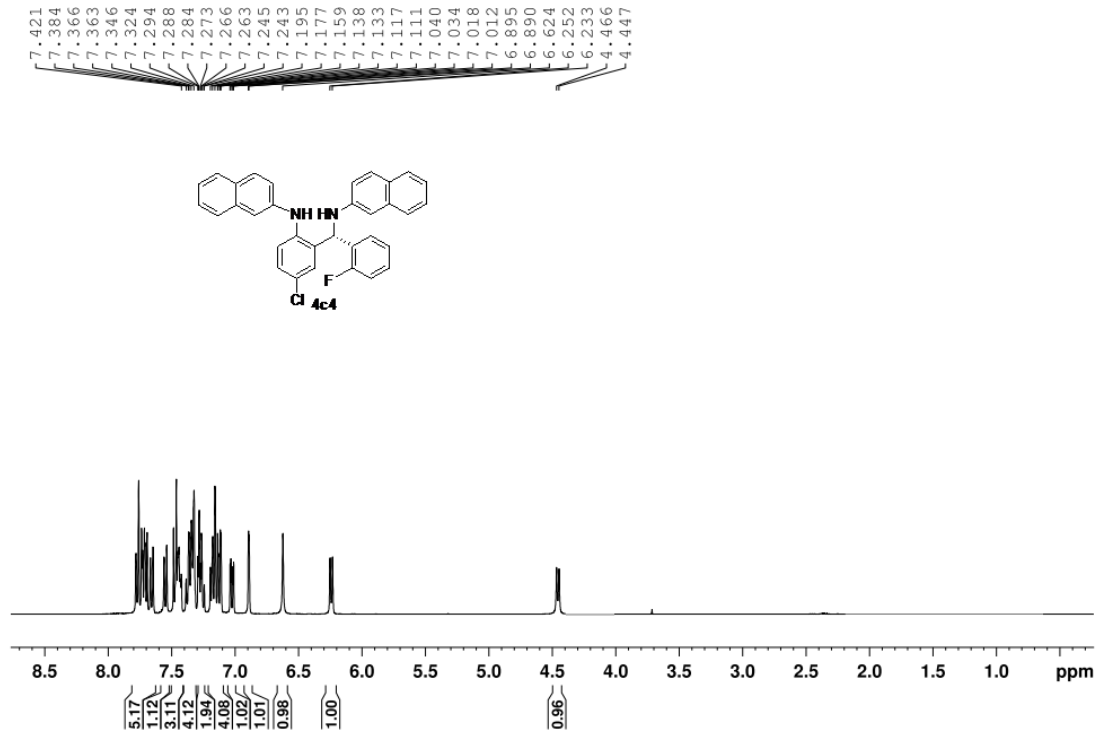

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.395
7.377
7.357
7.341
7.319
7.305
7.284
7.202
7.195
7.174
7.156
7.143
7.118
7.096
6.947
6.942
6.611
6.449
6.367
6.318
6.006
5.986
4.115
4.095
2.278
2.211


HN HN
F
Cl
4c3


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
ppm
3.22
3.69
1.10
3.11
1.02
0.98
2.05
1.05
1.00
6.38
6.13


146.27
143.04
140.94
139.15
139.02
132.35
129.55
129.46
128.99
128.39
128.09
127.13
126.99
125.97
124.64
122.99
121.08
120.16
116.05
115.97
115.83
112.16
77.34
77.02
76.70
52.77
21.45
21.36
HN
HN
F
Cl
4c3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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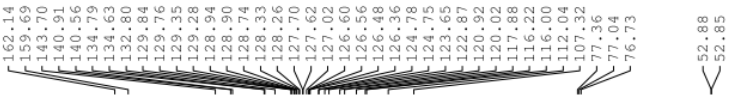
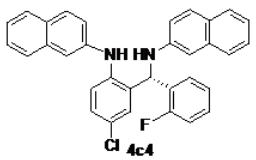
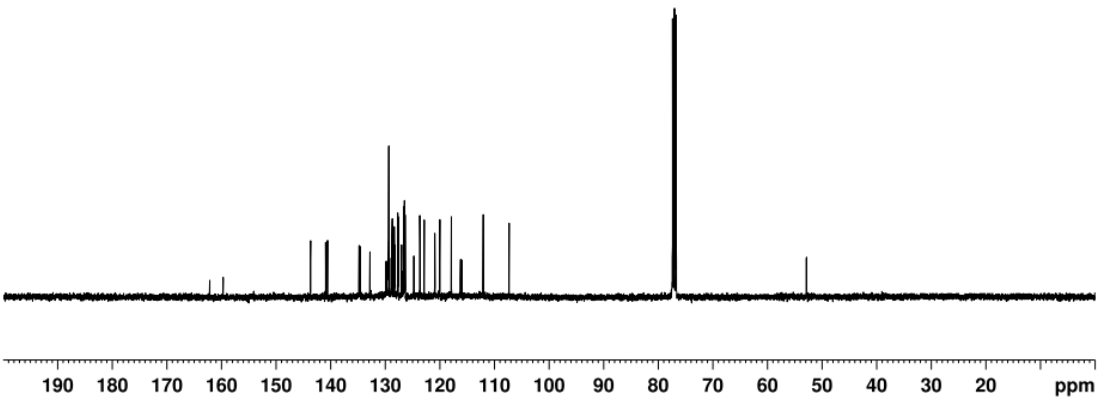
7.384
7.366
7.363
7.346
7.324
7.294
7.288
7.284
7.273
7.266
7.263
7.245
7.243
7.195
7.177
7.159
7.138
7.133
7.117
7.111
7.040
7.034
7.018
7.012
6.895
6.890
6.624
6.252
6.233
4.466
4.447
NH
HN
F
Cl
4c4
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.17
1.12
3.11
4.12
1.94
4.08
1.02
1.01
0.98
1.00
0.96


162.14
159.69
143.70
140.91
140.56
134.79
134.63
132.80
129.84
129.76
129.35
129.28
128.94
128.90
128.74
128.33
128.26
127.70
127.62
127.02
126.60
126.56
126.48
126.36
124.78
124.75
123.65
122.87
120.92
120.02
117.88
116.22
116.00
112.04
107.32
77.36
77.04
76.73
52.88
52.85


NH HN
F
Cl

4c4


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.751
7.955
7.942
7.742
7.725
7.598
7.583
7.564
7.544
7.446
7.429
7.321
7.317
7.300
7.285
7.281
7.269
7.258
7.238
7.197
7.193
7.182
7.175
7.170
7.165
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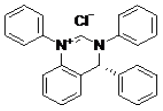
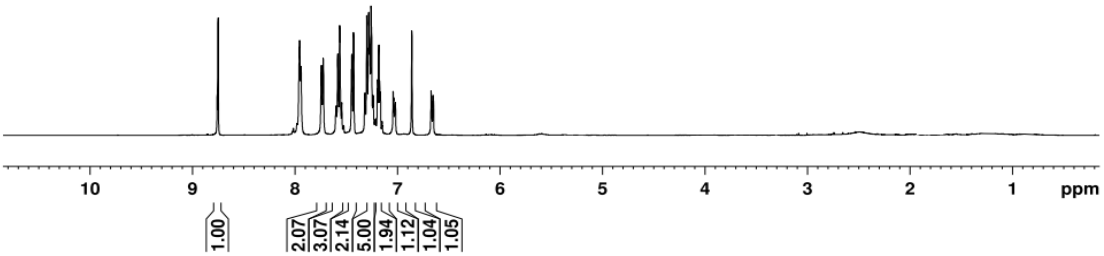
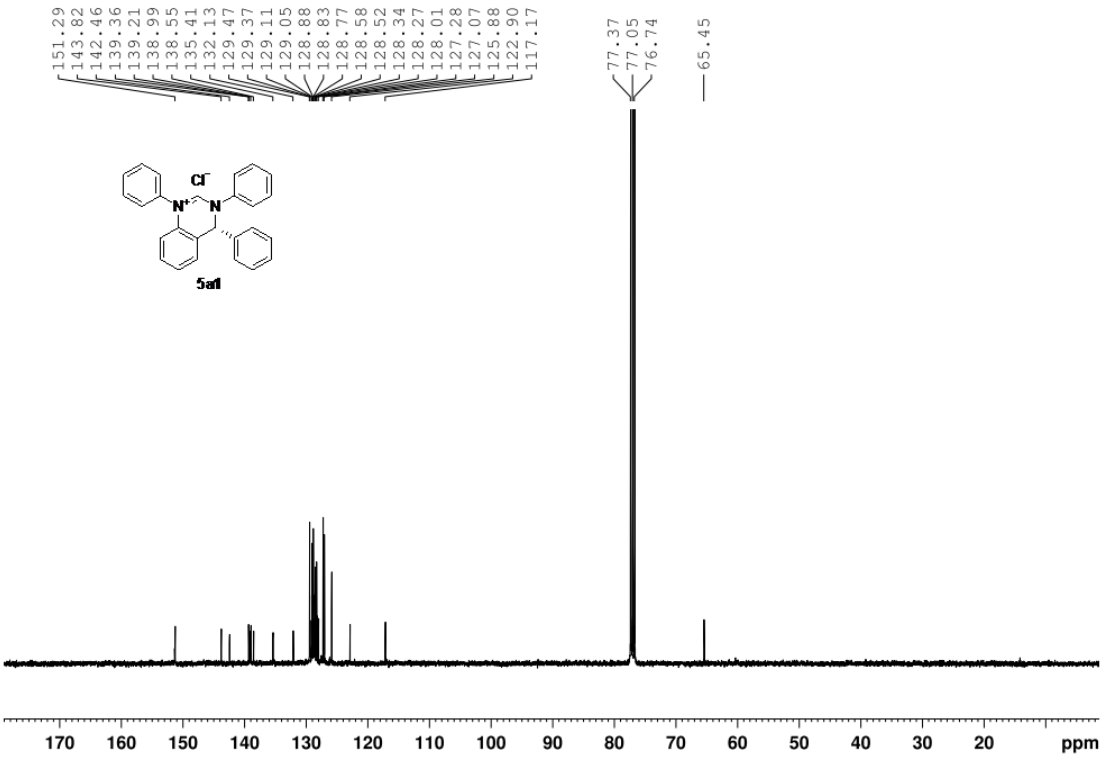
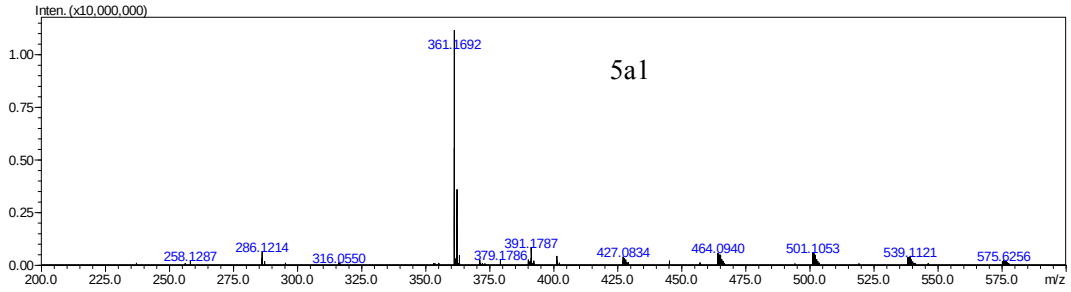
7.020
6.860
6.672
6.668
6.653
6.648


Cl⁻
N⁺
N

5a1


10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.07
3.07
2.14
5.00
1.94
1.12
1.04
1.05


151.29
143.82
142.46
139.36
139.21
138.99
138.55
135.41
132.13
129.47
129.37
129.11
129.05
128.88
128.83
128.77
128.58
128.52
128.34
128.27
128.01
127.28
127.07
125.88
122.90
117.17
77.37
77.05
76.74
65.45
Cl⁻
N⁺
N
5a1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


Inten. (x10,000,000)
1.00
0.75
0.50
0.25
0.00
361.1692
5a1
258.1287
286.1214
316.0550
379.1786
391.1787
427.0834
464.0940
501.1053
539.1121
575.6256
200.0
225.0
250.0
275.0
300.0
325.0
350.0
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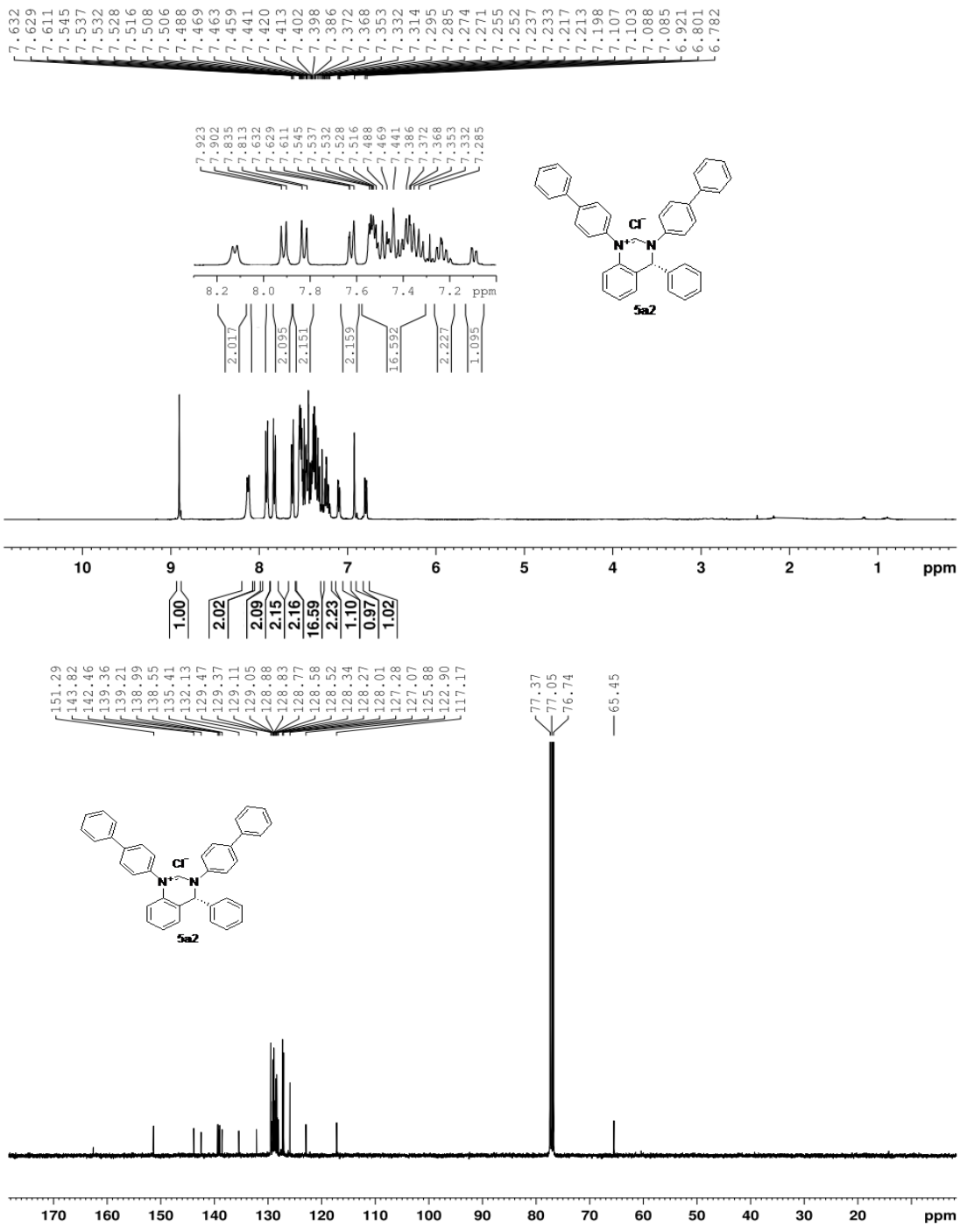
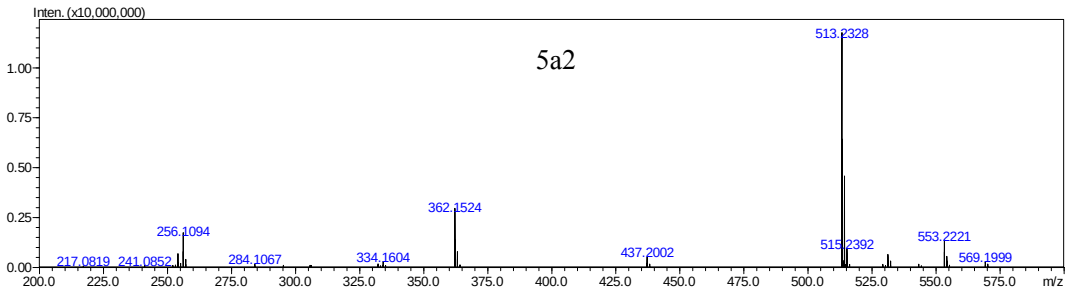
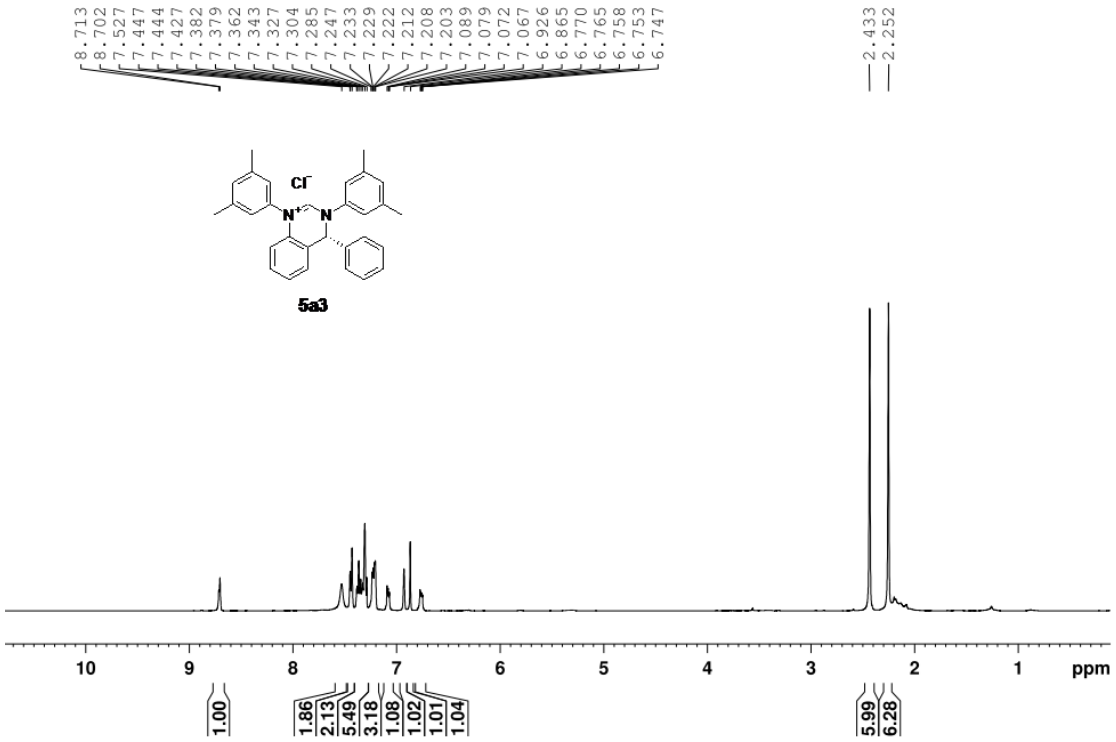
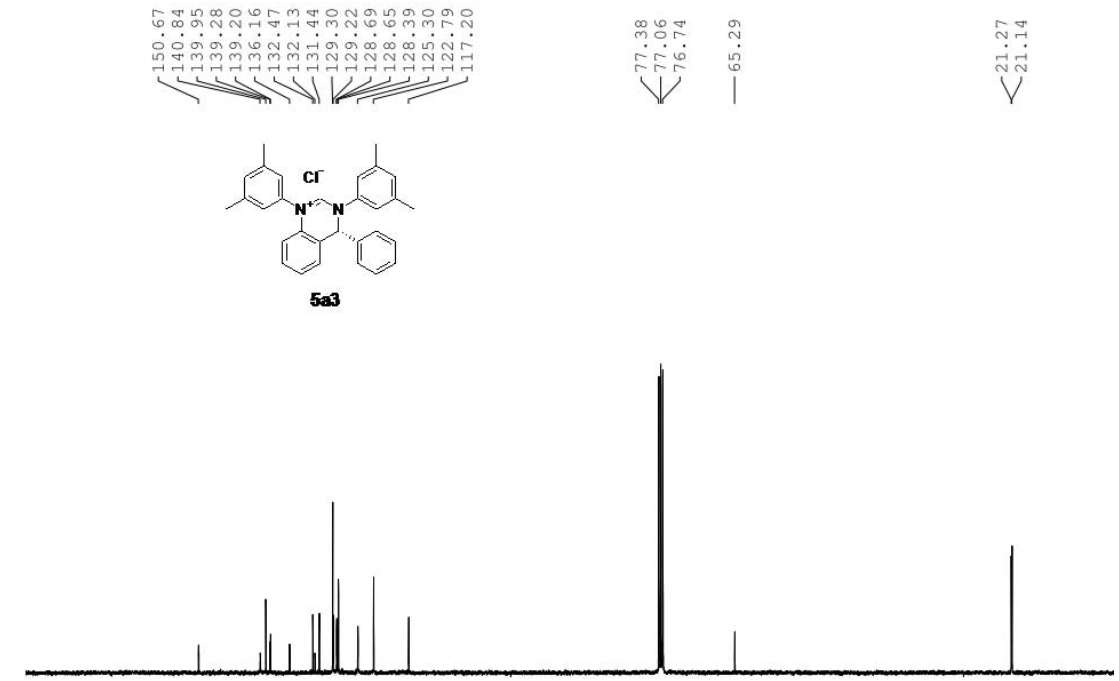
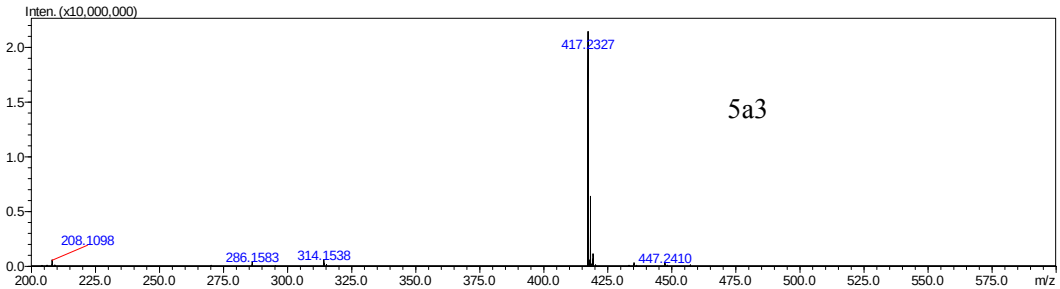
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z

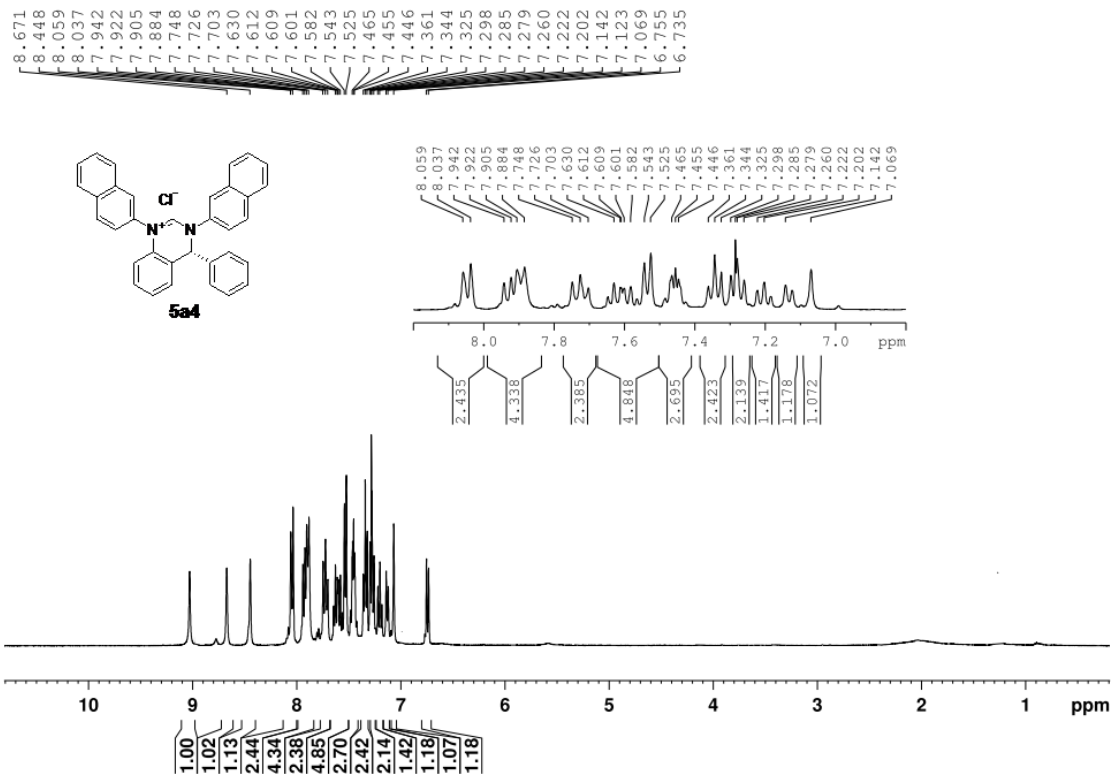

7.632 7.629 7.611 7.545 7.537 7.532 7.528 7.516 7.508 7.506 7.488 7.469 7.463 7.459 7.441 7.420 7.413 7.402 7.398 7.386 7.372 7.368 7.353 7.332 7.314 7.295 7.285 7.274 7.271 7.255 7.252 7.237 7.233 7.217 7.213 7.198 7.107 7.103 7.088 7.085 6.921 6.801 6.782
7.923 7.902 7.835 7.813 7.632 7.629 7.611 7.545 7.537 7.532 7.528 7.516 7.488 7.469 7.441 7.386 7.372 7.368 7.353 7.332 7.285
8.2 8.0 7.8 7.6 7.4 7.2 ppm
2.017 2.095 2.151 2.159 16.592 2.227 1.095
Cl⁻
5a2
10 9 8 7 6 5 4 3 2 1 ppm
1.00 2.02 2.09 2.15 2.16 16.59 2.23 1.10 0.97 1.02
151.29 143.82 142.46 139.36 139.21 138.99 138.55 135.41 132.13 129.47 129.37 129.11 129.05 128.88 128.83 128.77 128.58 128.52 128.34 128.27 128.01 127.28 127.07 125.88 122.90 117.17
77.37 77.05 76.74
65.45
Cl⁻
5a2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

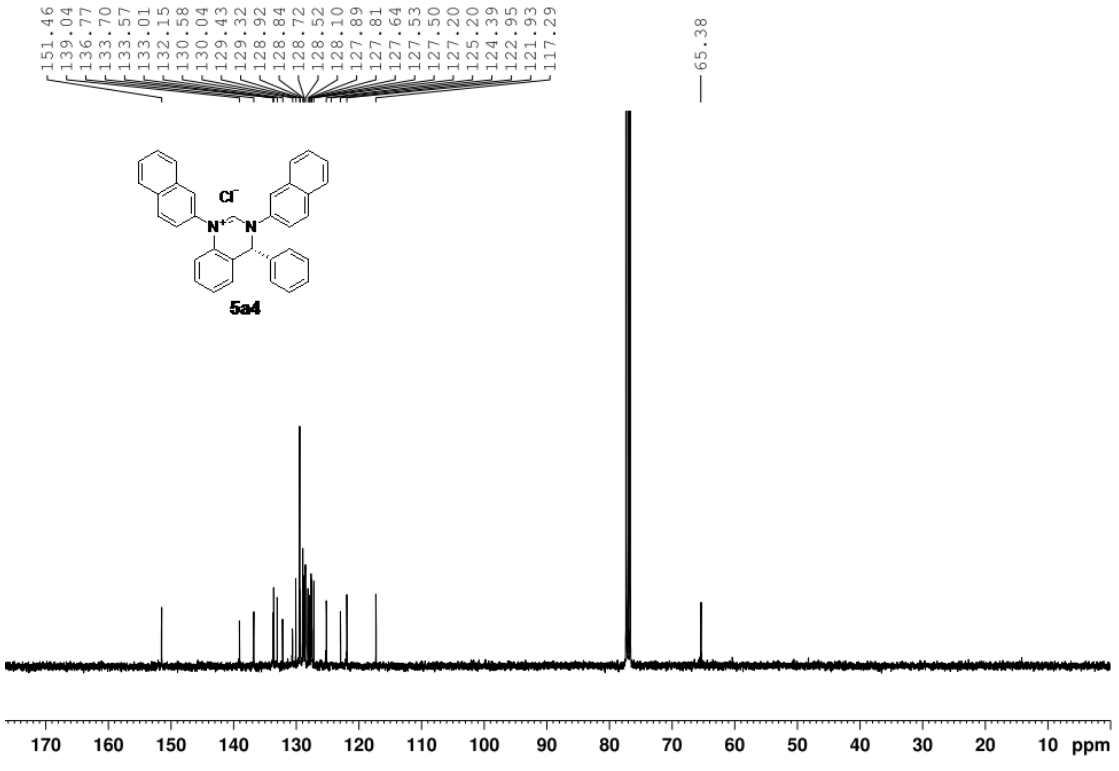

Inten. (x10,000,000)
5a2
513.2328
362.1524
256.1094
553.2221
515.2392
569.1999
437.2002
334.1604
284.1067
217.0819
241.0852
1.00
0.75
0.50
0.25
0.00
200.0 225.0 250.0 275.0 300.0 325.0 350.0 375.0 400.0 425.0 450.0 475.0 500.0 525.0 550.0 575.0 m/z

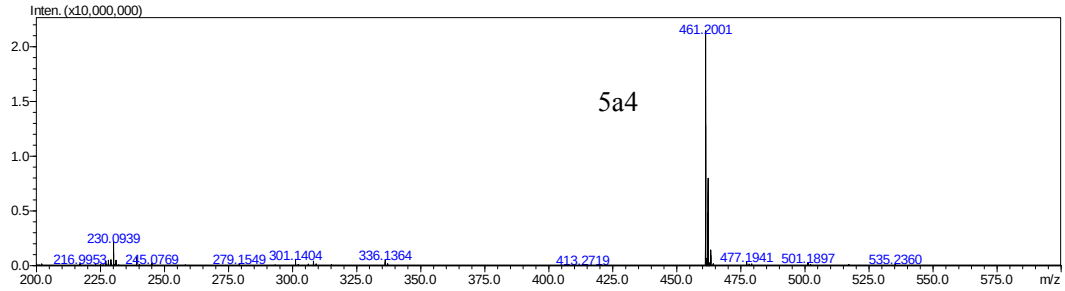

8.713
8.702
7.527
7.447
7.444
7.427
7.382
7.379
7.362
7.343
7.327
7.304
7.285
7.247
7.233
7.229
7.222
7.212
7.208
7.203
7.089
7.079
7.072
7.067
6.926
6.865
6.770
6.765
6.758
6.753
6.747
2.433
2.252
Cl⁻
5a3
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.86
2.13
5.49
3.18
1.08
1.02
1.01
1.04
5.99
6.28


150.67
140.84
139.95
139.28
139.20
136.16
132.47
132.13
131.44
129.30
129.22
128.69
128.65
128.39
125.30
122.79
117.20
77.38
77.06
76.74
65.29
21.27
21.14
Cl⁻
5a3

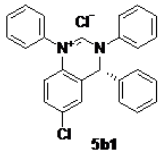

Inten. (x10,000,000)
2.0
1.5
1.0
0.5
0.0
417.2327
5a3
208.1098
286.1583
314.1538
447.2410
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z

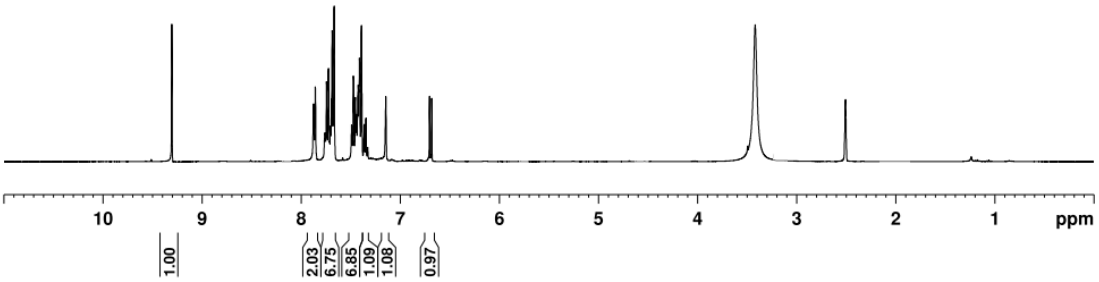

8.671
8.448
8.059
8.037
7.942
7.922
7.905
7.884
7.748
7.726
7.703
7.630
7.612
7.609
7.601
7.582
7.543
7.525
7.465
7.455
7.446
7.361
7.344
7.325
7.298
7.285
7.279
7.260
7.222
7.202
7.142
7.123
7.069
6.755
6.735
Cl⁻
N⁺
N
5a4
8.059
8.037
7.942
7.922
7.905
7.884
7.748
7.726
7.703
7.630
7.612
7.609
7.601
7.582
7.543
7.525
7.465
7.455
7.446
7.361
7.344
7.325
7.298
7.285
7.279
7.260
7.222
7.202
7.142
7.069
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.435
4.338
2.385
4.848
2.695
2.423
2.139
1.417
1.178
1.072
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.13
2.44
4.34
2.38
4.85
2.70
2.42
2.14
1.42
1.18
1.07
1.18

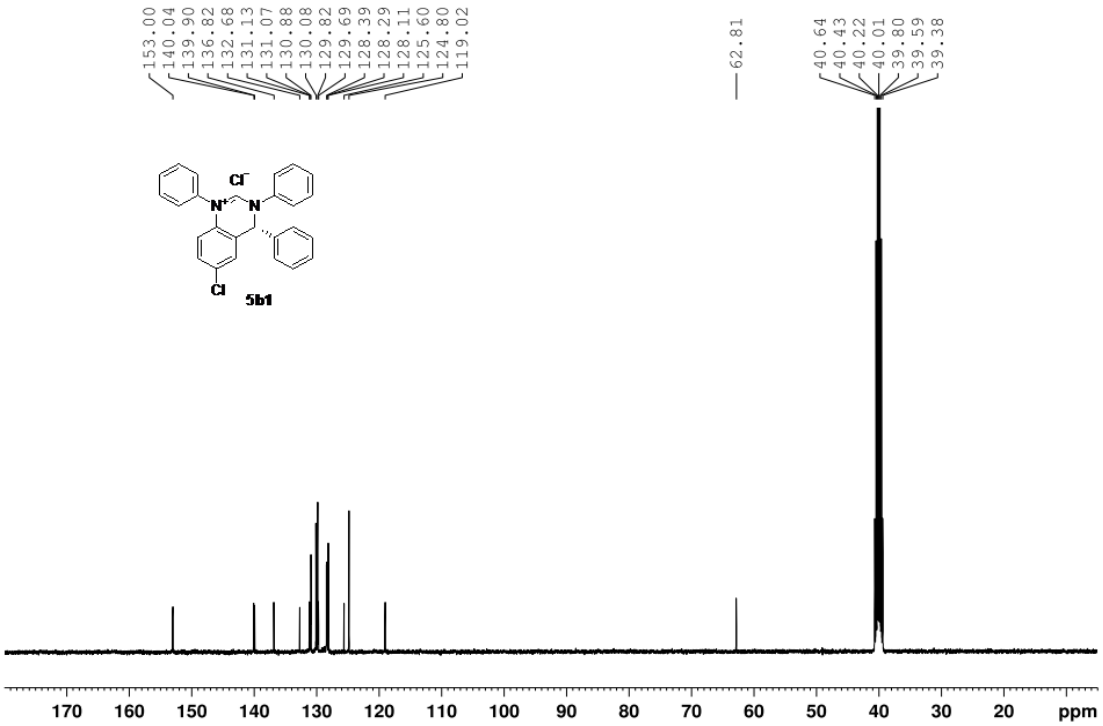

151.46
139.04
136.77
133.70
133.57
133.01
132.15
130.58
130.04
129.43
129.32
128.92
128.84
128.72
128.52
128.10
127.89
127.81
127.64
127.53
127.50
127.20
125.20
124.39
122.95
121.93
117.29
65.38
Cl⁻
N⁺
N
5a4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

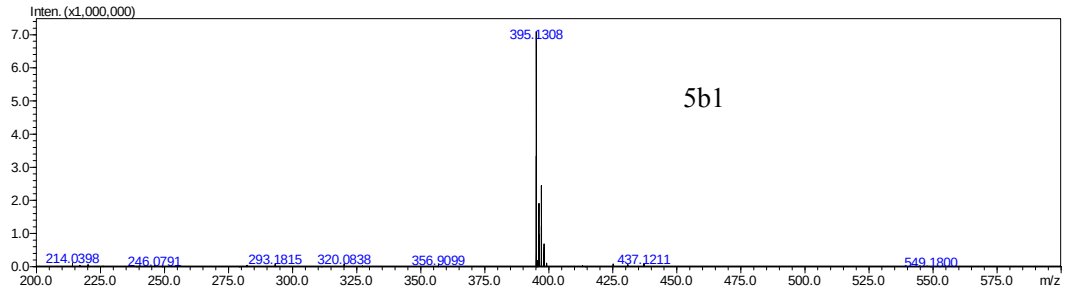

Inten. (x10,000,000)
461.2001
5a4
230.0939
216.9953
245.0769
279.1549
301.1404
336.1364
413.2719
477.1941
501.1897
535.2360
m/z

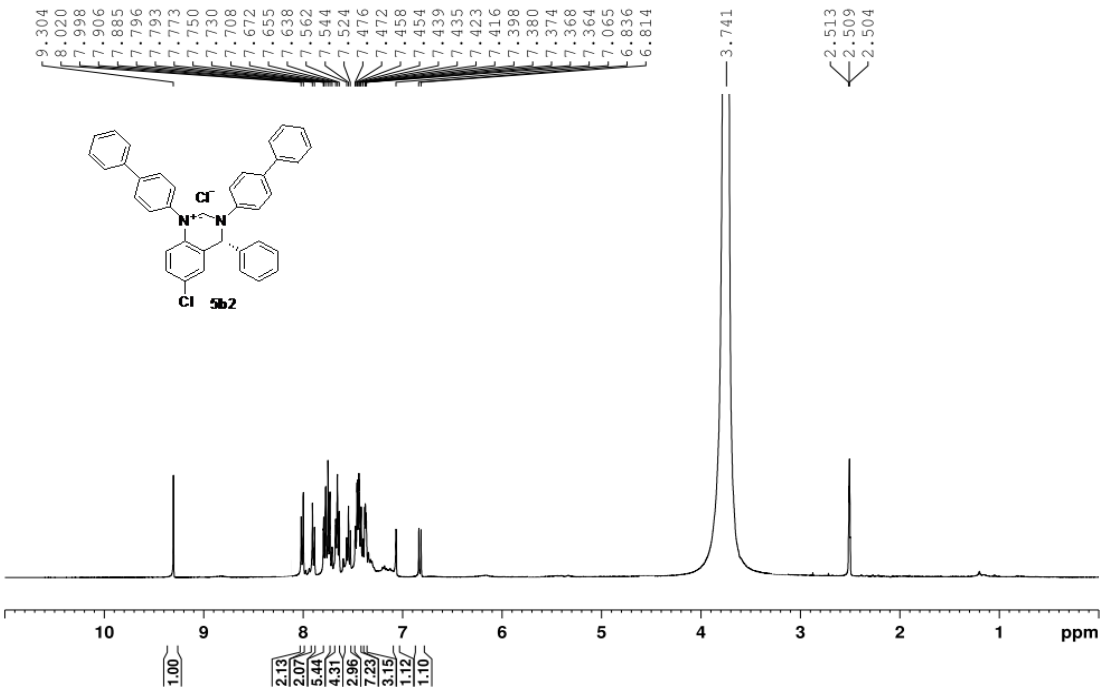

9.304
7.873
7.856
7.765
7.759
7.743
7.724
7.712
7.704
7.688
7.669
7.493
7.475
7.455
7.448
7.441
7.426
7.419
7.414
7.394
7.389
7.367
7.349
7.330
7.148
6.707
6.684
3.420
2.513
2.509
2.504

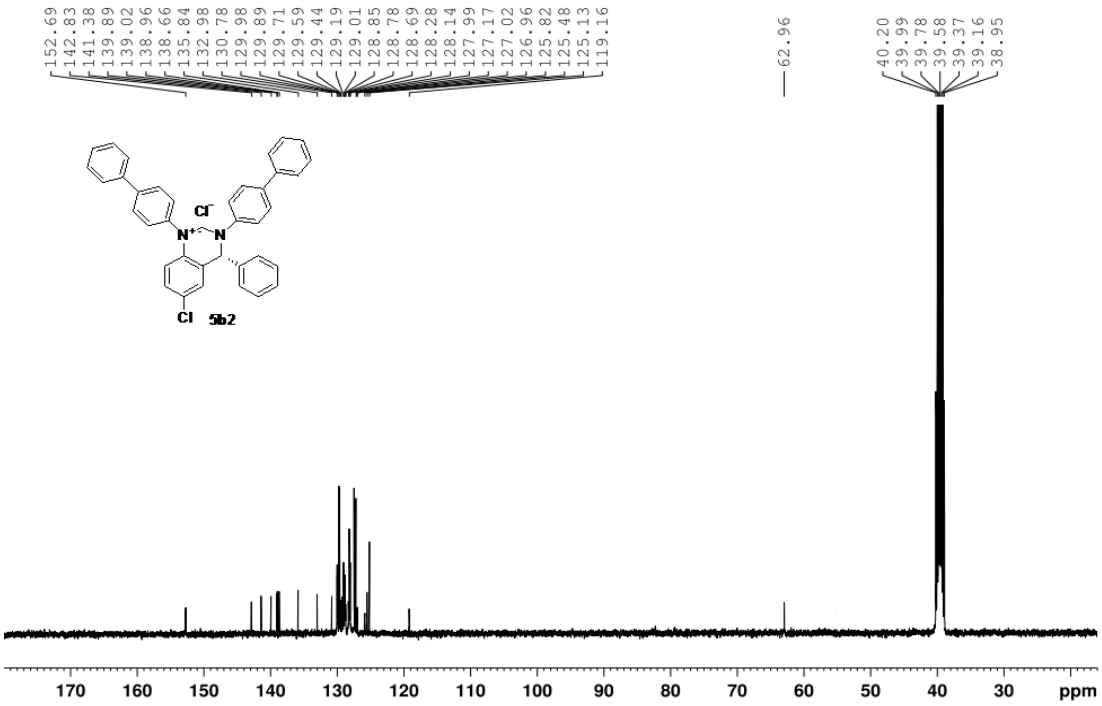

Cl
N
N
Cl
5b1

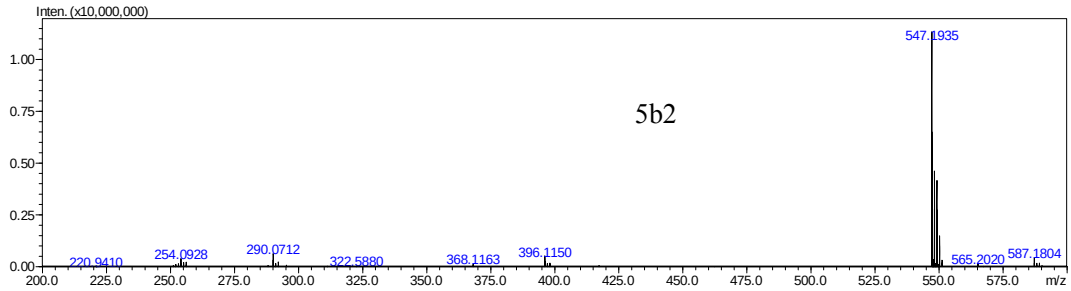

10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
6.75
6.85
1.09
1.08
0.97

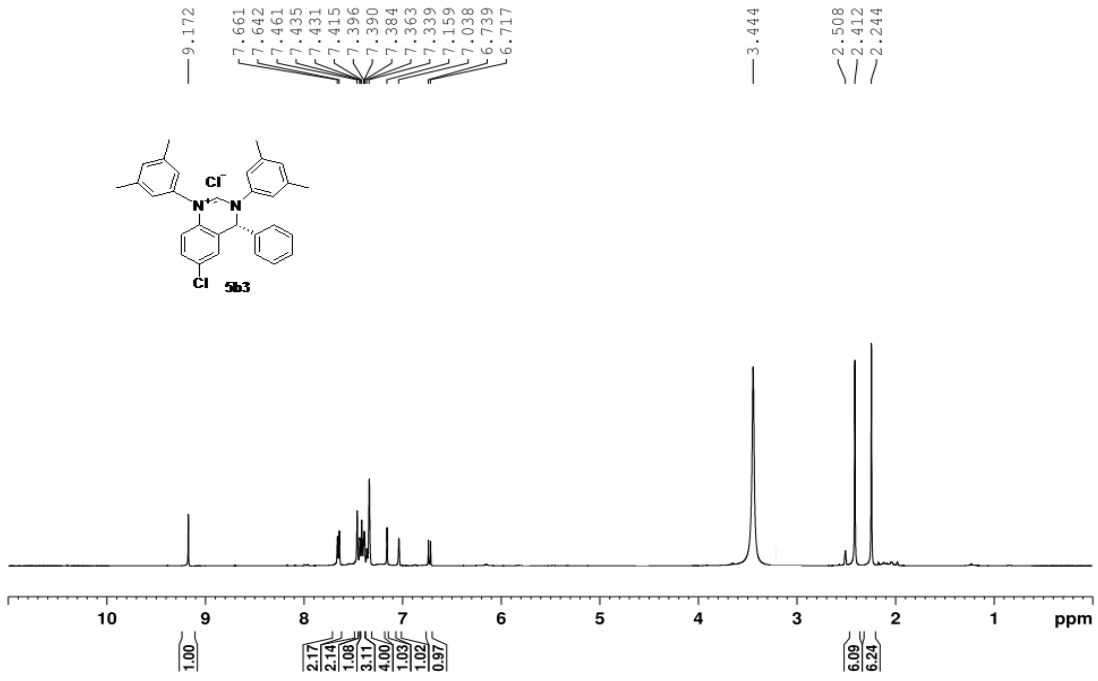

153.00
140.04
139.90
136.82
132.68
131.13
131.07
130.88
130.08
129.82
129.69
128.39
128.29
128.11
125.60
124.80
119.02
62.81
40.64
40.43
40.22
40.01
39.80
39.59
39.38
5b1
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

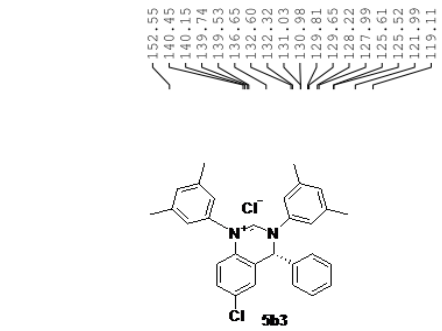

Inten. (x1,000,000)
395.1308
5b1
214.0398
246.0791
293.1815
320.0838
356.9099
437.1211
549.1800
m/z

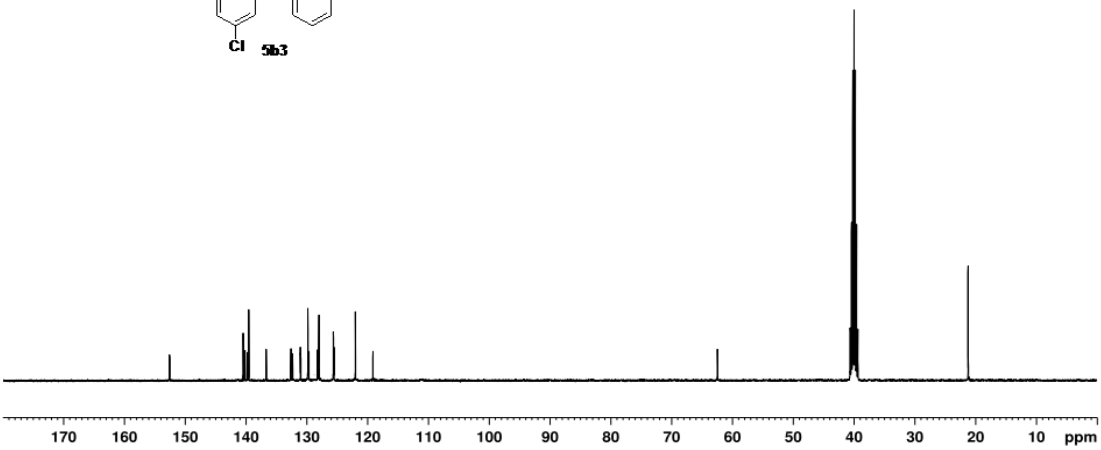

9.304
8.020
7.998
7.906
7.885
7.796
7.793
7.773
7.750
7.730
7.708
7.672
7.655
7.638
7.562
7.544
7.524
7.476
7.472
7.458
7.454
7.439
7.435
7.423
7.416
7.398
7.380
7.374
7.368
7.364
7.065
6.836
6.814
3.741
2.513
2.509
2.504
5b2
10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.13
2.07
5.44
4.31
2.96
7.23
3.15
1.12
1.10

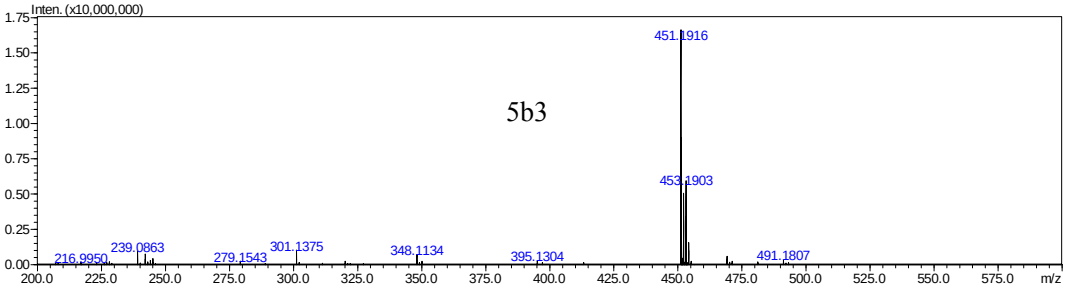

152.69
142.83
141.38
139.89
139.02
138.96
138.66
135.84
132.98
130.78
129.98
129.89
129.71
129.59
129.44
129.19
129.01
128.85
128.78
128.69
128.28
128.14
127.99
127.17
127.02
126.96
125.82
125.48
125.13
119.16
62.96
40.20
39.99
39.78
39.58
39.37
39.16
38.95
Cl⁻
N⁺
N
Cl
5b2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

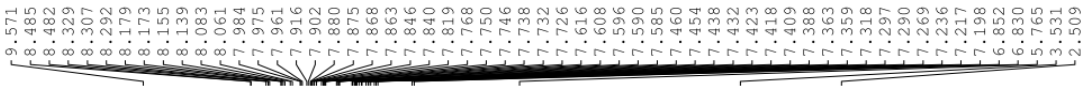

Inten. (x10,000,000)
1.00
0.75
0.50
0.25
0.00
547.1935
5b2
220.9410
254.0928
290.0712
322.5880
368.1163
396.1150
565.2020
587.1804
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z

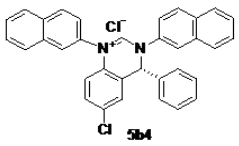

9.172
7.661
7.642
7.461
7.435
7.431
7.415
7.396
7.390
7.384
7.363
7.339
7.159
7.038
6.739
6.717
3.444
2.508
2.412
2.244
Cl⁻
N⁺
N
Cl
5b3
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.17
2.14
1.08
3.11
4.00
1.03
1.02
0.97
6.09
6.24

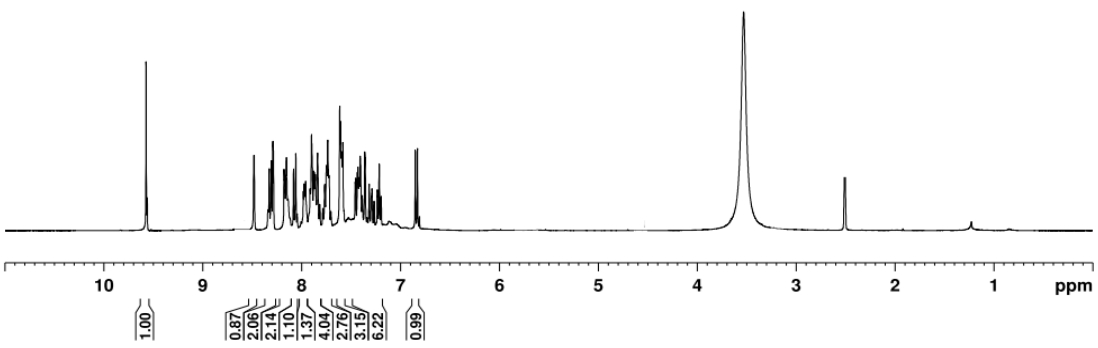

152.55
140.45
140.15
139.74
139.53
136.65
132.60
132.32
131.03
130.98
129.81
129.65
128.22
127.99
125.61
125.52
121.99
119.11
62.43
40.59
40.38
40.17
39.96
39.75
39.54
39.34
21.22
21.18
Cl⁻
N⁺
N
Cl
5b3

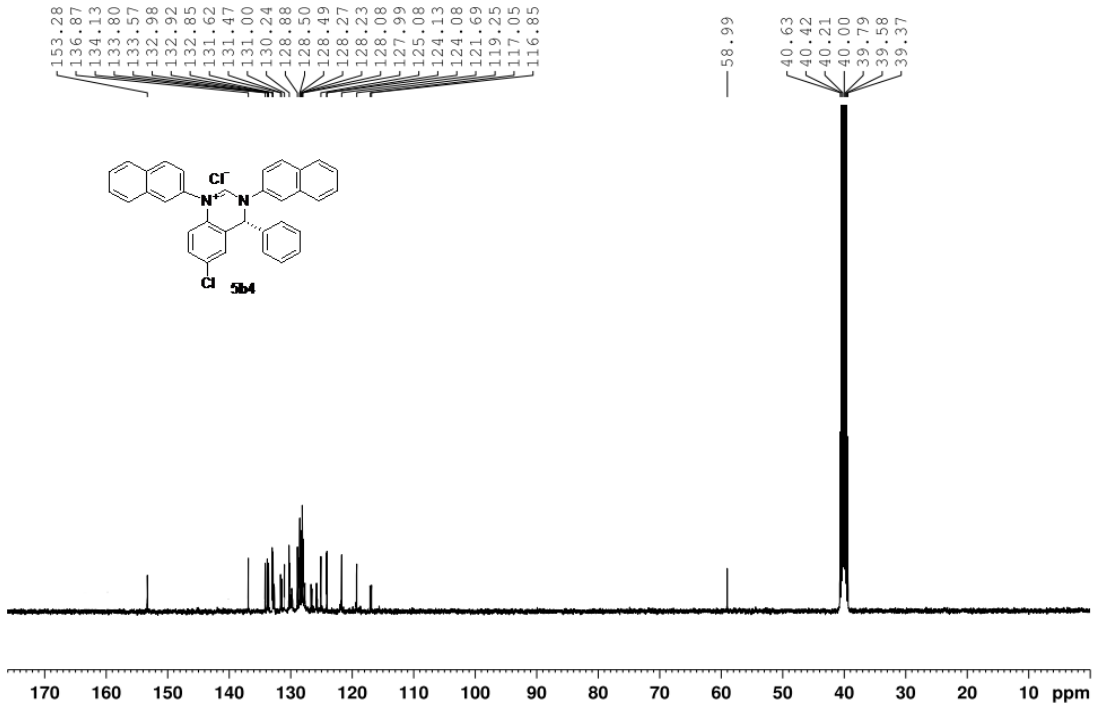

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

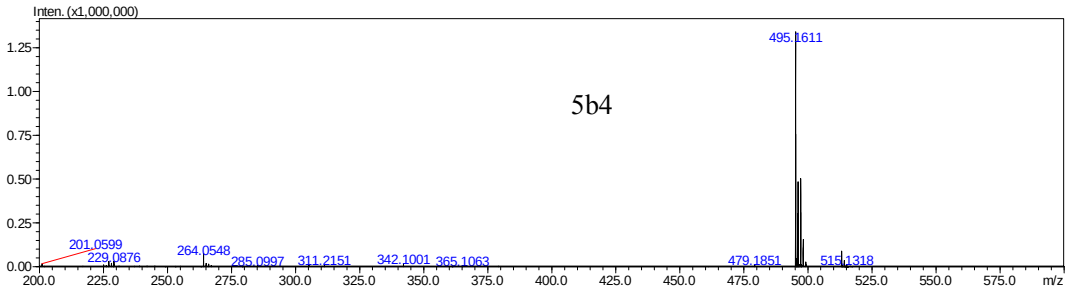

Inten. (x10,000,000)
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
5b3
451.1916
453.1903
216.9950
239.0863
279.1543
301.1375
348.1134
395.1304
491.1807
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z

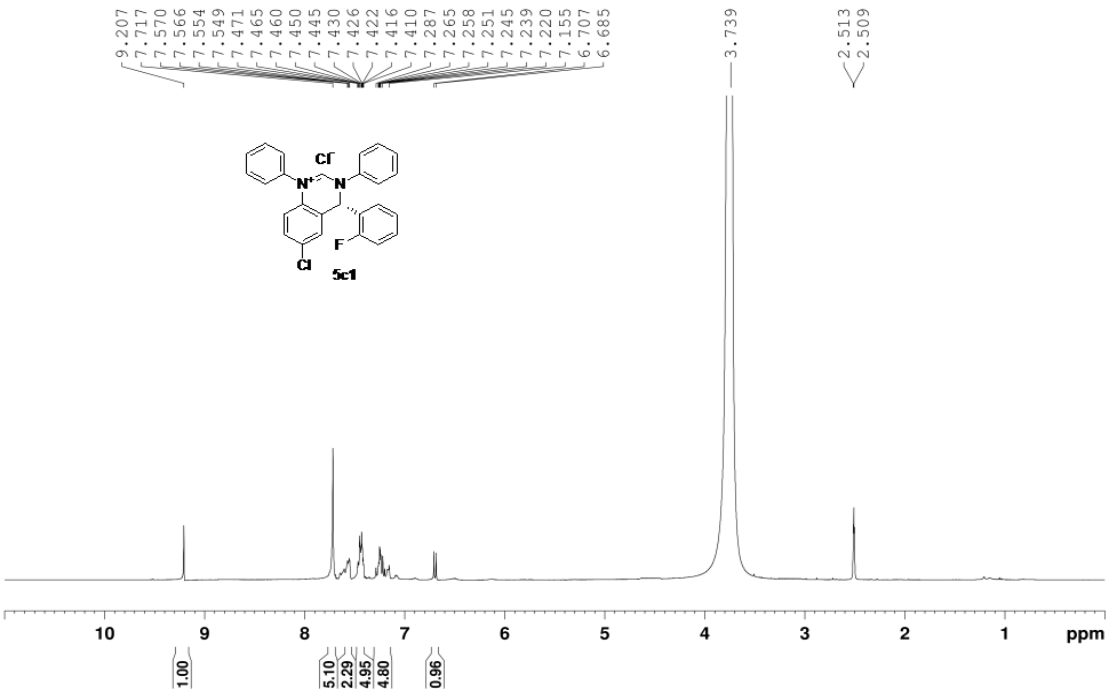

9.571
8.485
8.482
8.329
8.307
8.292
8.179
8.173
8.155
8.139
8.083
8.061
7.984
7.975
7.961
7.916
7.902
7.880
7.875
7.868
7.863
7.846
7.840
7.819
7.768
7.750
7.746
7.738
7.732
7.726
7.616
7.608
7.596
7.590
7.585
7.460
7.454
7.438
7.432
7.423
7.418
7.409
7.388
7.363
7.359
7.318
7.297
7.290
7.269
7.236
7.217
7.198
6.852
6.830
5.765
3.531
2.509

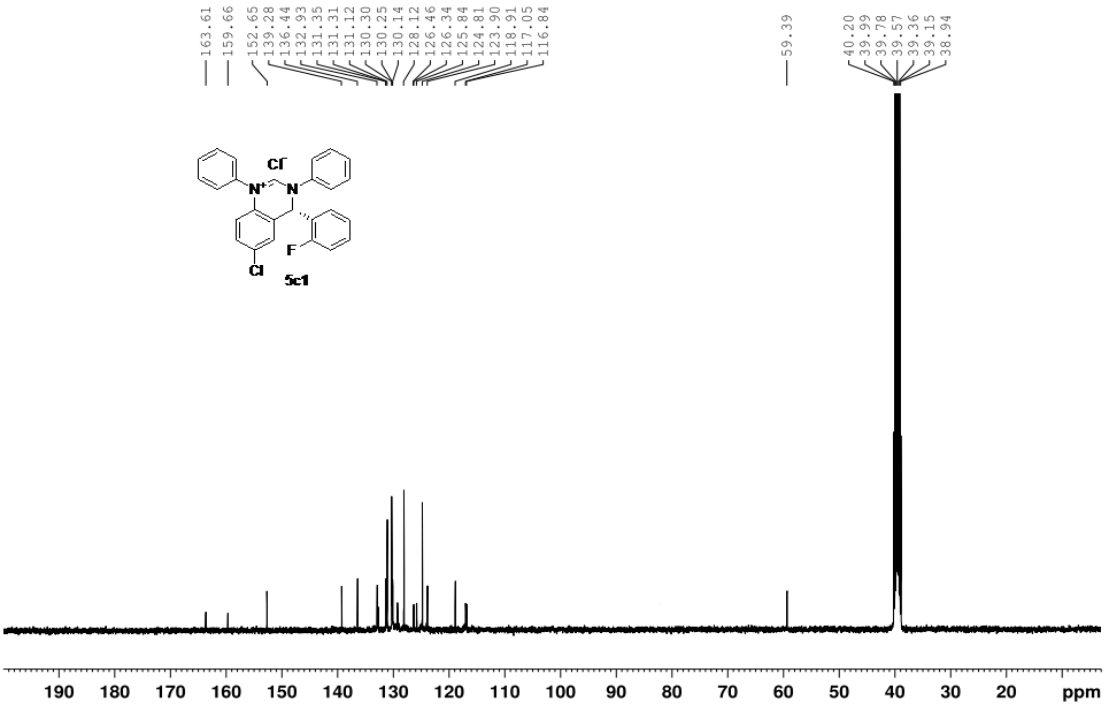

Cl⁻
N⁺
N
Cl
5b4


10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.87
2.06
2.14
1.10
1.37
4.04
2.76
3.15
6.22
0.99


153.28
136.87
134.13
133.80
133.57
132.98
132.92
132.85
131.62
131.47
131.00
130.24
128.88
128.50
128.49
128.27
128.23
128.08
127.99
125.08
124.13
124.08
121.69
119.25
117.05
116.85
58.99
40.63
40.42
40.21
40.00
39.79
39.58
39.37
Cl⁻
N⁺
N
Cl
5b4
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Inten. (x1,000,000)
1.25
1.00
0.75
0.50
0.25
0.00
5b4
495.1611
201.0599
229.0876
264.0548
285.0997
311.2151
342.1001
365.1063
479.1851
515.1318
200.0 225.0 250.0 275.0 300.0 325.0 350.0 375.0 400.0 425.0 450.0 475.0 500.0 525.0 550.0 575.0 m/z


9.207
7.717
7.570
7.566
7.554
7.549
7.471
7.465
7.460
7.450
7.445
7.430
7.426
7.422
7.416
7.410
7.287
7.265
7.258
7.251
7.245
7.239
7.220
7.155
6.707
6.685
3.739
2.513
2.509
Cl⁻
N⁺
N
F
Cl
5c1
10 9 8 7 6 5 4 3 2 1 ppm
1.00
5.10
2.29
4.95
4.80
0.96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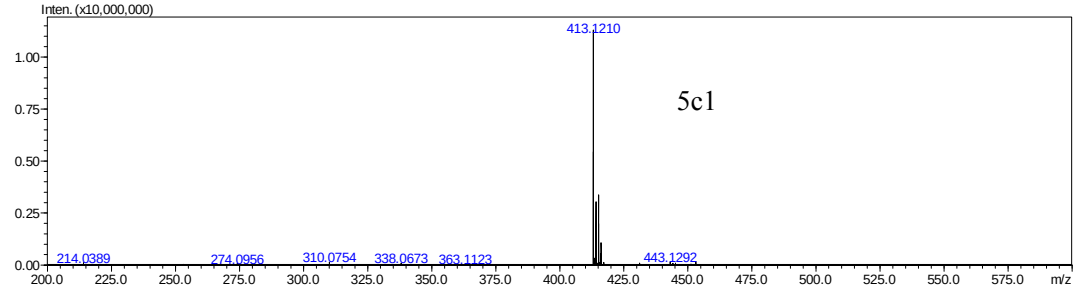
159.66
152.65
139.28
136.44
132.93
131.35
131.31
131.12
130.30
130.25
130.14
128.12
126.46
126.34
125.84
124.81
123.90
118.91
117.05
116.84
59.39
40.20
39.99
39.78
39.57
39.36
39.15
38.94
Cl⁻
N⁺
N
F
Cl
5c1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Inten. (x10,000,000)
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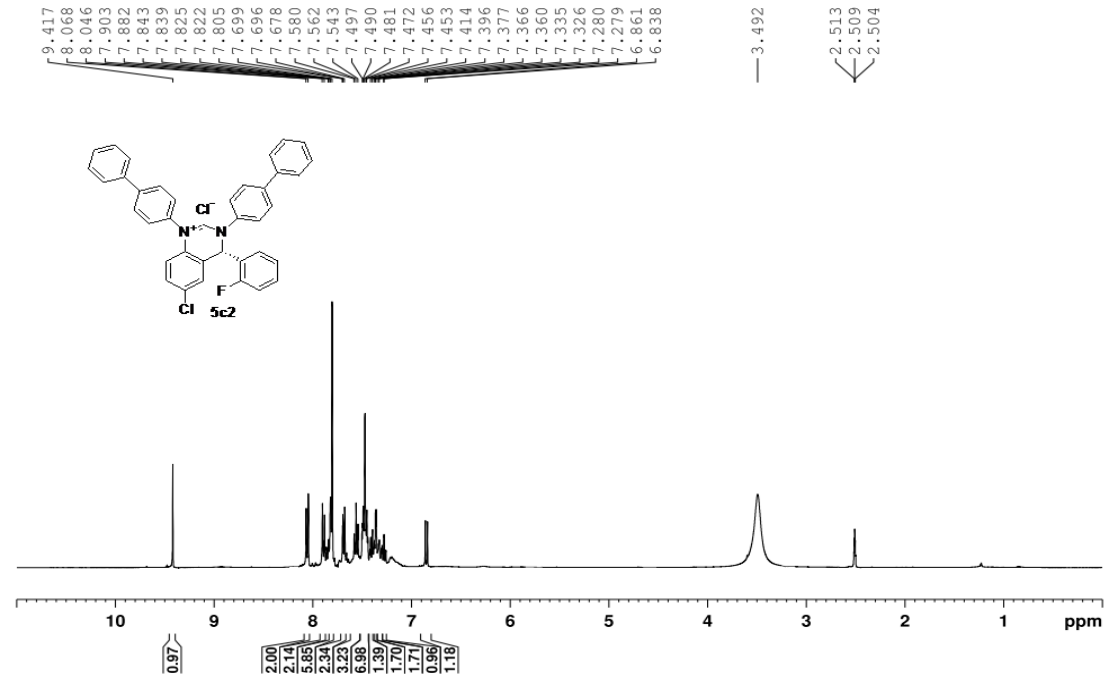
0.75
0.50
0.25
0.00
214.0389
274.0956
310.0754
338.0673
363.1123
443.1292
200.0 225.0 250.0 275.0 300.0 325.0 350.0 375.0 400.0 425.0 450.0 475.0 500.0 525.0 550.0 575.0 m/z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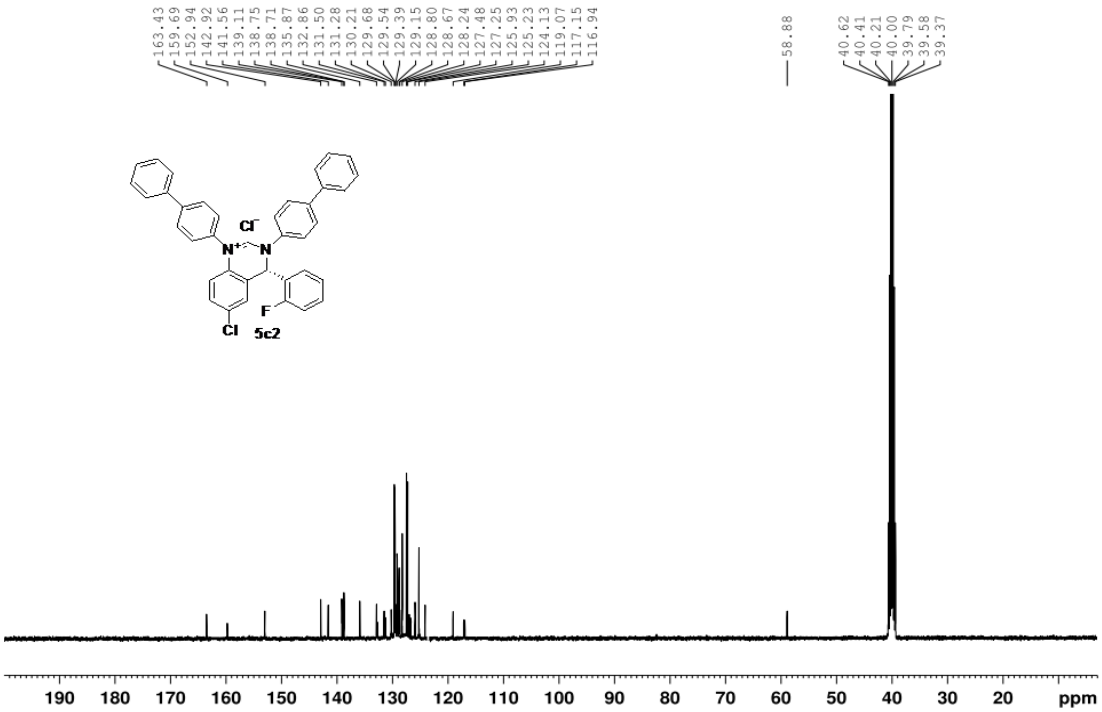
8.068
8.046
7.903
7.882
7.843
7.839
7.825
7.822
7.805
7.699
7.696
7.678
7.580
7.562
7.543
7.497
7.490
7.481
7.472
7.456
7.453
7.414
7.396
7.377
7.366
7.360
7.335
7.326
7.280
7.279
6.861
6.838
3.492
2.513
2.509
2.504
Cl⁻
N⁺
N
F
Cl
5c2
10 9 8 7 6 5 4 3 2 1 ppm
0.97
2.00
2.14
5.85
2.34
3.23
6.98
1.39
1.70
1.71
0.96
1.18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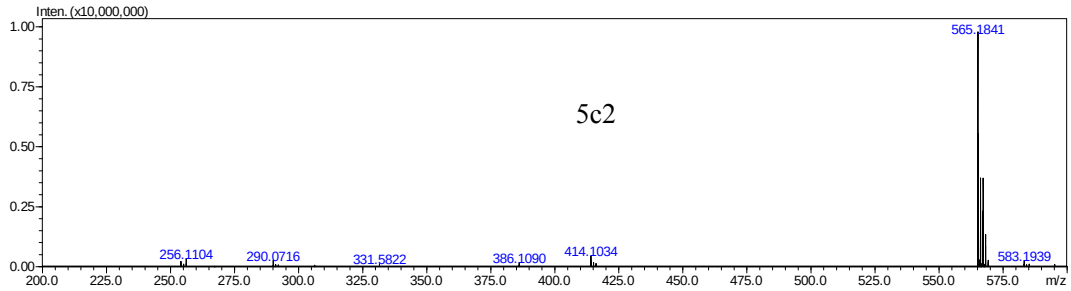
152.94
142.92
141.56
139.11
138.75
138.71
135.87
132.86
131.50
131.28
130.21
129.68
129.54
129.39
129.15
128.80
128.67
128.24
127.48
127.25
125.93
125.23
124.13
119.07
117.15
116.94
58.88
40.62
40.41
40.21
40.00
39.79
39.58
39.37
Cl
N
N
F
Cl
5c2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


Inten. (x10,000,000)
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0.75
0.50
0.25
0.00
5c2
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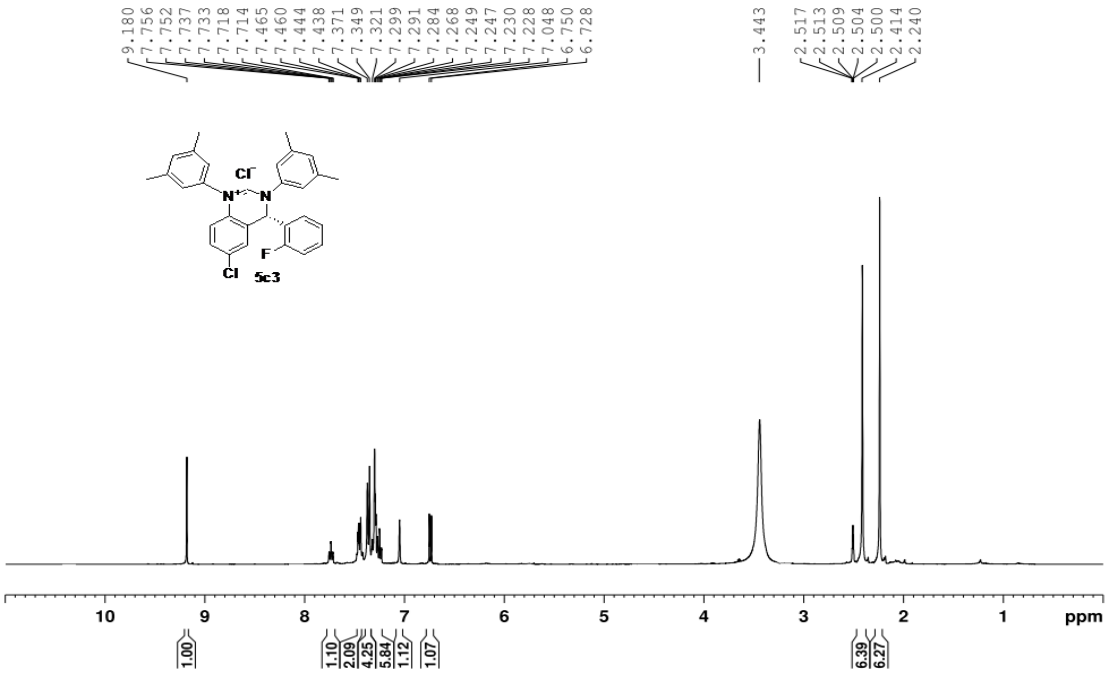
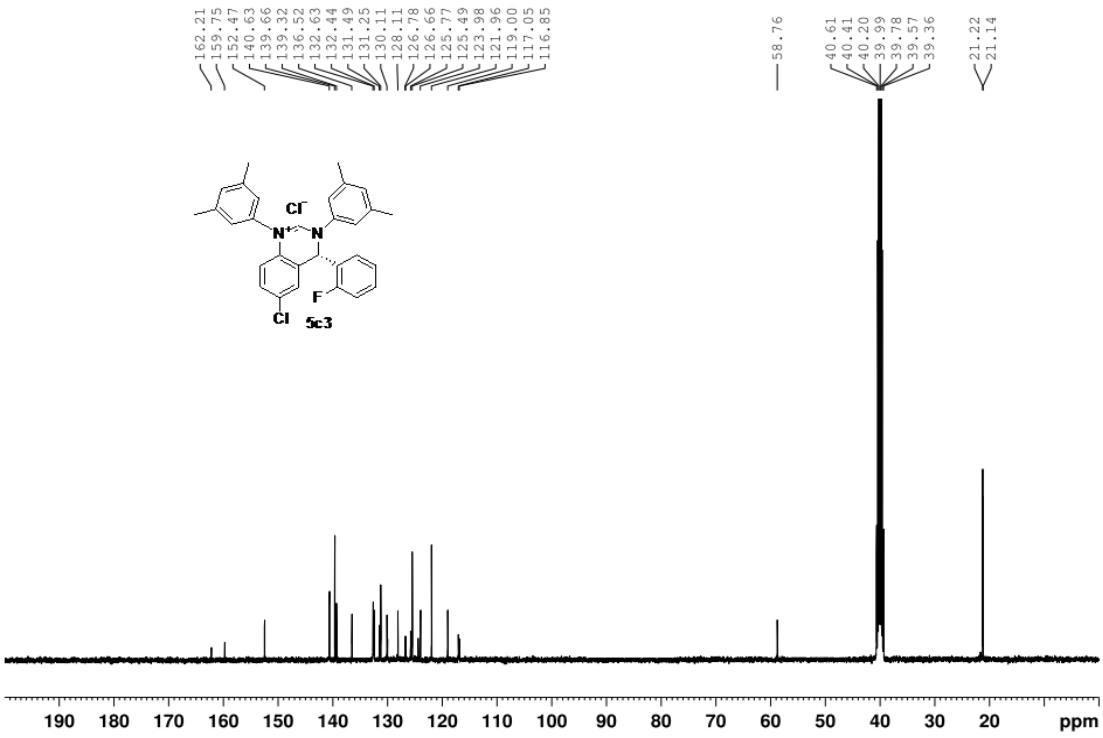
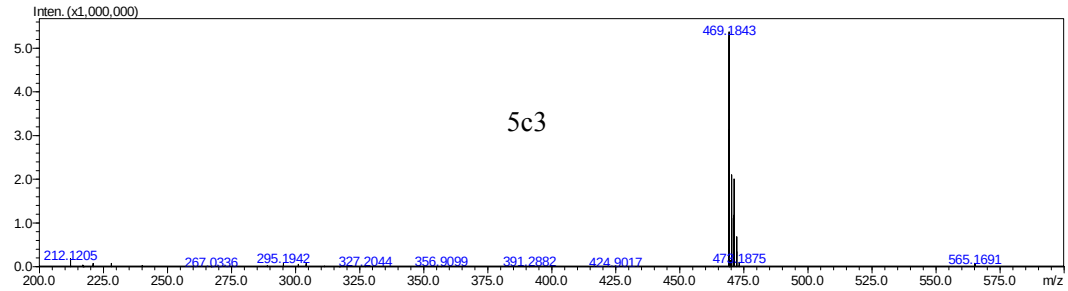
256.1104
290.0716
331.5822
386.1090
414.1034
583.1939
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z


9.180
7.756
7.752
7.737
7.733
7.718
7.714
7.465
7.460
7.444
7.438
7.371
7.349
7.321
7.299
7.291
7.284
7.268
7.249
7.247
7.230
7.228
7.048
6.750
6.728
3.443
2.517
2.513
2.509
2.504
2.500
2.414
2.240
Cl
N
N
F
Cl
5c3
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.10
2.09
4.25
5.84
1.12
1.07
6.39
6.27


162.21
159.75
152.47
140.63
139.66
139.32
136.52
132.63
132.44
131.49
131.25
130.11
128.11
126.78
126.66
125.77
125.49
123.98
121.96
119.00
117.05
116.85
58.76
40.61
40.41
40.20
39.99
39.78
39.57
39.36
21.22
21.14
Cl⁻
N⁺
N
F
Cl
5c3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Inten. (x1,000,000)
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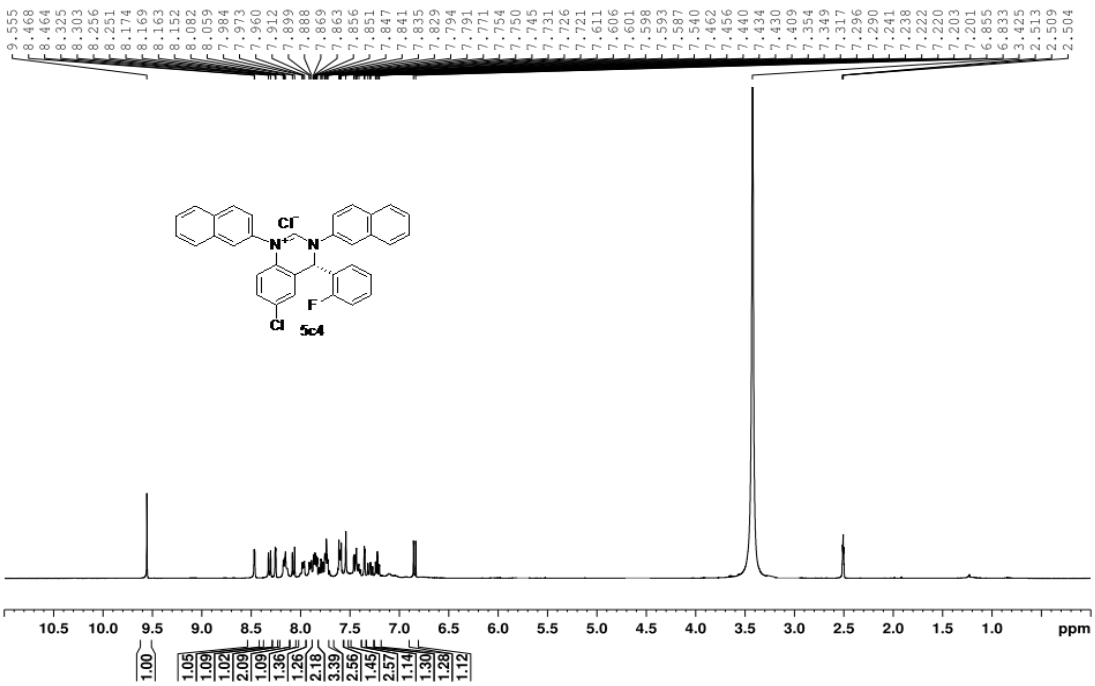
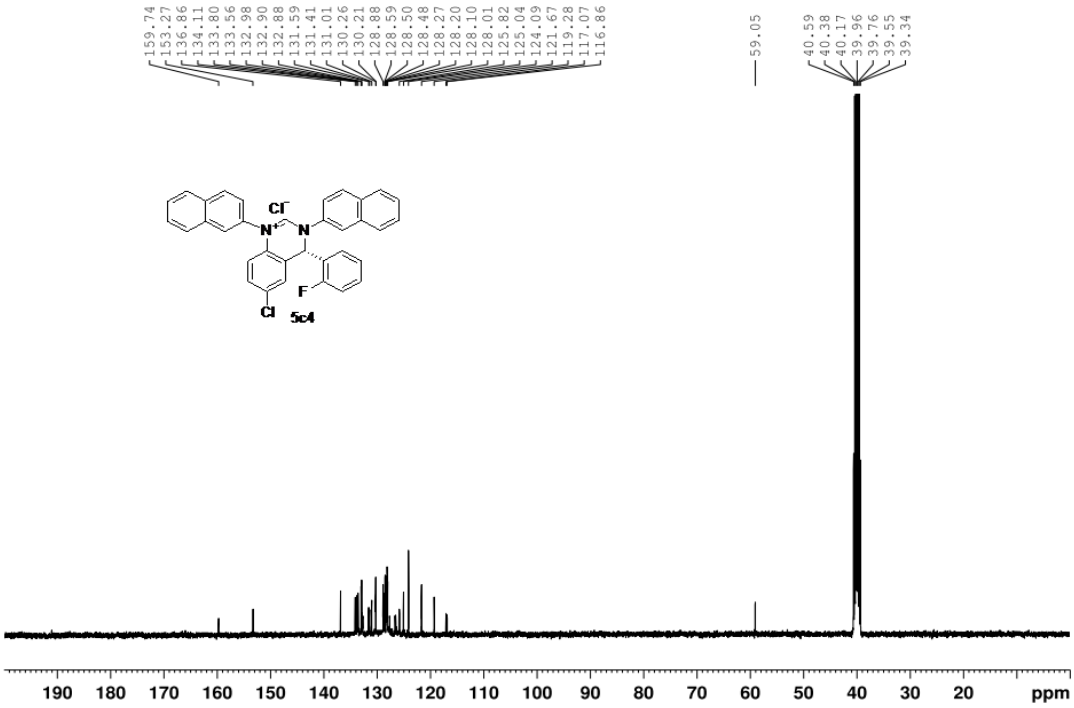
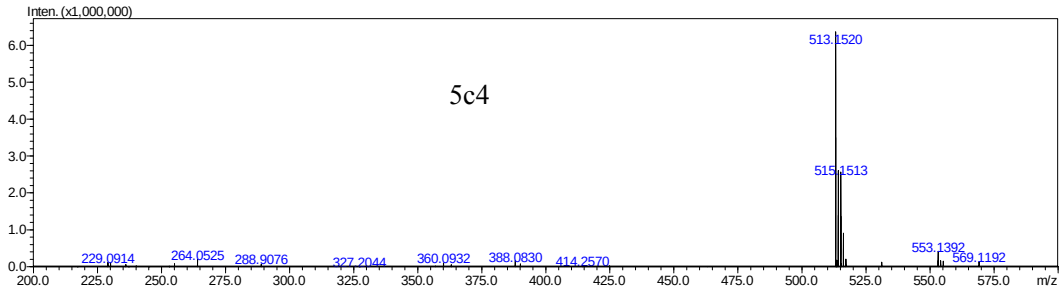
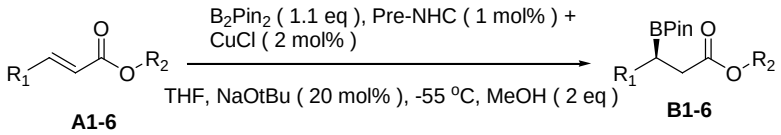
5c3
212.1205
267.0336
295.1942
327.2044
356.9099
391.2882
424.9017
471.1875
565.1691
200.0 225.0 250.0 275.0 300.0 325.0 350.0 375.0 400.0 425.0 450.0 475.0 500.0 525.0 550.0 575.0 m/z


Cl⁻
N⁺
N
F
Cl
5c4
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 ppm
1.00 1.05 1.09 1.02 2.09 1.09 1.36 1.26 2.18 3.39 2.56 1.45 2.57 1.14 1.30 1.28 1.12

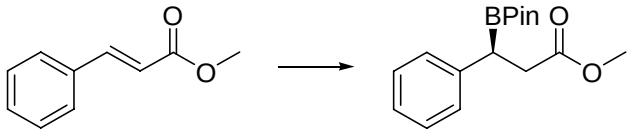

159.74
153.27
136.86
134.11
133.80
133.56
132.98
132.90
132.88
131.59
131.41
131.01
130.26
130.21
128.88
128.59
128.50
128.48
128.27
128.20
128.10
128.01
125.82
125.04
124.09
121.67
119.28
117.07
116.86
59.05
40.59
40.38
40.17
39.96
39.76
39.55
39.34
Cl⁻
N
N
F
Cl
5c4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

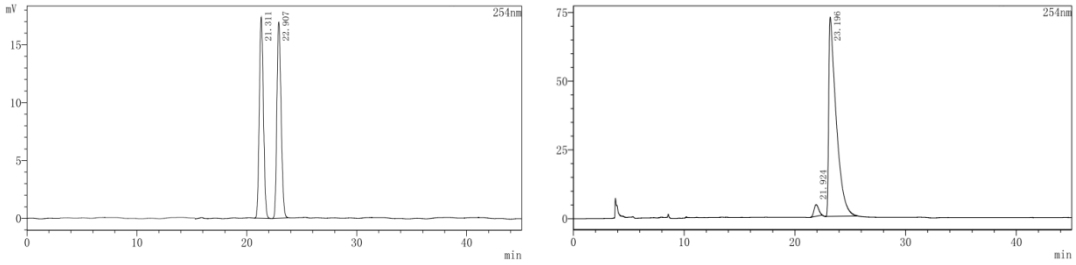

Inten. (x1,000,000)
5c4
513.1520
515.1513
553.1392
569.1192
229.0914
264.0525
288.9076
327.2044
360.0932
388.0830
414.2570
6.0
5.0
4.0
3.0
2.0
1.0
0.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0
525.0
550.0
575.0
m/z

HPLC analysis and NMR spectra for enantioselective β-borylated ester synthesis catalyzed by chiral RE-NHCs



(S)-methyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**B1**)

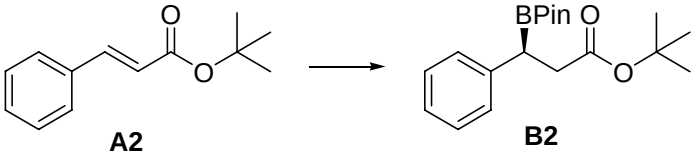


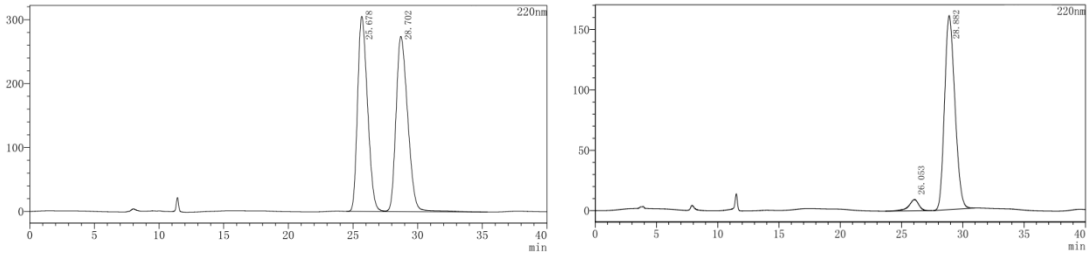


B1(Racemic) **B1**

B1(Racemic)	Peak#	Time (min)	Area (%)	**B1**	Peak#	Time (min)	Area (%)
	1	21.311	49.927		1	21.924	3.507
	2	22.907	50.073		2	23.196	96.493

(S)-tert-butyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**B2**)

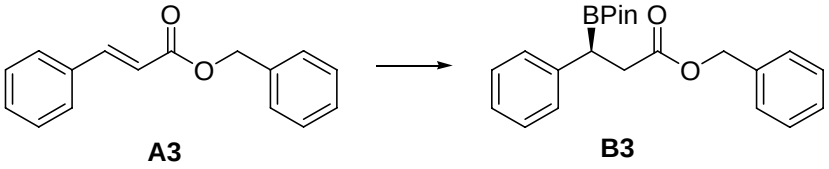




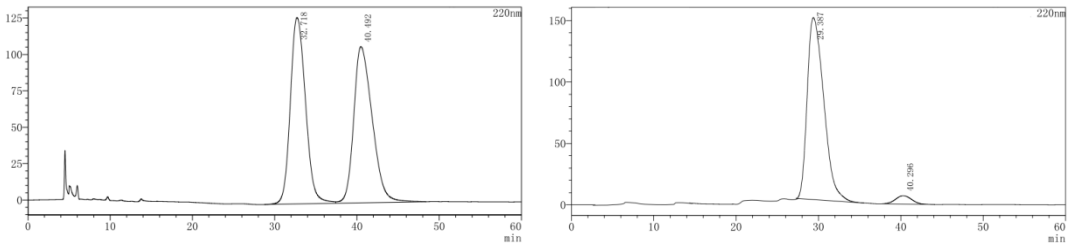
B2(Racemic) **B2**

B2(Racemic)	Peak#	Time (min)	Area (%)	**B2**	Peak#	Time (min)	Area (%)
	1	25.678	48.482		1	26.053	5.284
	2	28.702	51.518		2	28.882	94.716

(S)-benzyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**B3**)



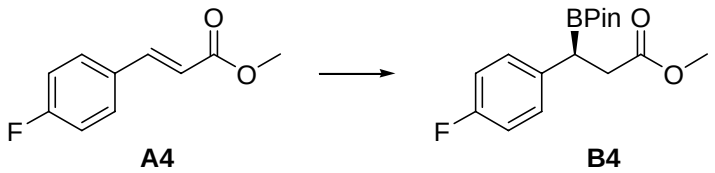
A3 **B3**



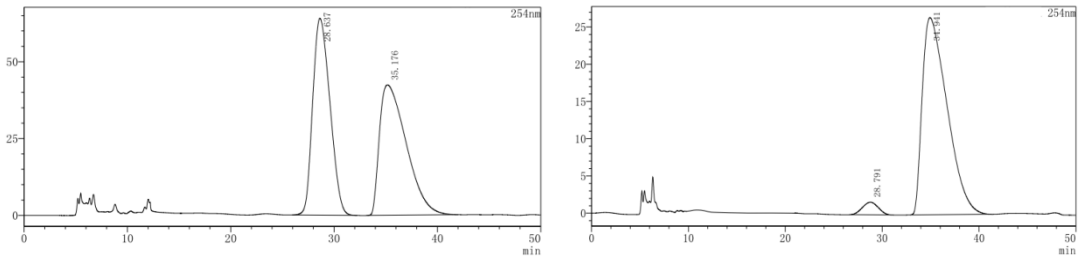
B3 (Racemic) **B3**

	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
B3(Racemic)	1	32.718	49.558	**B3**	1	29.387	95.676
	2	40.492	50.442		2	40.296	4.324

(S)-methyl 3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**B4**)



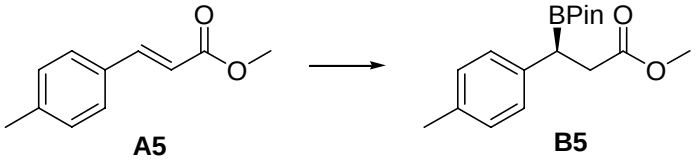
A4 **B4**



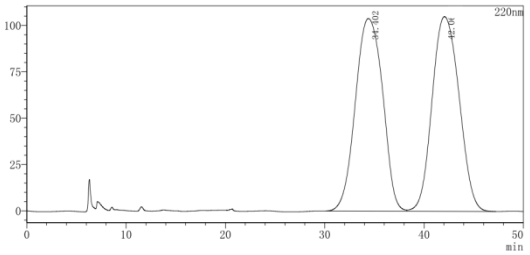
B4 (Racemic) **B4**

	Peak#	Time (min)	Area (%)		Peak#	Time (min)	Area (%)
B4(Racemic)	1	28.637	49.289	**B4**	1	28.791	3.884
	2	35.176	50.711		2	34.941	96.116

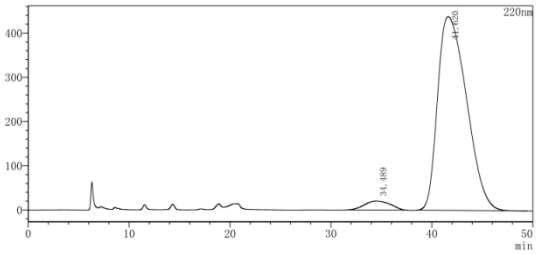
(S)-methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-p-tolylpropanoate (**B5**)



A5 **B5**



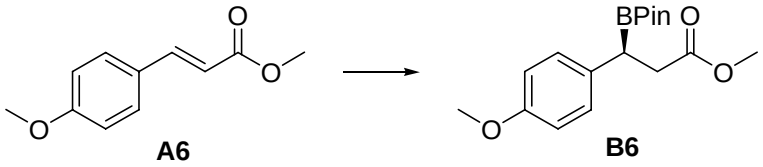
B5(Racemic)



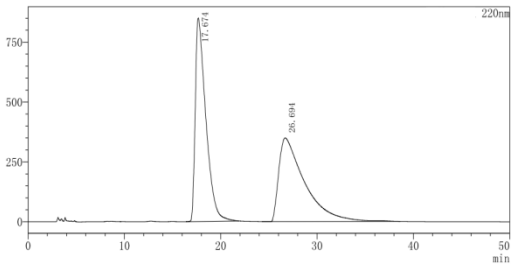
B5

B5(Racemic)	Peak#	Time (min)	Area (%)	**B5**	Peak#	Time (min)	Area (%)
	1	34.402	49.941		1	34.489	3.966
	2	42.066	50.059		2	41.620	96.034

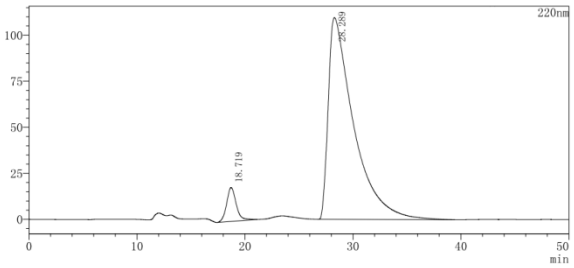
(S)-methyl 3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (**B6**)



A6 **B6**



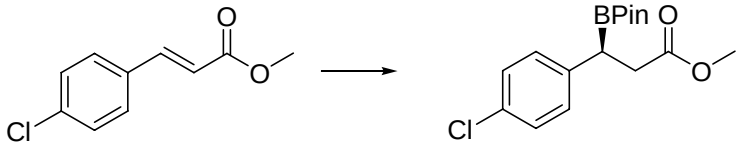
B6(Racemic)



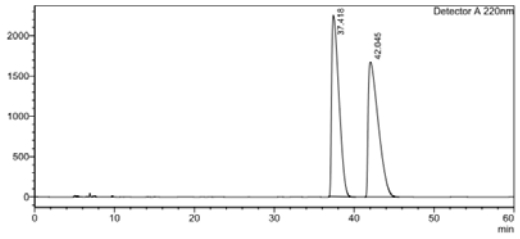
B6

B6(Racemic)	Peak#	Time (min)	Area (%)	**B6**	Peak#	Time (min)	Area (%)
	1	17.674	49.868		1	18.719	5.955
	2	26.694	50.132		2	28.289	94.045

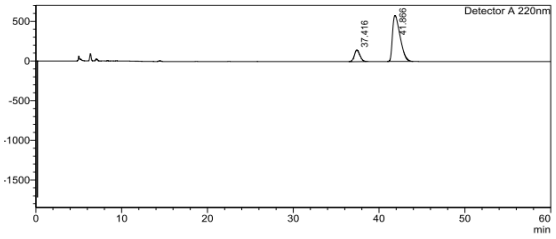
(S)-methyl-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate(**B7**)



A7 **B7**

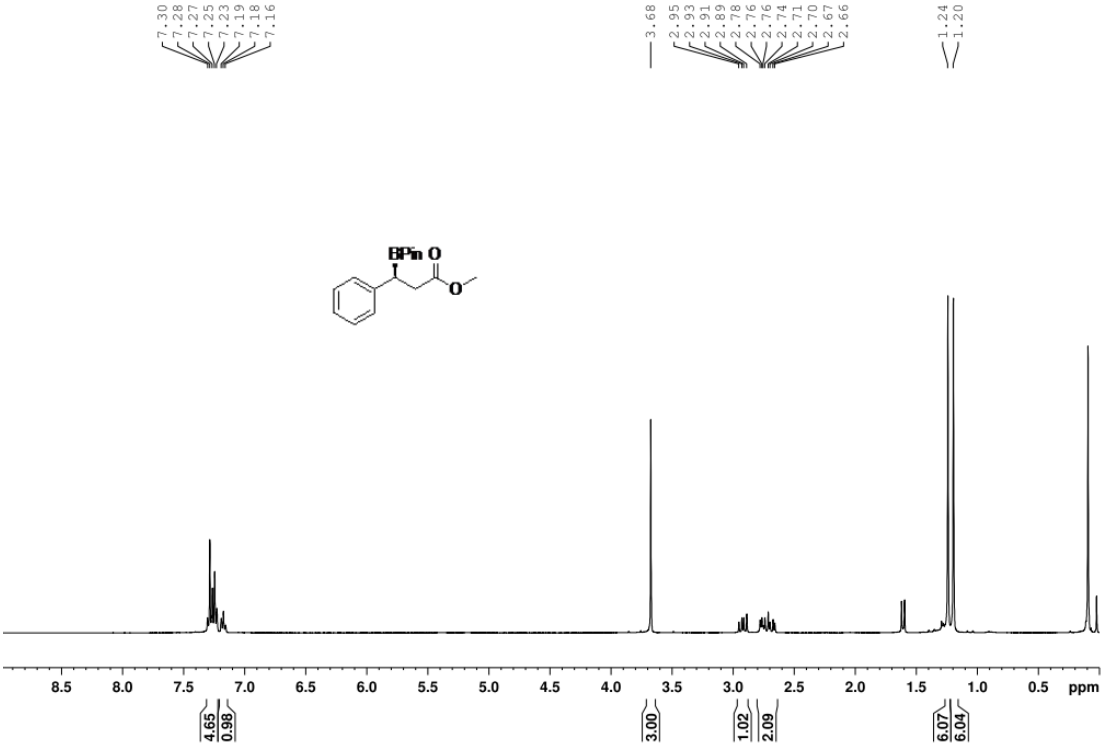


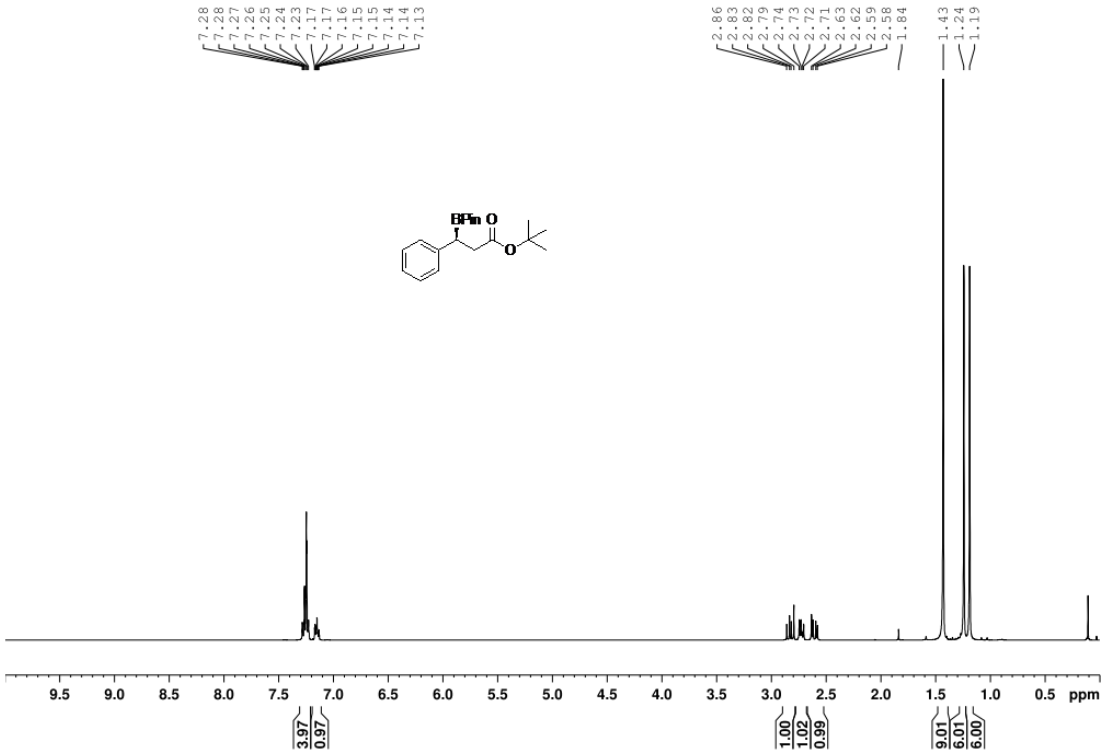
B7(Racemic)



B7

B7(Racemic)	Peak#	Time (min)	Area (%)	**B7**	Peak#	Time (min)	Area (%)
	1	37.418	49.288		1	37.416	9.071
	2	42.045	50.712		2	41.866	90.929

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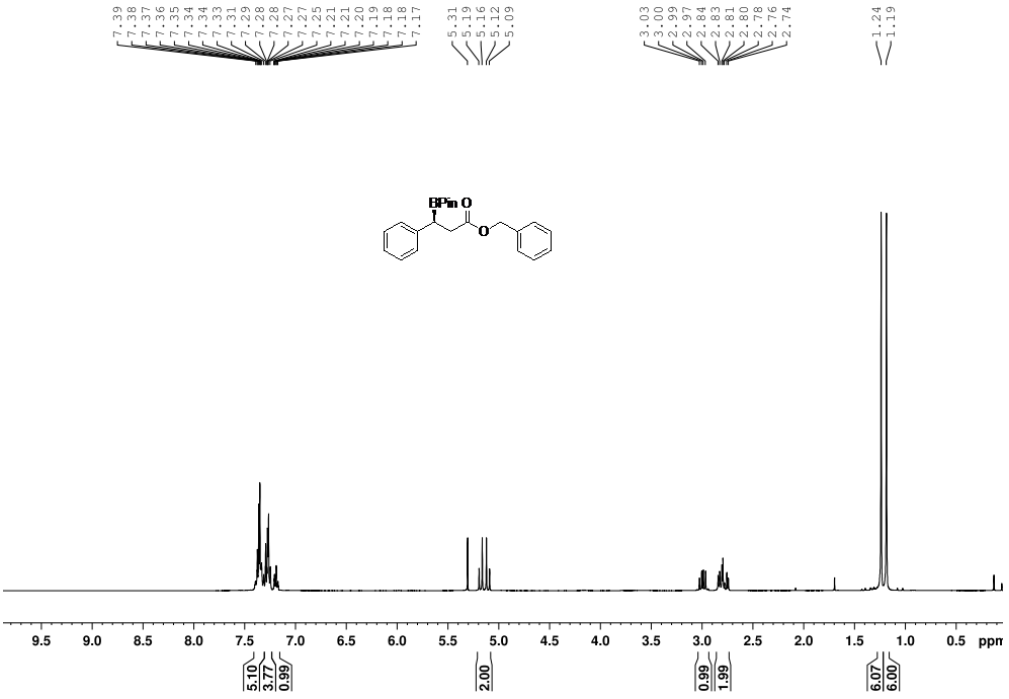
7.24
7.23
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
2.86
2.83
2.82
2.79
2.74
2.73
2.72
2.71
2.63
2.62
2.59
2.58
1.84
1.43
1.24
1.19
BPin
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.97
0.97
1.00
1.02
0.99
9.01
6.01
6.00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7.28
7.28
7.27
7.27
7.25
7.21
7.20
7.19
7.18
7.18
7.17
5.31
5.19
5.16
5.12
5.09
3.03
3.00
2.99
2.97
2.84
2.83
2.81
2.80
2.78
2.76
2.74
1.24
1.19
BPin
O
O
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 ppm
5.10
3.77
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2.00
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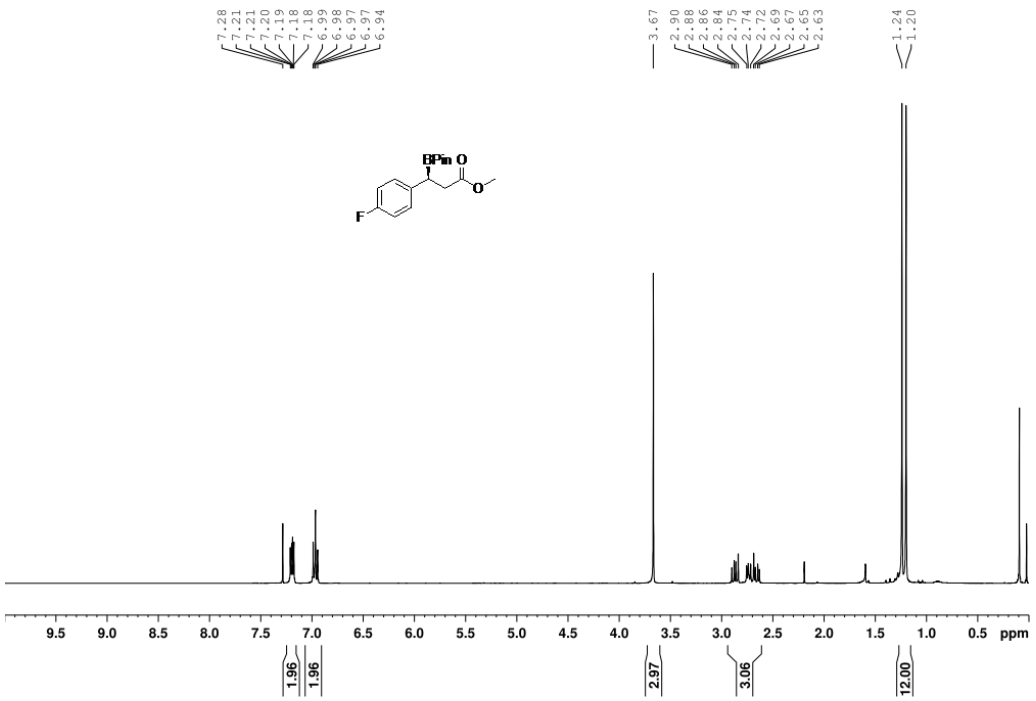
6.07
6.00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7.21
7.20
7.19
7.18
7.18
6.99
6.98
6.97
6.97
6.94
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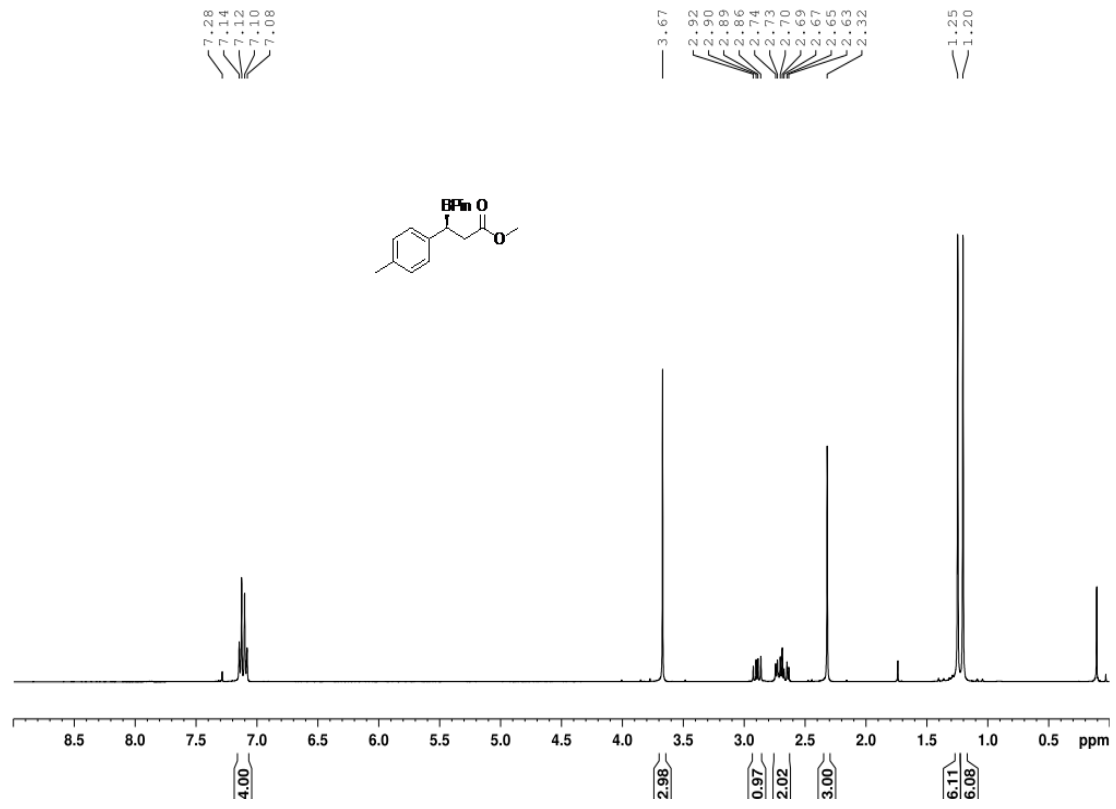
2.90
2.88
2.86
2.84
2.75
2.74
2.72
2.69
2.67
2.65
2.63
1.24
1.20
BPin
O
O
F
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.96
1.96
2.97
3.06
12.00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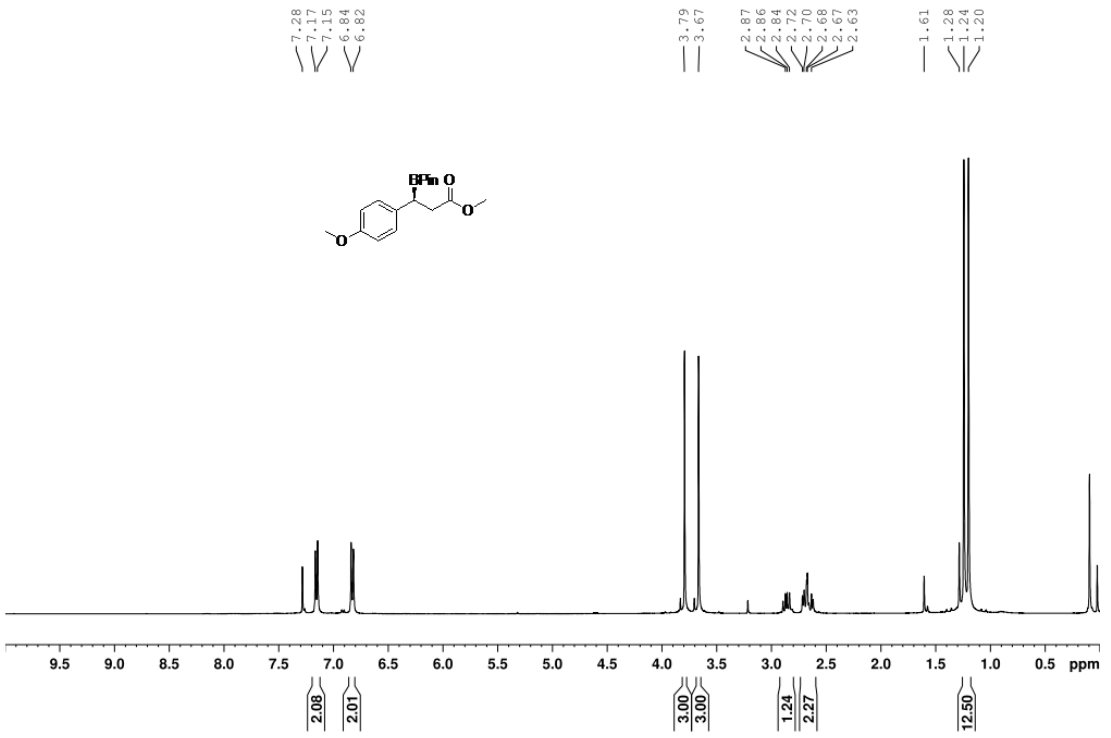
7.14
7.12
7.10
7.08
3.67
2.92
2.90
2.89
2.86
2.74
2.73
2.70
2.69
2.67
2.65
2.63
2.32
1.25
1.20
BPin
O
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.00
2.98
0.97
2.02
3.00
6.11
6.08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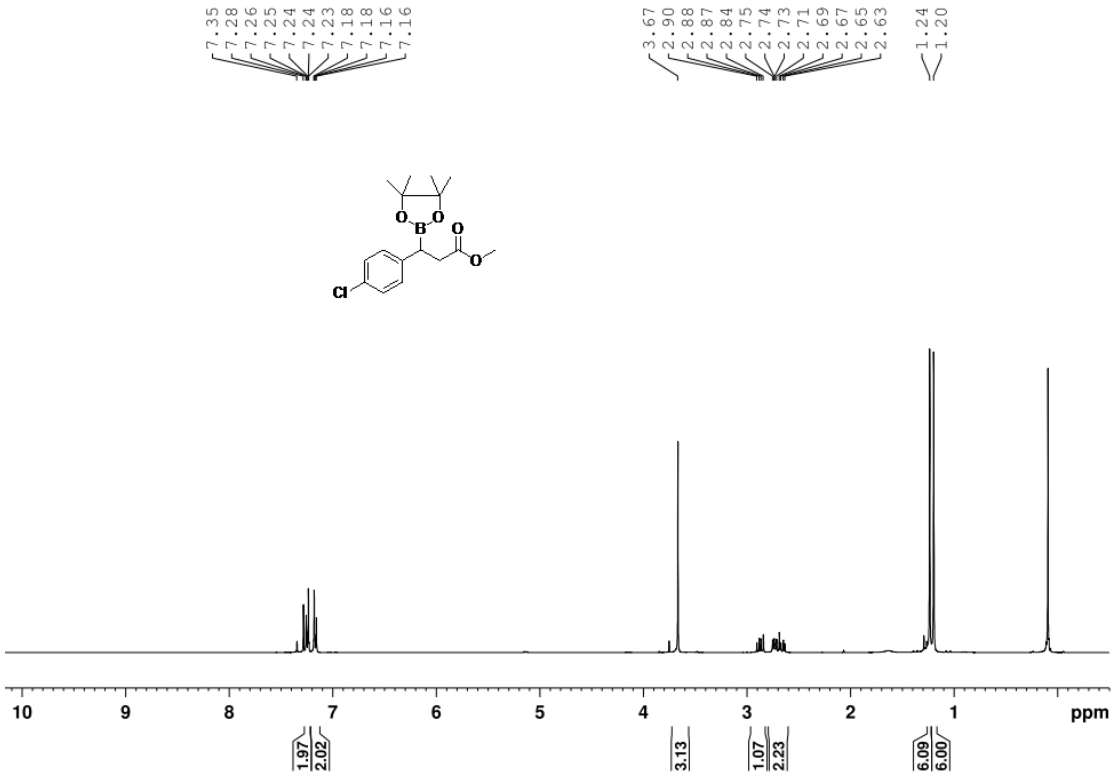
7.15
6.84
6.82
3.79
3.67
2.87
2.86
2.84
2.72
2.70
2.68
2.67
2.63
1.61
1.28
1.24
1.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.08
2.01
3.00
3.00
1.24
2.27
12.50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7.28
7.26
7.25
7.24
7.24
7.23
7.18
7.18
7.16
7.16
3.67
2.90
2.88
2.87
2.84
2.75
2.74
2.73
2.71
2.69
2.67
2.65
2.63
1.24
1.20
10 9 8 7 6 5 4 3 2 1 ppm
1.97
2.02
3.13
1.07
2.23
6.09
6.00