Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information

# A Free Radical Alkylation of Quinones with Olefins

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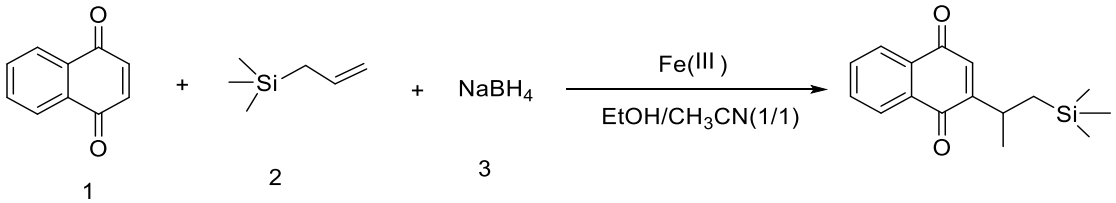
**General Information**

All commercial reagents were used without further purification unless otherwise noted. All kinds of alkene were commercially available or were synthesized by known procedures. All reactions were performed under air unless otherwise noted. $^{1}H$ and $^{13}C$ NMR was recorded on a Bruker 500 MHz, Varian 600 MHz spectrometer. Chemical shifts are reported in ppm from an internal standard of residual $CHCl_3$ (7.26 for 1H and 77 for $^{13}C$) with TMS as internal standard. Proton chemical data are reported as follows: chemical shift (δ), multiplicity (ovlp = overlapping, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. All products were identified by $^{1}H$ and $^{13}C$ NMR, MS, HRMS, and Element Analysis.

**Typical procedure**

Under the room temperature in an open flask, quinones (1equiv, 0.2mmol), alkene (4equiv, 0.8mmol) and $Fe(NO_3)_3 9\ H_2O$ (5equiv, 1mmol) was added to $CH_3CN$ (2 mL) and EtOH (2 mL). The mixture was stirred for 5 minutes to make $Fe(NO_3)_3 9\ H_2O$ dissolved. $NaBH_4$ (4equiv, 0.8mmol) was added to the mixture under the room temperature. The resulting mixture was stirred for 30 min before being quenched by addition of 5% aqueous HCl (5 mL). The mixture was extracted with $CH_2Cl_2$ and the organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure. Flash chromatography ($SiO_2$, PE/EA) provided product.

**The modification of the reaction condition of naphthoquinone with allyltrimethylsilane**




**Examination of 3**

| Entry | 1 (1eq) | 2 (eq) | 3 (eq) | $Fe(NO_3)_3•9H_2O$ (eq) | Solvent (mL) | T (℃) | Yield (%) | RSM (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.2mmol | 5 | 1 | 5 | 4 | RT | 22% | 73% |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2 | 0.2mmol | 5 | 2 | 5 | 4 | RT | 42% | 50% |
| 3 | 0.2mmol | 5 | 3 | 5 | 4 | RT | 45% | 42% |
| 4 | 0.2mmol | 5 | 4 | 5 | 4 | RT | 65% | 15% |
| 5 | 0.2mmol | 5 | 5 | 5 | 4 | RT | 68% | 10% |

**Examination of 2**

| Entry | 1 (1eq) | 2 (eq) | 3 (eq) | $Fe(NO_3)_3•9H_2O$ (eq) | Solvent (mL) | T (℃) | Yield (%) | RSM (%) |
|---|---|---|---|---|---|---|---|---|
| 6 | 0.2mmol | 2 | 4 | 5 | 4 | RT | 37% | 51% |
| 7 | 0.2mmol | 3 | 4 | 5 | 4 | RT | 52% | 32% |
| 8 | 0.2mmol | 4 | 4 | 5 | 4 | RT | 63% | 18% |
| 9 | 0.2mmol | 6 | 4 | 5 | 4 | RT | 62% | 16% |

**Examination of $Fe(NO_3)_3•9H_2O$**

| Entry | 1 (1eq) | 2 (eq) | 3 (eq) | $Fe(NO_3)_3•9H_2O$ (eq) | Solvent (mL) | T (℃) | Yield (%) | RSM (%) |
|---|---|---|---|---|---|---|---|---|
| 10 | 0.2mmol | 4 | 4 | 0 | 4 | rt | 0% | 100% |
| 11 | 0.2mmol | 4 | 4 | 1 | 4 | rt | 16% | 72% |
| 12 | 0.2mmol | 4 | 4 | 2 | 4 | rt | 20% | 60% |
| 13 | 0.2mmol | 4 | 4 | 3 | 4 | rt | 39% | 40% |
| 14 | 0.2mmol | 4 | 4 | 4 | 4 | rt | 53% | 24% |

**Examination of Solvent**

| Entry | 1 (1eq) | 2 (eq) | 3 (eq) | $Fe(NO_3)_3•9H_2O$ (eq) | Solvent (mL) | T (℃) | Yield (%) | RSM (%) |
|---|---|---|---|---|---|---|---|---|
| 15 | 0.2mmol | 4 | 4 | 5 | 4 | RT | 63% | 18% |
| 16 | 0.2mmol | 4 | 4 | 5 | 6 | RT | 48% | 33% |
| 17 | 0.2mmol | 4 | 4 | 5 | 8 | RT | 50% | 31% |
| 18 | 0.2mmol | 4 | 4 | 5 | 10 | RT | 57% | 22% |
| 19 | 0.2mmol | 4 | 4 | 5 | 12 | RT | 60% | 21% |
| 20 | 0.2mmol | 4 | 4 | 5 | 15 | RT | 52% | 23% |
| 21 | 0.2mmol | 4 | 4 | 5 | 20 | RT | 54% | 20% |

**Examination of Oxidant**

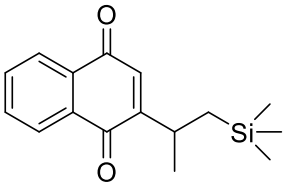
| Entry | 1 (1eq) | 2 (eq) | 3 (eq) | Oxidant (eq) | Solvent (mL) | T (℃) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 22 | 0.2mmol | 4 | 4 | $FeCl_3$(5) | 4 | RT | 10% |
| 23 | 0.2mmol | 4 | 4 | $Fe(acac)_3$(5) | 4 | RT | trance |
| 24 | 0.2mmol | 4 | 4 | $Fe_2(C_2O_4)_3$(5) | 4 | RT | 0 |
| 25 | 0.2mmol | 4 | 4 | $Mn(OAc)_3$(5) | 4 | RT | 43% |
| 26 | 0.2mmol | 4 | 4 | $Cu(OAc)_2$(5) | 4 | RT | 0 |

## Physical data for the following products

All known compounds are determined by $^{1}H$ and $^{13}C$ NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.


(1) E. Giorgini, G. Tommasi, P. Stipa, G. Tosi, G. Littarru and L. Greci, *Free Rad. Res.*, 2000, **35**, 63.
(2) E. R. Baral, S. H. Kim and Y. R. Lee, *Asian J. Org. Chem.*, 2016, **5**, 1134.
(3) Á. Gutiérrez-Bonet, C. Remeur, J. K. Matsui, G. A. Molander, *J. Am. Chem. Soc.*, 2017, **139**, 12251.
(4) D. R. Sutherland, M. Veguillas, C. L. Oates and A.-L. Lee, *Org. Lett.*, 2018, **20**, 6863.


**Compound 1**
**2-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

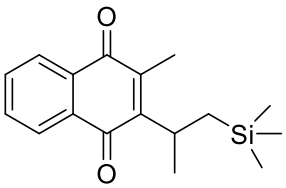



$^{1}H$ NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 1H), 8.08 – 8.04 (m, 1H), 7.76 – 7.70 (m, 2H), 6.79 (s, 1H), 3.31 – 3.23 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.91 (dd, *J* = 14.7, 5.4 Hz, 1H), 0.74 (dd, *J* = 14.5, 9.1 Hz, 1H), 0.04 (s, 9H).

$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 185.93, 185.08, 158.86, 133.85, 133.81, 132.88, 132.74, 132.11, 126.89, 126.14, 28.79, 24.70, 22.85, -0.52.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}O_2Si$ $(M+H)^+$ 273.1305, found 273.1306.

**Compound 2**
**2-methyl-3-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

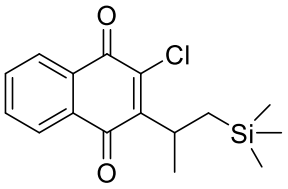



$^{1}H$ NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.71 – 7.64 (m, 2H), 3.25-3.27 (m, 1H), 2.22 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H), 1.17 (dd, *J* = 14.8, 7.1 Hz, 1H), 1.11 (dd, *J* = 14.8, 8.0 Hz, 1H), -0.03 (s, 9H).

$^{13}C$ NMR (126 MHz, $CDCl_3$) δ 185.98, 185.18, 152.56, 142.13, 133.61, 133.30, 133.05, 131.95, 126.38, 126.26, 23.72, 22.18, 12.72, -0.72.

HRMS (ESI, m/z): Calculated for $C_{17}H_{22}O_2Si$ $(M+H)^+$ 287.1462, found 287.1455.

**Compound 3**
**2-chloro-3-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

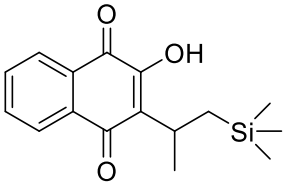



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 7.75-7.72 (m, 2H), 3.63-3.59 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.20 (dd, *J* = 7.0, 4.3 Hz, 1H), 1.14 (dd, *J* = 14.7, 8.1 Hz, 1H), -0.01 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.81, 178.29, 153.04, 142.02, 134.41, 133.90, 132.54, 131.10, 127.19, 127.14, 32.57, 23.14, 21.41, -0.75.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}ClO_2Si$ $(M+H)^+$ 307.0916, found 307.0911.

**Compound 4**
**2-hydroxy-3-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

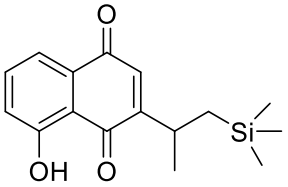



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.75 (dd, *J* = 10.9, 4.3 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.42 (s, 1H), 3.48 – 3.40 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.23 (dd, *J* = 14.7, 8.3 Hz, 1H), 1.00 (dd, *J* = 14.7, 7.1 Hz, 1H), -0.04 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 184.64, 182.03, 152.58, 135.16, 133.36, 132.97, 129.90, 129.34, 127.11, 126.17, 26.22, 22.77, 21.87, -0.78.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}ClO_2Si$ $(M+H)^+$ 289.1254, found 289.1254.

**Compound 5a**
**8-hydroxy-2-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

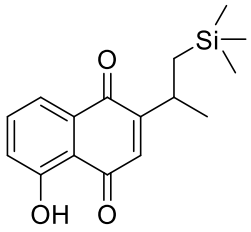



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 11.99 (s, 1H), 7.64 – 7.58 (m, 2H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.74 (s, 1H), 3.29 – 3.21 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.89 (dd, *J* = 14.5, 5.2 Hz, 1H), 0.72 (dd, *J* = 14.5, 9.3 Hz, 1H), 0.04 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 191.13, 184.30, 161.25, 160.34, 136.33, 132.68, 124.22, 119.56, 115.04, 28.90, 24.69, 22.72, -0.52.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}O_3Si$ $(M+H)^+$ 289.1254, found 289.1254.

**Compound 5b**
**5-hydroxy-2-(1-(trimethylsilyl)propan-2-yl)naphthalene-1,4-dione**

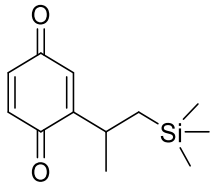



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 12.19 (s, 1H), 7.61-7.58 (m, 2H), 7.25 (d, *J* = 2.3 Hz, 1H), 6.76 (s, 1H), 3.26 (dd, *J* = 14.5, 6.8 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.91 (dd, *J* = 14.5, 5.2 Hz, 1H), 0.73 (dd, *J* = 14.5, 9.3 Hz, 1H), 0.05 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 190.52, 185.12, 161.87, 158.78, 136.52, 133.68, 132.18, 124.44, 118.78, 115.58, 28.25, 24.75, 22.72, -0.53.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}O_3Si$ $(M+H)^+$ 289.1254, found 289.1253.

**Compound 6**
**2-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

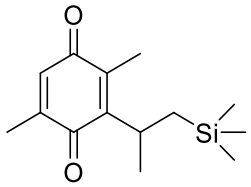



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.71 (dt, *J* = 10.1, 6.2 Hz, 2H), 6.55 (s, 1H), 3.10 – 2.99 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.82 (dd, *J* = 14.5, 5.4 Hz, 1H), 0.67 (dd, *J* = 14.5, 9.1 Hz, 1H), 0.02 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.51, 187.41, 156.51, 137.25, 136.10, 130.59, 28.57, 24.44, 22.68, -0.57.

HRMS (ESI, m/z): Calculated for $C_{12}H_{18}O_2Si$ $(M+H)^+$ 223.1149, found 223.1150.

**Compound 7**
**2,5-dimethyl-3-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

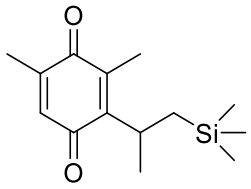



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.52 (d, *J* = 1.4 Hz, 1H), 3.08-3.12 (m, 1H), 2.04 (s, 3H), 2.00 (d, 3H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.09 (dd, *J* = 14.7, 7.4 Hz, 1H), 0.99 (dd, *J* = 14.8, 7.8 Hz, 1H), -0.05 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.36, 188.20, 150.03, 146.30, 139.43, 132.66, 23.63, 22.29, 16.08, 11.88, -0.80.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}O_2Si$ $(M+H)^+$ 251.1462, found 251.1462.

**Compound 8**
**3,5-dimethyl-2-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

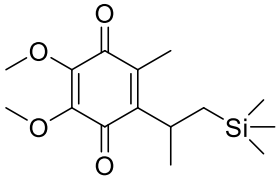


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.45 (s, 1H), 3.07-3.11 (m, 1H), 2.06 (s, 3H), 2.00 (s, 3H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.08 (dd, *J* = 14.8, 7.5 Hz, 1H), 0.98 (dd, *J* = 14.8, 7.7 Hz, 1H), -0.05 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.87, 187.89, 149.69, 144.62, 139.59, 134.28, 23.71, 22.32, 15.89, 12.27, -0.79.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}O_2Si$ $(M+H)^+$ 251.1462, found 251.1462.

**Compound 9**
**2,3-dimethoxy-5-methyl-6-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

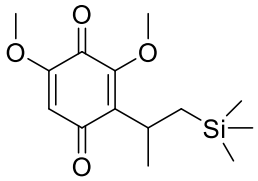


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 3H), 3.97 (s, 3H), 3.08-3.12 (m, 1H), 2.04 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.08 (dd, *J* = 14.8, 7.5 Hz, 1H), 0.99 (dd, *J* = 14.8, 7.8 Hz, 1H), -0.03 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.14, 184.35, 147.90, 144.59, 143.81, 137.72, 61.30, 61.26, 30.28, 23.64, 22.31, 12.01, -0.84.

HRMS (ESI, m/z): Calculated for $C_{15}H_{24}O_4Si$ $(M+H)^+$ 297.1517, found 297.1515.

**Compound 10**
**3,5-dimethoxy-2-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

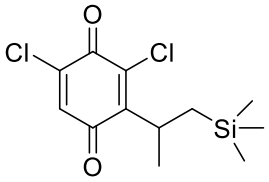


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.79 (s, 1H), 3.95 (s, 3H), 3.78 (s, 3H), 3.32 – 3.23 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.05 (dd, *J* = 14.7, 8.0 Hz, 1H), 0.90 (dd, *J* = 14.7, 7.3 Hz, 1H), -0.04 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 187.55, 178.91, 157.08, 154.43, 139.43, 107.66, 61.07, 56.53, 26.20, 23.65, 22.54, -0.78.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}O_4Si$ $(M+H)^+$ 283.1360, found 283.1357.

**Compound 11**
**3,5-dichloro-2-(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

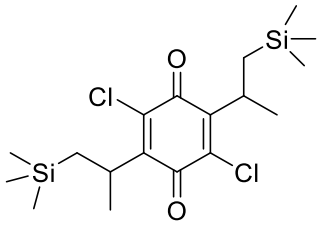



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 3.43 (dt, *J* = 14.5, 7.1 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.11 – 1.02 (m, 2H), -0.01 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 182.90, 173.38, 151.09, 142.58, 139.09, 134.66, 29.92, 23.07, 21.23, -0.79.

HRMS (ESI, m/z): Calculated for $C_{12}H_{16}Cl_2O_2Si$ $(M+H)^+$ 291.0369, found 291.0362.

**Compound 12**
**2,5-dichloro-3,6-bis(1-(trimethylsilyl)propan-2-yl)cyclohexa-2,5-diene-1,4-dione**

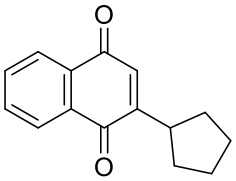



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 3.49 – 3.39 (m, 2H), 1.32 (dd, *J* = 7.0, 1.4 Hz, 6H), 1.12 – 1.01 (m, 4H), -0.02 (d, *J* = 2.3 Hz, 18H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 177.76, 149.65, 149.59, 140.02, 139.95, 23.07, 21.40, 21.23, -0.81.

HRMS (ESI, m/z): Calculated for $C_{18}H_{30}Cl_2O_2Si_2$ $(M+H)^+$ 405.1234, found 405.1230.

**Compound 13**
**2-cyclopentylnaphthalene-1,4-dione**

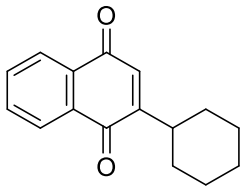



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 1H), 8.04-8.11 (m, *J* = 5.7, 3.2 Hz, 1H), 7.74 – 7.70 (m, 2H), 6.79 (s, 1H), 3.30 – 3.21 (m, 1H), 2.05 (m, 2H), 1.81 – 1.69 (m, 4H), 1.54 – 1.47 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.79, 185.51, 155.77, 133.79, 133.78, 132.73, 132.60, 132.17, 126.85, 126.13, 39.28, 32.45, 25.50.

HRMS (ESI, m/z): Calculated for $C_{15}H_{14}O_2$ $(M+H)^+$ 227.1067, found 227.1064.

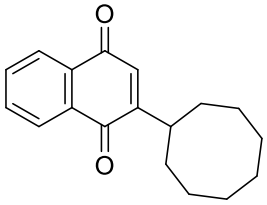
**Compound 14**
**2-cyclohexylnaphthalene-1,4-dione**



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 8.07 – 8.02 (m, 1H), 7.75 – 7.68 (m, 2H), 6.73 (s, 1H), 2.90 (t, *J* = 11.9 Hz, 1H), 1.84 (d, *J* = 10.8 Hz, 4H), 1.77 (d, *J* = 13.2 Hz, 1H), 1.51 – 1.39 (m, 2H), 1.27 – 1.18 (m, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.81, 184.99, 156.49, 133.78, 133.76, 133.25, 132.71, 132.11, 126.89, 126.11, 36.90, 32.45, 26.60, 26.25.

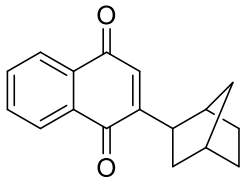
**Compound 15**
**2-cyclooctylnaphthalene-1,4-dione**



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 8.09 – 8.04 (m, 1H), 7.77 – 7.72 (m, 2H), 6.77 (s, 1H), 3.19-3.20 (m, 1H), 1.79 – 1.74 (m, 4H), 1.68 – 1.58 (m, 10H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.68, 184.90, 158.01, 133.59, 133.55, 133.06, 132.50, 131.88, 126.68, 125.89, 36.06, 31.90, 26.60, 26.35, 25.63.

**Compound 16**
**2-(bicyclo[2.2.1]heptan-2-yl)naphthalene-1,4-dione**

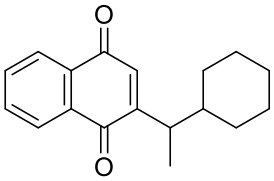


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 1H), 8.05-8.02 (m, 1H), 7.72 – 7.69 (m, 2H), 6.71 (s, 1H), 2.92 (dd, *J* = 8.2, 6.8 Hz, 1H), 2.34 (s, 1H), 2.28 (d, *J* = 3.4 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.66 – 1.54 (m, 2H), 1.46 – 1.39 (m, 2H), 1.37 – 1.29 (m, 2H), 1.22 (d, *J* = 9.9 Hz, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.78, 185.60, 155.67, 133.76, 132.67, 132.07, 132.03, 126.77, 126.10, 40.92, 40.86, 37.71, 37.05, 36.23, 30.29, 28.85.

HRMS (ESI, m/z): Calculated for $C_{17}H_{16}O_2$ $(M+H)^+$ 253.1223, found 253.1219

**Compound 17**
**2-(1-cyclohexylethyl)naphthalene-1,4-dione**

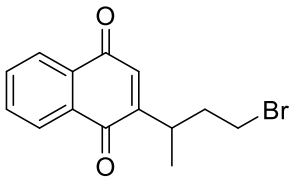


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 8.07-8.09 (m, 1H), 7.78 – 7.70 (m, 2H), 6.75 (s, 1H), 2.99-3.05 (m, 1H), 1.85 – 1.73 (m, 2H), 1.59-1.70 (m, 4H), 1.53 – 1.42 (m, 1H), 1.29 – 1.18 (m, 2H), 1.16 (d, *J* = 7.1 Hz, 3H), 1.08 – 0.92 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.38, 184.92, 156.16, 134.16, 133.58, 133.56, 132.42, 131.89, 126.81, 125.89, 42.53, 37.37, 31.73, 29.52, 26.48, 26.37, 16.22.

HRMS (ESI, m/z): Calculated for $C_{18}H_{20}O_2$ $(M+H)^+$ 269.1536, found 269.1536.

**Compound 18**
**2-(4-bromobutan-2-yl)naphthalene-1,4-dione**

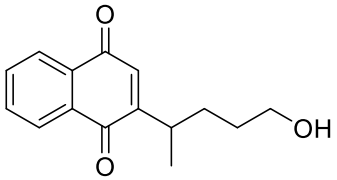


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 1H), 8.08 – 8.04 (m, 1H), 7.79 – 7.70 (m, 2H), 6.78 (s, 1H), 3.40 (t, *J* = 7.1 Hz, 2H), 3.37 – 3.28 (m, 1H), 2.21 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.04 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.24 (d, *J* = 7.0 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.37 , 184.78 , 154.78 , 134.23 , 134.01, 134.00, 132.56 , 132.00 , 127.00 , 126.23 , 38.65 , 31.98 , 30.92 , 19.33 .

HRMS (ESI, m/z): Calculated for $C_{14}H_{13}BrO_2$ $(M+H)^+$ 293.0172, found 293.0169.

**Compound 19**
**2-(5-hydroxypentan-2-yl)naphthalene-1,4-dione**

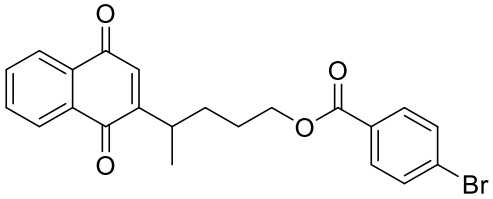


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 1H), 8.08 – 8.03 (m, 1H), 7.77 – 7.70 (m, 2H), 6.77 (s, 1H), 3.67 (t, *J* = 3.7 Hz, 2H), 3.13-3.18 (m, 1H), 1.74 – 1.60 (m, 4H), 1.21 (d, *J* = 6.9 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.63 , 185.20 , 156.37 , 133.93, 133.92, 133.68 , 132.61 , 132.09 , 126.98 , 126.20 , 62.77 , 32.41 , 31.76 , 30.53 , 19.58 .

HRMS (ESI, m/z): Calculated for $C_{15}H_{16}O_3$ $(M+H)^+$ 245.1172, found 245.1171.

## Compound 20
## 4-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)pentyl 4-bromobenzoate

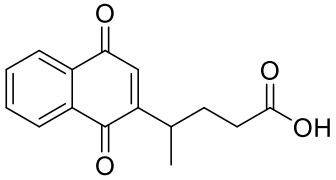



$^1$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 8.10-8.06 (m, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.78 – 7.72 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 1H), 4.33 (t, *J* = 5.9 Hz, 2H), 3.23 (dd, *J* = 13.5, 6.8 Hz, 1H), 1.90 – 1.73 (m, 3H), 1.70 – 1.60 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.51, 184.92, 166.00, 155.95, 133.91, 133.75, 132.55, 132.03, 131.88, 131.28, 129.33, 128.20, 126.94, 126.17, 65.16, 32.49, 31.93, 26.78, 19.75.

HRMS (ESI, m/z): Calculated for $C_{22}H_{19}BrO_4$ $(M+H)^+$ 427.0539, found 427.0535.

## Compound 21
## 4-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)pentanoic acid

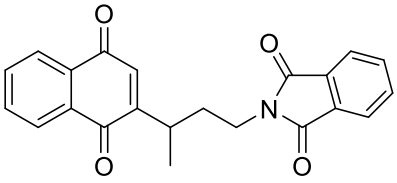



$^1$H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 8.10 – 8.05 (m, 1H), 7.80 – 7.72 (m, 2H), 6.80 (s, 1H), 3.21 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.39 (dt, *J* = 8.6, 6.7 Hz, 2H), 2.01 – 1.83 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.45, 184.85, 179.13, 155.33, 133.98, 133.95, 133.91, 132.54, 132.00, 127.00, 126.20, 31.98, 31.76, 30.55, 19.58.

HRMS (ESI, m/z): Calculated for $C_{15}H_{14}O_4$ $(M+H)^+$ 259.0965, found 259.0963.

## Compound 22
## 2-(3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)butyl)isoindoline-1,3-dione



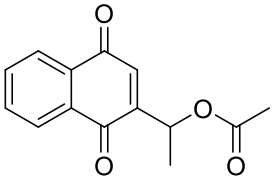
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 1H), 8.03 – 7.98 (m, 1H), 7.81 – 7.75 (m, 2H), 7.72 – 7.65 (m, 4H), 6.79 (s, 1H), 3.73 (dd, *J* = 10.7, 4.9 Hz, 2H), 3.16 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.04 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.87 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.34, 184.68, 168.42, 155.12, 134.12, 133.84, 133.81, 133.70, 132.53, 132.19, 131.97, 126.93, 126.11, 123.42, 36.15, 34.01, 30.19, 19.92.

HRMS (ESI, m/z): Calculated for $C_{22}H_{17}NO_4$ $(M+H)^+$ 360.1230, found 360.1226.

## Compound 23
## 1-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)ethyl acetate

.

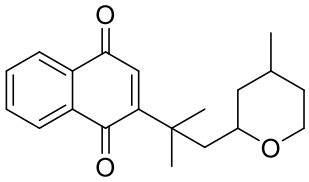


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 1H), 8.07 – 8.03 (m, 1H), 7.79 – 7.70 (m, 2H), 6.89 (s, 1H), 6.00 (q, *J* = 6.6 Hz, 1H), 2.14 (s, 3H), 1.51 (d, *J* = 6.6 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.17, 183.88, 169.81, 150.78, 134.19, 134.14, 132.73, 132.25, 132.01, 126.80, 126.37, 66.52, 21.26, 20.83.

HRMS (ESI, m/z): Calculated for $C_{14}H_{12}O_4$ $(M+H)^+$ 245.0808, found 245.0807.

## Compound 24
## 2-(2-methyl-1-(4-methyltetrahydro-2*H*-pyran-2-yl)propan-2-yl)naphthalene-1,4-dione

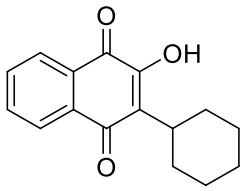


$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.02 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.69 (m, 2H), 6.74 (s, 1H), 3.32 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.03 (dd, *J* = 10.9, 9.8 Hz, 1H), 2.91 (td, *J* = 12.3, 2.2 Hz, 1H), 2.29 (dd, *J* = 14.4, 9.6 Hz, 1H), 1.64 (dd, *J* = 14.4, 1.1 Hz, 1H), 1.44 (s, 3H), 1.41 – 1.37 (m, 1H), 1.30 (s, 4H), 1.01 (dd, *J* = 12.5, 4.5 Hz, 1H), 0.92 (d, *J* = 12.6 Hz, 1H), 0.90 – 0.85 (m, 1H), 0.83 (d, *J* = 6.5 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 186.21, 185.21, 158.60, 134.11, 133.74, 133.05, 133.03, 131.66, 127.02, 125.63, 75.59, 67.45, 47.77, 41.40, 38.30, 34.19, 30.55, 29.28, 28.42, 22.44.

HRMS (ESI, m/z): Calculated for $C_{20}H_{24}O_3$ $(M+H)^+$ 313.1798, found 313.1795.

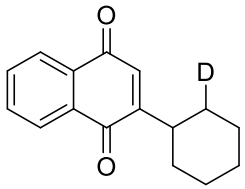
## Compound 25
## 2-cyclohexyl-3-hydroxynaphthalene-1,4-dione




$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.74 (td, *J* = 7.6, 1.3 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.45 (s, 1H), 3.07 (tt, *J* = 12.3, 3.4 Hz, 1H), 2.01-1.93 (m, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.69 (m, 1H), 1.64 – 1.56 (m, 2H), 1.43 – 1.27 (m, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 184.78, 182.14, 153.03, 135.10, 133.33, 132.92, 129.38, 128.07, 127.12, 126.11, 35.32, 29.40, 26.94, 26.16.

## Compound 26
## 2-(cyclohexyl-2-*d*)naphthalene-1,4-dione

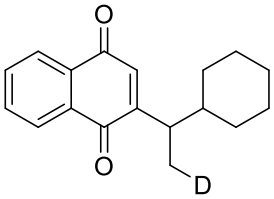



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 1H), 8.06 – 8.01 (m, 1H), 7.74 – 7.69 (m, 2H), 6.72 (s, 1H), 2.94 – 2.84 (m, 1H), 1.80 (dd, *J* = 34.5, 13.7 Hz, 5H), 1.48 – 1.39 (m, 2H), 1.25 – 1.19 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.79, 184.97, 156.48, 133.77, 133.74, 133.23, 132.70, 132.10, 126.88, 126.09, 36.81, 32.43, 32.37, 26.48(m).

HRMS (ESI, m/z): Calculated for $C_{16}H_{15}DO_2$ $(M+H)^+$ 242.1286, found 242.1284.

## Compound 27
## 2-(1-cyclohexylethyl-2-*d*)naphthalene-1,4-dione

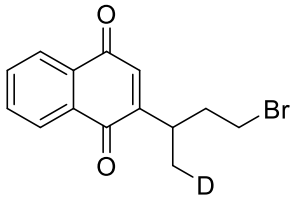



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.14 – 7.99 (m, 2H), 7.79 – 7.65 (m, 2H), 6.71 (s, 1H), 2.97 (q, *J* = 7.0 Hz, 1H), 1.74 (dd, *J* = 26.4, 13.1 Hz, 2H), 1.68 – 1.54 (m, 3H), 1.49 – 1.39 (m, 1H), 1.28 – 1.12 (m, 3H), 1.11 (d, *J* = 7.7 Hz, 2H), 1.02-0.89 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.51, 185.06, 156.29, 134.31, 133.74, 133.73, 132.57, 132.05, 126.97, 126.04, 42.65, 37.45, 31.88, 29.66, 26.64, 26.52, 16.07(m).

HRMS (ESI, m/z): Calculated for $C_{16}H_{15}DO_2$ $(M+H)^+$ 270.1599, found 270.1592.

**Compound 28**
**2-(4-bromobutan-2-yl-1-*d*)naphthalene-1,4-dione**

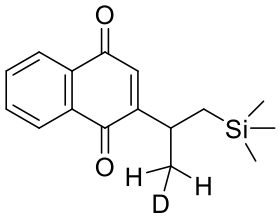



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 1H), 8.07 – 8.02 (m, 1H), 7.76 – 7.70 (m, 2H), 6.77 (s, 1H), 3.40 (t, *J* = 7.1 Hz, 2H), 3.31 (p, *J* = 6.9 Hz, 1H), 2.20 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.04 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.34, 184.76, 154.75, 134.20, 133.99, 133.97, 132.54, 131.98, 126.98, 126.20, 38.61, 31.90, 30.92, 19.03(m).

HRMS (ESI, m/z): Calculated for $C_{14}H_{12}DBrO_2$ $(M+H)^+$ 294.0234, found 294.0233.

**Compound 29**
**2-(1-(trimethylsilyl)propan-2-yl-3-*d*)naphthalene-1,4-dione**

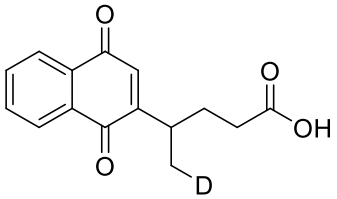



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.75 – 7.69 (m, 2H), 6.78 (s, 1H), 3.24-3.27 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 2H), 0.91 (dd, *J* = 14.5, 5.4 Hz, 1H), 0.73 (dd, *J* = 14.5, 9.2 Hz, 1H), 0.04 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.90, 185.06, 158.83, 133.83, 133.79, 132.86, 132.73, 132.10, 126.87, 126.12, 28.71, 24.66, 22.54 (m), -0.53.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}DO_2Si$ $(M+H)^+$ 274.1368, found 274.1368.

**Compound 30**
**4-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)pentanoic-5-*d* acid**

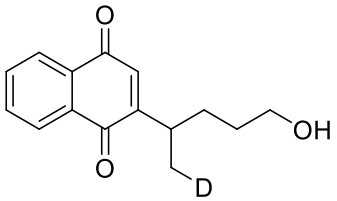



$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.76 – 7.68 (m, 2H), 6.76 (s, 1H), 3.26 – 3.09 (m, 1H), 2.43 – 2.31 (m, 2H), 1.97 – 1.80 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.43, 184.81, 179.39, 155.29, 133.95, 133.91, 133.87, 132.49, 131.95, 126.97, 126.17, 31.99, 31.66, 30.47, 19.26(m).

HRMS (ESI, m/z): Calculated for $C_{15}H_{13}DO_4$ $(M+H)^+$ 260.1028, found 260.1028.

## Compound 31
## 2-(5-hydroxypentan-2-yl-1-*d*)naphthalene-1,4-dione

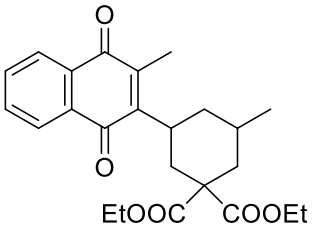



$^1$H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.70 (dd, *J* = 5.2, 3.7 Hz, 2H), 6.74 (s, 1H), 3.64 (t, *J* = 5.5 Hz, 2H), 3.17 – 3.07 (m, 1H), 1.70 – 1.59 (m, 2H), 1.58 – 1.48 (m, 2H), 1.16 (d, *J* = 6.8 Hz, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.57, 185.11, 156.34, 133.86, 133.60, 132.53, 131.99, 126.89, 126.11, 62.63, 32.31, 31.66, 30.47, 19.25(m).

HRMS (ESI, m/z): Calculated for $C_{15}H_{15}DO_3$ $(M+H)^+$ 246.1235, found 246.1233.

## Compound 32
## diethyl 3-methyl-5-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)cyclohexane-1,1-dicarboxylate




$^1$H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.68 (dd, *J* = 5.7, 3.3 Hz, 2H), 4.17 (q, *J* = 6.2 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.73 – 2.66 (m, 1H), 2.62 – 2.54 (m, 1H), 2.36 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.27 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.21 (d, *J* = 5.5 Hz, 2H), 2.19 (s, 3H), 2.10 (dd, *J* = 13.7, 4.8 Hz, 1H), 2.00 (dd, *J* = 18.1, 6.2 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H).

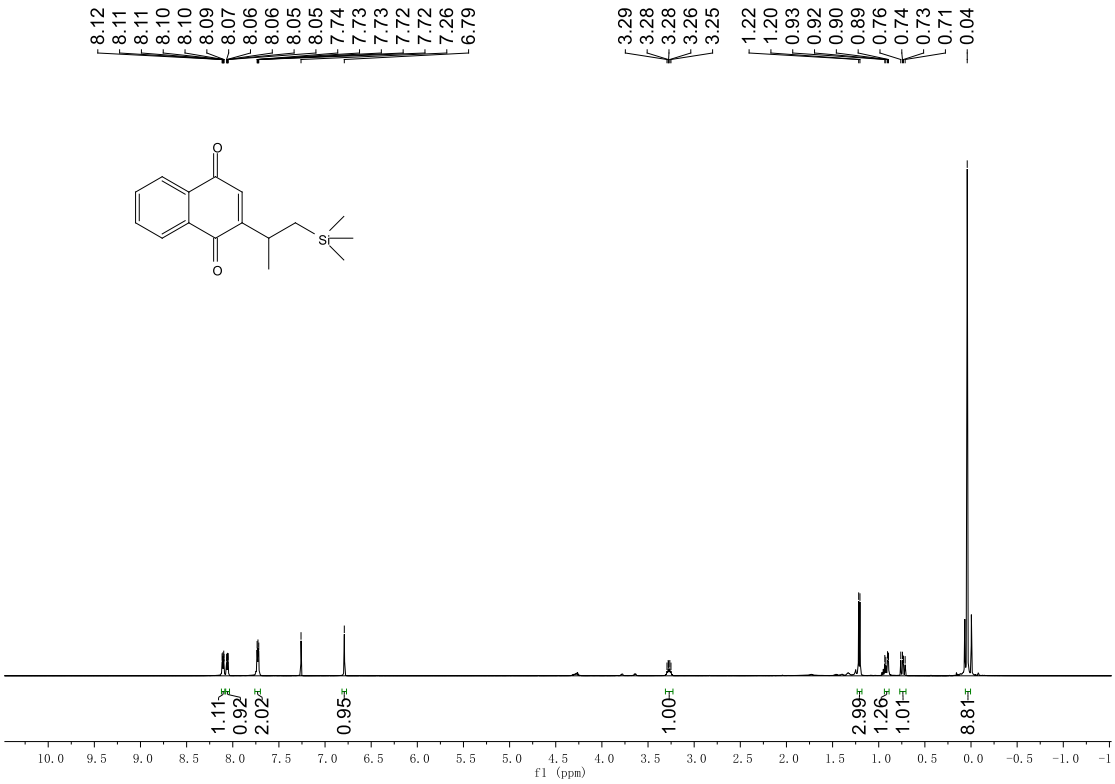
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 185.36, 184.87, 172.94, 172.78, 146.79, 144.07, 133.55, 133.53, 132.30, 132.27, 126.53, 126.37, 61.63, 61.57, 59.03, 42.60, 41.31, 37.66, 37.12, 27.46, 15.33, 14.21, 14.14, 13.37.

HRMS (ESI, m/z): Calculated for $C_{24}H_{28}O_6$ $(M+H)^+$ 413.1959, found 413.1959.

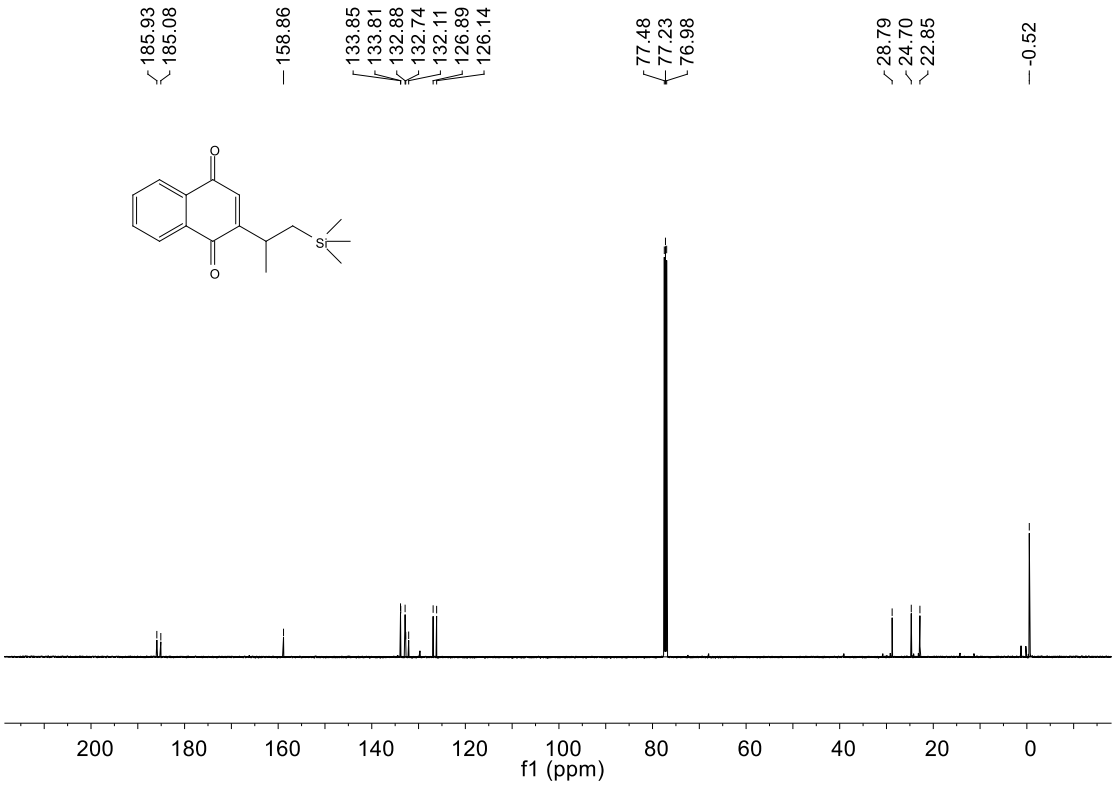
## Copies of the $^{1}$H NMR, $^{13}$C NMR

### Compound 1

$^{1}$H NMR

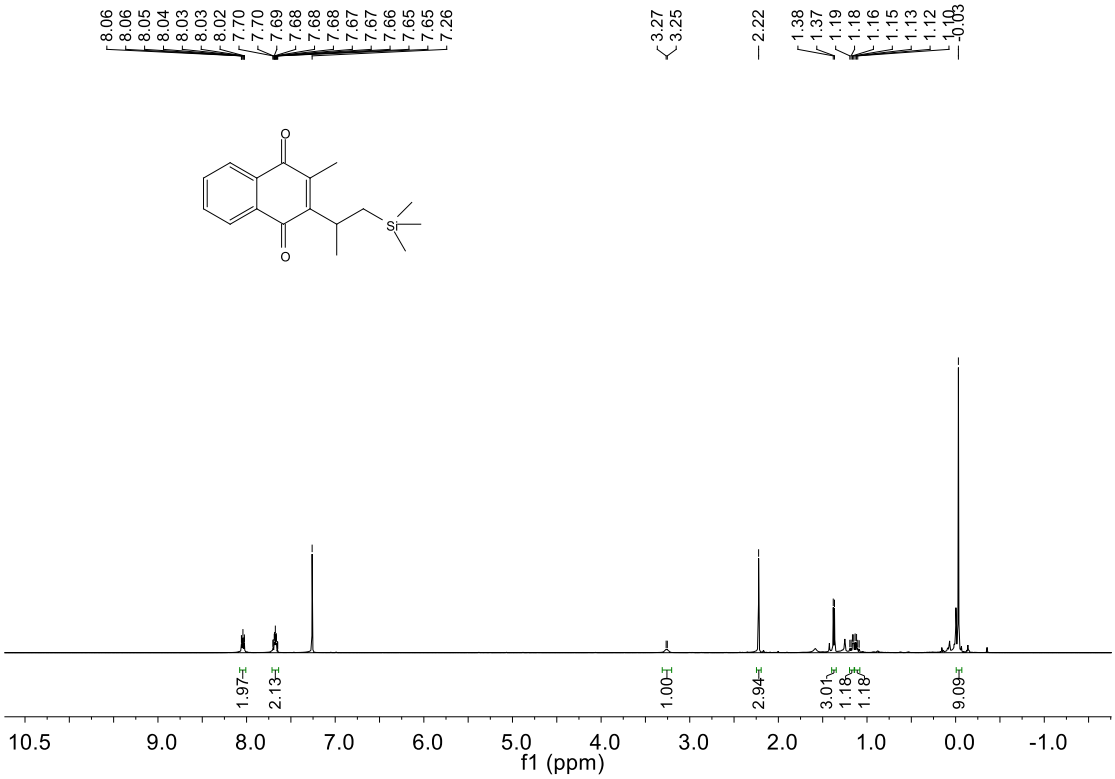



$^{13}$C NMR

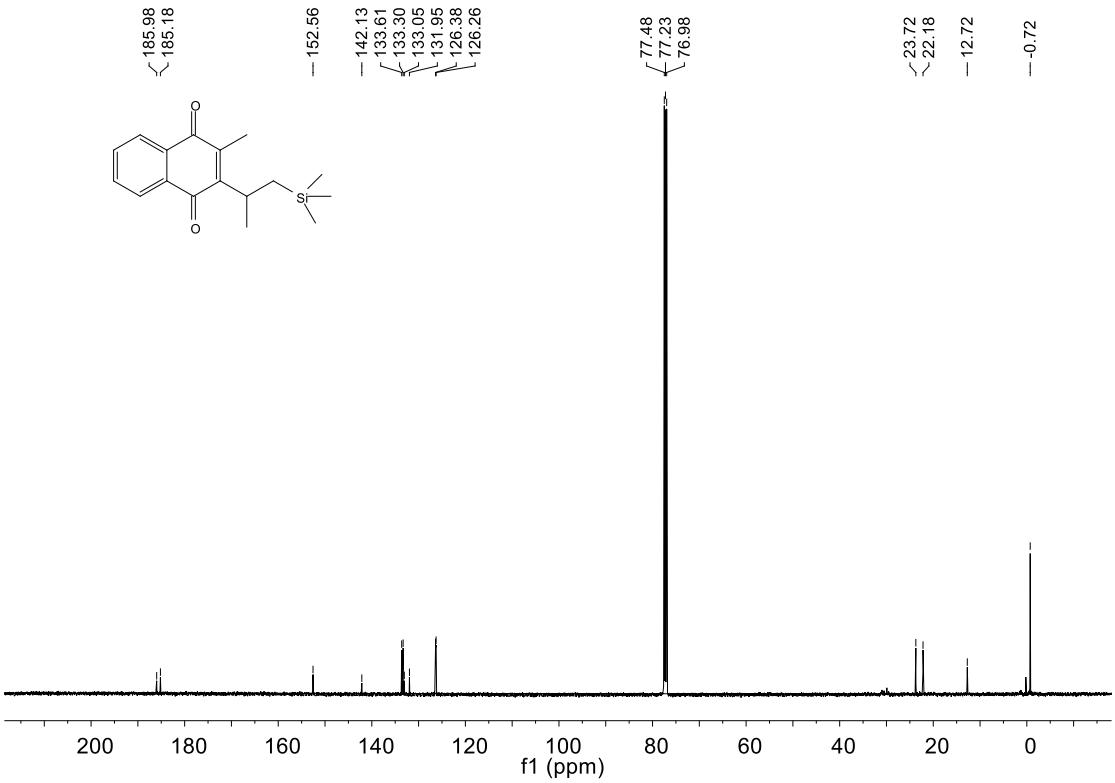


**Compound 2**

$^{1}$H NMR

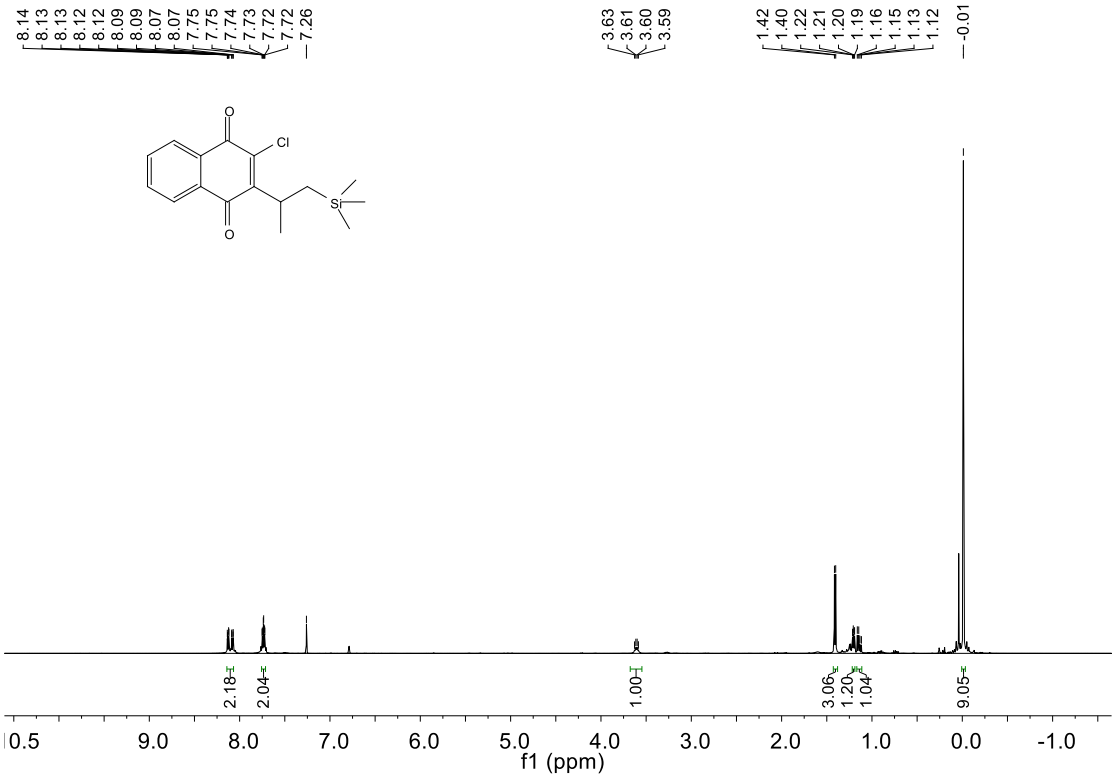



$^{13}$C NMR

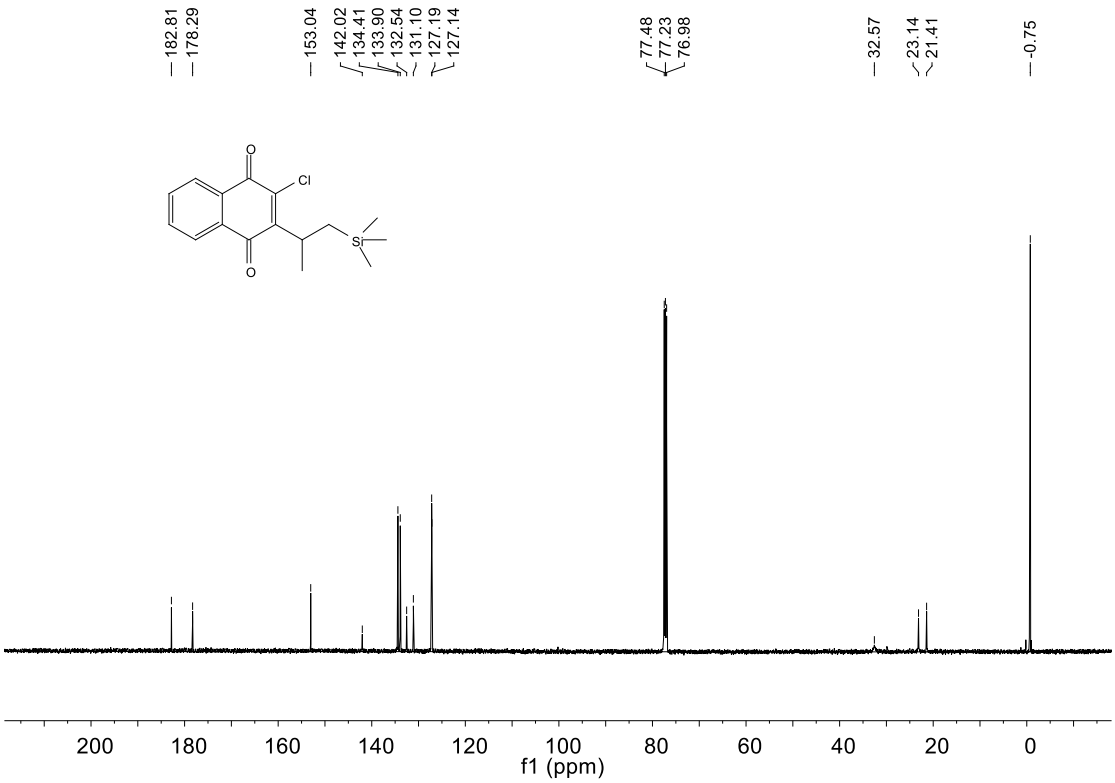


**Compound 3**

$^{1}$H NMR

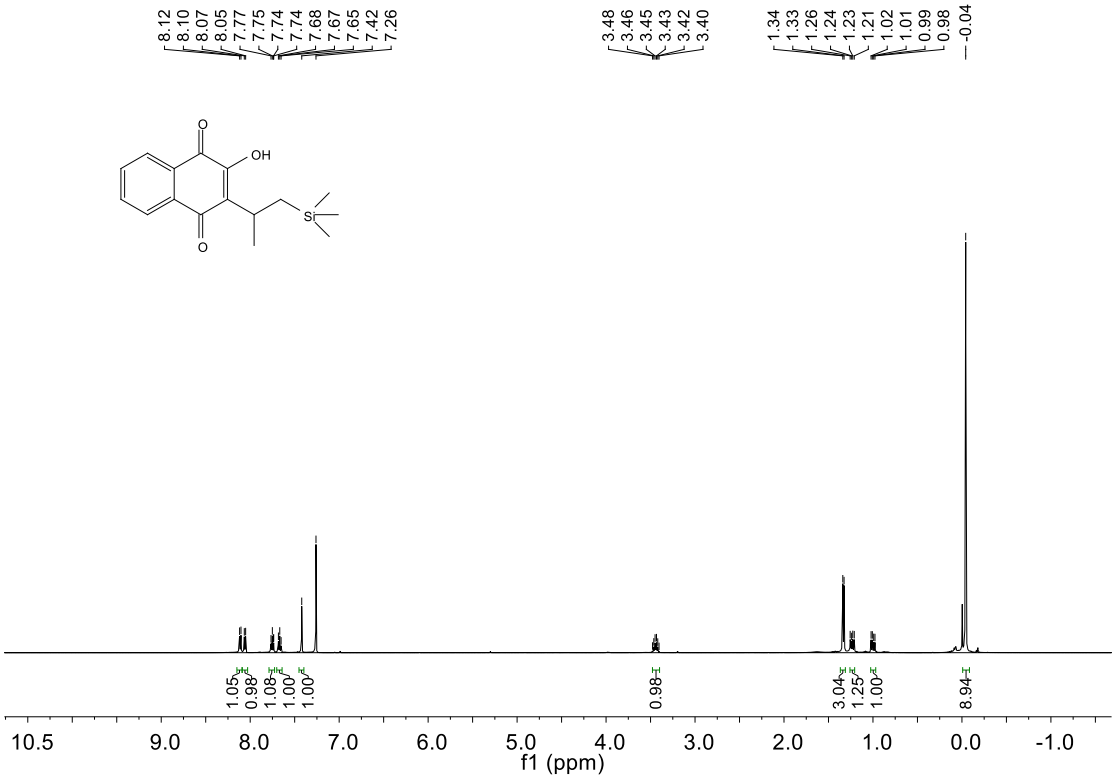



$^{13}$C NMR

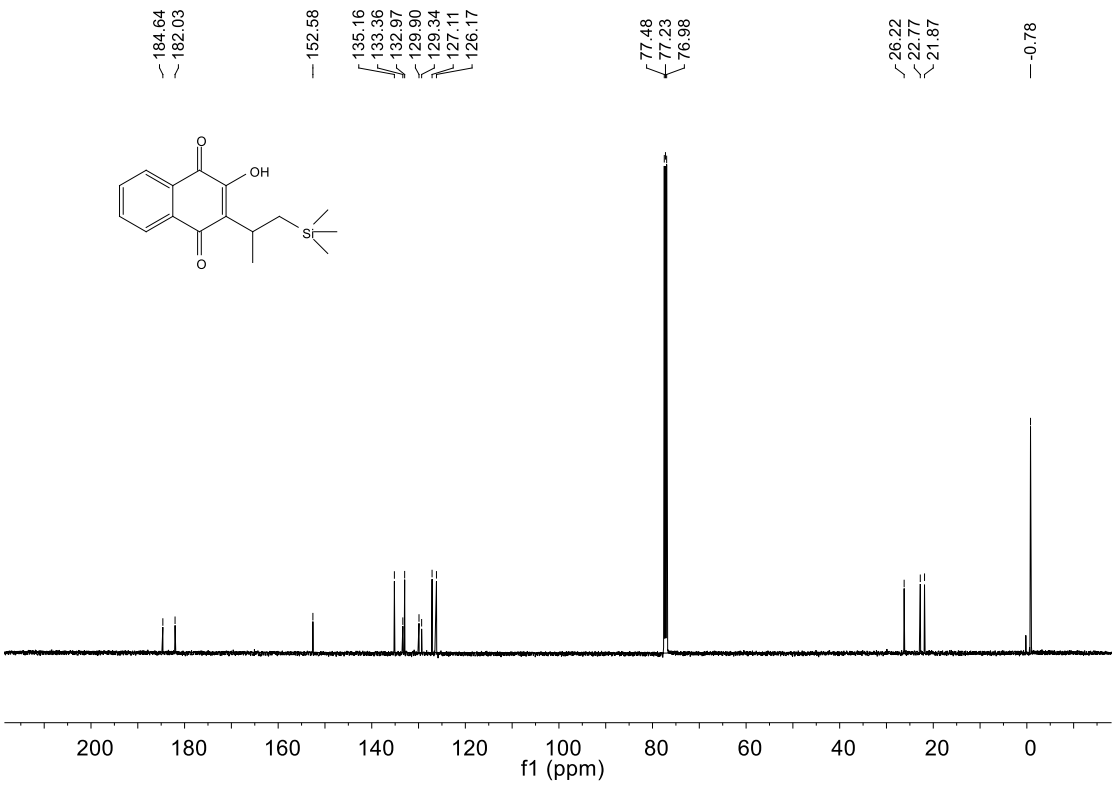


**Compound 4**

$^{1}$H NMR

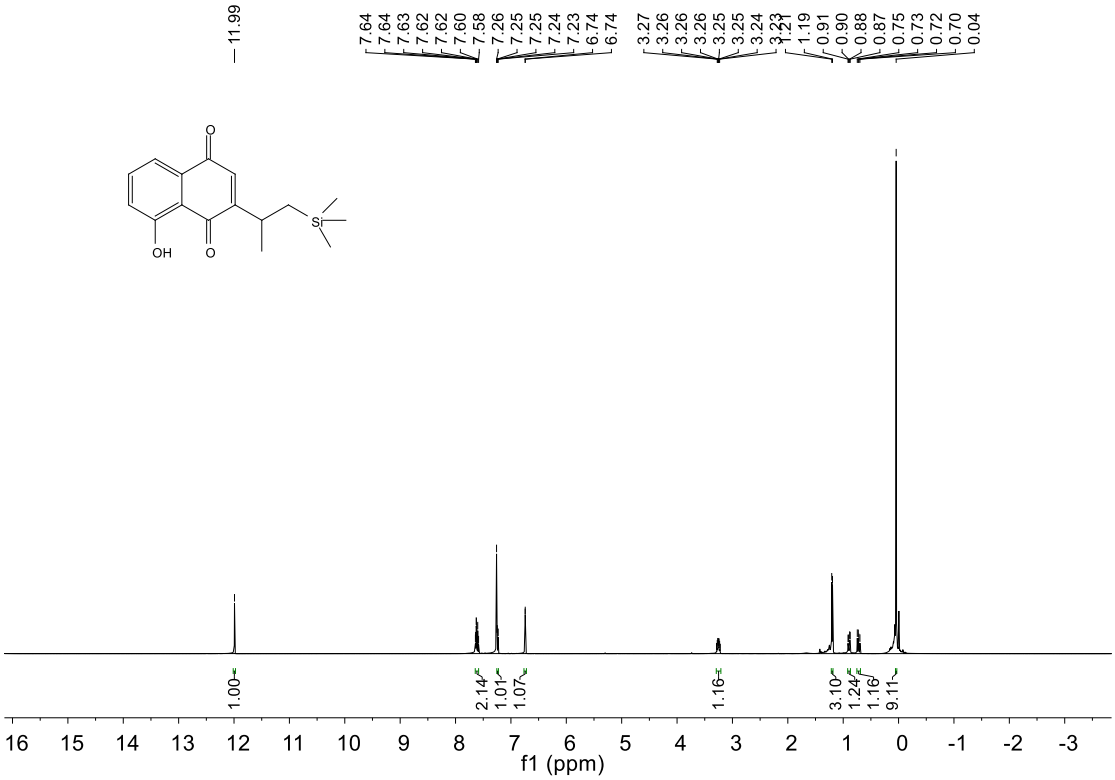



$^{13}$C NMR

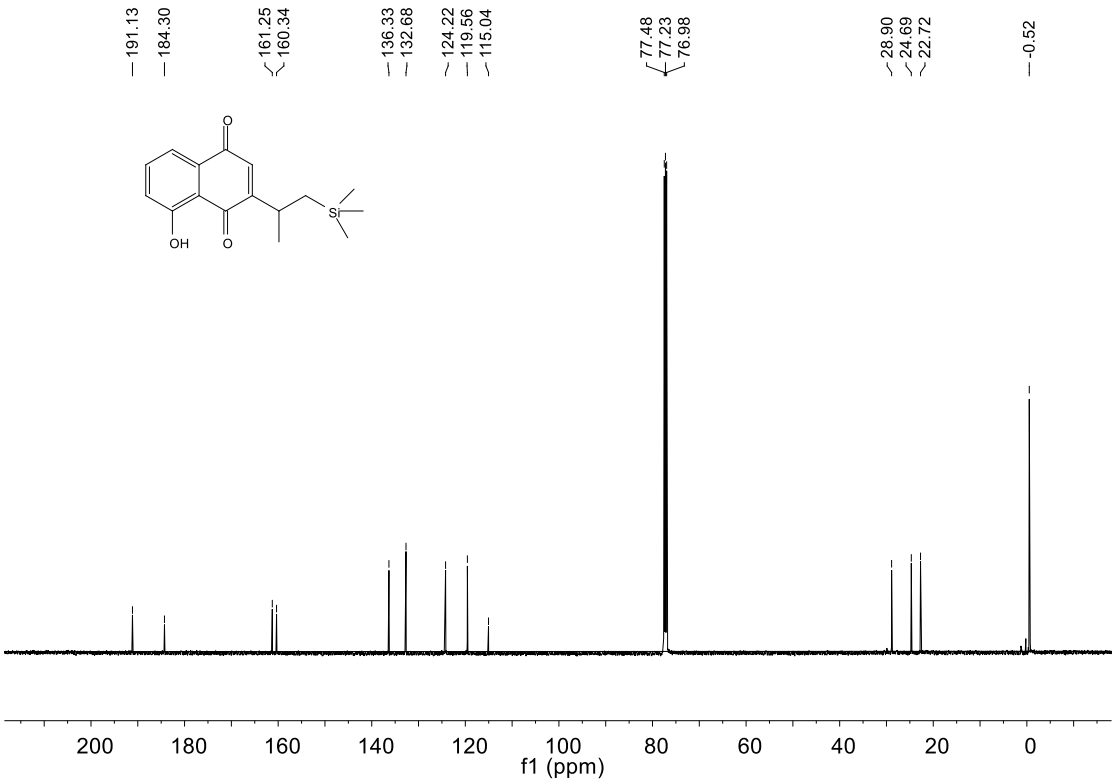


**Compound 5a**

$^{1}$H NMR

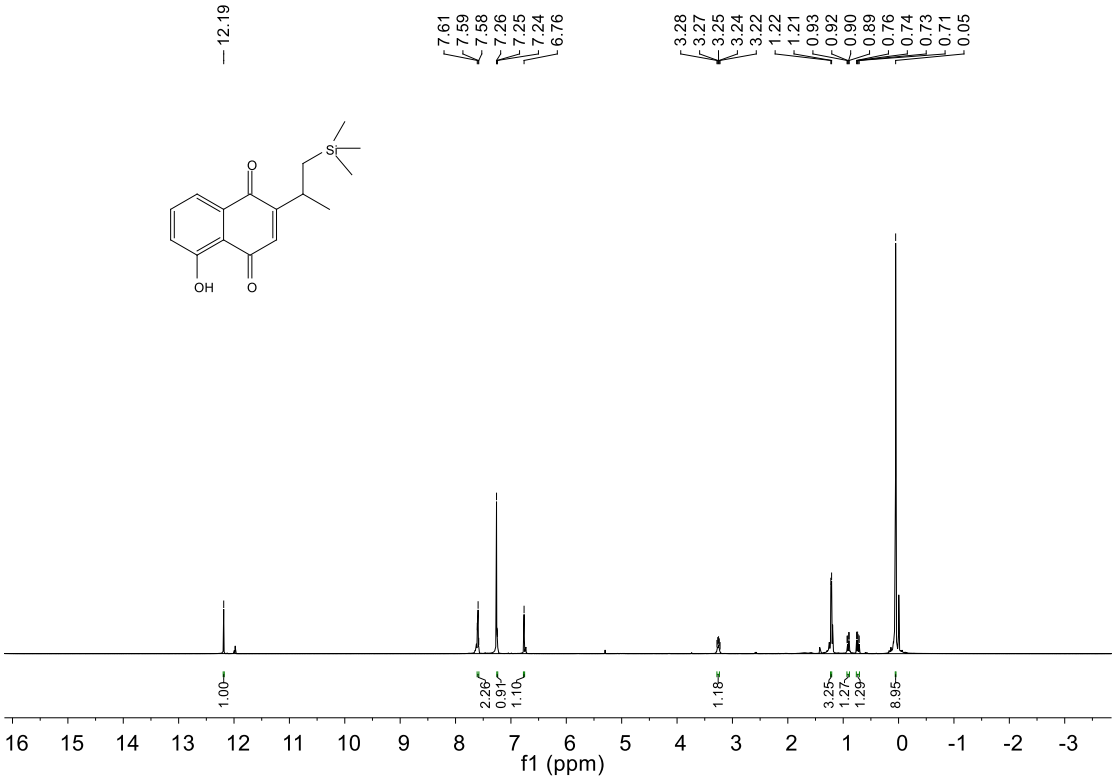



$^{13}$C NMR

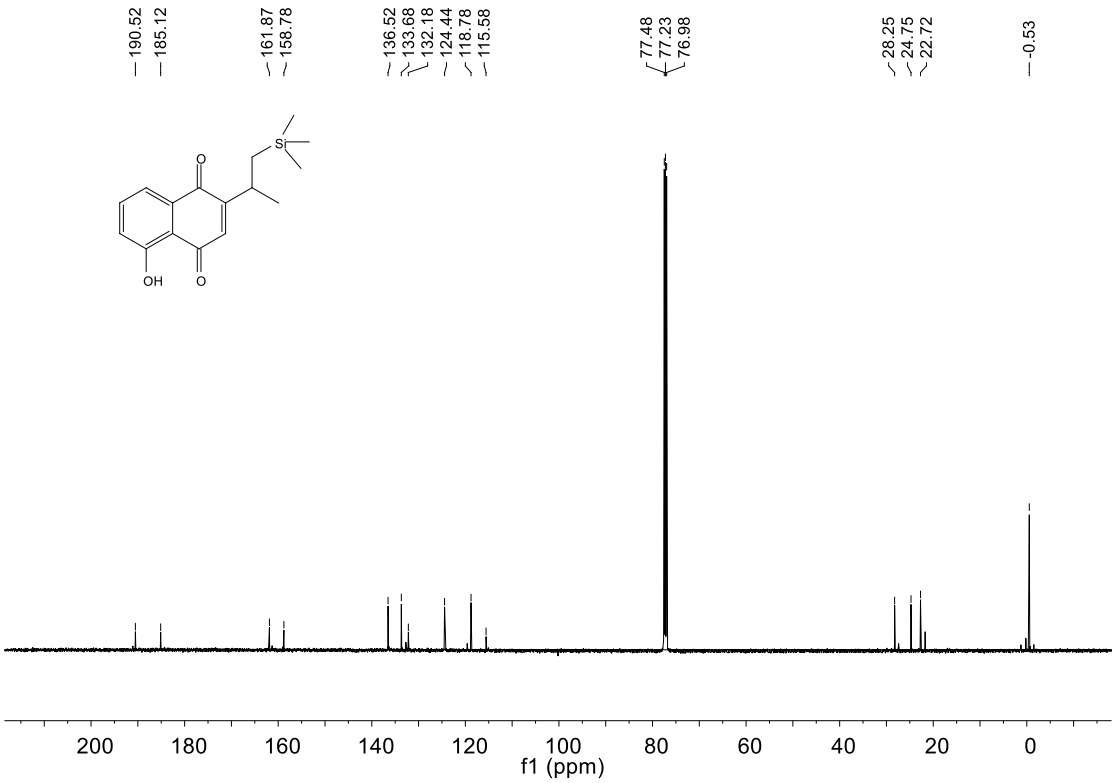


**Compound 5b**

$^{1}$H NMR

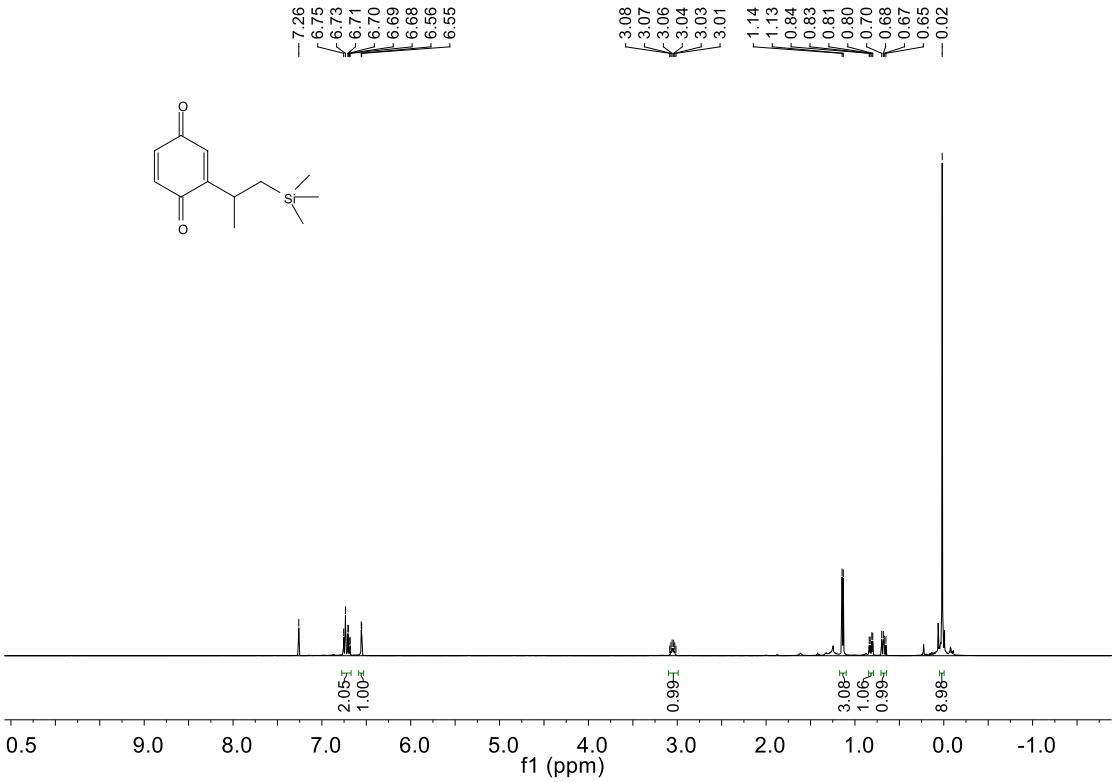



$^{13}$C NMR

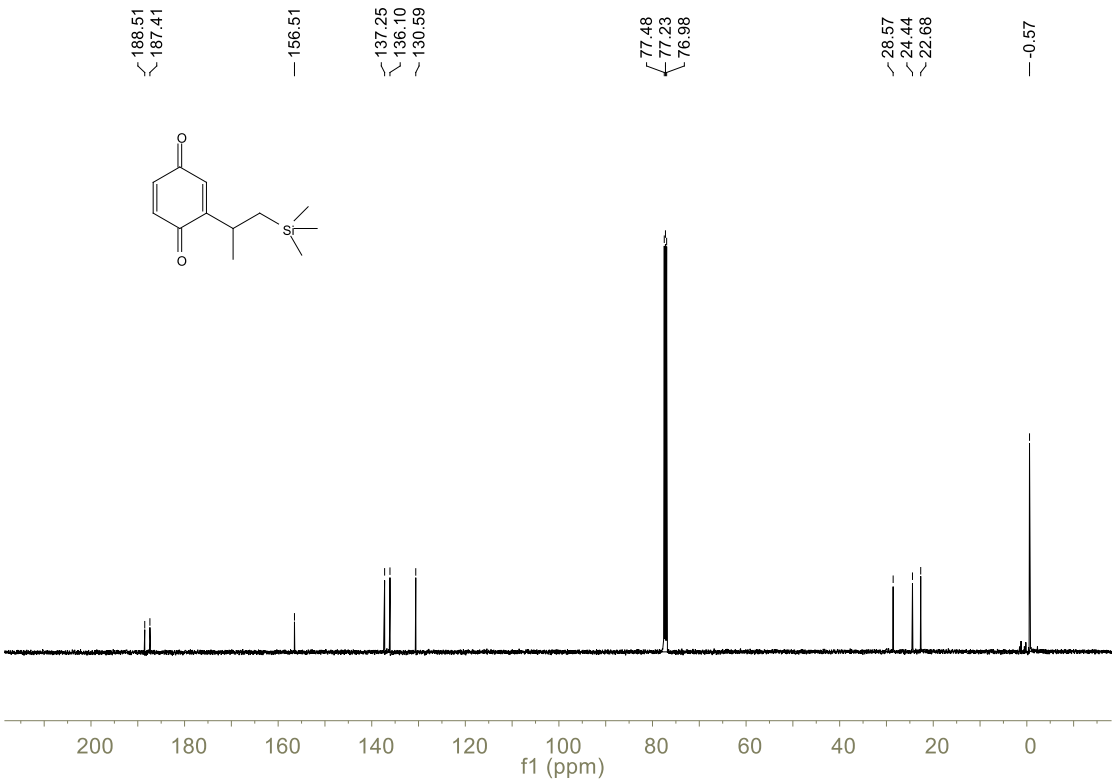


**Compound 6**

$^{1}$H NMR

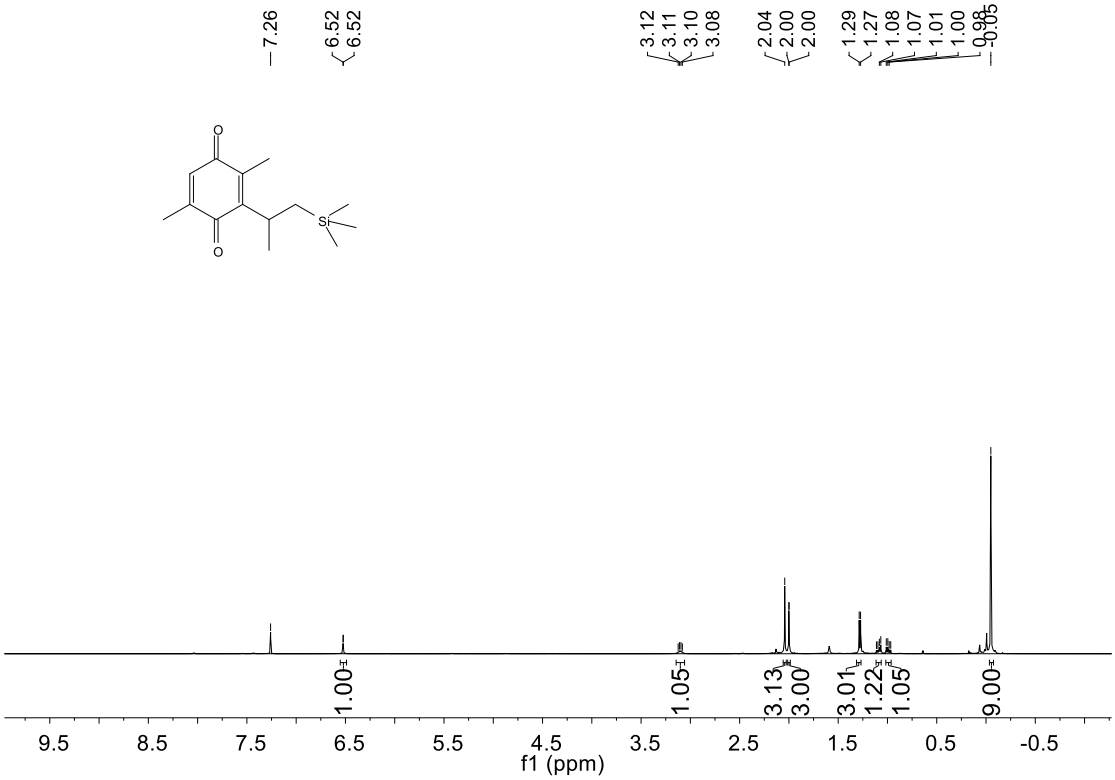



$^{13}$C NMR

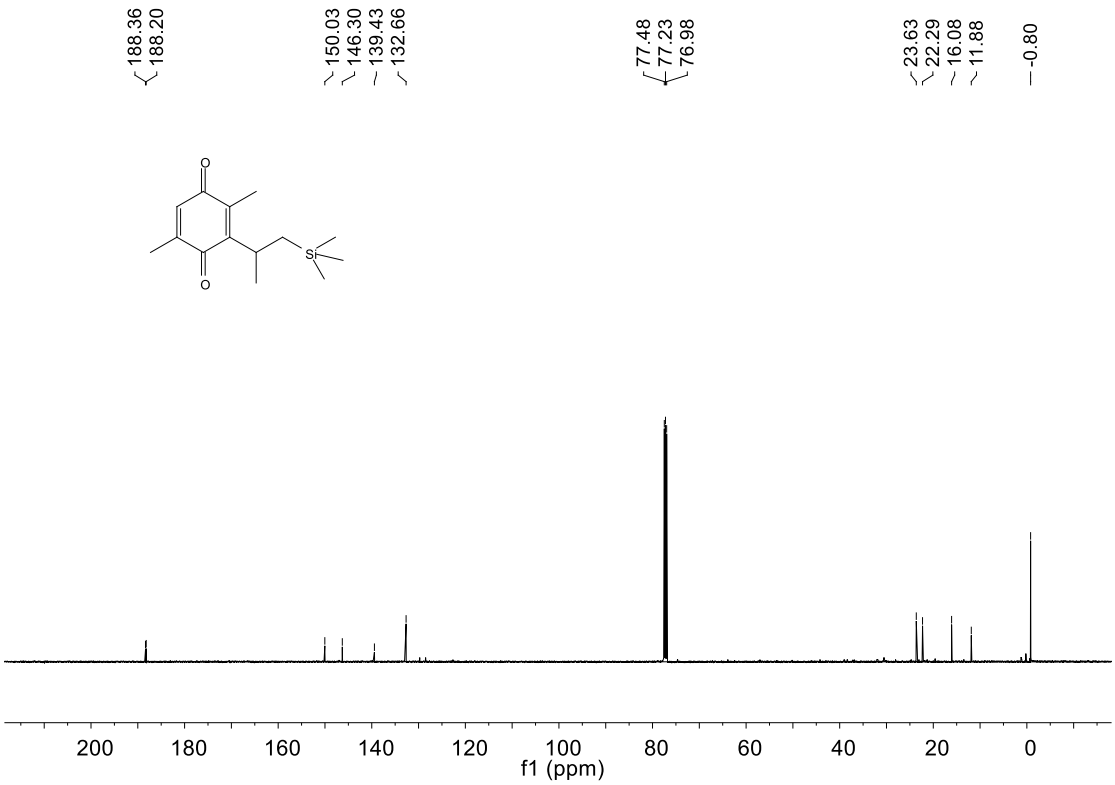


**Compound 7**

$^{1}$H NMR

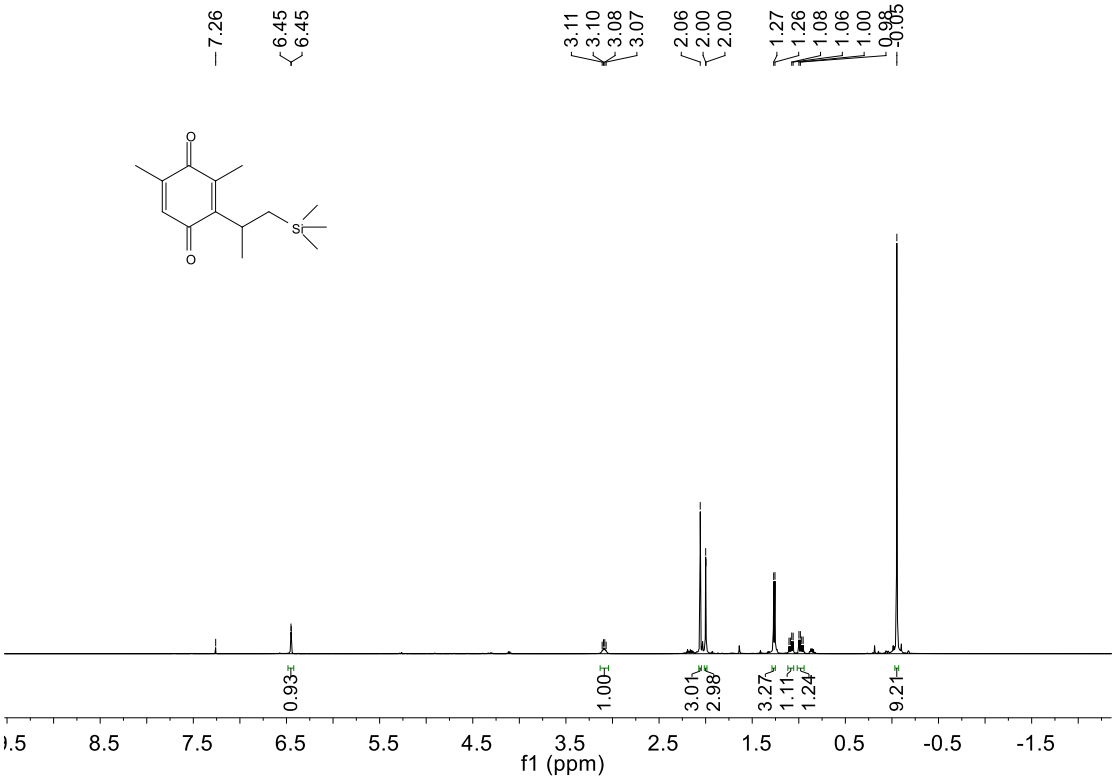



$^{13}$C NMR

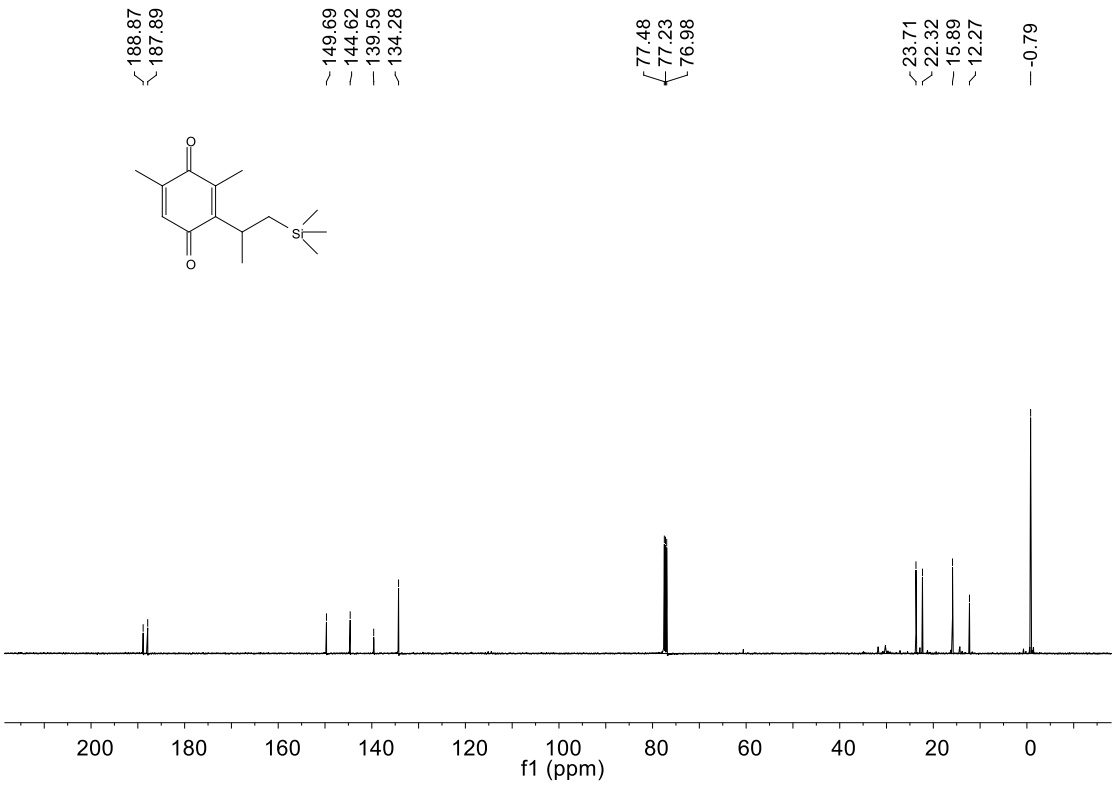


**Compound 8**

$^{1}$H NMR

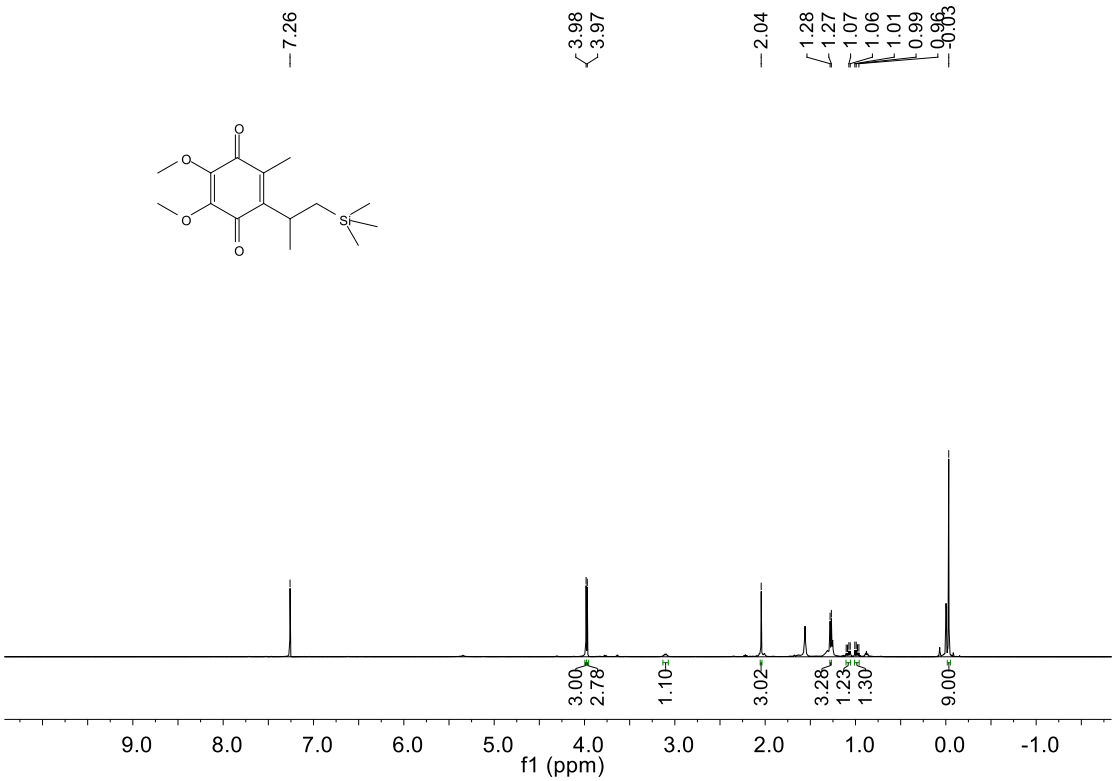



$^{13}$C NMR

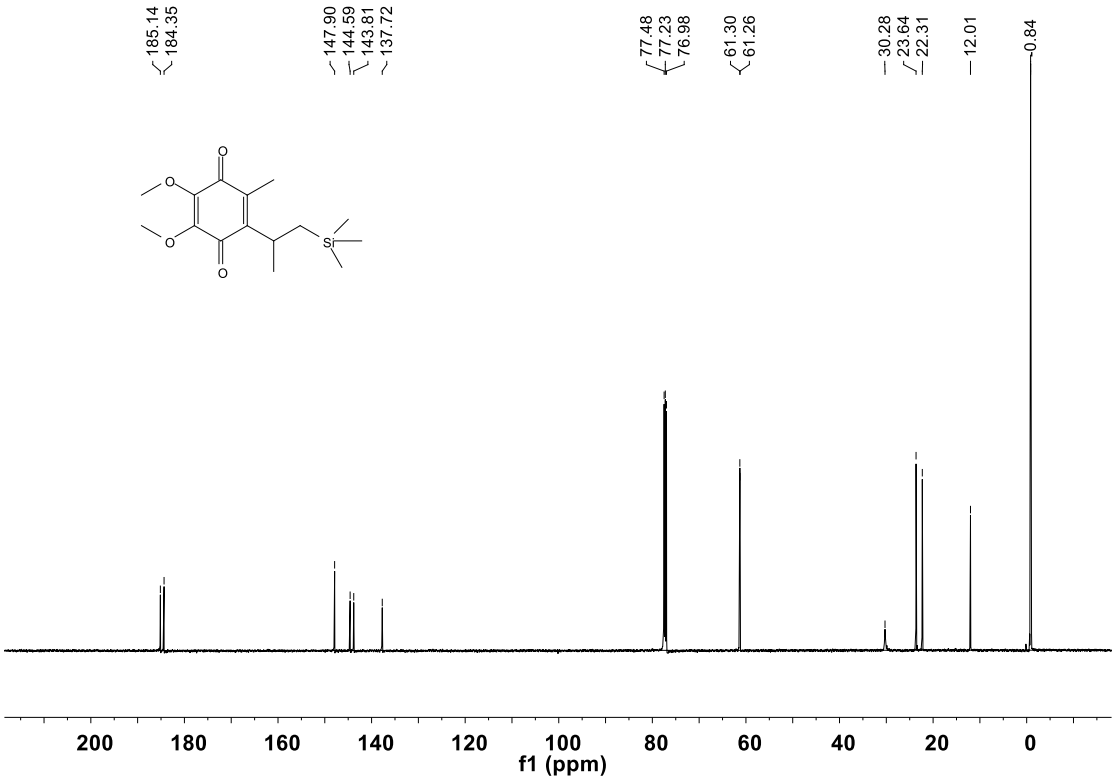


**Compound 9**

$^{1}$H NMR

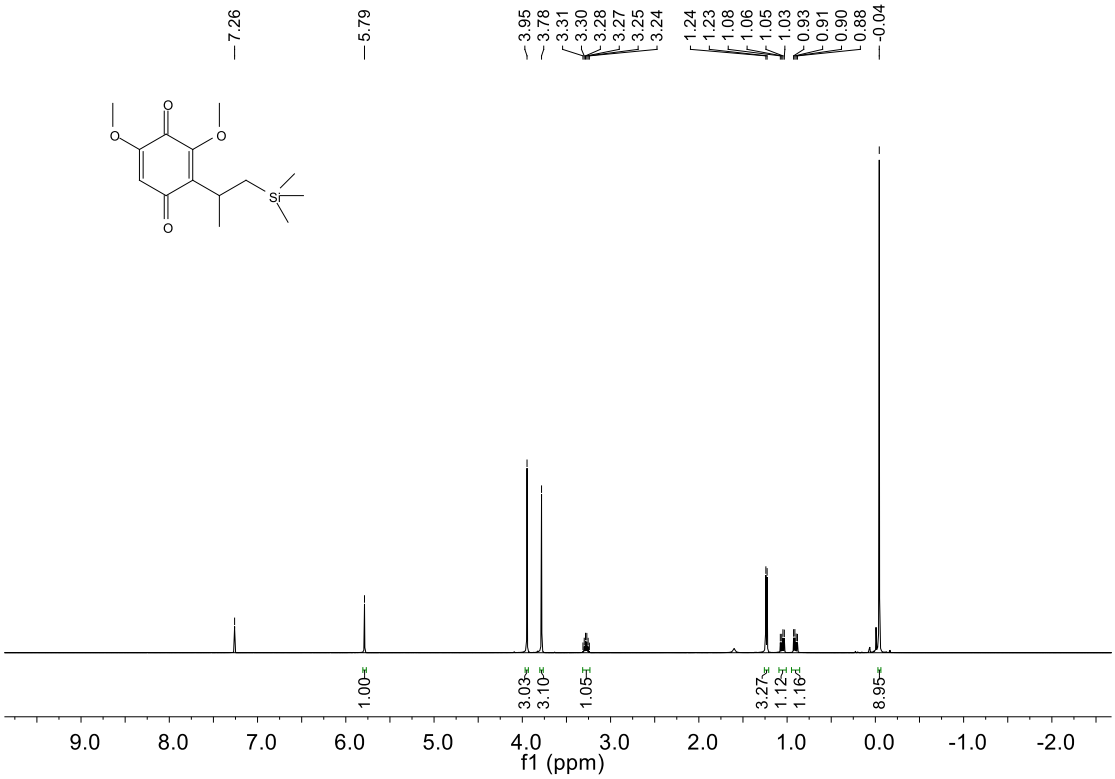



$^{13}$C NMR

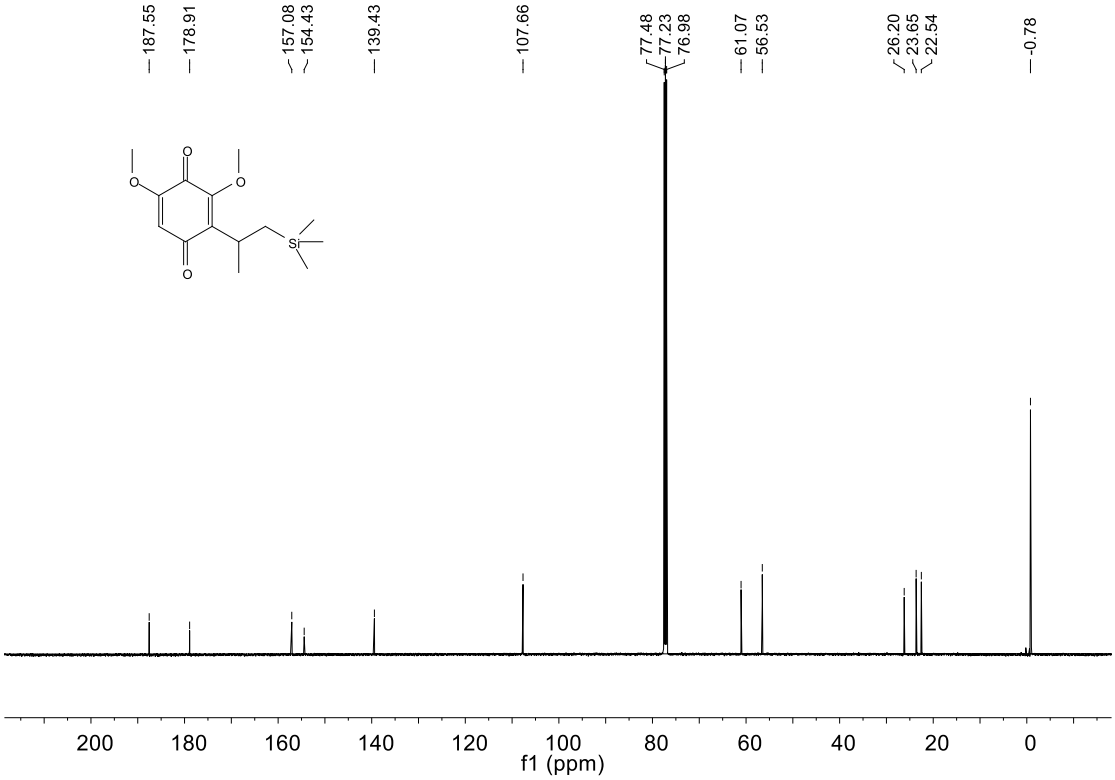


**Compound 10**

$^{1}$H NMR

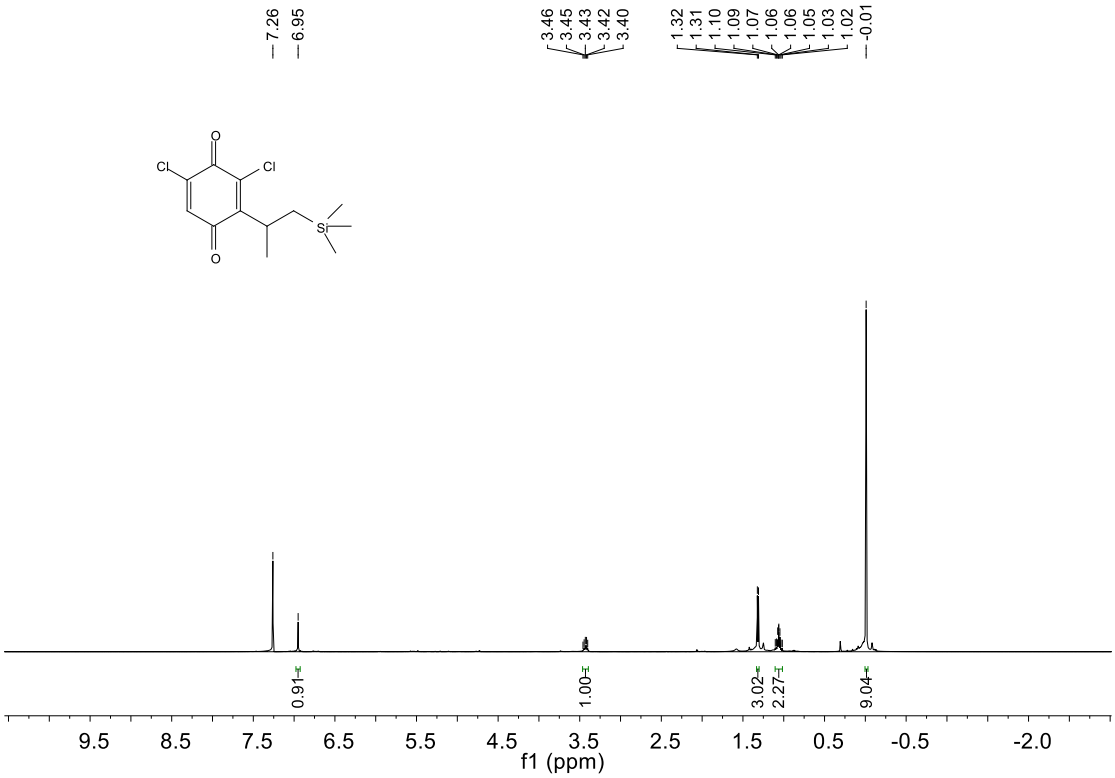



$^{13}$C NMR

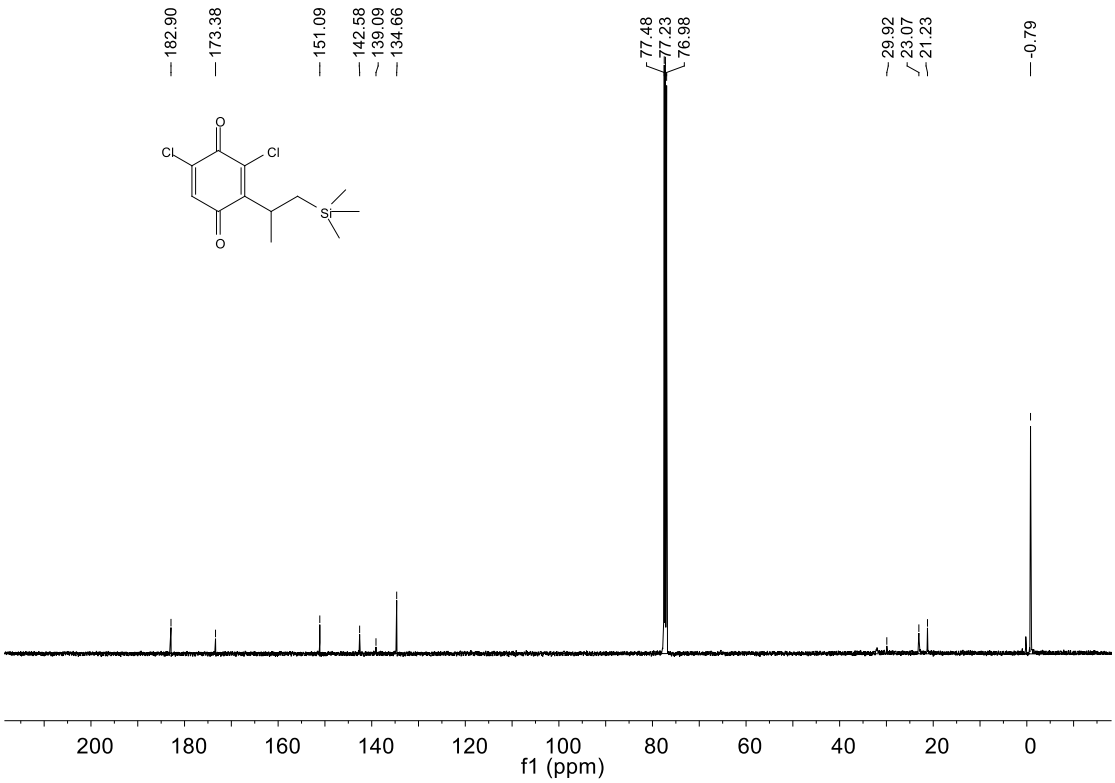


**Compound 11**

$^{1}$H NMR

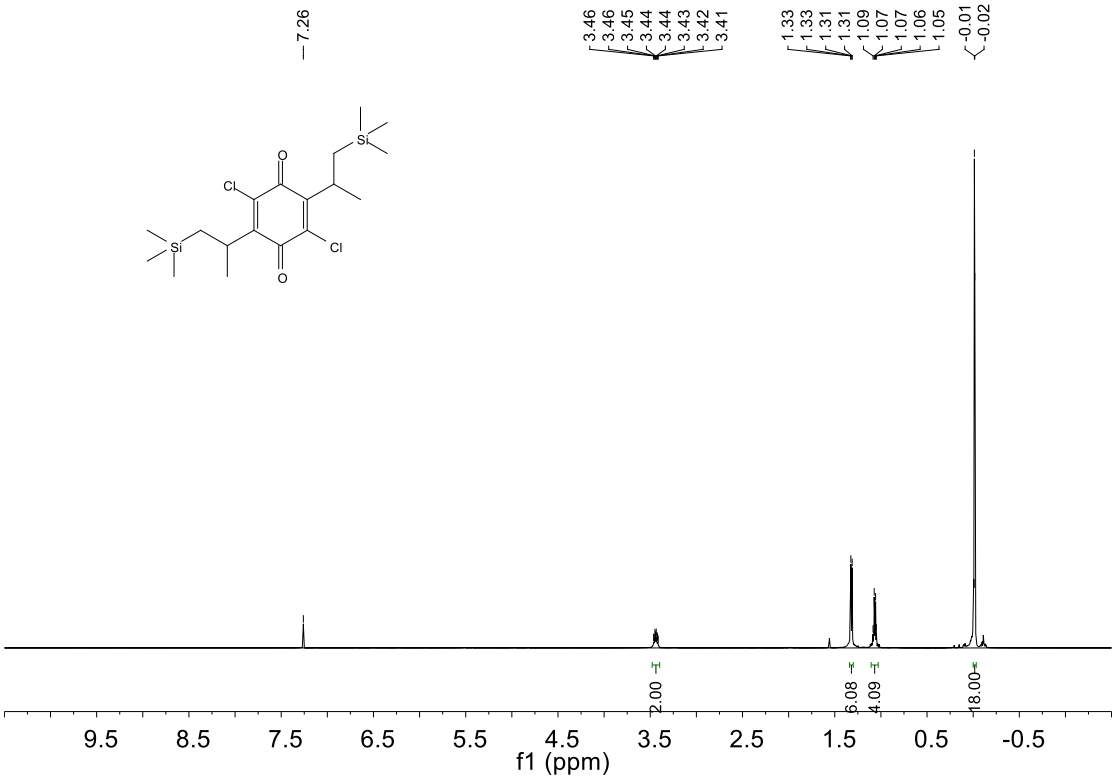



$^{13}$C NMR

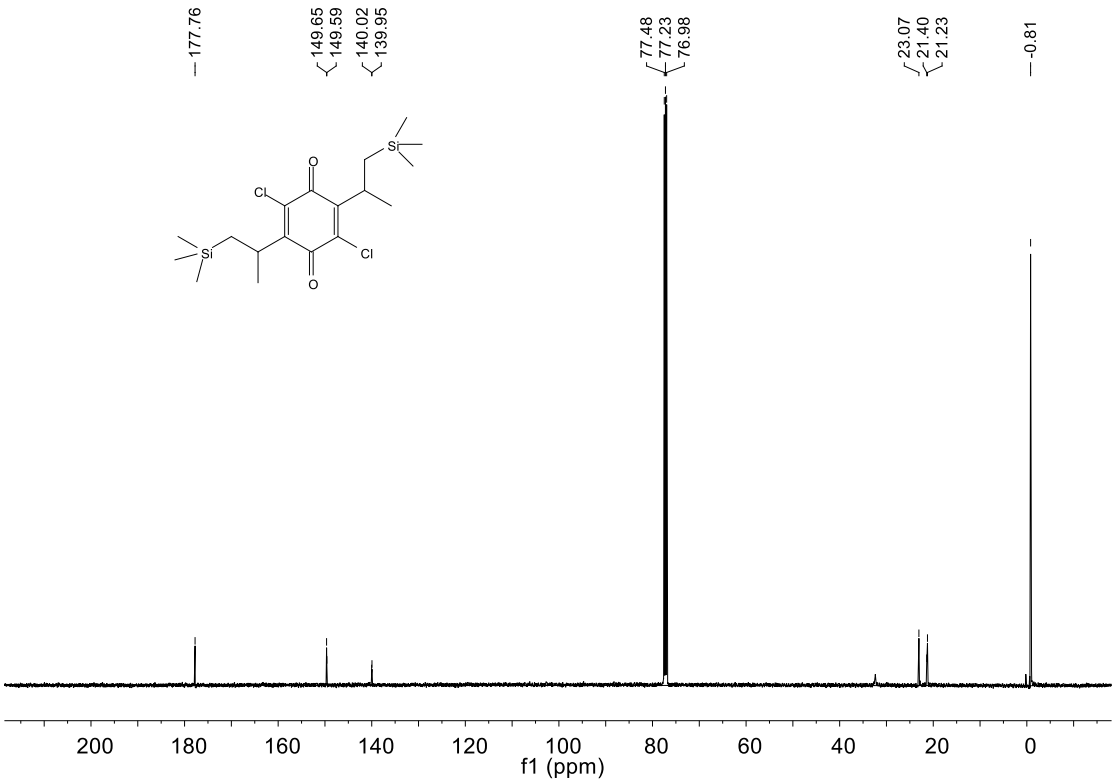


**Compound 12**

$^{1}$H NMR

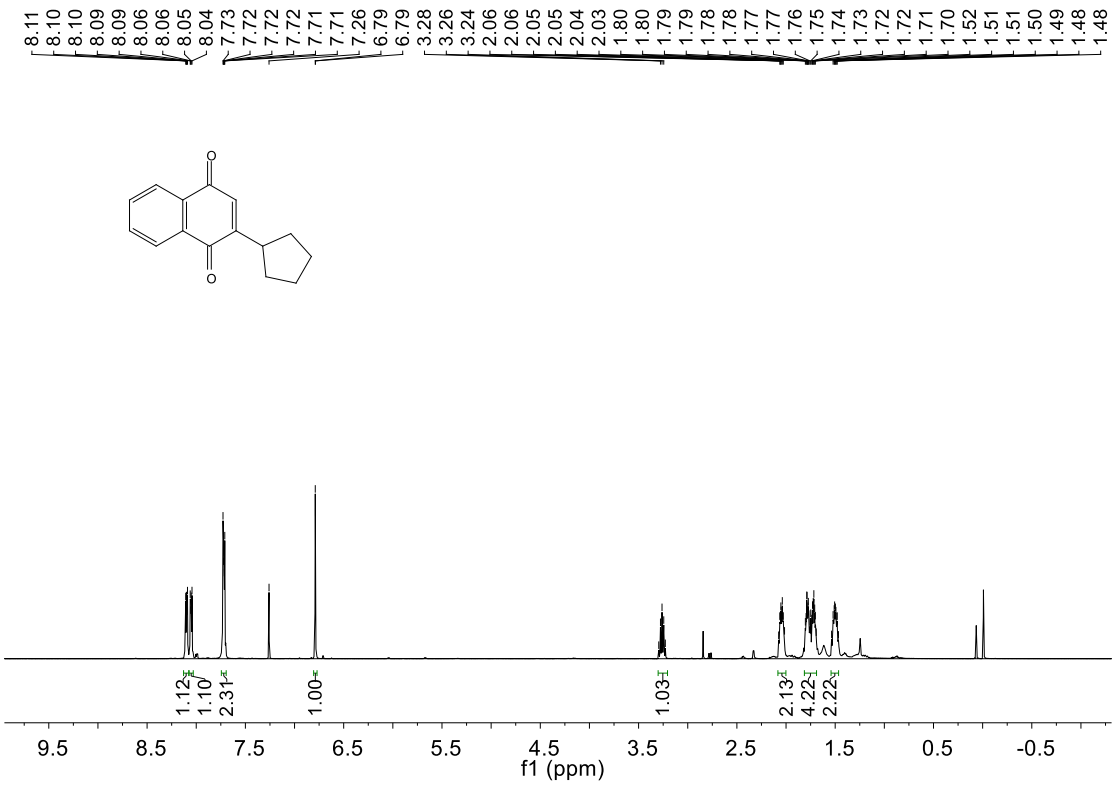



$^{13}$C NMR

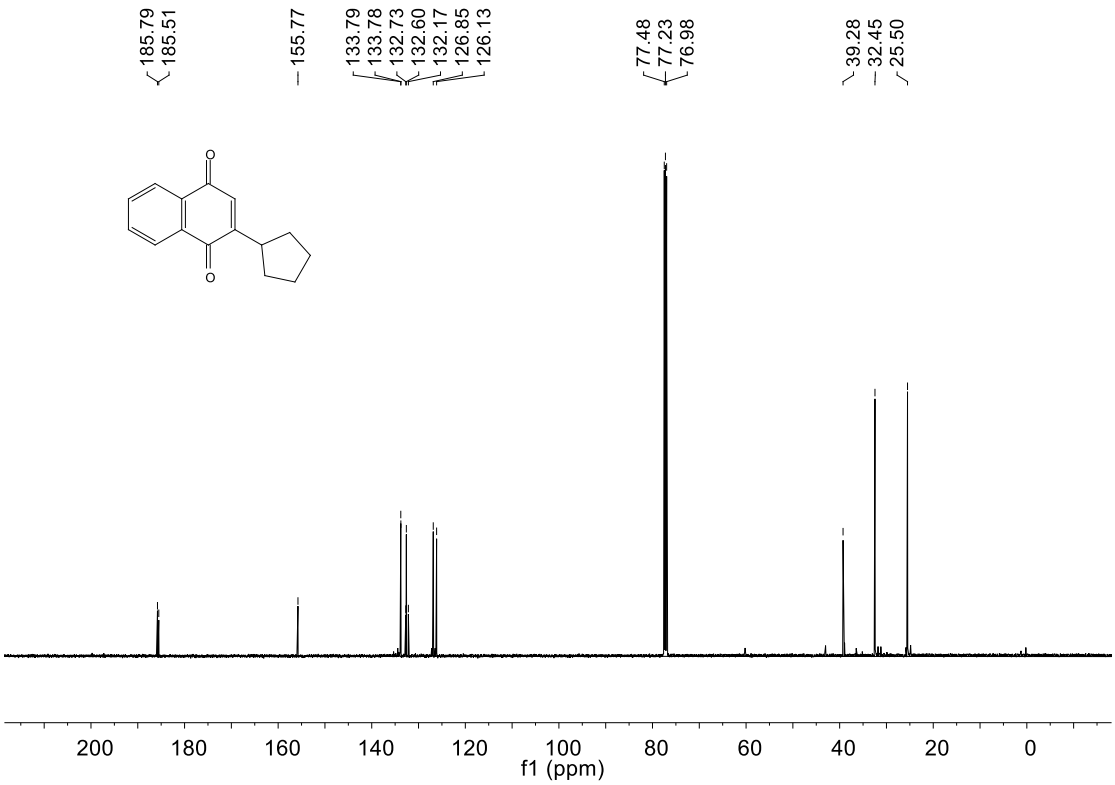


**Compound 13**

$^{1}$H NMR

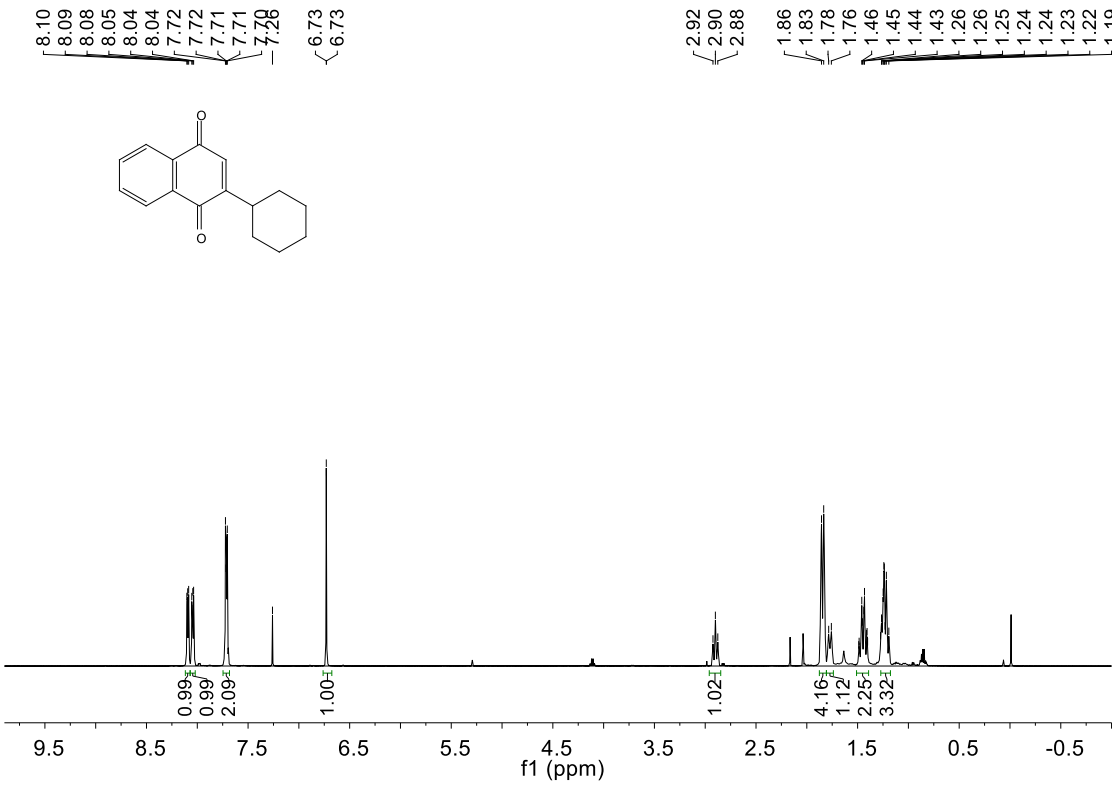



$^{13}$C NMR

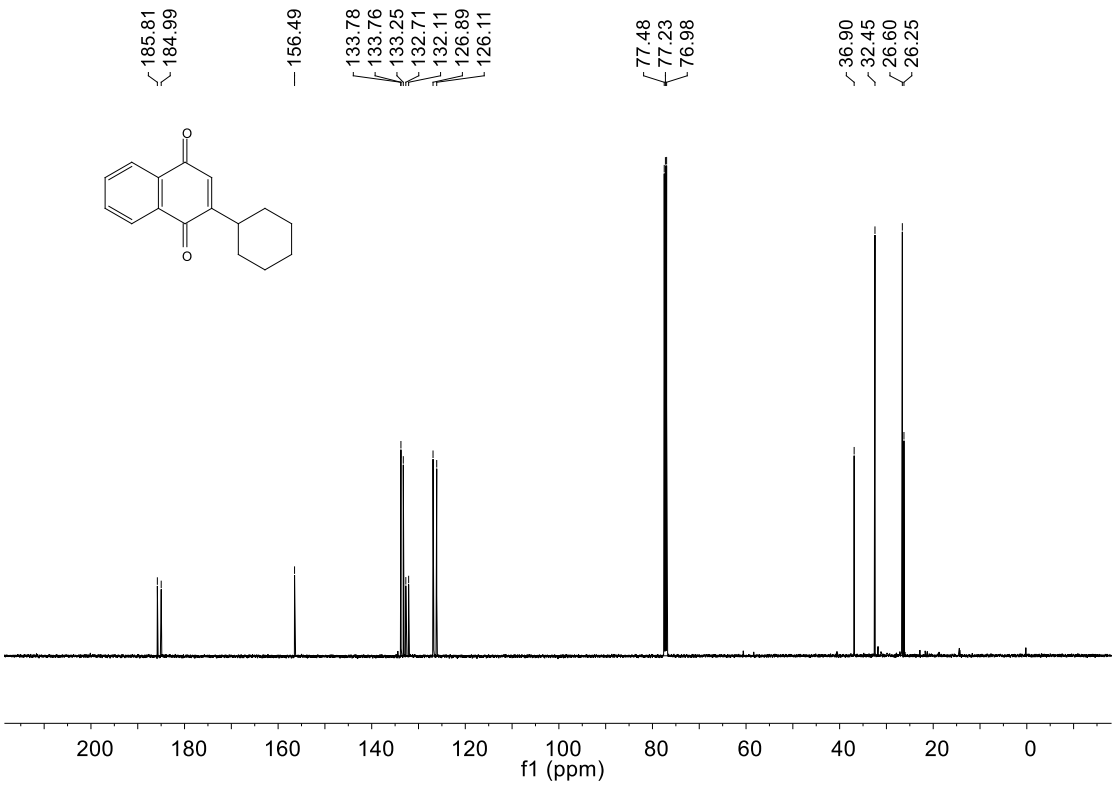


**Compound 14**

$^{1}$H NMR

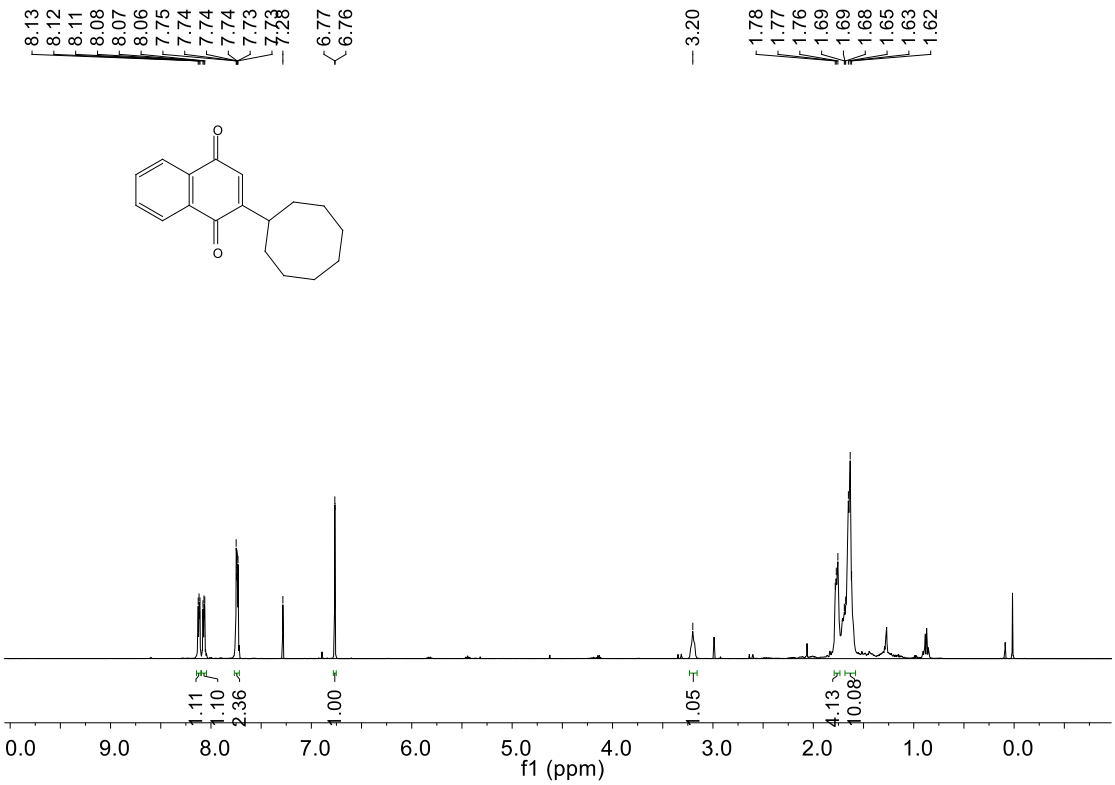



$^{13}$C NMR

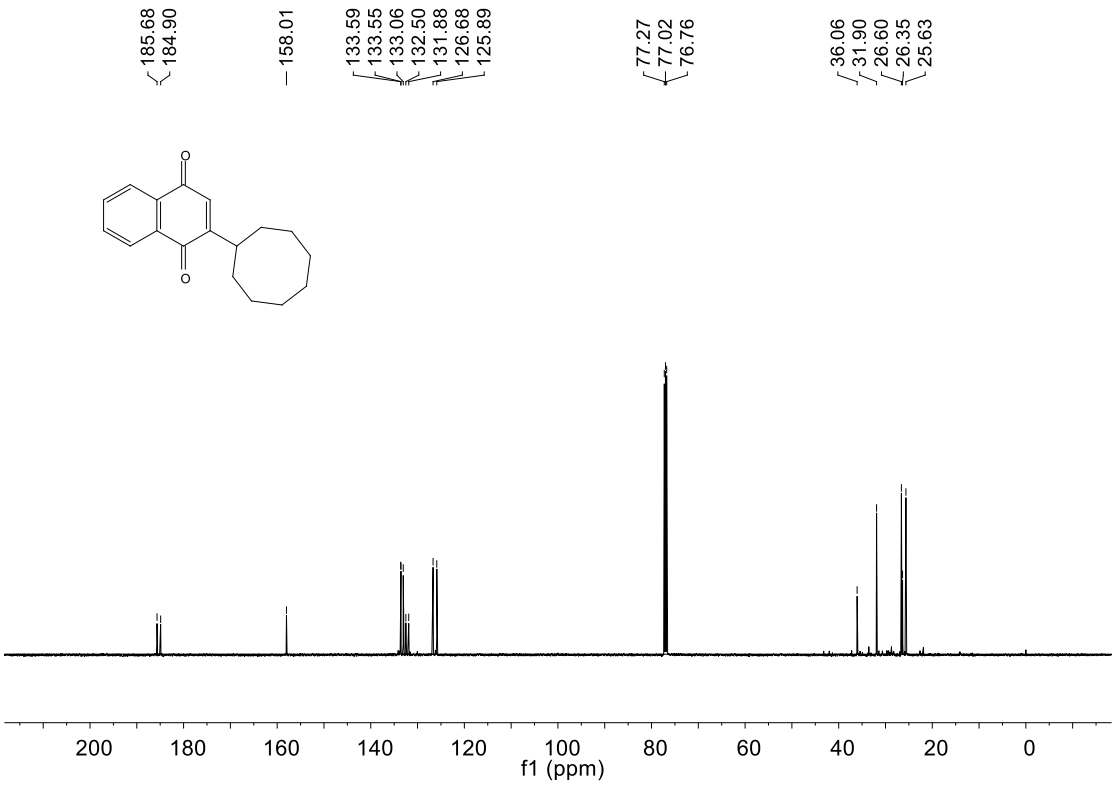


**Compound 15**

$^{1}$H NMR

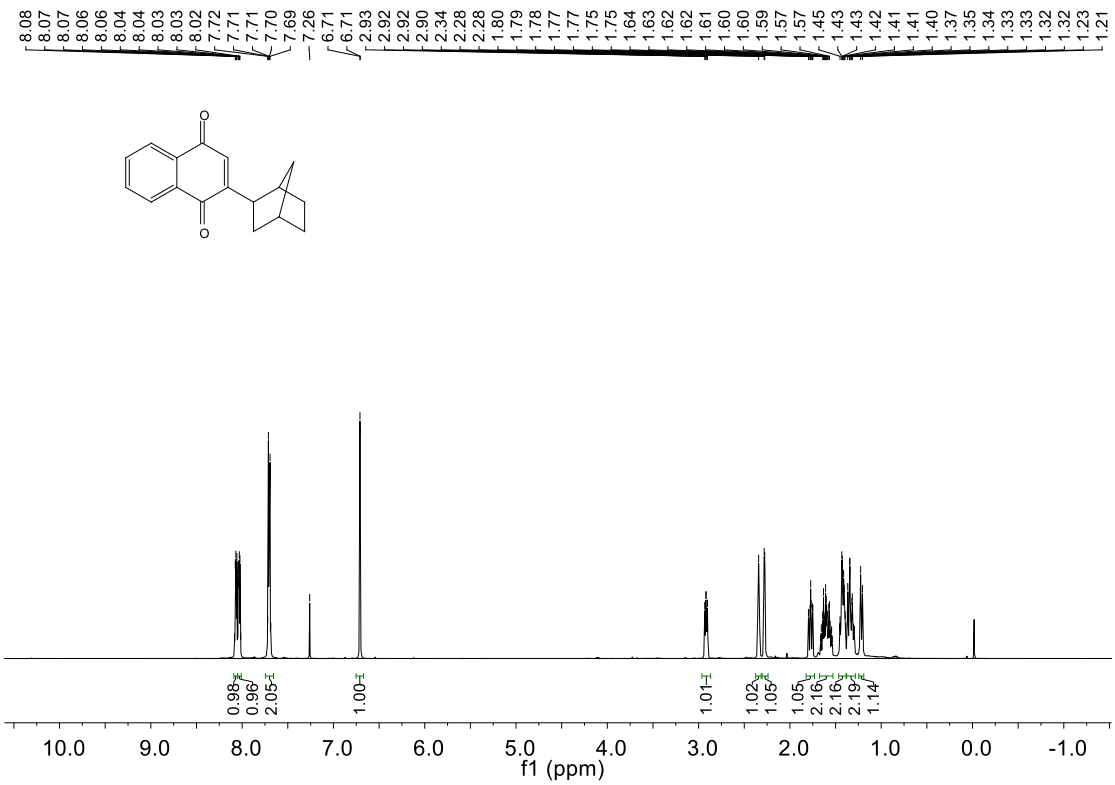



$^{13}$C NMR

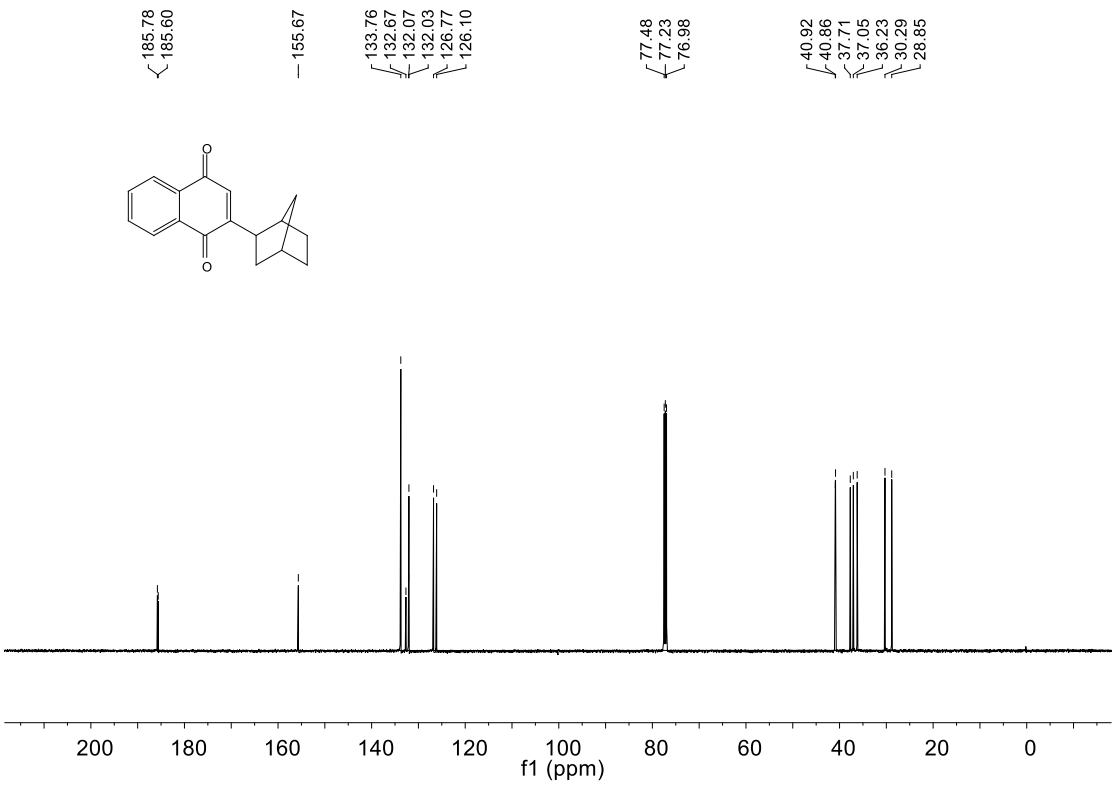


**Compound 16**

$^{1}$H NMR

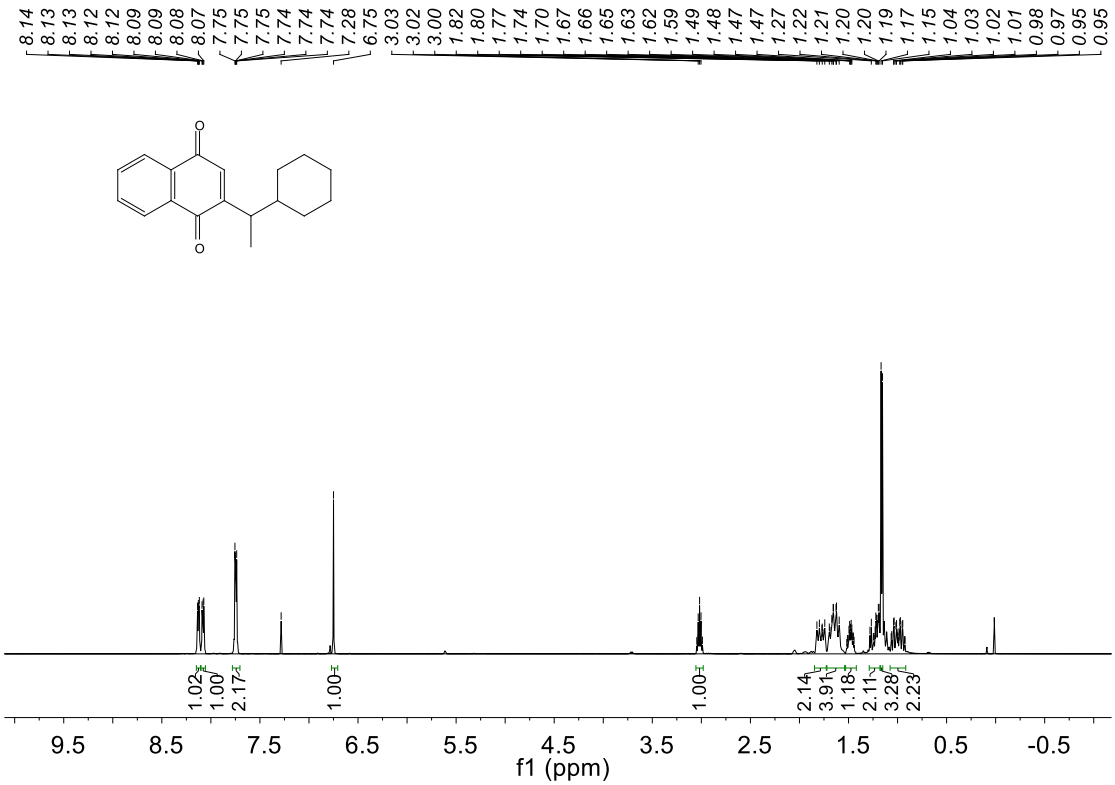



$^{13}$C NMR

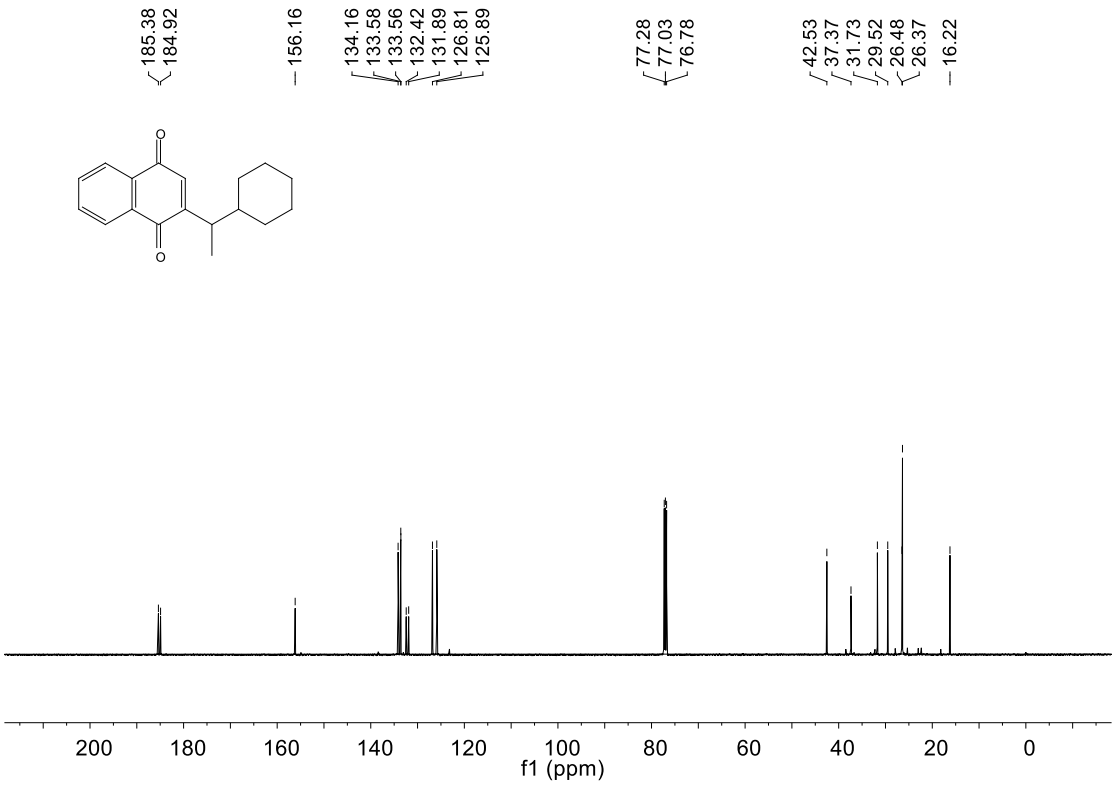


**Compound 17**

$^{1}$H NMR

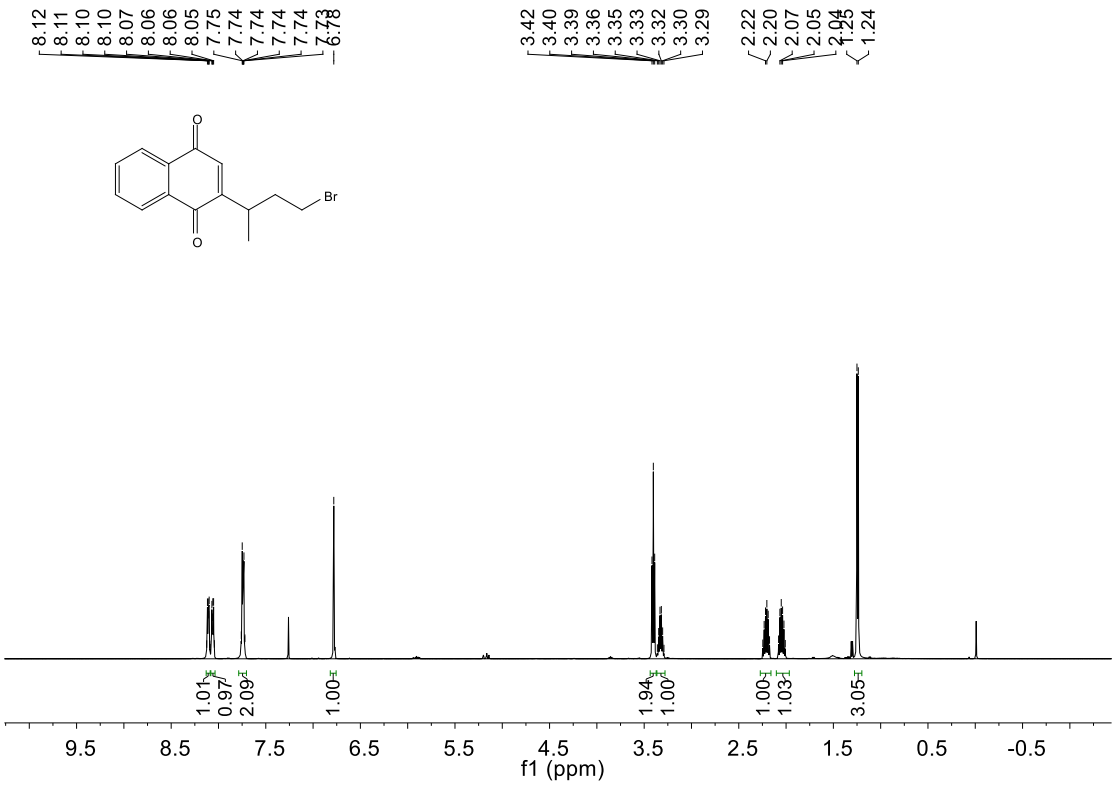



$^{13}$C NMR

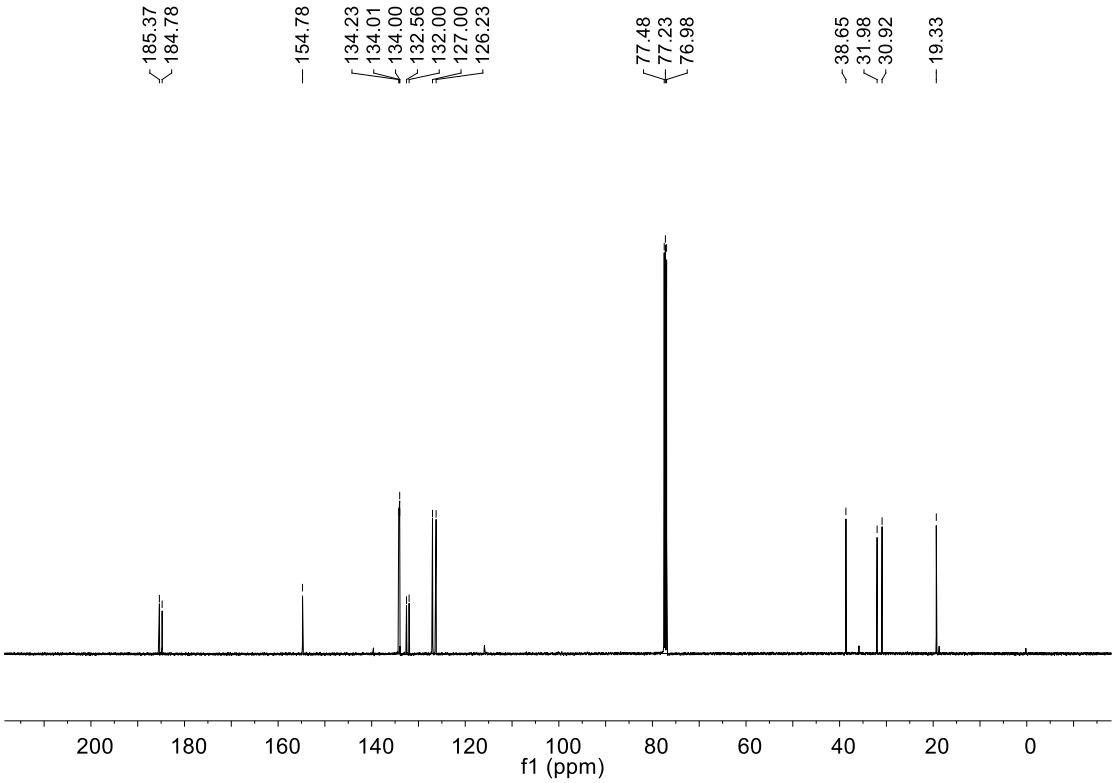


**Compound 18**

$^{1}$H NMR

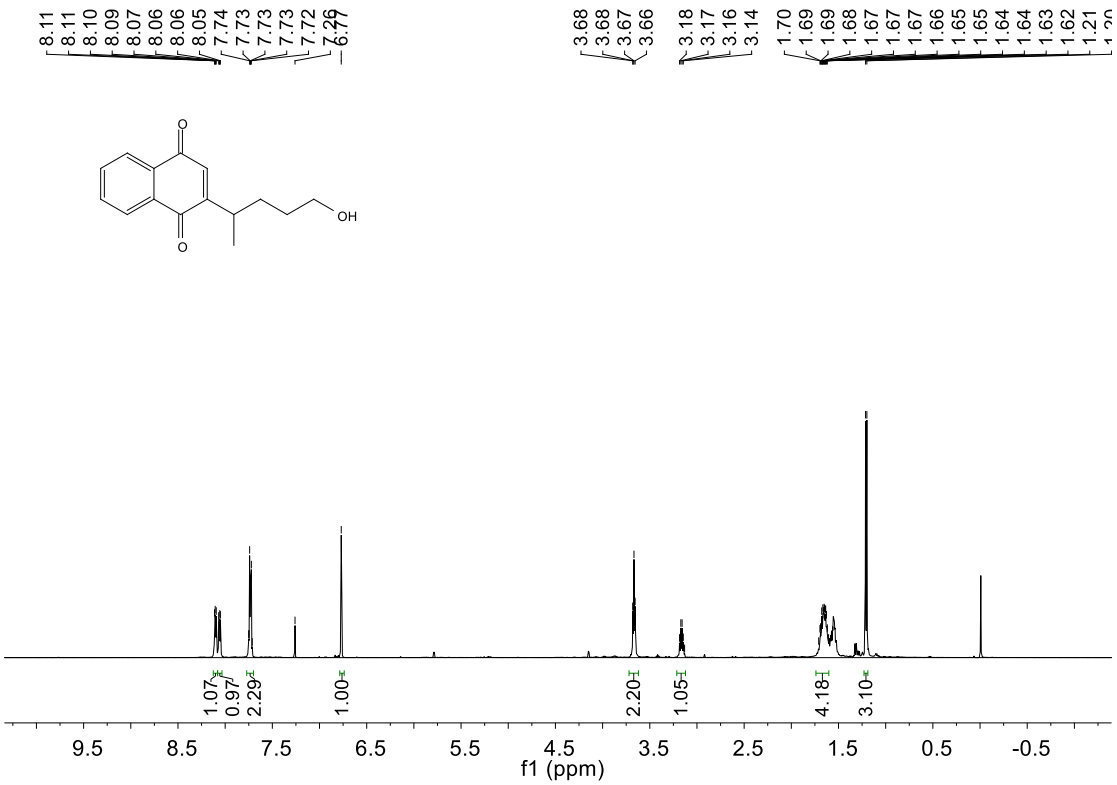



$^{13}$C NMR

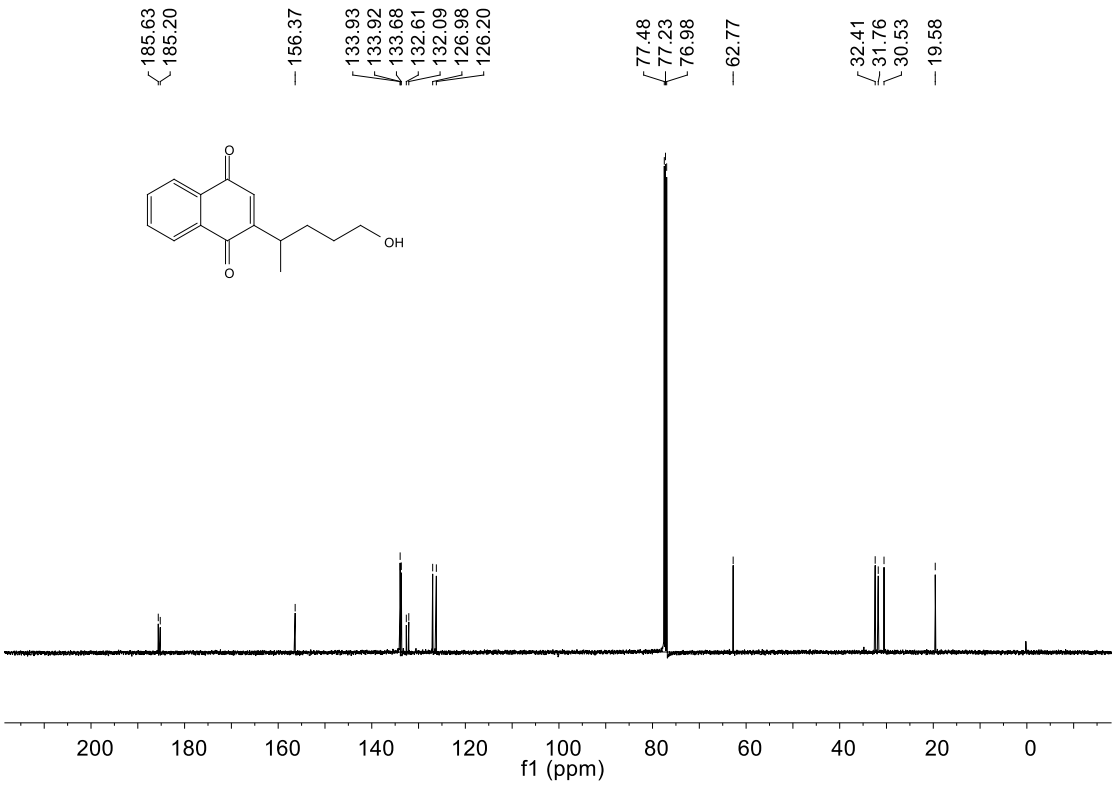


**Compound 19**

$^{1}$H NMR

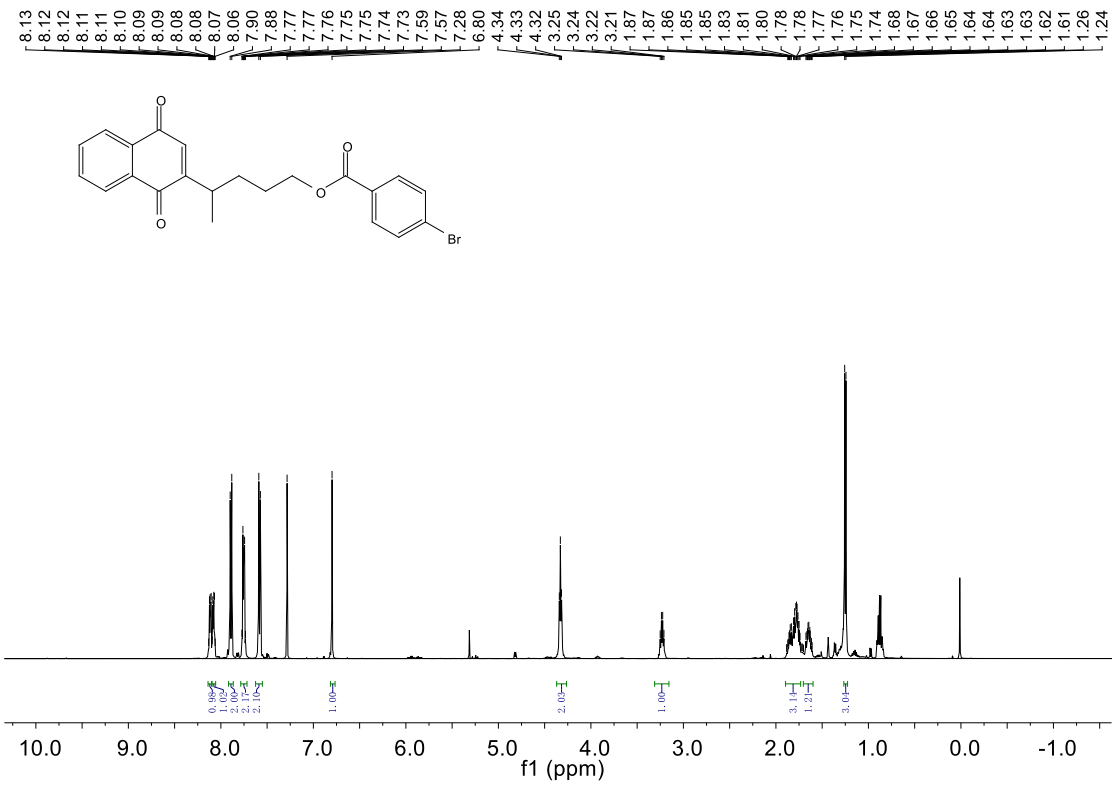



$^{13}$C NMR

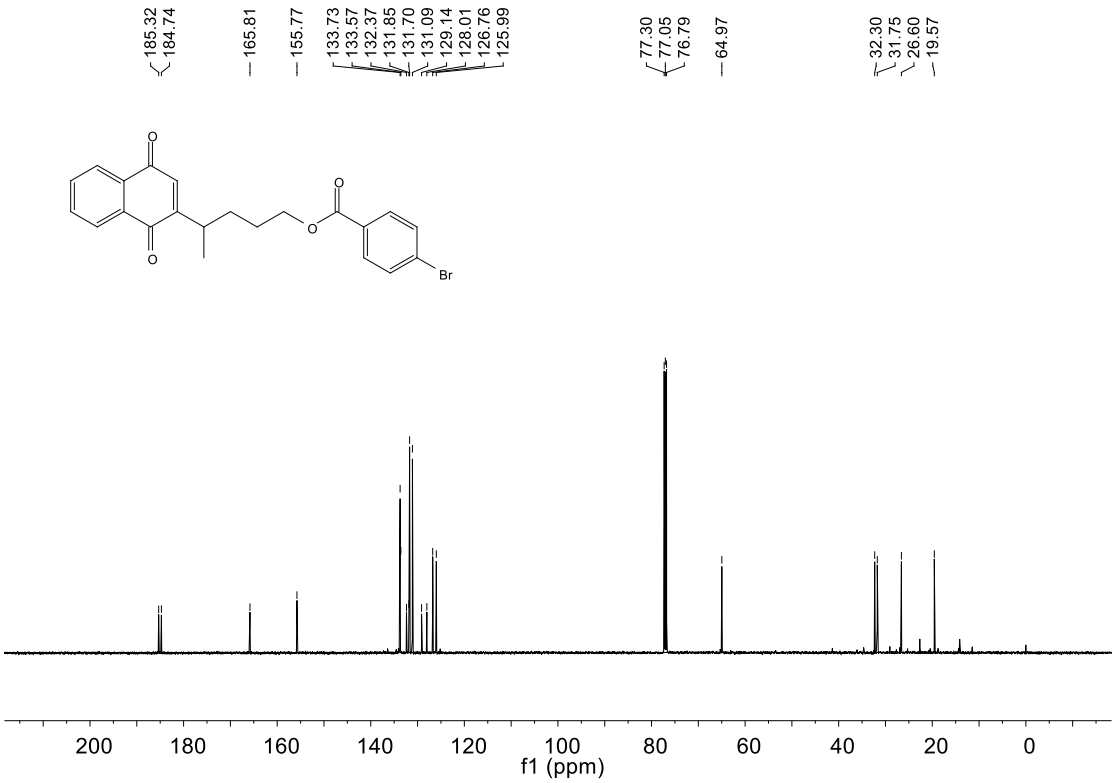


**Compound 20**

$^{1}$H NMR

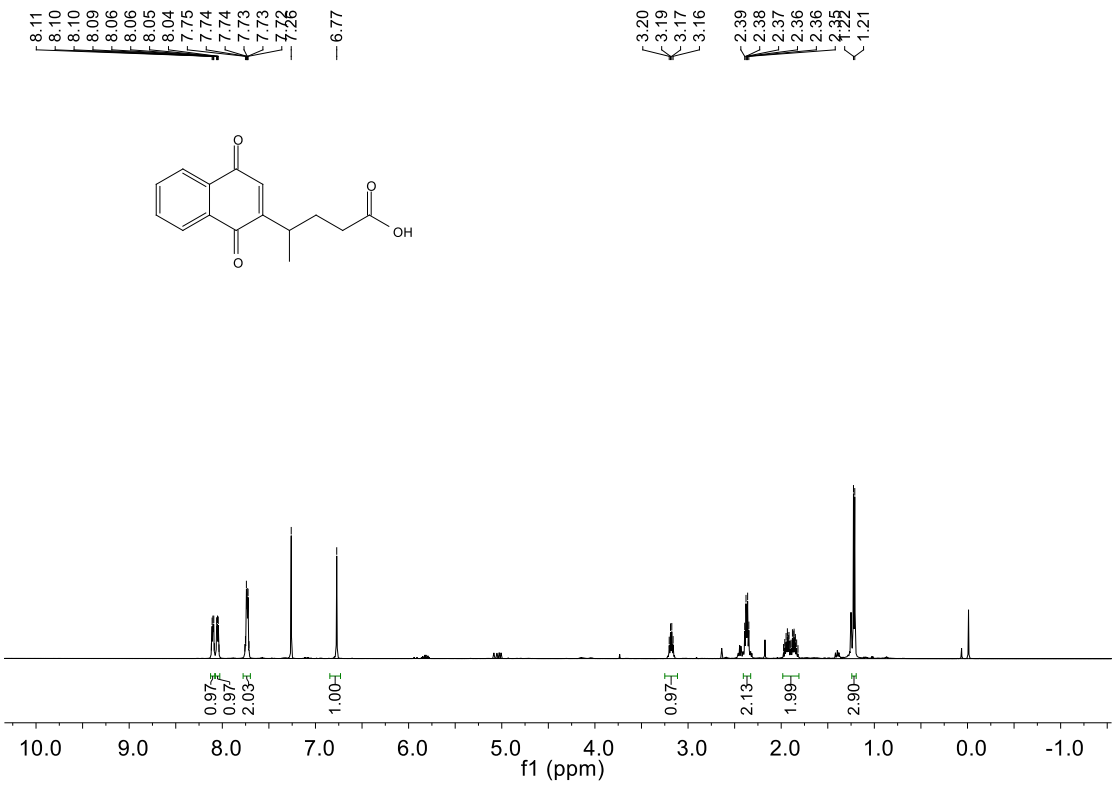



$^{13}$C NMR

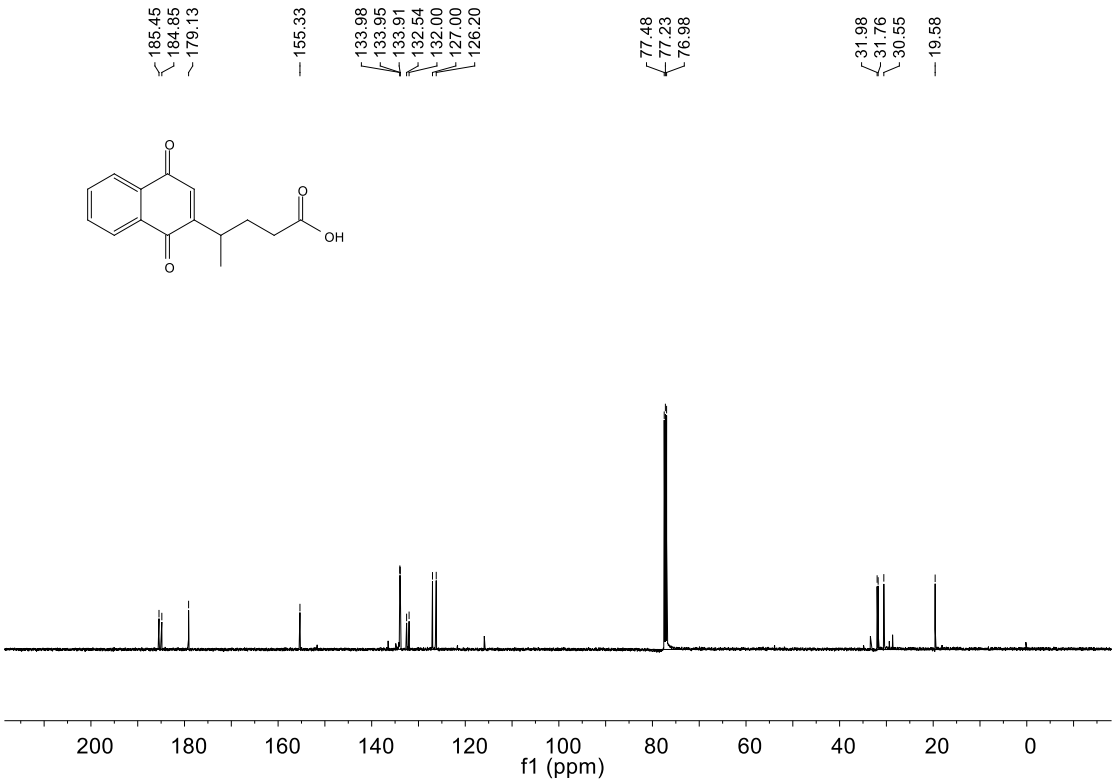


**Compound 21**

$^{1}$H NMR

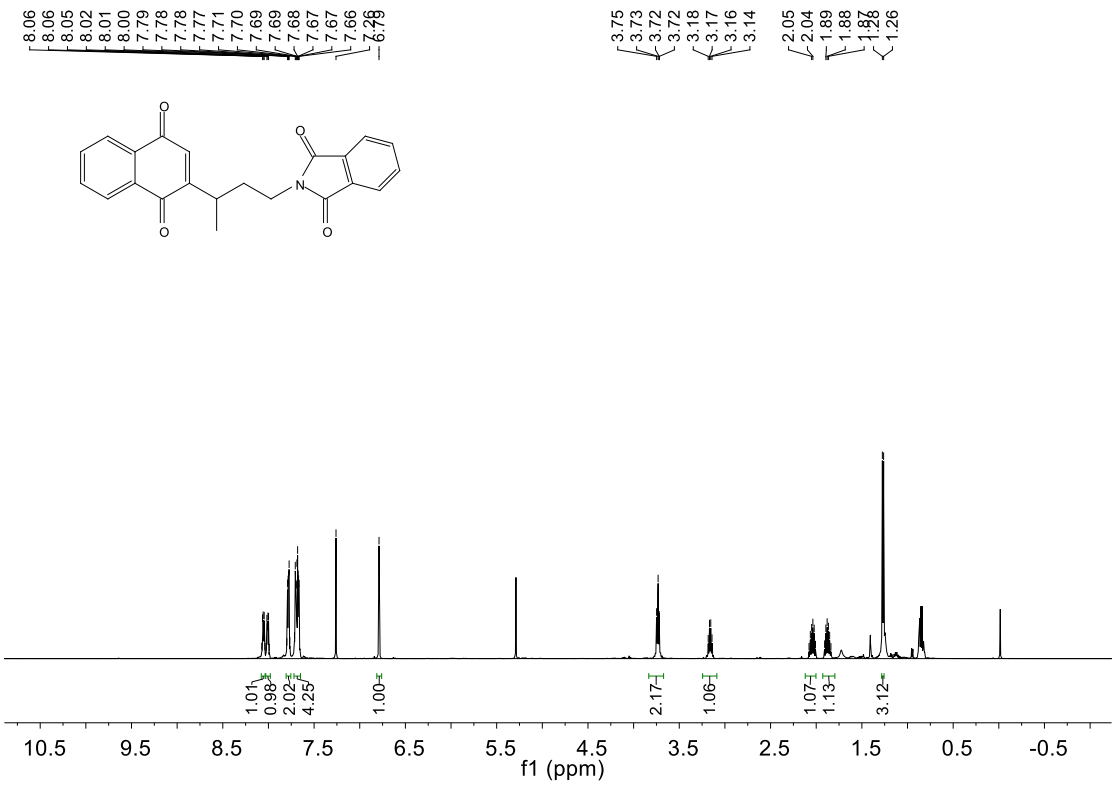



$^{13}$C NMR

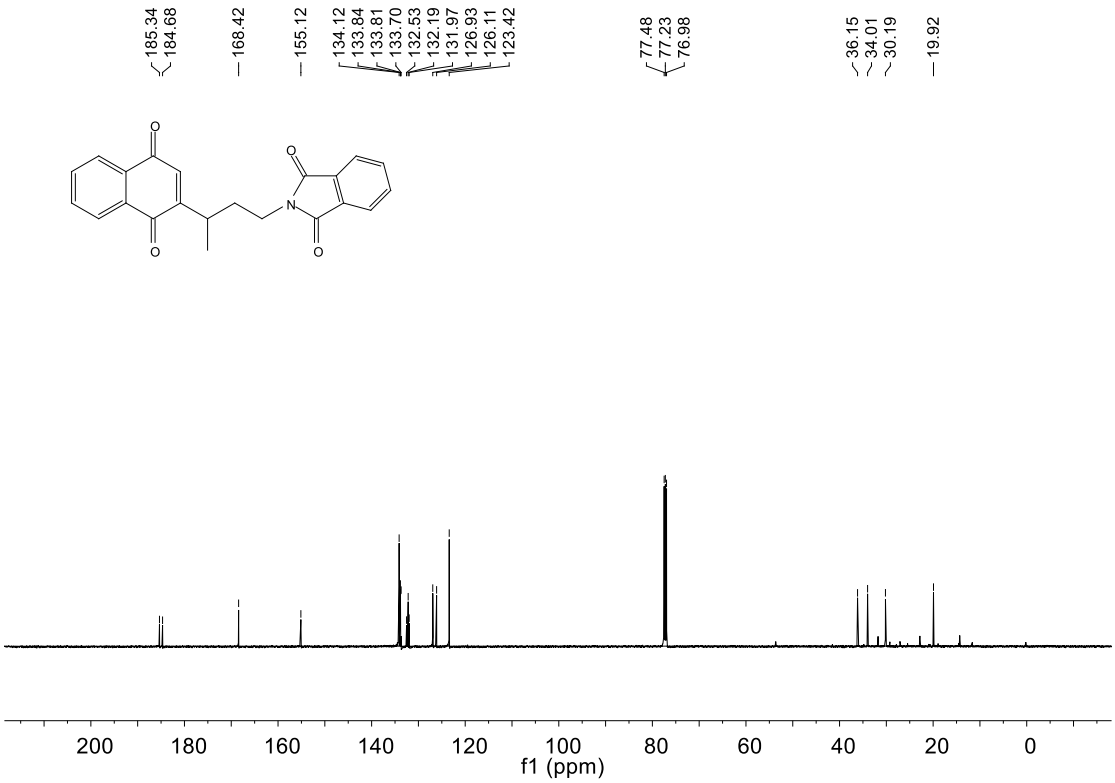


**Compound 22**

$^{1}$H NMR

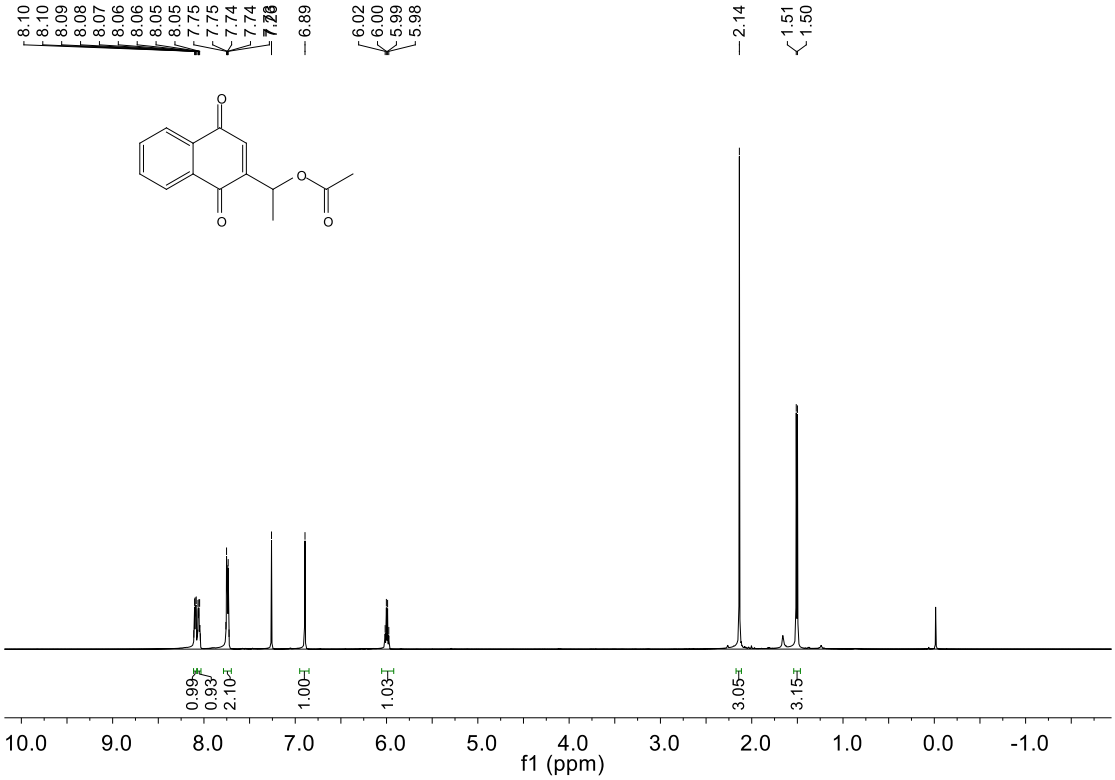



$^{13}$C NMR

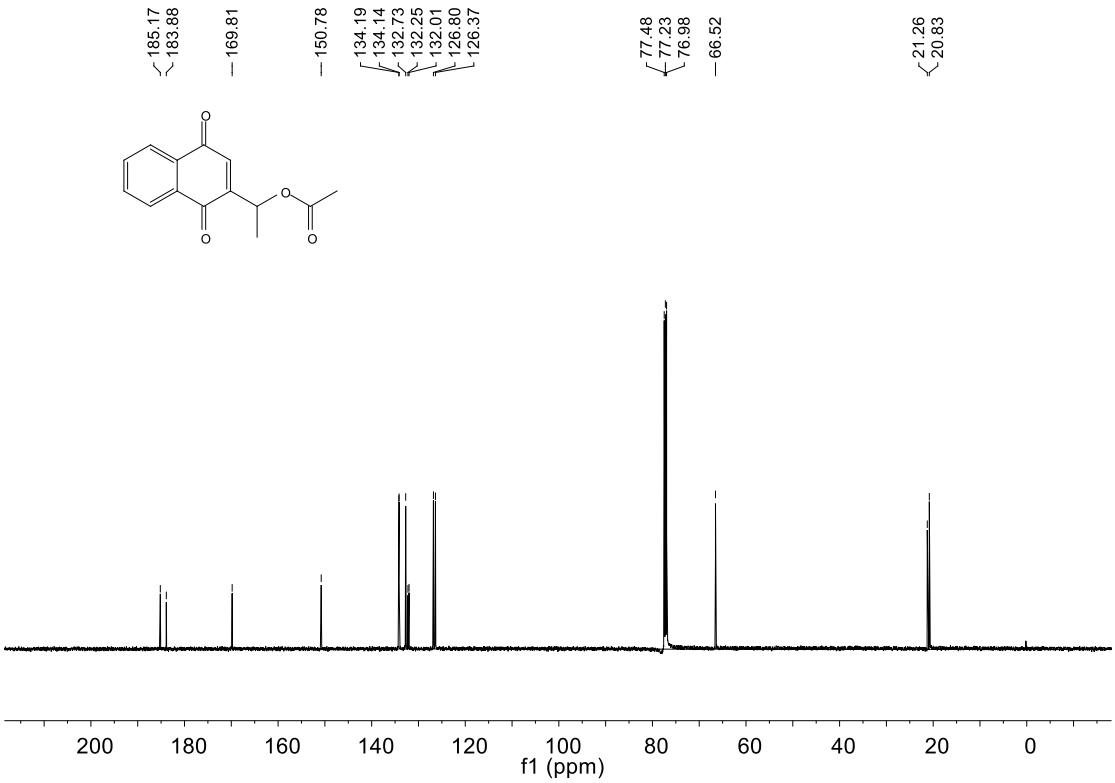


**Compound 23**

$^{1}$H NMR

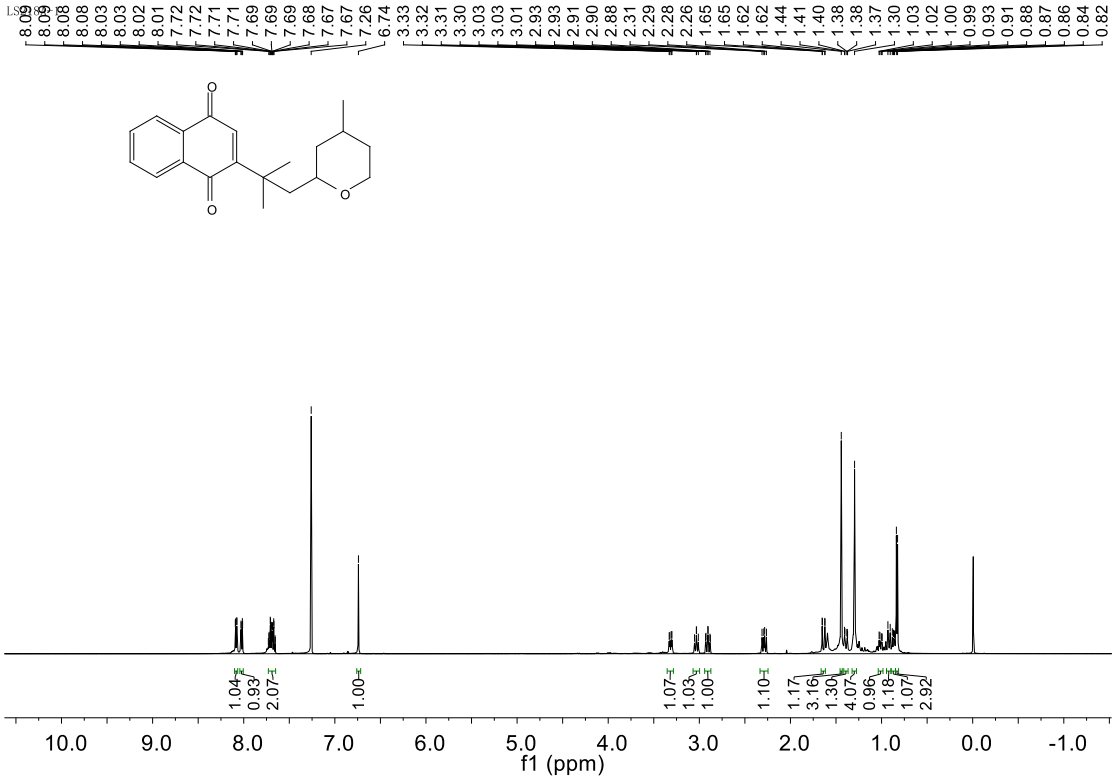



$^{13}$C NMR

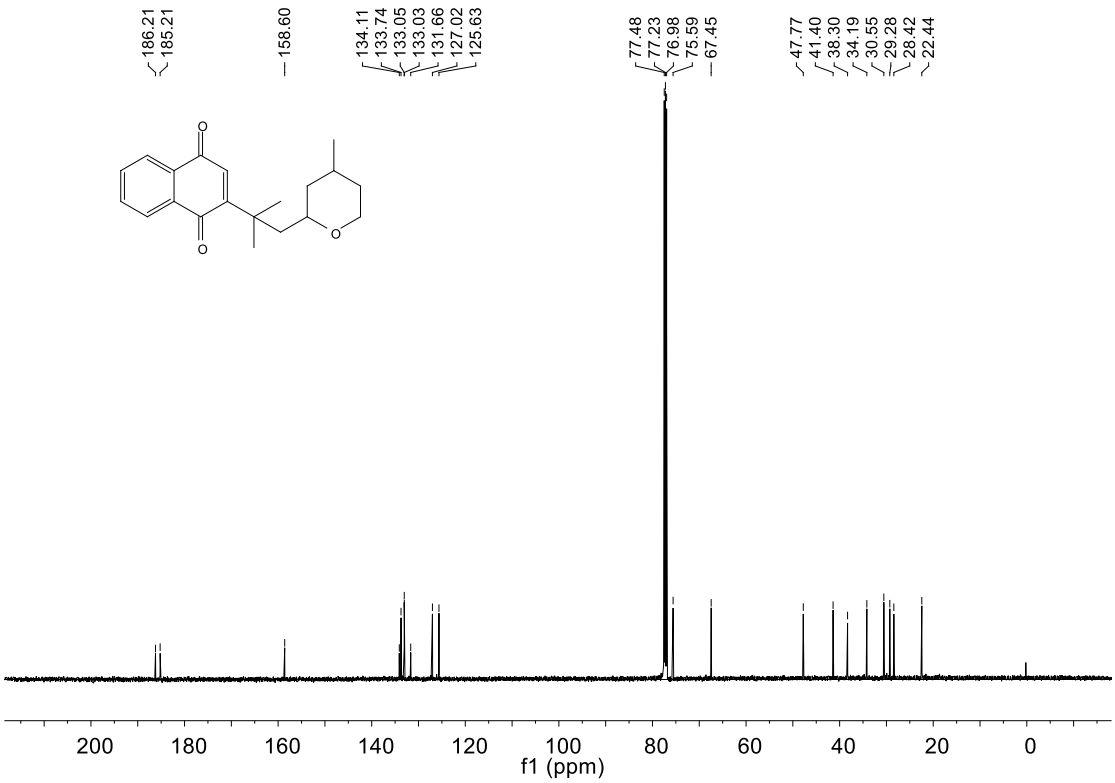


**Compound 24**

$^{1}$H NMR

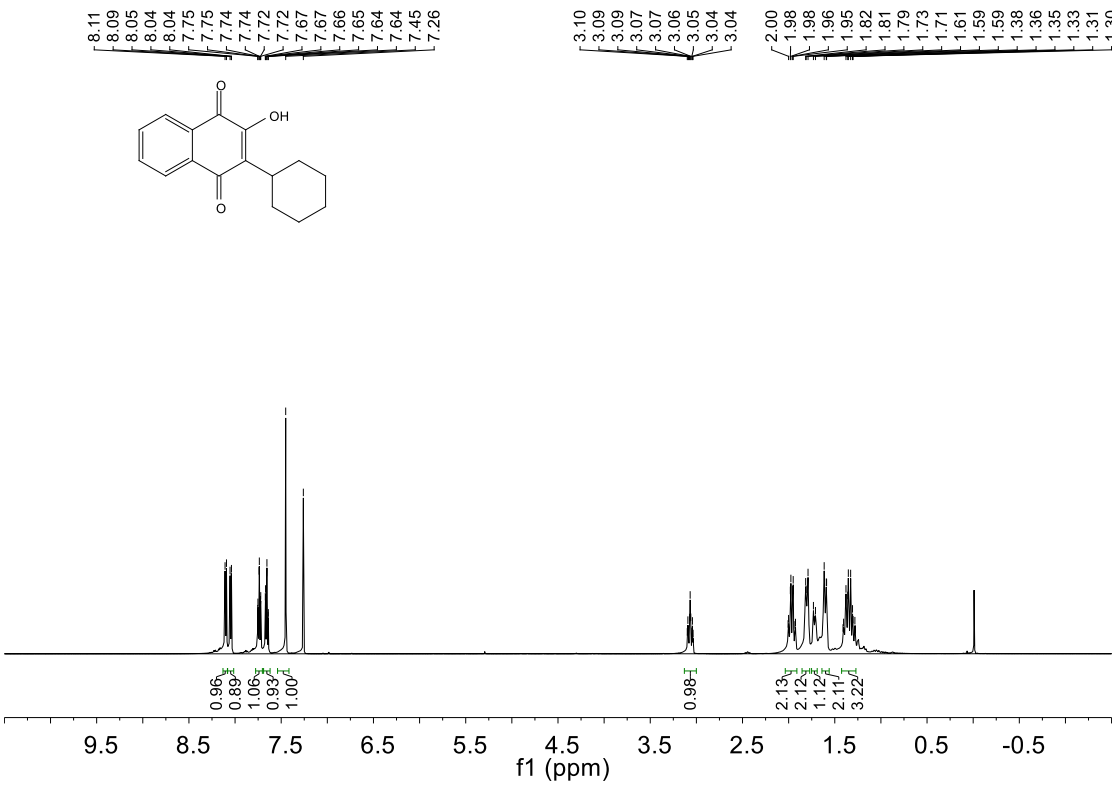



$^{13}$C NMR

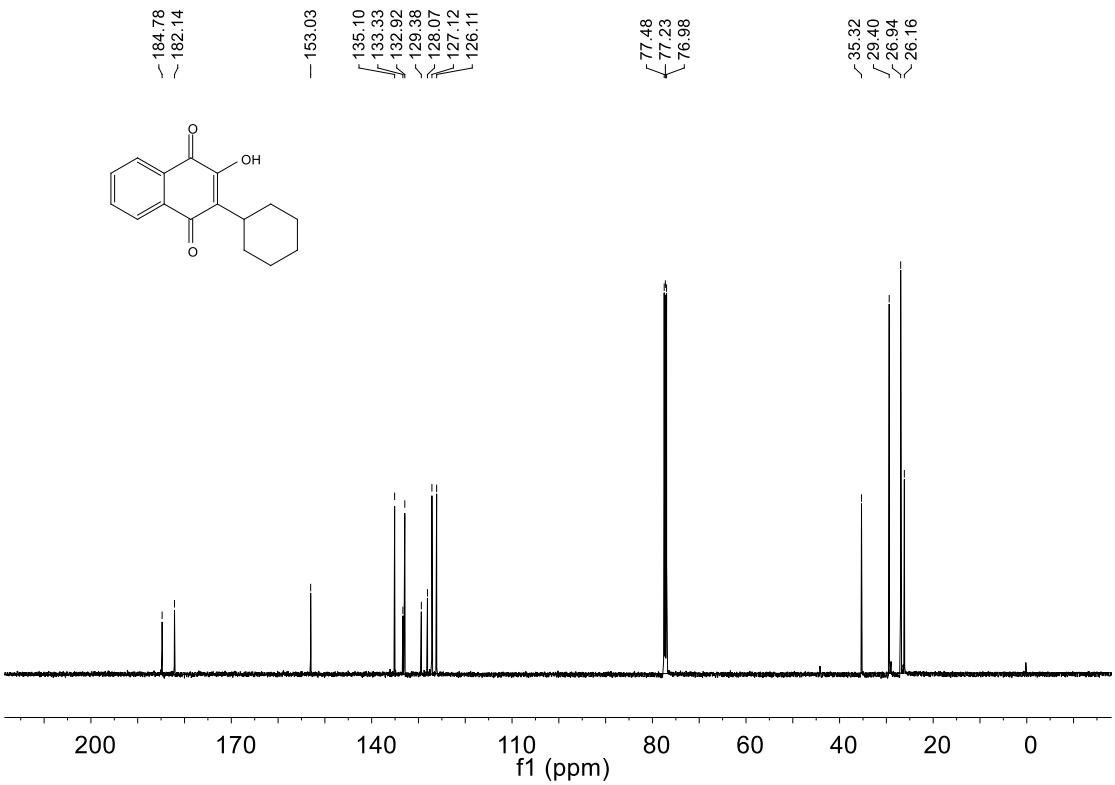


**Compound 25**

$^{1}$H NMR

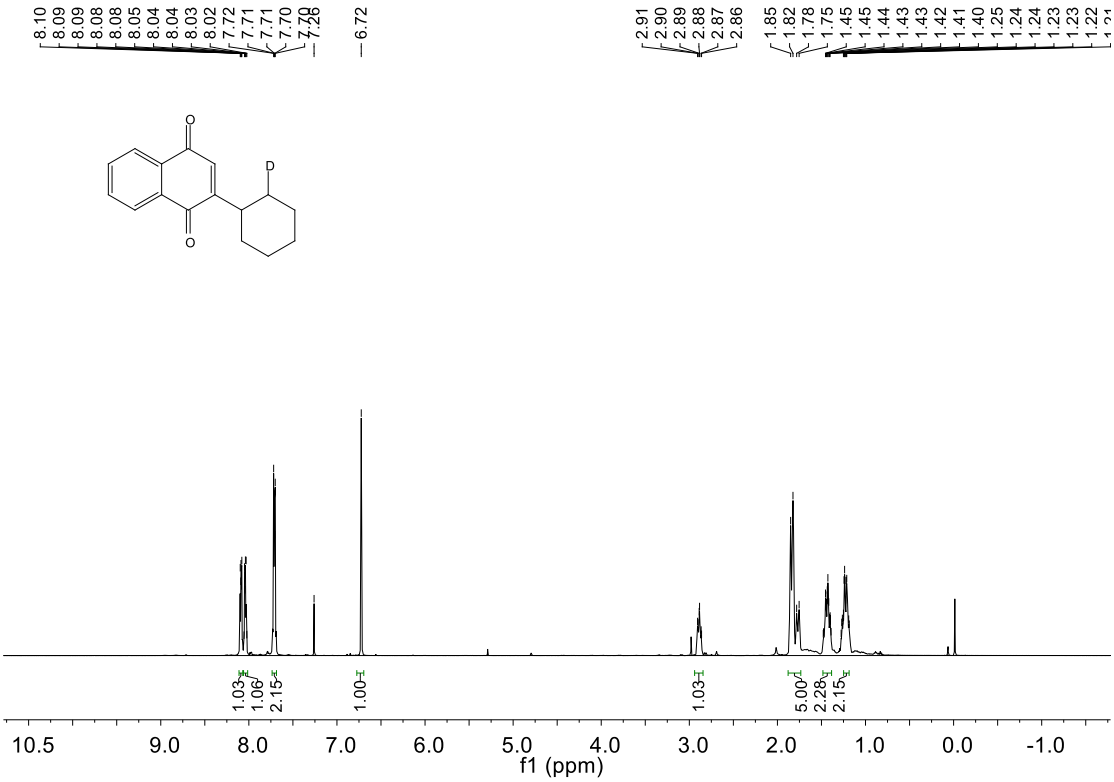



$^{13}$C NMR

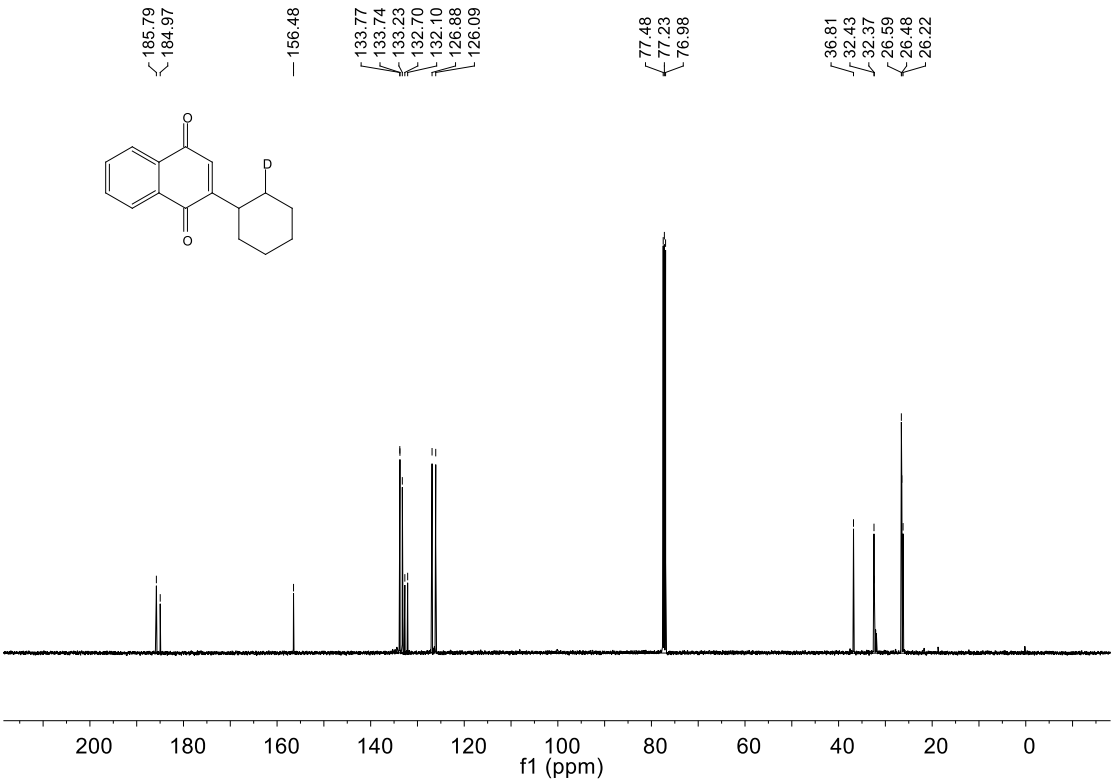


**Compound 26**

$^{1}$H NMR

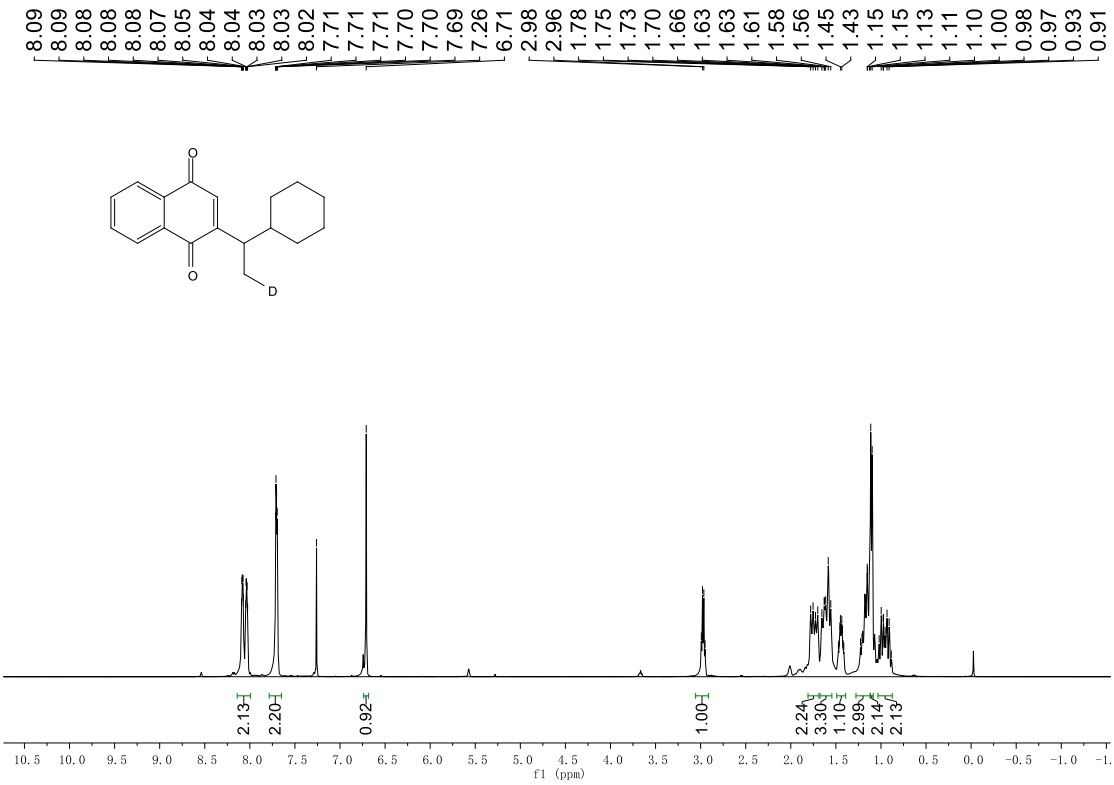



$^{13}$C NMR

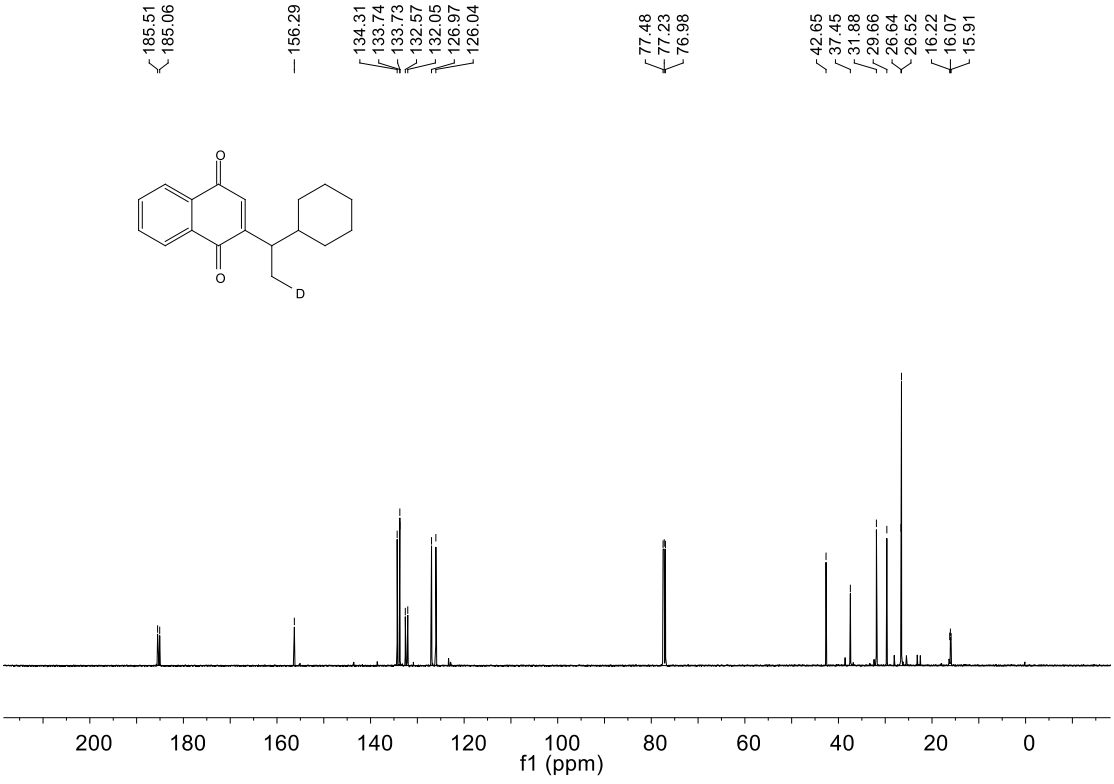


**Compound 27**

$^{1}$H NMR

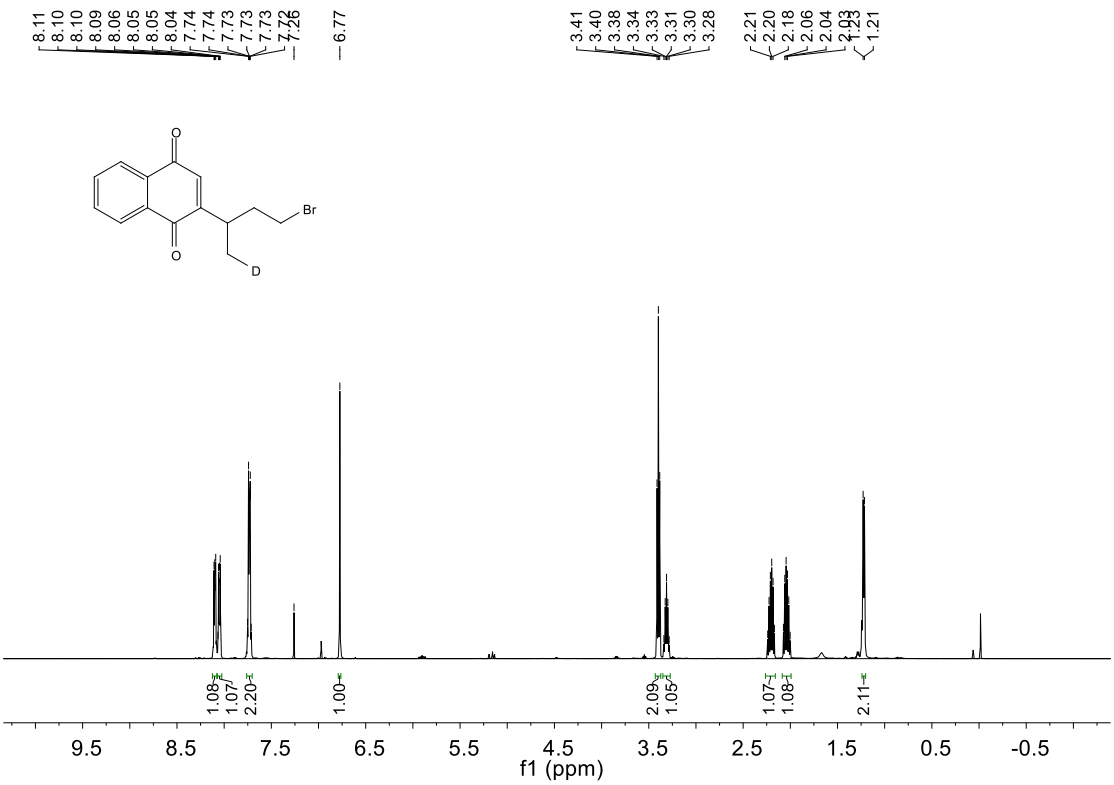



$^{13}$C NMR

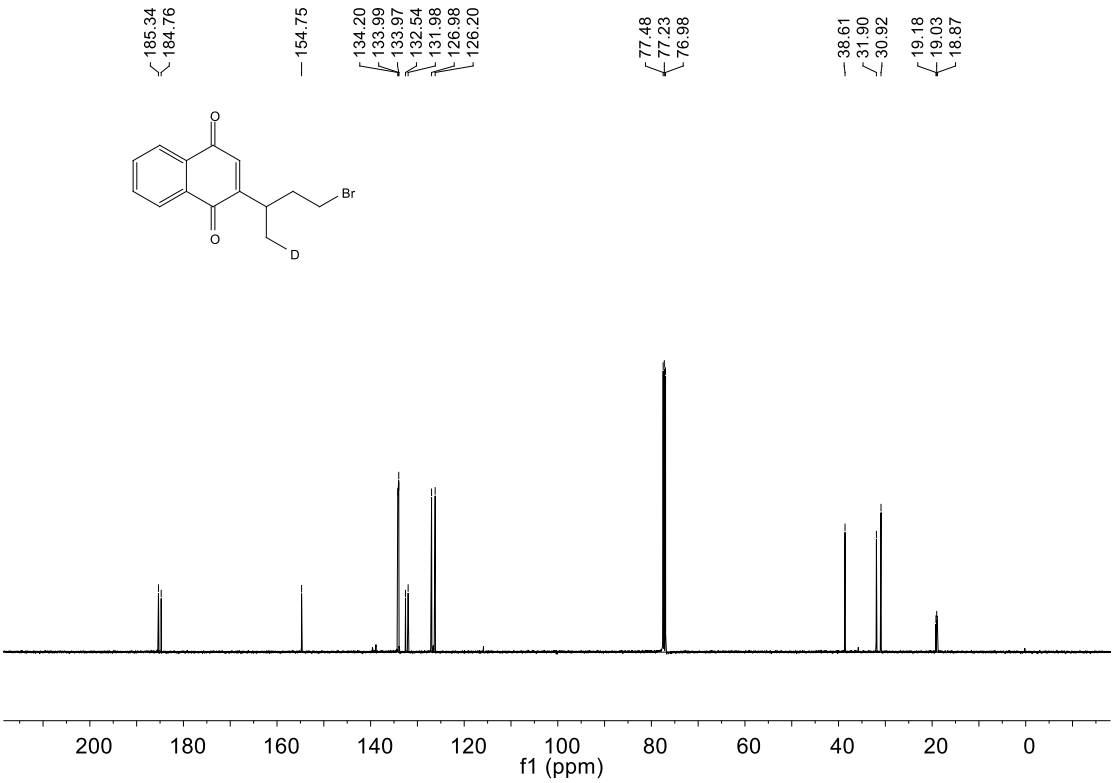


**Compound 28**

$^{1}$H NMR

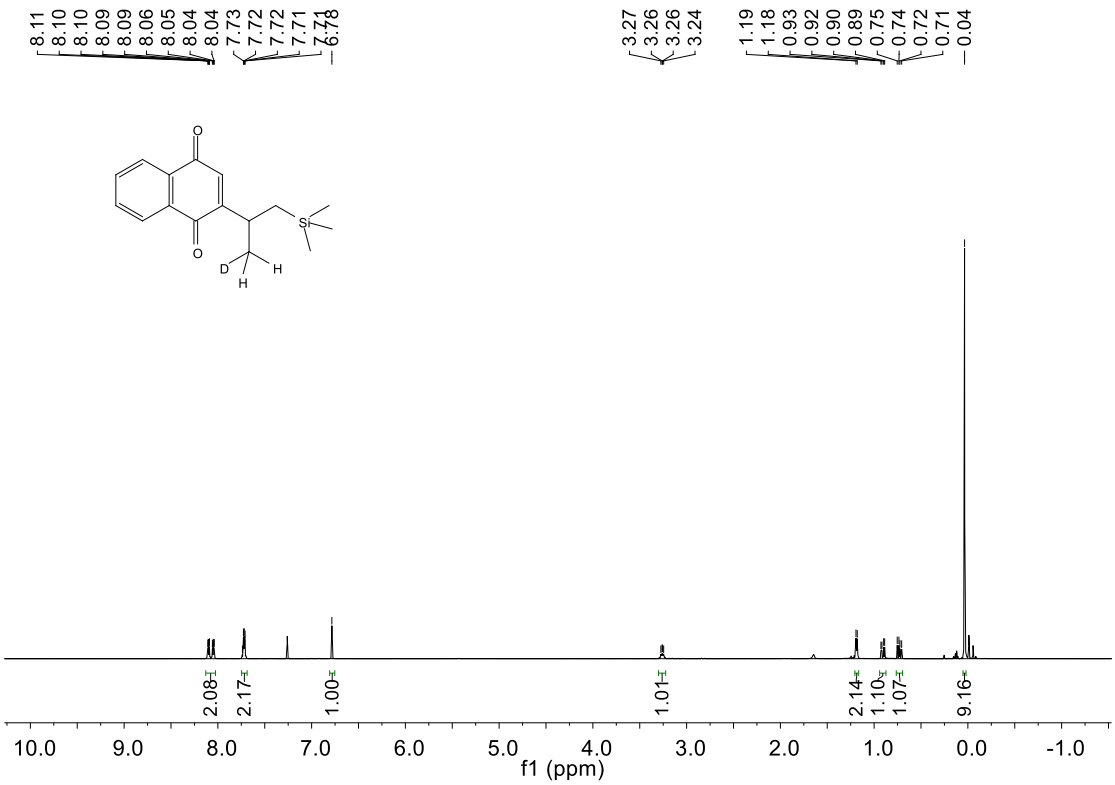



$^{13}$C NMR

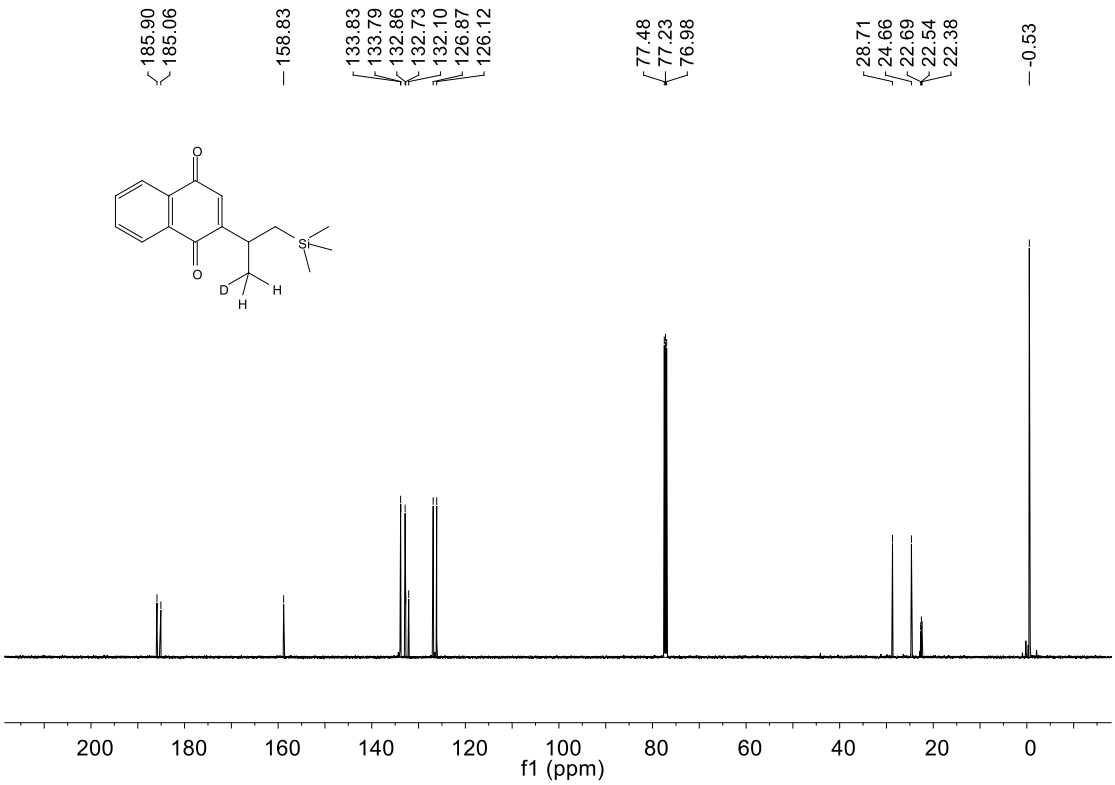


**Compound 29**

$^{1}$H NMR

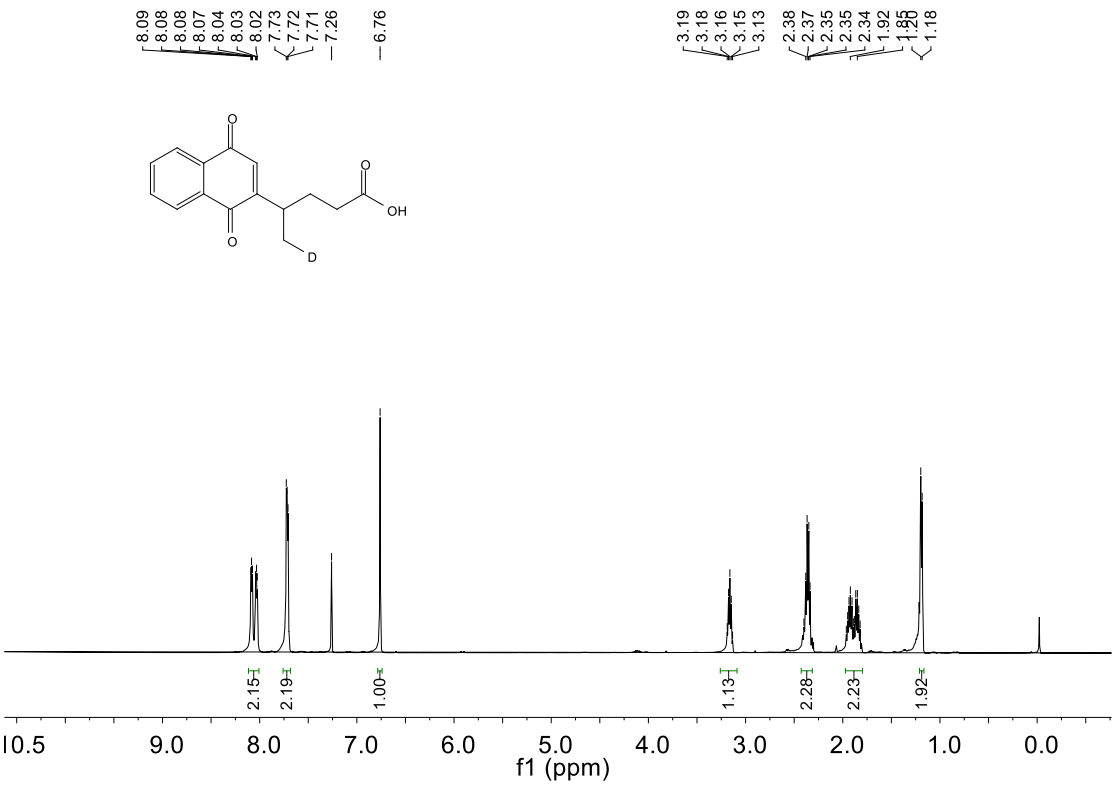



$^{13}$C NMR

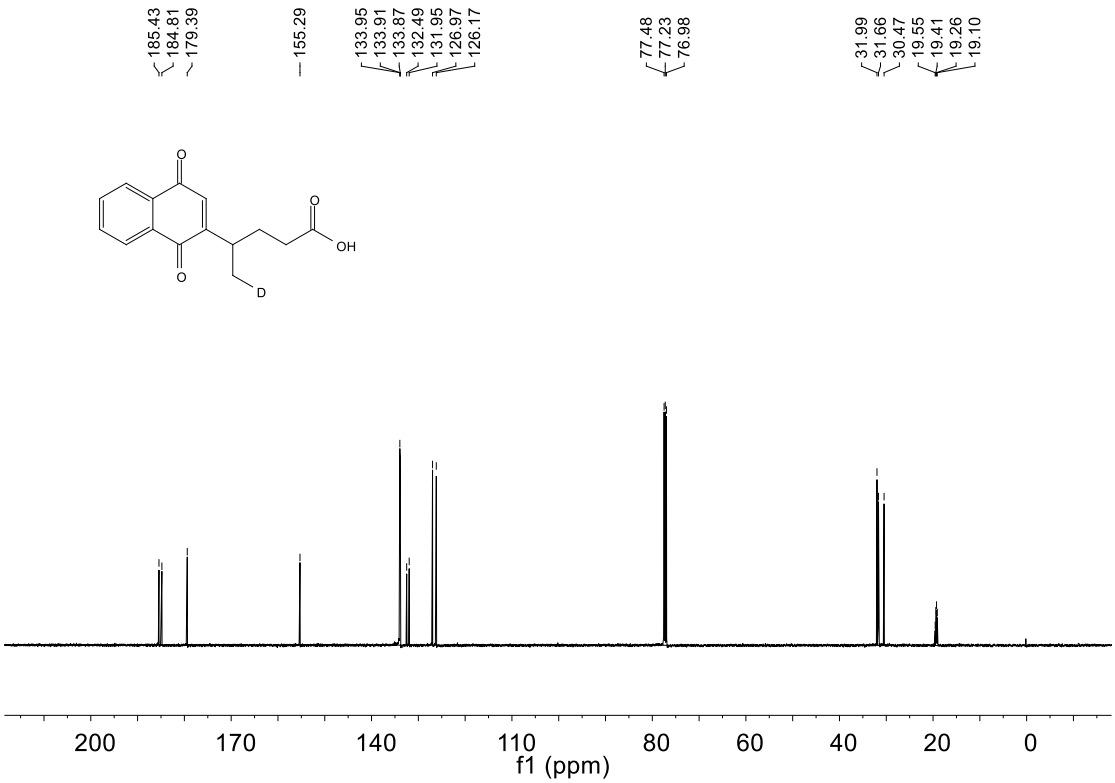


**Compound 30**

$^{1}$H NMR

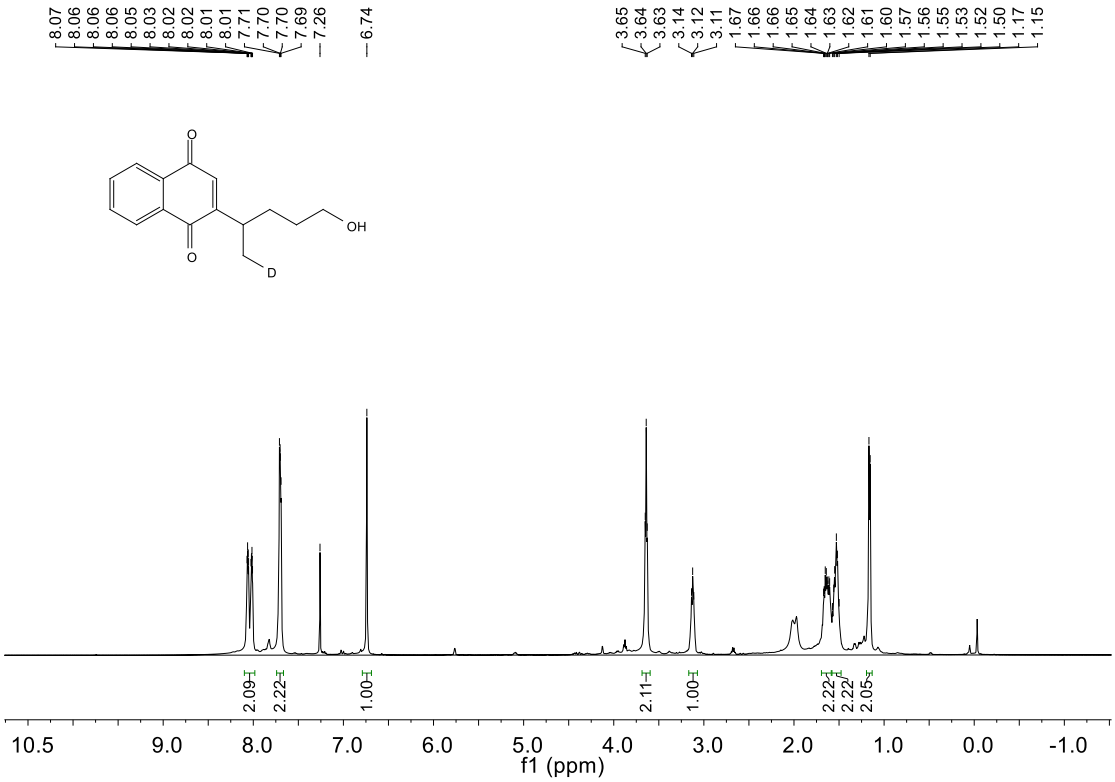



$^{13}$C NMR

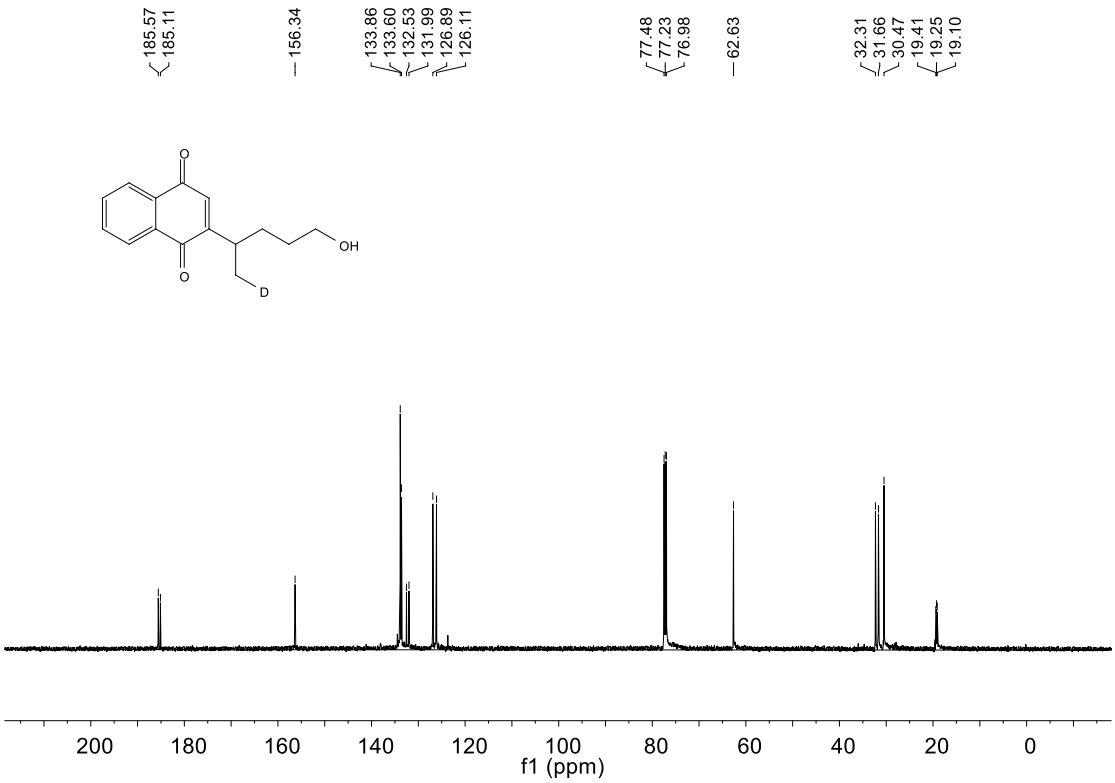


**Compound 31**

$^{1}$H NMR

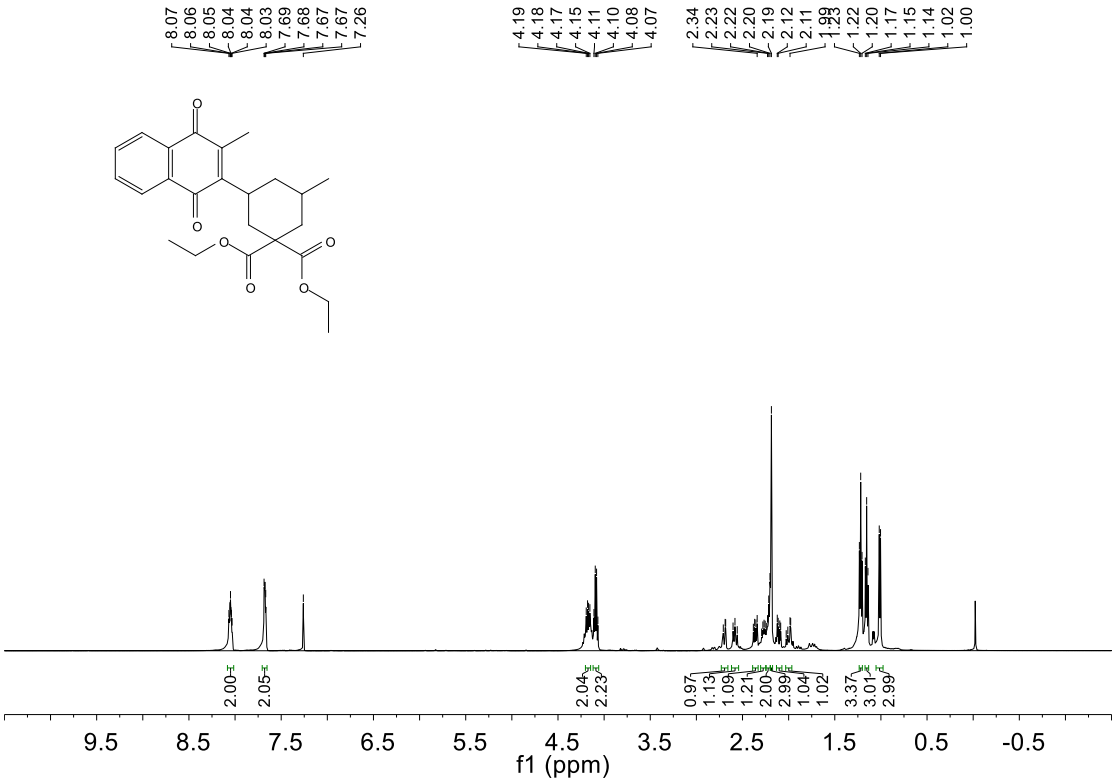



$^{13}$C NMR



**Compound 32**

$^{1}$H NMR




$^{13}$C NMR