Supplementary Material (ESI) for Chemical Communications

Supporting Information

Enantioselective Organocatalytic Michael Additions to Acrylic Acid Derivatives: Generation of All-Carbon Quaternary Stereocentres

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Contents

General Experimental

For all reactions conducted under anhydrous conditions glassware was dried in an oven at 100^{o}C and carried out under a nitrogen atmosphere, unless otherwise stated.

Solvents and Reagents

Bulk solutions were evaporated under reduced pressure using a Büchi rotary evaporator. Reagents used were obtained from commercial suppliers or purified according to standard procedures. Petrol refers to distilled light petroleum of fraction (40 – 65 °C). Anhydrous tetrahydrofuran and diethyl ether were freshly distilled from sodium-benzophenone.

Chromatography

Flash column chromatography was performed with commercial solvents using Merck Kieselgel 60 silica gel (200-400 mesh). Thin layer chromatography (TLC) was performed on aluminium or glass plates pre-coated with Merck Kieselgel 60 F254 and visualised by ultra-violet radiation or by staining with either aqueous basic potassium permanganate or vanillin. Enantiomeric excesses were determined using high performance liquid chromatography (HPLC) performed on a Hewlett-Packard Series 1050 series system (column conditions are given with the compound).

Melting Points

Melting points were recorded on a Gallenkamp melting point apparatus with the sample contained in a thin glass tube at ambient pressure and are uncorrected.

Polarimetry

Optical rotations were recorded using an Optical Activity AA-1000 polarimeter; specific rotations ($[\alpha]_D$) are reported in 10^{-1} deg•cm^2•g^{-1}; concentrations (c) are quoted in g•(100 mL)$^{-1}$; *D* refers to the D-line of sodium (589 nm); temperatures (*T*) are given in degrees Celsius (^{o}C).

Infra-Red Spectroscopy

Infrared spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrometer (thin film deposited onto a sodium chloride plate). Only selected absorbencies (ν_{max}) are reported.

NMR Spectroscopy

^{1}H, ^{13}C, DEPT, COSY and HMQC NMR spectra were recorded on Brucker 500 MHz and Varian 300 MHz spectrometers Chemical shifts (δ_H) are quoted in parts per million (ppm $\pm$ 0.01 ppm) downfield of tetramethylsilane, relative to the residual protiosolvent (δ_H (C**H**Cl_3) = 7.26 ppm) against an internal deuterium lock. Coupling constants (*J*) are given in Hertz (Hz $\pm$ 0.1 Hz). The ^{1}H NMR spectra are reported as follows: δ / ppm (multiplicity, coupling constants *J* / Hz, number of protons, assignment). DEPT and two-dimensional NMR spectroscopy (COSY and HMQC) were used where appropriate to assist the assignment of the signals in the ^{1}H NMR and ^{13}C NMR spectra.

Mass Spectrometry

Low resolution mass spectrometry (electron impact / chemical ionisation) was recorded on a Micromass Trio 2000 quadropole mass spectrometer and (electrospray) on a Micromass Platform II spectrometer. High resolution mass spectra (accurate mass) were recorded on a Thermo Finnigan Mat95XP mass spectrometer.

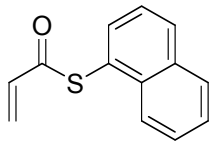
Starting Materials

Michael acceptor **3b** was prepared by the treatment of 1,2-dibromopropionyl chloride with ethanethiol followed by the elimination of bromine.[S1] Michael acceptors **3e** and **3h** were prepared by the treatment of acryloyl chloride with thiophenol or phenol.[S2,S3] Michael acceptor **3i** was prepared by the treatment of carbonyl dipyrrole with vinyl magnesium bromide.[S4] β-Keto esters **2**, **5**, **6** and **7** were prepared by acylation of the parent indanone followed by Sn-catalysed transesterification.[S5] β-Keto esters **8**, **9** and **10** were prepared by Dieckmann cyclisation of the corresponding open chain diester.[S6]

Michael Acceptors 3c, 3d, 3f, 3g

Michael acceptors **3c, 3d, 3f** and **3g** were prepared using a modified literature procedure as described here:[S2]

1-Naphthyl Thioacrylate 3c:

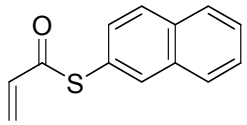


Acryloyl chloride (1.14 mL, 14 mmol) was added to a suspension of 1-thionaphthol (1 mL, 7 mmol) in 5 % aqueous NaOH solution (20 mL) at 0 °C. The mixture was stirred at 0°C for 2 minutes. It was then extracted into CH_2Cl_2 (20 mL x 2), washed with $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4. The solvent was removed *in vacuo* and the crude reaction mixture was subjected to flash column chromatography (eluting with 95:5 petrol:Et_2O) to furnish the title compound as a pale yellow oil (1.04 g, 69 %).

IR ν_{max} (film): 3056 (CH), 1685 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.19 (d, *J* = 8.2, 1H, Ar-*H*), 7.99 (d, *J* = 8.3, 1H, Ar-*H*), 7.92 (d, *J* = 7.6, 1H, Ar-*H*), 7.76 (dd, *J* = 7.1, 1.1, 1H, Ar-*H*), 7.63-7.48 (m, 3H, Ar-*H*), 6.56 (dd, *J* = 17.2, 10.2, 1H, C*H*$_2$=CH), 6.46 (dd, *J* = 17.2, 0.9, 1H, CH_2=C*H*), 5.83 (dd, *J* = 10.2, 0.9, 1H, C*H*$_2$=CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 188.3 (*C*=O), 135.2 (CH_2=*C*H), 134.3 (*C*H_2=CH), 134.2, 131.1, 128.7,

127.7, 127.3, 126.5, 125.6, 125.3, 124.6 (Ar-*C*); **MS**: *m/z* (CI) 232 (M + NH_4^+); **HRMS**: (ES^+) Found 232.0790. $C_{13}H_{14}ONS$ requires *M* 232.0791.

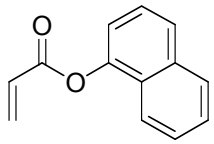
2-Naphthyl Thioacrylate 3d:



Acryloyl chloride (2.44 mL, 30 mmol) was added to a suspension of 2-thionaphthol (500 mg, 3 mmol) in 5% aqueous NaOH solution (25 mL) at 0 °C. The mixture was stirred at 0 °C for 5 minutes. It was then extracted into CH_2Cl_2 (20 mL x 2), washed with $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4 before being filtered. The solvent was removed *in vacuo* and the crude reaction mixture was subjected to flash column chromatography (eluting with 95:5 petrol:Et_2O) to furnish the title compound as a colourless solid (230 mg, 33 %).

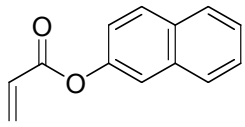
m.p. 75-77°C; **IR** ν_{max} (film): 3028, 3016 (CH), 1677 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.00 (s, 1H, Ar-*H*), 7.93-7.80 (m, 3H, Ar-*H*), 7.62-7.42 (m, 3H, Ar-*H*), 6.51 (dd, *J* = 17.2, 9.9, 1H, C*H*$_2$=CH), 6.44 (dd, *J* = 17.2, 1.1, 1H, CH_2=C*H*), 5.81 (dd, *J* = 9.9, 1.1, 1H, C*H*$_2$=CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 188.8 (*C*=O), 134.5 (CH_2=*C*H), 134.4 (*C*H_2=CH), 133.6, 133.4, 130.9, 128.9, 128.0, 127.8, 127.6, 127.2, 126.6, 124.5 (Ar-*C*); **MS**: *m/z* (CI) 232 (M + NH_4^+); **HRMS**: (ES^+) Found 232.0792. $C_{13}H_{14}ONS$ requires *M* 232.0791.

1-Naphthyl Acrylate 3f:



Acryloyl chloride (1.14 mL, 14 mmol) was dissolved in CH_2Cl_2 (5 mL) and added dropwise to a solution of 1-naphthol (2 g, 14 mmol) and Et_3N (2.5 mL, 18 mmol) in CH_2Cl_2 (10 mL) under an atmosphere of N_2. The mixture was stirred at room temperature for 30 minutes. The reaction mixture was extracted into CH_2Cl_2 (20 mL x 2) and washed with brine (20 mL); it was then dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude reaction mixture was subjected to flash column chromatography on silica gel (eluting with 9:1 petrol:EtOAc) to afford the title compound as a yellow oil (2.445 g, 88 %).
IR ν_{max} (film): 3062 (CH), 1742 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.92-7.84 (m, 2H, Ar-*H*), 7.77 (d, *J* = 8.29, 1H, Ar-*H*), 7.55-7.45 (m, 3H, Ar-*H*), 7.30 (dd, *J* = 7.45, 0.86, 1H, Ar-*H*), 6.75 (dd, *J* = 17.3, 1.1, 1H, C*H*$_2$=CH), 6.50 (dd, *J* = 17.3, 10.5, 1H, CH_2=C*H*), 6.12 (dd, *J* = 10.5, 1.1, 1H, C*H*$_2$=CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 164.6 (*C*=O), 146.5 (CH_2=*C*H), 134.7 (*C*H_2=CH), 133.0, 128.1, 127.8, 126.8, 126.5, 126.5, 126.1, 125.4, 121.2, 118.1 (Ar-*C*); **MS**: *m/z* (CI) 216 (M + NH_4^+); **HRMS**: (ES^+) Found 216.1022. $C_{13}H_{14}O_2N$ requires *M* 216.1019.

2-Naphthyl Acrylate 3g:

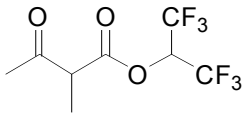


Acryloyl chloride (1.14 mL, 14 mmol) was dissolved in CH_2Cl_2 (5 mL) and added dropwise to a solution of 2-naphthol (2 g, 14 mmol) and Et_3N (2.5 mL, 18 mmol) in CH_2Cl_2 (10 mL) under an atmosphere of N_2. The mixture was stirred at room temperature for 30 minutes. The reaction mixture was extracted into CH_2Cl_2 (20 mL x 2) and washed with brine (20 mL); it was then dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude reaction mixture was

subjected to flash column chromatography on silica gel (eluting with 9:1 petrol:EtOAc) to afford the title compound as a colourless solid (2.285 g, 82 %).

m.p. 43-45°C; **IR** ν_{max} (film): 3058, 3034 (CH), 1742 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.90-7.79 (m, 3H, Ar-*H*), 7.62 (d, *J* = 2.3, 1H, Ar-*H*), 7.52-7.45 (m, 2H, Ar-*H*), 7.28 (dd, *J* = 8.8, 2.3, 1H, Ar-*H*), 6.66 (dd, *J* = 17.3, 1.2, 1H, CH_2=CH), 6.39 (dd, *J* = 17.3, 10.4, 1H, CH_2=C*H*), 6.06 (dd, *J* = 10.4, 1.2, 1H, CH_2=CH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 164.8 (*C*=O), 148.2 (CH_2=*C*H), 133.8 (*C*H_2=CH), 132.7, 131.5, 129.5, 128.0, 127.8, 127.7, 126.6, 125.8, 121.1, 118.5 (Ar-*C*); **MS**: *m/z* (CI) 216 (M + NH_4^+); **HRMS**: (ES^+) Found 216.1028. $C_{13}H_{14}O_2N$ requires *M* 216.1019.

1,1,1,3,3,3-hexafluoropropan-2-yl 2-methyl-3-oxobutanoate 11:

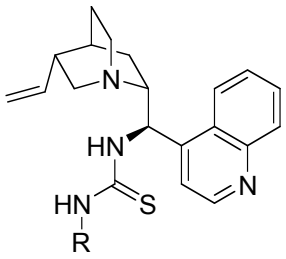


2-Methyl-3-oxobutanoic acid (1.99 g, 17 mmol), was dissolved in CH_2Cl_2 (50 ml) and cooled to 0°C. DMAP (1.04 g, 8.5 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (1.99 ml, 19 mmol) were added followed by EDC.HCl (3.58 g, 18.7 mmol) and the mixture was stirred for two hours. It was then warmed to room temperature, extracted into EtOAc (50 ml x 2) and washed with 1M HCl (30 ml), 1M $NaHCO_3$ (30 ml) and brine (30 ml). The combined organics were dried over Na_2SO_4, the solvent removed *in vacuo*, and the crude reaction mixture subjected to flash column chromatography on silica gel (eluting with 9:1 petrol:EtOAc) to afford the title compound as a pale yellow liquid (859 mg, 19 %).

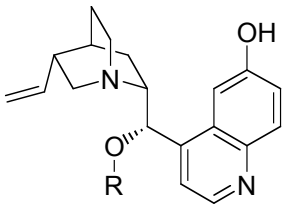
IR ν_{max} (film): 3439 (OH), 2950, 2973, 2888 (CH), 1790, 1726 (C=O); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H ppm: 11.81 (s, 0.1H, enol O*H*), 5.80 (sept., *J* = 6.2, 0.1H, C*H*(CF_3)$_2$), 5.73 (sept., *J* = 6.0, 0.9H, C*H*(CF_3)$_2$), 3.66 (q, *J* = 7.2, 0.9H, C*H*CH_3), 2.21 (s, 2.7H, COCH_3), 2.02 (s, 0.3H, COCH_3), 1.76 (s, 0.3H, CCH_3), 1.38 (d, *J* = 7.2, 2.7H, CHCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 201.1 (*C*=O), 167.5 (*C*=O), 120.2 (q, *J* = 282.2, CH(*C*F_3)$_2$), 66.9 (sept., *J* = 34.9, (*C*H(CF_3)$_2$), 52.7 (*C*HCH_3), 28.2 (C=O*C*H_3), 12.6 (CH*C*H_3); **MS**: *m/z* (ES^-) 265 (M – H^+); **HRMS**: (ES^-) Found 265.0299. $C_{13}H_{14}O_3F_6$ requires *M* 265.0305.

Structure of the Catalysts

Cinchona alkaloid based catalysts **1b**, **1c** and **1d** were prepared according to literature procedures.[S7,S8]

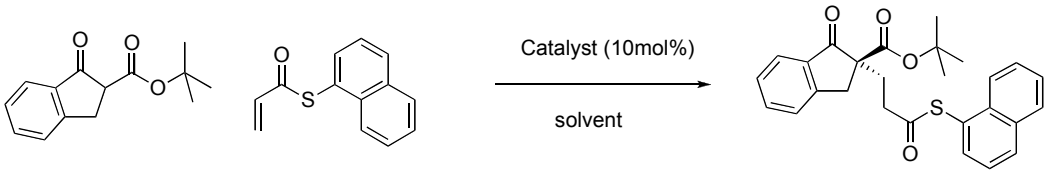


1b: R = 3,5-$(CF_3)_2$Ph



1c: R = Bn
1d: R =

Optimisation



2A **3b** **4Ab**

Michael acceptor **3c** (3 equivalents) was added to a solution of β-keto ester **2** (1 equivalent) followed by catalyst (10 mol %); the mixture was stirred until TLC analysis showed that all **2** had been consumed. The solvent was then removed *in vacuo* and the crude product subjected to flash column chromatography on silica gel (eluting with 95:5 petrol:Et_2O followed by 9:1 petrol:EtOAc) to afford the desired product **4c**.

Details of optimisation of Michael addition of **2** to **3c** are shown below:

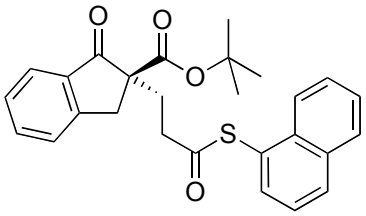
Entry	Catalyst	**Solvent**	**Conc. (M)**	**Reaction Time**	**Temp (°C)**	**Conv. (%)**	**e.e. (%)**
1	**1b**	CH_2Cl_2	1	30 mins	r.t.	>95	40
2	**1c**	CH_2Cl_2	1	30 mins	r.t.	>95	82
3	**1c**	CH_2Cl_2	1	30 mins	0	>95	86
4	**1c**	CH_2Cl_2	1	30 mins	-20	>95	88
5	**1c**	CH_2Cl_2	⅓	90 mins	-20	>95	90

6	**1c**	Toluene	⅓	2 hours	-20	>95	82
7	**1c**	THF	⅓	90 mins	-20	>95	74
8	**1c**	TBME	⅓	2 hours	-20	80	85
9	**1c**	EtOAc	⅓	90 mins	-20	>95	79
10	**1c**	$CHCl_3$	⅓	90 mins	-20	>95	90
11	**1c**	Me_2CO	⅓	2 hours	-20	>95	70
12	**1c**	Et_2O	⅓	2 hours	-20	>95	84
13	**1c**	MeCN	⅓	2 hours	-20	>95	76
14	**1d**	CH_2Cl_2	⅓	2 hours	-20	>95	96

Optimised General procedure for Michael addition

A ⅓M solution of β-keto ester (1 equivalent) in CH_2Cl_2 was cooled to -20°C. Michael acceptor (3 equivalents) was added followed by catalyst **1d** (10 mol %) and the mixture was stirred at -20 °C until TLC analysis showed that all β-keto ester had been consumed. The solvent was then removed *in vacuo* and the crude product subjected to flash column chromatography on silica gel (eluting with 95:5 petrol:Et_2O followed by 9:1 petrol:EtOAc) to afford the desired product.

(*S*)-*tert*-butyl 2-(3-(naphthalen-1-ylthio)-3-oxopropyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4c:



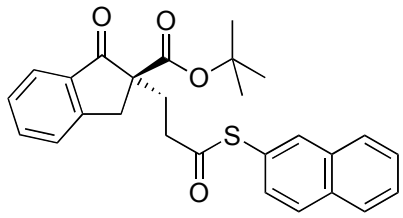
The product was isolated as a colourless solid (38 mg, 83 %).

e.e.: 96 % (Chiralcel OD, 96:4 hexanes:IPA, 1mL/min, t_R = 34.6 min (minor), 40.2 min (major)).

m.p. 104-108°C; **IR** ν_{max} (film): 3054, 2975, 2930 (CH), 1734, 1708 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.14 (d, *J* = 8.3, 1H, Ar-*H*), 7.93 (d, *J* = 8.2, 1H, Ar-*H*), 7.87 (d, *J* = 7.7, 1H, Ar-*H*), 7.78 (d, *J* = 7.7, 1H, Ar-*H*), 7.68-7.60 (m, 2H, Ar-*H*), 7.58-7.45 (m, 4H, Ar-

H), 7.41 (t, *J* = 7.5, 1H, Ar-*H*), 3.65 (d, *J* = 17.2, 1H, indanone CH_AH$_B$), 3.04 (d, *J* = 17.2, 1H, indanone CH$_A$$H_B$), 2.92 (ddd, *J* = 14.2, 9.4, 3.8, 1H, CH$_2$CH_AH$_B$COSAr), 2.83 (ddd, *J* = 16.1, 11.0, 5.2, 1H, CH$_2$CH$_A$$H_B$COSAr), 2.43 (ddd, *J* = 14.0, 11.0, 5.1, 1H, CH_AH$_B$CH$_2$COSAr), 2.28 (ddd, *J* = 14.0, 11.1, 5.2, 1H, CH$_A$$H_BCH_2$COSAr), 1.41 (s, 9H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, CDCl$_3$) δ_C ppm: 202.3 (*C*=O), 196.5 (*C*=O), 169.7 (*C*=O), 152.7, 135.4, 135.1, 135.0, 134.2, 134.1, 131.0, 128.6, 127.9, 127.2, 126.4, 126.4, 125.6, 125.3, 125.0, 124.8 (Ar-*C*), 82.3 (quaternary *C*), 60.2 (*C*(CH$_3$)$_3$), 39.3 (indanone *C*H$_2$), 37.5 (CH$_2$*C*H$_2$COSAr), 30.0 (*C*H$_2$CH$_2$COSAr), 27.9 (C(*C*H$_3$)$_3$); **MS:** *m/z* (ES$^+$) 464 (M + NH$_4^+$); **HRMS:** (ES$^+$) Found 464.1887. $C_{27}H_{30}O_4NS$ requires *M* 464.1890; **$[\alpha]_D^{23}$:** -28.4 (c 1, CHCl$_3$).

(*S*)-*tert*-butyl 2-(3-(naphthalen-2-ylthio)-3-oxopropyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4d:



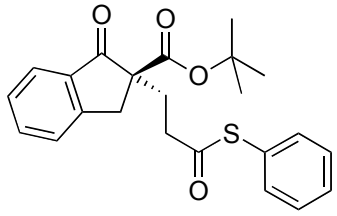
The product was isolated as a colourless solid (33 mg, 75 %).

e.e.: 95% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/min, t_R = 23.3 min (minor), 29.9 min (major)).

m.p. 92-95°C; **IR** ν_{max} (film): 3054, 2977, 2930 (CH), 1732, 1710 (C=O); **^{1}H NMR** (500 MHz, CDCl$_3$) δ_H ppm: 7.92 (s, 1H, Ar-*H*), 7.88-7.74 (m, 4H, Ar-*H*), 7.63 (dt, *J* = 7.6, 1.1, 1H, Ar-*H*), 7.55-7.45 (m, 3H, Ar-*H*), 7.44-7.38 (m, 2H, Ar-*H*), 3.65 (d, *J* = 17.2, 1H, indanone CH_AH$_B$), 3.05 (d, *J* = 17.2, 1H, indanone CH$_A$$H_B$), 2.87 (ddd, *J* = 15.9, 11.1, 5.1, 1H, CH$_2$CH_AH$_B$COSAr), 2.76 (ddd, *J* = 16.0, 11.0, 5.1, 1H, CH$_2$CH$_A$$H_B$COSAr), 2.43 (ddd, *J* = 14.0, 11.0, 5.1, 1H, CH_AH$_B$CH$_2$COSAr), 2.27 (ddd, *J* = 14.0, 11.1, 5.2, 1H, CH$_A$$H_BCH_2$COSAr), 1.41 (s, 9H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, CDCl$_3$) δ_C ppm: 202.2 (*C*=O), 196.9 (*C*=O), 169.7 (*C*=O), 152.7, 135.4, 135.2, 134.4, 133.5, 133.3, 130.9, 128.8, 128.0, 127.9, 127.8, 127.2, 126.6, 126.4, 124.9, 124.8 (Ar-*C*), 82.3 (quaternary *C*), 60.2 (*C*(CH$_3$)$_3$), 39.3 (indanone *C*H$_2$), 37.5 (CH$_2$*C*H$_2$COSAr), 30.0 (*C*H$_2$CH$_2$COSAr), 27.8

($C(CH_3)_3$); **MS:** *m/z* (ES^+) 464 ($M + NH_4^+$); **HRMS:** (ES^+) Found 464.1884. $C_{27}H_{30}O_4NS$ requires *M* 464.1890; $[\alpha]_D^{23}$**:** -16.8 (c 0.5, $CHCl_3$).

(*S*)-*tert*-butyl 1-oxo-2-(3-oxo-3-(phenylthio)propyl)-2,3-dihydro-1*H*-indene-2-carboxylate 4e:

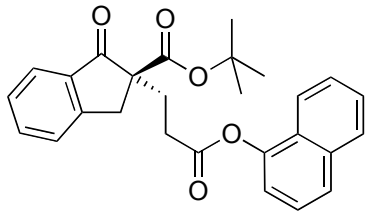


The product was isolated as a yellow oil (314 mg, 83 %).

e.e.: 95% (Chiralpak AS, 98:2 hexanes:IPA, 1mL/min, t_R = 16.3 min (major), 19.0 min (minor)).

IR ν_{max} (film): 2976, 2928 (CH), 1734, 1709 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.77 (d, *J* = 7.7, 1H, Ar-*H*), 7.63 (dt, *J* = 7.5, 1.2, 1H, Ar-*H*), 7.48 (d, *J* = 7.7, 1H, Ar-*H*), 7.43-7.35 (m, 6H, Ar-*H*), 3.64 (d, *J* = 17.2, 1H, indanone CH_AH_B), 3.03 (d, *J* = 17.2, 1H, indanone CH_AH_B), 2.83 (ddd, *J* = 16.0, 11.1, 5.1, 1H, $CH_2CH_AH_BCOSAr$), 2.72 (ddd, *J* = 16.2, 11.0, 5.2, 1H, $CH_2CH_AH_BCOSAr$), 2.40 (ddd, *J* = 14.0, 11.0, 5.1, 1H, $CH_AH_BCH_2COSAr$), 2.24 (ddd, *J* = 14.0, 11.1, 5.2, 1H, $CH_AH_BCH_2COSAr$), 1.41 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.2 (*C*=O), 196.7 (*C*=O), 169.7 (*C*=O), 152.7, 135.4, 135.1, 134.5, 129.4, 129.2, 127.9, 127.5, 126.4, 124.8 (Ar-*C)*, 82.3 (quaternary *C*), 60.2 ($C(CH_3)_3$) , 39.2 (indanone CH_2), 37.5 (CH_2CH_2COSAr), 30.0 (CH_2CH_2COSAr), 27.8 ($C(CH_3)_3$); **MS:** *m/z* (ES^+) 414 ($M + NH_4^+$); **HRMS:** (ES^+) Found 414.1736. $C_{27}H_{30}O_4NS$ requires *M* 414.1734; $[\alpha]_D^{22}$**:** -29.6 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 2-(3-(naphthalen-1-yloxy)-3-oxopropyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4f:

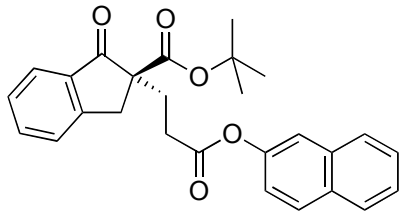


The product was isolated as a pale yellow oil (34 mg, 83 %).

e.e. 94% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/min, t_R = 27.7 min (minor), 37.9 min (major)).

IR ν_{max} (film): 3063, 2977, 2932 (CH), 1760, 1735, 1711 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.88-7.80 (m, 3H, Ar-*H*), 7.73 (d, *J* = 8.3, 1H, Ar-*H*), 7.65 (dt, *J* = 7.6, 0.9, 1H, Ar-*H*), 7.54-7.39 (m, 5H, Ar-*H*), 7.23 (dd, *J* = 7.5, 0.4, 1H, Ar-*H*), 3.71 (d, *J* = 17.2, 1H, indanone CH_AH$_B$), 3.15 (d, *J* = 17.2, 1H, indanone CH$_A$$H_B$), 2.96 (ddd, *J* = 16.4, 10.3, 5.3, 1H, CH$_2$CH_AH$_B$CO$_2$Ar), 2.83 (ddd, *J* = 16.4, 10.9, 5.4, 1H, CH$_2$CH$_A$$H_BCO_2$Ar), 2.53 (ddd, *J* = 14.1, 10.9, 5.3, 1H, CH_AH$_B$CH$_2$CO$_2$Ar), 2.45 (ddd, *J* = 14.1, 11.0, 5.4, 1H, CH$_A$$H_BCH_2CO_2$Ar), 1.44 (s, 1H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.5 (*C*=O), 171.5 (*C*=O), 170.0 (*C*=O), 152.7, 146.5, 135.4, 135.3, 134.6, 128.0, 127.9, 126.7, 126.5, 126.4, 126.4, 126.0, 125.4, 124.9, 121.2, 118.0 (Ar-*C*), 82.3 (quaternary *C*), 60.1 (*C*(CH$_3$)$_3$), 37.8 (indanone *C*H$_2$), 30.0 (CH$_2$*C*H$_2$CO$_2$Ar), 29.7 (*C*H$_2$CH$_2$CO$_2$Ar), 27.9 (C(*C*H$_3$)$_3$); **MS** *m/z* (ES$^+$) 453 (M + Na$^+$); **HRMS** (ES$^+$) Found 453.1681. $C_{27}H_{26}O_5Na$ requires *M* 453.1672; **$[\alpha]_D^{22}$:** -24 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 2-(3-(naphthalen-2-yloxy)-3-oxopropyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4g:

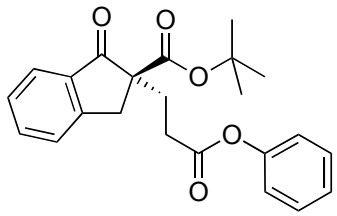


The product was isolated as a colourless solid (31 mg, 76 %).

e.e.: 94% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/min, t_R = 30.3 min (minor), 47.6 (major)).

m.p. 92-94°C; **IR** ν_{max} (film): 3058, 2976, 2930 (CH), 1756, 1736, 1710 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.86-7.76 (m, 4H, Ar-*H*), 7.64 (dt, *J* = 7.5, 1.1, 1H, Ar-*H*), 7.55-7.39 (m, 5H, Ar-*H*), 7.21 (dd, *J* = 8.9, 2.3, 1H, Ar-H), 3.69 (d, *J* = 17.2, 1H, indanone CH_AH$_B$), 3.12 (d, *J* = 17.2, 1H, indanone CH$_A$$H_B$), 2.82 (ddd, *J* = 16.3, 10.9, 5.4, 1H, CH$_2$CH_AH$_B$CO$_2$Ar), 2.69 (ddd, *J* = 16.3, 10.8, 5.4, 1H, CH$_2$CH$_A$$H_BCO_2$Ar), 2.47 (ddd, *J* = 14.1, 10.8, 5.4, 1H, CH_AH$_B$CH$_2$CO$_2$Ar), 2.38 (ddd, *J* = 14.1, 10.9, 5.4, 1H, CH$_A$$H_BCH_2CO_2$Ar), 1.43 (s, 1H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.5 (*C*=O), 171.7 (*C*=O), 169.9 (*C*=O), 152.7, 148.3, 135.4, 135.3, 133.7, 131.4, 129.4, 127.9, 127.8, 127.7, 126.5, 126.4, 125.7, 124.8, 121.1, 118.5 (Ar-*C*), 82.3 (quaternary *C*), 60.1 (*C*(CH$_3$)$_3$), 37.7 (indanone *C*H$_2$), 30.1 (CH$_2$*C*H$_2$CO$_2$Ar), 29.6 (*C*H$_2$CH$_2$CO$_2$Ar), 27.9 (C(*C*H$_3$)$_3$); **MS** *m/z* (ES$^+$) 453 (M + Na$^+$); **HRMS** (ES$^+$) Found 453.1675. $C_{27}H_{26}O_5Na$ requires *M* 453.1672; **$[\alpha]_D^{22}$:** -20 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 1-oxo-2-(3-oxo-3-phenoxypropyl)-2,3-dihydro-1*H*-indene-2-carboxylate 4h:

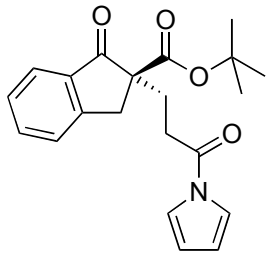


The product was isolated as a colourless solid (28 mg, 78 %).

e.e. 94% (Chiralpak IA, 97:3 hexanes:IPA, 1mL/min, t_R = 21.1 min (minor), 22.4 min (major)).

m.p. 102-104°C; **IR** ν_{max} (film): 3039, 2977, 2932 (CH), 1756, 1736, 1711 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.79 (d, *J* = 7.7, 1H, Ar-*H*), 7.63 (dt, *J* = 7.5, 1.1, 1H, Ar-*H*), 7.49 (d, *J* = 7.7, 1H, Ar-*H*), 7.41 (t, *J* = 7.4, 1H, Ar-*H*), 7.38-7.33 (m, 2H, Ar-*H*), 7.21 (t, *J* = 7.4, 1H, Ar-*H*), 7.08-7.02 (m, 2H, Ar-*H*), 3.67 (d, *J* = 17.2, 1H, indanone CH_AH_B), 3.10 (d, *J* = 17.2, 1H, indanone CH_AH_B), 2.76 (ddd, *J* = 16.3, 10.9, 5.3, 1H, $CH_2CH_AH_BCO_2Ar$), 2.62 (ddd, *J* = 16.3, 10.8, 5.4, 1H, $CH_2CH_AH_BCO_2Ar$), 2.43 (ddd, *J* = 14.1, 10.8, 5.3, 1H, $CH_AH_BCH_2CO_2Ar$), 2.33 (ddd, *J* = 14.1, 11.0, 5.4, 1H, $CH_AH_BCH_2CO_2Ar$), 1.41 (s, 1H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.4 (*C*=O), 171.5 (*C*=O), 169.9 (*C*=O), 152.7, 150.6, 135.4, 135.3, 129.4, 127.9, 126.4, 125.8, 124.8, 121.5 (Ar-*C*), 82.3 (quaternary *C*), 60.1 ($C(CH_3)_3$), 37.6 (indanone CH_2), 30.0 ($CH_2CH_2CO_2Ar$), 29.5 ($CH_2CH_2CO_2Ar$), 27.8 ($C(CH_3)_3$); **MS** *m/z* (ES^+) 403 ($M + Na^+$); **HRMS** (ES^+) Found 403.1520. $C_{23}H_{24}O_5Na$ requires *M* 403.1516; **$[\alpha]_D^{22}$:** -32 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 1-oxo-2-(3-oxo-3-(1H-pyrrol-1-yl)propyl)-2,3-dihydro-1*H*-indene-2-carboxylate 4i:

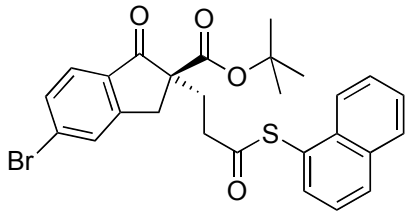


The product was isolated as a colourless solid (32 mg, 96 %).

e.e. 95% (Chiralpak AS-H, 98:2 hexanes:IPA, 1mL/min, t_R = 22.4 min (major), 29.2 min (minor)).

m.p. 86-90°C; **IR** ν_{max} (film): 3147, 2978, 2932 (CH), 1717 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 7.78 (d, *J* = 7.7, 1H, Ar-*H*), 7.63 (t, *J* = 7.4, 1H, Ar-*H*), 7.48 (d, *J* = 7.7, 1H, Ar-*H*), 7.41 (t, *J* = 7.4, 1H, Ar-*H*), 7.35-7.27 (m, 2H, pyrrole-*H*), 6.28 (t, *J* = 2.2, 2H, pyrrole-*H*), 3.65 (d, *J* = 17.2, 1H, indanone- CH_AH$_B$), 3.13-3.04 (m, 2H, indanone CH$_A$$H_B$ and CH$_2$CH_AH$_B$CON), 3.01-2.91 (m, 1H, CH$_2$CH$_A$$H_B$CON), 2.37 (t, *J* = 8.0, 2H, CH_2CH$_2$CON), 1.38 (s, 9H, C(CH_3)$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.5 (*C*=O), 170.1 (*C*=O), 152.5 (*C*=O), 135.4, 135.6, 127.9, 126.4, 124.8 (Ar-*C*), 119.1, 113.2 (pyrrole-*C*), 82.3 (quaternary *C*), 59.9 (*C*(CH$_3$)$_3$), 38.2 (indanone *C*H$_2$), 30.3 (CH$_2$*C*H$_2$CON), 29.5 (*C*H$_2$CH$_2$CON), 27.8 (C(*C*H$_3$)$_3$); **MS** *m/z* (ES$^+$): 376 (M + Na$^+$), 412 (M + MeCN + NH$_4^+$); **HRMS** (ES$^+$): Found 376.1510. $C_{21}H_{23}O_4NNa$ requires *M* 376.1519; **$[\alpha]_D^{22}$:** -37.6 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 5-bromo-2-(3-(naphthalen-1-ylthio)-3-oxopropyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 12c:

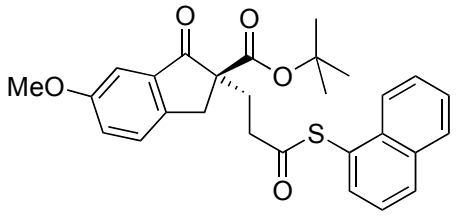


The product was isolated as a colourless solid (411 mg, 78 %).

e.e. 93% (Chiralcel OD, 95:5 hexanes:IPA, 1mL/min, t_R = 50.3 min (minor), 76.4 min (major)).

m.p. 103-105°C; **IR** ν_{max} (film): 3057, 2977, 2931 (CH), 1735, 1711 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.14 (d, *J* = 8.2, 1H, Ar-*H*), 7.94 (d, *J* = 8.2, 1H, Ar-*H*), 7.88 (d, *J* = 7.6, 1H, Ar-*H*), 7.70-7.63 (m, 3H, Ar-*H*), 7.60-7.48 (m, 4H, Ar-*H*), 3.61 (d, *J* = 17.5, 1H, indanone CH_AH$_B$), 2.99 (d, *J* = 17.4, 1H, indanone CH$_A$$H_B$), 2.90 (ddd, *J* = 15.9, 10.8, 5.1, 1H, CH$_2$CH_AH$_B$COSAr), 2.78 (ddd, *J* = 15.9, 10.8, 5.3, 1H, CH$_2$CH$_A$$H_B$COSAr), 2.41 (ddd, *J* = 14.2, 10.8, 5.1, 1H, CH_AH$_B$CH$_2$COSAr), 2.26 (ddd, *J* = 14.1, 10.9, 5.3, 1H, CH$_A$$H_BCH_2$COSAr), 1.41 (s, 9H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 201.0 (*C*=O), 196.4 (*C*=O), 169.3 (*C*=O), 154.2, 135.0, 134.2, 134.0, 131.6, 131.0, 130.9, 129.7, 128.7, 127.3, 126.5, 126.0, 125.6, 125.2, 124.9 (Ar-*C*), 82.6 (quaternary *C*), 60.3 (*C*(CH$_3$)$_3$), 39.1 (indanone *C*H$_2$), 37.1 (CH$_2$*C*H$_2$CO$_2$Ar), 29.8 (*C*H$_2$CH$_2$CO$_2$Ar), 27.8 (C(*C*H$_3$)$_3$); **MS** *m/z* (ES$^+$) 547 (M + Na$^+$); **HRMS** (ES$^+$) Found 547.0552. $C_{27}H_{25}O_4BrNaS$ requires *M* 547.0549; **$[\alpha]_D^{22}$:** -10 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 6-methoxy-2-(3-(naphthalen-1-ylthio)-3-oxopropyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 13c:

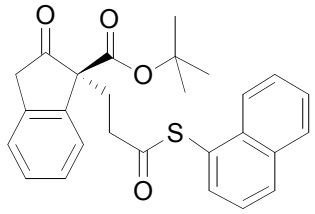


The product was isolated as a colourless solid (447 mg, 90 %).

e.e. 94% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/ min, t_R = 35.6 min (minor), 47.9 min (major)).

m.p. 84-86°C; **IR** ν_{max} (film): 3056, 2975, 2932, 2837 (CH), 1734, 1707 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.15 (d, *J* = 8.3, 1H, Ar-*H*), 7.93 (d, *J* = 8.2, 1H, Ar-*H*), 7.87 (d, *J* = 7.6, 1H, Ar-*H*), 7.67 (dd, *J* = 1.1, 7.1, 1H, Ar-*H*), 7.58-7.46 (m, 3H, Ar-*H*), 7.35 (d, *J* = 8.3, 1H, Ar-*H*), 7.24-7.17 (m, 2H, Ar-*H*), 3.84 (s, 1H, OCH_3), 3.55 (d, *J* = 17.0, 1H, indanone CH_AH_B), 2.99-2.86 (m, 2H, indanone CH_AH_B and $CH_2CH_AH_BCOSAr$), 2.78 (ddd, *J* = 15.8, 11.0, 5.2, 1H, $CH_2CH_AH_BCOSAr$), 2.41 (ddd, *J* = 14.0, 11.0, 5.1, 1H, $CH_AH_BCH_2COSAr$), 2.29 (ddd, *J* = 14.0, 11.1, 5.2, 1H, $CH_AH_BCH_2COSAr$), 1.38 (m, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.3 (*C*=O), 196.5 (*C*=O), 169.8 (*C*=O), 159.7, 145.6, 136.4, 135.0, 134.2, 134.1, 131.0, 128.6, 127.2, 127.1, 126.4, 125.6, 125.3, 125.0, 124.9, 105.7 (Ar-*C*), 82.3 (quaternary *C*), 60.9 ($C(CH_3)_3$), 55.6 (OCH_3), 39.3 (indanone CH_2), 36.9 ($CH_2CH_2CO_2Ar$), 30.0 ($CH_2CH_2CO_2Ar$), 27.9 ($C(CH_3)_3$); **MS** *m/z* (ES^+) 499 ($M + Na^+$); **HRMS** (ES^+) Found 499.1547. $C_{28}H_{28}O_5NaS$ requires *M* 499.1550; **$[\alpha]_D^{23}$:** -33.6 (c 1, $CHCl_3$).

(*S*)-*tert*-butyl 1-(3-(naphthalen-1-ylthio)-3-oxopropyl)-2-oxo-2,3-dihydro-1H-indene-1-carboxylate 14c:

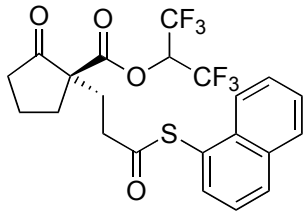


The product was isolated as a pale yellow oil (42 mg, 95 %).

e.e. 88% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/ min, t_R = 15.3 min (major), 35.4 min (minor)).

IR ν_{max} (film): 2977 (CH), 1757, 1728 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.09 (d, *J* = 8.0, 1H, Ar-*H*), 7.92 (d, *J* = 8.2, 1H, Ar-*H*), 7.87 (d, *J* = 7.4, 1H, Ar-*H*), 7.62 (dd, *J* = 7.1, 1.0, 1H, Ar-*H*), 7.57-7.44 (m, 3H, Ar-*H*), 7.38-7.26 (m, 4H, Ar-*H*), 3.79 (d, *J* = 22.5, 1H, indanone CH_AH$_B$), 3.51 (d, *J* = 22.5, 1H, indanone CH$_A$$H_B$), 2.67-2.47 (m, 4H, CH_2CH_2COSAr and CH_AH$_B$$CH_2$COSAr), 1.33 (m, 1H, C(C$H_3$)$_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 212.0 (*C*=O), 196.1 (*C*=O), 168.7 (*C*=O), 140.3, 137.3, 135.0, 134.2, 134.1, 130.9, 128.7, 128.1, 127.2, 126.4, 125.5, 125.3, 125.2, 125.0, 123.9 (Ar-*C*), 82.7 (quaternary *C*), 64.9 (*C*(CH$_3$)$_3$), 43.4 (indanone *C*H$_2$), 38.8 (CH_2CH_2COSAr), 28.7 (*C*H$_2$CH$_2$COSAr), 27.7 (C(*C*H$_3$)$_3$); **MS** *m/z* (ES$^+$) 469 (M + Na$^+$); **HRMS** (ES$^+$) Found 469.1447. $C_{27}H_{26}O_4NaS$ requires *M* 469.1444; **$[\alpha]_D^{23}$:** +19.2 (c 2, $CHCl_3$).

(*R*)-1,1,1,3,3,3-hexafluoropropan-2-yl 1-(3-(naphthalen-1-ylthio)-3-oxopropyl)-2-oxocyclopentanecarboxylate 15c:

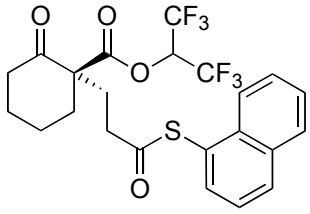


The product was isolated as a colourless oil (38 mg, 75 %).

e.e. 95% (Chiralpak AD, 98:2 hexanes:IPA, 1mL/min, t_R = 13.7 min (minor), 19.8 min (major)).

IR ν_{max} (film): 3059, 2971 (CH), 1780, 1745, 1708 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.16 (d, *J* = 8.3, 1H, Ar-*H*), 7.96 (d, *J* = 8.2, 1H, Ar-*H*), 7.89 (d, *J* = 7.7, 1H, Ar-*H*), 7.69 (d, *J* = 7.2, 1H, Ar-*H*), 7.54 (m, 3H, Ar-*H*), 5.78 (sept., 1H, *J* = 5.9, C*H*$(CF_3)_2$) 3.00 (ddd, 1H, *J* = 15.9, 9.9, 5.7, $CH_2CH_AH_BCOSAr$) 2.80 (m, 1H, $CH_2CH_AH_BCOSAr$) 2.43 (m, 4H, CH_2CH_2COSAr and 2 x cyclopentanone CH_2) 2.07 (m, 4H, cyclopentanone CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 211.6 (*C*=O), 196.3 (*C*=O), 168.2 (*C*=O), 135.1, 134.2, 131.1, 128.7, 127.3, 126.5, 125.6, 125.2, 124.7 (Ar-*C*), 120.2 (q, *J* = 275.9, $CH(CF_3)_2$), 66.9 (sept., *J* = 35.0, ($CH(CF_3)_2$), 58.9 (quaternary *C*), 38.6 (CH_2CH_2COSAr), 37.6 (CH_2CH_2COSAr), 33.7 (cyclopentanone CH_2), 28.2 (cyclopentanone CH_2), 19.6 (cyclopentanone CH_2); **MS** *m/z* (ES^+) 515 ($M + Na^+$), 551 ($M + MeCN + NH_4^+$); **HRMS** (EI) Found 492.0822. $C_{22}H_{18}O_4F_6S$ requires *M* 492.0825; **$[\alpha]_D^{22}$:** -2.4 (c 1, $CHCl_3$).

(*R*)-1,1,1,3,3,3-hexafluoropropan-2-yl 1-(3-(naphthalen-1-ylthio)-3-oxopropyl)-2-oxocyclohexanecarboxylate 16c:

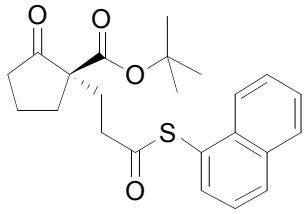


The product was isolated as a colourless oil (26 mg, 52 %).

e.e. 98% (Chiralcel OD, 96:4 hexanes:IPA, 1mL/min, t_R = 20.9 min (minor), 41.4 min (major)).

IR ν_{max} (film): 3058, 2950, 2870 (CH), 1769, 1728 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.14 (d, *J* = 8.3, 1H, Ar-*H*), 7.95 (d, *J* = 8.2, 1H, Ar-*H*), 7.89 (d, *J* = 7.6, 1H, Ar-*H*), 7.69 (dd, *J* = 7.1, 0.8, 1H, Ar-*H*), 7.53 (m, 3H, Ar-*H*), 5.83 (sept., *J* = 6.0, 1H, C*H*$(CF_3)_2$), 2.85 (ddd, *J* = 16.1, 10.9, 5.2, 1H, $CH_2CH_AH_BCOSAr$), 2.68 (ddd, 1H, *J* = 16.1, 10.9, 5.3, 1H, $CH_2CH_AH_BCOSAr$), 2.49 (m, 3H, cyclohexanone CH_2), 2.35 (ddd, 1H, *J* = 14.4, 10.9, 5.2, $CH_AH_BCH_2COSAr$), 2.14 (ddd, 1H, *J* = 14.4, 10.9, 5.3, $CH_AH_BCH_2COSAr$), 2.04 (m, 1H, cyclohexanone CH_2), 1.84 (m, 1H, cyclohexanone CH_2), 1.71 (m, 3H, cyclohexanone CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 205.3 (*C*=O), 196.1 (*C*=O), 169.1 (*C*=O), 135.1, 134.2, 131.0, 128.6, 127.2, 126.5, 125.6, 125.1, 124.8 (Ar-*C*), 120.2 (q, *J* = 284.9, CH(*C*$F_3)_2$), 66.8 (sept., *J* = 34.8, (*C*H$(CF_3)_2$), 58.4 (quaternary *C*), 40.5 (CH_2CH_2COSAr), 38.4 (CH_2CH_2COSAr), 36.0 (cyclohexanone *C*H_2), 29.7 (cyclohexanone *C*H_2), 27.2 (cyclohexanone *C*H_2), 21.9 (cyclohexanone *C*H_2); **MS** *m/z* (ES^+) 529 (M + Na^+), 565 (M + MeCN + NH_4^+); **HRMS** (ES^+) Found 529.0876. $C_{23}H_{20}O_4F_6NaS$ requires *M* 529.0879; **$[\alpha]_D^{22}$:** +7.85 (c 2, $CHCl_3$).

(*R*)-*tert*-butyl 1-(3-(naphthalen-1-ylthio)-3-oxopropyl)-2-oxocyclopentanecarboxylate 17c:

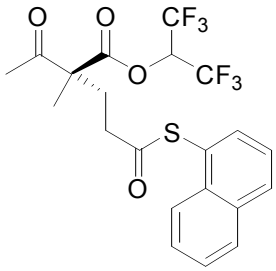


The product was isolated as a colourless oil (25 mg, 64 %).

e.e. 67% (Chiralcel AD, 95:5 hexanes:IPA, 1mL/ min, t_R = 10.8 min (minor), 12.2 min (major)).

IR ν_{max} (film): 2975 (CH), 1746, 1716 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.18 (d, *J* = 8.4, 1H, Ar-*H*), 7.94 (d, *J* = 8.2, 1H, Ar-*H*), 7.88 (d, *J* = 8.5, 1H, Ar-*H*), 7.69 (dd, *J* = 7.1, 1.0, 1H, Ar-*H*), 7.60-7-45 (m, 3H, Ar-*H*), 3.02 (ddd, *J* = 15.8, 10.5, 5.3, 1H, $CH_2CH_AH_BCOSAr$), 2.77 (ddd, 1H, *J* = 15.9, 10.6, 5.3, $CH_2CH_AH_BCOSAr$), 2.50-2.35 (m, 2H, $CH_AH_BCH_2COSAr$ and cyclopentanone CH_2), 2.31-2.15 (m, 2H, $CH_AH_BCH_2COSAr$ and cyclopentanone CH_2), 2.08-1.81 (m, 4H, cyclopentanone CH_2), 1.44 (m, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 214.6 (*C*=O), 196.7 (*C*=O), 170.2 (*C*=O), 135.0, 134.2, 134.2, 130.9, 128.6, 127.2, 126.4, 125.6, 125.3, 125.2 (Ar-*C*), 82.3 ($C(CH_3)_3$), 59.7 (quaternary *C*), 39.2 (CH_2CH_2COSAr), 37.9 (CH_2CH_2COSAr), 34.1 (cyclopentanone CH_2), 28.7 (cyclopentanone CH_2), 27.9 ($C(CH_3)_3$), 19.6 (cyclopentanone CH_2); **MS** *m/z* (ES^+) 421 ($M + Na^+$); **HRMS** (ES^+) Found 421.1445. $C_{23}H_{26}O_4NaS$ requires *M* 421.1444; **$[\alpha]_D^{23}$:** +5.6 (c 1, $CHCl_3$).

(*R*)-1,1,1,3,3,3-hexafluoropropan-2-yl 2-acetyl-2-methyl-5-(naphthalen-1-ylthio)-5-oxopentanoate 18c:

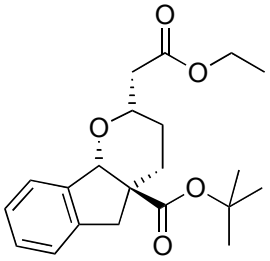


The product was isolated as a colourless oil (56 mg, 58%).

e.e. 71% (Chiralcel IA, 95:5 hexanes:IPA, 1mL/ min, t_R = 13.4 min (minor), 19.1 min (major)).

M.p. 59-62˚; **IR** ν_{max} (film): 3058, 2972 (CH), 1778, 1716 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H ppm: 8.15 (d, *J* = 8.2, 1H, Ar-*H*), 7.96 (d, *J* = 8.2, 1H, Ar-*H*), 7.90 (d, *J* = 7.6, 1H, Ar-H), 7.69 (dd, *J* = 7.2, 0.9, 1H, Ar-*H*), 7.60-7.48 (m, 1H, 3H), 5.82 (sept., *J* = 6.0, 1H, C*H*$(CF_3)_2$), 2.74 (t, *J* = 8.0, 2H, CH_2CH_2COSAr), 2.40-2.25 (m, 1H, CH_2CH_2COSAr), 2.20 (s, 1H, C=OCH_3), 1.46 (s, 1H, CCH_3) ; **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C ppm: 202.6 (*C*=O), 195.9 (*C*=O), 169.6 (*C*=O), 135.1, 134.2, 134.1, 131.1, 128.7, 127.3, 126.5, 125.6, 125.1, 124.6 (Ar-*C*), 120.0 (q, *J* = 281.2, CH(*C*$F_3)_2$), 67.0 (sept., *J* = 34.9, (*C*H$(CF_3)_2$), 59.1 (quaternary *C*), 38.2 (CH_2CH_2COSAr), 29.7 (CH_2CH_2COSAr), 25.9 (C=O*C*H_3), 18.9 (*C*H_3); **MS** *m/z* (ES^+) 505 (M + Na^+); **HRMS** (ES^+) Found 498.1159 (M + Na^+). $C_{21}H_{22}O_4NF_6S$ requires *M* 498.1168; **$[\alpha]_D^{23}$:** -1.2 (c 1, $CHCl_3$).

(*S, S, S)*-2-Ethoxycarbonylmethyl-3,4,5,9*b*-tetrahydro-2*H*-indeno[1,2-b]pyran-4a-carboxylic acid *tert*-butyl ester 20:



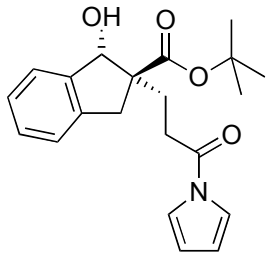
Adduct **4i** (100 mg, 0.3 mmol) was dissolved in dry Et_2O (10 mL) and cooled to 0 ^oC under N_2. Super-Hydride® (600 µl of a 1M solution in THF) was added dropwise and the mixture was stirred for 30 minutes until TLC analysis showed that all starting material had been consumed. The reaction mixture was quenched with saturated aqueous NH_4Cl (2 mL) and cooled to room temperature; it was then extracted into EtOAc (2 x 10 mL), washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*.

The crude reaction mixture was dissolved in THF (10 mL) and NaOMe (0.8 mg, 0.015 mmol) was added. It was stirred for 2 hours before being extracted into EtOAc (2 x 10 mL), washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Triethyl phosphonoacetate (118 µl, 0.59 mmol) was added to a suspension of NaH (24 mg, 0.6 mmol (60 % dispersion in mineral oil)) in dry THF (5 mL) at 0 ^oC under N_2. The mixture was warmed to room temperature over 30 minutes, cooled back to 0 ^oC and the crude reaction mixture in THF (5 mL) was added dropwise. The mixture was warmed to room temperature over 4 hours, quenched with NH_4Cl, extracted into EtOAc (2 x 10 mL), washed with brine and dried over Na_2SO_4. It was then filtered, concentrated *in vacuo*, and filtered through a pad of silica (eluting with 4:1 petrol EtOAc) to yield **20** as a colourless oil (81 mg, 75 % over three steps, 5:1 mixture of diastereoisomers).

IR ν_{max} (film): 2927, 2854 (CH), 1725 (C=O); **^{1}H NMR** (500 MHz, $CDCl_3$, major diastereoisomer) δ_H ppm: 7.34 (d, J = 7.3, 1H, Ar-*H*), 7.20 (m, 2H, Ar-*H*), 7.11 (d, J = 7.2, 1H, Ar-*H*), 5.68 (s, 1H, CC*H*O), 4.13 (q, J = 7.1, 2H, CH_2CH_3), 3.84 (m, 1H, $CHCH_2$), 3.09 (d, J = 15.2, 1H, indanone CH_AH_B), 2.63 (d, J = 15.3, 1H, indanone CH_AH_B), 2.52 (dd, J = 8.6, 1H, 15.5, $CHCH_AH_BCO$), 2.32 (dd, J = 15.5, 4.3, 1H $CHCH_AH_BCO$), 2.20 (dd, J = 10.1, 2.8, 1H, $CH_AH_BCH_2$), 1.43 (s, 1H, $C(CH_3)_3$), 1.36 (m, 3H, CH_2CH_2), 1.24 (t, J = 7.1, 1H, CH_2CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$ major diastereoisomer) δ_C ppm: 173.3 (*C*=O),

170.3 (*C*=O), 139.4, 137.9, 126.9, 126.0, 124.4, 123.2, (Ar-*C*), 82.1 (C*C*HO), 79.9 (quaternary *C*), 66.3 (*C*HCH$_2$), 59.5 (*C*H$_2$CH$_3$), 50.4 (*C*(CH$_3$)$_3$), 40.6 (indanone *C*), 40.1 (*C*H$_2$CO), 27.1 (C(*C*H$_3$)$_3$), 26.9 (*C*H$_2$CH$_2$), 26.7 (CH$_2$*C*H$_2$), 14.3 (CH$_2$*C*H$_3$); **MS** *m/z* (ES$^+$) 378 (M + NH$_4^+$), 383 (M + Na$^+$); **HRMS** (ES$^+$) Found 378.2266. $C_{21}H_{32}O_5N$ requires *M* 378.2275; **[α]$_D^{22}$:** +72 (c 1, CHCl$_3$).

(*S, S*)-1-Hydroxy-2-(3-oxo-3-pyrrol-1-yl-propyl)-indan-2-carboxylic acid *tert*-butyl ester 21:



Adduct **4i** (100 mg, 0.3 mmol) was dissolved in dry THF (10 mL) and cooled to –78^{o}C. Super-Hydride® (300 µl of a 1M solution in THF) was added dropwise and the mixture was stirred at –78^{o}C for 5 hours. It was then quenched with saturated aqueous NH$_4$Cl (2 mL), warmed to room temperature and extracted into EtOAc (2 x 10 mL). The combined organics were washed with brine, dried over Na$_2$SO$_4$ ad concentrated *in vacuo*; the crude product was then subjected to flash column chromatography on silica gel (eluting with 9:1 petrol:EtOAc) to yield **21** as a colourless oil (68 mg, 68 % (+ 9 % recovered starting material), 5:1 mixture of diastereoisomers).

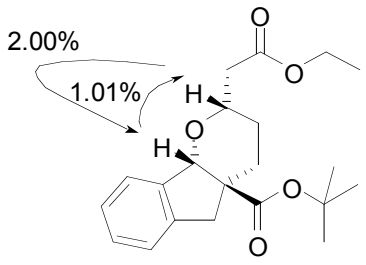
IR ν_{max} (film): 3488 (broad OH), 3248, 3074, 2977, 2933 (CH), 1718 (C=O); **^{1}H NMR** (500 MHz, CDCl$_3$) δ_H ppm: 7.20 (m, 6H, Ar-*H*), 6.21 (t, *J* = 2.1, 2H, pyrrole-*H* (minor diastereoisomer)), 6.17 (t, *J* = 2.1, 2H, pyrrole-*H* (major diastereoisomer)), 5.37 (d, *J* = 4.5, 1H, C*H*OH (major diastereoisomer)), 4.93 (d, *J* = 8.1, 1H, C*H*OH (minor diastereoisomer)), 3.42 (d, *J* = 16.3, 1H, indanone C*H$_A$*H$_B$ (minor diastereoisomer)), 3.25 (d, *J* = 16.2, 1H, indanone C*H$_A$*H$_B$ (major diastereoisomer)), 2.87 (d, *J* = 16.2, 1H, indanone CH$_A$*H$_B$*), 2.68 (ddd, 2H, *J* = 9.6, 6.0, 4.3, CH$_2$C*H$_2$*CON), 2.43 (d, *J* = 5.5, 1H, O*H*), 2.25 (ddd, *J* = 14.2, 10.3, 5.9, 1H, C*H$_A$*H$_B$CH$_2$CON), 2.05 (m, 1H, CH$_A$*H$_B$*CH$_2$CON), 1.36 (m, 9H, C(C*H$_3$*)$_3$); **^{13}C NMR** (126 MHz, CDCl$_3$) δ_C ppm: major diastereoisomer: 173.9 (*C*=O), 169.4 (*C*=O), 141.6, 138.4, 127.5, 126.2, 123.5, 123.1, 118.0, 112.1 (Ar-*C*), 80.6 (quaternary *C*), 77.9

(*C*HOH), 57.8 (*C*(CH_3)$_3$), 37.6 (indanone *C*), 30.0 (CH_2*C*H_2CON), 27.0 (C(*C*H_3)$_3$), 26.2 (*C*H_2CH_2CON); minor diastereoisomer: 173.2 (*C*=O), 168.9 (*C*=O), 141.9, 139.0, 127.6, 126.2, 123.4, 123.2, 117.9, 112.2 (Ar-*C*), 81.2 (quaternary *C*), 80.6 (*C*HOH), 58.2 (*C*(CH_3)$_3$), 38.3 (indanone *C*), 30.2 (CH_2*C*H_2CON), 26.9 (C(*C*H_3)$_3$), 26.2 (*C*H_2CH_2CON); **MS** *m/z* (ES^-) 354 ($M - H^+$); **HRMS** (ES^+) Found 356.1852. $C_{21}H_{26}O_4N$ requires *M* 356.1856; $[\alpha]_D^{22}$**:** +0.8 (c 0.5, $CHCl_3$).

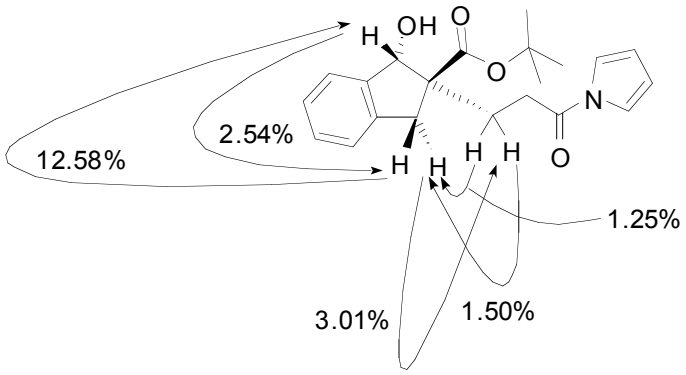
Determination of Relative Configuration of 20 and 21

The relative configuration of compounds **20** and **21** was determined by nOe experiments.

nOe of compound 20:



nOe of compound 21:



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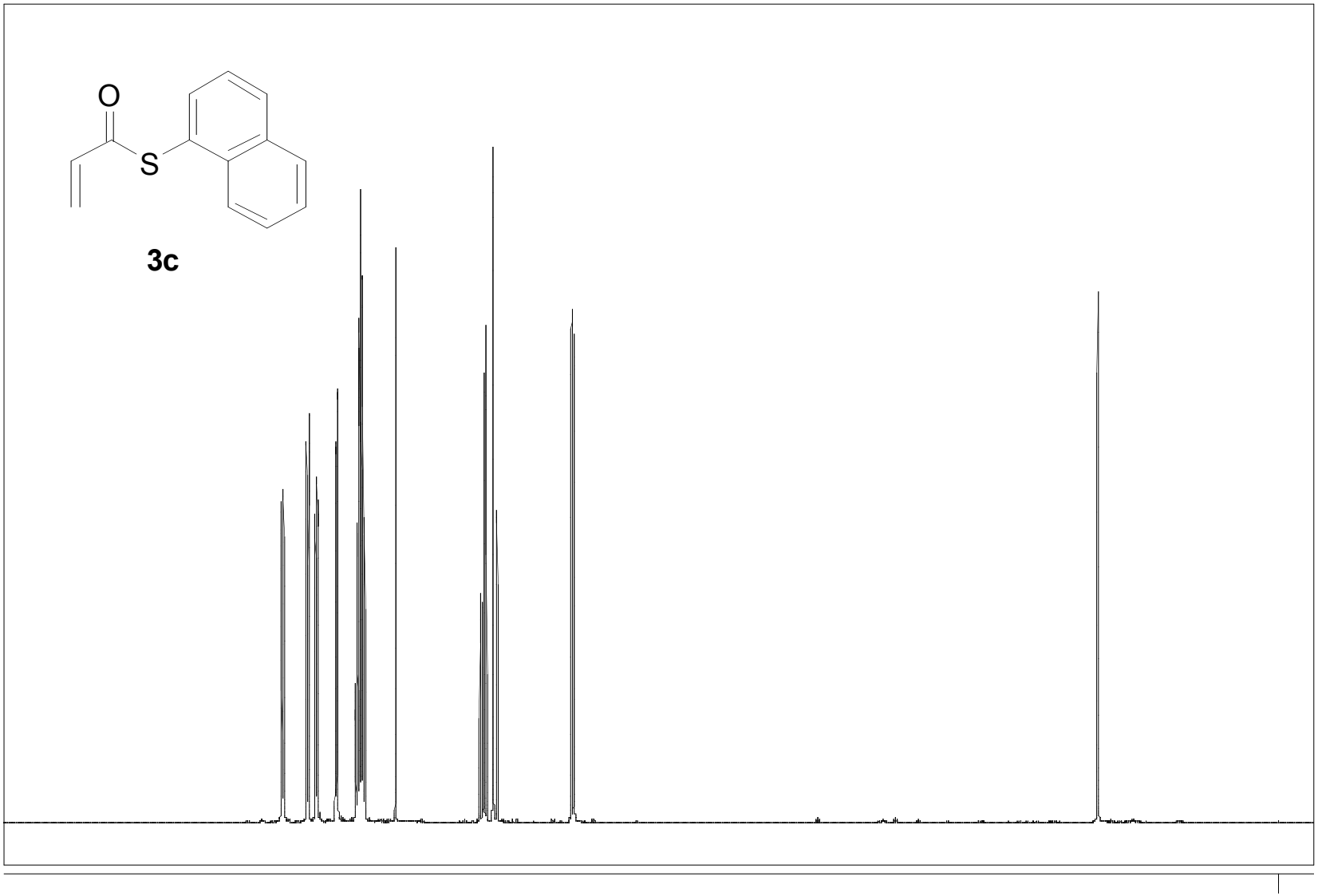
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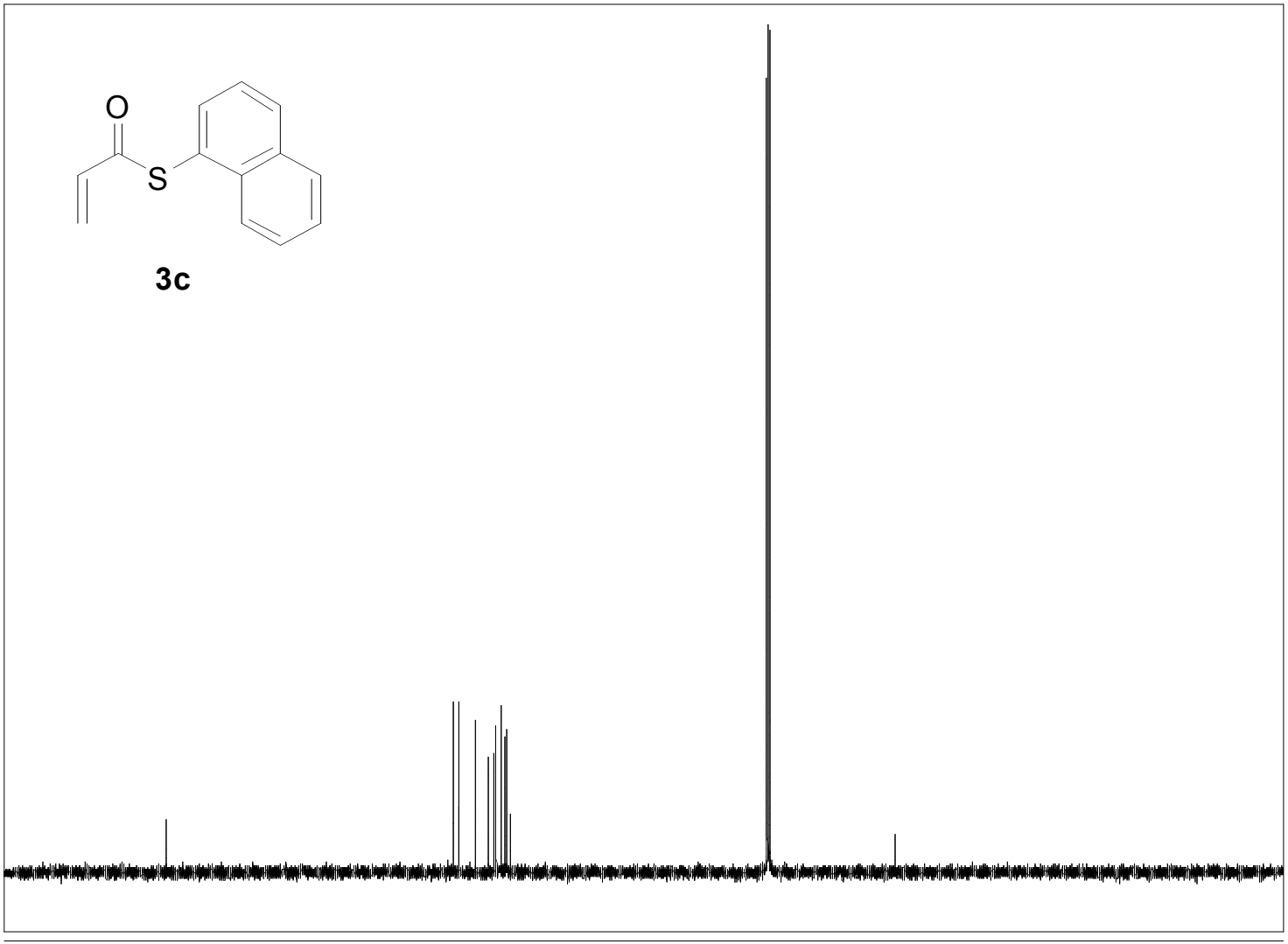
S
3c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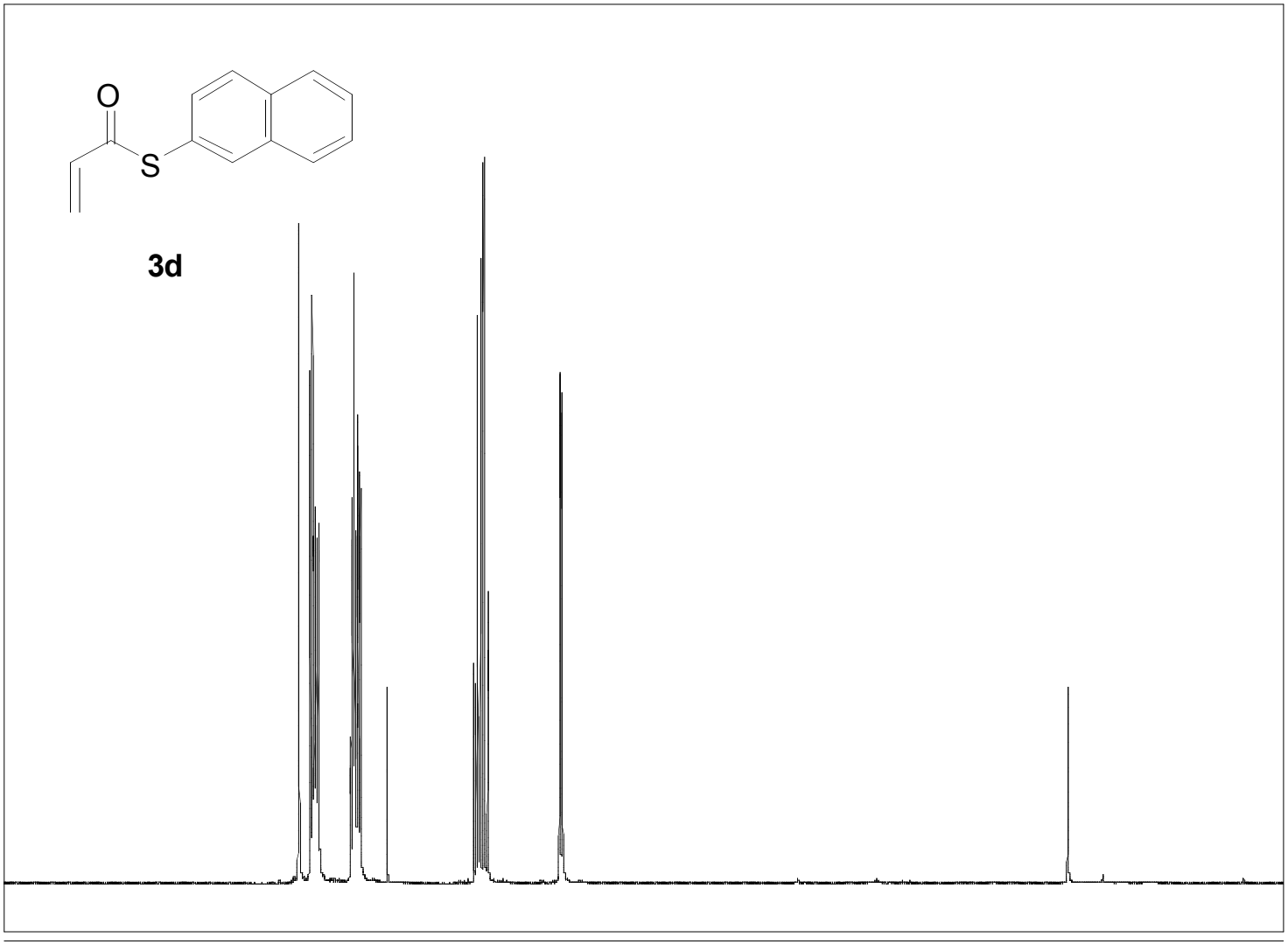
3c
ppm (t1)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3d
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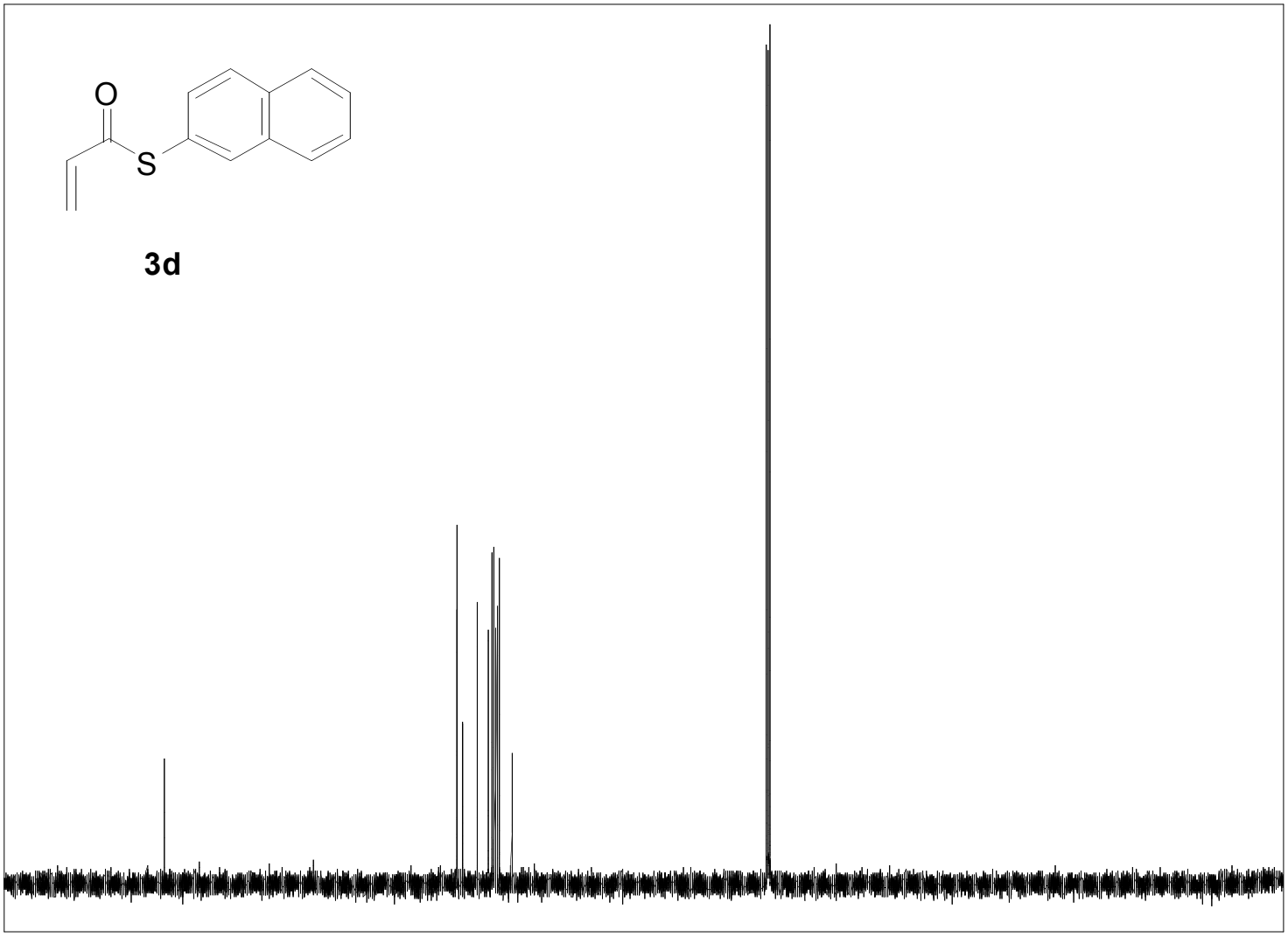
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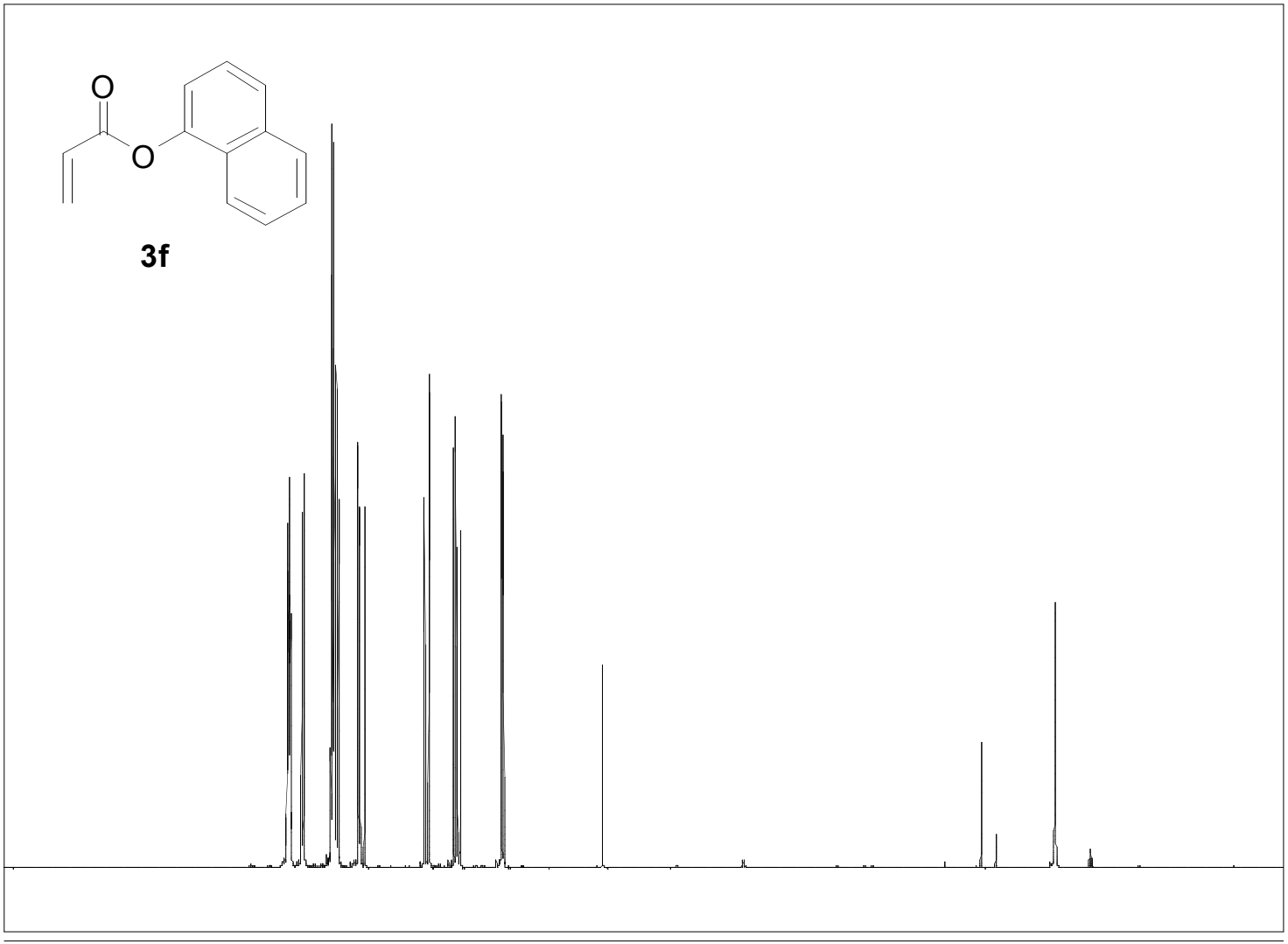
3d
ppm (t1)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O
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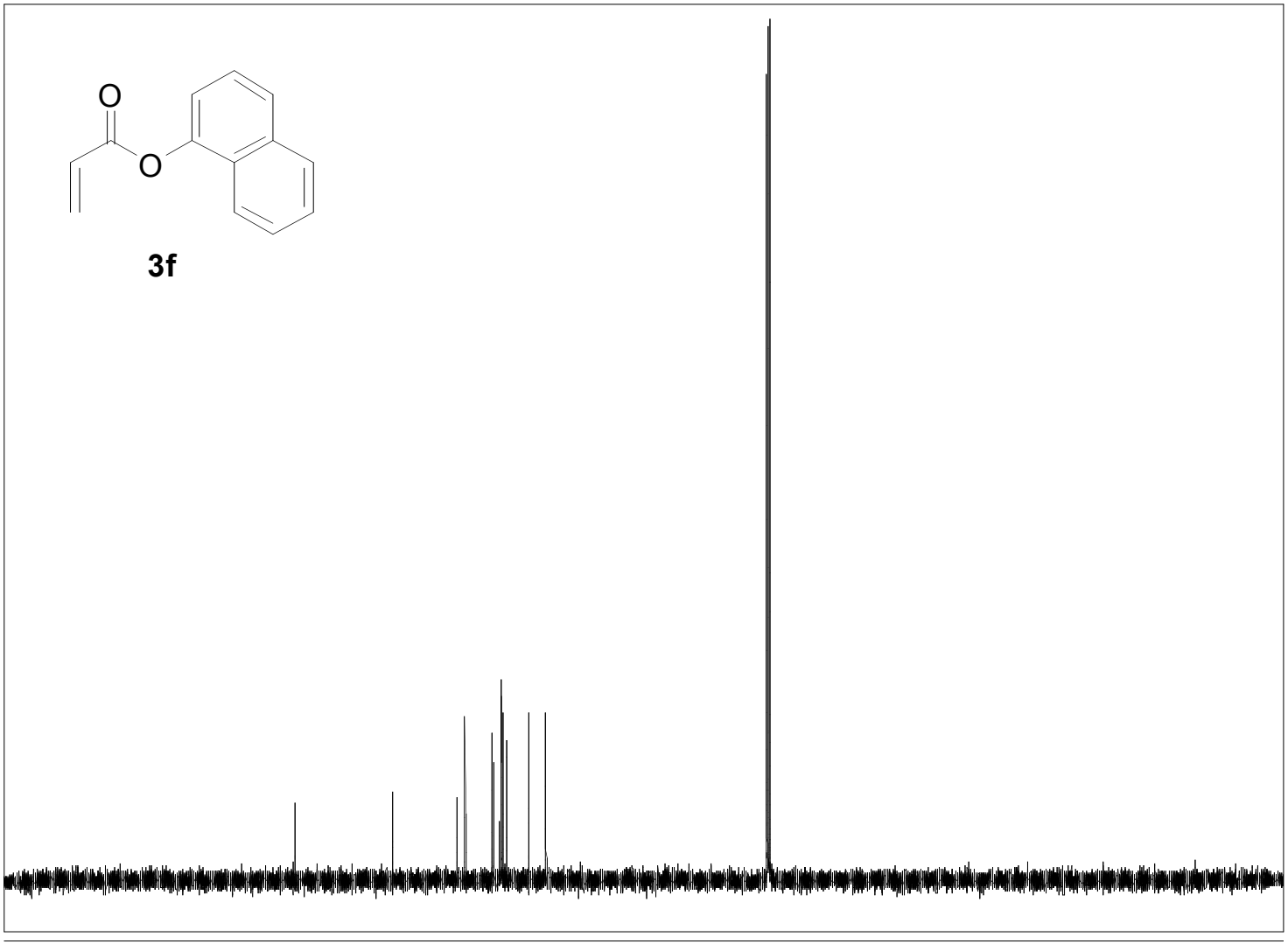
ppm (t1)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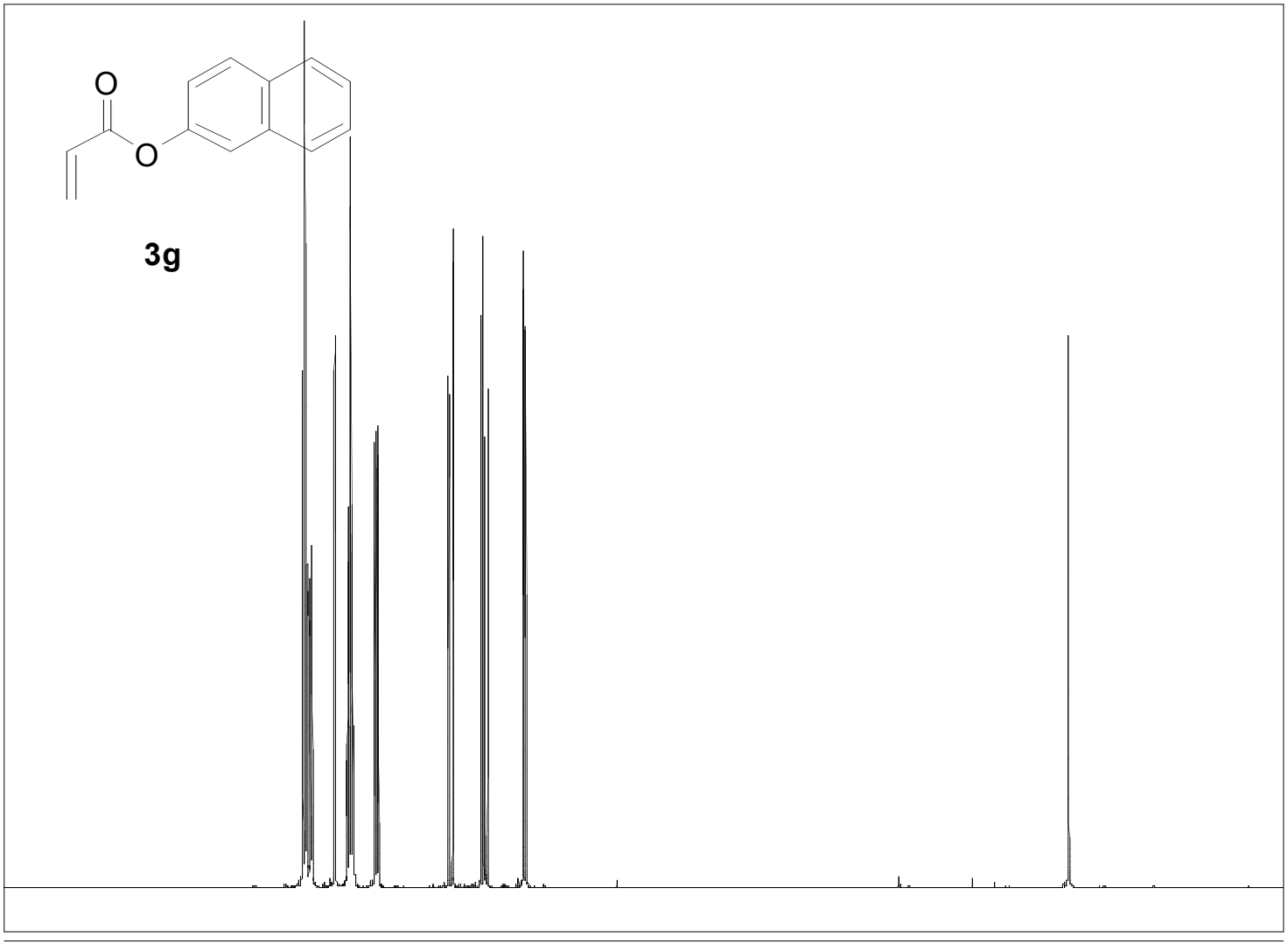
O
3f
ppm (t1)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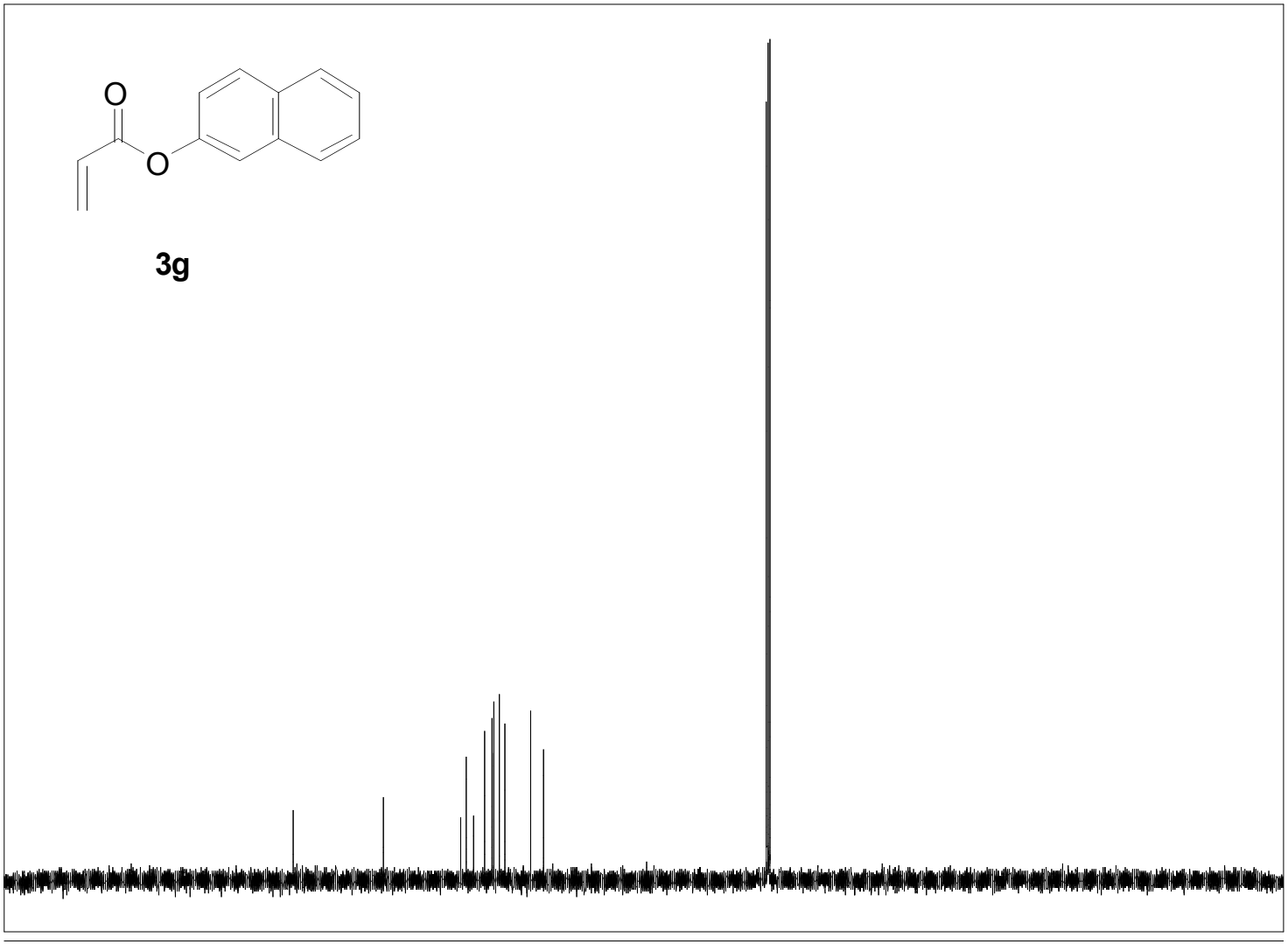
3g
ppm (t1)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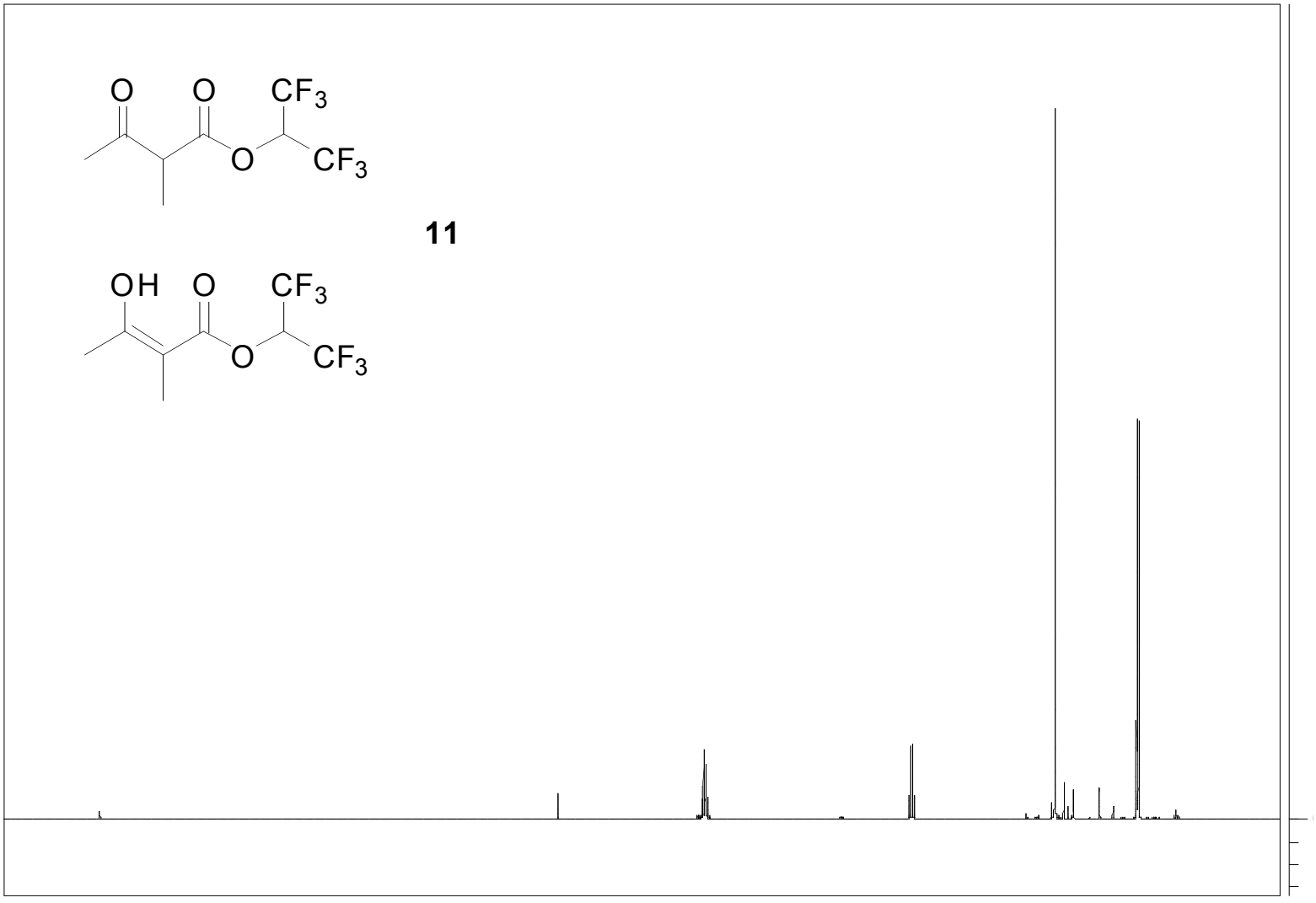
3g
ppm (t1)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CF3
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OH
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CF3
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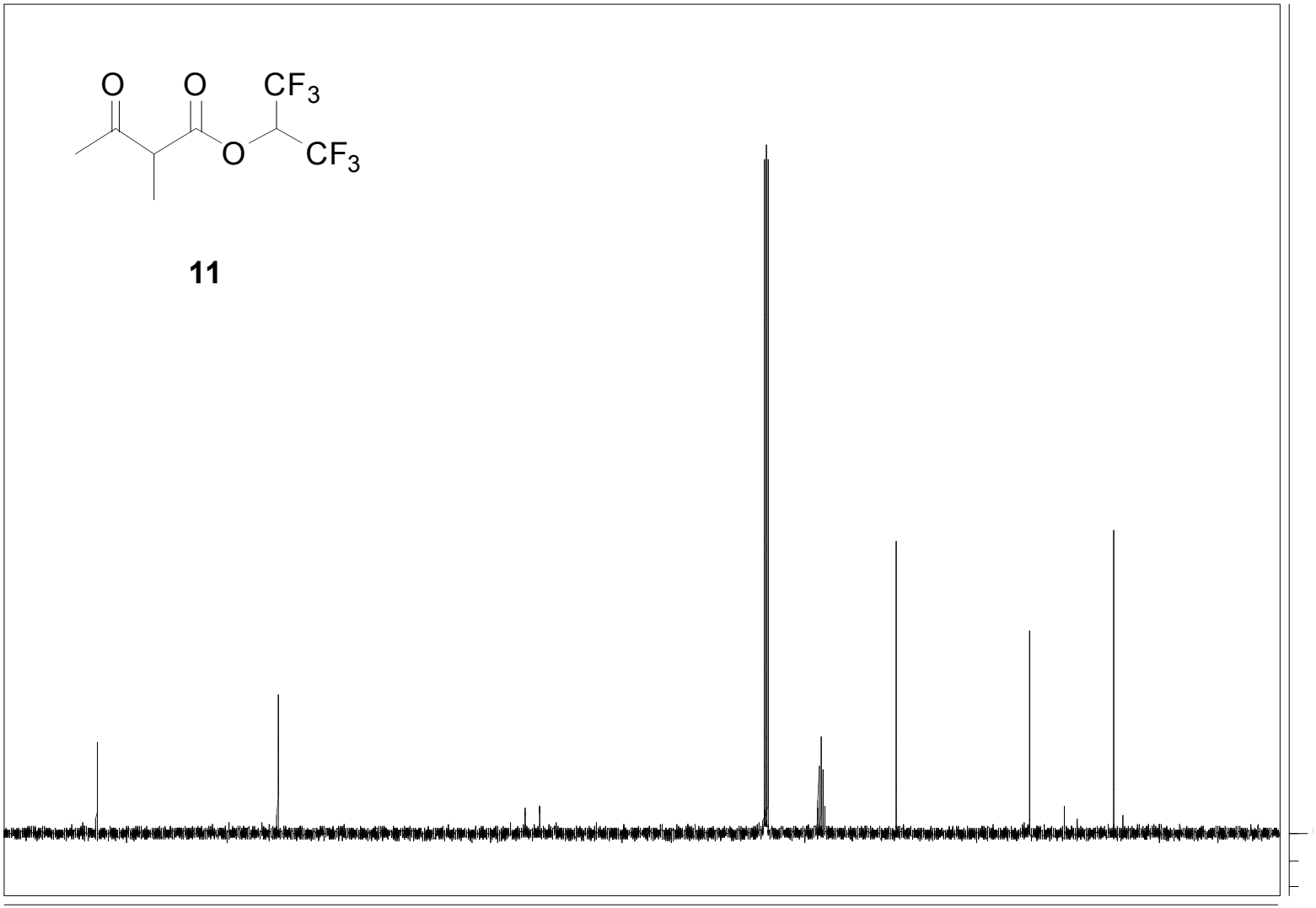
CF3
ppm (t1)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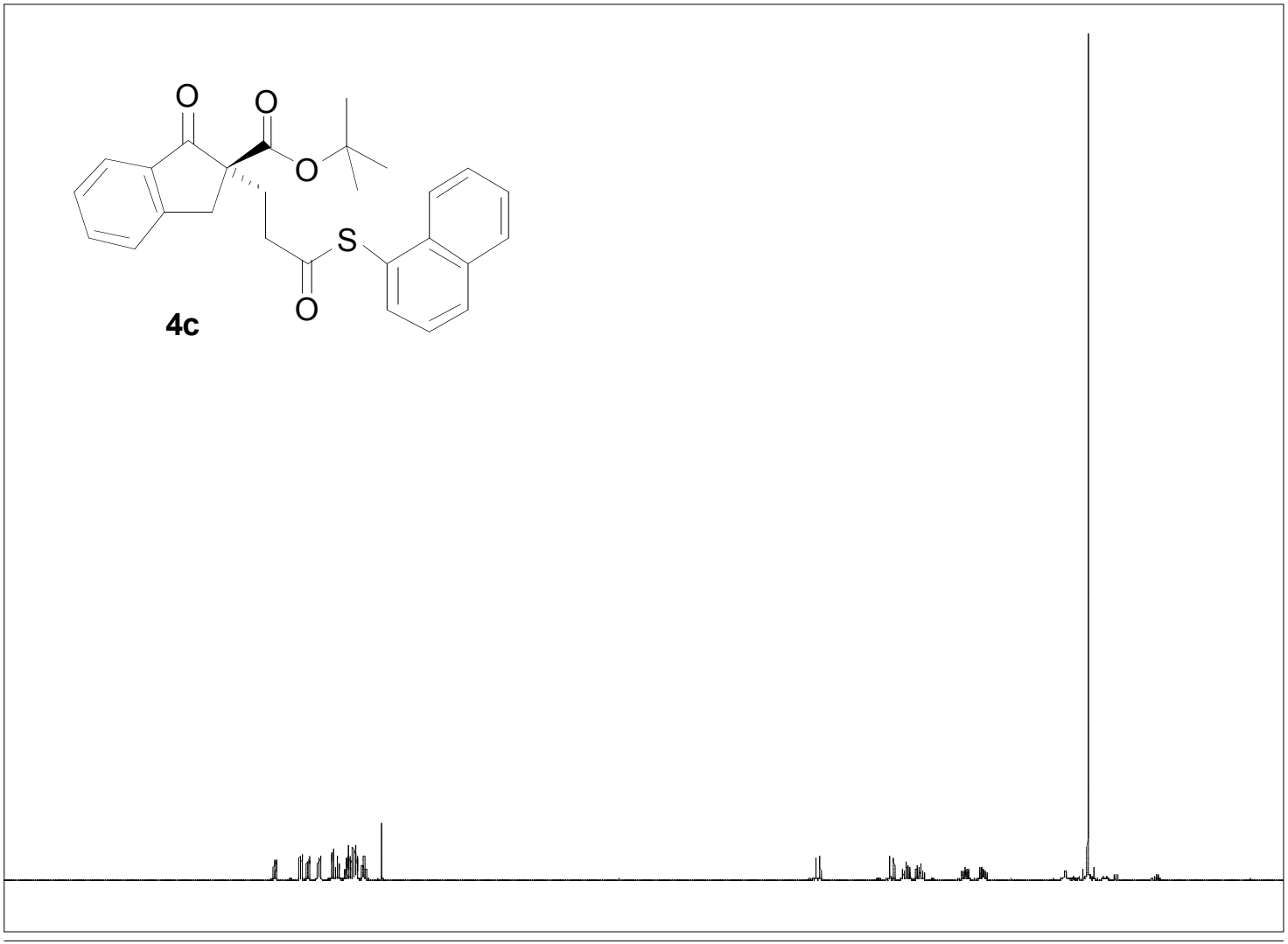
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S
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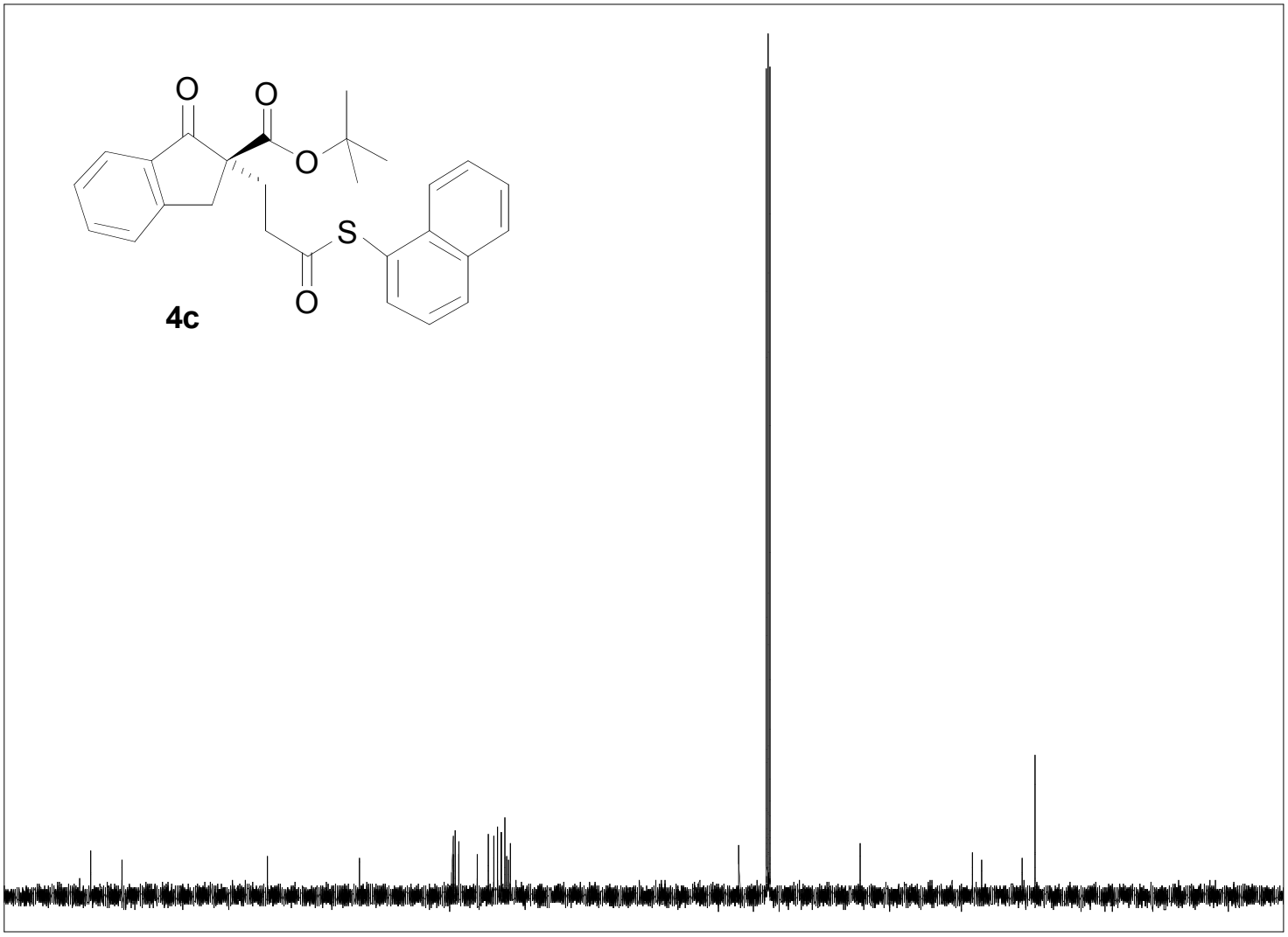
ppm (t1)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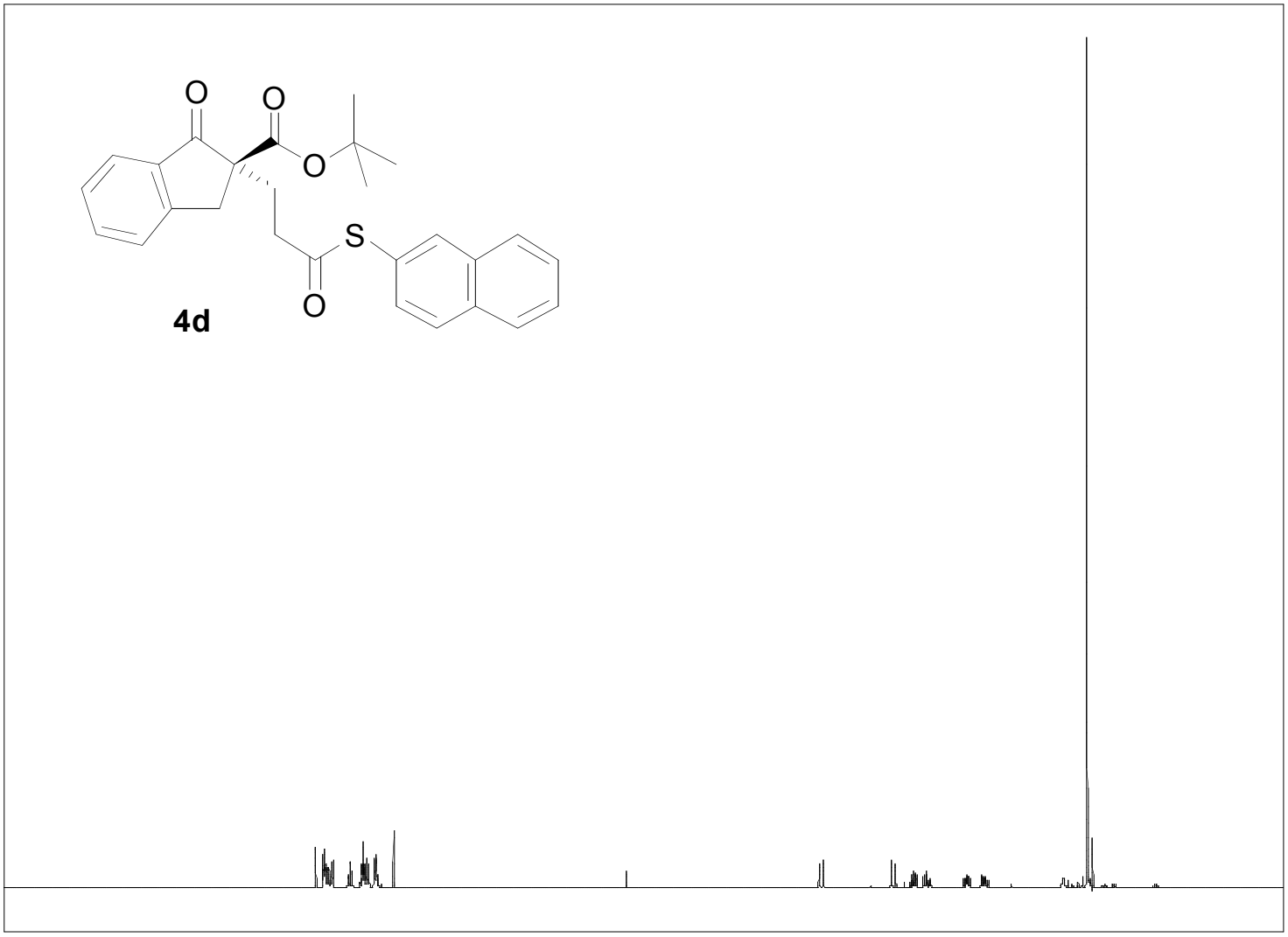
O
S
O
4c
ppm (t1)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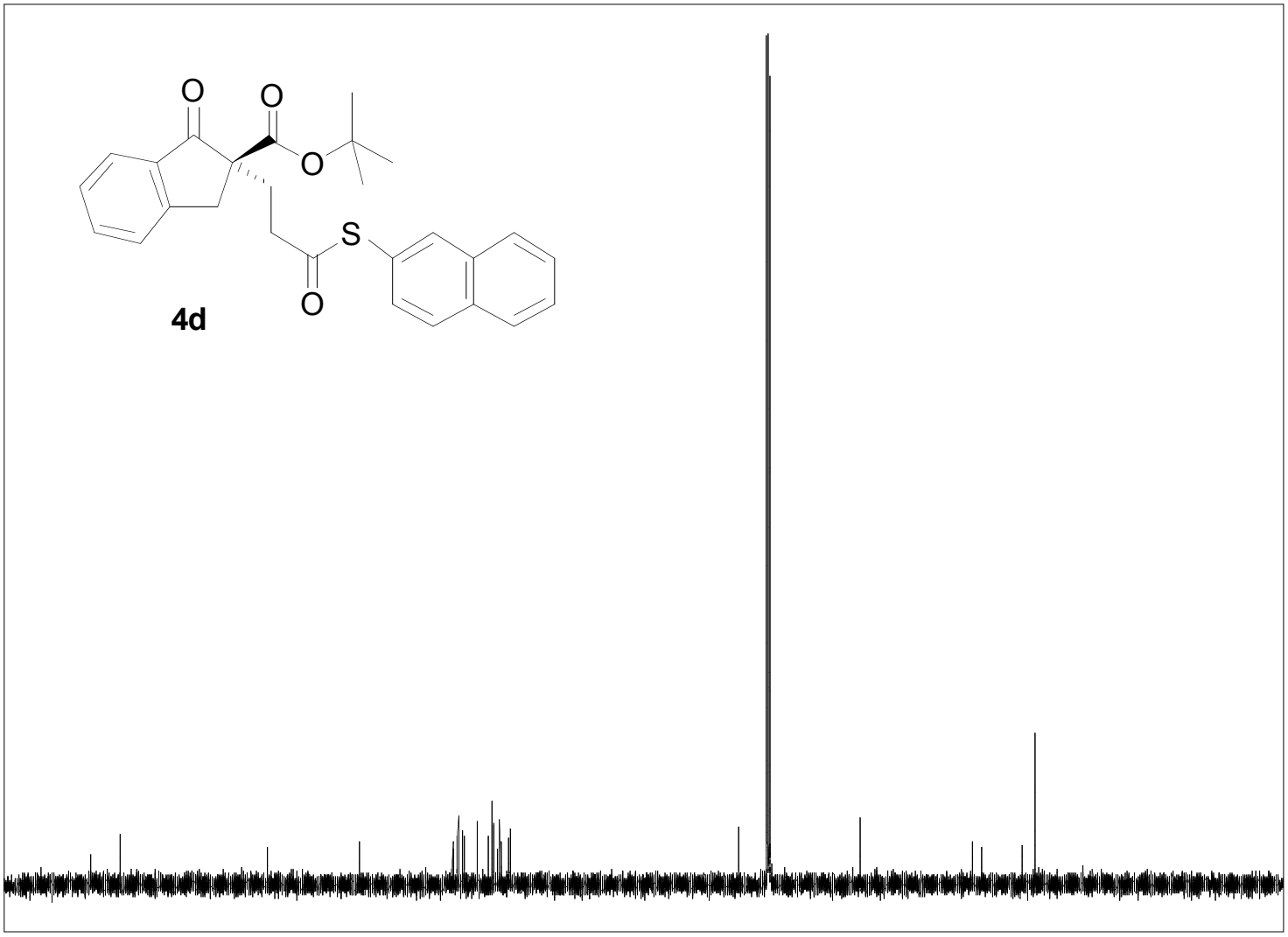
O
S
O
4d
ppm (t1)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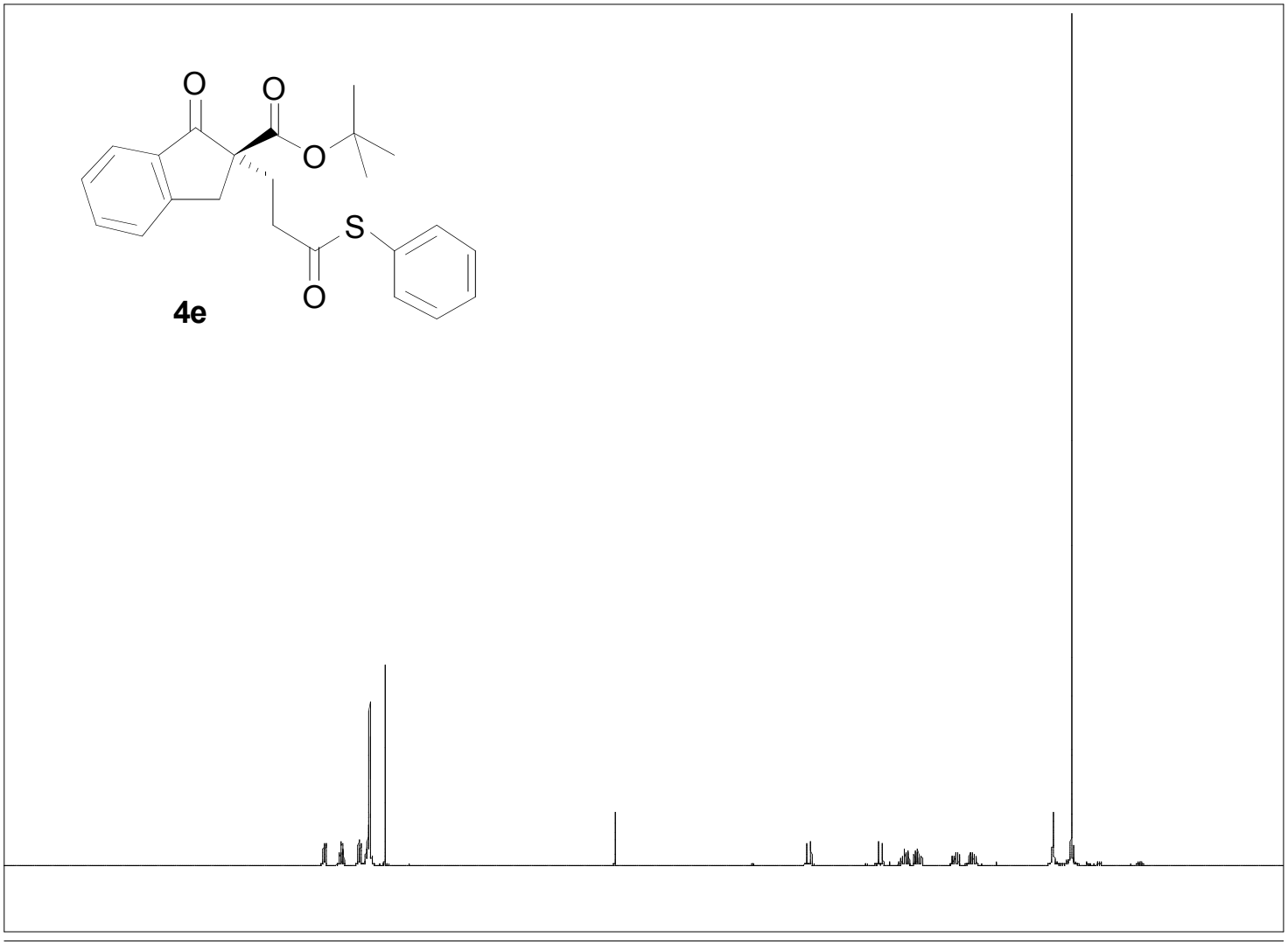
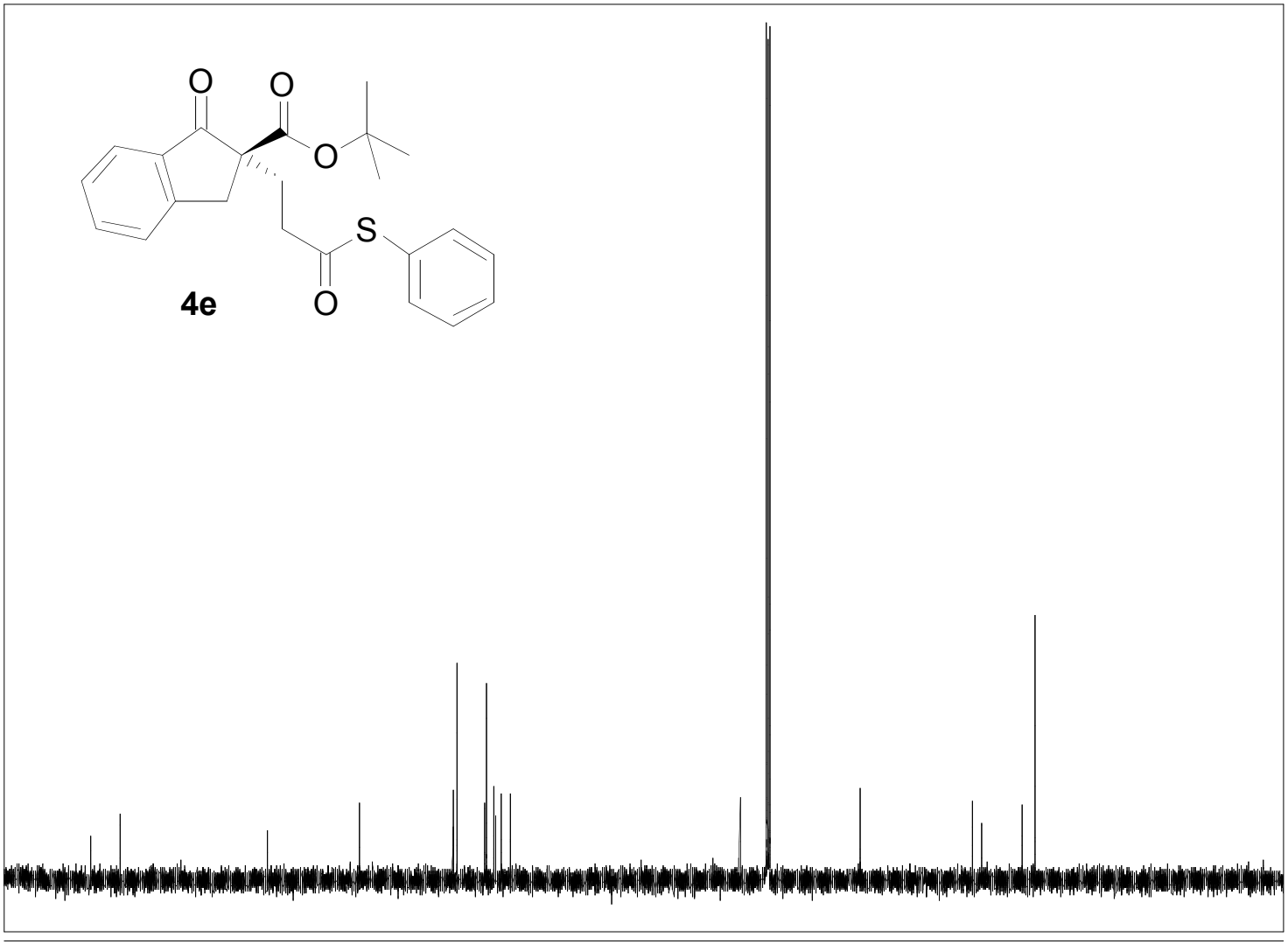
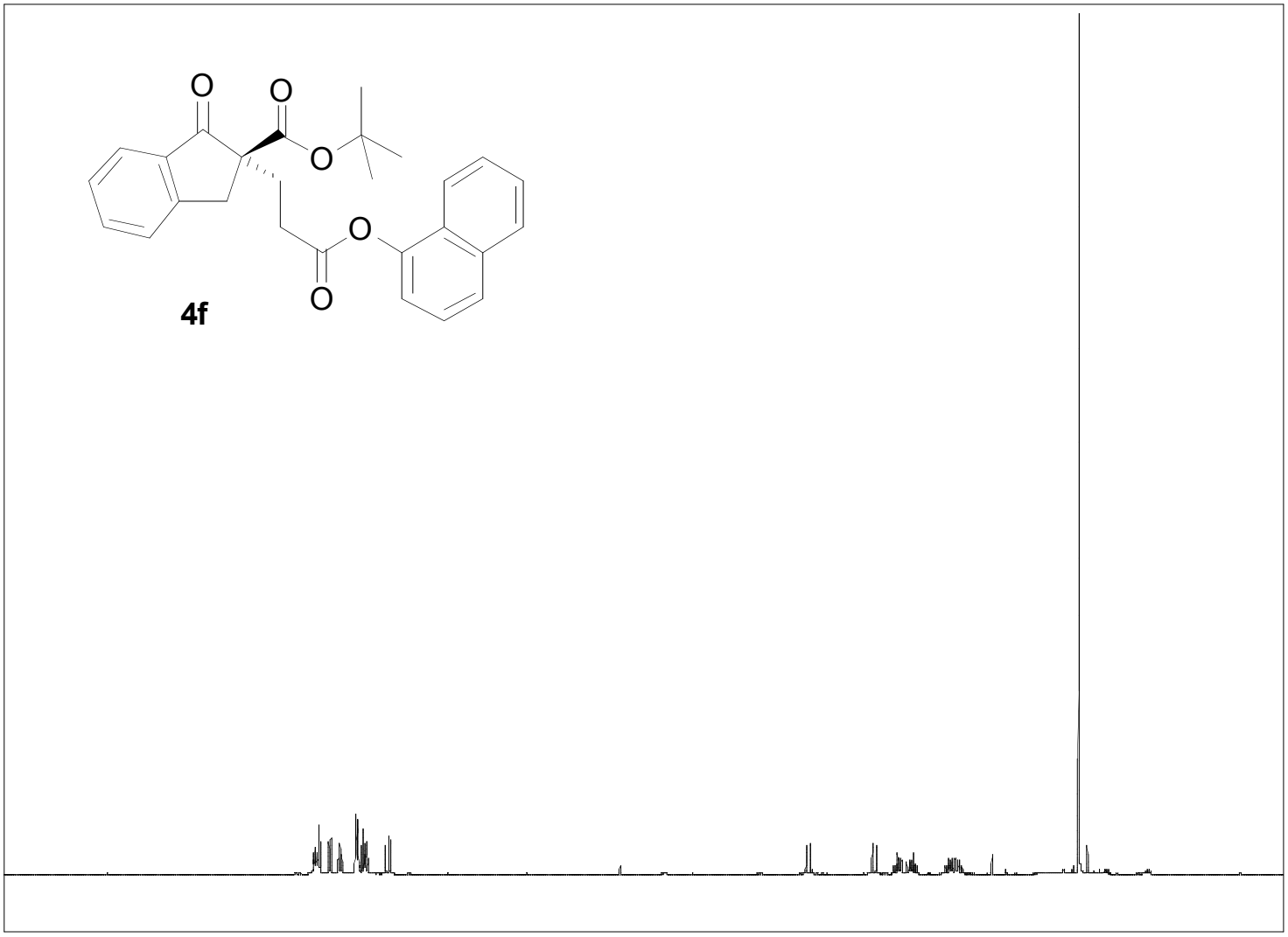
O
O
S
O
4d
ppm (t1)


O
O
O
S
O
4e
ppm (t1)



ppm (t1)


O
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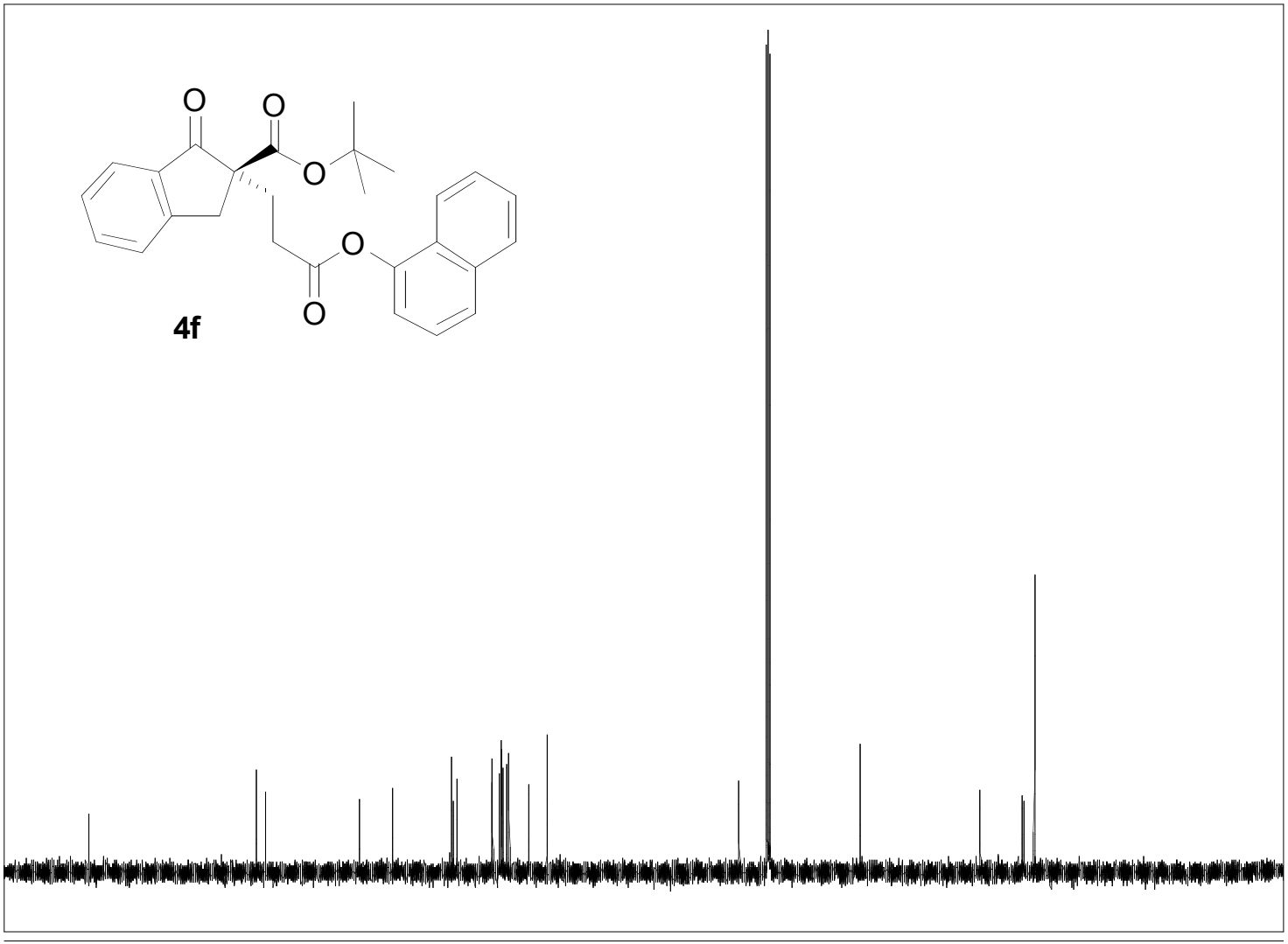
O
O
4f
ppm (t1)


O
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O
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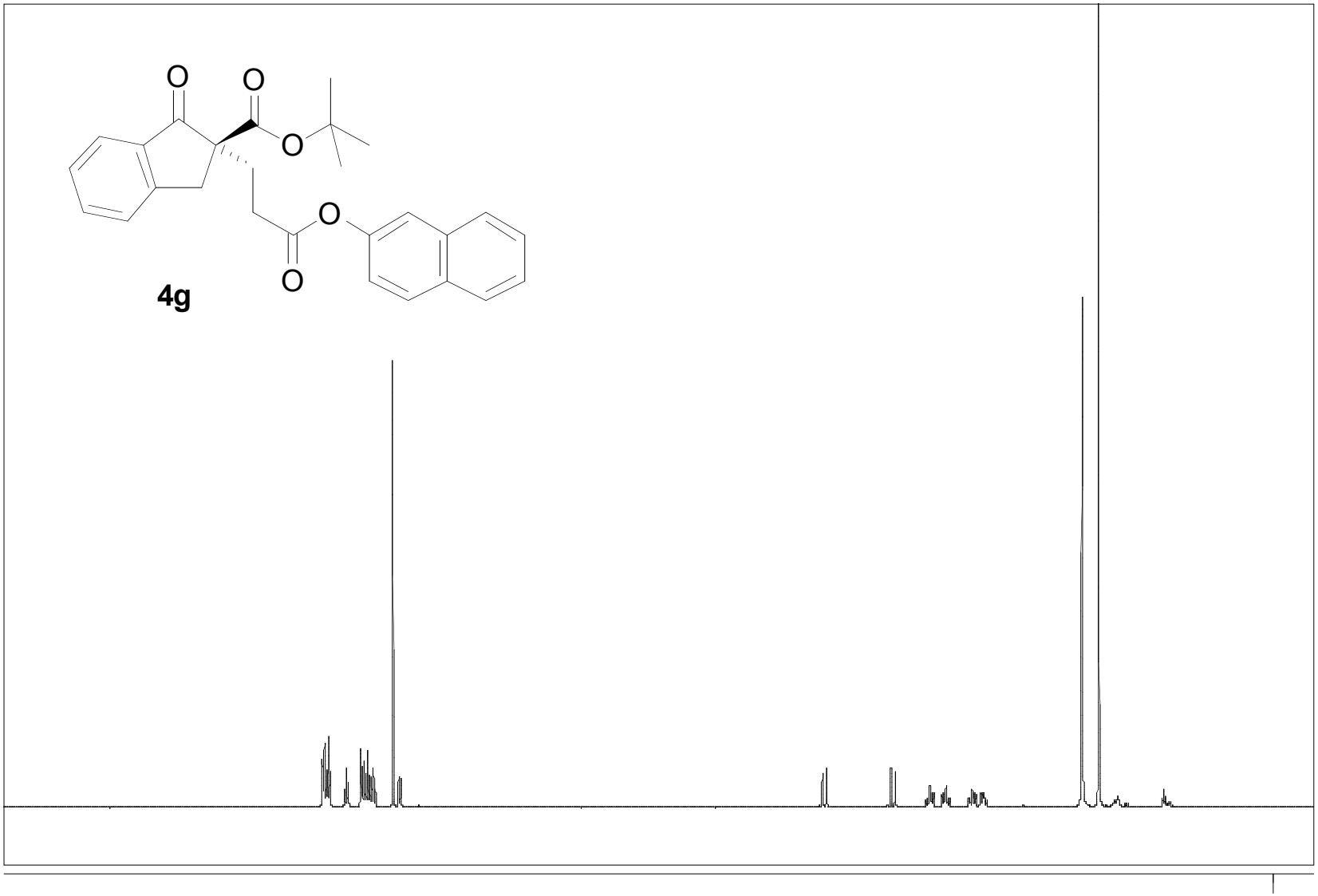
4f
ppm (t1)


O
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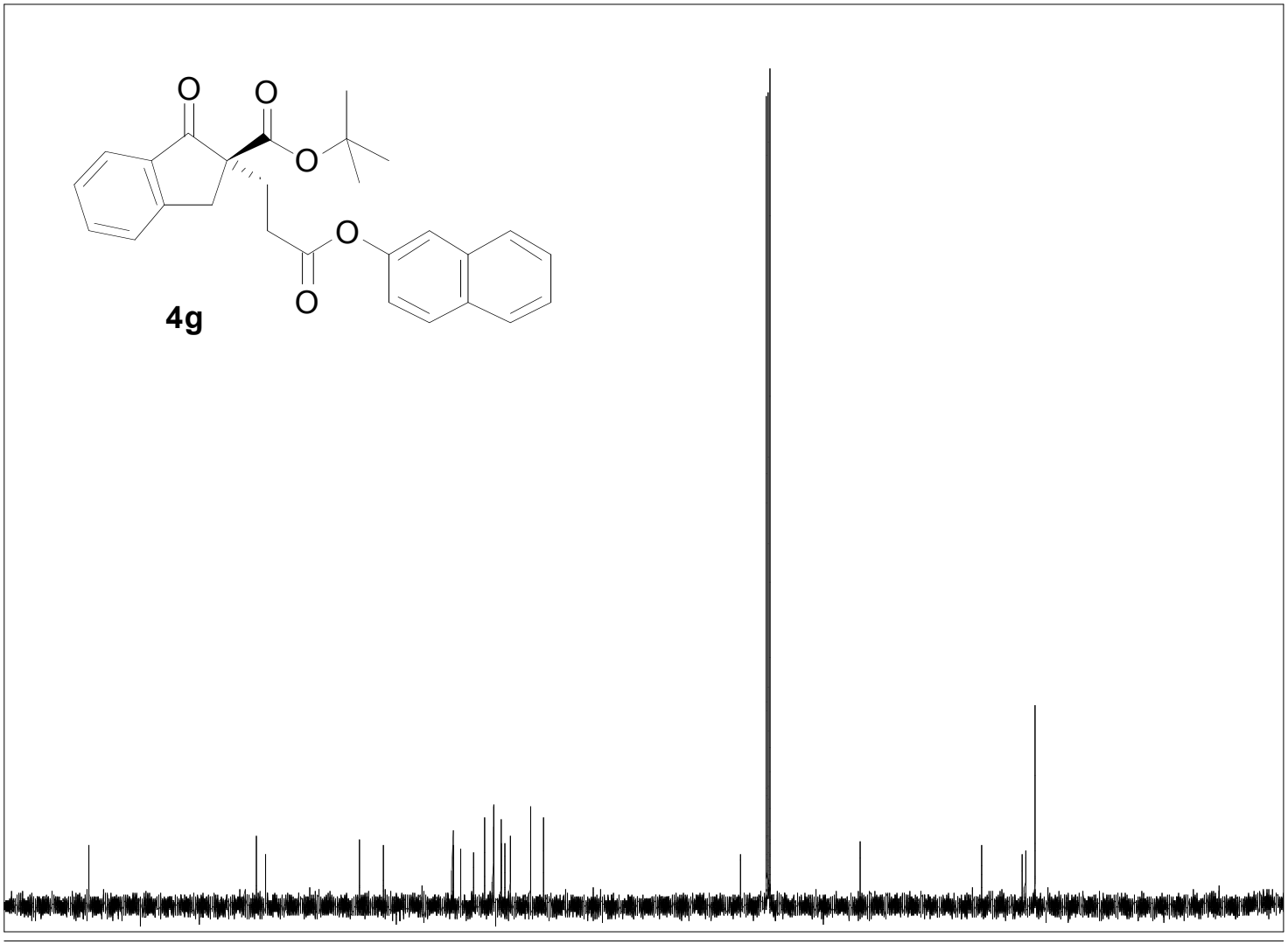
4g


O
O
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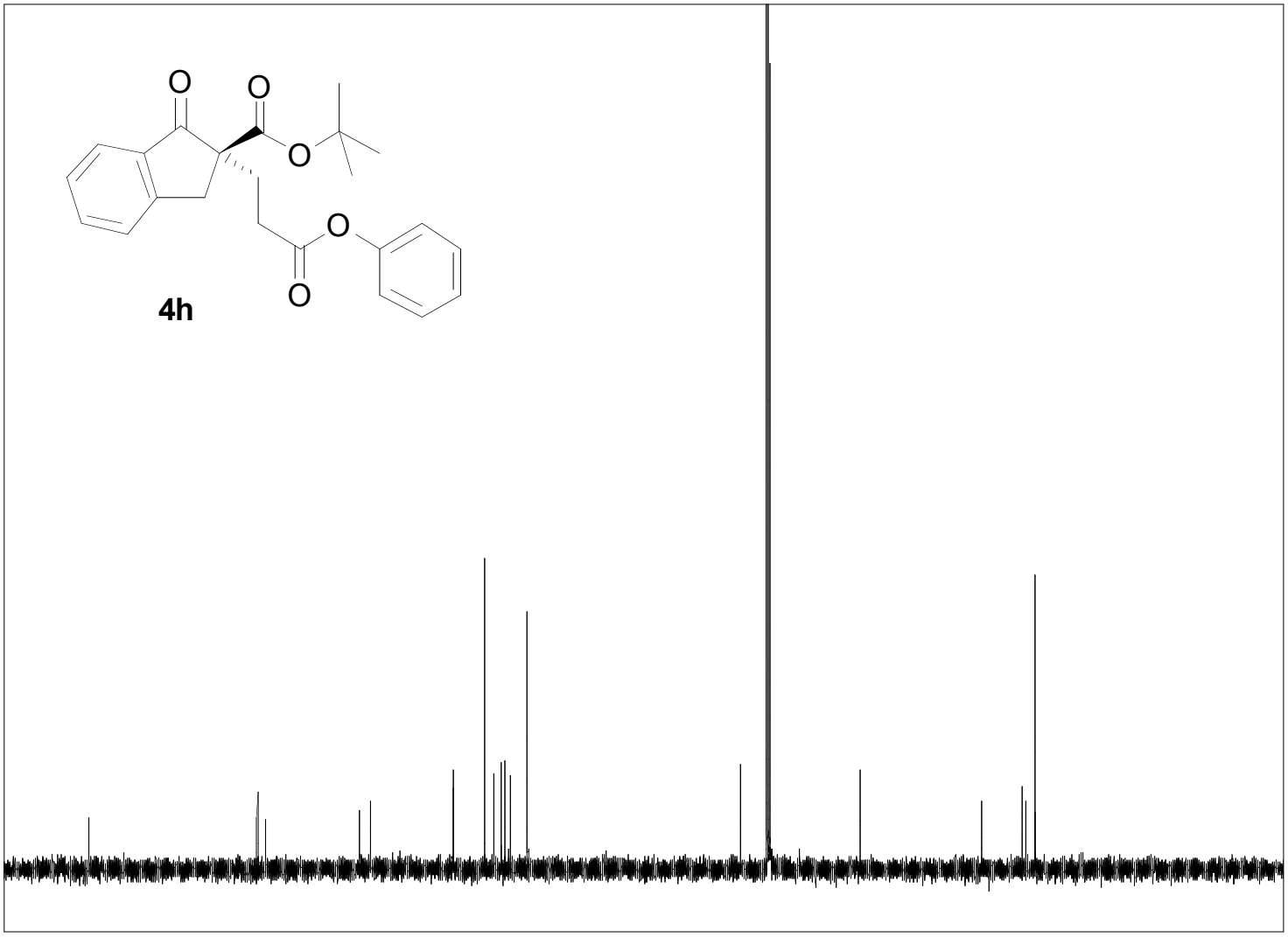
O
O
O
4g
ppm (t1)


O
O
O
O
O
O
4h
ppm (t1)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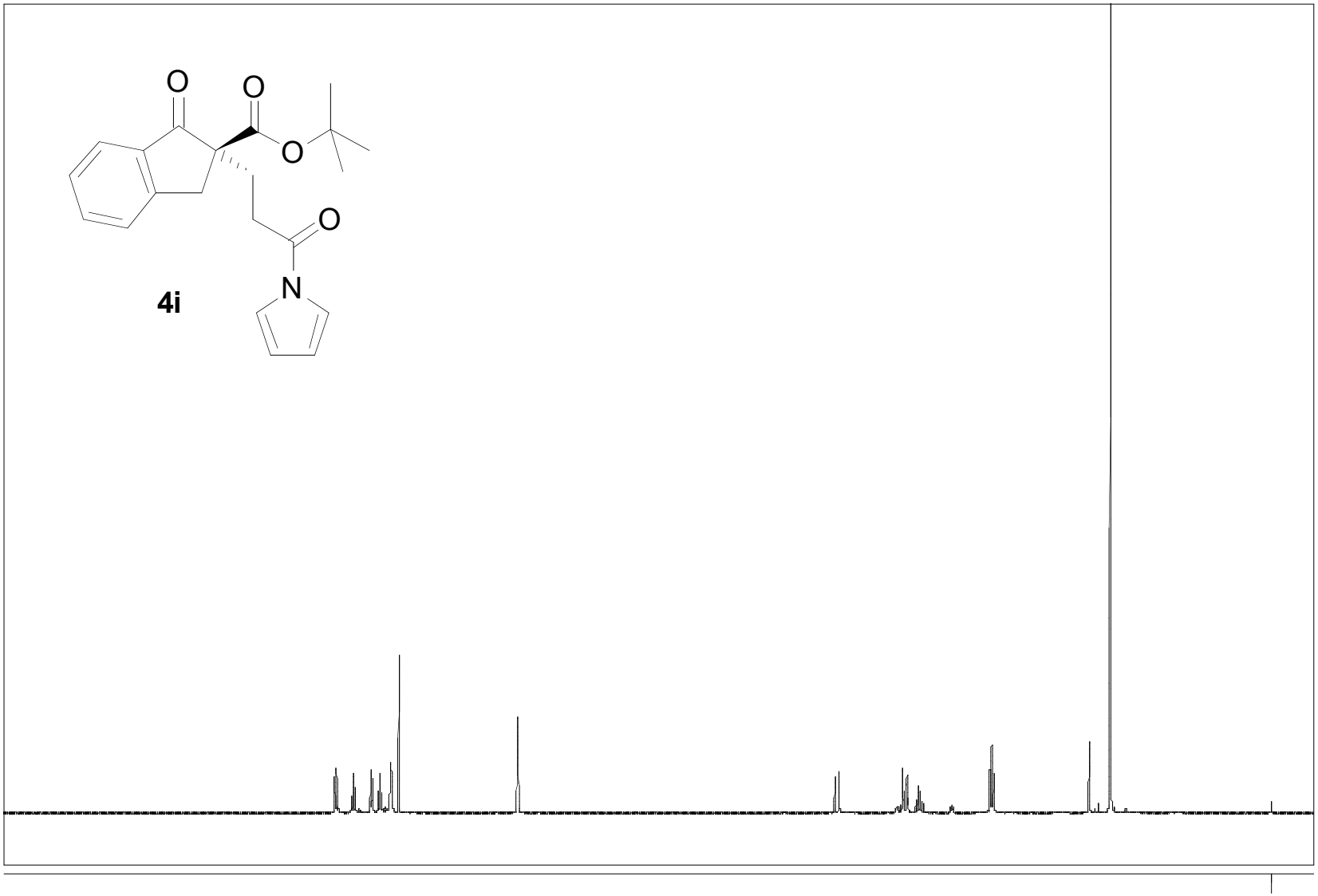
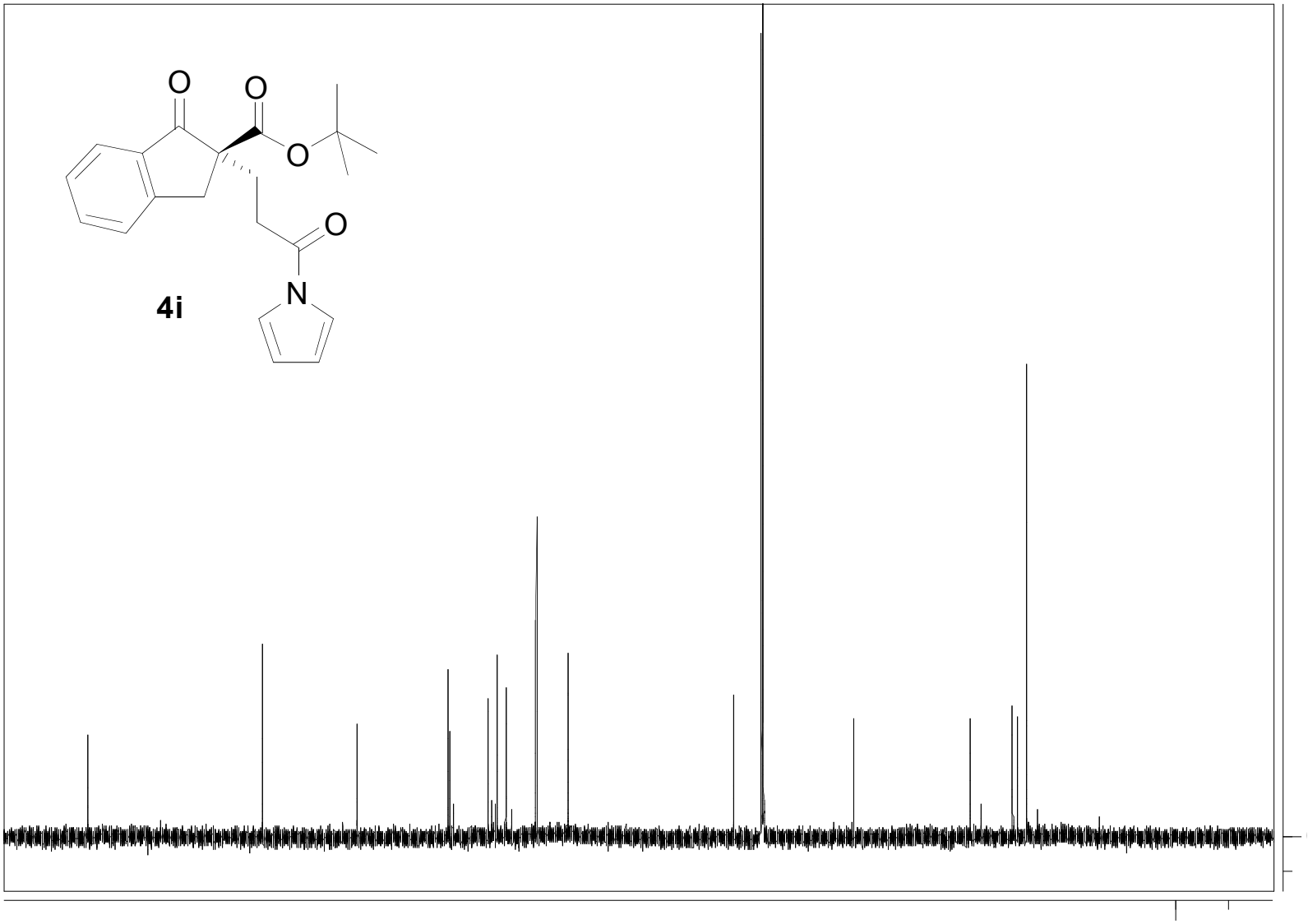
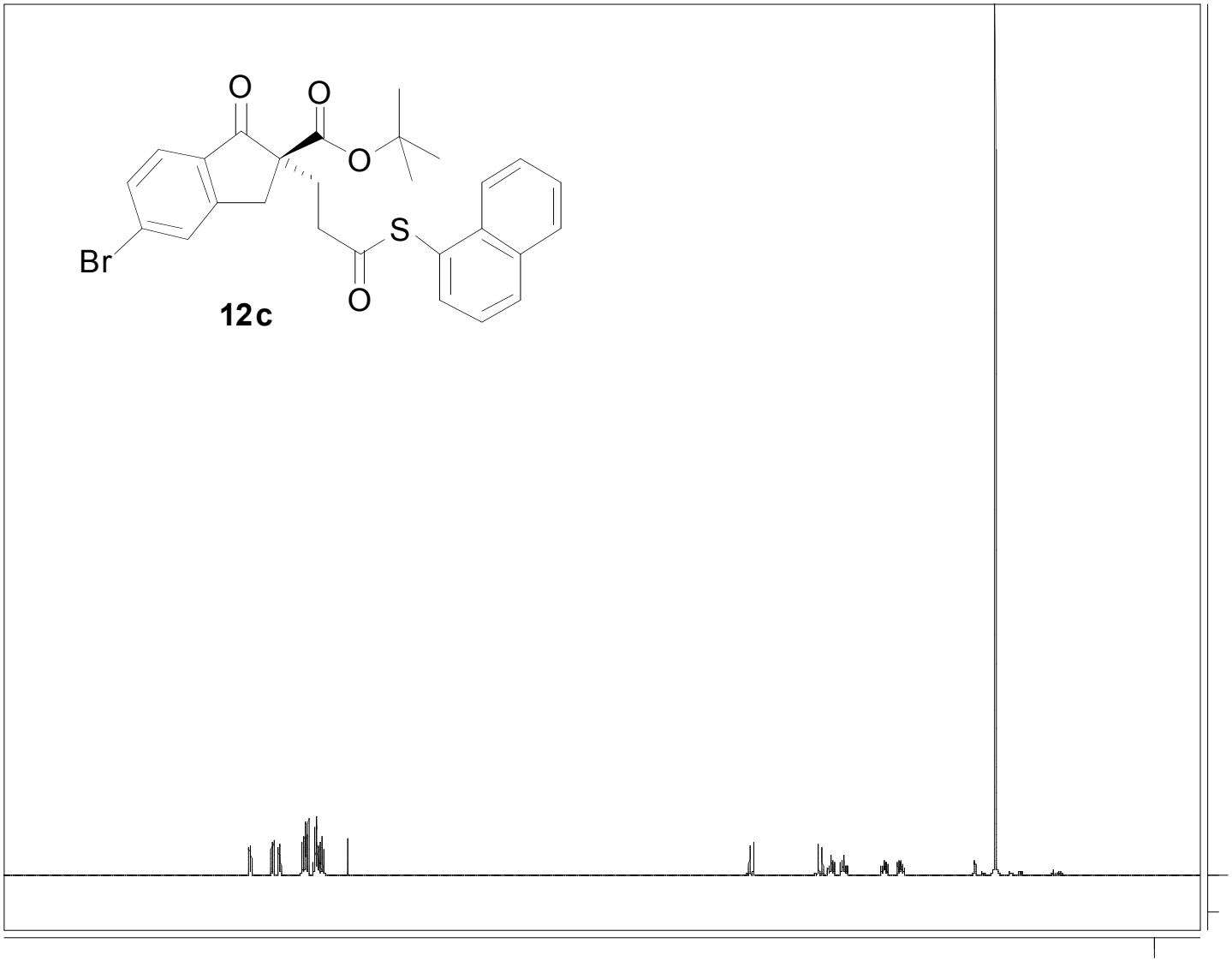
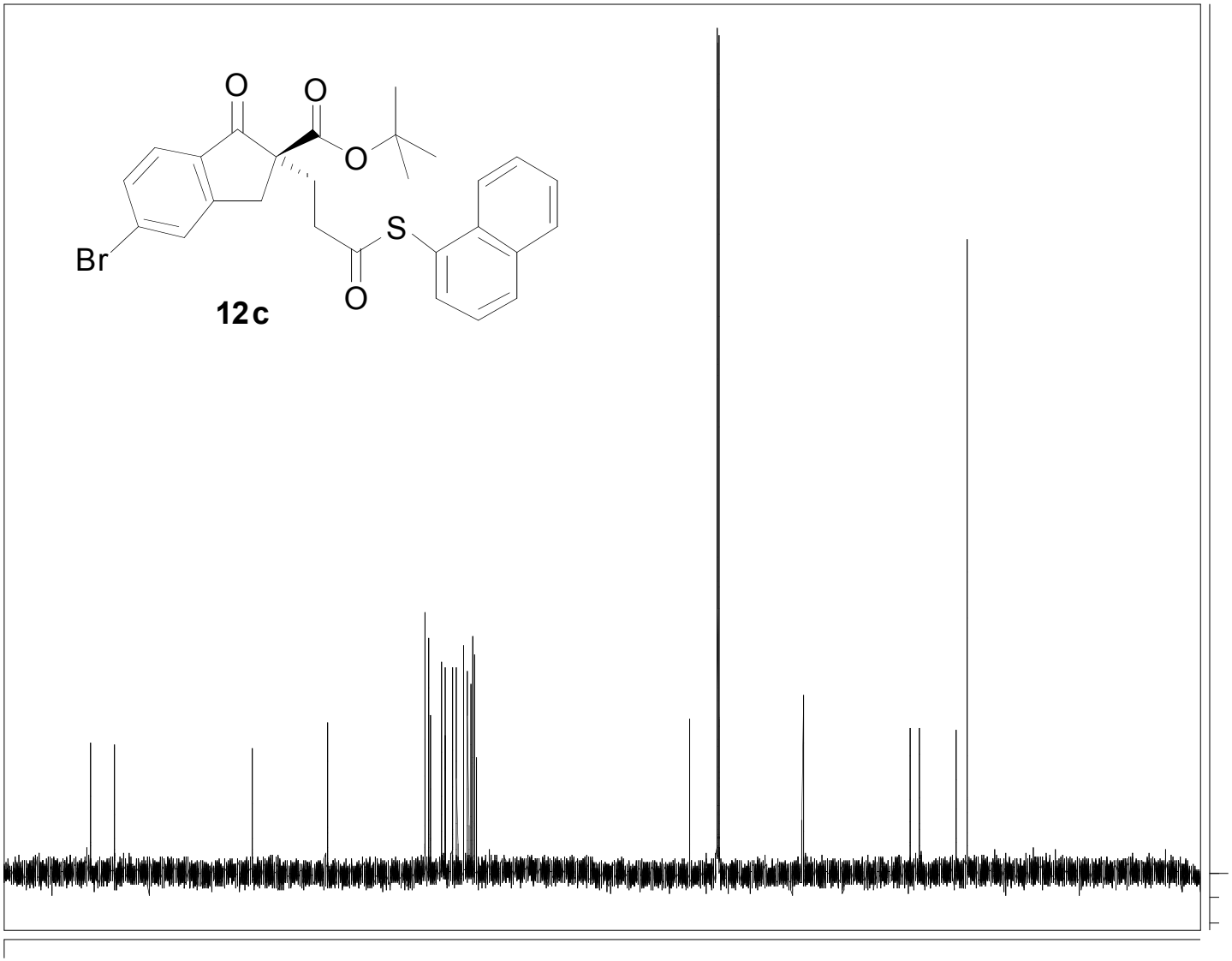
O
O
O
4h
ppm (t1)

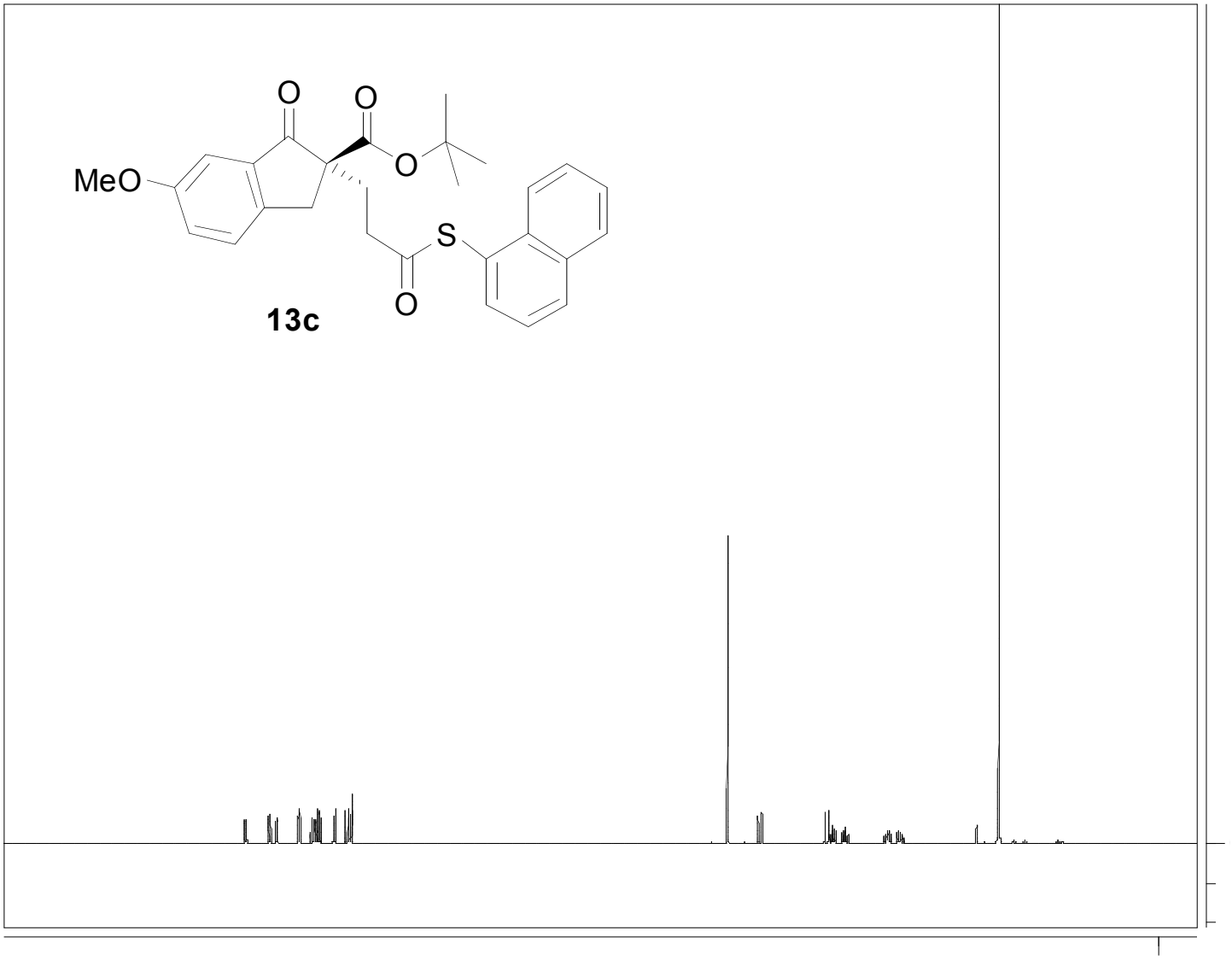

O
O
O
O
N
4i


O
O
O
O
N
4i

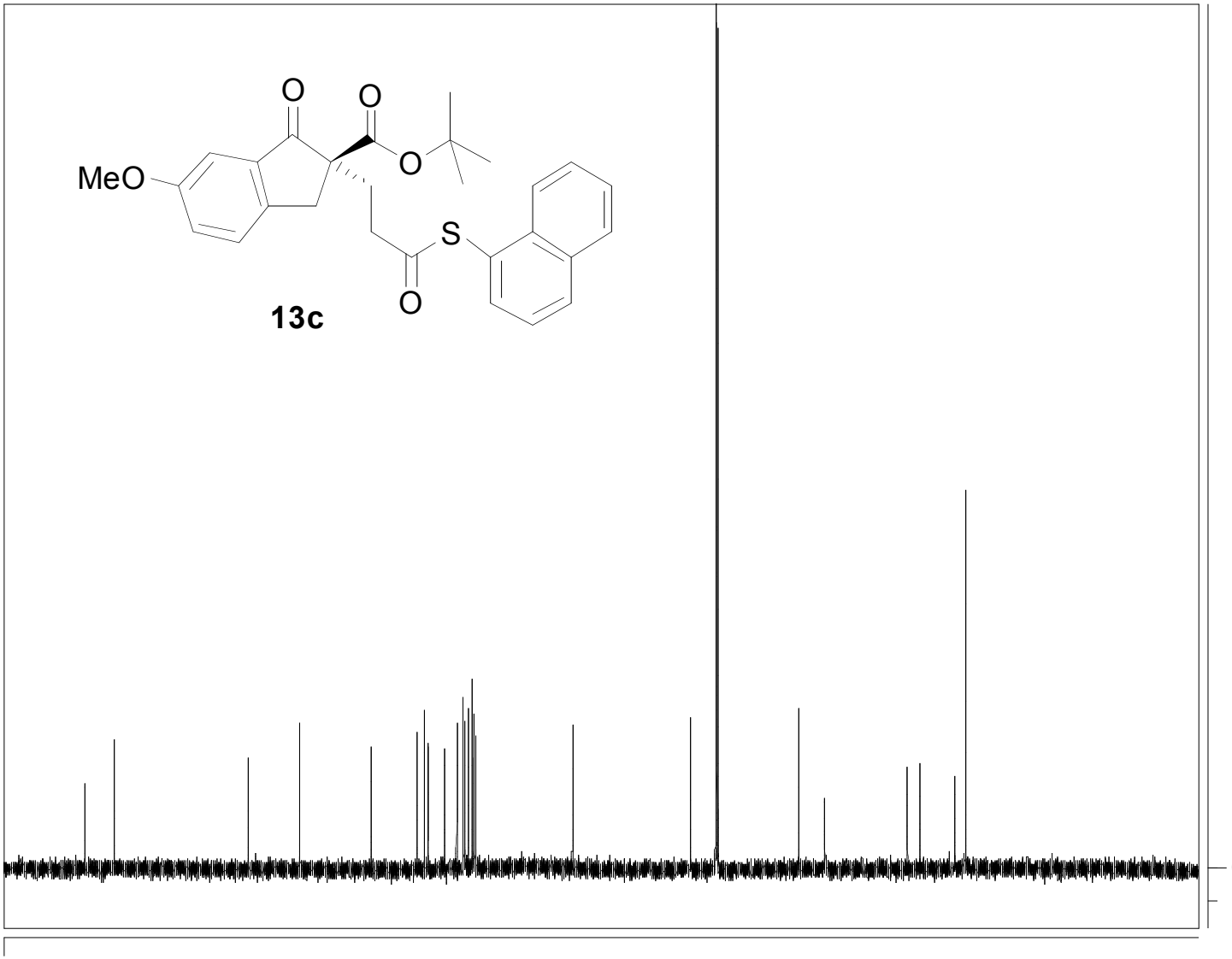


12c

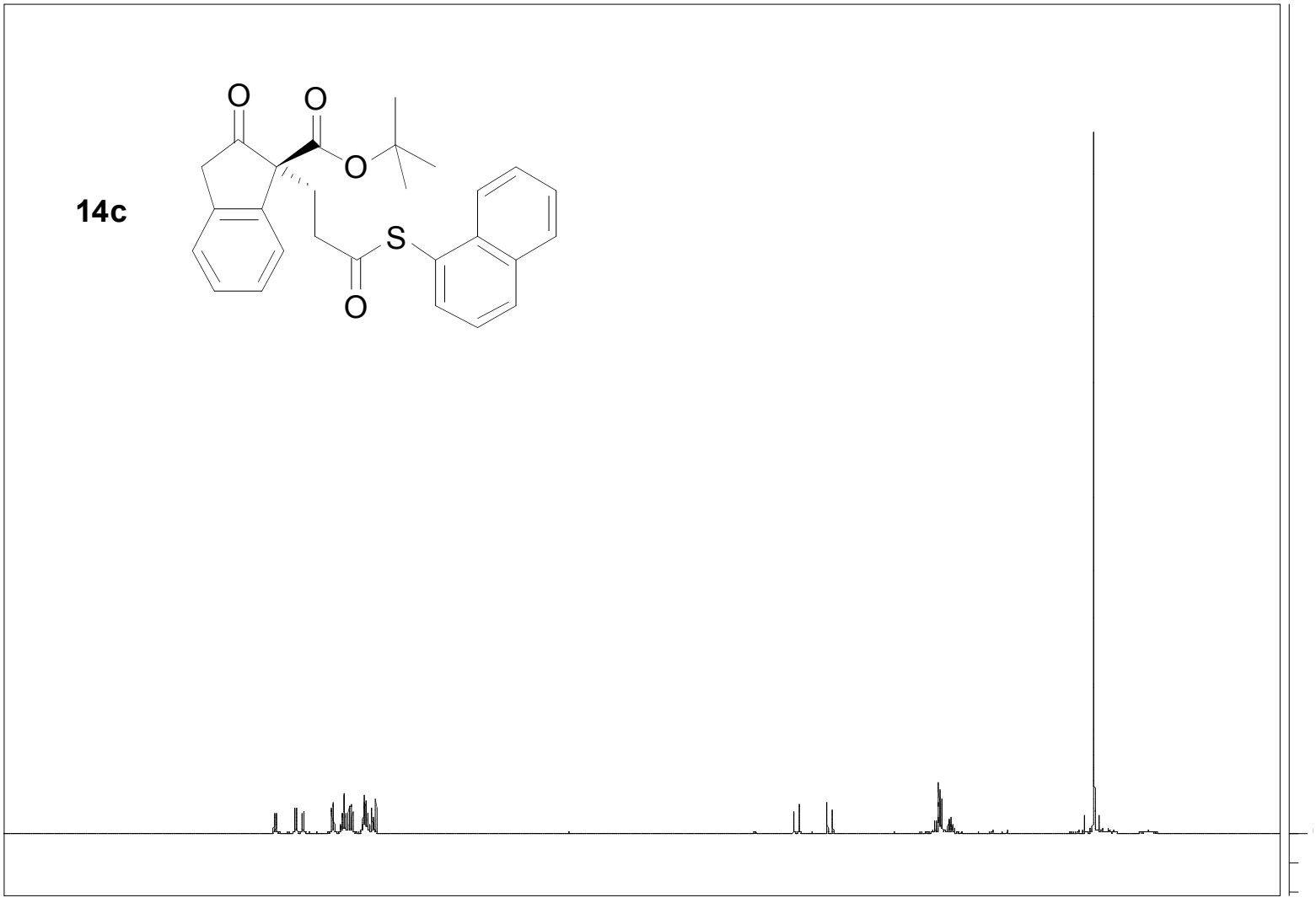

O
O
O
S
Br
O
12c

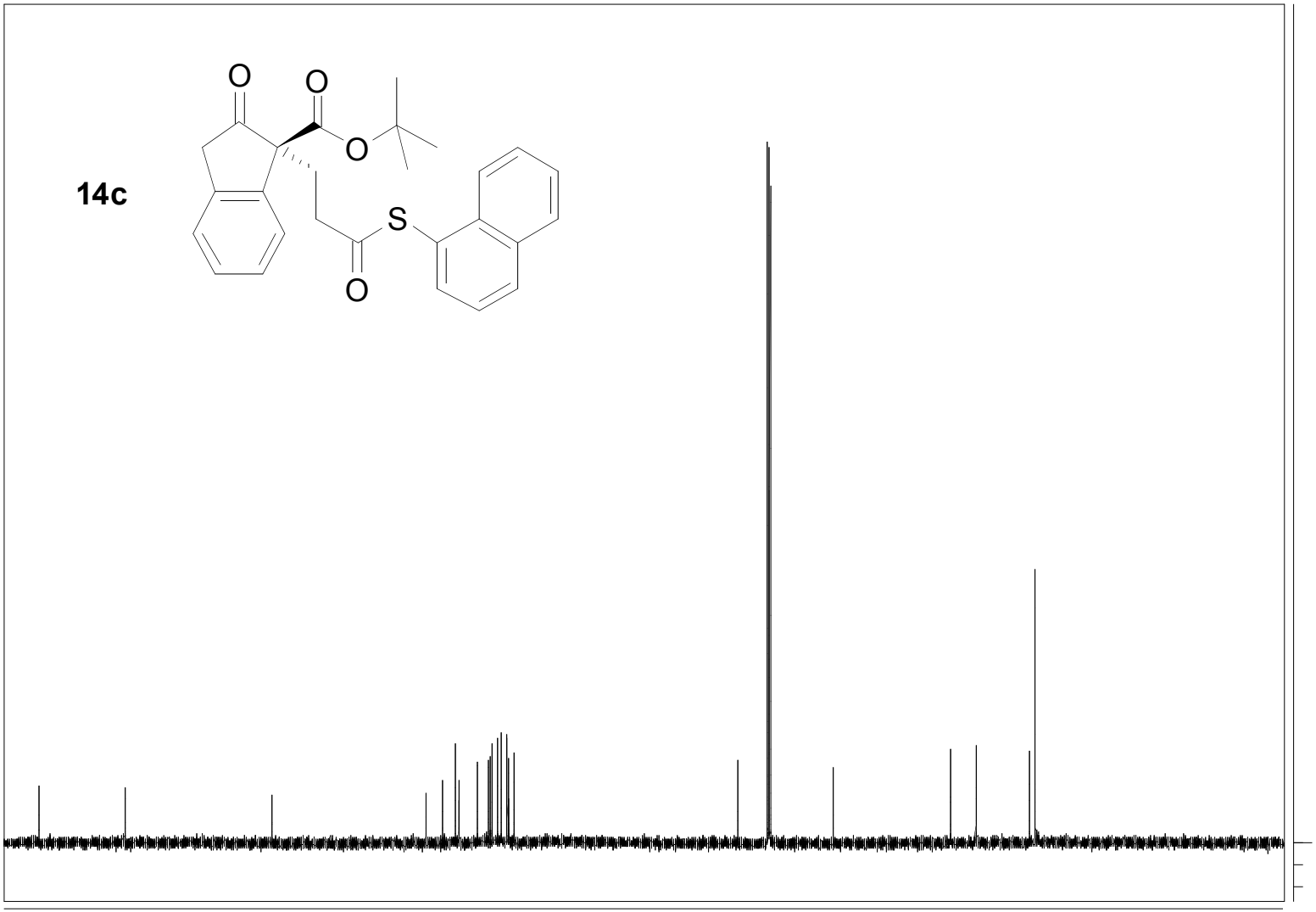


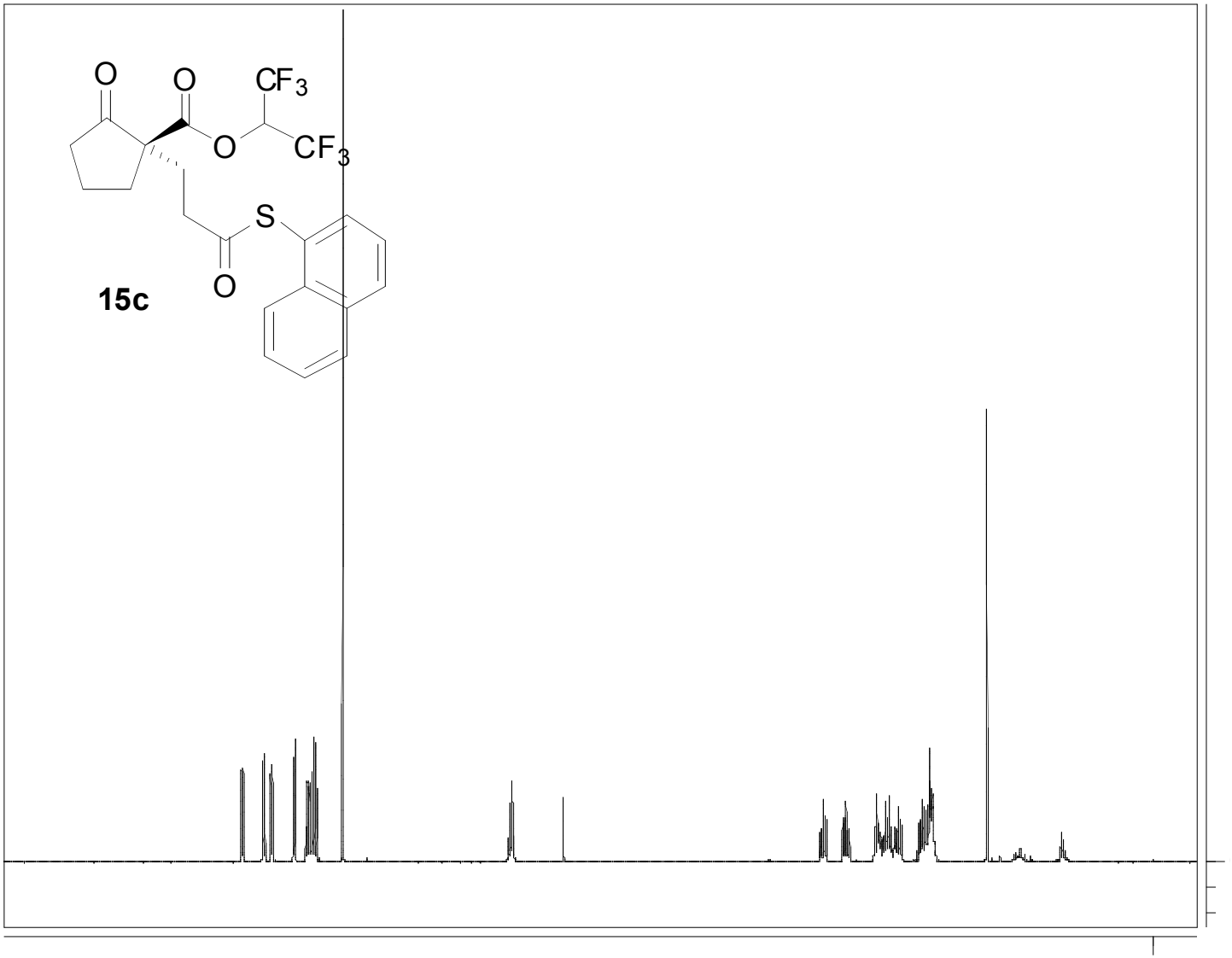
13c

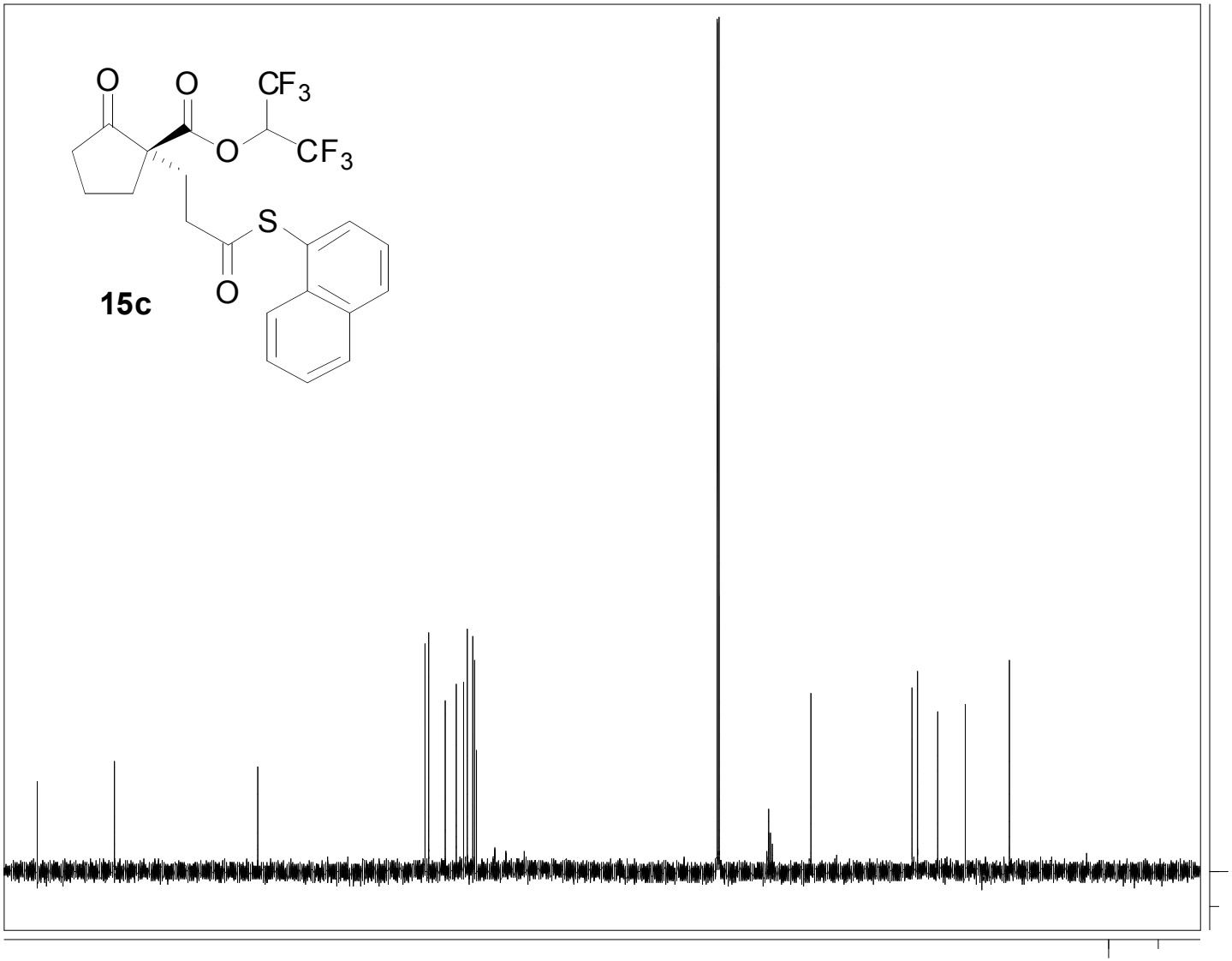


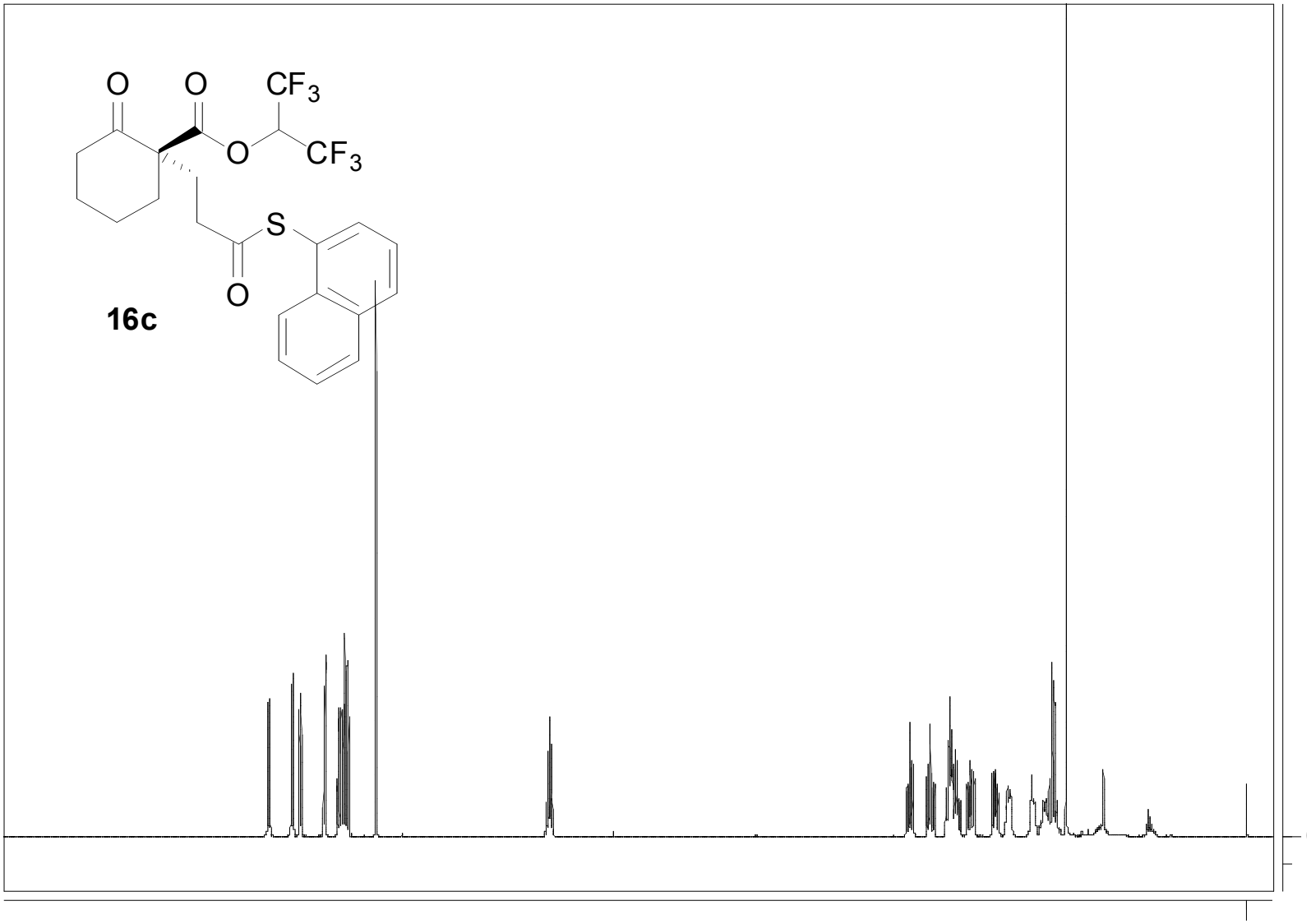
13c

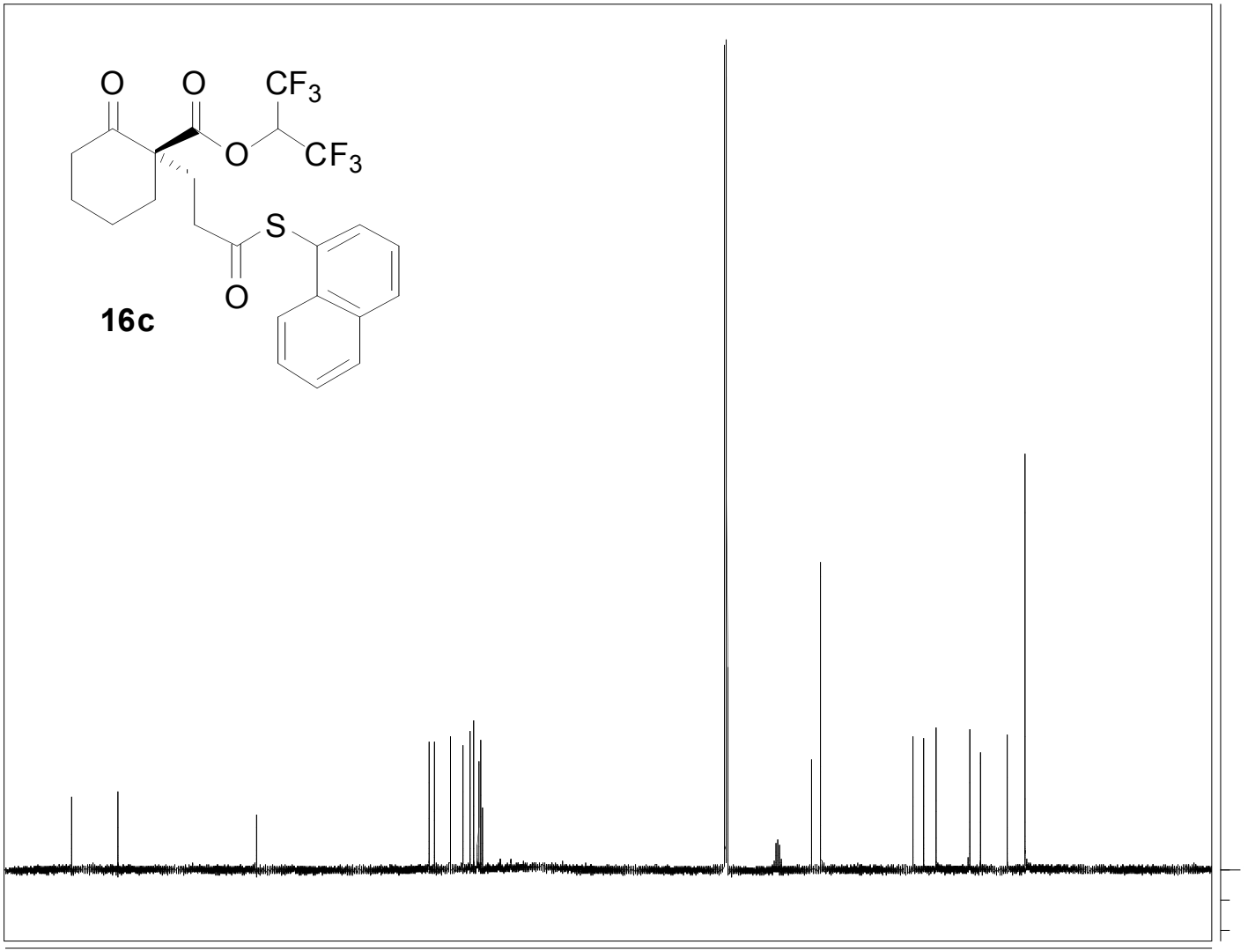

14c
O
O
O
S
O
ppm (t1)

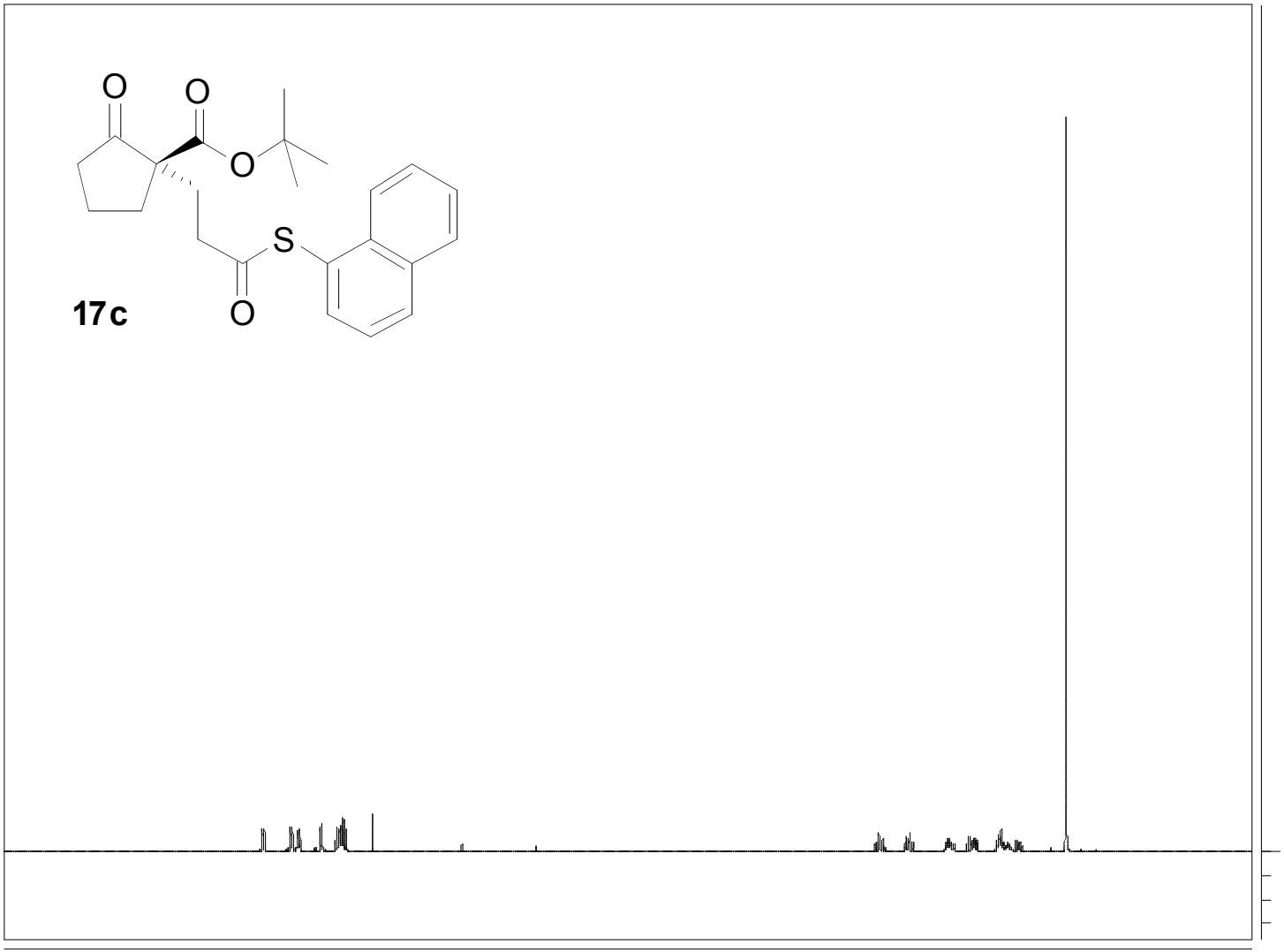

14c
O
O
O
S
O
pt (t1)

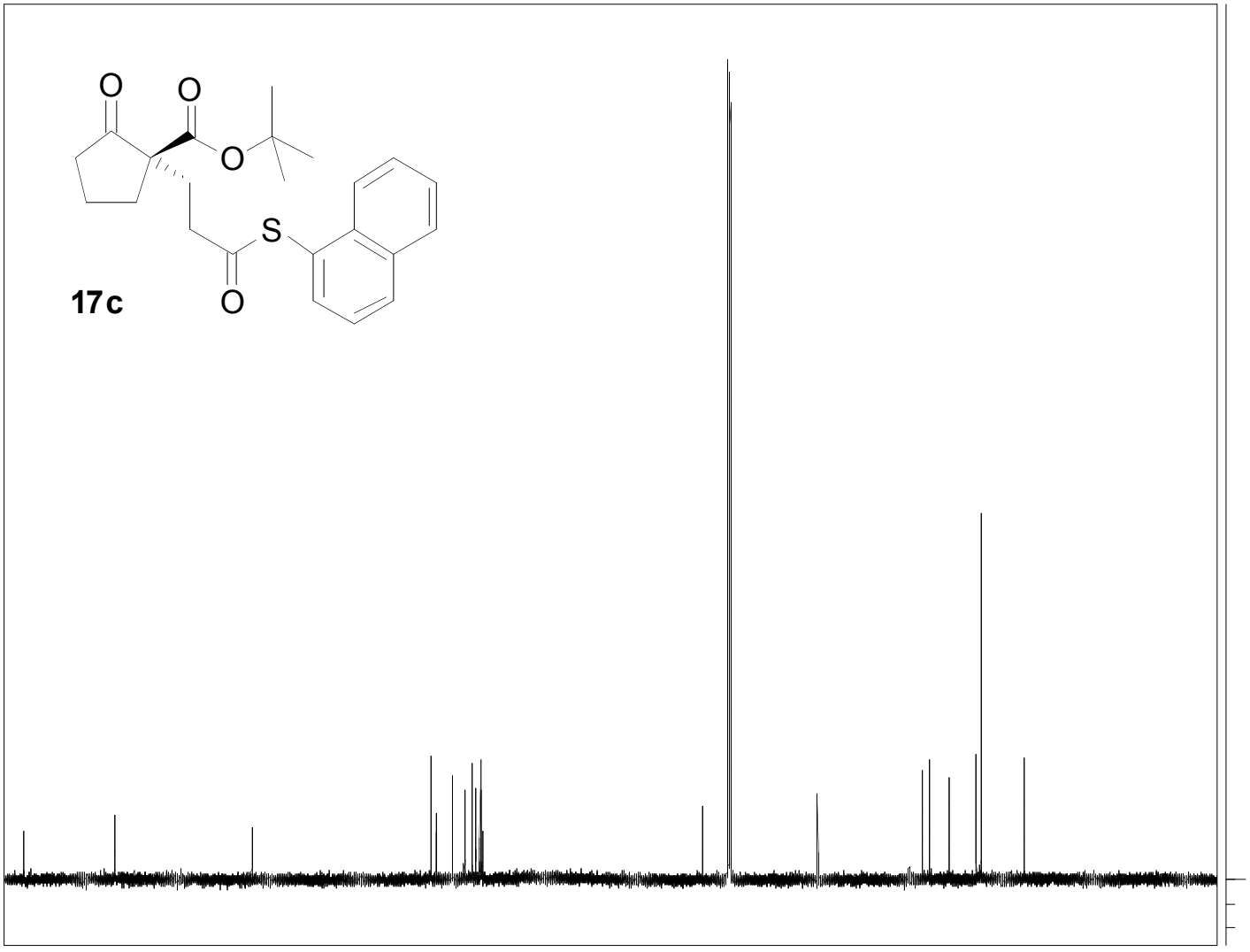

O
O
CF3
O
CF3
S
O
15c

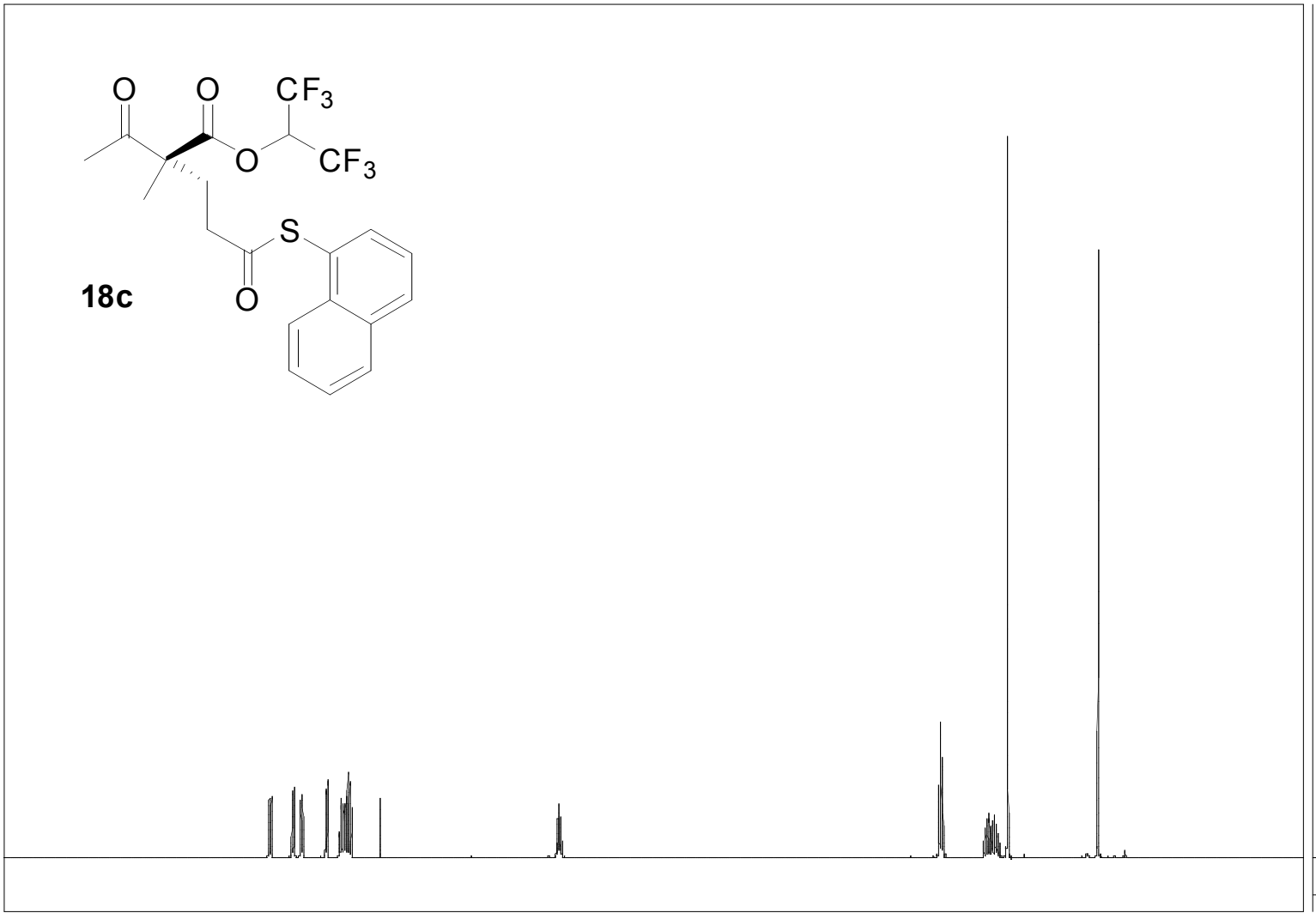

O
O
CF3
O
CF3
S
O
15c

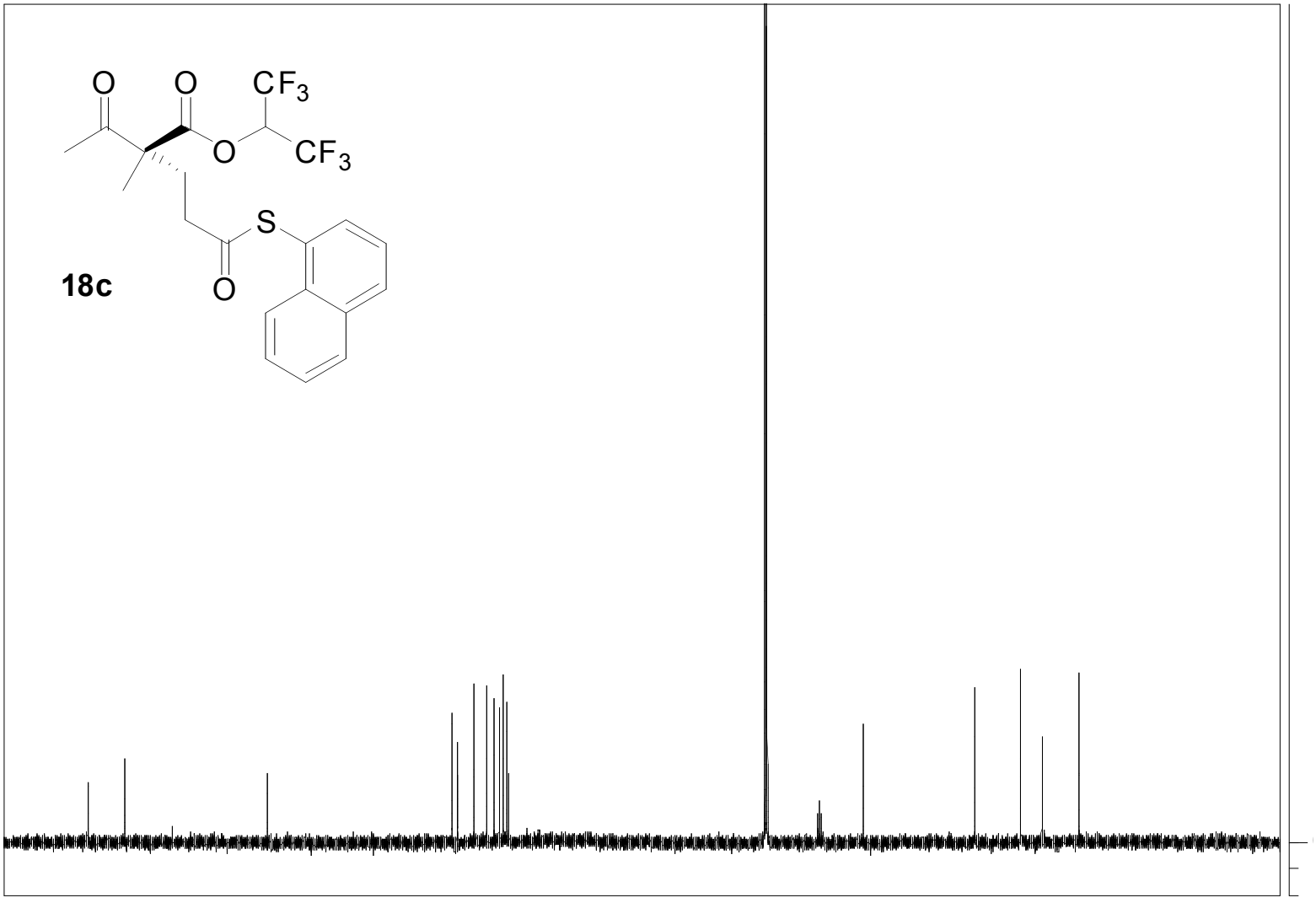

O
O
CF3
O
CF3
S
O
16c

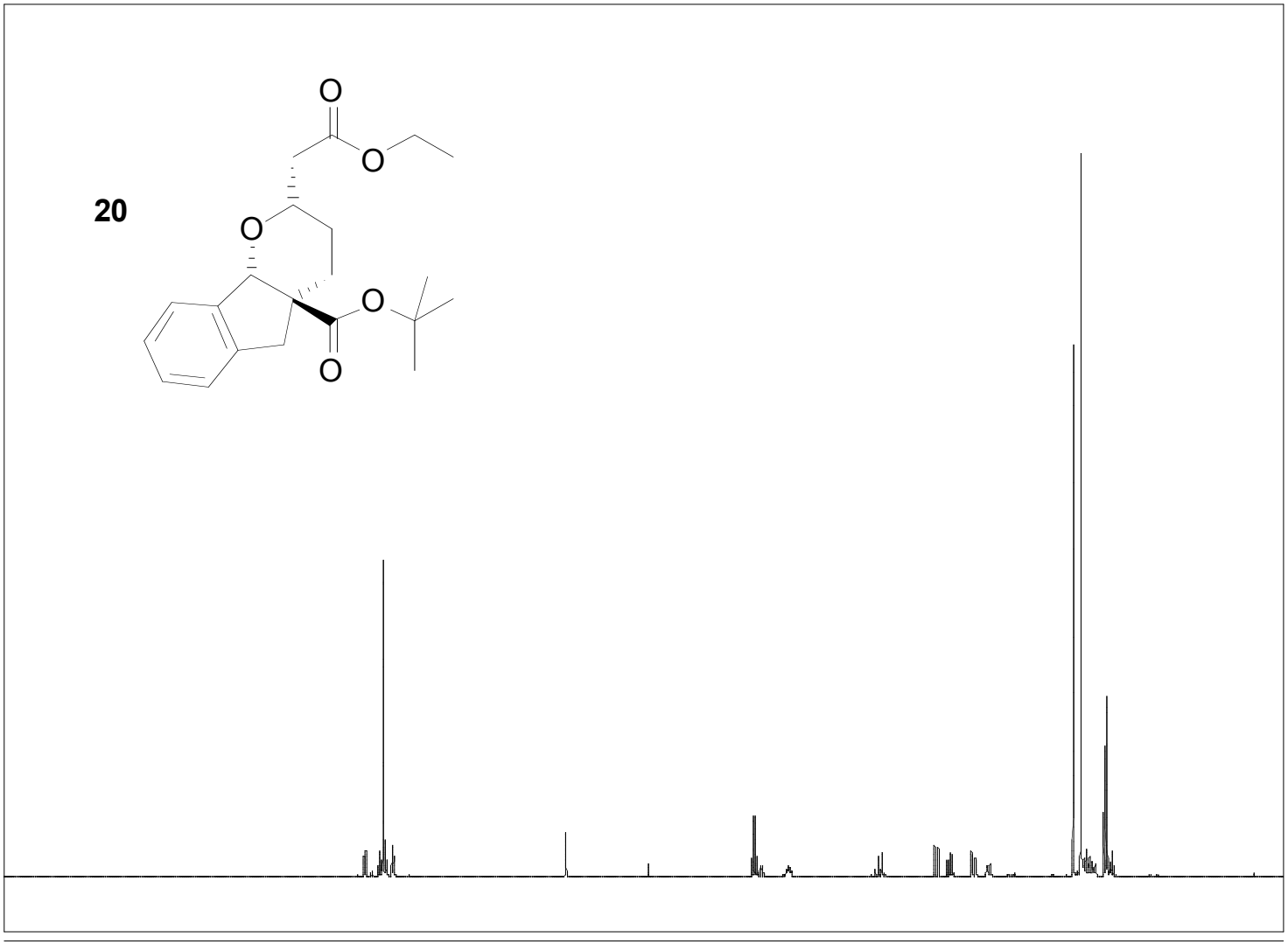

O
O
CF3
O
CF3
S
O
16c
ppm (t1)

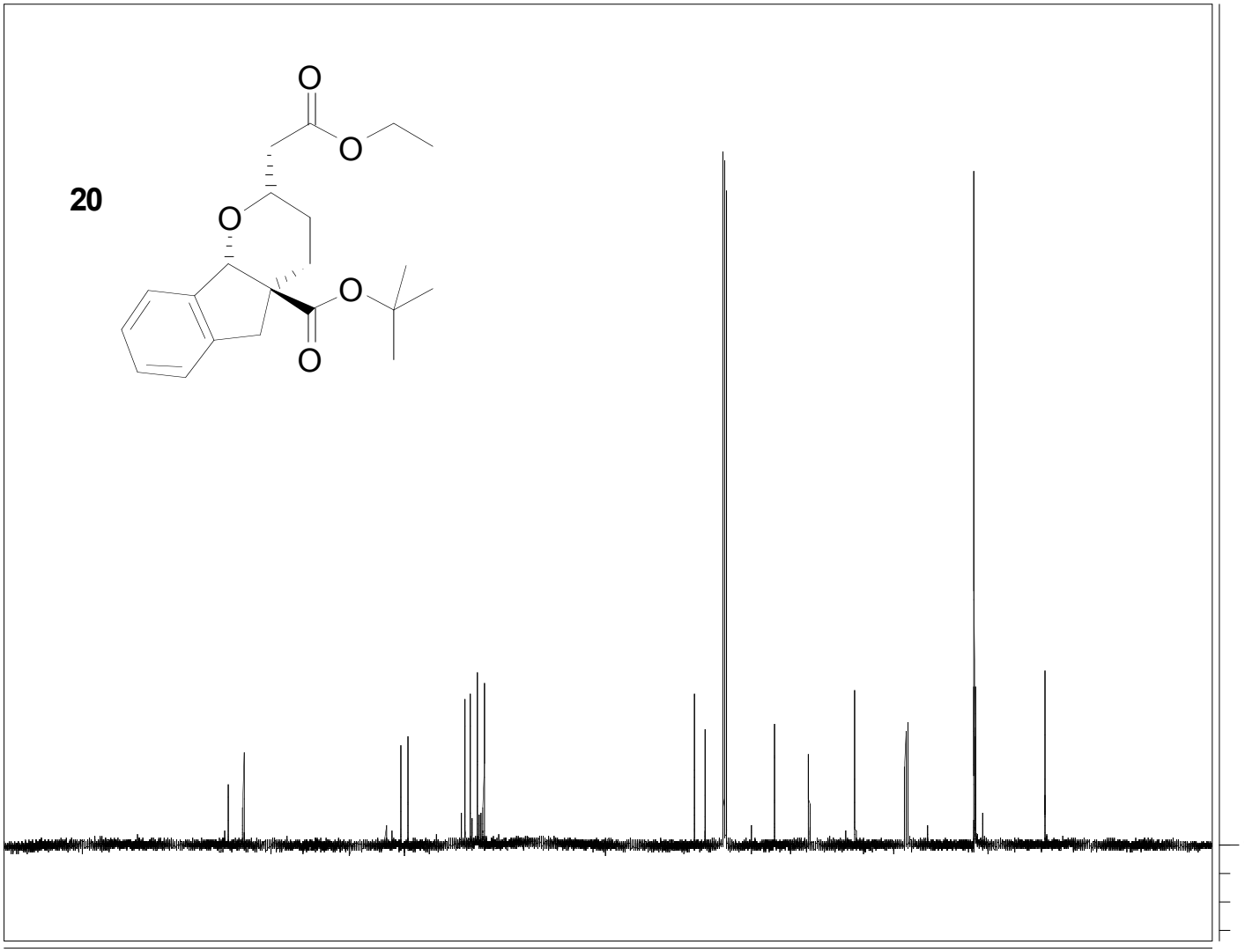

O
O
O
S
O
17c
ppm (t1)

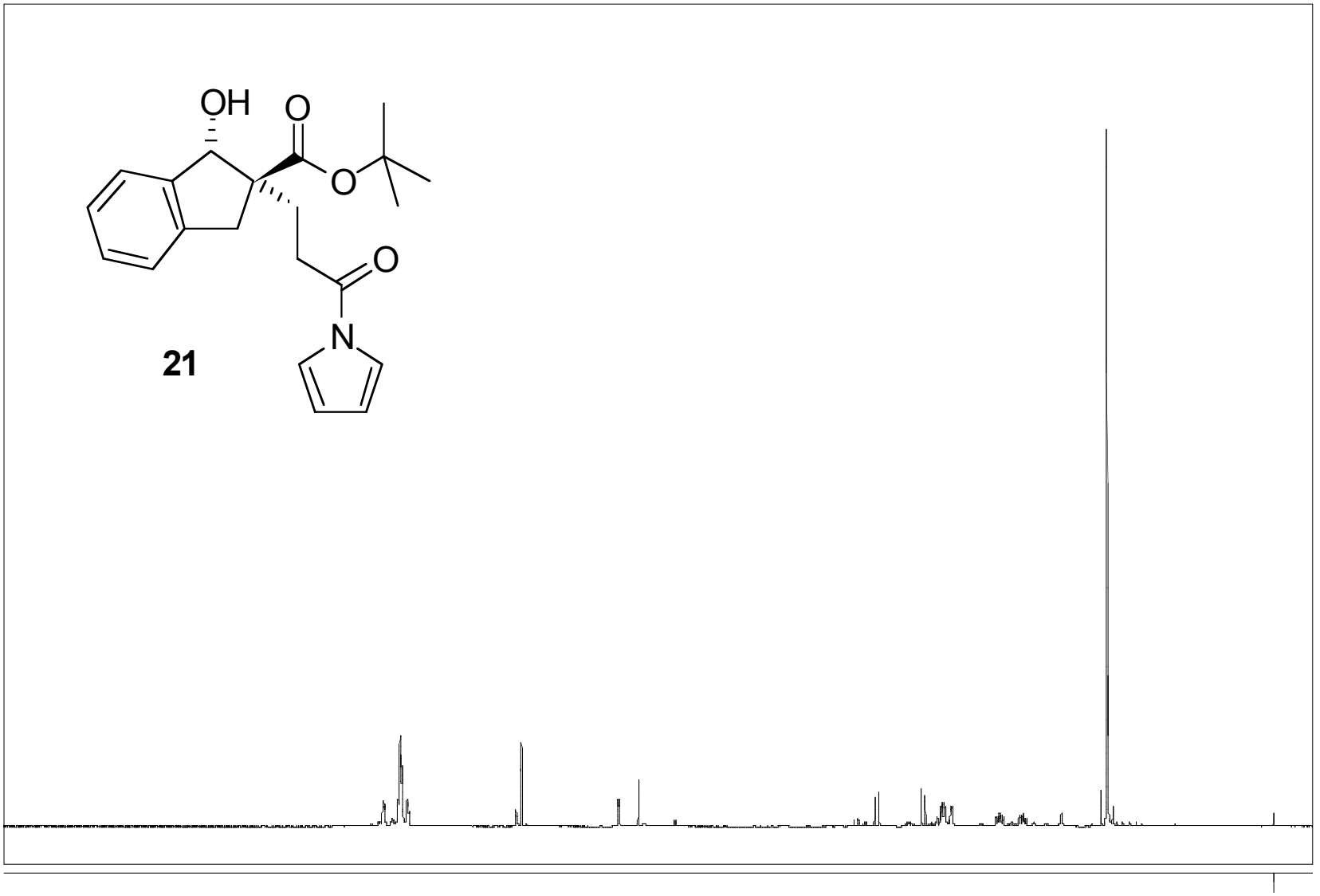

O
O
O
S
O
17c
ppm (t1)


O
O
CF3
O
CF3
S
O
18c
ppm (t1)

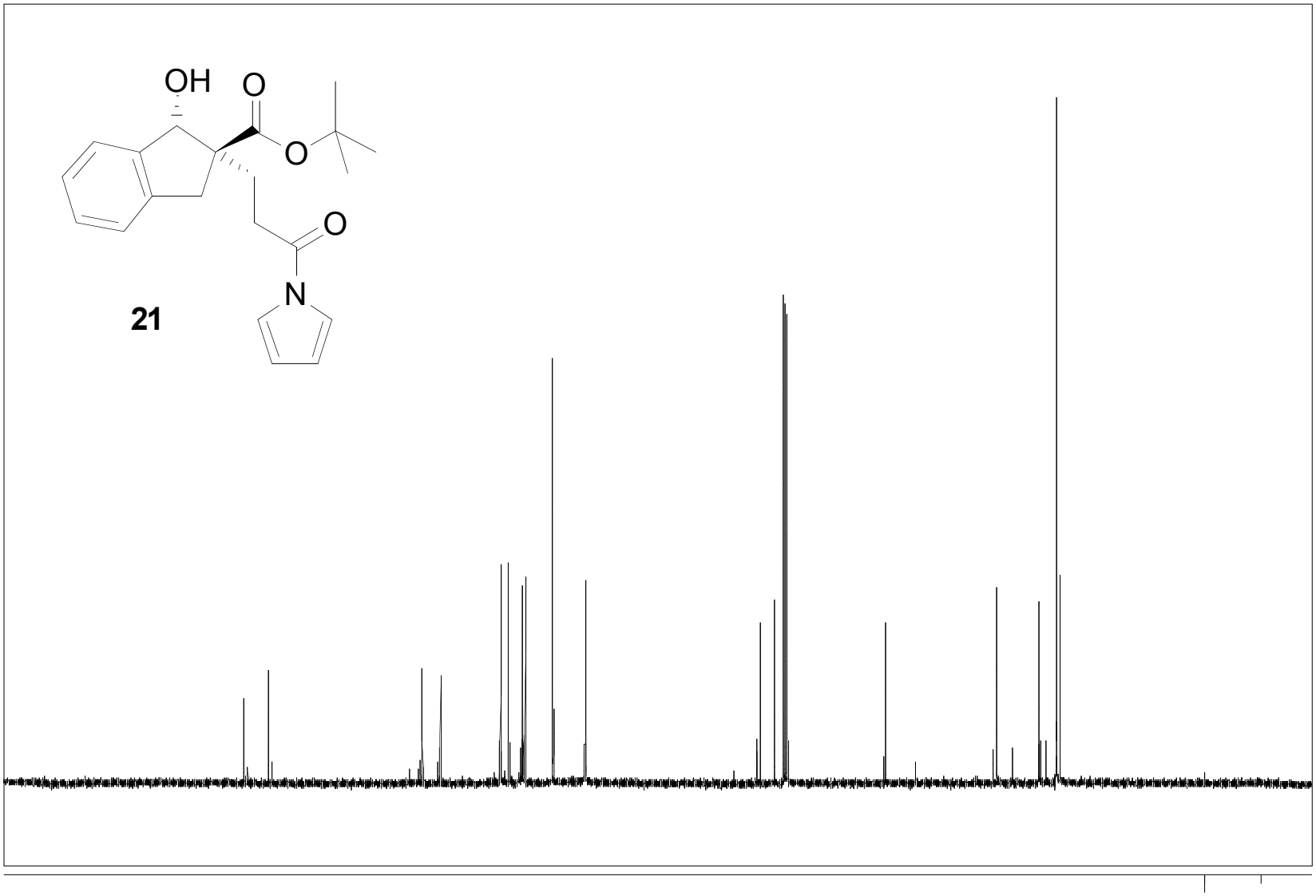

O
O
CF3
O
CF3
S
18c
O
ppm (t1)

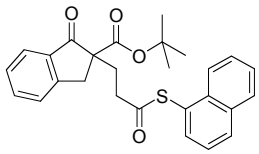

20
O
O
O
O
O
O
ppm (t1)


20
O
O
O
O
O
O
ppm (t1)

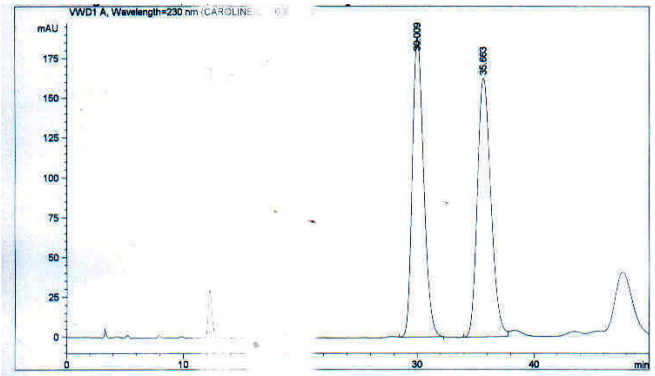


21


OH
O
O
O
N
21



4c

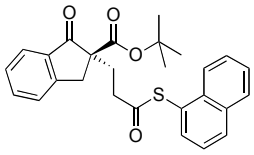


Area Percent Report

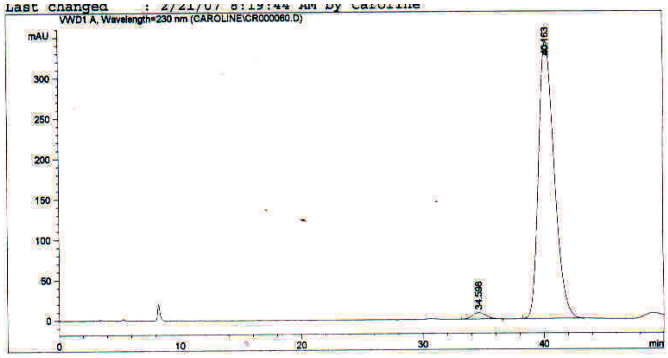
Sorted By :
Multiplier :
Dilution :

Signal 1: VWD1 A, Wavelength

Peak #	RetTime [min]	Type	Width [min]	Height [mAU]	Area %
1	30.009	VB	0.9795	188.43449	49.3543
2	35.663	BB	1.0182	162.74715	50.6457



4c

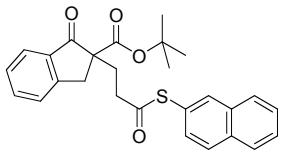


Area Percent Report

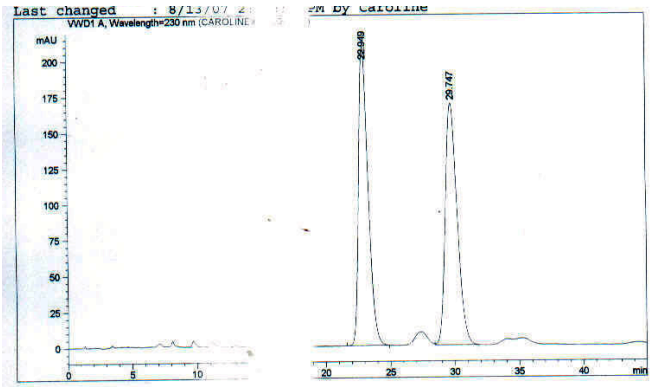
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.598	BB	0.9031	611.76093	7.95576	1.9324
2	40.163	BB	1.2331	3.10466e4	343.29404	98.0676



4d

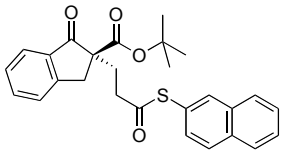


ent Report

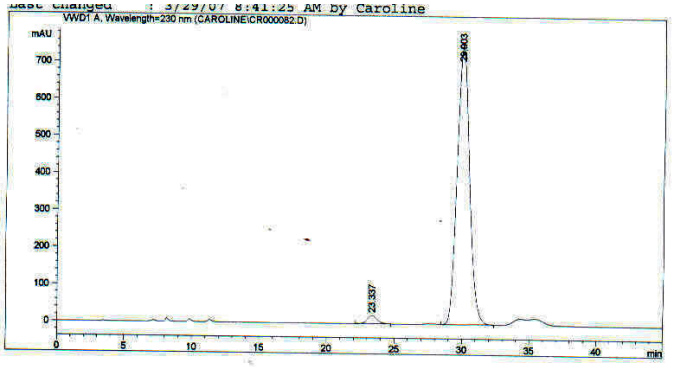
Sorted By : 1
Multiplier : 0
Dilution : 0

Signal 1: VWD1 A, Wavelengt

Peak #	RetTime [min]	Type	Width [min]	Height [mAU]	Area %
1	22.949	BB	0.7789	209.05835	50.0090
2	29.747	VB	0.8510	168.96202	49.9910



4d

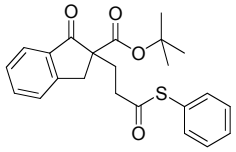


Area Percent Report

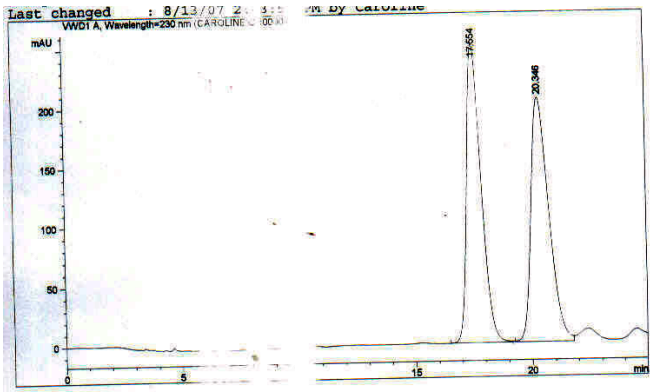
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.337	BB	0.6044	1154.09766	22.38729	2.3550
2	29.903	VB	0.9451	4.78520e4	748.23987	97.6450



4e



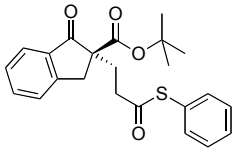
Last changed : 8/13/07 2:

Area Percent Report

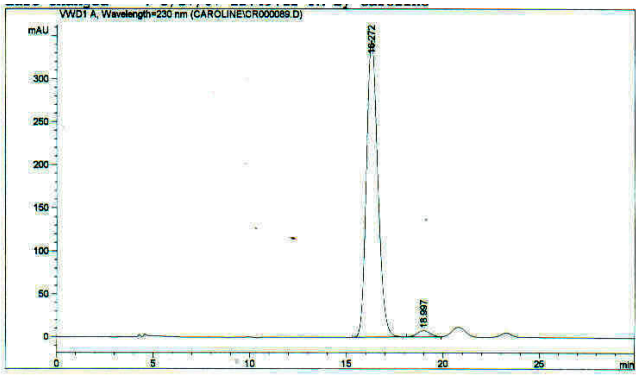
Sorted By :
Multiplier :
Dilution :

Signal 1: VWD1 A, Wavelengt

Peak #	RetTime [min]	Type	Width [min]	Height [mAU]	Area %
1	17.554	BB	0.6458	252.51056	49.8704
2	20.346	BV	0.7379	206.21405	50.1296



4e

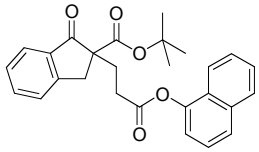


Area Percent Report

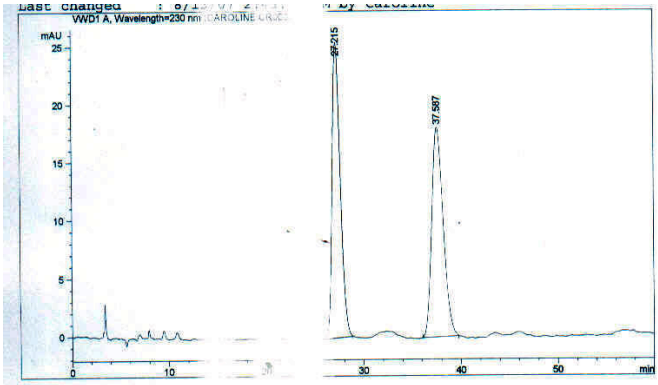
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.272	BB	0.6167	1.42163e4	345.74963	97.5663
2	18.997	BV	0.5661	354.60779	7.42654	2.4337



4f

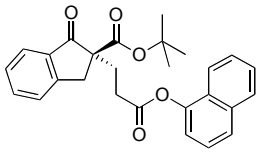


Area Percent Report

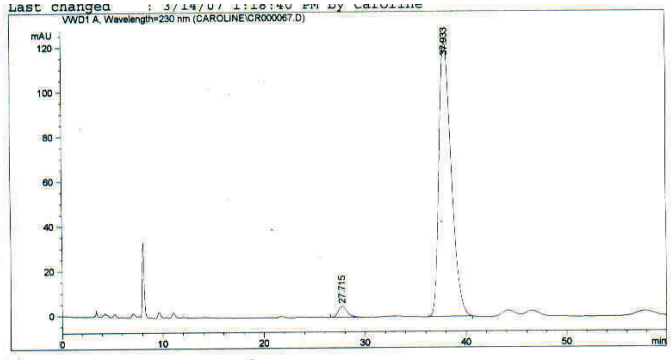
Sorted By
Multiplier
Dilution

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.215	BB	0.6877	1482.1	25.51475	50.0181
2	37.587	BB	0.9612	1482.1	18.08970	49.9819



4f

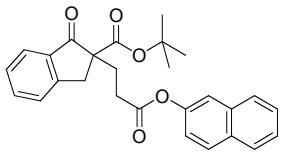


Area Percent Report

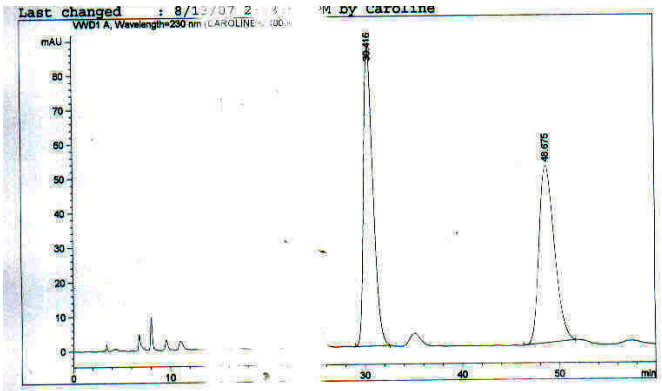
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.715	BB	0.7108	301.53870	4.97736	2.8141
2	37.933	BB	1.0303	1.04137e4	123.18063	97.1859



4g



Last changed : 8/12/07 2 PM By Caroline

VWD1 A, Wavelength=230 nm (CAROLINE

mAU

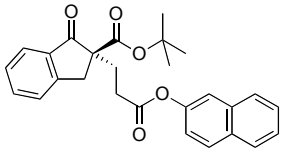
min

Area Percent Report

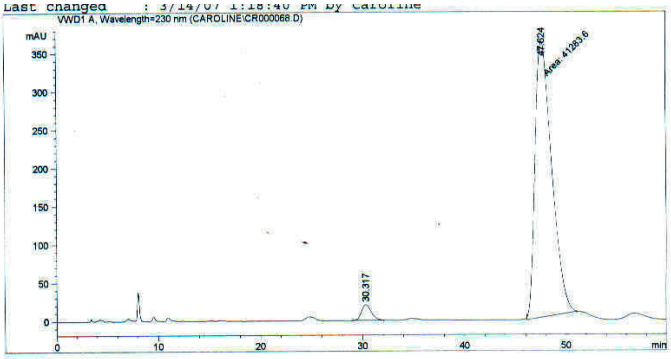
Sorted By :
Multiplier :
Dilution :

Signal 1: VWD1 A, Wavelength 23

Peak #	RetTime [min]	Type	Width [min]	Area	Height [mAU]	Area %
1	30.416	BB	0.8239	58	86.76334	50.6897
2	48.675	PB	1.2889	5	51.65387	49.3103



4g



Last changed : 3/14/07 1:18:40 PM By Caroline

VWD1 A, Wavelength=230 nm (CAROLINE\CR000068.D)

mAU

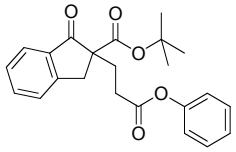
min

Area Percent Report

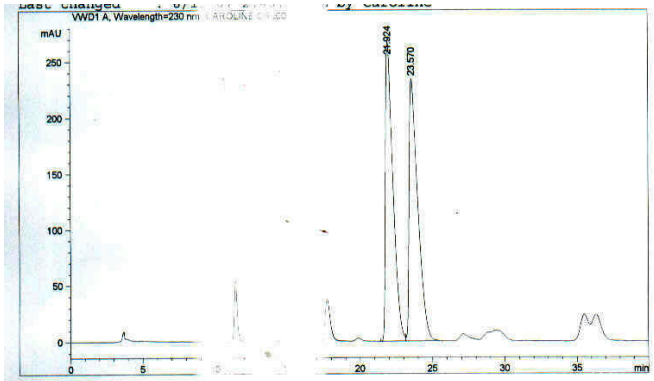
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.317	BB	0.7832	1374.40747	20.55238	3.2219
2	47.624	MM	1.9097	4.12836e4	360.29535	96.7781



4h

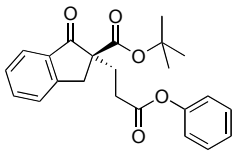


Area Percent Report

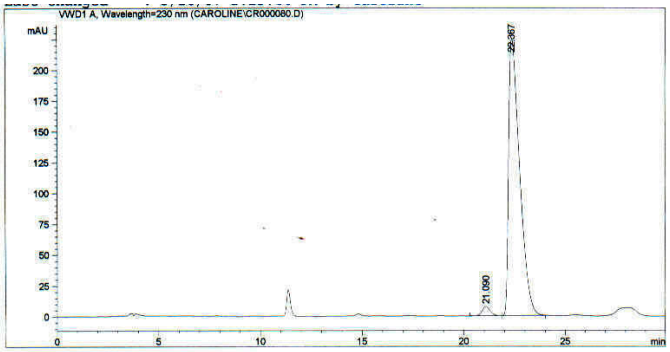
Sorted By
Multiplier
Dilution

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.924	PV	0.5524	9[illegible]	267.88077	49.7202
2	23.570	VB	0.5[illegible]	9[illegible]	234.03398	50.2798



4h

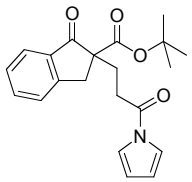


Area Percent Report

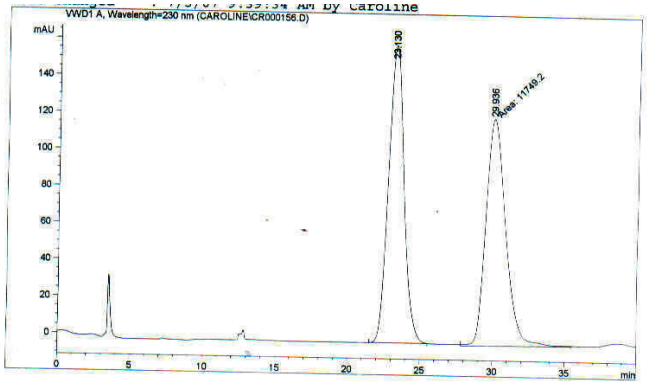
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.090	PB	0.3375	210.18501	7.55622	2.4259
2	22.367	PB	0.5387	8453.97168	225.34804	97.5741



4i

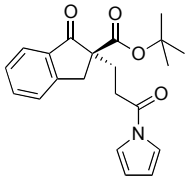


Area Percent Report

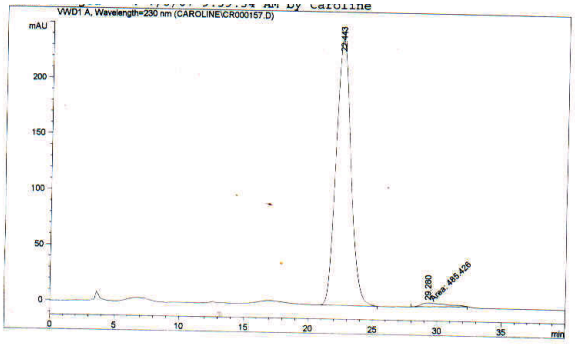
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.130	BB	0.9906	1.20040e4	161.22902	50.5362
2	29.936	MM	1.5918	1.17492e4	123.01839	49.4638



4i

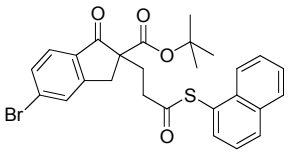


Area Percent Report

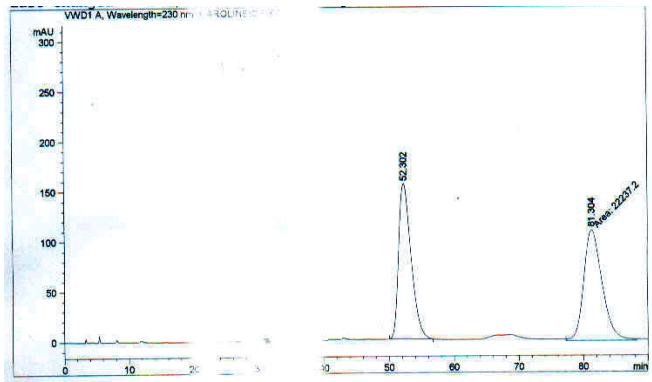
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.443	BB	1.1107	1.90979e4	238.62784	97.5212
2	29.280	MM	2.2555	485.42639	3.58693	2.4788



12c

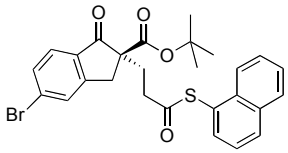


Area Percent Report

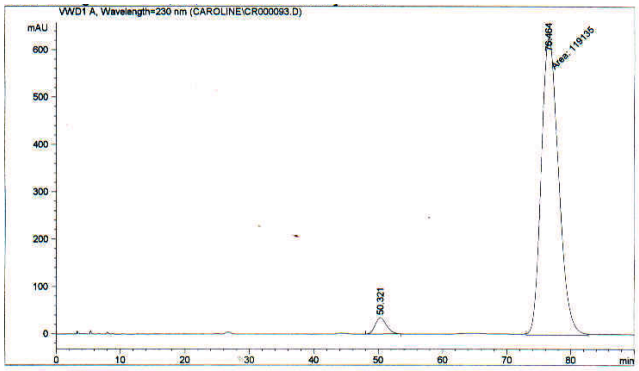
Sorted By
Multiplier
Dilution

Signal 1: VWD1 A, Wav

Peak #	RetTime [min]	Type	Wi [m	Height [mAU]	Area %
1	52.302	BB	1.	155.03372	48.1590
2	81.304	MM	3.	111.01462	51.8410



12c

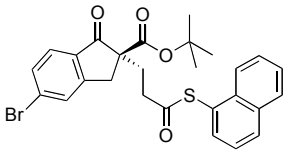


Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

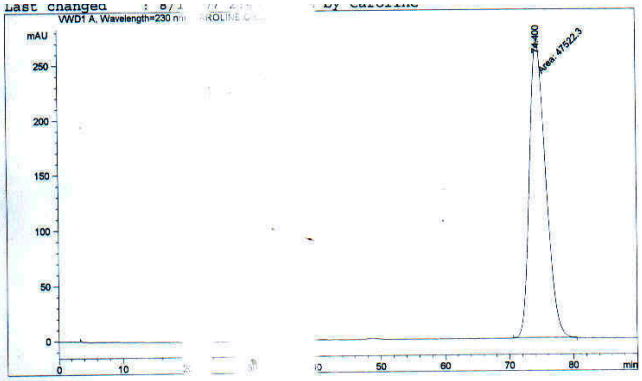
Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.321	BB	1.4369	4219.21533	34.54588	3.4204
2	76.464	MM	3.1552	1.19135e5	629.29779	96.5796



Recrystallised:

12c

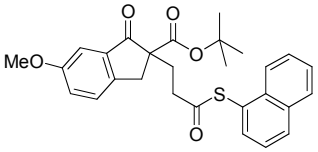


t Report

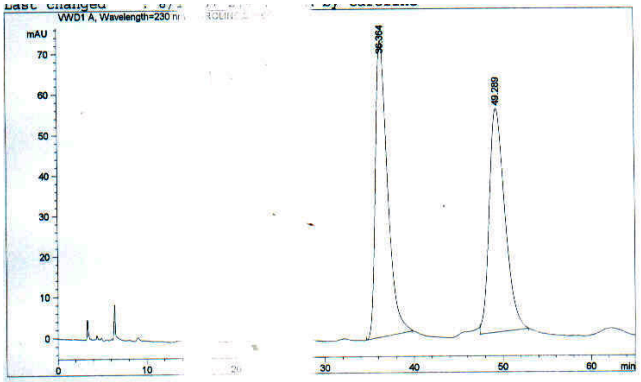
Sorted By
Multiplier
Dilution

Signal 1: VWD1 A, Wav

Peak #	RetTime [min]	Type	Height [mAU]	Area %
1	74.400	MM	270.34186	100.0000



13c

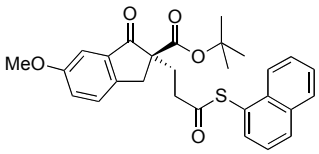


Area Percent Report

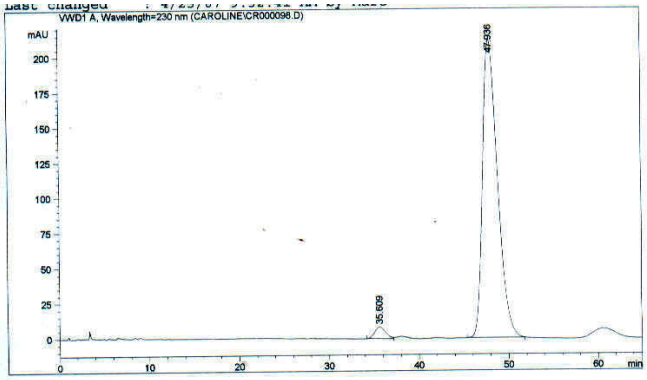
Sorted By
Multiplier
Dilution

Signal 1: VWD1 A, Wav

Peak #	RetTime [min]	Type	Wi [m	Height [mAU]	Area %
1	36.364	PB	1.	73.18456	50.4630
2	49.289	BB	1.	55.18302	49.5370



13c

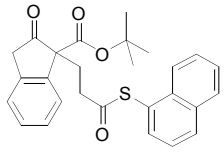


Area Percent Report

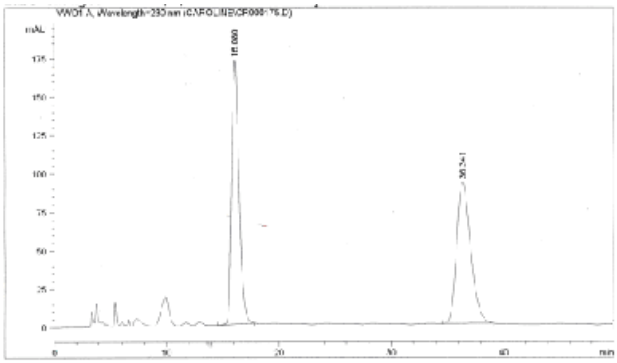
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.609	BV	0.9782	705.00073	8.43406	2.8040
2	47.936	BB	1.3706	2.44374e4	212.03166	97.1960



14c

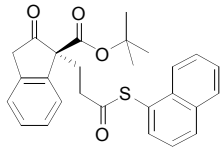


Area Percent Report

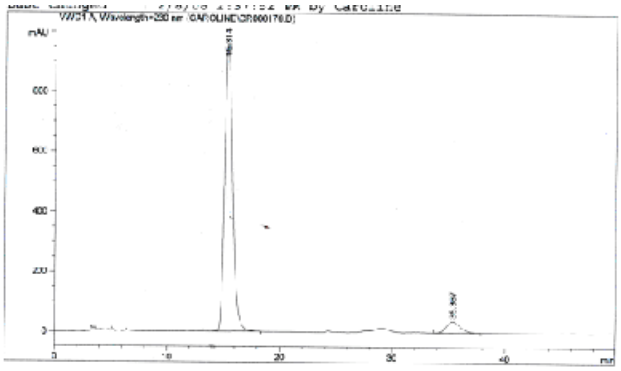
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.080	PB	0.6313	7978.30518	172.26911	19.8540
2	36.341	BB	1.0460	8025.04004	92.06383	80.1460



14c

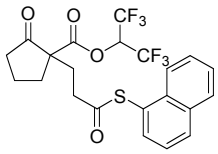


Area Percent Report

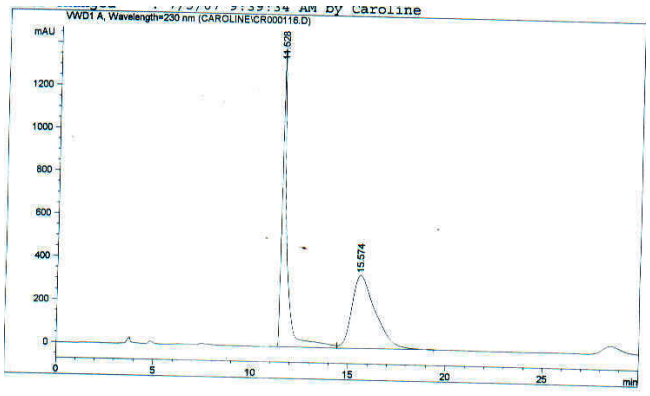
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.318	BB	0.7585	4.79579e4	960.69759	93.6688
2	35.367	VB	0.9881	3133.12085	37.21509	6.1312



15c

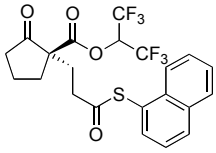


Area Percent Report

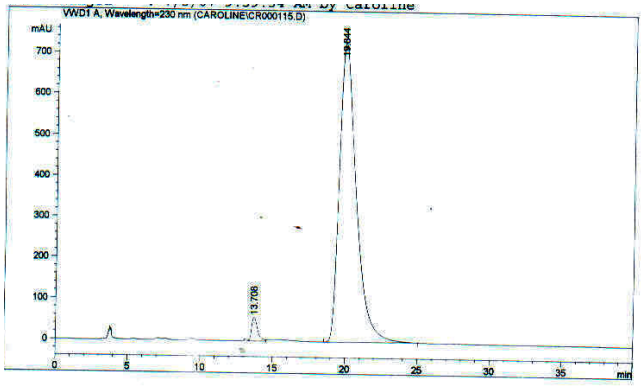
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.528	VV	0.2398	2.54882e4	1404.07910	47.1706
2	15.574	VB	1.1655	2.85459e4	340.00757	52.8294



15c

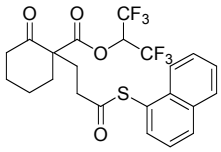


Area Percent Report

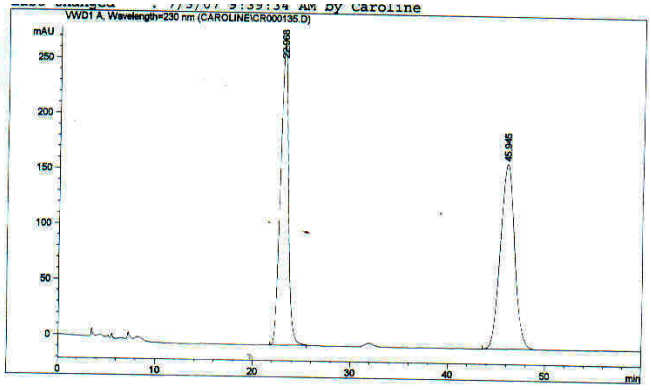
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.708	VB	0.4250	1621.87695	56.81702	2.6555
2	19.844	BB	1.1580	5.94542e4	730.89984	97.3445



16c

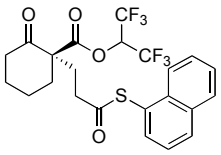


Area Percent Report

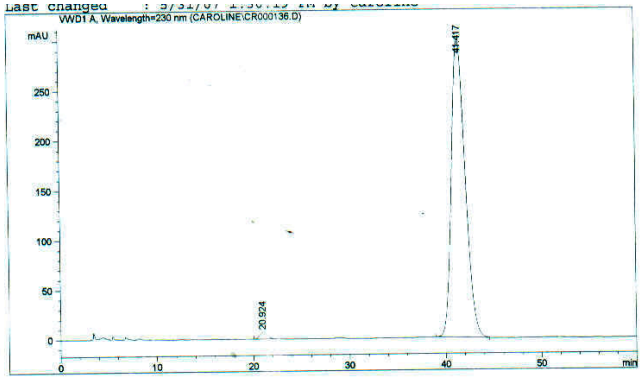
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.968	BB	0.8466	1.53483e4	271.07104	47.4567
2	45.945	BB	1.2083	1.69934e4	166.70271	52.5433



16c

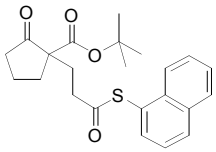


Area Percent Report

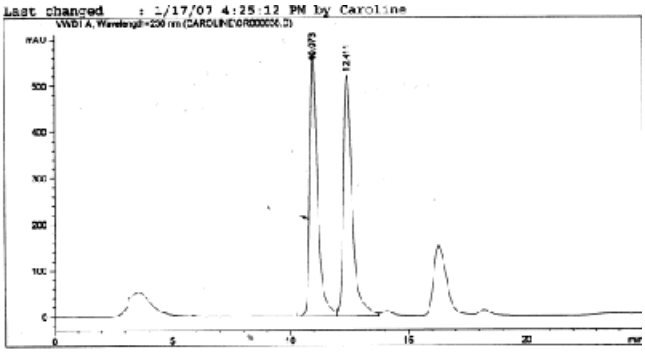
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.924	BB	0.6160	340.41757	6.46826	1.1270
2	41.417	BB	1.1972	2.98643e4	298.51648	98.8730



17c



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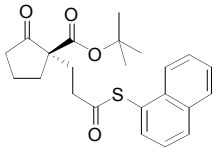
Area Percent Report

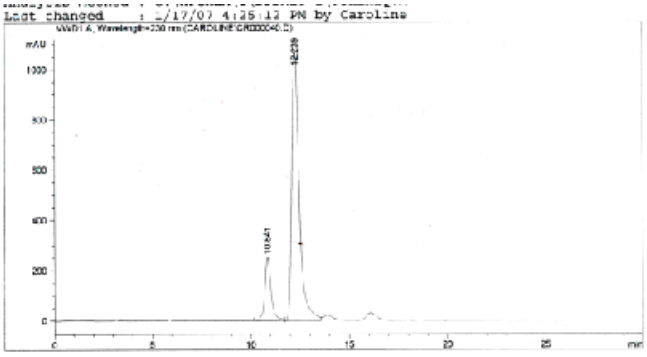
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.973	BV	0.3377	1.29534e4	584.10248	49.0238
2	12.411	VV	0.3826	1.34693e4	522.82843	50.9762



17c



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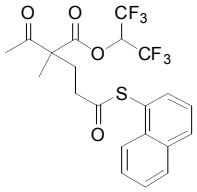
Area Percent Report

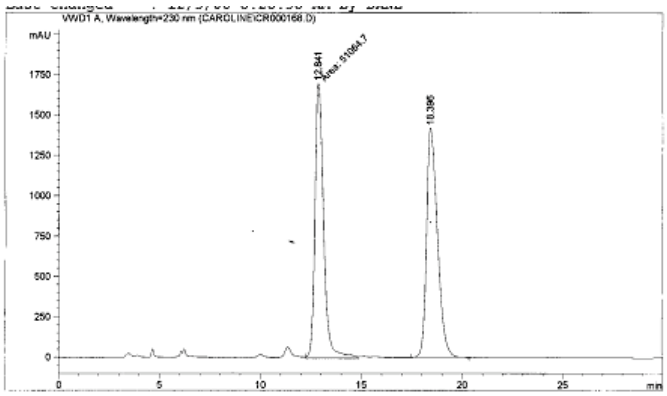
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.841	BV	0.3218	5596.84131	254.30280	16.5632
2	12.239	VV	0.4315	2.81939e4	1069.82910	83.4368



18c

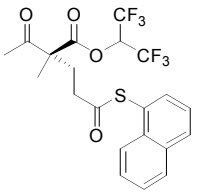


Area Percent Report

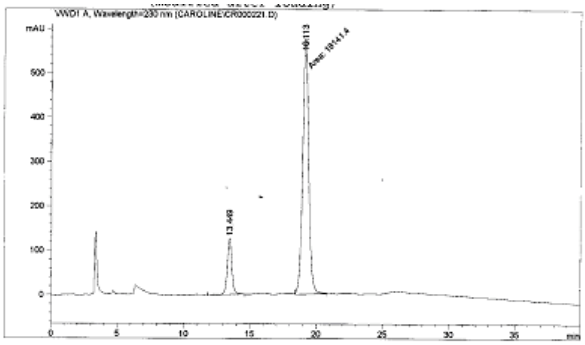
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.841	MM	0.4999	5.10647e4	1702.48413	49.0237
2	18.396	PB	0.5530	5.30987e4	1420.68518	50.9763



18c



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.449	VB	0.3551	3033.75439	127.26301	14.3269
2	19.113	MM	0.5227	1.81414e4	578.40253	85.6731