

Supporting Information:

Palladium triggered dienes formation from allylic nitro compounds: a versatile entry into aromatic derivatives.

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1. General Information

All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of argon. All commercial materials were used without further purification. Reactions were monitored by TLC on Merck silica gel 60-F₂₅₄ aluminium sheets (ref.1.05554.0001), using UV absorption then vanillin-H₂SO₄ (1% vanillin in ethanol + 2% H₂SO₄) or basic permanganate (1% KMnO₄ + 15% Na₂CO₃ in water) as staining system. Column chromatography was carried out on silica gel (40-63 μm). NMR spectra were recorded on a Bruker 400 MHz Avance III spectrometer. Proton chemical shifts are reported in ppm (δ) with the solvent resonance employed as the internal standard (CDCl₃ δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, Q = quintuplet, h = heptuplet, m = multiplet, br = broad), coupling constants (Hz) and integration. Carbon chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃ δ 77.16). IR spectra were performed on a Perkin-Elmer FT 1600 spectrometer with wavenumbers in cm⁻¹ and only peaks of interest are reported. High-Resolution Mass spectra (HRMS) were carried out with JEOL JMS-GCmate II spectrometer. Melting points (M_p) were determined on a Stuart SMP3 apparatus and were left uncorrected. 1-(Nitromethyl)cyclohex-1-ene,¹ 1-(nitromethyl)cyclopent-1-ene,² 4-(nitromethyl)-1,2-dihydronaphthalene² and 1-chloro-4-(1-nitrobut-2-en-2-yl)benzene² were synthesized according to literature.

2. Experimental procedures

2.1. Preparation of allylic nitro compounds

General procedure A: double Michael addition:

To a solution of nitro compound (1 eq.) in acetonitrile ($C = 0.5 \text{ M}$) was added the desired Michael acceptor (3 eq.) and DBU (0.5 eq.). The mixture was stirred for 2 h at r.t. under argon. After evaporation of solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel.

General procedure B: double Michael addition:

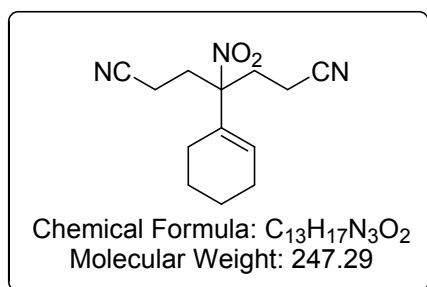
To a solution of nitro compound (1 eq.) in acetonitrile ($C = 0.33 \text{ M}$) was added the desired Michael acceptor (5 eq.) and DBU (0.5 eq.). The mixture was stirred for 3 h at r.t. under argon. After evaporation of solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel.

General procedure C: mono Michael addition:

To a solution of nitro compound (1 eq.) in acetonitrile ($C = 0.33 \text{ M}$) was added the desired Michael acceptor (3 eq.) and DBU (0.1 eq.). The mixture was stirred for 2 h at r.t. under argon. After evaporation of solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel.

4-(Cyclohex-1-en-1-yl)-4-nitroheptanedinitrile (2a):

Prepared from 1-(nitromethyl)cyclohex-1-ene (141 mg, 1 eq., 1 mmol) according to general procedure A (acrylonitrile as Michael acceptor). Purification by column chromatography on silica gel (Et₂O/petroleum ether = 70:30) to afford the desired product (89%, 220 mg) as a red oil.



R_f = 0.21 (Et₂O/petroleum ether, 7:3).

¹H NMR (400 MHz, CDCl₃) δ_H = 5.80 (t, *J* = 3.8 Hz, 1H), 2.49–2.28 (m, 8H), 2.18 (dt, *J* = 6.1, 3.8 Hz, 2H), 1.83–1.82 (m, 2H), 1.71–1.58 (m, 4H).

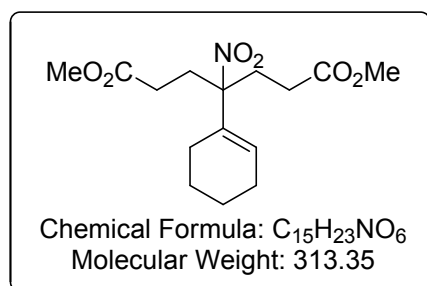
¹³C NMR (101 MHz, CDCl₃) δ_C = 131.7, 129.6, 118.2 (2C), 95.8, 29.8 (2C), 25.4, 24.8, 22.2, 21.4, 13.0 (2C).

HRMS: calculated for [M-NO₂]: 201.1386, found: 201.1387.

ν_{max} (thin film): 2935, 2862, 1538, 1449, 1423, 1339, 1276, 1159, 1143 cm⁻¹.

Methyl 6-acetoxy-4-(cyclohex-1-en-1-yl)-4-nitrohexanoate (2b):

Prepared from 1-(nitromethyl)cyclohex-1-ene (141 mg, 1 eq., 1 mmol) according to general procedure A (methyl acrylate as Michael acceptor). Purification by column chromatography on silica gel (Et₂O/petroleum ether = 30:70) to afford the desired product (92%, 288 mg) as a colorless oil.



R_f = 0.24 (Et₂O/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = 5.84–5.82 (m, 1H), 3.65 (s, 6H), 2.42–2.21 (m, 6H), 2.18–2.10 (m, 4H), 1.79–1.77 (m, 2H), 1.61–1.51 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ_C = 172.7 (2C), 133.5, 128.0, 96.7, 52.0 (2C), 29.0 (2C), 28.2 (2C), 25.4, 24.5, 22.5, 21.7.

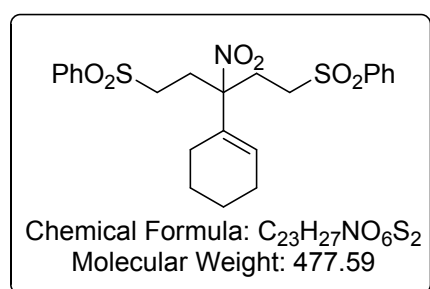
HRMS: calculated for [M-NO₂]: 267.1591, found: 267.1591.

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ν_{\max} (thin film): 2935, 2861, 1733, 1537, 1436, 1321, 1294, 1276, 1258, 1196, 1173, 1071 cm^{-1} .

(3-(Cyclohex-1-en-1-yl)-3-nitropentane-1,5-diylbisulfonyl)dibenzene (2c):

Prepared from 1-(nitromethyl)cyclohex-1-ene (141 mg, 1 eq., 1 mmol) according to general procedure A ((vinylsulfonyl)benzene as Michael acceptor). Purification by column chromatography on silica gel (EtOAc:petroleum ether = 30:70) to afford the desired product (99%, 473 mg) as a white solid.



$M_p = 139\text{ }^\circ\text{C}$.

$R_f = 0.23$ (EtOAc/petroleum ether, 3:7).

$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta_{\text{H}} = 7.90\text{--}7.88$ (m, 4H), 7.72-7.69 (m, 2H), 7.63-7.59 (m, 4H), 5.69 (br s, 1H), 3.05-2.88 (m, 4H), 2.46-2.31 (m, 4H), 2.09 (br s, 2H), 1.64 (br s, 2H), 1.53 (br s, 4H).

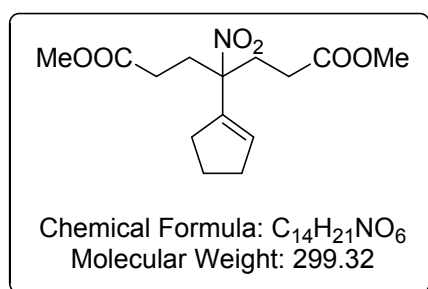
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta_{\text{C}} = 138.4$ (2C), 134.4 (2C), 131.9, 129.8 (4C), 129.3, 128.2 (4C), 95.2, 51.4 (2C), 27.3 (2C), 25.3, 24.4, 22.3, 21.5.

HRMS: calculated for $\text{C}_{23}\text{H}_{27}\text{NO}_6\text{S}_2$: 477.1280, not found.

ν_{\max} (thin film): 2933, 2861, 1540, 1446, 1305, 1289, 1145, 1085, 1072 cm^{-1} .

Dimethyl 4-(cyclopent-1-en-1-yl)-4-nitroheptanedioate (2d):

Prepared from 1-(nitromethyl)cyclopent-1-ene (127 mg, 1 eq., 1 mmol) according to general procedure A (methyl acrylate as Michael acceptor). Purification by column chromatography on silica gel (Et_2O /petroleum ether = 30:70) to afford the desired product (68%, 204 mg) as a light yellow oil.



$R_f = 0.27$ (Et_2O /petroleum ether, 3:7).

$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta_{\text{H}} = 5.89\text{--}5.87$ (m, 1H), 3.67 (s, 6H), 2.51-2.16 (m, 12H), 1.90 (dt, $J = 19.1, 7.5$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta_{\text{C}} = 172.6$ (2C), 140.1, 132.3, 93.5, 52.1 (2C), 32.7, 32.0, 29.1 (2C), 29.0 (2C), 23.2.

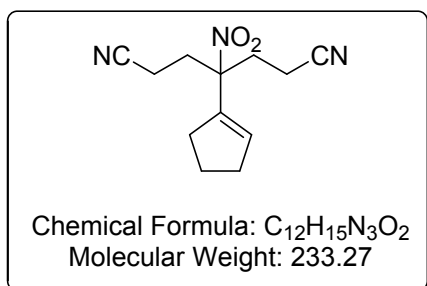
Supporting Information:

HRMS: calculated for [M-NO₂]: 253.1434, found: 253.1435.

ν_{\max} (thin film): 2953, 2849, 1733, 1538, 1436, 1375, 1349, 1320, 1298, 1259, 1196, 1175 cm⁻¹.

4-(Cyclopent-1-en-1-yl)-4-nitroheptanedinitrile (2e):

Prepared from 1-(nitromethyl)cyclopent-1-ene (127 mg, 1 eq., 1 mmol) according to general procedure A (acrylonitrile as Michael acceptor). Purification by column chromatography on silica gel (Et₂O/petroleum ether =70:30) to afford the desired product (65%, 150 mg) as a yellow oil.



R_f = 0.32 (Et₂O/petroleum ether, 7:3).

¹H NMR (400 MHz, CDCl₃) δ_{H} = 5.90–5.88 (m, 1H), 2.54–2.25 (m, 12H), 2.02–1.95 (m, 2H).

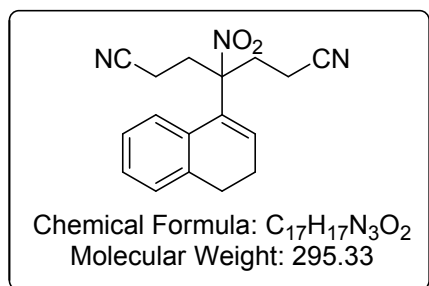
¹³C NMR (101 MHz, CDCl₃) δ_{C} = 137.8, 134.1, 118.1 (2C), 92.6, 32.8, 32.3, 30.4 (2C), 23.1, 12.9 (2C).

HRMS: calculated for [M-NO₂]: 187.1230, found: 187.1230.

ν_{\max} (thin film): 2958, 2849, 1539, 1447, 1422, 1348, 1332, 1302, 1276, 1045 cm⁻¹.

4-(3,4-Dihydronaphthalen-1-yl)-4-nitroheptanedinitrile (4a):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure B (acrylonitrile as Michael acceptor). Purification by column chromatography on silica gel (petroleum ether/Et₂O = 1:0 → 3:7) to afford the desired product (99%, 292 mg) as a colorless oil.



R_f = 0.22 (Et₂O/petroleum ether, 7:3).

¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.24–7.19 (m, 2H), 7.18–7.13 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.36 (t, *J* = 4.9 Hz, 1H), 2.80–2.66 (m, 6H), 2.45–2.34 (m, 4H), 2.32–2.24 (m, 2H).

Supporting Information:

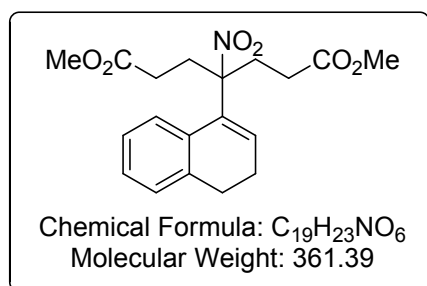
¹³C NMR (101 MHz, CDCl₃) δ_C = 137.5, 133.2, 131.8, 130.4, 129.0, 128.5, 127.1, 122.1, 118.0 (2C), 93.5, 30.9 (2C), 27.9, 23.4, 13.2 (2C).

HRMS: calculated for [M-NO₂]: 249.1386, found: 249.1386.

ν_{\max} (thin film): 2944, 2889, 2835, 1542, 1487, 1452, 1426, 1344, 1275, 1026 cm⁻¹.

Dimethyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedioate (4b):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure B (methyl acrylate as Michael acceptor). Purification by column chromatography on silica gel (Et₂O/petroleum ether = 40:60) to afford the desired product (98%, 177 mg) as a colorless oil.



R_f = 0.25 (Et₂O/petroleum ether, 4:6).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.19–7.05 (m, 3H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.38 (t, *J* = 4.8 Hz, 1H), 3.61 (s, 6H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.62–2.58 (m, 4H), 2.39–2.30 (m, 2H), 2.27–2.16 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ_C = 172.4 (2C), 137.3, 133.4, 131.8, 131.3, 128.4, 127.6, 126.7, 122.5, 94.1, 52.0, 51.9, 29.8 (2C), 29.1, 28.1, 23.3.

HRMS: calculated for C₁₉H₂₃NO₆: 361.1525, not found, fragment (-HNO₂): 314.1518.

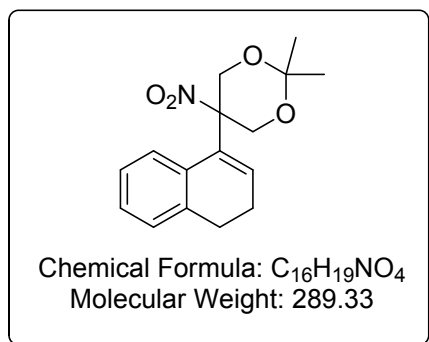
ν_{\max} (thin film): 3066, 3001, 2954, 2893, 2837, 1737, 1542, 1487, 1452, 1439, 1379, 1348, 1293, 1202, 1179 cm⁻¹.

5-(3,4-Dihydronaphthalen-1-yl)-2,2-dimethyl-5-nitro-1,3-dioxane (4c):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure B (formaldehyde as Michael acceptor). Purification by column chromatography on silica gel (EtOAc/petroleum ether = 4:6) to afford the 2-(3,4-dihydronaphthalen-1-yl)-2-nitropropane-1,3-diol (66%, 82 mg) as a colorless oil.

In a round-bottomed flask was added 2-(3,4-dihydronaphthalen-1-yl)-2-nitropropane-1,3-diol (125 mg, 1 eq., 0.5 mmol), *p*-toluenesulfonic acid (8 mg, 0.1 eq., 0.05 mmol), an excess of MgSO₄ (1 g) and 1.5 mL of acetone. The mixture was heated under reflux for 15 h. After

evaporation of solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel (Et₂O/petroleum ether = 30:70) to afford the desired product (45%, 65 mg) as a colorless oil.



R_f = 0.67 (EtOAc:petroleum ether, 4:6).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.17–7.12 (m, 3H), 7.07–7.05 (m, 1H), 6.47–6.45 (m, 1H), 4.84 (d, *J* = 12.8 Hz, 2H), 4.25 (d, *J* = 12.8 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.35 (dt, *J* = 12.7, 6.5 Hz, 2H), 1.46 (s, 3H), 1.43 (s, 3H).

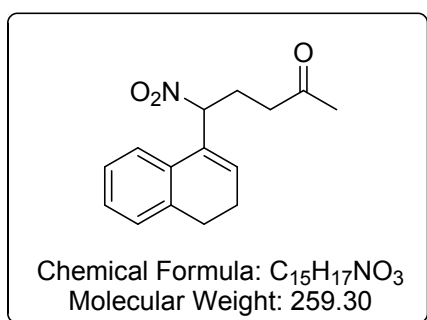
¹³C NMR (101 MHz, CDCl₃) δ_C = 137.4, 132.4, 132.3, 131.0, 128.5, 127.8, 126.8, 123.1, 100.0, 89.2, 65.0 (2C), 27.9, 25.7, 23.4, 21.6.

HRMS: calculated for [M-NO₂]:243.1380, found: 243.1380.

ν_{max} (thin film): 3413, 2986, 2938, 2852, 1542, 1485, 1445, 1370, 1223, 1200, 1155, 1080, 1015 cm⁻¹.

5-(3,4-Dihydronaphthalen-1-yl)-5-nitropentan-2-one (4e):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure C (but-3-en-2-one as Michael acceptor). Purification by column chromatography on silica gel (Et₂O/petroleum ether = 30:70) to afford the desired product (84%, 109 mg) as a colorless oil.



R_f = 0.26 (Et₂O/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.33 (d, *J* = 7.3 Hz, 1H), 7.25–7.13 (m, 3H), 6.37 (t, *J* = 4.7 Hz, 1H), 5.66–5.62 (m, 1H), 2.76–2.72 (m, 2H), 2.62–2.45 (m, 3H), 2.40–2.29 (m, 3H), 2.14 (s, 3H).

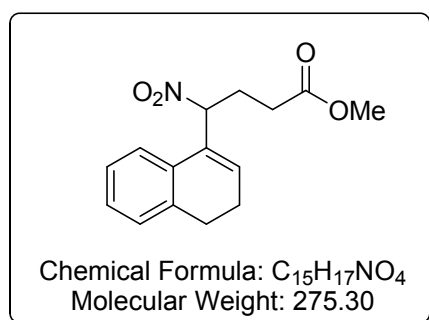
¹³C NMR (101 MHz, CDCl₃) δ_C = 206.7, 136.2, 132.2, 131.8, 130.4, 128.1, 127.8, 126.8, 122.1, 86.2, 39.3, 30.0, 27.5, 26.4, 23.0.

HRMS: calculated for C₁₅H₁₇NO₃: 259.1208, found: 259.1201.

ν_{max} (thin film): 3064, 3024, 2944, 2893, 2836, 1717, 1551, 1489, 1451, 1437, 1428, 1366, 1167, 1023 cm⁻¹.

Methyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitrobutanoate (**4f**):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure C (methyl acrylate as Michael acceptor). Purification by column chromatography on silica gel (CH₂Cl₂/petroleum ether = 40:60) to afford the desired product (71%, 98 mg) as a colorless oil.



R_f = 0.49 (CH₂Cl₂/petroleum ether, 5:5).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.25 (d, *J* = 7.6 Hz, 1H), 7.20–7.04 (m, 3H), 6.30 (t, *J* = 4.5 Hz, 1H), 5.63–5.59 (m, 1H), 3.61 (s, 3H), 2.69–2.65 (m, 2H), 2.60–2.51 (m, 1H), 2.38–2.25 (m, 5H).

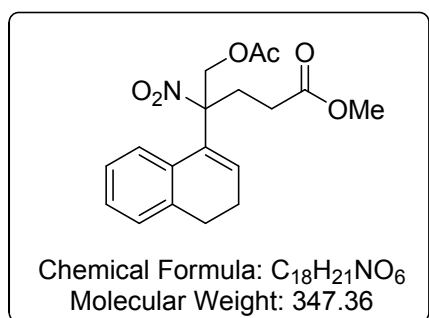
¹³C NMR (101 MHz, CDCl₃) δ_C = 172.5, 136.4, 132.2, 131.8, 130.6, 128.2, 127.9, 126.9, 122.2, 86.2, 52.0, 30.3, 27.8, 27.6, 23.1.

HRMS: calculated for C₁₅H₁₇NO₄: 275.1158, found: 275.1161.

ν_{max} (thin film): 2953, 2892, 2836, 1736, 1553, 1489, 1439, 1371, 1258, 1230, 1204, 1176, 1023 cm⁻¹.

Methyl 5-acetoxy-4-(3,4-dihydronaphthalen-1-yl)-4-nitropentanoate (**4g**):

Prepared from methyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitrobutanoate **4f** (138 mg, 1 eq., 0.5 mmol) according to general procedure C (formaldehyde as Michael acceptor). The crude residue was dissolved in dichloromethane (1.5 mL), and then acetic anhydride (94 μL, 2 eq., 1 mmol) and DMAP (6 mg, 0.1 eq., 0.05 mmol) were added. The mixture was stirred at r.t. for 2 h under Ar. After evaporation of solvent under reduced pressure, the crude was purified by column chromatography on silica gel (EtOAc/petroleum ether = 30:70) to afford the desired product (44%, 77 mg) as colorless oil.



R_f = 0.54 (EtOAc/petroleum ether, 4:6).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.19–7.06 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.26 (t, *J* = 4.9 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 3.56 (s, 3H), 2.87–2.61 (m, 4H), 2.36–2.12 (m, 4H), 2.06 (s, 3H).

Supporting Information:

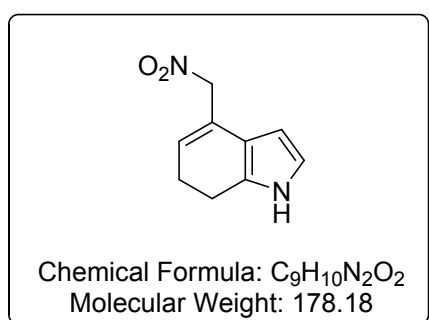
^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 172.2, 170.0, 137.2, 131.8, 131.8, 130.9, 128.4, 127.8, 126.8, 122.4, 92.8, 65.2, 51.9, 29.2, 27.8, 27.0, 23.2, 20.6.

HRMS: calculated for $\text{C}_{18}\text{H}_{21}\text{NO}_6$: 347.1369, not found.

ν_{max} (thin film): 2949, 2906, 1738, 1544, 1487, 1439, 1367, 1339, 1226, 1160, 1104, 1065 cm^{-1} .

4-(Nitromethyl)-6,7-dihydro-1H-indole (11):

In a round-bottomed flask, fitted with a Dean-Stark trap, was added 1,5,6,7-tetrahydro-4H-indol-4-one (676 mg, 1 eq., 5 mmol), nitromethane (2.68 mL, 10 eq., 50 mmol), *N,N*-dimethylethane-1,2-diamine (164 μL , 0.3 eq., 1.5 mmol), and toluene (25 mL). The mixture was stirred under reflux for 72h. After evaporation of solvent under reduced pressure, the crude residue was purified by column chromatography on silica gel (EtOAc/petroleum ether = 30:70) to afford the desired product 4-(nitromethyl)-6,7-dihydro-1H-indole (45%, 401 mg) as a yellow solid.



M_{p} = 146 $^{\circ}\text{C}$.

R_{f} = 0.57 (EtOAc/petroleum ether, 5:5).

^1H NMR (400 MHz, CDCl_3) δ_{H} = 8.54 (br s, 1H), 7.41 (t, J = 1.6 Hz, 1H), 6.76–6.68 (m, 1H), 6.31 (dd, J = 3.2, 2.4 Hz, 1H), 3.26–3.23 (m, 2H), 2.74 (t, J = 6.3 Hz, 2H), 2.02–1.96 (m, 2H).

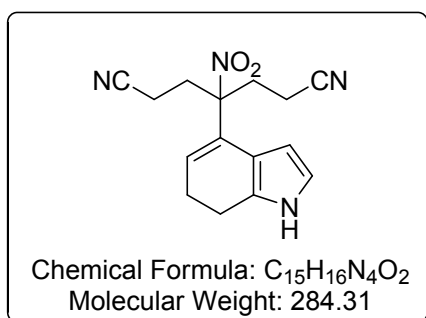
^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 149.3, 139.0, 127.7, 119.4, 115.2, 104.3, 26.5, 23.1, 22.7.

HRMS: calculated for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$: 178.0742, found: 178.0740.

ν_{max} (thin film): 3270, 2941, 1572, 1546, 1503, 1459, 1413, 1329, 1301, 1240, 1182, 1139, 1100, 1018 cm^{-1} .

4-(6,7-Dihydro-1H-indol-4-yl)-4-nitroheptanedinitrile (5a):

Prepared from 4-(nitromethyl)-6,7-dihydro-1H-indole **10** (89 mg, 1 eq., 0.5 mmol) according to general procedure B (acrylonitrile as Michael acceptor). Purification by column chromatography on silica gel (EtOAc/petroleum ether = 30:70) to afford the desired product (83%, 118 mg) as a yellow oil.



$R_f = 0.56$ (EtOAc/petroleum ether, 5:5).

$^1\text{H NMR}$ (400 MHz, CDCl₃) $\delta_{\text{H}} = 8.21$ (br s, 1H), 6.58 (t, $J = 2.5$ Hz, 1H), 5.80 (d, $J = 2.2$ Hz, 1H), 5.53 (t, $J = 4.5$ Hz, 1H), 2.74–2.57 (m, 6H), 2.53–2.42 (m, 4H), 2.38–2.28 (m, 2H).

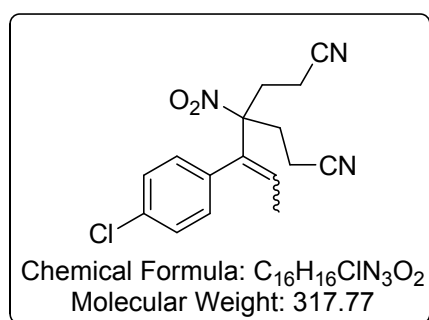
$^{13}\text{C NMR}$ (101 MHz, CDCl₃) $\delta_{\text{C}} = 130.4, 129.5, 119.7, 118.4$ (2C), 116.8, 112.9, 103.4, 94.1, 30.8 (2C), 24.2, 20.6, 13.1 (2C).

HRMS: calculated for C₁₅H₁₆N₄O₂: 284.1273, found: 284.1267.

ν_{max} (thin film): 3401, 2942, 1542, 1450, 1422, 1348, 1086 cm⁻¹.

4-(1-(4-Chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedinitrile (8a):

To a solution of 1-chloro-4-(1-nitrobut-2-en-2-yl)benzene (223 mg, 1 eq., 1.05 mmol) in acetonitrile (2.1 mL) was added acrylonitrile (345 μL , 5 eq., 5.27 mmol), K₂CO₃ (87 mg, 0.6 eq., 0.63 mmol) and benzyltriethylammonium chloride (120 mg, 0.5 eq., 0.53 mmol). The mixture was stirred for 24 h at r.t. under argon. Purification by column chromatography on silica gel (EtOAc/petroleum ether = 30:70) to afford the desired product (60%, 201 mg, *E/Z* mixture 63:37) as a white solid.



$M_p = 110$ °C.

$R_f = 0.3$ for the 1st isomer and 0.4 for the 2nd isomer (EtOAc/petroleum ether, 3:7).

$^1\text{H NMR}$ (400 MHz, CDCl₃) $\delta_{\text{H}} =$ (mixture of 2 isomers, signals of minor indicated by *) 7.41-7.37 (m, 2H), 7.37-7.33* (m, 2H), 7.13-7.07* (m, 2H), 6.49-6.88 (m, 2H), 6.10 (q, $J = 6.8$ Hz, 1H), 5.87* (q, $J = 7.7$ Hz, 1H), 2.60-2.33 (m, 8H of both isomers), 1.71* (d, $J = 7.7$ Hz, 3H), 1.53 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl₃) $\delta_{\text{C}} = 138.5$ (1C*), 135.8 (1C), 135.6 (1C*), 135.0 (1C*), 135.0 (1C), 134.5 (1C*), 132.9 (1C), 132.0 (1C), 130.5 (2C), 130.2 (2C*), 129.6 (2C), 129.0 (2C*), 117.9 (2C*), 117.8 (2C), 95.0 (1C), 93.1 (1C*), 32.6 (2C*), 29.4 (2C), 15.5 (1C), 14.8 (1C*), 13.0 (2C), 12.9 (2C*).

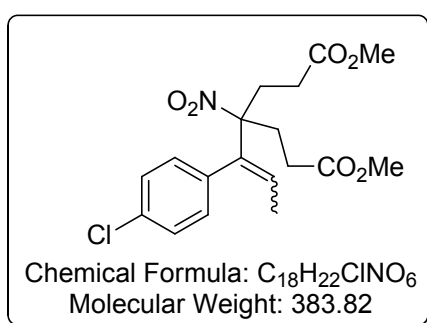
Supporting Information:

HRMS: calculated for $C_{16}H_{16}ClN_3O_2$: 317.0931, not found, fragment (-HNO₂): 271.1.

ν_{\max} (thin film): 2251, 1545, 1444, 1344, 1091, 1015, 829, 744, 581 cm^{-1} .

Dimethyl 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedioate (8b):

Prepared from 1-chloro-4-(1-nitrobut-2-en-2-yl)benzene (560 mg, 1eq., 2.65 mmol) according to general procedure B. Purification by column chromatography on silica gel (Et₂O/petroleum ether = 20:80) to afford the desired product (94%, 948 mg, *E/Z* mixture 54:46) as a colorless oil.



R_f = 0.3 for the 1st isomer and 0.5 for the 2nd isomer (EtOAc/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = (mixture of 2 isomers, signals of minor indicated by *) 7.37-7.25 (m, 2H of both isomers), 7.14* (dd, J = 6.5, 1.9 Hz, 2H), 6.90 (dd, J = 6.5, 1.8 Hz, 2H), 6.13 (q, J = 6.7 Hz, 1H), 5.73* (q, J = 7.6 Hz, 1H), 3.69 (s, 6H), 3.67* (s, 6H), 2.54-2.15 (m, 8H of both isomers), 1.70* (d, J = 7.7 Hz, 1H), 1.48 (d, J = 6.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ_C = 172.5 (2C*), 172.4 (2C), 139.9 (1C*), 137.8 (1C), 137.5 (1C), 134.3 (1C), 134.1 (1C*), 133.7 (1C*), 133.5 (1C*), 130.8 (2C), 130.6 (2C*), 130.4 (1C), 129.1 (2C), 128.5 (2C*), 96.0 (1C), 94.4 (1C*), 52.2 (2C), 52.2 (2C*), 31.8 (2C*), 29.1 (2C), 29.0 (2C*), 28.3 (2C), 15.4 (1C), 14.7 (1C*).

HRMS: calculated for $C_{18}H_{22}ClNO_6$: 383.1136, not found.

ν_{\max} (thin film): 2953, 1733, 1590, 1540, 1489, 1436, 1378, 1345, 1263, 1196, 1174, 1090, 1015, 986, 887, 826, 735, 703, 621, 579, 536 cm^{-1} .

2.2. Palladium catalyzed Tsuji-Trost elimination

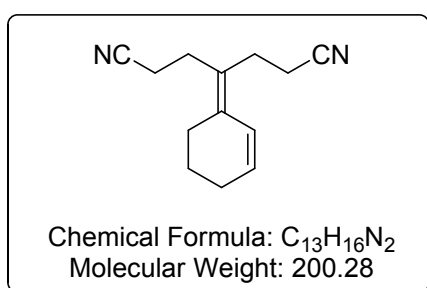
General procedure D:

To a solution of allylic nitro compound (1 eq.) in DMF (C = 0.5 M) was added Cs₂CO₃ (1 eq.), Pd(OAc)₂ (0.10 eq.) and dppe (0.10 eq.). The mixture was stirred for 30 min at 120°C

under Ar. After completion of reaction, water (10 mL) and Et₂O (20 mL) were added. The organic layer was separated, washed with water (2×10 mL), dried over MgSO₄ and evaporated. The residue was purified by column chromatography.

4-(Cyclohex-2-en-1-ylidene)heptanedinitrile (3a):

Prepared from 4-(cyclohex-1-en-1-yl)-4-nitroheptanedinitrile **2a** (124 mg, 1 eq., 0.5 mmol) according to general procedure D. The residue was purified by column chromatography (Et₂O/petroleum ether = 50:50) to give the desired product (83%, 83 mg) as a yellow oil.



R_f = 0.45 (Et₂O/petroleum ether, 6:4).

¹H NMR (400 MHz, CDCl₃) δ_H = 6.30 (dt, *J* = 10.2, 2.0 Hz, 1H), 5.95 (dt, *J* = 10.2, 4.1 Hz, 1H), 2.54–2.49 (m, 4H), 2.43–2.34 (m, 6H), 2.16–2.12 (m, 2H), 1.75–1.69 (m, 2H).

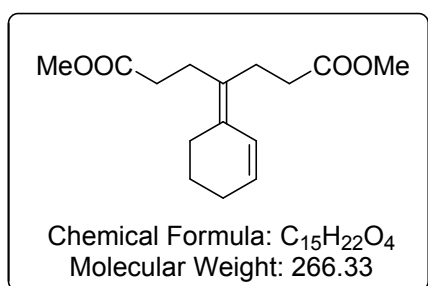
¹³C NMR (101 MHz, CDCl₃) δ_C = 135.0, 132.5, 125.6, 124.1, 119.3, 119.2, 28.0, 27.0, 26.6, 25.6, 22.7, 17.0, 16.4.

HRMS: calculated for C₁₃H₁₆N₂: 200.1313, found: 200.1310.

ν_{max} (thin film): 3478, 2930, 2864, 2832, 1670, 1544, 1453, 1423, 1338, 1254, 1059, 1041 cm⁻¹.

Methyl 6-acetoxy-4-(cyclohex-2-en-1-ylidene)hexanoate (3b):

Prepared from methyl 6-acetoxy-4-(cyclohex-1-en-1-yl)-4-nitrohexanoate **2b** (157 mg, 1 eq., 0.5 mmol) according to general procedure D. The residue was purified by column chromatography (Et₂O/petroleum ether = 20:80) to give the desired product (77%, 102 mg) as a colorless oil.



R_f = 0.32 (Et₂O/petroleum ether, 2:8).

¹H NMR (400 MHz, CDCl₃) δ_H = 6.36 (dt, *J* = 10.2, 2.0 Hz, 1H), 5.79 (dt, *J* = 10.2, 4.1 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.46–2.22 (m, 10H), 2.11–2.07 (m, 2H), 1.69–1.63 (m, 2H).

Supporting Information:

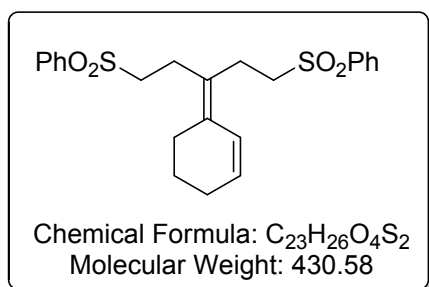
^{13}C NMR (101 MHz, CDCl_3) $\delta_{\text{C}} = 173.8, 173.8, 131.1, 130.0, 129.6, 125.2, 51.8, 51.8, 33.8, 33.1, 27.6, 26.8, 26.5, 25.7, 22.9$.

HRMS: calculated for $\text{C}_{15}\text{H}_{22}\text{O}_4$: 266.1518, found: 266.1524.

ν_{max} (thin film): 2950, 1731, 1673, 1435, 1365, 1297, 1255, 1194, 1166, 1068, 1019 cm^{-1} .

(3-(Cyclohex-2-en-1-ylidene)pentane-1,5-diyl)disulfonyl)dibenzene (3c):

Prepared from (3-(cyclohex-1-en-1-yl)-3-nitropentane-1,5-diyl)disulfonyl)dibenzene **2c** (239 mg, 1 eq., 0.5 mmol) according to general procedure D. The residue was purified by column chromatography (Et_2O /petroleum ether = 70:30) to give the desired product (78%, 167 mg) as colorless oil.



$R_f = 0.32$ (Et_2O /petroleum ether, 7:3).

^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 7.90\text{--}7.88$ (m, 4H), 7.69–7.65 (m, 2H), 7.60–7.55 (m, 4H), 6.04 (dt, $J = 10.2, 1.9$ Hz, 1H), 5.81 (dt, $J = 10.1, 4.1$ Hz, 1H), 3.05–2.99 (m, 4H), 2.47–2.40 (m, 4H), 2.12–2.03 (m, 4H), 1.66–1.55 (m, 2H).

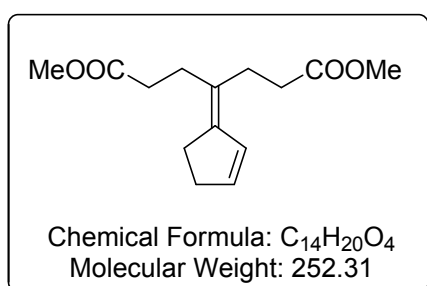
^{13}C NMR (101 MHz, CDCl_3) $\delta_{\text{C}} = 139.0, 139.0, 134.0, 134.0$ (2C), 132.1, 129.5 (2C), 129.5 (2C), 128.1 (2C), 128.1 (2C), 124.0, 123.9, 55.0, 54.4, 26.4, 25.5, 25.2, 24.3, 22.5.

HRMS: calculated for $\text{C}_{23}\text{H}_{26}\text{O}_4\text{S}_2$: 430.1273, not found.

ν_{max} (thin film): 3062, 2927, 2830, 1446, 1304, 1230, 1141, 1084, 1071, 1024 cm^{-1} .

Dimethyl 4-(cyclopent-2-en-1-ylidene)heptanedioate (3d):

Prepared from dimethyl 4-(cyclopent-1-en-1-yl)-4-nitroheptanedioate **2d** (150mg, 1 eq., 0.5 mmol) according to general procedure D. The residue was purified by column chromatography (Et_2O /petroleum ether = 20:80) to give the desired product (89%, 112 mg) as a pale yellow oil.



$R_f = 0.42$ (Et_2O /petroleum ether, 3:7).

Supporting Information:

^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 6.38\text{--}6.32$ (m, 1H), 6.07 (d, $J = 5.6$ Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H), 2.47–2.34 (m, 12H).

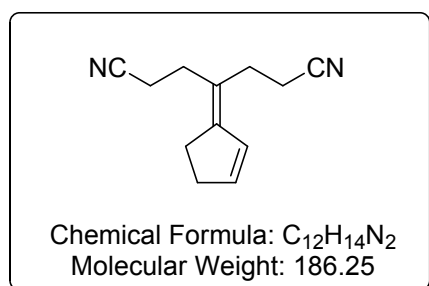
^{13}C NMR (101 MHz, CDCl_3) $\delta_{\text{C}} = 174.0, 173.9, 143.9, 137.9, 130.7, 124.3, 51.7, 51.7, 33.7, 32.5, 31.9, 28.4, 27.7, 27.2$.

HRMS: calculated for $\text{C}_{14}\text{H}_{20}\text{O}_4$: 252.1362, not found.

ν_{max} (thin film): 3458, 2951, 1775, 1730, 1436, 1366, 1297, 1255, 1194, 1166, 1108, 1055, 1021 cm^{-1} .

4-(Cyclopent-2-en-1-ylidene)heptanedinitrile (3e):

Prepared from 4-(cyclopent-1-en-1-yl)-4-nitroheptanedinitrile **2e** (117 mg, 1 eq., 0.5 mmol) according to general procedure D. The residue was purified by column chromatography (Et_2O /petroleum ether = 70:30) to give the desired product (79%, 74 mg) as a yellow oil.



$R_f = 0.33$ (Et_2O /petroleum ether, 7:3).

^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 6.34\text{--}6.33$ (m, 1H), 6.24–6.22 (m, 1H), 2.54–2.50 (m, 6H), 2.45–2.39 (m, 6H).

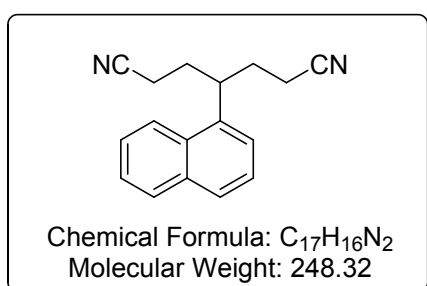
^{13}C NMR (101 MHz, CDCl_3) $\delta_{\text{C}} = 148.1, 140.9, 129.8, 120.0, 119.5, 119.4, 32.0, 28.8, 27.8, 27.4, 17.0, 15.9$.

HRMS: calculated for $\text{C}_{12}\text{H}_{14}\text{N}_2$: 186.1157, found: 186.1155.

ν_{max} (thin film): 3472, 2931, 2878, 2848, 1711, 1671, 1449, 1423, 1341, 1261, 1199, 1113, 1060, 1027 cm^{-1} .

4-(Naphthalen-1-yl)heptanedinitrile (6a):

Prepared from 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedinitrile **4a** (148 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (Et_2O /petroleum ether = 70:30) to afford the desired product (71%, 88 mg) as a colorless oil.



$R_f = 0.32$ (Et_2O /petroleum ether, 7:3).

Supporting Information:

^1H NMR (400 MHz, CDCl_3) δ_{H} = 8.18 (d, J = 7.8 Hz, 1H), 7.94–7.87 (m, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.61–7.49 (m, 3H), 7.36 (d, J = 7.1 Hz, 1H), 3.87 (br s, 1H), 2.27–2.08 (m, 8H).

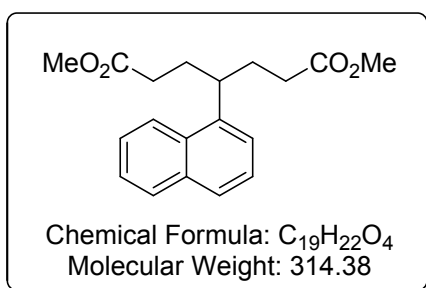
^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 136.7, 134.1, 132.6, 129.3, 128.1, 126.9, 126.2, 125.7, 122.7, 122.3, 119.4 (2C), 36.4, 32.4 (2C), 15.2 (2C).

HRMS: calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2$: 248.1313, found: 248.1313.

ν_{max} (thin film): 3047, 2934, 2871, 1596, 1511, 1454, 1422, 1397, 1362, 1257, 1168, 1028 cm^{-1} .

Dimethyl 4-(naphthalen-1-yl)heptanedioate (6b):

Prepared from dimethyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedioate **4b** (181mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (Et_2O /petroleum ether = 20:80) to afford the desired product (87%, 137 mg) as colorless oil.



R_f = 0.67 (Et_2O /petroleum ether, 4:6).

^1H NMR (400 MHz, CDCl_3) δ_{H} = 8.09 (d, J = 8.2 Hz, 1H), 7.89–7.82 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.54–7.42 (m, 3H), 7.38 (d, J = 6.6 Hz, 1H), 3.56 (s, 6H), 2.26–1.96 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 173.8 (2C), 139.6, 133.9, 132.6, 129.0, 126.9, 125.9, 125.6, 125.5 (2C), 122.8, 51.4 (2C), 36.7, 31.7 (2C), 31.5 (2C).

HRMS: calculated for $\text{C}_{19}\text{H}_{22}\text{O}_4$: 314.1518, found: 314.1528.

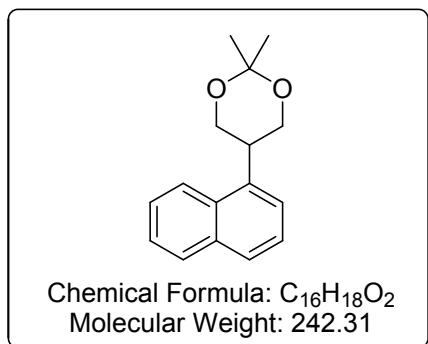
ν_{max} (thin film): 3047, 3001, 2953, 2848, 1731, 1597, 1511, 1457, 1438, 1419, 1396, 1368, 1326, 1259, 1202, 1174, 1014 cm^{-1} .

2,2-Dimethyl-5-(naphthalen-1-yl)-1,3-dioxane (6c):

Prepared from 5-(3,4-dihydronaphthalen-1-yl)-2,2-dimethyl-5-nitro-1,3-dioxane **4c** (145 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography

Supporting Information:

on silica gel (Et₂O/petroleum ether = 10:90) to afford the desired product (87%, 105 mg) as a white solid.



M_p = 108 °C.

R_f = 0.61 (Et₂O/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = 8.20 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.59–7.42 (m, 4H), 4.24–4.13 (m, 4H), 4.04–3.98 (m, 1H), 1.63 (s, 3H), 1.57 (s, 3H).

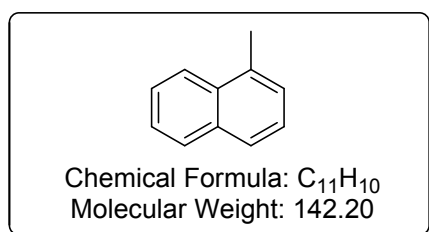
¹³C NMR (101 MHz, CDCl₃) δ_C = 135.1, 134.1, 131.9, 129.2, 127.7, 126.5, 125.9, 125.5, 123.7, 122.9, 98.3, 65.2 (2C), 36.2, 28.5, 20.1.

HRMS: calculated for C₁₆H₁₈O₂: 242.1307, found 242.1300.

ν_{max} (thin film): 3396, 3047, 2991, 2941, 2876, 1597, 1511, 1398, 1371, 1259, 1196, 1151, 1132, 1071, 1029 cm⁻¹.

1-Methylnaphthalene (6d):

Prepared from 4-(nitromethyl)-1,2-dihydronaphthalene (90 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (petroleum ether) to afford the desired product (35%, 25 mg) as a colorless oil.



R_f = 0.75 (Et₂O/petroleum ether, 0.5:9.5).

¹H NMR (400 MHz, CDCl₃) δ_H = 8.04 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.59–7.48 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 6.9 Hz, 1H), 2.74 (s, 3H).

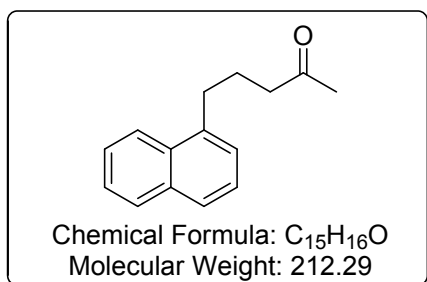
¹³C NMR (101 MHz, CDCl₃) δ_C = 134.4, 133.7, 132.7, 128.7, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 19.5.

HRMS: calculated for C₁₁H₁₀: 142.0783, found: 142.0784.

ν_{max} (thin film): 3071, 2949, 2865, 1598, 1509, 1465, 1441, 1398, 1382, 1264, 1215, 1167, 1077, 1020 cm⁻¹.

5-(Naphthalen-1-yl)pentan-2-one (6e):

Prepared from 5-(3,4-dihydronaphthalen-1-yl)-5-nitropentan-2-one **4e** (130 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (Et₂O/petroleum ether = 20:80) to afford the desired product (71%, 75 mg) as a colorless oil.



R_f = 0.51 (Et₂O/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = 8.11 (d, *J* = 8.4 Hz, 1H), 7.91–7.84 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.59–7.46 (m, 2H), 7.45–7.37 (m, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 2.06 (p, *J* = 8.0 Hz, 2H).

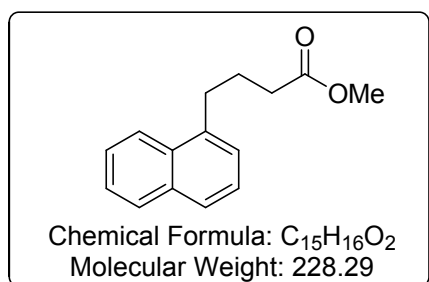
¹³C NMR (101 MHz, CDCl₃) δ_C = 208.9, 137.8, 133.9, 131.9, 128.8, 126.9, 126.2, 125.9, 125.6, 125.5, 123.9, 43.1, 32.3, 30.1, 24.6.

HRMS: calculated for C₁₅H₁₆O: 212.1201, found: 212.1205.

ν_{max} (thin film): 3044, 2941, 1710, 1595, 1509, 1396, 1354, 1262, 1218, 1180, 1162, 1080, 1027 cm⁻¹.

Methyl 4-(naphthalen-1-yl)butanoate (6f):

Prepared from methyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitrobutanoate **4f** (138 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (Et₂O/petroleum ether = 10:90) to afford the desired product (66%, 75 mg) as a colorless oil.



R_f = 0.46 (Et₂O/petroleum ether, 1:9).

¹H NMR (400 MHz, CDCl₃) δ_H = 8.09 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.56–7.47 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 1H), 3.70 (s, 3H), 3.13 (t, *J* = 7.7 Hz, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 2.11 (p, *J* = 7.4 Hz, 2H).

Supporting Information:

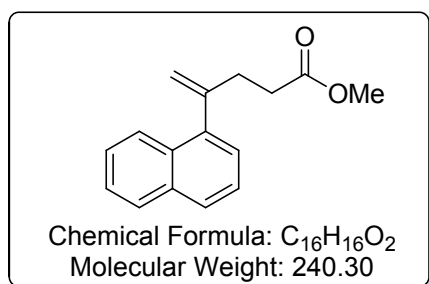
^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 174.1, 137.6, 134.0, 131.9, 128.9, 127.0, 126.3, 126.0, 125.6, 125.6, 123.9, 51.7, 33.8, 32.4, 25.9.

HRMS: calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$: 228.1150, found: 228.1144.

ν_{max} (thin film): 3065, 2953, 1731, 1597, 1511, 1438, 1395, 1367, 1251, 1220, 1168, 1147, 1011 cm^{-1} .

Methyl 4-(naphthalen-1-yl)pent-4-enoate (6g):

Prepared from methyl 5-acetoxy-4-(3,4-dihydronaphthalen-1-yl)-4-nitropentanoate **4g** (174 mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (CH_2Cl_2 /petroleum ether = 30:70) to afford the desired product (50%, 120 mg) as a colorless oil.



R_f = 0.60 (CH_2Cl_2 /petroleum ether, 5:5).

^1H NMR (400 MHz, CDCl_3) δ_{H} = 7.95–7.86 (m, 1H), 7.76–7.74 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.39–7.31 (m, 3H), 7.18 (d, J = 7.0 Hz, 1H), 5.34 (s, 1H), 5.03 (s, 1H), 3.53 (s, 3H), 2.76 (t, J = 7.6 Hz, 2H), 2.36 (t, J = 7.7 Hz, 2H).

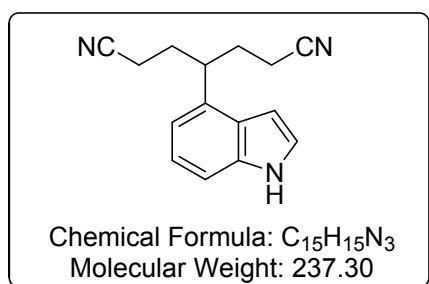
^{13}C NMR (101 MHz, CDCl_3) δ_{C} = 173.5, 147.1, 140.4, 133.8, 131.3, 128.4, 127.6, 126.0, 125.8, 125.7, 125.3 (2C), 116.1, 51.7, 33.6, 32.8.

HRMS: calculated for $\text{C}_{16}\text{H}_{16}\text{O}_2$: 240.1150, found 240.1147.

ν_{max} (thin film): 3043, 2989, 2949, 1734, 1638, 1590, 1506, 1435, 1361, 1252, 1194, 1156, 1062, 1024 cm^{-1} .

4-(1H-Indol-4-yl)heptanedinitrile (7a):

Prepared from methyl 4-(6,7-dihydro-1H-indol-4-yl)-4-nitroheptanedinitrile **5a** (142mg, 1 eq., 0.5 mmol) according to general procedure D. Purification by column chromatography on silica gel (EtOAc/petroleum ether = 30:70) to afford the desired product (67%, 80 mg) as a pale yellow oil.



R_f = 0.51 (EtOAc/petroleum ether, 4:6).

Supporting Information:

¹H NMR (400 MHz, CDCl₃) δ_{H} = 8.44 (br s, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.24–7.23 (m, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.61–6.60 (m, 1H), 3.26–3.20 (m, 1H), 2.22–2.05 (m, 8H).

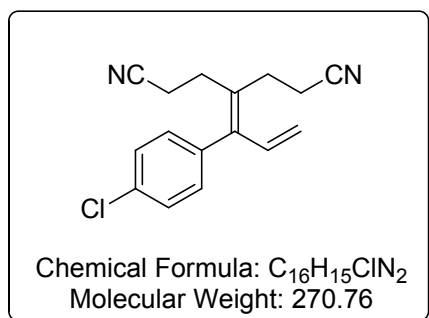
¹³C NMR (101 MHz, CDCl₃) δ_{C} = 136.2, 131.6, 127.1, 124.7, 122.5, 119.7 (2C), 117.9, 110.6, 100.5, 42.0, 31.6 (2C), 15.6 (2C).

HRMS: calculated for C₁₅H₁₅N₃: 237.1266, found: 237.1269.

ν_{max} (thin film): 3396, 2930, 1612, 1550, 1503, 1417, 1338, 1200, 1157, 1119, 1090 cm⁻¹.

4-(1-(4-Chlorophenyl)allylidene)heptanedinitrile (9a):

Prepared from 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedinitrile (56mg, 1eq., 0.18 mmol) according to general procedure D but with 0.05 eq. of Pd(OAc)₂ and dppe. Purification by column chromatography on silica gel (Et₂O/petroleum ether = 30:70) to afford the desired product (67%, 32 mg) as a yellow oil.



R_{f} = 0.37 (EtOAc/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.38 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.84 (dd, J = 16.9, 10.6 Hz, 1H), 5.29 (d, J = 10.6 Hz, 1H), 4.69 (d, J = 16.9 Hz, 1H), 2.75 (t, J = 7.3 Hz, 2H), 2.58 (t, J = 7.3 Hz, 2H), 2.30–2.19 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ_{C} = 141.5, 136.4, 133.6, 133.6, 132.4, 131.1 (2C), 129.0 (2C), 121.0, 118.8, 118.8, 29.3, 26.3, 17.1, 16.3.

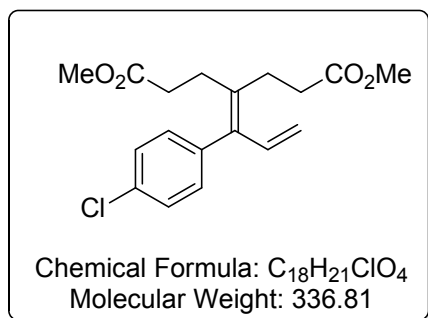
HRMS: calculated for C₁₆H₁₅ClN₂: 270.0924, found: 270.0914.

ν_{max} (thin film): 2928, 2246, 1591, 1488, 1451, 1422, 1393, 1221, 1088, 1055, 1016, 983, 917, 829, 737, 630, 578 cm⁻¹.

Dimethyl 4-(1-(4-chlorophenyl)allylidene)heptanedioate (9b):

Prepared from dimethyl 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedioate (53mg, 1eq., 0.14 mmol) according to general procedure D but with 0.05 eq. of Pd(OAc)₂ and dppe.

Purification by column chromatography on silica gel (Et₂O/petroleum ether = 10:90) to afford the desired product (75%, 35 mg) as a yellow oil.



R_f = 0.80 (EtOAc/petroleum ether, 3:7).

¹H NMR (400 MHz, CDCl₃) δ_H = 7.32 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.88 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 16.0 Hz, 1H), 3.70 (s, 3H), 3.59 (s, 3H), 2.68-2.58 (m, 2H), 2.55-2.44 (m, 2H), 2.31-2.22 (m, 2H), 2.22-2.14 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ_C = 173.3, 173.2, 137.7, 137.7, 137.1, 134.6, 132.8, 131.1 (2C), 128.6 (2C), 118.0, 51.9, 51.8, 33.5, 32.9, 29.0, 26.0.

HRMS: calculated for C₁₈H₂₁ClO₄: 336.1128, not found.

ν_{max} (thin film): 2951, 1732, 1622, 1592, 1488, 1435, 1392, 1364, 1252, 1194, 1167, 1099, 1088, 1061, 1016, 910, 830, 740, 630, 576 cm⁻¹.

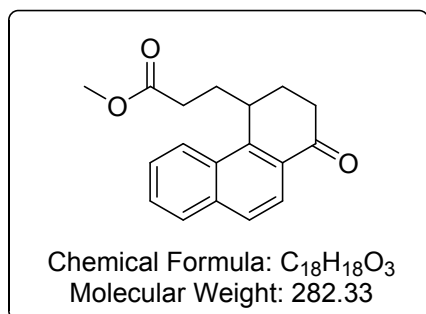
2.3. Product functionalization

Methyl 3-(1-oxo-1,2,3,4-tetrahydrophenanthren-4-yl)propanoate (10):

To dimethyl 4-(naphthalen-1-yl)heptanedioate **6b** (157 mg, 1 eq., 0.5 mmol) was added triflic acid (1.5 mL) at 0 °C. The mixture was stirred 48 h at r.t. and then was poured into a mixture of water and ice. The aqueous layer was extracted with CH₂Cl₂ (3 x 15 mL), and the organic layers were gathered, washed with brine and dried over MgSO₄. After evaporation of solvent under reduced pressure, the crude was purified by column chromatography on silica gel (petroleum ether/Et₂O = 9:1 → 1:1) to afford the desired product (70%, 99 mg) as colorless oil.

R_f = 0.36 (Et₂O/petroleum ether, 1:1).

¹H NMR (400 MHz, CDCl₃) δ_H = 8.29-8.22 (m, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.89-7.82 (m, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.66-7.56 (m, 2H), 3.81 (dq, *J* = 11.2, 3.7 Hz, 1H), 3.73 (s, 3H), 2.92-2.78 (m, 1H), 2.74-2.64 (m, 1H), 2.63-2.53 (m, 2H), 2.35-2.26 (m, 2H), 2.24-2.12 (m, 1H), 2.08-1.96 (m, 1H).



¹³C NMR (101 MHz, CDCl₃) δ_C = 198.0, 173.6, 146.9, 136.2, 130.6, 129.2, 129.1, 128.4, 127.5, 127.1, 125.2, 123.0, 51.9, 32.8, 32.4, 32.3, 27.7, 24.7.

Supporting Information:

HRMS: calculated for $C_{15}H_{17}NO_3$: 259.1208, found: 259.1201.

ν_{\max} (thin film): 3064, 3024, 2944, 2893, 2836, 1717, 1551, 1489, 1451, 1437, 1428, 1366, 1167, 1023 cm^{-1} .

3. References

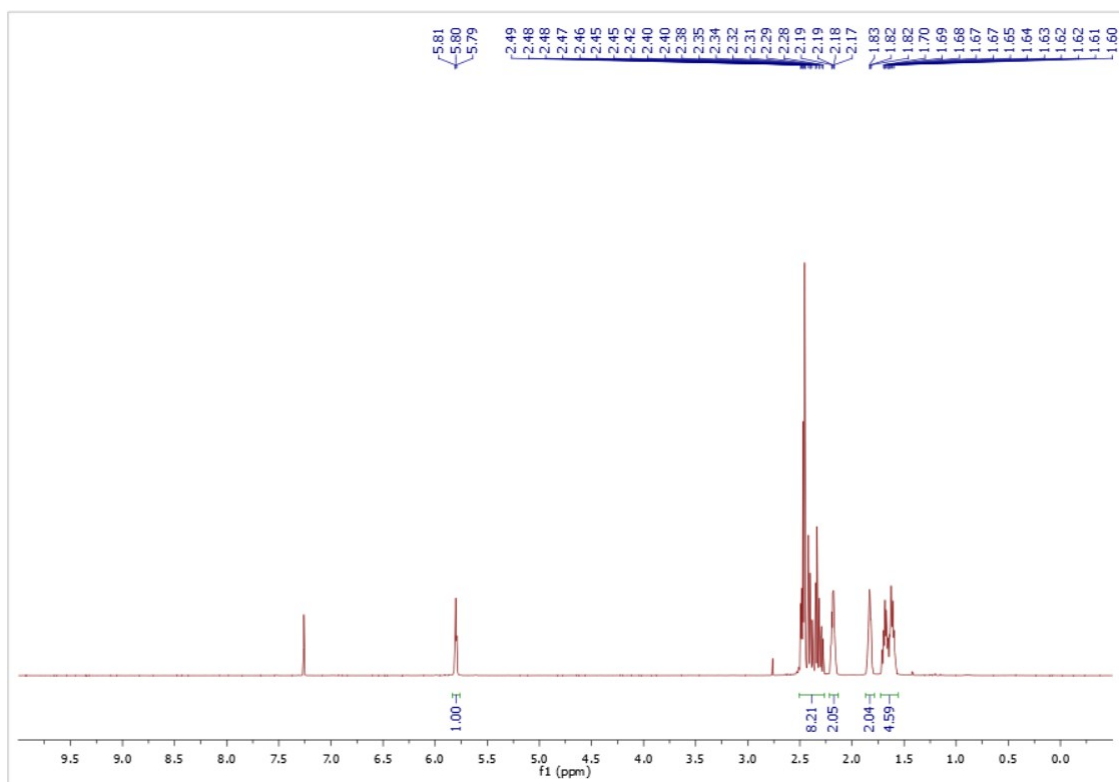
[1] Z. Li, C. Alameda-Angulo, B. Quiclet-Sire and S. Z. Zard, *Tetrahedron*, **2011**, *67*, 9844.

Supporting Information:

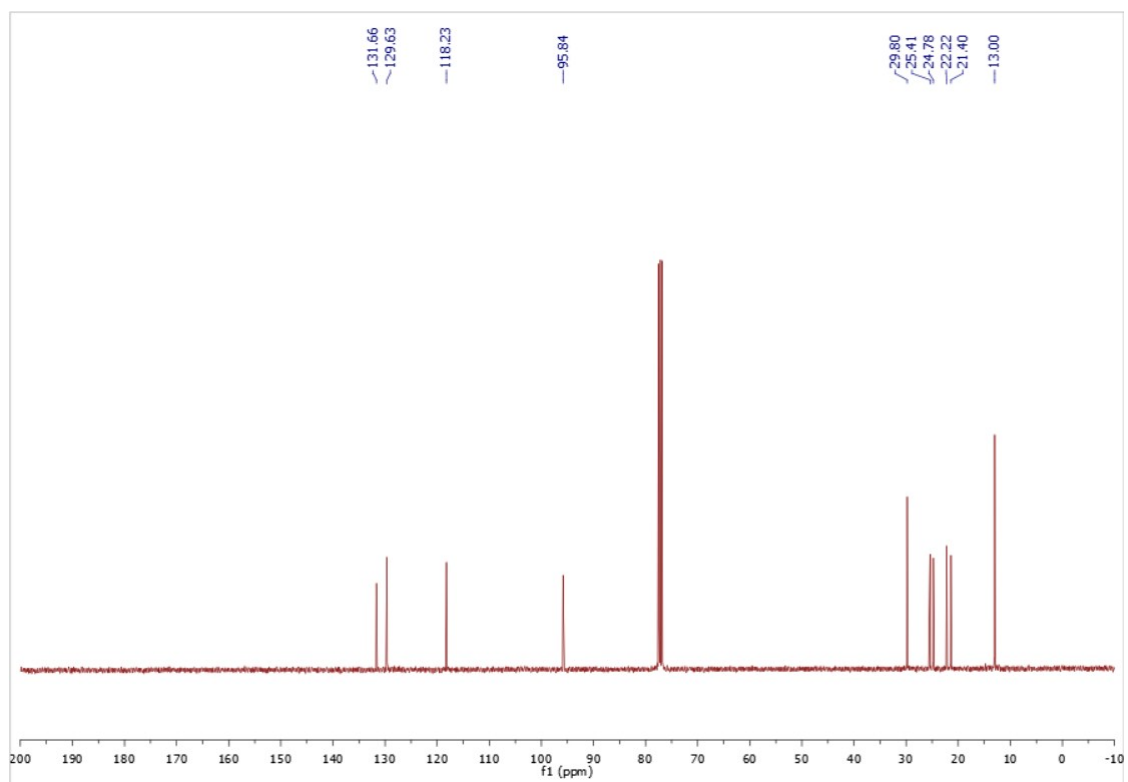
[2] R. Tamura, M. Sato and D. Oda, *J. Org. Chem.*, **1986**, *51*, 4368.

4. ^1H and ^{13}C spectra

Supporting Information:

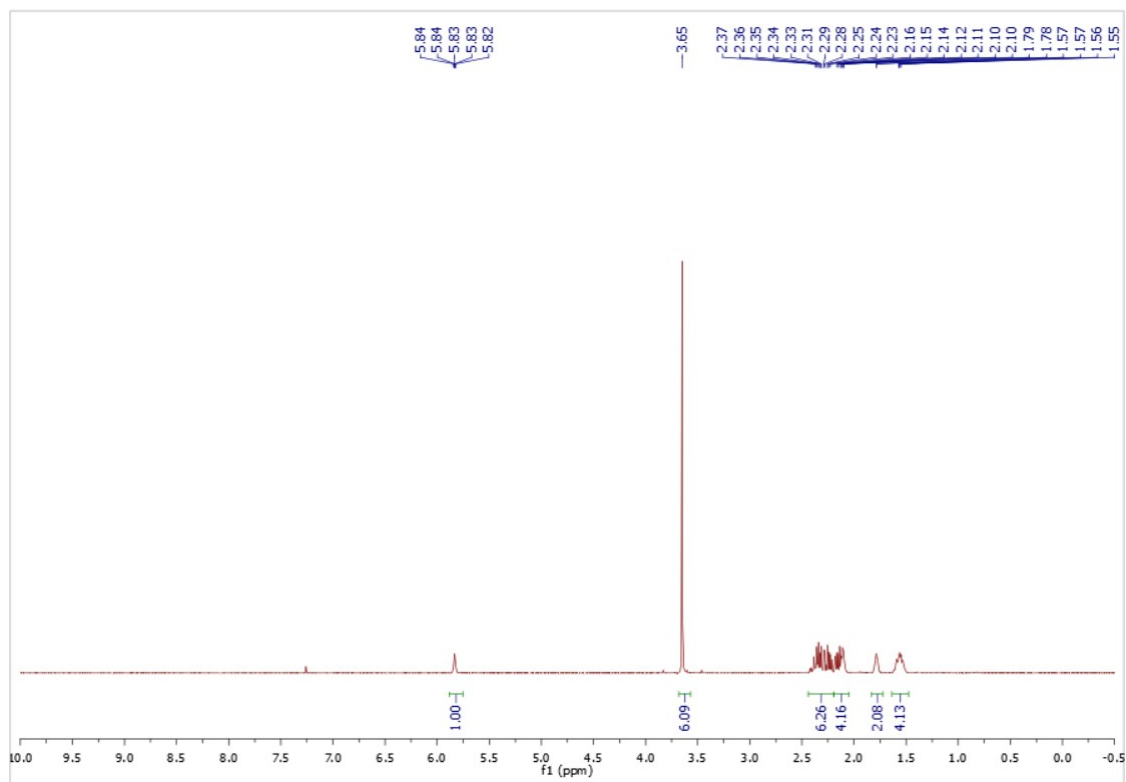


¹H NMR (CDCl₃, 400 MHz) of 4-(cyclohex-1-en-1-yl)-4-nitroheptanedinitrile (2a)

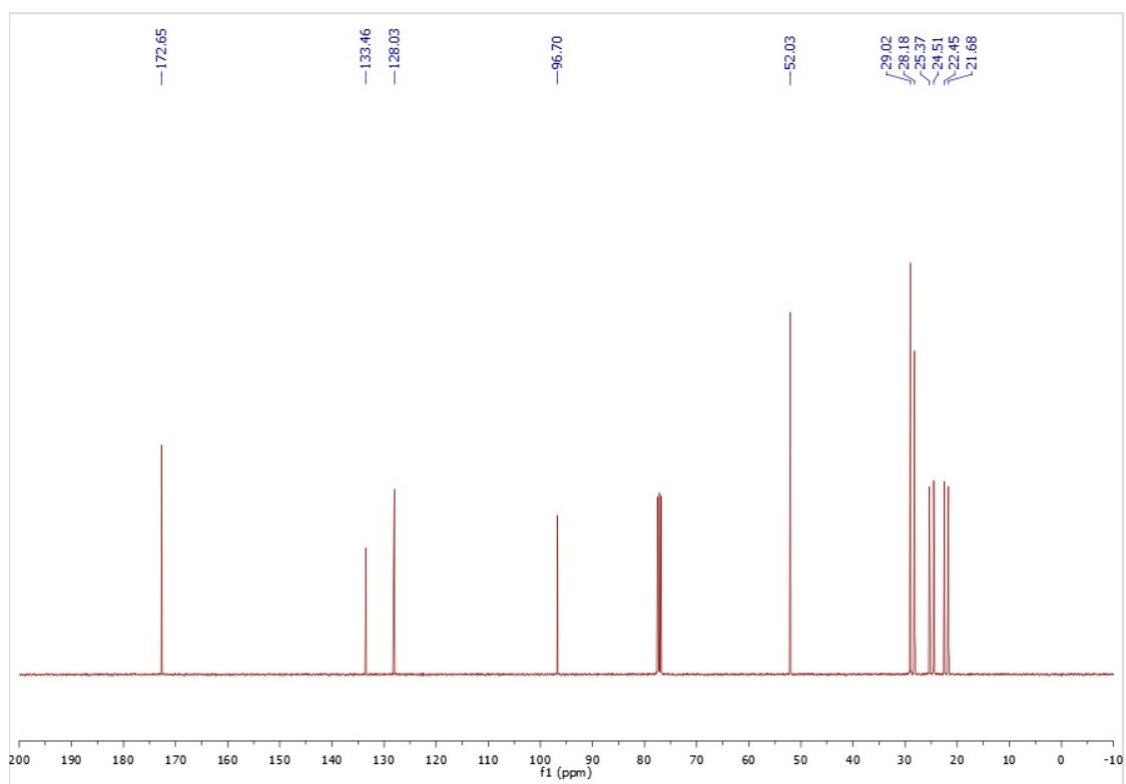


¹³C NMR (CDCl₃, 101 MHz) of 4-(cyclohex-1-en-1-yl)-4-nitroheptanedinitrile (2a)

Supporting Information:

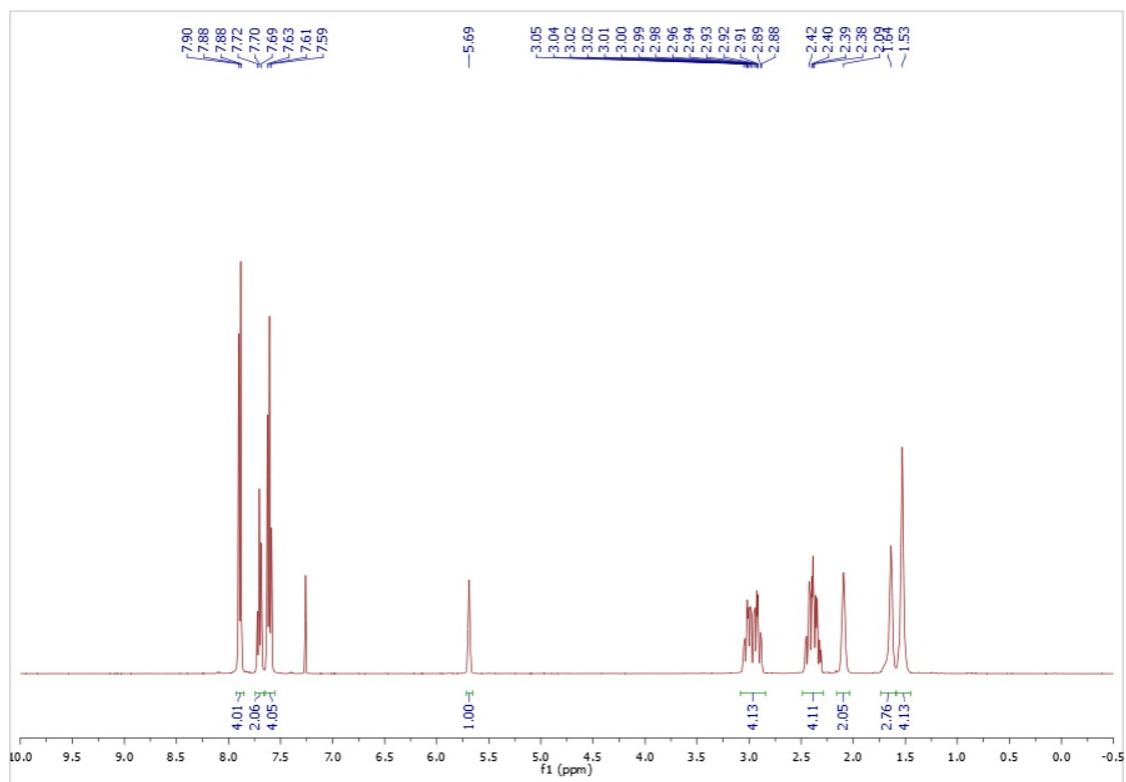


¹H NMR (CDCl₃, 400 MHz) of methyl 6-acetoxy-4-(cyclohex-1-en-1-yl)-4-nitrohexanoate (2b)

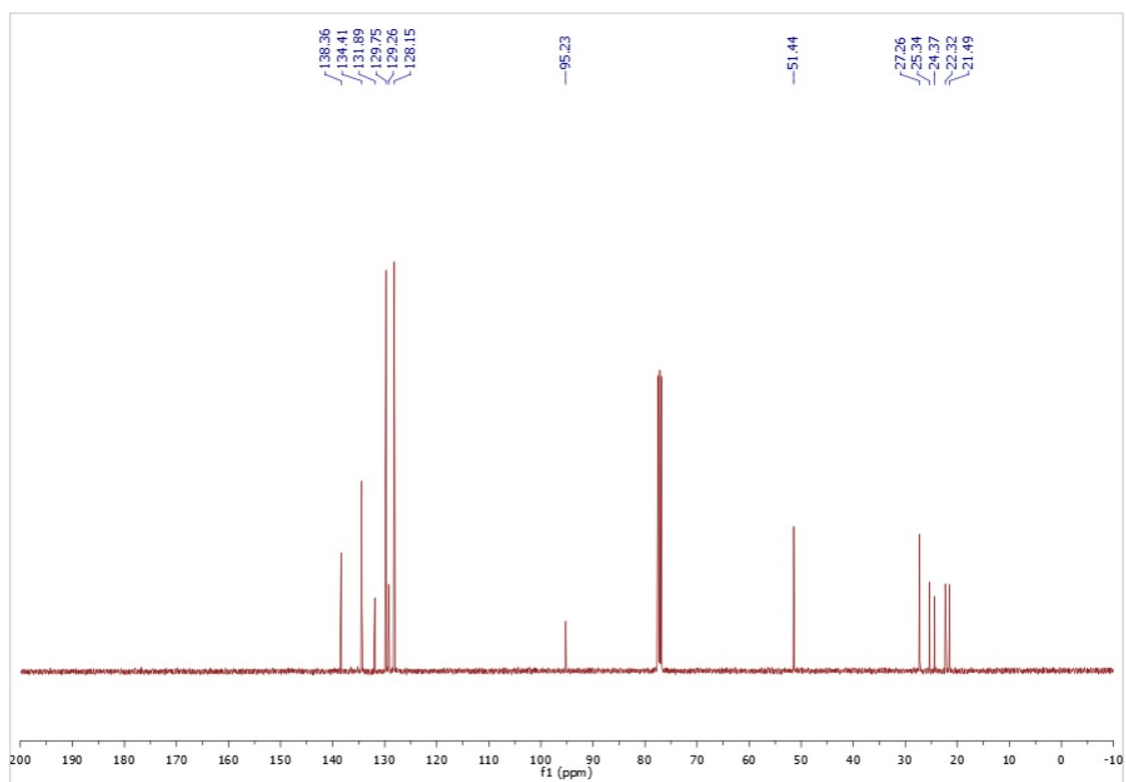


¹³C NMR (CDCl₃, 101 MHz) of methyl 6-acetoxy-4-(cyclohex-1-en-1-yl)-4-nitrohexanoate (2b)

Supporting Information:

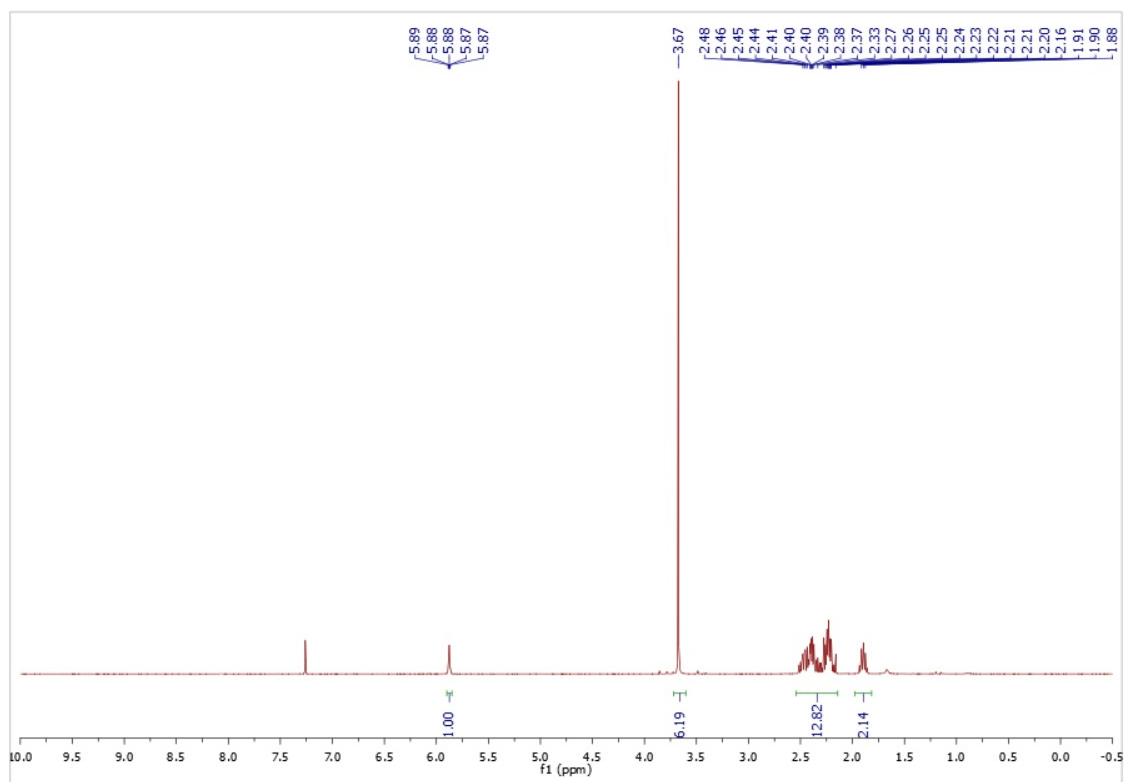


¹H NMR (CDCl₃, 400 MHz) of (3-(cyclohex-1-en-1-yl)-3-nitropentane-1,5-diyl)disulfonyldibenzene (2c)

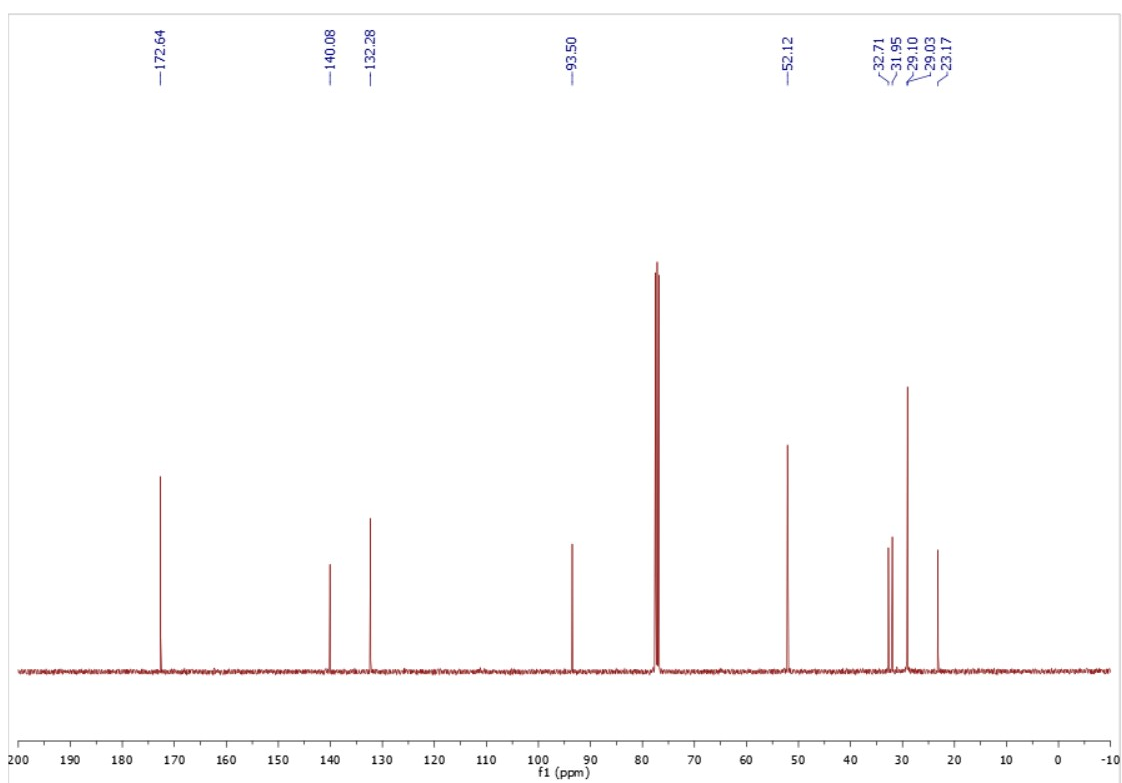


¹³C NMR (CDCl₃, 101 MHz) of (3-(cyclohex-1-en-1-yl)-3-nitropentane-1,5-diyl)disulfonyldibenzene (2c)

Supporting Information:

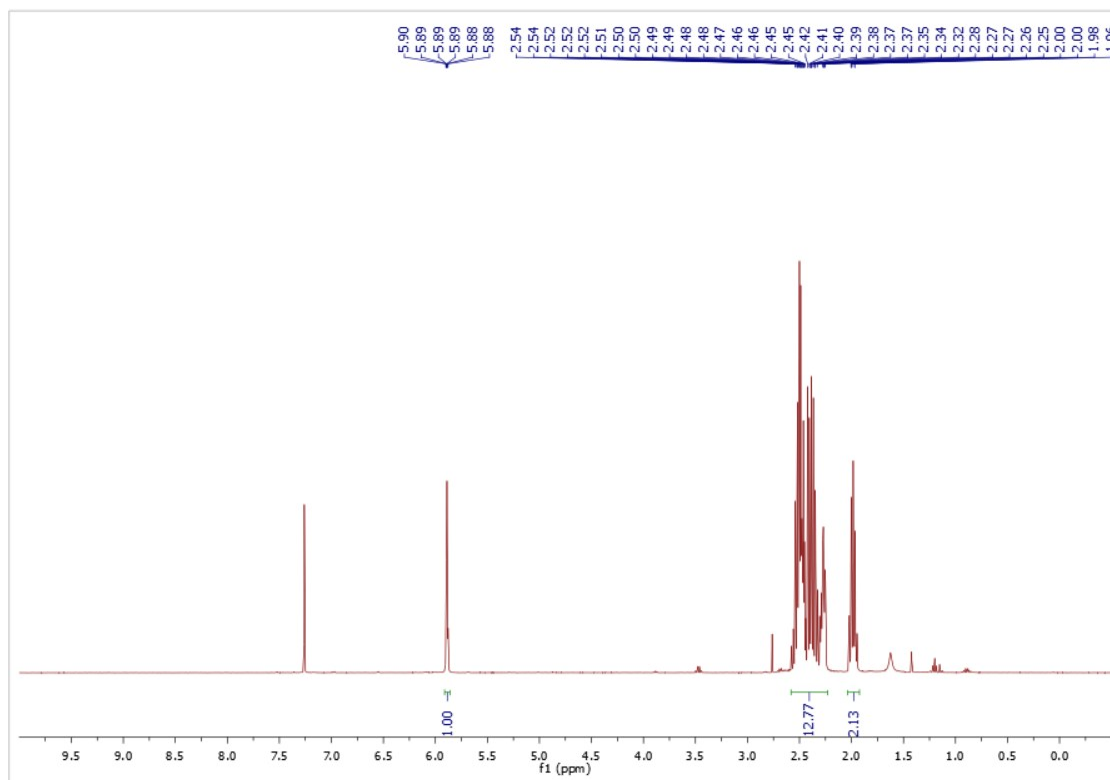


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(cyclopent-1-en-1-yl)-4-nitroheptanedioate (2d)

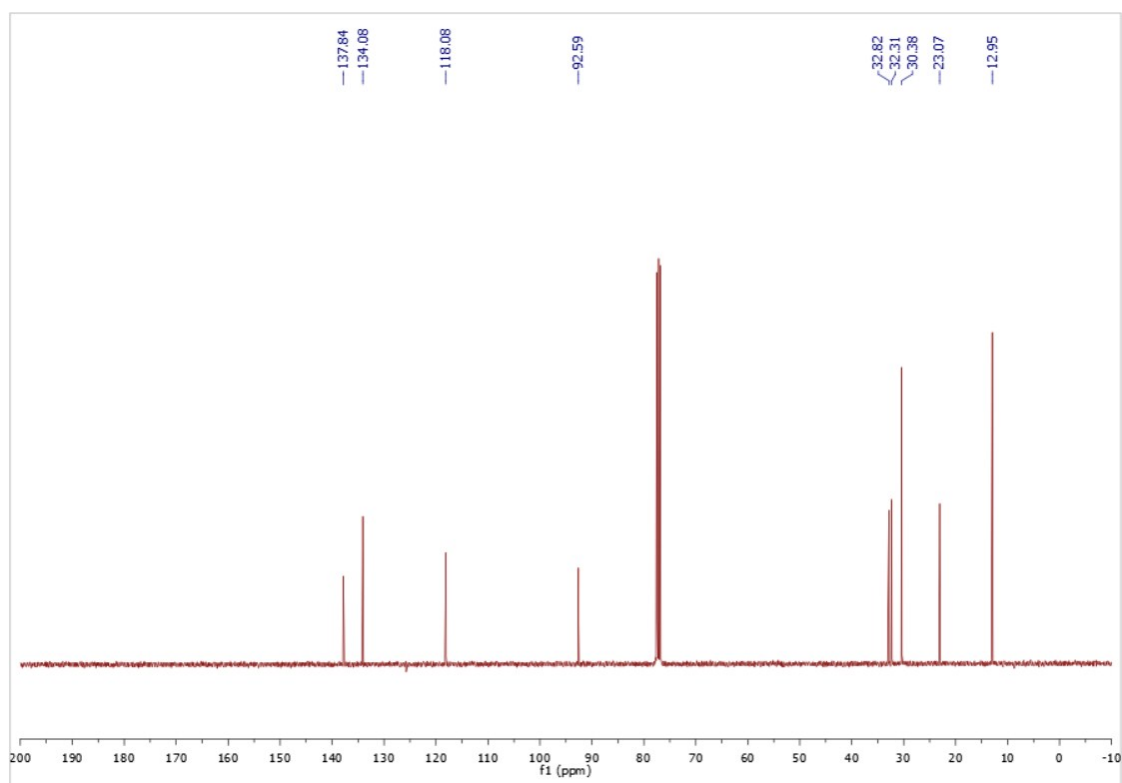


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(cyclopent-1-en-1-yl)-4-nitroheptanedioate (2d)

Supporting Information:

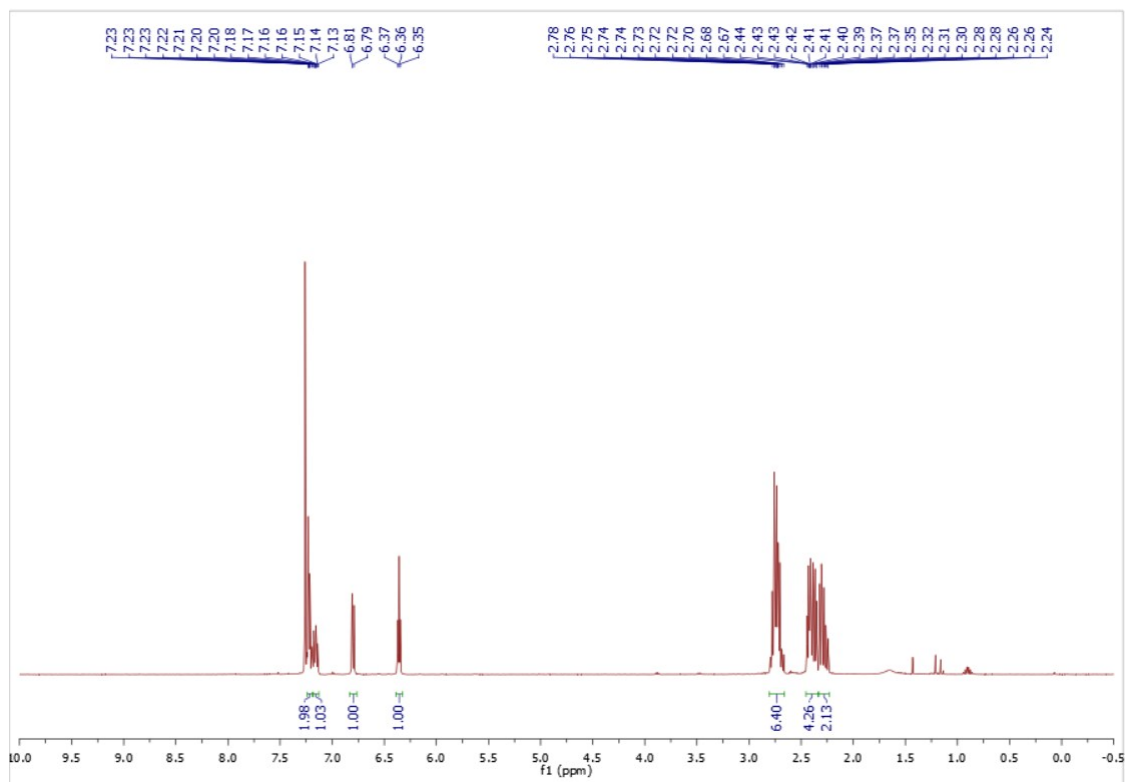


¹H NMR (CDCl₃, 400 MHz) of 4-(cyclopent-1-en-1-yl)-4-nitroheptanedinitrile (2e)

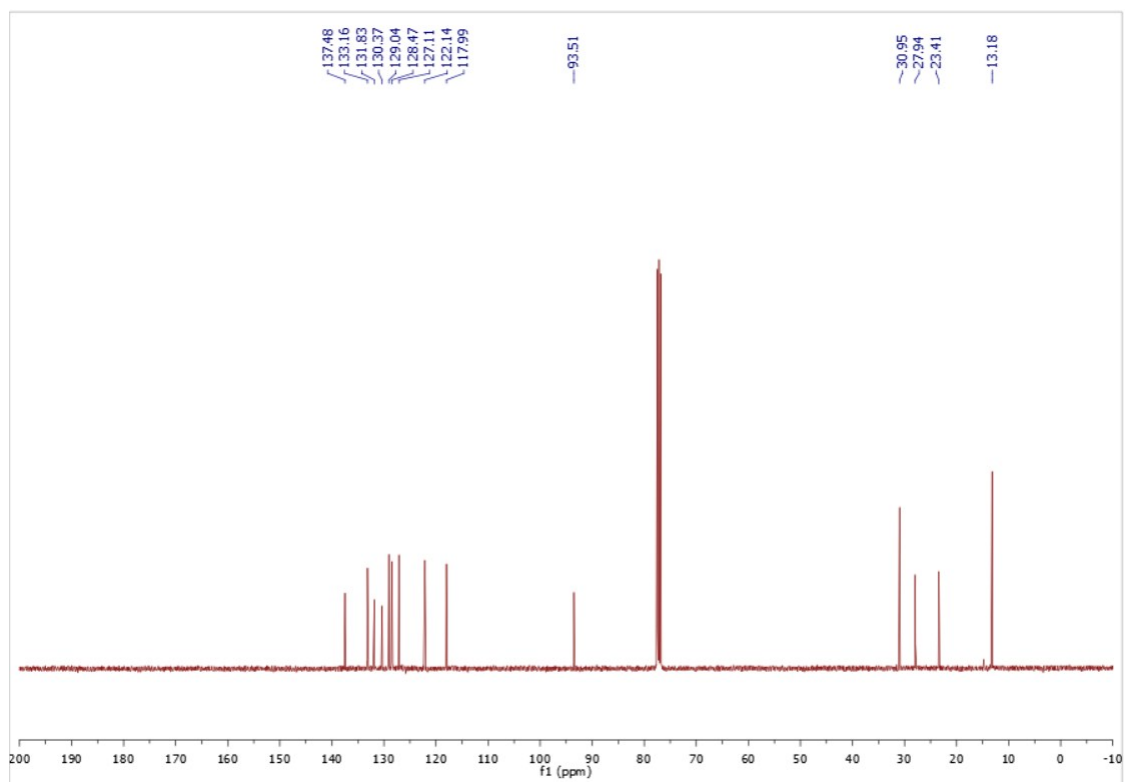


¹³C NMR (CDCl₃, 101 MHz) of 4-(cyclopent-1-en-1-yl)-4-nitroheptanedinitrile (2e)

Supporting Information:

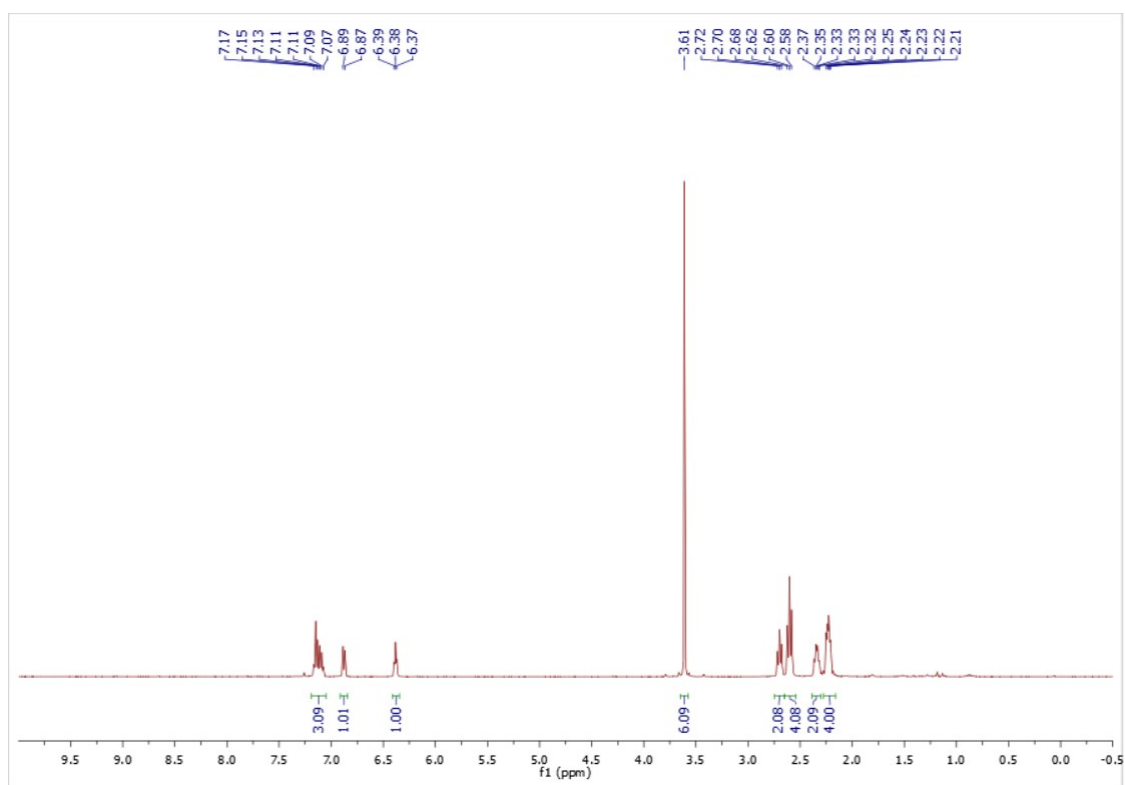


¹H NMR (CDCl₃, 400 MHz) of 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedinitrile (4a)

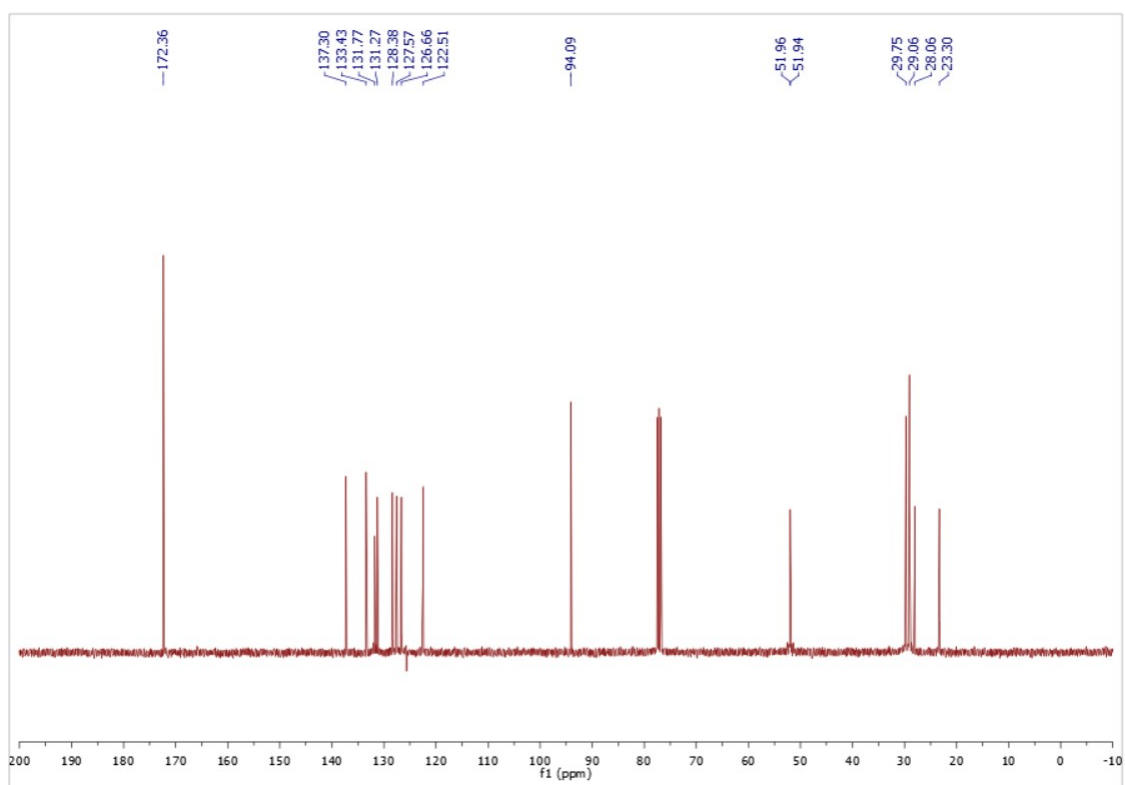


¹³C NMR (CDCl₃, 101 MHz) of 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedinitrile (4a)

Supporting Information:

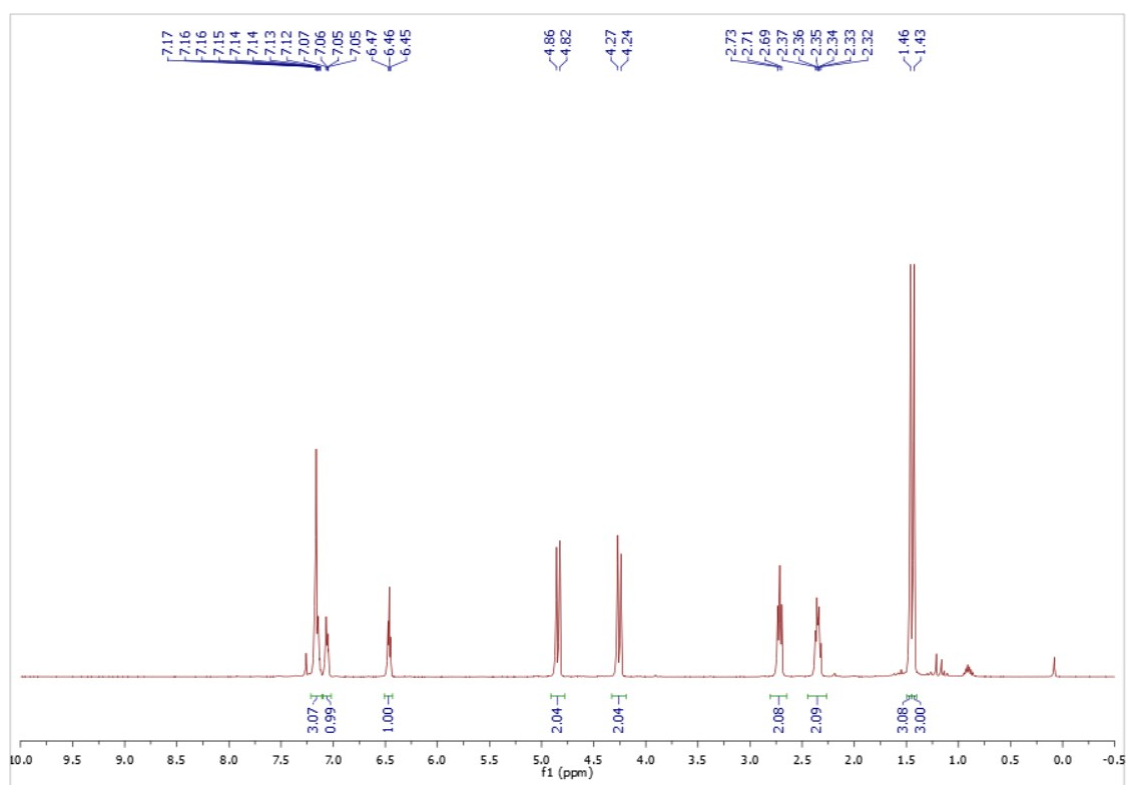


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedioate (4b)

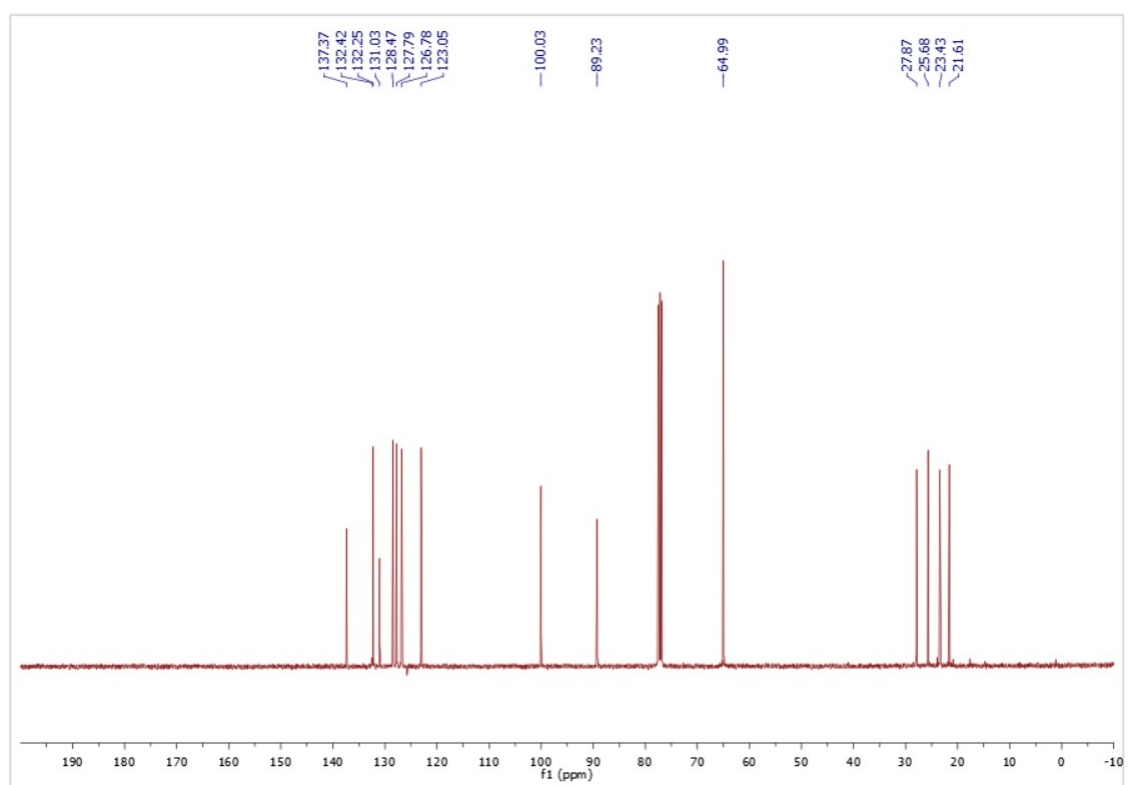


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitroheptanedioate (4b)

Supporting Information:

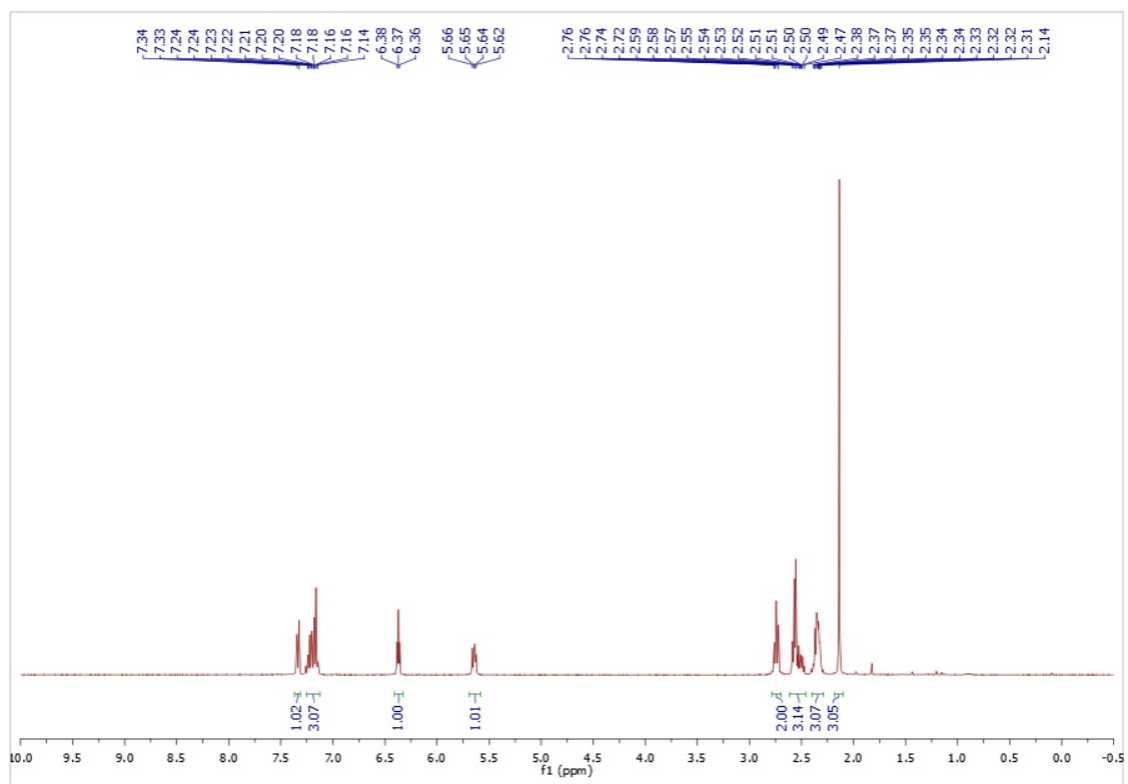


¹H NMR (CDCl₃, 400 MHz) of 5-(3,4-dihydronaphthalen-1-yl)-2,2-dimethyl-5-nitro-1,3-dioxane (4c)

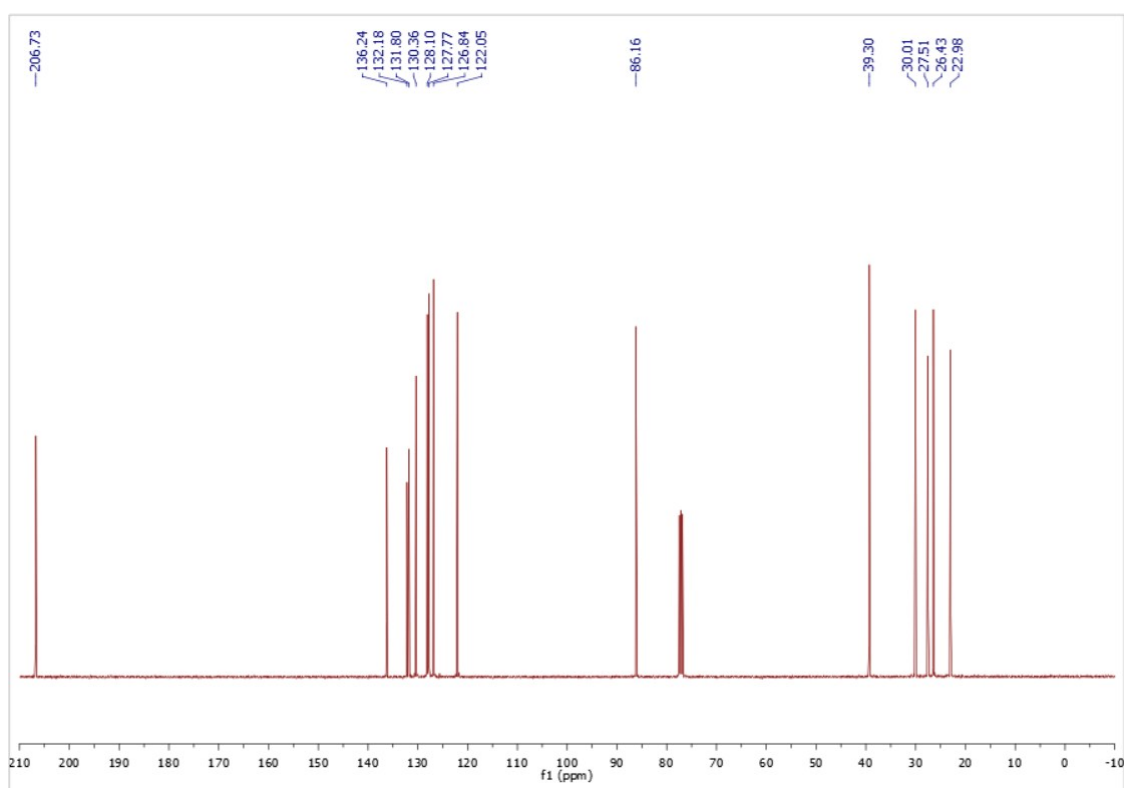


¹³C NMR (CDCl₃, 101 MHz) of 5-(3,4-dihydronaphthalen-1-yl)-2,2-dimethyl-5-nitro-1,3-dioxane (4c)

Supporting Information:

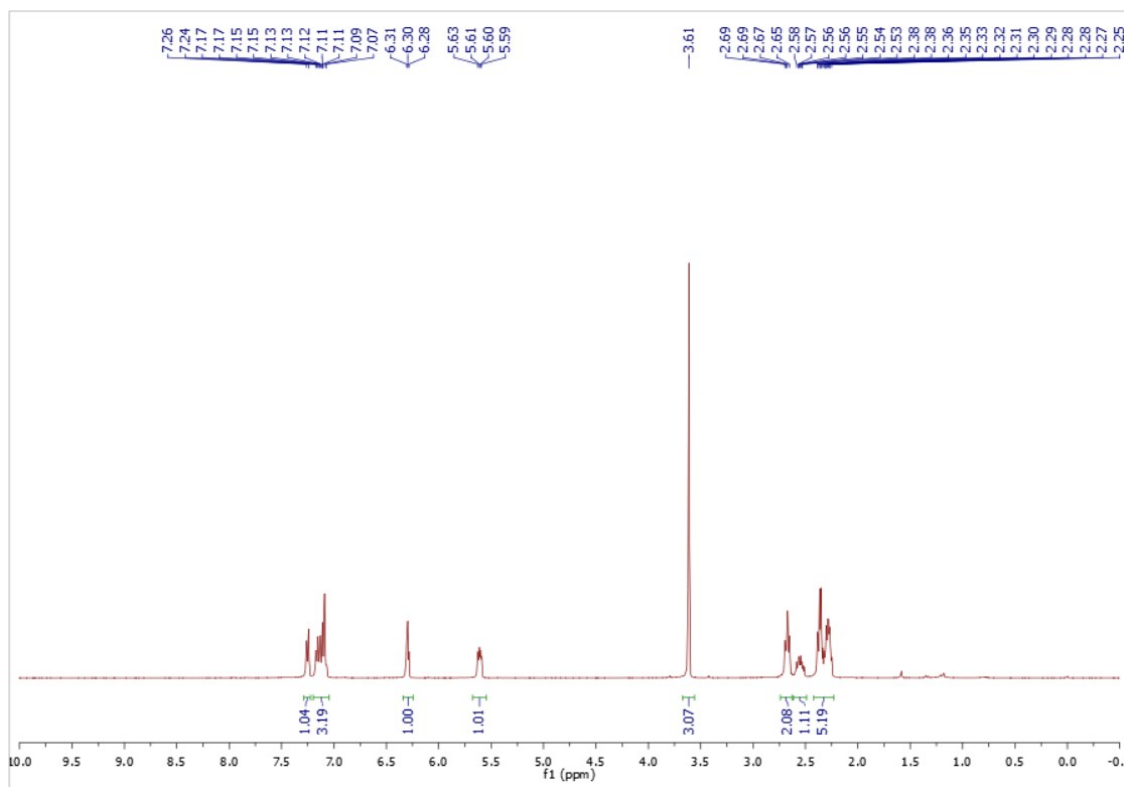


¹H NMR (CDCl₃, 400 MHz) of 5-(3,4-dihydronaphthalen-1-yl)-5-nitropentan-2-one (4e)

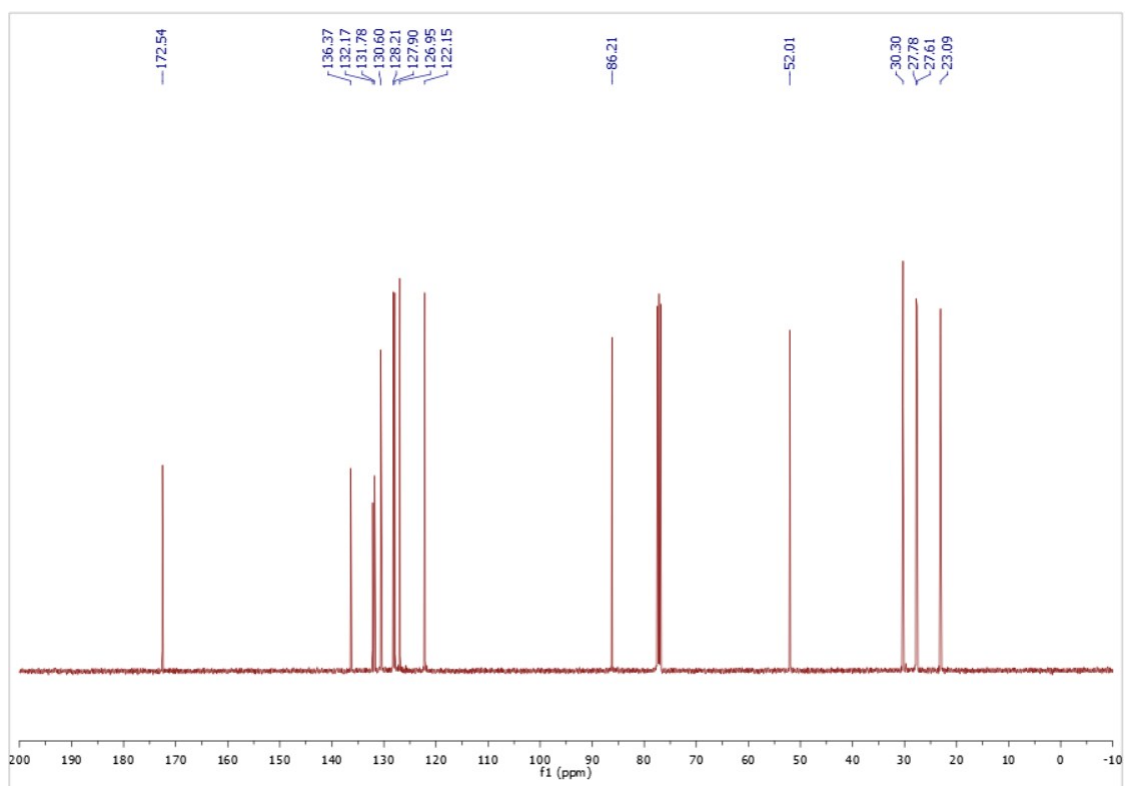


¹³C NMR (CDCl₃, 101 MHz) of 5-(3,4-dihydronaphthalen-1-yl)-5-nitropentan-2-one (4e)

Supporting Information:

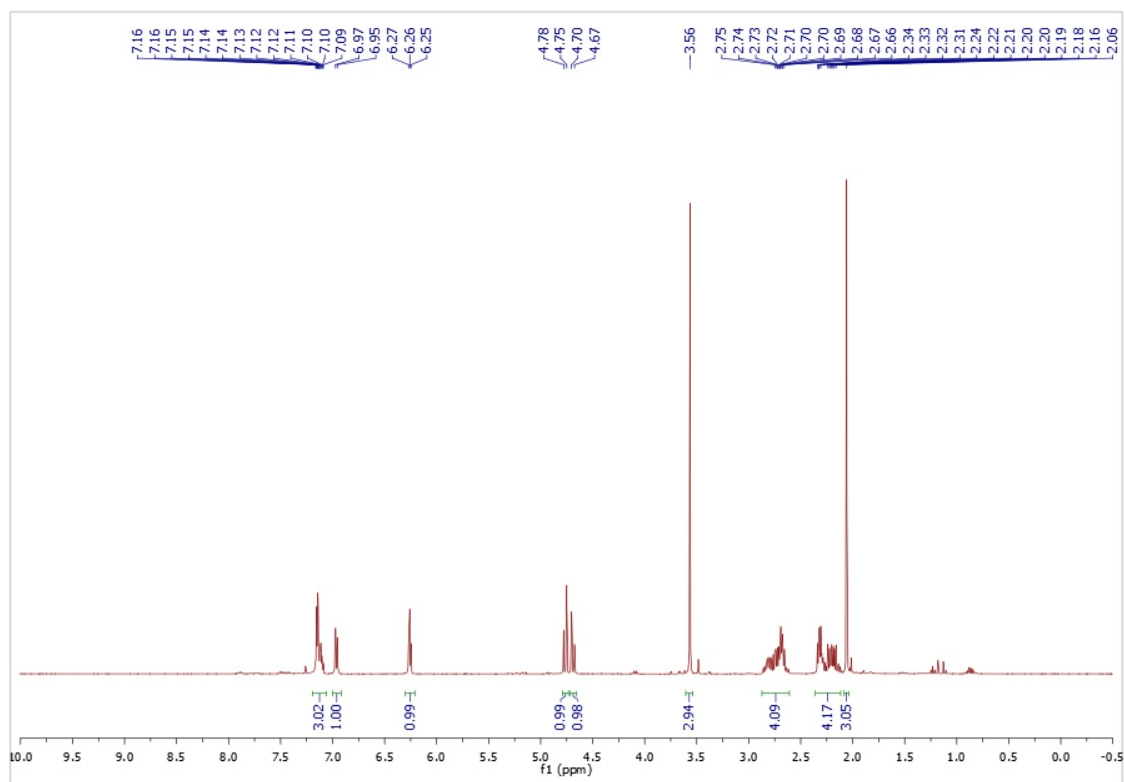


¹H NMR (CDCl₃, 400 MHz) of methyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitrobutanoate (4f)

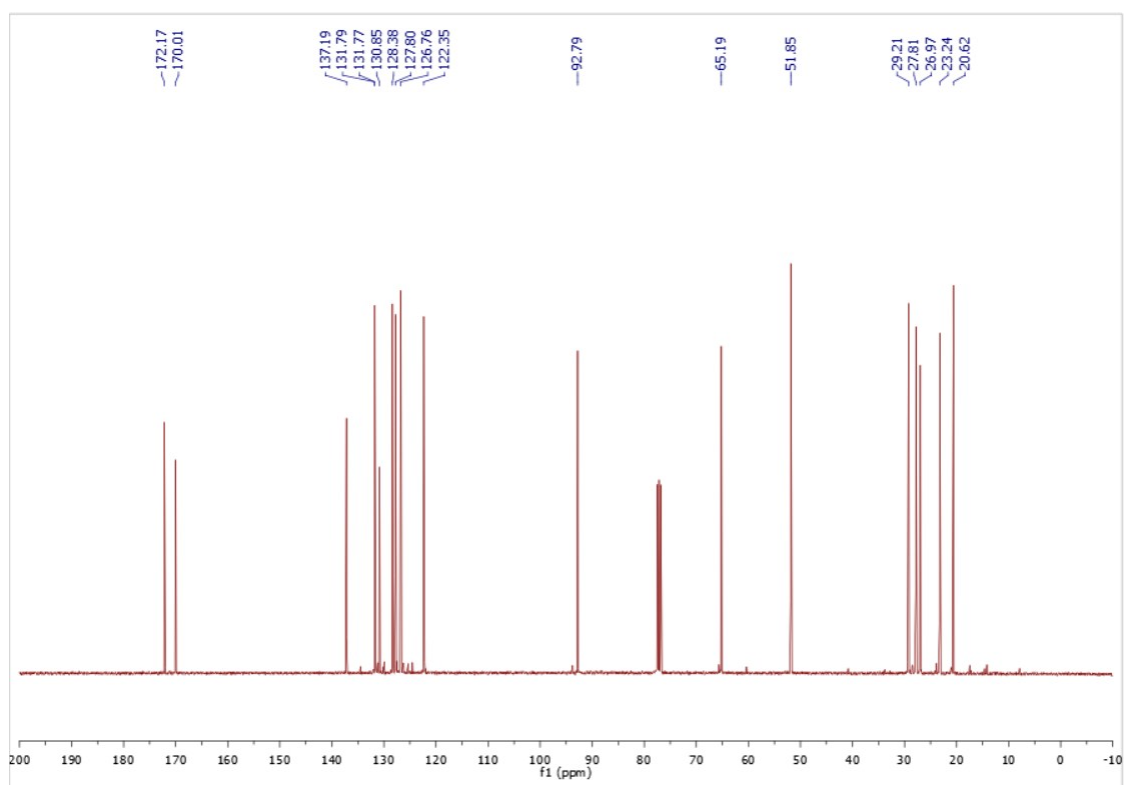


¹³C NMR (CDCl₃, 101 MHz) of methyl 4-(3,4-dihydronaphthalen-1-yl)-4-nitrobutanoate (4f)

Supporting Information:

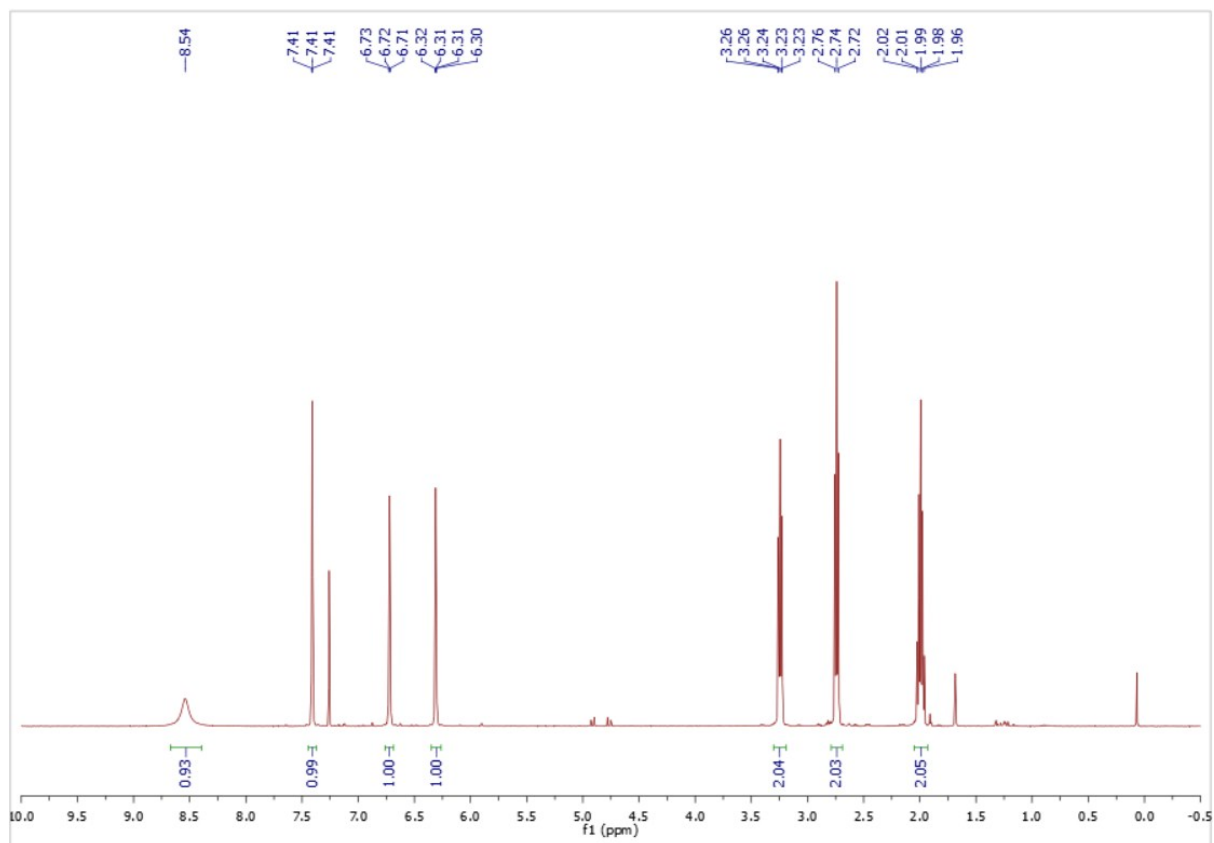


¹H NMR (CDCl₃, 400 MHz) of methyl 5-acetoxy-4-(3,4-dihydronaphthalen-1-yl)-4-nitropentanoate (4g)

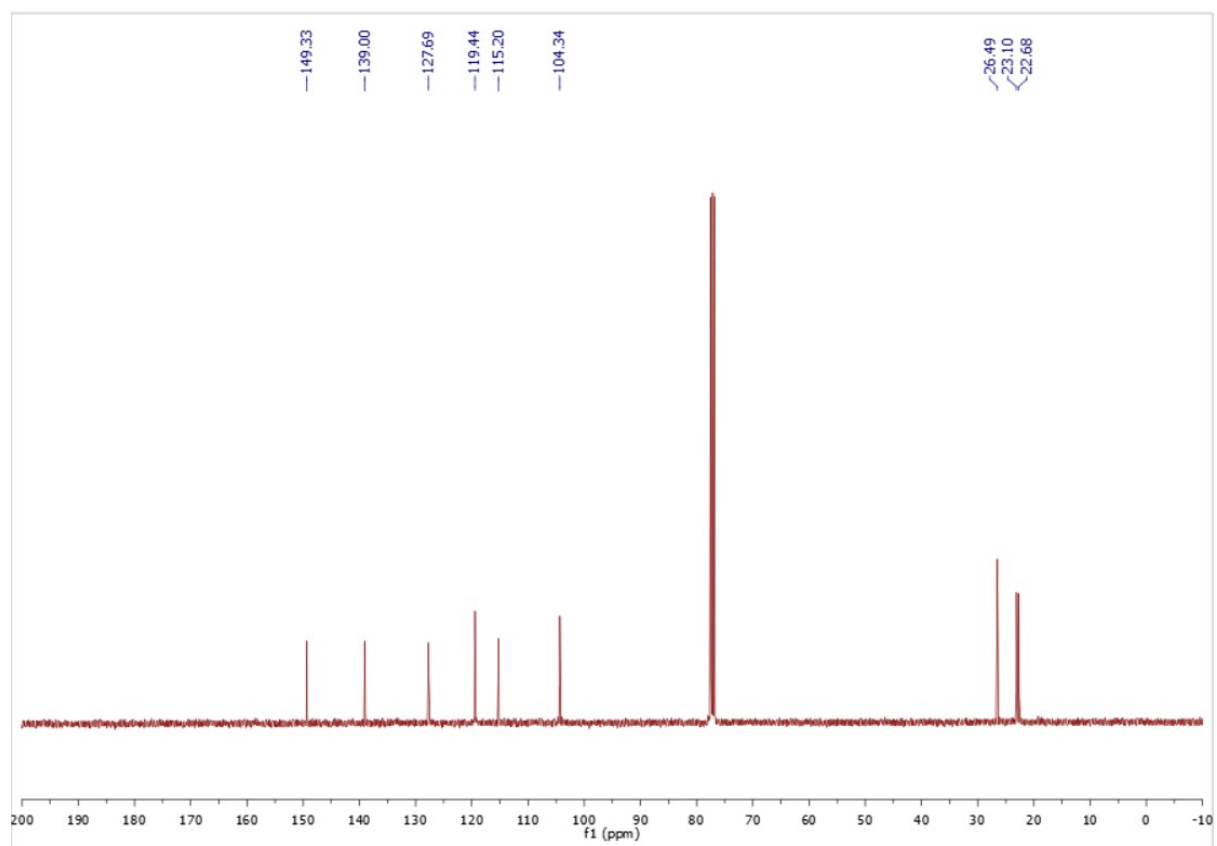


¹³C NMR (CDCl₃, 101 MHz) of methyl 5-acetoxy-4-(3,4-dihydronaphthalen-1-yl)-4-nitropentanoate (4g)

Supporting Information:

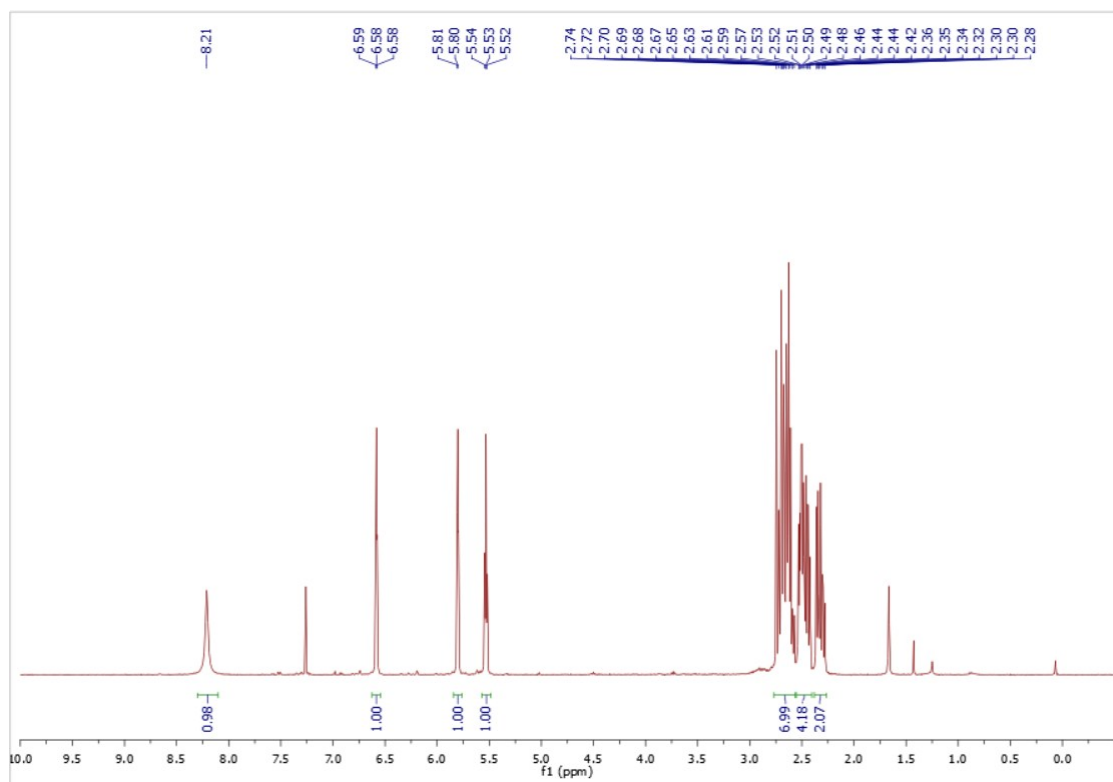


¹H NMR (CDCl₃, 400 MHz) of 4-(nitromethyl)-6,7-dihydro-1H-indole (10)

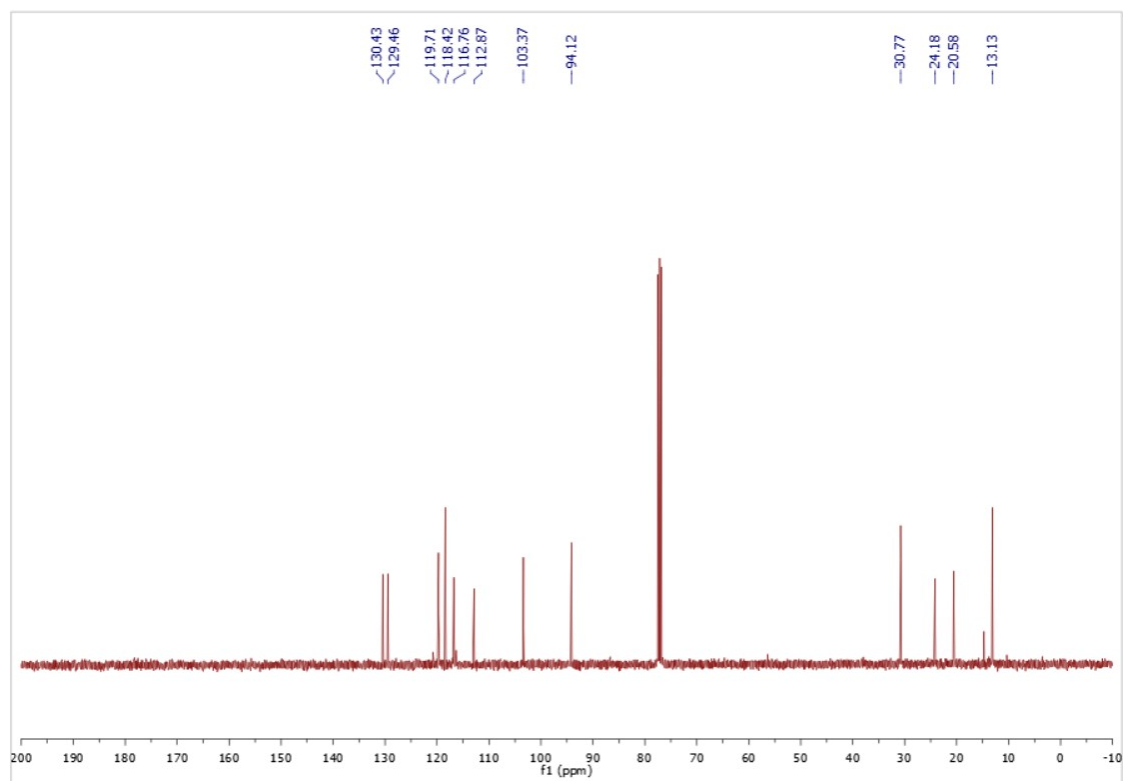


¹³C NMR (CDCl₃, 101 MHz) of 4-(nitromethyl)-6,7-dihydro-1H-indole (10)

Supporting Information:

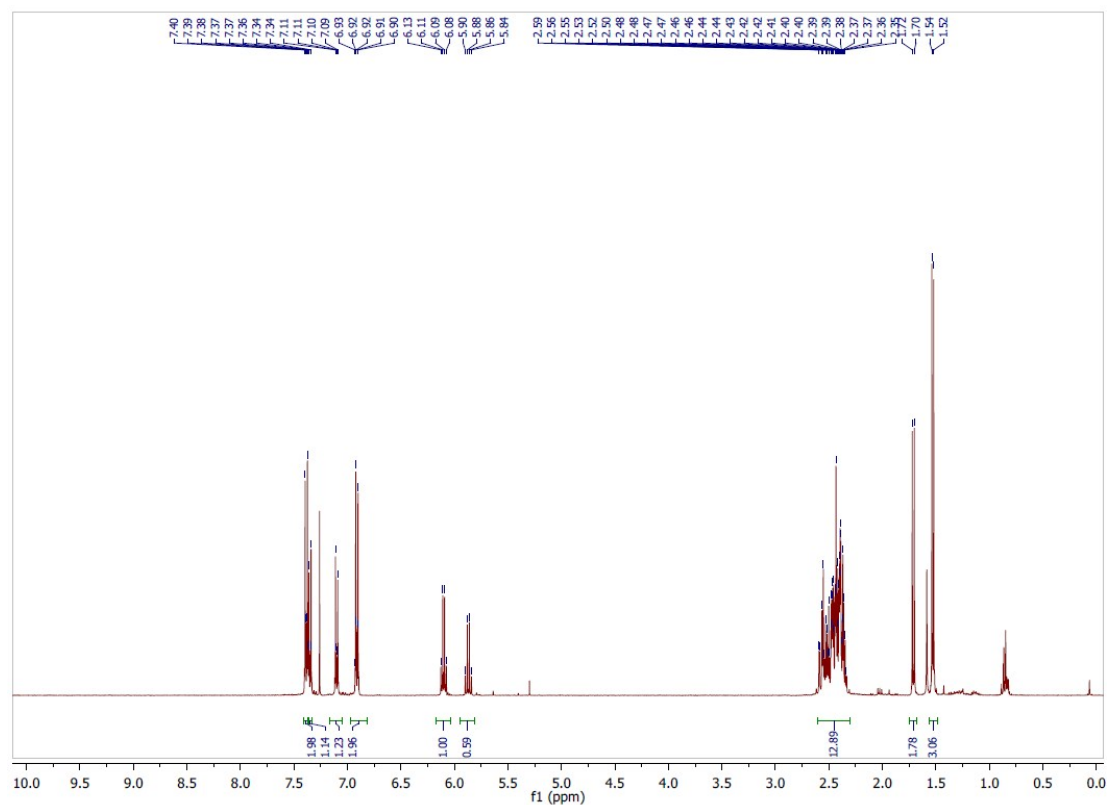


¹H NMR (CDCl₃, 400 MHz) of 4-(6,7-dihydro-1H-indol-4-yl)-4-nitroheptanedinitrile (5a)

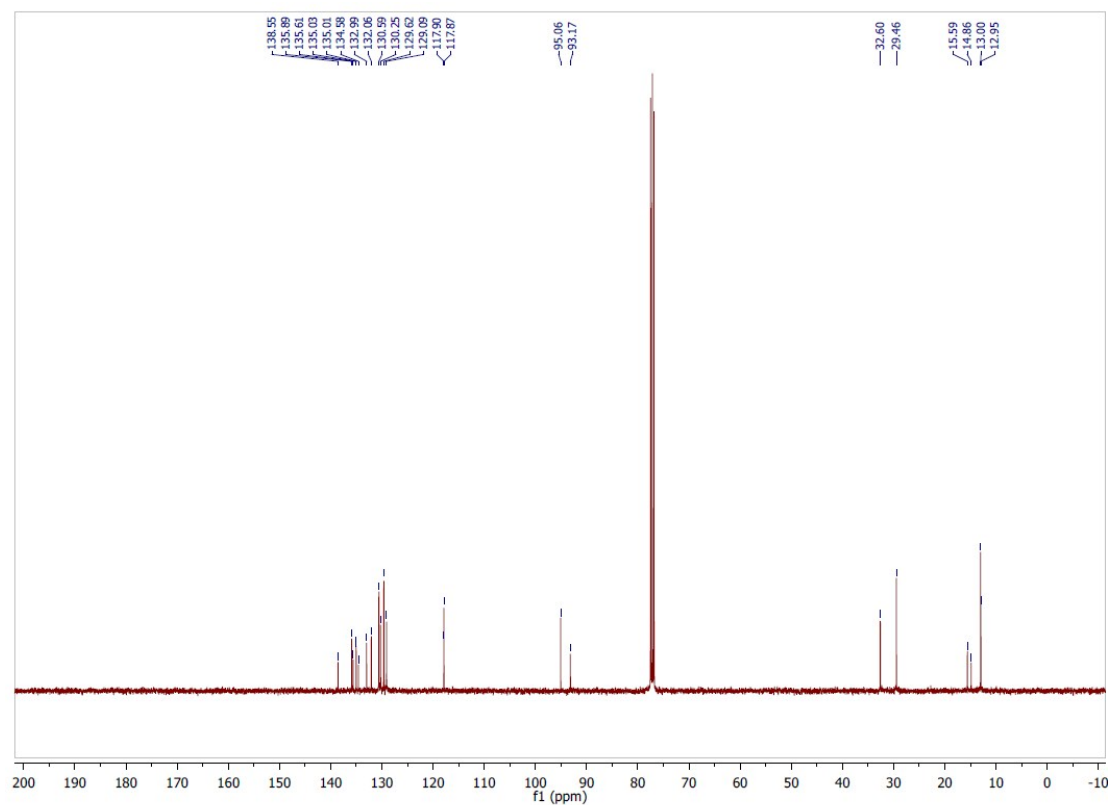


¹³C NMR (CDCl₃, 101 MHz) of 4-(6,7-dihydro-1H-indol-4-yl)-4-nitroheptanedinitrile (5a)

Supporting Information:

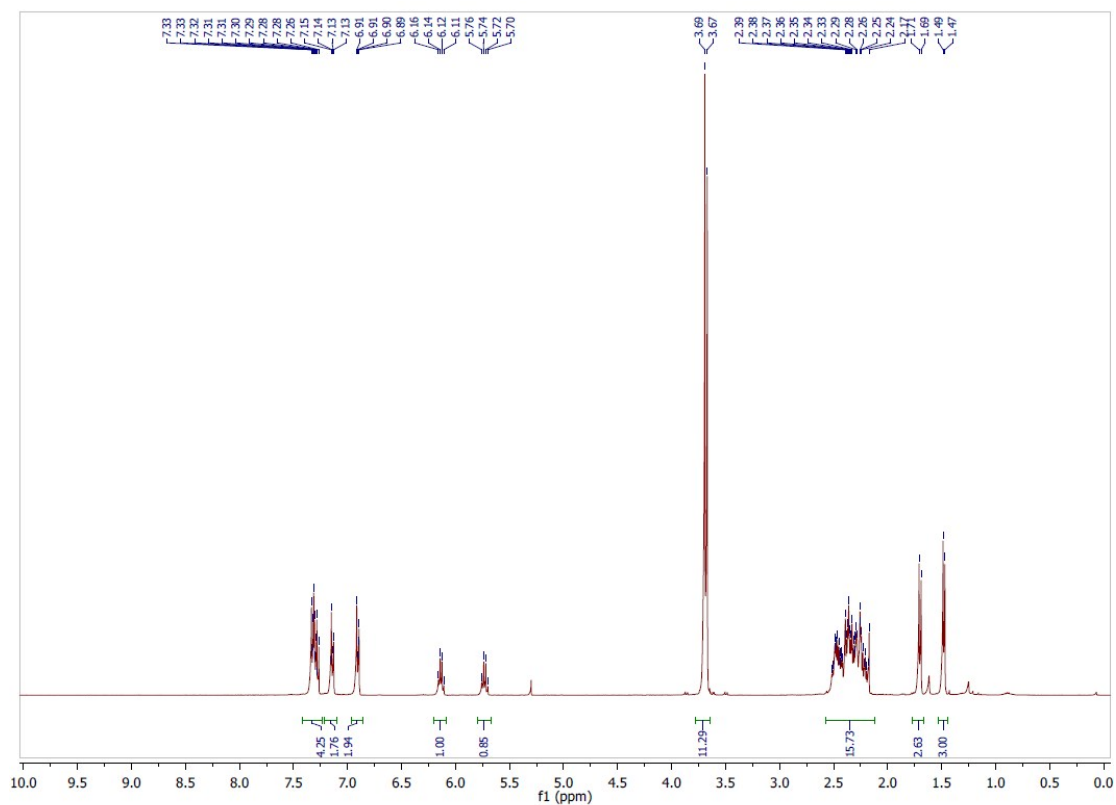


¹H NMR (CDCl₃, 400 MHz) of 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedinitrile (8a)

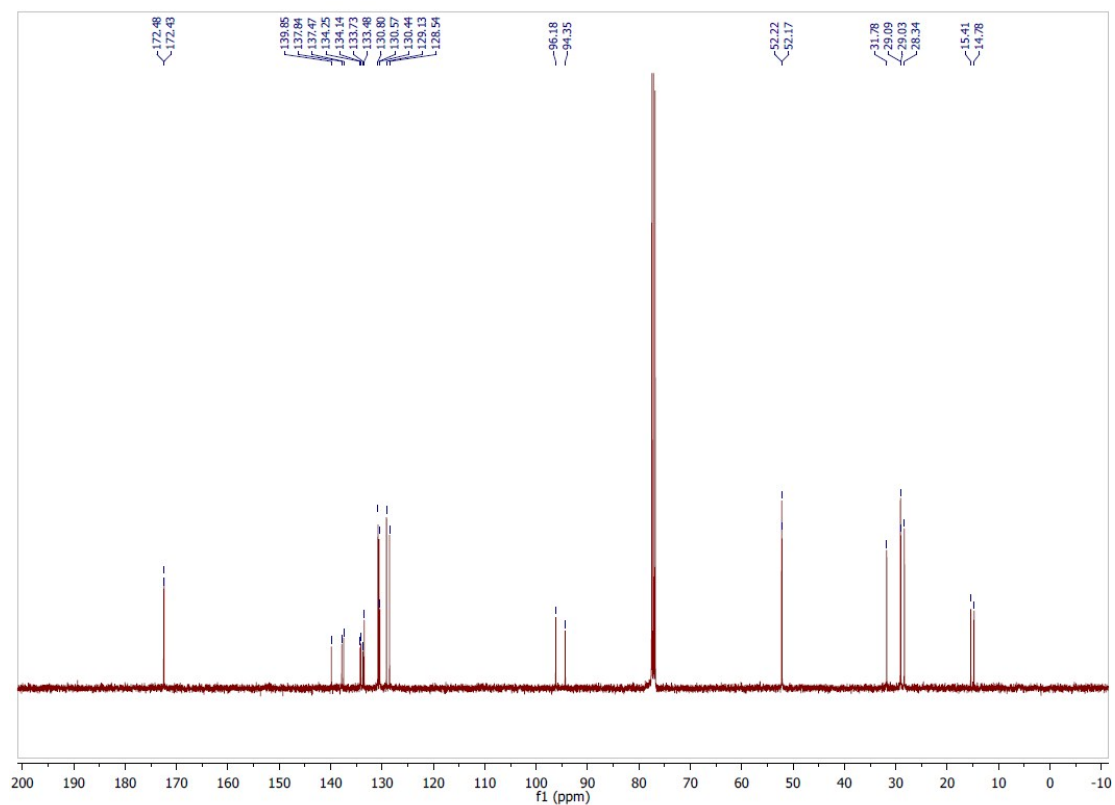


¹³C NMR (CDCl₃, 101 MHz) of 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedinitrile (8a)

Supporting Information:

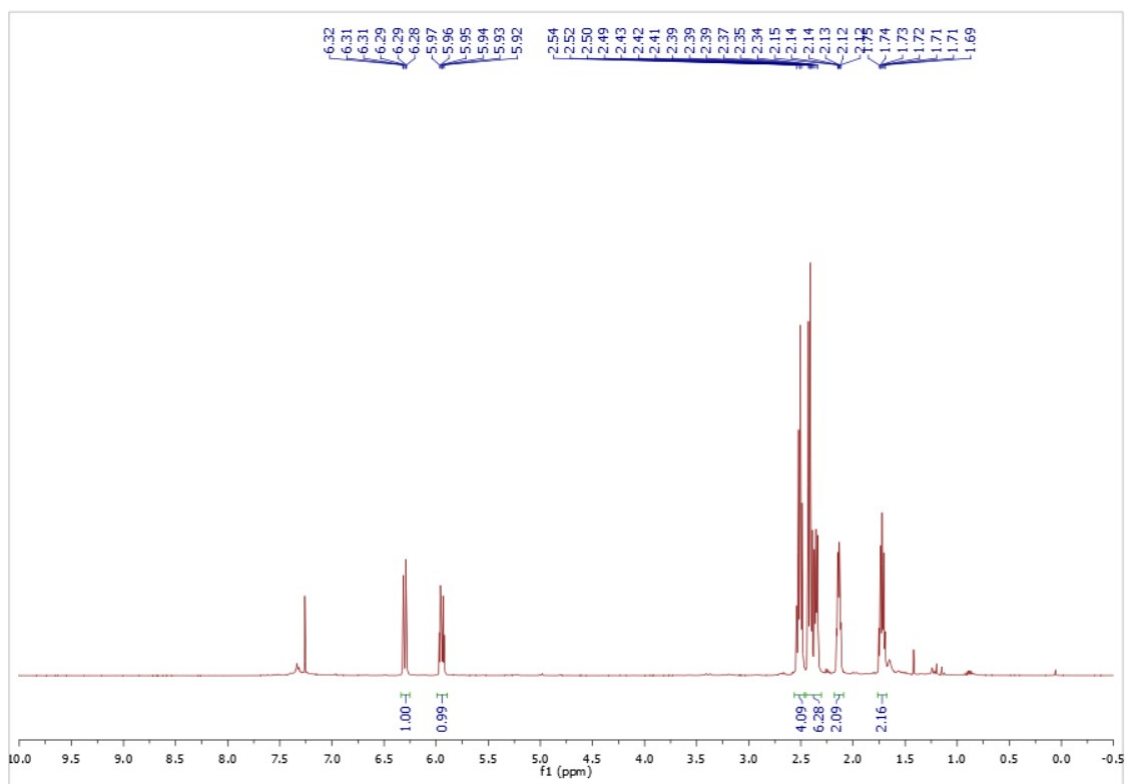


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedioate (8b)

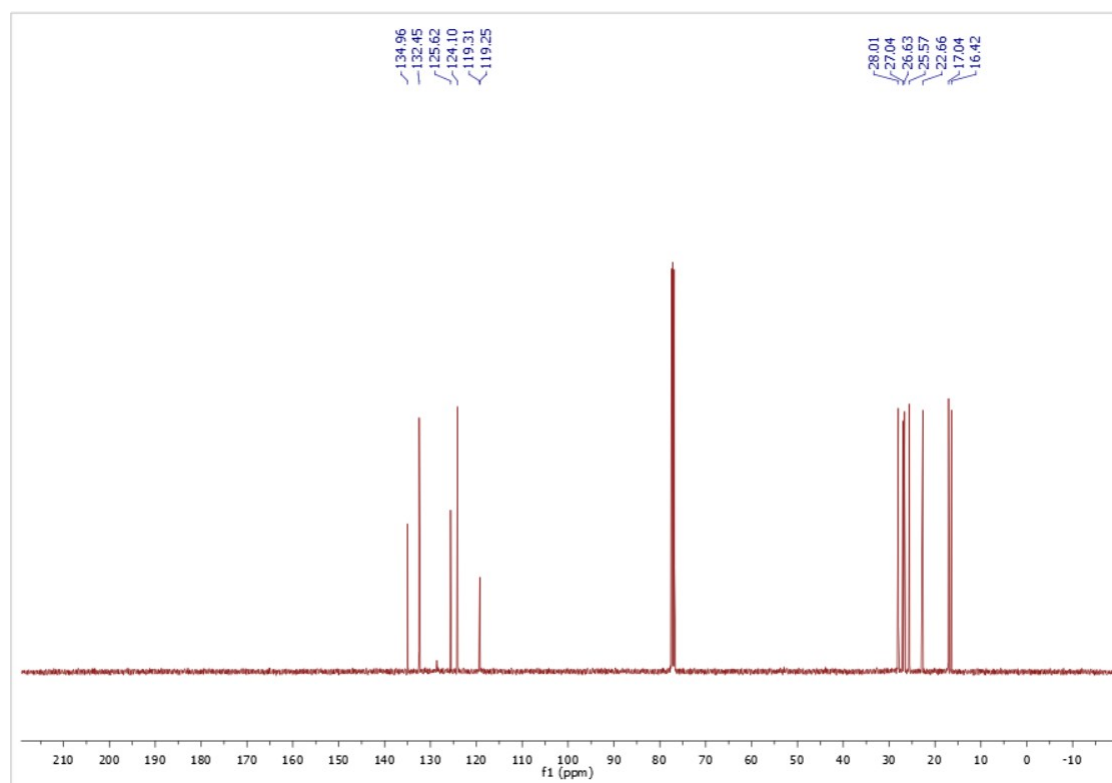


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(1-(4-chlorophenyl)prop-1-en-1-yl)-4-nitroheptanedioate (8b)

Supporting Information:

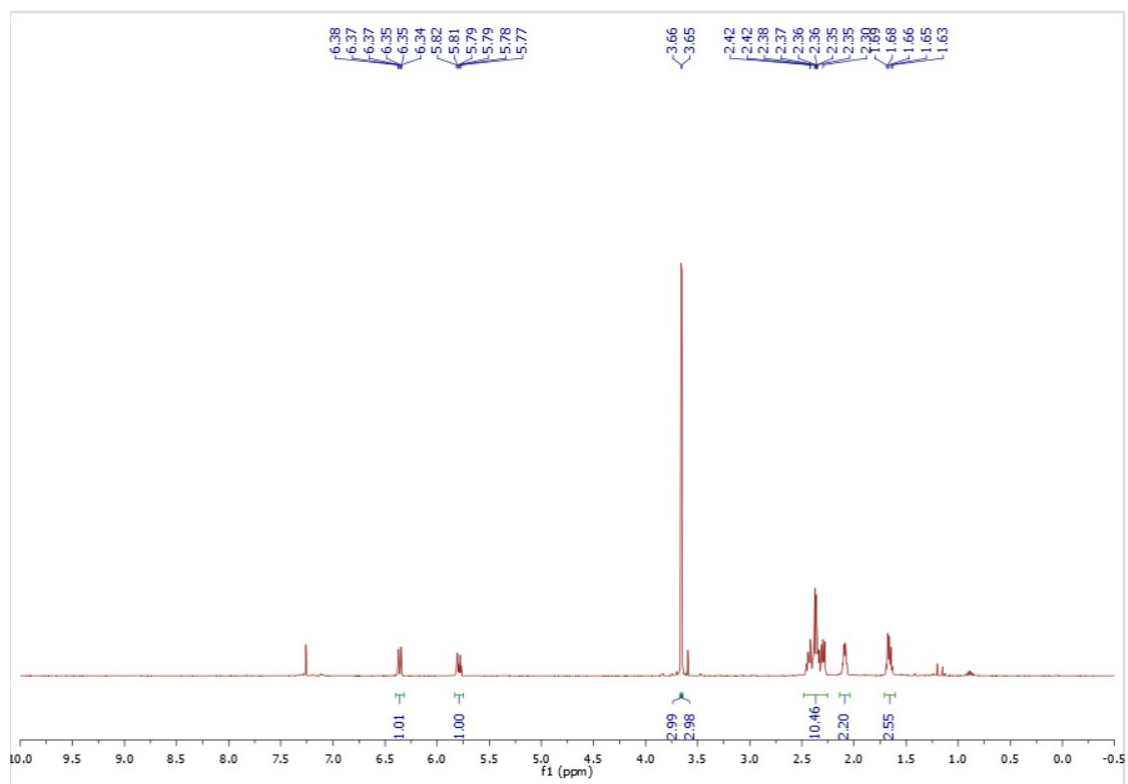


¹H NMR (CDCl₃, 400 MHz) of 4-(cyclohex-2-en-1-ylidene)heptanedinitrile (3a)

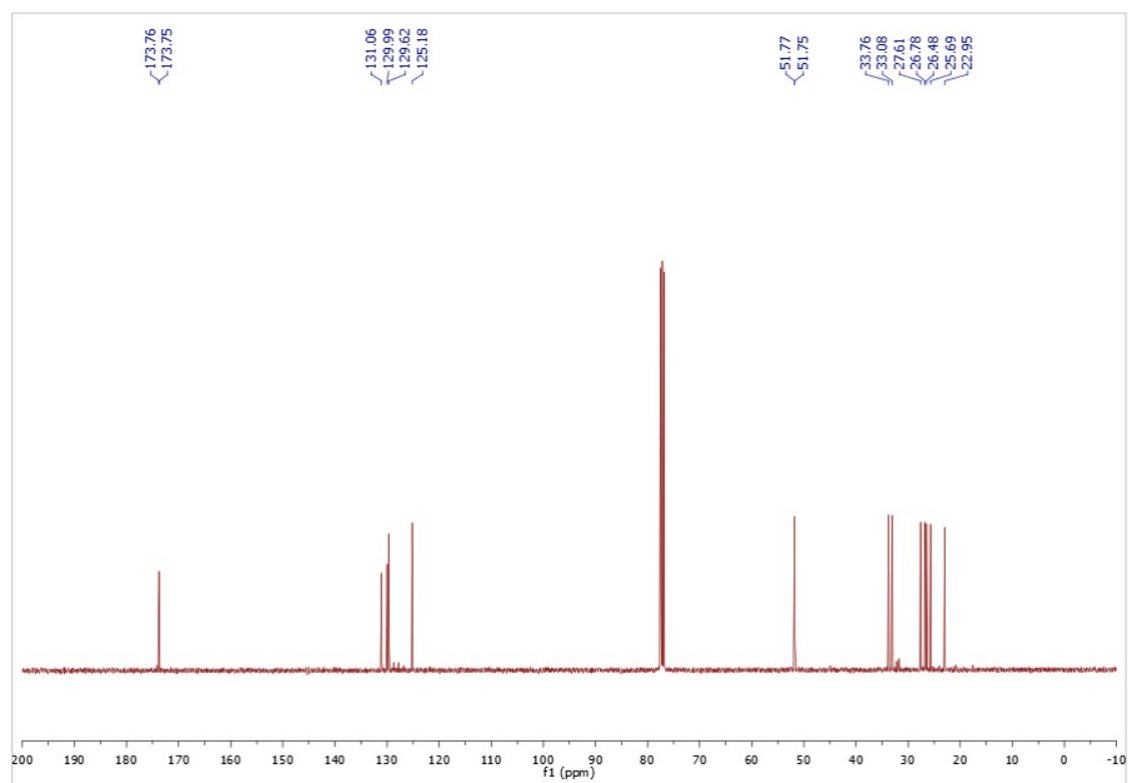


¹³C NMR (CDCl₃, 101 MHz) of 4-(cyclohex-2-en-1-ylidene)heptanedinitrile (3a)

Supporting Information:

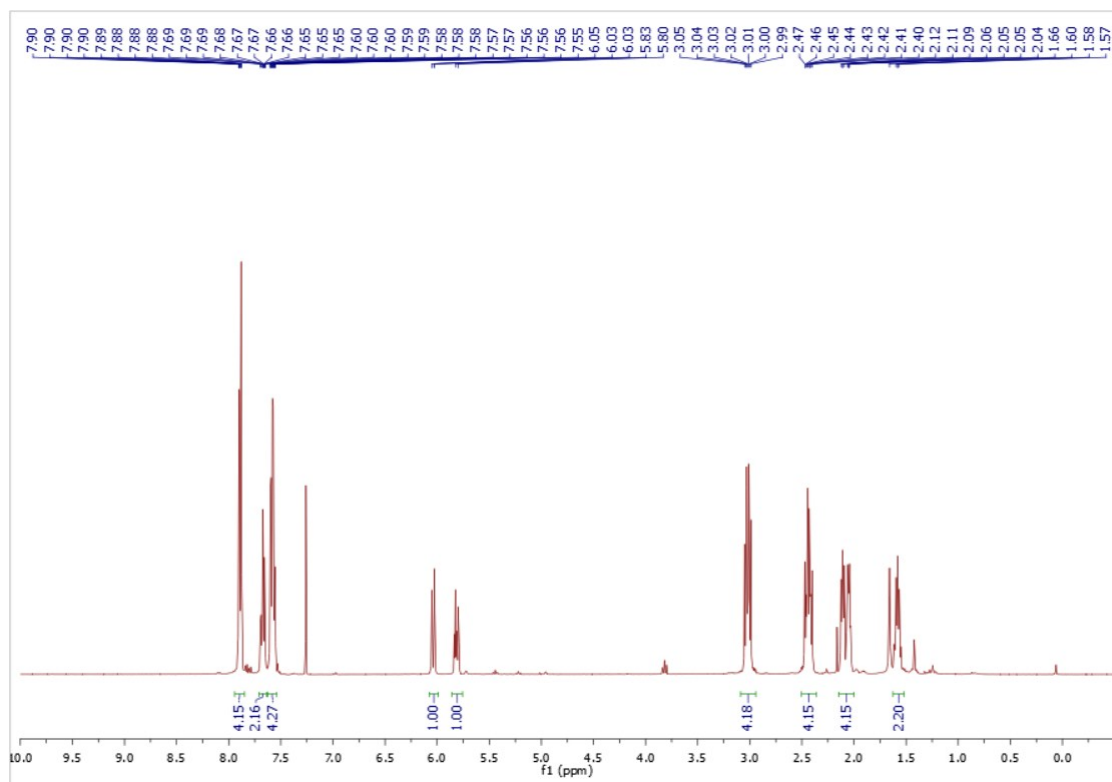


¹H NMR (CDCl₃, 400 MHz) of methyl 6-acetoxy-4-(cyclohex-2-en-1-ylidene)hexanoate (3b)

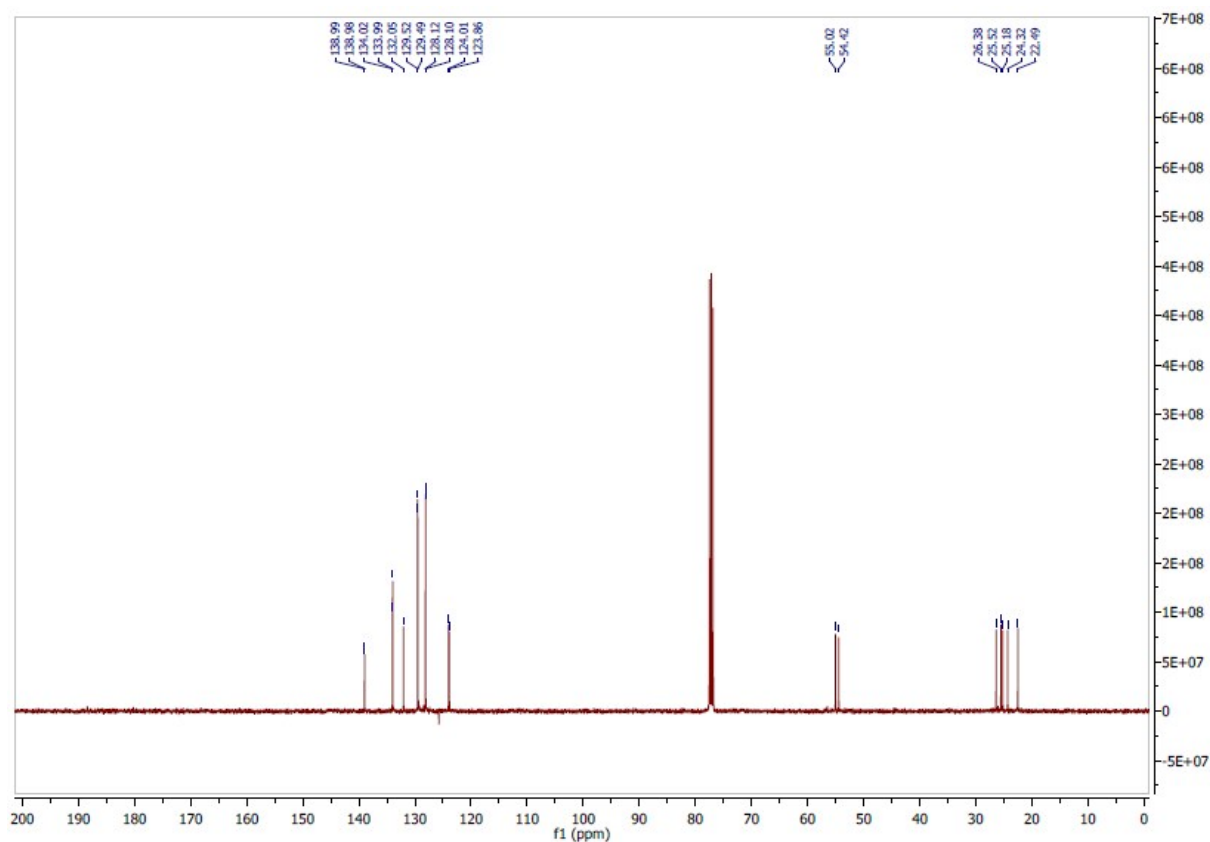


¹³C NMR (CDCl₃, 101 MHz) of methyl 6-acetoxy-4-(cyclohex-2-en-1-ylidene)hexanoate (3b)

Supporting Information:

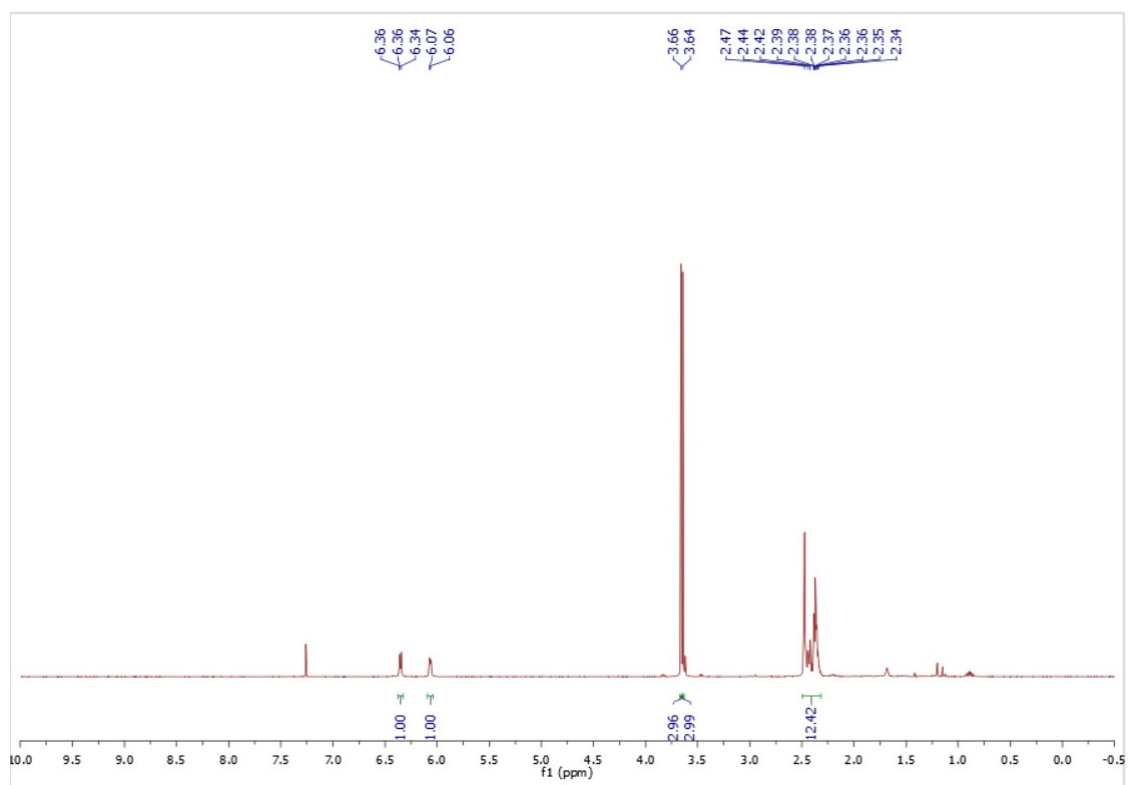


¹H NMR (CDCl₃, 400 MHz) of (3-(cyclohex-2-en-1-ylidene)pentane-1,5-diyl)disulfonyldibenzene (3c)

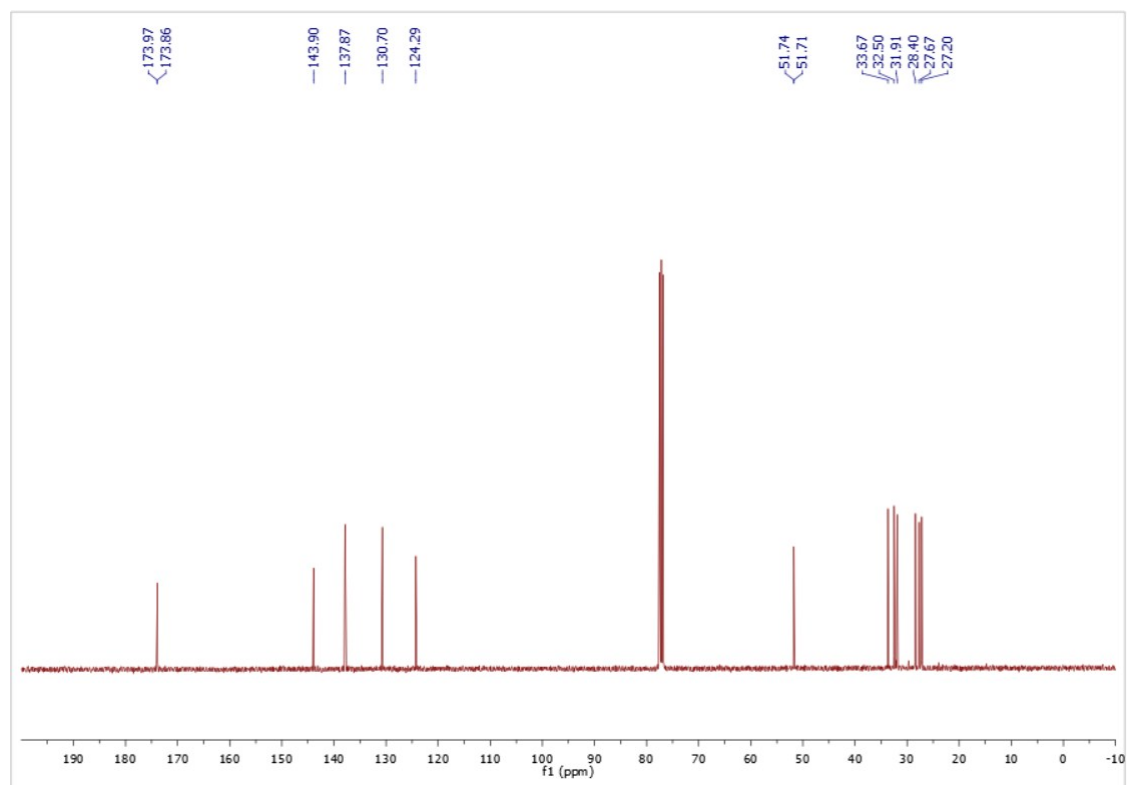


¹³C NMR (CDCl₃, 101 MHz) of (3-(cyclohex-2-en-1-ylidene)pentane-1,5-diyl)disulfonyldibenzene (3c)

Supporting Information:

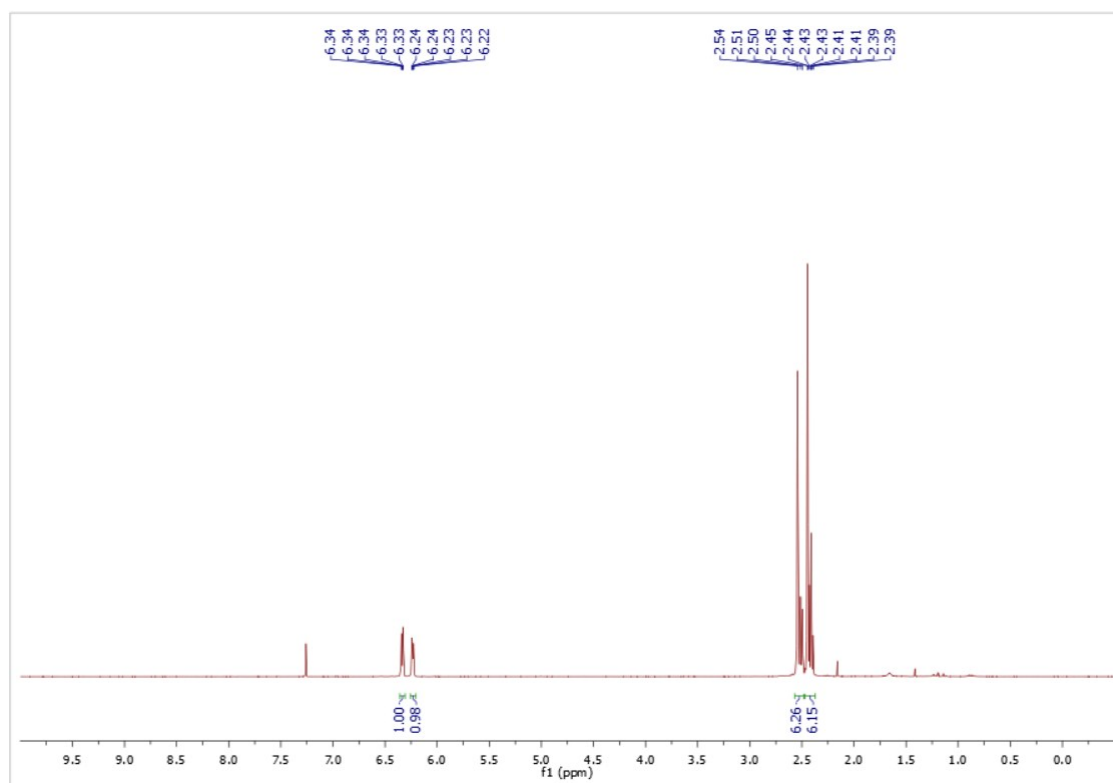


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(cyclopent-2-en-1-ylidene)heptanedioate (3d)

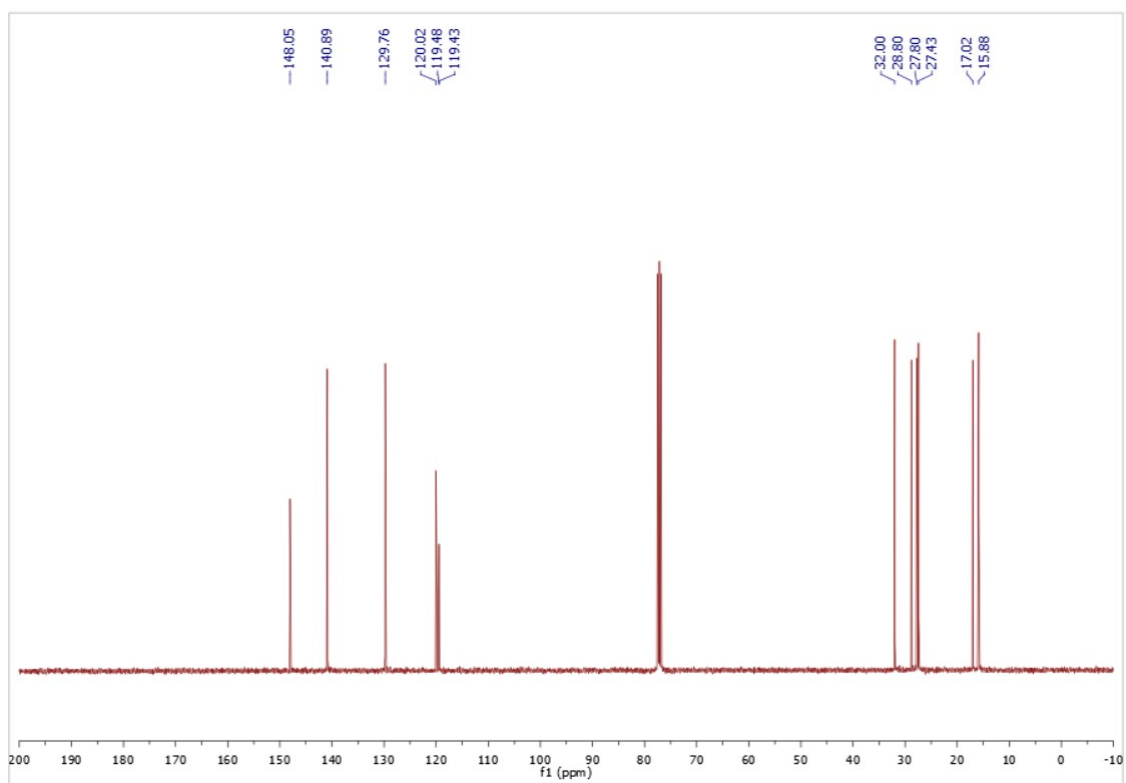


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(cyclopent-2-en-1-ylidene)heptanedioate (3d)

Supporting Information:

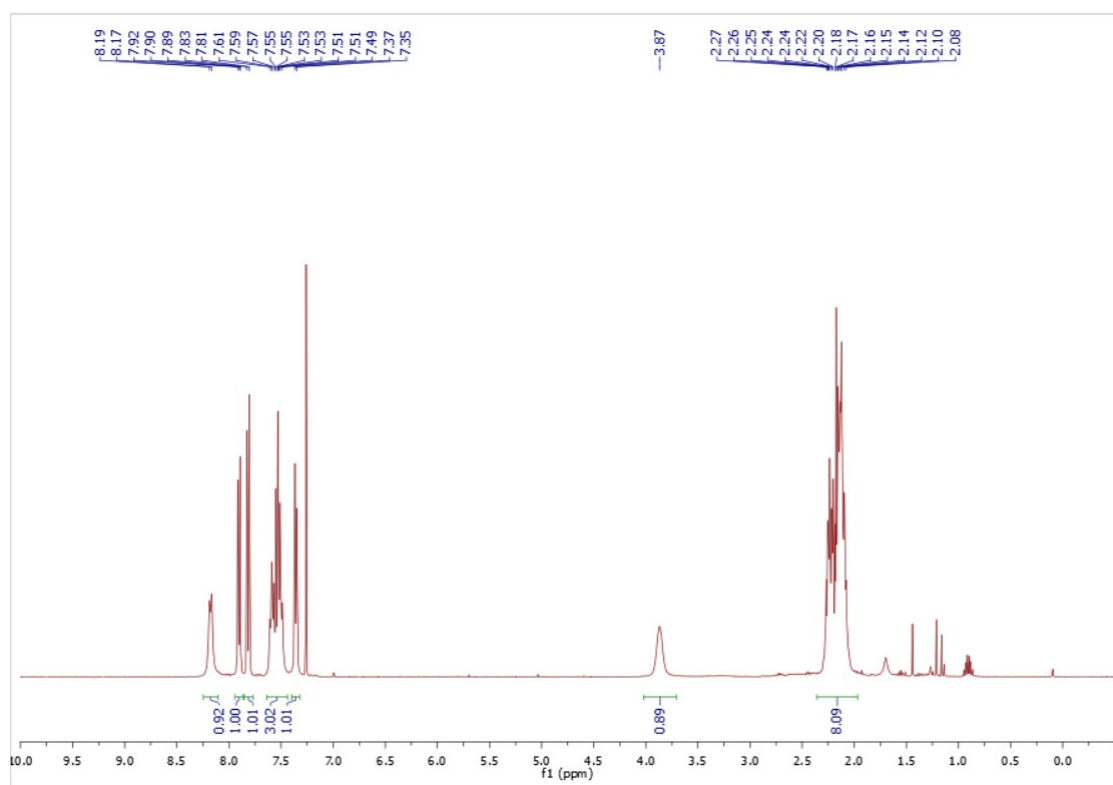


¹H NMR (CDCl₃, 400 MHz) of 4-(cyclopent-2-en-1-ylidene)heptanedinitrile (3e)

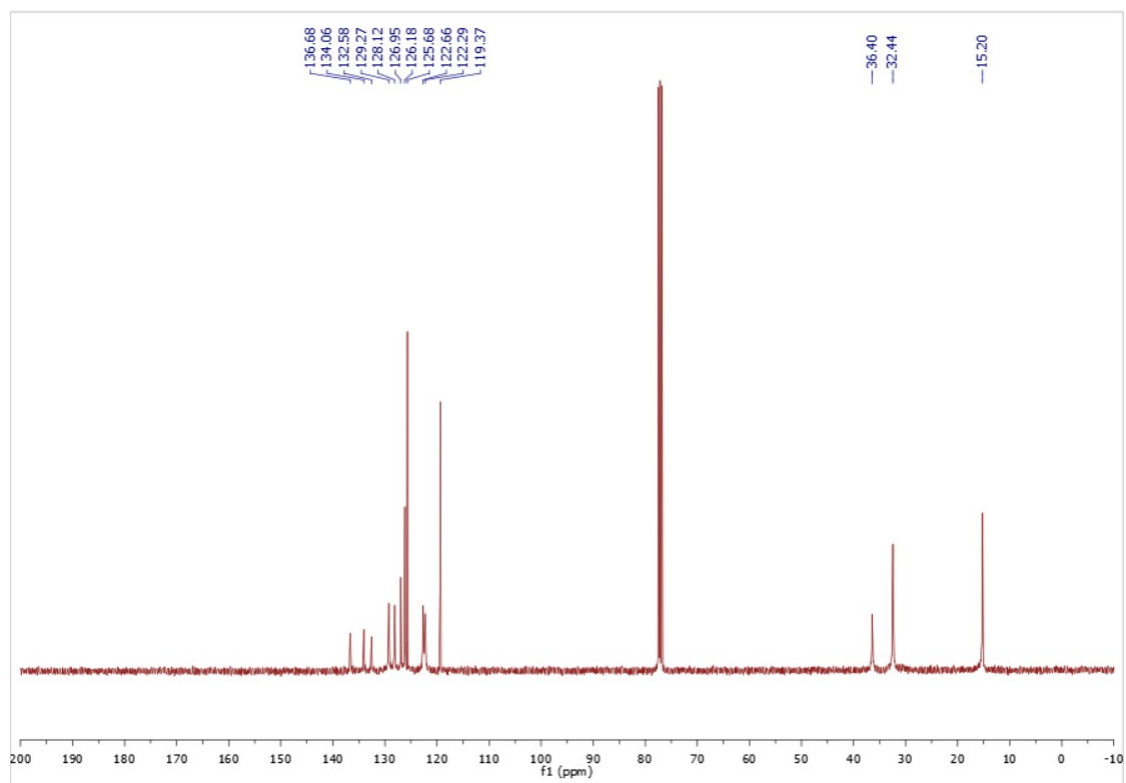


¹³C NMR (CDCl₃, 101 MHz) of 4-(cyclopent-2-en-1-ylidene)heptanedinitrile (3e)

Supporting Information:

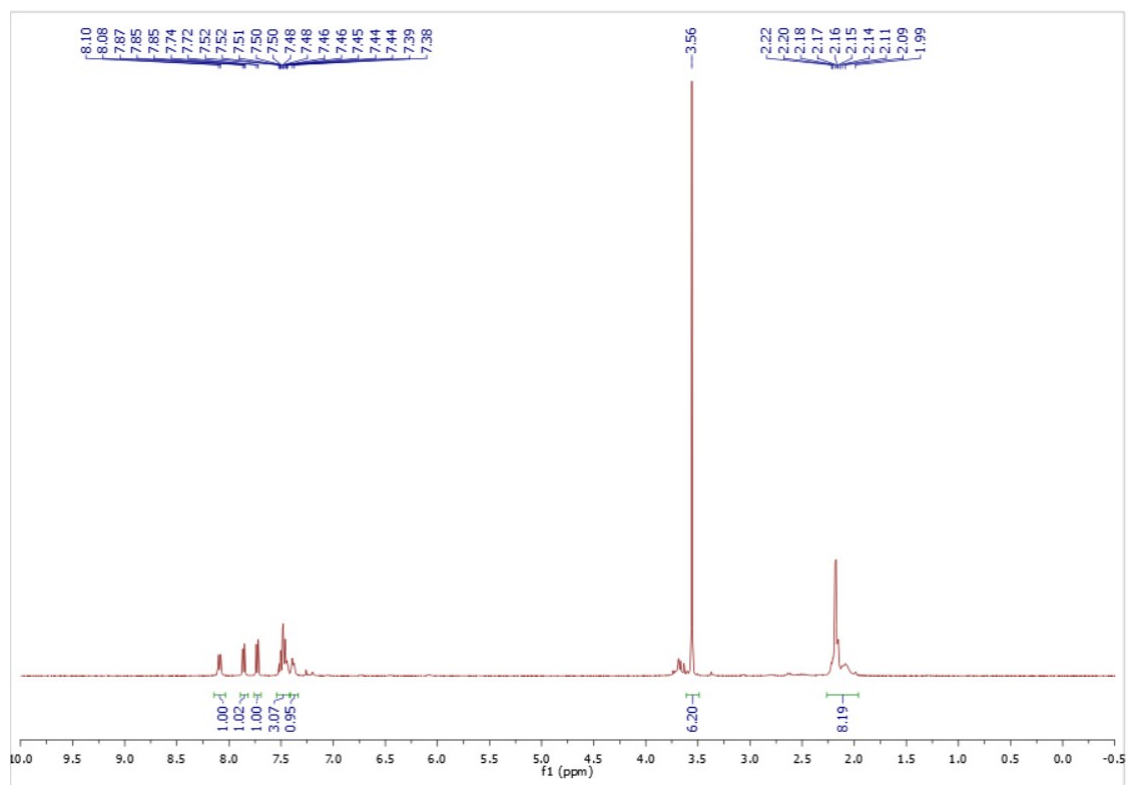


¹H NMR (CDCl₃, 400 MHz) of 4-(naphthalen-1-yl)heptanedinitrile (6a)

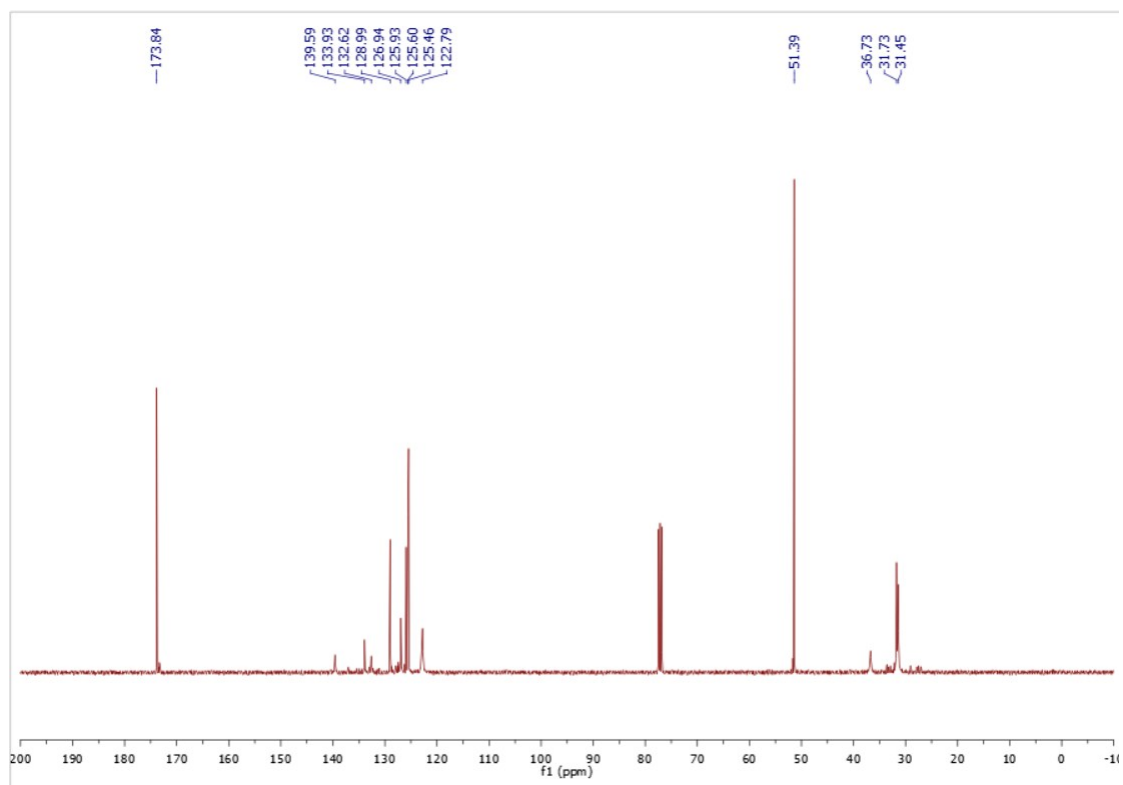


¹³C NMR (CDCl₃, 101 MHz) of 4-(naphthalen-1-yl)heptanedinitrile (6a)

Supporting Information:

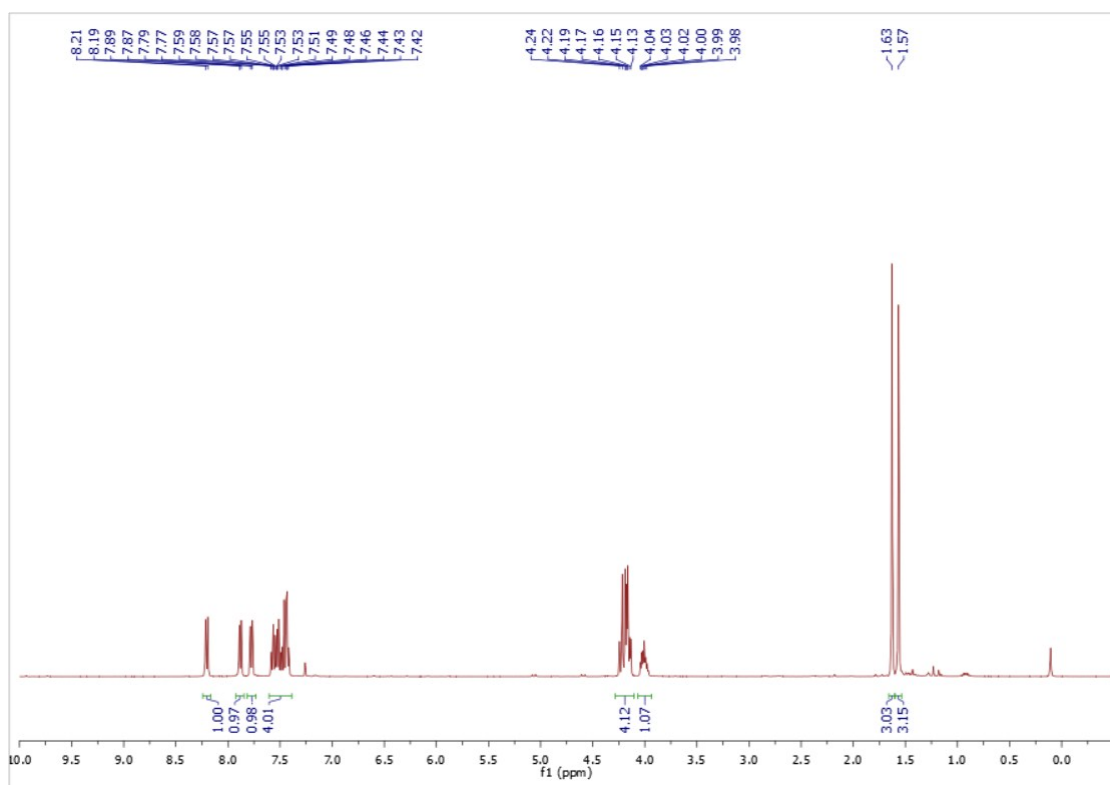


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(naphthalen-1-yl)heptanedioate (6b)

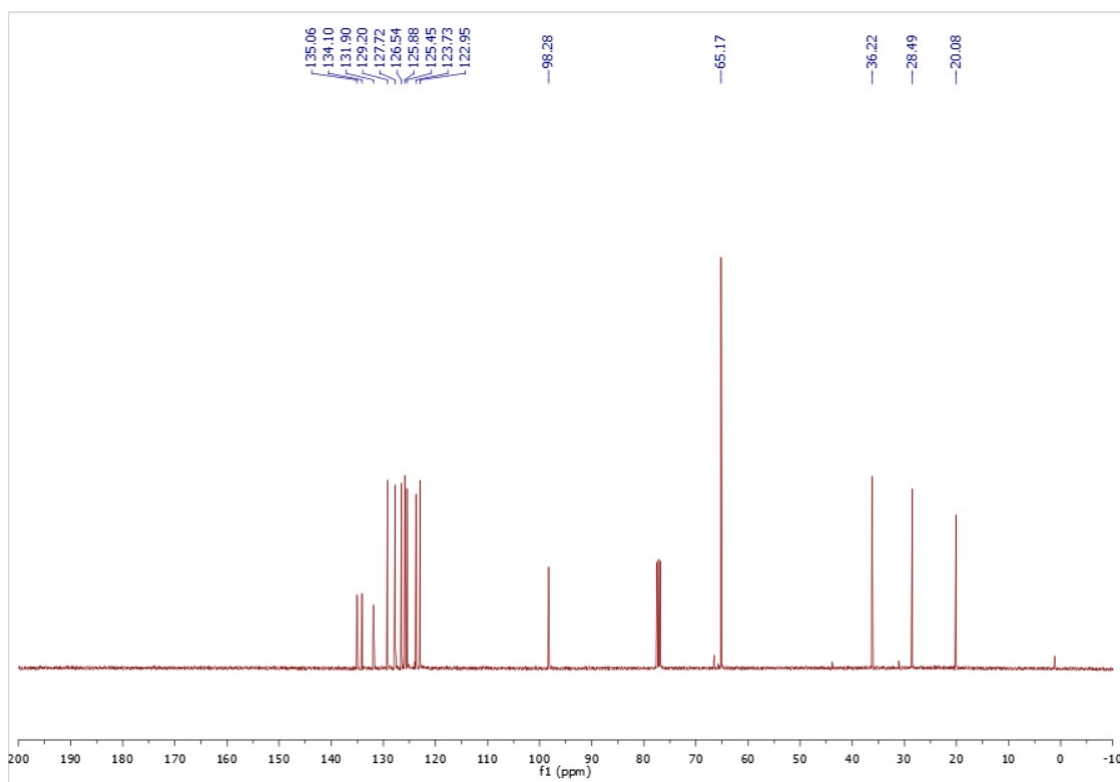


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(naphthalen-1-yl)heptanedioate (6b)

Supporting Information:

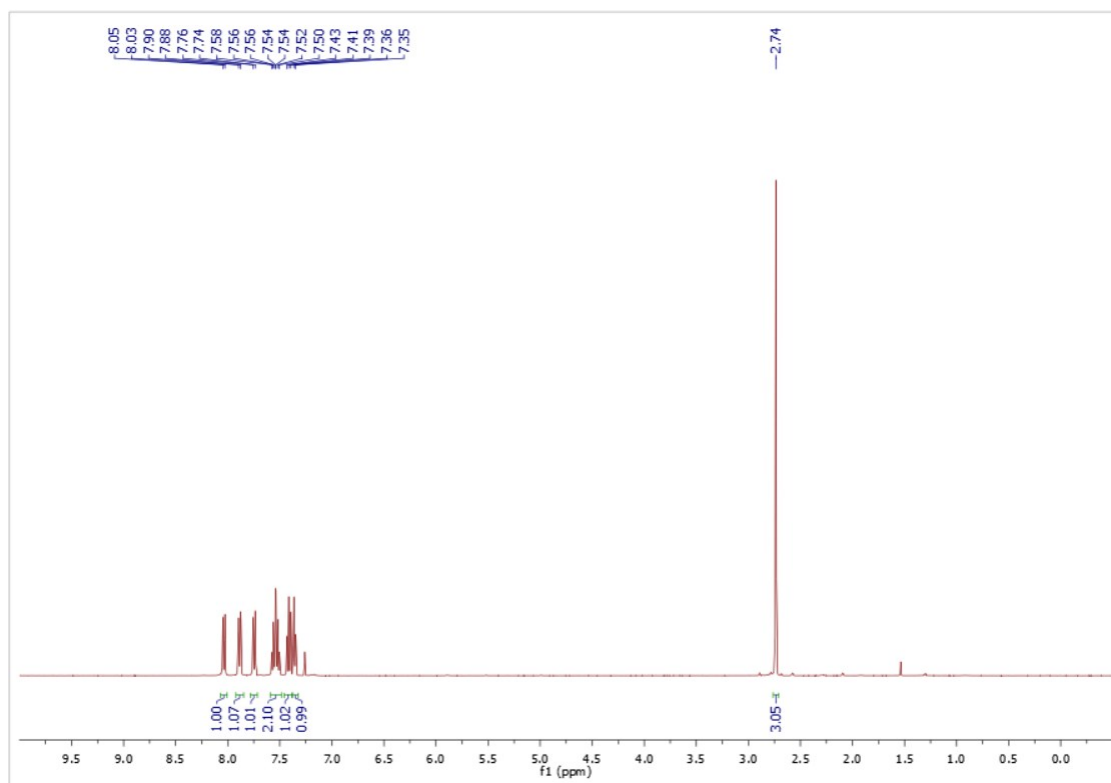


¹H NMR (CDCl₃, 400 MHz) of 2,2-dimethyl-5-(naphthalen-1-yl)-1,3-dioxane (6c)

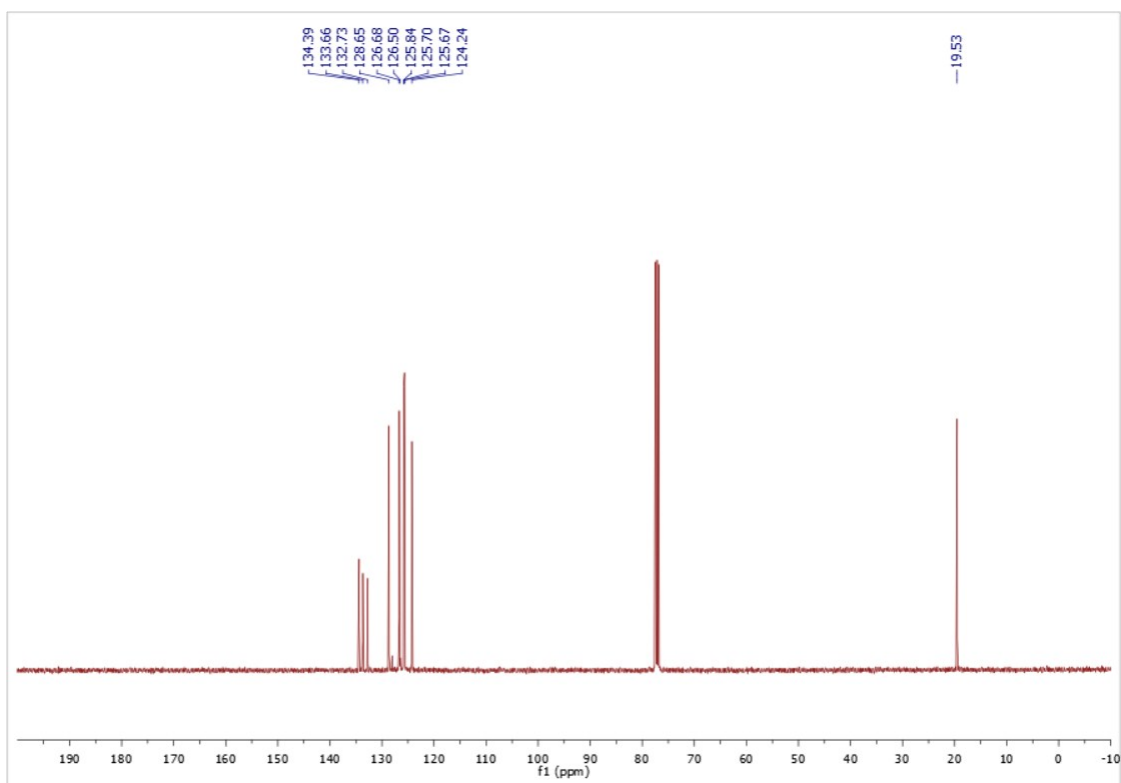


¹³C NMR (CDCl₃, 101 MHz) of 2,2-dimethyl-5-(naphthalen-1-yl)-1,3-dioxane (6c)

Supporting Information:

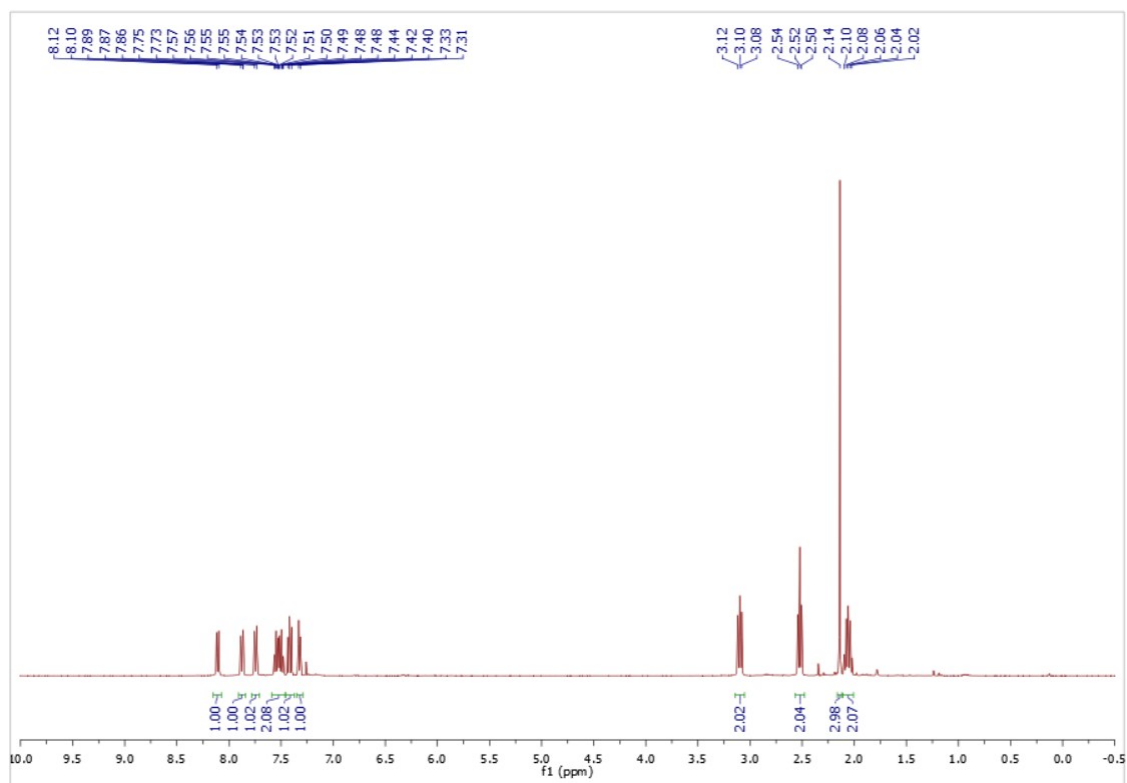


¹H NMR (CDCl₃, 400 MHz) of 1-methylnaphthalene (6d)

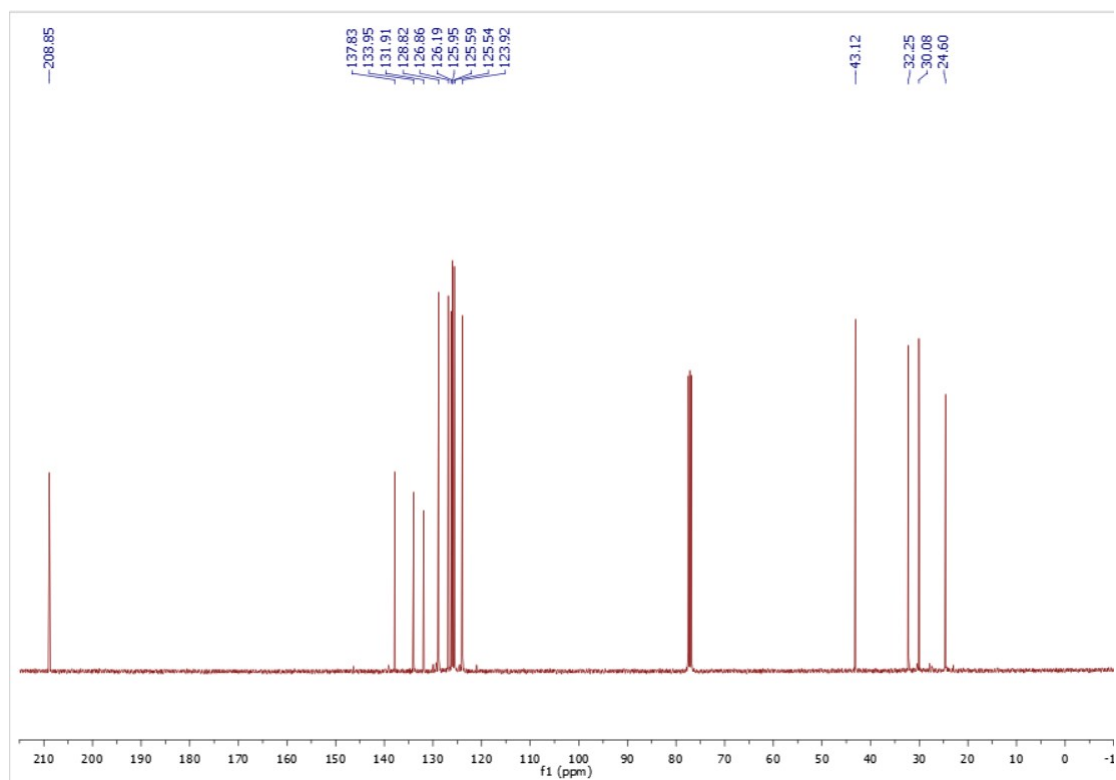


¹³C NMR (CDCl₃, 101 MHz) of 1-methylnaphthalene (6d)

Supporting Information:

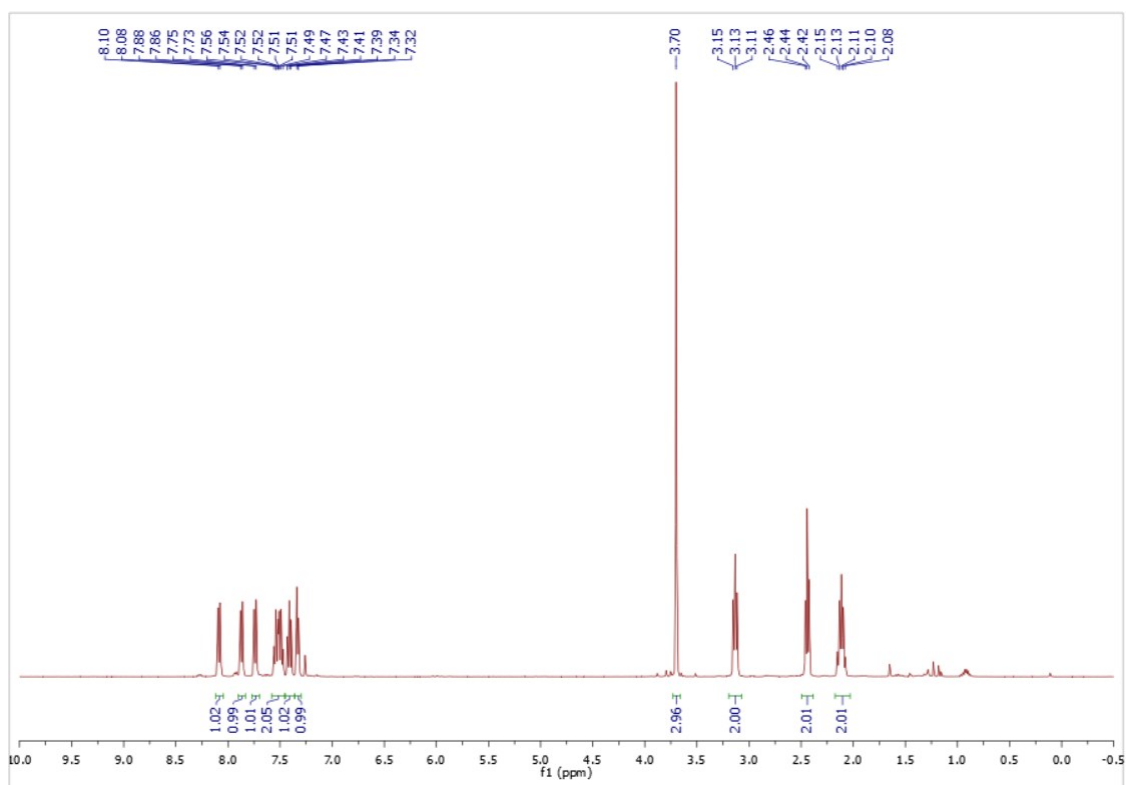


¹H NMR (CDCl₃, 400 MHz) of 5-(naphthalen-1-yl)pentan-2-one (6e)

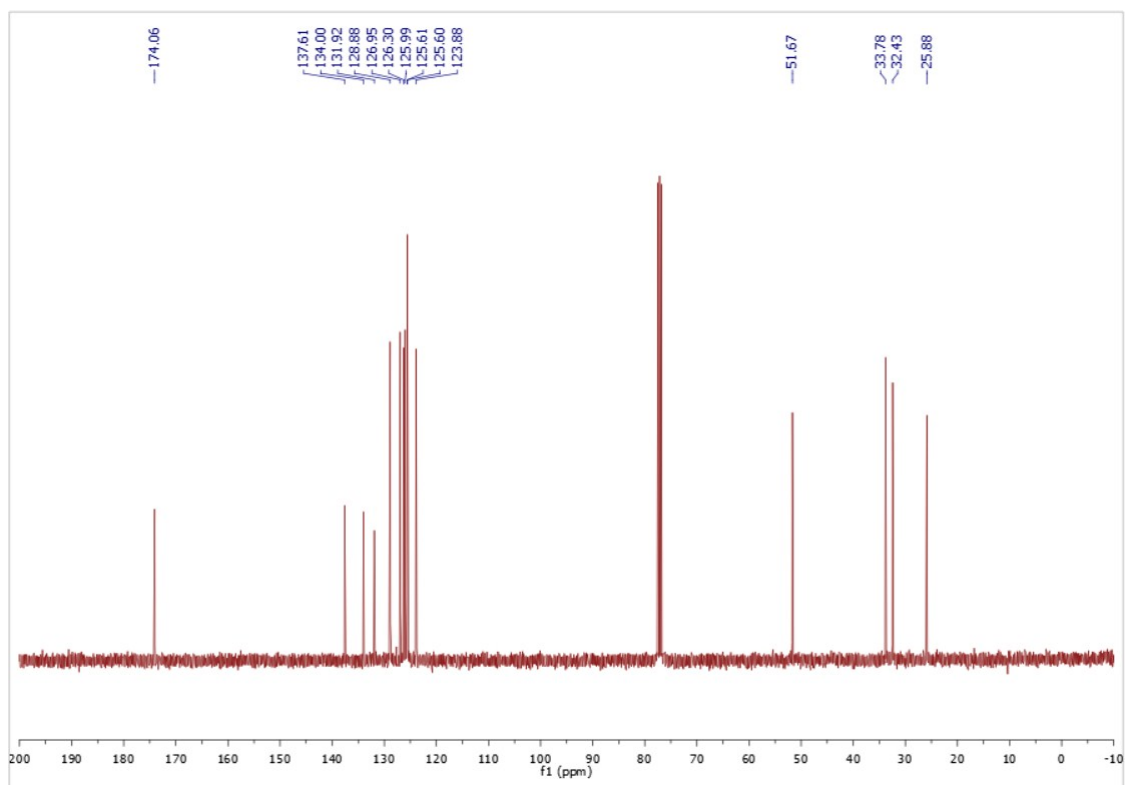


¹³C NMR (CDCl₃, 101 MHz) of 5-(naphthalen-1-yl)pentan-2-one (6e)

Supporting Information:

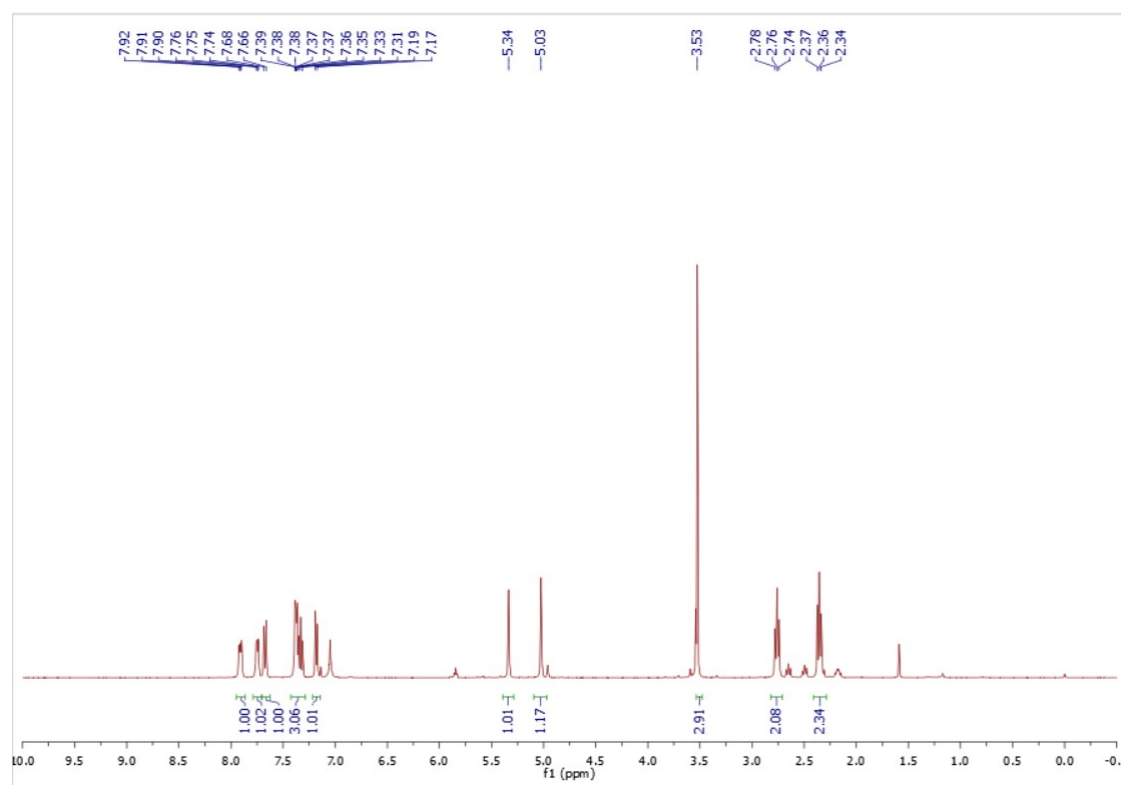


¹H NMR (CDCl₃, 400 MHz) of methyl 4-(naphthalen-1-yl)butanoate (6f)

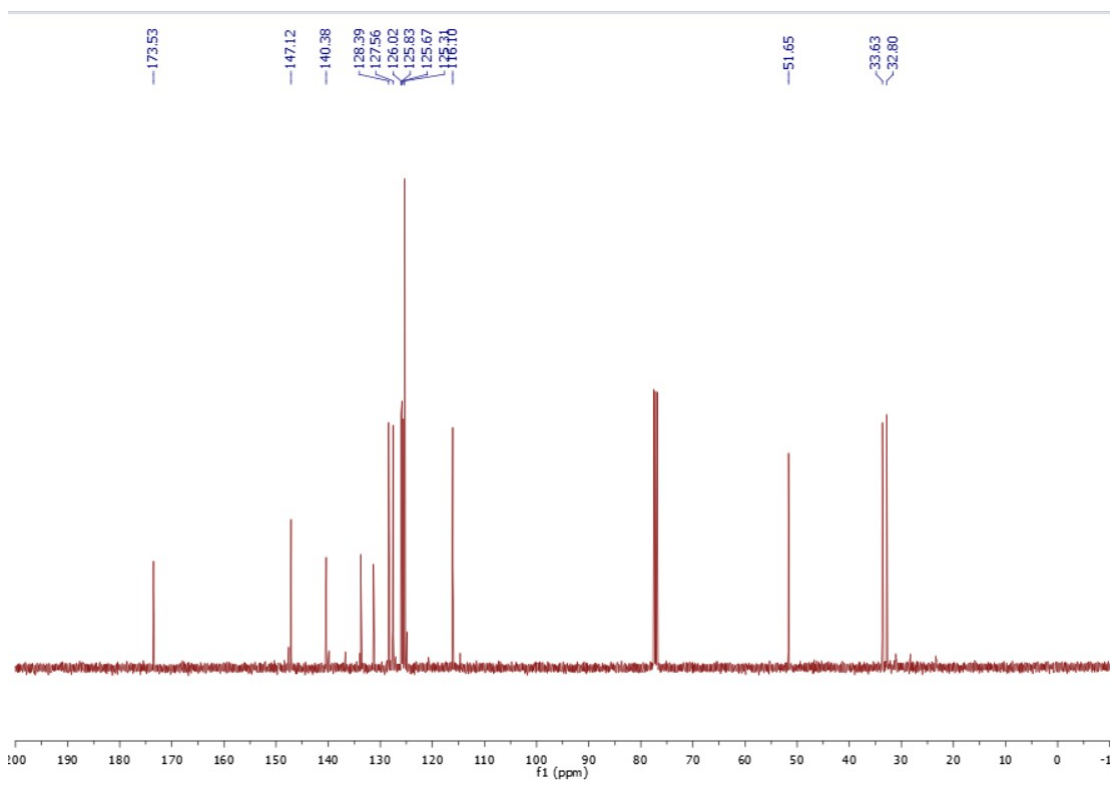


¹³C NMR (CDCl₃, 101 MHz) of methyl 4-(naphthalen-1-yl)butanoate (6f)

Supporting Information:

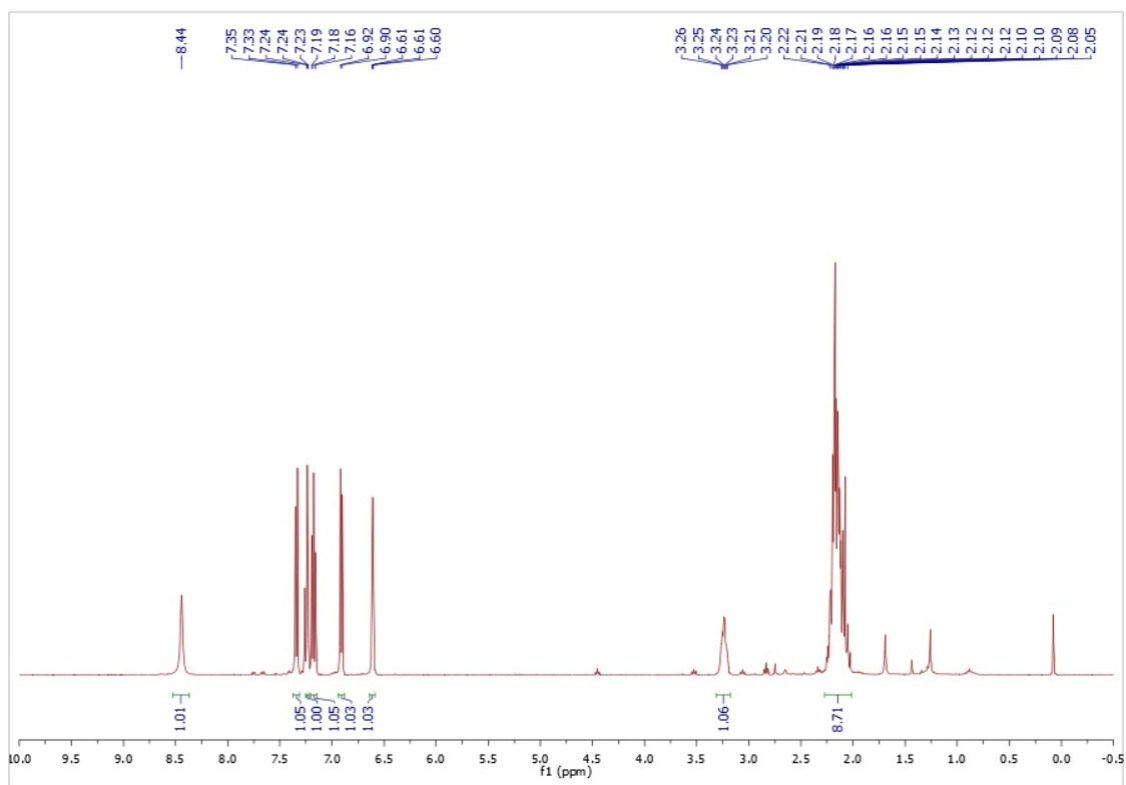


¹H NMR (CDCl₃, 400 MHz) of methyl 4-(naphthalen-1-yl)pent-4-enoate (6g)

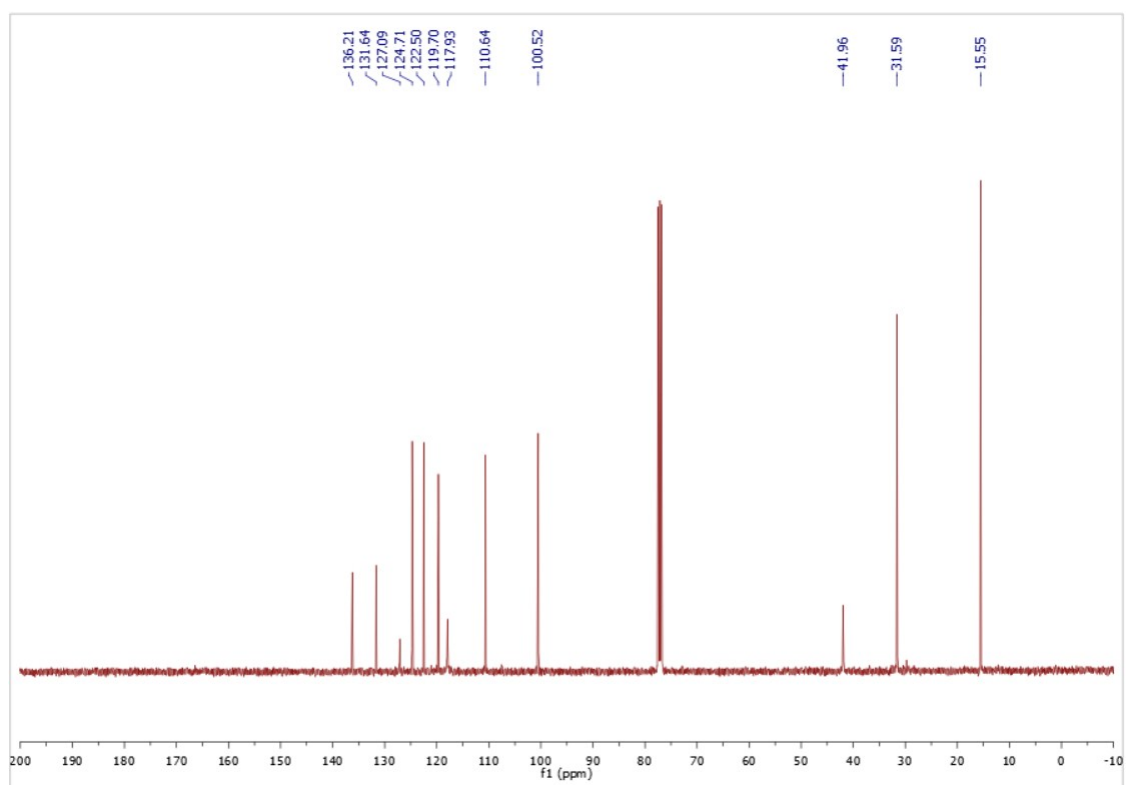


¹³C NMR (CDCl₃, 101 MHz) of methyl 4-(naphthalen-1-yl)pent-4-enoate (6g)

Supporting Information:

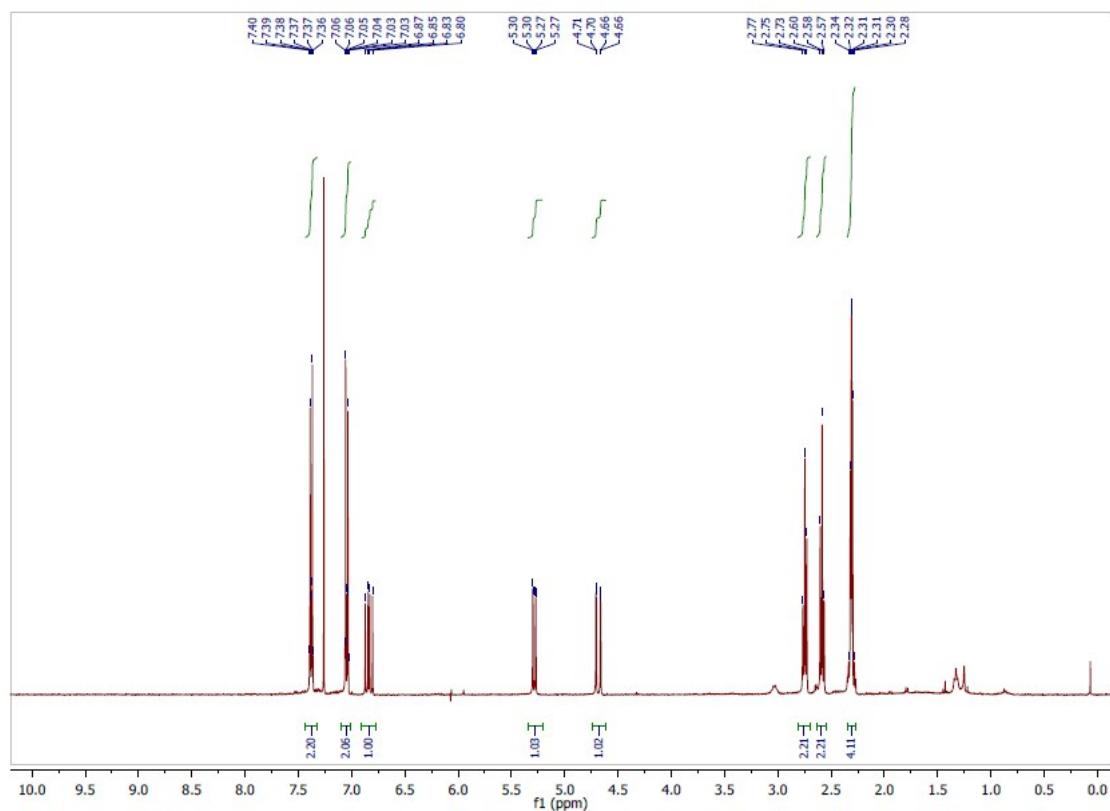


¹H NMR (CDCl₃, 400 MHz) of 4-(1H-indol-4-yl)heptanedinitrile (7a)

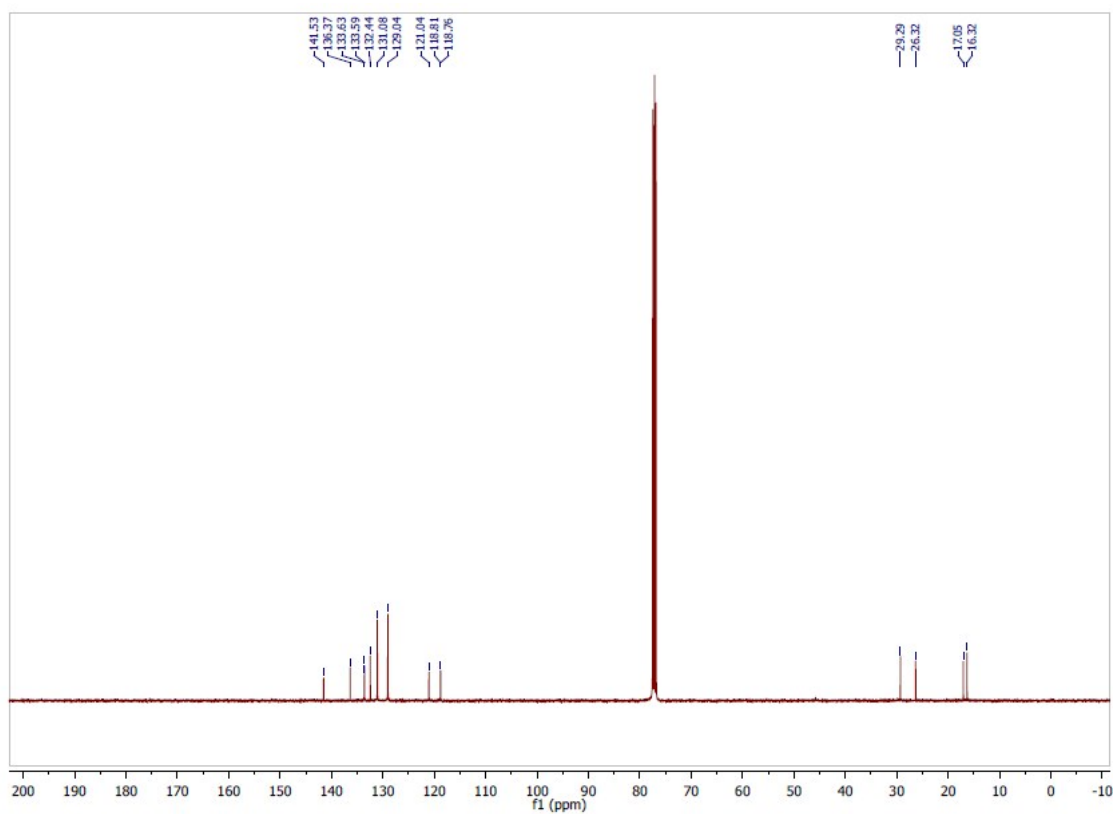


¹³C NMR (CDCl₃, 101 MHz) of 4-(1H-indol-4-yl)heptanedinitrile (7a)

Supporting Information:

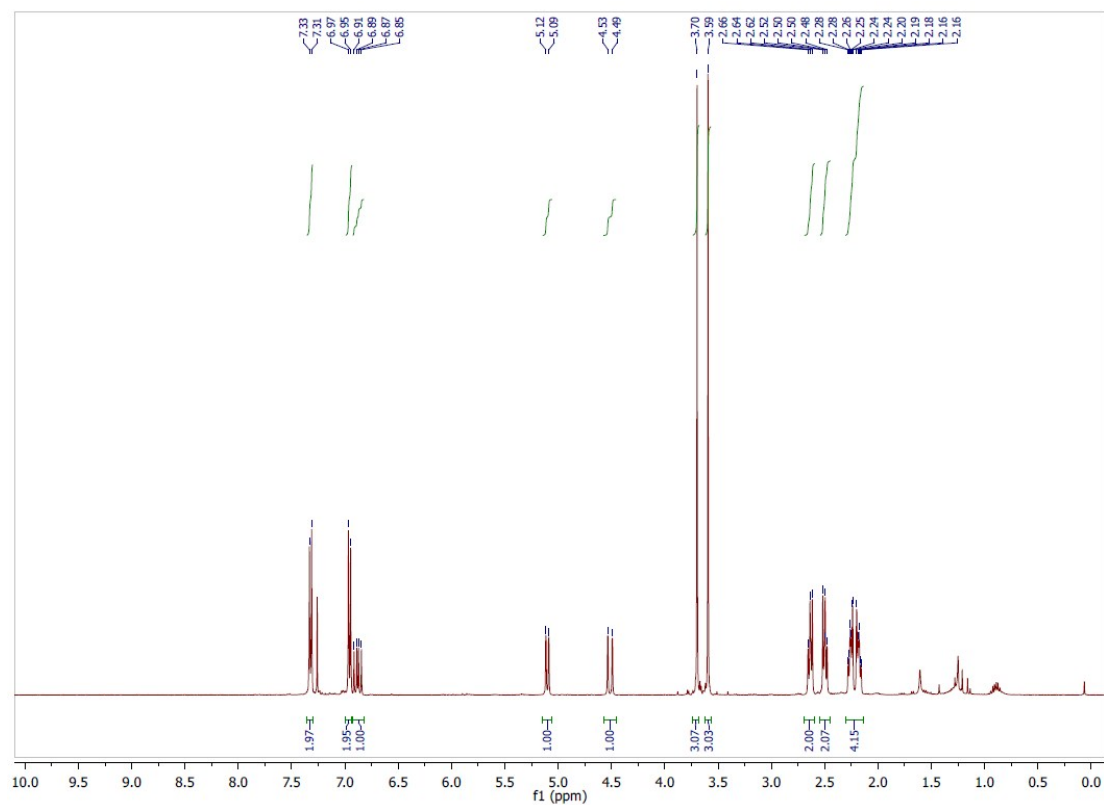


¹H NMR (CDCl₃, 400 MHz) of 4-(1-(4-chlorophenyl)allylidene)heptanedinitrile (9a)

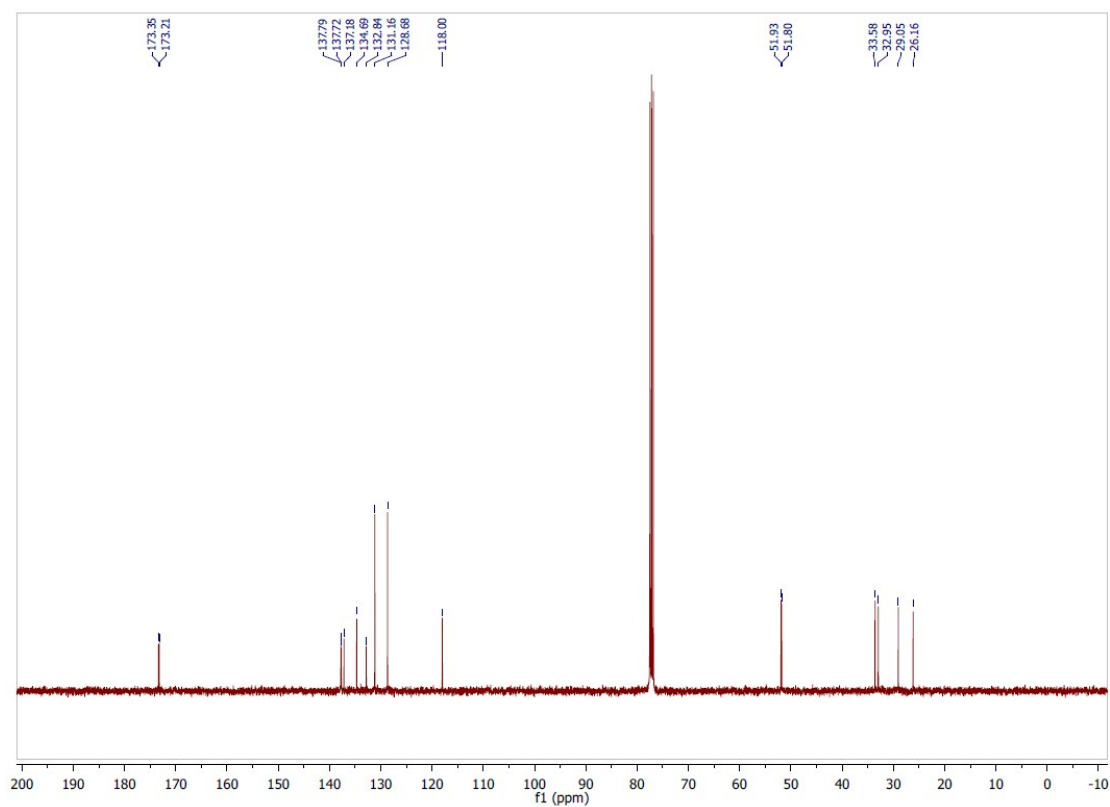


¹³C NMR (CDCl₃, 101 MHz) of 4-(1-(4-chlorophenyl)allylidene)heptanedinitrile (9a)

Supporting Information:

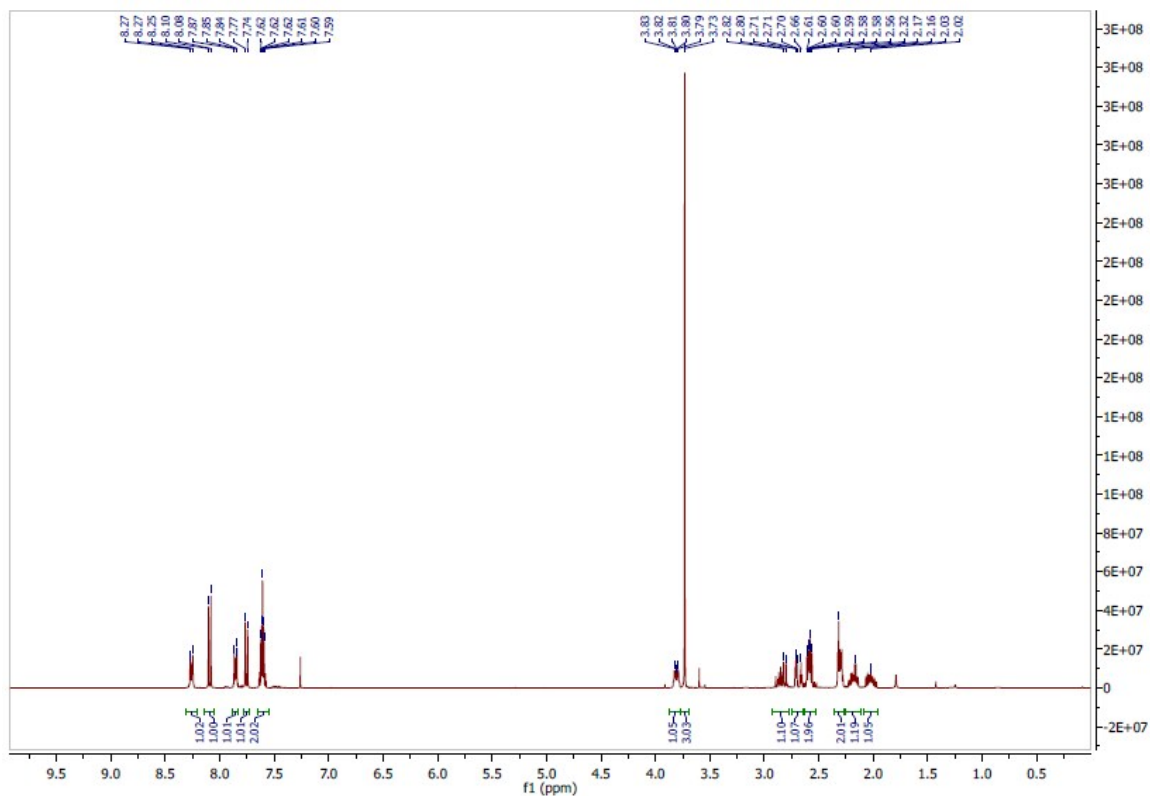


¹H NMR (CDCl₃, 400 MHz) of dimethyl 4-(1-(4-chlorophenyl)allylidene)heptanedioate (9b)

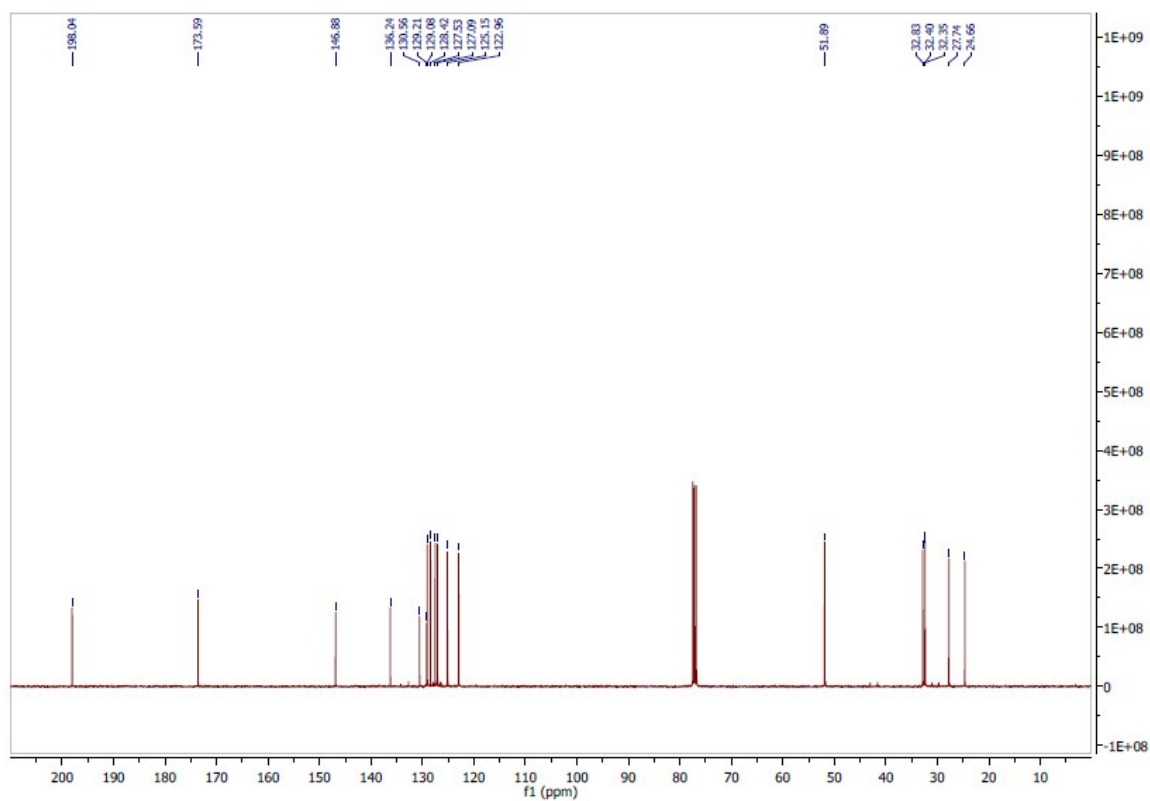


¹³C NMR (CDCl₃, 101 MHz) of dimethyl 4-(1-(4-chlorophenyl)allylidene)heptanedioate (9b)

Supporting Information:



¹H NMR (CDCl₃, 400 MHz) of methyl 3-(1-oxo-1,2,3,4-tetrahydrophenanthren-4-yl)propanoate (10)



¹³C NMR (CDCl₃, 101 MHz) of methyl 3-(1-oxo-1,2,3,4-tetrahydrophenanthren-4-yl)propanoate (10)