Electronic Supporting Information (ESI)

Palladium(II)-Catalyzed Hydroxy-involved Enolate-type Efficient C−C Functionalization of Hydroxynaphthoquinones at Room Temperature

Nan Wang [a], Xingsen Wu [a], Taoyu Qin [a], Jianrui Zhou [a], Qidong You [a,*], Xiaojin Zhang [a,b,*]

[a] State Key Laboratory of Natural Medicines, and Jiangsu Key Laboratory of Drug Design and Optimization, China Pharmaceutical University, Nanjing, 210009, China
[b] Department of Organic Chemistry, School of Science, China Pharmaceutical University, Nanjing, 210009, China
[*] Corresponding authors. E-mail: zxj@cpu.edu.cn (X. Zhang), youqd@163.com (Q. You).

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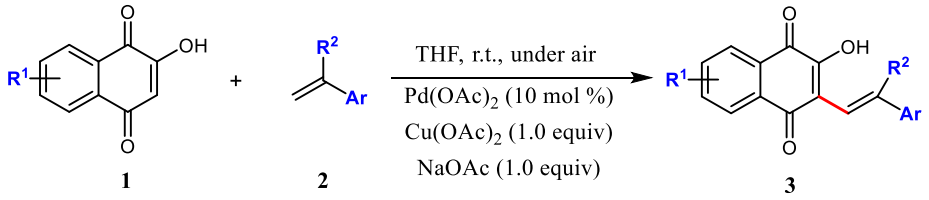
1 General Methods

Reactions were monitored by thin-layer chromatography on silica gel plates (650F-254) visualized under UV light. Melting points were determined on a Mel-TEMP II melting point apparatus without correction. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO on a Bruker Avance 300 MHz spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (TMS) using the residual solvent resonance ($CDCl_3$: 7.26 ppm, 1.56 ppm (HDO) for ^{1}H NMR, 77.16 ppm for ^{13}C NMR; DMSO: 3.30 ppm and 2.50 ppm for ^{1}H NMR; THF: 25.31 ppm, 67.21 ppm for ^{13}C NMR). Multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of double doublets, dt = doublet of triplet, dtd = doublet of triple doublets t = triplet, q = quartet, m = multiplet). MS spectra were recorded on a LC/MSD TOF HR-MS Spectrum. Flash column chromatography was performed with 100-200 mesh silica gel and yields refer to chromatographically and spectroscopically pure compounds.

All chemicals purchased from commercial suppliers were used as received unless otherwise stated. $Pd(OAc)_2$ was purchased from Aladdin. **1t-1w**[1], **2c**[2], **2g**[3], **2k**[2] and **4**[3] were prepared according to the literature procedures. All solvents were reagent grade and, when necessary, were purified and dried by standard methods.

2 Experimental Procedure

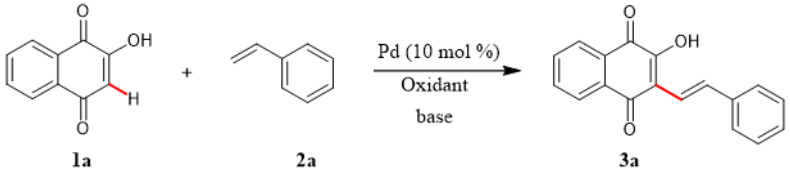
General experimental procedure for synthesis of 3a-3y



1 **2** **3**

A mixture of (substituted) 2-hydroxy-1,4-naphthoquinone (**1**, 0.30 mmol, 1.0 equiv), (substituted) terminal alkenes (**2**, 0.45 mmol, 1.5 equiv) , $Cu(OAc)_2$ (0.30 mmol, 54 mg, 1.0 equiv), NaOAc (0.30 mmol, 41 mg, 1.0 equiv), $Pd(OAc)_2$ (10 mol %) and THF (solvent, 10 mL) was stired for 4 h at 25 °C (**3r** and **3s** was conducted at 50 °C) under air condition. Upon completion of the reaction, as determined by TLC, the mixture was filtered through a celite pad, and then washed with cooled water (20 mL), extracted with dichloromethane (3 × 20 mL) and dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent to afford corresponding product.

3 Additional Reaction Optimization



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

Table S1 Optimization of oxidant amount[a]

Entry	**2a** equiv	Oxidant equiv	Oxidant	Catalyst	Solvent	Yield [%][b]

1	1.5	1	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	84
2	1.5	1.5	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	85
3	1.5	2	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	85

[a] Reaction condition: **1a (**0.30 mmol), Oxidant (1.0 equiv), Base (NaOAc, 1.0 equiv) and Pd catalyst (10 mol %) in solvent (10 ml) for 4 h under air.

[b] Isolated yield.

Table S2 Optimization of the base[a]

Entry	**2a** equiv	Base equiv	Base	Oxidant	Catalyst	Solvent	Yield [%][b]
1	1.5	2	K_2CO_3	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	32
2	1.5	2	Et_3N	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	Trace
3	1.5	2	NaOAc	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	85
4	1.5	2	K_3PO_4	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	Trace
5	1.5	1	NaOAc	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	84
6	1.5	1.5	NaOAc	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	84
7	1.5	2	NaOAc	$Cu(OAc)_2$	$Pd(OAc)_2$	THF	85

[a] Reaction condition: **1a (**0.30 mmol), Oxidant (1.0 equiv), Base (NaOAc, 1.0 equiv) and Pd catalyst (10 mol %) in solvent (10 ml) for 4 h under air.

[b] Isolated yield.

Table S3 Optimization of catalyst amount[a]

Entry	**2a** equiv	Oxidant	Catalyst equiv [mol %]	Catalyst	Solvent	Yield [%][b]
1	1.5	$Cu(OAc)_2$	5	$Pd(OAc)_2$	THF	43
2	1.5	$Cu(OAc)_2$	10	$Pd(OAc)_2$	THF	84
3	1.5	$Cu(OAc)_2$	15	$Pd(OAc)_2$	THF	84
4	1.5	$Cu(OAc)_2$	20	$Pd(OAc)_2$	THF	86

[a] Reaction condition: **1a (**0.30 mmol), Oxidant (1.0 equiv), Base (NaOAc, 1.0 equiv) and Pd catalyst (10 mol %) in solvent (10 ml) for 4 h under air.

[b] Isolated yield.

Table S4 Negative control[a]

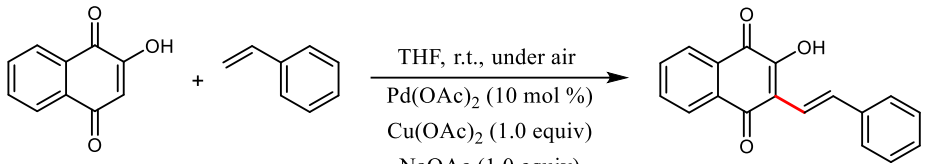
Entry	**2a** equiv	Oxidant	Catalyst	Solvent	Yield [%][b]
1	1.5	$Cu(OAc)_2$	-	THF	15
2	1.5	-	$Pd(OAc)_2$	THF	NR[c]
3	1.5	-	-	THF	NR[c]

[a] Reaction condition: **1a (**0.30 mmol), Oxidant (1.0 equiv), Base (NaOAc, 1.0 equiv) and Pd catalyst (10 mol %) in solvent (10 ml) for 4 h under air.

[b] Isolated yield.

[c] NR = No reaction.

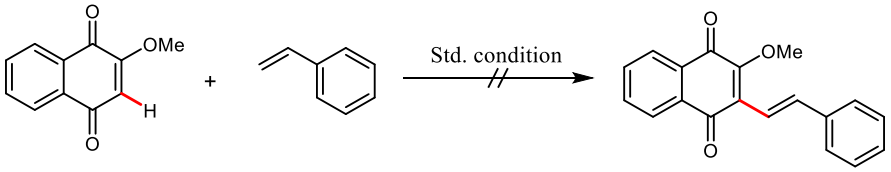
4 Large Scale Experiment



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

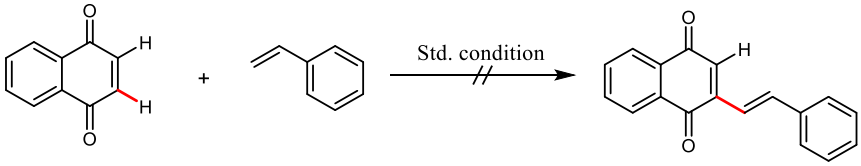
A 250 mL round-bottomed flask with a magnetic stir bar was charged with **1a** (2.61 g, 15 mmol), $Pd(OAc)_2$ (336 mg, 10.0 mol %), $Cu(OAc)_2$ (2.71 g, 15 mmol, 1.0 equiv), NaOAc (1.23 g, 15 mmol, 1.0 equiv), **2a** (2.34 g/2.57 ml, 22.5 mmol, 1.5 equiv), and THF (50 mL) was stired for 6 h at 25 °C under air condition. Upon completion of the reaction, as determined by TLC, the mixture was filtered through a celite pad, and then washed with cooled water (50 mL), extracted with dichloromethane (3 × 30 mL) and dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent to afford corresponding product.

5 Control Experiments



4 **2a** **5**

A mixture of 2-methoxynaphthalene-1,4-dione (**4**, 56.4 mg, 0.30 mmol, 1.0 equiv), terminal alkenes (**2a**, 0.45 mmol, 47mg/0.51 mL, 1.5 equiv) , $Cu(OAc)_2$ (0.30 mmol, 54 mg, 1.0 equiv), NaOAc (0.30 mmol, 41 mg, 1.0 equiv), $Pd(OAc)_2$ (10 mol %) and THF (solvent, 10 mL) was stired for 4 h at 25 °C under air condition and determined by TLC. No reaction was observed.

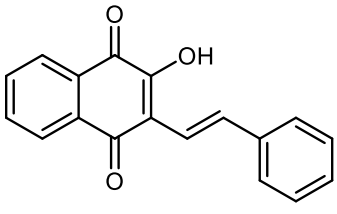


6 **2a** **7**

A mixture of naphthalene-1,4-dione (**6**, 56.4 mg, 0.30 mmol, 1.0 equiv), terminal alkenes (**2a**, 0.45 mmol, 47mg/0.51 mL, 1.5 equiv) , $Cu(OAc)_2$ (0.30 mmol, 54 mg, 1.0 equiv), NaOAc (0.30 mmol, 41 mg, 1.0 equiv), $Pd(OAc)_2$ (10 mol %) and THF (solvent, 10 mL) was stired for 4 h at 25 °C under air condition and determined by TLC. No reaction was observed.

6 Analytical Data for All Compounds

2-hydroxy-3-styrylnaphthalene-1,4-dione (3a)



3a

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 84% (70.2 mg)
Physical appearance: red solid

M.p. 145.2-146.8 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 8.02 (td, *J* = 7.5, 1.5 Hz, 2H), 7.90-7.77 (m, 3H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 6.7 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.67, 180.51, 151.18, 138.83, 137.29, 134.80, 134.50, 132.72, 132.24, 129.06, 128.23, 126.69, 126.22, 125.57, 118.21, 116.90; **HRMS** (ESI^-): calc. for $C_{18}H_{11}O_3$ $[M-H]^-$: 275.0714, found: 275.0701 *m/z*.

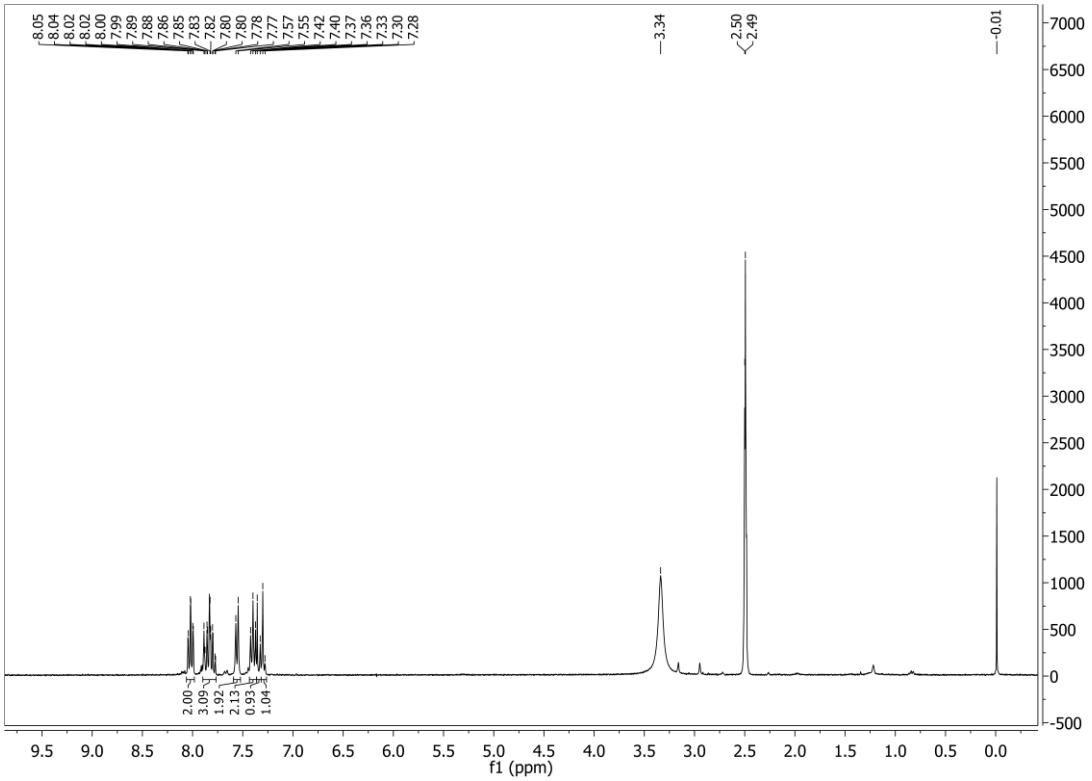


Figure E1 ^{1}H-NMR spectrum of **3a** in $CDCl_3$

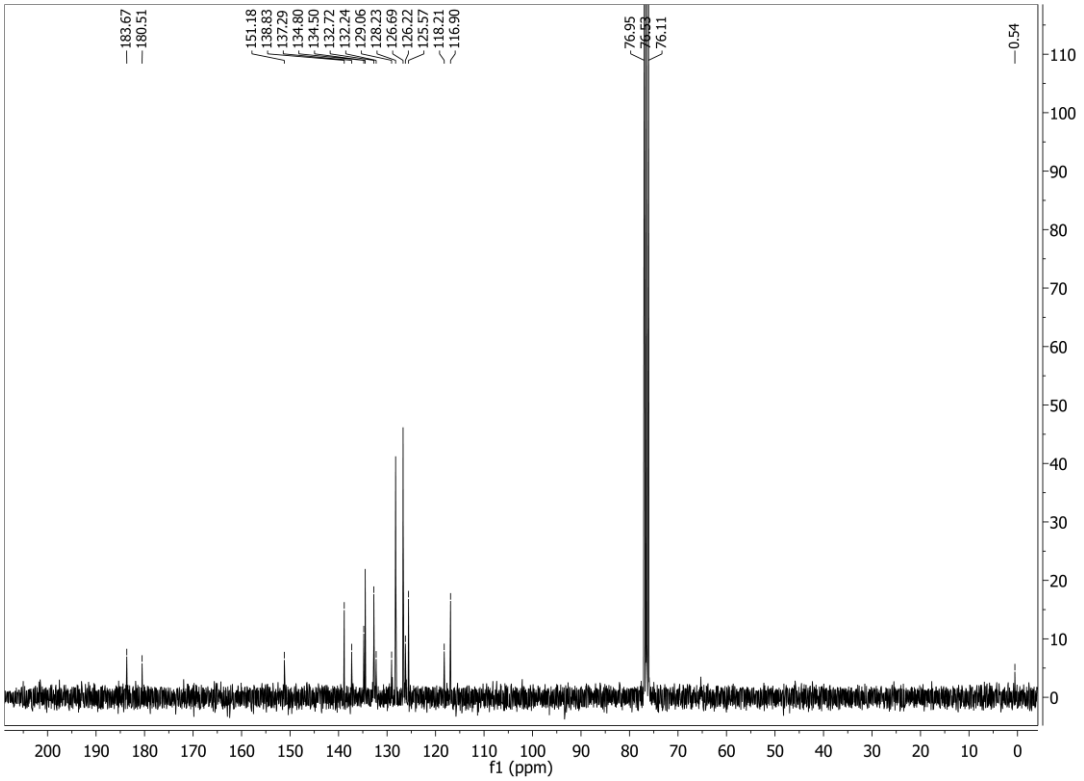
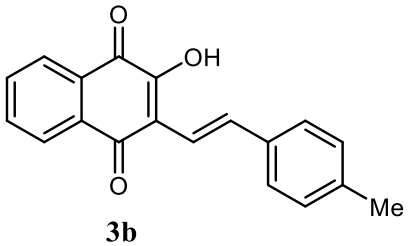


Figure E2 ^{13}C-NMR spectrum of **3a** in $CDCl_3$

2-hydroxy-3-(4-methylstyryl)naphthalene-1,4-dione (3b)



3b

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 87% (75.7 mg)
Physical appearance: red solid

M.p. 125.6-126.7 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 8.02 (td, *J* = 7.4, 1.5 Hz, 2H), 7.90 – 7.76 (m, 3H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 16.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.27, 180.97, 151.45, 139.41, 138.88, 135.08, 134.92, 133.20, 132.76, 129.61, 129.48, 127.21, 127.15, 126.03, 118.97, 116.43, 21.40; **HRMS** (ESI$^-$): calc. for $C_{19}H_{13}O_3$ $[M-H]^-$: 289.087, found: 289.0864 *m/z*.

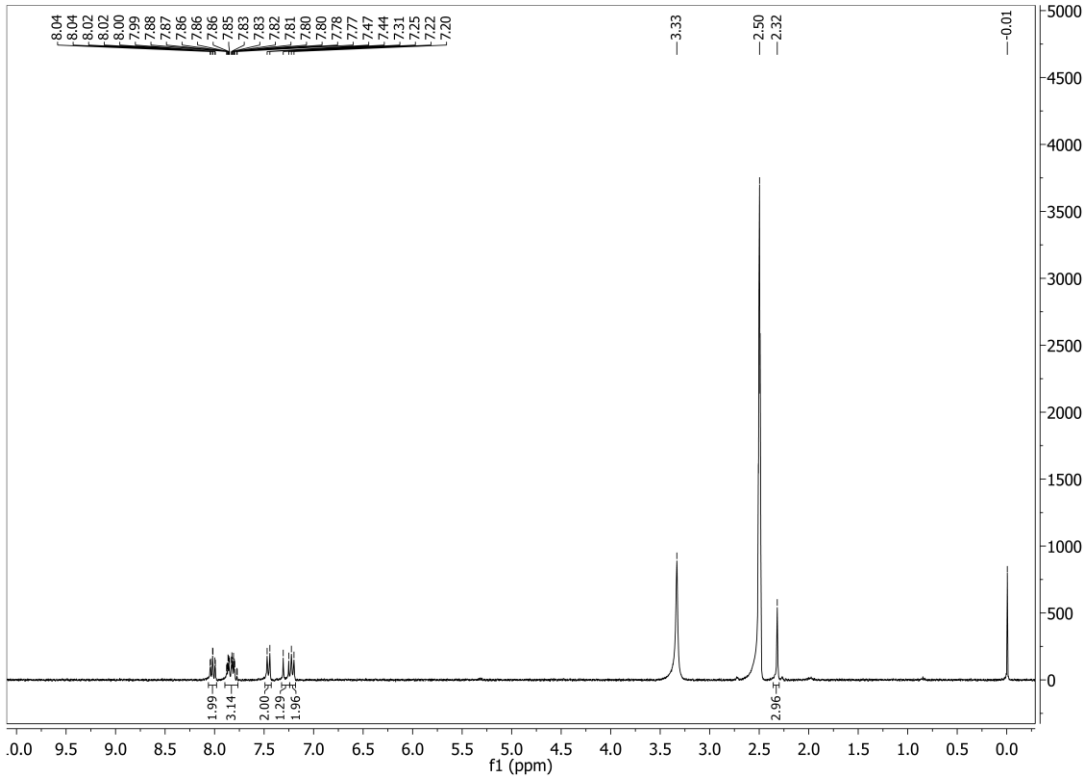


Figure E3 ^{1}H-NMR spectrum of **3b** in $CDCl_3$

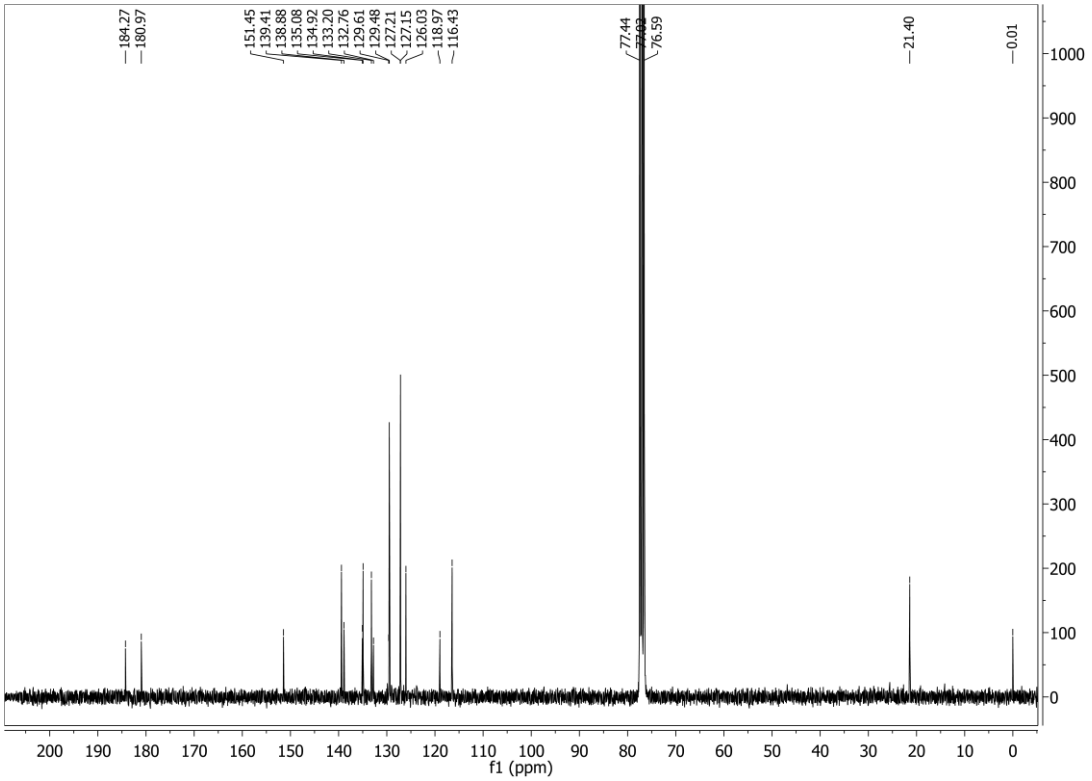
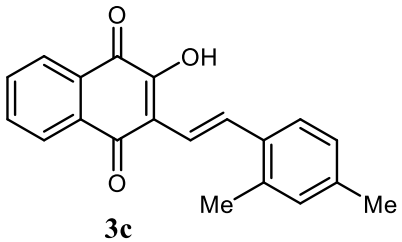


Figure E4 ^{13}C-NMR spectrum of **3b** in $CDCl_3$

2-(2,4-dimethylstyryl)-3-hydroxynaphthalene-1,4-dione (3c)



3c

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 89% (80.9 mg)
Physical appearance: red solid

M.p. 118.4-119.8 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.19 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.96 (s, 1H), 7.79 (d, *J* = 141 Hz, 1H),7.75 (dt, *J* = 20.9, 7.2 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 13.9 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.33, 181.08, 151.46, 138.61, 137.23, 136.62, 134.90, 134.09, 133.17, 132.87, 131.32, 129.69, 127.16, 127.11, 126.02, 125.37, 119.30, 117.43, 21.23, 19.76; **HRMS** (ESI^-): calc. for $C_{20}H_{15}O_3$ $[M-H]^-$: 303.1027, found: 303.1030 *m/z*.

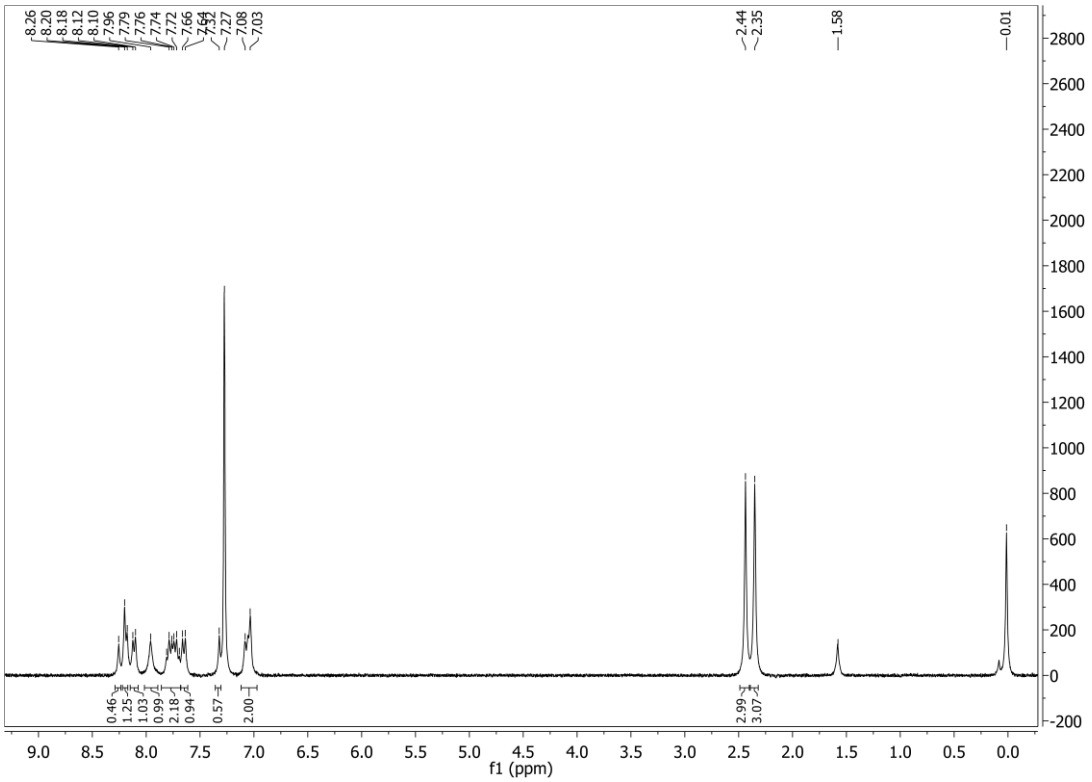


Figure E5 ^{1}H-NMR spectrum of **3c** in $CDCl_3$

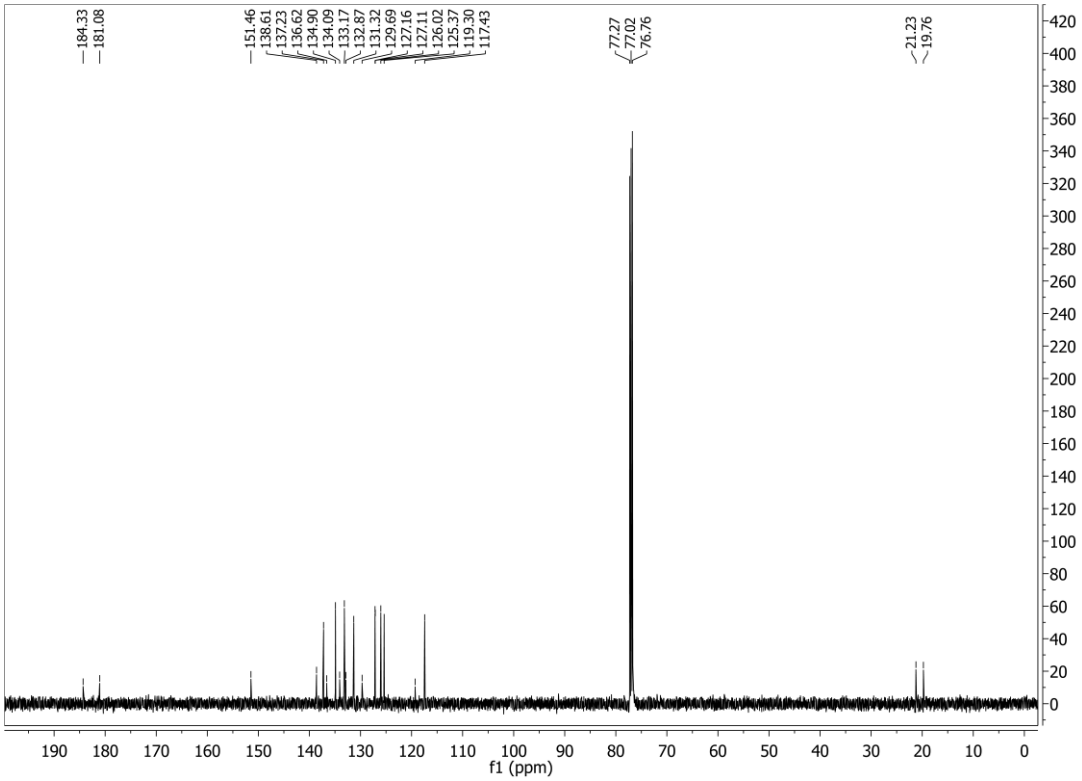
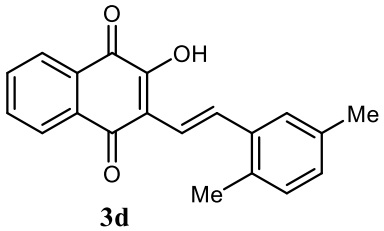


Figure E6 ^{13}C-NMR spectrum of **3c** in $CDCl_3$

2-(2,5-dimethylstyryl)-3-hydroxynaphthalene-1,4-dione (3d)



3d

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 88% (80.3 mg)
Physical appearance: red solid

M.p. 120.2-123.0 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.23 (d, *J* = 11.9 Hz, 1H), 8.19 (d, *J* = 2.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.76 (dt, *J* = 21.5, 7.4 Hz, 2H), 7.55 (s, 1H), 7.34 (d, *J* = 15 Hz, 1H), 7.07 (q, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.81, 180.58, 151.07, 136.83, 136.03, 135.15, 134.46, 133.18, 132.71, 132.25, 129.91, 129.09, 128.91, 126.66, 125.54, 125.39, 118.56, 117.50, 20.57, 18.89; **HRMS** (ESI^-): calc. for $C_{20}H_{15}O_3$ $[M-H]^-$: 303.1027, found: 303.1019 *m/z*.

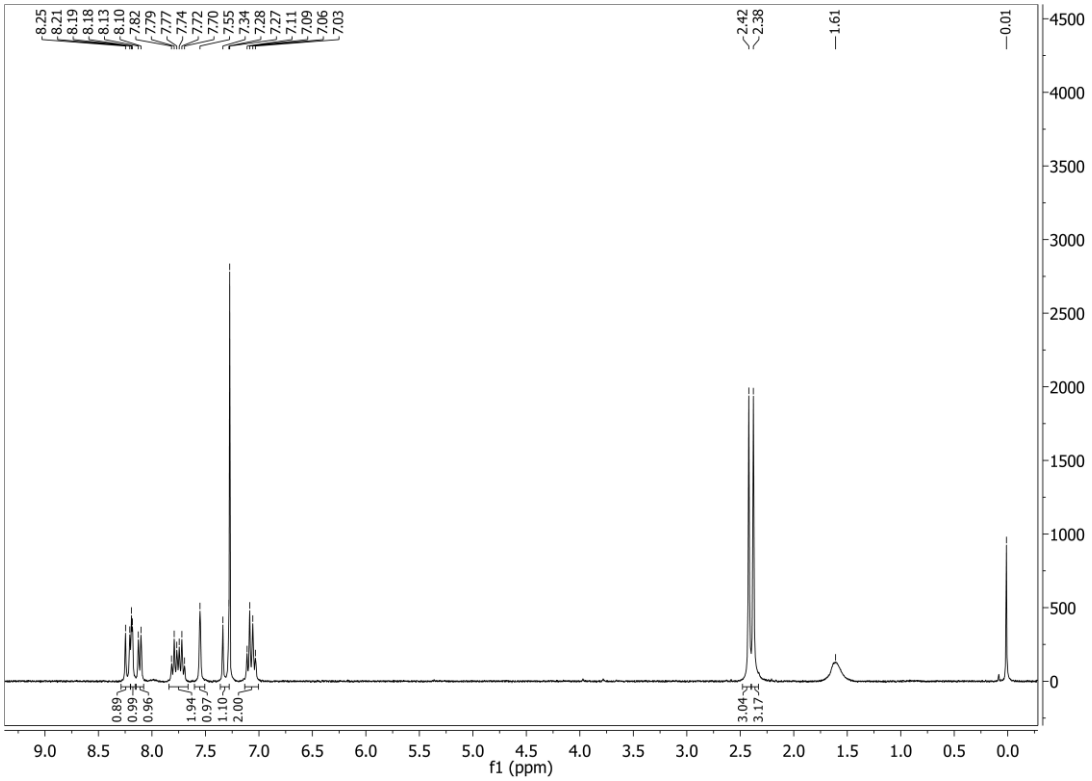


Figure E7 ^{1}H-NMR spectrum of **3d** in $CDCl_3$

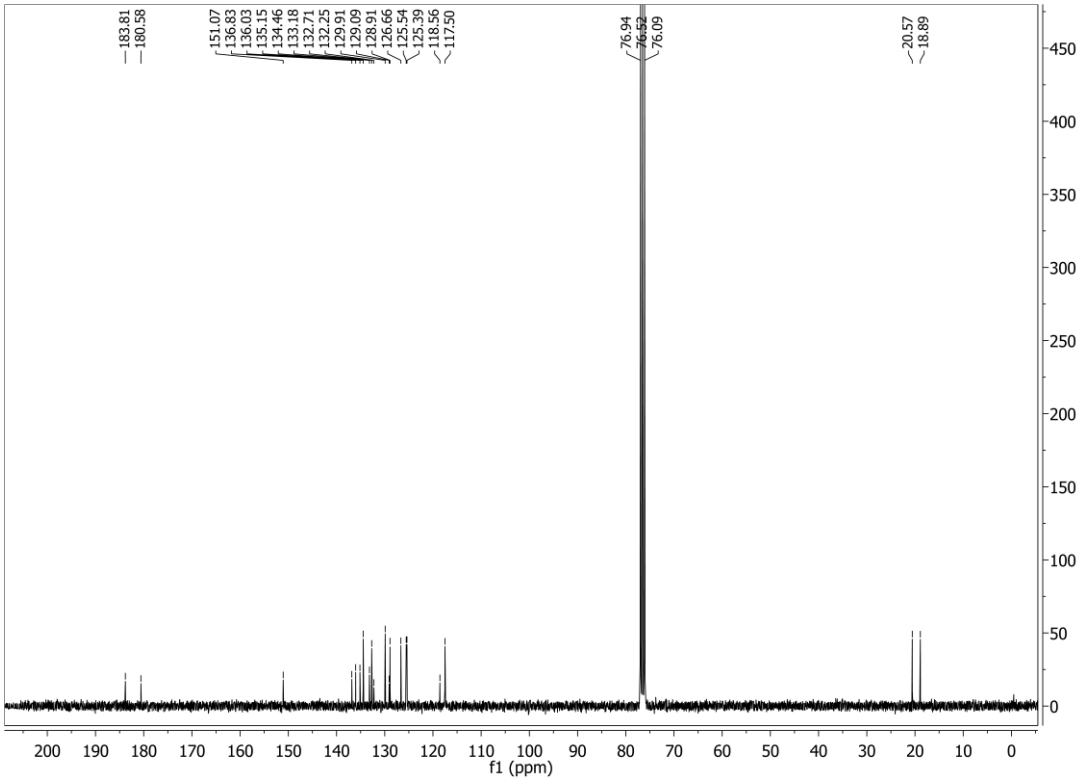
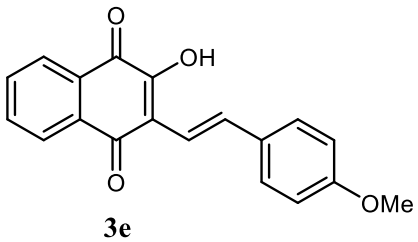


Figure E8 ^{13}C-NMR spectrum of **3d** in $CDCl_3$

2-hydroxy-3-(4-methoxystyryl)naphthalene-1,4-dione (3e)



3e

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 91% (83.5 mg)
Physical appearance: red solid

M.p. 143.2-145.8 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 8.01 (td, *J* = 7.2, 1.2 Hz, 2H), 7.89-7.78 (m, 3H), 7.51 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.32, 180.87, 160.24, 151.20, 139.08, 134.79, 133.14, 132.78, 130.73, 129.68, 128.62, 127.09, 125.96, 119.20, 115.30, 114.21, 55.34; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_4$ $[M-H]^-$: 305.0819, found: 305.0822 *m/z*.

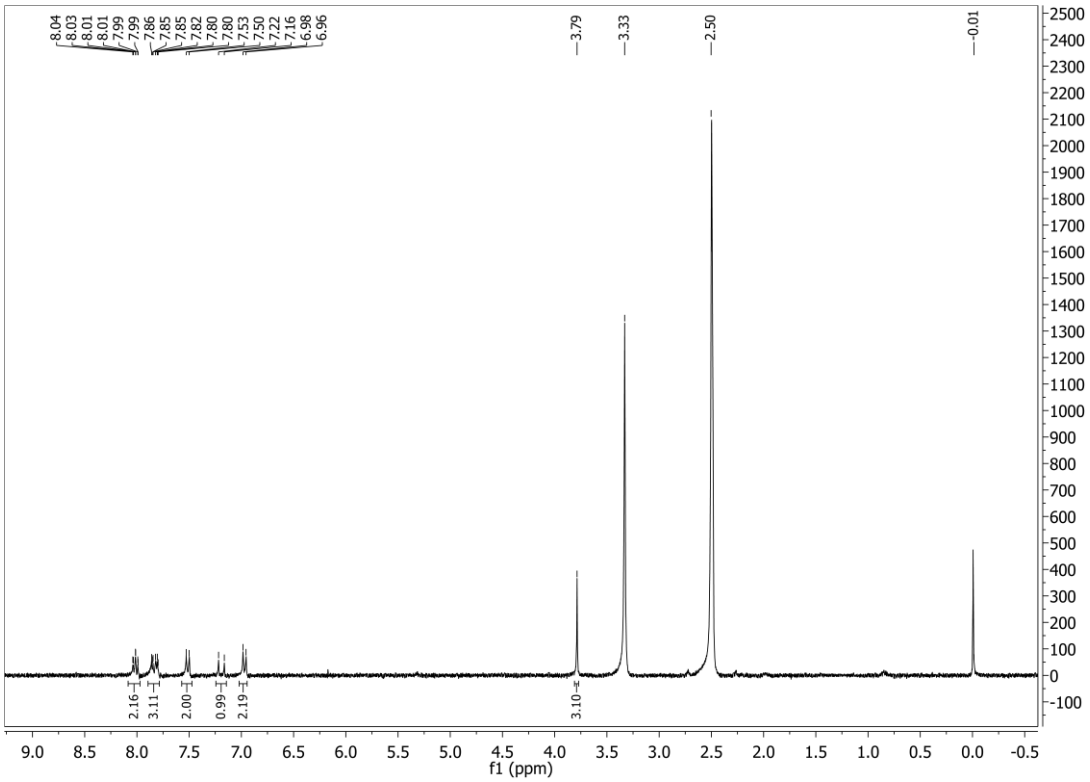


Figure E9 ^{1}H-NMR spectrum of **3e** in $CDCl_3$

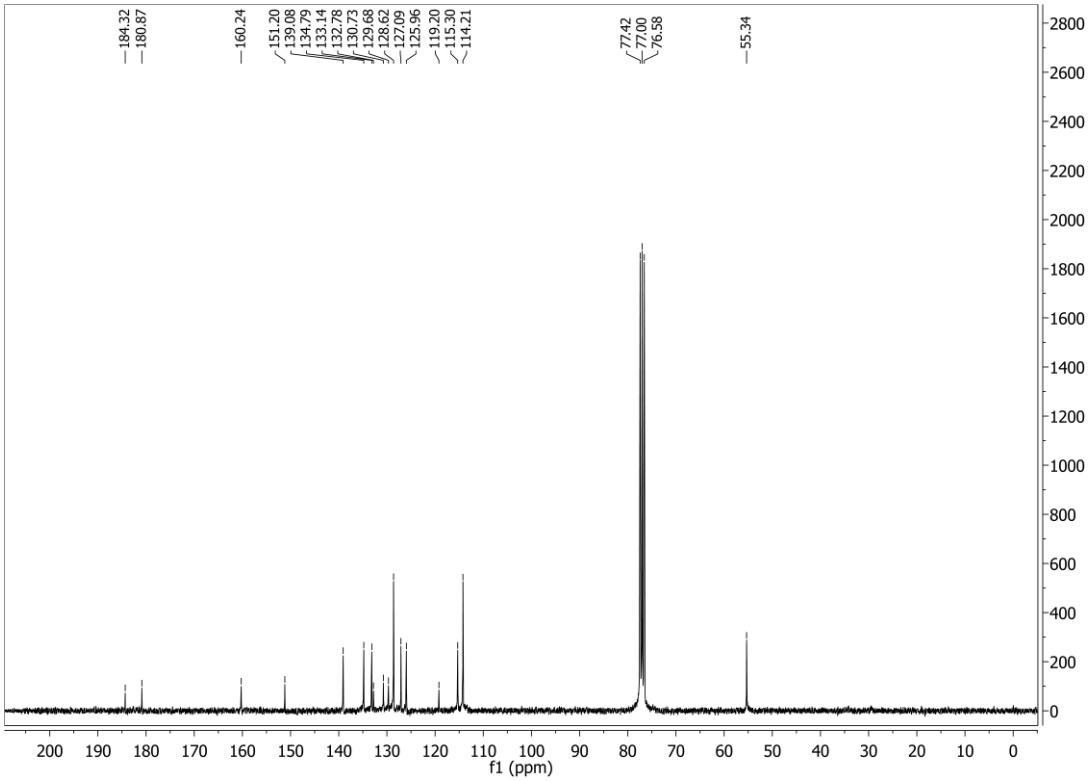
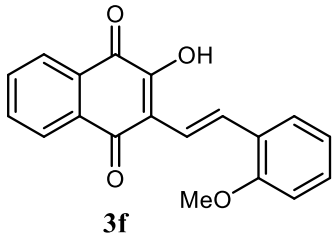


Figure E10 ^{13}C-NMR spectrum of **3e** in $CDCl_3$

2-hydroxy-3-(2-methoxystyryl)naphthalene-1,4-dione (3f)



3f

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 90% (82.6 mg)
Physical appearance: red solid

M.p. 144.5-146.2 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.32 (d, *J* = 16.9 Hz, 1H), 8.19 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.11 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.78 (td, *J* = 7.6, 1.6 Hz, 1H), 7.72 (ddd, *J* = 7.7, 4.3, 1.7 Hz, 2H), 7.64, (d, J = 99 Hz, 1H) 7.42 (d, *J* = 16.9 Hz, 1H), 7.01 (t, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.78, 180.52, 156.85, 151.00, 134.75, 134.37, 133.69, 132.64, 132.26, 129.36, 129.14, 126.63, 126.27, 125.50, 120.29, 118.81, 117.22, 110.45, 55.11; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_4$ $[M-H]^-$: 305.0819, found: 305.0809 *m/z*.

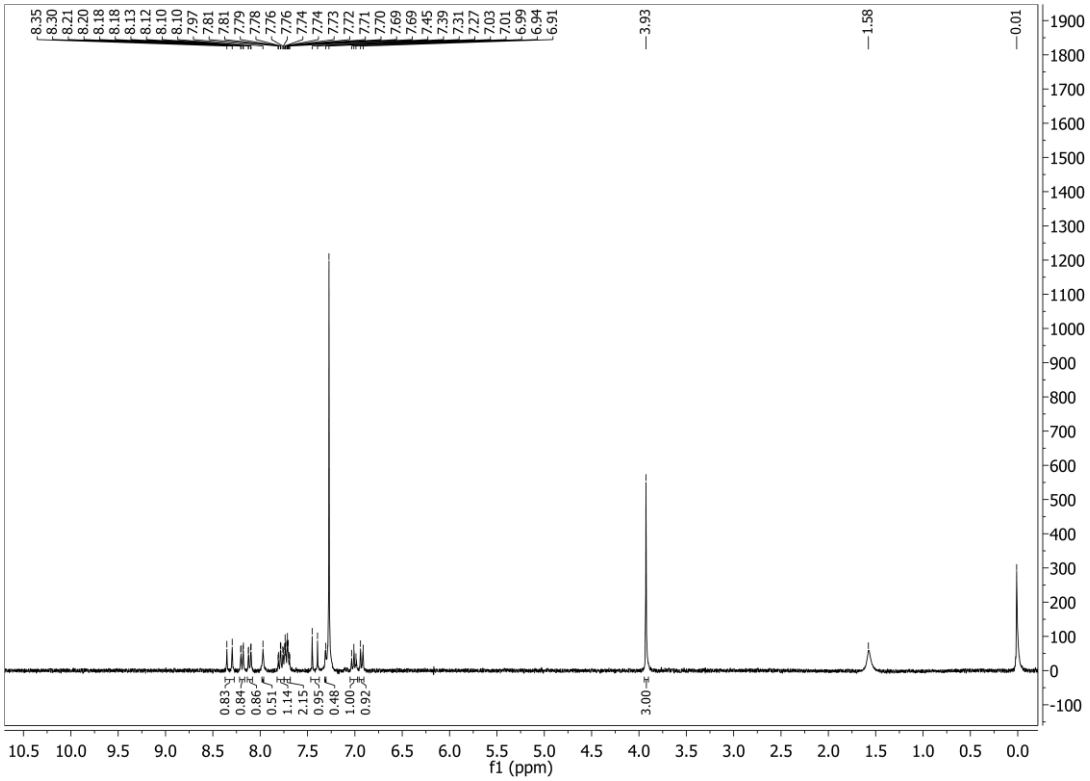


Figure E11 ^{1}H-NMR spectrum of **3f** in $CDCl_3$

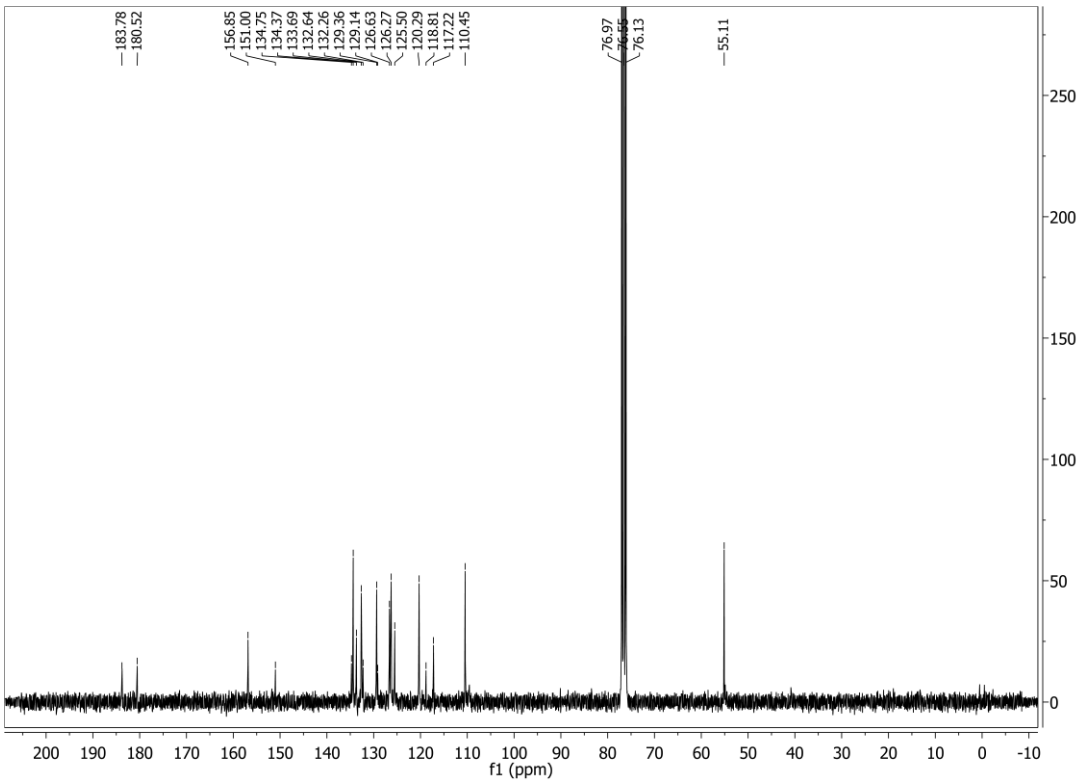
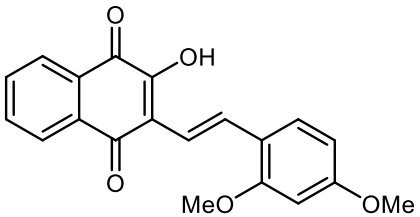


Figure E12 ^{13}C-NMR spectrum of **3f** in $CDCl_3$

2-(2,4-dimethoxystyryl)-3-hydroxynaphthalene-1,4-dione (3g)



3g

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 92% (92.8 mg)
Physical appearance: dark red solid

M.p. 132.5-133.8 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 2.2 Hz, 2H), 6.41 (d, *J* = 2.2 Hz, 1H), 6.39 (d, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.68, 180.92, 160.12, 157.28, 146.59, 134.93, 129.25, 128.89, 128.06, 127.89, 127.09, 126.49, 123.47, 122.68, 121.64, 115.02, 103.42, 98.82, 54.94, 54.74.; **HRMS** (ESI^-): calc. for $C_{20}H_{16}O_5$ $[M-H]^-$: 335.0925, found: 335.0916 *m/z*.

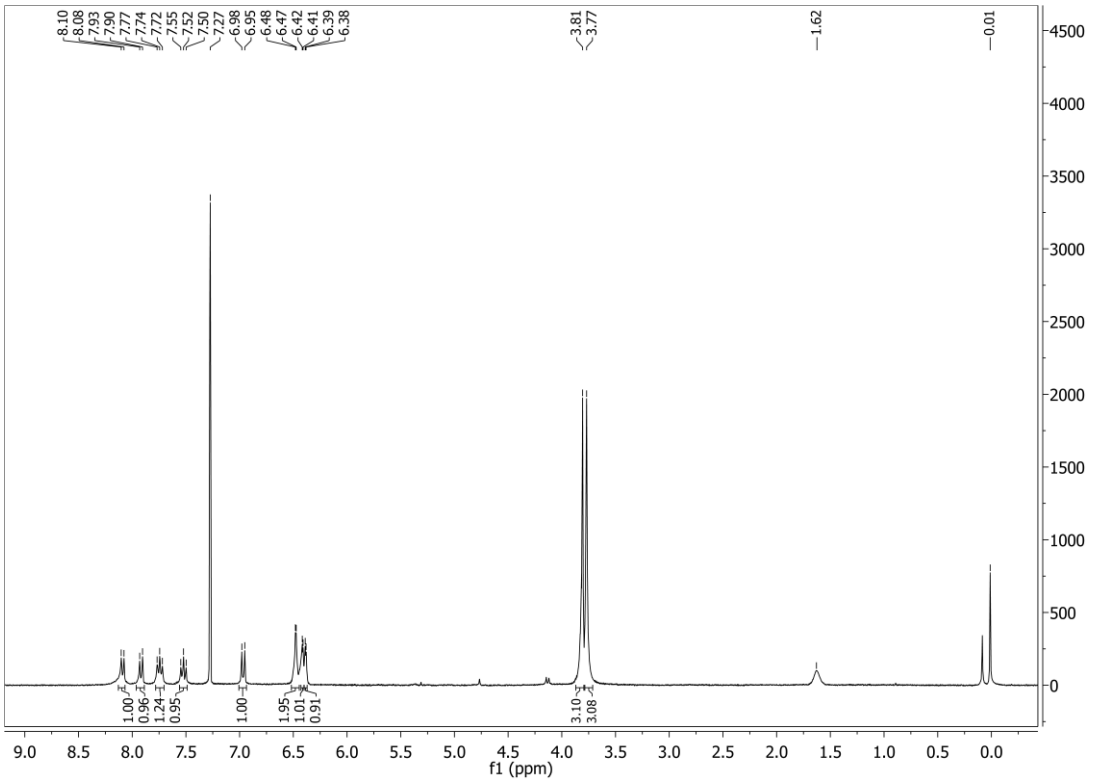


Figure E13 ^{1}H-NMR spectrum of **3g** in $CDCl_3$

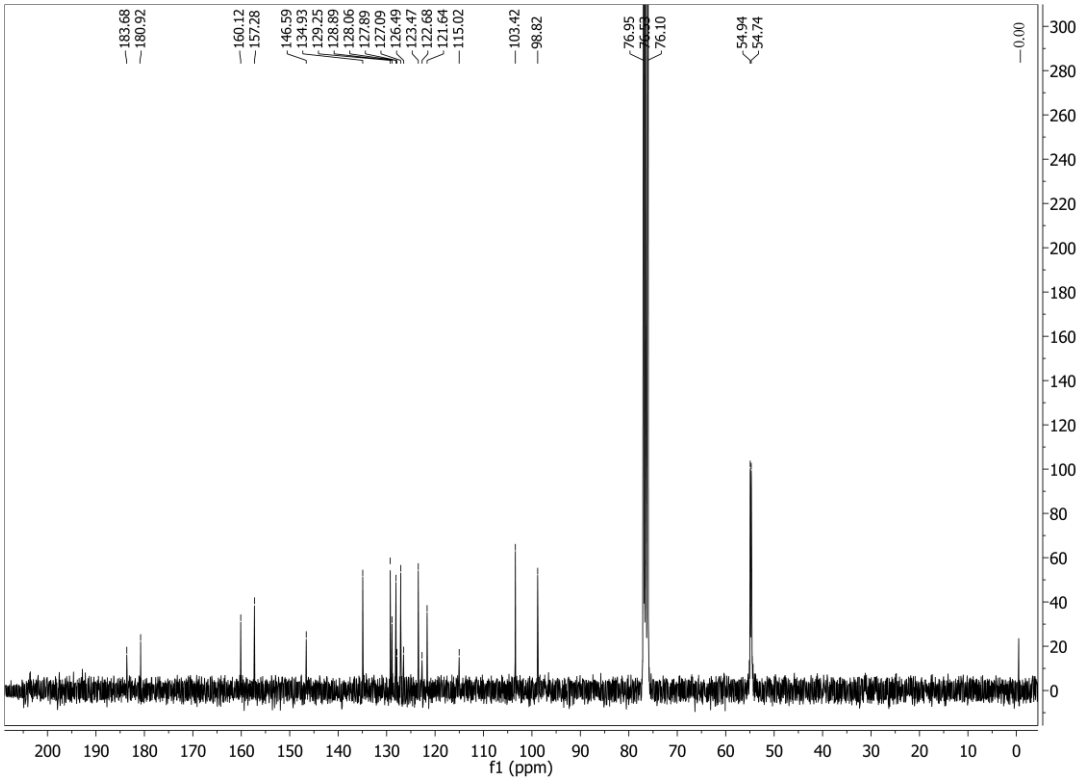
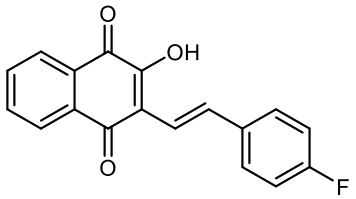


Figure E14 ^{13}C-NMR spectrum of **3g** in $CDCl_3$

2-(4-fluorostyryl)-3-hydroxynaphthalene-1,4-dione (3h)



3h

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 66% (58.4 mg)
Physical appearance: red solid

M.p. 202.2-204.5 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.17 (d, *J* = 7.4 Hz, 1H), 8.10 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 9.4 Hz, 1H), 7.75 (dt, *J* = 21.8, 7.4 Hz, 2H), 7.62 (d, *J* = 85.5 Hz, 1H) 7.57 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 2H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.63, 180.46, 162.48 ($^1J_{CF}$ = 123.8 Hz), 151.13, 137.48, 134.52, 133.53, 132.75, 132.20, 129.04, 128.30 ($^2J_{CF}$ = 4.1 Hz), 126.67, 125.59, 118.06, 116.63 ($^3J_{CF}$ = 1.1 Hz), 115.25 ($^4J_{CF}$ = 10.5 Hz); **HRMS** (ESI$^-$): calc. for $C_{18}H_{10}FO_3$ $[M-H]^-$: 293.0619, found: 293.0622 *m/z*.

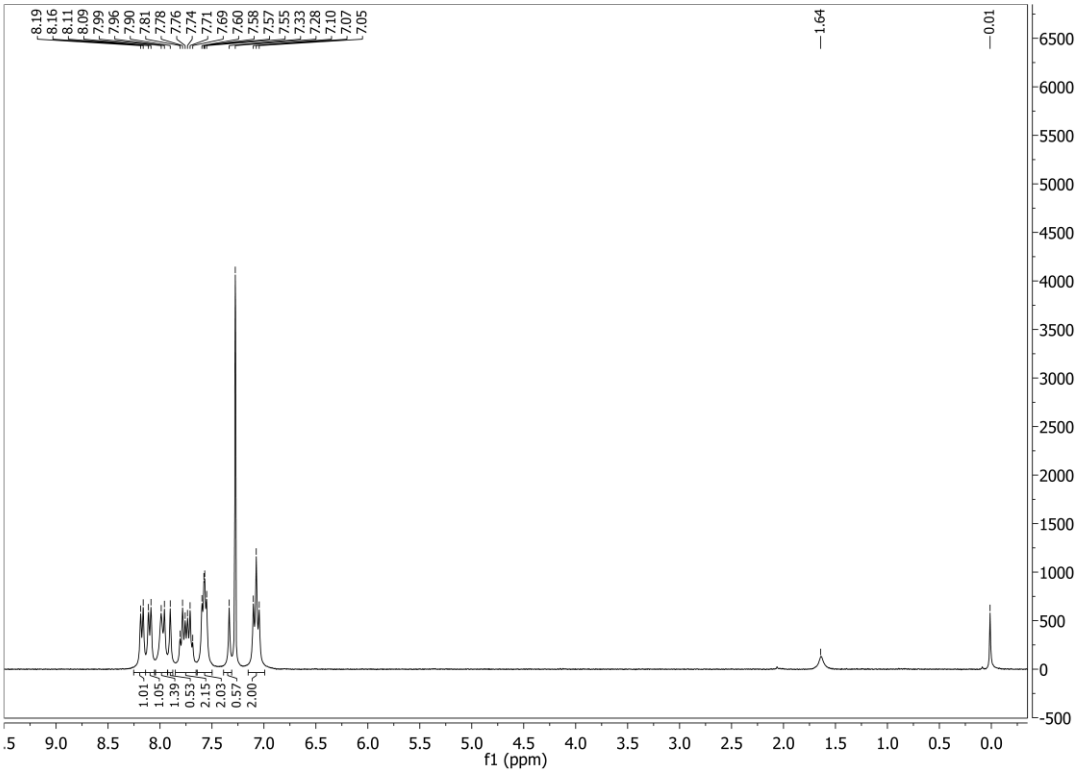


Figure E15 ^{1}H-NMR spectrum of **3h** in $CDCl_3$

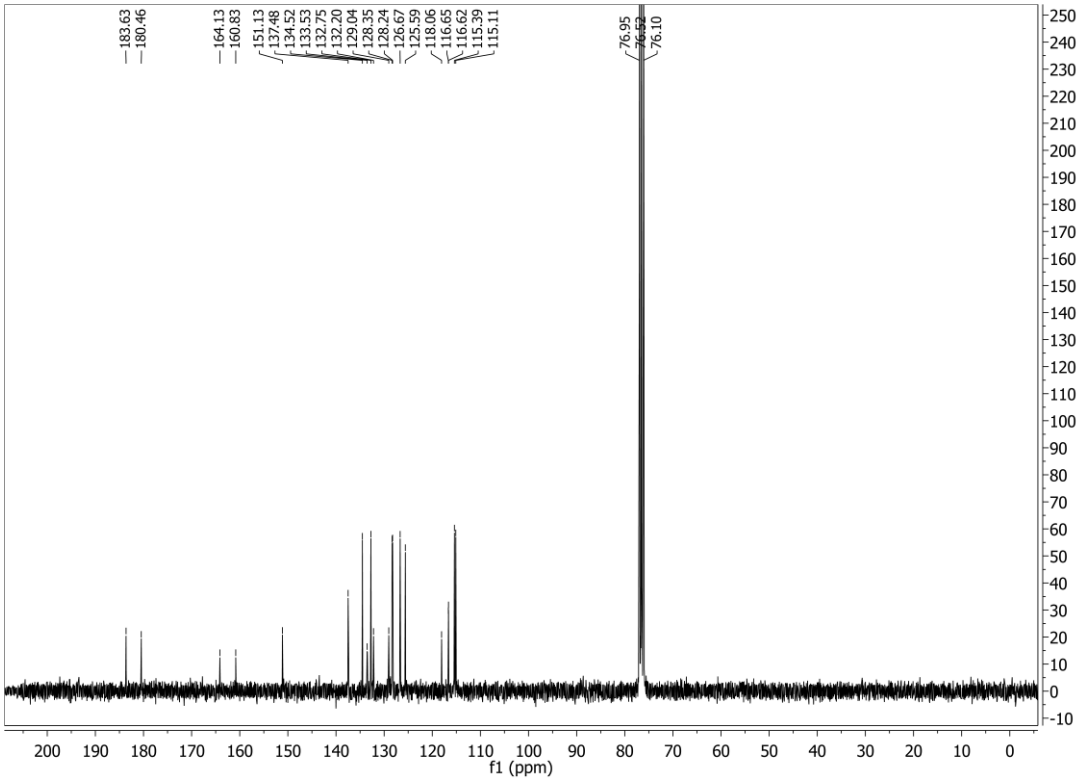
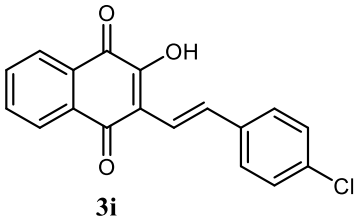


Figure E16 ^{13}C-NMR spectrum of **3h** in $CDCl_3$

2-(4-chlorostyryl)-3-hydroxynaphthalene-1,4-dione (3i)



3i

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 74% (69.6 mg)
Physical appearance: red solid

M.p. 192.3-194.8 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 7.1 Hz, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 16.6 Hz, 1H), 7.84- 7.69 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.42-7.33 (m, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.07, 180.98, 151.82, 137.80, 136.30, 135.10, 134.34, 133.30, 132.71, 129.53, 128.94, 128.31, 127.21, 126.14, 118.39, 117.96; **HRMS** (ESI^-): calc. for $C_{18}H_{10}ClO_3$ $[M-H]^-$: 309.0324, found: 309.0325 *m/z*.

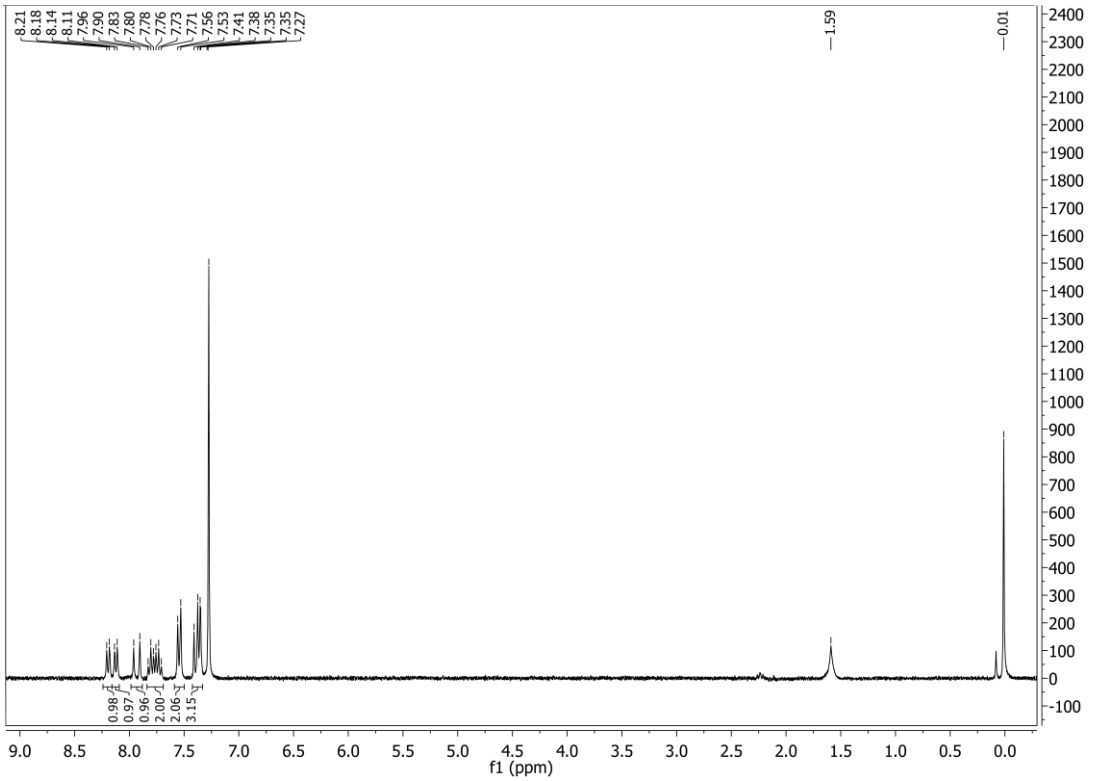


Figure E17 ^{1}H-NMR spectrum of **3i** in $CDCl_3$

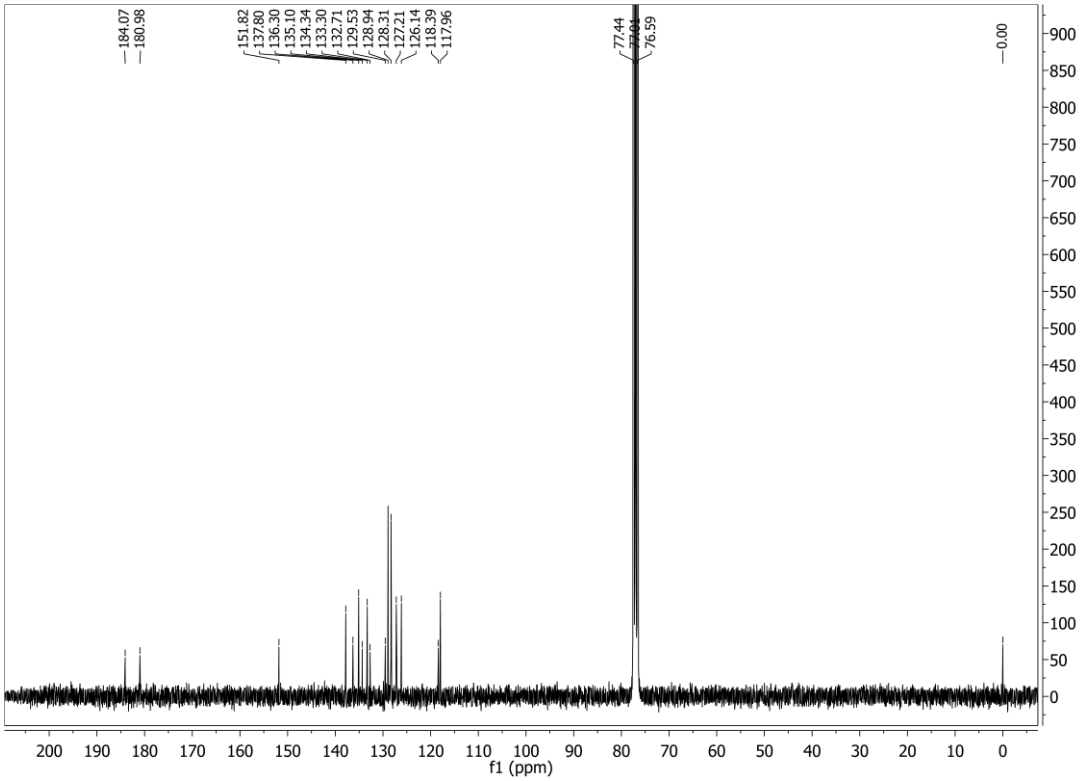
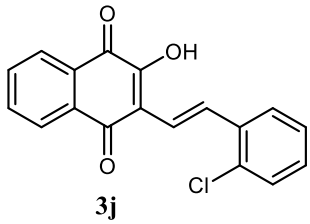


Figure E18 ^{13}C-NMR spectrum of **3i** in $CDCl_3$

2-(2-chlorostyryl)-3-hydroxynaphthalene-1,4-dione (3j)



3j

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 74% (68.8 mg)
Physical appearance: red solid

M.p. 193.8-195.7 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.36 (d, *J* = 17.2 Hz, 1H), 8.21 (d, *J* = 7.3 Hz, 1H), 8.18-8.02 (m, 2H), 7.88-7.67 (m, 3H), 7.48-7.30 (m, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.97, 181.11, 152.11, 136.03, 135.11, 134.17, 133.28, 132.79, 129.91, 129.60, 129.43, 127.27, 127.00, 126.76, 126.17, 119.80, 118.44, 113.58; **HRMS** (ESI^-): calc. for $C_{18}H_{10}ClO_3$ $[M-H]^-$: 309.0324, found: 309.0309 *m/z*.

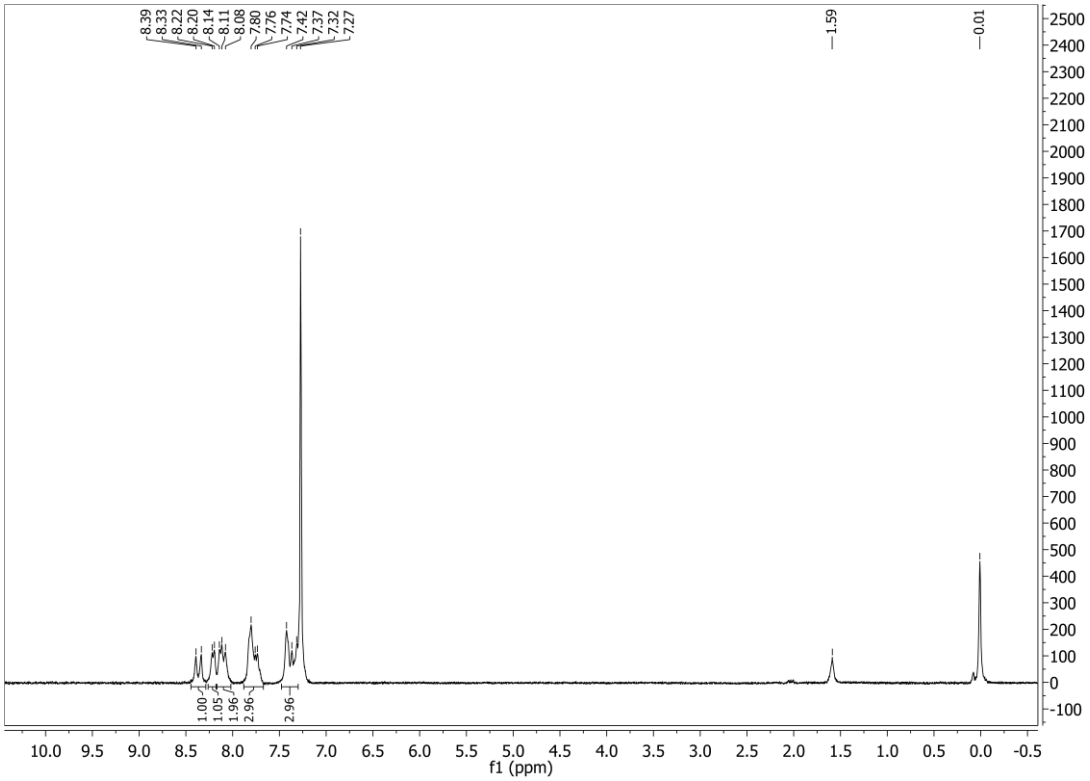


Figure E19 ^{1}H-NMR spectrum of **3j** in $CDCl_3$

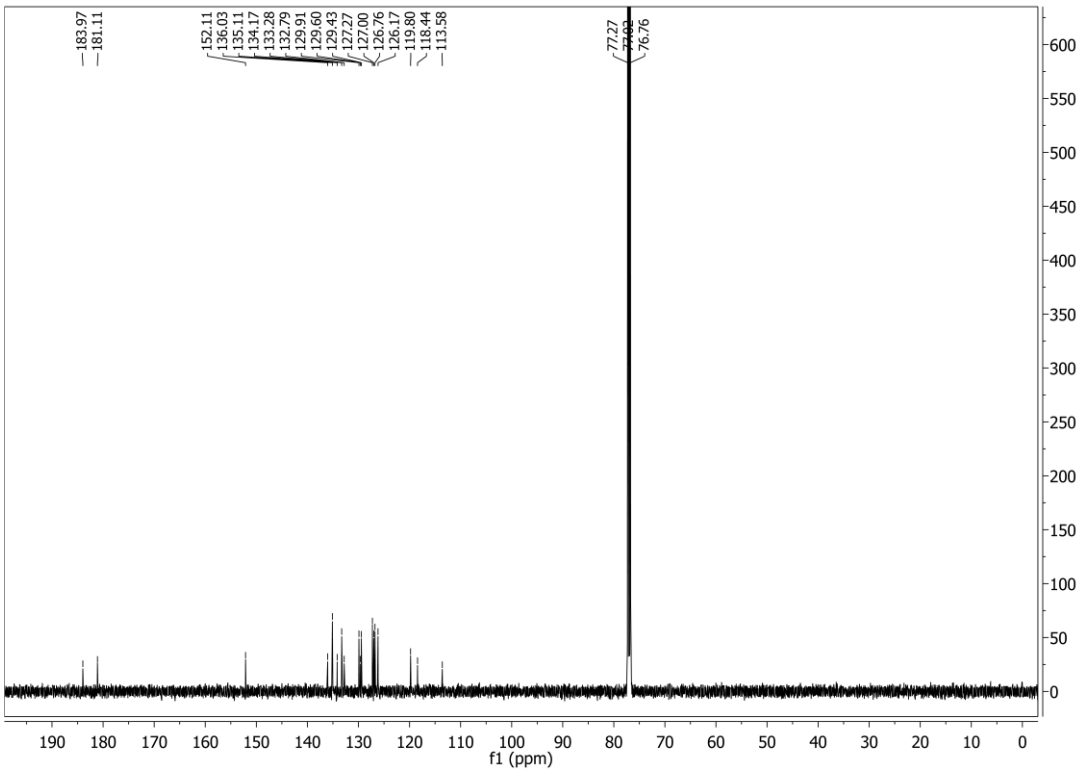
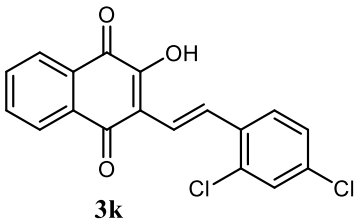


Figure E20 ^{13}C-NMR spectrum of **3j** in $CDCl_3$

2-(2,4-dichlorostyryl)-3-hydroxynaphthalene-1,4-dione (3k)



3k

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 65% (64.6 mg)
Physical appearance: red solid

M.p. 212.9-215.4 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 16.5 Hz, 1H), 8.20 (d, *J* = 6.8 Hz, 1H), 8.13 (d, *J* = 7.3 Hz, 1H), 7.81 (t, *J* = 7.3 Hz, 1H), 7.74 (dd, *J* = 7.8, 4.6 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.37 (d, *J* = 16.6 Hz, 1H), 7.32-7.28 (m, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.85, 180.99, 152.18, 135.19, 134.53, 134.45, 133.65, 133.34, 132.63, 129.64, 129.48, 127.40, 127.37, 127.26, 126.20, 120.17, 120.16, 118.04; **HRMS** (ESI$^-$): calc. for $C_{18}H_9Cl_2O_3$ $[M-H]^-$: 342.9934, found: 342.9926 *m/z*.

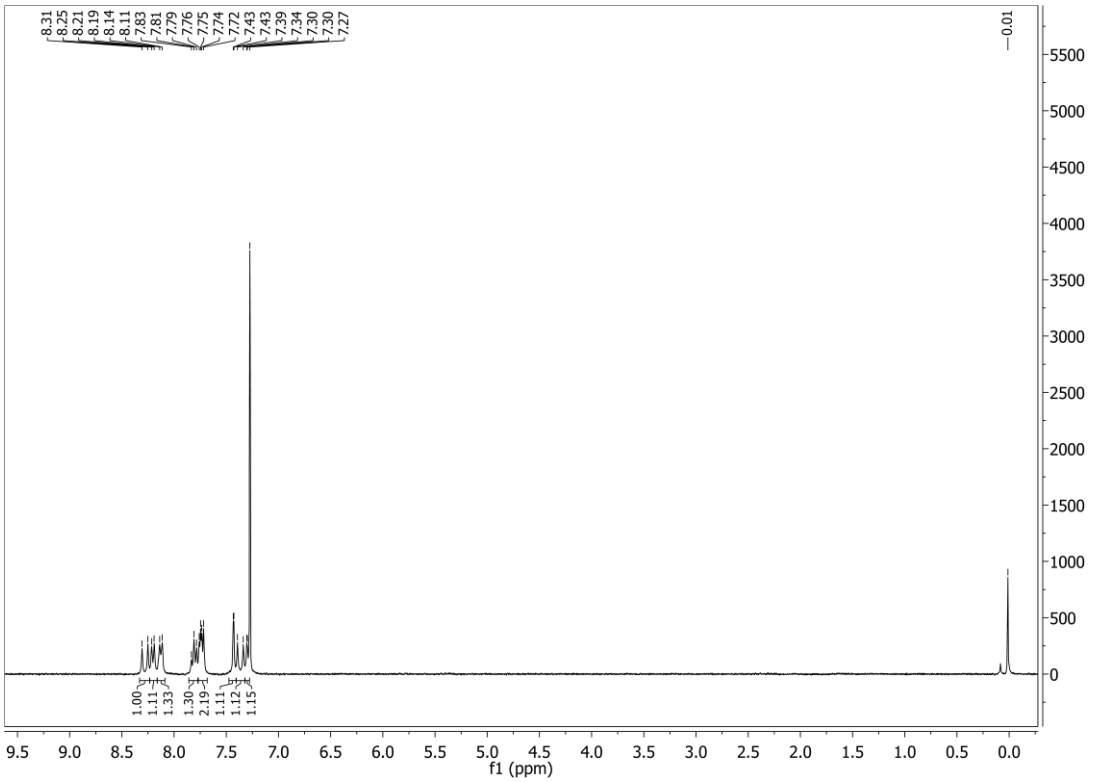


Figure E21 ^{1}H-NMR spectrum of **3k** in $CDCl_3$

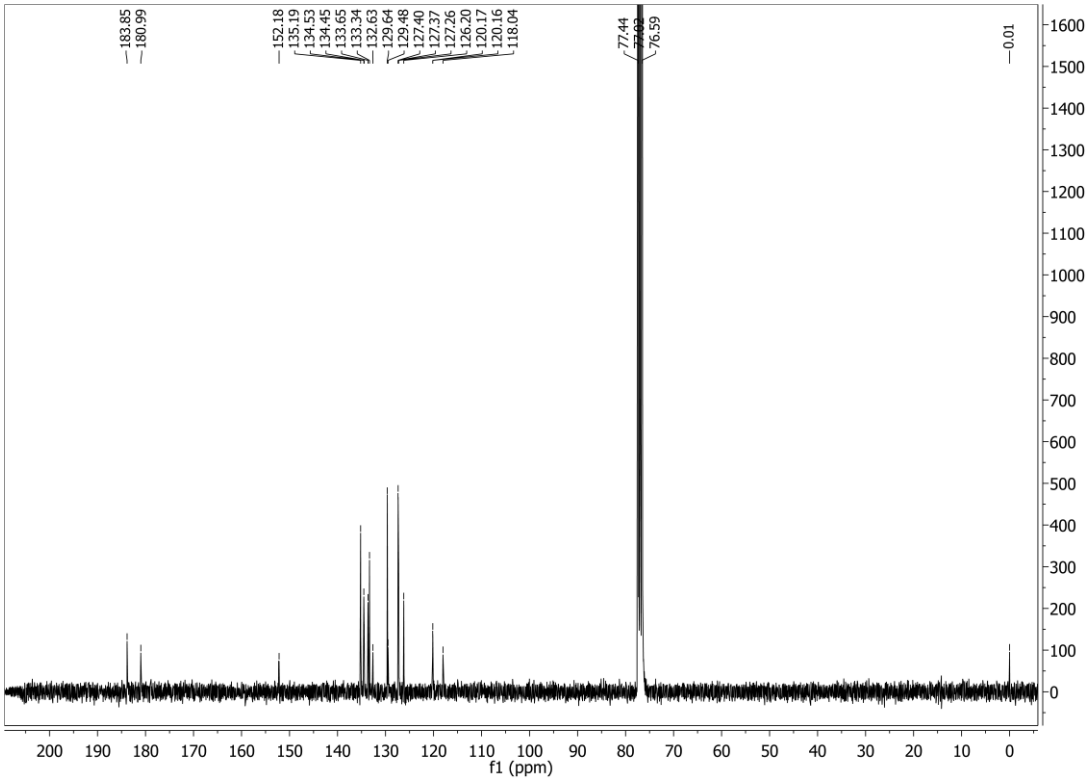
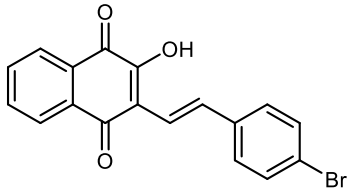


Figure E22 ^{13}C-NMR spectrum of **3k** in $CDCl_3$

2-(4-bromostyryl)-3-hydroxynaphthalene-1,4-dione (3l)



3l

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 70% (74.3 mg)
Physical appearance: red solid

M.p. 181.3-182.2 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.22-8.17, 7.86-7.95 (m, 1H), 8.15 (d, *J* = 0.45 Hz, 1H), 8.12 (d, *J* = 1.4 Hz, 1H), 7.91 (d, *J* = 16.7 Hz, 1H), 7.78 (dtd, *J* = 23.4, 7.5, 1.4 Hz, 4H), 7.56-7.44 (dd, *J* = 2H), 7.39 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 174.61, 171.69, 146.03, 127.62, 125.01, 124.82, 123.02, 122.85, 121.63, 118.32, 116.95, 116.47, 116.23, 115.87, 107.84, 100.43; **HRMS** (ESI^-): calc. for $C_{18}H_{10}BrO_3$ $[M-H]^-$: 353.9819, found: 353.9804 *m/z*.

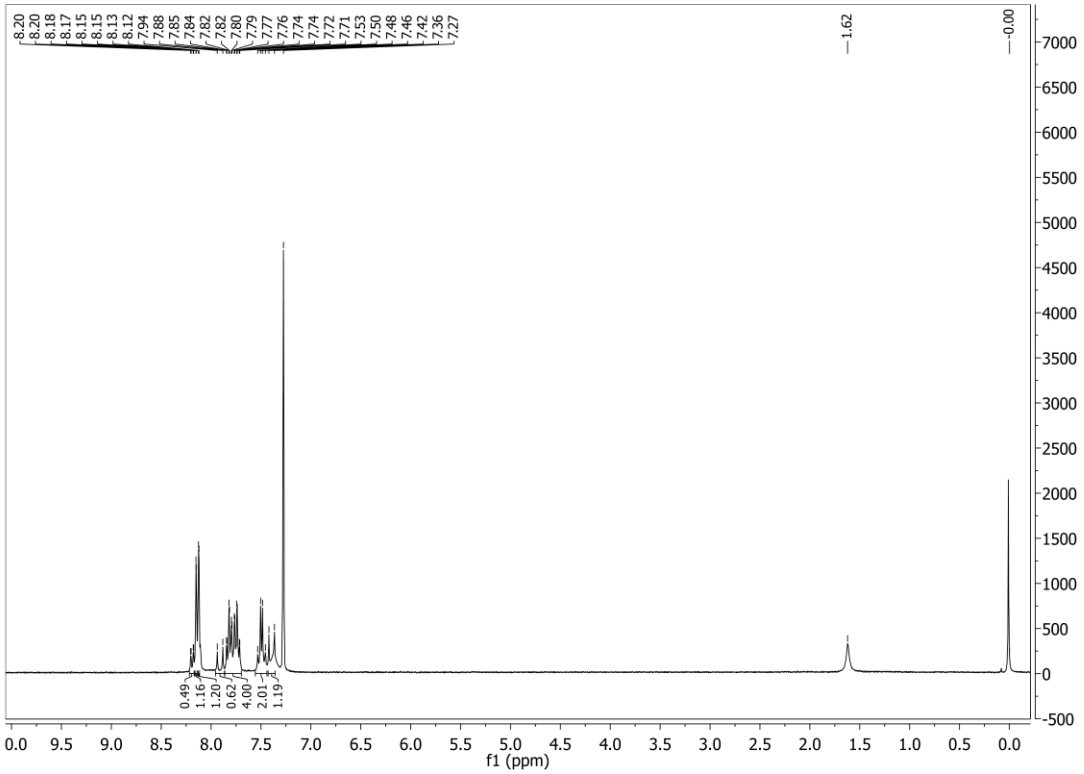


Figure E23 ^{1}H-NMR spectrum of **3l** in $CDCl_3$

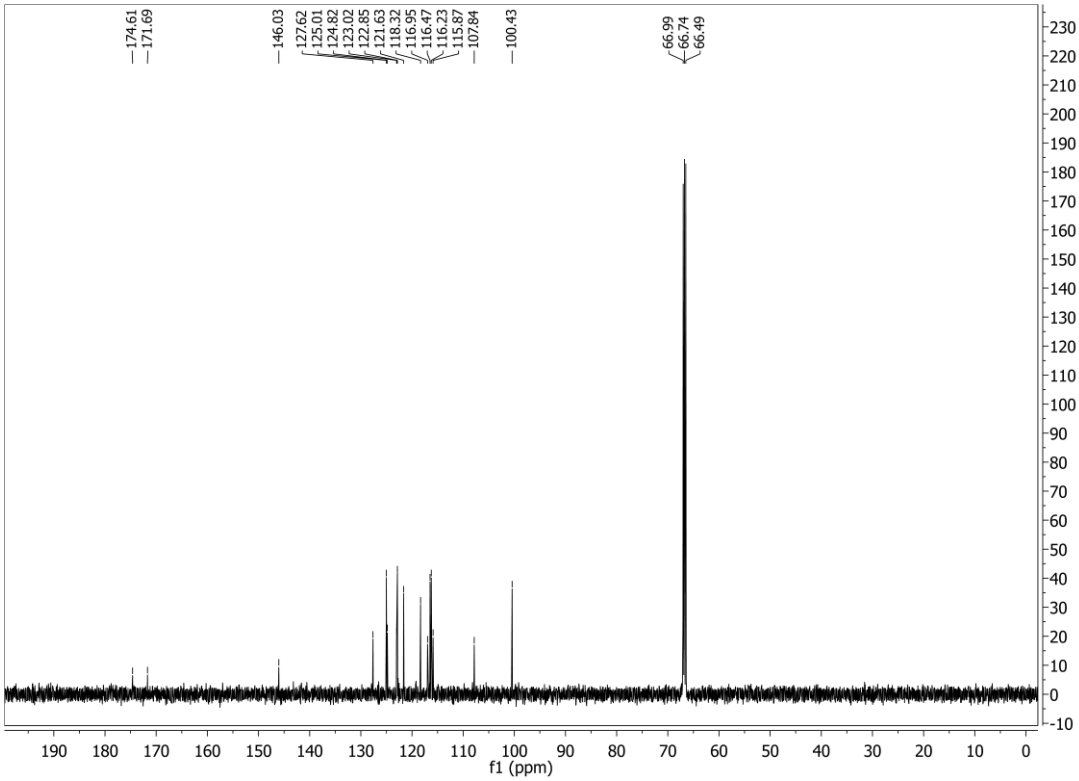
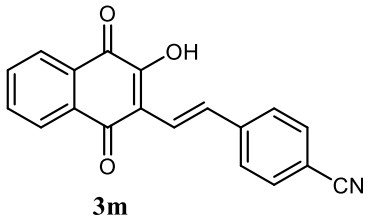


Figure E24 ^{13}C-NMR spectrum of **3l** in $CDCl_3$

4-(2-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)vinyl)benzonitrile (3m)



3m

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 87% (78.6 mg)
Physical appearance: red solid

M.p. 214.7-218.9 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.21 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 16.7 Hz, 1H), 7.79 (dt, *J* = 22.9, 7.6 Hz, 2H), 7.68 (s, 4H), 7.51 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.29, 180.48, 151.98, 141.68, 136.17, 134.85, 132.94, 132.14, 132.00, 128.93, 126.95, 126.80, 125.79, 120.46, 118.43, 117.13, 110.96; **HRMS** (ESI^-): calc. for $C_{19}H_{10}NO_3$ $[M-H]^-$: 300.0666, found: 300.0667 *m/z*.

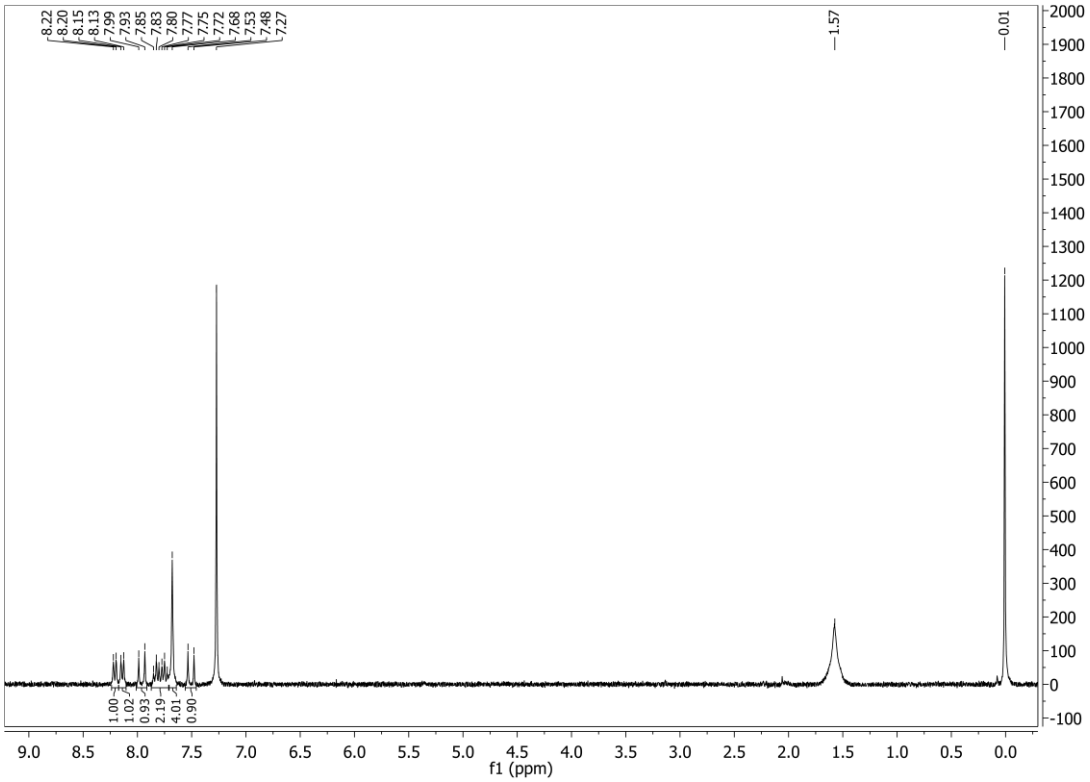


Figure E25 ^{1}H-NMR spectrum of **3m** in $CDCl_3$

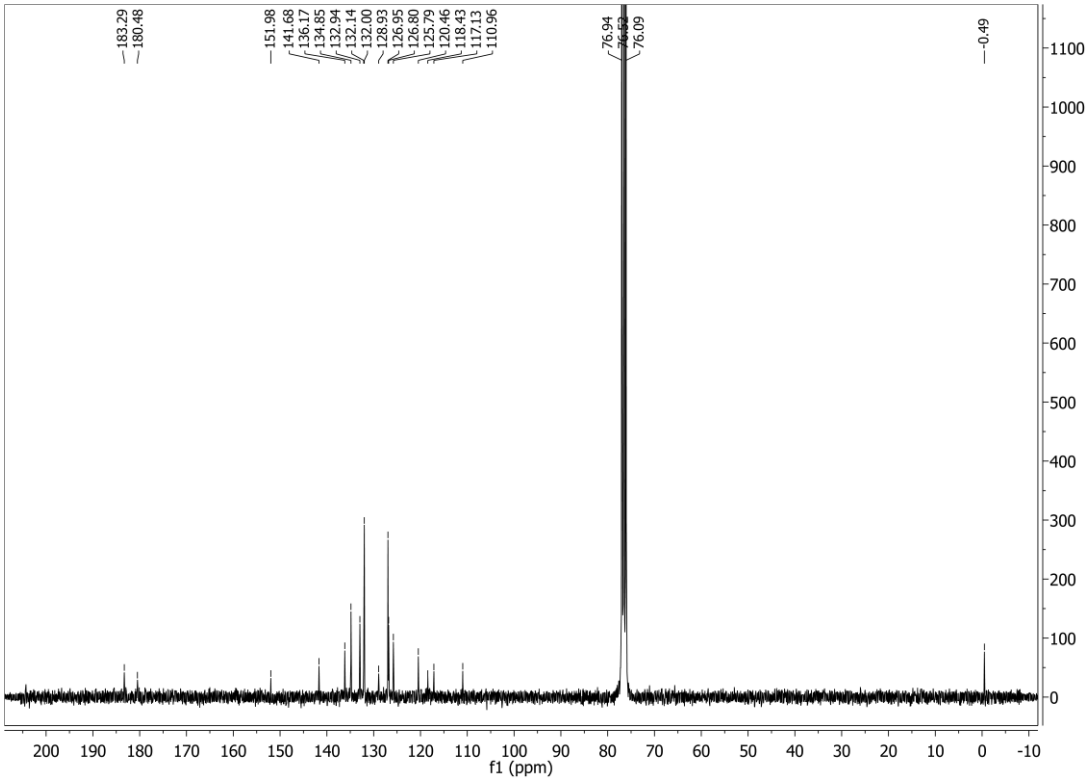
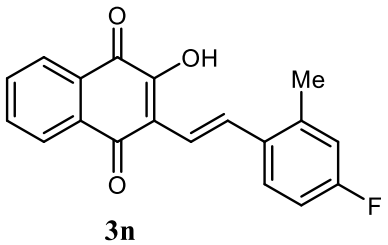


Figure E26 ^{13}C-NMR spectrum of **3m** in $CDCl_3$

2-(4-fluoro-2-methylstyryl)-3-hydroxynaphthalene-1,4-dione (3n)



3n

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 77% (71.1 mg)
Physical appearance: red solid

M.p. 165.7-168.2 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 8.05-7.97 (m, 2H), 7.88-7.78 (m, 2H), 7.57 (d, J = 7.0 Hz, 2H), 7.43-7.28 (m, 3H), 6.50 (s, 1H), 1.95 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.04, 180.95, 150.73, 142.83 ($^1J_{CF}$ = 59.3 Hz), 134.58 ($^2J_{CF}$ = 1.5 Hz), 132.61, 132.49 ($^3J_{CF}$ = 1.5 Hz), 129.07, 127.78, 127.68, 127.47 ($^4J_{CF}$ = 2.3 Hz), 127.33, 127.05, 126.51, 125.75, 120.33, 115.43 ($^5J_{CF}$ = 7.5 Hz), 114.60 ($^6J_{CF}$ = 10.9 Hz) 19.04; **HRMS** (ESI$^-$): calc. for $C_{19}H_{12}FO_3$ $[M-H]^-$: 307.0747, found: 307.0776 *m/z*.

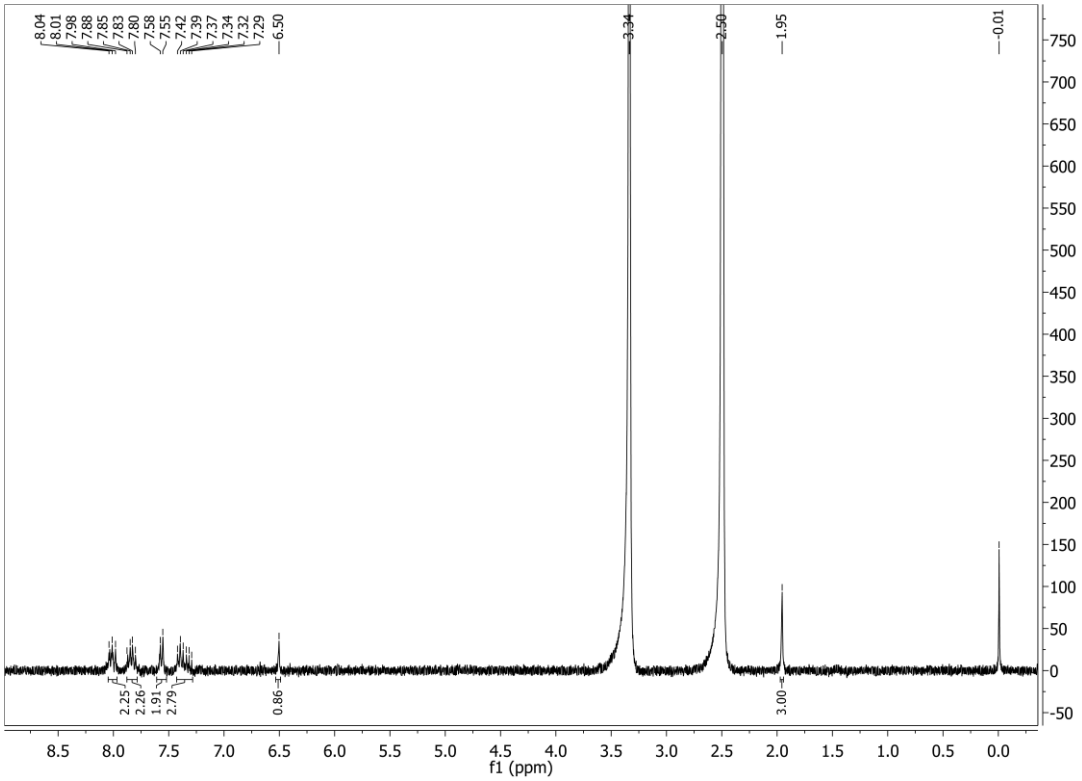


Figure E27 ^{1}H-NMR spectrum of **3n** in $CDCl_3$

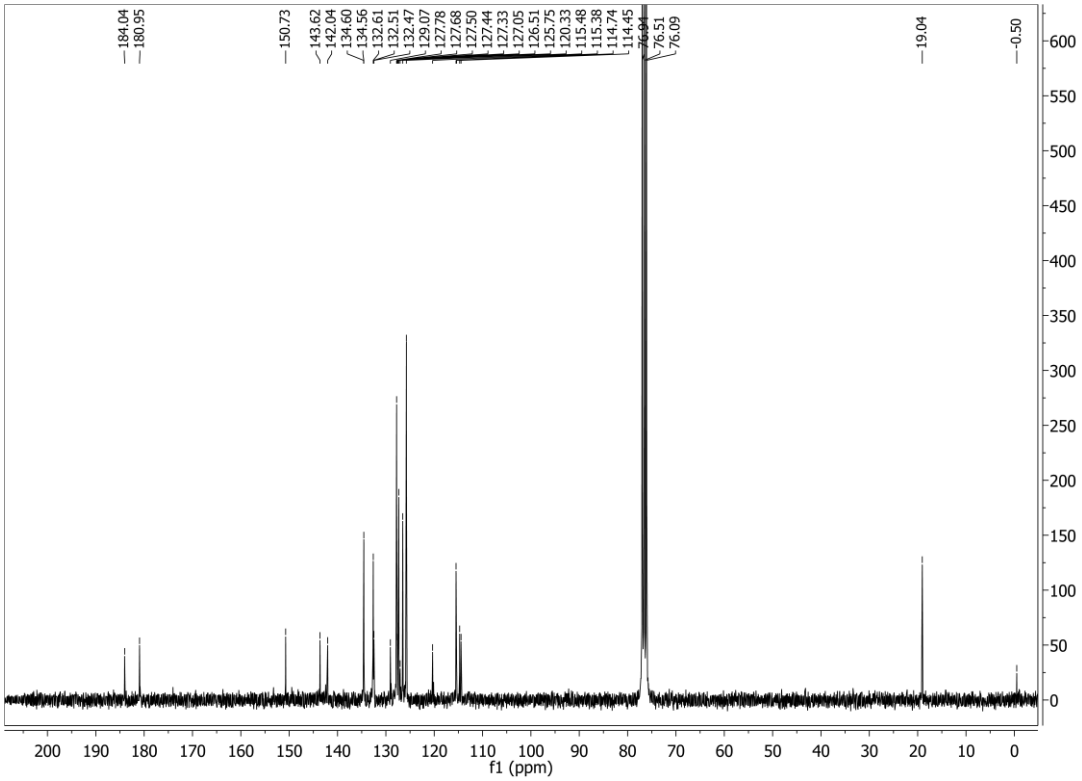
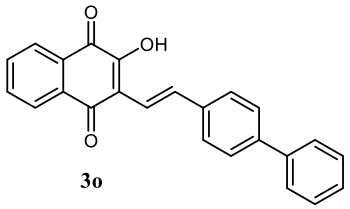


Figure E28 ^{13}C-NMR spectrum of **3n** in $CDCl_3$

2-(2-([1,1'-biphenyl]-4-yl)vinyl)-3-hydroxynaphthalene-1,4-dione (3o)



3o

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 91% (96.1 mg)
Physical appearance: dark red solid

M.p. 224.2-224.6 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.24-8.16 (m, 1H), 8.15-8.09 (m, 1H), 8.03 (d, *J* = 17.1 Hz, 2H), 7.77-7.82 (m, 1H), 7.75-7.71 (m, 1H), 7.70-7.61 (m, 5H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.68, 180.46, 151.16, 140.87, 140.00, 138.36, 136.38, 134.48, 132.72, 132.28, 129.11, 128.32, 127.15, 127.00, 126.88, 126.68, 126.46, 125.57, 118.29, 116.94; **HRMS** (ESI^-): calc. for $C_{24}H_{15}O_3$ $[M-H]^-$: 351.1027, found: 351.1025 *m/z*.

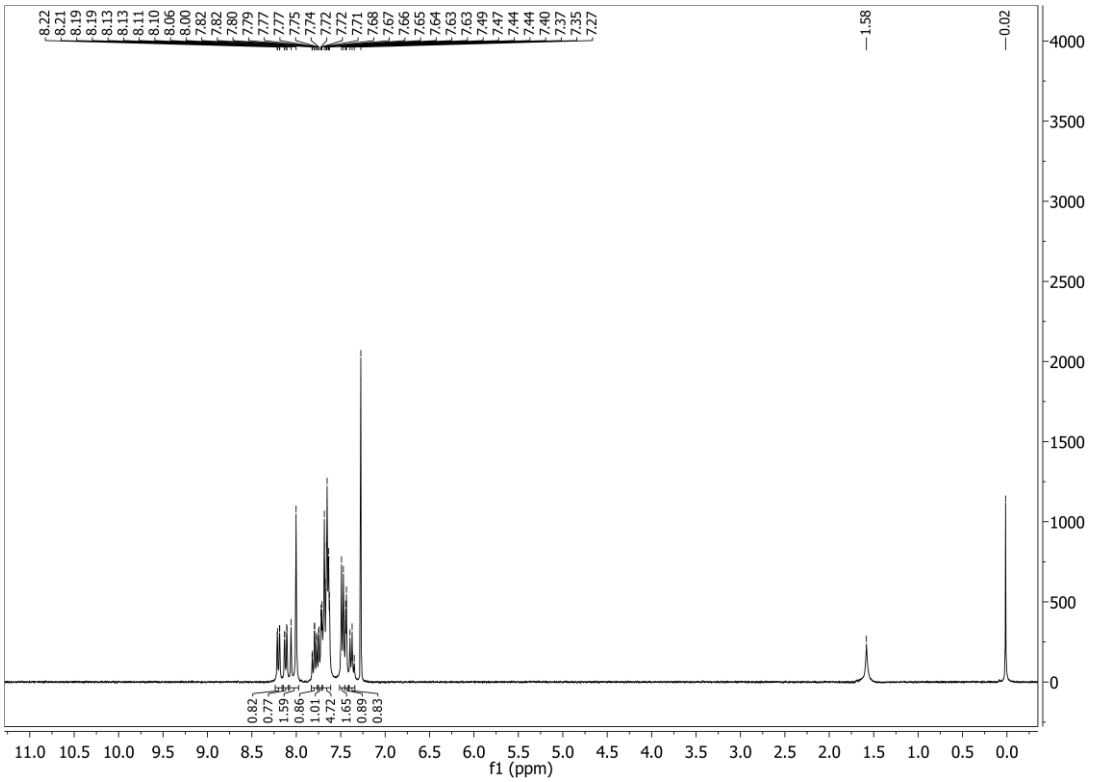


Figure E29 ^{1}H-NMR spectrum of **3o** in $CDCl_3$

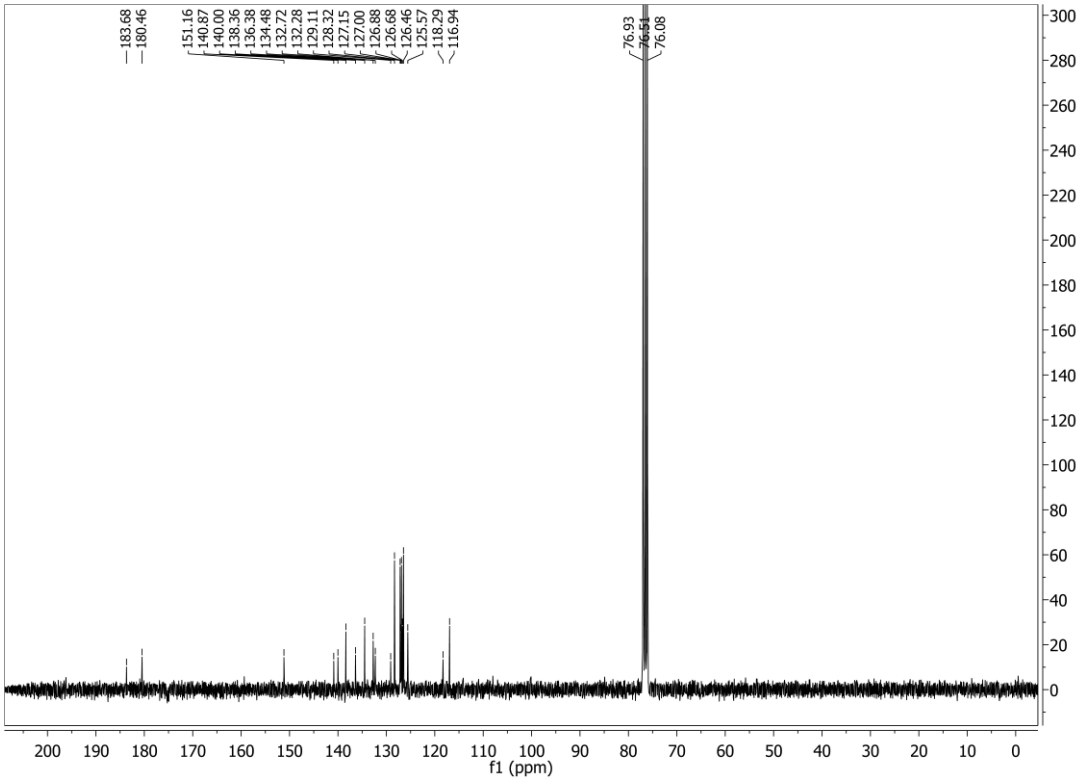
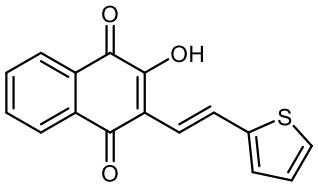


Figure E30 ^{13}C-NMR spectrum of **3o** in $CDCl_3$

2-hydroxy-3-(2-(thiophen-2-yl)vinyl)naphthalene-1,4-dione (3p)



3p

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 46% (38.8 mg)
Physical appearance: red solid

M.p. 196.5-199.2 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.11 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.85-7.68 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 5.0 Hz, 1H), 7.07-7.03 (m, 1H), 6.90 (d, *J* = 3.4 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.29, 180.55, 151.45, 139.69, 134.93, 133.25, 132.36, 129.72, 128.05, 127.93, 127.18, 126.55, 126.24, 126.08, 122.84, 116.91; **HRMS** (ESI^-): calc. for $C_{16}H_{19}O_3S$ $[M-H]^-$: 281.0278, found: 281.0250 *m/z*.

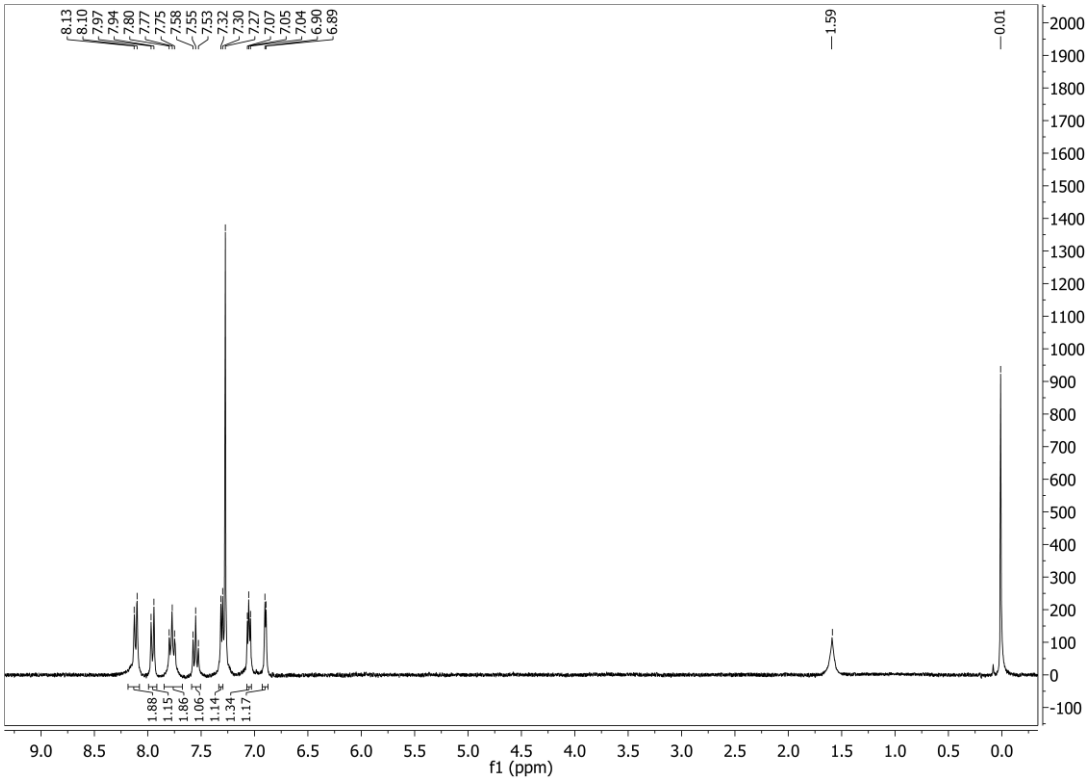


Figure E31 ^{1}H-NMR spectrum of **3p** in $CDCl_3$

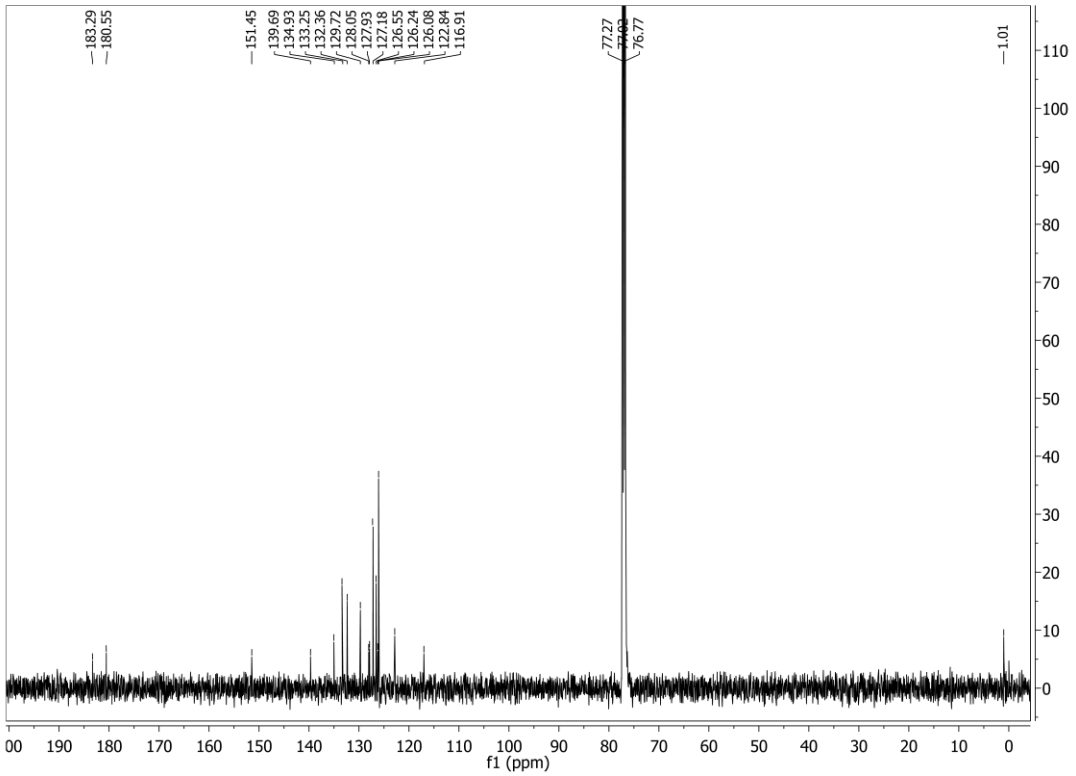
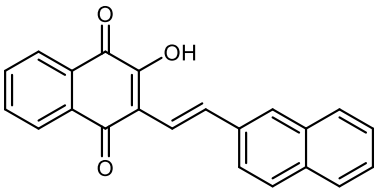


Figure E32 ^{13}C-NMR spectrum of **3p** in $CDCl_3$

2-hydroxy-3-(2-(naphthalen-2-yl)vinyl)naphthalene-1,4-dione (3q)



3q

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 88% (86.0 mg)
Physical appearance: red solid

M.p. 195.6-197.9 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 8.07 (d, J = 1.9 Hz, 1H), 8.06-7.99 (m, 3H), 7.99-7.86 (m, 4H), 7.85-7.79 (m, 2H), 7.567.44 (m, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.21, 180.97, 151.67, 139.39, 135.34, 135.00, 133.57, 133.26, 132.74, 129.60, 128.41, 128.36, 128.17, 128.06, 127.73, 127.20, 126.44, 126.09, 125.11, 123.48, 118.79, 117.73; **HRMS** (ESI$^-$): calc. for $C_{22}H_{13}O_3$ $[M-H]^-$: 325.0870, found: 325.0868 *m/z*.

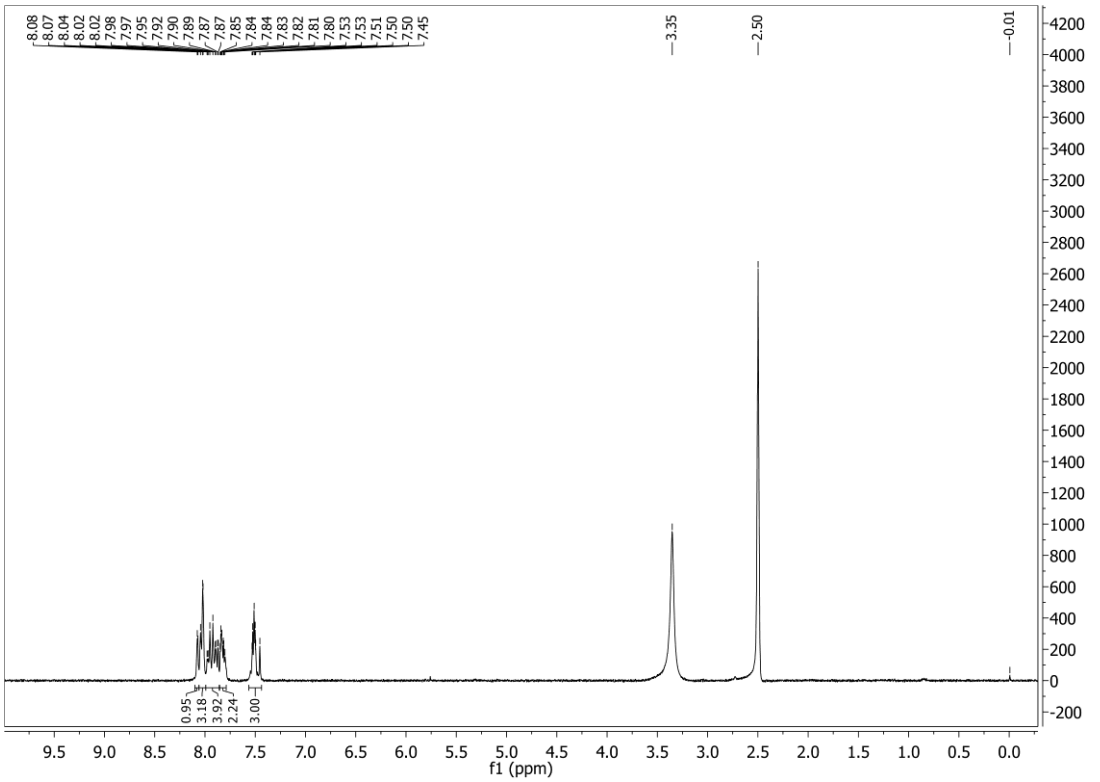


Figure E33 ^{1}H-NMR spectrum of **3q** in $CDCl_3$

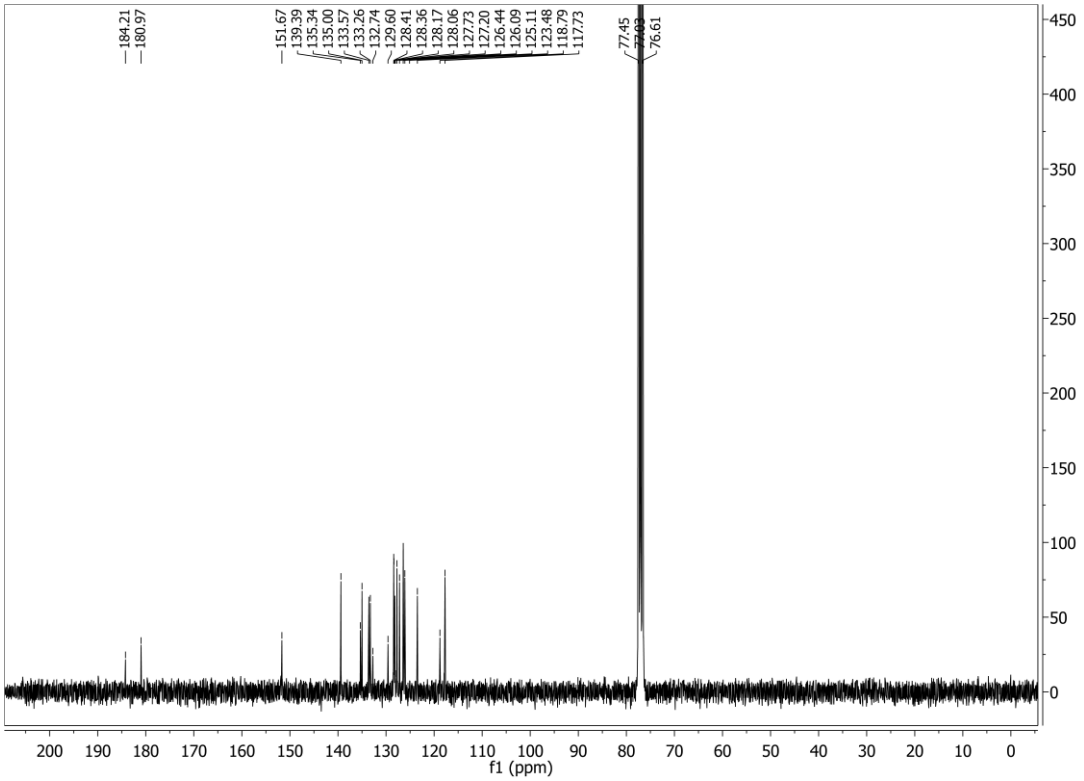
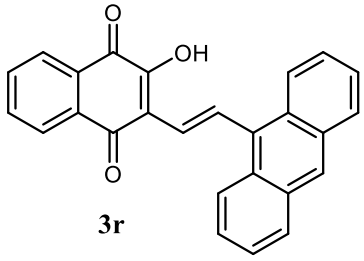


Figure E34 ^{13}C-NMR spectrum of **3q** in $CDCl_3$

2-(2-(anthracen-9-yl)vinyl)-3-hydroxynaphthalene-1,4-dione (3r)



3r

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 67% (75.6 mg)
Physical appearance: dark red solid

M.p. 219.7-221.6 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.80 (d, *J* = 16.9 Hz, 1H), 8.41 (d, *J* = 6.0 Hz, 2H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.04-7.97 (m, 2H), 7.86-7.68 (m, 2H), 7.54-7.43 (m, 4H), 7.29-7.20 (m, 2H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.81, 180.91, 151.59, 137.16, 136.16, 134.74, 132.85, 132.40, 131.08, 129.83, 129.14, 128.95, 128.29, 126.80, 126.71, 125.74, 125.55, 125.37, 124.82, 118.02; **HRMS** (ESI^-): calc. for $C_{26}H_{15}O_3$ $[M-H]^-$: 375.1027, found: 375.1029 *m/z*.

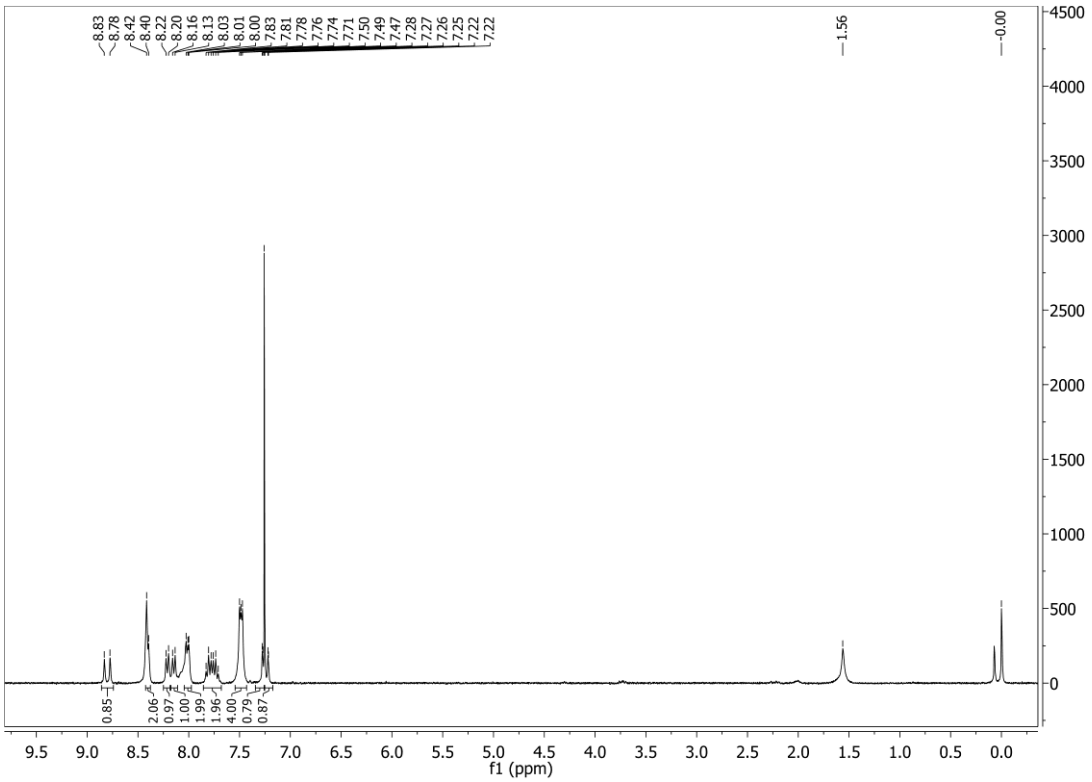


Figure E35 ^{1}H-NMR spectrum of **3r** in $CDCl_3$

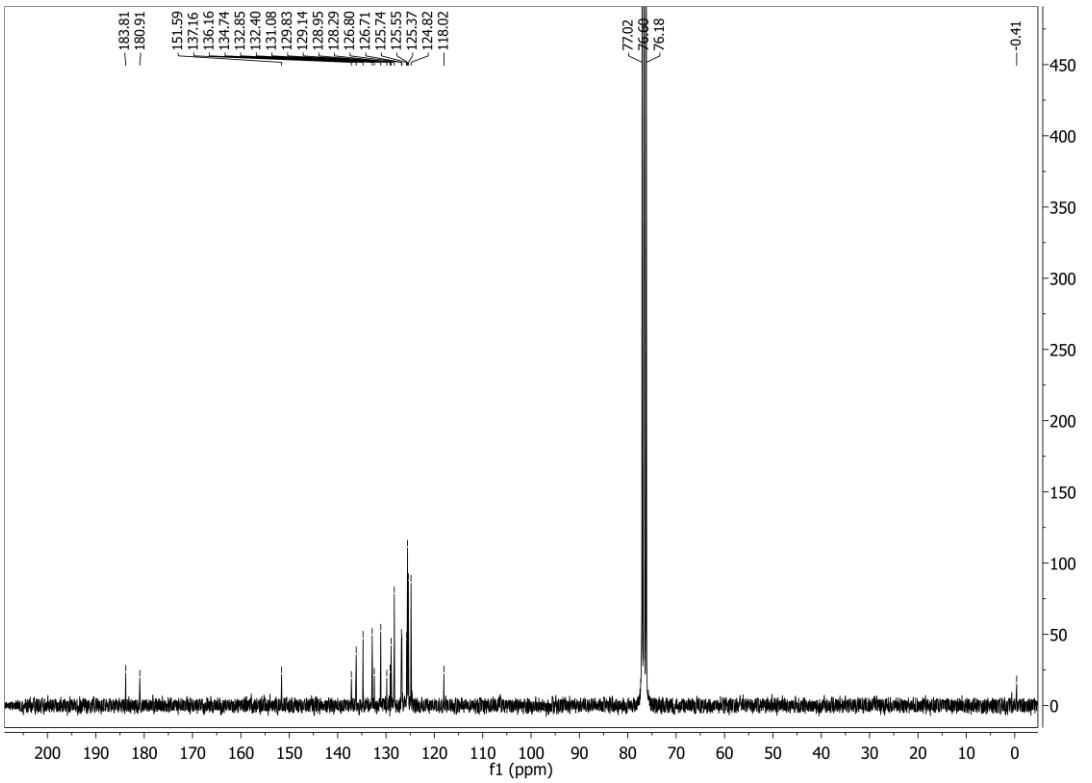
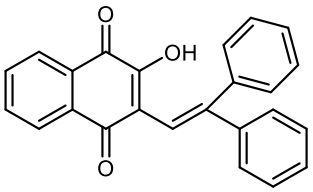


Figure E36 ^{13}C-NMR spectrum of **3r** in $CDCl_3$

2-(2,2-diphenylvinyl)-3-hydroxynaphthalene-1,4-dione (3s)



3s

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 48% (49.6 mg)
Physical appearance: red solid

M.p. 201.6-202.3 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.04 (dt, *J* = 7.4, 1.4 Hz, 2H), 7.70 (dtd, *J* = 18.8, 7.4, 1.5 Hz, 2H), 7.39 – 7.31 (m, 5H), 7.25 – 7.18 (m, 5H), 6.75 (s, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.44, 180.51, 151.07, 149.64, 141.99, 140.71, 134.73, 134.41, 132.65, 132.50, 129.03, 128.09, 127.76, 127.59, 127.50, 127.25, 126.43, 125.56, 120.63, 116.20; **HRMS** (ESI^-): calc. for $C_{24}H_{15}O_3$ $[M-H]^-$: 351.1027, found: 351.1019 *m/z*.

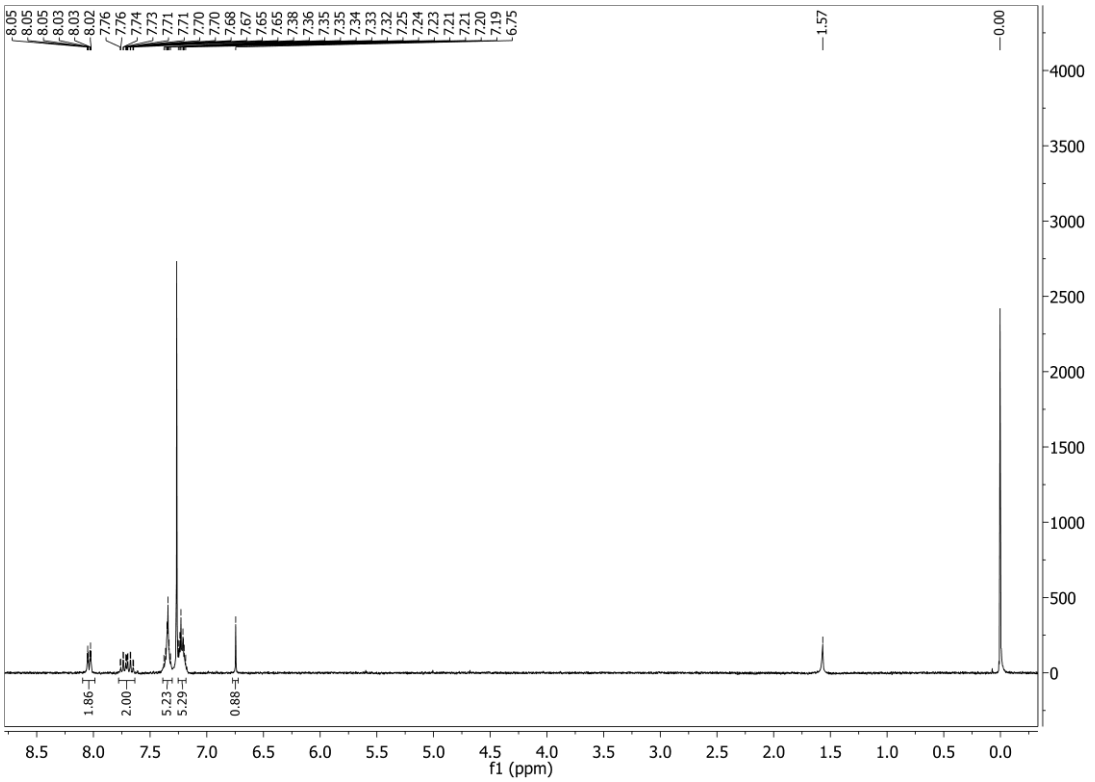


Figure E37 ^{1}H-NMR spectrum of **3s** in $CDCl_3$

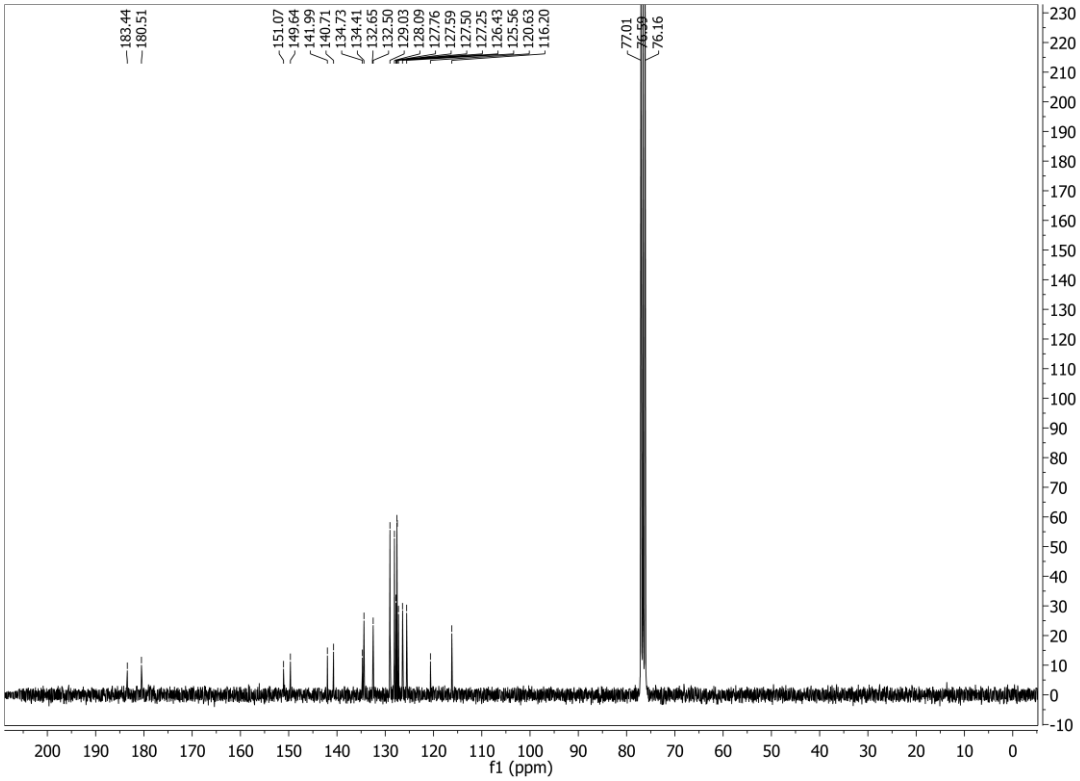
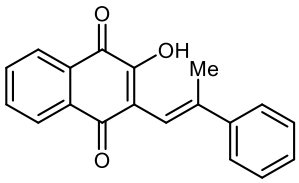


Figure E38 ^{13}C-NMR spectrum of **3s** in $CDCl_3$

2-hydroxy-3-(2-phenylprop-1-en-1-yl)naphthalene-1,4-dione (3t)



3t

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 50% (43.5 mg)
Physical appearance: red solid

M.p. 141.2-143.6 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.22-8.10 (m, 2H), 7.82-7.71 (m, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.36 (dt, *J* = 12.5, 6.6 Hz, 3H), 6.64 (s, 1H), 2.10 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 184.03, 180.96, 150.78, 143.60, 142.09, 134.51, 132.56, 132.42, 129.10, 127.76, 127.30, 126.50, 125.75, 125.68, 120.35, 115.51, 19.02; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_3$ $[M-H]^-$: 289.0870, found: 289.0857 *m/z*.

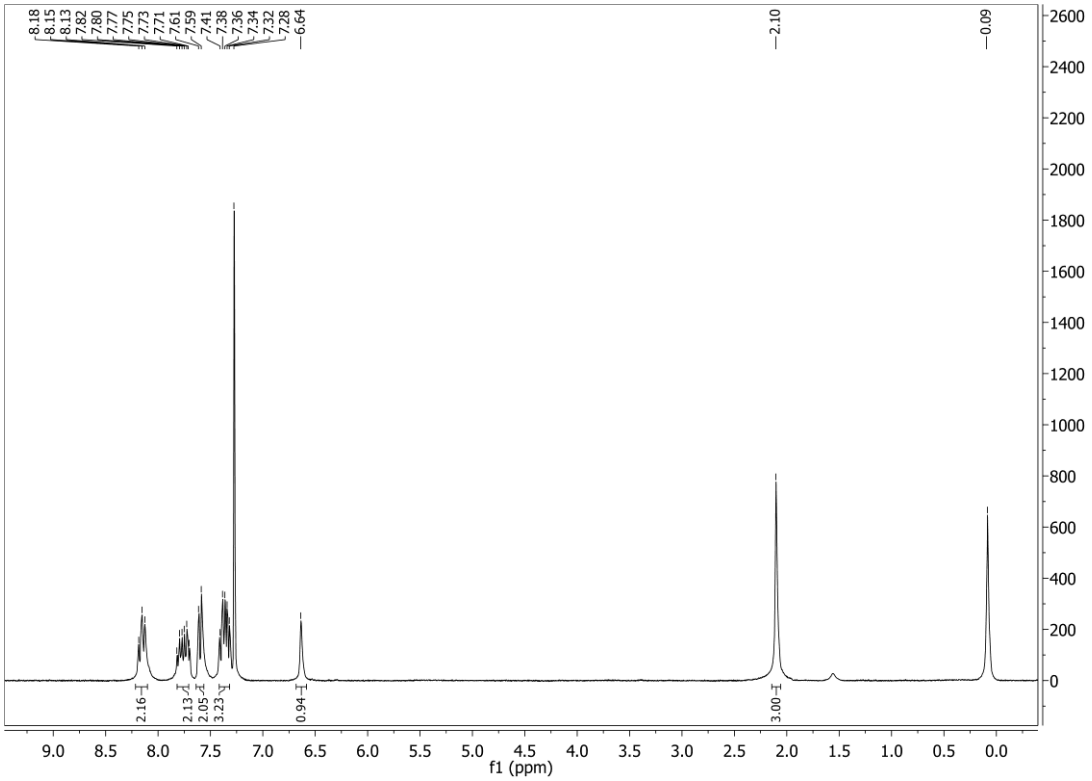


Figure E39 ^{1}H-NMR spectrum of **3t** in $CDCl_3$

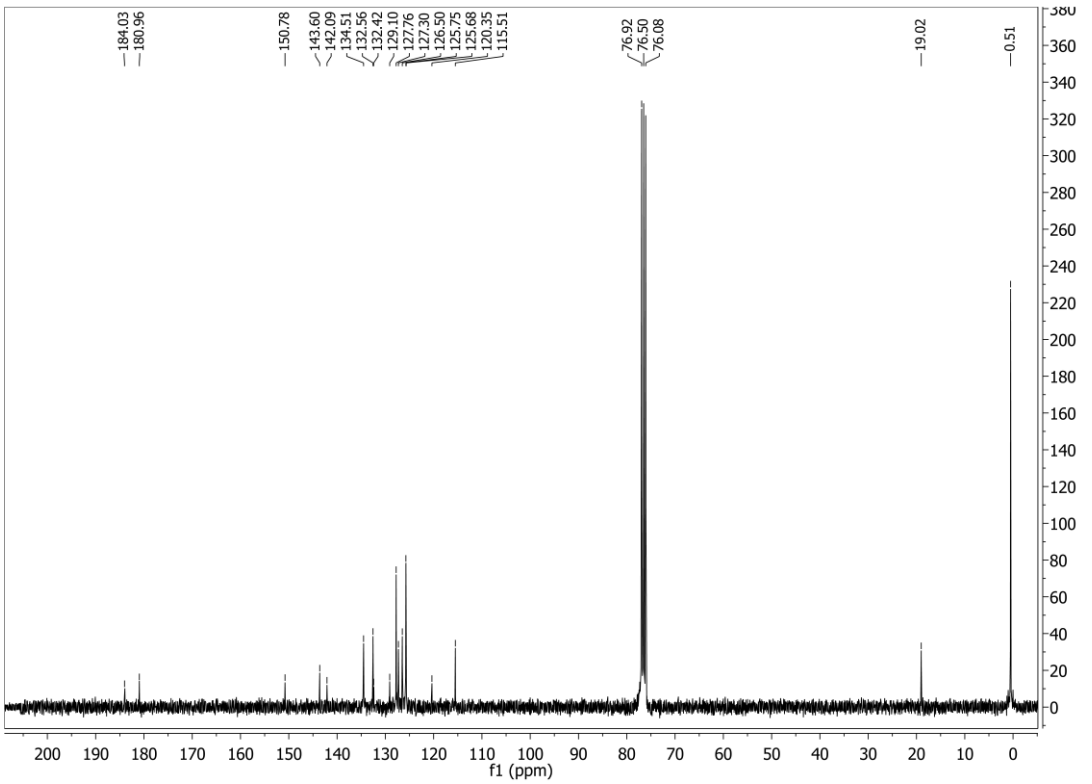
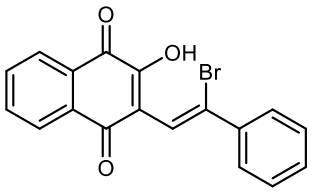


Figure E40 ^{13}C-NMR spectrum of **3t** in $CDCl_3$

2-(2-bromo-2-phenylvinyl)-3-hydroxynaphthalene-1,4-dione (3u)



3u

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 51% (54.2 mg)
Physical appearance: red solid

M.p. 220.5-222.1 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.09-8.01 (m, 1H), 7.80-7.74 (m, 1H), 7.74-7.68 (m, 2H), 7.67-7.61 (m, 1H), 7.50-7.43 (m, 2H), 7.43-7.34 (m, 2H), 6.99 (s, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 179.79, 173.86, 159.15, 156.21, 134.91, 130.06, 129.67, 128.71, 128.50, 128.37, 128.12, 127.89, 123.88, 122.80, 121.68, 102.29; **HRMS** (ESI^-): calc. for $C_{18}H_{10}BrO_3$ $[M-H]^-$: 353.9819, found: 353.9804 *m/z*.

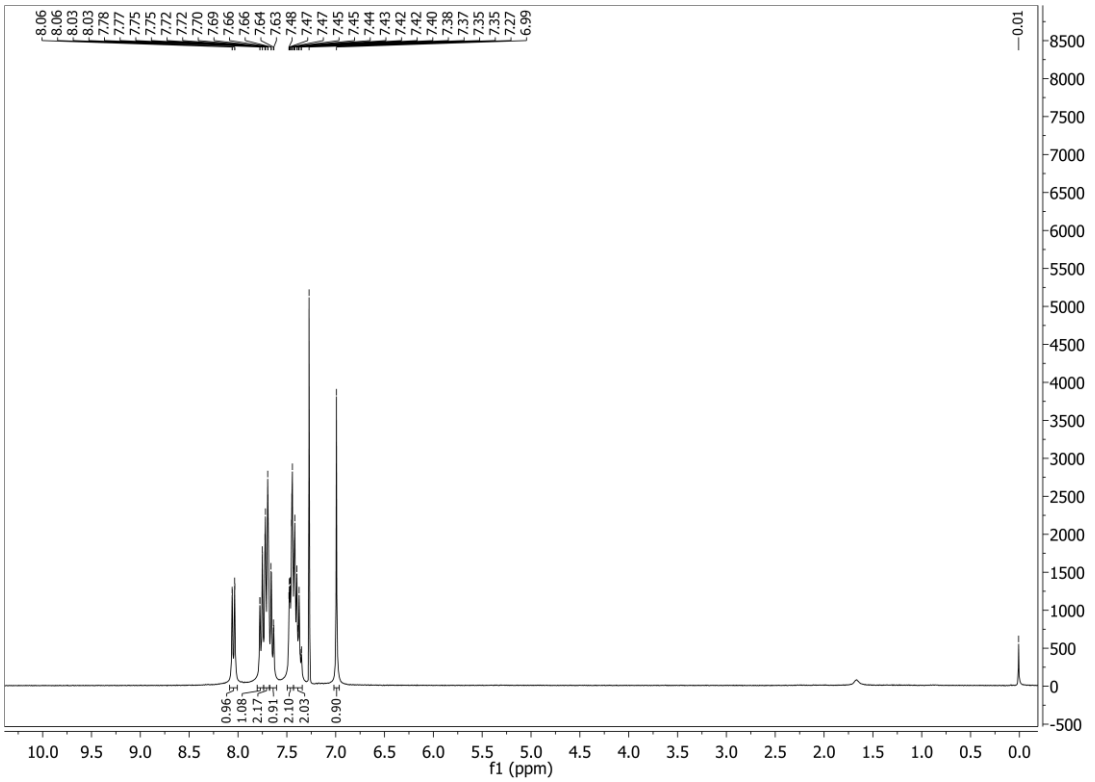


Figure E41 ^{1}H-NMR spectrum of **3u** in $CDCl_3$

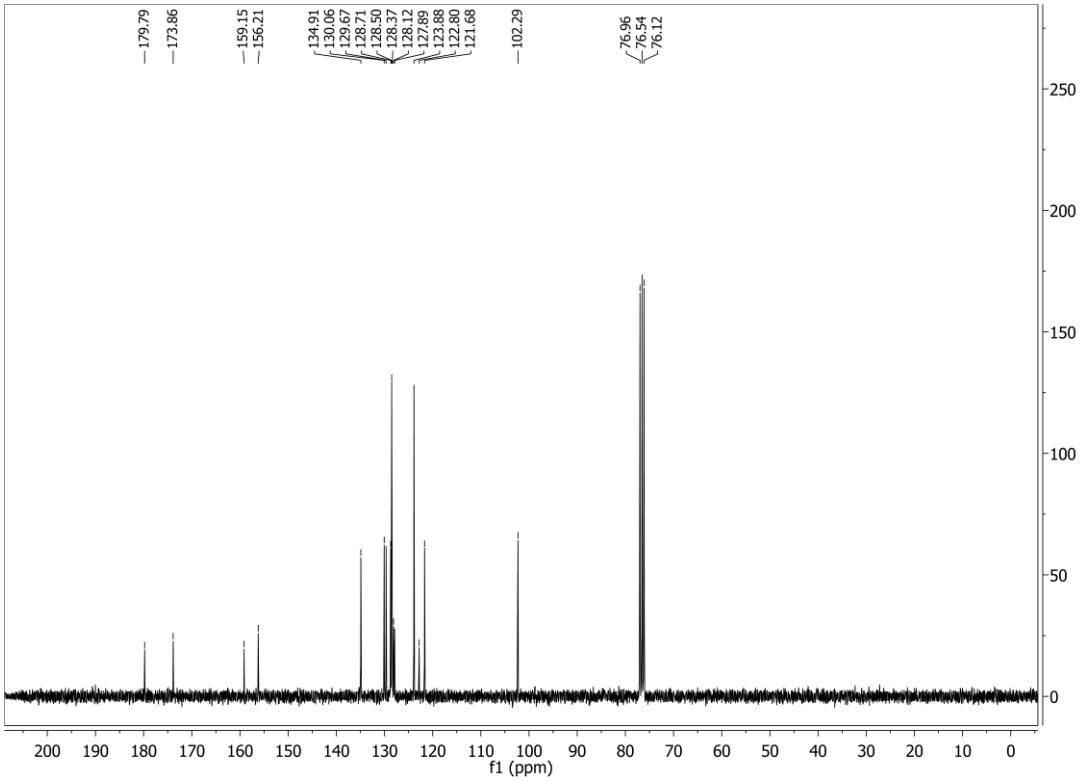
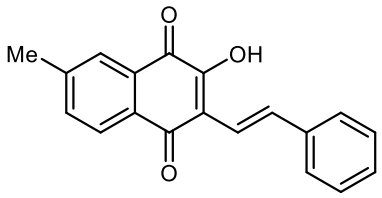


Figure E42 ^{13}C-NMR spectrum of **3u** in $CDCl_3$

3-hydroxy-6-methyl-2-styrylnaphthalene-1,4-dione (3v)



3v

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 86% (74.8 mg)
Physical appearance: red solid

M.p. 192.3-194.1 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 9.8 Hz, 1H), 7.91 (d, *J* = 13.7 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 3.5 Hz, 1H), 7.38 (d, *J* = 6.1 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 2.49 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.60, 180.75, 151.10, 143.74, 138.65, 137.37, 135.13, 129.96, 128.96, 128.20, 128.09, 126.82, 126.66, 125.94, 117.99, 117.02, 21.13; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_3$ $[M-H]^-$: 289.0870, found: 289.0864 *m/z*.

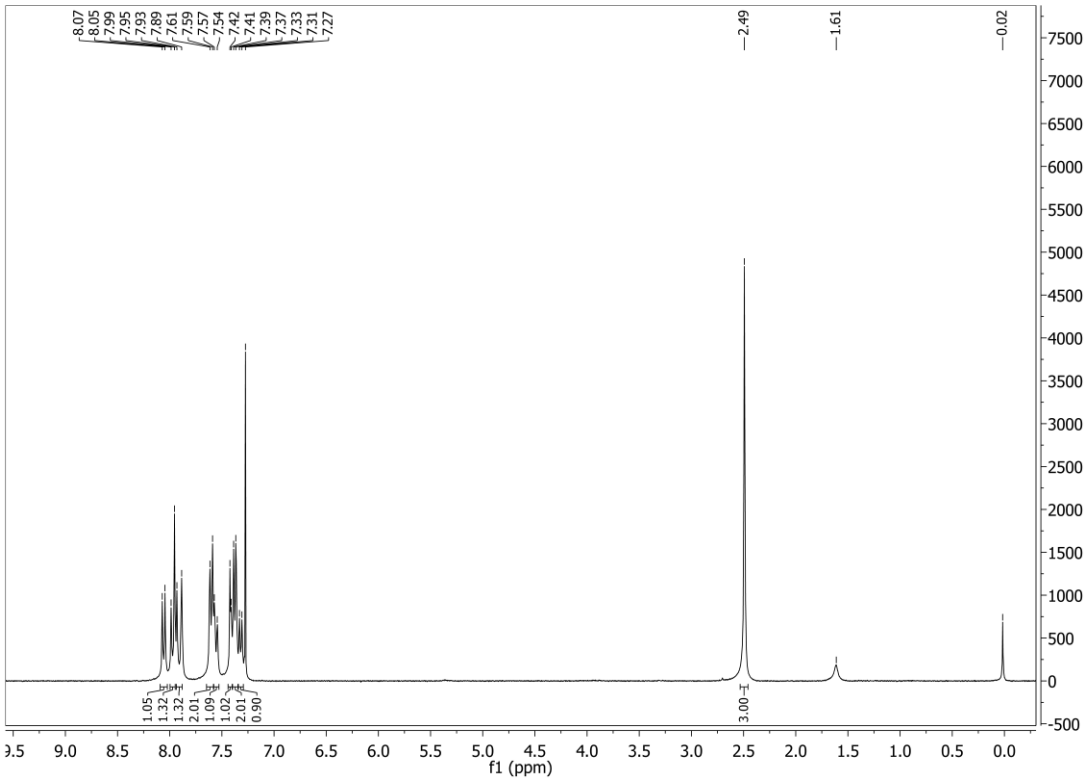


Figure E43 ^{1}H-NMR spectrum of **3v** in $CDCl_3$

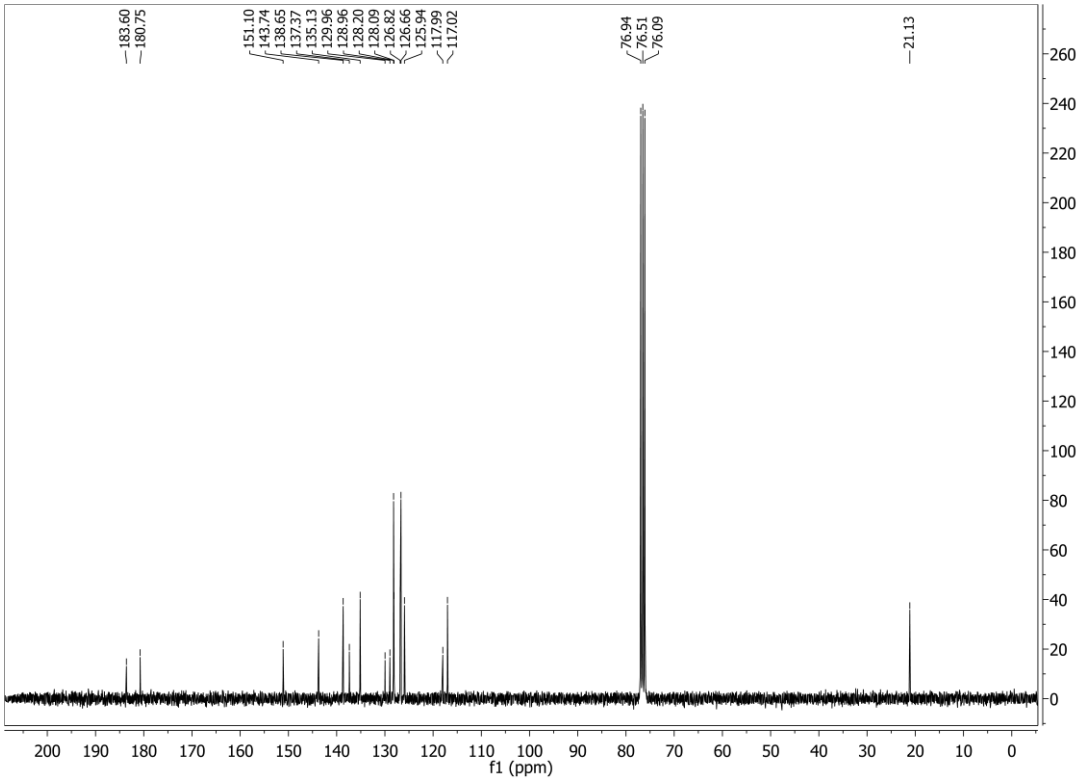
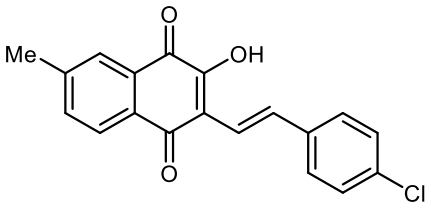


Figure E44 ^{13}C-NMR spectrum of **3v** in $CDCl_3$

2-(4-chlorostyryl)-3-hydroxy-6-methylnaphthalene-1,4-dione (3w)



3w

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 84% (81.6mg)
Physical appearance: red solid

M.p. 234.5-235.6 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.96-7.88 (m, 2H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.41-7.32 (m, 3H), 2.51 (s, 3H; **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 181.08, 178.41, 151.85, 141.40, 134.89, 133.26, 132.35, 130.98, 128.12, 128.04, 126.22, 125.63, 124.11, 123.29, 116.64, 115.39, 18.11; **HRMS** (ESI^-): calc. for $C_{19}H_{12}ClO_3$ $[M-H]^-$: 323.0480, found: 323.0475 *m/z*.

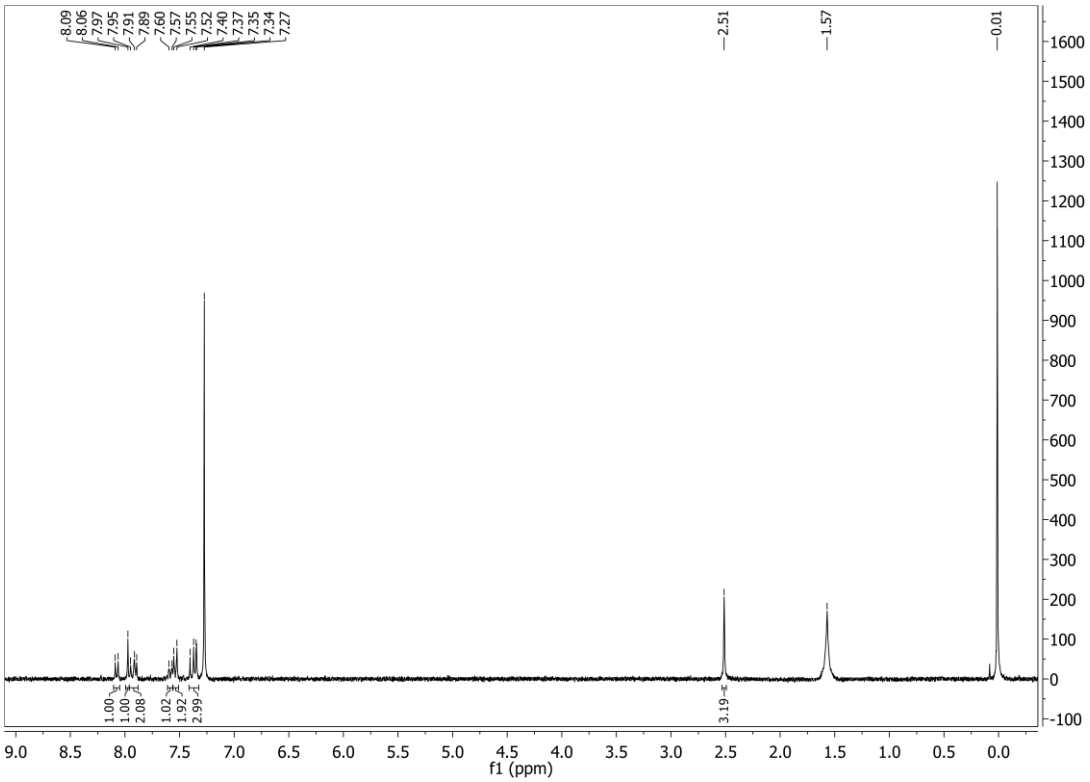


Figure E45 ^{1}H-NMR spectrum of **3w** in $CDCl_3$

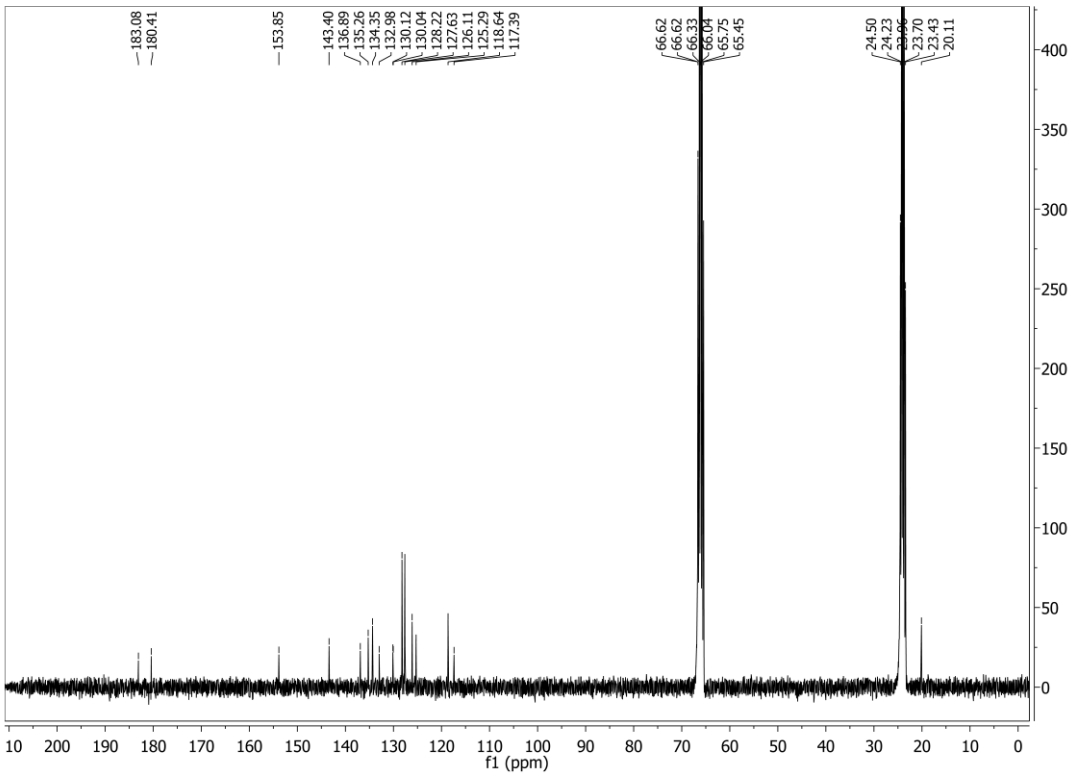
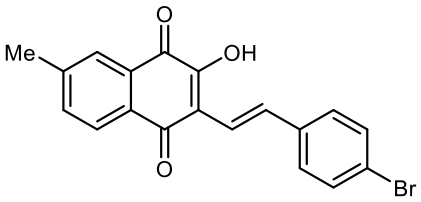


Figure E46 ^{13}C-NMR spectrum of **3w** in THF

-

2-(4-bromostyryl)-3-hydroxy-6-methylnaphthalene-1,4-dione (3x)



3x

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 83% (91.6 mg)
Physical appearance: red solid

M.p. 238.4-240.3 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 8.2 Hz, 1H), 8.02-7.85 (m, 3H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.53-7.45 (m, 3H), 7.39 (d, *J* = 17.2 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 181.08, 178.41, 151.89, 141.41, 135.28, 134.72, 133.31, 132.36, 129.22, 128.13, 128.04, 125.91, 124.11, 123.29, 116.71, 115.39, 18.10; **HRMS** (ESI^-): calc. for $C_{19}H_{12}BrO_3$ $[M-H]^-$: 366.9975, found: 366.9954*m/z*.

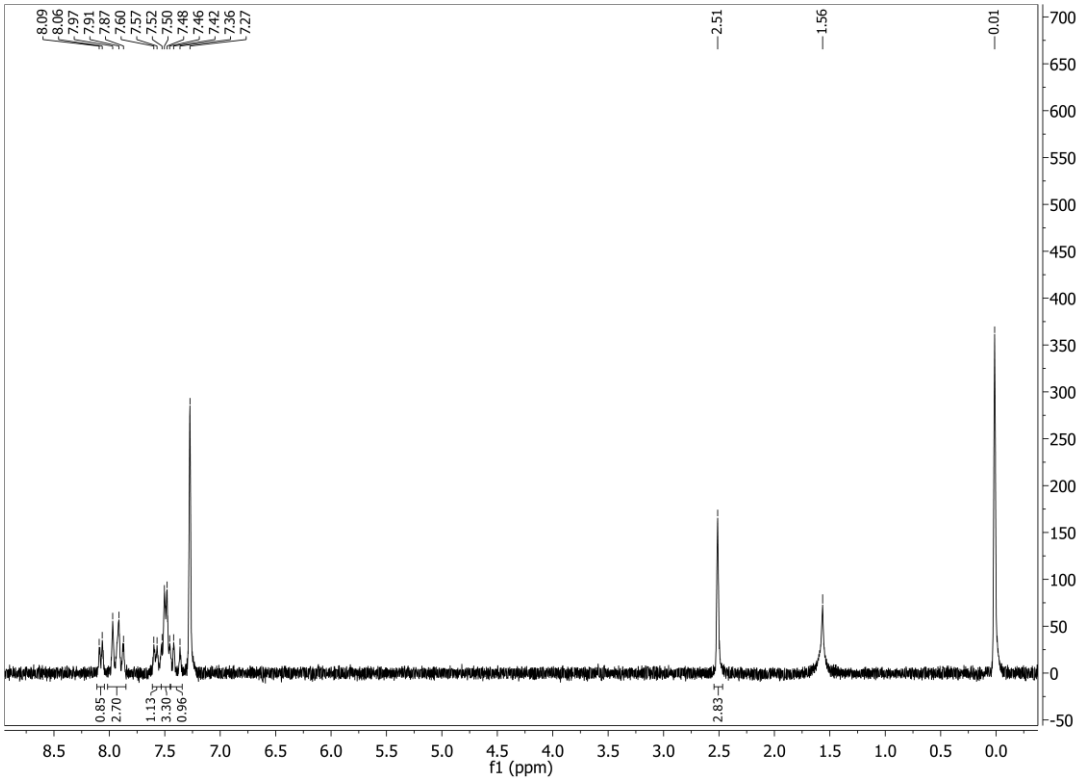


Figure E47 ^{1}H-NMR spectrum of **3x** in $CDCl_3$

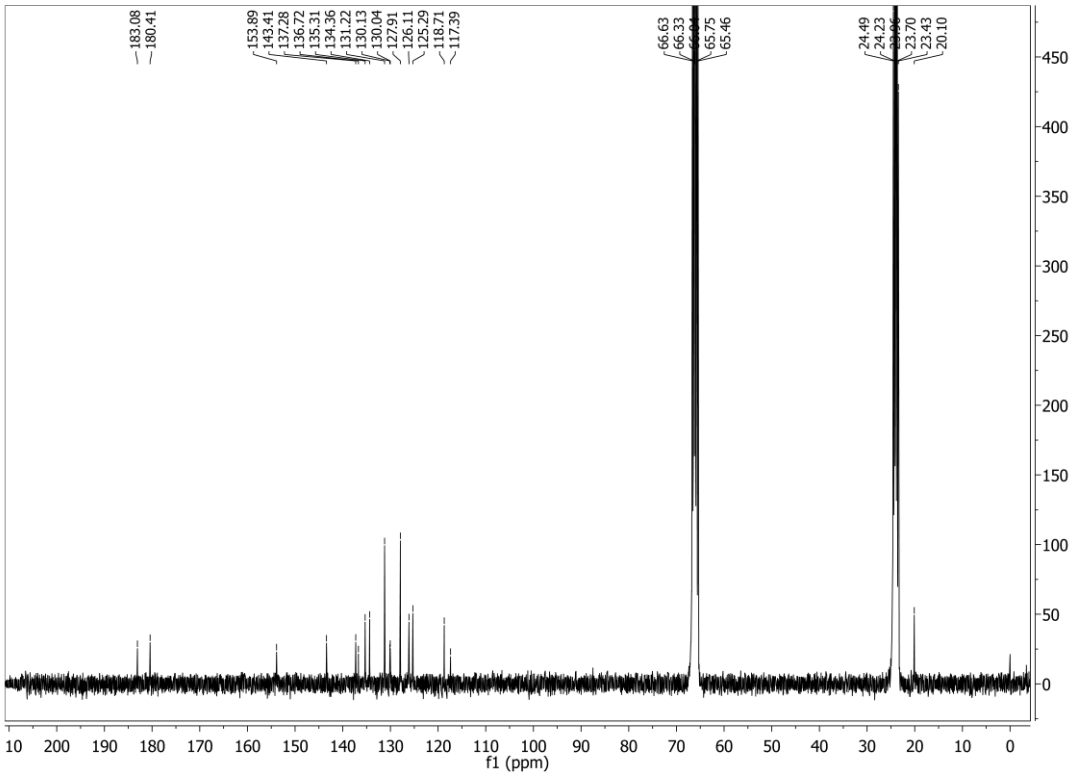
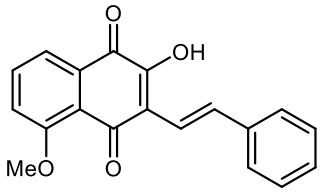


Figure E48 ^{13}C-NMR spectrum of **3x** in THF

2-hydroxy-5-methoxy-3-styrylnaphthalene-1,4-dione (3y)



3y

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 83% (76.2 mg)
Physical appearance: red solid

M.p. 156.2-157.3 ℃; **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) 7.81 (d, *J* = 16.4 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 3H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.35 (d, *J* = 5.5 Hz, 1H), 7.30 (d, *J* = 6.0 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.44, 180.78, 159.35, 153.67, 137.76, 135.99, 133.77, 130.94, 128.18, 127.93, 127.34, 126.65, 119.54, 119.02, 117.43, 114.66, 56.09; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_4$ $[M-H]^-$: 305.0819, found: 305.0800 *m/z*.

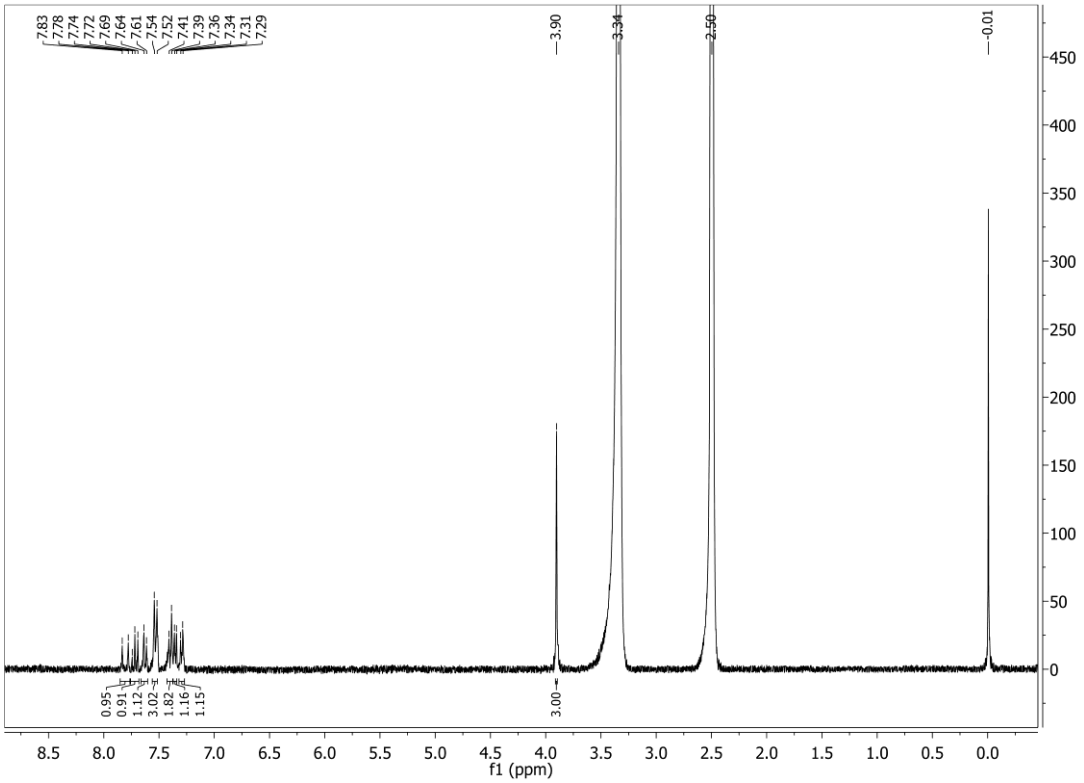


Figure E49 ^{1}H-NMR spectrum of **3y** in $CDCl_3$

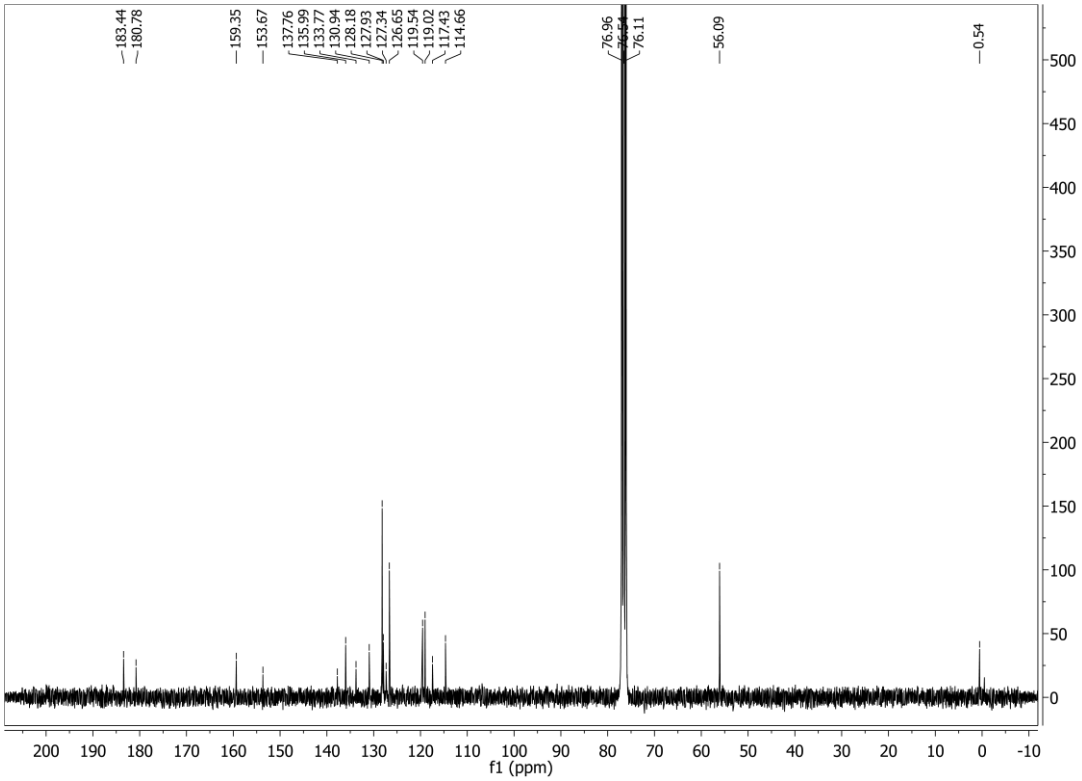
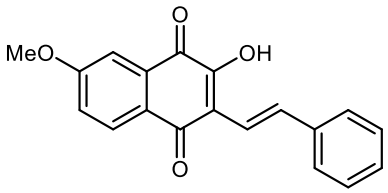


Figure E50 ^{13}C-NMR spectrum of **3y** in $CDCl_3$

3-hydroxy-6-methoxy-2-styrylnaphthalene-1,4-dione (3z)



3z

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 86% (78.8 mg)
Physical appearance: red solid

M.p. 141.3-143.9 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.11 (d, *J* = 8.6 Hz, 1H), 7.94 (t, *J* = 14.8 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.95 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.56, 181.16, 163.56, 151.52, 139.28, 137.87, 131.35, 129.49, 128.71, 128.63, 127.18, 125.99, 120.96, 118.44, 117.60, 109.70, 55.95; **HRMS** (ESI^-): calc. for $C_{19}H_{13}O_4$ $[M-H]^-$: 305.0819, found: 305.0815 *m/z*.

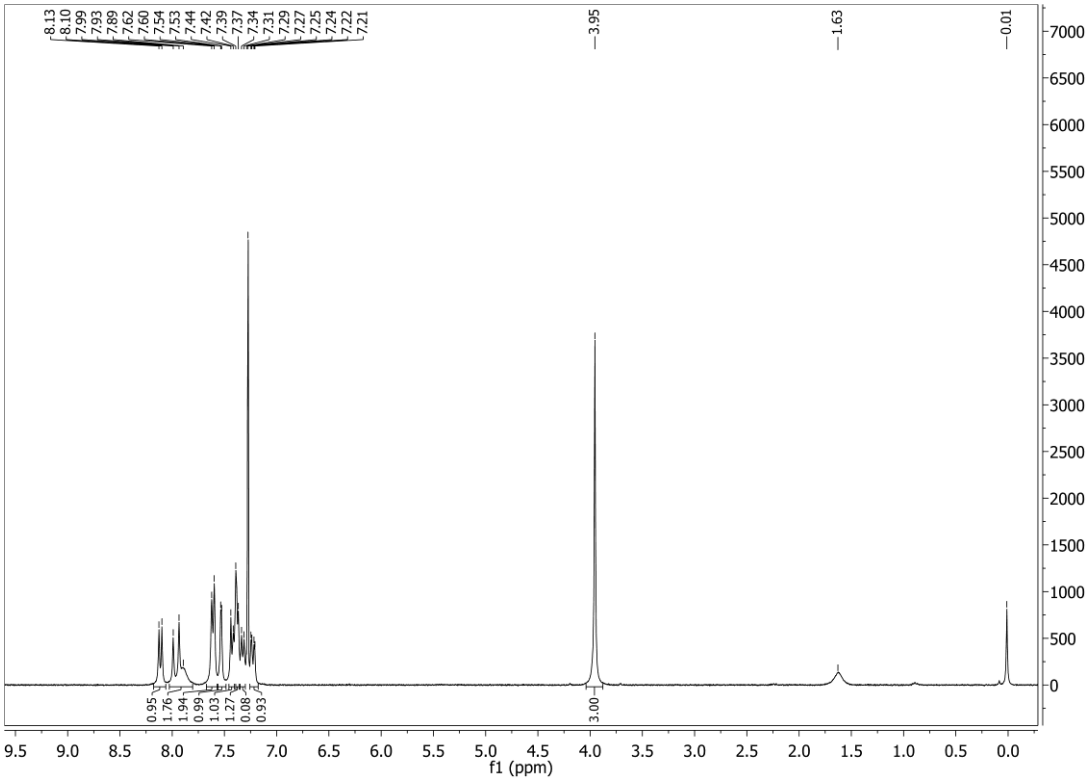


Figure E51 ^{1}H-NMR spectrum of **3z** in $CDCl_3$

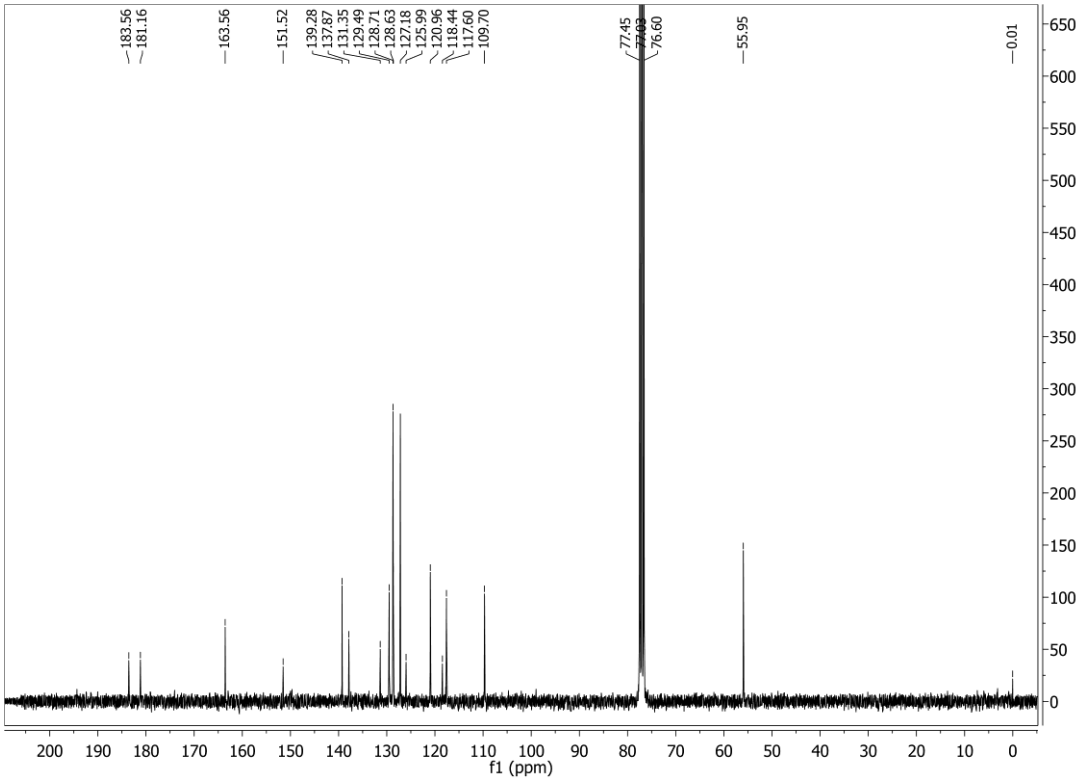
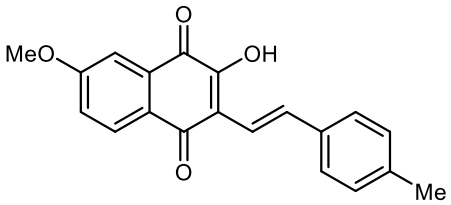


Figure E52 ^{13}C-NMR spectrum of **3z** in $CDCl_3$

3-hydroxy-6-methoxy-2-(4-methylstyryl)naphthalene-1,4-dione (3aa)



3aa

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 89% (85.5 mg)
Physical appearance: red solid

M.p. 133.5-136.3 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.12 (d, *J* = 11.0 Hz, 1H), 7.96 (d, *J* = 14.9 Hz, 1H), 7.63-7.44 (m, 3H), 7.38 (d, *J* = 15.8 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 3H), 3.97 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.16, 180.61, 163.04, 150.82, 138.87, 138.31, 134.66, 133.82, 130.91, 128.96, 126.64, 125.51, 120.37, 118.23, 116.14, 109.18, 55.45, 20.89; **HRMS** (ESI$^-$): calc. for $C_{20}H_{15}O_4$ $[M-H]^-$: 319.0976, found: 319.0958 *m/z*.

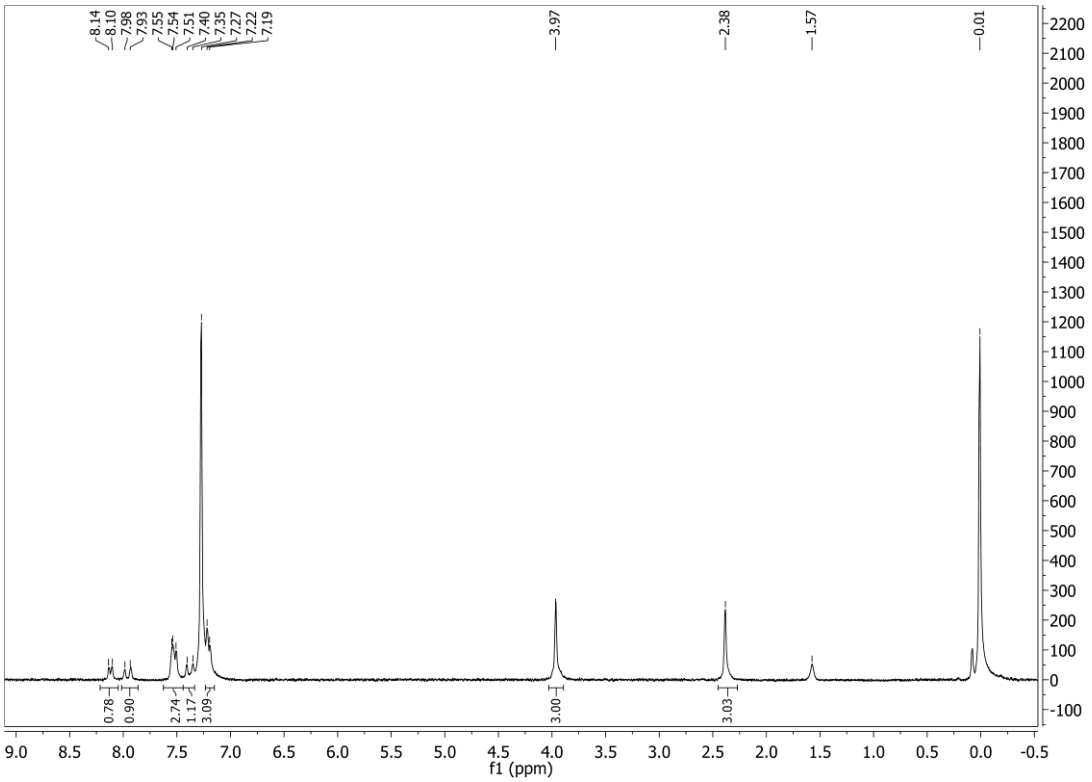


Figure E53 ^{1}H-NMR spectrum of **3aa** in $CDCl_3$

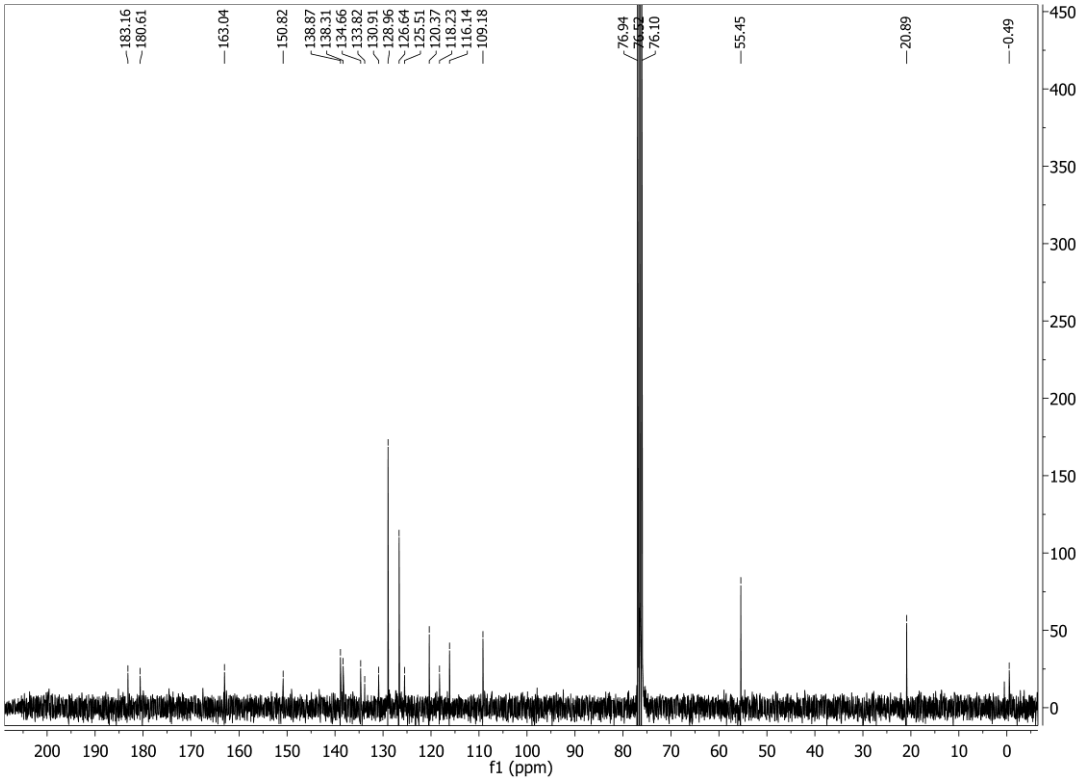
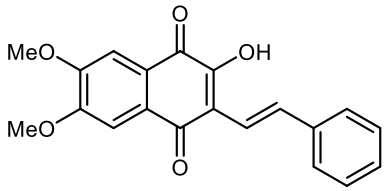


Figure E54 ^{13}C-NMR spectrum of **3aa** in $CDCl_3$

2-hydroxy-6,7-dimethoxy-3-styrylnaphthalene-1,4-dione (3ab)



3ab

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 89% (89.7 mg)
Physical appearance: red solid

M.p. 156.2-158.3 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 16.7 Hz, 1H), 7.59 (s, 2H), 7.51 (s, 1H), 7.40 (d, *J* = 3.7 Hz, 2H), 7.36 (d, *J* = 5.4 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 2H), 4.07 (s, 3H), 4.04 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.38, 179.74, 153.97, 152.31, 151.14, 137.90, 137.43, 133.82, 128.20, 127.98, 127.37, 126.58, 125.48, 117.03, 108.47, 107.03, 56.10, 56.03; **HRMS** (ESI^-): calc. for $C_{20}H_{15}O_5$ $[M-H]^-$: 335.0925, found: 335.0900 *m/z*.

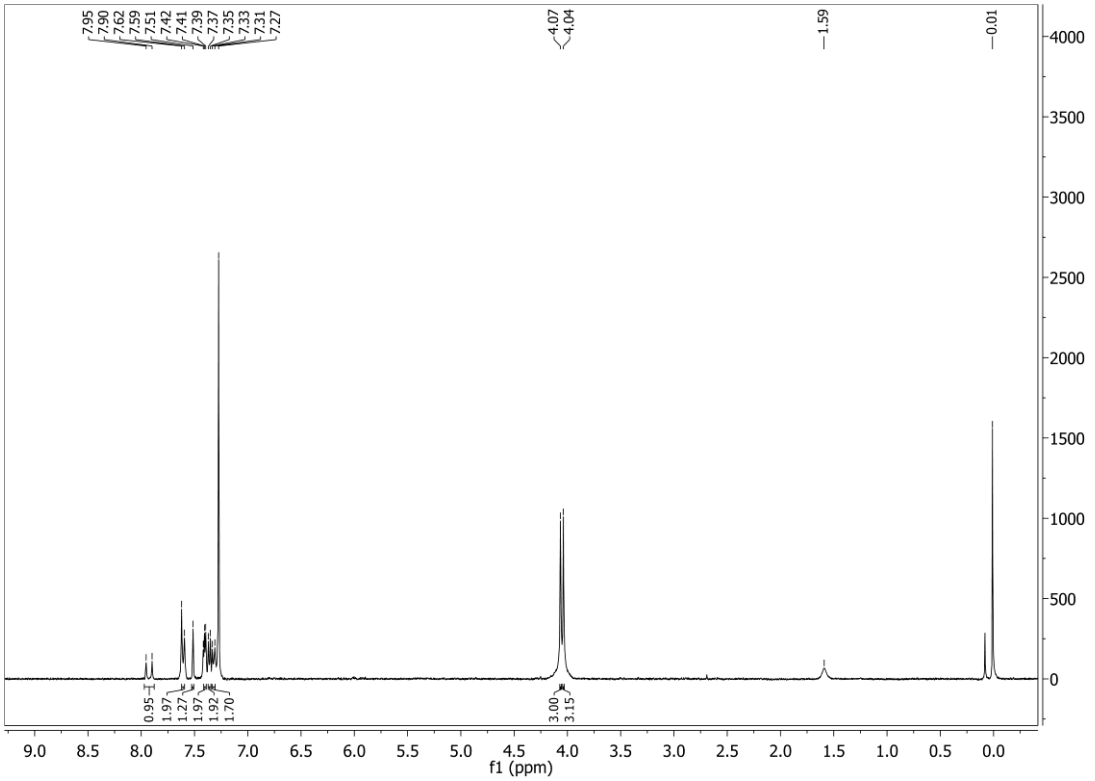


Figure E55 ^{1}H-NMR spectrum of **3ab** in $CDCl_3$

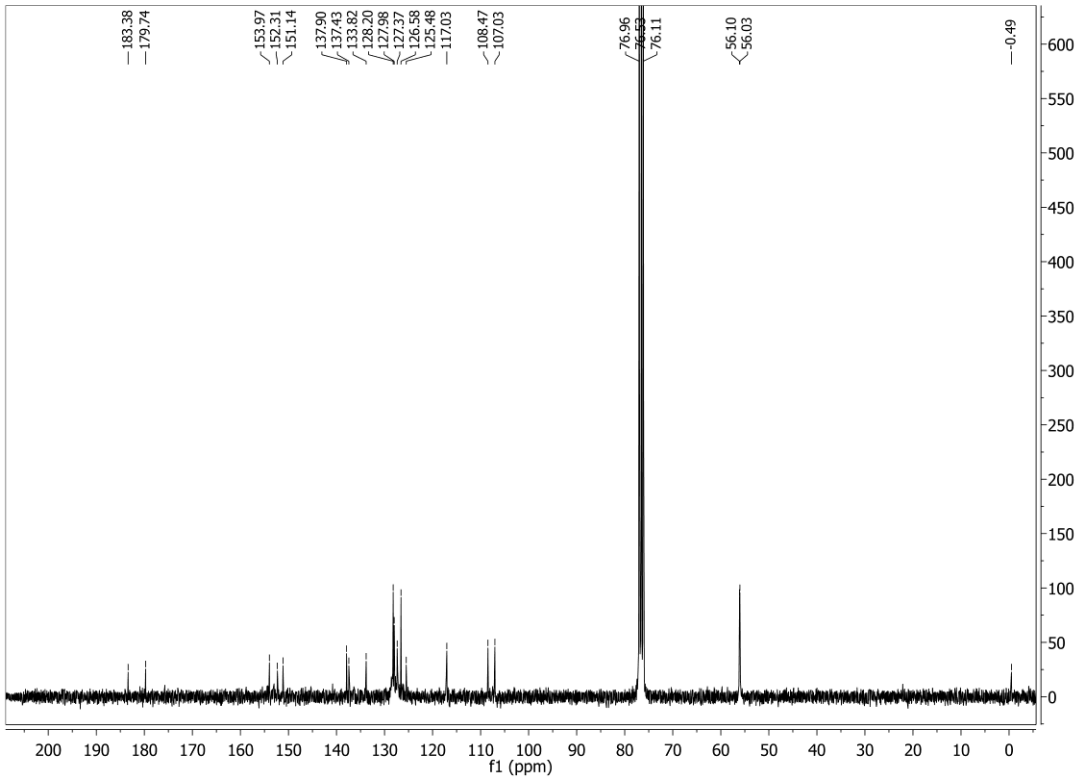
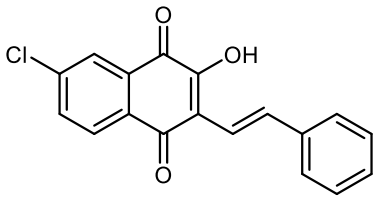


Figure E56 ^{13}C-NMR spectrum of **3ab** in $CDCl_3$

6-chloro-3-hydroxy-2-styrylnaphthalene-1,4-dione (3ac)



3ac

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 84% (78.1 mg)
Physical appearance: red solid

M.p. 208.3-209.2 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.13 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 13.1 Hz, 1H), 7.93 (d, *J* = 20.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.41 (d, *J* = 6.4 Hz, 2H), 7.39-7.28 (m, 2H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 182.71, 179.58, 151.01, 139.65, 139.48, 137.16, 134.81, 134.26, 130.37, 130.25, 128.35, 128.25, 126.75, 125.44, 118.60, 116.66; **HRMS** (ESI^-): calc. for $C_{18}H_{10}ClO_3$ $[M-H]^-$: 309.0324, found: 309.0325 *m/z*.

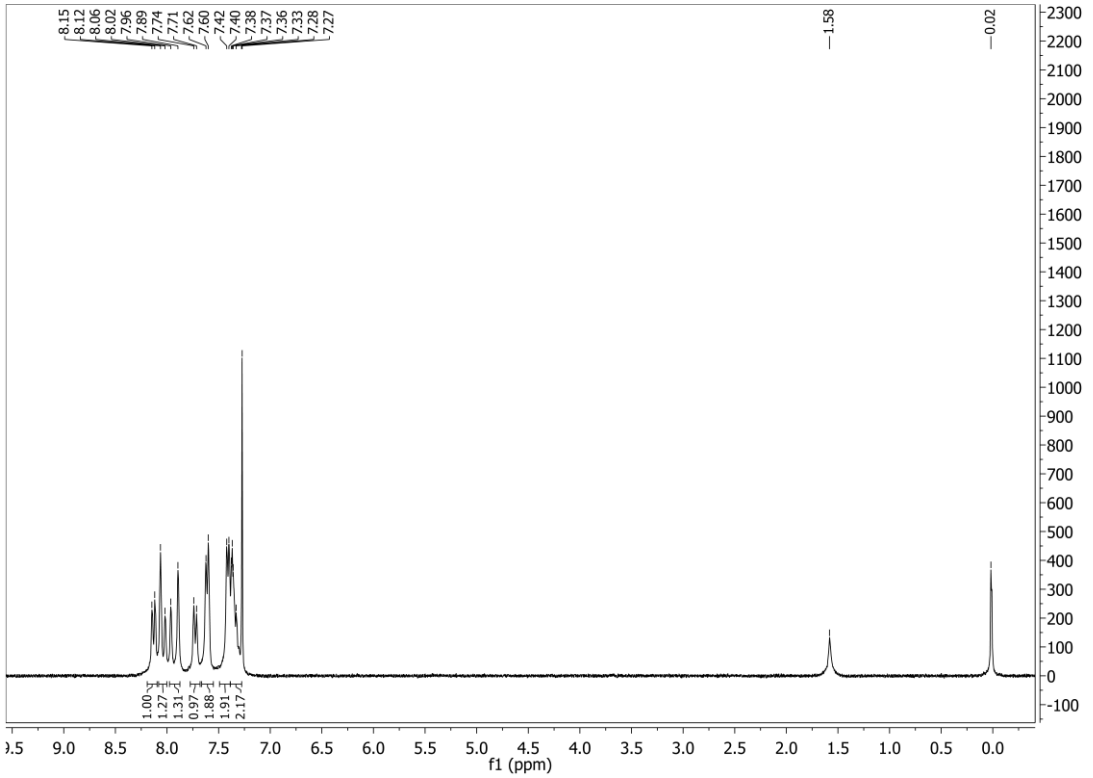


Figure E57 ^{1}H-NMR spectrum of **3ac** in $CDCl_3$

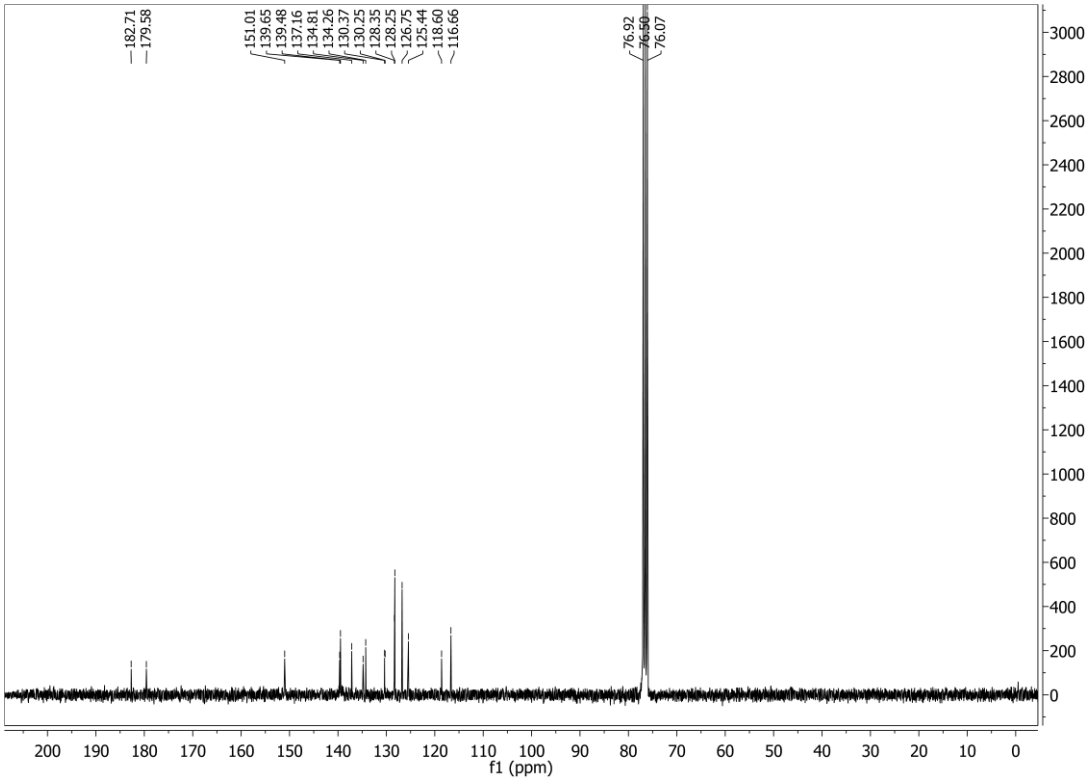
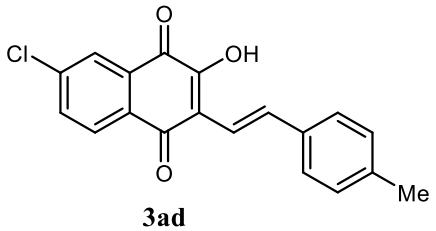


Figure E58 ^{13}C-NMR spectrum of **3ac** in $CDCl_3$

6-chloro-3-hydroxy-2-(4-methylstyryl)naphthalene-1,4-dione (3ad)



3ad

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 85% (82.6 mg)
Physical appearance: red solid

M.p. 232.5-234.8 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.13 (d, *J* = 9.6 Hz, 1H), 8.08-7.85 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 16.9, 2.2 Hz, 1H), 7.21 (d, *J* = 6.6 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 182.52, 179.22, 153.52, 138.65, 137.70, 137.53, 135.29, 133.37, 131.58, 129.85, 128.75, 127.85, 126.32, 124.56, 118.51, 116.55, 19.95; **HRMS** (ESI$^-$): calc. for $C_{19}H_{12}ClO_3$ $[M-H]^-$: 323.0480, found: 323.0475 *m/z*.

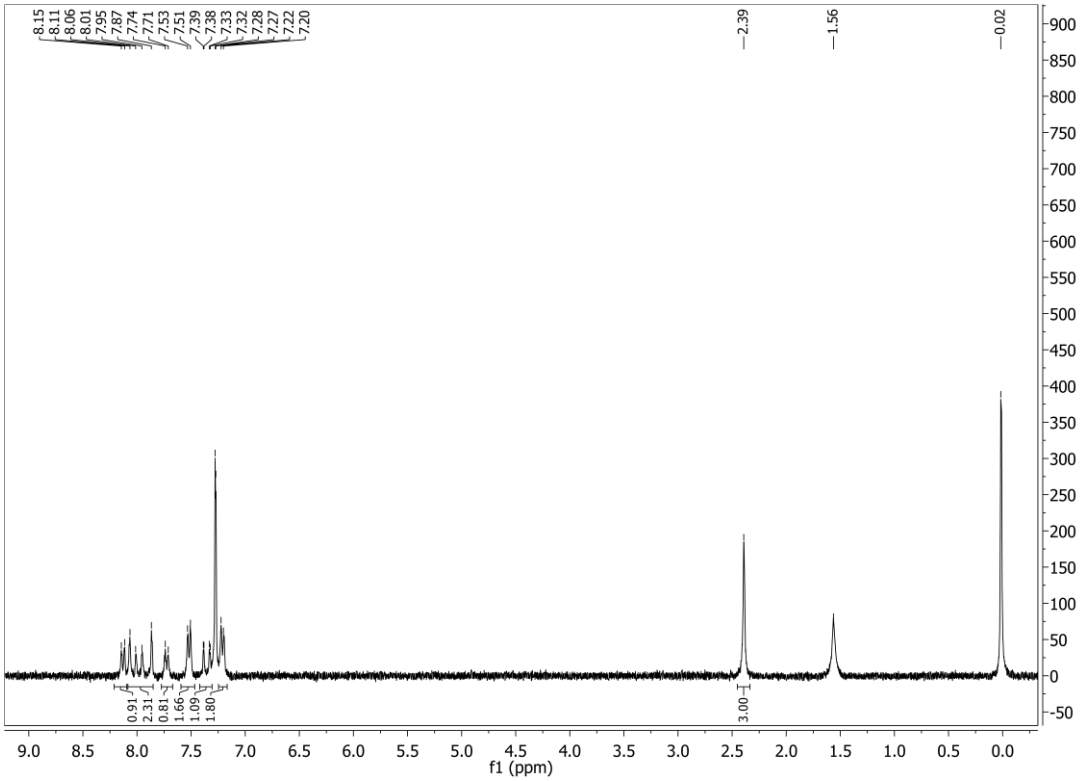


Figure E59 ^{1}H-NMR spectrum of **3ad** in $CDCl_3$

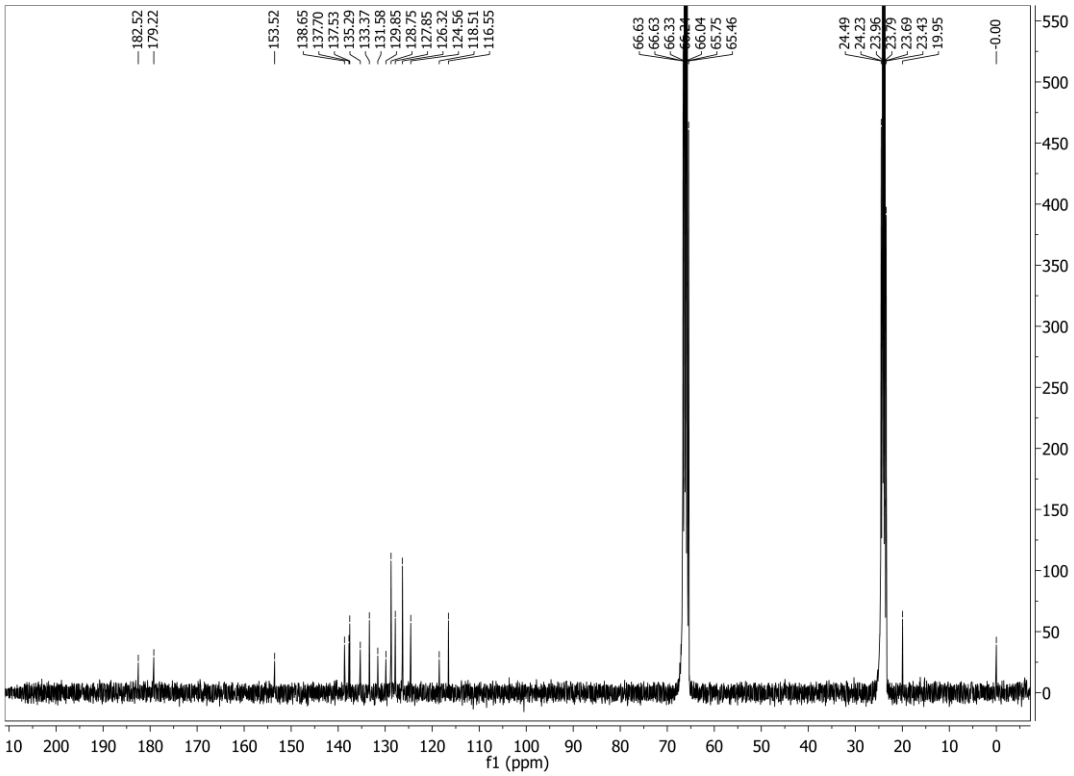
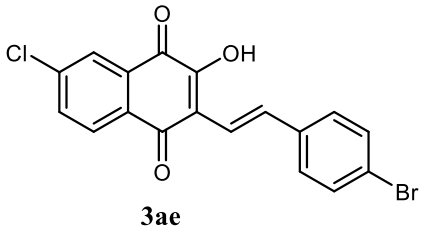


Figure E60 ^{13}C-NMR spectrum of **3ad** in THF

2-(4-bromostyryl)-6-chloro-3-hydroxynaphthalene-1,4-dione (3ae)



3ae

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 82% (95.4 mg)
Physical appearance: red solid

M.p. 238.7-239.2 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.13 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 7.96-7.87 (m, 2H), 7.74 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 16.5 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 182.35, 179.59, 151.43, 139.05, 137.98, 136.26, 134.57, 134.38, 131.43, 129.45, 128.37, 128.13, 125.51, 122.34, 117.31, 115.42; **HRMS** (ESI^-): calc. for $C_{18}H_9BrClO_3$ $[M-H]^-$: 386.9429, found: 386.9425 *m/z*.

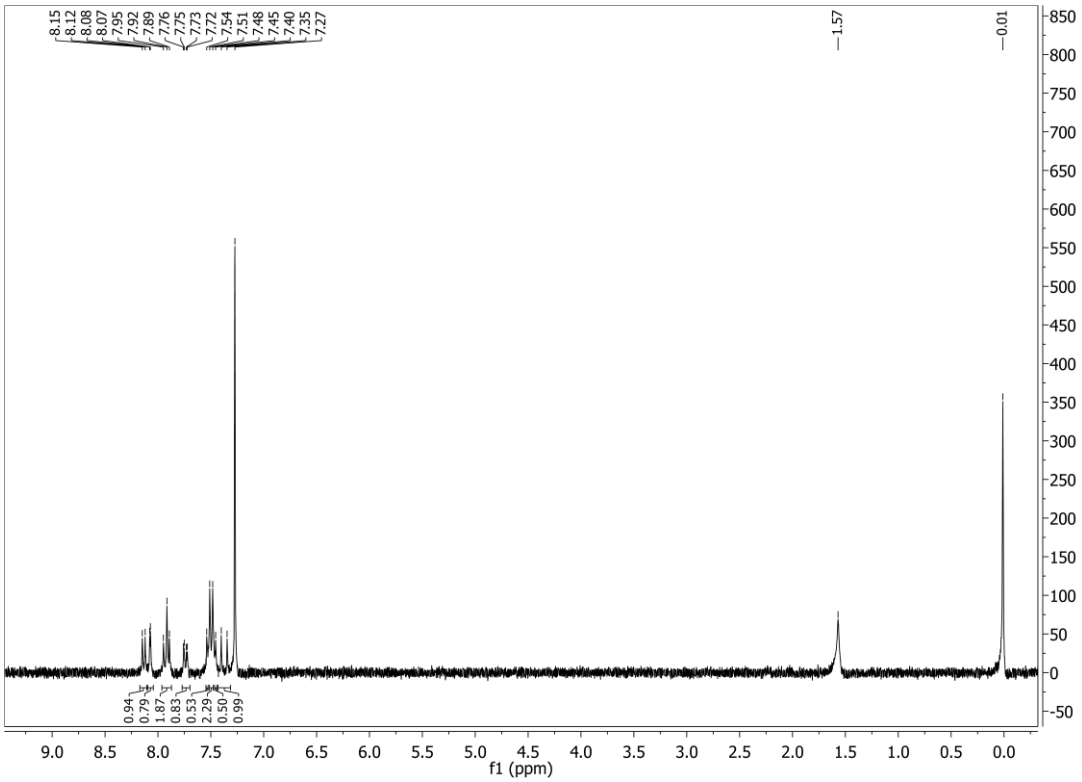


Figure E61 ^{1}H-NMR spectrum of **3ae** in $CDCl_3$

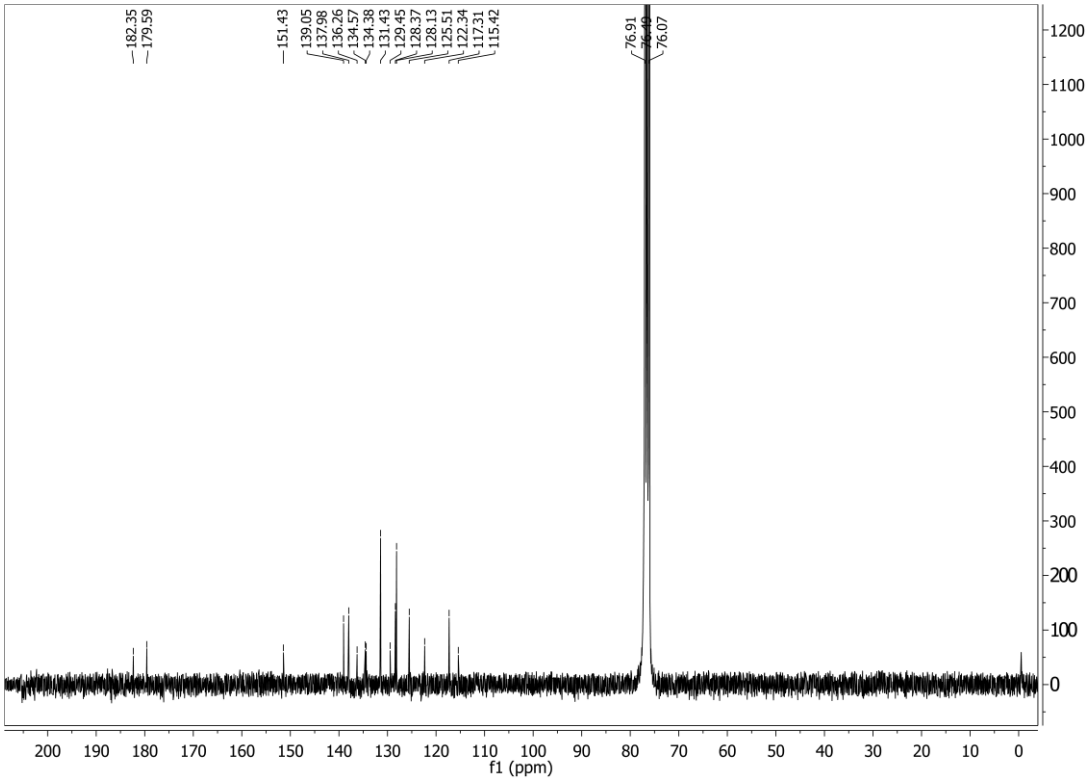
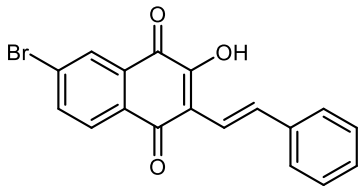


Figure E62 ^{13}C-NMR spectrum of **3ae** in $CDCl_3$

6-bromo-3-hydroxy-2-styrylnaphthalene-1,4-dione (3af)



3af

Purification: flash chromatography on silica gel (CH_2Cl_2 /MeOH : 500/1)
Yield: 83% (87.9 mg)
Physical appearance: red solid

M.p. 214.9-216.1 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 8.23 (s, 1H), 7.94 (dd, *J* = 13.4, 2.2 Hz, 1H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.68 (d, *J* = 121.5 Hz, 1H), 7.61 (d, *J* = 6.2 Hz, 2H), 7.41 (d, *J* = 5.6 Hz, 2H), 7.38-7.31 (m, 2H); **^{13}C NMR** (75 MHz, CDCl3): δ (ppm) 183.77, 180.53, 151.00, 134.75, 134.37, 133.69, 132.65, 132.26, 129.36, 129.13, 126.63, 126.43, 126.27, 125.50, 118.82, 117.22; **HRMS** (ESI^-): calc. for $C_{18}H_{10}BrO_3$ $[M-H]^-$: 352.9819, found: 352.9813 *m/z*.

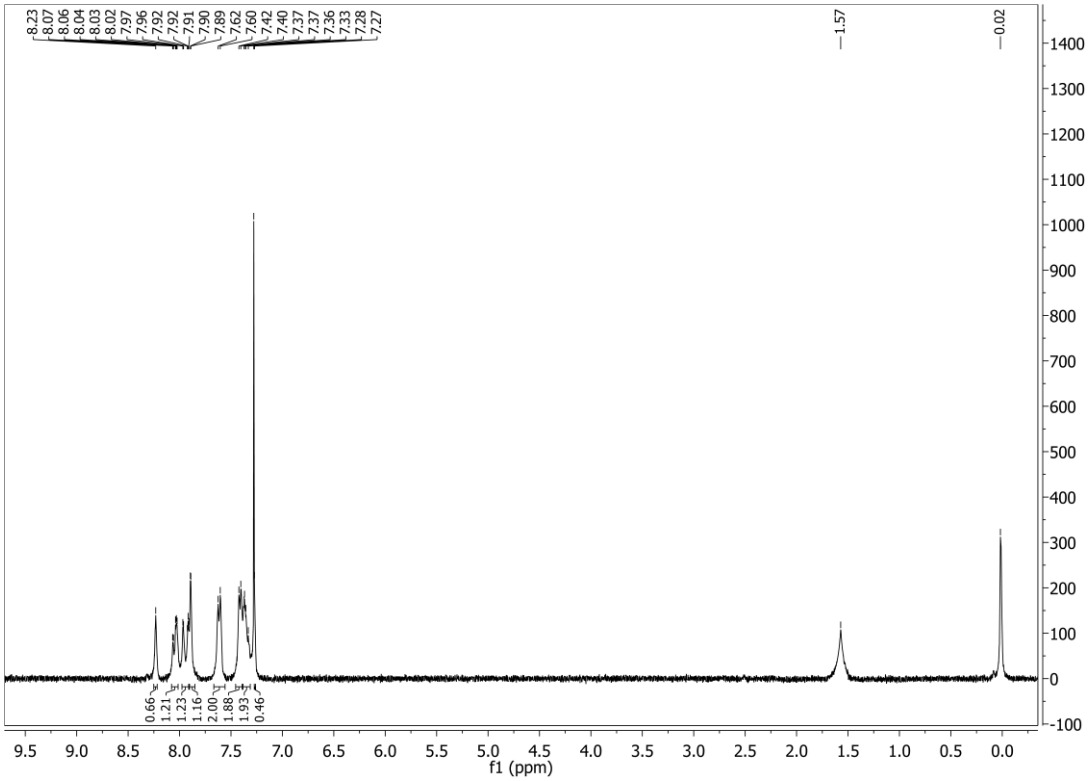


Figure E63 ^{1}H-NMR spectrum of **3af** in $CDCl_3$

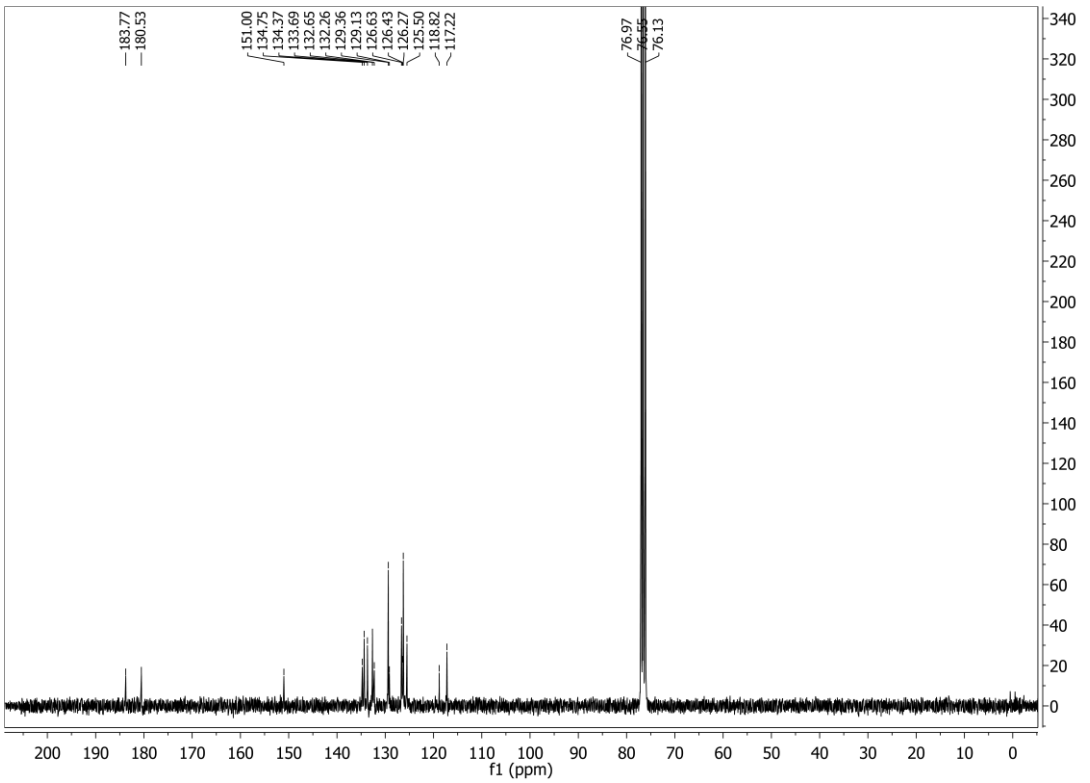


Figure E64 ^{13}C-NMR spectrum of **3af** in $CDCl_3$

7 Reference

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[3] T. Inui, H. Matsuda, Y. takegami, *J.C.S. Chem. Comm.* **1981,** 676, 906-907.