Supporting Information for

Pd-Catalyzed Carbonylative Lactonization of 2-Halidearomatic Aldehydes with H_2O as Nucleophile

Min Si,[a] Jiaqi Yan,[a] Yongzheng Ding[a] and Hanmin Huang[*,a,b]

[a]*Department of Chemistry, School of Chemistry and Material Science, Center for Excellence in Molecular Synthesis of CAS, University of Science and Technology of China, Hefei, 230026, P. R. China.*

[b]*State Key Laboratory of Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China*

**Corresponding author: hanmin@ustc.edu.cn*

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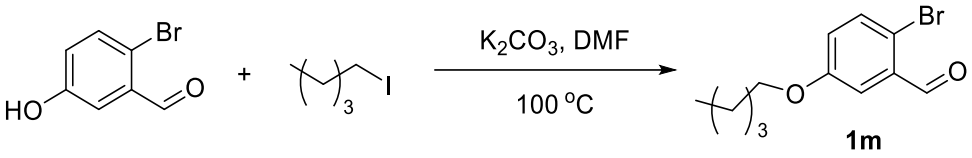
1. General experiment details and materials

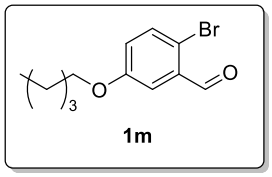
Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before used were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 400 or 500 spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. All the high-resolution mass spectra (HRMS) were carried out using Bruker Micro TOF-QII mass (ESI). Mass spectra were recorded by the mass spectrometry service at the University of Science and Technology of China. Gas chromatography (GC) analyses were performed on Agilent 7890B instrument with Hp-5 column. GC-MS analysis was performed with Agilent 7890B/5975B GC-MS system. Melting points were determined using a WRS-2A of shanghai INESA Physico optiacal instrument Co.,Ltd and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrophotometer. All chemicals were purchased from commercial sources.

2. Experimental procedure for synthesis of starting material[1]



A mixture of 2-bromo-5-hydroxybenzaldehyde (1.0 g, 4.4 mmol), K_2CO_3 (2.1 g, 15.4 mmol) and pentyl iodide (2.3 mL, 15.4 mmol) in DMF (15 mL) was stirred at 100 ℃ for 2 hours. The reaction mixture was diluted with ethyl acetate (50 mL), and washed with saturated NH_4Cl solution. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1) to afford 2-bromo-5-(pentyloxy)benzaldehyde **1m** (1.0 g, 85% yield) as a colorless liquid.

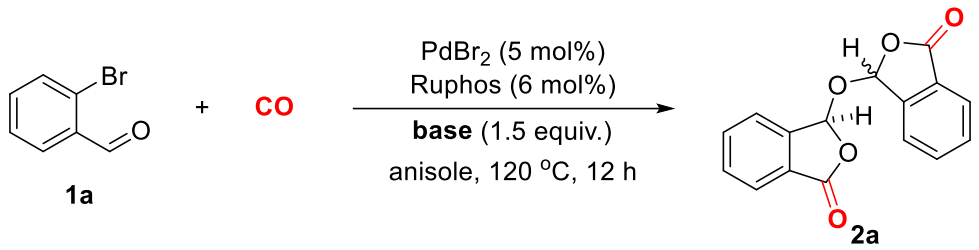
2-Bromo-5-(pentyloxy)benzaldehyde (1m): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless liquid. (1.0 g, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.82 -1.73 (m, 2H), 1.47 - 1.35 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.9, 158.9, 134.6, 133.9, 123.6, 117.8, 113.4, 68.7, 28.8, 28.2, 22.5, 14.1. **HRMS** (ESI) calcd. for $C_{12}H_{16}BrO_2$ $[M+H]^+$: 271.0334, found: 271.0331.



3. Optimization of the reaction conditions

In the glove box, a mixture of **1a** (184 mg, 1.0 mmol), Pd catalyst (0.025 mmol, 5 mol%), ligand (0.03 mmol, 6 mol%), base (0.75 mmol, 1.5 equiv.) and solvent (1.5 mL) was added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (20 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood. The dr value of the crude reaction mixture was determined by ^{1}H NMR. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to give the desired product **2a**.

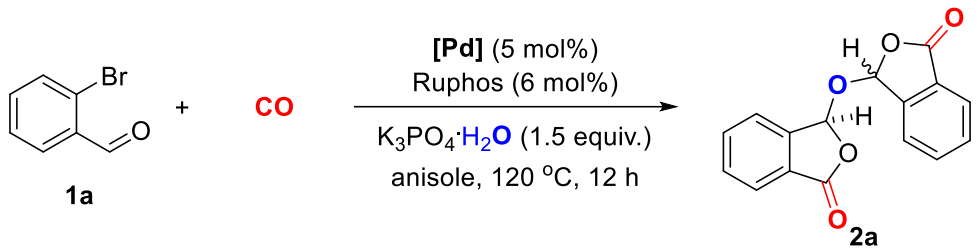
Table S1. Screening of base[a]



Entry	base	yield (%) **2a**	dr[b]
1	Na_2CO_3	32	2.2:1
2	K_2HPO_4	12	2.4:1
3	NaOH	11	3.1:1
4	$NaHCO_3$	trace	-
5	K_2CO_3	trace	-
6	C_2H_5ONa	0	-
7	Na_3PO_4	27	2.3:1
8	K_3PO_4	21	3.1:1
9	DBU	trace	-
10	(*i*-Pr)$_2$NEt	0	-
11	$K_3PO_4 \cdot H_2O$	60	2.6:1
12	NEt_3	0	-

[a]Reaction conditions: **1a** (1.0 mmol), $PdBr_2$ (0.025 mmol, 5 mol%), Ruphos (0.03 mmol, 6 mol%), base (0.75 mmol, 1.5 equiv.), CO (20 atm), anisole (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^{1}H NMR.

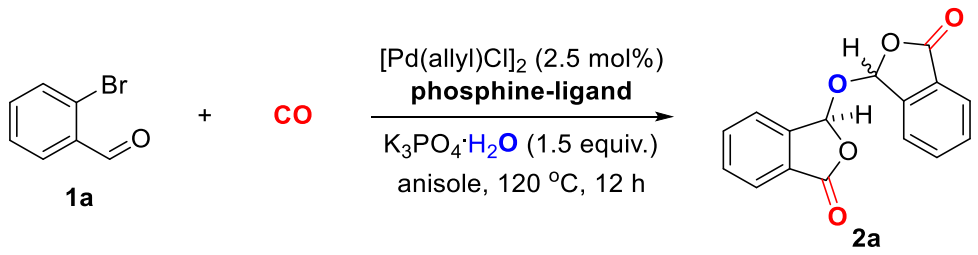
Table S2. Screening of the catalyst precursor[a]



Entry	[Pd]	yield (%) **2a**	dr[b]
1	$PdBr_2$	60	2.5:1
2	$Pd(acac)_2$	74	2.6:1
3	$[Pd(allyl)Cl]_2$	82	2.9:1
4	$Pd(TFA)_2$	72	4.1:1
5	$Pd(COD)Br_2$	80	2.7:1
6	$Pd(P(t\text{-}Bu)_3)_2$	46	2.1:1
7	$Pd(PPh_3)_4$	56	2.2:1
8	$Pd_2(dba)_3$	68	2.1:1
9	$Pd(OAc)_2$	58	3.4:1
10	$Pd(MeCN)_2Cl_2$	64	2.9:1

[a]Reaction conditions: **1a** (1.0 mmol), [Pd] (5 mol%), Ruphos (0.03 mmol, 6 mol%), $K_3PO_4·H_2O$ (0.75 mmol, 1.5 equiv.), CO (20 atm), anisole (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^1H NMR.

Table S3. Screening of ligand[a]



Entry	ligand	yield (%) **2a**	dr[b]
1	L1	76	1.9:1
2	L2	78	1.9:1
3	L3	75	2.2:1
4	L4	trace	-
5	L5	82	2.9:1
6	L6	77	2.3:1
7	L7	48	1.5:1
8	L8	65	2.2:1
9	L9	62	2.1:1

[a]Reaction conditions: **1a** (1.0 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%),

phosphine ligand (0.03 mmol, 6 mol%), $K_3PO_4·H_2O$ (0.75 mmol, 1.5 equiv.), CO (20 atm), anisole (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^1H NMR.

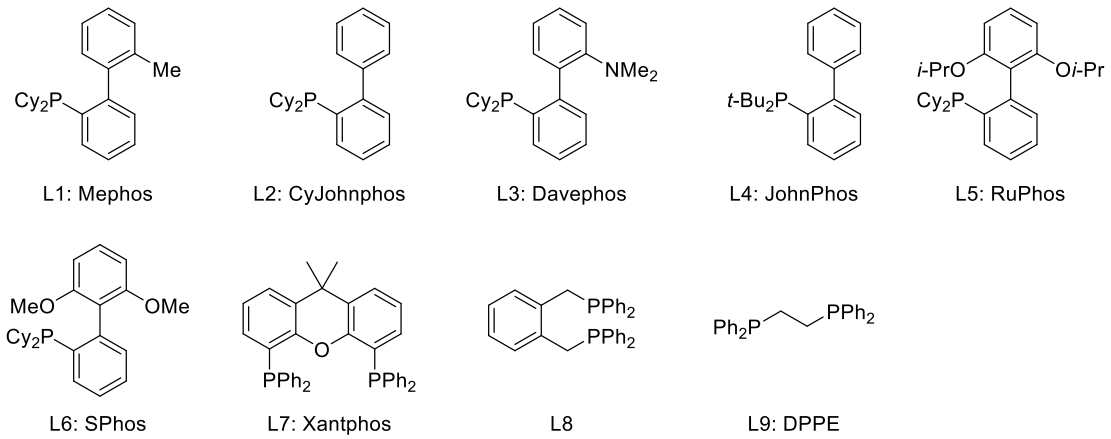
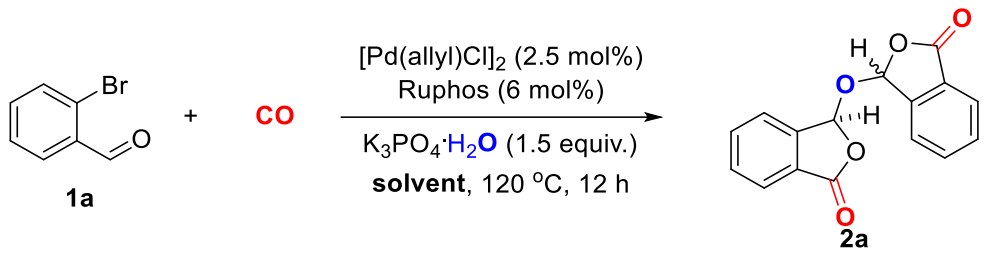


Figure S1. The structures of ligands

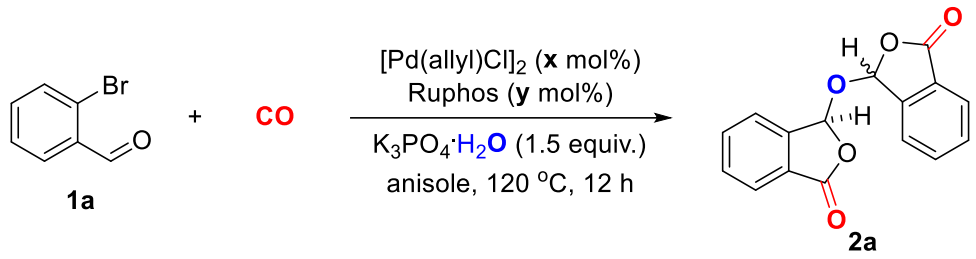
Table S4. Screening of solvent[a]



Entry	solvent	yield (%) **2a**	dr[b]
1	1,4-dioxane	72	2.0:1
2	toluene	82	1.5:1
3	NMP	78	2.1:1
4	anisole	82	2.9:1
5	THF	65	1.9:1
6	DCE	68	2.3:1

[a]Reaction conditions: **1a** (1.0 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), Ruphos (0.03 mmol, 6 mol%), $K_3PO_4·H_2O$ (0.75 mmol, 1.5 equiv.), CO (20 atm), solvent (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^1H NMR.

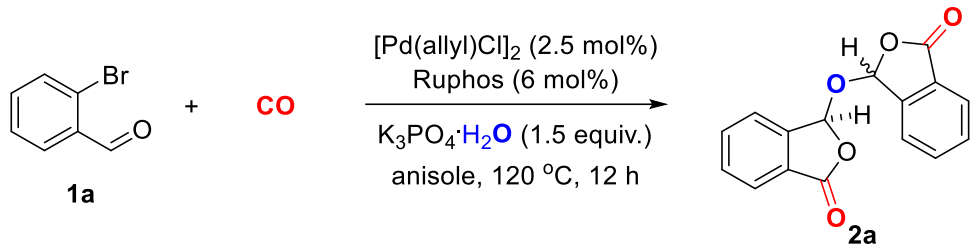
Table S5. Effect on the ratio of palladium to Ruphos[a]



Entry	**x** mol%	**y** mol%	yield (%) **2a**	dr[b]
1	2.5	6	82	2.9:1
2	2.5	11	61	2.1:1

[a]Reaction conditions: **1a** (1.0 mmol), $[Pd(allyl)Cl]_2$ (x mol%), RuPhos (y mol%), $K_3PO_4·H_2O$ (0.75 mmol, 1.5 equiv.), CO (20 atm), anisole (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^{1}H NMR.

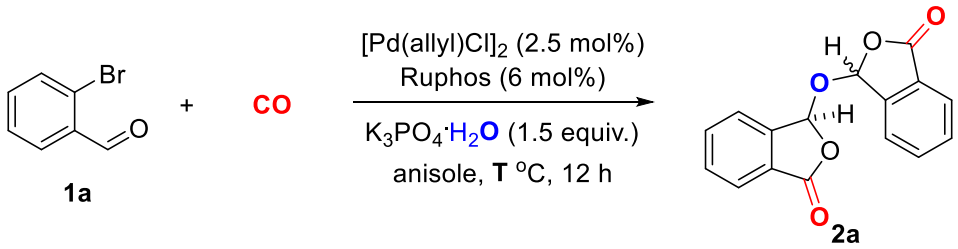
Table S6. Screening of pressures of CO[a]



Entry	CO (atm)	yield (%) **2a**	dr[b]
1	20	82	2.9:1
2	10	83	2.9:1
3	2	74	2.8:1

[a]Reaction conditions: **1a** (1.0 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), Ruphos (0.03 mmol, 6 mol%), $K_3PO_4·H_2O$ (0.75 mmol, 1.5 equiv.), CO (x atm), anisole (1.5 mL), 120 ℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^{1}H NMR.

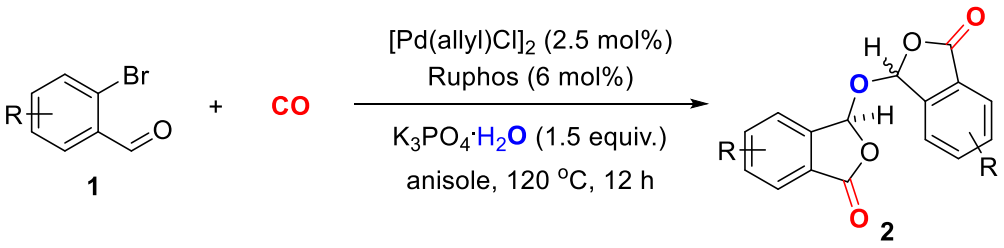
Table S7. Screening of temperature[a]



Entry	T (°C)	yield (%) **2a**	dr[b]
1	120	83	2.9:1
2	60	trace	-
3	RT	0	-

[a]Reaction conditions: **1a** (1.0 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol, 2.5 mol%), Ruphos (0.03 mmol, 6 mol%), $K_3PO_4 \cdot H_2O$ (0.75 mmol, 1.5 equiv.), CO (10 atm), anisole (1.5 mL), T/℃, 12 h. [b]The dr value of the crude reaction mixture was determined by ^1H NMR.

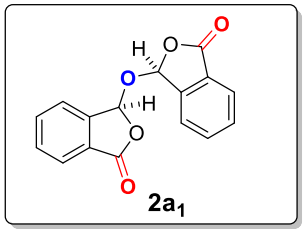
4. General procedure for carbonylative cyclization[2]



In the glove box, a mixture of **1** (1.0 mmol), $K_3PO_4 \cdot H_2O$ (173 mg, 0.75 mmol, 1.5 equiv.), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), Ruphos (14.0 mg, 0.03 mmol, 6 mol%) and anisole (1.5 mL) was added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (10 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood. The dr value of the crude reaction mixture was determined by ^1H NMR. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to afford the product **2**.

5. Spectral data of products

***Rac*-3,3'-oxybis(isobenzofuran-1(3*H*)-one) ($2a_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 87 mg, 62% yield. M. p.: 227-229 °C. **IR** (neat) ν(cm^{-1}): 3067, 2923, 1775, 1607, 1460, 1362, 1289, 1057, 935, 892, 752; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dt, *J* = 7.6, 1.1 Hz, 2H), 7.74 - 7.70 (m, 2H), 7.66 - 7.60 (m, 4H), 6.90 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 144.2, 135.0, 131.5, 126.7, 125.9, 124.1, 99.2; **HRMS** (ESI) calcd. for $C_{16}H_{10}O_5Na$ $[M+Na]^+$: 305.0420, found: 305.0427. The compound was confirmed by single-crystal X-ray analysis.



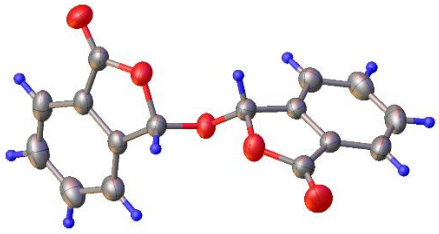
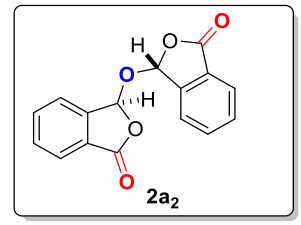


Figure S2. The structure of the product **$2a_1$**

***Meso*-3,3'-oxybis(isobenzofuran-1(3*H*)-one) ($2a_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 30 mg, 21% yield. M. p.: 204-207 °C. **IR** (neat) ν(cm^{-1}): 3067, 2924, 1775, 1607, 1467, 1356, 1289, 1060, 935, 895, 751; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 7.6, 1.0 Hz, 2H), 7.82 - 7.74 (m, 4H), 7.68 (td, *J* = 7.4, 1.2 Hz, 2H), 6.58 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 144.2, 135.1, 131.6, 127.0, 125.7, 124.6, 98.3; **HRMS** (ESI) calcd. for $C_{16}H_{10}O_5Na$ $[M+Na]^+$: 305.0420, found: 305.0429. The compound was confirmed by single-crystal X-ray analysis.



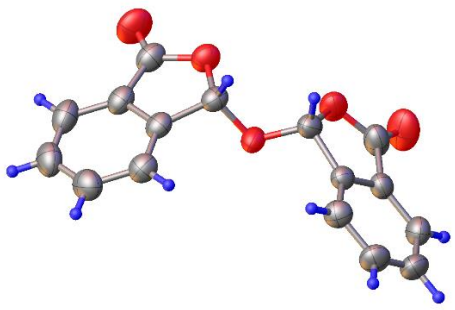
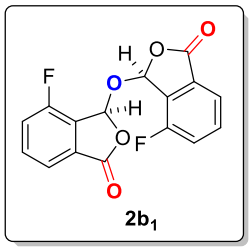


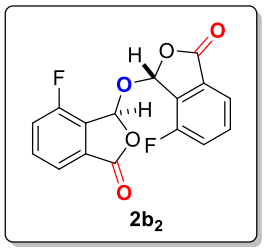
Figure S3. The structure of the product **$2a_2$**

***Rac*-3,3'-oxybis(4-fluoroisobenzofuran-1(3*H*)-one) (2b$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 63 mg, 40% yield. M. p.: 221-223 °C. **IR** (neat) ν(cm^{-1}): 3088, 2079, 1787, 1606, 1490, 1368, 1246, 1081, 925, 868, 751; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.68 (td, *J* = 7.9, 4.3 Hz, 2H), 7.39 (t, *J* = 8.3 Hz, 2H), 6.99 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7 (d, *J* = 1.6 Hz), 158.9 (d, *J* = 258.2 Hz), 134.2 (d, *J* = 6.6 Hz), 130.1 (d, *J* = 17.2 Hz), 129.6 (d, *J* = 2.9 Hz), 122.2 (d, *J* = 19.1 Hz), 121.9 (d, *J* = 4.3 Hz), 96.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.2; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0235.



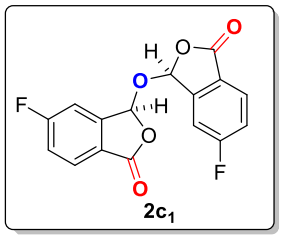
2b$_1$

***Meso*-3,3'-oxybis(4-fluoroisobenzofuran-1(3*H*)-one) (2b$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 53 mg, 33% yield. M. p.: 232-235 °C. **IR** (neat) ν(cm^{-1}): 3088, 2923, 1792, 1609, 1482, 1359, 1259, 1078, 932, 859, 748; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 - 7.77 (m, 4H), 7.76 - 7.71 (m, 2H), 7.35 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.6, 158.3 (d, *J* = 255.0 Hz), 134.8 (d, *J* = 3.1 Hz), 130.4 (d, *J* = 17.2 Hz), 128.9, 122.4 (d, *J* = 18.9 Hz), 121.6, 98.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.0; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0222.



2b$_2$

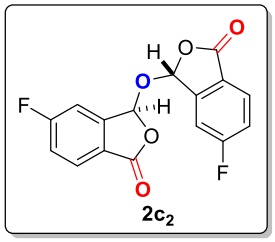
***Rac*-3,3'-oxybis(5-fluoroisobenzofuran-1(3*H*)-one) (2c$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 79 mg, 50% yield. M. p.: 187-189 °C. **IR** (neat) ν(cm^{-1}): 3076, 2969, 1781, 1610, 1488, 1356, 1258, 1051, 929, 843, 769; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 4.6 Hz, 2H), 7.37 (td, *J* = 8.6, 2.2 Hz, 2H), 7.31 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.85 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2 (d, *J* = 257.0 Hz), 166.8, 146.8(d, *J* = 10.4 Hz), 128.4 (d, *J* = 10.2 Hz), 122.6 (d, *J* = 2.2 Hz), 119.9 (d, *J* = 24.1 Hz), 111.7 (d, *J* = 24.8 Hz), 98.0 (d, *J* = 2.8 Hz); **^{19}F NMR** (376 MHz,



2c$_1$

$CDCl_3$) δ -100.5; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0238.

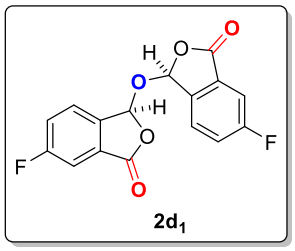
***Meso*-3,3'-oxybis(5-fluoroisobenzofuran-1(3*H*)-one) (2c$_2$)**: The title compound was



2c$_2$

prepared according to general procedure and purified by column chromatography to give a white solid, 34 mg, 21% yield. M. p.: 196-198 °C. **IR** (neat) ν(cm^{-1}): 3076, 2924, 1781, 1613, 1481, 1353, 1246, 1053, 929, 877, 776; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.99 (dd, *J* = 8.4, 4.7 Hz, 2H), 7.94 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.60 (ddd, *J* = 9.2, 8.4, 2.4 Hz, 2H), 7.13 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.5 (d, *J* = 252.3 Hz), 166.7, 147.7 (d, *J* = 11.0 Hz), 127.9 (d, *J* = 10.5 Hz), 122.3 (d, *J* = 1.9 Hz), 119.6 (d, *J* = 24.3 Hz), 112.2 (d, *J* = 25.2 Hz), 101.0 (d, *J* = 2.6 Hz); **^{19}F NMR** (376 MHz, DMSO-d_6) δ -102.7; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0230.

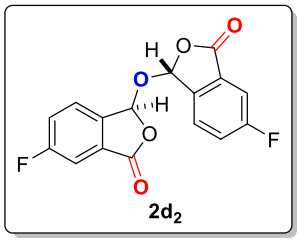
***Rac*-3,3'-oxybis(6-fluoroisobenzofuran-1(3*H*)-one) (2d$_1$)**: The title compound was



2d$_1$

prepared according to general procedure and purified by column chromatography to give a white solid yield, 61 mg, 38% yield. M. p.: 206-208 °C. **IR** (neat) ν(cm^{-1}): 3067, 2975, 1781, 1622, 1487, 1359, 1051, 931, 867, 721; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 - 7.58 (m, 4H), 7.46 (td, *J* = 8.5, 2.4 Hz, 2H), 6.86 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8 (d, *J* = 3.8 Hz), 165.9 (d, *J* = 253.1 Hz), 139.7 (d, *J* = 2.4 Hz), 129.0 (d, *J* = 9.3 Hz), 126.0 (d, *J* = 8.9 Hz), 123.0 (d, *J* = 24.0 Hz), 112.7 (d, *J* = 24.2 Hz), 98.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.3; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0223.

***Meso*-3,3'-oxybis(6-fluoroisobenzofuran-1(3*H*)-one) (2d$_2$)**: The title compound was

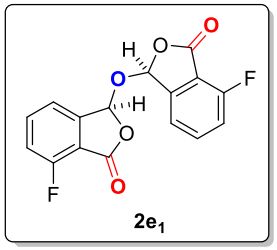


2d$_2$

prepared according to general procedure and purified by column chromatography to give a white solid, 27 mg, 17% yield. M. p.: 219-221 °C. **IR** (neat) ν(cm^{-1}): 3073, 2924, 1763, 1616, 1490, 1359, 1270, 1090, 940, 834, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.4, 4.2 Hz, 2H), 7.58 (dd, *J* = 6.9, 2.3 Hz, 2H), 7.53 (td, *J* = 8.5, 2.4 Hz, 2H), 6.55 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6 (d, *J* = 3.8

Hz), 165.9 (d, *J* = 253.2 Hz), 139.7 (d, *J* = 2.3 Hz), 129.3 (d, *J* = 9.3 Hz), 126.5 (d, *J* = 8.9 Hz), 123.2 (d, *J* = 23.9 Hz), 112.5 (d, *J* = 24.2 Hz), 97.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.1; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0240.

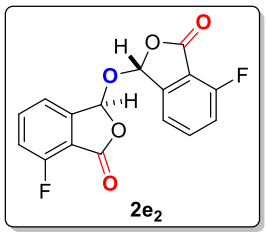
***Rac*-3,3'-oxybis(7-fluoroisobenzofuran-1(3*H*)-one) (2e$_1$)**: The title compound was



2e$_1$

prepared according to general procedure and purified by column chromatography to give a white solid, 53 mg, 33% yield. M. p.: 229-231 ºC. **IR** (neat) ν(cm^{-1}): 3067, 2923, 1778, 1622, 1481, 1311, 1262, 934, 803, 779; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.93 (td, *J* = 7.9, 4.7 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.57 - 7.52 (m, 2H), 7.05 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 163.7 (d, *J* = 2.6 Hz), 159.5 (d, *J* = 261.5 Hz), 146.5, 138.5 (d, *J* = 7.9 Hz), 120.6 (d, *J* = 4.0 Hz), 118.5 (d, *J* = 18.4 Hz), 113.5 (d, *J* = 14.3 Hz), 98.8; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -115.5; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0232.

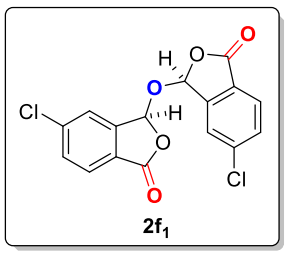
***Meso*-3,3'-oxybis(7-fluoroisobenzofuran-1(3*H*)-one) (2e$_2$)**: The title compound was



2e$_2$

prepared according to general procedure and purified by column chromatography to give a white solid, 12 mg, 8% yield. M. p.: 210-212 ºC. **IR** (neat) ν(cm^{-1}): 3082, 2923, 1778, 1609, 1485, 1359, 1261, 1069, 938, 797, 776; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.97 - δ 7.92 (m, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 8.9 Hz, 2H), 7.15 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 163.9 (d, *J* = 2.8 Hz), 159.4 (d, *J* = 259.8 Hz), 147.0, 138.2 (d, *J* = 7.9 Hz), 121.0 (d, *J* = 4.1 Hz), 118.4 (d, *J* = 18.5 Hz), 113.5 (d, *J* = 14.3 Hz), 100.9; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -115.8; **HRMS** (ESI) calcd. for $C_{16}H_8F_2O_5Na$ $[M+Na]^+$: 341.0232, found: 341.0238.

***Rac*-3,3'-oxybis(5-chloroisobenzofuran-1(3*H*)-one) (2f$_1$)**: The title compound was

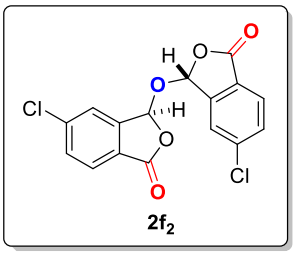


2f$_1$

prepared according to general procedure and purified by column chromatography to give a white solid, 65 mg, 37% yield. M. p.: 222-225 ºC. **IR** (neat) ν(cm^{-1}): 3088, 2969, 1772, 1613, 1426, 1344, 1212, 1054, 934, 840, 775; **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.64 - 7.60 (m, 4H), 6.84 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 145.6, 141.9, 132.4, 127.1, 125.0, 124.5, 98.1; **HRMS** (ESI) calcd. for $C_{16}H_8Cl_2O_5Na$ $[M+Na]^+$: 372.9641, found: 372.9649.

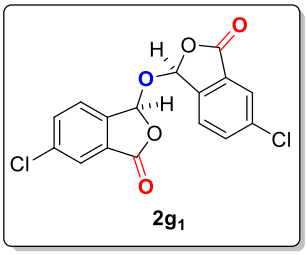
***Meso*-3,3'-oxybis(5-chloroisobenzofuran-1(3*H*)-one) (2f$_2$)**: The title compound was



2f$_2$

prepared according to general procedure and purified by column chromatography to give a white solid, 17 mg, 10% yield. M. p.: 228-230 °C. **IR** (neat) ν(cm^{-1}): 3082, 2923, 1781, 1609, 1432, 1341, 1215, 1069, 940, 885, 775; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 1.7 Hz, 2H), 7.65 (dd, *J* = 8.2, 1.8 Hz, 2H), 6.56 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 145.7, 142.0, 132.4, 127.0, 125.3, 124.8, 97.7; **HRMS** (ESI) calcd. for $C_{16}H_8Cl_2O_5Na$ $[M+Na]^+$: 372.9641, found: 372.9647.

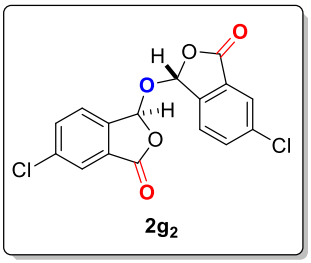
***Rac*-3,3'-oxybis(6-chloroisobenzofuran-1(3*H*)-one) (2g$_1$)**: The title compound was



2g$_1$

prepared according to general procedure and purified by column chromatography to give a white solid, 75 mg, 43% yield. M. p.: 228-230 °C. **IR** (neat) ν(cm^{-1}): 3082, 2923, 1781, 1609, 1432, 1341, 1215, 1069, 940, 885, 775; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.85 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 142.2, 138.1, 135.3, 128.5, 125.9, 125.3, 98.8; **HRMS** (ESI) calcd. for $C_{16}H_8Cl_2O_5Na$ $[M+Na]^+$: 372.9641, found: 372.9650.

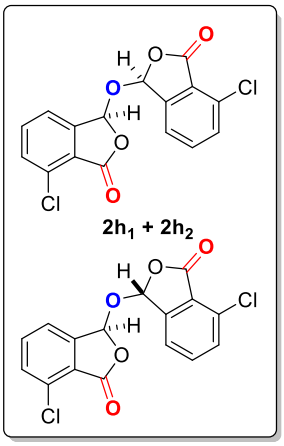
***Meso*-3,3'-oxybis(6-chloroisobenzofuran-1(3*H*)-one) (2g$_2$)**: The title compound was



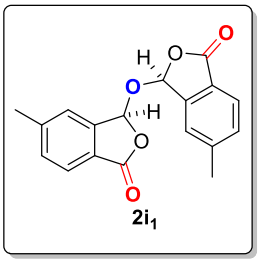
2g$_2$

prepared according to general procedure and purified by column chromatography to give a white solid, 30 mg, 17% yield. M. p.: 208-211 °C. **IR** (neat) ν(cm^{-1}): 3091, 2923, 1775, 1613, 1420, 1350, 1209, 1051, 923, 837, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.9 Hz, 2H), 7.77 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 6.55 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.3, 142.2, 138.2, 135.4, 128.7, 125.79, 125.77, 97.8; **HRMS** (ESI) calcd. for $C_{16}H_8Cl_2O_5Na$ $[M+Na]^+$: 372.9641, found: 372.9642.

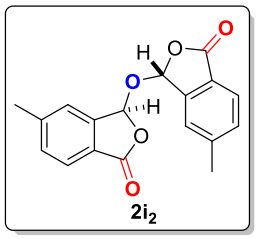
***Rac*-3,3'-oxybis(7-chloroisobenzofuran-1(3*H*)-one) / *Meso*-3,3'-oxybis(7-chloroisobenzofuran-1(3*H*)-one) (2h$_1$ + 2h$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid (**2h$_1$ + 2h$_2$**: 106.8 mg, 61% yield, dr = 5.0:1). M. p.: 209-211 °C. **IR** (neat) ν(cm^{-1}): 3085, 2945, 1784, 1594, 1469, 1356, 1209, 1060, 956, 893, 794; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.90 - 7.83 (m, 2H), 7.79 - 7.73 (m, 4H), 7.11 (s, 0.35H), 7.03 (s, 1.65H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 164.9, 164.7, 147.1, 146.7, 136.9, 136.7, 132.6, 132.5, 131.3, 131.0, 123.6, 123.2, 122.6, 100.2, 97.9; **HRMS** (ESI) calcd. for $C_{16}H_8Cl_2O_5Na$ $[M+Na]^+$: 372.9641, found: 372.9649.



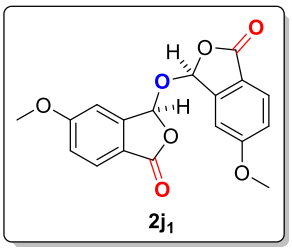
***Rac*-3,3'-oxybis(5-methylisobenzofuran-1(3*H*)-one) (2i$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 91 mg, 59% yield. M. p.: 184-186 °C. **IR** (neat) ν(cm^{-1}): 3061, 2920, 2853, 1771, 1616, 1487, 1353, 1276, 1050, 916, 834, 769; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.44 - 7.40 (m, 4H), 6.84 (s, 2H), 2.47 (s, 6H).; **^{13}C NMR** (100MHz, $CDCl_3$) δ 168.3, 146.6, 144.8, 132.5, 125.6, 124.4, 124.1, 99.0, 22.2; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_5Na$ $[M+Na]^+$: 333.0733, found: 333.0742.



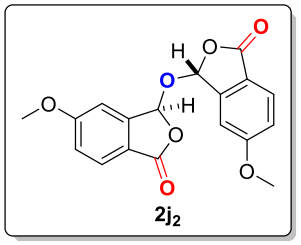
***Meso*-3,3'-oxybis(5-methylisobenzofuran-1(3*H*)-one) (2i$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 33 mg, 21% yield. M. p.: 212-214 °C. **IR** (neat) ν(cm^{-1}): 3067, 2923, 2853, 1771, 1613, 1487, 1344, 1280, 1050, 934, 843, 769; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.54 (s, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 6.51 (s, 2H), 2.55 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 146.6, 144.8, 132.6, 125.5, 124.8, 124.4, 98.2, 22.3; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_5Na$ $[M+Na]^+$: 333.0733, found: 333.0735.



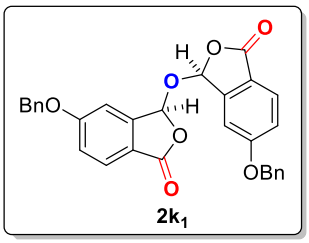
***Rac*-3,3'-oxybis(5-methoxyisobenzofuran-1(3H)-one) (2j$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 67 mg, 39% yield. M. p.: 226-228 ^{o}C. **IR** (neat) ν(cm^{-1}): 3073, 2954, 2853, 1784, 1609, 1493, 1356, 1255, 1072, 953, 837, 766; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.13 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.03 (d, *J* = 2.2 Hz, 2H), 6.80 (s, 2H), 3.88 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 165.5, 147.2, 127.3, 119.4, 118.6, 107.4, 98.5, 56.2; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_7Na$ $[M+Na]^+$: 365.0632, found: 365.0636.



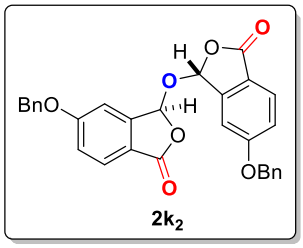
***Meso*-3,3'-oxybis(5-methoxyisobenzofuran-1(3H)-one) (2j$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 37 mg, 22% yield. M. p.: 209-212 ^{o}C. **IR** (neat) ν(cm^{-1}): 3070, 2926, 2850, 1778, 1606, 1493, 1353, 1255, 1078, 940, 837, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.16 (d, *J* = 2.2 Hz, 2H), 7.15 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.47 (s, 2H), 3.96 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 165.5, 147.2, 127.1, 119.2, 118.9, 108.2, 97.3, 56.3; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_7Na$ $[M+Na]^+$: 365.0632, found: 365.0638.



***Rac*-3,3'-oxybis(5-(benzyloxy)isobenzofuran-1(3*H*)-one) (2k$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 81 mg, 33% yield. M. p.: 246-248 ^{o}C. **IR** (neat) ν(cm^{-1}): 3030, 2935, 1778, 1490, 1322, 1259, 1072, 931, 852, 767; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.42 - 7.33 (m, 10H), 7.20 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.13 (d, *J* = 2.2 Hz, 2H), 6.80 (s, 2H), 5.16 – 5.10 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 164.6, 147.1, 135.5, 128.9, 128.6 127.7, 127.4, 119.9, 118.8, 108.4, 98.5, 70.9; **HRMS** (ESI) calcd. for $C_{30}H_{22}O_7Na$ $[M+Na]^+$: 517.1258, found: 517.1266.



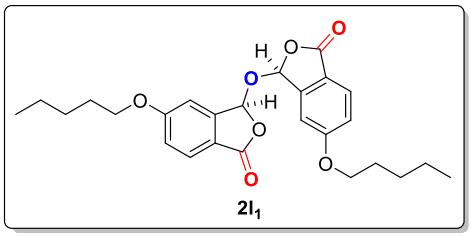
***Meso*-3,3'-oxybis(5-(benzyloxy)isobenzofuran-1(3*H*)-one) (2k$_2$)**: The title compound was prepared according to general procedure and purified by column



2k$_2$

chromatography to give a white solid, 50 mg, 20% yield. M. p.: 201-203 °C. **IR** (neat) ν(cm^{-1}): 3067, 2923, 1768, 1616, 1493, 1350, 1256, 1078, 934, 867, 775; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.35 (m, 10H), 7.24 - 7.19 (m, 4H), 6.47 (s, 2H), 5.24 - 5.16 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.6, 147.1, 135.5, 128.9, 128.7, 127.8, 127.2, 119.8, 119.1, 109.1, 97.4, 71.0; **HRMS** (ESI) calcd. for $C_{30}H_{22}O_7Na$ $[M+Na]^+$: 517.1258, found: 517.1260.

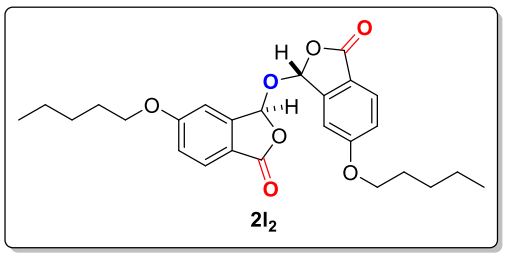
***Rac*-3,3'-oxybis(5-(pentyloxy)isobenzofuran-1(3*H*)-one) (2l$_1$)**: The title compound



2l$_1$

was prepared according to general procedure and purified by column chromatography to give a white solid, 90 mg, 40% yield. M. p.: 75-77 °C. **IR** (neat) ν(cm^{-1}): 3088, 2957, 2871, 1771, 1606, 1493, 1322, 1261, 1072, 934, 840, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.11 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.01 (d, *J* = 2.2 Hz, 2H), 6.79 (s, 2H), 4.02 (t, *J* = 6.5 Hz, 4H), 1.83 - 1.76 (m, 4H), 1.47 - 1.32 (m, 8H), 0.92 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 165.1, 147.2, 127.2, 119.6, 118.2, 107.9, 98.5, 69.1, 28.7, 28.1, 22.4, 14.1; **HRMS** (ESI) calcd. for $C_{26}H_{30}O_7Na$ $[M+Na]^+$: 477.1884, found: 477.1884.

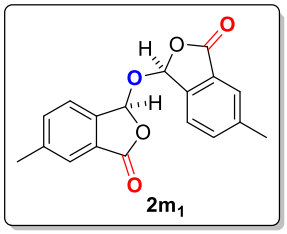
***Meso*-3,3'-oxybis(5-(pentyloxy)isobenzofuran-1(3*H*)-one (2l$_2$)**: The title compound



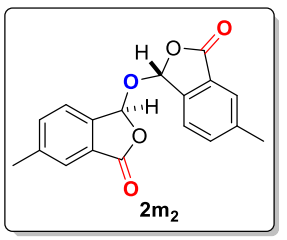
2l$_2$

was prepared according to general procedure and purified by column chromatography to give a white solid, 28 mg, 12% yield. M. p.: 107-109 °C. **IR** (neat) ν(cm^{-1}): 3064, 2954, 2868, 1765, 1606, 1490, 1347, 1261, 1078, 937, 773; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 2.2 Hz, 2H), 7.12 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.46 (s, 2H), 4.12 - 4.06 (m, 4H), 1.89 - 1.82 (m, 4H), 1.50 - 1.38 (m, 8H), 0.96 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 165.1, 147.1, 127.0, 119.4, 118.6, 108.6, 97.3, 69.2, 28.7, 28.2, 22.5, 14.1; **HRMS** (ESI) calcd. for $C_{26}H_{30}O_7Na$ $[M+Na]^+$: 477.1884, found: 477.1895.

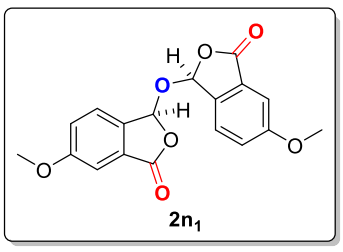
***Rac*-3,3'-oxybis(6-methylisobenzofuran-1(3*H*)-one) (2m$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 72 mg, 46% yield. M. p.: 169-171 ^{o}C. **IR** (neat) ν(cm^{-1}): 3055, 2926, 2865, 1781, 1619, 1496, 1347, 1298, 1054, 943, 816, 773; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.53 (q, *J* = 7.8 Hz, 4H), 6.85 (s, 2H), 2.48 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 142.0, 141.6, 135.9, 126.8, 125.7, 123.6, 99.1, 21.5; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_5Na$ $[M+Na]^+$: 333.0733, found: 333.0745.



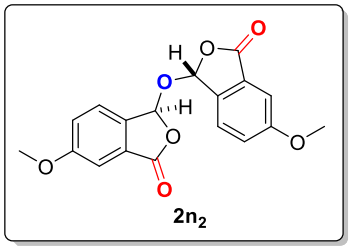
***Meso*-3,3'-oxybis(6-methylisobenzofuran-1(3*H*)-one) (2m$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 21 mg, 14% yield. M. p.: 158-161 ^{o}C. **IR** (neat) ν(cm^{-1}): 3021, 2923, 2856, 1763, 1628, 1496, 1283, 1054, 932, 825, 776; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.63 (q, *J* = 7.9 Hz, 4H), 6.51 (s, 2H), 2.49 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.2, 142.2, 141.7, 136.1, 127.2, 125.7, 124.3, 98.2, 21.6; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_5Na$ $[M+Na]^+$: 333.0733, found: 333.0738.



***Rac*-3,3'-oxybis(6-methoxyisobenzofuran-1(3*H*)-one) (2n$_1$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 66 mg, 39% yield. M. p.: 217-219 ^{o}C. **IR** (neat) ν(cm^{-1}): 3070, 2963, 2835, 1781, 1622, 1496, 1359, 1292, 1047, 937, 819, 773; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 2.3 Hz, 2H), 7.25 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.81 (s, 2H), 3.89 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 162.4 136.6, 128.4, 124.9, 123.3, 108.0, 99.2, 56.1; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_7Na$ $[M+Na]^+$: 365.0632, found: 365.0638.



***Meso*-3,3'-oxybis(6-methoxyisobenzofuran-1(3*H*)-one) (2n$_2$)**: The title compound was prepared according to general procedure and purified by column chromatography to give a white solid, 23 mg, 13% yield. M. p.: 157-160 ^{o}C. **IR** (neat) ν(cm^{-1}): 3076,

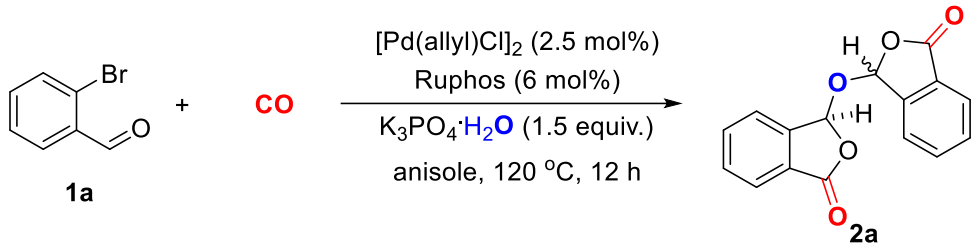


2n$_2$

2954, 2850, 1778, 1619, 1496, 1322, 1249, 1053, 943, 837, 773; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 - 7.60 (m, 2H), 7.32 - 7.30 (m, 4H), 6.50 (s, 2H), 3.89 (s, 6H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 168.1, 162.5, 136.5, 128.7, 125.5, 123.5, 107.8, 98.2, 56.1; **HRMS** (ESI) calcd. for $C_{18}H_{14}O_7Na$ $[M+Na]^+$: 365.0632, found: 365.0633.

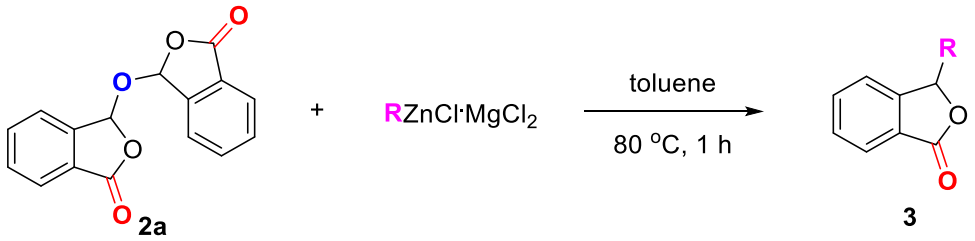
6. Synthetic transformations of product[3]

6.1. Large scale synthesis of 2a



In the glove box, a mixture of **1a** (2.56 g, 14.0 mmol), $K_3PO_4·H_2O$ (2.42 g, 10.5 mmol, 1.5 equiv.), $[Pd(allyl)Cl]_2$ (64 mg, 0.175 mmol, 2.5 mol%), Ruphos (196 mg, 0.42 mmol, 6 mol%) and anisole (15.0 mL) was added to a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (15 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood with an outlet system. The dr value of the crude reaction mixture was determined by ^1H NMR. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to afford the product **2a** (1.3 g, 68% yield, dr = 2.1:1).

6.2. General procedure for the synthesis of 3-substituted phthalides

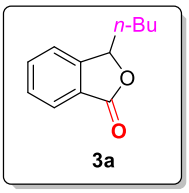


Magnesium turnings (110 mg, 4.5 mmol) and LiCl (153 mg, 3.6 mmol) were placed in a dry 25 mL Schlenk tube equipped with a magnetic stirrer under argon. After adding THF and I_2, the mixture was activated by adding $BrCH_2CH_2Br$ (11.3 mg, 0.06 mmol, 2.0 mol%) followed by gently heating. Aryl or alkyl bromide/iodide (3.0 mmol) was then added in one portion, the mixture was then allowed to reflux for 2 hours. After resulting mixture was stirred to be cooled to room temperature, the resulting

Grignard reagent was transferred with a syringe into a solution of $ZnCl_2$ (3.6 mL, 1M in THF, 3.6 mmol). This mixture was stirred at room temperature for 3 hours and the resulting organozinc reagent was titrated with iodine prior to use.

A dry and argon-flushed 25 mL Schlenk-tube was equipped with a stirring bar and a septum. Aryl or alkylzinc reagent (0.9 mmol) was transferred to the Schlenk-tube. Then, **2a** (84.6 mg, 0.3 mmol) was added in one portion at room temperature. Subsequent removal of THF in vacuum, toluene (1.0 mL) was added and the reaction mixture was heated typically at 80 °C for 1 hour. The reaction mixture was finally quenched with saturated NH_4Cl solution. The aqueous phase was extracted with ethyl acetate (3×10 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Finally, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 - 5/1) to give the desired product **3**.

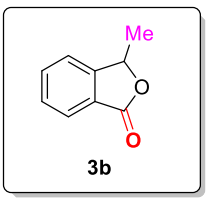
3-Butylisobenzofuran-1(3*H*)-one (3a): (colorless oil, 37.6 mg, 66% yield). **^{1}H NMR**



3a

(400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.70 (td, *J* = 7.5, 1.1 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 5.50 (dd, *J* = 7.9, 4.1 Hz, 1H), 2.10 - 2.01 (m, 1H), 1.81 - 1.72 (m, 1H), 1.53 - 1.29 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 150.2, 134.1, 129.1, 126.3, 125.8, 121.8, 81.6, 34.6, 27.0, 22.6, 14.0; **HRMS** (ESI) calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072, found: 191.1063.

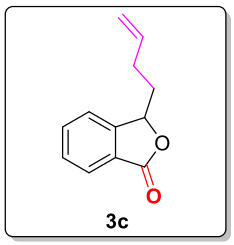
3-Methylisobenzofuran-1(3*H*)-one (3b): (colorless oil, 39.1 mg, 88% yield). **^{1}H NMR**



3b

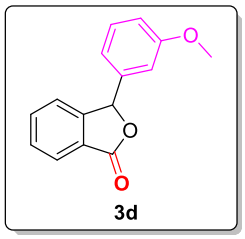
(400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.60 (q, *J* = 6.7 Hz, 1H), 1.66 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 151.3, 134.2, 129.2, 125.9, 125.8, 121.7, 77.9, 20.5; **HRMS** (ESI) calcd. for $C_9H_9O_2$ $[M+H]^+$: 149.0603, found: 149.0595.

3-(But-3-en-1-yl)isobenzofuran-1(3*H*)-one (3c): (colorless oil, 42.9 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.71 (td, *J* = 7.5, 1.1 Hz, 1H),

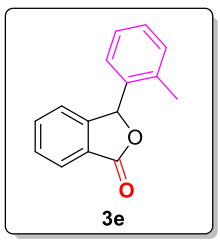


7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 5.89 - 5.79 (m, 1H), 5.52 (dd, *J* = 8.4, 3.7 Hz, 1H), 5.11 - 5.02 (m, 2H), 2.33 - 2.20 (m, 2H), 2.19 - 2.11 (m, 1H), 1.89 - 1.80 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 150.0, 136.9, 134.1, 129.2, 126.2, 125.8, 121.8, 116.1, 80.7, 34.1, 29.2; **HRMS** (ESI) calcd. for $C_{12}H_{13}O_2$ $[M+H]^+$: 189.0916, found: 189.0914.

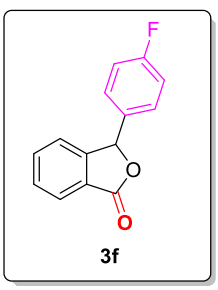
3-(3-Methoxyphenyl)isobenzofuran-1(3*H*)-one (3d): (colorless oil, 67.0 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.5, 2.8 Hz, 1H), 7.68 - 7.63 (m, 1H), 7.58 - 7.53 (m, 1H), 7.37 - 7.34 (m, 1H), 7.32 - 7.26 (m, 1H), 6.92 - 6.87 (m, 2H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.37 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 160.1, 149.7, 138.1, 134.4, 130.2, 129.5, 125.8, 125.6, 123.0, 119.2, 114.8, 112.5, 82.6, 55.4; **HRMS** (ESI) calcd. for $C_{15}H_{13}O_3$ $[M+H]^+$: 241.0865, found: 241.0854.



3-(*o*-Tolyl)isobenzofuran-1(3*H*)-one (3e): (colorless oil, 61.2 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.69 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.24 (m, 1H), 7.14 (td, *J* = 6.9, 6.0, 2.7 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.68 (s, 1H), 2.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 149.4, 137.2, 134.3, 134.2, 131.2, 129.44, 129.41, 127.3, 126.50, 126.46, 125.8, 123.1, 80.6, 19.4; **HRMS** (ESI) calcd. for $C_{15}H_{13}O_2$ $[M+H]^+$: 225.0916, found: 225.0908.

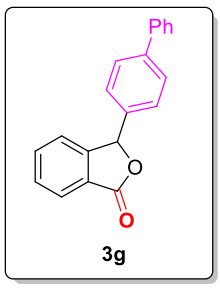


3-(4-Fluorophenyl)isobenzofuran-1(3*H*)-one (3e): (white solid, 65.7 mg, 96% yield). M. p.: 99-101 °C. **IR** (neat) ν(cm^{-1}): 3064, 2923, 1753, 1603, 1509, 1292, 1066, 978, 831, 736; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.69 (td, *J* = 7.5, 1.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.28 - 7.24 (m, 2H), 7.09 - 7.05 (m, 2H), 6.40 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 164.5 (d, *J* = 248.7 Hz), 149.5, 134.6, 132.4 (d, *J* = 3.2 Hz), 129.6, 129.2 (d, *J* = 8.5 Hz), 125.8, 125.7, 123.0, 116.2 (d, *J* = 21.9 Hz), 82.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ

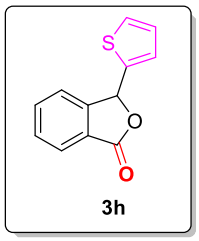


-111.8; **HRMS** (ESI) calcd. for $C_{14}H_{10}FO_2$ $[M+H]^+$: 229.0665, found: 229.0656.

3-([1,1'-Biphenyl]-4-yl)isobenzofuran-1(3*H*)-one (3g): (white solid, 76.4 mg, 89% yield). M. p.: 211-213 ^oC. **IR** (neat) ν(cm^{-1}): 3064, 2923, 1753, 1598, 1283, 1066, 968, 830, 721; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.70 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 - 7.56 (m, 4H), 7.46 - 7.42 (m, 2H), 7.40 - 7.34 (m, 4H), 6.46 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 149.7, 142.4, 140.4, 135.4, 134.5, 129.6, 129.0, 127.9, 127.8, 127.6, 127.3, 125.9, 125.8, 123.0, 82.7; **HRMS** (ESI) calcd. for $C_{20}H_{15}O_2$ $[M+H]^+$: 287.1072, found: 287.1064.

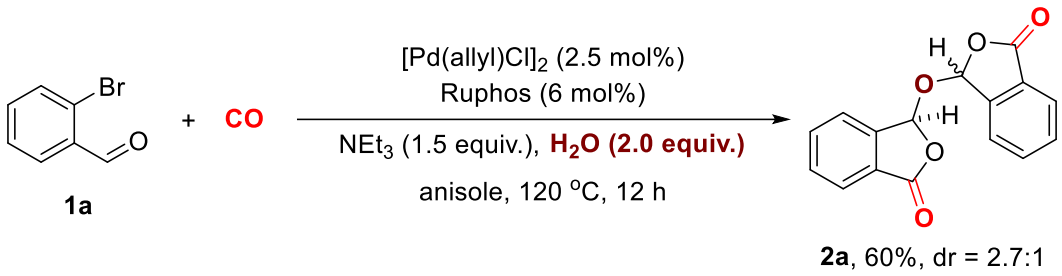


3-(Thiophen-2-yl)isobenzofuran-1(3*H*)-one (3h): (light yellow oil, 23.3 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 5.1 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.68 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 148.8, 139.0, 134.5, 123.0, 128.1, 127.7, 127.2, 126.1, 125.9, 123.3, 78.0; **HRMS** (ESI) calcd. for $C_{12}H_9O_2$ $[M+H]^+$: 217.0323, found: 217.0312.

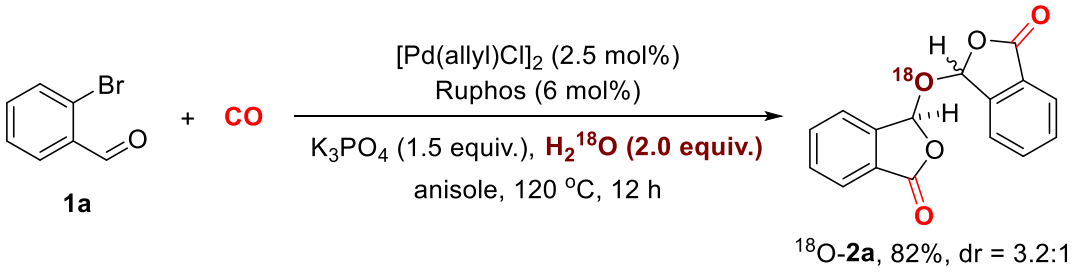


7. Control experiments

7.1. $H_2{}^{18}O$ labeling experiments



A mixture of **1a** (184 mg, 1.0 mmol), NEt_3 (76 mg, 0.75 mmol, 1.5 equiv.), H_2O (18 mg, 1.0 mmol, 2.0 equiv.), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), Ruphos (14.0 mg, 0.03 mmol, 6 mol%) and anisole (1.5 mL) was added to a dry glass vessel. The glass vessel was put into an autoclave. The autoclave was purged for three times and charged with CO (10 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood. The dr value of the crude reaction mixture was determined by ^1H NMR. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to **2a** (85 mg, 60% yield, dr = 2.7:1).



A mixture of **1a** (184 mg, 1.0 mmol), K_3PO_4 (160 mg, 0.75 mmol, 1.5 equiv.), $H_2{}^{18}O$ (20 mg, 1.0 mmol, 2.0 equiv.), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), Ruphos (14.0 mg, 0.03 mmol, 6 mol%) and anisole (1.5 mL) was added to a dry glass vessel. The glass vessel was put into an autoclave. The autoclave was purged for three times and charged with CO (10 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood. The dr value of the crude reaction mixture was determined by ^1H NMR. The solvent was

evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to ^{18}O-**2a** (116 mg, 82% yield, dr = 3.2:1). **HRMS** (ESI) calcd. for $C_{16}H_{10}{}^{18}O_5Na$ $[M+Na]^+$: 307.0463, found: 307.0467.

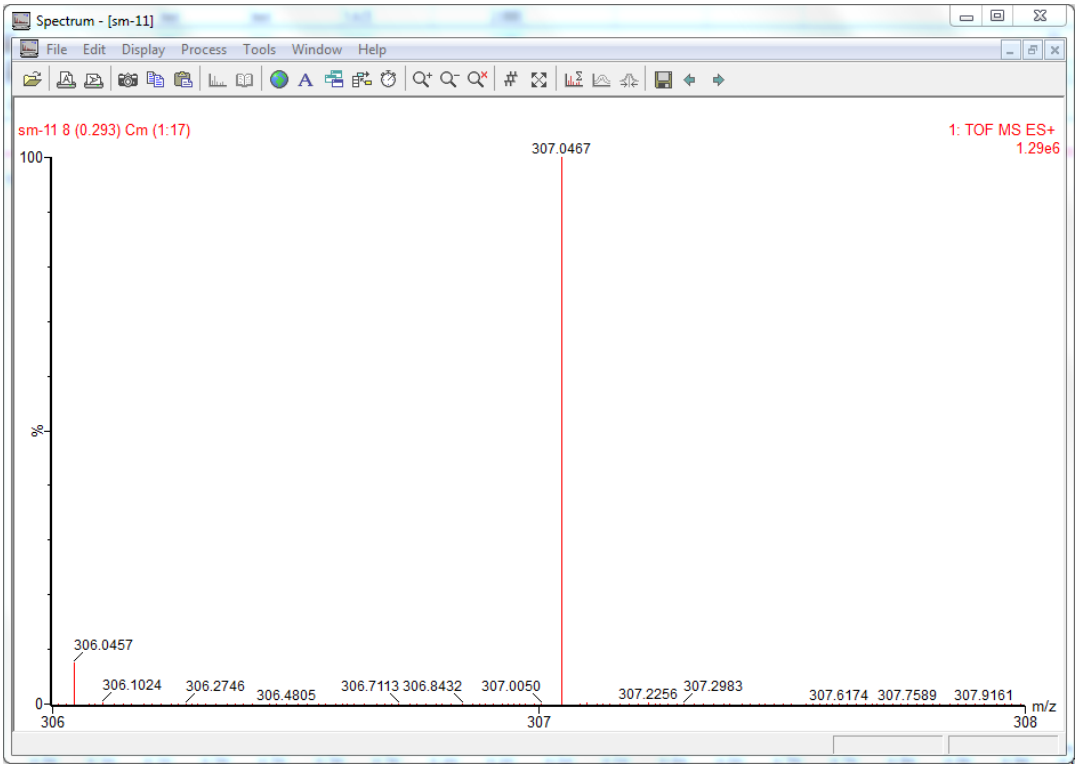
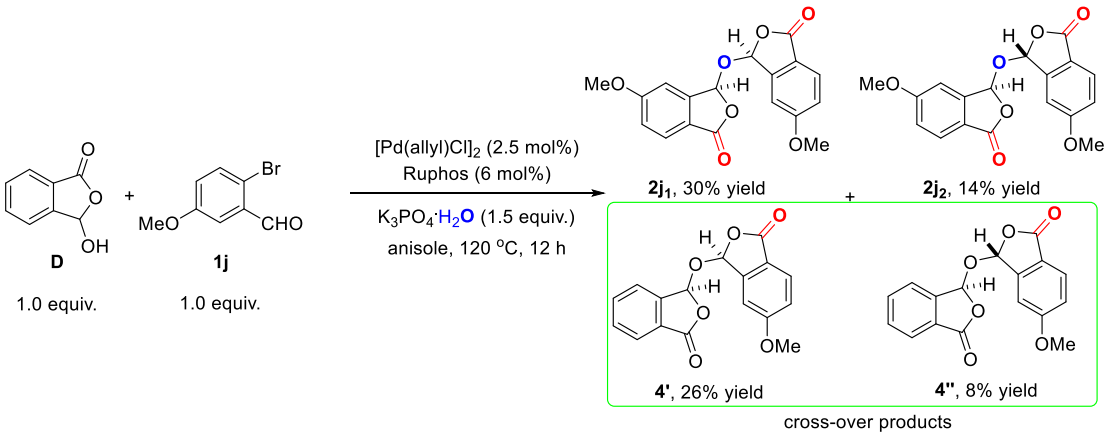


Figure S4. HRMS of $H_2{}^{18}O$ labeling experiment product ^{18}O-**2a**.

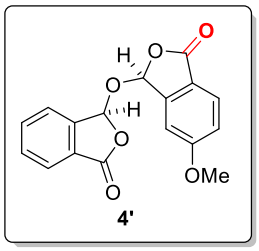
7.2. Cross-over experiment



In the glove box, a mixture of **D** (75 mg, 0.5 mmol), **1j** (54 mg, 0.5 mmol), $K_3PO_4{\cdot}H_2O$ (173 mg, 0.75 mmol, 1.5 equiv.), $[Pd(allyl)Cl]_2$ (4.6 mg, 0.0125 mmol, 2.5 mol%), Ruphos (14.0 mg, 0.03 mmol, 6 mol%) and anisole (1.5 mL) was added to

a dry glass vessel. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (10 atm). The reaction mixture was stirred at 120 ℃ for 12 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the well-ventilated fume hood. he solvent was evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 20/1/1 - 1/1/1) to **2j₁** (26 mg, 30% yield), **2j₂** (12 mg, 14% yield) and cross-over product **4**.

***Rac*-5-methoxy-3-((3-oxo-1,3-dihydroisobenzofuran-1-yl)oxy)isobenzofuran-**



1(*3H*)-one (4'): (a white solid, 37 mg, 26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.66 - 7.61 (m, 2H), 7.13 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.89 (s, 1H), 6.81 (s, 1H), 3.88 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 167.9, 165.5, 147.1, 144.3, 135.0, 131.5, 127.3, 126.7, 125.8, 124.1, 119.4, 118.6, 107.4, 99.2, 98.5, 56.2. **HRMS** (ESI) calcd. for $C_{17}H_{12}O_6$ $[M+Na]^+$: 335.0526, found: 335.0530.

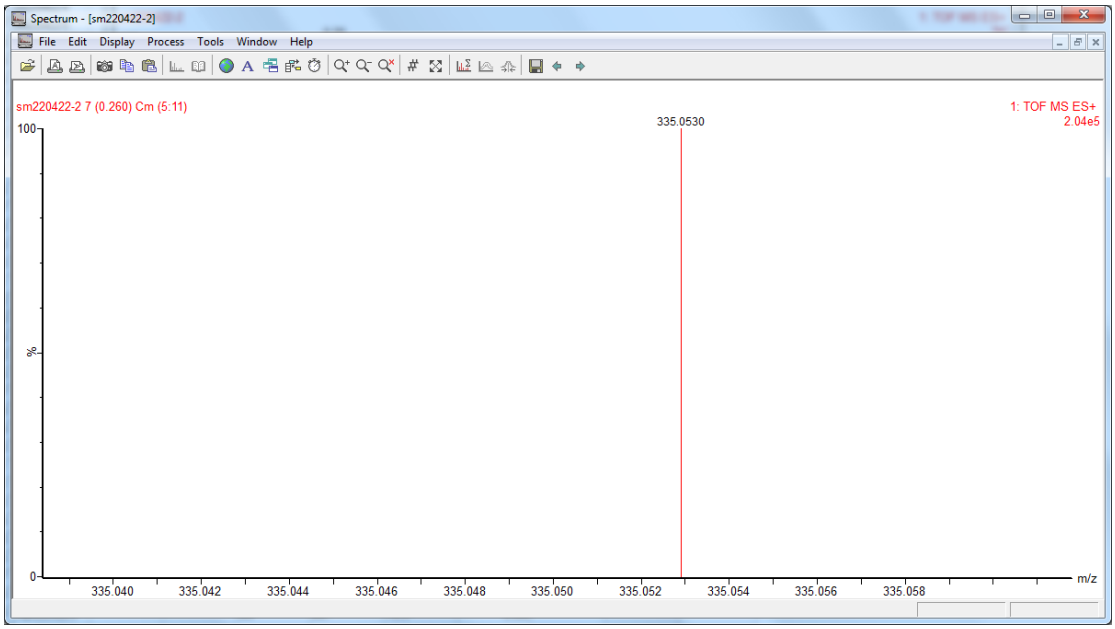
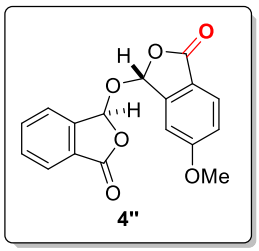


Figure S5. HRMS spectrum of the cross-over product **4'**

***Meso*-5-methoxy-3-((3-oxo-1,3-dihydroisobenzofuran-1-yl)oxy)isobenzofuran-**



1(*3H*)-one (4''): (a white solid, 12 mg, 8% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.82 - 7.76 (m, 3H), 7.68 (td, *J* = 7.4, 1.3 Hz, 1H), 7.15 - 7.13 (m, 2H), 6.58 (s, 1H), 6.46 (s, 1H), 3.96 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.0, 167.7, 165.5, 147.1, 144.3, 135.1, 131.6, 127.2, 127.0, 125.7, 124.7, 119.2, 118.9, 108.1, 98.2, 97.3, 56.3. **HRMS** (ESI) calcd. for $C_{17}H_{12}O_6$ $[M+Na]^+$: 335.0526, found: 335.0535.

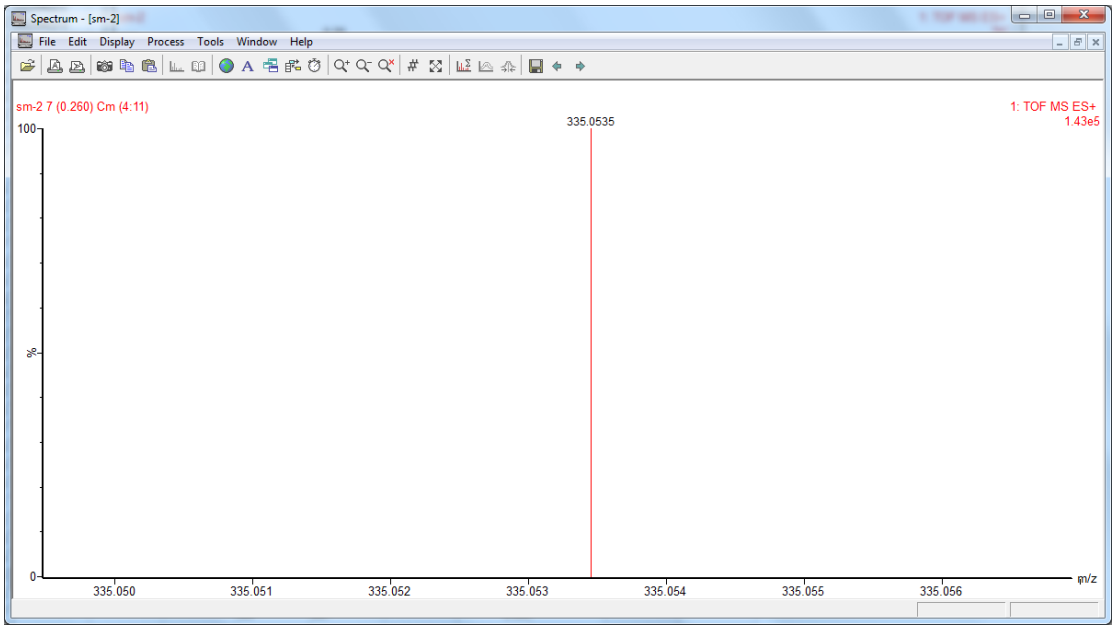
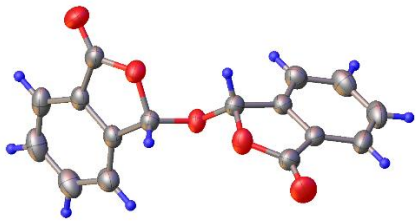


Figure S6. HRMS spectrum of the cross-over product **4''**

8. X-ray Single Crystal Data

Sample preparation: To a 10 mL sample vial, compound **2a$_1$** (20 mg), ethyl acetate (1 mL) was added successively at room temperature. The resulting solution was left open at room temperature until the colorless crystals precipitated.

Table S8. Crystal data and structure refinement for product **2a$_1$**



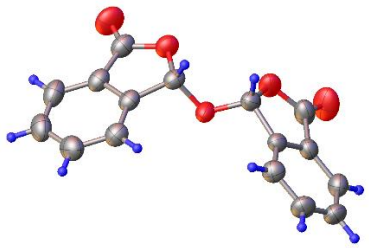
2a$_1$

The ellipsoid contour percent probability lever is 50%

Identification code	SM-UP_auto
Empirical formula	$C_{16}H_{10}O_5$
Formula weight	282.255
Temperature/K	298
Crystal system	monoclinic
Space group	I2/a
a/Å	15.3058(5)
b/Å	6.1080(2)
c/Å	28.2912(9)
α/°	90
β/°	101.503(3)
γ/°	90
Volume/Å^3	2591.76(15)
Z	8
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	0.915
F(000)	1172.4
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.8 to 145.82
Index ranges	$-18 \le h \le 17$, $-7 \le k \le 5$, $-32 \le l \le 34$
Reflections collected	4845
Independent reflections	2523 [R_{int} = 0.0210, R_{sigma} = 0.0300]
Data/restraints/parameters	2523/0/190
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0985
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1044
Largest diff. peak/hole / e Å^{-3}	0.17/-0.21

Sample preparation: To a 10 mL sample vial, compound **2a$_2$** (20 mg), ethyl acetate (1 mL) was added successively at room temperature. The resulting solution was left open at room temperature until the colorless crystals precipitated.

Table S9. Crystal data and structure refinement for product **2a$_2$**



2a$_2$

The ellipsoid contour percent probability lever is 50%

Identification code	SM-DOWN_auto
Empirical formula	$C_{16}H_{10}O_5$
Formula weight	282.255
Temperature/K	298
Crystal system	monoclinic
Space group	Pn
a/Å	4.4392(1)
b/Å	6.5027(1)
c/Å	22.2547(3)
α/°	90
β/°	91.313(1)
γ/°	90
Volume/Å^3	642.25(2)
Z	2
ρcalcg/cm^3	1.460
μ/mm^{-1}	0.923
F(000)	293.1
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.94 to 146
Index ranges	$-4 \le h \le 5$, $-8 \le k \le 8$, $-27 \le l \le 27$
Reflections collected	8918
Independent reflections	2317 [Rint = 0.0175, Rsigma = 0.0115]
Data/restraints/parameters	2317/2/190
Goodness-of-fit on F^2	1.155
Final R indexes [I>=2σ (I)]	R_1 = 0.0283, wR_2 = 0.0744
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0747
Largest diff. peak/hole / e Å^{-3}	0.10/-0.16
Flack parameter	0.35(13)

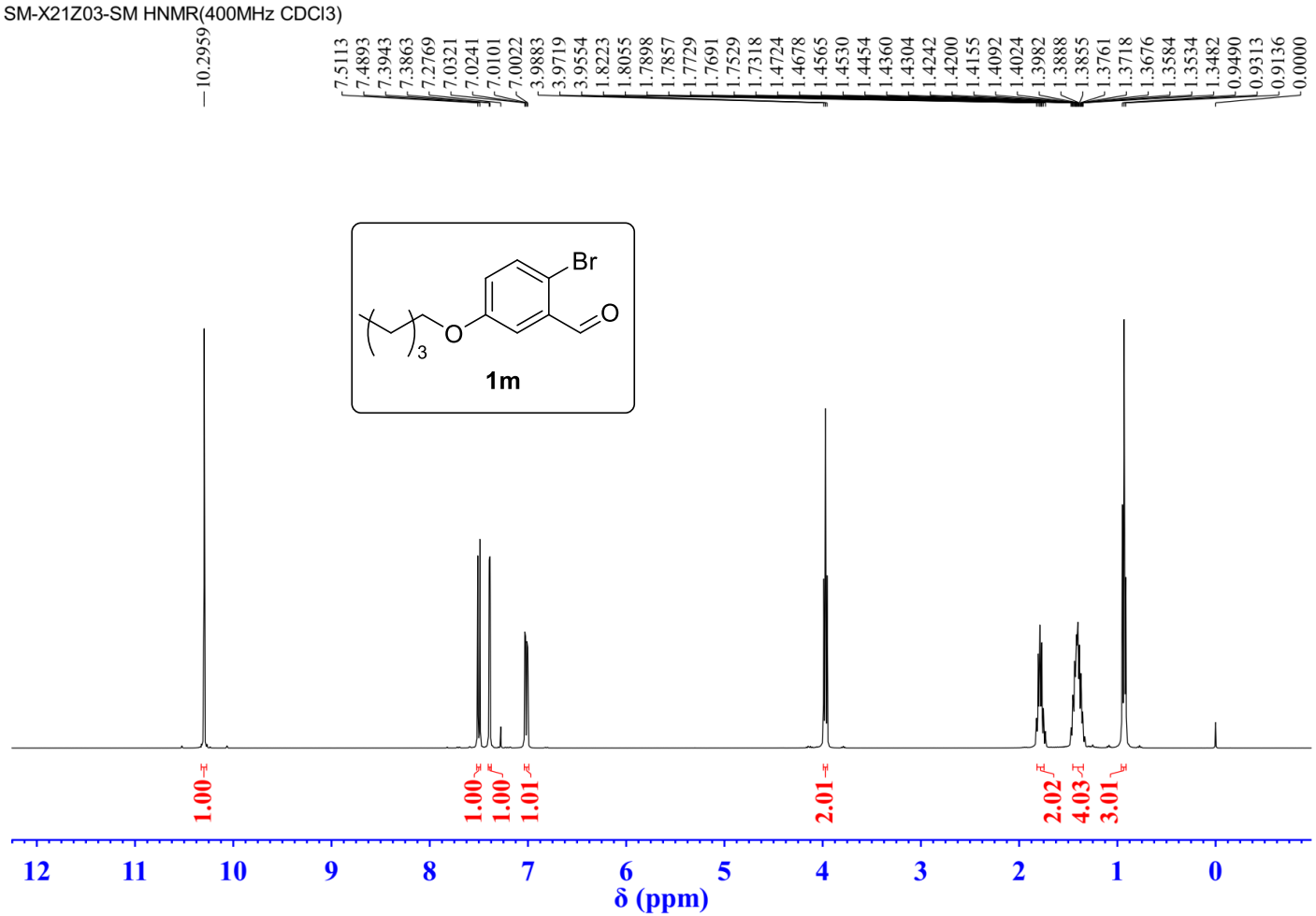
9. References

1. B. H. Ahn, I. Y. Lee and H. N. Lim, *Org. Biomol. Chem.*, 2018, **16**, 7851.

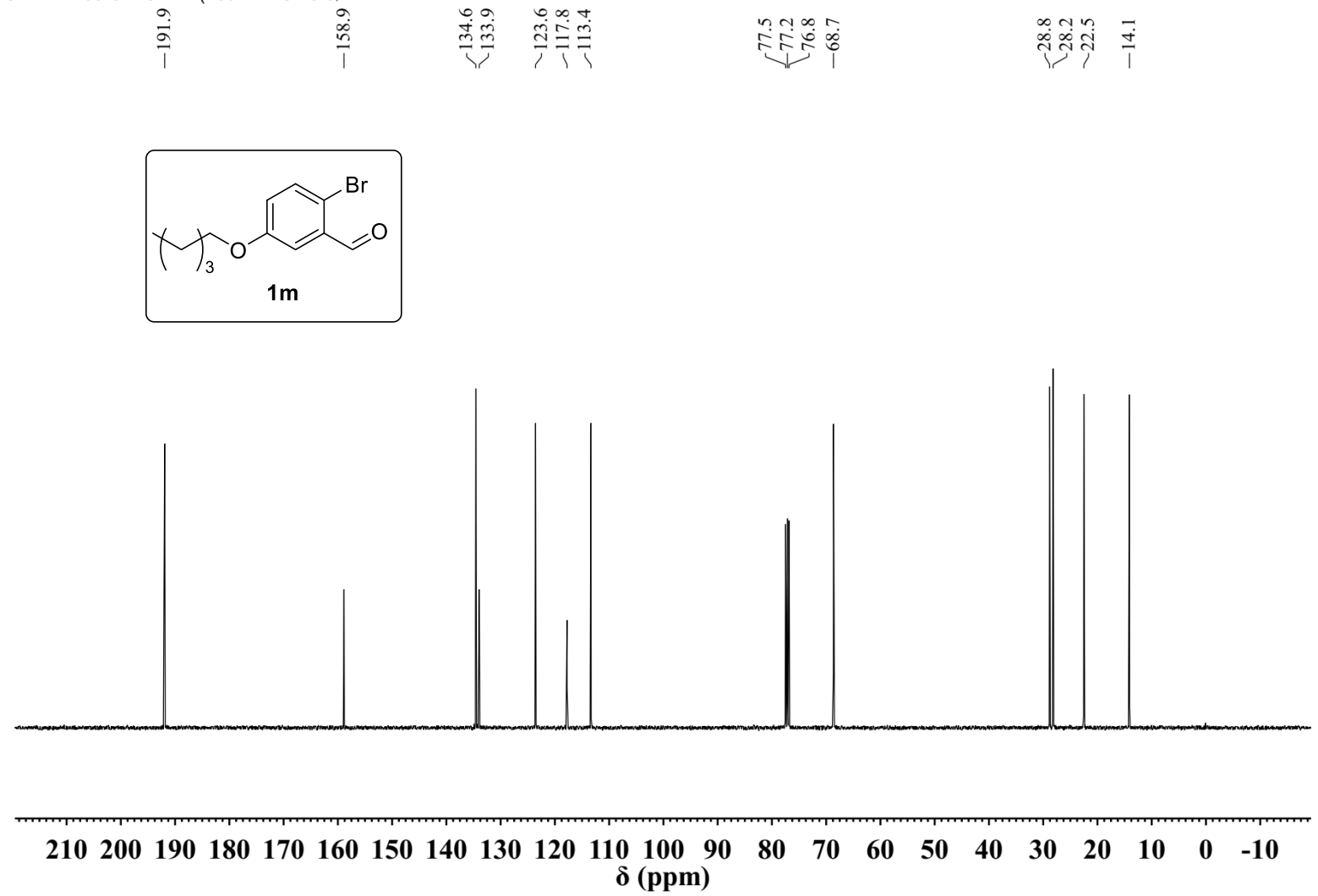
2. (a) B. Gao, S. Zou, G. Yang, Y. Ding and H. Huang, *Chem. Commun.*, 2020, **56**, 12198; (b) S. Wang, Y. Zhou and H. Huang, *Org. Lett.*, 2021, **23**, 2125; (c) Y. Ding, M. Si and H. Huang, *Org. Chem. Front.*, 2022, **9**, 715.

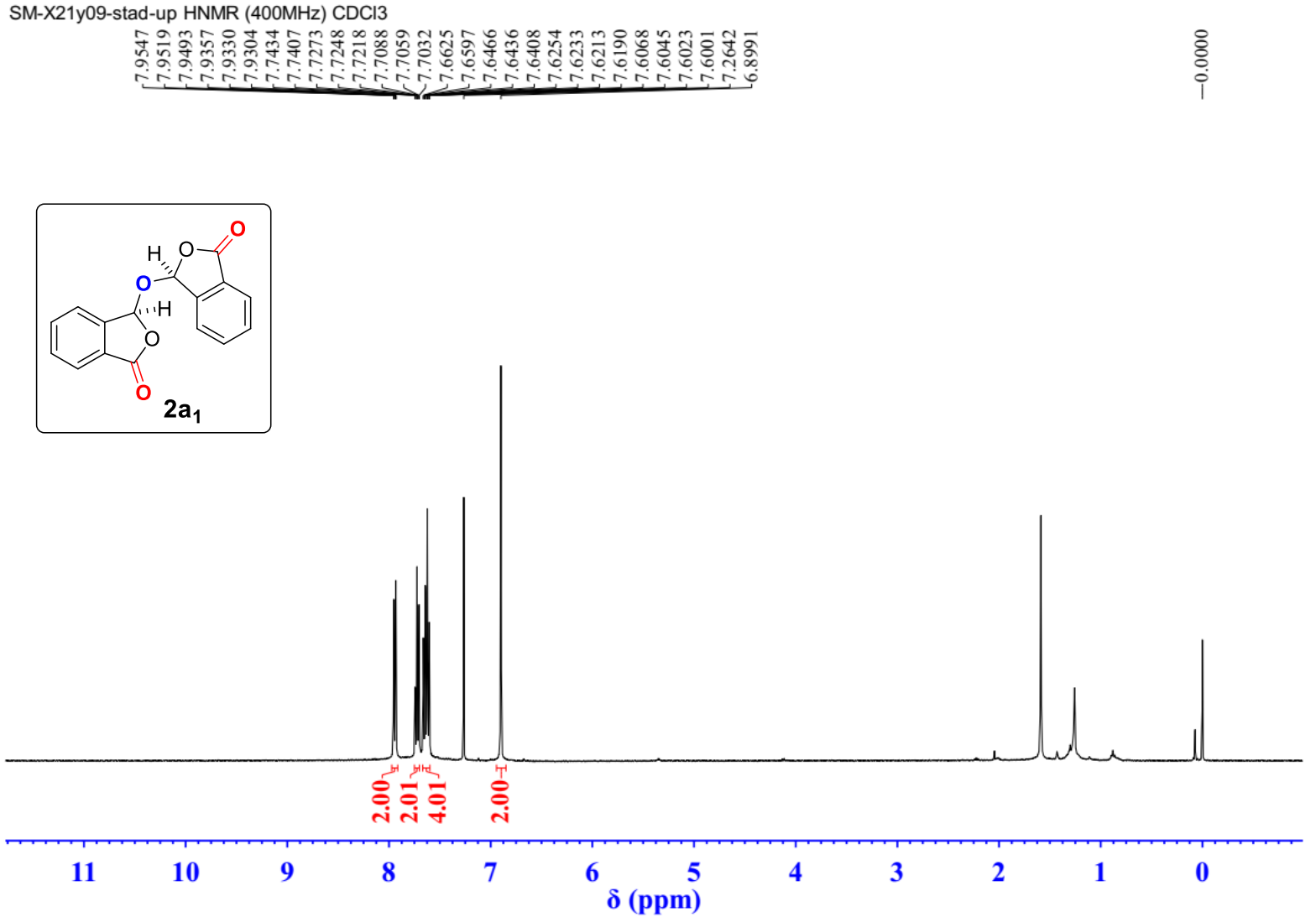
3. B. Wei, Q. Ren, T. Bein and P. Knochel, *Angew. Chem. Int. Ed.*, 2021, **60**, 10409.

10. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of the product

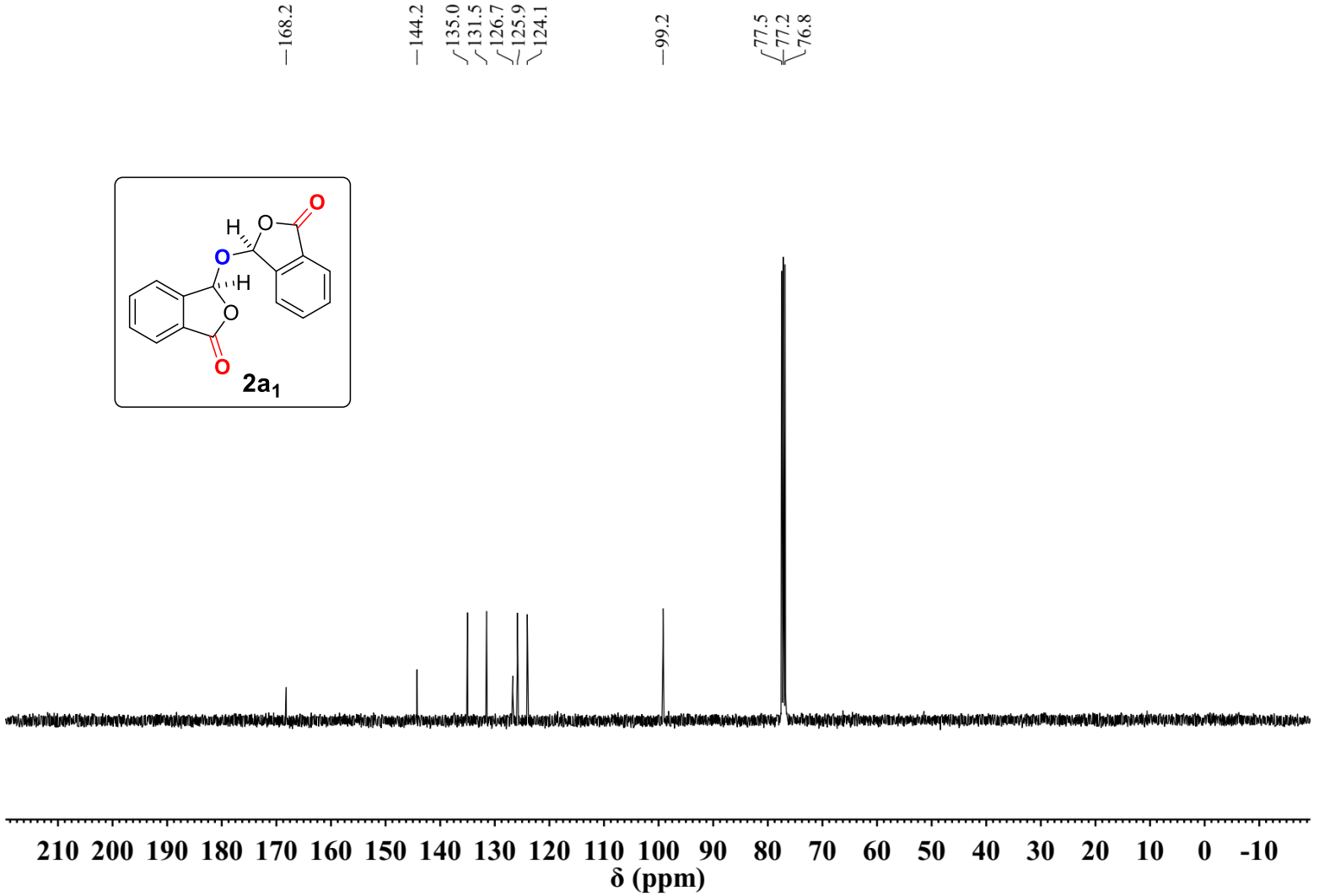


SM-X21Z03-SM CNMR(100MHz CDCl3)

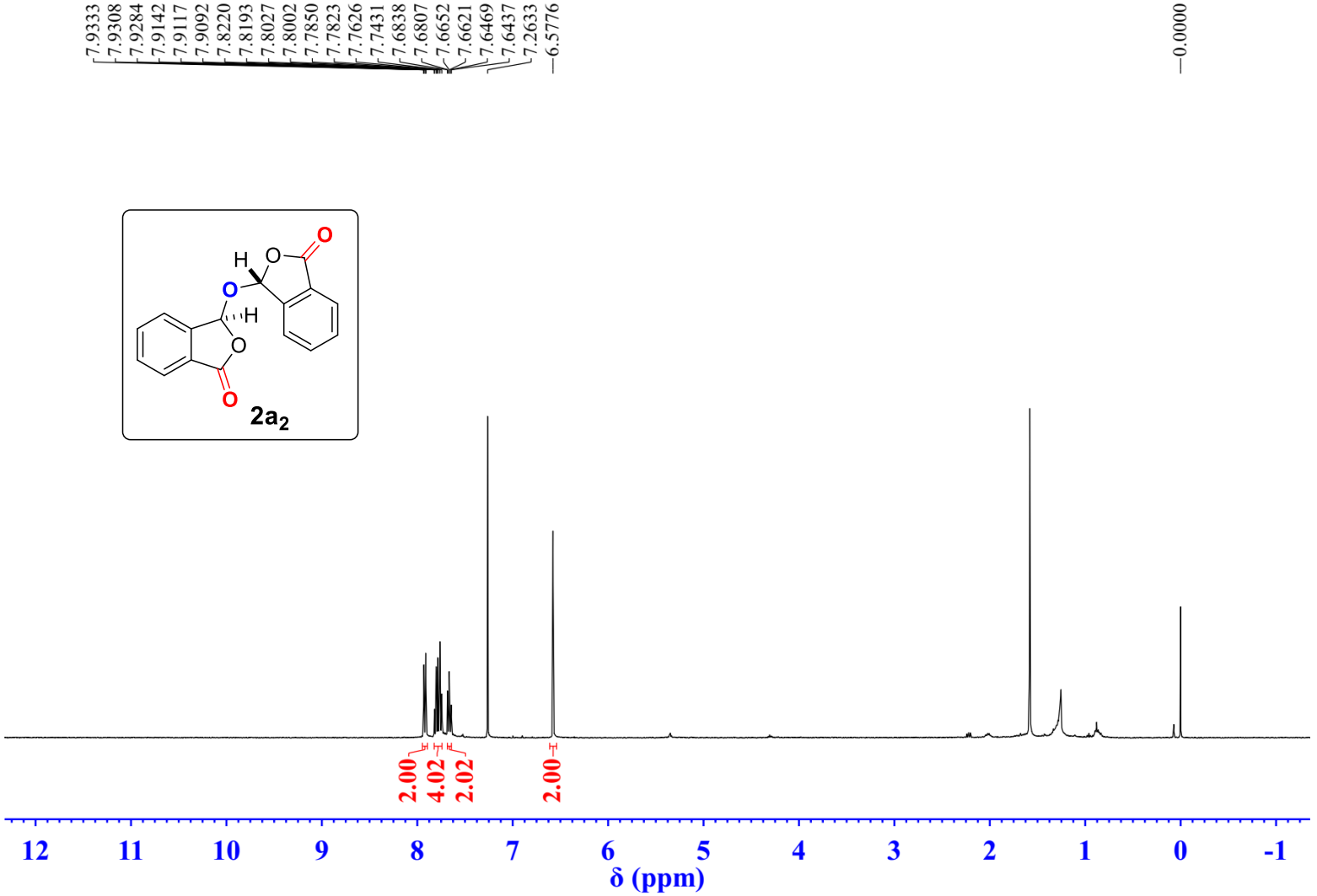


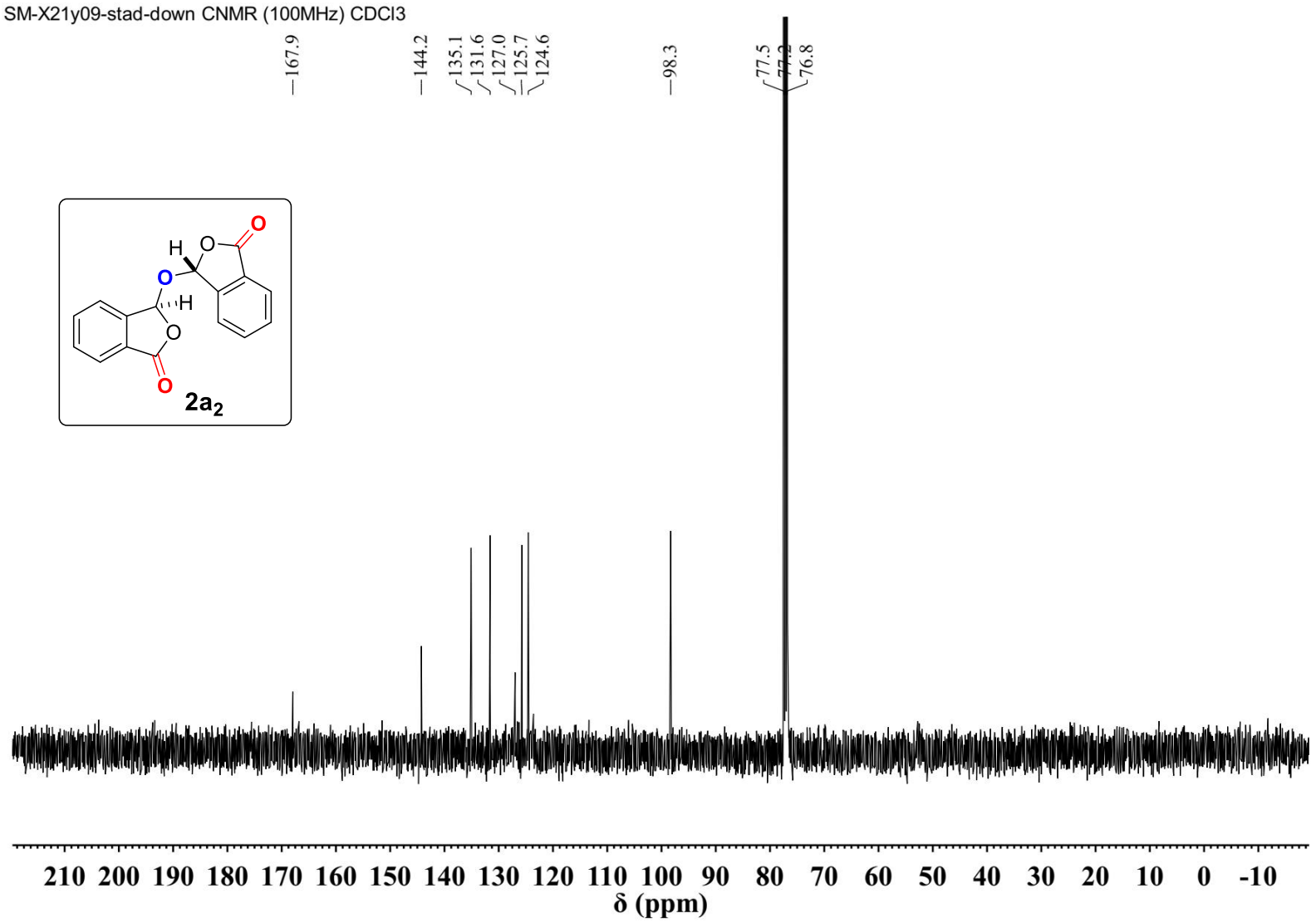

SM-X21y09-stad-up HNMR (400MHz) CDCl3
7.9547
7.9519
7.9493
7.9357
7.9330
7.9304
7.7434
7.7407
7.7273
7.7248
7.7218
7.7088
7.7059
7.7032
7.6625
7.6597
7.6466
7.6436
7.6408
7.6254
7.6233
7.6213
7.6190
7.6068
7.6045
7.6023
7.6001
7.2642
6.8991
0.0000
2a1
2.00
2.01
4.01
2.00
11
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

SM-X21y09-stad-up CNMR (100MHz) CDCl3

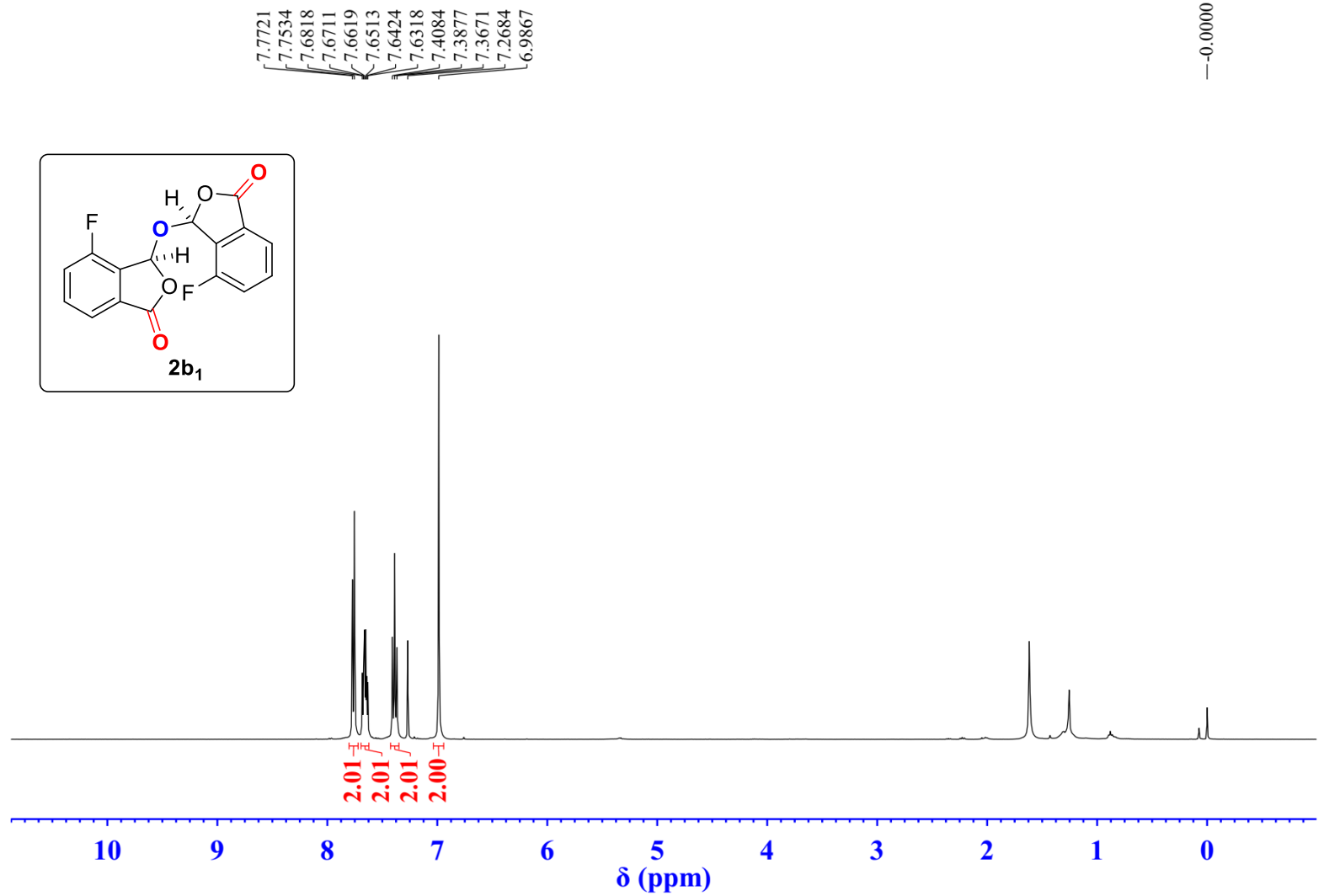


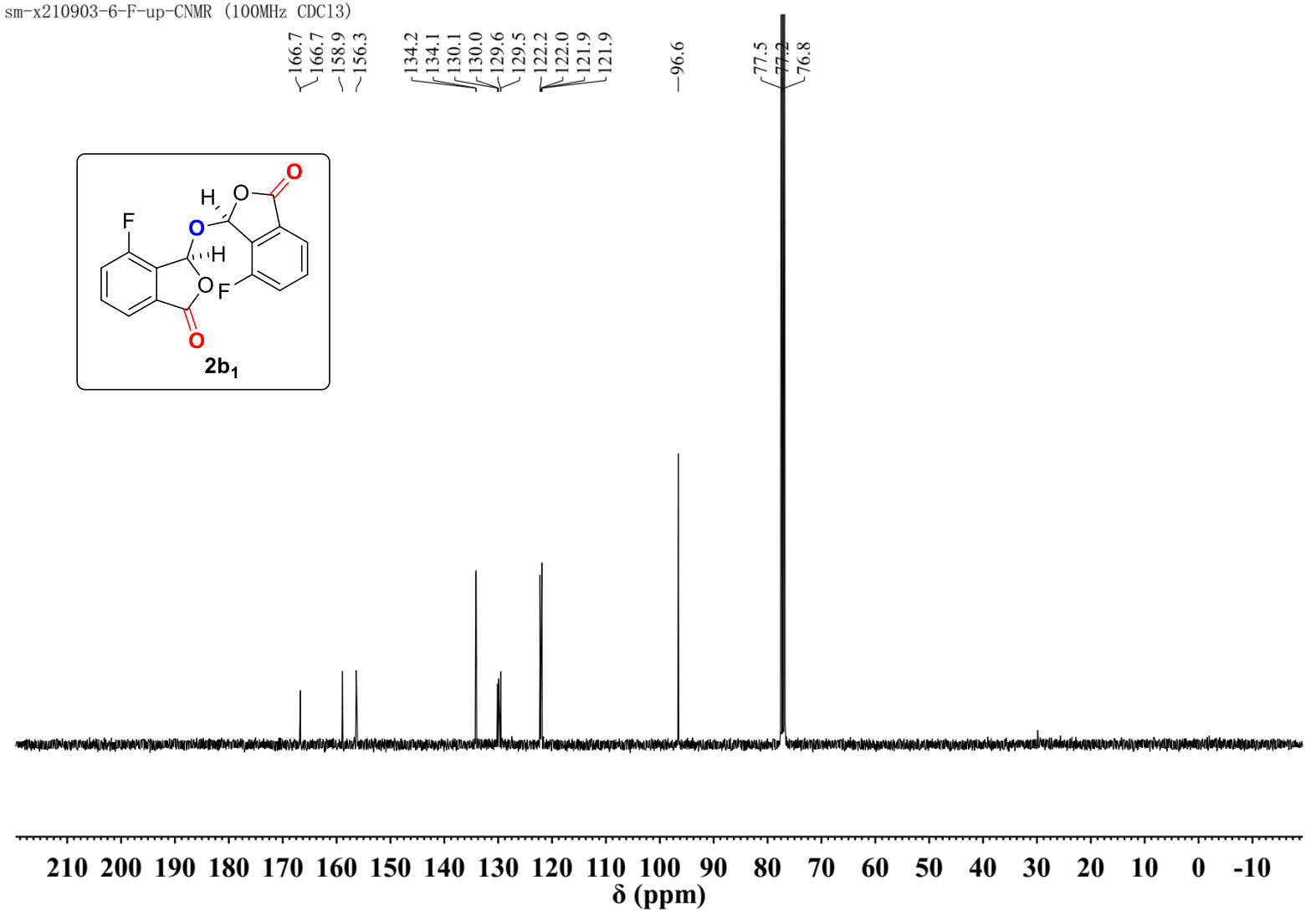
SM-X21y09-stad-down HNMR (400MHz) CDCl3



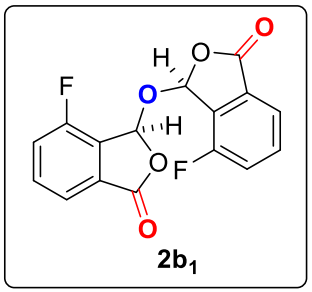

SM-X21y09-stad-down CNMR (100MHz) CDCl3
167.9
144.2
135.1
131.6
127.0
125.7
124.6
98.3
77.5
77.2
76.8
2a2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

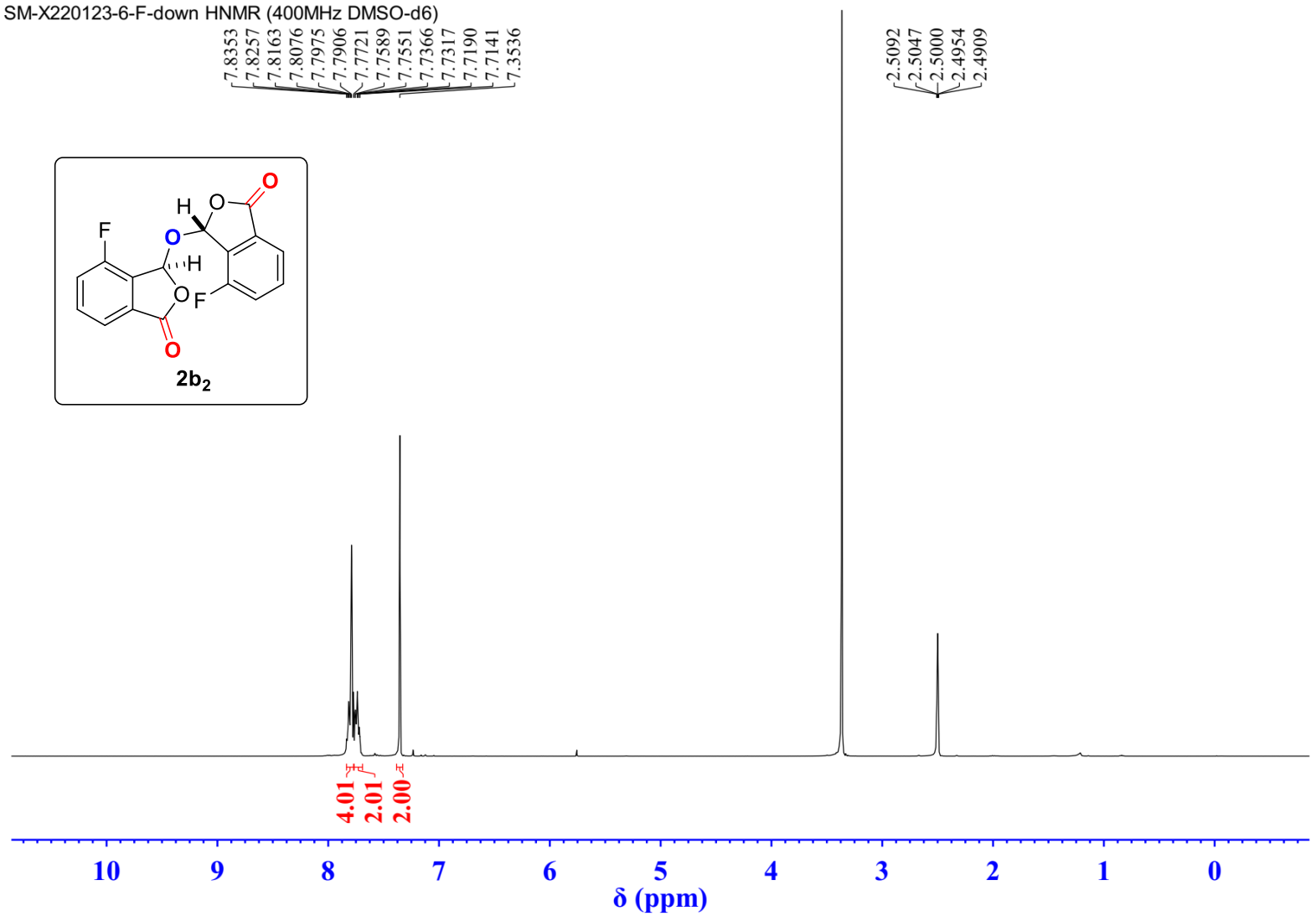
sm-x210903-6-F-up HNMR (400MHz CDCl3)



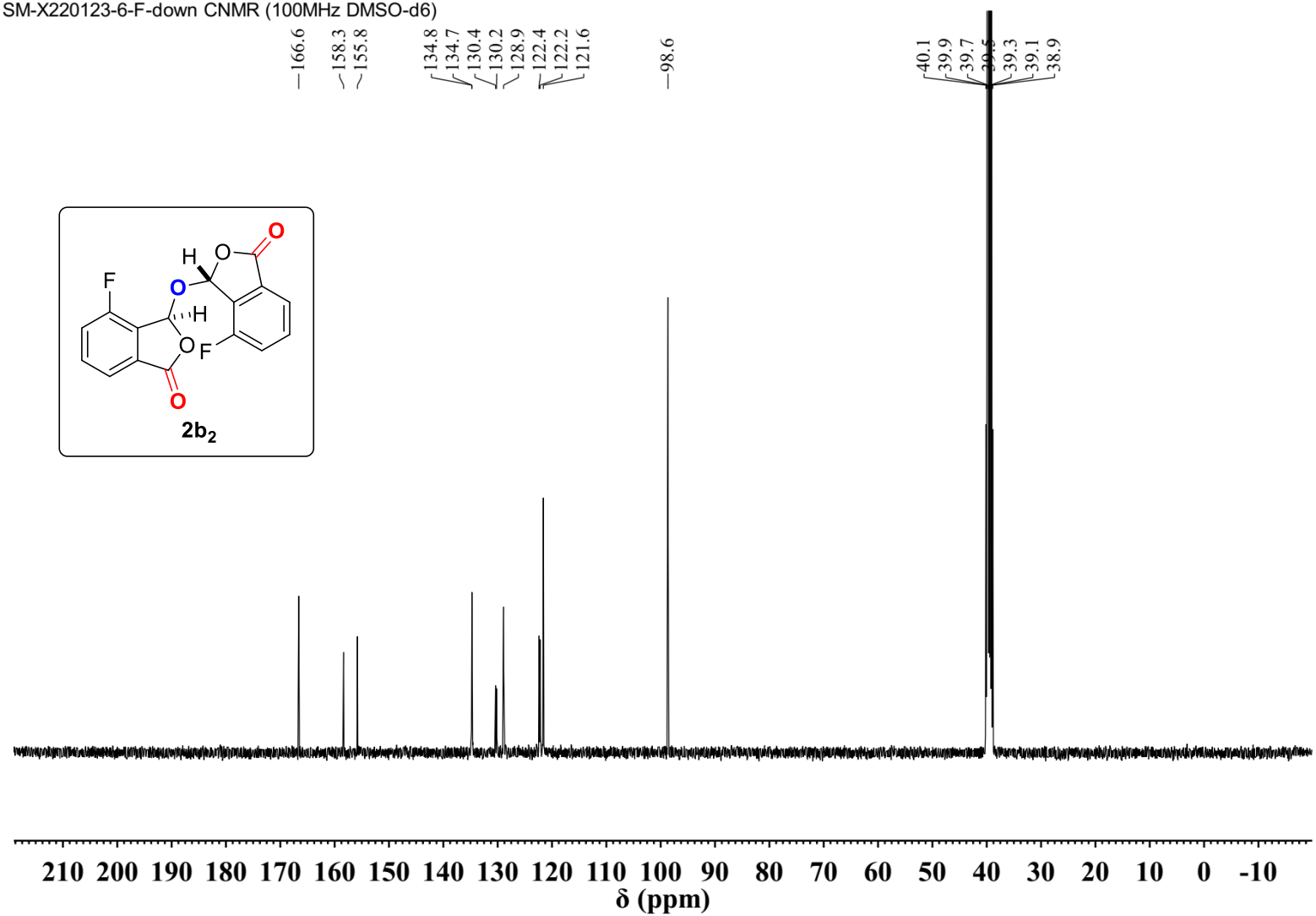

sm-x210903-6-F-up-CNMR (100MHz CDCl3)
166.7
166.7
158.9
156.3
134.2
134.1
130.1
130.0
129.6
129.5
122.2
122.0
121.9
121.9
96.6
77.5
77.2
76.8
2b1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

sm-x210903-6-F-up FNMR (376MHz CDCl3)

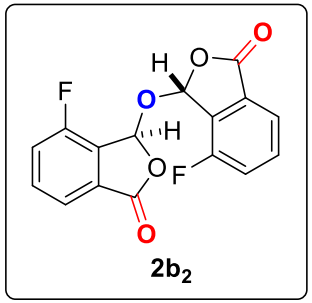



SM-X220123-6-F-down HNMR (400MHz DMSO-d6)
7.8353
7.8257
7.8163
7.8076
7.7975
7.7906
7.7721
7.7589
7.7551
7.7366
7.7317
7.7190
7.7141
7.3536
2.5092
2.5047
2.5000
2.4954
2.4909
2b2
4.01
2.01
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

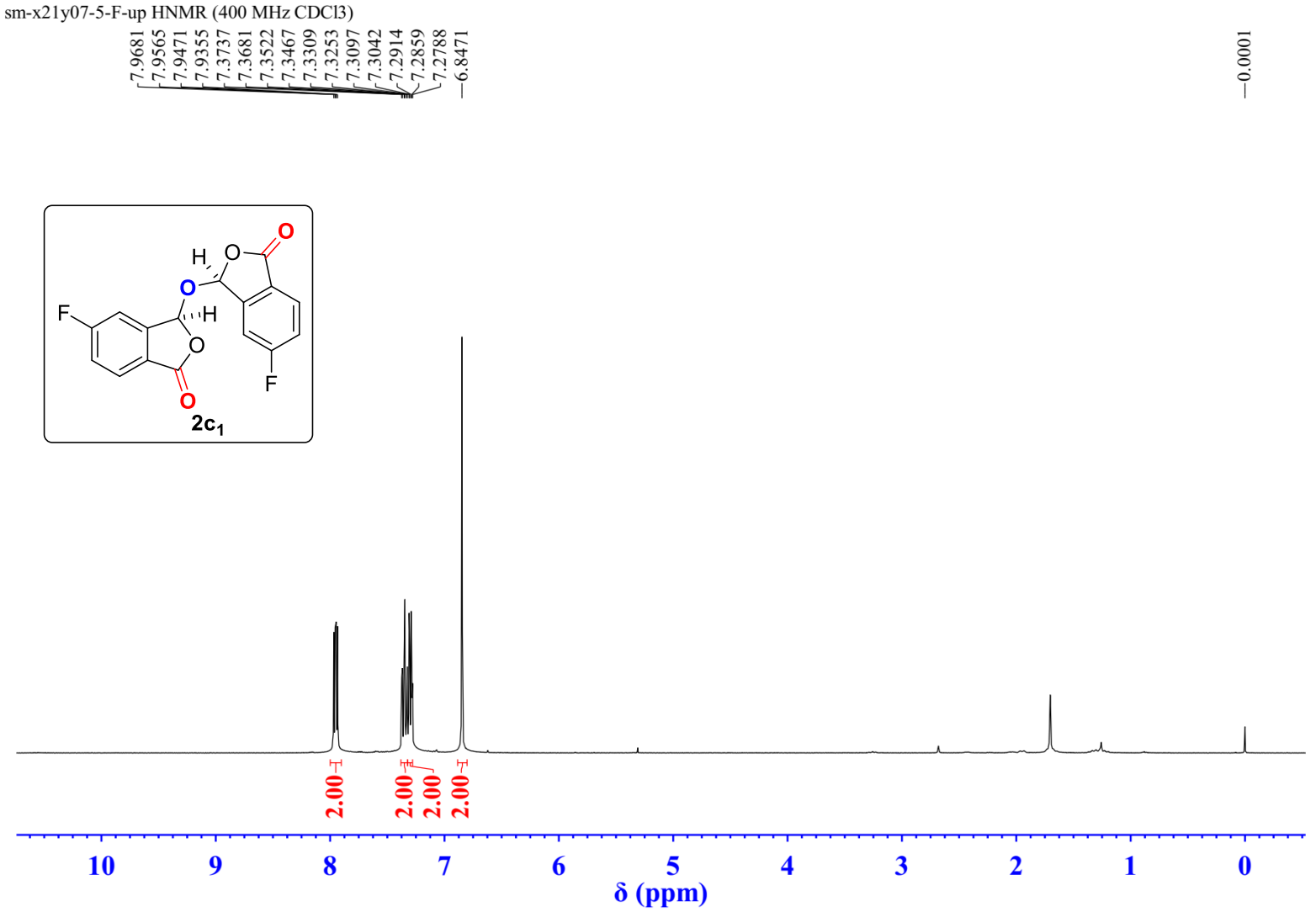
SM-X220123-6-F-down CNMR (100MHz DMSO-d6)



SM-X220123-6-F-down FNMR (376MHz DMSO-d6)

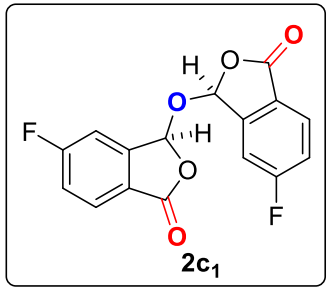


2b$_2$


sm-x21y07-5-F-up HNMR (400 MHz CDCl3)
7.9681
7.9565
7.9471
7.9355
7.3737
7.3681
7.3522
7.3467
7.3309
7.3253
7.3097
7.3042
7.2914
7.2859
7.2788
6.8471
0.0001
2c1
2.00
2.00
2.00
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

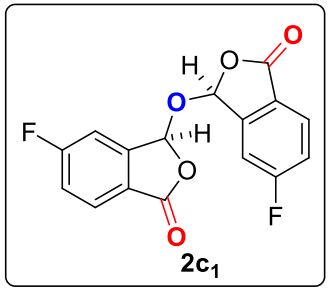
sm-x21y07-5-F-up CNMR (100MHz CDCl3)

168.2
166.8
165.7
146.8
146.7
128.4
128.3
122.6
122.6
119.9
119.6
111.7
111.5
98.0
97.9
77.5
77.2
76.8

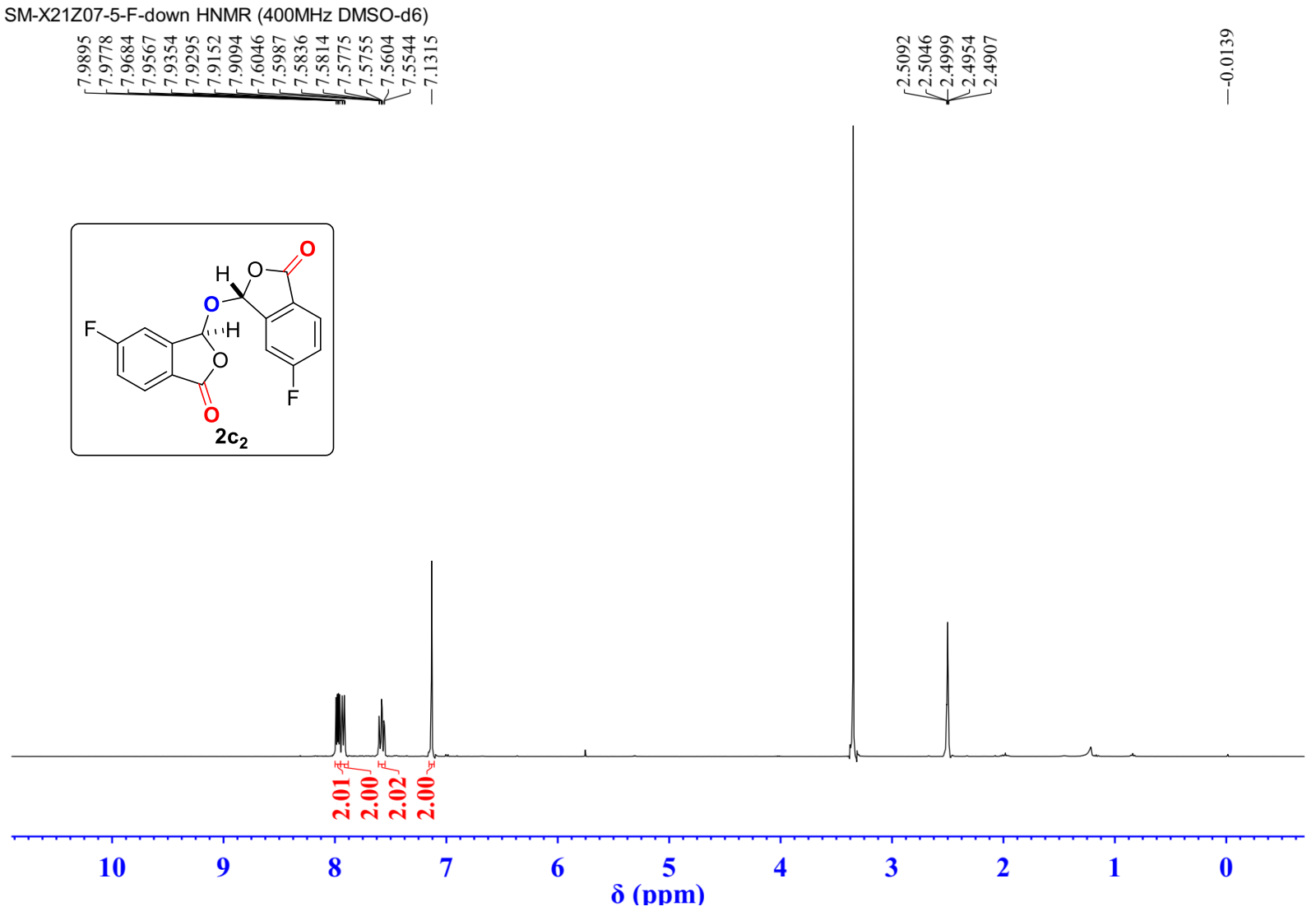


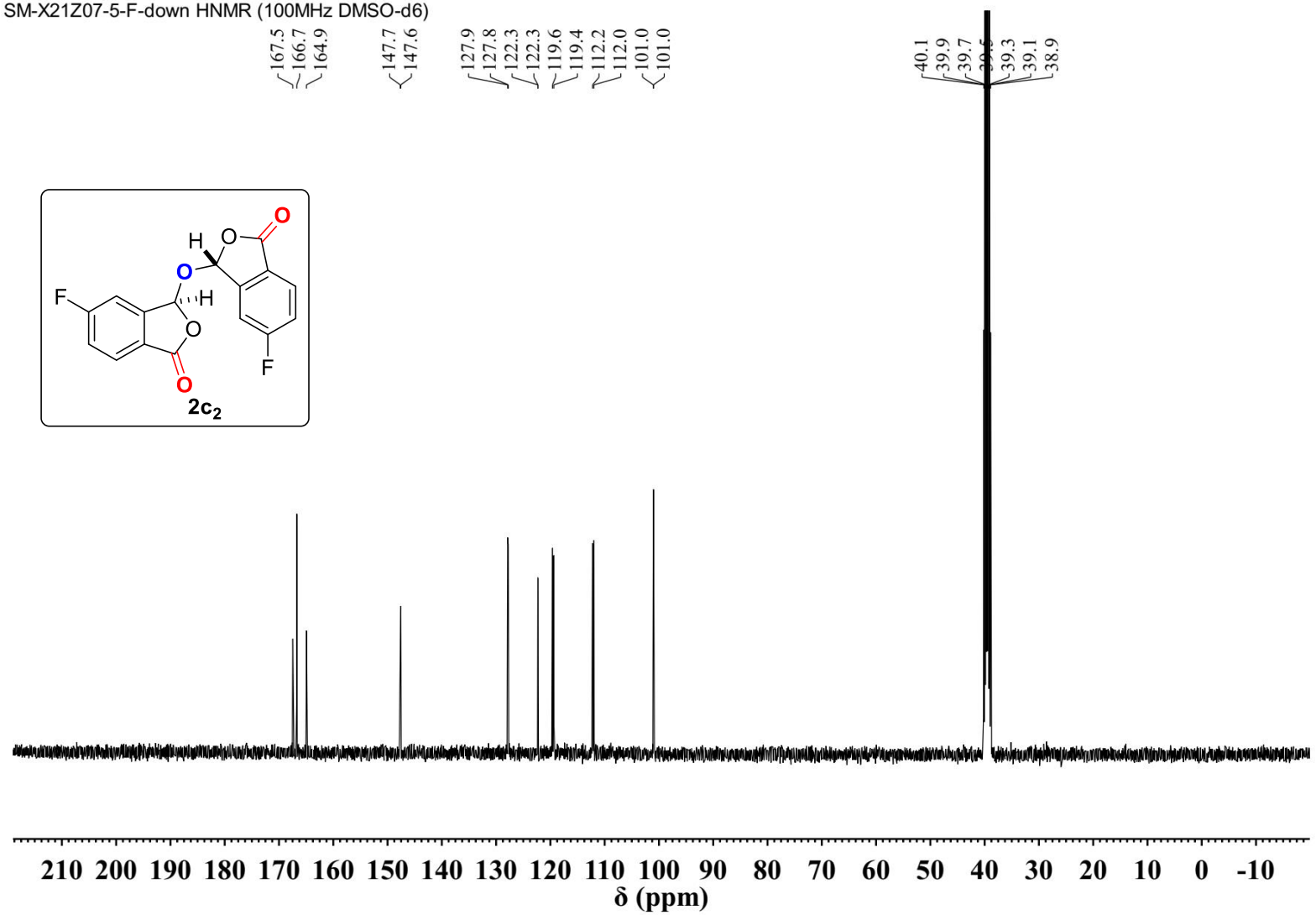
2c$_1$

sm-x21y07-5-F-up FNMR (376MHz CDCl3)

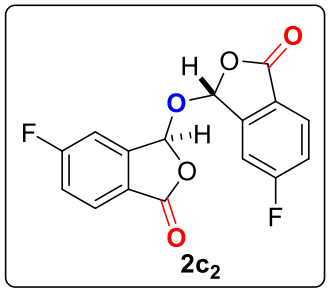


$2c_1$

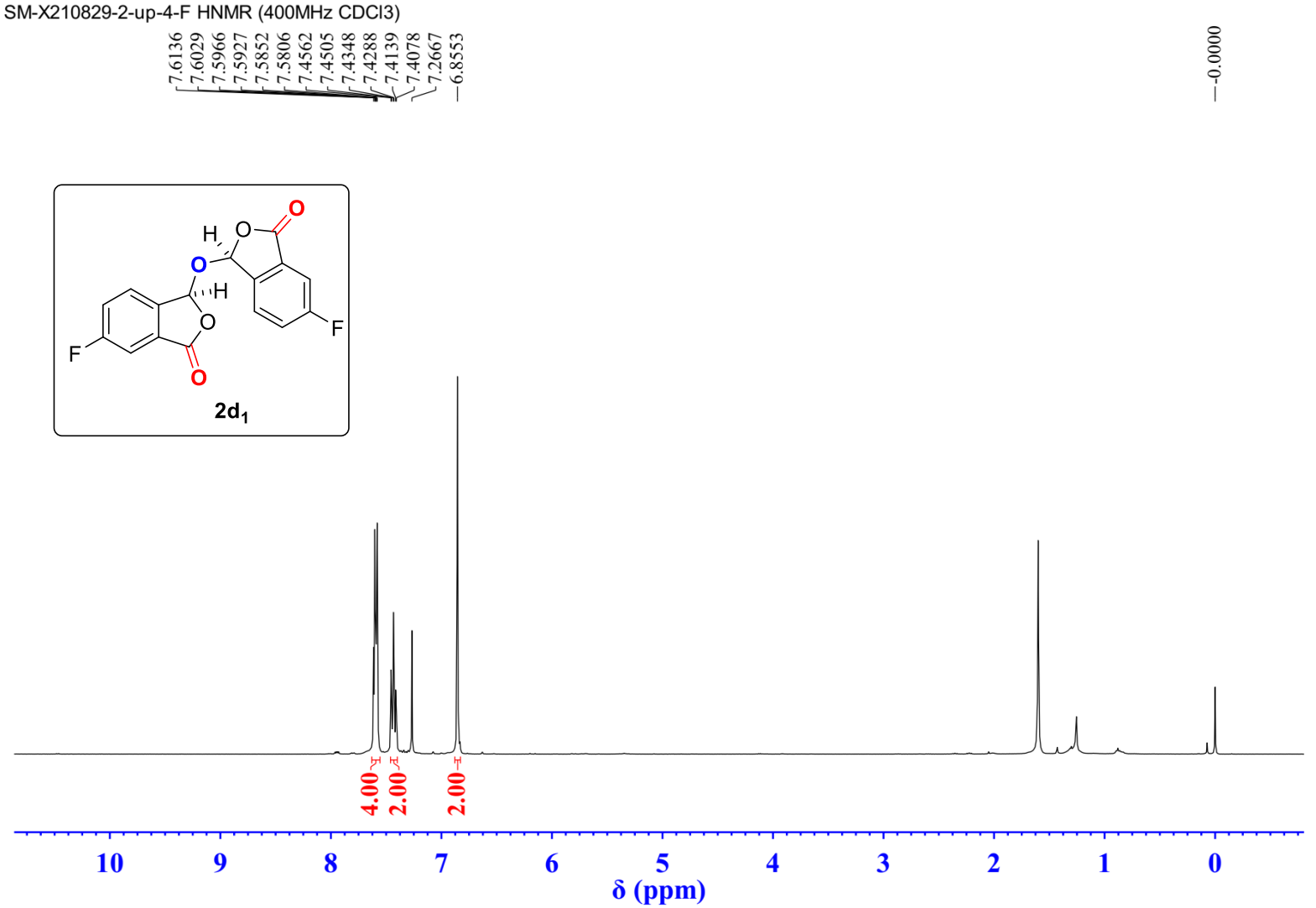

SM-X21Z07-5-F-down HNMR (400MHz DMSO-d6)
7.9895
7.9778
7.9684
7.9567
7.9354
7.9295
7.9152
7.9094
7.6046
7.5987
7.5836
7.5814
7.5775
7.5755
7.5604
7.5544
7.1315
2.5092
2.5046
2.4999
2.4954
2.4907
-0.0139
2c2
2.01
2.00
2.02
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


SM-X21Z07-5-F-down HNMR (100MHz DMSO-d6)
167.5
166.7
164.9
147.7
147.6
127.9
127.8
122.3
122.3
119.6
119.4
112.2
112.0
101.0
101.0
40.1
39.9
39.7
39.3
39.1
38.9
2c2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

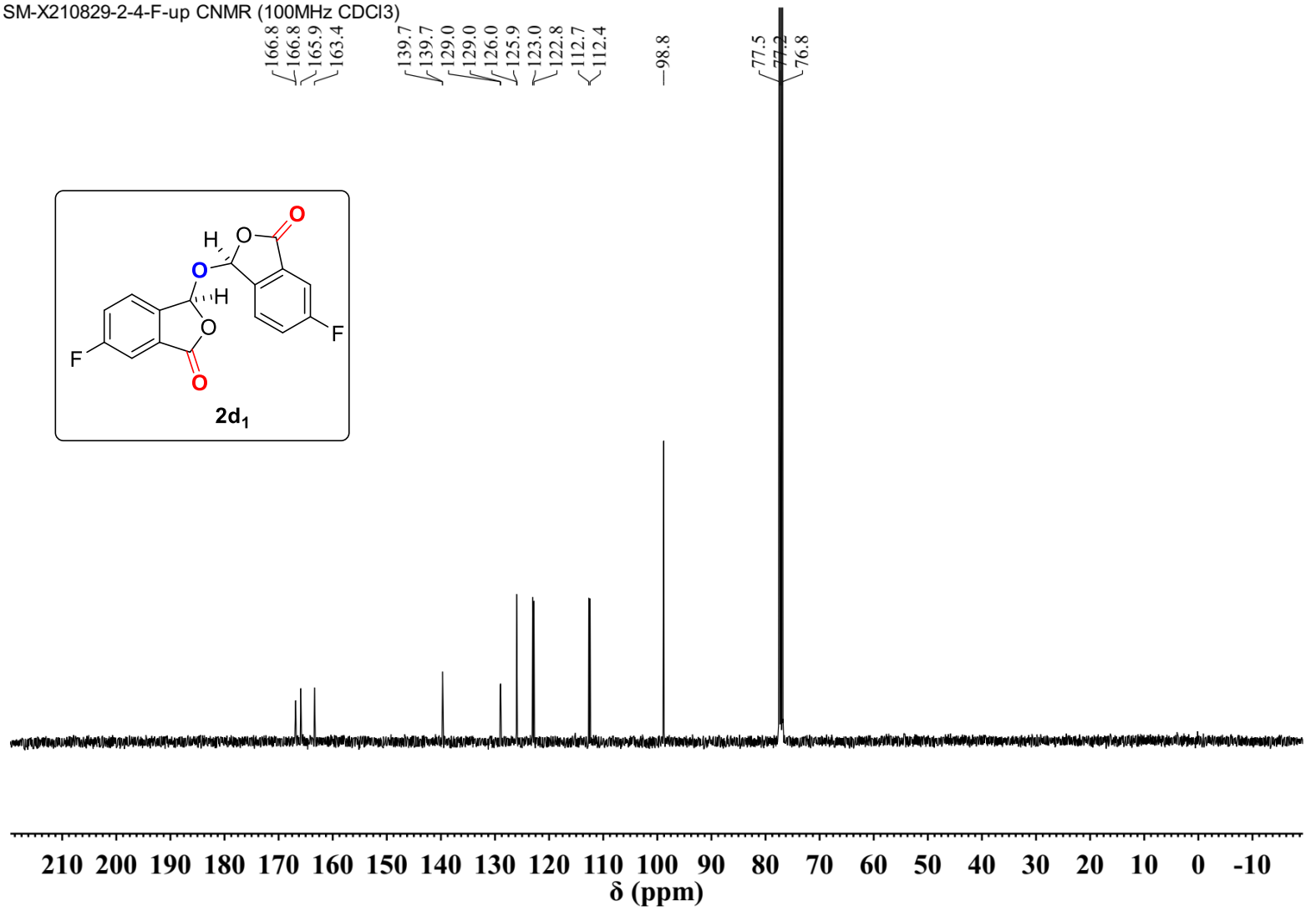
SM-X21Z07-5-F-down FNMR (376MHz DMSO-d6)



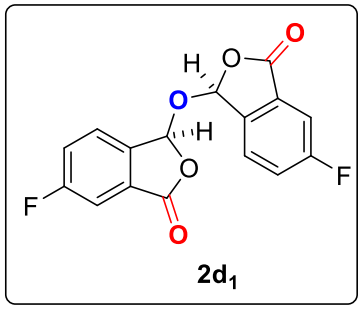
$2c_2$


SM-X210829-2-up-4-F HNMR (400MHz CDCl3)
7.6136
7.6029
7.5966
7.5927
7.5852
7.5806
7.4562
7.4505
7.4348
7.4288
7.4139
7.4078
7.2667
6.8553
0.0000
2d1
4.00
2.00
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

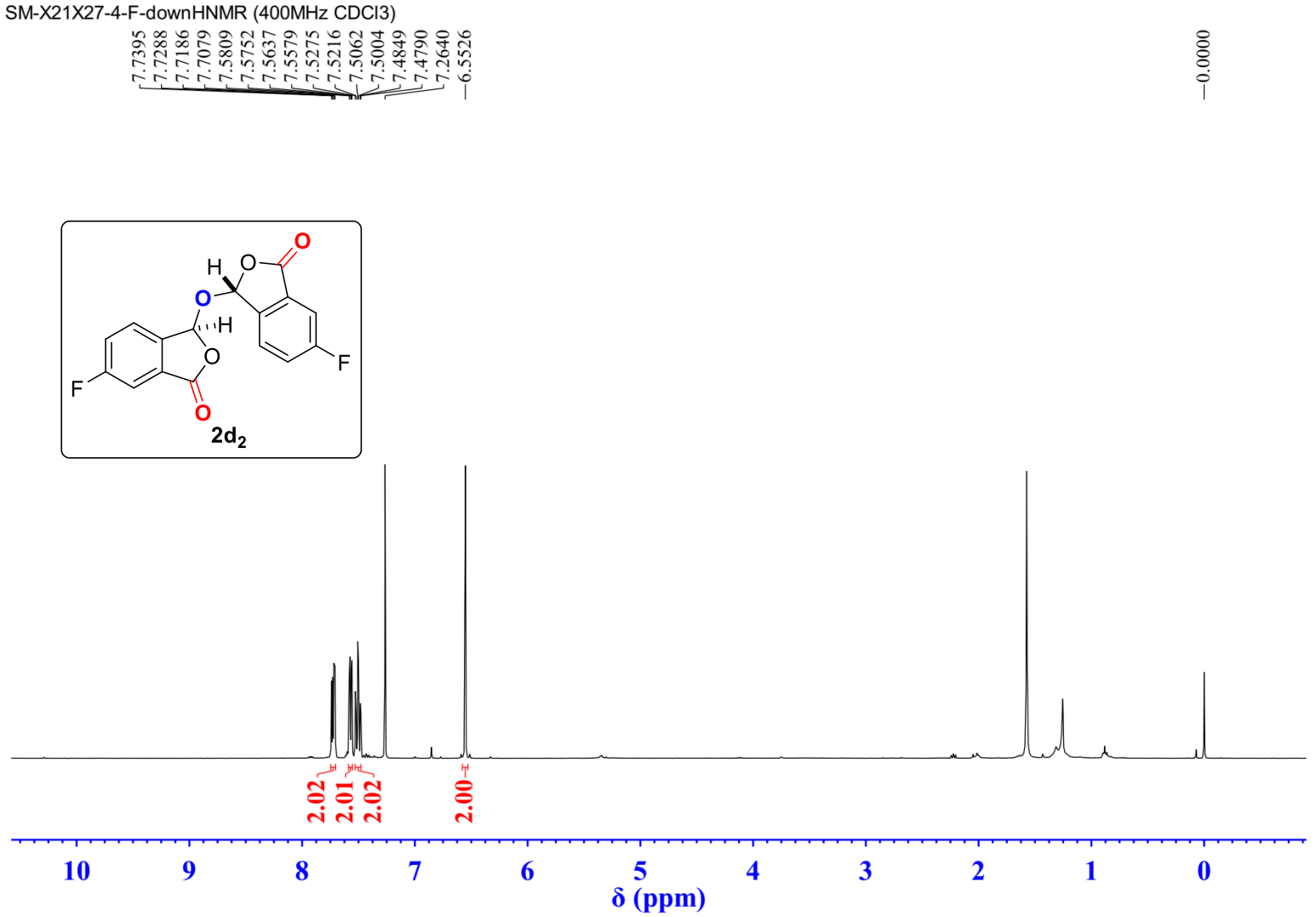
SM-X210829-2-4-F-up CNMR (100MHz CDCl3)

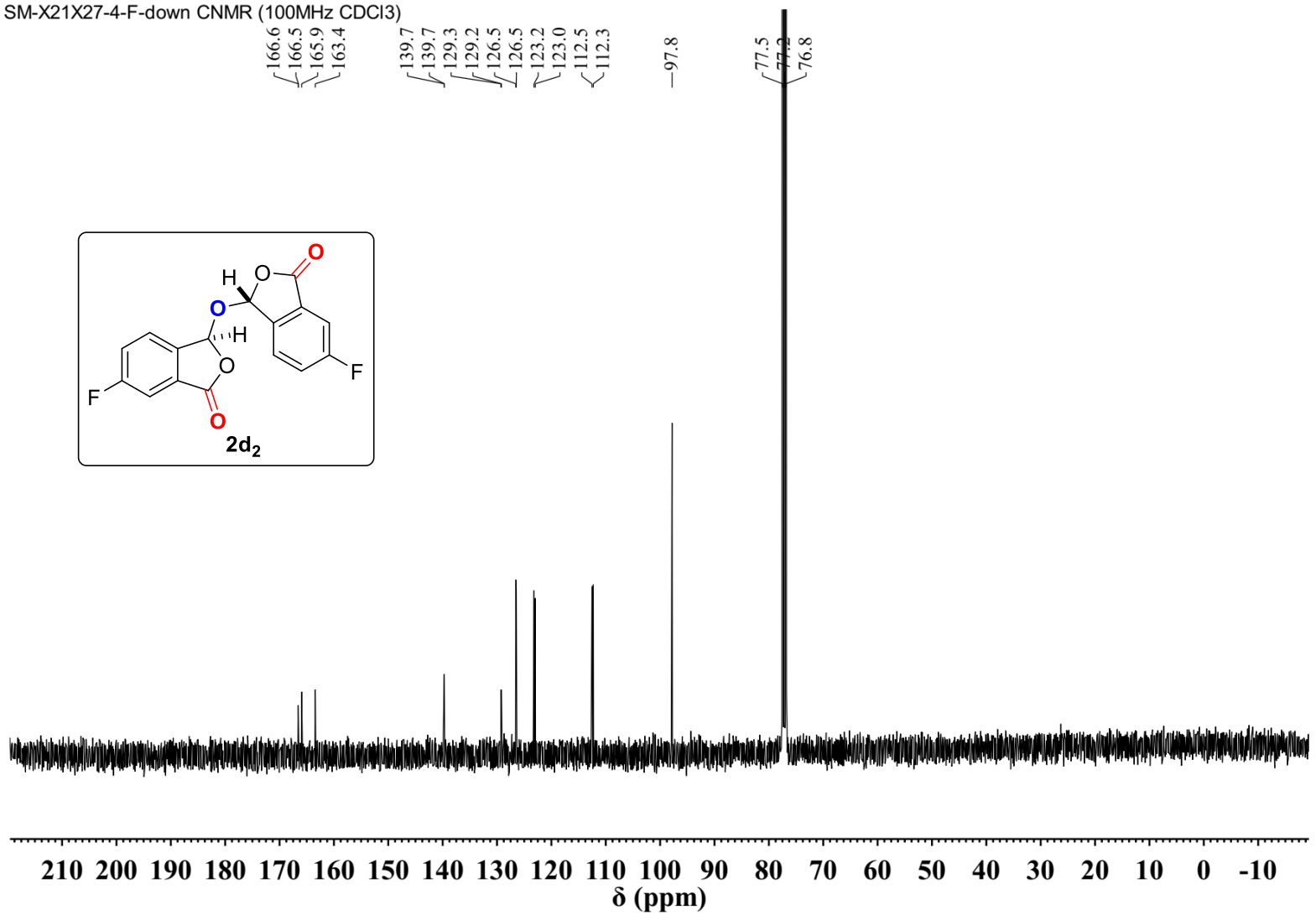


SM-X210829-2-up-4-F FNMR (376MHz CDCl3)

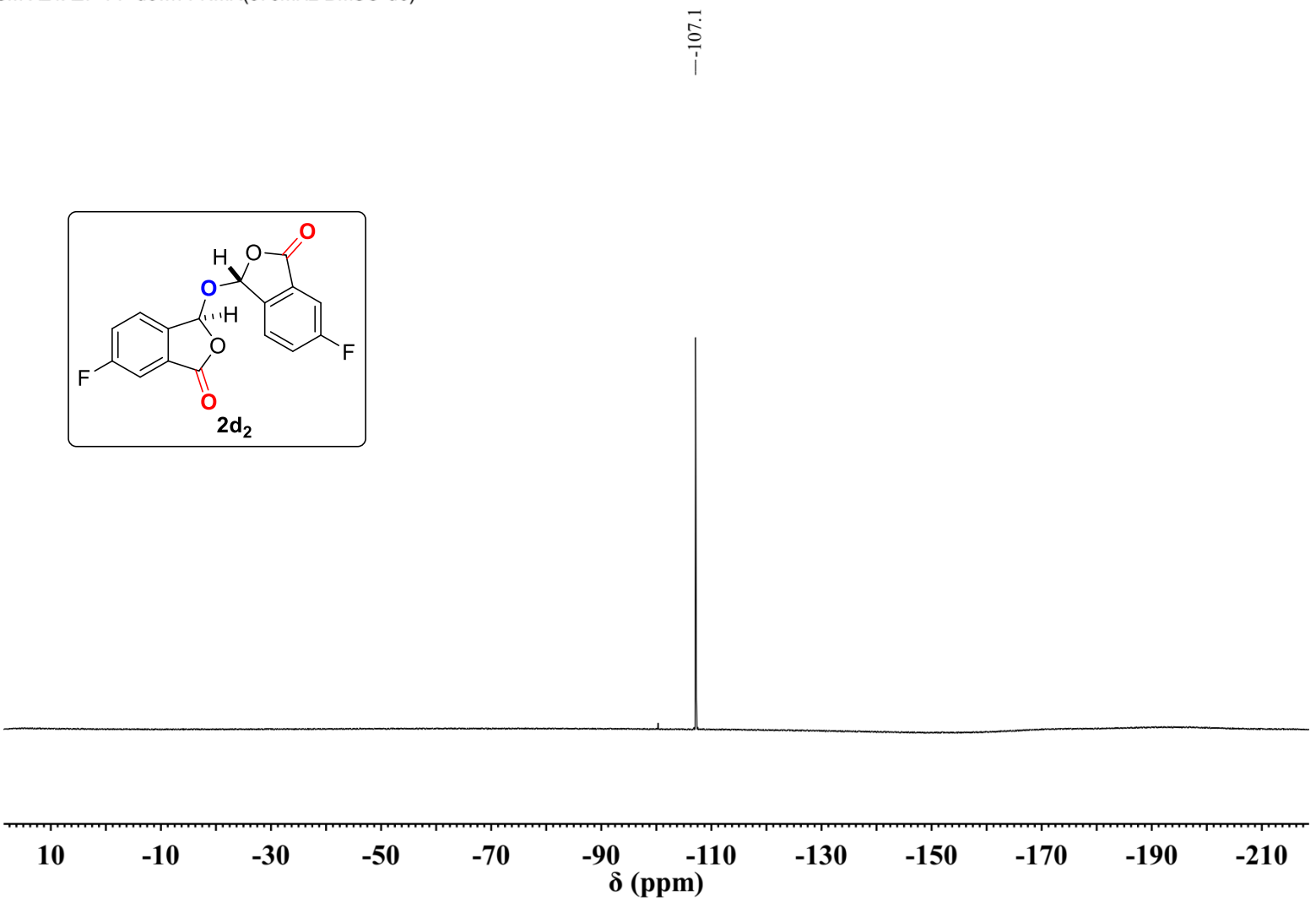


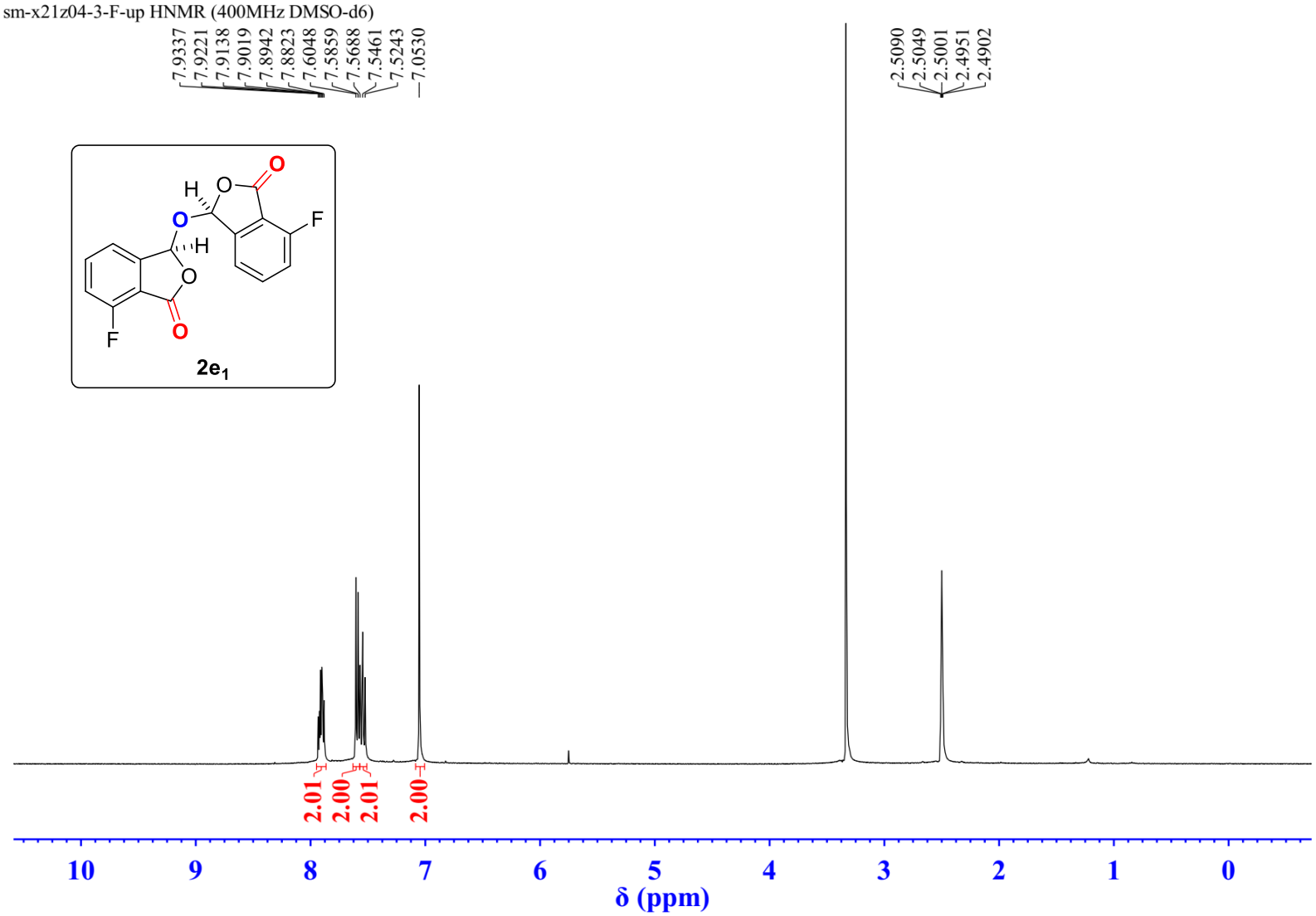
2d$_1$

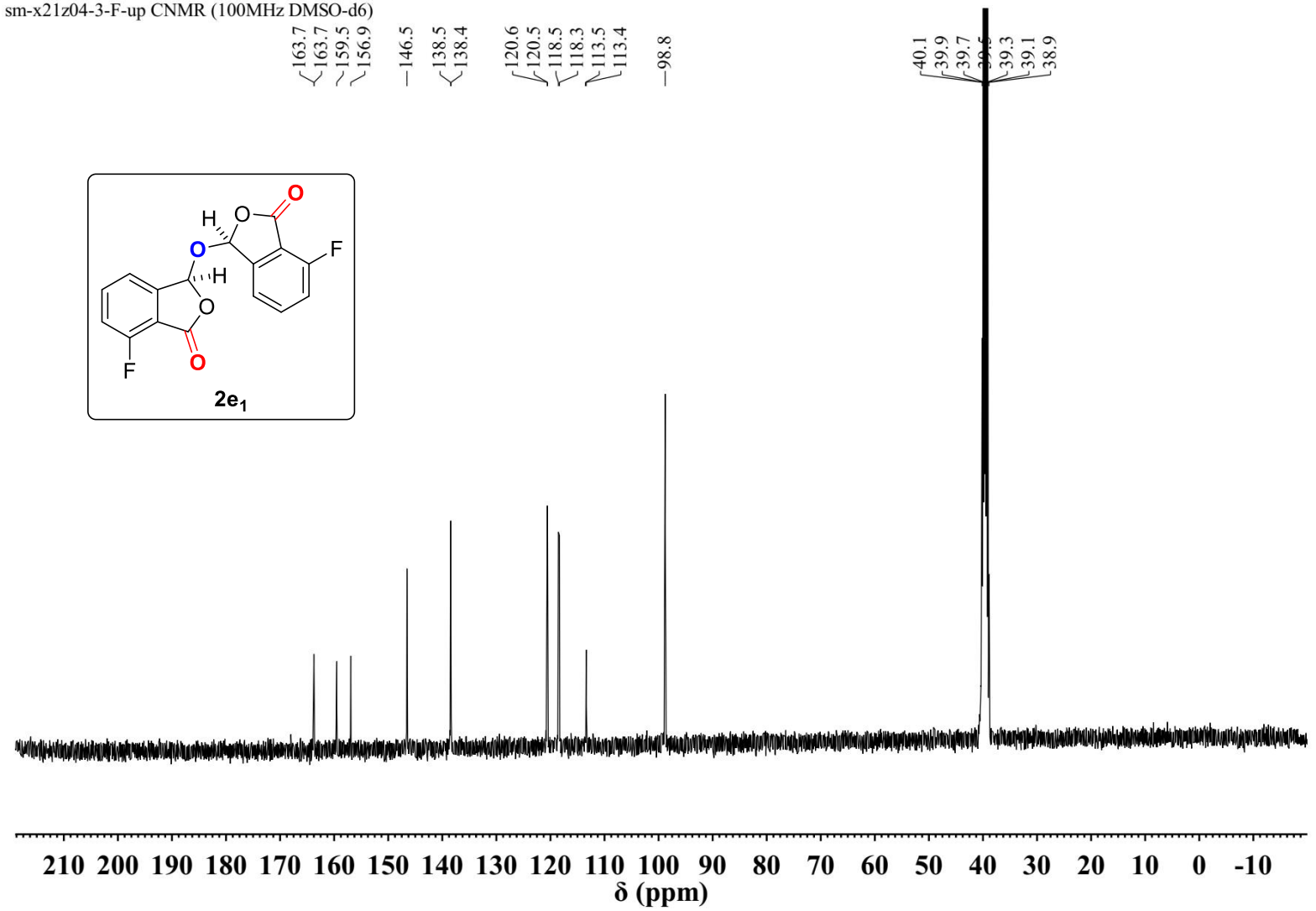

SM-X21X27-4-F-downHNMR (400MHz CDCl3)
7.7395
7.7288
7.7186
7.7079
7.5809
7.5752
7.5637
7.5579
7.5275
7.5216
7.5062
7.5004
7.4849
7.4790
7.2640
6.5526
0.0000
2d2
2.02
2.01
2.02
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


SM-X21X27-4-F-down CNMR (100MHz CDCl3)
166.6
166.5
165.9
163.4
139.7
139.7
129.3
129.2
126.5
126.5
123.2
123.0
112.5
112.3
97.8
77.5
77.2
76.8
H
O
O
O
O
H
F
F
O
2d2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

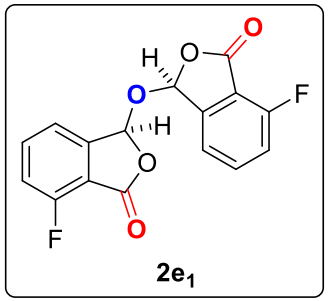
SM-X21X27-4-F-down FNMR(376MHz DMSO-d6)



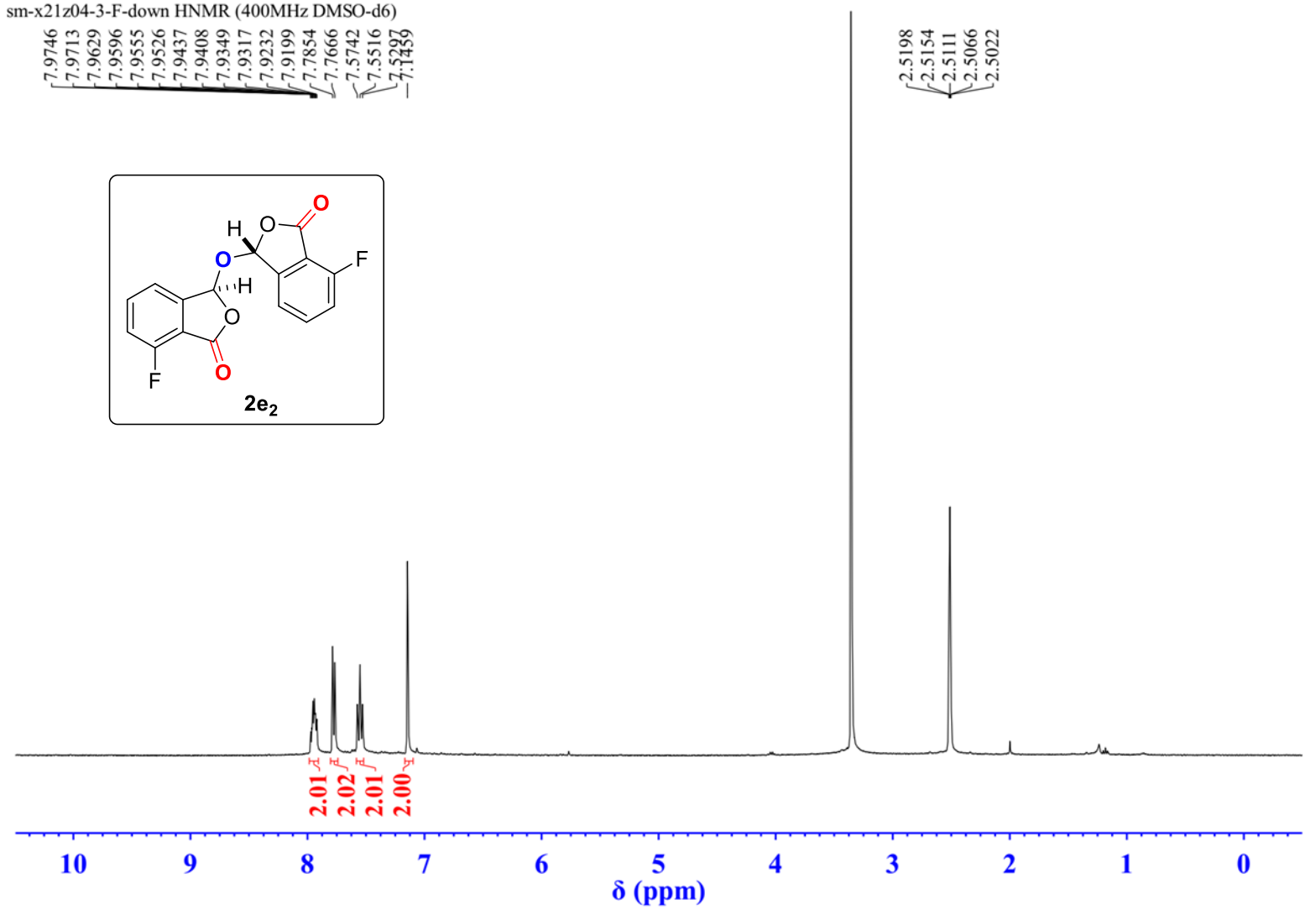

sm-x21z04-3-F-up HNMR (400MHz DMSO-d6)
7.9337
7.9221
7.9138
7.9019
7.8942
7.8823
7.6048
7.5859
7.5688
7.5461
7.5243
7.0530
2.5090
2.5049
2.5001
2.4951
2.4902
2e1
2.01
2.00
2.01
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


sm-x21z04-3-F-up CNMR (100MHz DMSO-d6)
163.7
163.7
159.5
156.9
146.5
138.5
138.4
120.6
120.5
118.5
118.3
113.5
113.4
98.8
40.1
39.9
39.7
39.3
39.1
38.9
2e1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

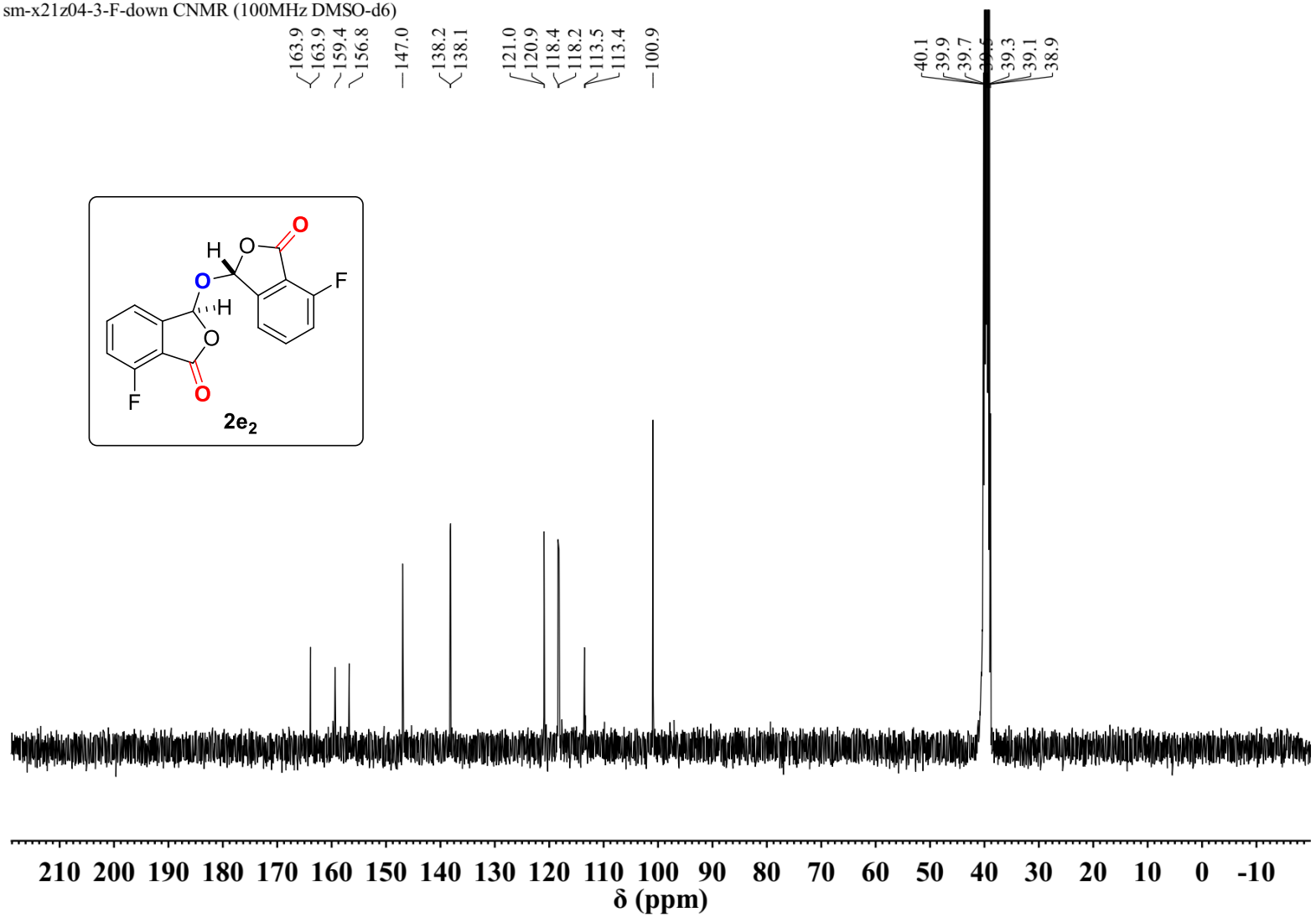
SM-X21Z04-3-F-up FNMR(376MHz DMSO-d6)



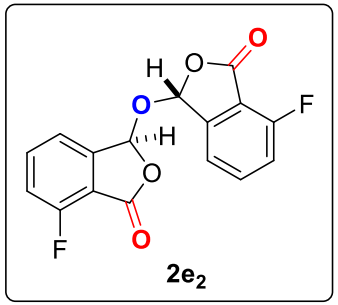
2e$_1$


sm-x21z04-3-F-down HNMR (400MHz DMSO-d6)
7.9746
7.9713
7.9629
7.9596
7.9555
7.9526
7.9437
7.9408
7.9349
7.9317
7.9232
7.9199
7.7854
7.7666
7.5742
7.5516
7.5297
7.1459
2.5198
2.5154
2.5111
2.5066
2.5022
2e2
2.01
2.02
2.01
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

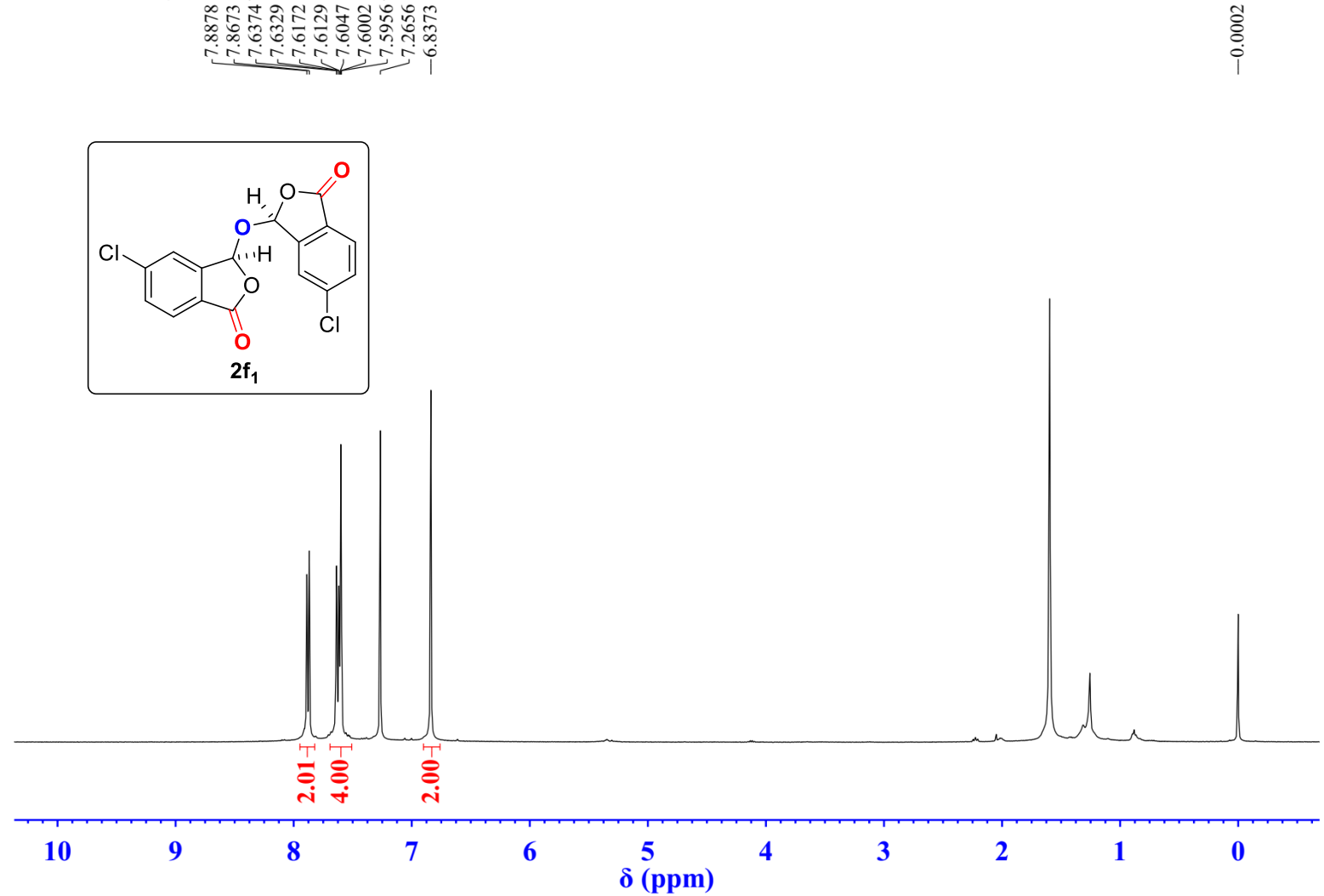
sm-x21z04-3-F-down CNMR (100MHz DMSO-d6)

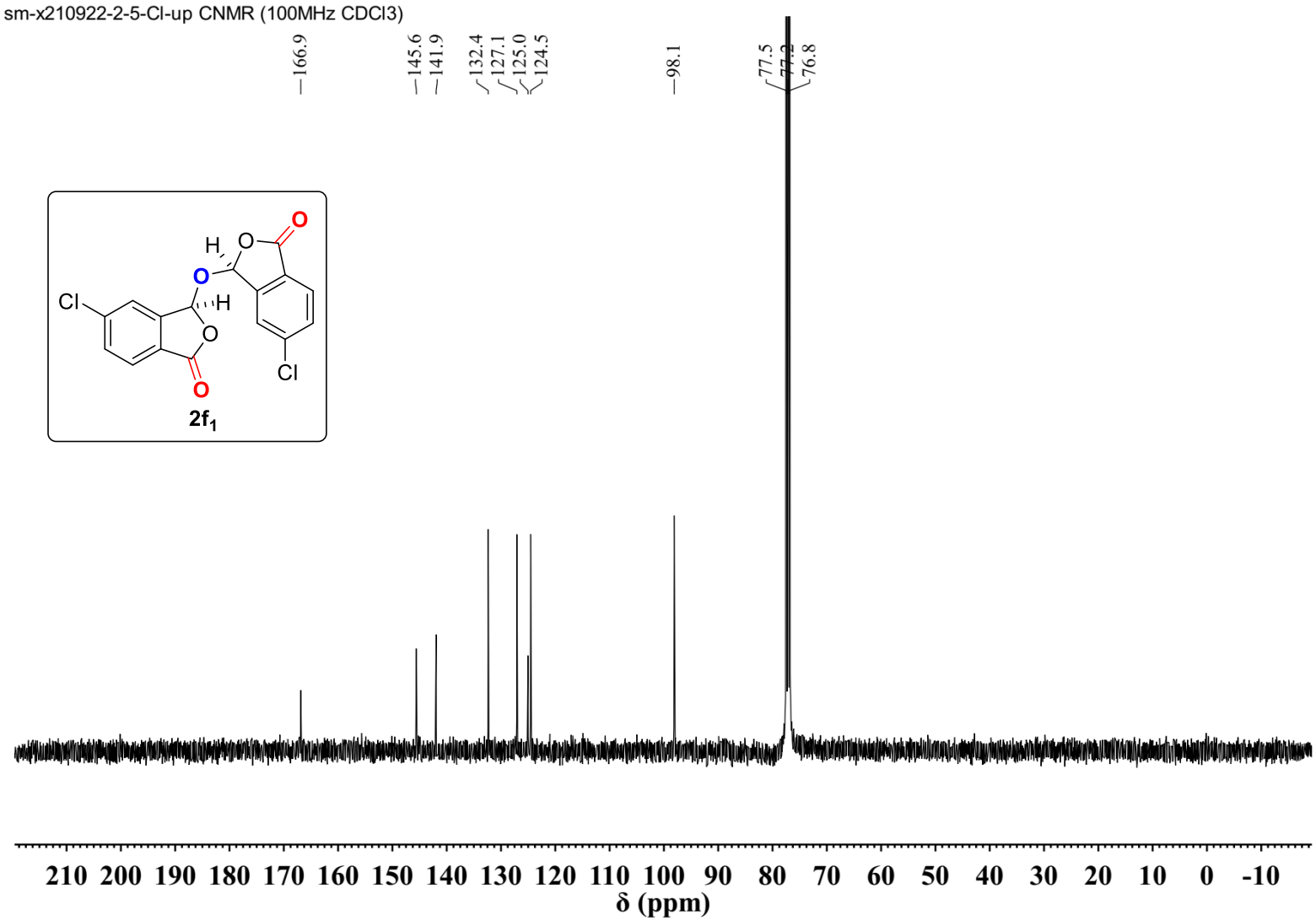


SM-X22Z04-3-F-down FNMR(376MHz DMSO-d6)

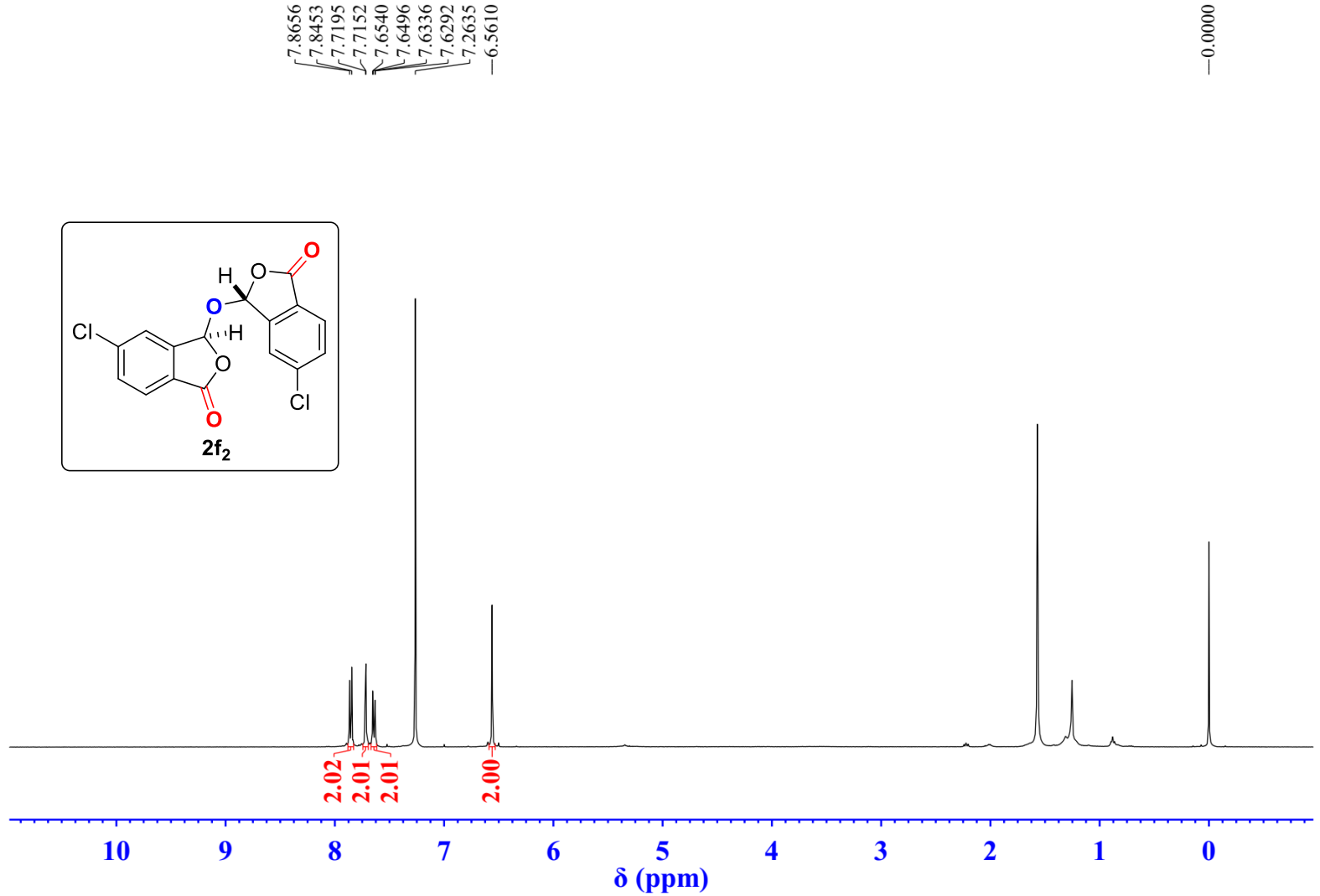


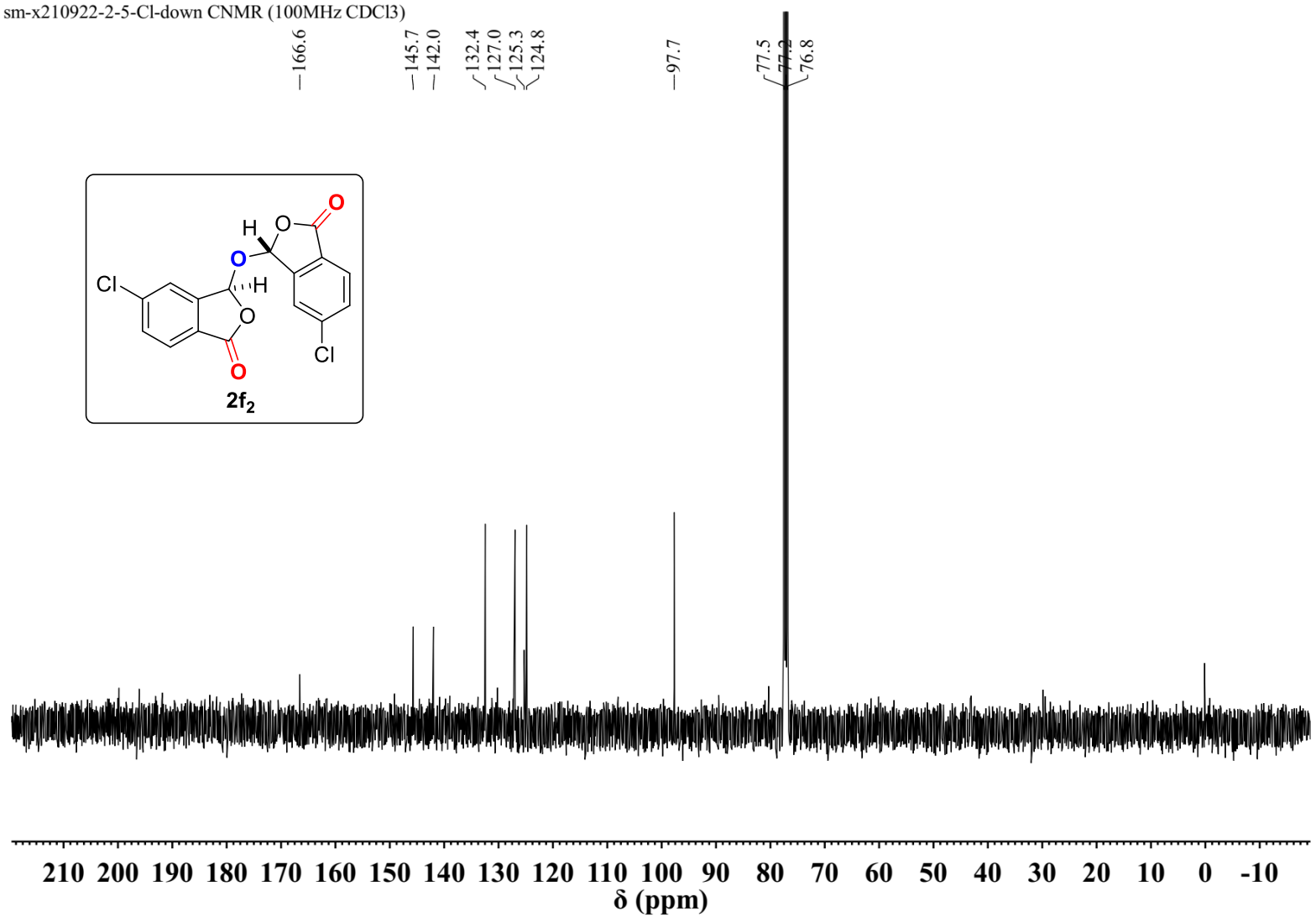
2e$_2$


sm-x210922-5-Cl-up HNMR (400MHz CDCl3)
7.8878
7.8673
7.6374
7.6329
7.6172
7.6129
7.6047
7.6002
7.5956
7.2656
6.8373
0.0002
Cl
H
O
O
O
O
H
O
Cl
2f1
2.01
4.00
2.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

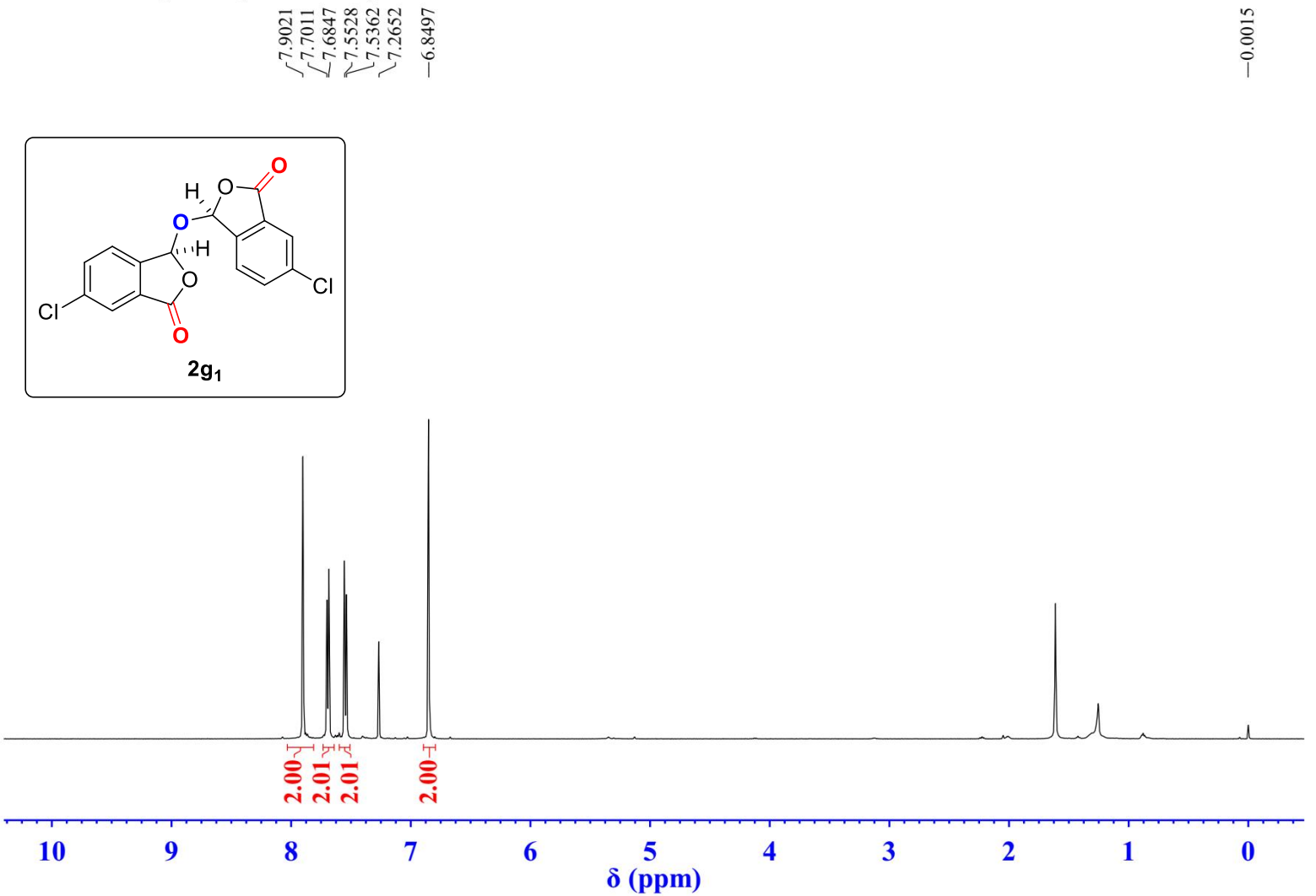

sm-x210922-2-5-Cl-up CNMR (100MHz CDCl3)
166.9
145.6
141.9
132.4
127.1
125.0
124.5
98.1
77.5
77.2
76.8
Cl
H
O
O
O
O
H
Cl
O
2f1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

sm-x210922-2-5-Cl-down HNMR (400 MHz CDCl3)

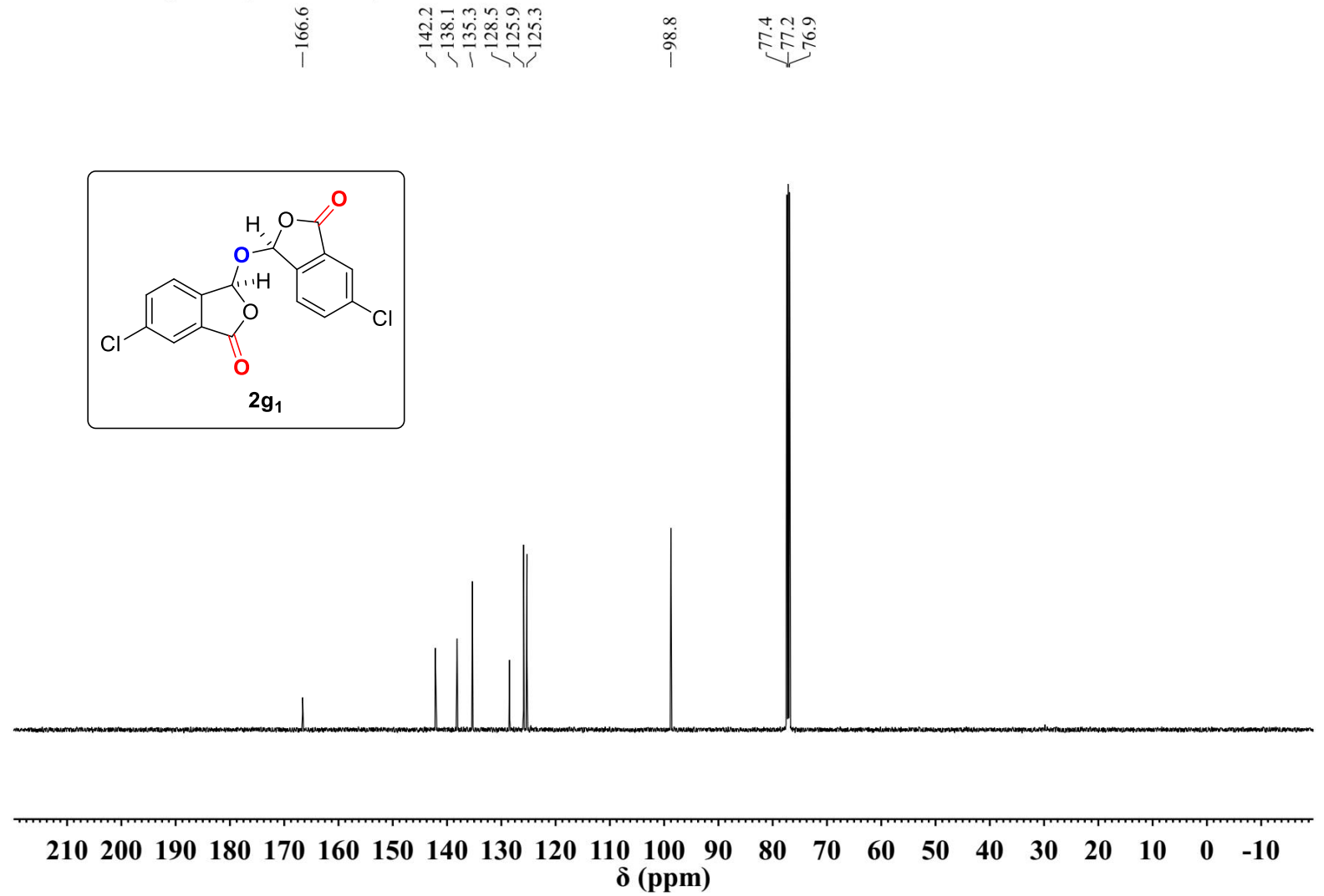



sm-x210922-2-5-Cl-down CNMR (100MHz CDCl3)
166.6
145.7
142.0
132.4
127.0
125.3
124.8
97.7
77.5
77.2
76.8
Cl
H
O
O
O
O
H
O
Cl
2f2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

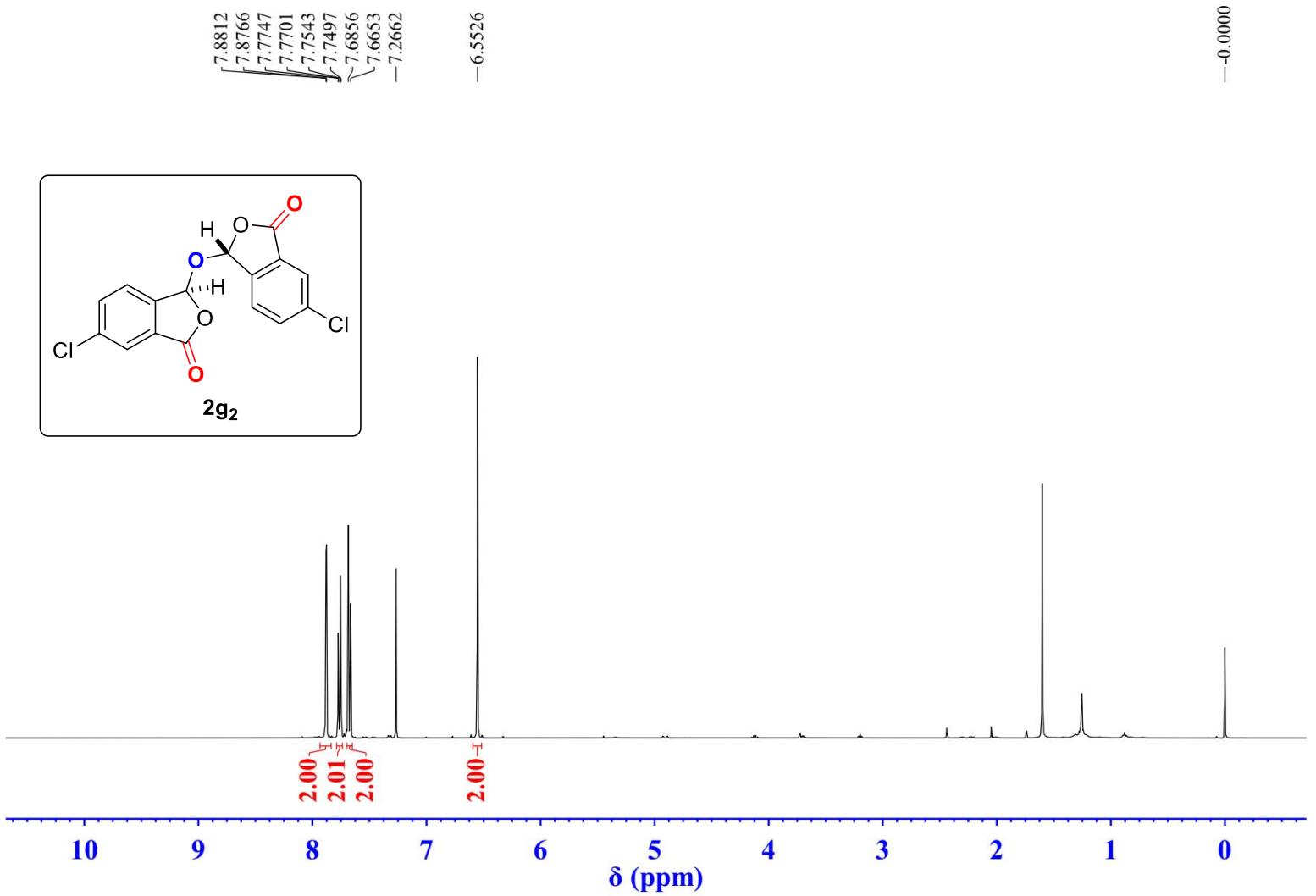
sm-x210903-7-4-Cl-up HNMR (500MHz CDCl3)

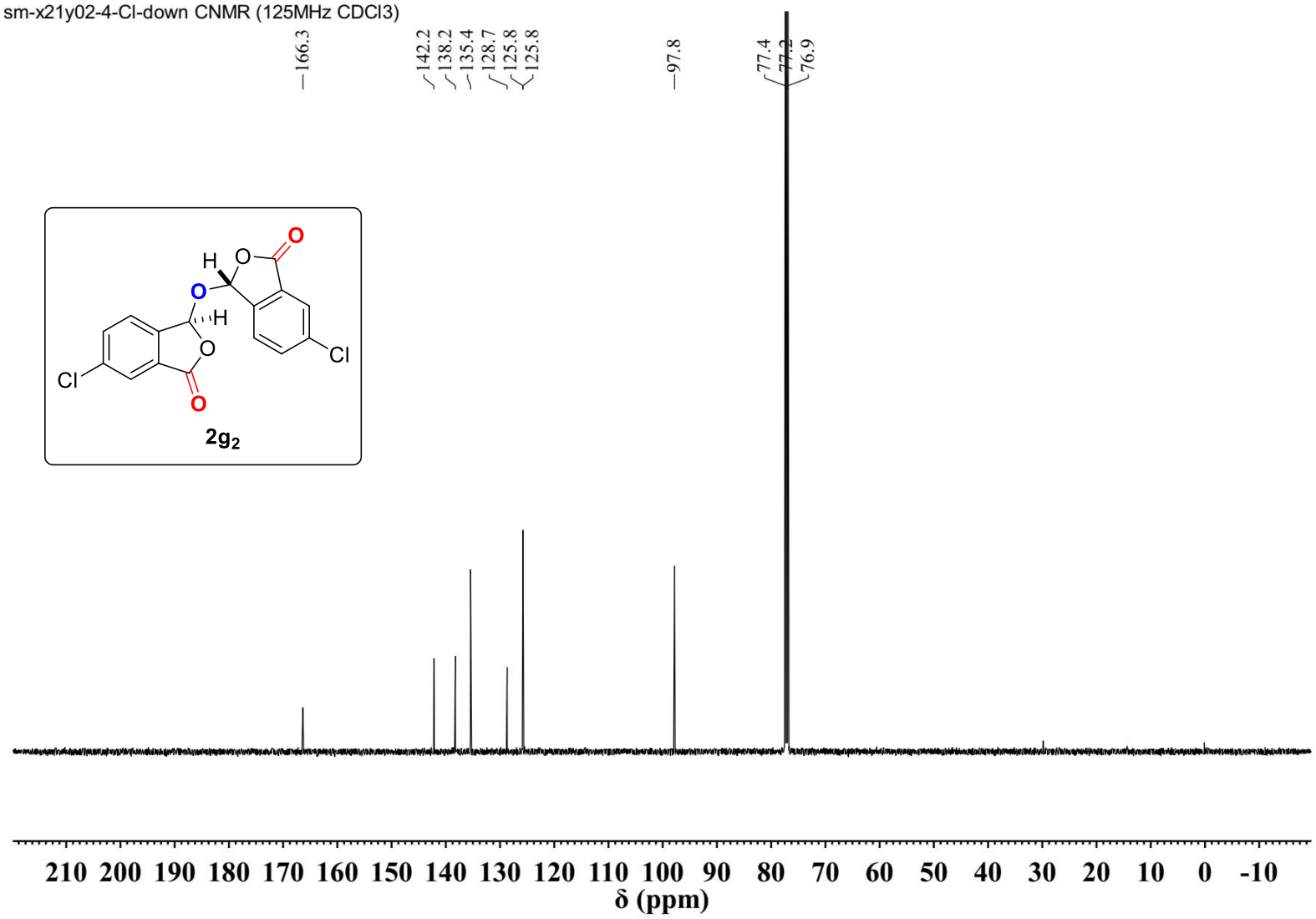


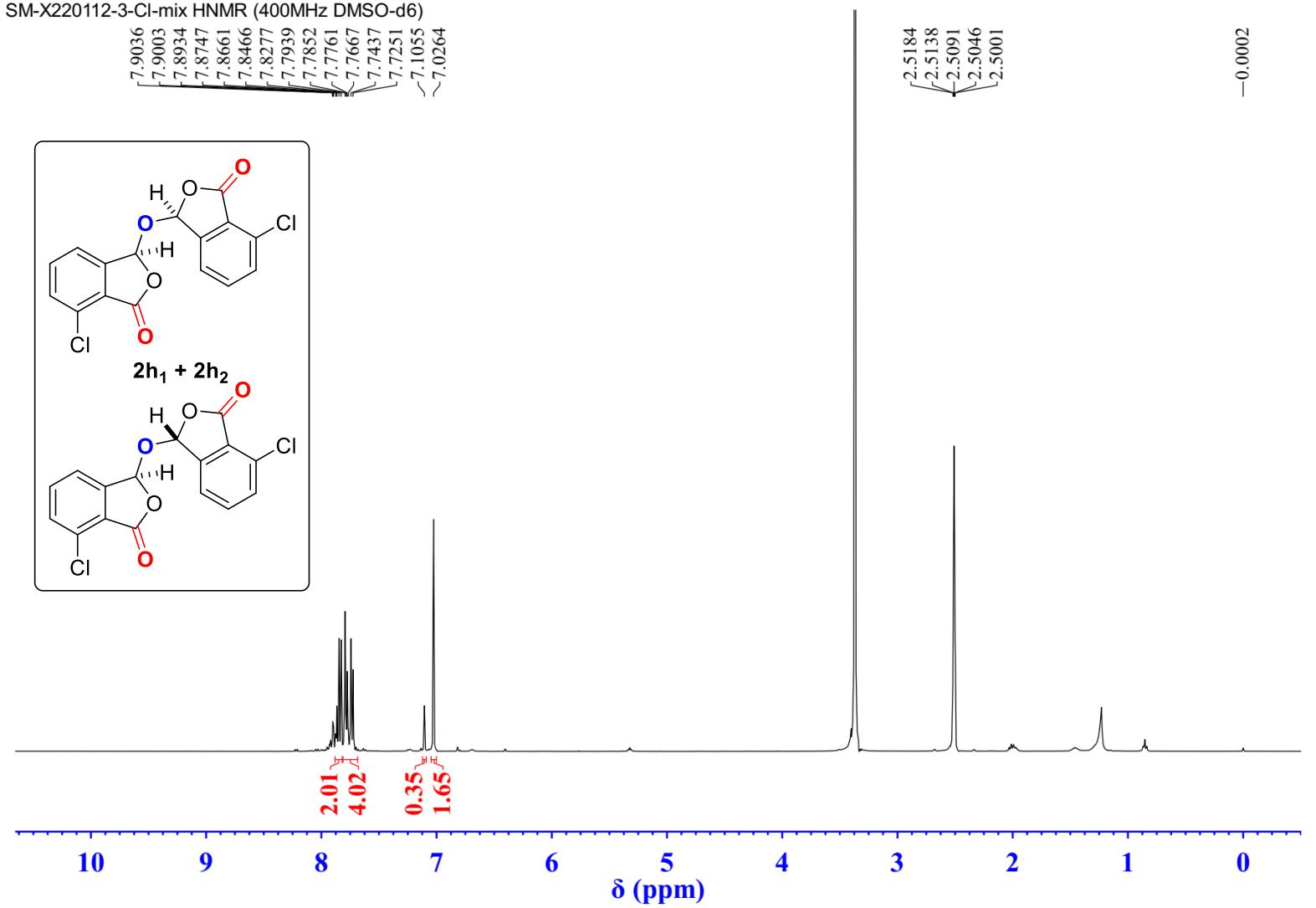
sm-x210903-7-4-Cl-up CNMR (125MHz CDCl3)

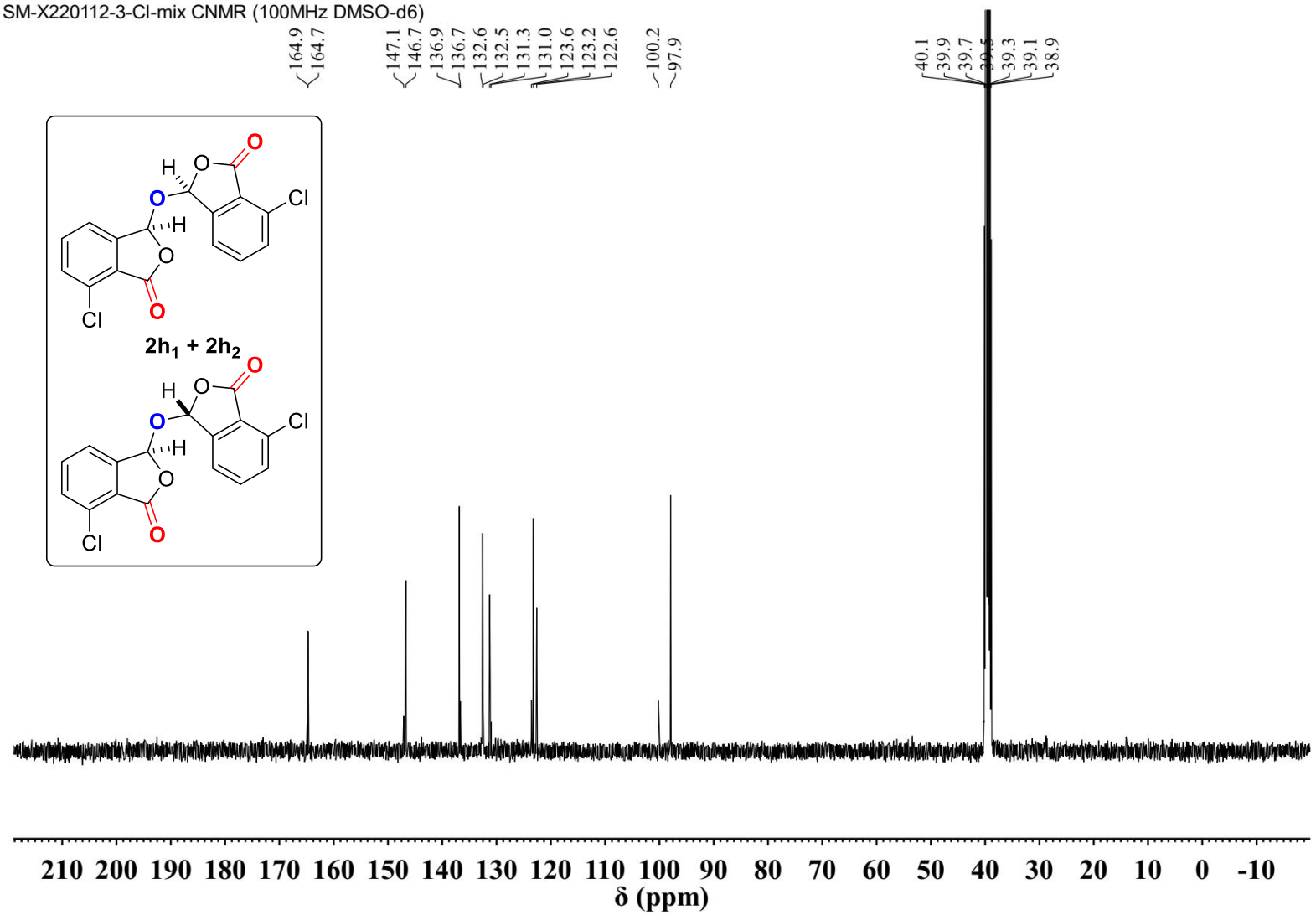


sm-x21y02-4-Cl-down HNMR (400MHz CDCl3)

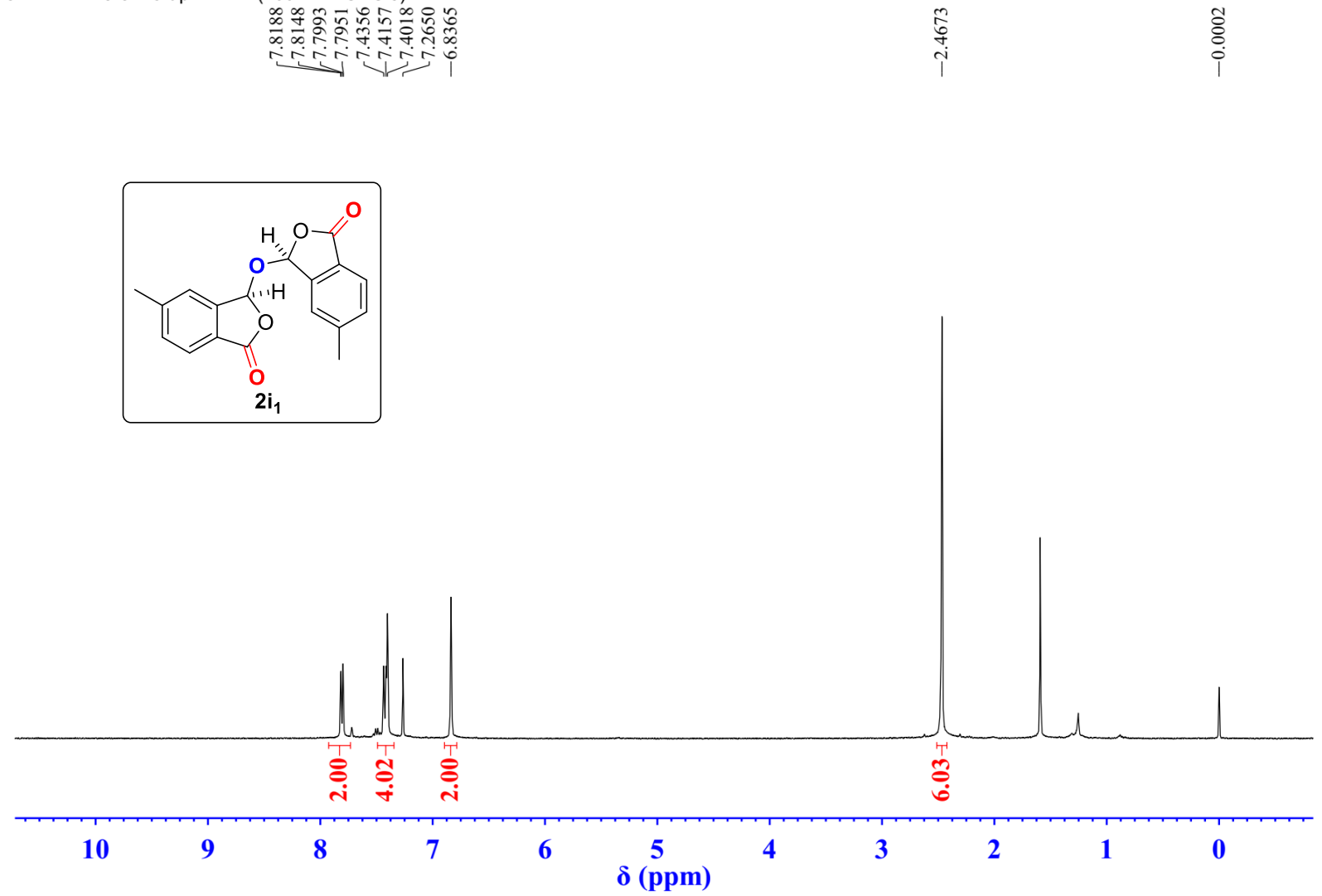


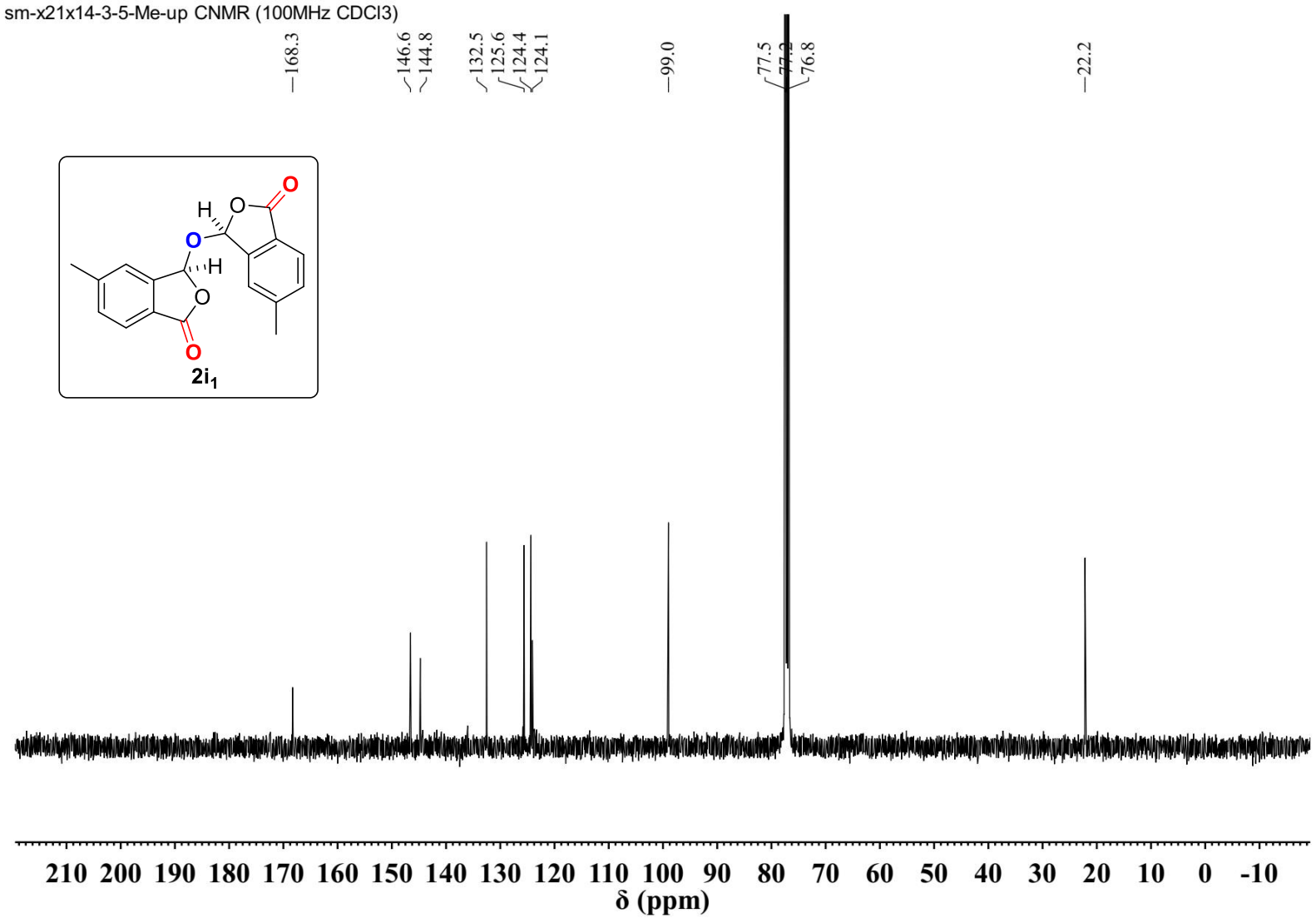

sm-x21y02-4-Cl-down CNMR (125MHz CDCl3)
166.3
142.2
138.2
135.4
128.7
125.8
125.8
97.8
77.4
77.2
76.9
H
O
O
O
O
H
Cl
Cl
O
2g2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


SM-X220112-3-Cl-mix HNMR (400MHz DMSO-d6)
7.9036
7.9003
7.8934
7.8747
7.8661
7.8466
7.8277
7.7939
7.7852
7.7761
7.7667
7.7437
7.7251
7.1055
7.0264
2.5184
2.5138
2.5091
2.5046
2.5001
0.0002
2h1 + 2h2
2.01
4.02
0.35
1.65
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

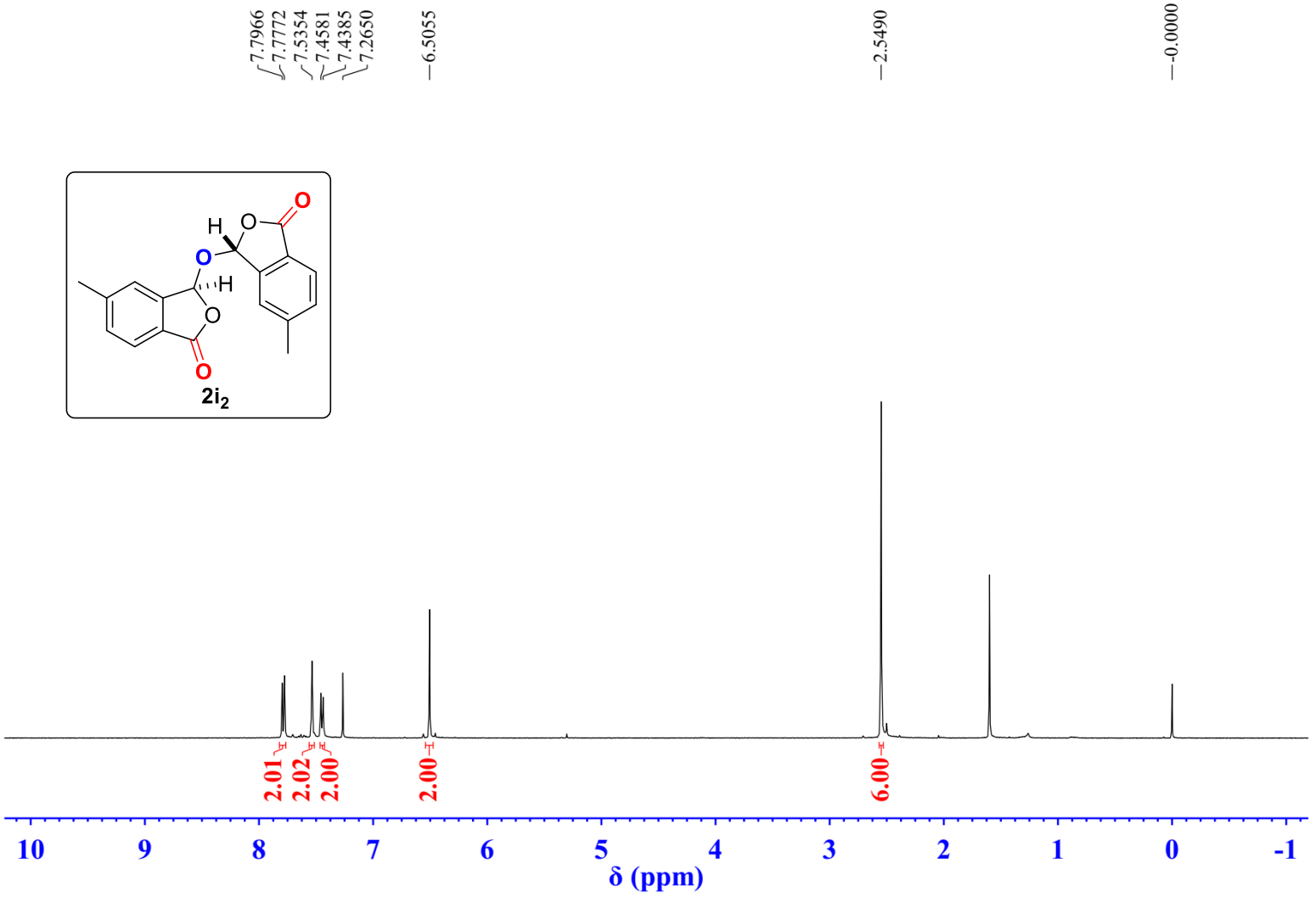

SM-X220112-3-Cl-mix CNMR (100MHz DMSO-d6)
164.9
164.7
147.1
146.7
136.9
136.7
132.6
132.5
131.3
131.0
123.6
123.2
122.6
100.2
97.9
40.1
39.9
39.7
39.5
39.3
39.1
38.9
2h1 + 2h2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

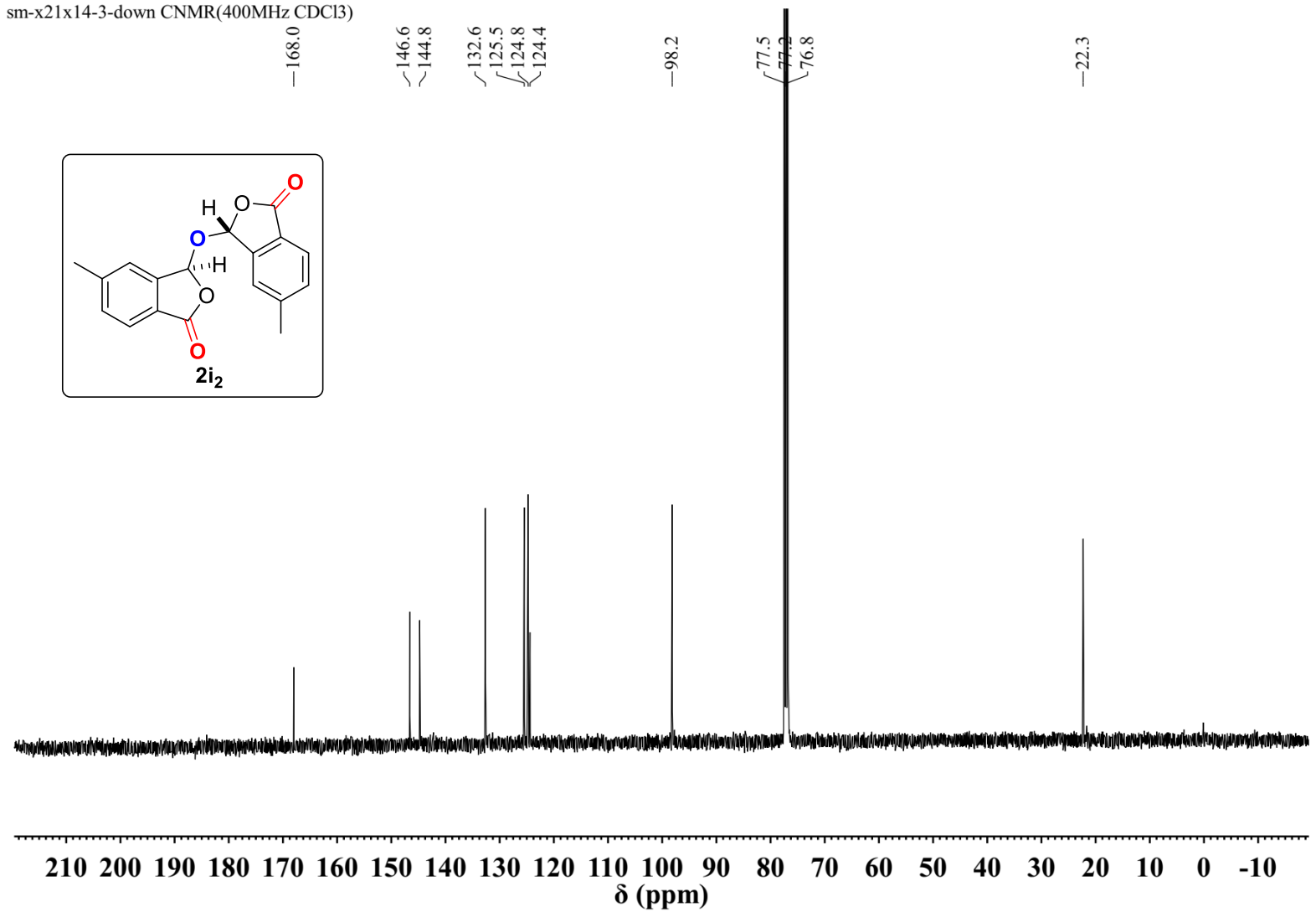
sm-x21x14-3-5-Me-up HNMR (400 MHz CDCl3)



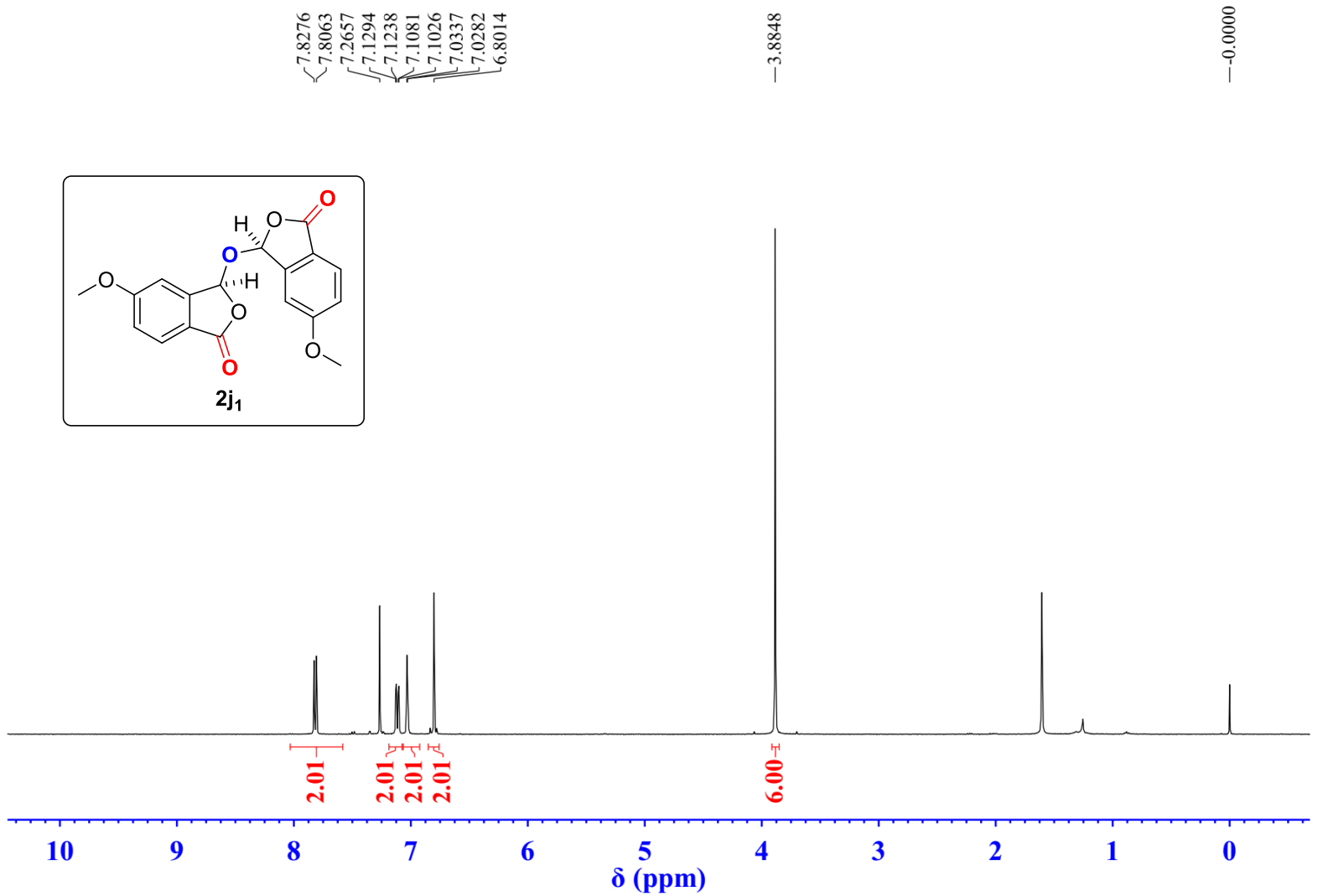

sm-x21x14-3-5-Me-up CNMR (100MHz CDCl3)
168.3
146.6
144.8
132.5
125.6
124.4
124.1
99.0
77.5
77.2
76.8
22.2
2i1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

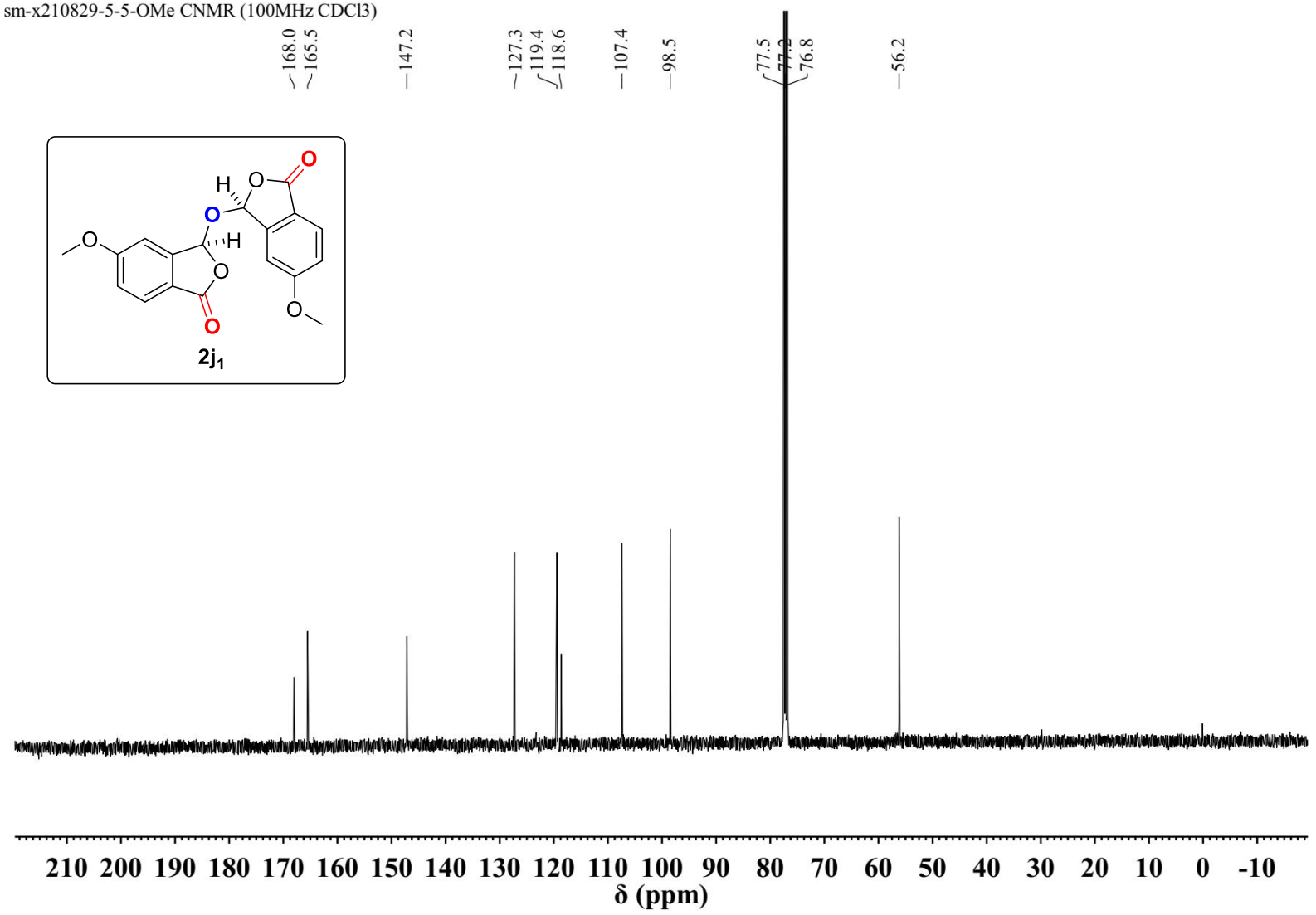
sm-x21x14-3-down HNMR(400MHz CDCl3)



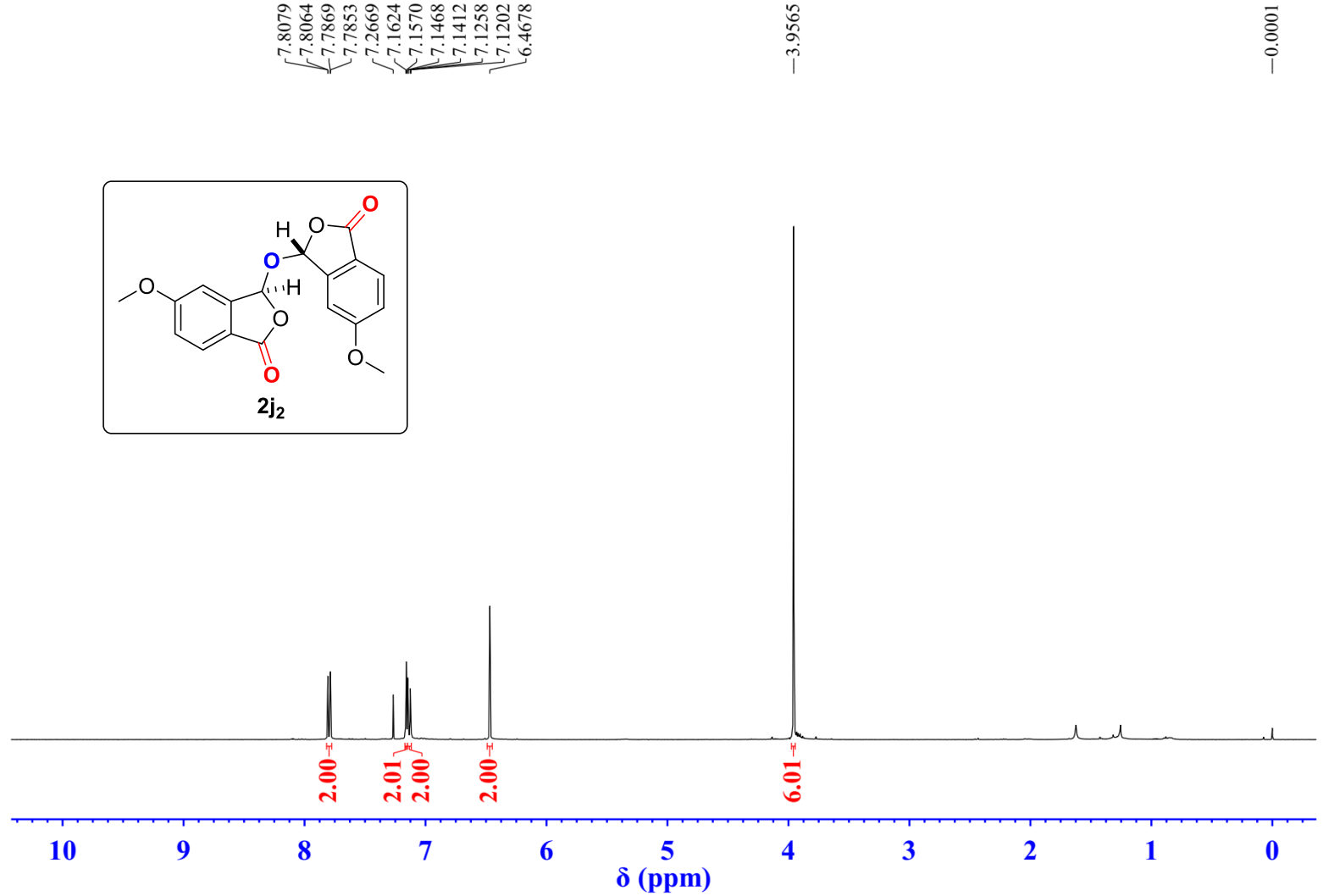

sm-x21x14-3-down CNMR(400MHz CDCl3)
168.0
146.6
144.8
132.6
125.5
124.8
124.4
98.2
77.5
76.8
22.3
2i2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

sm-x210829-5-5-OMe HNMR (400MHz CDCl3)

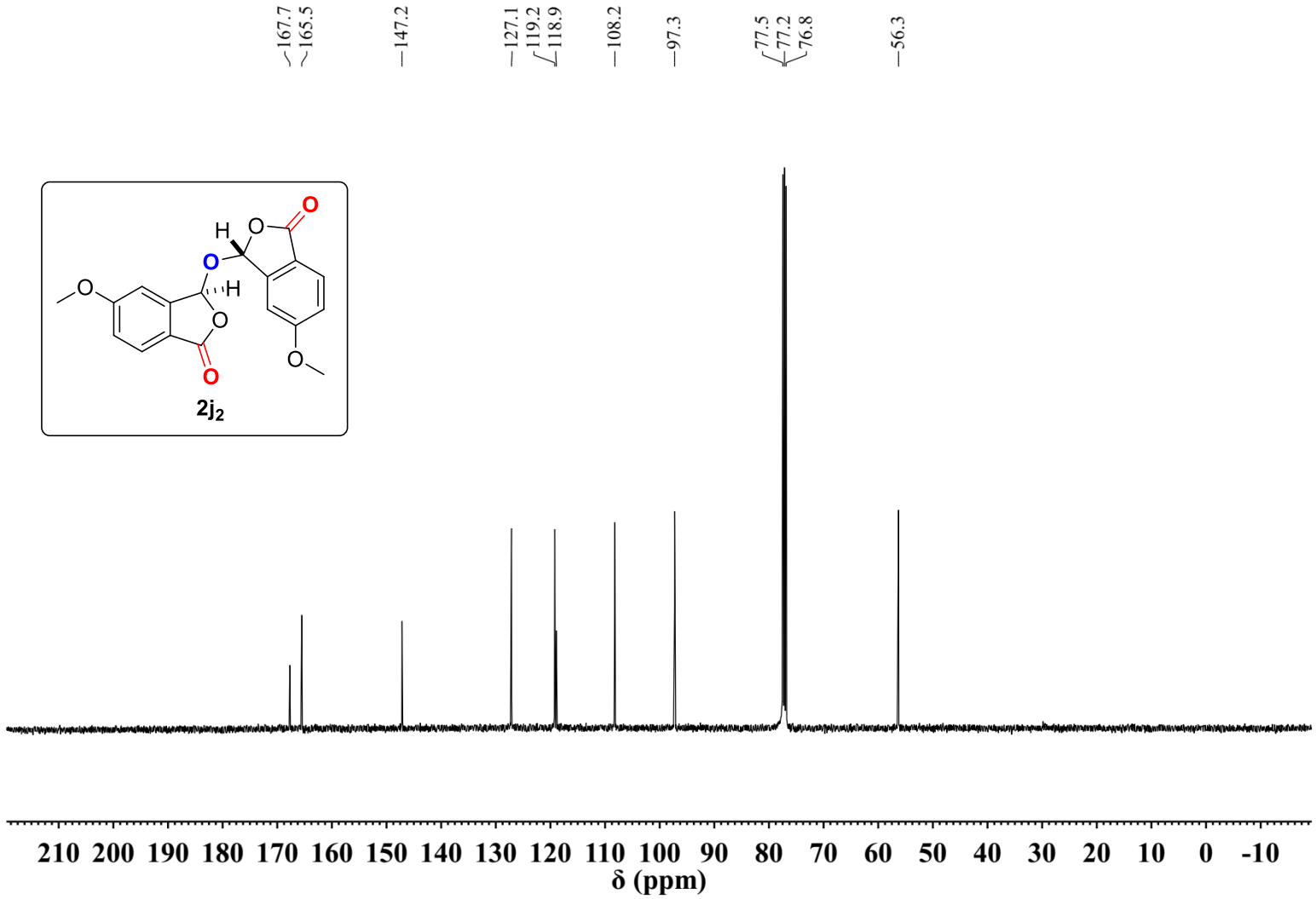


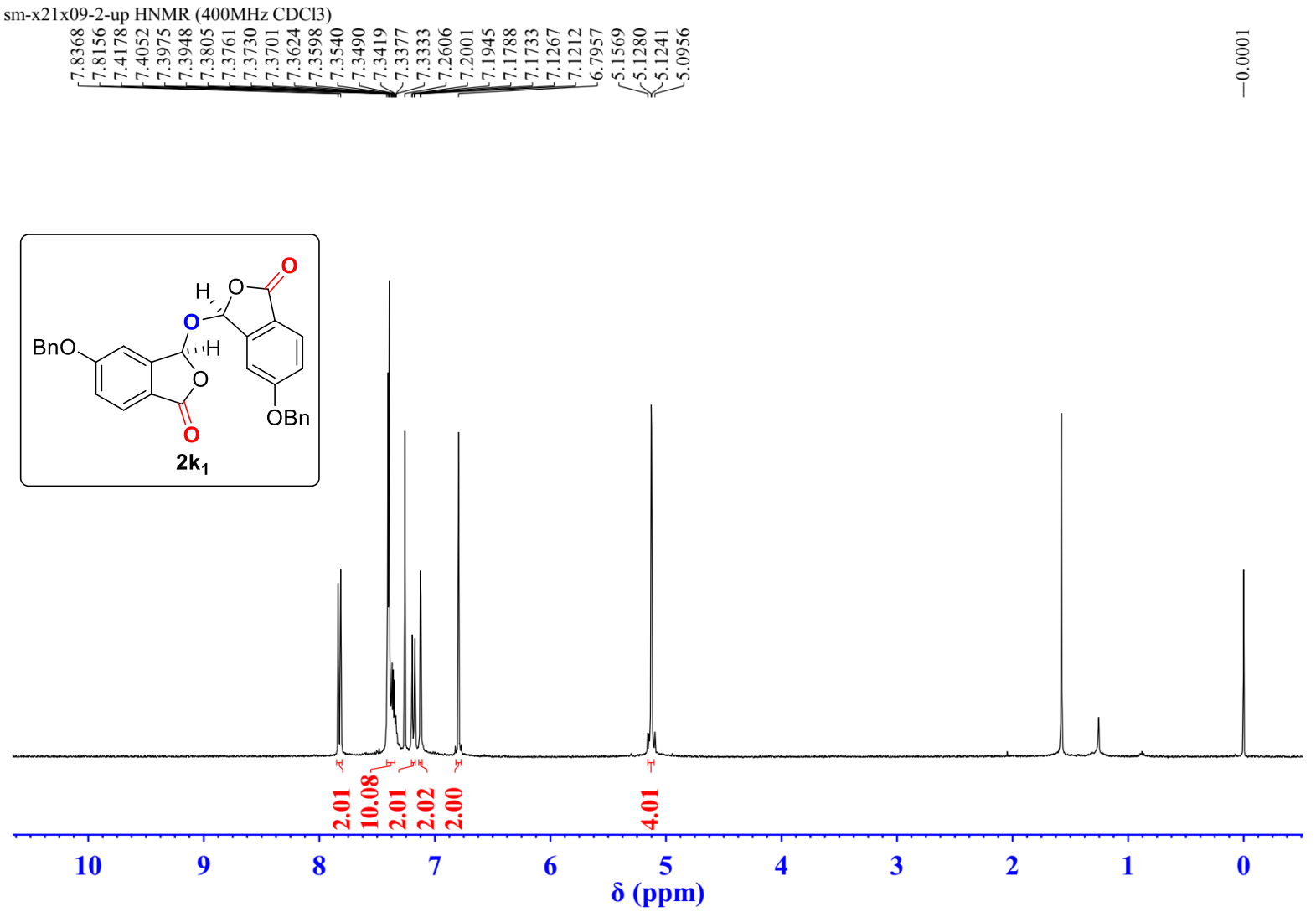

sm-x210829-5-5-OMe CNMR (100MHz CDCl3)
168.0
165.5
147.2
127.3
119.4
118.6
107.4
98.5
77.5
76.8
56.2
2j1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

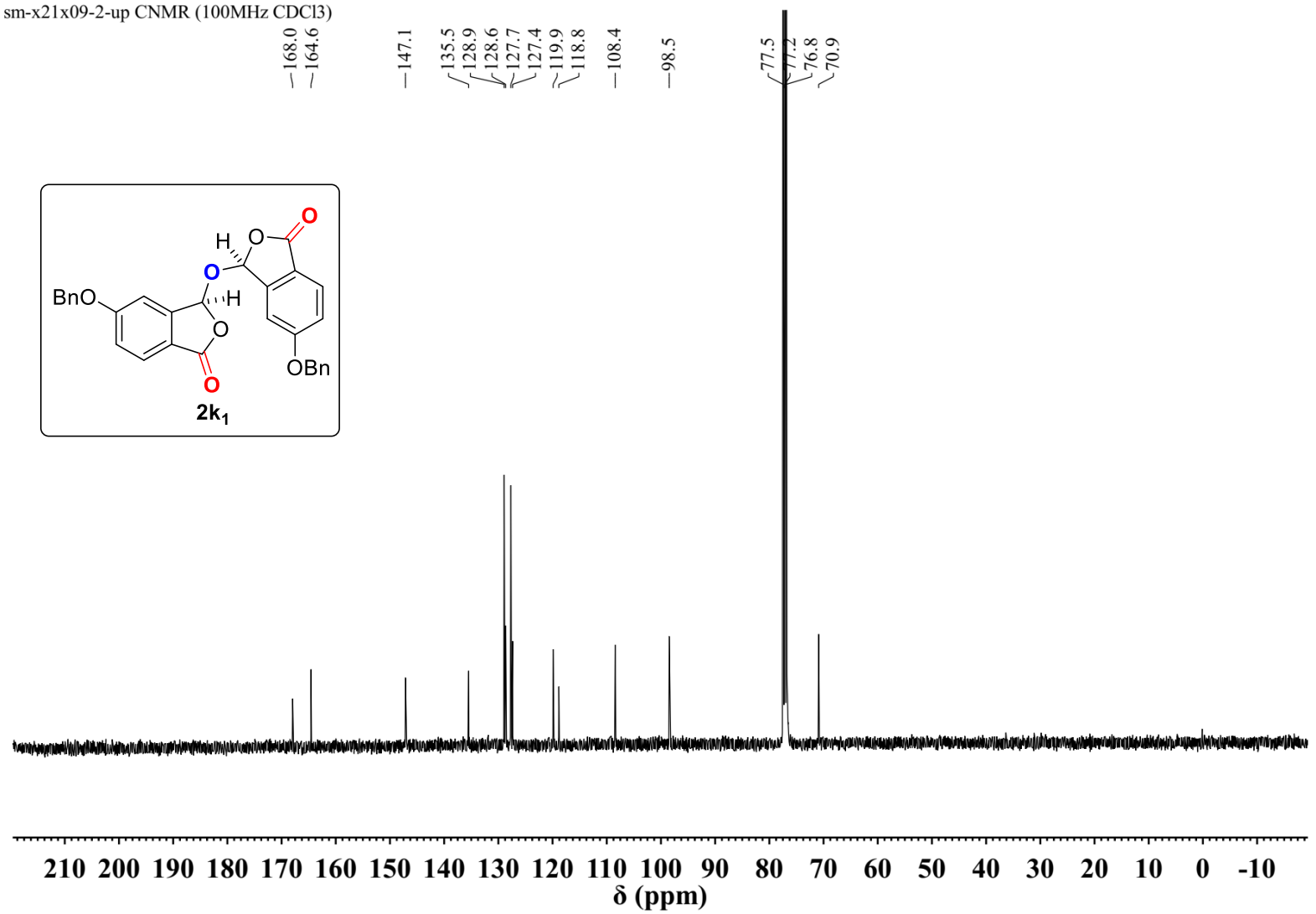
sm-x21y03-5-OMe-down HNMR(400MHz CDCl3)



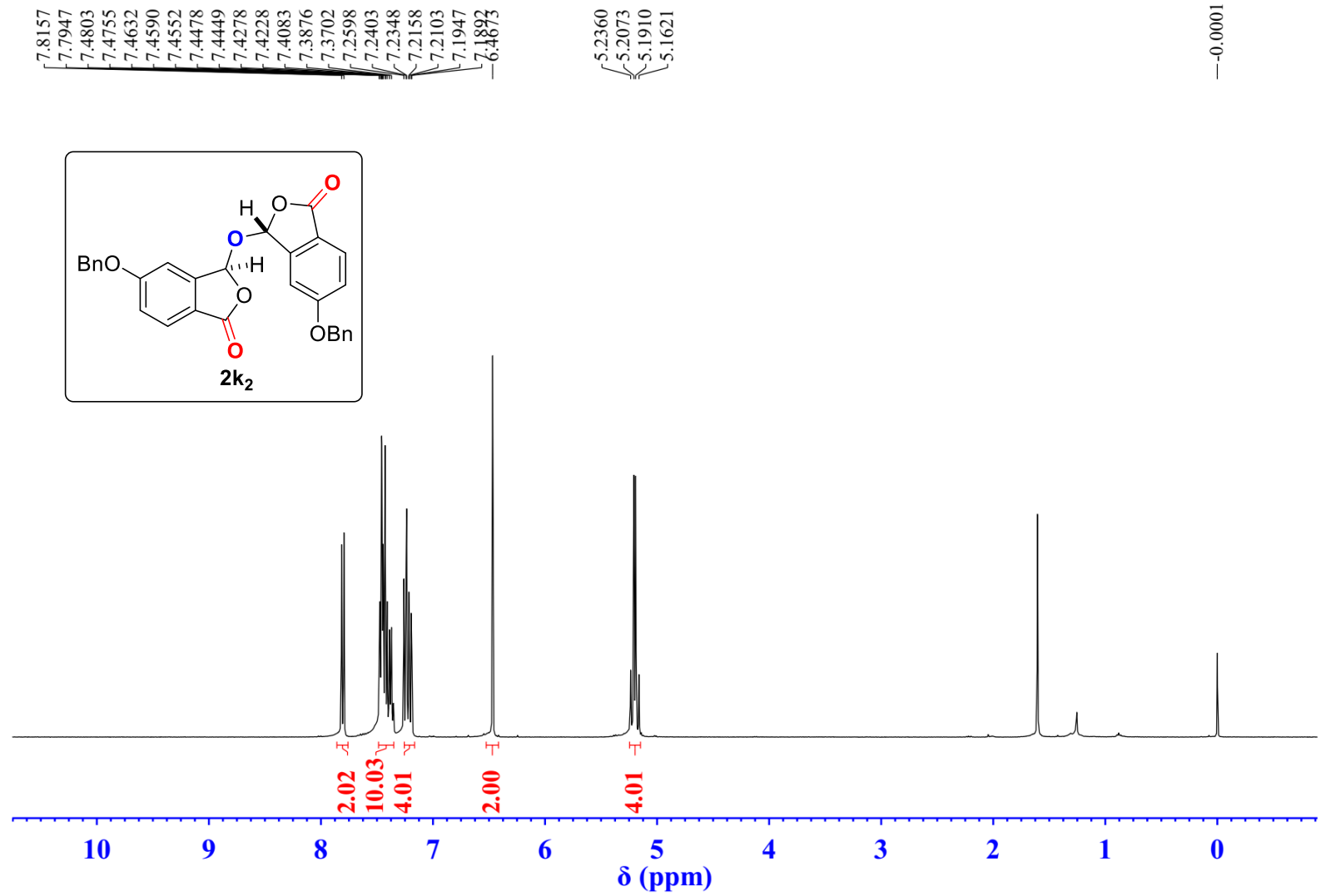
sm-x21y03-5-OMe-down CNMR(100MHz CDCl3)



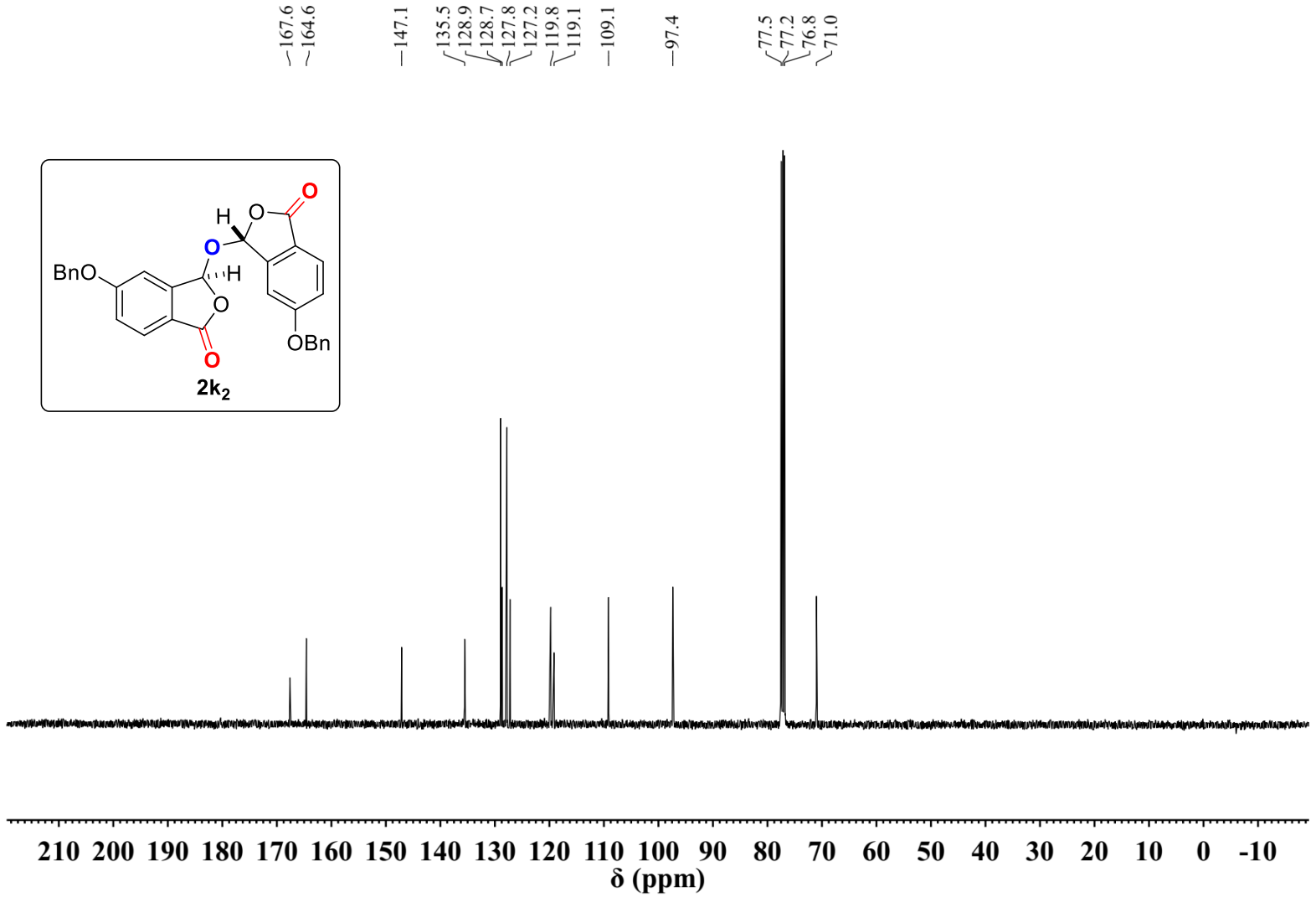

sm-x21x09-2-up HNMR (400MHz CDCl3)
7.8368
7.8156
7.4178
7.4052
7.3975
7.3948
7.3805
7.3761
7.3730
7.3701
7.3624
7.3598
7.3540
7.3490
7.3419
7.3377
7.3333
7.2606
7.2001
7.1945
7.1788
7.1733
7.1267
7.1212
6.7957
5.1569
5.1280
5.1241
5.0956
0.0001
BnO
OBn
2k1
2.01
10.08
2.01
2.02
2.00
4.01
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


sm-x21x09-2-up CNMR (100MHz CDCl3)
168.0
164.6
147.1
135.5
128.9
128.6
127.7
127.4
119.9
118.8
108.4
98.5
77.5
76.8
70.9
BnO
OBn
2k1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

sm-x21z09-2-down HNMR (400MHz CDCl3)

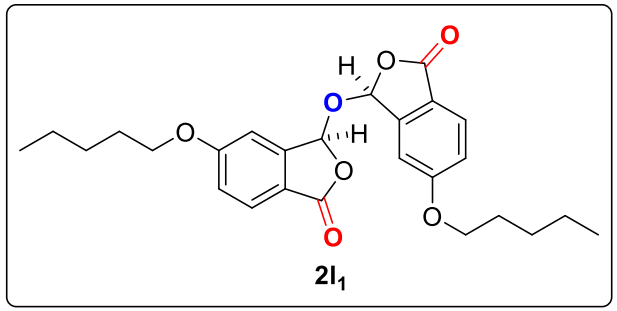


sm-x21z09-2-down CNMR (100MHz CDCl3)

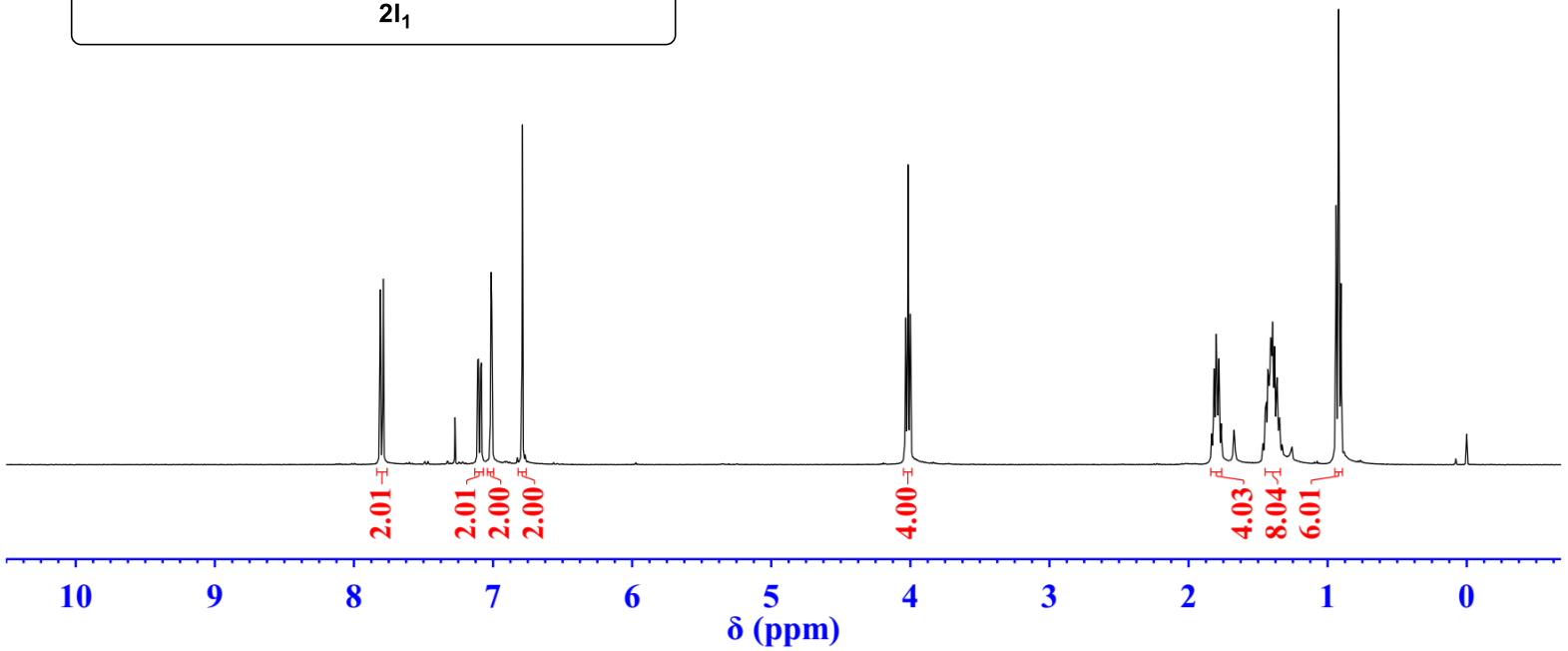


sm-x21x14-5-O5C-up HNMR (400MHz CDCl3)

7.8100 7.7889 7.2731 7.1100 7.1046 7.0887 7.0833 7.0147 7.0093 6.7883 4.0323 4.0161 3.9996 1.8337 1.8172 1.8008 1.7971 1.7818 1.7648 1.4665 1.4618 1.4481 1.4398 1.4297 1.4242 1.4186 1.4134 1.4095 1.4032 1.3957 1.3805 1.3690 1.3645 1.3604 1.3494 1.3461 1.3412 1.3277 1.3238 0.9388 0.9210 0.9040 0.0000

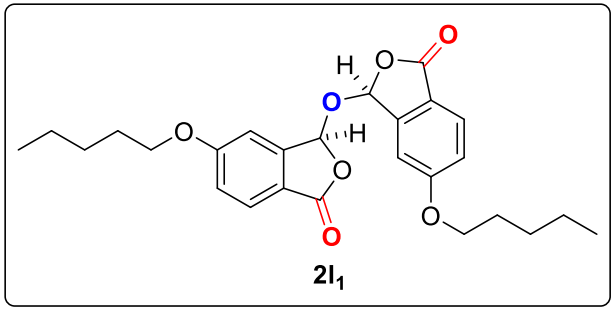


2l$_1$



sm-x21x14-5-05C-up CNMR (100MHz CDCl3)

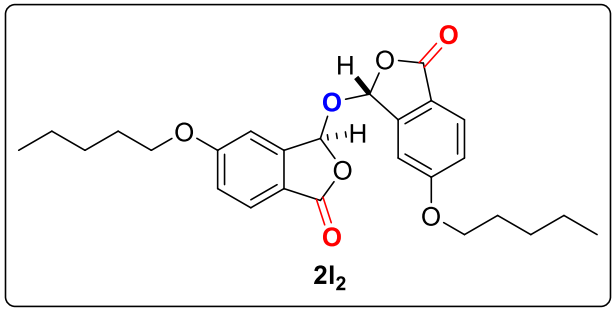
168.1
165.1
147.2
127.2
119.6
118.2
107.9
98.5
77.5
77.2
76.8
69.1
28.7
28.1
22.4
14.1



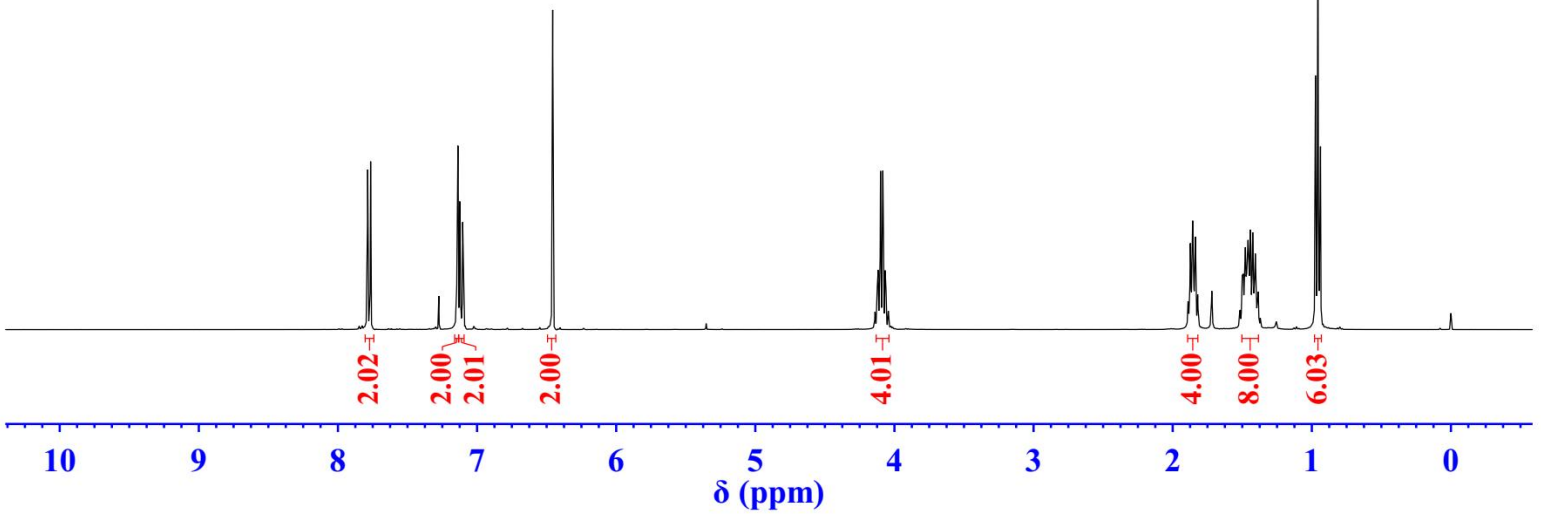
2l$_1$

sm-x21x14-5-05C-down HNMR (400MHz CDC13)

7.7862 7.7652 7.2747 7.1426 7.1373 7.1247 7.1192 7.1038 7.0983 6.4564 4.1234 4.1169 4.1072 4.1002 4.0834 4.0763 4.0668 4.0602 1.8896 1.8730 1.8570 1.8529 1.8402 1.8363 1.8201 1.5003 1.4919 1.4828 1.4775 1.4704 1.4664 1.4619 1.4580 1.4538 1.4507 1.4448 1.4420 1.4390 1.4302 1.4252 1.4214 1.4125 1.4073 1.4041 1.4006 1.3938 1.3887 1.3842 0.9736 0.9559 0.9382 0.0001

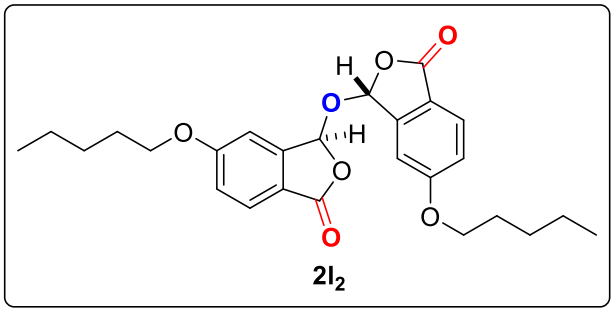


2l$_2$

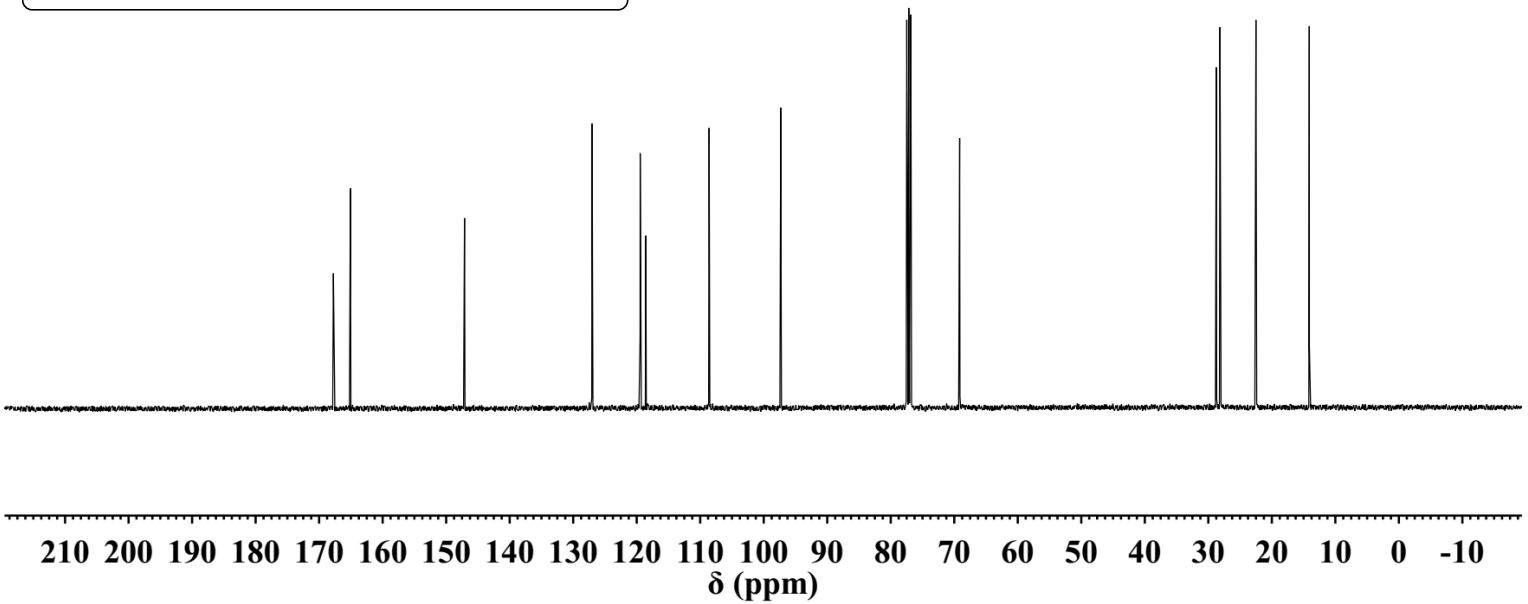


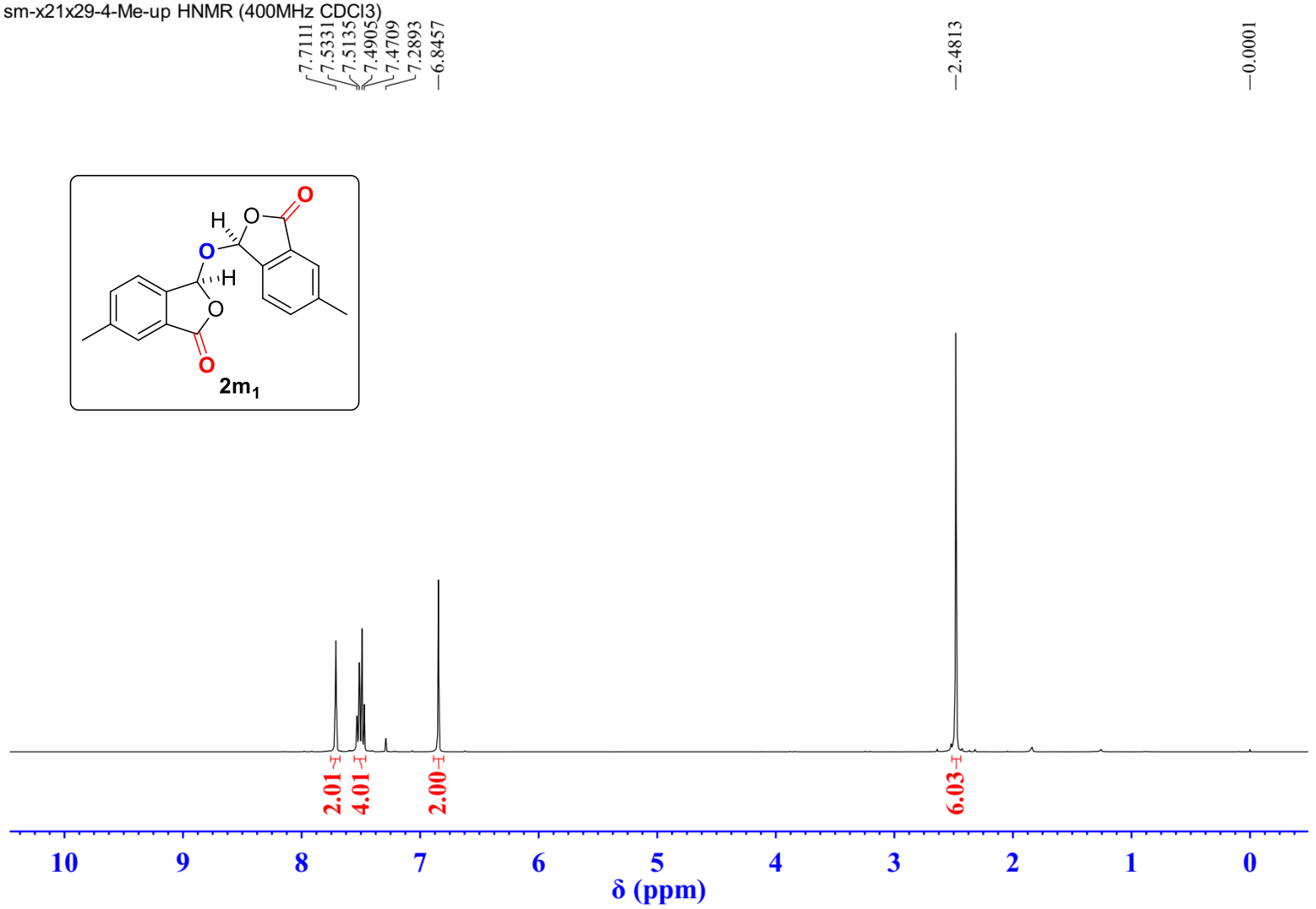
sm-x21x14-5-05C-down CNMR (100MHz CDCl3)

167.8
165.1
147.1
127.0
119.4
118.6
108.6
97.3
77.5
77.2
76.8
69.2
28.7
28.2
22.5
14.1

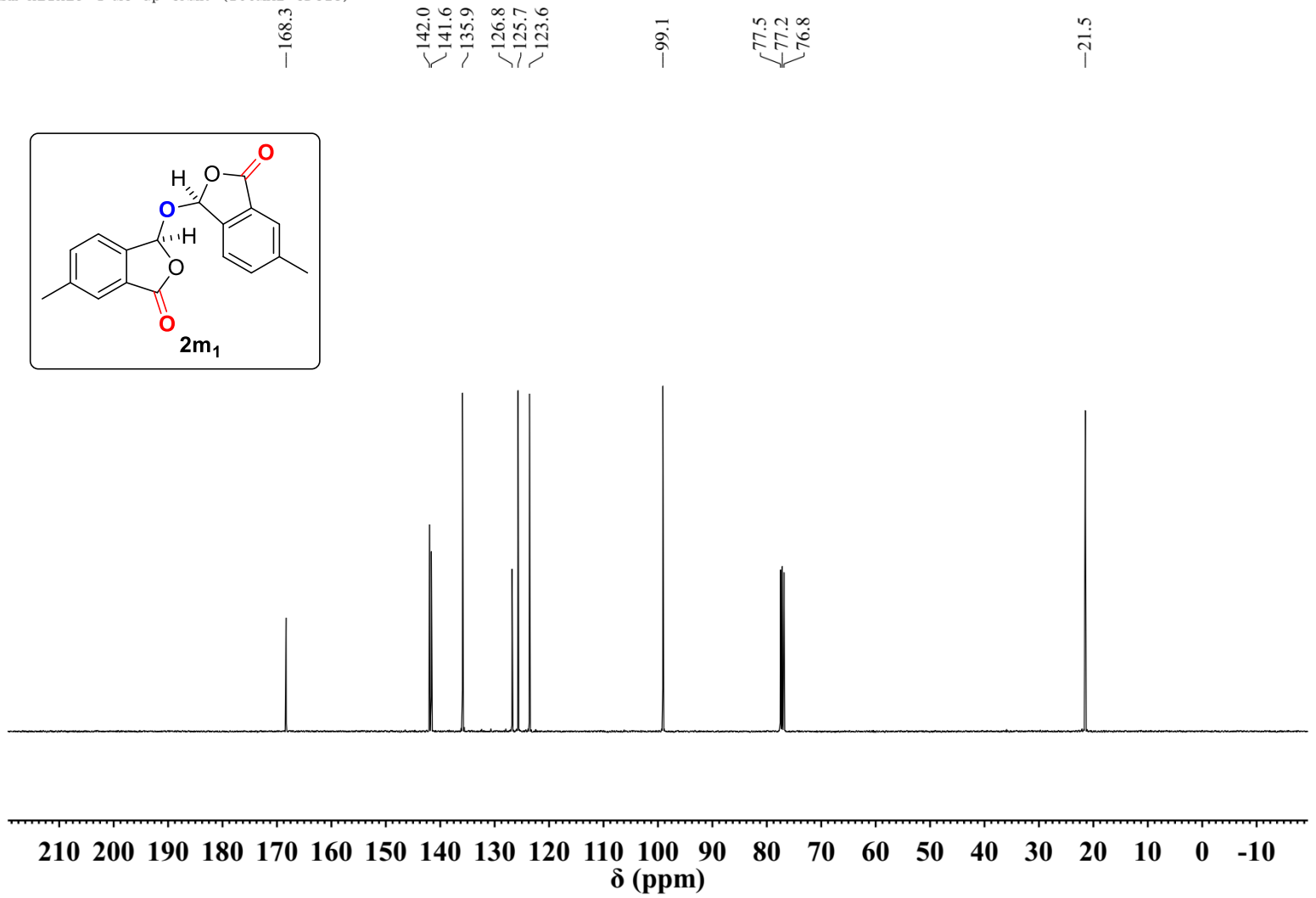


2I$_2$

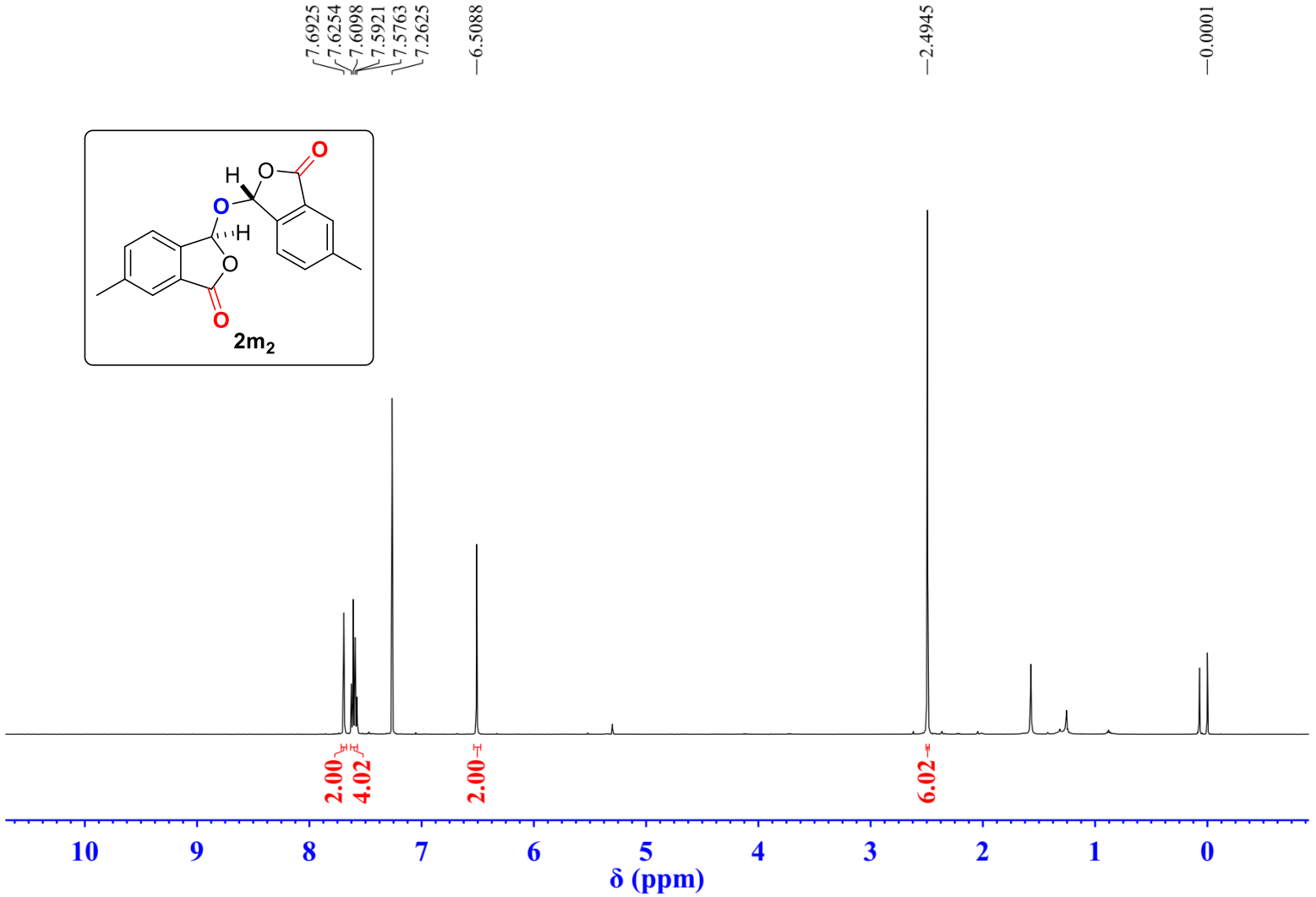



sm-x21x29-4-Me-up HNMR (400MHz CDCl3)
7.7111
7.5331
7.5135
7.4905
7.4709
7.2893
6.8457
2.4813
0.0001
2m1
2.01
4.01
2.00
6.03
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

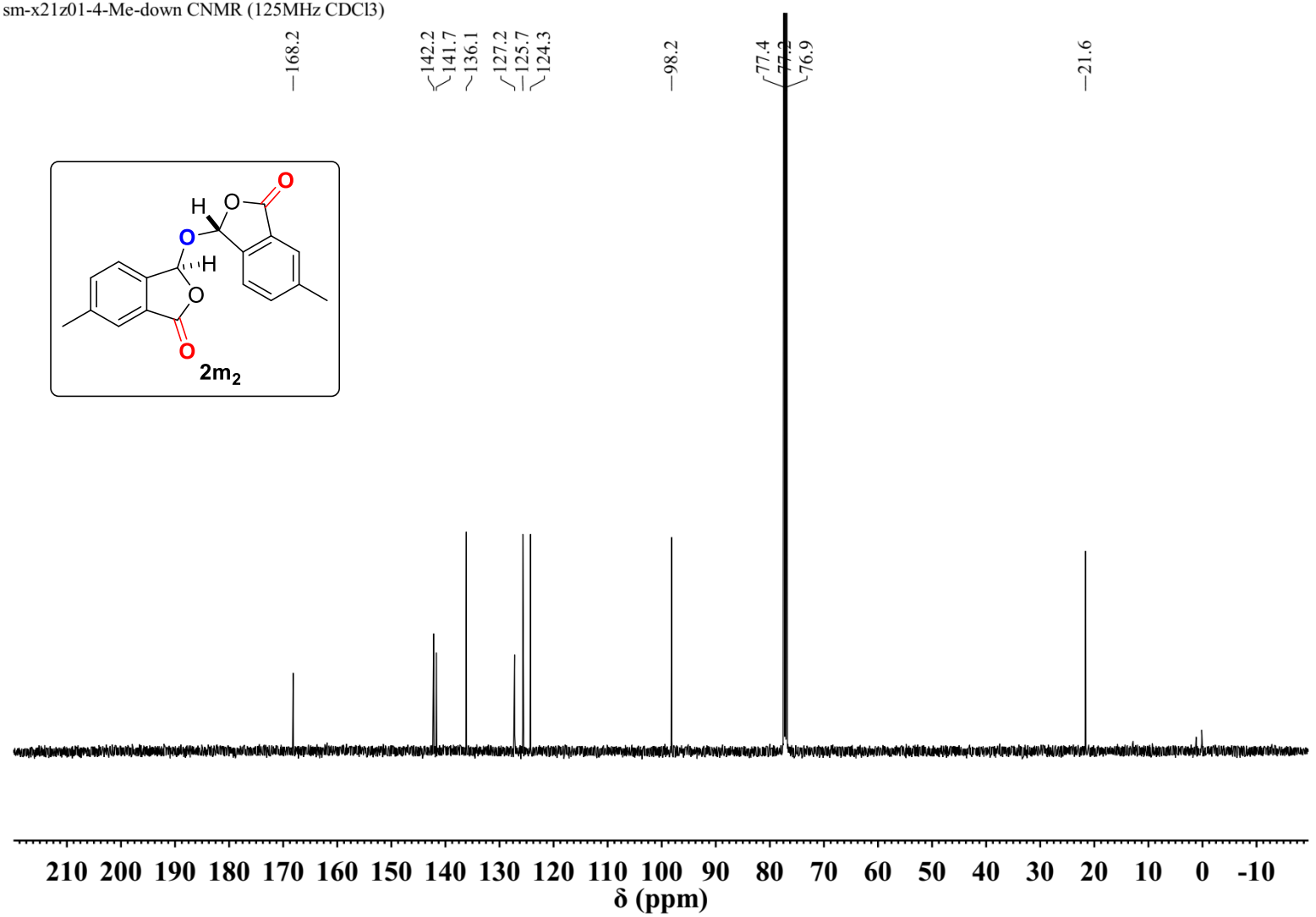
sm-x21x29-4-Me-up CNMR (100MHz CDCl3)



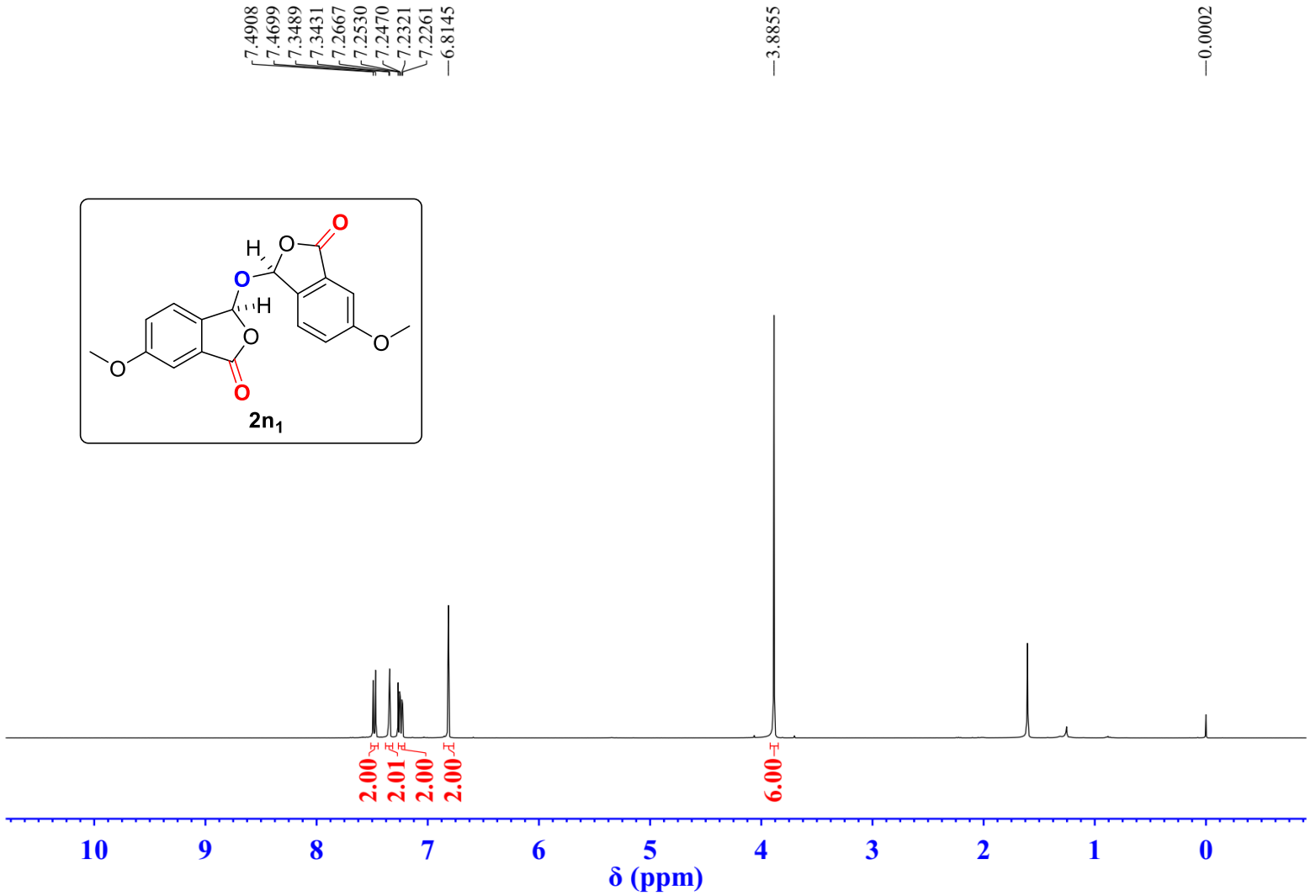
sm-x21z01-4-Me-down HNMR (500MHz CDCl3)

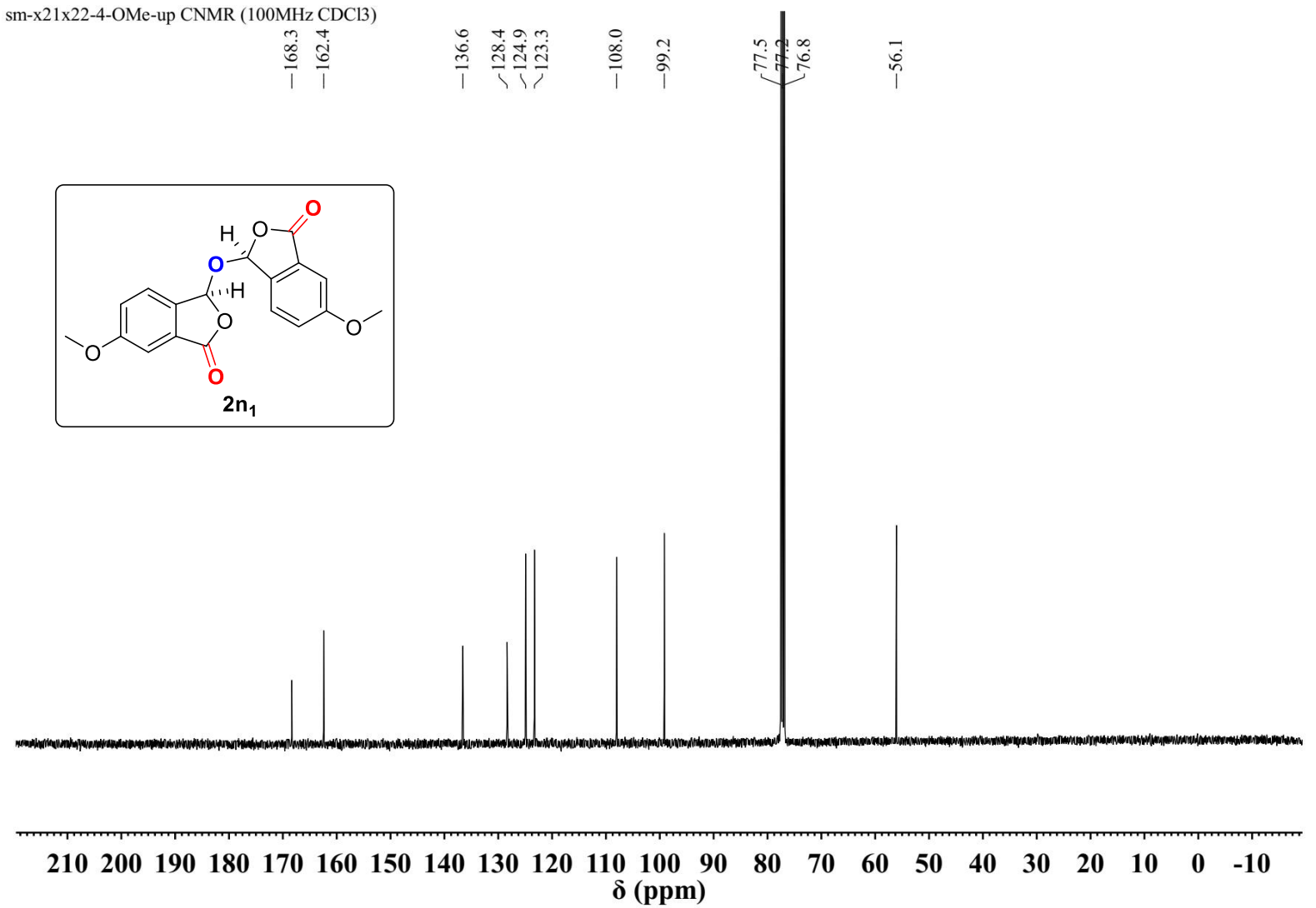


sm-x21z01-4-Me-down CNMR (125MHz CDCl3)

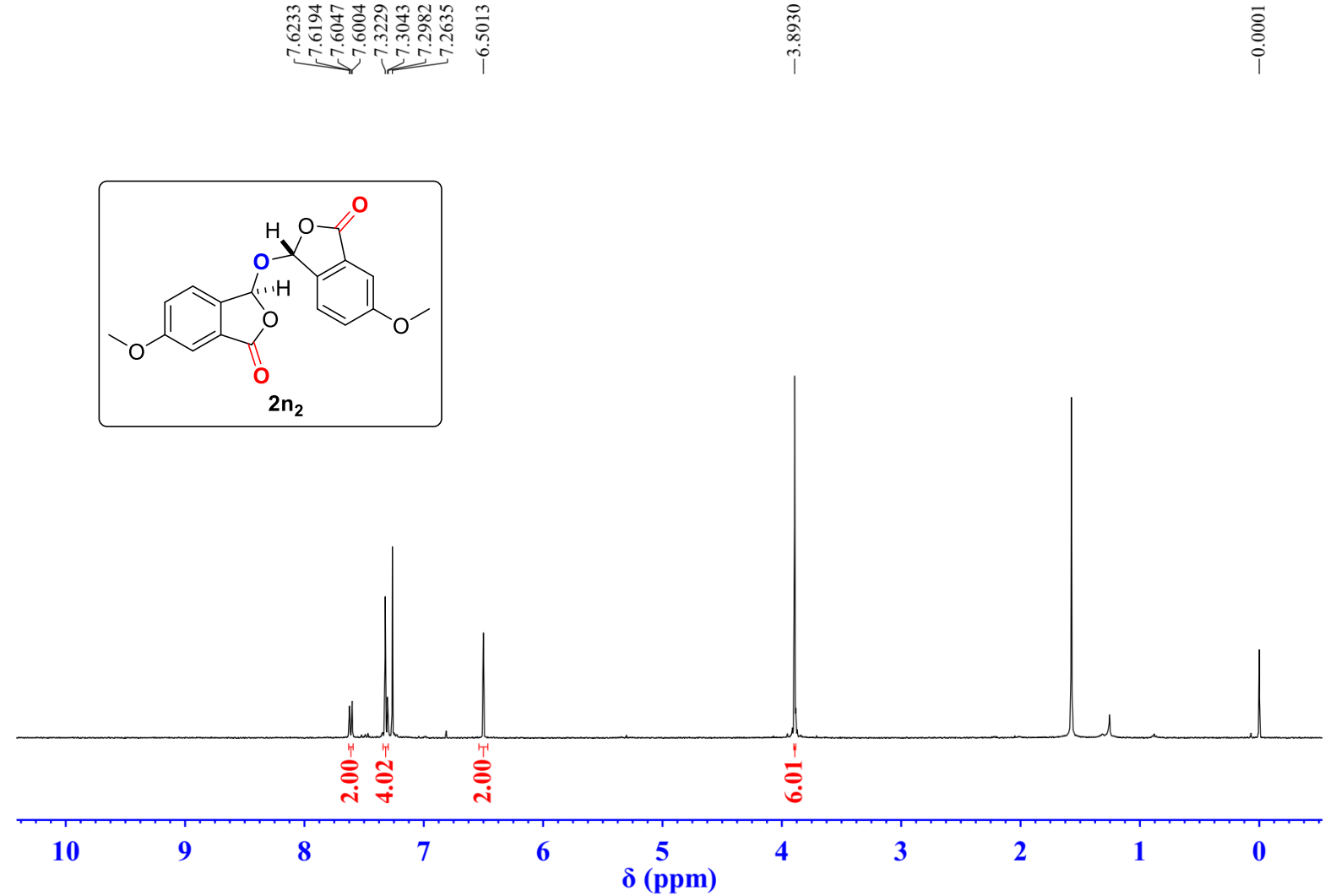


sm-x21x22-4-OMe-up HNMR (400MHz CDCl3)

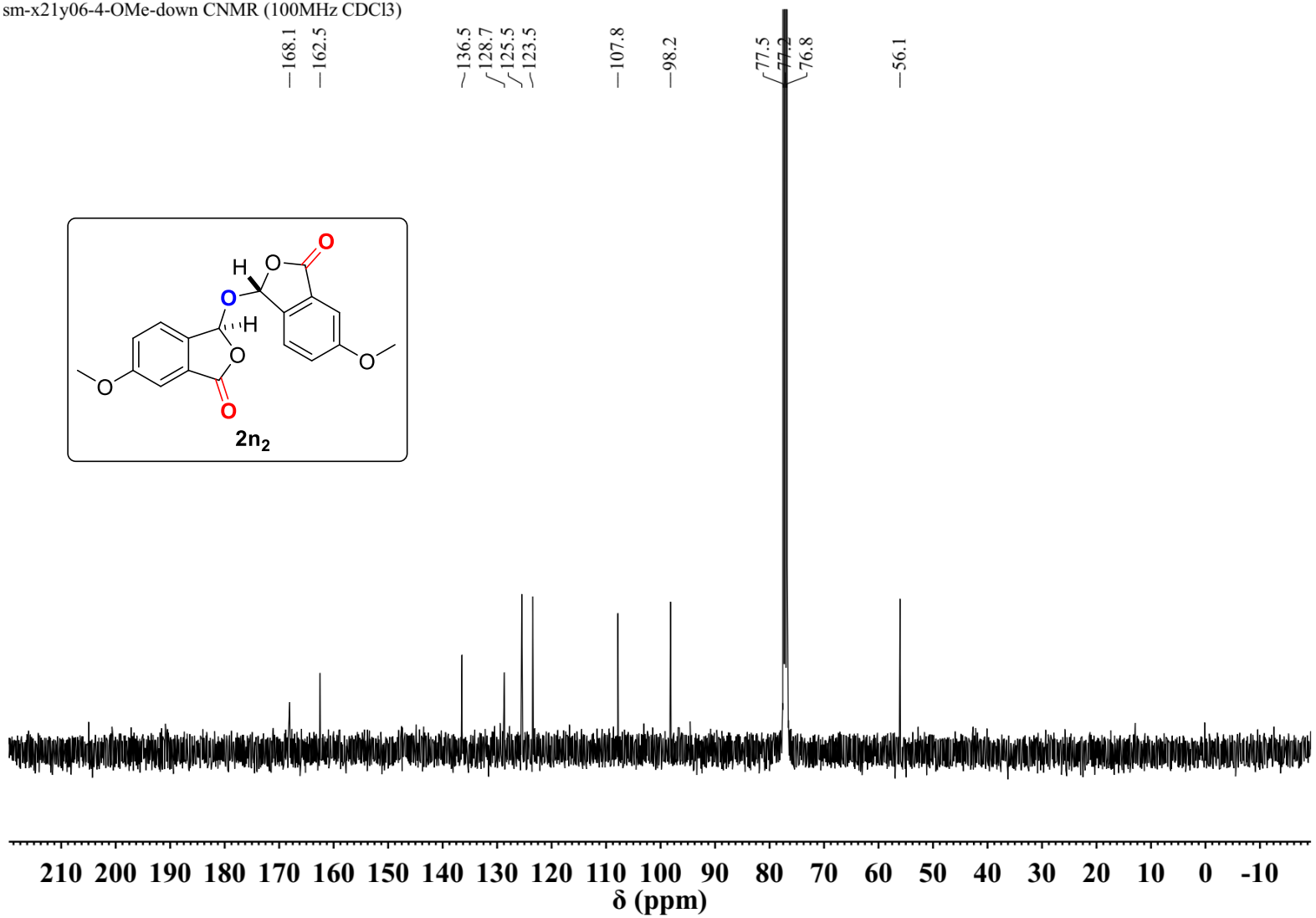



sm-x21x22-4-OMe-up CNMR (100MHz CDCl3)
168.3
162.4
136.6
128.4
124.9
123.3
108.0
99.2
77.5
77.2
76.8
56.1
2n1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

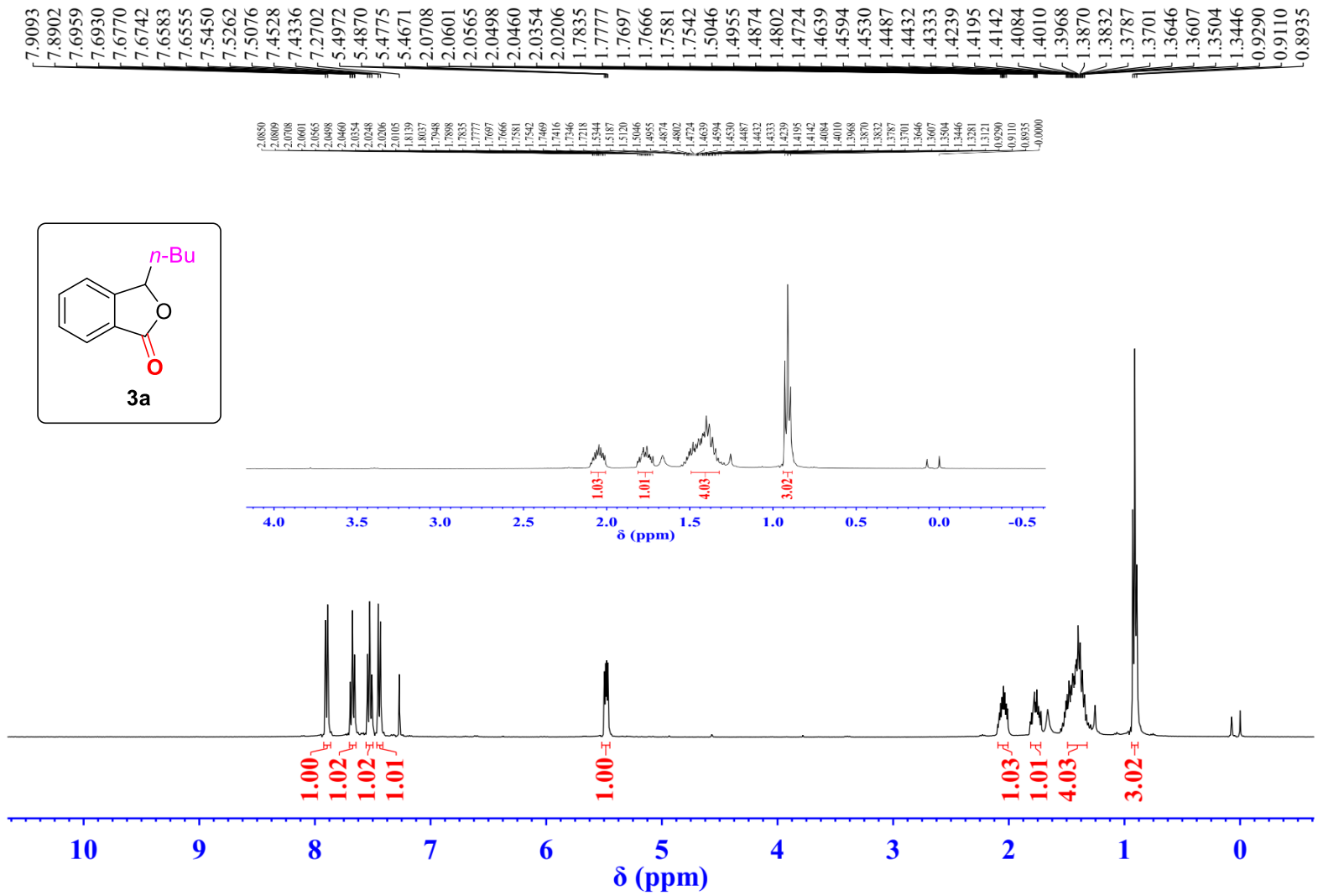
sm-x21y06-4-OMe-down HNMR (400MHz CDCl3)



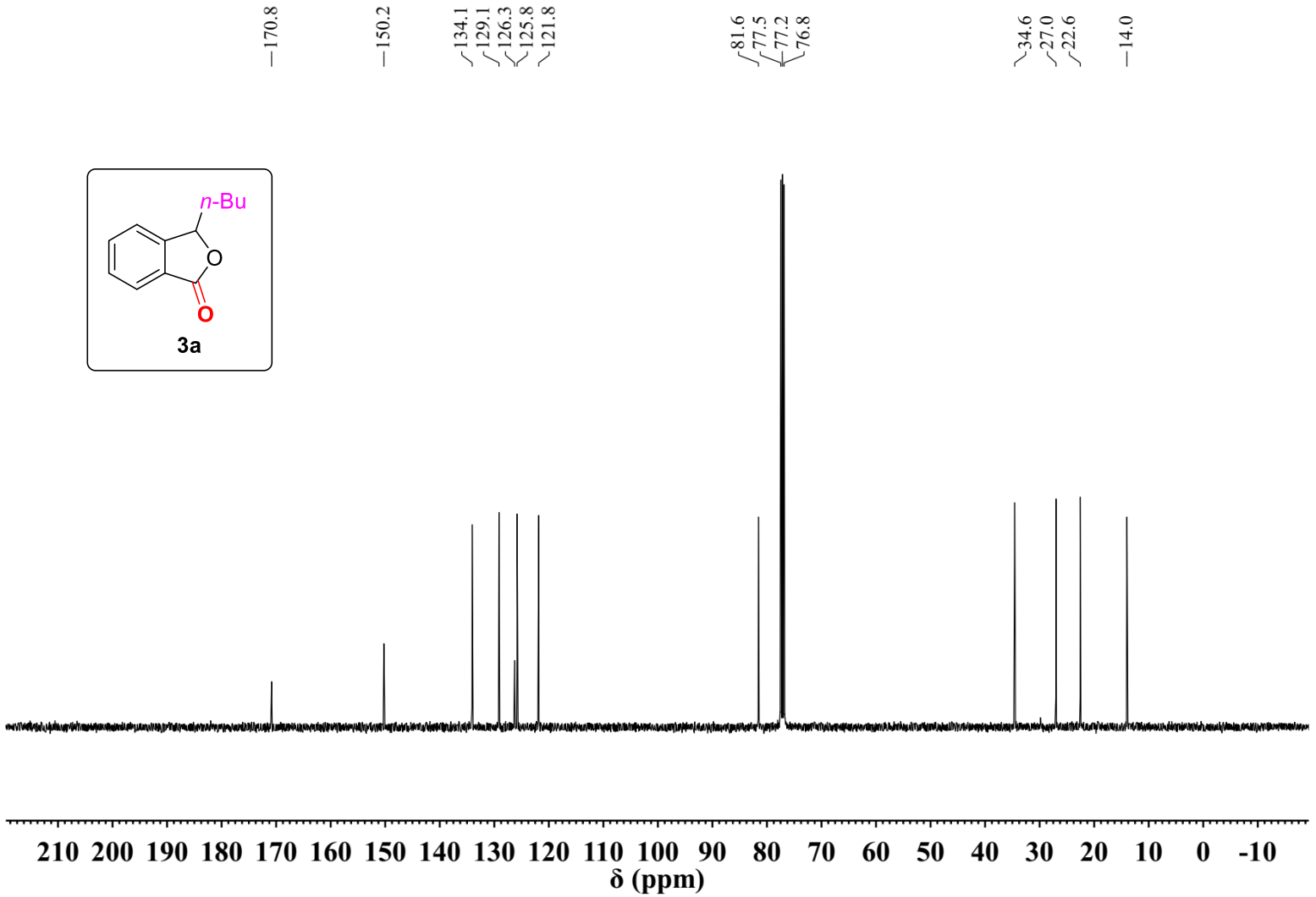
sm-x21y06-4-OMe-down CNMR (100MHz CDCl3)



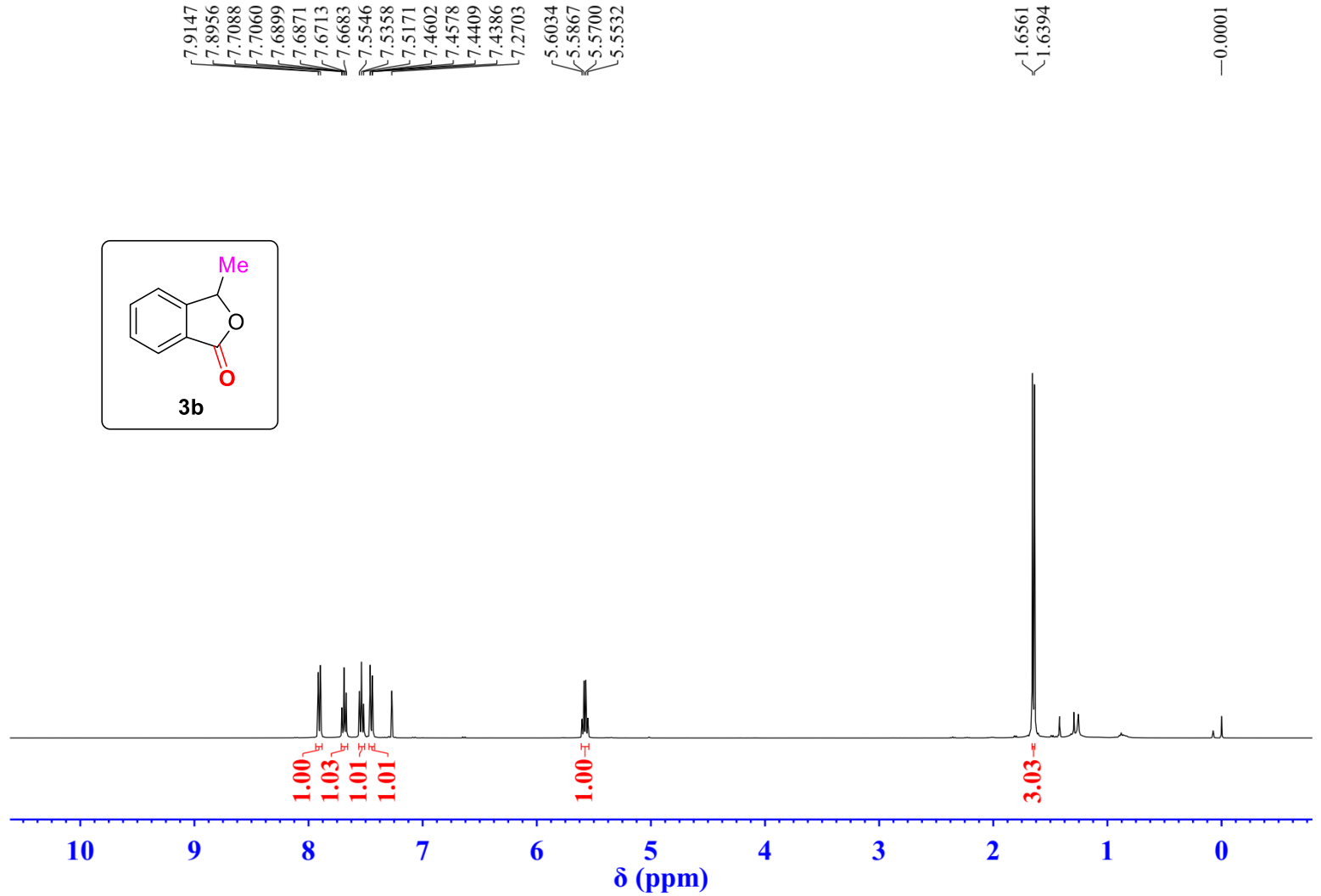
SM-X220108-nBu HNMR (400MHz CDCl3)



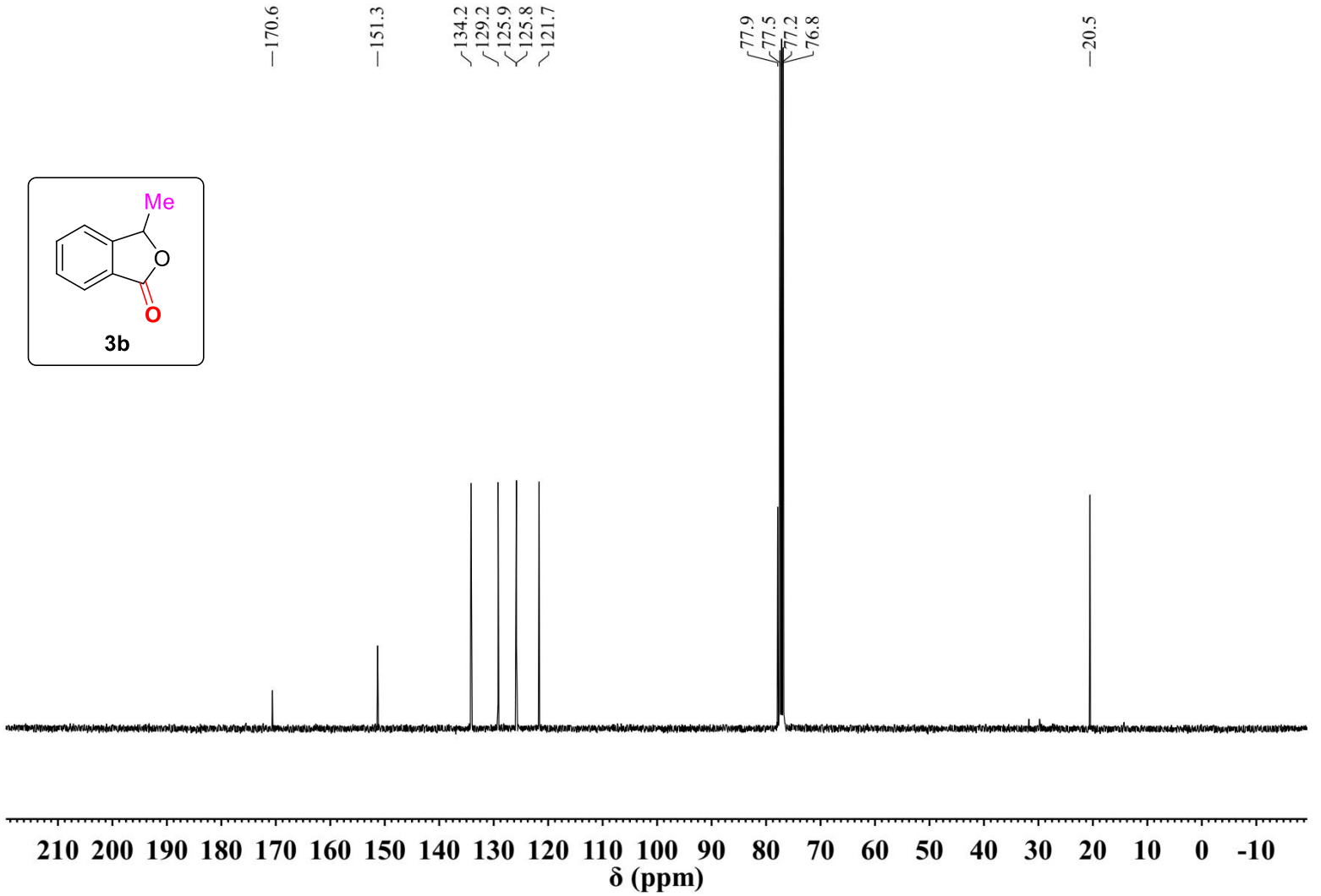
SM-X220108-nBu CNMR (100MHz CDCl3)



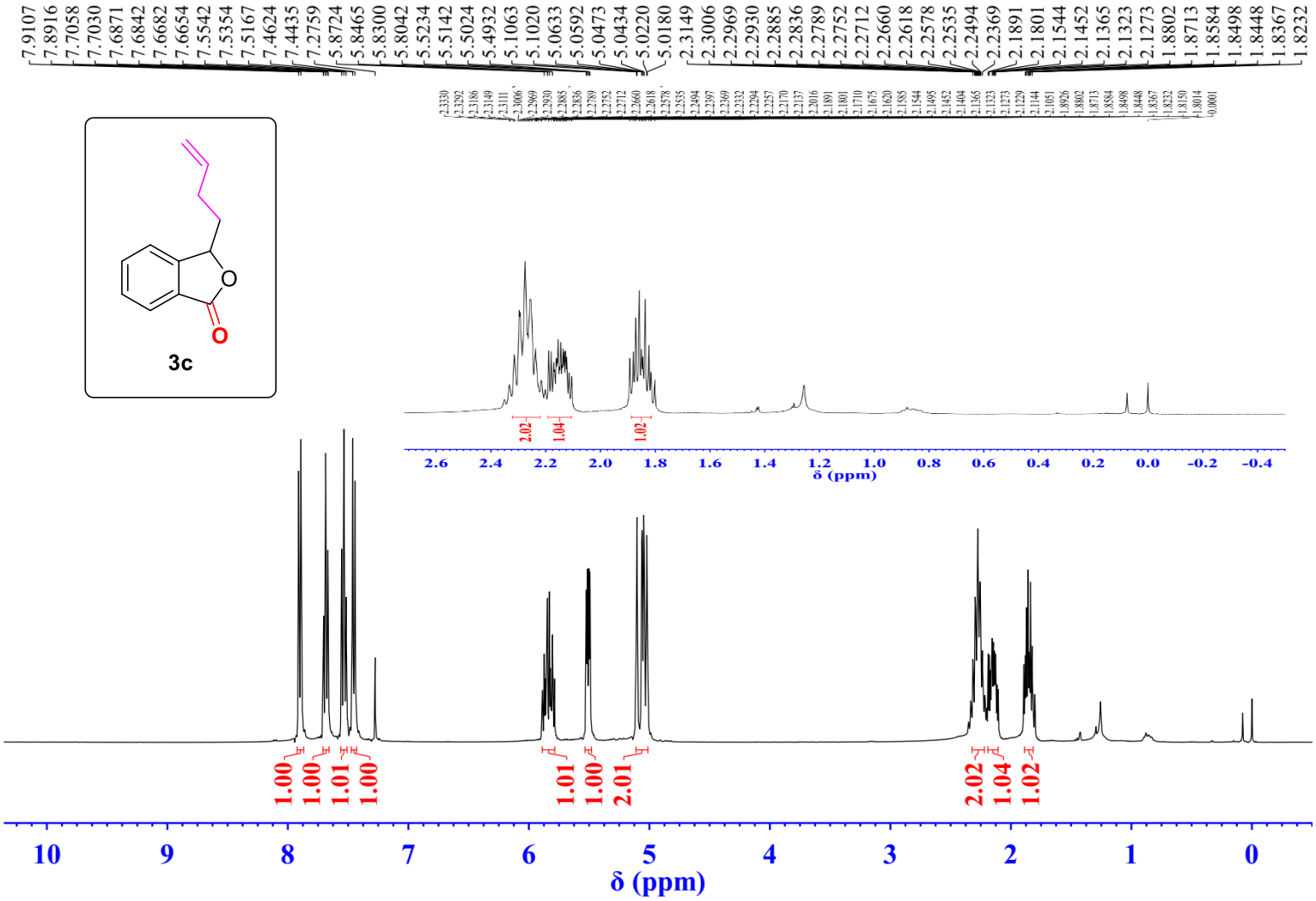
SM-X220112-CH3 HNMR (400MHz CDCl3)



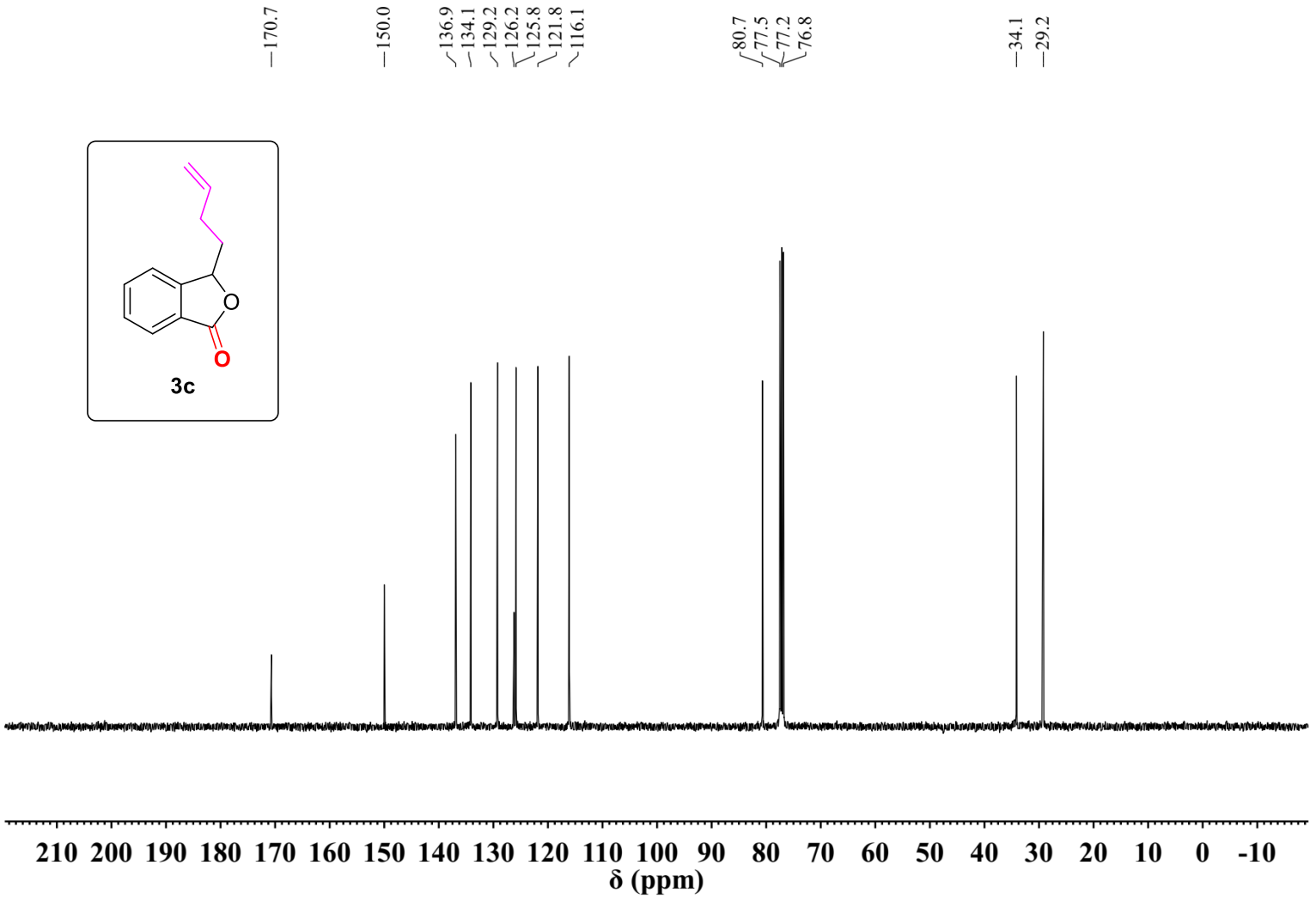
SM-X220112-CH3 CNMR (100MHz CDCl3)



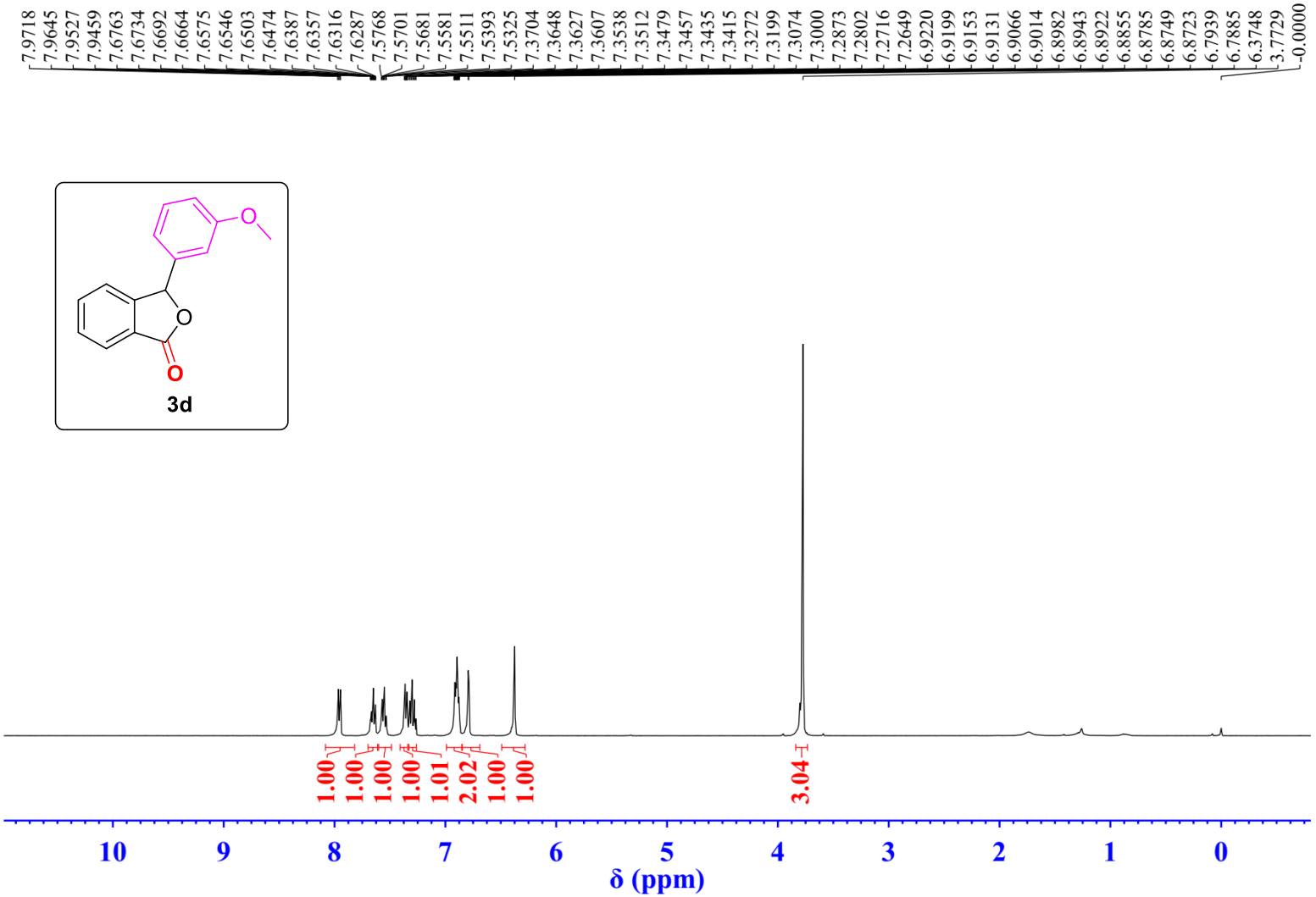
SM-X220108-nBuenyl HNMR (400MHz CDCl3)



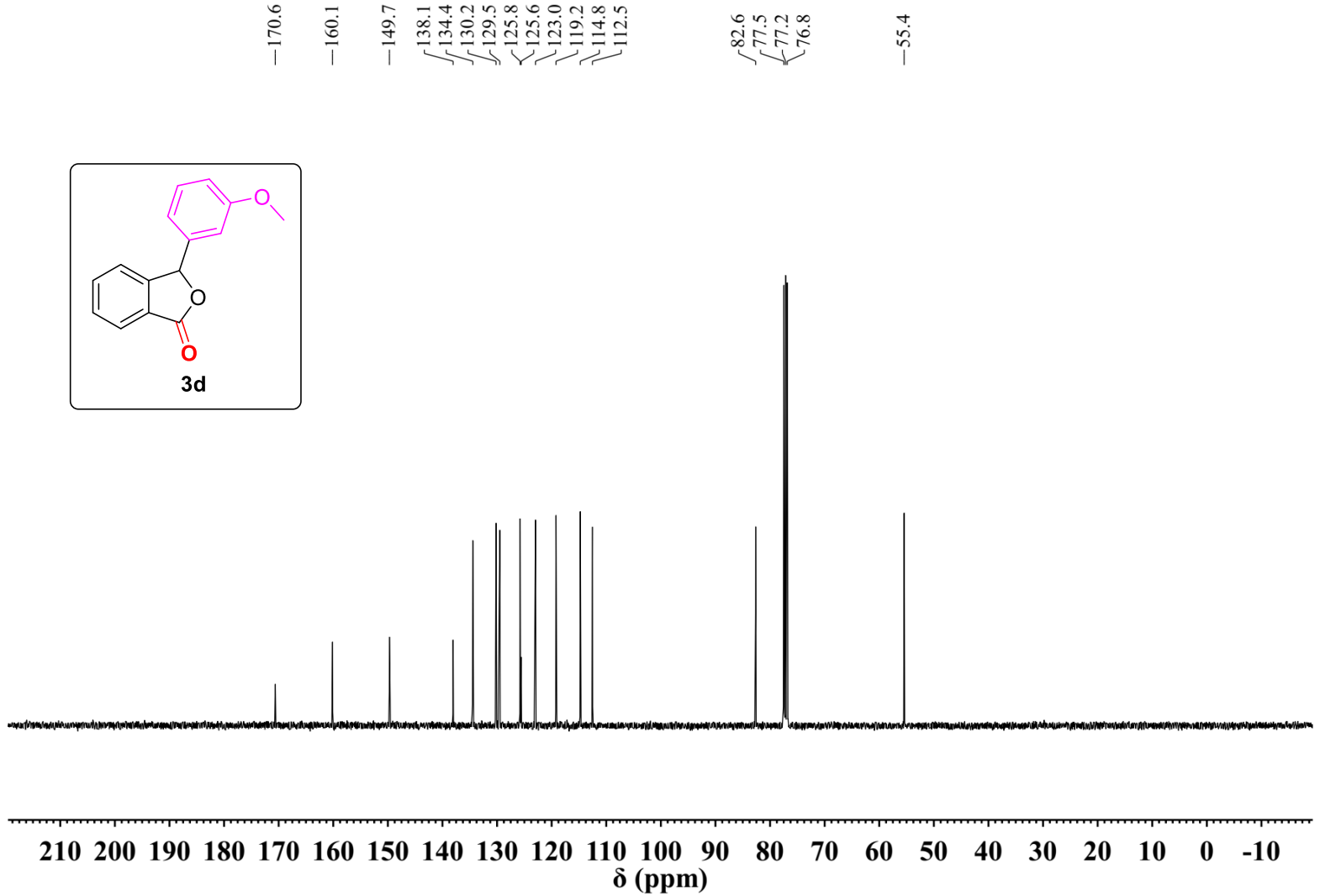
SM-X220108-nBuenyl CNMR (100MHz CDCl3)



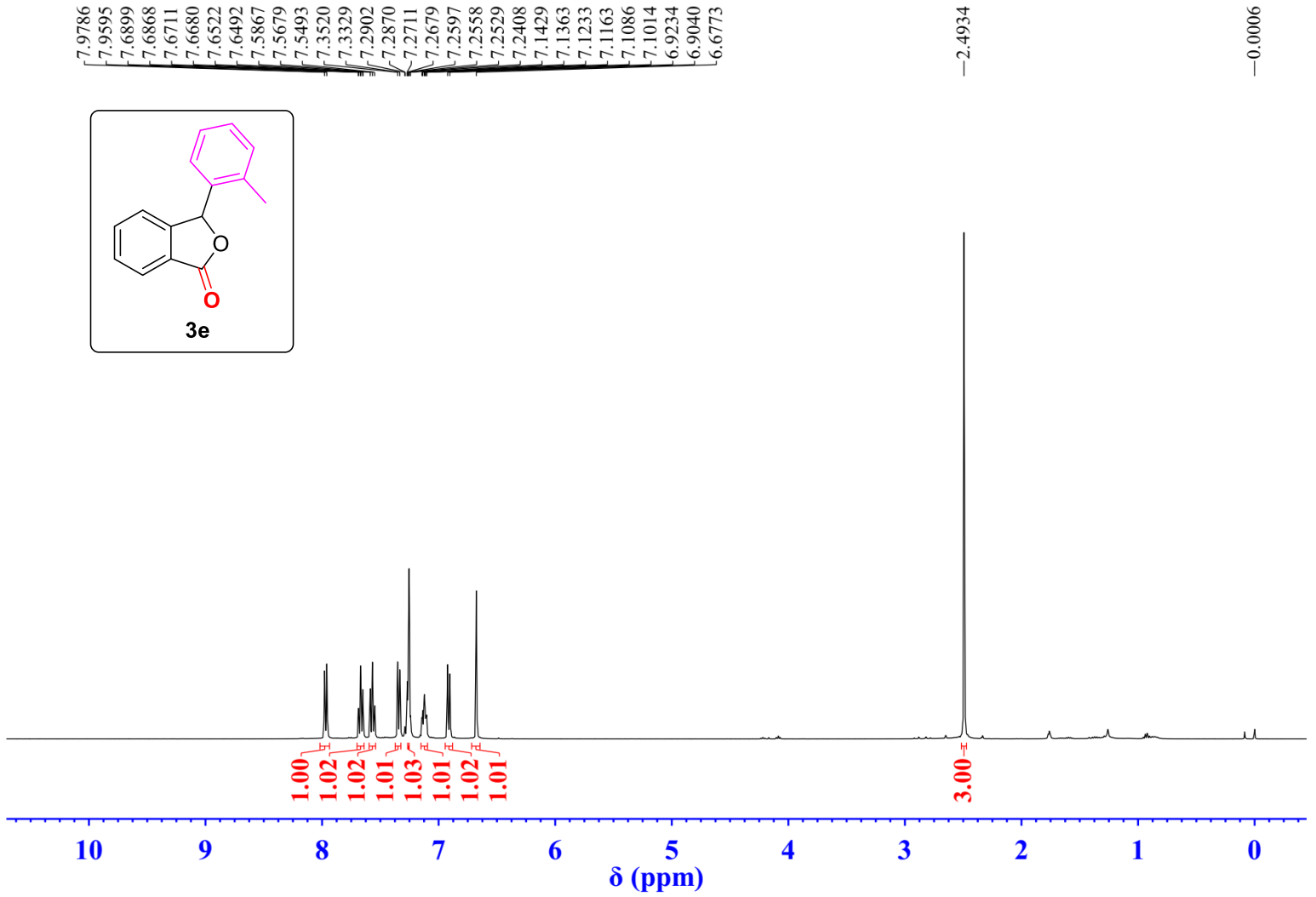
SM-X220104-PHOCH3 HNMR (400MHz CDCl3)



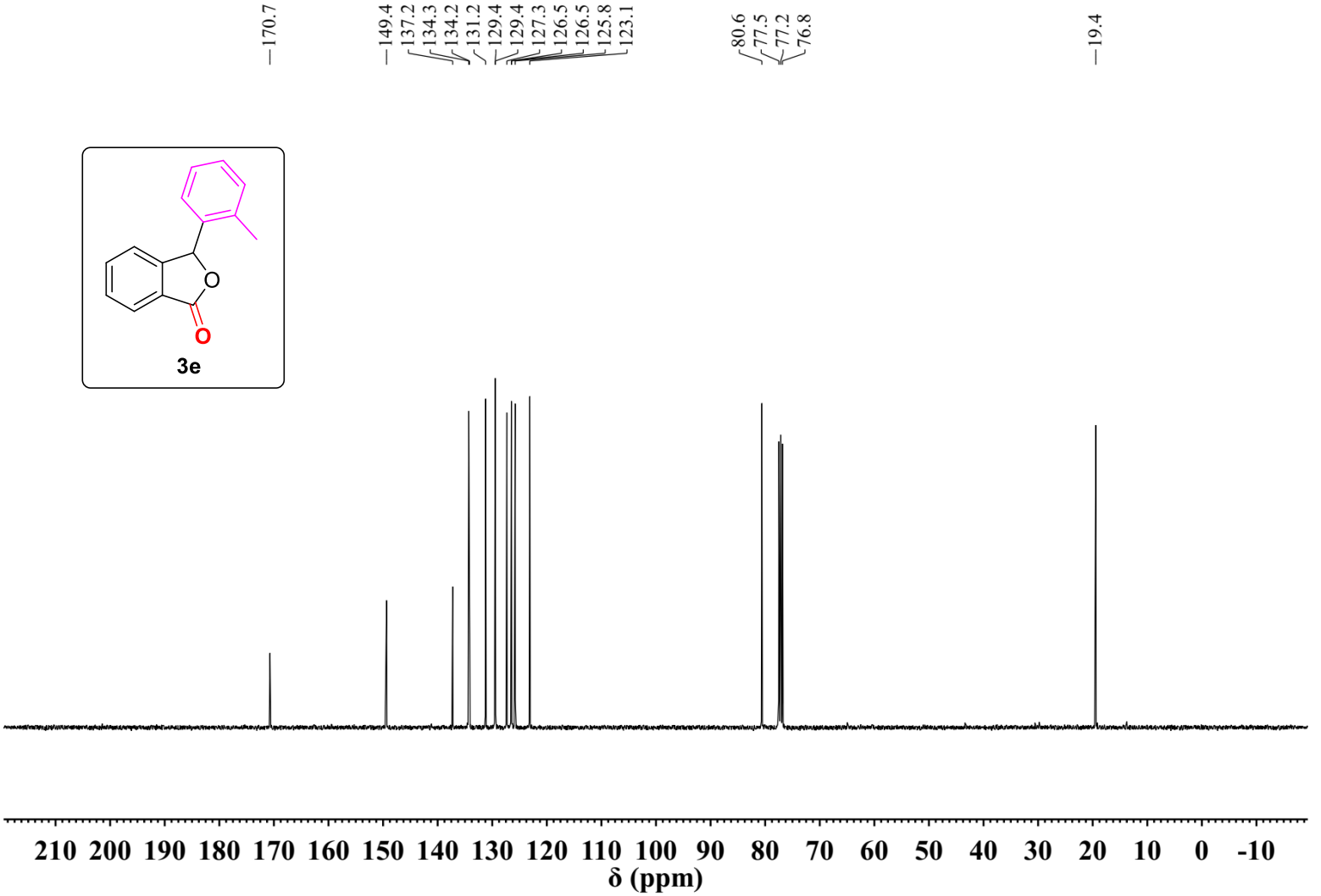
SM-X220104-PHOCH3 CNMR (100MHz CDCl3)

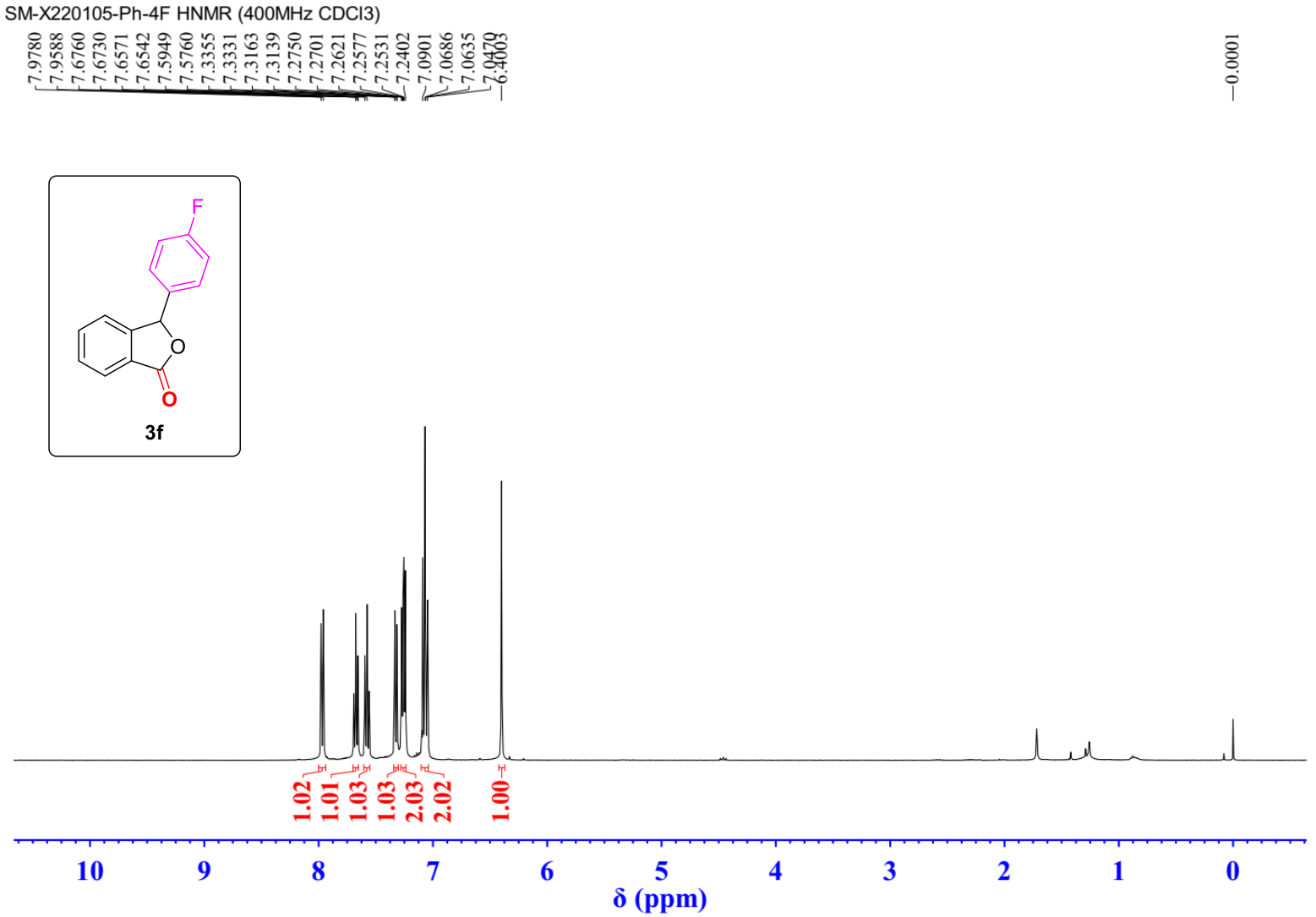


SM-X21Z31-PHCH3 HNMR (400MHz CDCl3)

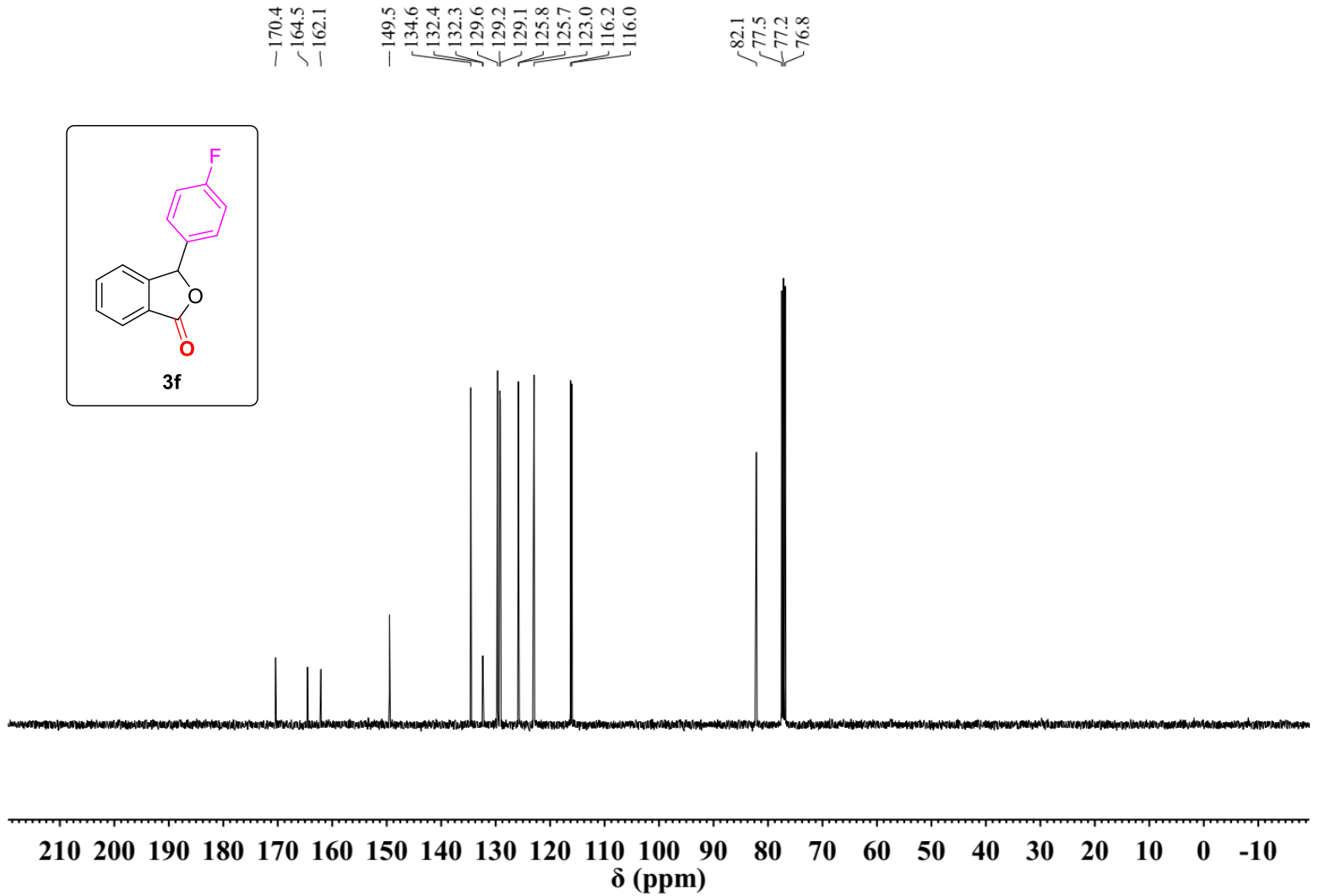


SM-X21Z31-PHCH3 CNMR (100MHz CDCl3)

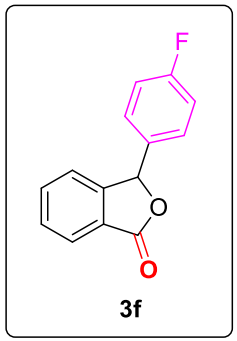



SM-X220105-Ph-4F HNMR (400MHz CDCl3)
7.9780
7.9588
7.6760
7.6730
7.6571
7.6542
7.5949
7.5760
7.3355
7.3331
7.3163
7.3139
7.2750
7.2701
7.2621
7.2577
7.2531
7.2402
7.0901
7.0686
7.0635
7.0470
6.4003
0.0001
F
O
O
3f
1.02
1.01
1.03
1.03
2.03
2.02
1.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

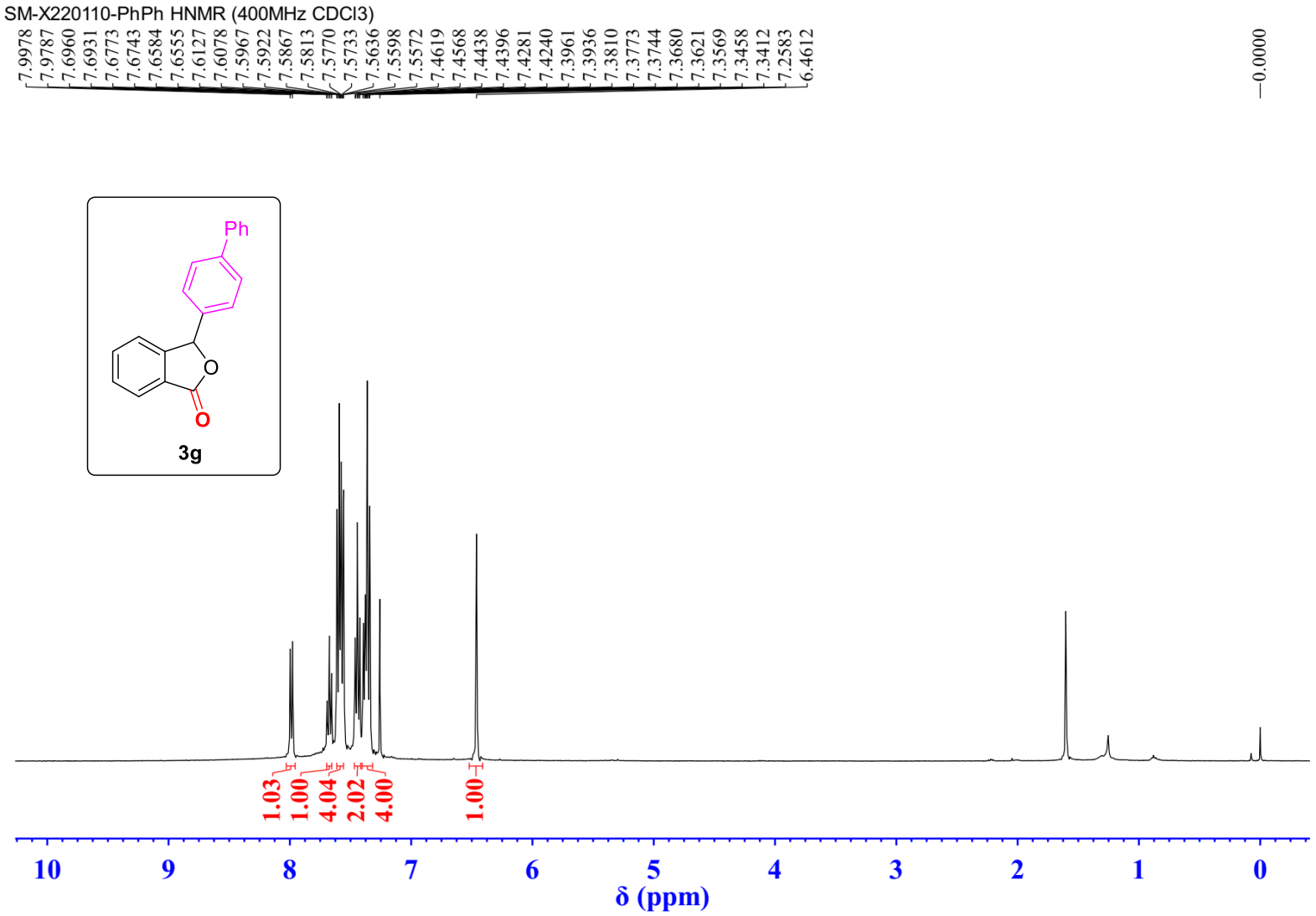
SM-X220105-Ph-4F CNMR (100MHz CDCl3)



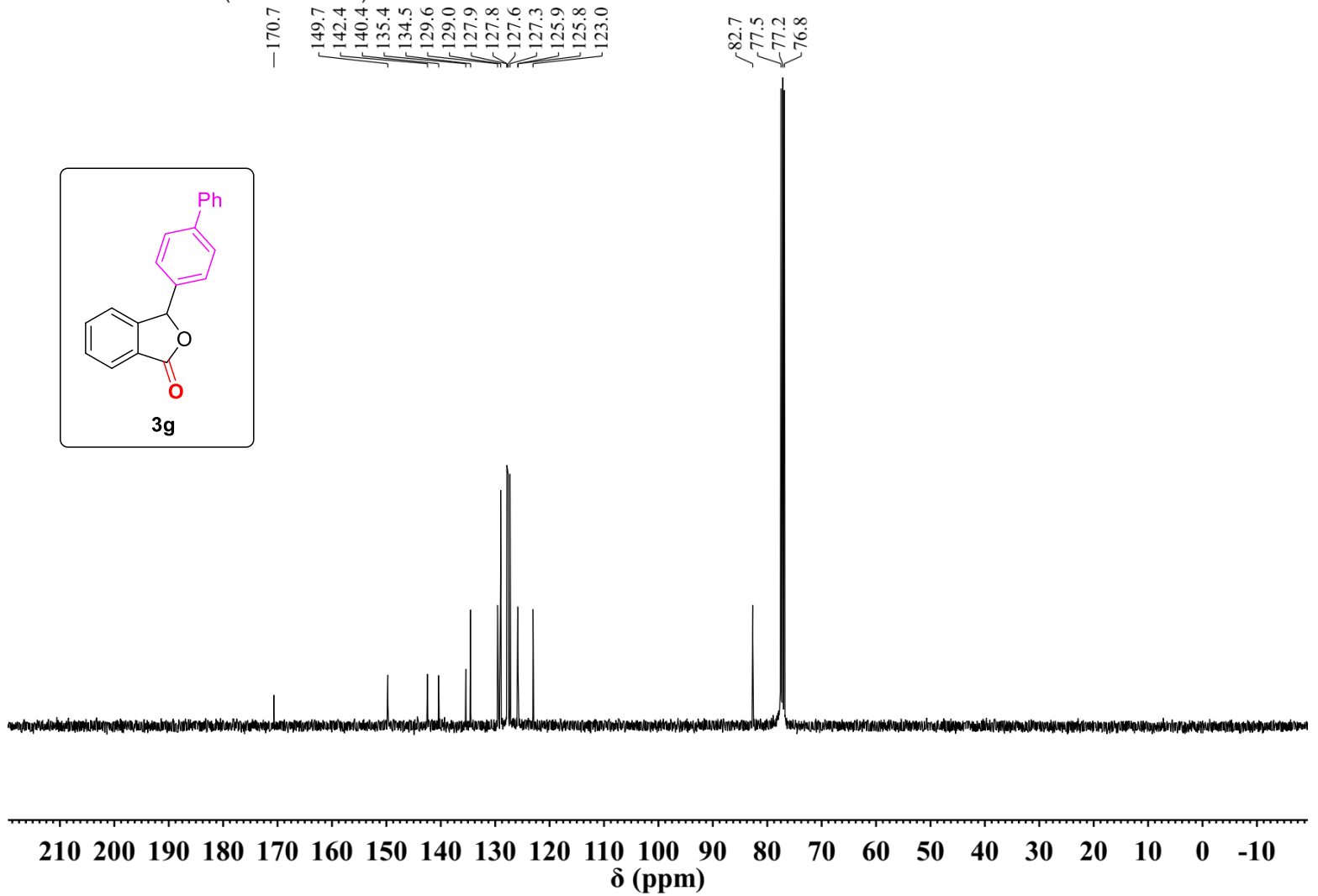
SM-X220105-Ph-4F FNMR (376MHz CDCl3)



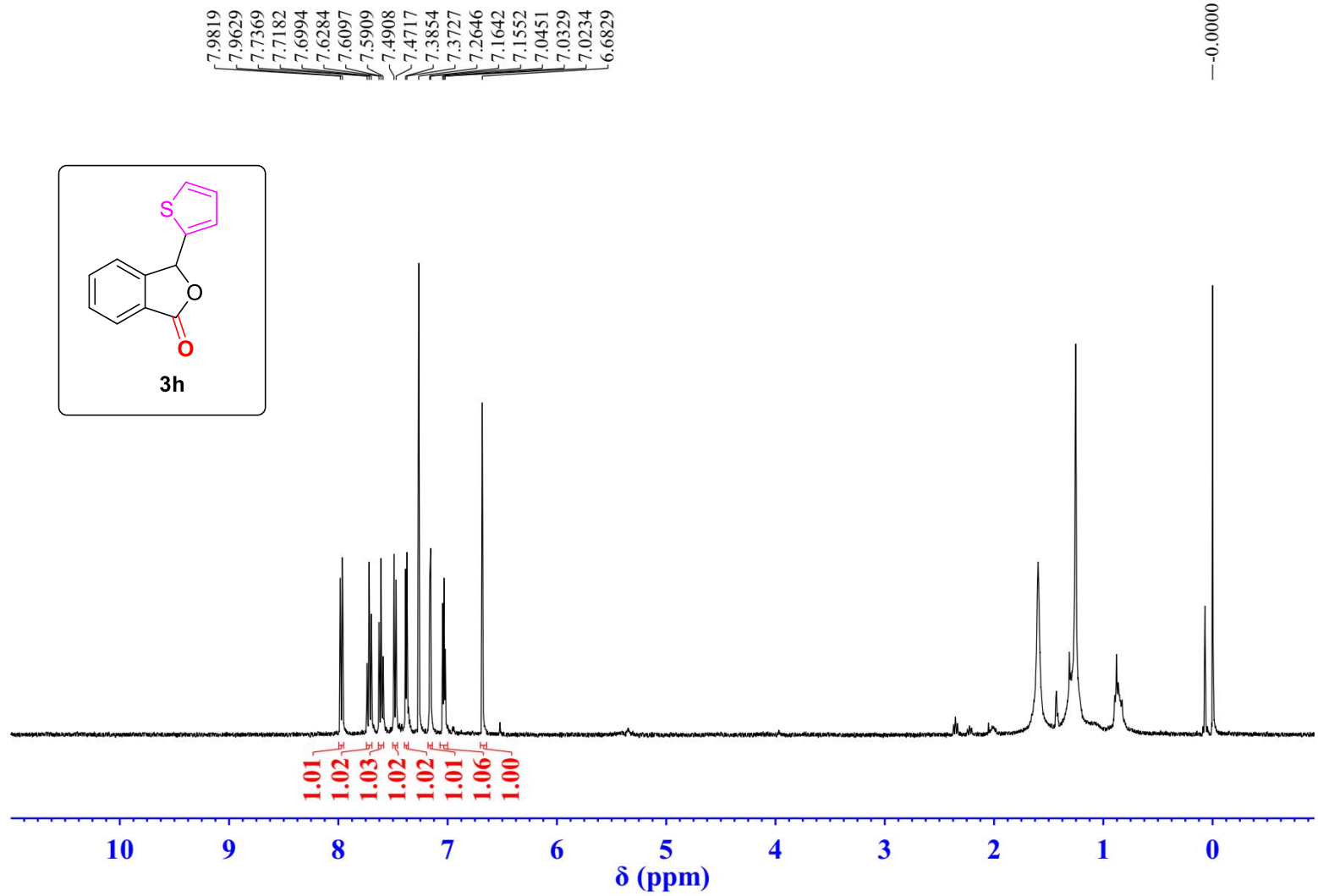
3f

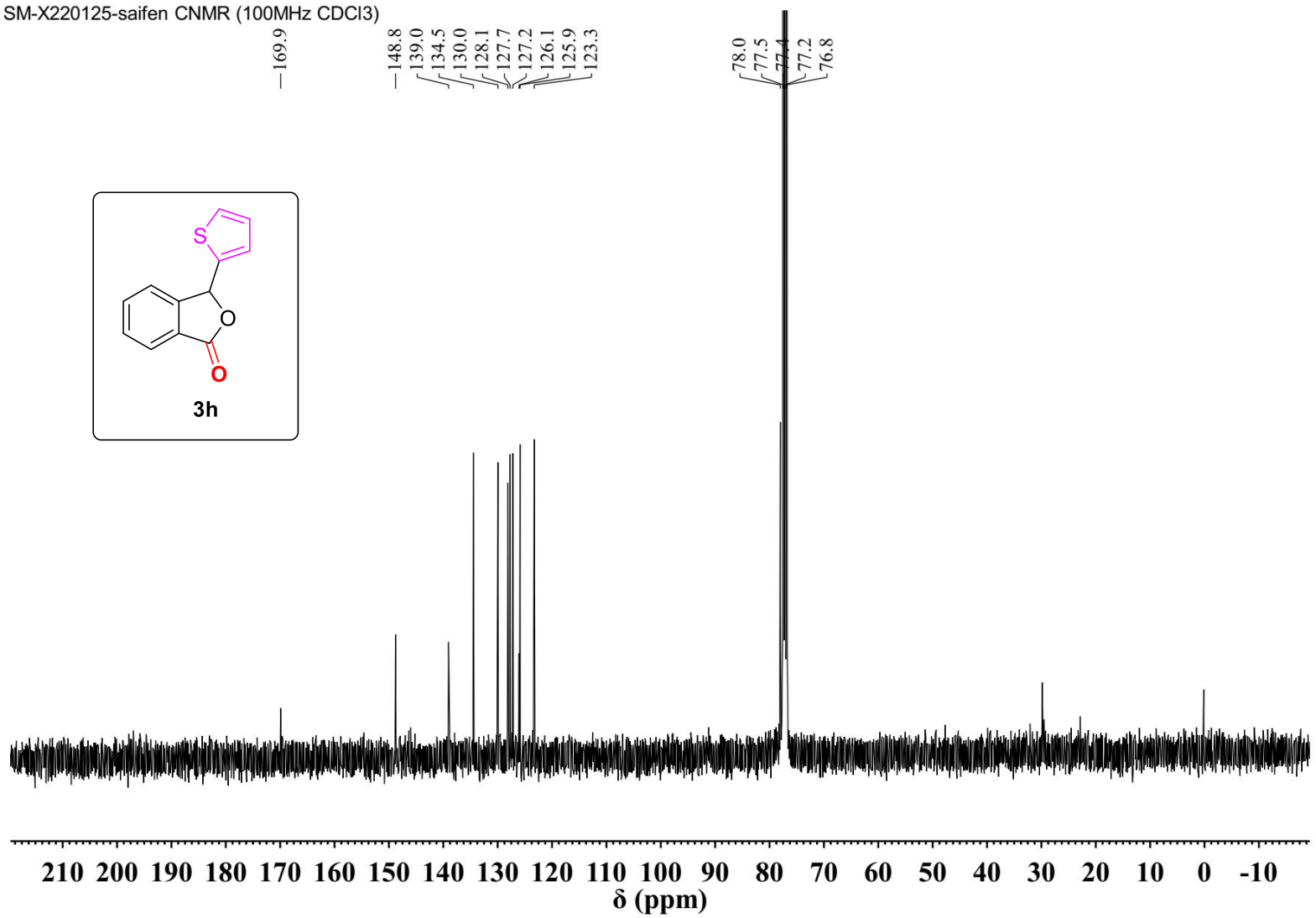

SM-X220110-PhPh HNMR (400MHz CDCl3)
7.9978
7.9787
7.6960
7.6931
7.6773
7.6743
7.6584
7.6555
7.6127
7.6078
7.5967
7.5922
7.5867
7.5813
7.5770
7.5733
7.5636
7.5598
7.5572
7.4619
7.4568
7.4438
7.4396
7.4281
7.4240
7.3961
7.3936
7.3810
7.3773
7.3744
7.3680
7.3621
7.3569
7.3458
7.3412
7.2583
6.4612
0.0000
Ph
O
O
3g
1.03
1.00
4.04
2.02
4.00
1.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

SM-X220110-PhPh CNMR (100MHz CDCl3)

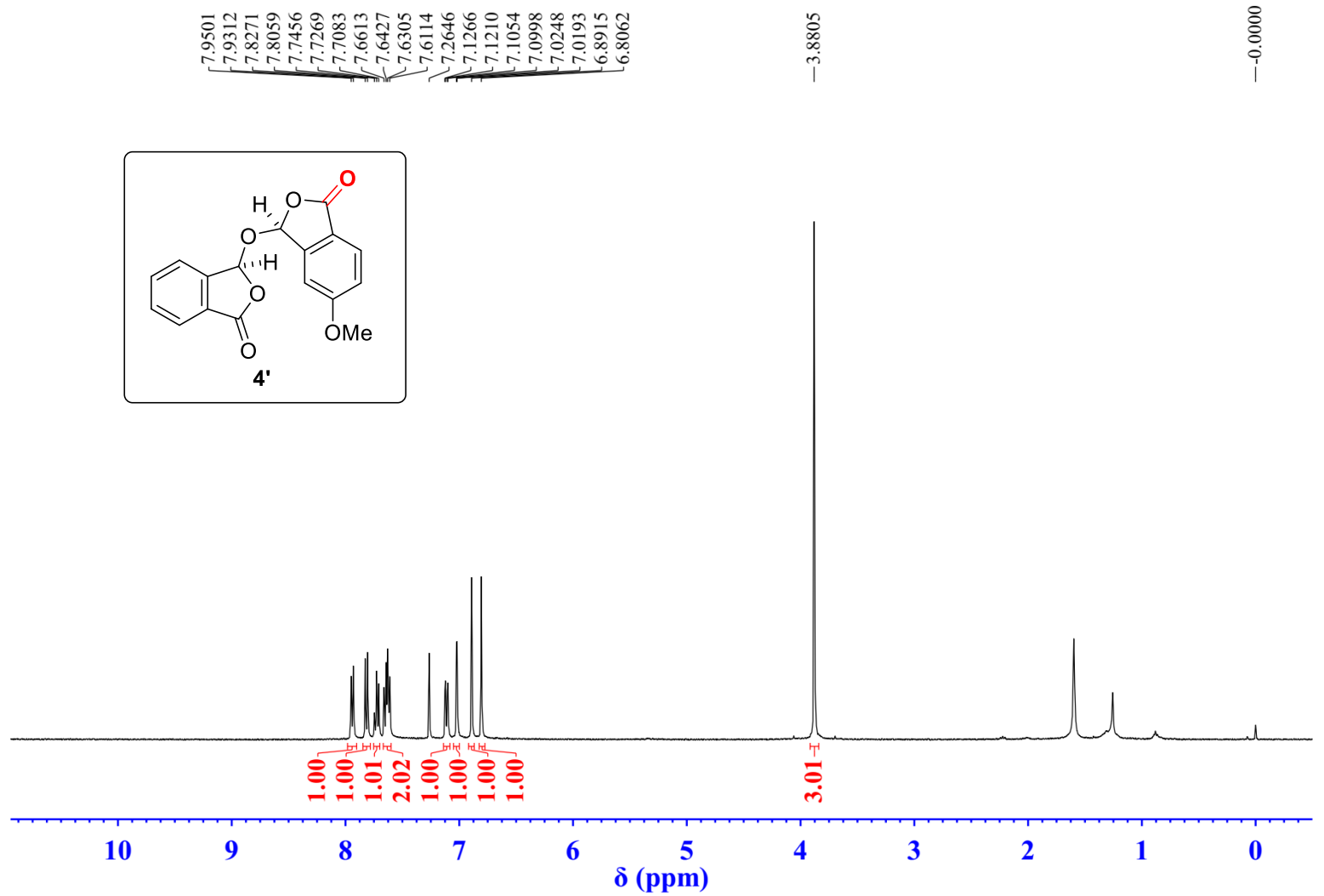


SM-X220125-saifen HNMR (400MHz CDCl3)

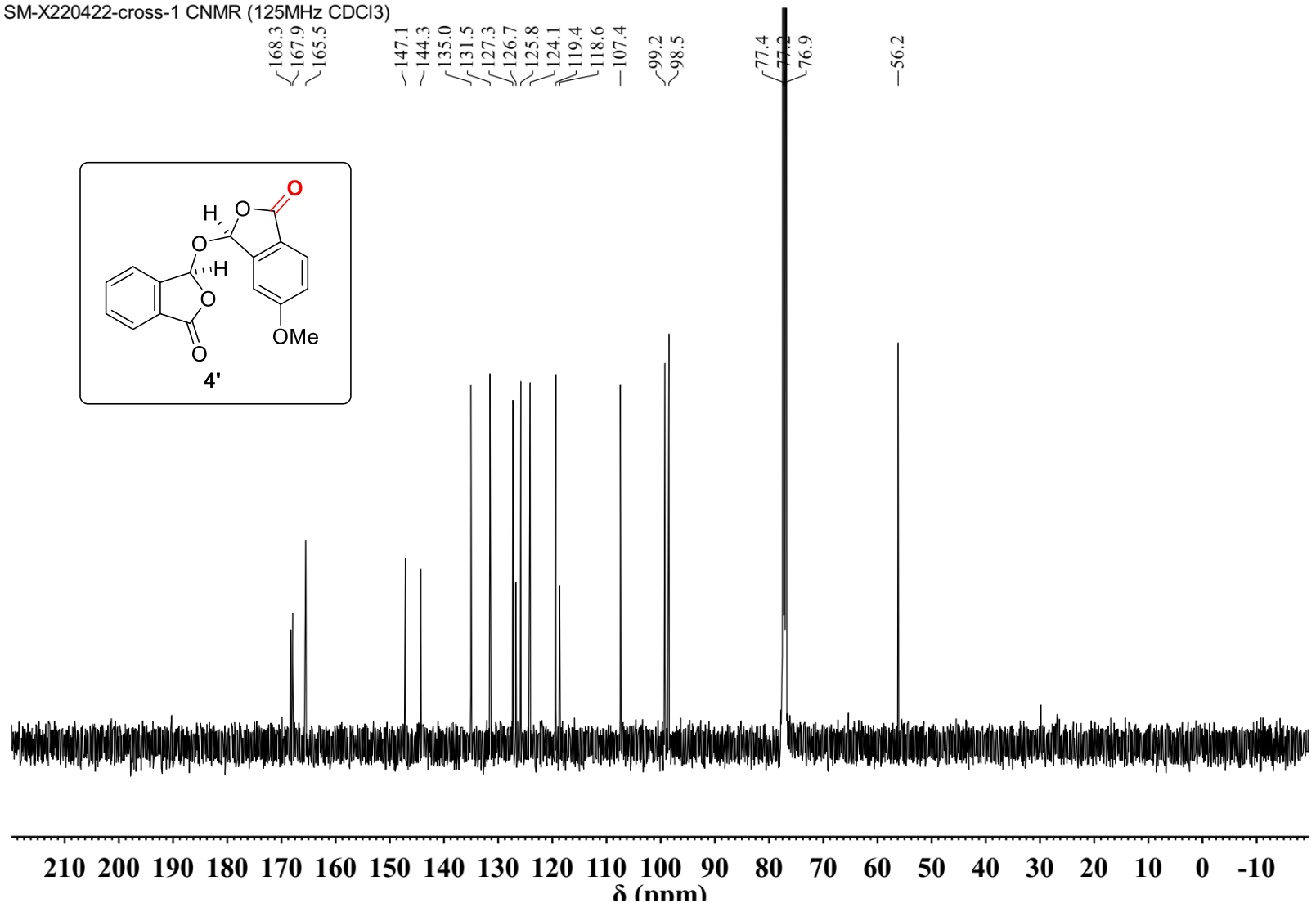


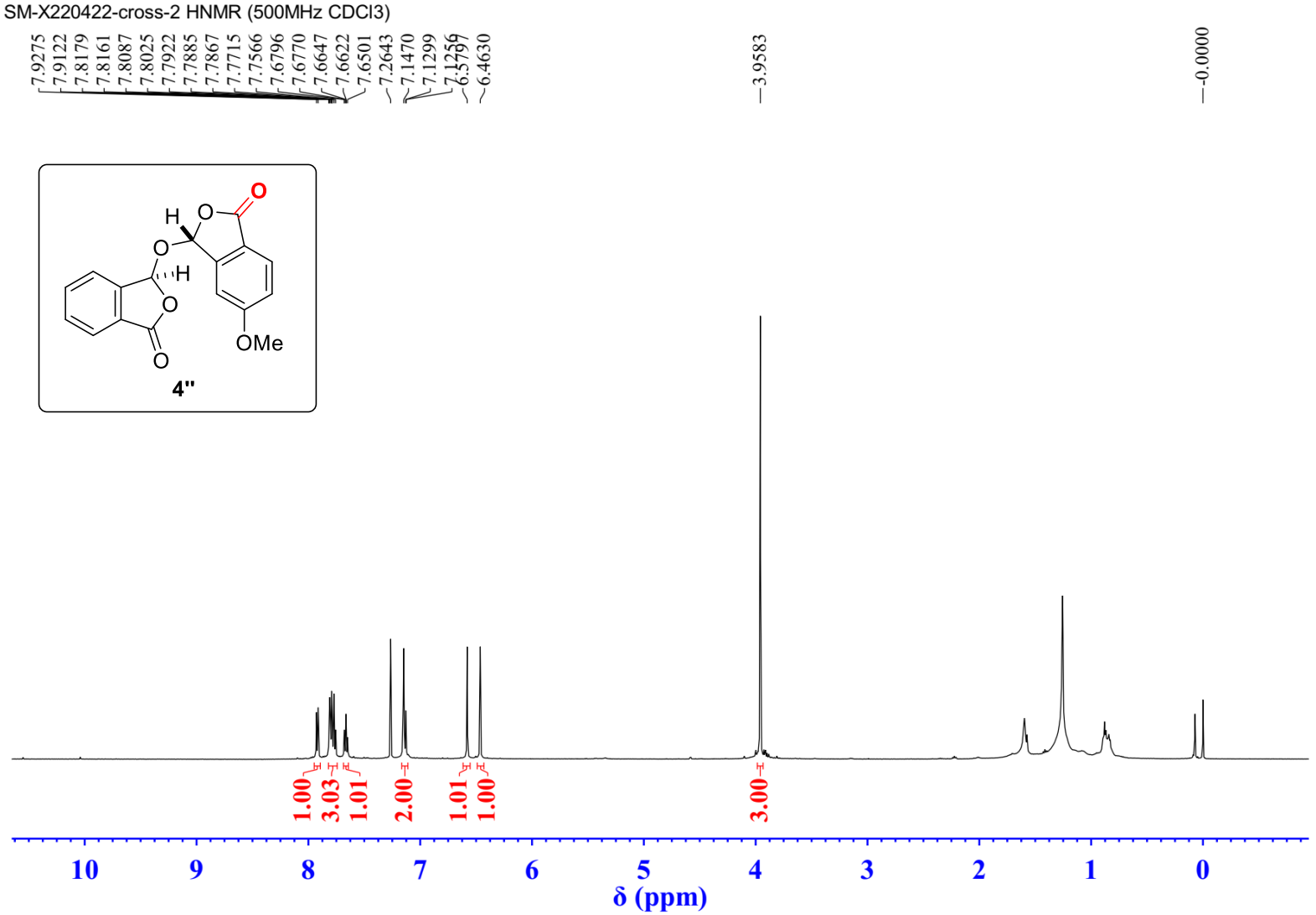

SM-X220125-saifen CNMR (100MHz CDCl3)
169.9
148.8
139.0
134.5
130.0
128.1
127.7
127.2
126.1
125.9
123.3
78.0
77.5
77.2
76.8
S
O
O
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

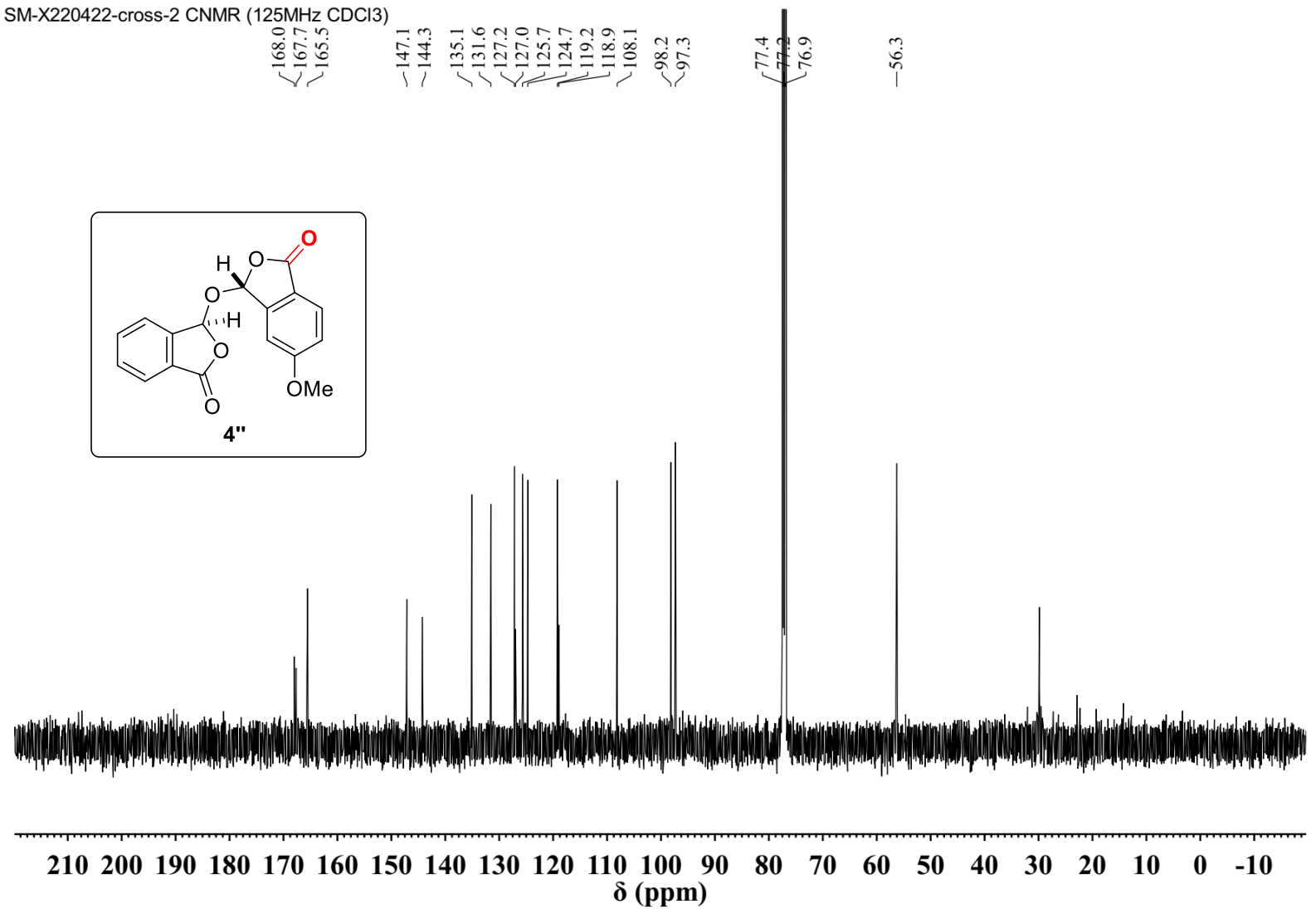
SM-X220422-cross-1 HNMR (400MHz CDCl3)



SM-X220422-cross-1 CNMR (125MHz CDCl3)




SM-X220422-cross-2 HNMR (500MHz CDCl3)
7.9275
7.9122
7.8179
7.8161
7.8087
7.8025
7.7922
7.7885
7.7867
7.7715
7.7566
7.6796
7.6770
7.6647
7.6622
7.6501
7.2643
7.1470
7.1299
7.1256
6.5797
6.4630
3.9583
-0.0000
H
O
O
O
H
O
O
OMe
4"
1.00
3.03
1.01
2.00
1.01
1.00
3.00
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


SM-X220422-cross-2 CNMR (125MHz CDCl3)
168.0
167.7
165.5
147.1
144.3
135.1
131.6
127.2
127.0
125.7
124.7
119.2
118.9
108.1
98.2
97.3
77.4
77.2
76.9
56.3
OMe
4"
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)