Supplementary information

for

Bioinspired Intramolecular Spirocyclopropanation of Quinones as an Interrupted Photoredox Process

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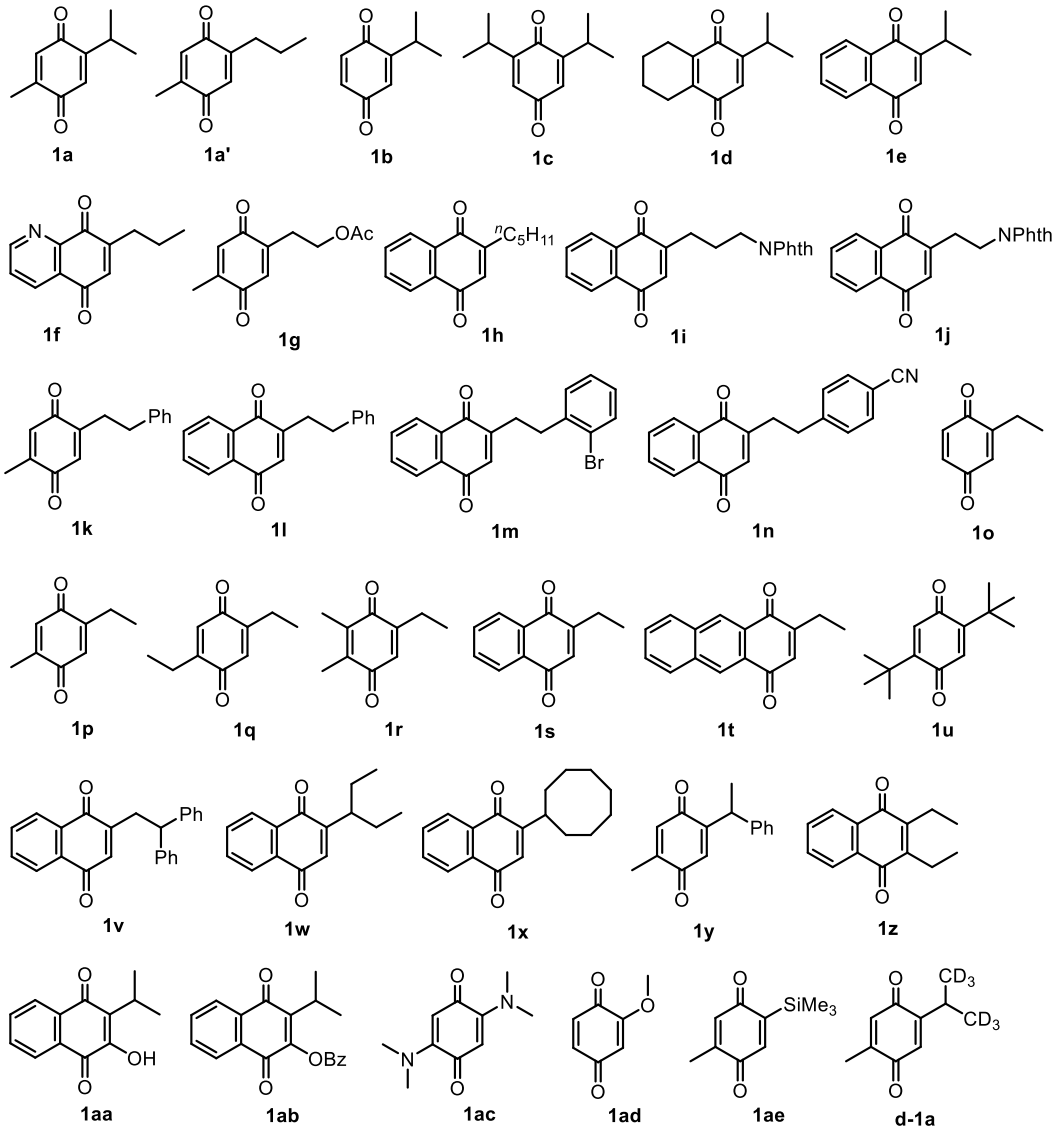
1. General

All reagents were purchased form commercial sources (Sigma-Aldrich, Fluorochem, TCI Chemicals, BLDPharm). Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane and dichloroethane from calcium hydride. Other solvents and all reagents were used without further purification unless otherwise noted. The room temperature was maintained between 20 and 25 °C. Column chromatography was performed on silica gel SiliaFlash® P60 (40−63 μm) from Silicycle. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 coated aluminum sheets (254 nm UV light and neutral aqueous $KMnO_4$ were used for visualization). The enantiomeric induction was measured by chiral HPLC (CHIRALPAK IA, 250×4.6 mm; 9/1 ^{n}heptane/^{i}PrOH as eluent; flow 1 mL/min; UV detection at 223 nm). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD Spectrometer (^{1}H at 400 MHz and ^{13}C at 101 MHz) as solutions in $CDCl_3$, acetone-d6 and C_6D_6. Chemical shifts are given in parts per million (ppm) and referenced to the residual solvent peaks: $CDCl_3$ (^{1}H, δ = 7.26; ^{13}C, δ = 77.2), acetone-d6 (^{1}H, δ = 2.05; ^{13}C, δ = 29.8) and C_6D_6 (^{1}H, δ = 7.16; ^{13}C, δ = 128.1), coupling constants *J* are given in Hz (Hertz), splitting patterns are abbreviated as s (singlet), br. s (broad singlet), d (doublet), t (triplet), q (quartet), hept (septet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), qd (quartet of doublets), hetptd (septet of doublets), ddd (doublet of doublets of doublets), ddt (doublet of doublets of triplets), dtt (doublet of triplets of triplets), and ddq (doublet of doublets of quartets). The IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer in KBr powder and are reported in wave numbers (cm^{-1}). The HRMS spectra were measured using Bruker amaZon SL and Bruker Esquire 3000. UV-Vis spectra were recorded on Unicam 340 spectrometer. Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTONIII by IμS micro-focus sealed tube. All melting points were determined on a meting point apparatus KB T3000.

2. Experimental procedures and compound characterization

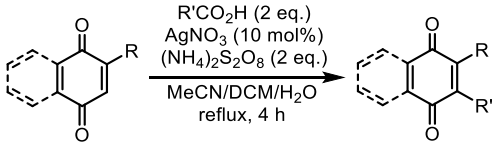
2.1 Synthesis of the starting quinones

The quinones used in this study are depicted on Scheme S1. Quinones **1a**, **1c**, **1u** and **1ad** were obtained from commercial sources and used without further purification. Quinones **1b**, **1d**, **1e**, **1h**, **1i**, **1j**, **1l**, **1m**, **1n**, **1o**, **1r**, **1s**, **1t**, **1v**, **1w**, **1z**, and **1aa** were synthesized by Minisci reaction according to the General Procedure A. Quinones **1a'**, **1g**, **1k**, **1p**, **1q**, **1y**, **1ae**, and **1af** were synthesized by oxidation of the corresponding dimethoxyarenes with ceric ammonium nitrate (CAN) according to the General Procedure B. Other quinones (**1f**, **1x**, **1ab**, and **1ac**) were prepared according to the previously reported methods as described below.



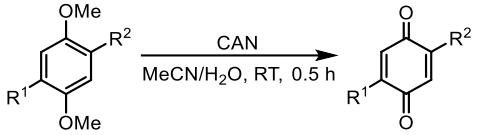
Scheme S1. Quinones used as the starting materials.

General procedure A: synthesis of quinones 1 by Minisci reaction



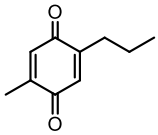
Following the literature method,[1] a biphasic solution containing a quinone (10 mmol), a carboxylic acid (20 mmol), $AgNO_3$ (1 mmol, 170 mg), $(NH_4)_2S_2O_8$ (20 mmol, 4.56 g) in DCM/MeCN/H_2O (20/20/40 mL, respectively) was stirred under reflux for 4 h. Next, water (100 mL) was added, the organic phase was separated, and the aqueous phase was extracted with DCM (2×30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography to give the corresponding monoalkylated quinone as the major product.

General procedure B: synthesis of quinones 1 by oxidation of *p*-dimethoxyarenes



Following the literature method,[2] to a solution of a *p*-dimethoxyarene (1 mmol) in MeCN (10 mL) was added a solution of CAN (2.2 mmol, 1.2 g) in water (10 mL) at room temperature and the resulting mixture was stirred for 0.5 h after addition. Next, the reaction mixture was quenched with 0.2 M aqueous KH_2PO_4 (10 mL), diluted with water (50 mL) and the product was extracted with Et_2O (3×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel gave the corresponding quinone.

2-Methyl-5-propyl-1,4-benzoquinone (1a')



To a solution of 1-bromo-2,5-dimethoxy-4-methylbenzene[3] (5 mmol, 1155 mg) in THF (20 mL) under Ar atmosphere was added ^{n}BuLi (2.5 M in hexanes, 5 mmol, 2 mL) dropwise at -78 °C. After stirring for 0.5 h at this temperature *n*-propyl iodide (5.5 mmol, 935 mg, 0.55 mL) was added dropwise. The reaction mixture was allowed to reach room temperature over 2 h and the stirring was continued for the next 24 h. Water (50 mL) was added and the product was extracted with EtOAc (3×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in hexanes/EtOAc (75/1, 20 mL), vacuum filtered through a pad of silica gel, which was then washed with hexanes/EtOAc (75/1, 200 mL). The solution was concentrated under reduced pressure to give the crude arene, which was directly

[1] a) Coppa, F.; Fontana, F.; Lazzarini, E.; Minisci, F. *Chem. Lett.* **1992**, *21*, 1299–1302; b) Bauch, M.; Fudickar, W.; Linker, T. *Molecules*, **2021**, *26*, 804.
[2] Lumb, J.-P.; Trauner, D. *Org. Lett.* **2005**, *7*, 5865–5868.
[3] Klein, R.; Sunassee, S. N.; Davies-Coleman, M. T. *J. Chem. Res.* **2009**, *8*, 468–472.

oxidized with CAN according to the General Procedure B (5 mmol scale). Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 640 mg (78% overall) of the title compound as a yellow oil.

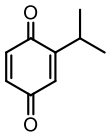
TLC R_f = 0.55 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (q, *J* = 1.6 Hz, 1H), 6.53 (t, *J* = 1.5 Hz, 1H), 2.37 (td, *J* = 7.4, 1.5 Hz, 2H), 2.02 (d, *J* = 1.6 Hz, 3H), 1.52 (sextet, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.4, 188.0, 149.5, 145.6, 133.7, 132.6, 30.8, 21.2, 15.6, 13.9.

The recorded spectroscopic values agree with the previously reported data.[4]

2-Isopropyl-1,4-benzoquinone (1b)



General procedure A was followed using *p*-benzoquinone (5 mmol, 540 mg) and isobutyric acid (10 mmol, 881 mg). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 100 mg (13%) of the title compound as a yellow oil.

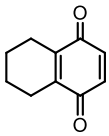
TLC R_f = 0.50 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 10.1 Hz, 1H), 6.70 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.54 (dd, *J* = 2.4, 1.2 Hz, 1H), 3.04 (heptd, *J* = 6.9, 1.2 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.3, 187.3, 155.2, 137.2, 136.1, 130.5, 27.0, 21.5 (2C).

The recorded spectroscopic values agree with the previously reported data.[5]

5,6,7,8-Tetrahydronaphthoquinone



The title compound was prepared by Co-catalyzed oxidation of 5,6,7,8-tetrahydro-1-naphthol (2.5 mmol, 370 mg) according to the literature procedure.[6] Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 173 mg (43%) of the title compound as a yellow solid.

TLC R_f = 0.50 (4/1 hexanes/EtOAc);

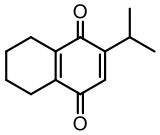
M.p. 55 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (s, 2H), 2.45 – 2.39 (m, 4H), 1.72 – 1.66 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.6 (2C), 142.6 (2C), 136.4 (2C), 22.7 (2C), 21.1 (2C).

The recorded spectroscopic values agree with the previously reported data.[7]

2-Isopropyl-5,6,7,8-tetrahydronaphthalene-1,4-dione (1d)



General procedure A was followed using 5,6,7,8-tetrahydronaphthoquinone (1 mmol, 162 mg) and propionic acid (2 mmol, 185 μL). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 114 mg (56%) of the title compound as a yellow oil.

[4] Hargreaves, R. H. J.; O'Hare, C. C.; Hartley, J. A.; Ross, D.; Butler, J. *J. Med. Chem.* **1999**, *42*, 2245–2250.
[5] Abreu, B. L.; Boufroura, H.; Moore, J. C.; Poliakoff, M.; George, M. W. *Synthesis* **2022**, *54*, 3651–3657.
[6] van Dort, H. M.; Geursen, H. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 520–526.
[7] Mal, D.; Ray, S.; Sharma, I. *J. Org. Chem.* **2007**, *72*, 4981–4984.

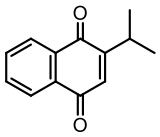
TLC R_f = 0.55 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (d, *J* = 1.2 Hz, 1H), 3.03 (heptd, *J* = 6.9, 1.2 Hz, 1H), 2.45 – 2.37 (m, 4H), 1.71 – 1.65 (m, 4H), 1.11 (d, *J* = 6.9 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.3, 187.4, 154.7, 142.8, 141.9, 130.1, 26.8, 22.9, 22.5, 21.6 (2C), 21.4, 21.2;

HRMS (ESI): m/z calcd for $C_{13}H_{16}NaO_2^+$: 227.1043 $[M+Na]^+$; found: 227.1046.

2-Isopropyl-1,4-naphthoquinone (1e)



General procedure A was followed using 1,4-naphthoquinone (5 mmol, 790 mg) and isobutyric acid (10 mmol, 0.90 mL). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 450 mg (45%) of the title compound as a yellow oil.

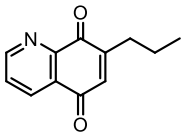
TLC R_f = 0.52 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.08 (m, 1H), 8.07 – 8.02 (m, 1H), 7.74 – 7.69 (m, 2H), 6.77 (d, *J* = 1.1 Hz, 1H), 3.24 (heptd, *J* = 6.9, 1.1 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.7, 184.9, 157.4, 133.8, 133.7, 132.8, 132.7, 132.1, 126.8, 126.1, 27.2, 21.7 (2C).

The recorded spectroscopic values agree with the previously reported data.[1b]

7-Propylquinoline-5,8-dione (1f)



The title compound was prepared according to the literature procedure[8] using 8-hydroxy-7-propylquinoline (3 mmol, 561 mg) and (bis(trifluoroacetoxy)iodo)benzene (4.5 mmol, 1.94 g). Column chromatography on silica gel (1/7 hexanes/Et_2O) gave 383 mg (63%) of the title compound as an orange solid.

TLC R_f = 0.35 (Et_2O);

M.p. 75 °C;

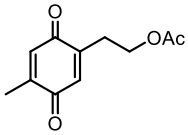
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.39 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.67 (dd, *J* = 7.9, 4.6 Hz, 1H), 6.85 (t, *J* = 1.3 Hz, 1H), 2.61 (td, *J* = 7.4, 1.3 Hz, 2H), 1.64 (sextet, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.5, 183.4, 154.5, 152.8, 147.9, 134.4, 134.2, 129.1, 127.7, 31.8, 21.3, 13.9;

HRMS (ESI): m/z calcd for $C_{12}H_{11}NNaO_2^+$: 224.0682 $[M+Na]^+$; found: 224.0681.

[8] Morin, C.; Besset, T.; Moutet, J.-C.; Fayolle, M.; Brückner, M.; Limosin, D.; Becker, K.; Davioud-Charvet, E. *Org. Biomol. Chem.* **2008**, *6*, 2731–2742.

2-(4-Methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)ethyl acetate (1g)



To a stirred solution of 2,5-dimethoxy-4-methylphenethyl alcohol[9] (1 mmol, 196 mg) and Et_3N (1.5 mmol, 152 mg, 210 µl) in DCM (5 mL) was added Ac_2O (1.25 mmol, 120 µl) at 0 °C. The reaction mixture was stirred for 1 h at this temperature and for 8 h at room temperature. Next, water (10 mL) was added, the organic phase was separated, and the aqueous phase was extracted with DCM (2×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude 2,5-dimethoxy-4-methylphenethyl acetate, which was directly oxidized with CAN according to the General Procedure B (1 mmol scale). Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 134 mg (64% overall) of the title compound as a yellow solid.

TLC R_f = 0.37 (3/1 hexanes/EtOAc);

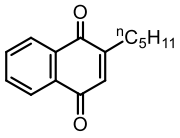
M.p. 36 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (q, *J* = 1.6 Hz, 1H), 6.60 (t, *J* = 1.3 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 2.73 (td, *J* = 6.3, 1.3 Hz, 2H), 2.04 (d, *J* = 1.6 Hz, 3H), 2.02 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.0, 187.3, 170.9, 146.0, 145.4, 134.1, 133.6, 61.9, 28.7, 21.0, 15.7;

HRMS (ESI): m/z calcd for $C_{11}H_{12}NaO_4^+$: 231.0628 $[M+Na]^+$; found: 231.0630.

2-Pentyl-1,4-naphthoquinone (1h)



General procedure A was followed using 1,4-naphthoquinone (10 mmol, 1.58 g) and caproic acid (20 mmol, 2.50 mL). Column chromatography on silica gel (150/1 hexanes/EtOAc) gave 1.16 g (51%) of the title compound as a yellow oil.

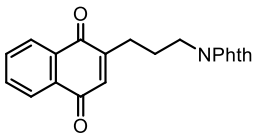
TLC R_f = 0.57 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.03 (m, 2H), 7.75 – 7.69 (m, 2H), 6.79 (t, *J* = 1.4 Hz, 1H), 2.56 (td, *J* = 7.6, 1.4 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.42 – 1.32 (m, 4H), 0.94 – 0.87 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.41, 185.39, 152.1, 134.9, 133.75, 137.72, 132.5, 132.3, 126.7, 126.2, 31.7, 29.7, 27.9, 22.6, 14.1.

The recorded spectroscopic values agree with the previously reported data.[10]

2-(3-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)propyl)isoindoline-1,3-dione (1i)



General procedure A was followed using 1,4-naphthoquinone (4 mmol, 632 mg) and *N*-phthaloyl-γ-aminobutyric acid[1111] (8 mmol, 1.98 g). Crystallization of the crude product from EtOAc gave 497 mg (36%) of the title compound as a yellow powder.

TLC R_f = 0.45 (1/1 hexanes/EtOAc);

[9] Nilsson, J. L. G.; Sievertsson, H.; Selander, H. *Acta Chem. Scand.* **1968**, *22*, 3160–3170.
[10] Yamashita, M.; Ohishi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1187–1190.
[11] Guénin, E.; Monteil, M.; Bouchemal, N.; Prangé, T.; Lecouvey, M. *Eur. J. Org. Chem.* **2007**, 3380–3391.

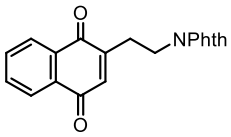
M.p. 178 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 – 8.00 (m, 2H), 7.86 – 7.80 (m, 2H), 7.73 – 7.68 (m, 4H), 6.84 (t, *J* = 1.3 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 2H), 2.66 – 2.60 (m, 2H), 2.04 – 1.95 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.0 (2C), 168.4 (2C), 150.4, 135.2, 134.1, 133.82, 133.78, 132.3, 132.2, 132.1 (2C), 126.7, 126.2, 123.4 (2C), 37.6, 27.1, 26.9;

HRMS (ESI): m/z calcd for $C_{21}H_{15}NNaO_4^+$: 368.0893 [M+Na]$^+$; found: 368.0896.

2-(2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl)isoindoline-1,3-dione (1j)



General procedure A was followed using 1,4-naphthoquinone (4 mmol, 632 mg) and *N*-phthaloyl-β-alanine[11] (8 mmol, 1.68 g). Column chromatography on silica gel (10/10/1 hexanes/DCM/EtOAc) gave 379 mg (29%) of the title compound as a yellow solid.

TLC R_f = 0.41 (1/1 hexanes/EtOAc);

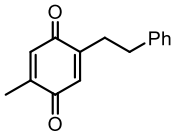
M.p. 186 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 8.06 (m, 1H), 8.01 – 7.96 (m, 1H), 7.79 – 7.74 (m, 2H), 7.73 – 7.65 (m, 4H), 6.70 (br. s, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.95 – 2.89 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.8, 184.7, 168.2 (2C), 148.1, 136.0, 134.2 (2C), 133.9, 133.8, 132.2, 132.1, 131.9 (2C), 126.8, 126.2, 123.5 (2C), 36.6, 30.0;

HRMS (ESI): m/z calcd for $C_{20}H_{13}NNaO_4^+$: 354.0737 [M+Na]$^+$; found: 354.0732.

2-Methyl-5-phenethyl-1,4-benzoquinone (1k)



Following a literature procedure,[12] a solution of 1-bromo-2,5-dimethoxy-4-methylbenzene (3 mmol, 693 mg), styrene (4.5 mmol, 515 µl), piperidine (1 mL), $Pd(PPh_3)_4$ (0.09 mmol, 104 mg) and LiCl (0.1 mmol, 4 mg) in dry DMF (6 mL) was stirred under Ar atmosphere at 180 °C for 3 h in a microwave reactor (Anton Paar Monowave 400). After cooling to room temperature, the reaction mixture was poured into water (50 mL), and the product was extracted with EtOAc (3×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in hexanes/EtOAc (75/1, 20 mL), vacuum filtered through a pad of silica gel, which was then washed with hexanes/EtOAc (75/1, 200 mL). The solution was concentrated under reduced pressure to give the crude stilbene, which was dissolved in MeOH (20 mL) and hydrogenated at room temperature for 2 h (1 atm H_2, 150 mg Pd/C (10% Pd by weight)). The volatiles were removed under reduced pressure, and the residue was dissolved in hexanes/Et_2O (20/1, 20 mL), vacuum filtered through a pad of silica gel, which was then washed with hexanes/Et_2O (20/1, 200 mL). The solution was concentrated under reduced pressure to give crude 1,4-dimethoxy-2-methyl-5-phenethylbenzene, which was oxidized with CAN according to the General

[12] Martí-Centelles, R.; Falomir, E., Murga, J.; Carda, M.; Marco, J. A. *Eur. J. Med. Chem.* **2015**, *103*, 488–496.

Procedure B (2 mmol scale). Column chromatography on silica gel (30/1 hexanes/EtOAc) gave 315 mg (46% overall) of the title compound as a yellow solid.

TLC R_f = 0.48 (4/1 hexanes/EtOAc);

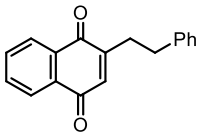
M.p. 79 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.60 (q, *J* = 1.6 Hz, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 2.86 – 2.79 (m, 2H), 2.76 – 2.70 (m, 2H), 2.03 (d, *J* = 1.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.2, 187.8, 148.4, 145.8, 140.5, 133.7, 133.1, 128.7 (2C), 128.5 (2C), 126.5, 34.2, 30.8, 15.6;

HRMS (ESI): m/z calcd for $C_{15}H_{14}NaO_2^+$: 249.0886 $[M+Na]^+$; found: 249.0888.

2-Phenethyl-1,4-naphthoquinone (1l)



General procedure A was followed using 1,4-naphthoquinone (4 mmol, 632 mg) and hydrocinnamic acid (8 mmol, 1.20 g). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 657 mg (63%) of the title compound as a yellow oil.

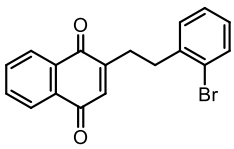
TLC R_f = 0.45 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.03 (m, 2H), 7.76 – 7.71 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 6.73 (br. s, 1H), 2.94 – 2.86 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.24, 185.16, 150.7, 140.6, 135.4, 133.83, 133.79, 132.4, 132.2, 128.7 (2C), 128.5 (2C), 126.7, 126.5, 126.2, 34.4, 31.7.

The recorded spectroscopic values agree with the previously reported data.[13]

2-(2-Bromophenethyl)-1,4-naphthoquinone (1m)



General procedure A was followed using 1,4-naphthoquinone (5 mmol, 790 mg) and 3-(2-bromophenyl)propionic acid (10 mmol, 2.29 g). Column chromatography on silica gel (20/1 hexanes/EtOAc) gave a yellow oil, which was crystallized from hexanes/benzene to give 961 mg (56%) of the title compound as yellow prisms.

TLC R_f = 0.39 (4/1 hexanes/EtOAc);

M.p. 104 °C;

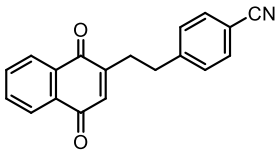
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.09 (m, 1H), 8.09 – 8.03 (m, 1H), 7.76 – 7.71 (m, 2H), 7.56 – 7.50 (m, 1H), 7.25 – 7.19 (m, 2H), 7.12 – 7.04 (m, 1H), 6.72 (t, *J* = 1.2 Hz, 1H), 3.07 – 3.00 (m, 2H), 2.92 – 2.85 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.22, 185.16, 150.4, 139.9, 135.5, 133.9, 133.8, 133.1, 132.4, 132.2, 130.6, 128.3, 127.8, 126.8, 126.2, 124.6, 34.9, 30.3.

HRMS (ESI): m/z calcd for $C_{18}H_{13}BrNaO_2^+$: 362.9991 $[M+Na]^+$; found: 362.9989.

[13] Baxter, I.; Sanders, J. K. M.; Evans, G. E. *J. Chem. Soc. Perkin Trans. 1*, **1974**, 2574–2577.

4-(2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl)benzonitrile (1n)



General procedure A was followed using 1,4-naphthoquinone (5 mmol, 790 mg) and 3-(4-cyanophenyl)propionic acid (10 mmol, 1.75 g). Column chromatography on silica gel (1/1 DCM/EtOAc) gave a yellow oil, which was crystallized from EtOAc/Et_2O to give 313 mg (22%) of the title compound as yellow solid.

TLC R_f = 0.55 (1/1 hexanes/EtOAc);

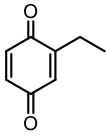
M.p. 157 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.01 (m, 2H), 7.78 – 7.70 (m, 2H), 7.62 – 7.55 (m, 2H), 7.36 – 7.30 (m, 2H), 6.78 – 6.67 (m, 1H), 3.01 – 2.92 (m, 2H), 2.92 – 2.85 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.1, 184.9, 149.8, 146.2, 135.6, 134.05, 133.96, 132.6 (2C), 132.23, 132.16, 129.4 (2C), 126.8, 126.3, 119.0, 110.5, 34.5, 31.2.

HRMS (ESI): m/z calcd for $C_{19}H_{13}NNaO_2^+$: 310.0838 $[M+Na]^+$; found: 310.0834.

2-Ethyl-1,4-benzoquinone (1o)



General procedure A was followed using *p*-benzoquinone (7.5 mmol, 810 mg) and propionic acid (15 mmol, 1.12 mL). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 510 mg (50%) of the title compound as a yellow solid.

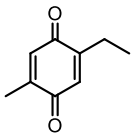
TLC R_f = 0.34 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 10.1 Hz, 1H), 6.71 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.56 (dt, *J* = 2.4, 1.7 Hz, 1H), 2.46 (qd, *J* = 7.4, 1.7 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.0, 187.6, 151.0, 136.9, 136.4, 131.8, 22.2, 11.7.

The recorded spectroscopic values agree with the previously reported data.[5]

2-Ethyl-5-methyl-1,4-benzoquinone (1p)



The title product was prepared starting from 1-bromo-2,5-dimethoxy-4-methylbenzene[3] and iodoethane following the procedure for the synthesis of **1a'** (3 mmol scale). Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 332 mg (74%) of the title compound as a yellow oil.

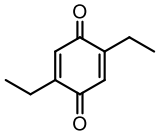
TLC R_f = 0.50 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.58 (q, *J* = 1.6 Hz, 1H), 6.53 (t, *J* = 1.6 Hz, 1H), 2.44 (qd, *J* = 7.4, 1.6 Hz, 2H), 2.03 (d, *J* = 1.6 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.5, 187.9, 151.0, 145.7, 133.7, 131.8, 22.0, 15.6, 11.8.

The recorded spectroscopic values agree with the previously reported data.[4]

2,5-Diethyl-1,4-benzoquinone (1q)



The title product was prepared starting from 1,4-dibromo-2,5-dimethoxybenzene[14] and iodoethane following the procedure for the synthesis of **1a'** on 5 mmol scale, except double amounts of ^{n}BuLi and iodoethane were used. Column chromatography on silica gel (20/1 hexanes/EtOAc) gave 170 mg (21%) of the title compound as a yellow oil.

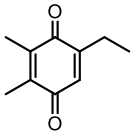
TLC R_f = 0.59 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (t, *J* = 1.5 Hz, 2H), 2.44 (qd, *J* = 7.4, 1.5 Hz, 4H), 1.12 (t, *J* = 7.4 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.2 (2C), 150.7 (2C), 132.0 (2C), 21.9 (2C), 11.8 (2C).

The recorded spectroscopic values agree with the previously reported data.[4]

5-Ethyl-2,3-dimethyl-1,4-benzoquinone (1r)



General procedure A was followed using 2,3-dimethyl-1,4-benzoquinone (2 mmol, 272 mg) and propionic acid (4 mmol, 296 mg). Column chromatography on silica gel (200/1 hexanes/EtOAc) gave 146 mg (44%) of the title compound as a yellow solid.

TLC R_f = 0.59 (4/1 hexanes/EtOAc);

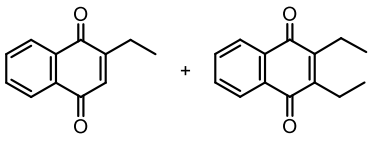
M.p. 34 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.49 (t, *J* = 1.6 Hz, 1H), 2.45 (qd, *J* = 7.4, 1.6 Hz, 2H), 2.03 – 1.99 (m, 6H), 1.11 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 187.9, 187.7, 150.5, 141.2, 140.6, 131.5, 22.3, 12.5, 12.2, 11.8;

HRMS (APPI): m/z calcd for $C_{10}H_{12}O_2^{\bullet+}$: 164.0832 $[M]^{\bullet+}$; found: 164.0835.

2-Ethyl-1,4-naphthoquinone (1s) and **2,3-diethyl-1,4-naphthoquinone (1z)**



1s **1z**

General procedure A was followed using 1,4-naphthoquinone (10 mmol, 1.58 g) and propionic acid (20 mmol, 1.50 mL). Column chromatography on silica gel (150/1 hexanes/EtOAc) furnished 95 mg (4%) the doubly alkylated quinone **1z** as a yellow solid and further elution 125/1 hexanes/EtOAc) gave 853 mg (46%) of the monoalkylated quinone **1s** as a yellow solid.

Compound **1s**

TLC R_f = 0.52 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.04 (m, 2H), 7.75 – 7.69 (m, 2H), 6.79 (t, *J* = 1.6 Hz, 1H), 2.62 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.21 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.42, 185.37, 153.3, 134.1, 133.8, 133.7, 132.5, 132.2, 126.7, 126.2, 22.8, 12.0.

The recorded spectroscopic values agree with the previously reported data.[1b]

[14] Royuela, S.; Almarza, J.; Mancheño, M. J.; Pérez-Flores, J. C.; Michel, E. G.; Ramos, M. M.; Zamora, F.; Ocón, P.; Segura, J. L. *Chem. Eur. J.* **2019**, *25*, 12394–12404.

Compound **1z**

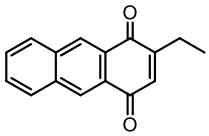
TLC R_f = 0.59 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 – 8.05 (m, 2H), 7.71 – 7.65 (m, 2H), 2.65 (q, *J* = 7.5, 4H), 1.15 (t, *J* = 7.5 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.2 (2C), 148.2 (2C), 133.4 (2C), 132.4 (2C), 126.3 (2C), 20.3 (2C), 14.1 (2C).

The recorded spectroscopic values agree with the previously reported data.[15]

2-Ethyl-1,4-anthraquinone (1t)



General procedure A was followed using 1,4-anthraquinone (2 mmol, 416 mg) and propionic acid (4 mmol, 0.30 mL). Column chromatography on silica gel (30/1 hexanes/EtOAc) gave 130 mg (27%) of the title compound as an orange solid.

TLC R_f = 0.65 (3/1 hexanes/EtOAc);

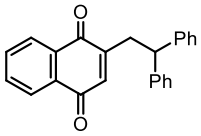
M.p. 136 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 8.55 (s, 1H), 8.04 – 7.99 (m, 2H), 7.67 – 7.63 (m, 2H), 6.86 (t, *J* = 1.5 Hz, 1H), 2.65 (qd, *J* = 7.4, 1.5 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.0, 184.9, 154.7, 135.6, 134.92, 134.85, 130.25, 130.22, 129.5, 129.4, 129.0, 128.9, 128.8, 128.4, 23.0, 12.0;

HRMS (APPI): m/z calcd for $C_{16}H_{13}O_2^+$: 237.0910 $[M+H]^+$; found: 237.0909.

2-(2,2-Diphenylethyl)-1,4-naphthoquinone (1v)



General procedure A was followed using 1,4-naphthoquinone (5 mmol, 790 mg) and 3,3-diphenylpropionic acid (10 mmol, 2.26 g). Column chromatography on silica gel (70/1 hexanes/EtOAc) gave a yellow oil that upon crystallization from hexanes/C_6H_6 furnished 833 mg (49%) of the title compound as yellow prisms.

TLC R_f = 0.35 (4/1 hexanes/EtOAc);

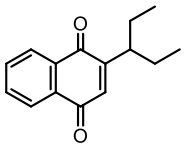
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 – 8.10 (m, 1H), 8.05 – 7.99 (m, 1H), 7.75 – 7.67 (m, 2H), 7.36 – 7.28 (m, 8H), 7.25 – 7.18 (m, 2H), 6.59 (br. s, 1H), 4.44 (t, *J* = 7.9 Hz, 1H), 3.38 (dd, *J* = 7.9, 1.3 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.1, 184.7, 149.2, 143.4 (2C), 136.5, 133.7, 133.6, 132.2, 132.0, 128.7 (4C), 127.9 (4C), 126.7 (2C), 126.6, 126.0, 49.5, 35.8.

The recorded spectroscopic values agree with the previously reported data.[16]

[15] Wu, C.; Berbasov, D. O.; Wulff, W. D *J. Org. Chem.* **2010**, *75*, 4441–4452.
[16] Osuka, A. *J. Org. Chem.* **1982**, *47*, 3131–3139.

2-(3-Pentyl)-1,4-naphthoquinone (1w)



General procedure A was followed using 1,4-naphthoquinone (4 mmol, 632 mg) and diethylacetic acid (8 mmol, 928 mg). Column chromatography on silica gel (150/1 hexanes/EtOAc) gave 622 mg (68%) of the title compound as a yellow oil.

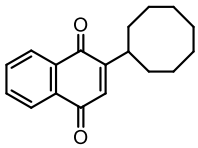
TLC R_f = 0.59 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.05 (m, 2H), 7.75 – 7.70 (m, 2H), 6.72 (d, *J* = 0.8 Hz, 1H), 2.98 – 2.88 (m, 1H), 1.71 – 1.51 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.5, 185.3, 155.1, 134.4, 133.75, 133.72, 132.6, 132.0, 126.9, 126.1, 40.8, 26.9 (2C), 11.8 (2C);

HRMS (APPI): m/z calcd for $C_{15}H_{16}O_2^{\bullet+}$: 228.1145 $[M]^{\bullet+}$; found: 228.1145.

2-Cyclooctyl-1,4-naphthoquinone (1x)



The title compound was prepared according to the literature procedure[17] using 1,4-naphthoquinone (1 mmol, 158 mg) and cyclooctene (4 mmol, 441 mg). Column chromatography on silica gel (100/1 hexanes/EtOAc) followed by preparative TLC on silica gel (20/1 hexanes/EtOAc) furnished 43 mg (16%) of the title compound as a yellow oil.

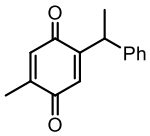
TLC R_f = 0.62 (4/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.08 (m, 1H), 8.07 – 8.03 (m, 1H), 7.73 – 7.70 (m, 2H), 6.74 (d, *J* = 1.0 Hz, 1H), 3.23 – 3.13 (m, 1H), 1.77 – 1.71 (m, 4H), 1.66 – 1.57 (m, 10H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.8, 185.0, 158.2, 133.73, 133.69, 133.2, 132.6, 132.0, 126.8, 126.0, 36.2, 32.0 (2C), 26.7, 26.5 (2C), 25.8 (2C).

The recorded spectroscopic values agree with the previously reported data.[17]

2-Methyl-5-(1-phenylethyl)-1,4-benzoquinone (1y)



The title compound was prepared by alkylation of 2,5-dimethoxytoluene with styrene[18] followed by oxidation of the crude product with CAN. In a sealed 10 mL pressure vial, a solution of 2,5-dimethoxytoluene (2 mmol, 304 mg), styrene (1 mmol, 115 µl), anhydrous $FeCl_3$ (0.1 mmol, 16 mg) in DCM (5 mL) was stirred under Ar atmosphere at 80 °C for 4 h. After cooling to room temperature, the volatiles were evaporated under reduced pressure and the residue was dissolved in hexanes/EtOAc (40/1, 10 mL), vacuum-filtered through a pad of silica gel, which was then washed with hexanes/EtOAc (40/1, 100 mL). The solution was concentrated under reduced pressure to give crude 1,4-dimethoxy-2-methyl-5-(1-phenylethyl)benzene, which was oxidized with CAN according to the General Procedure B (2 mmol scale). Column chromatography on silica gel (30/1 hexanes/EtOAc) gave 173 mg (76% overall) of the title compound as a yellow solid.

TLC R_f = 0.52 (4/1 hexanes/EtOAc);

[17] Liu, S.; Shen, T.; Luo, Z.; Liu, Z.-Q. *Chem. Commun.* **2019**, *55*, 4027–4030.
[18] Kischel, J.; Jovel, I.; Mertins, K.; Zapf, A.; Beller, M. *Org. Lett.* **2006**, *8*, 19–22.

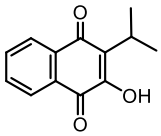
M.p. 52 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 6.55 (q, *J* = 1.5 Hz, 1H), 6.52 (d, *J* = 1.2 Hz, 1H), 4.26 (qd, *J* = 7.1, 1.2 Hz, 1H), 2.02 (d, *J* = 1.5 Hz, 3H), 1.47 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.6, 187.2, 152.8, 145.4, 142.7, 133.8, 131.9, 128.8 (2C), 127.7 (2C), 127.0, 37.6, 20.0, 15.5;

HRMS (ESI): m/z calcd for $C_{15}H_{14}NaO_2^+$: 249.0886 $[M+Na]^+$; found: 249.0889.

2-Hydroxy-3-isopropyl-1,4-naphthoquinone (1aa)



General procedure A was followed using lawsone (2 mmol, 348 mg) and isobutyric acid (3 mmol, 264 mg, 275 µL). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 58 mg (13%) of the title compound as a yellow oil.

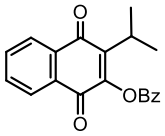
TLC R_f = 0.55 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.75 (td, *J* = 7.6, 1.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.4 Hz, 1H), 7.42 (s, 1H), 3.42 (hept, *J* = 7.1 Hz, 1H), 1.31 (d, *J* = 7.1 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.6, 182.0, 152.9, 135.1, 133.3, 132.9, 129.3, 128.9, 127.0, 126.1, 24.8, 20.0 (2C).

The recorded spectroscopic values agree with the previously reported data.[19]

2-Benzoyloxy-3-isopropyl-1,4-naphthoquinone (1ab)



To a stirred solution of **1aa** (0.1 mmol, 22 mg) and 2,6-lutidine (0.2 mmol, 22 mg, 23 µl) in DCM (1 mL) was added benzoyl chloride (0.15 mmol, 21 mg, 18 µl) at room temperature. After stirring for 1 h, water (10 mL) was added, the organic phase was separated, and the aqueous phase was extracted with DCM (2×5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (100/1 hexanes/EtOAc) gave 23 mg (72%) of the title compound as a pale yellow solid.

TLC R_f = 0.45 (3/1 hexanes/EtOAc);

M.p. 117 °C;

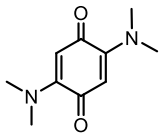
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 – 8.18 (m, 2H), 8.16 – 8.13 (m, 1H), 8.12 – 8.05 (m, 1H), 7.79 – 7.66 (m, 3H), 7.58 – 7.52 (m, 2H), 3.44 (hept, *J* = 7.1 Hz, 1H), 1.38 – 1.25 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.6, 178.5, 164.1, 151.5, 144.0, 134.34, 134.27, 133.8, 132.6, 130.9, 130.7 (2C), 128.9 (2C), 128.3, 127.0, 126.7, 25.9, 20.6 (2C).

The recorded spectroscopic values agree with the previously reported data.[20]

[19] Dong, J.; Yue, F.; Xu, W.; Song, H.; Liu, Y.; Wang, Q. *Green Chem*. **2020**, *22*, 5599–5604.
[20] Matsumoto, T.; Imai, S.; Yamamoto, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 911–920.

2,5-Bis(dimethylamino)-1,4-benzoquinone (1ac)



The title compound was prepared according to the literature procedure[21] using *p*-benzoquinone (10 mmol, 1.08 g) and dimethylamine solution (5.6 M in ethanol, 50 mmol, 9 mL). Recrystallization of the precipitate from EtOAc gave 442 mg (23%) of the pure product as a dark red solid.

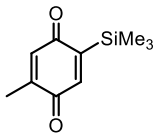
M.p. 182 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.35 (s, 2H), 3.19 (s, 12H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.7 (2C), 152.4 (2C), 102.1 (2C), 42.8 (2C).

The recorded spectroscopic values agree with the previously reported data.[22]

2-Methyl-5-(trimethylsilyl)-1,4-benzoquinone (1ae)



The title product was prepared starting from 1-bromo-2,5-dimethoxy-4-methylbenzene[3] and trimethylsilyl chloride following the procedure for the synthesis of **1a'** (5 mmol scale). Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 650 mg (67% overall) of the title compound as a yellow solid.

TLC R_f = 0.62 (3/1 hexanes/EtOAc);

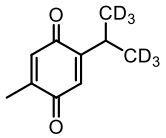
M.p. 74 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 1H), 6.59 (q, *J* = 1.5 Hz, 1H), 2.02 (d, *J* = 1.5 Hz, 3H), 0.23 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.2, 187.5, 152.4, 145.6, 143.5, 134.9, 15.7, -1.6;

HRMS (APPI): m/z calcd for $C_{10}H_{14}O_2Si^{\bullet+}$: 194.0758 $[M]^{\bullet+}$; found: 194.0754.

2-Methyl-5-(prop-2-yl-1,1,1,3,3,3-d6)-1,4-benzoquinone (d-1a)



To a solution of 1-bromo-2,5-dimethoxy-4-methylbenzene[3] (3 mmol, 693 mg) in THF (6 mL) under Ar atmosphere was added ^{n}BuLi (1.6 M in hexanes, 3.04 mmol, 1.9 mL) dropwise at -78 °C. After stirring for 0.5 h at this temperature acetone-d6 (3.3 mmol, 192 mg, 220 μL) was added dropwise. The reaction mixture was allowed to reach room temperature over 2 h and the stirring was continued for the next 24 h. Water (30 mL) was added and the product was extracted with Et_2O (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solution was concentrated under reduced pressure to give the crude alcohol, which was dissolved in MeOH (30 mL) and hydrogenated at room temperature for 3 h (1 atm H_2, 160 mg Pd/C (10% Pd by weight)). The volatiles were removed under reduced pressure, and the residue was dissolved in hexanes/Et_2O (10/1, 10 mL), vacuum filtered through a pad of silica gel, which was then washed with hexanes/Et_2O (10/1, 100 mL). The solution was concentrated under

[21] Mylius, F. *Chem. Ber.* **1885**, *18*, 463–481.
[22] Schäfer, W., Schlude, H. *Tetrahedron Lett.* **1967**, *8*, 4307–4312.

reduced pressure to give the crude arene, which was directly oxidized with CAN according to the General Procedure B (3 mmol scale). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 352 mg (69% overall) of the title compound as a yellow solid.

TLC R_f = 0.55 (4/1 hexanes/EtOAc);

M.p. 44 °C;

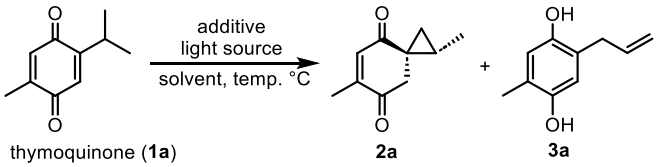
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (q, *J* = 1.5 Hz, 1H), 6.51 – 6.49 (m, 1H), 2.97 (br. s, 1H), 2.02 (d, *J* = 1.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.7, 187.6, 155.1, 145.3, 134.0, 130.5, 26.2, 20.6 (hept, *J* = 20 Hz, 2C), 15.5;

HRMS (ESI): m/z calcd for $C_{10}H_7D_6O_2^+$: 171.1287 $[M+H]^+$; found: 171.1287.

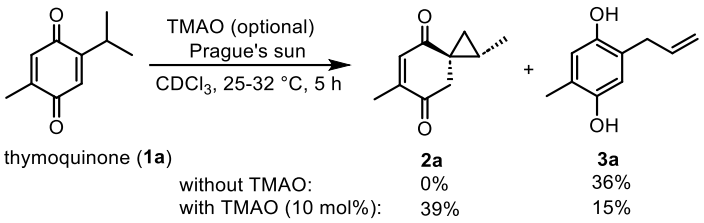
2.2 Screening of the spirocyclopropanation reaction conditions

Table S1. Screening of the reaction conditions for the synthesis of spirocyclopropane **2a**.[a]

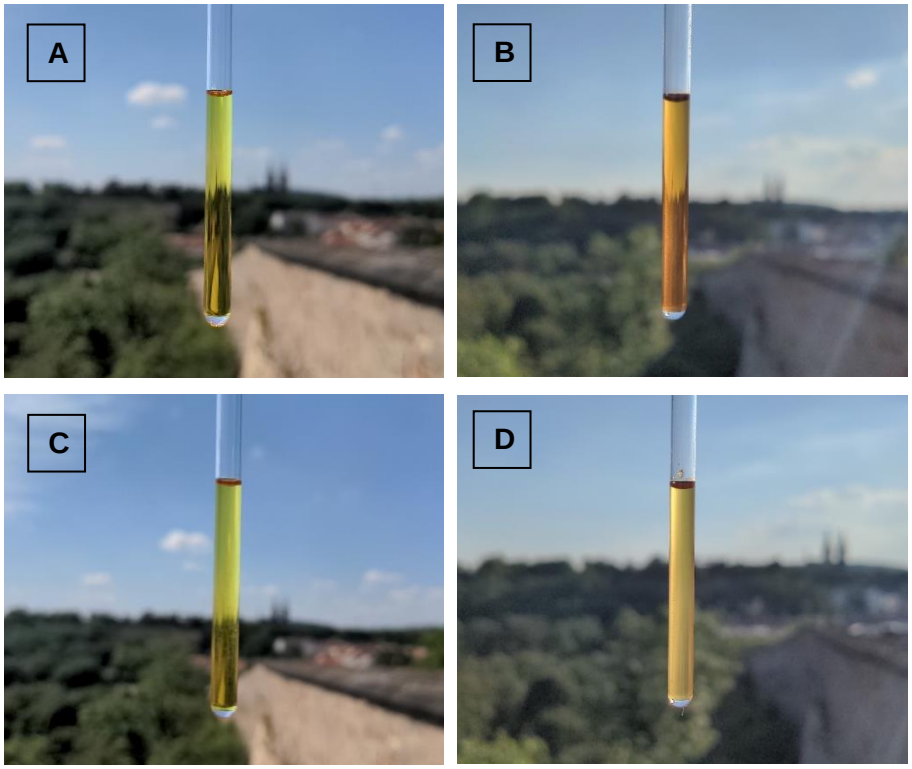


Entry	Additive	Yield of 2a, %	Yield of 3a, %
1	-	0	49
2	$Ph_2C=O$	0	42
3	$Ph_2C=NH$	6	34
4	*n*-$Bu_4N^+Cl^-$	48	<5
5	Fluorene	0	48
6	Bn_2O	0	48
7	**TMAO**	**84 (51)[b]**	**14**
8	PPTS	48	33
9	$[bmim]^+Cl^-$	54	<5
10	Berberine	64	8
11	NMO	72	18
12	TEMPO	70	11
13	L-phenylalanine	0	41
14	Caffeine	0	46
15	Coumarin	0	50
16	Betaine·HCl	0	48
17	$Me_3S^+(O)I^-$	64	19
18	Et_3N	82	12
19	Canadine	44	27
20	Canadine methiodide	56	<5
21	Berberine (5 mol%)	68	13
22	Berberine (3 mol%)	64	17
23	Berberine (1 mol%)	48	27
24	Berberine (no light)	0	0
25	TMAO (5 mol%)	76	19
26	TMAO (15 mol%)	84	14
27	TMAO (no light)	0	0
28	TMAO[c]	0	49
29	TEMPO (1 eq.)	80	<5
30	Galvinoxyl (1 eq.)	0	0
31	TMAO, in THF	<5	<5
32	TMAO, in MeCN	12	<5
33	TMAO, in EtOAc	14	<5
34	TMAO, in toluene	6	34
35	TMAO, in DCM	84	12
36	TMAO, in DCE	70	12
37	TMAO, 0.2 M $CDCl_3$	74	16
38	TMAO, 0 °C	74	22
39	TMAO, green LEDs	<5	<5
40	TMAO, red LEDs	0	0

[a] 0.05 mmol scale, 10 mol% of the additive unless noted otherwise, blue LEDs, 0.1 M $CDCl_3$, 20−25 °C, 1 h; [b] isolated yield on 0.5 mmol scale; [c] additive was added after 1 h of irradiation and the irradiation was continued for 1 h



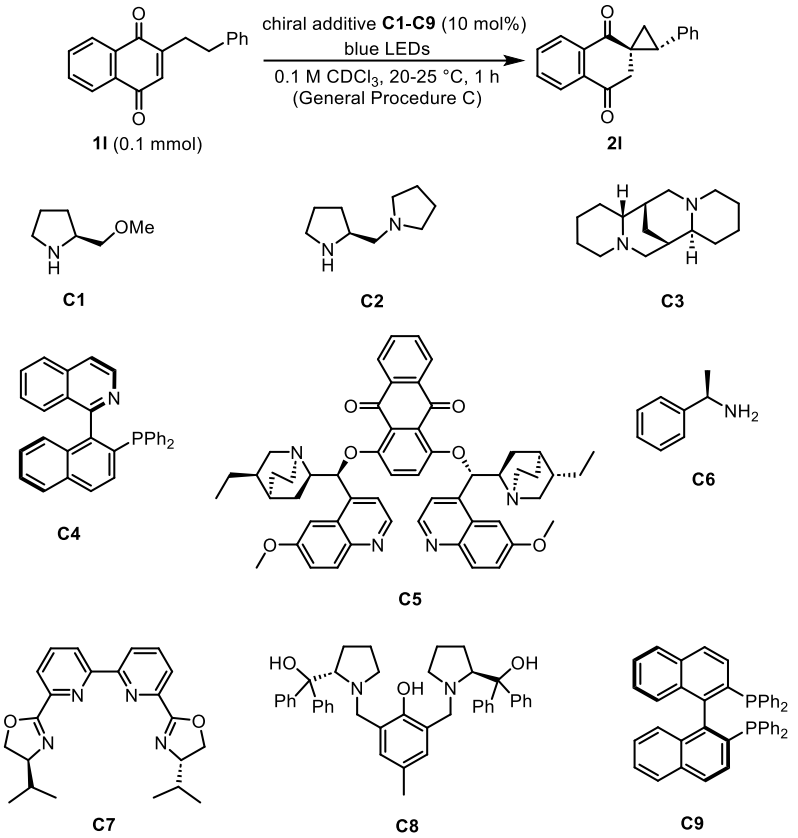
Scheme S2. Transformation of thymoquinone (**1a**) into **2a** and **3a** under ambient sunlight.



Picture 1. Exposure of the solutions of thymoquinone (**1a**) to sunlight.
A – **1a** in chloroform (0.1M); B – solution A after 5 h exposure;
C – **1a** in chloroform (0.1M) containing TMAO (10 mol%); D – solution C after 5 h exposure.

2.3 Screening of the chiral additives in the spirocyclopropanation reaction

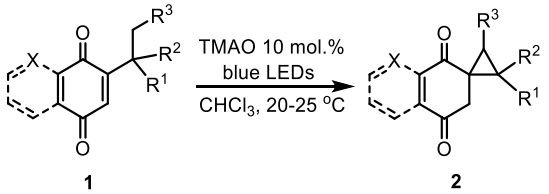
Table S2. Screening of the chiral additives **C1**–**C9** in the synthesis of **2l**.



Entry	Chiral additive	NMR yield, %	*dr*	*ee*
1	**C1**	88	1.6:1	0
2	**C2**	99	2:1	0
3	**C3**	99	4.8:1	0
4	**C4**	34	2.8:1	0
5	**C5**	96	2.4:1	0
6	**C6**	29	3.8:1	0
7	**C7**	<5	-	-
8	**C8**	82	2.7:1	0
9	**C9**	62	3:1	0

2.4 Synthesis of spirocyclopropanes 2

General procedure C: synthesis of spirocyclopropanes 2

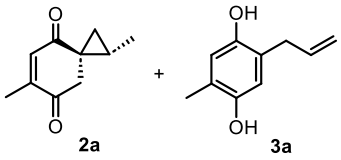


1 2

A solution of quinone **1** (0.5 mmol) and trimethylamine *N*-oxide (0.05 mmol, 3.8 mg) in $CHCl_3$ (5 mL) was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere (1–24 h, TLC control).[23] After the given time the volatiles were removed under reduced pressure and the residue was purified by column chromatography to afford the desired product **2**.

The labile spirocyclopropanes **2b**, **2f**, **2k**, **2o**, **2v** and cyclobutane **5** could not be isolated in pure state, therefore only spectral yields are given. The reactions were run on 0.15 mmol scale in an NMR tube. After the given time, the reaction mixture was concentrated to 0.5–0.6 mL and NMR and HRMS spectra were recorded. The yields were measured by ^{1}H NMR with dibromomethane as an internal standard.

1,6-Dimethylspiro[2.5]oct-5-ene-4,7-dione (2a) and **2-allyl-5-methylhydroquinone (3a)**



2a 3a

The title compounds were prepared from thymoquinone (**1a**, 0.5 mmol, 82 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (15/1 hexanes/EtOAc) gave 42 mg (51%) of the title compound (*dr* >20/1) as a pale yellow oil. Further elution (10/1 hexanes/EtOAc) gave 18 mg (22%) of hydroquinone **3a** as a colorless solid. When the reaction was performed starting from linear quinone **1a'**, **2a** was obtained in 82% spectral yield (*dr* 15/1) and 44% isolated yield (*dr* 12/1). Pure **2a** should be stored at -20 °C or below to minimize decomposition.

Compound **2a**

TLC R_f = 0.35 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (q, *J* = 1.4 Hz, 1H), 2.89 (d, *J* = 18.0 Hz, 1H), 2.73 (d, *J* = 18.0 Hz, 1H), 2.03 (d, *J* = 1.4 Hz, 3H), 1.70 (ddq, *J* = 9.1, 6.8, 6.2 Hz, 1H), 1.62 (dd, *J* = 9.1, 3.7 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.55 (dd, *J* = 6.8, 3.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.1, 198.0, 149.8, 139.1, 40.6, 30.3, 27.1, 24.7, 16.3, 13.6;

IR (KBr): ṽ = 2962, 2922, 2883, 1680, 1655, 1618, 1421, 1309, 1257, 1196, 1099, 1001, 935, 893, 762 cm^{-1};

HRMS (ESI): m/z calcd for $C_{10}H_{13}O_2^+$: 165.0910 $[M+H]^+$; found: 165.0909.

[23] The experimental setup was described in details in our previous work: Fadeev, A. A.; Kotora, M. *Org. Biomol. Chem.* **2023**, *21*, 6174–6179.

Compound **3a**

TLC R_f = 0.23 (3/1 hexanes/EtOAc);

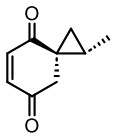
M.p. 139 °C;

^{1}H NMR (400 MHz, acetone-d6): δ = 7.41 (s, 1H), 7.36 (s, 1H), 6.58 (s, 1H), 6.55 (s, 1H), 5.95 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.03 (ddt, *J* = 16.8, 2.1, 1.7 Hz, 1H), 4.96 (ddt, *J* = 10.0, 2.1, 1.3 Hz, 1H), 3.27 (ddd, *J* = 6.7, 1.7, 1.3 Hz, 2H), 2.09 (s, 3H);

^{13}C NMR (101 MHz, acetone-d6): δ = 149.0, 148.3, 138.4, 124.9, 123.2, 118.1, 116.9, 115.1, 34.6, 15.9;

The recorded spectroscopic values agree with the previously reported data.[24]

1-Methylspiro[2.5]oct-5-ene-4,7-dione (2b)



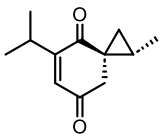
The title compound was prepared as a solution in chloroform from 2-isopropyl-1,4-benzoquinone (**1b**, 0.15 mmol, 22.5 mg) in 44% spectral yield (*dr* >20/1) according to the General Procedure C. The reaction took 1 h to complete (visible loss of yellow color).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 – 6.72 (m, 2H), 2.90 (d, *J* = 18.2 Hz, 1H), 2.74 (d, *J* = 18.2 Hz, 1H), 1.73 (ddq, *J* = 9.1, 6.7, 6.2 Hz, 1H), 1.66 (dd, *J* = 9.1, 3.7 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.60 (dd, *J* = 6.7, 3.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.6, 197.9, 141.9, 140.2, 40.5, 30.0, 27.8, 25.6, 13.6;

HRMS (APPI): m/z calcd for $C_9H_{10}O_2^{\bullet+}$: 150.0675 $[M]^{\bullet+}$; found: 150.0678.

5-Isopropyl-1-methylspiro[2.5]oct-5-ene-4,7-dione (2c)



The title compound was prepared from 2,6-diisopropyl-1,4-benzoquinone (**1c**, 0.5 mmol, 96 mg) according to the General Procedure C. The reaction took 4 h to complete (TLC monitoring; visible loss of yellow color). Analysis of the reaction mixture by ^{1}H NMR showed 58% yield of **2c** (*dr* >20/1). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 40 mg (42%) of the title compound (*dr* >20/1) as a pale yellow oil.

TLC R_f = 0.43 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (br. s, 1H), 3.07 – 2.96 (m, 1H), 2.85 (d, *J* = 18.1 Hz, 1H), 2.69 (d, *J* = 18.1 Hz, 1H), 1.70 (ddq, *J* = 9.1, 6.6, 6.2 Hz, 1H), 1.62 (dd, *J* = 9.1, 3.6 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 6H), 0.54 (dd, *J* = 6.6, 3.6 Hz, 1H);

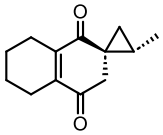
^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.9, 197.0, 160.3, 134.5, 40.6, 30.0, 27.5, 27.2, 25.1, 21.51, 21.49, 13.7;

IR (KBr): $\tilde{\nu}$ = 2964, 2933, 2873, 1662, 1614, 1464, 1415, 1377, 1269, 1192, 1149, 1057, 916, 843 cm^{-1};

HRMS (ESI): m/z calcd for $C_{12}H_{16}NaO_2^+$: 215.1043 $[M+Na]^+$; found: 215.1044.

[24] Benharref, A.; Fdil, R.; El Hanbali, F.; Zeroual, A.; Dakir, M.; Mazoir, N. *Nat. Prod. Commun*. **2017**, *12*, 881–882.

2-Methyl-5',6',7',8'-tetrahydro-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2d)



The title compound was prepared from 2-isopropyl-5,6,7,8-tetrahydronaphthalene-1,4-dione (**1d**, 0.5 mmol, 102 mg) according to the General Procedure C. The reaction took 21 h to complete (TLC monitoring; visible loss of yellow color). Analysis of the reaction mixture by ^{1}H NMR showed 58% yield of **2d** (*dr* >20/1). Column chromatography on silica gel (30/1 hexanes/EtOAc) gave 48 mg (47%) of the title compound (*dr* >20/1) as a pale yellow oil.

TLC R_f = 0.45 (3/1 hexanes/EtOAc);

M.p. 70 °C;

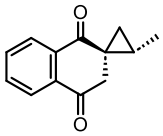
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.86 (d, *J* = 17.8 Hz, 1H), 2.69 (d, *J* = 17.8 Hz, 1H), 2.49 – 2.32 (m, 4H), 1.72 – 1.59 (m, 5H), 1.60 (dd, *J* = 9.1, 3.6 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.52 (dd, *J* = 6.7, 3.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.5, 197.6, 147.9, 146.7, 40.5, 29.5, 27.1, 24.7, 23.9, 23.3, 21.3, 21.1, 13.7;

IR (KBr): $\tilde{\nu}$ = 2958, 2929, 2871, 1653, 1614, 1419, 1379, 1286, 1263, 1203, 1174, 1099, 972, 908, 864, 777, 721 cm^{-1};

HRMS (APPI): m/z calcd for $C_{13}H_{16}O_2^{\bullet+}$: 204.1145 $[M]^{\bullet+}$; found: 204.1143.

2-Methyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2e)



The title compound was prepared from 2-isopropyl-1,4-naphthoquinone (**1e**, 0.5 mmol, 100 mg) according to the General Procedure C. The reaction took 3 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 71 mg (71%) of the title compound (*dr* 7/1) as a pale yellow oil, which was crystallized from hexanes to give 53 mg (53%) of the major isomer (*dr* >20/1) as a pale yellow solid.

TLC R_f = 0.48 (3/1 hexanes/EtOAc);

M.p. 73 °C;

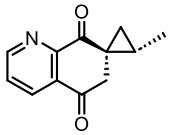
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.07 (m, 1H), 8.07 – 8.00 (m, 1H), 7.77 – 7.70 (m, 2H), 3.04 (d, *J* = 17.3 Hz, 1H), 2.97 (d, *J* = 17.3 Hz, 1H), 1.86 – 1.76 (m, 2H), 1.20 (d, *J* = 6.0 Hz, 3H), 0.68 – 0.61 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8, 196.4, 135.4, 135.2, 134.2, 134.0, 127.0, 126.5, 41.3, 30.7, 26.3, 25.0, 13.6;

IR (KBr): $\tilde{\nu}$ = 3064, 2962, 1685, 1664, 1591, 1412, 1323, 1284, 1248, 1167, 1074, 1049, 1011, 912, 818, 756, 681 cm^{-1};

HRMS (APPI): m/z calcd for $C_{13}H_{12}O_2^{\bullet+}$: 200.0832 $[M]^{\bullet+}$; found: 200.0836.

2-Methyl-6'*H*-spiro[cyclopropane-1,7'-quinoline]-5',8'-dione (2f)



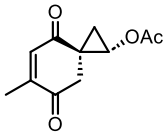
The title compound was prepared as a solution in chloroform from 7-propylquinoline-5,8-dione (**1f**, 0.15 mmol, 30.2 mg) in 80% spectral yield (*dr* >20/1) according to the General Procedure C. The reaction took 1 h to complete (visible loss of yellow color). When the reaction was performed in the absence of trimethylamine *N*-oxide, **2f** was formed in 52% spectral yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.37 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.65 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.10 (d, *J* = 17.5 Hz, 1H), 3.03 (d, *J* = 17.5 Hz, 1H), 2.01 – 1.81 (m, 2H), 1.24 – 1.18 (m, 3H), 0.75 – 0.67 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.8, 194.6, 155.2, 150.4, 135.2, 132.2, 127.8, 41.1, 30.8, 27.0, 26.0, 13.7;

HRMS (ESI): m/z calcd for $C_{12}H_{12}NO_2^+$: 202.0863 $[M+H]^+$; found: 202.0862.

6-Methyl-4,7-dioxospiro[2.5]oct-5-en-1-yl acetate (2g)



The title compound was prepared from 2-(4-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)ethyl acetate (**1g**, 0.35 mmol, 73 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (12/1 hexanes/EtOAc) gave 26 mg (36%) of the title compound (*dr* >20/1) as a pale yellow oil of ~90% purity according to ^{1}H NMR.

TLC R_f = 0.21 (3/1 hexanes/EtOAc);

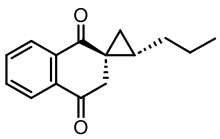
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (q, *J* = 1.4 Hz, 1H), 4.23 (dd, *J* = 7.2, 4.7 Hz, 1H), 2.91 (d, *J* = 18.1 Hz, 1H), 2.68 (d, *J* = 18.1 Hz, 1H), 2.09 (s, 3H), 2.03 (d, *J* = 1.4 Hz, 3H), 1.96 (dd, *J* = 7.2, 6.2 Hz, 1H), 1.06 (dd, *J* = 6.2, 4.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.2, 195.1, 170.9, 150.6, 138.3, 60.0, 39.0, 30.6, 20.53, 20.49, 16.5;

IR (KBr): $\tilde{\nu}$ = 3018, 2929, 1749, 1460, 1417, 1373, 1186, 1047, 1007, 941, 874, 750 cm^{-1};

HRMS (ESI): m/z calcd for $C_{11}H_{12}NaO_4^+$: 231.0628 $[M+Na]^+$; found: 231.0631.

2-Propyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2h)



The title compound was prepared from 2-pentyl-1,4-naphthoquinone (**1h**, 0.5 mmol, 114 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (40/1 hexanes/EtOAc) gave 101 mg (89%) of the title compound (*dr* 6/1) as a pale yellow oil. Successive chromatographic separation (100/1 hexanes/EtOAc) gave 85 mg (75%) of the major isomer (*dr* 14/1) as a pale yellow oil.

TLC R_f = 0.50 (3/1 hexanes/EtOAc);

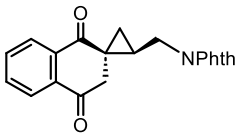
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.09 (m, 1H), 8.06 – 8.02 (m, 1H), 7.77 – 7.70 (m, 2H), 3.04 (d, *J* = 17.4 Hz, 1H), 2.99 (d, *J* = 17.3 Hz, 1H), 1.80 (dd, *J* = 9.1, 3.7 Hz, 1H), 1.76 – 1.68 (m, 1H), 1.52 – 1.34 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.66 (dd, *J* = 6.8, 3.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.8, 196.5, 135.3, 135.2, 134.3, 134.0, 127.0, 126.5, 41.5, 31.1, 31.0, 30.7, 24.9, 22.7, 14.0;

IR (KBr): ṽ = 2958, 2929, 2871, 1693, 1672, 1593, 1284, 1250, 1205, 1068, 1020, 980, 752, 696 cm^{-1};

HRMS (APPI): m/z calcd for $C_{15}H_{16}O_2^{\bullet+}$: 228.1145 $[M]^{\bullet+}$; found: 228.1148.

2-((1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)methyl)isoindoline-1,3-dione (2i)



The title compound was prepared from 2-(3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)propyl)isoindoline-1,3-dione (**1i**, 0.5 mmol, 172 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 142 mg (82%) of the title compound (*dr* 3/1) as a pale yellow solid. Recrystallization from hexanes/EtOAc provided 74 mg (43%) the major isomer (*dr* >20/1) as colorless needles.

TLC R_f = 0.45 (1/1 hexanes/EtOAc);

M.p. 147 °C;

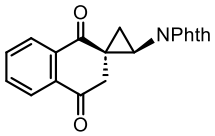
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 – 8.07 (m, 1H), 7.98 – 7.90 (m, 1H), 7.71 – 7.58 (m, 6H), 3.83 (dd, *J* = 14.4, 6.2 Hz, 1H), 3.66 (dd, *J* = 14.4, 7.1 Hz, 1H), 3.36 (d, *J* = 16.9 Hz, 1H), 2.54 (d, *J* = 16.9 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.04 (dd, *J* = 8.1, 4.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.6, 194.0, 167.9 (2C), 135.8, 134.9, 134.1, 134.0, 133.9 (2C), 131.9 (2C), 127.0, 126.4, 123.2 (2C), 47.2, 36.1, 31.73, 31.66, 18.5;

IR (KBr): ṽ = 2883, 1763, 1695, 1674, 1591, 1408, 1390, 1361, 1279, 1246, 1076, 901, 791, 750, 714, 694 cm^{-1};

HRMS (ESI): m/z calcd for $C_{21}H_{15}NNaO_4^+$: 368.0893 $[M+Na]^+$; found: 368.0890.

1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)isoindoline-1,3-dione (2j)



The title compound was prepared from 2-(2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)ethyl)isoindoline-1,3-dione (**1j**, 0.5 mmol, 165 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 134 mg (81%) of the title compound (*dr* 3.5/1) as a pale yellow solid. Successive chromatographic separation (50/1 DCM/EtOAc) provided 89 mg (54%) of the major isomer (*dr* >20/1) as a colorless solid.

TLC R_f = 0.42 (20/1 DCM/EtOAc);

M.p. 277 °C;

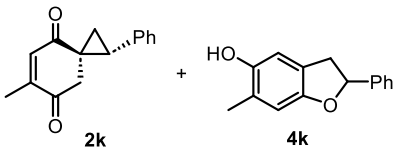
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.06 (m, 1H), 7.94 – 7.87 (m, 1H), 7.78 – 7.63 (m, 6H), 3.42 (d, *J* = 17.0 Hz, 1H), 3.06 (dd, *J* = 7.5, 6.1 Hz, 1H), 2.82 (d, *J* = 17.0 Hz, 1H), 2.71 (dd, *J* = 6.5, 6.1 Hz, 1H), 1.60 (dd, *J* = 7.5, 6.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.0, 191.4, 168.1 (2C), 135.42, 135.37, 134.3 (2C), 134.2, 134.1, 131.6 (2C), 126.7, 126.6, 123.5 (2C), 45.6, 38.5, 31.3, 19.5;

IR (KBr): $\tilde{\nu}$ = 2920, 1776, 1709, 1672, 1593, 1400, 1358, 1282, 1248, 1205, 1149, 1047, 916, 756, 717, 708, 694 cm^{-1};

HRMS (ESI): m/z calcd for $C_{20}H_{13}NNaO_4^+$: 354.0737 $[M+Na]^+$; found: 354.0735.

6-Methyl-1-phenylspiro[2.5]oct-5-ene-4,7-dione (2k) and **6-methyl-2-phenyl-2,3-dihydrobenzofuran-5-ol (4k)**



The compound **2k** was prepared as a solution in chloroform from 2-methyl-5-phenethyl-1,4-benzoquinone (**1k**, 0.15 mmol, 33.9 mg) in 75% spectral yield (*dr* 13/1) according to the General Procedure C. The reaction took 1 h to complete (visible loss of yellow color). When the reaction was carried out on 0.5 mmol scale, attempted isolation by column chromatography on silica gel (10/1 hexanes/EtOAc) only furnished 34 mg (30%) of dihydrobenzofuran **4k** as a colorless solid.

Compound **2k**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.14 – 7.10 (m, 2H), 6.60 (q, *J* = 1.5 Hz, 1H), 2.99 (dd, *J* = 9.1, 7.5 Hz, 1H), 2.54 (d, *J* = 18.3 Hz, 1H), 2.42 (d, *J* = 18.3 Hz, 1H), 2.01 (d, *J* = 1.5 Hz, 3H), 1.96 (dd, *J* = 9.1, 4.7 Hz, 1H), 1.39 (dd, *J* = 7.5, 4.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.2, 196.9, 150.2, 138.9, 135.4, 129.1 (2C), 128.8 (2C), 127.6, 40.7, 35.2, 32.5, 22.3, 16.3;

HRMS (ESI): m/z calcd for $C_{15}H_{14}NaO_2^+$: 249.0886 $[M+Na]^+$; found: 249.0884.

Compound **4k**

TLC R_f = 0.40 (2/1 hexanes/EtOAc);

M.p. 185 °C;

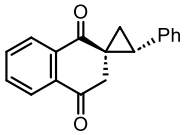
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.28 (m, 5H), 6.70 – 6.58 (m, 2H), 5.71 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.35 (br. s, 1H), 3.56 (dd, *J* = 15.5, 9.3 Hz, 1H), 3.14 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.23 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.8, 147.9, 142.3, 128.7 (2C), 128.1, 125.9 (2C), 124.8, 123.3, 111.9, 111.1, 84.3, 38.8, 16.3;

IR (KBr): $\tilde{\nu}$ = 3375, 2906, 2850, 1510, 1495, 1462, 1417, 1360, 1180, 1003, 931, 864, 845, 762, 744 cm^{-1};

HRMS (APPI): m/z calcd for $C_{15}H_{14}O_2^{\bullet+}$: 226.0988 $[M]^{\bullet+}$; found: 226.0989.

2-Phenyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2l)



The title compound was prepared from 2-phenethyl-1,4-naphthoquinone (**1l**, 0.5 mmol, 131 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 92 mg (70%) of the title compound (*dr* >20/1) as a colorless solid.

TLC R_f = 0.43 (3/1 hexanes/EtOAc);

M.p. 87 °C;

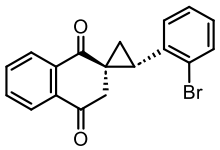
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 – 8.15 (m, 1H), 8.06 – 7.99 (m, 1H), 7.81 – 7.72 (m, 2H), 7.34 – 7.25 (m, 3H), 7.17 – 7.12 (m, 2H), 3.14 (dd, *J* = 9.1, 7.5 Hz, 1H), 2.74 (d, *J* = 17.7 Hz, 1H), 2.60 (d, *J* = 17.7 Hz, 1H), 2.11 (dd, *J* = 9.1, 4.6 Hz, 1H), 1.48 (dd, *J* = 7.5, 4.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.9, 195.5, 135.5, 135.4, 135.1, 134.3, 134.2, 129.3 (2C), 128.8 (2C), 127.6, 127.1, 126.7, 41.5, 35.2, 32.8, 21.9;

IR (KBr): ṽ = 3059, 2943, 2883, 1682, 1668, 1589, 1379, 1321, 1282, 1248, 1201, 1009, 812, 775, 750, 723, 700 cm^{-1};

HRMS (ESI): m/z calcd for $C_{18}H_{14}NaO_2^+$: 285.0886 $[M+Na]^+$; found: 285.0890.

2-(2-Bromophenyl)-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2m)



The title compound was prepared from 2-(2-bromophenethyl)-1,4-naphthoquinone (**1m**, 0.5 mmol, 171 mg) according to the General Procedure C. The reaction took 2 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (25/1 hexanes/EtOAc) gave 137 mg (80%) of the title compound (*dr* 6/1) as a colorless solid. Recrystallization from hexanes/EtOAc provided 92 mg (54%) of the title compound (*dr* 17/1) as a colorless solid (1:1 diastereomeric mixture had crystallized first and was filtered off).

TLC R_f = 0.38 (3/1 hexanes/EtOAc);

M.p. 112 °C (for 17/1 diastereoisomeric mixture);

^{1}H NMR (400 MHz, $CDCl_3$), major diastereomer: δ = 8.25 – 8.16 (m, 1H), 8.05 – 7.99 (m, 1H), 7.80 – 7.71 (m, 2H), 7.59 – 7.51 (m, 1H), 7.33 – 7.29 (m, 1H), 7.21 – 7.14 (m, 2H), 3.08 (dd, *J* = 9.0, 7.6 Hz, 1H), 2.66 (d, *J* = 17.8 Hz, 1H), 2.47 (d, *J* = 17.8 Hz, 1H), 2.18 (dd, *J* = 9.0, 4.7 Hz, 1H), 1.45 (dd, *J* = 7.6, 4.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$), major diastereomer: δ = 195.7, 195.3, 135.9, 135.5, 135.0, 134.22, 134.20, 132.9, 130.3, 129.4, 127.7, 127.4, 127.1, 126.6, 41.3, 36.9, 32.2, 22.4;

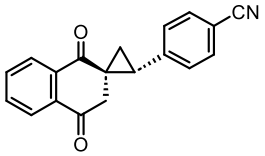
^{1}H NMR (400 MHz, $CDCl_3$), minor diastereomer: δ = 8.07 – 8.04 (m, 1H), 7.84 – 7.79 (m, 1H), 7.73 – 7.60 (m, 2H), 7.34 – 7.26 (m, 3H), 7.09 – 7.00 (m, 1H), 3.56 (d, *J* = 17.1 Hz, 1H), 2.96 (d, *J* = 17.1 Hz, 1H), 2.74 (dd, *J* = 8.5, 7.8 Hz, 1H), 2.47 (dd, *J* = 7.8, 5.1 Hz, 1H), 1.38 (dd, *J* = 8.5, 5.1 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$), minor diastereomer: δ = 195.9, 192.1, 135.8, 135.5, 135.1, 134.01, 133.99, 132.1, 131.1, 128.8, 127.4, 127.0, 126.8, 126.4, 47.5, 40.3, 34.5, 18.2;

IR (KBr): $\tilde{\nu}$ = 3060, 3012, 1691, 1666, 1591, 1437, 1358, 1279, 1246, 1205, 1157, 1007, 771, 750, 739, 715 cm^{-1};

HRMS (ESI): m/z calcd for $C_{18}H_{13}BrNaO_2^+$: 362.9991 $[M+Na]^+$; found: 362.9990.

4-(1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)benzonitrile (2n)



The title compound was prepared from 4-(2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)ethyl)benzonitrile (**1n**, 0.5 mmol, 144 mg) according to the General Procedure C. The reaction took 2 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 110 mg (76%) of the title compound (*dr* >20/1) as a colorless solid.

TLC R_f = 0.24 (3/1 hexanes/EtOAc);

M.p. 133 °C;

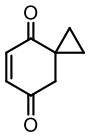
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 – 8.14 (m, 1H), 8.05 – 7.99 (m, 1H), 7.82 – 7.74 (m, 2H), 7.65 – 7.60 (m, 2H), 7.30 – 7.26 (m, 2H), 3.17 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.74 (d, *J* = 17.4 Hz, 1H), 2.55 (d, *J* = 17.4 Hz, 1H), 2.11 (dd, *J* = 9.2, 4.9 Hz, 1H), 1.50 (dd, *J* = 7.2, 4.9 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1, 194.7, 141.3, 135.3, 134.8, 134.55, 134.53, 132.5 (2C), 130.0 (2C), 127.2, 126.8, 118.6, 111.5, 41.4, 33.7, 33.1, 21.7;

IR (KBr): $\tilde{\nu}$ = 3039, 3008, 2964, 2224, 1691, 1670, 1595, 1506, 1415, 1377, 1319, 1290, 1254, 1211, 1165, 1086, 999, 852, 754, 698 cm^{-1};

HRMS (ESI): m/z calcd for $C_{19}H_{13}NNaO_2^+$: 310.0838 $[M+Na]^+$; found: 310.0837.

Spiro[2.5]oct-5-ene-4,7-dione (2o)



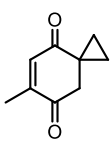
The title compound was prepared as a solution in chloroform from 2-ethyl-1,4-benzoquinone (**1o**, 0.15 mmol, 20.4 mg) in 64% spectral yield according to the General Procedure C. The reaction took 1 h to complete (visible loss of yellow color). When the reaction was performed in the absence of trimethylamine *N*-oxide, **2o** was formed in 1% spectral yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 – 6.74 (m, 2H), 2.81 (s, 2H), 1.46 (dd, *J* = 7.1, 4.0 Hz, 2H), 0.87 (dd, *J* = 7.1, 4.0 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.0, 197.7, 141.7, 140.8, 45.5, 25.9, 19.6 (2C);

HRMS (APPI): m/z calcd for $C_8H_8O_2^{\bullet+}$: 136.0519 $[M]^{\bullet+}$; found: 136.0522.

6-Methylspiro[2.5]oct-5-ene-4,7-dione (2p)



The title compound was prepared from 2-ethyl-5-methyl-1,4-benzoquinone (**1p**, 0.5 mmol, 75 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (25/1 hexanes/EtOAc) gave 58 mg (77%) of the title compound as a colorless solid. When the reaction was performed in the absence of trimethylamine *N*-oxide, **2p** was formed in 2% spectral yield.

TLC R_f = 0.30 (3/1 hexanes/EtOAc);

M.p. 62 °C;

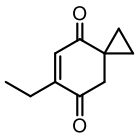
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 – 6.64 (m, 1H), 2.80 (s, 2H), 2.03 (d, *J* = 1.4 Hz, 3H), 1.42 (dd, *J* = 7.0, 4.0 Hz, 2H), 0.84 (dd, *J* = 7.0, 4.0 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.6, 197.8, 150.5, 139.0, 45.6, 26.2, 19.0 (2C), 16.4;

IR (KBr): ṽ = 3008, 2871, 1680, 1653, 1620, 1415, 1379, 1350, 1308, 1261, 1200, 1171, 1007, 962, 937, 910, 808, 698 cm^{-1};

HRMS (APPI): m/z calcd for $C_9H_{10}O_2^{\bullet+}$: 150.0675 $[M]^{\bullet+}$; found: 150.0672.

6-Ethylspiro[2.5]oct-5-ene-4,7-dione (2q)



The title compound was prepared from 2,5-diethyl-1,4-benzoquinone (**1q**, 0.5 mmol, 82 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (30/1 hexanes/EtOAc) gave 60 mg (73%) of the title compound as a pale yellow oil. When the reaction was performed in the absence of trimethylamine *N*-oxide, **2q** was formed in 4% spectral yield.

TLC R_f = 0.37 (3/1 hexanes/EtOAc);

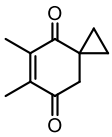
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (t, *J* = 1.6 Hz, 1H), 2.80 (s, 2H), 2.44 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.43 (dd, *J* = 7.0, 3.9 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H), 0.84 (dd, *J* = 7.0, 3.9 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.4, 198.1, 155.6, 137.1, 45.9, 26.1, 22.6, 18.9 (2C), 11.7;

IR (KBr): ṽ = 2970, 2937, 2877, 1666, 1616, 1414, 1377, 1257, 1186, 904, 823 cm^{-1};

HRMS (ESI): m/z calcd for $C_{10}H_{12}NaO_2^+$: 187.0730 $[M+Na]^+$; found: 187.0737.

5,6-Dimethylspiro[2.5]oct-5-ene-4,7-dione (2r)



The title compound was prepared from 5-ethyl-2,3-dimethyl-1,4-benzoquinone (**1r**, 1 mmol, 164 mg) according to the General Procedure C. The reaction took 24 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (35/1 hexanes/EtOAc) gave 67 mg (41%) of the title compound as a pale yellow solid. When the reaction was performed in the absence of trimethylamine *N*-oxide, **2r** was formed in 5% spectral yield.

TLC R_f = 0.42 (3/1 hexanes/EtOAc);

M.p. 52 °C;

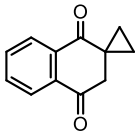
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.78 (s, 2H), 2.03 – 1.99 (m, 6H), 1.42 (dd, *J* = 7.0, 4.0 Hz, 2H), 0.81 (dd, *J* = 7.0, 4.0 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.0, 197.4, 146.5, 145.9, 45.6, 25.5, 18.9 (2C), 13.4, 13.3;

IR (KBr): ṽ = 2999, 2879, 1672, 1655, 1614, 1415, 1377, 1360, 1300, 1259, 1227, 1070, 1043, 937, 872, 818, 746 cm^{-1};

HRMS (APPI): m/z calcd for $C_{10}H_{12}O_2^{\bullet+}$: 164.0832 $[M]^{\bullet+}$; found: 164.0828.

1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2s)



The title compound was prepared from 2-ethyl-1,4-naphthoquinone (**1s**, 0.5 mmol, 93 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (15/1 hexanes/EtOAc) gave 67 mg (72%) of the title compound as a colorless solid. When the reaction was conducted on 5 mmol scale, the product was obtained in 73% yield (the reaction took 3 h to complete). When the reaction was performed in the absence of trimethylamine *N*-oxide, **2s** was formed in 36% spectral yield.

TLC R_f = 0.48 (3/1 hexanes/EtOAc);

M.p. 77 °C;

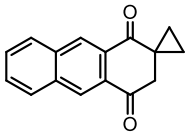
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.09 (m, 1H), 8.08 – 8.03 (m, 1H), 7.78 – 7.71 (m, 2H), 2.99 (s, 2H), 1.56 (dd, *J* = 6.9, 3.9 Hz, 2H), 0.94 (dd, *J* = 6.9, 3.9 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.3, 196.2, 135.7, 135.2, 134.2, 134.1, 126.9, 126.6, 46.3, 26.5, 18.7 (2C);

IR (KBr): ṽ = 3005, 2875, 1682, 1670, 1587, 1427, 1360, 1290, 1244, 1207, 1068, 1036, 997, 787, 748, 692 cm^{-1};

HRMS (APPI): m/z calcd for $C_{12}H_{10}O_2^{\bullet+}$: 186.0675 $[M]^{\bullet+}$; found: 186.0679.

1*H*-Spiro[anthracene-2,1'-cyclopropane]-1,4(3*H*)-dione (2t)



The title compound was prepared from 2-ethyl-1,4-anthraquinone (**1t**, 0.5 mmol, 118 mg) according to the General Procedure C. The reaction was stopped after 24 h (TLC monitoring). Column chromatography on silica gel (25/1 hexanes/EtOAc) gave 47 mg (40%) of the title compound as a pale yellow solid. The starting quinone (40 mg, 34%) was recovered. When the reaction was performed in the absence of trimethylamine *N*-oxide, **2t** was formed in 26% spectral yield.

TLC R_f = 0.31 (3/1 hexanes/EtOAc);

M.p. 131 °C;

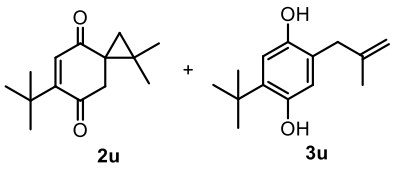
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 8.59 (s, 1H), 8.08 – 8.02 (m, 2H), 7.70 – 7.64 (m, 2H), 3.04 (s, 2H), 1.60 (dd, *J* = 6.9, 3.9 Hz, 2H), 0.97 (dd, *J* = 6.9, 3.9 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.4, 196.2, 135.3, 135.1, 131.9, 131.1, 130.2, 130.0, 129.43, 129.41, 128.8, 128.4, 46.5, 26.8, 18.5 (2C);

IR (KBr): ṽ = 3055, 3005, 2941, 1685, 1676, 1618, 1583, 1446, 1390, 1360, 1304, 1261, 1174, 1057, 993, 966, 903, 808, 760, 744 cm^{-1};

HRMS (APPI): m/z calcd for $C_{16}H_{12}O_2^{\bullet+}$: 236.0832 $[M]^{\bullet+}$; found: 236.0824.

6-(*tert*-Butyl)-1,1-dimethylspiro[2.5]oct-5-ene-4,7-dione (2u) and **2-(*tert*-butyl)-5-(2-methylallyl)hydroquinone (3u)**



2u **3u**

The title compounds were prepared from 2,6-di-*tert*-butyl-1,4-benzoquinone (**1u**, 0.5 mmol, 110 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (100/1 hexanes/EtOAc) funished 27 mg (25%) of compound **2u** as a pale yellow oil, further elution (30/1 hexanes/EtOAc) gave 76 mg (69%) of hydroquinone **3u** as a colorless solid.

Compound **2u**

TLC R_f = 0.55 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, C_6D_6): δ = 6.55 (s, 1H), 2.52 (d, *J* = 15.8 Hz, 1H), 2.37 (d, *J* = 15.8 Hz, 1H), 1.66 (d, *J* = 4.4 Hz, 1H), 1.10 (s, 9H), 1.03 (s, 3H), 0.89 (s, 3H), 0.08 (d, *J* = 4.4 Hz, 1H);

^{13}C NMR (101 MHz, C_6D_6): δ = 199.0, 197.0, 159.5, 137.2, 45.0, 36.9, 35.0, 29.9, 28.8 (3C), 26.6, 22.0, 19.6;

IR (KBr): $\tilde{\nu}$ = 2956, 2912, 2870, 1689, 1647, 1595, 1414, 1360, 1184, 1136, 876, 758 cm^{-1};

HRMS (APPI): m/z calcd for $C_{14}H_{20}O_2^{\bullet+}$: 220.1458 [M]$^{\bullet+}$; found: 220.1460.

Compound **3u**

TLC R_f = 0.41 (3/1 hexanes/EtOAc);

M.p. 116 °C;

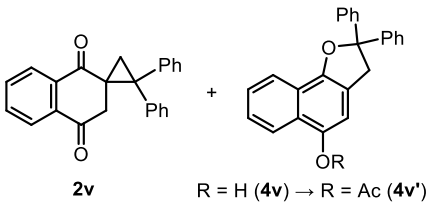
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (s, 1H), 6.42 (s, 1H), 4.91 (br. s, 1H), 4.84 (br. s, 1H), 4.75 (br. s, 1H), 4.49 (br. s, 1H), 3.26 (s, 2H), 1.74 (s, 3H), 1.38 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.01, 147.97, 144.7, 136.0, 122.9, 118.7, 115.3, 112.4, 39.4, 34.5, 29.7 (3C), 22.3;

IR (KBr): $\tilde{\nu}$ = 3278, 2958, 2910, 2871, 1410, 1225, 1188, 1134, 891, 872, 808, 752 cm^{-1};

HRMS (APPI): m/z calcd for $C_{14}H_{20}O_2^{\bullet+}$: 220.1458 [M]$^{\bullet+}$; found: 220.1451.

2,2-Diphenyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2v) and **2,2-diphenyl-2,3-dihydronaphtho[1,2-b]furan-5-yl acetate (4v')**



2v R = H (**4v**) → R = Ac (**4v'**)

The title compound was prepared from 2-(2,2-diphenylethyl)-1,4-naphthoquinone (**1v**, 0.15 mmol, 50.7 mg) in 52% spectral yield according to the General Procedure C. The reaction took 2 h to complete (^{1}H NMR monitoring). The resulting solution containing **2v** was allowed to stand for 6 days at room temperature without irradiation. After this time, ^{1}H NMR showed that **2v** was almost fully consumed, and signals corresponding to 2,2-diphenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (**4v**) were observed. Earlier attempts to isolate **4v** in pure state were not successful, therefore this product was isolated as *O*-acetate derivative **4v'**. The solution was cooled to 0 °C, treated with Et_3N (0.45 mmol, 45 mg, 63 μl)

followed by Ac_2O (0.3 mmol, 31 mg, 28 µl), shaken, and held at 0 °C for 1 h. After another 3 h at room temperature, the solution was concentrated under reduced pressure. Column chromatography of the residue on silica gel (25/1 hexanes/EtOAc) furnished 26.1 mg (46% overall) of compound **4v'** as a pale yellow oil.

Compound **2v**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 – 8.17 (m, 1H), 7.96 – 7.93 (m, 1H), 7.81 – 7.73 (m, 2H), 7.33 – 7.04 (m, 10H), 3.33 (d, *J* = 17.4 Hz, 1H), 2.78 (d, *J* = 4.9 Hz, 1H), 2.47 (d, *J* = 17.4 Hz, 1H), 1.64 (d, *J* = 4.9 Hz, 1H);

^{13}C NMR signals could not be unequivocally assigned due to a high concentration of **4v**.

HRMS (ESI): m/z calcd for $C_{24}H_{18}NaO_2^+$: 361.1199 $[M+Na]^+$; found: 361.1194.

Compound **4v'**

TLC R_f = 0.35 (3/1 hexanes/EtOAc);

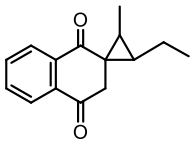
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 – 8.18 (m, 1H), 7.83 – 7.76 (m, 1H), 7.59 – 7.48 (m, 6H), 7.37 – 7.31 (m, 4H), 7.29 – 7.24 (m, 2H), 7.12 (s, 1H), 4.12 (s, 2H), 2.44 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.1, 151.9, 145.5 (2C), 140.5, 128.5 (4C), 127.6 (2C), 126.8, 126.4, 126.12 (4C), 126.08, 122.1, 121.7, 120.8, 118.4, 115.4, 93.6, 45.7, 21.1;

IR (KBr): $\tilde{\nu}$ = 3060, 3024, 2925, 1763, 1597, 1446, 1365, 1188, 1082, 1028, 999, 903, 752, 731 cm^{-1};

HRMS (ESI): m/z calcd for $C_{26}H_{20}NaO_3^+$: 403.1305 $[M+Na]^+$; found: 403.1305.

2-Ethyl-3-methyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2w)



The title compound was prepared from 2-(3-pentyl)-1,4-naphthoquinone (**1w**, 0.5 mmol, 114 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (100/1 hexanes/EtOAc) gave 85 mg (75%) of the title compound (*dr* 3/2/1) as a pale yellow oil.

TLC R_f = 0.53 (3/1 hexanes/EtOAc);

^{1}H NMR signals of the 1st diastereomer (400 MHz, $CDCl_3$): δ = 8.13 – 8.08 (m, 1H), 8.07 – 7.99 (m, 1H), 7.76 – 7.69 (m, 2H), 3.31 (d, *J* = 16.8 Hz, 1H), 2.56 (d, *J* = 16.8 Hz, 1H), 2.09 – 1.87 (m, 1H), 1.52 – 0.98 (m, 6H), 0.64 (t, *J* = 7.3 Hz, 3H);

^{1}H NMR signals of the 2nd diastereomer (400 MHz, $CDCl_3$): δ = 8.13 – 8.08 (m, 1H), 8.07 – 7.99 (m, 1H), 7.76 – 7.69 (m, 2H), 2.92 (d, *J* = 17.6 Hz, 1H), 2.85 (d, *J* = 17.6 Hz, 1H), 2.09 – 1.87 (m, 1H), 1.79 (dt, *J* = 9.7, 7.4 Hz, 1H), 1.52 – 0.98 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 3H);

^{1}H NMR signals of the 3rd diastereomer (400 MHz, $CDCl_3$): δ = 8.13 – 8.08 (m, 1H), 8.07 – 7.99 (m, 1H), 7.76 – 7.69 (m, 2H), 3.31 (d, *J* = 16.8 Hz, 1H), 2.60 (d, *J* = 16.8 Hz, 1H), 2.09 – 1.87 (m, 1H), 1.52 – 0.98 (m, 9H);

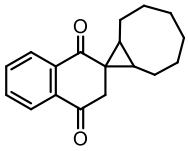
^{13}C NMR signals of all 3 isomers (101 MHz, $CDCl_3$): δ = 197.29, 197.26, 197.21, 196.7, 194.8, 136.1, 135.3, 135.1, 135.0, 134.31, 134.27, 133.85, 133.84, 127.0, 126.9, 126.7, 126.43, 126.38, 45.0, 43.5,

43.3, 36.8, 36.1, 36.0, 35.8, 35.6, 33.1, 33.0, 27.6, 24.5, 21.9, 20.0, 16.7, 14.04, 13.96, 13.7, 13.2, 12.1, 7.9;

IR (KBr): $\tilde{\nu}$ = 2960, 2931, 2871, 1693, 1668, 1593, 1456, 1417, 1282, 1252, 1205, 1061, 1022, 806, 752, 715 cm^{-1};

HRMS (APPI): m/z calcd for $C_{15}H_{16}O_2^{\bullet+}$: 228.1145 $[M]^{\bullet+}$; found: 228.1153.

1'*H*-spiro[bicyclo[6.1.0]nonane-9,2'-naphthalene]-1',*4*'(3'*H*)-dione (2x)



The title compound was prepared from 2-cyclooctyl-1,4-naphthoquinone (**1x**, 0.25 mmol, 67 mg) according to the General Procedure C. The reaction took 1 h to complete (TLC monitoring; visible loss of yellow color). Column chromatography on silica gel (50/1 hexanes/EtOAc) gave 39 mg (58%) of the title compound (*dr* 4/2/1) as a pale yellow oil.

TLC R_f = 0.46 (3/1 hexanes/EtOAc);

^{1}H NMR signals of the 1st diastereomer (400 MHz, $CDCl_3$): δ = 8.14 – 8.07 (m, 1H), 8.06 – 7.99 (m, 1H), 7.77 – 7.66 (m, 2H), 3.30 (d, *J* = 17.0 Hz, 1H), 2.59 (d, *J* = 17.0 Hz, 1H), 2.14 – 0.67 (m, 14H);

^{1}H NMR signals of the 2nd diastereomer (400 MHz, $CDCl_3$): δ = 8.14 – 8.07 (m, 1H), 8.06 – 7.99 (m, 1H), 7.77 – 7.66 (m, 2H), 2.96 (s, 2H), 2.14 – 0.67 (m, 14H);

^{1}H NMR signals of the 3rd diastereomer (400 MHz, $CDCl_3$): δ = 8.14 – 8.07 (m, 1H), 8.06 – 7.99 (m, 1H), 7.77 – 7.66 (m, 2H), 2.90 (s, 2H), 2.14 – 0.67 (m, 14H);

^{13}C NMR signals of all 3 isomers (101 MHz, $CDCl_3$): δ = 197.3, 197.2, 196.5, 196.4, 194.9, 137.3, 135.9, 135.4, 135.1, 135.0, 134.5, 134.24, 134.20, 134.15, 133.8, 133.6, 127.0, 126.8, 126.5, 126.4, 126.3, 126.2, 50.0, 43.3, 42.1, 37.3, 35.7, 33.9, 33.7, 33.22, 33.19, 31.6, 31.5, 30.8, 29.4, 29.1, 28.9, 28.8, 28.4, 27.0, 26.4, 26.3, 22.0, 21.3;

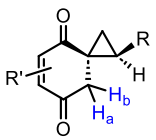
IR (KBr): $\tilde{\nu}$ = 2922, 2852, 1693, 1670, 1593, 1454, 1415, 1281, 1254, 1205, 1068, 1020, 966, 918, 796, 752, 696 cm^{-1};

HRMS (APPI): m/z calcd for $C_{18}H_{20}O_2^{\bullet+}$: 268.1458 $[M]^{\bullet+}$; found: 268.1461.

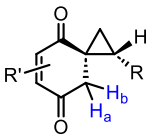
2.5 Structural assignment of diastereomeric spirocyclopropanes 2a-2n

The structures of pure diastereomers *syn*-**2j** and *anti*-**2l** were confirmed by single crystal X-ray diffraction analysis and their spectra were used as the reference points. The analysis of the ^{1}H NMR data of compounds **2** given in the Table S3 reveals that the chemical shift of the methylene hydrogens located in the 6-memebered ring could be used to assign the relative stereochemistry of the diastereomers. Thus, the methylene hydrogens in *syn*-**2** are noticeably downshifted compared to those in *anti*-**2**. In addition, the difference between the chemical shifts of H_a and H_b ($\Delta\delta_{Ha/b}$) is considerably higher in *syn*-**2** compared to *anti*-**2**.

Table S3. ^{1}H NMR analysis of diastereomeric products **2a-n**.



syn-**2**



anti-**2**

2	R	*syn*-**2**		*anti*-**2**	
		$\delta_{Ha/b}$, ppm	$\Delta\delta_{Ha/b}$, ppm	$\delta_{Ha/b}$, ppm	$\Delta\delta_{Ha/b}$, ppm
2a	Me	NA	-	2.89, 2.73	0.16
2b	Me	NA	-	2.90, 2.74	0.16
2c	Me	NA	-	2.85, 2.69	0.16
2d	Me	NA	-	2.86, 2.69	0.17
2e	Me	3.47, 2.43	1.04	3.04, 2.97	0.07
2f	Me	NA	-	3.10, 3.03	0.07
2g	OAc	NA	-	2.91, 2.68	0.23
2h	*n*-Pr	3.48, 2.42	1.06	3.04, 2.99	0.05
2i	CH_2NPhth	3.36, 2.54	0.82	3.40, 3.10	0.30
2j	NPhth	3.42, 2.82	0.60	3.08, 2.71	0.37
2k	Ph	3.35, 2.59	0.76	2.54, 2.42	0.12
2l	Ph	3.62, 2.69	0.93	2.74, 2.60	0.14
2m	2-Br-C_6H_4	3.56, 2.96	0.60	2.66, 2.47	0.19
2n	4-CN-C_6H_4	3.63, 2.72	0.91	2.74, 2.55	0.19

NA – the signal could not be assigned unequivocally due to low intensity.

2.6 Mechanistic experiments

2.6.1 Analysis of interaction between thymoquinone (1a) and TMAO by UV-Vis spectroscopy

The recorded UV-Vis spectra (Figure S1) show absorption of thymoquinone (0.01 M in chloroform), TMAO (0.01 M in chloroform) and a solution of thymoquinone (0.01 M in chloroform) containing TMAO (10 mol%). The absence of a noticeable bathochromic shift in the spectra indicates that EDA complexation between thymoquinone and TMAO is unlikely.

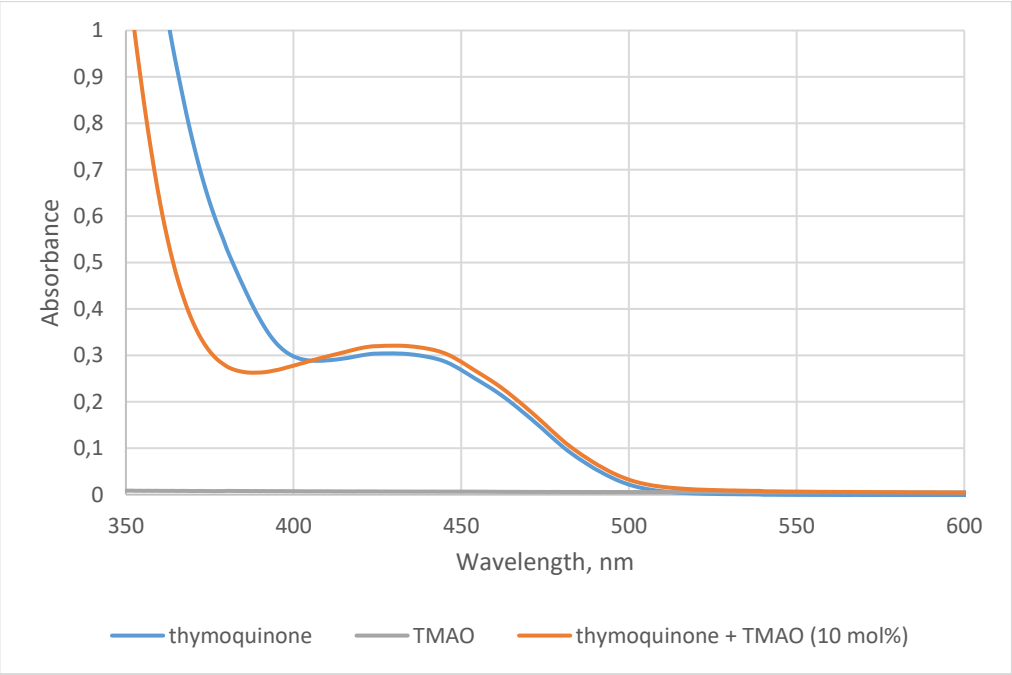
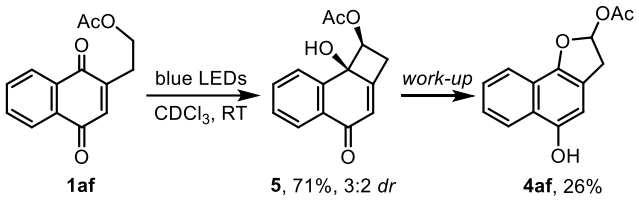


Figure S1. UV-Vis spectra of thymoquinone (**1a**) in $CHCl_3$ with and without TMAO.

2.6.2 Detection of cyclobutane 5 by NMR.



Scheme S3. Formation of **4af** from **1af** through intermediate **5**.

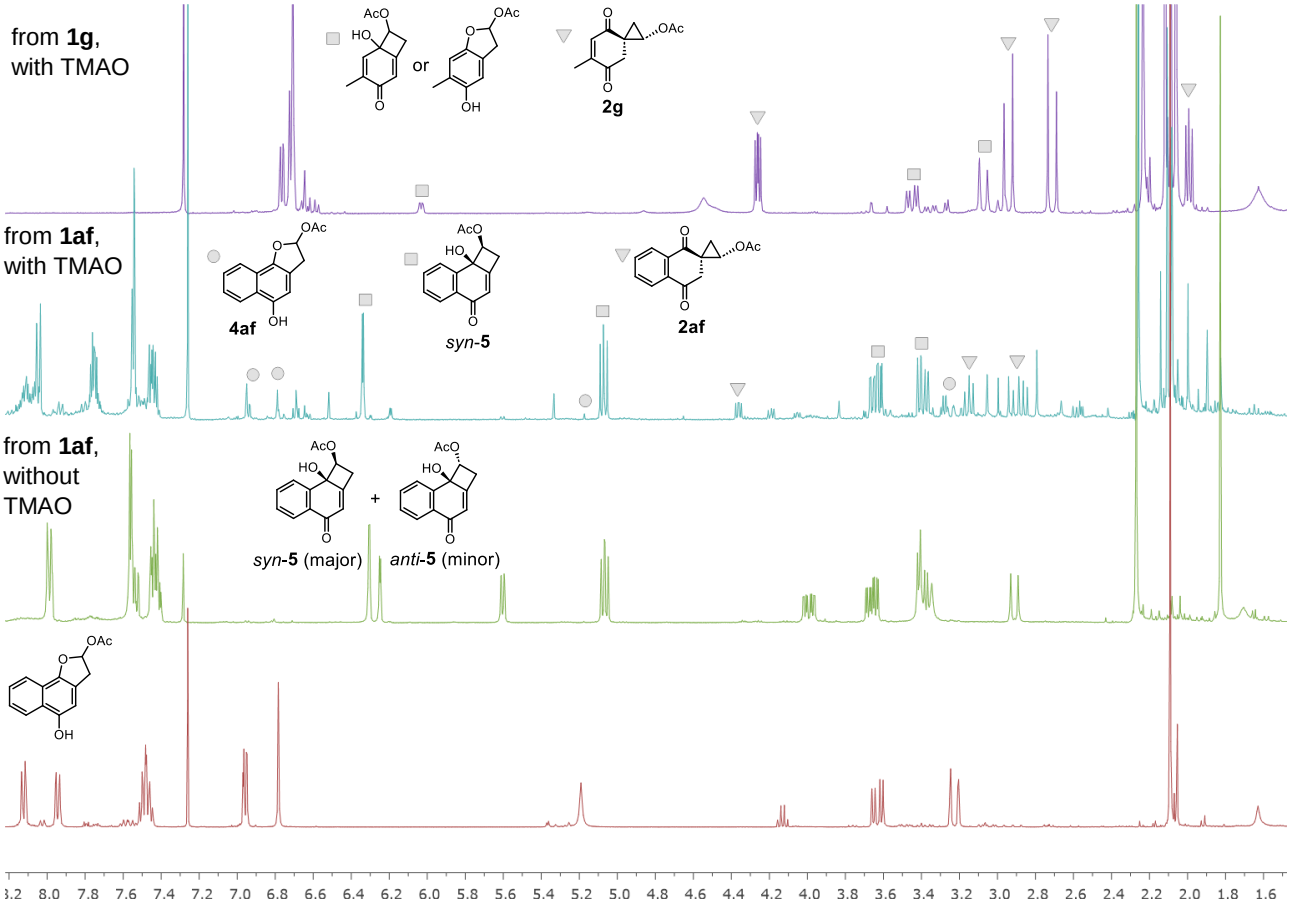
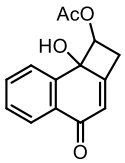


Figure S2. Spectral comparison of the reaction outcome with and without TMAO.

8b-Hydroxy-4-oxo-1,2,4,8b-tetrahydrocyclobuta[a]naphthalen-1-yl acetate (5)



A solution of 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)ethyl acetate (0.15 mmol, 36.6 mg) in $CHCl_3$ was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere. The reaction took 1 h to complete (NMR monitoring). Exclusive formation of diastereomeric product **5** was observed (71% spectral yield, *dr* 3/2). The relative stereochemistry of diastereomers was assigned using Karplus equation. Attempted isolation of this product by preparative TLC on silica gel (3/1 hexanes/EtOAc) only afforded dihydrobenzofuran **4af** as a pinkish oil (9.5 mg, 26% yield).

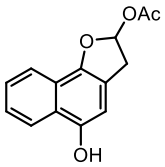
^{1}H NMR (400 MHz, $CDCl_3$), major *syn*-diastereomer: δ = 8.00 – 7.92 (m, 1H), 7.58 – 7.48 (m, 2H), 7.45 – 7.36 (m, 1H), 6.28 (dd, *J* = 2.8, 0.7 Hz, 1H), 5.04 (dd, *J* = 8.0, 6.8 Hz, 1H), 3.64 (ddd, *J* = 15.0, 8.0, 2.8 Hz, 1H), 3.37 (ddd, *J* = 15.0, 6.8, 0.7 Hz, 1H), 2.25 (s, 3H);

^{1}H NMR (400 MHz, $CDCl_3$), minor *anti*-diastereomer: δ = 8.00 – 7.92 (m, 1H), 7.58 – 7.48 (m, 2H), 7.45 – 7.36 (m, 1H), 6.24 – 6.21 (m, 1H), 5.58 (dd, *J* = 6.7, 0.7 Hz, 1H), 3.97 (ddd, *J* = 15.9, 6.7, 2.5 Hz, 1H), 2.89 (ddd, *J* = 15.9, 1.2, 0.7 Hz, 1H), 1.80 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$), both diastereomers: δ = 185.5, 185.3, 170.6, 170.5, 161.8, 156.2, 142.3, 140.5, 133.4, 132.8, 132.5, 132.3, 129.0, 128.9, 127.33, 127.31, 127.0, 126.7, 124.3, 122.8, 78.1, 77.7, 73.8, 68.0, 40.4, 40.2, 21.0, 20.8;

HRMS (ESI): m/z calcd for $C_{14}H_{12}NaO_4^+$: 267.0628 $[M+Na]^+$; found: 267.0629.

5-Hydroxy-2,3-dihydronaphtho[1,2-b]furan-2-yl acetate (4af)



The title compound was prepared as described above under the preparation of **5**.

TLC R_f = 0.45 (1/1 hexanes/EtOAc);

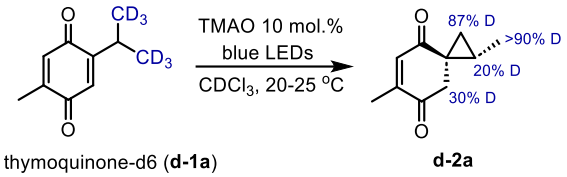
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.10 (m, 1H), 7.98 – 7.91 (m, 1H), 7.52 – 7.44 (m, 2H), 6.96 (dd, *J* = 6.7, 1.5 Hz, 1H), 6.78 (s, 1H), 5.19 (br. s, 1H), 3.63 (dd, *J* = 16.9, 6.7 Hz, 1H), 3.23 (dd, *J* = 16.9, 1.5 Hz, 1H), 2.09 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.4, 147.4, 146.8, 126.5, 125.4, 124.4, 122.2, 121.5, 120.9, 116.9, 105.5, 98.9, 37.5, 21.4;

IR (KBr): $\tilde{\nu}$ = 3363, 2924, 2850, 1720, 1599, 1394, 1228, 1155, 1072, 989, 949, 833, 766, 733 cm^{-1};

HRMS (ESI): m/z calcd for $C_{14}H_{12}NaO_4^+$: 267.0628 $[M+Na]^+$; found: 267.0623.

2.6.3 Labelling experiment



Scheme S4. Transformation of deuterated thymoquinone **d-1a** under the benchmark conditions.

According to the General Procedure C, a solution of deuterated quinone **d-1a** (0.15 mmol, 24.6 mg) in 0.1 M $CDCl_3$ containing TMAO (0.015 mmol, 1.1 mg) was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere. The recorded ^{1}H NMR spectrum shows the following distribution of deuterium atoms in the product **d-2a**: cyclopropylmethyl group (>90% D), methine position of the cyclopropane ring (20% D), methylene group of the 3-membered ring (87% D), and methylene group of the 6-membered ring (30% D).

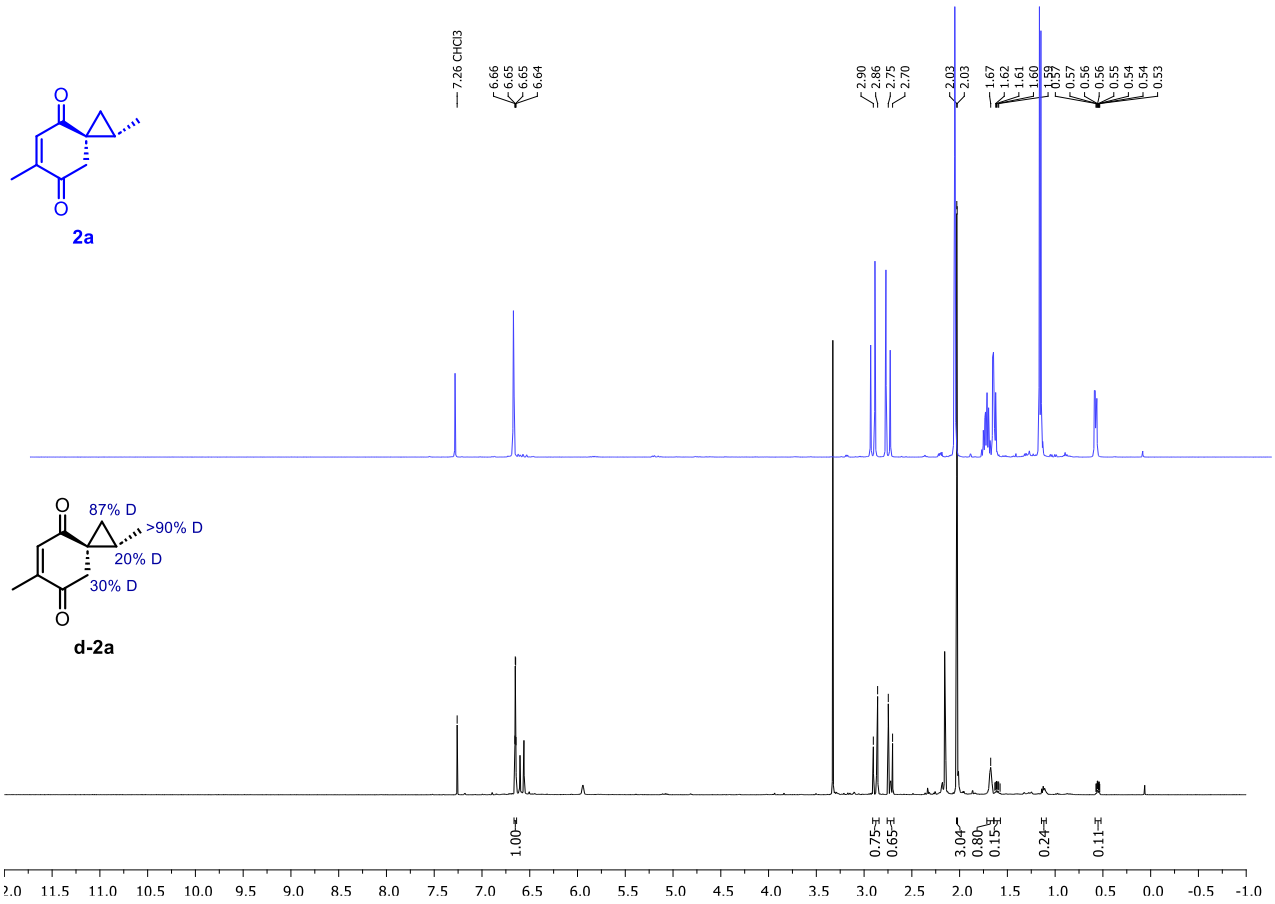
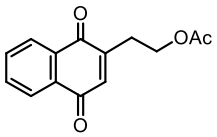


Figure S3. ^{1}H NMR spectrum of the reaction mixture compared to the spectrum of **2a.**

2.7 Transformations of spirocyclopropanes 2

2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl acetate (1ah)



First, a solution of **1s** in chloroform was prepared from 2-ethyl-1,4-naphthoquinone (0.5 mmol, 93 mg) according to General Procedure C. This solution was then vacuum-filtered through a pad of silica gel, which was then washed with hexanes/EtOAc (10/1, 100 mL). The solution was concentrated under reduced pressure and redissolved in AcOH (4 mL). Next, a solution of methanesulfonic acid in AcOH (0.05 M, 0.05 mmol, 1 mL) was added. The reaction mixture was stirred at 80 °C for 3h, cooled to room temperature, treated with 30% aqueous H_2O_2 (0.5 mL), and the stirring was continued for 12 h. The yellow solution was poured into water (50 mL) and extracted with EtOAc (3×20 mL). The combined organic extracts were washed with water (2×50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) gave 49 mg (40% overall) of the title compound as a yellow solid.

TLC R_f = 0.35 (3/1 hexanes/EtOAc);

M.p. 67 °C;

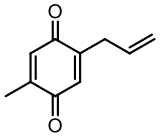
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.04 (m, 2H), 7.76 – 7.71 (m, 2H), 6.84 (t, *J* = 1.1 Hz, 1H), 4.33 (t, *J* = 6.3 Hz, 2H), 2.90 (td, *J* = 6.3, 1.1 Hz, 2H), 2.02 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.94, 184.90, 171.0, 147.7, 136.4, 134.0, 133.9, 132.23, 132.19, 126.8, 126.3, 62.0, 29.5, 21.0.

IR (KBr): ṽ = 3049, 1736, 1655, 1620, 1591, 1308, 1240, 1144, 1039, 951, 924, 891, 771 cm^{-1};

HRMS (ESI): m/z calcd for $C_{14}H_{12}NaO_4^+$: 267.0628 $[M+Na]^+$; found: 267.0632.

2-Allyl-5-methyl-1,4-benzoquinone (1ag)



A solution of a thymoquinone (0.5 mmol, 82 mg) and trimethylamine *N*-oxide (0.05 mmol, 3.8 mg) in $CHCl_3$ (5 mL) was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere for 1 h. After that, (diacetoxyiodo)benzene (0.75 mmol, 242 mg) was added and the reaction mixture was stirred for 48 h at 20–25 °C in the dark. Next, the volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (50/1 hexanes/EtOAc) gave 39 mg (48%) of the title compound as a yellow oil.

TLC R_f = 0.50 (3/1 hexanes/EtOAc);

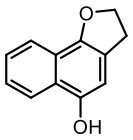
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (q, *J* = 1.5 Hz, 1H), 6.55 (t, *J* = 1.3 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.21 – 5.12 (m, 2H), 3.19 – 3.13 (m, 2H), 2.03 (d, *J* = 1.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 188.2, 187.5, 147.7, 145.9, 133.6, 133.05, 133.00, 119.0, 32.9, 15.6.

IR (KBr): ṽ = 2981, 2924, 1653, 1612, 1427, 1348, 1282, 1240, 1134, 1003, 903 cm^{-1};

HRMS (APPI): m/z calcd for $C_{10}H_{10}O_2^{\bullet+}$: 162.0675 $[M]^{\bullet+}$; found: 162.0680.

2,3-Dihydronaphtho[1,2-b]furan-5-ol (4s)



A solution of a 2-ethyl-1,4-naphthoquinone (0.5 mmol, 93 mg) and trimethylamine *N*-oxide (0.05 mmol, 3.8 mg) in $CHCl_3$ (5 mL) was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere for 1 h. After that, the volatiles were removed under reduced pressure and the residue was redissolved in MeCN (5 mL). Next, *para*-toluenesulfonic acid monohydrate (9.5 mg, 0.05 mmol) was added and the reaction mixture was stirred at 150 °C under Ar atmosphere (6-8 bar) for 3 h in a microwave reactor (Anton Paar Monowave 400). After cooling down to room temperature, the reaction mixture was concentrated under reduced pressure. Column chromatography of the residue on silica gel (25/1 hexanes/EtOAc) gave 64 mg (69%) of the title compound as a colorless oil.

TLC R_f = 0.35 (2/1 hexanes/EtOAc);

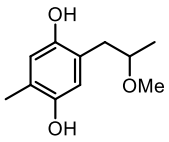
^{1}H NMR (400 MHz, acetone-d6): δ = 8.45 (s, 1H), 8.21 – 8.13 (m, 1H), 7.84 – 7.75 (m, 1H), 7.46 – 7.36 (m, 2H), 6.86 (s, 1H), 4.66 (t, *J* = 8.8 Hz, 2H), 3.30 (t, *J* = 8.8 Hz, 2H);

^{13}C NMR (101 MHz, acetone-d6): δ = 149.0, 147.8, 126.3, 125.3, 125.0, 123.6, 121.8, 121.7, 120.6, 106.3, 71.8, 31.8;

IR (KBr): $\tilde{\nu}$ = 3386, 2962, 2895, 2862, 1595, 1471, 1385, 1306, 1259, 1221, 1186, 1147, 1065, 1003, 920, 835, 808, 764 cm^{-1};

HRMS (APPI): m/z calcd for $C_{12}H_{10}O_2^{\bullet+}$: 186.0675 $[M]^{\bullet+}$; found: 186.0674.

2-(2-Methoxypropyl)-5-methylhydroquinone (6)



A solution of a thymoquinone (0.5 mmol, 82 mg) and trimethylamine *N*-oxide (0.05 mmol, 3.8 mg) in $CHCl_3$ (5 mL) was irradiated at 20–25 °C with a blue LED strip (470 nm, 14.4 W/m, 1 m) under Ar atmosphere for 1 h. After that, MeOH (5 mL) was added and the reaction mixture was stirred for 4 h at 60 °C without irradiation. Next, the volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexanes/EtOAc) funished 13 mg (16%) of **3a** as a colorless solid and further elution (6/1 hexanes/EtOAc) gave 77 mg (79%) of the title compound as a pinkish solid.

TLC R_f = 0.27 (2/1 hexanes/EtOAc);

M.p. 95 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (s, 1H), 6.46 (s, 1H), 3.69 – 3.61 (m, 1H), 3.36 (s, 3H), 2.71 (d, *J* = 5.1 Hz, 2H), 2.18 (s, 3H), 1.18 (d, *J* = 5.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.3, 147.1, 123.7, 123.6, 119.5, 117.9, 79.7, 56.5, 39.7, 18.2, 15.7.

HRMS (ESI): m/z calcd for $C_{11}H_{16}NaO_3^+$: 219.0992 $[M+H]^+$; found: 219.0993.

The recorded spectroscopic values agree with the previously reported data.[25]

[25] Enomoto, S.; Asano, R.; Iwahori, Y.; Narui, T.; Okada, Y.; Singab, A. N. B.; Okuyama, T. *Biol. Pharm. Bull.* **2001**, *24*, 307–310.

2.8 Crystallographic data

The diffraction data of single crystals of **2l**, **2m** and **2j** were obtained on Bruker D8 VENTURE Kappa Duo PHOTONIII by IμS micro-focus sealed tube either with MoKα (0.71073) or CuKα (λ= 1.54178) radiation at low temperature preserved by Cryostream Cooler. The structures were solved by direct methods (XT)[26] and refined by full matrix least squares based on F^2 (SHELXL2019)[27] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom). Two compound (**2l** and **2j**) crystallized in non-centrosymmetric space group $P2_1$, however determination of absolute configuration[28] is not reliable due to lack of atoms with significant anomalous dispersion. Basic crystallographic data are given in Table S4.

The specific details for sample **2m** are as follows: the crystal was refined as two component twin with twin matrix : -0.999 0.0 0.0; 0.0 -0.999 0.0; 0.585 0.335 0.999, the volume ration of domains 0.529:0.471.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), the deposition numbers are in Table S4 and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/structures/).

[26] SHELXT: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3–8
[27] SHELXL: Sheldrick, G.M. *Acta Cryst.* **2015**, *C71*, 3–8.
[28] Parsons,S., Flack, H.D., Wagner, T. *Acta Cryst*. **2013**, *B69*, 249–259.

Table S4. Crystal data, data collection, and refinement parameters for **2j, 2l,** and **2m**.

Compound	**2j**	**2l**	**2m**
CCDC	2352748	2352747	2352749
Formula	$C_{20}H_{13}NO_4$	$C_{18}H_{14}O_2$	$C_{18}H_{13}BrO_2$
M.w.	331.31	262.29	341.19
Crystal system Space group	Monoclinic $P2_1$ (No. 4)	Monoclinic $P2_1$ (No. 4)	Triclinic P -1 (No.2)
a [Å]	9.7795 (3)	10.3866 (9)	8.2511 (6)
b [Å]	14.7456 (4)	5.6440 (5)	11.6841 (9)
c [Å]	11.7028 (3)	12.0776 (10)	15.8119 (14)
α [°]			94.173 (3)°
β [°]	113.180 (1)°	114.196 (5)°	96.426 (3)°
γ [°]			109.320 (2)°
Z	4	2	4
$V[Å^3]$	1551.36 (8)	645.81 (10)	1419.7 (2)
Temperature	120	120	120
D_x [g cm^{-3}]	1.419	1.349	1.596
Wavelength, Å	0.71073	1.54178	0.71073
Crystal size [mm]	0.37 × 0.23 × 0.14	0.57 × 0.04 × 0.04	0.31 × 0.18 × 0.11
Crystal color, shape	Prism, colorless	Needle, colorless	Plate, colorless
μ [mm^{-1}]	0.10	0.69	2.90
T_{min},T_{max}	0.95, 0.99	0.78, 0.98	0.56, 0.74
Measured reflections	36082	9349	105383
Independent diffractions (R_{int}[a])	7077, (0.026)	2357, (0.054)	11973, (0.041)
Observed diffract. [I>2σ(I)]	6977	2148	11269
No. of parameters	451	181	380
R[b]	0.029	0.046	0.030
$wR(F^2)$ for all data	0.074	0.132	0.081
GOF[c]	1.05	1.09	1.11
Residual electron density [e/Å^3]	0.27, −0.16	0.18, −0.28	0.56, −0.50
Absolute structure parameter	0.08 (18)	-0.2 (3)	

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$; [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

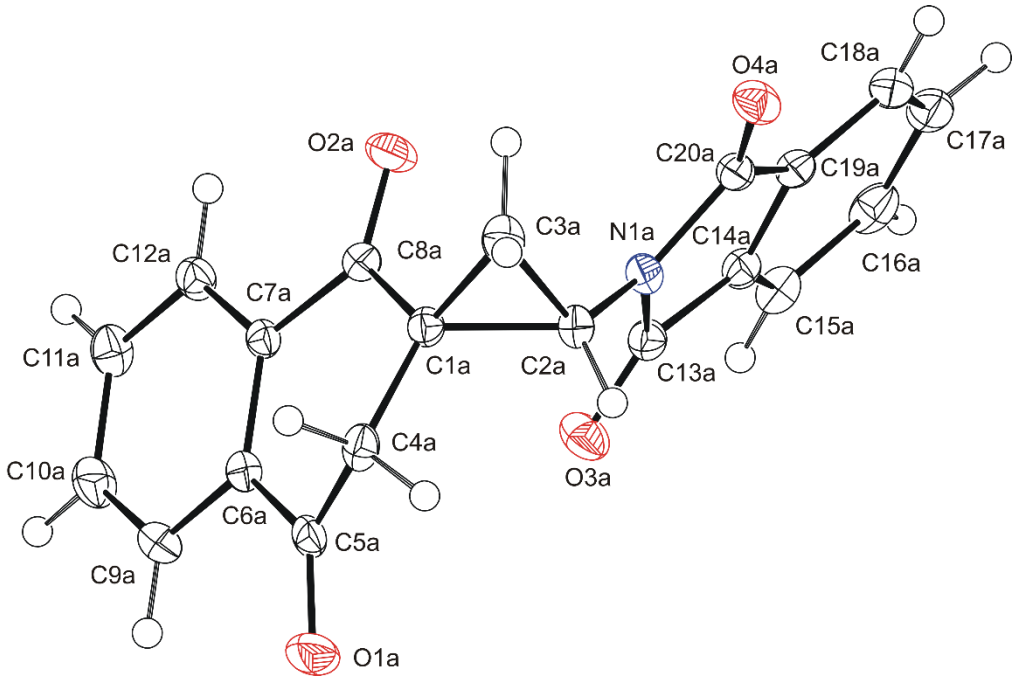


Figure S4. View on the molecule of **2j** with atom numbering schema. The displacement ellipsoids are drawn on 30% probability level.

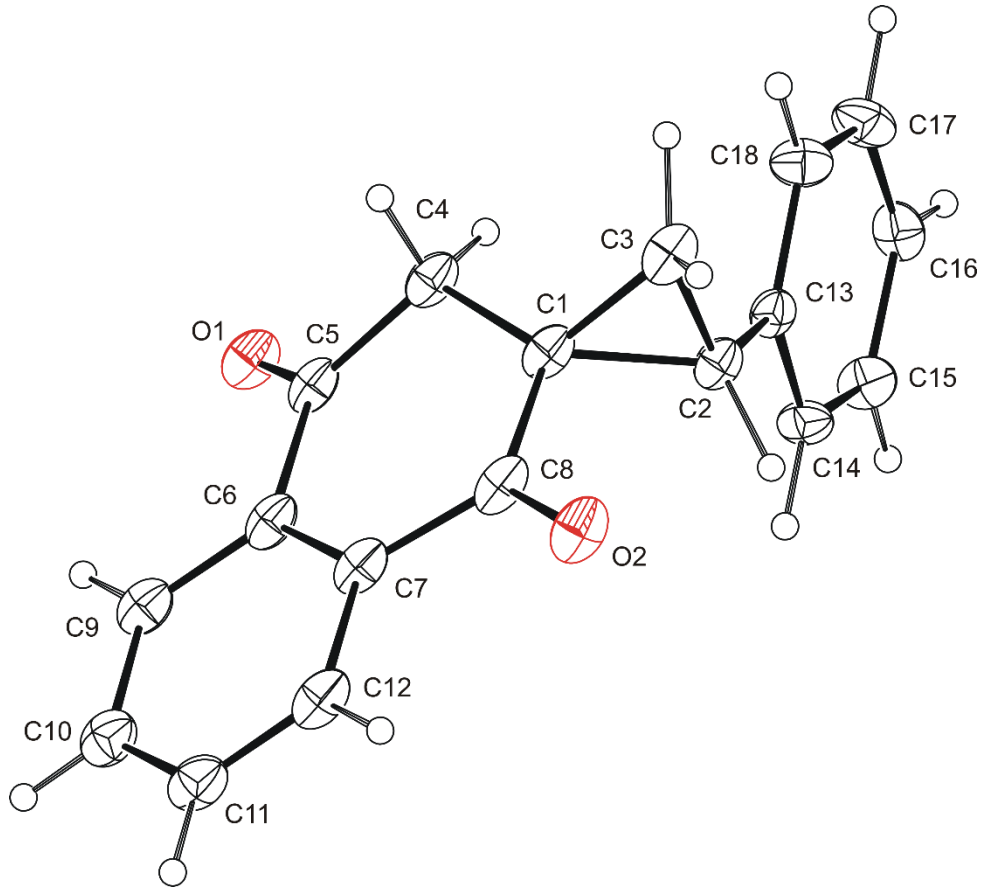


Figure S5. View on the molecule of **2l** with atom numbering schema. The displacement ellipsoids are drawn on 50% probability level.

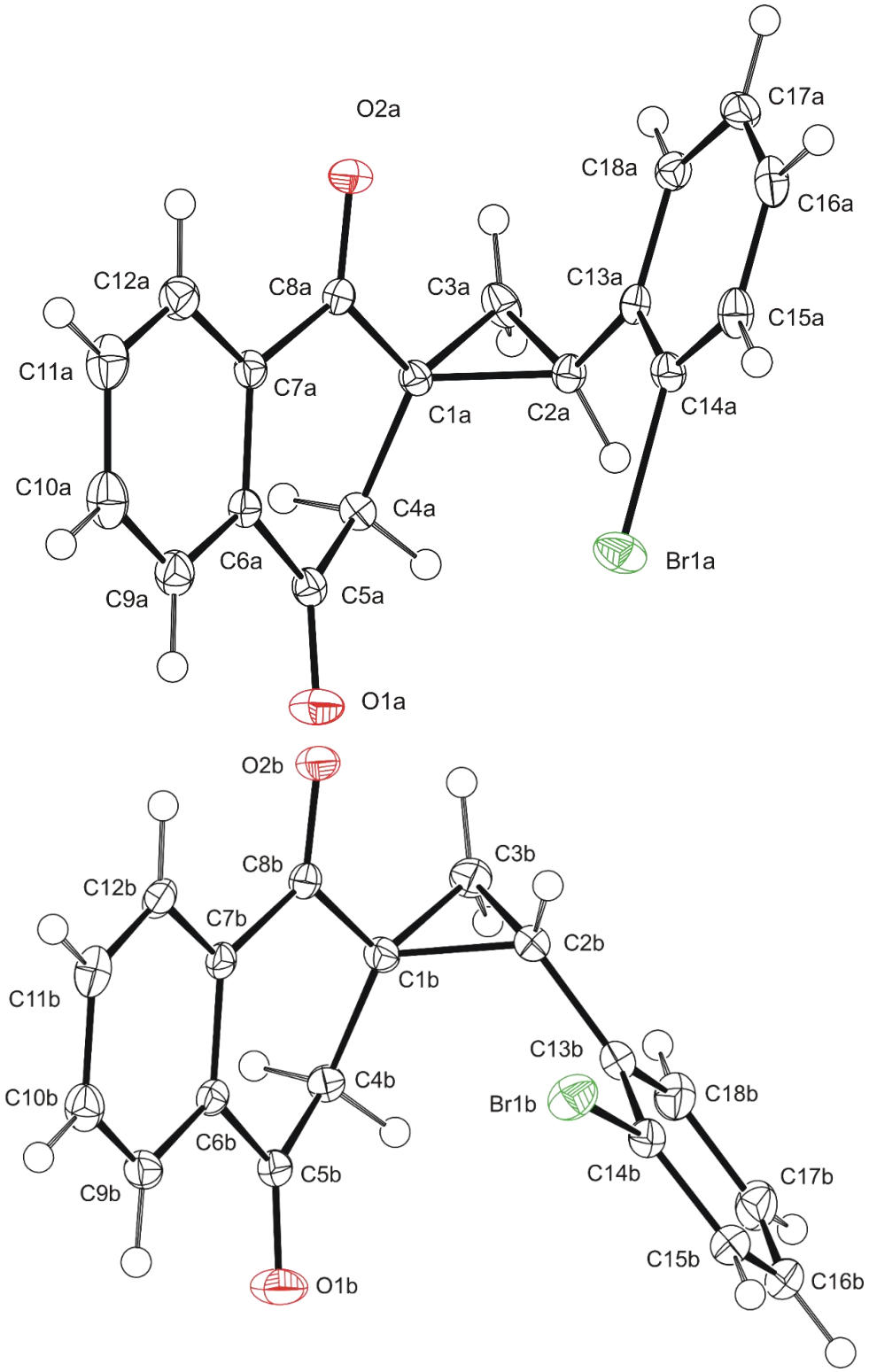


Figure S6. View on the molecules of **2m** with atom numbering schema. The displacement ellipsoids are drawn on 50% probability level. The displacement ellipsoids are drawn on 50% probability level. There are two diastereomers in asymmetric unit, differing in the configuration on atoms C2a and C2b.

3. Computational analysis by DFT and TD-DFT

3.1 General

All calculations were carried out using ORCA 5.0.3 program.[29] The structures were optimized using the PBE0 functional,[30] the def2-TZVP basis set,[31] and the D3BJ dispersion correction.[32] The effect of solvation in chloroform on geometry optimizations was included by employing the conductor-like polarizable continuum model (CPCM).[33] The calculations were accelerated by resolution-of-identity approximation (RIJCOSX).[34] The unrestricted Kohn-Sham formalism was used to approximate the lowest-energy broken-symmetry singlet (BSS) and triplet states. Transition states were located by performing geometry optimizations to the first-order saddle point, and confirmed by the analytic frequency calculations.

The terms contributing to Gibbs free energy were calculated as follows:

$$G = E_{el} + G_{solv} + [E_{ZPVE} + RT - RTlnQ], \quad (1)$$

where:

i) E_{el} is the *in vacuo* electronic energy, calculated using the methodology described above,

ii) G_{solv} is the free energy of solvation; calculated using the conductor-like polarizable continuum model (CPCM),

iii) $[E_{ZPVE} + RT - RT \ln Q]$ corresponds to the thermal enthalpic and entropic contributions to the solute energy with E_{ZPVE} and Q being the zero-point vibrational energy and the molecular partition function, respectively; obtained from frequency calculations with the rigid rotor/harmonic oscillator approximation (for p = 1 bar, T = 298 K).

To obtain excited-state energies along the H-atom transfer coordinate, we have performed relaxed one-dimensional potential energy surface scans along O…H distance, followed by the TD-DFT calculations using the same methodology as above.

The energy of biradical **III**, which is a higher-energy structure than relaxed closed-shell **IV/V** intermediate, was obtained by optimizing the triplet (S = 1) state to minimum, followed by the single-point BSS calculation.

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[29] Neese, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78.
[30] Adamo, C.; Barone, F. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
[31] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297–3305.
[32] a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104; b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem*. **2011**, *32*, 1456–1465.
[33] a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001; b) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
[34] Helmich-Paris, B.; de Souza, B.; Neese, F.; Izsák, R. *J. Chem. Phys.* **2021**, *155*, 104109.

Sample ORCA inputs

Example Geometry Optimization

```
! UKS PBE0 def2-TZVP def2/J RIJCOSX
!D3BJ Opt Freq CPCM(chloroform)
%maxcore 3000
*xyzfile 0 1 geom.xyz
```

Example TS Optimization

```
! UKS PBE0 def2-TZVP def2/J RIJCOSX
!D3BJ OptTS Freq CPCM(chloroform)
%maxcore 3000
%geom
Calc_Hess true
end
*xyzfile 0 1 geom.xyz
```

Example TD-DFT Calculation

```
! UKS PBE0 def2-TZVP def2/J RIJCOSX
!D3BJ TightSCF CPCM(chloroform) Normalprint
%maxcore 3000
%tddft
 maxdim 5
 nroots 15
 end
*xyzfile 0 1 geom.xyz
```

3.2 Computational mechanistic studies

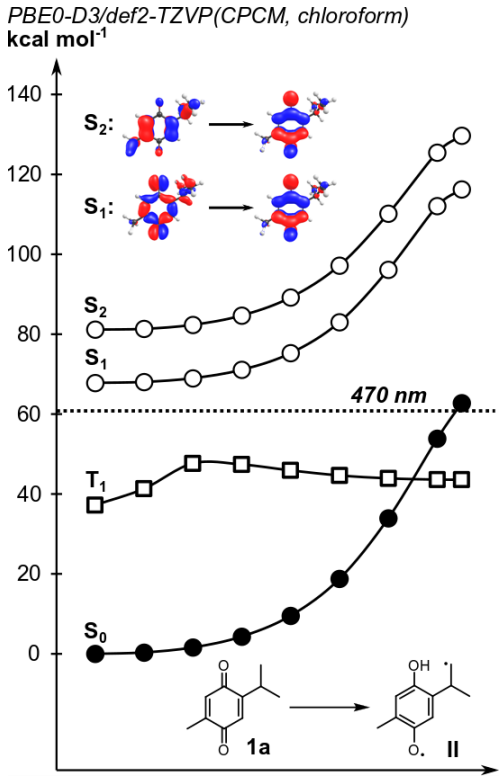


Figure S7. DFT and TD-DFT calculations along the 1,5-HAT coordinate of **1a** (the irradiation wavelength of 470 nm is showed as a dashed horizontal line).

3.2.1 Alternative reactivity of 1a toward cyclobutane ring closure

Beside the spirocyclopropane ring closure pathway discussed in the main text (pathway A in Scheme 3), we have evaluated the possibility of cyclobutane ring closure from biradical intermediate **II**. Two possible cyclobutanes were investigated (structures **7a** and **VI** in Figures S8 and S9).

For the formation of **7a** with and without TMAO, we have found transition states for the direct cyclobutane ring closure by radical recombination from **II**. However, these transition states are significantly higher in free energy than the corresponding transition states for the spirocyclopropyl ring closure (Figure S8). Based on these energy requirements, the direct ring-closure pathway toward cyclobutane **7a** is unlikely. Regarding cyclobutane **VI**, we were unable to locate the transition states directly connecting biradical **II** and **VI**. Instead, all of the attempts resulted in the spirocyclopropane ring closure and yielded **IV/V** intermediate.

The possible pathway to cyclobutanes **7a** and **VI** was found from the intermediate **IV/V** through ring expansion. However, for both **7a** and **VI**, we have found the transition states to be too high in energy. Therefore, the conversion to **7a** and **VI** is kinetically unfavorable and will be likely outcompeted by the H^+ transfer leading to **2a**. We hypothesize the H^+ transfer process to be essentially barrierless when TMAO is present.

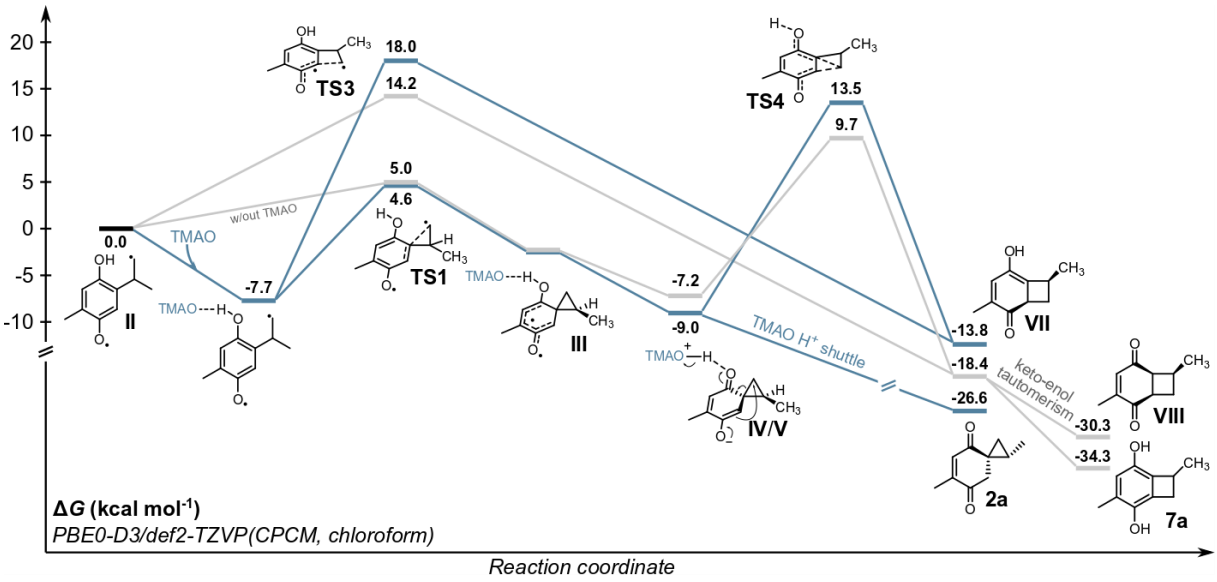


Figure S8. Computed energy profile for the formation of **2a** and **7a** from **II**.

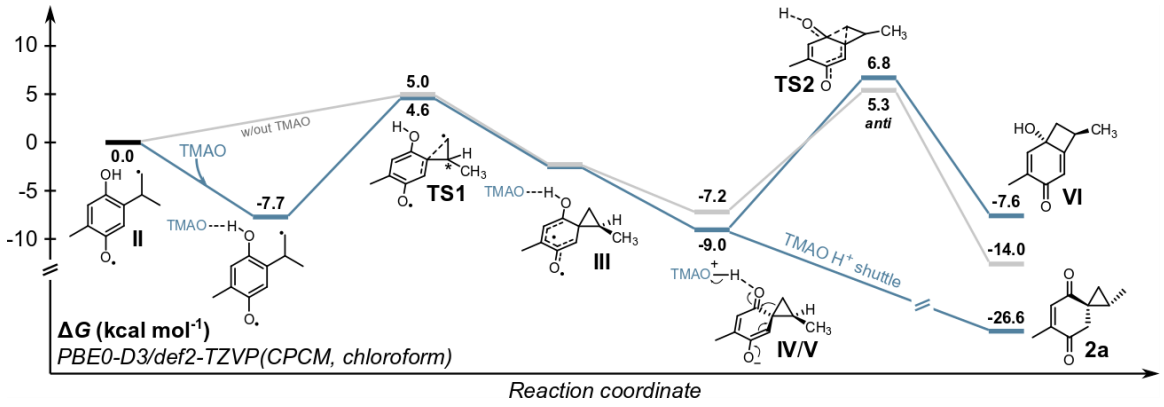


Figure S9. Computed energy profile for the formation of **2a** and **VI** from **II**.

Interestingly, cyclobutane **5** (analogous to the proposed intermediate **VI** in Figure S9) was obtained experimentally from quinone **1af**. We attribute this observation to the enhanced stabilization of the cyclobutane **5** compared to **IV**/**V**, which lowers the transition state energy for connecting **IV**/**V** with **5**. Indeed, DFT calculations reveal that **5** is substantially more stable than **IV**/**V** analogue of **1af** by ~17-19 kcal mol^{-1} (Figure S10). This is also reflected in a small activation free energy of only ~2-3 kcal mol^{-1} for the conversion of **IV**/**V** to **5**, which is expected to outcompete the other TMAO-unassisted alternatives. We have also found a direct ring-closure pathway from **II** analogue of **1af** to **5** with comparable energy requirements as in the case of **IV**/**V** formation. This pathway might also represent a viable option of how the spirocyclopropane derivative is avoided in case of **1af**. The experimental

observation of *syn*-**5** as the major stereoisomer in the reaction mixture can likely be attributed to the enhanced stabilization induced by the benzene ring and the acetate group.

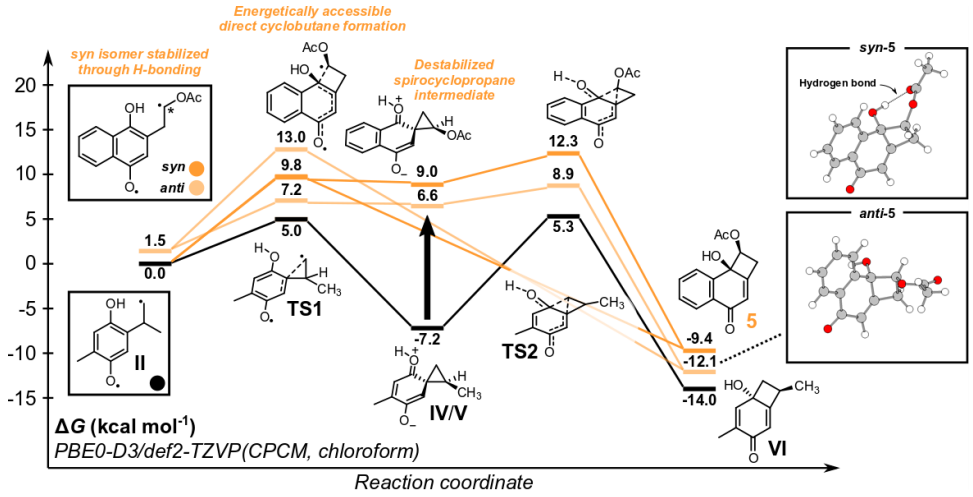


Figure S10. Comparison of the energy profiles for the conversion of intermediate **II** derived from **1a** *vs.* **1af** to **VI** *vs.* **5**.

3.2.2 Computation of the diastereomeric ratio of 2a

Diastereomeric ratio of **2a** was determined spectroscopically as >20:1. We have evaluated the expected diastereomeric ratio from the computed values of pro-*anti* and pro-*syn* transition-states free energies. From Eyring equation, the diastereomeric ratio can be computed as:

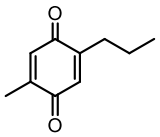
$$\frac{k_1}{k_2} = e^{\frac{\Delta G_2^{\neq} - \Delta G_1^{\neq}}{RT}} \qquad (2)$$

From the difference in the free energy barriers ($\Delta\Delta G^{\neq}$ = 1.8 kcal mol^{-1}), we find that k_1/k_2 = 19.3–20.3 for T = 293–298 K.

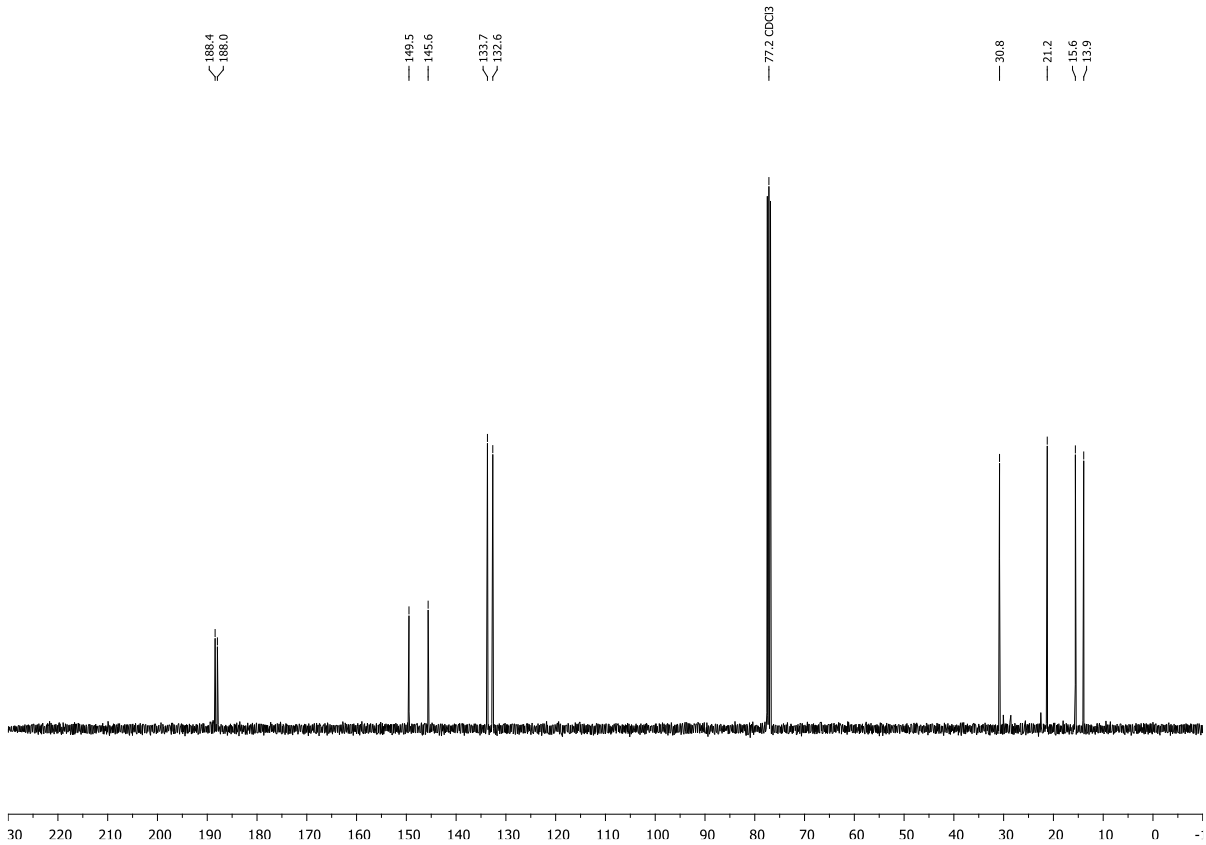
4. Copies of NMR spectra

2-Methyl-5-propyl-1,4-benzoquinone (1a')

^{1}H NMR (400 MHz, $CDCl_3$)

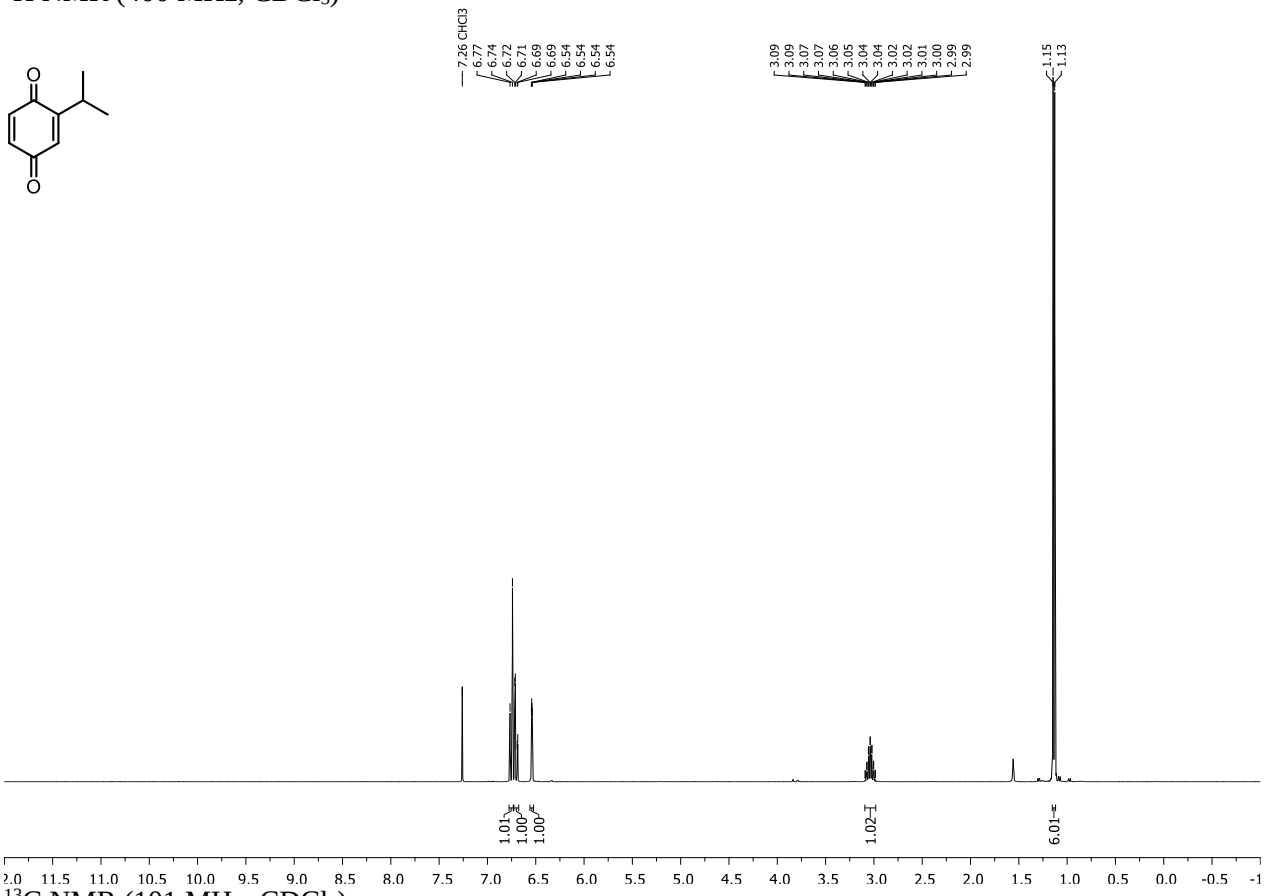


^{13}C NMR (101 MHz, $CDCl_3$)

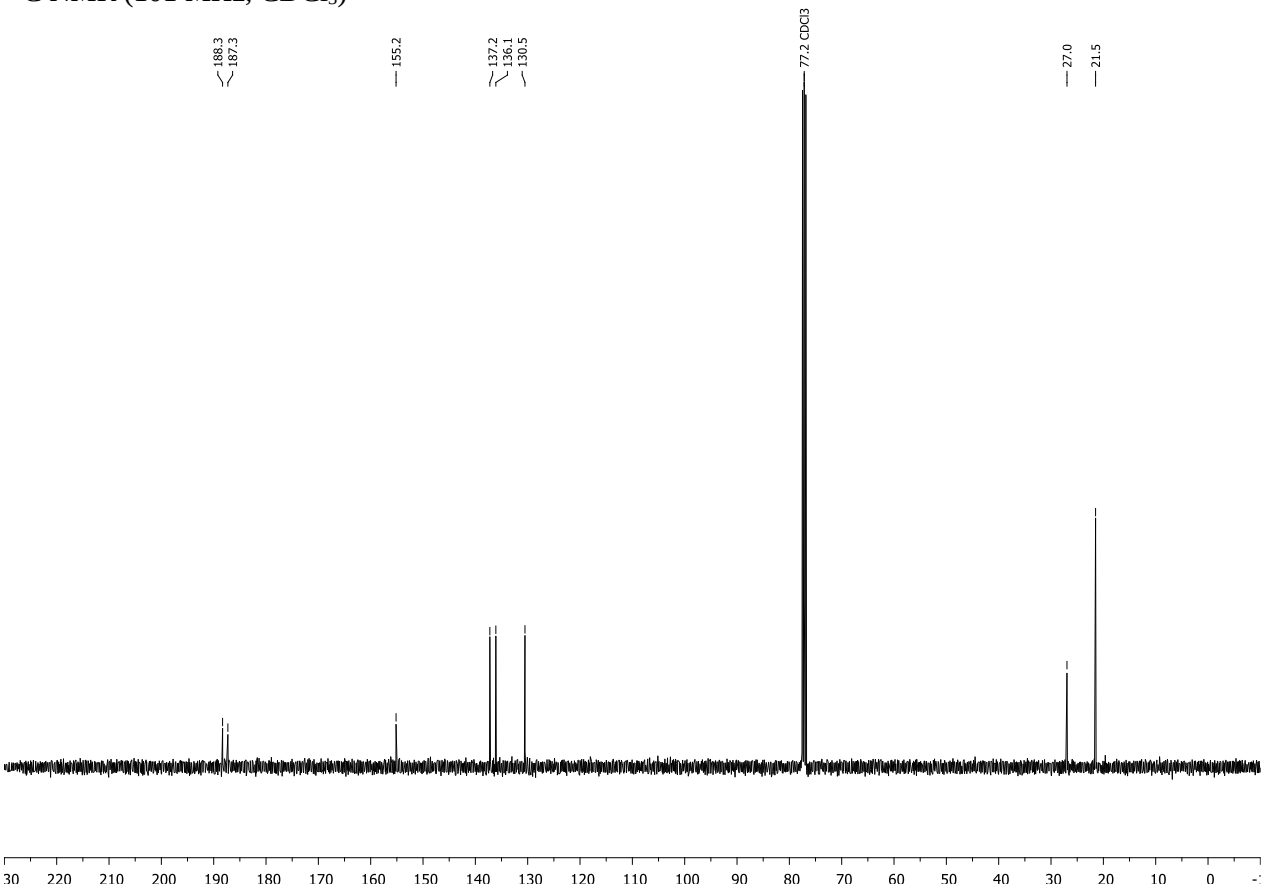


2-Isopropyl-1,4-benzoquinone (1b)

^{1}H NMR (400 MHz, $CDCl_3$)

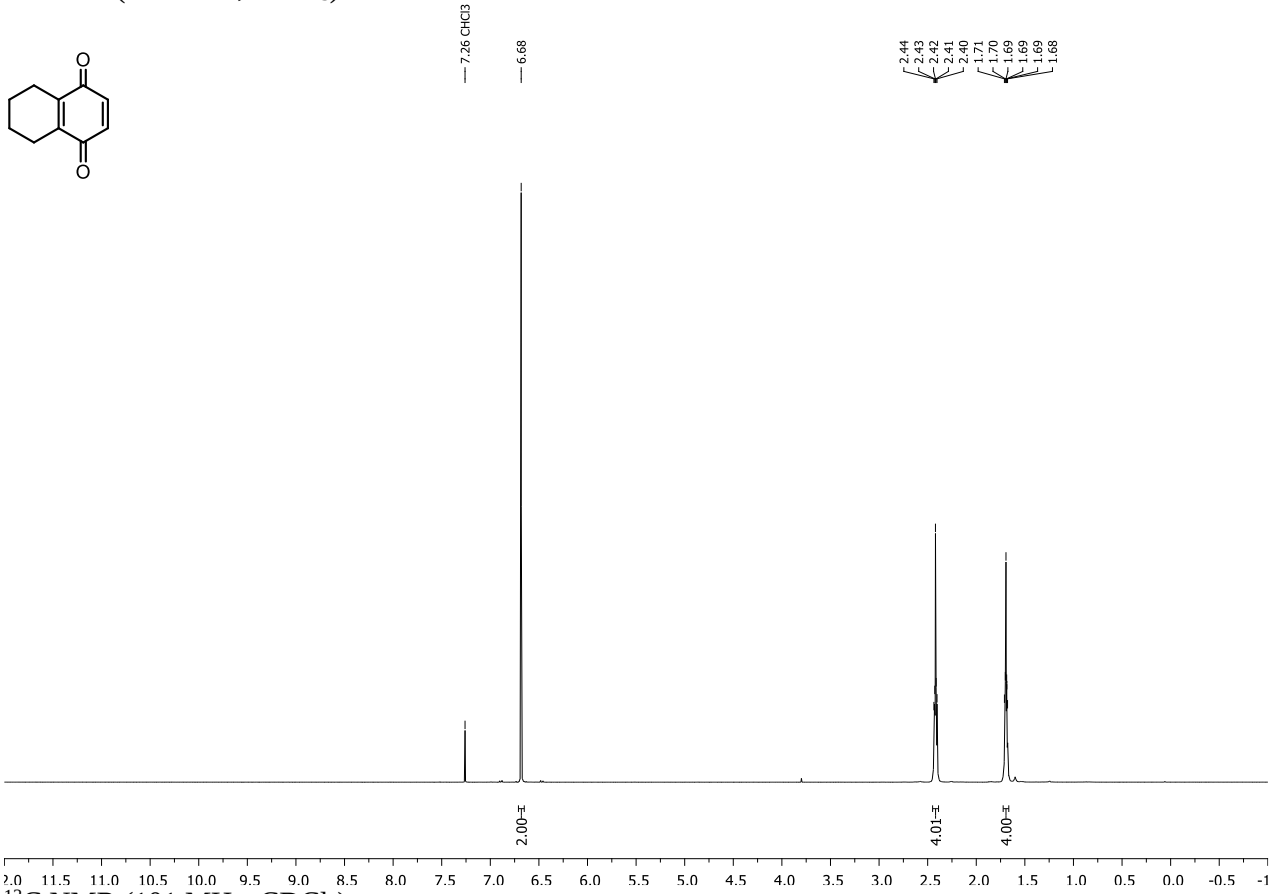


^{13}C NMR (101 MHz, $CDCl_3$)

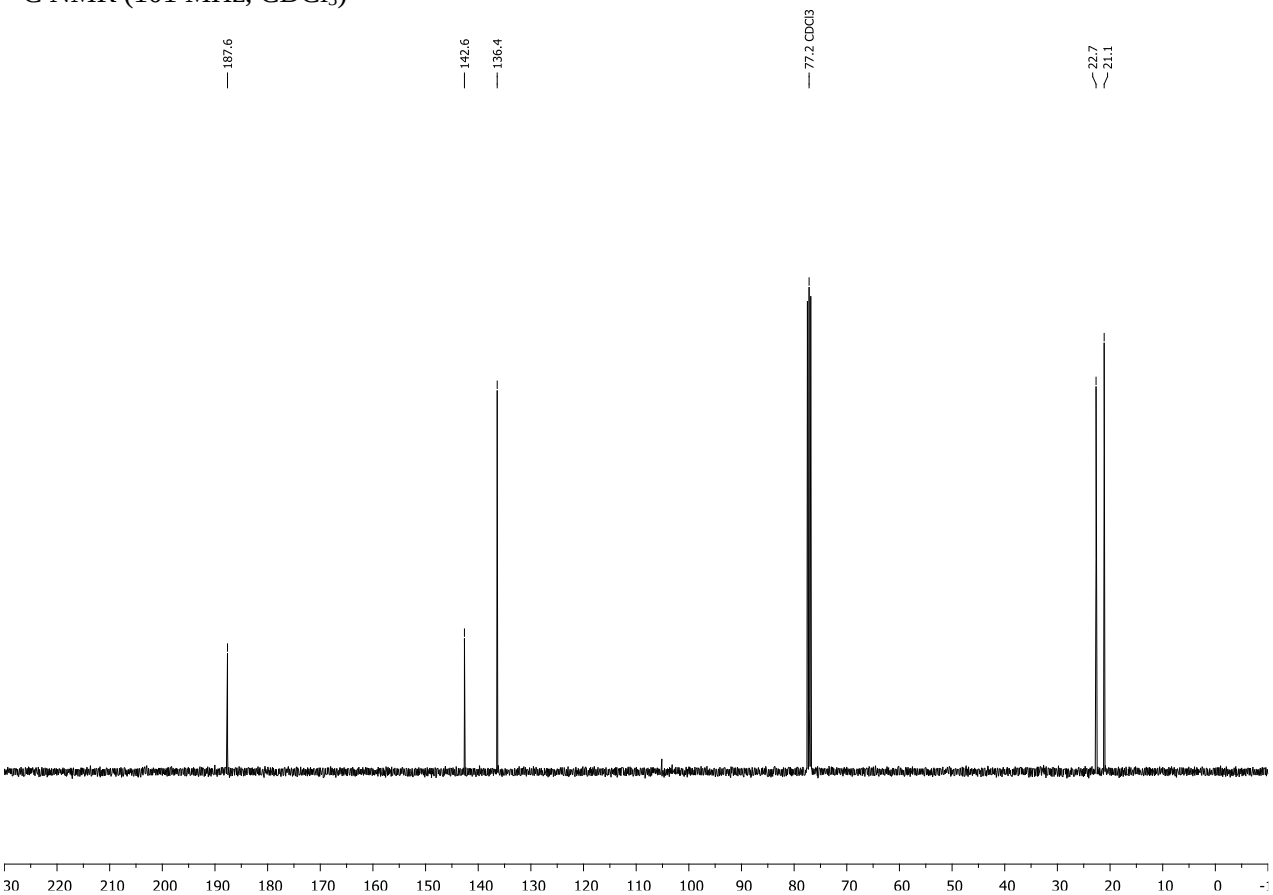


5,6,7,8-Tetrahydronaphthoquinone

^{1}H NMR (400 MHz, $CDCl_3$)

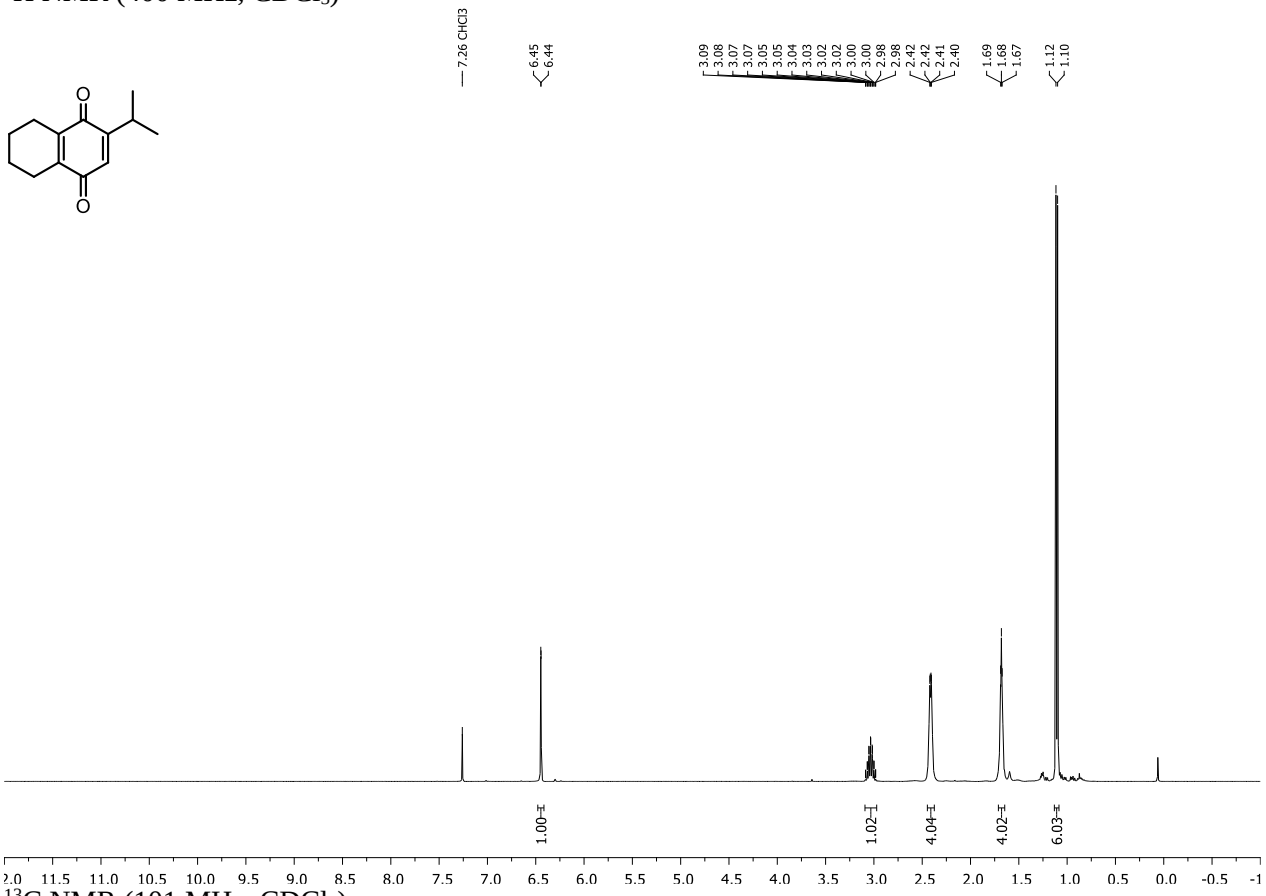


^{13}C NMR (101 MHz, $CDCl_3$)

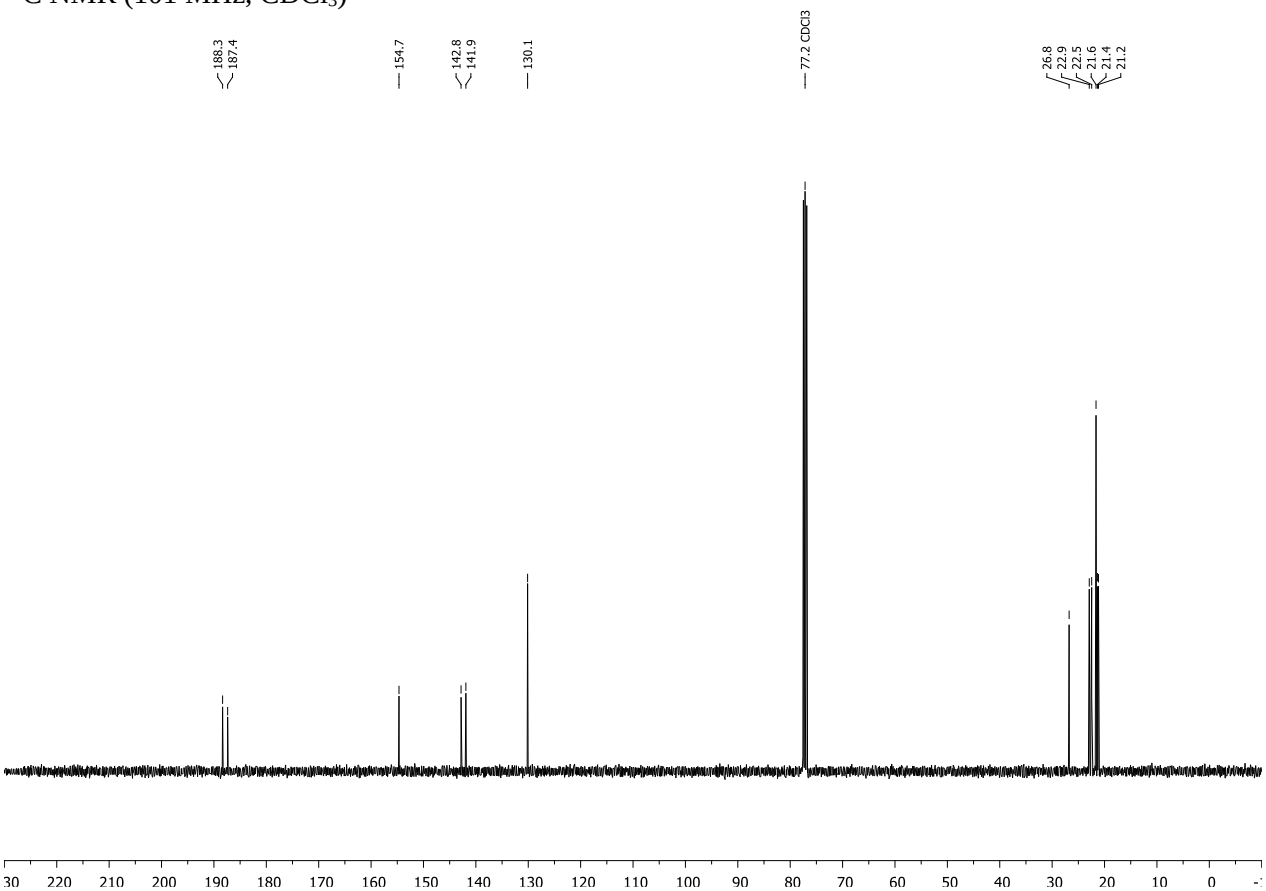


2-Isopropyl-5,6,7,8-tetrahydronaphthalene-1,4-dione (1d)

^{1}H NMR (400 MHz, $CDCl_3$)

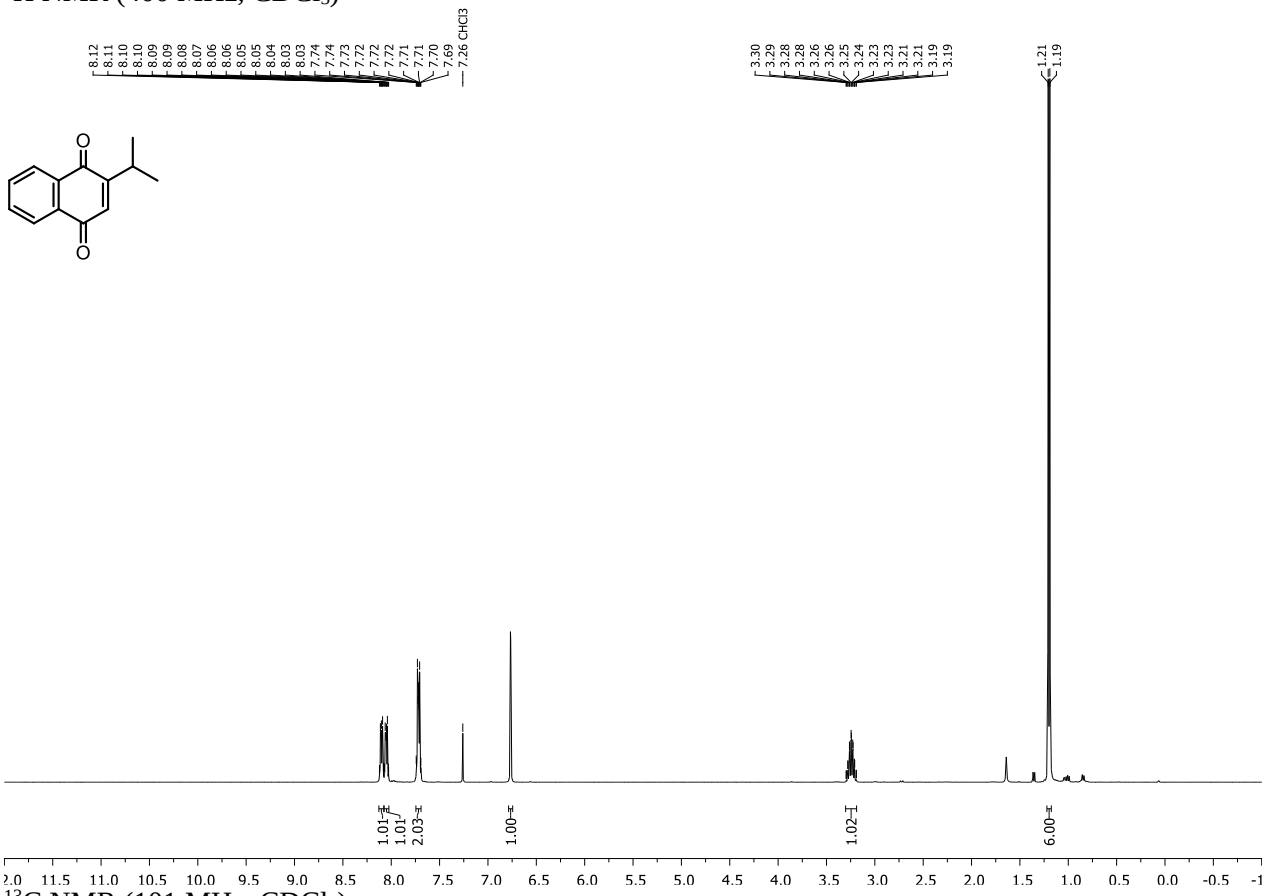


^{13}C NMR (101 MHz, $CDCl_3$)

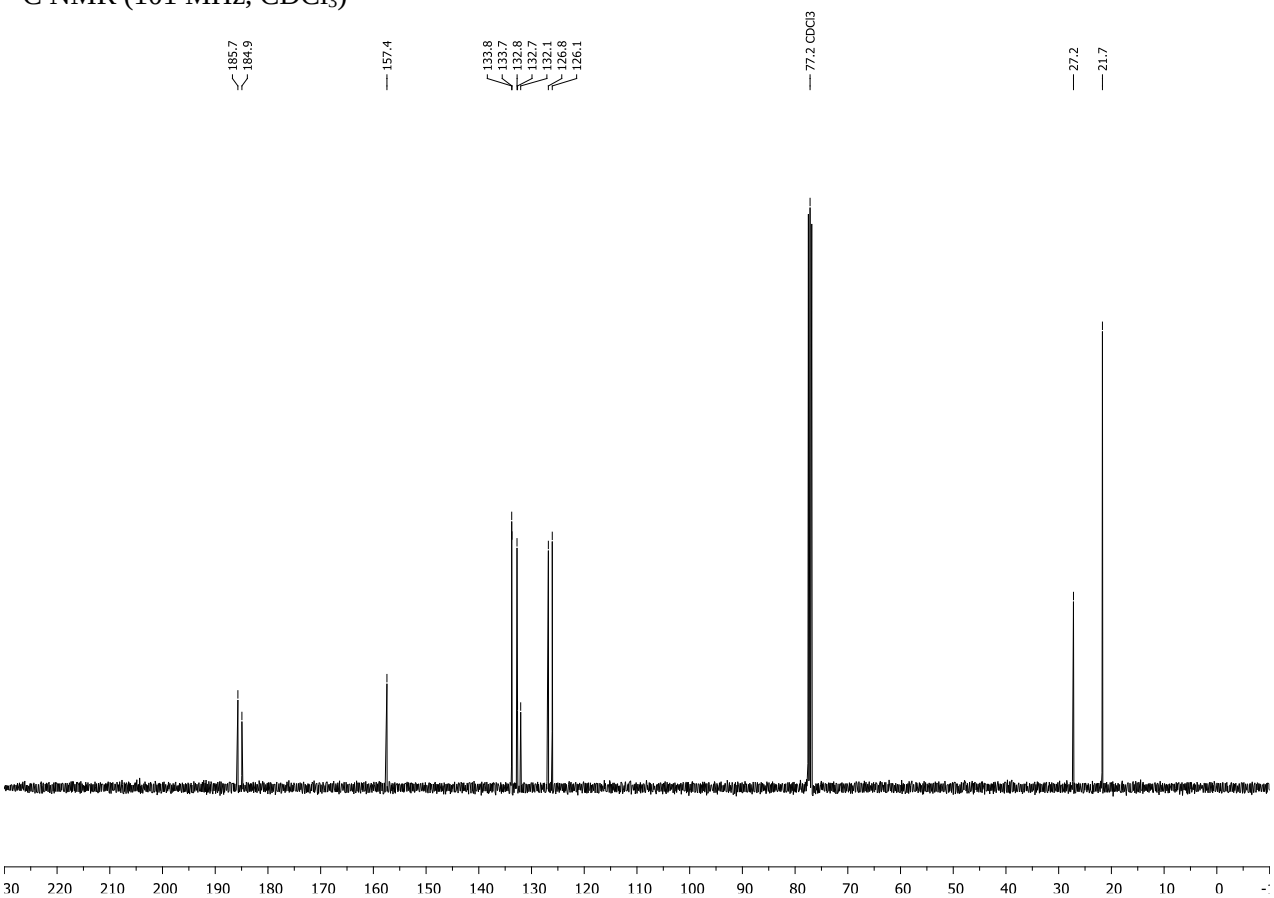


2-Isopropyl-1,4-naphthoquinone (1e)

^{1}H NMR (400 MHz, $CDCl_3$)

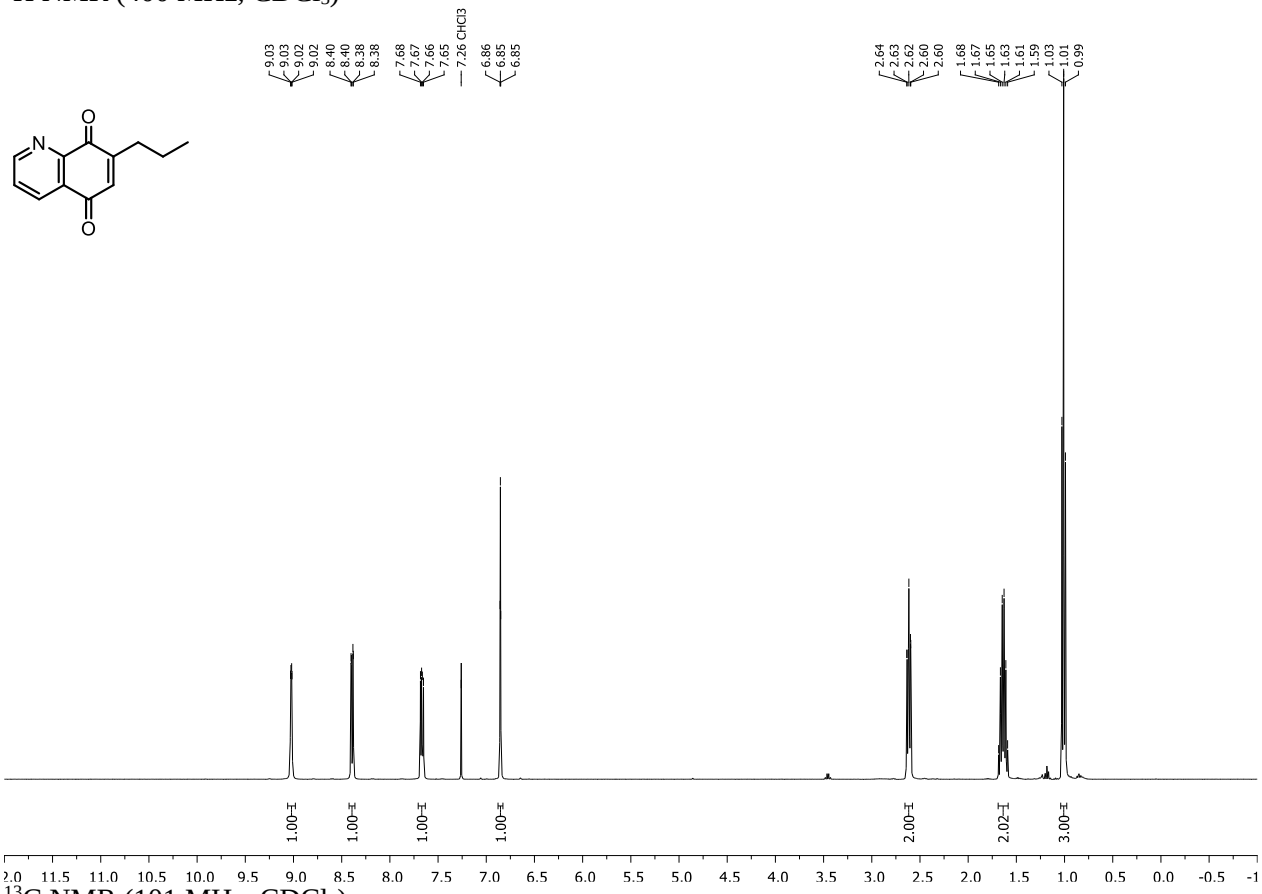


^{13}C NMR (101 MHz, $CDCl_3$)

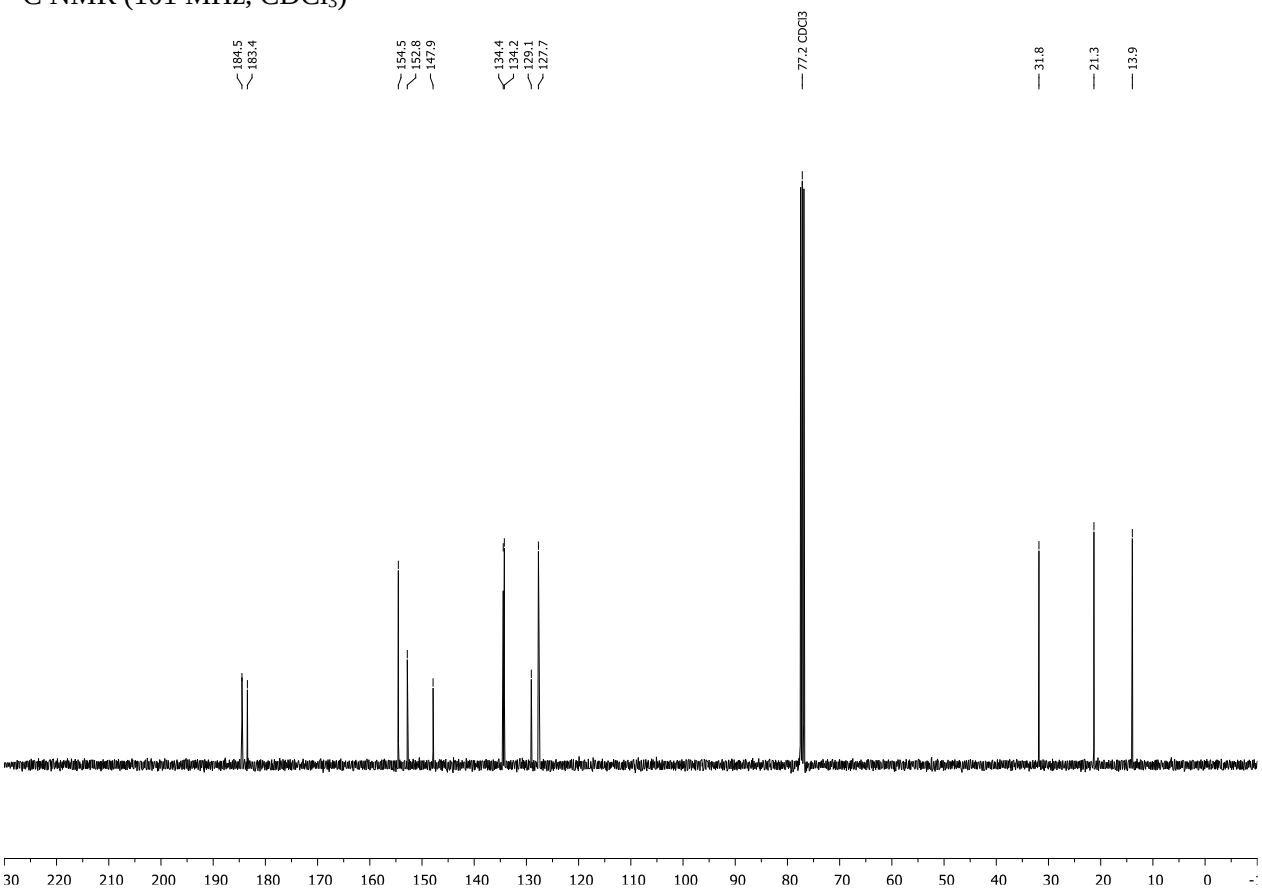


7-Propylquinoline-5,8-dione (1f)

^{1}H NMR (400 MHz, $CDCl_3$)

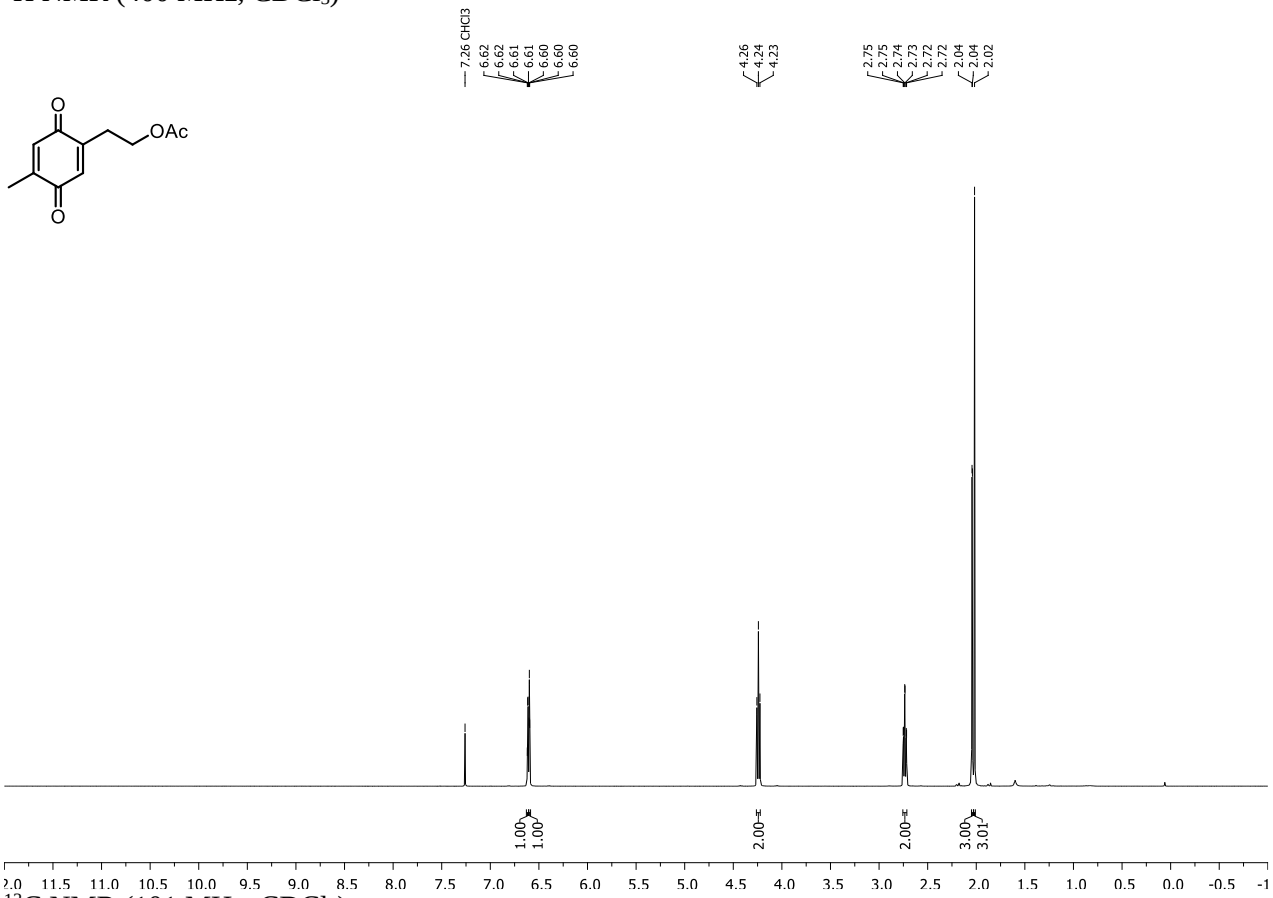


^{13}C NMR (101 MHz, $CDCl_3$)

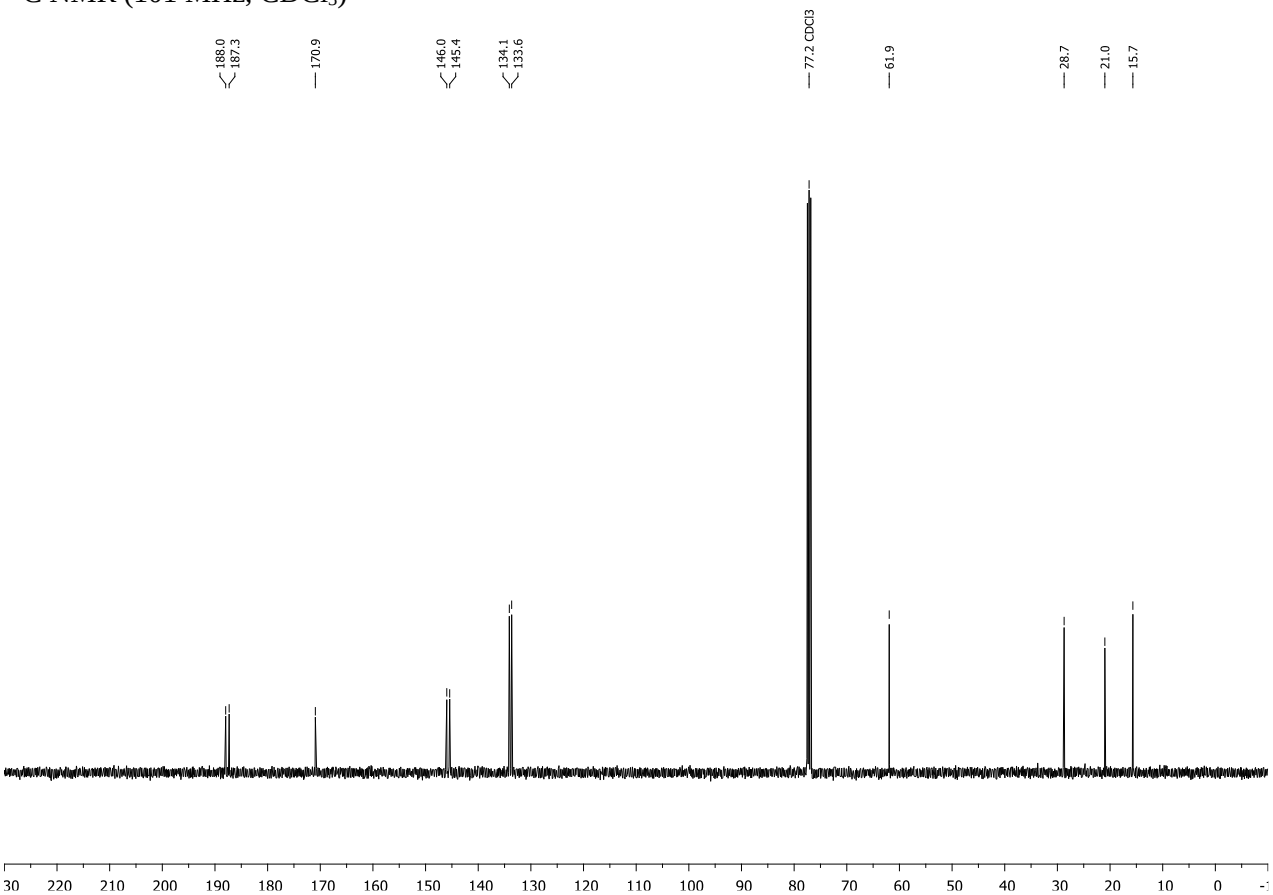


2-(4-Methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)ethyl acetate (1g)

^{1}H NMR (400 MHz, $CDCl_3$)

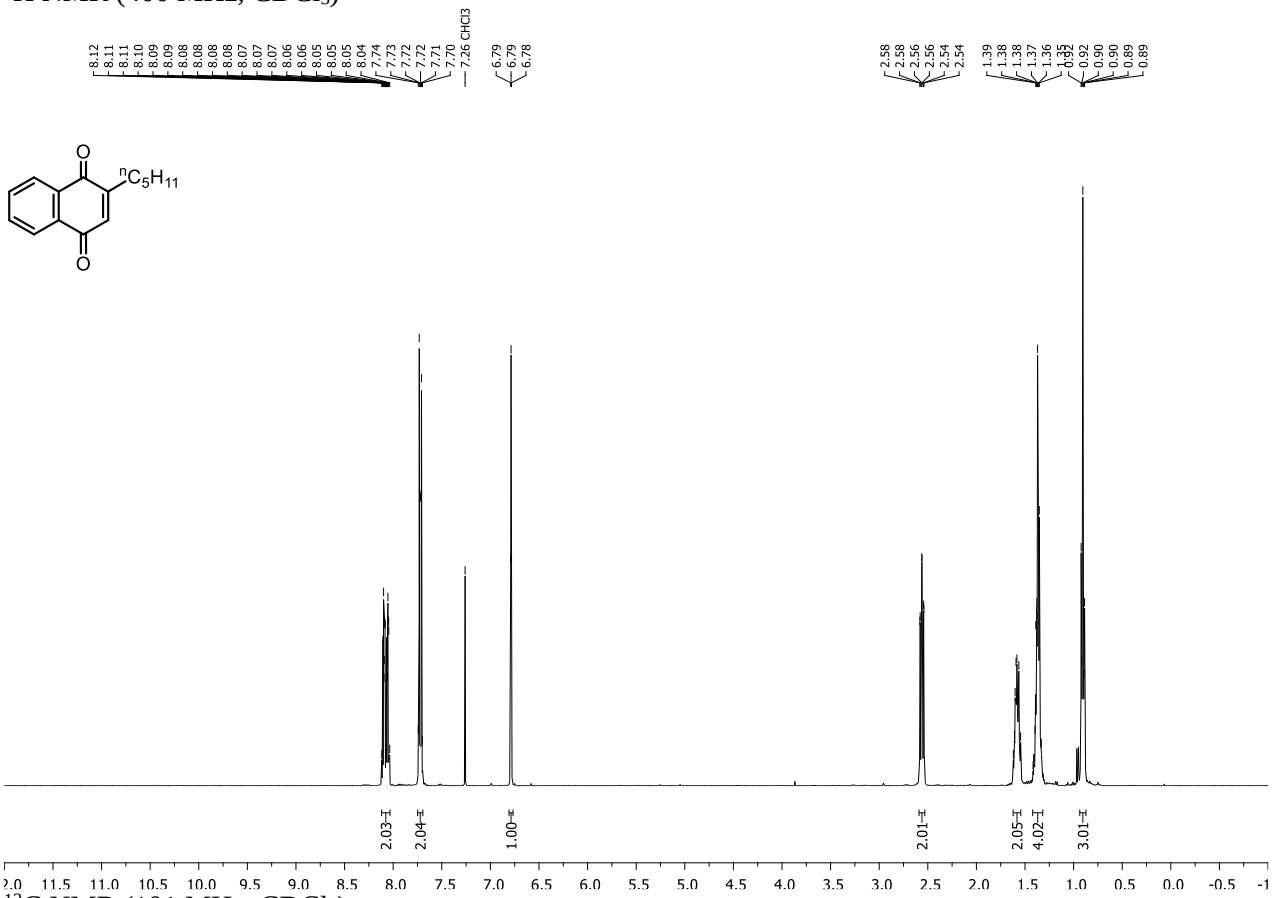


^{13}C NMR (101 MHz, $CDCl_3$)

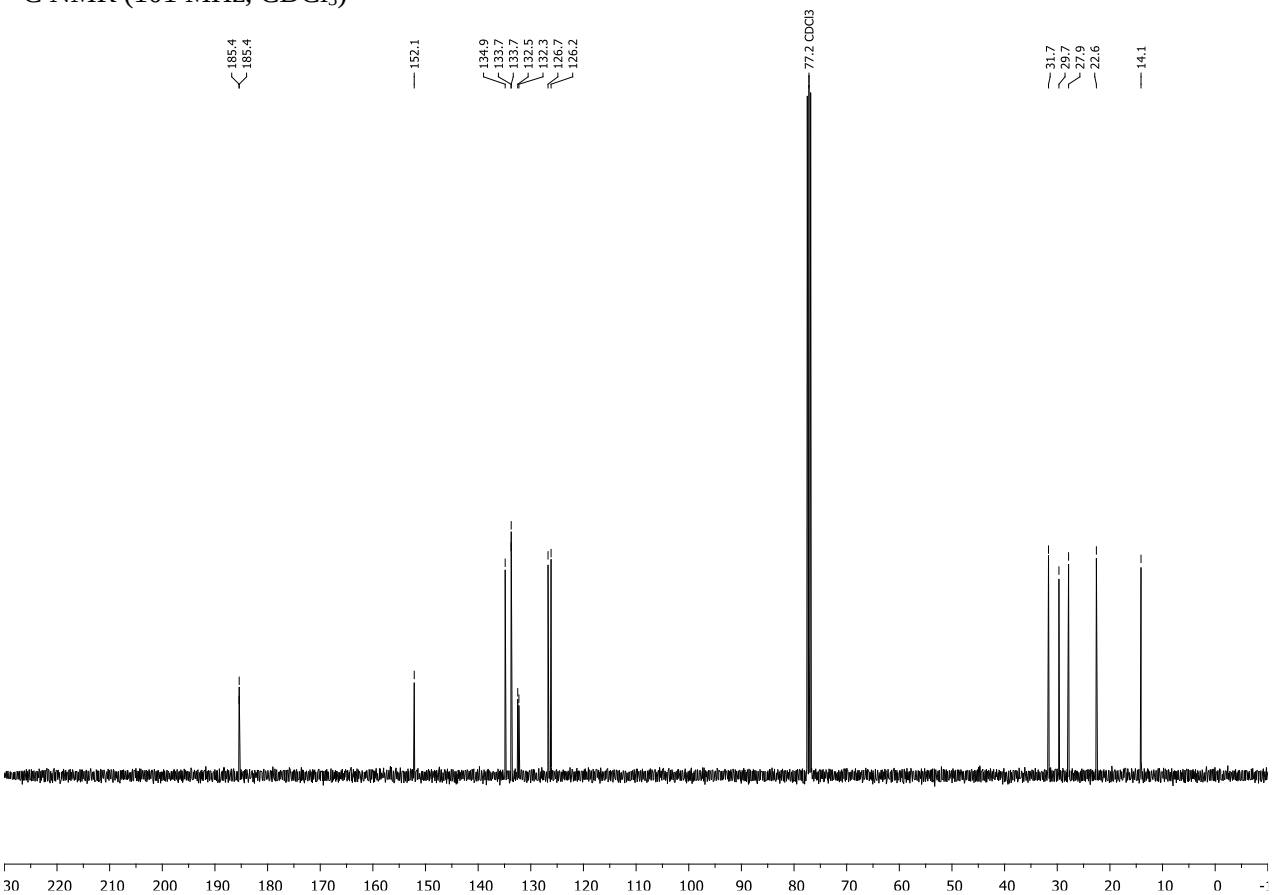


2-Pentyl-1,4-naphthoquinone (1h)

^{1}H NMR (400 MHz, $CDCl_3$)

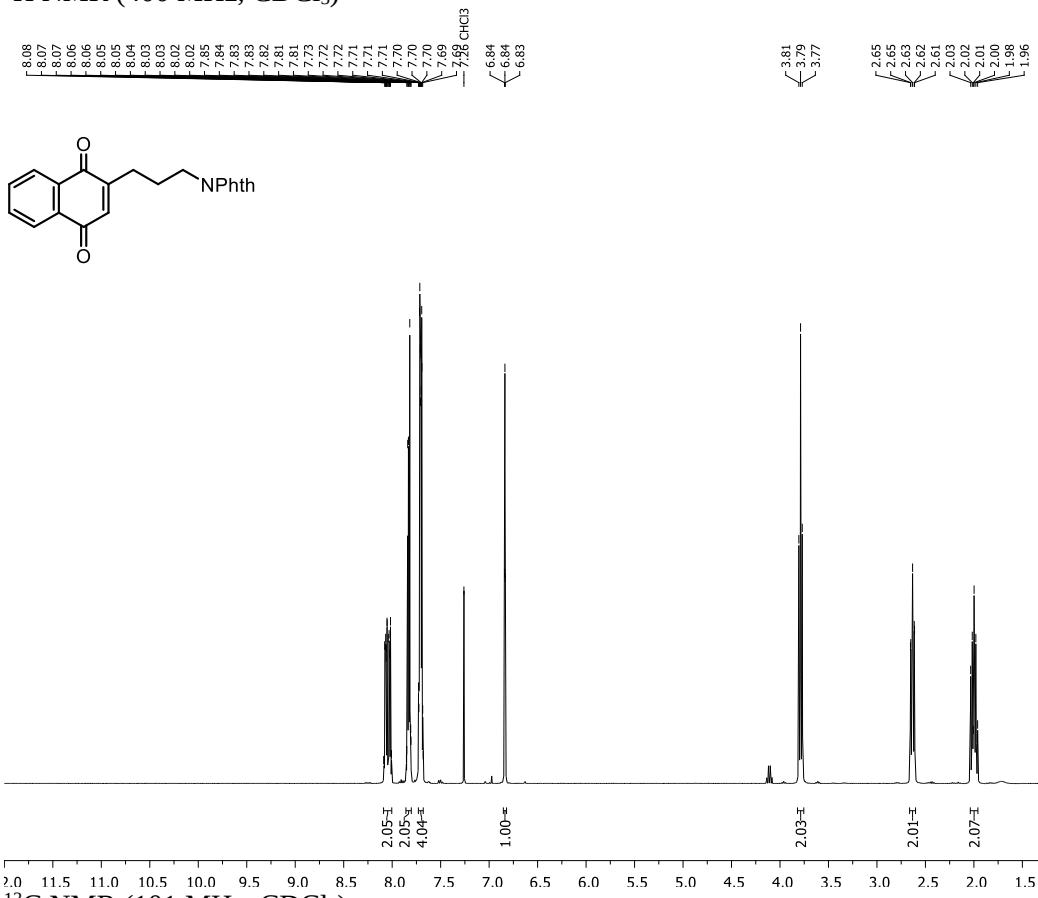


^{13}C NMR (101 MHz, $CDCl_3$)

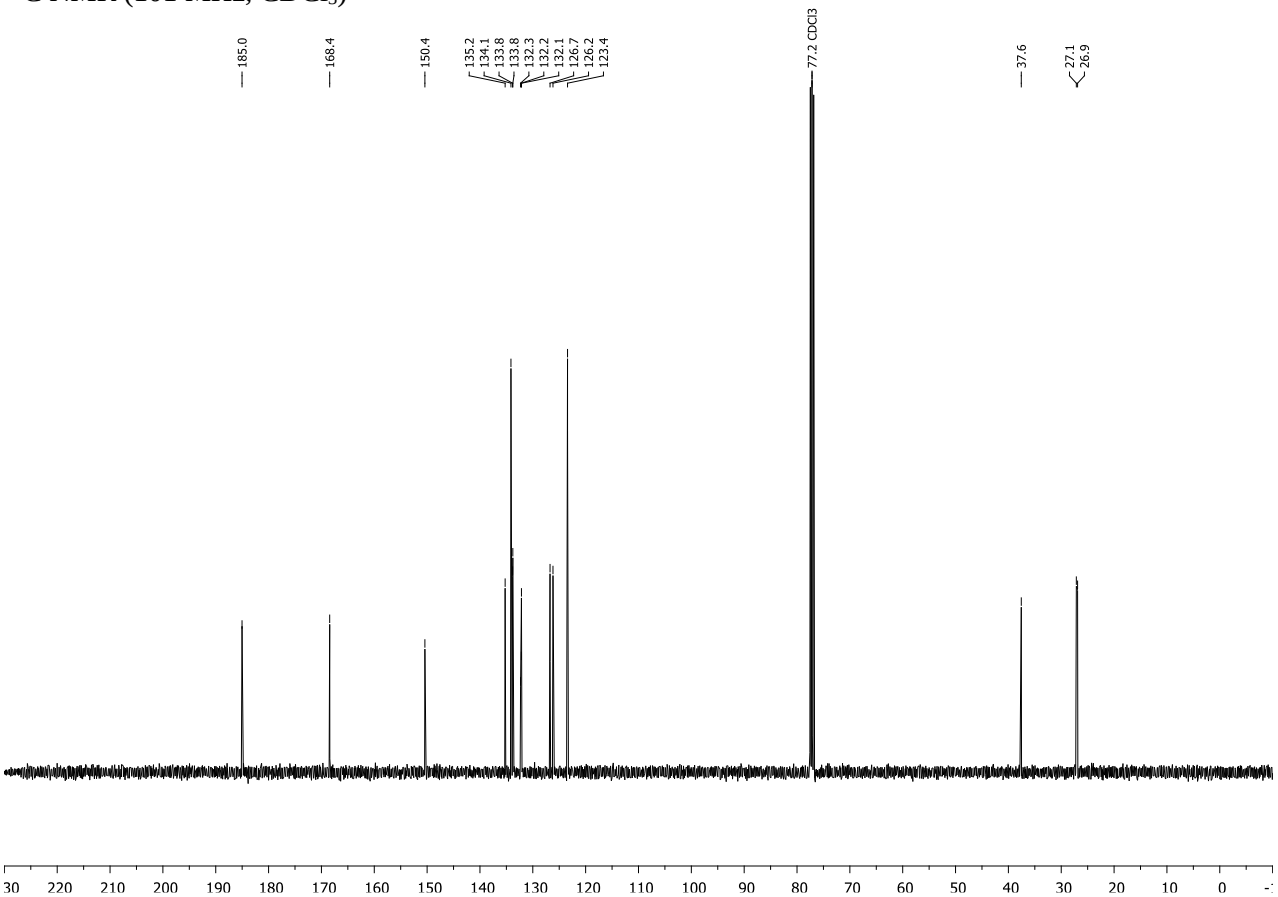


2-(3-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)propyl)isoindoline-1,3-dione (1i)

^{1}H NMR (400 MHz, $CDCl_3$)

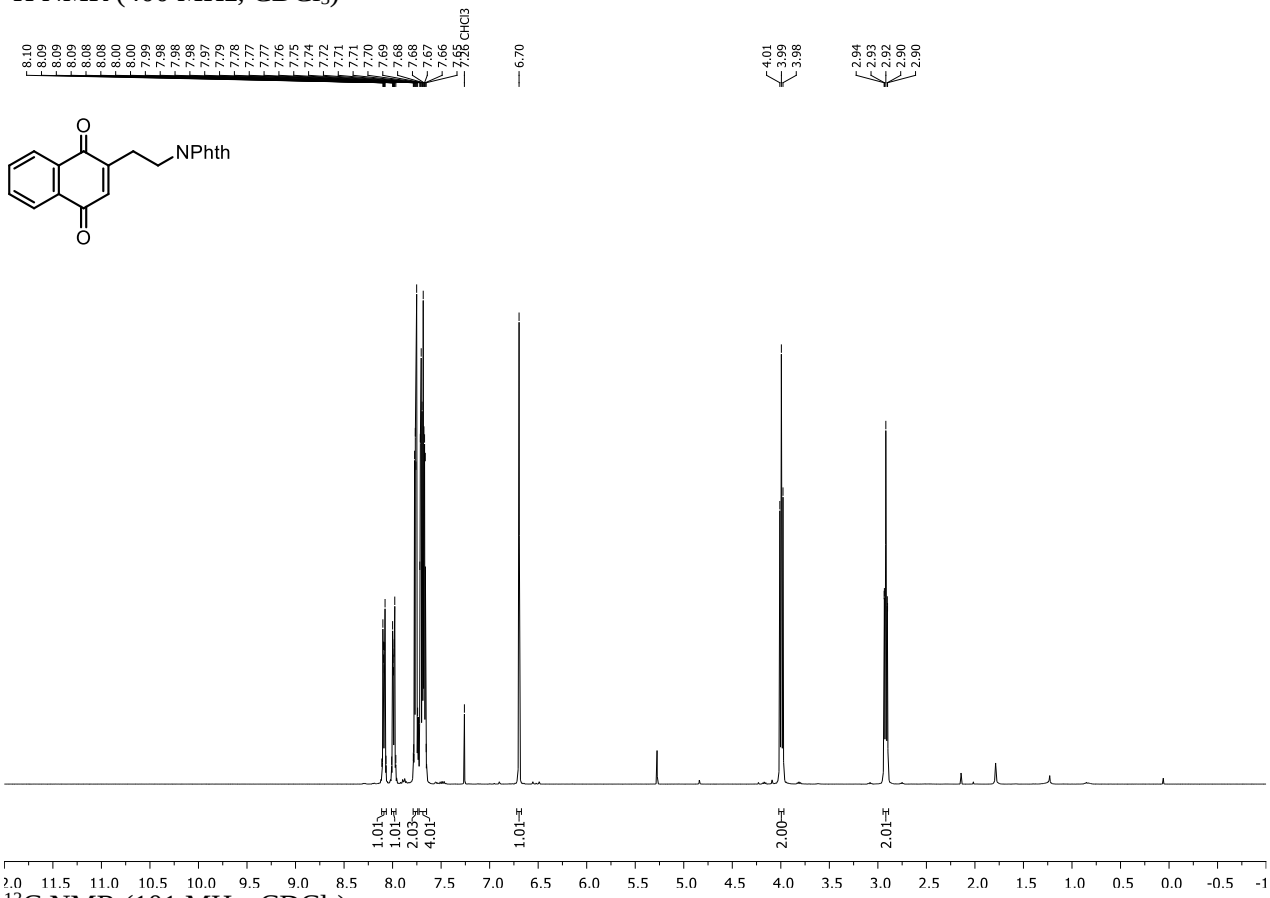


^{13}C NMR (101 MHz, $CDCl_3$)

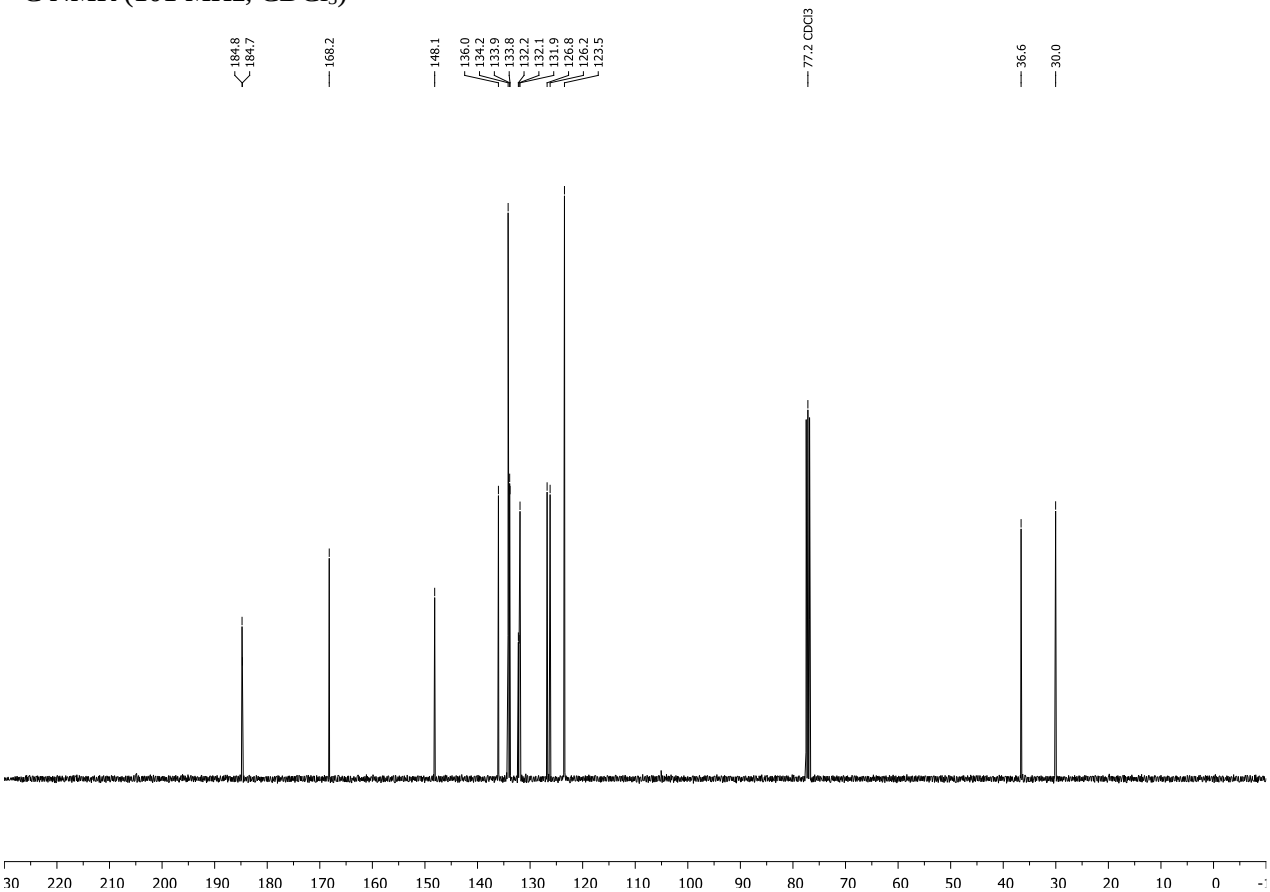


2-(2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl)isoindoline-1,3-dione (1j)

^{1}H NMR (400 MHz, $CDCl_3$)

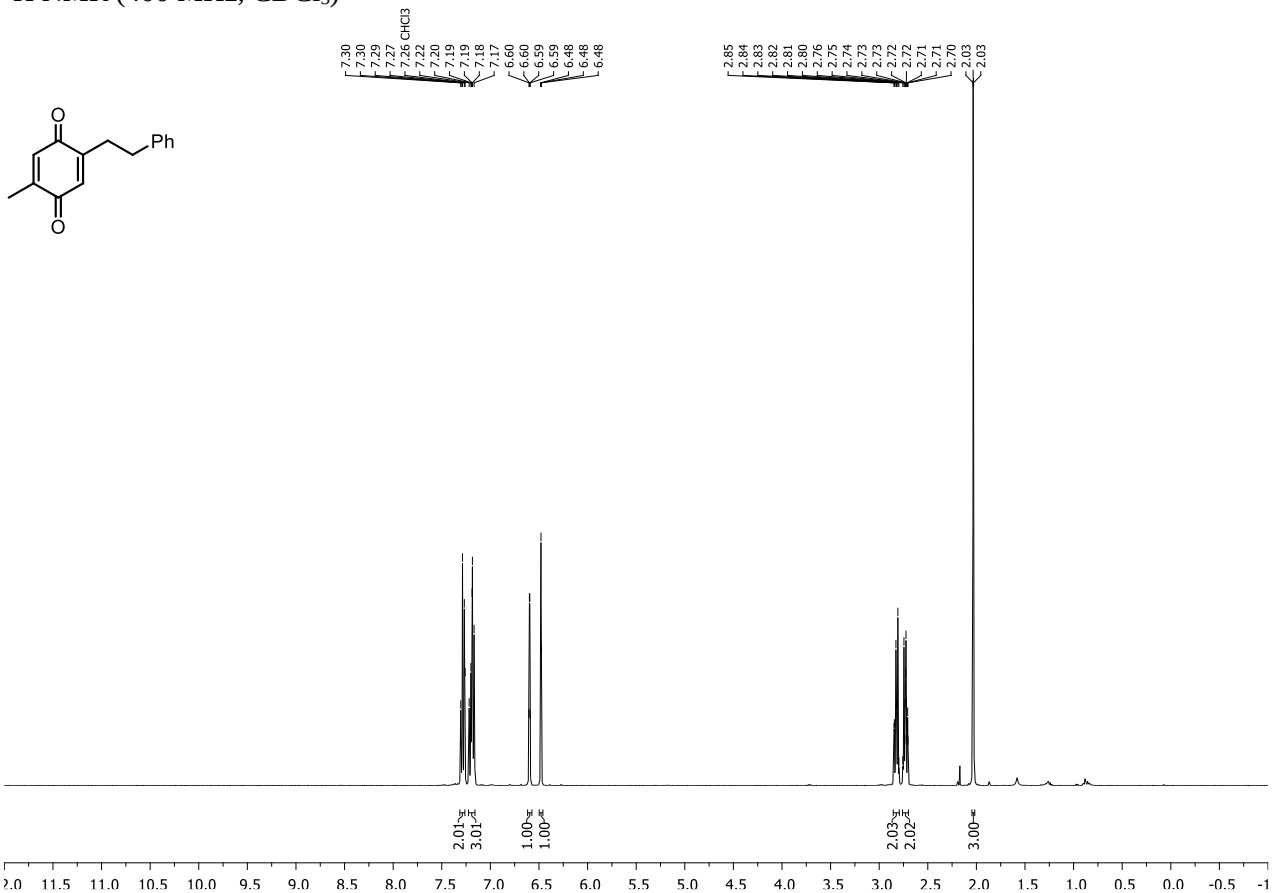


^{13}C NMR (101 MHz, $CDCl_3$)

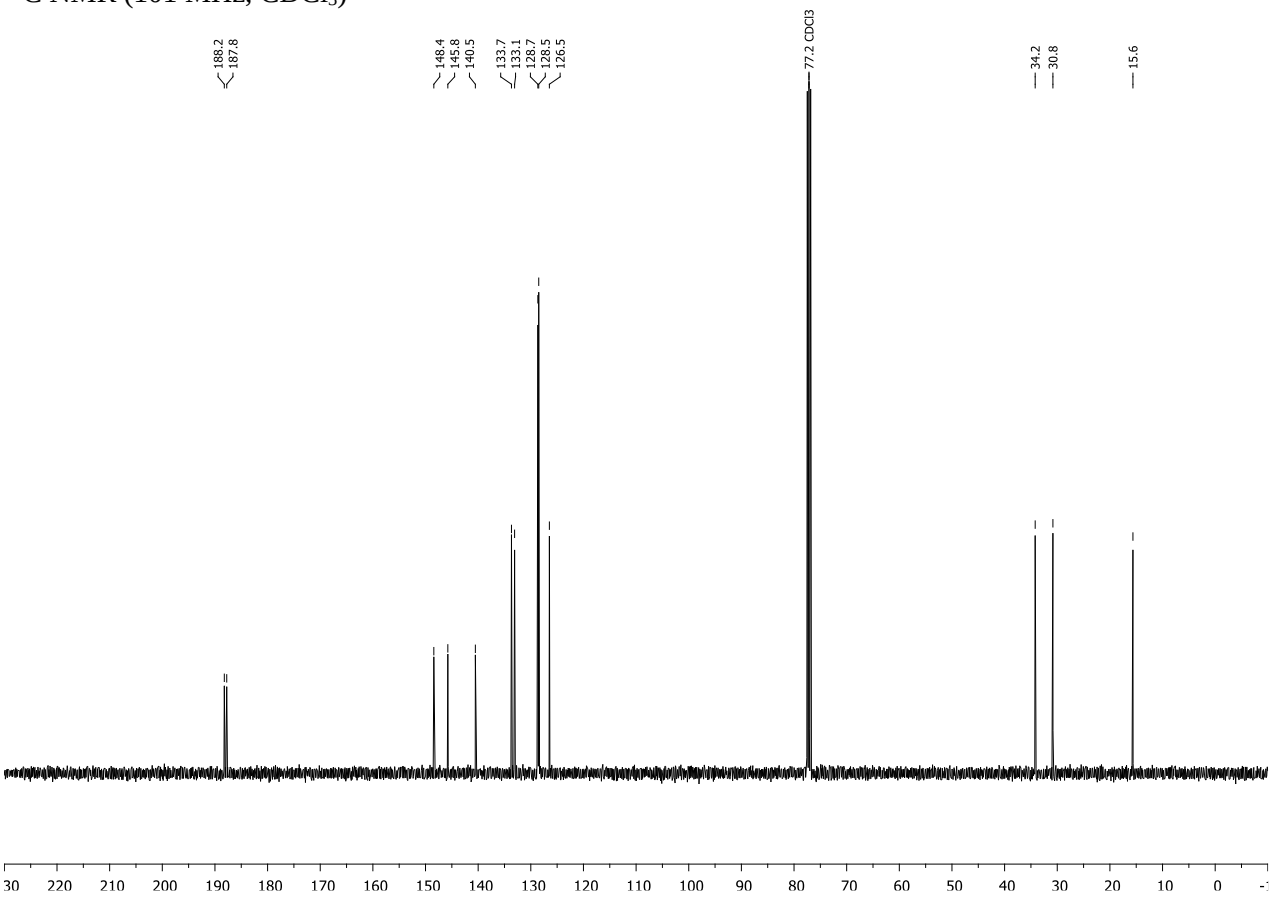


2-Methyl-5-phenethyl-1,4-benzoquinone (1k)

^{1}H NMR (400 MHz, $CDCl_3$)

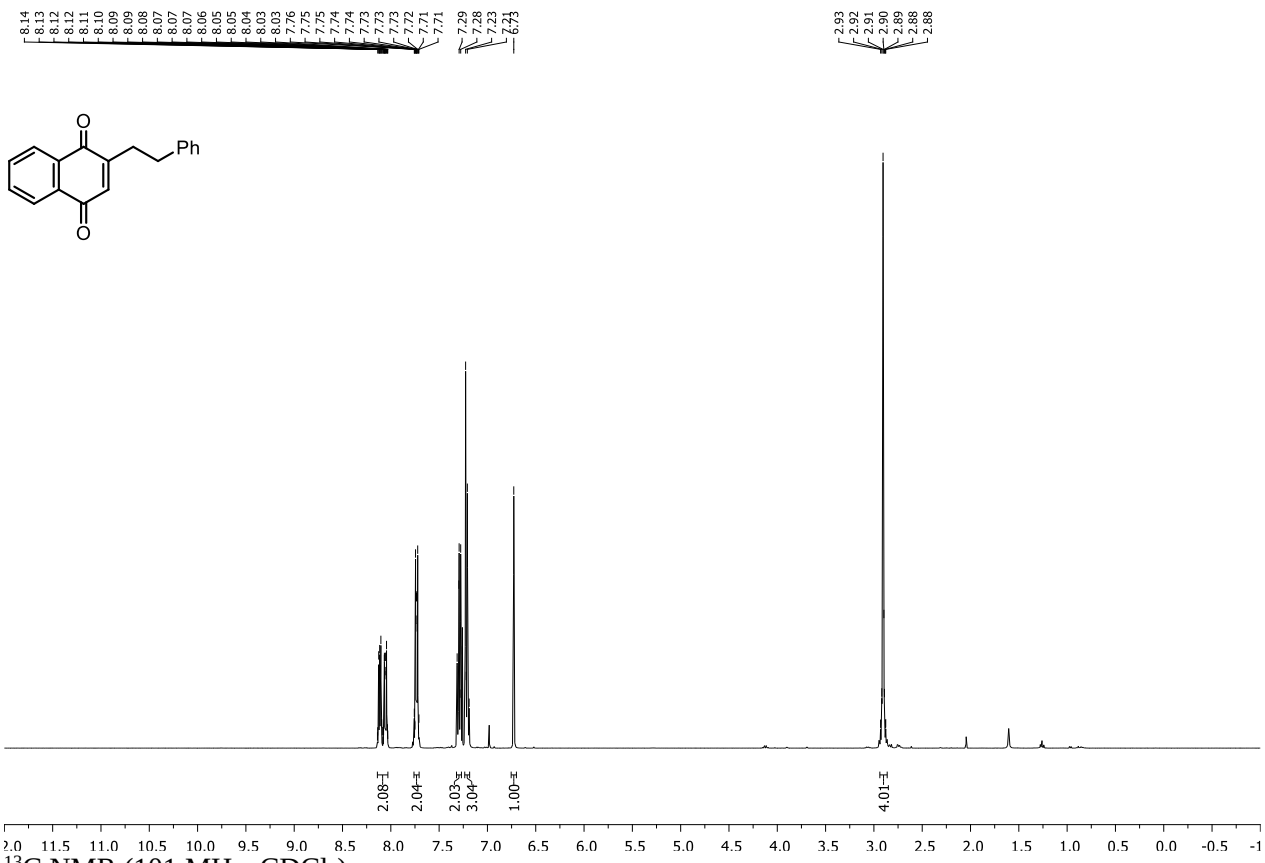


^{13}C NMR (101 MHz, $CDCl_3$)

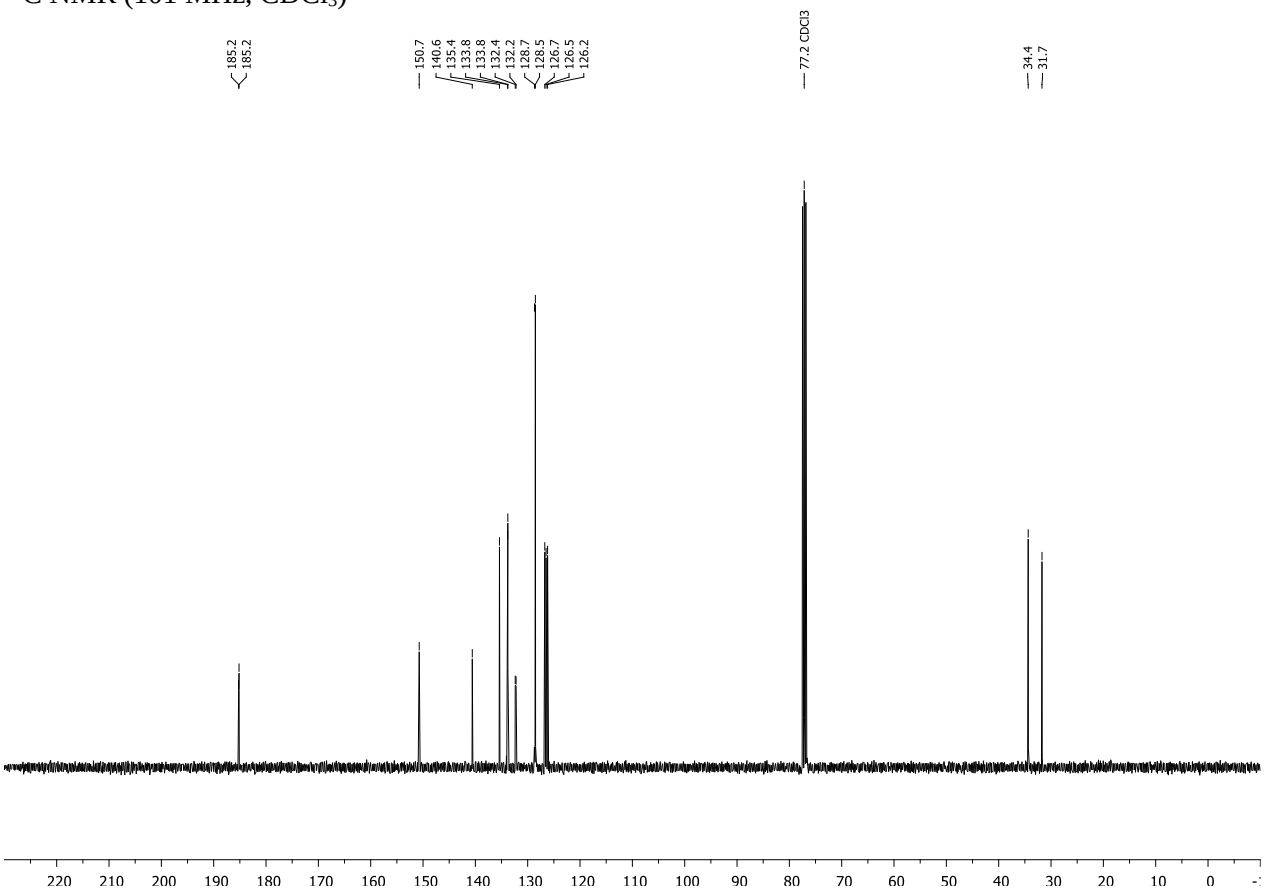


2-Phenethyl-1,4-naphthoquinone (1l)

^{1}H NMR (400 MHz, $CDCl_3$)

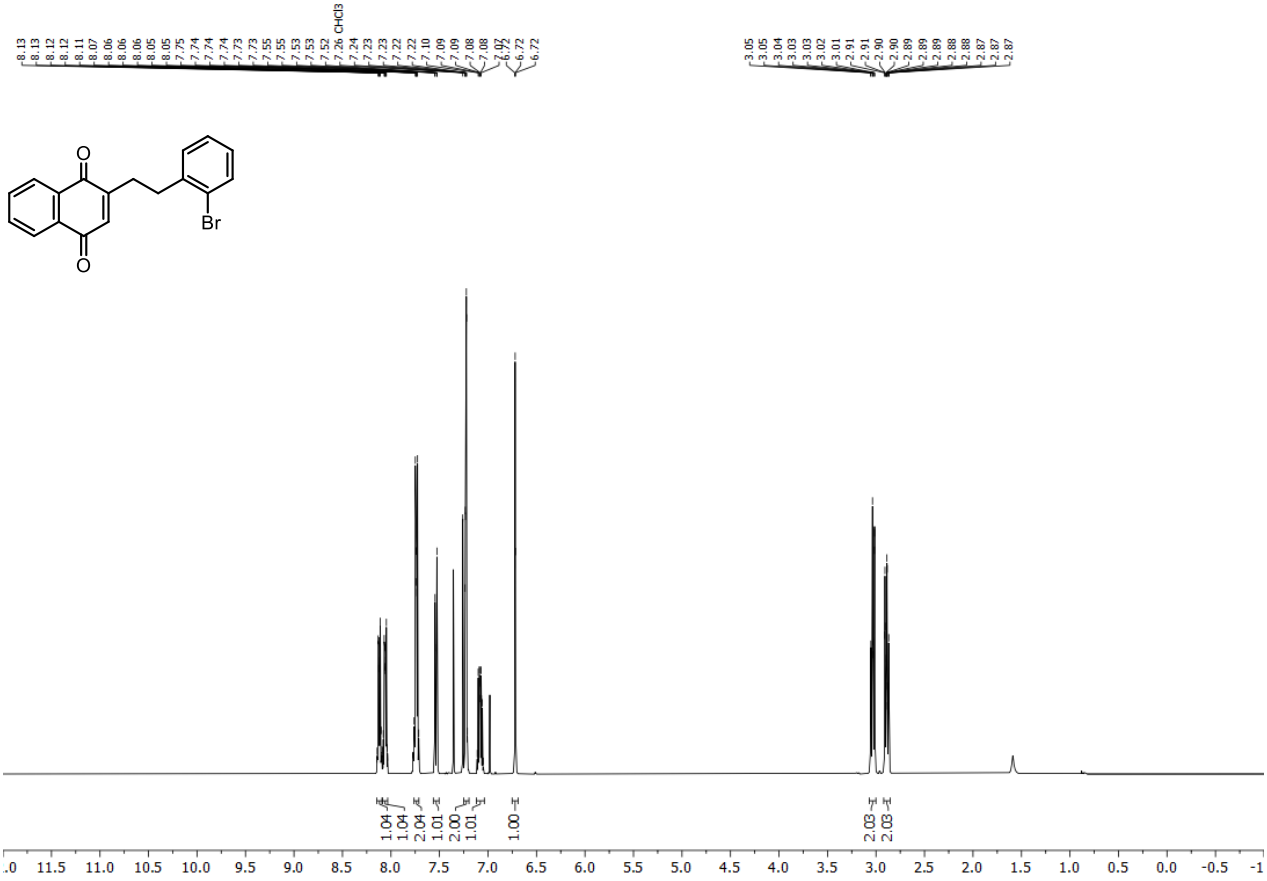


^{13}C NMR (101 MHz, $CDCl_3$)

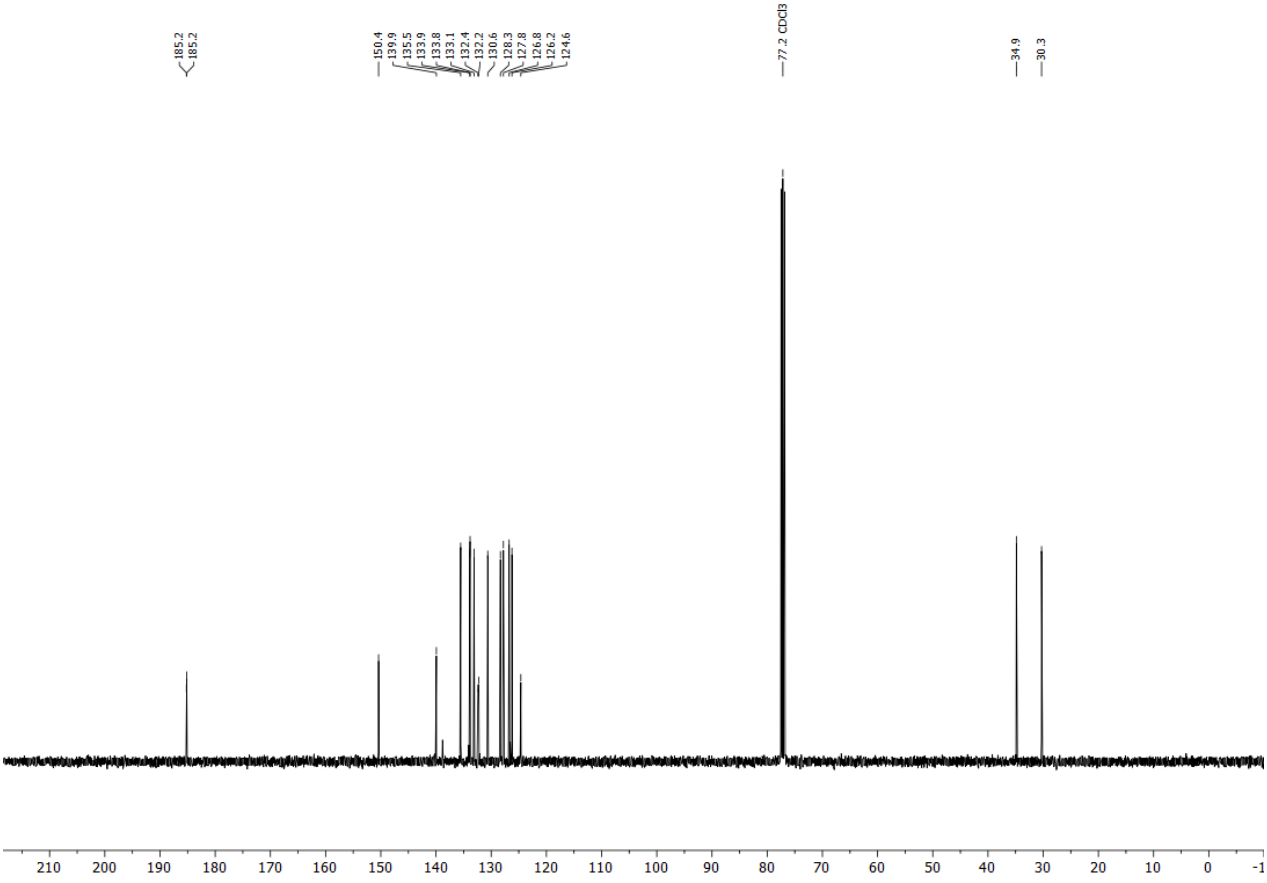


2-(2-Bromophenethyl)-1,4-naphthoquinone (1m)

^{1}H NMR (400 MHz, $CDCl_3$)

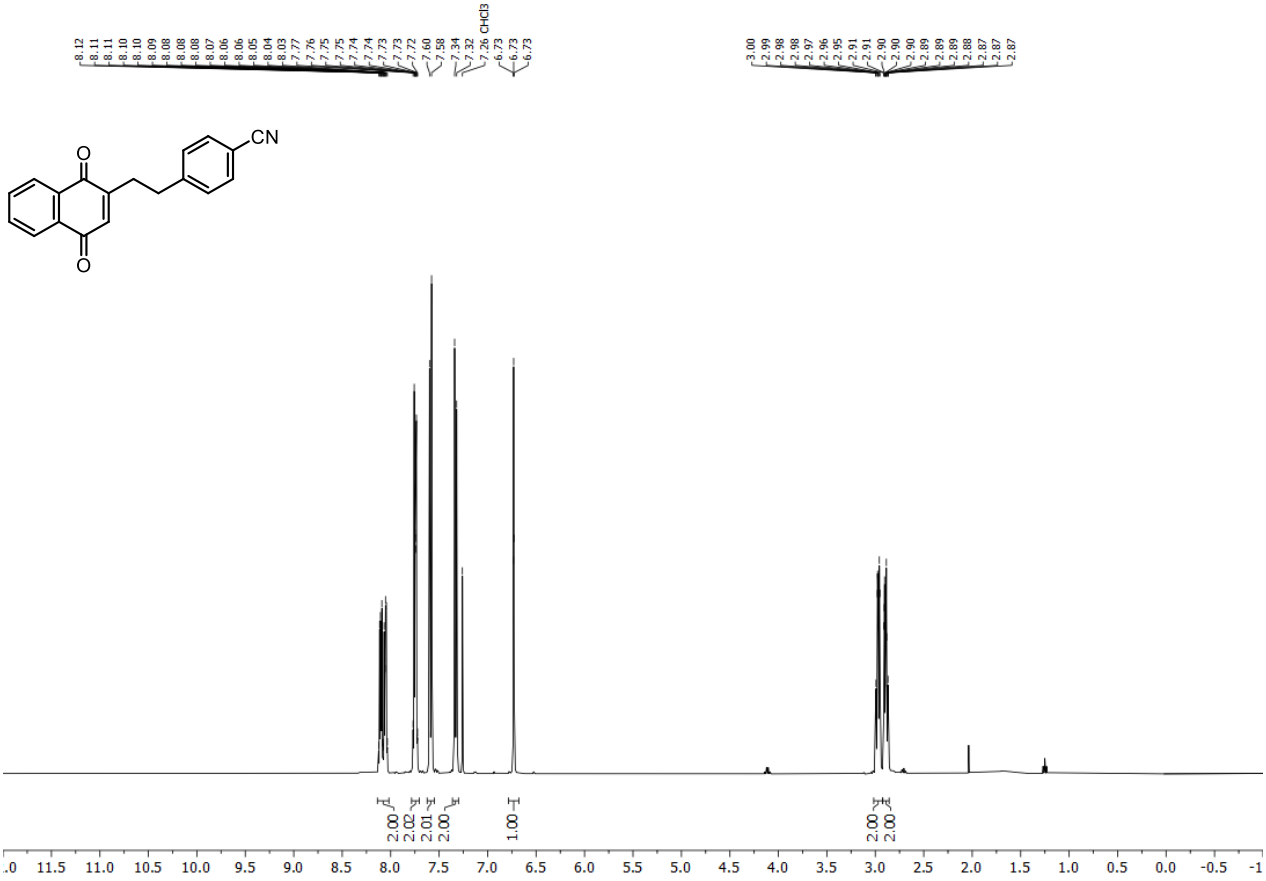


^{13}C NMR (101 MHz, $CDCl_3$)

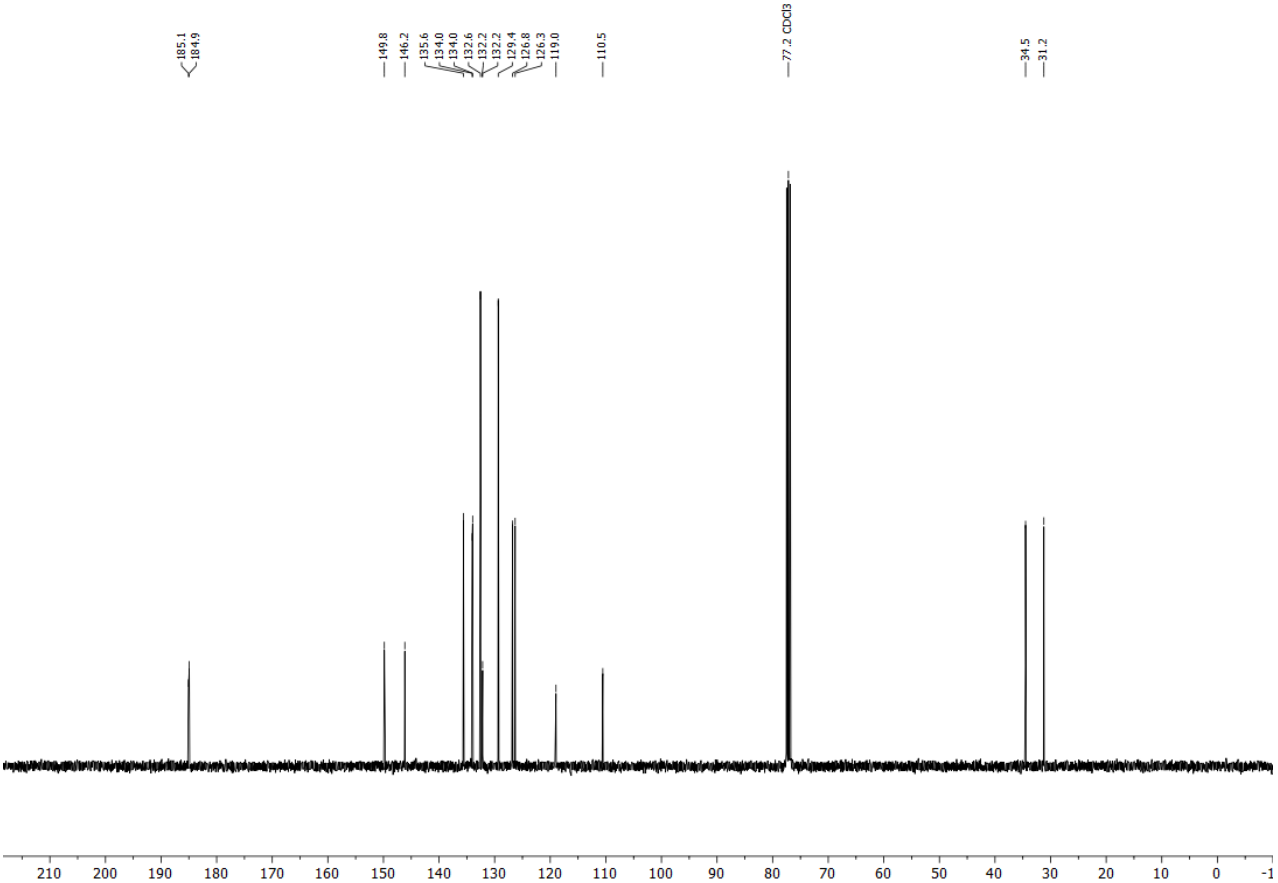


4-(2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl)benzonitrile (1n)

^{1}H NMR (400 MHz, $CDCl_3$)

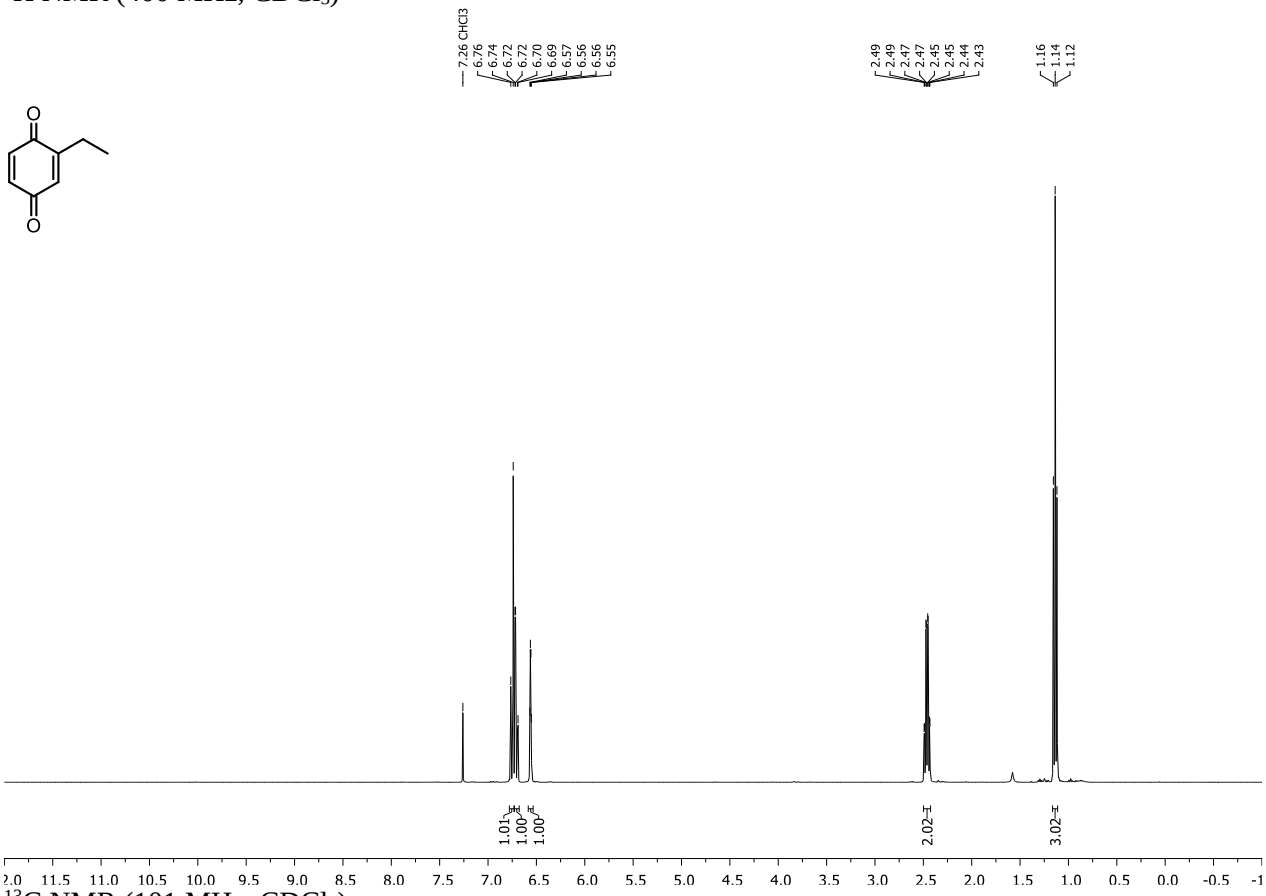


^{13}C NMR (101 MHz, $CDCl_3$)

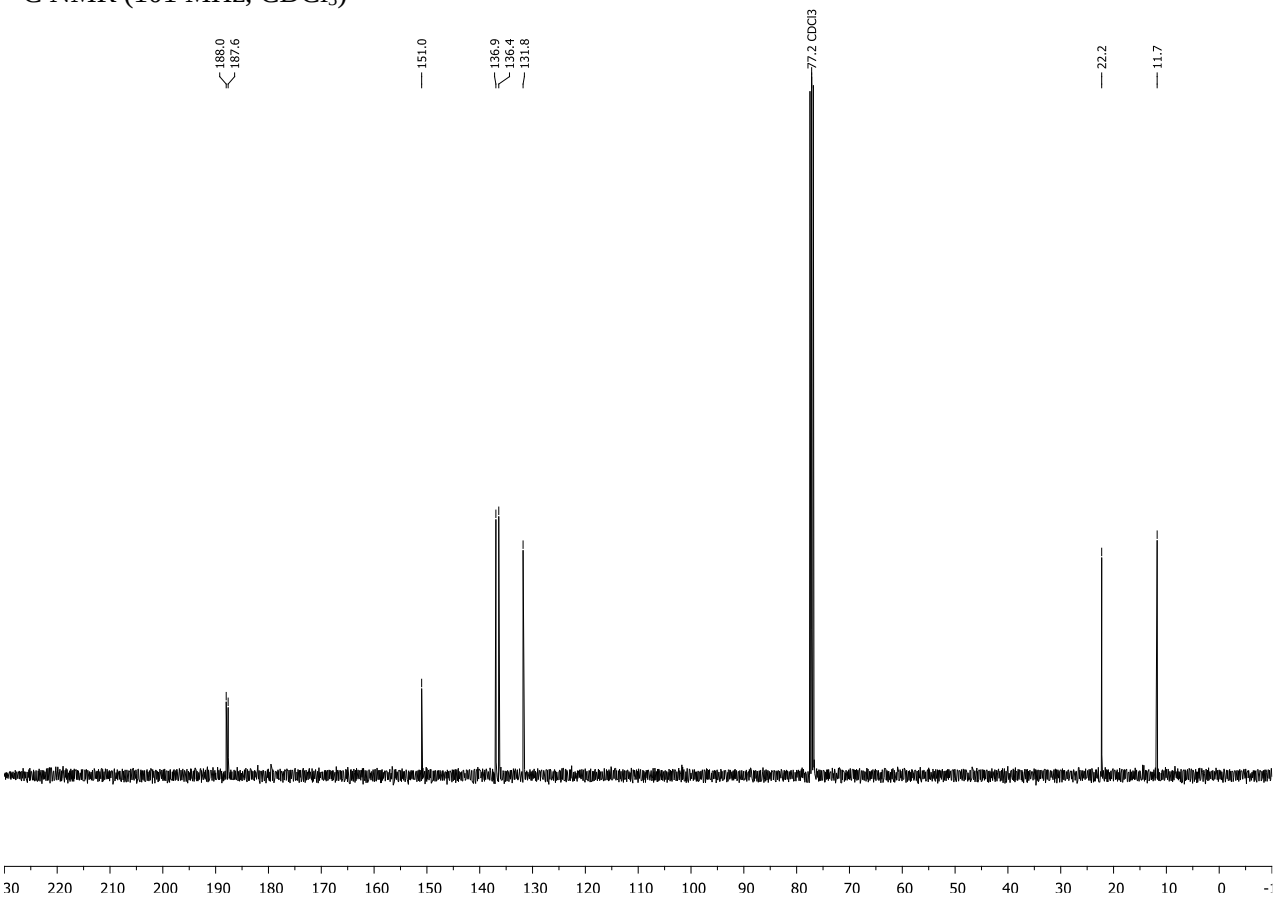


2-Ethyl-1,4-benzoquinone (1o)

^{1}H NMR (400 MHz, $CDCl_3$)

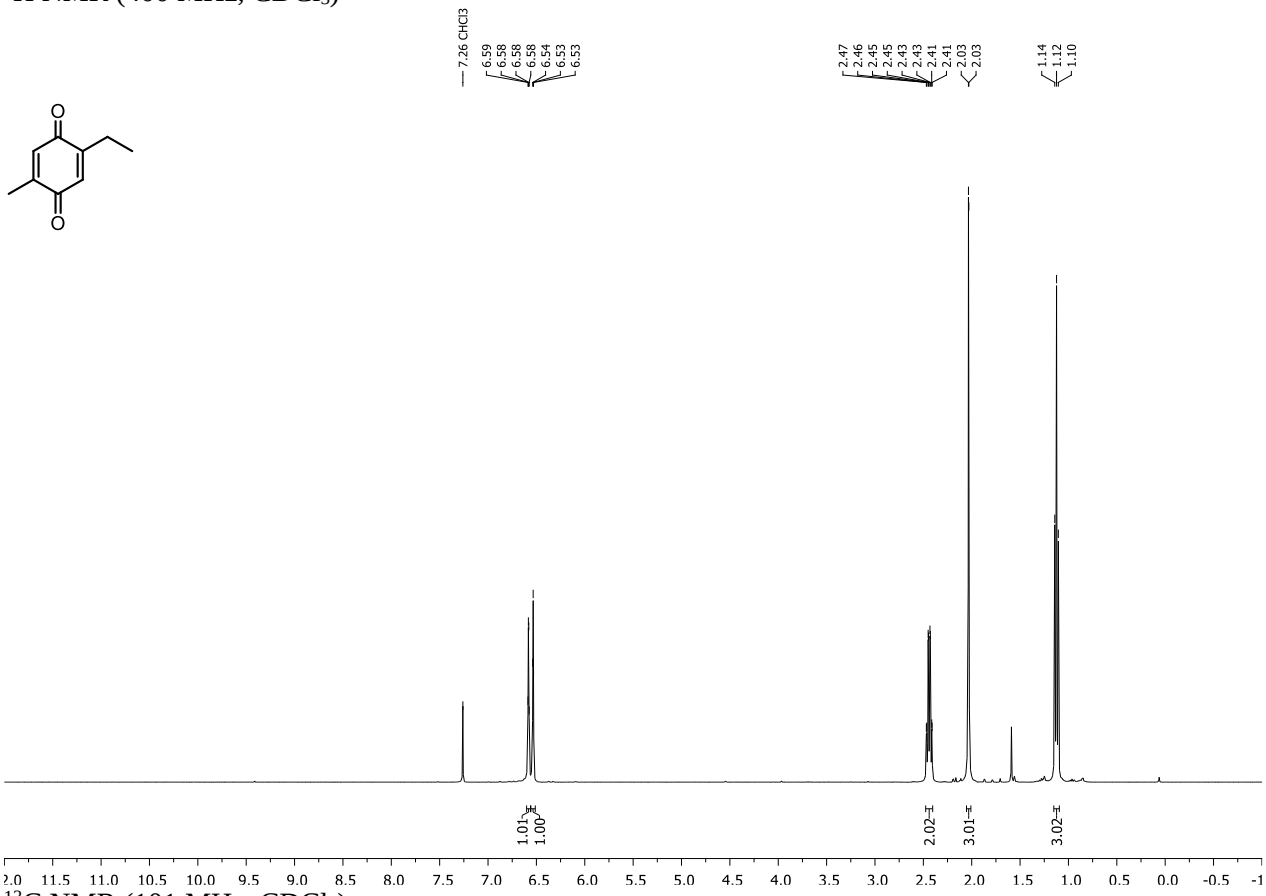


^{13}C NMR (101 MHz, $CDCl_3$)

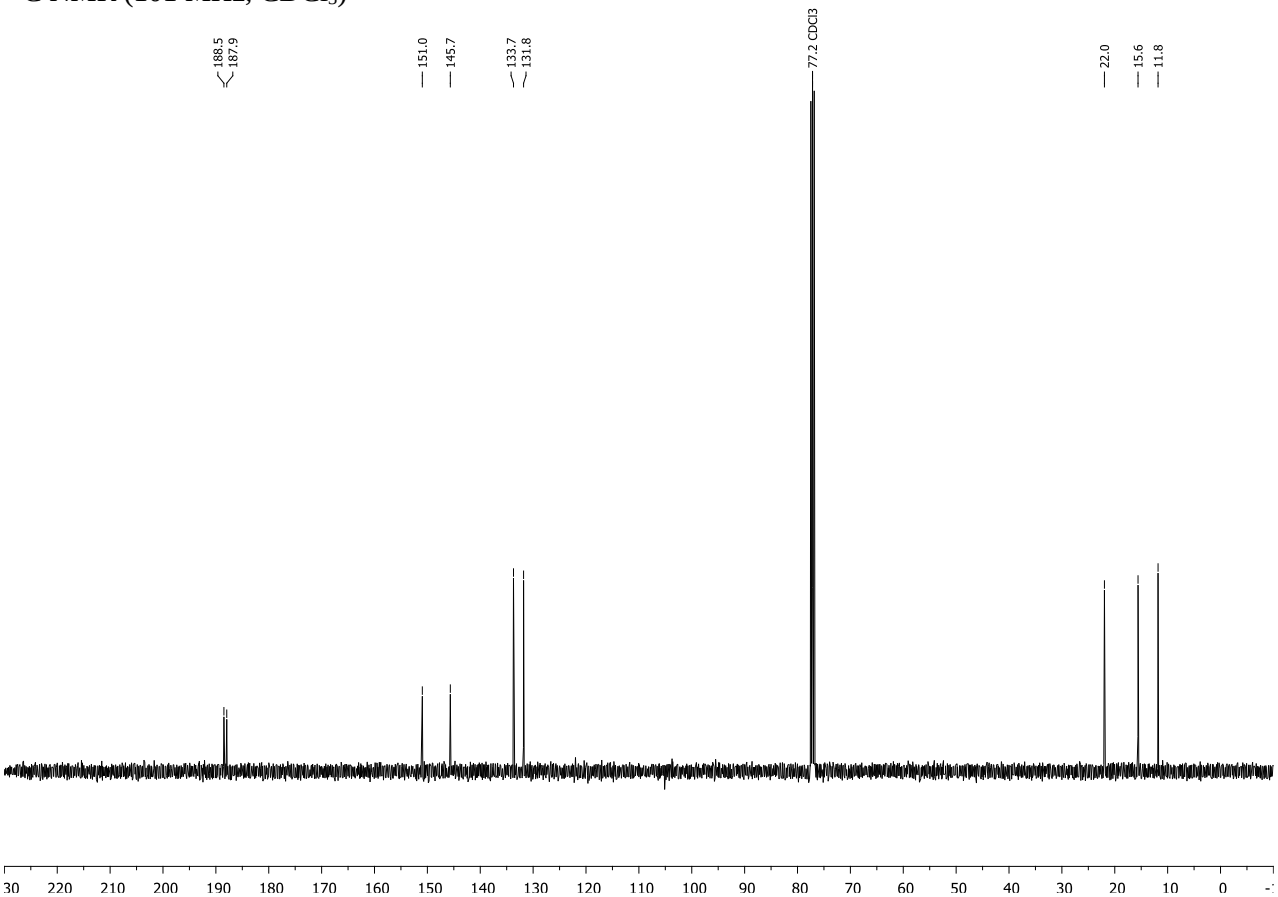


2-Ethyl-5-methyl-1,4-benzoquinone (1p)

^{1}H NMR (400 MHz, $CDCl_3$)

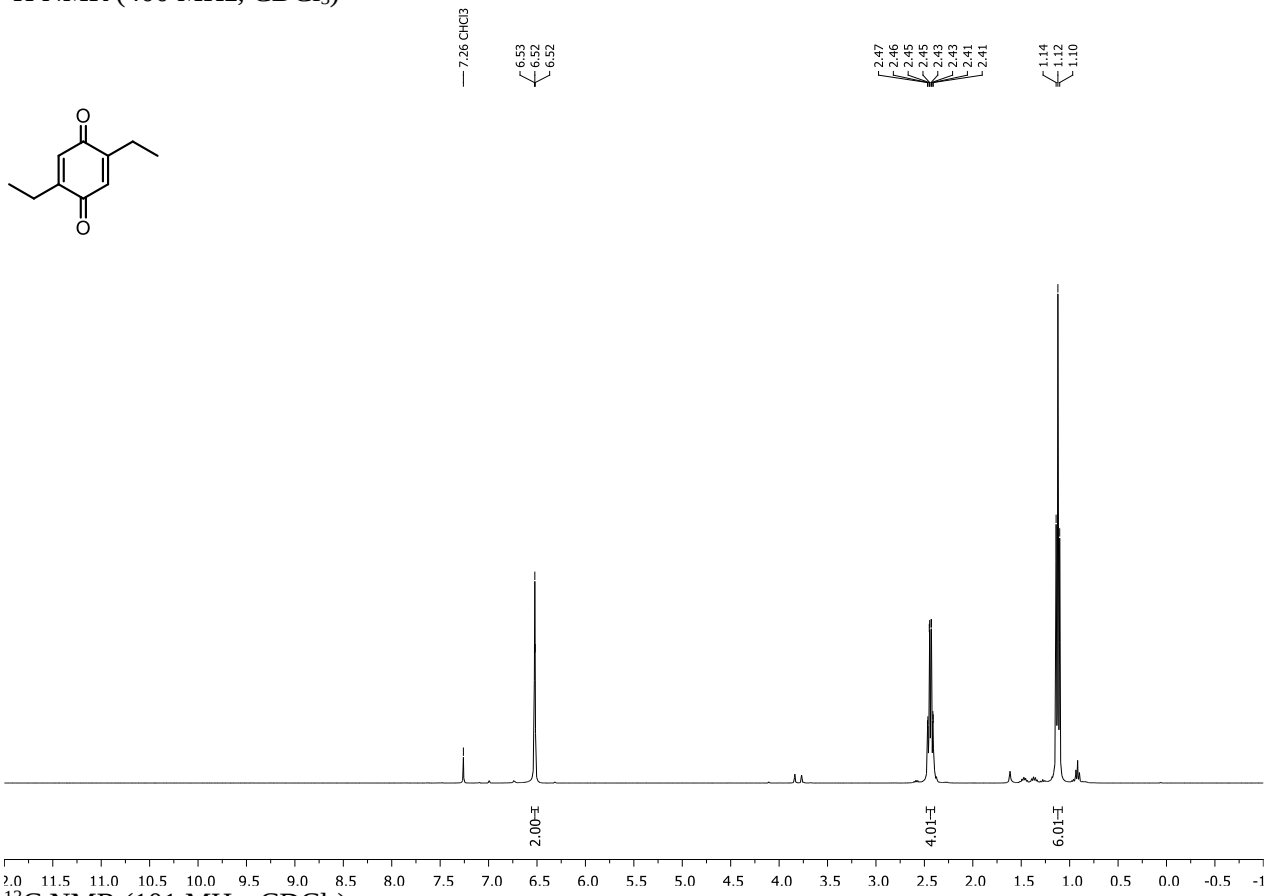


^{13}C NMR (101 MHz, $CDCl_3$)

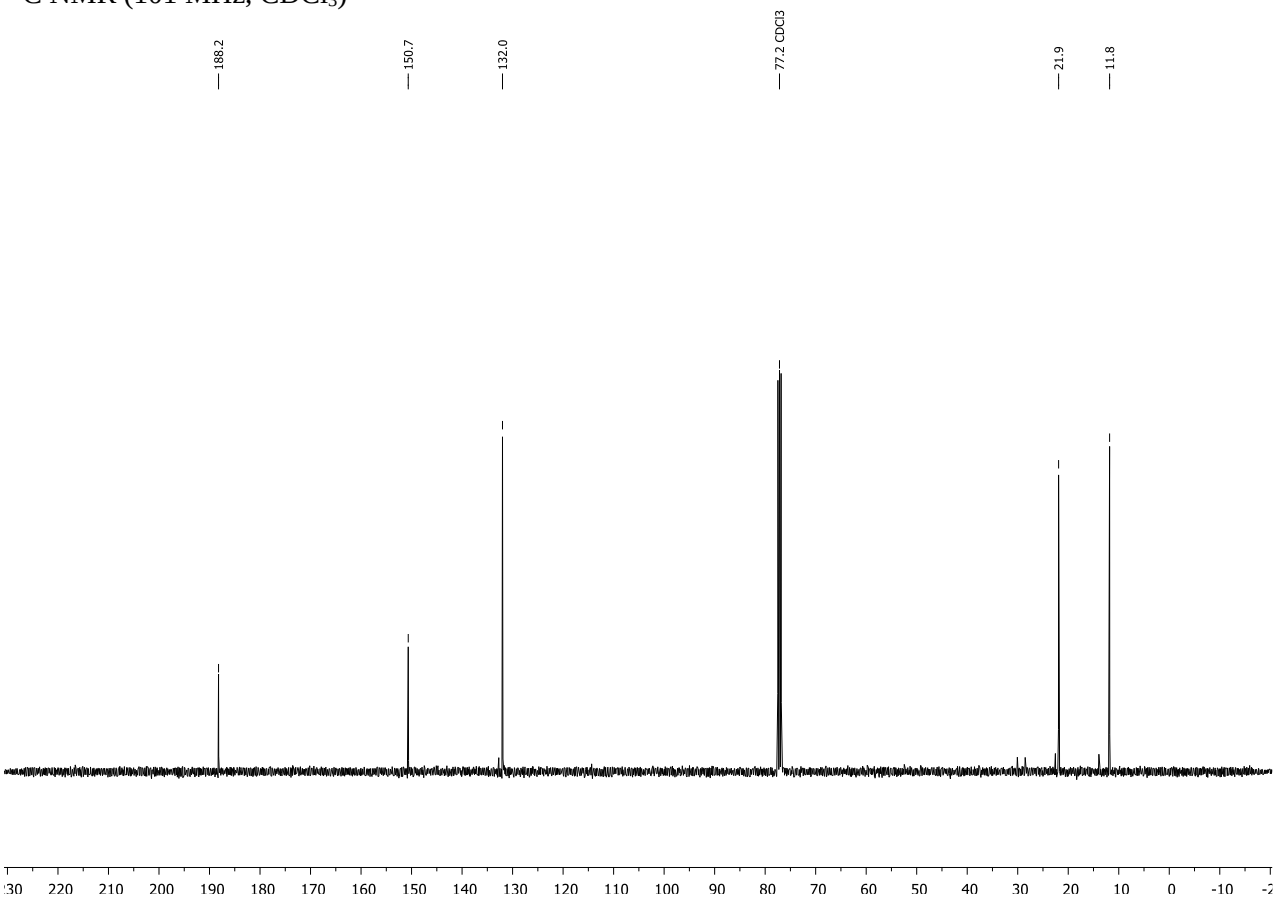


2,5-Diethyl-1,4-benzoquinone (1q)

^{1}H NMR (400 MHz, $CDCl_3$)

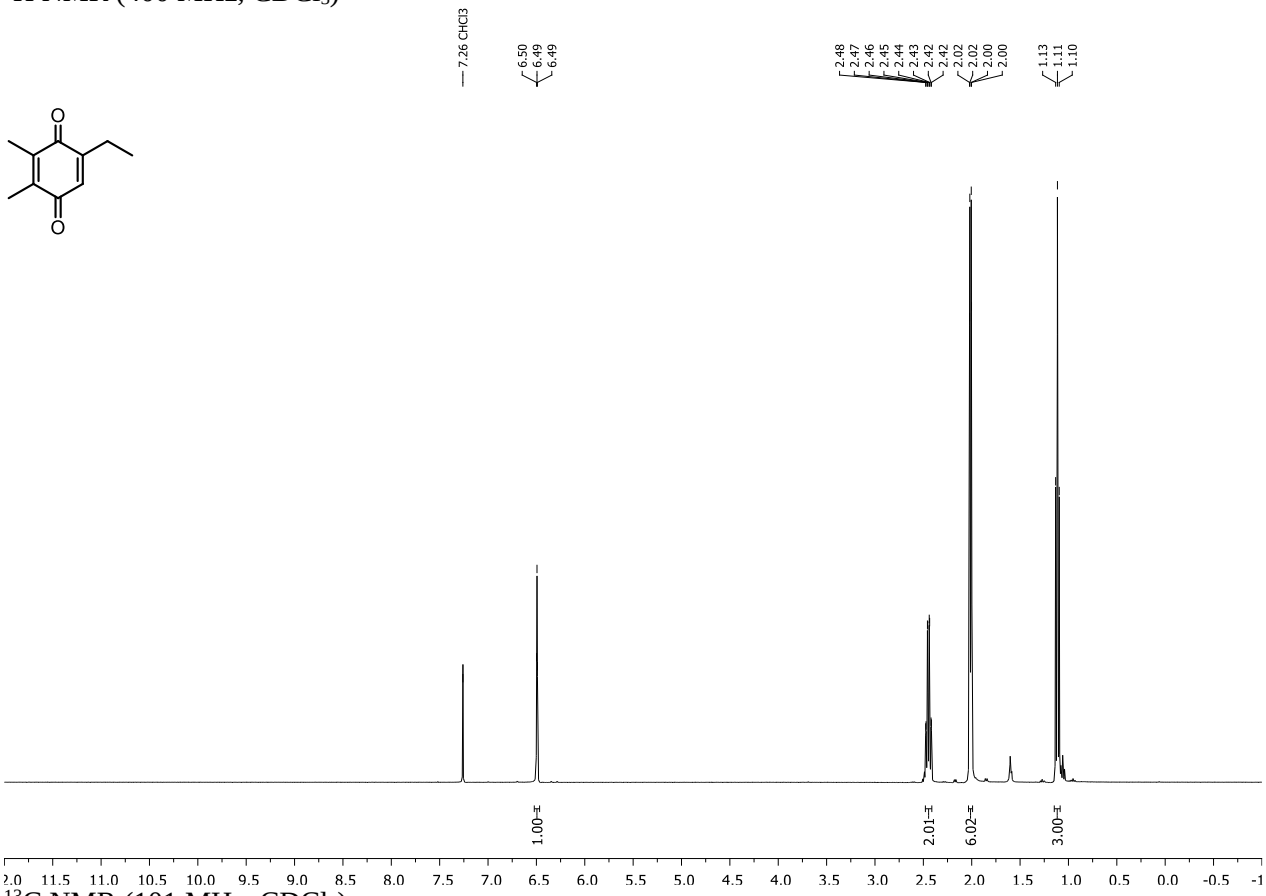


^{13}C NMR (101 MHz, $CDCl_3$)

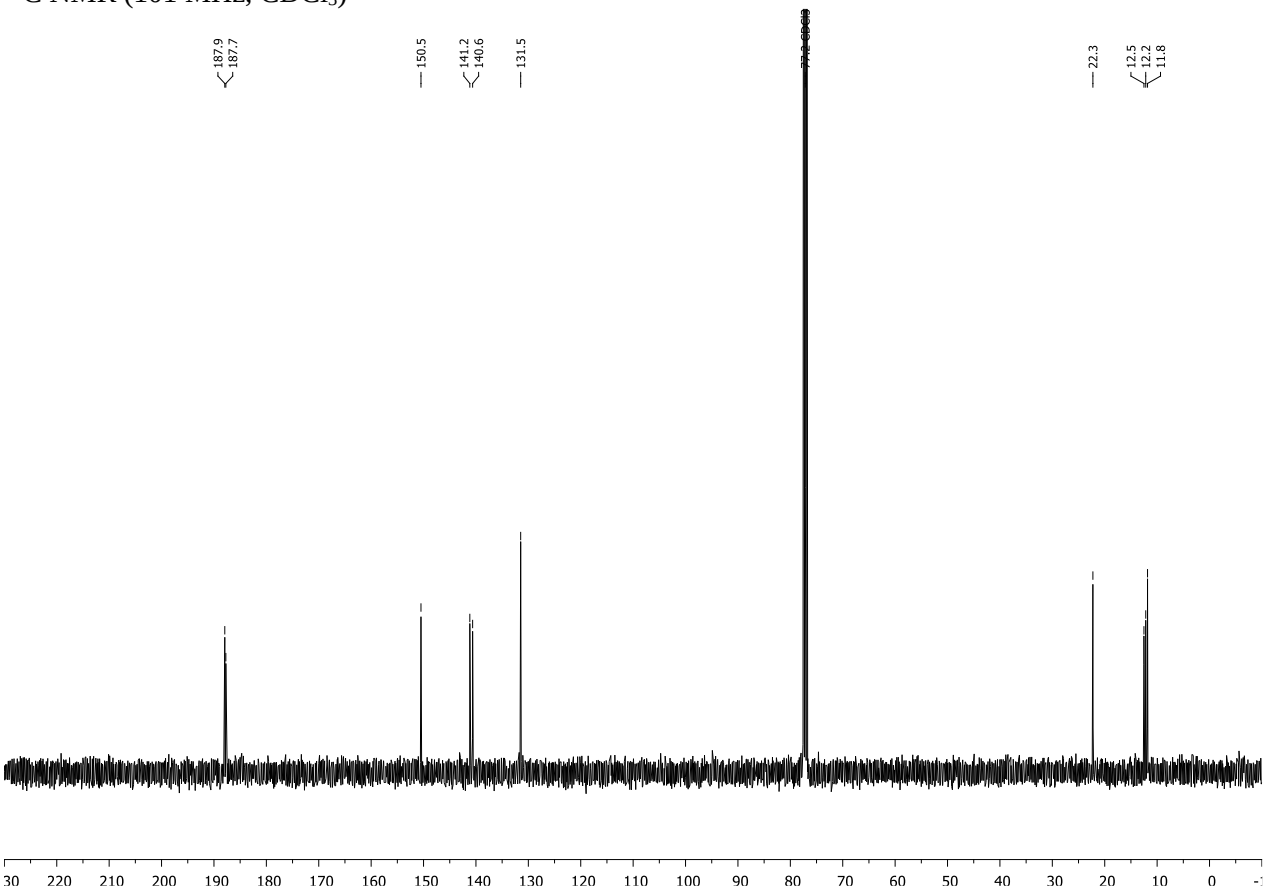


5-Ethyl-2,3-dimethyl-1,4-benzoquinone (1r)

^{1}H NMR (400 MHz, $CDCl_3$)

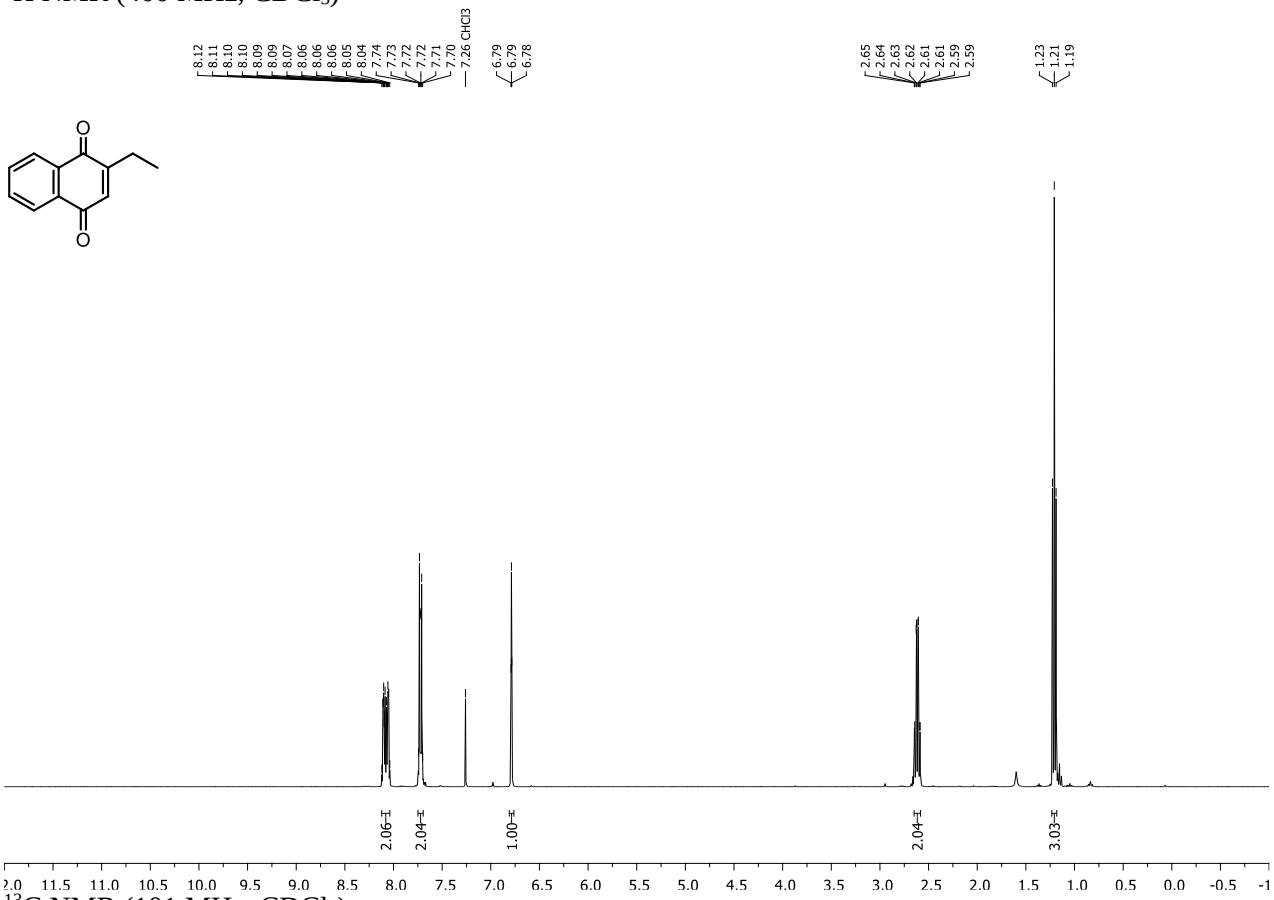


^{13}C NMR (101 MHz, $CDCl_3$)

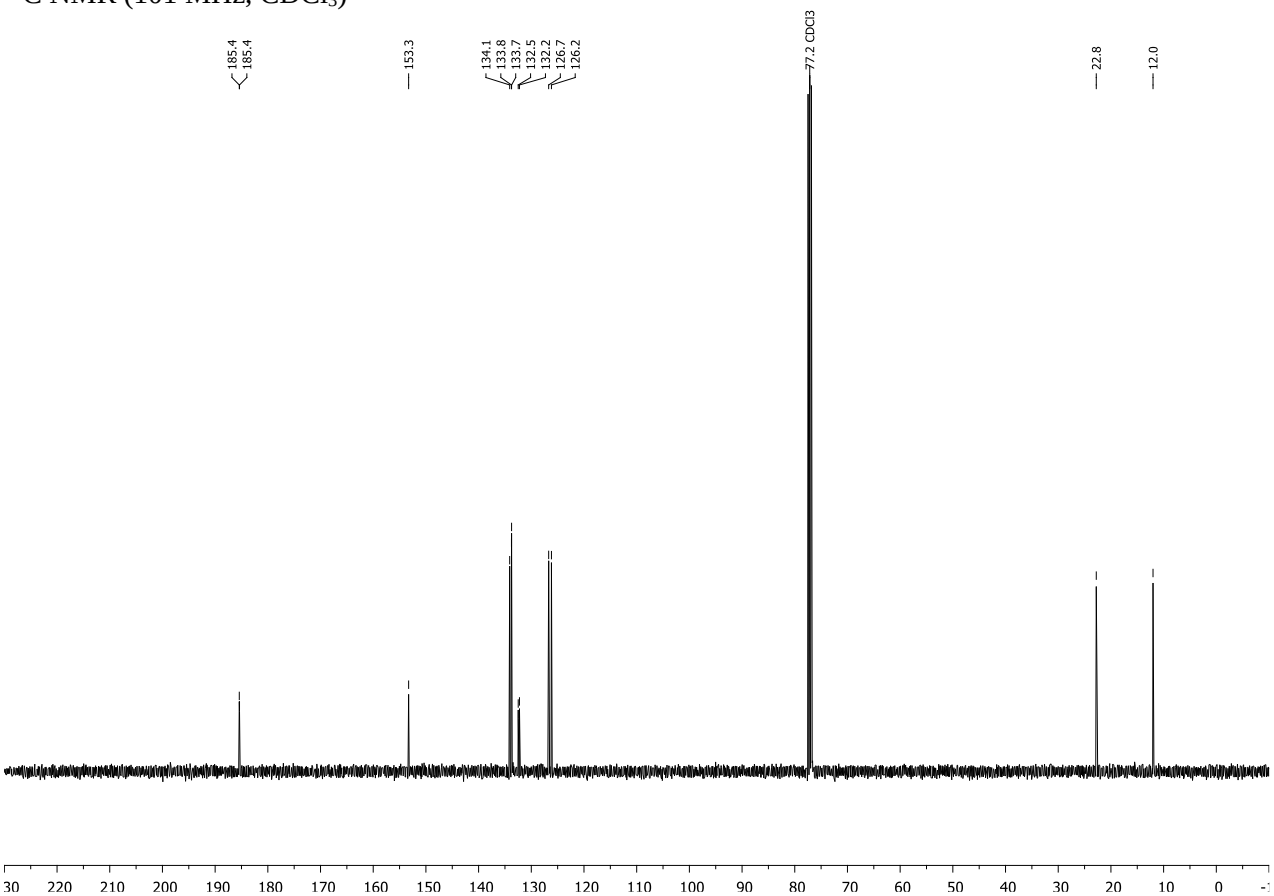


2-Ethyl-1,4-naphthoquinone (1s)

^{1}H NMR (400 MHz, $CDCl_3$)

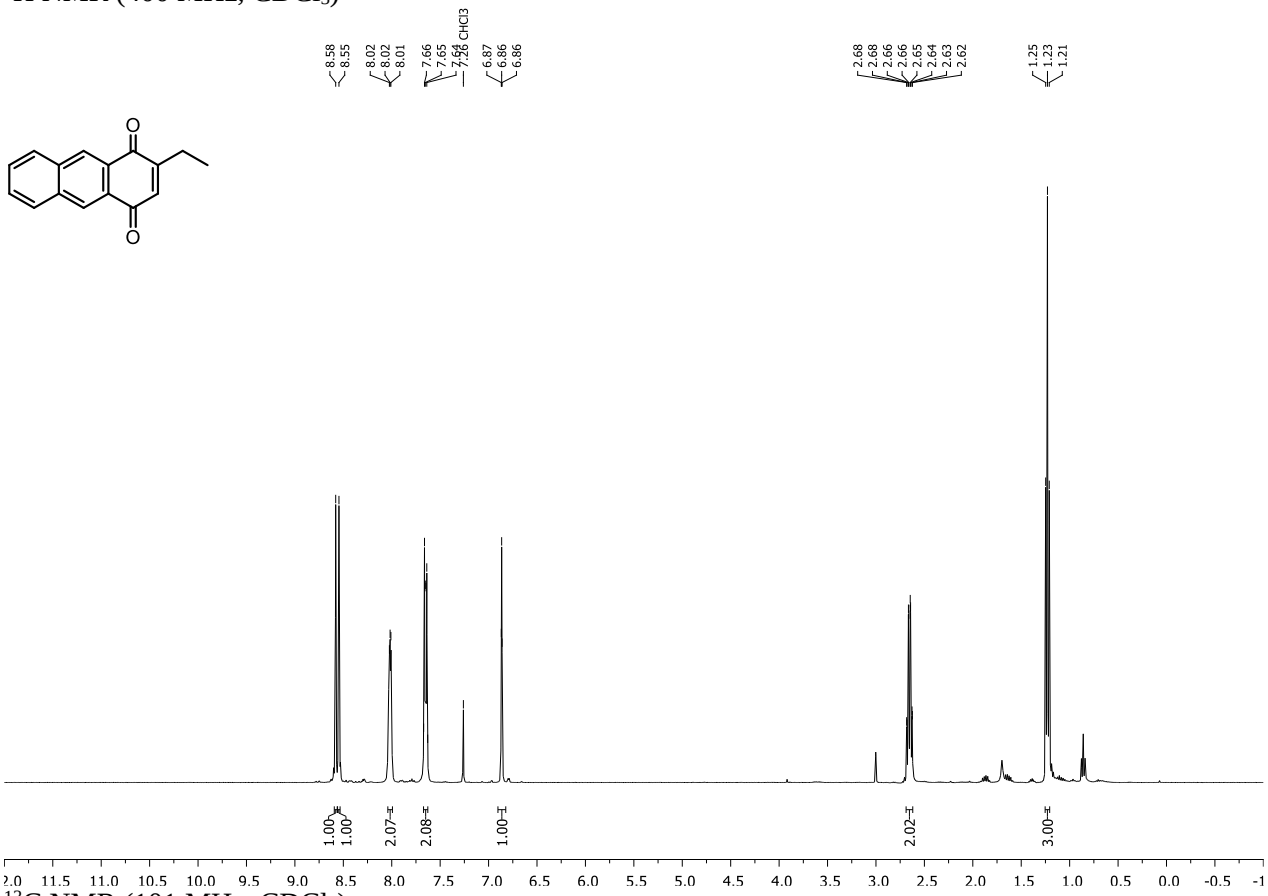


^{13}C NMR (101 MHz, $CDCl_3$)

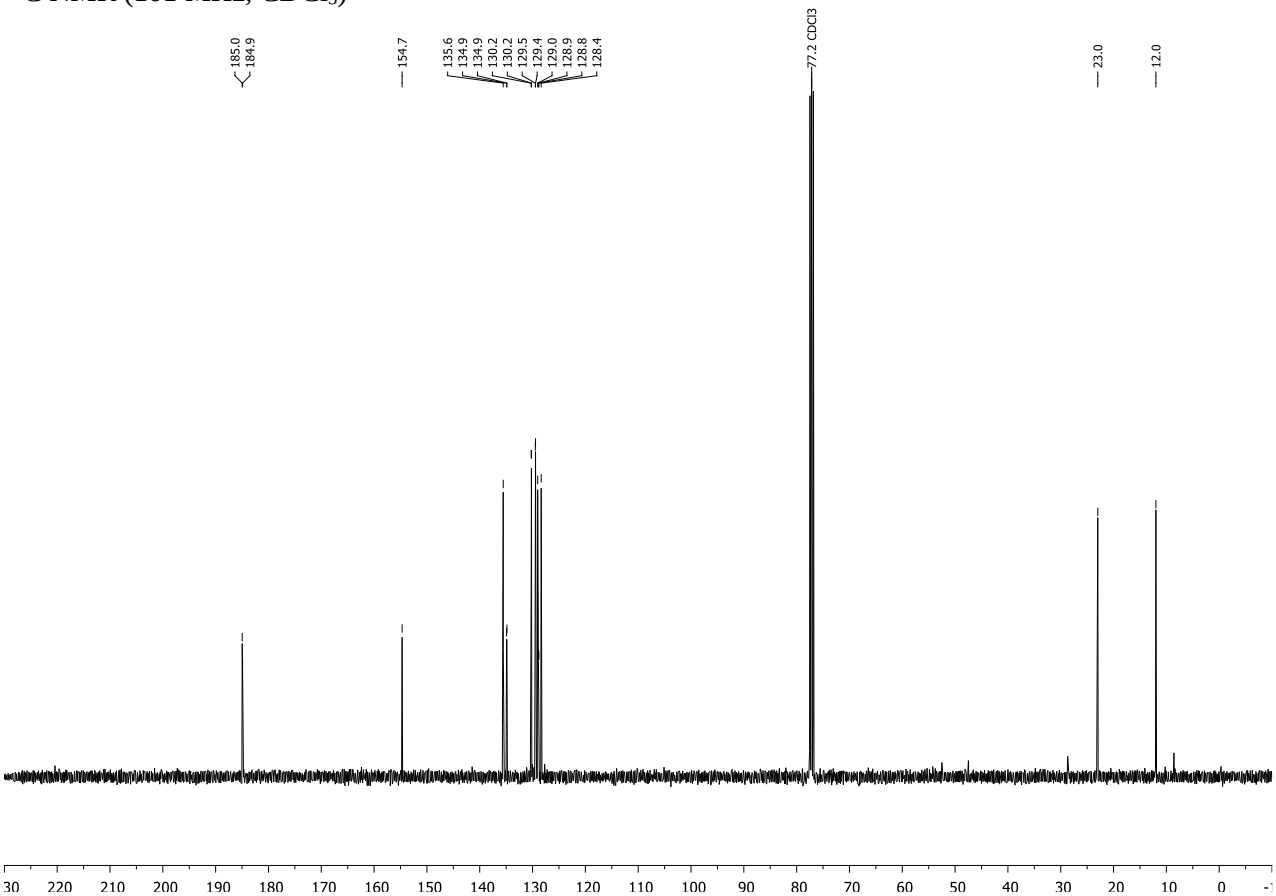


2-Ethyl-1,4-anthraquinone (1t)

^{1}H NMR (400 MHz, $CDCl_3$)

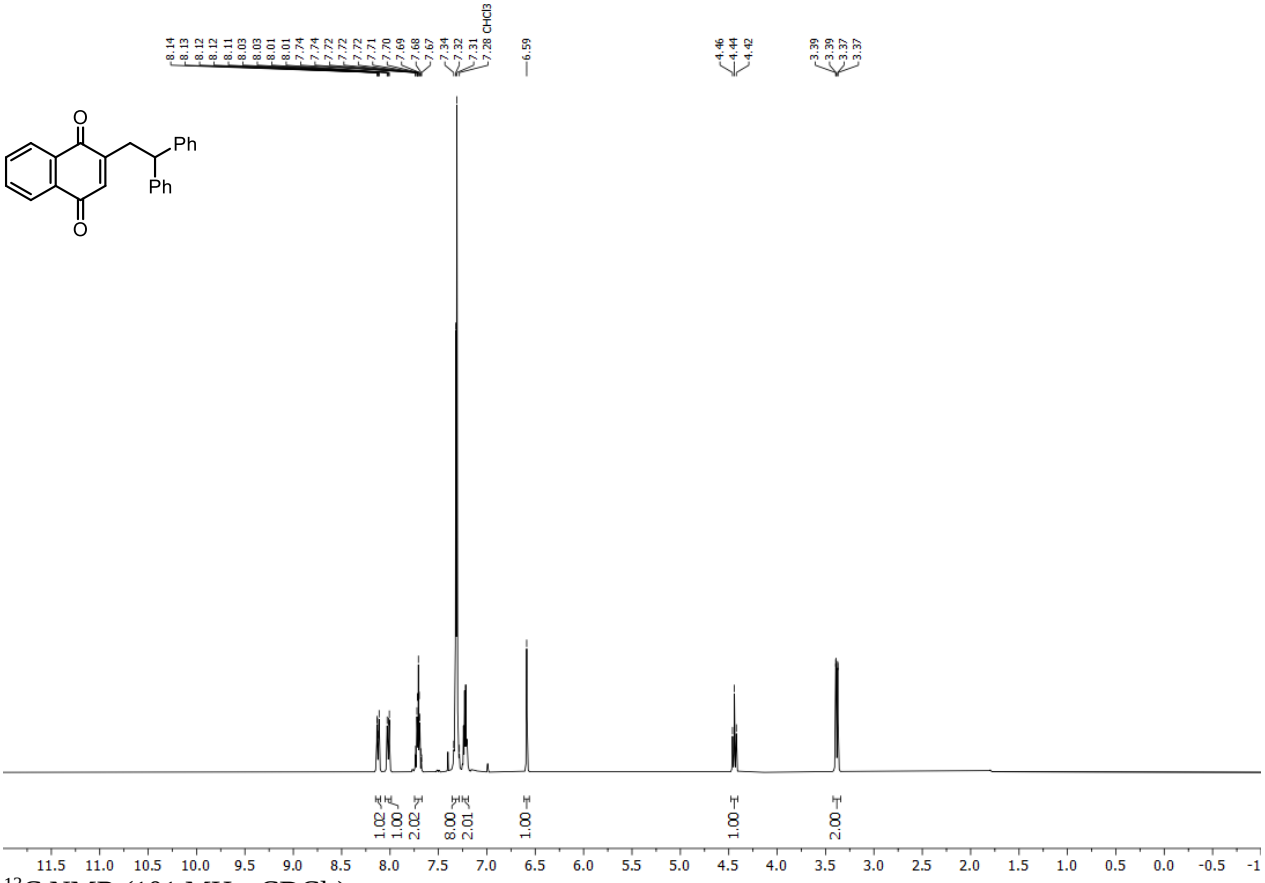


^{13}C NMR (101 MHz, $CDCl_3$)

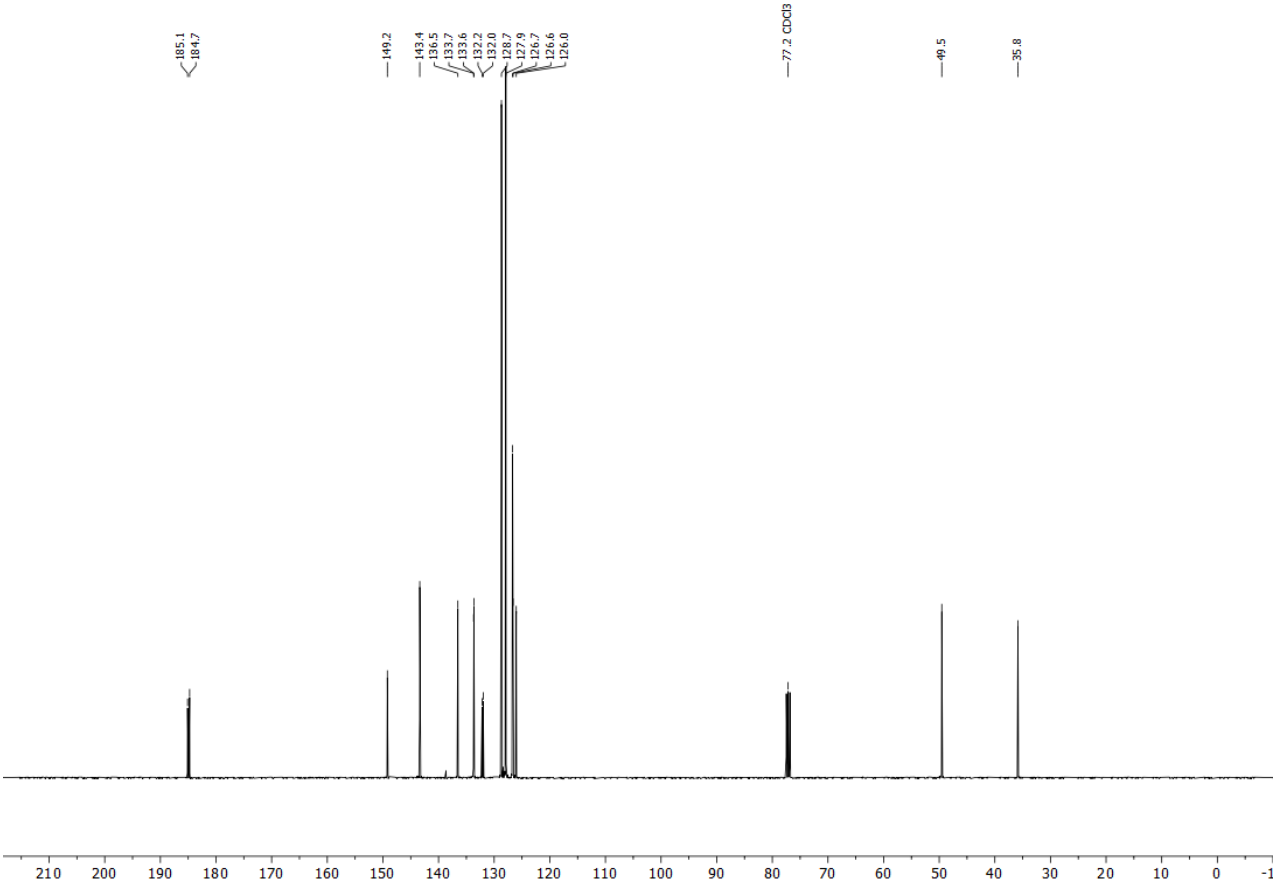


2-(2,2-Diphenylethyl)-1,4-naphthoquinone (1v)

^{1}H NMR (400 MHz, $CDCl_3$)

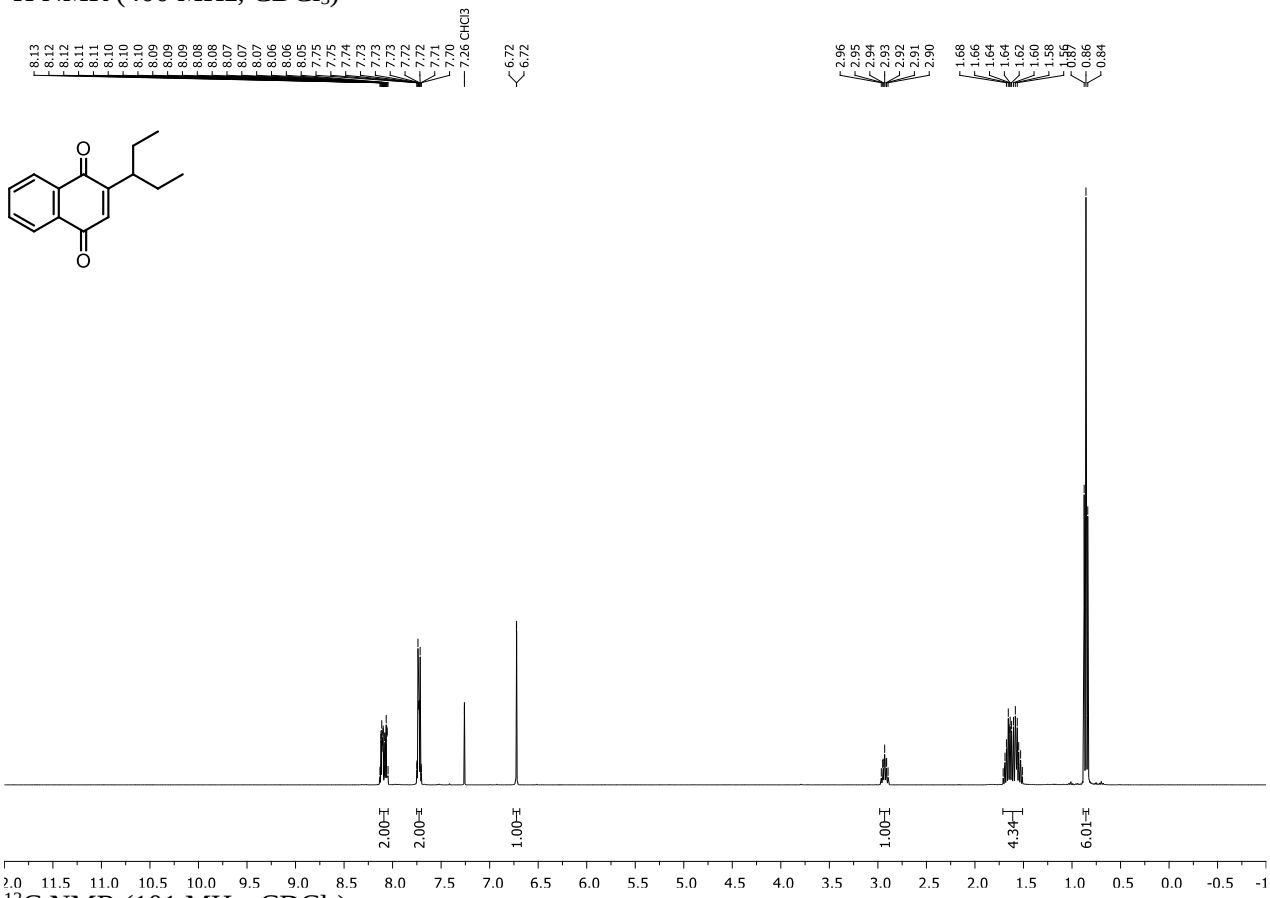


^{13}C NMR (101 MHz, $CDCl_3$)

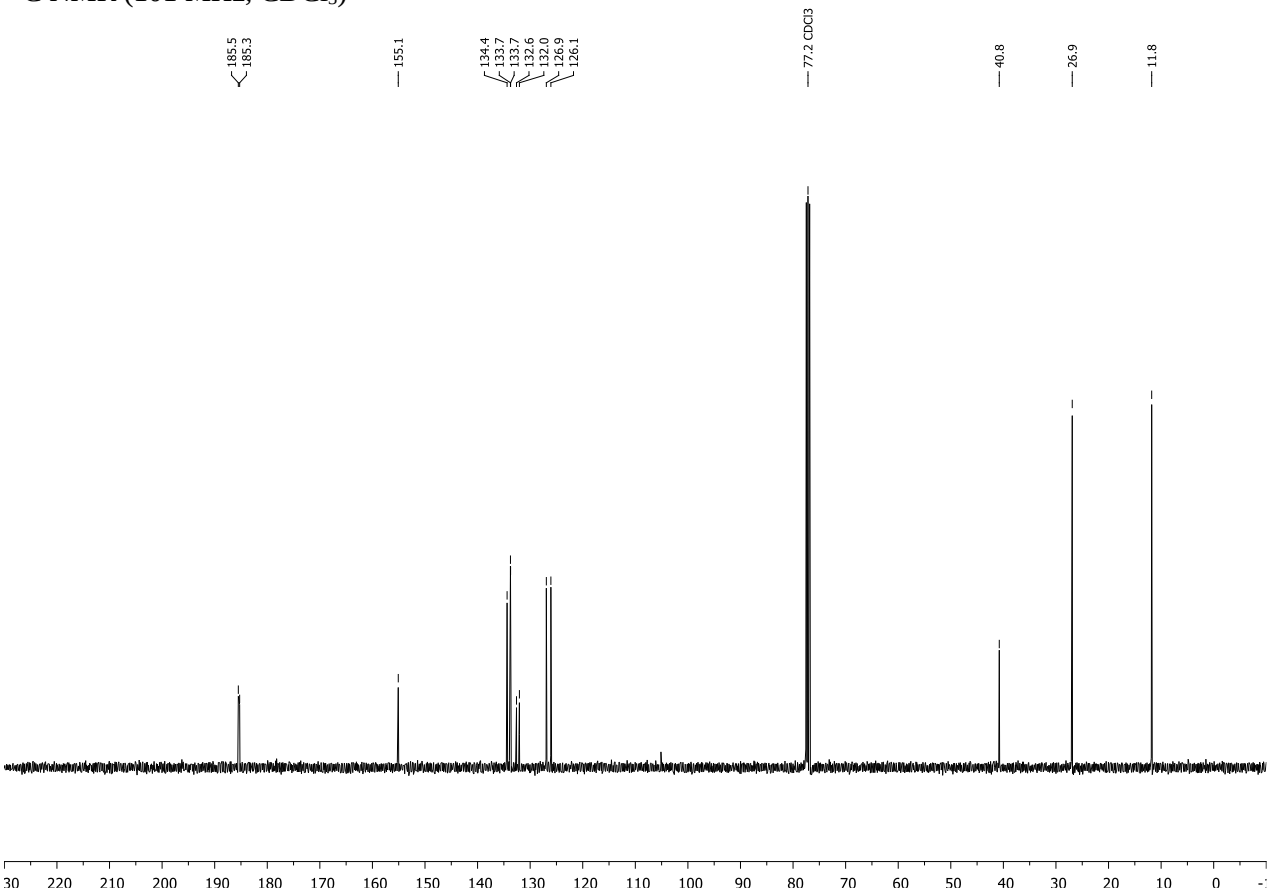


2-(3-Pentyl)-1,4-naphthoquinone (1w)

^{1}H NMR (400 MHz, $CDCl_3$)

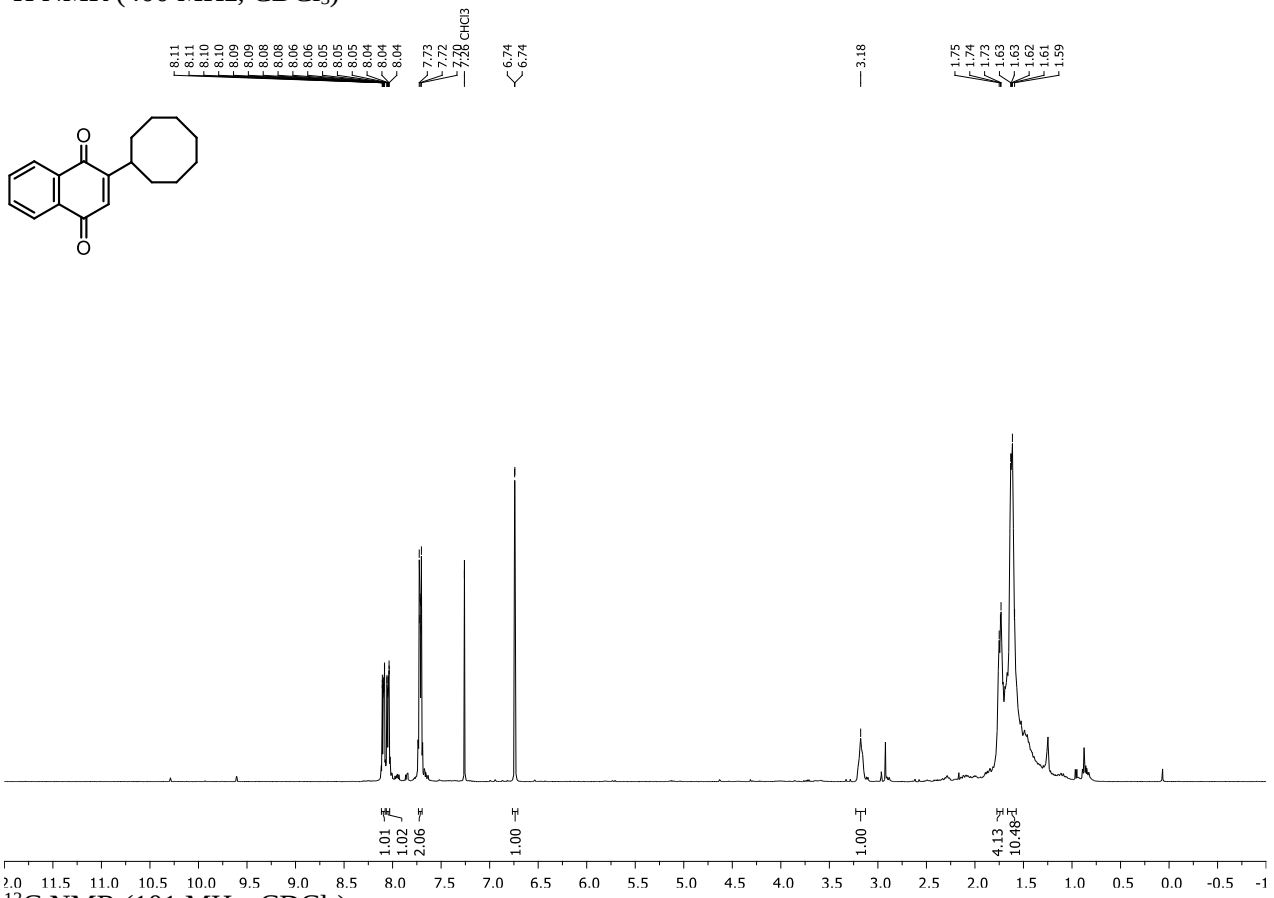


^{13}C NMR (101 MHz, $CDCl_3$)

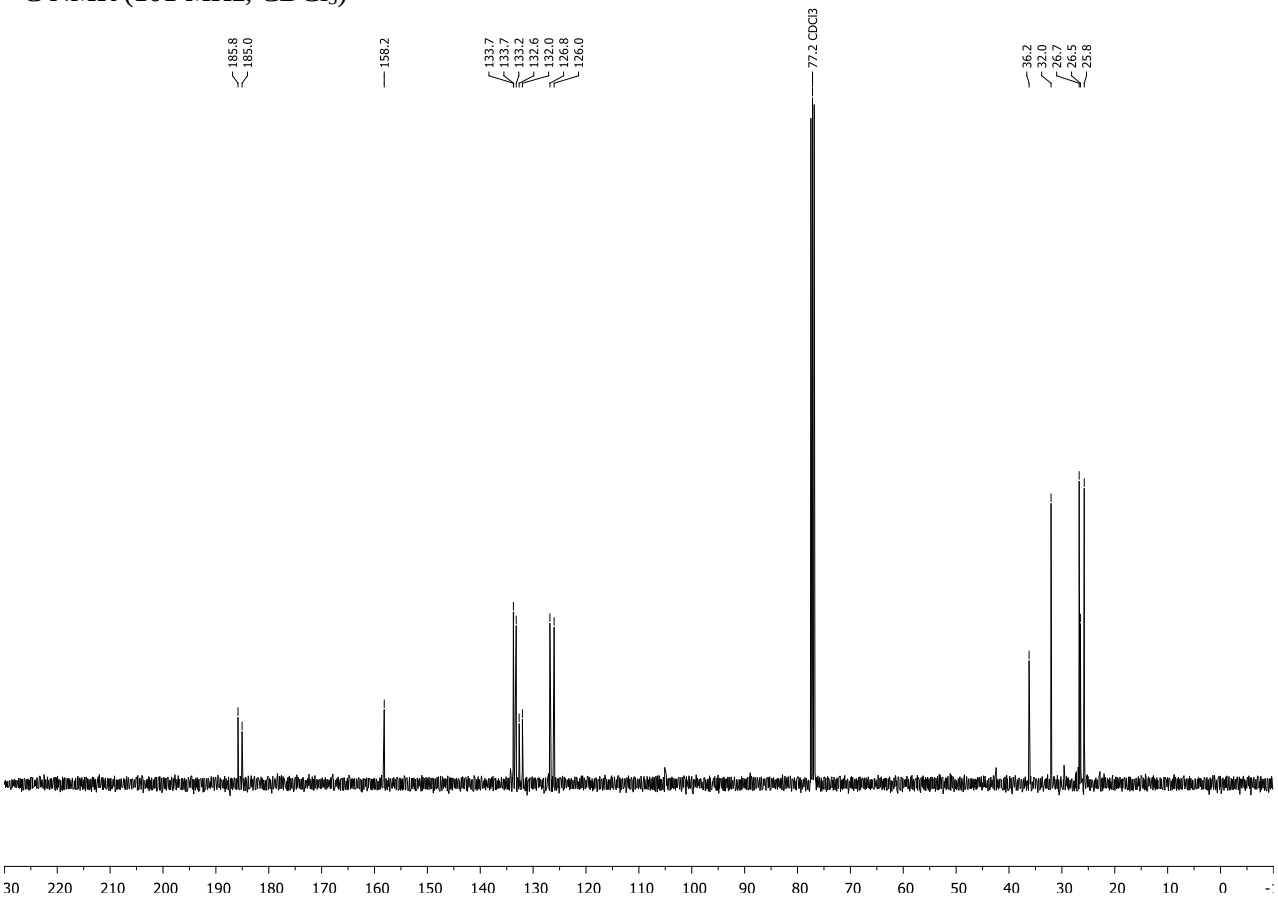


2-Cyclooctyl-1,4-naphthoquinone (1x)

^{1}H NMR (400 MHz, $CDCl_3$)

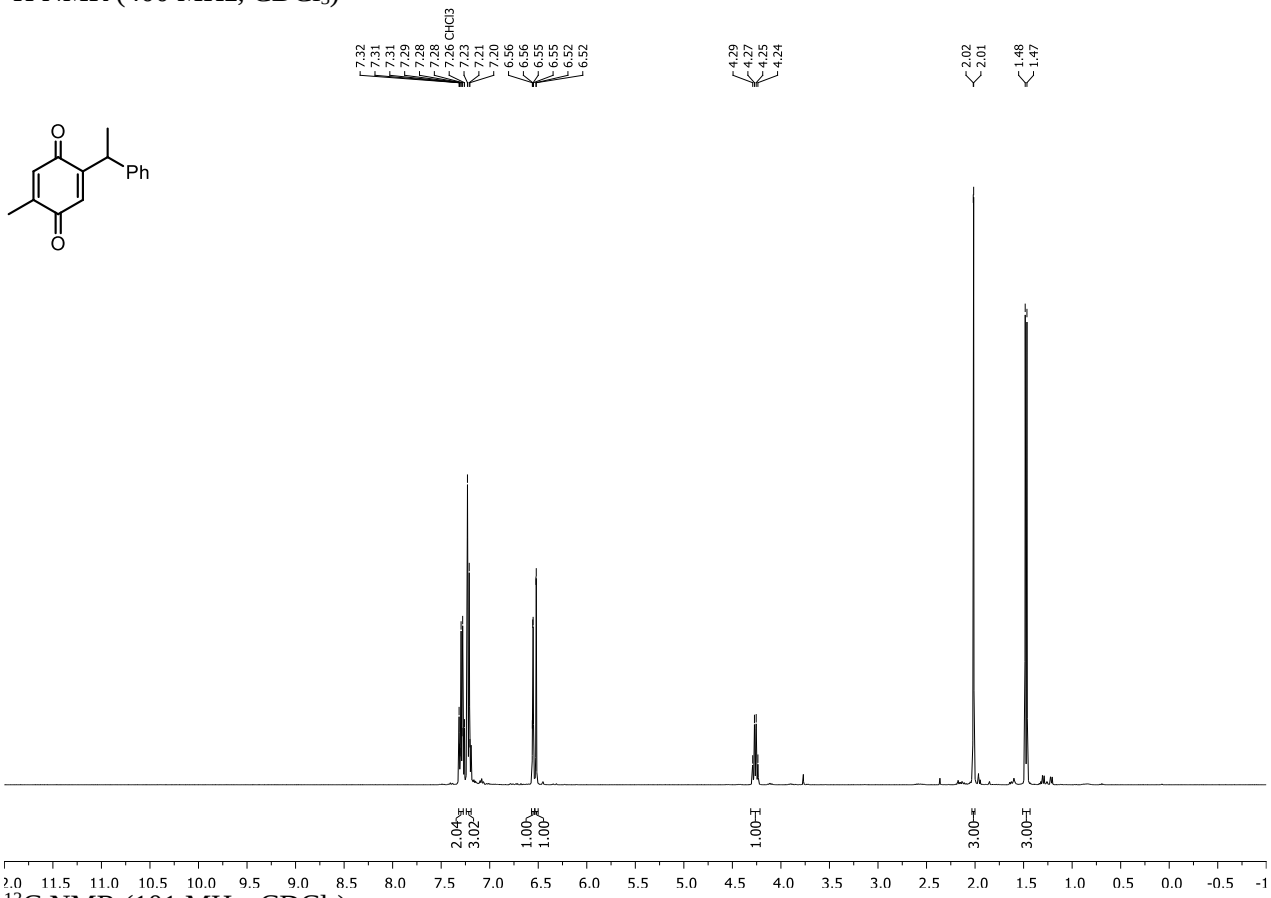


^{13}C NMR (101 MHz, $CDCl_3$)

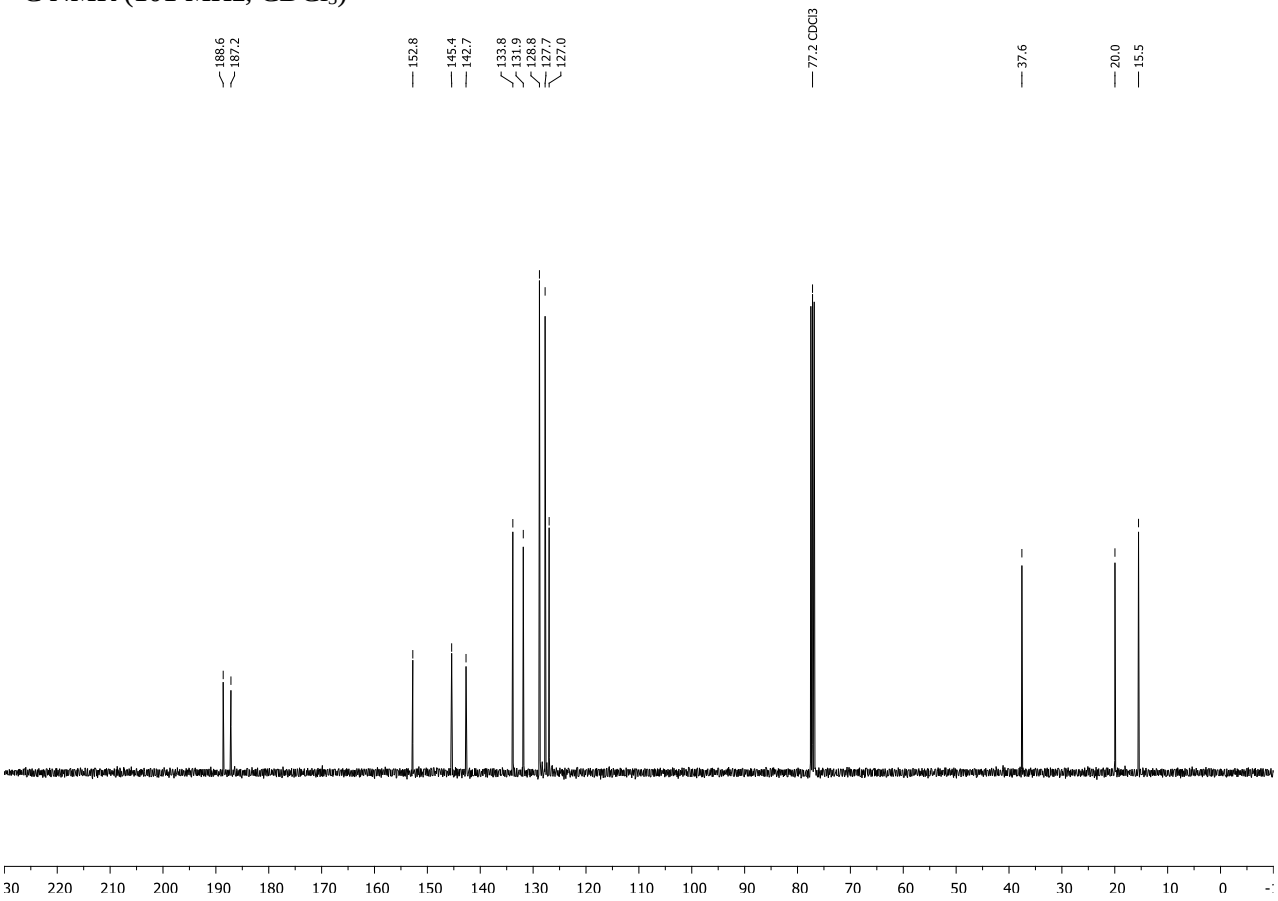


2-Methyl-5-(1-phenylethyl)-1,4-benzoquinone (1y)

^{1}H NMR (400 MHz, $CDCl_3$)

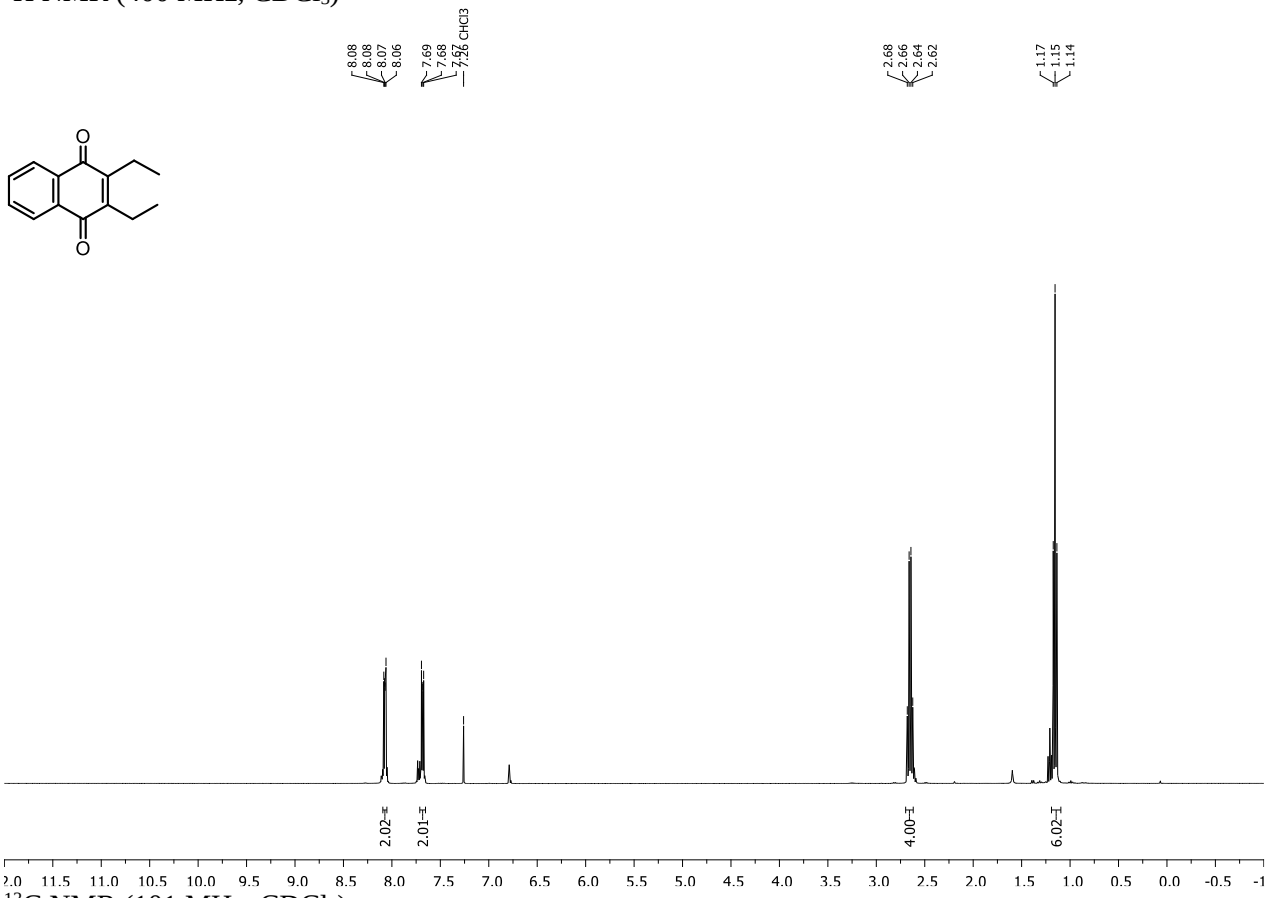


^{13}C NMR (101 MHz, $CDCl_3$)

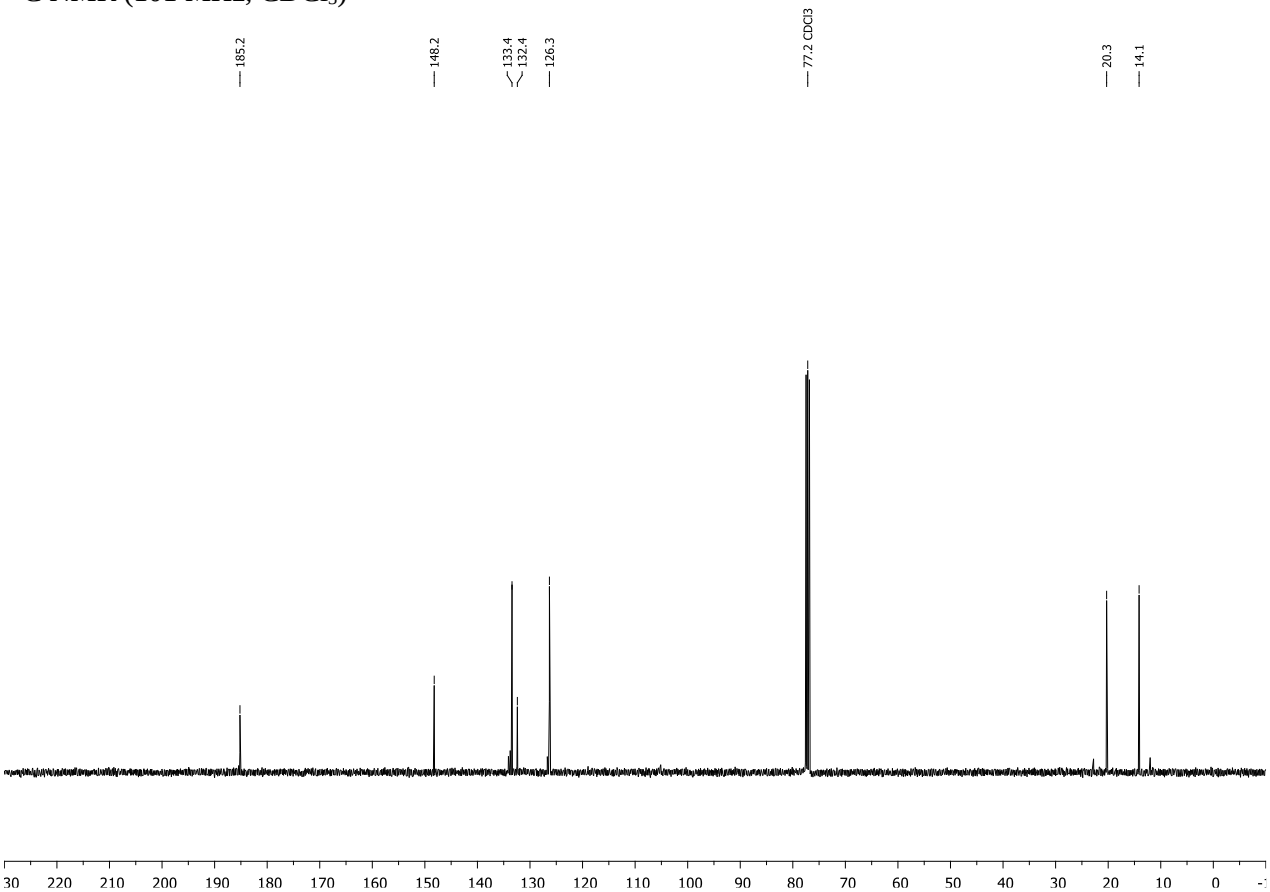


2,3-Diethyl-1,4-naphthoquinone (1z)

^{1}H NMR (400 MHz, $CDCl_3$)

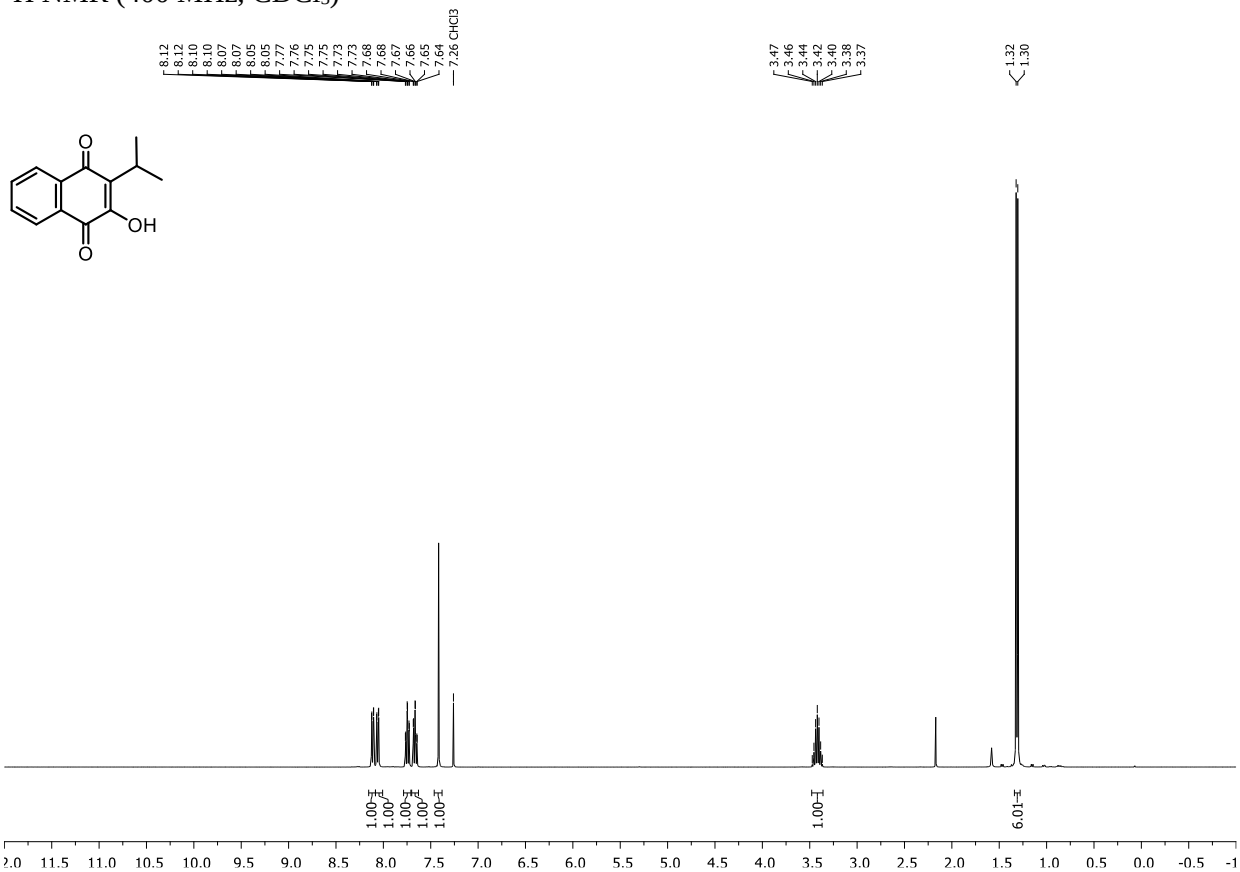


^{13}C NMR (101 MHz, $CDCl_3$)

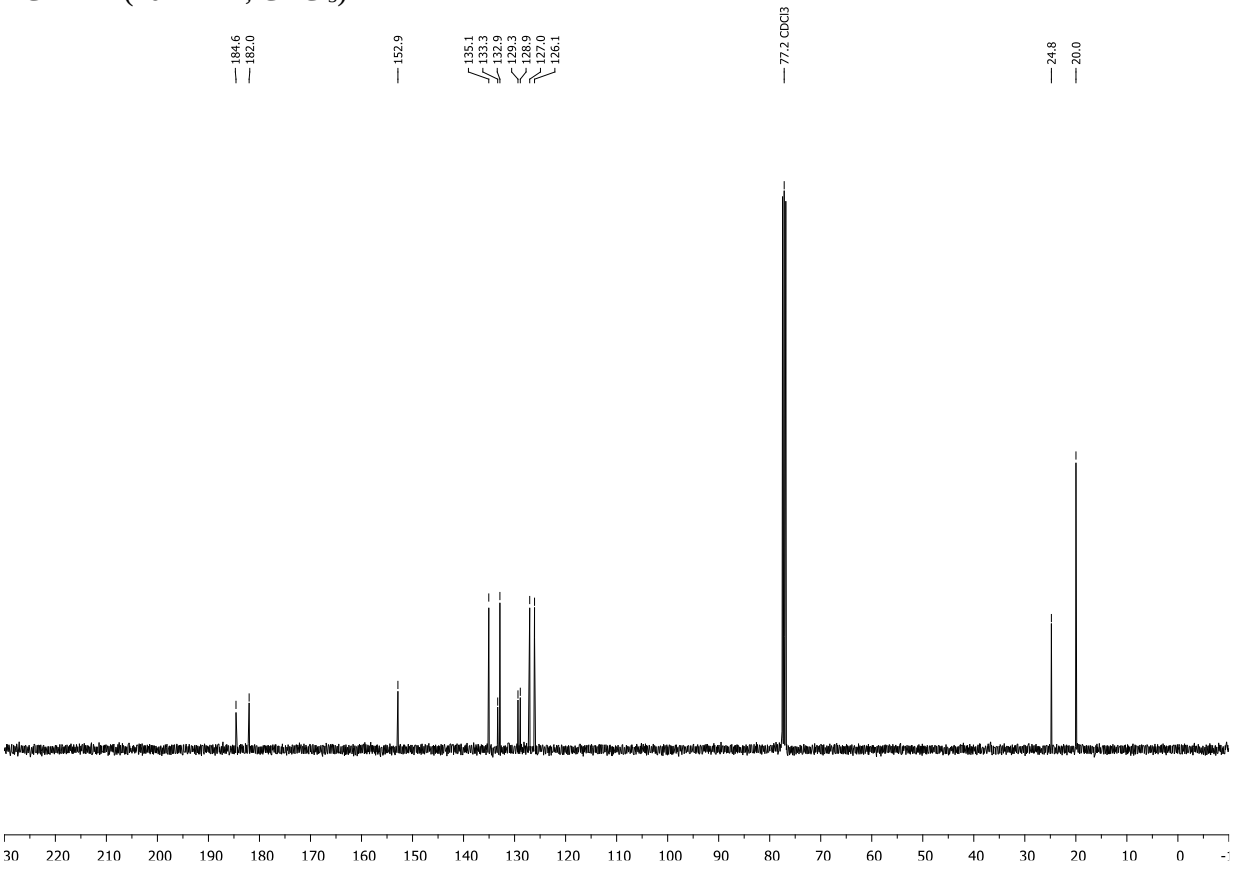


2-Hydroxy-3-isopropyl-1,4-naphthoquinone (1aa)

^{1}H NMR (400 MHz, $CDCl_3$)

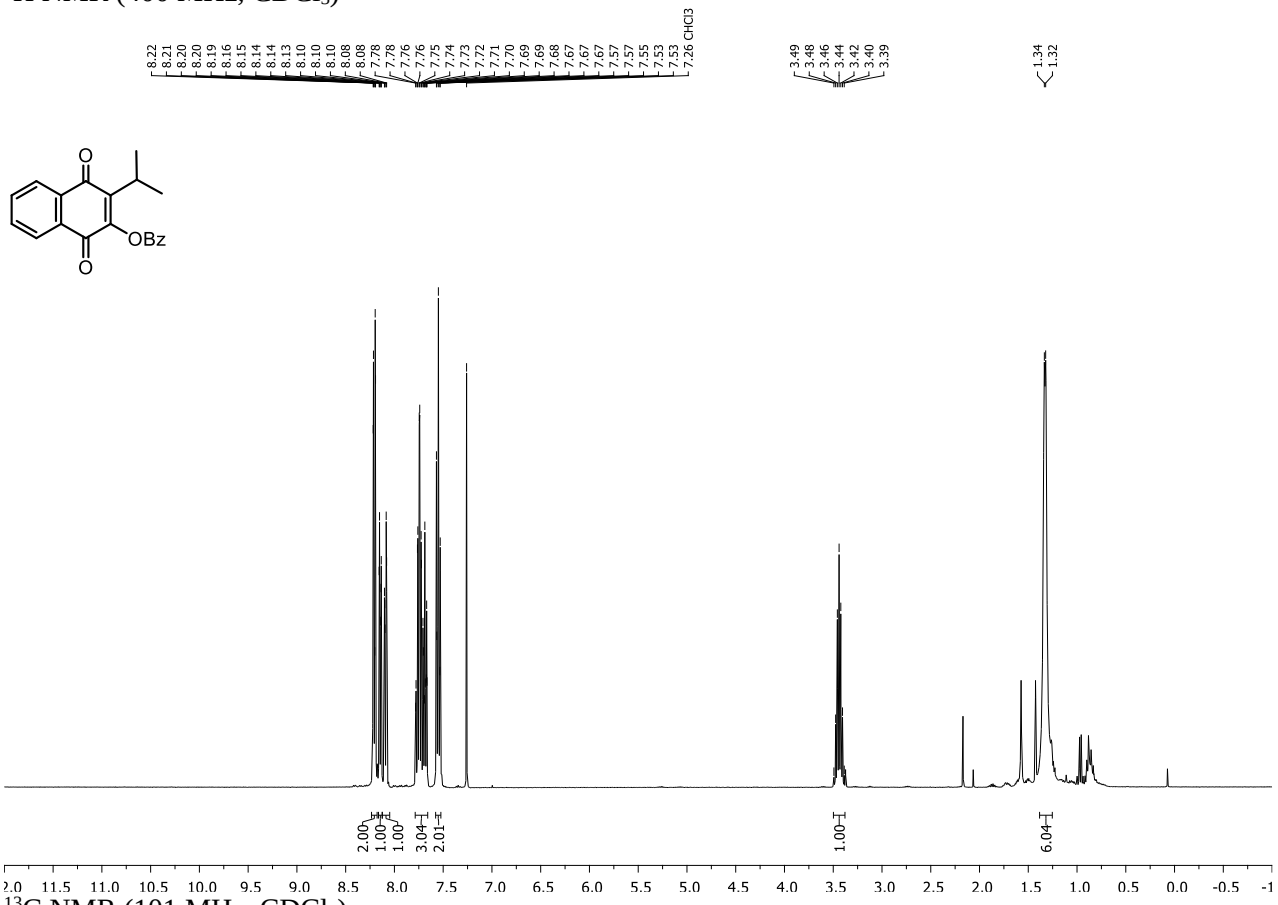


^{13}C NMR (101 MHz, $CDCl_3$)

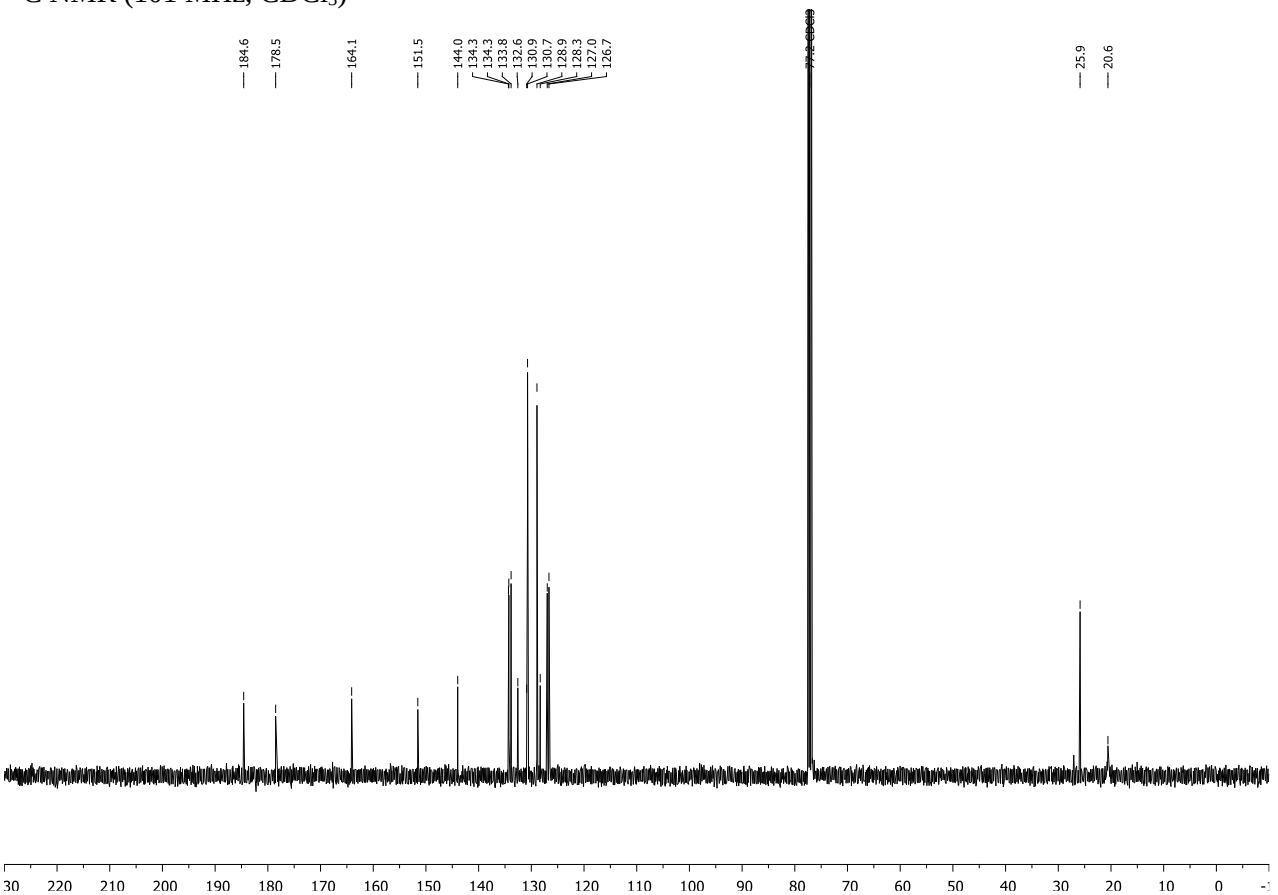


2-Benzoyloxy-3-isopropyl-1,4-naphthoquinone (1ab)

^{1}H NMR (400 MHz, $CDCl_3$)

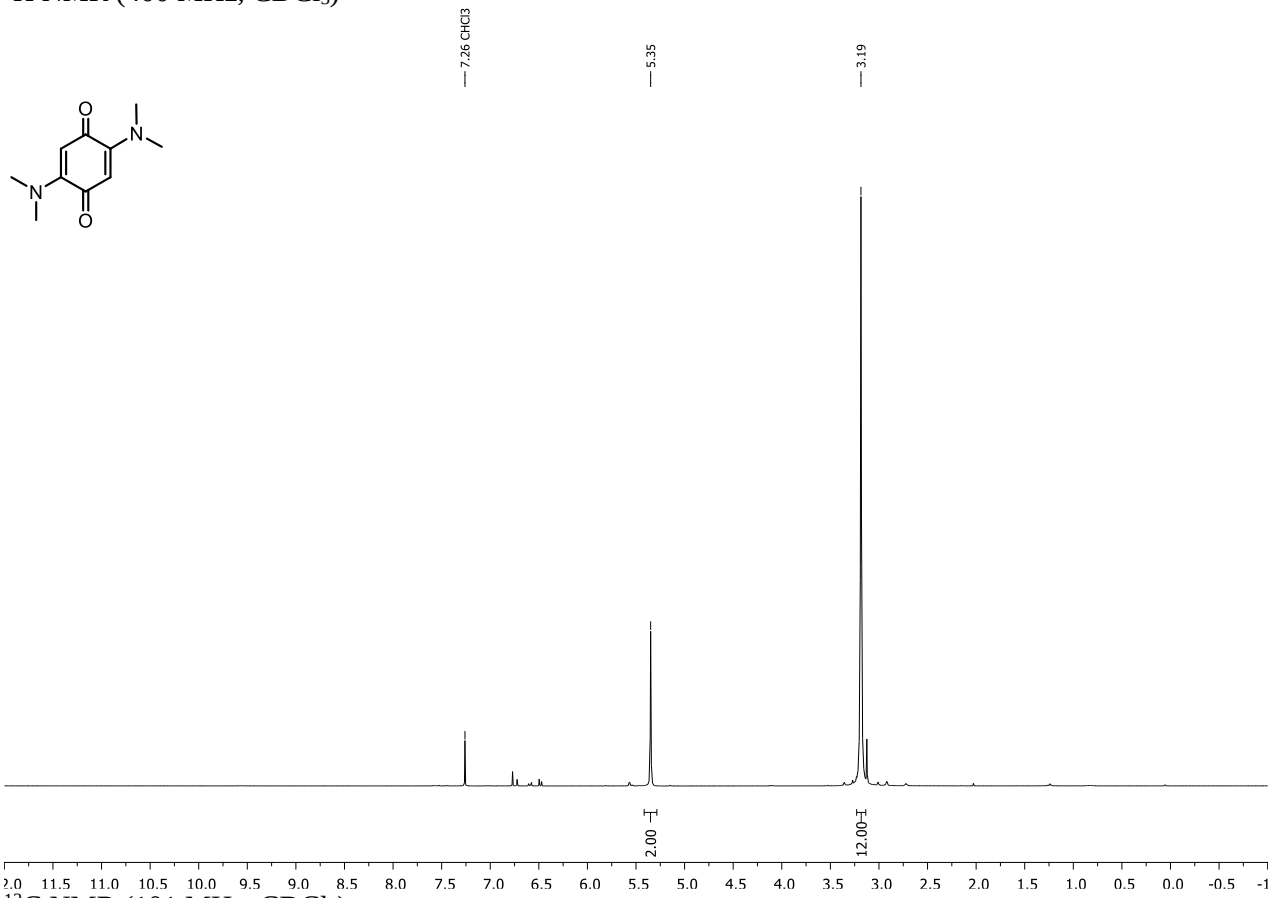


^{13}C NMR (101 MHz, $CDCl_3$)

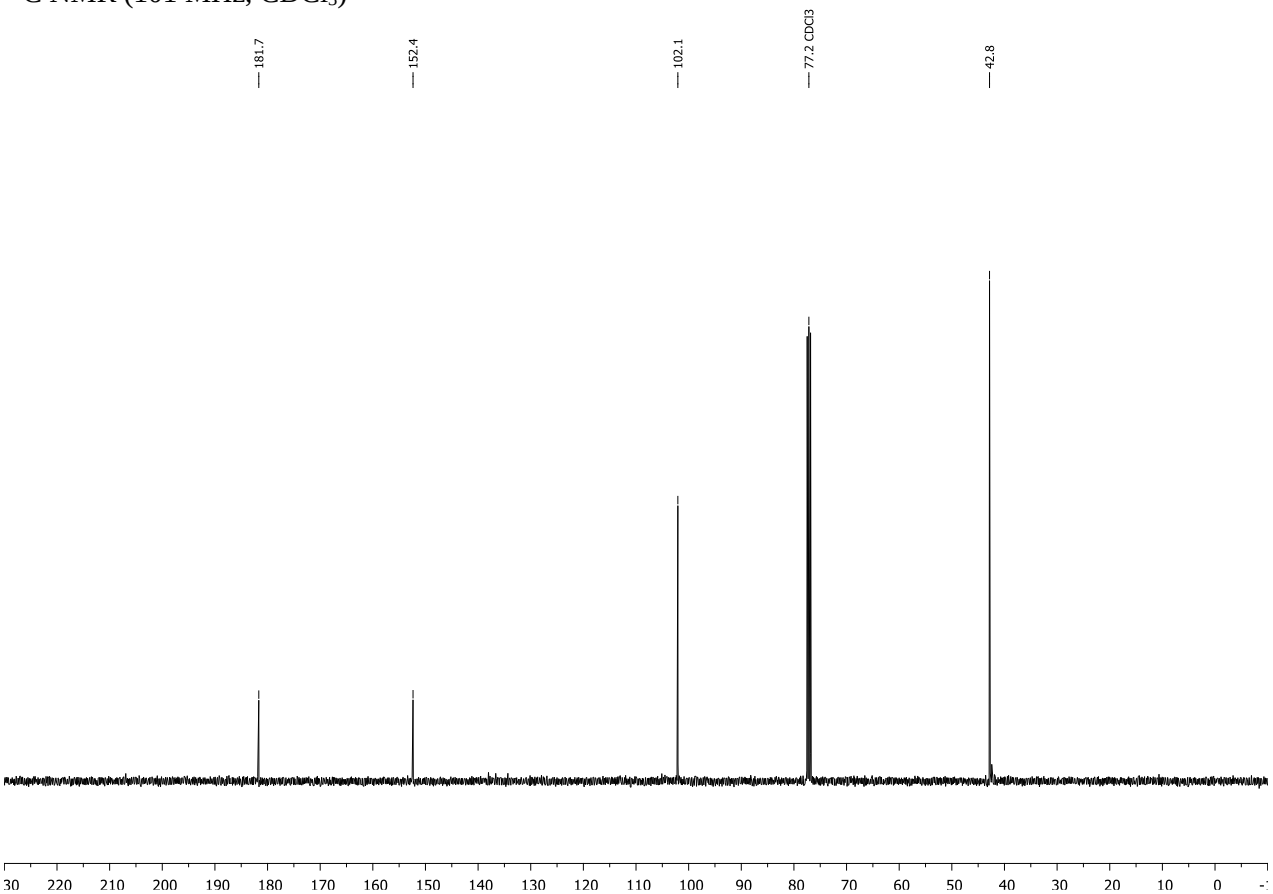


2,5-Bis(dimethylamino)-1,4-benzoquinone (1ac)

^{1}H NMR (400 MHz, $CDCl_3$)

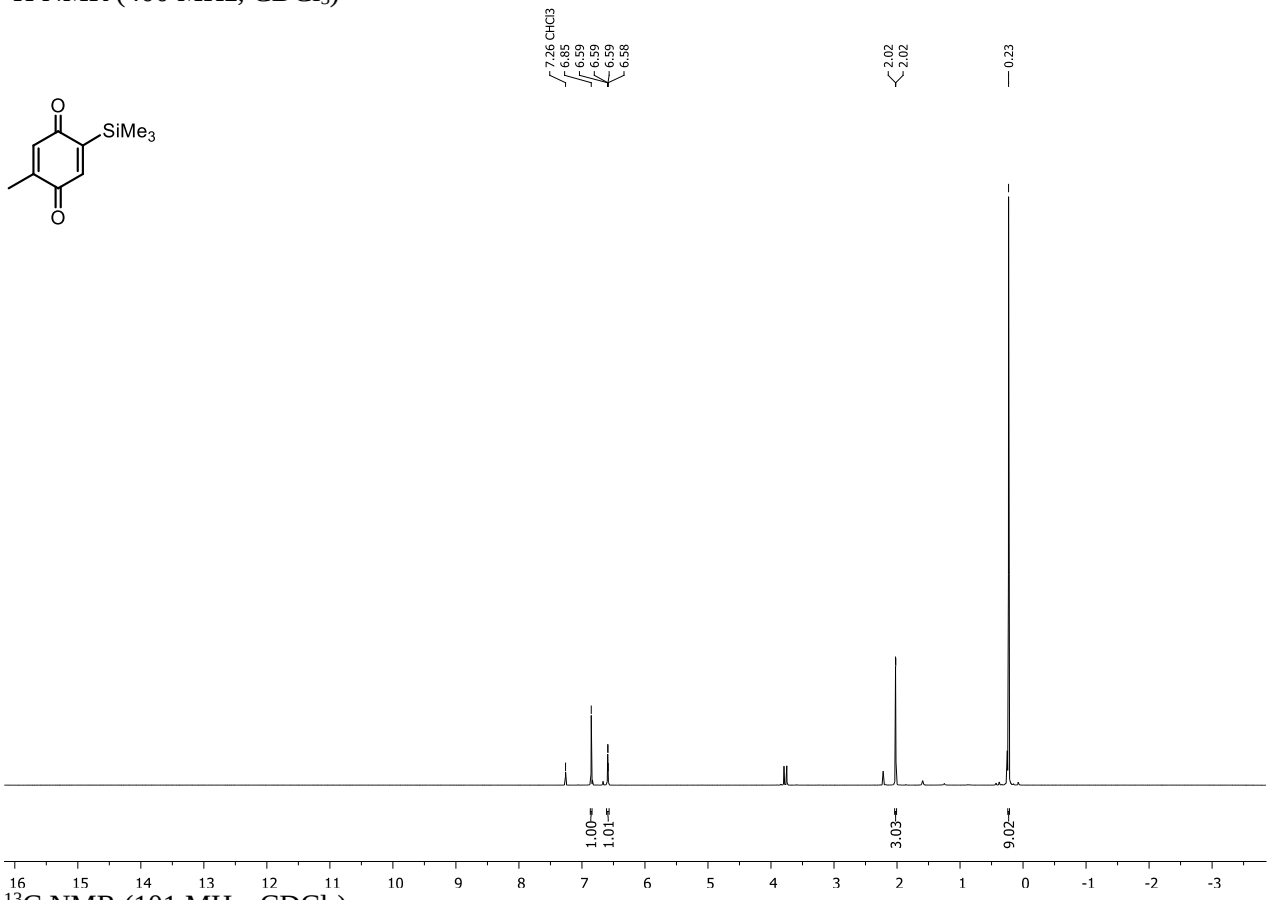


^{13}C NMR (101 MHz, $CDCl_3$)

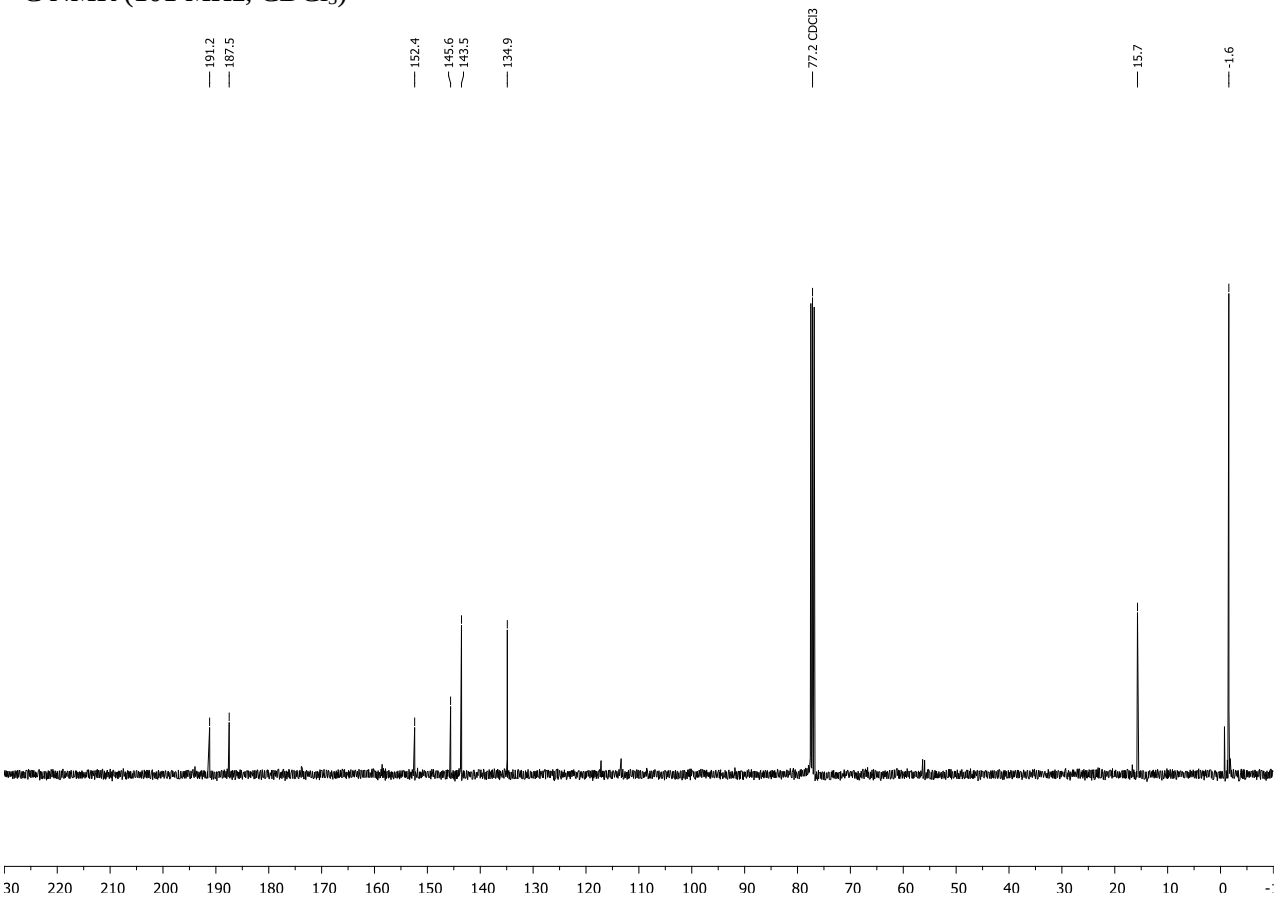


2-Methyl-5-(trimethylsilyl)-1,4-benzoquinone (1ae)

^{1}H NMR (400 MHz, $CDCl_3$)

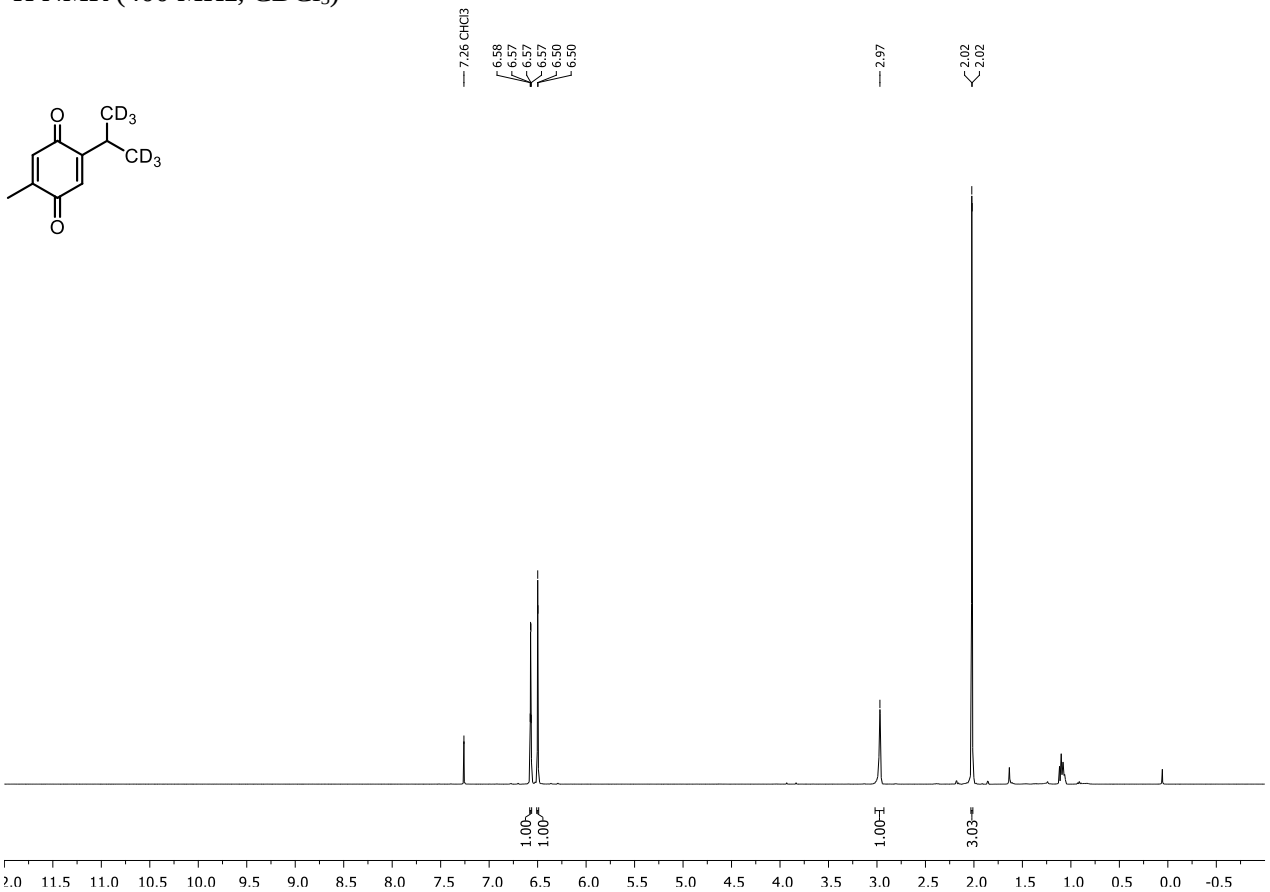


^{13}C NMR (101 MHz, $CDCl_3$)

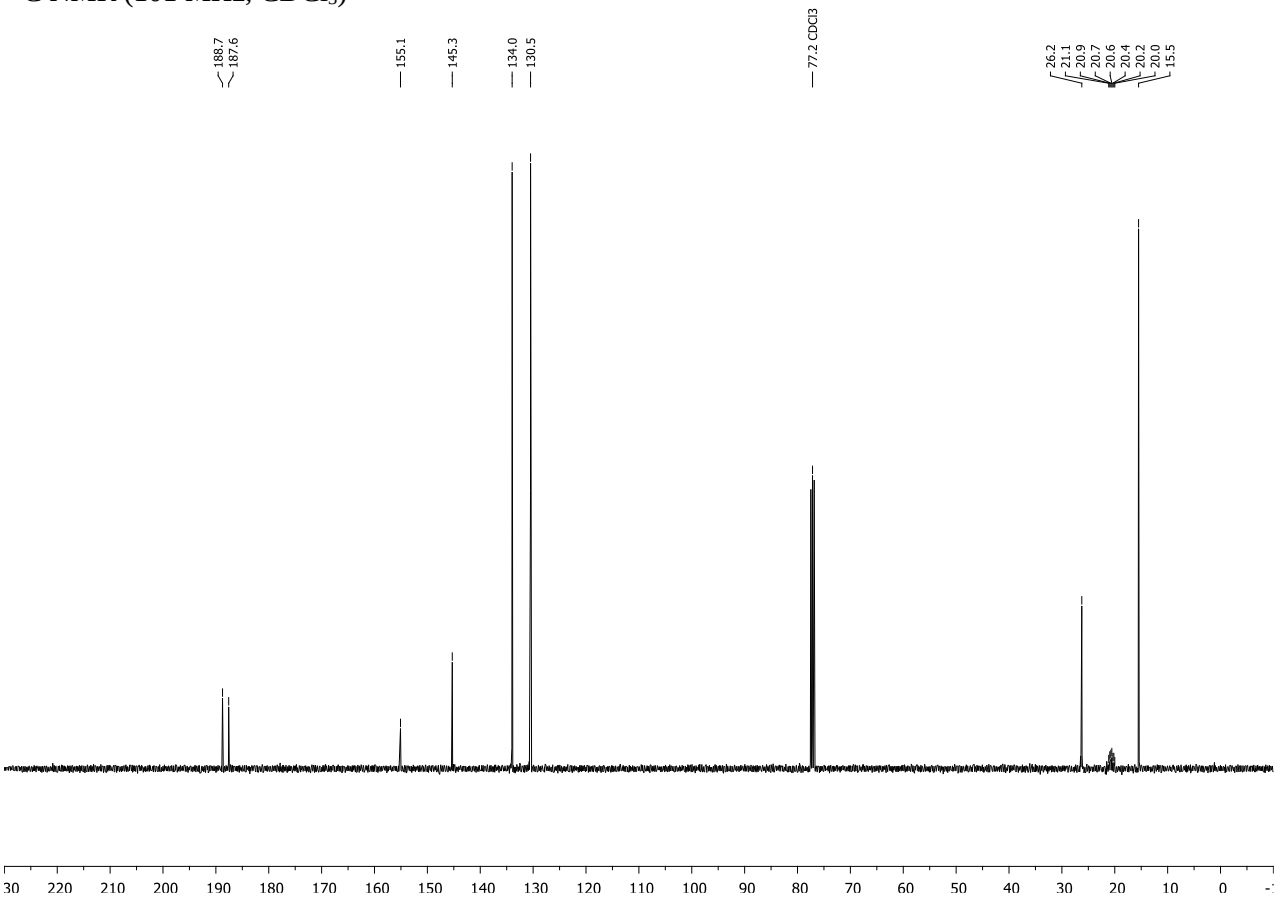


2-Methyl-5-(prop-2-yl-1,1,1,3,3,3-d6)-1,4-benzoquinone (d-1a)

^{1}H NMR (400 MHz, $CDCl_3$)

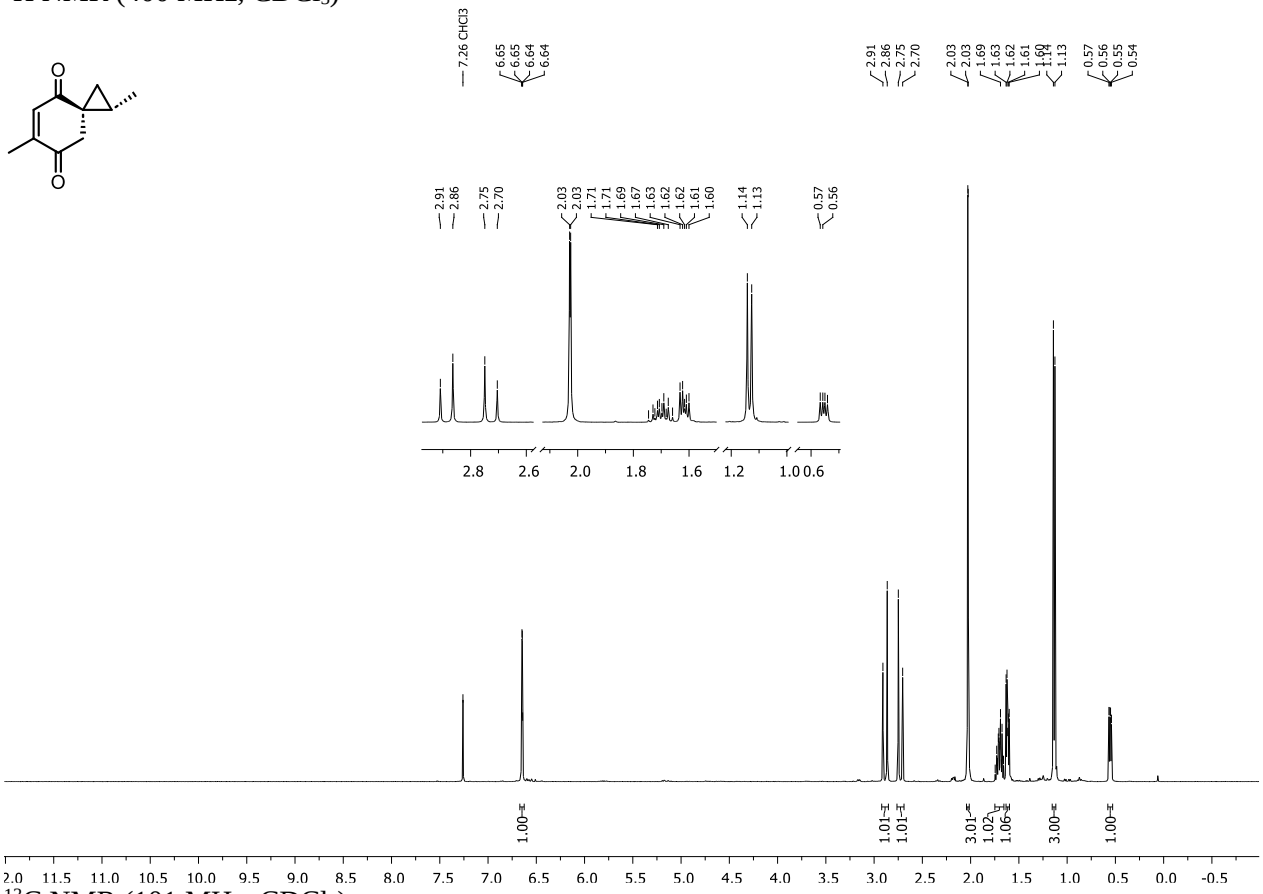


^{13}C NMR (101 MHz, $CDCl_3$)

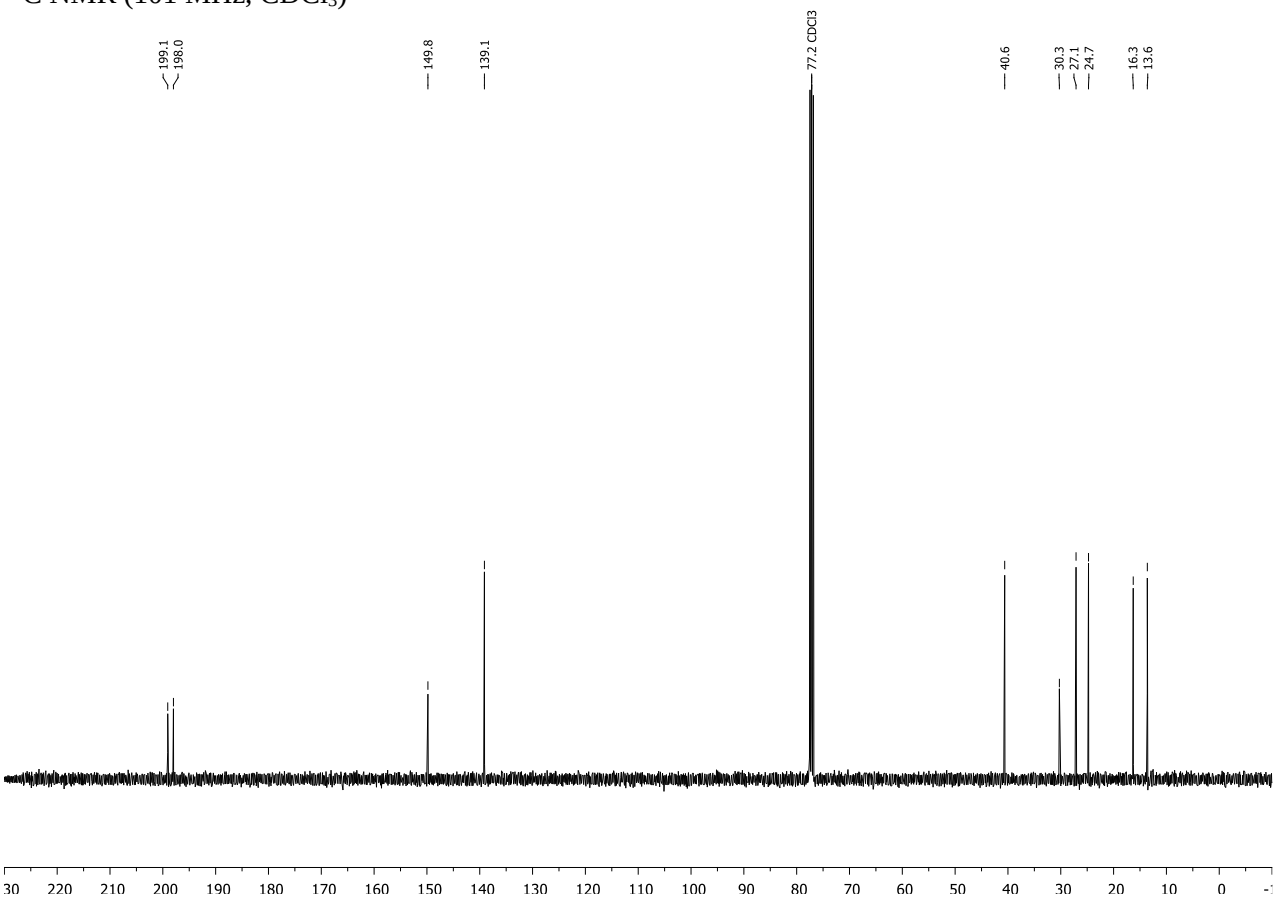


1,6-Dimethylspiro[2.5]oct-5-ene-4,7-dione (2a)

^{1}H NMR (400 MHz, $CDCl_3$)

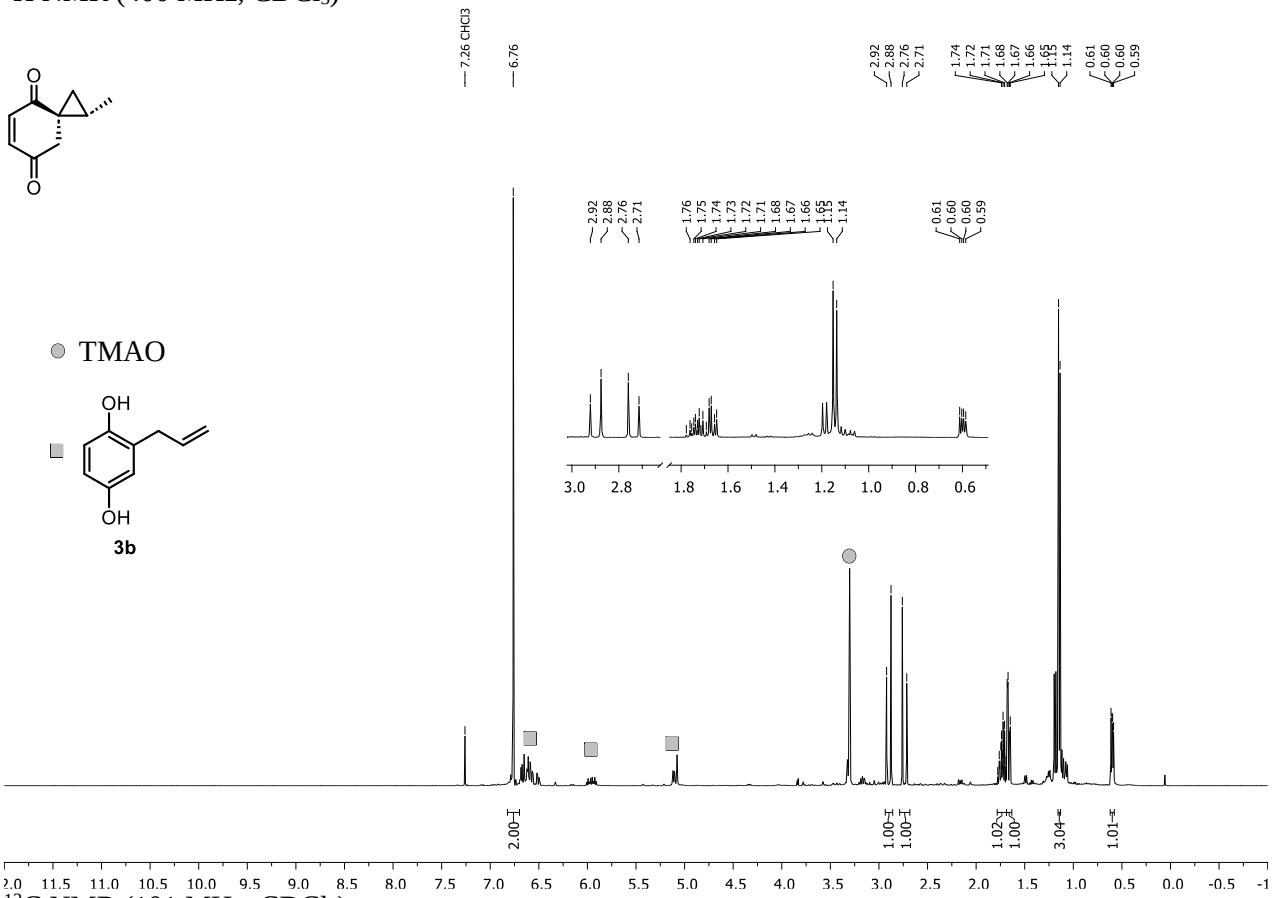


^{13}C NMR (101 MHz, $CDCl_3$)

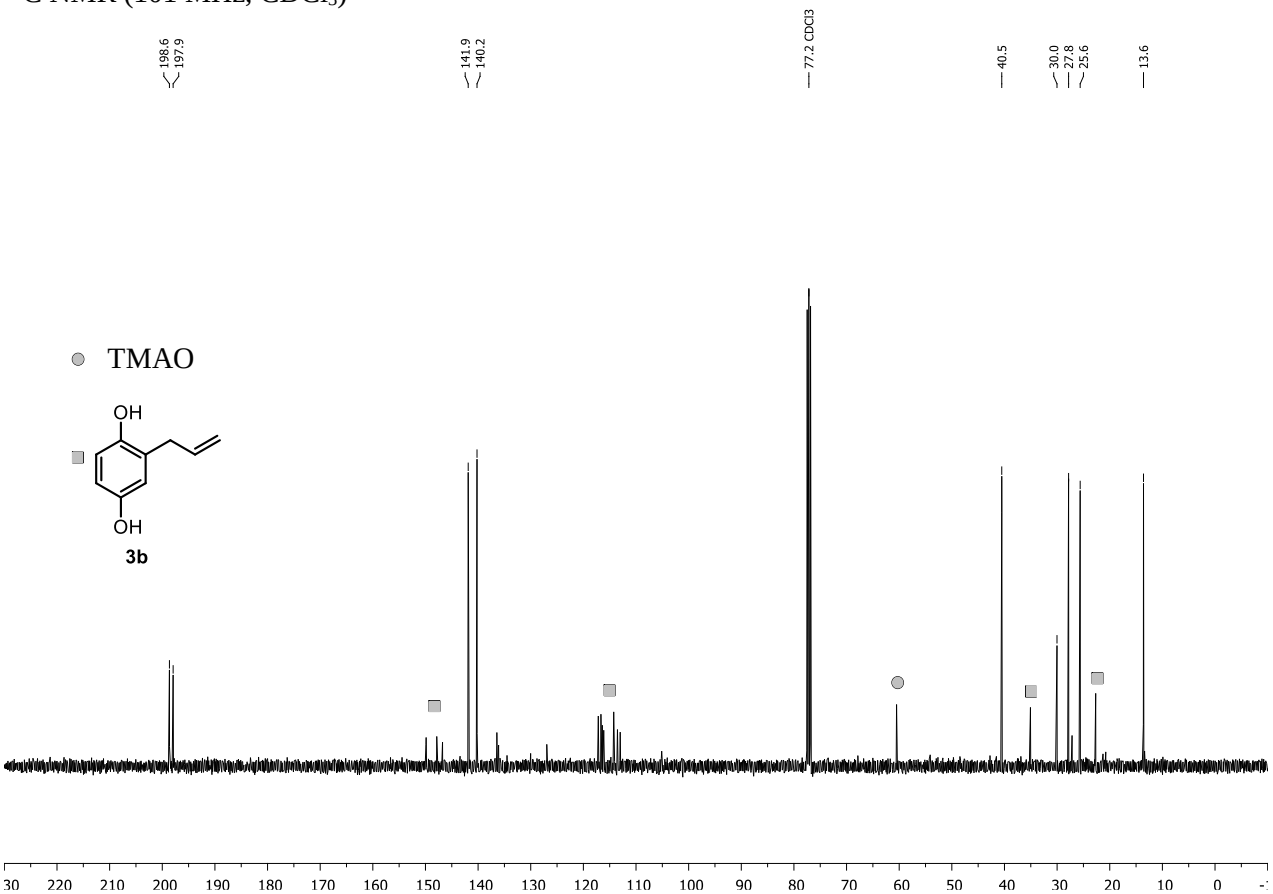


1-Methylspiro[2.5]oct-5-ene-4,7-dione (2b)

^{1}H NMR (400 MHz, $CDCl_3$)

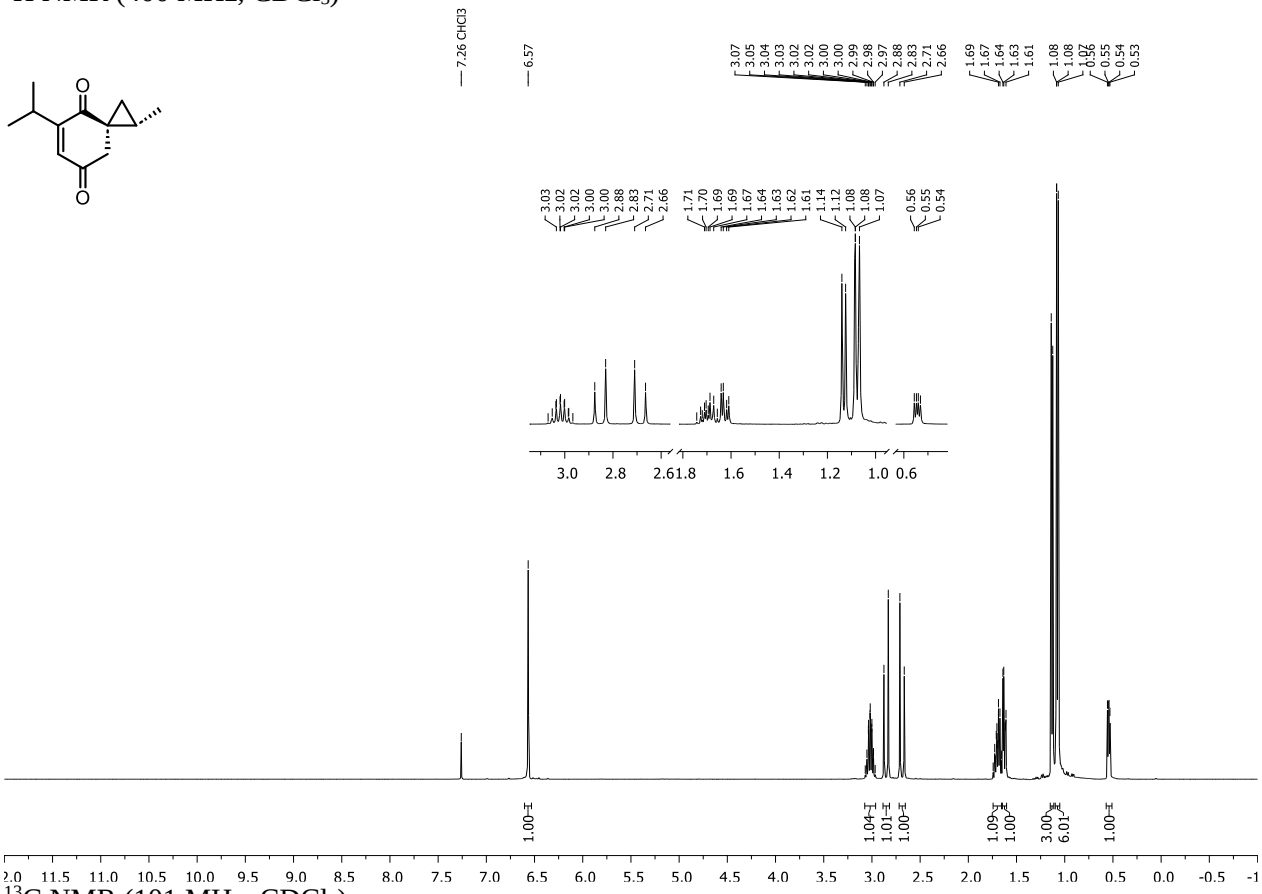


^{13}C NMR (101 MHz, $CDCl_3$)

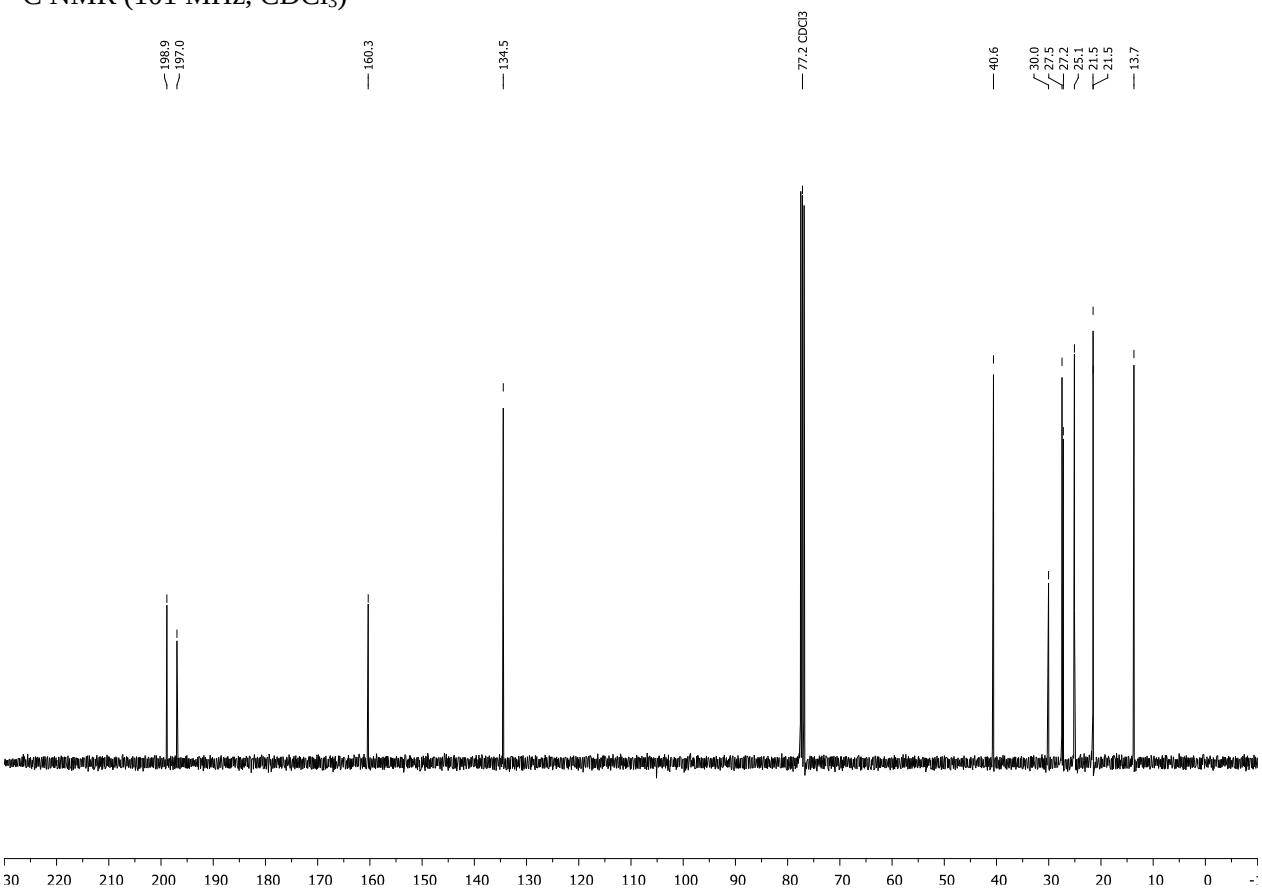


5-Isopropyl-1-methylspiro[2.5]oct-5-ene-4,7-dione (2c)

^{1}H NMR (400 MHz, $CDCl_3$)

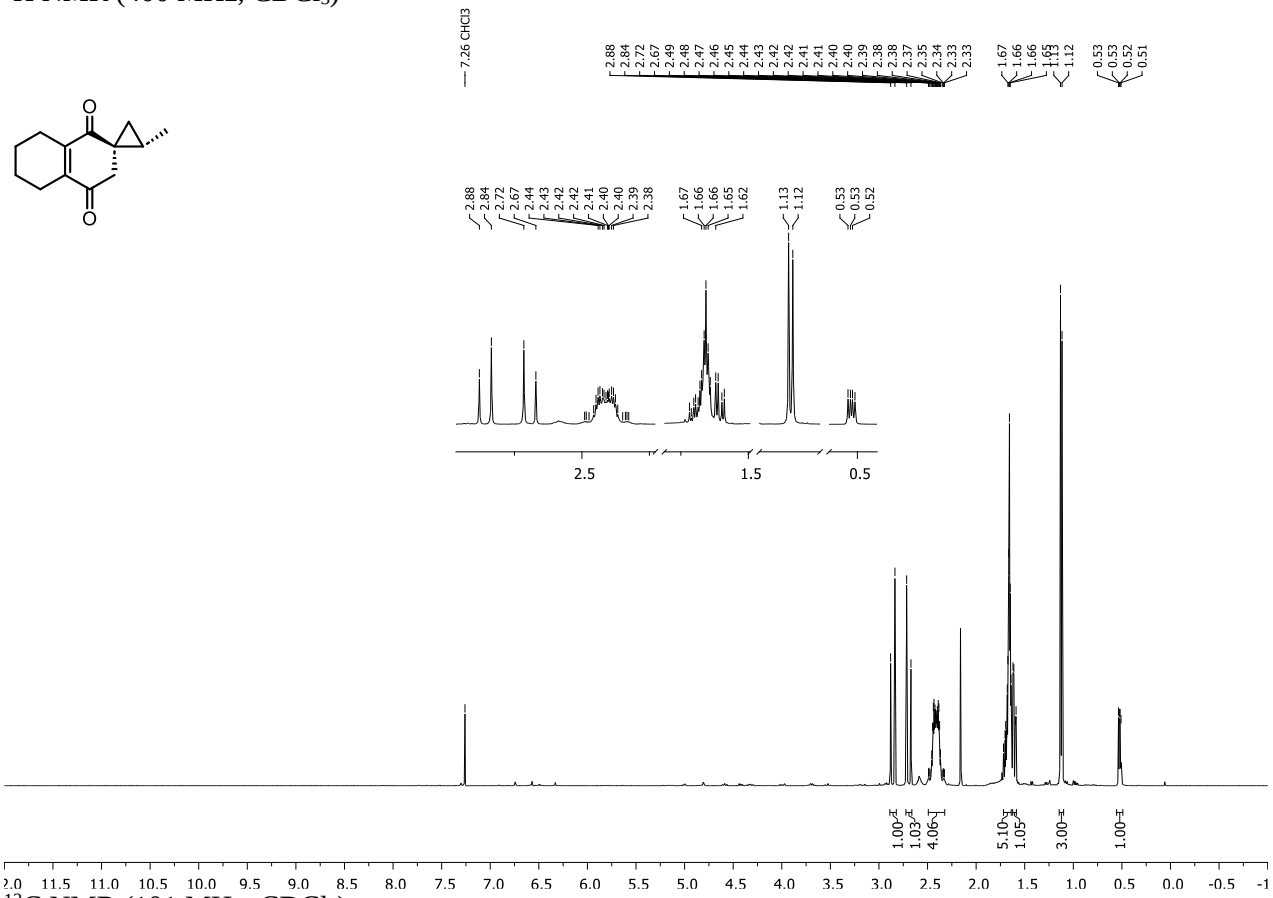


^{13}C NMR (101 MHz, $CDCl_3$)

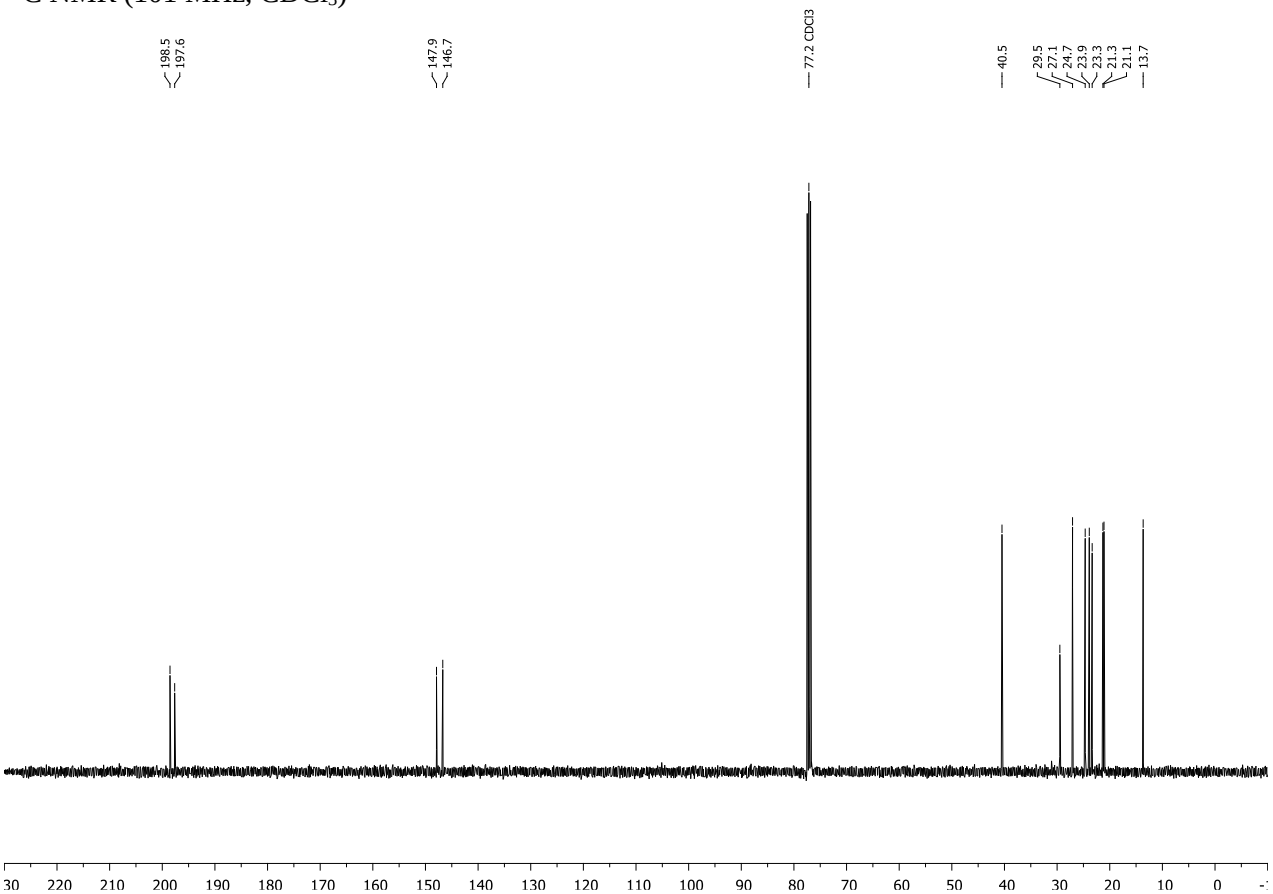


2-Methyl-5',6',7',8'-tetrahydro-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2d)

^{1}H NMR (400 MHz, $CDCl_3$)

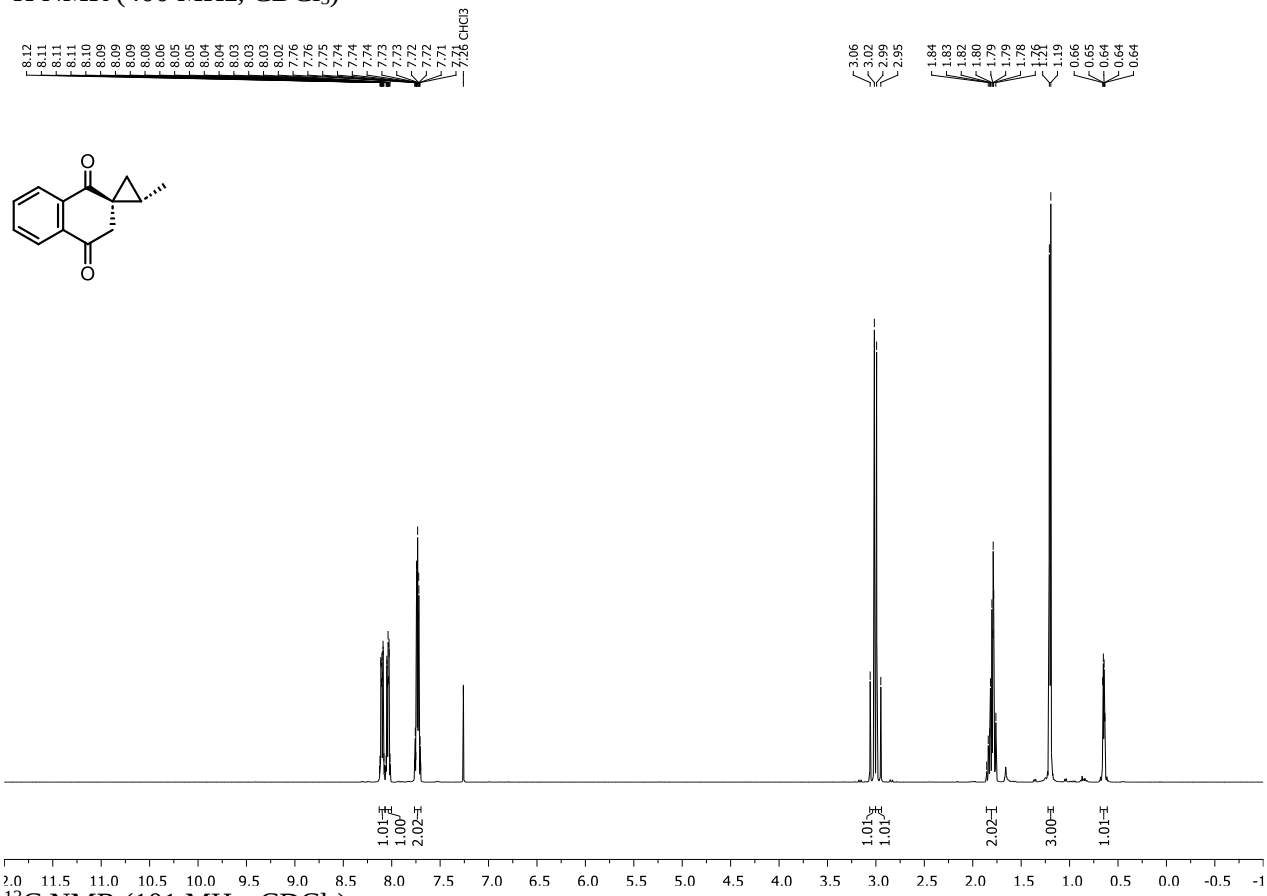


^{13}C NMR (101 MHz, $CDCl_3$)

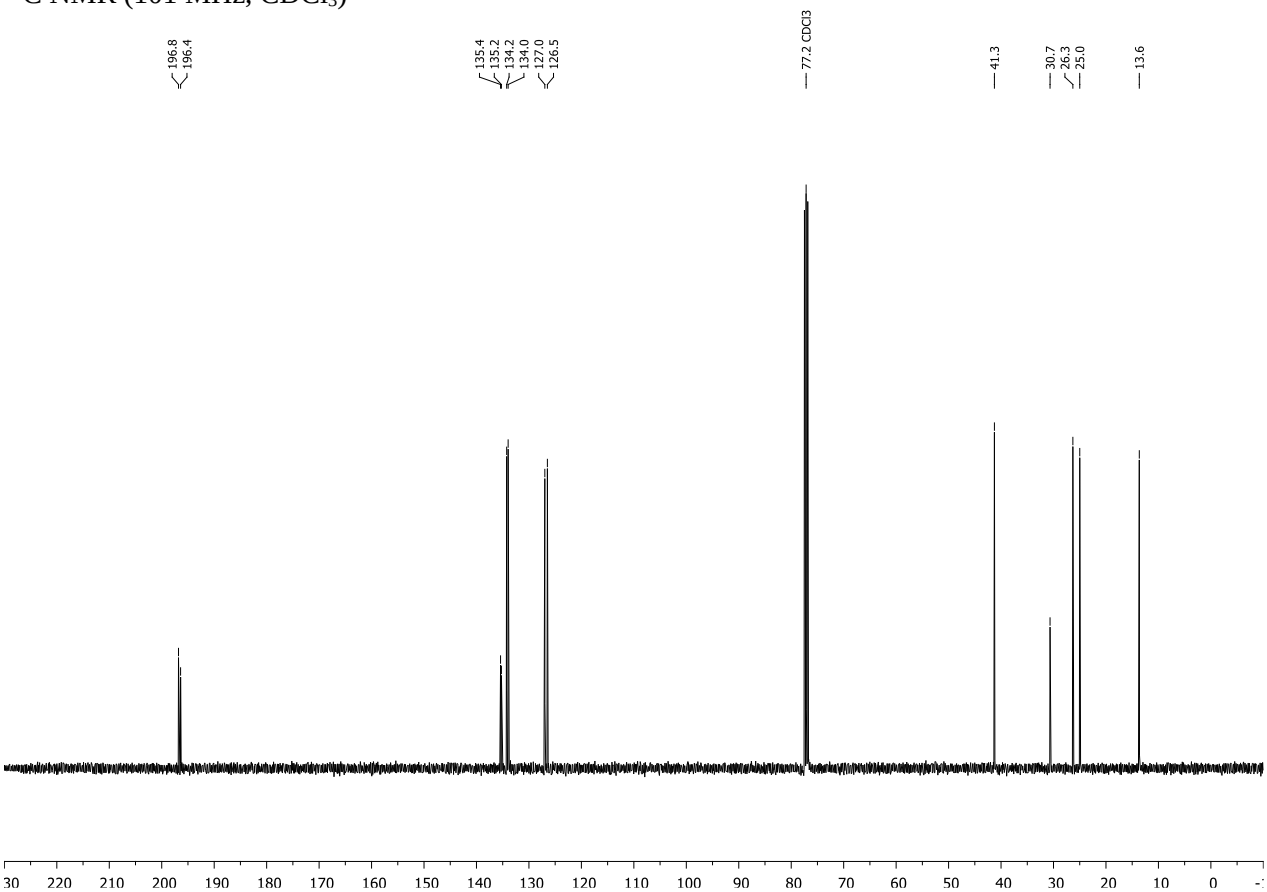


2-Methyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2e)

^{1}H NMR (400 MHz, $CDCl_3$)

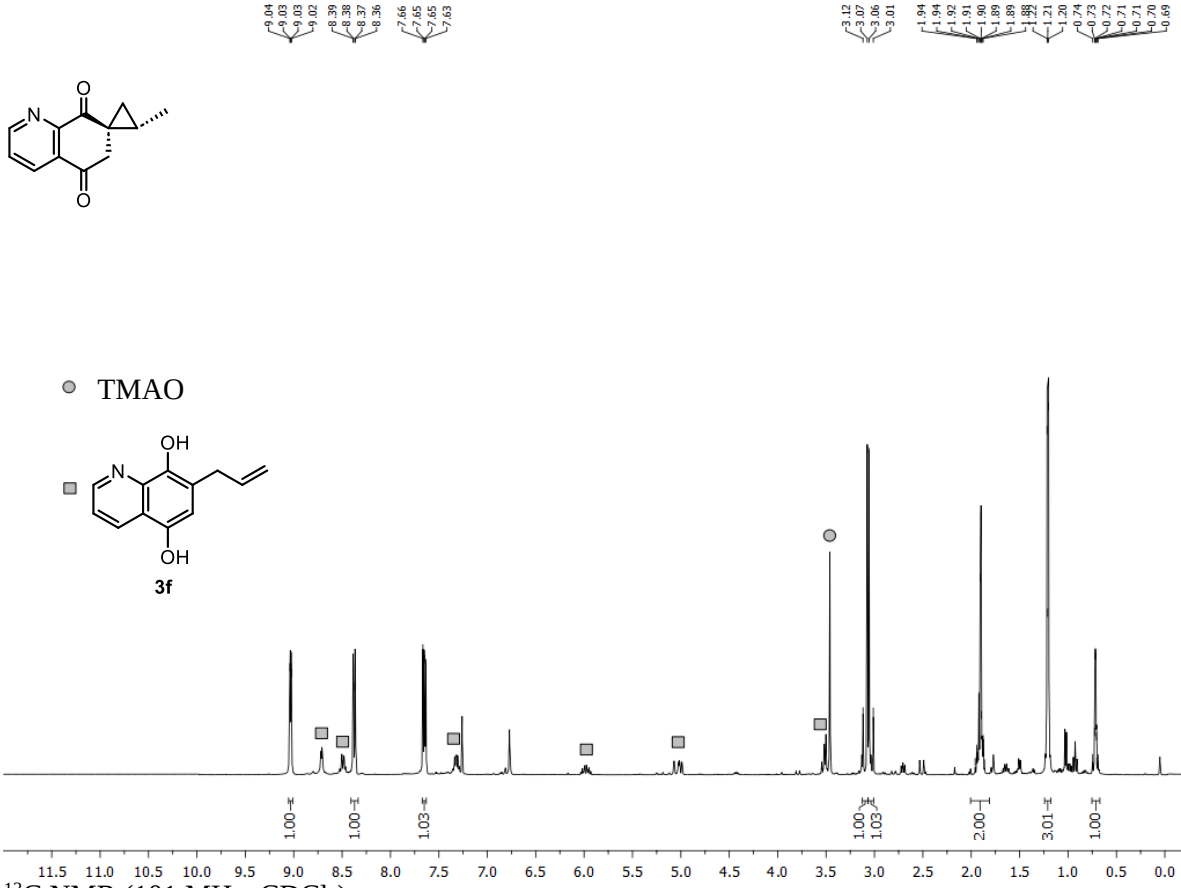


^{13}C NMR (101 MHz, $CDCl_3$)

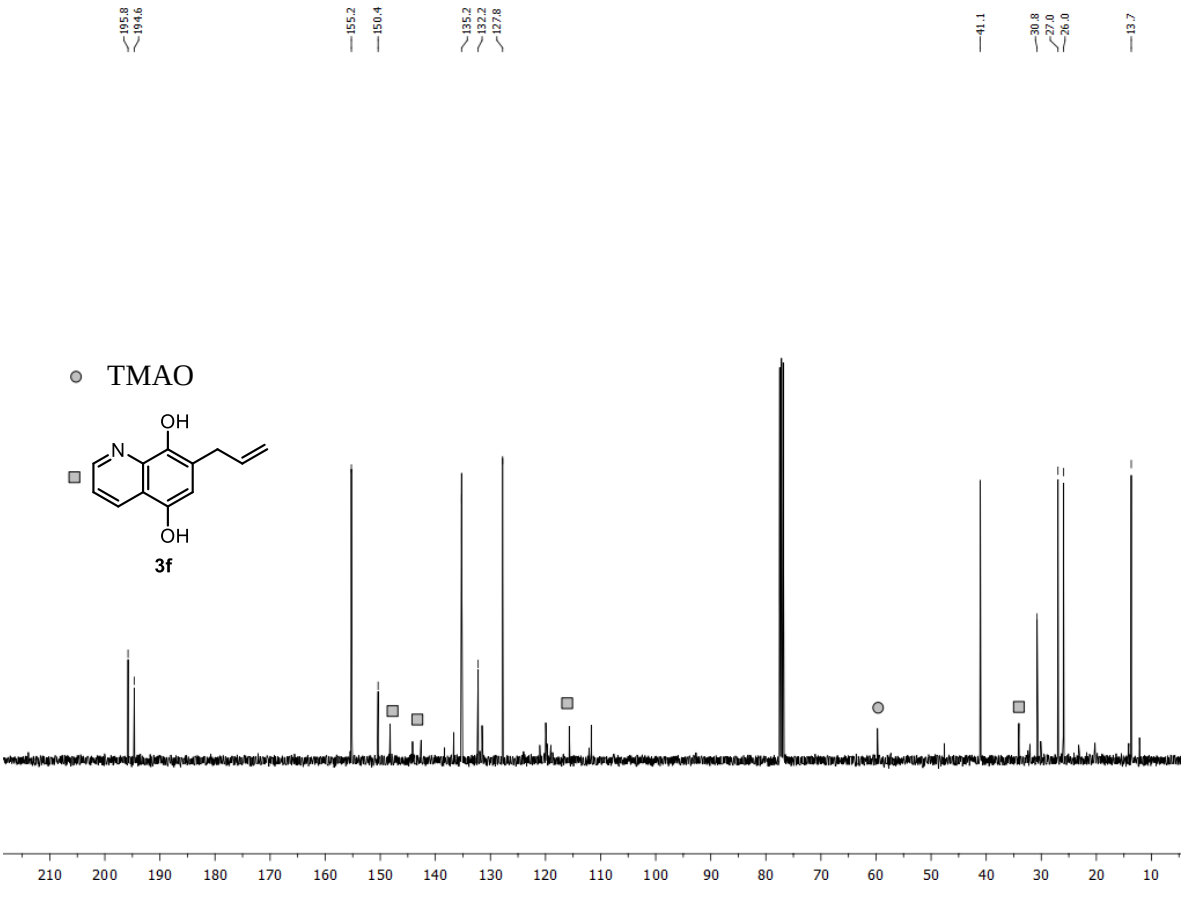


2-Methyl-6'*H*-spiro[cyclopropane-1,7'-quinoline]-5',8'-dione (2f)

^{1}H NMR (400 MHz, $CDCl_3$)

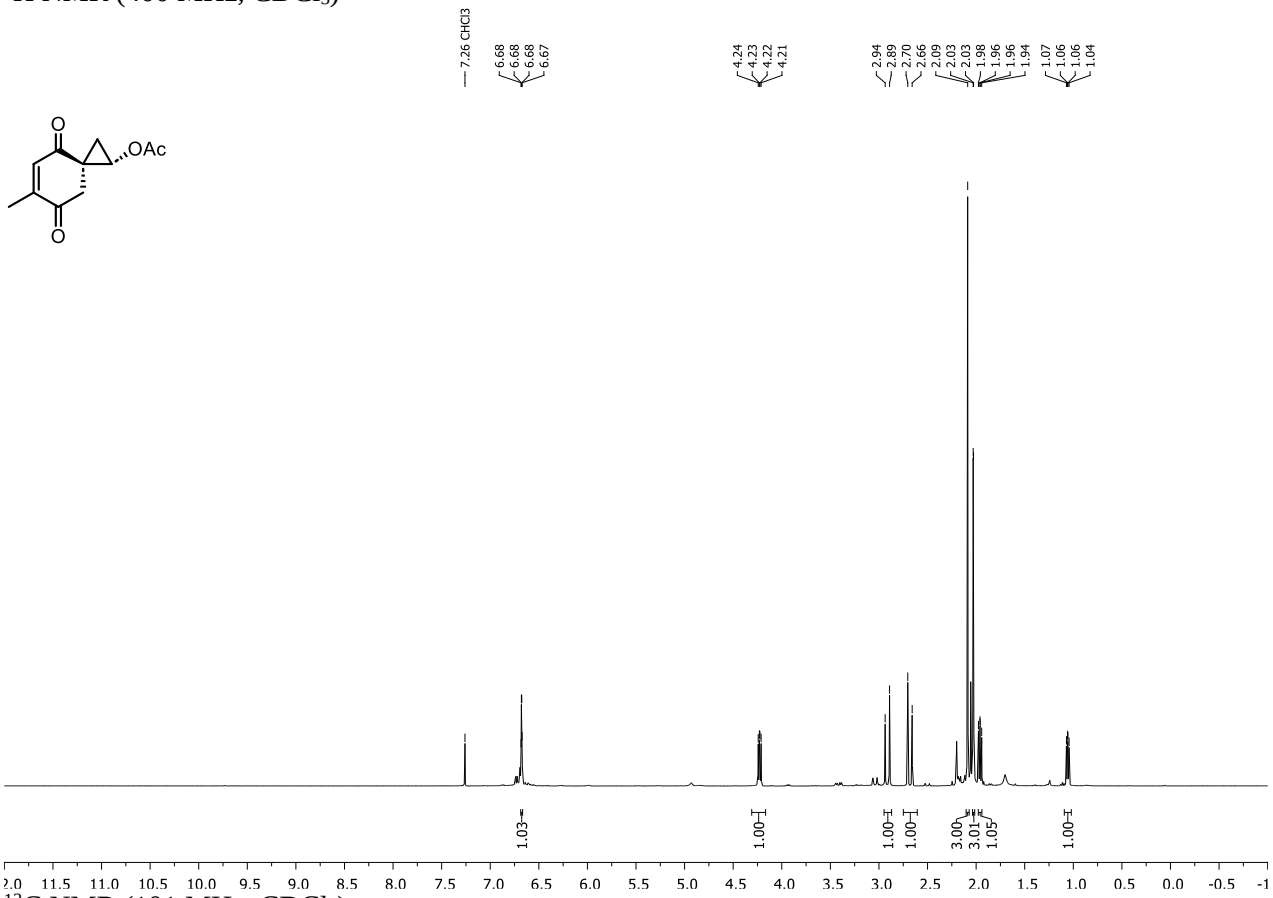


^{13}C NMR (101 MHz, $CDCl_3$)

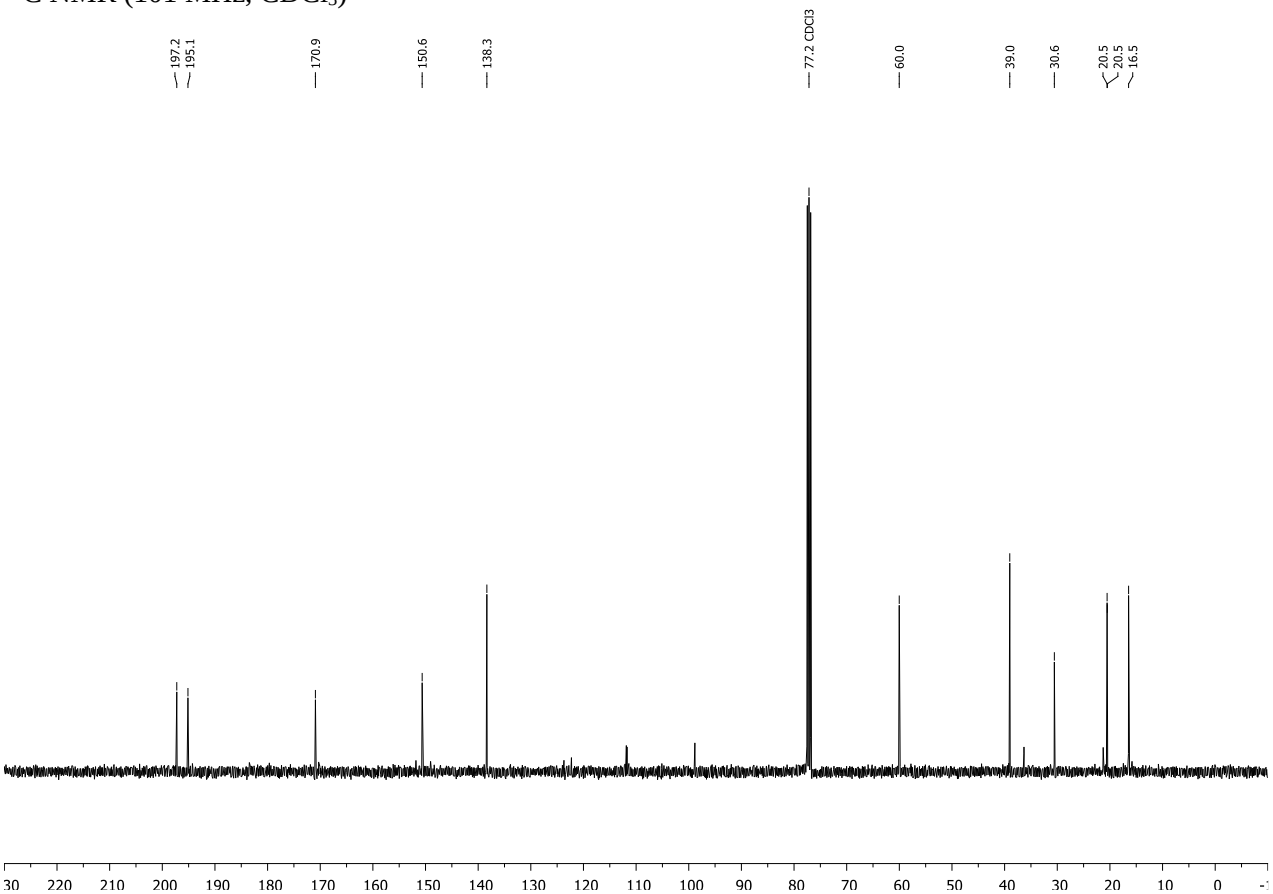


6-Methyl-4,7-dioxospiro[2.5]oct-5-en-1-yl acetate (2g)

^{1}H NMR (400 MHz, $CDCl_3$)

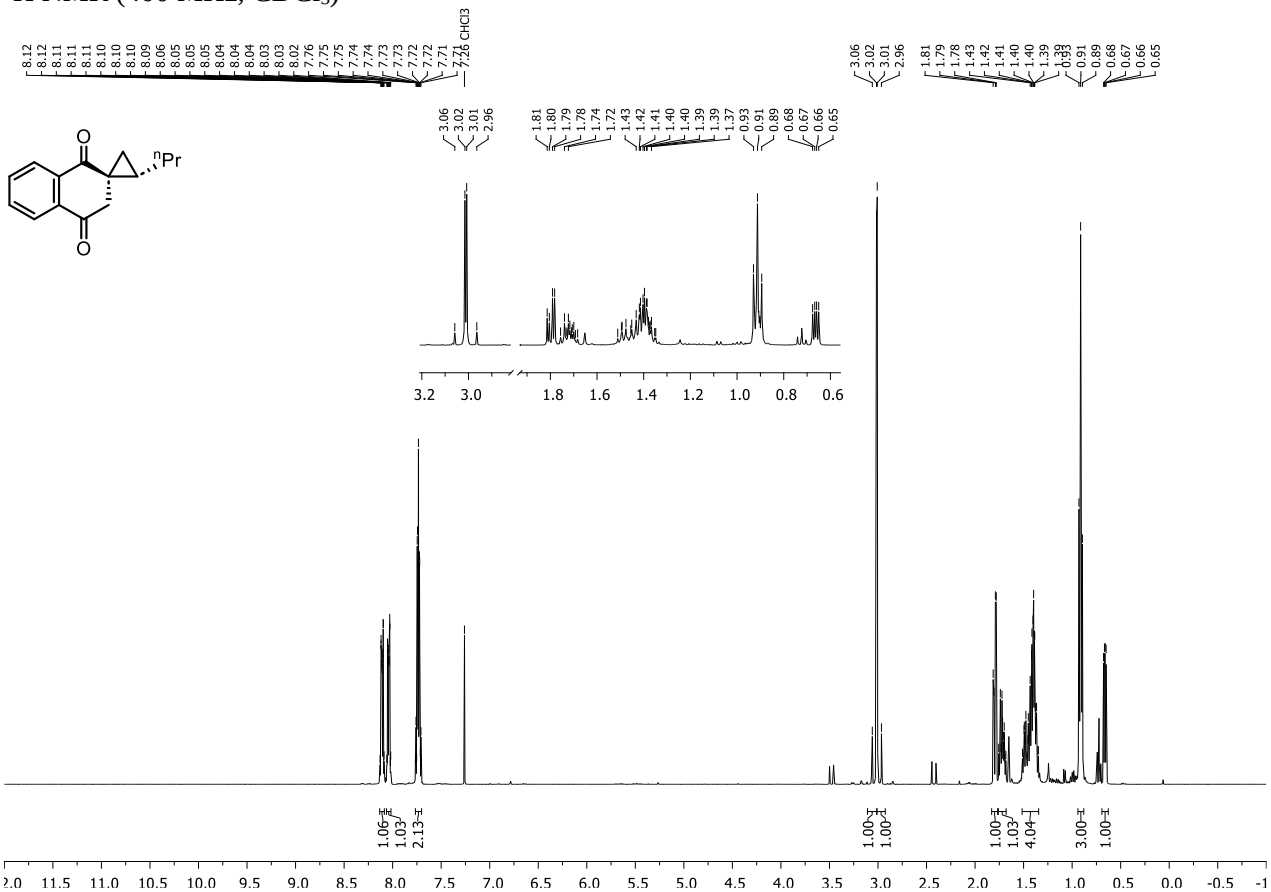


^{13}C NMR (101 MHz, $CDCl_3$)

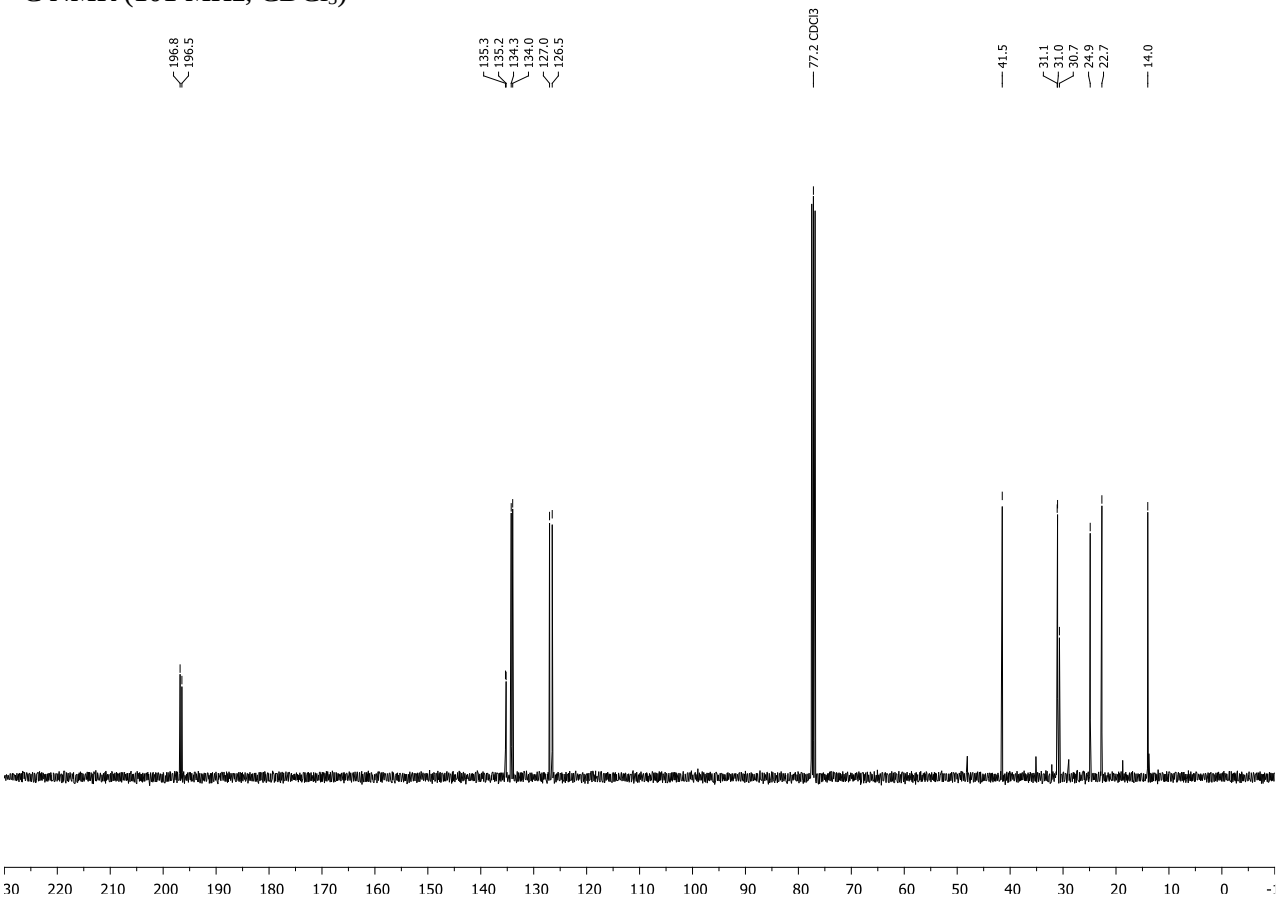


2-Propyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2h)

^{1}H NMR (400 MHz, $CDCl_3$)

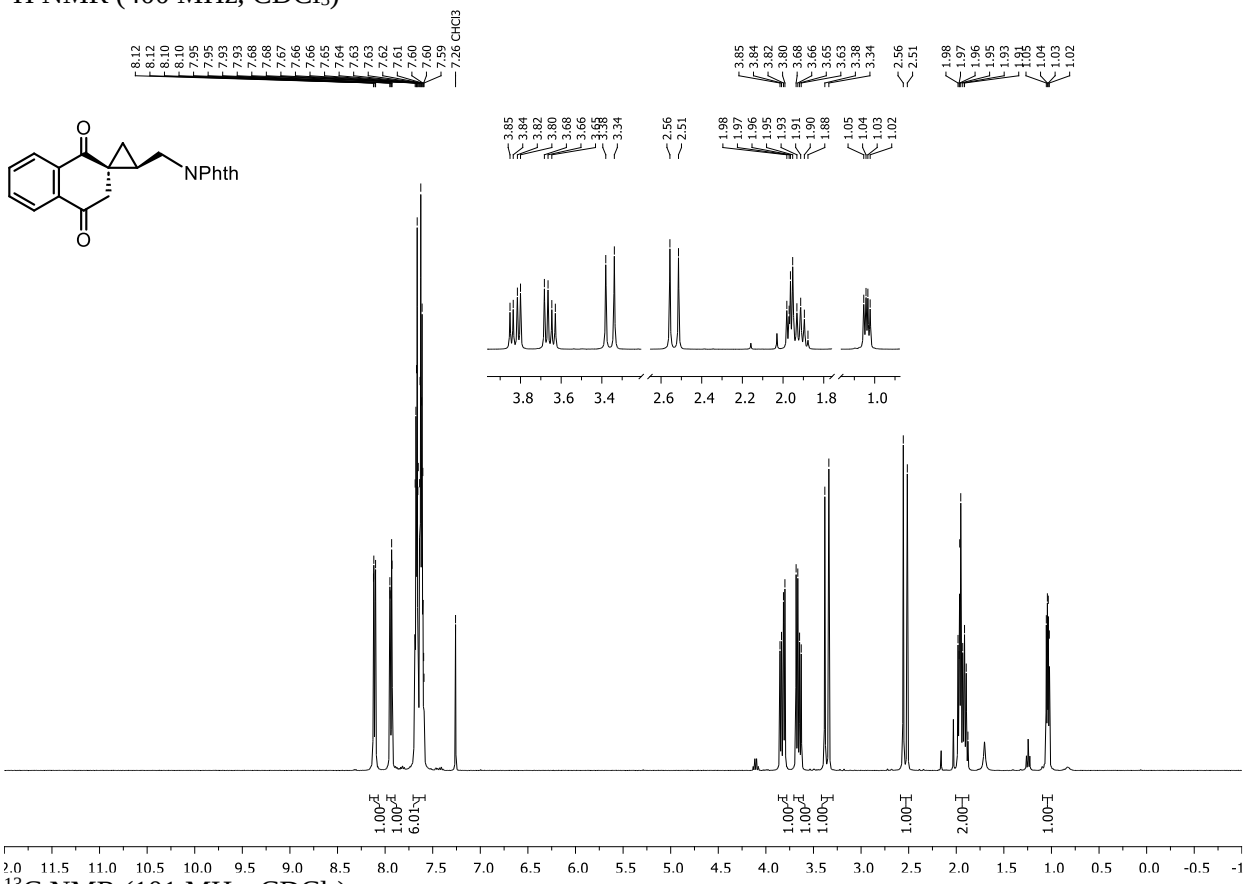


^{13}C NMR (101 MHz, $CDCl_3$)

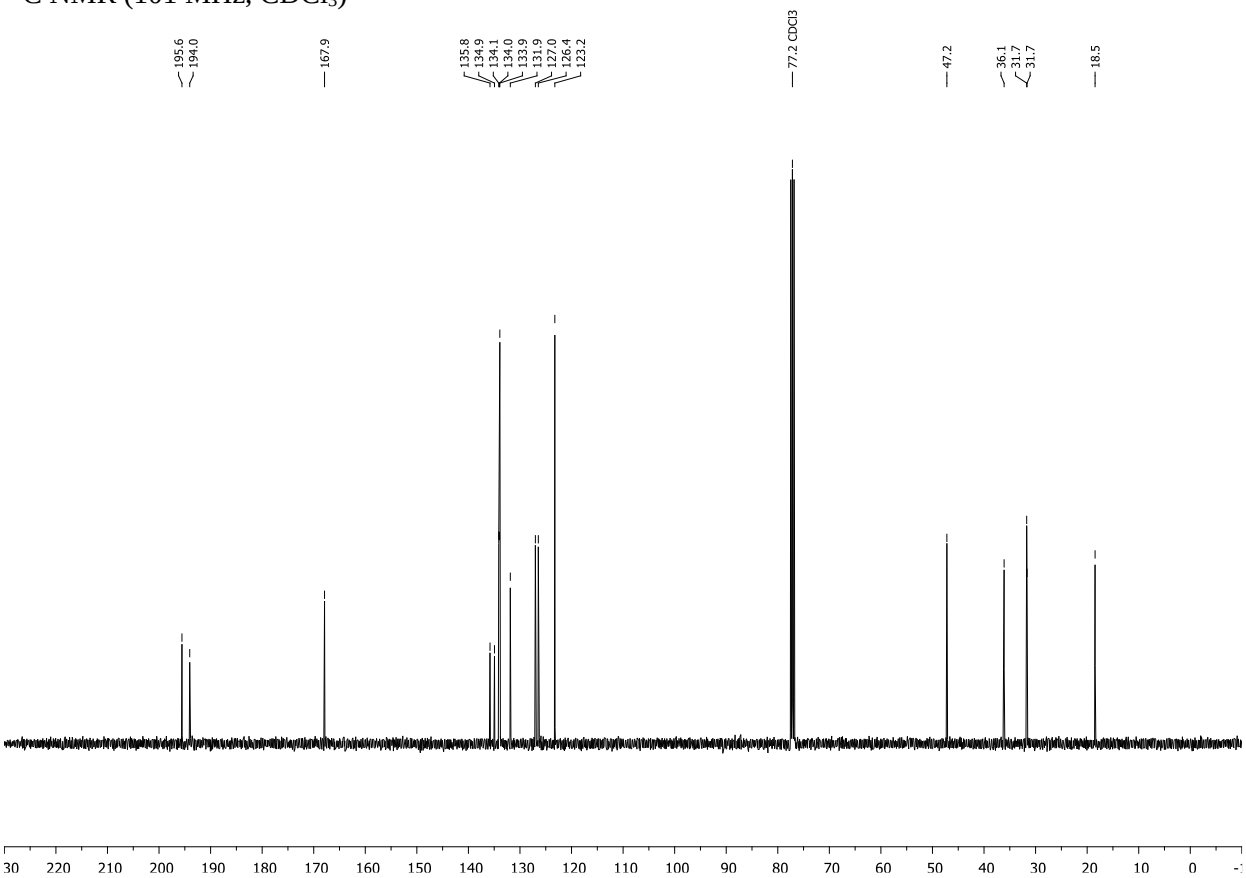


2-((1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)methyl)isoindoline-1,3-dione (2i)

^{1}H NMR (400 MHz, $CDCl_3$)

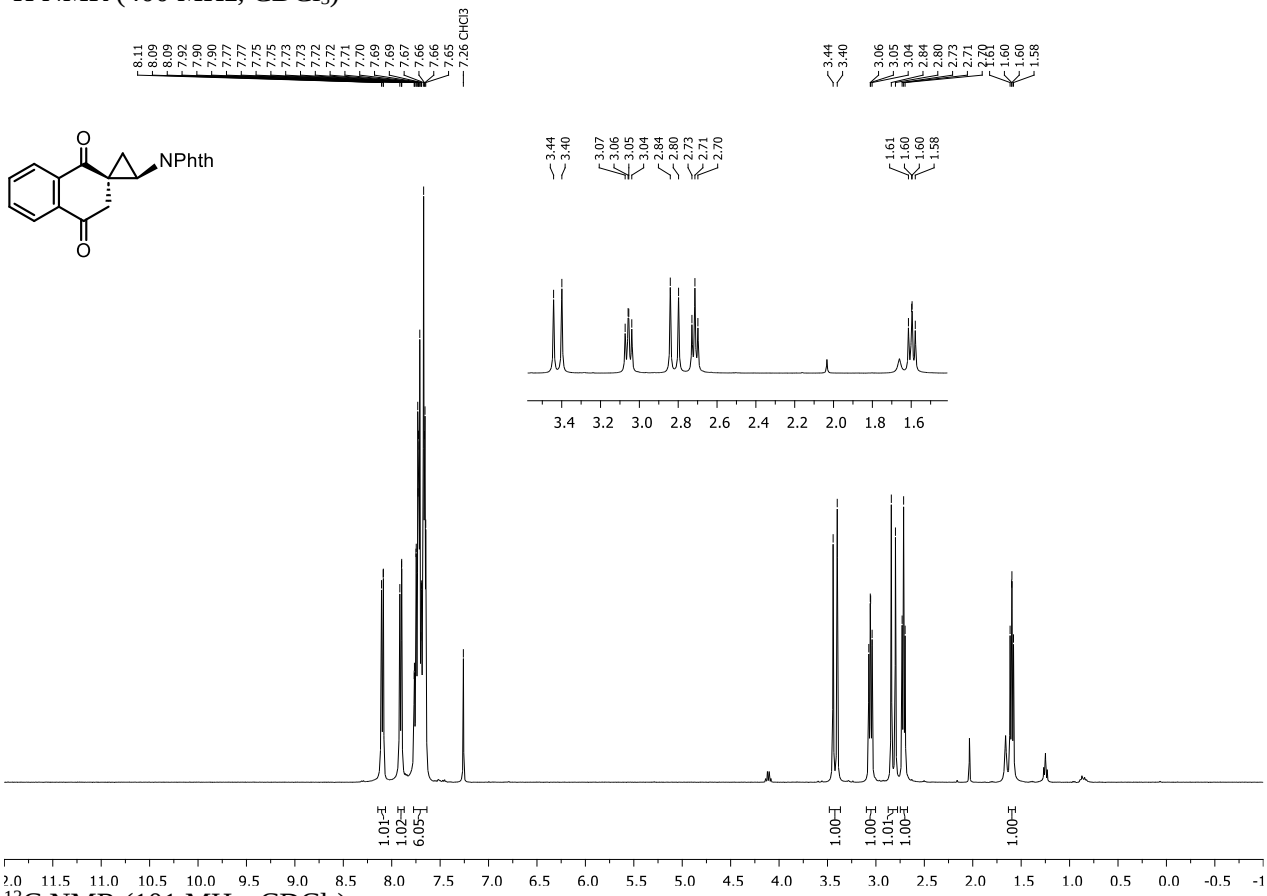


^{13}C NMR (101 MHz, $CDCl_3$)

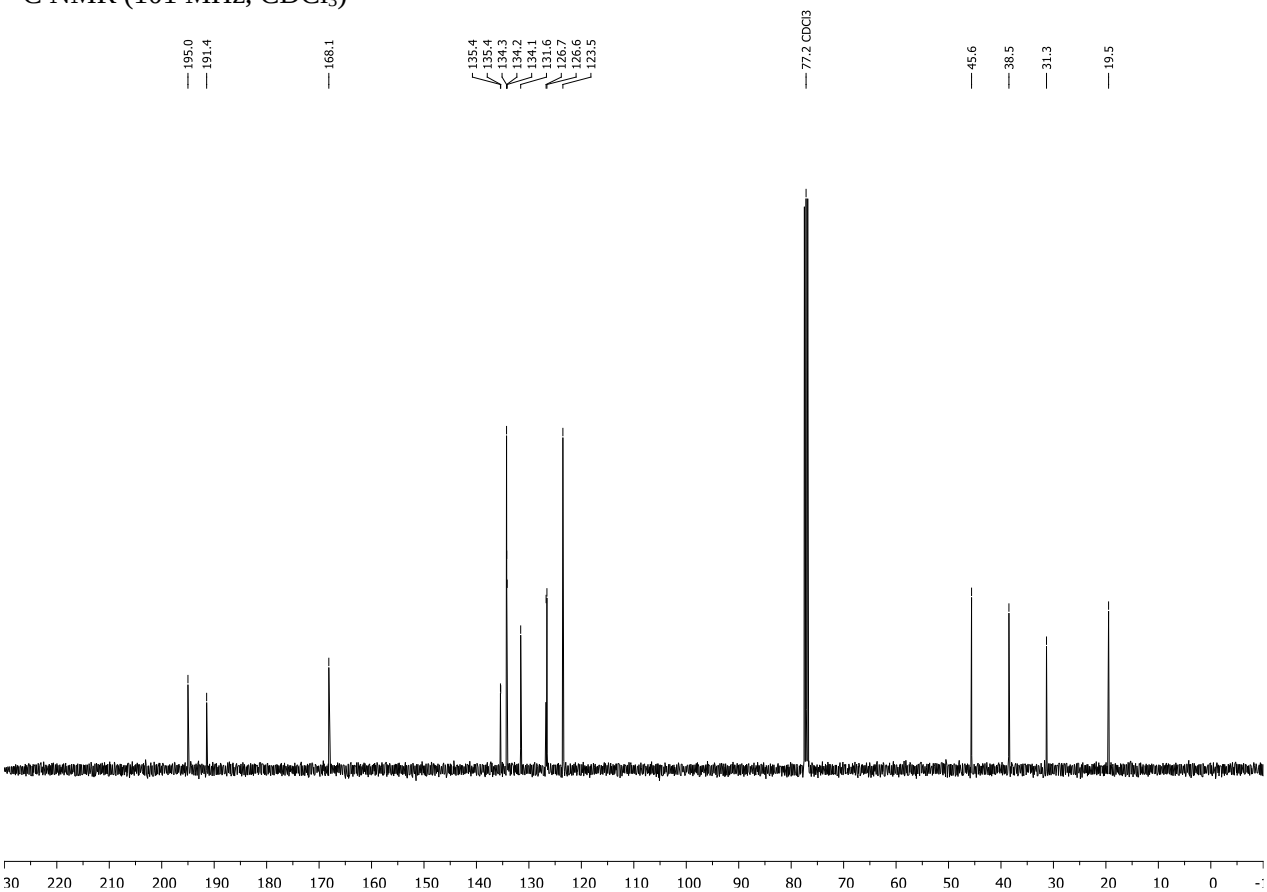


1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)isoindoline-1,3-dione (2j)

^{1}H NMR (400 MHz, $CDCl_3$)

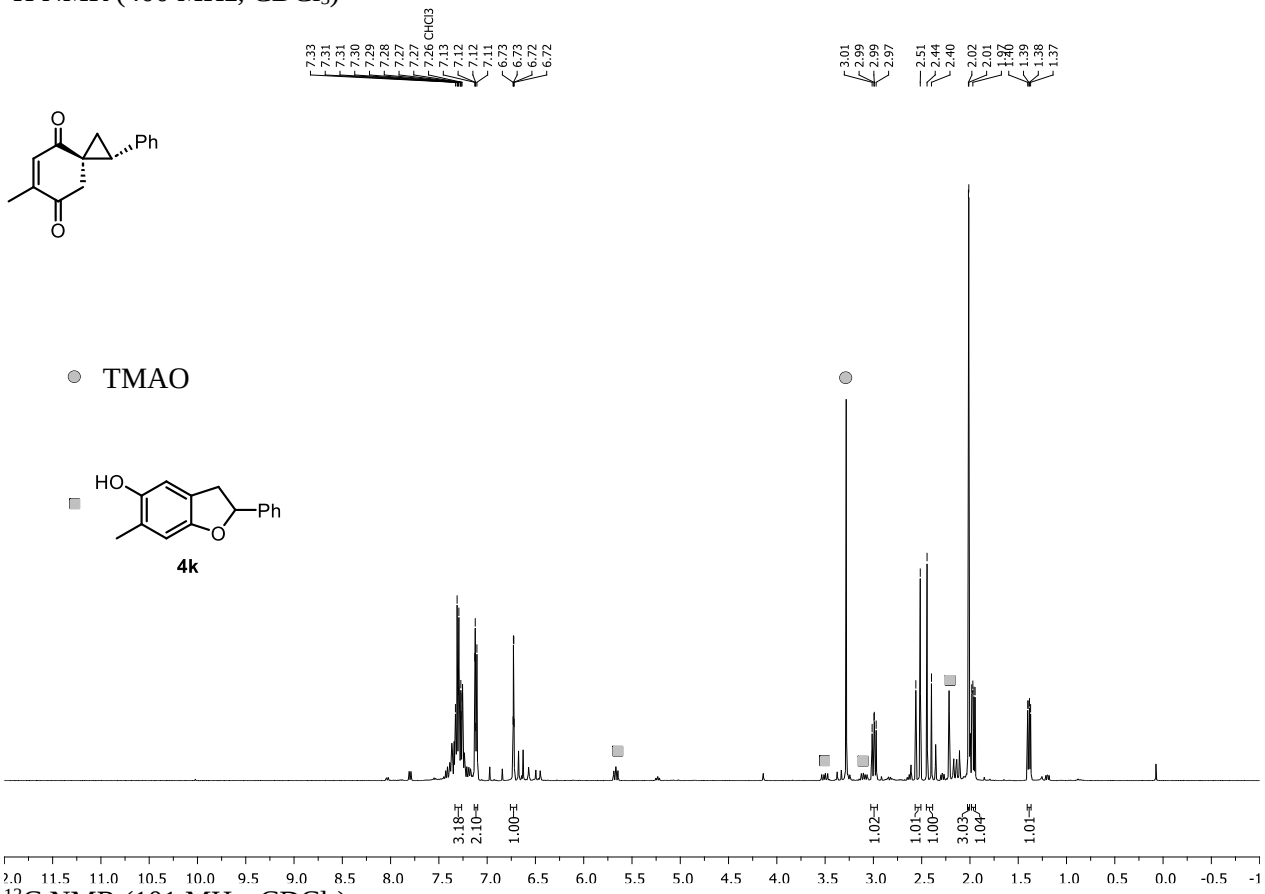


^{13}C NMR (101 MHz, $CDCl_3$)

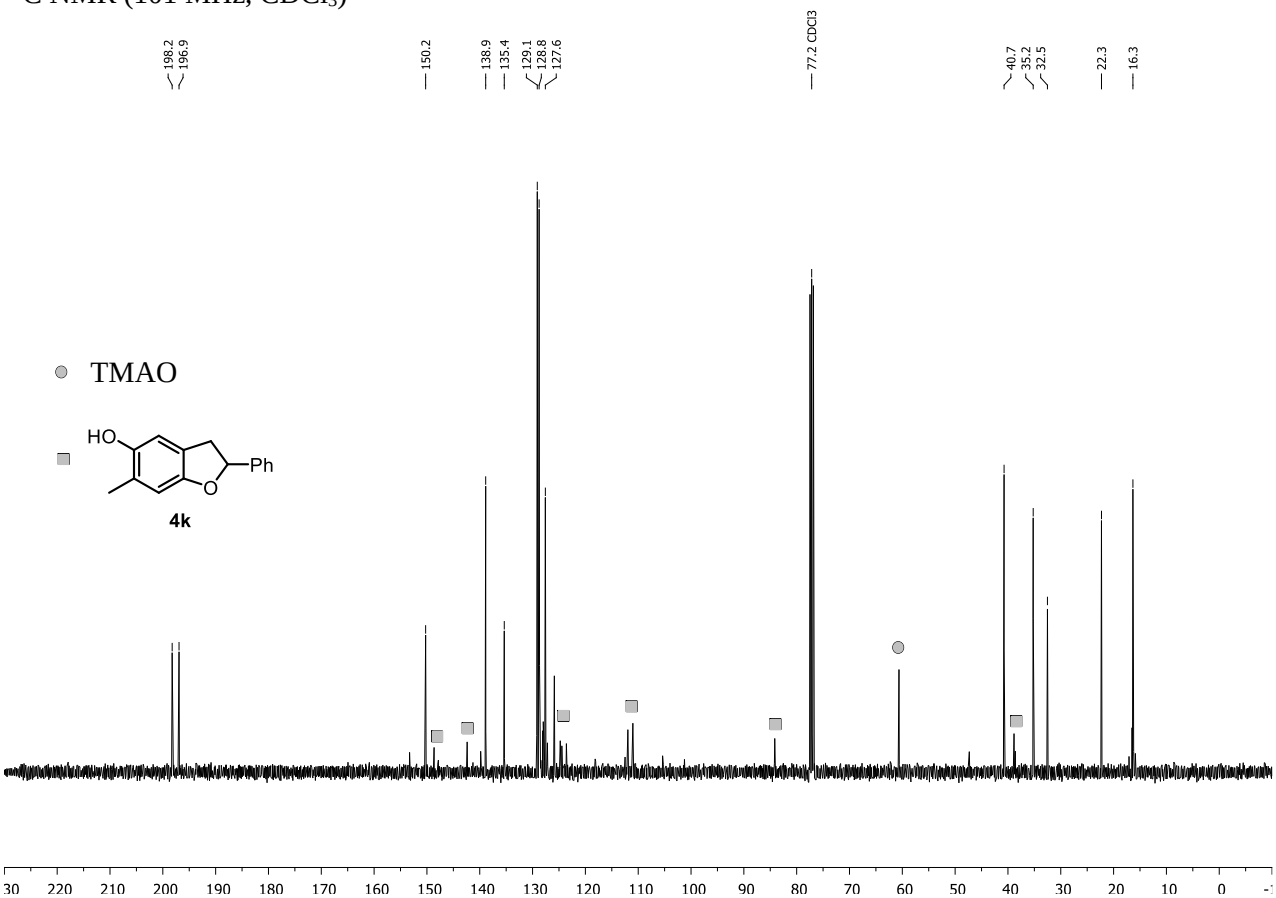


6-Methyl-1-phenylspiro[2.5]oct-5-ene-4,7-dione (2k)

^{1}H NMR (400 MHz, $CDCl_3$)

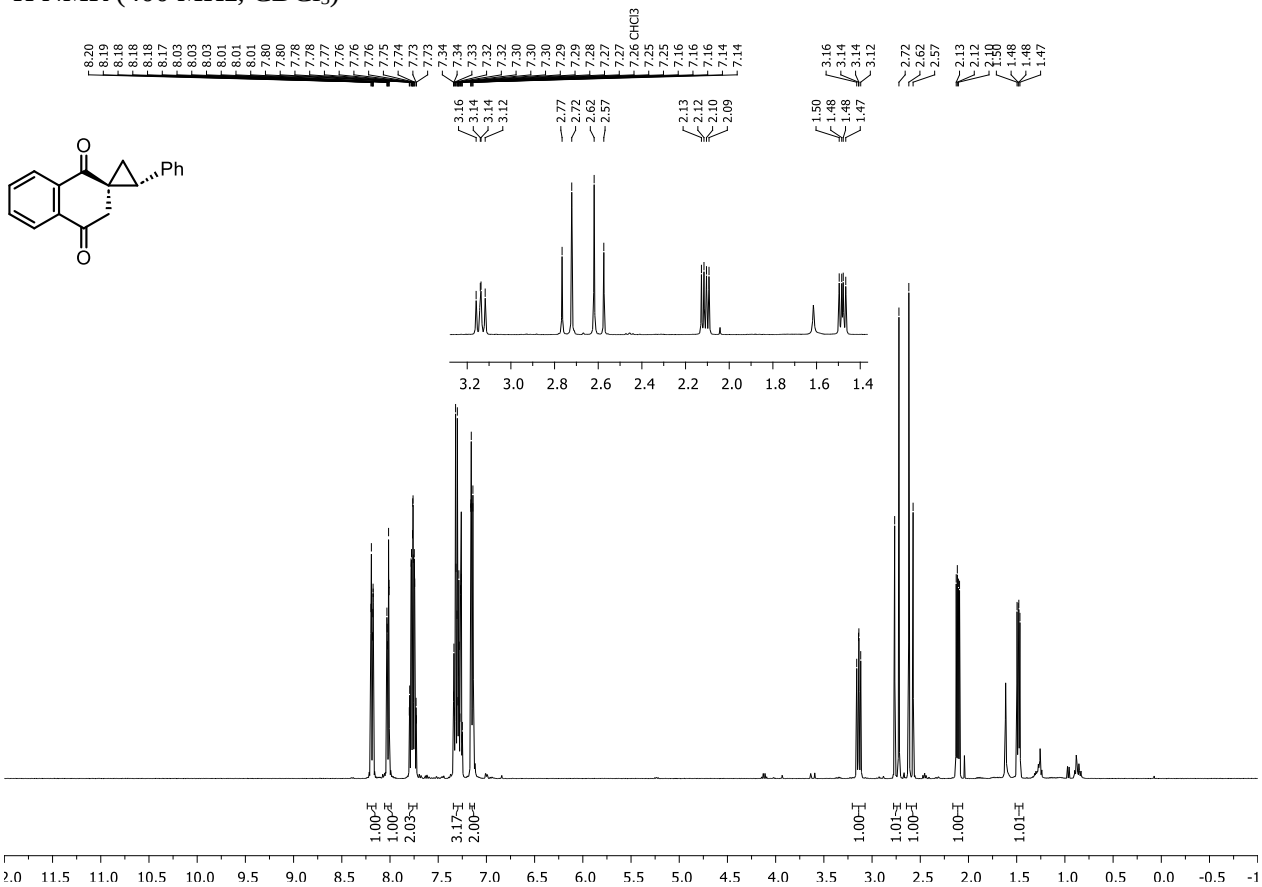


^{13}C NMR (101 MHz, $CDCl_3$)

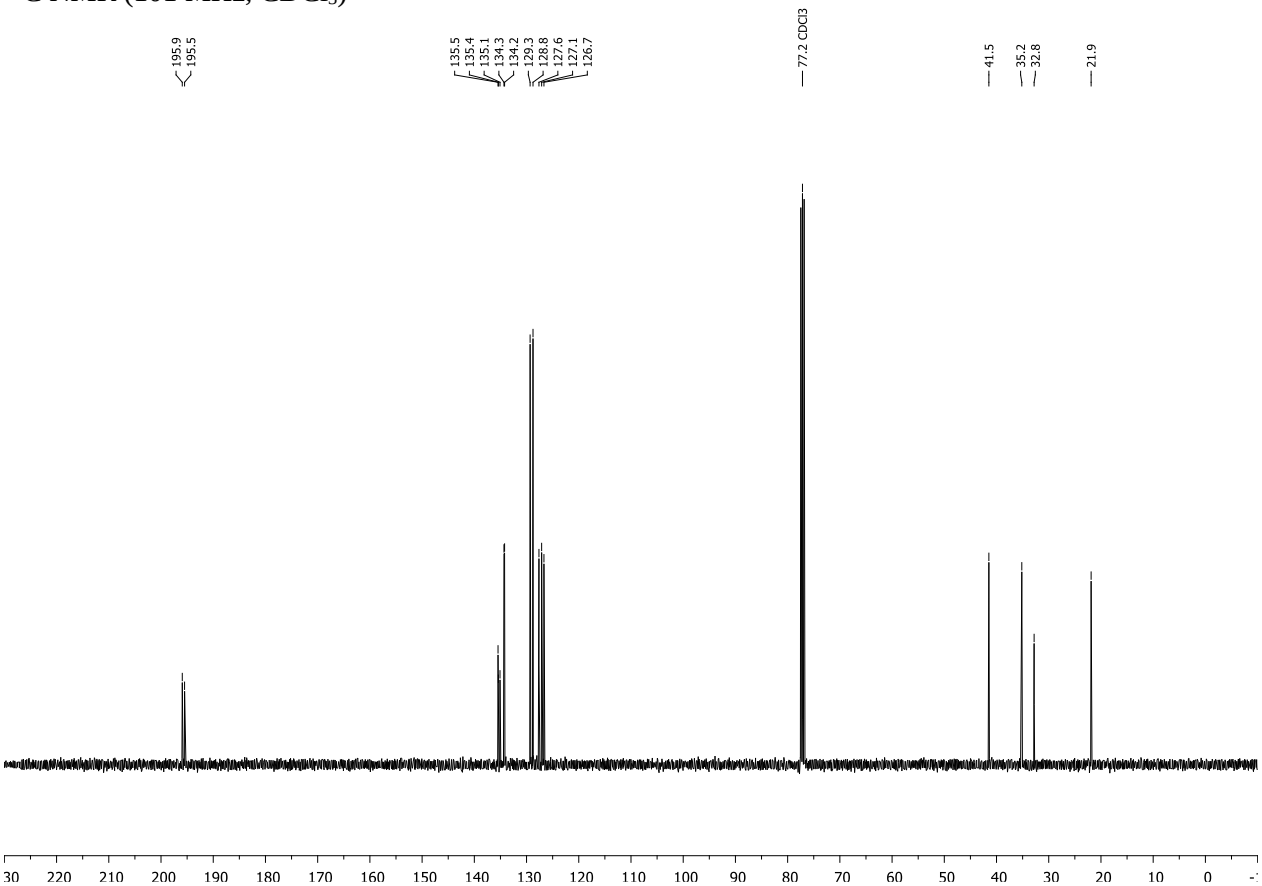


2-Phenyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2l)

^{1}H NMR (400 MHz, $CDCl_3$)

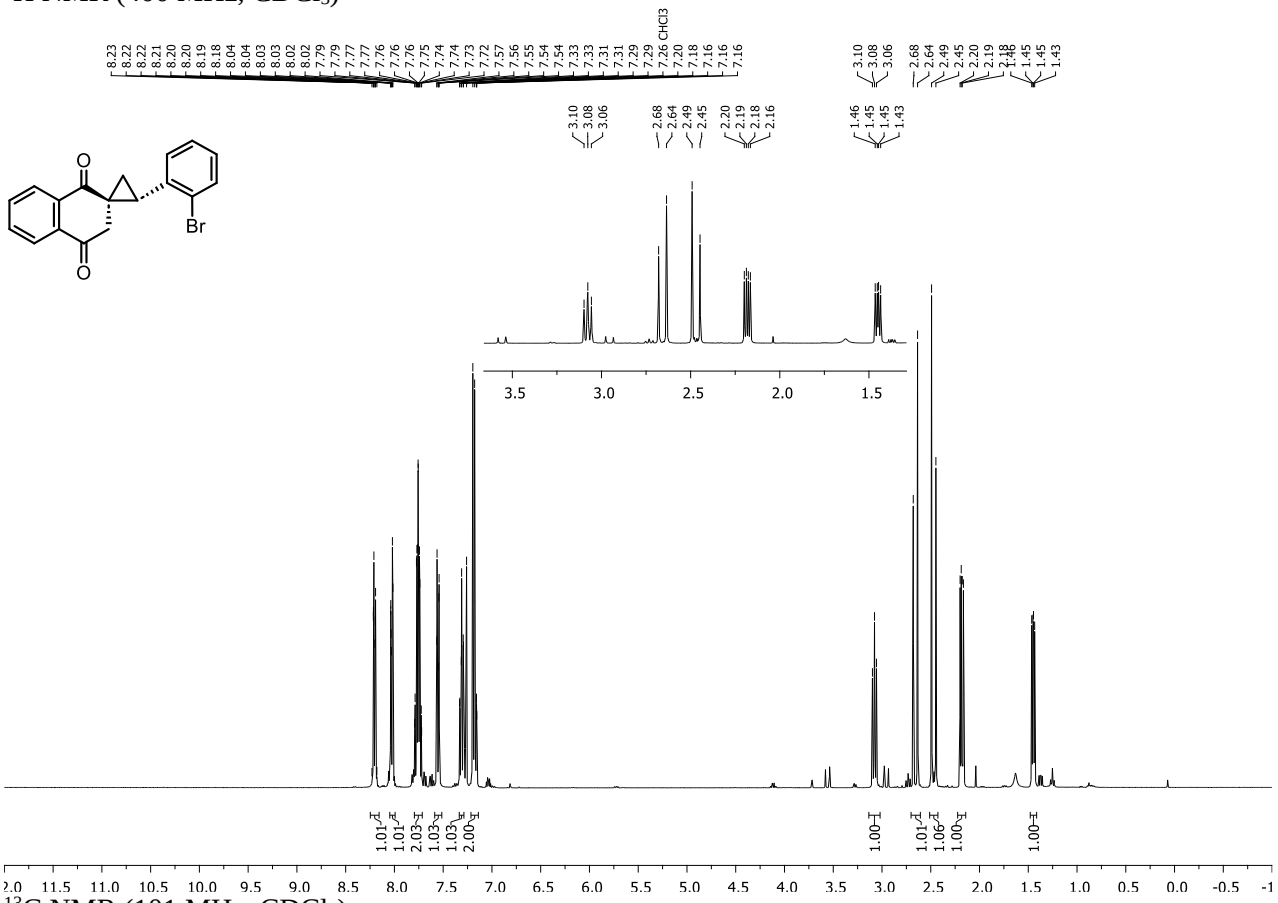


^{13}C NMR (101 MHz, $CDCl_3$)

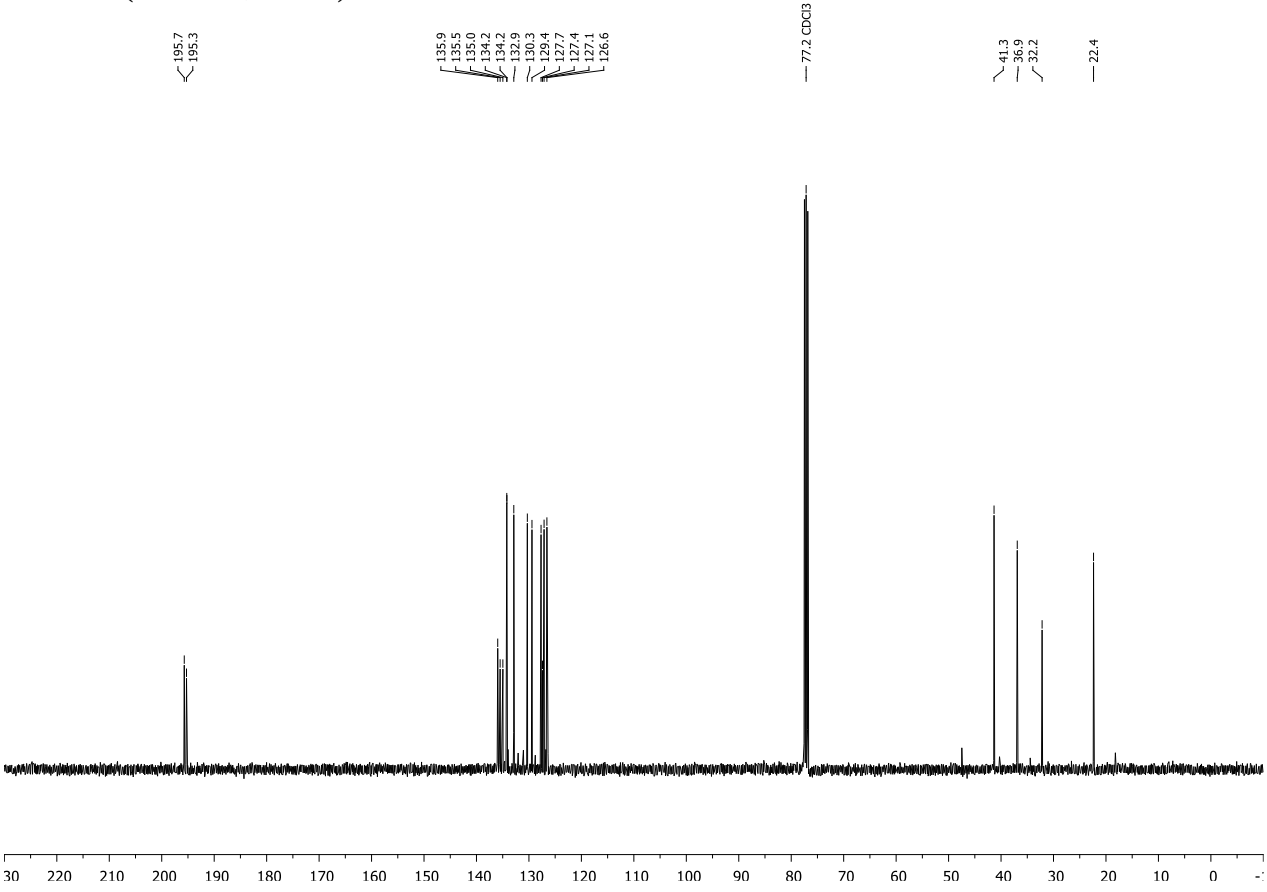


2-(2-Bromophenyl)-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2m)

^{1}H NMR (400 MHz, $CDCl_3$)

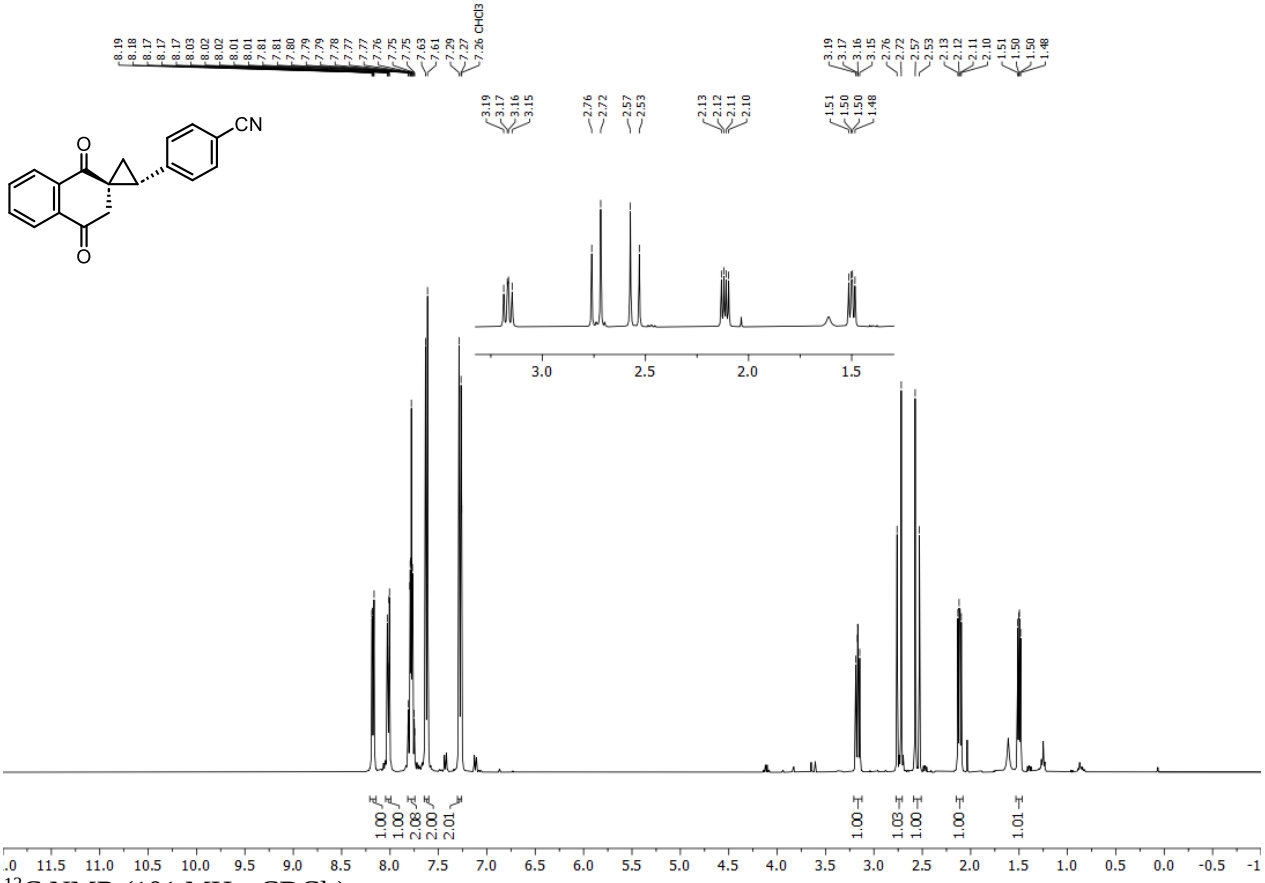


^{13}C NMR (101 MHz, $CDCl_3$)

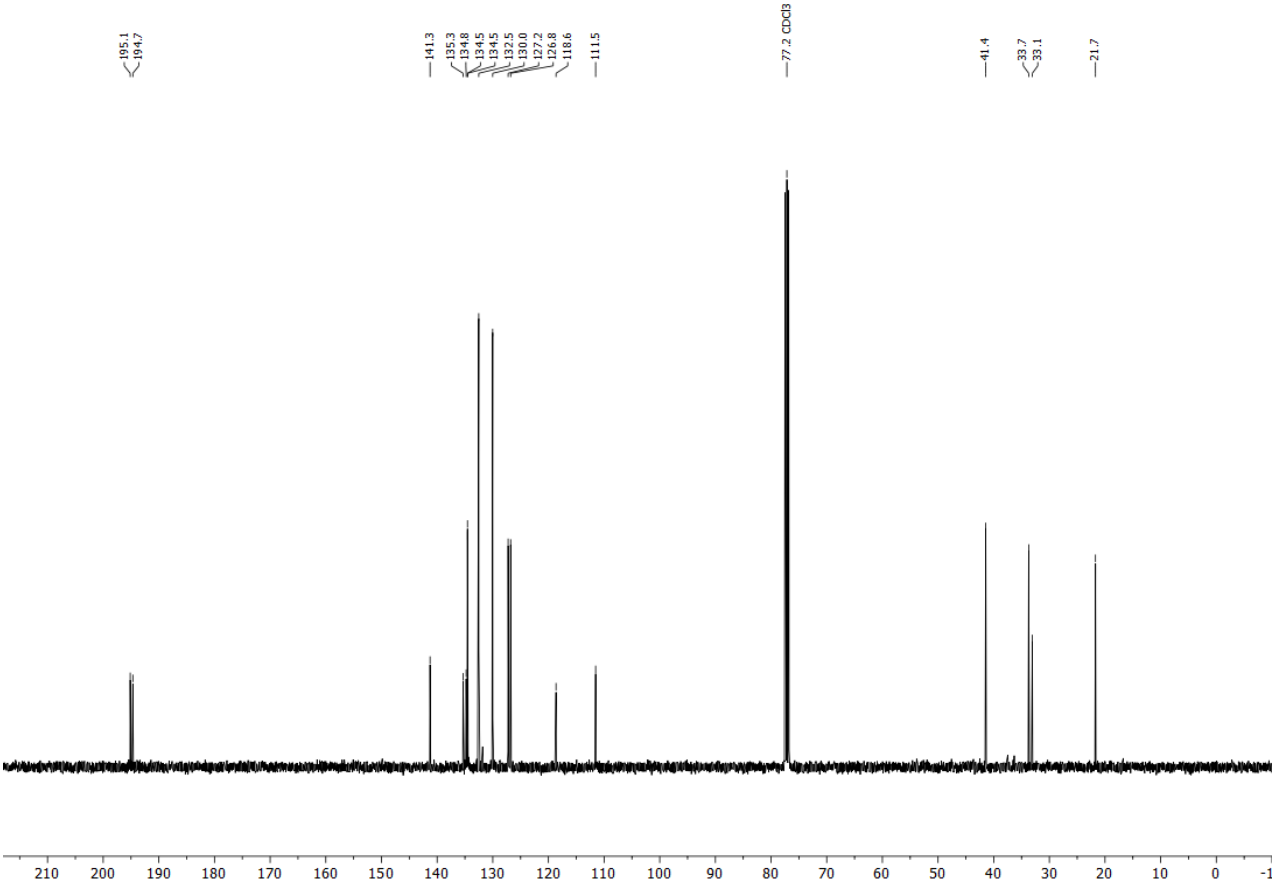


4-(1',4'-Dioxo-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-2-yl)benzonitrile (2n)

^{1}H NMR (400 MHz, $CDCl_3$)

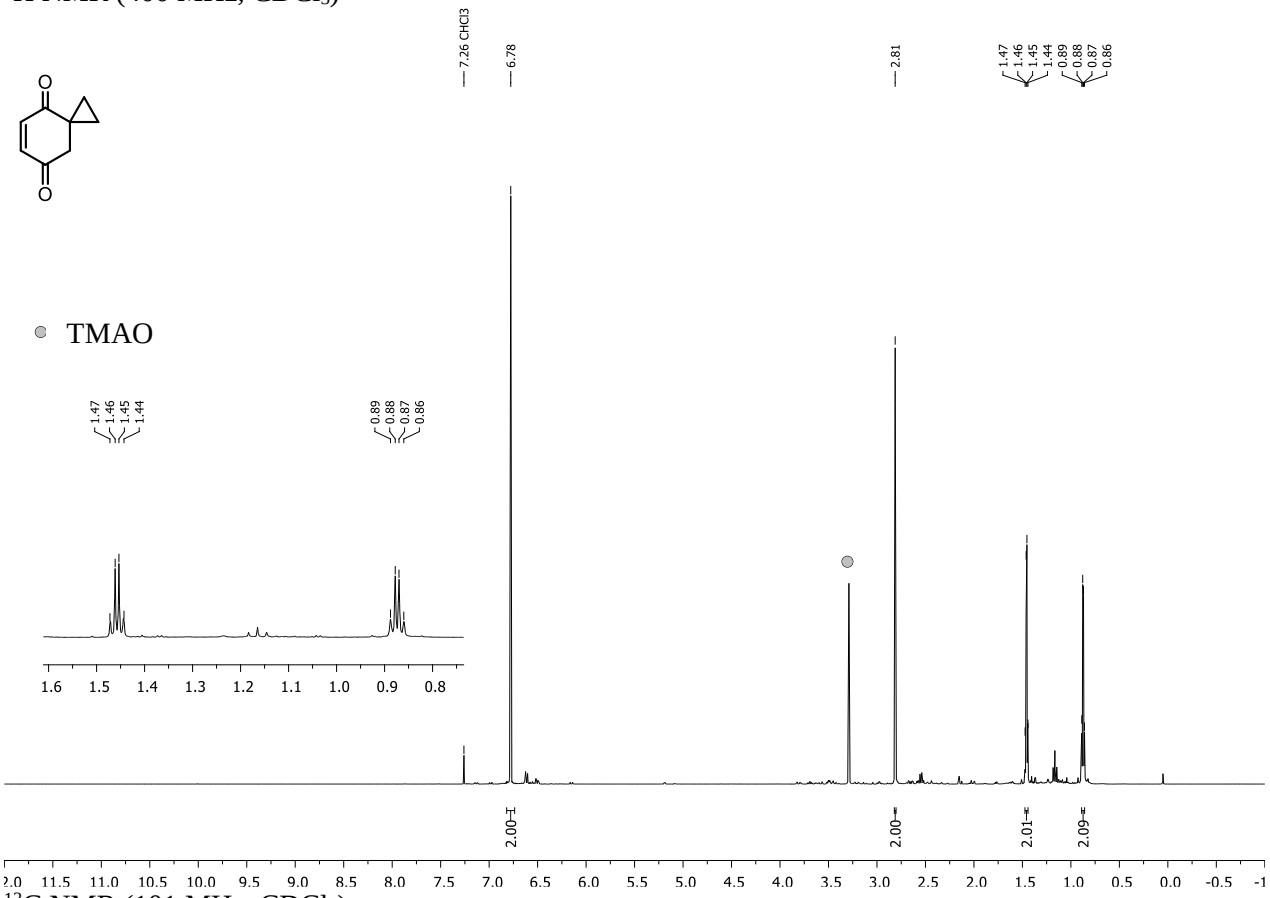


^{13}C NMR (101 MHz, $CDCl_3$)

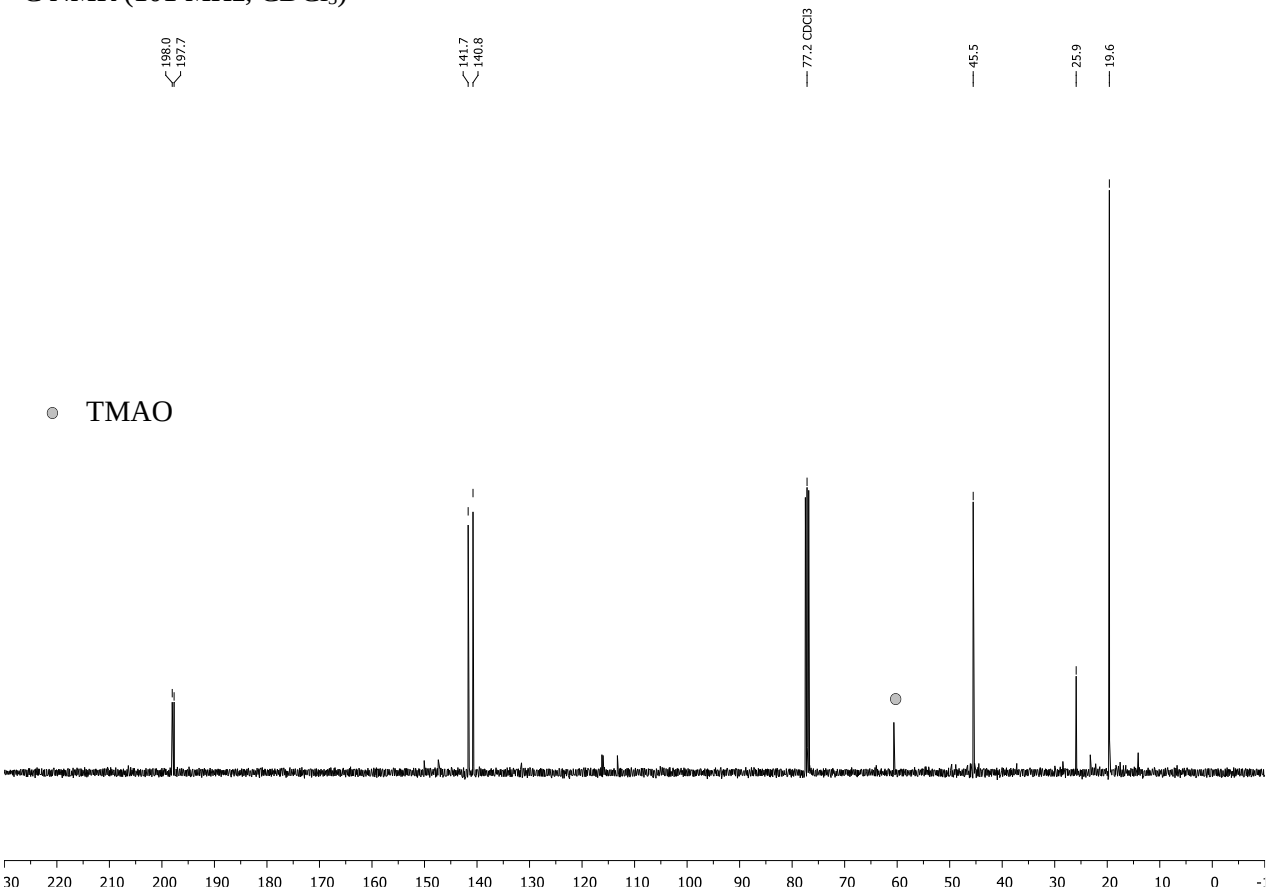


Spiro[2.5]oct-5-ene-4,7-dione (2o)

^{1}H NMR (400 MHz, $CDCl_3$)

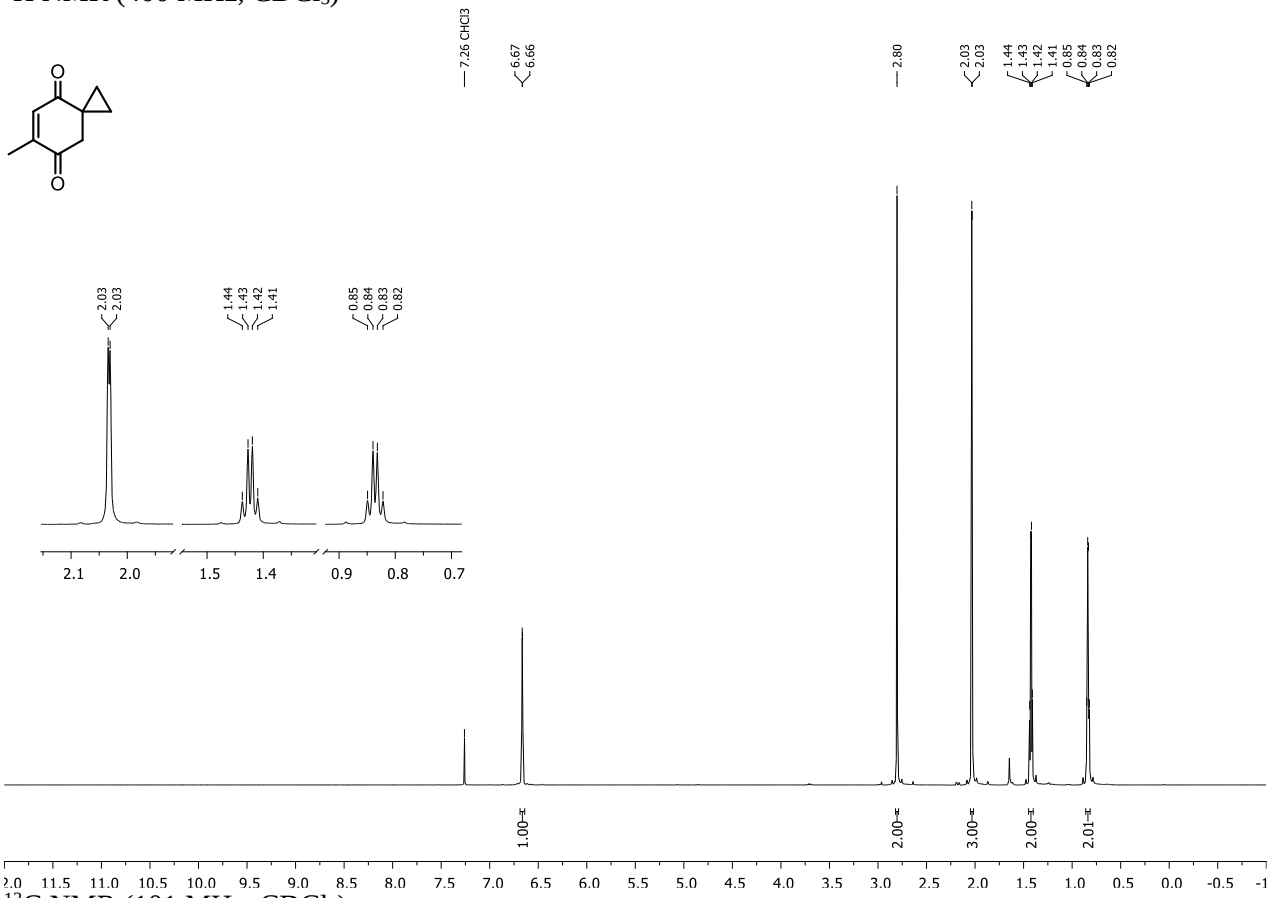


^{13}C NMR (101 MHz, $CDCl_3$)

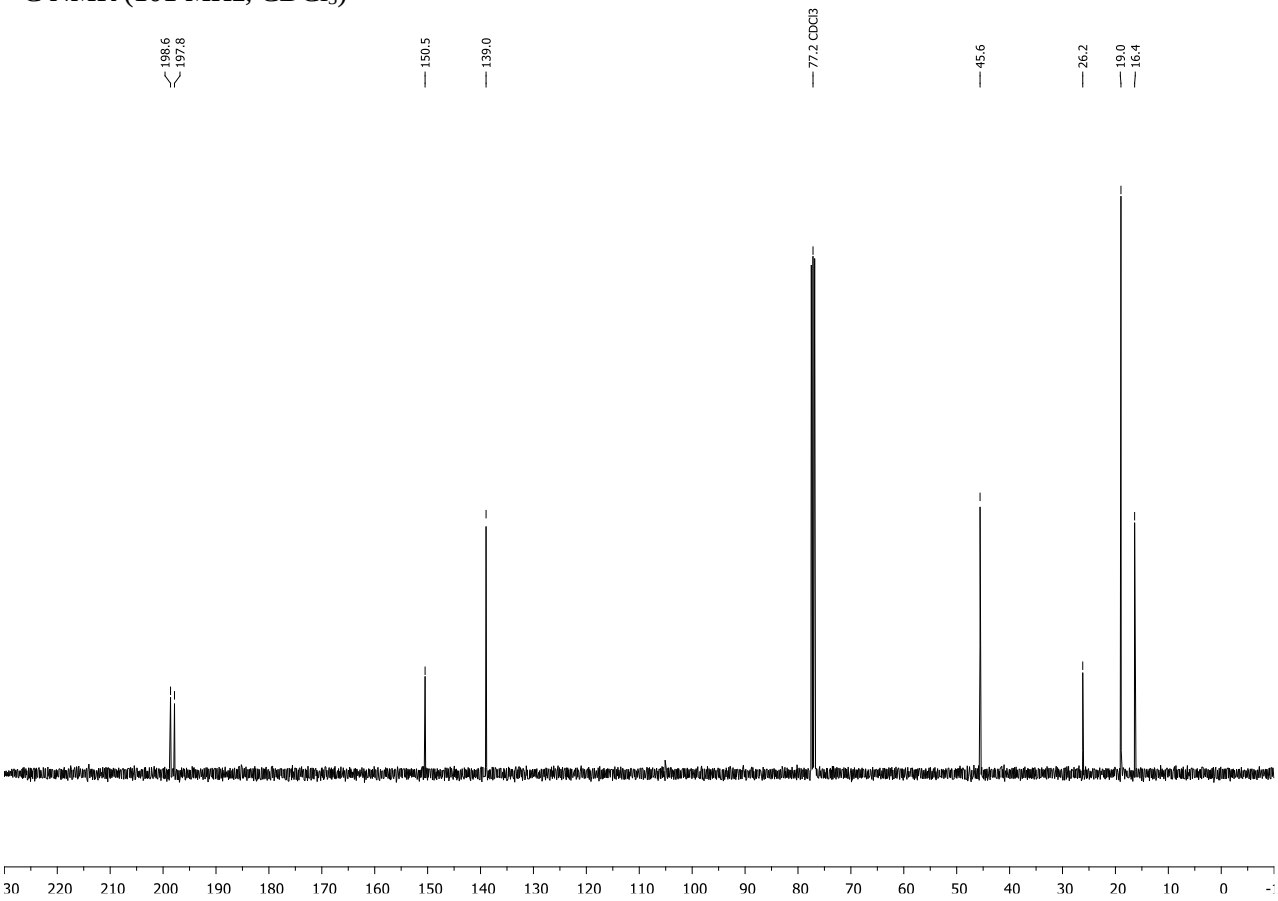


6-Methylspiro[2.5]oct-5-ene-4,7-dione (2p)

^{1}H NMR (400 MHz, $CDCl_3$)

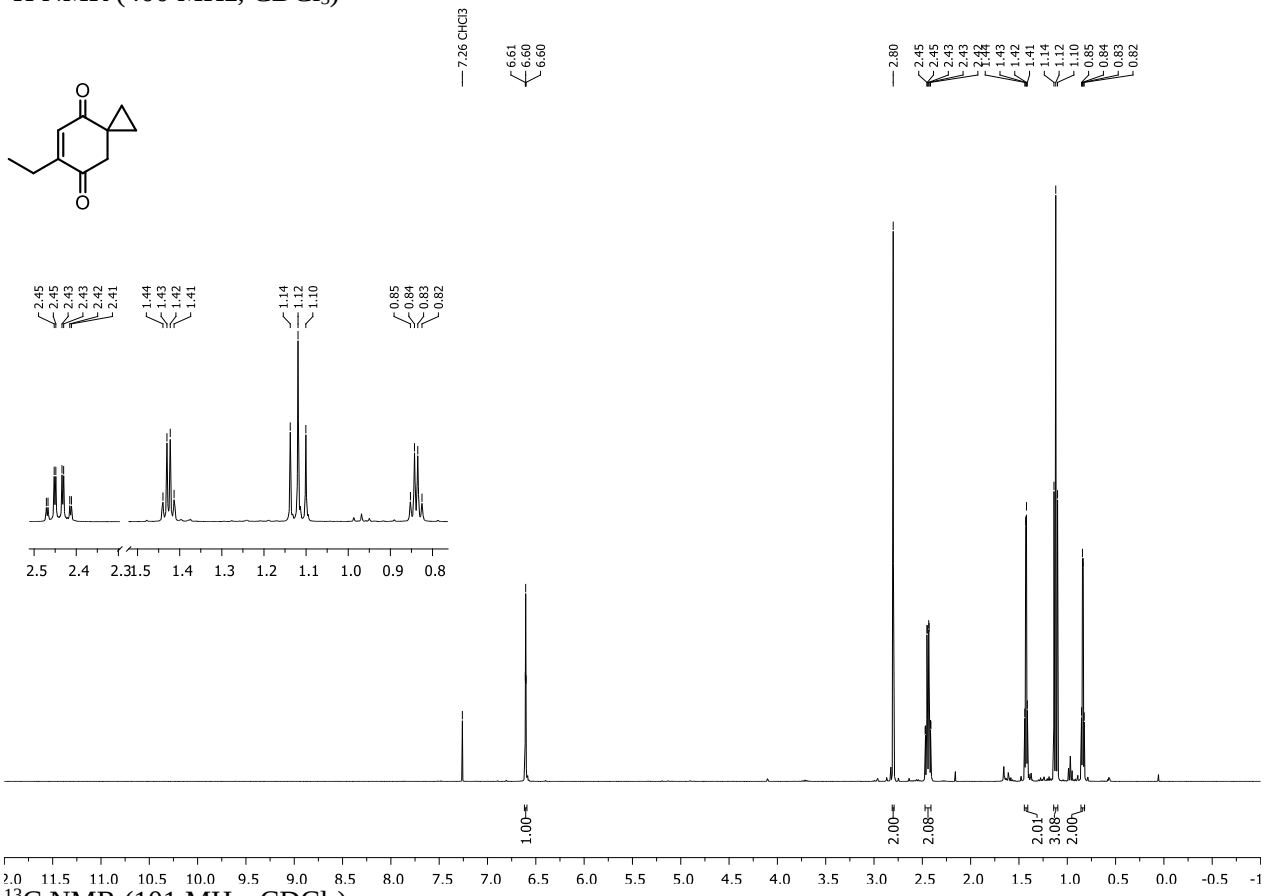


^{13}C NMR (101 MHz, $CDCl_3$)

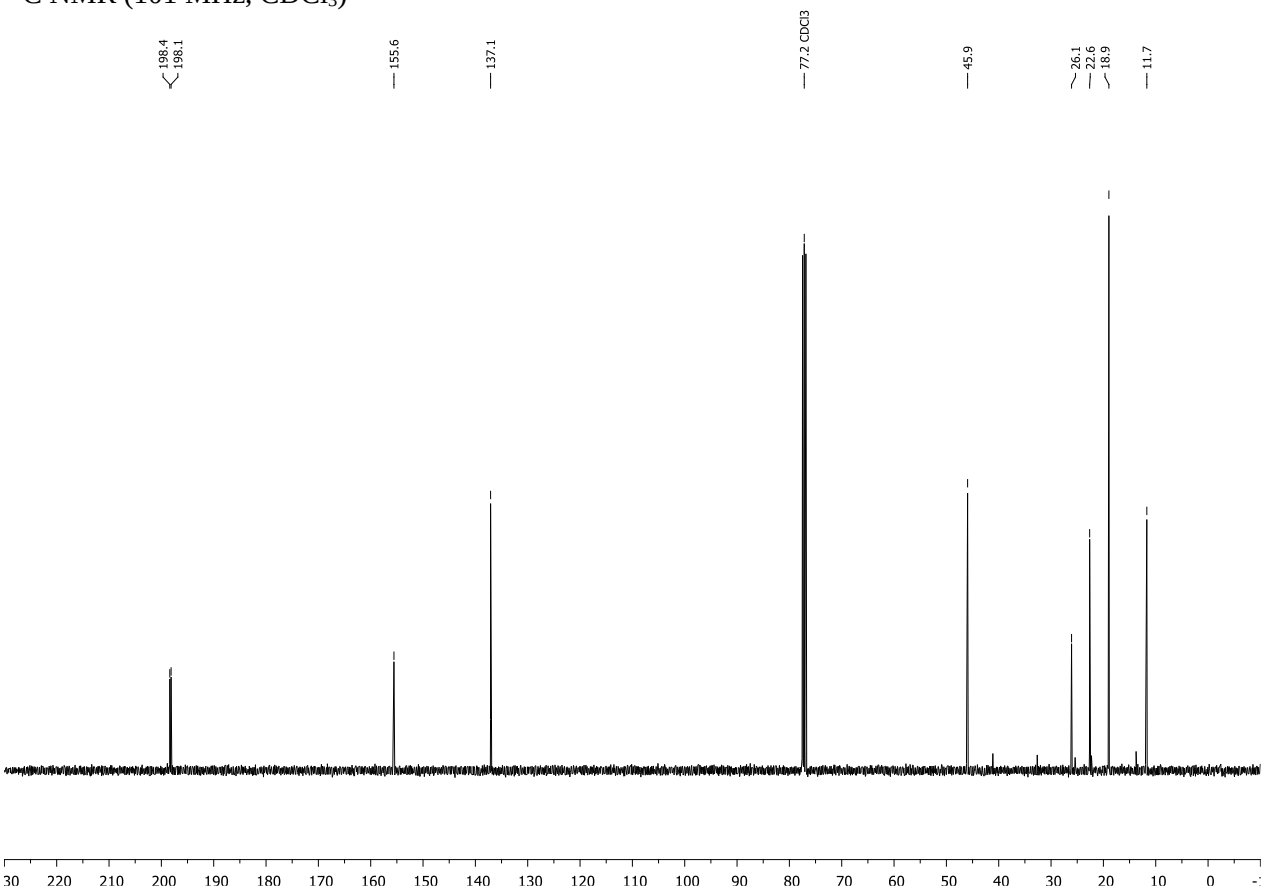


6-Ethylspiro[2.5]oct-5-ene-4,7-dione (2q)

^{1}H NMR (400 MHz, $CDCl_3$)

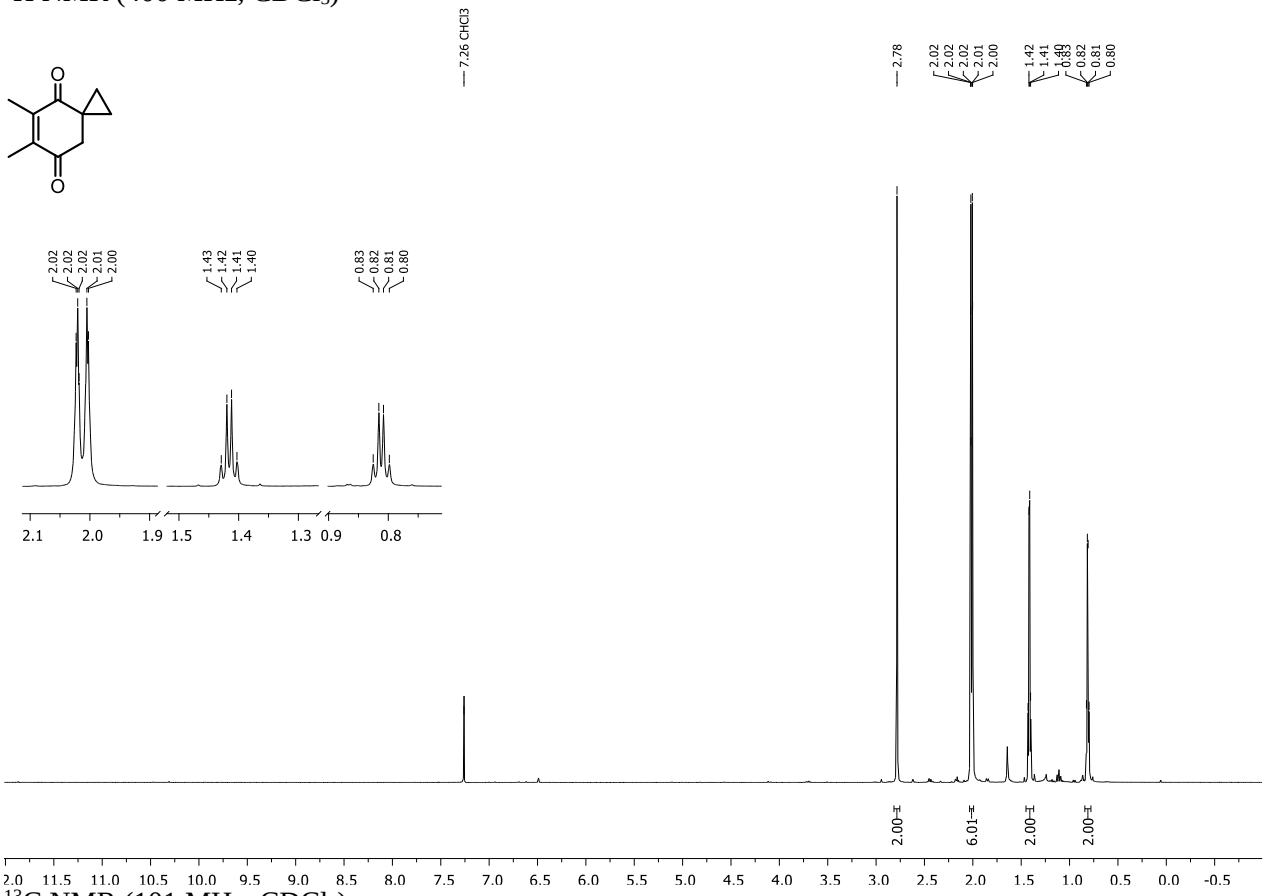


^{13}C NMR (101 MHz, $CDCl_3$)

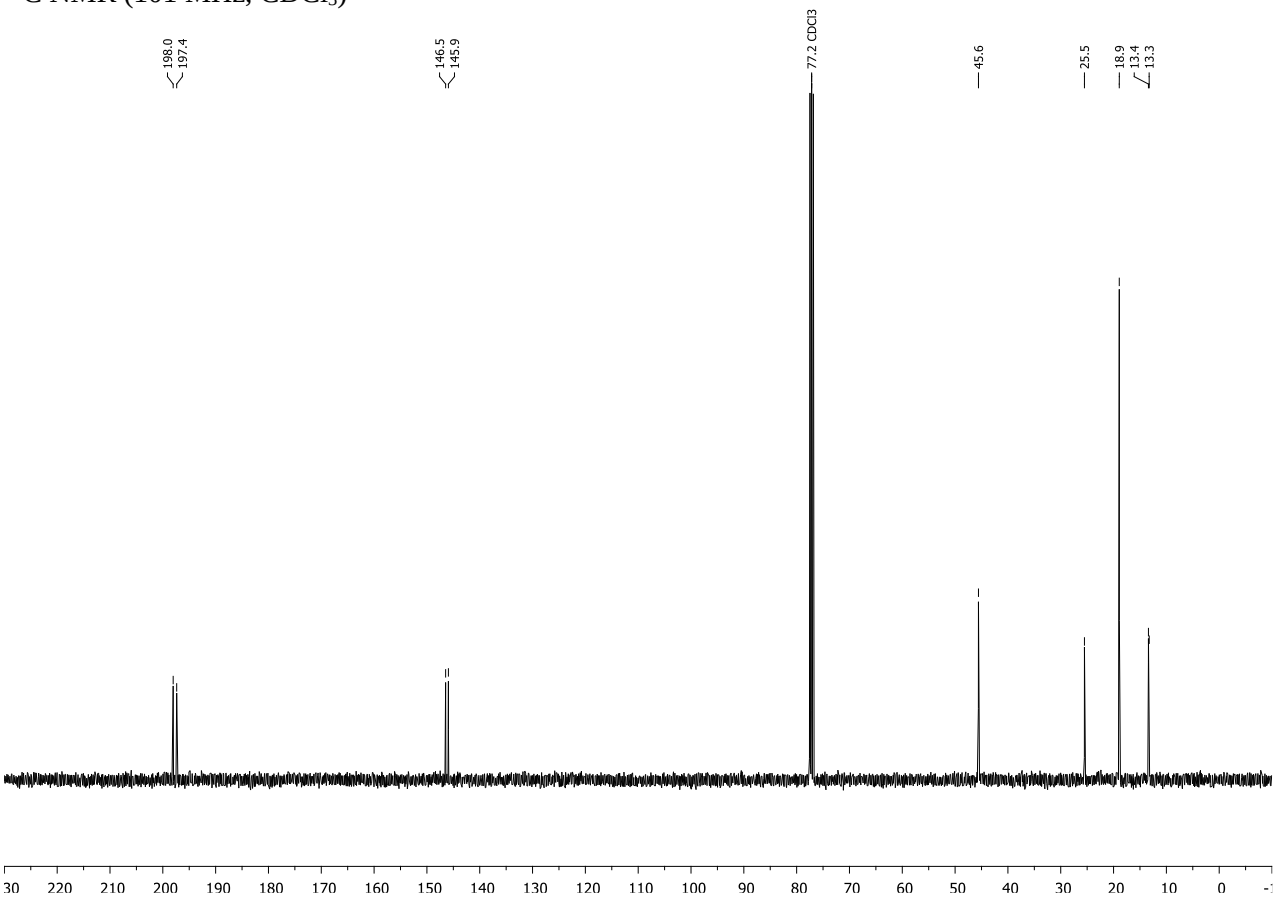


5,6-Dimethylspiro[2.5]oct-5-ene-4,7-dione (2r)

^{1}H NMR (400 MHz, $CDCl_3$)

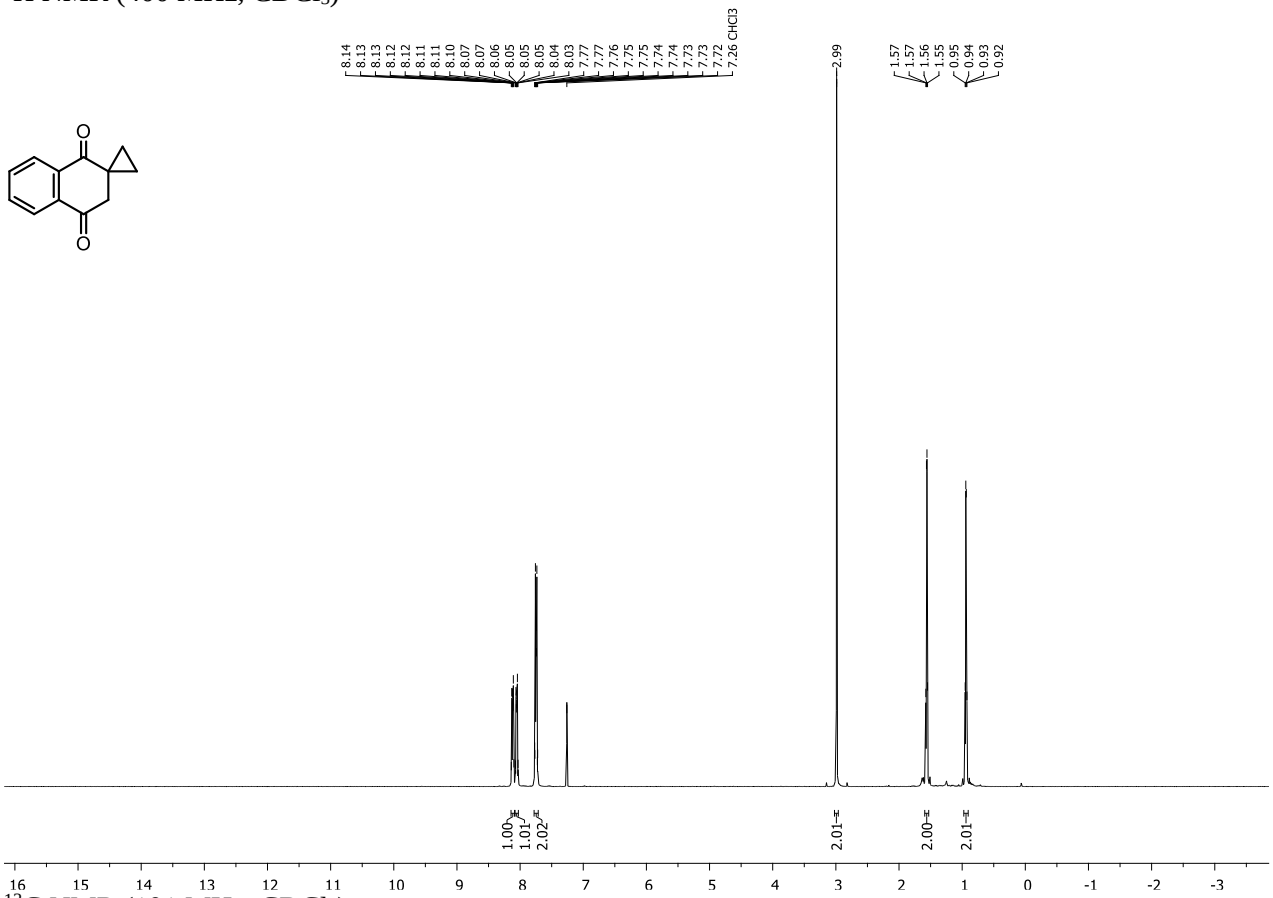


^{13}C NMR (101 MHz, $CDCl_3$)

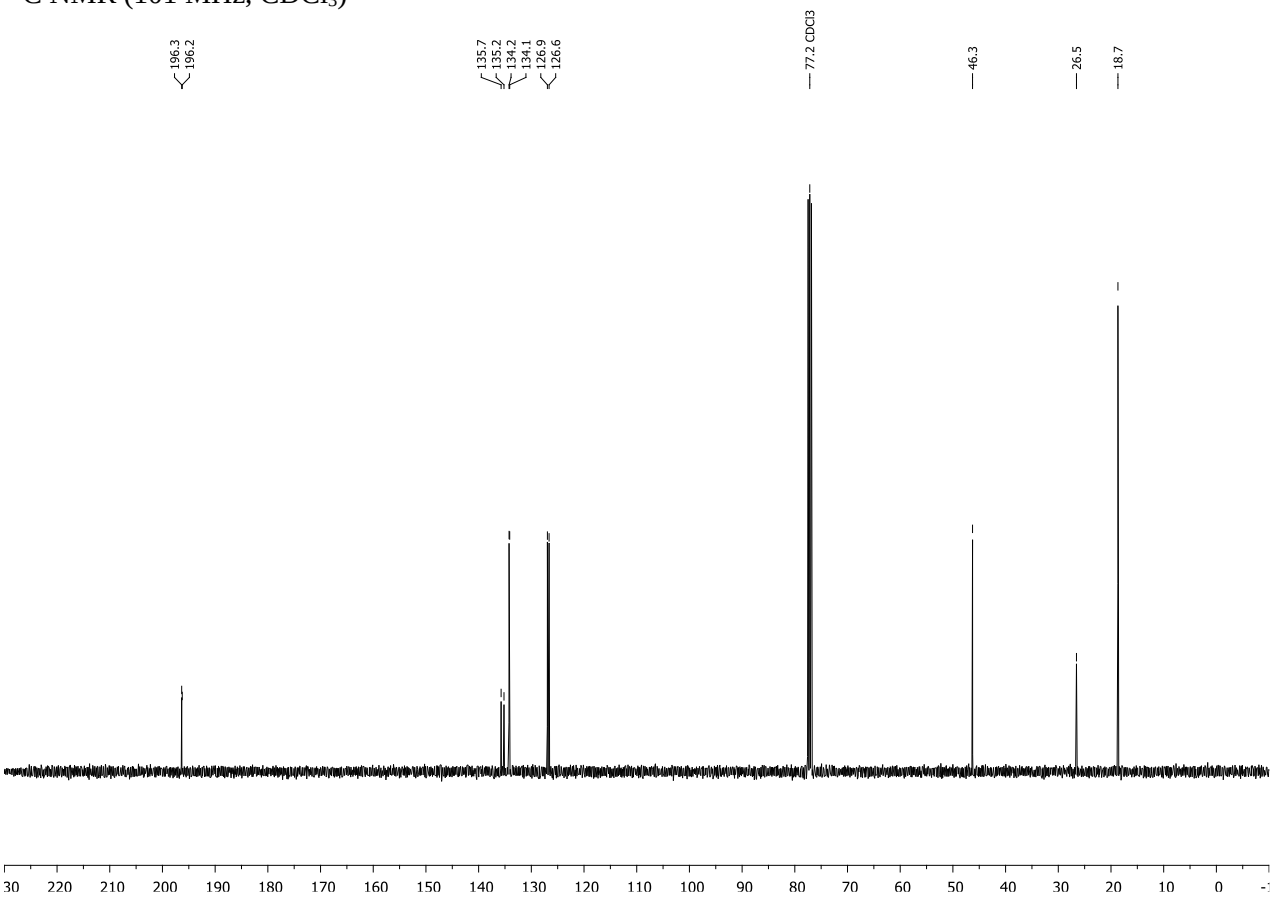


1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2s)

^{1}H NMR (400 MHz, $CDCl_3$)

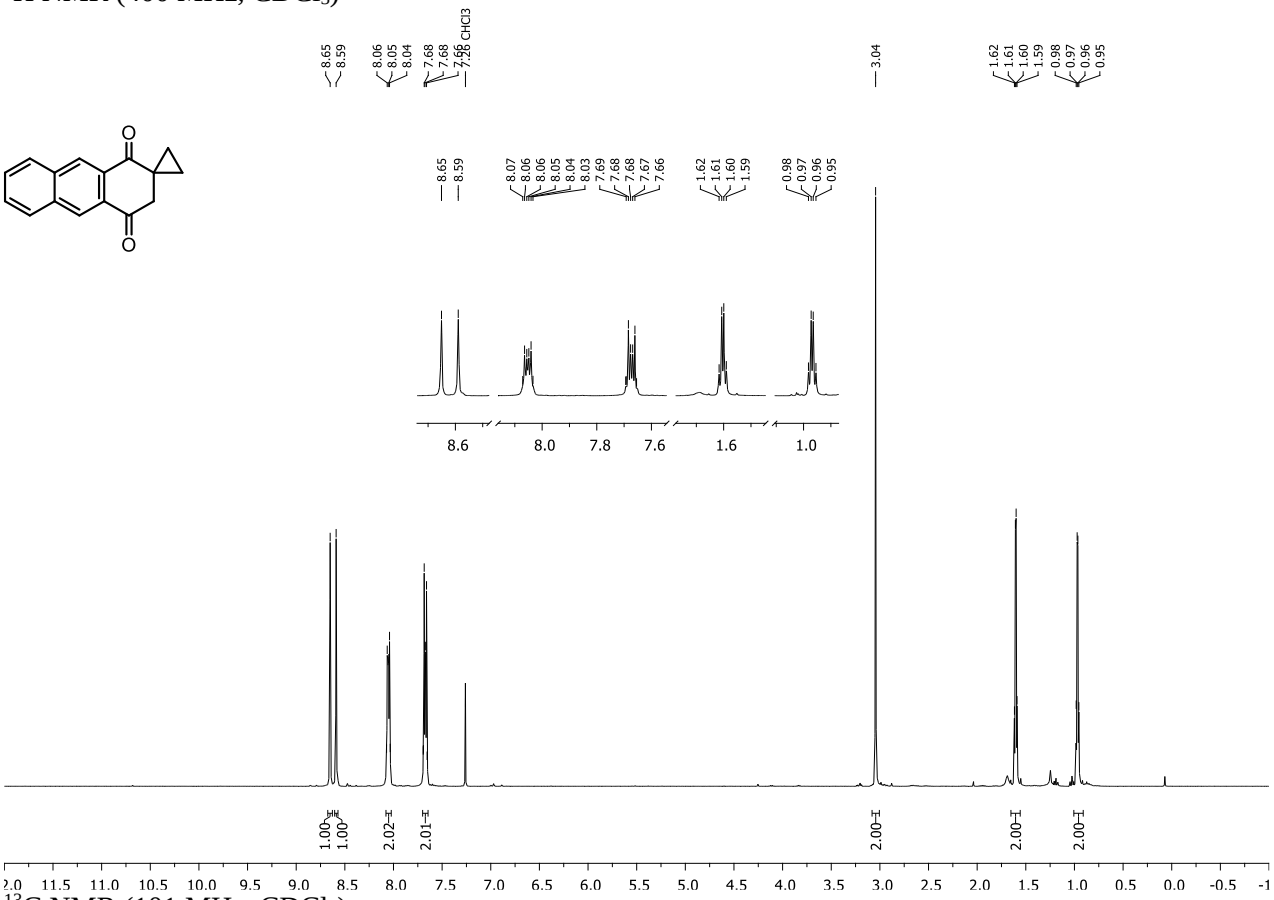


^{13}C NMR (101 MHz, $CDCl_3$)

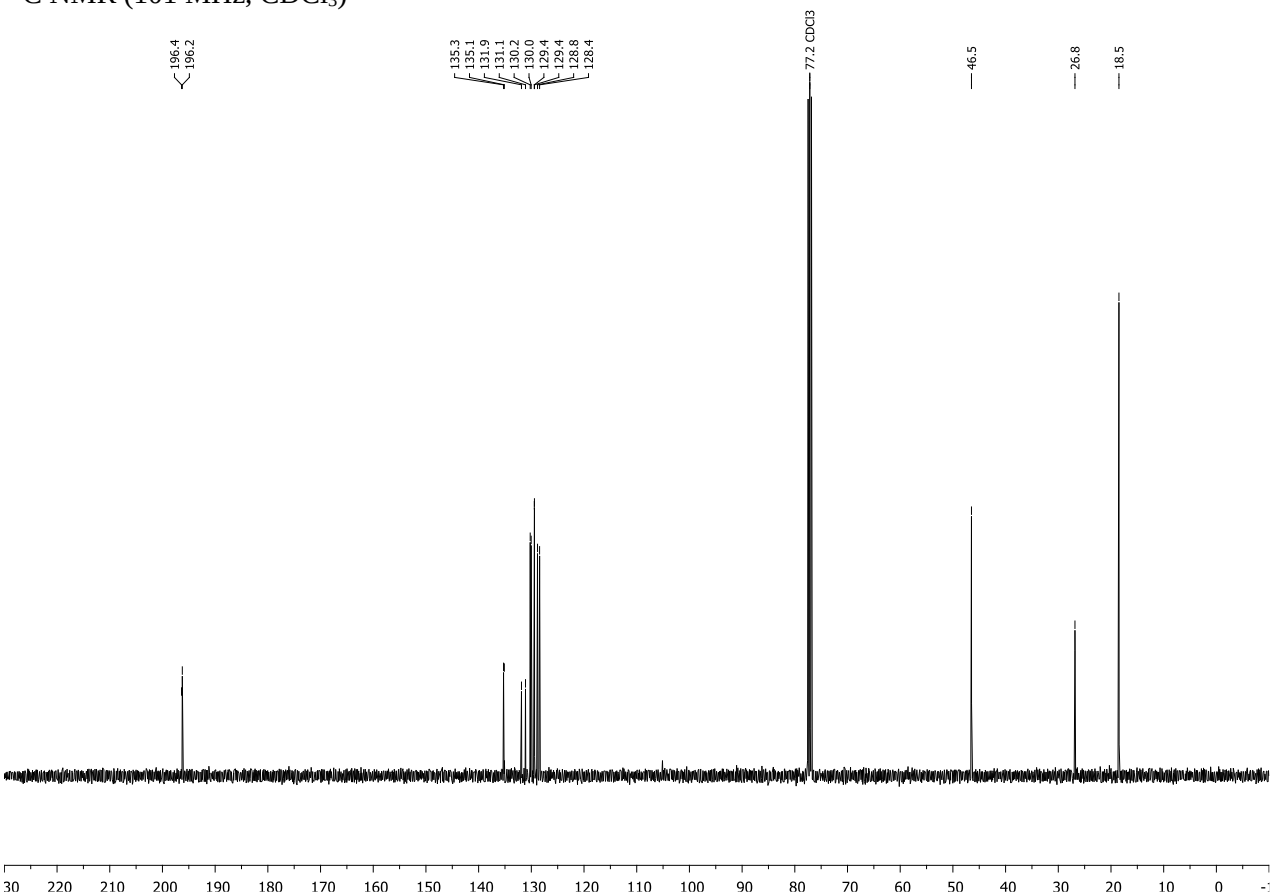


1*H*-Spiro[anthracene-2,1'-cyclopropane]-1,4(3*H*)-dione (2t)

^{1}H NMR (400 MHz, $CDCl_3$)

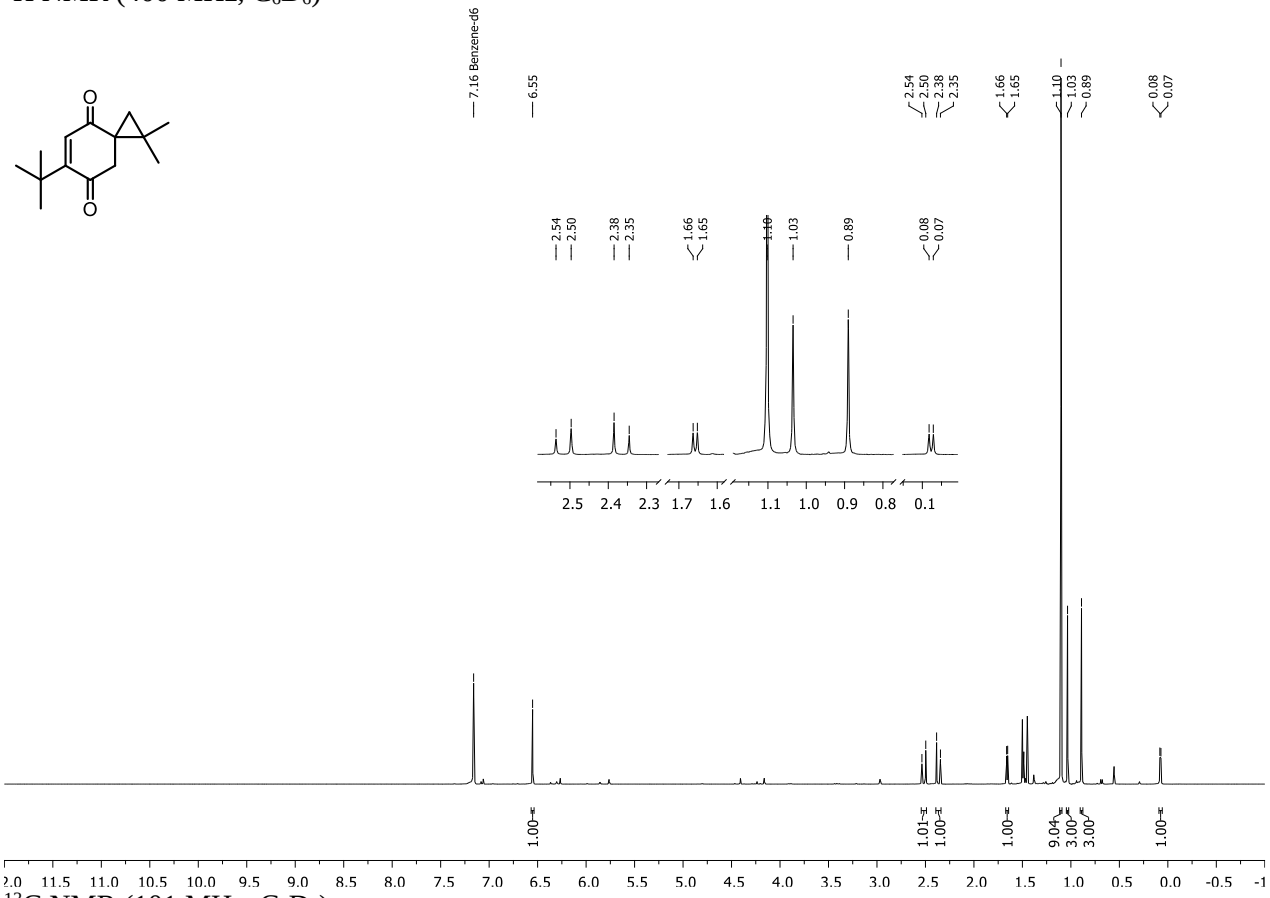


^{13}C NMR (101 MHz, $CDCl_3$)

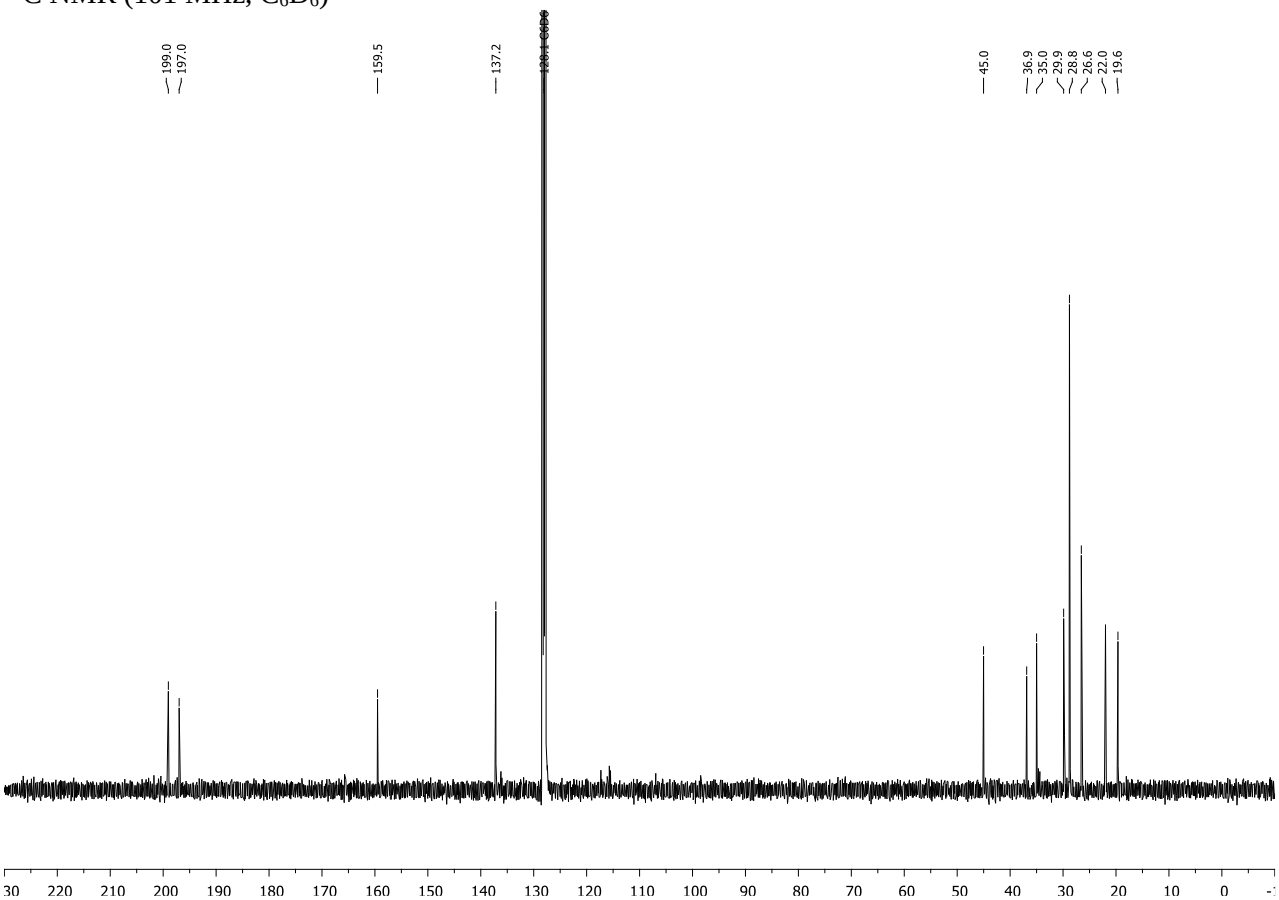


6-(*tert*-Butyl)-1,1-dimethylspiro[2.5]oct-5-ene-4,7-dione (2u)

^{1}H NMR (400 MHz, C_6D_6)

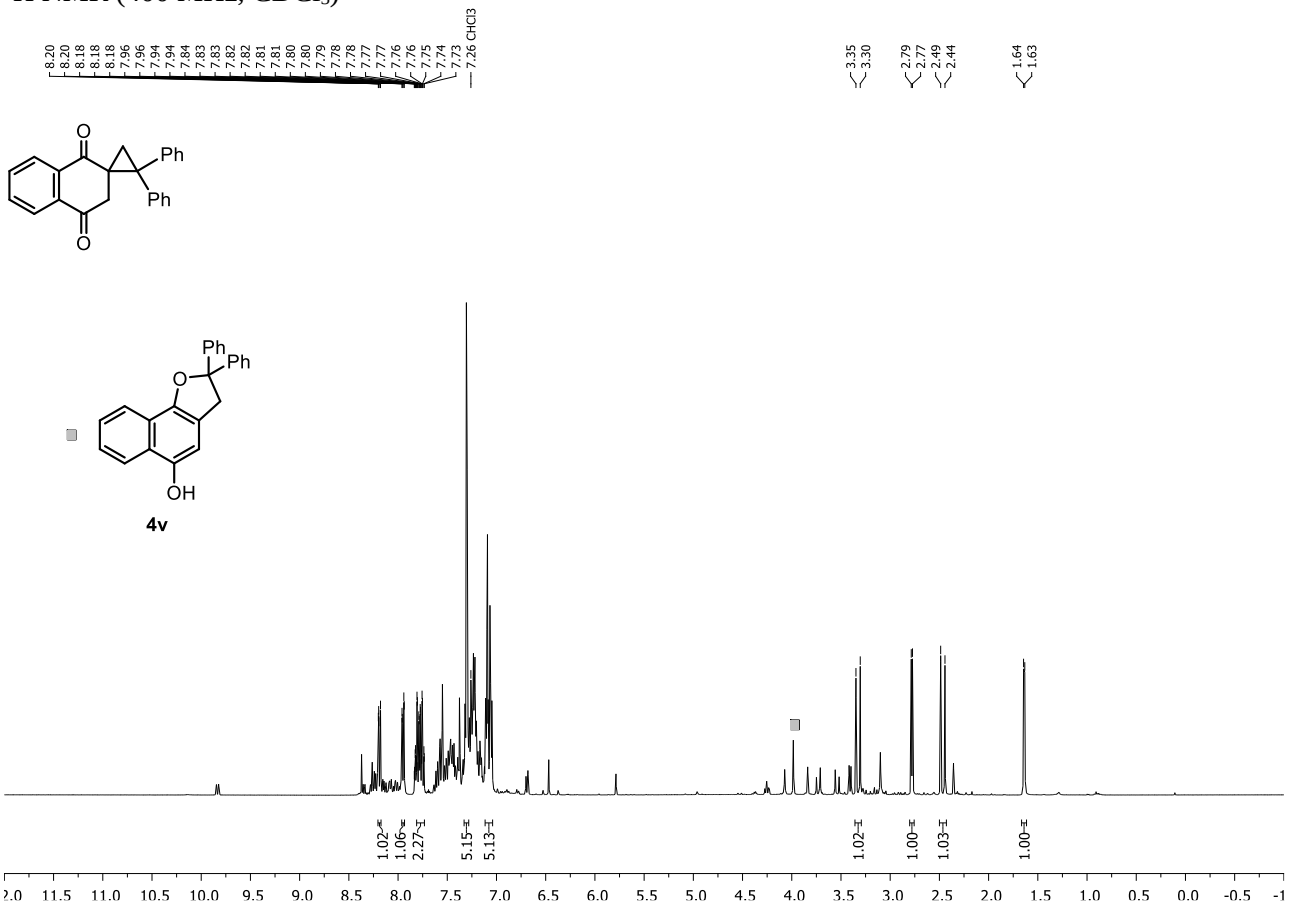


^{13}C NMR (101 MHz, C_6D_6)



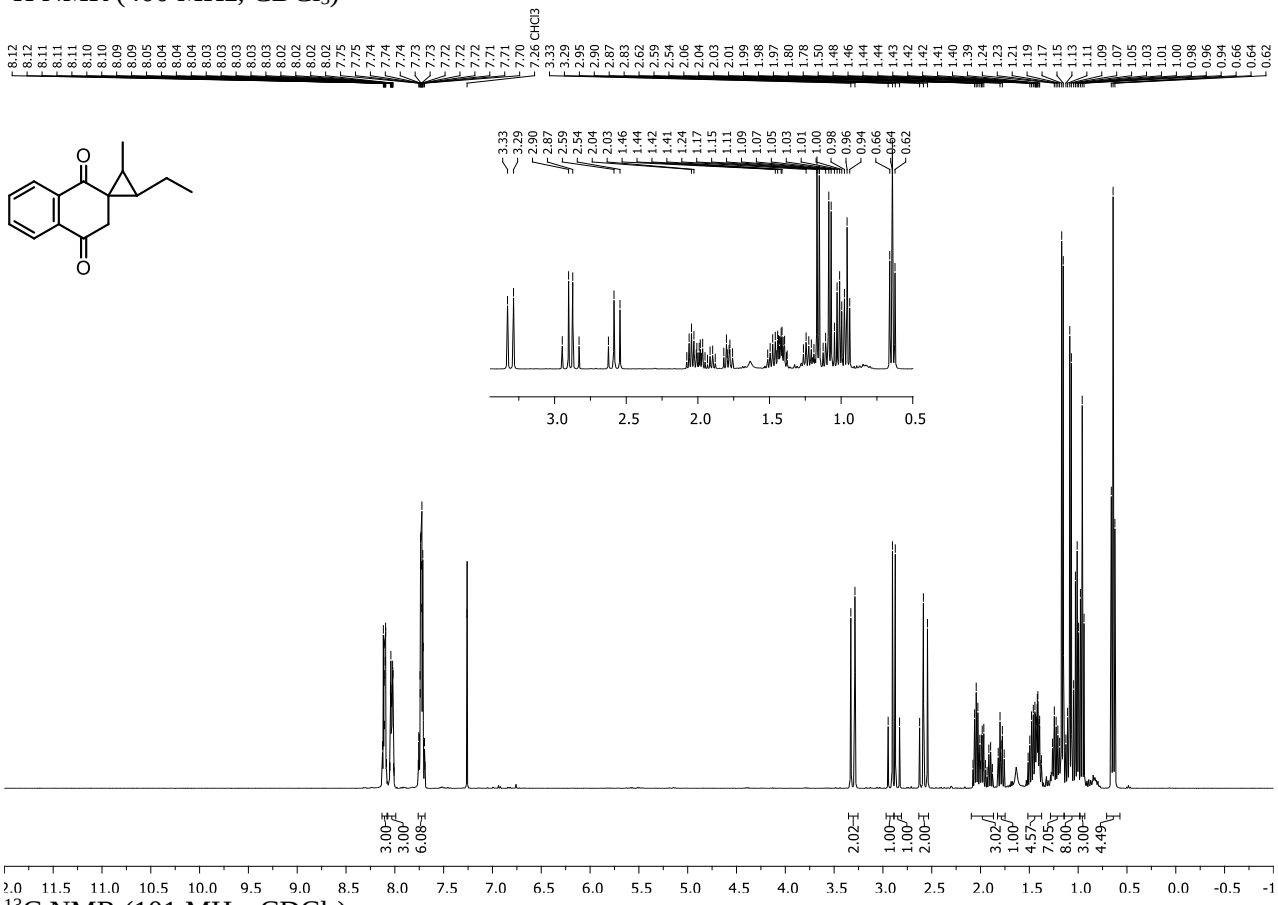
2,2-Diphenyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2v)

^{1}H NMR (400 MHz, $CDCl_3$)

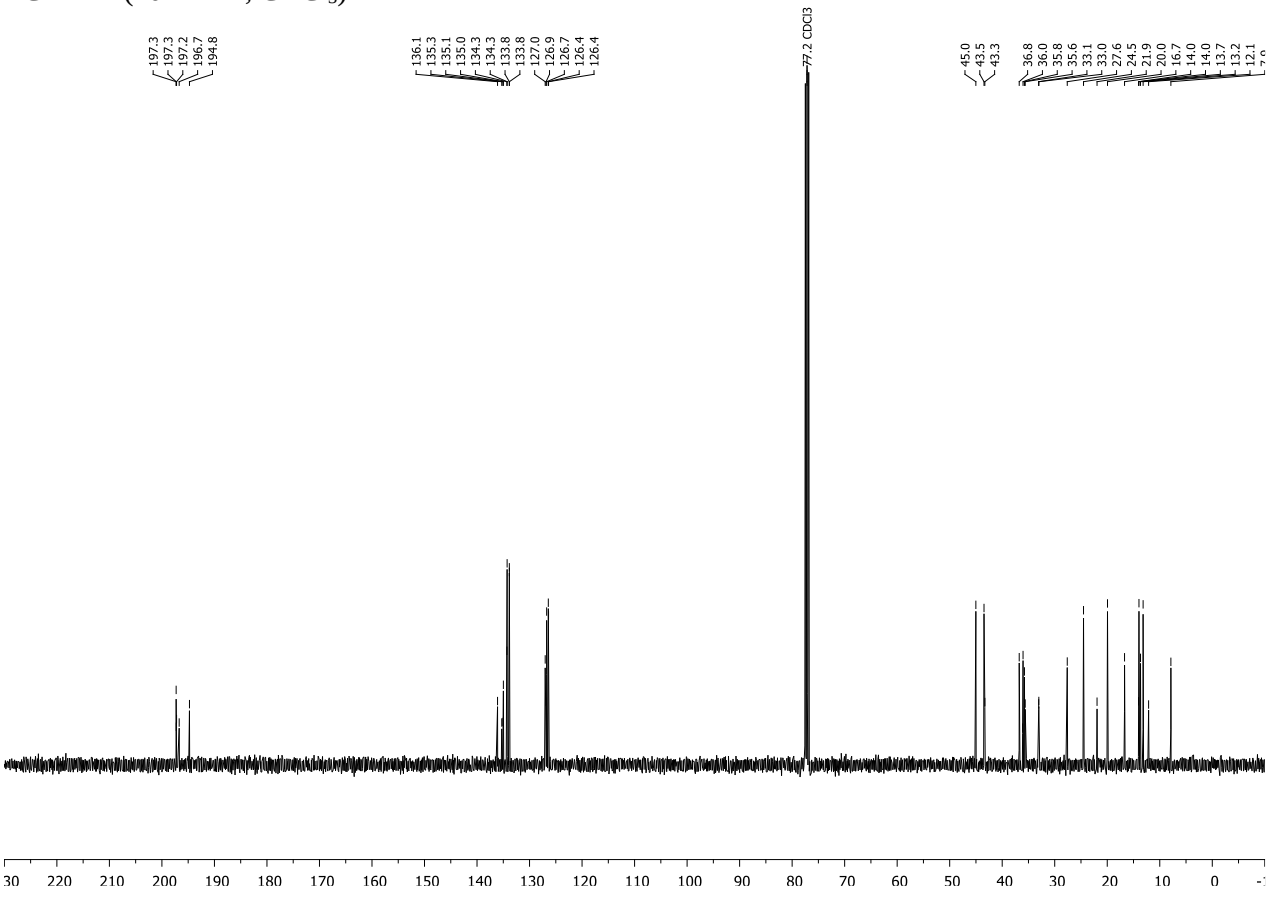


2-Ethyl-3-methyl-1'*H*-spiro[cyclopropane-1,2'-naphthalene]-1',4'(3'*H*)-dione (2w)

^{1}H NMR (400 MHz, $CDCl_3$)

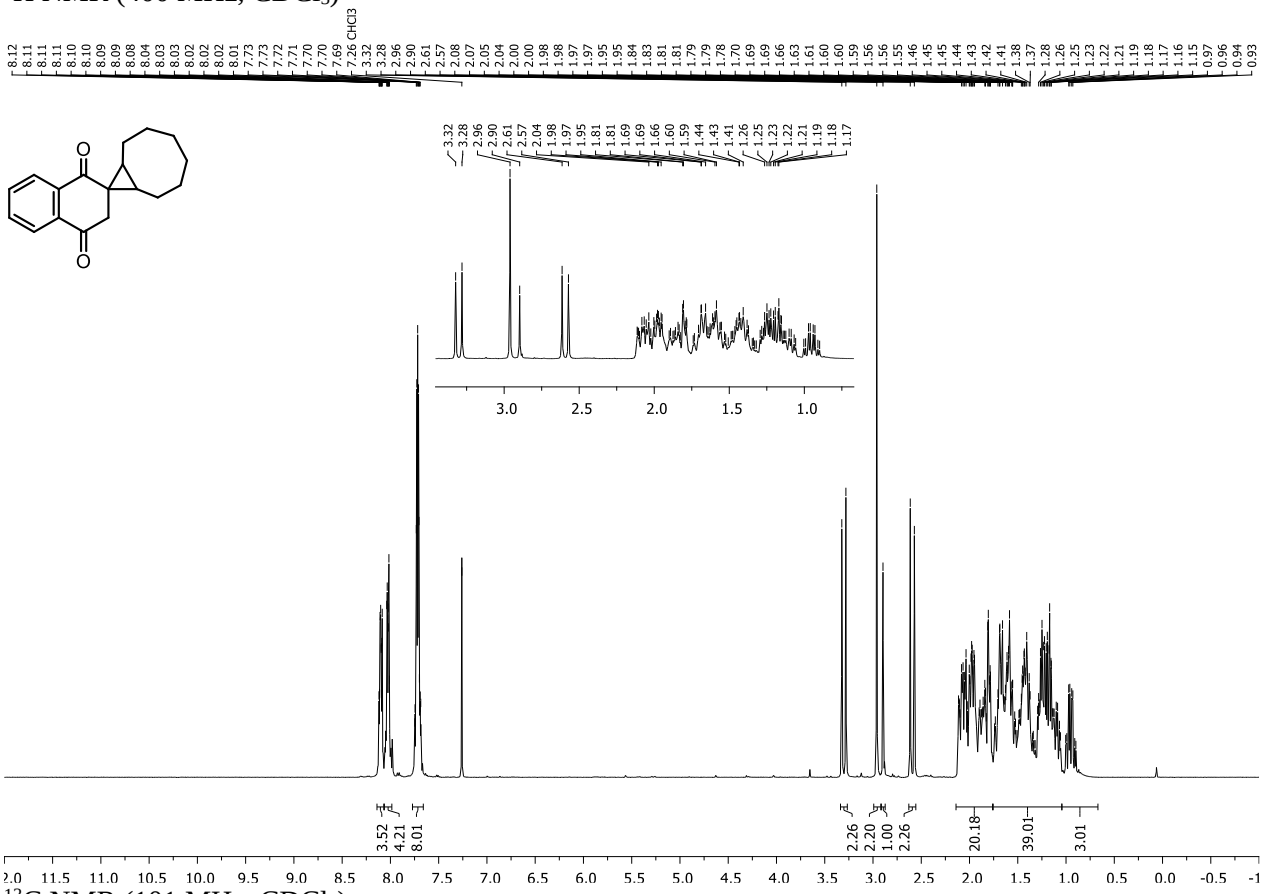


^{13}C NMR (101 MHz, $CDCl_3$)

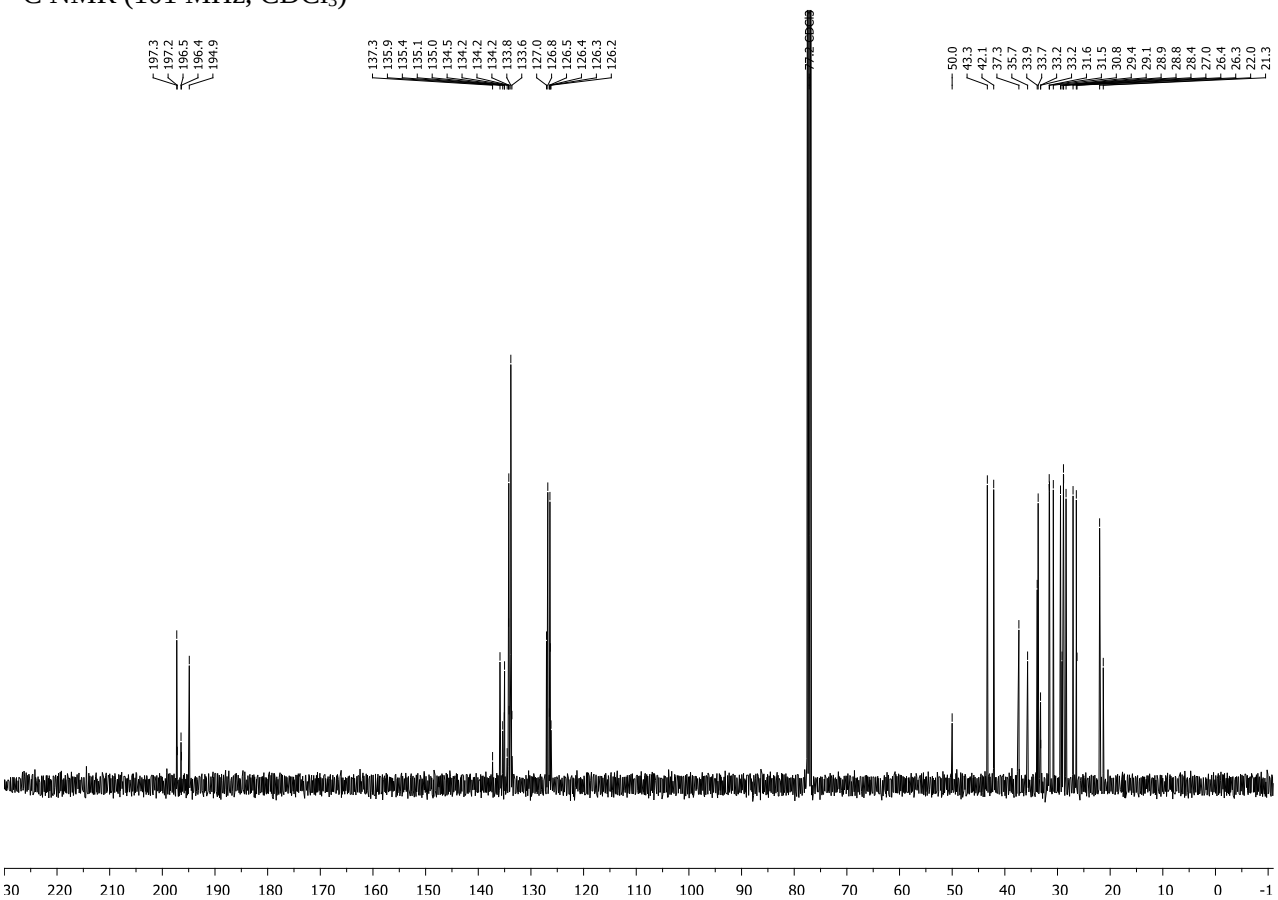


1'*H*-spiro[bicyclo[6.1.0]nonane-9,2'-naphthalene]-1',4'(3'*H*)-dione (2x)

^{1}H NMR (400 MHz, $CDCl_3$)

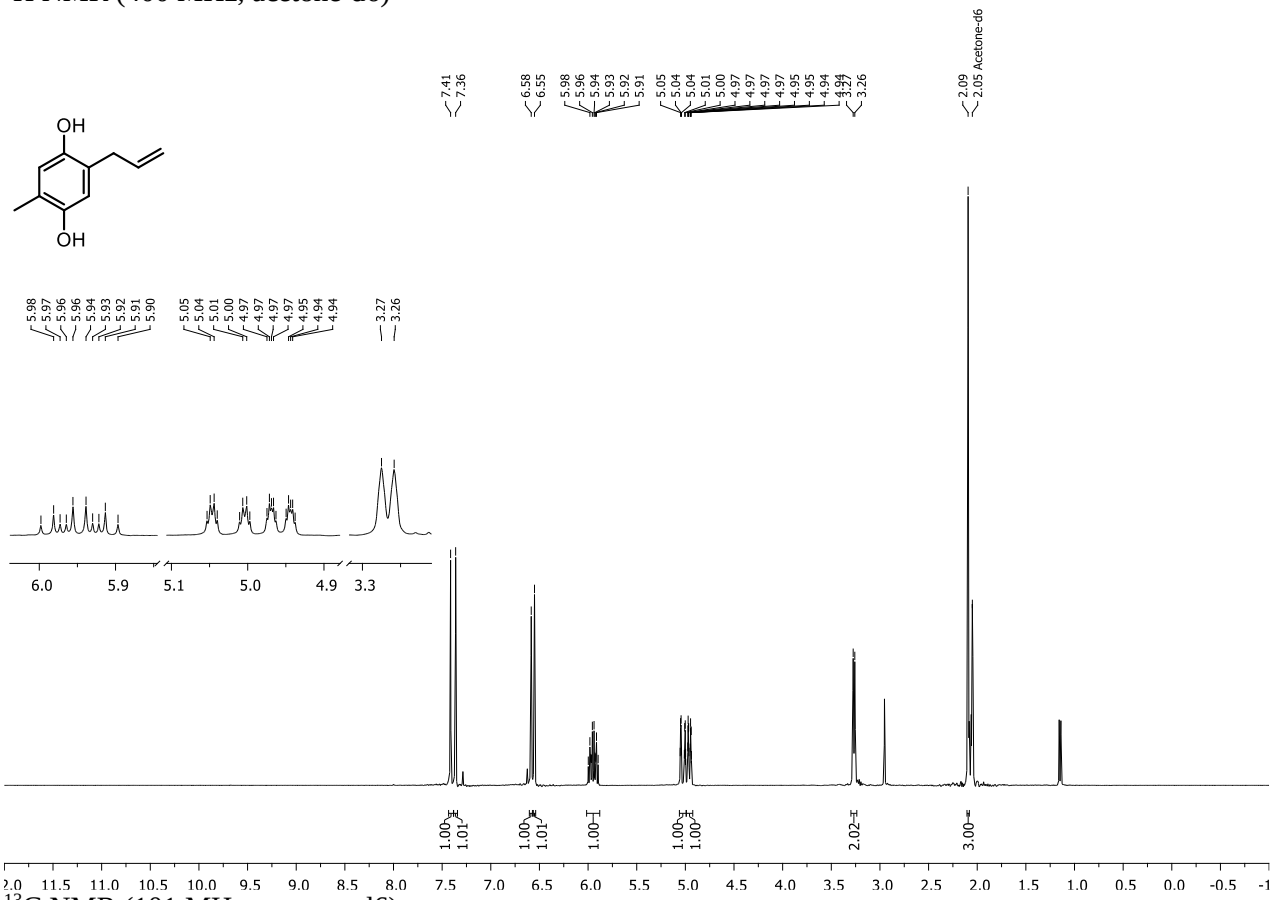


^{13}C NMR (101 MHz, $CDCl_3$)

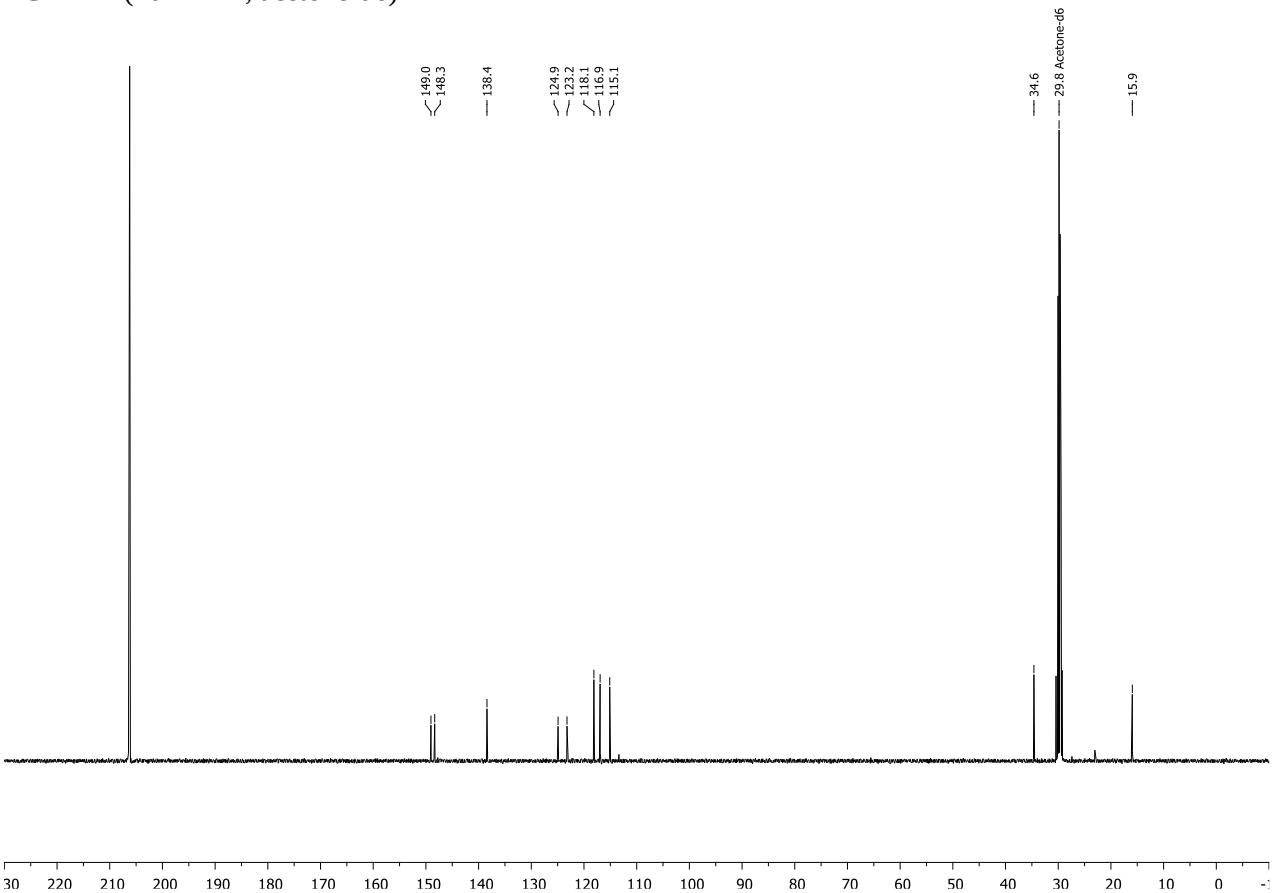


2-Allyl-5-methylhydroquinone (3a)

^{1}H NMR (400 MHz, acetone-d6)

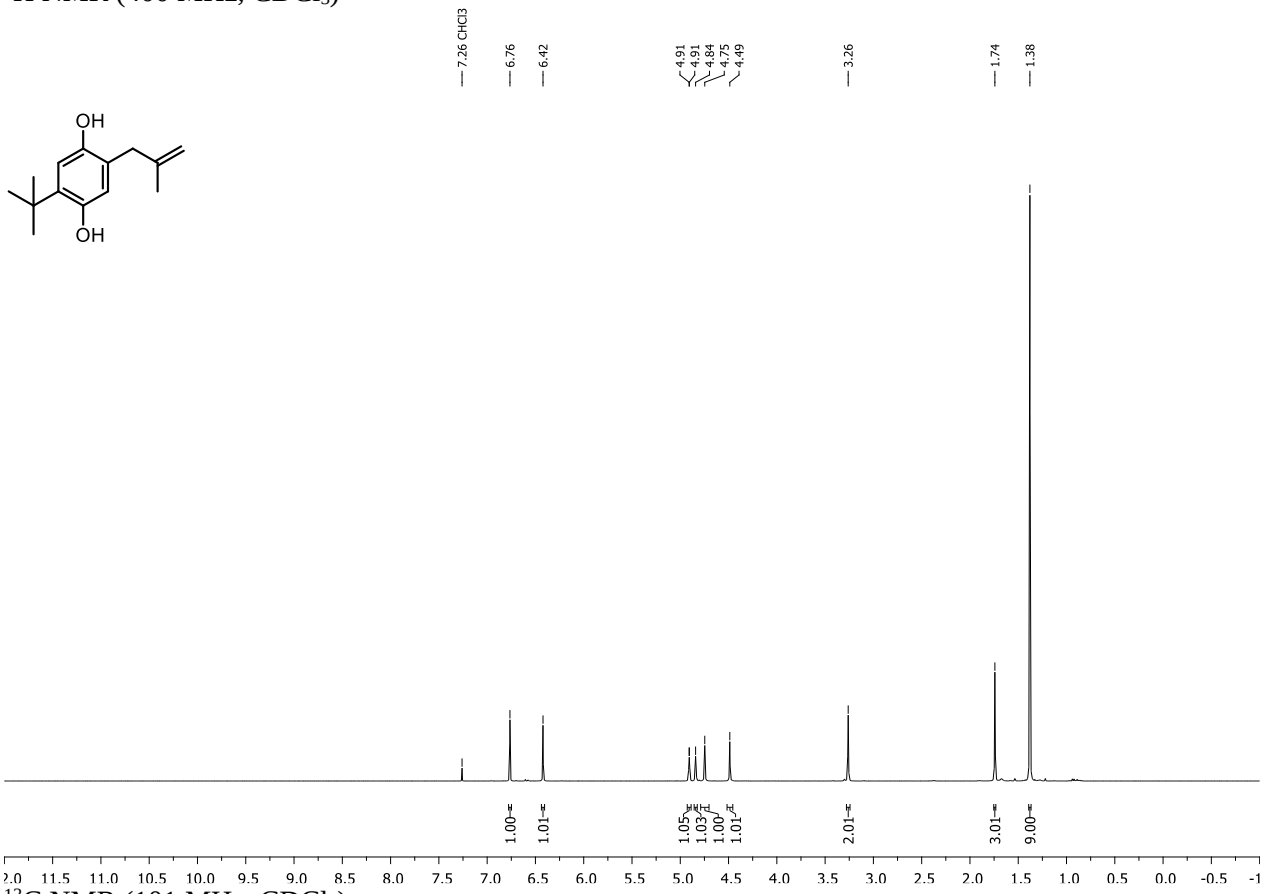


^{13}C NMR (101 MHz, acetone-d6)

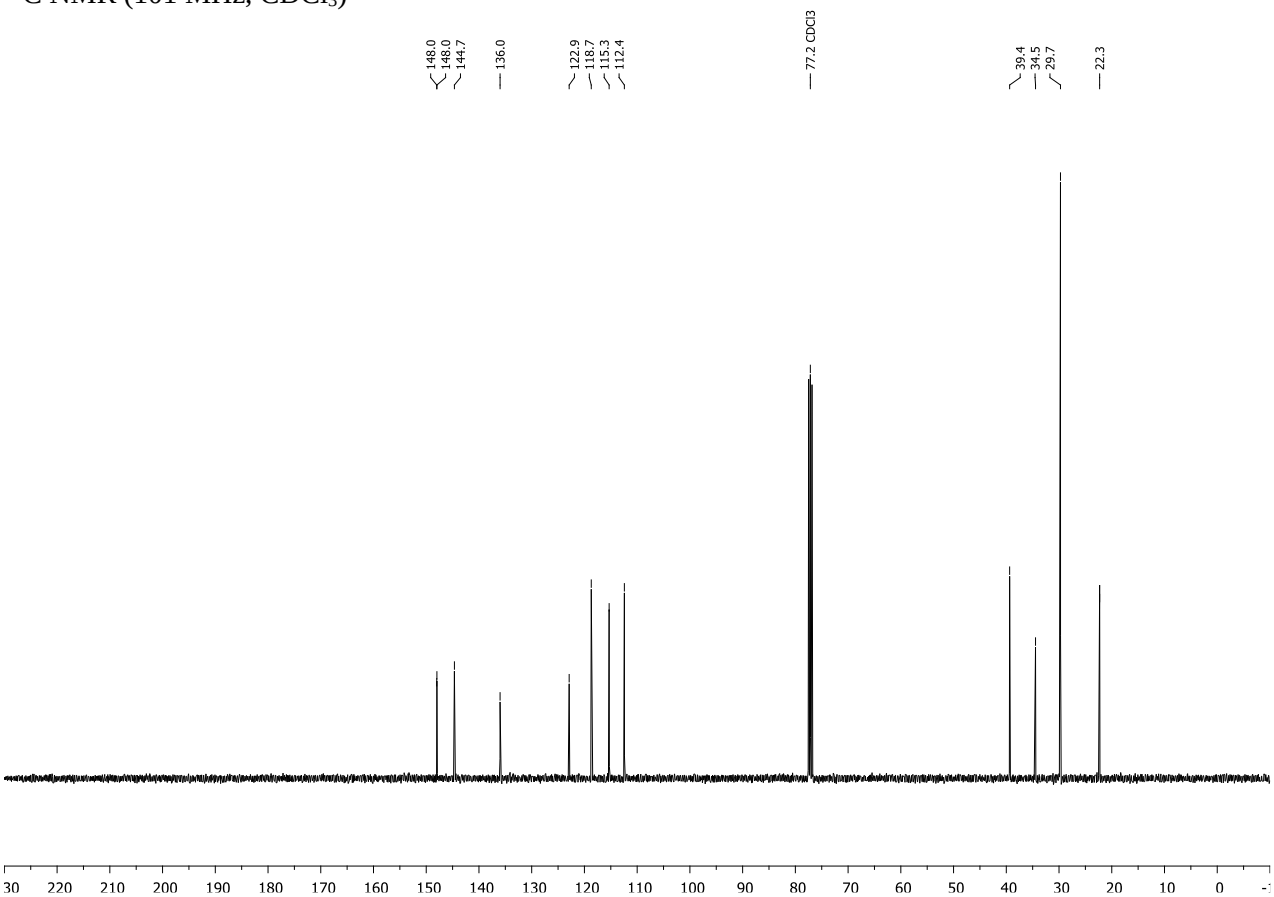


2-(*tert*-Butyl)-5-(2-methylallyl)hydroquinone (3u)

^{1}H NMR (400 MHz, $CDCl_3$)

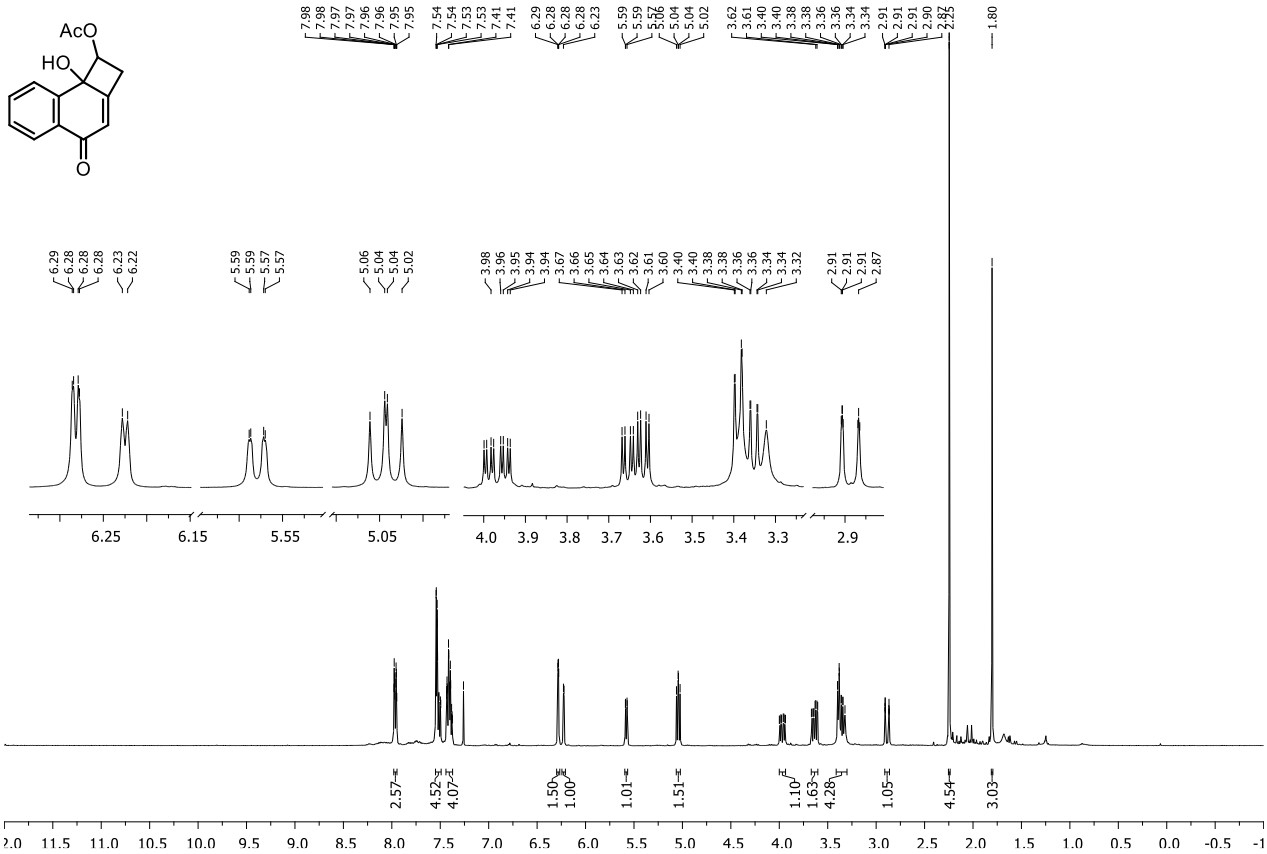


^{13}C NMR (101 MHz, $CDCl_3$)

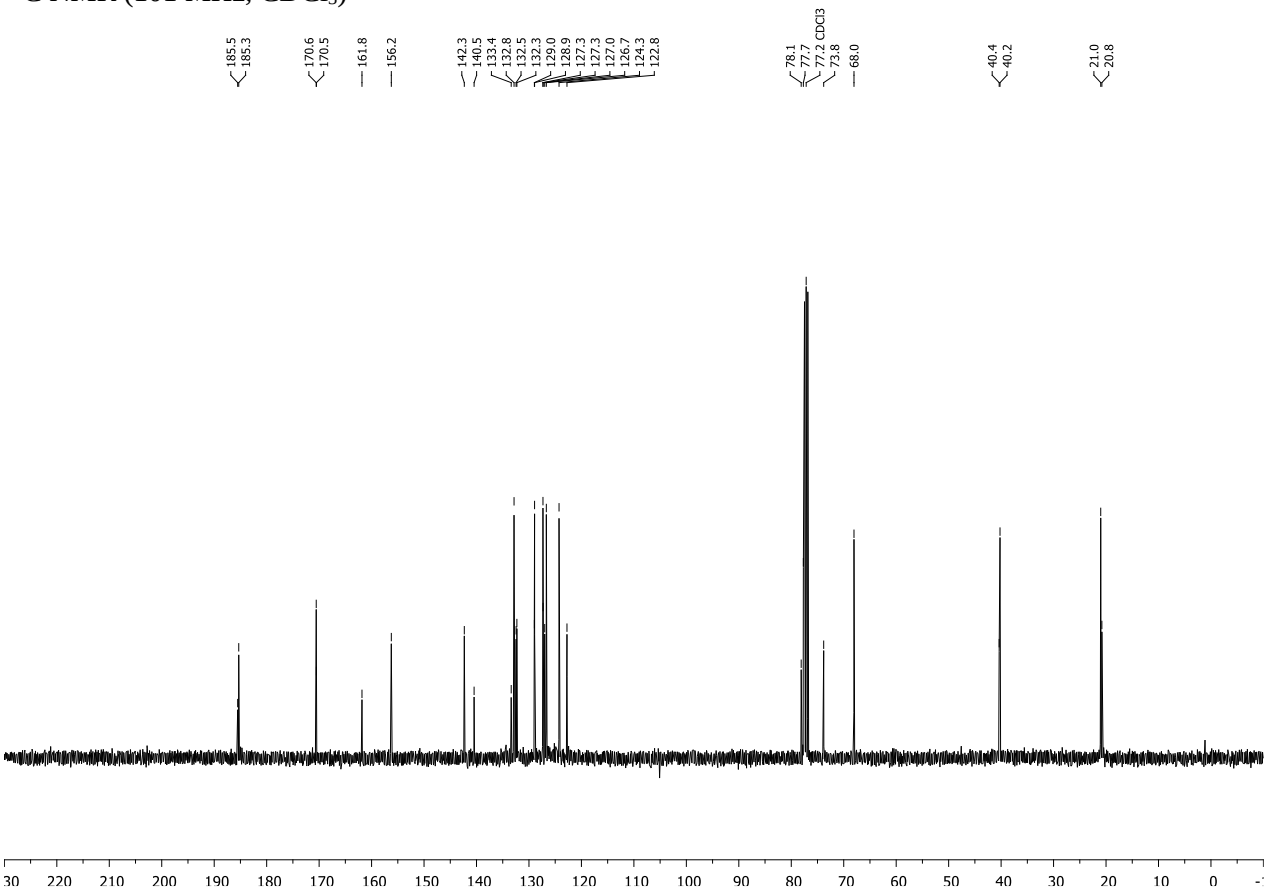


8b-Hydroxy-4-oxo-1,2,4,8b-tetrahydrocyclobuta[a]naphthalen-1-yl acetate (5)

^{1}H NMR (400 MHz, $CDCl_3$)

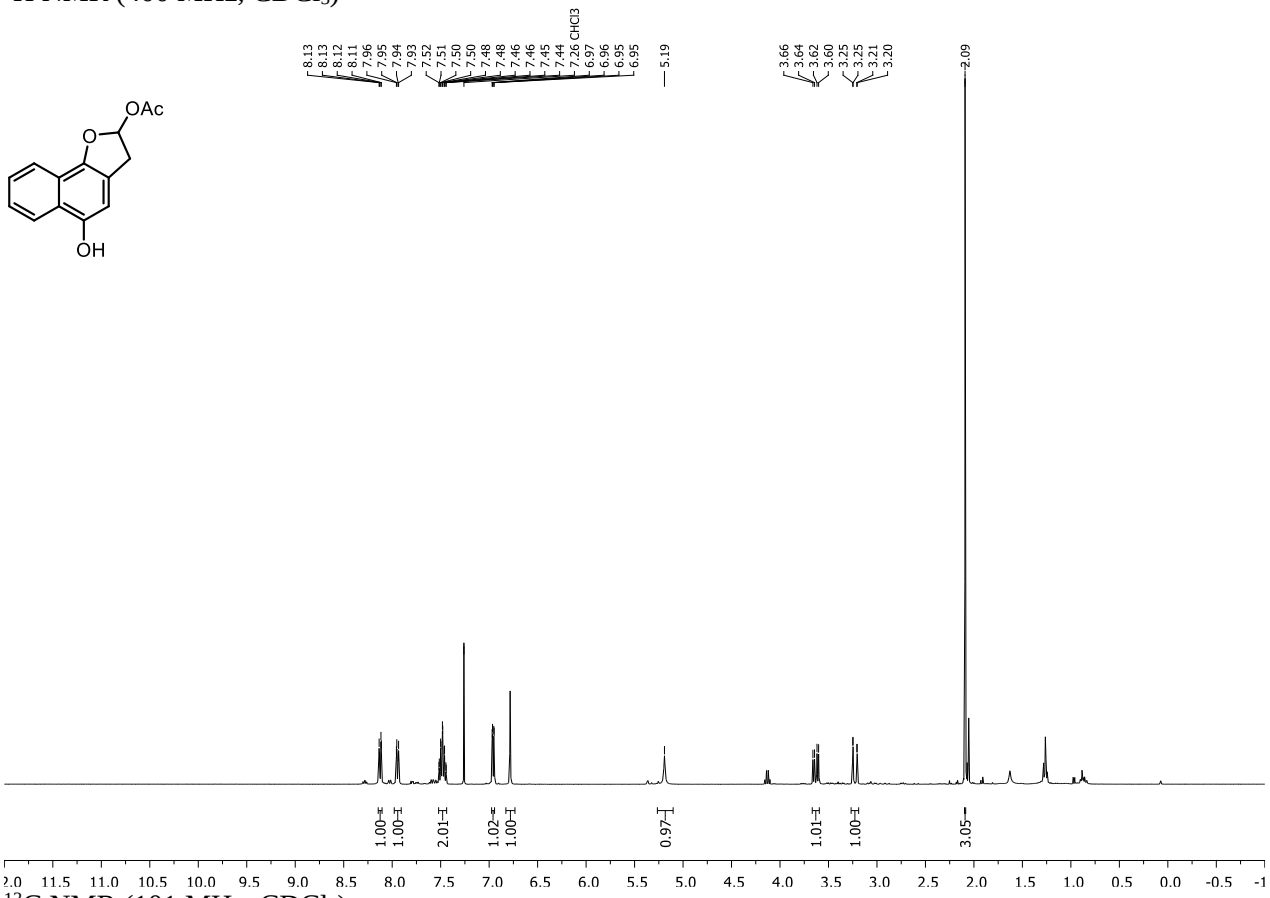


^{13}C NMR (101 MHz, $CDCl_3$)

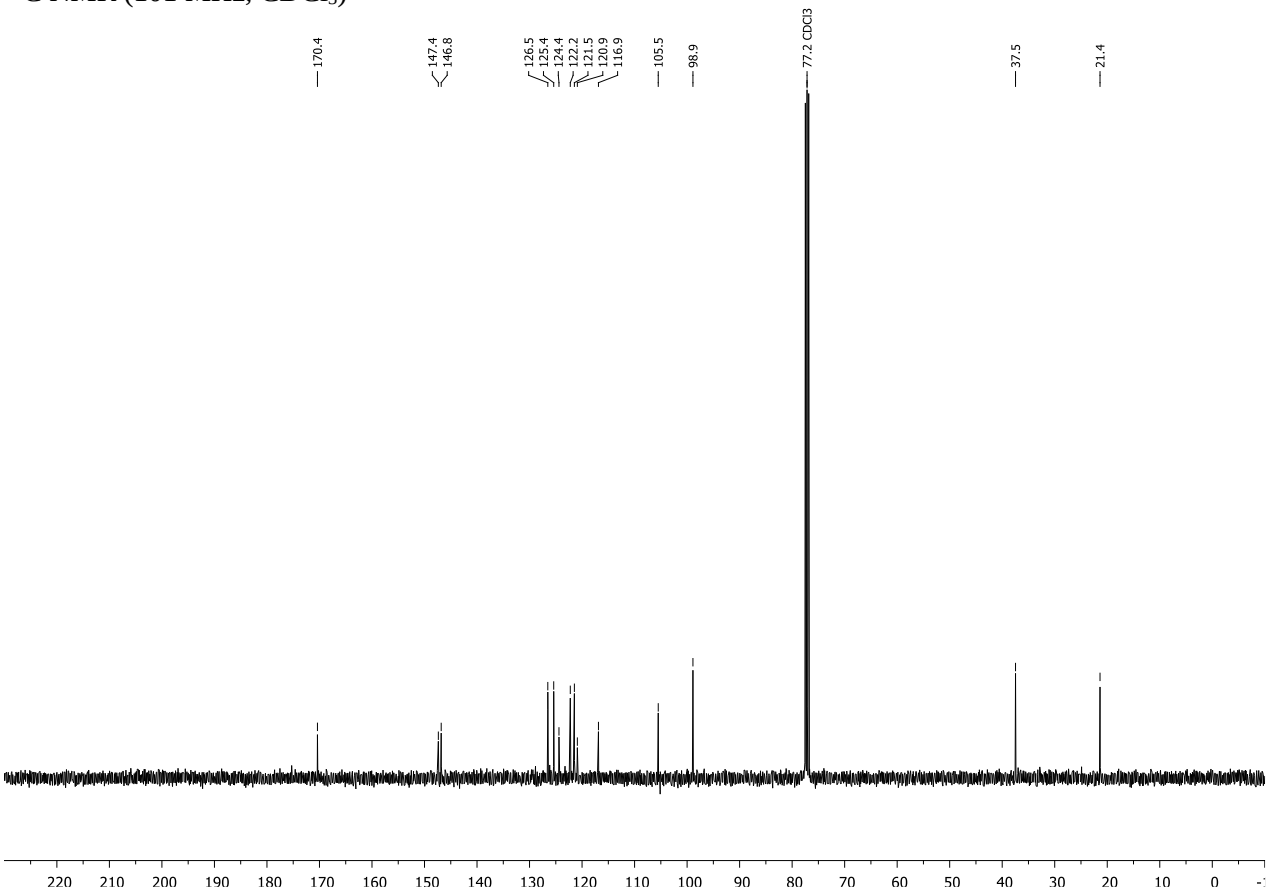


5-Hydroxy-2,3-dihydronaphtho[1,2-b]furan-2-yl acetate (4af)

^{1}H NMR (400 MHz, $CDCl_3$)

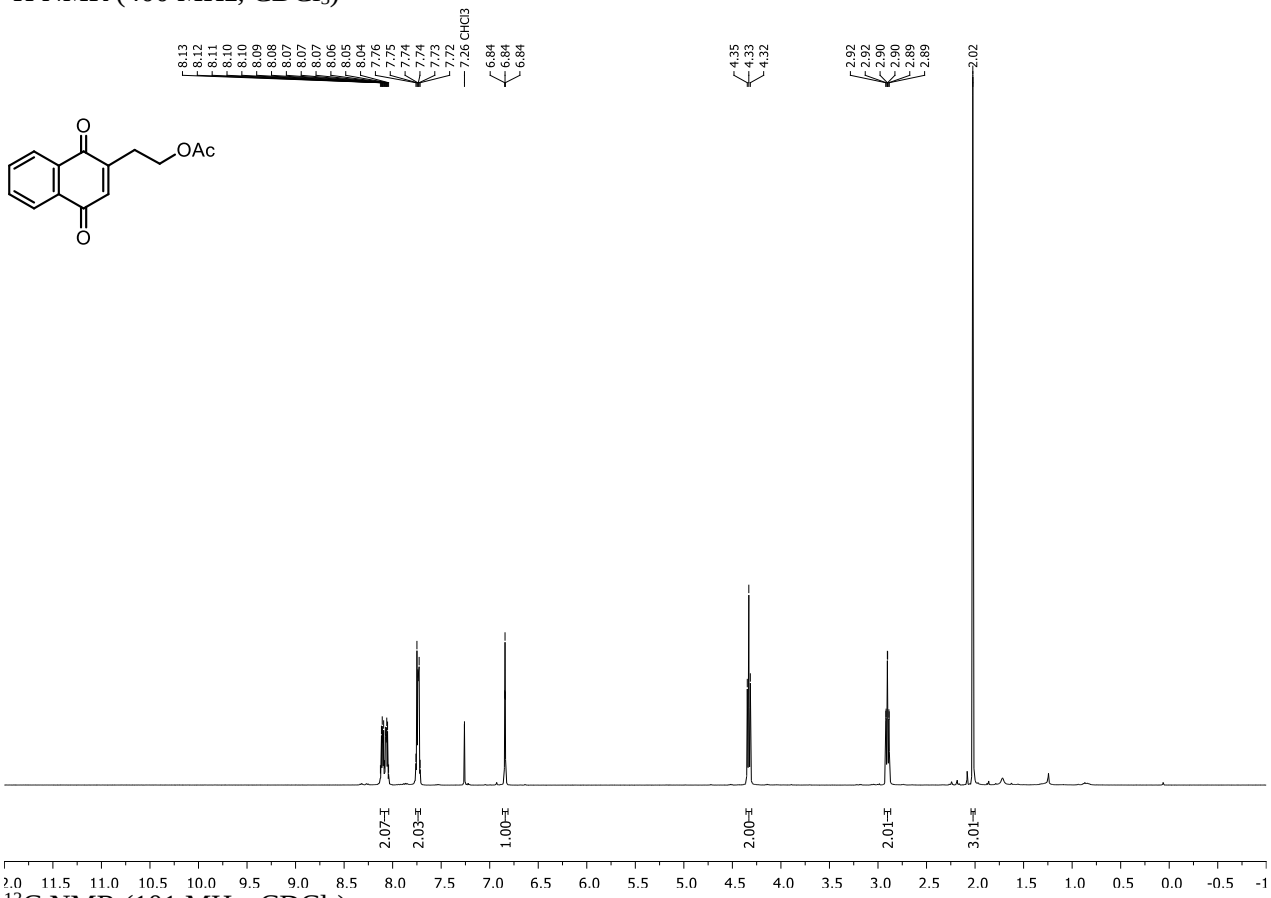


^{13}C NMR (101 MHz, $CDCl_3$)

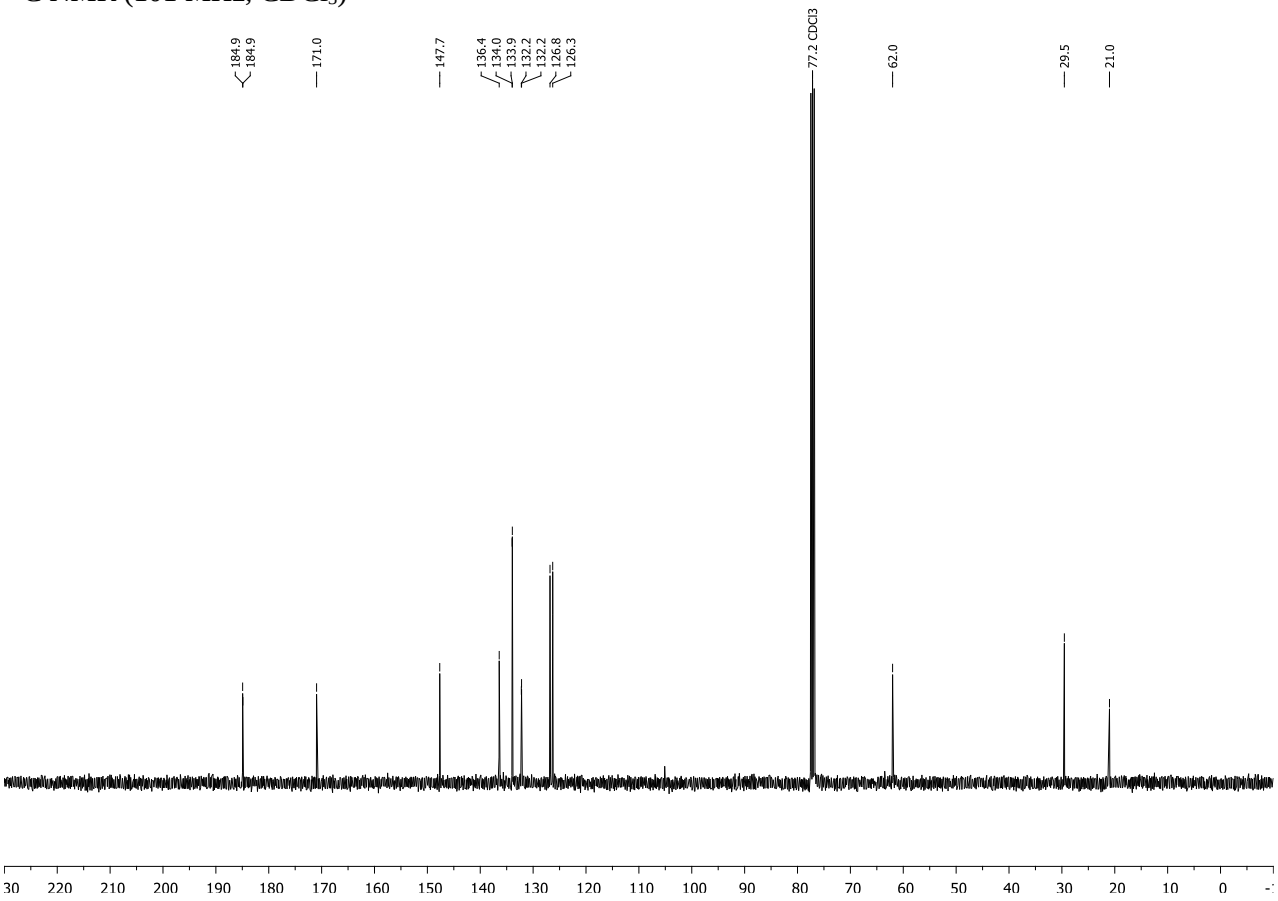


2-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)ethyl acetate (1ah)

^{1}H NMR (400 MHz, $CDCl_3$)

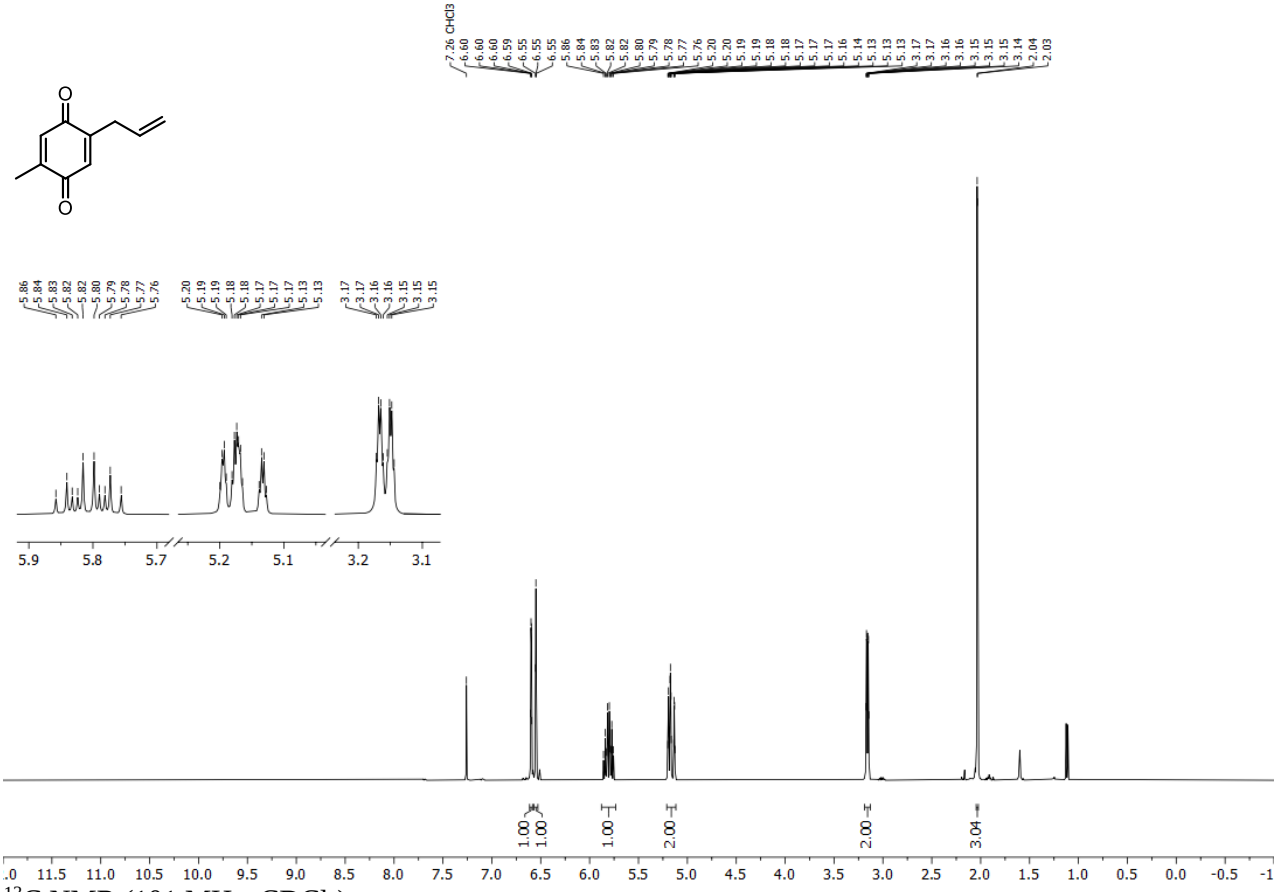


^{13}C NMR (101 MHz, $CDCl_3$)

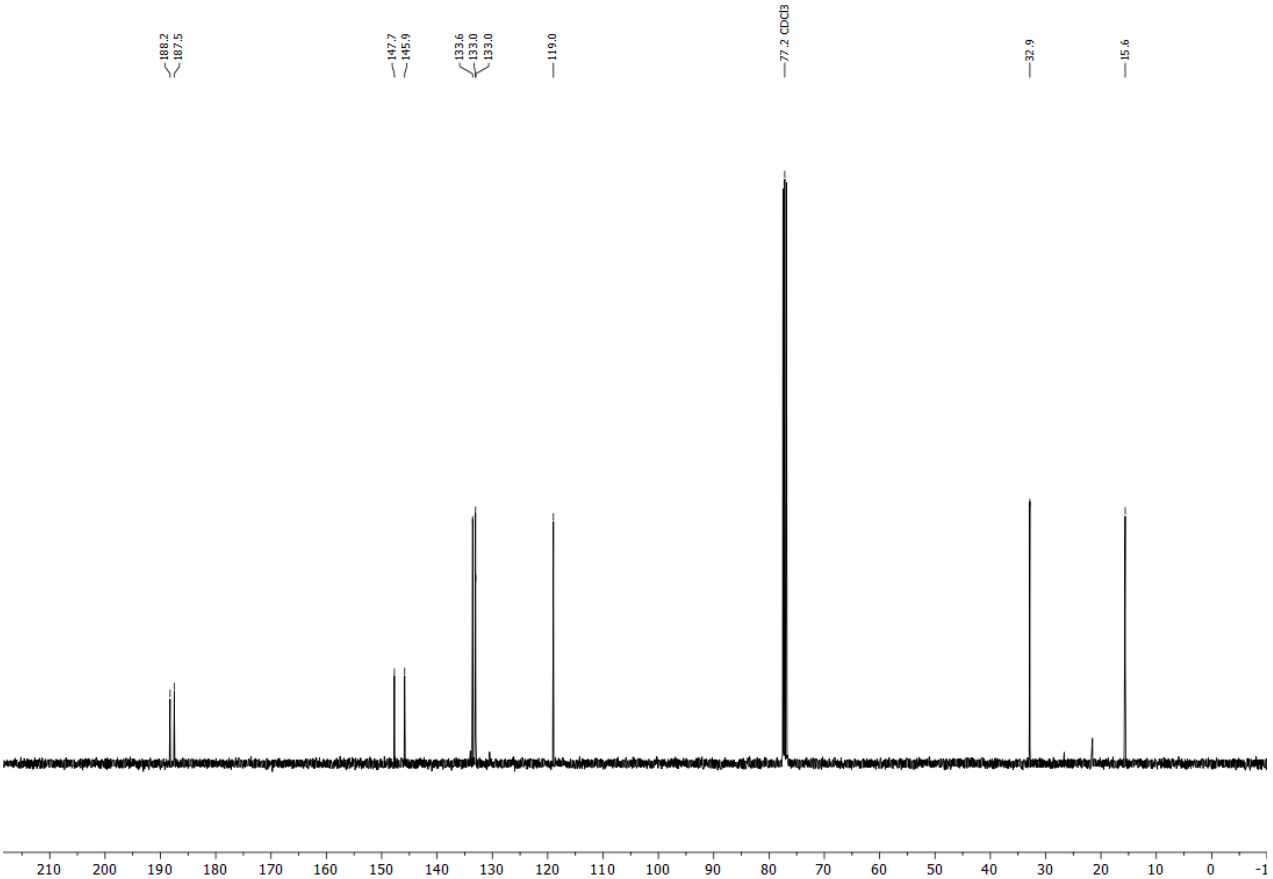


2-Allyl-5-methyl-1,4-benzoquinone (1ag)

^{1}H NMR (400 MHz, $CDCl_3$)

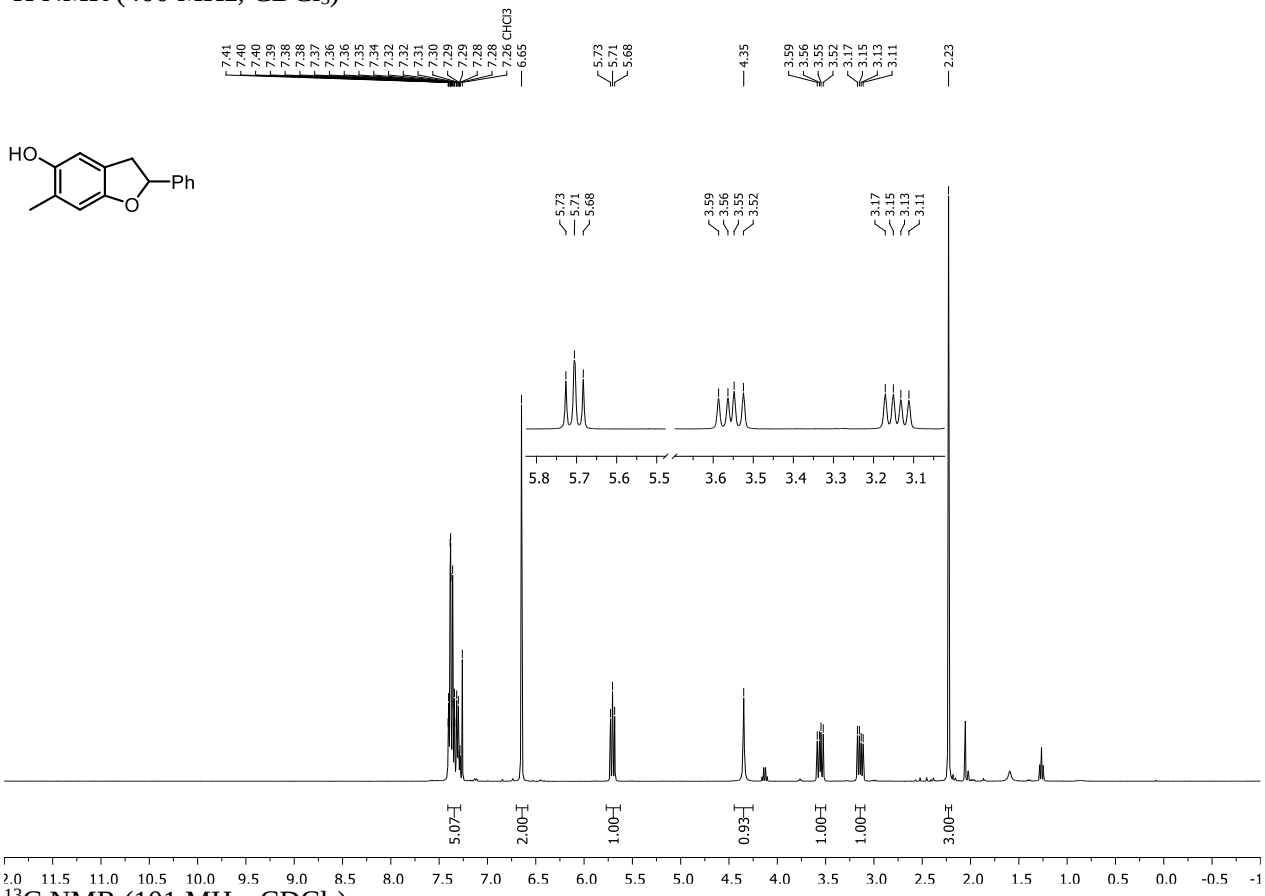


^{13}C NMR (101 MHz, $CDCl_3$)

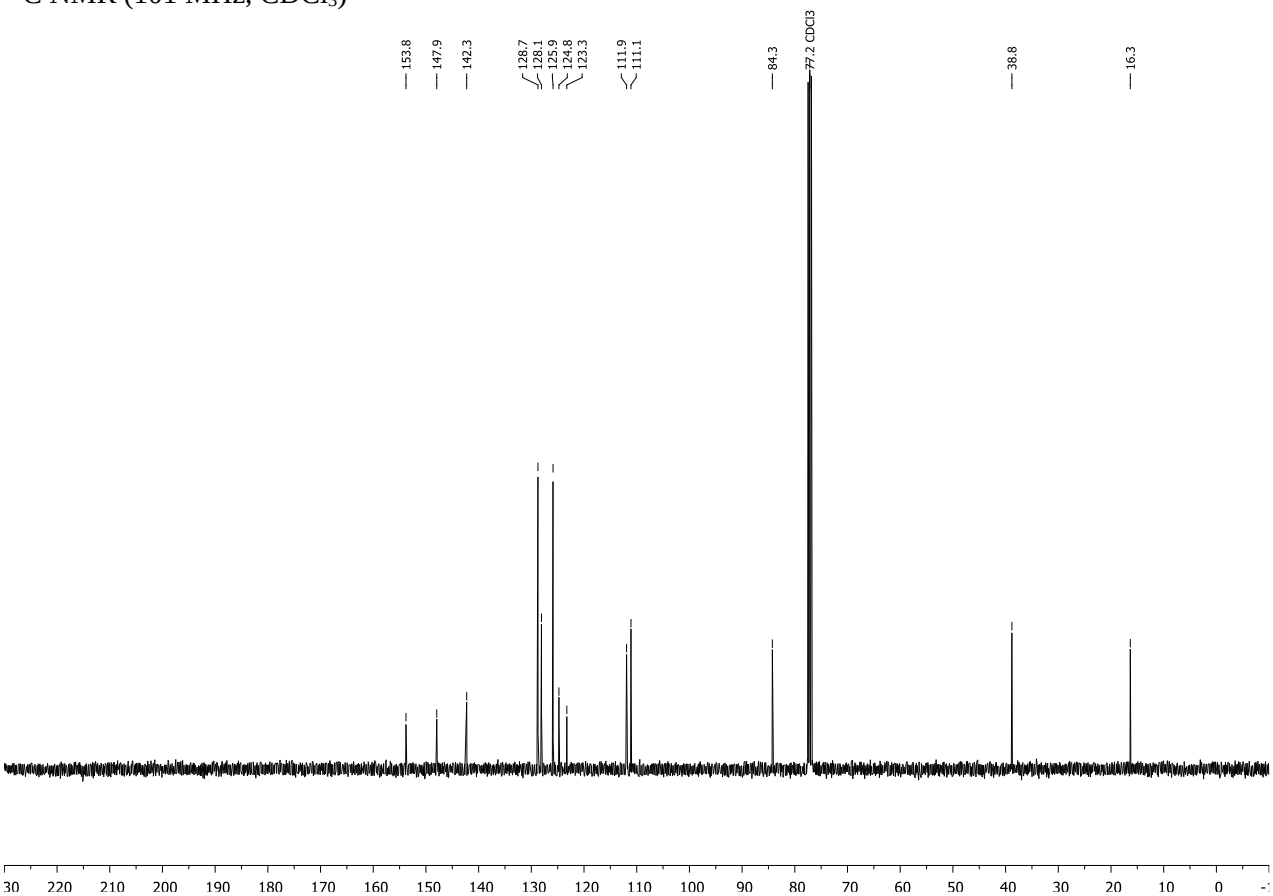


6-Methyl-2-phenyl-2,3-dihydrobenzofuran-5-ol (4k)

^{1}H NMR (400 MHz, $CDCl_3$)

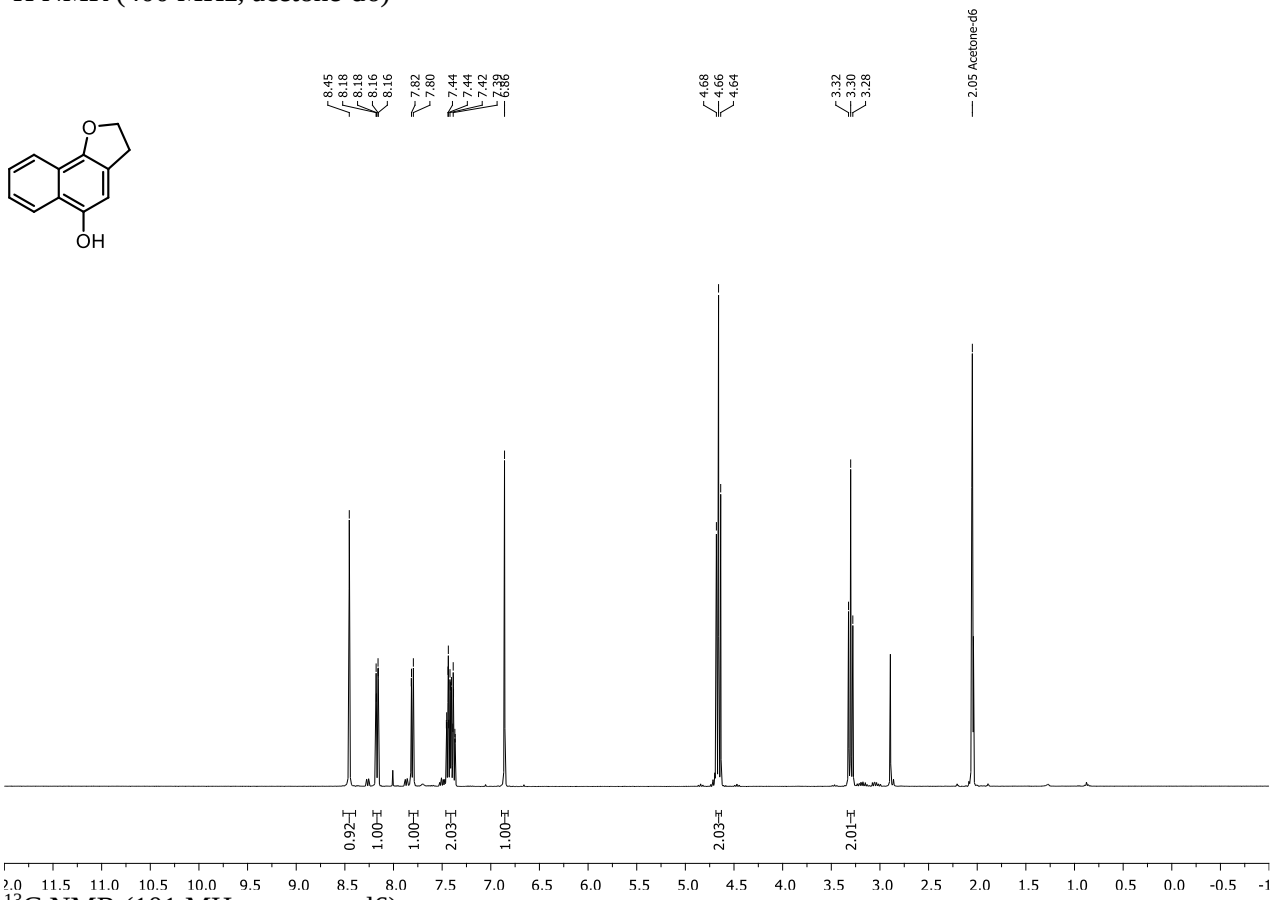


^{13}C NMR (101 MHz, $CDCl_3$)

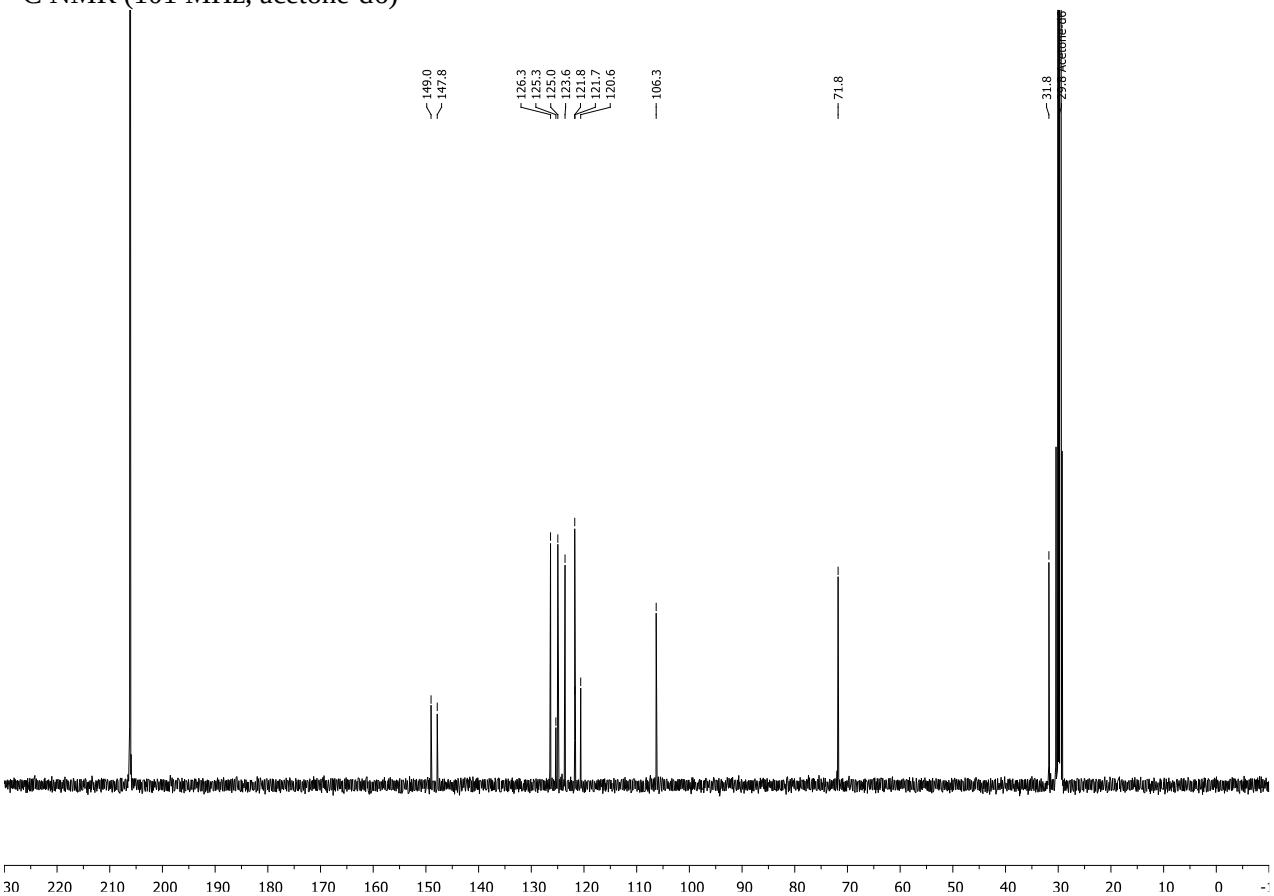


2,3-Dihydronaphtho[1,2-b]furan-5-ol (4s)

^{1}H NMR (400 MHz, acetone-d6)

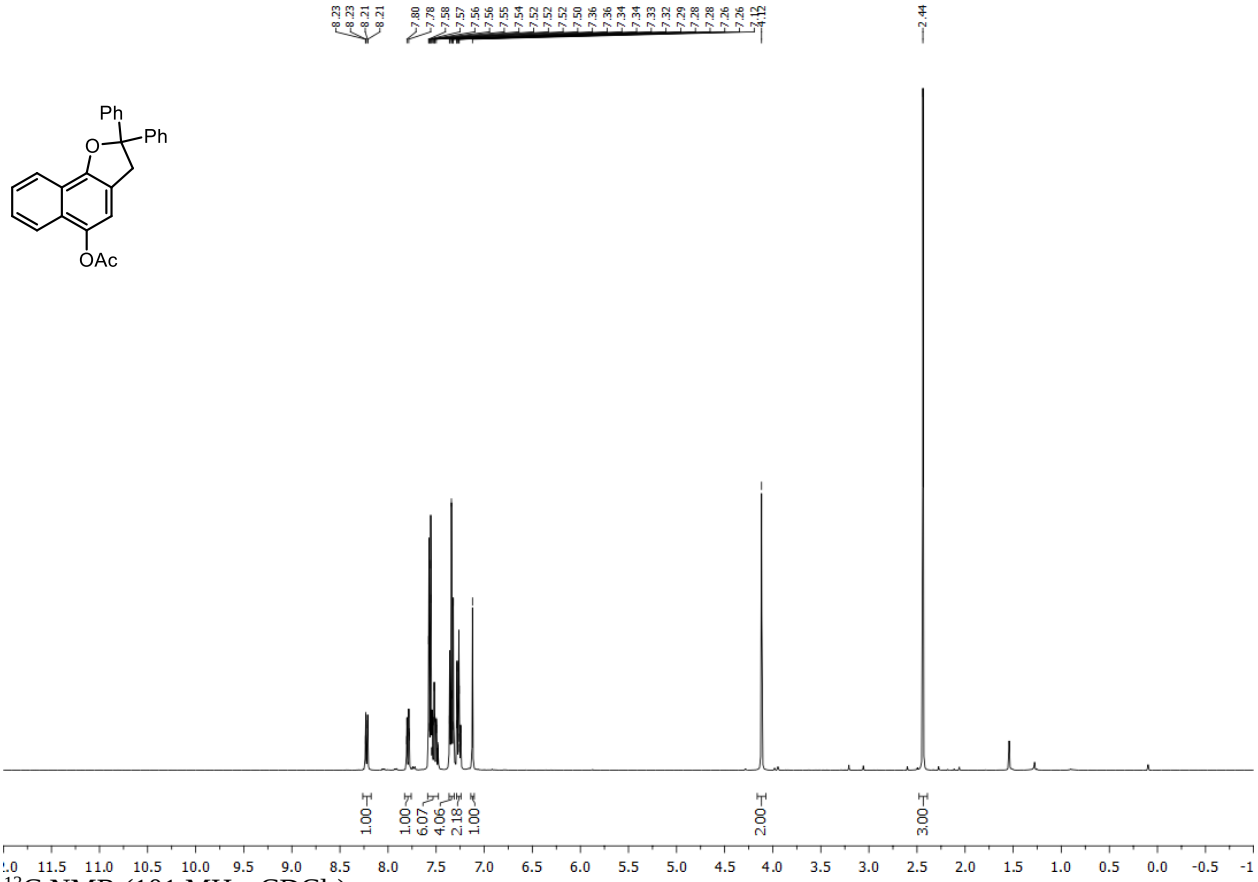


^{13}C NMR (101 MHz, acetone-d6)

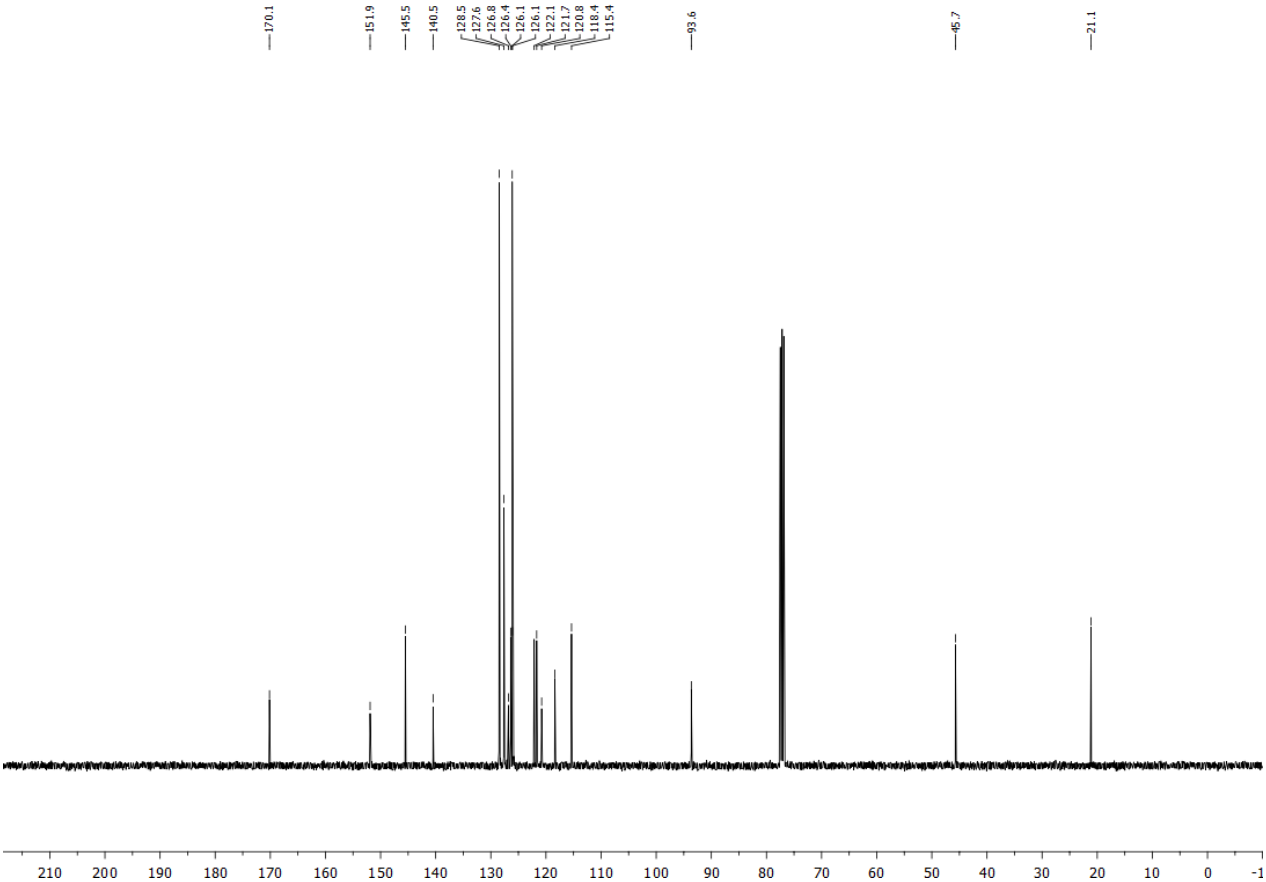


2,2-Diphenyl-2,3-dihydronaphtho[1,2-b]furan-5-yl acetate (4v')

^{1}H NMR (400 MHz, $CDCl_3$)

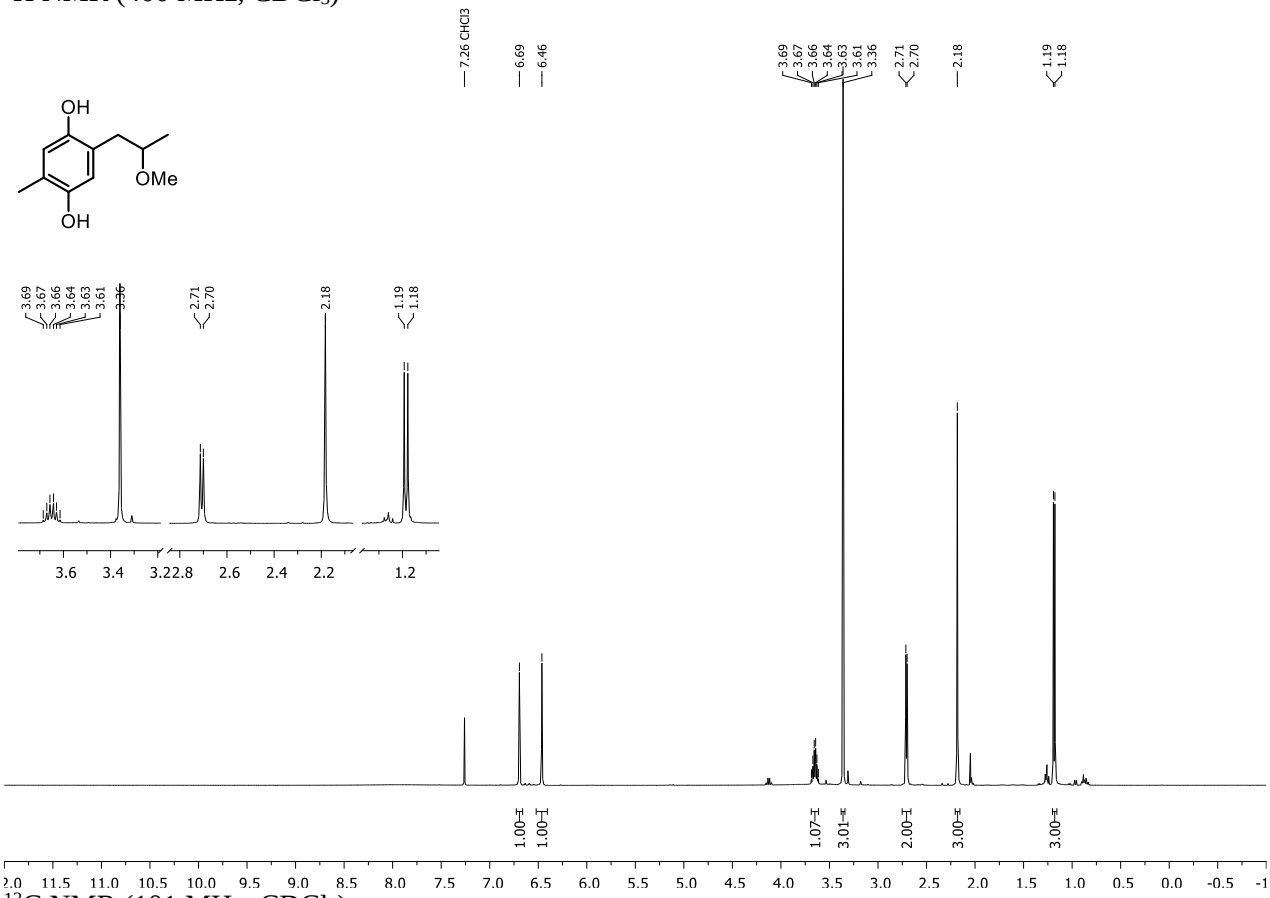


^{13}C NMR (101 MHz, $CDCl_3$)

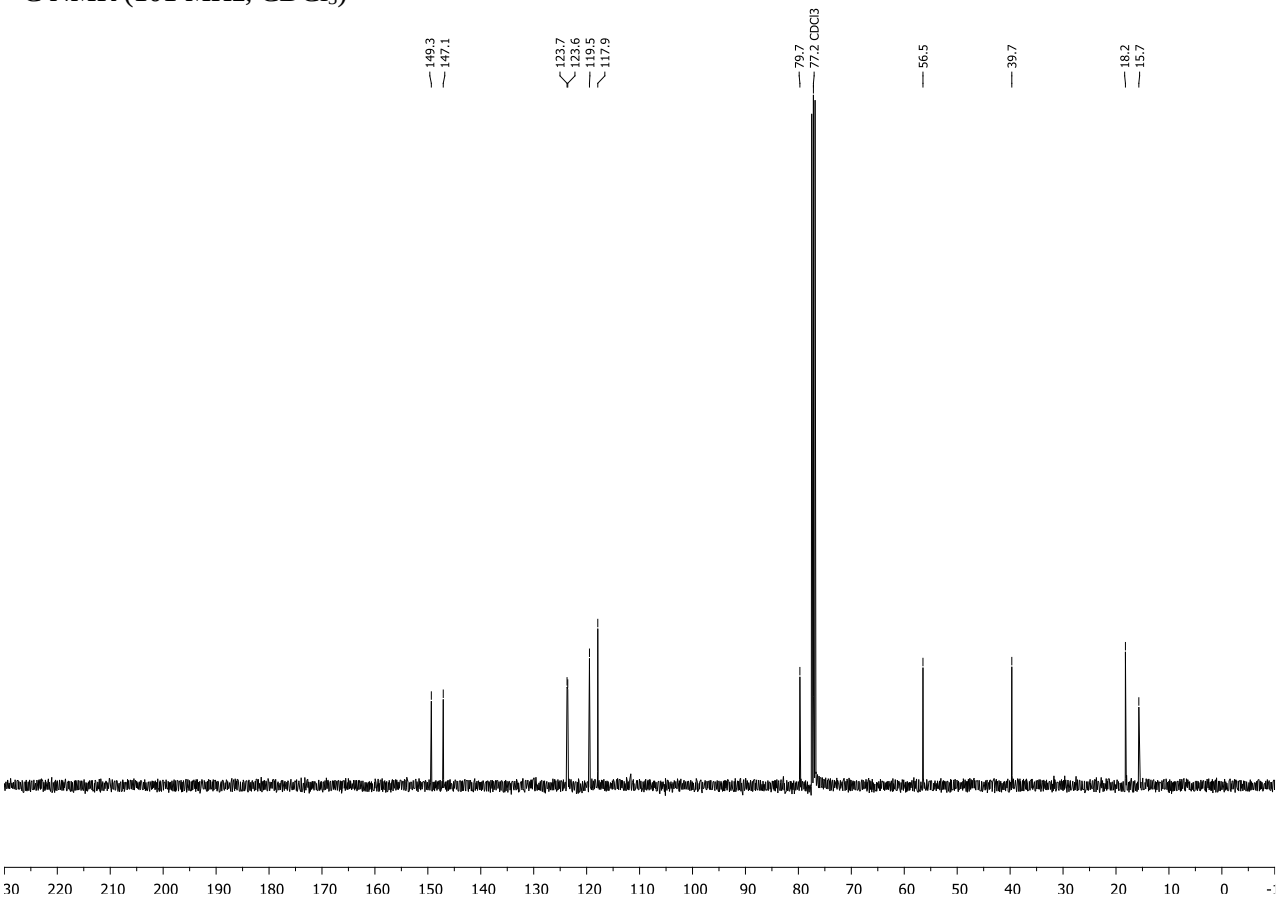


2-(2-Methoxypropyl)-5-methylhydroquinone (6)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



5. Computed XYZ coordinates of structures optimized at DFT (PBE0-D3BJ/def2-TZVP+CPCM) level

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II

C	0.47014421590999	0.03323063529520	1.53580419289233
C	-0.24311792141018	-0.77275712645374	0.55731607044171
C	0.36580047518194	-1.05306283617691	-0.63679110107960
C	1.64846870538296	-0.57354141148571	-0.93607719484078
C	2.38127439330665	0.22045861841235	-0.01277093068498
C	1.78736194757445	0.49719194567828	1.18357955531025
C	-1.60621983492090	-1.26241269016914	0.89138054440171
H	-0.14672904951275	-1.65816322455921	-1.38037822375129
O	2.23747034031274	-0.85868012431399	-2.10335861301459
C	3.74884460874829	0.74203514495574	-0.41554324918235
H	2.29973419516045	1.08549716270514	1.93505340014461
O	-0.03983918763304	0.30310327982919	2.64368784022739
H	4.26070184215555	-0.07887381005333	-0.92826890848416
C	3.55229153290853	1.85615275696238	-1.38890994887911
C	4.59700756279807	1.17958977027281	0.77015238819297
H	3.33593606394940	2.85069674105078	-1.01464146913840
H	3.43062696022461	1.66013465793092	-2.44599677304391
H	1.65920196017323	-1.41338915574231	-2.64158252364971
H	5.59583613371457	1.45184286999538	0.42527293328181
H	4.16810061853318	2.05456922122348	1.26460653265687
H	4.69165816697490	0.38047415831697	1.50858406766524
H	-2.01602645494956	-1.87103063645193	0.08524218380021
H	-1.58780867390285	-1.85242949185294	1.81143419757692
H	-2.28025660068033	-0.42214245536939	1.07950402915687

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II + TMAO

C	0.05909769564820	0.23006020711553	1.34420999924537
C	-0.40177436986390	-0.77569566960207	0.40300964981667
C	0.34235631635490	-1.03791630345529	-0.71374564688555
C	1.55327779460078	-0.36113233573034	-0.98664375234792
C	2.03893554736000	0.62363886265358	-0.07464182802707
C	1.29971455926403	0.89355155267506	1.03968930331084
C	-1.67314432622162	-1.49343877571454	0.69607082082825
H	0.01153103319904	-1.78692848620585	-1.42604734273774
O	2.25165960464705	-0.61273705149636	-2.06966996280215
C	3.35990642780493	1.29428168842348	-0.36124412751074
H	1.63710183267333	1.63942571275074	1.75192169200646
O	-0.59536538408303	0.50541648273382	2.37604012955214
H	3.41946074008018	1.39994287638674	-1.45681898436727
C	3.48590673977921	2.64283315334598	0.24245821014316
C	4.52081111672964	0.38124958466118	0.04958456528510
H	4.46757132732776	3.04535240677407	0.46116833935759
H	2.63172715153152	3.30519522464422	0.31191590812872
H	1.75971427784003	-1.28060512887538	-2.76634900245944
H	5.47677283083461	0.83908335911595	-0.21611427387536
H	4.50684459947333	0.21419968132137	1.12922914244409
H	4.45041134115023	-0.58528323762712	-0.45149558892156
H	-1.90784718411629	-2.21379420501326	-0.08826955429628

H	-1.60733791930307	-2.02088241484770	1.65180913739261
H	-2.50386586377846	-0.78893270934425	0.79198866720201
O	1.19221305982945	-2.09959007221755	-3.69754158242338
N	0.75636236021641	-1.38061201023517	-4.78589033753398
C	0.13837056924126	-2.33180238105624	-5.73744326511032
C	-0.24827603208207	-0.37346457299212	-4.36041450680713
C	1.90516176510274	-0.70142617461005	-5.43620516812017
H	-0.61987590173429	0.16217883274368	-5.23330147720888
H	-1.05384562484146	-0.90511903428444	-3.86017820433095
H	0.23615915742191	0.31420602226185	-3.67117790125316
H	-0.20927640436194	-1.79185628879476	-6.61744435070072
H	0.89570213107762	-3.06411952279537	-6.00571073232849
H	-0.69054398735484	-2.81657601804519	-5.22763617891721
H	1.55607108881370	-0.15492494575526	-6.31170939227422
H	2.34599731989335	-0.02117306442126	-4.71099153524435
H	2.62116460984564	-1.46935424448758	-5.71817086822872

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TMAO

O	1.06830107140868	-2.10092126254285	-3.85240412923574
N	0.53272454381723	-1.30180267374820	-4.81153641572467
C	-0.10242873775798	-2.13131900917493	-5.86661835172612
C	-0.49402762464595	-0.41173313293739	-4.21343594723406
C	1.59552838304276	-0.46801993217510	-5.42771882760442
H	-0.93327435400375	0.23453117197084	-4.97471776249072
H	-1.25210465628041	-1.04950445985247	-3.76490167916727
H	-0.00172405876804	0.17804694760300	-3.44375340113660
H	-0.53039028812374	-1.49929941094115	-6.64602518018375
H	0.66863658108662	-2.77963397774205	-6.27622495327301
H	-0.87445128115653	-2.72908338579538	-5.38773138387629
H	1.17732533948403	0.18134619161940	-6.19815633576869
H	2.04741841849657	0.11921549712541	-4.63169969157701
H	2.33232073937843	-1.14527076995278	-5.85339189872229

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TS1: pro-*syn*

C	0.46048721237008	0.19345580122744	1.42821701833841
C	-0.17074900787748	-0.69280616980056	0.44983272905808
C	0.48617895714454	-1.03594754763826	-0.70781449086171
C	1.75782239425661	-0.54746941304292	-1.00357245867407
C	2.42479643502223	0.31462663113244	-0.06901840438194
C	1.76349226835284	0.65321169198763	1.10297024387498
C	-1.53151513143589	-1.20117678614237	0.75153376729372
H	0.00808010426304	-1.69855823662875	-1.42493227657275
O	2.38059173390219	-0.90156748231616	-2.13458797468447
C	3.78608732876335	0.90816912284018	-0.36553218005575
H	2.26577886317931	1.28838260328897	1.82438614031980
O	-0.13761856035401	0.48789411062675	2.48973822867190
H	4.10242256403963	1.43798547973768	0.53369608563240
C	3.10559377685275	1.80835057756266	-1.30483165188269
C	4.90413328487204	0.02302463581409	-0.87154908858683
H	2.65262733665904	2.72344190169965	-0.94819051173011
H	2.99138804779838	1.53482459279120	-2.34573144689368
H	1.81027656225784	-1.48613795919068	-2.64908437048310
H	5.80468898838875	0.62614201582289	-1.00577186026040

H	5.12476764046514	-0.75979958953058	-0.14307849208568
H	4.66016880012567	-0.44749154145825	-1.82167264617243
H	-1.89666244681919	-1.86710525221763	-0.03022499860018
H	-1.53237751046794	-1.72852039545354	1.70964929816221
H	-2.22881364175907	-0.36681679111189	0.87028234057426

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TS1: pro-*anti*

C	0.50105463971955	0.10994631671798	1.51121982969106
C	-0.18887537844162	-0.69923337992292	0.50607739344114
C	0.43656250995896	-1.03674213856184	-0.67265193923900
C	1.72889646794410	-0.60470247175324	-0.95250919809701
C	2.44478807806773	0.19747620285081	-0.00057347723989
C	1.82558542078090	0.51856914350427	1.19474258238332
C	-1.57364111225379	-1.14107364787558	0.80388066441368
H	-0.07996075473040	-1.65129467666749	-1.40537827263349
O	2.36257715703032	-0.95528305146992	-2.07806864486565
C	3.82383837710907	0.67957141735960	-0.38659440415837
H	2.35669591866207	1.09433923877934	1.94218725036207
O	-0.07011344795457	0.39149991488763	2.59053069942381
H	4.32564412899479	-0.06319384635904	-1.00556755063735
C	3.15449711485752	1.71428018593886	-1.19249085377945
C	4.71178657398443	1.15803087689864	0.73837586613631
H	2.84675884096474	2.63715864948843	-0.71661737654722
H	2.88830245234628	1.53806087719772	-2.22520647214871
H	1.78410800660374	-1.50145827916610	-2.62453402314569
H	5.65907222537700	1.51363344486702	0.32937683717589
H	4.25498644984871	1.98177033190743	1.28958806153266
H	4.92042233047361	0.34765084616152	1.43957107069238
H	-1.97542095590584	-1.77123119405489	0.01047645291335
H	-1.60028229074860	-1.68529423031136	1.75195288634614
H	-2.22682075268877	-0.27398653041694	0.93951161798001

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TS1: pro-*syn* + TMAO

C	0.46393900757587	0.16999482390981	1.41129372040608
C	-0.17236080035189	-0.72880353801813	0.44769601348643
C	0.46226529875247	-1.07625327799204	-0.71496360804500
C	1.73577040866236	-0.57952769973779	-1.05855402729487
C	2.39689146649141	0.30483966253632	-0.12600486002727
C	1.75331691259735	0.63816921050704	1.06126133897010
C	-1.52398471463721	-1.25053501104021	0.77874025584958
H	-0.01688171504721	-1.75441295101783	-1.41335503380079
O	2.31780606268219	-0.92659140587708	-2.17690327338829
C	3.74142319193751	0.91609163139941	-0.44341062375837
H	2.26150031065651	1.28152868303447	1.77232949944422
O	-0.12181639437371	0.46518891258886	2.48449279925024
H	4.07360820751566	1.45039496610670	0.44776963250561
C	3.02198366543319	1.80952384262318	-1.36360075757020
C	4.86225211392035	0.05234850658031	-0.97943382435110
H	2.57611291168285	2.72390721836975	-0.99663005351532
H	2.86669906525263	1.52192145130049	-2.39476169556709
H	1.67296803338513	-1.47026090757115	-2.86863024643080
H	5.74455669358341	0.67302390587626	-1.15291851052083
H	5.12722197541220	-0.71737748161751	-0.25113469924000

H	4.58830566186892	-0.43604755112315	-1.91187251929610
H	-1.89586534244869	-1.92133319839592	0.00378131076681
H	-1.50299784960746	-1.77892448583728	1.73595926782151
H	-2.22890501648409	-0.42431746804754	0.90897895742050
O	0.94777374553519	-2.13865210496067	-3.79166652634044
N	0.46900937904630	-1.29316047023427	-4.76639778645195
C	-0.15236169127003	-2.12767168660503	-5.82013644948541
C	-0.54874942394698	-0.37902464723987	-4.18949423584129
C	1.58276018509303	-0.50272394999420	-5.34839090357635
H	-0.95181800414895	0.25811615052189	-4.97588272158376
H	-1.32994712154849	-0.99414703553906	-3.75016585981894
H	-0.06722109102370	0.22251547456742	-3.42193980982529
H	-0.54182829278998	-1.48610885185975	-6.60981437356193
H	0.61469023293034	-2.79495141356524	-6.20486599949267
H	-0.95211154491699	-2.70001427575118	-5.35665919643631
H	1.19755039452682	0.14045218750768	-6.13867769044038
H	2.02254337146955	0.09188915207341	-4.55113293424329
H	2.31289570658388	-1.20548136747804	-5.74219557601658

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TS1: pro-*anti* + TMAO

C	0.49049126046852	0.08885855959611	1.48645673913371
C	-0.19805350074427	-0.74164536601057	0.49804600219267
C	0.41198201032471	-1.09192460212123	-0.67882600219023
C	1.70878172891434	-0.65292981774023	-1.00153928345658
C	2.40909409833177	0.18678198142966	-0.05589247956300
C	1.80133499688321	0.51062299135222	1.14807038214662
C	-1.57576346047722	-1.19682915537839	0.82045943479834
H	-0.10249454291783	-1.72924817291761	-1.39036428653538
O	2.31024043530859	-1.00579542240704	-2.10637390022336
C	3.76862452399561	0.69144649312210	-0.46613047919109
H	2.33318206905035	1.10454472156867	1.88170910206825
O	-0.07441019418784	0.37587936570640	2.57274308262793
H	4.26645648028673	-0.04324344043775	-1.09773056148412
C	3.06033875655298	1.71267712655818	-1.26008657144217
C	4.67645014027374	1.18946811191524	0.63395273862505
H	2.75030356733302	2.63372179781921	-0.78229654119220
H	2.75848097741009	1.51672753928267	-2.27910052661404
H	1.67134278590203	-1.53486278821520	-2.82680405530959
H	5.60126255059199	1.57619220119671	0.20145524547078
H	4.21272456806632	1.99528049004373	1.20591549149969
H	4.92977439285244	0.38177652215440	1.32389222161884
H	-1.98186248591713	-1.83302268171882	0.03353657858055
H	-1.58437934075735	-1.74158312385739	1.76851771416522
H	-2.23682484052749	-0.33707429823605	0.96401926565873
O	0.95804630805398	-2.16452832597589	-3.76635673017764
N	0.54978610615381	-1.28308404852401	-4.74221714606794
C	-0.10601289263315	-2.07067056210985	-5.81104607253077
C	-0.41809785908345	-0.31063239393803	-4.17449710758232
C	1.72117092790811	-0.56129368449293	-5.30006759615573
H	-0.75974898296139	0.36182994493701	-4.96047061313887
H	-1.24837494967204	-0.87767781911231	-3.76132670681696
H	0.08452046504569	0.24862115466113	-3.38848502651445
H	-0.44517468642311	-1.40049789194507	-6.60019935525172
H	0.62435693091782	-2.78031132251845	-6.19167499523234

H	-0.94509161480808	-2.59713418470550	-5.36294928733955
H	1.39036274854549	0.10777450713544	-6.09332091060776
H	2.18324469140754	0.00191937064584	-4.49248469464592
H	2.41278583053123	-1.30688277676231	-5.68429606932220

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IV/V: *syn*

C	0.39116777211266	0.41411086084477	1.29547733853868
C	-0.07346975176935	-0.66859067573796	0.43454128180514
C	0.54760070915966	-0.99953176445549	-0.76000755497062
C	1.67208707655985	-0.33193172611199	-1.20128809633707
C	2.23025156939709	0.69808841579731	-0.38006326682874
C	1.54417295575668	1.05276352054042	0.83345399683566
C	-1.27201056014729	-1.41054442660832	0.88638129641824
H	0.13170598935240	-1.79177242578110	-1.37717670993805
O	2.23896051004971	-0.58584064643240	-2.38406028330261
C	3.83068196655988	0.81007665922513	-0.26609464417992
H	1.97940072144375	1.84449448095520	1.43502974702574
O	-0.22810640673790	0.70047199846128	2.36263706716659
H	4.06863058565934	1.12826610320138	0.74204512129100
C	3.11260380843614	1.77173667717338	-1.07390078595736
C	4.73720162281754	-0.24628410787918	-0.81081727014180
H	2.94781705063993	2.77251228265907	-0.69750429397650
H	3.15225300484723	1.66510206487490	-2.15141024633928
H	1.76399275137270	-1.29898826365616	-2.82903418449069
H	5.75418108598078	0.15718006447313	-0.81750334656941
H	4.73612776205375	-1.13266192490001	-0.17399142559365
H	4.48021172703547	-0.53626458569918	-1.82677883863046
H	-1.54843737593041	-2.21265151207598	0.20273315928220
H	-1.09457303752370	-1.81639232185031	1.88736330812156
H	-2.11080553712601	-0.71723674701791	1.00468163077135

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IV/V: *anti*

C	0.42568442327818	0.38992046639081	1.37618516010678
C	-0.10085195539482	-0.66059015010450	0.50701176898881
C	0.48950642250730	-1.00994836801898	-0.69717504125205
C	1.63574245069573	-0.38173038847324	-1.13958393949538
C	2.23595386725303	0.62907558104699	-0.32457429827572
C	1.59584026039803	0.99263348946318	0.90766962474439
C	-1.32516736772667	-1.35328310182947	0.96759195938246
H	0.04422092858579	-1.79089481452204	-1.30774409946834
O	2.22838184639207	-0.67686596098987	-2.29946586768080
C	3.83634165625764	0.61615069229429	-0.38539038203990
H	2.04608411355771	1.77667975957922	1.50486107684986
O	-0.16907402724161	0.68707077375435	2.45359878515226
H	4.16479951138592	-0.20326270081339	-1.01538188060837
C	3.12075766540542	1.67917615953036	-1.05606819414724
C	4.62170359241988	0.81741952935077	0.87030105922824
H	3.08825631386909	2.65577016247891	-0.58957296332939
H	3.02286684017453	1.65744381154242	-2.13388729741888
H	1.75314968118080	-1.39103803899752	-2.74211958211561
H	5.66874999887320	0.97692068827776	0.59725998088729
H	4.28520975784961	1.68660751541157	1.43388324068651
H	4.57232347801113	-0.06143734467401	1.51513621448870

H	-1.64706806205454	-2.13319961430739	0.27812804968863
H	-1.15292775115413	-1.77965954344694	1.96076212043865
H	-2.13002164452339	-0.62446460294330	1.10587350518906

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IV/V: *syn* + TMAO

C	0.37540561950312	0.45452552186787	1.27942597112333
C	-0.05989836151584	-0.66702134278829	0.42940519475779
C	0.56883911118281	-1.01475310333556	-0.73786483692941
C	1.69873628095202	-0.32155177621451	-1.22825074854060
C	2.24804777813108	0.71767447698575	-0.36617103448901
C	1.52320595737290	1.08968872395431	0.83919411957844
C	-1.25017064683279	-1.42279807333289	0.89305987432088
H	0.18114232322062	-1.83613454197231	-1.33277289149105
O	2.20647797561972	-0.56604527062751	-2.37227780566630
C	3.81869942981160	0.78420302291556	-0.23983061211343
H	1.94437399592863	1.89082471110366	1.44015896557479
O	-0.29266441148618	0.74177247923031	2.32701032362428
H	4.07657250098299	1.10938624332485	0.76208425894448
C	3.12217812946676	1.77467186529634	-1.05704784266612
C	4.72436478182232	-0.26918963123528	-0.79798373865748
H	2.99716699751230	2.78180136104041	-0.68045106347678
H	3.17757656737384	1.66327718436865	-2.13387166304444
H	1.56550588017033	-1.44591722330842	-3.21000963968975
H	5.72908882748421	0.14930454398604	-0.91160862640706
H	4.79390565164319	-1.12322822445147	-0.12045914426459
H	4.38634115164748	-0.62023972556532	-1.77139807918544
H	-1.50696351652757	-2.24075039406386	0.21955856948728
H	-1.06914120351146	-1.81327000703079	1.89887580864288
H	-2.10231932229653	-0.74482438215664	0.99676106464136
O	1.09829596509253	-2.09583419397502	-3.93281098060385
N	0.45991229810777	-1.27663388438462	-4.85624676157668
C	-0.15317229424758	-2.18392559055939	-5.85105332248383
C	-0.58992355492756	-0.47371999135810	-4.17885158107739
C	1.45321611387299	-0.38779797233586	-5.51050962348207
H	-1.11232304502818	0.11817751414843	-4.92849911998731
H	-1.26870342747162	-1.16539113395501	-3.68674703008876
H	-0.10708757210319	0.17228731394957	-3.44992927695576
H	-0.66654032479835	-1.58316624580871	-6.59926525814362
H	0.64369161416755	-2.76969887434446	-6.30199786448711
H	-0.85164158757518	-2.82968523240410	-5.32500832674681
H	0.93945547404906	0.21877740724143	-6.25439019778648
H	1.89980442121501	0.23851386938609	-4.74180368767175
H	2.20553942199109	-1.01972442359110	-5.97571439298235

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IV/V: *anti* + TMAO

C	0.42418426621457	0.41600590380799	1.37722402179277
C	-0.09530662743311	-0.65221267480189	0.50372754452605
C	0.49064569849913	-1.00723900476347	-0.68337185279795
C	1.65959215214331	-0.37622707644378	-1.16283437415784
C	2.26099339956697	0.63533074697165	-0.30271086189501
C	1.59747219870734	1.00338808569719	0.93486796078682
C	-1.32189568687185	-1.34643934734307	0.96908898470100
H	0.05326806621339	-1.79770658996911	-1.28579175363822

O	2.19071200403624	-0.66238193457694	-2.28648052475376
C	3.82927068042269	0.59851744803599	-0.35941615198213
H	2.04490271800366	1.78451050067423	1.53973938666368
O	-0.21059965664307	0.71266527681744	2.44174661342524
H	4.16368626885140	-0.20760758262238	-1.00444100434231
C	3.12048119027608	1.68085698225467	-1.03581980099997
C	4.63374555587619	0.80820224728955	0.88541226633034
H	3.11606441884885	2.65986508062794	-0.57211172813018
H	3.03737334616918	1.65396449140165	-2.11544010995956
H	1.53731262513528	-1.51380323848106	-3.13563201784393
H	5.67761041478053	0.98791022615232	0.61262778818609
H	4.28507575690851	1.66663661936830	1.45933124039103
H	4.60200492218230	-0.07209498801521	1.53112268601076
H	-1.63102642909943	-2.13823621465743	0.28630607702656
H	-1.15475935615547	-1.76036110197447	1.96762756854379
H	-2.13435870623522	-0.62381992183075	1.08917975565270
O	1.05890448474449	-2.13984324765123	-3.87449369817082
N	0.52397653279540	-1.28613102257857	-4.83201682375815
C	-0.09855093444598	-2.15592118069163	-5.85374931440303
C	-0.50126528381851	-0.40864270502967	-4.21146485827745
C	1.60667710608263	-0.47106942518043	-5.43884348848547
H	-0.94825204940416	0.20711828431765	-4.99002440829916
H	-1.24595649113768	-1.04881289862580	-3.74569210692834
H	-0.01125138598008	0.21346421864976	-3.46678465154416
H	-0.52522098251081	-1.52638625504353	-6.63220436206965
H	0.67702301371602	-2.80184069973801	-6.25706114749512
H	-0.87006222868161	-2.74463106325123	-5.36393017593010
H	1.17291735252151	0.16860198700887	-6.20559304046068
H	2.05991812454896	0.12299482128025	-4.64865655070543
H	2.33354352117210	-1.15537374708577	-5.86920008700790

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2a: ***syn***

C	0.58927299788543	0.25036404295541	1.38294118347046
C	-0.10042461634454	-0.69126621827350	0.46020012524834
C	0.29223484405486	-0.76746966529860	-0.82094742489024
C	1.42744995711616	-0.02587673149948	-1.39260811287182
C	2.22124289518459	0.80425031049650	-0.46063847519182
C	1.47871921005218	1.28543383945653	0.76024948744892
C	-1.19802718668322	-1.51482227515616	1.03001287805847
H	-0.21145942542405	-1.43626719096582	-1.51288838457157
O	1.70111445057665	-0.15791553229784	-2.57451864477100
C	3.69224598059652	0.41793755655427	-0.28127928024104
H	0.81296899130346	2.11415781181991	0.47998671436271
O	0.38238391703314	0.20795480862456	2.57798182368831
C	4.31931636594062	-0.75818971792659	-0.96876102299048
C	3.32391781055766	1.65417262348132	-1.01970181670409
H	4.01857345563976	0.56578357131050	0.74415481664089
H	3.48096379166449	2.61584450348602	-0.54589249423356
H	3.43246610666169	1.63469129936437	-2.09767137564034
H	2.16146702312653	1.66777595417083	1.52033123764396
H	-1.64375560300661	-2.15616650923751	0.27067483480002
H	-0.81807056787930	-2.13423645148599	1.84661522759702
H	-1.97058234685585	-0.87409760786487	1.46343036353254
H	5.40205986012371	-0.61772297526407	-1.02286032104910

H	4.12893681219217	-1.68449488544511	-0.42087182834504
H	3.94547827648390	-0.87578756100469	-1.98608651099154

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2a: *anti*

C	0.38048888667625	0.35095639581373	1.37168163208419
C	-0.17667042572935	-0.70513399975312	0.49496061070203
C	0.44743516820022	-1.01786144732345	-0.65005971205061
C	1.68073861279306	-0.38810597934455	-1.13467816294303
C	2.33634028626457	0.63041730587251	-0.29117438573923
C	1.66310067346563	1.03916353953382	0.99736749775321
C	-1.43187058241956	-1.36292017819255	0.94250864707066
H	0.04259032501558	-1.78301316460916	-1.30623422863691
O	2.13546437817360	-0.72824610671781	-2.21746096184439
C	3.86738244954032	0.58757138752423	-0.36047100461776
H	1.43336431818069	2.10917786549819	0.99605509002339
O	-0.19705690184458	0.65938100054837	2.39558510672508
H	4.22647590283459	-0.21861178412951	-0.99188981700739
C	3.13946025174335	1.65972367136455	-1.06573731541498
C	4.69407140490627	0.86948020312855	0.85794615762266
H	3.15780127931641	2.65300715008596	-0.63110055544907
H	3.05748972799989	1.60941827974917	-2.14426021658769
H	2.32643619374330	0.88715218082032	1.85455693805907
H	5.72919031581809	1.05762299736438	0.56222479447923
H	4.34102592171947	1.75148740753547	1.39540617534067
H	4.69436506025436	0.02254172322216	1.54932538324134
H	-1.74693700936172	-2.12824349455061	0.23432570990158
H	-1.29315890453393	-1.81508340754429	1.92775713521192
H	-2.22868833275653	-0.62277354589632	1.05256048207603

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3a

C	0.20146989859863	0.33538773505987	1.28648692317422
C	-0.36810358676299	-0.66957102158505	0.50397122962340
C	0.26755250572419	-0.99957288970064	-0.68631913161845
C	1.43191594422215	-0.36373634339161	-1.09798462804422
C	1.99590501811337	0.64205035231365	-0.31730989584191
C	1.36261876233491	0.97190822848806	0.87561603217466
C	-1.62119177686957	-1.35761162940125	0.94272382945310
H	-0.15989682426496	-1.77853207462798	-1.31235854381081
O	2.05804880987693	-0.69198515651091	-2.26534588386030
C	4.48110672522511	0.52156829430340	-0.37953863214684
H	1.79026005320834	1.75276982436391	1.49931814222347
O	-0.42864037356226	0.65786894707674	2.45266333099808
H	4.53465153190101	-0.46967515946452	-0.82467397587975
C	3.26930324664193	1.32919218631344	-0.73198850356229
C	5.44670441723311	0.93082538598862	0.43275057212376
H	3.32978081309818	2.30749706233605	-0.24926894934569
H	3.25015477343976	1.49290826644849	-1.81455243303681
H	1.55448339807072	-1.38073259247844	-2.71109436164507
H	5.41656506949525	1.91314499685155	0.89549255479566
H	0.06577994436079	1.35418225714217	2.89710760737783
H	6.29981763485522	0.30152642674078	0.66101666760061
H	-1.92515858414235	-2.10976808105460	0.21420364959424
H	-1.48404236195053	-1.84863748916710	1.91011792843721

H	-2.44117103884710	-0.64478652604464	1.06619047121590

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TS2: pro-*anti*

C	0.40133979651237	0.06330209728341	1.49950463600946
C	-0.20261476397444	-0.62711714442980	0.33973031047086
C	0.52555909541304	-0.92067106516975	-0.76851322518563
C	1.90012026715994	-0.58312550000803	-0.86277809480338
C	2.49707446238338	0.15757248432418	0.20960915763601
C	1.74673471207870	0.46581113781156	1.34503164238293
C	-1.63717183511501	-0.99612413040652	0.44776235981823
H	0.07867570169822	-1.47836666176403	-1.58778289306582
O	2.69492623638479	-1.20710720801480	-1.75831646945773
C	3.69582131878378	0.92563330530258	-0.24577284382097
H	2.19101844681134	1.07654049255176	2.12097396965071
O	-0.29143773780024	0.28351389616932	2.51716484230713
C	4.29620755316856	1.93683160362718	0.69223266133899
C	2.57884290532417	1.33117196960710	-1.15330558176100
H	4.43648552401074	0.31705104469672	-0.75817307005368
H	1.94858704866270	2.15826567969944	-0.85167476033037
H	2.64128585284089	1.10214588436614	-2.20964035903648
H	2.15612590269112	-1.56316793466944	-2.47521797437232
H	-1.98898472421580	-1.51591050655795	-0.44351048969545
H	-1.79784389291287	-1.62587642463066	1.32670773314495
H	-2.24375610518904	-0.10018311891010	0.60800752018195
H	5.03321474567562	2.54226097210967	0.16189020808158
H	3.53699190059182	2.60454098413042	1.10195577121378
H	4.80013258901622	1.43938414288163	1.52367994934625

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TS2: pro-*anti* + TMAO

C	0.87564923169949	-0.30687142691780	1.89688088216944
C	-0.14620939249942	-0.45968964399976	0.83819354231451
C	0.19818770506209	-0.59181526514183	-0.46498674749458
C	1.56681666802840	-0.61848211120882	-0.88884389032790
C	2.57141123918853	-0.38644722514487	0.11968400723202
C	2.21676363445720	-0.23138853935620	1.45687735556156
C	-1.56868916499515	-0.47547887930446	1.27392903763506
H	-0.56332924398983	-0.75866425436325	-1.22073476826933
O	1.89238809747459	-1.17102424927802	-2.05415701784994
C	3.79463412139216	0.19230697014885	-0.50591655484010
H	2.98046527621775	0.01637293961841	2.18408374527835
O	0.51838818148149	-0.21291382637430	3.09226371291188
H	4.18908423479436	-0.40987316300135	-1.32072833775797
C	2.66138763527565	1.06539692988520	-0.96713095063952
C	4.86471155314753	0.76149750185980	0.38420704743095
H	2.38276082650867	1.90085218139478	-0.33655313863305
H	2.45032504909352	1.14320184345030	-2.02645543085024
H	1.08584825323923	-1.15207686009621	-2.72527723794776
H	5.58747072962245	1.32371589407100	-0.21021064162673
H	4.44514392744174	1.43217238963934	1.13572391003054
H	5.40040090593515	-0.03785016185165	0.90170584847930
H	-2.24399010529936	-0.60582745040964	0.42781195947123
H	-1.73377607997287	-1.27766065371633	1.99814551831808
H	-1.81692211477744	0.45413033113222	1.79379396794526

O	-0.03193350629035	-1.13288427455346	-3.63185322782153
N	0.33047893427038	-0.91731443174694	-4.93749031712454
C	1.15088318303491	-2.05389911785224	-5.42541480636254
C	-0.90534767753990	-0.81281701325820	-5.74757067632679
C	1.10574269525382	0.34356240459514	-5.04738663843522
H	-0.64589067686780	-0.64400343199474	-6.79240839132838
H	-1.45274170517462	-1.74462700341130	-5.62937829521559
H	-1.48599757549509	0.01747762853751	-5.35341674536393
H	1.41801705939032	-1.89303381783703	-6.46956627295140
H	2.04327717862679	-2.11041627271015	-4.80620890516197
H	0.55671380826057	-2.95724258611829	-5.31214595823824
H	1.36879622893879	0.52430149838824	-6.08919057396961
H	0.48147066691830	1.14547688816393	-4.66090044977170
H	2.00192529412563	0.23688305221855	-4.44039051818987

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VI

C	0.53733462617685	-0.22927367271316	1.59896727018427
C	-0.18717261360927	-0.57263139575659	0.33919202945348
C	0.44675855645255	-0.54857947633370	-0.83904071732241
C	1.90117876221657	-0.27919192971552	-0.93965535896745
C	2.54110015488625	0.19976513534071	0.32393800403737
C	1.90604484027974	0.28580265014678	1.48981232225821
C	-1.62477052082640	-0.94191016880499	0.48384415782469
H	-0.07855999857746	-0.83016610579995	-1.74967350884940
O	2.58025126313568	-1.42597215479598	-1.43499393973811
C	3.56465506084511	1.02525224735787	-0.40028546182348
H	2.30832068360809	0.81105255113957	2.35000013708772
O	-0.03559337340637	-0.30043053413421	2.67686658685913
C	4.01407608543604	2.32974556406491	0.20493492521566
C	2.51026736137316	1.01927810297001	-1.55382392523298
H	4.41588711140968	0.41137485104871	-0.70655352646172
H	1.82731090329918	1.86554212550671	-1.46979621372094
H	2.88387167547797	0.92012455775661	-2.57425933228264
H	2.36108649567947	-1.51453276838624	-2.36963475648535
H	-2.06815833667358	-1.15885376948815	-0.48821116833664
H	-1.73397446826079	-1.81847289320352	1.12748813928574
H	-2.18775423056715	-0.13504401532247	0.95957632126929
H	4.61238201568556	2.90034404559233	-0.50921868597641
H	3.15369149590300	2.93724187569438	0.49727096488731
H	4.62679245005610	2.15893617783589	1.09350773683468

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TS3

C	0.15420511099840	0.45186317116646	-0.40523317065015
C	-0.14326516628539	-0.56648374614739	0.59033002044346
C	0.87544803854423	-1.11649758906529	1.30702062817560
C	2.23135990962939	-0.71068615069511	1.16491229649844
C	2.56812888223546	0.23455715867027	0.23735962668962
C	1.55127241870872	0.81336482912382	-0.55608066272116
C	-1.56435272286235	-0.97736650168978	0.76714195707481
H	0.66405174119853	-1.88634155897010	2.04350616500566
O	3.10930542562989	-1.26944964695493	2.03697926926993
C	3.78012168414928	1.13238870127080	0.23027756081061
H	1.80522419700993	1.36606987302405	-1.45330847340071

O	-0.73058540653994	0.96638132814281	-1.11390736331533
H	4.37062911281868	1.00424167151354	1.14630671896580
C	3.00562448036152	2.41697596078990	0.27555193466444
C	4.68902812137991	1.00148052334234	-0.98134124924596
H	2.52426104846174	2.70324966930713	1.20228907841670
H	3.11175195244414	3.16804211996002	-0.49975441593479
H	4.00590608886844	-0.98956374679712	1.82339722611873
H	5.46851382457699	1.76631756903999	-0.95885966429762
H	5.16804466108951	0.02099566876381	-0.99945021063713
H	4.12372114869597	1.12059298872100	-1.90871786049138
H	-1.65614884193061	-1.75813211892204	1.52271899875261
H	-2.18084306325268	-0.12444442837757	1.06426453221485
H	-1.98106864593036	-1.34500074521670	-0.17480494240710

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TS3 + TMAO

C	0.31648754358962	0.42662052897510	1.15223833026941
C	-0.28793687281330	-0.52394792448428	0.23549049772378
C	0.32790853166301	-0.80335077787755	-0.94932979689692
C	1.58568935034894	-0.24664015425194	-1.33840700922685
C	2.17895348045684	0.67162321068379	-0.51040560421413
C	1.56987053294460	1.01601203072874	0.71745478767468
C	-1.58109959120044	-1.15532895496612	0.62762393410113
H	-0.13194926629794	-1.51110530810851	-1.63383049493566
O	2.20672824995748	-0.65631970359344	-2.45217427938610
C	3.64599010106738	1.00413361074058	-0.43920480468878
H	1.87983719313165	1.90903718934420	1.24924816576501
O	-0.21544677839887	0.74791777825633	2.23414050016768
H	4.20991302386076	0.34512140584277	-1.10773131241914
C	3.80076888577067	0.60039523140849	0.99919439083987
C	4.01346236864816	2.45304747791044	-0.71450263217457
H	3.81116032069492	-0.45455032643837	1.24413973492811
H	4.15769371811797	1.29870997224096	1.74910241952941
H	1.64666833766116	-1.35023017760181	-2.97144350637909
H	5.07779370237417	2.62221882827216	-0.53419368964034
H	3.79490773630406	2.71390938315440	-1.75173161706036
H	3.44958753312769	3.13031618634856	-0.06792223314686
H	-1.93357569837105	-1.83784027480102	-0.14671769194512
H	-1.47557225752958	-1.71100878697400	1.56378625913373
H	-2.34895841693995	-0.39674939885677	0.80524678663648
O	0.86817933453873	-2.33543110176156	-3.77233777771466
N	0.59084284884497	-1.86048993808853	-5.02806221343627
C	-0.29213306054920	-2.83504750401396	-5.70947807165376
C	-0.09797291981600	-0.54809704979066	-4.93666407768888
C	1.85198547690845	-1.70977519827146	-5.79600797090949
H	-0.34000732807861	-0.18935976411935	-5.93689432629942
H	-1.00094772037202	-0.69406691803265	-4.34875518612668
H	0.57109270996015	0.14527806150278	-4.43248499748219
H	-0.52104166504607	-2.48495371781543	-6.71587988153798
H	0.23312300857353	-3.78644047786047	-5.74044046289439
H	-1.19863390334289	-2.92570946219644	-5.11604209564359
H	1.63166266299731	-1.35504349370191	-6.80268369896952
H	2.47833997853734	-0.99532675969999	-5.26671924547518
H	2.33362384867608	-2.68394272210302	-5.82491212882264

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TS4

C	0.43710887100241	0.37314663622859	1.29031497542926
C	-0.15914979441216	-0.59062202889585	0.41985453922722
C	0.56792618301824	-1.18533940978923	-0.60865269954884
C	1.88832286095390	-0.88648319335468	-0.87949968397286
C	2.55938849003629	0.00445336055297	-0.02793435696605
C	1.82955303990133	0.62381750045842	1.04209313900689
C	-1.58005569465928	-0.96292324207438	0.66900585793161
H	0.06152601066520	-1.90706111226302	-1.24674780750907
O	2.57592410314927	-1.37154359863787	-1.95380838602772
C	3.79582030006230	0.74200624078282	-0.44603352195514
H	2.36672500902675	1.18112532591851	1.79882529498567
O	-0.17088062357880	0.92657497255496	2.24694559076119
H	4.12820604161820	0.39413319785582	-1.41921979343266
C	2.65525699633218	1.68620104696193	-0.49501560413341
C	4.91072288425584	1.00676362044213	0.53037588009327
H	2.64811344944458	2.54372320490016	0.16724996596887
H	2.06038715143834	1.77055667525407	-1.39470053835172
H	1.99012803229489	-1.92749023876009	-2.47827627314413
H	5.56929105331039	1.78518928289688	0.14012309009585
H	4.53484520193825	1.33842988230824	1.49925293216352
H	5.50150751768226	0.10219361918214	0.68230721541789
H	-1.93931234048912	-1.69306775450301	-0.05740147240822
H	-1.69860458654787	-1.37769216687813	1.67520192911913
H	-2.22228815644356	-0.07759782114145	0.63303872724940

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TS4 + TMAO

C	0.42031754156657	0.22409801155601	1.29225257219393
C	-0.14765524331460	-0.73751229008388	0.40274358151906
C	0.57577788559637	-1.26239092763335	-0.66571480339822
C	1.87267524947903	-0.88530898728287	-0.97966620610973
C	2.51734201791490	0.00505890876167	-0.09846720640125
C	1.78991626523128	0.54959527772798	1.01808983863992
C	-1.54321803172522	-1.18866172021403	0.67137552011787
H	0.08736124565459	-1.98089441710739	-1.31789409154118
O	2.52630172679273	-1.27904697567346	-2.08778562932707
C	3.68194758937515	0.83892207311241	-0.53289260667992
H	2.32505263556831	1.09343034985858	1.78684449746947
O	-0.19130004008288	0.71370939920521	2.28571579337889
H	3.98606044239687	0.54905449867062	-1.53388799851069
C	2.47889928965327	1.70534165811220	-0.48672593626008
C	4.82428392192572	1.14147277921663	0.39965182957343
H	2.45738794490017	2.54227636051435	0.20200780677223
H	1.84287176229372	1.79170078412232	-1.35798598282768
H	1.87500761395137	-1.68247048018634	-2.77974265964034
H	5.41181936156712	1.97630648125410	0.01199073281122
H	4.47614418850897	1.41031635559105	1.39829863085926
H	5.47969823860278	0.27340140947858	0.48741493036975
H	-1.87786301669345	-1.92026624786928	-0.06545531696348
H	-1.62162487148057	-1.63109932497200	1.66970258000057
H	-2.23241020958404	-0.33819330837448	0.66722384663504
O	0.97409543120688	-2.24277355733514	-3.82370082966427

N	0.58321752455614	-1.29569576680181	-4.73450341789280
C	-0.40535533204624	-1.91009054454980	-5.65105291616645
C	-0.04168508440368	-0.14271346930832	-4.03825594622860
C	1.75909531018136	-0.83101470762848	-5.51149989103302
H	-0.37513116526256	0.59188434133365	-4.77077065500204
H	-0.88038630470372	-0.52384153664734	-3.46123984472944
H	0.70259420210619	0.29070856966796	-3.37417621821717
H	-0.72845136507695	-1.17761307580406	-6.39059452800471
H	0.07592478813069	-2.75891903474884	-6.13064778999298
H	-1.24502831201316	-2.24654972771013	-5.04788541736233
H	1.44653900180302	-0.09218979569072	-6.24919079025511
H	2.46794135974988	-0.39645414377713	-4.81041485675755
H	2.19469921727611	-1.70155615240379	-5.99557633490975

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VII

C	0.18510279901961	0.89075755444604	0.05452023143571
C	-0.06142364041607	-0.48230520444659	0.53546906516086
C	0.96782232650982	-1.21947055973636	1.01218172366289
C	2.34265671325984	-0.76268043302298	1.07186047326097
C	2.58544850071309	0.53222906343122	0.85721293423829
C	1.50641720313406	1.47183726927629	0.44830899319010
C	-1.44378051682635	-1.02284157004374	0.39578014575709
H	0.78752392599087	-2.24963784125675	1.31014818845388
O	3.25600188512798	-1.75482040850869	1.26873532421494
C	3.67422152909721	1.41505021578017	0.29647581705902
H	1.28124722642284	2.19054064113941	1.25052203999337
O	-0.65788758947026	1.52398984164072	-0.56042148991580
H	4.04501557035989	2.11451669502401	1.05452994488653
C	2.54026637050940	2.09657095638779	-0.52753829324149
C	4.82841009967202	0.78705009161705	-0.45020598616357
H	2.55457265440050	3.18287360518114	-0.60635073335918
H	2.45989146382171	1.64943005260183	-1.51975935951803
H	4.13645518305384	-1.37182349772466	1.34436134140407
H	5.40277252203227	1.55325818462762	-0.97682257507583
H	5.51453151040196	0.27285144004668	0.22884145962211
H	4.46880695299905	0.06425561743865	-1.18696331594199
H	-1.50747740628254	-2.04101612213435	0.78020536361493
H	-2.16222022159175	-0.39629414921194	0.93198764431608
H	-1.75404106193932	-1.02176644255266	-0.65248093705503

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VII + TMAO

C	0.34190792500433	0.44660518625738	0.77726891693536
C	-0.21115060961870	-0.77481968293732	0.17045146443571
C	0.57550428502646	-1.54892919974382	-0.61520898400358
C	1.95948403576852	-1.25172044058510	-0.96239755302980
C	2.56001338450789	-0.28566310474738	-0.25570749233524
C	1.83451739662970	0.54106341081233	0.74573984935516
C	-1.65907125457171	-1.06179307121805	0.38854112310549
H	0.13231025749991	-2.41516477503982	-1.10114964552669
O	2.53643920708322	-1.91122180331550	-1.98433604587362
C	3.64071354895076	0.74619538132797	-0.44967706936524
H	2.15790730040749	0.30859391744175	1.77238640905575
O	-0.36542374248358	1.28270676821721	1.32126294260088

H	4.49081399497359	0.57493891441580	0.22145554045862
C	2.64684104870136	1.75138818280299	0.20895295806291
C	4.12677694450760	1.03446751700766	-1.85123372175494
H	3.04295504183165	2.44833553263830	0.94692207077333
H	2.08362989476425	2.29565457989963	-0.55157303586658
H	1.83450263688612	-2.16915770383193	-2.69020729719412
H	4.76124727981066	1.92475292224352	-1.86404580262311
H	4.70488186097163	0.19784185379778	-2.24884348684915
H	3.28051595705946	1.20723581920483	-2.52178763164582
H	-1.94767738011968	-1.99704441134575	-0.09214256556329
H	-1.88945228590762	-1.12728861552953	1.45574265529330
H	-2.27983884079524	-0.25579794242455	-0.01284838699035
O	0.83707621945512	-2.48792269226927	-3.76607606032486
N	0.65977761698955	-1.43406949840611	-4.62539980096492
C	-0.26127432214098	-1.86601541079596	-5.70152294729953
C	0.06935667049163	-0.27702205733002	-3.90602550526285
C	1.96338800497701	-1.03674610438133	-5.21408115657805
H	-0.11103334152108	0.53683772347234	-4.60786584946819
H	-0.86024956572429	-0.61233437092165	-3.45278826961580
H	0.77047480799248	0.03591708373472	-3.13571669492328
H	-0.41653507533326	-1.04999175836355	-6.40715435427752
H	0.19186926872138	-2.72311207229637	-6.19354868012325
H	-1.19857570248146	-2.15556720593226	-5.23259446094077
H	1.81764613225556	-0.20988923014175	-5.90911123397843
H	2.61810987711527	-0.74135622657303	-4.39723138070732
H	2.36861652231467	-1.90632241514407	-5.72573981698953

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VIII

C	0.50784294269526	0.30283223447251	1.24509769004484
C	-0.11374657872056	-0.59384477287312	0.23069961293062
C	0.65527720398659	-1.30671669008610	-0.60981141306138
C	2.12133087398779	-1.28650875630048	-0.62552562799902
C	2.84857419773928	-0.38914484359000	0.32616029213385
C	1.96954849774246	0.56690582567115	1.14657973881296
C	-1.59750186114588	-0.66805553383276	0.22276035994533
H	0.19760389328290	-1.96899364699465	-1.33969335951078
O	2.73373658001910	-1.98945629197124	-1.41058697609873
C	3.50739106718011	0.83665477337279	-0.37221901353434
H	2.36076126356836	0.74645776755196	2.14752902685661
O	-0.18204265997252	0.83400564381172	2.09332414975335
H	3.55155683919126	0.75735774617566	-1.46010921849209
C	2.36200036791594	1.71457911221875	0.17078436769036
C	4.87080177344002	1.18213849730942	0.18286587016862
H	2.64232012602867	2.65736197953174	0.64067747452314
H	1.58636773245218	1.90262923256184	-0.57380150202123
H	3.54175243336870	-1.00926453078445	0.89957715646452
H	5.21203559611320	2.14396869722753	-0.20871518094774
H	4.84388902678312	1.25342063580096	1.27414921950831
H	5.60661826381079	0.42151144216272	-0.08904454652677
H	-1.95360897177398	-1.34485618784124	-0.55280462760037
H	-1.96405160797030	-1.00641870867396	1.19525708564774
H	-2.02514399972253	0.32532437507922	0.06218342131219

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C	0.29765637296067	0.66695266645312	0.62514421346303
C	-0.14588829410560	-0.59410074696095	0.20438062903719
C	0.70796231956776	-1.41886624464528	-0.53149204927175
C	2.00849514143066	-1.05125891466073	-0.88366553614004
C	2.41818977742403	0.19556932914583	-0.45775434123103
C	1.58389362372398	1.02292796229514	0.27580136153345
C	-1.53144684250715	-1.04381222455108	0.55101145290114
H	0.33579266182970	-2.39193552560236	-0.84292591305755
O	2.84156561246096	-1.85069969108079	-1.60495195587941
C	3.56481359717710	1.18597323545268	-0.45241967620465
H	-0.11194675922388	2.27536717176324	1.56502796790720
O	-0.55544518376456	1.44936588729676	1.34623099353235
H	3.77671087343058	1.60078280625786	-1.44288679418515
C	2.61722112121475	2.12182982922078	0.38518698022347
C	4.85031564945229	0.75719828135146	0.22150727923326
H	2.98080632743766	2.32356298424614	1.39639428287590
H	2.36053802408330	3.06912314628577	-0.09532650793031
H	2.39328610817710	-2.67901287206491	-1.80632549330566
H	5.53726119593422	1.60180457468854	0.32107494893386
H	4.64875552862104	0.35993871082515	1.22020327294302
H	5.35284420995714	-0.02189208344731	-0.35673455883746
H	-1.72481452433295	-2.04222479946682	0.15799921090770
H	-1.68193518675640	-1.06406372555703	1.63408095785120
H	-2.28241635419242	-0.36113875724517	0.14326427470023

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1af/II: *syn*

C	0.41948919999804	0.01405756071391	1.58462674760996
C	-0.41409693334665	-0.18720676835950	0.39305240712788
C	0.18039473376456	-0.49973375425597	-0.84618886847449
C	1.60664497562413	-0.61798424182827	-0.94057677578889
C	2.41767114147043	-0.43374756446180	0.19489716305657
C	1.83501880212221	-0.12643703085912	1.40241139697101
C	-0.63720557932148	-0.68376490000491	-1.97302898770322
O	2.08714609995881	-0.92174059875950	-2.13832890158147
C	3.91222737199492	-0.55977327169558	0.08267192867318
H	2.45678637798850	0.01480422781959	2.27996393165682
O	-0.07179225919179	0.28783114860869	2.69236351615457
H	4.18467961284584	-1.51263152763283	-0.37853527723322
C	4.48075012022633	0.57356128710514	-0.69011427280572
H	4.33772282114213	-0.57564411022576	1.09491757916818
H	4.32378989689489	1.60165185374198	-0.39196338420206
O	5.64195468539089	0.41252491883900	-1.41304045701321
H	3.07134226127909	-0.93146413575867	-2.19485291423161
C	-2.00474526850974	-0.56138515600476	-1.86648463872555
H	-0.17963626571426	-0.92086194277219	-2.92465294177405
H	-2.62739619277147	-0.70440705047260	-2.74213067493897
C	-2.59209490184033	-0.25221256248662	-0.63654736132153
C	-1.80097702953529	-0.06715208007366	0.47832668434222
H	-3.66900144934563	-0.15650293068887	-0.56026505415032
H	-2.23618773571280	0.17470685560014	1.44043221656776
C	5.67266533032970	-0.49045758337740	-2.40466845119077
O	4.69097421511861	-1.10045315449128	-2.76604366326855
C	7.03570934928544	-0.64604998202957	-2.97525401950555

H	7.51665568760348	0.32550310648492	-3.08768905874524
H	7.63762467323215	-1.23624423677583	-2.27857988377338
H	6.97900625901920	-1.16497637589870	-3.92864798490031

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1af/II: *anti*

C	0.52294103387132	-0.00140800887808	1.39393810687252
C	-0.06059630320946	-0.06669411766485	0.04574058777995
C	0.72662570114782	-0.45747835473788	-1.06037509180628
C	2.10656807155027	-0.77088639560808	-0.84553891540214
C	2.67827509951653	-0.72716023688440	0.43749730313421
C	1.90762241610642	-0.35423071625859	1.51069364808436
C	0.12566288100906	-0.51630375205081	-2.33005466684070
O	2.91634051494865	-1.12471979872762	-1.84801378530403
C	4.14783396421867	-1.03613688965743	0.60306328615714
H	2.34101229152758	-0.32475758678498	2.50441019850452
O	-0.15527939299529	0.33060386121039	2.37913544975254
H	4.41674137268733	-1.91683644244076	0.01767256102174
C	4.98879987570385	0.09838582826128	0.16026293446589
H	4.33799132366888	-1.25637448117580	1.65727801394420
H	5.31008613176946	0.26442042511024	-0.85766562154284
O	4.93280857423613	1.19176850754881	0.97309567893240
H	2.45429813390135	-1.11236656789056	-2.69395664172567
C	-1.20356116549239	-0.19615143748466	-2.49354320139054
H	0.68751687449021	-0.81710473320763	-3.20849743466534
H	-1.64978570266896	-0.24833578254320	-3.47957837298087
C	-1.97500182949429	0.19355590154093	-1.39659335742149
C	-1.40312651336386	0.25549333188029	-0.14270086185934
H	-3.02022013589965	0.44525730893363	-1.53211107985678
H	-1.98153218962624	0.55433982561041	0.72301589493204
C	5.43494588328277	2.37075919175834	0.52506285550208
O	5.93308970985759	2.49311375074923	-0.56192751112300
C	5.26635350028405	3.43871947556206	1.55013934964364
H	4.20113469244782	3.61910376834946	1.71303318270091
H	5.69312048816037	3.11612814497149	2.50133779993303
H	5.74714569836350	4.35245998050872	1.21045369055790

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1af/TS1: pro-*syn*

C	0.76705168014584	0.06920109429523	1.51035376444671
C	0.16746782619349	0.03033309931864	0.15511916439871
C	0.86452886353513	-0.45355229564734	-0.97802351695205
C	2.20922529639566	-0.89933656829450	-0.81742390413607
C	2.80806003597048	-0.82492969115737	0.45434337261361
C	2.09558633443641	-0.36483198641029	1.58238809259679
C	0.21376170692449	-0.48090766293697	-2.22750252793941
O	2.90841912854587	-1.42960562900147	-1.82435853481763
C	4.28369071431862	-1.12333593883655	0.58099674036167
H	2.60041809096174	-0.35360426636412	2.54160037362721
O	0.08181543634463	0.46467301271444	2.48568771037877
H	4.66680973190682	-1.92231253011413	-0.04552407426279
C	4.35888533744096	0.19311367369574	-0.02189014865696
H	4.59097499953510	-1.19399053226021	1.61999428843425
H	4.15990919419670	1.10291938043842	0.52987371408550
O	4.85385038515625	0.30654471887744	-1.24904309539447

H	2.44123489358767	-1.32189333207470	-2.66104126052311
C	-1.07616006521673	-0.02841223531031	-2.35833245195655
H	0.71169150339523	-0.86003943840276	-3.11467807928509
H	-1.56150291594791	-0.05207280159360	-3.32672316116989
C	-1.76057667308272	0.45968973808571	-1.23949727776526
C	-1.14419153608732	0.48244082702579	-0.00857190186081
H	-2.77904726992935	0.81595742102218	-1.34476268188207
H	-1.65486322341528	0.84923866683055	0.87343677326069
C	4.54874327290806	1.46115195769667	-1.96697418082507
O	3.76121370240477	2.25392183304137	-1.55418051315190
C	5.32286465068737	1.49225587952317	-3.23104713890554
H	6.38874881889118	1.55333803084120	-2.99836610589399
H	5.16194893430346	0.56456012720400	-3.78312959334360
H	5.02035514549332	2.34976144779377	-3.82585184548160

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1af/TS1: pro-*anti*

C	0.81300045147919	0.10175531318794	1.47398029692187
C	0.25793276885876	0.08616916085198	0.10007486901375
C	0.96840107267211	-0.45753701689824	-0.99752178225048
C	2.28165008244906	-0.96347950513471	-0.77323559781676
C	2.82270400214517	-0.94698771407013	0.52746910633565
C	2.10621591300198	-0.43782030938018	1.61174409476074
C	0.36642161492765	-0.46326950002341	-2.27078259198115
O	3.01427703862475	-1.52174281497897	-1.74911221657638
C	4.28624737921546	-1.30129372956522	0.65449650966274
H	2.55356026935599	-0.46231795546033	2.59854534193791
O	0.13231118286944	0.55854470886069	2.42047767139779
H	4.60194022611263	-2.13917859181594	0.04020134429524
C	4.56825555548482	0.00304218654069	0.06363841433453
H	4.59996931338193	-1.39905792988129	1.69050369088110
H	4.62173161128311	0.18498446572647	-1.00090411492164
O	4.72182792604227	1.02905123866972	0.88434031132501
H	2.60463046625447	-1.38264559093740	-2.61021933673476
C	-0.88891090008228	0.06436657545270	-2.45677113665372
H	0.87429684653963	-0.88724009488403	-3.13131277965019
H	-1.33780921199153	0.05352206754631	-3.44289476710933
C	-1.58442214968447	0.61124783845681	-1.37371624337658
C	-1.01433437722317	0.61594792443344	-0.11890006360062
H	-2.57463065867761	1.02625202904221	-1.52307826751465
H	-1.53736894230226	1.02677512434855	0.73606359240163
C	4.59129281492335	2.31574173161528	0.35699682532726
O	4.36406411796802	2.49043004843465	-0.79962680798447
C	4.77212770959181	3.32112670008749	1.43012762275156
H	3.99484711789629	3.18085731587704	2.18511514316522
H	5.73587043728632	3.16881757519266	1.92013671841379
H	4.71171132159661	4.32110274870514	1.00943815324496

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1af/IV/V: *syn*

C	0.88367881365402	0.30112539839985	1.40871356982458
C	0.22392195871844	0.12415999389356	0.09589791886891
C	0.86698646392084	-0.44165950099166	-1.03699135620004
C	2.21470343200844	-0.85052894369403	-0.92432706064730
C	2.90653024550852	-0.62503151668236	0.29601772004063

C	2.21644261744968	-0.09009169930863	1.44084342971767
C	0.14628403195577	-0.58595255711168	-2.24515916963393
O	2.87928350427289	-1.43090951193838	-1.91212665891631
C	4.26407236881899	-1.31677102824548	0.51773844200108
H	2.78520620435743	0.03318801422240	2.35589406452522
O	0.23329783785169	0.77402656611513	2.38044117474117
H	4.50513377007326	-2.09425231250062	-0.19607291969362
C	4.39545982295927	0.04180924606769	0.06100494966458
H	4.46098183096398	-1.53385925306464	1.55917609691999
H	4.51337557459555	0.86958004077135	0.74758329446128
O	4.88611640772203	0.25133732432889	-1.19905193450941
H	2.34580439692626	-1.47016849375175	-2.71591283839908
C	-1.15577972603806	-0.17501840561959	-2.33717877645761
H	0.60699144167519	-1.02005162452823	-3.12721666113395
H	-1.69525586632001	-0.28610219030739	-3.26992203922583
C	-1.78780233997245	0.39225559545166	-1.21948286005387
C	-1.10793970183402	0.53379263697320	-0.03387729109716
H	-2.81927506596553	0.71737457361763	-1.29612471174955
H	-1.57653770930555	0.96445793948230	0.84237677463356
C	4.52173049837656	1.41885997559537	-1.80899146479305
O	3.71696231133317	2.16179111990688	-1.32539608810633
C	5.25103140548217	1.59160259783548	-3.09338243425987
H	6.31084183608815	1.75370295064496	-2.88203375582541
H	5.17026547065560	0.68535894545170	-3.69509654056084
H	4.84840216406772	2.44625011898640	-3.63047087413551

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1af/IV/V: *anti*

C	0.92653591339233	0.33656670025944	1.38385817779873
C	0.32357731663106	0.17752756087743	0.03883291810819
C	0.99293981442569	-0.43194693626486	-1.05497482165476
C	2.31709858390306	-0.88729315468230	-0.86659646538283
C	2.94670766766328	-0.70082603743587	0.39198517163027
C	2.22909192140757	-0.13690415250306	1.49921207439333
C	0.32804357987771	-0.56481723283708	-2.29503811494594
O	3.03603061551377	-1.46457968736107	-1.82081694953053
C	4.30729333873527	-1.37073548414712	0.62481253700287
H	2.74279796482431	-0.05025668871221	2.44875532325843
O	0.25374667667173	0.85993033346496	2.31256558006414
H	4.53458154660145	-2.20299110572989	-0.02827921844916
C	4.44141421939211	-0.04193376967803	0.08463378856730
H	4.53377865866704	-1.50442380412151	1.67507836871008
H	4.60598987688318	0.12801235165956	-0.97112371149081
O	4.80602144183484	0.96699293557263	0.92400185012370
H	2.59697309515504	-1.40553547325392	-2.67854487385869
C	-0.94858108048564	-0.09659071326367	-2.45608820743219
H	0.80880398490720	-1.04633855743999	-3.14099141415925
H	-1.44963923178893	-0.20294438504253	-3.41058157172864
C	-1.60446550597352	0.52017445800483	-1.37997701725744
C	-0.97774697643303	0.64851253938660	-0.16292918784810
H	-2.61424554634407	0.89232761193889	-1.51188590537612
H	-1.46905919817374	1.11493488930078	0.68189719343923
C	4.41386380079551	2.22668485534562	0.54930398634687
O	3.82150907493397	2.42803737016038	-0.47077792361744
C	4.81319475300213	3.22541036287544	1.57387164363124

H	4.21496373494801	3.05787732970164	2.47329954651177
H	5.86147973363927	3.09319803841681	1.84462286070989
H	4.63511122539297	4.22909384550808	1.19714836243588

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5: ***syn***

C	0.58697795174580	-0.55295720362037	1.75091638469414
C	0.01834124446976	-0.34153842908992	0.38365077106121
C	0.82774264653228	-0.30780068375123	-0.75636641474450
C	2.27776178464616	-0.63231045717429	-0.61029411430459
C	2.79723340981316	-0.49231983375911	0.80053766184866
C	2.04647527378293	-0.44436764033293	1.89389780149842
C	0.26297310383810	-0.06658432020702	-2.00016307434797
O	2.48528975881118	-1.90404776658908	-1.17879904443350
C	4.14484890152425	-0.01092517735185	0.35210403830331
H	2.43528968166977	-0.24901758745341	2.88794835851013
O	-0.13637396258953	-0.70683850506222	2.72013371023208
H	4.85209623925795	-0.82387589115496	0.18598567959835
C	3.40350867892274	0.39983278183551	-0.94963870317987
H	4.61476063392947	0.78098650918570	0.93303409893562
H	3.00304650711725	1.40676889825155	-0.84413548478922
O	4.04105862479378	0.42063883517284	-2.21973436772421
H	3.44122295737806	-2.02758420410650	-1.32057980523413
C	-1.09972116057048	0.16197312187920	-2.11341056343224
H	0.89511324739878	-0.05818742574827	-2.88124626154720
H	-1.53361484284891	0.36800878085634	-3.08525620277136
C	-1.90994571101927	0.12265362747089	-0.98406686622555
C	-1.35311000697818	-0.13276310873642	0.25639019502457
H	-2.97598447742473	0.29534997146615	-1.07474870194368
H	-1.96811484012180	-0.16435755946539	1.14771017570782
C	4.87132205261140	-0.54168556824936	-2.62611285713040
O	5.04515149033727	-1.58560454226622	-2.03782303044169
C	5.55273387282351	-0.16153133444153	-3.89631168215832
H	4.80543267534019	0.08703681534102	-4.65205945363933
H	6.16088944771899	0.73005377758198	-3.73054525172206
H	6.17667581709009	-0.98232188048109	-4.23976199564450

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5: ***anti***

C	0.59137941631776	-0.91874235714830	1.61913180848440
C	0.26628576652882	-0.26932003266001	0.31101941447514
C	1.21766158919784	-0.12808394609360	-0.70557909334586
C	2.54756486276527	-0.77585812179607	-0.52275587121829
C	2.87256396437345	-1.16691025298609	0.89186304264503
C	2.00287424666148	-1.21696017335242	1.89438073474765
C	0.87743114788869	0.51383410626700	-1.88865831663256
O	2.74923272038596	-1.84076137943118	-1.43810953848254
C	4.33698709565990	-0.91255558933707	0.69096463660648
H	2.28445432383607	-1.38562130643344	2.92852879454194
O	-0.27412678375449	-1.10889486094391	2.45762243208351
H	4.88900645936422	-1.78152687741095	0.33022881894476
C	3.90260071219746	-0.01509209146377	-0.50310180655526
H	4.87985299283294	-0.43578198897333	1.50552198213825
H	4.48852640991092	-0.07101317544842	-1.41922914617543
O	3.67577871744464	1.32938495651105	-0.12235456214795

H	2.06617350151889	-2.50268856673055	-1.27741822358054
C	-0.39763211416200	1.02910299693188	-2.05878254857801
H	1.61585480993213	0.60685934681139	-2.67723251626033
H	-0.65402688130608	1.54308869874968	-2.97813195399715
C	-1.34900514365949	0.88419496393663	-1.05440201287713
C	-1.01855929036812	0.23534009053526	0.12136207849357
H	-2.34796530708014	1.28121657090872	-1.19193820436565
H	-1.74508528020155	0.11576580300644	0.91590591131624
C	4.76672533475217	2.10665173314473	-0.02268407139279
O	5.87905028859242	1.70103175814957	-0.24377564881131
C	4.40263810621951	3.49288299906005	0.39215207645266
H	3.64960303471587	3.89885502136643	-0.28533857919241
H	3.96356028510503	3.46602492514382	1.39189917125965
H	5.28840601433027	4.12274074968647	0.39418519142393

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1af/TS2: pro-*syn*

C	0.69387861142658	-0.11978842807391	1.59890139207648
C	0.13684289569229	-0.03468229533985	0.22642955280118
C	0.87968779632607	-0.41389075350701	-0.91409893318802
C	2.21946249473092	-0.89474296506942	-0.73493102582927
C	2.76915969402941	-0.93001207964350	0.56781352077631
C	2.04033466579941	-0.53781793556645	1.68258604081221
C	0.28292814437437	-0.31246992482604	-2.18278575110765
O	2.89212579016060	-1.48612925733142	-1.73663912373755
C	4.26945403518743	-0.98870913292350	0.60456854423433
H	2.52477574214208	-0.53518133456423	2.65218923449343
O	-0.01115842652497	0.18611850522238	2.58188716540074
H	4.72757640511957	-1.79343397193412	0.03479445671557
C	4.24822255396115	0.27910900185121	-0.13450648867630
H	4.66202613404005	-0.93385792438272	1.61793244652401
H	3.90438787675514	1.20515138987757	0.30884674025977
O	4.83106415981196	0.32960740656749	-1.32382340103023
H	2.43577341137966	-1.36205581781759	-2.57595816552383
C	-1.00198813408587	0.15960895771656	-2.32160778088801
H	0.82429954861565	-0.58496246937093	-3.08321337173178
H	-1.44242211245610	0.23970401560126	-3.30841146733688
C	-1.73419013586517	0.53513997382010	-1.19285856346092
C	-1.16599263451030	0.43622640665812	0.05896278155631
H	-2.74738913234496	0.90387420502957	-1.30407529436956
H	-1.71306860379962	0.71954888403341	0.94994403164791
C	4.54234481223311	1.41595547823970	-2.14775547042945
O	3.71821179575868	2.22139796981082	-1.84374347135172
C	5.39108543074509	1.37295480254317	-3.36271609601087
H	6.43697500197142	1.50317321282748	-3.07357093849311
H	5.30357320655326	0.39640321309232	-3.84185602557622
H	5.09293297277303	2.16403686745952	-4.04543253855682

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1af/TS2: pro-*anti*

C	0.74783813626180	0.19052005429520	1.45661417103524
C	0.12654848590212	0.01911799241180	0.11676223818496
C	0.84097769973729	-0.49489291193816	-0.98635401116650
C	2.23122333082531	-0.81545866412449	-0.81145678096679
C	2.83782494981080	-0.60060019143888	0.45789755213342

C	2.13130758513968	-0.10305322772821	1.53583944374171
C	0.17754710516361	-0.67257256297303	-2.21138880486153
O	2.89683137194742	-1.57718032195618	-1.70718319266358
C	4.32286422914173	-0.44262589306505	0.31555199857802
H	2.65670879124733	0.12281183652164	2.45585886812516
O	0.06267430608273	0.59330195832855	2.41253452283661
H	4.85408419513357	-1.27477877196257	-0.13496113700080
C	3.93097893086948	0.61378961235138	-0.64866129149423
H	4.80821215886238	-0.07179749015771	1.21371645915591
O	3.83779449831773	1.84691116582033	-0.14523999103014
H	4.04282777211539	0.49026738990380	-1.71840717626075
H	2.47677351392450	-1.52956306854307	-2.57324356811619
C	-1.14640434540295	-0.32040645813349	-2.34961003507310
H	0.69291411556335	-1.08075735907046	-3.07492318582413
H	-1.64264080092283	-0.45554257966853	-3.30335930643360
C	-1.84666657054788	0.20708881106196	-1.26290334197705
C	-1.21409223278376	0.36681848033436	-0.04836021364017
H	-2.88871253162985	0.48358761697941	-1.37483731429490
H	-1.73866877332796	0.76174398609179	0.81308716210601
C	3.23926954860335	2.88905350837447	-0.83664936378594
O	3.31040930366339	3.96557460420361	-0.33016290733134
C	2.57408906225661	2.56002176742913	-2.12533579610733
H	3.31415595346710	2.24201181859742	-2.86458154307638
H	1.85844313147359	1.74667257975808	-1.99321958370039
H	2.06798907910487	3.45112031829686	-2.48631987109215

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1af/TS3: pro-*anti*

C	0.91422510562900	-0.07754466955111	1.61606050141687
C	0.46992867872041	0.13029259191581	0.21266954075687
C	1.18932434466849	-0.37622815738170	-0.89069376982093
C	2.41836121341776	-1.07708031208364	-0.64459042641292
C	2.86641863224954	-1.23931800121922	0.69380298535444
C	2.13996091900692	-0.76004788478140	1.77514684858735
C	0.68684802236078	-0.18294053188290	-2.18734481093834
O	3.02654201746262	-1.79577404676456	-1.60907773442473
C	4.35245702567603	-1.44555373625100	0.76159950721864
H	2.56098827203711	-0.84417039170589	2.76979447793328
O	0.22714884850578	0.36294145044195	2.55814490653215
H	4.75358112516270	-2.27791342991874	0.19323075927136
C	4.33181872253523	-0.16776392723606	0.01904444605967
H	4.75042336484270	-1.38782980393984	1.77013244935760
H	4.54623277887531	-0.08824389869980	-1.03764606525706
O	4.37382012641950	0.95446458537586	0.74449447508646
H	2.79475427908855	-1.45801365029538	-2.48192857336786
C	-0.47638393673721	0.52399389487307	-2.39055838757219
H	1.20529536187608	-0.57753377953759	-3.05480426879781
H	-0.84707335879273	0.67330874952303	-3.39774790431895
C	-1.17640255888582	1.04458253306192	-1.30018704384538
C	-0.70743548888672	0.84181226579823	-0.01976637773299
H	-2.09277743615759	1.60038961408480	-1.46259511960395
H	-1.24110714425264	1.22287794277957	0.84223565433379
C	4.05963406838583	2.13799744629132	0.09790284650324
O	3.78532870412244	2.16219784421644	-1.06387438320670
C	4.11936881825797	3.27302669182774	1.05085241201529

H	3.37235714204535	3.12014252685576	1.83346017464398
H	5.09846481938824	3.30116982510393	1.53257443888114
H	3.92570853297789	4.20392225909934	0.52494244134777