Supporting Information

Ruthenium Catalyzed Hydrohydroxyalkylation of Acrylates with Diols and α-Hydroxycarbonyl Compounds to Form Spiro- and α-Methylene-γ-Butyrolactones

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General Information: All reactions were run under an atmosphere of argon. Anhydrous solvents were distilled using solvent stills, and solvents were transferred by oven-dried syringe. Sealed tubes (13×100 mm^2) were purchased from Fisher Scientific (catalog number 14-959-35C) and were dried in an oven overnight and cooled under a stream of argon prior to use. $Ru_3(CO)_{12}$, DPPP (1,3-Bis(diphenylphosphinopropane), and all other ligands were used without purification. All starting materials were used without purification. Diols **1c**, **1g**, **1h**, and **1i** were prepared from the corresponding alkene using the protocol described by Hayashi et al.[1] Diol **1j** was prepared from **5j** according to the method described by Rodrigues *et al*.[2] Diol **1k** was prepared according to the method of Dakdouki et al.[3] Diol **1l** was prepared from the corresponding chromene[4] by OsO_4 catalyzed dihydroxylation. Hydroxy ester **7b** was prepared by reduction of the corresponding oxoester[5] by the method described by Hui *et al*.[6] Hydroxyoxindole **1o** was prepared according to the method described by Autry and Tahk.[7] Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Silicycle Siliaplate, F-254). Visualization was accomplished with UV light followed by dipping in a *p*-anisaldehyde solution and heating. Purification of reaction products was carried out by flash column chromatography using Silicycle silica gel (40-63 μm), according to the method described by Still.[8]

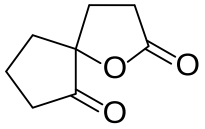
Spectroscopy and Spectrometry: Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M or M-H) or a suitable fragment ion. Melting points were obtained on a Stuart SMP3 apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian Gemini (400 MHz) spectrometer at ambient temperature unless otherwise noted. Chemical shifts are reported in delta (δ) units, parts per million (ppm), relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. ^{13}C NMR spectra were recorded on a Varian Gemini (100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in ppm, with the residual solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm).

Computational Analysis: All structures were optimized and characterized to determine each atom's contribution to the LUMO orbital. Density functional theory (DFT) calculations were carried out with QChem 4.0 using the B3LYP hybrid functional and 6-311G(d,p) basis set.

References:

1. Hayashi, M.; Terashima, S.; Koga, K. *Tetrahedron,* **1981**, *37*, 2797.
2. Lunardi, I.; Cazetta, T.; Conceição, G. J. A.; Moran, P. J. S.; Rodrigues, J. A. R. *Adv. Synth. Catal.* **2007**, *349*, 925.
3. Dakdouki, S.C.; Villemin, D.; Bar, N. *Eur. J. Org. Chem.* **2011,** *23,* 4448.
4. de Boer, J. W.; Browne, W. R.; Harutyunyan, S. R.; Bini, L.; Tiemersma-Wegman, T. D.; Alsters, P. L.; Hage, R.; Feringa, B. L. *Chem. Comm.* **2008**, 3747.
5. Hlasta, D. J.; Luttinger, D.; Perrone, M. H.; Silbernagel, M. J.; Ward, S. J.; Haubrich, D. R. *J. Med. Chem.* **1987**, *30*, 1555.
6. Chiba, S.; Zhang, L.; Ang, G. Y.; Hui, B. W-Q. *Org. Lett.* **2010**, *12*, 2052.
7. Autry, R.L.; Tahk, F.C. *Tetrahedron* **1967**, *23*, 901.
8. Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

1-oxaspiro[4.4]nonane-2,6-dione (3a)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis*-cyclopentane-1,2-diol (**1a**) (31 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (109 µL, 1.20 mmol, 400 mol%) and *m*-xylenes (0.19 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (39.3 mg, 0.25 mmol, 85%) as a colorless solid. All spectral data was consistent with literature reported values.[9]

TLC (SiO_2): R_f = 0.17 (hexanes:ethyl acetate = 3:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.81 (dt, *J* = 9.7, 9.6 Hz, 1H), 2.57 (ddd, J = 17.8, 9.8, 4.0 Hz, 1H), 2.48-2.31 (m, 4H), 2.19-2.01 (m, 3H), 1.98-1.88 (m, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 213.6, 175.8, 86.6, 35.2, 35.0, 28.7, 28.1, 17.8.

MP: 103 – 104 °C

HRMS: (ESI) Calculated for $C_8H_{10}O_3$ $[M+Na]^+$ = 177.05220, Found 177.05180.

FTIR: (neat): 1981, 1772, 1745, 1454, 1398, 1246, 1222, 1156, 1037 cm^{-1}.

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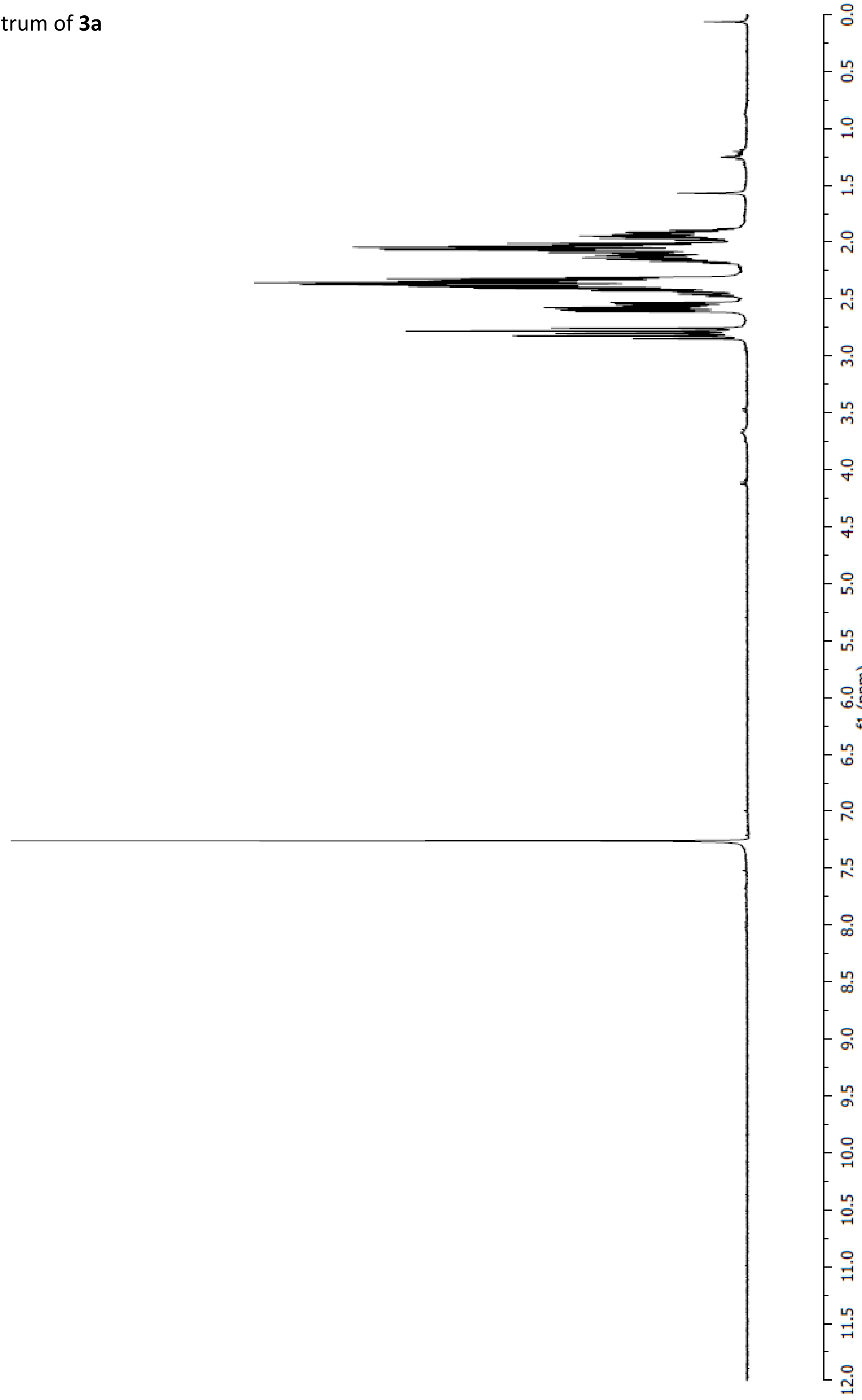
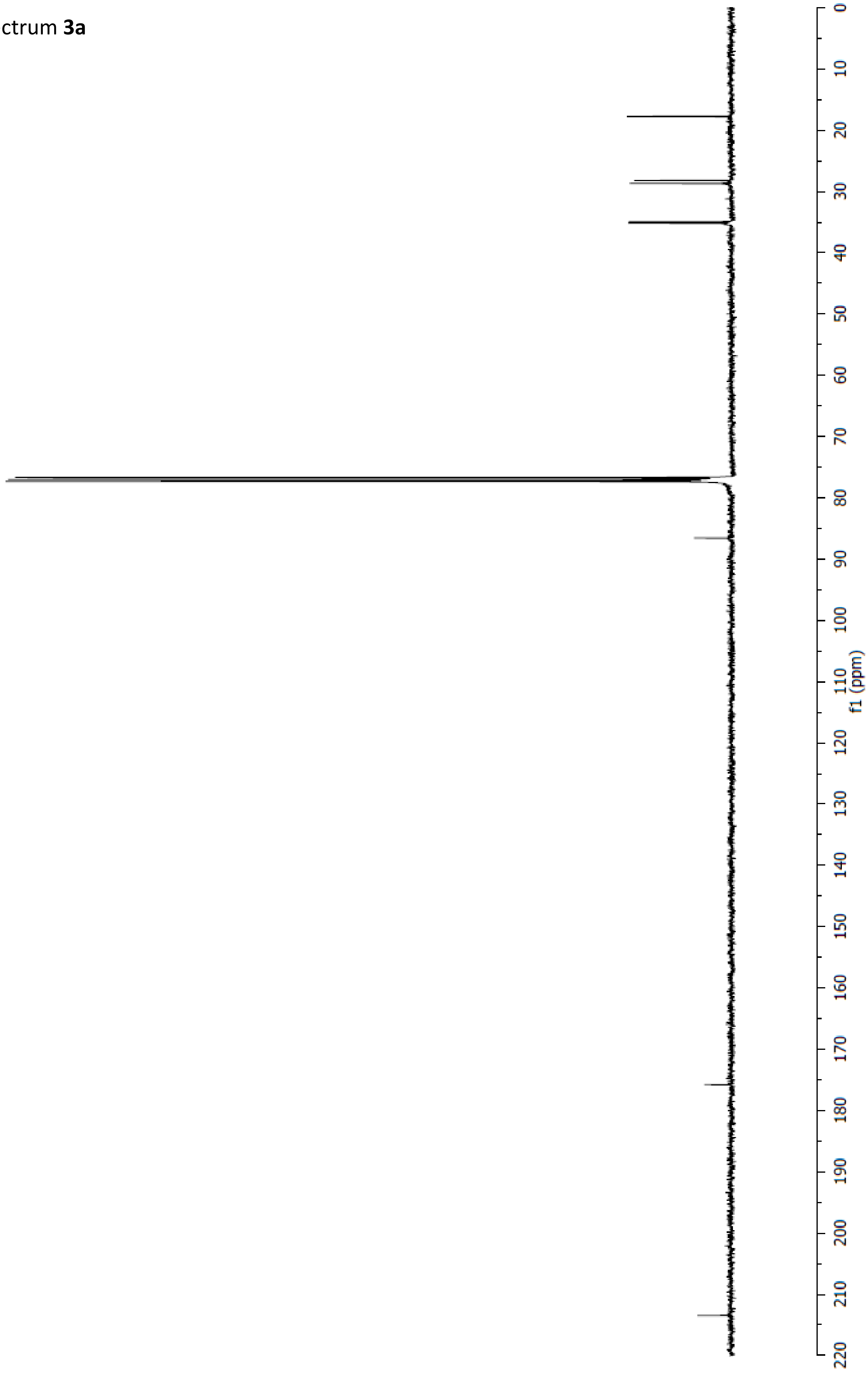
[9] Bigi, M.A.; Reed, S.A.; White, M.C. *Nature Chemistry,* **2011**, *3,* 216.

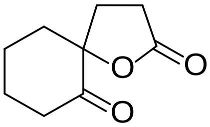
^{1}H NMR Spectrum of **3a**



^{13}C NMR Spectrum **3a**



1-oxaspiro[4.5]decane-2,6-dione (3b)



General Protocol:

To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-1,2-cyclohexanediol (**1b**) (35 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 1:1) to furnish the title compound (48.4 mg, 0.29 mmol, 96%) as a clear yellow oil. All spectral data was consistent with literature reported values.[10]

Procedure using Preformed Ru(CO)(dppp)($C_{15}H_{10}CO_2$)$_2$ complex:

To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-1,2-cyclohexanediol (**1b**) and Ru(CO)(dppp)($C_{15}H_{10}CO_2$)$_2$ (16.2 mg, 0.018 mMol, 6 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 1:1) to furnish the title compound (43.3 mg, 0.26 mmol, 86%) as a clear yellow oil. All spectral data was consistent with literature reported values.[10]

TLC (SiO_2): R_f = 0.23 (hexanes:ethyl acetate = 1:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.77-2.67 (m, 2H) 2.53 (dd, *J* = 9.5, 2.1 Hz, 1H), 2.52-2.50 (m, 1H), 2.47-2.41 (m, 1H), 2.20 (dddd, *J* = 13.2, 6.6, 3.5, 1.8 Hz, 1H), 2.04-1.67 (m, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 206.0, 175.5, 88.3, 39.2, 38.8, 28.7, 28.2, 26.8, 21.5.

HRMS: (ESI) Calculated for $C_9H_{12}O_3$ $[M+Na]^+$ = 191.06790, Found 191.06790.

FTIR: (neat): 3538, 2943, 2868, 1776, 1718, 1451, 1421, 1339, 1316, 1253, 1201, 1171, 1145, 1131, 1112, 1094, 1057, 1024 cm^{-1}.

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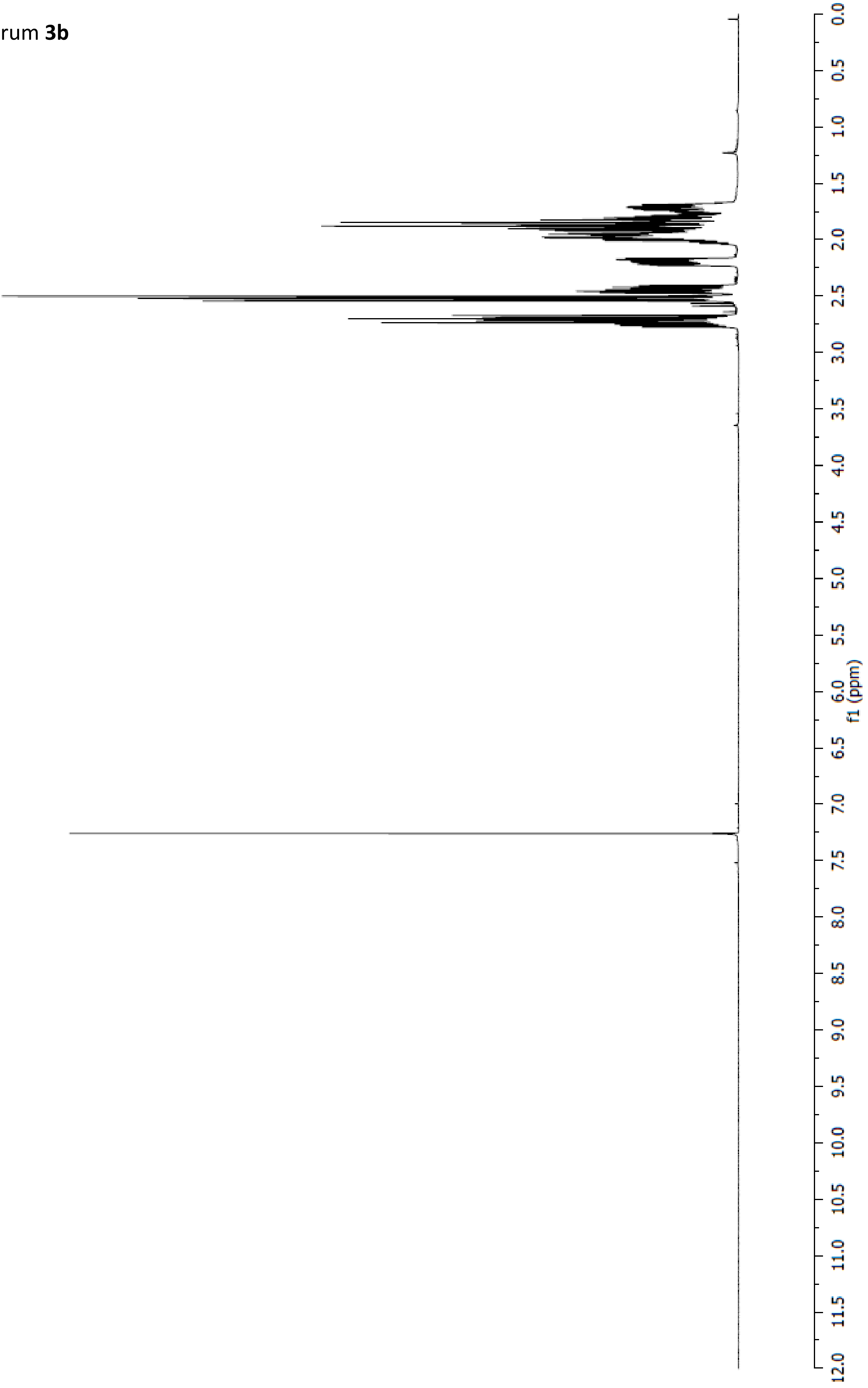
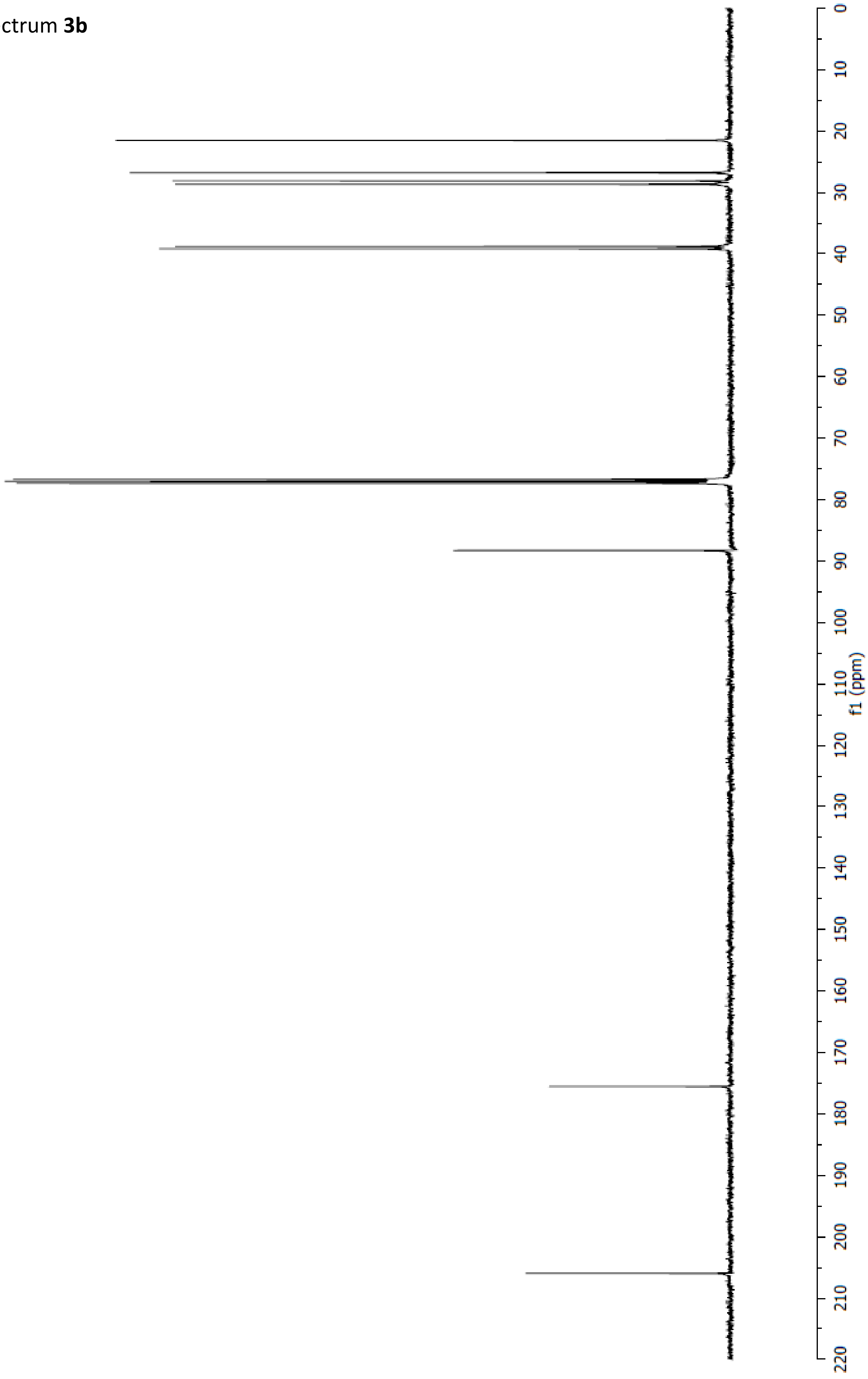
[10] Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331.

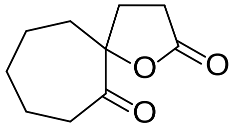
^{1}H NMR Spectrum **3b**



^{13}C NMR Spectrum **3b**



1-oxaspiro[4.6]undecane-2,6-dione (3c)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-1,2-cycloheptanediol (**1c**) (39 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:2) to furnish the title compound (35 mg, 0.19 mmol, 64%) as a colorless solid. All spectral data was consistent with literature reported values.[11]

TLC (SiO_2): R_f = 0.3 (hexanes:ethyl acetate = 1:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.68 (m, 1H), 2.63 – 2.49 (m, 3H), 2.42 (ddd, *J* = 13.0, 8.8, 4.1 Hz, 1H), 2.13 (ddd, *J* = 15.0, 7.1, 1.8 Hz, 1H), 1.99 (m, 1H), 1.94 – 1.56 (m, 6H), 1.41 (m, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 209.2, 176.0, 90.7, 40.1, 37.1, 31.3, 29.0, 27.9, 25.2, 24.7.

MP: 64 - 65 °C

HRMS: (ESI) Calculated for $C_{10}H_{14}O_3$ $[M+Na]^+$ = 205.08350, Found 205.08390.

FTIR: (neat): 2930, 2860, 1773, 1713, 1455, 1227, 1150, 943, 694 cm^{-1}.

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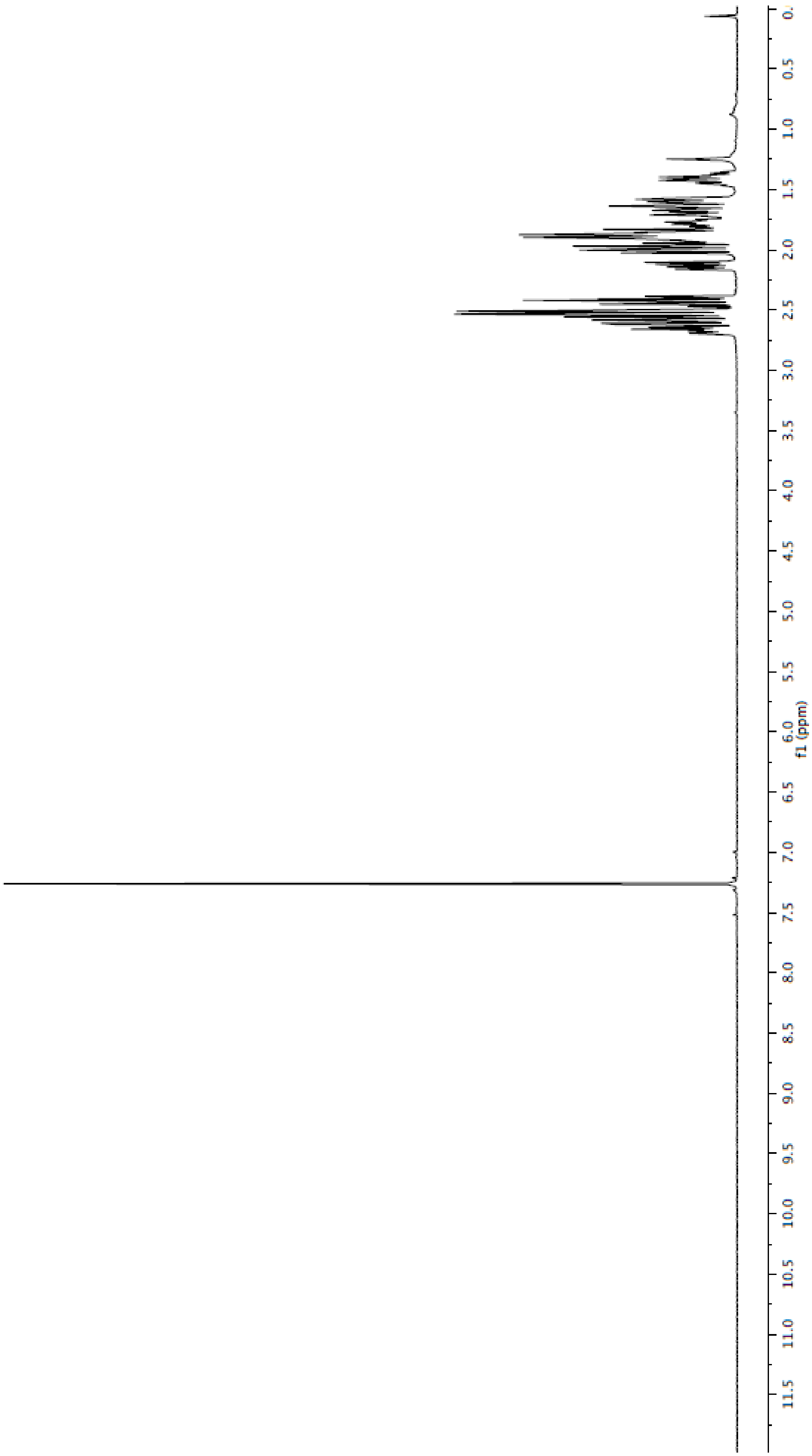
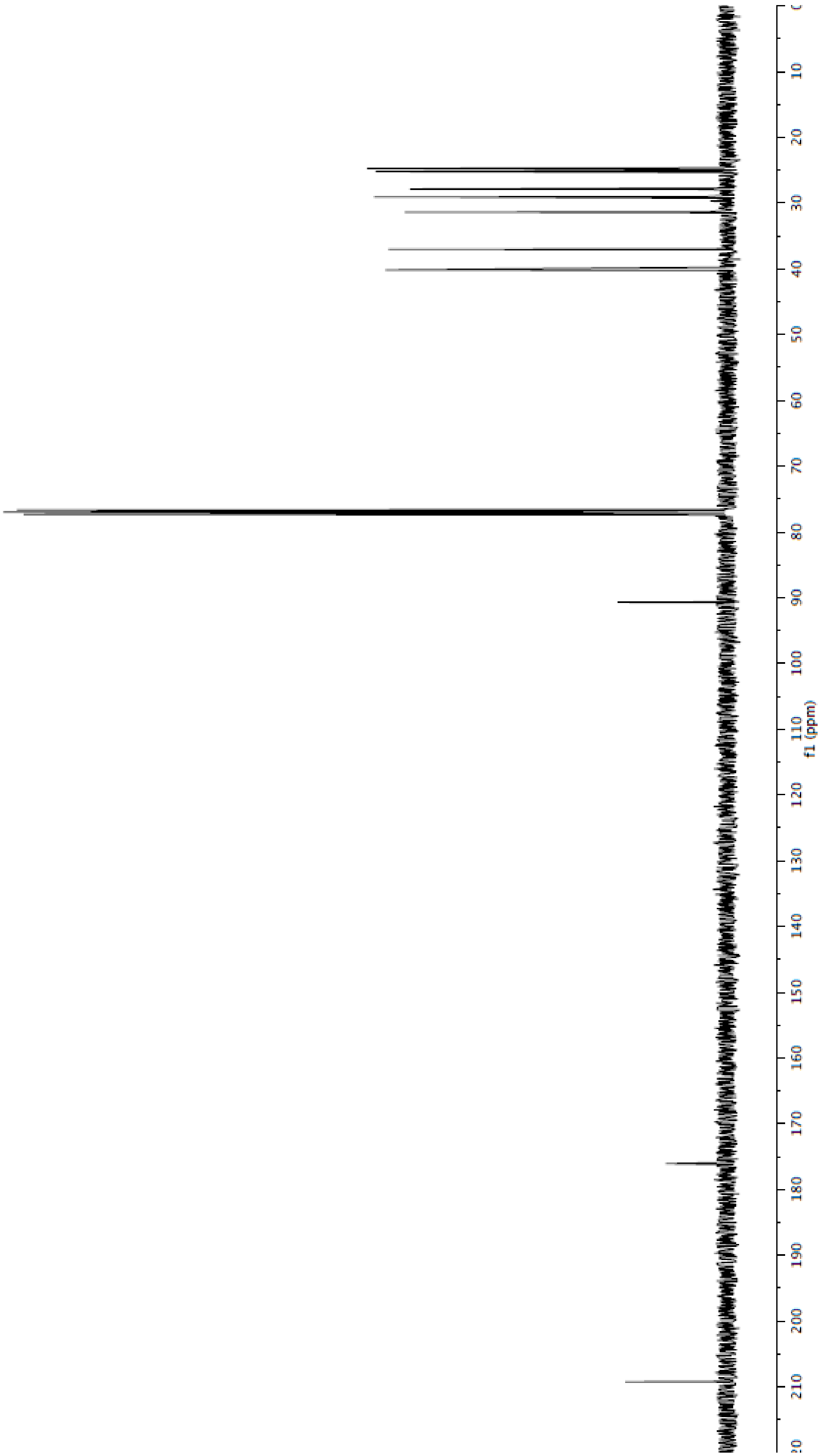
[11] Mandal, A.K.; Jawalker, D.G. *J. Org. Chem.* **1989**, *54,* 2364.

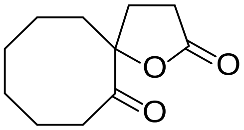
^{1}H NMR Spectrum **3c**



^{13}C NMR Spectrum **3c**



1-oxaspiro[4.7]dodecane-2,6-dione (3d)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis*-1,2-cyclooctanediol (**1d**) (43 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:2) to furnish the title compound (46.5 mg, 0.24 mmol, 79%) as a clear yellow oil.

TLC (SiO_2): R_f = 0.27 (hexanes:ethyl acetate = 3:2).

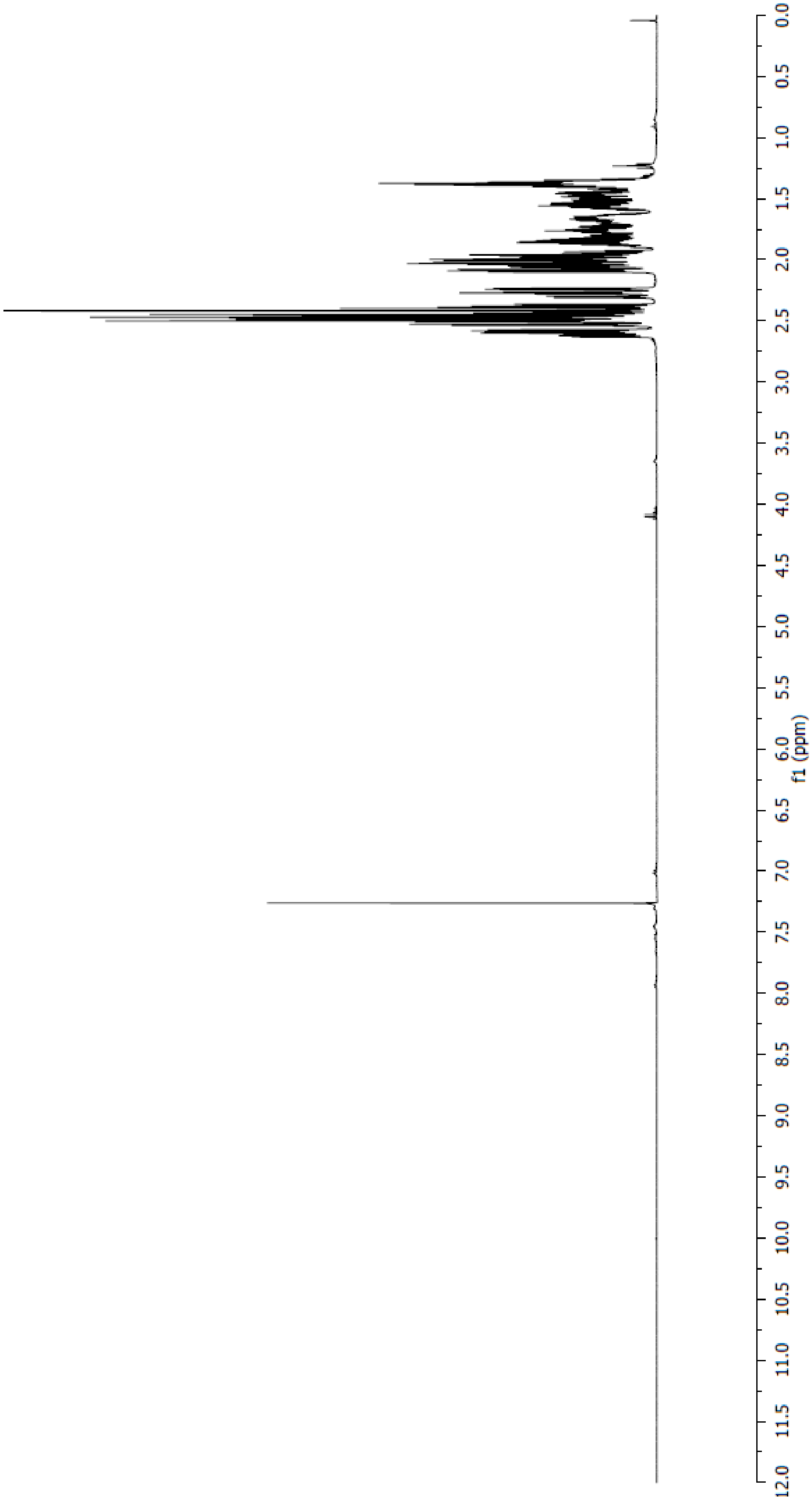
^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.60 (ddd, *J* = 12.2, 7.1, 4.0 Hz, 1H), 2.54-2.37 (m, 4H), 2.27 (ddd, *J* = 14.9, 11.7, 4.0 Hz, 1H), 2.10-1.92 (m, 3H), 1.90-1.62 (m, 3H), 1.60-1.34 (m, 4H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 212.6, 176.0, 90.3, 38.1, 36.4, 31.0, 28.1, 27.7, 26.3, 24.4, 22.8.

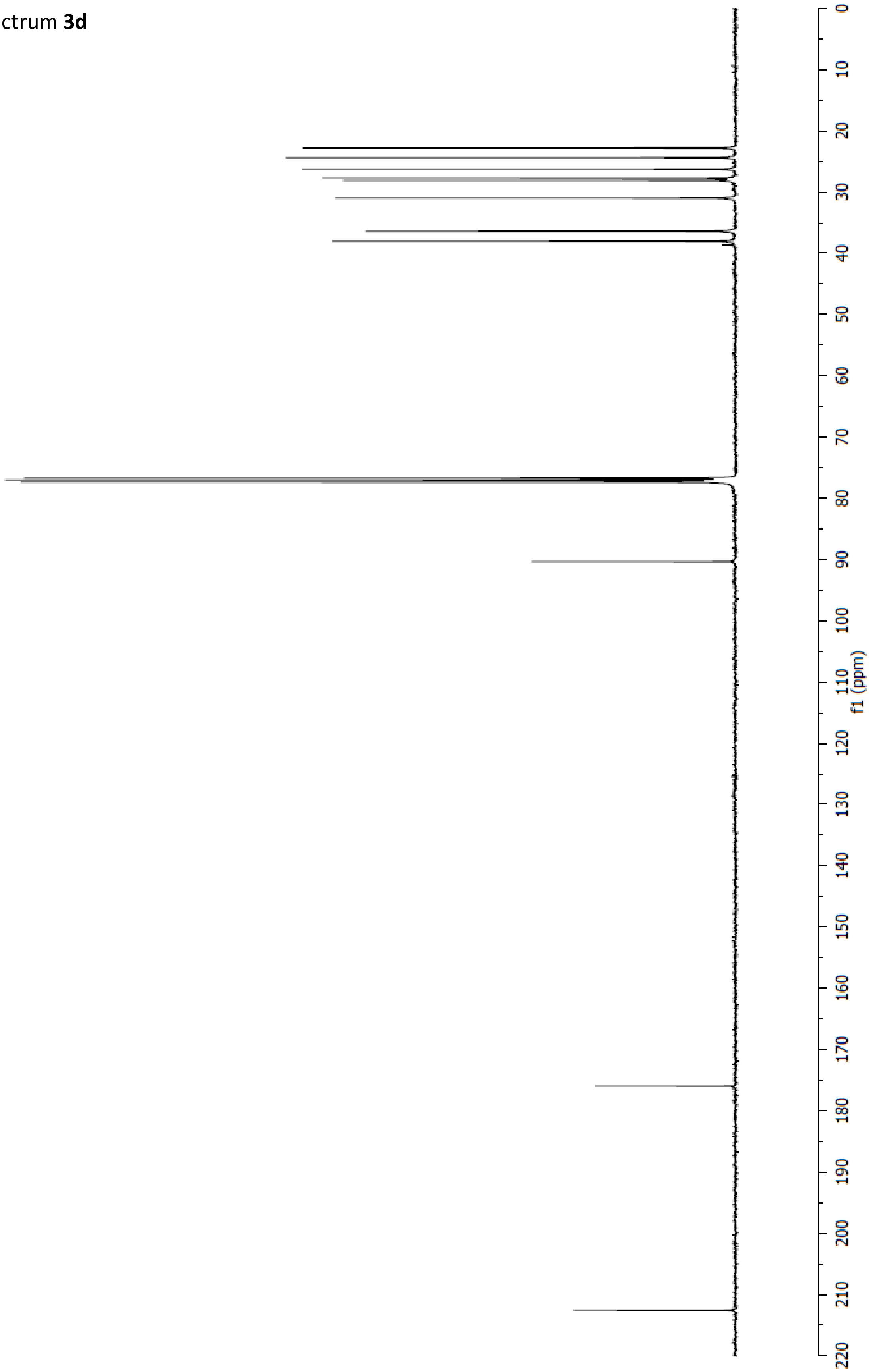
HRMS: (ESI) Calculated for $C_{11}H_{16}O_3$ $[M+Na]^+$ = 219.09920, Found 219.09890.

FTIR: (neat): 2923, 2854, 1708, 1438, 1408, 1205, 1170, 1032 cm^{-1}.

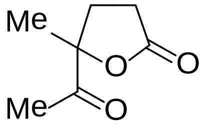
^{1}H NMR Spectrum **3d**



^{13}C NMR Spectrum **3d**



5-acetyl-5-methyldihydrofuran-2(3H)-one (3e)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis/trans*-2,3-butanediol (**1e**) (27 µL, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (108 µL, 0.90 mmol, 400 mol%) and *m*-xylenes (0.19 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:2) to furnish the title compound (39.7 mg, 0.28 mmol, 93%) as a colorless solid. All spectral data was consistent with literature reported values.[12]

TLC (SiO_2): R_f = 0.3 (hexanes:ethyl acetate = 2:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.63-2.46 (m, 3H), 2.27 (s, 3H), 2.08-2.02 (m, 1H), 1.51 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 207.1, 174.6, 88.2, 39.8, 27.3, 24.3, 22.4.

HRMS: (ESI) Calculated for $C_7H_{10}O_3$ $[M+Na]^+$ = 165.05220, Found 165.05200.

FTIR: (neat): 1774, 1718, 1361, 1234, 1209, 1166, 1139, 1092, 10003, 947, 903,
667 cm^{-1}.

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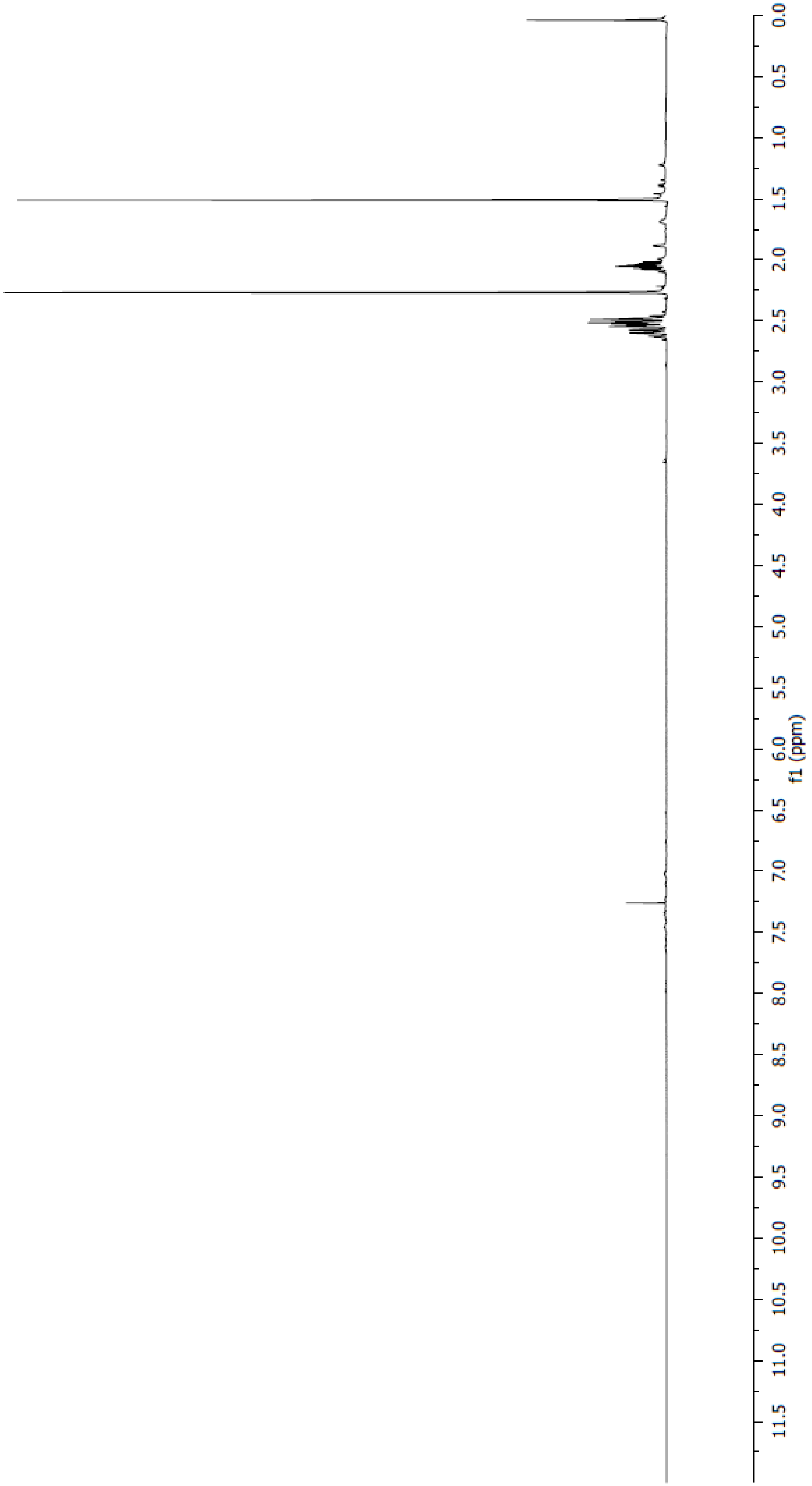
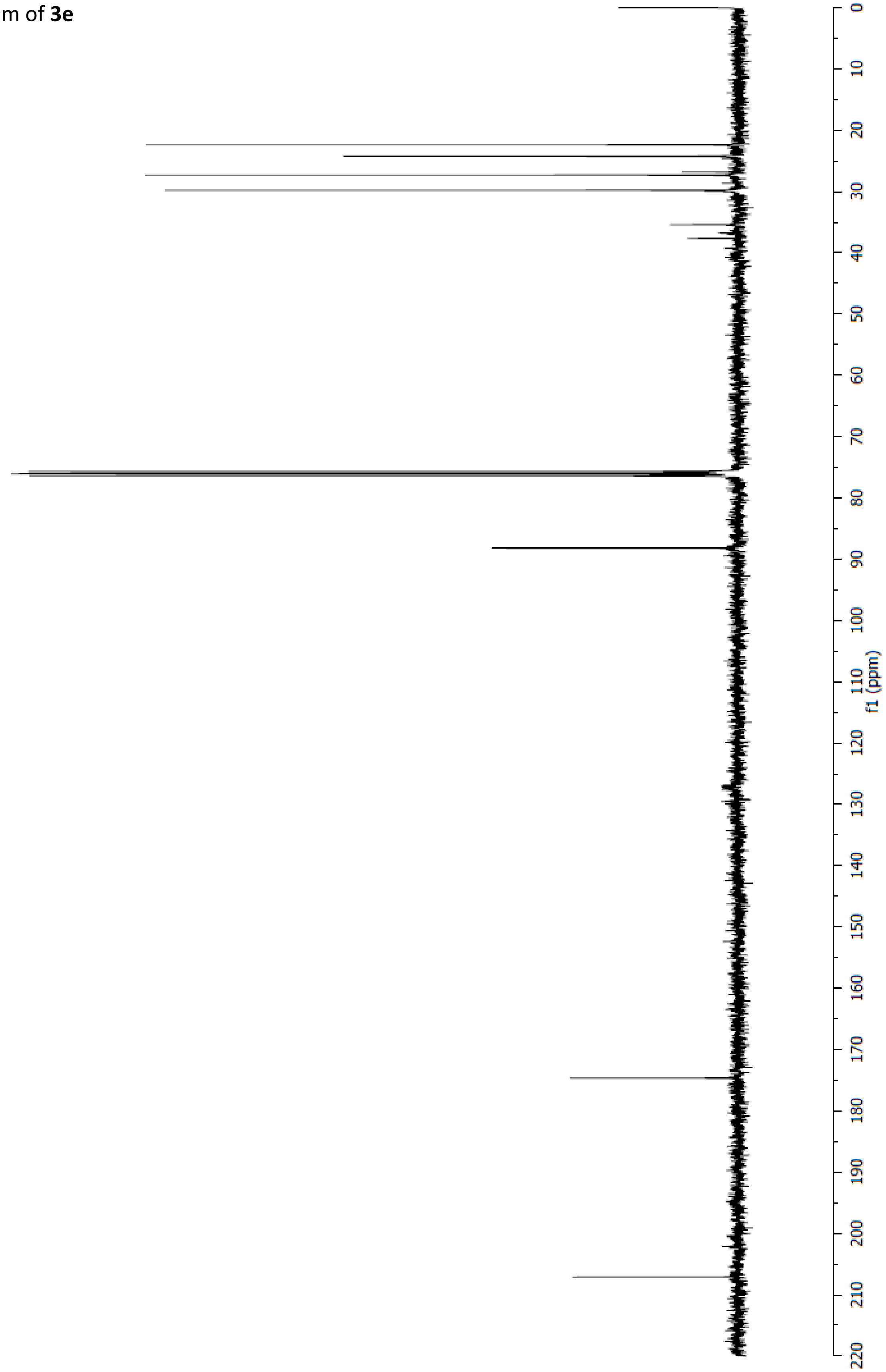
[12] Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12663.

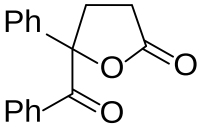
^{1}H NMR Spectrum **3e**



^{13}C Spectrum of **3e**



5-benzoyl-5-phenyldihydrofuran-2(3H)-one (3f)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis/trans*-hydrobenzoin (**1f**) (64 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:2) to furnish the title compound (71.9 mg, 0.27 mmol, 90%) as a colorless oil. All spectral data was consistent with literature reported values.[12]

TLC (SiO_2): R_f = 0.14 (hexanes:ethyl acetate = 9:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.49-7.44 (m, 3H), 7.42-7.37 (m, 2H), 7.36-7.30 (m, 3H), 3.43 (ddd, *J* = 13.0, 8.3, 7.1 Hz, 1H), 2.60-2.55 (m, 2H), 2.34 (dt, *J* = 13.0, 8.3 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 195.2, 175.6, 139.3, 133.5, 133.4, 13.7, 129.3, 128.5, 128.3, 123.7, 92.1, 34.3, 28.0.

HRMS: (ESI) Calculated for $C_{17}H_{14}O_3$ $[M+Na]^+$ = 289.08350, Found 289.08430.

FTIR: (neat): 3062, 1784, 1580, 1597, 1448, 1268, 1159, 1086, 1056, 899, 758, 701, 687 cm^{-1}.

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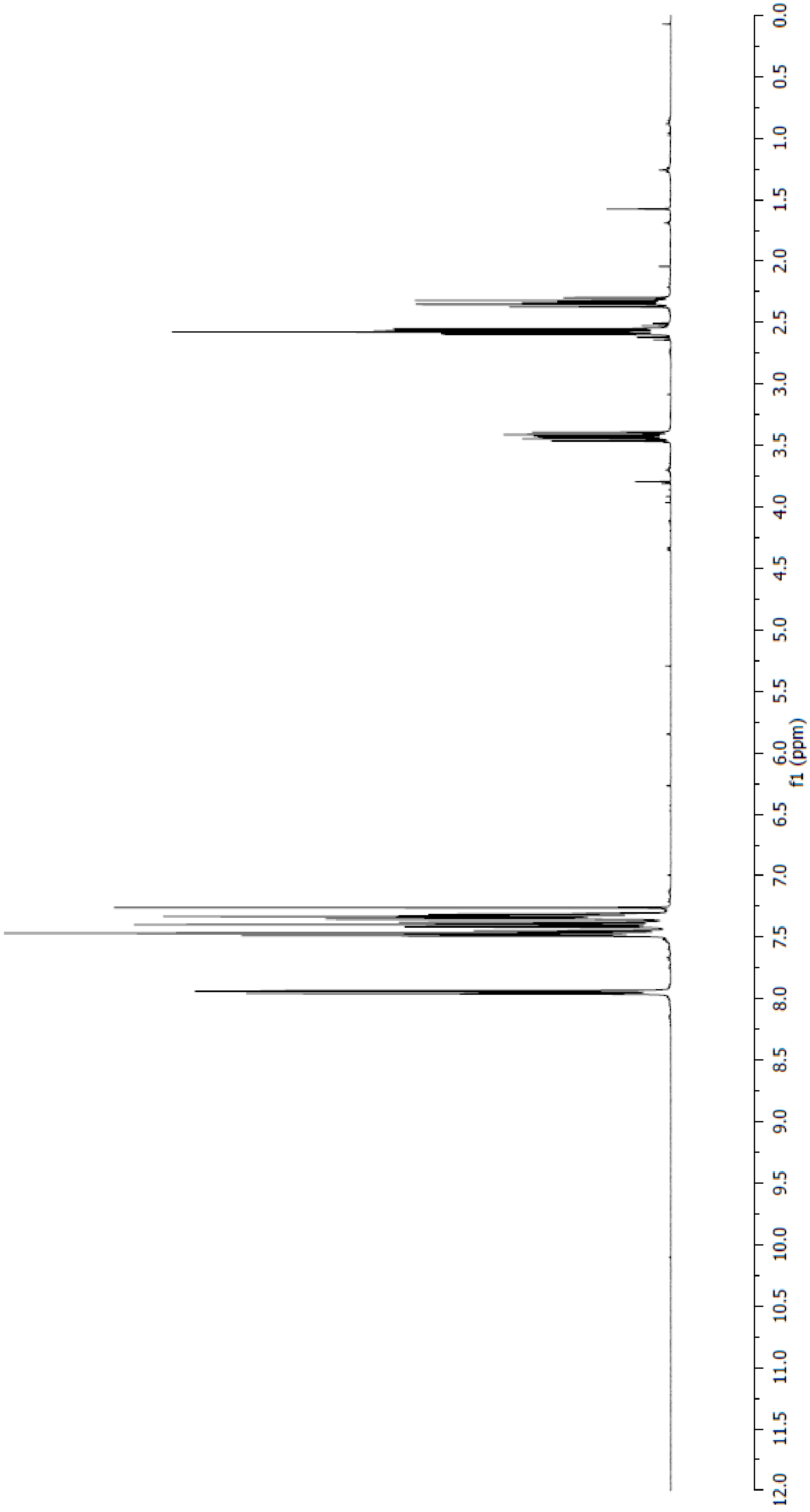
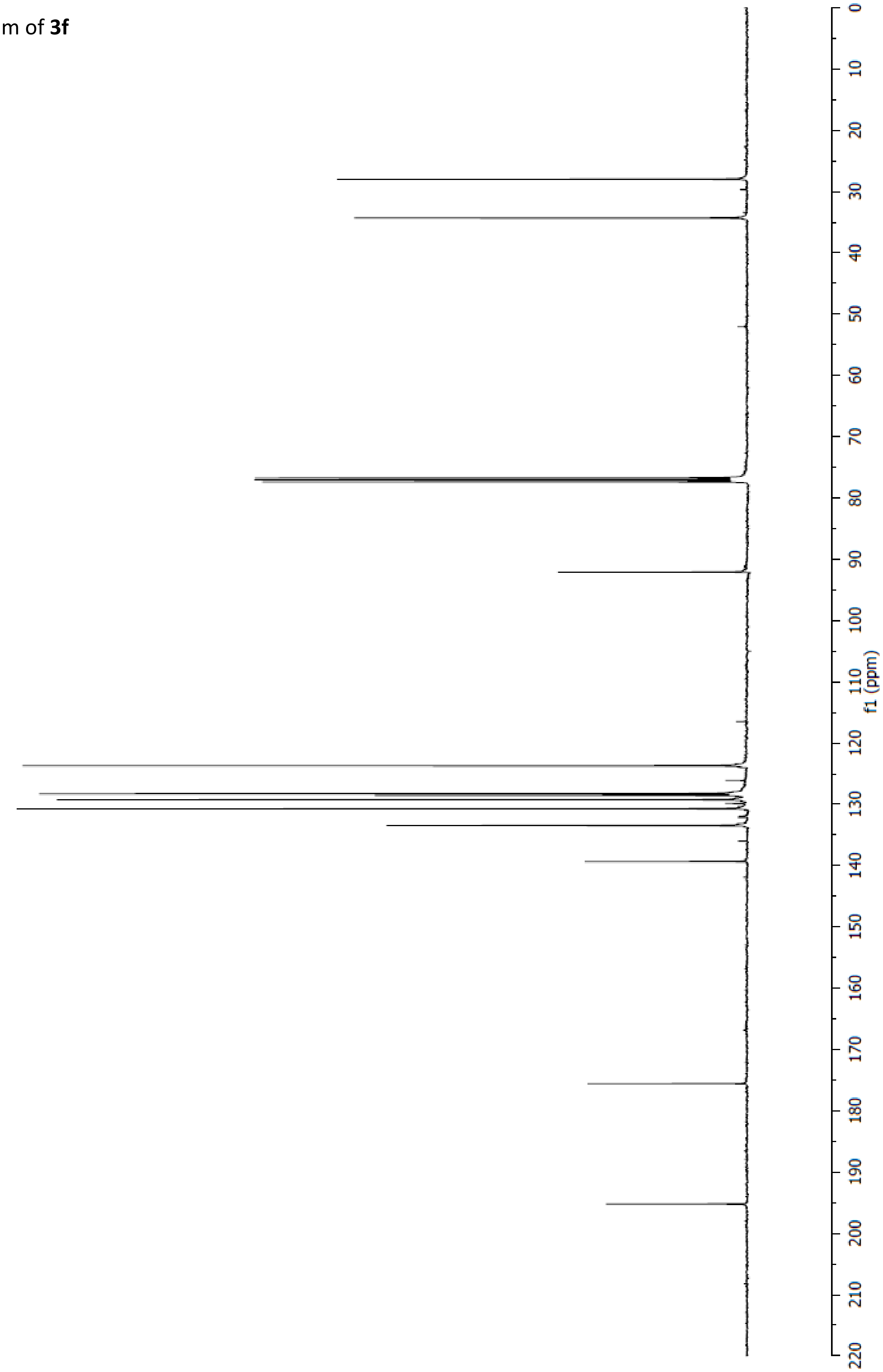
[12] Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12663.

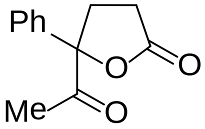
^{1}H NMR Spectrum **3f**



^{13}C Spectrum of **3f**



5-acetyl-5-phenyldihydrofuran-2(3H)-one (3g)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-1-phenyl-propan-1,2-diol (**1g**) (46 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactones (r.r = 4:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) afforded the title compound **3g** (36 mg, 0.18 mmol, 59%) and the regioisomer 5-benzoyl-5-methyloxolan-2-one (9 mg, 0.044 mmol, 15%) as colorless oils in 74% overall yield. All spectral data was consistent with literature reported values.[12]

TLC (SiO_2): R_f = 0.57 (hexanes:ethyl acetate = 1:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.46 – 7.33 (m, 5H), 3.12 (ddd, *J* = 12.9, 8.7, 7.0 Hz, 1H), 2.64 – 2.45 (m, 2H), 2.35 (m, 1H), 2.19 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 204.7, 175.2, 137.7, 129.0, 128.8, 124.4, 92.1, 31.6, 28.2, 25.1.

HRMS: (ESI) Calculated for $C_{12}H_{12}O_3$ $[M+Na]^+$ = 227.06790, Found 227.06790.

FTIR: (neat): 3062, 2922, 2852, 1783, 1719, 1682, 1449, 1235, 1153, 1091, 700 cm^{-1}.

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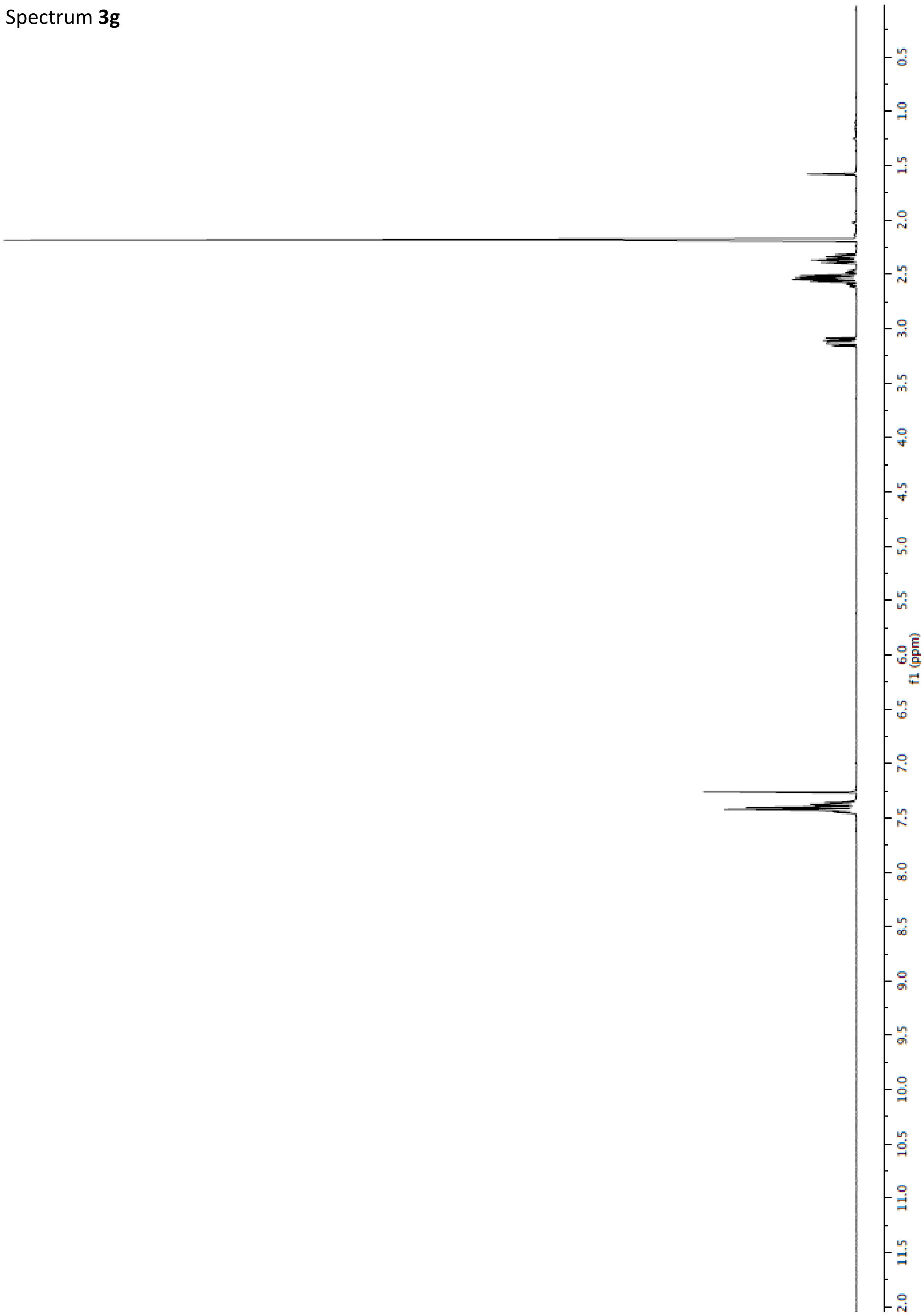
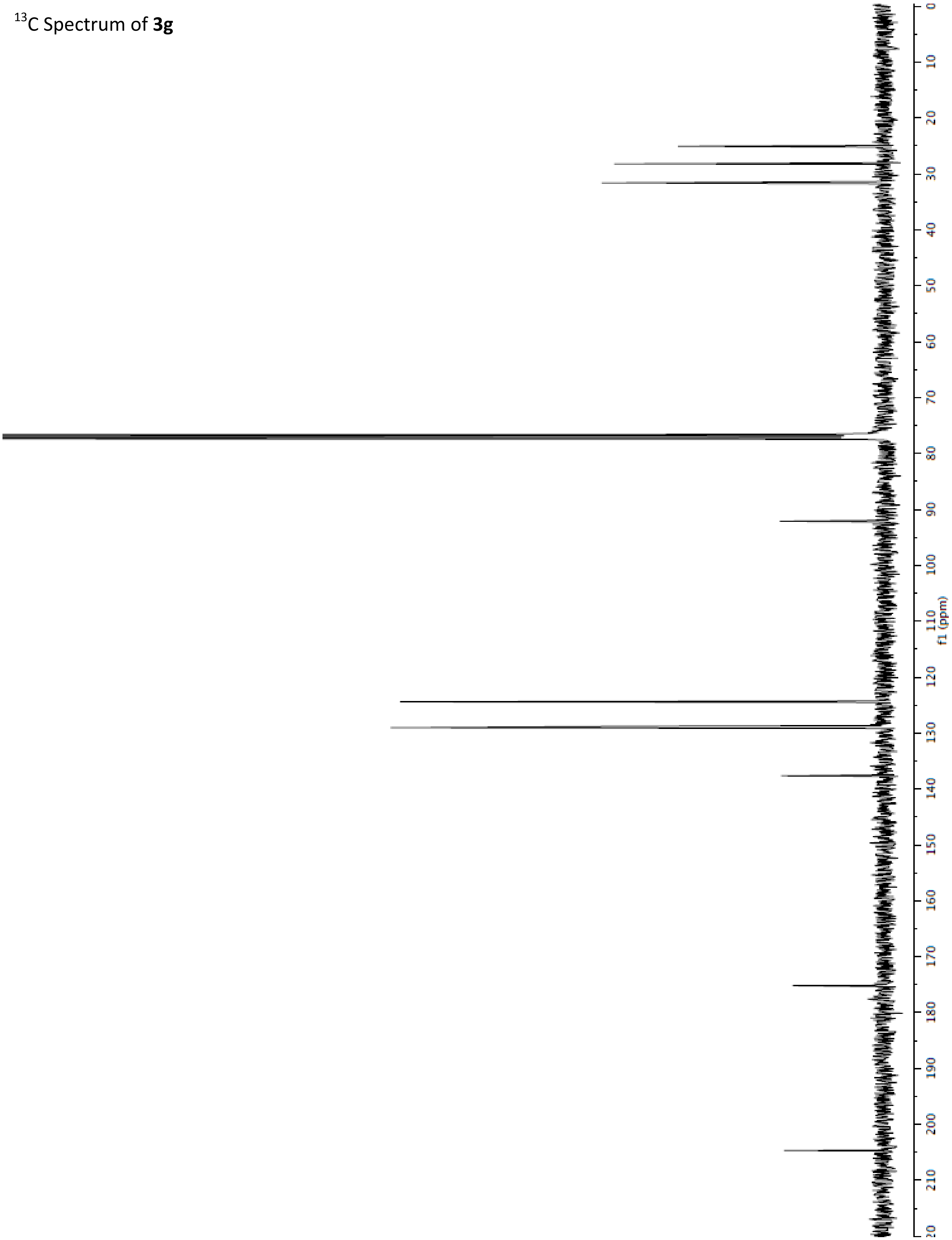
[12] Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12663.

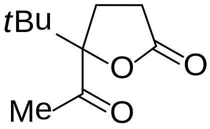
^{1}H NMR Spectrum **3g**



^{13}C Spectrum of **3g**



5-acetyl-5-(tert-butyl)dihydrofuran-2(3H)-one (3h)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-diol **1h** (40 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (108 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.19 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactones (r.r = 1.3:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 4:1) furnished the title compound as an inseparable mixture of regioisomer (41.6 mg, 0.25 mmol, 75%) as a colorless oil.

TLC (SiO_2): R_f = 0.50 (hexanes:ethyl acetate = 2:1).

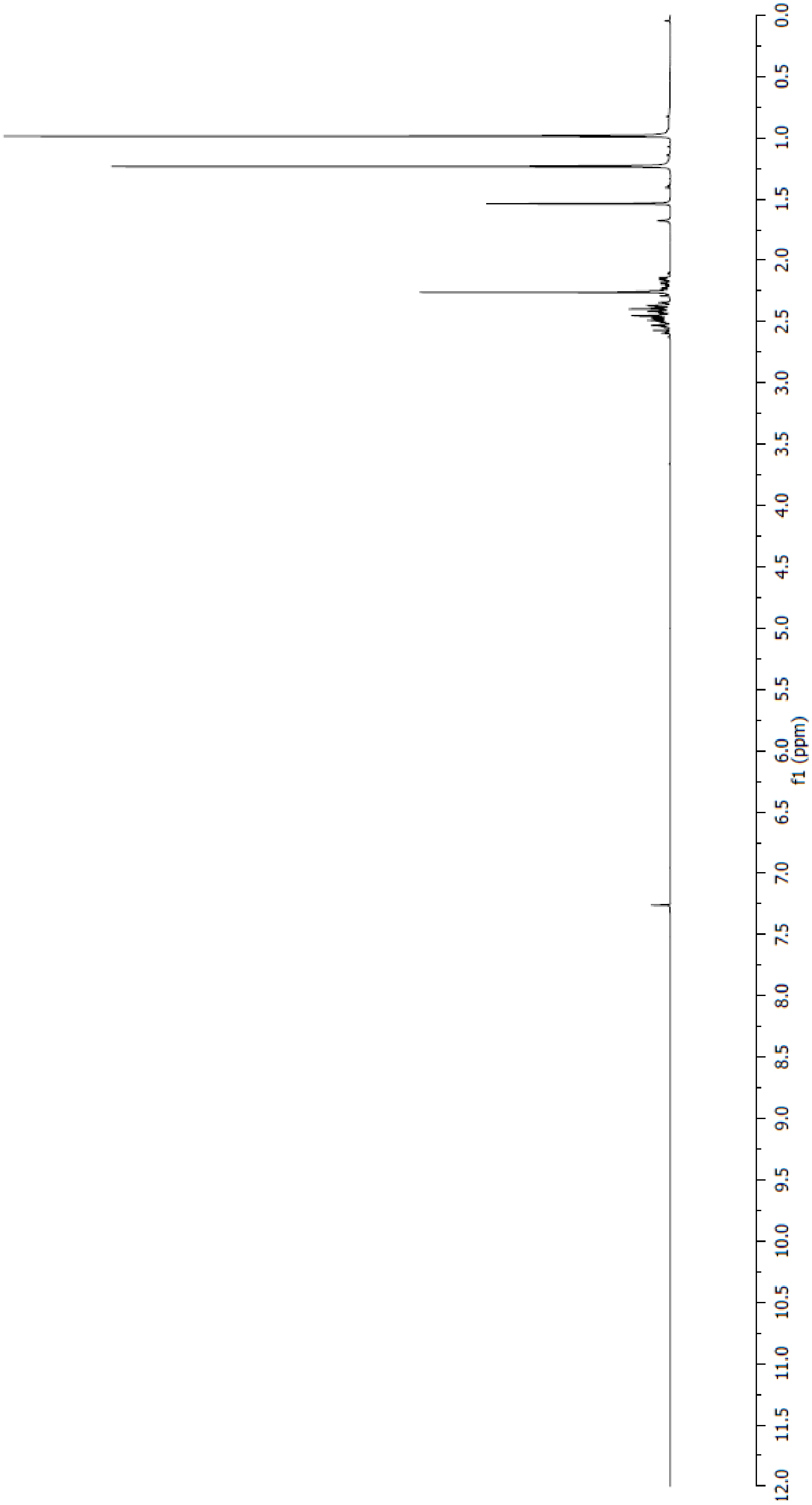
^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.59-2.10 (m, 7.4H), 2.26 (s, 3H, *major*), 1.54 (s, 2.3H, *minor*), 1.24 (s, 7.4H, *minor*), 0.99 (s, 9H, *major*).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 214.9, 211.1, 175.9, 175.9, 96.8, 90.8, 44.9, 37.1, 33.4, 29.6, 28.8, 27.8, 26.9, 26.3, 26.3, 24.8.

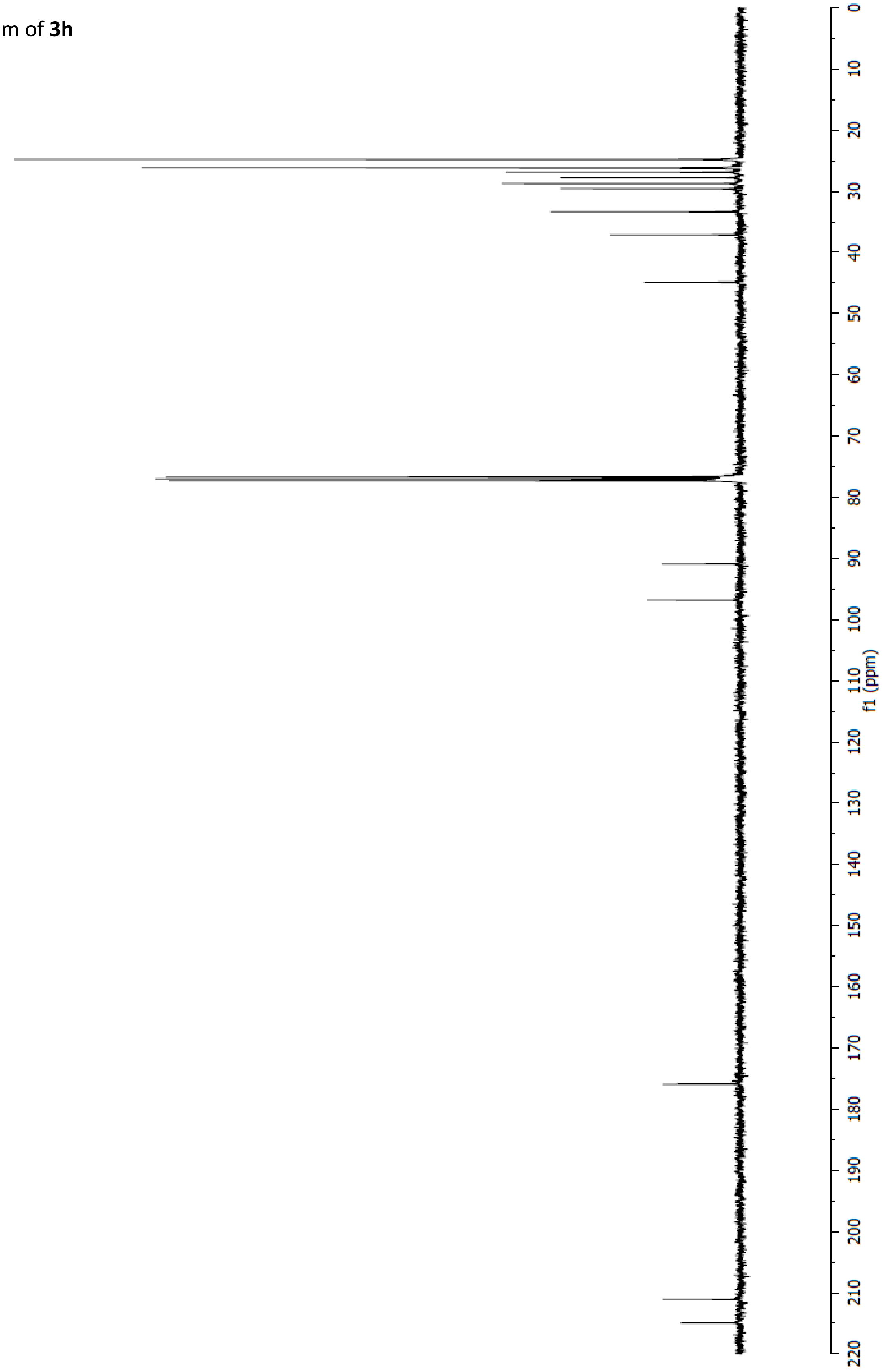
HRMS: (ESI) Calculated for $C_{10}H_{16}O_3$ $[M+Na]^+$ = 207.09920, Found 207.09910.

FTIR: (neat): 2971, 1778, 1714, 1699, 1370, 1251, 1153, 1128, 1053, 1008, 904, 675 cm^{-1}.

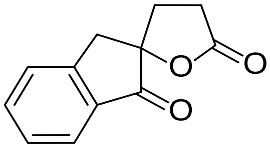
^{1}H NMR Spectrum **3h**



^{13}C Spectrum of **3h**



1,3-dihydrospiro[indene-2,2'-oxolane]-1,5'-dione (3i)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-2,3-dihydro-1*H*-indene-1,2-diol (**1i**) (45 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactone (r.r = >20:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 1:1) furnished the title compound (54 mg, 0.27 mmol, 89%) as a colorless solid.

TLC (SiO_2): R_f = 0.35 (hexanes:ethyl acetate = 1:1).

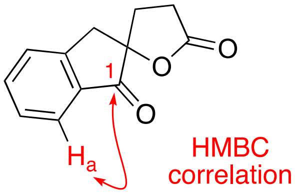
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.46 (m, 2H), 3.61 (d, *J* = 17.4 Hz, 1H), 3.33 (d, *J* = 17.4 Hz, 1H), 3.02 (dt, *J* = 17.7, 9.6 Hz, 1H), 2.67 (ddd, *J* = 17.7, 9.5, 4.0 Hz, 1H), 2.51 (ddd, *J* = 13.6, 9.7, 4.0 Hz, 1H), 2.27 (dt, *J* = 13.1, 9.6 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 201.5, 176.2, 150.1, 136.5, 133.1, 128.5, 126.6, 125.2, 86.4, 39.7, 31.2, 28.6.

MP: 68 - 70 °C

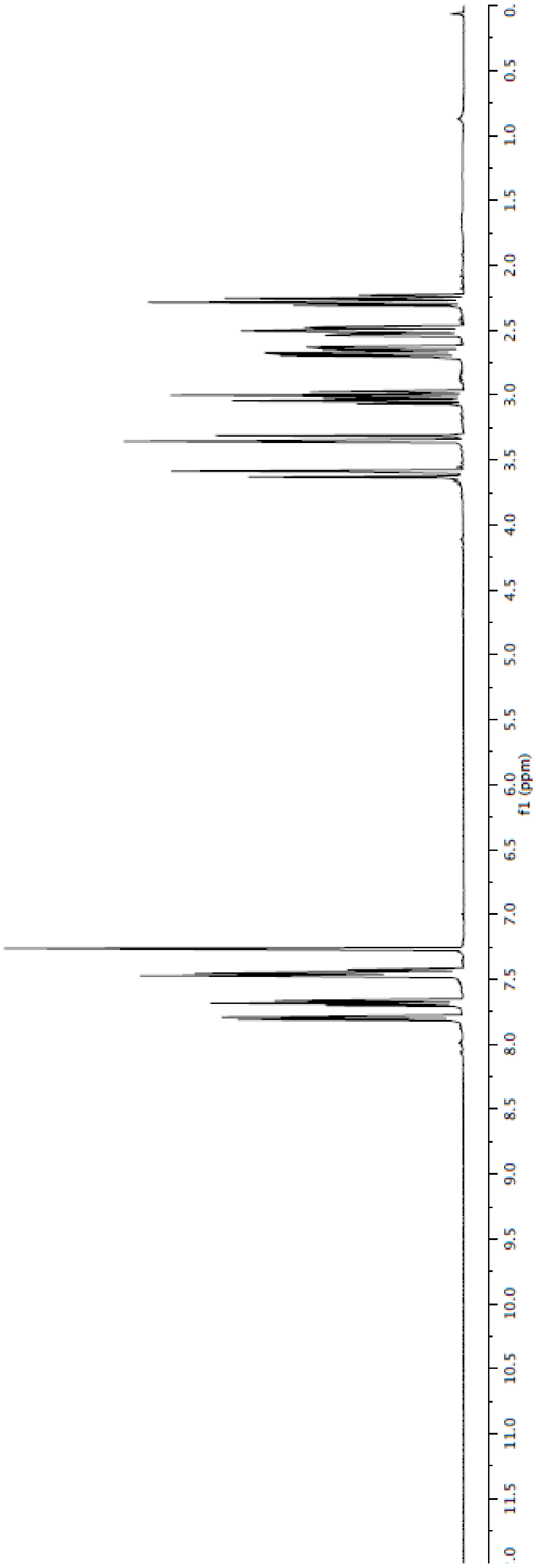
HRMS: (ESI) Calculated for $C_{12}H_{10}O_3$ $[M+Na]^+$ = 225.05220, Found 225.05190.

FTIR: (neat): 2942, 1776, 1713, 1603, 1462, 1227, 1167, 1061, 940, 759 cm^{-1}.

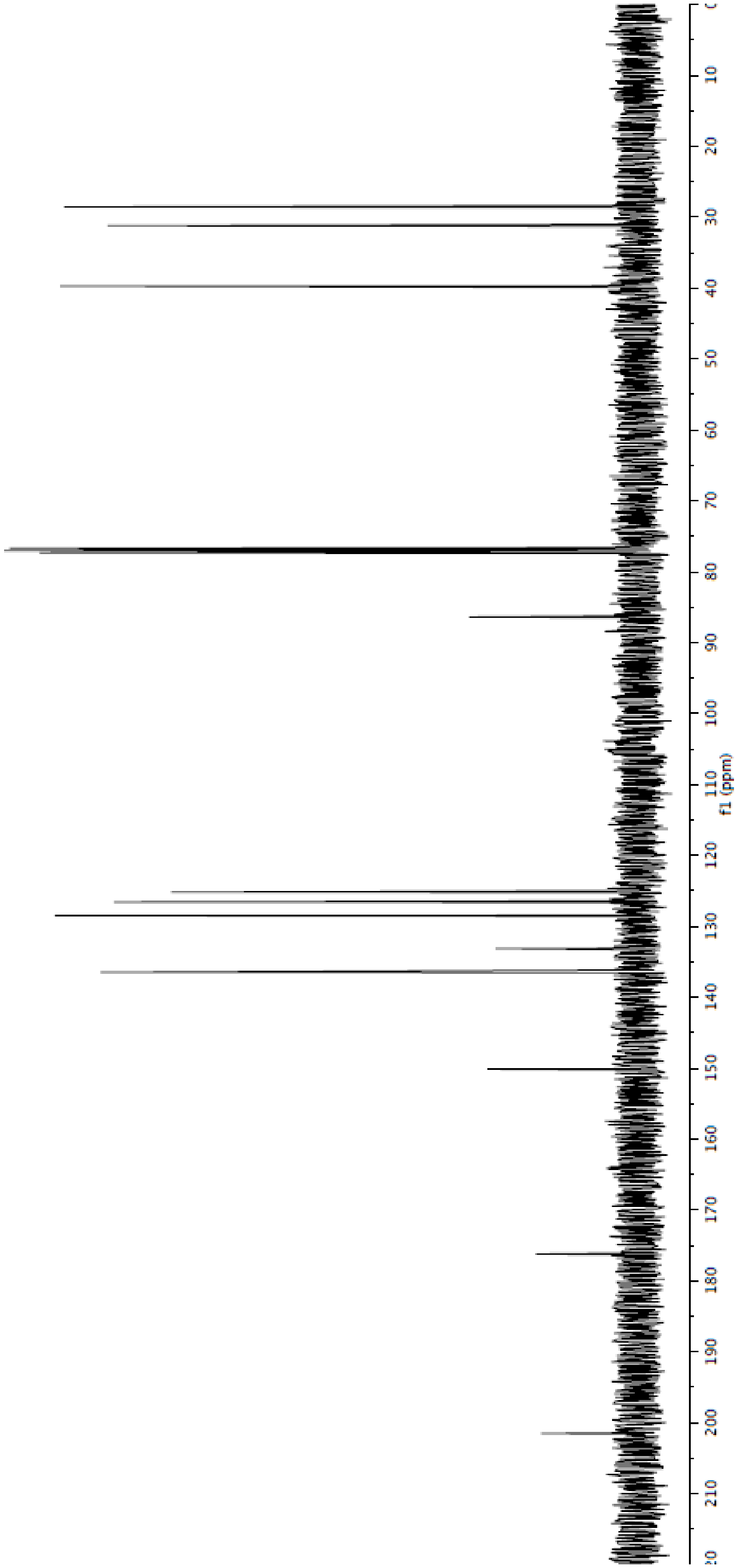


The regioselectivity of the spirolactone formation was determined by HMBC analysis which showed a correlation between the aromatic proton H_a at δ 7.80 ppm and the ketone carbon C1 at δ 201.5 ppm.

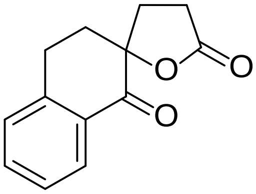
^{1}H NMR Spectrum **3i**



^{13}C Spectrum of **3i**



3,4-dihydro-1H-spiro[naphthalene-2,2'-oxolane]-1,5'-dione (3j)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis/trans*-1,2,3,4-tetrahydronaphthalene-1,2-diol (**1j**) (49 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactone (r.r = >20:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) furnished the title compound (57 mg, 0.26 mmol, 88%) as a colorless solid. All spectral data was consistent with literature reported values.[10]

TLC (SiO_2): R_f = 0.38 (hexanes:ethyl acetate = 1:1).

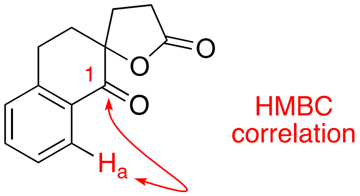
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 3.20 (dt, *J* = 17.2, 5.3 Hz, 1H), 3.09 (ddd, *J* = 17.2, 9.9, 4.7 Hz, 1H), 2.80 (ddd, *J* = 17.9, 10.8, 9.8 Hz, 1H), 2.59 (m, 3H), 2.31 (ddd, *J* = 13.5, 5.5, 5.0 Hz, 1H), 2.15 (ddd, *J* = 13.0, 10.8, 9.7 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ193.5, 176.1, 143.0, 134.4, 130.0, 128.7, 128.5, 127.3, 85.0, 34.5, 29.6, 27.9, 25.7.

MP: 94 - 95 °C

HRMS: (ESI) Calculated for $C_{13}H_{12}O_3$ $[M+Na]^+$ = 239.06790, Found 239.08610.

FTIR: (neat): 2951, 2937, 1772, 1687, 1602, 1454, 1217, 1067, 949, 743 cm^{-1}.



The regioselectivity of the spirolactone formation was determined by HMBC analysis which showed a correlation between the aromatic proton H_a at δ 8.07 ppm and the ketone carbon C1 at δ 193.5 ppm.

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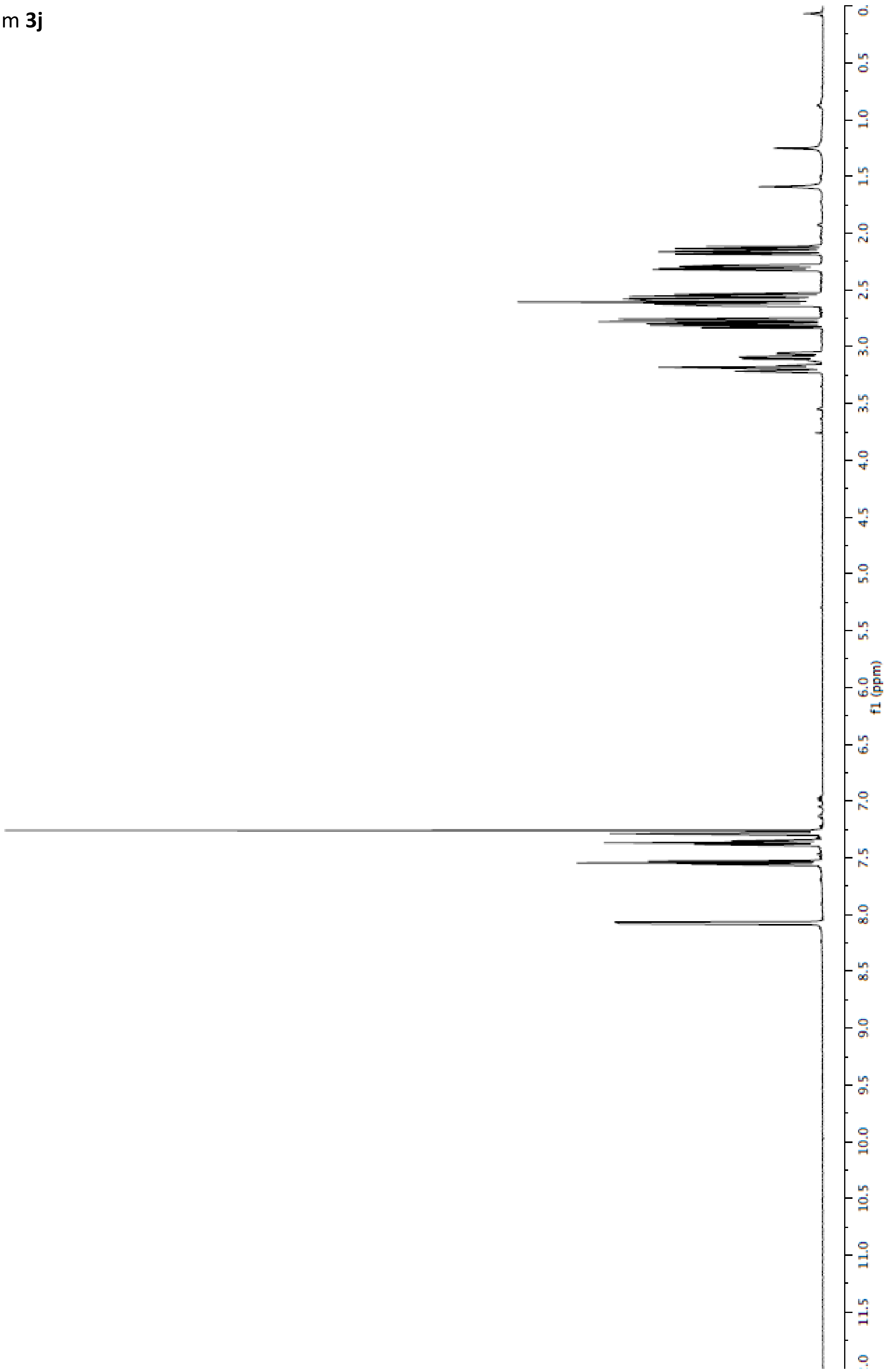
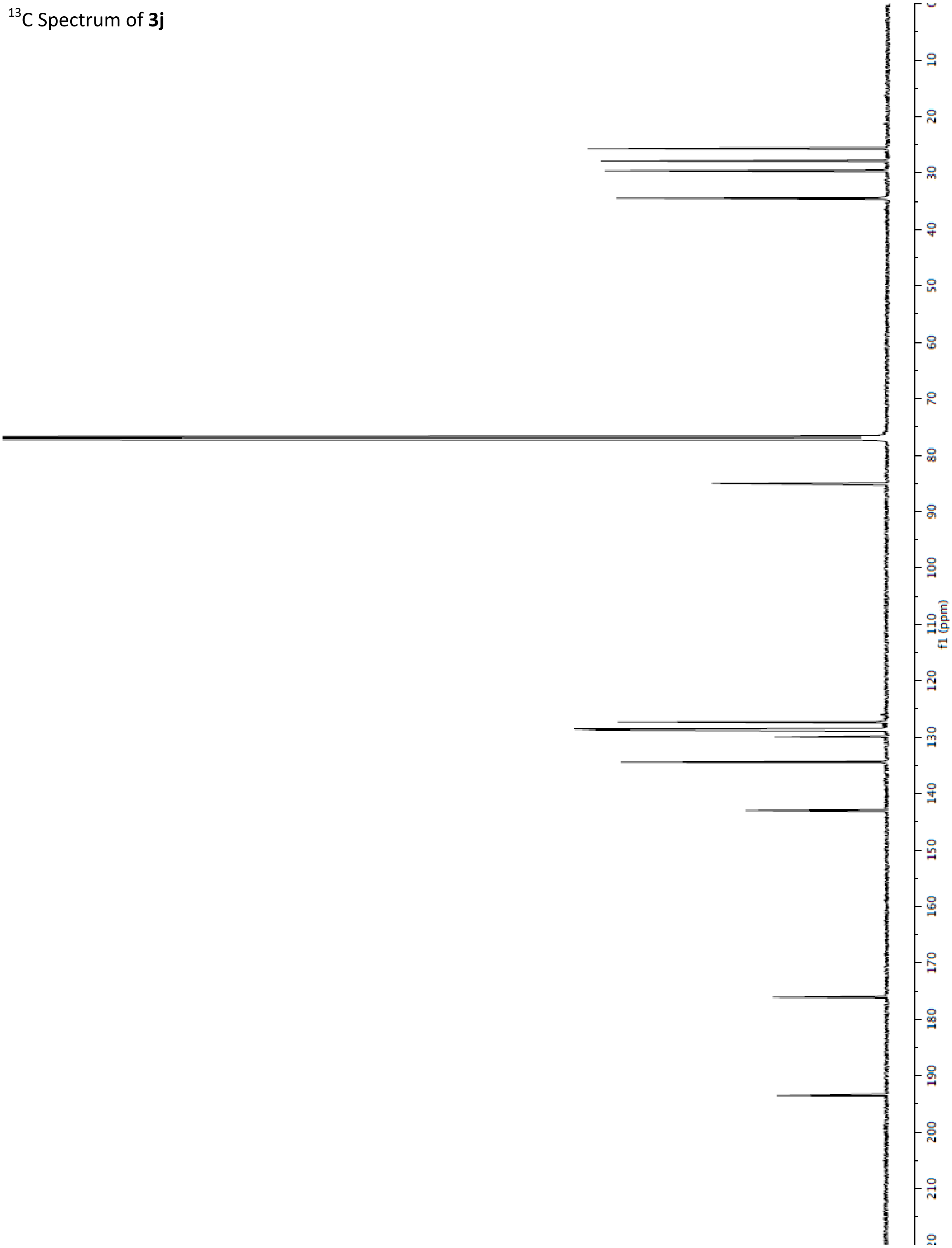
[10] Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331.

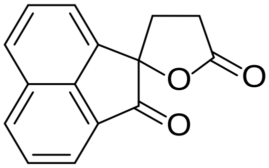
^{1}H NMR Spectrum **3j**



^{13}C Spectrum of **3j**



2H,3'H-spiro[acenaphthylene-1,2'-furan]-2,5'(4'H)-dione (3k)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added cis/*trans*-1,2-dihydroacenapthylene-1,2-diol (**1k**) (56 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 4:1) to furnish the title compound (42.4 mg, 0.18 mmol, 59%) as a tan solid.

TLC (SiO_2): R_f = 0.28 (hexanes:ethyl acetate = 3:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 8.3, 0.6 Hz, 1H), 8.03 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.98 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.80 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.74 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.66 (dd, *J* = 7.1, 0.7 Hz, 1H), 3.25 (ddd, *J* = 17.7, 9.7, 10.4 Hz, 1H), 2.87 (ddd, *J* = 17.7, 9.0, 3.9 Hz, 1H), 2.68-2.55 (m, 2H).

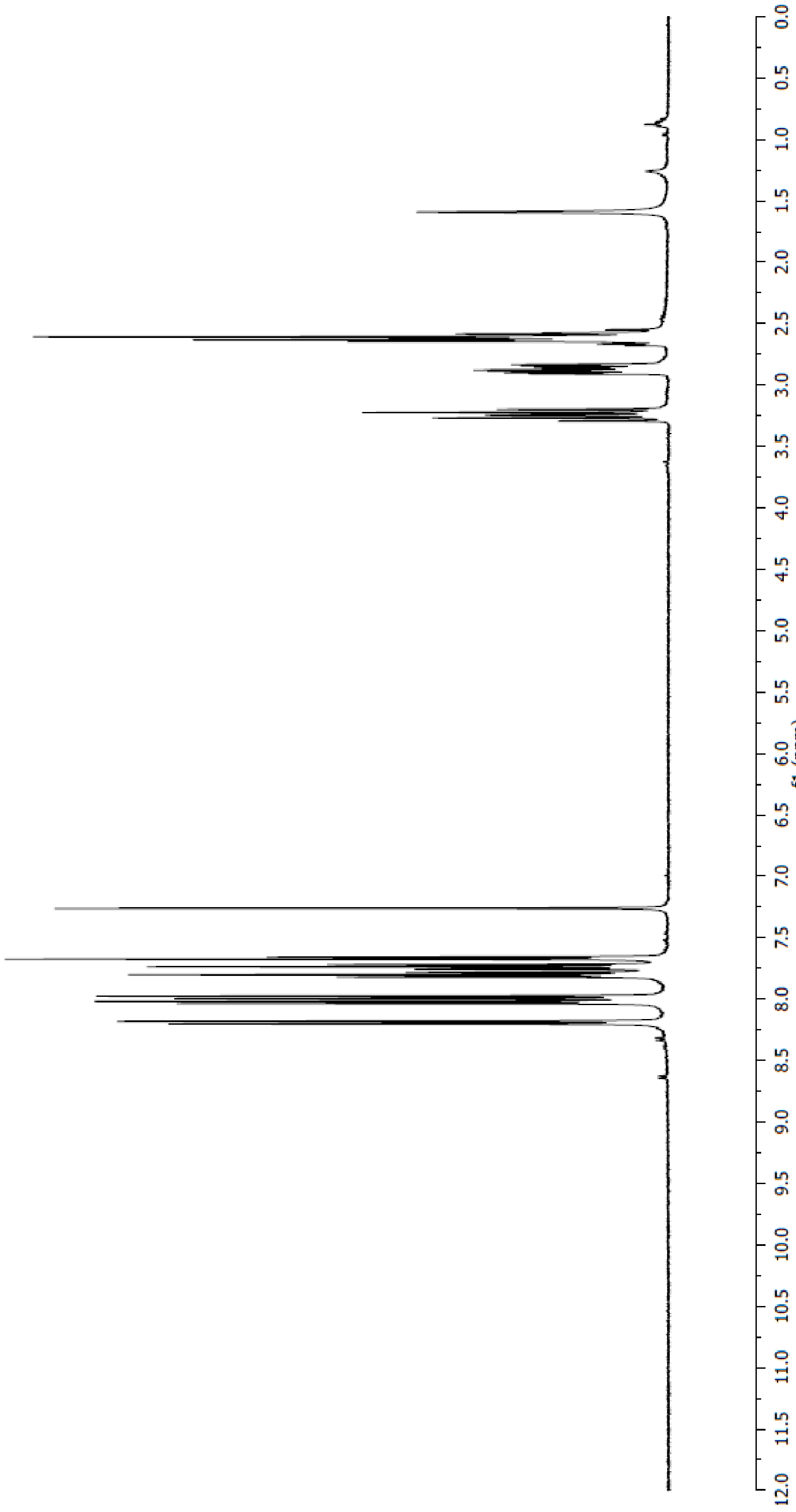
^{13}C NMR: (100 MHz, $CDCl_3$): δ 200.2, 176.3, 142.1, 136.1, 132.4, 130.6, 129.6, 128.9, 128.8, 126.6, 123.0, 120.8, 86.0, 31.3, 28.6.

MP: 131 - 132 °C

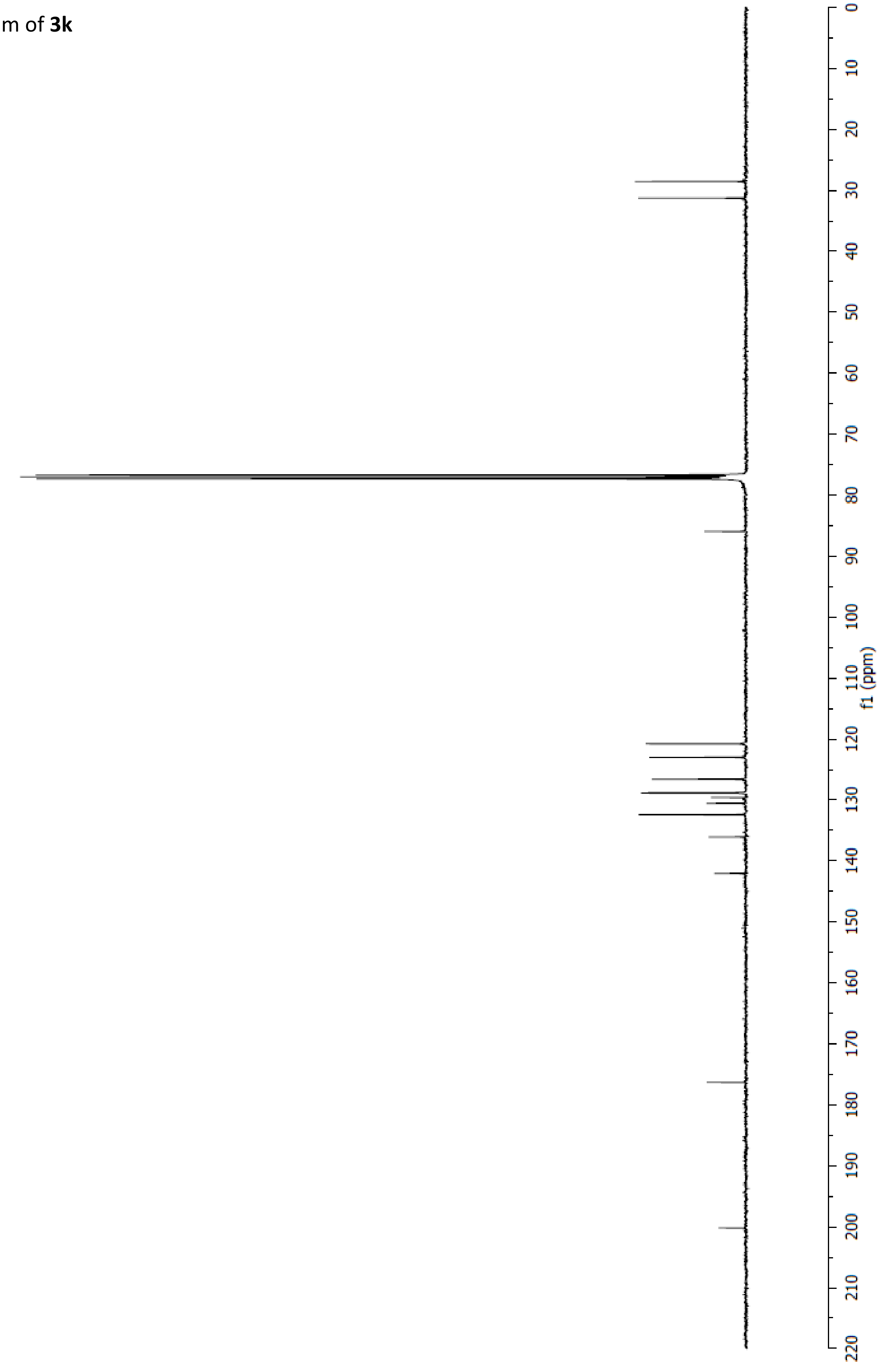
HRMS: (ESI) Calculated for $C_{15}H_{10}O_3$ $[M+Na]^+$ = 261.05220, Found 261.05230.

FTIR: (neat): 1778, 1719, 1493, 1452, 1203, 1179, 1160, 1135, 1029, 919, 876, 782 cm^{-1}.

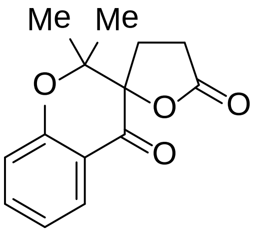
^{1}H NMR Spectrum **3k**



^{13}C Spectrum of **3k**



2,2-dimethyl-2,4-dihydrospiro[1-benzopyran-3,2'-oxolane]-4,5'-dione (3l)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis*-2,2-dimethylchroman-3,4-diol (**1l**) (58 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactone (r.r = >20:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 4:1) furnished the title compound (55 mg, 0.22 mmol, 74%) as a colorless solid.

TLC (SiO_2): $R_f = 0.54$ (hexanes:ethyl acetate = 1:1)

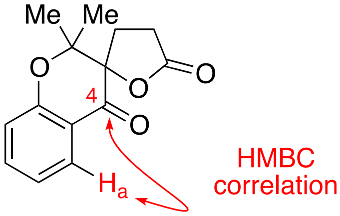
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53 (td, *J* = 8.5, 1.8 Hz, 1H), 7.05 (dt, *J* = 7.9, 0.9 Hz, 1H), 6.94 (dd, *J* = 8.4, 0.5 Hz, 1H), 2.74 (dt, *J* = 18.1, 10.0 Hz, 1H), 2.61 (ddd, *J* = 18.0, 9.4, 4.2 Hz, 1H), 2.36 (m, 2H), 1.49 (s, 3H), 1.46 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 189.6, 175.4, 158.6, 137.0, 127.6, 121.7, 118.4, 118.2, 86.5, 81.8, 28.0, 24.6, 21.3, 21.2.

MP: 145 - 147 °C

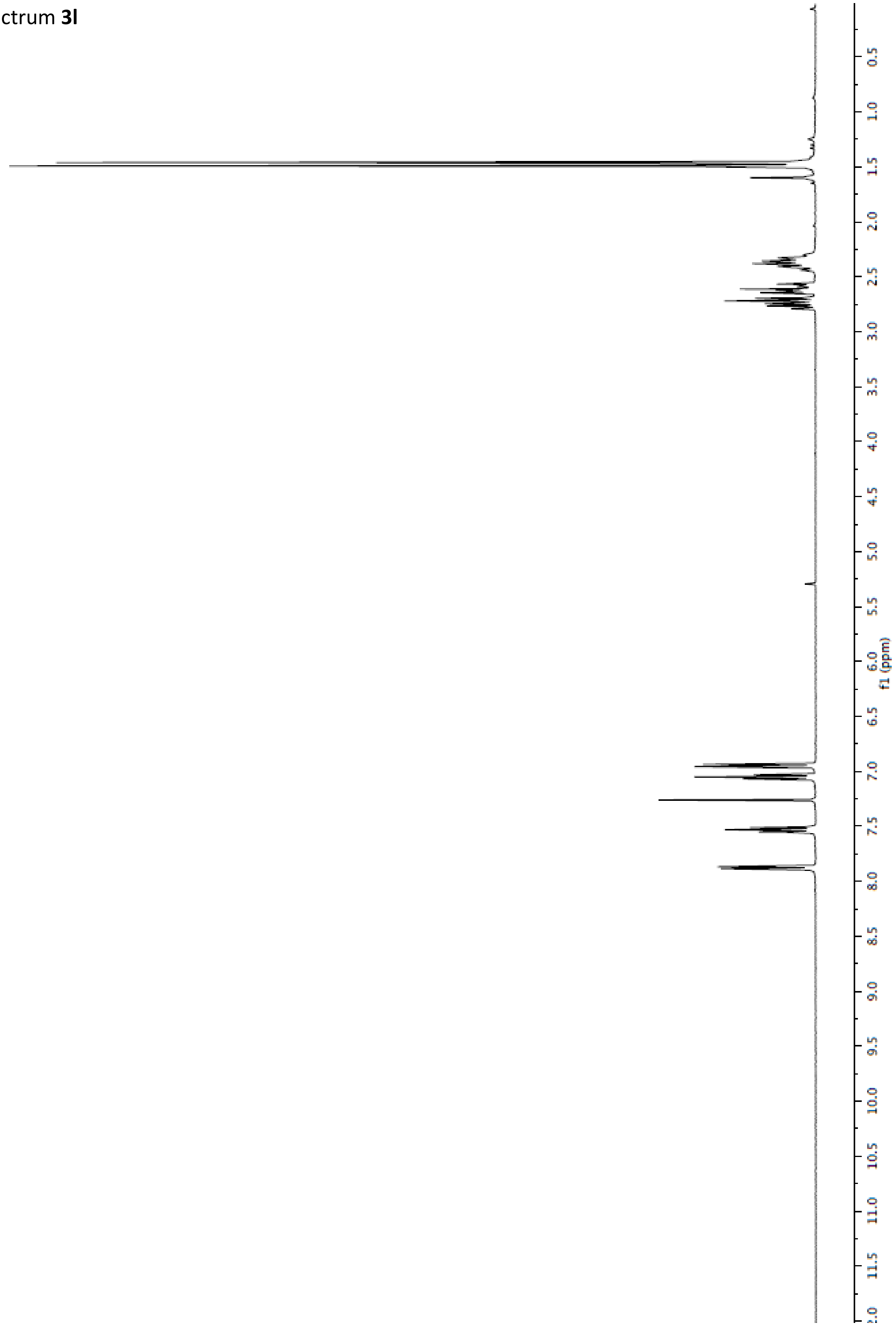
HRMS: (ESI) Calculated for $C_{14}H_{14}O_4$ $[M+Na]^+$ = 269.07840, Found 269.07820.

FTIR: (neat):2982, 2921, 1776, 1703, 1610, 1462, 1424, 1327, 1307, 1165, 1138, 1065, 922, 749. cm^{-1}.

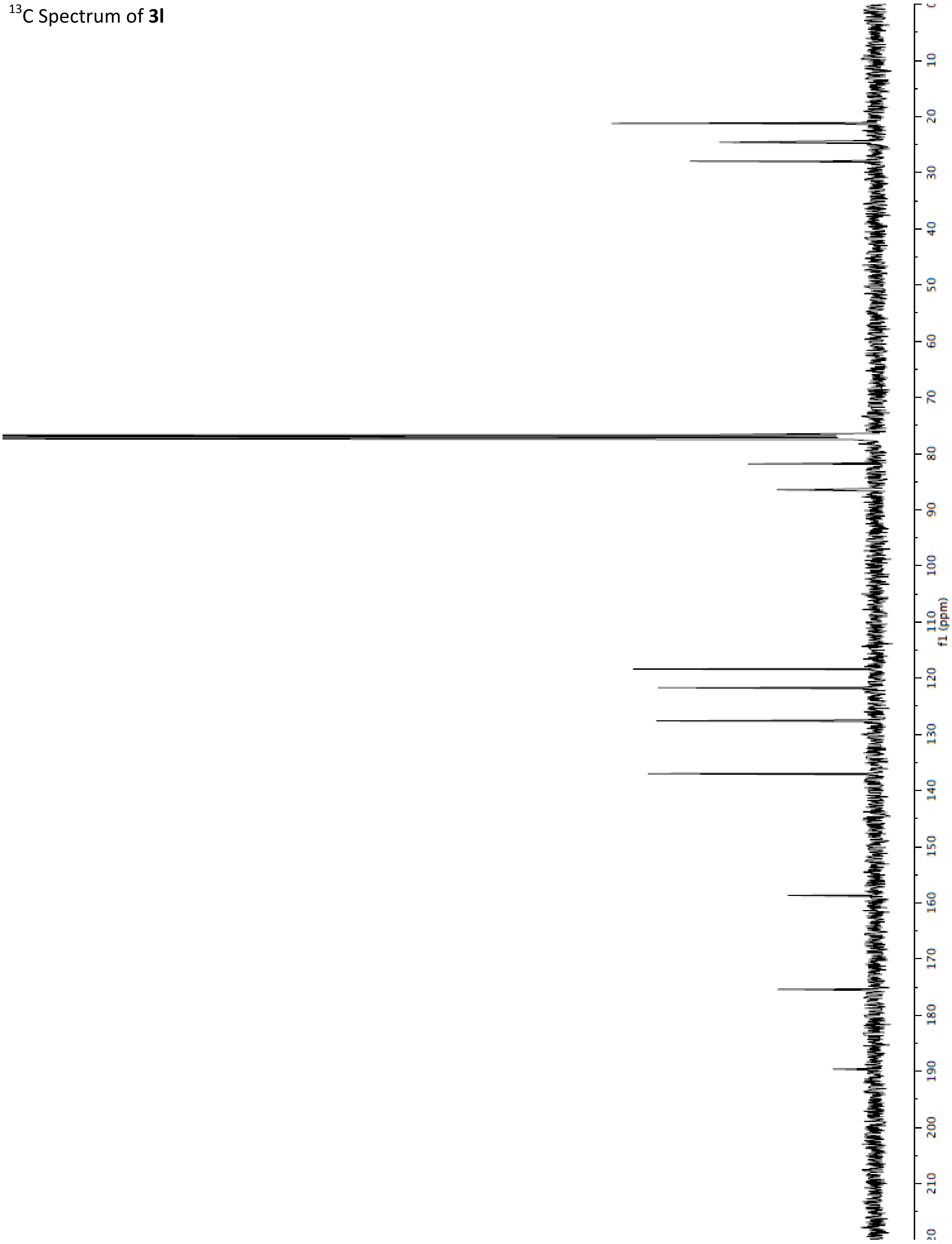


The regioselectivity of the spirolactone formation was determined by HMBC analysis which showed a correlation between the aromatic proton H_a at δ 7.88 ppm and the ketone carbon C4 at δ 189.6 ppm.

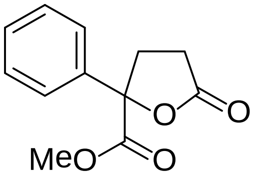
^{1}H NMR Spectrum **3l**



^{13}C Spectrum of **3l**



methyl 5-oxo-2-phenyltetrahydrofuran-2-carboxylate (3m)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added methyl-DL-mandelate (**1m**) (50 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) to furnish the title compound (63.9 mg, 0.29 mmol, 97%) as a colorless solid. All spectral data was consistent with literature reported values.[13]

TLC (SiO_2): R_f = 0.31 (hexanes:ethyl acetate = 3:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.42-7.34 (m, 3H), 3.75 (s, 3H), 3.10 (ddd, *J* = 10.5, 8.6, 3.1 Hz), 2.72-2.51 (m, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 174.9, 170.8, 138.0, 128.8, 128.7, 125.0, 53.4, 33.4, 28.1.

MP: 48 °C

HRMS: (ESI) Calculated for $C_{12}H_{12}O_4$ $[M+Na]^+$ = 243.06280, Found 243.06260.

FTIR: (neat): 2957, 1783, 1737, 1450, 1262, 1228, 1190, 1156, 1091, 1058, 1005, 905, 742, 700 cm^{-1}.

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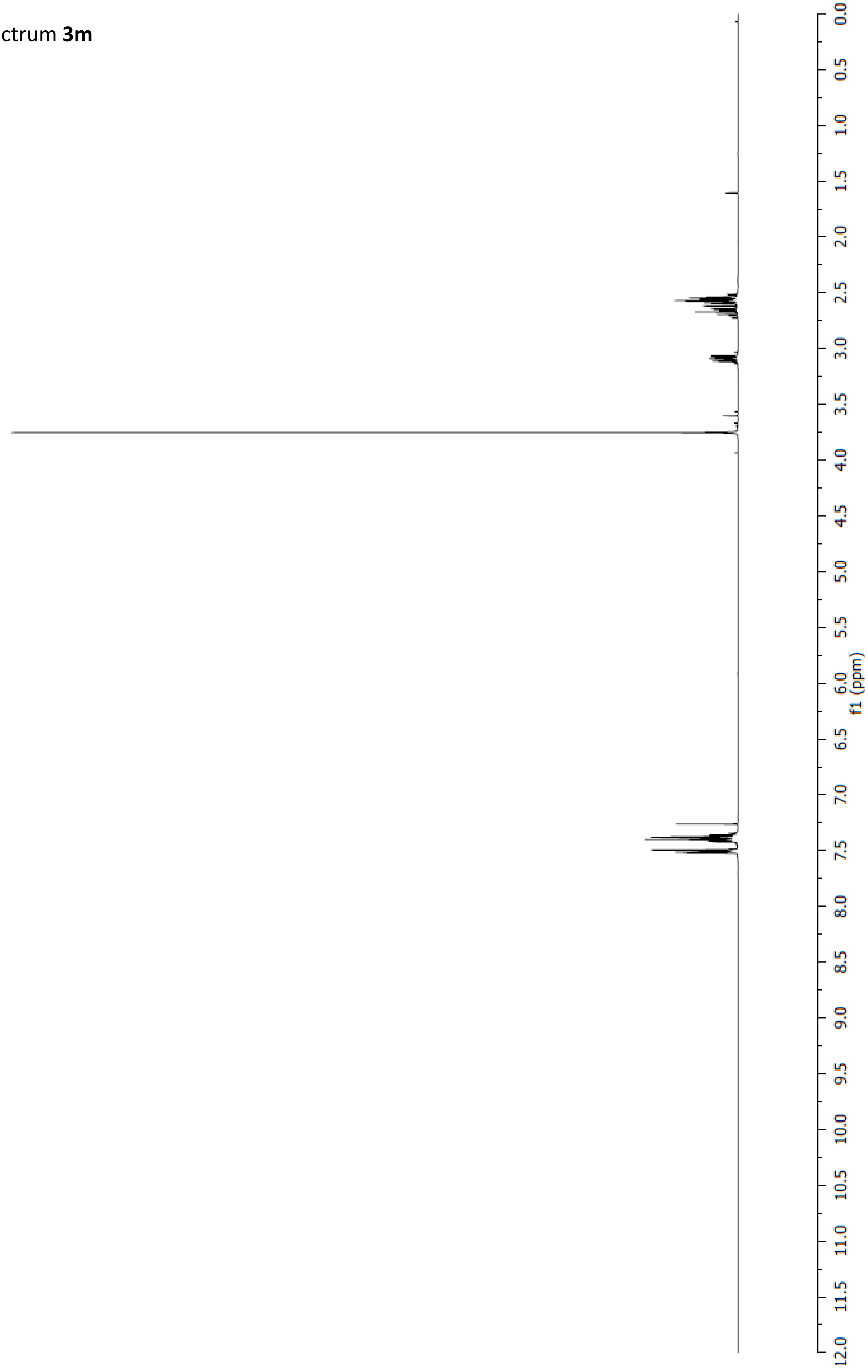
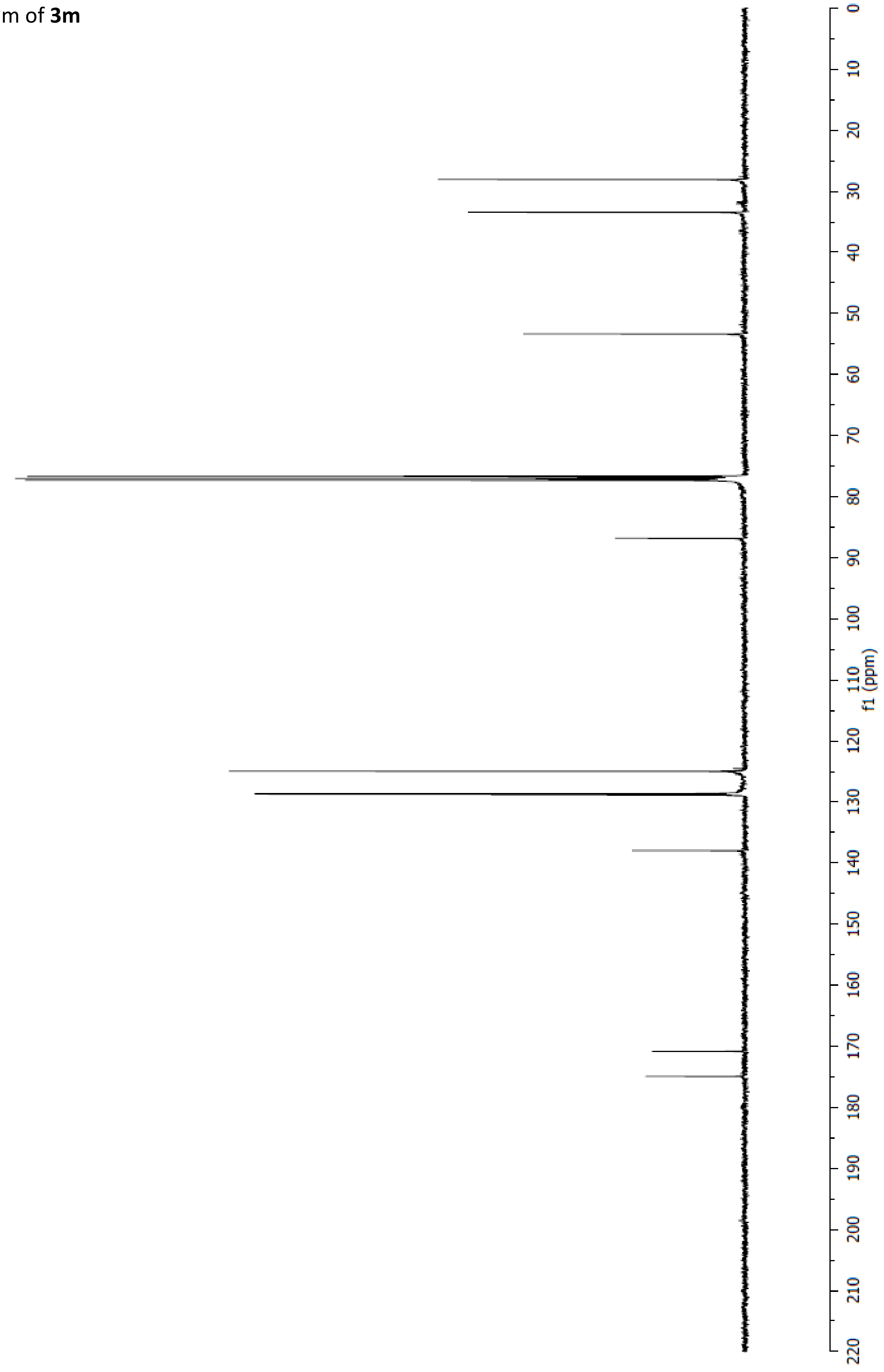
[13] Chatani, N.; Tobisu, M.; Asaumi, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.,* **1999**, *121,* 7160.

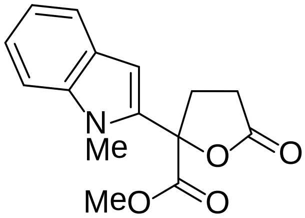
^{1}H NMR Spectrum **3m**



^{13}C Spectrum of **3m**



methyl 2-(1-methyl-1*H*-indol-2-yl)-5-oxotetrahydrofuran-2-carboxylate (3n)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added methyl 2-hydroxy-2-(1-methyl-1*H*-indol-2-yl)acetate (**1n**) (66 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (81 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) to furnish the title compound (48 mg, 0.18 mmol, 58%) as a yellow solid.

TLC (SiO_2): R_f = 0.29 (hexanes:ethyl acetate = 2:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.14 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 6.66 (d, *J* = 0.5 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.06 (ddd, *J* = 12.1, 9.5, 8.2 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.78 – 2.65 (m, 2H).

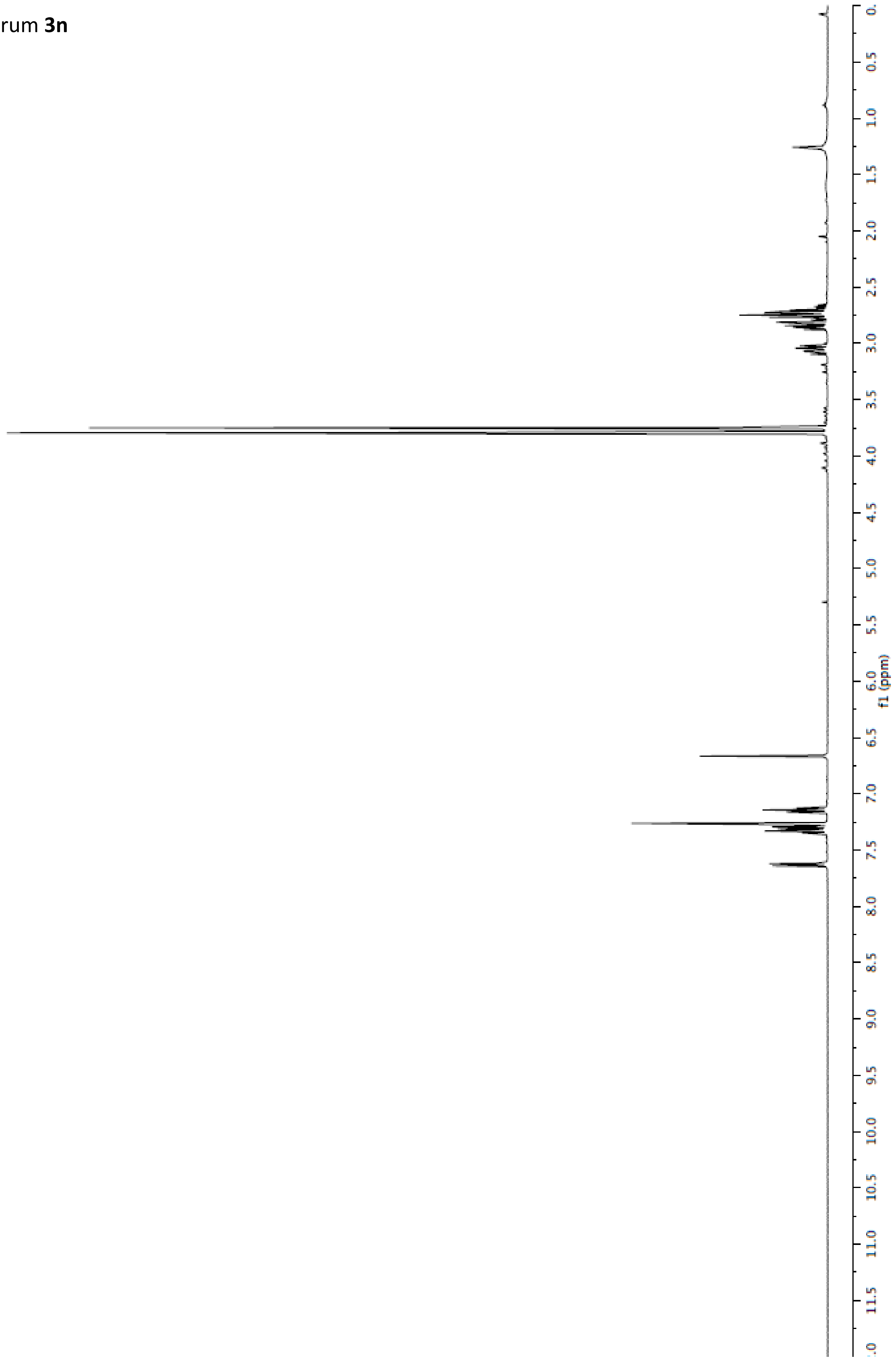
^{13}C NMR: (100 MHz, $CDCl_3$): δ 174.9, 170.6, 138.8, 134.4, 126.3, 123.1, 121.2, 120.1, 109.5, 102.2, 82.5, 53.6, 31.5, 31.1, 27.8.

MP: 109 - 110 °C

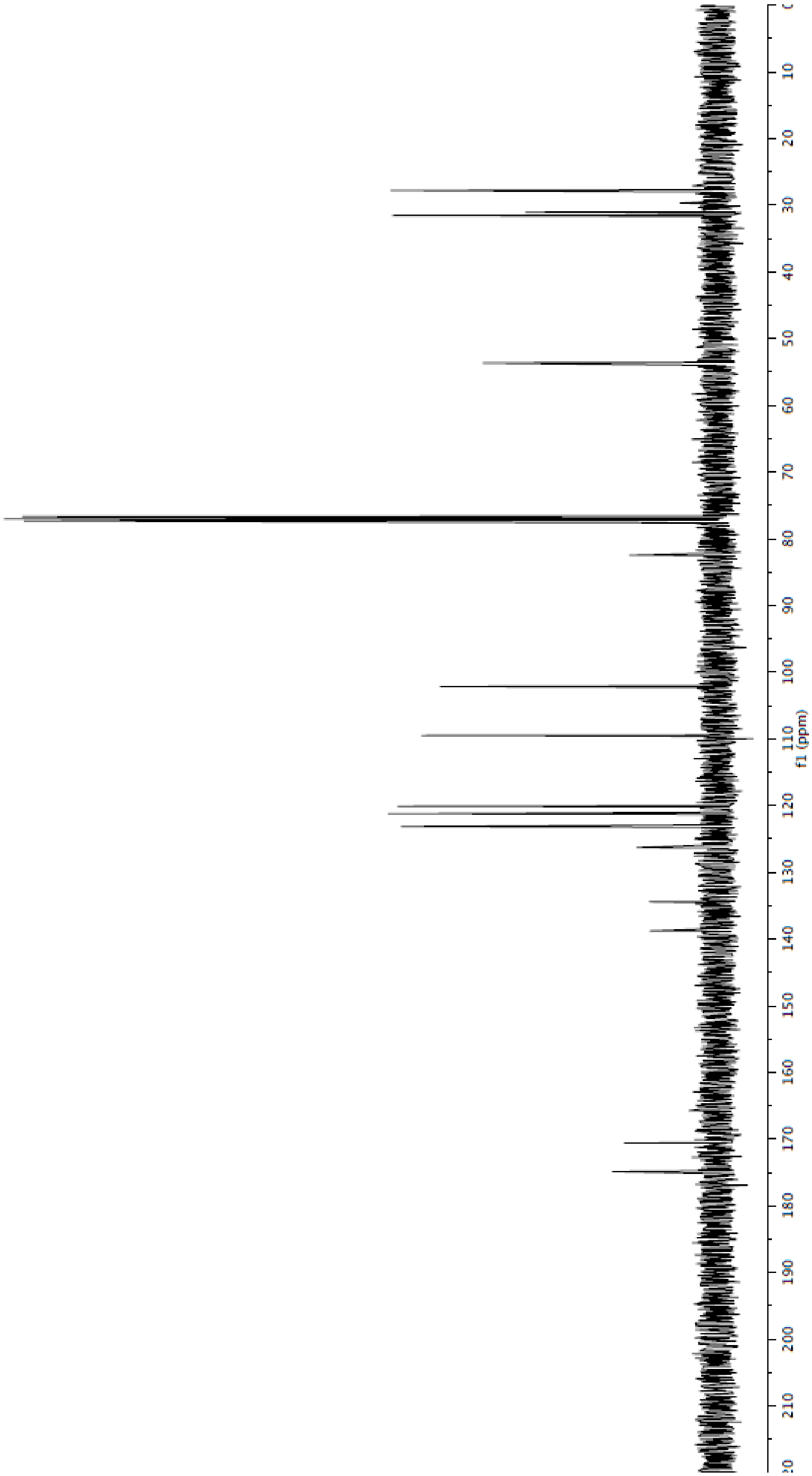
HRMS: (ESI) Calculated for $C_{15}H_{15}NO_4$ $[M+Na]^+$ = 296.08930, Found 296.08980.

FTIR: (neat): 2958, 2920, 1771, 1745, 1614, 1460, 1262, 1199, 1170, 1047, 800 cm^{-1}.

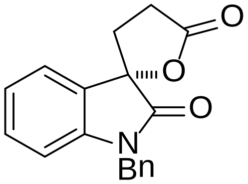
^{1}H NMR Spectrum **3n**



^{13}C Spectrum of **3n**



1'-benzyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4a)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (82 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) furnished the title compound (87.8 mg, 0.30 mmol, 99%) as a colorless solid.

TLC (SiO_2): R_f = 0.44 (hexanes:ethyl acetate = 5:2).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.76-7.37 (m, 7H), 7.10 (td, J = 7.7, 0.9 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.88 (s, 2H), 3.26 (ddd, *J* = 17.6, 10.8, 9.7 Hz, 1H), 2.80 (ddd, *J* = 17.6, 9.6, 3.0 Hz, 1H), 2.64 (ddd, *J* = 13.4, 9.7, 3.0 Hz, 1H), 2.50 (ddd, *J* = 13.4, 10.8, 9.6 Hz, 1H).

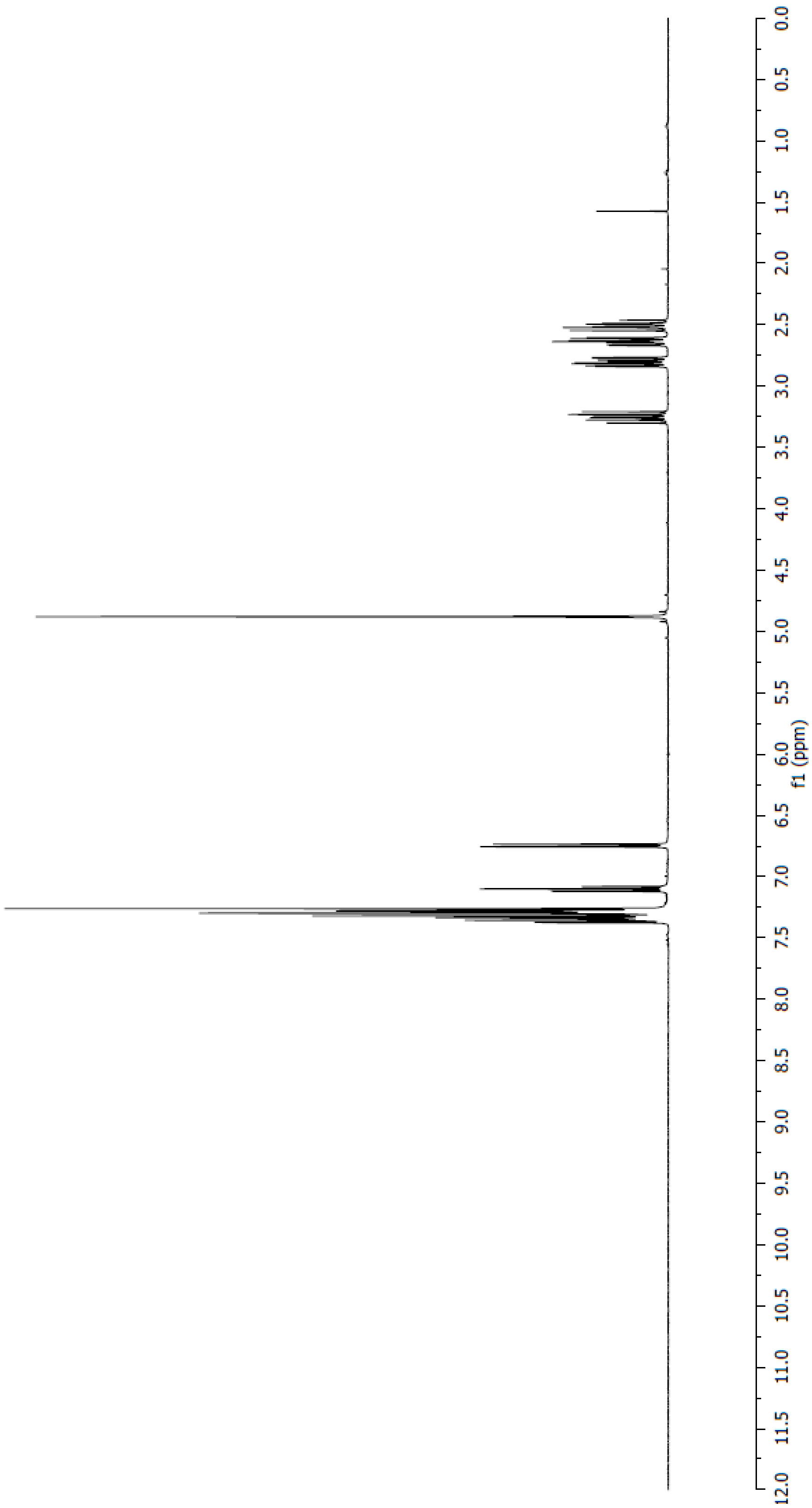
^{13}C NMR: (100 MHz, $CDCl_3$): δ 176.0, 174.4, 143.0, 134.9, 131.1, 128.9, 127.9, 127.2, 126.3, 124.3, 123.6, 109.9, 82.3, 43.9, 31.4, 28.3.

MP: 118 – 119 °C

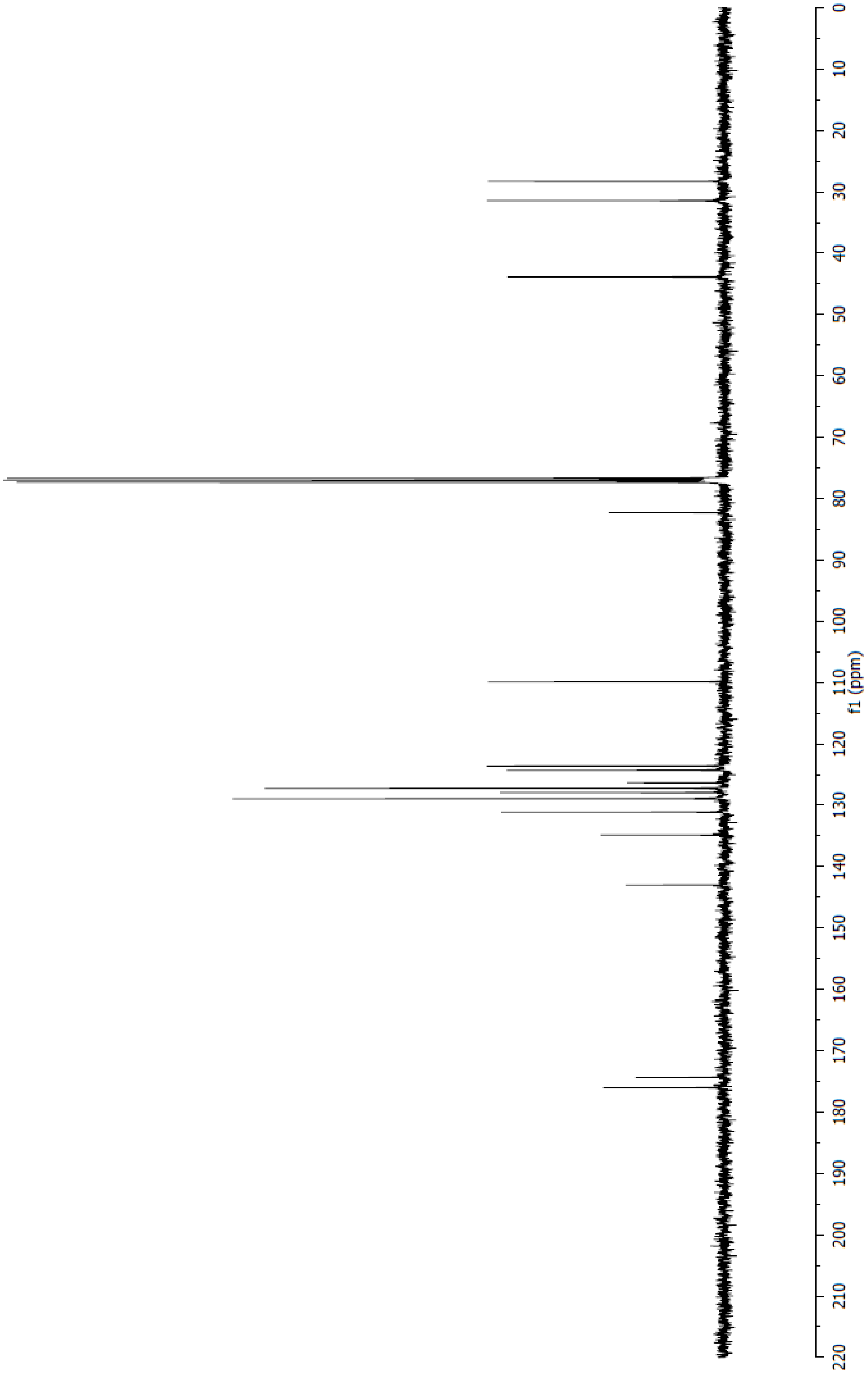
HRMS: (ESI) Calculated for $C_{18}H_{15}NO_3$ $[M+Na]^+$ = 316.09440, Found 316.09430.

FTIR: (neat): 1782, 1720, 1615, 1468, 1367, 1175, 1054, 983, 753, 723, 697, 680 cm^{-1}.

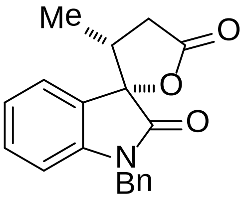
^{1}H NMR Spectrum **4a**



^{13}C NMR Spectrum **4a**



1'-benzyl-3-methyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4b)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl crotonate (**2b**) (96 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.20 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = >20:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (85.0 mg, 0.28 mmol, 92%) as a colorless solid.

TLC (SiO_2): R_f = 0.50 (hexanes:ethyl acetate = 5:2).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 7H), 7.07 (td, J = 7.7, 1.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.90 (dd, J = 62.3, 15.7 Hz, 2H), 3.28 (dd, *J* = 17.4, 8.4, 1H), 3.08-2.99 (m, 1H), 2.53 (dd, *J* = 17.4, 7.5 Hz, 1H), 1.04 (d, *J* = 7.0 Hz, 1H).

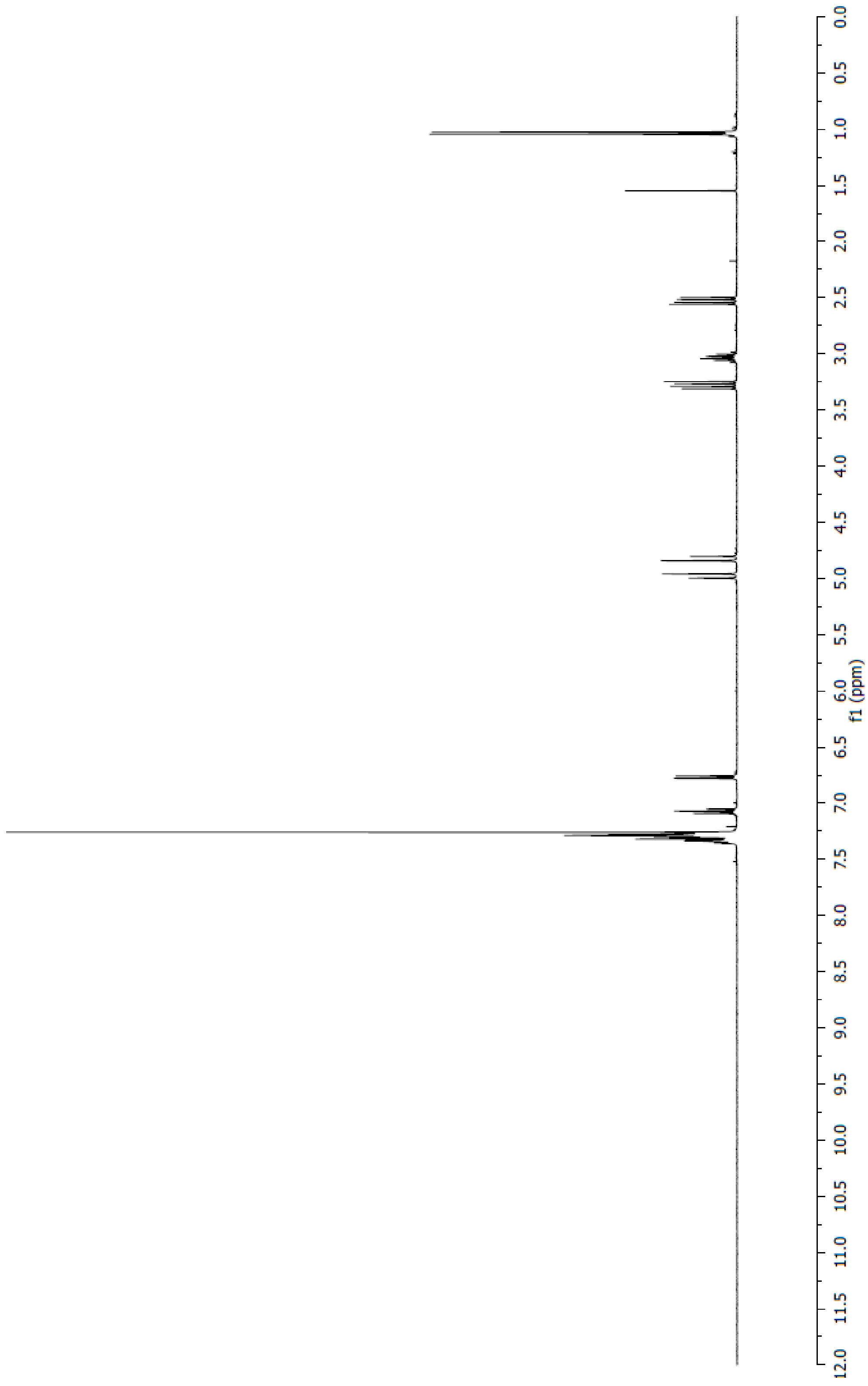
^{13}C NMR: (100 MHz, $CDCl_3$): δ 175.4, 174.2, 143.0, 135.0, 130.9, 129.0, 127.9, 127.2, 137.2, 124.0, 123.0, 110.1, 85.8, 44.1, 37.3, 35.9, 16.2.

MP: 146 – 147 °C

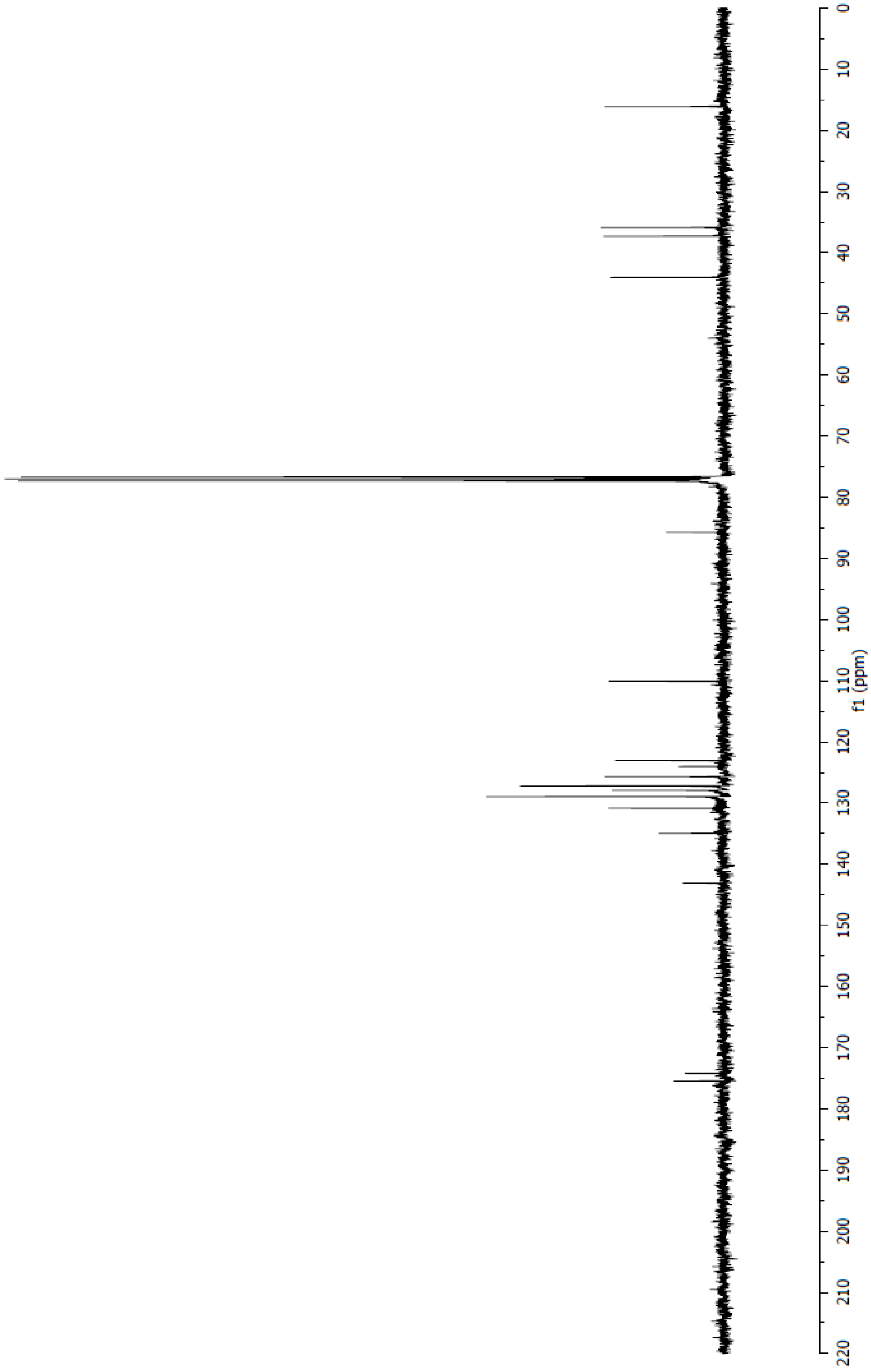
HRMS: (ESI) Calculated for $C_{19}H_{17}NO_3$ $[M+H]^+$ = 308.12810, Found 308.12830.

FTIR: (neat): 1783, 1727, 1612, 1490, 1471, 1373, 1212, 1164, 1004, 969, 767, 757, 734, 693, 673 cm^{-1}.

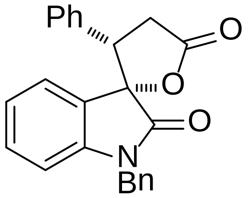
^{1}H NMR Spectrum **4b**



^{13}C NMR Spectrum **4b**



1'-benzyl-3-phenyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4c)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl cinnamate (146 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.30 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = >20:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (91.2 mg, 0.25 mmol, 82%) as a colorless solid. All spectral data was consistent with literature reported values.[15]

TLC (SiO_2): R_f = 0.62 (hexanes:ethyl acetate = 5:2).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.35-7.19 (m, 7H), 7.10 (td, *J* = 7.8, 1.2 Hz, 1H), 7.02-6.99 (m, 2H), 6.73 (td, *J* = 7.6, 1.0 Hz, 1H), 6.62 (d, *J* = 7.8, 1H), 6.42 (dq, *J* = 7.6, 0.6 Hz, 1H), 4.98 (d, *J* = 15.8 Hz, 1H), 4.81 (d, *J* = 15.8 Hz, 1H), 4.08 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.67 (dd, *J* = 17.4, 8.6 Hz, 1H) 3.15 (3d, *J* = 17.4, 5.8 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 175.7, 174.2, 142.9, 136.3, 134.8, 130.7, 128.9, 128.7, 128.2, 128.0, 127.9, 127.2, 126.0, 123.4, 122.7, 109.6, 86.0, 48.3, 44.0, 34.0.

MP: 176 – 177 °C

HRMS: (ESI) Calculated for $C_{24}H_{10}NO_3$ $[M+Na]^+$ = 392.12570, Found 392.12580.

FTIR: (neat): 1793, 1723, 1614, 1468, 1365, 1182, 1153, 1029, 1001, 752, 699 cm^{-1}.

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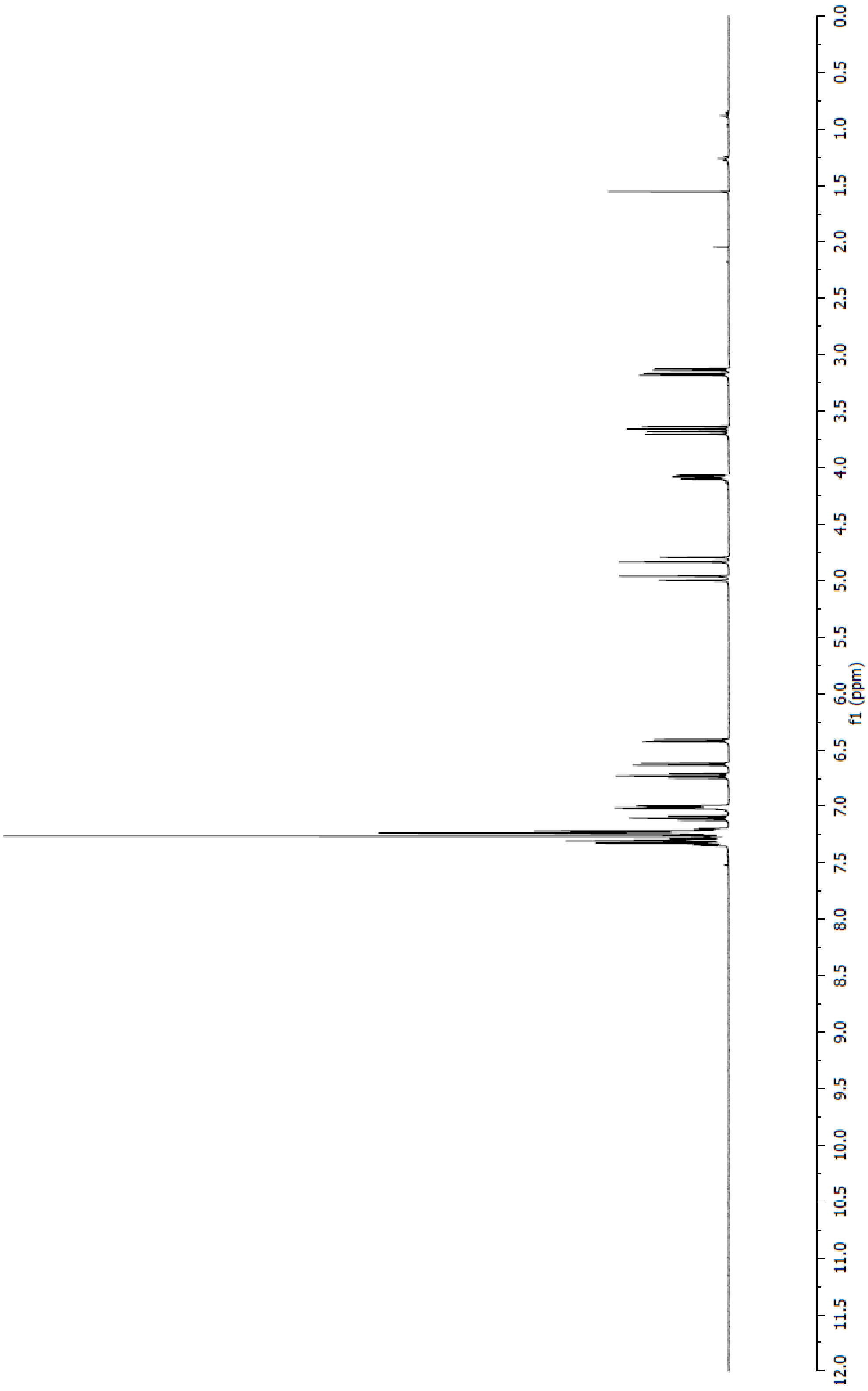
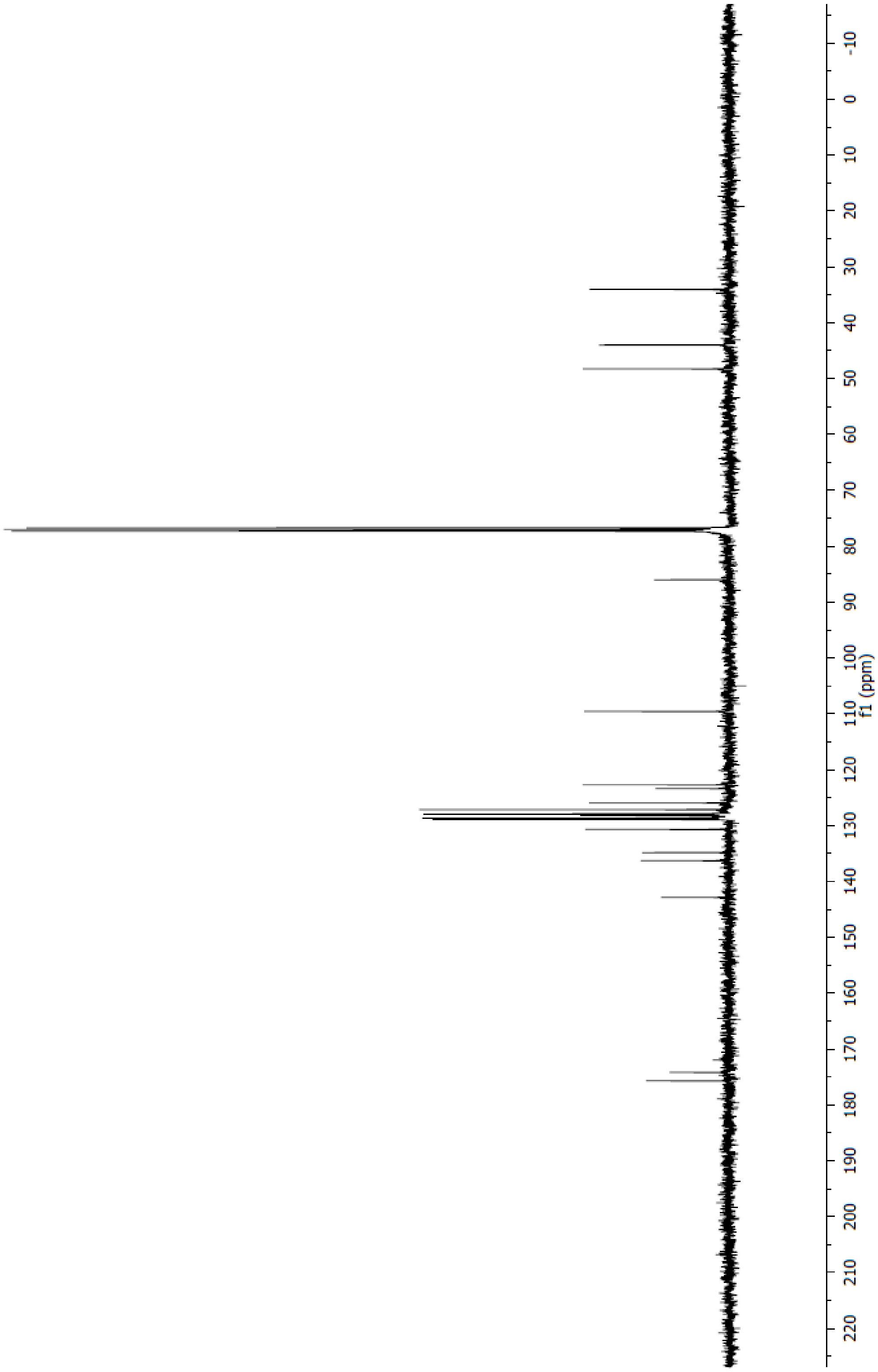
[15] Autrey, R.L.; Talk, F.C. *Tetrahedron* **1967**, *23*, 901.

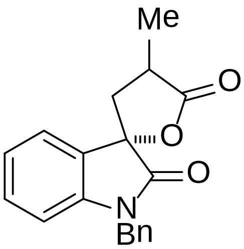
^{1}H NMR Spectrum **4c**



^{13}C NMR Spectrum **4c**



1'-benzyl-4-methyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4d)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl methacrylate (96.1 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.20 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = 2.2:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (91.7 mg, 0.30 mmol, 99%) as a colorless solid. All spectral data was consistent with literature reported values.[15]

TLC (SiO_2): $R_{f\,(minor)}$= 0.62, $R_{f\,(major)}$= 0.47 (hexanes:ethyl acetate = 5:2).

Spectral Data for Major Isomer:
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 7H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 3.20-3.10 (m, 1H), 2.62 (dd, *J* = 13.1, 9.5 Hz, 1H), 2.46 (dd, *J* = 13.1, 9.5 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 173.8, 142.6, 134.9, 130.9, 128.9, 127.9, 127.8, 127.2, 123.7, 123.5, 110.0, 80.6, 44.1, 38.4, 34.7, 16.5.

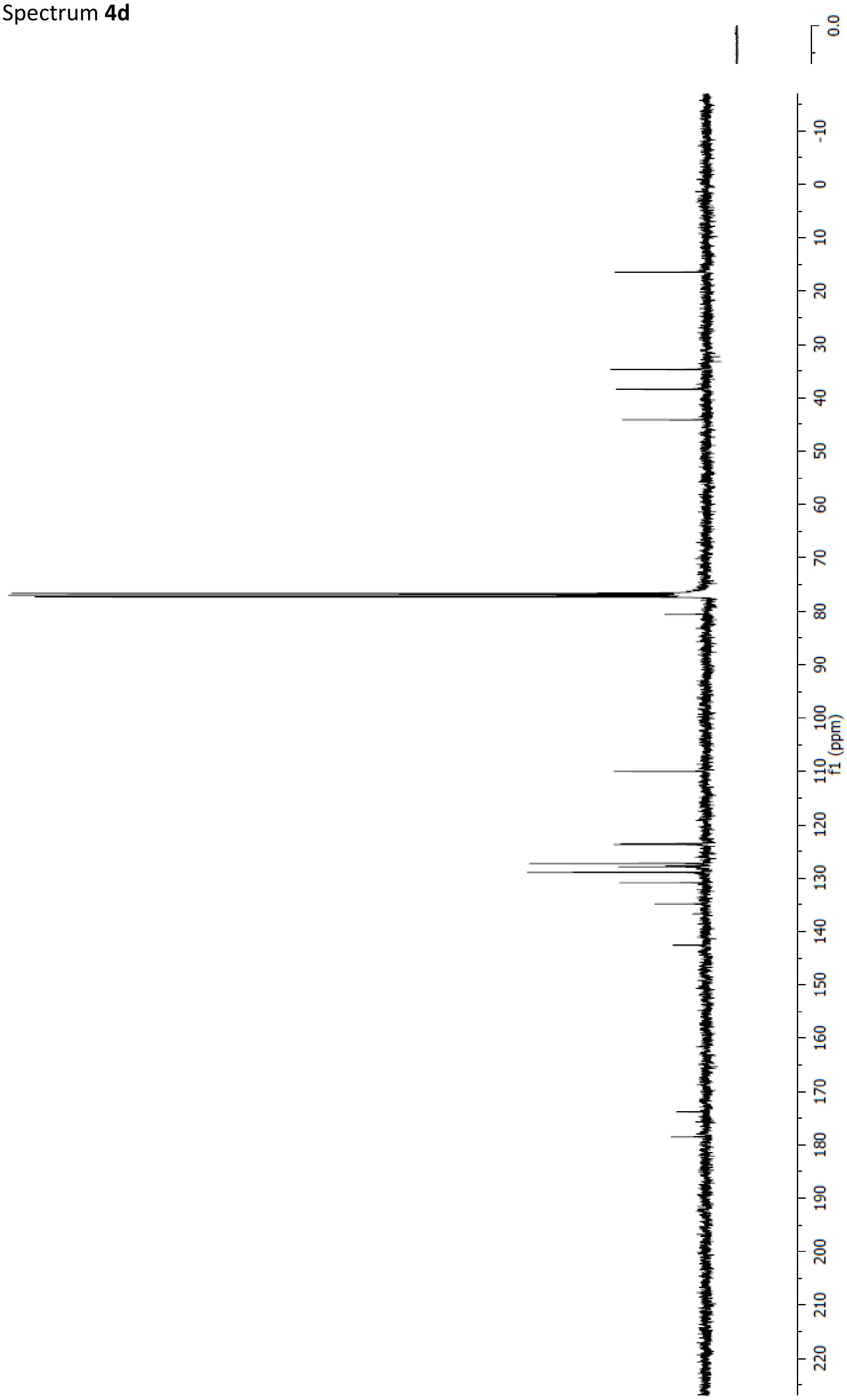
MP: 122 – 123 °C

HRMS: (ESI) Calculated for $C_{19}H_{17}NO_3$ $[M+Na]^+$ = 330.11010, Found 330.11050.

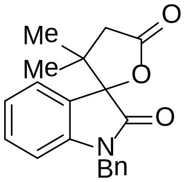
FTIR: (neat): 1783, 1727, 1615, 1489, 1469, 1369, 1178, 1024, 984, 752, 697 cm^{-1}.

^{1}H NMR Spectrum **4d**

^{13}C NMR Spectrum **4d**



1'-benzyl-3,3-dimethyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4e)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 3-methyl-2-butenoate (117 µL, 0.90 mmol, 300 mol%) and *m*-xylenes (0.18 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) furnished the title compound (50.1 mg, 0.156 mmol, 52%) as a colorless solid.

TLC (SiO_2): R_f = 0.59 (hexanes:ethyl acetate = 5:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 7H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.66 (d, *J* = 15.6 Hz, 1H), 3.46 (d, *J* = 16.6 Hz, 1H), 2.41 (d, *J* = 16.6 Hz, 1H), 1.32 (s, 3H), 1.10 (2, 3H).

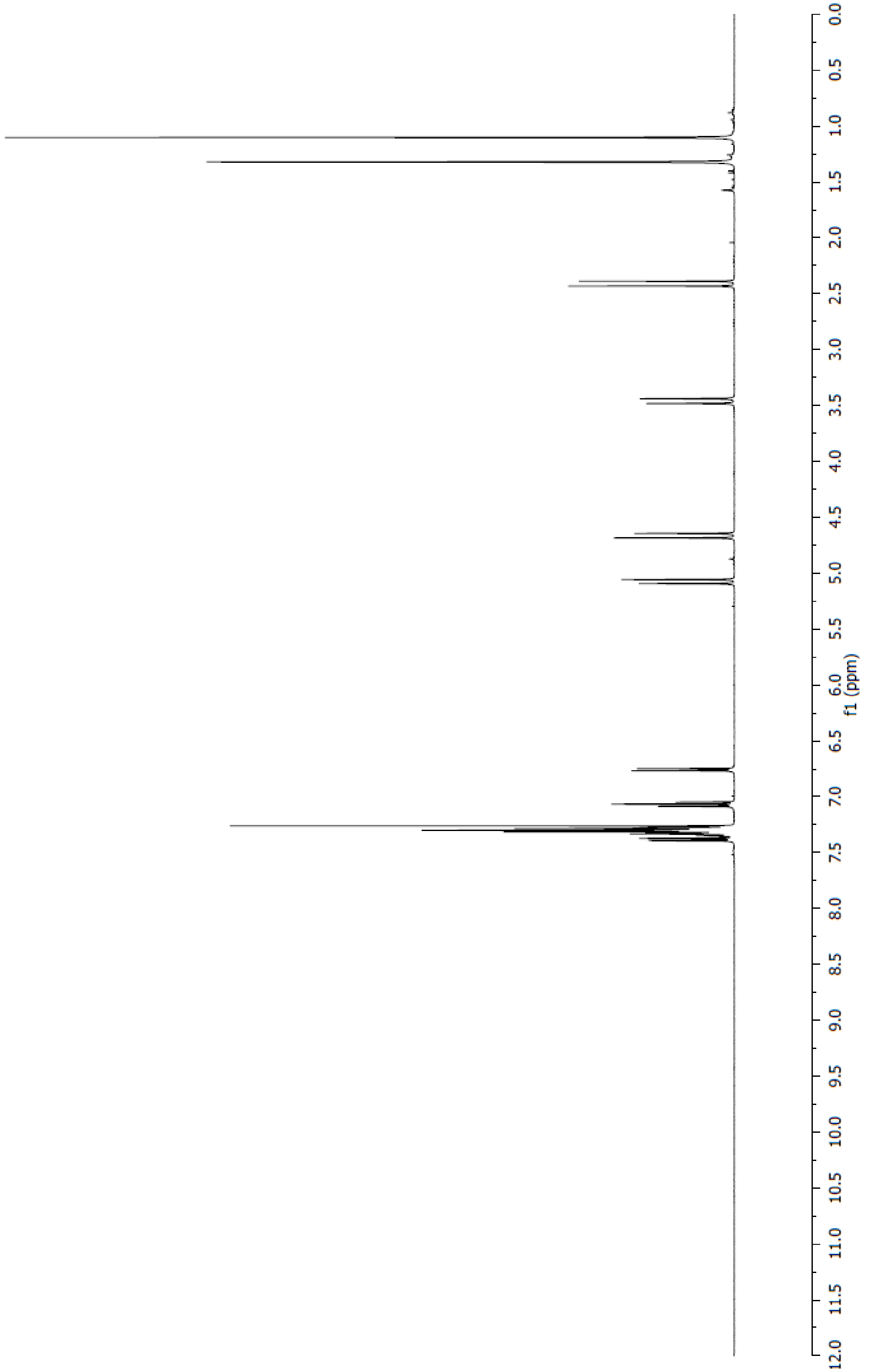
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 174.9, 144.1, 135.1, 130.9, 128.9, 127.9, 127.3, 127.1, 122.7, 122.2, 109.8, 88.4, 44.0, 43.4, 41.7, 26.0, 21.7.

MP: 142 – 143 °C

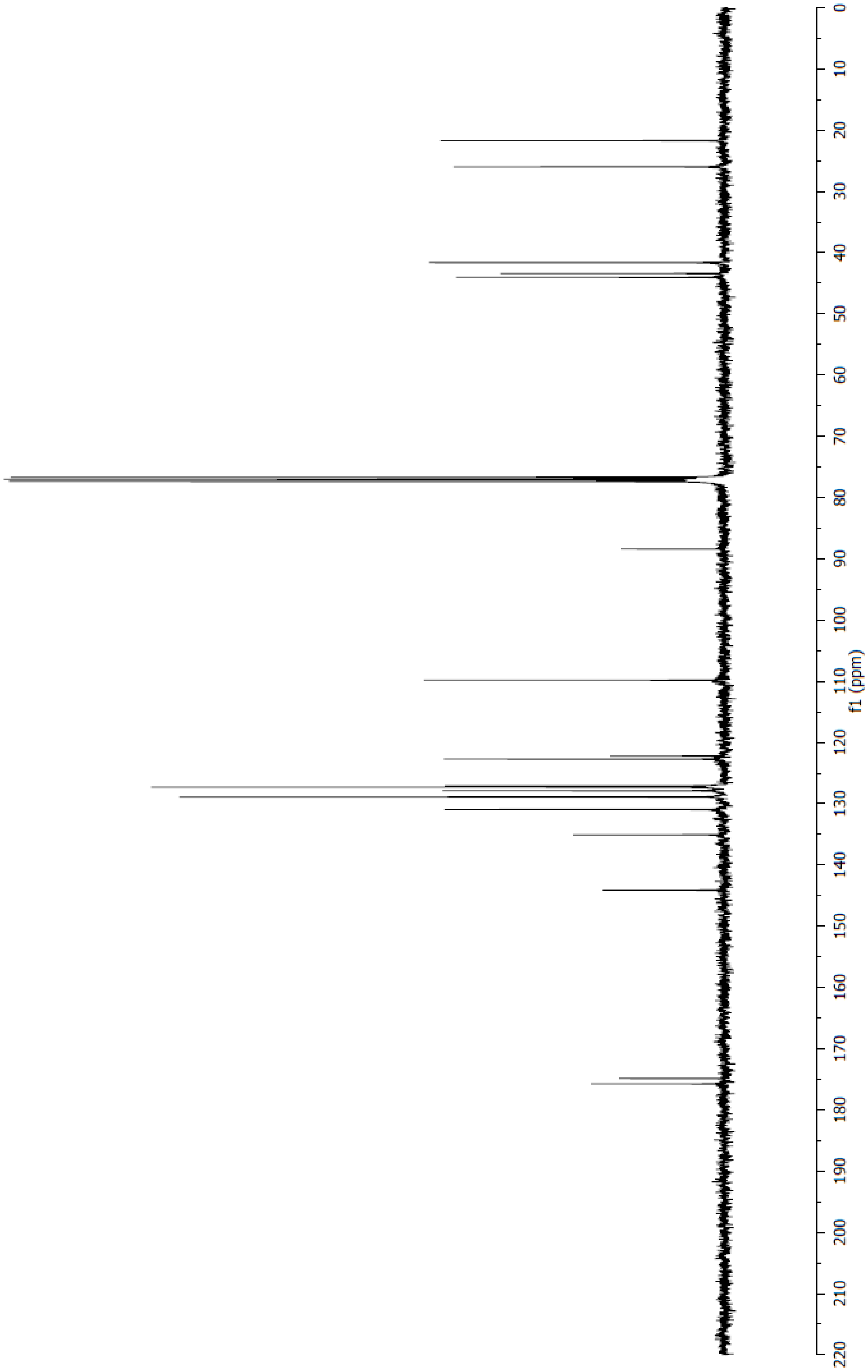
HRMS: (ESI) Calculated for $C_{20}H_{19}NO_3$ $[M+Na]^+$ = 344.12570, Found 344.12580.

FTIR: (neat): 1793, 1723, 1614, 1467, 1368, 1224, 1185, 1017, 755 cm^{-1}.

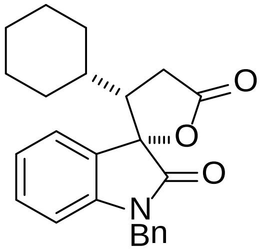
^{1}H NMR Spectrum **4e**



^{13}C NMR Spectrum **4e**



1'-benzyl-3- cyclohexyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4f)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon, (*E*)-methyl-3-cyclohexylacrylate (146 µL, 0.900 mmol, 300 mol%) and *m*-xylenes (0.15 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = >20:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (86.3 mg, 0.23 mmol, 77%) as a light brown solid.

TLC (SiO_2): R_f = 0.34 (hexanes:ethyl acetate = 7:3).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.34-7.23 (m, 7H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 15.4 Hz, 1H), 4.83 (d, *J* = 15.5 Hz, 1H), 3.00-2.86 (m, 2H), 2.74-2.60 (m, 1H), 1.73-1.62 (m, 2H), 1.53-1.46 (m, 1H), 1.36-1.21 (m, 2H), 1.17-0.98 (m, 3H), 0.93-0.84 (m, 1H), 0.77-0.67 (m, 2H).

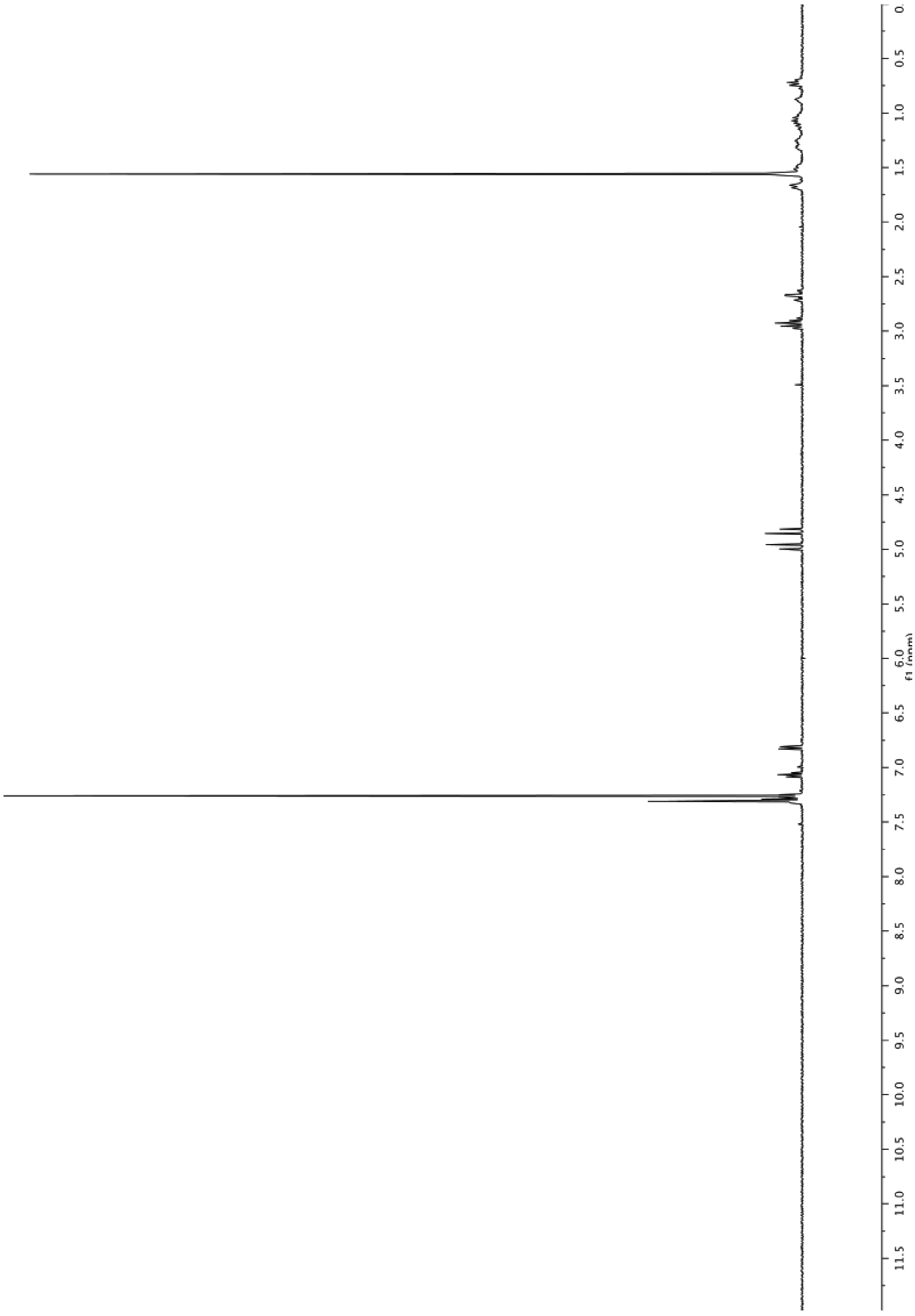
^{13}C NMR: (100 MHz, $CDCl_3$): δ 174.8, 173.2, 143.3, 134.9, 131.1, 128.9, 128.1, 127.8, 125.2, 124.7, 123.3, 110.3, 85.2, 47.9, 44.5, 38.8, 33.8, 31.8, 30.5, 25.8, 25.6, 25.2.

MP: 161 – 163 °C

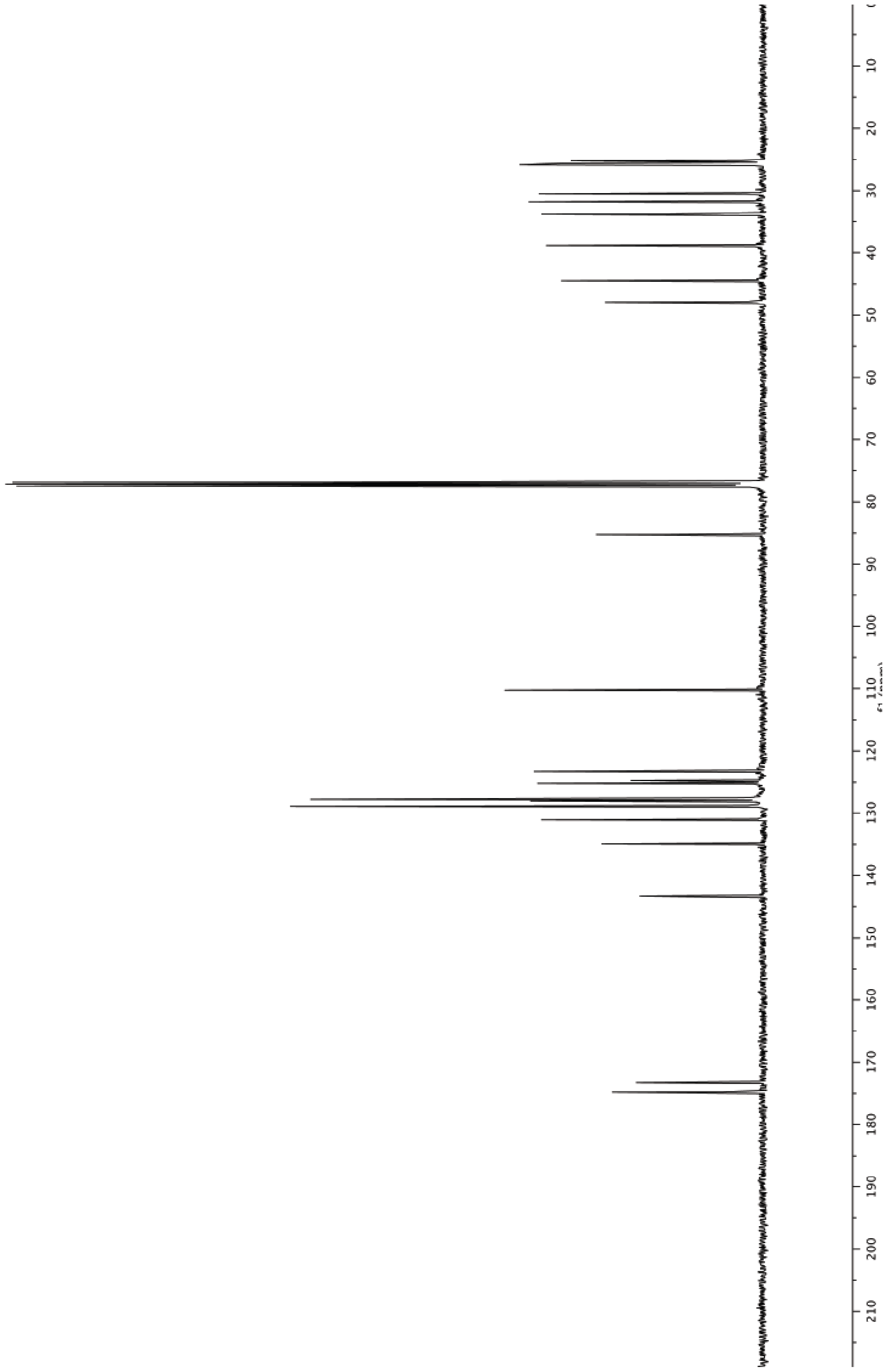
HRMS: (ESI) Calculated for $C_{24}H_{25}NO_3$ $[M+Na]^+$ = 398.17270, Found 398.17290.

FTIR: (neat):2934, 1788, 1731, 1614, 1487, 1350, 1206, 1184, 1159, 976, 770, 753, 708 cm^{-1}.

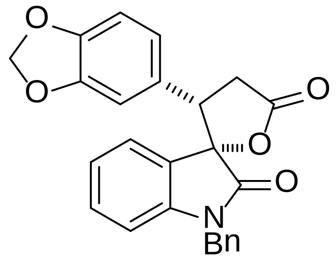
^{1}H NMR Spectrum **4f**



^{13}C NMR Spectrum **4f**



(3-(benzo[d][1,3]dioxol-5-yl)-1'-benzyl-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4g)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), acrylic ester (**2g**) $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon, and *m*-xylenes (0.30 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = >20:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (112 mg, 0.27 mmol, 90%) as a pale pink solid.

TLC (SiO_2): R_f = 0.28 (hexanes:ethyl acetate = 7:3).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.34-7.22 (m, 5H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 6.82 (td, *J* = 7.6, 0.9 Hz, 1H), 6.66-6.61 (m, 3H), 6.50-6.48 (m, 2H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.99 (d, *J* = 15.8 Hz, 1H), 4.80 (d, *J* = 15.8, 1H), 4.03 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.60 (dd, *J* = 17.5, 8.6 Hz, 1H), 3.08 (dd, *J* = 17.5, 6.4 Hz, 1H).

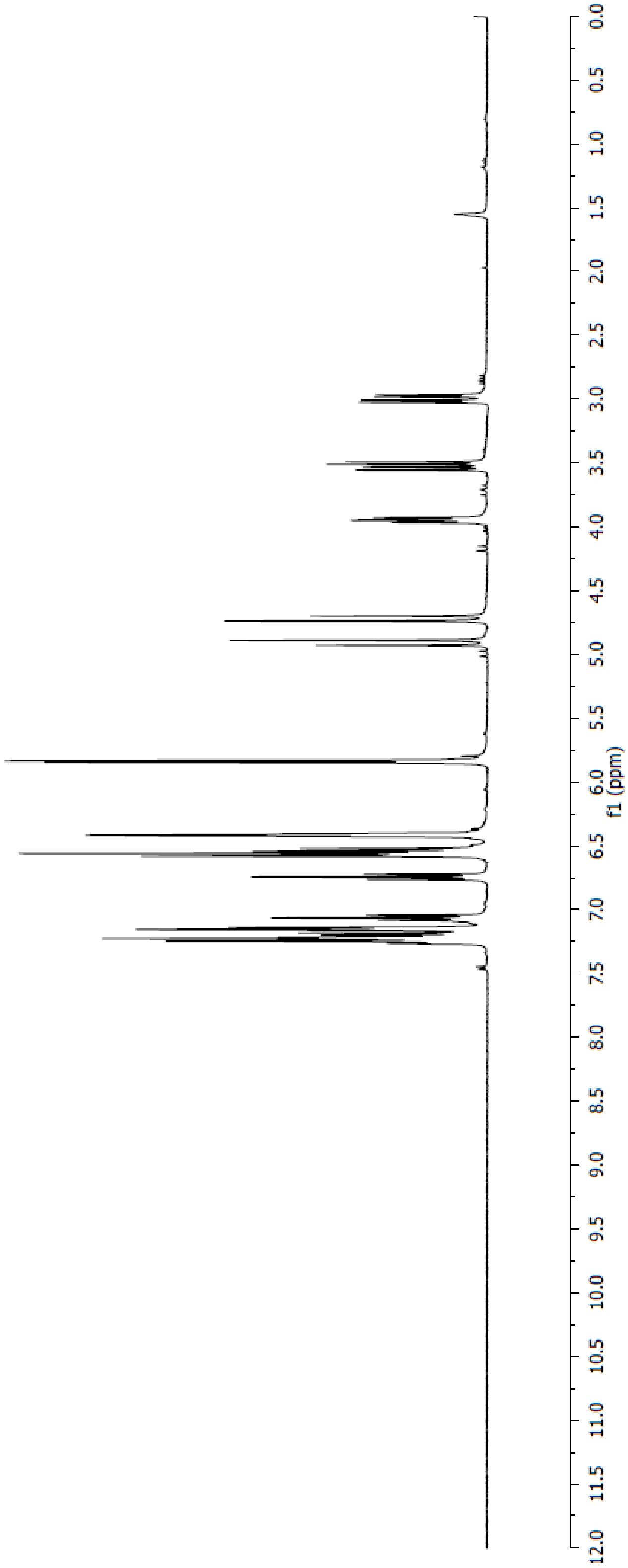
^{13}C NMR: (100 MHz, $CDCl_3$): δ 175.5, 174.0, 147.9, 147.4, 142.9, 134.8, 130.8, 129.8, 128.9, 127.9, 127.1, 125.9, 123.5, 122.9, 121.3, 109.7, 108.3, 101.3, 86.1, 48.1, 44.0, 34.3, 14.2.

MP: 177 – 178 °C

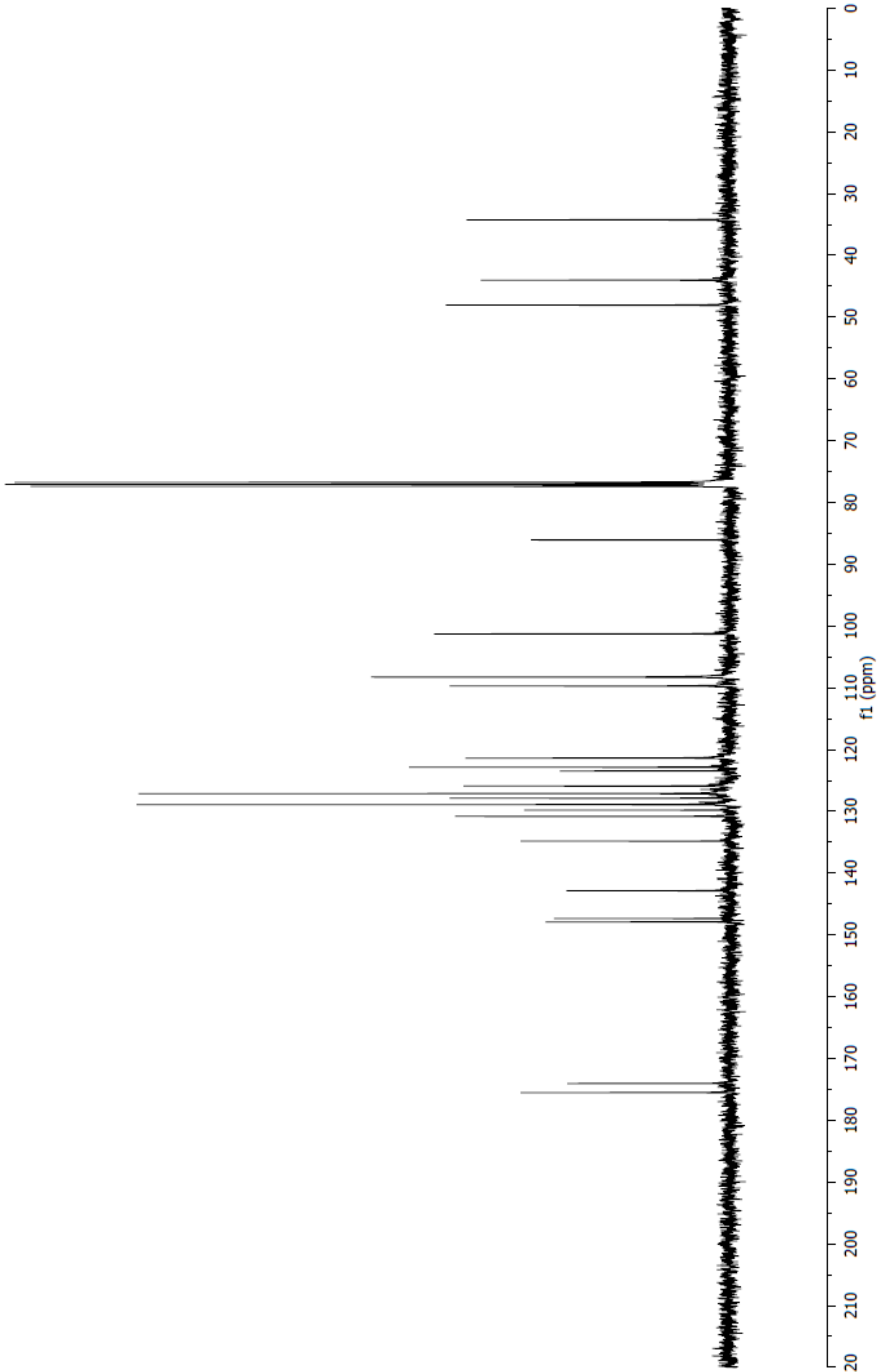
HRMS: (ESI) Calculated for $C_{25}H_{19}NO_5$ $[M+Na]^+$ = 436.11550, Found 436.11510.

FTIR: (neat): 1791, 1730, 1489, 1468, 1368, 1234, 1184, 1155, 1035, 1000, 760, cm^{-1}

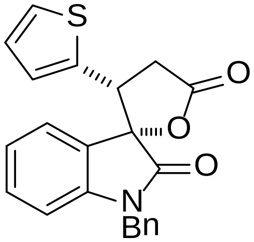
^{1}H NMR Spectrum **4g**



^{13}C NMR Spectrum **4g**



1'-benzyl-3-(thiophen-2-yl)-3H-spiro[furan-2,3'-indoline]-2',5(4H)-dione (4h)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added 1-benzyl-3-hydroxyindolin-2-one (**1o**) (72 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 2,2';6'2"-terpyridine (4.2 mg, 0.018 mmol, 6 mol%) and KO*t*Bu (3.3 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 3-(thiophen-2-yl)acrylate (151 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.30 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude product (d.r = >20:1, as determined by ^{1}H NMR spectroscopy). The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 3:1) to furnish the title compound (97.8 mg, 0.26 mmol, 87%) as a pale pink solid. All spectral data was consistent with literature reported values.

TLC (SiO_2): R_f = 0.49 (hexanes:ethyl acetate = 2:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 3H), 7.22-7.19 (m, 2H), 7.16 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.6 Hz 1H), 6.85 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.79 (ddd, *J* = 3.6, 1.1, 0.6 Hz, 1H), 6.72 (ddd, *J* = 7.6, 1.2, 0.6 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.96 (d, *J* = 15.8 Hz, 1H), 4.85 (d, *J* = 15.8 Hz, 1H), 4.38 (m, 1H), 3.65 (dd, *J* = 17.5, 8.7 Hz, 1H), 3.15 (dd, *J* = 17.5, 7.2 Hz, 1H).

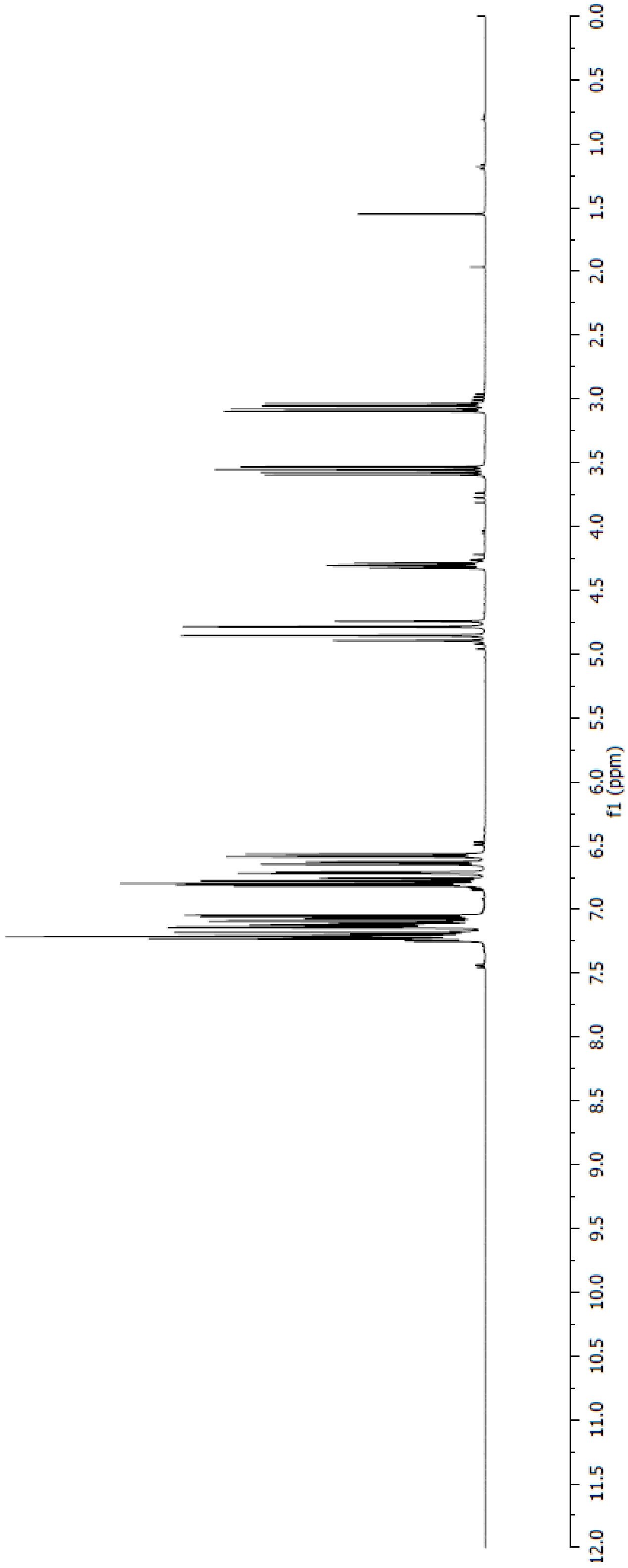
^{13}C NMR: (100 MHz, C_6D_6): δ 173.5, 173.3, 143.0, 138.7, 135.1, 130.5, 128.6, 126.9, 126.6, 126.2, 125.4, 124.7, 123.8, 122.5, 109.5, 85.2, 44.1, 43.4, 35.4.

MP: 158 – 159 °C

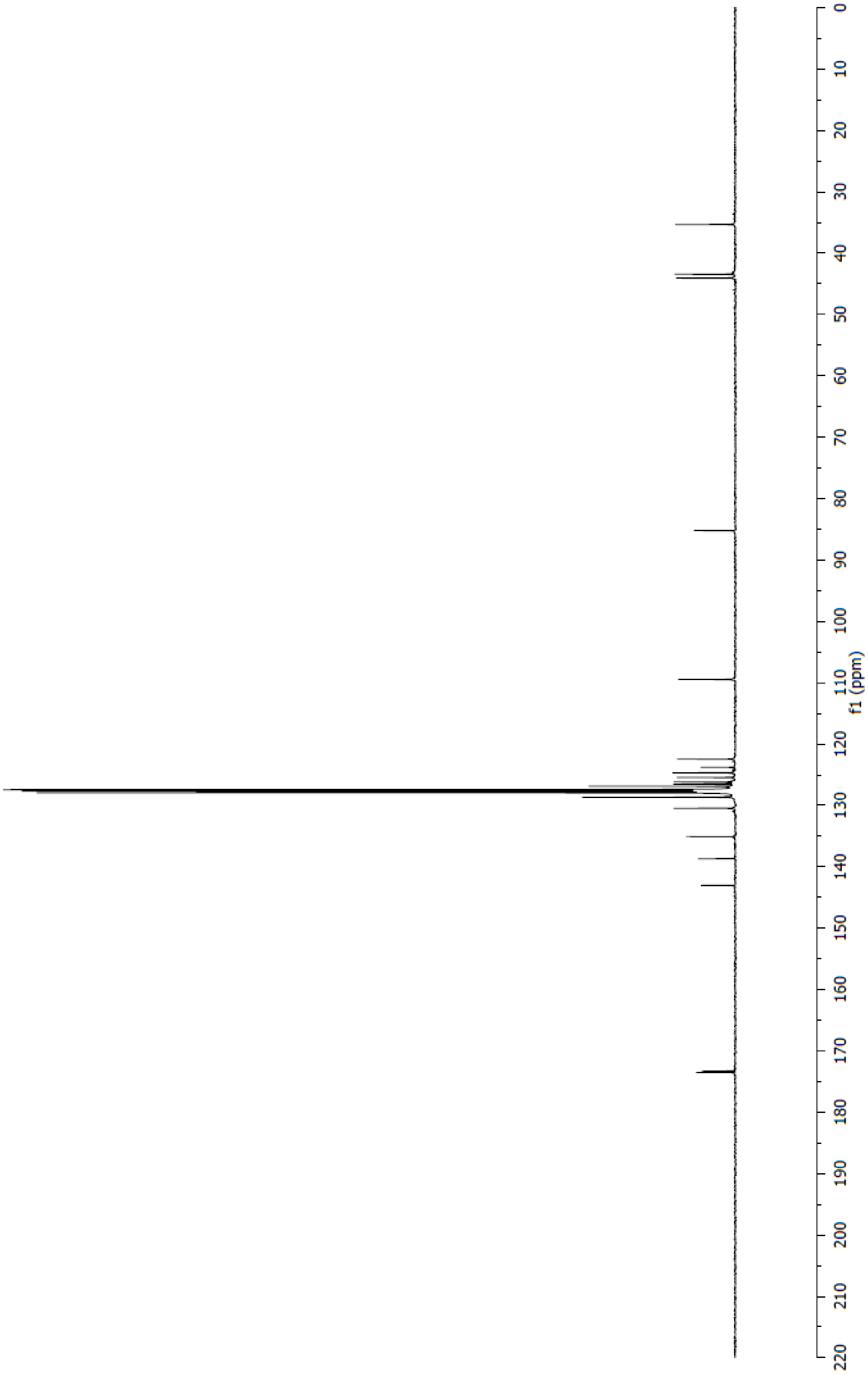
HRMS: (ESI) Calculated for $C_{22}H_{17}NO_3S$ $[M+Na]^+$ = 398.08210, Found 398.08200.

FTIR: (neat): 1790, 1722, 1614, 1467, 1379, 1368, 1194, 1183, 1155, 999, 768, 757, 732, 709, 694, 676 cm^{-1}.

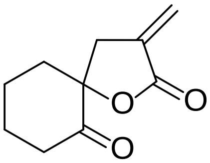
^{1}H NMR Spectrum **4h**



^{13}C NMR Spectrum **4h**



3-methylene-1-oxaspiro[4.5]decane-2,6-dione (5b)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *trans*-1,2-cyclohexanediol (**1b**) (35 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 2-(hydroxymethyl)acrylate (**2i**) (104 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 2.5:1) to furnish the title compound (32 mg, 0.18 mmol, 59%) as a colorless oil.

TLC (SiO_2): R_f = 0.23 (hexanes:ethyl acetate = 2:1).

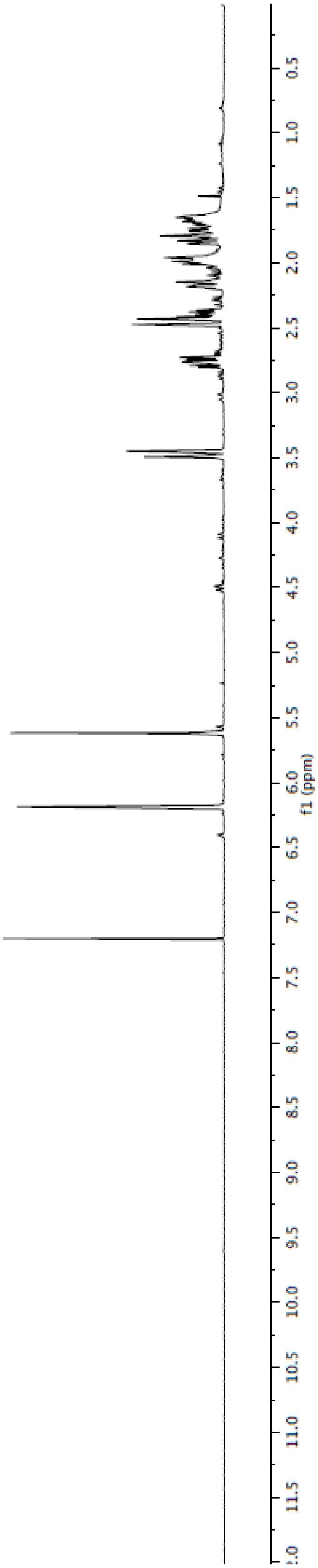
^{1}H NMR: (400 MHz, $CDCl_3$): δ 6.24 (t, *J* = 2.9 Hz, 1H), 5.67 (t, *J* = 2.5 Hz, 1H), 3.53 (dt, *J* = 17.3, 2.6 Hz, 1H), 2.83 (ddd, *J* = 13.9, 10.9, 6.0 Hz, 1H), 2.51 (d, *J* = 17.3, 2.9Hz, 1H), 2.45 (m, 1H), 2.22 (m, 1H), 2.09 – 2.00 (m, 2H), 1.92 – 1.67 (m, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 205.1, 168.5, 133.4, 123.5, 85.3, 39.9, 38.8, 33.6, 27.1, 21.3.

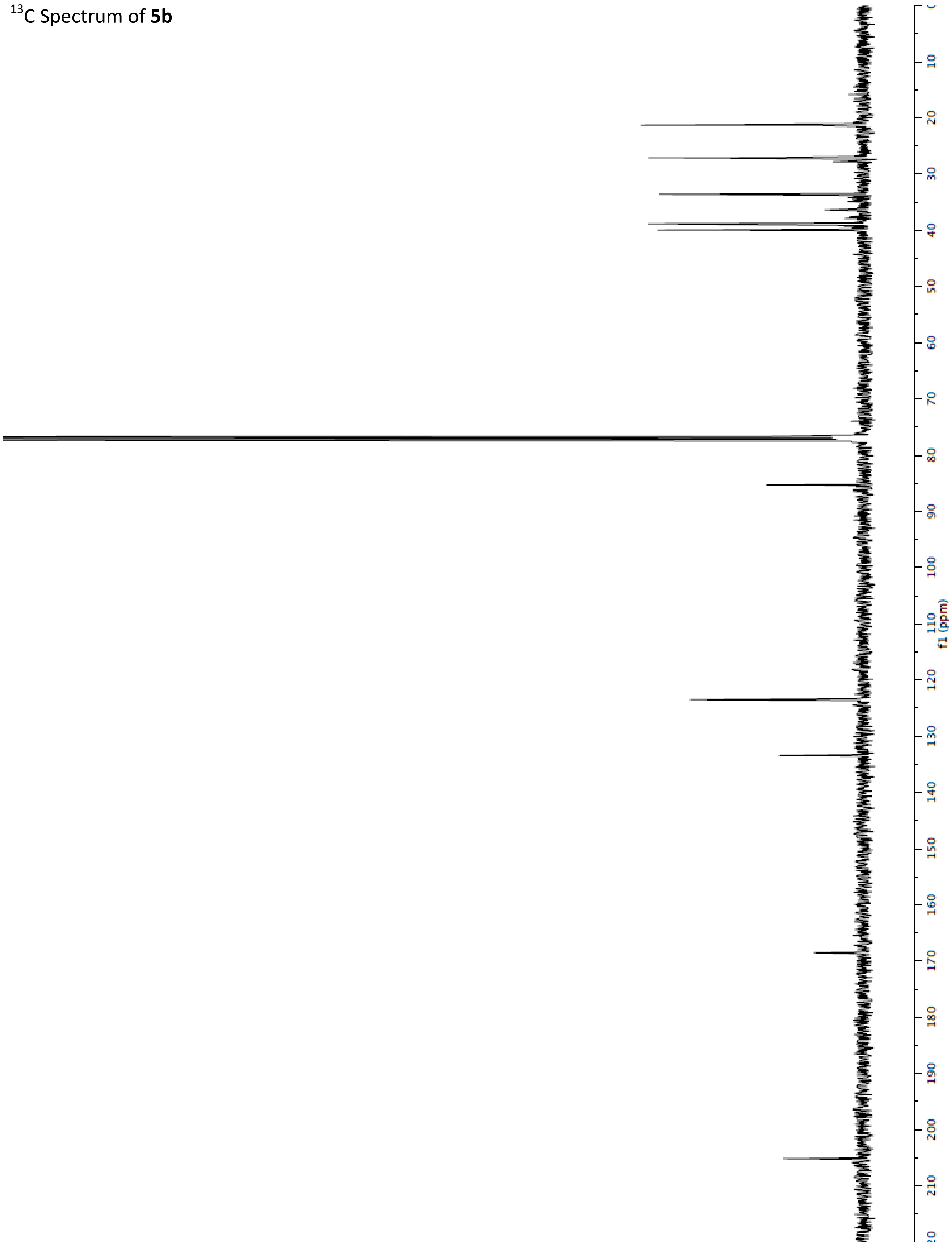
HRMS: (ESI) Calculated for $C_{10}H_{12}O_3$ $[M+Na]^+$ = 203.06790, Found 203.06750.

FTIR: (neat): 2941, 2868, 1767, 1724, 1665, 1452, 1265, 1083, 957 cm^{-1}.

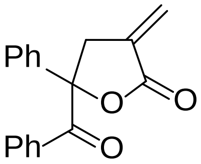
^{1}H NMR Spectrum **5b**



^{13}C Spectrum of **5b**



5-benzoyl-3-methylene-5-phenyldihydrofuran-2(3H)-one (5f)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis/trans*-hydrobenzoin (**1f**) (64 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 2-(hydroxymethyl)acrylate (**2i**) (104 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 6:1) to furnish the title compound (57 mg, 0.20 mmol, 68%) as a colorless solid. All spectral data was consistent with literature reported values.[14]

TLC (SiO_2): R_f = 0.38 (hexanes:ethyl acetate = 4:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.96 (m, 2H), 7.46 (m, 2H), 7.42 – 7.29 (m, 6H), 6.29 (t, *J* = 2.7 Hz, 1H), 5.71 (t, *J* = 2.7 Hz, 1H), 4.23 (dt, *J* = 17.4, 2.7 Hz, 1H), 3.01 (dt, *J* = 17.4, 2.7 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 194.9, 168.8, 140.0, 133.4, 132.8, 130.8, 129.3, 128.5, 128.2, 124.0, 123.8, 123.7, 89.1, 40.0.

MP: 63 - 66 °C

HRMS: (ESI) Calculated for $C_{18}H_{14}O_3$ $[M+Na]^+$ = 301.08350, Found 301.08370.

FTIR: (neat): 3061, 1775, 1681, 1597, 1447, 1249, 1155, 1069, 699 cm^{-1}.

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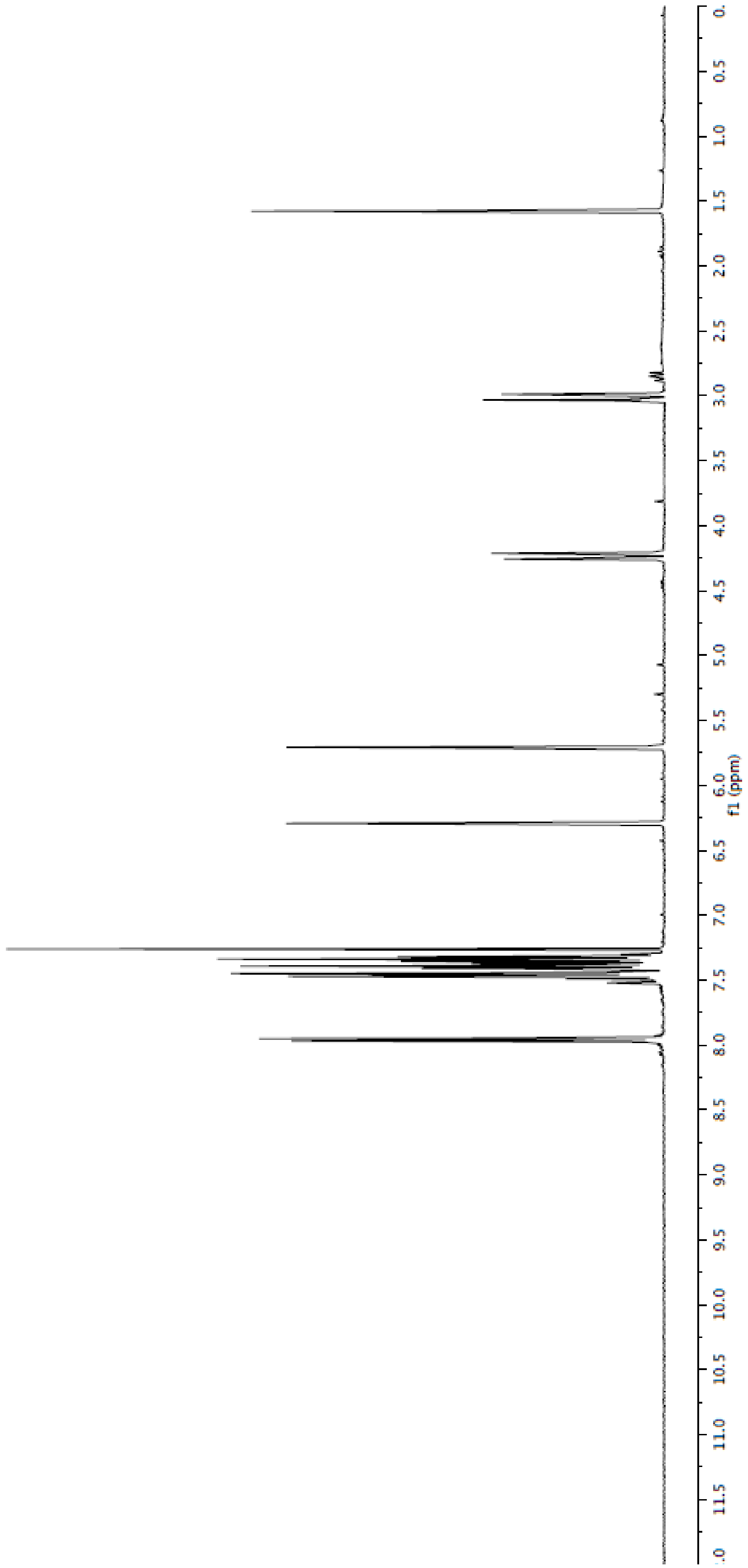
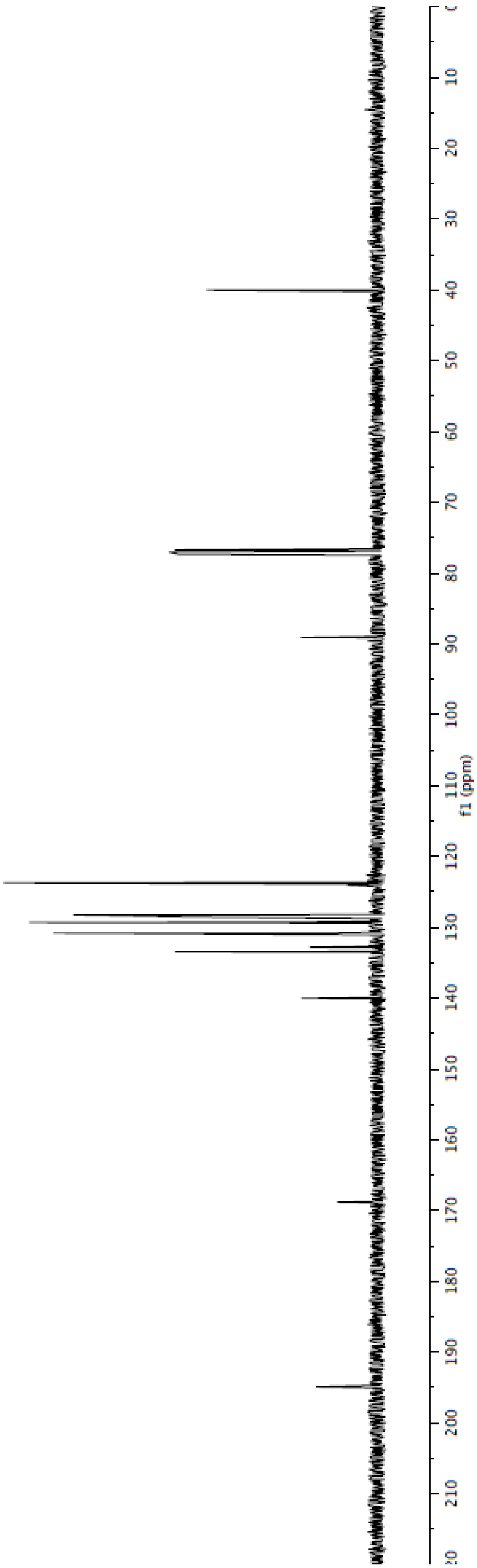
[14] Hegedus, L.S.; Wagner, S.D.; Waterman, E.L.; Siirala-Hansen, K. *J. Org. Chem.* **1974,** *40,* 593.

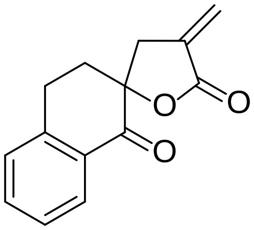
^{1}H NMR Spectrum **5f**



^{13}C Spectrum of **5f**



4-methylene-3',4'-dihydro-1'H,3H-spiro[furan-2,2'-naphthalene]-1',5(4H)-dione (5j)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis/trans*-1,2,3,4-tetrahydronaphthalene-1,2-diol (**1j**) (49 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 2-(hydroxymethyl)acrylate (**2i**) (104 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactone (r.r = >20:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) furnished the title compound (48 mg, 0.21 mmol, 70%) as a colorless oil.

TLC (SiO_2): R_f = 0.26 (hexanes:ethyl acetate = 2:1).

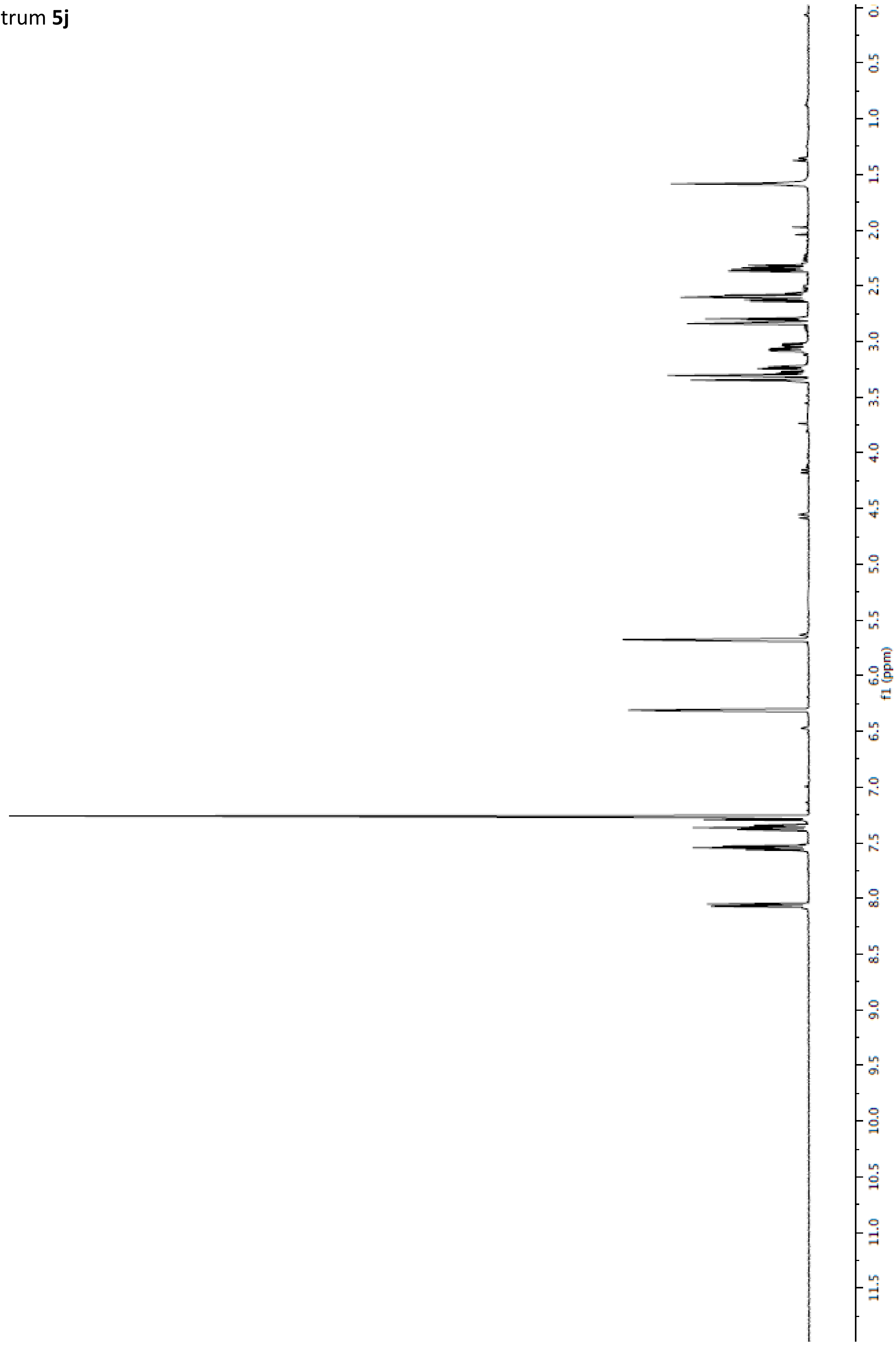
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.30 (dd, *J* = 3.2, 2.4 Hz, 1H), 5.68 (dd, *J* = 2.7, 2.2 Hz, 1H), 3.32 (dt, *J* = 16.9, 2.2 Hz, 1H), 3.25 (m, 1H), 3.06 (ddd, *J* = 17.2, 8.8, 4.8 Hz, 1H), 2.82 (dt, *J* = 17.0, 3.0 Hz, 1H), 2.60 (ddd, *J* = 13.7, 8.9, 4.9 Hz, 1H), 2.33 (ddd, *J* = 13.6, 6.5, 4.9 Hz, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 192.4, 169.1, 143.1, 134.5, 133.2, 130.0, 128.7, 128.7, 127.3, 122.9, 82.0, 35.0, 34.4, 25.5.

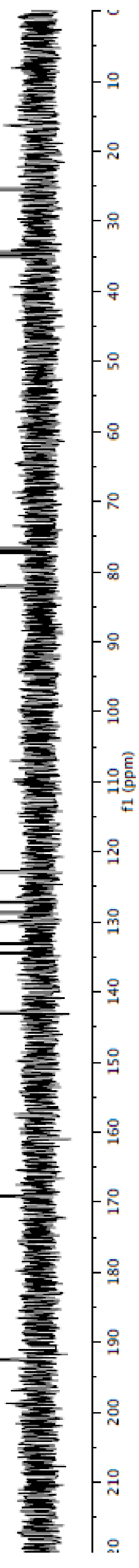
HRMS: (ESI) Calculated for $C_{14}H_{12}O_3$ $[M+Na]^+$ = 251.06790, Found 251.06790.

FTIR: (neat): 2937, 1769, 1692, 1602, 1456, 1227, 1150, 1004, 750 cm^{-1}.

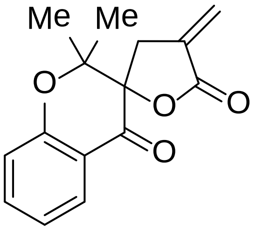
^{1}H NMR Spectrum **5j**



^{13}C Spectrum of **5j**



2,2-dimethyl-4'-methylene-3'H-spiro[chroman-3,2'-furan]-4,5'(4'H)-dione (5l)



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added *cis*-2,2-dimethylchroman-3,4-diol (**1l**) (58 mg, 0.30 mmol), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 1,3-bis(diphenylphosphino)propane (7.4 mg, 0.018 mmol, 6 mol%), and 1-adamantanecarboxylic acid (5.4 mg, 0.03 mmol, 10 mol%). The tube was sealed with a rubber septum and purged with argon. Methyl 2-(hydroxymethyl)acrylate (**2i**) (104 mg, 0.90 mmol, 300 mol%) and *m*-xylenes (0.22 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo* to afford the crude spirolactone (r.r = >20:1, as determined by ^{1}H NMR spectroscopy). Purification of the crude product by flash column chromatography (SiO_2; hexanes:ethyl acetate = 4:1) furnished the title compound (46 mg, 0.18 mmol, 60%) as a colorless solid.

TLC (SiO_2): $R_f = 0.39$ (hexanes:ethyl acetate = 2:1).

^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 1H), 7.05 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.32 (t, *J* = 2.9 Hz, 1H), 5.72 (t, *J* = 2.6 Hz, 1H), 3.09 (br. s, 2H), 1.48 (s, 3H), 1.42 (s, 3H).

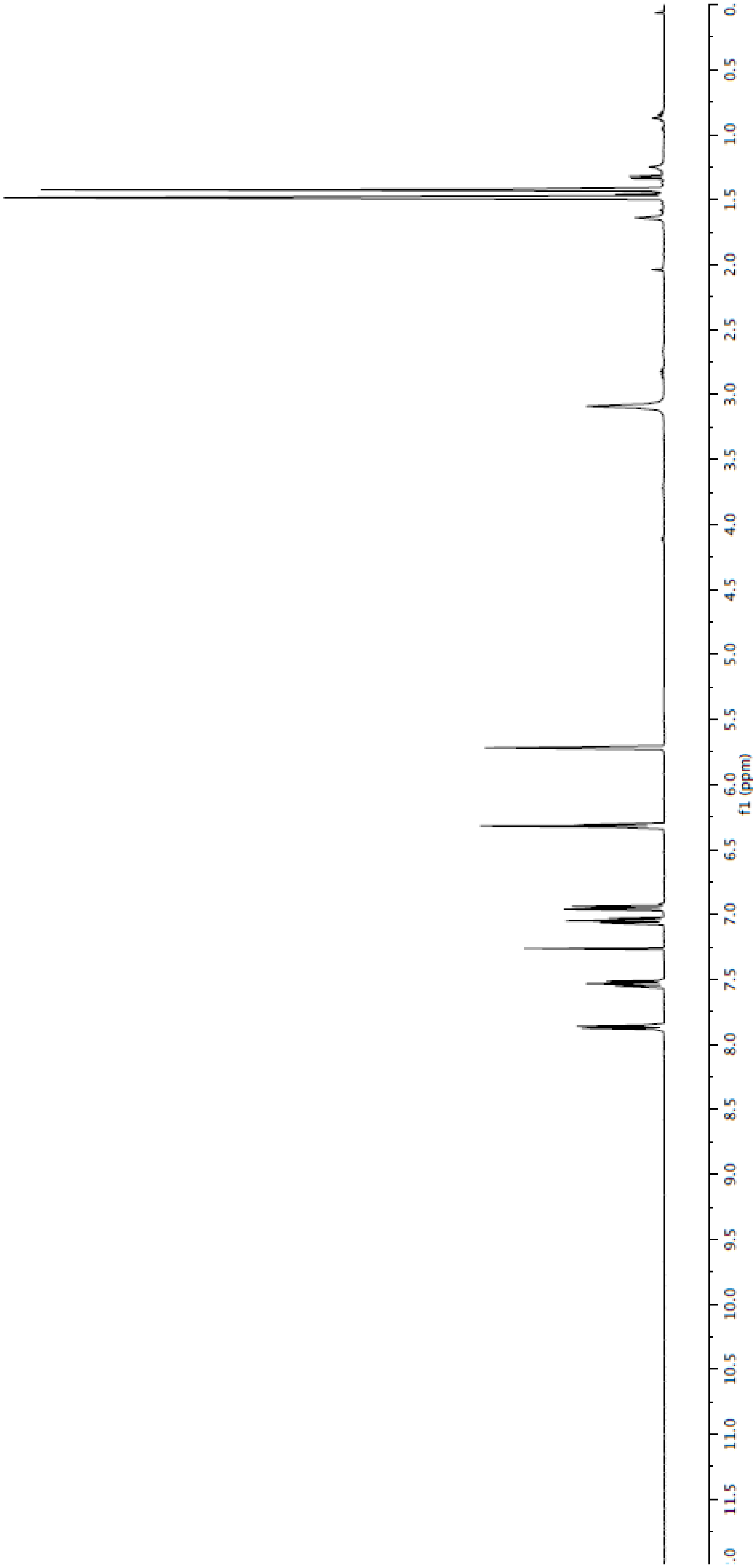
^{13}C NMR: (100 MHz, $CDCl_3$): δ 188.6, 168.5, 158.6, 137.0, 132.5, 127.7, 123.8, 121.7, 121.6, 118.3, 83.5, 81.9, 30.1, 21.0, 20.9.

MP: 97 °C

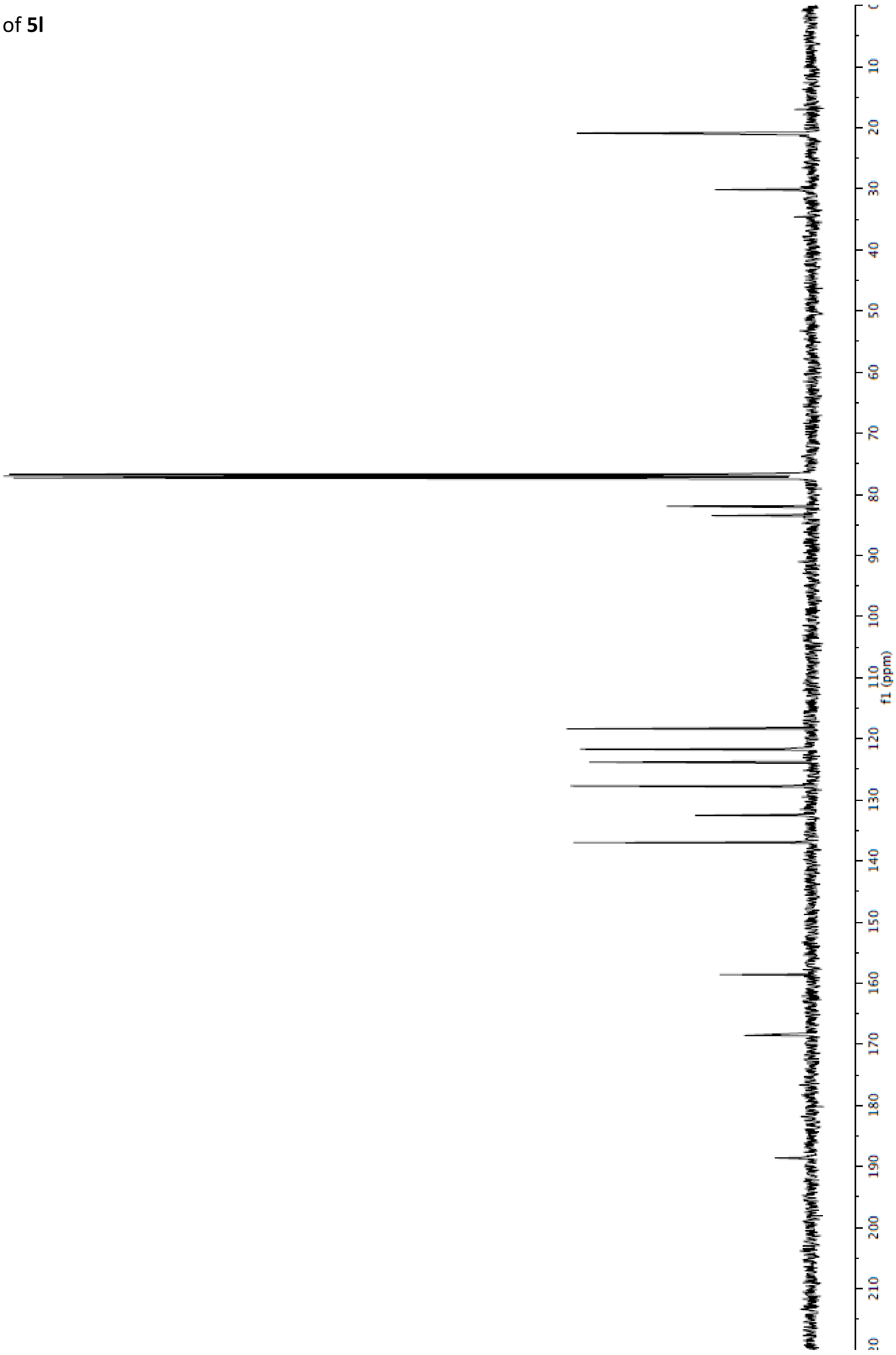
HRMS: (ESI) Calculated for $C_{14}H_{12}O_3$ $[M+Na]^+ = 281.07840$, Found 281.07880.

FTIR: (neat): 2985, 1764, 1702, 1608, 1463, 1242, 1063, 928, 757 cm^{-1}.

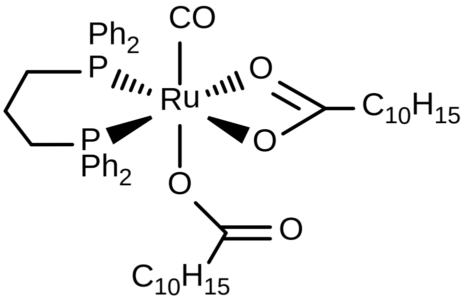
^1H NMR Spectrum **5l**



^{13}C Spectrum of **5l**



Preparation of Ru(CO)(dppp)($C_{10}H_{15}CO_2$)$_2$



To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added $Ru_3(CO)_{12}$ (38.3 mg, 0.060 mmol, 100 mol%), 1,3-bis(diphenylphosphino)propane (74.1 mg, 0.18 mmol, 300 mol%), and 1-adamantanecarboxylic acid (64.8 mg, 0.36 mmol, 600 mol%). The tube was sealed with a rubber septum and purged with argon and *m*-xylenes (0.60 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature and concentrated *in vacuo*. The material was recrystallized from dichloromethane and pentane *via* vapor diffusion to afford yellow crystals for single crystal x-ray diffraction spectroscopy. This complex was found to be a catalytically competent precatalyst to generate product **3b**(eq. 2 in manuscript).

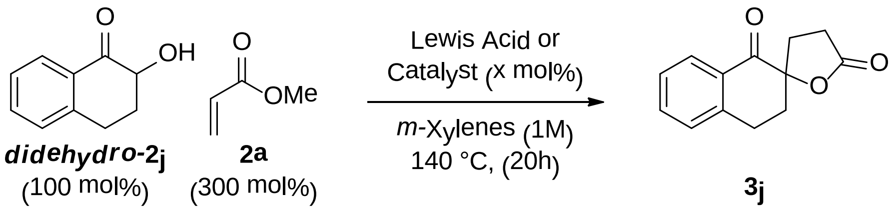
MP: 188 – 194 °C decomposed

HRMS: (ESI) Calculated for $C_{50}H_{56}O_5P_2Ru$ $[M+Na]^+$ = 917.25710, Found 917.25760.

FTIR: (neat): 2901, 2847, 1952, 1485, 1435, 1446, 1344, 1305, 1099, 743, 692, 681 cm^{-1}.

Experimental Details for Control Experiments

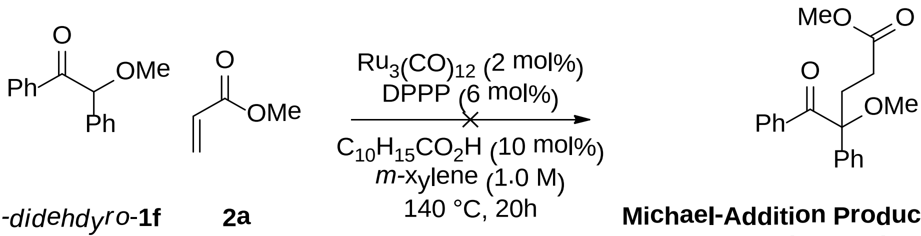
Lewis Acid Screen: *These control experiments were performed to probe the feasibility of spirolactone formation via a Lewis Acid catalyzed pathway, initiating from the hydroxy ketone formed upon initial oxidation of the diol starting material. Based on the poor reactivity, this reaction pathway seems unlikely.*



Entry	Lewis Acid or Catalyst	Catalyst Loading (x mol%)	Yield (%)
1	$Ru_3(CO)_{12}$	2	26
2	$RuCl_3$-H_2O	6	6
3	$B(OMe)_3$	6	No Reaction
4	$InCl_3$	6	No Reaction
5	ZnI_2	6	No Reaction
6	$MgCl_2$	6	16

To a resealable pressure tube (13 x 100 mm) equipped with a magnetic stir bar was added α-hydroxy ketone (didehydro-**2j**) (32.4 mg, 0.20 mmol) and Lewis Acid/Catalyst (0.012 mmol, 6 mol%, see table below).The tube was sealed with a rubber septum and purged with argon. Methyl acrylate (**2a**) (54 µL, 0.60 mmol, 300 mol%) and *m*-xylenes (0.15 mL) were added. The rubber septum was quickly replaced with a screw cap. The mixture was heated at 140 °C (oil bath temperature) for 20 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated and subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 2:1) to yield product **3j**. Spectroscopic data was consistent with that listed for this compound using the general procedure for spirolactonization of diol **1j**.

Michael Addition Probe: *This control experiment was performed to further evaluate the possibility of an anionic cyclization pathway, via enolate formation followed by Michael addition. Methylation of the hydroxyl group of didehydro-***1f** *renders the substrate incapable of oxidation to the dione, while still allowing the possibility for enolate formation. However, subjecting O-Me-didehydro-***1f** *to the Ru-catalysis conditions reported in this account only resulted in recovery of the starting material. No Michael addition product was observed, ruling out the possibility of a Ru-catalyzed enolate formation/Michael addition reaction pathway.*



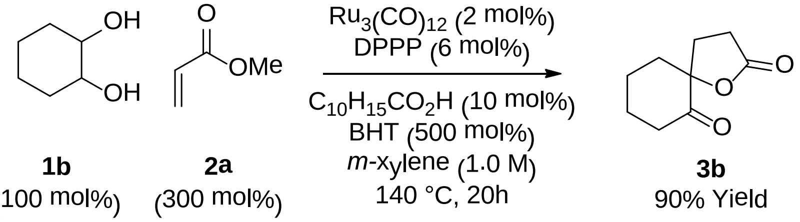
O-Me-*didehdyro*-**1f** (100 mol%)

2a (300 mol%)

Michael-Addition Product was Not Observed

Starting Material *O*-Me-*didehydro*-1f was Recovered Quantitatively

Radical Mechanism Probe: *Addition of 1, 3 or 5 equivalents of butylated hydroxyl toluene (BHT), a radical inhibitor, should slow or halt reaction progress if it proceeds through a radical mechanism. TLC evaluation of the reactions showed high conversion. The yield of the reaction with 5 equivalents of BHT additive is shown below. This suggests that a radical pathway does not account for the observed reactivity.*



1b (100 mol%)

2a (300 mol%)

3b 90% Yield