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Palladium-catalyzed enol/enolate directed oxidative annulation: functionalized naphthofuroquinones synthesis and bioactivity evaluation

*Shuaipeng Lv[1, †], Haitao Liu[1, †], Jie Kang[2], Yun Luo[1], Ting Gong[2], Zhengqi Dong[1], Chunnian He[1], Xiaobo Sun[1], *, Lei Wang[1], **

[1]*Institute of Medicinal Plant Development, Chinese Academy of Medical Science & Peking Union Medical College, Beijing 100193 (P. R. China)*

[2]*Institute of Materia Medica, Chinese Academy of Medical Sciences & Peking Union Medical College, Beijing 100050 (P. R.China*

Corresponding Author: *E-mail: lwang@implad.ac.cn; siquanwl@gmail.com

Contents

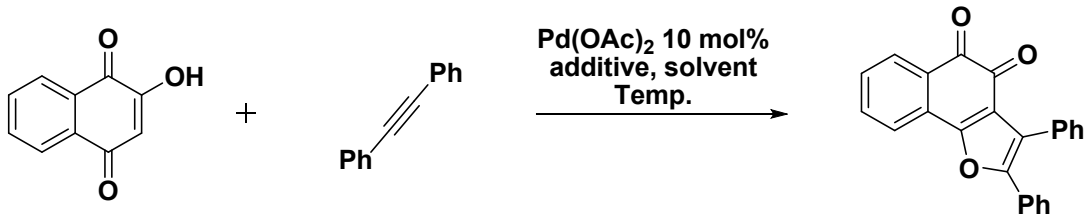
1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Inova 400 or Bruker VNMRS 600 spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high-resolution mass spectra were obtained on a a ThermoFisher Scientific LTQ-Orbitrap XL. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

2. Preparation of Starting Materials

2-Hydroxy-1,4-naphthoquinone **1a** and diphenylacetylene **2a** were commercially available. Others 2-hydroxy-1,4-naphthoquinones[1] and alkynes[2, 3] were prepared according to literature, respectively.

3. Optimization of reaction conditions



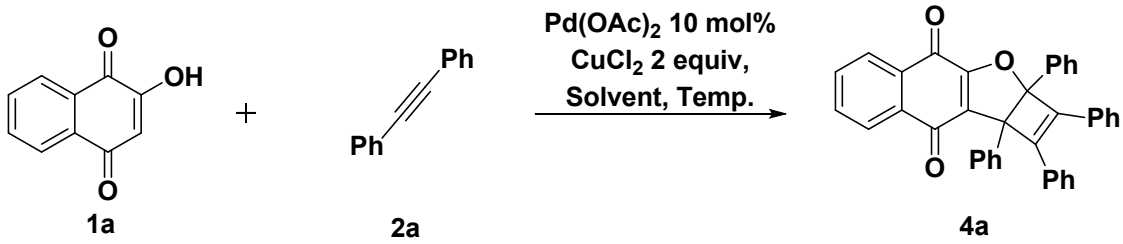
1a **2a** **3a**

Entry	Solvent	Catalyst	Additives	Temp/°C	Yield/%
1	MeCN	$Pd(OAc)_2$	Oxone	100	42 %
2	MeCN	$Pd(OAc)_2$	Oxone/Cs_2CO_3	100	No reaction
3	IPA	$Pd(OAc)_2$	Oxone	100	No reaction

4	MeOH	$Pd(OAc)_2$	Oxone	100	17 %
5	Diethyl ether	$Pd(OAc)_2$	Oxone	80	No reaction
6	$CHCl_3$	$Pd(OAc)_2$	Oxone	80	14 %
7	DCE	$Pd(OAc)_2$	Oxone	100	22 %
8	Toluene	$Pd(OAc)_2$	Oxone	100	21 %
9	1,4-Dioxane	$Pd(OAc)_2$	Oxone	100	No reaction
10	THF	$Pd(OAc)_2$	Oxone	80	No reaction
11	DMF	$Pd(OAc)_2$	Oxone	100	No reaction
12	DMA	$Pd(OAc)_2$	Oxone	100	No reaction
13	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone	100	61 %
14	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ	100	71 %
15	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/DDQ	100	No reaction
16	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/PPh_3	100	69 %
17	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/$CuCl_2$	100	No reaction
18	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/CuOAc	100	No reaction
19	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/AgOAc	100	No reaction
20	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/PCy_3	100	<10 %
21	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/dppe	100	No reaction
22	**MeCN/HOAc (v/v = 3:1)**	**$Pd(OAc)_2$**	**Oxone/BQ/O_2**	**100**	**77 %**
23	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	120	75 %
24	MeCN/HOAc (v/v = 1:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	100	50 %
25	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/N_2	100	64 %
26	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	60	55 %
27	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	80	59 %
28	MeCN/HOAc (v/v = 1:2)	$Pd(OAc)_2$	Oxone/BQ/O_2	100	61 %
29[a]	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	100	52 %
30[b]	MeCN/HOAc (v/v = 3:1)	$Pd(OAc)_2$	Oxone/BQ/O_2	100	68 %

Reaction condition: HOAc/MeCN (1:3, v/v) 2 mL, 2-hydroxy-1,4-naphthoquinone **1a** (0. 2 mmol, 1 equiv.),

diphenylacetylene **2a** (1.0 mmol, 3 equiv.), $Pd(OAc)_2$ 10 mol%, Oxone 2 equiv., BQ 1 equiv., O_2 1 atm, reaction time 24 hours; [a] BQ 2 equiv.; [b] Oxone 4 equiv.

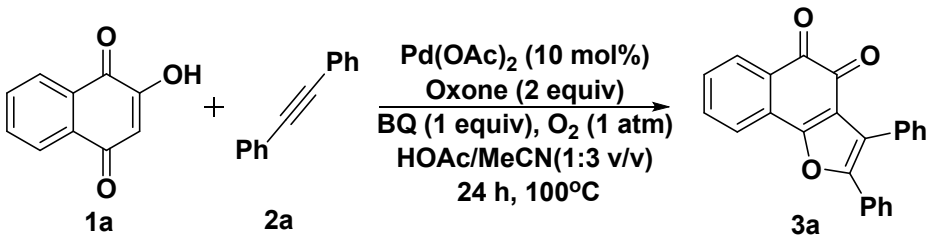


Entry	Solvent	Catalyst	Additives	Temp/°C	Yield/%
1	MeCN	$Pd(OAc)_2$	$CuCl_2$	100	58 %
2	IPA	$Pd(OAc)_2$	$CuCl_2$	100	Trace product
3	MeOH	$Pd(OAc)_2$	$CuCl_2$	100	Trace product
4	ether	$Pd(OAc)_2$	$CuCl_2$	100	No reaction
5	$CHCl_3$	$Pd(OAc)_2$	$CuCl_2$	100	Trace product
6	Toluene	$Pd(OAc)_2$	$CuCl_2$	100	No reaction
8	1,4-Dioxane	$Pd(OAc)_2$	$CuCl_2$	100	No reaction
8	DCE	$Pd(OAc)_2$	$CuCl_2$	100	Trace product
9	THF	$Pd(OAc)_2$	$CuCl_2$	100	No reaction
10	DMF	$Pd(OAc)_2$	$CuCl_2$	100	Trace product
11	DMA	$Pd(OAc)_2$	$CuCl_2$	100	57 %
12	MeCN	$Pd(OAc)_2$	$CuCl_2$ /O_2	100	49 %
13	MeCN	$Pd(OAc)_2$	$CuCl_2$ /N_2	100	22%
14	DMA	$Pd(OAc)_2$	$CuCl_2$ /O_2	100	47%
15	**DMA**	**$Pd(OAc)_2$**	**$CuCl_2$ /N_2**	**100**	**68 %**
16[a]	DMA	$Pd(OAc)_2$	$CuCl_2$ /N_2	100	51 %
17[b]	DMA	$Pd(OAc)_2$	$CuCl_2$ /N_2	100	65 %
18	MeCN	$Pd(OAc)_2$	$CuBr_2$	100	No product
19	MeCN	$Pd(OAc)_2$	$Cu(OAc)_2$	100	No product
20	DMA	$Pd(OAc)_2$	$Cu(ClO_4)_2$ /O_2	100	Trace product

Reaction condition: Solvent 2 mL, 2-hydroxy-1,4-naphthoquinone **1a** (0. 2 mmol, 1 equiv.), diphenylacetylene **2a** (1.0 mmol, 5 equiv.), $Pd(OAc)_2$ 10 mol%, $CuCl_2$ 2 equiv., N_2 1 atm, reaction time 24-40 hours. [a] $Pd(OAc)_2$ 5 mol%. [b] $CuCl_2$ 4 equiv.

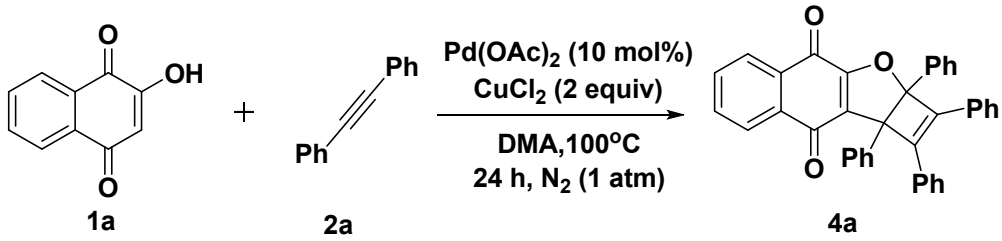
4. Representative Procedure for Palladium-Catalyzed Oxidative Annulation Reaction

a) Procedure for palladium-catalyzed 1,2-naphthofuroquinone synthesis (Typical Procedure A)



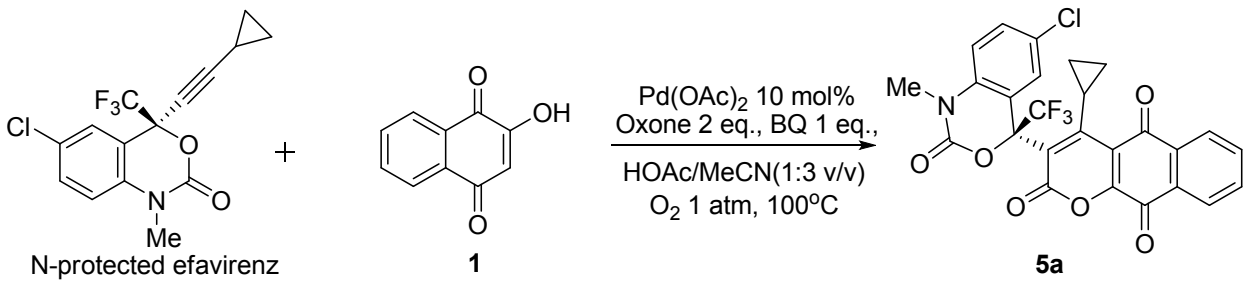
To a solution of diphenylacetylene **2a** (178.0 mg, 1.0 mmol) and 2-hydroxy-1,4-naphthoquinone **1a** (34.8 mg, 0.2 mmol) in 2.0 ml MeCN/HOAc (v/v = 3:1), palladium acetate (4.5 mg, 0.02 mmol) as catalyst, oxone (245.6 mg, 0.4 mmol) and benzoquinone (21.7 mg, 0.2 mmol) as an oxidant were added. The reaction was refluxed at 100 ^{o}C for 24 h under O_2. The reaction mixture was cooled to room temperature and the solvent was removed by evaporation and the residue was directly purified by silica gel flash chromatography, eluted by hexane/EtOAc=25:1 then 10:1 to afford 51.8 mg (74 % yield) of the desired product **3a** as dark red solid.

b) Procedure for palladium-catalyzed cyclobutene fused 1,4-naphthofuroquinone synthesis (Typical Procedure B)



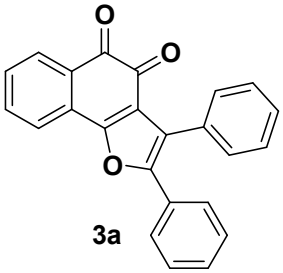
To a solution of diphenylacetylene **2a** (178.0 mg, 1.0 mmol) and 2-hydroxy-1,4-naphthoquinone **1a** (34.8 mg, 0.2 mmol) in 2.0 ml DMA, palladium acetate (4.5 mg, 0.02 mmol) as catalyst and copper (II) chloride (57.2 mg, 0.4 mmol) as an oxidant were added. The reaction was refluxed at 100 ^{o}C for 24 h under N_2. The reaction mixture was cooled to room temperature and the solvent was removed by evaporation and the residue was directly purified by silica gel flash chromatography, eluted by hexane/EtOAc=25:1 then 10:1 to afford 71.8 mg (68 % yield) of the desired product **8** as pale yellow solid.

c) Procedure for palladium-catalyzed late-stage functionalization (Typical Procedure C)



To a solution of N-protected efavirenz (197.4 mg, 3.0 mmol) and 2-hydroxy-1,4-naphthoquinone **1a** (34.8 mg, 0.2 mmol) in 2.0 ml MeCN/HOAc (v/v = 3:1), palladium acetate (4.5 mg, 0.02 mmol) as catalyst, oxone (245.6 mg, 0.4 mmol) and benzoquinone (21.7 mg, 0.2 mmol) as an oxidant were added. The reaction was refluxed at 100 °C for 24 h under O_2. The reaction mixture was cooled to room temperature and the solvent was removed by evaporation and the residue was directly purified by silica gel flash chromatography, eluted by hexane/EtOAc=10:1 then 4:1 to afford 47.6 mg (45 % yield) of the desired product **5a** as pale-yellow solid.

2,3-Diphenylnaphtho[1,2-*b*]furan-4,5-dione (3a)



3a

Following the procedure **A**, **3a** was obtained as a dark red solid (53.9 mg, 77%).

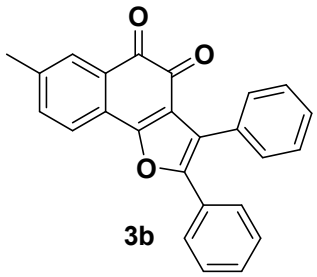
Melting Point: 199-201°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.41 (m, 7H), 7.33 – 7.32 (m, 3H), 6.85 – 6.83 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.04, 174.94, 159.65, 152.01, 135.90, 131.89, 130.89, 130.66, 130.61, 130.40, 129.56, 129.42, 129.39, 129.08, 129.02, 128.91, 127.08, 127.04, 122.87, 122.31, 122.25.

HRMS (ESI): calcd for $C_{24}H_{15}O_3$ $[M+H]^+$: 351.1016, found 351.1019.

7-Methyl-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3b)



3b

Following the procedure **A**, **3b** was obtained as a dark red solid (57.5 mg, 79%).

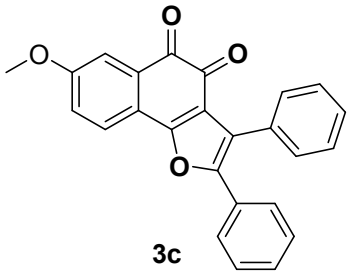
Melting Point: 206-208°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.44 – 7.40 (m, 4H), 7.32 – 7.30 (m, 2H), 6.87 – 6.81 (m, 2H), 2.44 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.36, 175.04, 160.22, 151.61, 141.41, 136.48, 131.91, 131.53, 130.75, 130.43, 129.69, 129.42, 129.26, 129.06, 128.99, 128.85, 127.05, 126.50, 125.66, 122.92, 122.23, 121.59, 21.94;

HRMS (ESI): calcd for $C_{25}H_{17}O_3$ $[M+H]^+$ 365.1172, found 365.1178.

7-Methoxy-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3c)



3c

Following the procedure **A**, **3c** was obtained as a dark red solid (61.6 mg, 81%).

Melting Point: 218-220°*C*.

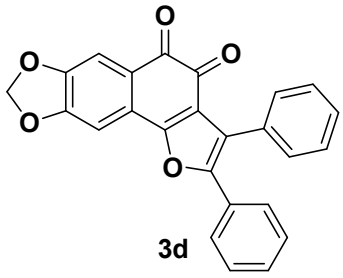
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* =2 .6 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.45 – 7.43 (m, 2H), 7.42 – 7.40 (m, 2H), 7.31 – 7.30 (m, 3H), 7.19 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.85 – 6.83 (m, 2H), 3.91 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.16, 174.96, 161.96, 160.65, 151.19, 131.91, 131.14, 130.79, 130.41, 129.72, 129.16, 129.04, 128.97, 128.82, 127.04, 126.97, 125.66, 124.65, 122.36, 122.11, 122.08, 120.43, 115.10,

56.36;

HRMS (ESI): calcd for $C_{25}H_{17}O_4$ $[M+H]^+$ 381.1121, found 381.1122.

[7,8-*d*] [1,3] dioxole-2,3-diphenylnaphtho[1,2-*b*] furan-4,5-dione (3d)



3d

Following the procedure **A**, **3d** was obtained as a dark red solid (55.9 mg, 71%).

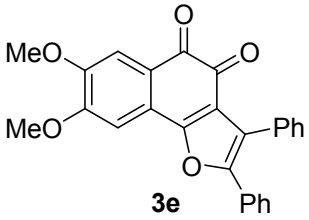
Melting Point: 237-239°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 – 7.42 (m, 7H), 7.36 – 7.28 (m, 5H), 6.15 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.29, 174.97, 159.63, 154.15, 151.43, 150.01, 130.64, 130.43, 130.39, 129.62, 129.26, 129.07, 129.02, 128.99, 128.88, 126.99, 126.13, 125.27, 123.47, 122.31, 110.73, 103.16, 103.01.

HRMS (ESI): calcd for $C_{25}H_{15}O_5$ $[M+H]^+$ 395.0914, found 395.0906.

7,8-Dimethoxy-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3e)



3e

Following the procedure **A**, **3e** was obtained as a dark red solid (59.1 mg, 72%).

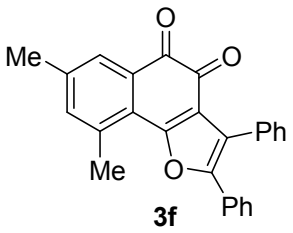
Melting Point: 228-230°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.50 – 7.48 (m, 2H), 7.45 – 7.42 (m, 2H), 7.41 – 7.38 (m, 3H), 7.33 – 7.31 (m, 3H), 7.22 (s, 1H), 4.09 (s, 3H), 3.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.78, 175.35, 159.96, 155.57, 151.35, 151.01, 130.65, 130.41, 129.70, 129.22, 129.04, 128.94, 128.83, 127.12, 124.10, 123.29, 122.41, 120.76, 112.93, 104.89, 57.13, 56.88.

HRMS (ESI): calcd for $C_{26}H_{19}O_5$ $[M+H]^+$ 411.1227, found 411.1230.

7,9-Dimethyl-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3f)



3f

Following the procedure **A**, **3f** was obtained as a dark red solid (38.6 mg, 51%).

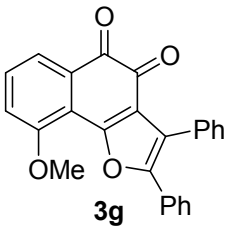
Melting Point: 239-241°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.48 – 7.41 (m, 7H), 7.32 – 7.30 (m, 4H), 2.80 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.79, 175.31, 161.48, 151.22, 140.74, 139.89, 135.71, 130.85, 130.40, 130.21, 129.68, 129.11, 129.08, 129.00, 128.83, 126.58, 124.60, 122.02, 121.80, 22.31, 21.63.

HRMS (ESI): calcd for $C_{26}H_{19}O_3$ $[M+H]^+$ 379.1329, found 379.1332.

9-Methoxy-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3g)



3g

Following the procedure **A**, **3g** was obtained as a dark red solid (44.1 mg, 58%).

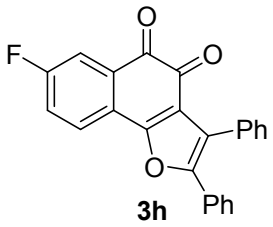
Melting Point: 220-222°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.45 – 7.38 (m, 6H), 7.31 – 7.28 (m, 3H), 7.26 – 7.23 (m, 1H), 4.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.38, 175.04, 159.31, 156.21, 151.30, 131.52, 131.00, 130.91, 130.44, 129.83, 128.98, 128.94, 128.75, 126.62, 123.68, 122.36, 121.56, 119.42, 117.20, 57.04.

HRMS (ESI): calcd for $C_{25}H_{17}O_4$ $[M+H]^+$ 381.1121, found 381.1125.

7-Fluoro-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3h)



3h

Following the procedure **A**, **3h** was obtained as a dark red solid (36.8 mg, 50%).

Melting Point: 224-226°*C*.

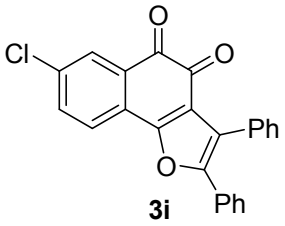
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 8.5, 4.9 Hz, 1H), 7.77 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.43 – 7.40 (m, 6H), 7.34 – 7.31 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.05, 174.52, 165.49, 162.96, 159.12, 151.98, 131.51 (d, $J_{C\text{-}F}$ = 6.6 Hz), 130.42, 130.35, 129.45, 129.40, 129.11, 129.05, 128.99, 127.06, 125.55 (d, $J_{C\text{-}F}$ = 4.6 Hz), 125.06 (d, $J_{C\text{-}F}$ = 8.0 Hz), 123.12, 122.89, 122.21, 121.53, 121.51, 118.14, 117.90.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -107.36 (s, F) ppm.

HRMS (ESI): calcd for $C_{24}H_{14}O_3F$ $[M+H]^+$ 369.0922, found 369.0923.

7-Chloro-2,3-diphenylnaphtho[1,2-b]furan-4,5-dione (3i)



3i

Following the procedure **A**, **3i** was obtained as a dark red solid (42.3 mg, 55%).

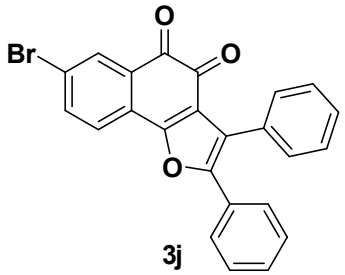
Melting Point: 232-234°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 2.1 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.47 – 7.43 (m, 4H), 7.36 – 7.34 (m, 3H), 7.21 – 7.20 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.07, 174.21, 158.77, 152.32, 137.26, 135.80, 130.89, 130.49, 130.39, 130.35, 130.30, 129.54, 129.33, 129.12, 129.06, 129.02, 128.76, 127.31, 127.09, 124.15, 122.38, 122.25.

HRMS (ESI): calcd for $C_{24}H_{14}O_3Cl$ $[M+H]^+$ 385.0626, found 385.0628.

7-Bromo-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3j)



3j

Following the procedure **A**, **3j** was obtained as a dark red solid (48.8 mg, 57%).

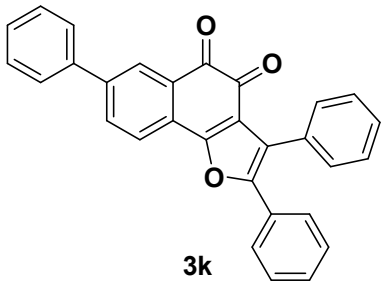
Melting Point: 245-247°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 2.0 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.45 – 7.41 (m, 4H), 7.33 – 7.29 (m, 3H), 7.19 – 7.17 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.06, 174.14, 158.82, 152.44, 138.74, 133.83, 130.50, 130.43, 130.37, 130.32, 129.57, 129.38, 129.13, 129.08, 129.04, 128.77, 127.73, 127.13, 125.25, 124.23, 122.48.

HRMS (ESI): calcd for $C_{24}H_{13}BrNaO_3$ $[M+Na]^+$ 450.9940, found 450.9949.

2,3,7-Triphenylnaphtho[1,2-*b*]furan-4,5-dione (3k)



3k

Following the procedure **A**, **3k** was obtained as a dark red solid (45.2 mg, 53%).

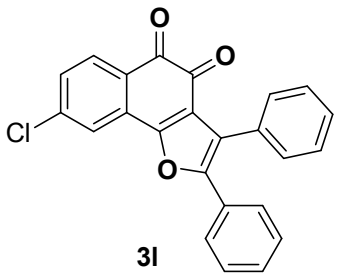
Melting Point: 269-271°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.93 (s, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.41 (m, 10H), 7.34 – 7.32 (m, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.12, 174.95, 159.72, 152.03, 143.56, 139.13, 134.00, 130.60, 130.42, 129.81, 129.62, 129.57, 129.41, 129.39, 129.11, 129.09, 129.02, 128.92, 127.55, 127.35, 127.10, 123.46, 122.38, 122.14.

HRMS (ESI): calcd for $C_{30}H_{18}NaO_3$ $[M+Na]^+$ 449.1148, found 449.1164.

8-Chloro-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3l)



3l

Following the procedure **A**, **3l** was obtained as a dark red solid (36.9 mg, 48%).

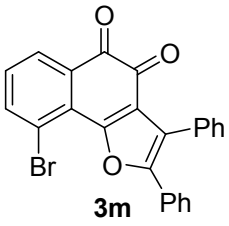
Melting Point: 223-225°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 1.9 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.45 – 7.42 (m, 6H), 7.35 – 7.32 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.95, 174.50, 157.95, 152.64, 142.85, 132.32, 130.53, 130.35, 130.32, 130.29, 129.63, 129.25, 129.14, 129.07, 129.04, 127.46, 127.13, 123.02, 122.89, 122.47.

HRMS (ESI): calcd for $C_{24}H_{14}O_3Cl$ $[M+H]^+$ 385.0626, found 385.0629.

8-Chloro-2,3-diphenylnaphtho[1,2-*b*]furan-4,5-dione (3m)



3m

Following the procedure **A**, **3m** was obtained as a dark red solid (51.4 mg, 46%).

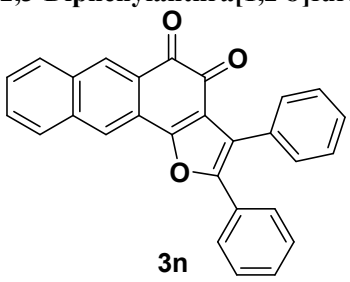
Melting Point: 233-235°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.44 (s, 5H), 7.33 – 7.28 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.42, 174.66, 157.18, 152.22, 142.10, 132.03, 130.70, 130.60, 130.57, 130.36, 129.47, 129.29, 129.14, 129.05, 128.23, 126.82, 124.00, 121.96, 118.23.

HRMS (ESI): calcd for $C_{24}H_{14}O_3Br$ $[M+H]^+$ 429.0120, found 429.0126.

2,3-Diphenylanthra[1,2-*b*]furan-4,5-dione (3n)



3n

Following the procedure **A**, **3n** was obtained as a dark red solid (49.6 mg, 62%).

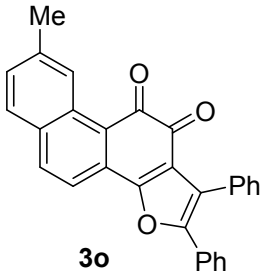
Melting Point: 267-269°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.41 (d, *J* = 8.7 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1Hz, 1H), 7.71 – 7.68 (m, 1H), 7.56 – 7.42 (m, 8H), 7.35 – 7.34 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$):δ = 183.69, 175.26, 160.26, 152.47, 137.66, 132.85, 131.56, 130.59, 130.53, 130.37, 129.63, 129.46, 129.12, 129.06, 128.99, 128.10, 127.17, 127.14, 123.56, 122.63, 121.62, 119.68.

HRMS (ESI): calcd for $C_{28}H_{17}O_3$ $[M+H]^+$ 401.1172, found 401.1168.

6-Methyl-1,2-diphenylphenanthro[1,2-*b*]furan-10,11-dione (3o)



3o

Following the procedure **A**, **3o** was obtained as a dark red solid (43.9 mg, 53%).

Melting Point: 258-260°*C*.

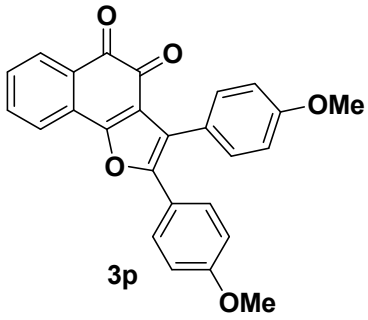
^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.20 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.42 (m, 7H), 7.39 – 7.29 (m, 4H), 2.54 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.71, 175.35, 160.39, 152.25, 142.19, 137.34, 133.35, 133.08, 130.57, 130.49, 130.35, 130.25, 129.63, 129.42, 129.38, 129.09, 129.03, 128.93, 127.10, 126.08, 122.88, 122.50, 121.44,

118.78, 22.99.

HRMS (ESI): calcd for $C_{29}H_{19}O_3$ $[M+H]^+$ 415.1328, found 415.1331.

2,3-Bis(4-methoxyphenyl)naphtho[1,2-*b*]furan-4,5-dione (3p)



Following the procedure **A**, **3p** was obtained as a dark red solid (63.1 mg, 77%).

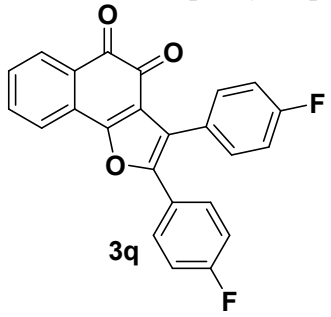
Melting Point: 212-214°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.46 – 7.44 (m, 3H), 7.37 – 7.36 (m, 2H), 6.94 – 6.93 (m, 2H), 6.86 – 6.84 (m, 2H), 3.86 (s, 3H), 3.82 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.23, 175.09, 160.48, 160.03, 159.23, 152.02, 135.83, 131.72, 130.79, 130.37, 129.30, 129.23, 128.60, 122.86, 122.69, 122.33, 120.56, 114.57, 114.46, 55.79, 55.73;

HRMS (ESI): calcd for $C_{26}H_{19}O_5$ $[M+H]^+$ 411.1227, found 411.1232.

2,3-Bis(4-fluorophenyl)naphtho[1,2-*b*]furan-4,5-dione (3q)



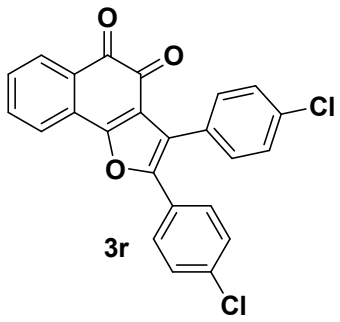
Following the procedure **A**, **3q** was was obtained as a dark red solid (47.9 mg, 62%).

Melting Point: 231-233°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.13 – 7.02 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.85, 174.96, 164.40, 162.32, 159.76, 151.26, 135.96, 132.27, 132.20, 130.99, 130.85, 129.37, 129.13 (d, J_{C-F} = 6.6 Hz), 128.80, 126.29, 125.57, 122.87, 122.01, 121.00, 116.51, 116.33, 116.18; **HRMS (ESI)**: calcd for $C_{24}H_{13}F_2O_3$ $[M+H]^+$ 387.0627, found 387.0629.

2,3-Bis(4-chlorophenyl)naphtho[1,2-*b*]furan-4,5-dione (3r)



Following the procedure **A**, **3r** was obtained as a dark red solid (49.3 mg, 59%).

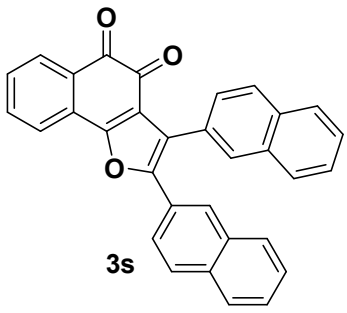
Melting Point: 237-239°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.31 (m, 7H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.73, 174.88, 160.01, 151.09, 135.99, 135.63, 135.17, 132.06, 131.74, 131.04, 131.01, 129.55, 129.47, 129.42, 129.38, 128.76, 128.67, 128.35, 127.70, 122.95, 121.89, 121.52.

HRMS (ESI): calcd for $C_{24}H_{12}Cl_2NaO_3$ $[M+Na]^+$ 441.0056, found 441.0055.

2,3-Di(naphthalen-2-yl)naphtho[1,2-*b*]furan-4,5-dione (3s)



Following the procedure **A**, **3s** was obtained as a dark red solid (61.2 mg, 68%).

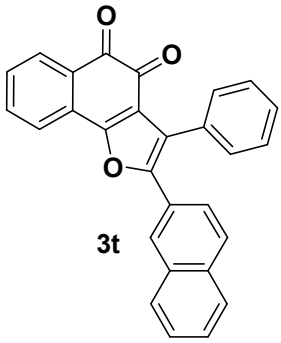
Melting Point: 258-260°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 2H), 8.04 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.72 (m, 3H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.46 (m, 7H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.07, 175.00, 159.99, 152.35, 135.93, 133.86, 133.74, 133.69, 133.57, 132.92, 130.93, 130.76, 130.02, 129.51, 129.05, 128.90, 128.83, 128.76, 128.61, 128.29, 128.23, 128.13, 127.97, 127.47, 127.19, 126.98, 126.73, 126.71, 124.40, 123.03, 122.67, 122.39, 112.66.

HRMS (ESI): calcd for $C_{32}H_{18}NaO_3$ $[M+Na]^+$ 473.1148, found 473.1157.

2-(Naphthalen-2-yl)-3-phenylnaphtho[1,2-*b*]furan-4,5-dione (3t)



3t

Following the procedure **A**, **3t** was obtained as a dark red solid (48.0 mg, 60%), regioisomer ratio ≈ 1:1.

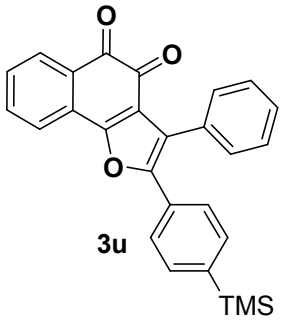
Melting Point: 241-243°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.7 Hz, 1H), 8.07 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.80 – 7.71 (m, 4H), 7.54 – 7.48 (m, 5H), 7.44 – 7.42 (m, 2H), 7.31 – 7.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.06, 174.97, 159.84, 152.14, 135.91, 133.65, 133.54, 130.93, 130.72, 130.64, 130.54, 129.83, 129.48, 129.14, 129.04, 129.02, 128.89, 128.79, 128.71, 128.63, 128.23, 128.04, 127.44, 127.18, 126.98, 126.66, 124.33, 122.98, 122.71, 122.35.

HRMS (ESI): calcd for $C_{28}H_{16}NaO_3$ $[M+Na]^+$ 423.0992, found 423.1008.

3-Phenyl-2-(4-(trimethylsilyl)phenyl)naphtho[1,2-*b*]furan-4,5-dione (3u)



Following the procedure **A**, **3u** obtained as a dark red solid (67.5 mg, 80%), regioisomer ratio ≈ 5:3.

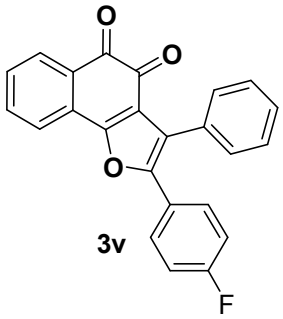
Melting Point: 207-209°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.56 – 7.42 (m, 16H), 7.35 – 7.33 (m, 4H), 0.31 (s, 9H), 0.26 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.07, 174.99, 159.74, 152.07, 142.36, 141.23, 135.90, 133.99, 133.91, 130.90, 130.87, 130.80, 130.69, 130.66, 130.40, 129.65, 129.54, 129.46, 129.39, 129.10, 129.07, 129.04, 128.92, 127.20, 126.01, 122.87, -0.59, -0.77.

HRMS (ESI): calcd for $C_{27}H_{23}O_3Si$ $[M+H]^+$ 423.0907, found 423.0909.

2-(4-Fluorophenyl)-3-phenylnaphtho[1,2-*b*]furan-4,5-dione (3v).



Following the procedure **A**, **3v** obtained as a dark red solid (46.6 mg, 63%), regioisomer ratio ≈ 3:2.

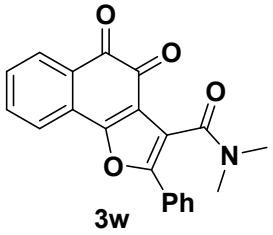
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.47 (m, 3H), 7.44 – 7.40 (m, 4H), 7.35 – 7.33 (m, 1H), 7.11 (t, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 8.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.96, 174.91, 162.35, 159.63, 151.18, 135.92 (d, $J_{C\text{-}F}$ = 4.2 Hz), 132.28 (d, $J_{C\text{-}F}$ = 6.6 Hz), 130.94, 130.78, 130.73, 130.43, 130.36, 129.55, 129.42, 129.18, 129.09 (d, $J_{C\text{-}F}$ = 6.6 Hz), 129.02,

127.12, 125.78, 122.91, 122.83, 122.21, 122.07, 121.26, 116.39, 116.24, 116.22, 116.07.

HRMS(ESI): calcd for $C_{24}H_{14}FO_3$ $[M+H]^+$ 369.0921, found 369.0931.

***N*, *N*-Dimethyl-4,5-dioxo-2-phenyl-4,5-dihydronaphtho[1,2-*b*]furan-3-carboxamide (3w)**



3w

Following the procedure **A**, **3w** was obtained as a red solid (28.3 mg, 41%).

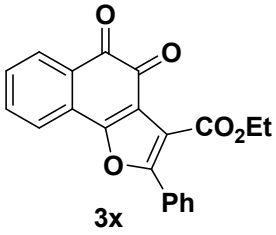
Melting Point: 284 – 286°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 – 8.24 (m, 1H), 8.17 – 8.15 (m, 1H), 7.90 – 7.87 (m, 2H), 7.79 – 7.76 (m, 2H), 7.49 – 7.47 (m, 3H), 3.28 (s, 3H), 2.95 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.73, 173.57, 163.90, 155.73, 151.13, 134.68, 134.48, 133.38, 132.99, 131.19, 129.85, 129.72, 128.19, 127.51, 127.43, 126.80, 115.46, 38.55, 35.59.

HRMS (ESI): calcd for $C_{21}H_{16}O_4N$ $[M+H]^+$ 346.1073, found 346.1076.

Ethyl 4,5-dioxo-3-phenyl-4,5-dihydronaphtho[1,2-*b*]furan-2-carboxylate (3x).



3x

Following the procedure **A**, **3x** was obtained as a yellow solid (24.6 mg, 37%).

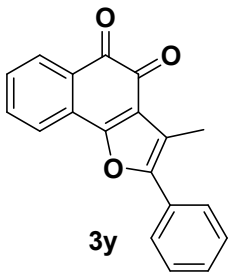
Melting Point: 196 – 198°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.7 Hz, 1H), 7.90 – 7.88 (m, 3H), 7.84 – 7.69 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 4H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.46, 173.76, 163.43, 159.31, 156.67, 135.98, 131.23, 131.17, 130.87, 129.56, 129.26, 128.39, 128.35, 127.84, 123.14, 121.44, 113.86, 62.65, 14.42.

HRMS (ESI): calcd for $C_{21}H_{15}O_5$ $[M+H]^+$ 347.0495, found 347.0500.

3-Methyl-2-phenylnaphtho[1,2-*b*]furan-4,5-dione (3y)



3y

Following the procedure **A**, **3y** was obtained as a yellow solid (20.0 mg, 33%).

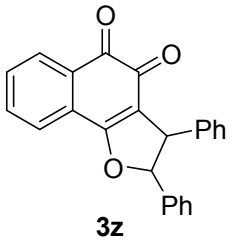
Melting Point: 123 – 125°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.39 (m, 4H), 2.54 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.25, 176.21, 159.30, 152.20, 135.88, 130.91, 130.42, 130.13, 129.38, 129.32, 129.08, 128.98, 128.88, 126.64, 123.35, 122.67, 117.50, 10.58.

HRMS (ESI): calcd for $C_{19}H_{13}O_3$ $[M+H]^+$ 289.0859, found 289.0857.

2,3-Diphenyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (3a').



3z

Following the procedure **A**, **3z** was obtained as a pale-yellow solid (21.8 mg, 31%).

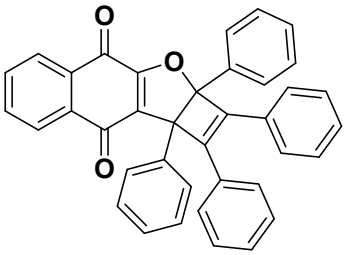
Melting Point: 163 – 165°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 6.6, 2.3 Hz, 1H), 8.01 – 7.99 (m, 1H), 7.72 – 7.70 (m, 2H), 7.42 – 7.29 (m, 10H), 5.83 (d, *J* = 6.6 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.04, 178.63, 160.09, 140.76, 139.73, 134.84, 133.61, 133.55, 132.16, 129.67, 129.47, 129.44, 128.31, 127.98, 126.84, 126.75, 126.38, 125.96, 95.25, 55.93.

HRMS (ESI): calcd for $C_{24}H_{17}O_3$ $[M+H]^+$ 353.1172, found 353.1176.

1,2,2a,9b-Tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4a)



4a

Following the procedure **B**, **4a** was prepared according to the general procedure. The product was obtained as a pale-yellow solid (71.8 mg, 68%).

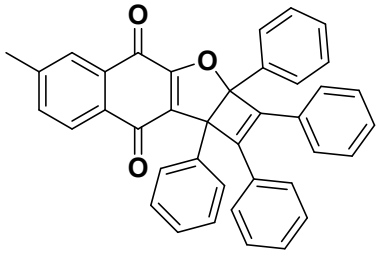
Melting Point: 281-283°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 – 8.18 (m, 1H), 8.10 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.02 – 8.01 (m, 2H), 7.75 – 7.71 (m, 3H), 7.33 – 7.28 (m, 8H), 7.10– 7.09 (m, 3H), 7.03 – 6.99 (m, 4H), 6.88 – 6.86 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.12, 179.19, 163.30, 148.98, 138.65, 135.44, 134.76, 134.68, 133.69, 133.46, 132.99, 132.61, 132.20, 132.04, 131.91, 130.33, 130.08, 129.35, 129.11, 129.00, 128.98, 128.77, 128.68, 128.64, 128.59, 128.23, 128.19, 127.53, 127.40, 127.16, 127.05, 126.69, 125.66, 100.30, 69.30.

HRMS (ESI): calcd for $C_{38}H_{25}O_3$ $[M+H]^+$ 529.1747, found 529.1752.

6-Methyl-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4b)



4b

Following the procedure **B**, **4b** was obtained as a pale-yellow solid (76.9 mg, 71%).

Melting Point: 293-295°*C*.

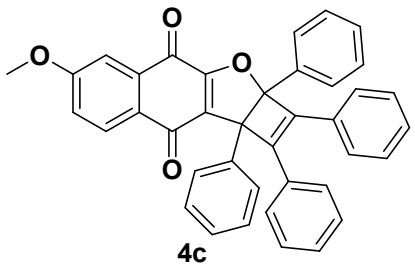
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 – 8.05 (m, 2H), 8.01 – 7.99 (m, 2H), 7.76 – 7.74 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.30 (m, 8H), 7.12 – 7.11 (m, 3H), 7.04 – 7.02 (m, 4H), 6.91 – 6.30 (m, 1H), 2.51 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.08, 179.42, 163.17, 148.99, 144.42, 138.55, 135.48, 135.30, 134.72,

132.59, 132.20, 131.89, 131.86, 131.37, 130.01, 129.28, 128.52, 128.17, 128.12, 127.44, 127.26, 127.07, 127.02, 125.63, 100.17, 69.29, 22.06.

HRMS (ESI): calcd for $C_{39}H_{27}O_3$ $[M+H]^+$ 543.1955, found 543.1980.

6-Methoxy-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4c)



4c

Following the procedure **B**, **4c** obtained as a pale-yellow solid (87.1 mg, 78%).

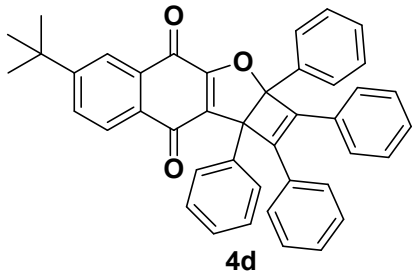
Melting Point: >300°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 – 8.02 (m, 2H), 7.72 – 7.70 (m, 2H), 7.63 (d, *J* = 2.6 Hz, 1H), 7.39 – 7.28 (m, 7H), 7.20 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.11 – 7.09 (m, 2H), 7.03 – 6.97 (m, 4H), 6.88 – 6.86 (m, 4H), 3.97 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.60, 179.24, 164.00, 163.07, 149.03, 141.10, 140.79, 138.55, 135.56, 134.79, 133.87, 132.65, 132.25, 131.90, 130.03, 129.41, 129.30, 129.09, 129.01, 128.96, 128.64, 128.59, 128.21, 128.15, 127.47, 127.40, 127.05, 127.00, 125.66, 110.56, 100.17, 69.36, 56.46.

HRMS (ESI): calcd for $C_{39}H_{27}O_4$ $[M+H]^+$ 559.1904, found 559.1910.

6-*Tert*-butyl-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4d)



4d

Following the procedure **B**, **4d** was obtained as a pale-yellow solid (87.1 mg, 78%).

Melting Point: 275-277 °*C*.

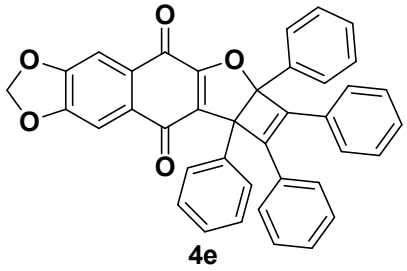
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 2.0 Hz, 1H), 8.01 – 7.97 (m, 3H), 7.74 (dd, *J* = 8.1, 2.0 Hz, 1H),

7.69 – 7.67 (m, 2H), 7.35 – 7.28 (m, 6H), 7.26 – 7.24 (m, 2H), 7.07 – 7.06 (m, 3H), 7.00 – 6.94 (m, 5H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.14, 179.57, 163.35, 157.60, 149.03, 138.54, 135.52, 134.78, 132.66, 132.21, 131.90, 131.84, 131.67, 131.35, 130.02, 129.29, 129.09, 129.00, 128.95, 128.64, 128.58, 128.21, 128.15, 127.47, 127.40, 127.23, 123.78, 100.20, 69.30, 35.95, 31.50.

HRMS (ESI): calcd for $C_{42}H_{33}O_3$ $[M+H]^+$ 585.2424, found 585.2431.

[6,7-*d*][1,3]dioxole-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4e).



4e

Following the procedure **B**, **4e** was obtained as a pale-yellow solid (78.9 mg, 69%).

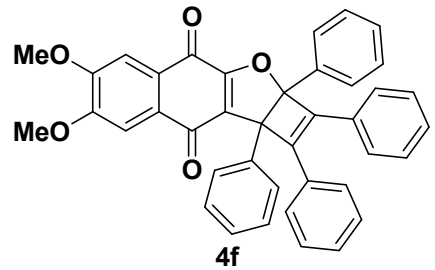
Melting Point: >300°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 – 8.00 (m, 2H), 7.72 – 7.70 (m, 2H), 7.57 (s, 1H), 7.49 (s, 1H), 7.38 – 7.27 (m, 6H), 7.10 – 6.97 (m, 6H), 6.88 – 6.86 (m, 2H), 6.14 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.17, 178.02, 163.22, 153.13, 151.97, 149.00, 141.09, 140.78, 138.53, 135.50, 134.71, 132.61, 132.23, 131.90, 131.05, 130.04, 129.31, 129.09, 128.97, 128.62, 128.57, 128.48, 128.20, 128.16, 127.62, 127.49, 127.38, 127.04, 125.65, 107.14, 106.28, 103.14, 100.42, 69.27.

HRMS (ESI): calcd for $C_{39}H_{25}O_5$ $[M+H]^+$ 573.1697, found 573.1719.

6,7-Dimethoxy-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4f)



4f

Following the procedure **B**, **4f** was obtained as a pale-yellow solid (76.4 mg, 65%).

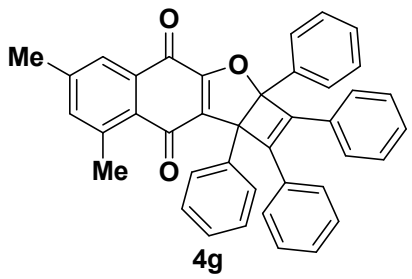
Melting Point: >300°*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.70 – 7.67 (m, 2H), 7.57 (s, 1H), 7.52 (s, 1H), 7.37 – 7.33 (m, 3H), 7.32 – 7.28 (m, 3H), 7.27 – 7.24 (m, 2H), 7.07 – 7.06 (m, 3H), 7.01 – 6.94 (m, 5H), 4.03 (s, 3H), 3.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.89, 178.60, 163.36, 154.14, 152.93, 148.97, 138.46, 135.55, 134.72, 132.60, 132.24, 130.01, 129.30, 129.08, 128.96, 128.62, 128.57, 128.55, 128.19, 128.13, 127.44, 127.38, 126.20, 109.06, 108.34, 100.28, 69.22, 57.07, 56.93.

HRMS (ESI): calcd for $C_{40}H_{29}O_5$ $[M+H]^+$ 589.2009, found 589.2017.

6,8-Dimethyl-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4g).



4g

Following the procedure **B**, **4g** was obtained as a pale-yellow solid (67.8 mg, 61%).

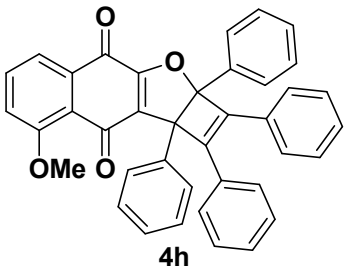
Melting Point: 284-286 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.94 (d, *J* = 1.3 Hz, 1H), 7.70 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.39 – 7.27 (m, 9H), 7.10 – 6.97 (m, 8H), 2.68 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 184.51, 179.72, 161.77, 148.86, 143.21, 142.08, 139.84, 135.74, 134.86, 132.63, 132.38, 129.94, 129.26, 129.06, 129.01, 128.91, 128.63, 128.59, 128.53, 128.15, 128.13, 127.42, 127.36, 126.37, 99.94, 69.79, 23.60, 21.84.

HRMS (ESI): calcd for $C_{40}H_{29}O_3$ $[M+H]^+$ 557.2111, found 557.2119.

8-Methoxy-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4h)



4h

Following the procedure **B**, **4h** was obtained as a pale-yellow solid (61.4 mg, 55%).

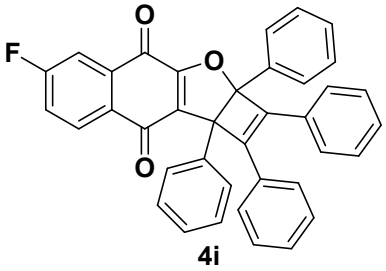
Melting Point: >300 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 – 8.01 (m, 2H), 7.84 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.36 – 7.27 (m, 7H), 7.25 – 7.22 (m, 2H), 7.06 – 7.04 (m, 3H), 6.97 – 6.94 (m, 5H), 3.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.88, 179.31, 161.13, 160.33, 148.88, 138.54, 135.68, 134.88, 134.45, 134.40, 132.71, 132.30, 130.20, 129.92, 129.21, 129.15, 129.06, 128.91, 128.63, 128.56, 128.51, 128.13, 128.08, 127.38, 127.22, 120.59, 119.69, 99.84, 69.88, 56.89.

HRMS (ESI): calcd for $C_{39}H_{27}O_4$ $[M+H]^+$ 559.1903, found 559.1912.

6-Fluoro-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4i)



4i

Following the procedure **B**, **4i** was obtained as a pale-yellow solid (54.6 mg, 50%).

Melting Point: >300 °*C*.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.99 – 7.97 (m, 2H), 7.81 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.40 – 7.30 (m, 7H), 7.25 – 7.23 (m, 2H), 7.09 – 7.07 (m, 3H), 7.03 – 7.00 (m, 3H), 6.98 – 6.94 (m, 2H).

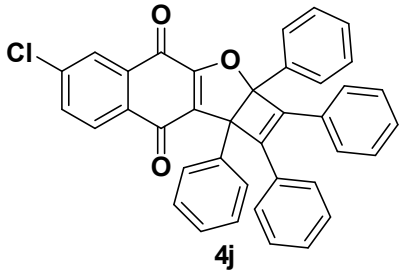
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.95, 178.09, 167.41, 164.87, 163.28, 148.85, 138.69, 135.28, 134.50, 134.39, 132.50, 132.10, 130.18, 130.14, 130.09, 129.41, 129.13, 128.97 (d, J_{C-F} = 3.2 Hz), 128.87, 128.74, 128.61, 128.55, 128.23 (d, J_{C-F} = 3.2Hz), 127.60, 127.36, 121.49 (d, J_{C-F} = 22.2 Hz), 113.56 (d, J_{C-F} = 24.2 Hz), 100.48,

69.21.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -103.68 (s, F) ppm.

HRMS (ESI): calcd for $C_{38}H_{24}O_3F$ $[M+H]^+$ 547.1704, found 547.1712.

6-Chloro-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4j).



4j

Following the procedure **B**, **4j** was obtained as a pale-yellow solid (58.5 mg, 52%).

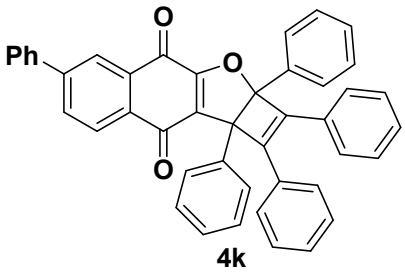
Melting Point: >300 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 2.1 Hz, 1H), 8.02 – 7.96 (m, 3H), 7.70 – 7.66 (m, 3H), 7.36 – 7.30 (m, 6H), 7.26 – 7.20 (m, 2H), 7.08 – 7.06 (m, 2H), 7.02 – 7.00 (m, 3H), 6.96 – 6.94 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.13, 178.12, 163.09, 148.81, 140.39, 138.67, 135.20, 134.56, 134.43, 133.11, 132.45, 132.06, 131.81, 130.16, 129.43, 129.14, 129.00, 128.93, 128.81, 128.75, 128.59, 128.52, 128.26, 128.23, 127.62, 127.34, 126.64, 100.49, 69.16.

HRMS (ESI): calcd for $C_{38}H_{24}O_3Cl$ $[M+H]^+$ 563.1408, found 563.1416.

1,2,2a,6,9b-Pentaphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4k)



4k

Following the procedure **B**, **4k** was obtained as a pale-yellow solid (70.1 mg, 58%).

Melting Point: >300 °*C*.

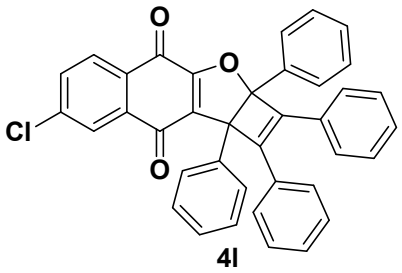
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.00 – 7.93 (m, 3H), 7.73 – 7.67 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.35 – 7.34 (m, 4H), 7.28 – 7.26 (m, 2H), 7.12 – 7.10 (m, 2H), 7.00 (s, 4H), 6.85 – 6.82 (m,

7H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.37, 175.48, 172.70, 150.28, 145.62, 141.08, 140.77, 139.11, 137.95, 135.03, 134.79, 133.24, 132.87, 132.08, 131.89, 131.82, 130.17, 129.66, 129.35, 129.25, 129.14, 129.10, 129.05, 128.80, 128.60, 128.42, 128.34, 128.17, 127.58, 127.46, 127.42, 127.04, 126.01, 125.65, 120.33, 101.73, 68.29.

HRMS (ESI): calcd for $C_{44}H_{29}O_3$ $[M+H]^+$ 605.2111, found 605.2124.

7-Chloro-1,2,2a,9b-tetraphenylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4l)



4l

Following the procedure **B**, **4l** was obtained as a pale-yellow solid (53.9 mg, 48%).

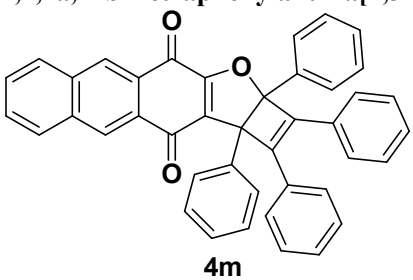
Melting Point: >300 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 2.1 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.70 – 7.64 (m, 3H), 7.36 – 7.30 (m, 6H), 7.26 – 7.23 (m, 2H), 7.09 – 7.07 (m, 3H), 7.03 – 7.00 (m, 3H), 6.97 – 6.94 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.89, 178.17, 163.40, 148.81, 141.88, 138.62, 135.12, 134.91, 134.39, 133.39, 132.44, 132.00, 130.19, 130.17, 129.41, 129.13, 129.00, 128.91, 128.76, 128.65, 128.58, 128.50, 128.29, 128.25, 128.23, 127.64, 127.39, 127.35, 100.56, 69.10.

HRMS (ESI): calcd for $C_{38}H_{24}O_3Cl$ $[M+H]^+$ 563.1408, found 563.1420.

1,2,2a,11b-Tetraphenylanthra[2,3-*b*]cyclobuta[*d*]furan-4,11(2a*H*,11b*H*)-dione (4m)



4m

Following the procedure **B**, **4m** was obtained as a pale-yellow solid (69.4 mg, 60%).

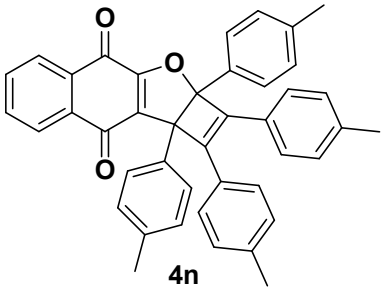
Melting Point: >300 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.06 – 8.04 (m, 1H), 7.92 – 7.87 (m, 2H), 7.77 – 7.75 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.40 – 7.32 (m, 7H), 7.23 – 7.19 (m, 4H), 7.13 – 7.10 (m, 2H), 7.06 – 7.02 (m, 3H), 6.89 – 6.86 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.50, 181.91, 163.99, 149.06, 145.04, 138.46, 136.88, 136.69, 136.08, 135.74, 135.38, 134.75, 134.44, 133.45, 132.66, 132.22, 131.90, 130.50, 130.31, 129.33, 129.22, 129.12, 129.01, 128.98, 128.84, 128.76, 128.65, 128.63, 128.24, 128.20, 128.02, 127.54, 127.43, 127.04, 125.60, 122.99, 100.45, 69.22.

HRMS (ESI): calcd for $C_{42}H_{27}O_3$ $[M+H]^+$ 579.1955, found 579.1971.

1,2,2a,9b-Tetrap-tolylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4n).



4n

Following the procedure **B**, **4n** was obtained as a pale-yellow solid (89.9 mg, 77%).

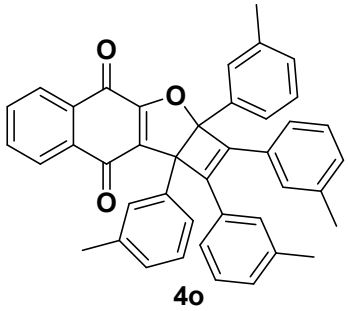
Melting Point: 276-278 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.06 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.16 (m, 6H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.81 (m, 4H), 2.35 (s, 3H), 2.33 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.15, 177.30, 161.14, 146.17, 142.10, 142.06, 137.92, 137.03, 136.13, 135.94, 134.84, 132.62, 131.30, 130.59, 129.92, 128.67, 128.11, 128.04, 127.81, 127.67, 127.58, 127.54, 127.43, 126.96, 126.91, 126.89, 126.52, 126.46, 125.33, 125.07, 124.56, 98.43, 66.75, 19.98, 19.90, 19.58, 19.52.

HRMS (ESI): calcd for $C_{42}H_{33}O_3$ $[M+H]^+$ 585.2424, found 585.2448.

1,2,2a,9b-tetra*m*-tolylcyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4o)



4o

Following the procedure **B**, **4o** was obtained as a pale-yellow solid (83.1 mg, 71%).

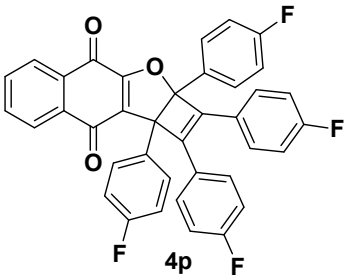
Melting Point: 269-271 °*C*.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.20 – 8.19 (m, 1H), 8.12 – 8.10 (m, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.56 – 7.52 (m, 2H), 7.29 – 7.18 (m, 4H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.97 – 6.89 (m, 3H), 6.84 – 6.77 (m, 2H), 2.35 (s, 3H), 2.32 (s, 31H), 2.18 (s, 3H), 2.12 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.02, 179.31, 163.18, 148.86, 138.62, 138.57, 138.35, 137.54, 137.37, 135.49, 134.68, 134.62, 133.73, 133.33, 132.71, 132.28, 132.00, 130.73, 130.03, 129.40, 129.25, 129.22, 129.05, 128.87, 128.82, 128.80, 128.17, 127.99, 127.82, 127.46, 127.10, 126.59, 126.27, 125.83, 125.71, 124.41, 100.41, 69.16, 21.89, 21.87, 21.77, 21.72.

HRMS (ESI): calcd for $C_{42}H_{33}O_3$ $[M+H]^+$ 585.2424, found 585.2425.

1,2,2a,9b-Tetrakis(4-fluorophenyl)cyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4p).



4p

Following the procedure **B**, **4p** was prepared according to the general procedure. The product was obtained as a pale-yellow solid (72.0 mg, 60%).

Melting Point: >300 °*C*.

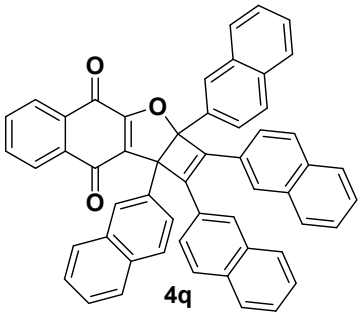
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.08 – 8.06 (m, 1H), 7.95 – 7.92 (m, 2H), 7.75 –

7.70 (m, 2H), 7.64 – 7.61 (m, 2H), 7.21 – 7.19 (m, 2H), 7.06 – 7.00 (m, 4H), 6.92 – 6.89 (m, 2H), 6.82 – 6.73 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.20, 178.93, 164.90, 164.34, 164.14, 163.36, 163.12, 162.90, 162.35, 162.17, 161.38, 147.52, 136.77, 134.99, 133.75, 133.43, 131.90, 131.03, 130.97, 130.93, 130.91, 130.49, 130.43, 130.16, 130.13, 130.05, 129.99, 129.17, 129.10, 129.07, 128.24, 128.22, 128.06, 127.78 (d, $J_{C\text{-}F}$ = 3.2 Hz), 127.18, 126.83, 116.60, 116.43, 116.27, 115.71, 115.61, 115.54, 115.44, 99.61, 68.57.

HRMS (ESI): calcd for $C_{38}H_{21}F_4O_3$ $[M+H]^+$ 601.1421, found 601.1442.

1,2,2a,9b-Tetra(naphthalen-2-yl)cyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione (4q)



4q

Following the procedure **B**, **4q** was obtained as a pale-yellow solid (84.1 mg, 58%).

Melting Point: >300 °*C*.

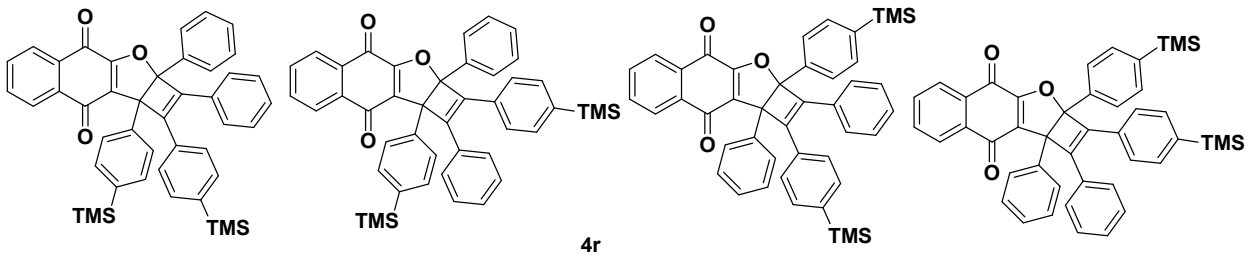
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 8.25 – 8.20 (m, 2H), 8.13 – 8.11 (m, 1H), 8.05 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.87 – 7.80 (m, 4H), 7.77 – 7.70 (m, 5H), 7.57 – 7.28 (m, 16H), 7.18 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.21, 179.36, 163.34, 149.42, 139.51, 134.83, 134.29, 133.88, 133.69, 133.51, 133.38, 133.27, 133.09, 132.85, 132.30, 132.09, 130.14, 129.76, 129.62, 129.06, 128.79, 128.71, 128.50, 128.42, 128.27, 128.18, 128.11, 128.03, 127.94, 127.60, 127.24, 126.98, 126.90, 126.76, 126.63, 126.39, 126.25, 126.15, 126.01, 125.87, 124.61, 100.75, 69.78.

HRMS (ESI): calcd for $C_{54}H_{33}O_3$ $[M+H]^+$ 729.2274, found 729.2286.

2,2a-Diphenyl-1,9b-bis(4-(trimethylsilyl)phenyl)cyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione and **1,2a-Diphenyl-2,9b-bis(4-(trimethylsilyl)phenyl)cyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione** and **2,9b-Diphenyl-1,2a-bis(4-(trimethylsilyl)phenyl)cyclobuta[*d*]naphtho[2,3-*b*]furan-4,9(2a*H*,9b*H*)-dione** and **1,9b-Diphenyl-2,2a-bis(4-(trimethylsilyl)phenyl)cyclobuta[*d*]naphtho[2,3-**

***b*]furan-4,9(2a*H*,9b*H*)-dione (4r)**



Following the procedure **B**, **4r** was obtained as a pale-yellow solid (105.8 mg, 79%), regioisomer ratio ≈ 5:5:7:8.

Melting Point: no determined.

Regioisomer mixture A

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.0 Hz, 2H), 8.11 (d, *J* = 7.2 Hz, 2H), 8.03 – 7.98 (m, 5H), 7.76 – 7.67 (m, 10H), 7.55 – 7.53 (m, 3H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 9H), 7.29 – 7.27 (m, 4H), 7.25 – 7.19 (m, 6H), 7.17 – 7.13 (m, 4H), 7.08 – 6.91 (m, 12H), 0.29 (m, 9H), 0.28 (s, 6H), 0.15 – 0.15 (m, 6H), 0.14 (s, 5H), 0.13 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.23, 182.07, 179.18, 163.38, 163.31, 149.23, 148.86, 143.12, 142.23, 140.96, 139.35, 138.96, 138.53, 135.88, 135.79, 135.42, 134.97, 134.71, 134.00, 133.88, 133.66, 133.45, 133.09, 133.06, 132.97, 132.87, 132.41, 132.34, 132.00, 130.02, 129.29, 129.09, 129.07, 128.99, 128.78, 128.69, 128.65, 128.56, 128.50, 128.16, 128.11, 127.93, 127.81, 127.74, 127.62, 127.36, 127.31, 127.28, 127.15, 126.67, 126.56, 126.51, 100.45, 100.28, 69.37, 69.28, 69.26, -0.75, -0.82.

HRMS (ESI): calcd for $C_{44}H_{41}O_3Si_2$ $[M+H]^+$ 673.2589, found 673.2617.

Regioisomer mixture B

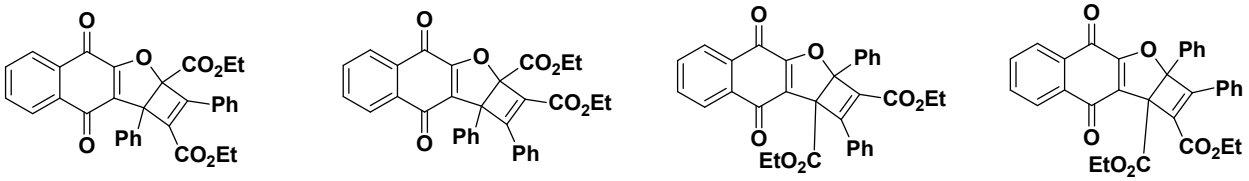
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.6 Hz, 2H), 7.98 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.93 – 7.91 (m, 4H), 7.72 – 7.70 (m, 5H), 7.67 – 7.61 (m, 4H),7.49 – 7.46 (m, 4H), 7.37 – 7.32 (m, 7H), 7.22 – 7.15 (m, 8H), 7.09 – 7.07 (m, 5H), 6.97 (s, 5H), 6.89 (d, *J* = 8.1 Hz, 2H), 0.26 (s, 8H), 0.24 (s, 10H), 0.13 (s, 8H), 0.09 (s, 7H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 181.28, 175.51, 175.39, 172.66, 172.53, 150.52, 150.09, 143.27, 142.11, 141.22, 139.24, 138.32, 137.94, 135.48, 135.23, 135.20, 135.04, 135.02, 134.82, 134.01, 133.99, 133.22, 133.16, 133.08, 133.02, 132.95, 132.57, 132.07, 131.95, 131.66, 130.12, 130.06, 129.97, 129.17, 129.13, 129.10, 129.06,

128.59, 128.55, 128.50, 128.26, 128.12, 128.00, 127.93, 127.82, 127.74, 127.43, 127.35, 127.29, 126.69, 125.42, 125.35, 125.30, 120.63, 120.29, 101.89, 101.68, 68.41, 68.28, -0.73, -0.77, -0.83.

HRMS (ESI): calcd for $C_{44}H_{41}O_3Si_2$ $[M+H]^+$ 673.2589, found 673.2617.

Diethyl 4,9-dioxo-2,9b-diphenyl-2a,4,9,9b-tetrahydrocyclobuta[*d*]naphtho[2,3-*b*]furan-1,2a-dicarboxylate and **Diethyl 4,9-dioxo-1,9b-diphenyl-2a,4,9,9b-tetrahydrocyclobuta[*d*]naphtho[2,3-*b*]furan-2,2a-dicarboxylate** and **Diethyl 4,9-dioxo-1,2a-diphenyl-2a,4,9,9b-tetrahydrocyclobuta[*d*]naphtho[2,3-*b*]furan-2,9b-dicarboxylate** and **Diethyl 4,9-dioxo-2,2a-diphenyl-2a,4,9,9b-tetrahydrocyclobuta[*d*]naphtho[2,3-*b*]furan-1,9b-dicarboxylate (4s)**.



4s

Following the procedure **B**, **4s** was prepared according to the general procedure. The product was obtained as a pale-yellow solid (36.4 mg, 34%), regioisomer ratio ≈ 8:7:4:1.

Melting Point: no determined.

Regioisomer mixture

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.59 – 7.28 (m, 8H), 7.27 – 7.07 (m, 3H), 4.21 – 4.10 (m, 2H), 4.03 – 3.93 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 2H), 0.84 (t, *J* = 3.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.09, 191.73, 165.48, 165.39, 164.87, 163.21, 154.76, 149.09, 140.71, 137.66, 133.90, 133.74, 133.58, 133.56, 130.02, 129.98, 129.79, 129.71, 129.56, 129.40, 129.30, 129.17, 129.10, 129.00, 128.89, 128.88, 128.86, 128.84, 128.81, 128.66, 128.46, 128.39, 128.26, 128.22, 128.19, 128.10, 115.08, 82.13, 63.04, 62.81, 61.85, 61.14, 14.16, 14.03, 14.03, 14.02.

HRMS (ESI): calcd for $C_{32}H_{24}O_7Na$ $[M+Na]^+$ 543.1414, found 543.1423.

Regioisomer mixture

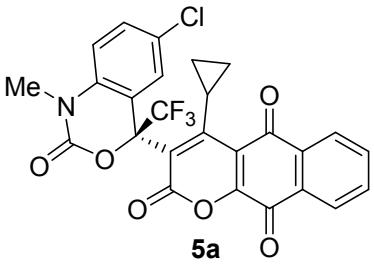
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 – 7.87 (m, 1H), 7.74 – 7.30 (m, 11H), 7.25 – 7.22 (m, 2H), 4.43 – 4.30 (m,

1H), 4.04 – 3.85 (m, 3H), 1.38 (t, *J* = 7.1 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 2H), 0.80 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.84, 167.54, 163.08, 161.66, 154.85, 153.17, 142.59, 142.12, 136.91, 134.38, 133.24, 132.69, 129.36, 129.30, 129.16, 128.82, 128.80, 128.58, 128.52, 128.41, 121.92, 70.33, 62.52, 61.73, 61.39, 14.69, 14.03, 13.79.

HRMS (ESI): calcd for $C_{32}H_{24}O_7Na$ $[M+Na]^+$ 543.1414, found 543.1424.

(*R*)-3-(6-chloro-1-methyl-2-oxo-4-(trifluoromethyl)-2,4-dihydro-1H-benzo[*d*][1,3]oxazin-4-yl)-4-cyclopropyl-1*H*-benzo[*g*]chromene-2,5,10-trione (5a)



5a

Following the procedure **C**, **5a** was prepared according to the general procedure. The product was obtained as a pale-yellow solid (47.6 mg, 45%).

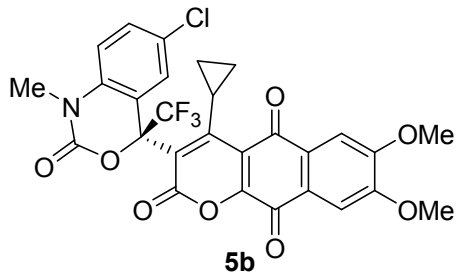
Melting Point: 285-287 °*C*.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 – 8.14 (m, 2H), 7.87 – 7.79 (m, 2H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.49 (s, 3H), 2.77 (ddd, *J* = 15.3, 8.8, 6.5 Hz, 1H), 0.99 (tt, *J* = 9.3, 5.6 Hz, 1H), 0.63 (tt, *J* = 8.8, 5.6 Hz, 1H), 0.10 (dt, *J* = 17.0, 6.5 Hz, 1H), -0.42 (td, *J* = 11.3, 6.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 180.60, 175.96, 162.18, 156.97, 153.35, 148.59, 136.51, 135.92, 134.73, 133.21, 132.25, 132.20, 130.45, 130.02, 127.85, 127.64, 127.24, 123.85 (q, $J_{C\text{-}F}$ = 289.9 Hz), 122.50, 117.45, 115.25, 85.58 (q, $J_{C\text{-}F}$ = 31.8 Hz), 32.34, 18.58, 10.28, 10.19.

HRMS (ESI): calcd for $C_{26}H_{15}O_6NClF_3Na$ $[M+Na]^+$ 552.0432, found 552.0438.

(*R*)-3-(6-Chloro-1-methyl-2-oxo-4-(trifluoromethyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazin-4-yl)-4-cyclopropyl-7,8-dimethoxy-1*H*-benzo[*g*]chromene-2,5,10-trione (5b).



5b

Following the procedure **C**, **5b** was obtained as a pale-yellow solid (60.1 mg, 51%).

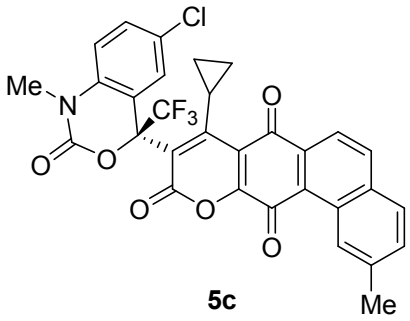
Melting Point: 288-290 °*C*.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 – 7.53 (m, 3H), 7.46 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 4.06 (s, 3H), 4.05 (s, 3H), 2.79 – 2.71 (m, 1H), 0.97 (ddd, *J* = 14.8, 9.1, 5.5 Hz, 1H), 0.62 (ddd, *J* = 13.9, 8.8, 5.5 Hz, 1H), 0.11 (td, *J* = 11.6, 5.9 Hz, 1H), -0.43 (dt, *J* = 11.2, 5.9 Hz, 1H)..

^{13}C NMR (151 MHz, $CDCl_3$): δ = 180.05, 175.16, 162.32, 157.17, 155.35, 154.19, 153.62, 148.68, 136.47, 132.21, 131.55, 130.02, 128.11, 127.69, 125.06, 123.83 (q, $J_{C\text{-}F}$ = 289.9 Hz), 121.87, 117.59, 115.22, 109.17, 108.17, 85.61 (q, $J_{C\text{-}F}$ = 31.8 Hz), 57.21, 32.33, 18.60, 10.38, 10.17, 0.48.

HRMS (ESI): calcd for $C_{28}H_{19}O_8NClF_3Na$ $[M+Na]^+$ 612.0644, found 612.0653.

(*R*)-10-(6-Chloro-1-methyl-2-oxo-4-(trifluoromethyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazin-4-yl)-11-cyclopropyl-4-methyl-1*H*-naphtho[1,2-*g*]chromene-7,9,12-trione.



5c

Following the procedure **C**, **5c** was obtained as a pale-yellow solid (49.8 mg, 42%).

Melting Point: 294-296 °*C*.

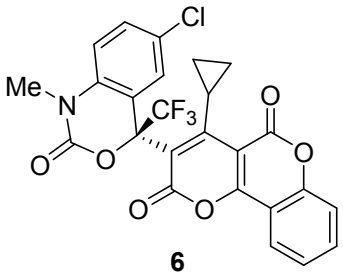
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.37 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.49 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.52 (s, 3H), 2.80 (ddd, *J* = 16.3, 7.4, 5.6 Hz, 1H), 2.66 (s, 3H), 1.04 (ddd, *J* = 11.4, 7.4, 4.5 Hz, 1H), 0.67 (ddd, *J* = 14.1, 8.8, 5.6 Hz, 1H), 0.16

(td, *J* = 11.4, 6.0 Hz, 1H), -0.38 (td, *J* = 11.4, 6.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 181.57, 177.92, 161.75, 157.35, 153.70, 148.66, 142.55, 137.07, 136.51, 135.22, 134.18, 132.22, 131.97, 131.35, 130.45, 130.01, 129.24, 127.72, 127.00, 125.14, 123.89 (q, $J_{C\text{-}F}$ = 289.9 Hz), 122.05, 120.50, 117.62, 115.22, 85.60 (q, $J_{C\text{-}F}$ = 33.2 Hz), 32.34, 23.06, 18.31, 10.35, 10.09.

HRMS (ESI): calcd for $C_{31}H_{19}O_6NClF_3Na$ $[M+Na]^+$ 616.0745, found 616.0750.

(*R*)-3-(6-chloro-1-methyl-2-oxo-4-(trifluoromethyl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazin-4-yl)-4-cyclopropylpyrano[3,2-*c*]chromene-2,5-dione (6).



6

Following the procedure **C** (4-hydroxycoumarin as starting material), **5a** was obtained as a pale-yellow solid (56.7 mg, 55%).

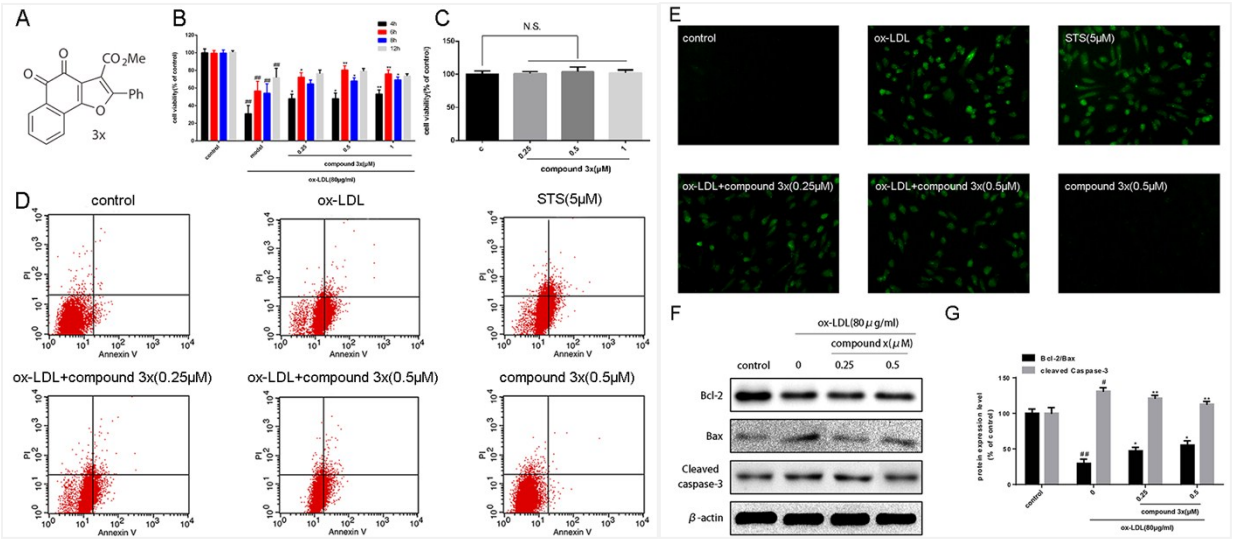
Melting Point: 285-287 °*C*.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.47 – 7.39 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.49 (s, 3H), 2.69 – 2.61 (m, 1H), 1.18 – 1.10 (m, 1H), 0.68 – 0.61 (m, 1H), 0.32 – 0.25 (m, 1H), -0.33 – -0.40 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.97, 161.39, 157.41, 156.58, 154.04, 148.72, 136.58, 135.69, 132.10, 129.85, 127.67, 126.98, 126.22, 125.59, 125.05, 124.62, 123.12, 121.20, 117.98, 117.37, 115.17, 112.68, 106.62, 85.87, 85.65, 85.44, 85.22, 32.30, 18.70, 10.20, 10.08.

HRMS (ESI): calcd for $C_{25}H_{15}O_6NClF_3Na$ $[M+Na]^+$ 540.0432, found 540.0440.

5. Endothelial protective Assay of 3x



Protective effects of compound 3x on endothelial cell injury. (A) Chemical structure of compound **3x**. (B) Human umbilical endothelial cells (HUVECs) were pretreated with various concentrations (0.25, 0.5 and 1 μM) and time (4, 6, 8 and 12 h), then the cells were exposed to ox-LDL (80 μg/ml) for another 24 h. Cell viability was measured by MTT assay. (C) HUVECs were treated with different concentrations of compound **3x** (0.25, 0.5 and 1μM) for 12 h, then cell viability was measured by MTT assay. (D-G) HUVECs were pretreated with compound **3x** (0.25 and 0.5 μM) for 6 h, followed by treatment with ox-LDL (80 μg/ml) for another 24 h. (D) After that, HUVECs were stained with Annexin V/PI kit, and the cell apoptosis was detected by a flow cytometry. (E) Representative images of HUVECs stained with Carboxy-H2DCFDA. (F) Bcl-2, Bax, Cleaved-caspase-3 and β-actin were evaluated by western blot analysis. (G) Densitometric analysis was used to quantify the levels of Bcl-2/Bax and Cleaved caspase-3. Values are expressed as the mean ± SD, n = 3. $^{\#}p < 0.05$, $^{\#\#}p < 0.01$ ox-LDL group *vs.* control group; $^{*}p < 0.05$, $^{**}p < 0.01$ vs. ox-LDL group. STS: sodium tanshinone IIA silate.

a) Ethics statement

This study was administrated according to the Declaration of Helsinki, and the research protocol was permitted by the Ethics Committee of Peking Union Medical College (Beijing, China).

b) Reagents

Ox-LDL (by copper ion-induced LDL oxidation, Malondialdehyde N-40 nmol/ml) was obtained from Union-Bio Technology (Beijing, China). 3-(4, 5-dimethylthiazol-2yl-)-2, 5-diphenyl tetrazolium bromide (MTT) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The VascuLife Basal Medium and growth supplement were obtained from Lifeline Cell Technology (Carlsbad, CA, USA). The ROS fluorometric assay and annexin V/PI assay kits were purchased from BioVision (Milpitas, CA, USA). Antibodies against Bcl-2, Bax, Cleaved-caspase-3 and β-actin were obtained from Santa Cruz Biotechnology (Santa Cruz, CA, USA).

c) Cell culture and treatment

Human umbilical vein endothelial cells (HUVECs) were separated from fresh human umbilical veins and cultured on 1% gelatin-coated plastic dishes as previously described [1]. The neonate cords were donated by the Maternal and Child Care Service Centre in Beijing, China. The study protocol was explained and all participating donors gave written informed consents. Briefly, the VascuLife Basal Medium with growth supplements, streptomycin (100 μg/ml) and penicillin (100 U/ml) were used for the HUVECs culture. Passages 3 to 5 of the HUVECs isolated from different donors were used for the experiments. The cells were incubated in a humidified atmosphere at 37°C containing 5% CO2. Compound **3x** was dissolved in DMSO to make a stock solution and diluted to the concentration of working solutions before administration.

d) Measurement of cell viability

Cell viability was measured by MTT assay. Briefly, the cells cultured on 96-well cell culture plates were pretreated with different concentrations and time of compound a followed by treatment with ox-LDL. To measure cell viability, 1 mg/ml MTT assay solution was added, and the plates were incubated for an additional 4 h. The formazan crystals were dissolved in 150 μl of DMSO. Then, the absorbance was measured at 570 nm on a microplate reader (Tecan, Switzerland). The percentage of living cells was calculated by the ratio of optical density compared with that of the normal wells.

e) Flow cytometry detection of apoptosis

After all treatment, the cells were harvested, washed with PBS, and then incubated with 100 μl 1× Annexin V work solution containing for 15 min in the dark at 37 ℃. After stained with PI and washed by PBS, the cells were immediately analyzed using a flow cytometer (Becton, Dickinson and Company, CA, USA).

f) Determination of reactive oxygen species (ROS) production

The effects of **3x** on intracellular ROS levels were detected using a total ROS detection kit according to the manufacturer's brochure. Briefly, the HUVECs were harvested and washed with PBS. Subsequently, the cells were incubated with 300 μl ROS detection solution (Carboxy-H2DCFDA) and stained at 37 °C for 30 min in the dark. The staining solution was replaced by PBS, and the samples were photographed by a fluorescence microscope.

g) Western blot analysis

Briefly, the cell extracts were lysed in RIPA lysis buffer containing 1% protease inhibitor (Beyotime, Shanghai, China). Protein content was measured with a BCA Protein Assay Kit (Cwbiotech, Beijing, China). 12% sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) was used for protein separation and then transferred onto polyvinylidene difluoride membranes. The membranes were incubated over night with 1:500-diluted primary antibodies at 4 °C, then washed with TBST thrice followed by secondary antibodies at room temperature for 1.5 h. Then, the proteins were developed by an enhanced chemiluminescence detection system. Finally, the blots were scanned, and densitometric analysis was performed using Gel Pro software (Media Cybernetics, Rockville, MD, USA).

h) Statistical analysis

Data are presented as the means ± standard deviation (SD) of three independent experiments. Differences between groups were analyzed by one-way analysis of variance (ANOVA), and the means of two groups were compared by Tukey method using Graphpad 6.0 statistical software. Statistical significance was defined as $p < 0.05$.

6. Crystallographic data for 3a, 3s, 3y, 4a, 5a

a) X-ray crystallographic data of 3a (CCDC 1909884)

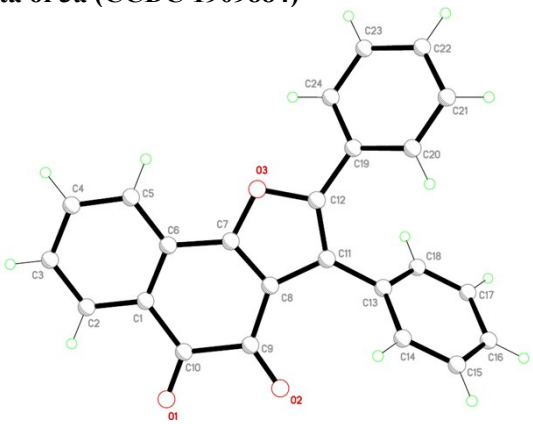


Table 1. Crystal data and structure refinement for **3a**.

Identification code	3a	
Empirical formula	$C_{24}H_{14}O_3$	
Formula weight	350.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.2578(19) Å	a= 90°.
	b = 13.3992(18) Å	b= 93.734(2)°.
	c = 9.5225(13) Å	g = 90°.
Volume	1688.0(4) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	728	
Crystal size	0.26 x 0.22 x 0.16 mm^3	
Theta range for data collection	1.54 to 27.50°.	
Index ranges	-15<=h<=17, -17<=k<=14, -11<=l<=12	
Reflections collected	11846	
Independent reflections	3876 [R(int) = 0.0448]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6663	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3876 / 0 / 244
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1129
R indices (all data)	R1 = 0.0635, wR2 = 0.1208
Largest diff. peak and hole	0.373 and -0.247 e.$Å^{-3}$

Note: The crystal is monoclinic, space group P2(1)/c. The asymmetric unit contains one molecule of the compound $C_{24}H_{14}O_3$. Final R values are R1=0.0483 and wR2=0.1129 for 2-theta up to 55º.

b) X-ray crystallographic data of 3s (CCDC 1909885)

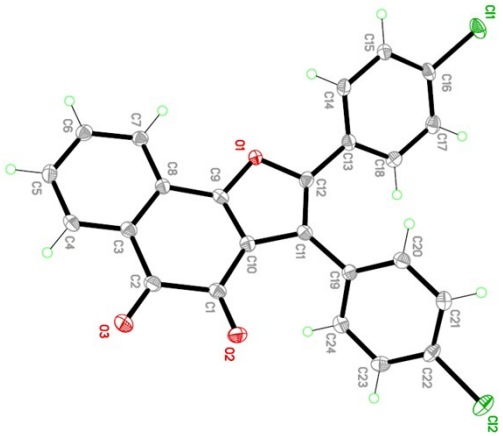


Table 2. Crystal data and structure refinement for **3s**.

Identification code	3s	
Empirical formula	$C_{24}H_{12}Cl_2O_3$	
Formula weight	419.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2581(15) Å	a= 75.829(4)°.
	b = 14.444(3) Å	b= 84.143(4)°.
	c = 17.808(4) Å	g = 87.362(5)°.
Volume	1800.2(6) $Å^3$	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	0.386 mm^{-1}	
F(000)	856	
Crystal size	0.40 x 0.20 x 0.15 mm^3	

Theta range for data collection	1.18 to 27.50°.
Index ranges	-9<=h<=9, -18<=k<=18, -23<=l<=23
Reflections collected	23747
Independent reflections	8254 [R(int) = 0.0340]
Completeness to theta = 27.50°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6173
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8254 / 0 / 523
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1066
R indices (all data)	R1 = 0.0511, wR2 = 0.1159
Largest diff. peak and hole	0.523 and -0.298 e.Å^{-3}

Note: The crystal is triclinic, space group P-1. The asymmetric unit contains two molecules of the compound $C_{24}H_{12}O_3Cl_2$. Final R values are R1=0.0439 and wR2=0.1066 for 2-theta up to 55º.

c) X-ray crystallographic data of 3y (CCDC 1909886)

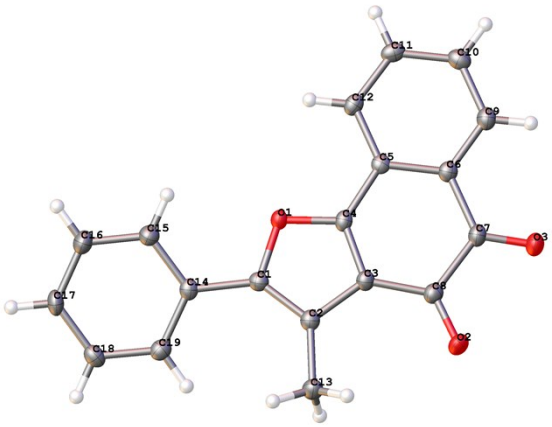


Table 3: Crystal data and structure refinement for **3y**

Identification code	3y
Empirical formula	$C_{19}H_{12}O_3$
Formula weight	288.29
Temperature / K	107.70(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å, b / Å, c / Å	13.3669(16), 6.5367(3), 16.8120(14)

α/°, β/°, γ/°	90.00, 112.656(12), 90.00
Volume / Å^3	1355.6(2)
Z	4
ρ_{calc} / mg mm^{-3}	1.413
μ / mm^{-1}	0.095
F(000)	600
Crystal size / mm^3	0.40 × 0.37 × 0.25
2Θ range for data collection	6.6 to 52°
Index ranges	-11 ≤ h ≤ 16, -8 ≤ k ≤ 7, -20 ≤ l ≤ 20
Reflections collected	5832
Independent reflections	2657[R(int) = 0.0281 (inf-0.9Å)]
Data/restraints/parameters	2657/0/200
Goodness-of-fit on F^2	1.035
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0467, wR_2 = 0.1033
Final R indexes [all data]	R_1 = 0.0618, wR_2 = 0.1141
Largest diff. peak/hole / e Å^{-3}	0.258/-0.233
Flack Parameters	N
Completeness	0.9964

Note: Single crystals of $C_{19}H_{12}O_3$ M =288.29, monoclinic, a = 13.3669(16) Å, b = 6.5367(3) Å, c = 16.8120(14) Å, β = 112.656(12)°, U = 1355.6(2) Å^3, T = 107.70(10), space group P2$_1$/c (no. 14), Z = 4, μ(Mo Kα) = 0.095, 5832 reflections measured, 2657 unique (R_{int} = 0.0281) which were used in all calculations. The final $wR(F_2)$ was 0.1141 (all data).

d) X-ray crystallographic data of 4a (CCDC 876846)

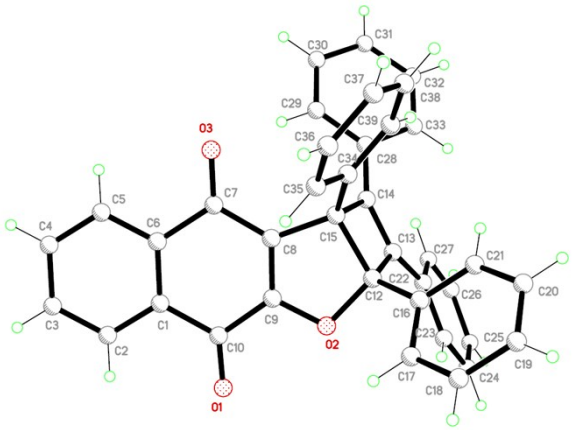


Table 4. Crystal data and structure refinement for **4a**.

Identification code	4a
Empirical formula	C_{38} H_{24} O_3
Formula weight	528.57
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4942(8) Å	a= 94.8310(10)°.
	b = 10.2513(9) Å	b= 96.6810(10)°.
	c = 15.9443(15) Å	g = 104.8190(10)°.
Volume	1323.7(2) $Å^3$	
Z	2	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	552	
Crystal size	0.60 x 0.54 x 0.10 mm^3	
Theta range for data collection	1.29 to 27.50°.	
Index ranges	-11<=h<=11, -13<=k<=13, -20<=l<=20	
Reflections collected	17382	
Independent reflections	6076 [R(int) = 0.0221]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6728	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6076 / 0 / 370	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1159	
R indices (all data)	R1 = 0.0480, wR2 = 0.1219	
Largest diff. peak and hole	0.399 and -0.230 $e.Å^{-3}$	

Note: The crystal is triclinic, space group P-1. The asymmetric unit contains one molecule of the compound C38H24O3. Final R values are R1=0.0433 and wR2=0.1159 for 2-theta up to 55º.

e) X-ray crystallographic data of 5a (CCDC 1909889)

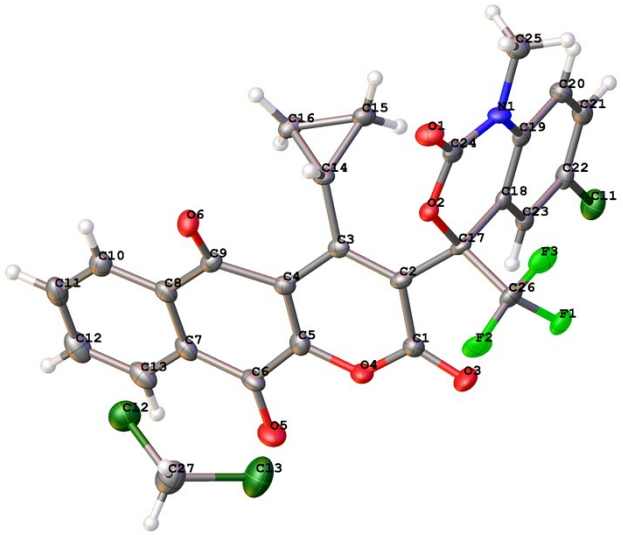


Table 5: Crystal data and structure refinement for **5a**

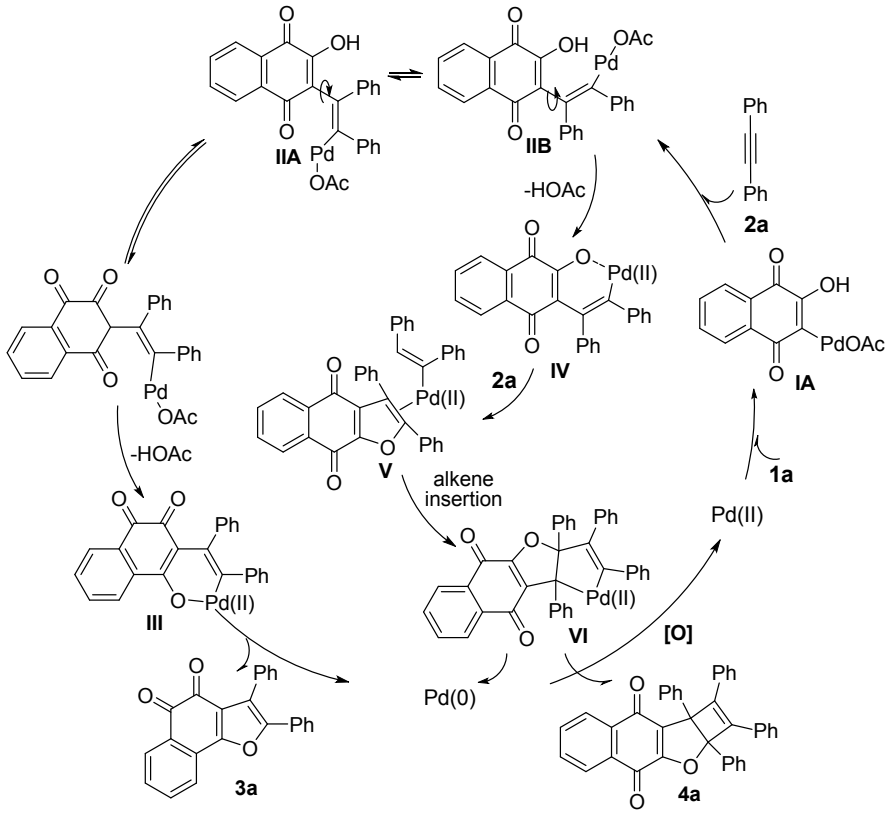
Identification code	5a
Empirical formula	$C_{27}H_{17}Cl_3F_3NO_6$
Formula weight	614.77
Temperature / K	110.60(14)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a / Å, b / Å, c / Å	6.9362(5), 16.8867(11), 21.0716(11)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / Å^3	2468.1(3)
Z	4
ρ_{calc} / mg mm^{-3}	1.654
μ / mm^{-1}	0.442
F(000)	1248
Crystal size / mm^3	0.40 × 0.11 × 0.09
2Θ range for data collection	6.18 to 52°
Index ranges	-8 ≤ h ≤ 8, -20 ≤ k ≤ 20, -25 ≤ l ≤ 22
Reflections collected	12224
Independent reflections	4844[R(int) = 0.0441 (inf-0.9Å)]
Data/restraints/parameters	4844/0/362
Goodness-of-fit on F^2	1.047
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0518, wR_2 = 0.1180
Final R indexes [all data]	R_1 = 0.0625, wR_2 = 0.1266
Largest diff. peak/hole / e Å^{-3}	0.385/-0.465
Flack Parameters	-0.01(8)
Completeness	0.9966

Single crystals of $C_{27}H_{17}Cl_3F_3NO_6$, M =614.77, orthorhombic, a = 6.9362(5) Å, b = 16.8867(11) Å, c = 21.0716(11) Å, U = 2468.1(3) Å^3, T = 110.60(14), space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo Kα) = 0.442,

12224 reflections measured, 4844 unique (R_{int} = 0.0441) which were used in all calculations. The final $wR(F_2)$ was 0.1266 (all data).

7. Postulated mechanism

On the basis of the known palladium-catalyzed oxidative annulation reactions, a possible mechanism for this switchable transformation is shown as follows. The formation of angular and linear naphthofuroquinones begins with the palladation of **1a** to yield the vinyl-palladium intermediate **IIA** and **IIB**. From intermediate **IIA** the reaction proceeds via an enolate intermediate to form six-membered metallacyclic species **III** then undergoes cyclization to release the palladium catalyst and furnish the 1,2-naphthofuroquinone **3a**. A similar catalytic pathway is postulated for the assembly of **4a** via an enol-directed route to form palladacycle **IV**, which then undergoes carbopalladation of second diphenylacetylene **2a** and leads to an intermediate **V**. A subsequent alkene insertion leads to the palladacycle species **VI** which regenerates the palladium catalyst through reduction elimination and affords the aim product **4a**.



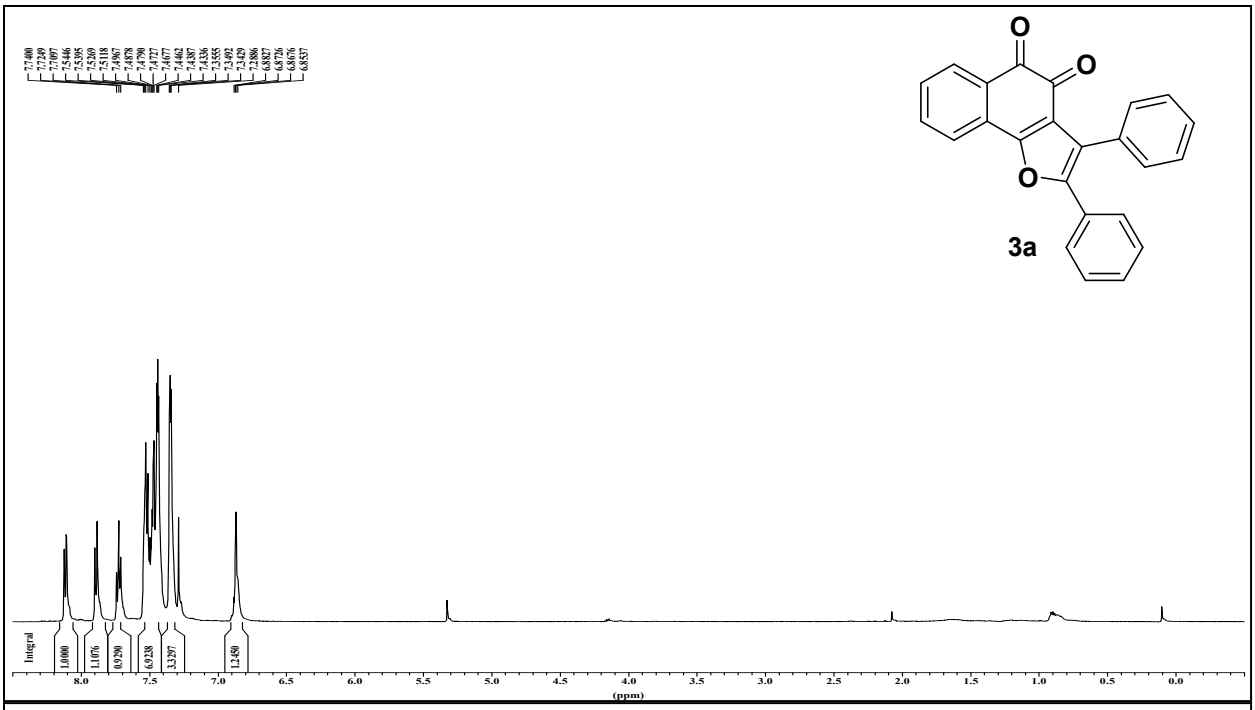
8. Reference

1) G. Sartori, F. Bigi, G. Canali, R. Maggi, G. Casnati, X. C. Tao, *J. Org. Chem.*, **1993**, *58*, 840.

2) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. W. Lee, *J. Org. Chem.,* **2010**, *75*, 624.

3) C. H. Tseng, S. L. Chang, P. K. Shih, C. M. Cheng, Y. L. Chen, *Bioorg. Med. Chem.* **2009**, *17*, 6773.

9. NMR Spectrum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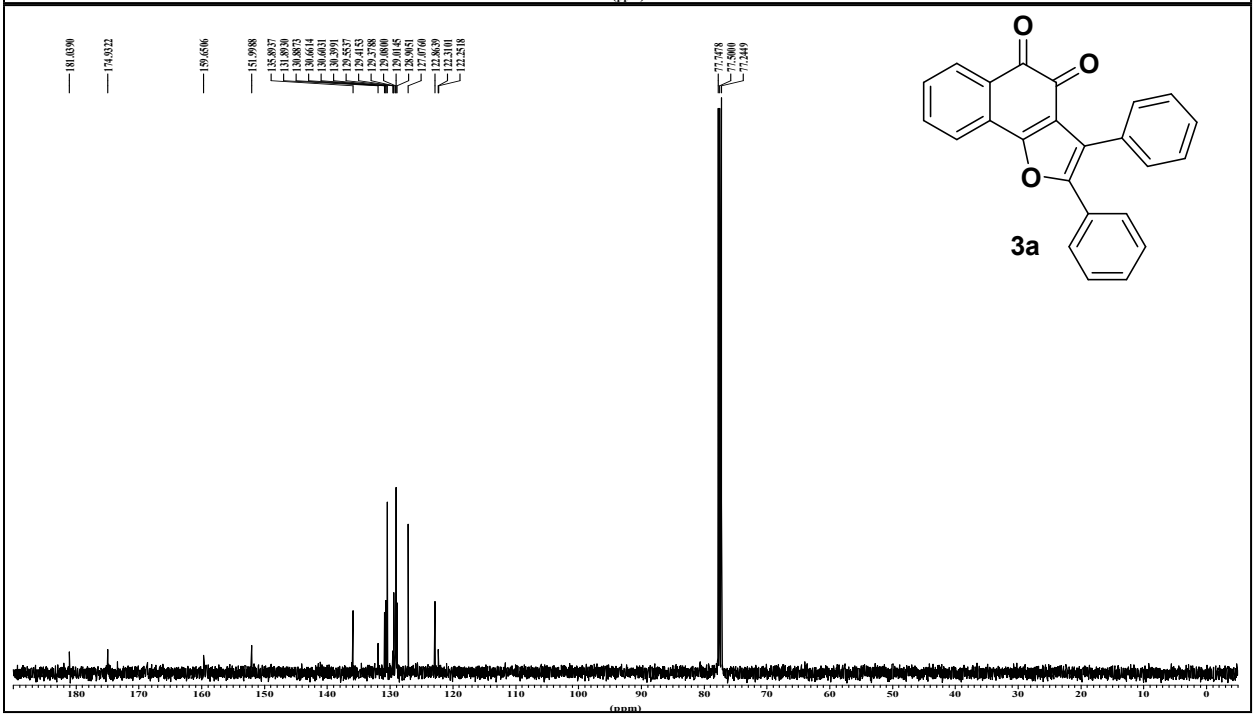
(ppm)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O
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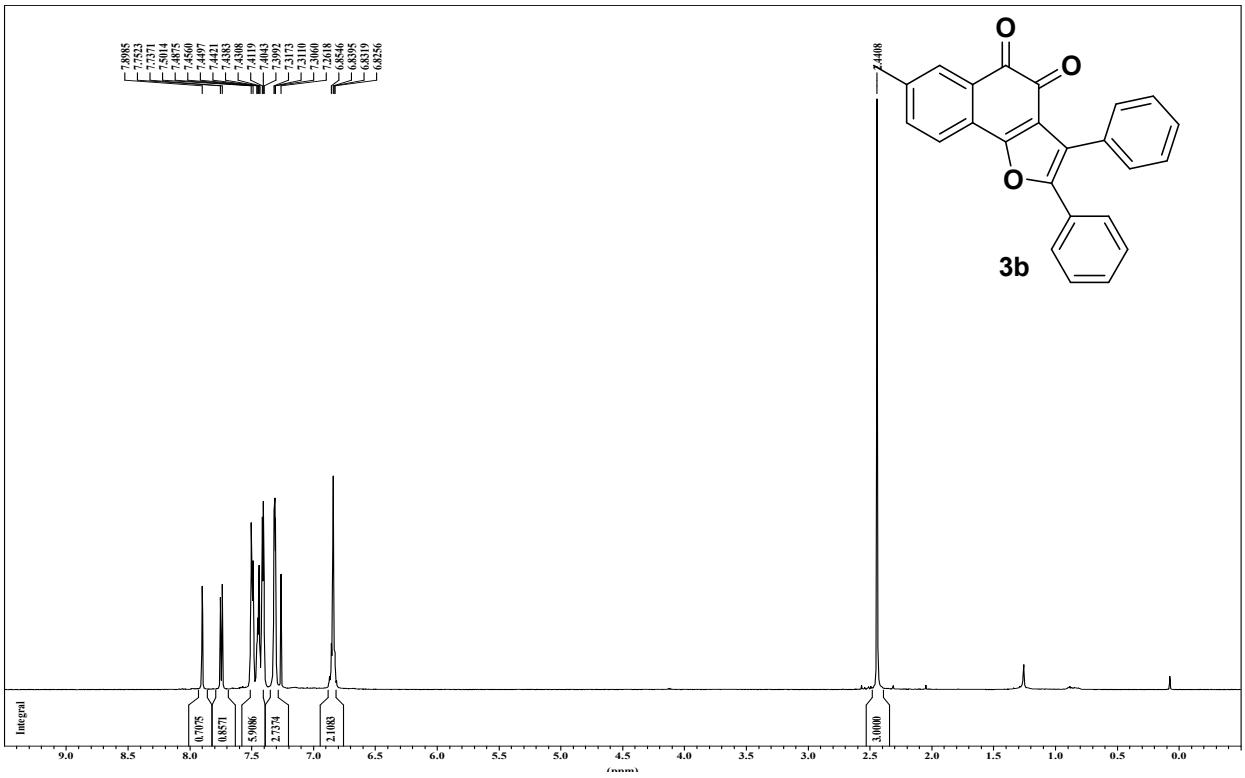
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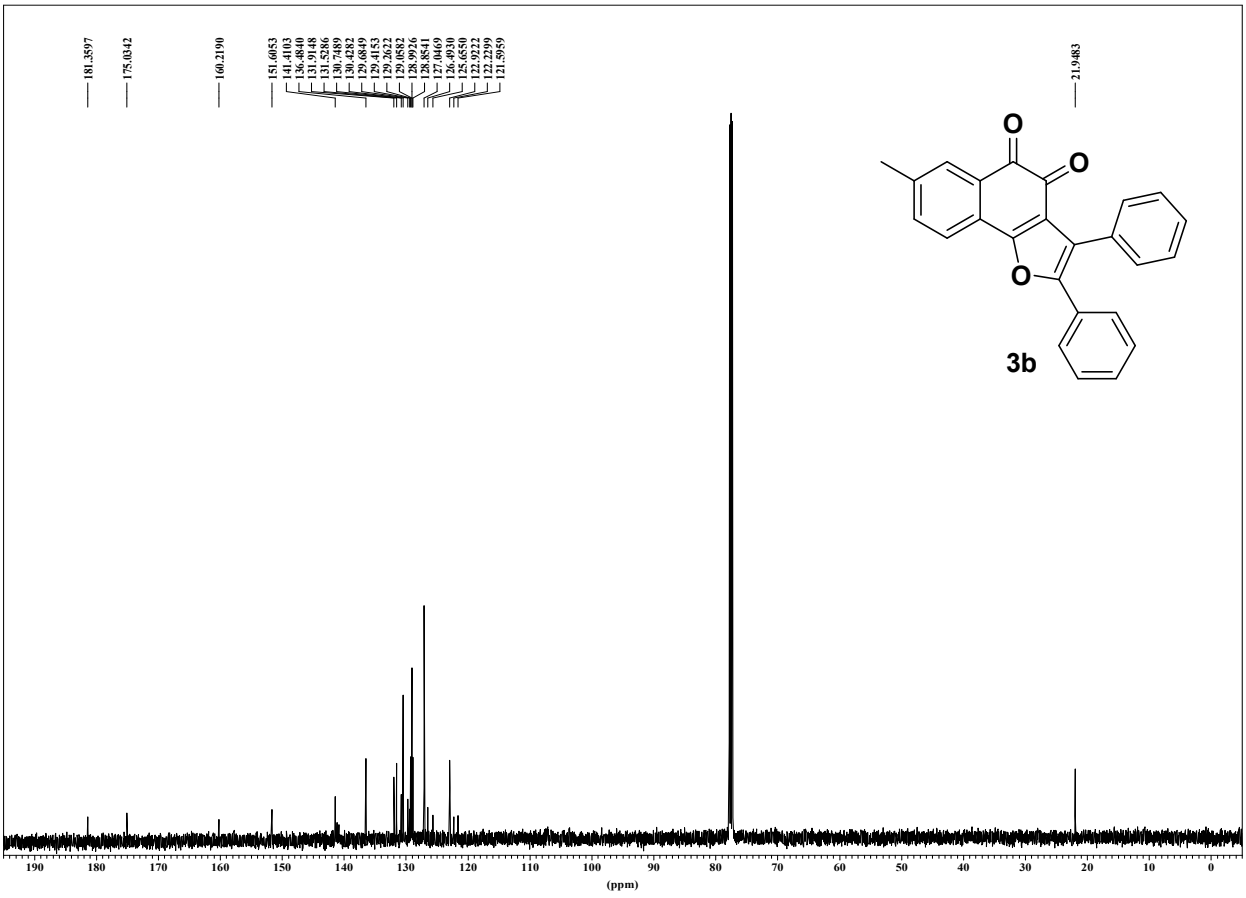
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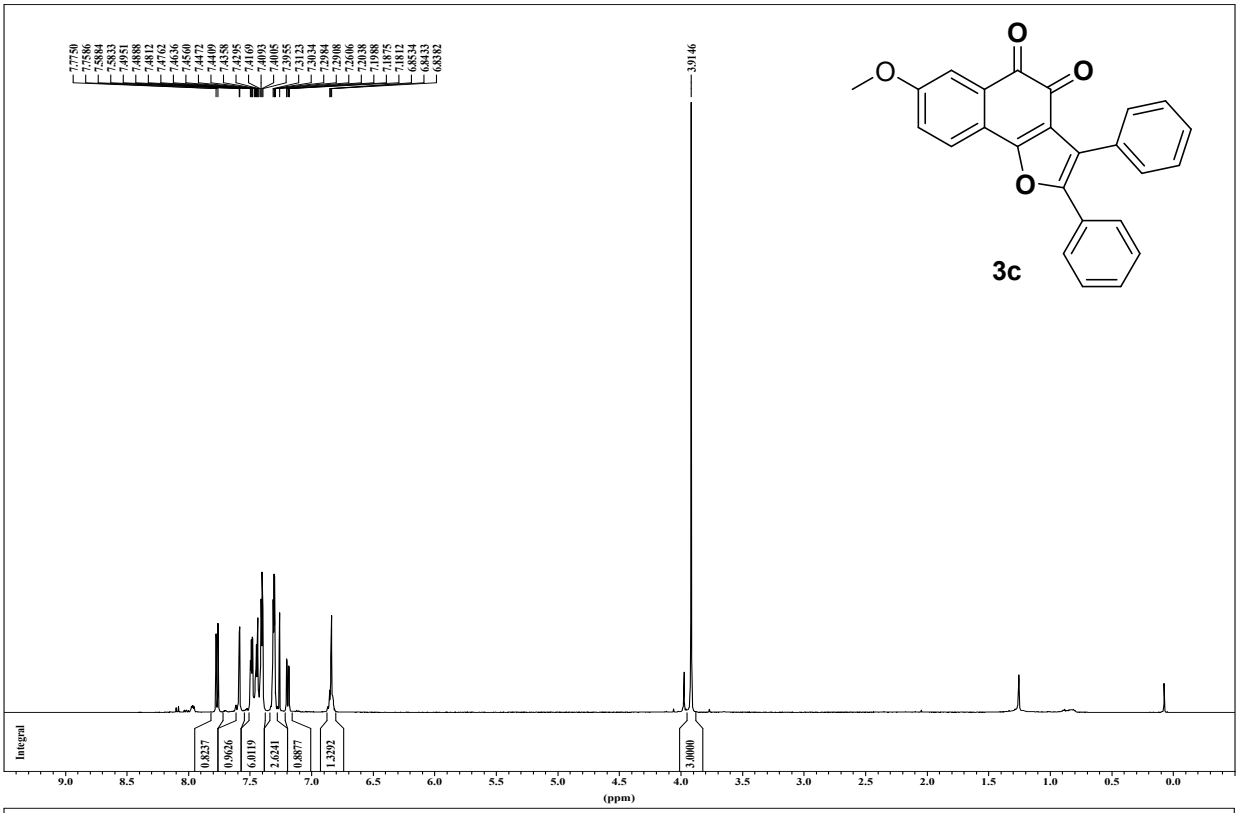
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Integral
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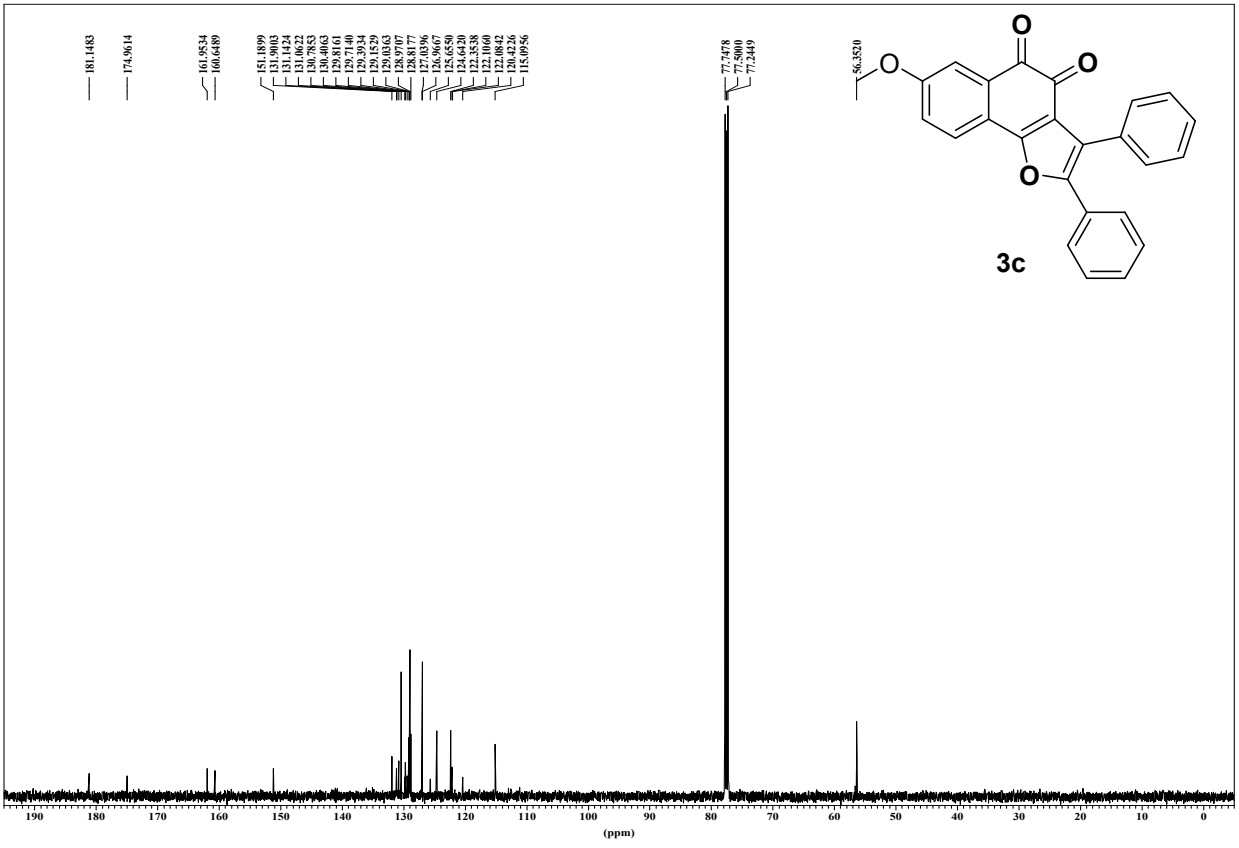
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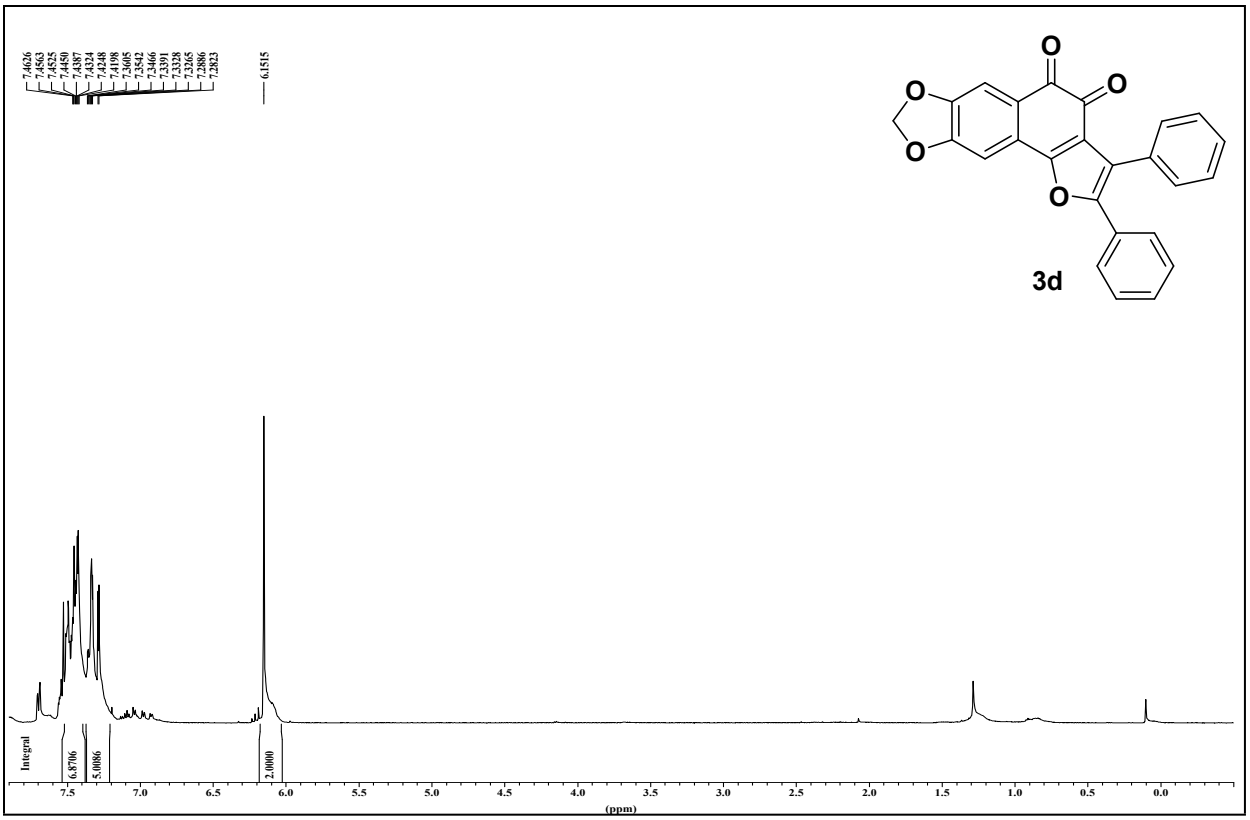
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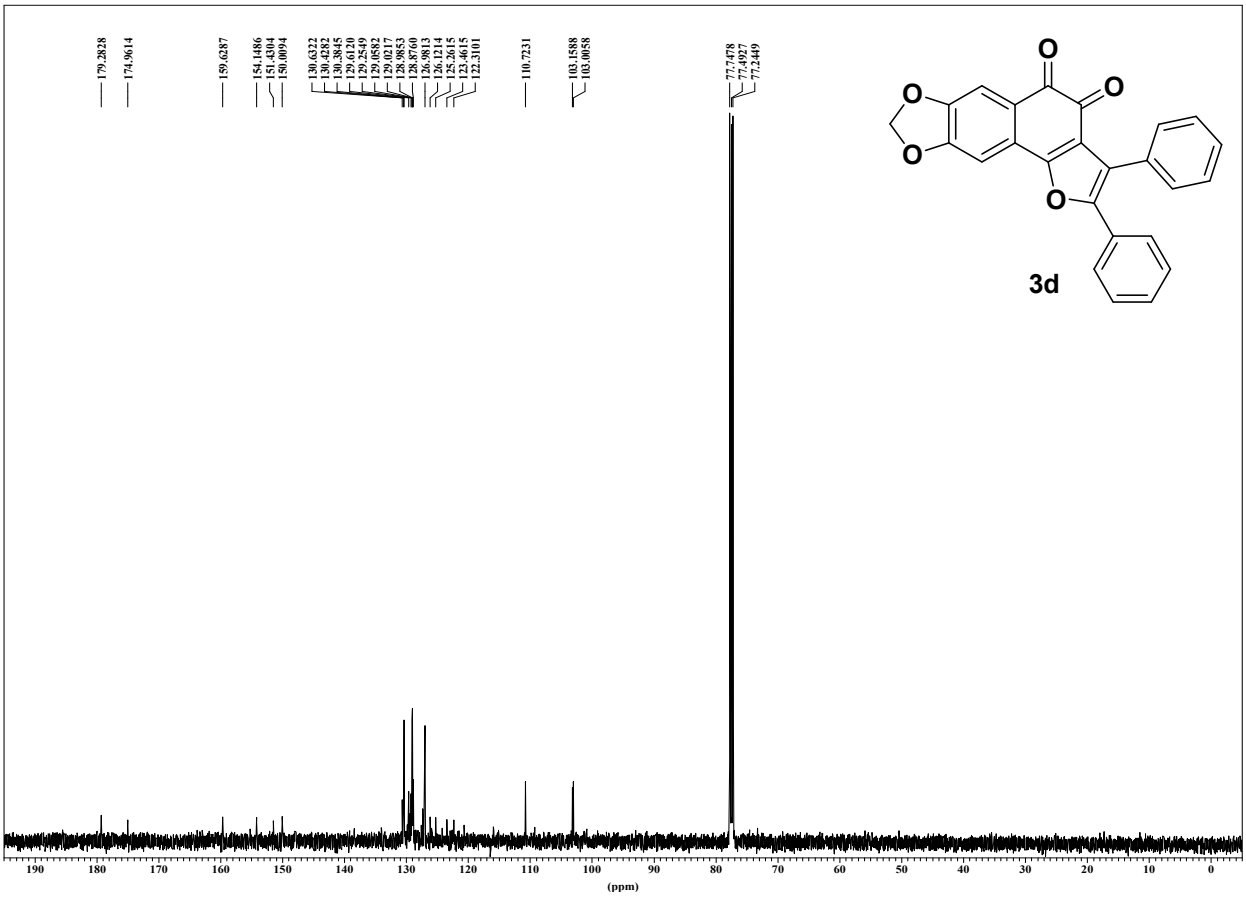
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129.0217
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126.1214
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103.0058
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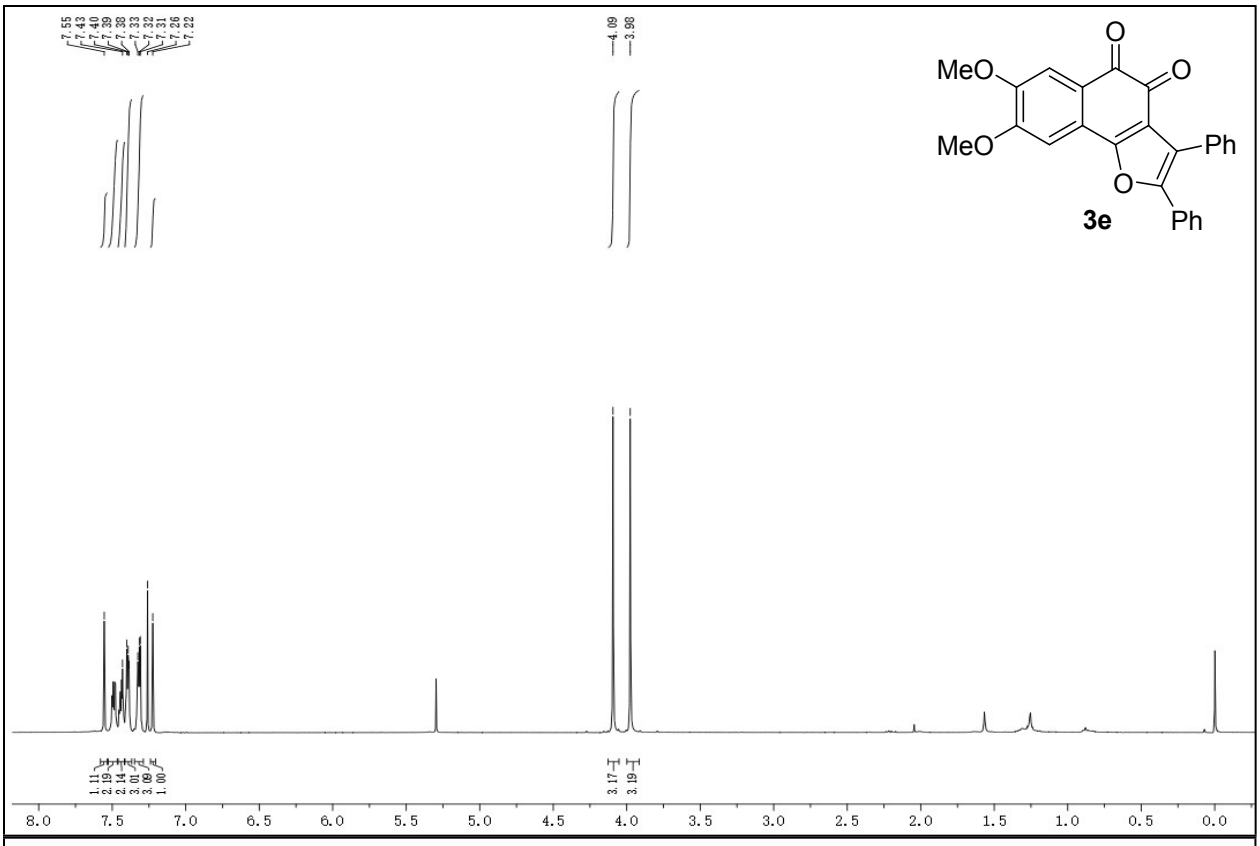
(ppm)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MeO
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Ph
Ph
O
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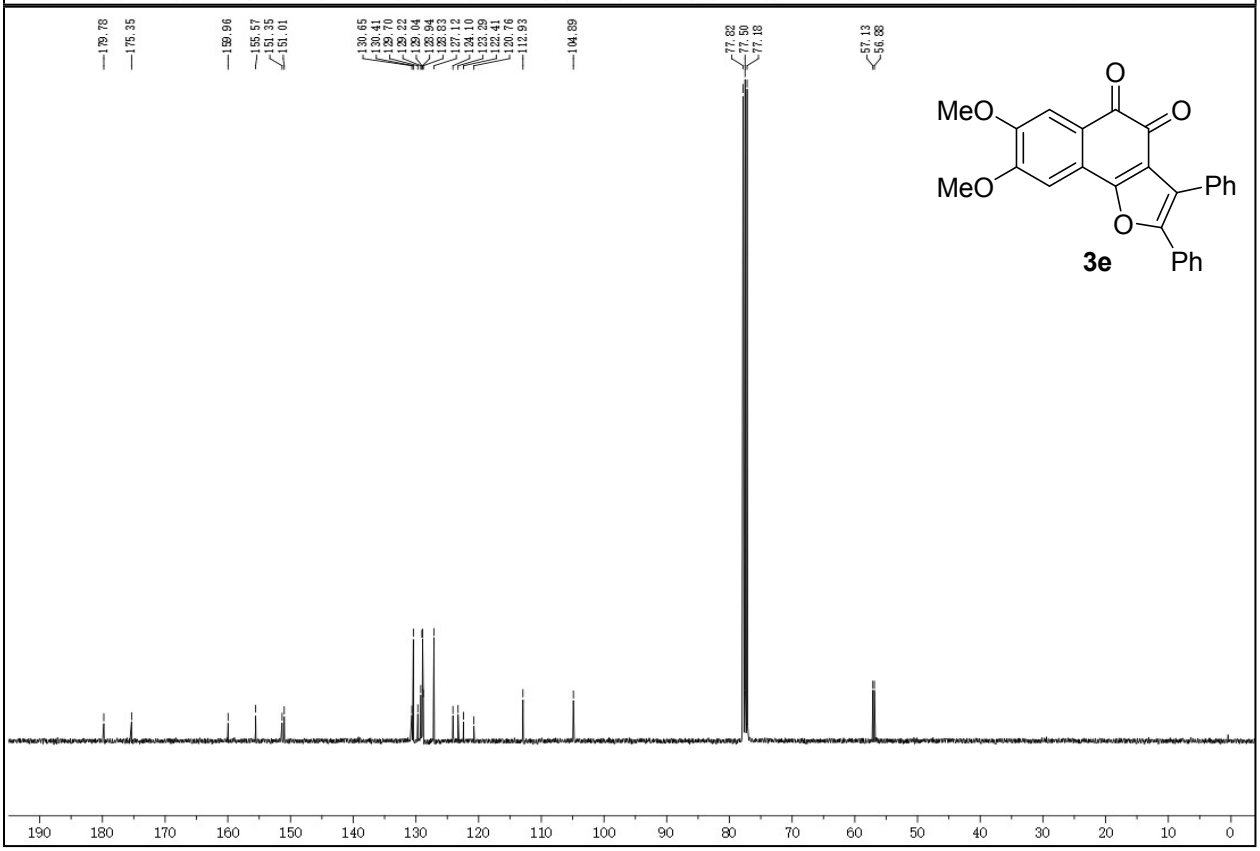
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MeO
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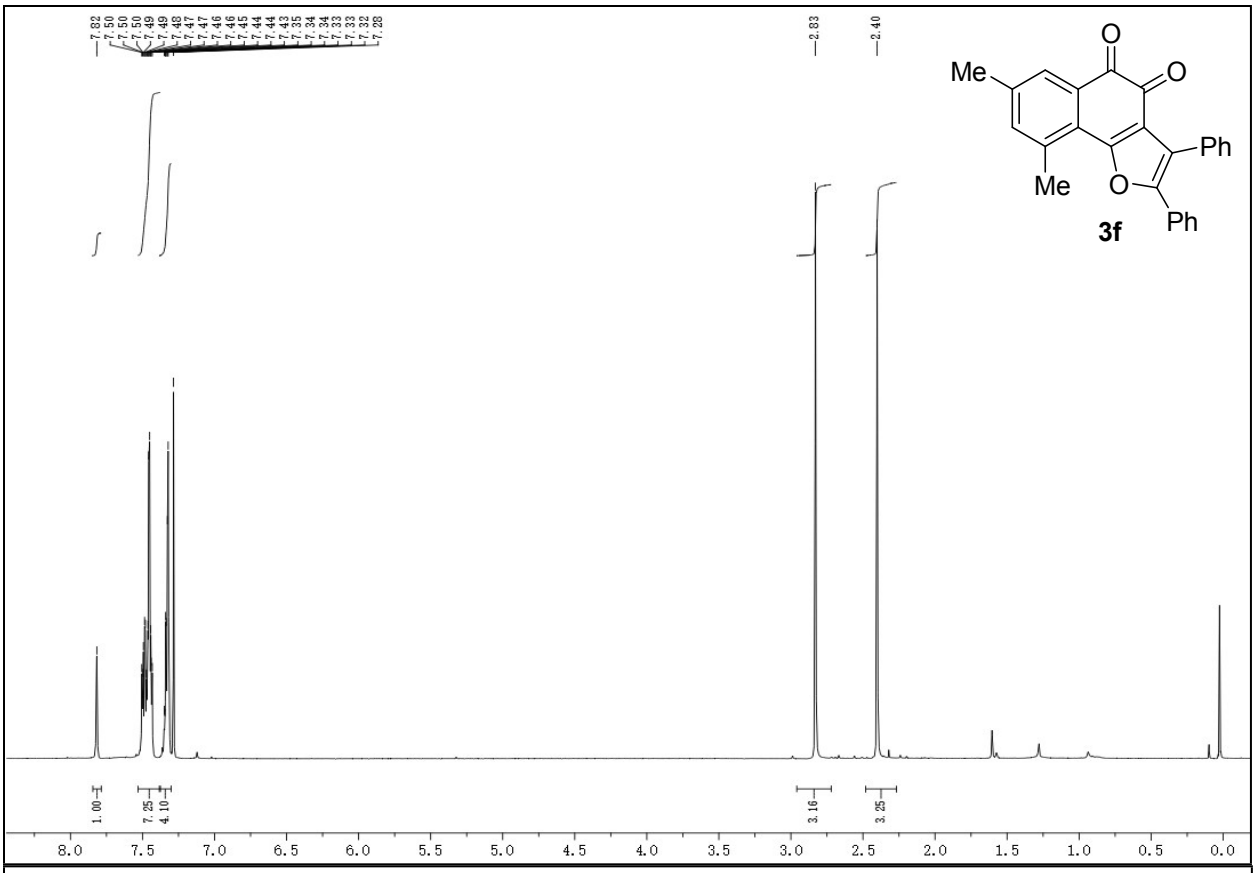
Ph
Ph
O
3e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7.45
7.45
7.44
7.44
7.43
7.35
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7.34
7.33
7.33
7.32
7.28
2.83
2.40
1.00
7.25
4.10
3.16
3.25
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7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
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Ph
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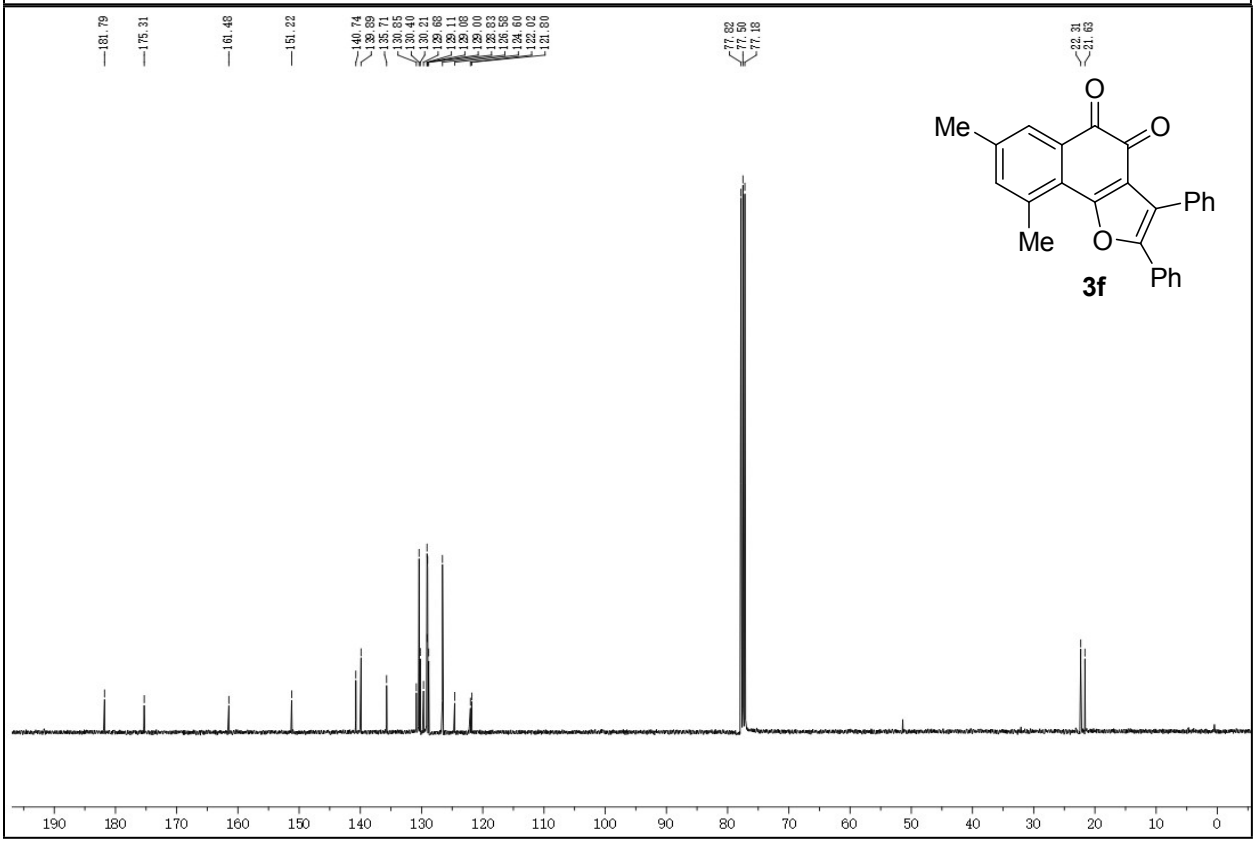
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129.08
129.00
128.83
126.58
124.60
122.02
121.80
77.82
77.50
77.18
22.31
21.63
Me
O
O
Ph
Me
O
Ph
3f
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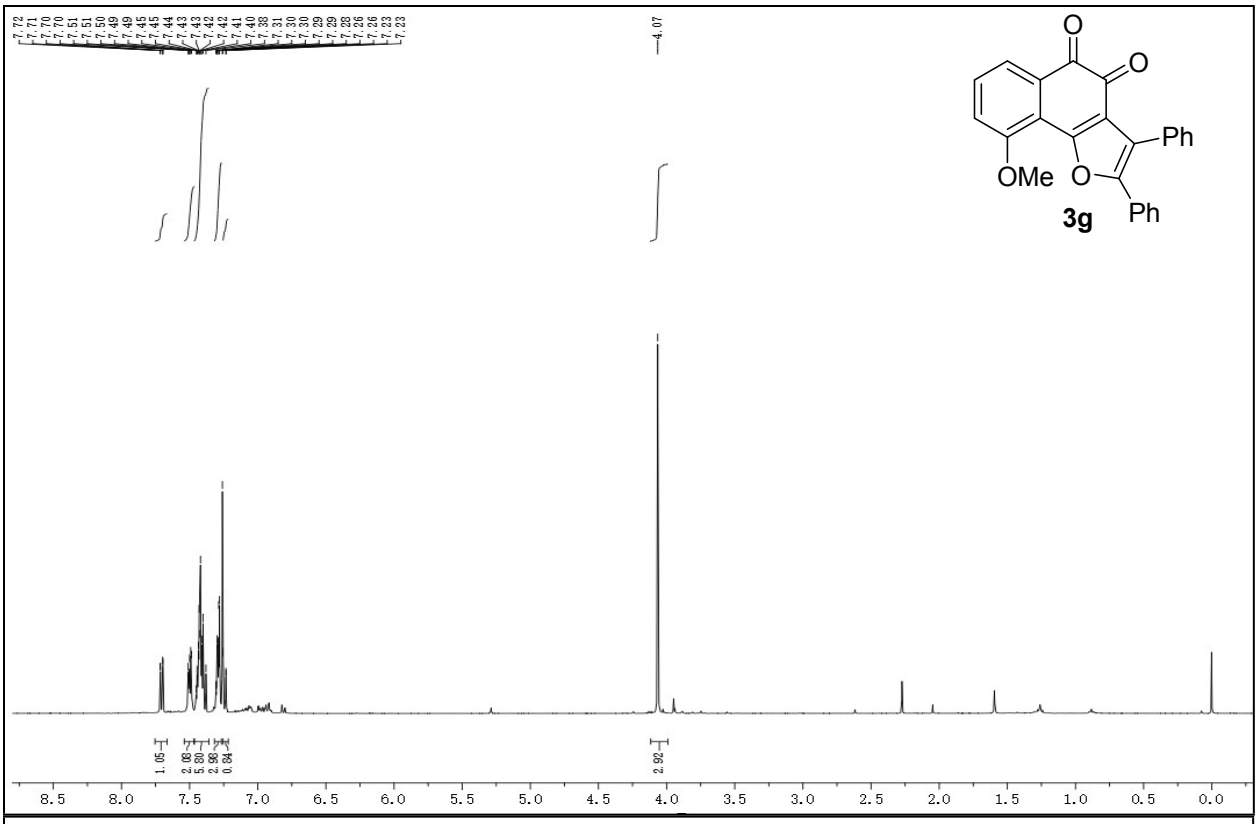
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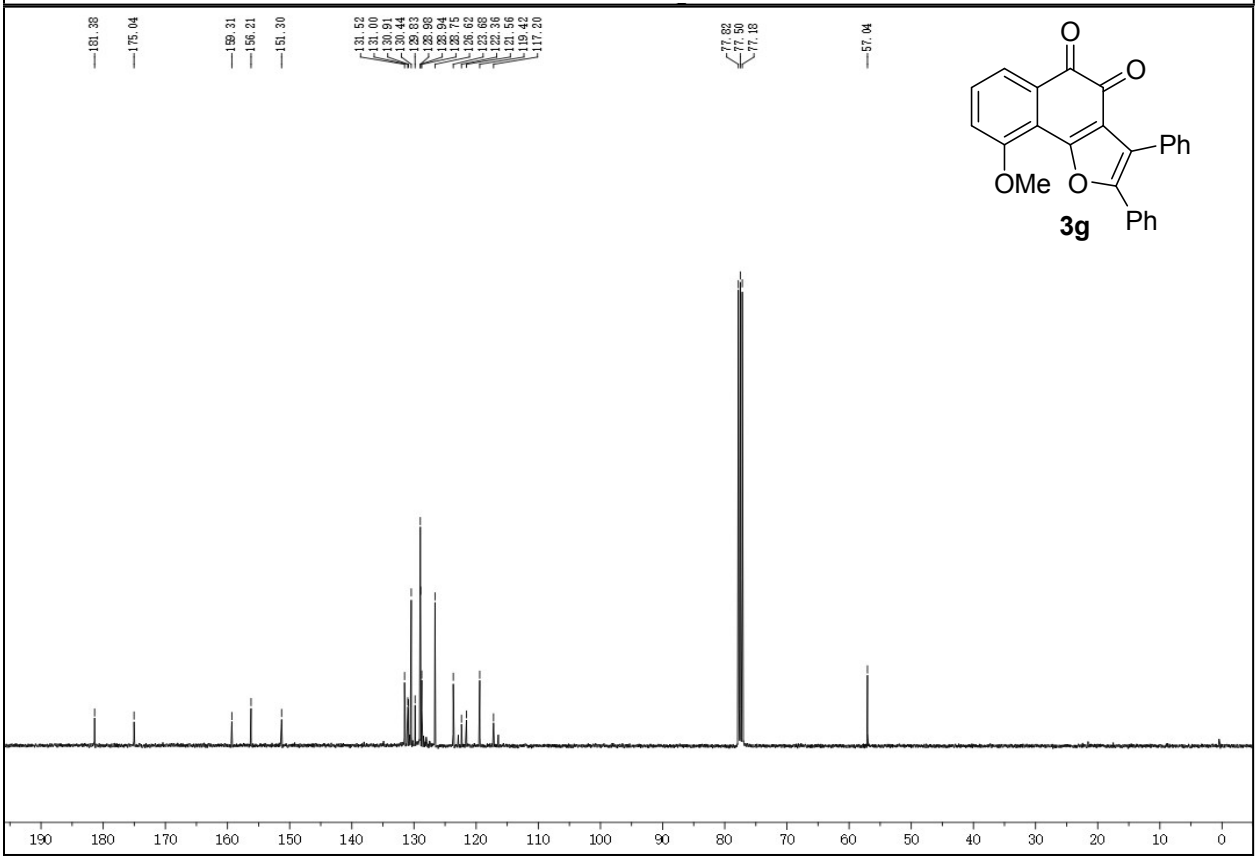
O
Ph
OMe
O
Ph
3g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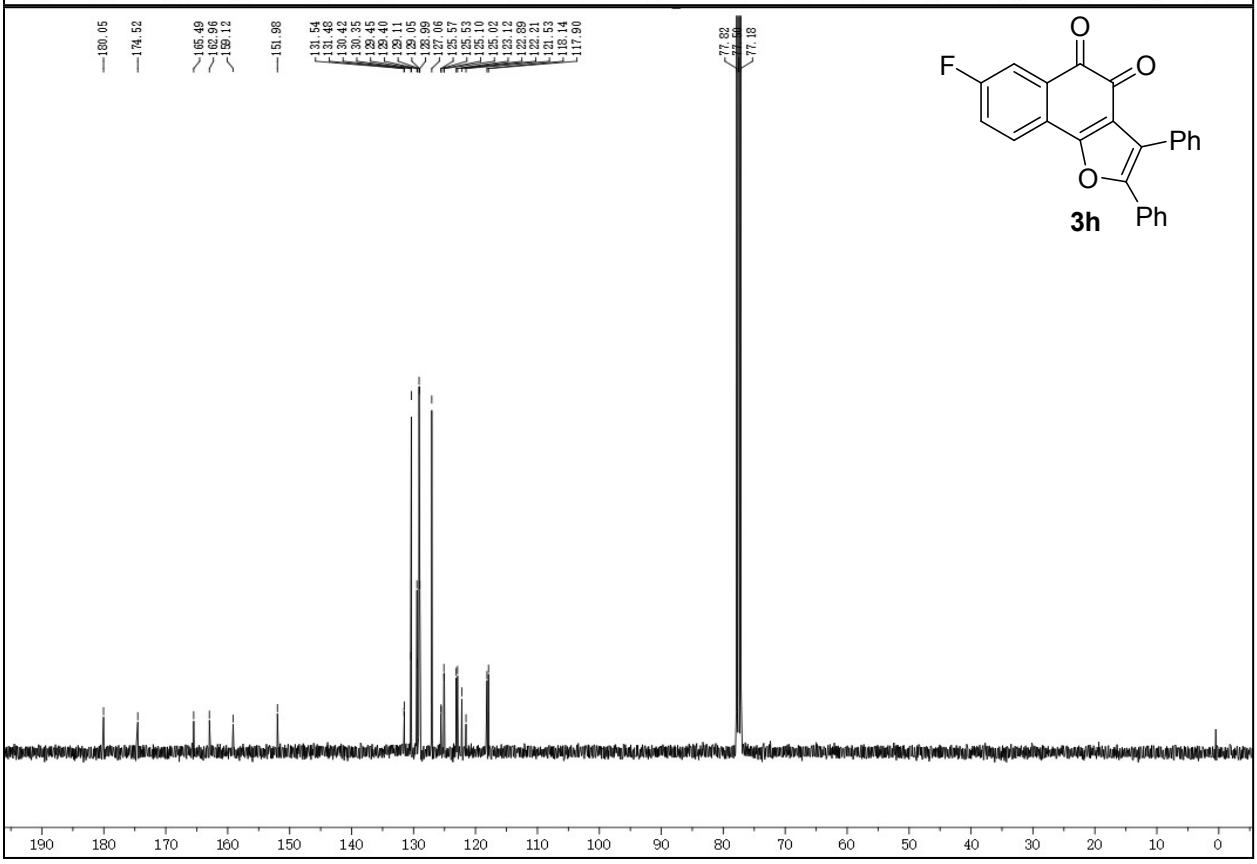
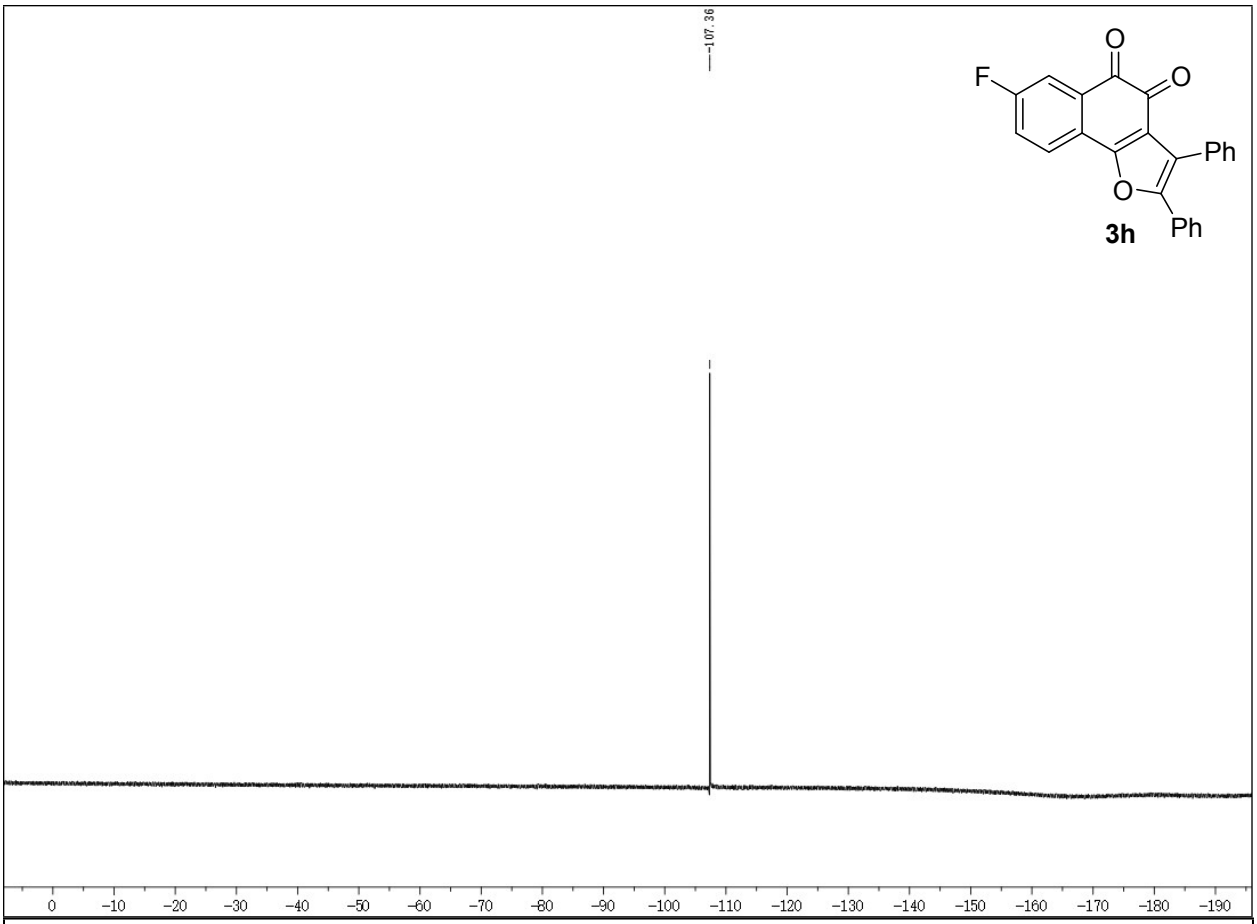
Ph
OMe
O
Ph
3g


F
O
O
Ph
O
Ph
3h


F
O
O
Ph
O
Ph
3h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Ph
3h
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-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


8.05
8.04
7.82
7.80
7.68
7.67
7.66
7.65
7.51
7.50
7.49
7.49
7.48
7.44
7.44
7.43
7.42
7.42
7.40
7.33
7.33
7.32
7.31
7.26
7.18
7.18
Cl
O
O
Ph
O
Ph
3i
0.89
0.91
1.00
1.92
4.20
3.13
0.92
8.5
8.0
7.5
7.0
6.5
6.0
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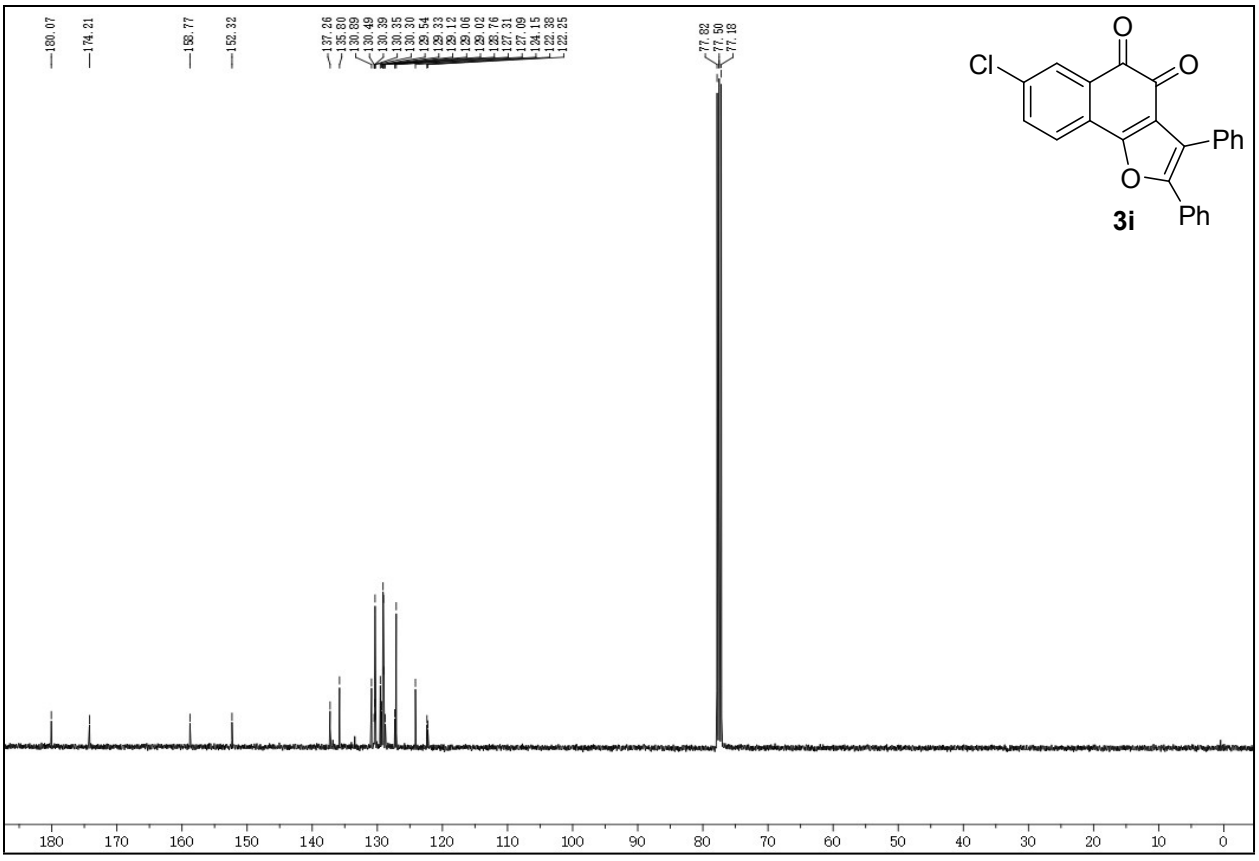
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130.49
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129.33
129.12
129.06
129.02
128.76
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127.09
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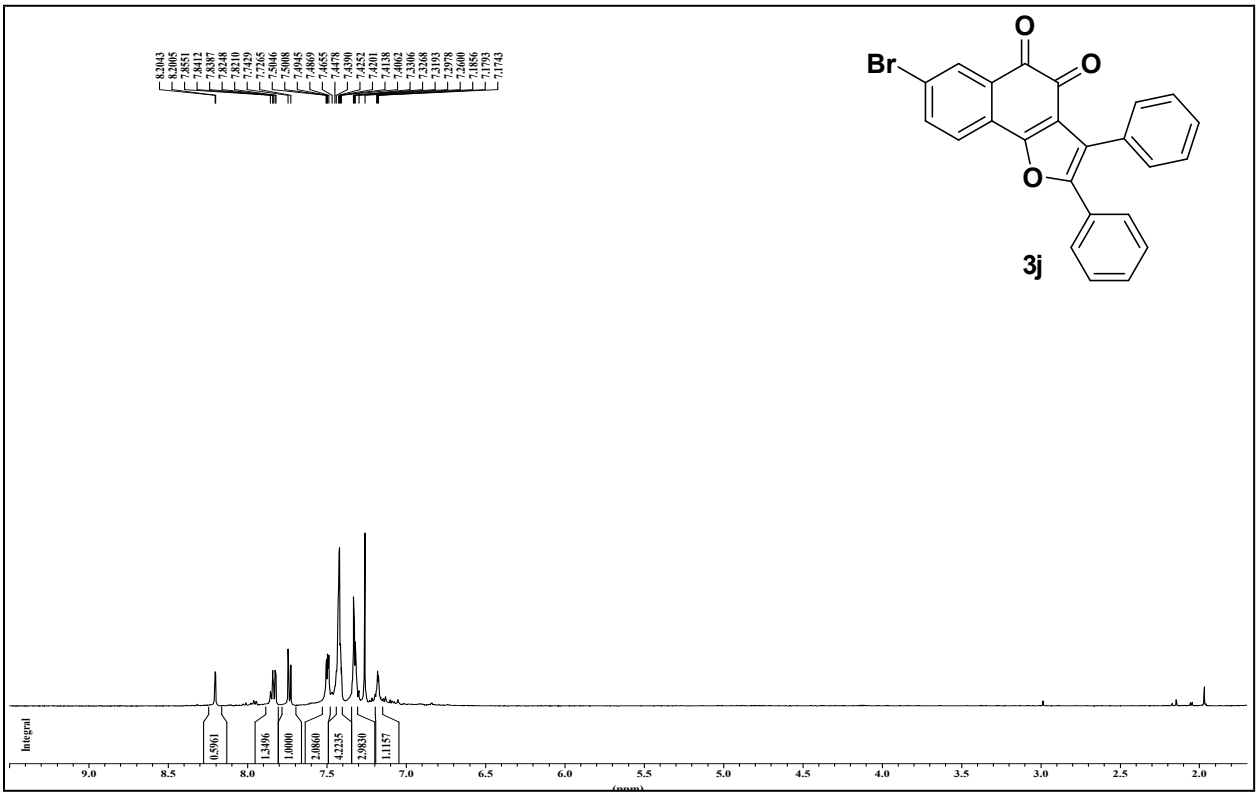
122.38
123.25
77.82
77.50
77.18
Cl
O
O
Ph
O
Ph
3i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7.4945
7.4869
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7.4478
7.4390
7.4252
7.4201
7.4158
7.4062
7.3306
7.3268
7.3193
7.2978
7.2600
7.1856
7.1793
7.1743
Br
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O
O
3j
Integral
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2.0860
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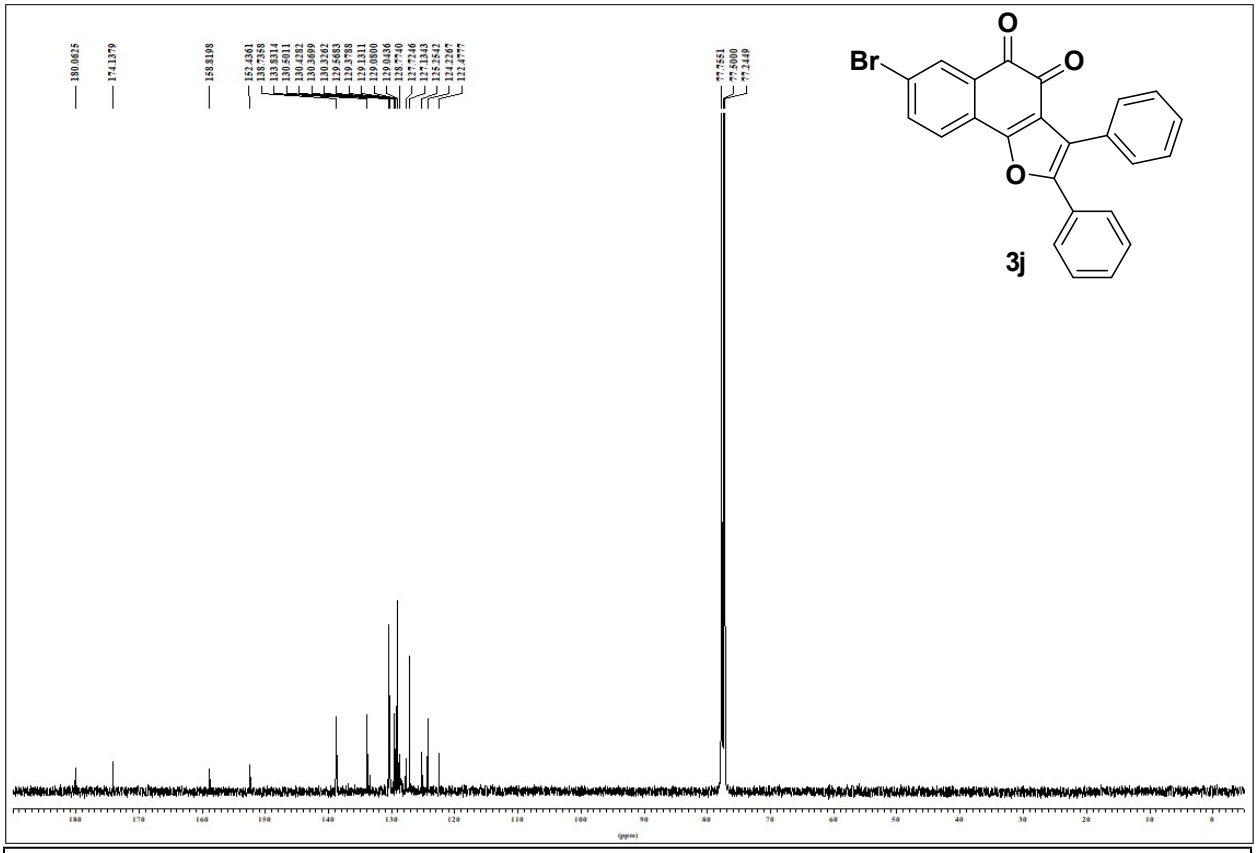
2.9830
1.1157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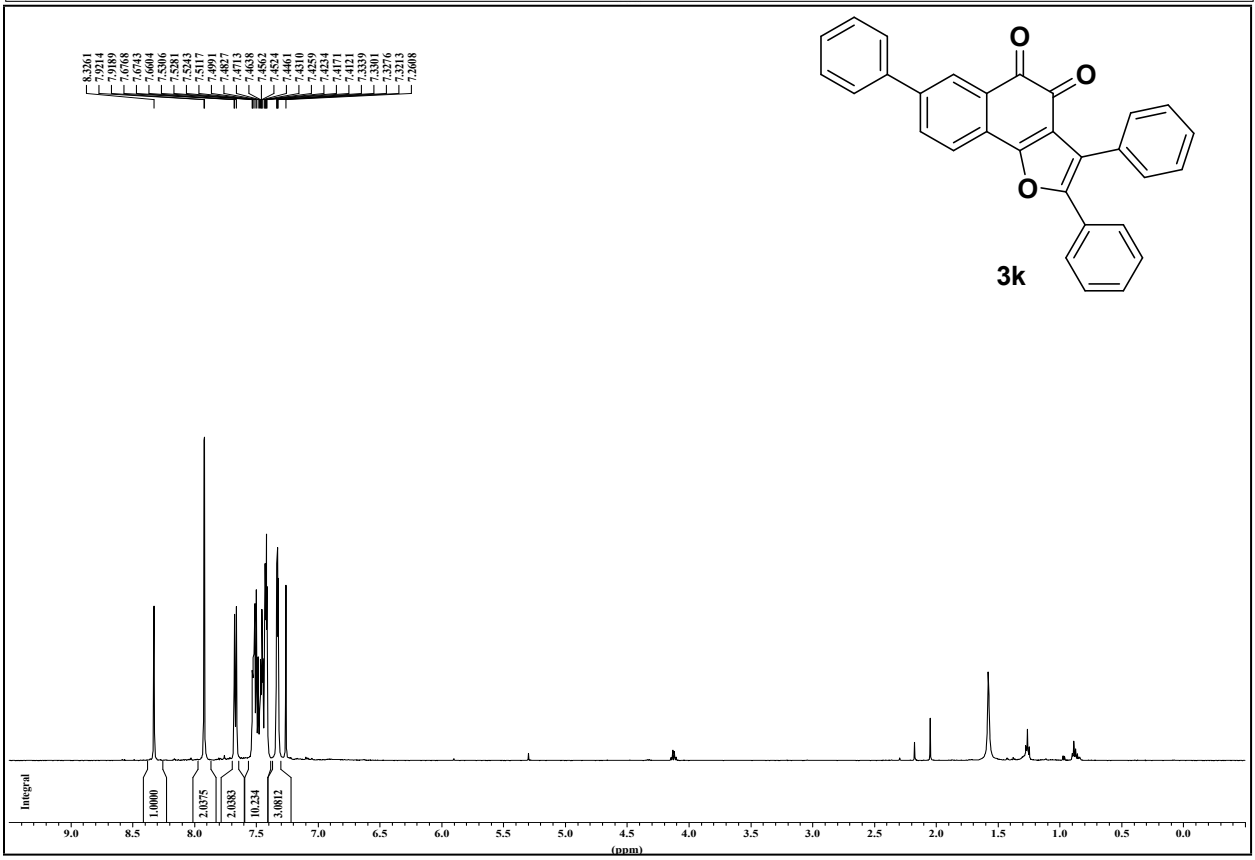
77.5000
77.2349
Br
O
O
O
3j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7.4991
7.4827
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7.4638
7.4562
7.4524
7.4464
7.4410
7.4259
7.4234
7.4171
7.4121
7.3339
7.3301
7.3276
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O
O
3k
Integral
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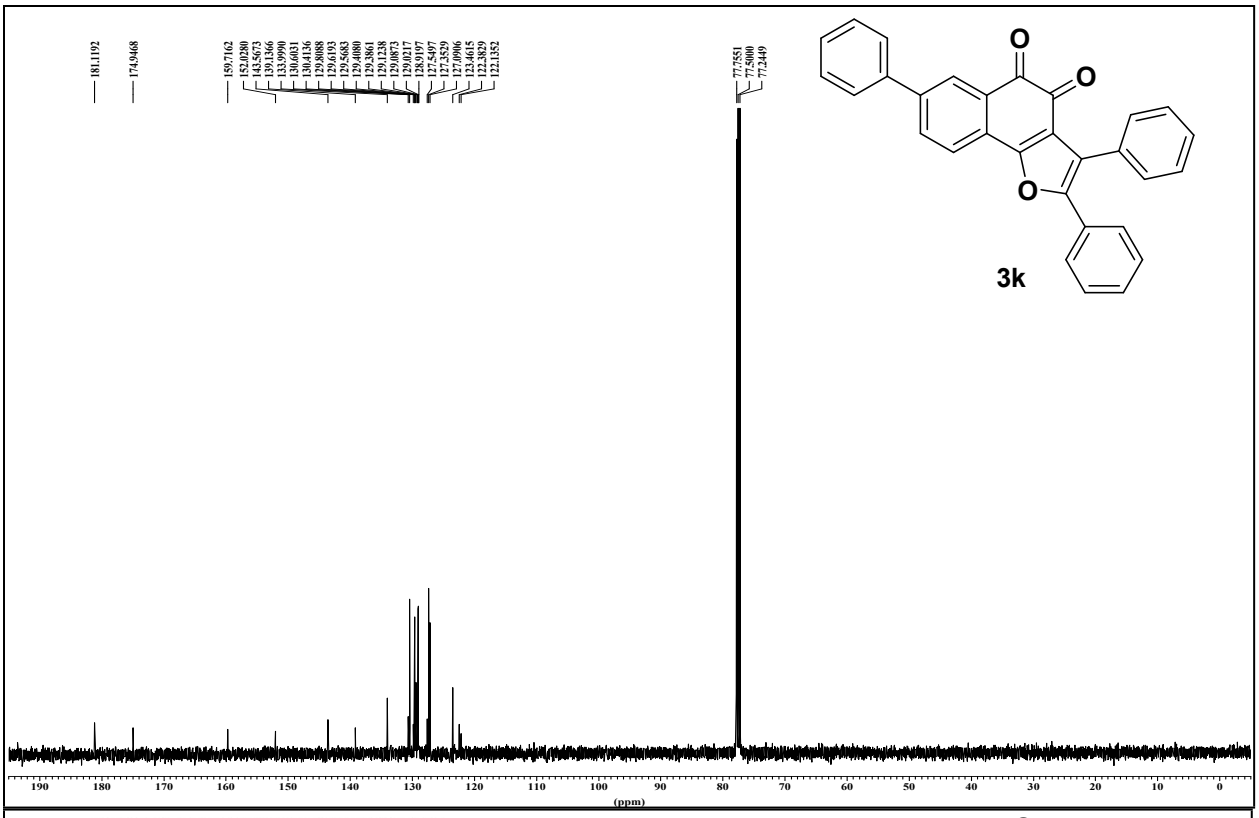
(ppm)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127.3529
127.0996
123.4615
123.3839
122.1352
77.7551
77.3000
77.2449
O
O
O
3k
190
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120
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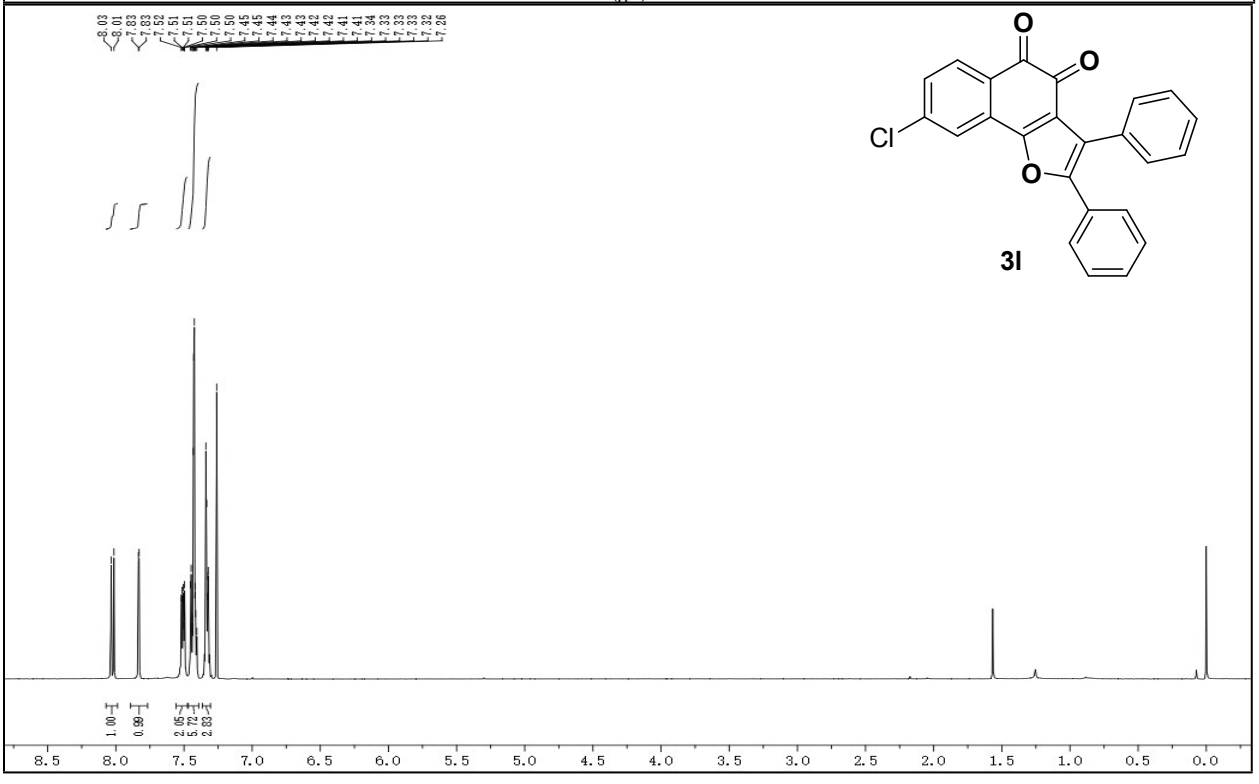
(ppm)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7.50
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7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.34
7.33
7.33
7.33
7.32
7.28
O
O
Cl
O
3l
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0.99
2.05
5.72
2.83
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8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
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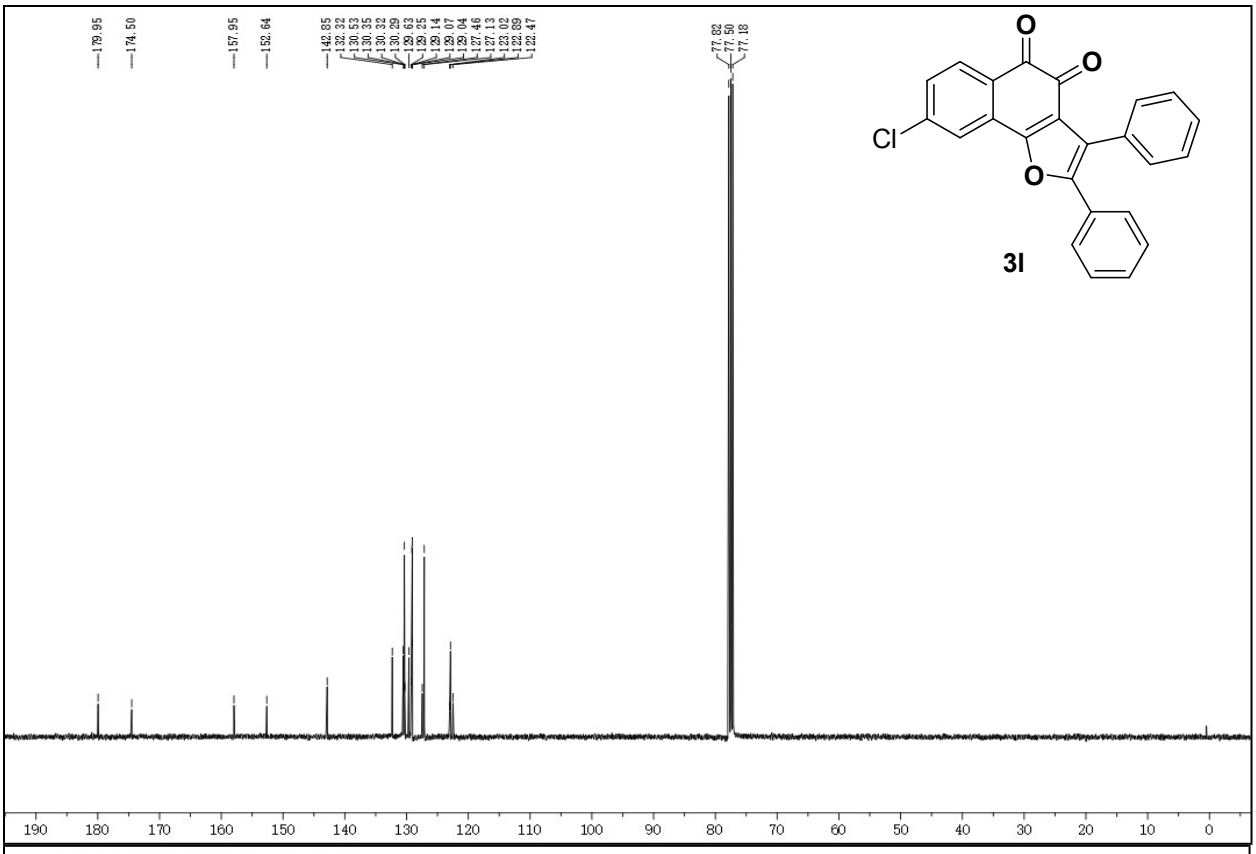
0.0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129.14
129.07
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123.02
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122.47
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77.50
77.18
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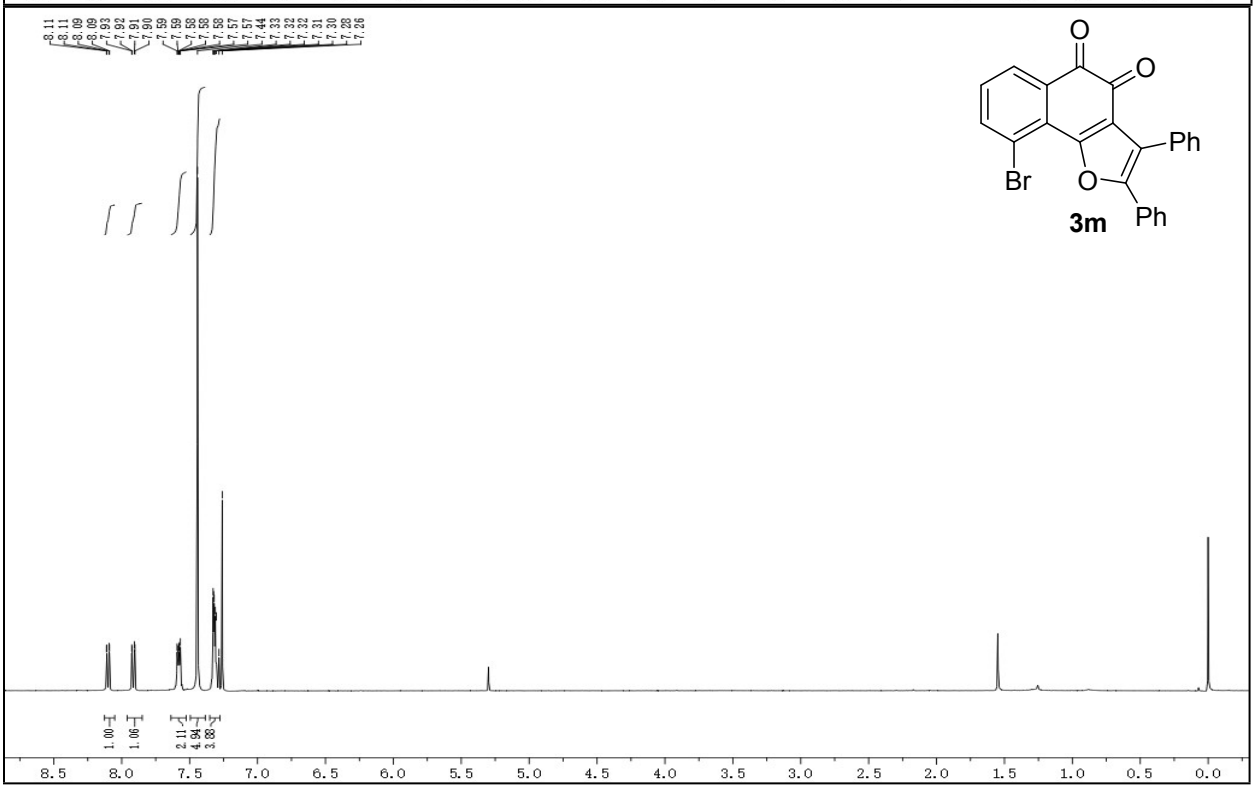
O
Cl
O
3l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7.90
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7.59
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7.58
7.58
7.58
7.57
7.57
7.44
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7.32
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7.31
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O
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Br
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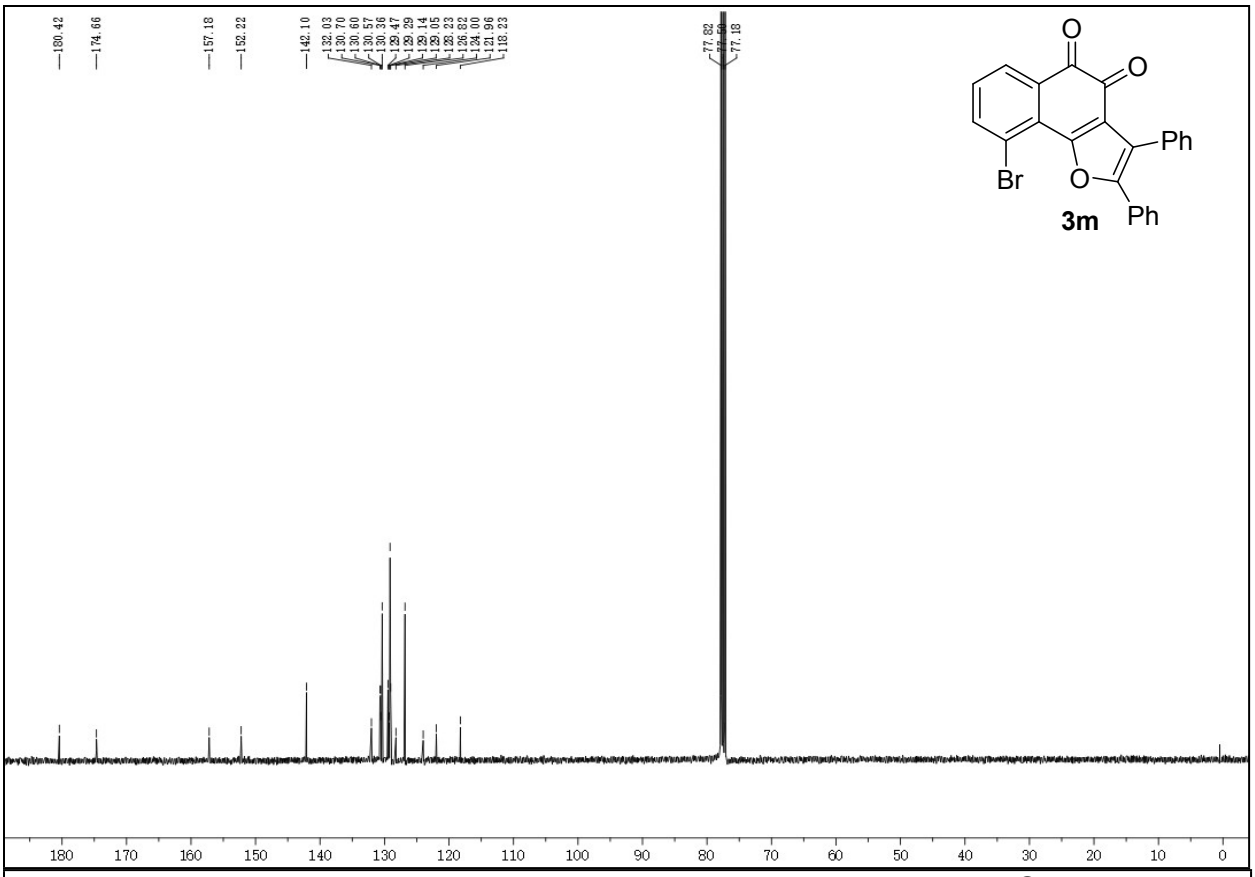
3.88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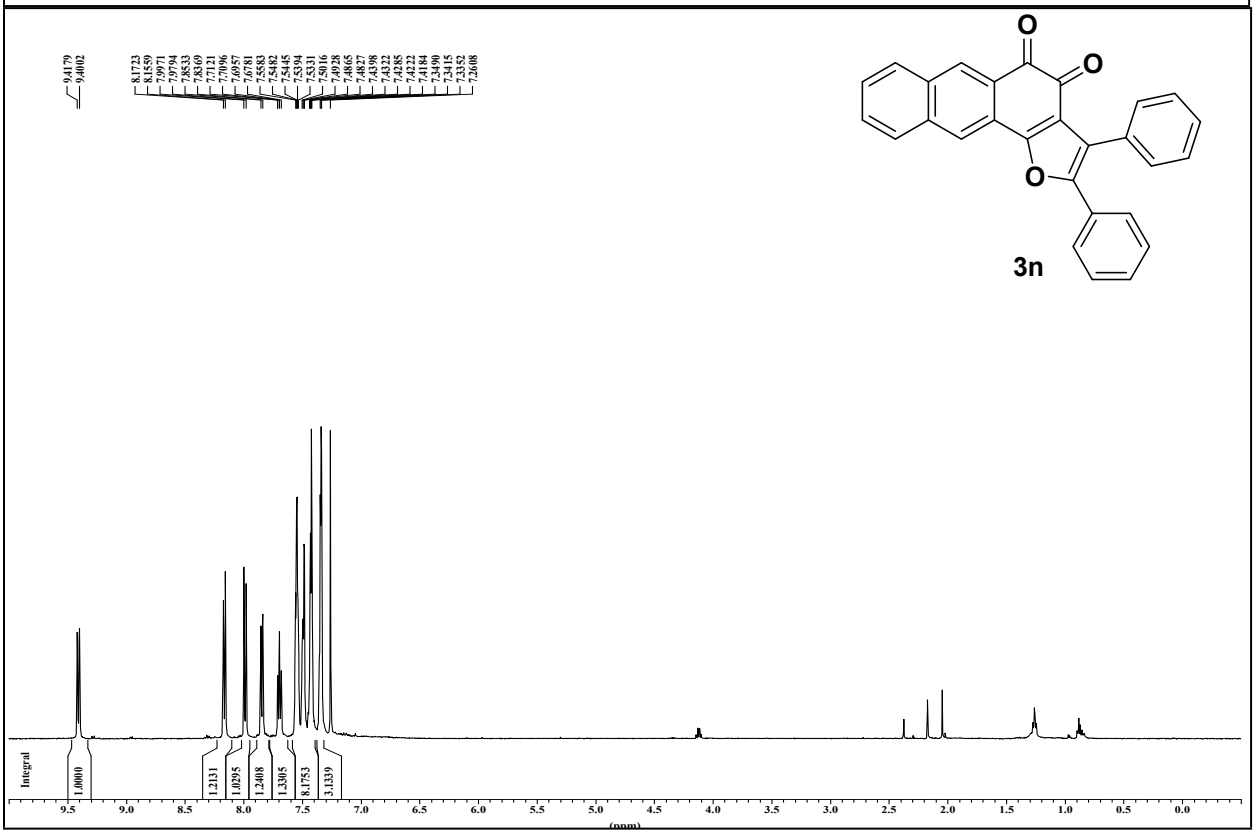
Br
O
Ph
3m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7.3352
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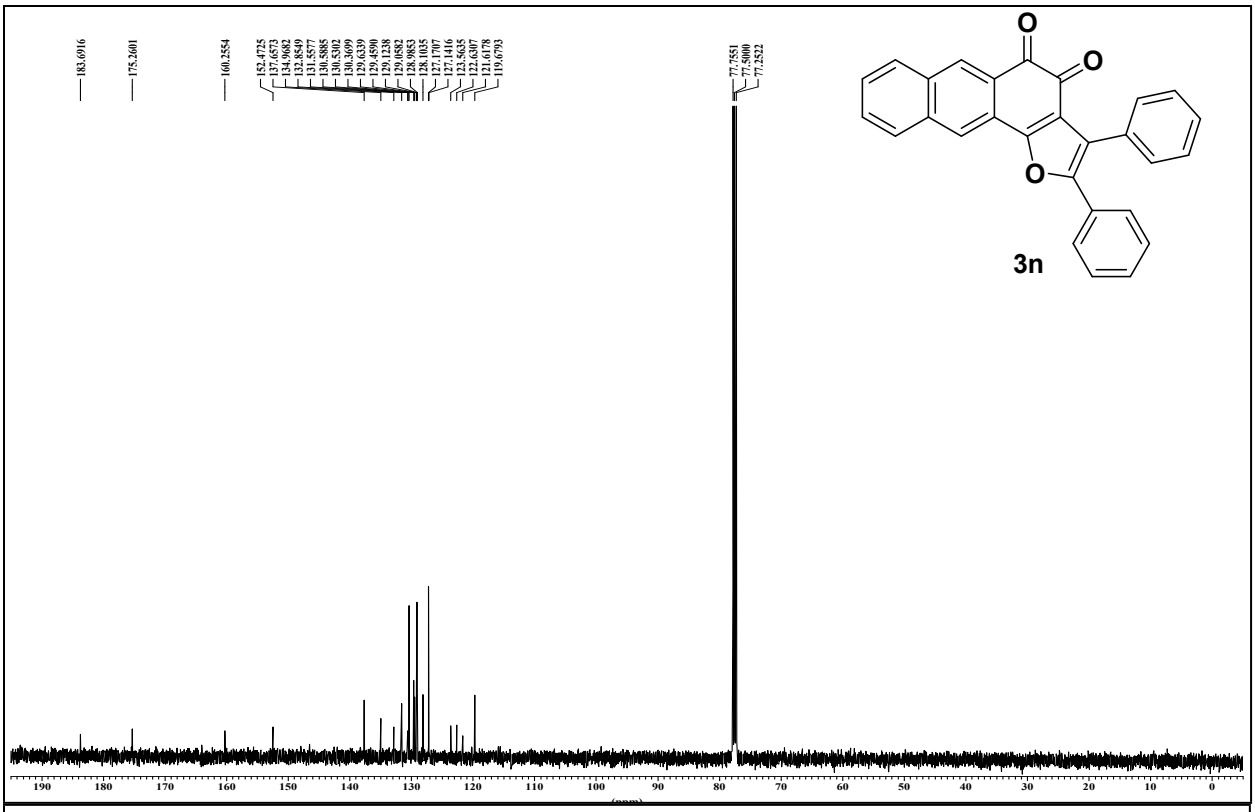
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O
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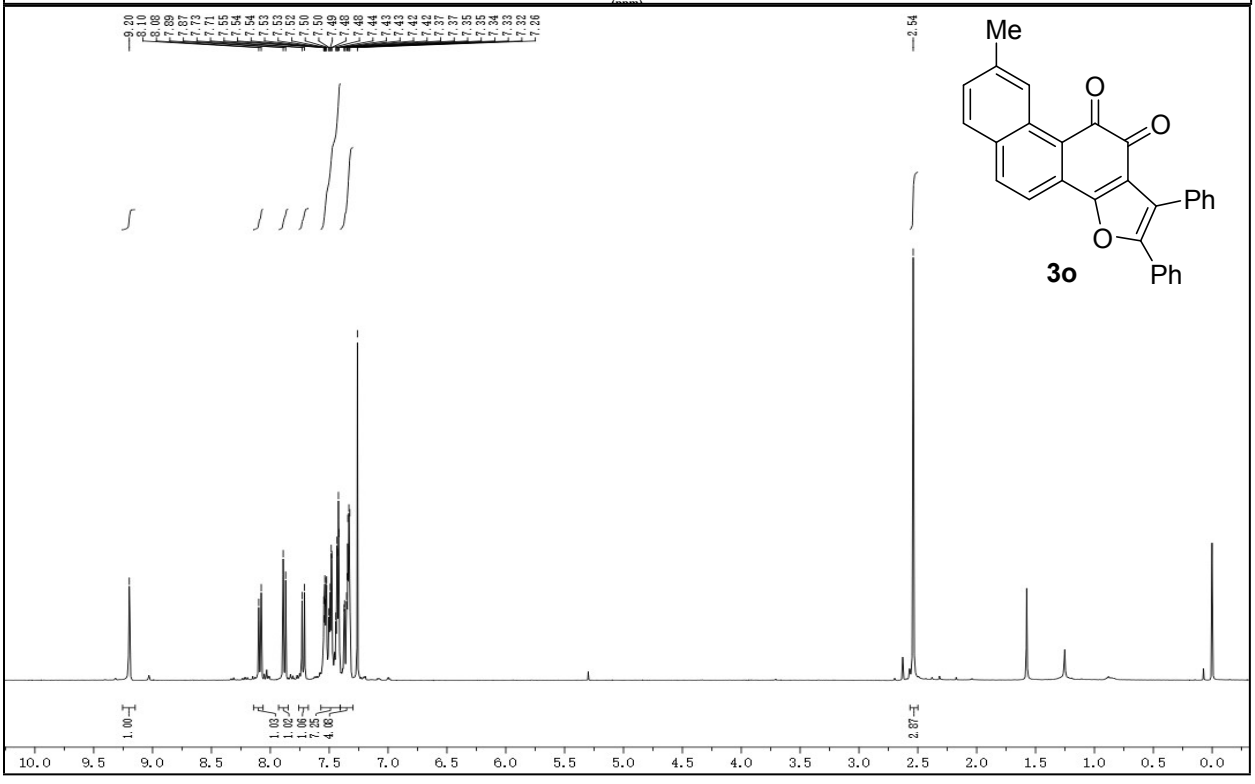
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7.48
7.44
7.43
7.43
7.42
7.42
7.37
7.37
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7.35
7.34
7.33
7.32
7.26
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Ph
O
Ph
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1.02
1.05
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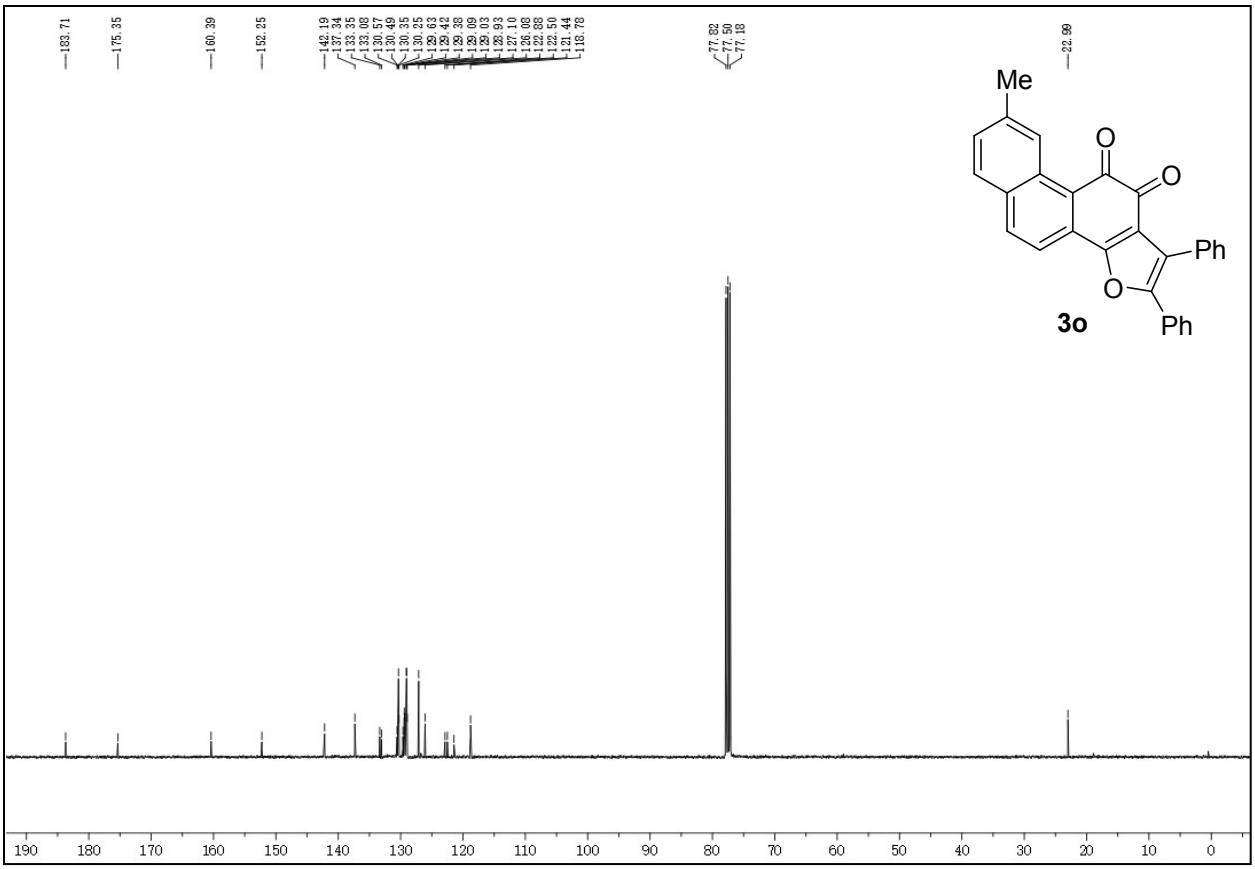
4.00
2.87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129.38
129.09
128.03
127.93
127.10
126.08
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121.44
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77.82
77.50
77.18
22.99
Me
O
O
Ph
O
Ph
3o
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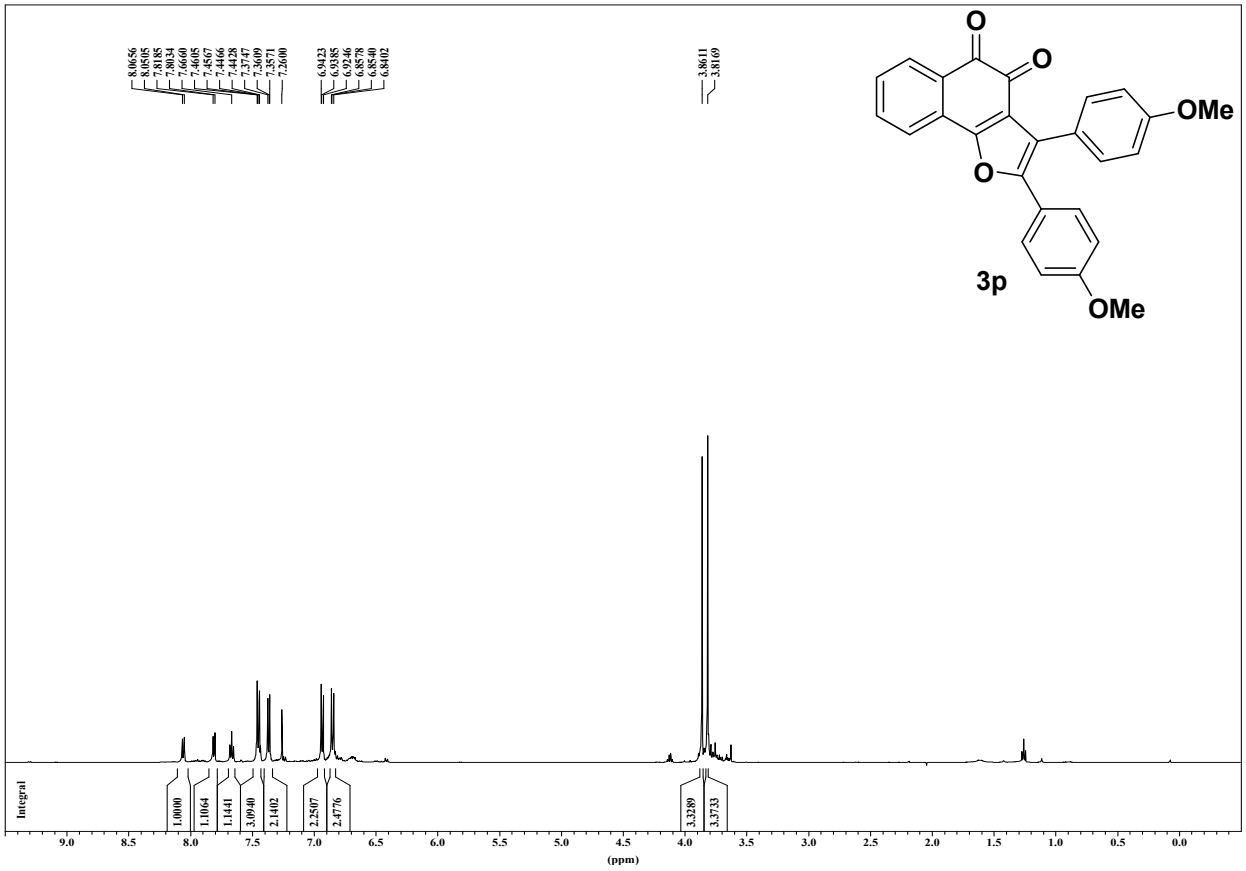
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6.9246
6.8578
6.8540
6.8402
3.8611
3.8169
O
O
OMe
O
3p
OMe
Integral
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6.0
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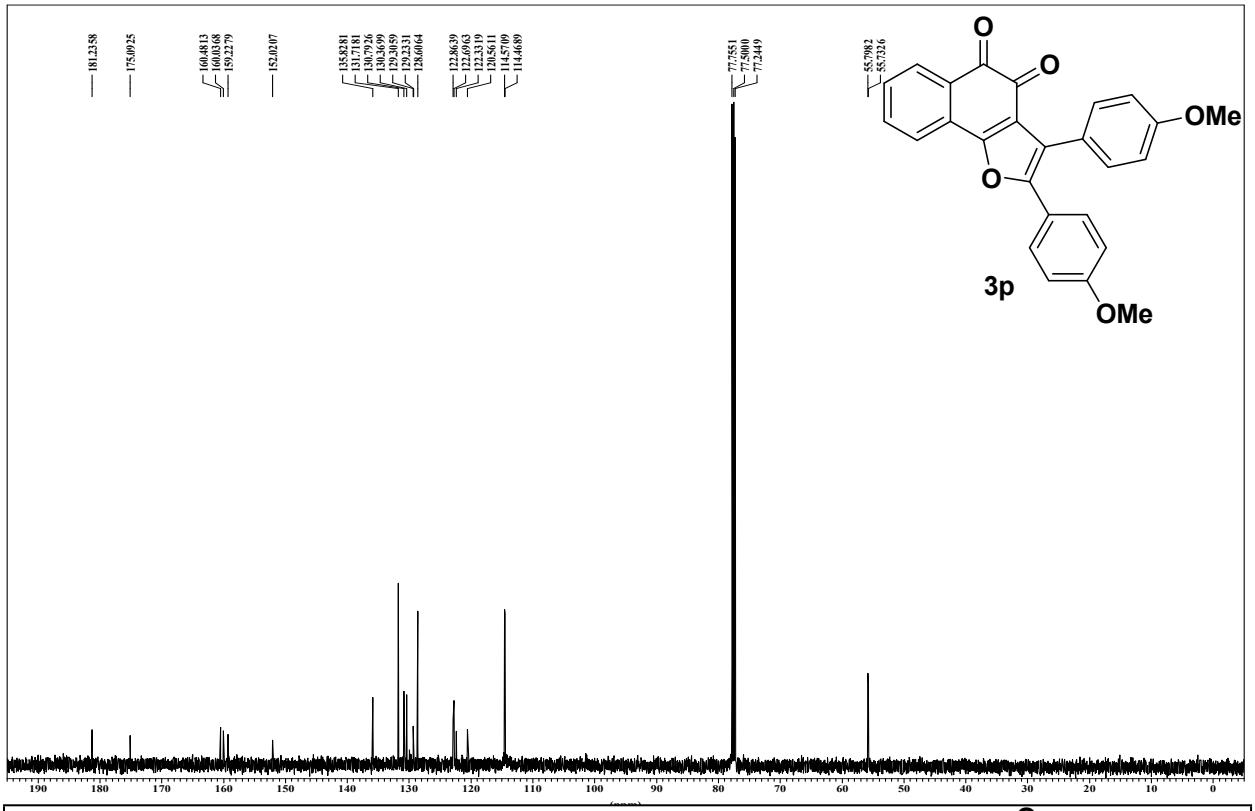
(ppm)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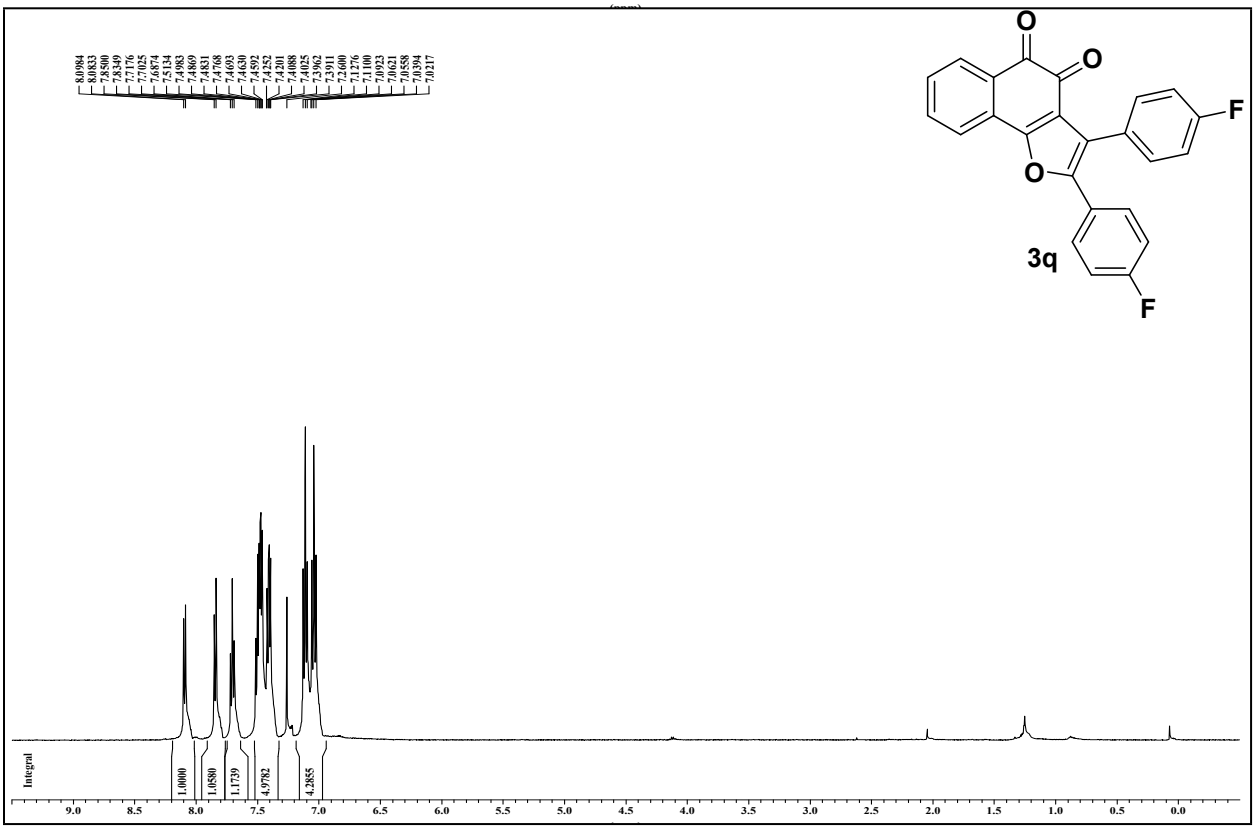
O
OMe
OMe
3p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7.1100
7.0923
7.0621
7.0558
7.0394
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O
F
F
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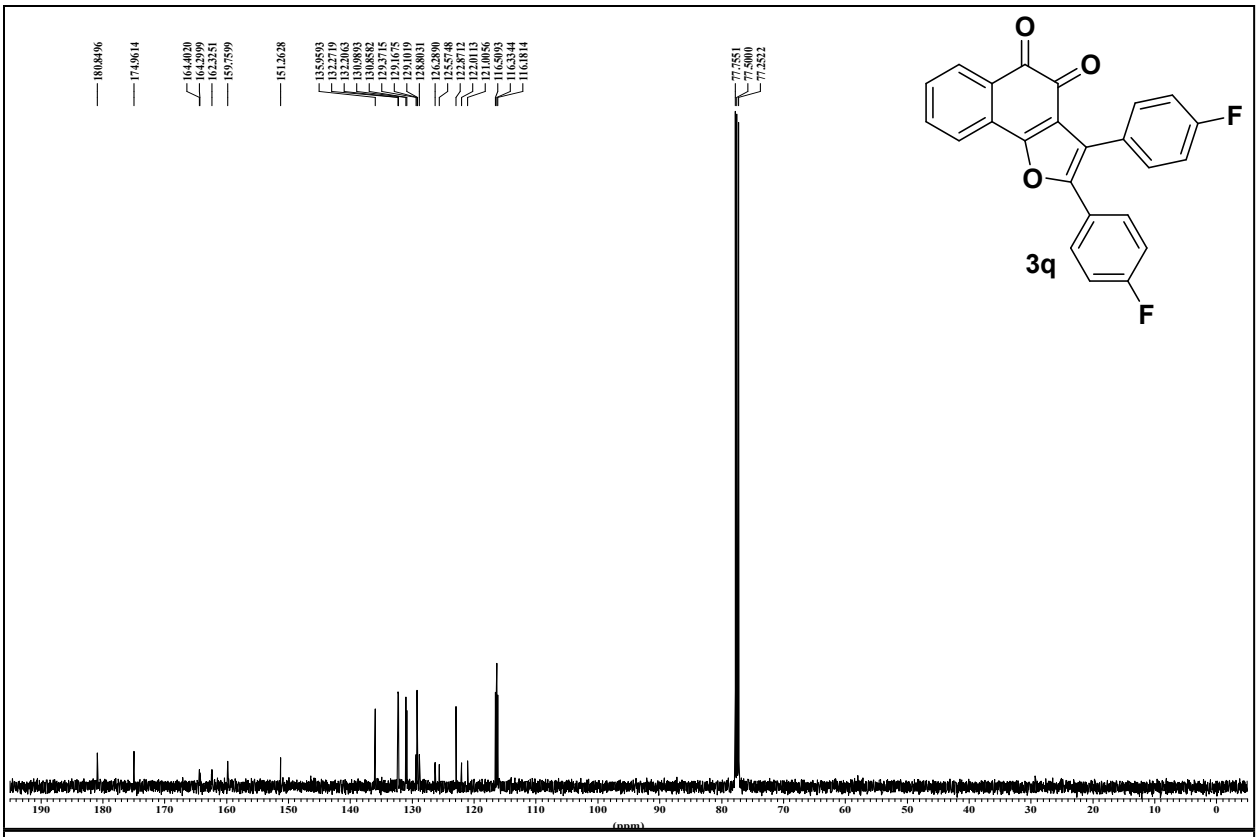
4.2855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121.0056
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O
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O
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3q
190
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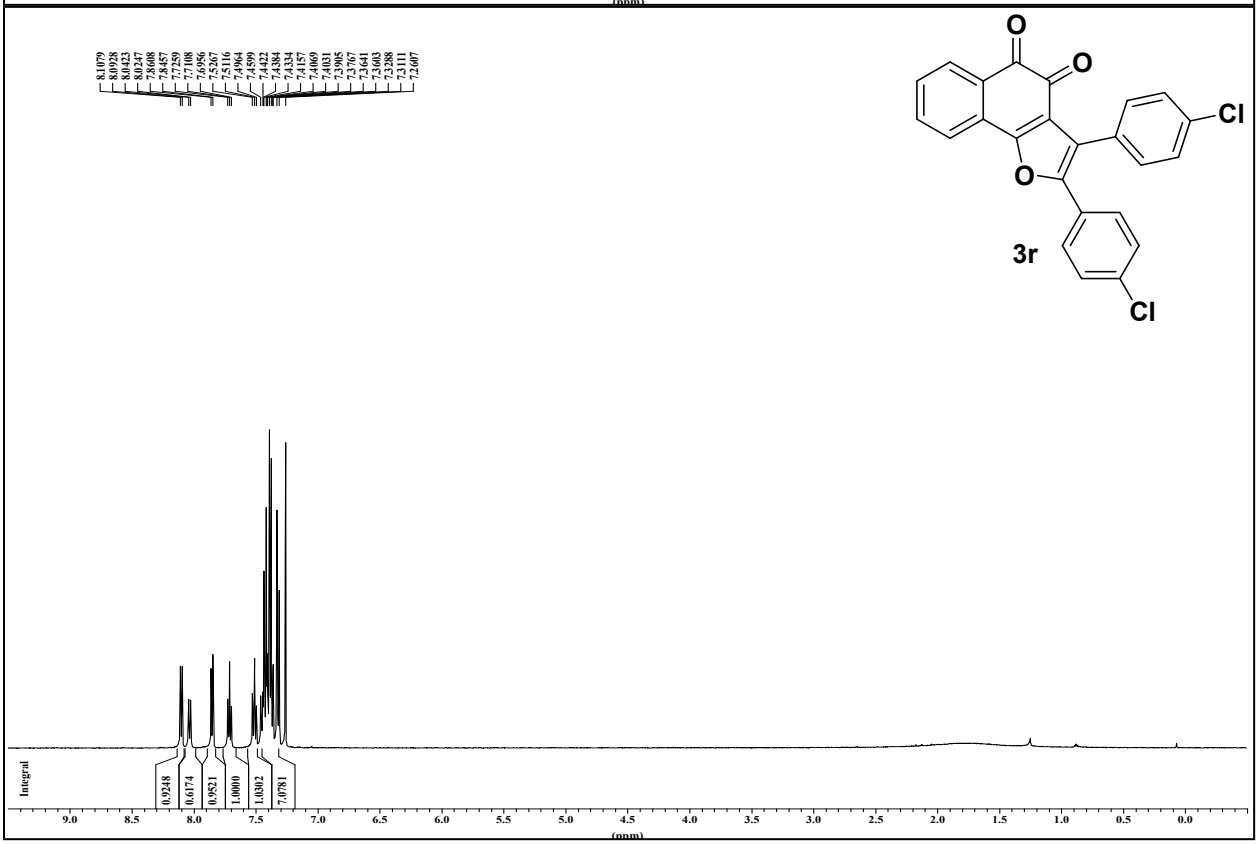
(ppm)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7.4031
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7.3641
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7.3111
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O
O
Cl
O
3r
Cl
Integral
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6.0
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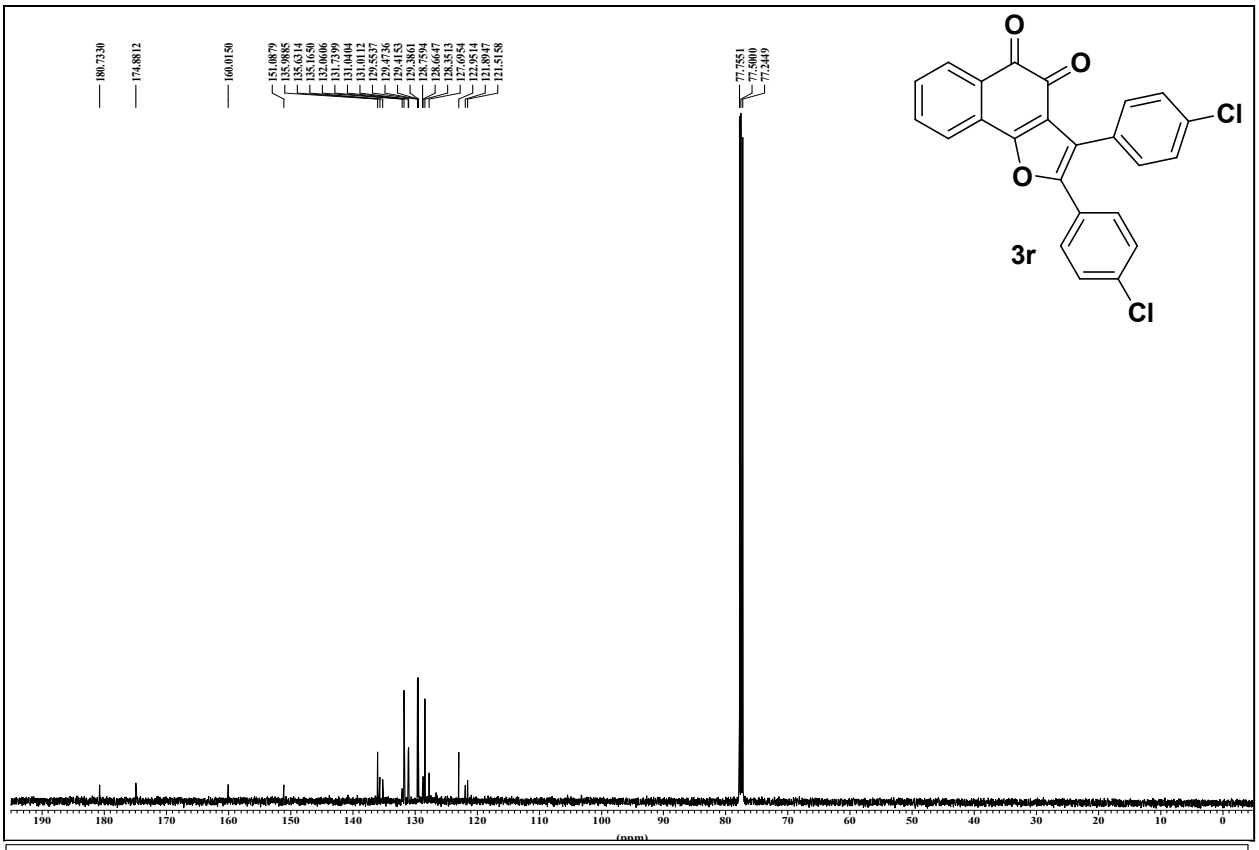
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O
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Cl
3r
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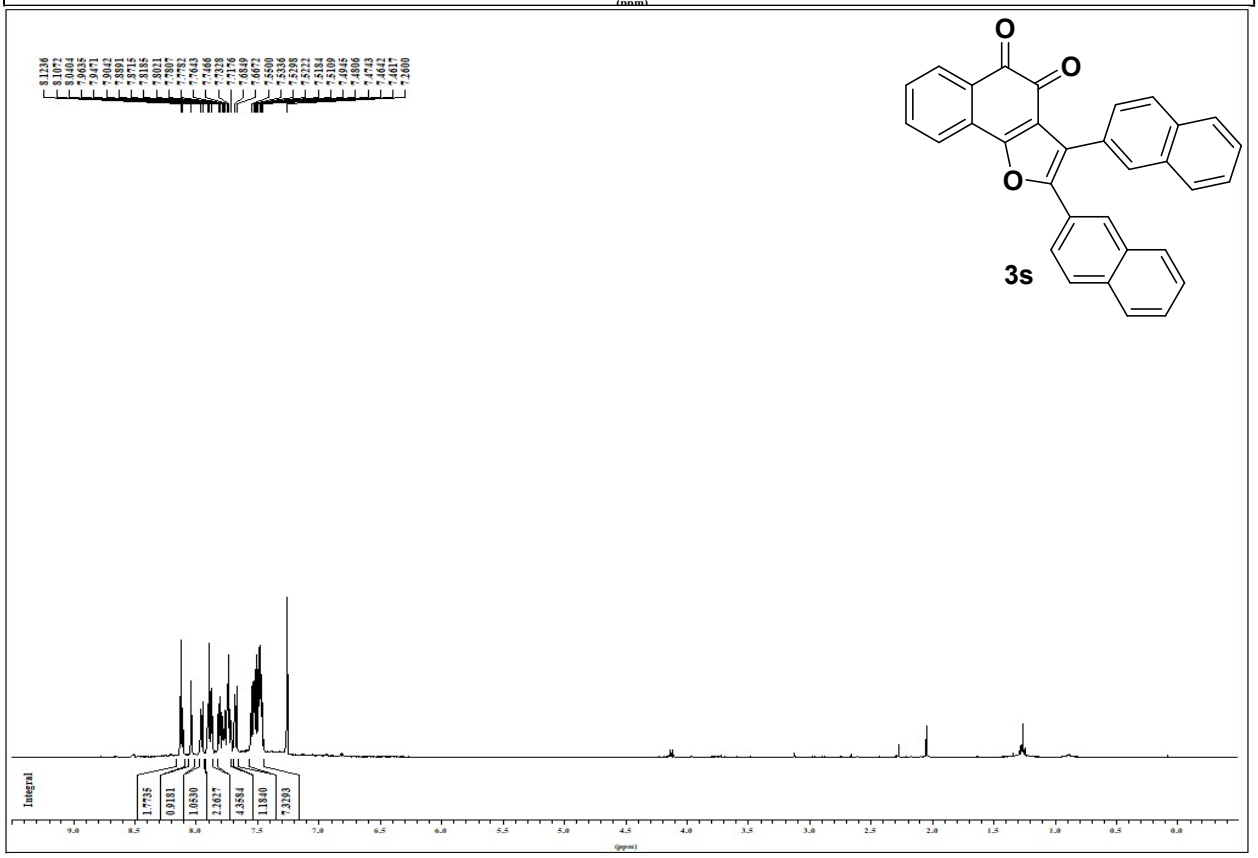
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O
O
3s
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6.0
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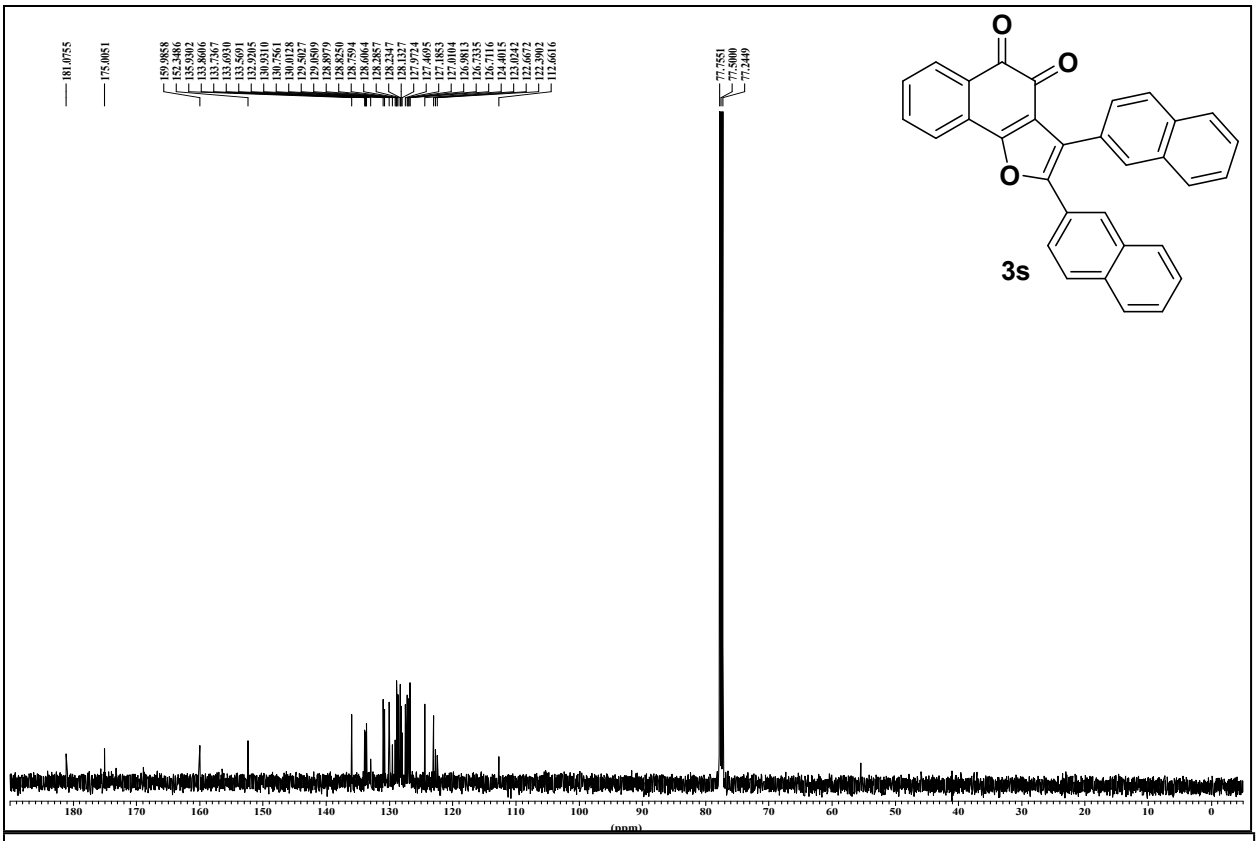
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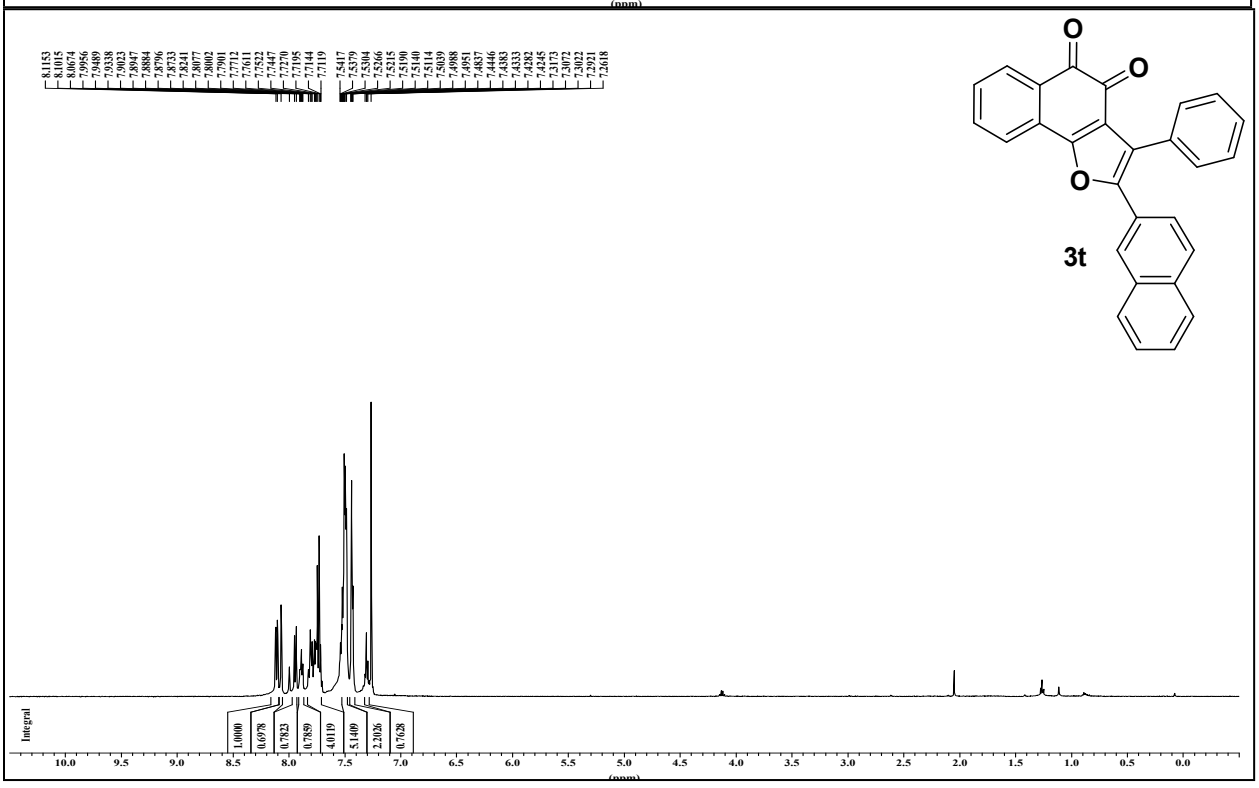
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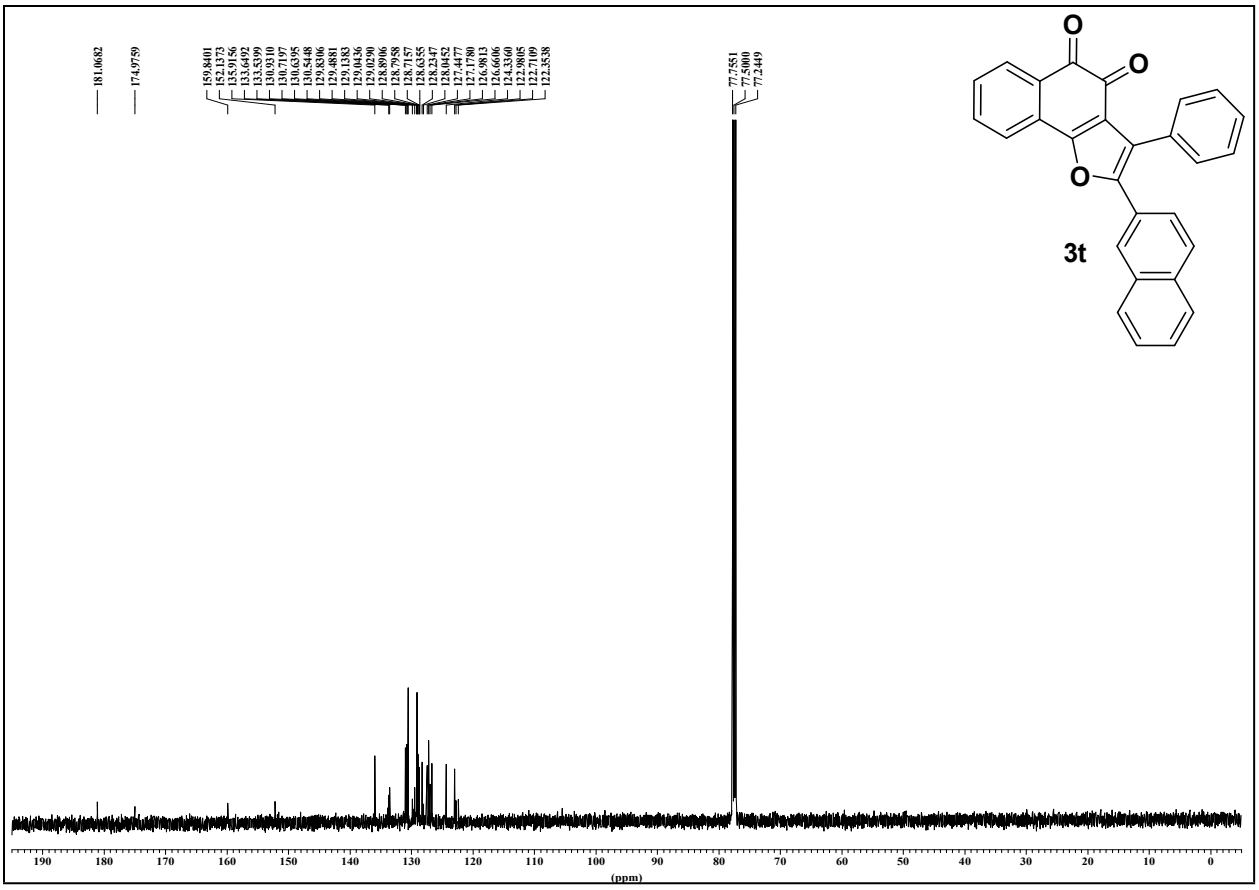
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127.1780
126.8013
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122.3538
77.7551
77.5000
77.2449
O
O
O
3t
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120
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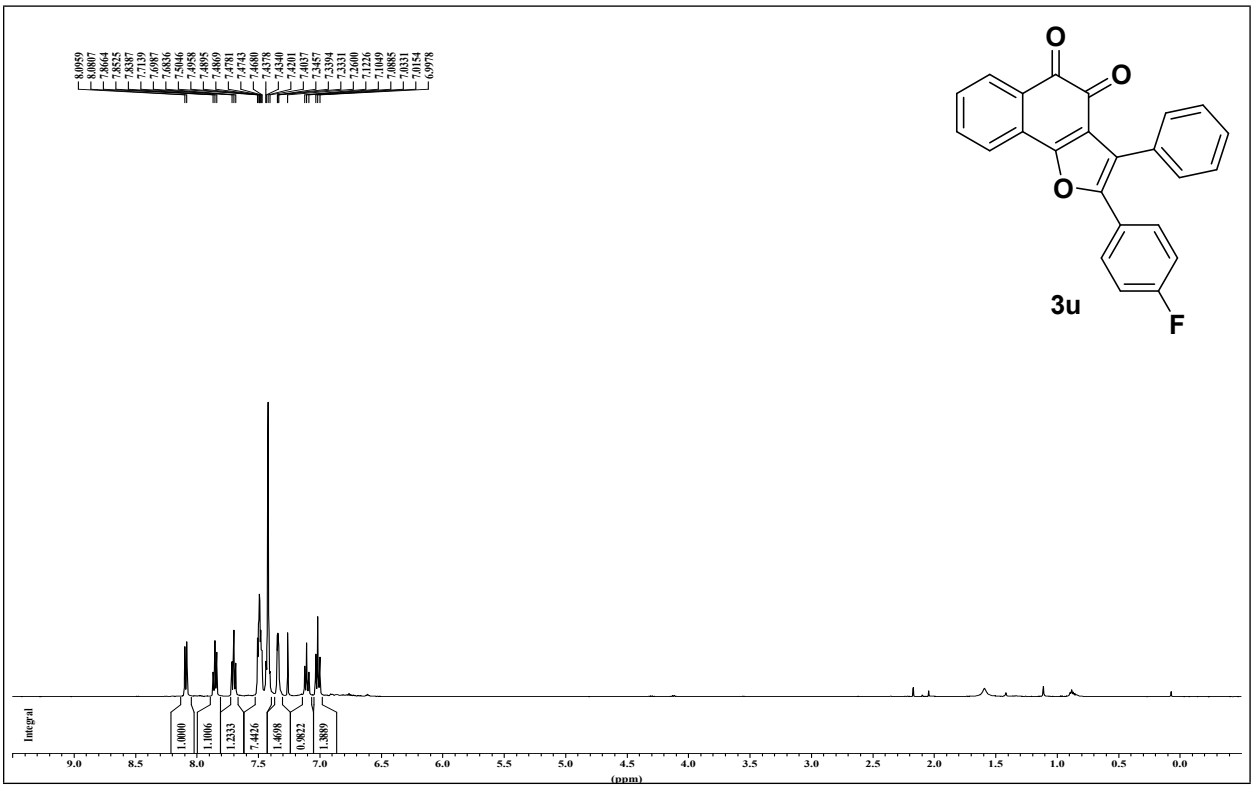
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7.4743
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7.0154
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O
O
3u
F
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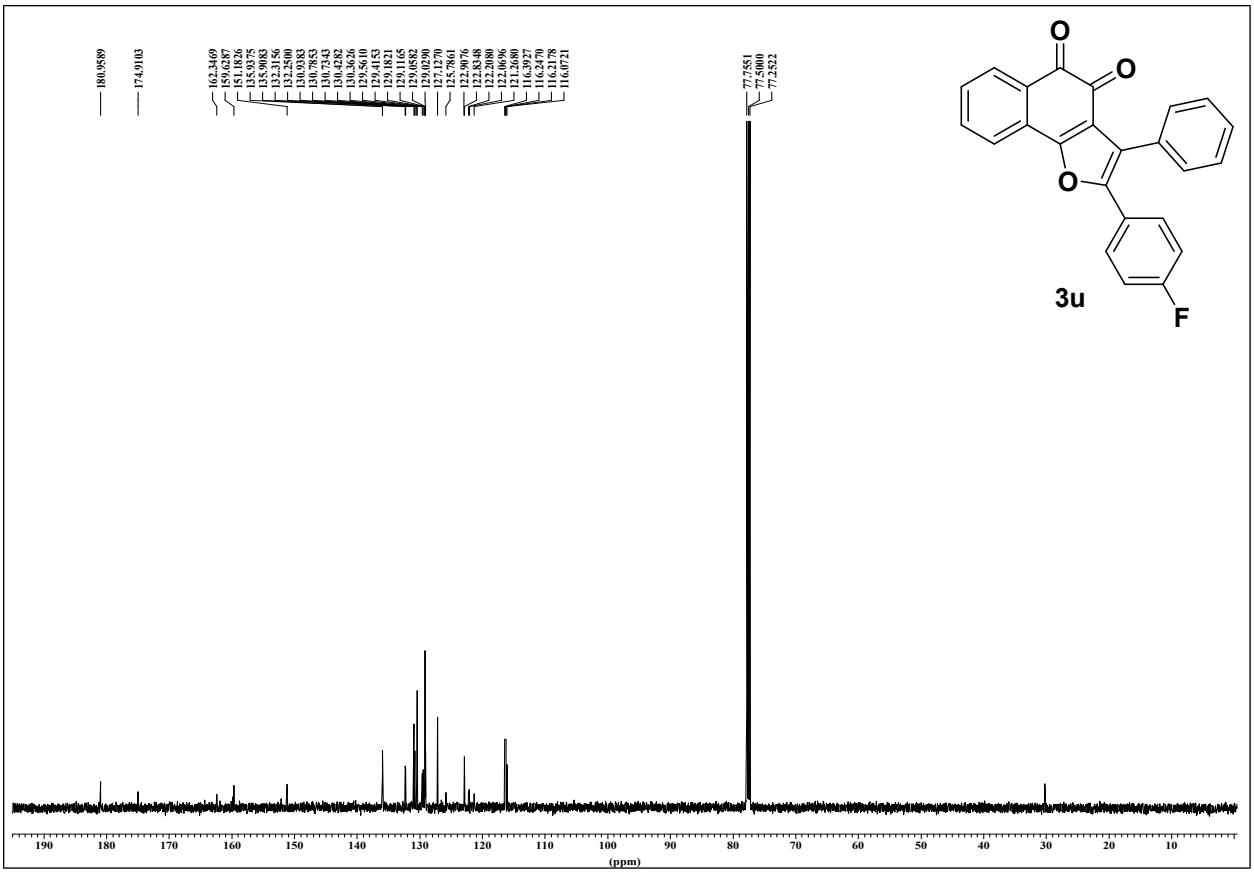
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122.0696
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116.2470
116.1798
116.0721
77.7551
77.5000
77.2522
O
O
O
3u
F
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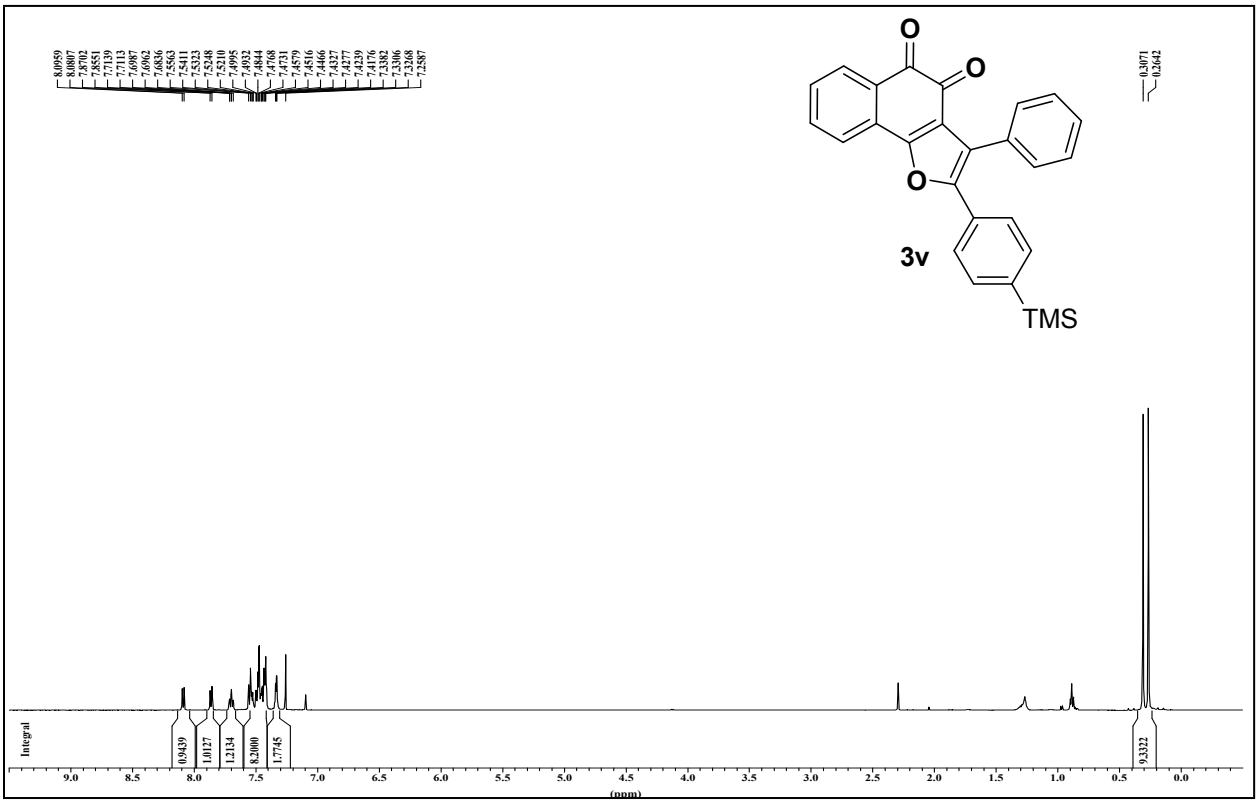
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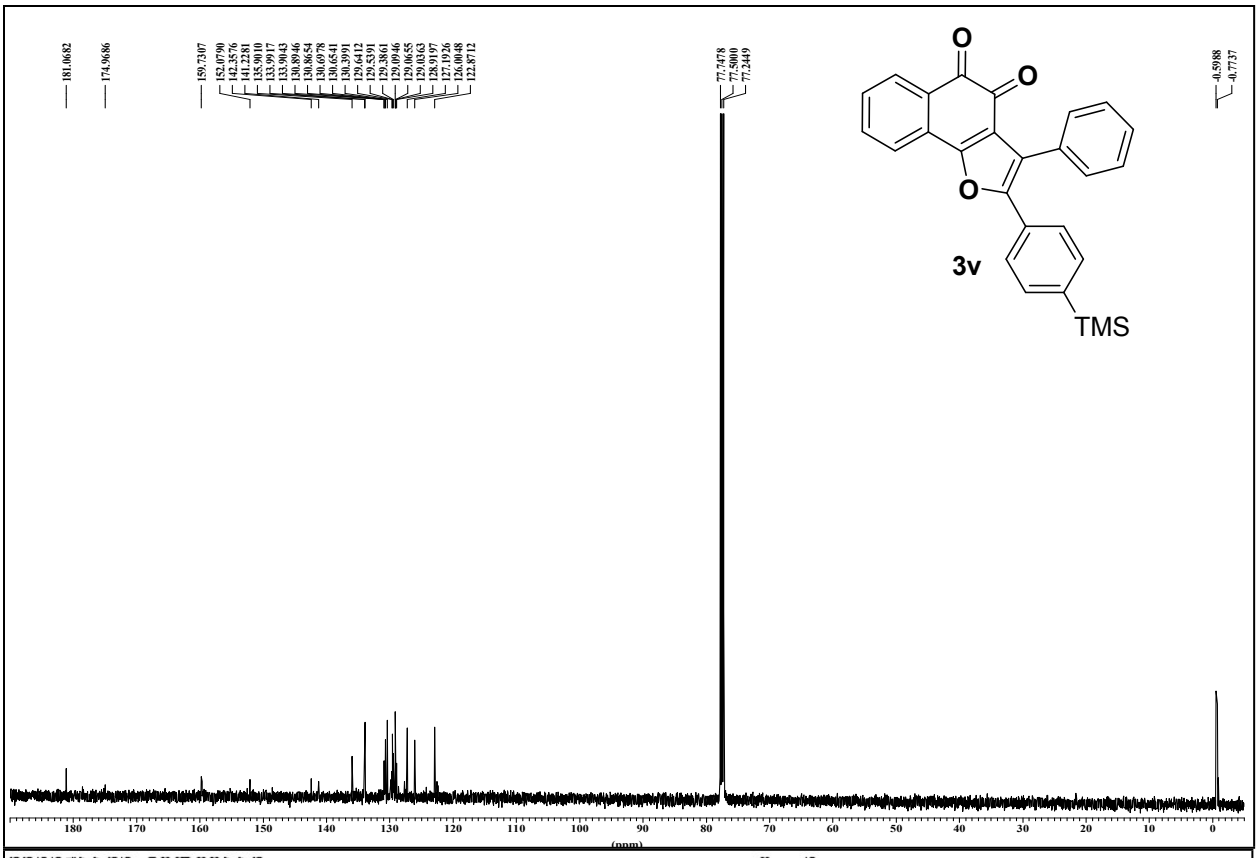
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-0.7737
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O
O
3v
TMS


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8.25
8.24
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8.17
8.16
8.15
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7.48
7.48
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7.47
7.26
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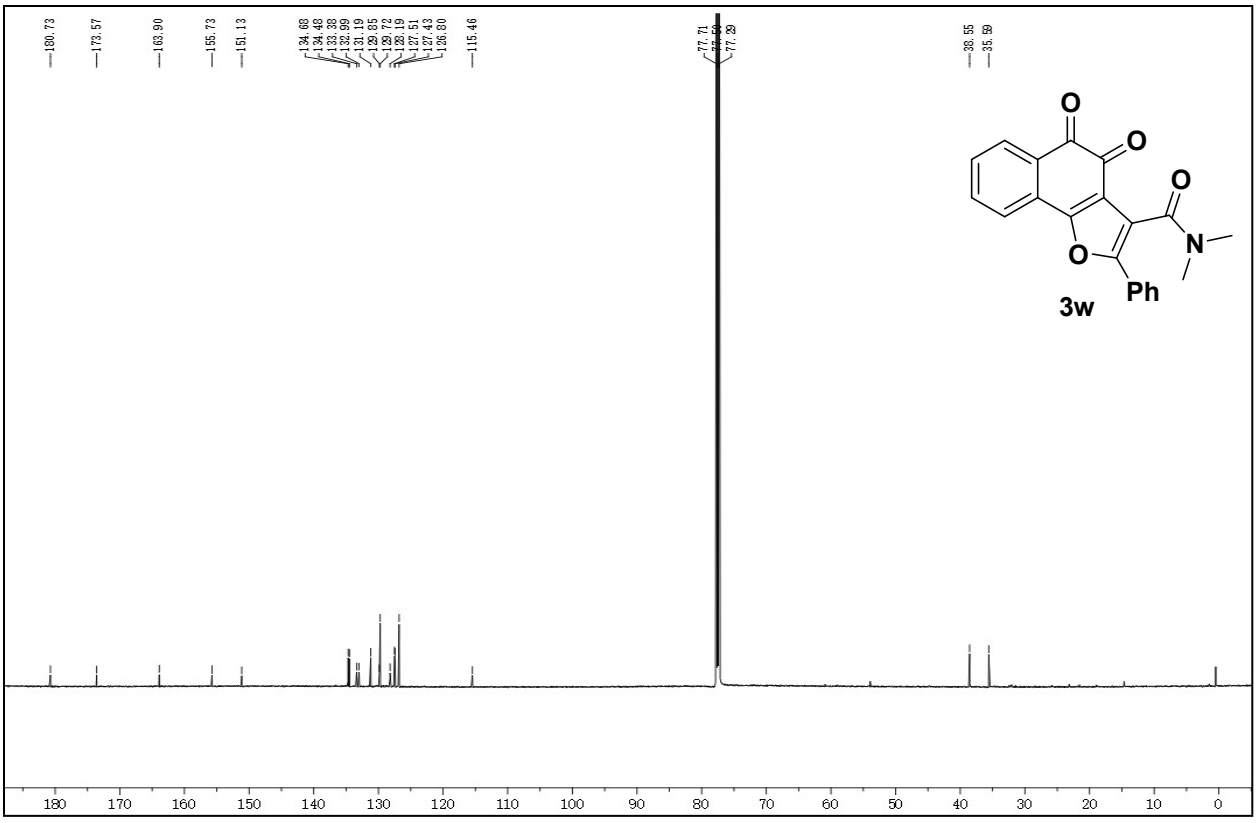
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77.29
38.55
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O
O
O
N
O
Ph
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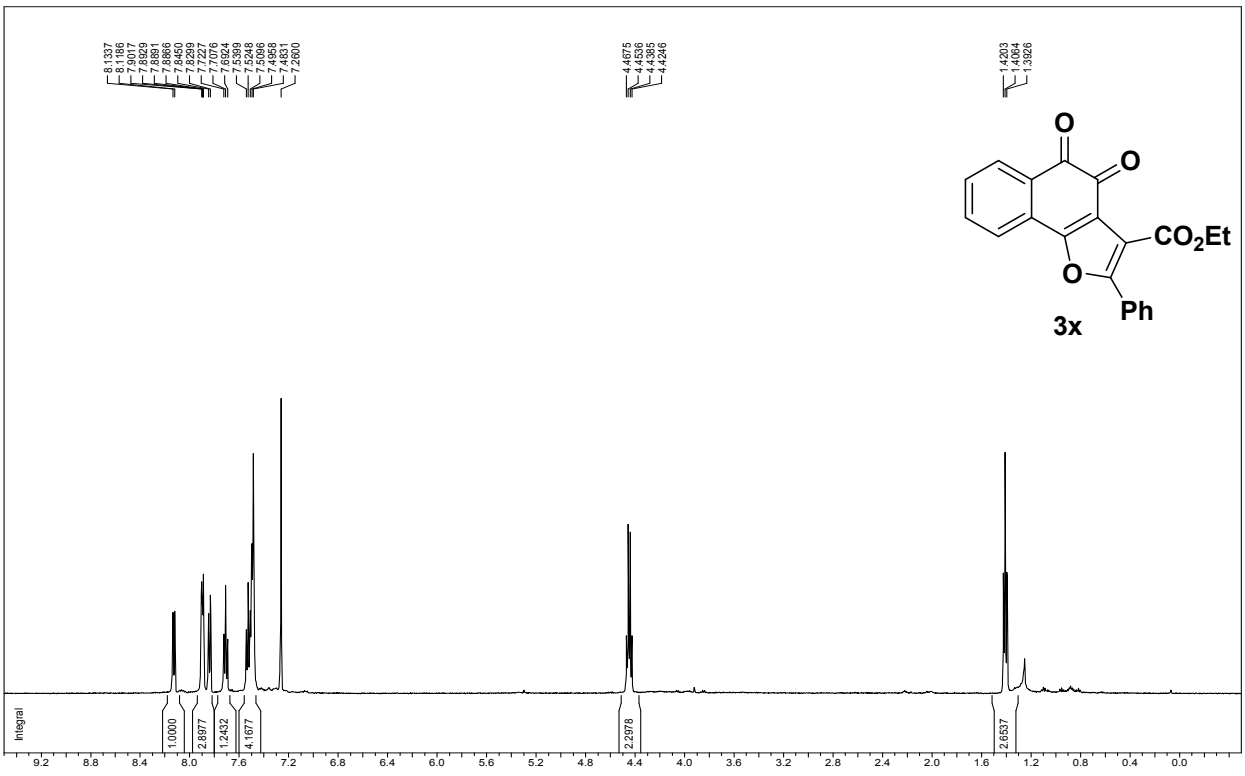
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7.2600
4.4675
4.4536
4.4385
4.4246
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1.3926
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O
O
CO2Et
Ph
3x
Integral
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7.2
6.8
6.4
6.0
5.6
5.2
4.8
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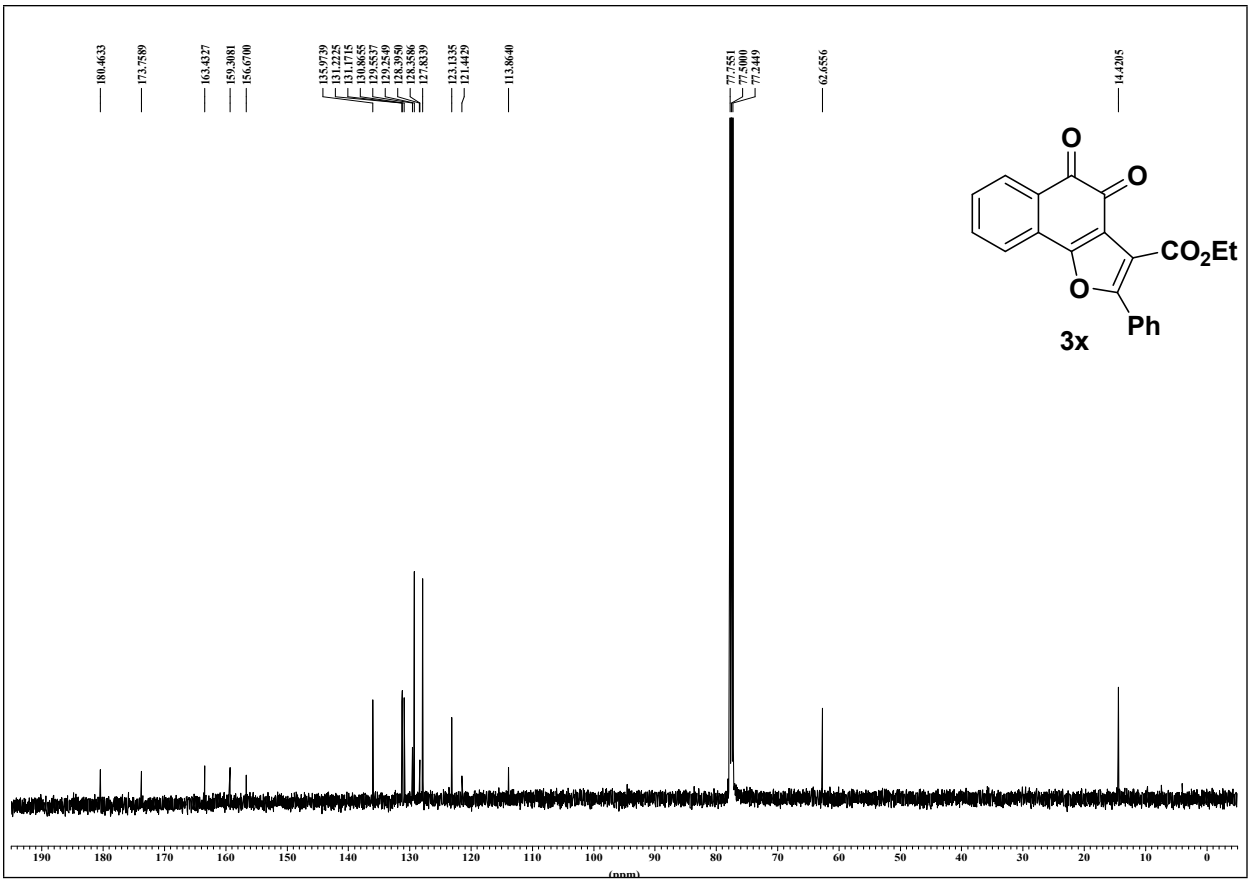
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O
O
CO2Et
O
Ph
3x
190
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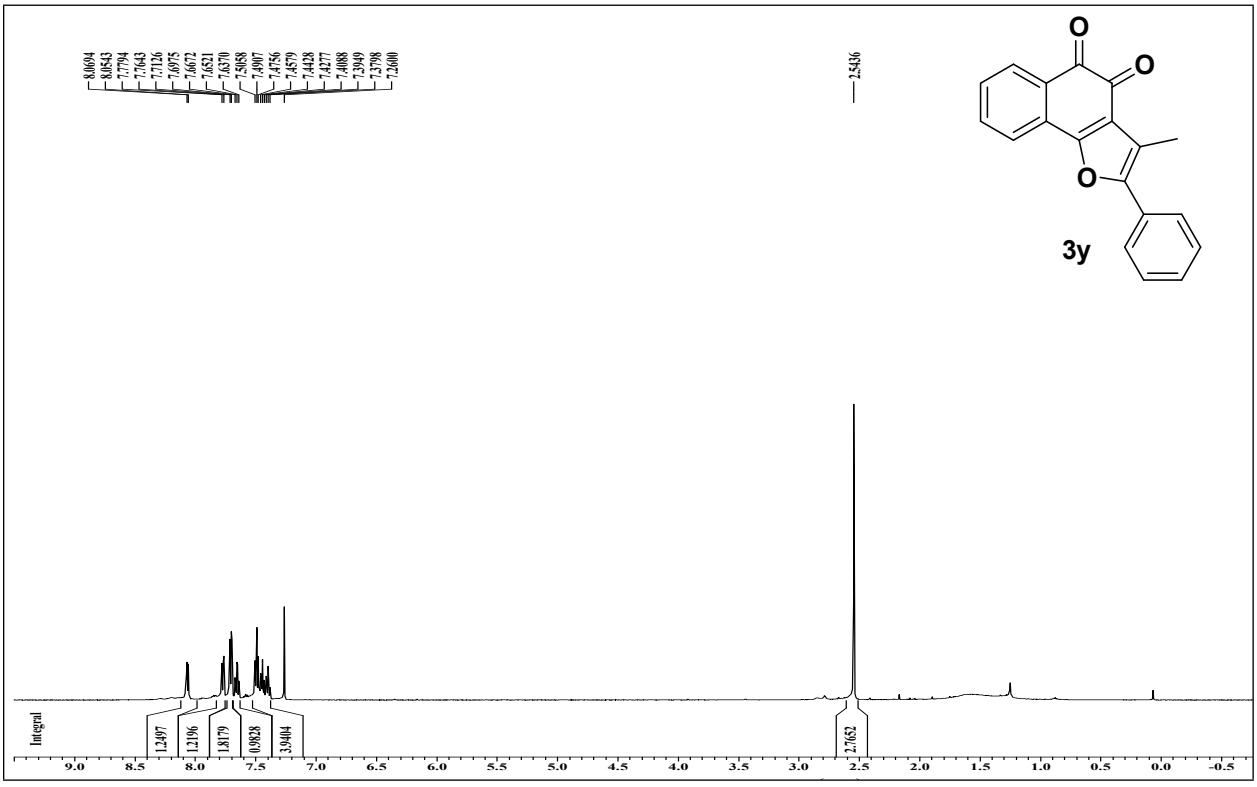
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7.4277
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7.3949
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7.2600
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O
O
3y
Integral
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6.0
5.5
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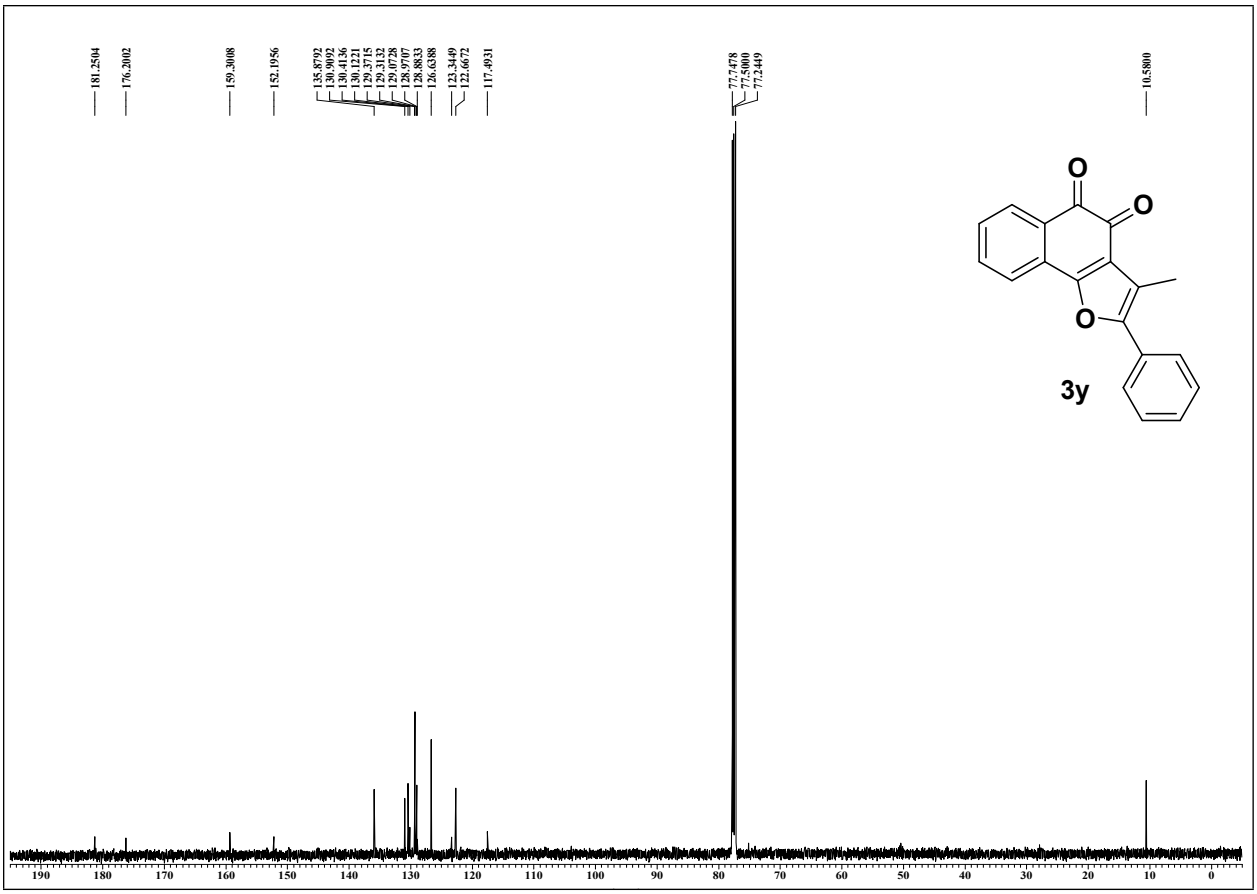
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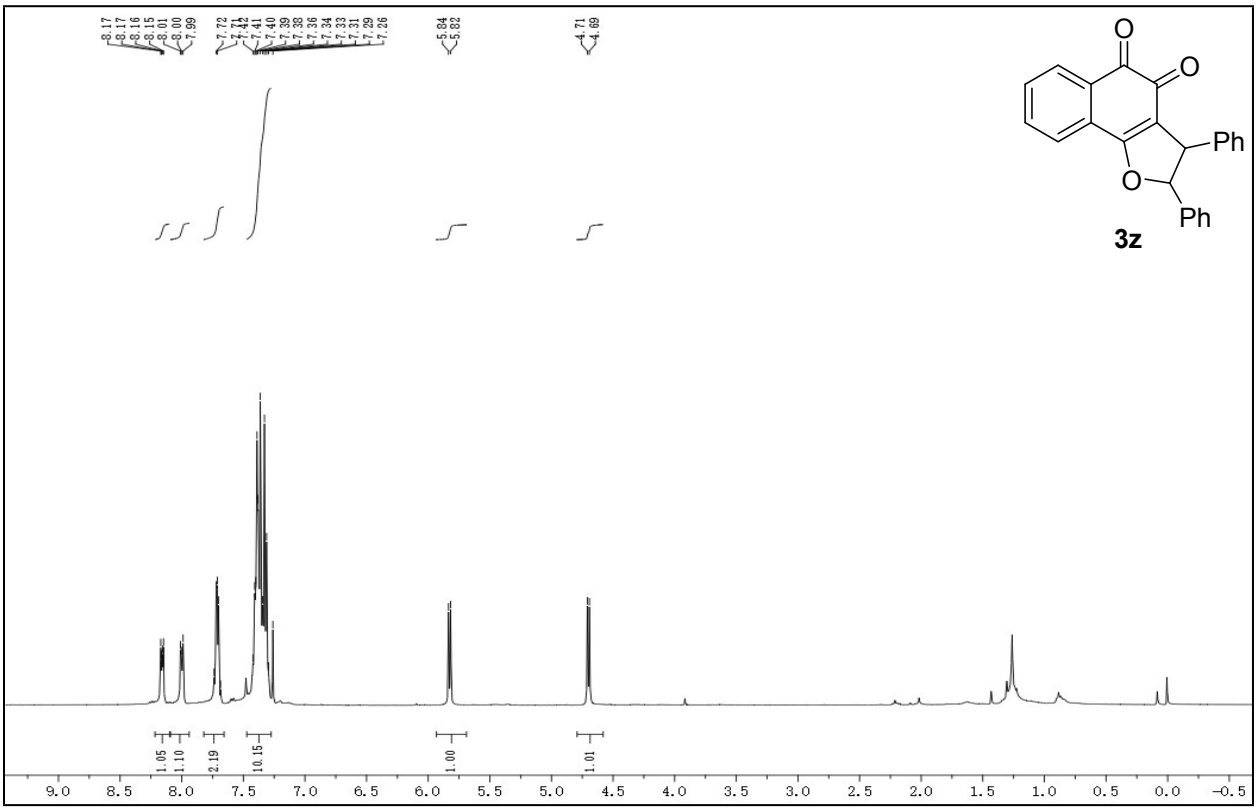
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5.82
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Ph
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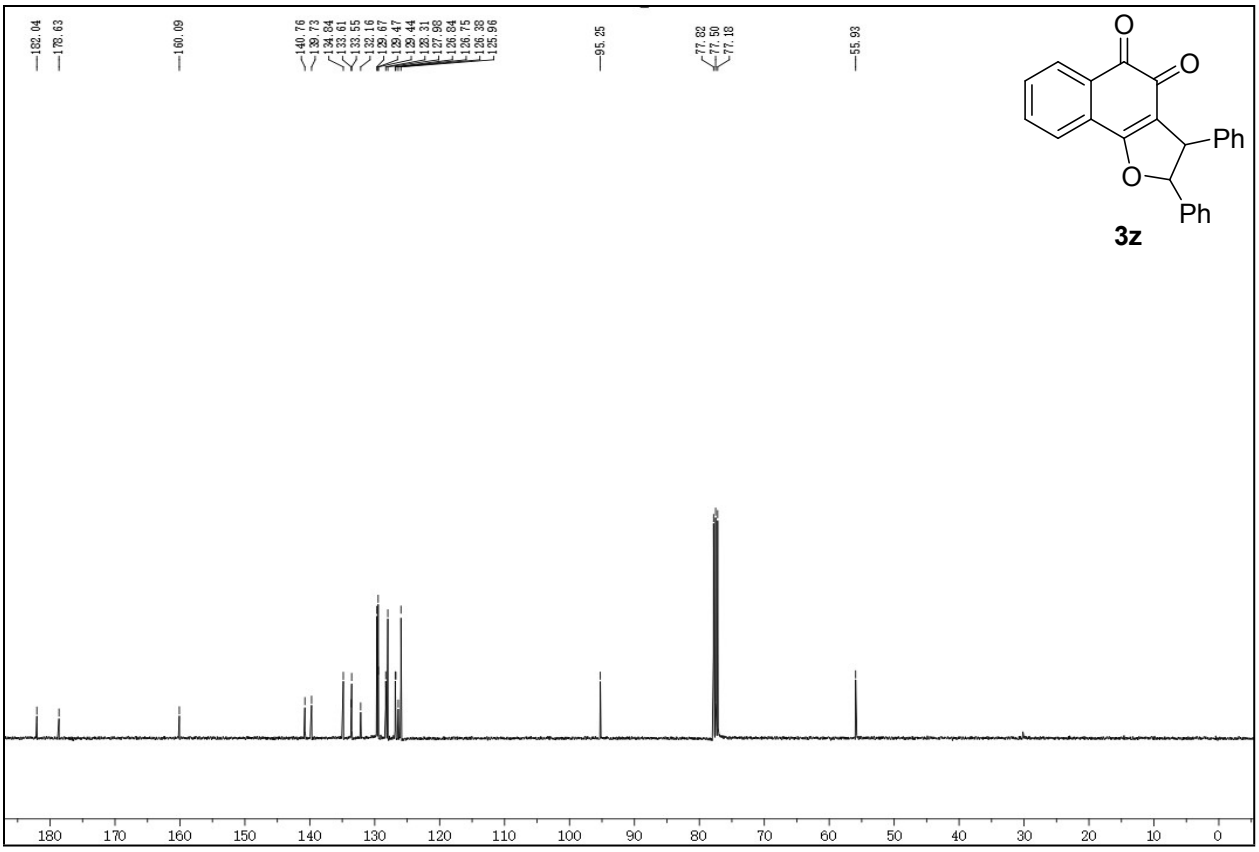
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Ph
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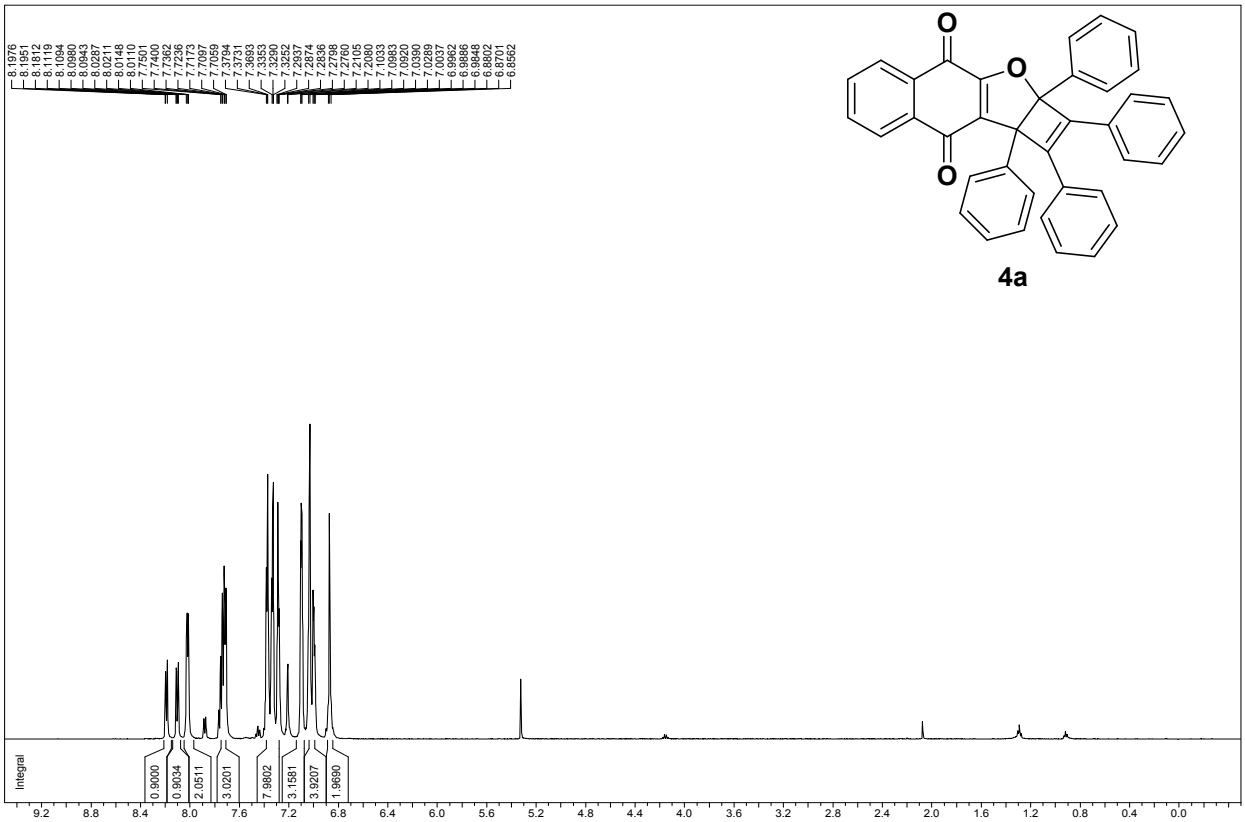
Ph
3z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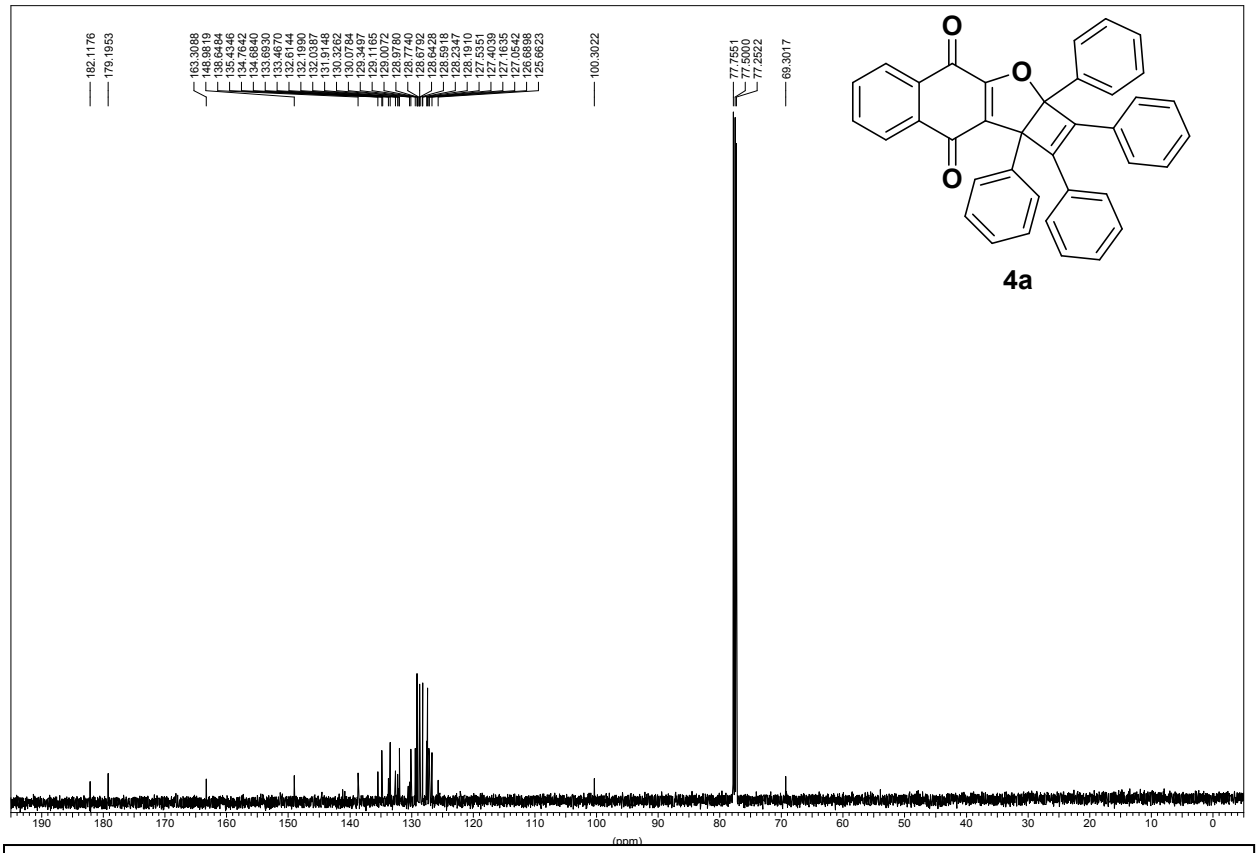
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O
O
O
4a
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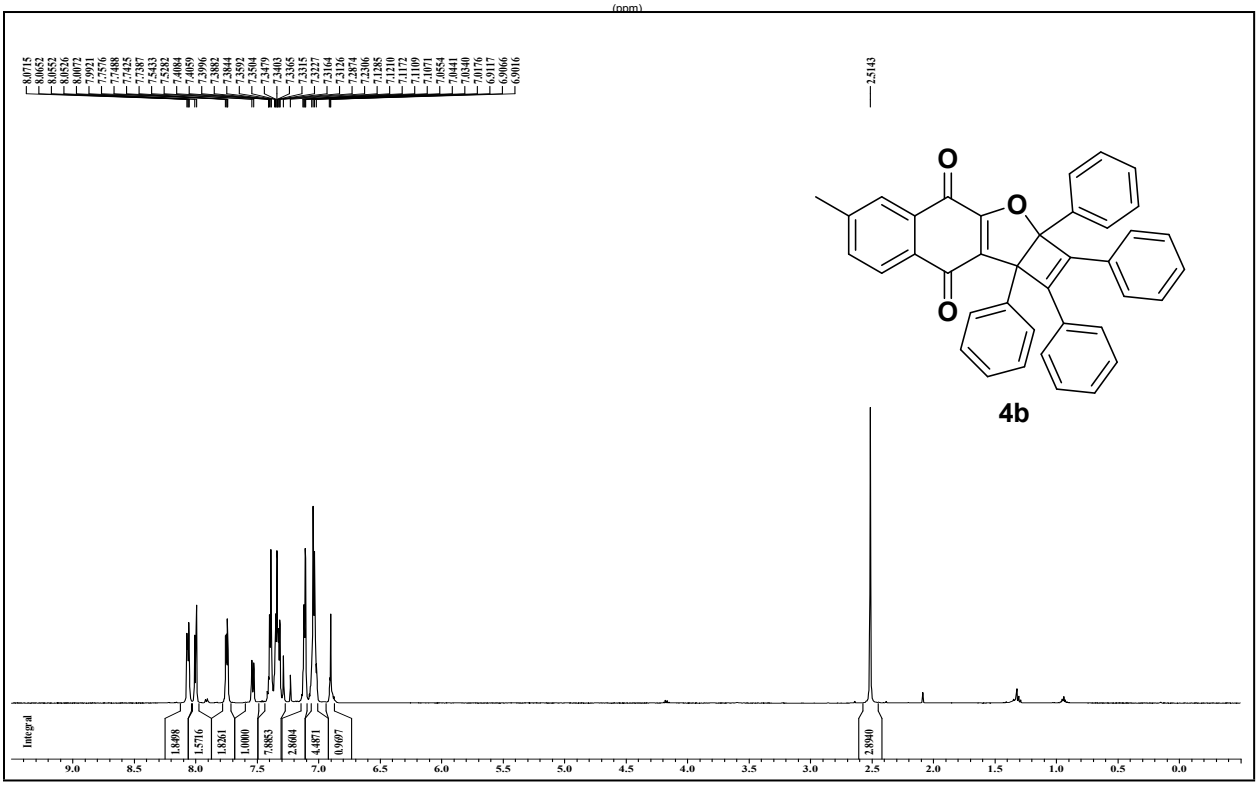
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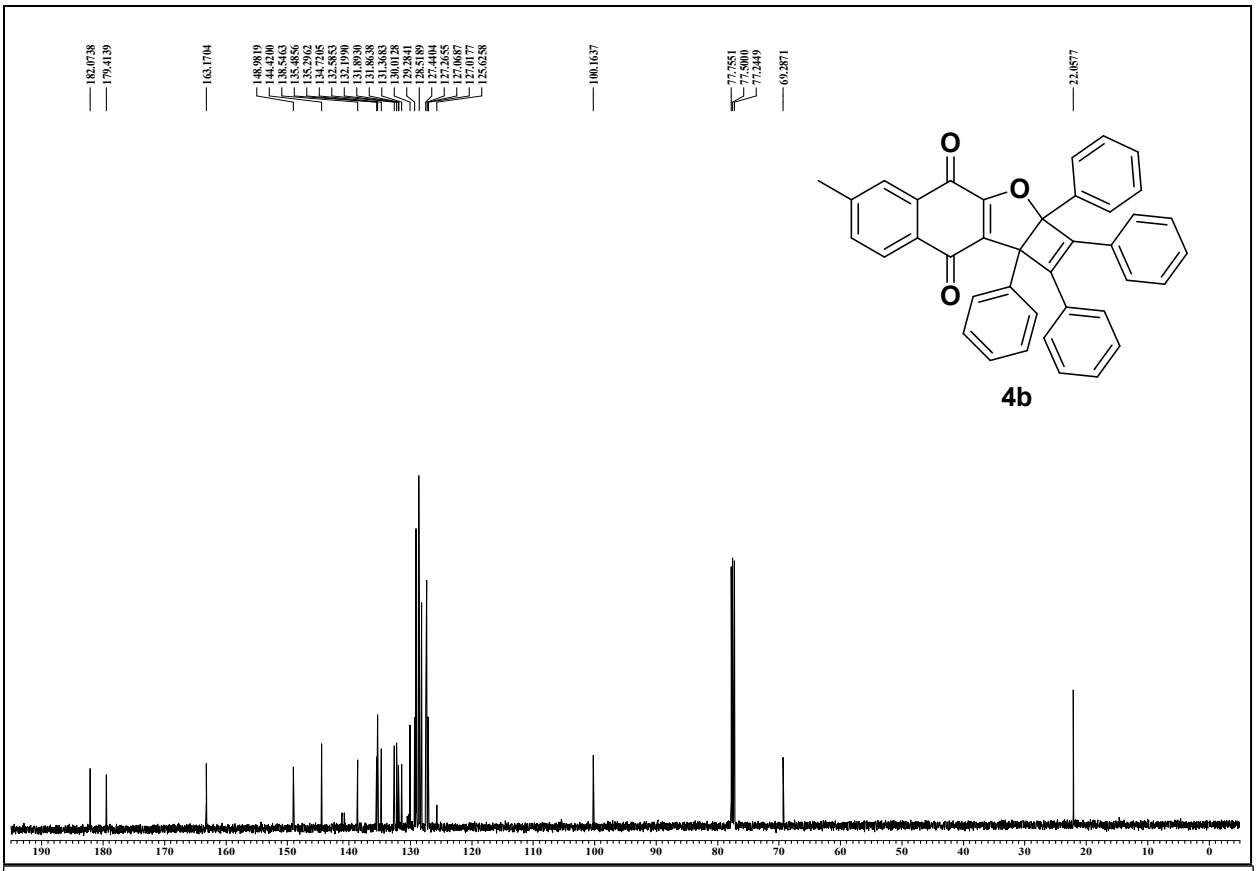
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132.1990
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130.0128
129.2841
128.5189
127.4404
127.2655
127.0687
127.0177
125.6258
100.1637
77.7551
77.5000
77.2449
69.2871
22.0577
O
O
O
4b
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110
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70
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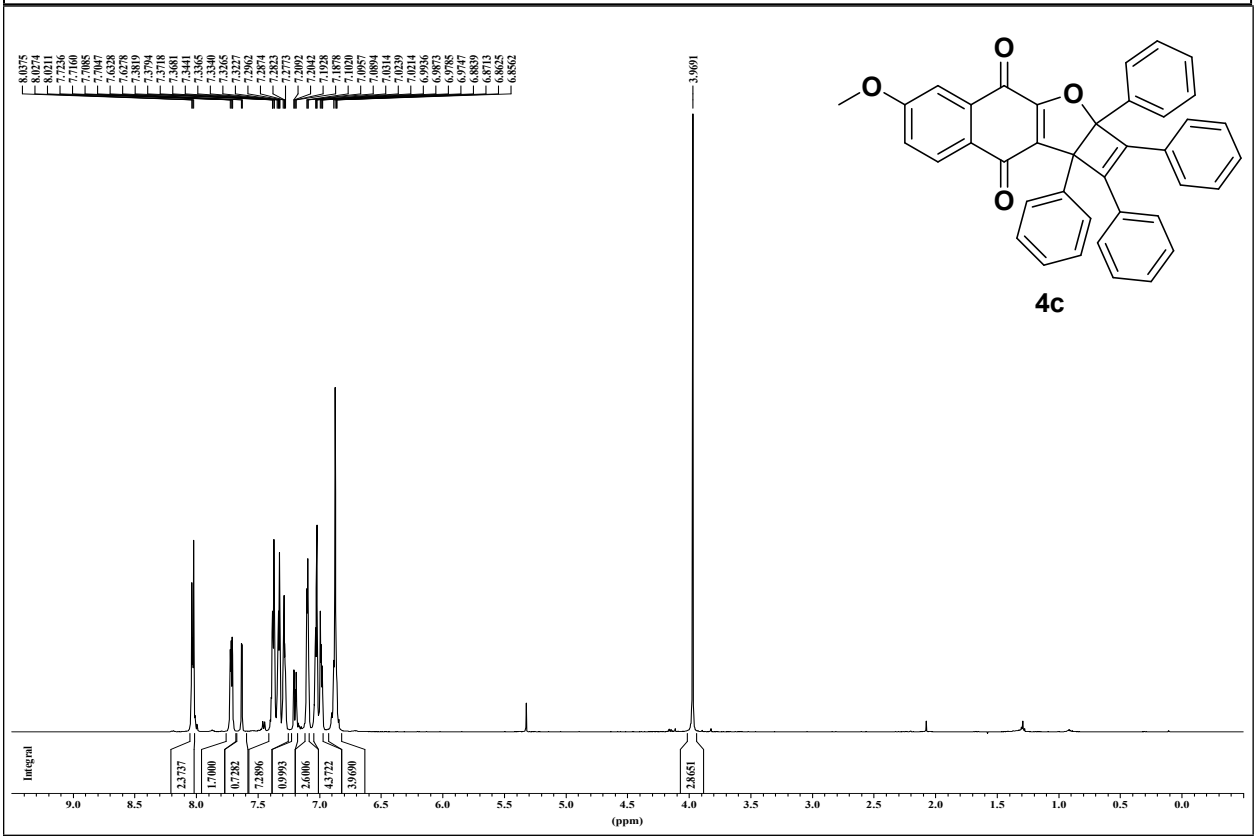
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7.3718
7.3681
7.3441
7.3365
7.3340
7.3265
7.3227
7.2962
7.2874
7.2823
7.2773
7.2092
7.2042
7.1928
7.1878
7.1020
7.0957
7.0894
7.0314
7.0210
7.0214
6.9936
6.9873
6.9785
6.9747
6.8839
6.8713
6.8625
6.8562
3.9691
O
O
O
O
4c
Integral
2.3737
1.7000
0.7382
2.2896
0.9993
2.6086
4.3722
3.9690
2.8651
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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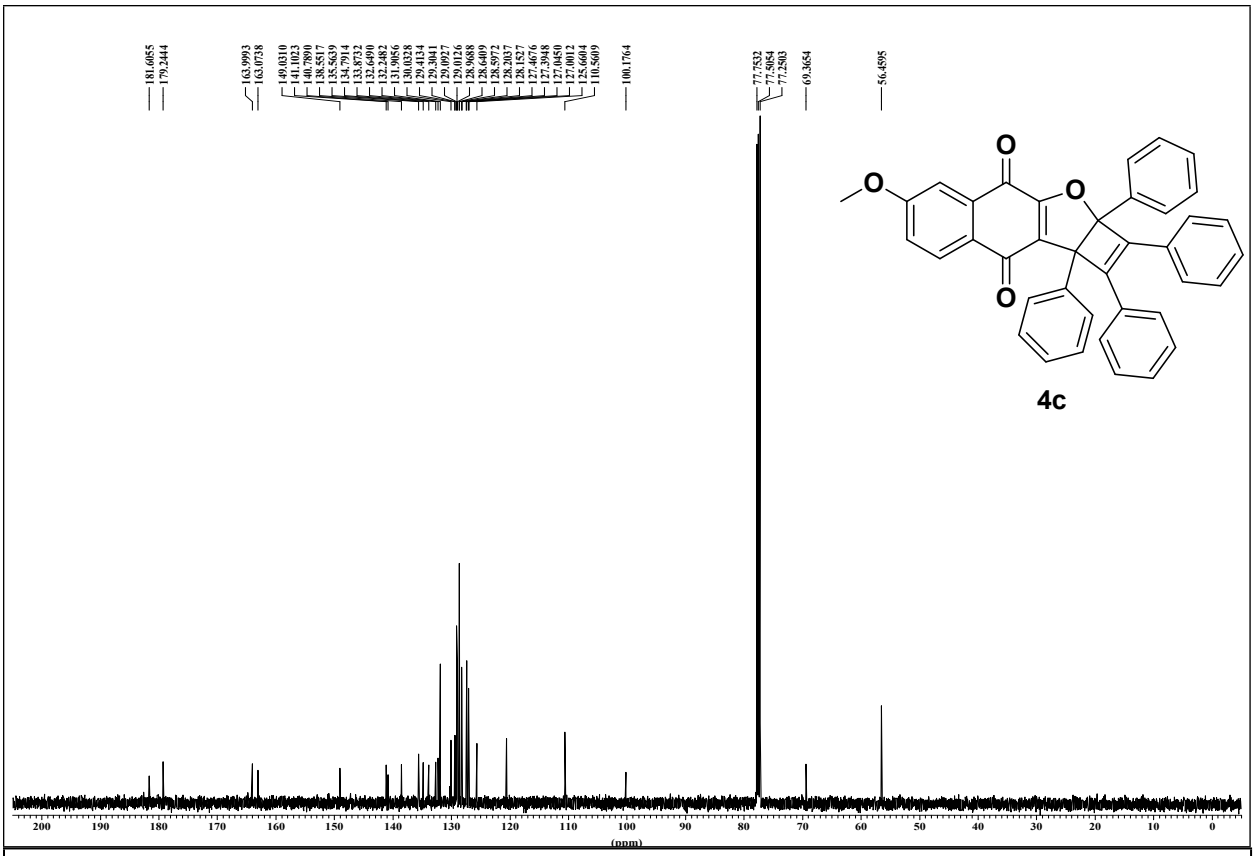
(ppm)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132.6040
132.2482
131.9056
130.0328
129.4134
129.3041
129.0927
129.0126
128.9088
128.6040
128.5972
128.2037
128.1527
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127.3948
127.0450
127.0012
125.6604
110.5609
100.1764
77.7532
77.5054
77.2503
69.3654
56.4595
O
O
O
O
4c
200
190
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120
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100
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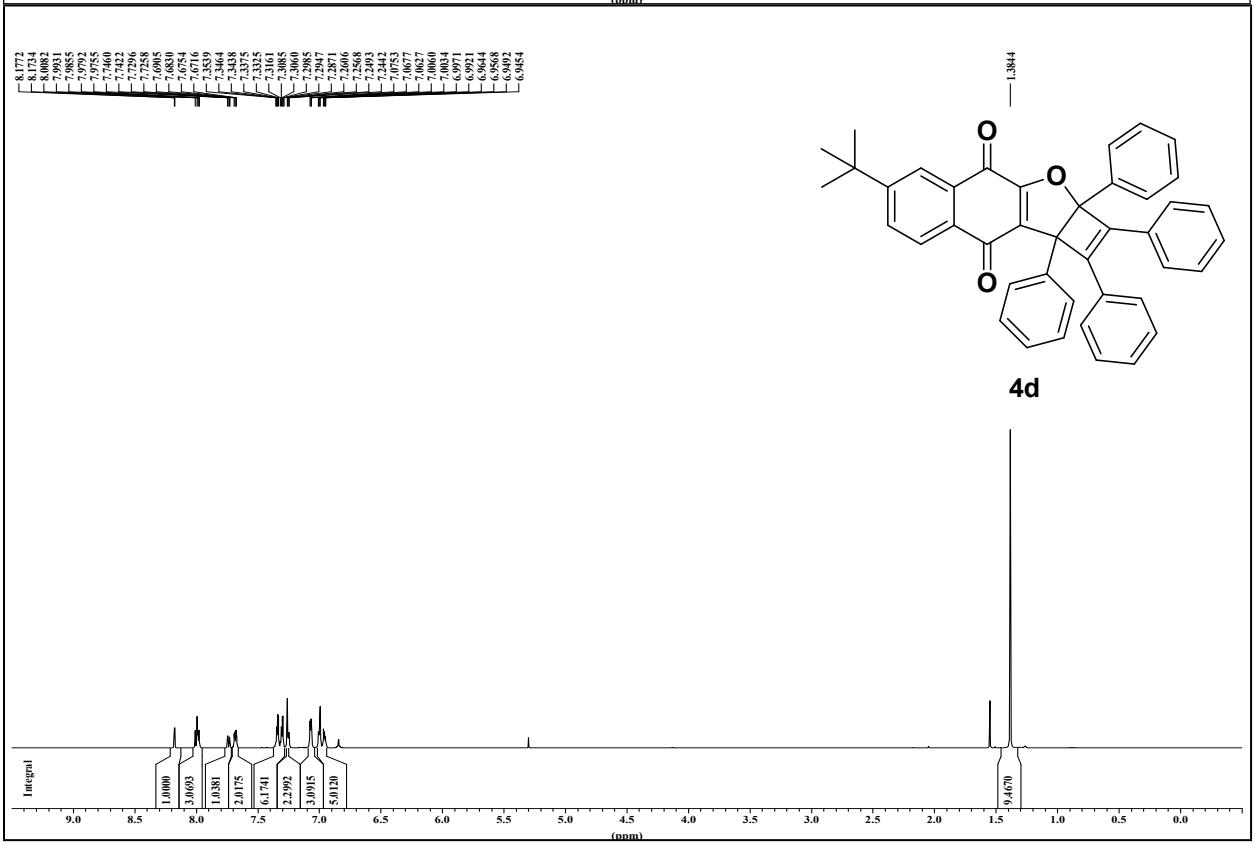
(ppm)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7.6905
7.6830
7.6754
7.6716
7.3559
7.3464
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7.3375
7.3325
7.3161
7.3085
7.3060
7.2985
7.2947
7.2871
7.2606
7.2568
7.2503
7.2442
7.0753
7.0677
7.0627
7.0060
7.0034
6.9971
6.9921
6.9644
6.9568
6.9492
6.9454
1.3844
O
O
O
4d
Integral
1.0000
3.0693
1.0381
2.0175
6.1741
2.2992
3.0915
5.0120
9.4670
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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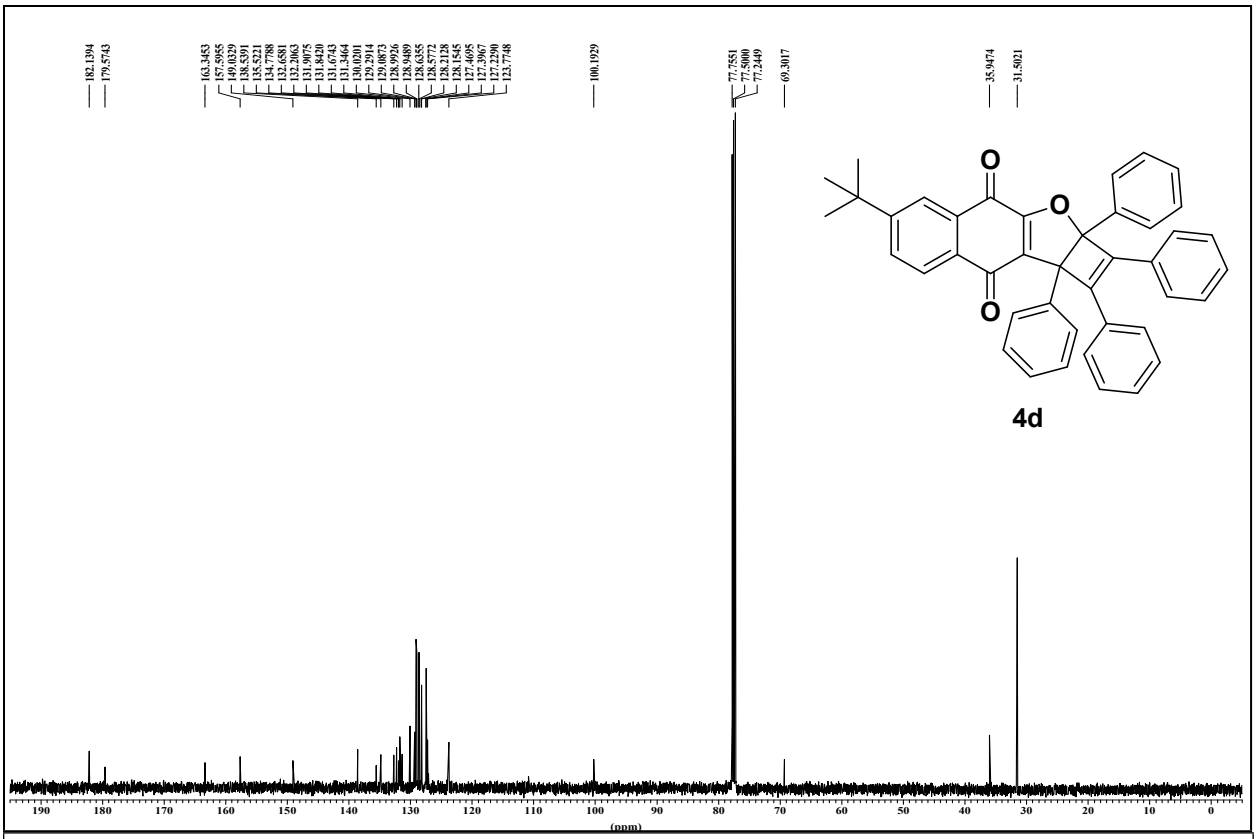
0.0
(ppm)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131.8420
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131.3464
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128.9926
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128.6355
128.5772
128.2128
128.1545
127.6695
127.3967
127.2290
123.7748
100.1929
77.7551
77.5000
77.3449
69.3017
35.9474
31.5021
O
O
O
4d
190
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130
120
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100
90
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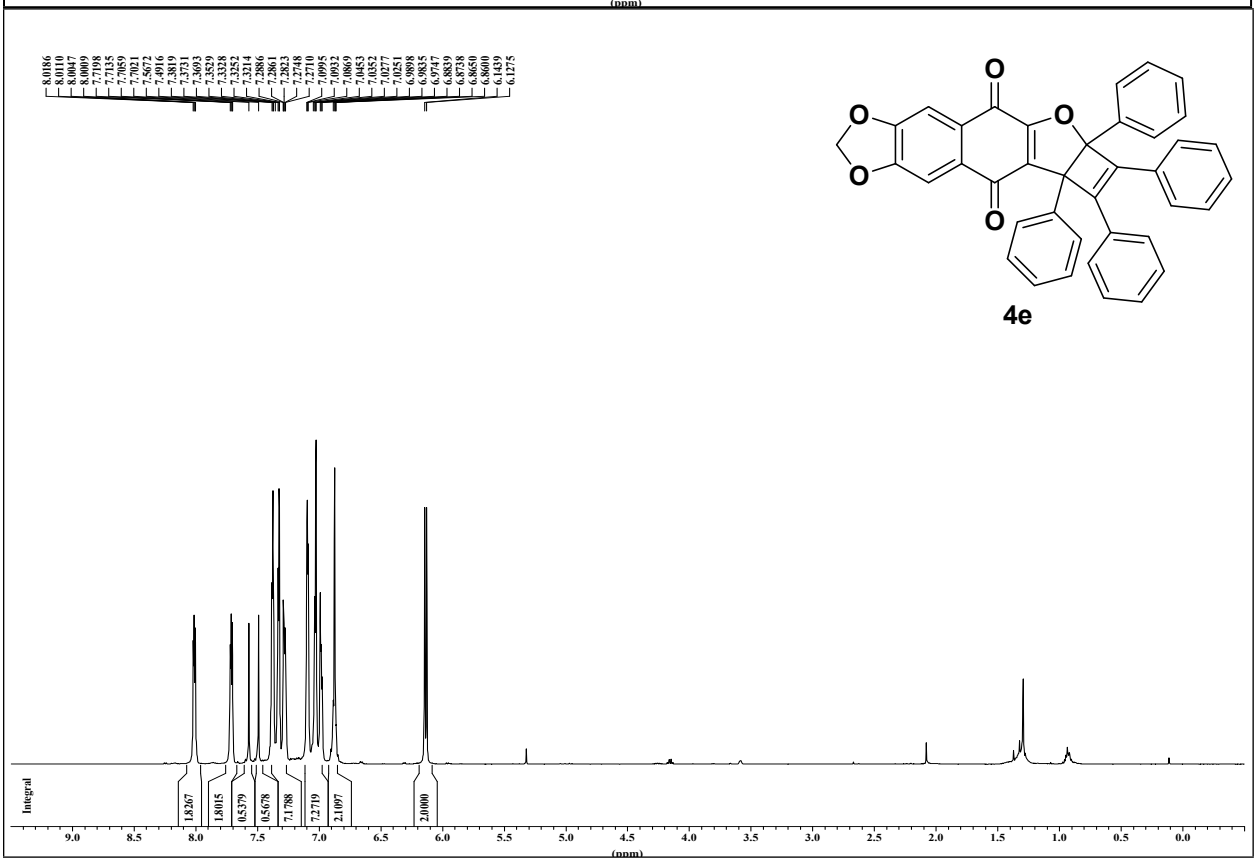
(ppm)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7.3731
7.3693
7.3529
7.3328
7.3252
7.3214
7.2886
7.2861
7.2823
7.2748
7.2710
7.0995
7.0932
7.0869
7.0453
7.0352
7.0277
7.0251
6.9898
6.9835
6.9747
6.8839
6.8738
6.8650
6.8600
6.1459
6.1375
O
O
O
O
O
4e
Integral
1.8267
1.8015
0.5379
0.5678
7.1788
7.2719
2.1097
2.0000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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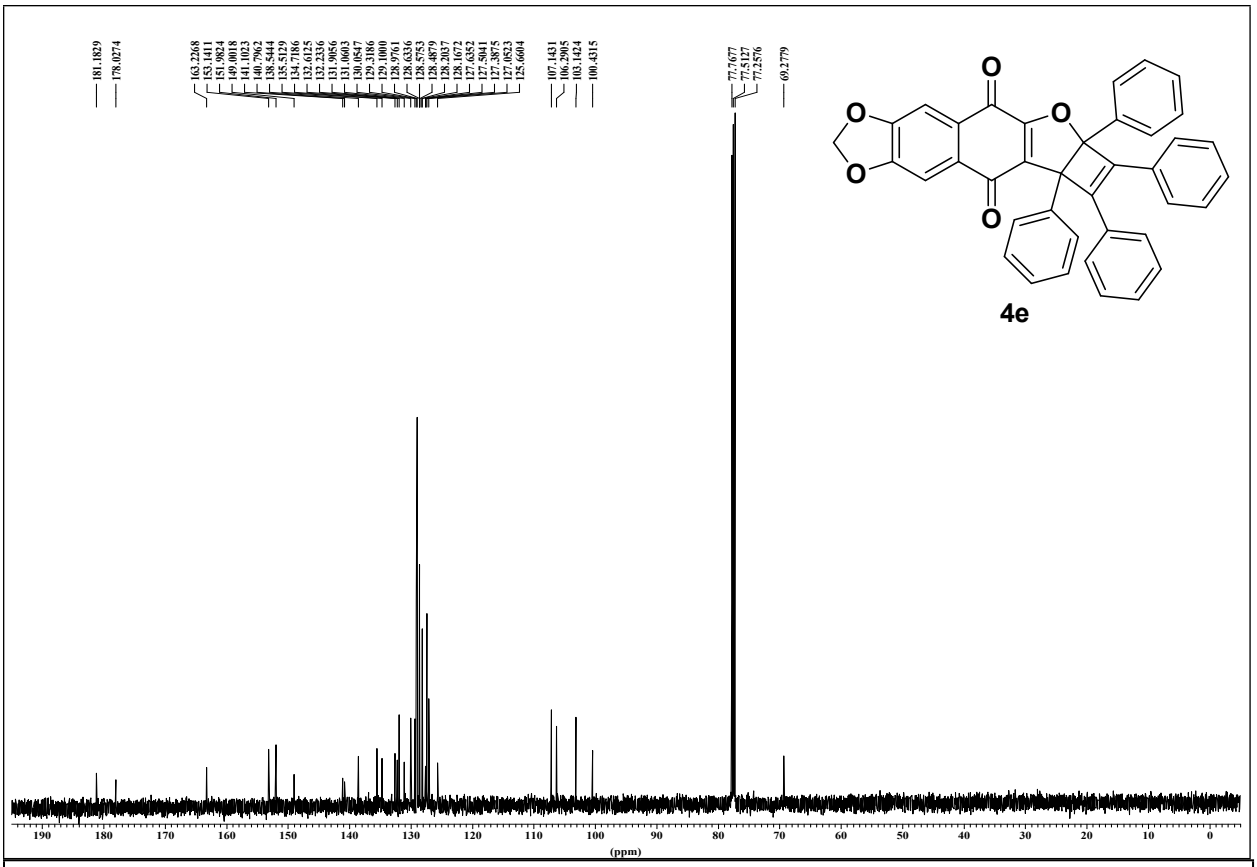
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)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140.7962
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135.5129
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132.2336
131.9056
131.0003
130.1647
129.3156
129.1000
128.9761
128.6336
128.5753
128.4879
128.2037
128.1672
127.6352
127.5041
127.3875
127.0523
125.6604
107.1431
106.2905
103.1424
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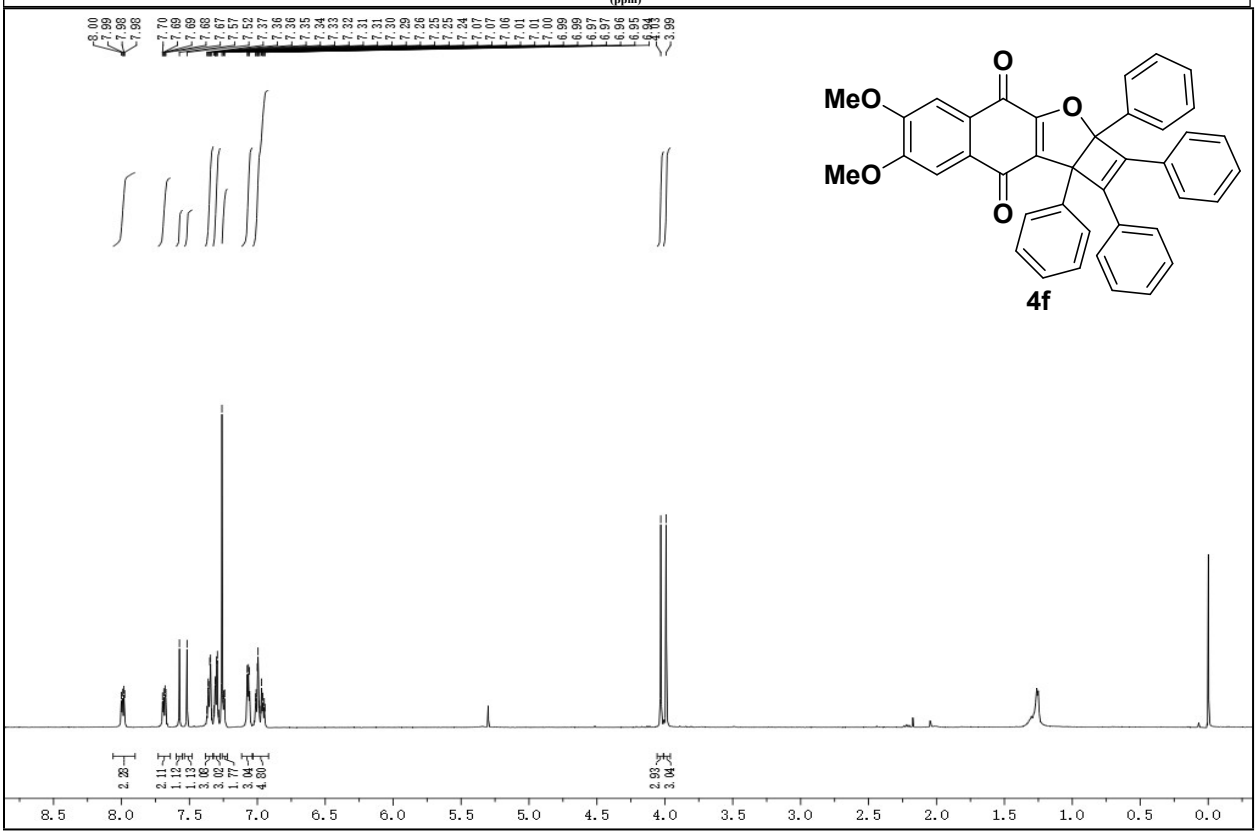
77.7677
77.5127
77.2576
69.2779
O
O
O
O
O
4e
(ppm)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7.69
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7.57
7.52
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.26
7.25
7.25
7.24
7.07
7.07
7.06
7.01
7.01
7.00
6.99
6.99
6.97
6.97
6.96
6.95
6.94
4.03
3.99
MeO
MeO
O
O
O
4f
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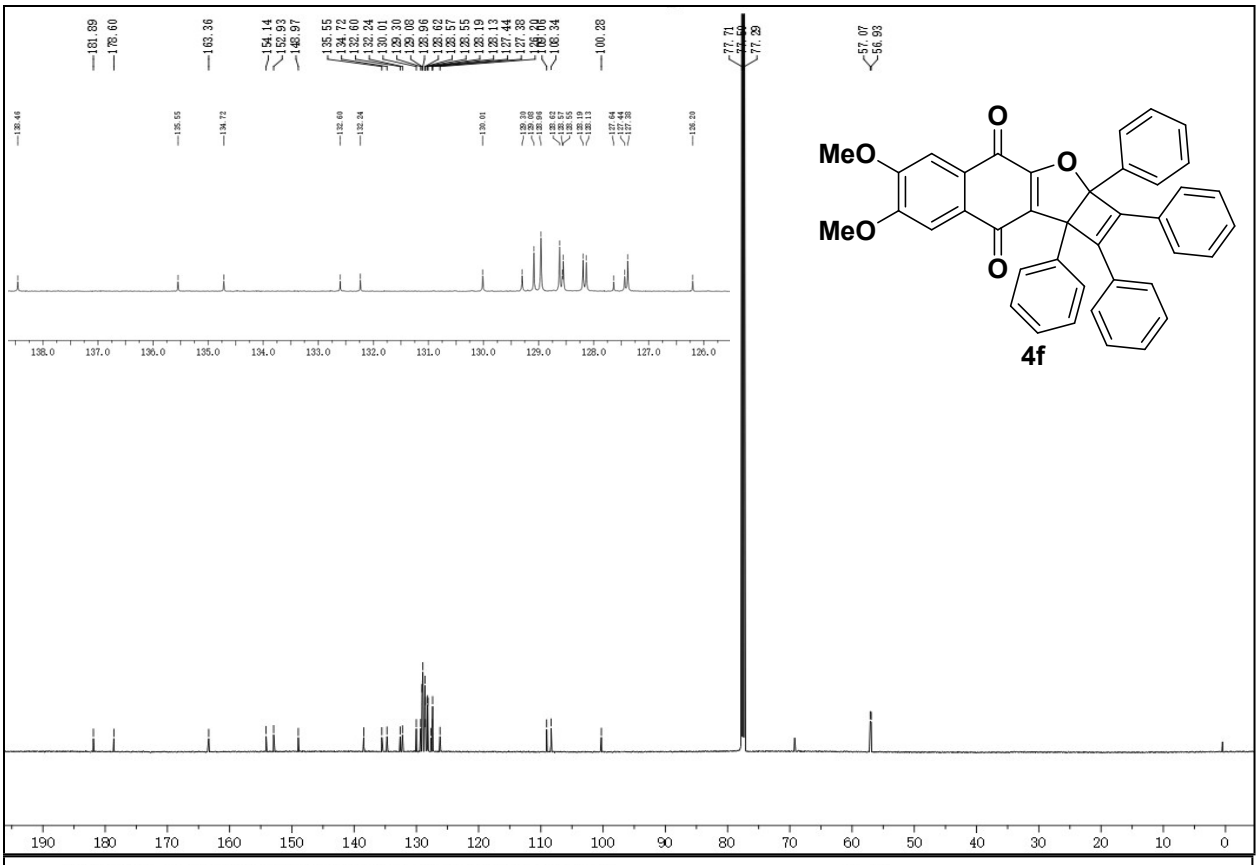
2.11
1.12
1.13
3.08
3.02
1.77
3.04
4.80
2.93
3.04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MeO
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O
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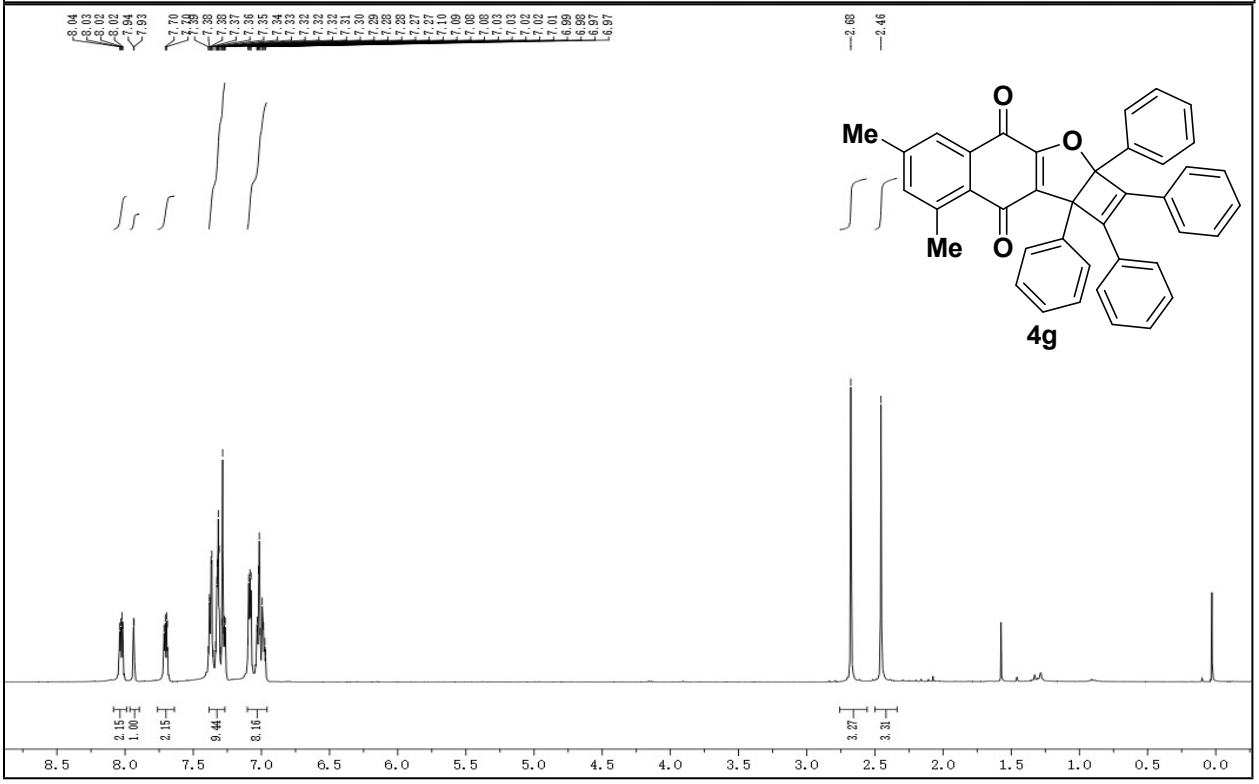
4f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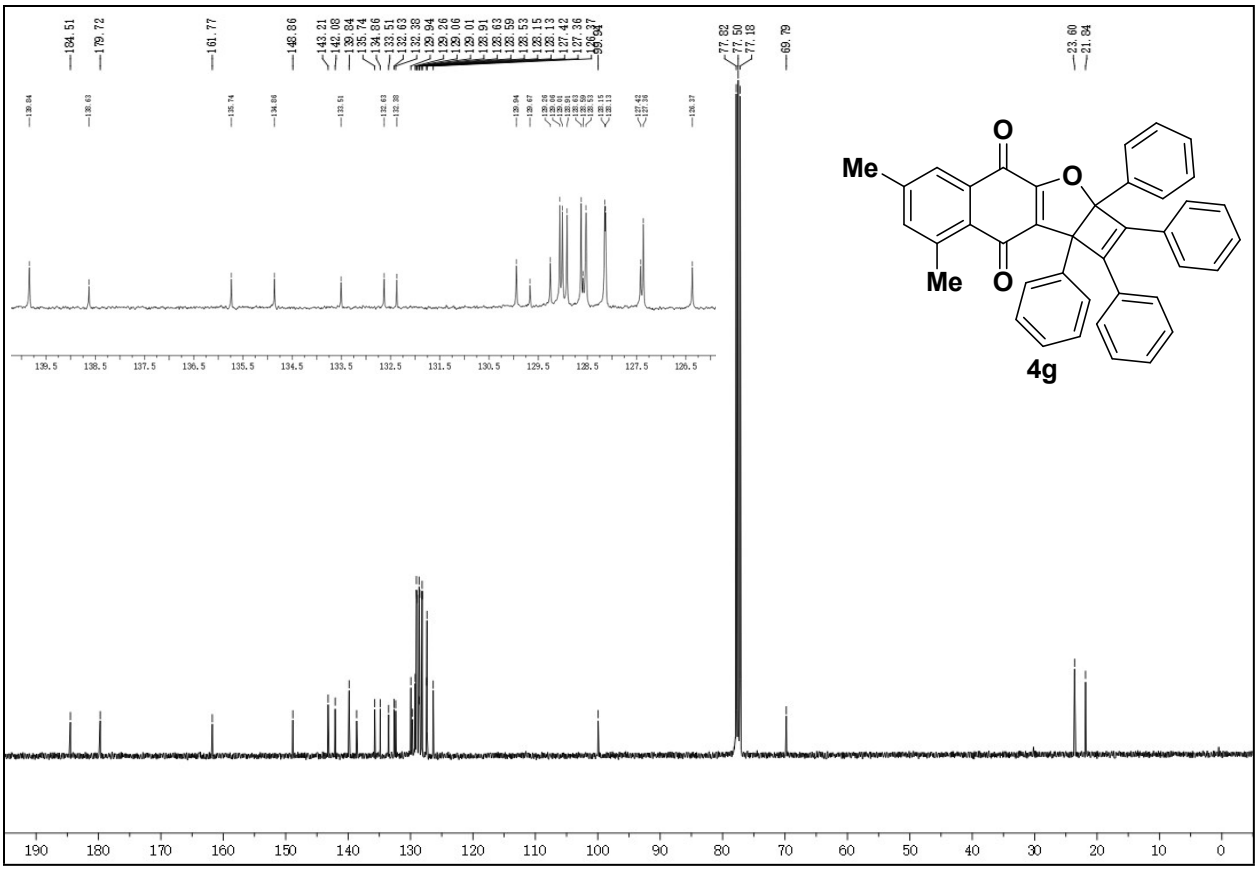
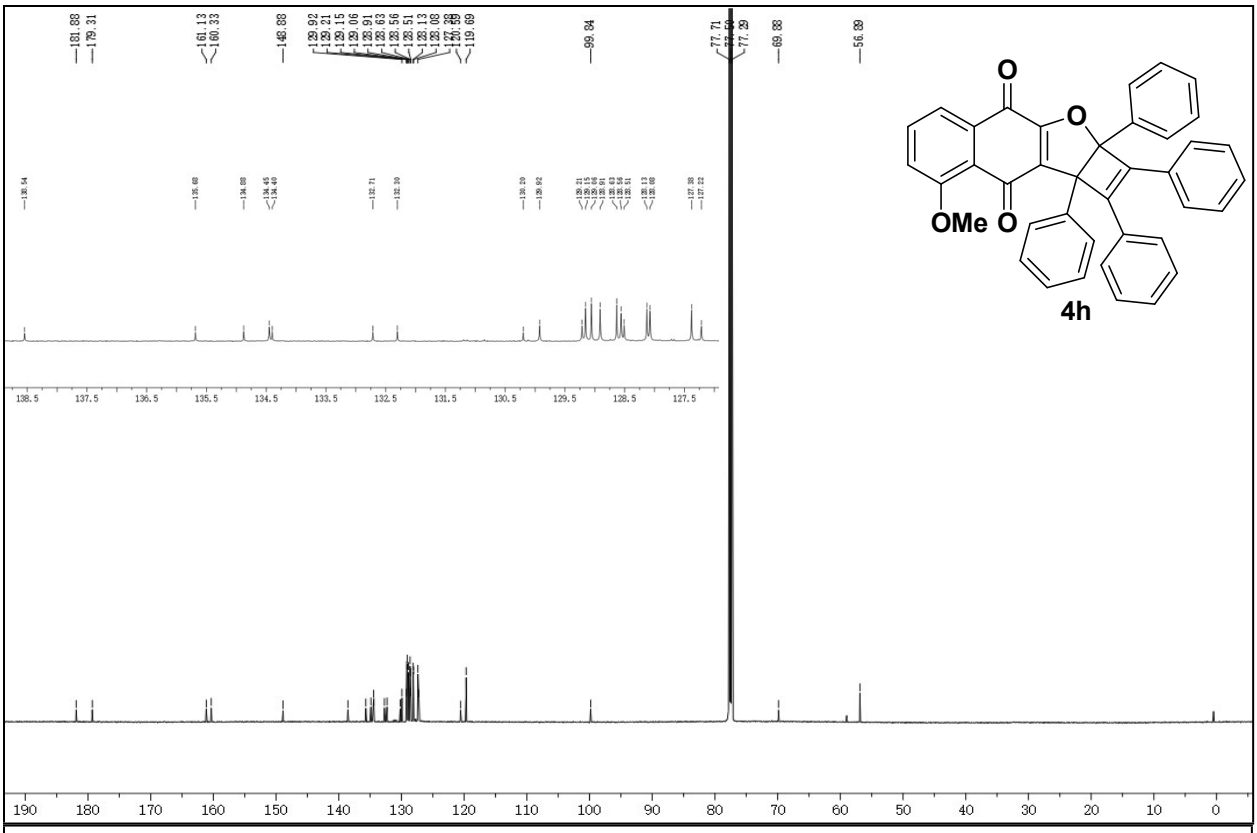
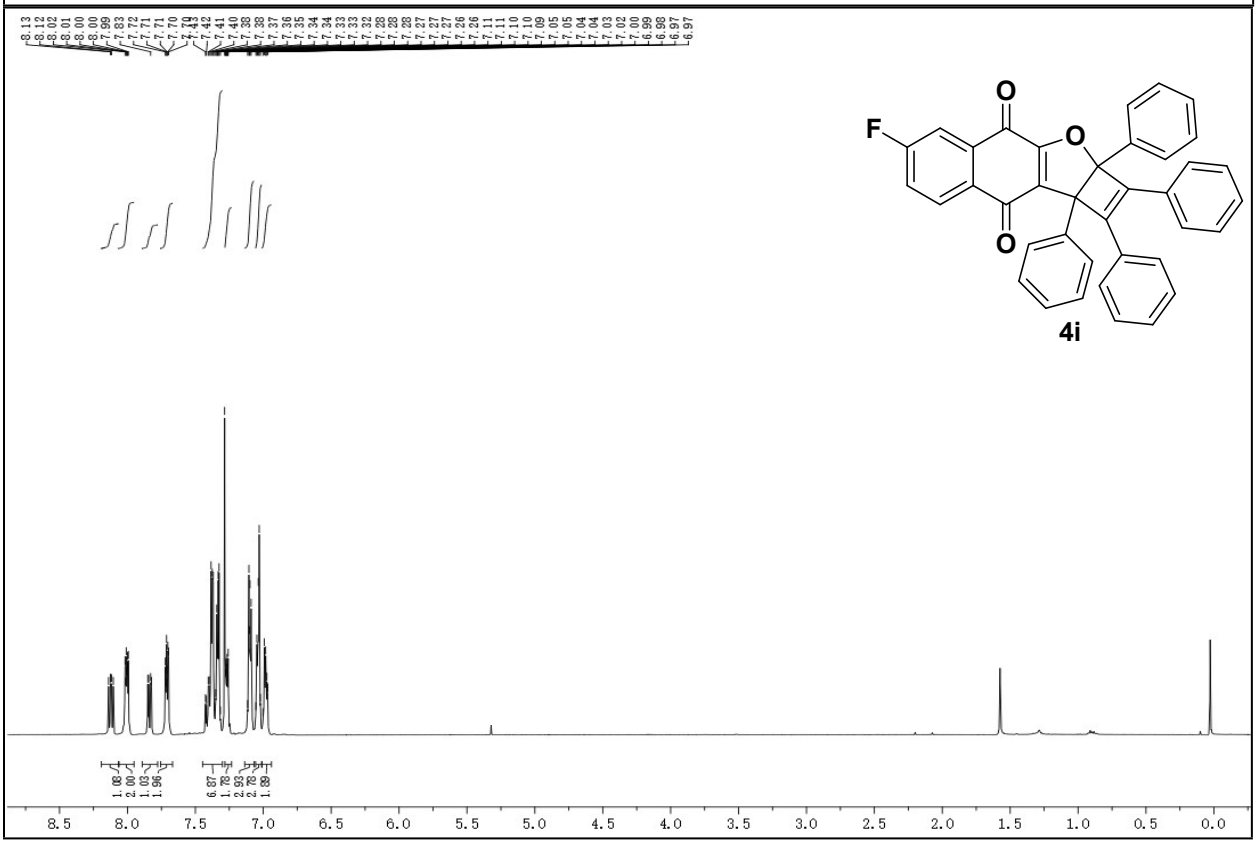
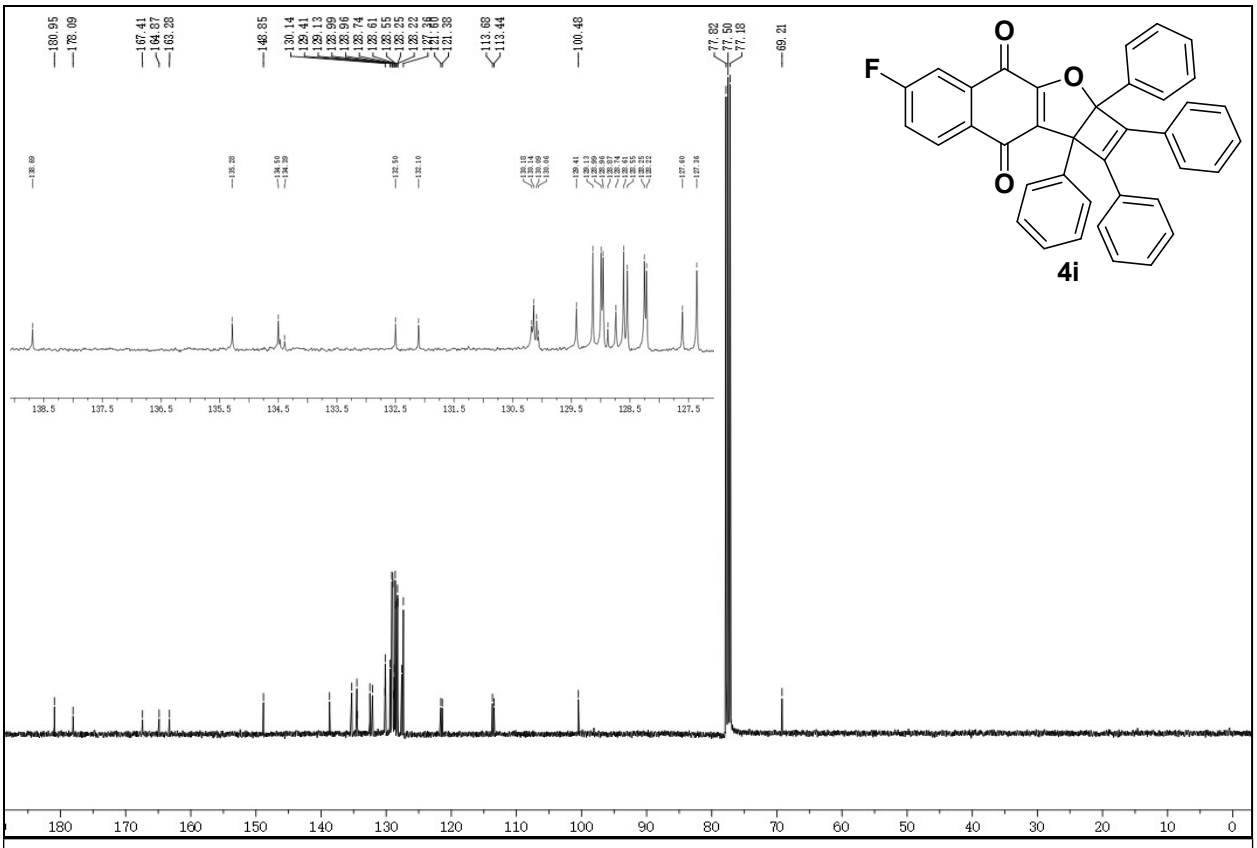
Me
O
O
O
4g


Me
Me
O
O
O
O
4g


OMe
O
O
O
4h


OMe
O
4h


F
O
4i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129.41
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125.25
122.22
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121.38
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113.44
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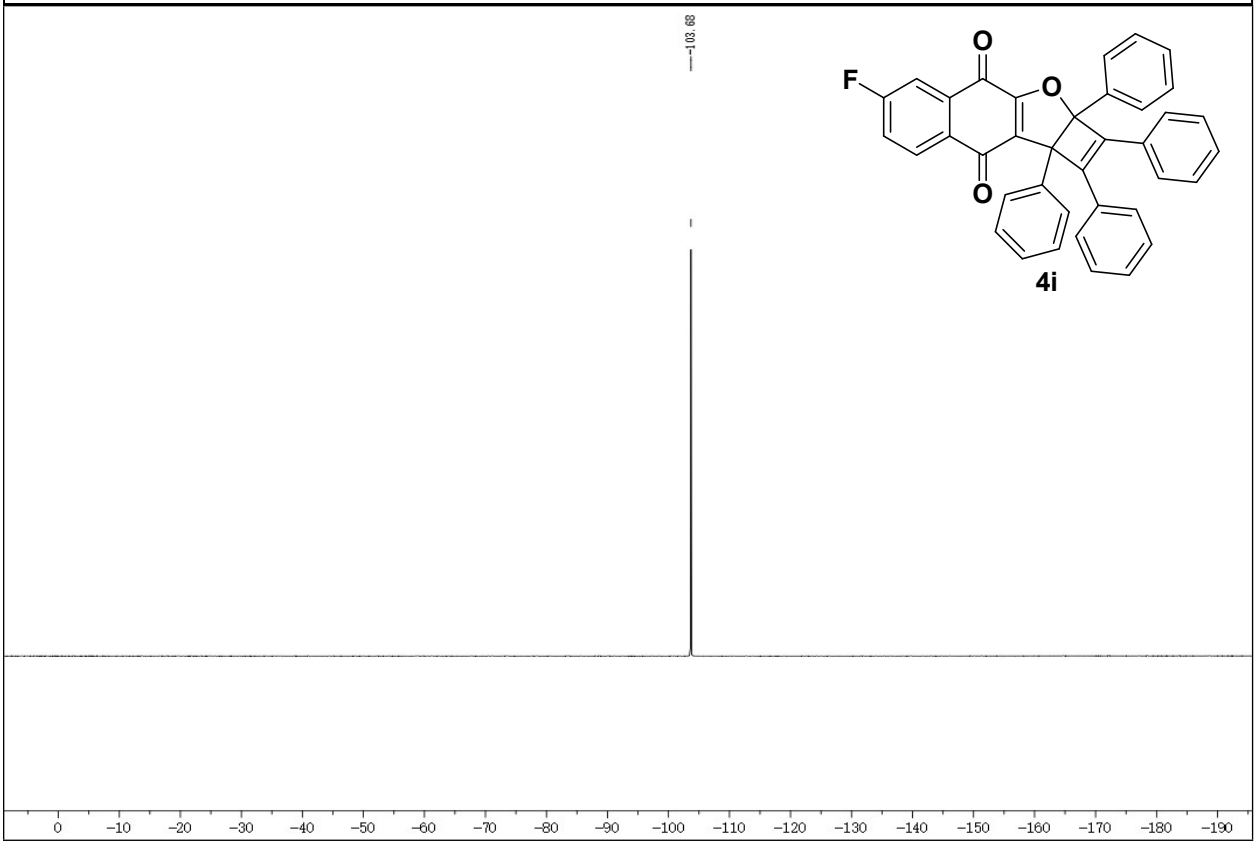
77.62
77.50
77.18
69.21
O
F
O
O
4i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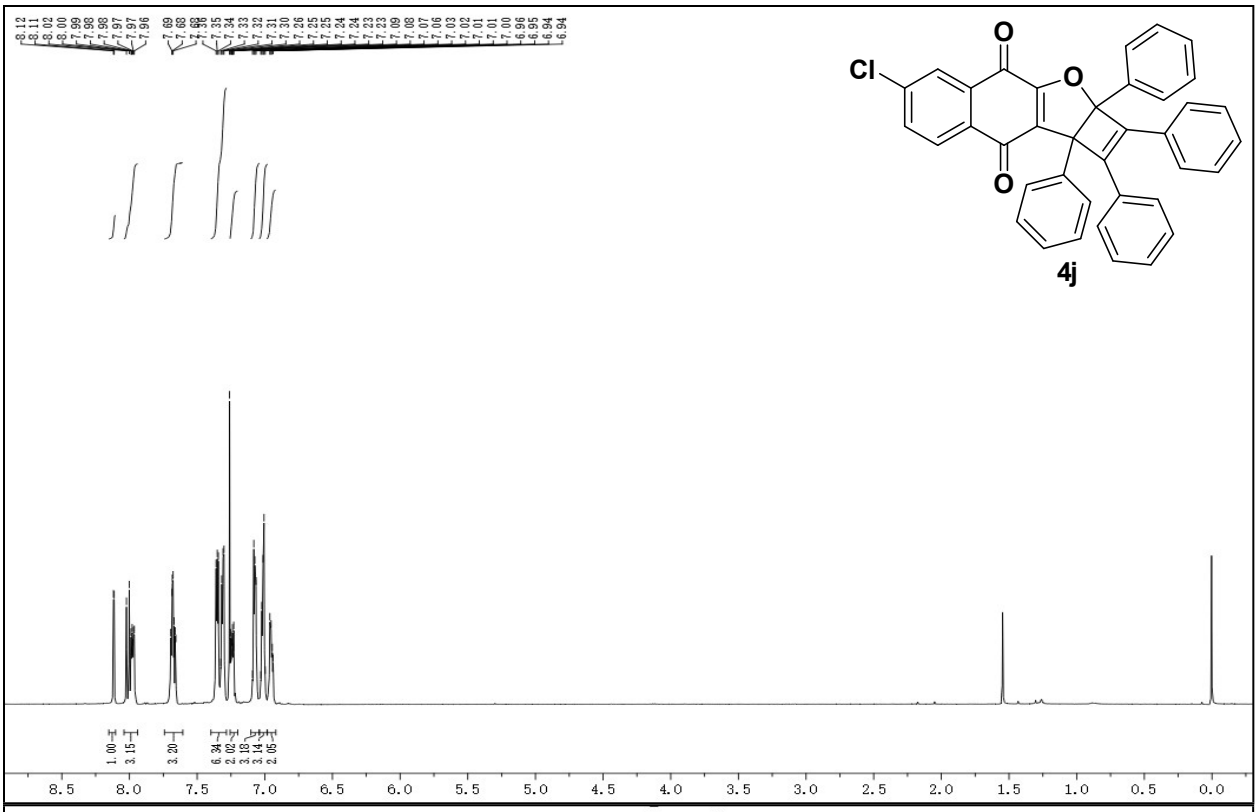
O
O
4i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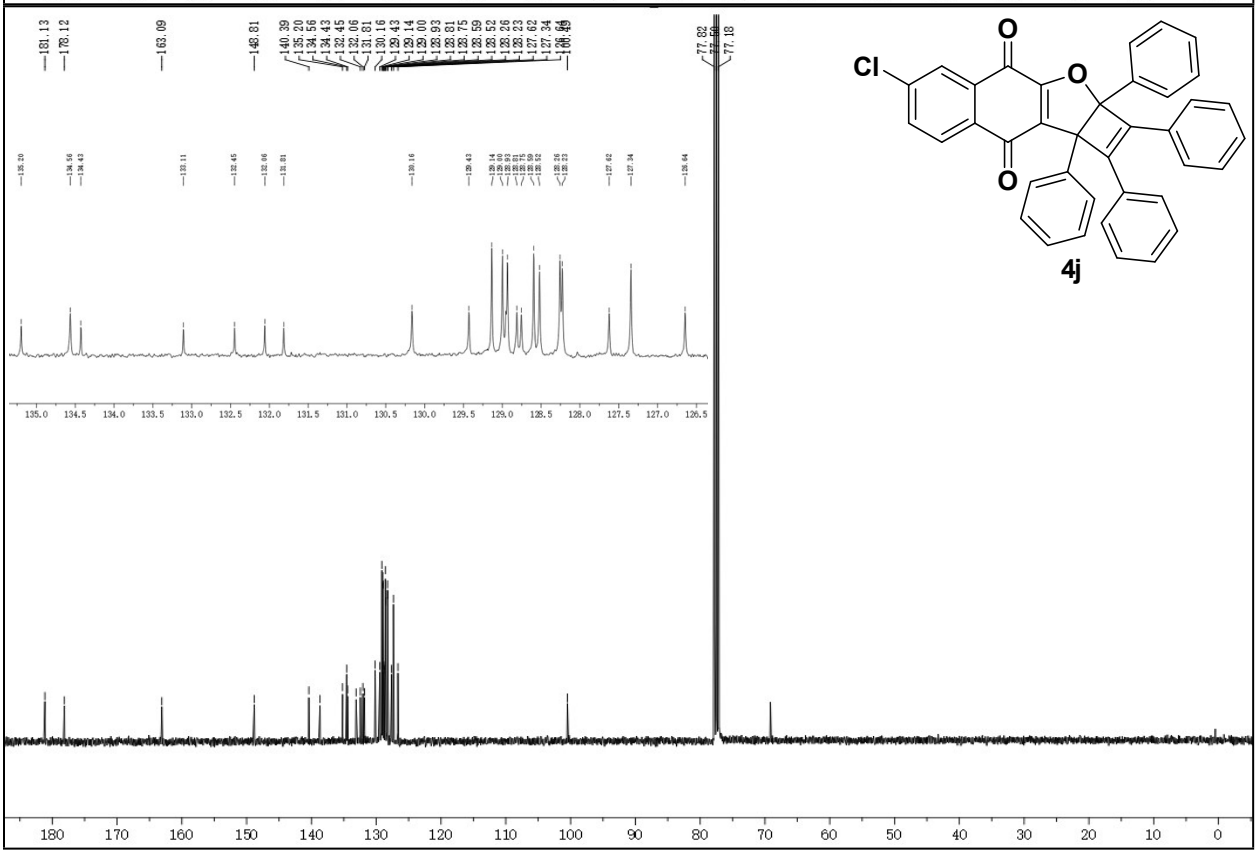
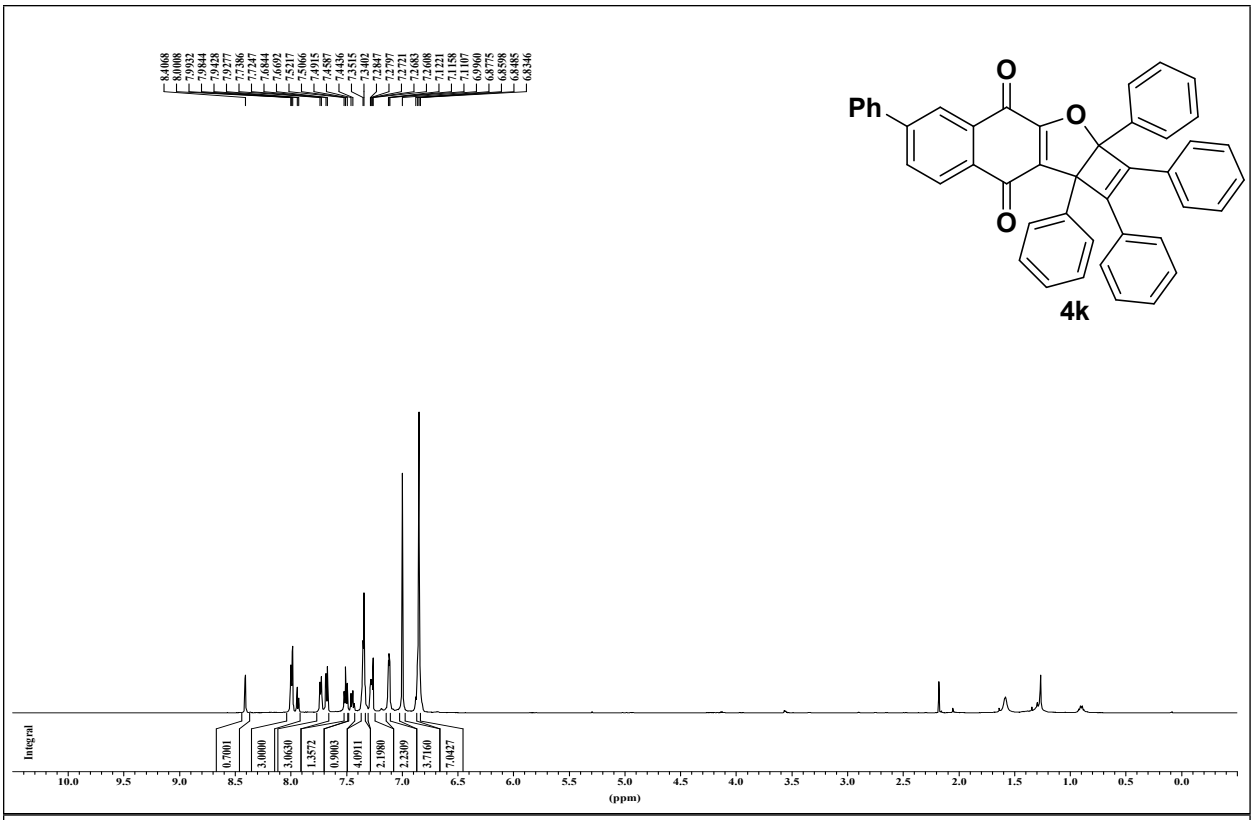
4j


Cl
O
O
O
4j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O
O
4k
Integral
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4.0911
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2.2309
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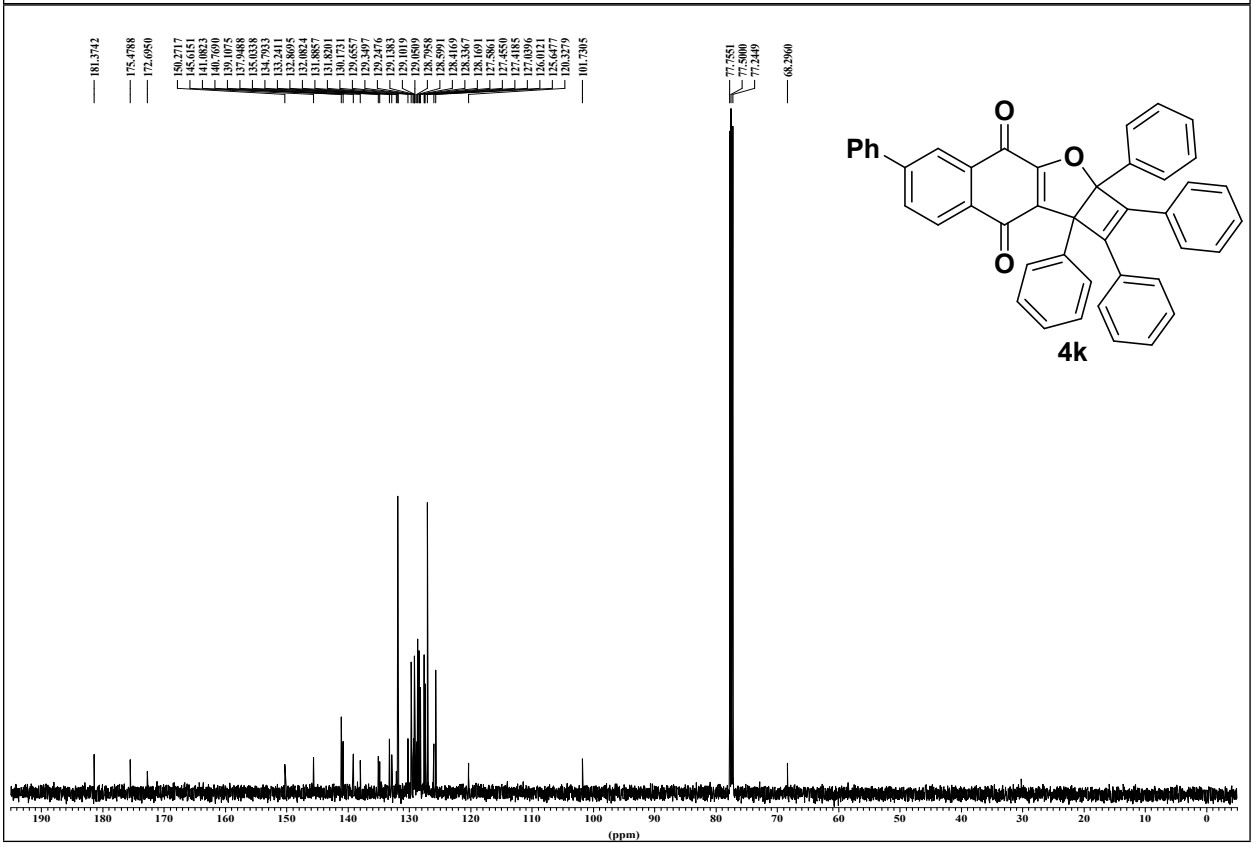
7.0427
(ppm)


Ph
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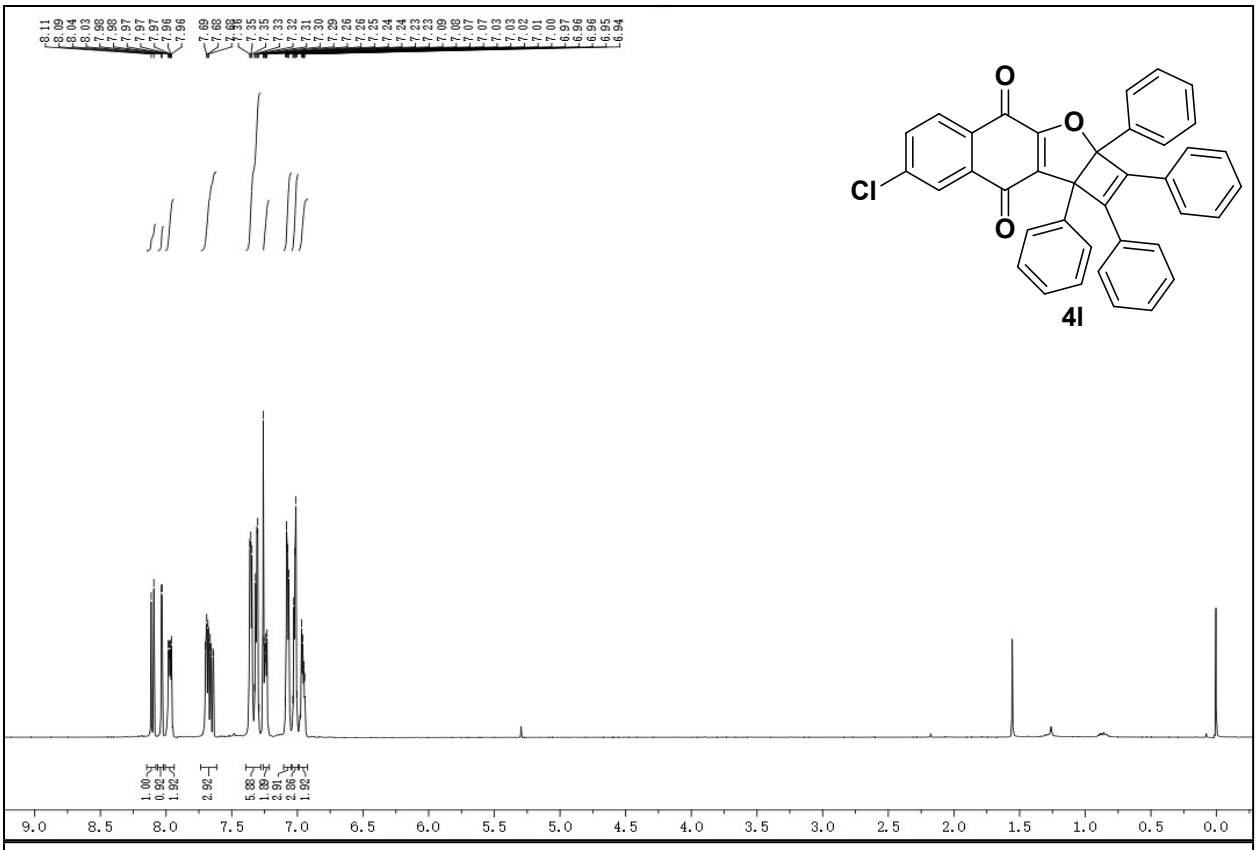
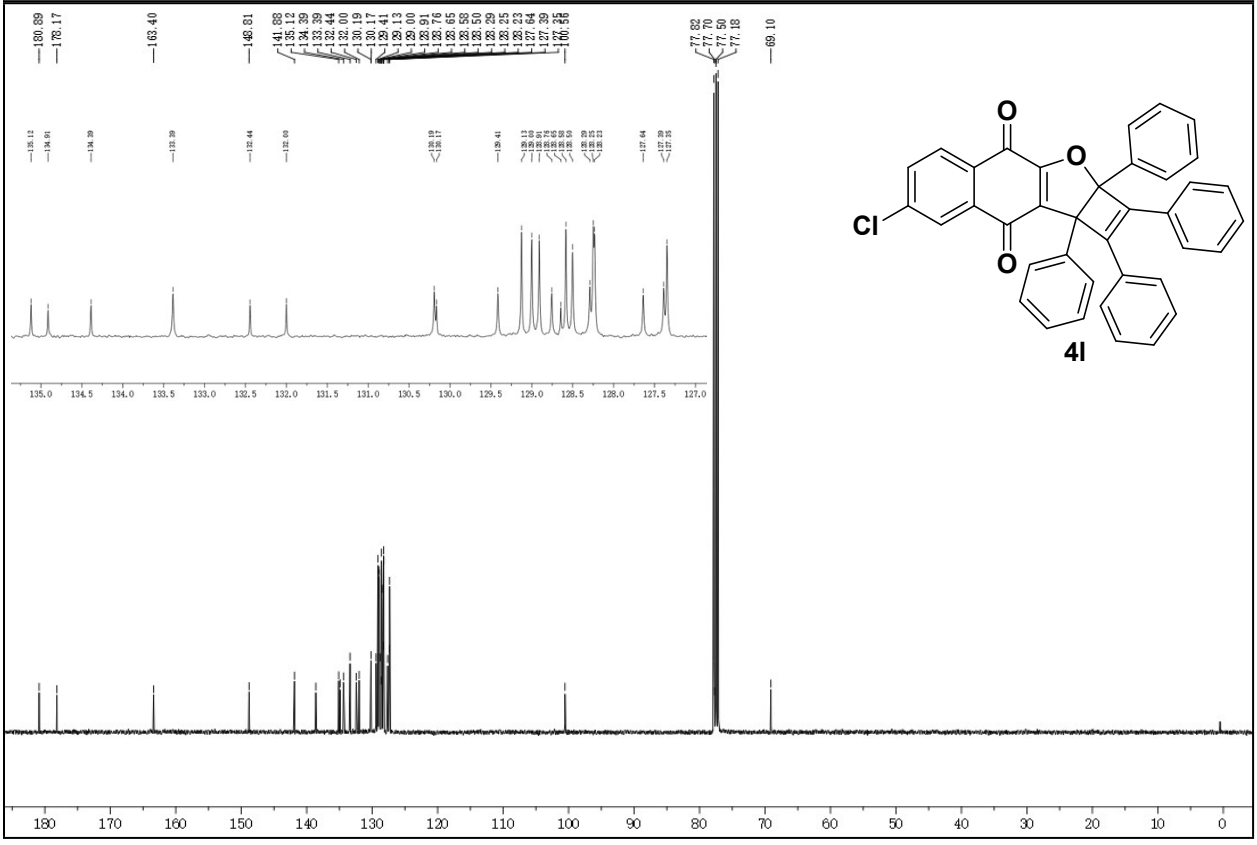
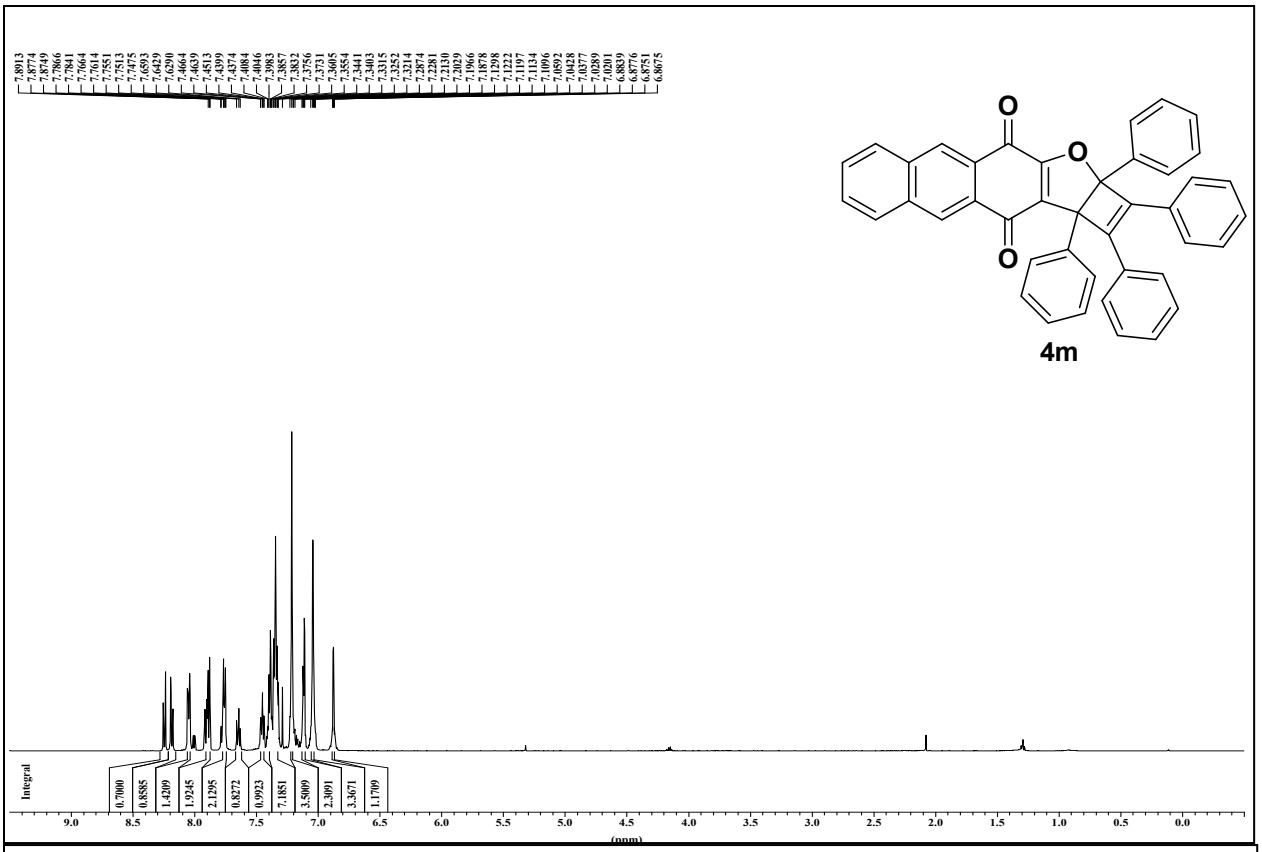
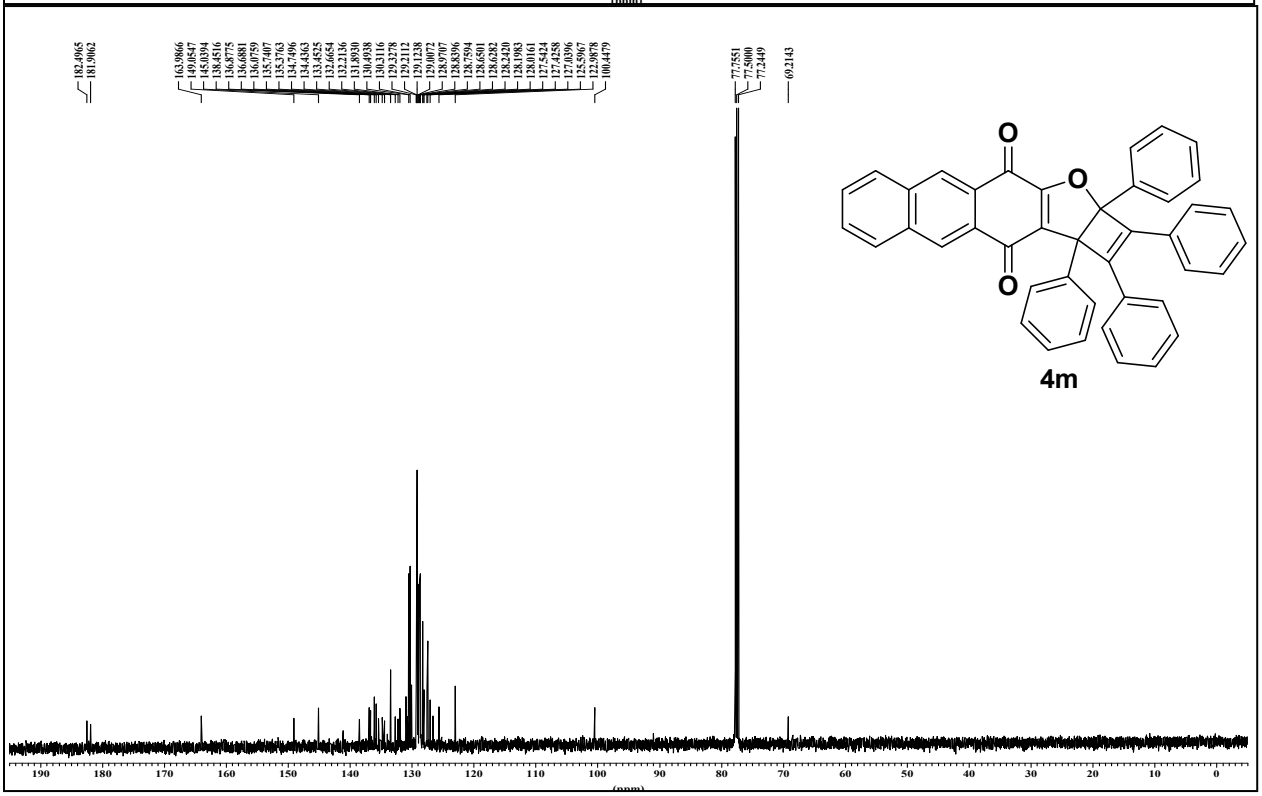
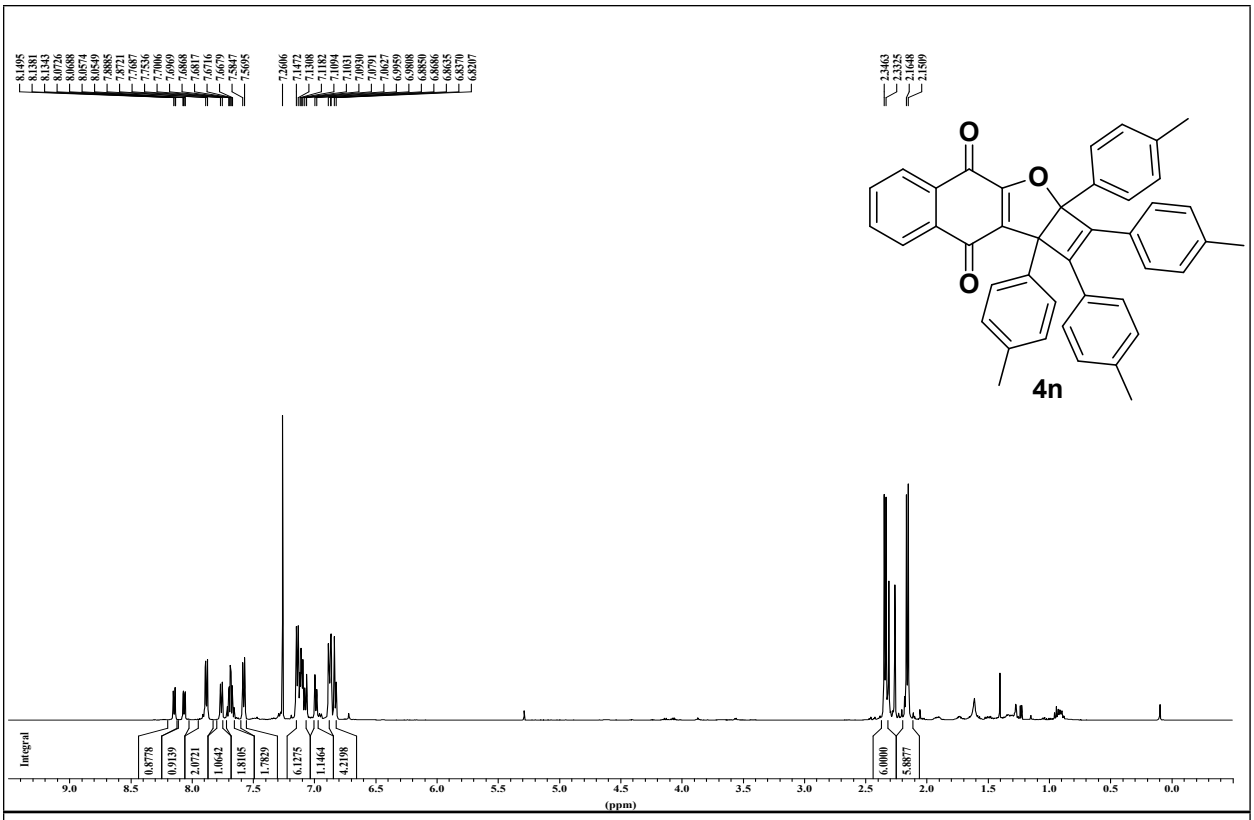
O
O
4k
(ppm)


O
O
Cl
O
4l


O
O
Cl
O
4l


4m
Integral
(ppm)


4m
(ppm)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7.6817
7.6716
7.6679
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7.5695
7.2606
7.1472
7.1308
7.1182
7.1094
7.1031
7.0930
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7.0637
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6.8850
6.8686
6.8635
6.8370
6.8207
2.3463
2.3325
2.1648
2.1509
O
O
O
4n
Integral
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0.9139
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1.8105
1.7829
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1.1464
4.2198
6.0000
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9.0
8.5
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6.5
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2.0
1.5
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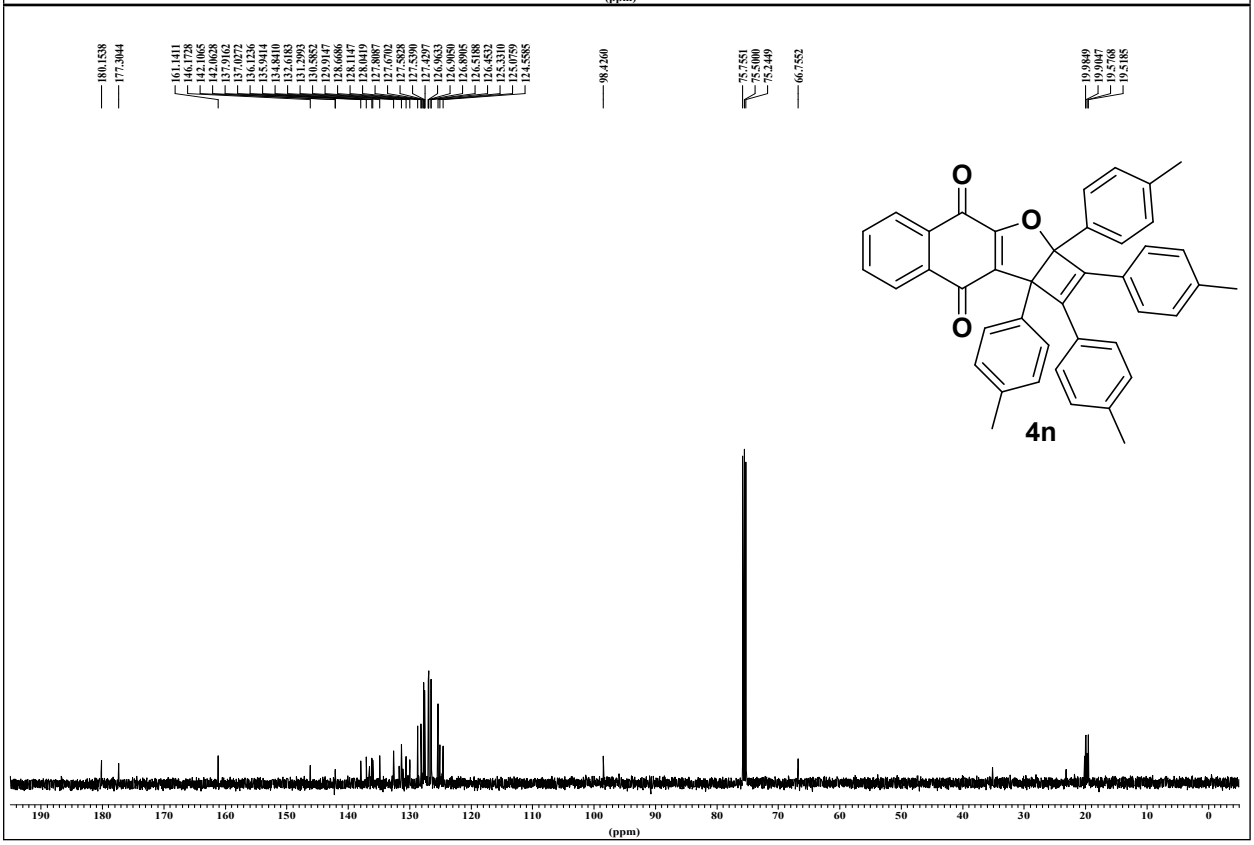
(ppm)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161.1228
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132.6163
131.7989
130.5852
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128.6686
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128.0419
127.8087
127.6702
127.5828
127.5390
127.4297
126.9633
126.9050
126.8905
126.5188
126.4532
125.3310
125.0759
124.5585
98.4260
75.7551
75.5000
75.2449
66.7552
19.9849
19.9647
19.5768
19.5185
O
O
O
4n
190
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120
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100
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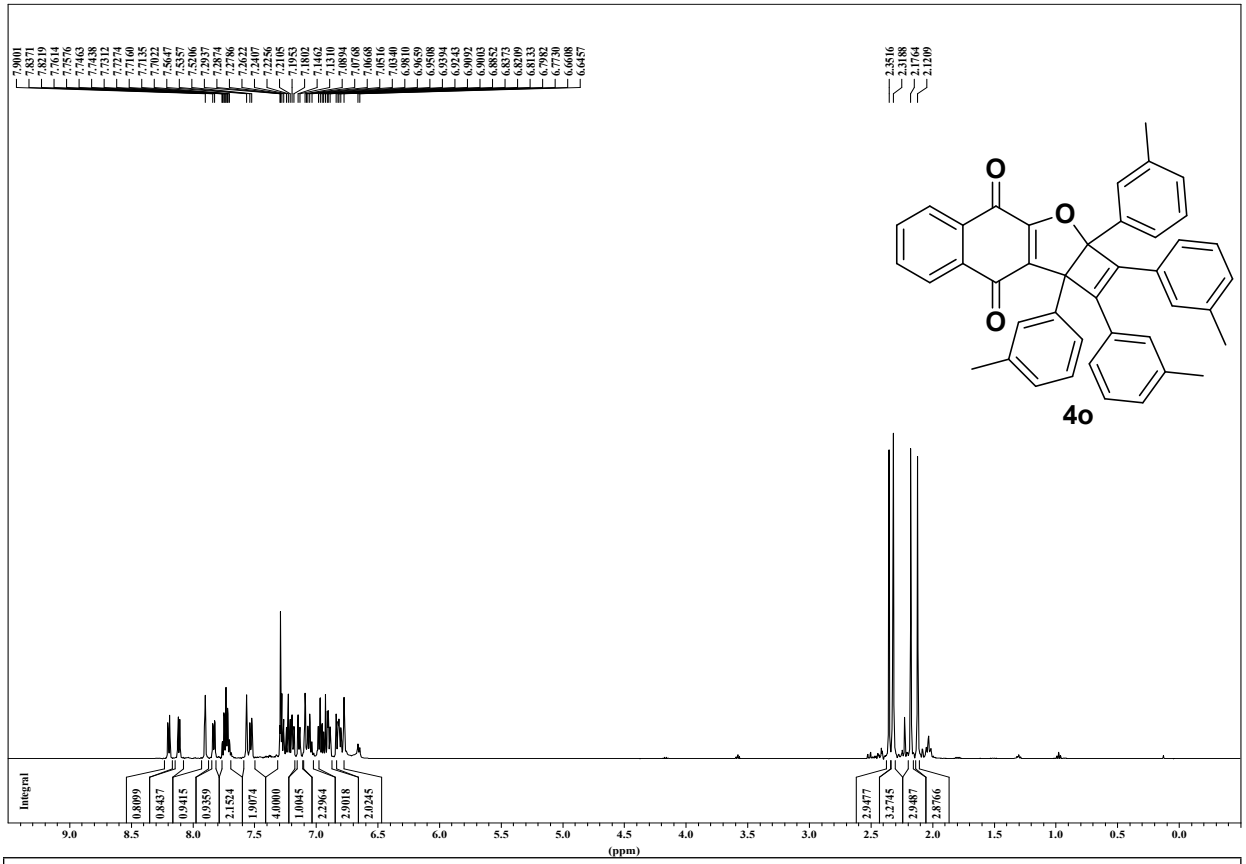
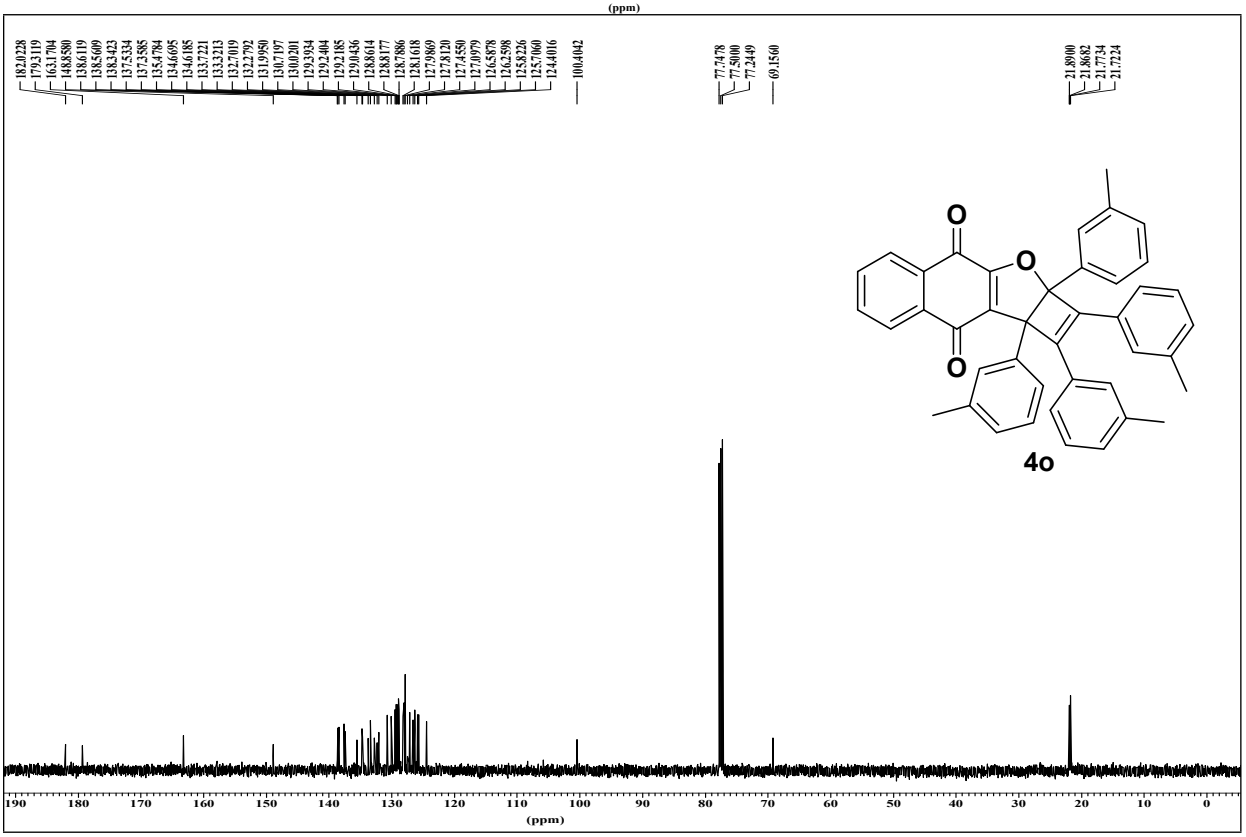
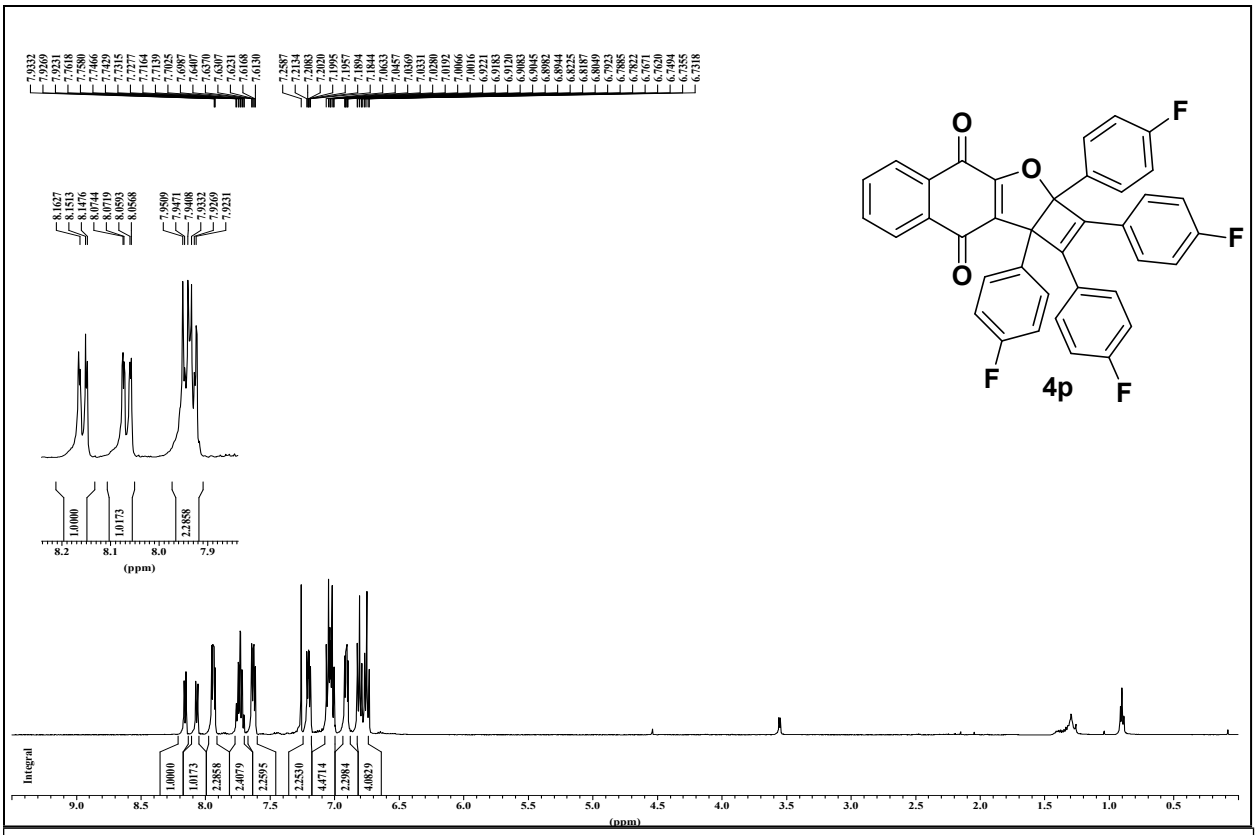
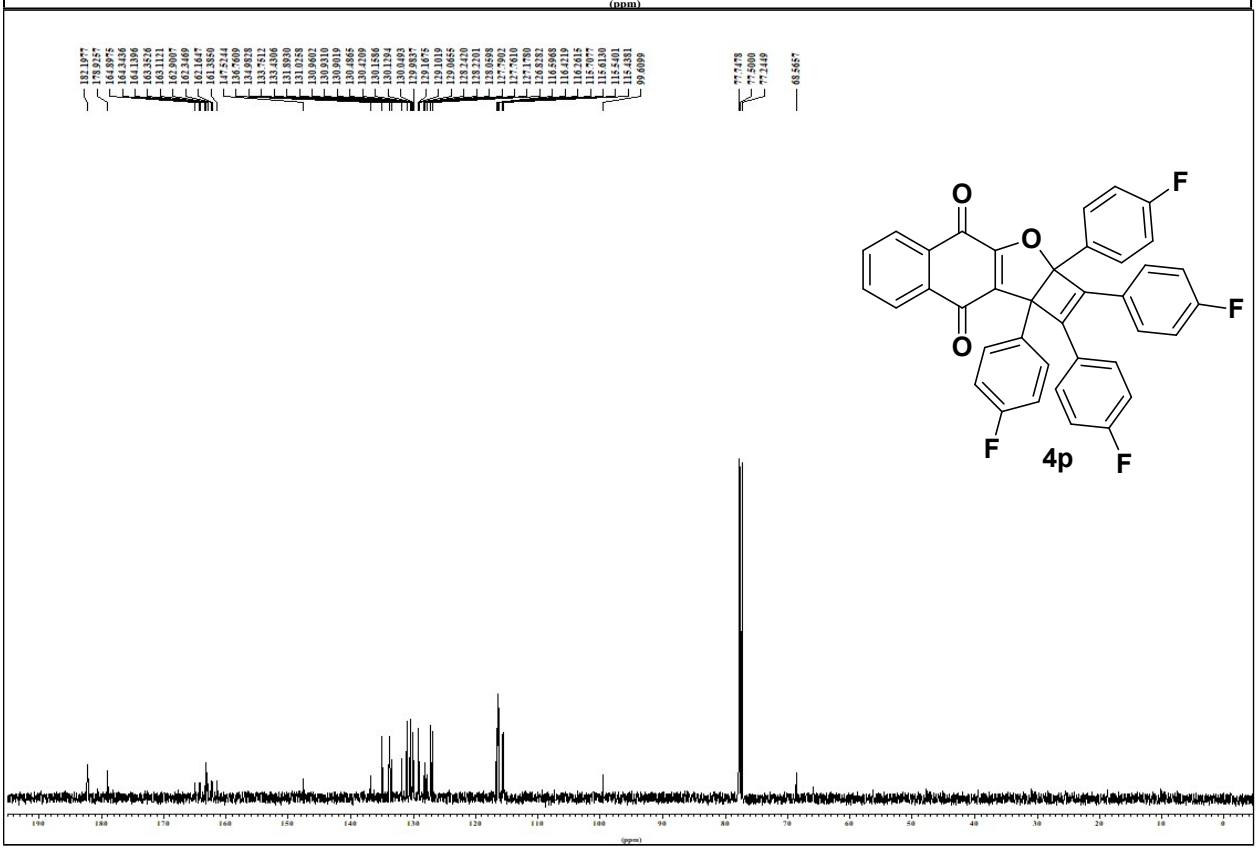
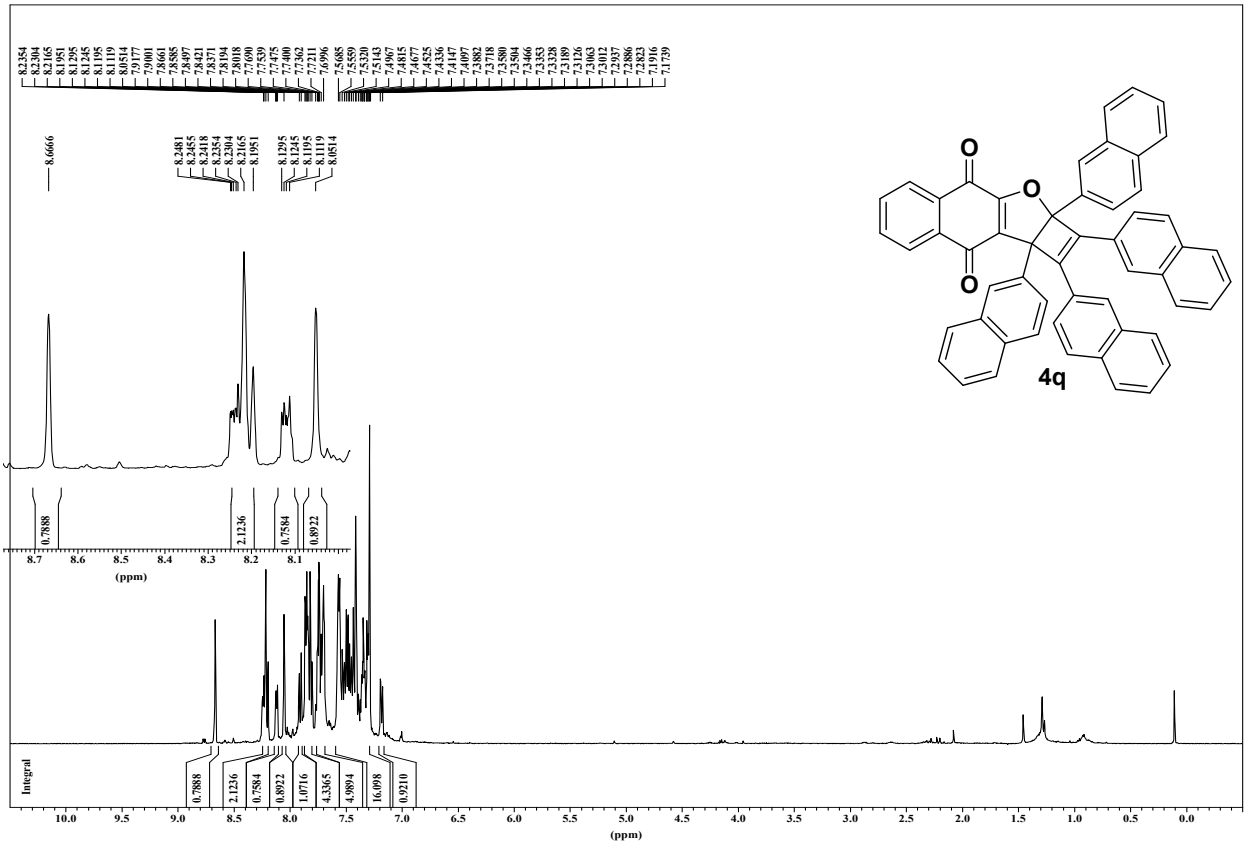
60
50
40
30
20
10
0
(ppm)

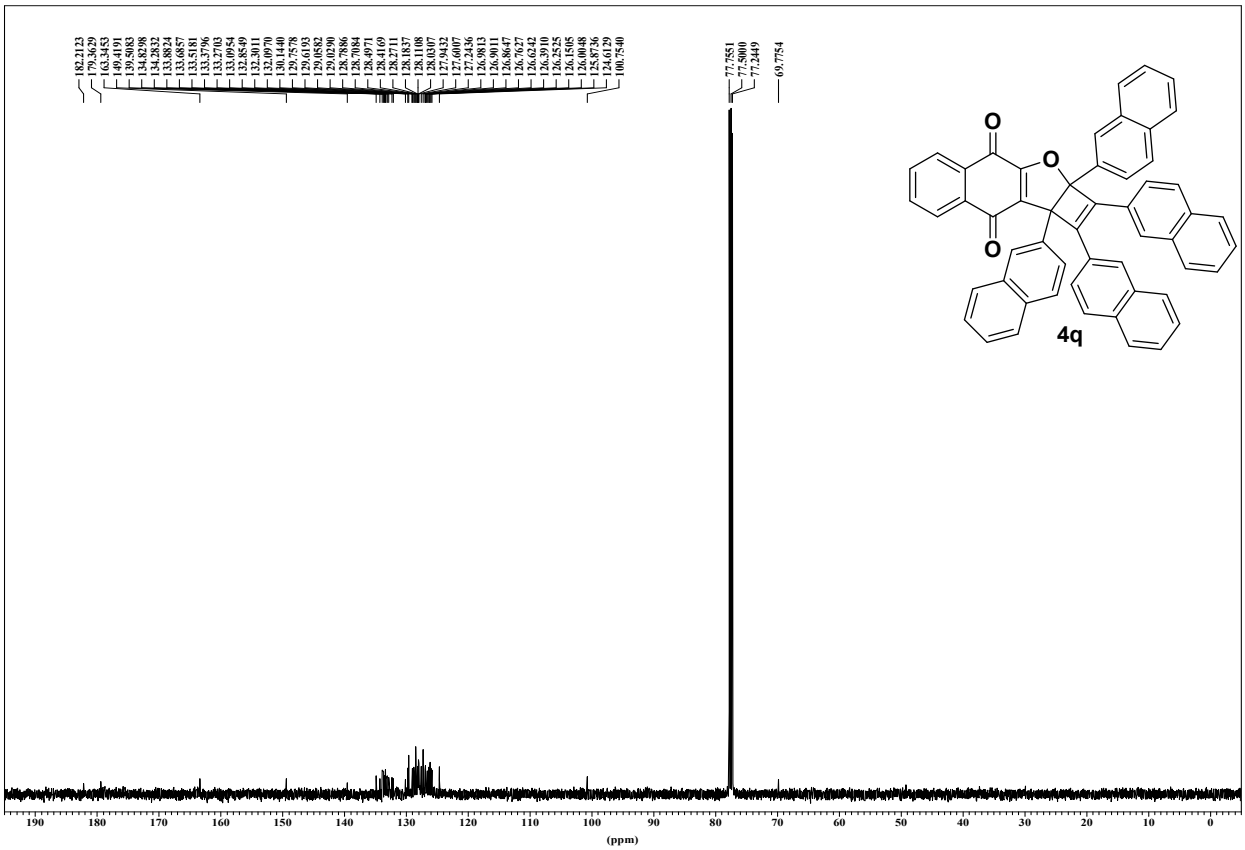

4o
Integral
(ppm)

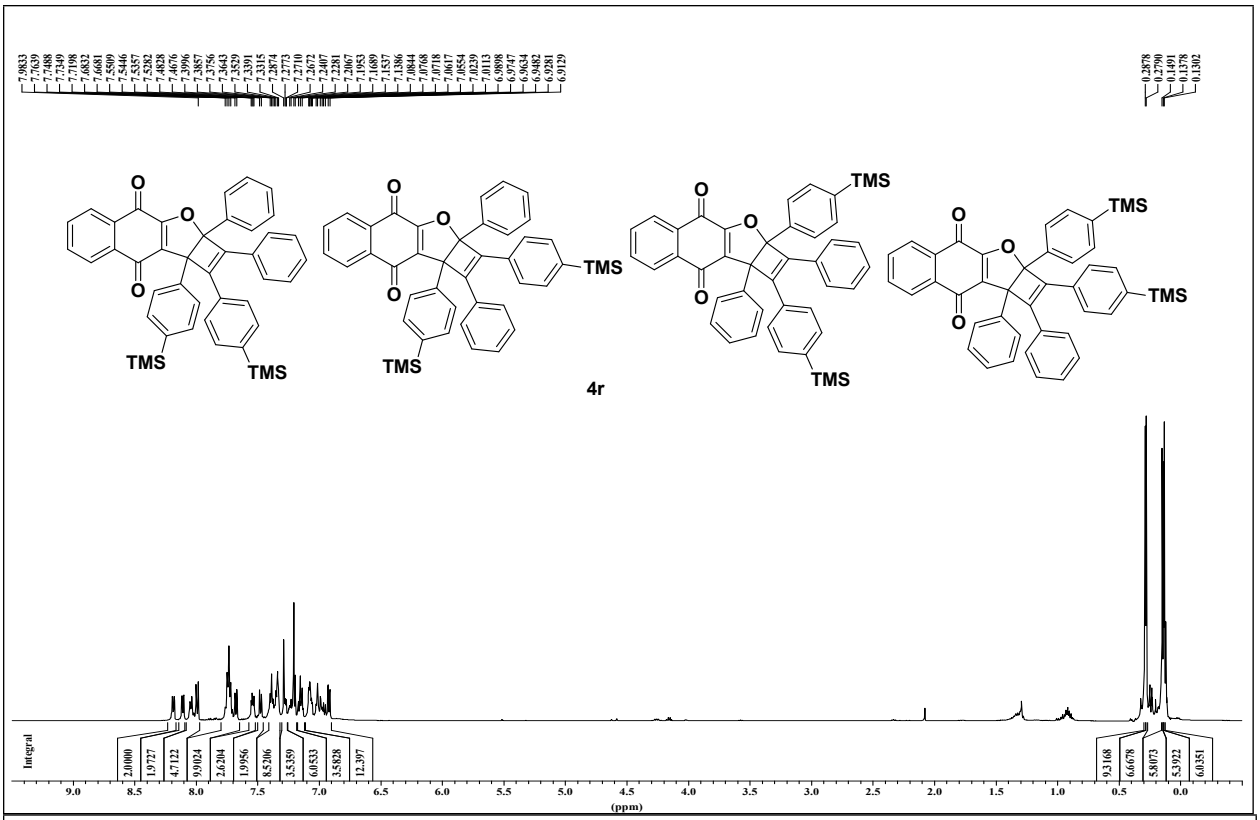

4o
(ppm)

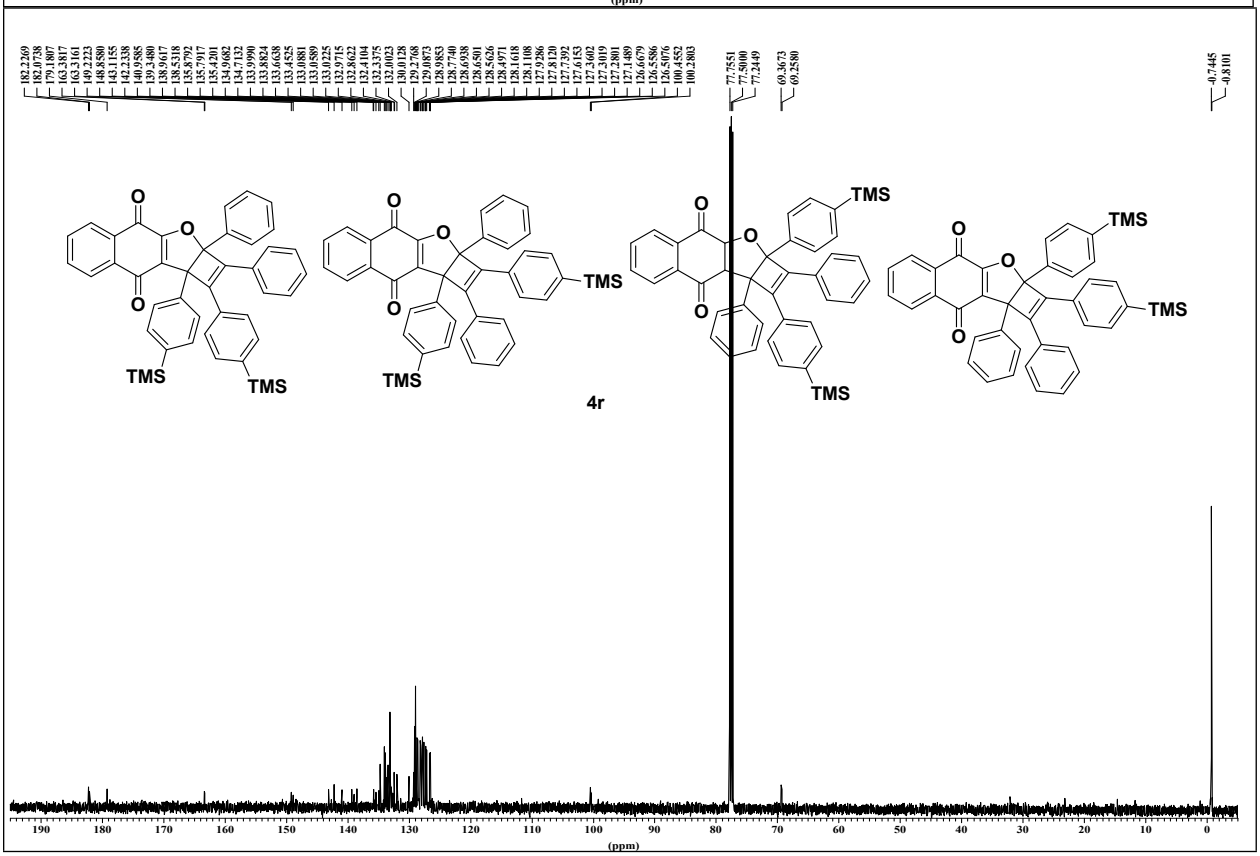

4p
(ppm)
Integral

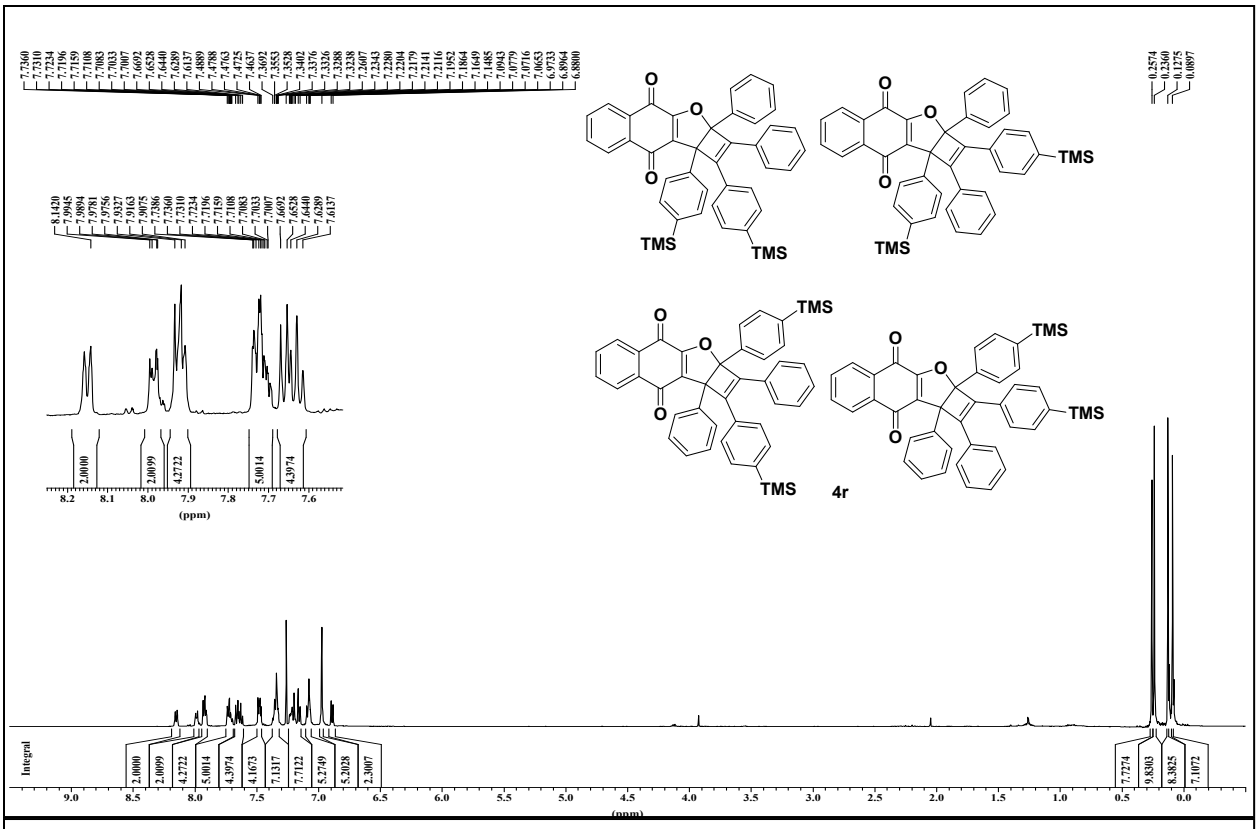

4p
(ppm)

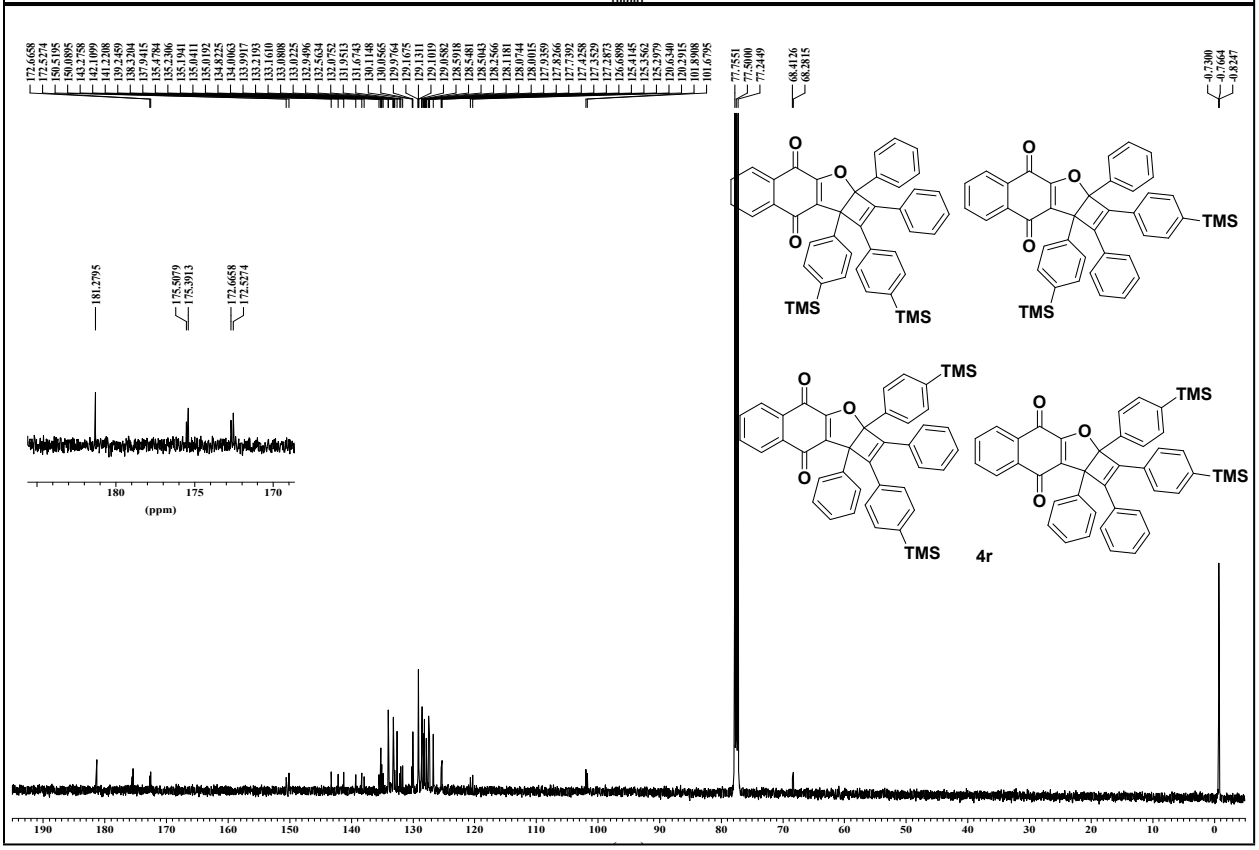

4q
(ppm)

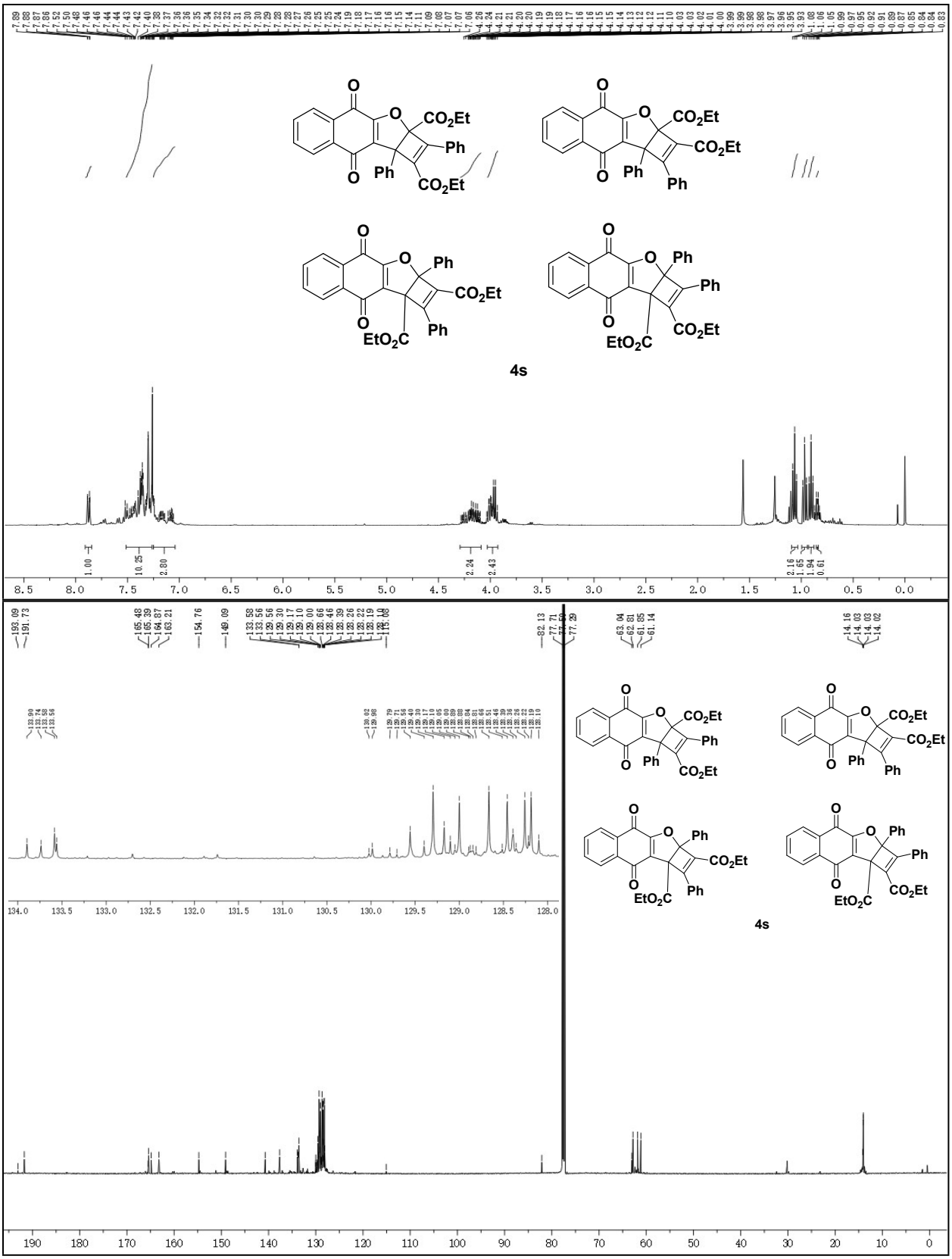

4q
(ppm)

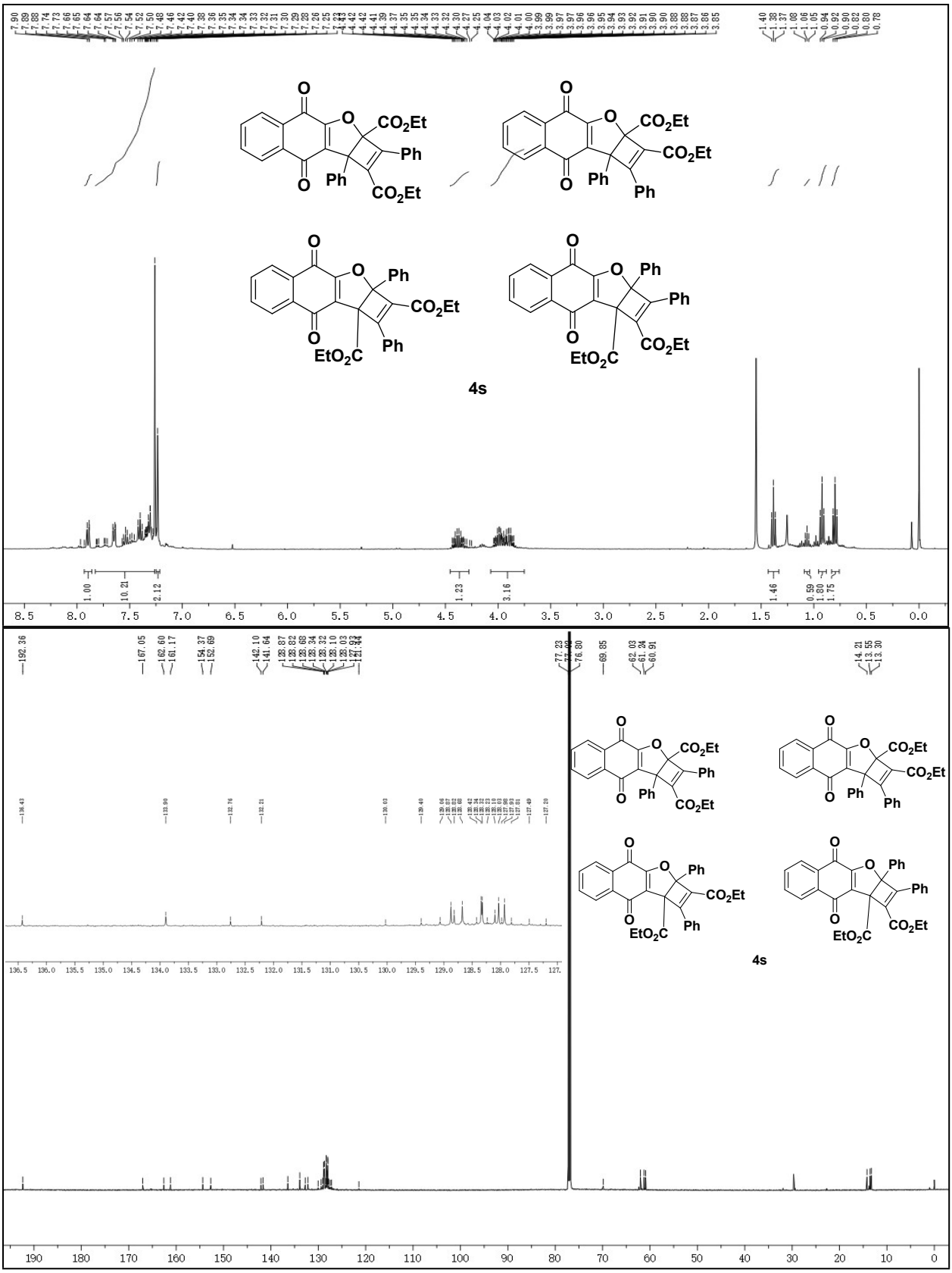

TMS
4r
Integral
(ppm)

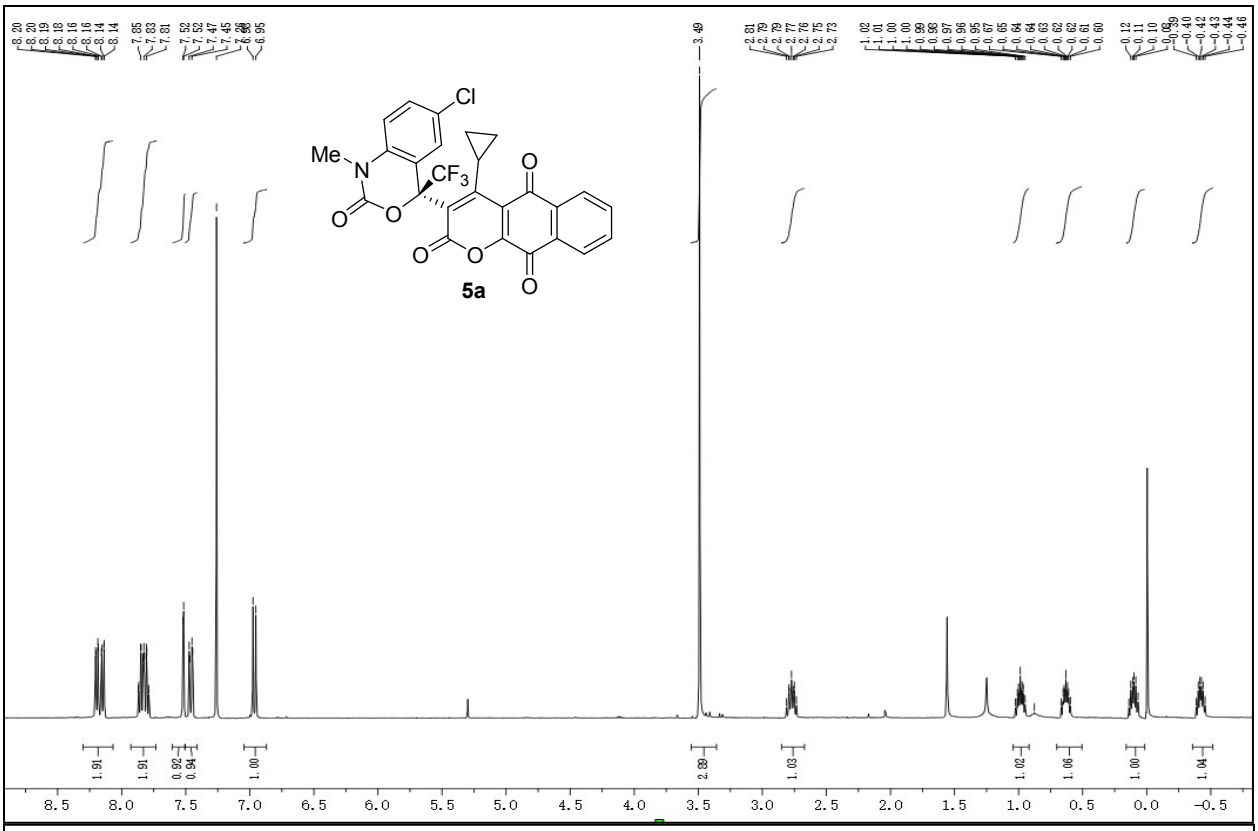

TMS
4r
(ppm)

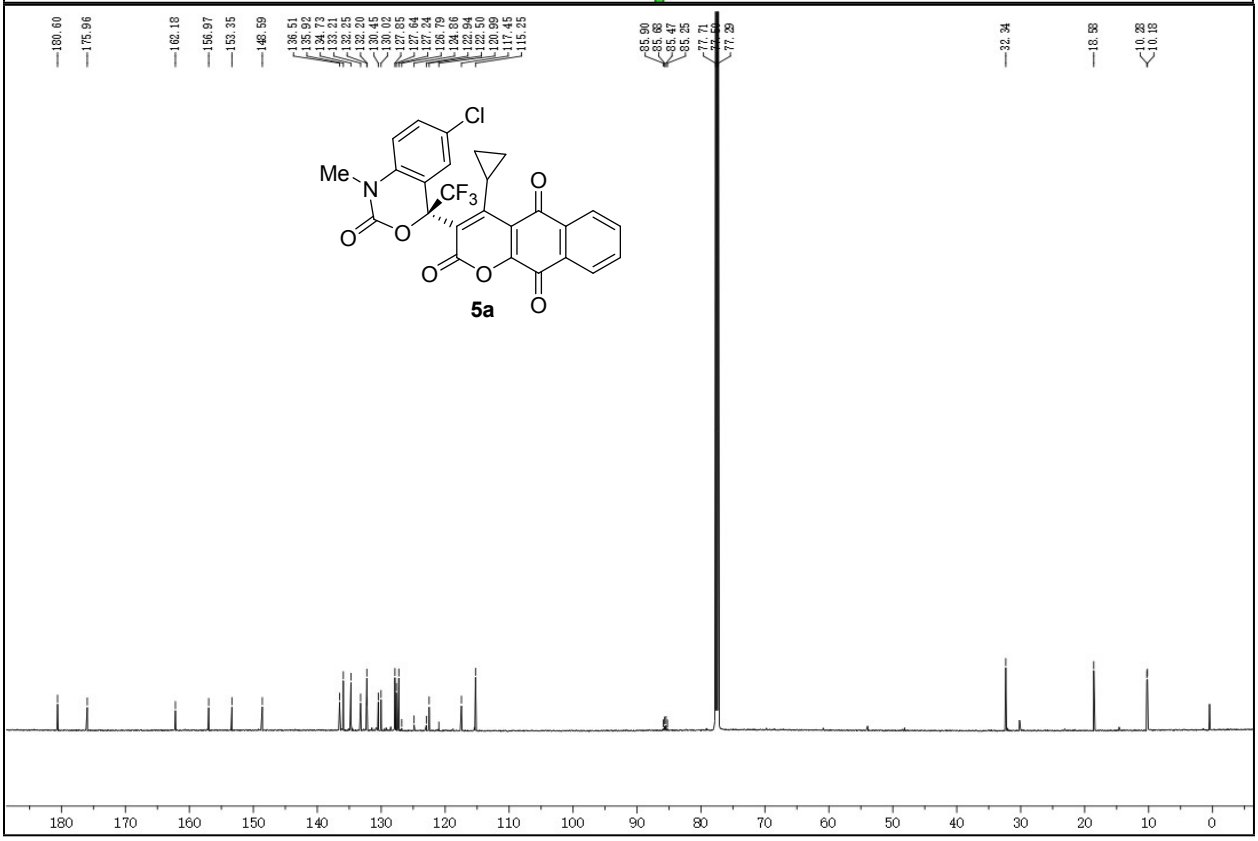

TMS
4r
Integral
(ppm)


TMS
4r
(ppm)

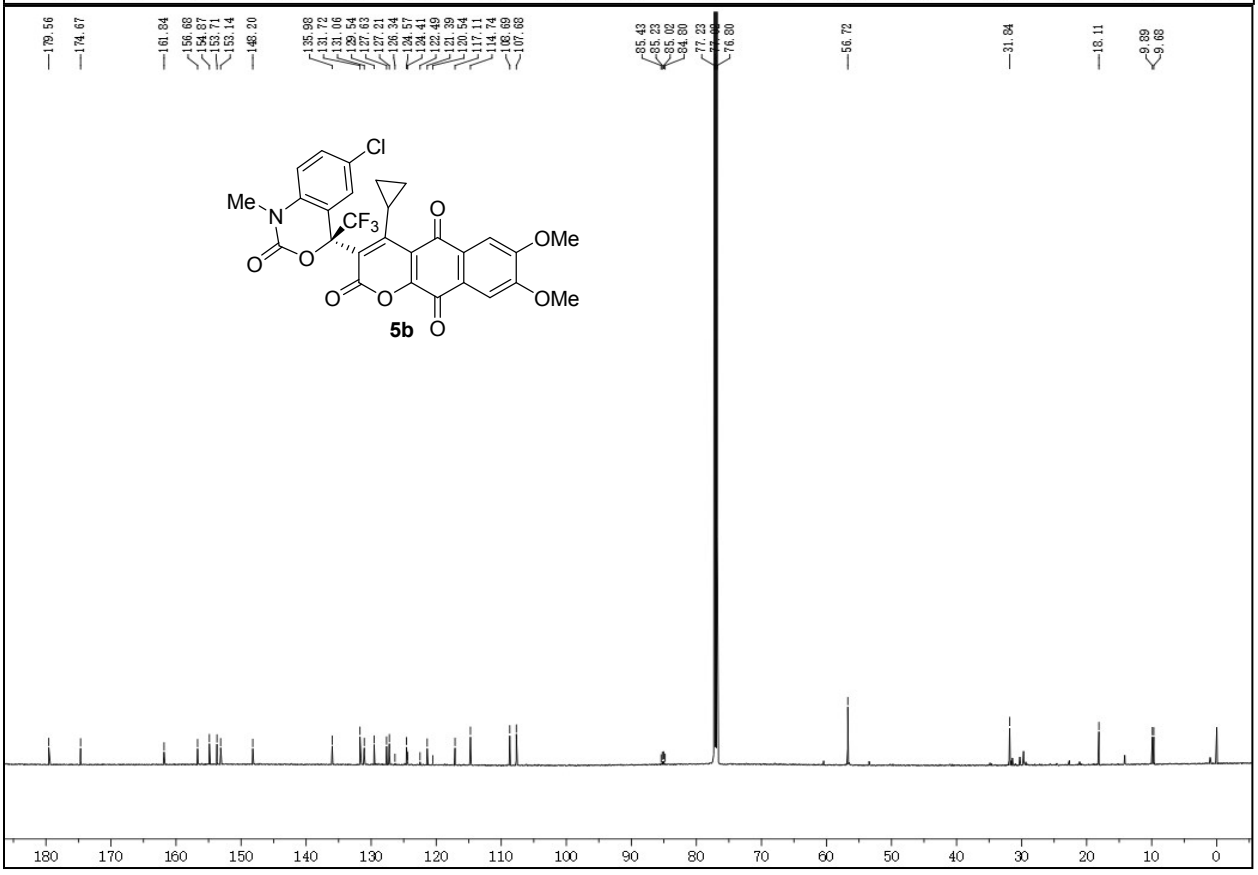

4s
4s

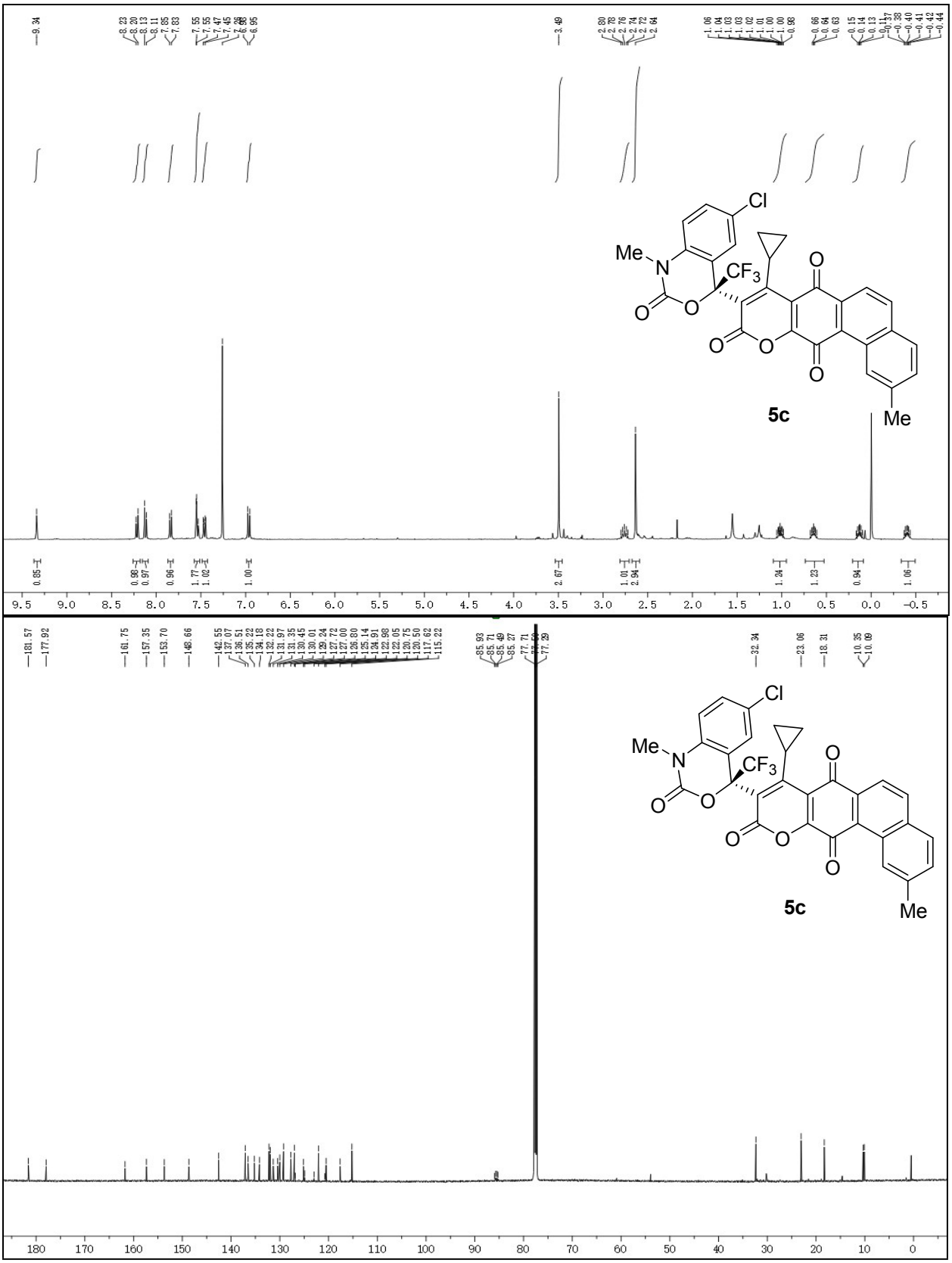

4s
4s

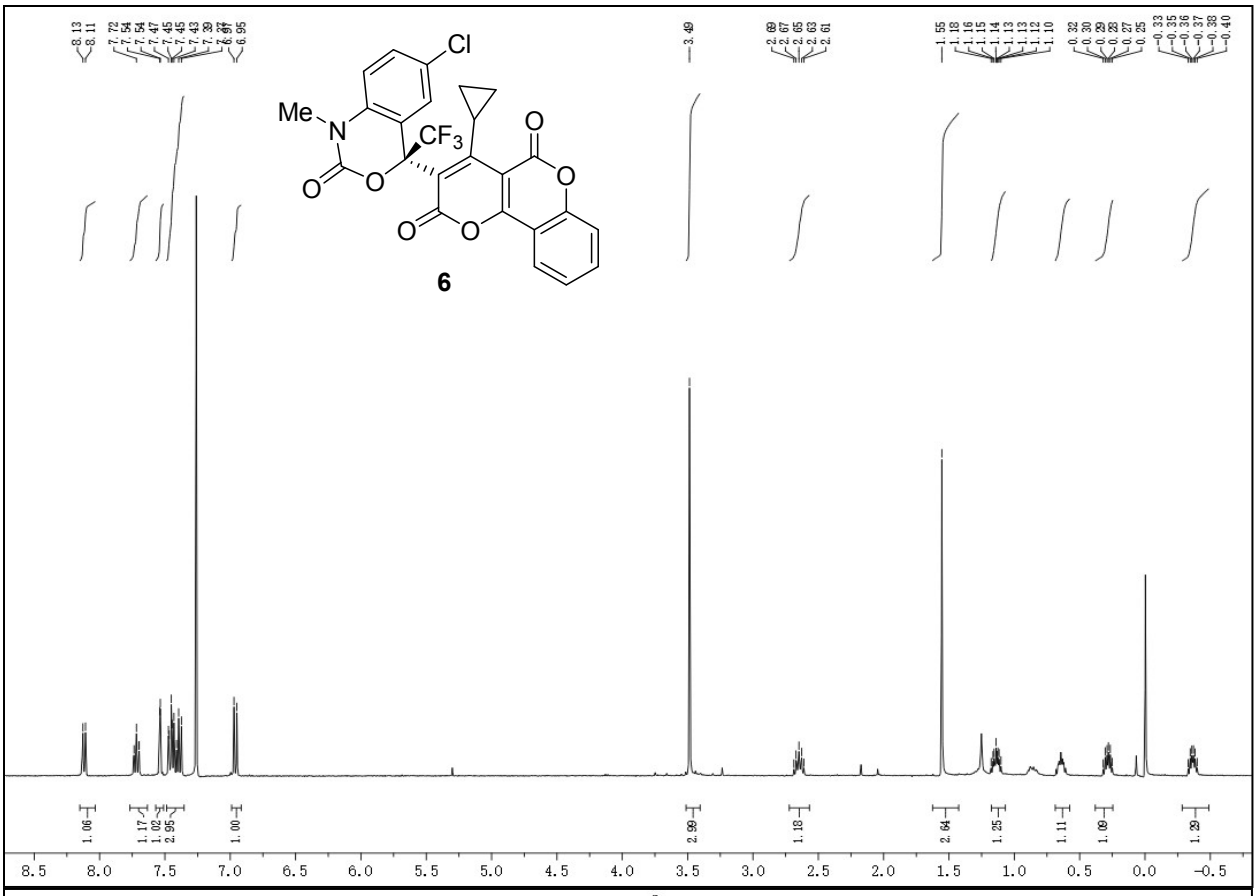

Cl
Me
N
CF3
O
O
O
O
O
O
5a

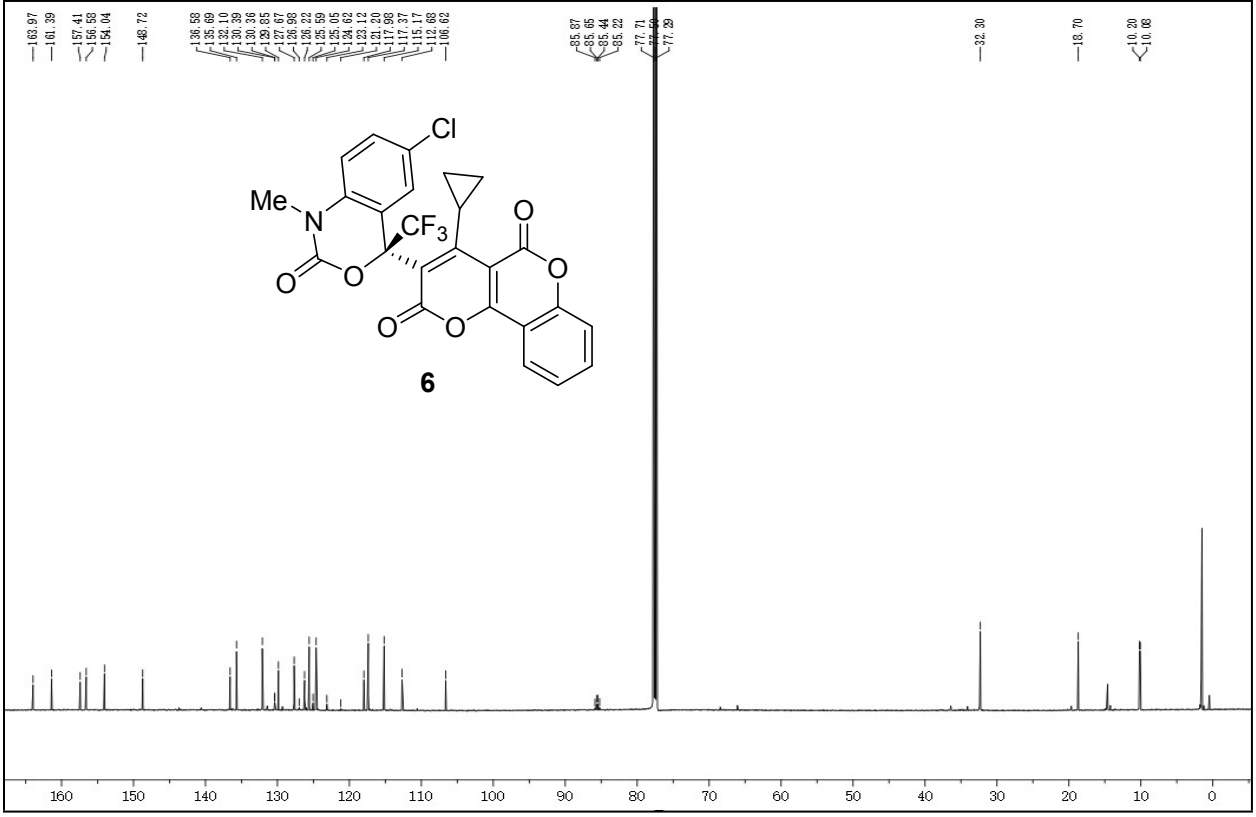

Cl
Me
N
CF3
O
O
O
O
O
O
5a


Cl
Me
N
CF3
O
OMe
OMe
5b


Cl
Me
N
CF3
O
OMe
OMe
5b


Cl
Me
N
CF3
O
O
O
O
O
O
Me
5c
Cl
Me
N
CF3
O
O
O
O
O
O
Me
5c


Cl
Me
N
CF3
O
O
O
O
O
6


Cl
Me
N
CF3
O
O
O
O
O
6