Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

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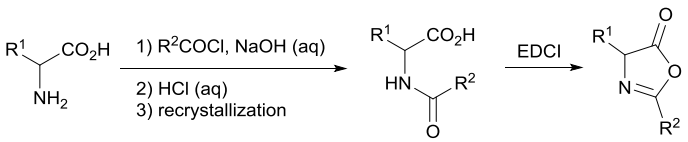
1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard [$CDCl_3$, δ = 7.26), $(CD_3)_2SO$, δ = 2.50, MeOD, δ = 2.64, $(CD_3)_2CO$, δ = 2.05]. Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants (Hz), integration and assignment. $^{13}C\{^{1}H\}$ NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. $^{19}F\{^{1}H\}$ NMR: chemical shifts δ are given relative to $CFCl_3$ [external reference, δ $^{19}F(CFCl_3)$ = 0]. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard [$CDCl_3$, δ = 77.0, $(CD_3)_2SO$, δ = 39.5, MeOD, δ = 49.0, $(CD_3)_2CO$, δ = 206.3， δ = 29.8]. Enantiomeric excesses (ee) were determined by high-performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) on systems of an Agilent 1100 or 1200 series with chiral stationary phases (Chiralpak IA, Chiralpak IB, Chiralpak ADH) from Chiral Technologies Inc in the experimental procedures at 35 ℃. Optical rotations were reported as follows: $[\alpha]_D^T$(*c*: g/100 mL, in solvent). The unit is deg•cm^3•g^{-1}•dm^{-1}. IR spectra were recorded on Pierkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm^{-1}. High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode. HRMS was recorded on a commercial apparatus (FTMS+c ESI). Reactions were monitored by thin layer chromatography (TLC) from Merck. Column chromatography was performed using silica gel 60 (63–200 μm) from Merck. All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Ethyl acetate, CH_2Cl_2 was distilled over CaH_2. $NaBAr^F_4$ and $NaBPh_4$ was purchased from Alfa, used after recrystallization. Chiral guanidine catalysts was prepared according to previously reported method.[1]

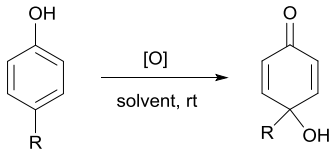
2. Substrates synthesis

2.1 General procedure for the synthesis of azlactones according to the literature procedure.[2]

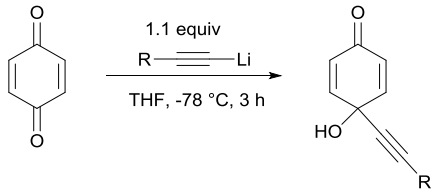


2.2 General procedure for the synthesis of *p*-quinols

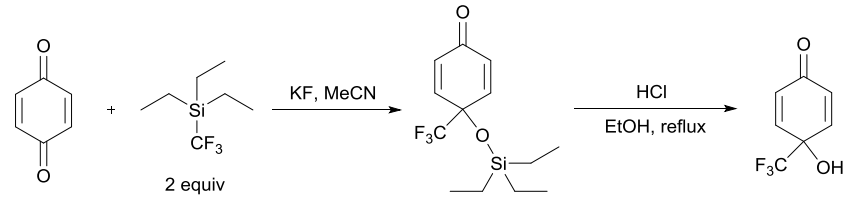
a) Method A: *p*-quinols (**1a**, **1c**, **1d**, **1e**, **1g** ang **1h**) were prepared by oxidative dearomatization according to the literature procedure.[3]



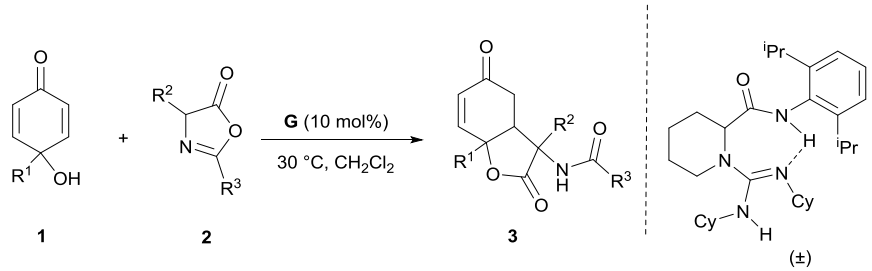
b) Method B: *p*-quinol (**1f**) was prepared according to the literature procedure.[4]



c) Method C: *p*-quinol (**1b**) was prepared according to the literature procedure.[5]



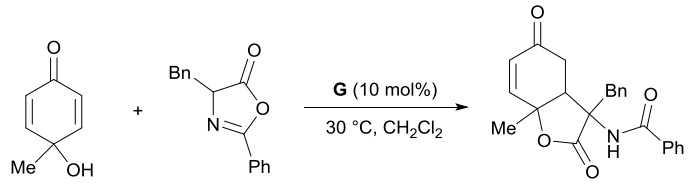
2.3 General procedure for the synthesis of racemic products 3



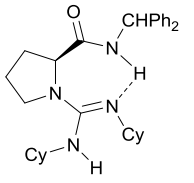
In a dry tube was charged with the racemic catalyst (10 mol%), **1** (0.10 mmol), and **2** (0.10 mmol) in CH_2Cl_2 (1.0 mL) were stirred at 30 ℃ for 24 h. After completion, flash column chromatography provided the desired racemic products **3** (petroleum ether/ethyl acetate = 4/1 as eluent).

3. Optimization of the reaction conditions

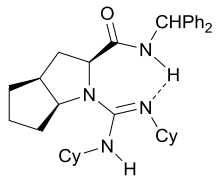
Table S1. Screening of guanidines[a]



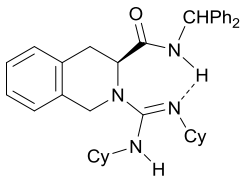
1a **2a** **3aa**



G-1

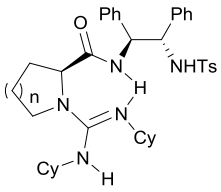


G-2

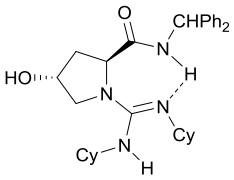


G-3

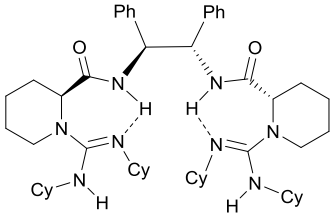
(Cy = Cyclohexyl)



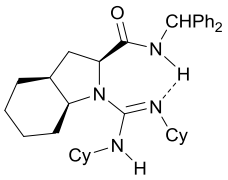
G-4: n = 0
G-5: n = 1



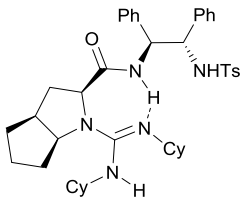
G-6



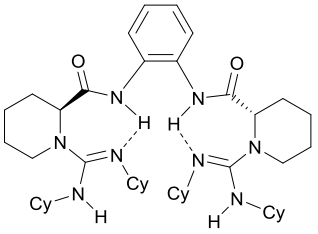
BG-1



G-7



G-8

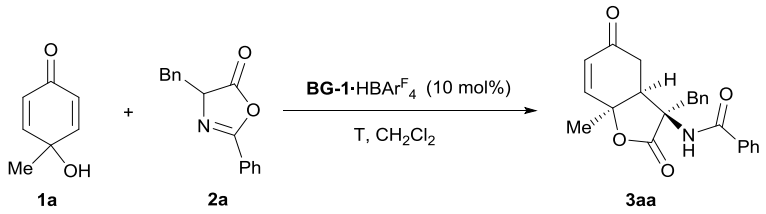


BG-2

entry	cat.	yield (%)[b]	ee (%)[c]
1	**G-1**	17	−5
2	**G-2**	24	−10
3	**G-3**	11	−11
4	**G-4**	22	40
5	**G-5**	23	41
6	**G-6**	11	−3
7	**G-7**	22	−13
8	**G-8**	14	−17
9	**BG-1**	33	46
10	**BG-2**	31	6
11	**BG-1**•$HBAr^F_4$	64	86

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.20 mmol) and **G** (10 mol%) in CH_2Cl_2 (1.0 mL) at 30 ℃ under N_2 for 24 h. Dr values (>19:1) were determined by ^1H NMR. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. $HBAr^F_4$ = $HB[3,5\text{-}(F_3C)_2C_6H_3]_4$. **BG-1**•$HBAr^F_4$ is prepared from a mixture of **BG-1** (50%) and **BG-1**•$2HBAr^F_4$ (50%).

Table S2. Screening of the temperature[a]

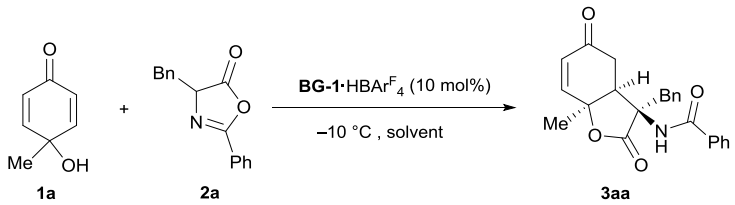


1a 2a 3aa

entry	T (℃)	yield (%)[b]	ee (%)[c]
1	0	55	95
2	−10	42	99
3	−20	43	99
4	−30	trace	99
5	−40	N.R.[d]	—
6	−78	N.R.	—

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **BG-1**•HBAr$^F_4$ (10 mol%) in CH_2Cl_2 (1.0 mL) at the indicated temperature under N_2 for 24 h. Dr values (>19:1) were determined by ^{1}H NMR. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] N.R. = no reaction.

Table S3. Screening of the solvents[a]



1a 2a 3aa

entry	solvent	yield (%)[b]	ee (%)[c]
1[d]	Toluene	26	75
2	THF	N.R.	—
3[f]	CH_2Cl_2	50	99
4[d,e,f]	CH_2Cl_2	71	99
5	Et_2O	N.R.[g]	—
6	CH_3CN	N.R.	—
7	Ethyl acetate	N.R.	—
8	$CHCl_3$	28	99
9	CCl_3CH_3	44	96
10	CH_2ClCH_2Cl	39	99
11[d,e,f]	CH_2ClCH_2Cl	50	99
12	$CHCl_2CH_2Cl$	16	98

[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **BG-1**•HBAr$^F_4$ (10 mol%) in

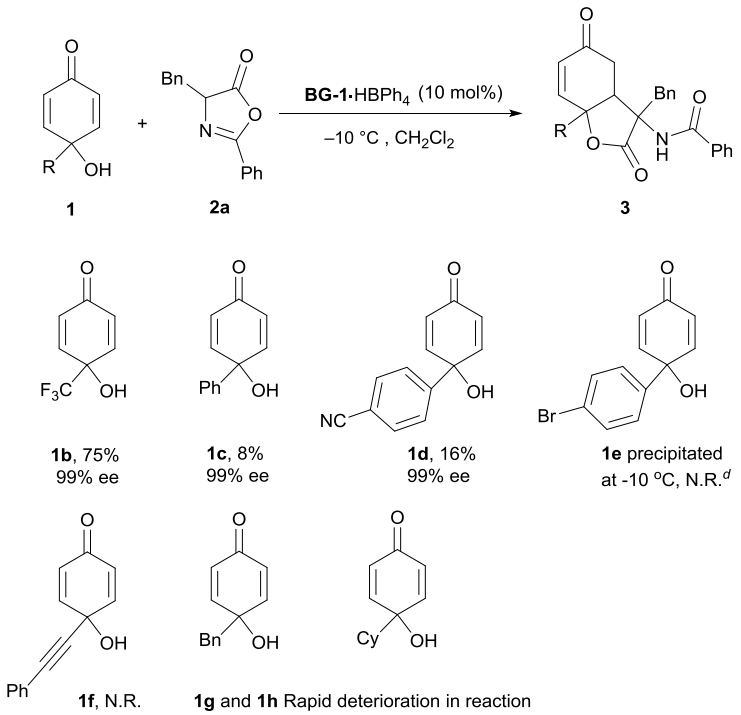
solvent (1.0 mL) at −10 ℃ under N_2 for 24 h. Dr values (>19:1) were determined by ^{1}H NMR. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] for 72 h. [e] **2a** (0.20 mmol) was used. [f] Using 10 mol% of **BG-1**•$HBPh_4$. [g] N.R. = no reaction.

Table S4. Screening of the additives[a]

entry	additive	yield (%)[b]	ee (%)[c]
1	Et_3N (10 mol%)	N.R.[d]	—
2	Imidazole (10 mol%)	N.R.	—
3	Benzoic acid (10 mol%)	N.R.	—
4	Pyridine (10 mol%)	N.R.	—
5	*tert*-Butanol (10 mol%)	N.R.	—
6	*N*-Methylmorpholine (10 mol%)	N.R.	—
7	4 Å M.S. (20 mg)	N.R.	—
8	water (10 μL)	33	93
9	Adamantanol (10 mol%)	49	95
10	$MgSO_4$ (10 mol%)	39	99
11	KBr (10 mol%)	41	91
12	$K_4P_2O_7$ (10 mol%)	52	99
13	K_2HPO_4 (10 mol%)	51	99

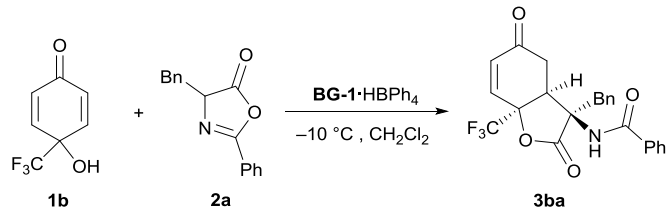
[a] The reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), and **BG-1**•$HBPh_4$ (10 mol%) and daaitive in CH_2Cl_2 (1.0 mL) at −10 ℃ under N_2 for 24 h. Dr values (>19:1) were determined by ^{1}H NMR. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] N.R. = no reaction.

Schem 1. Screening of the *p*-quinols[a]



[a] The reactions were carried out with **1** (0.10 mmol), **2a** (0.20 mmol) and **BG-1•**$HBPh_4$ (10 mol%) in CH_2Cl_2 (1.0 mL) at −10 ℃ under N_2 for 72 h. Dr values (>19:1) were determined by ^1H NMR. [b] Isolated yield. [c] Determined by HPLC/SFC analysis on a chiral stationary phase. [d] N.R. = no reaction.

Table S5. Screening of the amount of catalyst[a]

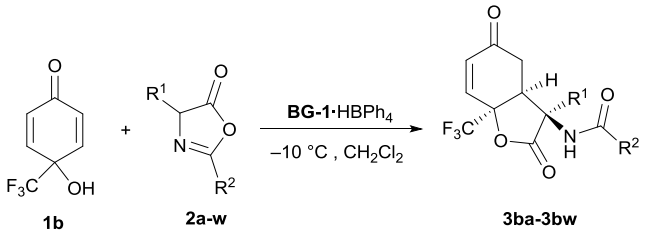


entry	cat (mol%)	yield (%)[b]	ee (%)[c]
1	10	75	99
2	5	80	99
3	2.5	98	98
4	1	50	97
5[d]	2.5	80	98
6[e]	2.5	94	98

[a] The reactions were carried out with **1b** (0.10 mmol), **2a** (0.20 mmol) and **BG-1•**$HBPh_4$ (10 mol%) in CH_2Cl_2 (1.0 mL) at −10 ℃ under N_2 for 72 h. Dr values (>19:1) were determined by ^1H NMR. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] **2a** (0.12 mmol) was used. [e] **2a** (0.15 mmol) was used.

4. Substrate scope

Table S6. Substrate scope with azlactones **2**[a]



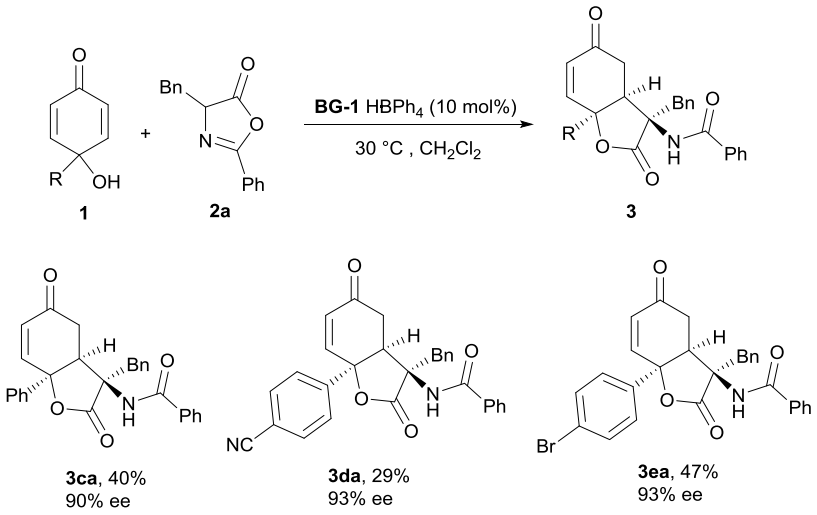
1b **2a-w** **3ba-3bw**

entry	cat. (mol%)	R^1, R^2	yield (%)[b]	ee (%)[c]
1	2.5	Bn, C_6H_5	**3ba**, 94	98
2	10	Phenethyl, C_6H_5	**3bb,** 75	99
3	10	Methyl, C_6H_5	**3bc,** 76	93
4	10	Isobutyl, C_6H_5	**3bd,** 77	99
5	10	2-(Methylthio)ethyl, C_6H_5	**3be,** 67	94
6	10	1H-indol-3-yl, C_6H_5	**3bf,** 91	94
7	5	4-chlorobenzyl, C_6H_5	**3bg,** 99	99
8	5	4-bromobenzyl, C_6H_5	**3bh,** 83	99
9	5	4-methylbenzyl, C_6H_5	**3bi,** 66	99
10	5	3-methylbenzyl, C_6H_5	**3bj,** 73	99
11	5	3-methoxybenzyl, C_6H_5	**3bk,** 64	98
12	5	Bn, 4-EtC_6H_4	**3bl,** 82	99
13	2.5	Bn, 4-MeC_6H_4	**3bm,** 87	99
14	2.5	Bn, 4-BrC_6H_4	**3bn,** 90	95
15	2.5	Bn, 4-ClC_6H_4	**3bo,** 86	97
16	5	Bn, 4-MeOC_6H_4	**3bp,** 74	99
17	5	Bn, 3,5-$(Me)_2C_6H_3$	**3bq,** 77	97

18	10	Bn, 2-naphthyl	**3br,** 73	99
19	10	Bn, 1-adamantyl	**3bs,** 72	99
20	10	Bn, 2-furyl	**3bt,** 72	99
21	10	Bn, 2-thienyl	**3bu,** 67	99
22	10	Bn, cyclopentyl	**3bv,** 57	99
23	10	Bn, cyclohexyl	**3bw,** 60	99

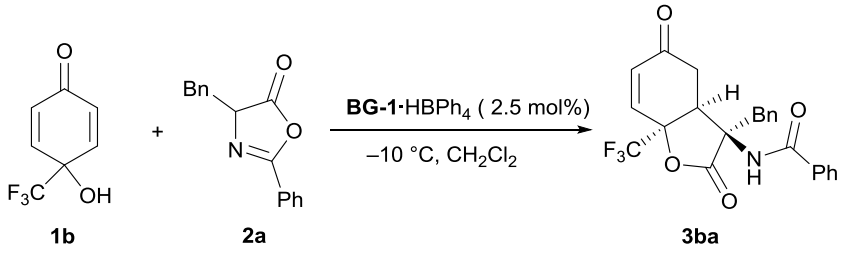
[a] Unless otherwise noted, the reactions were carried out **BG-1**•$HBPh_4$ (10 mol%), **1b** (0.10 mmol) and **2** (0.15 mmol) in CH_2Cl_2 (1.0 mL) at −10 ℃ for 72 h. Dr values (>19:1) were determined by ^1H NMR. [b] Isolated yield. [c] Determined by HPLC/SFC analysis on a chiral stationary phase.

Schem 2. Substrate scope with *p*-quinols[a]



[a] Unless otherwise noted, the reactions were carried out **BG-1**•$HBPh_4$ (10 mol%), **1** (0.10 mmol) and **2a** (0.15 mmol) in CH_2Cl_2 (1.0 mL) at 30 ℃ for 72 h. Dr values (>19:1) were determined by ^1H NMR. [b] Isolated yield. [c] Determined by SFC analysis on a chiral stationary phase.

5. Typical procedure for the asymmetric reaction



5.1. Representative experimental procedure for the asymmetricreaction of *p*-quinols with azlactones

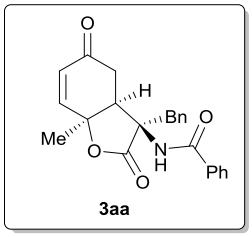
A dry tube was charged with **BG-1**•$HBPh_4$ (2.9 mg, 0.0025 mmol, 2.5 mol%) and **1b** (17.8 mg, 0.1 mmol). Under N_2 atmosphere, CH_2Cl_2 (1.0 mL) was added. The mixture was stirred at 30 ℃ for 30 min and then cooled to −10 ℃. Then azlactone **2a** (37.7 mg, 0.15 mmol) was added under stirring and the mixture continued stirring at −10 ℃ for 72 h. After completion, flash column chromatography provided the desired product **3ba** (petroleum ether/ethyl acetate = 4/1 as eluent). The product **3ba** was obtained in 94% yield (40.4 mg). The enantiomeric excess (ee) was determined by HPLC with Daicel Chiralcel **IB** (98% ee).

5.2. Typical experimental procedure for the scale-up reaction

A dry round-bottom flask was charged with **BG-1**•$HBPh_4$ (72.5 mg, 0.0625 mmol, 2.5 mol%) and **1b** (445.3 mg, 2.5 mmol). Under N_2 atmosphere, CH_2Cl_2 (25.0 mL) was added. The mixture was stirred at 30 ℃ for 30 min and then cooled to −10 ℃. Then azlactone **2a** (942.5 mg, 3.75 mmol) was added under stirring and the mixture continued stirring at −10 ℃ for 72 h. After completion, flash column chromatography provided the desired product **3ba** (petroleum ether/ethyl acetate = 4/1 as eluent). The product **3ba** was obtained in 92% yield (987.6 mg). The enantiomeric excess (ee) was determined by HPLC with Daicel Chiralcel **IB** (98% ee).

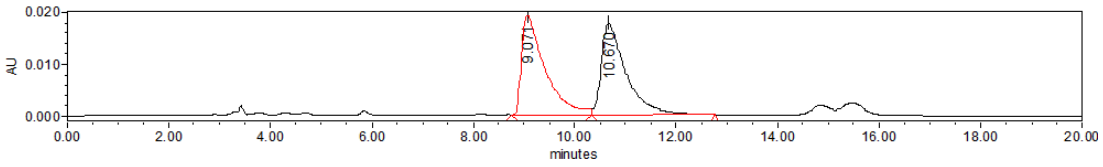
6. The analytical and spectral characterization data of the products

***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-7a-methyl-2,5-dioxo-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide**

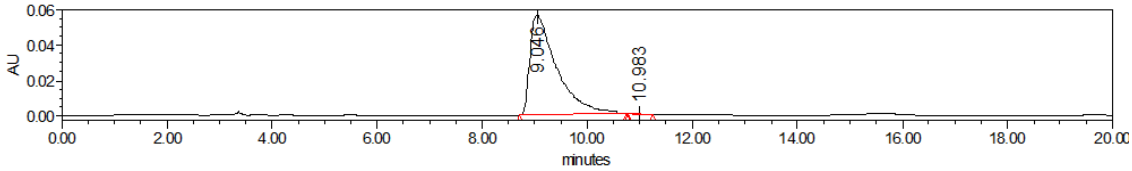


3aa

The compound **3aa** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1) to afford a white solid in 71% yield. **HPLC** (Daicel Chiralcel **IA**, *n*-hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t (major) = 9.05 min, t (minor) =10.98 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 98−100 ℃. $[\alpha]^{21}_D$ = –64.2 (*c*: 0.746, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.42 –7.36 (m, 4H), 7.35 – 7.29 (m, 2H), 7.28 –7.20 (m, 2H), 6.84 – 6.67 (m, 2H), 5.74 (d, *J* = 10.4 Hz, 1H), 3.35 – 3.23 (dd, *J* = 18.4 Hz, 13.2 Hz,2H), 3.05 (m, 1H), 2.67 –2.45 (m, 1H), 2.56 – 2.44 (m, 1H), 1.42 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.2, 173.4, 166.6, 148.3, 133.9, 132.9, 131.9, 130.5, 129.2, 128.5, 128.2, 127.8, 127.0, 79.3, 62.3, 47.3, 44.3, 34.0, 26.5. **IR** (neat) 3327, 1757, 1668, 1531, 1483, 1028 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{22}NO_4$ [(M+H$^+$)]** = 376.1543, Found 376.1546.

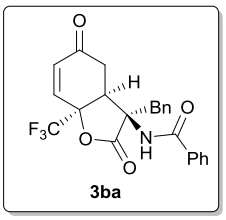


	Retention Time	Area	% Area
1	9.071	611277	50.59
2	10.670	596947	49.41

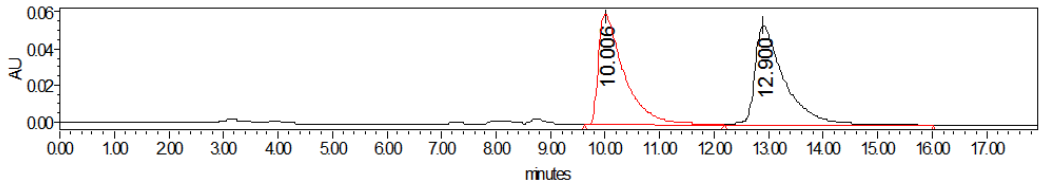


	Retention Time	Area	% Area
1	9.046	1980701	99.91
2	10.983	1870	0.09

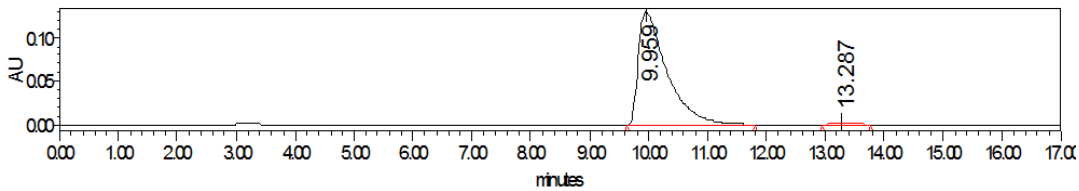
_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide



The compound **3ba** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 94% yield. **HPLC** (Daicel Chiralcel **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 9.96 min, t (minor) = 13.29 min, ee = 98%. dr >19:1 (by ^{1}H NMR). mp 190—192 ℃. $[\alpha]^{19}_{D}$ = +37.4 (*c*: 0.882, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53—7.42 (m, 6H), 7.41—7.35 (m, 2H), 7.31 (d, *J* = 6.9 Hz, 2H), 6.81 (d, *J* = 10.5 Hz, 1H), 6.37 (s, 1H), 6.21 (d, *J* = 10.4 Hz, 1H), 3.55 (d, *J* = 8.3 Hz, 1H), 3.32—3.20 (m, 2H), 2.67—2.57 (m, 1H), 2.20 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.2, 171.4, 166.4, 137.1, 134.0, 132.7, 132.6, 129.9, 129.9, 129.0, 128.9, 126.9, 126.9, 123.4 (q, *J* = 284.8 Hz, 1C), 77.9 (q, *J*= 32.3 Hz, 1C), 60.6, 45.1, 41.2, 34.2. **^{19}F{1H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (neat) 3339, 1803, 1663, 1393, 1196, 1175 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{19}F_3NO_4$ [(M+H^{+})]** = 430.1261, Found 430.1264.

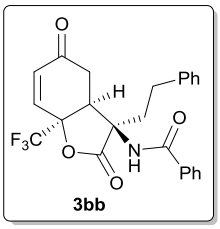


	Retention Time	Area	% Area
1	10.006	1963562	49.28
2	12.900	2020570	50.72



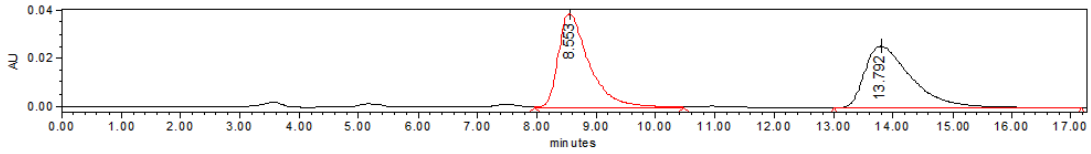
	Retention Time	Area	% Area
1	9.959	4352550	98.92
2	13.287	47405	1.08

_N_-[(3_R_,3a_S_,7a_S_)-2,5-Dioxo-3-phenethyl-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide

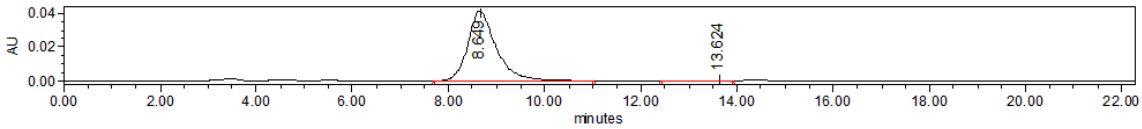


3bb

The compound **3bb** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 75% yield. **HPLC** (Daicel Chiralcel **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 8.65 min, t (minor) = 13.62 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 72—74 ℃. $[\alpha]^{18}_{D}$ = +106.1 (*c*: 0.390, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.38 –7.33 (m, 2H), 7.33 – 7.25 (m, 5H), 7.20 – 7.14 (m, 2H), 6.80 (d, *J* = 12 Hz, 1H), 6.35 (s, 1H), 6.30 (d, *J*= 10.5 Hz, 1H), 3.36 (m, 1H), 2.99 (m, 1H), 2.85 (m, 1H), 2.75 (m, 1H), 2.63 (m, 1H), 2.39 (m, 1H), 2.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.1, 171.6, 167.1, 139.6, 136.4, 134.1, 132.4, 131.5, 129.3, 128.5, 128.5, 127.0, 127.0, 123.7(q, *J* = 287.9, 1C), 77.6(q, *J* = 32.3, 1C), 61.8, 41.2, 39.8, 33.9, 29.7. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.2. **IR** (thin film, NaCl) 3298, 1799, 1691, 1647, 1528, 1309, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{24}H_{21}F_3NO_4$ [(M+H^{+})]** = 444.1417. Found 444.1408.

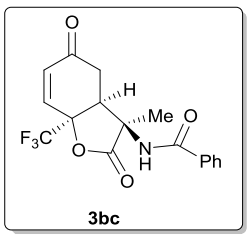


	Retention Time	Area	% Area
1	8.553	1407084	50.25
2	13.792	1393109	49.75



	Retention Time	Area	% Area
1	8.649	1694151	99.59
2	13.624	7013	0.41

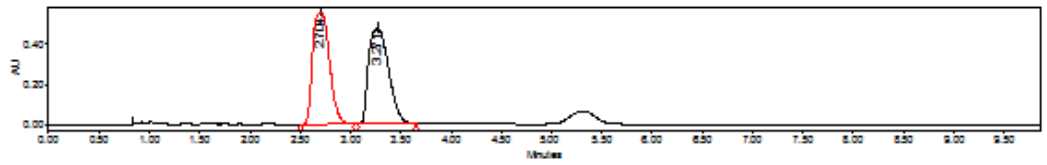
_N_-[(3_R_,3a_S_,7a_S_)-3-Methyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide



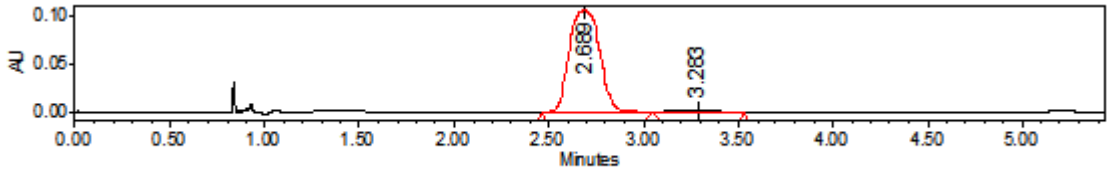
3bc

The compound **3bc** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1) to afford a white solid in 76% yield. **SFC** (Daicel Chiralcel **IA**, scCO$_2$/MeOH = 90/10, 1.5 mL/min, λ = 254nm), t (major) = 2.69 min, t (minor) = 3.28 min, ee = 93%. dr >19:1 (by ^{1}H NMR). mp 124—126 ℃. $[\alpha]^{23}$ = +113.0 (*c*: 0.554, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.7

Hz, 2H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.70 (s, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 3.22 – 3.15 (m, 1H), 2.79 – 2.60 (m, 2H), 1.62 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 172.4, 167.5, 136.5, 134.2, 132.5, 132.0, 128.7, 127.2, 123.5 (q, *J* = 283.8 Hz, 1C), 77.7 (q, *J* = 32.3 Hz, 1C), 58.5, 43.5, 33.7, 26.4. **$^{19}F\{^{1}H\}$ NMR** (376 MHz, $CDCl_3$) δ −80.2. **IR** (thin film, NaCl) 3303, 1802, 1692, 1648, 1530, 1316, 1182cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{17}H_{14}F_3NO_4$ [(M+H$^+$)]** = 354.0948. Found 354.0942.

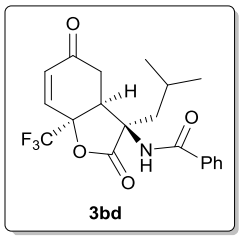


	Retention Time	Area	% Area
1	2.704	6495464	49.49
2	3.271	6628572	50.51



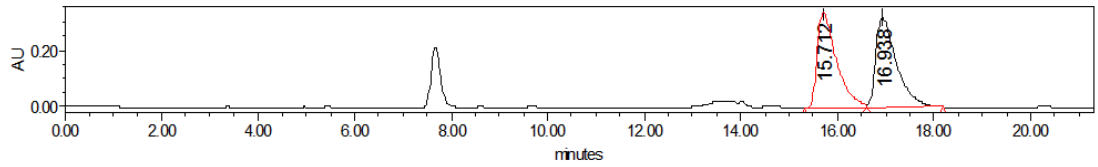
	Retention Time	Area	% Area
1	2.689	1197646	96.48
2	3.283	43697	3.52

***N*-[(3*R*,3a*S*,7a*S*)-3-Isobutyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide**

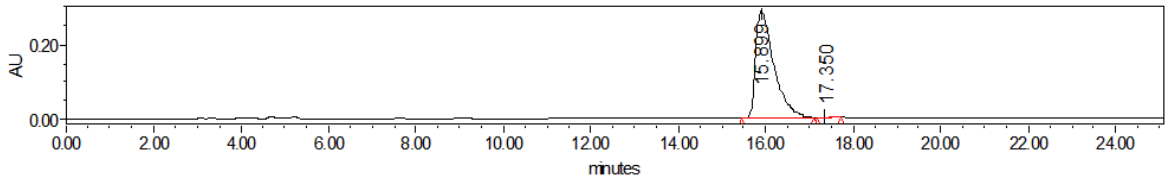


3bd

The compound **3bd** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 77% yield. **HPLC** (Daicel Chiralcel. **IA**, *n*-hexane ^{i}PrOH = 98/2, 1.0 mL/min, λ = 254nm), t (major) = 15.90 min, t (minor) = 17.66 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 144—146 ℃. $[\alpha]^{16}$ = +413.3 (*c*: 0.620, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.52 – 7.47 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.37 (s, 1H), 6.28 (d, *J* = 10.5 Hz, 1H), 3.41 – 3.30 (m, 1H), 2.73 (m, 1H), 2.65 (m, 1H), 1.86 (m, 3H), 1.09 (d, *J* = 6.1 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 193.2, 171.7, 167.1, 136.8, 134.0, 132.5, 132.1, 128.8, 127.1, 123.7(q, *J* = 284.8, 1C), 77.7 (q, *J* = 32.3, 1C), 61.5, 46.9, 40.4, 33.9, 24.6, 24.5, 23.7. **^{19}F NMR$\{^{1}H\}$** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3335, 1811, 1695, 1655, 1528, 1315, 1188, 1080 cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{20}H_{21}F_3NO_4$ [(M+H$^+$)]** = 396.1417. Found 396.1420.

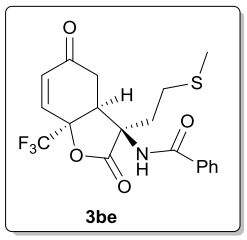


	Retention Time	Area	% Area
1	15.712	9345954	49.61
2	16.938	9492989	50.39

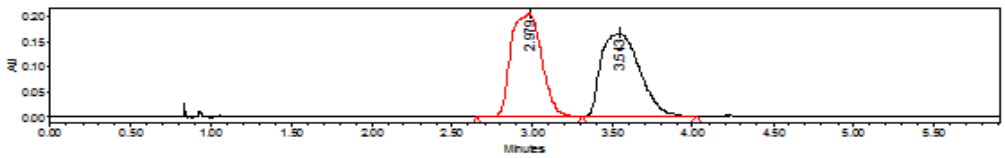


	Retention Time	Area	% Area
1	15.899	8375510	99.75
2	17.350	21355	0.25

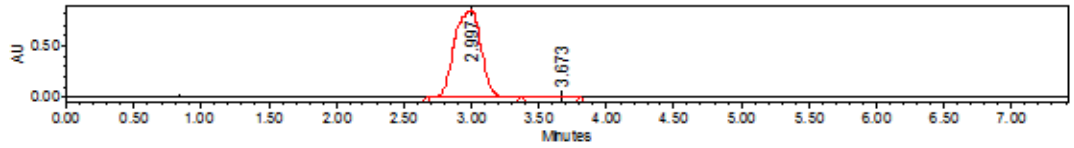
_N_-{(3_R_,3a_S_,7a_S_)-3-[2-(Methylthio)ethyl]-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl}benzamide



The compound **3be** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 67% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 254nm), t (major) = 3.00 min, t (minor) = 3.67 min, ee = 94%. dr >19:1 (by ^{1}H NMR). mp 40—42 ℃. $[\alpha]^{16}$ = +124.5 (*c*: 0.430, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.72 – 7.64 (m, 2H), 7.56 – 7.47 (m, 1H), 7.40 (td, *J* = 7.7, 1.5 Hz, 2H), 6.79 (d, *J* = 10.5 Hz, 1H), 6.30 (dd, *J* = 10.5, 1.4 Hz, 1H), 3.28 – 3.22 (m, 1H), 2.95 – 2.86 (m, 1H), 2.80 – 2.64 (m, 3H), 2.37 – 2.28 (m, 1H), 2.20 (d, *J* = 1.5 Hz, 3H), 2.16 – 2.08 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 192.8, 171.4, 167.2, 136.3, 134.2, 132.6, 131.6, 128.8, 127.3, 123.6 (q, *J* = 284.8, 1C), 77.6 (q, *J* = 32.3, 1C), 61.7, 42.1, 36.8, 34.1, 28.1, 15.7, 15.7. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.2. **IR** (thin film, NaCl) 3319, 1798, 1692, 1660, 1526, 1316, 1185, 1090cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{19}H_{18}F_3NO_4S$ [(M+H$^+$)]**= 414.0981. Found 414.0993.

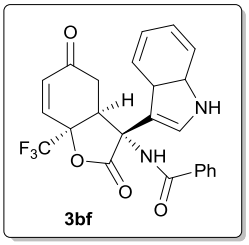


	Retention Time	Area	% Area
1	2.979	2733262	49.43
2	3.543	2795885	50.57

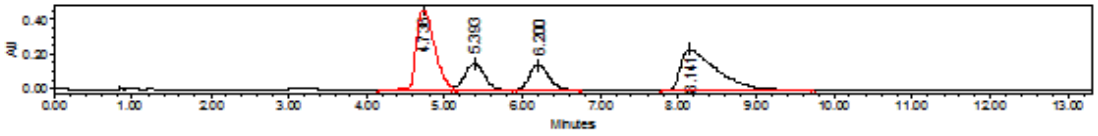


	Retention Time	Area	% Area
1	2.997	11643832	96.99
2	3.673	361544	3.01

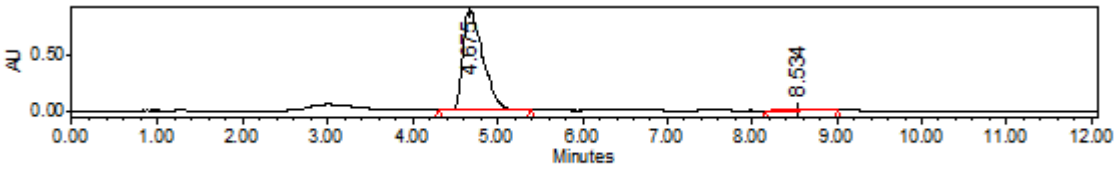
_N_-((3_R_,3a_S_,7a_S_)-3-(3a,7a-Dihydro-1H-indol-3-yl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl)benzamide



The compound **3bf** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1) to afford a white solid in 91% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 85/15, 1.5 mL/min, λ = 254nm), t (major) = 4.68 min, t (minor) = 8.53 min, ee = 94%. dr >19:1 (by ^{1}H NMR). mp 86—88 ℃. $[\alpha]^{26}$ = +130.3(*c*: 0.122, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.61 – 7.58 (m, 1H), 7.46 – 7.38 (m, 4H), 7.30 – 7.24 (s, 2H), 7.20 – 7.13 (m, 2H), 6.85 (s, 1H), 6.74 (d, *J* = 10.5 Hz, 1H), 6.16 (d, *J* = 10.5 Hz, 1H), 3.61 – 3.50 (m, 1H), 3.36 – 3.25 (m, 1H), 2.58 – 2.46 (m, 8.4 Hz, 1H), 2.31 – 2.21 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 171.8, 166.5, 137.0, 136.4, 134.1, 132.5, 131.7, 128.7, 127.1, 124.1, 123.3, 121.4 (q, *J* = 245.4, 1C), 121.1, 117.5, 112.3, 106.6, 77.8 (q, *J* = 32.3, 1C), 61.4, 41.9, 35.4, 34.4. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.1. **IR** (thin film, NaCl) 3319, 1731, 1680, 1482, 1466, 1245, 1178, 1138cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{24}H_{19}F_3N_2O_4$ [(M+H$^+$)]** = 457.1370. Found 457.1370.



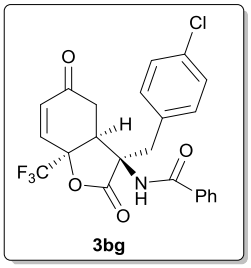
	Retention Time	Area	% Area
1	4.736	7438613	37.51
2	5.393	2569901	12.96
3	6.200	2459327	12.40
4	8.141	7361906	37.13



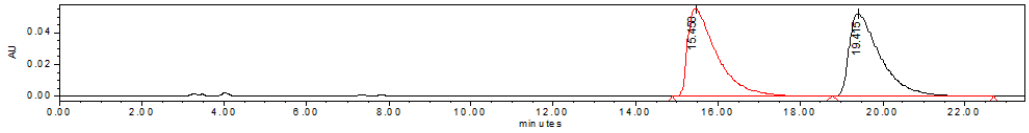
	Retention Time	Area	% Area
1	4.675	14652433	96.85

2	8.534	476948	3.15

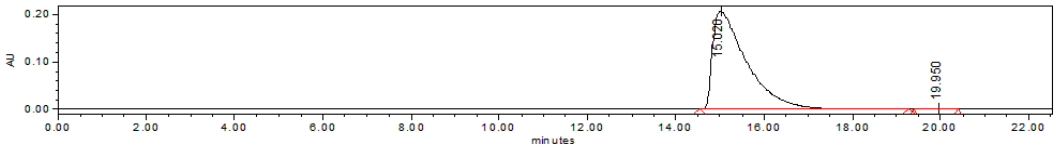
***N*-[(3*R*,3a*S*,7a*S*)-3-(4-Chlorobenzyl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide**



The compound **3bg** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 99% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 15.02 min, t (minor) = 19.95 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 196—198 ℃. $[\alpha]^{14}_{D}$ = —156.9 (*c*: 0.378, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 7.29 – 7.24 (m, 4H), 6.91 (d, *J* = 10.5 Hz, 1H), 6.73 (s, 1H), 6.17 (d, *J* = 10.5 Hz, 1H), 3.45 (dt, *J* = 8.1, 1.6 Hz, 1H), 3.24 (q, *J* = 13.7 Hz, 2H), 2.69 (dd, *J* = 18.0, 8.0 Hz, 1H), 2.55 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 171.3, 167.1, 137.4, 134.9, 134.1, 132.5, 131.9, 131.7, 131.2, 129.7, 128.7, 127.0, 123.2 (q, *J* = 280.0 Hz, 1C), 78.0 (q, *J* = 32.3 Hz, 1C), 61.5, 43.3, 40.3, 33.8. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -80.0. **IR** (thin film, NaCl) 3302, 1803, 1691, 1655, 1535, 1491, 1193 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{18}ClF_3NO_4$ [(M+H^{+})]** = 464.0871, 466.0841 Found 464.0876, 466.0856.

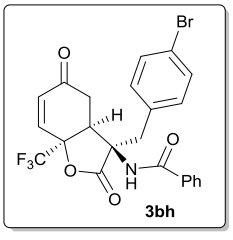


	Retention Time	Area	% Area
1	15.458	2757713	50.16
2	19.415	2740452	49.84



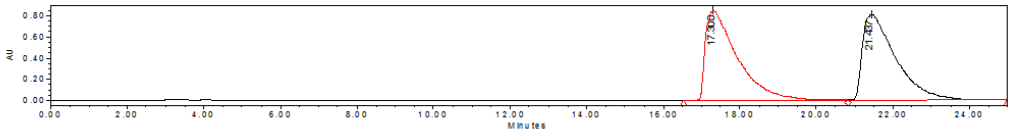
	Retention Time	Area	% Area
1	15.020	11215563	99.63
2	19.950	41824	0.37

***N*-[(3*R*,3a*S*,7a*S*)-3-(4-Bromobenzyl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide**

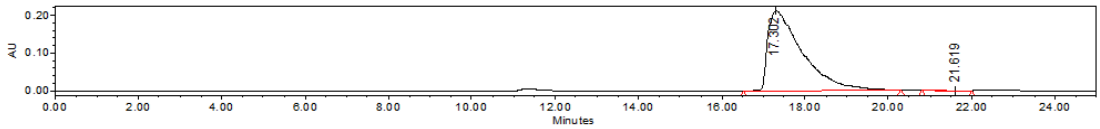


The compound **3bh** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 83% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) =17.30 min, t (minor) =21.62 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 124—126 ℃. $[\alpha]^{14}_{D}$ = —423.5 (*c*: 0.370, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.36 (m, 3H), 7.31 – 7.17 (m,

4H), 6.99 – 6.62 (m, 2H), 6.17 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.45 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.32 – 3.16 (m, 2H), 2.76 – 2.48 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.5, 171.3, 167.3, 137.4, 134.1, 132.6, 132.4, 132.2, 131.9, 131.8, 128.7, 127.0, 123.2 (q, *J* = 283.8 Hz, 1C), 122.9, 77.9 (q, *J* = 32.3 Hz, 1C), 61.7, 43.0, 40.0, 33.7. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –79.9. **IR** (thin film, NaCl) 3298, 1800, 1691, 1605, 1524, 1491, 1196 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{18}BrF_3NO_4$ [(M+H$^+$)]** = 508.0366, 510.0345. Found 508.0372, 510.0351.

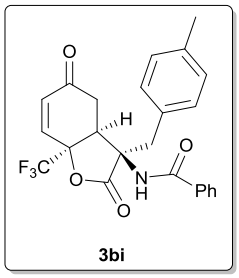


	Retention Time	Area	% Area
1	17.300	49290421	50.10
2	21.437	49090907	49.90



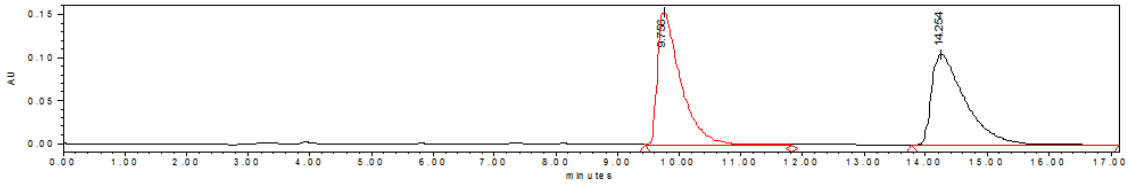
	Retention Time	Area	% Area
1	17.302	12111540	99.86
2	21.619	16874	0.14

_N_-[(3_R_,3a_S_,7a_S_)-3-(4-Methylbenzyl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide

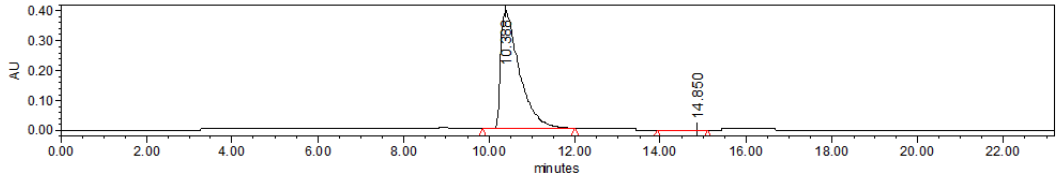


3bi

The compound **3bi** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 66% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 10.39 min, t (minor) = 14.85 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 89—91 ℃. $[\alpha]^{18}_{D}$ = —29.3 (*c*: 0.478, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 6.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.77 (m, 1H), 6.45 (s, 1H), 6.20 (d, *J* = 10.5 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 3.21 (q, *J* = 13.8 Hz, 2H), 2.69 – 2.54 (m, 1H), 2.40 (s, 3H), 2.20 (d, *J* = 18.0 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.3, 171.5, 166.4, 138.9, 137.2, 134.0, 132.5, 131.9, 130.6, 129.8, 129.5, 128.9, 127.0, 123.5 (q, *J* = 283.8 Hz, 1C), 77.9 (q, *J* = 32.3 Hz, 1C), 60.5, 44.8, 41.3, 34.2, 21.2.**^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –80.0. **IR** (thin film, NaCl) 3302, 1800, 1691, 1655, 1528, 1182 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{24}H_{21}F_3NO_4$ [(M+H$^+$)]** = 444.1417, Found 444.1422.

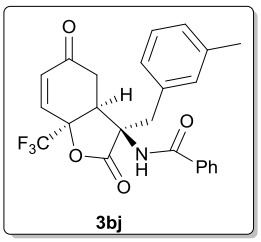


	Retention Time	Area	% Area
1	9.756	4062084	50.11
2	14.254	4044101	49.89

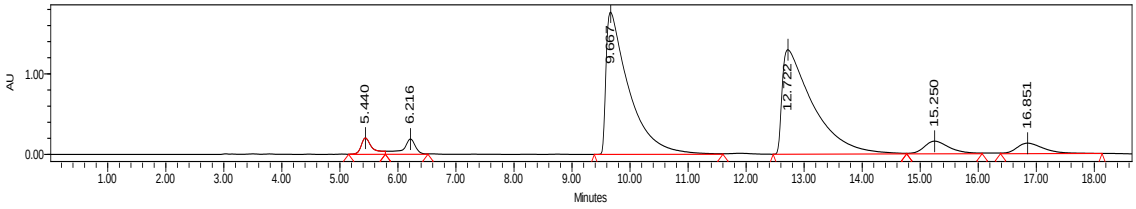


	Retention Time	Area	% Area
1	10.388	12070710	99.99
2	14.850	639	0.01

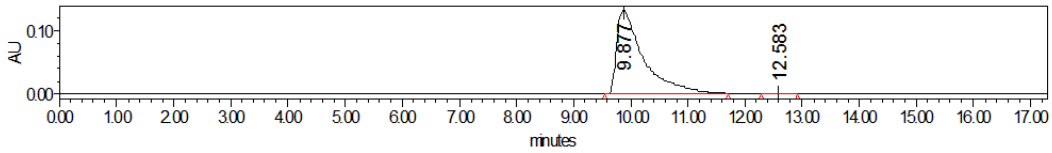
***N*-[(3*R*,3a*S*,7a*S*)-3-(3-Methylbenzyl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide**



The compound **3bj** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 73% yield. **HPLC** (Daicel Chiralcel. **IA**, *n*-hexane/^{i}PrOH = 90/10, 1.0 mL/min, λ = 254 nm), t (major) = 9.88 min, t (minor) = 12.58 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 185 −187 ℃. $[\alpha]^{15}_{D}$ = −53.3 (*c*: 0.242, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.39 – 7.31 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.82 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.48 (s, 1H), 6.19 (d, *J* = 10.5 Hz, 1H), 3.55 (dt, *J* = 8.4, 1.6 Hz, 1H), 3.21 (q, *J* = 13.7 Hz, 2H), 2.67 – 2.57 (m, 1H), 2.40 (s, 3H), 2.21 (d, *J* = 18.0 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.3, 171.5, 166.3, 139.8, 137.2, 134.0, 132.7, 132.5, 131.9, 130.6, 129.7, 129.7, 128.9, 127.0, 126.9, 123.5 (q, *J* = 277.8 Hz, 1C), 77.9 (q, *J* = 32.3 Hz, 1C), 60.5, 45.2, 41.4, 34.2, 21.5, 21.5. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –80.0. **IR** (thin film, NaCl) 3302, 1800, 1688, 1659, 1528, 1196 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{24}H_{21}F_3NO_4$ [(M+H^{+})]** = 444.1417, Found 444.1417.

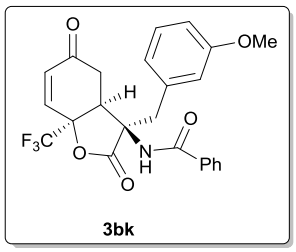


	Retention Time	Area	% Area
1	5.440	2725789	2.46
2	6.216	2886640	2.60
3	9.667	48291641	43.54
4	12.722	47940243	43.22
5	15.250	4834777	4.36
6	16.851	4238692	3.82

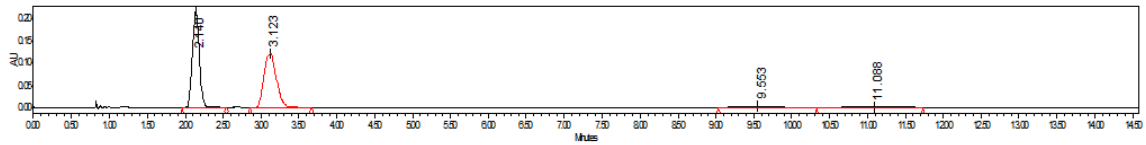


	Retention Time	Area	% Area
1	9.877	4321352	99.95
2	12.583	1960	0.05

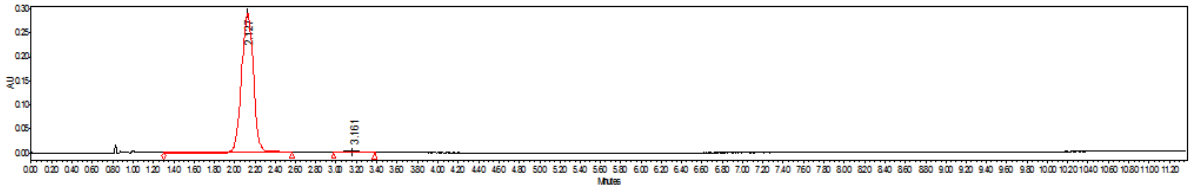
_N_-[(3_R_,3a_S_,7a_S_)-3-(3-Methoxybenzyl)-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide



The compound **3bk** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 64% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 80/20, 1.5 mL/min, λ = 254 nm), t (major) = 2.13 min, t (minor) = 3.16 min, ee = 98%. dr >19:1 (by ^{1}H NMR). mp 73—75 ℃. $[\alpha]^{15}_D$ = −31.7 (*c*: 0.334, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 3H), 7.32 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 7.08 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.05 – 6.95 (m, 2H), 6.82 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.42 (s, 1H), 6.23 (d, *J* = 10.5 Hz, 1H), 3.78 (s, 3H), 3.53 (dt, *J* = 8.4, 1.6 Hz, 1H), 3.25 (d, *J* = 2.4 Hz, 2H), 2.72 – 2.57 (m, 1H), 2.23 (d, *J* = 18.0 Hz, 1H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.2, 166.4, 159.9, 137.1, 134.0, 133.3, 132.7, 130.0, 129.9, 129.8, 128.9, 123.6 (q, *J* = 236.3 Hz, 1C), 118.9, 118.5, 112.2, 77.9 (q, *J* = 32.3 Hz, 1C), 60.7, 45.0, 41.1.**^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3285, 1803, 1691, 1651, 1522, 1184 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{24}H_{21}F_3NO_5$ [(M+H$^+$)]** = 460.1366, Found 460.1368.

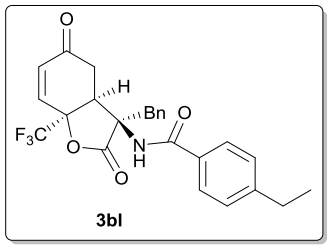


	Retention Time	Area	% Area
1	2.140	1407750	45.48
2	3.123	1394853	45.07
3	9.553	155557	5.03
4	11.088	136935	4.42

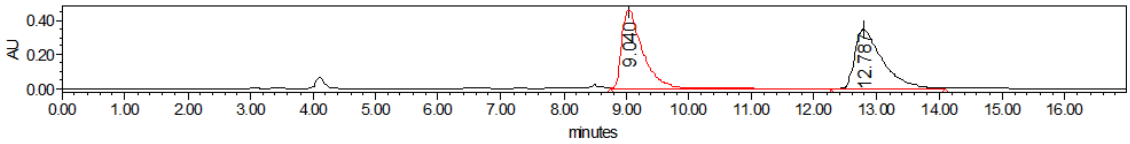


	Retention Time	Area	% Area
1	2.127	2371673	99.13
2	3.161	20832	0.87

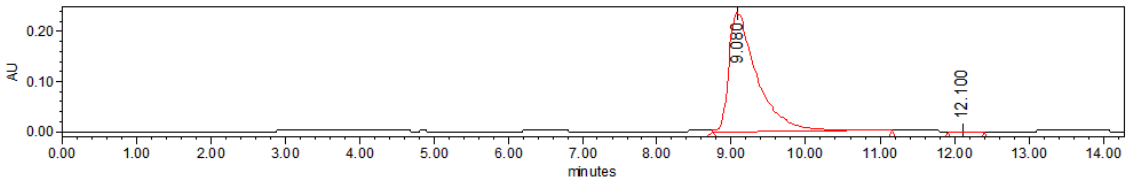
***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-4-ethylbenzamide**



The compound **3bl** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 82% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 9.08 min, t (minor) = 12.10 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 130—132 ℃. $[\alpha]^{17}_{D}$ = –20.5 (*c*: 0.650, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 5H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 6.78 (d, J = 10.5 Hz, 1H), 6.28 (s, 1H), 6.20 (d, J = 10.5 Hz, 1H), 3.59 – 3.49 (m, 1H), 3.35 – 3.18 (m, 2H), 2.74 – 2.50 (m, 3H), 2.15 (d, J = 18.0 Hz, 1H), 1.22 (t, J = 7.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 171.5, 166.6, 149.3, 137.2, 134.0, 132.9, 130.1, 129.7, 129.3, 128.8, 128.3, 127.1, 123.4(q, *J* = 284.8 HZ, 1C), 78.0(q, *J* = 32.3 HZ, 1C), 60.9, 44.7, 40.8, 28.8, 15.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ –80.1. **IR** (thin film, NaCl) 3294, 1796, 1680, 1531, 1315, 1188, 1088 cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{25}H_{23}F_3NO_4$ [(M+H^{+})]** = 458.1574. Found 458.1570.

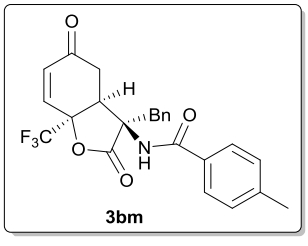


	Retention Time	Area	% Area
1	9.040	10649022	50.39
2	12.787	10483287	49.61



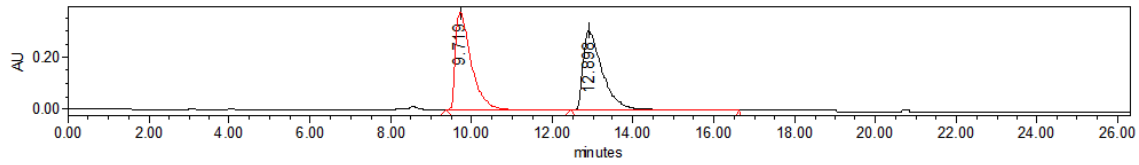
	Retention Time	Area	% Area
1	9.080	6225611	100.00
2	12.100	274	0.00

***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-4-methylbenzamide**

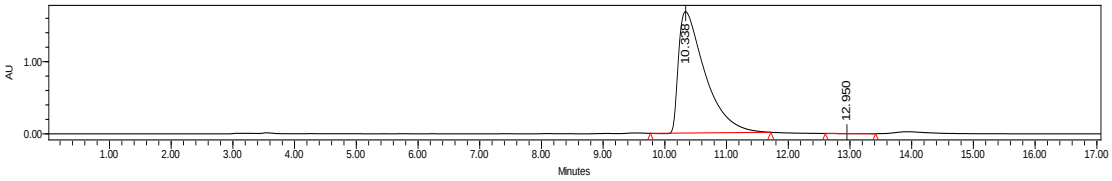


The compound **3bm** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 87% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 10.34 min, t (minor) = 12.95 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 165—167 ℃. $[\alpha]^{15}_{D}$ = –273.2 (*c*:

0.444, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.84 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.54 (s, 1H), 6.18 (d, *J* = 10.5 Hz, 1H), 3.53 (dt, *J* = 8.3, 1.6 Hz, 1H), 3.30 – 3.21 (m, 2H), 2.67–2.57 (m, 1H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 171.5, 166.6, 143.1, 137.3, 134.0, 132.9, 130.1, 129.7, 129.4, 129.1, 128.8, 127.0, 123.4 (q, *J* = 284.8 Hz, 1C), 77.9 (q, *J* = 32.3 Hz, 1C), 60.8, 44.7, 40.9, 34.0, 21.5. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3323, 1803, 1688, 1531, 1182 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{24}H_{21}F_3NO_4$ [(M+H$^+$)]** = 444.1237, Found 444.1237.

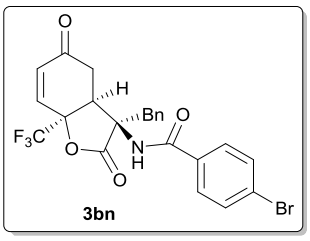


	Retention Time	Area	% Area
1	9.719	10445333	49.88
2	12.898	10495547	50.12

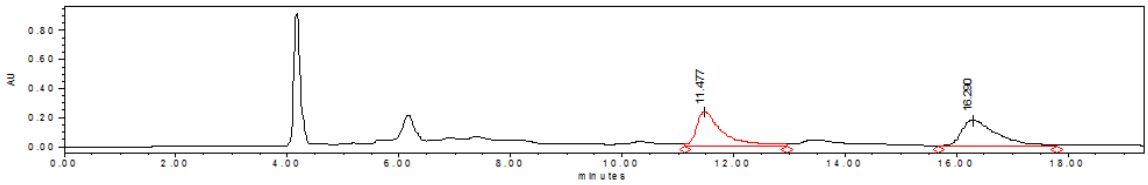


	Retention Time	Area	% Area
1	10.338	50309445	99.97
2	12.950	13465	0.03

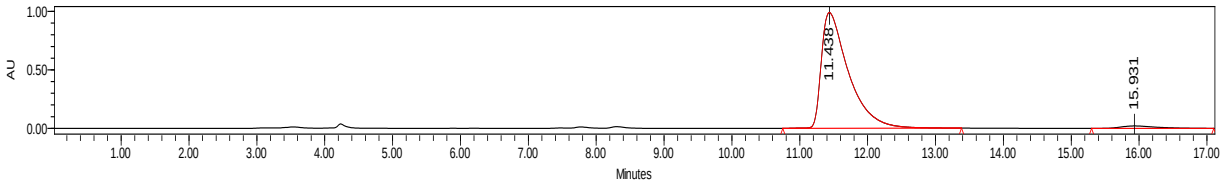
***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-4-bromobenzamide**



The compound **3bn** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 90% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 11.44 min, t (minor) = 15.93 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 118—120 ℃. $[\alpha]^{17}_D$ = −53.2 (*c*: 0.728, λ = 589 nm, in CH_2Cl_2).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 5H), 7.34 – 7.27 (m, 4H), 6.85 (dd, *J* = 10.5, 1.4 Hz, 1H), 6.58 (s, 1H), 6.20 (d, *J* = 10.5 Hz, 1H), 3.54 (dt, *J* = 8.3, 1.6 Hz, 1H), 3.26 (s, 2H), 2.66 (m, 1H), 2.34 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$) δ 193.5, 171.3, 165.9, 137.2, 134.1, 132.6, 132.1, 130.7, 130.1, 129.8, 128.9, 128.5, 127.4, 123.3 (q, *J* = 284.8 Hz, 1C), 78.0 (q, *J* = 32.3 Hz, 1C) , 61.1, 44.6, 40.9, 34.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3323, 1790, 1676, 1528, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{18}BrF_3NO_4$ [(M+H$^+$)]** = 508.0366, 510.0345. Found 508.0377, 510.0357.

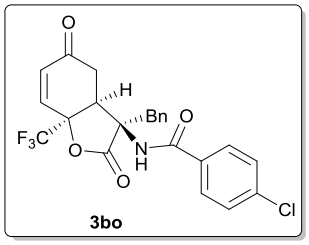


	Retention Time	Area	% Area
1	11.477	7552097	50.51
2	16.290	7398117	49.49

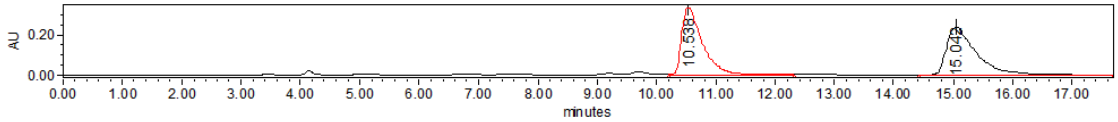


	Retention Time	Area	% Area
1	11.438	27498785	97.37
2	15.931	741658	2.63

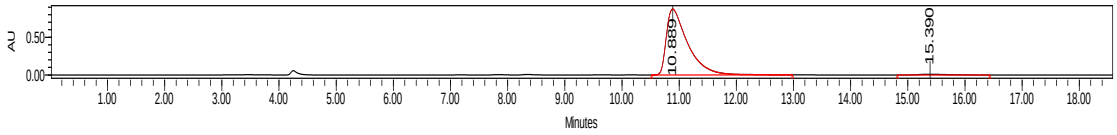
_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-4-chlorobenzamide



The compound **3bo** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 86% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 10.89 min, t (minor) = 15.39 min, ee = 97%. dr >19:1 (by ^{1}H NMR). mp 172−174 ℃. $[\alpha]^{17}_{D}$ = −31.1 (*c*: 0.626, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 5H), 7.35 – 7.27 (m, 4H), 6.82 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.46 (s, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 3.55 (dt, *J* = 8.3, 1.6 Hz, 1H), 3.26 (s, 2H), 2.65 (dd, *J* = 17.9, 8.3 Hz, 1H), 2.27 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$) δ 193.4, 171.3, 165.6, 138.9, 137.2, 134.1, 132.6, 130.3, 130.0, 129.9, 129.1, 129.0, 128.4, 123.3 (q, *J* = 284.8 Hz, 1C), 78.0 (q, *J* = 32.3 Hz, 1C), 60.9, 44.8, 41.1, 34.2. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3323, 1780, 1680, 1531, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{18}ClF_3NO_4$ [(M+H^{+})]** = 464.0871, 466.0841 Found 464.0879, 466.0850.

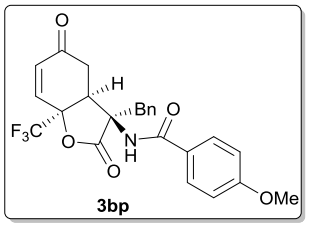


	Retention Time	Area	% Area
1	10.538	8047701	49.86
2	15.042	8092129	50.14

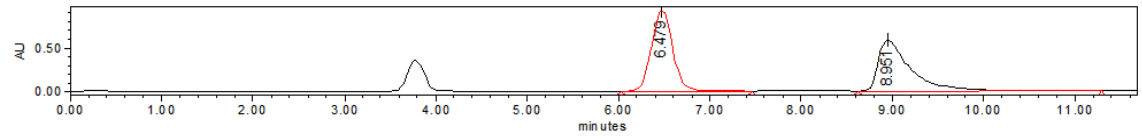


	Retention Time	Area	% Area
1	10.889	22688914	98.55
2	15.390	333792	1.45

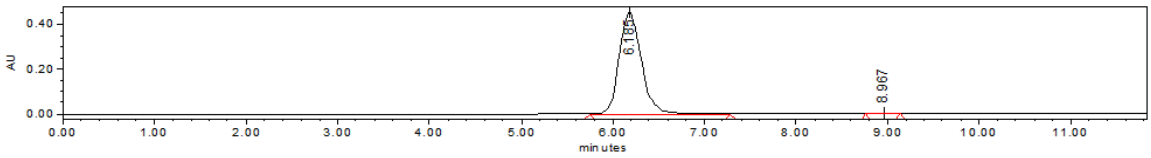
***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-4-methoxybenzamide**



The compound **3bp** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1) to afford a white solid in 74% yield. **HPLC** (Daicel Chiralcel. **ADH**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254nm), t (major) = 6.19 min, t (minor) = 8.97 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp decomposed at 183 ℃. $[\alpha]^{17}_{D}$ = −47.6 (*c*: 0.636, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 5H), 7.36 – 7.27 (m, 2H), 6.81 (dd, *J* = 9.0, 2.2 Hz, 2H), 6.45 (s, 1H), 6.19 (d, *J* = 10.5 Hz, 1H), 3.80 (s, 3H), 3.53 (dt, *J* = 8.3, 1.6 Hz, 1H), 3.26 (d, *J* = 2.6 Hz, 2H), 2.62 (m, 1H), 2.28 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 171.6, 166.0, 162.9, 137.2, 134.0, 132.9, 130.0, 129.7, 129.0, 128.8, 123.9,124.0, 123.0 (q, *J* = 282.8 Hz, 1C), 78.0 (q, *J* = 32.3 Hz, 1C), 60.7, 55.4, 55.4, 44.8, 41.0, 34.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (neat) 3408, 1796, 1684, 1606, 1495, 1306, 1261, 1182, 1028 cm^{-1}. **HRMS** (FTMS+cESI) caled for **$C_{24}H_{21}F_3NO_5$ [(M+H^{+})]** = 460.1366, Found 460.1369.

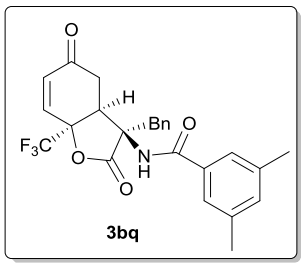


	Retention Time	Area	% Area
1	6.479	15092286	50.22
2	8.951	14959009	49.78

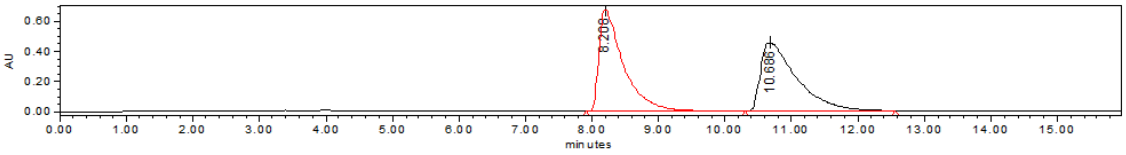


	Retention Time	Area	% Area
1	6.185	7670630	99.96
2	8.967	2840	0.04

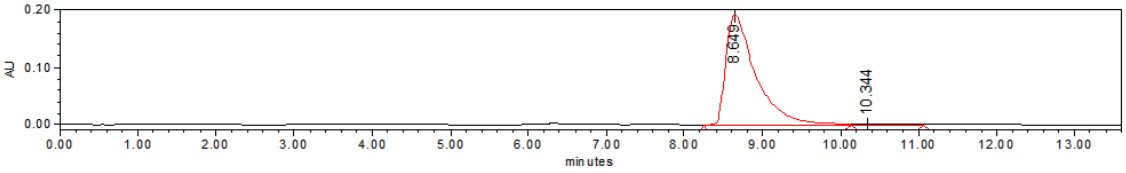
***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-3,5-dimethylbenzamide**



The compound **3bq** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 77% yield. **HPLC** (Daicel Chiralcel. **IB**, *n*-hexane/^{i}PrOH = 80/20, 1.0 mL/min, λ = 254 nm), t (major) = 8.65 min, t (minor) = 10.34 min, ee = 97%. dr >19:1 (by ^{1}H NMR). mp decomposed at 192 ℃. $[\alpha]^{17}_{D}$ = −239.7 (*c*: 0.292, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (tt, *J* = 4.2, 2.2 Hz, 3H), 7.33 – 7.28 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 3H), 6.78 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.29 (d, *J* = 3.0 Hz, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 3.53 (dt, *J* = 8.5, 1.6 Hz, 1H), 3.25 (s, 2H), 2.70 – 2.52 (m, 1H), 2.30 (s, 6H), 2.21 (d, *J* = 18.1 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.2, 171.5, 166.8, 138.6, 137.1, 134.2, 134.0, 132.8, 131.8, 130.0, 129.7, 129.0, 124.9, 123.4 (q, *J* = 284.8 Hz, 1C), 77.9 (q, *J* = 32.3 Hz, 1C), 60.8, 45.0, 40.9, 34.0, 21.2, 21.2. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3314, 1800, 1695, 1651, 1531, 1188 cm^{-1}.**HRMS** (FTMS+c ESI) caled for **$C_{25}H_{23}F_3NO_4$ [(M+H^{+})]** = 458.1574. Found 458.1567.

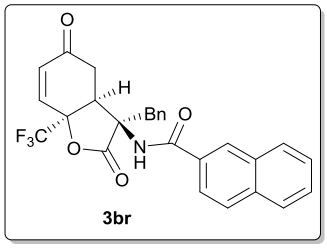


	Retention Time	Area	% Area
1	8.208	16977809	50.30
2	10.686	16776771	49.70



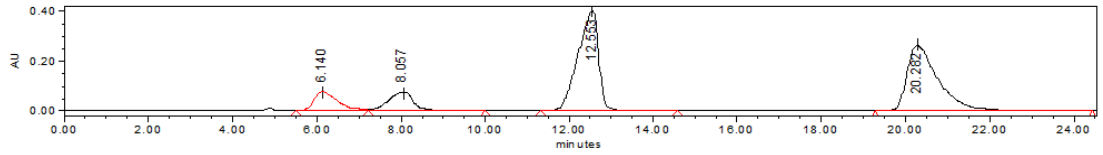
	Retention Time	Area	% Area
1	8.649	5070643	98.58
2	10.344	73110	1.42

_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]-2-naphthamide

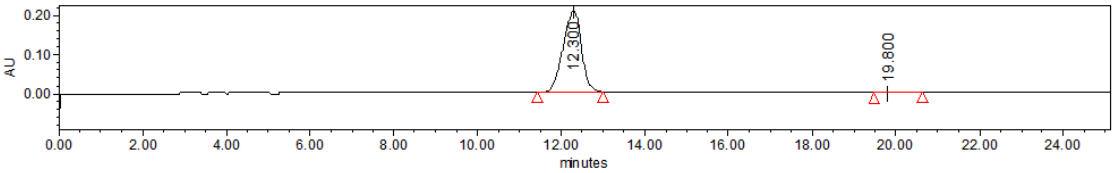


The compound **3br** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 73% yield. **HPLC** (Daicel Chiralcel. **ADH**, *n*-hexane/^{i}PrOH = 90/10, 1.0 mL/min, λ = 254 nm), t (major) = 12.30 min, t (minor) = 19.80 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 197—199 ℃. $[\alpha]^{16}_{D}$ = −142.8 (*c*: 0.430, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.8 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 3H), 7.60 – 7.41 (m, 6H), 7.33 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.82 (dd, *J* = 10.6, 1.3 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 3.56 (dt, *J* = 8.4, 1.6 Hz, 1H), 3.30 (d, *J* = 4.0 Hz, 2H), 2.60 –2.70 (m, 1H), 2.29 (d, *J* = 17.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ193.22, 171.46, 166.51, 137.10, 135.11, 134.09, 132.78, 132.45, 130.01, 129.88,

129.13, 129.01, 128.92, 128.31, 128.16, 127.79, 127.09, 123.5 (q, *J* = 283.8 Hz, 1C), 122.84, 77.9 (q, *J* = 32.3 Hz, 1C),60.75, 45.22, 41.29, 34.23. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.0. **IR** (thin film, NaCl) 3323, 1800, 1691, 1659, 1524, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) calcd for **$C_{27}H_{21}F_3NO_4$ [(M+H$^+$)]** = 480.1417. Found 480.1414.

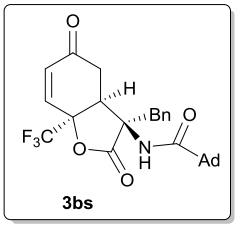


	Retention Time	Area	% Area
1	6.140	3202035	9.45
2	8.057	3280532	9.68
3	12.553	13698834	40.41
4	20.282	13718507	40.47

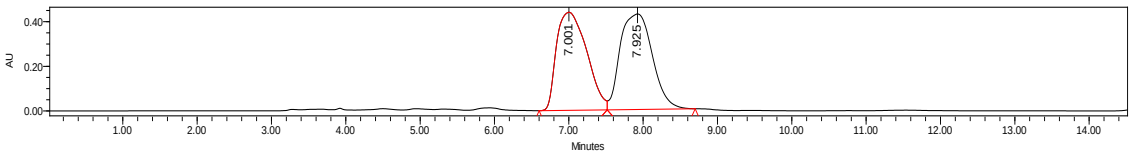


	Retention Time	Area	% Area
1	12.300	6405975	99.99
2	19.800	909	0.01

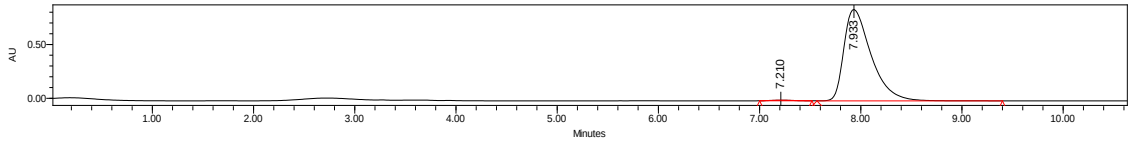
***N*-[(3*R*,3a*S*,7aS)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]adamantane-1-carboxamide**



The compound **3bs** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5/1) to afford a white solid in 72% yield. **HPLC** (Daicel Chiralcel. **ADH**, *n*-hexane/^{i}PrOH = 90/10, 1.0 mL/min, λ = 254 nm), t (major) = 7.93 min, t (minor) = 7.21 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 212−214 ℃. $[\alpha]^{14}_{D}$ = +386.8 (*c*: 0.386, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.9 Hz, 3H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 10.5 Hz, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 5.83 (s, 1H), 3.45 (d, *J* = 8.8 Hz, 1H), 3.23 – 3.06 (m, 2H), 2.60 – 2.48 (m, 1H), 2.00 (t, *J* = 8.8 Hz, 4H), 1.72 (s, 1H), 1.66 (t, *J* = 4.6 Hz, 9H), 1.62 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.1, 176.6, 171.7, 137.1, 133.8, 132.8, 129.8, 129.7, 128.9, 123.5 (q, *J* = 280.8 Hz, 1C), 77.6 (q, *J* = 32.3 Hz, 1C), 59.8, 45.4, 40.7, 40.5, 38.7, 36.2, 33.8, 27.8. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.1. **IR** (thin film, NaCl) 2913, 2855, 1798, 1695, 1510, 1184 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{27}H_{29}F_3NO_4$ [(M+H$^+$)]** = 488.2043, Found 488.2057.

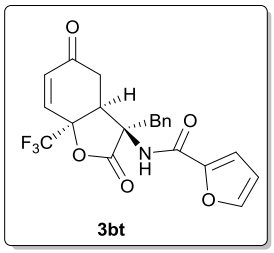


	Retention Time	Area	% Area
1	7.001	12406566	49.03
2	7.925	12898056	50.97

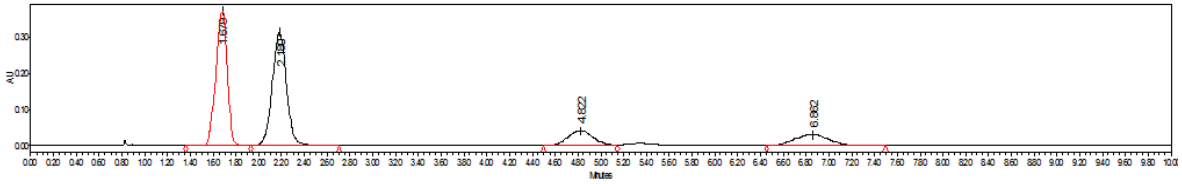


	Retention Time	Area	% Area
1	7.210	84047	0.53
2	7.933	15873706	99.47

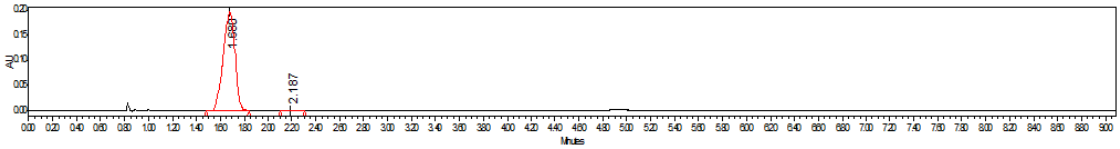
_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]furan-2-carboxamide



The compound **3bt** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1) to afford a white solid in 72% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 80/20, 1.5 mL/min, λ = 254 nm), t (major) = 1.68 min, t (minor) = 2.19 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 161 −163 ℃. $[\alpha]^{14}_D$ = −239.9 (*c*: 0.328, λ = 589 nm,in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 4H), 7.34 – 7.28 (m, 2H), 7.05 (d, *J* = 3.4 Hz, 1H), 6.78 (dd, *J* = 10.5, 1.4 Hz, 1H), 6.61 (d, *J* = 7.1 Hz, 1H), 6.48 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 3.53 (dt, *J* = 8.5, 1.6 Hz, 1H), 3.30 – 3.18 (m, 2H), 2.68 – 2.51 (m, 1H), 2.17 (d, *J* = 18.1 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.0, 171.3, 156.8, 145.7, 145.1, 137.0, 134.1, 132.5, 130.0, 129.8, 128.9, 123.4 (q, *J* = 284.8 Hz, 1C), 116.6, 112.7, 77.9 (q, *J* = 32.3 Hz, 1C),60.4, 45.1, 40.7, 33.9. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.1. **IR** (neat) 3258, 1803, 1695, 1645, 1531, 1514, 1177 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{21}H_{17}F_3NO_5$ [(M+H^+)]** = 420.1053, Found 420.1049.

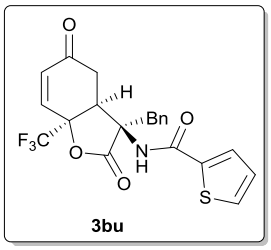


	Retention Time	Area	% Area
1	1.679	2591023	39.31
2	2.180	2720281	41.27
3	4.822	638708	9.69
4	6.862	640669	9.72

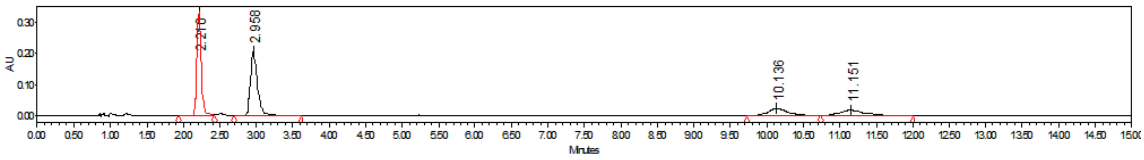


	Retention Time	Area	% Area
1	1.680	1314989	99.65
2	2.187	4645	0.35

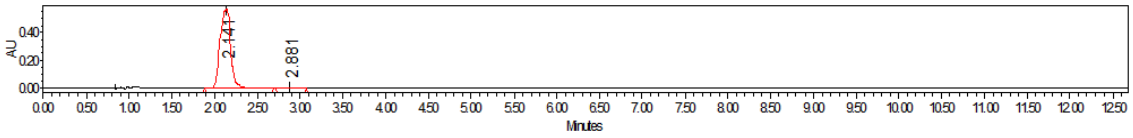
***N*-[(3*R*,3a*S*,7a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]thiophene-2-carboxamide**



The compound **3bu** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1) to afford a white solid in 67% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 254 nm), t (major) = 2.14 min, t (minor) = 2.88 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 165 −167 ℃. $[\alpha]^{14}_D$ = −270.3 (*c*: 0.212, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, MeOD) δ 7.68 (ddd, *J* = 5.4, 4.4, 1.2 Hz, 2H), 7.36 (qd, *J* = 7.8, 6.8, 3.6 Hz, 3H), 7.29 – 7.25 (m, 2H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.72 (dd, *J* = 10.5, 1.5 Hz, 1H), 6.16 (d, *J* = 10.5 Hz, 1H), 3.44 – 3.37 (m, 2H), 3.25 (d, *J* = 13.6 Hz, 1H), 2.93 – 2.73 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 195.3, 172.5, 163.1, 138.7, 137.8, 135.1, 135.0, 133.0, 132.1, 131.0, 130.0, 129.1, 128.9, 124.7 (q, *J* = 283.8 Hz, 1C), 79.2 (q, *J* = 32.3 Hz, 1C), 64.1, 43.2, 40.2, 33.9. **^{19}F{^{1}H} NMR** (376 MHz, MeOD) δ −81.4. **IR** (thin film, NaCl) 3277, 1807, 1699, 1637, 1539, 1180 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{21}H_{17}F_3NO_4S$ [(M+H$^+$)]** = 436.0825, Found 436.0821.

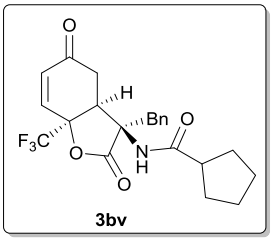


	Retention Time	Area	% Area
1	2.210	1434929	37.47
2	2.958	1420929	37.11
3	10.136	491144	12.83
4	11.151	482155	12.59

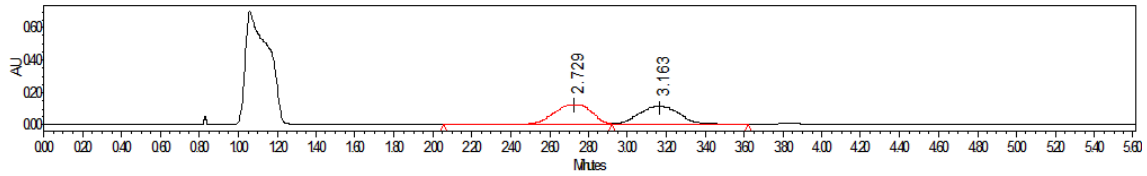


	Retention Time	Area	% Area
1	2.141	4848192	99.41
2	2.881	28867	0.59

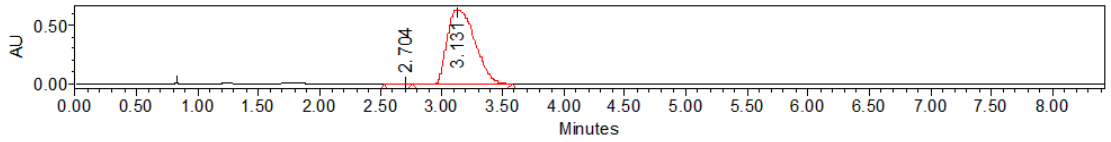
***N*-[(3*R*,3a*S*,3a*S*)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]cyclopentanecarboxamide**



The compound **3bv** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5/1) to afford a white solid in 57% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 254 nm), t (major) = 3.13 min, t (minor) = 2.70 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 175—177 ℃. $[\alpha]^{18}_D$ = +36.4 (*c*: 0.294, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.47 – 7.38 (m, 3H), 7.26 – 7.22 (m, 2H), 6.77 (d, *J* = 10.5 Hz, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 5.79 (s, 1H), 3.43 (d, *J* = 8.3 Hz, 1H), 3.15 (q, *J* = 13.7 Hz, 2H), 2.65 – 5.54 (m, 1H), 2.39 (q, *J* = 7.8 Hz, 1H), 2.19 (d, *J* = 18.0 Hz, 1H), 1.74 – 1.45 (m, 8H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 175.1, 171.6, 137.4, 133.9, 132.8, 130.0, 129.7, 128.8, 123.4 (q, *J* = 284.8 Hz, 1C), 77.8 (q, *J* = 32.3 Hz, 1C), 60.5, 44.9, 40.4, 33.9, 30.2, 29.9, 25.9, 25.7. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.1. **IR** (thin film, NaCl) 3265, 1802, 1695, 1659, 1533, 1513, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{22}H_{23}F_3NO_4$ [(M+H$^+$)]** = 422.1574, Found 422.1581.

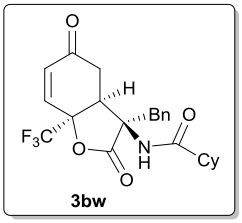


	Retention Time	Area	% Area
1	2.729	1834435	50.91
2	3.163	1768997	49.09



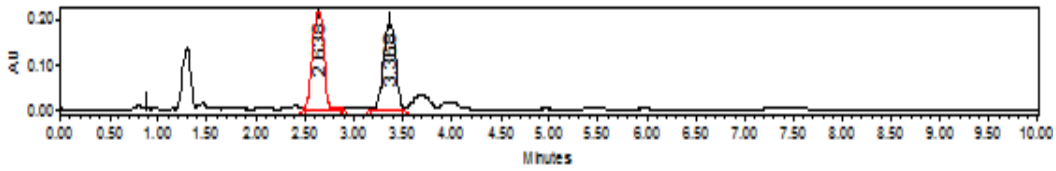
	Retention Time	Area	% Area
1	2.704	5549	0.06
2	3.131	9991571	99.94

_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-(trifluoromethyl)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]cyclohexanecarboxamide

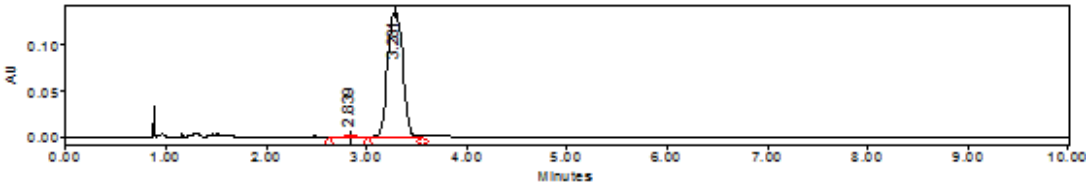


The compound **3bw** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 60% yield. **SFC** (Daicel Chiralcel **IB**, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 254 nm), t (major) = 3.28 min, t (minor) = 2.84 min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp 170—172 ℃. $[\alpha]^{22}_D$ = −106.1 (*c*: 0.130, λ = 405 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.26 – 7.22 (m, 2H), 6.76 (dd, *J* = 10.5, 1.3 Hz, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 5.72 (s, 1H), 3.44 (dt, *J* = 8.5, 1.6 Hz, 1H), 3.19 – 3.09 (m, 2H), 2.62 – 2.52 (m, 1H), 2.12 (d, *J* = 18.1 Hz, 1H), 1.81 – 1.63 (m, 5H), 1.33 – 1.10 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 174.7, 171.5, 137.3, 133.9, 132.7, 129.9, 129.7, 128.8, 123.4 (q, *J* =

283.8 Hz, 1C), 77.7 (q, *J* = 32.3 Hz, 1C), 60.2, 45.1, 44.3, 40.4, 33.9, 29.2, 28.9, 25.5, 25.4. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ −80.1. **IR** (thin film, NaCl) 3285, 1794, 1692, 1651, 1535, 1510, 1190 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{25}F_3NO_4$ [(M+H$^+$)]** = 436.1730, Found 436.1737.

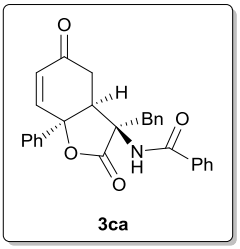


	Retention Time	Area	% Area
1	2.638	1730469	50.35
2	3.368	1706405	49.65



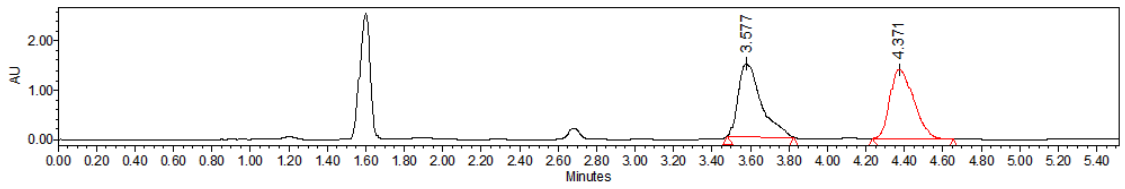
	Retention Time	Area	% Area
1	2.839	4963	0.35
2	3.281	1411842	99.65

_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-2,5-dioxo-7a-phenyl-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl] benzamide



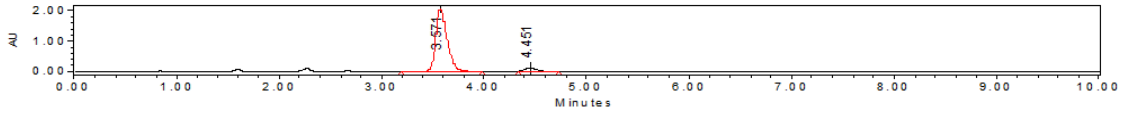
3ca

The compound **3ca** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1) to afford a white solid in 40% yield. **SFC** (Daicel Chiralcel **IB**, $scCO_2$/MeOH = 80/20, 1.5 mL/min, λ = 254nm), t (major) = 3.57 min, t (minor) = 4.45 min, ee = 90%. dr >19:1 (by ^{1}H NMR). mp 128—130 ℃. $[\alpha]^{22}_D$ = −129.5 (*c*: 0.244, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, CDCl3) δ 7.61 – 7.57 (m, 2H), 7.54 – 7.38 (m, 8H), 7.3 – 7.25 (m, 3H), 7.07 – 7.01 (m, 2H), 6.73 (d, *J* = 10.1 Hz, 1H), 6.36 (d, *J* = 3.3 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 3.69 (t, *J* = 7.2 Hz, 1H), 3.41 (d, *J* = 13.8 Hz, 1H), 2.91 (d, *J* = 13.8 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.51 – 2.35 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, CDCl3) δ 196.2, 173.6, 167.0, 145.0, 141.0, 133.9, 133.0, 132.3, 130.2, 129.4, 129.0, 128.8, 128.8, 127.9, 127.0, 124.8, 82.2, 64.2, 49.8, 41.9, 35.1. **IR** (thin film, NaCl) 3298, 1778, 1688, 1659, 1535, 1493, 1246 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{28}H_{24}NO_4H$ [(M+H$^+$)]** = 438.1700, Found 438.1702.



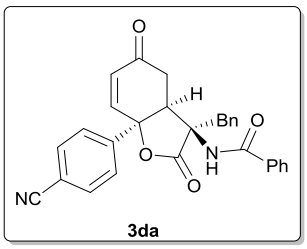
	Retention Time	Area	% Area

1	3.577	12111248	50.05
2	4.371	12088901	49.95

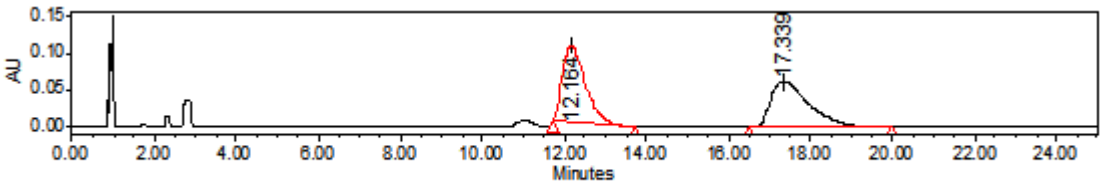


	Retention Time	Area	% Area
1	3.571	16063977	94.81
2	4.451	879376	5.19

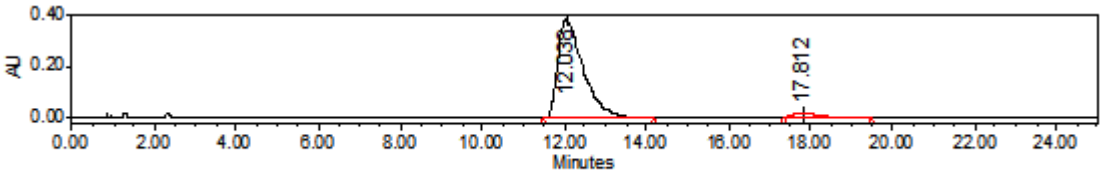
_N_-[(3_R_,3a_S_,7a_S_)-3-Benzyl-7a-(4-cyanophenyl)-2,5-dioxo-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl] benzamide



The compound **3da** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1) to afford a white solid in 29% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 85/15, 1.5 mL/min, λ = 254nm), t (major) = 12.04 min, t (minor) = 17.81 min, ee = 93%. dr >19:1 (by ^{1}H NMR). mp 158—160 ℃. $[\alpha]^{21}_D$ = −132.1 (*c*: 0.290, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, Acetone) δ 7.87 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.64 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.33 – 7.24 (m, 5H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.68 (dd, *J* = 10.4, 1.6 Hz, 1H), 6.09 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.48 (d, *J* = 13.3 Hz, 1H), 3.30 (d, *J* = 13.3 Hz, 1H), 2.87 (d, *J* = 1.5 Hz, 2H), 2.83 – 2.80 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Acetone) δ 194.9, 173.2, 167.1, 147.3, 144.6, 135.4, 134.6, 133.4, 132.5, 132.1, 131.0, 129.7, 129.2, 128.6, 128.4, 126.5, 118.9, 112.9, 81.9, 64.6, 48.3, 43.0, 34.0. **IR** (thin film, NaCl) 3335, 1782, 1678, 1653, 1531, 1510, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{29}H_{23}N_2O_4H$ [(M+H$^+$)]** = 463.1652, Found 463.1652.

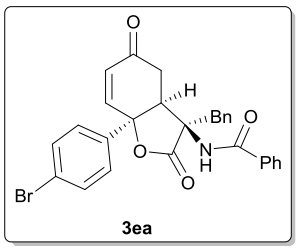


	RetentionTime	Area	% Area
1	12.164	3947402	49.42
2	17.339	4.39492	50.58



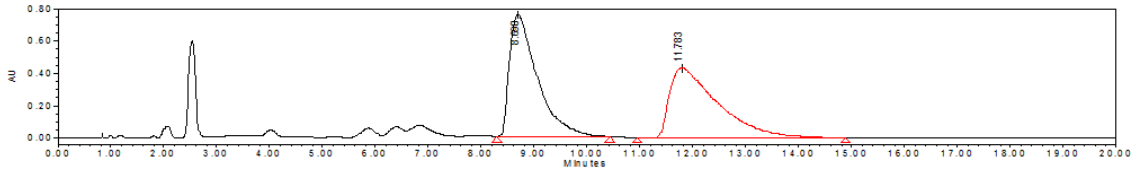
	RetentionTime	Area	% Area
1	12.038	16397754	96.37
2	17.812	616835	3.63

_N_-[(3_R_,3a_S_,7a_S_)-3-benzyl-7a-(4-bromophenyl)-2,5-dioxo-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide

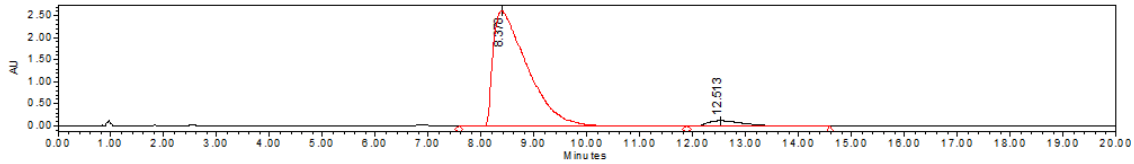


3ea

The compound **3ea** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3/1) to afford a white solid in 47% yield. **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 80/20, 1.5 mL/min, λ = 254 nm), t (major) = 8.38 min, t (minor) = 12.51min, ee = 93%. dr >19:1 (by ^{1}H NMR). mp 144—146 ℃. $[\alpha]^{21}_D$ = −117.7 (*c*: 0.232, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 5H), 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 3H), 7.20 – 7.15 (m, 2H), 7.11 – 7.02 (m, 2H), 6.72 (d, *J* = 10.2 Hz, 1H), 6.38 (s, 1H), 6.12 (dd, *J* = 10.2, 1.3 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 2.96 (d, *J* = 13.7 Hz, 1H), 2.80 – 2.61 (m, 1H), 2.51 – 2.38 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.6, 173.3, 167.0, 144.6, 139.9, 133.6, 132.9, 132.5, 132.3, 130.3, 129.3, 129.0, 128.8, 128.1, 127.0, 126.5, 123.2, 81.8, 63.8, 49.6, 42.5, 34.7. **IR** (thin film, NaCl) 3302, 1780, 1688, 1653, 1535, 1493, 1188 cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{28}H_{23}BrNO_4$ [(M+H$^+$)]** = 516.0805, 518.0785, Found 516.0814, 518.0793.

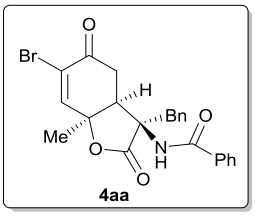


	Retention Time	Area	% Area
1	8.690	27658883	50.60
2	11.783	27001430	49.40



	Retention Time	Area	% Area
1	8.378	114762766	96.53
2	12.511	4130975	3.47

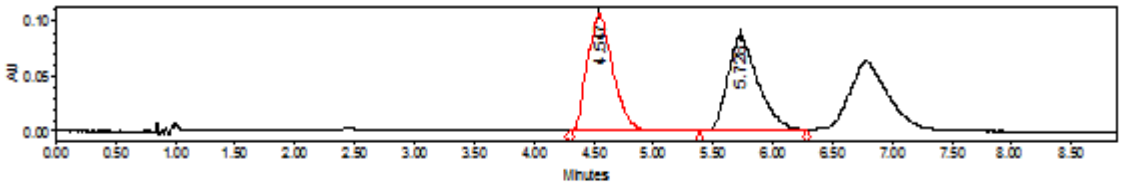
_N_-[(3_R_,3a_S_,7a_R_)-3-Benzyl-6-bromo-7a-methyl-2,5-dioxo-2,3,3a,4,5,7a-hexahydrobenzofuran-3-yl]benzamide



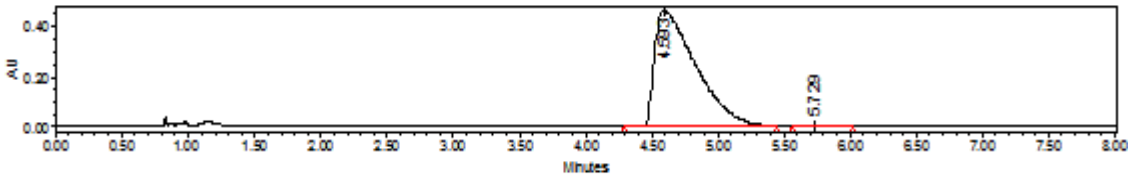
4aa

To a solution of **3aa** (37.5 mg, 0.10 mmol, 1 eq) in 1 mL DCM at 0 ℃ was added Br_2 (7 μL, 1.3 eq). The reaction was allowed to stir for 24 h and then 0.5 mL of NEt_3 was added and the reaction was warmed to room temperature. The crude residue was purified by column chromatography on silica gel to afford **4aa** as a pale White solid in 60% yield. **TLC** (petroleum ether/ethyl

acetate = 3/1): R_f = 0.25. Analytical data for **4aa** : **SFC** (Daicel Chiralcel **IA**, $scCO_2$/MeOH = 80/20, 1.5 mL/min, λ = 254 nm), t (major) = 4.59 min, t (minor) = 5.73min, ee = 99%. dr >19:1 (by ^{1}H NMR). mp decomposed at 172 ℃. $[\alpha]^{25}_D$ = −87.3 (*c*: 0.546, λ = 589 nm, in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.36 (m, 4H), 7.32 – 7.23 (m, 3H), 7.19 (d, *J* = 1.4 Hz, 1H), 6.15 (s, 1H), 3.37 – 3.21 (m, 2H), 3.13 – 3.04 (m, 1H), 2.72 – 2.66 (m, 1H), 2.56 – 2.44 (m, 1H), 1.55 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 187.3, 173.1, 166.2, 148.4, 133.5, 132.4, 132.2, 130.3, 129.5, 128.7, 128.5, 127.1, 123.7, 104.7, 80.9, 61.8, 48.1, 44.9, 26.3. **IR** (thin film, NaCl) 3349, 1770, 1677, 1508, 1269cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{21}BrNO_4$ [(M+H$^+$)]** = 454.0648, 456.0628, Found 454.0645, 456.0630.

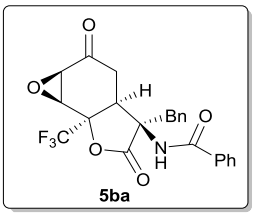


	Retention Time	Area	% Area
1	4.547	1591135	50.61
2	5.728	1552956	49.39



	Retention Time	Area	% Area
51	4.593	9971302	99.96
2	5.728	3495	0.04

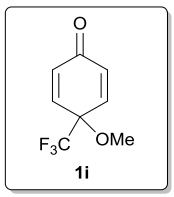
***N*-[(1a*R*,3a*S*,4*R*,6a*R*,6b*S*)-4-Benzyl-2,5-dioxo-6a-(trifluoromethyl)octahydrooxireno[2,3-g]benzofuran-4-yl]benzamide**



Into a mixed solution of **3ba** (0.1 mmol), *tert*-$BuNH_2$ (3 μL, 30 mol%) and CH_3OH (1 mL) was slowly added 50 μL of H_2O_2 (30%, 0.44 mmol) under stirring at 30 ℃. The reaction was allowed to stir for 24 h and then the solution was treated with 2 mL of ethyl acetate, 1 mL of H_2O and 2 mL of brine, the formed organic layer was separated. The water layer was extracted with ethyl acetate (3×3 mL). The extract was washed with brine and dried by Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel to afford **5ba** as a white solid in 82% yield. **TLC** (petroleum ether/ethyl acetate = 3/1): R_f = 0.10. Analytical data for **5ba**: mp decomposed at 158 ℃. $[\alpha]^{25}_D$ = −21.6 (*c*: 0.334, λ = 365 nm, in acetone). **^{1}H NMR** (400 MHz, acetone-d_6) δ 7.94 – 7.89 (m, 2H), 7.74 (s, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.47 (m, 2H), 7.42 – 7.32 (m, 5H), 4.11 (d, *J* = 4.4 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.61 – 3.58 (m, 1H), 3.51 (d, *J* = 25.2 Hz, 1H), 3.33 – 3.27 (m, 1H), 3.08 (dd, *J* = 14.4, 8.9 Hz, 1H), 2.30 (dd, *J* = 14.5, 10.1 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Acetone) δ 203.1, 171.9, 167.1, 78.9 (q, *J* = 307.0 Hz, 1C), 63.4, 58.7 (q, *J* = 115.1 Hz, 1C), 56.0, 55.6, 43.4, 40.8, 33.0. **^{19}F{^{1}H} NMR** (376 MHz, Acetone) δ 98.0. **IR** (neat)

3413, 1805, 1726, 1703, 1677, 1497, 1278, 1191cm^{-1}. **HRMS** (FTMS+c ESI) caled for **$C_{23}H_{19}F_3NO_5$ [(M+H^+)]** = 446.1210, Found 446.1199.

4-Methoxy-4-(trifluoromethyl)cyclohexa-2,5-dien-1-one

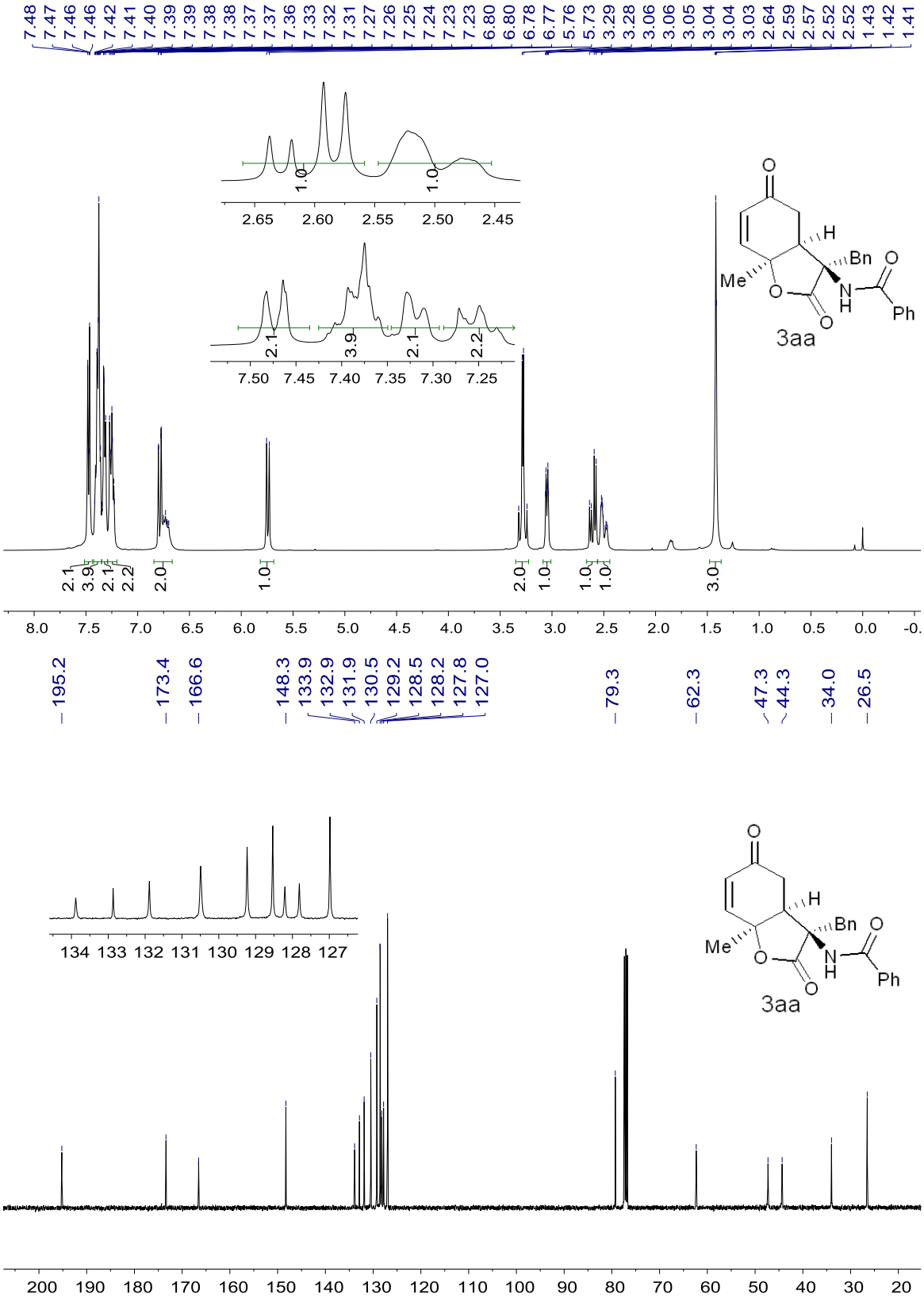


1i

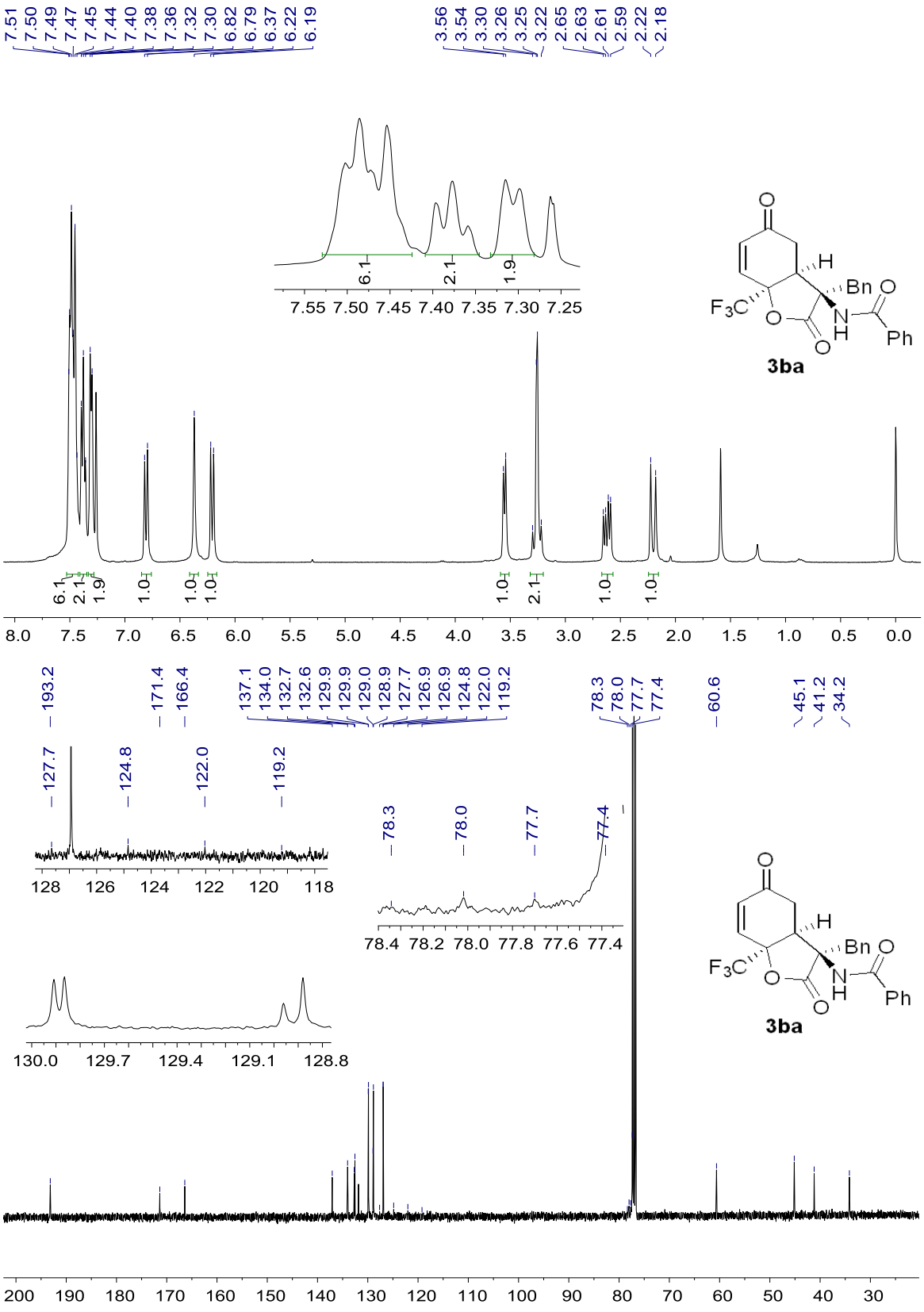
Into a mixed solution of **1b** (0.67 mmol), KOH (1.0 mol) and DMSO (10 mL) was slowly added CH_3I (6.7 mmol) under stirring at 30 ℃. The reaction was allowed to stir for 24 h and then the solution was treated with 10 mL of water, the water layer was extracted with DCM (3×10 mL). The extract was washed with brine and dried by Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel to afford **1i** as a yellow solid in 30% yield. **TLC** (petroleum ether/ethyl acetate = 3/1): R_f = 0.80. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 10.3 Hz, 2H), 6.59 (d, *J* = 10.4 Hz, 2H), 3.31 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 140.7, 135.3, 122.8 (q, *J* = 285.8 Hz, 1C), 74.8 (q, *J* = 31.3 Hz, 1C), 52.8. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ 77.6.

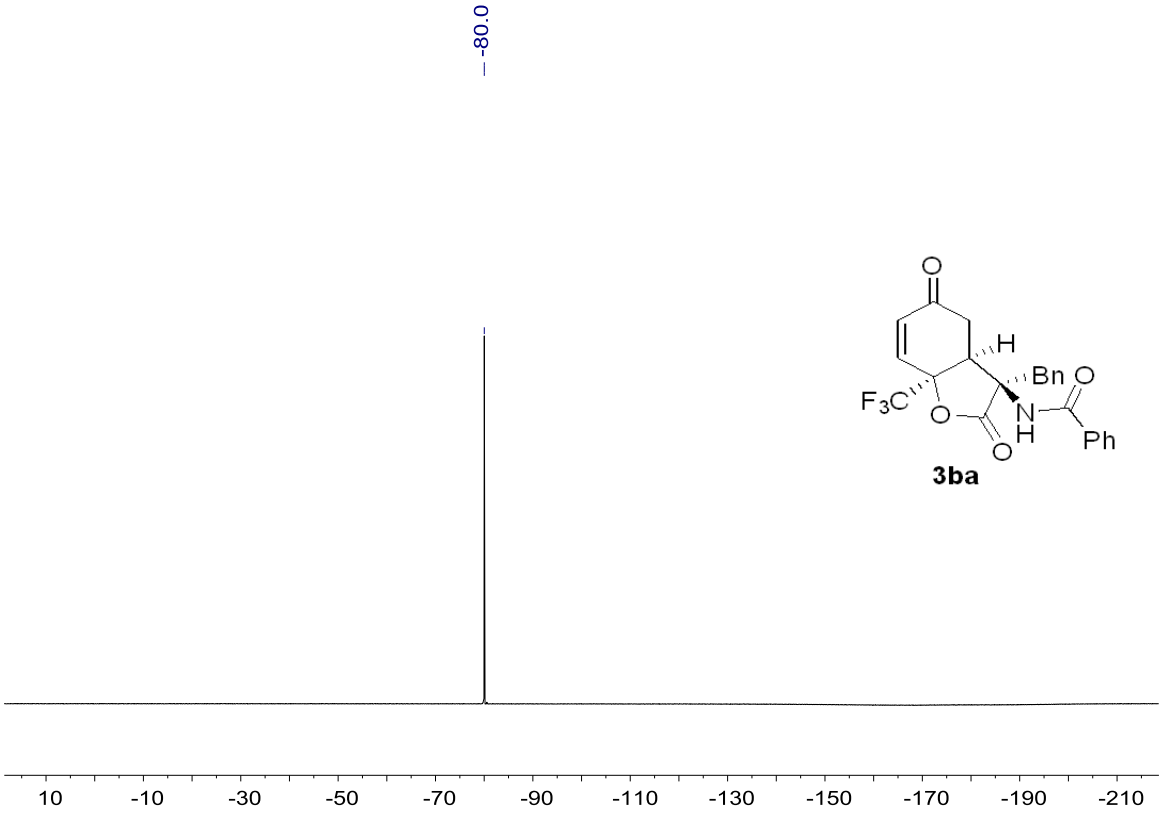
7. NMR spectra

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz), $CDCl_3$, compound **3aa**

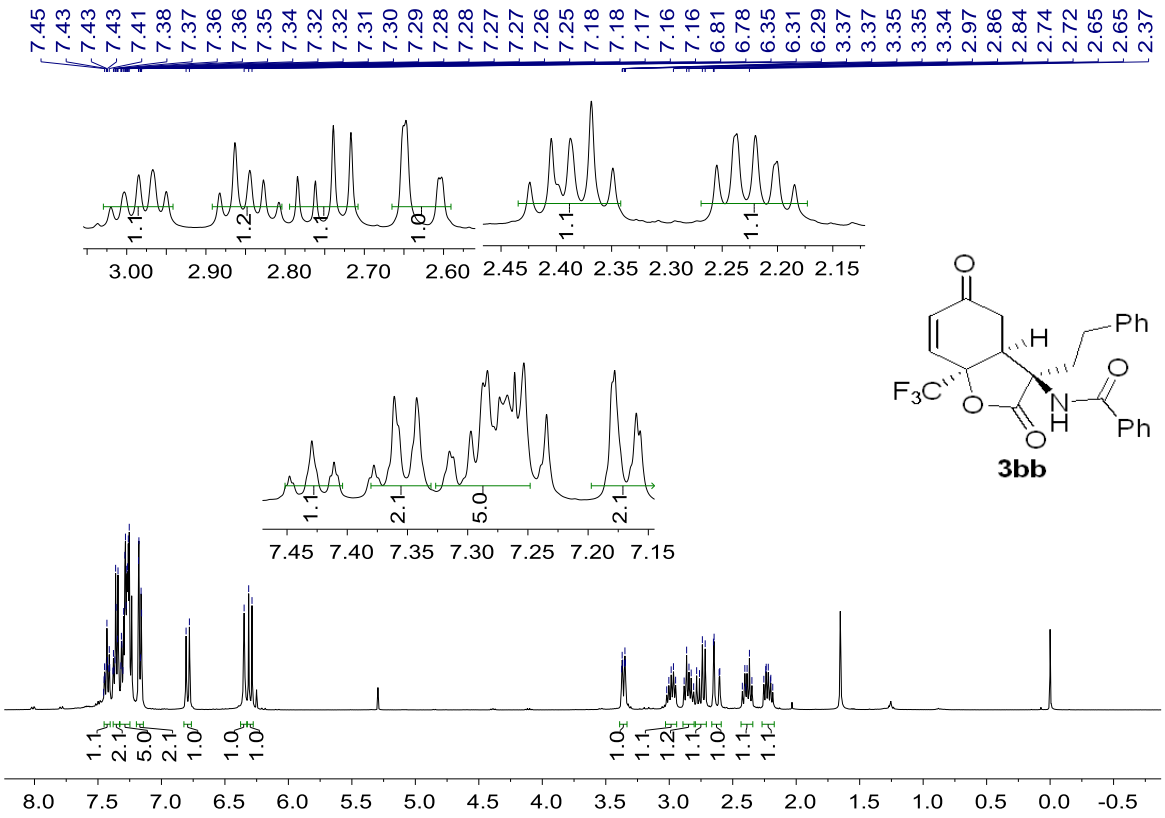


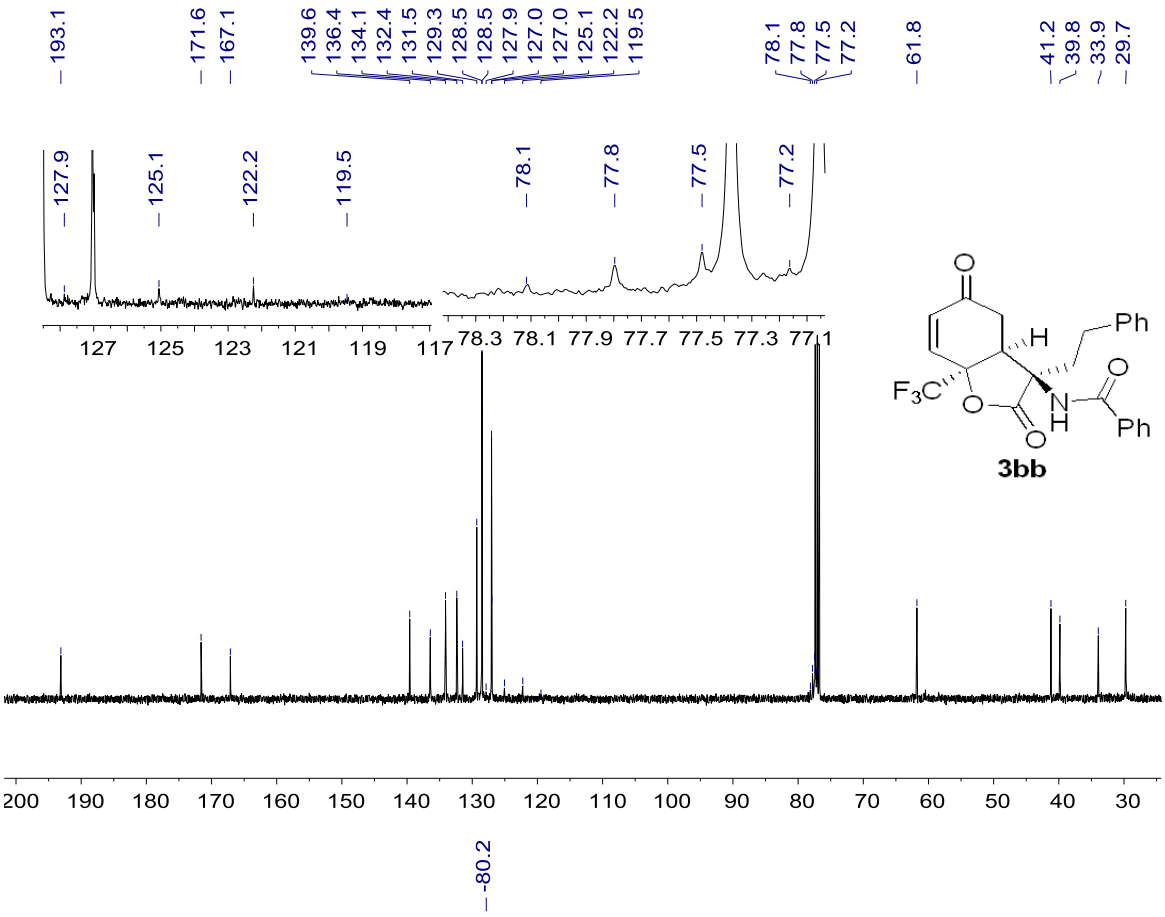
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3ba**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bb**

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33.9
29.7
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78.3 78.1 77.9 77.7 77.5 77.3 77.1
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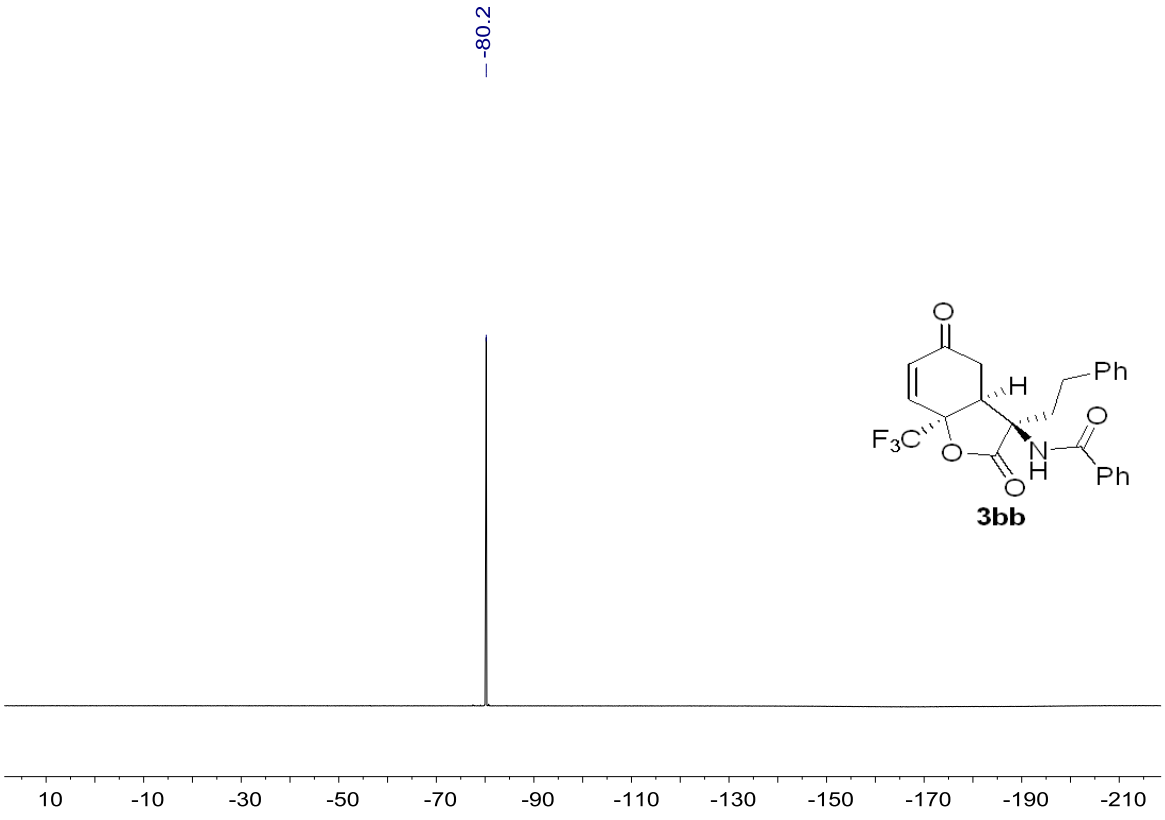
O
N
H
Ph
3bb


-80.2
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
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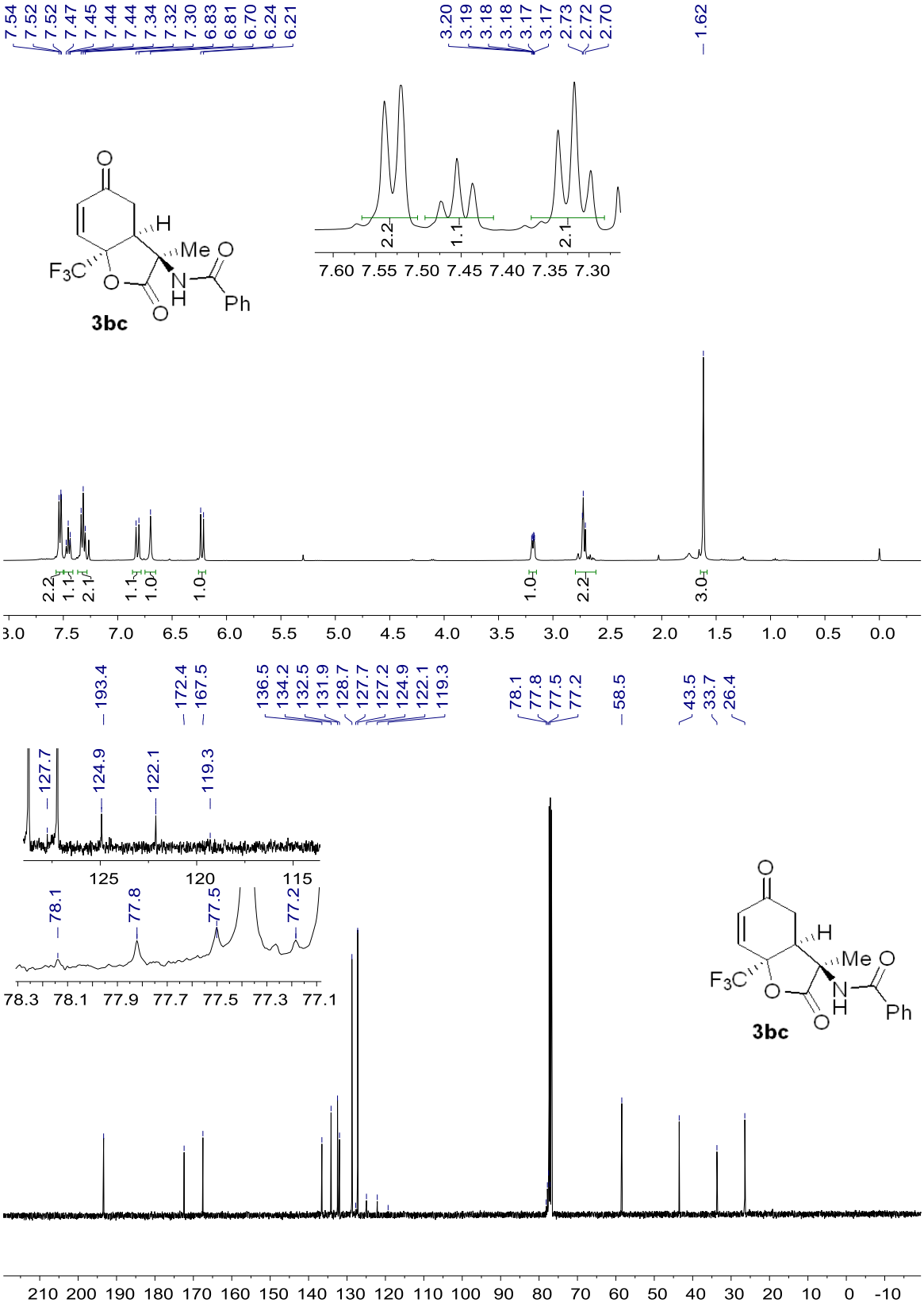
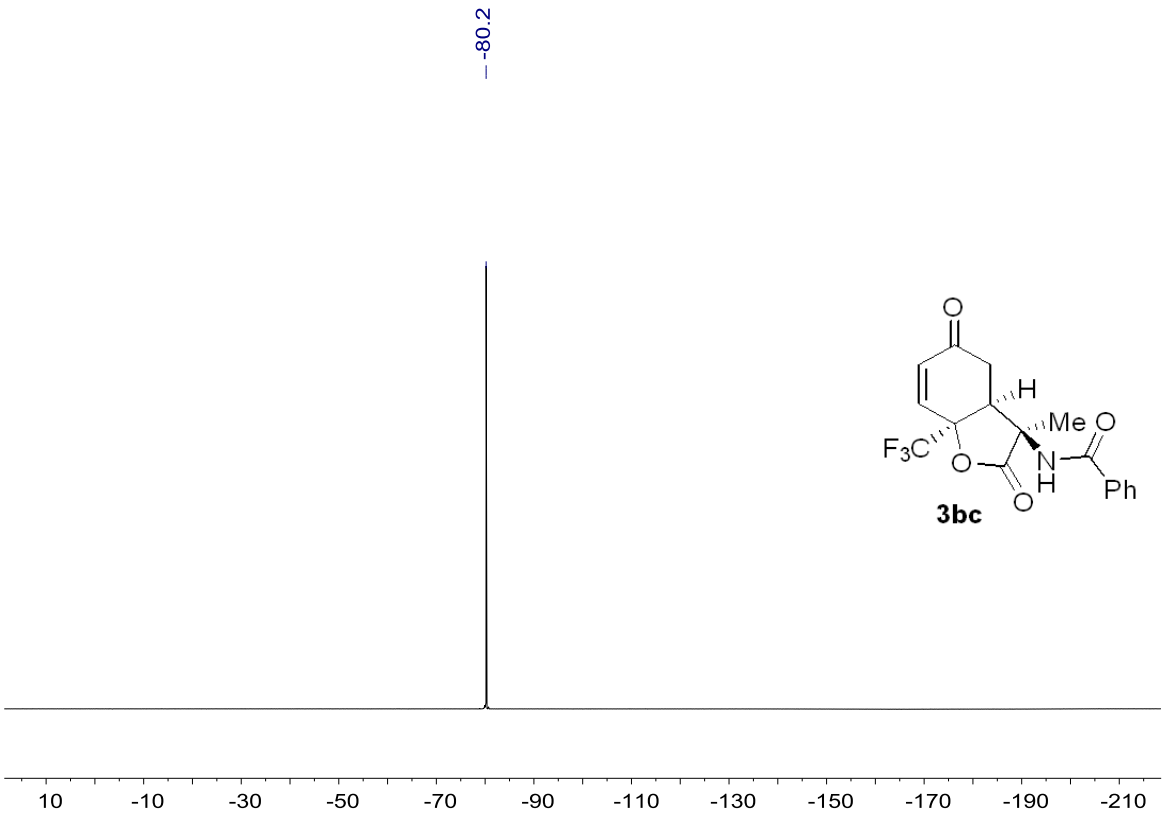
F3C
O
N
H
Ph
3bb

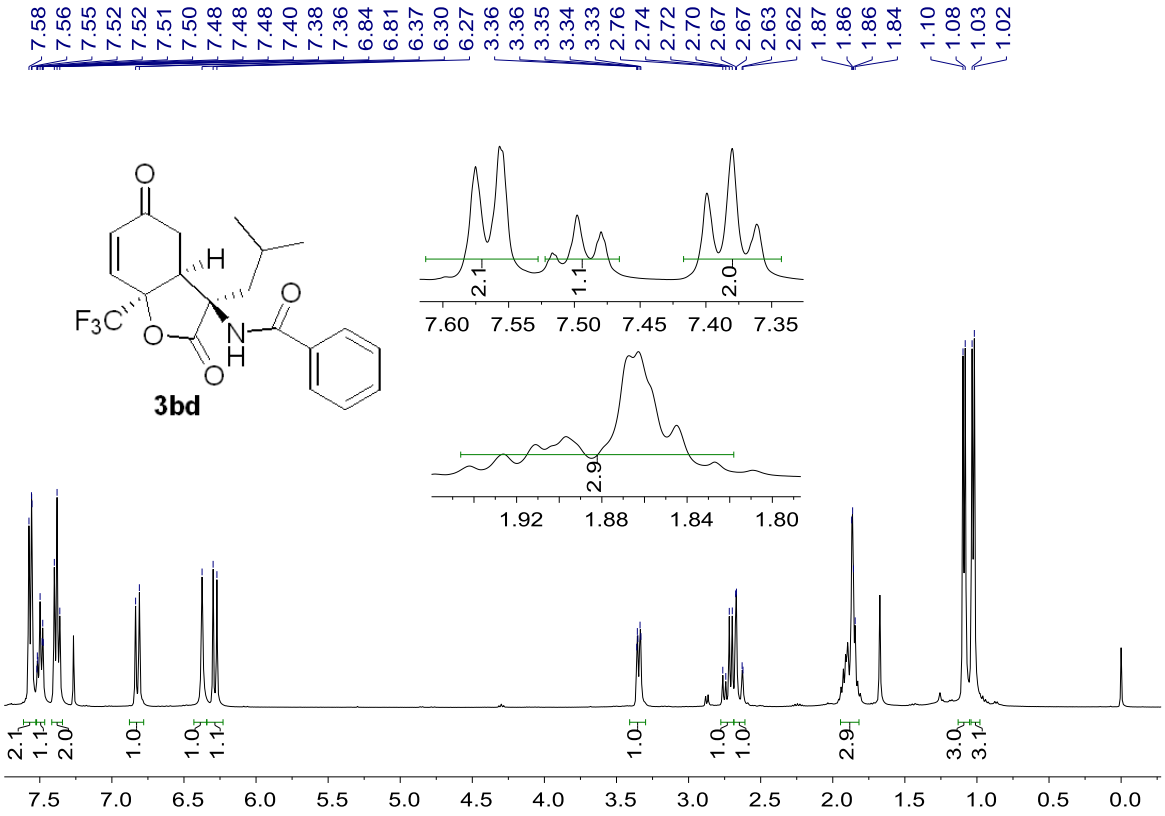
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bc**



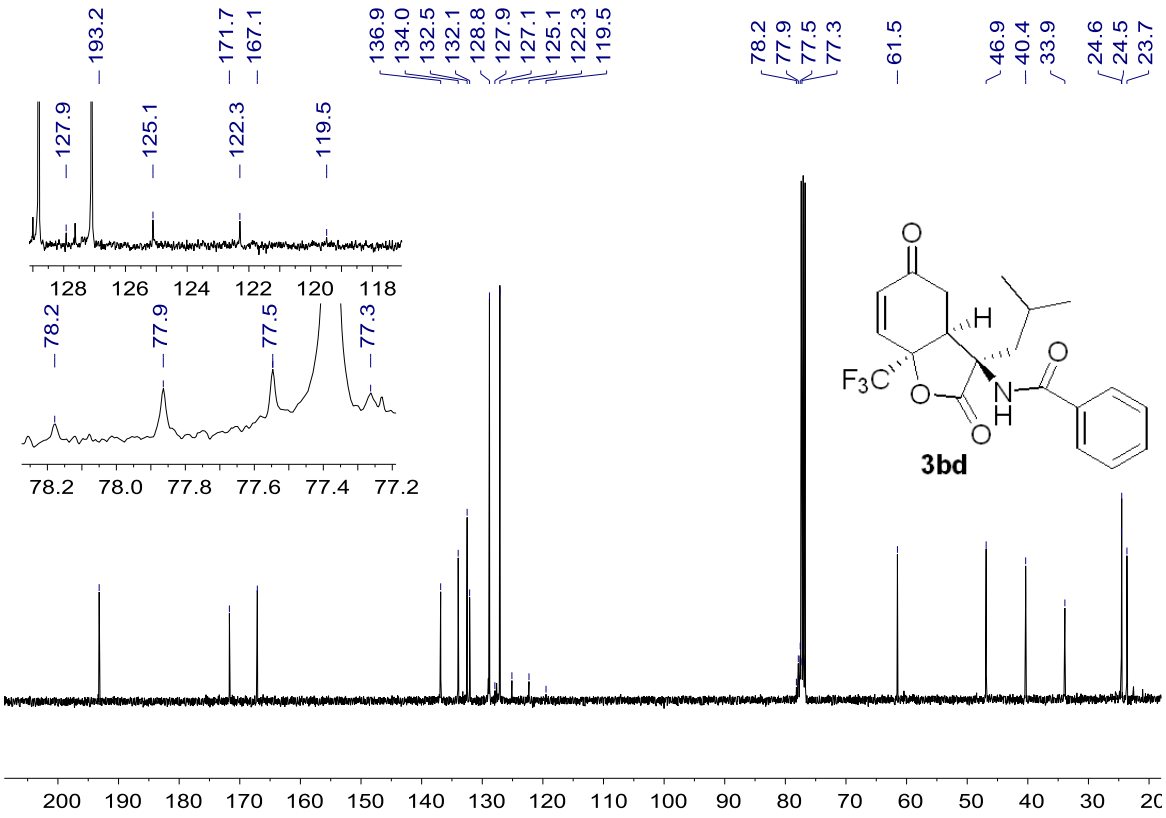


3bc

^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bd**



3bd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24.5
23.7
127.9
125.1
122.3
119.5
128 126 124 122 120 118
78.2
77.9
77.5
77.3
78.2 78.0 77.8 77.6 77.4 77.2
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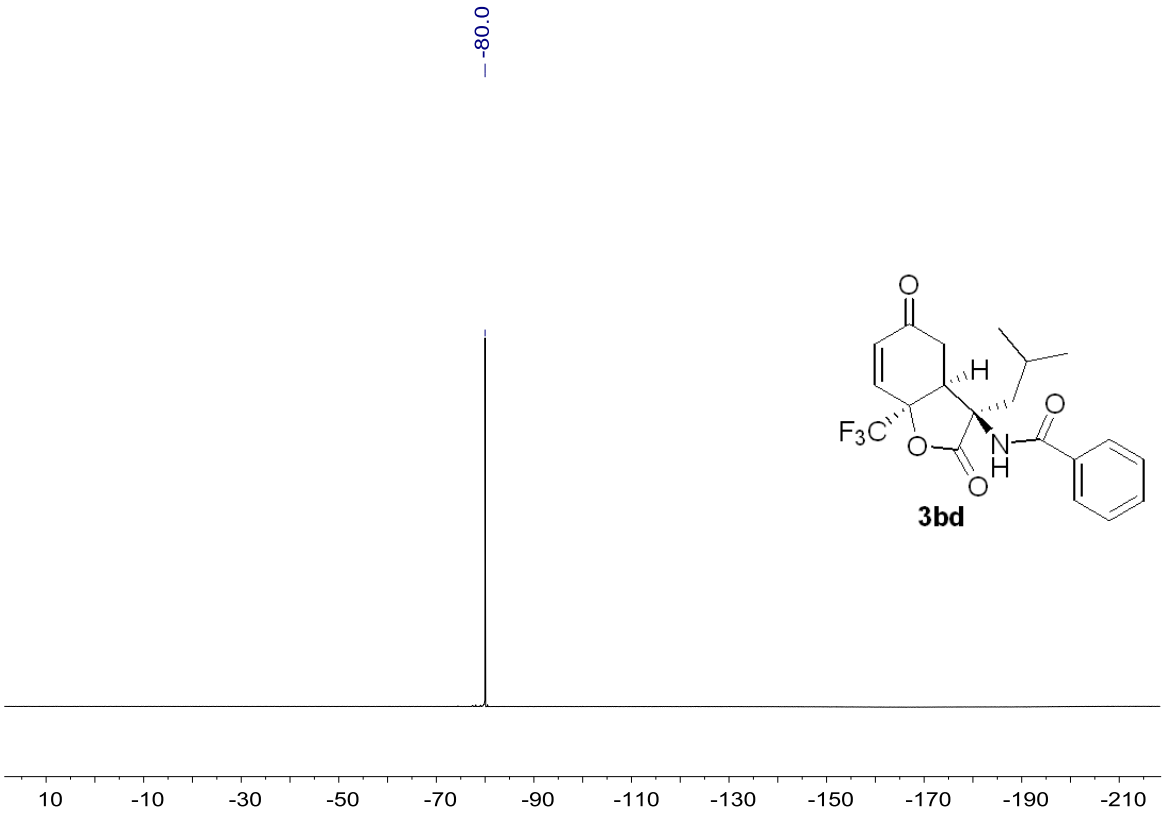
O
N
H
O
O
3bd


-80.0
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
O
H
F3C
O
N
H
O
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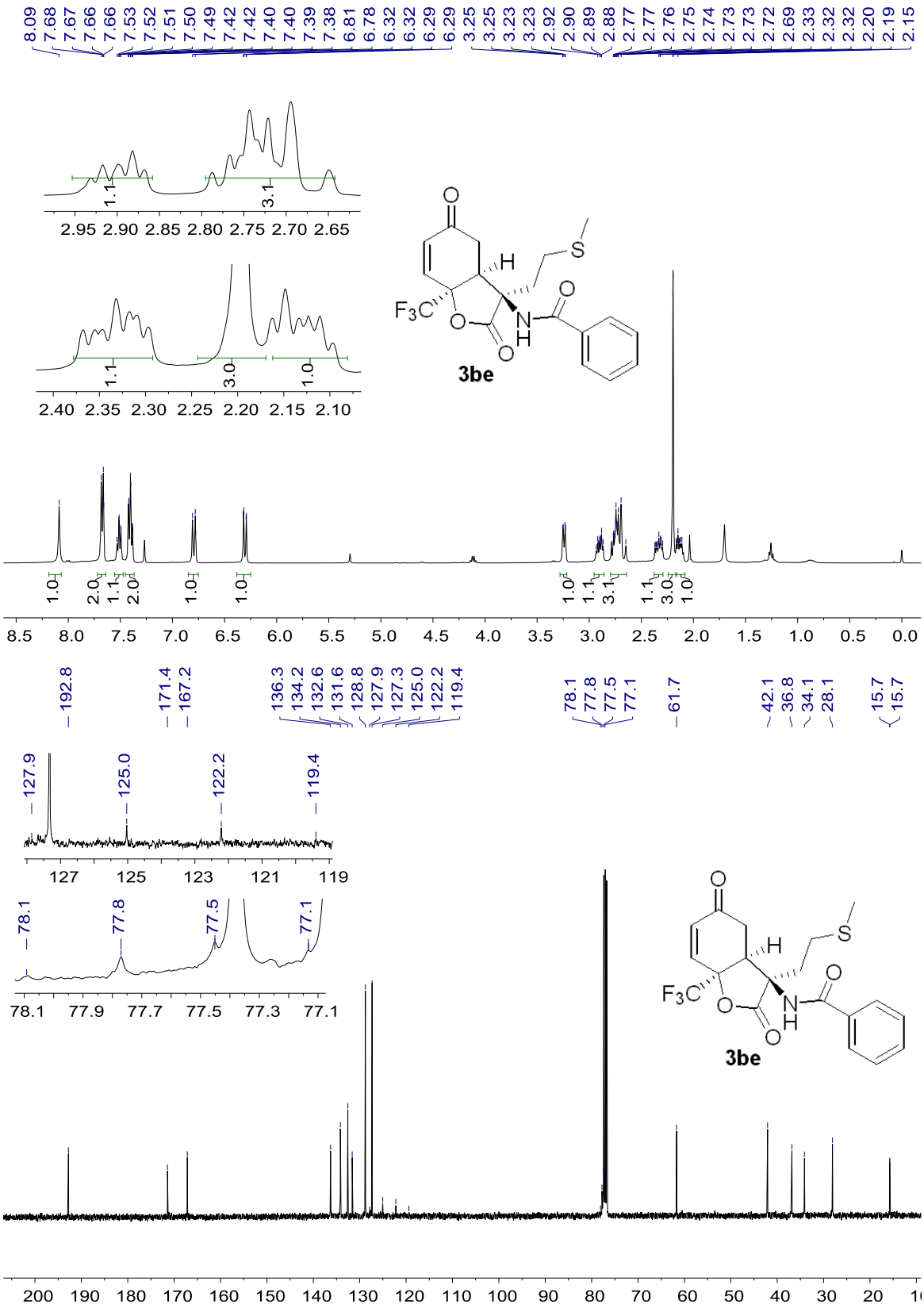
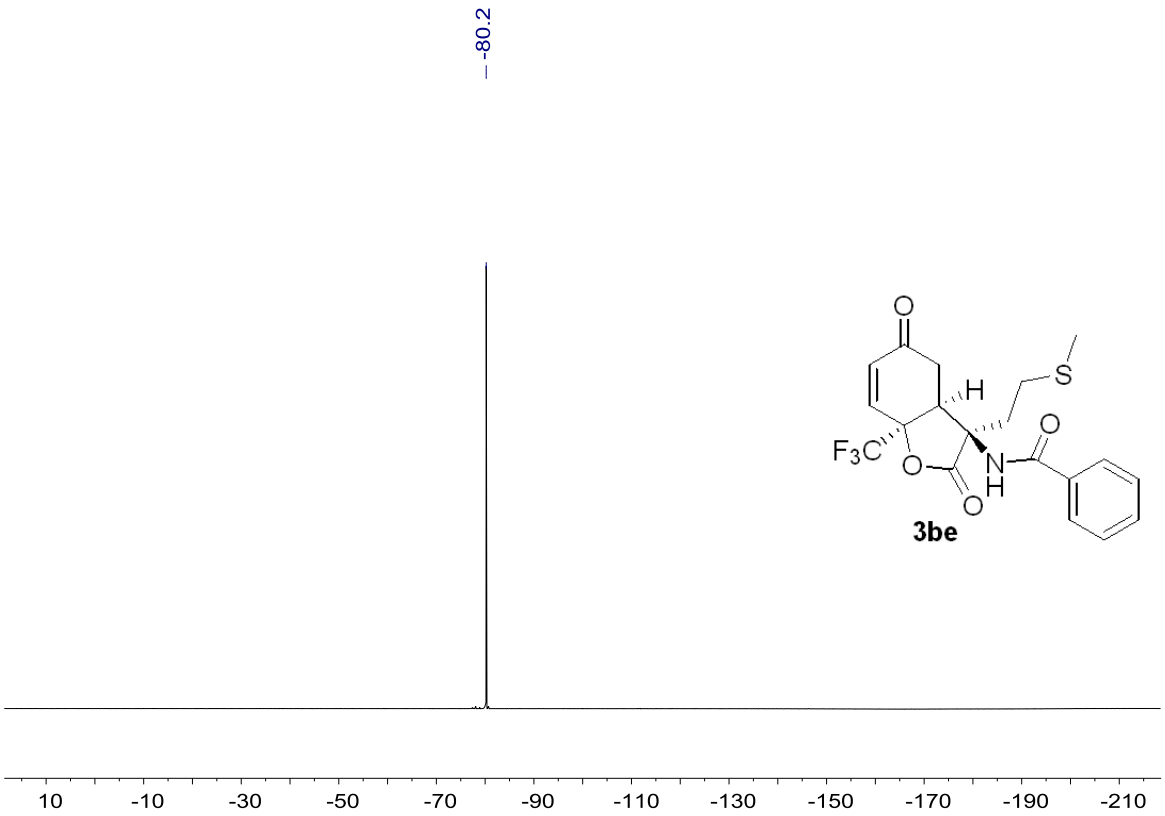
3bd

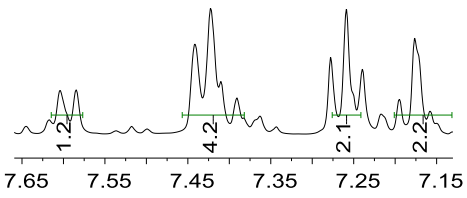
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3be**

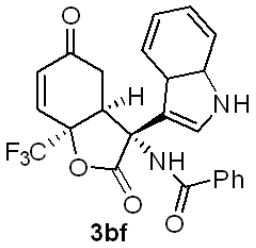




3be

^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bf**





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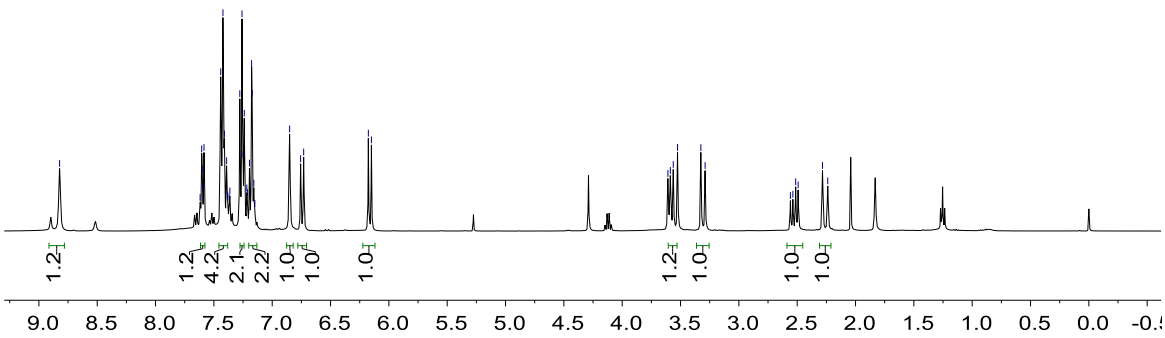

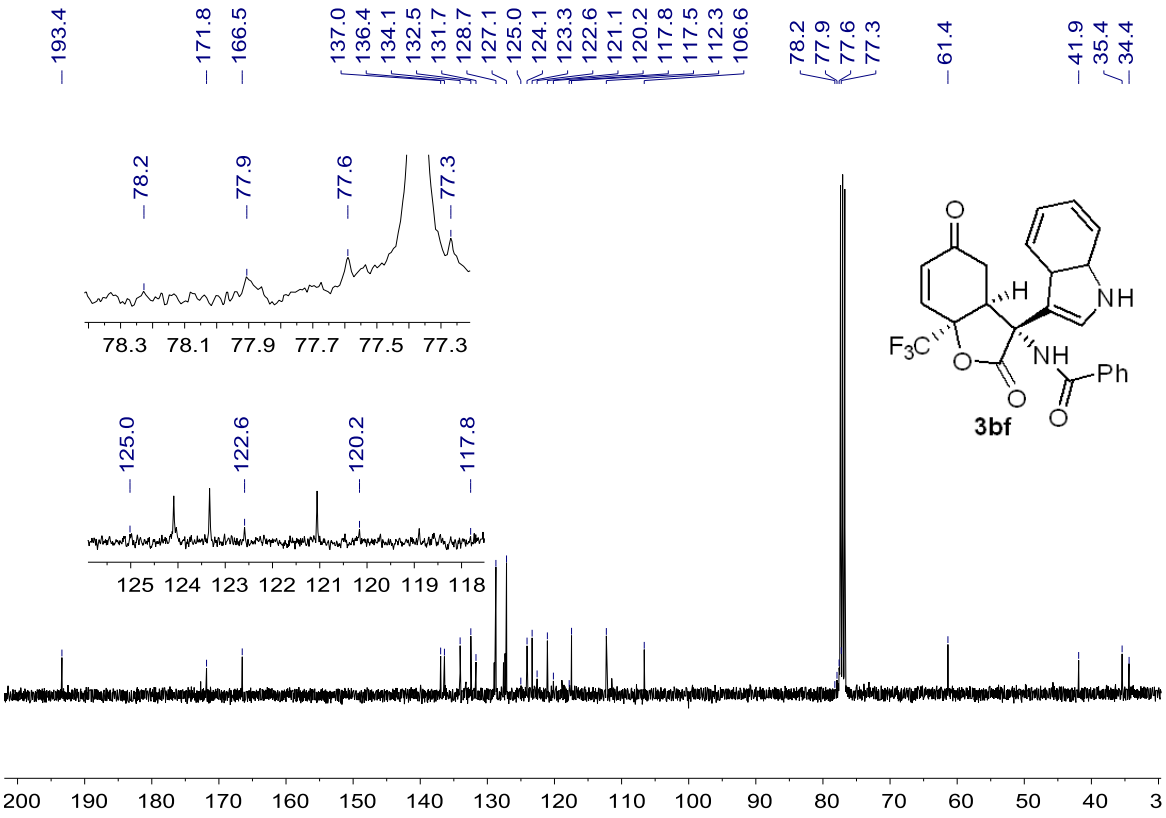
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125.0
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121.1
120.2
117.8
117.5
112.3
106.6
78.2
77.9
77.6
77.3
61.4
41.9
35.4
34.4
78.3 78.1 77.9 77.7 77.5 77.3
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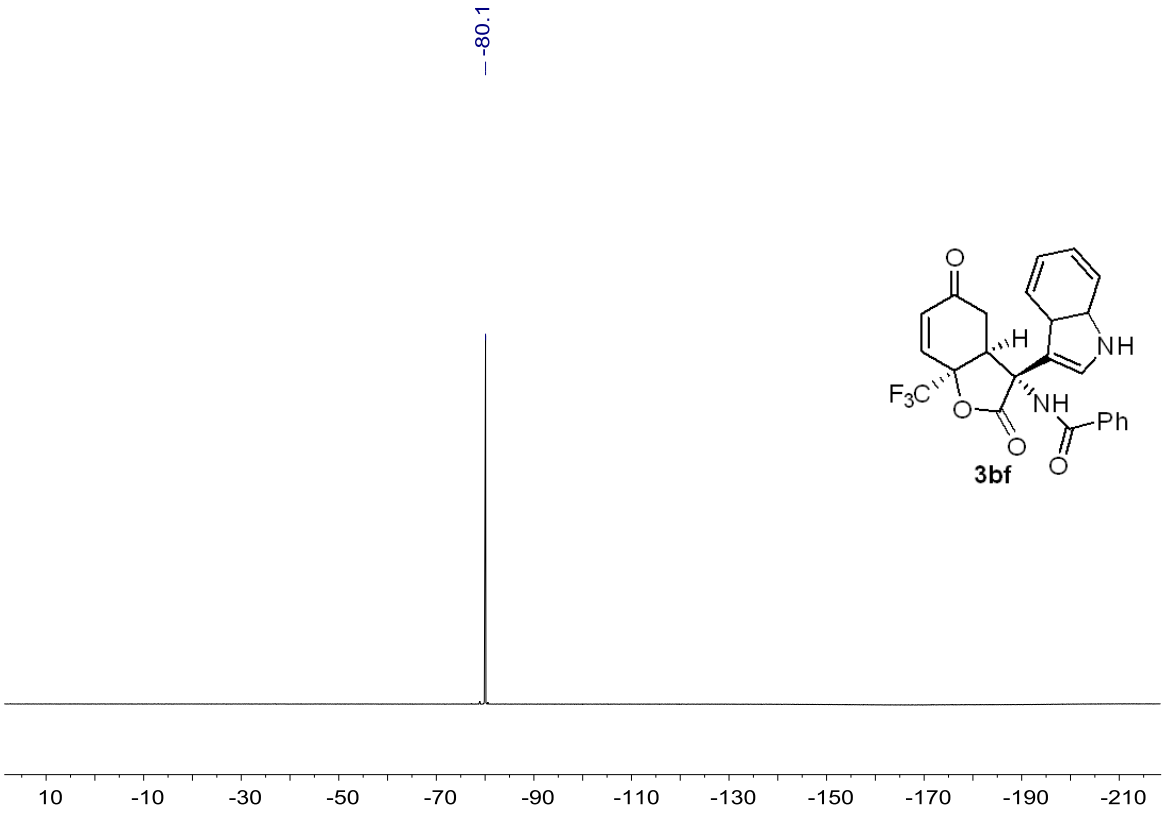
F3C
O
NH
Ph
3bf


-80.1
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
H
NH
F3C
O
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Ph
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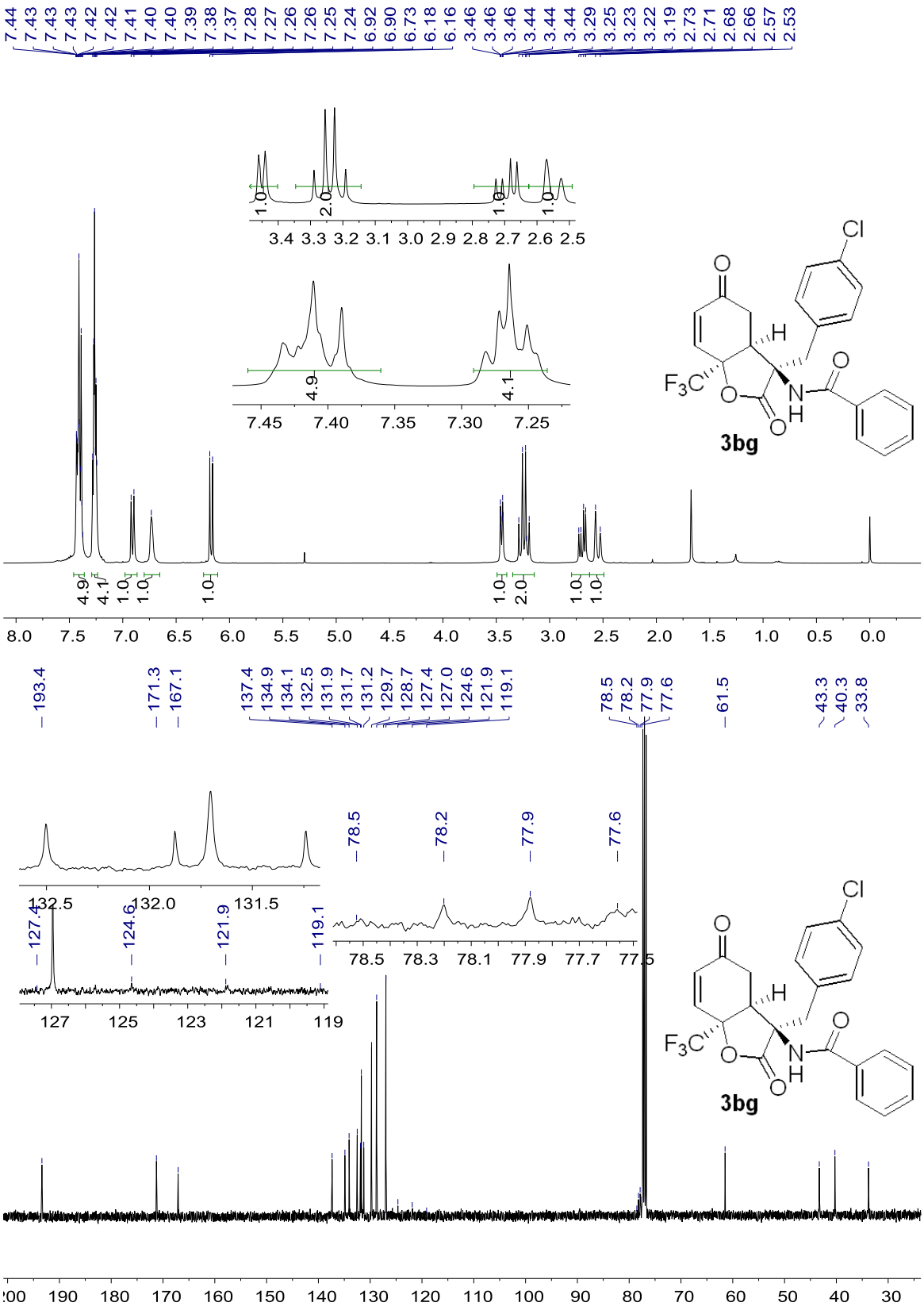
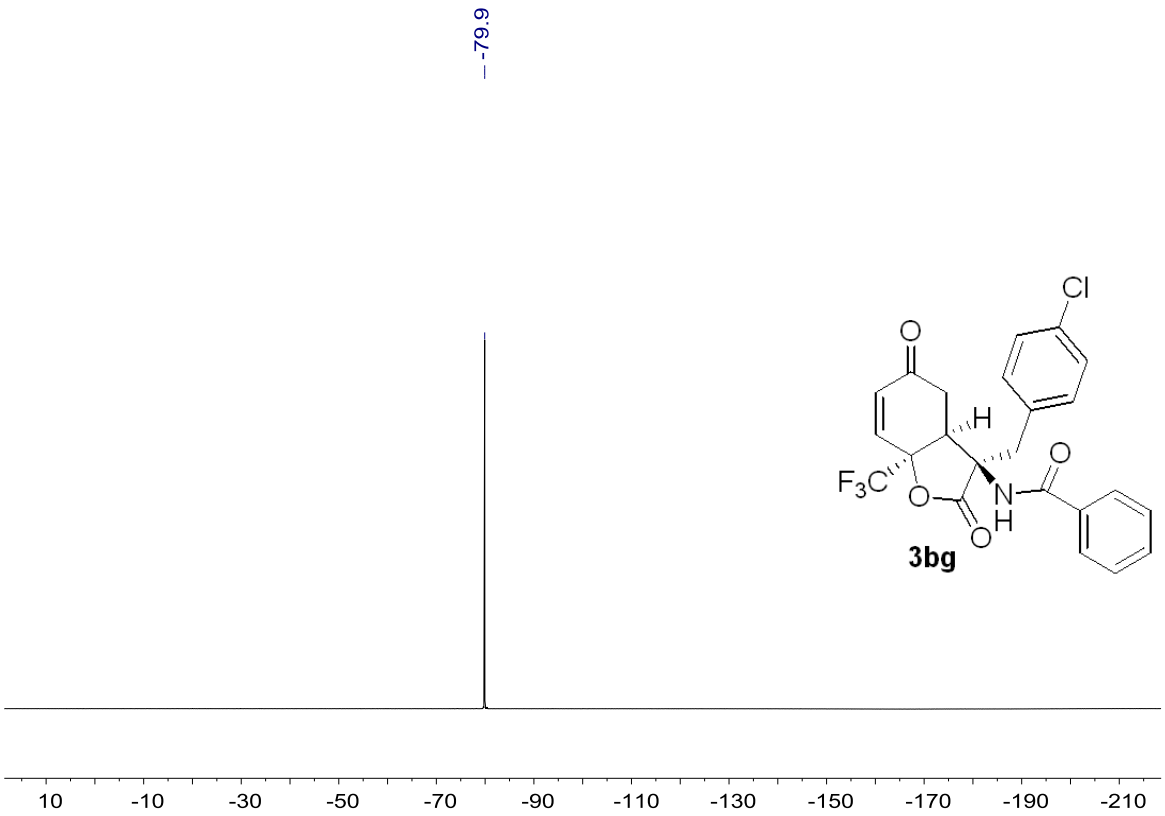
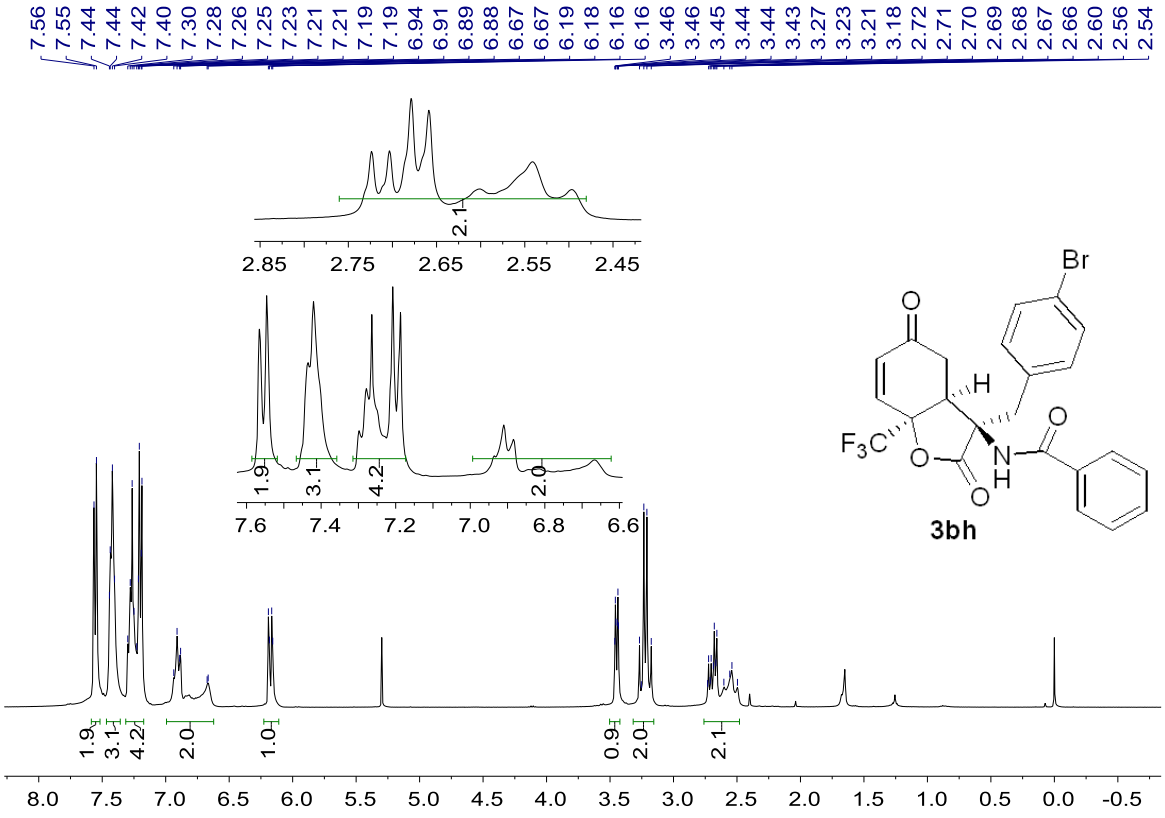
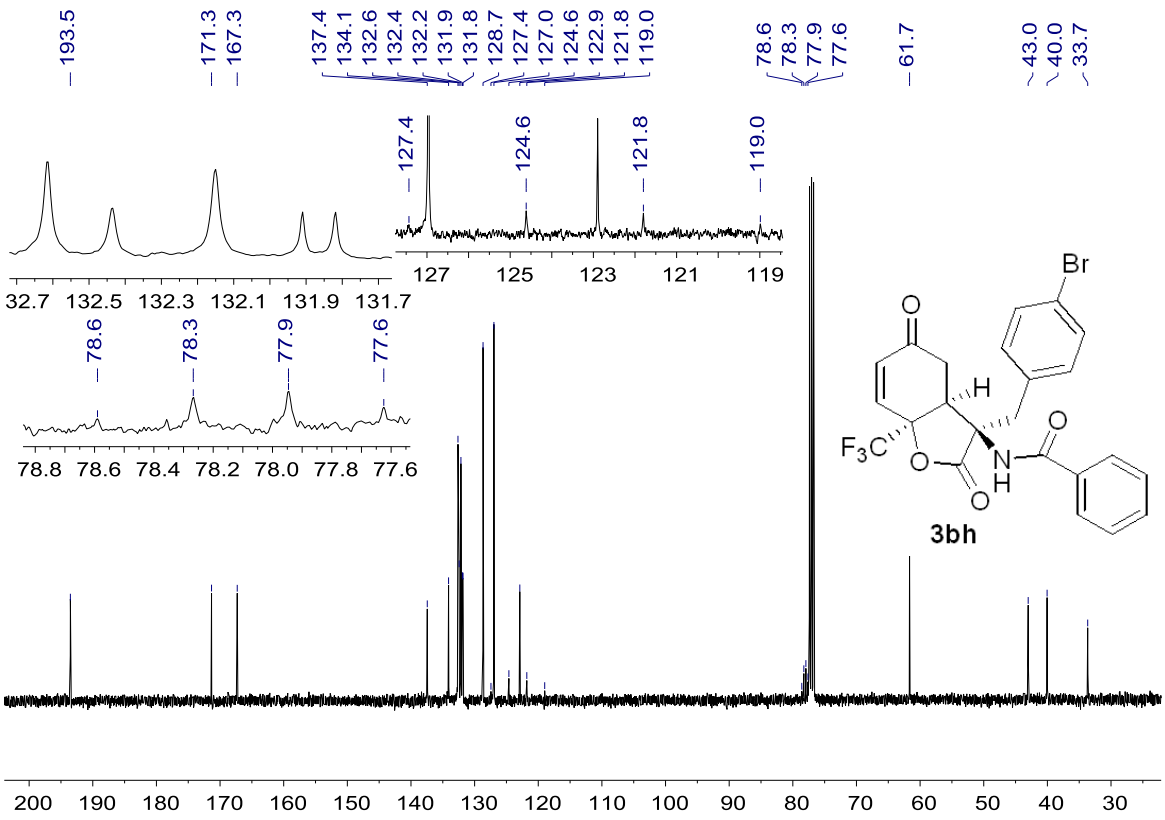
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bg**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bh**

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78.3
77.9
77.6
61.7
43.0
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Br
O
H
F3C
O
N
H
O
O
3bh
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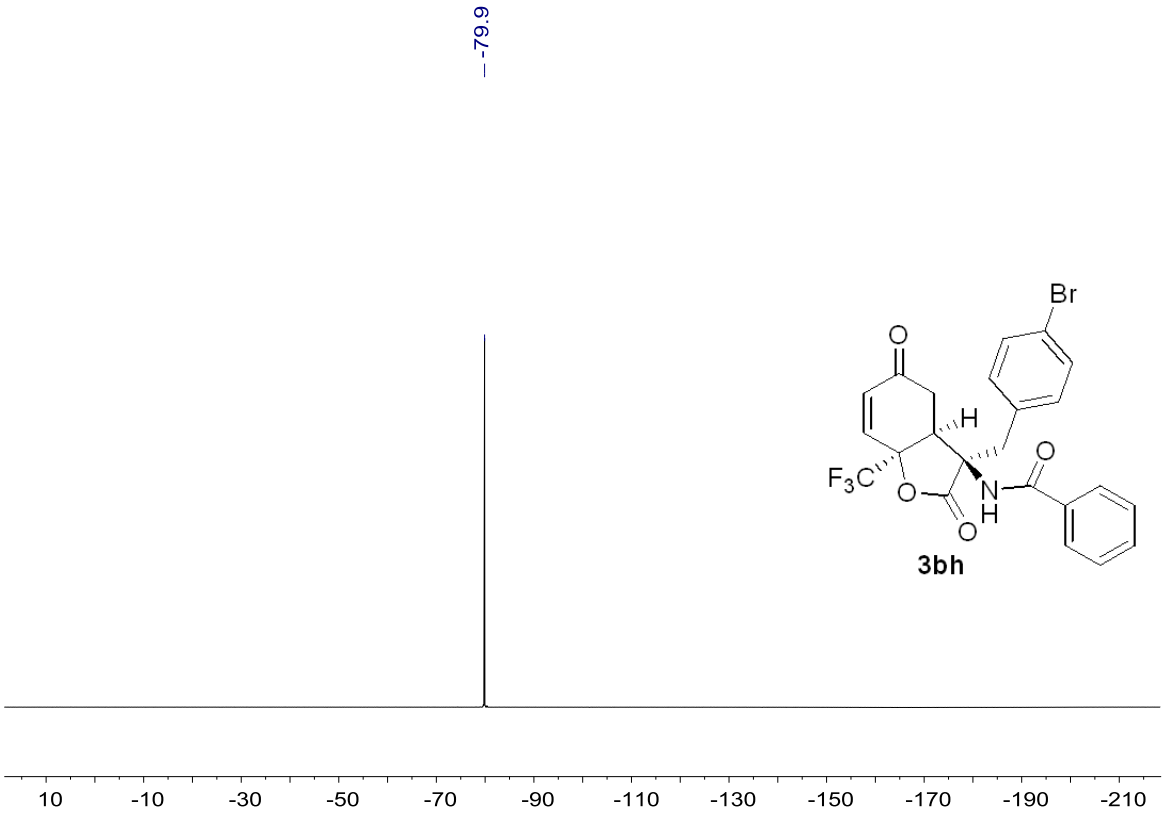
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Br
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H
F3C
O
N
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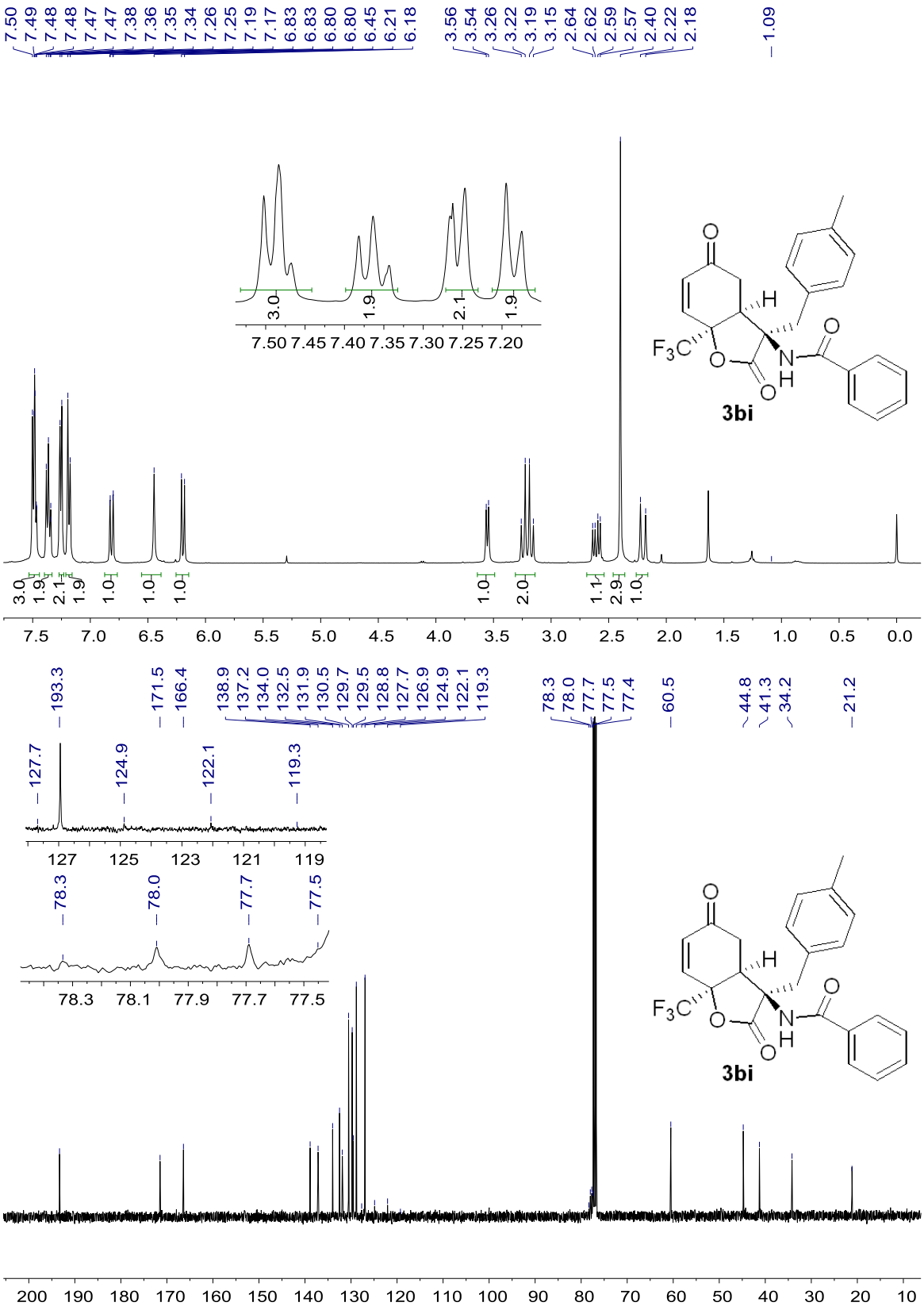
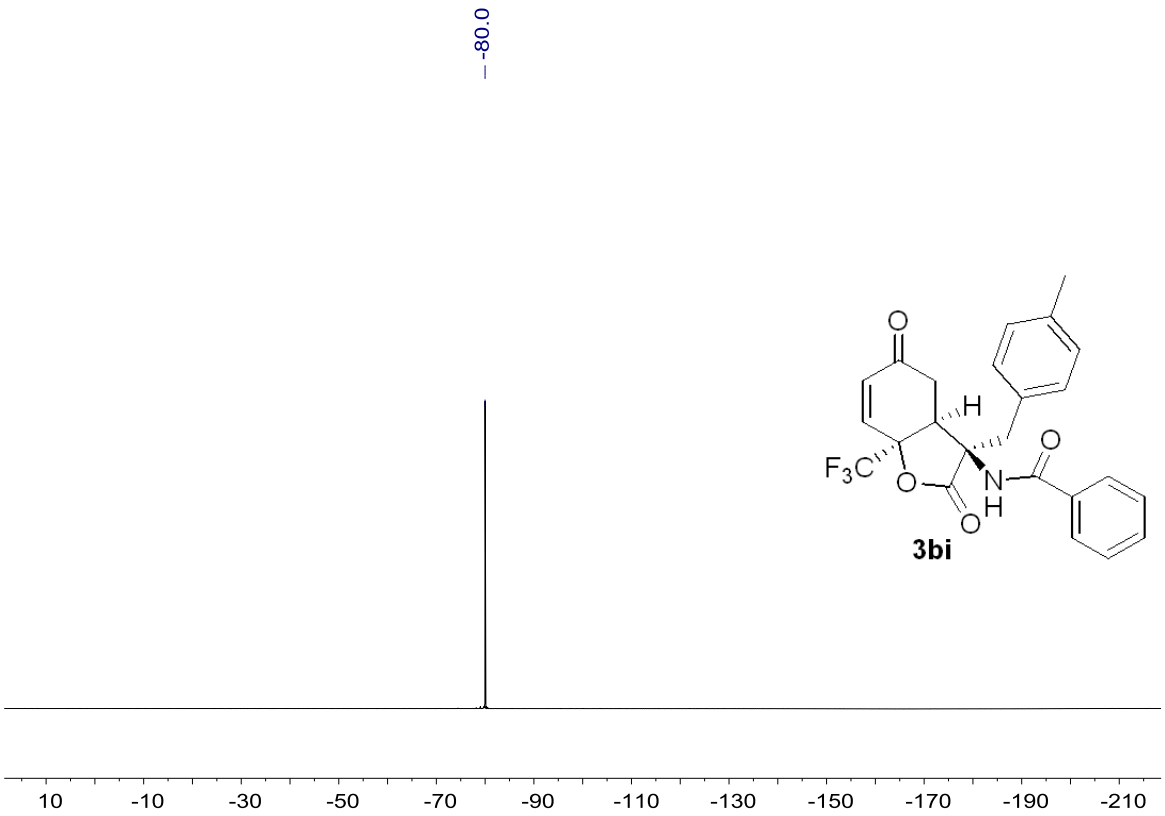
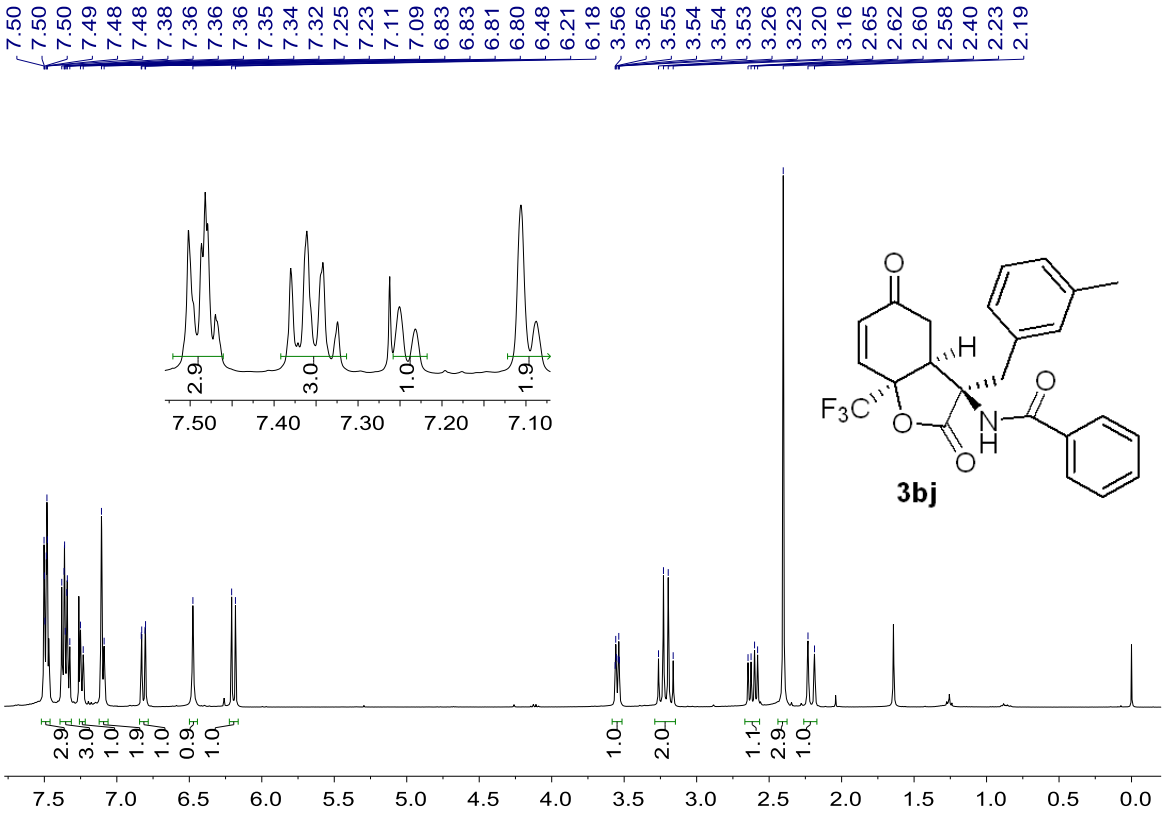
O
O
3bh
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

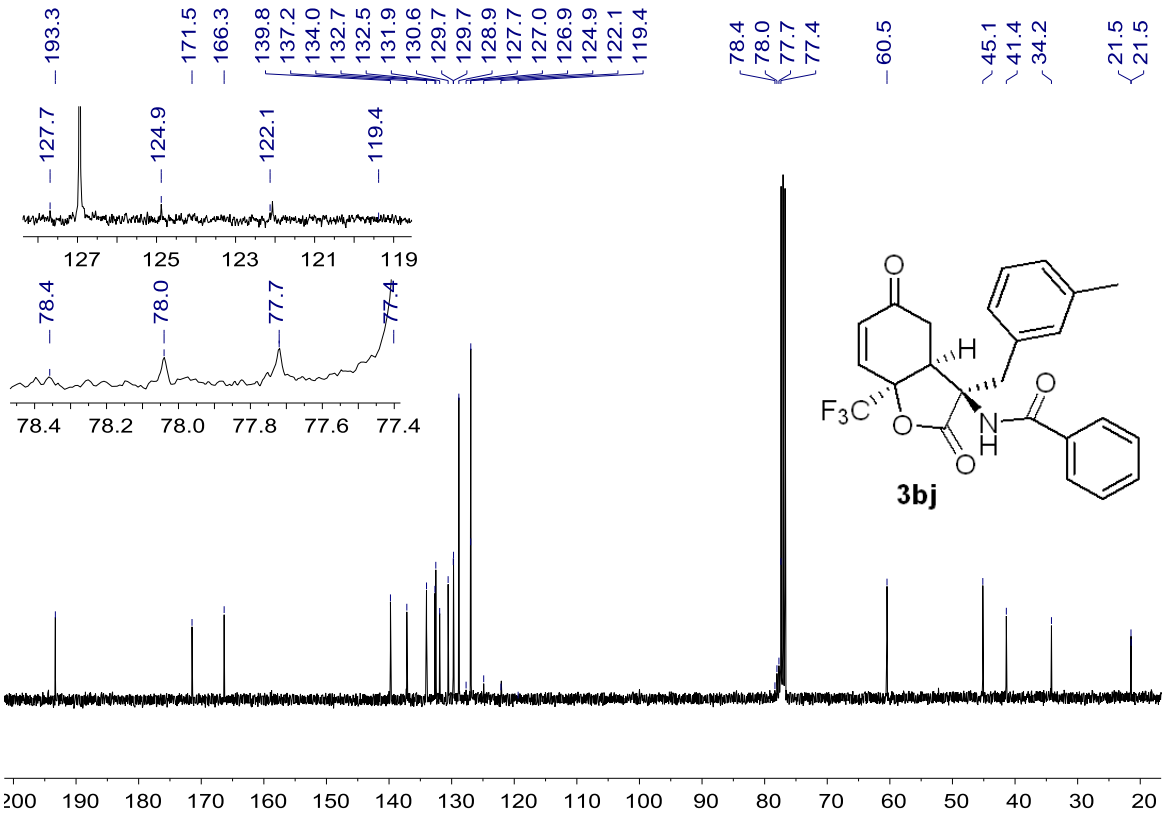
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bi**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bj**

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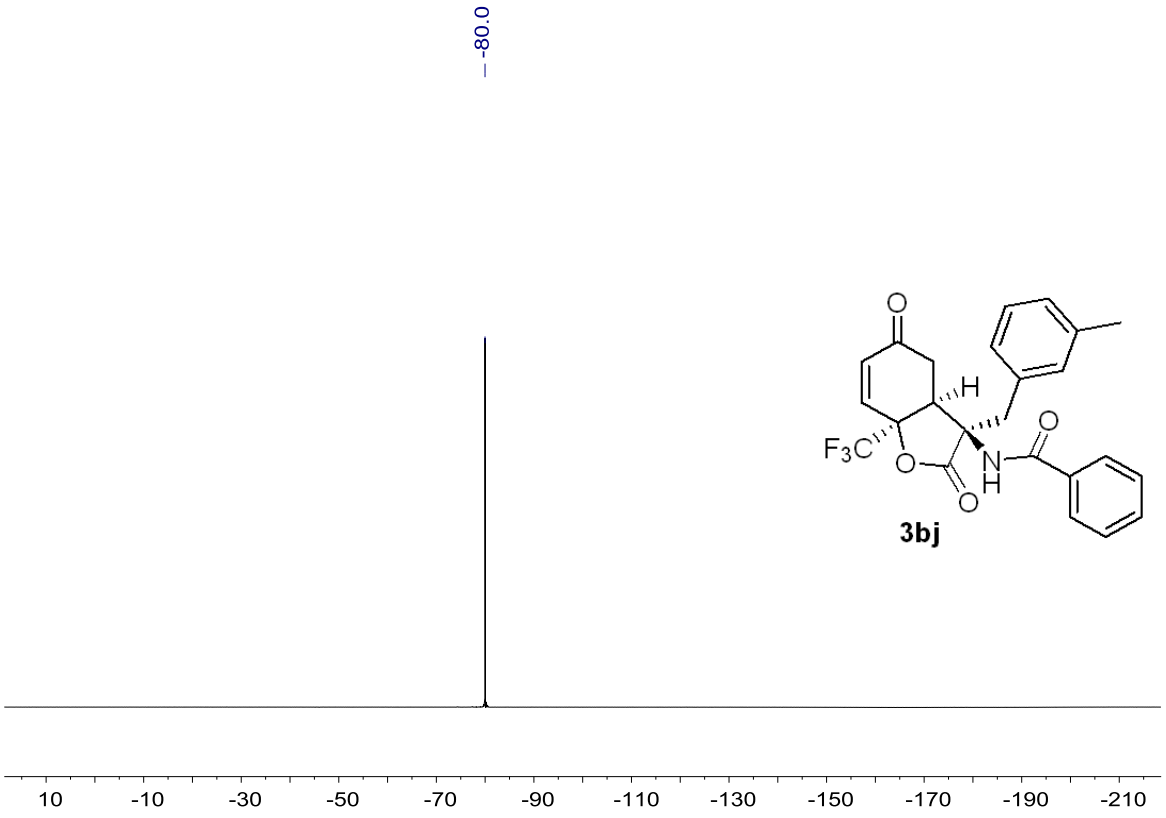
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F3C
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H
O
O
3bj
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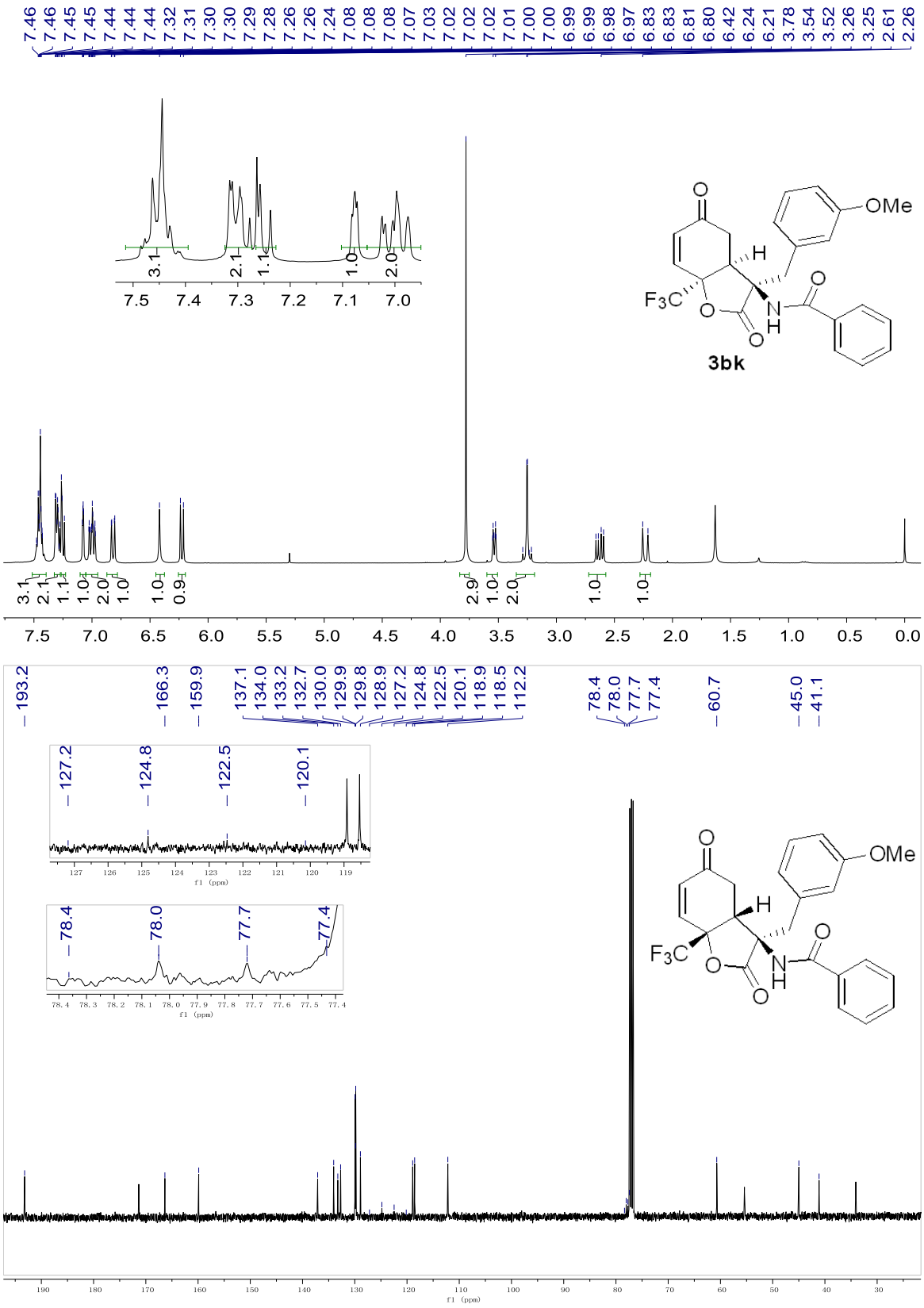
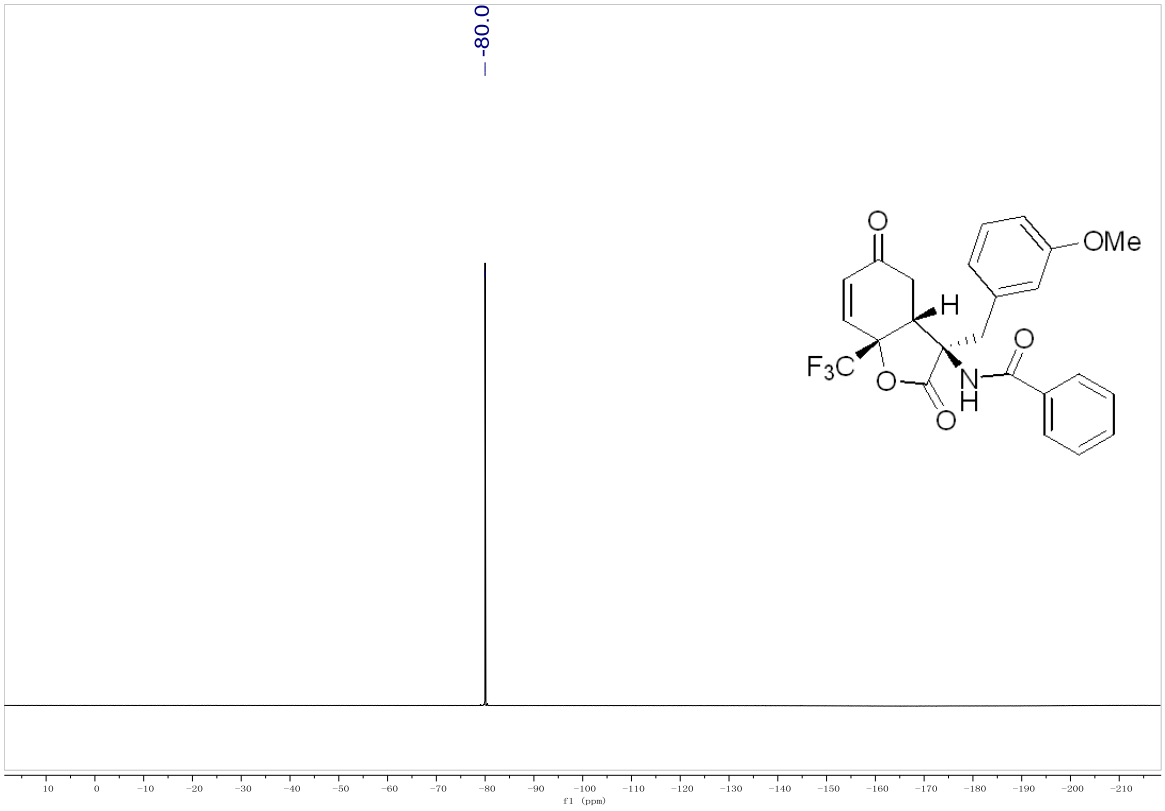
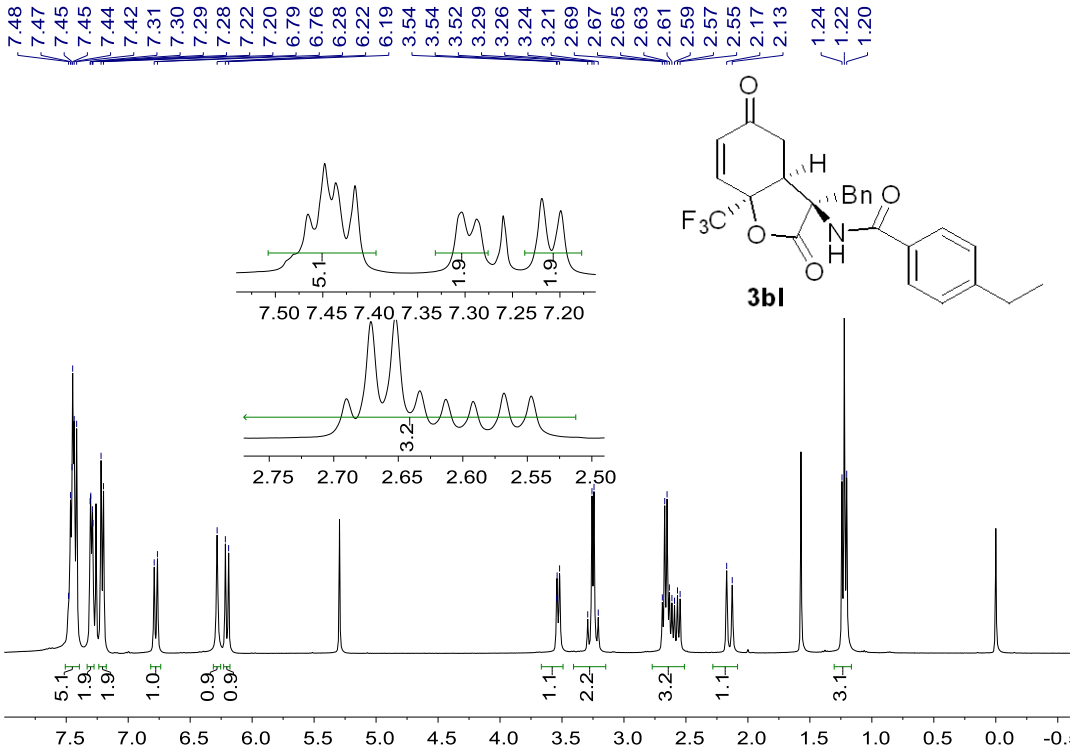
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210

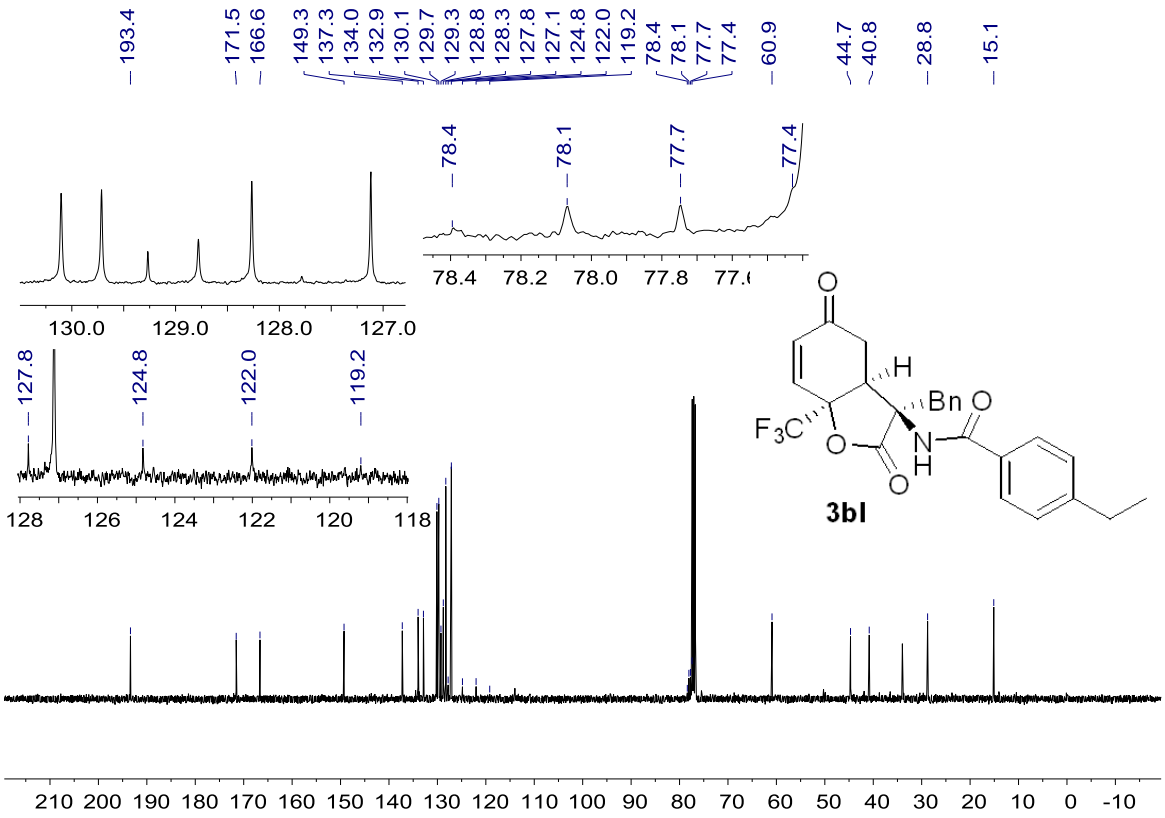
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bk**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bl**

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122.0
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15.1
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78.4
78.2
78.0
77.8
127.8
124.8
122.0
119.2
128
126
124
122
120
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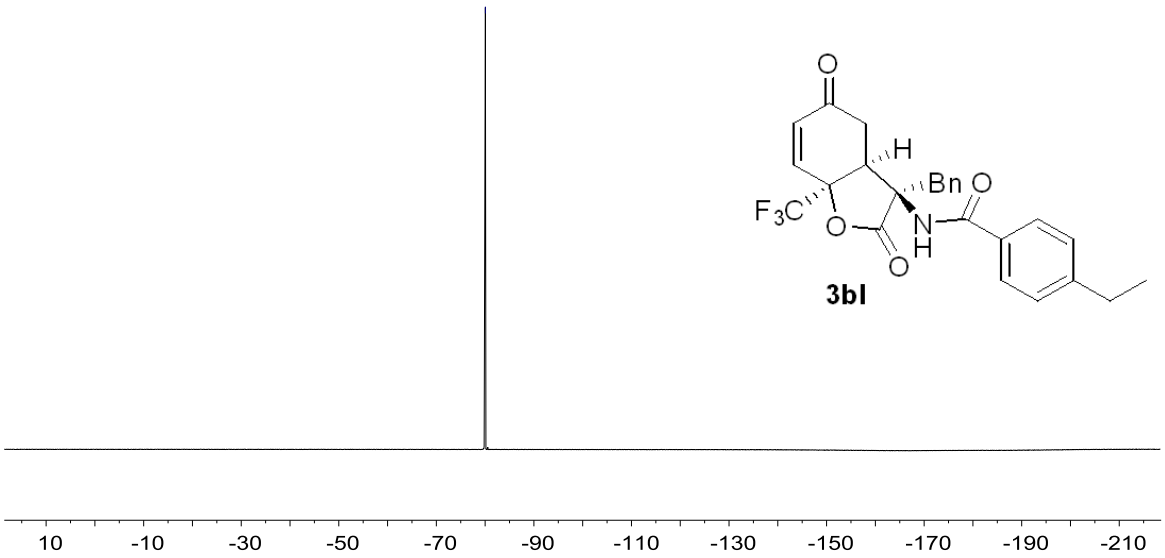
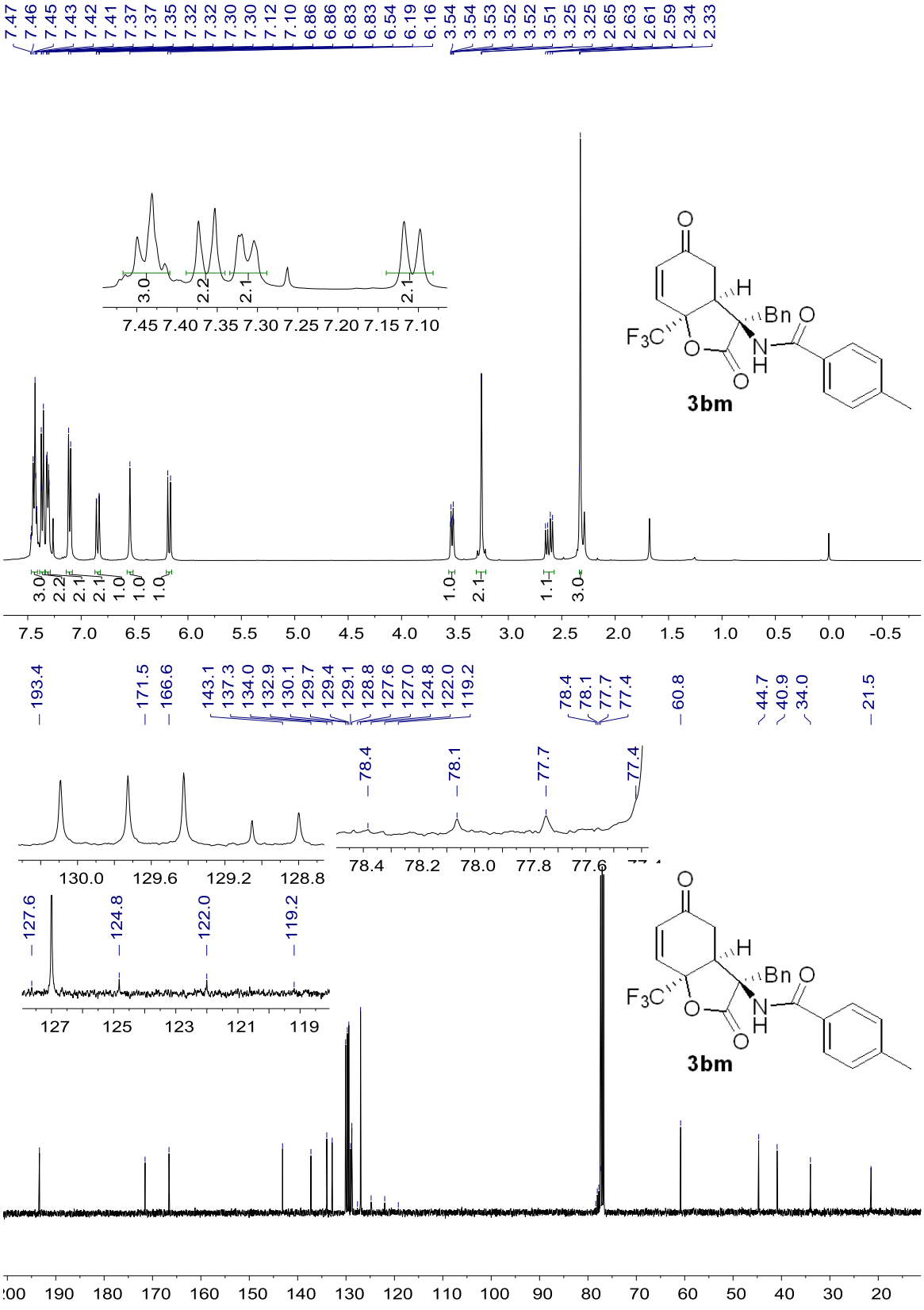
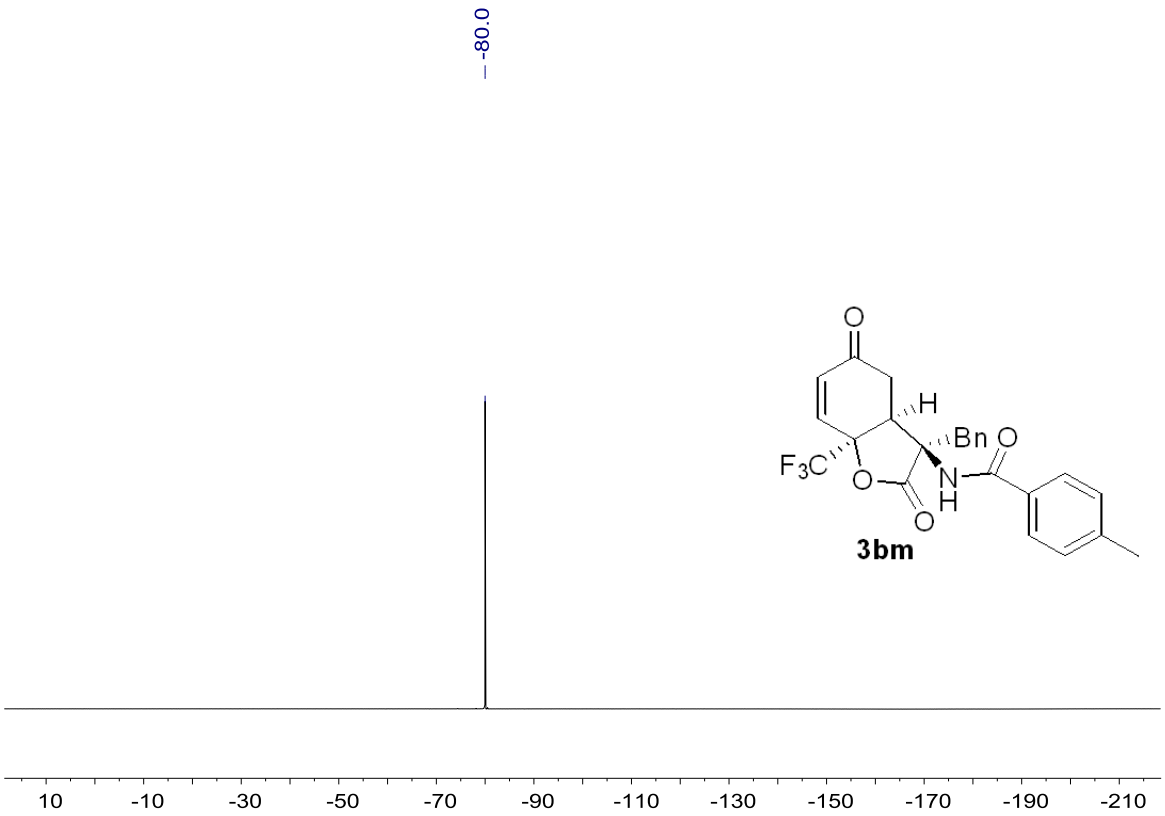
O
F3C
O
N
H
O
O
3bl

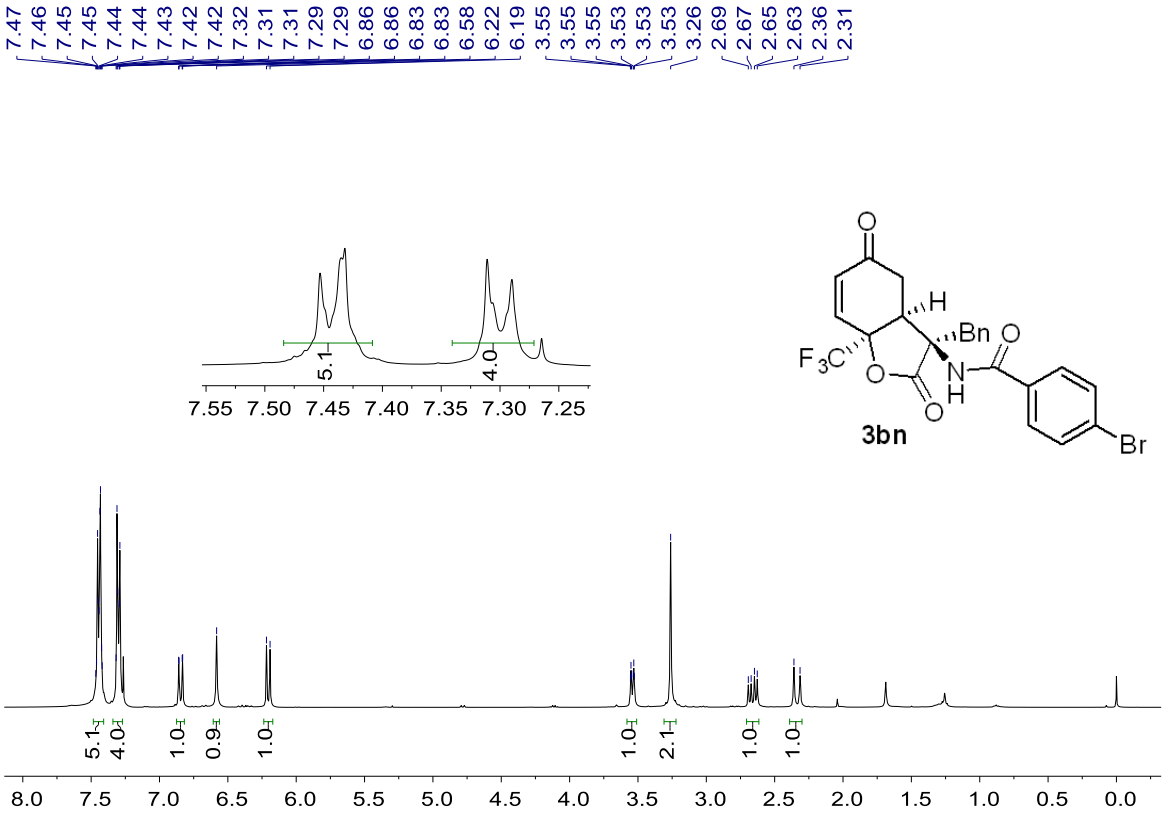

-80.1
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
H
Bn
O
F3C
O
N
H
O
O
3bl

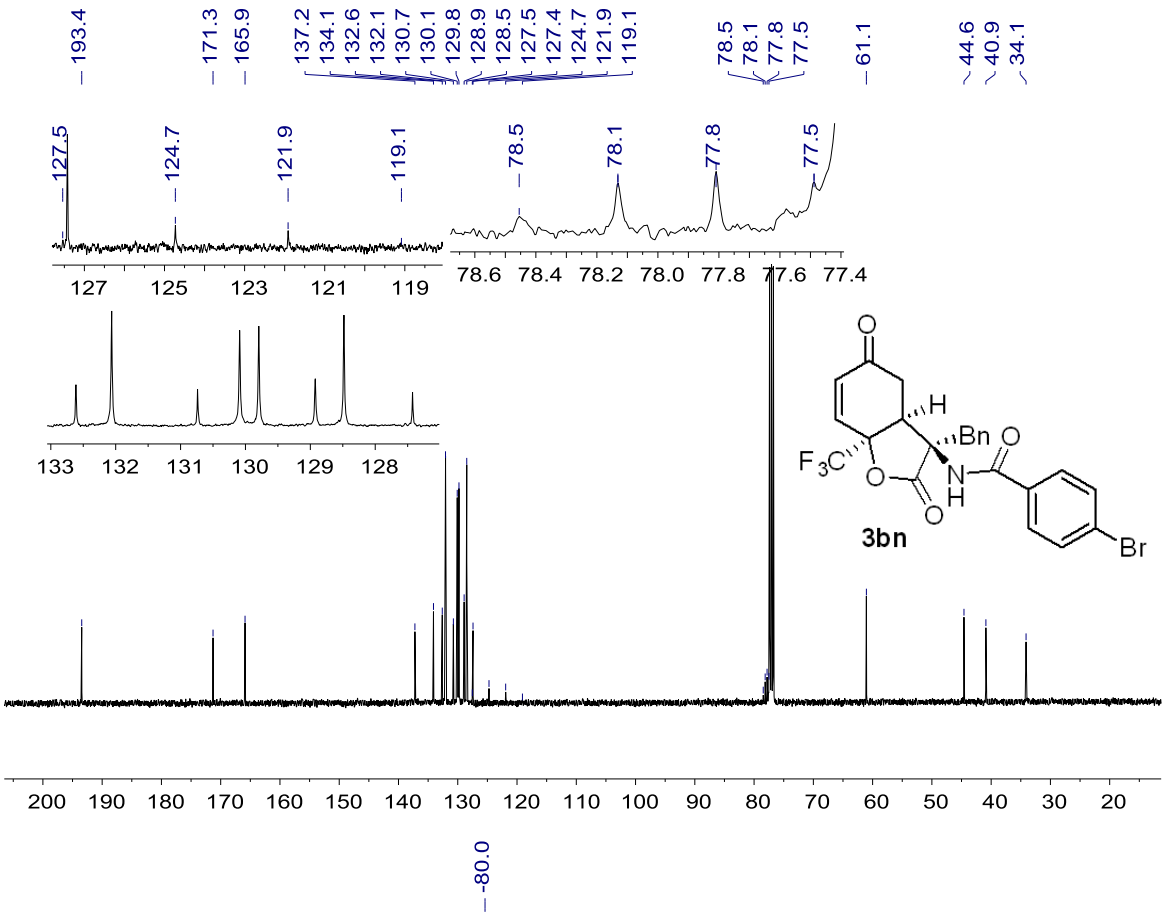
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bm**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bn**

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77.6
77.4
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132
131
130
129
128
O
H
Bn
O
F3C
O
N
H
O
3bn
Br
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90
80
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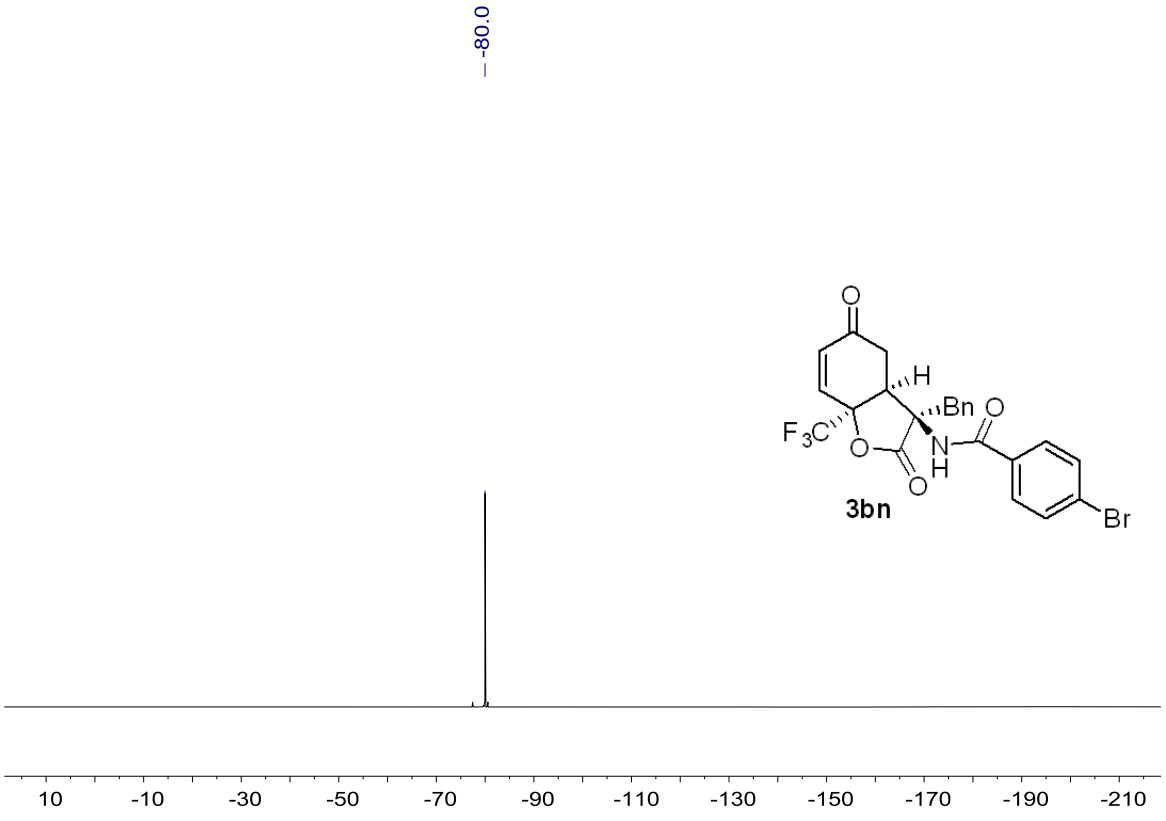
30
20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O
N
H
O
3bn
Br
10
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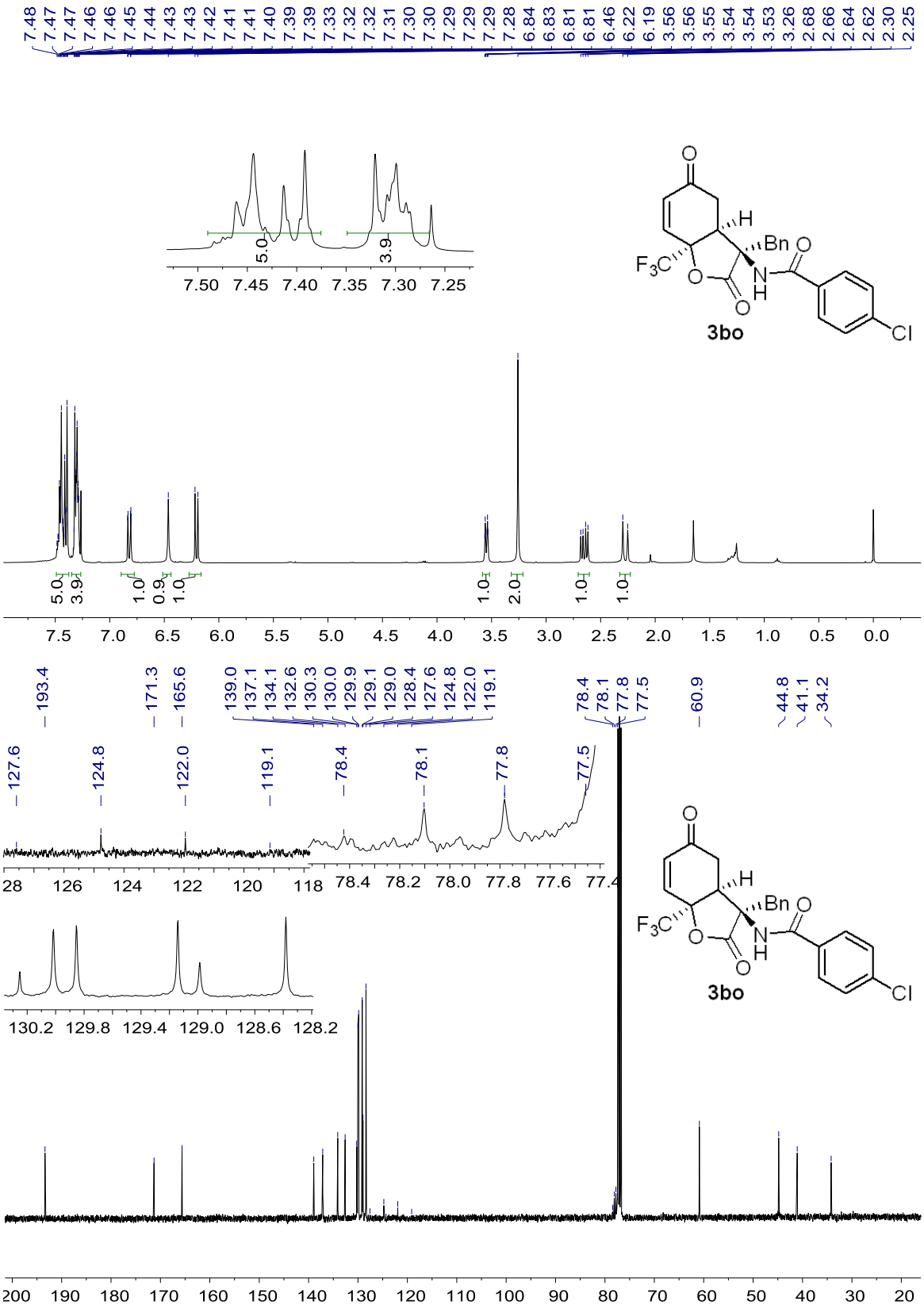
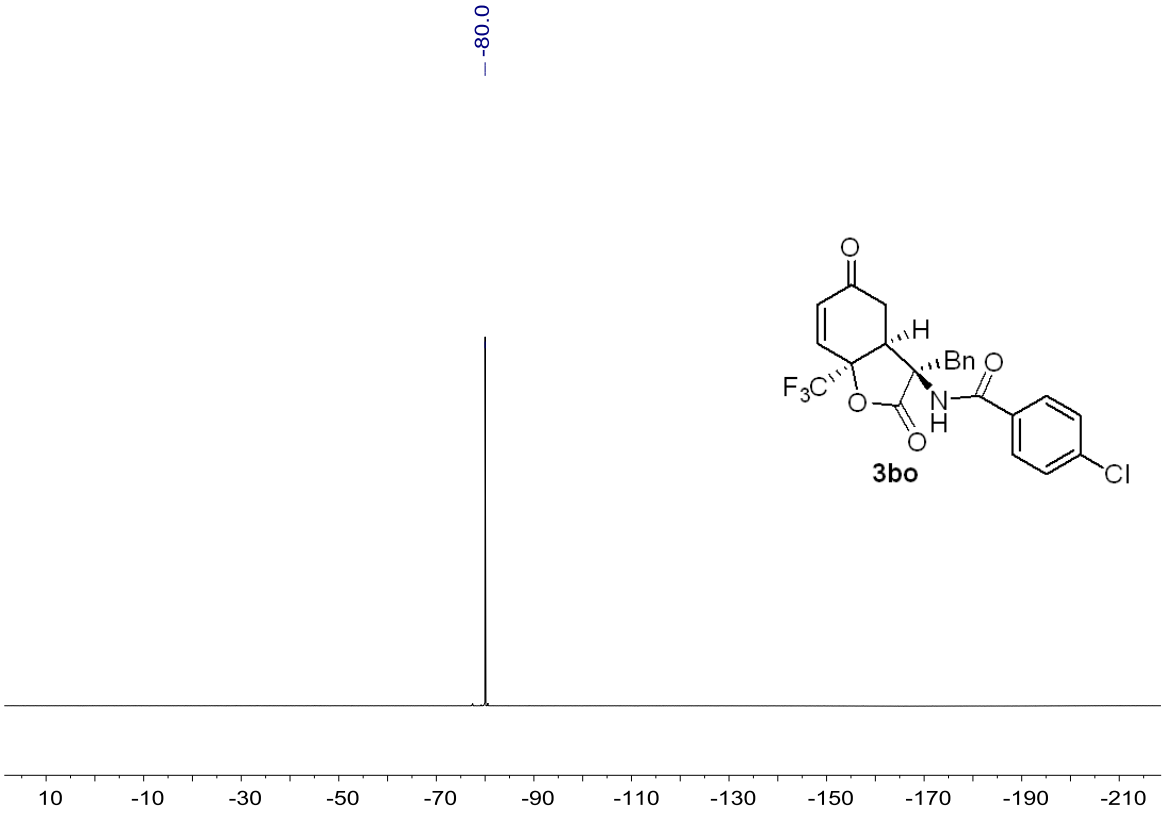
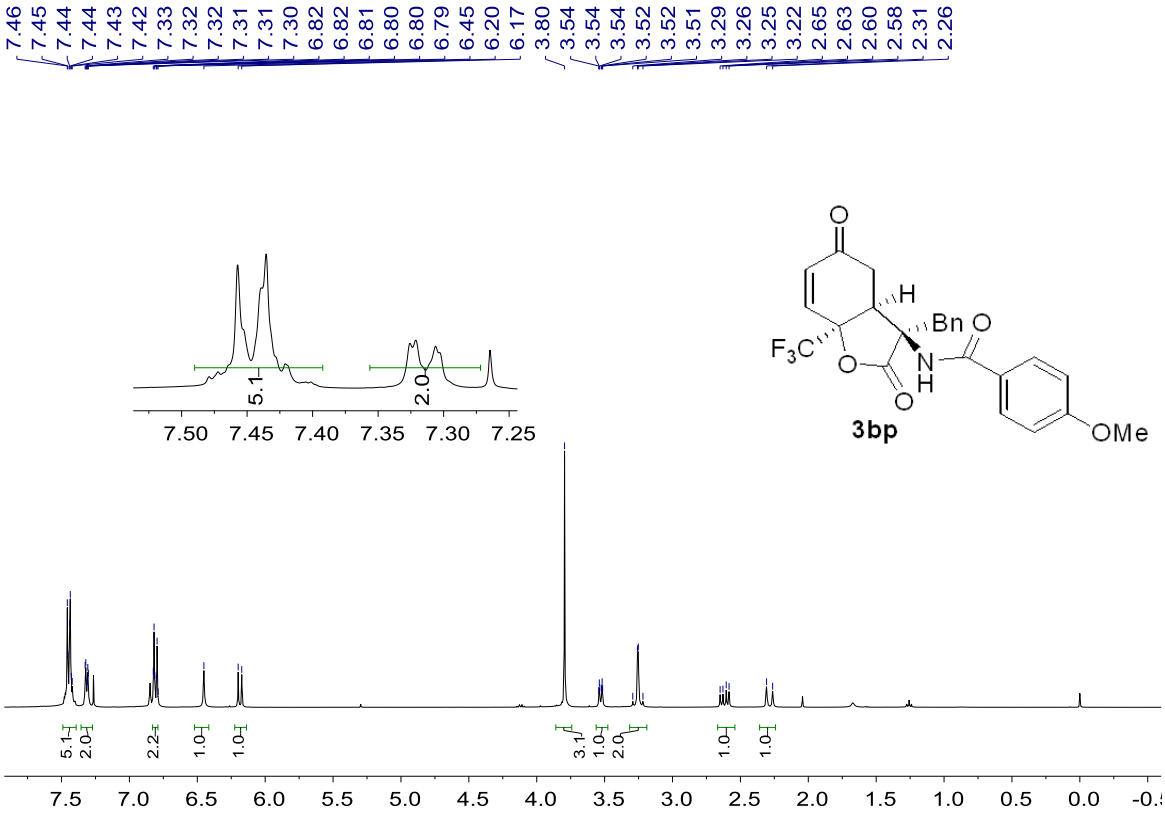
-70
-90
-110
-130
-150
-170
-190
-210

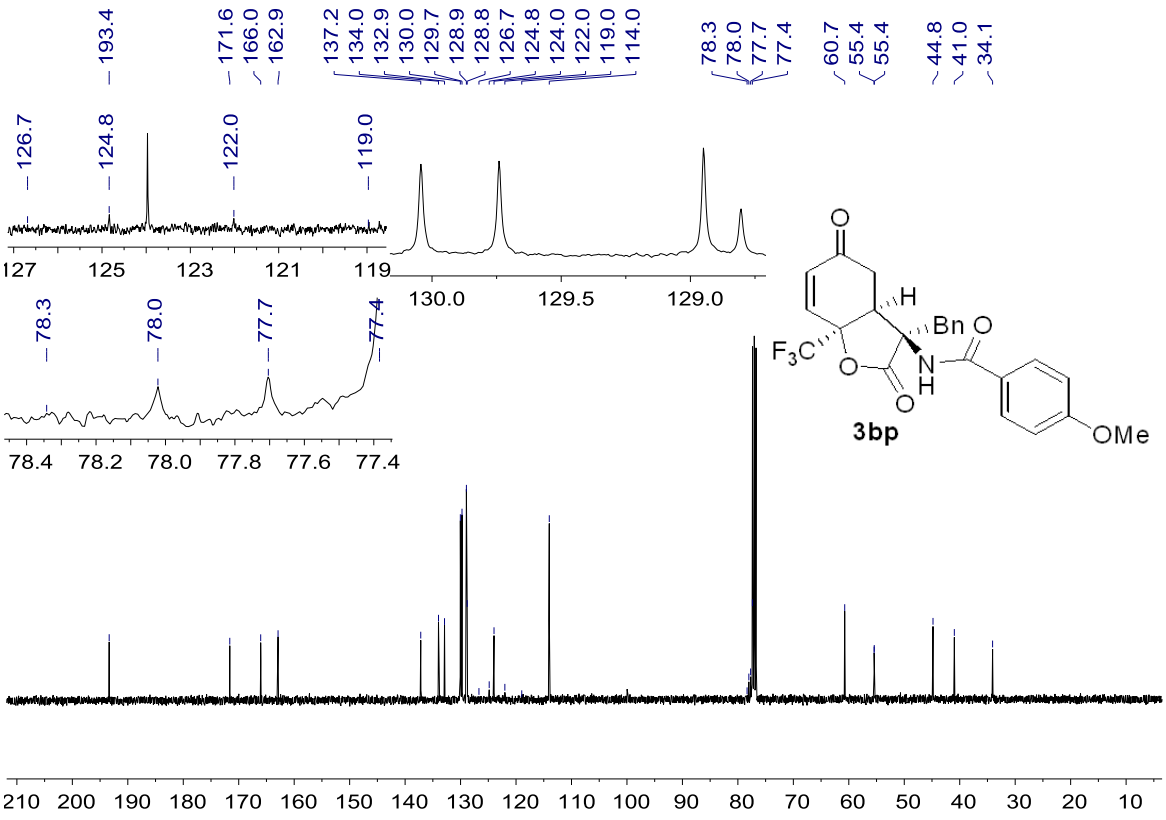
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bo**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bp**

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122.0
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129.0
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78.0
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78.0
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77.6
77.4
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H
Bn
O
F3C
O
N
H
O
3bp
OMe
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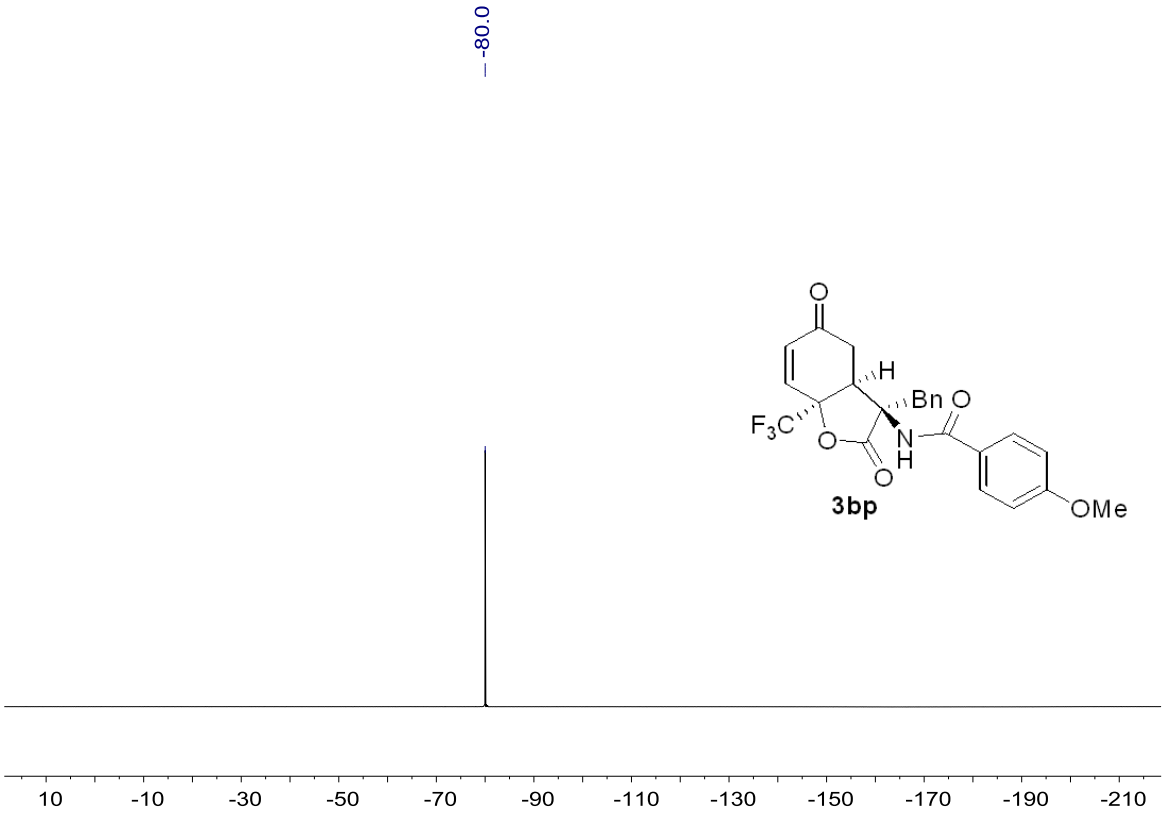
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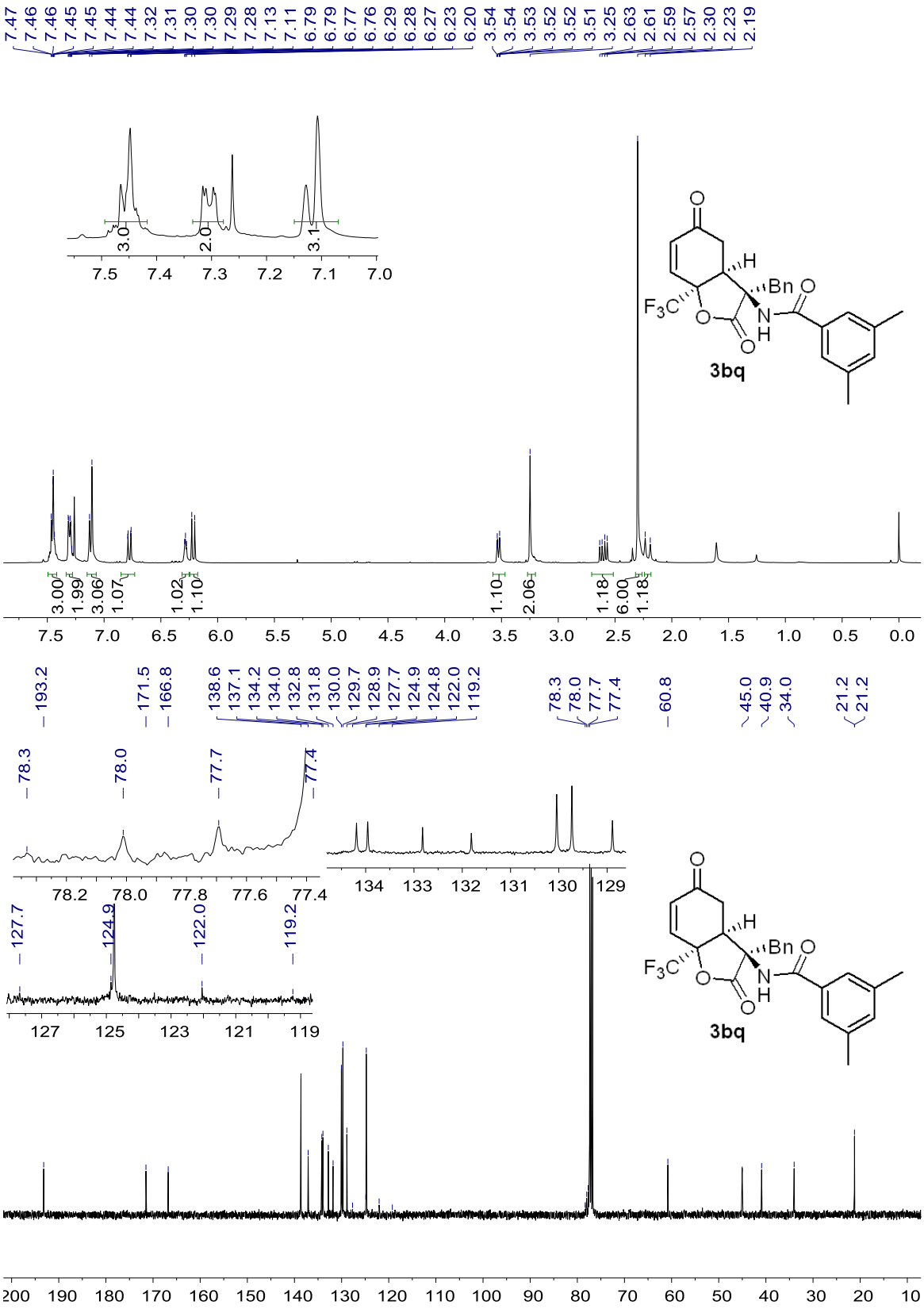
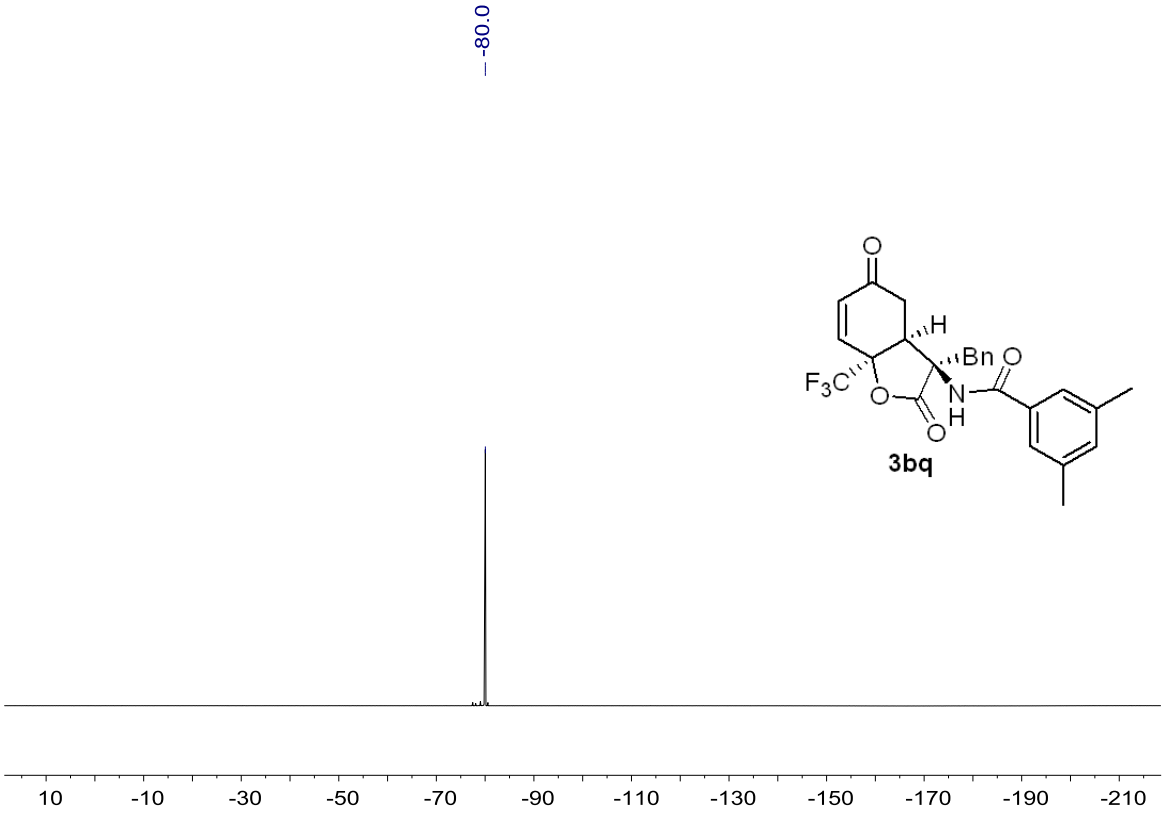
N
H
O
3bp
OMe
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210

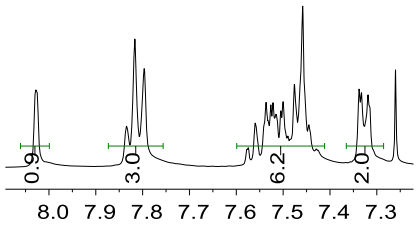
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bq**

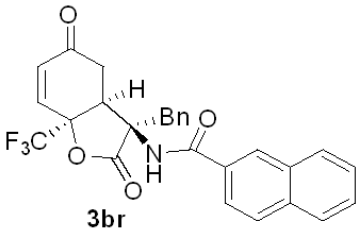




3bq

^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$,compound **3br**





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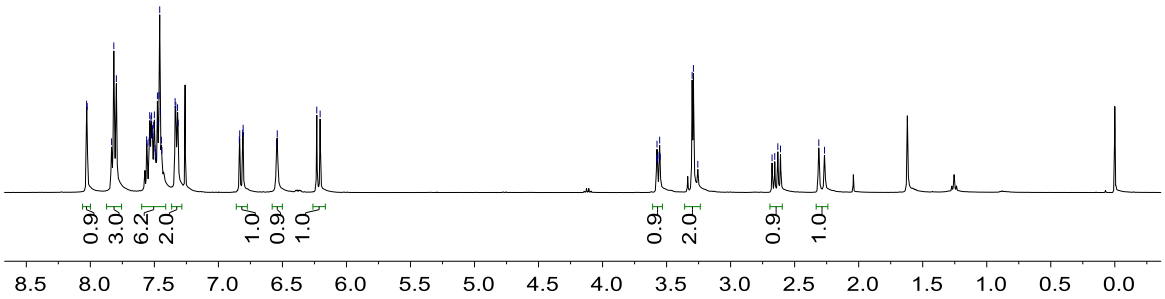

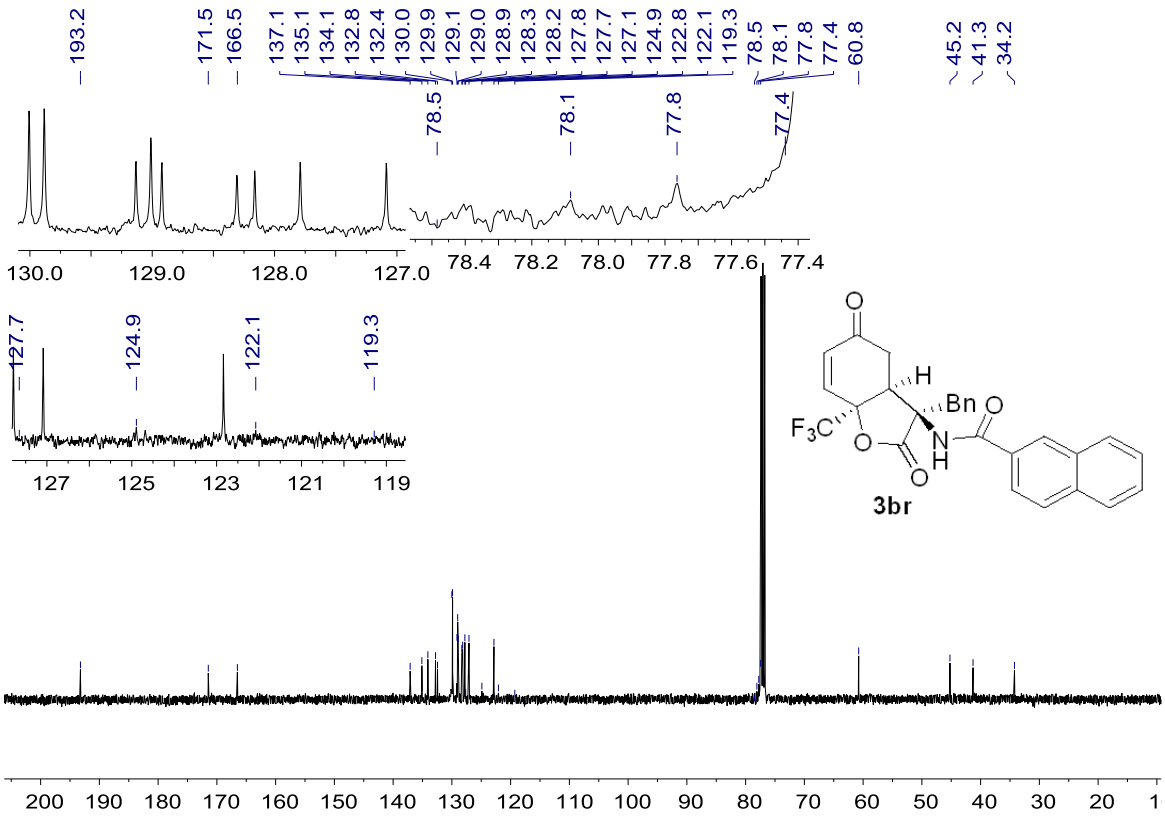
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127.7
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77.4
77.4
60.8
45.2
41.3
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77.8
77.6
77.4
127.7
124.9
122.1
119.3
127
125
123
121
119
H
Bn
O
F3C
O
N
H
O
O
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30
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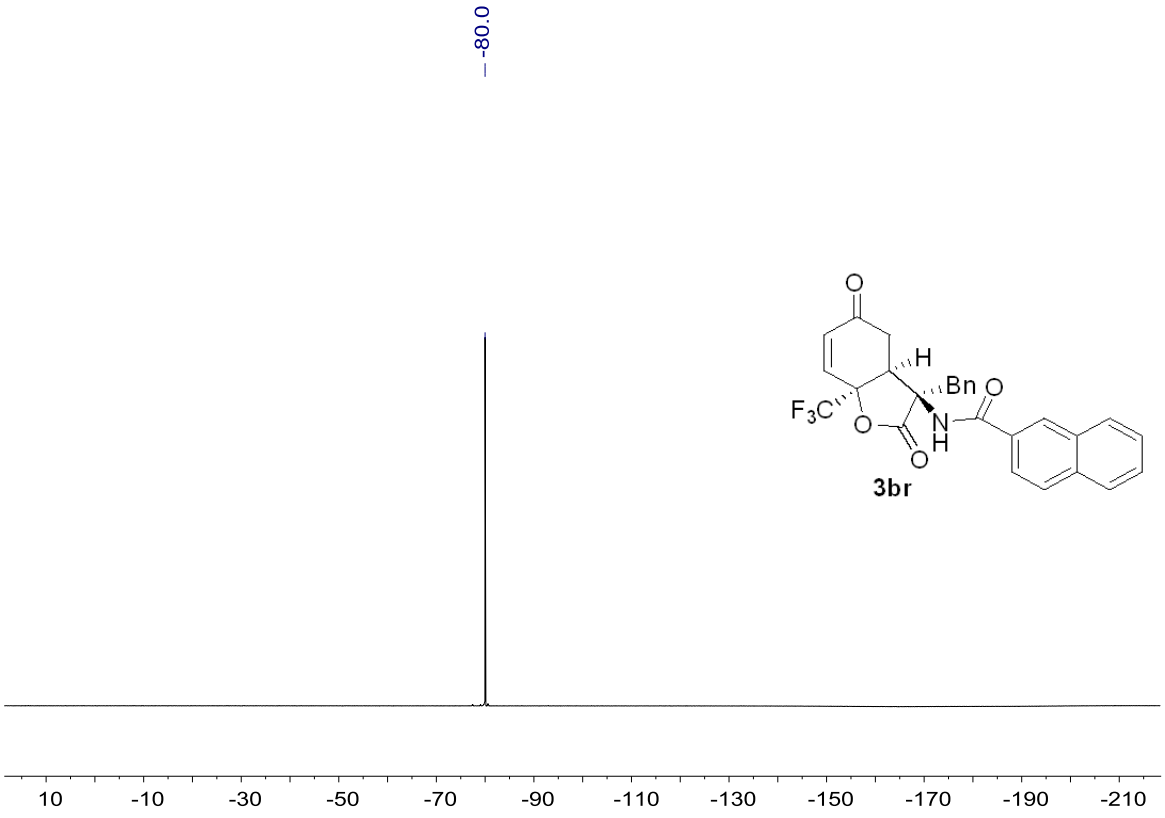
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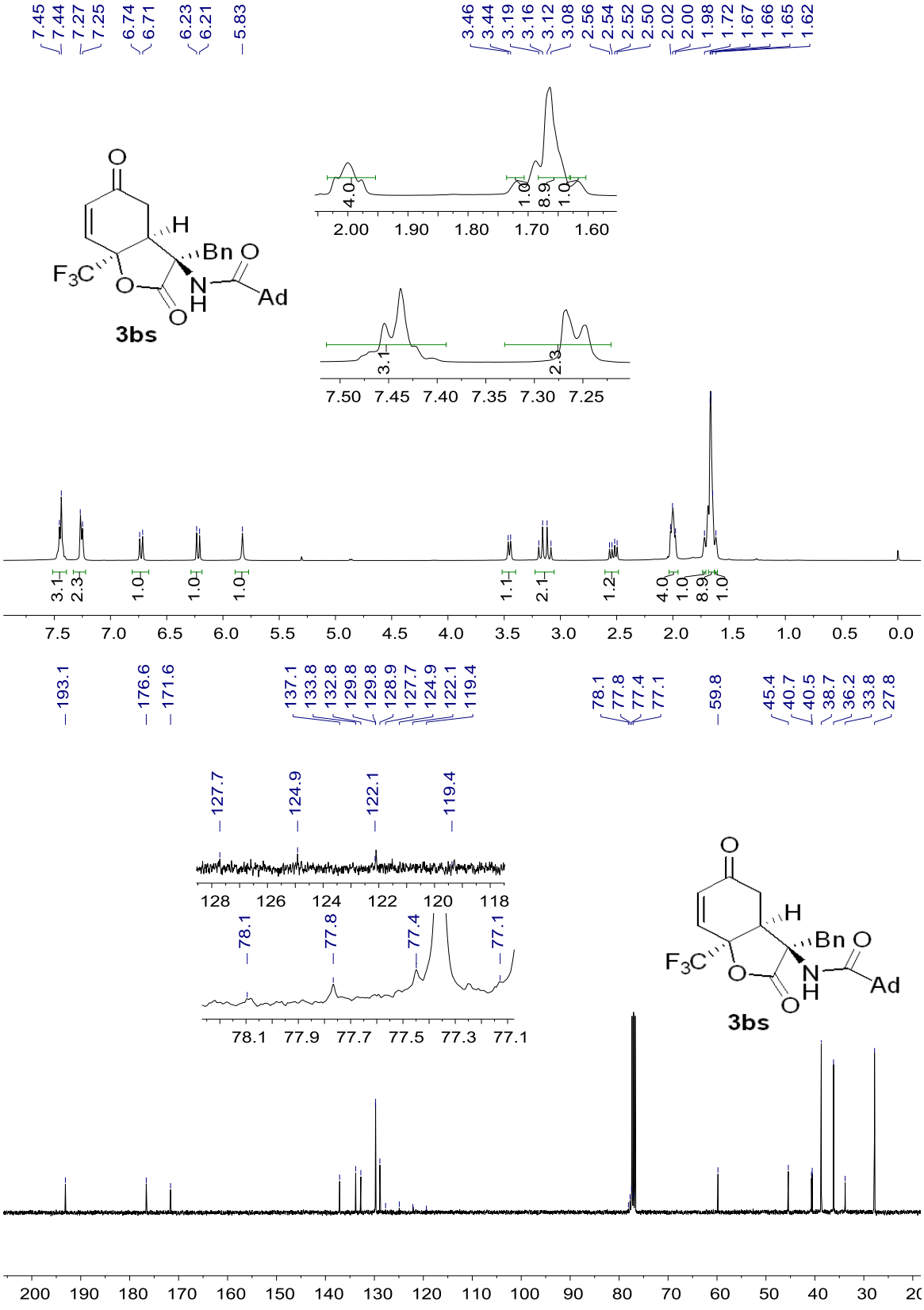
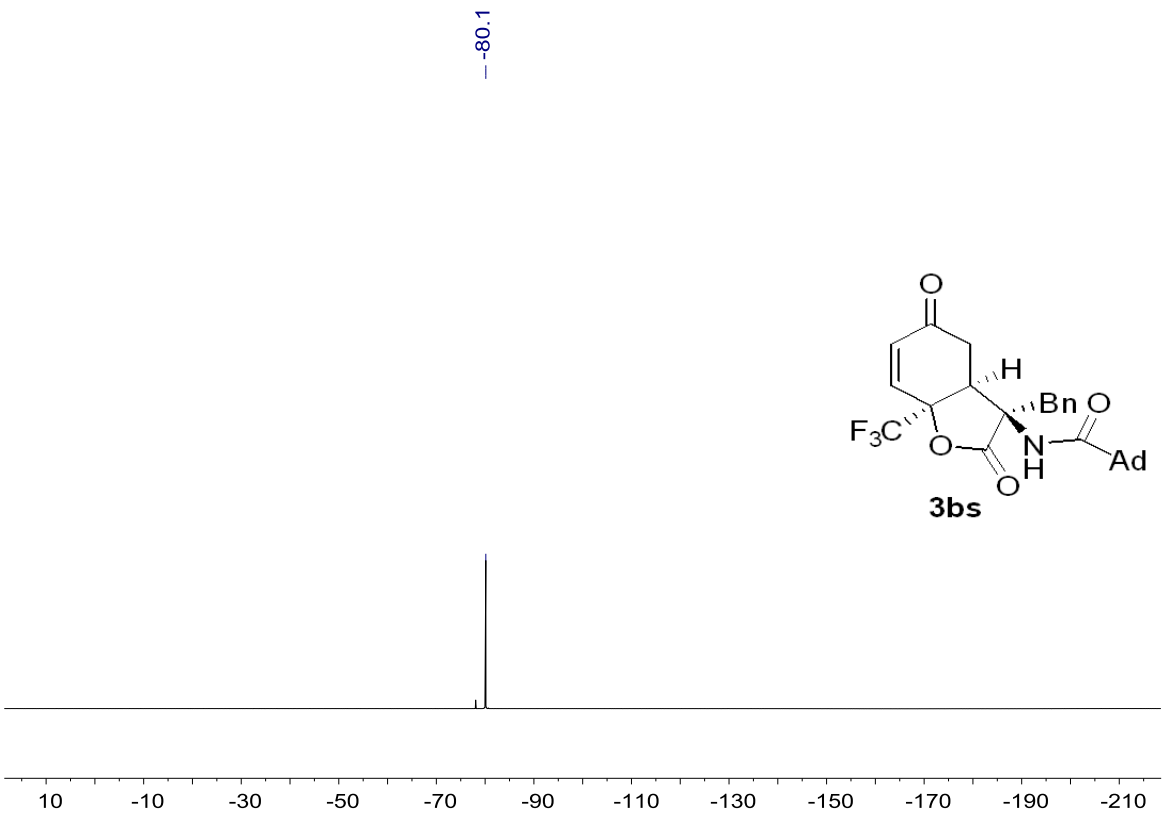
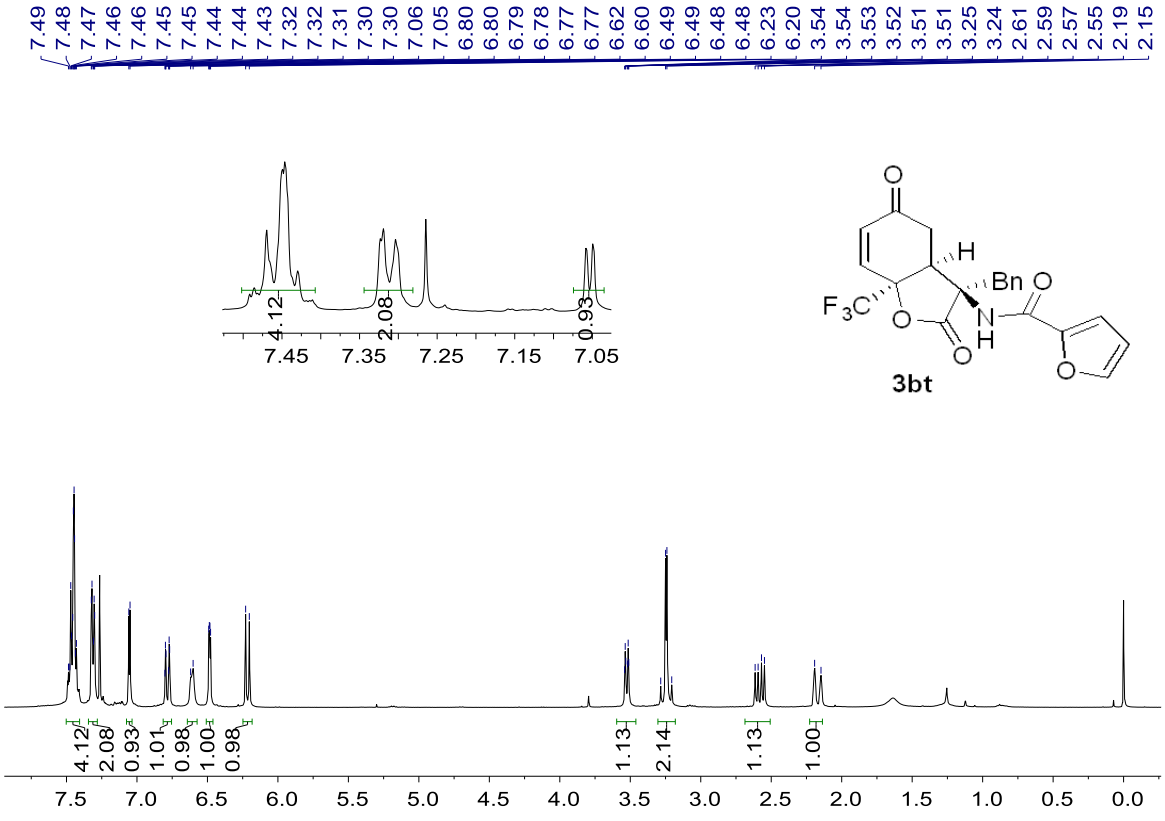
Bn
O
F3C
O
N
H
O
O
3br
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210

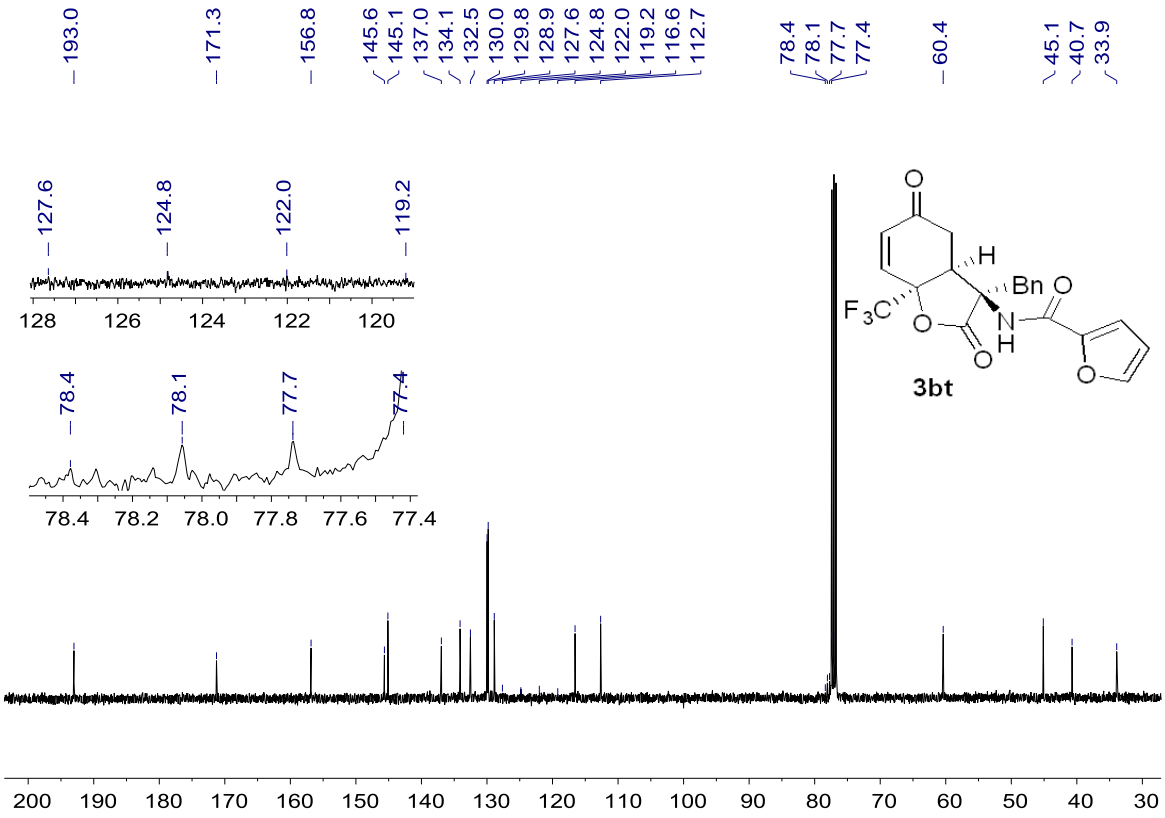
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bs**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bt**

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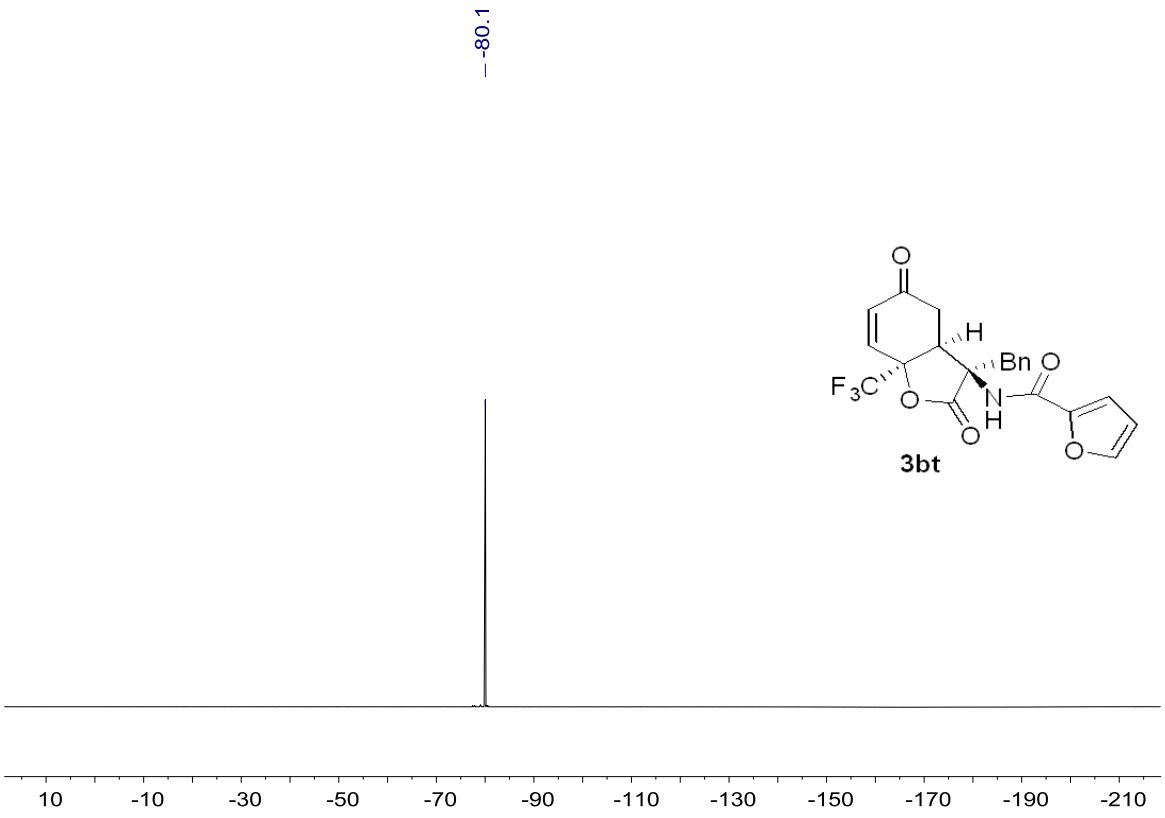
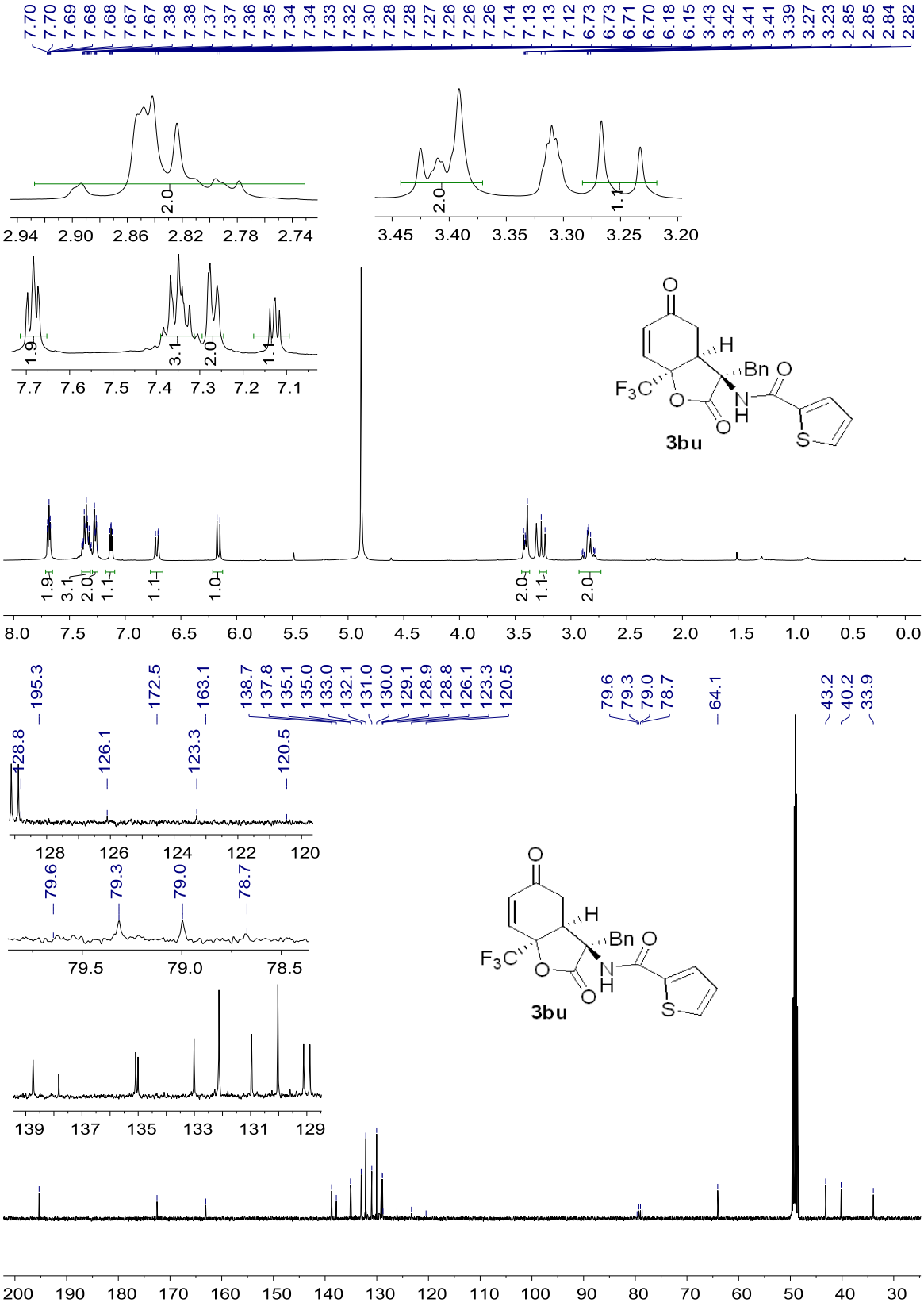
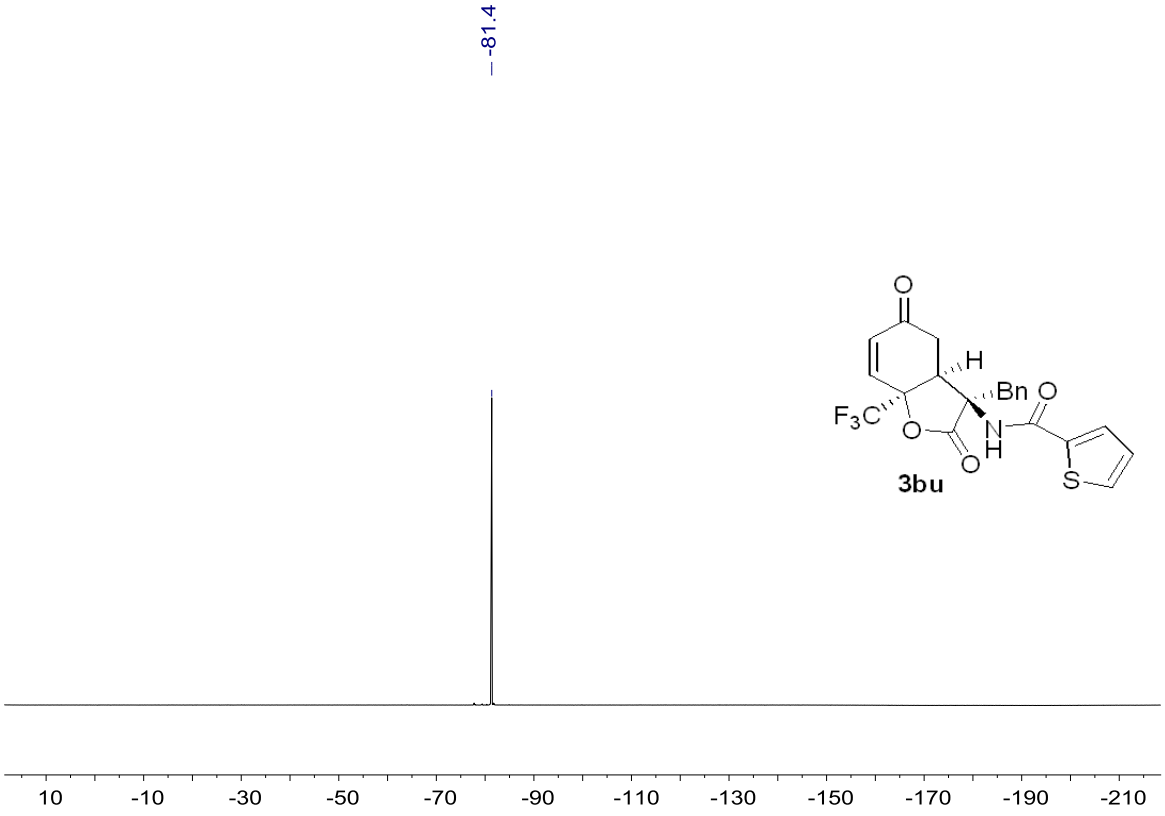
45.1
40.7
33.9
3bt

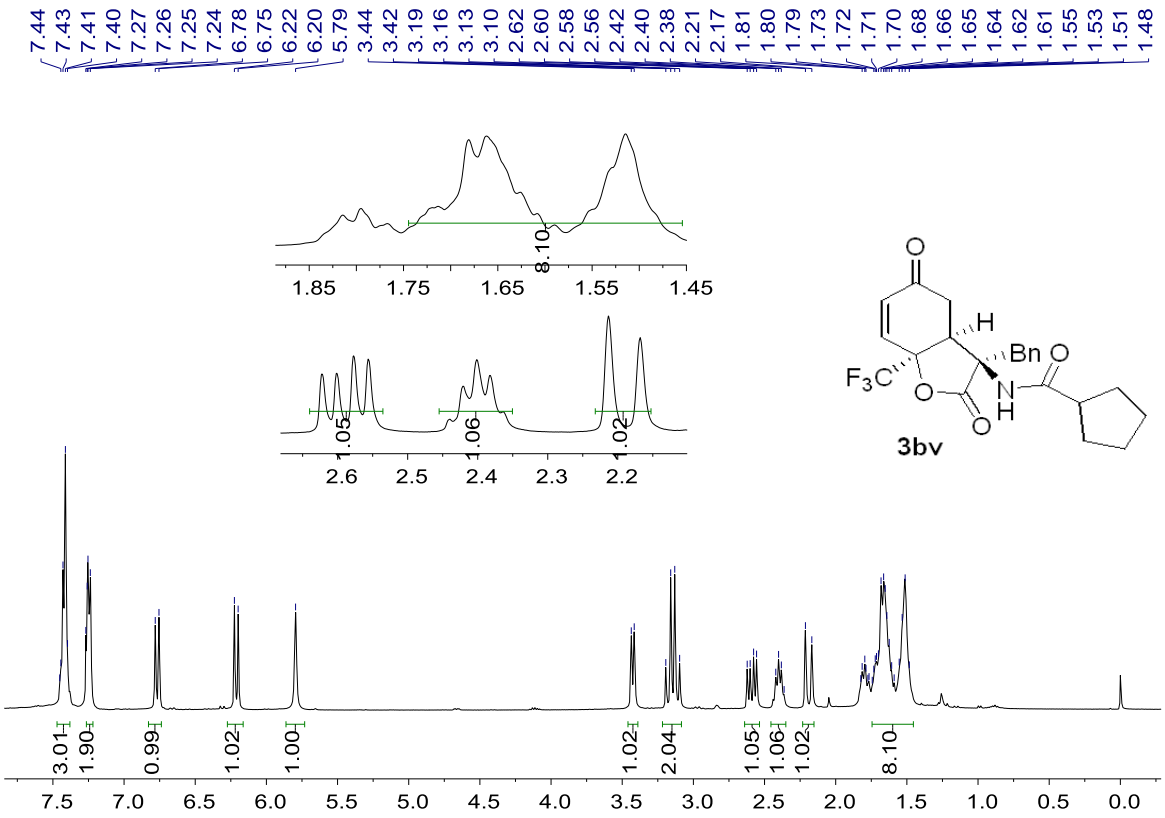

-80.1
3bt

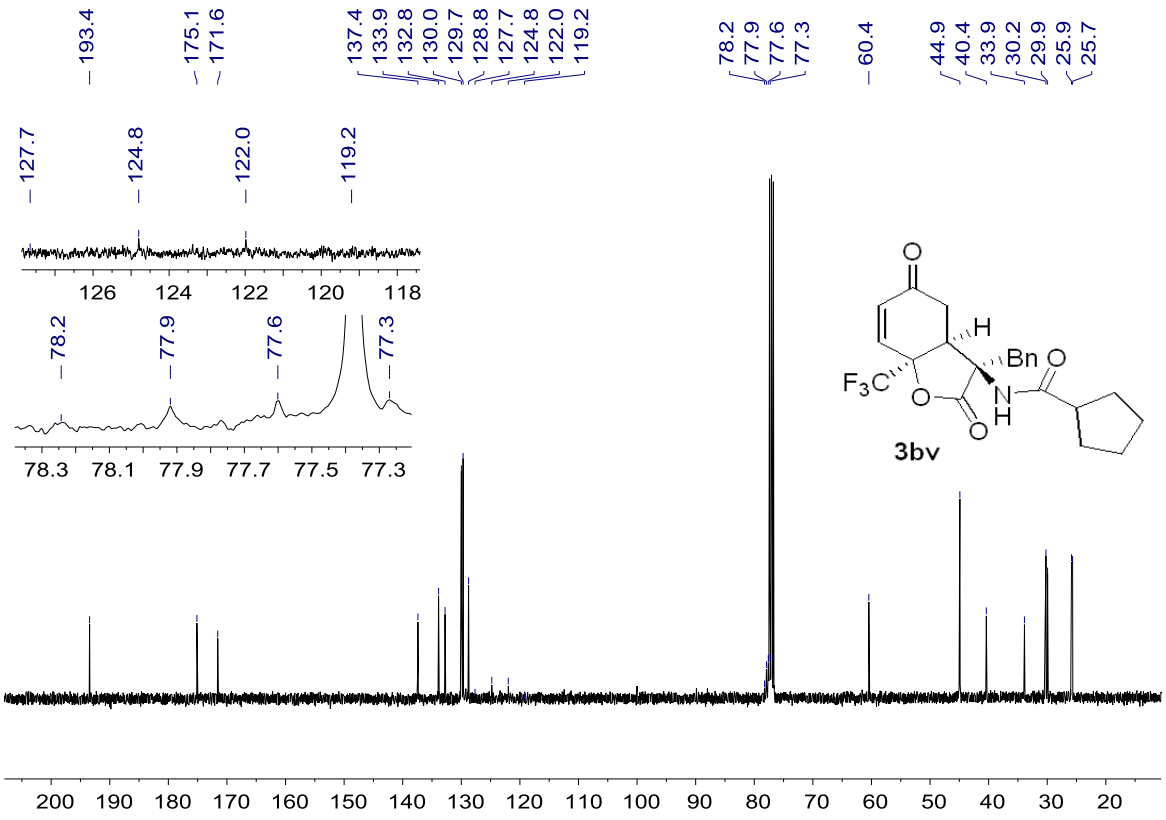
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), MeOD, compound **3bu**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bv**

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77.9
77.6
77.3
60.4
44.9
40.4
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30.2
29.9
25.9
25.7
127.7
124.8
122.0
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122
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78.2
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77.9
77.7
77.5
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O
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Bn
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F3C
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H
O
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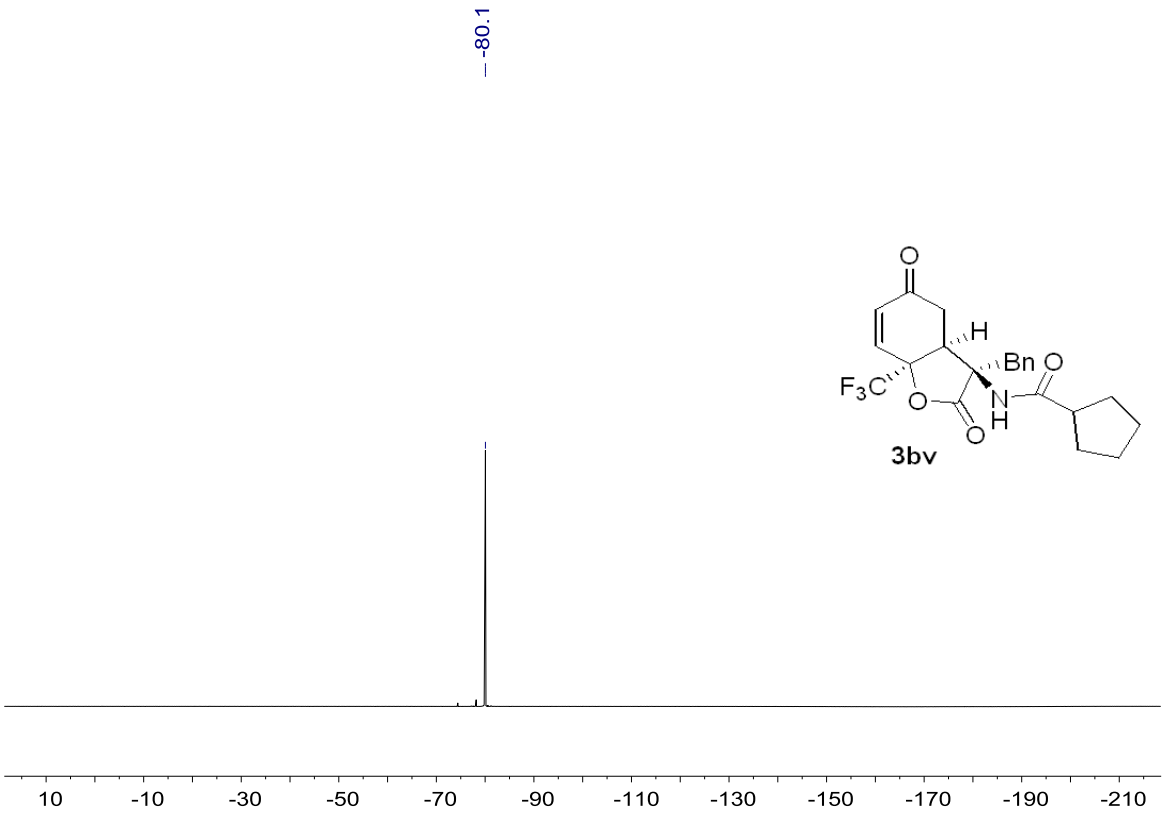
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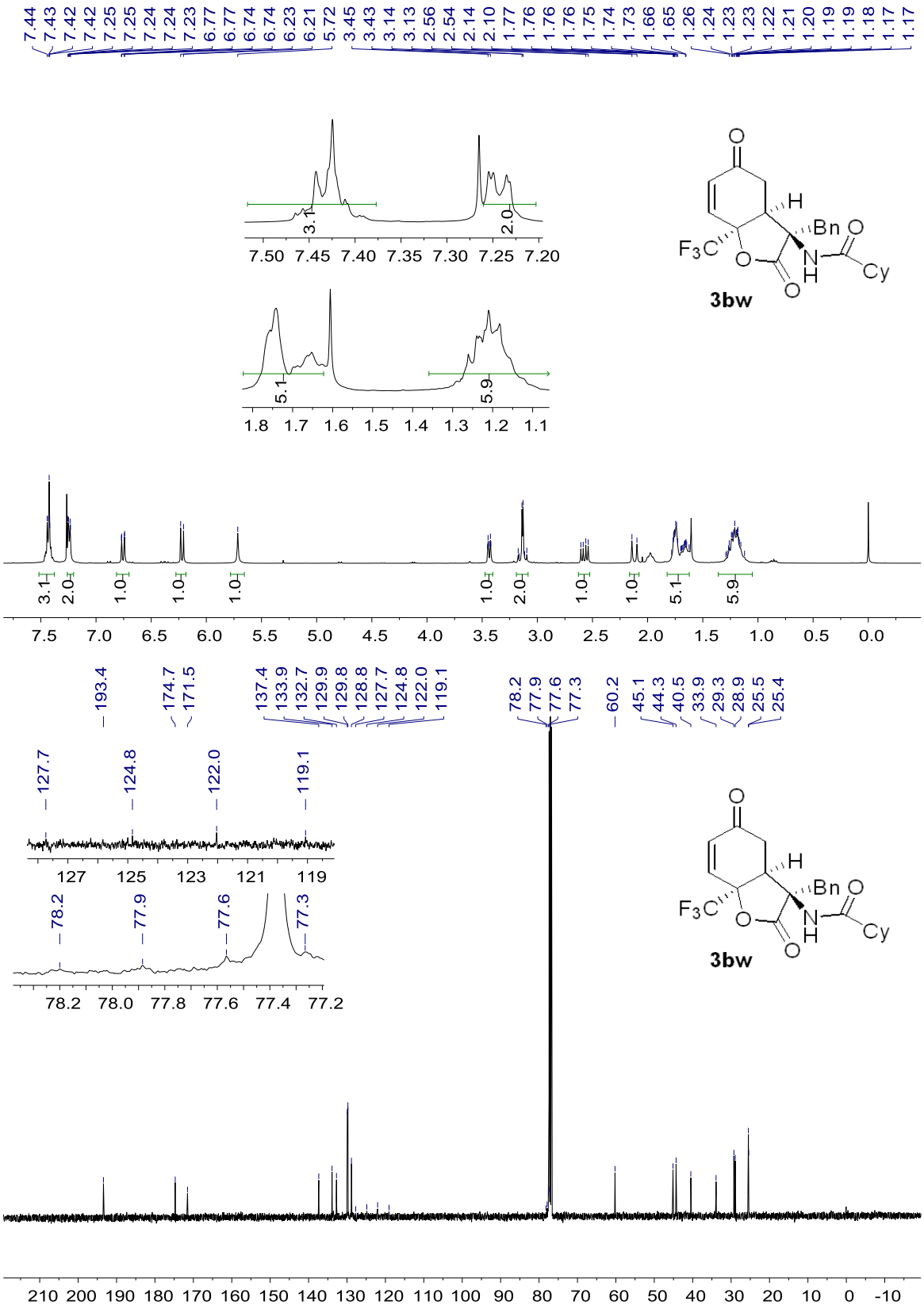
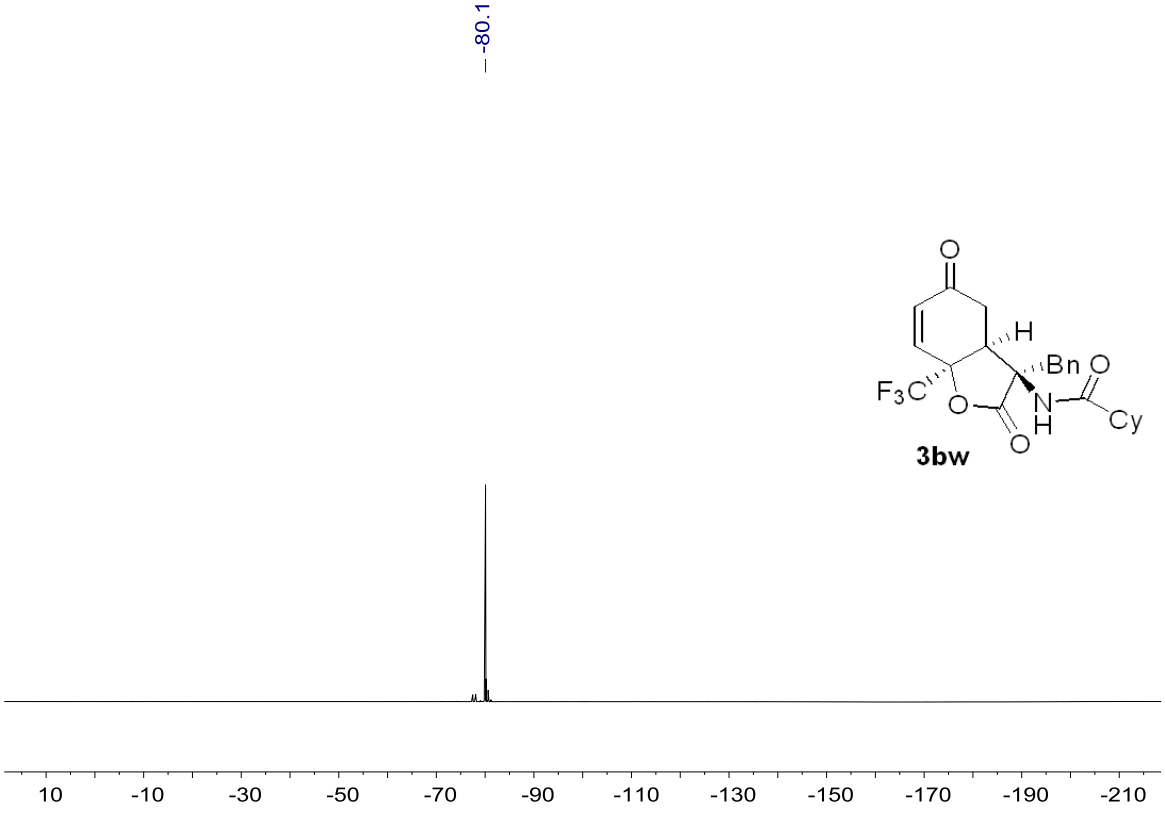
H
Bn
O
F3C
O
N
H
O
3bv
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210

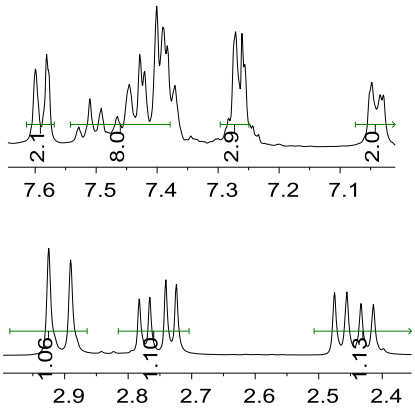
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3bw**

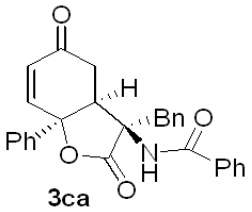




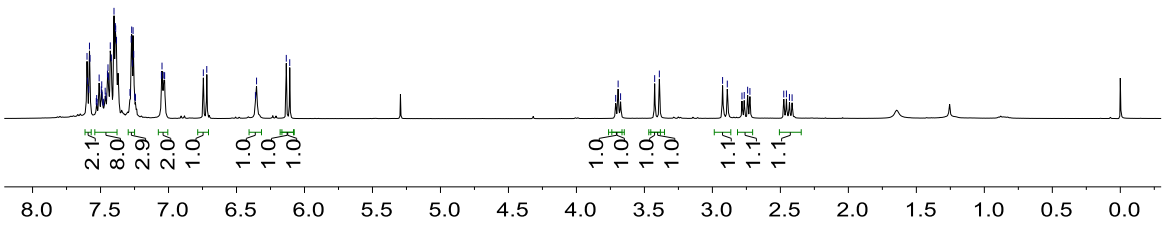
3bw

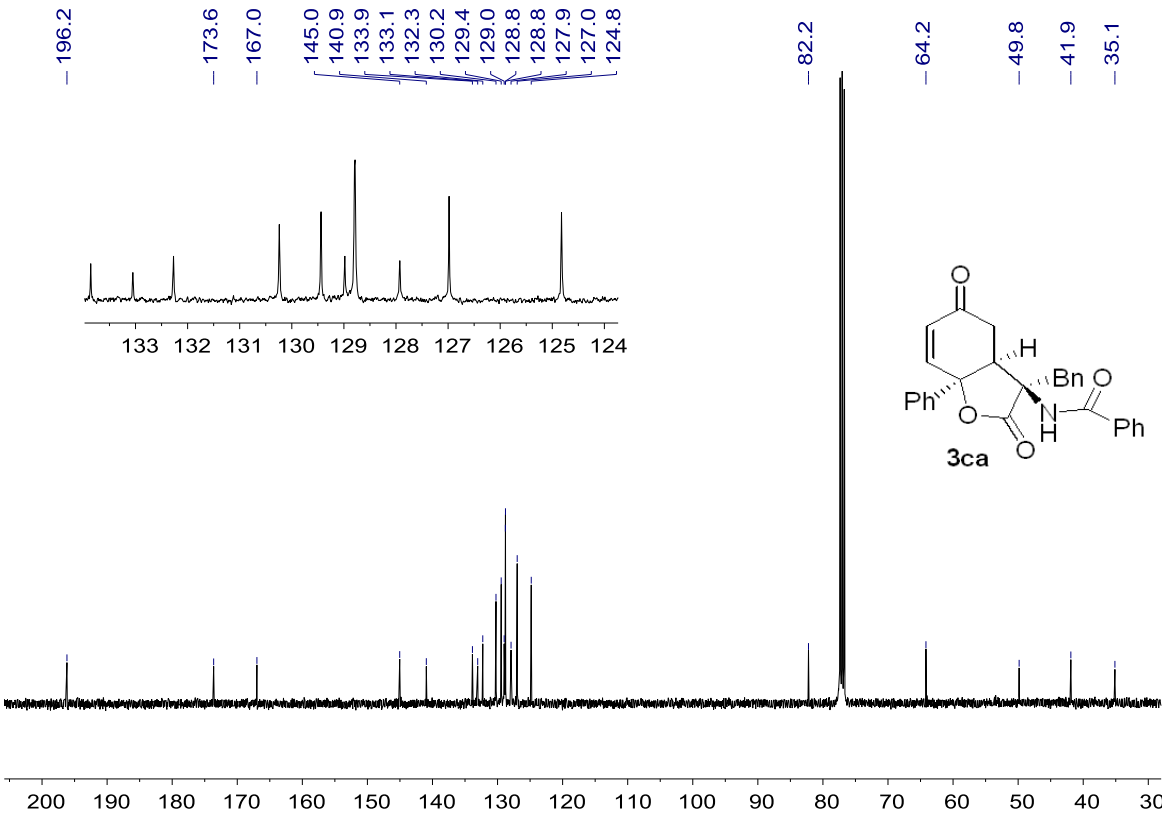
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **3ca**



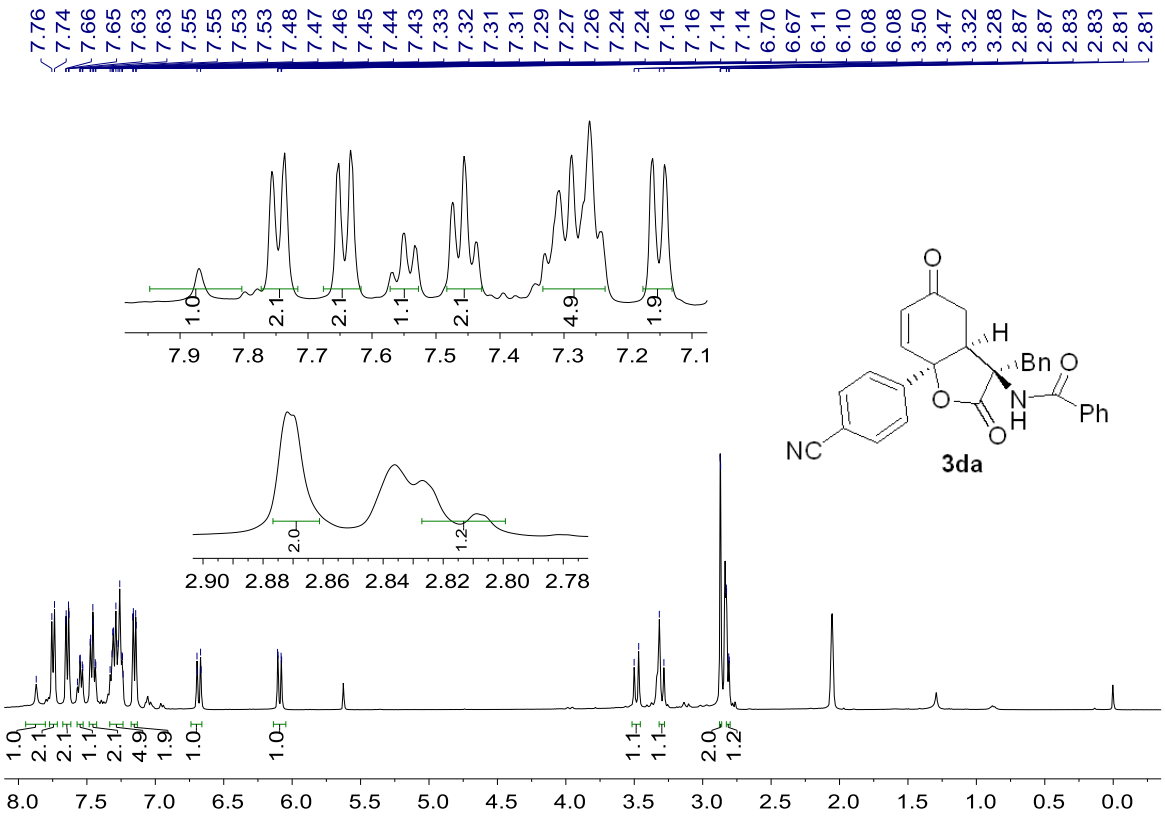


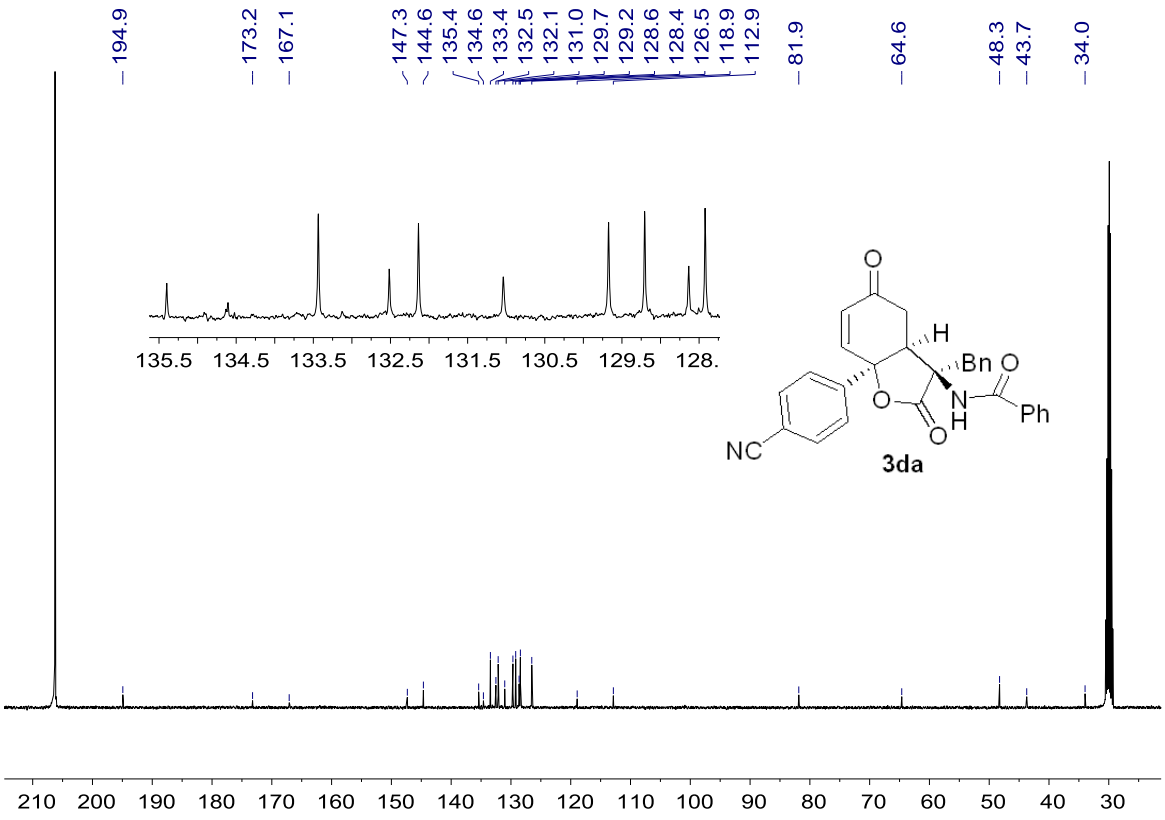
3ca



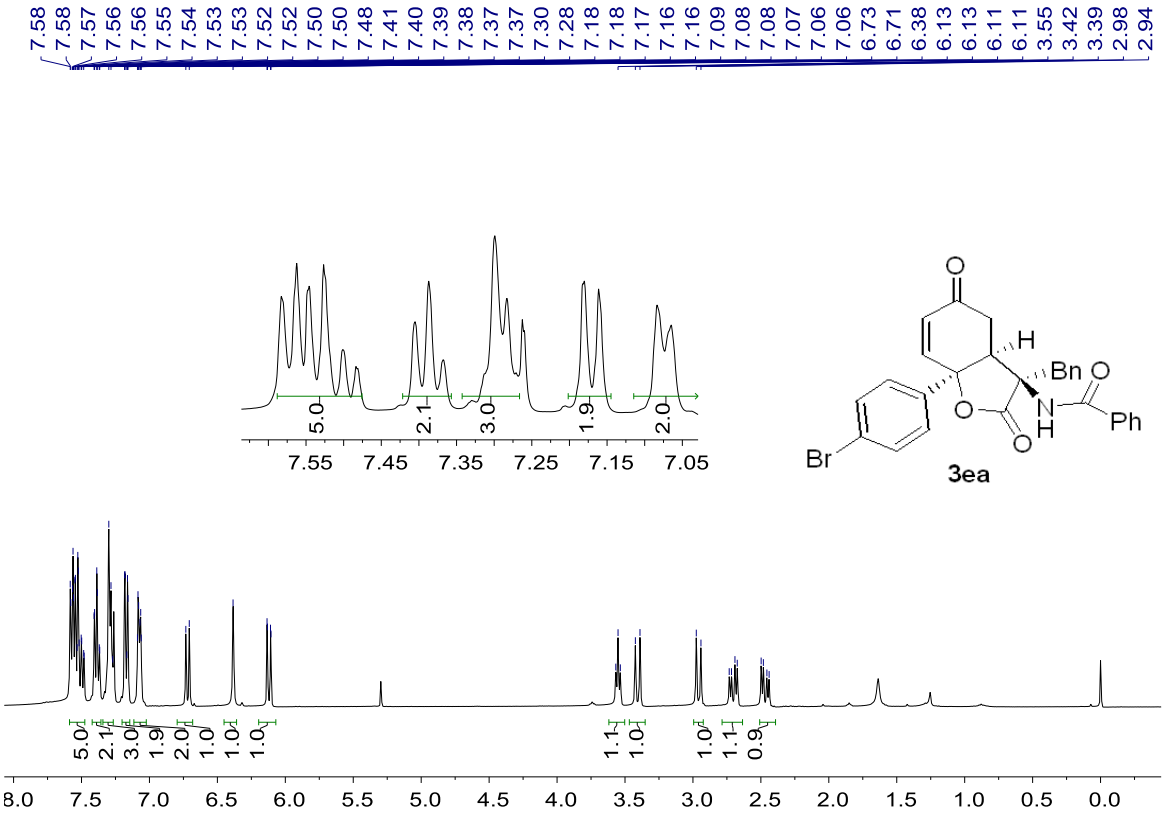


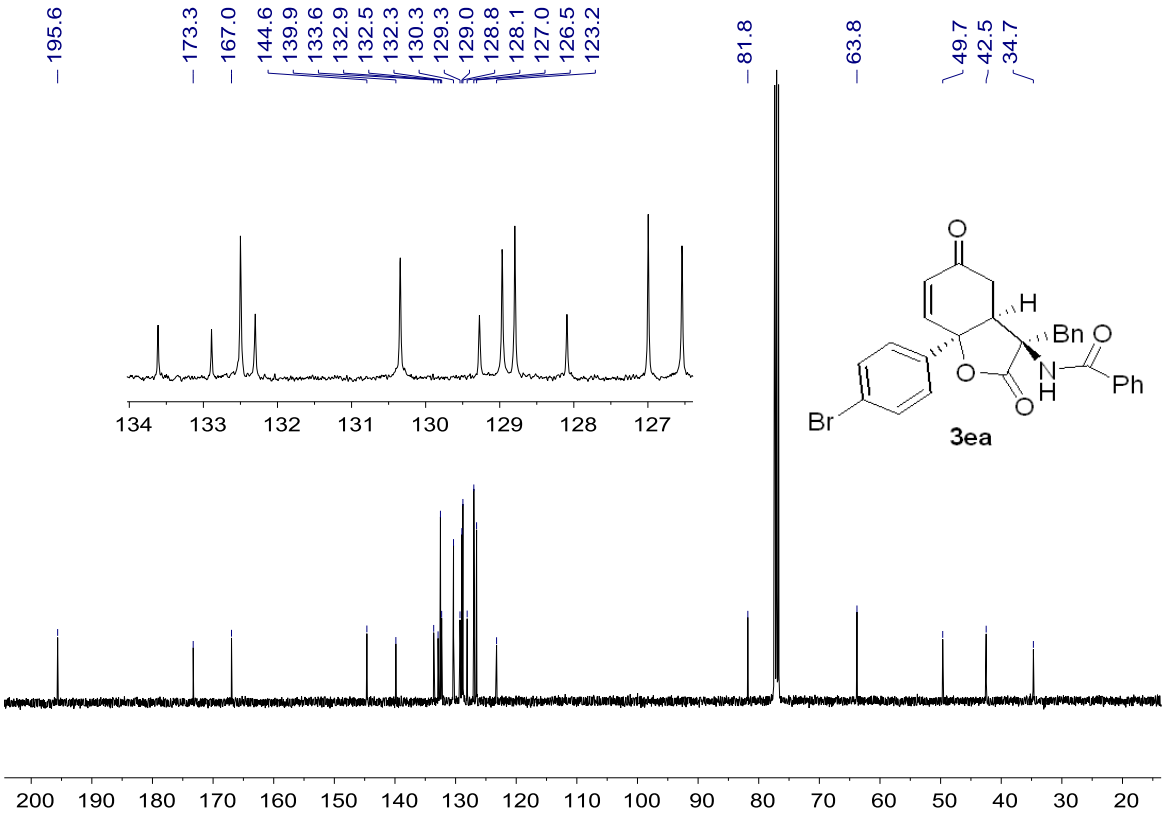
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), Acetone, compound **3da**



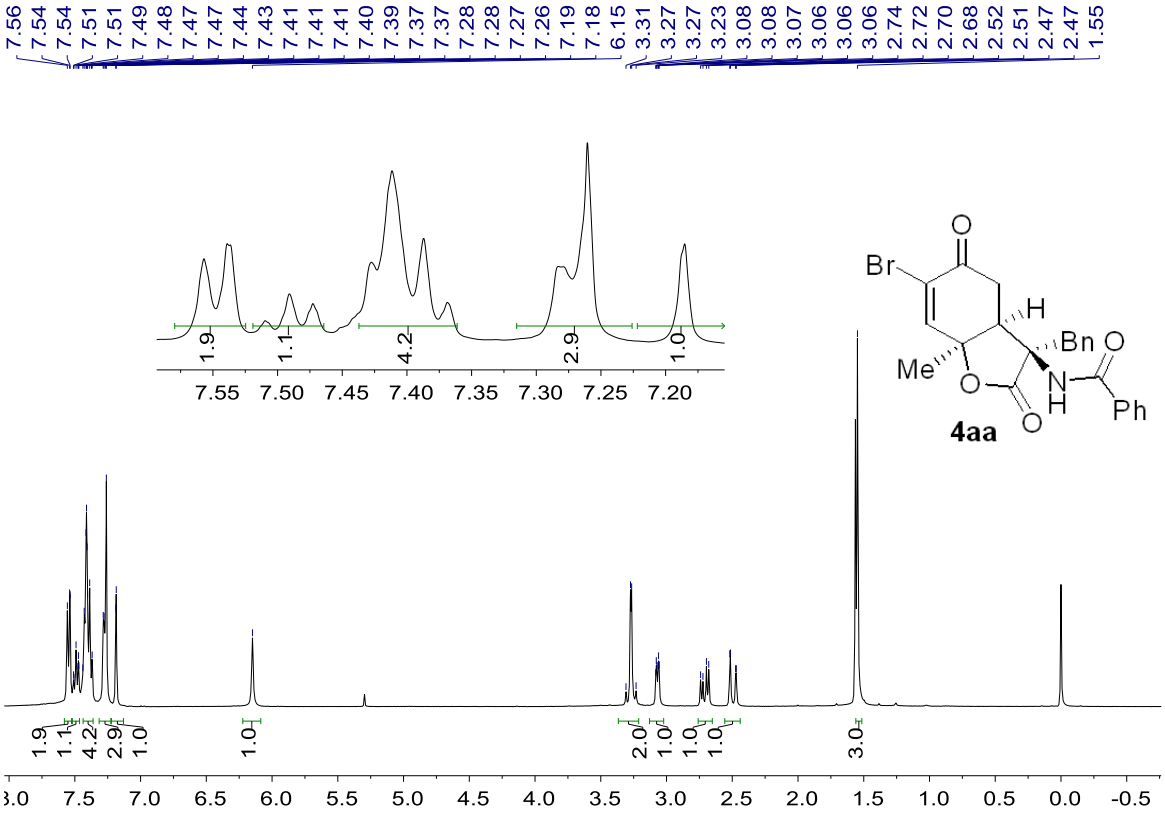


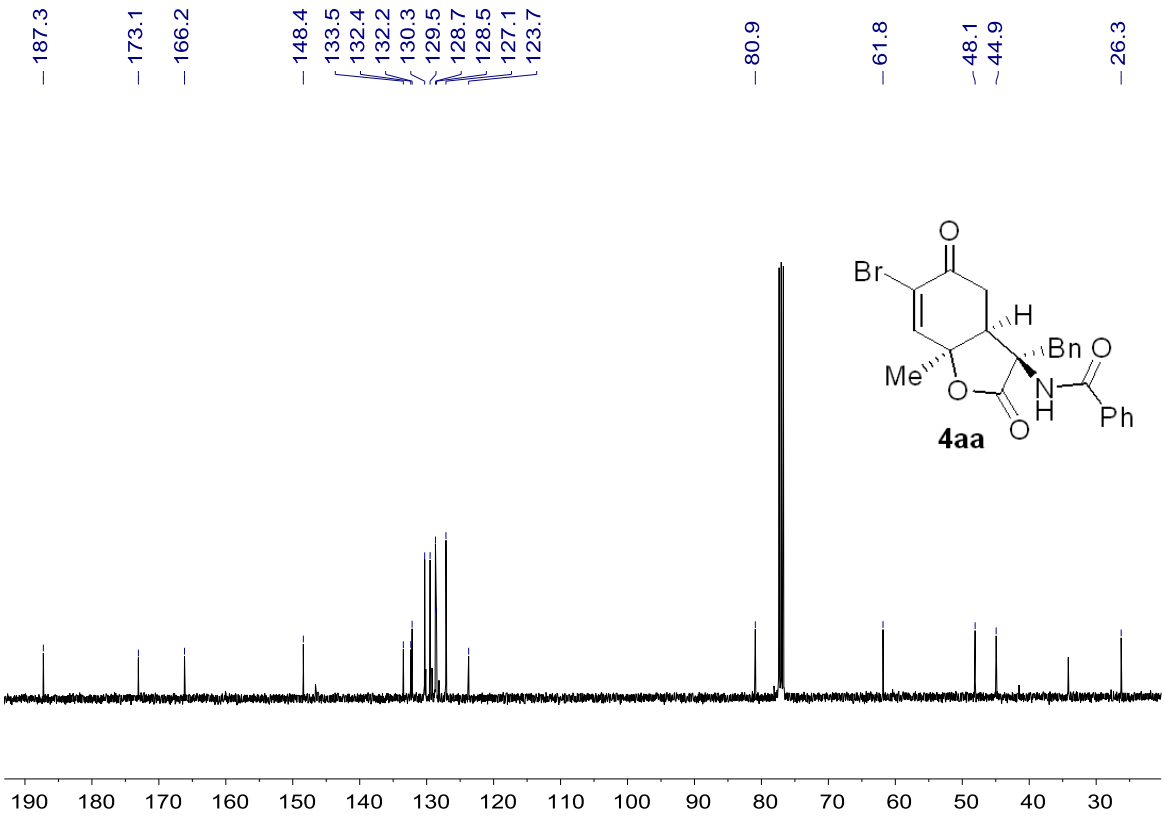
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$,compound **3ea**



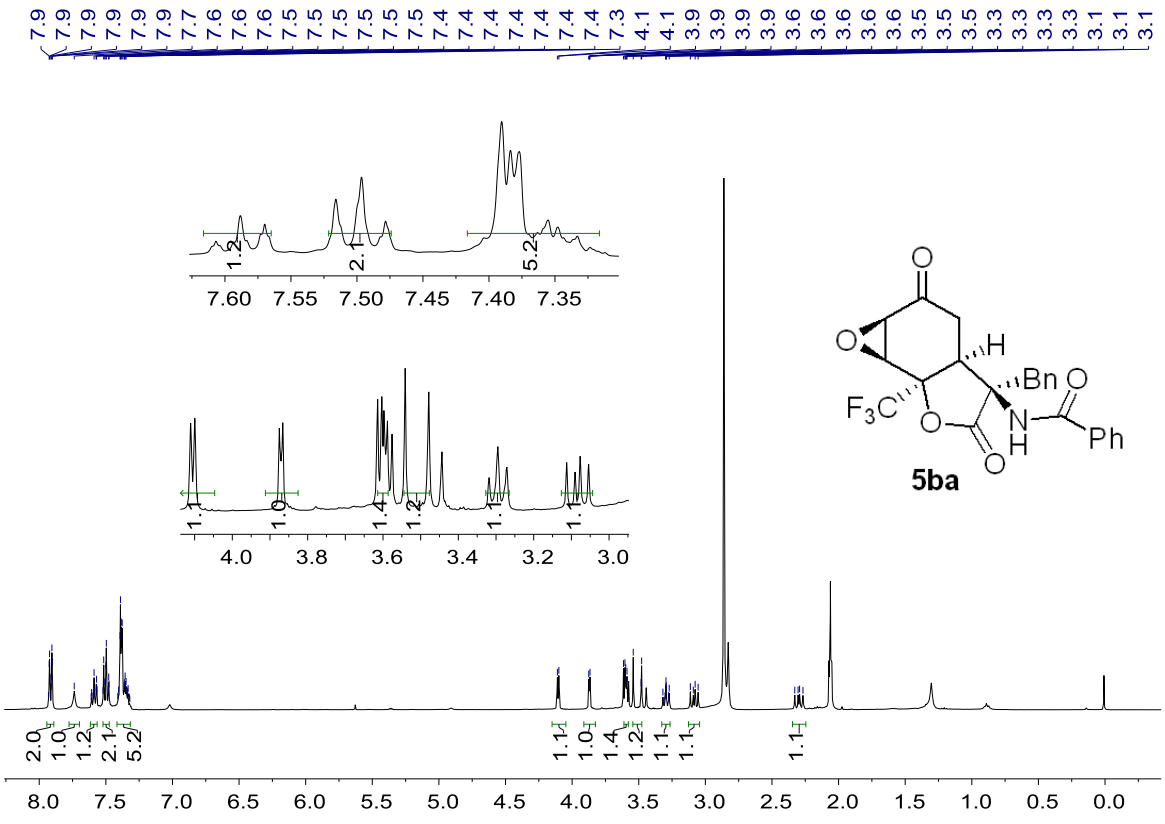


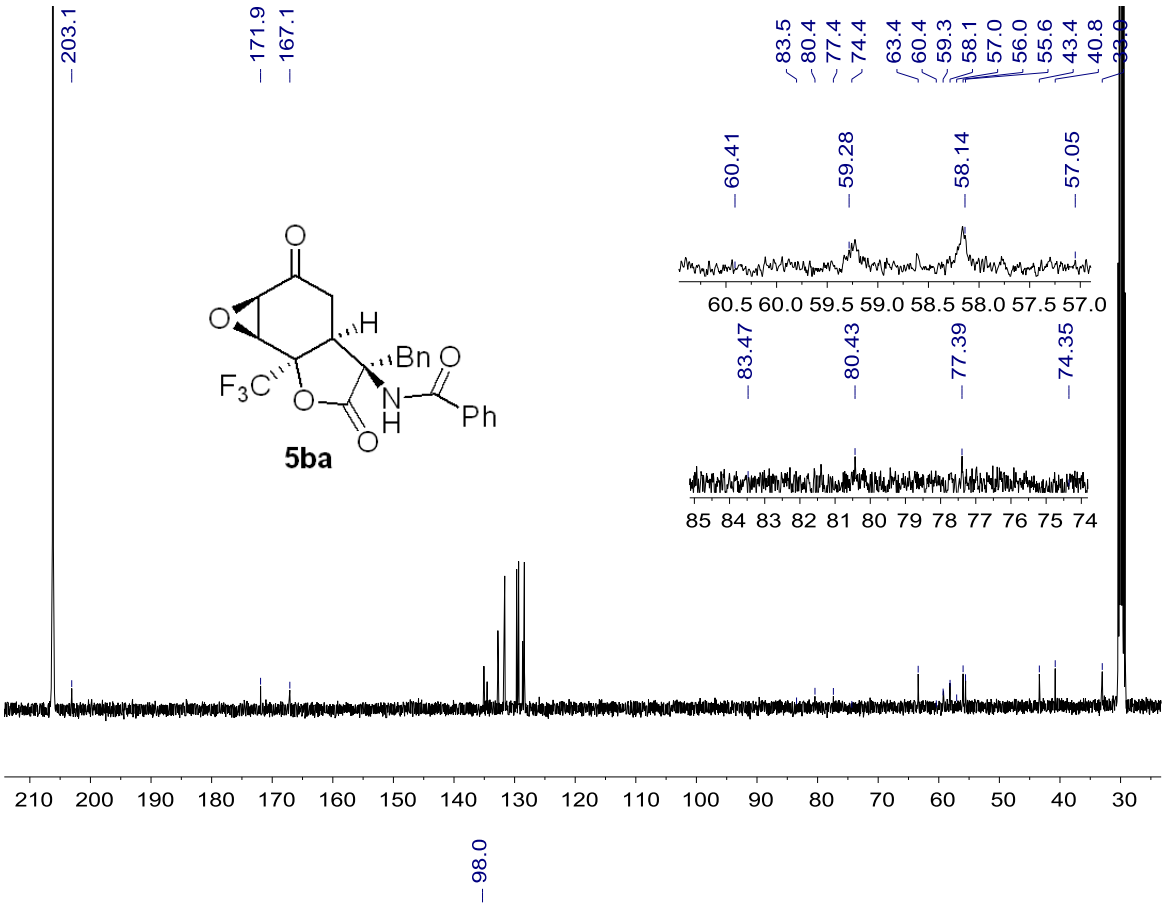
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **4aa**





^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), Acetone, compound **5ba**

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58.1
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56.0
55.6
43.4
40.8
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60.41
59.28
58.14
57.05
60.5 60.0 59.5 59.0 58.5 58.0 57.5 57.0
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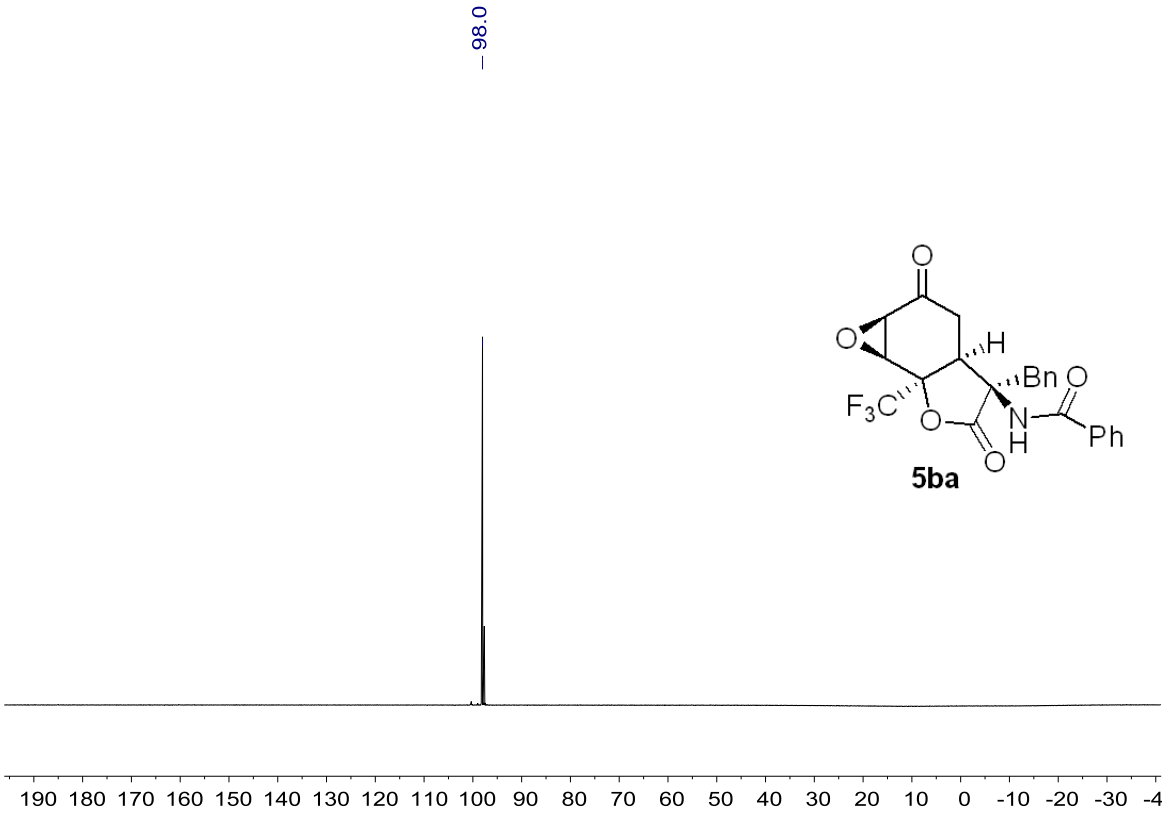
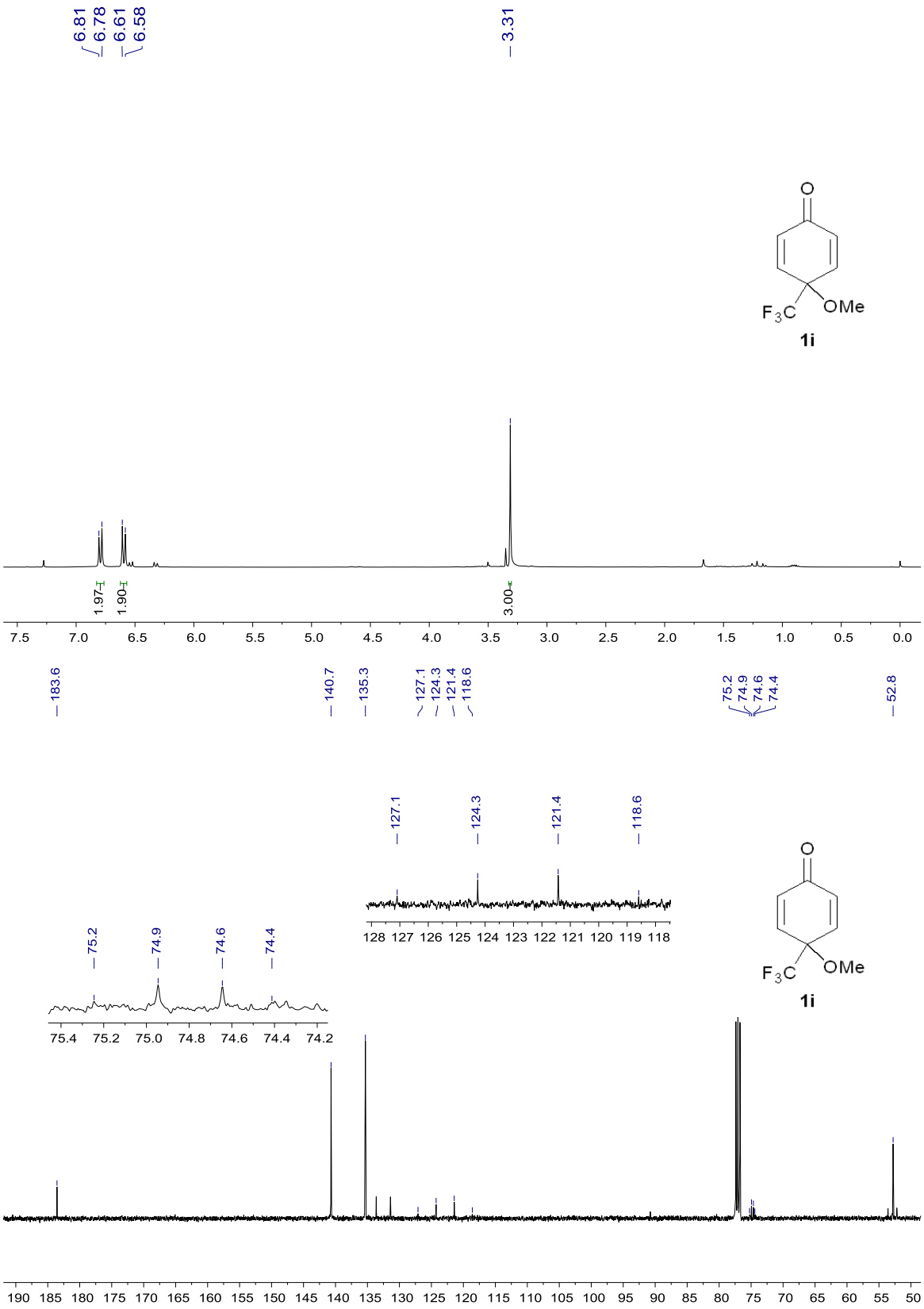
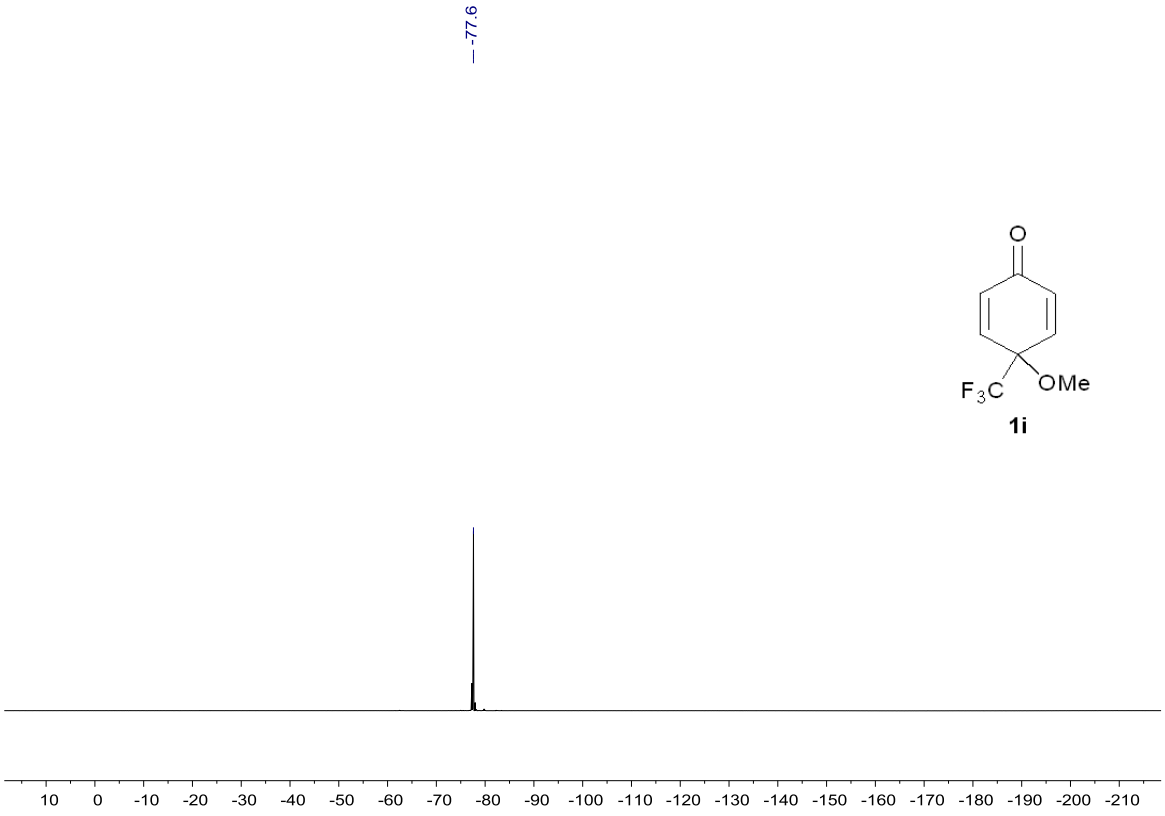
80.43
77.39
74.35
85 84 83 82 81 80 79 78 77 76 75 74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30


98.0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4

^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), ^{19}F{^{1}H} NMR (376 MHz), $CDCl_3$, compound **1i**.

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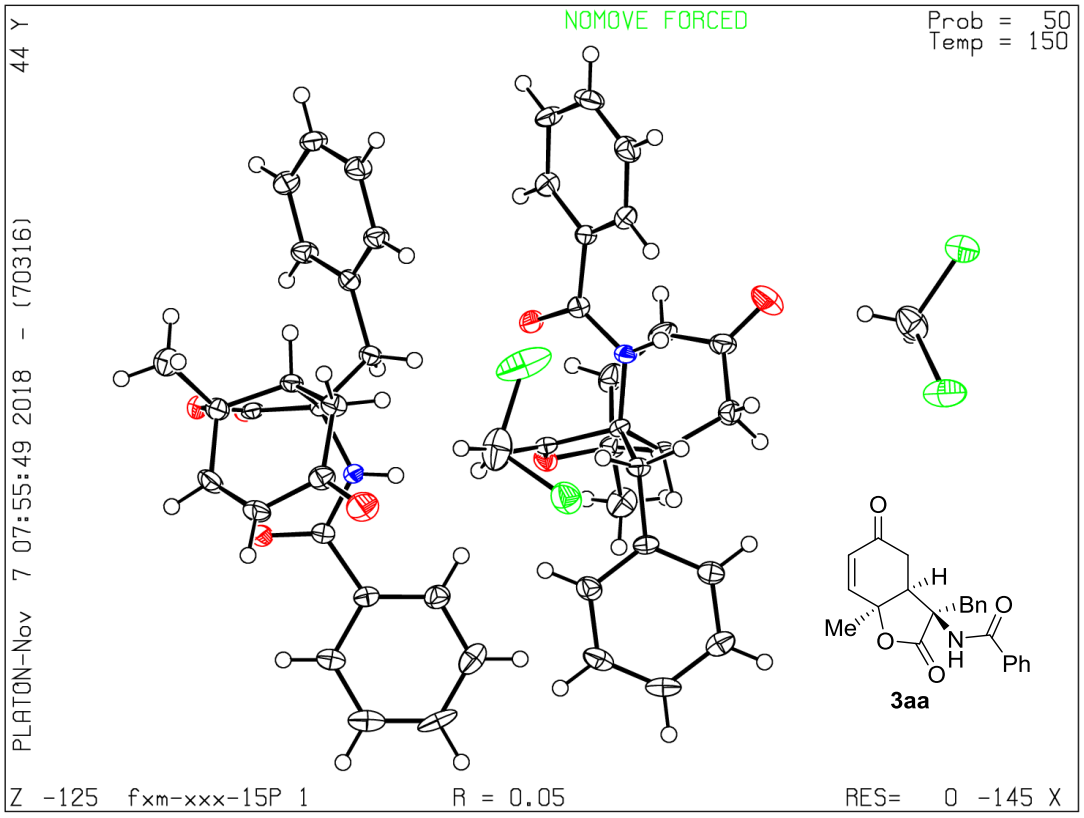
O
F3C
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

1i

8. Mechanism studies

8.1 CCDC 1836787

3aa was recrystallized from mixed solvents of CH_2Cl_2, *n*-hexane, ethanol, isopropanol, toluene at 0 ℃. The absolute configuration of the product **3aa** was determined to be (3*R*, 3a*S*, 7a*S*) according to X-ray crystal structural analysis.

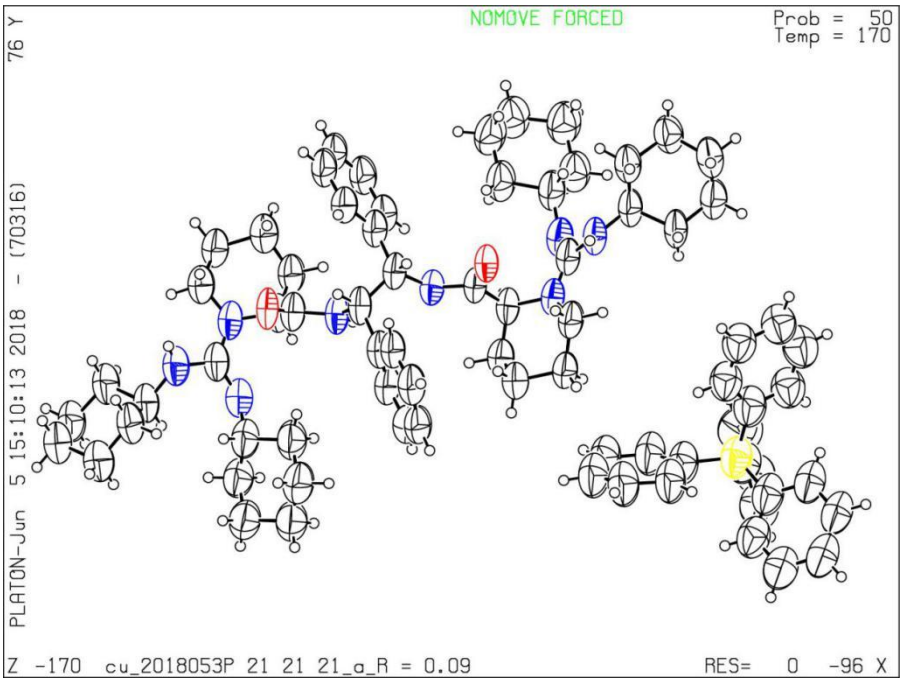


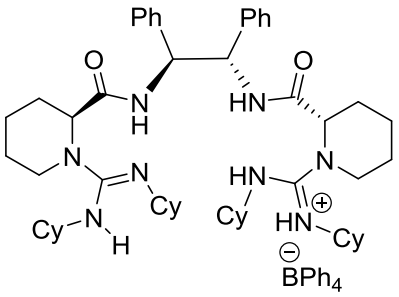
Identification code	fxm-xxx-150k
Empirical formula	$C_{24}H_{23}Cl_2NO_4$
Formula weight	460.33
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P1
a/Å	9.4955(4)
b/Å	11.2983(5)
c/Å	11.3062(5)
α/°	75.516(4)
β/°	69.837(4)
γ/°	89.852(3)
Volume/Å^3	1097.76(8)

Z	2
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	2.923
F(000)	480.0
Crystal size/mm^3	0.5 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.116 to 145.982
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 13, -13 ≤ l ≤ 14
Reflections collected	22281
Independent reflections	7754 [R_{int} = 0.0580, R_{sigma} = 0.0576]
Data/restraints/parameters	7754/3/561
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1360
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1402
Largest diff. peak/hole / e Å^{-3}	0.45/-0.41
Flack parameter	-0.002(11)

8.2 CCDC 1847525

Catalyst was recrystallized from mixed solvents of CH_2Cl_2, alcohol and *n*-hexane at 0 ℃. We synthesized the catalyst using L-Pipecolinic acid and (1S,2S)-1,2-Diphenyl-1,2-ethanediamine of known absolute configuration, So the absolute configuration of the catalyst is deterministic.





Identification code	cat.cu_20180530xlhbp_0ma_a_sq
Empirical formula	$C_{76}H_{99}BN_8O_2$
Formula weight	1167.44
Temperature/K	170(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	20.6886(6)
b/Å	21.2747(5)
c/Å	21.4491(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9440.7(5)
Z	4
ρ_{calc}g/cm^3	0.820
μ/mm^{-1}	0.378
F(000)	2520.0
Crystal size/mm^3	0.600 × 0.040 × 0.040
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/ °	5.936 to 108.766
Index ranges	-21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -21 ≤ l ≤ 22
Reflections collected	39183
Independent reflections	11357 [R_{int} = 0.0561, R_{sigma} = 0.0516]
Data/restraints/parameters	11357/1902/756
Goodness-of-fit on F^2	0.954
Final R indexes [I>=2σ (I)]	R_1 = 0.0950, wR_2 = 0.2222
Final R indexes [all data]	R_1 = 0.1186, wR_2 = 0.2388
Largest diff. peak/hole / e Å^{-3}	0.24/-0.25
Flack parameter	0.45(13)

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.5273

Author Response: The dataset was cut at 0.95 Angstroms as at this point the average I/sigama(I) drop to below 2. Increase the exposure time didn't help.

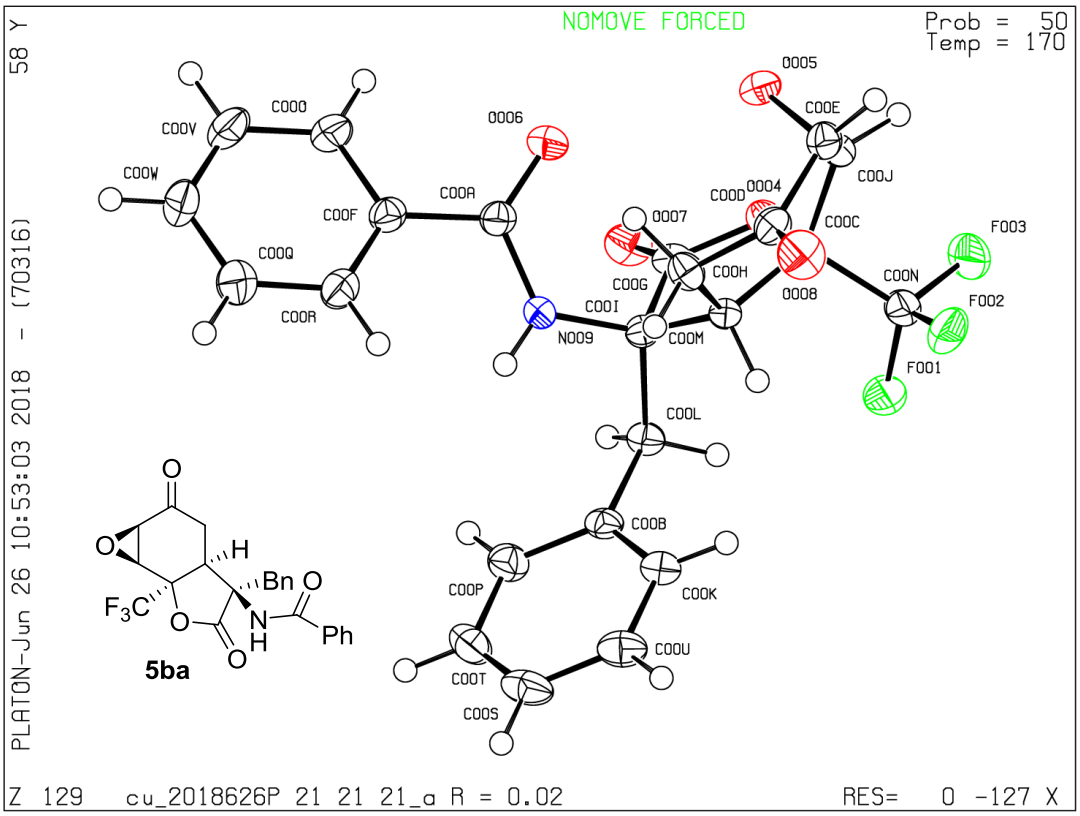
Alert level B

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01588 Ang.

Author Response: The resolution is low, hard to get high precision on C-C Bonds

8.3 CCDC 1851705

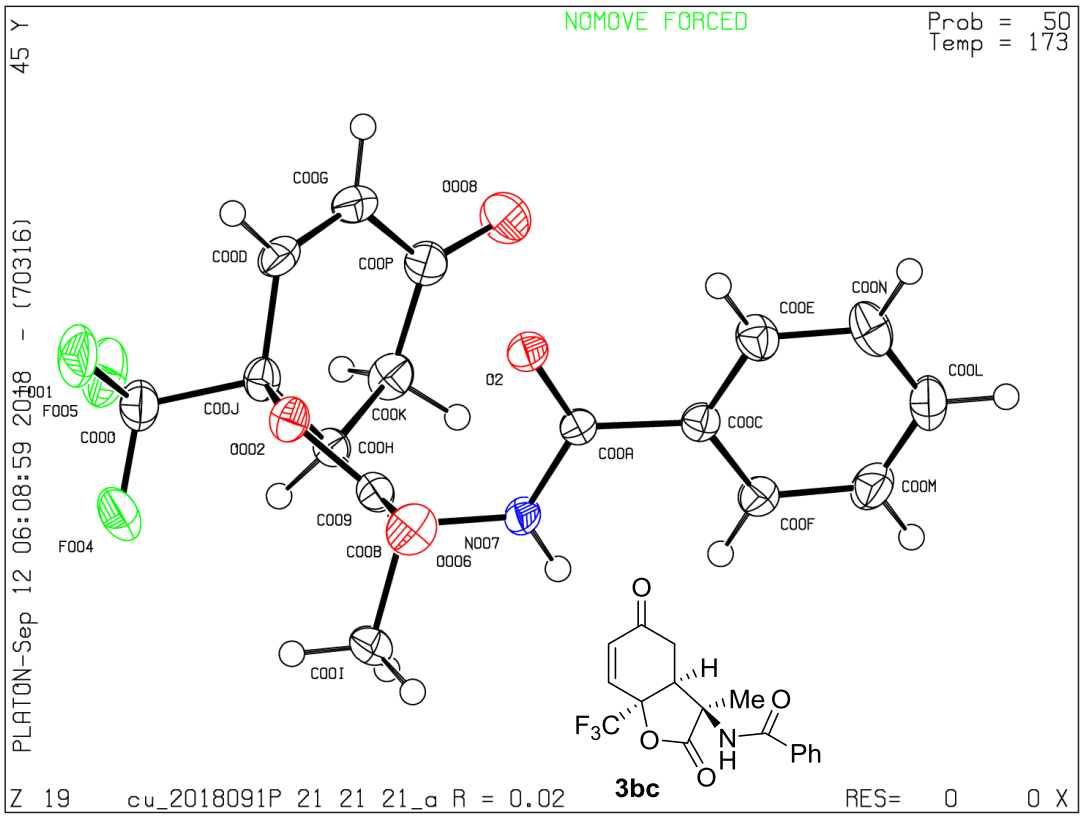
5ba was recrystallized from missed solvents of CH_2Cl_2 and *n*-hexane. The absolute configuration of **5ba** was determined to be (1a*R*, 3a*S*, 4*R*, 6a*R*, 6b*S*) according to X-ray crystal structural analysis.



Identification code	cu_2018626_XLH_01_0m_a
Empirical formula	$C_{23}H_{18}F_3NO_5$
Formula weight	445.38
Temperature/K	170(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.8880(14)
b/Å	7.800(2)
c/Å	36.992(16)
α/°	90

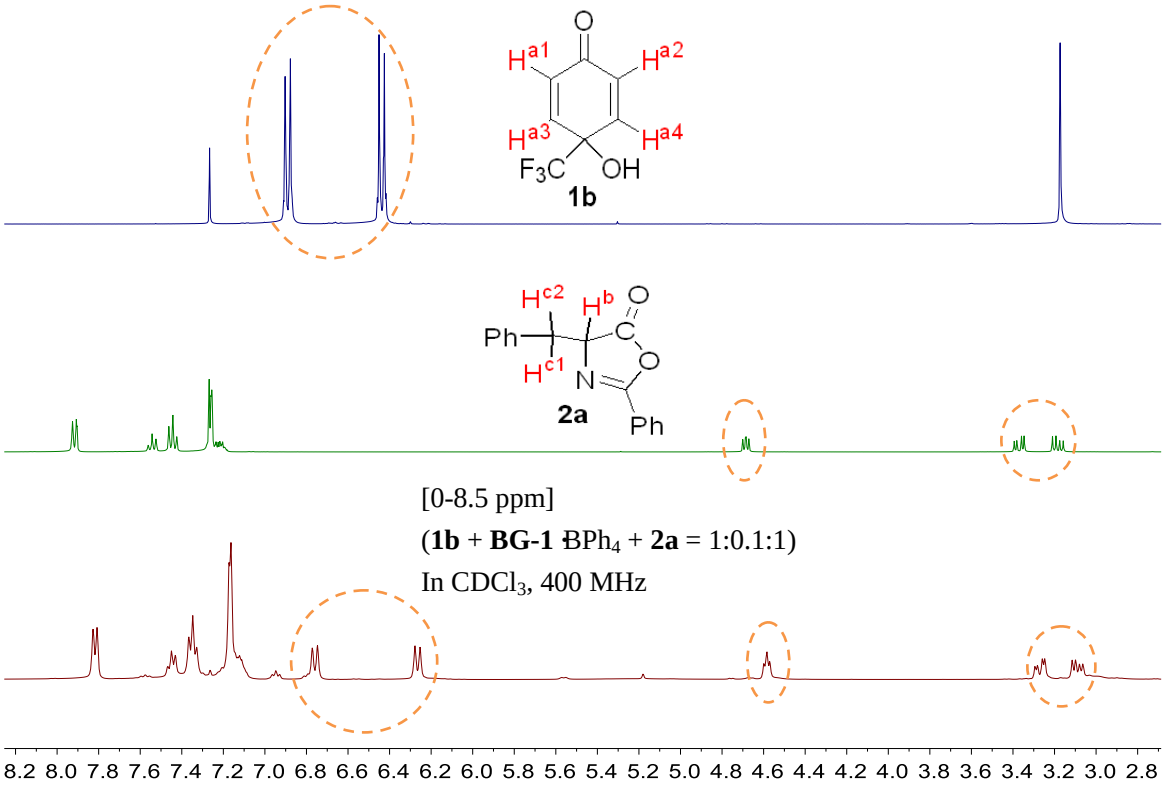
β/°	90
γ/°	90
Volume/Å^3	1987.4(11)
Z	4
ρ_{calc}g/cm^3	1.489
μ/mm^{-1}	1.060
F(000)	920.0
Crystal size/mm^3	0.360 ×0.110 ×0.110
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	12.316 to 129.886
Index ranges	-8 ≤ h ≤ 6, -9 ≤ k ≤ 9, -43 ≤ l ≤ 40
Reflections collected	11558
Independent reflections	3350 [R_{int} = 0.0253, R_{sigma} = 0.0237]
Data/restraints/parameters	3350/0/293
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0240, wR_2 = 0.0597
Largest diff. peak/hole / e Å^{-3}	0.15/-0.16
Flack parameter	0.03(3)

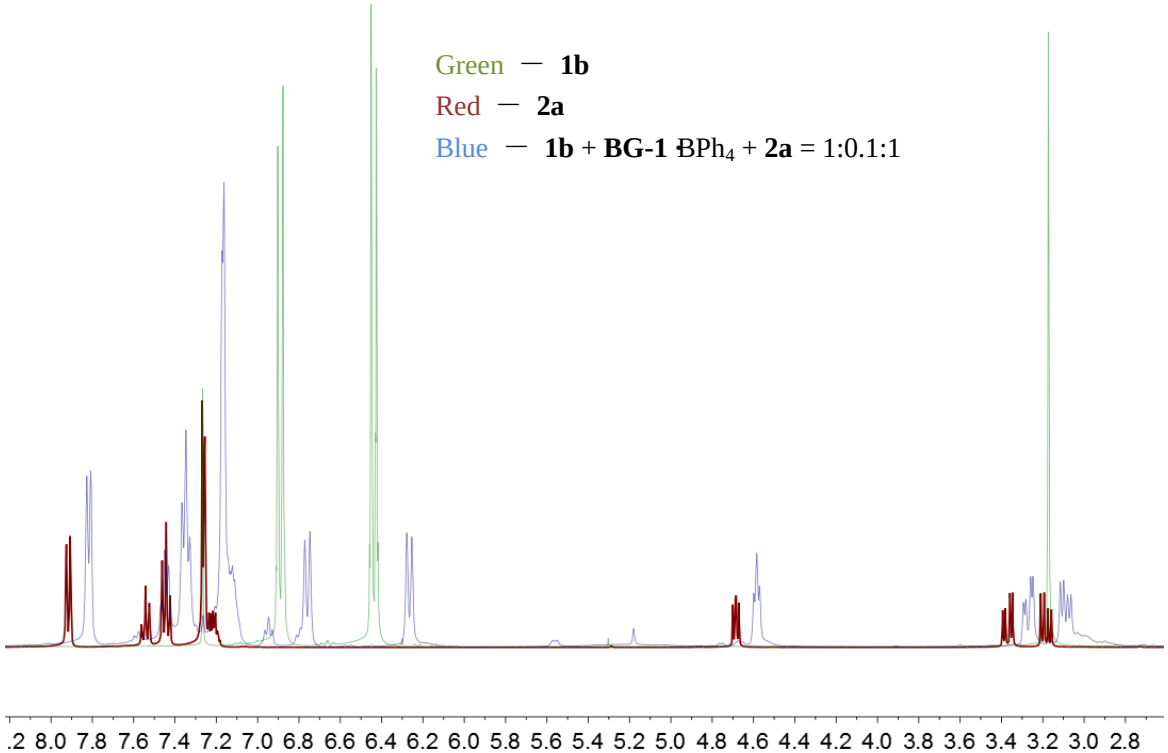
8.4 CCDC 1866762



Identification code	3bc. cu_20180910_XLH_2_0m_a
Empirical formula	$C_{17}H_{14}F_3NO_4$
Formula weight	353.29
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.2742(16)
b/Å	10.476(2)
c/Å	18.592(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1611.5(6)
Z	4
ρ_{calc}g/cm^3	1.456
μ/mm^{-1}	1.097
F(000)	728.0
Crystal size/mm^3	0.330 × 0.220 × 0.150
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.69 to 130.182
Index ranges	$-8 \le h \le 9$, $-12 \le k \le 12$, $-21 \le l \le 21$
Reflections collected	9036
Independent reflections	2641 [R_{int} = 0.0258, R_{sigma} = 0.0250]
Data/restraints/parameters	2641/0/227
Goodness-of-fit on F^2	0.714
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0653
Final R indexes [all data]	R_1 = 0.0247, wR_2 = 0.0656
Largest diff. peak/hole / e Å^{-3}	0.12/-0.14
Flack parameter	0.08(3)

8.5 ^{1}H NMR experiments



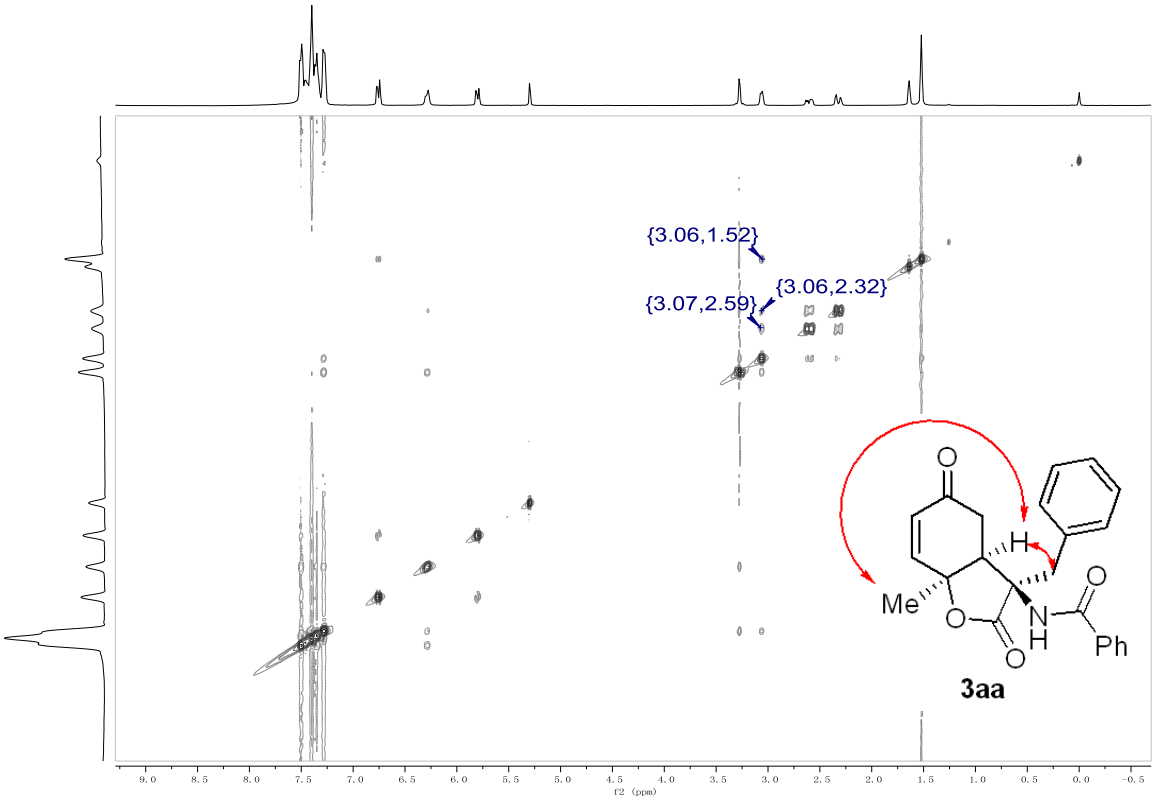


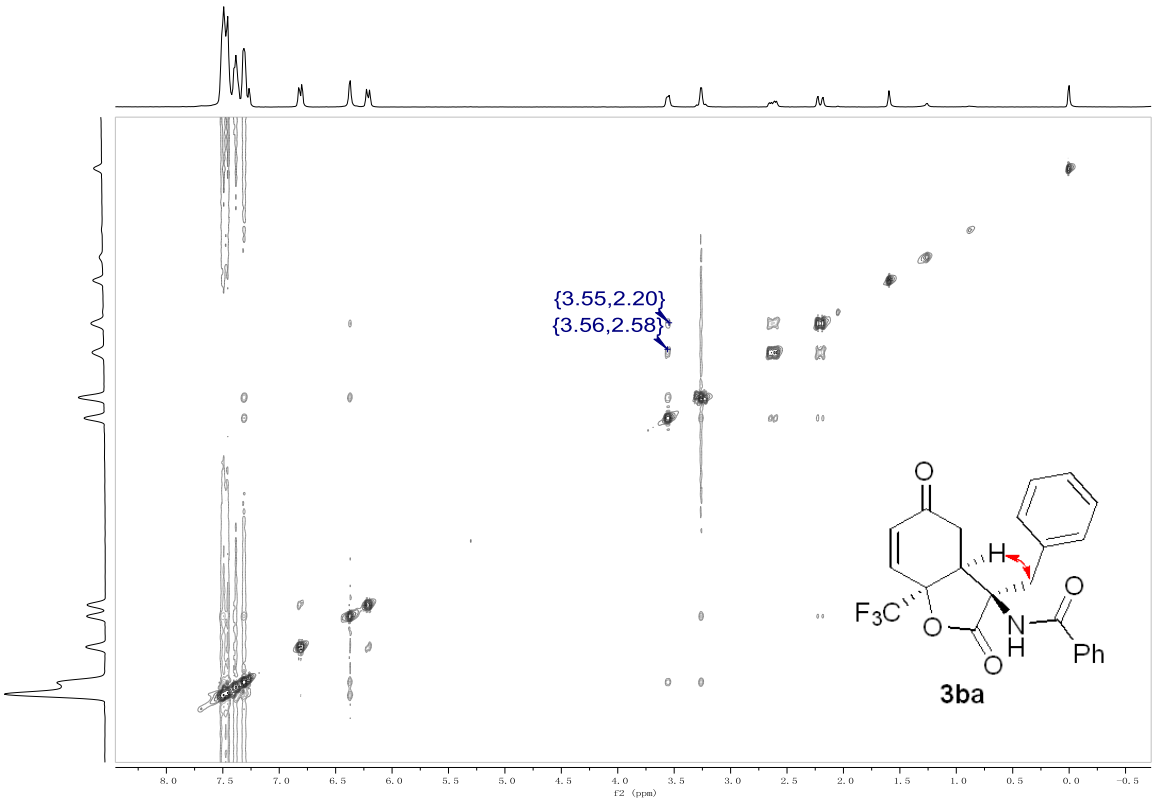
1b H^{a} = 6.92 — 6.23 ppm (m), **1b** + **BG-1** ⊖BPh$_4$ + **2a H^{a}** = 6.79 — 6.23 ppm (m).

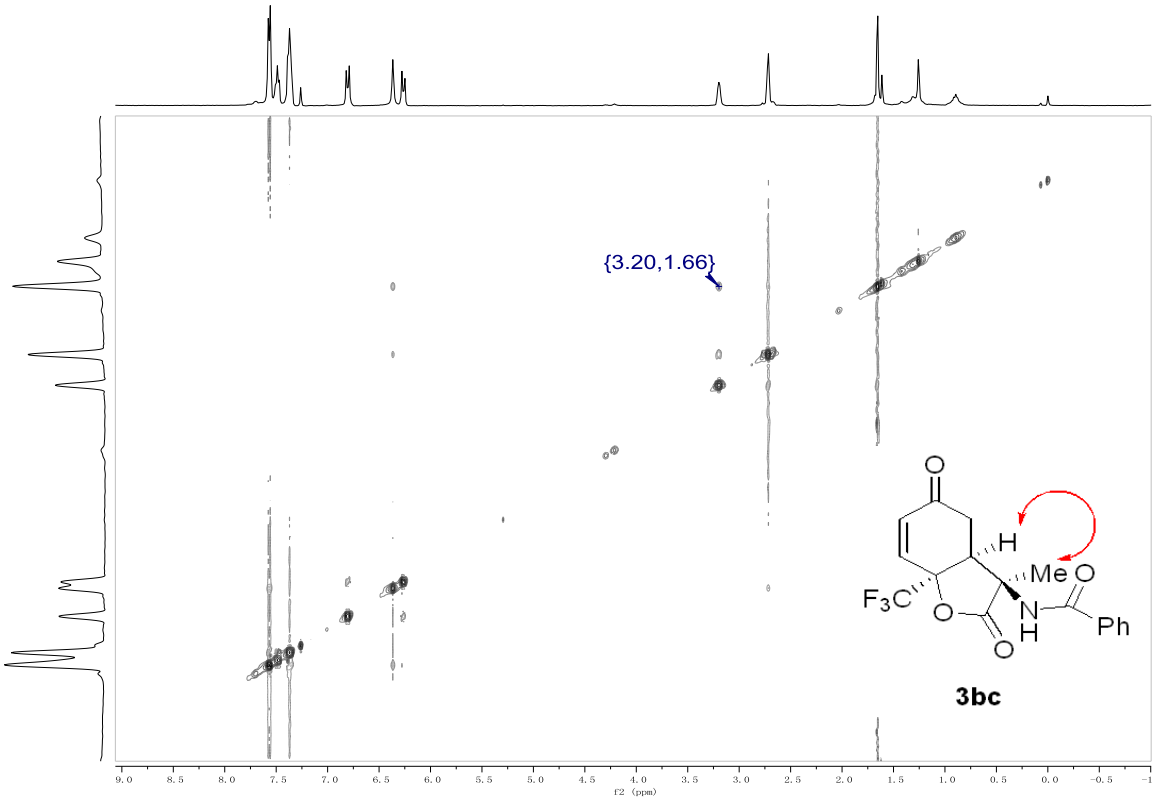
2a H^{b} = 4.72 — 4.66 ppm (m), **1b** + **BG-1** ⊖BPh$_4$ + **2a H^{b}** = 4.62 — 4.58 ppm (m).

2a H^c = 3.41 — 3.15 ppm (m), **1b** + **BG-1** BPh_4 + **2a H^c** = 3.31 — 3.05 ppm (m).

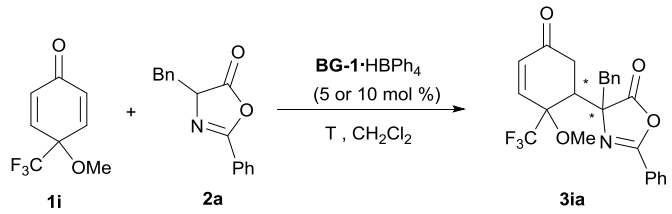
8.6 NOE studies







8.7 control experiments

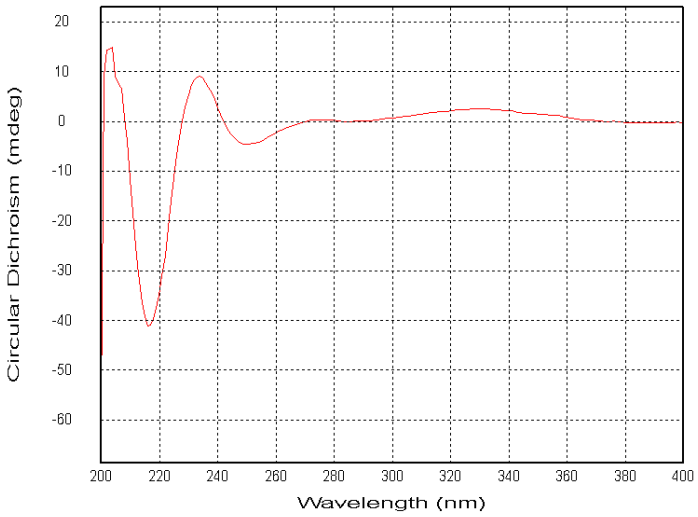


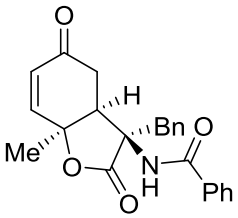
entry	T (℃)	yield (%)[b]	ee (%)[c]
1	30	N.R.[d]	—
2	0	N.R.	—
3	−10	N.R.	—

[a] The reactions were carried out **1i** (0.10 mmol), **2a** (0.15 mmol) and **BG-1**•$HBPh_4$ (5 or 10 mol%) in CH_2Cl_2 (1.0 mL) at the indicated temperature under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] N.R. = no reaction.

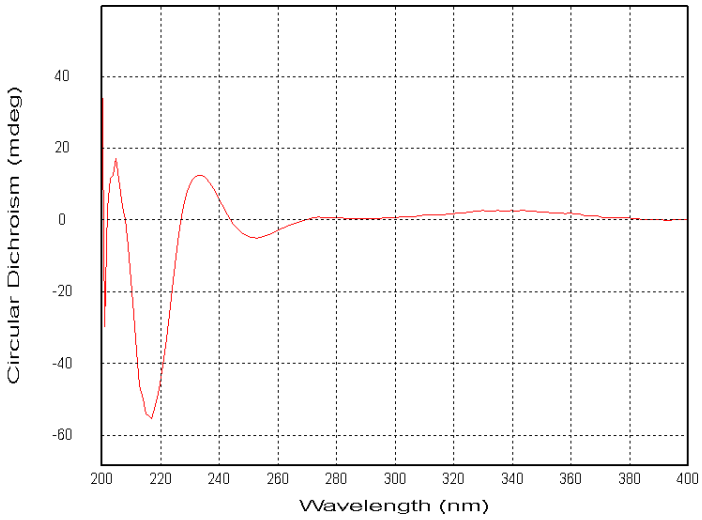
9. CD spectra of the products

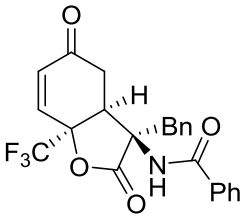
(3*R*, 3a*S*, 7a*S*)-3aa (standard) in MeOH



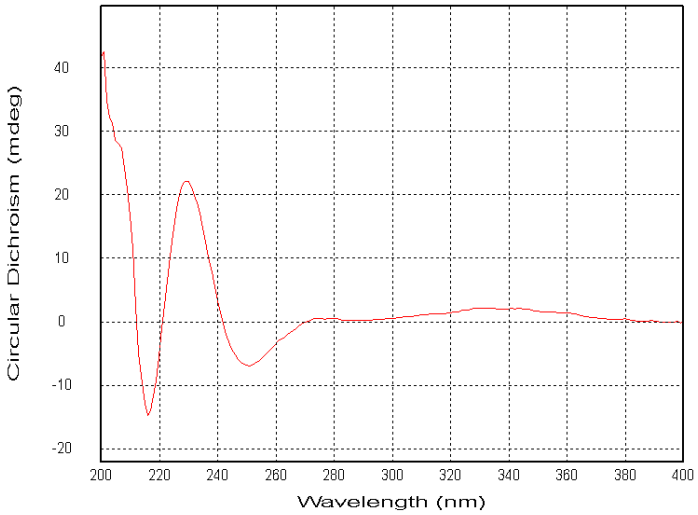


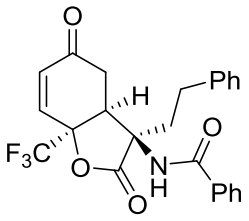
3aa



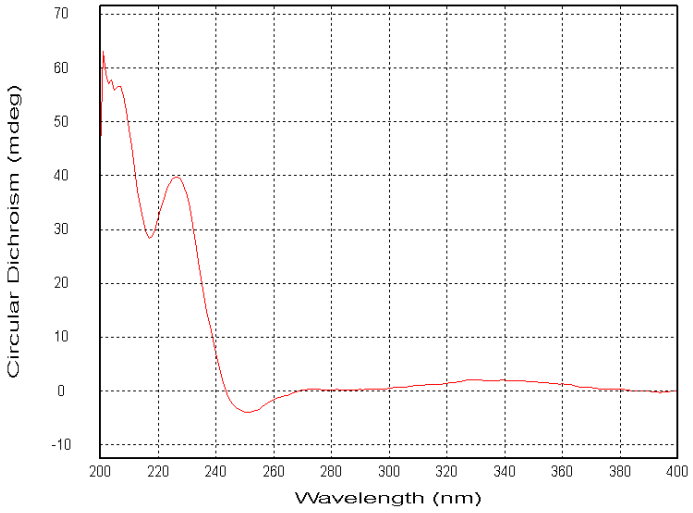


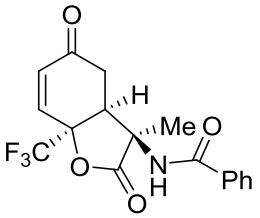
3ba


Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

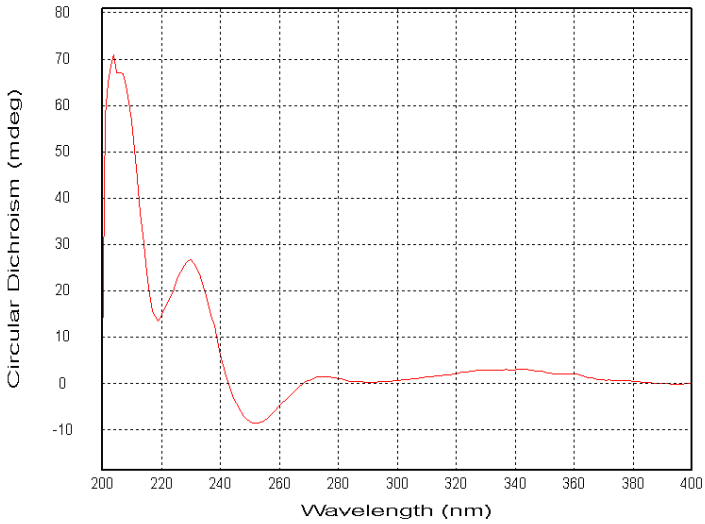

O
H
Ph
O
F3C
O
N
H
O
Ph

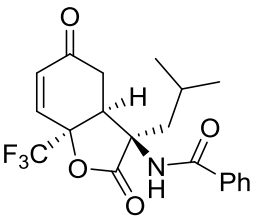
3bb


Circular Dichroism (mdeg)
70
60
50
40
30
20
10
0
-10
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

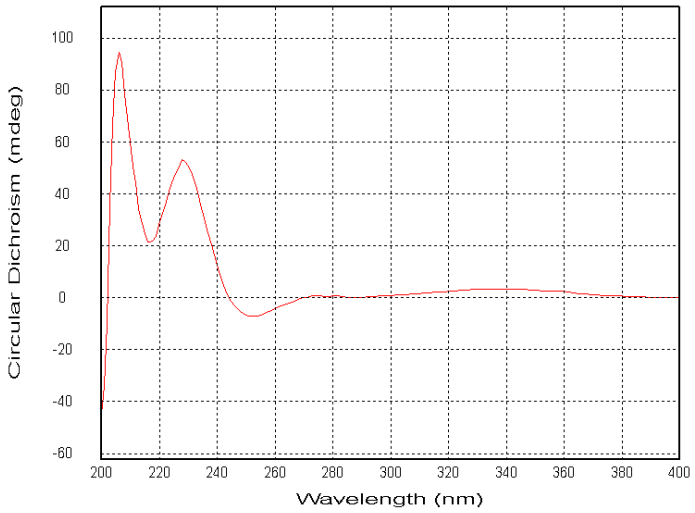

O
H
Me
O
F3C
O
N
H
O
Ph

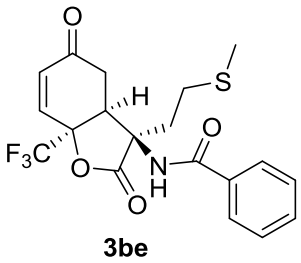
3bc


Circular Dichroism (mdeg)
80
70
60
50
40
30
20
10
0
-10
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

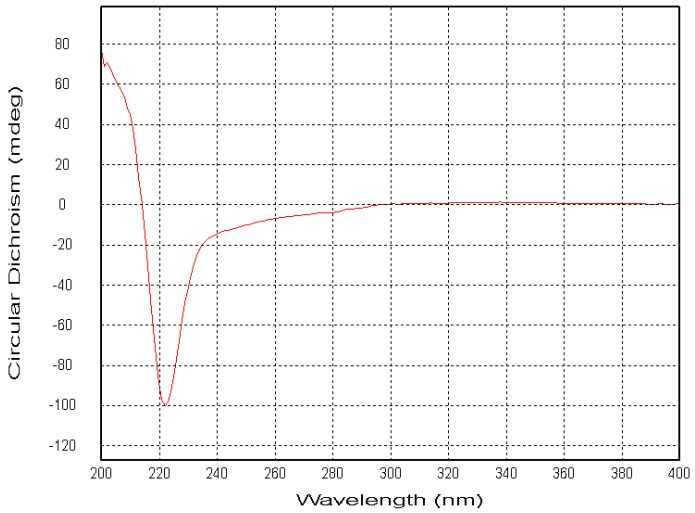

O
H
O
F3C
O
N
H
O
Ph

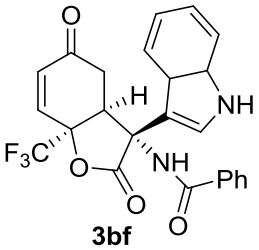
3bd


Circular Dichroism (mdeg)
100
80
60
40
20
0
-20
-40
-60
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

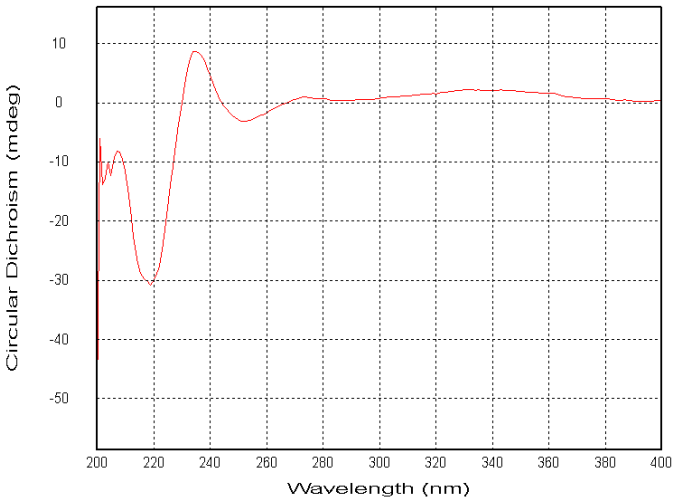

O
H
S
O
F3C
O
N
H
O

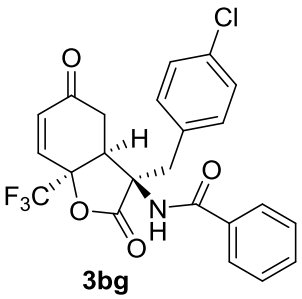
3be


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
-120
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

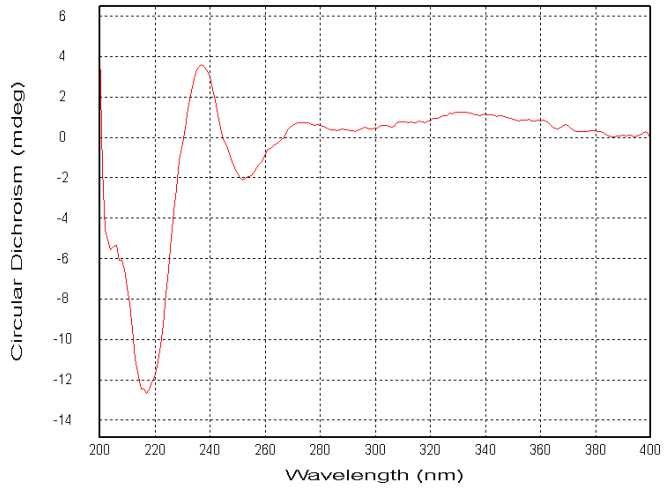

O
H
NH
F3C
O
NH
Ph
O
O

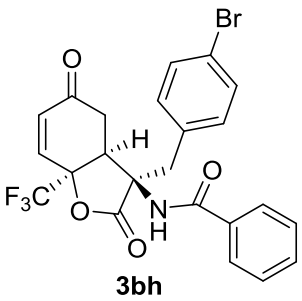
3bf


Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

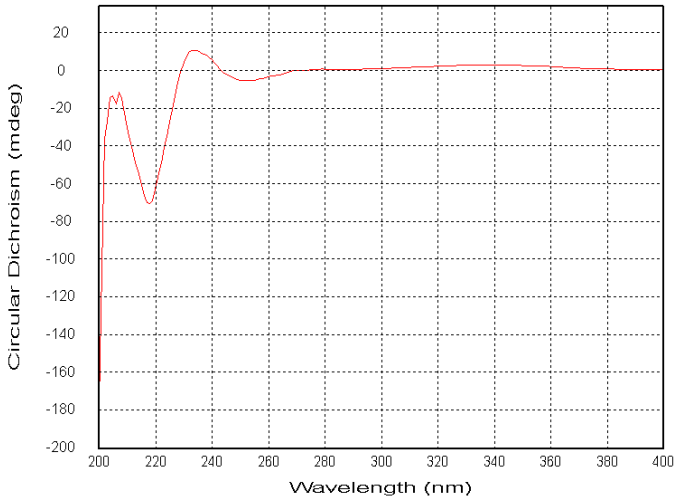

Cl
O
H
F3C
O
O
N
H
O

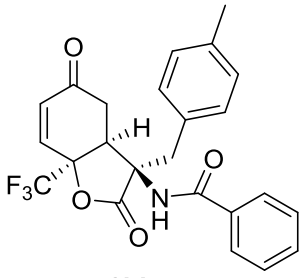
3bg


Circular Dichroism (mdeg)
Wavelength (nm)

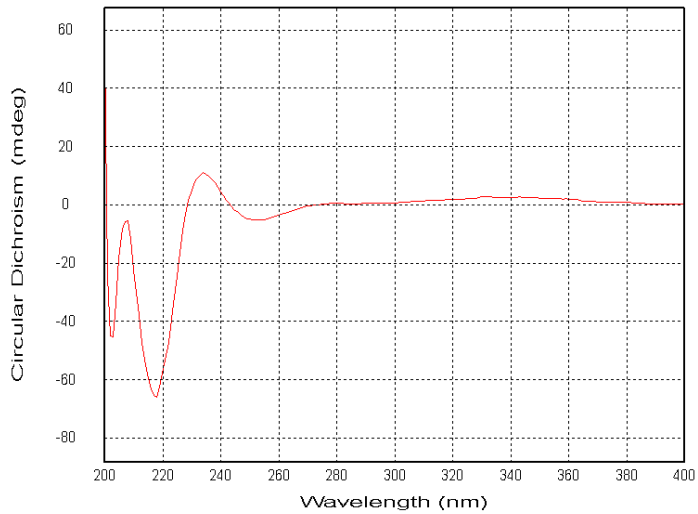

Br
O
H
O
F3C
O
N
H
O

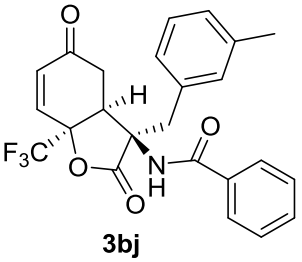
3bh


Circular Dichroism (mdeg)
Wavelength (nm)

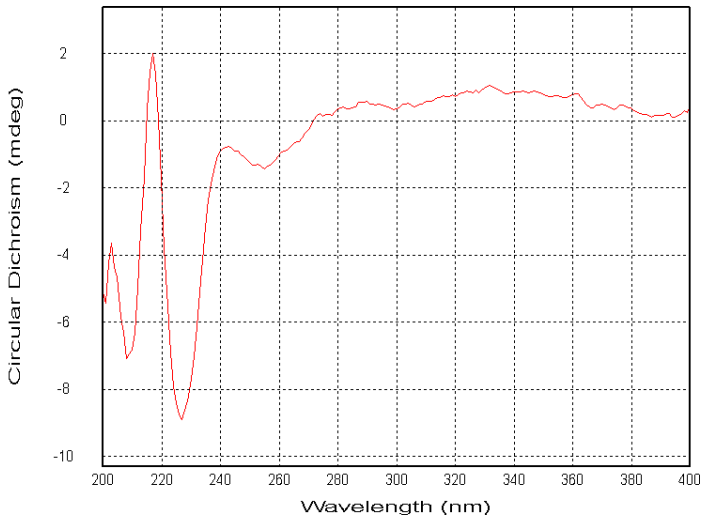

O
H
O
F3C
O
N
H
O

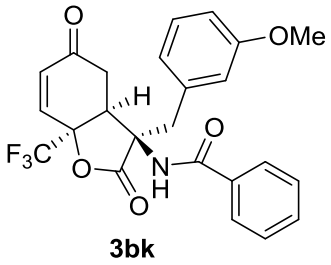
3bi


Circular Dichroism (mdeg)
Wavelength (nm)

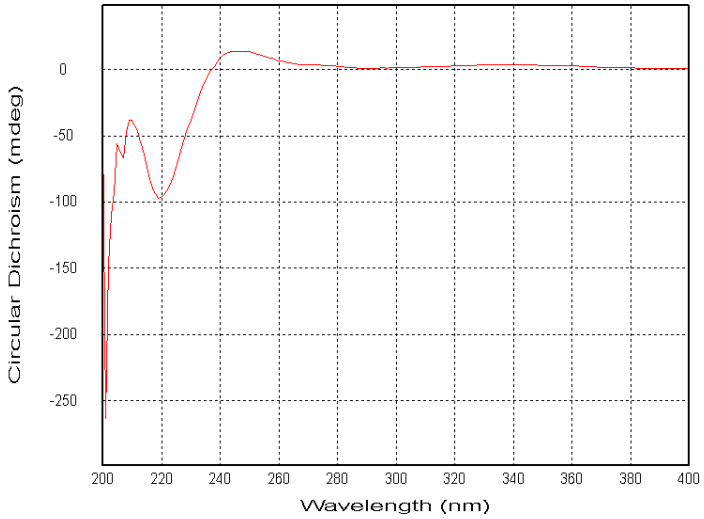

O
H
O
F3C
O
N
H
O

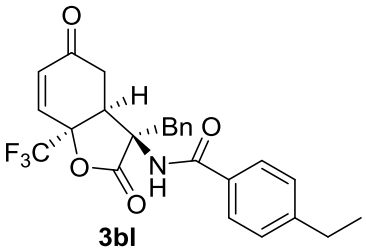
3bj


Circular Dichroism (mdeg)
2
0
-2
-4
-6
-8
-10
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

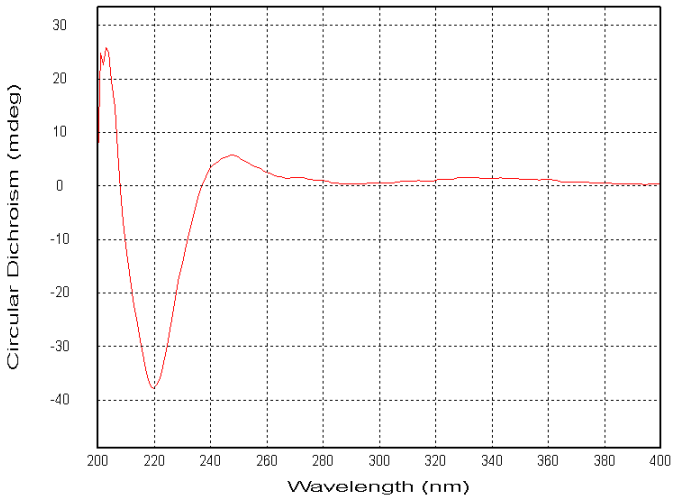

O
OMe
H
O
F3C
O
N
H
O

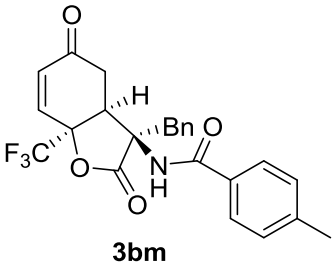
3bk


Circular Dichroism (mdeg)
0
-50
-100
-150
-200
-250
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

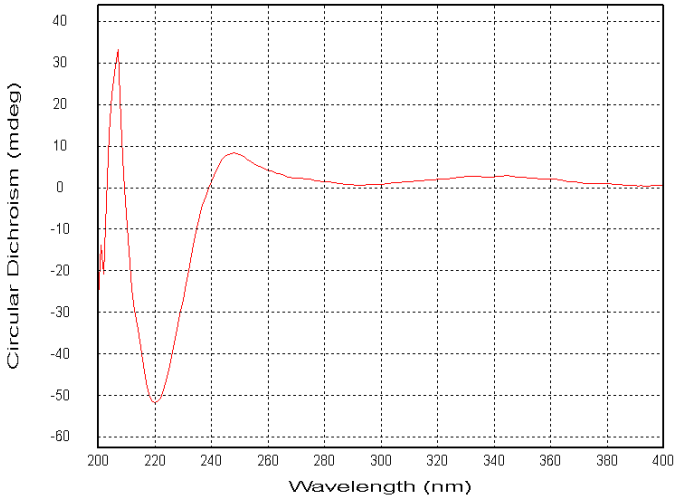

O
H
Bn
O
F3C
O
N
H
O

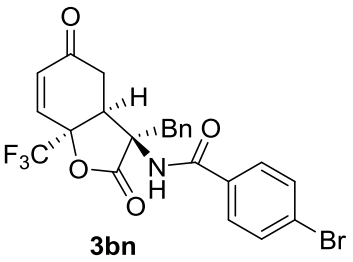
3bl


Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
-40
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

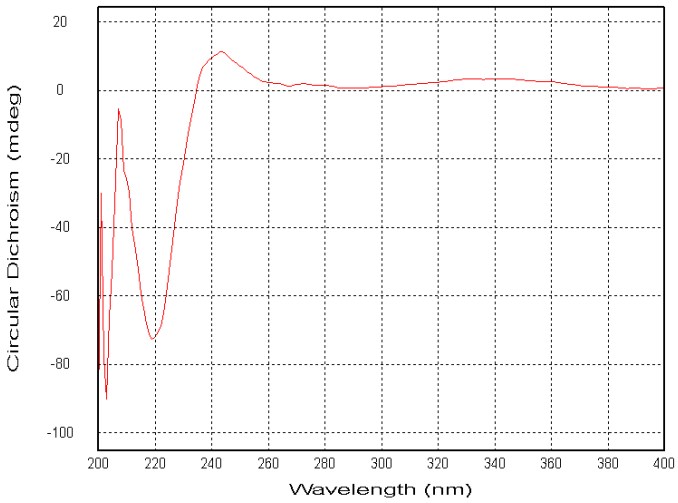

O
H
Bn
O
F3C
O
N
H
O

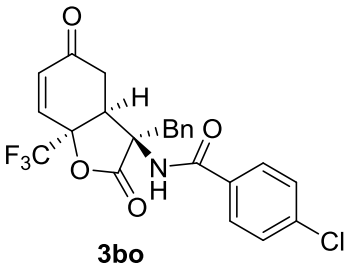
3bm


Circular Dichroism (mdeg)
Wavelength (nm)

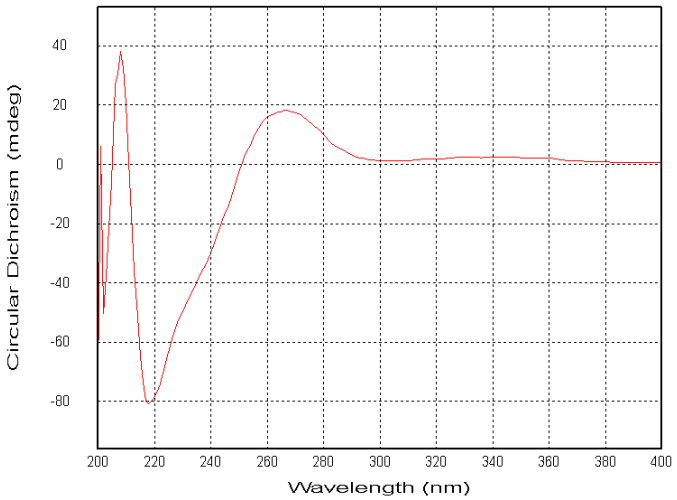

O
H
Bn
O
F3C
O
N
H
O
Br

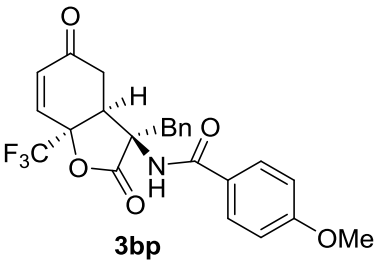
3bn


Circular Dichroism (mdeg)
Wavelength (nm)

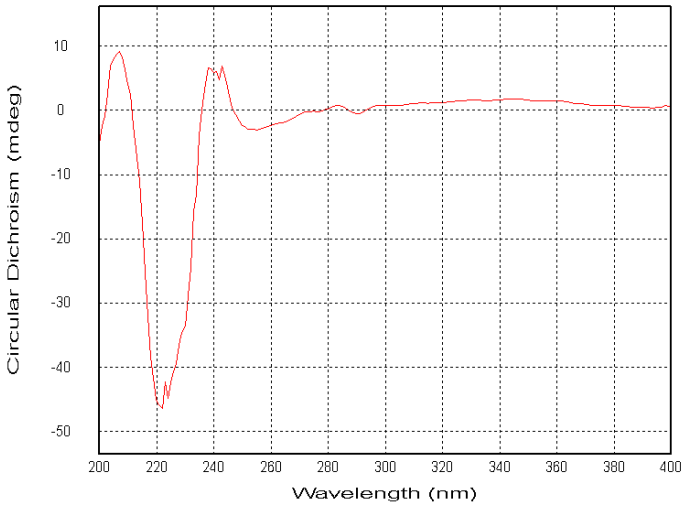

O
H
Bn
O
F3C
O
N
H
O
Cl

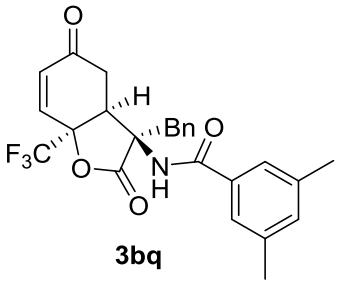
3bo


Circular Dichroism (mdeg)
Wavelength (nm)

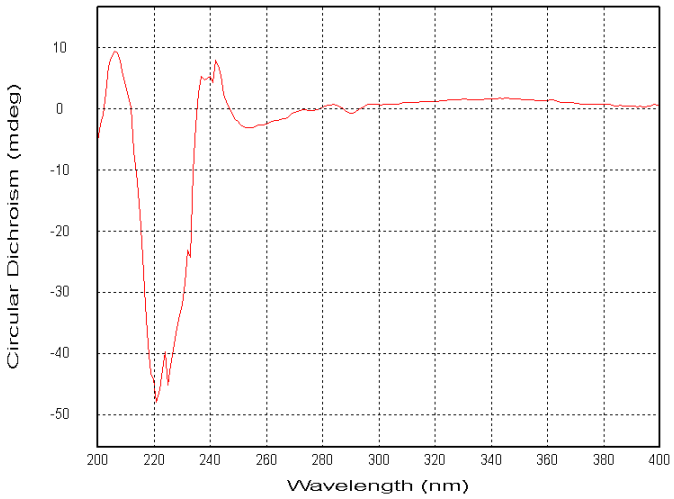

O
H
Bn
O
F3C
O
N
H
O
OMe

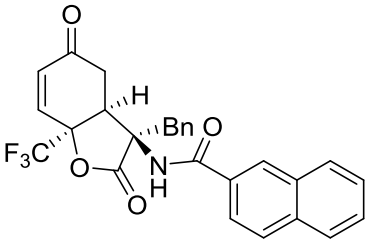
3bp


Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

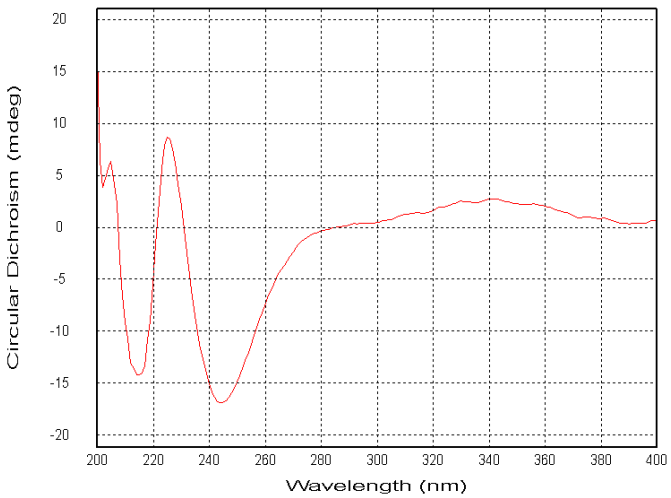

O
H
Bn O
F3C
O
N
H
O

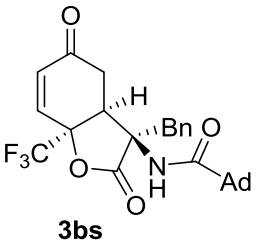
3bq


Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
-50
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

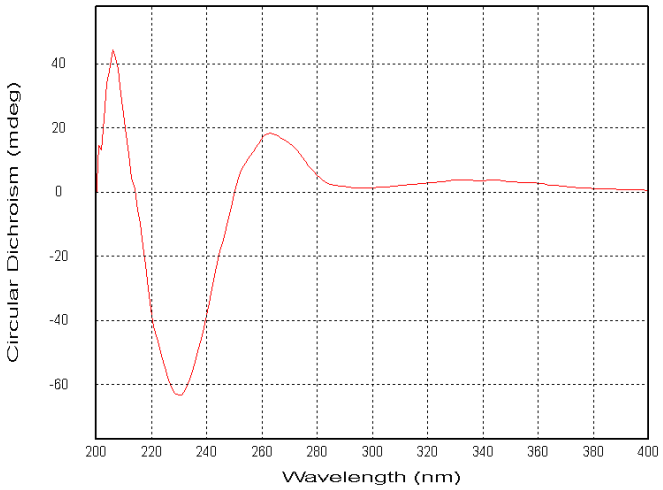

O
H
Bn O
F3C
O
N
H
O

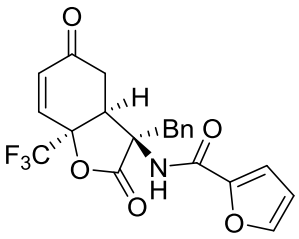
3br


Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

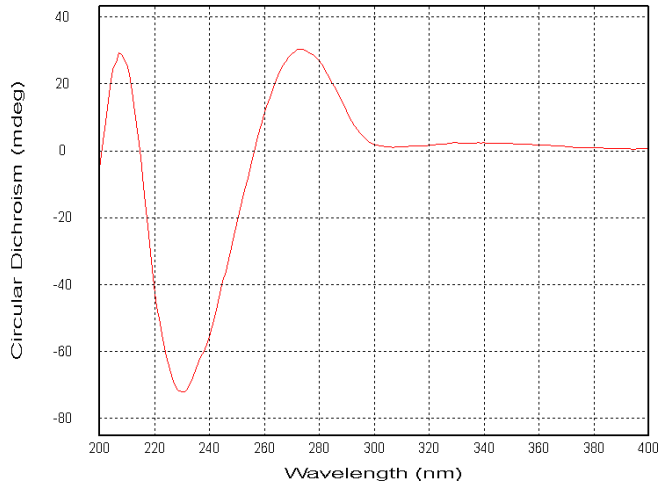

O
H
Bn O
F3C
O
N
H
Ad
O

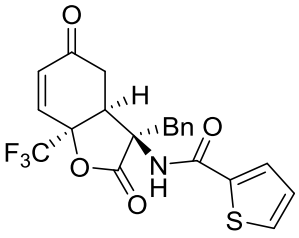
3bs


Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

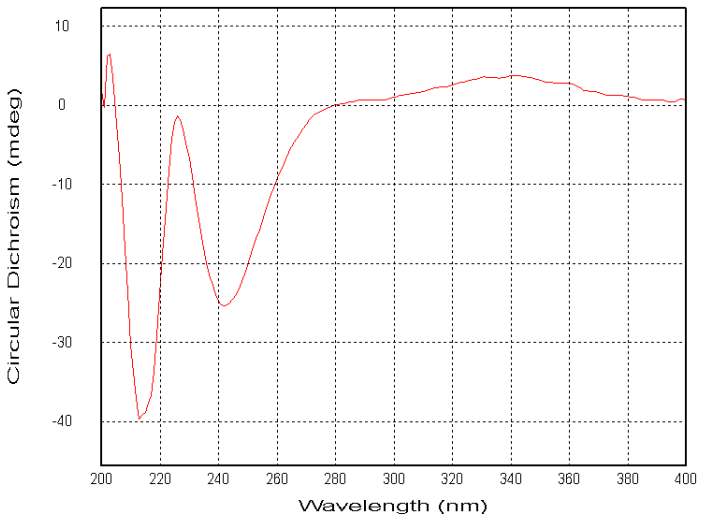

O
H
Bn
O
F3C
O
N
H
O
O

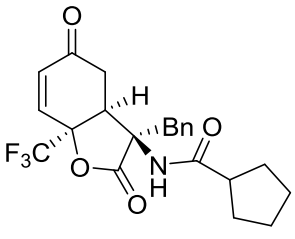
3bt


Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
-80
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

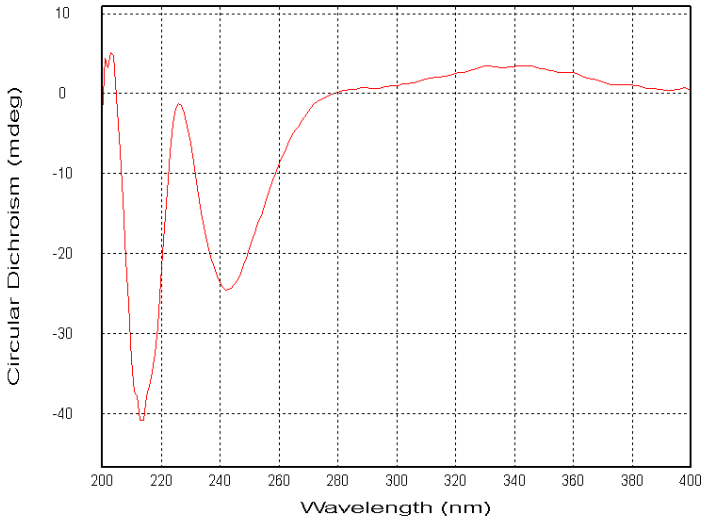

O
H
Bn
O
F3C
O
N
H
O
S

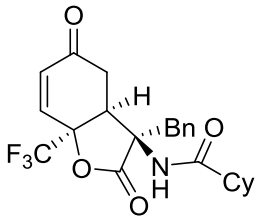
3bu


Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
200 220 240 260 280 300 320 340 360 380 400
Wavelength (nm)

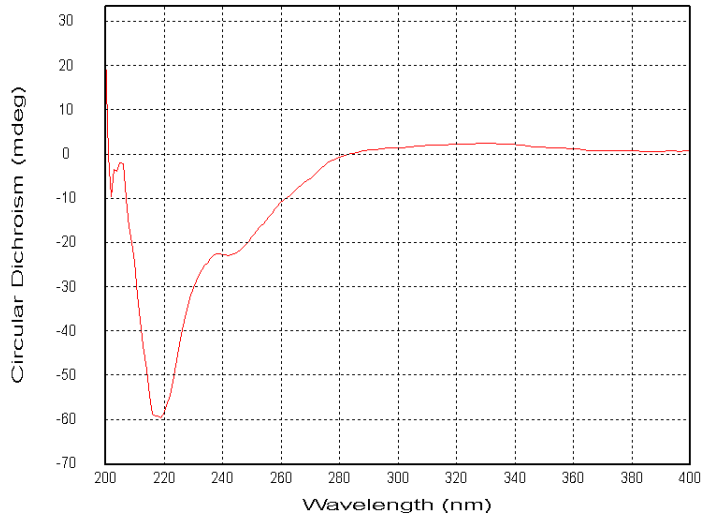

O
H
Bn
O
F3C
O
N
H
O

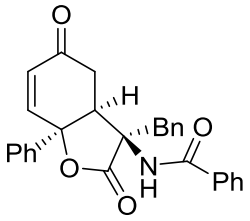
3bv


Circular Dichroism (mdeg)
Wavelength (nm)

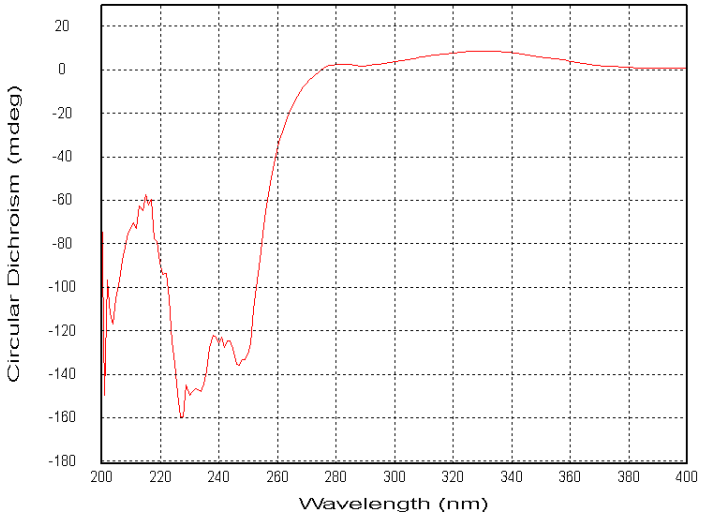

O
H
Bn
O
F3C
O
N
H
Cy
O

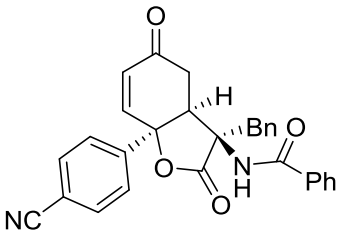
3bw


Circular Dichroism (mdeg)
Wavelength (nm)

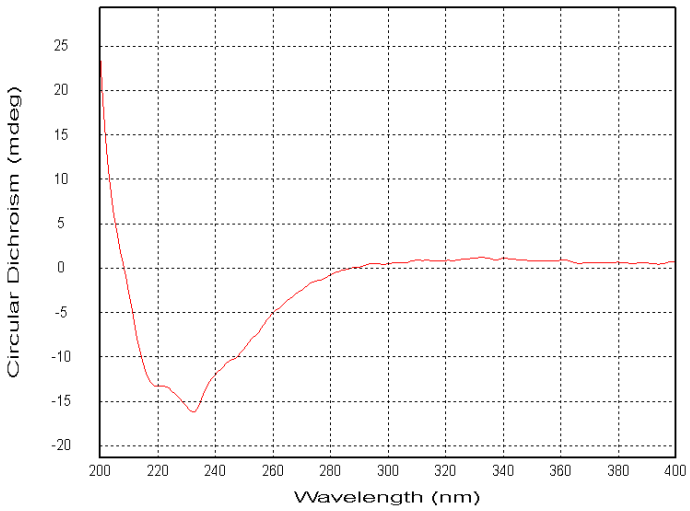

O
H
Bn
O
Ph
O
N
H
Ph
O

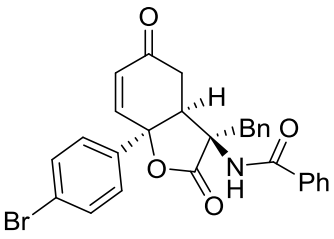
3ca


Circular Dichroism (mdeg)
Wavelength (nm)

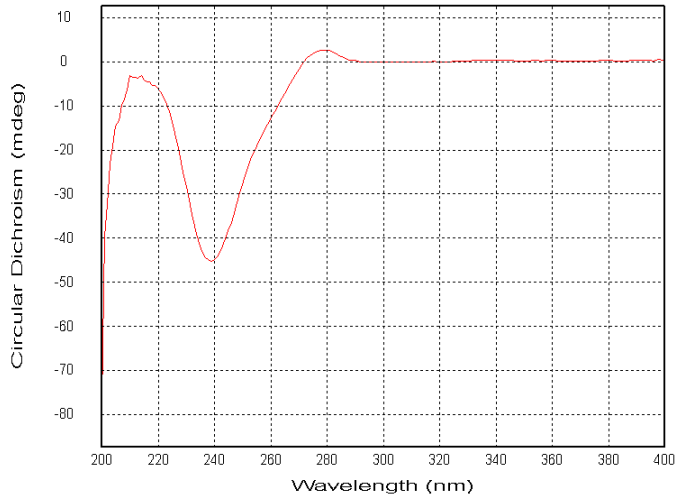

O
H
Bn
O
O
N
H
Ph
NC
O

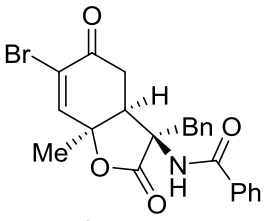
3da


Circular Dichroism (mdeg)
Wavelength (nm)

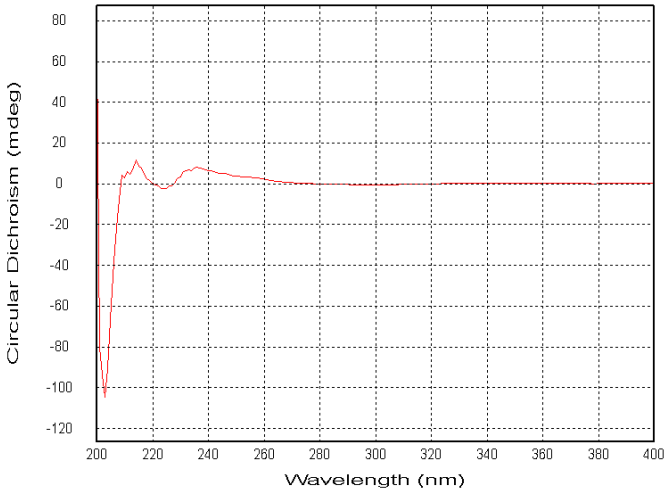

O
H
Bn
O
N
H
Ph
O
O
Br

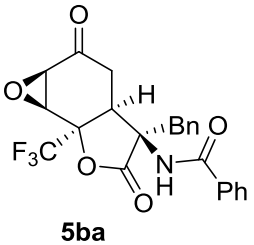
3ea


Circular Dichroism (mdeg)
Wavelength (nm)


O
Br
H
Bn
O
Me
O
N
H
Ph
O

4aa


Circular Dichroism (mdeg)
Wavelength (nm)


O
O
H
Bn
O
F3C
O
N
H
Ph
O

5ba

10. References

1. Z. P. Y, X. H. Liu, L. Zhou, L. L. Lin, X. M. Feng, *Angew. Chem., Int. Ed.*, 2009, **48**, 5195.
2. (a) S. X. Dong, X. H. Liu, X. H. Chen, F. Mei, Y. L. Zhang, B. Gao, L. L. Lin, X. M. Feng, *J. Am. Chem. Soc.*, 2010, **132**, 10650; (b) S. X. Dong, X. H. Liu, L. Zhou, L. L. Lin, X. M. Feng, *Org. Lett.*, 2011, **13**, 5060.
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